Sulfone mediated olefination and allylation reactions

Inaugural dissertation

of the Faculty of Science,

University of Bern

presented by

Remo Arnold

Supervisor of the doctoral thesis:

Prof. Dr. Philippe Renaud

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Accepted by the Faculty of Science.

Bern, **02.12.2024**

The Dean

Prof. Dr. Jean-Louis Reymond



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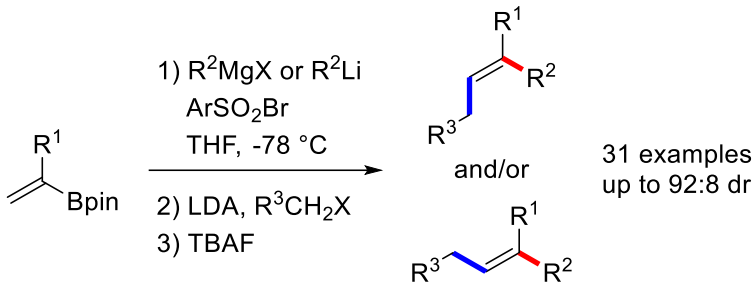
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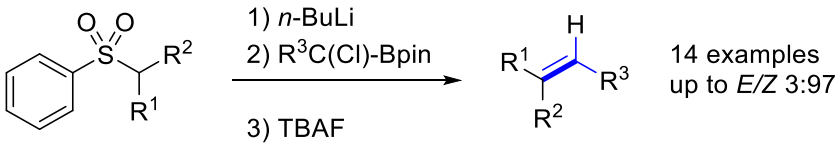
Lastly, and most importantly, I would like to thank my parents, my sister and my friends for their support over the years in all kinds of matters, without you none of this would have been possible!

Abstract

In the first chapter a stepwise, Zweifel-type olefination reaction between alkenylboronic acid pinacol esters, alkyllithium (or alkyl Grignard) reagents and alkyl halides is reported. The reaction sequence involves a three-component coupling reaction, followed by an alkylation reaction under basic conditions and subsequent β-elimination triggered with a fluoride source. With the developed protocol, a variety of tri-substituted alkenes were prepared in high yield, possibly with a stereogenic centre at the allylic position and with high enantiomeric purity thanks to the robust chemistry of the organoboron species. Separation of the diastereomers of the alkylated intermediates allowed for the preparation of *E*- or *Z*-olefins with high levels of stereoselectivity, pointing at a stereospecific (*anti*)-elimination mechanism. The usefulness of the overall process was illustrated by the introduction of stereodefined olefin moieties on a short selection of natural products. The sequence can also be performed in a one pot protocol.



In the second chapter, an olefination reaction is reported, which made it possible to use α-haloalkyl boronic acid esters as starting materials. Under basic conditions α-haloalkyl boronic esters were coupled with sulfones leading to β-borylated sulfones. These intermediates can be isolated or directly treated with TBAF to provide the desired alkenes. In most cases, *Z*-alkenes are preferentially formed and a particularly high *Z* stereoselectivity was achieved for arene substituted alkenes.



In the last chapter, allylation reactions were investigated with complex α,β-disubstituted bicyclic allylic sulfones. Two different approaches were tested. In the first approach, triethylborane was used as an initiator and chain transfer reagent. In the second approach, photoredox catalysis was tested. Although the isomerisation of the allyl sulfone could not be completely avoided, the photoredox results with the model substrate are promising for future photoredox reactions with the bicyclic allyl sulfones.

List of abbreviations

$[\propto]_D^{25}$	Optical rotation
aq.	aqueous
AIBN	Azobisisobutyronitrile
Bu_6Sn_2	Bis(tributyltin)
Br_2	Bromine
CCl_4	Carbon tetrachloride
$CDCl_3$	Deuterated chloroform
C_6H_5Cl	Chlorobenzene
Cs_2CO_3	Caesium carbonate
δ	Chemical shift (ppm)
DCE	1,2-dichloroethane
DCM	Dichloromethane
DIPA	Diisopropylamine
DLP	Dilauroyl peroxide
DMP	2,2-dimethoxypropane
Dr	Diastereomeric ratio
DTBHN	di-*tert*-butylhyponitrite
dppm	Bis(diphenylphosphino)methane
Et_3B	Triethylborane
Ee	Enantiomeric excess
EI	Electron Impact
ESI	Electrospray ionization
FCC	Flash column chromatography
HBpin	pinacolborane
HMPA	Hexamethylphosphoramide
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectroscopy
HSQC	Heteronuclear Single Quantum Coherence (2D NMR experiment)
IR	Infrared spectroscopy
J	Coupling constant (in Hz)
LDA	Lithium diisopropylamide
$LiAlH_4$	Lithium aluminium hydride

MeI	Methyl iodide
MeLi	Methyl lithium
MeMgCl	Methylmagnesium chloride
Mp	Melting point
MsCl	Methanesulfonyl chloride
m/z	Mass to charge ratio
NEP	*N*-ethyl-2-pyrrolidone
NMO	*N*-methylmorpholine *N*-oxide
NMR	Nuclear Magnetic Resonance
NOESY	Nuclear Overhauser Effect Spectroscopy (2D NMR experiment)
OsO_4	Osmium tetroxide
PhSH	Thiophenol
PMA	Phosphomolybdic Acid
PPh_3	Triphenylphosphine
PPTS	Pyridinium *p*-toluenesulfonate
R	Rest or substituent
Sat.	Saturated
Soln.	Solution
TBAF	Tetrabutylammonium fluoride
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMEDA	Tetramethylethylenediamine
ZnI_2	Zinc iodide

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Chapter 1

Modular approach to trisubstituted alkenes

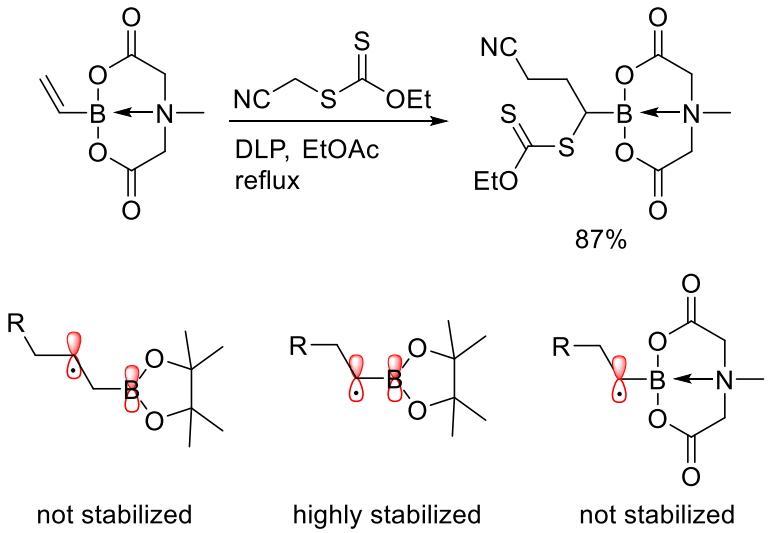
1. Modular approach to trisubstituted alkenes

1.1 Introduction

In this project, vinyl boronic acid esters are used for three-component coupling reactions and the intermediates formed are further modified to obtain trisubstituted olefins. Therefore, first an introduction to the three-component coupling reactions and then to the trisubstituted olefins formed from boronic intermediates is given.

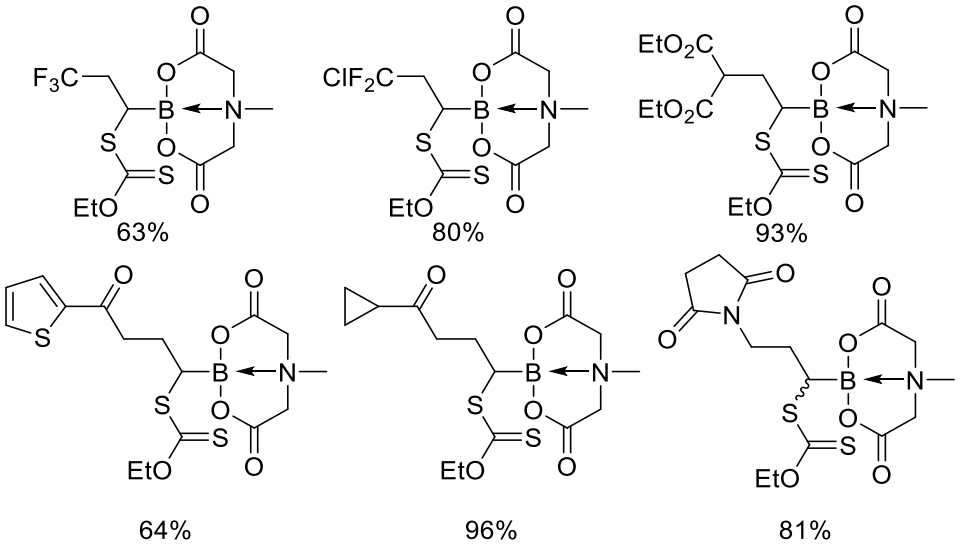
1.1.1 Radical addition to ate complexes of vinylboronic esters

In 2016, Zard published a method for radical addition onto *N*-methyliminoacetic acid (MIDA) boronates (**Scheme 1-1**).[1]



Scheme 1-1 Addition of xanthates to vinyl MIDA boronates by Zard.[1]

Zard has performed radical-mediated xanthate transfers using DLP as a radical initiator, with different boron compounds. Almost no yield was observed when vinylboronic pinacol esters were used, whereas good yields were achieved with allylboronic pinacol esters.[1] As shown in **Scheme 1-1** the boron atom has an empty p-orbital which has an stabilizing effect. While a stabilised intermediate is formed by the addition of vinylboronic pinacol esters, the radical intermediate formed with allylboronic pinacol esters is not stabilised at all. Zard showed that with using MIDA esters, the p-orbital of the boron atom is occupied with the lone pair of the amine, which in turn leads to an unstable intermediate. The change from pinacol to MIDA ester enabled the radical-mediated xanthate transfer to vinyl boronates and selected examples are shown in **Scheme 1-2**.[1]

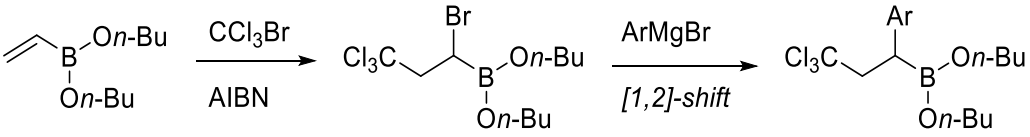


Scheme 1-2 Selected results for the radical addition of xanthates to vinyl MIDA boronates by Zard.[1]

The change to MIDA boronates not only accelerated the addition of electrophilic radicals to the vinyl group, the destabilising effect also benefits the xanthate transfer. With this method in total 24 xanthates were successfully synthesized with yields of up to 95%.[1]

1.1.2 Three-component coupling reactions with ate complexes of vinyl boronic esters

In 1963, Matteson discovered the [1,2]-metalate rearrangement (**Scheme 1-3**).[2]



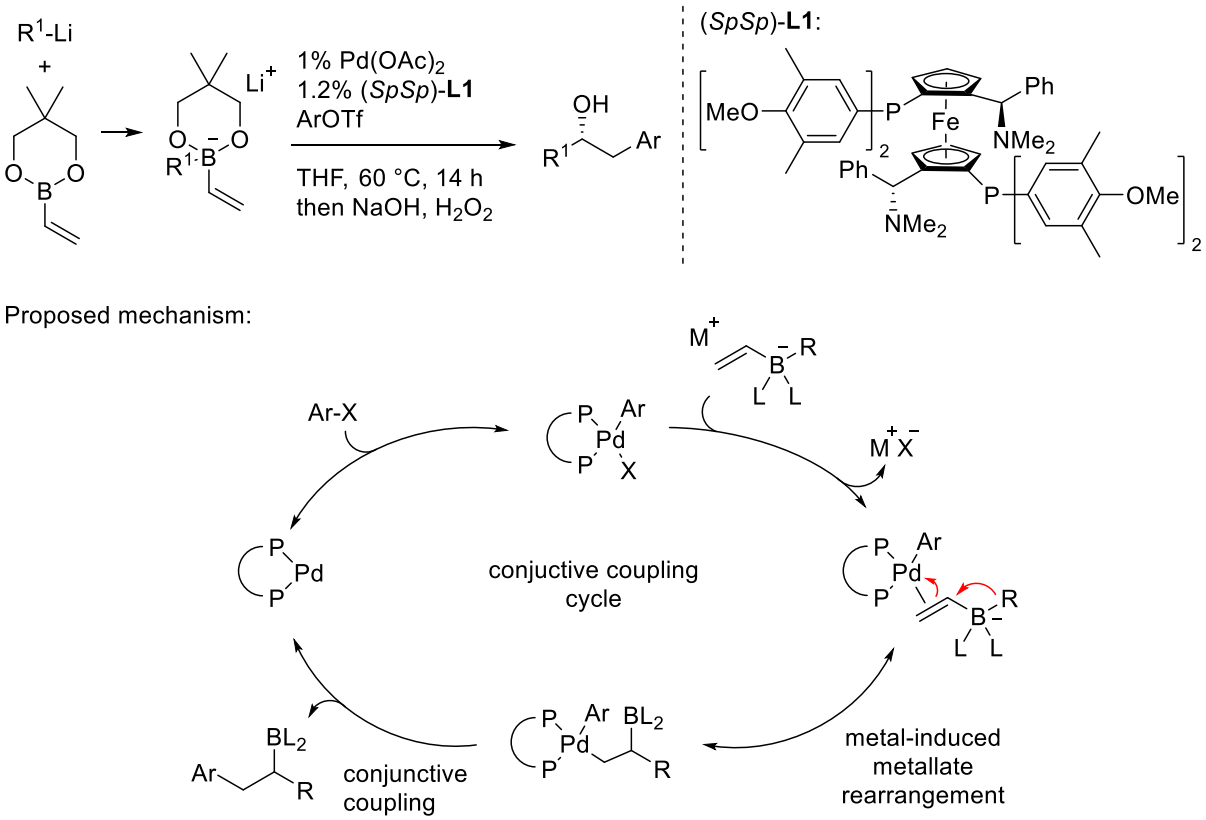
Scheme 1-3 [1,2]-metalate rearrangement discovered by Matteson.

In a first step, Matteson developed the radical addition of bromo trichloromethane to dibutyl ethyleneboronate using AIBN.[3,4] When treating this intermediate with aryl Grignard-compounds, Matteson proposed the formation of an tetracovalent boron anion, which rearranges to the desired product with expulsion of bromide ion. Matteson observed the [1,2]-metalate rearrangement, with aryl and alkyl groups migrating upon mild base treatment.[2]

The groups of Morken[5–7], Studer[8–10], Aggarwal[11–13], Shi[14,15] and Renaud[16,17] presented different approaches for the [1,2]-metalate rearrangement of boronate complexes roughly in the same time frame. In the following, the approaches are categorised according to research groups and discussed.

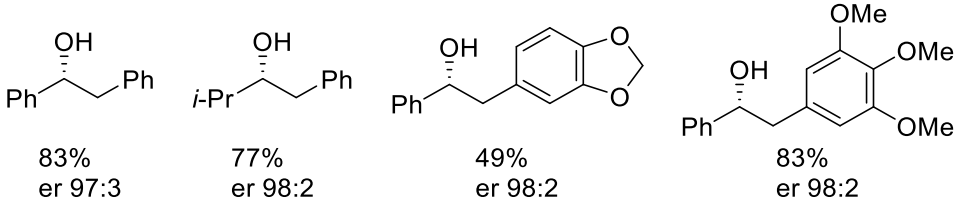
Approach by the group of James P. Morken

In 2016, Morken presented a metal-induced [1,2]-rearrangement on vinyl boron-ate complexes (**Scheme 1-4**).[5]



Scheme 1-4 Metal-induced [1,2]-rearrangement on vinyl boronate complexes by Morten and proposed mechanism.[5]

First, a lithium compound is added to a vinyl boronic ester forming a vinyl boron-ate complex. The formed boron-ate complex takes part then in a conjunctive coupling cycle, in which the conjunctive coupling product or the three-component coupling product is formed. Treatment with NaOH and H_2O_2 oxidises the boronic ester and the desired alcohol is formed.[5] With this protocol Morken synthesized 20 enantioenriched alcohols with yields of 41-83% and enantiomeric ratios of up to 98:2. Selected examples are shown in **Scheme 1-5**.[5]

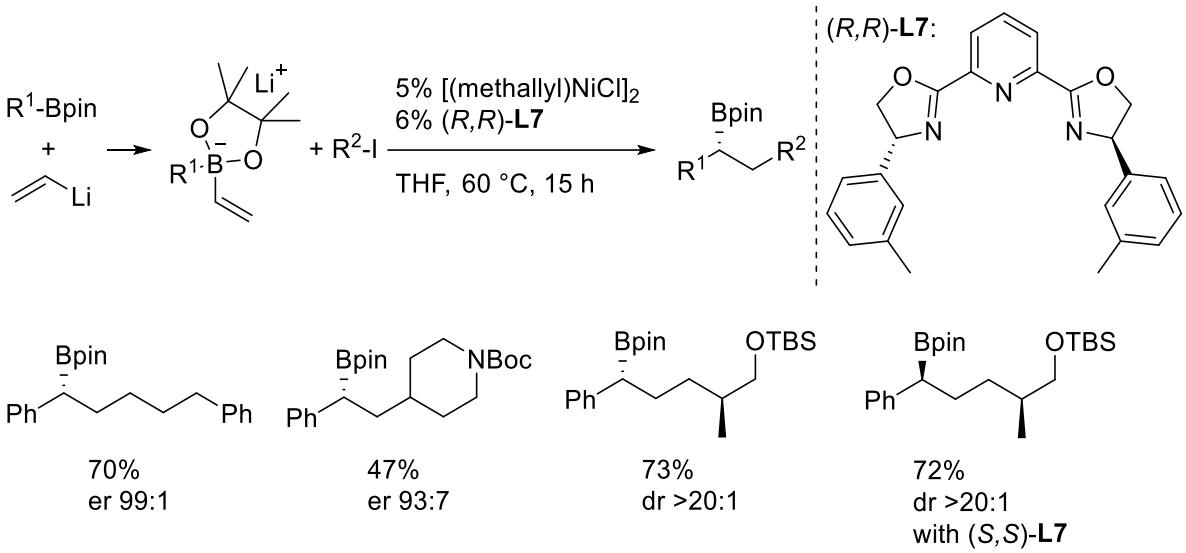


Scheme 1-5 Selected examples of [1,2]-metallate rearrangement reaction by Morken.[5]

Adjusting the protocol by increasing the amount of palladium catalyst and ligand allowed to use vinyl boron-ate complexes generated by vinyl lithium and aryl/alkyl boronic esters for the

conjunctive coupling cycle. This adjustment allows a broader reaction scope and with the optimized protocol further 12 enantioenriched alcohols were synthesized.[5]

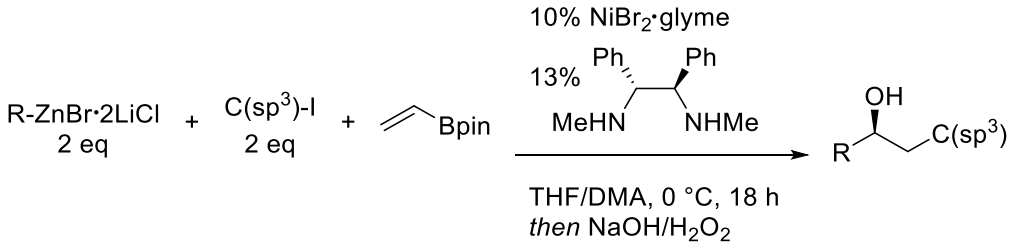
In 2017, Morken presented a modified version using Ni-catalyst allowing to introduce C(sp^3)-electrophiles (**Scheme 1-6**).[6]



Scheme 1-6 Optimized method for [1,2]-metallate rearrangement by Morken.[6]

With the initially designed palladium protocol by Morken C(sp^2)-electrophiles could be introduced via the conjunctive coupling cycle.[5] By changing the catalyst and ligand, Morken presented a similar method which allowed to introduce also C(sp^3)-electrophiles.[6] The Ni protocol requires a higher catalyst and ligand loading, however, it also provides products with high yields and high enantiomeric purity as shown in **Scheme 1-6**. The use of the other enantiomers of the ligand was also possible and led to comparable results.[6]

Another modification was introduced by Morken in 2019 (**Scheme 1-7**).[7]

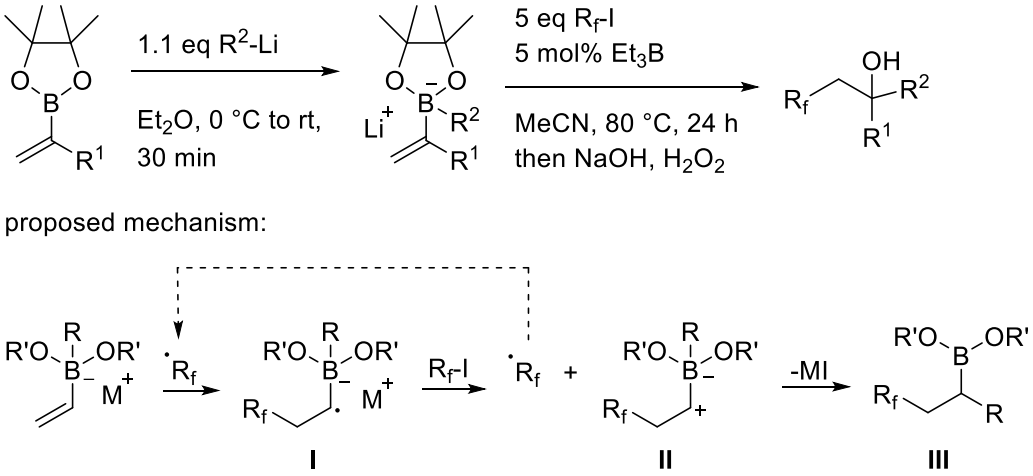


Scheme 1-7 Enantioselective radical addition/cross-coupling reaction by Morken.[7]

The modification included a sequential radical addition cross-coupling reaction with organozinc reagents. In contrast to the first modification[6], where the nickel catalyst acts primarily to initiate the radical reaction, in this modification the nickel catalyst takes on an additional role. After initiation of the radical reaction, it can recombine with the radical boron intermediate and thus influence the stereoselectivity of the reaction.[7]

Approach by the group of Armido Studer

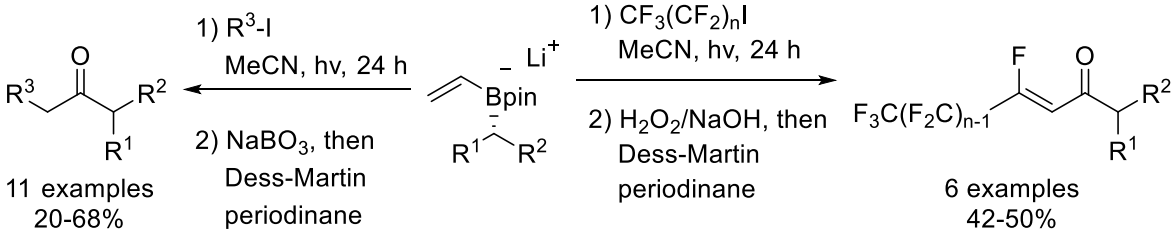
In 2017, Studer presented a radical-induced [1,2]-metalate rearrangement on vinylboron-ate complexes (**Scheme 1-8**).[8]



Scheme 1-8 Radical-induced [1,2]-metalate rearrangement reaction by Studer and proposed mechanism.

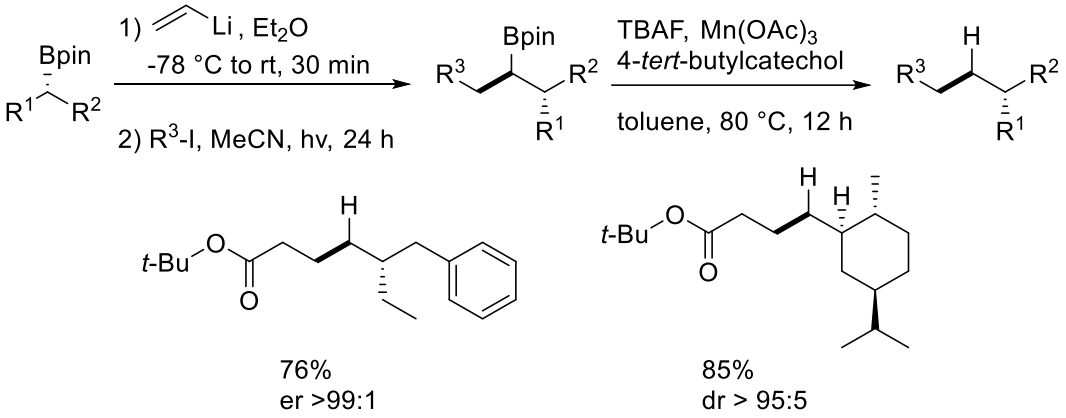
In contrast to Morken[5], who induced the [1,2]-metalate shift with metals, Studer presented a new method in which the rearrangement is induced by radicals.[8] With Studer's protocol first the boron-ate complex is formed in diethyl ether. After a solvent-switch to acetonitrile, perfluorinated alkyl halides were added to the reaction mixture and the radical reaction was started with triethylborane as radical initiator. After oxidation, the desired alcohol was obtained. Studer proposed two possible reaction mechanisms, however, experiments carried out suggest the mechanism shown in **Scheme 1-8**. According to this mechanism, an outer-sphere electron transfer proceeds. First, **I** undergoes an single-electron oxidation to form **II** and generates the perfluorinated radical Rf which can sustain the chain. Ionic [1,2]-rearrangement on **II** should afford **III** and form the final boronic ester. With this method in total 35 examples were prepared in yields of 23-94%.[8]

In 2018, Studer published modified versions of the protocol described above for the synthesis of α-chiral ketones and chiral alkanes (**Scheme 1-9**).[9]



Scheme 1-9 Modified protocols for synthesis of α-chiral ketones and β-fluorinated Michael acceptors by Studer.[9]

Based on the first version of the protocol[8], the boron-ate complex formation was made in diethyl ether, followed by a solvent-switch to acetonitrile. The change in the protocol occurs particularly in the second step, in which the radical initiation of triethylborane is switched to initiation by light. After the boronic ester was formed, various functionalizations were made. Treatment of the boronic ester with sodium perborate yielded the alcohol, which was subsequently oxidised to the ketone using Dess-Martin periodinane. Since the perfluorinated alcohols tend to dehydrofluorinate, treatment of the perfluorinated intermediate with $NaOH/H_2O_2$ yielded an allyl alcohol and, upon oxidation by Dess-Martin periodinane, beta-fluorinated Michael acceptors were obtained in yields of up to 50%. Despite the moderate yields of both functionalizations, high enantiomeric ratios were achieved with both protocols.

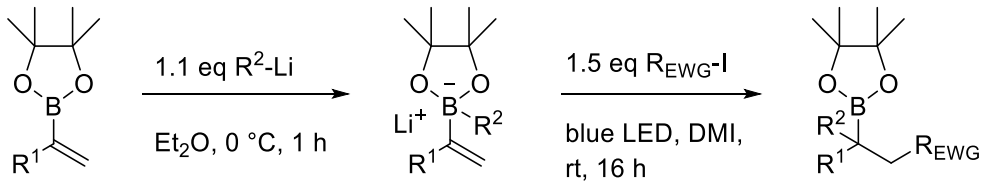


Scheme 1-10 Protodeborylation reaction by Studer.[9]

As shown in **Scheme 1-10**, also a defunctionalization in form of the protodeborylation was possible, whereby four examples were made with yields of up to 85%.

Approach by the group of Varinder K. Aggarwal

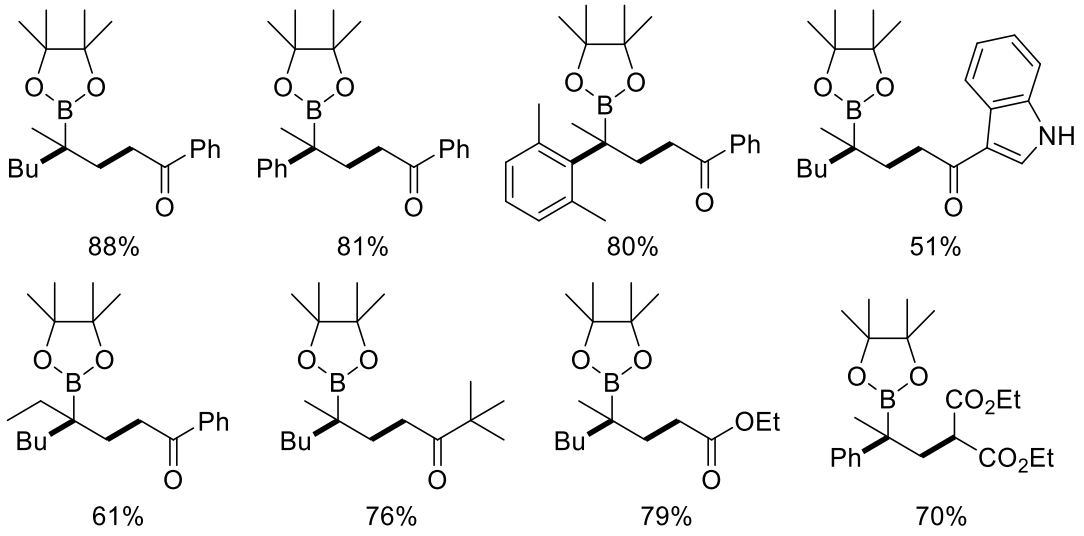
In 2017, Aggarwal presented a similar method for radical-induced [1,2]-metalate rearrangement reaction to Studer based on photochemistry (**Scheme 1-11**).[11]



Scheme 1-11 Radical-induced [1,2]-rearrangement reaction by Aggarwal.[11]

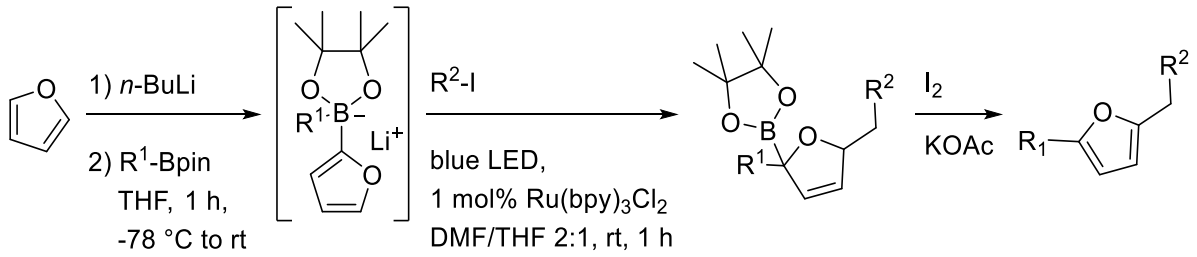
Like for Studer's protocol[8,9] the first step included the formation of the boron-ate complex in diethyl ether, followed by a solvent-switch. After adding 1,3-dimethyl-2-imidazolidinone (DMI) and alkyl halide, the reaction is initiated by blue light and irradiated for 16 h. Here too, the formation of a radical boronic intermediate is proposed, followed by a one-electron transfer to

obtain an ionic boronic intermediate, which undergoes a [1,2]-metalate rearrangement to give the desired product.[11] Interestingly, Aggarwal showed that in some examples the additional use of ruthenium catalyst ($Ru(bpy)_3Cl_2•6H_2O$) can have a supporting impact to obtain higher yields. Furthermore, when alkyl bromides were used for the reaction, addition of sodium iodide (NaI) as an additive increased the yield as well. With this method 27 compounds were successfully synthesized with yields from 25-95% and selected compounds are shown in **Scheme 1-12**.[11]



Scheme 1-12 Selected results with protocol of Aggarwal.[11] Newly formed bonds are in bold print.

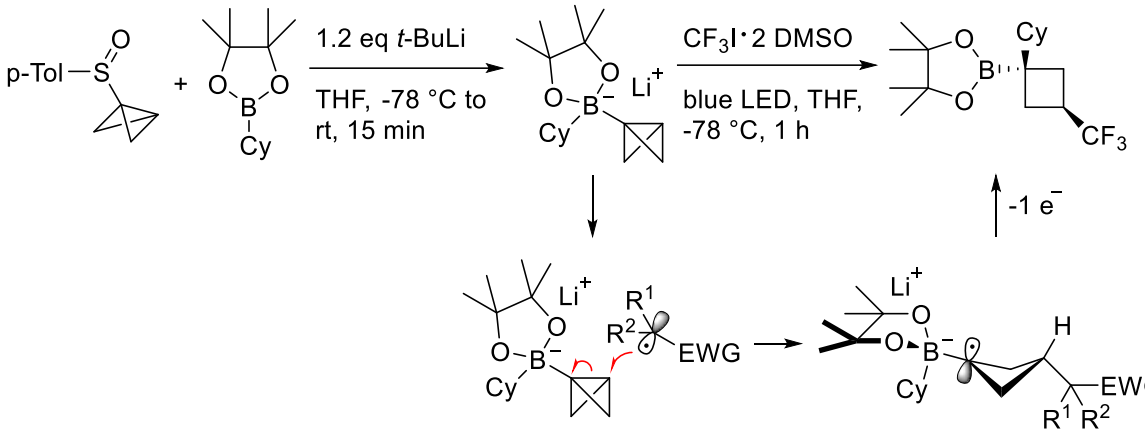
In 2018, Aggarwal used the similar methodology for the enantiospecific three-component alkylation of furan and indole (**Scheme 1-13**).[12]



Scheme 1-13 Enantiospecific three-component alkylation of furan by Aggarwal.[12]

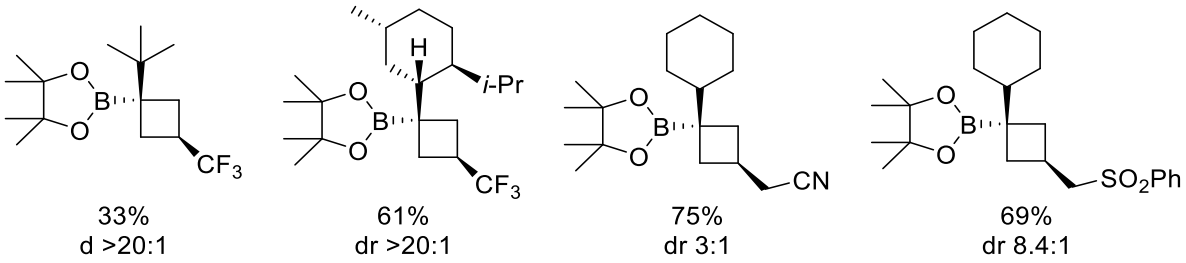
First, furan was deprotonated with *n*-BuLi and reacted with boronic pinacol ester to form a boron-ate complex. After addition of alkyl halide and ruthenium(II) photoredox catalyst, the reaction was irradiated with blue light for one hour. Followed oxidation with I_2/KOAc delivered the desired compound under rearomatization. With this protocol 11 furan derivatives were synthesized in yields of 45-82%. Interestingly, when indole was used, no ruthenium(II) catalyst and no blue light were required for the reaction. In this case, a polar reaction pathway was followed and 8 indole derivatives in yields of 18-93% were synthesized.[12]

In 2019, Aggarwal presented a modified method which allowed to do radical additions to σ-bonds to form cyclobutyl boronic esters (**Scheme 1-14**).[13]



Scheme 1-14 Stereocontrolled synthesis of cyclobutyl boronic esters by Aggarwal.[13]

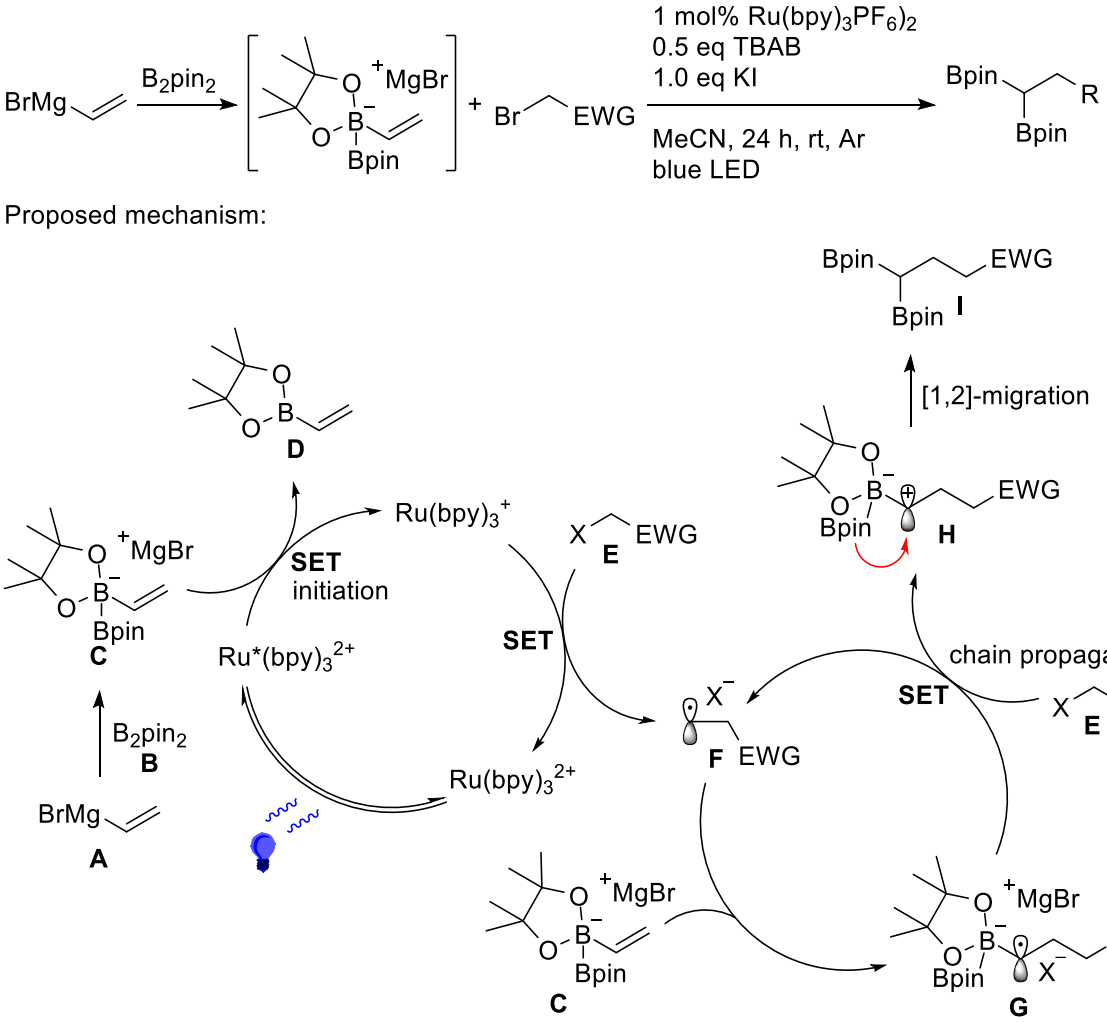
After formation of boron-ate complex, an electron deficient radical is added to open the strained bicyclobutyl boron-ate complex. Followed one-electron oxidation initiates [1,2]-metalate rearrangement and completes formation of the cyclobutyl boronic pinacol ester. With this method, different electron deficient radicals were possible to add containing electron withdrawing groups such as nitriles, esters, amides or sulfones. In total 23 examples were synthesized in yields of 33-90% and dr of up to >20:1. Selected examples are shown in **Scheme 1-15**.[13]



Scheme 1-15 Cyclobutyl boronic pinacol esters synthesized by the method of Aggarwal.[13]

Approach by the group of Zhuangzhi Shi

In 2019, Shi presented a protocol for the synthesis of *gem*-bis(boryl)alkanes based on [1,2]-metalate rearrangement (**Scheme 1-16**).[14]

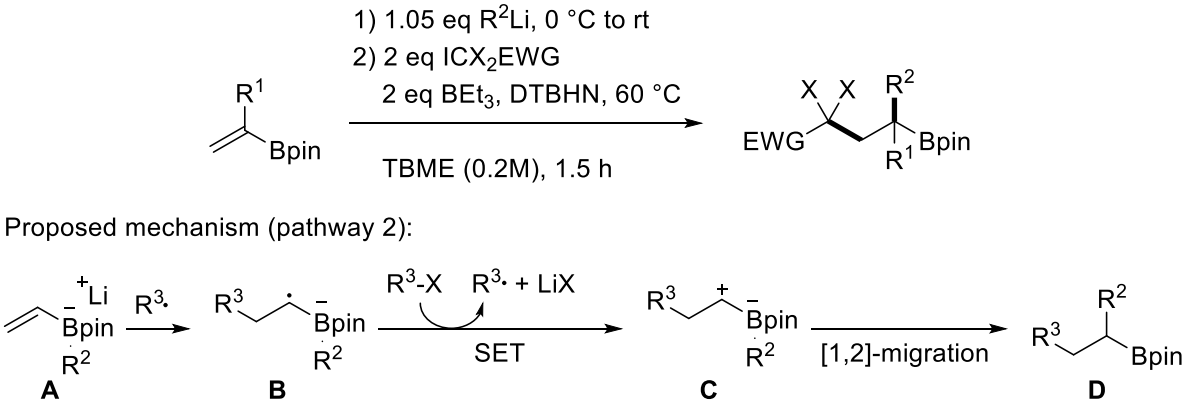


Scheme 1-16 Synthesis of *gem*-bis(boryl)alkanes with proposed mechanism by Shi.[14]

With Shi's protocol commercially or self-made Grignard reagents form with bis(pinacolato)diboron **B** a boron-ate complex. This complex is formed *in situ* during the reaction and participates in the photoredox mediated radical addition process. In the first step a single-electron transfer (SET) takes places where the excited Ru^{2+} is reduced to Ru^{+} and boron-ate complex **C** is oxidized to vinyl boronic pinacol ester **D**. Another SET takes place whereby electrophilic radical **F** is formed and Ru^{2+} regenerated. Intermediate **G** is formed via radical addition of the electrophilic radical **F** to the boron-ate complex **C**. Radical intermediate **G** undergoes another SET delivering ionic intermediate **H** alongside with radical **F**, which sustains the radical chain reaction. Finally, [1,2]-metalate rearrangement of **H** delivers the desired product **I**. A total of 37 compounds were synthesised using this protocol with yields of up to 80%.[14]

Approach by the group of Philippe Renaud

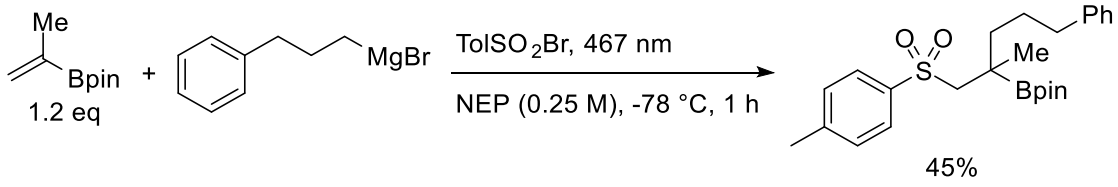
Our group also developed a protocol using the [1,2]-metalate rearrangement. In 2018, Renaud published a radical-triggered three-component coupling reaction of alkenylboronates, α-halocarbonyl compounds, and organolithium reagents (**Scheme 1-17**).[16]



Scheme 1-17 [1,2]-metalate rearrangement reaction by Renaud and proposed mechanism.[16] Newly formed bond are shown in bold.

Like the protocols of Studer[8] and Aggarwal[11], the developed method follows a radical initiated [1,2]-metalate rearrangement.[16] However, by using TBME as solvent, no solvent-switch after the boron-ate complex formation is necessary for the addition reaction. By using an initiator combination of DTBHN and triethylborane, less triethylborane can be used for the three-component reaction and the use of photoredox catalysts and/or co-solvents is not required. Renaud proposed three different mechanism pathways for the three-component reaction, with pathway 2 shown in **Scheme 1-17** being the most supported by mechanistic test reactions. After formation of boron-ate complex **A**, addition of electrophilic radical gives radical anion **B**. The subsequent SET oxidises the radical anion **B** to an inverse ylid **C** and generates an electrophilic radical of R_3-X to sustain the chain reaction. The inverse ylid **C** undergoes [1,2]-metalate rearrangement and the desired three-component coupling product **D** is formed. With this method 29 examples were synthesized in yields of up to 95%. [16]

Later in the group, in the doctoral thesis of Manuel Gnägi-Lux[18], a modified protocol for the three-component coupling reaction using Grignard reagents instead of organolithium reagents is presented (**Scheme 1-18**).



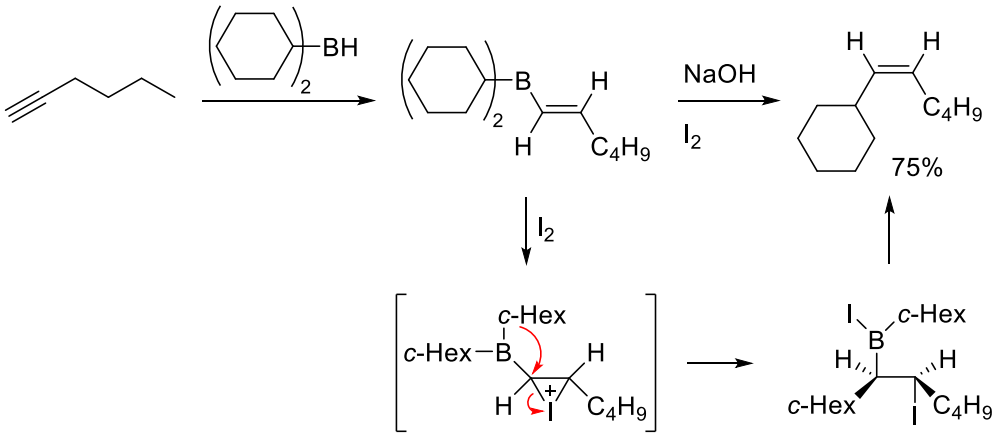
Scheme 1-18 Optimized method for three-component coupling reaction with Grignard reagents.[18]

With this optimized method, first the boron-ate complex is formed with vinyl boronic pinacol ester and the Grignard reagent. After addition of toluene sulfonyl bromide and cooling to -78 °C, radical addition was initiated by irradiation of the reaction mixture with blue light (467 nm), producing toluene sulfonyl radicals that add to the boron-ate complex. SET and followed [1,2]-metalate rearrangement delivered three-component coupling product in 45%. As with the organolithium reagents in the original protocol, no solvent change is required for the reaction, but it was found that the best results were obtained with *N*-ethyl-2-pyrrolidone (NEP).[18]

1.1.3 Trisubstituted olefins from boronic intermediates

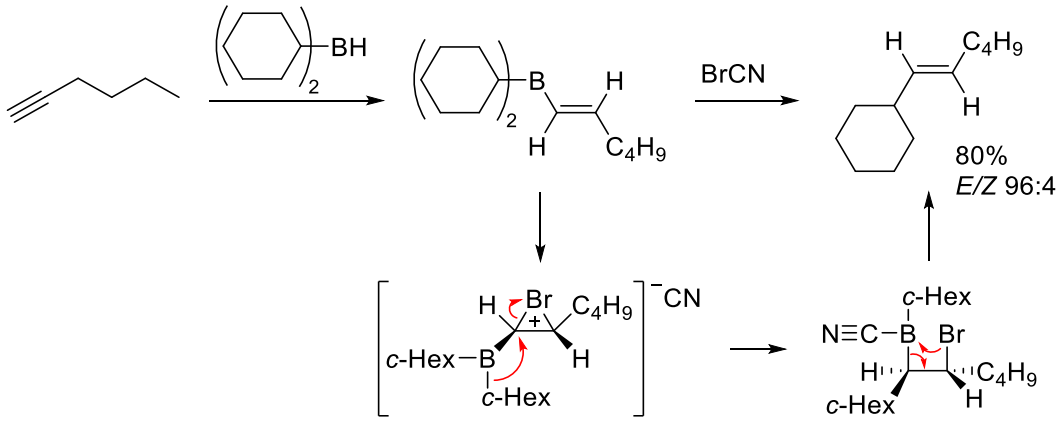
The Wittig[19] and Julia-Kocienski[20,21] olefinations are amongst the most reliable reactions to access disubstituted alkenes. Despite significant advances in the field[22], the preparation of trisubstituted alkenes via one of the afore-mentioned methods still remains challenging. For this purpose, the olefin metathesis[23,24] and cross-coupling reactions[25] with transition metal catalysts have demonstrated their utility. Reactions based upon the use of transition metal-free conditions are also very appealing as alternative approaches and, in this context, organoboron chemistry proved particularly efficient.

In the 1960s, Zweifel and co-workers reported an olefination reaction allowing the preparation of disubstituted alkenes through the coupling of a terminal alkyne and the alkyl residue of a dialkylborane (**Scheme 1-19**).[26]



Scheme 1-19 Zweifel's approach for synthesis of *Z*-selective olefins.[26]

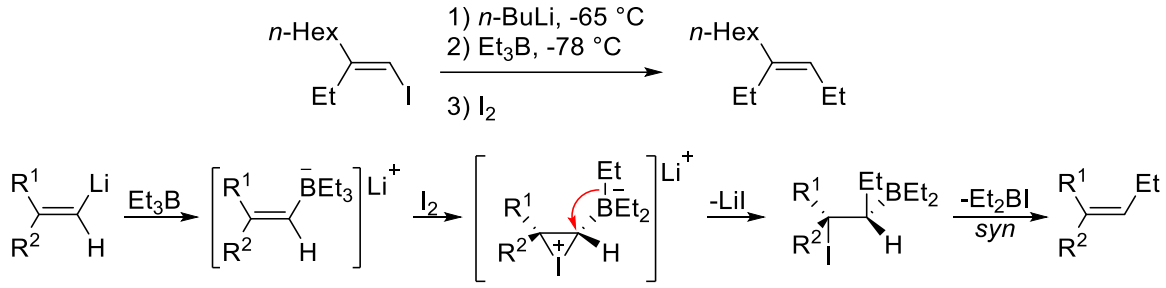
The reaction proceeds via hydroboration of the alkyne, followed by NaOH/I_2–promoted migration of the alkyl residue from the alkenylboron species intermediate. The stereospecificity of the overall process (overall retention of configuration via two consecutive steps taking place with inversion) allowed for the preparation of disubstituted alkenes with very high level of diastereoselectivity in favour of the *Z*-isomer. Interestingly, the stereoselectivity could be reversed simply by using cyanogen bromide in the absence of a base (**Scheme 1-20**).[27]



Scheme 1-20 Zweifel's approach for synthesis of *E*-selective olefins.[27]

Thus, the stereochemical outcome can be explained by a *syn*-elimination process. Alternatively, disubstituted *E*-alkenes could also be obtained by replacing the terminal alkyne by a 1-bromoalkyne. In this case, the hydroboration/1,2-metalate shift sequence delivers a new trisubstituted, alkenylborane intermediate, which undergoes protodeboronation upon heating in the presence of acetic acid.[28]

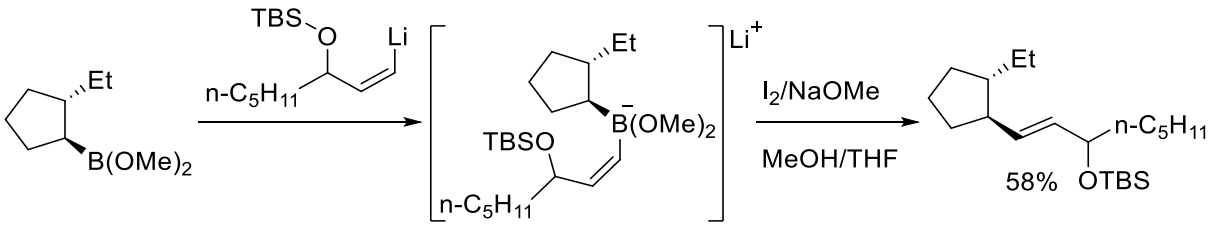
The main limitation of this original Zweifel approach is the access to the dialkylboranes as hydroborating agent and source of alkyl group. In a related process, Levy and co-workers showed that trisubstituted alkenes could be obtained from trisubstituted alkenyl lithium and trialkylboranes in high yields and with excellent levels of retention of configuration (**Scheme 1-21**).[29]



Scheme 1-21 Levy's method for trisubstituted olefins.[29]

In this case, the higher electrophilicity of the alkenyl dialkylborane intermediate compared to borinic esters (as in the original *Z*-selective Zweifel olefination) accounts for a *syn*-elimination process. The main limitation in this case is due to the loss of two alkyl groups on the boron.[29] Brown proposed a solution to circumvent this limitation by using alkylbromoboranes to perform the hydroboration of alkynes, with conversion of the intermediate into the corresponding borinic esters before initiating the [1,2]-migration with I_2/NaOMe.[30] The method proved efficient to access *E*-alkenes.

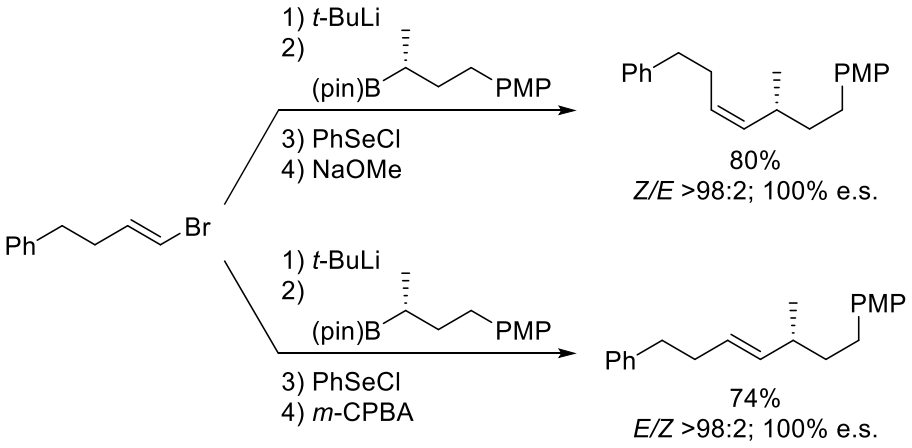
The major improvement however really came when Matteson[31,32] and, shortly later, Evans[33] reported independently a modified Zweifel olefination that used boronic esters as substrates (**Scheme 1-22**).



Scheme 1-22 Modified Zweifel olefination by Evans.[33]

In the modified method, vinyl-lithium compounds were added to boronic acid esters to form a boron-ate intermediate. Treatment with I_2/NaOMe initiated [1,2]-migration and the desired olefin was formed. This approach has significantly contributed to extend the scope of the reaction as not only alkenyl boronic esters, but also alkylboronic esters can now be used.[33]

Thanks to the development of robust methods to access enantio-enriched secondary alkylboronic ester derivatives, the Zweifel olefination has witness a revival in the recent years.[34] Numerous elegant variations of the original Zweifel olefination have been reported in the last 10 years, and the Aggarwal group has been particularly active in this field. For instance in 2017, Aggarwal and co-workers showed that the use of phenylselenyl chloride to trigger the [1,2]-metalate shift could be very useful for the synthesis of *E* or *Z* olefins (**Scheme 1-23**).[35]

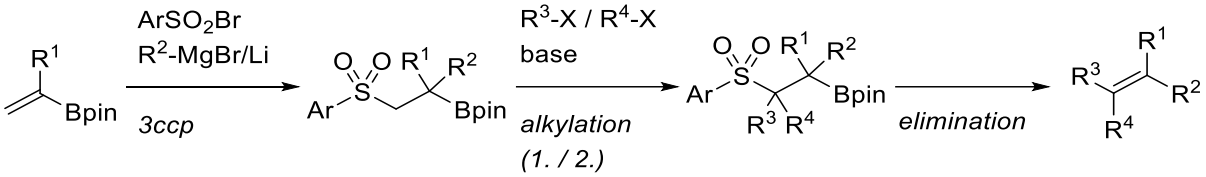


Scheme 1-23 Aggarwal's method using phenylselenyl chloride to trigger the [1,2]-migration.[35]

Depending on the reaction conditions, *syn* or *anti* elimination could be performed, giving access the *E* and *Z* olefins from the same β-selenoboronic ester intermediate, without the need for an alkenyllithium reagent of the opposite configuration. For instance, by using NaOMe, the classical *anti*-elimination is observed, while oxidation with *m*-CPBA led to the formation of a selenoxide intermediate, which is reactive enough to trigger the β-fragmentation via a *syn* elimination mechanism.[35,36]

1.2 Aim of the project

Despite its efficiency, the modern Zweifel olefination still requires the coupling between an alkenyl moiety (alkenylBpin or alkenyllithium), on which all the substituents but one are already present.[34] One possibility to circumvent this limitation was found in a modular, sequential approach to make olefins as shown in **Scheme 1-24**.



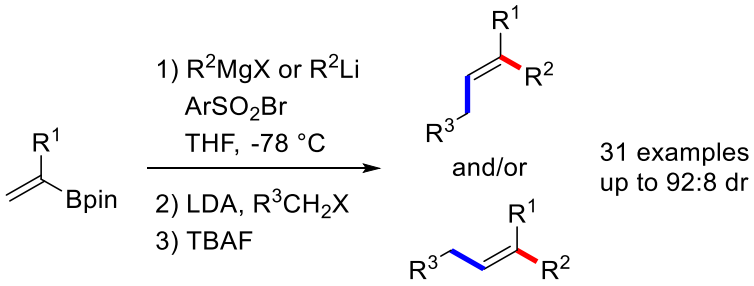
Scheme 1-24 Modular approach to tri-/tetra-substituted olefins.

Starting from vinyl boronic pinacol ester, three-component coupling with aryl sulfonyl bromide and Grignard or organolithium reagent leads to β-borylated sulfones. Alkylation under classical reaction conditions, followed by an elimination reaction, should yield tri- and tetra-substituted olefins. The aim of the project is to develop a suitable protocol to convert alkenyl boronic ester to poly substituted alkenes via the alkylation of β-borylated sulfones and their elimination

1.3 Draft manuscript « modular approach to trisubstituted olefins »

This work was made in collaboration with Dr. Manuel Gnägi-Lux. Dr. Gnägi-Lux made the experiments described in subchapter 1.3.3.a and contributed to subchapter 1.3.3.b. The experimental part only describes the work I carried out myself.

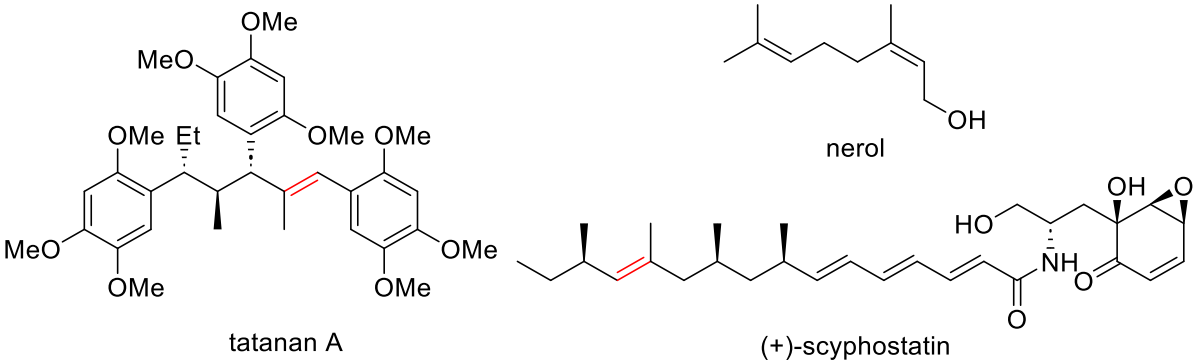
1.3.1 Abstract



A stepwise, Zweifel-type olefination reaction between alkenylboronic acid pinacol esters, alkyllithium (or alkylGrignard) reagents and alkyl halides is reported. The reaction sequence involves a three-component coupling between bromosulfones and the ate-complex of an alkenylboronic acid pinacol ester and an organometalic species. The ate-complexes intermediates could be accessed either from alkenylboronic acid pinacol esters and an organolithium (or organomagnesium) species or, alternatively, from alkylBpin and alkenyllithium reagents. The addition of the sulfonyl radical promotes the migration of the alkyl group leading to β-borosulfones. Unlike previously reported modified Zweifel olefination, the intermediate (here a β-borosulfone) is stable enough to be isolated and can undergo alkylation with alkyl halides under basic conditions. The β-elimination can then be triggered using a source of fluoride, delivering a variety of tri-substituted alkenes in high yields, possibly with a stereogenic centre at the allylic position and with high levels of enantiomeric purity thanks to the robust chemistry of organoboron species. Separation of the diastereomers of the alkylated intermediates allowed for the preparation of *E*- or *Z*-olefins with high levels of stereoselectivity, pointing at a stereospecific (*anti*)-elimination mechanism. The usefulness of the overall process was illustrated by the introduction of stereodefined olefin moieties on a short selection of natural products. The sequence can also be performed in a one pot protocol.

1.3.2 Introduction

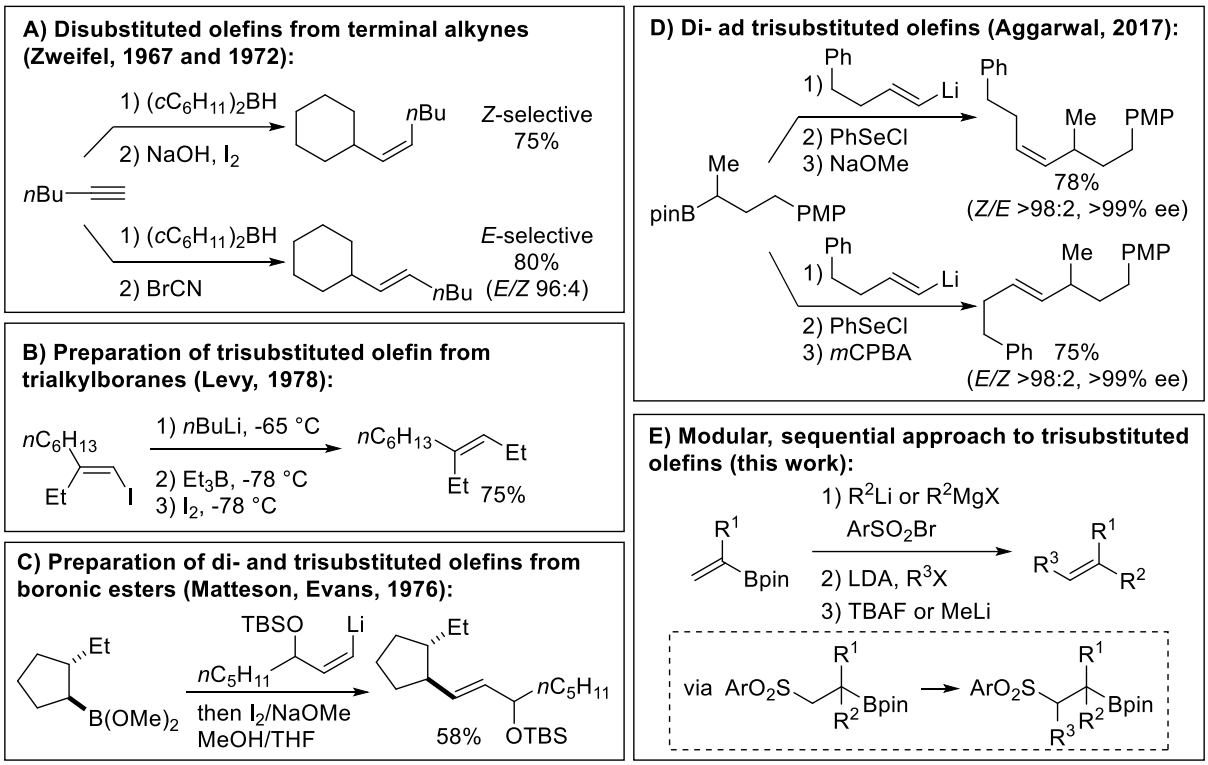
Trisubstituted alkenes are broadly used in the industries in the fields of petrochemicals, oleochemicals, polymers and speciality chemicals.[37] They can also often be found in nature like in terpenes or natural compounds such as those depicted in **Scheme 1-25**.[38–40] Alkenes are successfully produced in industries in large scale and many different methods are known to do this.



Scheme 1-25 Natural compounds containing trisubstituted alkenes.

The Wittig[19] and Julia-Kocienski[20,21] olefinations are amongst the most reliable reactions to access disubstituted alkenes. Despite significant advances in the field,[22] the preparation of trisubstituted alkenes via one of the afore-mentioned methods still remains challenging. For this purpose, the olefin metathesis[23,24] and cross-coupling reactions[25] with transition metal catalysts have demonstrated their utility. Reactions based upon the use of transition metal-free conditions are also very appealing as alternative approaches and, in this context, organoboron chemistry proved particularly efficient. In the 1960s, Zweifel and co-workers reported an olefination reaction allowing the preparation of disubstituted alkenes through the coupling of a terminal alkyne and the alkyl residue of a dialkylborane (**Scheme 1-26**, **A**).[26] The reaction proceeds via hydroboration of the alkyne, followed by NaOH/I_2–promoted migration of the alkyl residue from the alkenylboron species intermediate. The stereospecificity of the overall process (overall retention of configuration via two consecutive steps taking place with inversion) allowed for the preparation of disubstituted alkenes with very high level of diastereoselectivity in favour of the *Z*-isomer. Interestingly, the stereoselectivity could be reversed simply by using cyanogen bromide in the absence of a base (**Scheme 1-26**, **A**).[27] In this case, the stereochemical outcome can be explained by a *syn*-elimination process. Alternatively, disubstituted *E*-alkenes could also be obtained by replacing the terminal alkyne by a 1-bromoalkyne. In this case, the hydroboration/1,2-metalate shift sequence delivers a new trisubstituted, alkenylborane intermediate, which undergoes protodeboronation upon heating in the presence of acetic acid.[28] The main limitation of this original Zweifel approach is the access to the dialkylboranes as hydroborating agent and source of alkyl group. In a related process, Levy and co-workers showed that trisubstituted alkenes could be obtained from trisubstituted alkenyl lithium and trialkylboranes in high yields and with excellent levels of retention of configuration (**Scheme 1-26**, **B**).[29] In this case, the higher electrophilicity of the alkenyl dialkylborane intermediate compared to borinic esters (as in the original *Z*-selective Zweifel olefination) accounts for a *syn*-elimination process. The main limitation in this case is due to the loss of two alkyl groups on the boron. Brown proposed a solution to circumvent this limitation by using alkylbromoboranes to perform the hydroboration of alkynes, with conversion of the intermediate into the corresponding borinic esters before initiating the 1,2-migration with

I_2/NaOMe.[30] The method proved efficient to access *E*-alkenes. The major improvement however really came when Matteson[31,32] and, shortly later, Evans[33] reported independently a modified Zweifel olefination that used boronic esters as substrates (**Scheme 1-26**, **C**). This approach has significantly contributed to extend the scope of the reaction as not only alkenyl boronic esters, but also alkylboronic esters can now be used.



Scheme 1-26 Olefination with boron compounds.

Thanks to the development of robust methods to access enantio-enriched secondary alkylboronic ester derivatives, the Zweifel olefination has witness a revival in the recent years.[34] Numerous elegant variations of the original Zweifel olefination have been reported in the last 10 years, and the Aggarwal group has been particularly active in this field. For instance, Aggarwal and co-workers showed that the use of phenylselenyl chloride to trigger the 1,2-metallate shift could be very useful as, depending on the reaction conditions, *syn* or *anti* elimination could be performed, giving access the *E* and *Z* olefins from the same β-selenoboronic ester intermediate, without the need for an alkenyllithium reagent of the opposite configuration. For instance, by using NaOMe, the classical *anti*-elimination is observed, while oxidation with *m*CPBA led to the formation of a selenoxide intermediate, which is reactive enough to trigger the β-fragmentation via a *syn* elimination mechanism (**Scheme 1-26**, **D**).[35,36] Despite its efficiency, the modern Zweifel olefination still requires the coupling between an alkenyl moiety (alkenylBpin or alkenyllithium), on which all the substituents but one are already present. We present herein a stepwise Zweifel-type olefination reaction giving access to di- and tri-substituted alkenes, in which the substituents are introduced via three different partners,

an organolithium (or organomagnesium species), an alkenylBpin and an electrophile such as an alkyl halide, using a sulfonyl bromide (**Scheme 1-26**, **E**). The reaction proceeds via the formation of β-sulfonoboronic ester intermediate, which, unlike previous related intermediates of the Zweifel reaction, can be alkylated under classical reaction conditions, before elimination to give the desired alkenes.

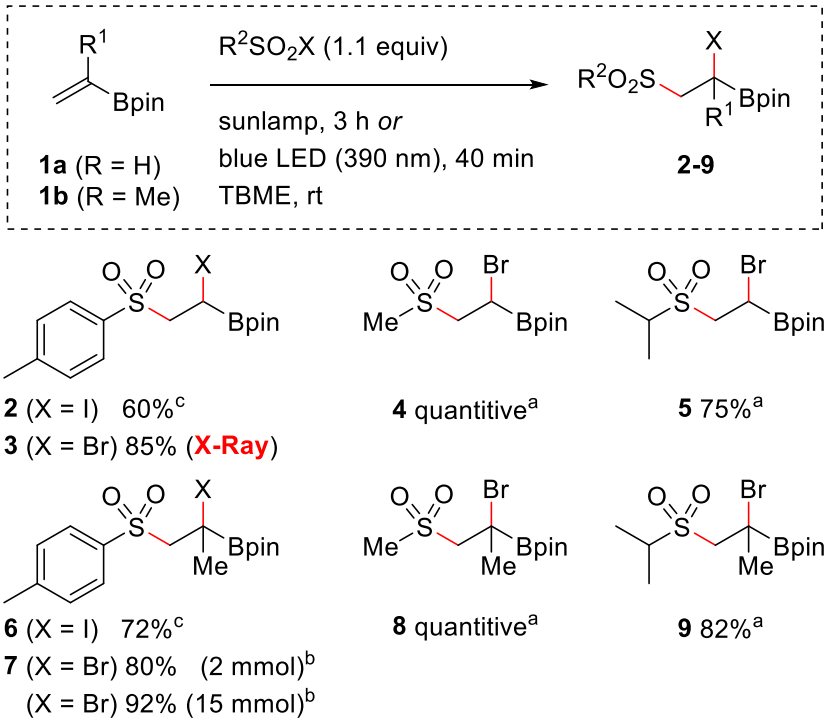
1.3.3 Results and discussion

a) Bromosulfonylation of alkenylboronic esters

The radical addition of electrophilic radicals to boron-substituted alkenes can be dated back to the 1950s with Matteson's report on the radical addition of electrophilic radicals derived from polyhalomethanes to dibutyl ethylene boronate and dibutyl propene-2-boronate.[4,3] Similarly, the use of bromomalonitrile delivered the corresponding atom transfer radical addition (ATRA) product in good to high yields.[41] The addition of sulfonyl halides, and mainly sulfonyl iodides, to alkenylboronic acid pinacol ester has been pioneered by Carboni and co-worker.[42] The dehydroiodination of α-iodo β-sulfonyl alkylboronic ester ATRA adducts could be achieved in the presence of a mild base and, depending on the reaction conditions, delivered the corresponding β-sulfonyl vinylboronic esters, or borylated allylsulfones.[42] We acknowledged that these α-halo β-sulfonyl alkylboronic ester could serve as platform to introduce two new substituents, sequentially, first by taking advantage of the well-known reactivity of α-haloBpin derivatives in presence of nucleophiles, then by using the classical chemistry of sulfones to introduce an electrophile at the α-position. We decided then to start our study by exploring the reactivity of the α-halo β-sulfonyl alkylboronic esters in the presence of organometallic species.[43,44]

In our first attempts, the use of arylsulfonyl chloride proved inefficient upon prolongated irradiation with a sunlamp. On the contrary, as reported by Carboni and co-workers, tosyl iodide reacted with vinylBpin at room temperature in CH_2Cl_2 to give the corresponding ATRA product **2** in 60% yield (**Scheme 1-27**). The UV-VIS spectrum of tosylbromide suggested that the reaction could be efficiently initiated upon blue LED irradiation (390 nm). Based on our recent work on three-component coupling reaction between alkenylboronic esters, organolithium reagents and sources of electrophilic radicals,[16] TBME was rapidly selected as the solvent of choice for this ATRA reaction. The reaction proved efficient for representative primary, secondary, and aromatic sulfonylbromides (**Scheme 1-27**). For instance, the addition on tosylbromide to vinylBpin **1a** was achieved at room temperature upon irradiation with blue LEDs, delivering the ATRA product **3** in 85% yield. Likewise, the addition of tosylbromide to 4,4,5,5-tetramethyl-2-(prop-1-en-2-yl)-1,3,2-dioxaborolane (propenylBpin) gave the corresponding adduct **7** in 80% yield (2 mmol scale). Gratifyingly, **7** was isolated in excellent

yield by running the reaction on a larger scale (92%, 15 mmol scale). The addition of tosyliodide to isopropenylBpin also delivered the ATRA adduct **6**, albeit in slightly lower yield (72%). Alkanesulfonyl bromides also gave excellent results, as illustrated by the addition of methanesulfonyl bromide to vinylBpin **1a** and propenylBpin **1b**, the corresponding ATRA products **4** and **8** being isolated in quantitative yields. Under these mild reaction conditions, even secondary alkanesulfonyl bromides could be used without noticeable fragmentation of the sulfonyl radical intermediate. For instance, the addition of isopropylsulfonyl brimide to vinylBpin **1a** and propenylBpin **1b** furnished **5** and **9** in 75% and 82% yields, respectively. On the contrary, the use of tertiary sulfonylbromides did not allow for the preparation of the ATRA adducts, presumably either because of the decomposition of the reagent,[45] or the fast desulfonylation of the sulfonyl radical intermediate.[46,47] It should be noted that commercially available vinyl- and isopropenylboronic acid pinacol esters sometimes contain stabilizer that efficiently inhibit the reaction.

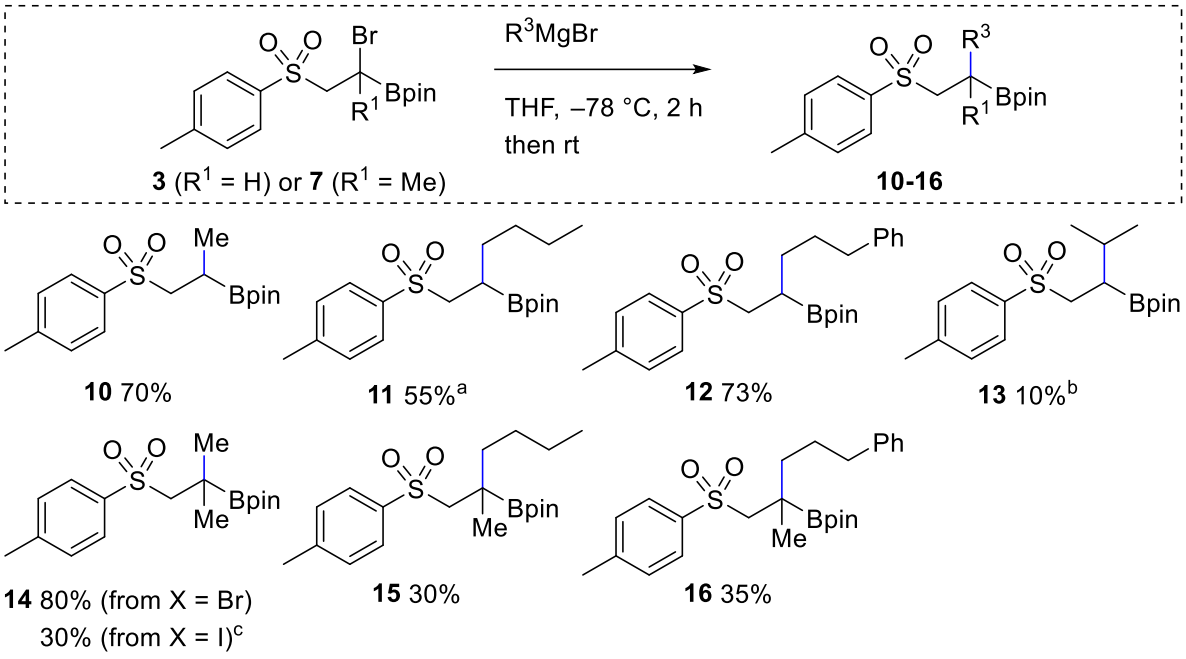


Scheme 1-27 Bromosulfonylation of alkenylboronic esters. [a] 3 h & sunlamp, [b] 40 min & blue LED, [c] 3.0 eq $TolSO_2I$, DCM, 2 h, rt

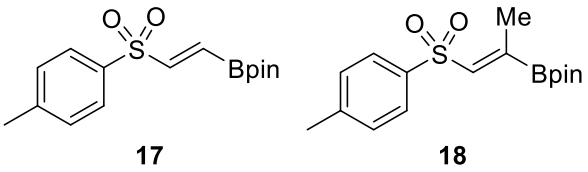
Under our reaction conditions, no ATRA product was observed with tosylsulfonyl bromide and non-terminal alkenylboronic acid pinacol esters, such as (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. This is in contrast with the pioneering report of Carboni and co-workers, in which the radical addition of tosyliodide was observed with the same boron-substituted alkene, albeit without yield and a significant drop in the regioselectivity.[42]

The reactivity of these α-bromo β-sulfonylalkylboronic esters in the presence of organometallic species was investigated next. The main difficulties reside in the possible and unwanted β-elimination of the ate-complex intermediate leading to alkenes prior to the desired 1,2-metalate shift, or the deprotonation α to the sulfonyl group that would deliver β-sulfonyl alkeneboronic esters via the elimination of the bromine atom.

The α-bromo β-sulfonylalkylboronic esters engaged in reaction with alkylmagnesium bromides to give substituted β-sulfonyl alkenylBpin derivatives **10-16** (**Scheme 1-28**). Using secondary boronic ester **3**, primary alkylmagnesium bromides reacted smoothly at low temperature to give the intermediate ate-complexes, which underwent spontaneous 1,2-metalate shift, delivering the desired products **10-12** in moderate to good yields. The use of bulkier reagents proved less successful, as illustrated by the reaction of isopropylmagnesium bromide with **3**, which gave adduct **13** in very low yield. In this case, the major product was the borylated alkenylsulfone resulting from HBr elimination. Counter-intuitively, the use of the more nucleophilic organolithium reagents proved more problematic. For instance, the use of *n*-butyllithium delivered **11** in only 7% yield. The addition of methyl magnesium bromide to **7** gave the product of 1,2-metallate shift **14** in high yield (80%). Surprisingly, other primary Grignard reagents such as *n*-butylmagnesium bromide and 3-phenylpropyl magnesium bromide gave deceiving results, the products **15** and **16** being isolated in only poor yields (30% and 35%, respectively). Worthy of note, the use of the corresponding iodo-derivative analogue to **7** in this reaction led a mixture of products containing the desired functionalized β-borosulfone **14**, the borylated alkenylsulfone resulting from HBr elimination and an unexpected product, propenylBpin **1b**, which presumably arises from iodine-magnesium exchange (**Scheme 1-28**).



a: 7% with *n*BuLi instead of *n*BuMgBr
b: borylated alkenysulfone **17** resulting from HBr elimination was obtained as the major product
c: mixture containing **14** (30%), borylated alkenysulfone **18** (40%) and isopropenylBpin (25%) (ratio determined by NMR)



Scheme 1-28 Reaction of α-bromo β-sulfonylalkylboronic esters with organometallic reagents.

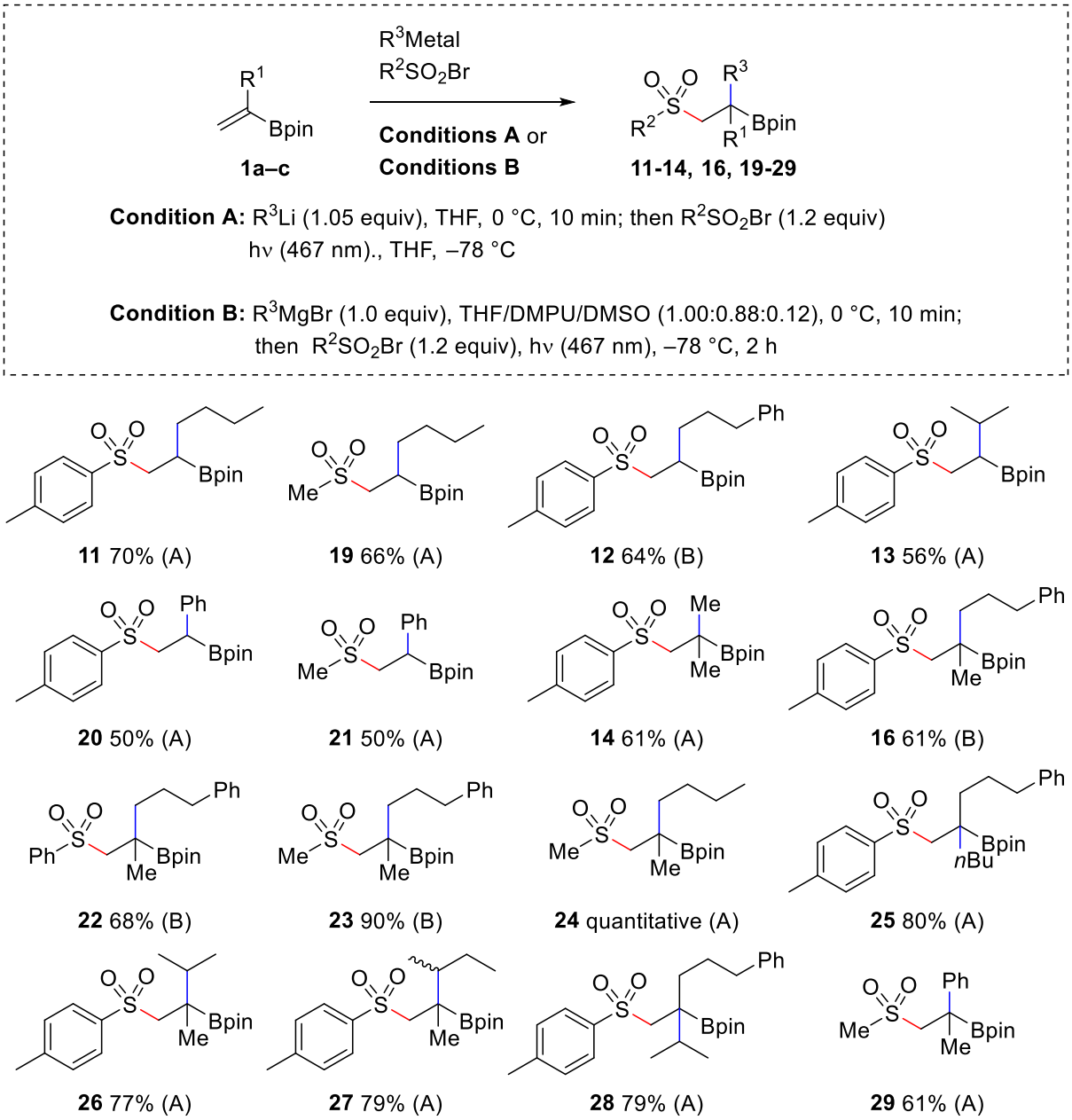
It is noteworthy that a certain time at low temperature was required before addition of the sulfonylbromide, presumably to complete the formation of the ate-complex. Addition of $ZnCl_2$ to facilitate the 1,2-alkylmigration proved ineffective.

b) Three-component coupling reaction:

The afore-mentioned limitations with some substituted α-bromo β-sulfonylalkylboronic esters not reacting with primary alkyl Grignard reagents other than MeMgBr or with alkyllithium reagents, prompted us to explore a three-component coupling involving transient alkenylboron ate-complexes as radical traps. It has been demonstrated that alkenylboron ate-complexes species participated efficiently in ATRA processes, with a halogen atom (or xanthate) transfer step favoured by the lack of stabilization of the α-boryl radical intermediate.[1,48–52] Since 2017, a series of three-component coupling processes involving an initial ATRA process involving electrophilic radicals and ate-complexes of vinylboronic pinacol ester and organolithium (or

organomagnesium) reagents, followed by a subsequent 1,2-metallate shifts of alkyl residues have been developed.[8–13,16,17,51,53–58]

The three-component coupling reaction was tested first with ate-complexes of alkenyl boronic esters **1a–b** and alkyllithium reagents (**Scheme 1-29**). Pleasingly, when vinylBpin **1a** was treated with *n*-butyllithium (1.05 equivalents) in THF at 0 °C, then with tosylbromide (1.2 equivalents) at –78 °C, the three-component adduct **11** was obtained in 70% yield. Using methanesulfonyl bromide, the corresponding adduct **19** was obtained in a comparable 66% yield. The use of phenyllithium delivered the three-component coupling product **21** in a moderate 50% yield. Primary alkyllithium (MeLi and *n*-butyllithium) were suitable partners for the three-component coupling using isopropenylBpin **1b** with tosylbromide and methylsulfonylbromide, delivering **14** and **24** in 61% and quantitative yields, respectively. The primary alkylmagnesium bromide (3-phenylpropyl magnesium bromide) failed to give the desired coupling products in satisfactory yields in THF, presumably due to incomplete boron ate complex formation. This limitation was overcome by using a ternary solvent system (THF/DMPU/DMSO 1.00:0.88:0.12)[59–61] and the adducts **16**, **22** and **23** were obtained in moderate to excellent yields (61–90%).

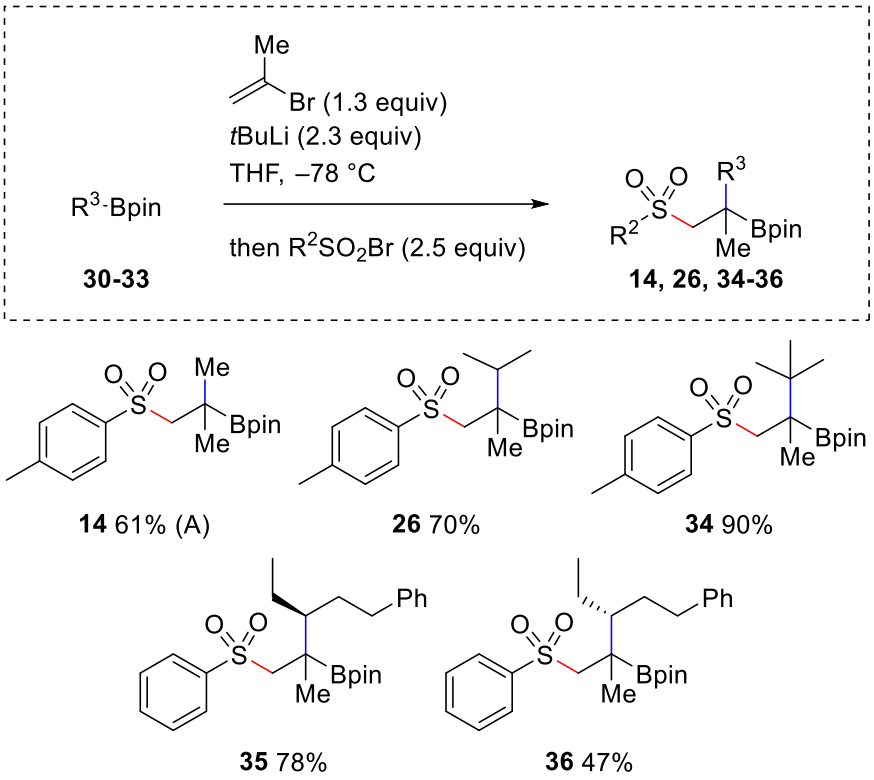


Scheme 1-29 Three-component coupling reactions.

Interestingly, unlike what was observed in the two-step process (vide supra), secondary alkyl lithium reagents participated in the three-component coupling, delivering **26** in 44% and **27** in 79% yields from isopropyllithium and sec-butyllithium, respectively. The methanesulfonyl bromide-mediated coupling between the boron-ate complex of phenyllithium and isopropenylBpin **1b** gave the expected product **29** in 61% yield. Additionally, the three-component coupling with 4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane **1c** (R^1=$CH_2CH_2CH_2Ph$) delivered **25** in 80% and **28** in 79% yields from *n*-butyllithium and isopropyllithium, respectively.

To extend the scope of the three-component coupling reaction, possibly to include substrates presenting a controlled stereogenic centre, we briefly explore the possibility of performing the

reaction using alkylBpin precursors and alkenyl lithium reagents. Pleasingly, the reaction of methylBpin **30**, isopropylBpin **31**, phenylpentan-3-ylBpin **32a** & **32b** and *tert*-butylBpin **33** with tosylsulfonyl bromide **2a** and in situ prepared isopropenyllithium, delivered the desired three-component coupling products in moderate to good yields (52–90% yields) (**Scheme 1-30**).

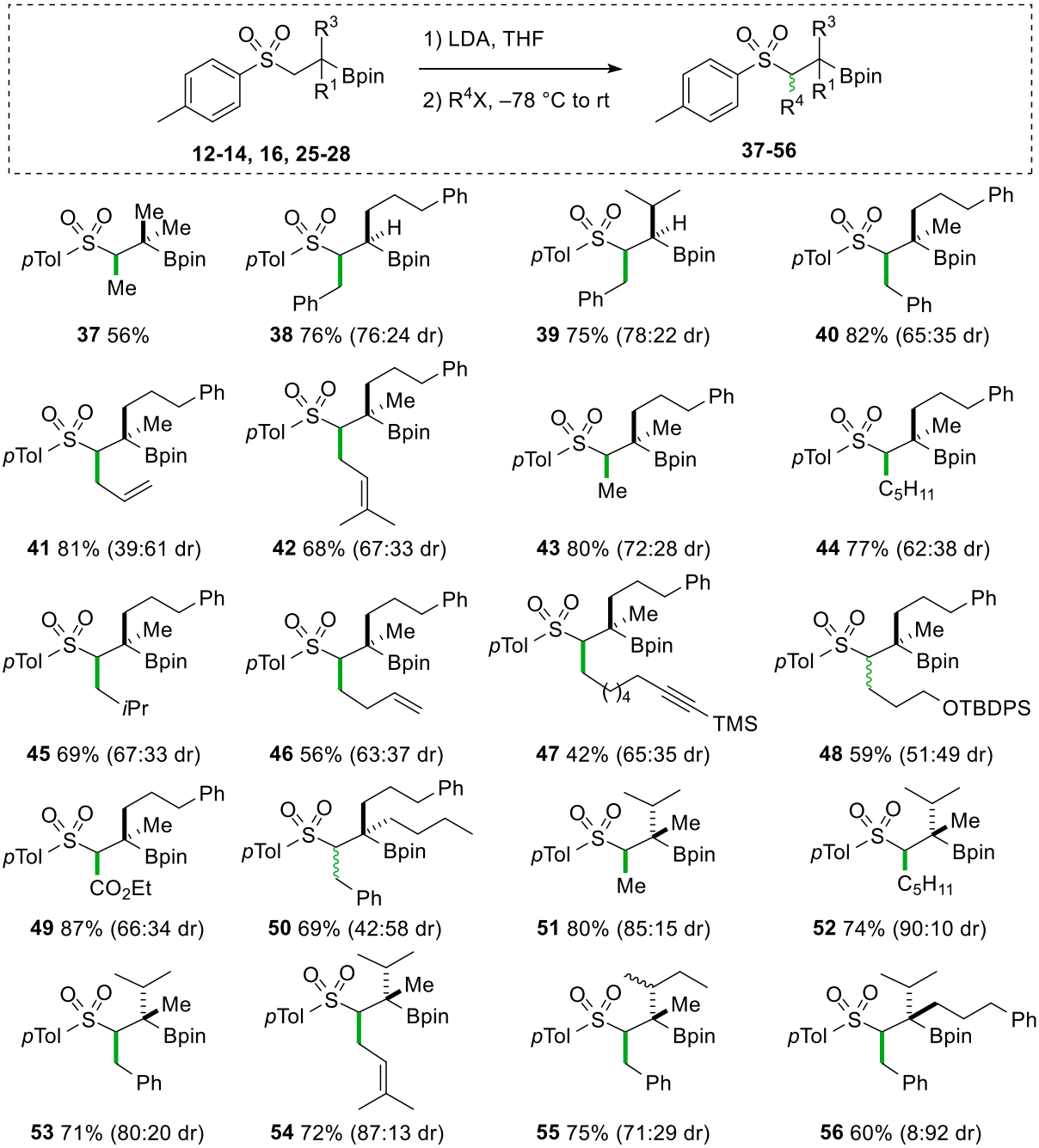


Scheme 1-30 Three-component coupling reaction with alkyl boronic ester.

c) β-Alkylation

Alkylation of enolates presenting a Bpin moiety at the β-position have been reported.[62–65] Borylated allylic sulfones have been alkylated in fair to good yields with alkyl iodides or allyl- and benzyl bromides via α-deprotonation of the sulfonyl moiety with LDA.[66,67] The authors showed that, amongst the different solvent tested, THF gave the best results and that the concentration had a dramatic influence on the yields. The introduction of an electrophile via α-deprotonation of the β-borosulfones was initially tested on precursors prepared using arenesulfonyl bromides to avoid any complications due to the regioselectivity of the deprotonation step. A rapid screening of the base showed that deprotonation with LDA or LiHMDS gave the best results in terms of yields, while the use of *n*BuLi, a base commonly used to achieve the α-deprotonation of sulfones, led to decomposition of the starting material. In this case, the olefin resulting from a β-elimination process was obtained, presumably via the formation of a boron-ate complex intermediate. Under the optimized reaction conditions (LDA, 1.0 equivalents; electrophile, 1.2 equivalents, THF, –78 °C to rt), the α-alkylated β-

borosulfones **37-56** (**Scheme 1-31**) were obtained in moderate to good yields with primary alkyl iodides (42–80 % yields) and in good to high yields with activated electrophiles such as benzyl bromide, allyl- and 1-bromo-3-methylbut-2-ene, and ethylchloroformate (68–87%). The alkylated products were obtained in all case with moderate levels of diastereoselectivity (from 61:39 dr to 72:28), presumably because the similar size of two substituents at the α-position (Me vs. primary alkyl chain). Gratifyingly, as illustrated by the preparation of **51-55**, increasing the steric hindrance at the β-position (precursors presenting a methyl and a branched alkyl chain), did not affect the yield of the alkylation step but the levels of diastereoselectivity (up to 90:10 dr) in this case were noticeable higher than those observed when both a methyl and a primary alkyl chain were present at the β-position. When a primary or secondary alkyl chain and a proton were present in the β-position, as in **38** and **39**, good yields were obtained in both cases (75 and 76%, respectively), but again with moderate diastereoselectivity (from 76:24 dr to 78:22). Fortunately, by introducing a secondary group next to the primary alkyl chain in the β-position as in **56**, the best diastereoselectivity of 8:92 dr could be achieved with 60% yield.



Scheme 1-31 β-Alkylation reactions.

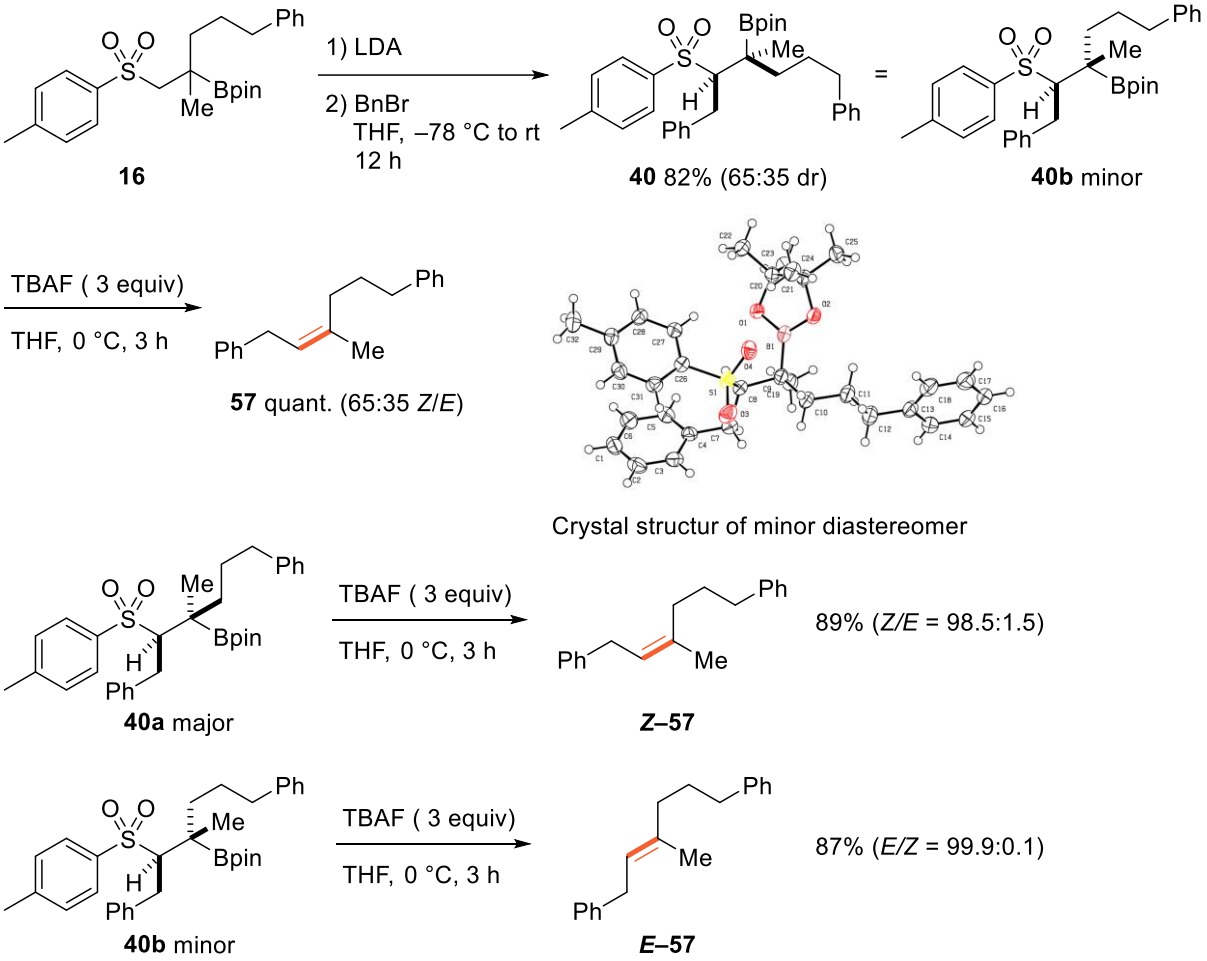
d) Second alkylation

The metalation of α-branched alkylarylsulfones has been studied in great details. Jahn reported a comprehensive study of the metalation of sterically hindered sulfones and showed that sulfone-directed ortho-metalation was the main pathway at –78 °C in THF using LDA as a base, while metalation at 0 °C delivered the α-metalated sulfones.[68] Beside the effect of the temperature, the substitution pattern and the presence of additives (TMEDA, HMPA...) also proved to dramatically influence the course of the reaction. The configurational stability of the lithiated anion has been studied by Gais and co-workers and it was found that certain sulfones

had relatively long (several hours) at very low temperature. Additives such as HMPA or TMEDA were not found to influence greatly this configurational stability.[69] The alkylation of branched allylic α-borosulfones has also been reported but in a cyclic systems, in which β-elimination via the formation of a boron-ate complex could not compete with the desired α-deprotonation.[66] Unfortunately, in our hands the introduction of a second electrophile at the α-position through the metalation of the α-branched, β-borosulfones presenting of a quaternary centre failed, making this approach inefficient to access tetrasubstituted alkenes.

e) Elimination reaction

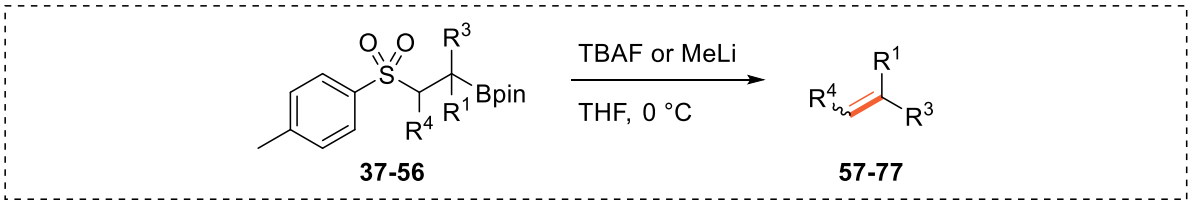
As already discussed in the introduction, two possible mechanisms can operate for the β-elimination of boronic esters presenting a leaving group at the β-position. In our case, the moderate selectivity of the alkylation step, resulted in the formation of a mixture of *E* and *Z*-alkenes after elimination. In most cases, the *E*/*Z* ratio correlated very well with the levels of diastereoselectivity observed for the alkylation step (**Scheme 1-32**). For instance, the 65:35 mixture of diastereomers **40** led, upon treatment with TBAF (3 equivalents), to a mixture of *Z* and *E*-alkenes in a 65:35 ratio. As the diastereomers of the β-borosulfones can usually be separated by flash column chromatography on silica gel, the stereospecificity of the elimination could be demonstrated by treating the two diastereomers with TBAF separately. Moreover, the structure of the minor isomer of **40b** could be ascertain by X-ray diffraction crystallography and assigned as *like*. Unlike allylic β-borosulfones studied by Harmata,[66] an interaction between the boron atom and one of the oxygen atoms of the sulfonyl group could be observed in the crystal structure of **40b**. Treatment of this diastereomer as previously delivered ***E*-57** (*E*/*Z* = 99.9:0.1) (**Scheme 1-32**). Based upon the relative configuration in **40b**, an anti-elimination mechanism can be proposed for the formation of the alkenes from β-borosulfones. Likewise, the major isomer **40a** was converted to the corresponding alkene, obtained this time as the *Z*-isomer (*Z*/*E* = 98.5:1). This contrast with the elimination of selenoxide, for which a *syn*-elimination mechanism is taking place,[35] indicating that the complexation of the sulfone with the boron atom, if taking place (see X-ray diffraction structure), is not sufficient to trigger a *syn*-elimination process.



Scheme 1-32 Elimination reaction of the diastereomer mixture and the main and minor diastereomers separately.

The sequence resembles the "stereocontrolled Horner-Wittig Reaction" reported by Warren and co-workers, which involved in the second case the Horner-Wittig addition, the purification of the intermediate, and finally the Horner-Wittig elimination.[70,71] One can take advantage of the poor stereoselectivity of the alkylation step by accessing both *E* and *Z*-alkenes separately from the separated diastereomer obtained after the alkylation step (vide infra).

The leaving group ability of the sulfonyl moiety was then exploited to access the desired alkenes. Treatment of the α-alkyl β-sulfonyl alkylboronic ester with either TBAF (3 equivalent) or MeLi (for **68**) in THF at 0 °C afforded the olefins **57**-**77** in good to excellent yields (**Scheme 1-33**). Interestingly, the method allows for the preparation of skipped dienes in high yields as for **63** and **64**. In addition, depending on the choice of substituents at R^1 and R^3, either the *Z*-olefin or the *E*-olefin was favoured. Secondary groups with methyl groups or primary alkyl chains led to *E*-olefins. Proton against secondary or primary groups resulted in *Z*-olefins, as well as when methyl groups were used with primary alkyl chains.



37-56 57-77

58 93%

59 >98% (32:68 *E/Z*)

60 81% (32:68 *E/Z*)

61 82% (29:71 *E/Z*)

57 >98% (35:65 *E/Z*)

62 82% (36:64 *E/Z*)

63 82% (38:62 *E/Z*)

64 >98% (29:71 *E/Z*)

65 80% (26:74 *E/Z*)

66 89% (30:70 *E/Z*)

67 85% (33:67 *E/Z*)

68 86% (43:57 *E/Z*)

69 81% (55:45 *E/Z*)

70 >98% (85:15 *E/Z*)

71 81% (83:17 *E/Z*)

72a 91% (77:23 *E/Z*)

73 90% (83:17 *E/Z*)

74 94% (94:6 *E/Z*)

75 81% (35:65 *E/Z*)

76 73% (25:75 *E/Z*)[a]

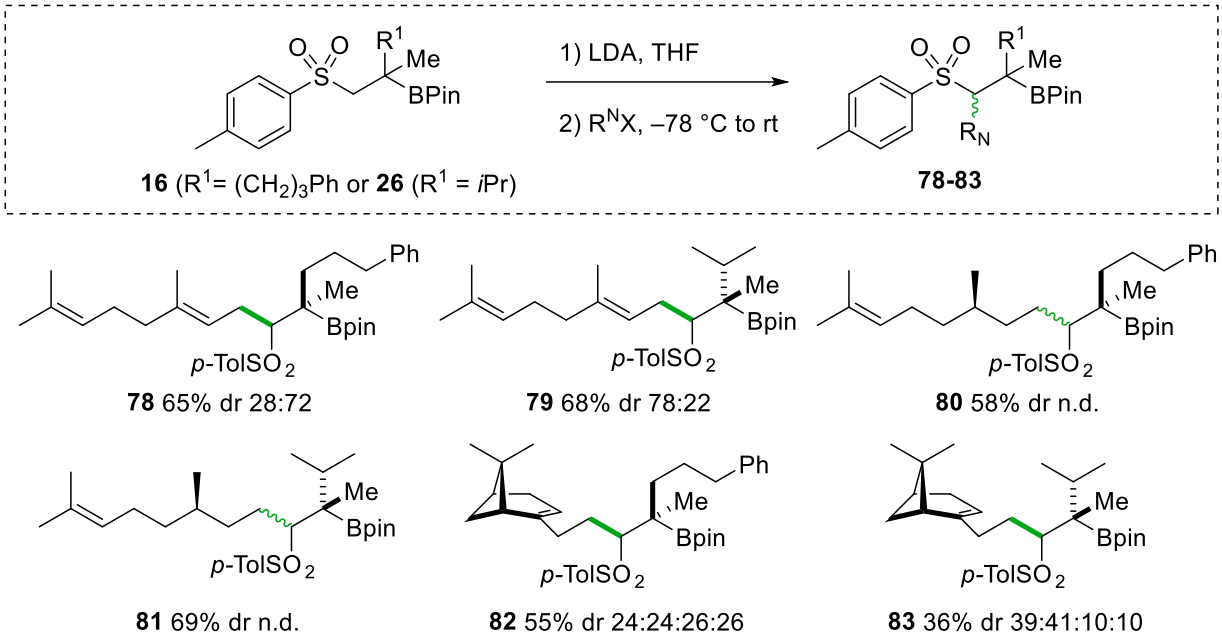
77 60% (23:77 *E/Z*)[a]

a: yield over the two steps (alkylation/elimination)

Scheme 1-33 Olefination reactions with TBAF and for **68** with MeLi. **76** and **77** were made one-pot because of partial elimination in the alkylation step.

f) Application to natural product-derived substrates

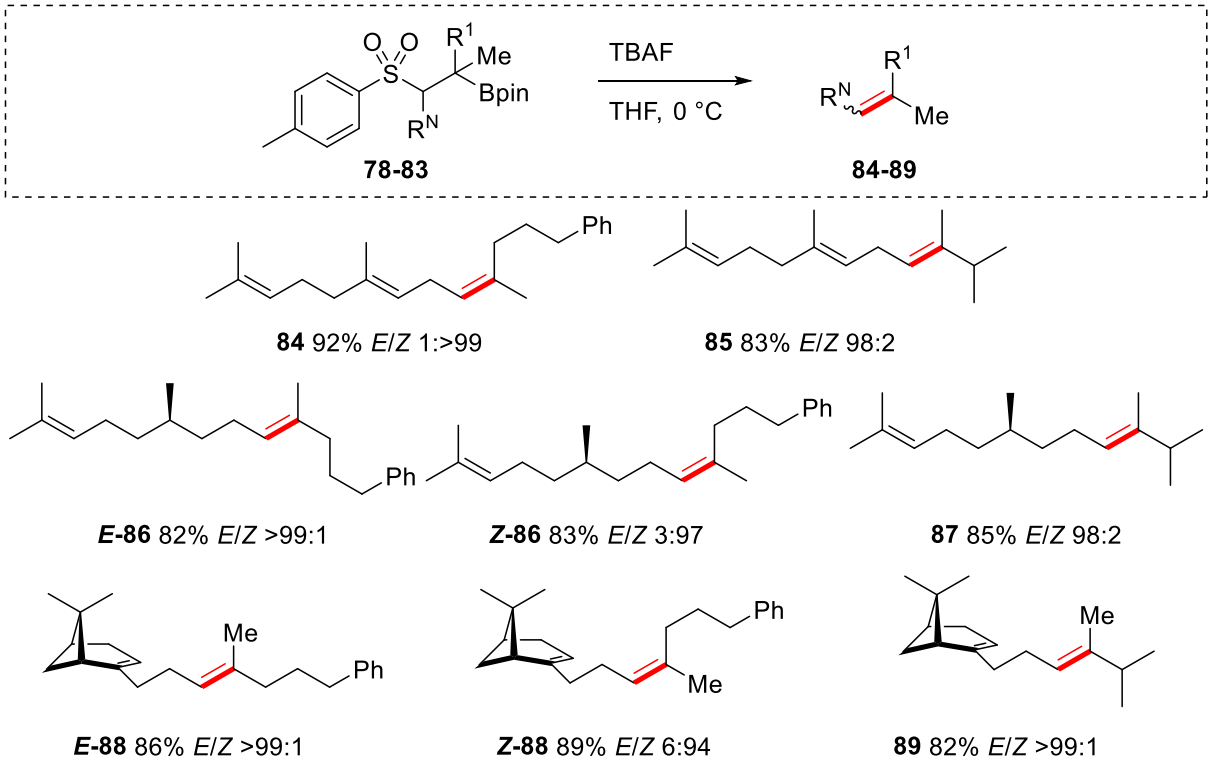
Finally, we were able to use the developed methods for the alkylation and olefination in late-stage modification of natural products. For this the three natural products (*R*)-(-)-nopol, (*S*)-(+)-citronellol and geraniol bromide were used on two different substrates. First, (*S*)-(+)-citronellol and (*R*)-(-)-nopol were converted into an electrophile in one step, while geraniol bromide was used as such, and then used in the alkylation step (**Scheme 1-34**).



Scheme 1-34 Alkylation reactions of β-borylated sulfones with natural products.

The alkylation reaction was successful with all three converted natural products and yields of 36-69% were obtained. The lower yields in the alkylation reaction with (*R*)-(-)-nopol iodide are most likely due to the instability of (*R*)-(-)-nopol iodide. Due to overlapping NMR signals, no information on the diastereomer ratio could be obtained for the alkylation reactions with (*S*)-(+)-citronellyl iodide (**80** and **81**).

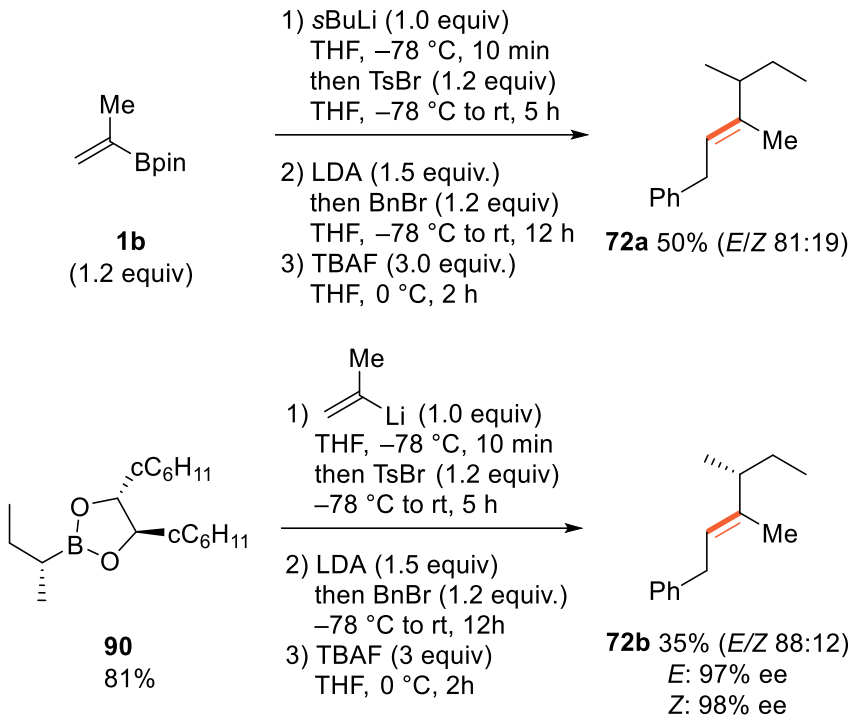
With flash column chromatography the two diastereomers were separated and treated each with excess TBAF to obtain either the *E*- or *Z*-olefin in high yields of 82-92% (**Scheme 1-35**). As the elimination reaction is completely selective, only one isomer was obtained in each case. Small deviations are due to unclean separation during flash column chromatography.



Scheme 1-35 Obtained olefins from late stage functionalization reactions with natural compounds.

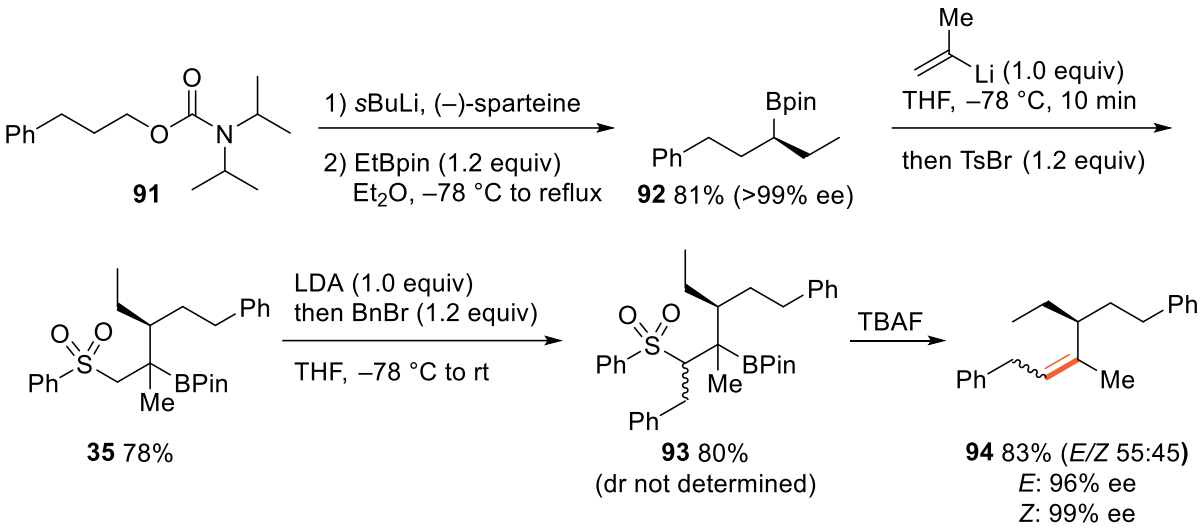
g) Synthesis of enantioenriched alkenes

Interestingly, the three steps could be carried out in a one pot sequence, which proved to be equally efficient as the stepwise procedure in terms of yields. For instance, reaction of isopropenylBpin **1b** with sec-butyllithium, followed by addition of tosylbromide gave the β-borosulfone intermediate, which could be deprotonated in situ with LDA (1.5 equivalents) at –78 °C and the resulting α-sulfonyl anion trapped with benzyl bromide (**Scheme 1-36**). The temperature was allowed to rise to room temperature slowly overnight and an excess of TBAF was then added, giving alkene **72a** in 50% yield over the three steps and with a level of diastereoselectivity of 81:19. Taking advantage of the possibility to perform this reaction starting from alkylBpin precursors, tri-substituted alkenes presenting a stereogenic centre at the allylic position could be prepared in an enantio-enriched form using two different routes based on the work of Matteson[72] and Aggarwal.[73] Using the enantioselective Matteson homologation approach, enantio-enriched alkyl boronic ester **90** was prepared in 81% from (4*R*,5*R*)-4,5-dicyclohexyl-2-methyl-1,3,2-dioxaborolane (**Scheme 1-36**). The afore-mentioned one-pot protocol for the olefination was applied to enantio-enriched alkyl boronic ester **90** and alkene **72b** was obtained in 35% yield over the three steps (88:12 dr), with both diastereomers obtained in high enantiomeric excess (98% ee for the *Z*-isomer; 97% for the *E*-isomer).



Scheme 1-36 One-pot protocol for the preparation of trisubstituted alkenes.

A complementary approach based upon the enantioselective borylation of diisopropylcarbamates was also explored (**Scheme 1-37**). Inspired by Hoppe's pioneering work, Aggarwal and co-workers showed that enantio-enriched secondary alkylBpin derivatives could be obtained by asymmetric metalation of diisopropylcarbamates with sec-butyllithium in the presence of (–)-sparteine and subsequent trapping with an alkylBpin reagent. This methodology was applied to 3-phenylpropyl diisopropylcarbamate **91** and ethylBpin and enantio-enriched (*S*)-4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane **92** was obtained in 81% yield (>99% ee). The latter engaged in the three-component coupling reaction with isopropenyllithium and phenylsulfonylbromide and gave the excepted β-borosulfone **93** in 78% yield. The latter was alkylated in good yield using benzyl bromide as the electrophile, and subsequent TBAF-promoted elimination took place smoothly to give alkene **95** in 83% yield. Surprisingly, the level of diastereoselectivity for the formation of the alkene was particularly deceiving when compared to the one previously observed in the racemic series. As this ratio reflects the diastereoselectivity of the alkylation step, we cannot exclude neither a low selectivity for the trapping of the α-sulfonyl anion, nor an epimerization of the alkylated adduct in the presence of the excess of LDA.



Scheme 1-37 Synthesis of trisubstituted, enantio-enriched alkenes.

1.3.4 Conclusion

In conclusion we have developed a bromosulfonylation of isopropenylboronic ester under controlled conditions. The α-bromo β-sulfonyl boronic ester obtained may serve for the same purposes as the corresponding iodinated ones. Additionally, they may serve as precursors to access the corresponding products of α-alkyl β-sulfonyl addition. This reaction can be shortcutted to obtain these products directly via the three-component coupling reaction. The α-alkyl-β-sulfonyl boronic acid esters serve as precursors for alkylation and subsequent olefination reactions, whereby a total of 31 alkenes were synthesised that tolerate various functional groups such as protected alcohols, cyanides, esters, etc. The three reaction steps of three-component coupling, alkylation and elimination were successfully implemented in a one-pot protocol, making it possible to prepare olefins with unstable intermediates and thus without loss of yield or selectivity. Although the modular approach for olefins was limited to di- and trisubstituted olefins, the developed methods were successfully used as late-stage functionalization of the natural products (1*R*)-(-)-nopol, geraniol and (*S*)-(+)-citronellol or synthesis of enantioenriched alkenes.

1.4 Experimental section

1.4.1 General information

Techniques

All reactions requiring anhydrous conditions were performed in heat-gun, oven or flame dried glassware under an argon atmosphere. An ice bath was used to obtain a temperature of 0 °C. To obtain a temperature of –78 °C, a bath of acetone was cooled with dry ice or in case of light reactions ethanol/dry ice was used instead. Silica gel 60 Å (40–63 µm) from Sigma Aldrich or Macherey Nagel and 60 Å (15-40 µm) from Macherey Nagel was used for flash column chromatography. Thin layer chromatography (TLC) was performed on Silicycle silica gel 60 F_{254} plates, visualization under UV light (254 nm) and/or by dipping in a solution of $(NH_4)_2MoO_4$ (15.0 g), $Ce(SO_4)_2$ (0.5 g), H_2O (90 mL), conc. H_2SO_4 (10 mL); or $KMnO_4$ (3 g), K_2CO_3 (20 g) and NaOH 5% (3 mL) in H_2O (300 mL) and subsequent heating. Anhydrous sodium sulfate was used as drying reagent.

Deactivated silica gel for the purification of bicyclic amines:

The abovementioned silica gel was suspended in in Et_2O and 20w% of HMDS, then filtered, washed with Et_2O and dried on HV overnight. Deactivated TLC plates: silica plates are dipped in 7M NH_3 in MeOH and then dried.

Materials

Commercial reagents were used without further purification unless otherwise stated. Dry solvents for reactions were filtered over columns of dried alumina under a positive pressure of argon. Solvents for extractions (Et_2O, heptanes, *n*-pentane, CH_2Cl_2, EtOAc) and flash column chromatography were of technical grade and distilled prior to use. Commercial dry DMF was used without further purification.

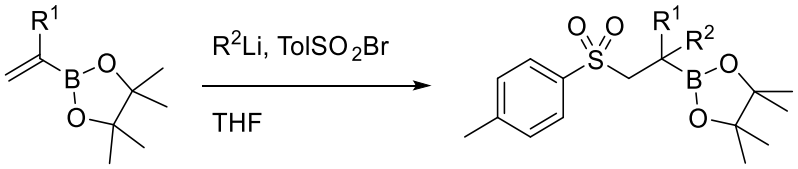
Instrumentation

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance IIIHD-300 spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C at room temperature (24-25°C) unless otherwise stated. Some ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance IIIHD-400 or a Bruker Avance II-400 spectrometer (^1H: 400 MHz; ^{13}C: 75 MHz). Chemical shifts (δ) are reported in parts per million (ppm) using the residual solvent or $Si(CH_3)_4$ (δ = 0.00 for ^1H NMR spectra) as an internal standard. Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), and br (broad). Coupling constant (J) is reported in Hz. In ^{13}C-NMR spectra, the peak positions are reported on one decimal unless the difference in chemical shift between two signals is small and required two decimals. Infrared spectra were recorded on a Jasco FT-IR-460 plus spectrometer equipped with a Specac MKII Golden Gate Single Reflection

Diamond ATR system and are reported in wave numbers (cm^{-1}). At maximum, the ten most prominent peaks are reported. Chiral GC spectra were recorded on a Thermo fisher Trace GC Ultra spectrometer fitted with a Restek Rt-bDEXm capillary column (30m, 0.25mmID, 0.25µm df); gas carrier: He 1.2 mL/min; injector: 220 °C split mode. Chiral HPLC spectra were recorded on an Agilent Technologies 1260 Infinity. Low resolution mass spectra were recorded on a Waters Micromass Autospec Q mass spectrometer in EI mode at 70 eV or were taken from GC-MS analyses performed on a Thermofisher GC-MS (quadrupole mass analyzer using EI mode at 70 eV) fitted with a Macherey-Nagel Optima delta-3-0.25 µm capillary column (20 m, 0.25 mm); gas carrier: He 1.4 mL/min; injector: 220 °C split mode. HRMS analyses and accurate mass determinations were performed on a Thermo Scientific LTQ Orbitrap XL mass spectrometer using ESI mode or a Thermo Scientific Trace 1310 Q Exactive GC mass spectrometer using EI mode fitted with a Macherey-Nagel Optima delta-3-0.25 µm capillary column (20 m, 0.25 mm); gas carrier: He 1.0 mL/min; injector: 200 °C split mode. Melting points were measured on a Büchi B-545 apparatus and are corrected. Syringe filters with polytetrafluoroethylene membrane were used with a pore size of 0.45 µm (or 5 µm) from Machery-Nagel (CHROMAFIL®Xtra PTFE 0.45). Medium pressure liquid chromatography (MPLC) was performed with a CombiFlash® Rf+ system from Teledyne Isco using RediSep® single-use normal phase columns.

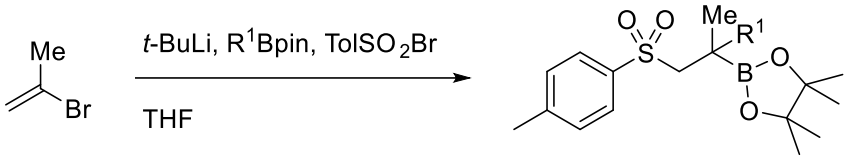
1.4.2 General Procedures

General Procedure A: Three-component coupling with alkyllithium and alkenylBpin



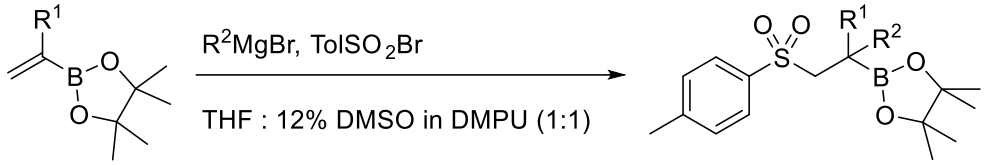
In a flame dried round bottom flask was placed dry THF (10 mL) and vinylic boronic acid pinacol ester (1.0 mmol). At -78 °C, R^2-Li (1.05 mmol) was added dropwise and stirred for 30 min. Then, tosyl bromide (282 mg, 1.2 mmol) dissolved in dry THF (3 mL) was added and the reaction mixture was irradiated for 2 h at 467 nm. After irradiation, the reaction mixture was allowed to reach rt and was stirred for 1 h. Then, the reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product is purified by flash column chromatography.

General Procedure B: Three-component coupling with propenyllithium and alkylBpin



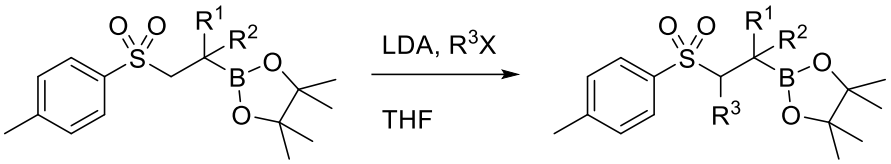
In a flame dried round bottom flask was placed dry THF (20 mL) and 2-bromoprop-1-ene (315 mg, 2.6 mmol). At -78 °C was added dropwise *t*-BuLi (1.7 M in pentane, 3.0 mL, 5.2 mmol) and stirred for 30 minutes. Then, alkylboronic acid pinacol ester (2.0 mmol) was added and the reaction mixture was warmed up to rt (removing cooling bath, ca. 30 min). After reaching rt, the reaction mixture was cooled again to -78 °C, tosyl bromide (1.41 g, 6.0 mmol) dissolved in dry THF (5 mL) was added slowly and the solution was stirred overnight allowing to reach rt. Then, the reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with Et_2O (3 ×). The combined organic phase were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was purified by flash column chromatography.

General Procedure C: Three-component coupling with alkylmagnesium bromide and alkenylBpin



In a flame dried round bottom flask was placed dry THF (4 mL), dry DMSO (0.7 mL), dry DMPU (freshly distilled over CaH_2, 5.3 mL) and vinylic boronic acid pinacol ester (2.6 mmol). At 0 °C, R^2-MgBr (2.0 mmol) was added dropwise and stirred for 30 min. Then, the reaction mixture was cooled down to -78 °C, tosyl bromide (0.56 g, 2.4 mmol) dissolved in dry THF (2 mL) was added and the reaction mixture was irradiated for 2 h at 467 nm. After the irradiation the reaction mixture was stirred overnight allowing to reach rt. Then, the reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with Et_2O (3 ×). The combined organic phase were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was purified by flash column chromatography.

General Procedure D: Alkylation of β-borylated sulfones

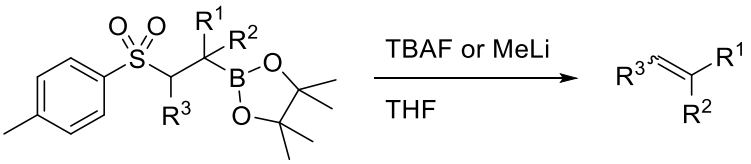


LDA preparation:

In a flame dried round bottom flask was placed dry THF (10 mL) and diisopropylamine (0.14 mL, 1.0 mmol). The reaction mixture was cooled down to –78 °C, then *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) was added dropwise and stirred for 15 min. The reaction mixture was warmed up to rt and stirred for another 15 min.

The freshly prepared LDA solution was cooled down to –78 °C and under stirring was added the β-borylated sulfone (1.0 mmol) dissolved in dry THF (2 mL). After 1 h, R^3-X (1.2 mmol) was added slowly and the reaction mixture was stirred overnight allowing to reach rt. Then, the reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with Et_2O (3 ×). The organic phase were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was purified by flash column chromatography.

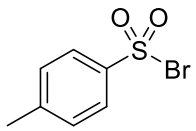
General Procedure E: Elimination reaction



In a dry round bottom flask was placed dry THF (10 mL) and alkylated β-borylated sulfones (1.0 mmol). Then, reaction mixture was cooled down to 0 °C, TBAF (1.0 M in THF, 3.0 mL, 3.0 mmol.) was added slowly and stirred for 2-3 h. The reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with Et_2O (3 ×). The organic phase were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was purified by flash column chromatography.

1.4.3 Three-component-coupling reactions

Tosyl bromide (95)

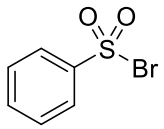


Chemical Formula: $C_7H_7BrO_2S$
Molecular Weight: 235,10

To a solution of *p*-toluenesulfinate (17.8 g, 100 mmol) in DCM/water (150 mL / 150 mL) was added dropwise Br_2 (6.2 mL, 120 mmol) in DCM (150 mL) via dropping funnel at 0 °C. After complete addition, the reaction mixture was stirred for 2 h at 0 °C, protected from light (covered with aluminium foil). Then, the reaction mixture was treated with sat. aq. $Na_2S_2O_3$ soln. and the aqueous phase was extracted three times with DCM. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated. Recrystallization in pentane afforded **95** (15.1 g, 64%).

Appearance white crystals; **Rf** 0.4 (EtOAc/heptanes=1:9); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.91 – 7.85 (m, 2H), 7.43 – 7.36 (m, 2H), 2.49 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 146.9 (C_q), 144.7 (C_q), 130.3 (2 x CH), 126.6 (2 x CH), 22.0 (CH_3). Physical and spectral data are in accordance with literature data[74].

Phenylsulfonyl bromide (96)

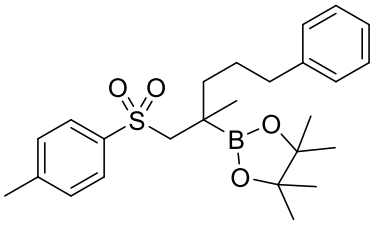


Chemical Formula: $C_6H_5BrO_2S$
Molecular Weight: 221,07

To a solution of benzenesulfinate (16.5 g, 100 mmol) in DCM/water (150 mL / 150 mL) was added dropwise Br_2 (5.2 mL, 100 mmol) via dropping funnel at 0 °C. After complete addition, the reaction mixture was stirred for 2 h at 0 °C, protected from light (covered with aluminium foil). Then, the reaction mixture was treated with sat. aq. $NaHCO_3$ soln. and washed with 5% aq. $Na_2S_2O_3$ soln.. The aqueous phase was extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated. The crude product was redisolved in benzene, filtered through a POR3 filter and concentrated again to afford **96** (17.3 g, 78%).

Appearance brown oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.03 – 7.95 (m, 2H), 7.78 – 7.70 (m, 1H), 7.66 – 7.57 (m, 2H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 147.2 (C_q), 135.3 (CH), 129.7 (2 x CH), 126.5 (2 x CH). Physical and spectral data are in accordance with literature data[74].

4,4,5,5-tetramethyl-2-(2-methyl-5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (16)

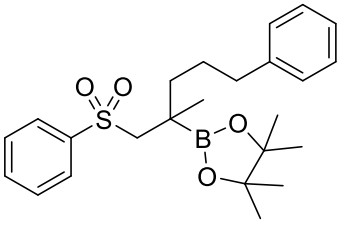


Chemical Formula: $C_{25}H_{35}BO_4S$
Molecular Weight: 442,42

The reaction was performed according to **General Procedure C** with 3-phenylpropyl-magnesium bromide solution (0.65 M in THF, 32 mL, 20.8 mmol), 2-isopropenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.7 mL, 25 mmol), tosyl bromide (5.87 g, 25 mmol), DMSO (5.8 mL), DMPU (43 mL), and THF (33 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane= 15:85, stained in PMA solution) to afford **16** (6.28 g, 68%).

Appearance white solid; **Mp** 70-72 °C; **Rf** 0.3 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.22 Hz, 2H), 7.32 (d, *J* = 8.07 Hz, 2H), 7.25 (t, *J* = 7.40 Hz, 3H), 7.19 – 7.10 (m, 3H), 3.30 (d, *J* = 13.69 Hz, 1H), 3.05 (d, *J* = 13.81 Hz, 1H), 2.54 (t, *J* = 7.30 Hz, 2H), 2.43 (s, 3H), 1.68 – 1.42 (m, 4H), 1.30 (s, 6H), 1.29 (s, 6H), 1.20 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ =144.0 (C_q), 142.4 (C_q), 139.3 (C_q), 129.7 (2 x CH), 128.4 (2 x CH), 128.3 f(2 x CH), 127.6 (2 x CH), 125.8 (CH), 83.8 (2 x C_q), 64.9 (CH_2), 38.0 (CH_2), 36.5 (CH_2), 26.8 (CH_2), 25.1 (2 x CH_3), 25.0 (2 x CH_3), 21.6 (CH_3), 20.9 CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.7; **FT-IR (cm^{-1}, neat)** 2976, 2930, 1738, 1599, 1454, 1371, 1312, 1302, 1202, 1141, 1086, 967, 848, 817, 748, 697, 658, 571, 507; **HRMS (ESI)** m/z calculated for $C_{25}H_{36}O_4BS$ $[M+H]^+$: 433.2422, found: 433.2421.

4,4,5,5-tetramethyl-2-(2-methyl-5-phenyl-1-(phenylsulfonyl)pentan-2-yl)-1,3,2-dioxaborolane (22)



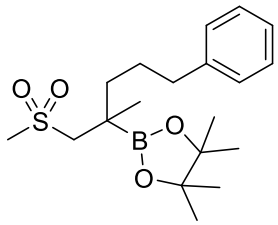
Chemical Formula: $C_{24}H_{33}BO_4S$
Molecular Weight: 428,39

The reaction was performed according to **General Procedure C** with 3-phenylpropyl-magnesium bromide solution (0.57 M in THF, 38 mL, 21.7 mmol), 2-isopropenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.9 mL, 26 mmol), Phenylsulfonyl bromide (5.75 g, 26 mmol), DMSO (16 mL), DMPU (117 mL), and THF (88 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford **22** (6.05 g, 65%).

Appearance colorless oil; **Rf** 0.2 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.91 (dd, *J* = 7.01, 1.68 Hz, 2H), 7.65 – 7.49 (m, 3H), 7.30 – 7.22 (m, 2H), 7.20 – 7.10 (m, 2H), 3.33 (d, *J* = 13.70 Hz, 1H), 3.07 (d, *J* = 13.71 Hz, 1H), 2.55 (t, *J* = 7.18 Hz, 2H), 1.70 – 1.44 (m, 4H), 1.31 (d, *J* = 2.32 Hz, 6H), 1.30 (s, 6H), 1.21 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.5 (C_q),

142.3 (C_q), 133.3 (CH), 129.2 (2 x CH), 128.5 (2 x CH), 128.4 (2 x CH), 127.6 (2 x CH), 125.8 (CH), 84.0 (2 x C_q), 64.9 (CH_2), 38.1 (CH_2), 36.6 (CH_2), 26.9 (CH_2), 25.1 (2 x CH_3), 25.1 (2 x CH_3), 21.0 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 34.0; **FT-IR (cm^{-1}, neat)** 2975, 2923, 2864, 1449, 1372, 1306, 1204, 1141, 1085, 1026, 1001, 967, 846, 793, 772, 736, 720, 687, 637, 599, 550, 528, 514, 452, 419; **HRMS (ESI)** m/z calculated for $C_{24}H_{34}O_4BS$ $[M+H]^+$: 429.2260, found: 429.2265.

4,4,5,5-tetramethyl-2-(2-methyl-1-(methylsulfonyl)-5-phenylpentan-2-yl)-1,3,2-dioxaborolane (23)

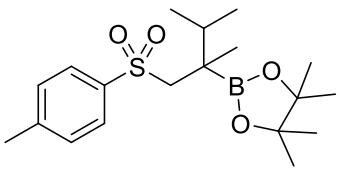


Chemical Formula: $C_{19}H_{31}BO_4S$
Molecular Weight: 366,32

The reaction was performed according to **General Procedure C** with 3-phenylpropyl-magnesium bromide solution (0.62 M in THF, 3.3 mL, 2.0 mmol), 2-isopropenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.45 mL, 2.4 mmol), methanesulfonyl bromide (0.2 mL, 2.4 mmol), DMSO (0.8 mL), DMPU (5.2 mL), and THF (6.4 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=25:75, stained in PMA solution) to afford **23** (662 mg, 90%).

Appearance white solid; **Mp** 74-76 °C; **Rf** 0.1 (Et_2O/pentane=25:75); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.34 – 7.23 (m, 2H), 7.17 (tt, *J* = 7.92, 1.47 Hz, 3H), 3.29 (d, *J* = 13.95 Hz, 1H), 2.97 (d, *J* = 13.95 Hz, 1H), 2.89 (s, 3H), 2.59 (t, *J* = 7.31 Hz, 2H), 1.75 – 1.38 (m, 4H), 1.25 (s, 12H), 1.20 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.3 (C_q), 128.5 (2 x CH), 128.4 (2 x CH), 125.9 (CH), 84.0 (2 C_q), 63.6 (CH_2), 44.1 (CH_3), 38.3 (CH_2), 36.6 (CH_2), 26.9 (CH_2), 25.0 (2 x CH_3), 24.9 (2 x CH_3), 21.1 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.3; **FT-IR (cm^{-1}, neat)** 2981, 2928, 2912, 2877, 2837, 1496, 1469, 1460, 1414, 1389, 1370, 1320, 1298, 1286, 1207, 1163, 1143, 1122, 1098, 1027, 1001, 966, 933, 865, 849, 826, 793, 755, 717, 699; **HRMS (ESI)** m/z calculated for $C_{19}H_{32}O_4BS$ $[M+H]^+$: 367.2112, found: 367.2109.

2-(2,3-dimethyl-1-tosylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26)

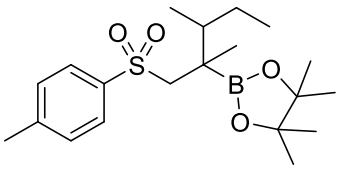


Chemical Formula: $C_{19}H_{31}BO_4S$
Molecular Weight: 366,32

The reaction was performed according to **General Procedure A** with Isopropyl lithium solution (0.7 M in pentane, 25 mL, 17.3 mmol), 2-isopropenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.1 mL, 16.5 mmol), tosyl bromide (4.27 g, 17.3 mmol), and THF (110 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford **26** (4.62 g, 77%). (**GPC**: 70%).

Appearance white solid; **Mp** 63-65 °C; **Rf** 0.2 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.83 – 7.77 (m, 2H), 7.35 – 7.29 (m, 2H), 3.37 (d, *J* = 13.5 Hz, 1H), 3.05 (d, *J* = 13.5 Hz, 1H), 2.43 (s, 3H), 1.68 (hept, *J* = 6.8 Hz, 1H), 1.34 (s, 6H), 1.32 (s, 6H), 1.20 (s, 3H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.0 (C_q), 139.7 (C_q), 129.8 (2 x CH), 127.6 (2 x CH), 83.9 (2 x C_q), 64.6 (CH_2), 34.7 (CH), 25.5 (2 x CH_3), 25.3 (2 x CH_3), 21.7 (CH_3), 19.2 (CH_3), 17.7 (CH_3), 16.6 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.7; **FT-IR (cm^{-1}, neat)** 2970, 2925, 2878, 1597, 1470, 1450, 1392, 1381, 1371, 1358, 1308, 1287, 1215, 1194, 1164, 1116, 1083, 1028, 1017, 971, 955, 919, 874, 858, 831, 817, 799, 770, 748, 703, 686, 658, 573, 554, 543, 499, 472, 455, 420, 408; **HRMS (ESI)** m/z calculated for $C_{19}H_{32}O_4BS$ $[M+H]^+$: 367.2106, found: 367.2109.

2-(2,3-dimethyl-1-tosylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27)



Chemical Formula: $C_{20}H_{33}BO_4S$
Molecular Weight: 380,35

The reaction was performed according to **General Procedure A** with *s*-BuLi (1.4 M in cyclohexane, 19.2 mL, 26.8 mmol), 2-isopropenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.8 mL, 25.5 mmol), tosyl bromide (7.21 g, 30.6 mmol), and THF (37 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford **27** (7.71 g, 79%) as an inseparable racemic mixture.

Appearance white solid; **Mp** 74-76 °C; **Rf** 0.4 (Et_2O/pentane=2:8).

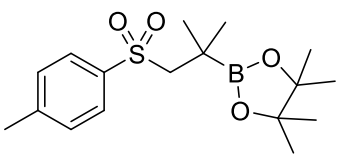
Major diastereomer: **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.04 Hz, 2H), 7.31 (d, *J* = 8.06 Hz, 2H), 3.34 (d, *J* = 13.52 Hz, 1H), 3.09 (d, *J* = 13.45 Hz, 1H), 2.42 (s, 3H), 1.57 - 1.46 (m, 1H), 1.33 (s, 6H), 1.31 (s, 6H), 1.40 – 1.29 (m, 1H), 1.17 (s, 3H), 1.08 – 0.94 (m, 1H), 0.91 – 0.85 (m, 3H), 0.80 (d, *J* = 6.78 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.01 (C_q), 139.60 (C_q), 129.79 (2 x CH), 127.59 (2 x CH), 83.91 (2 x C_q), 64.70 (CH_2), 41.77 (CH), 26.24 (CH_2), 25.49 (2 x CH_3), 25.23 (2 x CH_3), 21.68 (CH_3), 16.18 (CH_3), 13.24 (CH_3), 13.02 (CH_3). Due to

coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Minor diastereomer: **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.04 Hz, 2H), 7.31 (d, *J* = 8.06 Hz, 2H), 3.36 (d, *J* = 13.51 Hz, 1H), 3.09 (d, *J* = 13.50 Hz, 1H), 2.42 (s, 3H), 1.57 – 1.46 (m, 1H), 1.33 (s, 6H), 1.31 (s, 6H), 1.20 (s, 3H), 0.96 – 0.85 (m, 1H), 0.94 – 0.85 (m, 1H), 0.91 – 0.83 (m, 3H), 0.80 (d, *J* = 6.78 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.99 (C_q), 139.65 (C_q), 129.79 (2 x CH), 127.59 (2 x CH), 83.90 (2 x C_q), 64.29 (CH_2), 41.98 (CH), 25.50 (2 x CH_3), 25.27 (2 x CH_3), 24.34 (CH_2), 21.68 (CH_3), 17.01 (CH_3), 15.00 (CH_3), 12.92 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mixture of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.7; **FT-IR (cm^{-1}, neat)** 2972, 2929, 2875, 1598, 1455, 1360, 1313, 1260, 1197, 1139, 1085, 1018, 968, 903, 852, 816, 748, 675, 657, 603, 573, 544, 531, 503, 472, 415; **HRMS (ESI)** m/z calculated for $C_{20}H_{34}O_4BS$ $[M+H]^+$: 381.2280, found: 381.2265.

4,4,5,5-tetramethyl-2-(2-methyl-1-tosylpropan-2-yl)-1,3,2-dioxaborolane (14)

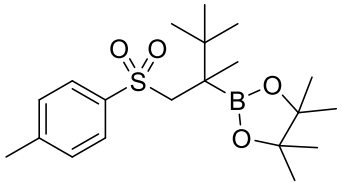


Chemical Formula: $C_{17}H_{27}BO_4S$
Molecular Weight: 338,27

The reaction was performed according to **General Procedure B** with *t*-BuLi (1.7 M in pentane, 2.7 mL, 4.5 mmol), 2-bromoprop-1-ene (315 mg, 2.6 mol), 2,4,4,5,5-pentamethyl-1,3,2-dioxaborolane (280 mg, 2.0 mmol), tosyl bromide (1.42 g, 5.9 mmol), and THF (20 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford **14** (407 mg, 61%).

Appearance white solid; **Mp** 92-93 °C; **Rf** 0.6 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 8.28 Hz, 2H), 7.32 (d, *J* = 8.01 Hz, 2H), 3.17 (s, 2H), 2.43 (s, 3H), 1.30 (s, 12H), 1.14 (s, 6H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.11 (C_q), 139.34 (C_q), 129.82 (2 x CH), 127.71 (2 x CH), 83.87 (2 x C_q), 66.91 (CH_2), 24.91 (4 x CH_3), 24.58 (2 x CH_3), 21.73 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.34; **FT-IR (cm^{-1}, neat)** 2978, 2958, 2872, 1598, 1475, 1368, 1323, 1298, 1264, 1212, 1192, 1134, 1083, 1040, 967, 936, 915, 865, 843, 813, 761, 702, 673, 634; **HRMS (ESI)** m/z calculated for $C_{17}H_{28}O_4BS$ $[M+H]^+$: 339.1806, found: 339.1796.

4,4,5,5-tetramethyl-2-(2,3,3-trimethyl-1-tosylbutan-2-yl)-1,3,2-dioxaborolane (34)

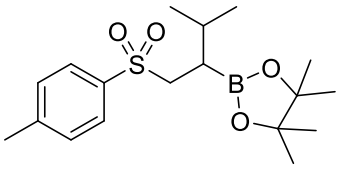


Chemical Formula: $C_{20}H_{33}BO_4S$
Molecular Weight: 380,35

The reaction was performed according to **General Procedure B** with *t*-BuLi (1.7 M in pentane, 3.0 mL, 5.2 mmol), 2-bromoprop-1-ene (316 mg, 2.6 mmol), 2-tert-butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (414 mg, 2.25 mmol), tosyl bromide (1.59 g, 6.75 mmol), and THF (20 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford **34** (767 mg, 90%).

Appearance yellow oil; **Rf** 0.3 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.80 (d, J = 8.28 Hz, 2H), 7.33 (d, J = 8.64 Hz, 2H), 3.49 (d, J = 13.26 Hz, 1H), 3.02 (d, J = 13.26 Hz, 1H), 2.43 (s, 3H), 1.36 (s, 6H), 1.34 (s, 6H), 1.29 (s, 3H), 0.89 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.93 (C_q), 139.91 (C_q), 129.82 (2 x CH), 127.57 (2 x CH), 84.01 (2 x C_q), 62.45 (CH_2), 35.27 (C_q), 26.68 (3 x CH_3), 25.79 (2 x CH_3), 25.28 (2 x CH_3), 21.71 (CH_3), 16.47 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.30; **FT-IR (cm^{-1}, neat)** 2969, 2873, 1596, 1477, 1457, 1401, 1391, 1370, 1345, 1319, 1308, 1289, 1267, 1208, 1192, 1141, 1087, 1037, 1017, 967, 899, 864, 846, 819, 799, 763, 740, 654; **HRMS (ESI)** m/z calculated for $C_{20}H_{34}O_4BS$ $[M+H]^+$: 381.2276, found: 381.2265.

4,4,5,5-tetramethyl-2-(3-methyl-1-tosylbutan-2-yl)-1,3,2-dioxaborolane (13)



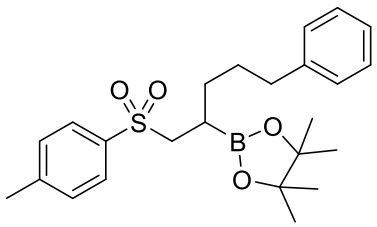
Chemical Formula: $C_{18}H_{29}BO_4S$
Molecular Weight: 352,30

The reaction was performed according to **General Procedure A** with isopropyl lithium solution (0.7 M in pentane, 30 mL, 21.0 mmol), 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (3.26 g, 20.0 mmol), tosyl bromide (5.65 g, 24.0 mmol), and THF (45 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **13** (3.93 g, 56%).

Appearance white solid; **Mp** 69-71 °C; **Rf** 0.5 (Et_2O/pentane=3:7); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.80 – 7.74 (m, 2H), 7.34 – 7.30 (m, 2H), 3.37 (dd, *J* = 13.85, 10.80 Hz, 1H), 3.02 (dd, *J* = 13.92, 3.42 Hz, 1H), 2.43 (s, 3H), 1.87 – 1.71 (m, 1H), 1.32 (ddd, *J* = 10.65, 5.48, 3.50 Hz, 1H), 1.26 (s, 12H), 0.86 (dd, *J* = 6.70, 5.33 Hz, 6H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 144.35 (C_q), 136.83 (C_q), 129.86 (2 x CH), 128.31 (2 x CH), 83.88 (2 x C_q), 56.77 (CH_2), 29.59 (CH), 25.11(4 x CH_3), 21.90 (CH_3), 21.72 (CH_3), 20.93 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.64; **FT-IR (cm^{-1}, neat)** 2974, 2929, 2871, 1598, 1465, 1408,

1372,z 1315, 1302, 1288, 1234, 1213, 1140, 1087, 1039, 1019, 972, 905, 861, 836, 816, 763, 705, 661, 634; **HRMS (ESI)** m/z calculated for $C_{18}H_{29}O_4BSNa$ $[M+Na]^+$: 375.1767, found: 375.1772.

4,4,5,5-tetramethyl-2-(5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (12)

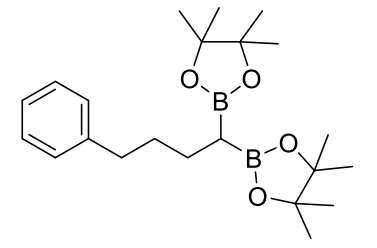


Chemical Formula: $C_{24}H_{33}BO_4S$
Molecular Weight: 428,39

The reaction was performed according to **General Procedure C** with 3-phenylpropyl-magnesium bromide solution (0.55 M in THF, 14.5 mL, 7.98 mmol), 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (1.8 mL, 9.57 mmol), tosyl bromide (2.264 g, 9.57 mmol), DMSO (2.0 mL), DMPU (14.5 mL), and THF (11.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=35:65, stained in PMA solution) to afford **12** (2.18 g, 64%).

Appearance colorless solid; **Mp** 68-70 °C; **Rf** 0.4 (Et_2O/pentane=35:65); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.80 – 7.76 (m, 2H), 7.35 – 7.31 (m, 2H), 7.27 – 7.21 (m, 2H), 7.18 – 7.13 (m, 1H), 7.11 – 7.07 (m, 2H), 3.32 (dd, *J* = 14.00, 9.13 Hz, 1H), 3.02 (dd, *J* = 13.92, 4.34 Hz, 1H), 2.61 – 2.45 (m, 2H), 2.43 (s, 3H), 1.63 – 1.40 (m, 4H), 1.51 – 1.42 (m, 1H), 1.25 (s, 12H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 144.55 (C_q), 142.35 (C_q), 136.99 (C_q), 130.01 (2 x CH), 128.57 (2 x CH), 128.50 (2 x CH), 128.40 (2 x CH), 125.96 (CH), 84.02 (2 x C_q), 58.26 (CH_2), 35.97 (CH_2), 30.37 (CH_2), 30.19 (CH_2), 25.11 (2 x CH_3), 25.08 (2 x CH_3), 21.85 (CH_3), 18.40 (CH, broad signal). **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.78; **FT-IR (cm^{-1}, neat)** 2979, 2924, 2861, 1596, 1487, 1450, 1413, 1378, 1336, 1317, 1291, 1257, 1230, 1141, 1085, 1050, 1019, 964, 893, 856, 820, 758, 700, 674, 594, 563; **HRMS (ESI)** m/z calculated for $C_{24}H_{33}O_4BSNa$ $[M+Na]^+$: 451.2087, found: 451.2085.

2,2'-(4-phenylbutane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (97)



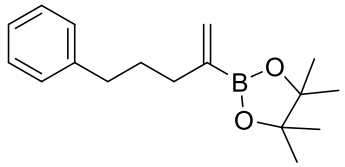
Chemical Formula: $C_{22}H_{36}B_2O_4$
Molecular Weight: 386,15

Intermediate **97** was prepared by a reported procedure[75].

In a flame dried Schlenk tube was placed 4-phenyl-1-butyne (3.760 g, 26.1 mmol), [H-*B*-9-BBN]$_2$ (1.29 g, 5.29 mmol), and HBpin (11.3 mL, 78.2 mmol). Then, the Schlenk tube was placed in a preheated oil bath at 120 °C and stirred for 20 h. The reaction mixture was concentrated under reduced pressure and the obtained crude product purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford **97** (5.61 g, 54%).

Appearance colorless liquid; **Rf** 0.57 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.31 – 7.20 (m, 2H), 7.19 – 7.11 (m, 3H), 2.65 – 2.54 (m, 2H), 1.63 (d, J = 3.9 Hz, 2H), 1.61 (d, J = 4.3 Hz, 2H), 1.23 (s, 12H), 1.22 (s, 12H), 0.82 – 0.72 (m, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.19 (C_q), 128.48 (2 x CH), 128.30 (2 x CH), 125.55 (CH), 83.08 (4 x C_q), 36.18 (CH_2), 34.49 (CH_2), 25.72 (CH_2), 25.02 (4 x CH_3), 24.67 (4 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.80. Physical and spectral data are in accordance with literature data[75].

4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (98)



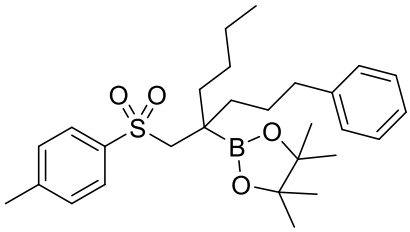
Chemical Formula: $C_{17}H_{25}BO_2$
Molecular Weight: 272,20

Intermediate **98** was prepared by a reported procedure[76].

In a flame dried round bottom flask were placed dry THF (22 mL) and tetramethylpiperidine (2.3 mL, 13.9 mmol). The reaction mixture was cooled to 0 °C, *n*-BuLi (1.6 M in hexanes, 8.7 mL, 13.9 mmol) was added slowly and stirred for 15 min. Then, 4,4,5,5-tetramethyl-2-[4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl]-1,3,2-dioxaborolane (4.46 g, 11.5 mmol) dissolved in dry THF (18 mL) was added slowly at 0 °C and stirred for 5 min. Diiodomethane (6.22 g, 23.2 mmol) dissolved in dry THF (13 mL) was added to the reaction mixture, the cooling bath was removed, and the reaction mixture was heated up to 70 °C and stirred for 2 h at 70 °C. After cooling to rt, the reaction mixture was filtered through a silica plug, washed with Et_2O, and concentrated under reduced pressure. The obtained crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=5:95, stained in PMA solution) to afford **98** (1.24 g, 40%).

Appearance yellowish oil; **Rf** 0.8 (Et_2O/pentane=1:9); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.37 – 7.29 (m, 2H), 7.28 – 7.19 (m, 3H), 5.87 (d, *J* = 3.46 Hz, 1H), 5.71 – 5.65 (m, 1H), 2.72 – 2.63 (m, 2H), 2.28 (t, *J* = 7.53 Hz, 2H), 1.89 – 1.76 (m, 2H), 1.33 (s, 12H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.95 (C_q), 129.40 (CH_2), 128.55 (2 x CH), 128.33 (2 x CH), 125.66 (CH), 83.46 (2 x C_q), 35.64 (CH_2), 35.22 (CH_2), 31.02 (CH_2), 24.88 (4 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 30.25. Physical and spectral data are in accordance with literature data[77].

4,4,5,5-tetramethyl-2-(1-phenyl-4-(tosylmethyl)octan-4-yl)-1,3,2-dioxaborolane (25)

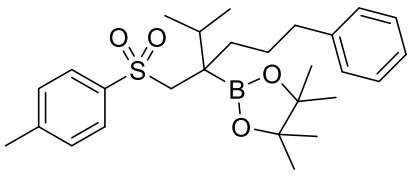


Chemical Formula: $C_{28}H_{41}BO_4S$
Molecular Weight: 484,50

The reaction was performed according to **General Procedure A** with *n*-BuLi (1.6 M in hexanes, 1.3 mL, 2.1 mmol), 4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (544 mg, 2.0 mmol), tosyl bromide (552 mg, 2.4 mmol), and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford **25** (773 mg, 80%).

Appearance colorless oil; **Rf** 0.4 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 8.30 Hz, 2H), 7.37 – 7.23 (m, 4H), 7.21 – 7.12 (m, 3H), 3.23 (s, 2H), 2.55 (t, *J* = 7.52 Hz, 2H), 2.43 (s, 3H), 1.75 – 1.64 (m, 2H), 1.64 – 1.48 (m, 4H), 1.30 (s, 12H), 1.26 – 1.08 (m, 4H), 0.86 (t, *J* = 7.00 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.04 (C_q), 142.79 (C_q), 139.59 (C_q), 129.79 (2 x CH), 128.48 (2 x CH), 128.34 (2 x CH), 127.66 (2 x CH), 125.75 (CH), 83.88 (2 x C_q), 61.40 (CH_2), 36.65 (CH_2), 33.11 (CH_2), 32.99 (CH_2), 26.43 (2 x CH_2), 25.21 (2 x CH_3), 25.19 (2 x CH_3), 23.35 (CH_2), 21.67 (CH_3), 14.17 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.69; **FT-IR (cm^{-1}, neat)** 2983, 2952, 1794, 1732, 1638, 1438, 1414, 1389, 1371, 1353, 1309, 1290, 1255, 1227, 1212, 1200, 1167, 1144, 1132, 1071, 1026, 1007, 984, 965, 950, 918, 876, 847, 827, 804, 790, 765, 744, 722, 696, 668, 619, 578; **HRMS (ESI)** m/z calculated for $C_{28}H_{42}O_4BS$ $[M+H]^+$: 485.2894, found: 485.2891.

4,4,5,5-tetramethyl-2-(2-methyl-6-phenyl-3-(tosylmethyl)hexan-3-yl)-1,3,2-dioxaborolane (28)



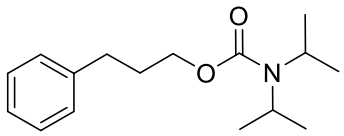
Chemical Formula: $C_{27}H_{39}BO_4S$
Molecular Weight: 470,48

The reaction was performed according to **General Procedure A** with isopropyl lithium solution (0.7 M in pentane, 3.0 mL, 2.0 mmol), 4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (516 mg, 1.9 mmol), tosyl bromide (539 mg, 2.3 mmol), and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford **28** (735 mg, 79%).

Appearance colorless oil; **Rf** 0.4 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.26 Hz, 2H), 7.33 (d, *J* = 8.02 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.21 – 7.13 (m, 3H), 3.43 (d, *J* = 14.08 Hz, 1H), 3.20 (d, *J* = 14.13 Hz, 1H), 2.67 – 2.50 (m, 2H), 2.44 (s, 3H), 2.03 – 1.92

(m, 2H), 2.03 – 1.90 (m, 1H), 1.73 – 1.44 (m, 2H), 1.31 (s, 6H), 1.30 (s, 6H), 0.95 (d, *J* = 6.92 Hz, 3H), 0.92 (d, *J* = 6.88 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.97 (C_q), 143.32 (C_q), 140.00 (C_q), 129.84 (2 x CH), 128.51 (2 x CH), 128.31 (2 x CH), 127.61 (2 x CH), 125.64 (CH), 83.91 (C_q), 60.21 (CH_2), 36.93 (CH_2), 31.83 (CH), 31.26 (CH_2), 26.65 (CH_2), 25.46 (2 x CH_3), 25.20 (2 x CH_3), 21.69 (CH_3), 19.48 (CH_3), 19.27 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.29; **FT-IR (cm^{-1}, neat)** 3471, 2983, 2952, 1991, 1732, 1638, 1438, 1414, 1371, 1353, 1309, 1290, 1255, 1227, 1200, 1167, 1144, 1132, 1071, 1026, 1007, 984, 965, 950, 876, 847, 827, 804, 790, 765, 744, 722, 696, 669, 619, 578; **HRMS (ESI)** m/z calculated for $C_{27}H_{40}O_4BS$ $[M+H]^+$: 471.2740, found: 471.2735.

3-phenylpropyl diisopropylcarbamate (91)



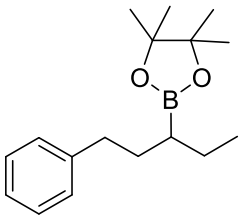
Chemical Formula: $C_{16}H_{25}NO_2$
Molecular Weight: 263,38

Intermediate **91** was prepared by a reported procedure[78].

In a dry two neck round bottom flask were placed N,N-diisopropylcarbamoyl chloride (8.12 g, 49.5 mmol), triethylamine (7.5 mL, 54.0 mmol), 3-phenylpropan-1-ol (6.1 mL, 45.0 mmol), dry DCM (45 mL) and was refluxed overnight. After cooling down to room temperature, the reaction mixture was treated with aq. 1M NaOH soln. and extracted with DCM (3 ×). The combined organic phases were washed with aq. 1M HCl soln. and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was purified by flash chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford **91** (10.91 g, 92%).

Appearance yellow liquid; **Rf** 0.4 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.38 – 7.30 (m, 2H), 7.28 – 7.20 (m, 3H), 4.18 (t, *J* = 6.50 Hz, 2H), 4.13 – 3.66 (m, 2H), 2.81 – 2.73 (m, 2H), 2.09 – 1.97 (m, 2H), 1.29 (s, 6H), 1.26 (s, 6H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 155.91 (C=O), 141.67 (C_q), 128.52 (2 x CH), 128.49 (2x CH), 126.03 (CH), 64.14 (CH_2), 45.84 (broad, 2 x CH), 32.68 (CH_2), 31.02 (CH_2), 21.19 (broad, 4 x CH_3). Physical and spectral data are in accordance with literature data[78].

4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (99)



Chemical Formula: $C_{17}H_{27}BO_2$
Molecular Weight: 274,21

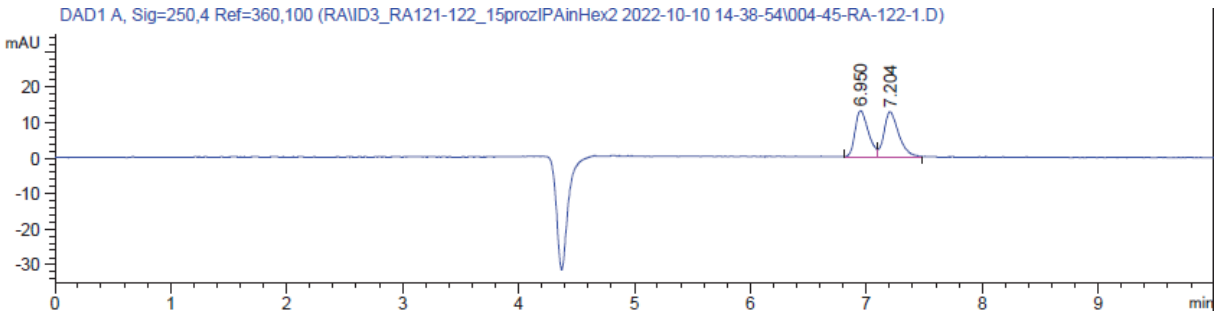
Intermediate **99** was prepared by a reported procedure[9].

In a dry two neck round bottom flask were placed dry Et_2O (30 mL), TMEDA (0.85 mL, 5.54 mmol) and 3-phenylpropyl N,N-diisopropylcarbamate (**91**) (1.22 g, 4.61 mmol), and cooled down to -78 °C. *S*-BuLi (1.4 M in hexanes, 3.6 mL, 5.07 mmol) was added slowly to the reaction mixture and stirred for 5 h at -78 °C. Then, 2-ethyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (957 mg, 6.13 mmol) was added dropwise to the reaction mixture and was stirred for 1 hour at -78 °C. The reaction mixture was warmed up to room temperature and refluxed overnight. After cooling down to room temperature, the reaction mixture was treated with water and extracted with Et_2O (3 ×). The combined organic phases were washed with aq. 1M HCl soln., aq. 1M NaOH soln., water, and brine. Then, the organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude products was purified by flash chromatography on silica gel (Et_2O/pentane=2:98, stained in PMA solution) to afford **99** (666 mg, 53%).

Appearance yellow liquid; **Rf** 0.3 (Et_2O/pentane=2:98); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.36 – 7.29 (m, 2H), 7.28 – 7.19 (m, 3H), 2.76 – 2.58 (m, 2H), 1.90 – 1.64 (m, 2H), 1.63 – 1.46 (m, 2H), 1.31 (s, 12H), 1.15 – 0.99 (m, 1H), 0.98 (t, *J* = 7.41 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.28 (C_q), 128.54 (2 x CH), 128.35 (2 x CH), 125.66 (CH), 83.05 (2 x C_q), 35.77 (CH_2), 33.37 (CH_2), 25.01 (2 x CH_3), 24.97 (2 x CH_3), 24.25 (CH_2), 13.73 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 34.50. Physical and spectral data are in accordance with literature data[9].

chiral HPLC analysis (oxidized with $NaOH/H_2O_2$, corresponding alcohol analysed):

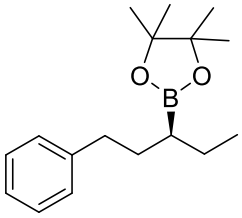
CHIRALPAK ID-3, hexane/IPA 85:15, 0.8 mL min^{-1}, λ = 250 nm



Signal 1: DAD1 A, Sig=250,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.950	BV	0.1183	102.81834	12.99076	48.2268
2	7.204	VB	0.1308	110.37907	12.64649	51.7732
Totals :				213.19742	25.63725	

(*S*)-4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (92)



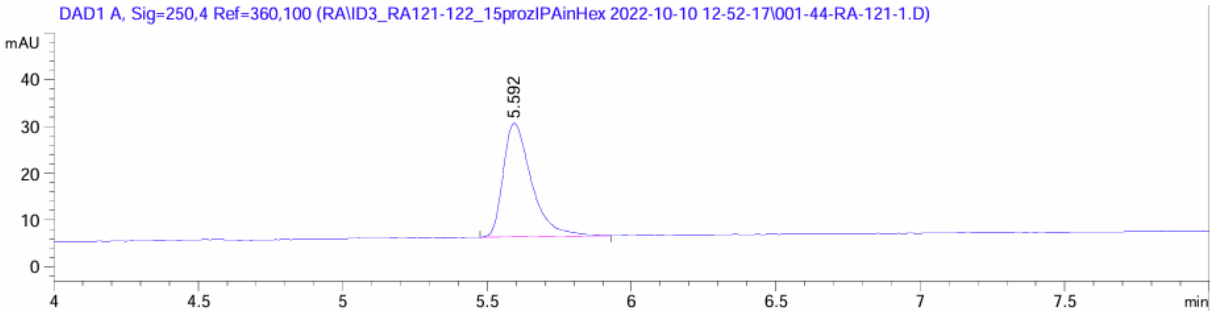
Chemical Formula: $C_{17}H_{27}BO_2$
Molecular Weight: 274,21

Intermediate **92** was prepared by a reported procedure[9].

In a dry two neck round bottom flask were placed dry Et_2O (20 mL), (-)-sparteine (0.95 mL, 4.11 mmol) and 3-phenylpropyl N,N-diisopropylcarbamate (**91**) (903 mg, 3.43 mmol) and cooled down to -78 °C. *S*-BuLi (1.4 M in hexanes, 2.7 mL, 3.77 mmol) was added slowly to the reaction mixture and stirred for 5 h at -78 °C. Then, 2-ethyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (684 mg, 4.38 mmol) was added dropwise, stirred for 1 hour at -78 °C, warmed up to room temperature and then refluxed overnight. The reaction mixture was cooled down to room temperature, treated with water and extracted with Et_2O (3 ×). The combined organic phases were washed with aq. 1M HCl soln., aq. 1M NaOH soln., water, and brine. Then, the organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was purified by flash chromatography on silica gel (Et_2O/pentane=2:98, stained in PMA solution) to afford **92** (763 mg, 81%).

Appearance colorless liquid; **Rf** 0.3 (Et_2O/pentane=2:98); $[\propto]_D^{25}$= +8.3° (c=1.04 g/100 mL $CHCl_3$) ; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.32 – 7.23 (m, 2H), 7.23 – 7.13 (m, 3H), 2.71 – 2.53 (m, 2H), 1.85 – 1.59 (m, 2H), 1.58 – 1.41 (m, 2H), 1.28 (s, 12H), 1.09 – 0.97 (m, 1H), 0.93 (t, *J* = 7.41 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.27 (C_q), 128.53 (2 x CH), 128.34 (2 x CH), 125.65 (CH), 83.04 (2 x C_q), 35.76 (CH_2), 33.36 (CH_2), 25.01 (2 x CH_3), 24.97 (2 x CH_3), 24.25 (CH_2), 13.73 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 34.50. Physical and spectral data are in accordance with literature data[9]. **EE** >99% was determined by chiral HPLC analysis (oxidized with NaOH/H_2O_2, corresponding alcohol analysed):

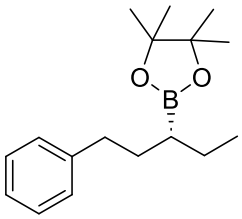
CHIRALPAK ID-3, hexane/IPA 85:15, 0.8 mL min^{-1}, λ = 250 nm



Signal 1: DAD1 A, Sig=250,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.592	BB	0.1048	166.44765	24.32172	100.0000
Totals :				166.44765	24.32172	

(*R*)-4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (100)



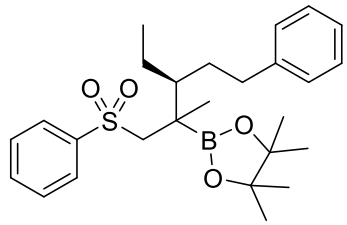
Chemical Formula: $C_{17}H_{27}BO_2$
Molecular Weight: 274,21

Intermediate **100** was prepared by a reported procedure[9].

In a dry two neck round bottom flask were placed dry Et_2O (25 mL), (+)-sparteine (1.1 mL, 4.7 mmol) and 3-phenylpropyl N,N-diisopropylcarbamate (**91**) (1.03 g, 3.91 mmol) and cooled down to -78 °C. *S*-BuLi (1.4 M in hexanes, 3.3 mL, 4.3 mmol) was added slowly to the reaction mixture and stirred for 5 h at -78 °C. Then, 2-ethyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (773 mg, 4.95 mmol) was added dropwise, stirred for 1 hour at -78 °C, warmed up to room temperature and then refluxed overnight. The reaction mixture was cooled down to room temperature, treated with water and extracted with Et_2O (3 ×). The combined organic phases were washed with aq. 1M HCl soln., aq. 1M NaOH soln., water, and brine. Then, the organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was purified by flash chromatography on silica gel (Et_2O/pentane=2:98, stained in PMA solution) to afford **100** (645 mg, 60%).

Appearance colorless liquid; **Rf** 0.3 (Et_2O/pentane=2:98); $[\propto]_D^{25}$= -7.2° (c=1.0 g/100 mL $CHCl_3$) ; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.37 – 7.29 (m, 2H), 7.28 – 7.18 (m, 3H), 2.76 – 2.58 (m, 2H), 1.91 – 1.64 (m, 2H), 1.62 – 1.48 (m, 2H), 1.33 (s, 12H), 1.13 – 1.02 (m, 1H), 1.01 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.28 (C_q), 128.54 (2 x CH), 128.35 (2 x CH), 125.66 (CH), 83.05 (2 x C_q), 35.77 (CH_2), 33.37 (CH_2), 29.85 (CH), 25.01 (2 x CH_3), 24.97 (2 x CH_3), 24.25 (CH_2), 13.73 (CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 34.57. Physical and spectral data are in accordance with literature data[9].

2-((3*S*)-3-ethyl-2-methyl-5-phenyl-1-(phenylsulfonyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (35)

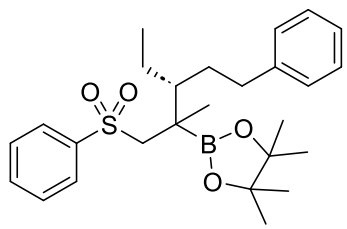


Chemical Formula: $C_{26}H_{37}BO_4S$
Molecular Weight: 456,45

The reaction was performed according to **General Procedure B** with *t*-BuLi (1.7 M in pentane, 2.7 mL, 4.58 mmol), (*S*)-4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (**92**) (546 mg, 2.0 mmol), phenylsulfonyl bromide (1.32 g, 6.0 mmol), and THF (15 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford **35** (708 mg, 78%) as an inseparable mixture

Mix of diastereomer (characteristic peaks): **Appearance** colorless oil; **Rf** 0.5 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.05 – 7.98 (m, 4H), 7.75 – 7.59 (m, 6H), 7.39 – 7.30 (m, 4H), 7.29 – 7.20 (m, 6H), 3.51 (d, *J* = 13.52 Hz, 1H), 3.45 (d, *J* = 13.52 Hz, 1H), 3.20 (d, *J* = 4.49 Hz, 1H), 3.16 (d, *J* = 4.48 Hz, 1H), 2.90 – 2.73 (m, 2H), 2.72 – 2.49 (m, 2H), 1.96 – 1.81 (m, 2H), 1.80 – 1.20 (m, 8H), 1.43 (s, 24H), 1.36 (s, 3H), 1.35 (s, 3H), 1.09 (t, *J* = 7.18 Hz, 3H), 1.05 (t, *J* = 7.44 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.77, 142.67, 142.39, 142.35, 133.23, 129.22, 128.44, 128.39, 128.36, 127.57, 125.91, 125.86, 84.02, 64.36, 64.33, 46.94, 46.91, 36.33, 35.88, 34.95, 33.20, 29.81, 25.83, 25.51, 25.45, 25.35, 23.89, 17.43, 17.21, 14.52, 14.11; **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.82; **FT-IR (cm^{-1}, neat)** 3061, 2970, 2930, 2872, 1597, 1453, 1363, 1308, 1199, 1141, 1084, 1031, 967, 923, 849, 730, 691, 596, 544, 515, 456; **HRMS (ESI)** m/z calculated for $C_{26}H_{38}O_4BS$ $[M+H]^+$: 457.2577, found: 457.2578.

2-((3*R*)-3-ethyl-2-methyl-5-phenyl-1-(phenylsulfonyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36)



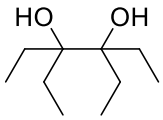
Chemical Formula: $C_{26}H_{37}BO_4S$
Molecular Weight: 456,45

The reaction was performed according to **General Procedure B** with *t*-BuLi (1.7 M in pentane, 1.2 mL, 2.08 mmol), (*R*)-4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (**100**) (248 mg, 0.9 mmol), phenylsulfonyl bromide (604 mg, 2.74 mmol), and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford **36** (192 mg, 47%) as an inseparable mixture.

Mix of diastereomer (characteristic peaks): **Appearance** colorless oil; **Rf** 0.4 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.95 – 7.87 (m, 4H), 7.66 – 7.44 (m, 6H),

7.29 – 7.21 (m, 4H), 7.19 – 7.09 (m, 6H), 3.40 (d, *J* = 13.51 Hz, 1H), 3.34 (d, *J* = 13.53 Hz, 1H), 3.10 (d, *J* = 4.26 Hz, 1H), 3.05 (d, *J* = 4.26 Hz, 1H), 2.78 – 2.62 (m, 2H), 2.61 – 2.40 (m, 2H), 1.85 – 1.69 (m, 2H), 1.69 – 1.10 (m, 8H), 1.33 (s, 24H), 1.25 (s, 3H), 1.24 (s, 3H), 0.96 (dt, *J* = 10.17, 7.26 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ =142.81, 142.43, 133.25, 129.25, 128.48, 128.39, 127.61, 125.94, 125.89, 84.07, 64.39, 64.35, 46.99, 46.96, 35.91, 34.98, 33.23, 25.87, 25.53, 25.48, 25.38, 23.92, 17.45, 17.23, 14.55, 14.14; **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.82; **FT-IR (cm^{-1}, neat)** 2970, 2931, 2873, 1717, 1596, 1452, 1362, 1308, 1199, 1140, 1082, 1028, 969, 920, 849, 730, 690, 595, 548, 514; **HRMS (ESI)** m/z calculated for $C_{26}H_{38}O_4BS$ $[M+H]^+$: 457.2575, found: 457.2578.

3,4-diethylhexane-3,4-diol (101)



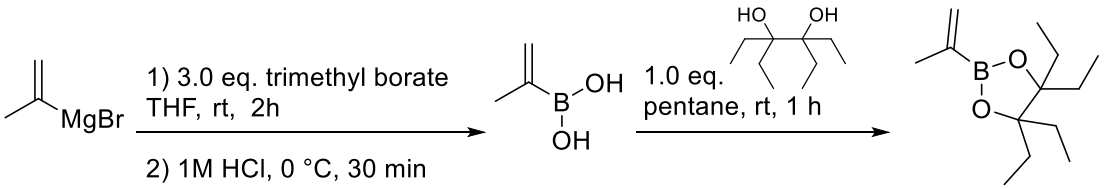
Chemical Formula: $C_{10}H_{22}O_2$
Molecular Weight: 174,28

Intermediate **101** was prepared by a reported procedure[79].

In a dry three neck round bottom flask were placed dry THF (50 mL) and pentan-3-one (1.70 g, 19.7 mmol). The reaction mixture was cooled down to -60 °C, tetrachloro titanium (3.3 mL, 29.6 mmol) was added slowly and stirred for 30 min at -60 °C. Then, Zn powder (3.86 g, 59.0 mmol) was added in one shot, the reaction mixture was warmed up to room temperature and after, refluxed for 3 h. Then, the reaction mixture was cooled down to 0 °C and treated with sat. aq. K_2CO_3 soln. (30 mL). The sticky suspension was filtrated through a buchner funnel, and the filter cake washed with EtOAc. The combined organic phases were washed with water and brine, dried over Na_2SO_3 and concentrated under reduced pressure to afford **101** (1.37 g, 80%). The obtained crude was used without purification for the next step.

Appearance yellow oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 1.96 (s, 2H), 1.61 (qd, *J* = 7.53, 1.97 Hz, 8H), 0.94 (t, *J* = 7.54 Hz, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 78.99, 27.46, 9.17. Physical and spectral data are in accordance with literature data[79].

4,4,5,5-tetraethyl-2-(prop-1-en-2-yl)-1,3,2-dioxaborolane (102)



Chemical Formula: $C_{13}H_{25}BO_2$
Molecular Weight: 224,15

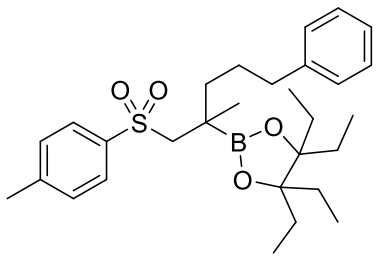
Intermediate **102** was prepared by a reported procedure[80,81].

To a solution of dry THF (10 mL) and isopropenyl magnesium bromide solution (0.5 M in THF, 20 mL, 10.0 mmol) was added trimethyl borate (3.4 mL, 30.0 mmol) and stirred for 2 h at room temperature. Then, the reaction mixture was cooled down to 0 °C, aq. 1M HCl soln. (12 mL) was added and stirred for 30 min at 0 °C. The reaction mixture was extracted with Et_2O (3 ×), the combined organic phases washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

The obtained crude product was added to a solution of pentane (20 mL) and 3,4-diethylhexane-3,4-diol (871 mg, 5.0 mmol). Under stirring was added dry Na_2SO_4 and stirred for 1 h. The reaction mixture was filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **102** (535 mg, 24% over 2 steps).

Appearance colorless liquid; **Rf** 1.0 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.77 – 5.71 (m, 1H), 5.64 – 5.58 (m, 1H), 1.82 (t, *J* = 1.51 Hz, 3H), 1.67 (h, *J* = 7.41 Hz, 8H), 0.92 (t, *J* = 7.49 Hz, 12H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 129.70 (CH_2), 88.50 (2 x C_q), 29.86 (C_q), 26.53 (4 x CH_2), 21.35 (CH_3), 8.93 (4 x CH_3); **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 29.46; **FT-IR (cm^{-1}, neat)** 2970, 2941, 2884, 1622, 1455, 1433, 1416, 1382, 1358, 1287, 1179, 1128, 1114, 1041, 1003, 975, 918, 858, 819, 771, 738, 637, 584, 559, 538, 472, 444, 432, 418; **HRMS (EI)** m/z calculated for $C_{13}H_{25}O_2B$ $[M+H]^+$: 224.1943, found: 224.1942.

4,4,5,5-tetraethyl-2-(2-methyl-5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (103)



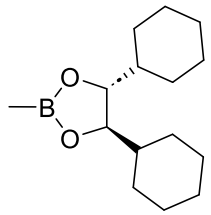
Chemical Formula: $C_{29}H_{43}BO_4S$
Molecular Weight: 498,53

The reaction was performed according to **General Procedure C** with 3-phenylpropyl-magnesium bromide solution (0.7 M in THF, 17 mL, 11.9 mmol), 2-isopropenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3219, 14.3 mmol), tosyl bromide (3.41 g, 14.5 mmol), DMSO (2.4 mL), DMPU (17.3 mL), and THF (13 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford **103** (2.45 g, 41%).

Appearance yellow oil; **Rf** 0.4 (Et_2O/pentane=2:8); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.82 – 7.76 (m, 2H), 7.31 (d, *J* = 8.01 Hz, 2H), 7.29 – 7.21 (m, 2H), 7.20 – 7.09 (m, 3H), 3.28 (d, *J* = 13.84 Hz, 1H), 3.08 (d, *J* = 13.83 Hz, 1H), 2.53 (t, *J* = 7.16 Hz, 2H), 2.43 (s, 3H), 1.87 – 1.38 (m, 12H), 1.19 (s, 3H), 0.90 (td, *J* = 7.48, 1.40 Hz, 12H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 144.04 (C_q), 142.60 (C_q), 139.59 (C_q), 129.79 (2 x CH), 128.46 (2 x CH), 128.38 (2 x CH), 127.68 (2 x CH), 125.80 (CH), 89.07 (2 x Cq), 64.63 (CH_2), 38.04 (CH_2), 36.72 (CH_2), 27.15 (CH_2), 25.82 (2 x CH_2), 25.70 (2 x CH_2), 24.67 (C_q), 21.70 (CH_3), 21.20 (CH_3), 8.96 (2 x CH_3), 8.79 (2 x CH_3);

^{11}B NMR (96 MHz, $CDCl_3$) δ = 33.06; **FT-IR (cm^{-1}, neat)** 2973, 2938, 2881, 1599, 1495, 1455, 1384, 1351, 1312, 1302, 1201, 1183, 1145, 1113, 1086, 1028, 970, 914, 851, 816, 800, 748, 697, 682, 658, 634, 571, 546, 508, 470, 416, 404; **HRMS (ESI)** m/z calculated for $C_{29}H_{47}O_4BSN$ $[M+NH_4]^+$: 516.3306, found: 516.3313.

(4*R*,5*R*)-4,5-dicyclohexyl-2-methyl-1,3,2-dioxaborolane (104)



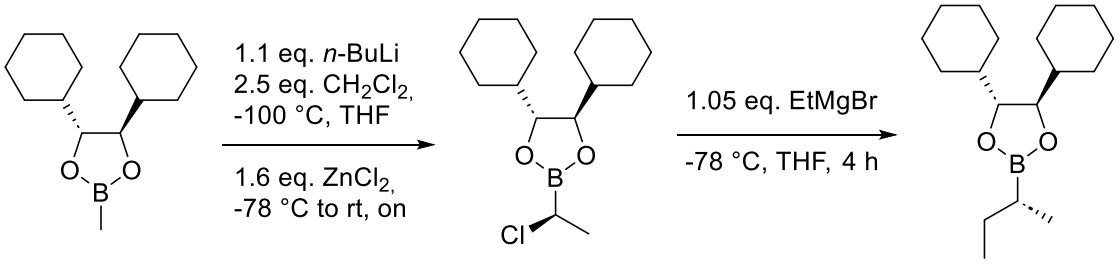
Chemical Formula: $C_{15}H_{27}BO_2$
Molecular Weight: 250,19

Intermediate **104** was prepared by a reported procedure[82].

To a solution of trimethyl boroxine (648 mg, 5.16 mmol) and (4*R*,5*R*)-4,5-dicyclohexyl-2-methyl-1,3,2-dioxaborolane (3.40 g, 15.0 mmol) in pentane (20 mL) was added Na_2SO_4 and stirred for 30 min. Then, the reaction mixture was filtered and concentrated to afford **104** (3.76 g, 97%).

Appearance colorless liquid; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 3.85 – 3.79 (m, 2H), 1.84 – 1.53 (m, 10H), 1.41 – 0.84 (m, 12H), 0.26 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 83.49 (2 x CH), 43.14 (2 x CH), 28.53 (2 x CH_2), 27.44 (2 x CH_2), 26.59 (2 x CH_2), 26.19 (2 x CH_2), 26.03 (2 x CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected; **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.48. Physical and spectral data are in accordance with literature data[82].

(4*R*,5*R*)-2-((*R*)-sec-butyl)-4,5-dicyclohexyl-1,3,2-dioxaborolane (90)



Chemical Formula: $C_{18}H_{33}BO_2$
Molecular Weight: 292,27

Intermediate **90** was prepared by a reported procedure[82].

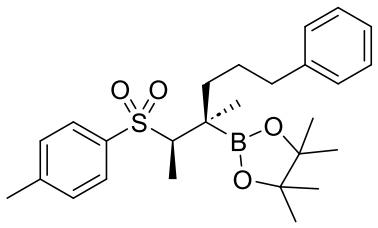
In a three neck round bottom flask were placed dry THF (8 mL) and dry DCM (0.8 mL, 12.5 mmol). After cooling down to -100 °C, *n*-BuLi (2.5 M in hexanes, 2.2 mL, 5.5 mmol) was added very slowly without exceeding -100 °C. The reaction mixture was stirred for 10 min, (4*R*,5*R*)-4,5-dicyclohexyl-2-methyl-1,3,2-dioxaborolane (**104**) (1.25 g, 5.0 mmol) dissolved in dry THF (4 mL) was added also very slowly and stirred for another 10 min continued by slowly warming up to -78 °C. Then, zinc chloride (1.41 g, 10.3 mmol) was added in one shot to the reaction

mixture and warmed up slowly to room temperature overnight. The reaction mixture was concentrated, dissolved in Et_2O (20 mL), treated with aq. Sat. NH_4Cl soln., and extracted with Et_2O (3 ×). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was dissolved in dry THF (5 mL) and at -78 °C was added dropwise ethyl magnesium bromide solution (1 M in THF, 5.3 mL, 5.25 mmol). After 1 h stirring at -78 °C, the reaction mixture was warmed up to room temperature and continued to stir for 4 h. Then, the reaction mixture was treated with aq. 1M HCl soln. and extracted with cold pentane (3 ×). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford **90** (1.19 g, 81%).

Appearance colorless liquid; **Rf** 0.4 (Et2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 3.87 – 3.79 (m, 2H), 1.84 – 0.85 (m, 31H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 83.29 (2 x CH), 43.23 (2 x CH), 28.44 (2 x CH_2), 27.51 (2 x CH_2), 26.64 (2 x CH_2), 26.35 (CH_2), 26.20 (2 x CH_2), 26.10 (2 x CH_2), 15.58 (CH_3), 13.56 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected; **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.98. Physical and spectral data are in accordance with literature data[82].

1.4.4 Alkylation of β-borylated sulfones

4,4,5,5-tetramethyl-2-((2*R*,3*S*)-3-methyl-6-phenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (43)



Chemical Formula: $C_{26}H_{37}BO_4S$
Molecular Weight: 456,45

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-[1-methyl-4-phenyl-1-(p-tolylsulfonylmethyl)butyl]-1,3,2-dioxaborolane (**16**) (422 mg, 0.95 mmol), diisopropylamine (0.14 mL, 1.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), methyl iodide (0.07 mL, 1.14 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two inseparable isomers of **43** (348 mg, 80%, dr 28:72). Dr was determined on crude product by quantitative NMR analysis.

Appearance colorless oil; **Rf** 0.3 (Et_2O/pentane=15:85);

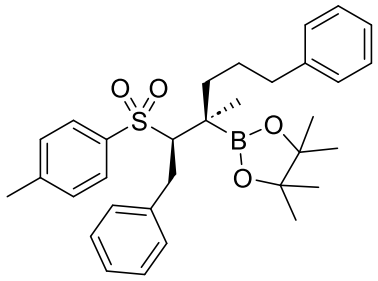
Minor diastereomer: **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.81 – 7.74 (m, 2H), 7.34 – 7.29 (m, 2H), 7.29 – 7.09 (m, 5H), 3.40 (q, *J* = 7.00 Hz, 1H), 2.64 – 2.51 (m, 2H), 2.43 (s, 3H), 1.86 – 1.75 (m, 1H), 1.50 – 1.36 (m, 1H), 1.43 – 1.29 (m, 2H), 1.34 (s, 6H), 1.33 (s, 6H), 1.18 (s, 3H), 1.09 (d, *J* = 7.06 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.00 (C_q), 142.31 (C_q), 137.62 (C_q), 129.71 (2 x CH), 128.47 (2 x CH), 128.43 (4 x CH), 125.89 (CH), 83.74 (2 x C_q), 65.42 (CH),

37.64 (CH_2), 36.82 (CH_2), 27.26 (CH_2), 25.59 (2 x CH_3), 25.39 (2 x CH_3), 21.71 (CH_3), 16.68 (CH_3), 7.91 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomer: **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.80 – 7.74 (m, 2H), 7.35 – 7.24 (m, 4H), 7.24 – 7.13 (m, 3H), 3.38 (q, J = 7.09 Hz, 1H), 2.76 – 2.51 (m, 2H), 2.43 (s, 3H), 2.04 – 1.86 (m, 2H), 1.75 – 1.48 (m, 2H), 1.30 (s, 6H), 1.28 (s, 6H), 1.15 (d, J = 7.09 Hz, 3H), 1.05 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.01 (C_q), 143.32 (C_q), 137.77 (C_q), 129.68 (2 x CH), 128.59 (2 x CH), 128.48 (2 x CH), 128.33 (2 x CH), 125.62 (CH), 83.53 (2 x C_q), 66.44 (CH), 37.19 (CH_2), 33.50 (CH_2), 27.99 (CH_2), 25.06 (4 x CH_3), 21.71 (CH_3), 19.54 (CH_3), 10.29 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 34.33; **FT-IR (cm^{-1}, neat)** 2975, 2930, 1598, 1495, 1454, 1389, 1370, 1310, 1299, 1256, 1213, 1120, 1086, 1056, 1031, 1019, 966, 909, 852, 816, 800, 777, 697, 648, 570, 534, 510, 491, 470, 431, 414; **HRMS (ESI)** m/z calculated for $C_{26}H_{38}O_4BS$ $[M+H]^+$: 457.2571, found: 457.2578.

4,4,5,5-tetramethyl-2-((2*R*,3*S*)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (40)



Chemical Formula: $C_{32}H_{41}BO_4S$
Molecular Weight: 532,55

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-[1-methyl-4-phenyl-1-(p-tolylsulfonylmethyl)butyl]-1,3,2-dioxaborolane (**16**) (259 mg, 0.6 mmol), diisopropylamine (0.08 mL, 0.6 mmol), *n*-BuLi (2.5 M in hexanes, 0.25 mL, 0.6 mmol), benzyl bromide (0.07 mL, 0.6 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two separable isomers of **40** (256 mg, 82%, dr 35:65). Dr was determined on crude product by quantitative NMR analysis.

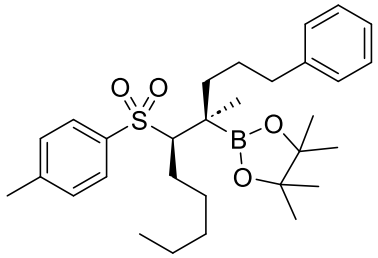
Minor diastereomer: **Appearance** white solid; **Mp** 139 °C; **Rf** 0.5 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, CD_2Cl_2) δ = 7.41 (d, *J* = 8.21 Hz, 2H), 7.33 – 7.21 (m, 4H), 7.21 – 7.13 (m, 1H), 7.04 (d, *J* = 8.06 Hz, 2H), 7.02 – 6.95 (m, 3H), 6.89 – 6.82 (m, 2H), 3.82 (dd, *J* = 8.31, 4.21 Hz, 1H), 3.19 – 3.00 (m, 2H), 2.76 – 2.52 (m, 2H), 2.31 (s, 3H), 2.14 – 1.85 (m, 2H), 1.73 – 1.59 (m, 2H), 1.30 (s, 6H), 1.28 (s, 6H), 1.08 (s, 3H); **^{13}C-NMR** (75 MHz, CD_2Cl_2) δ = 143.95 (C_q), 143.77 (C_q), 139.34 (2 x C_q), 129.61 (2 x CH), 129.43 (2 x CH), 129.00 (2 x CH), 128.73 (2 x CH), 128.54 (2 x CH), 128.32 (2 x CH), 126.48 (CH), 126.05 (CH), 83.95 (2 x C_q), 74.24

(CH), 37.64 (CH_2), 33.75 (CH_2), 31.61 (CH_2), 28.22 (CH_2), 25.34 (2 x CH_3), 25.17 (2 x CH_3), 21.71 (CH_3), 21.16 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.4 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, CD_2Cl_2) δ = 7.40 – 7.33 (m, 2H), 7.28 – 7.19 (m, 2H), 7.19 – 7.11 (m, 1H), 7.11 – 6.95 (m, 7H), 6.88 – 6.81 (m, 2H), 3.85 (dd, *J* = 8.84, 4.40 Hz, 1H), 3.06 (qd, *J* = 15.20, 6.63 Hz, 2H), 2.58 – 2.40 (m, 2H), 2.32 (s, 3H), 1.92 – 1.73 (m, 1H), 1.57 – 1.36 (m, 3H), 1.32 (s, 6H), 1.30 (s, 6H), 1.22 (s, 3H); **^{13}C-NMR** (75 MHz, CD_2Cl_2) δ = 143.76 (C_q), 142.88 (C_q), 139.47 (C_q), 138.79 (C_q), 129.62 (2 x CH), 129.59 (2 x CH), 128.95 (2 x CH), 128.78 (2 x CH), 128.61 (2 x CH), 128.16 (2 x CH), 126.64 (CH), 126.22 (CH), 84.17 (2 x C_q), 72.50 (CH), 38.46 (CH_2), 37.11 (CH_2), 30.10 (CH_2), 27.85 (CH_2), 25.86 (2 x CH_3), 25.56 (2 x CH_3), 21.72 (CH_3), 18.01 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.46; **FT-IR (cm^{-1}, neat)** 2930, 1600, 1493, 1454, 1297, 1241, 1146, 1125, 1030, 968, 859, 813, 751, 695, 655, 570, 505, 473; **HRMS (ESI)** m/z calculated for $C_{32}H_{42}O_4BS$ $[M+H]^+$: 533.2891, found: 533.2890.

4,4,5,5-tetramethyl-2-((4*S*,5*R*)-4-methyl-1-phenyl-5-tosyldecan-4-yl)-1,3,2-dioxaborolane (44)



Chemical Formula: $C_{30}H_{45}BO_4S$
Molecular Weight: 512,56

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-[1-methyl-4-phenyl-1-(p-tolylsulfonylmethyl)butyl]-1,3,2-dioxaborolane (**16**) (447 mg, 1.0 mmol), diisopropylamine (0.14 mL, 1.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), 1-iodopentane (0.16 mL, 1.2 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two separable isomers of **44** (397 mg, 77%, dr 38:62). Dr was determined on crude product by quantitative NMR analysis.

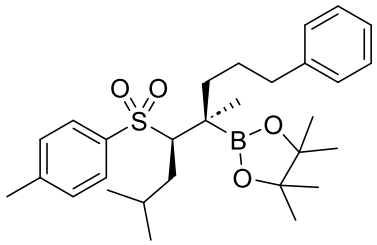
Minor diastereomer: **Appearance** colorless oil; **Rf** 0.55 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.85 – 7.82 (m, 2H), 7.34 – 7.11 (m, 7H), 3.37 (dd, *J* = 8.07, 3.04 Hz, 1H), 2.42 (s, 3H), 2.01 – 1.87 (m, 1H), 2.00 – 1.87 (m, 1H), 1.97 – 1.77 (m, 1H), 1.67 – 1.54 (m, 1H), 1.64 – 1.53 (m, 1H), 1.58 – 1.38 (m, 1H), 1.51 – 1.33 (m, 2H), 1.33 (s, 6H), 1.32 (s, 6H), 1.18 – 0.99 (m, 2H), 1.16 (s, 3H), 1.15 – 0.92 (m, 2H), 1.07 – 0.90 (m, 2H), 0.74 – 0.70 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ =143.77 (C_q), 142.33 (C_q), 139.81 (C_q), 129.59 (2 x CH),

128.49 (2 x CH), 128.42 (2 x CH), 128.09 (2 x CH), 125.87 (CH), 83.65 (2 x C_q), 71.17 (CH), 37.66 (CH_2), 31.67 (CH_2), 28.42 (CH_2), 27.27 (CH_2), 26.19 (CH_2), 25.66 (2 x CH_3), 25.34 (2 x CH_3), 23.70 (CH_2), 22.25 (CH_2), 21.67 (CH_3), 17.25 (CH_3), 13.90 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.45 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.82 – 7.79 (m, 2H), 7.36 – 7.10 (m, 7H), 3.28 (dd, *J* = 7.00, 2.89 Hz, 1H), 2.75 – 2.65 (m, 1H), 2.64 – 2.54 (m, 1H), 2.64 – 2.54 (m, 2H), 2.43 (s, 3H), 2.04 – 1.89 (m, 1H), 2.01 – 1.90 (m, 1H), 1.71 – 1.58 (m, 1H), 1.70 -1.55 (m, 1H), 1.30 (s, 6H), 1.28 (s, 6H), 1.18 – 0.99 (m, 2H), 1.06 (s, 3H), 1.06 – 0.96 (m, 1H), 1.05 – 0.96 (m, 2H), 0.87 – 0.76 (m, 1H), 0.71 (t, *J* = 6.74 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.88 (C_q), 143.36 (C_q), 139.33 (C_q), 129.61 (2 x CH), 128.57 (2 x CH), 128.33 (2 x CH), 128.29 (2 x CH), 125.57 (CH), 83.45 (2 x Cq), 72.15 (CH), 37.22 (CH_2), 36.87 (CH_2), 33.81 (CH_2), 31.70 (CH_2), 29.35 (CH_2), 28.02 (CH_2), 25.05 (4 x CH_3), 22.25 (CH_2), 21.67 (CH_3), 19.68 (CH_3), 13.90 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 34.51; **FT-IR (cm^{-1}, neat)** 2954, 2927, 2858, 1598, 1495, 1454, 1371, 1353, 1298, 1285, 1260, 1213, 1084, 1030, 1019, 967, 910, 854, 817, 800, 732, 712, 698, 680, 631, 572, 541, 511, 467, 437, 421, 411; **HRMS (ESI)** m/z calculated for $C_{30}H_{46}O_4BS$ $[M+H]^+$: 513.3204, found: 513.3204.

2-((4*S*,5*R*)-4,7-dimethyl-1-phenyl-5-tosyloctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (45)



Chemical Formula: $C_{29}H_{43}BO_4S$
Molecular Weight: 498,53

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-[1-methyl-4-phenyl-1-(p-tolylsulfonylmethyl)butyl]-1,3,2-dioxaborolane (**16**) (432 mg, 1.0 mmol), diisopropylamine (0.14 mL, 1.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), 1-iodo-2-methyl-propane (0.14 mL, 1.2 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two separable isomers of **45** (336 mg, 69%, dr 33:67). Dr was determined on crude product by quantitative NMR analysis.

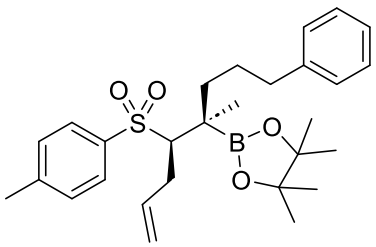
Minor diastereomer: **Appearance** colorless oil; **Rf** 0.4 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ =7.88 – 7.82 (m, 2H), 7.33 – 7.09 (m, 7H), 3.47 (dd, *J* = 7.48, 3.06 Hz, 1H), 2.56 (t, *J* = 7.43 Hz, 2H), 2.42 (s, 3H), 2.00 – 1.82 (m, 1H), 1.86 – 1.76 (m, 1H), 1.63 – 1.54 (m, 1H),

1.59 – 1.49 (m, 1H), 1.46 – 1.31 (m, 2H), 1.41 – 1.33 (m, 1H), 1.33 (s, 6H), 1.32 (s, 6H), 1.15 (s, 3H), 0.56 (d, *J* = 5.98 Hz, 3H), 0.48 (d, *J* = 5.89 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.80 (C_q), 142.34 (C_q), 139.58 (C_q), 129.60 (2 x CH), 128.50 (2 x CH), 128.42 (2 x CH), 128.17 (2 x CH), 125.86 (CH), 83.67 (2 x C_q), 68.83 (CH), 37.58 (CH_2), 36.88 (CH_2), 32.82 (CH_2), 27.18 (CH_2), 26.05 (CH), 25.72 (2 x CH_3), 25.38 (2 x CH_3), 23.08 (CH_3), 21.71 (CH_3), 21.44 (CH_3), 17.01 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.3 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.85 – 7.80 (m, 2H), 7.33 – 7.13 (m, 7H), 3.42 (dd, *J* = 7.27, 3.42 Hz, 1H), 2.75 – 2.63 (m, 1H), 2.62 – 2.50 (m, 1H), 2.43 (s, 3H), 2.09 – 1.94 (m, 1H), 1.93 – 1.84 (m, 1H), 1.89 – 1.76 (m, 1H), 1.67 – 1.55 (m, 1H), 1.60 – 1.48 (m, 1H), 1.53 – 1.45 (m, 1H), 1.32 (s, 6H), 1.30 (s, 6H), 1.25 – 1.16 (m, 1H), 0.98 (s, 3H), 0.57 (d, *J* = 12.18 Hz, 3H), 0.55 (d, *J* = 12.21 Hz, 3H) **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.90 (C_q), 143.54 (C_q), 139.26 (C_q), 129.63 (2 x CH), 128.62 (2 x CH), 128.36 (2 x CH), 128.30 (2 x CH), 125.56 (CH), 83.35 (2 x C_q), 70.50 (CH), 37.35 (CH_2), 33.82 (CH_2), 32.84 (CH_2), 27.87 (CH_2), 26.73 (CH), 25.14 (2 x CH_3), 25.09 (2 x CH_3), 22.89 (CH_3), 21.75 (CH_3), 21.71 (CH_3), 20.31 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.61; **FT-IR (cm^{-1}, neat)** 2961, 2864, 1598, 1496, 1465, 1453, 1378, 1368, 1340, 1312, 1298, 1287, 1241, 1211, 1177, 1084, 1042, 1031, 1019, 964, 908, 854, 822, 800, 747, 734, 715, 698, 653, 626, 574, 510, 467, 455, 435, 416, 404; **HRMS (ESI)** m/z calculated for $C_{29}H_{44}O_4BS$ $[M+H]^+$: 499.3049, found: 499.3048.

4,4,5,5-tetramethyl-2-((4*S*,5*R*)-4-methyl-1-phenyl-5-tosyloct-7-en-4-yl)-1,3,2-dioxaborolane (41)



Chemical Formula: $C_{28}H_{39}BO_4S$
Molecular Weight: 482,49

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-[1-methyl-4-phenyl-1-(p-tolylsulfonylmethyl)butyl]-1,3,2-dioxaborolane (**16**) (443 mg, 1.0 mmol), diisopropylamine (0.14 mL, 1.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), allyl iodide (0.11 mL, 1.2 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two separable isomers of **41** (389 mg, 81%, dr 39:61). Dr was determined on crude product by quantitative NMR analysis.

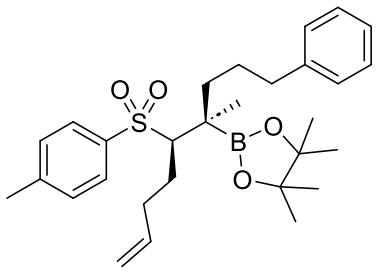
Minor diastereomer: **Appearance** colorless oil; **Rf** 0.4 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.81 – 7.74 (m, 2H), 7.33 – 7.24 (m, 4H), 7.24 – 7.13 (m, 3H), 5.37 – 5.21

(m, 1H), 4.82 (dq, *J* = 17.03, 1.59 Hz, 1H), 4.70 (dq, *J* = 10.00, 1.42 Hz, 1H), 3.44 (dd, *J* = 7.47, 3.78 Hz, 1H), 2.77 – 2.67 (m, 1H), 2.75 – 2.64 (m, 1H), 2.66 – 2.56 (m, 1H), 2.54 – 2.44 (m, 1H), 2.42 (s, 3H), 2.07 – 1.95 (m, 1H), 2.05 – 1.94 (m, 1H), 1.72 – 1.60 (m, 1H), 1.70 – 1.57 (m, 1H), 1.30 (s, 6H), 1.29 (s, 6H), 1.06 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.96 (C_q), 143.36 (C_q), 138.91 (C_q), 136.16 (CH), 129.55 (2 x CH), 128.66 (2 x CH), 128.61 (2 x CH), 128.33 (2 x CH), 125.62 (CH), 116.77 (CH_2), 83.52 (2 x C_q), 71.93 (CH), 37.23 (CH_2), 33.46 (CH_2), 30.01 (CH_2), 27.85 (CH_2), 25.13 (2 x CH_3), 25.05 (2 x CH_3), 21.74 (CH_3), 20.16 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.3 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.82 – 7.76 (m, 2H), 7.31 – 7.22 (m, 4H), 7.20 – 7.09 (m, 3H), 5.40 – 5.24 (m, 1H), 4.89 (dq, *J* = 17.01, 1.58 Hz, 1H), 4.75 (dq, *J* = 10.00, 1.38 Hz, 1H), 3.50 – 3.43 (m, 1H), 2.72 – 2.59 (m, 1H), 2.55 (t, *J* = 6.91 Hz, 2H), 2.48 – 2.38 (m, 1H), 2.42 (s, 3H), 1.89 – 1.71 (m, 1H), 1.58 – 1.44 (m, 1H), 1.53 – 1.36 (m, 2H), 1.33 (s, 6H), 1.32 (s, 6H), 1.19 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.88 (C_q), 142.31 (C_q), 139.19 (C_q), 135.77 (CH), 129.52 (2 x CH), 128.60 (2 x CH), 128.53 (2 x CH), 128.45 (2 x CH), 125.92 (CH), 117.26 (CH_2), 83.76 (2 x C_q), 70.62 (CH), 37.75 (CH_2), 36.82 (CH_2), 28.39 (CH_2), 27.27 (CH_2), 25.67 (2 x CH_3), 25.33 (2 x CH_3), 21.73 (CH_3), 17.52 CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.21; **FT-IR (cm^{-1}, neat)** 2975, 2929, 2360, 1639, 1599, 1495, 1454, 1370, 1298, 1287, 1247, 1212, 1084, 1030, 1019, 992, 967, 911, 853, 816, 800, 732, 698, 680, 572, 532, 509, 492, 466, 437, 409; **HRMS (ESI)** m/z calculated for $C_{28}H_{40}O_4BS$ $[M+H]^+$: 483.2736, found: 483.2735.

4,4,5,5-tetramethyl-2-((4*S*,5*R*)-4-methyl-1-phenyl-5-tosylnon-8-en-4-yl)-1,3,2-dioxaborolane (46)



Chemical Formula: $C_{29}H_{41}BO_4S$
Molecular Weight: 496,51

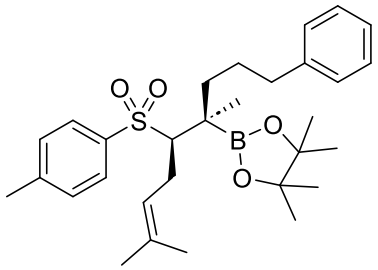
The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-[1-methyl-4-phenyl-1-(p-tolylsulfonylmethyl)butyl]-1,3,2-dioxaborolane (**16**) (221 mg, 0.5 mmol), diisopropylamine (0.07 mL, 0.5 mmol), *n*-BuLi (2.5 M in hexanes, 0.2 mL, 0.5 mmol), allyl iodide (0.11 mL, 1.2 mmol) and THF (7 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two separable isomers of **46** (138 mg, 56%, dr 37:63). Dr was determined on crude product by quantitative NMR analysis.

Minor diastereomer: **Appearance** colorless oil; **Rf** 0.31 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.88 – 7.82 (m, 2H), 7.34 – 7.23 (m, 3H), 7.22 – 7.10 (m, 4H), 5.50 – 5.35 (m, 1H), 4.77 (dd, *J* = 10.28, 1.81 Hz, 1H), 4.61 – 4.52 (m, 1H), 3.41 (dd, *J* = 8.59, 2.33 Hz, 1H), 2.56 (t, *J* = 7.18 Hz, 2H), 2.43 (s, 3H), 2.13 – 1.98 (m, 1H), 1.80 – 1.70 (m, 1H), 1.77 – 1.66 (m, 1H), 1.65 – 1.53 (m, 1H), 1.64 – 1.51 (m, 1H), 1.46 – 1.27 (m, 1H), 1.41 – 1.23 (m, 2H), 1.32 (s, 6H), 1.31 (s, 6H), 1.15 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.92 (C_q), 142.34 (C_q), 139.92 (C_q), 137.21 (CH), 129.71 (2 x CH), 128.51 (2 x CH), 128.46 (2 x CH), 128.14 (2 x CH), 125.91 (CH), 115.70 (CH_2), 83.72 (2 x C_q), 70.11 (CH), 37.74 (CH_2), 36.88 (CH_2), 32.45 (CH_2), 27.22 (CH_2), 25.68 (2 x CH_3), 25.35 (2 x CH_3), 23.38 (CH_2), 21.72 (CH_3), 17.40 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.37 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.88 – 7.82 (m, 2H), 7.38 – 7.27 (m, 4H), 7.26 – 7.16 (m, 3H), 5.56 – 5.40 (m, 1H), 4.83 (dd, *J* = 10.22, 1.92 Hz, 1H), 4.67 (dt, *J* = 17.08, 1.69 Hz, 1H), 3.36 (dd, *J* = 7.32, 1.98 Hz, 1H), 2.63 – 2.53 (m, 1H), 2.53 – 2.43 (m, 1H), 2.46 (s, 3H), 2.17 – 2.02 (m, 1H), 2.03 – 1.87 (m, 2H), 1.68 – 1.50 (m, 1H), 1.68 – 1.48 (m, 2H), 1.59 – 1.48 (m, 1H), 1.58 – 1.44 (m, 1H), 1.32 (s, 6H), 1.31 (s, 6H), 1.09 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.01 (C_q), 143.28 (C_q), 139.37 (C_q), 137.22 (CH), 129.70 (2 x CH), 128.57 (2 x CH), 128.33 (2 x CH), 128.30 (2 x CH), 125.59 (CH), 115.50 (CH_2), 83.49 (2 x C_q), 71.15 (CH), 37.19 (CH_2), 33.88 (CH_2), 33.38 (CH_2), 27.97 (CH_2), 25.59 (CH_2), 25.07 (2 x CH_3), 25.03 (2 x CH_3), 21.70 (CH_3), 19.77 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.63; **FT-IR (cm^{-1}, neat)** 3027, 2974, 2929, 2857, 1640, 1598, 1495, 1454, 1428, 1389, 1371, 1353, 1311, 1297, 1286, 1257, 1213, 1140, 1110, 1084, 1030, 1019, 997, 967, 909, 853, 817, 731, 699, 682; **HRMS (ESI)** m/z calculated for $C_{29}H_{42}O_4BS$ $[M+H]^+$: 497.2890, found: 497.2891.

2-((4*S*,5*R*)-4,8-dimethyl-1-phenyl-5-tosylnon-7-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (42)



Chemical Formula: $C_{30}H_{43}BO_4S$
Molecular Weight: 510,54

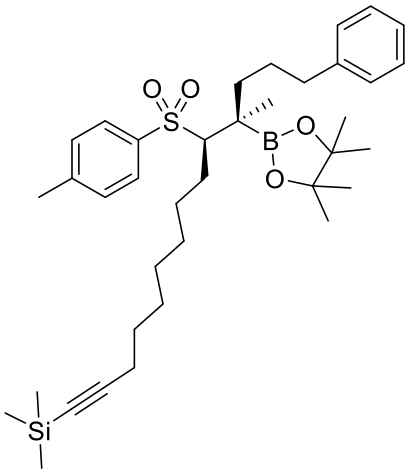
The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-[1-methyl-4-phenyl-1-(p-tolylsulfonylmethyl)butyl]-1,3,2-dioxaborolane (**16**) (441 mg, 1.0 mmol), diisopropylamine (0.14 mL, 1.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), 1-bromo-3-methyl-but-2-ene (0.15 mL, 1.2 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two separable isomers of **42** (347 mg, 68%, dr 33:67). Dr was determined on crude product by quantitative NMR analysis.

Minor diastereomer: **Appearance** colorless oil; **Rf** 0.5 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ =7.77 – 7.71 (m, 2H), 7.32 – 7.14 (m, 7H), 4.55 – 4.46 (m, 1H), 3.45 (dd, *J* = 8.58, 3.62 Hz, 1H), 2.78 – 2.67 (m, 1H), 2.75 – 2.62 (m, 1H), 2.67 – 2.56 (m, 1H), 2.41 (s, 3H), 2.40 – 2.31 (m, 1H), 2.14 – 1.96 (m, 1H), 2.06 – 1.94 (m, 1H), 1.71 – 1.59 (m, 1H), 1.71 – 1.57 (m, 1H), 1.49 (s, 3H), 1.35 (s, 3H), 1.31 (s, 6H), 1.29 (s, 6H), 1.05 (s, 3H) ; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.54 (C_q), 143.46 (C_q), 139.58 (C_q), 132.93 (C_q), 129.24 (2 x CH), 128.60 (2 x CH), 128.34 (2 x CH), 128.30 (2 x CH), 125.56 (CH), 122.50 (CH), 83.39 (2 x C_q), 72.70 (CH), 37.27 (CH_2), 33.14 (CH_2), 27.86 (CH_2), 25.64 (CH_3), 25.13 (2 x CH_3), 25.00 (2 x CH_3), 24.18 (CH_2), 21.66 (CH_3), 20.47 (CH_3), 17.90 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.45 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ =7.77 – 7.70 (m, 2H), 7.30 – 7.22 (m, 4H), 7.20 – 7.09 (m, 3H), 4.56 – 4.47 (m, 1H), 3.46 (dd, *J* = 8.95, 3.71 Hz, 1H), 2.72 – 2.59 (m, 1H), 2.54 (t, *J* = 7.18 Hz, 2H), 2.41 (s, 3H), 2.37 – 2.24 (m, 1H), 1.92 – 1.77 (m, 1H), 1.59 – 1.41 (m, 1H), 1.55 – 1.33 (m, 2H), 1.53 (s, 3H), 1.38 (s, 3H), 1.33 (s, 6H), 1.32 (s, 6H), 1.21 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.49 (C_q), 142.32 (C_q), 139.76 (C_q), 133.24 (C_q), 129.22 (2 x CH), 128.51 (2 x CH), 128.42 (2 x CH), 128.31 (2 x CH), 125.87 (CH), 122.07 (CH), 83.67 (2 x C_q), 71.02 (CH), 37.96 (CH_2), 36.90 (CH_2), 27.29 (CH_2), 25.75 (CH_3), 25.66 (2 x CH_3), 25.33 (2 x CH_3), 22.77 (CH_2), 21.66 (CH_3), 17.93 (CH_3), 17.67 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.78; **FT-IR (cm^{-1}, neat)** 3026, 2973, 2925, 2360, 1599, 1495, 1453, 1370, 1318, 1297, 1247, 1213, 1139, 1084, 1019, 967, 910, 855, 816, 735, 713, 697, 680, 631, 574, 509, 467, 448, 419; **HRMS (ESI)** m/z calculated for $C_{30}H_{44}O_4BS$ $[M+H]^+$: 511.3042, found: 511.3048.

trimethyl((10*R*,11*S*)-11-methyl-14-phenyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10-tosyltetradec-1-yn-1-yl)silane (47)



Chemical Formula: $C_{37}H_{57}BO_4SSi$
Molecular Weight: 636,81

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-[1-methyl-4-phenyl-1-(p-tolylsulfonylmethyl)butyl]-1,3,2-dioxaborolane (**16**) (220 mg, 1.0 mmol), diisopropylamine (0.07 mL, 1.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.2 mL, 1.0 mmol), 9-iodonon-1-ynyl(trimethyl)silane (203 mg, 1.2 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two separable isomers of **47** (134 mg, 42%, dr 35:65). Dr was determined on crude product by quantitative NMR analysis.

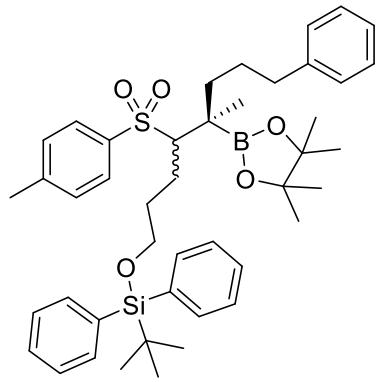
Appearance colorless oil; **Rf** 0.4 & 0.5 (Et_2O/pentane=15:85);

Minor diastereomer (characteristic signals): **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 3.33 (dd, J = 8.1, 3.0 Hz, 1H), 2.39 (s, 3H), 1.29 (s, 6H), 1.28 (s, 6H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 107.66 (C_q), 84.44 (C_q), 83.48 (2 x C_q), 21.72 (CH_3), 19.93 (CH_2), 0.30 (3 x CH_3).

Major diastereomer: **^{1}H-NMR** (300 MHz, $CDCl_3$) δ =7.83 – 7.77 (m, 2H), 7.34 – 7.24 (m, 4H), 7.24 – 7.13 (m, 3H), 3.27 (dd, *J* = 6.97, 2.91 Hz, 1H), 2.73 – 2.50 (m, 2H), 2.44 (s, 3H), 2.14 (t, *J* = 7.22 Hz, 2H), 1.99 – 1.83 (m, 3H), 1.69 – 1.47 (m, 4H), 1.40 (p, *J* = 7.22 Hz, 2H), 1.29 (s, 6H), 1.27 (s, 6H), 1.23 – 1.10 (m, 1H), 1.05 (s, 3H), 1.03 – 0.93 (m, 6H), 0.15 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.92 (C_q), 143.37 (C_q), 139.33 (C_q), 129.65 (2 x CH), 128.59 (2 x CH), 128.34 (2 x CH), 128.31 (2 x CH), 125.59 (CH), 107.70 (C_q), 84.45 (C_q), 83.47 (2 x C_q), 72.13 (CH), 37.23 (CH_2), 33.75 (CH_2), 29.65 (CH_2), 29.35 (CH_2), 28.69 (2 x CH_2), 28.64 (CH_2), 28.02 (CH_2), 26.12 (CH_2), 25.07 (4 x CH_3), 21.72 (CH_3), 19.93 (CH_2), 19.74 (CH_3), 0.33 (3 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 34.25; **FT-IR (cm^{-1}, neat)** 2929, 2856, 2172, 1598, 1496, 1455, 1371, 1312, 1298, 1286, 1248, 1212, 1141, 1084, 1030, 1019, 967, 910, 840, 817, 732, 698, 667, 643, 573, 511, 492, 467, 453, 438; **HRMS (ESI)** m/z calculated for $C_{37}H_{58}O_4BSSi$ $[M+H]^+$: 637.3914, found: 637.3913.

***tert*-butyl(((4*R*,5*S*)-5-methyl-8-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-tosyloctyl)oxy)diphenylsilane (48)**



Chemical Formula: $C_{44}H_{59}BO_5SSi$
Molecular Weight: 738.91

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-[1-methyl-4-phenyl-1-(p-tolylsulfonylmethyl)butyl]-1,3,2-dioxaborolane (**16**) (223 mg, 1.0 mmol), diisopropylamine (0.07 mL, 1.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.2 mL, 1.0 mmol), *tert*-butyl-(3-iodopropoxy)-diphenyl-silane (550 mg, 1.3 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two separable isomers of **48** (305 mg, 59%, dr 49:51). Dr was determined on crude product by quantitative NMR analysis.

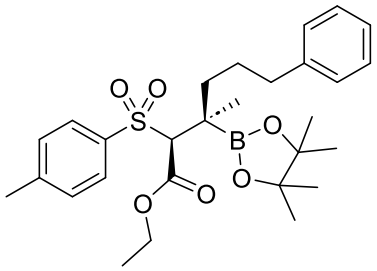
First diastereomer: **Appearance** colorless oil; **Rf** 0.35 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.80 – 7.75 (m, 2H), 7.59 – 7.53 (m, 4H), 7.45 – 7.29 (m, 6H), 7.29 – 7.13 (m, 7H), 3.37 (t, *J* = 6.01 Hz, 2H), 3.30 (dd, *J* = 6.79, 3.20 Hz, 1H), 2.73 – 2.64 (m, 1H), 2.62 – 2.53 (m, 1H), 2.38 (s, 3H), 2.04 – 1.92 (m, 1H), 2.01 – 1.89 (m, 1H), 1.99 – 1.88 (m, 1H), 1.88 – 1.76 (m, 1H), 1.68 – 1.58 (m, 1H), 1.67 – 1.54 (m, 1H), 1.30 (s, 6H), 1.28 (s, 6H), 1.30 – 1.18 (m, 1H), 1.17 – 1.05 (m, 1H), 1.04 (s, 3H), 1.00 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.89 (C_q), 143.41 (C_q), 139.14 (C_q), 135.64 (2 x CH), 135.63 (2 x CH), 133.94 (C_q), 133.90 (C_q), 129.71 (2 x CH), 128.60 (2 x CH), 128.34 (4 x CH), 127.74 (4 x CH), 125.60 (3 x CH), 83.48 (2 x C_q), 72.18 (CH), 63.46 (CH_2), 37.29 (CH_2), 33.52 (CH_2), 32.77 (CH_2), 27.94 (CH_2), 26.95 (3 x CH_3), 25.11 (2 x CH_3), 25.08 (2 x CH_3), 22.44 (CH_2), 21.72 (CH_3), 19.90 (CH_3), 19.30 (C_q). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Second diastereomer: **Appearance** colorless oil; **Rf** 0.3 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.83 – 7.76 (m, 2H), 7.62 – 7.55 (m, 4H), 7.46 – 7.32 (m, 6H), 7.27 – 7.20 (m, 4H), 7.18 – 7.07 (m, 3H), 3.44 – 3.39 (m, 2H), 3.40 – 3.35 (m, 1H), 2.52 (t, *J* = 7.23 Hz, 2H), 2.38 (s, 3H), 2.03 – 1.90 (m, 1H), 1.90 – 1.80 (m, 1H), 1.85 – 1.76 (m, 1H), 1.54 – 1.38 (m, 1H), 1.49 – 1.35 (m, 2H), 1.32 (s, 6H), 1.32 (s, 6H), 1.32 – 1.12 (m, 2H), 1.17 (s, 3H), 1.03 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ =143.82 (C_q), 142.39 (C_q), 139.60 (C_q), 135.65 (2 x CH), 135.63 (2 x CH), 133.93 (C_q), 129.76 (C_q), 129.73 (CH), 129.70 (CH), 128.49 (2 x CH), 128.44 (2 x CH), 128.13 (2 x CH), 127.78 (2 x CH), 127.77 (2 x CH), 125.88 (3 x CH), 83.72 (2 x C_q), 71.33 (CH), 63.52 (CH_2), 37.75 (CH_2), 36.92 (CH_2), 32.06 (CH_2), 27.44 (CH_2), 27.00 (3 x CH_3), 25.71 (2 x CH_3), 25.41 (2 x CH_3), 21.70 (CH_3), 20.52 (CH_2), 19.35 (C_q), 17.11 (CH_3). Due to

coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.03; **FT-IR (cm^{-1}, neat)** 2929, 2857, 1597, 1467, 1428, 1373, 1293, 1212, 1140, 1107, 1001, 967, 853, 818, 740, 700, 611, 571, 503, 424; **HRMS (ESI)** m/z calculated for $C_{44}H_{60}O_5BSSi$ $[M+H]^+$: 739.4026, found: 739.4018.

ethyl (2*S*,3*S*)-3-methyl-6-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-tosylhexanoate (49)



Chemical Formula: $C_{28}H_{39}BO_6S$
Molecular Weight: 514,48

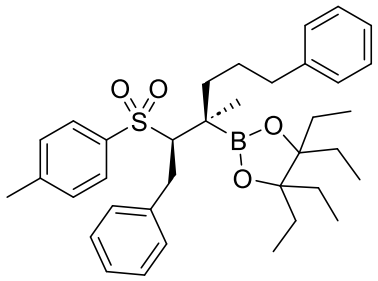
The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-[1-methyl-4-phenyl-1-(p-tolylsulfonylmethyl)butyl]-1,3,2-dioxaborolane (**16**) (201 mg, 0.45 mmol), diisopropylamine (0.14 mL, 1.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), ethyl chloroformate (0.4 mL, 4.5 mmol) and THF (7 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two inseparable isomers of **49** (203 mg, 87%, dr 34:66). Dr was determined on crude product by quantitative NMR analysis.

Minor diastereomer: **Appearance** yellow oil; **Rf** 0.2 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.79 – 7.72 (m, 2H), 7.36 – 7.07 (m, 7H), 4.32 (s, 1H), 4.05 (q, *J* = 7.16 Hz, 2H), 2.57 – 2.47 (m, 2H), 2.51 (s, 3H), 1.83 – 1.69 (m, 1H), 1.57 – 1.38 (m, 2H), 1.57 – 1.37 (m, 1H), 1.53 (s, 3H), 1.33 (s, 6H), 1.30 (s, 6H), 1.07 (q, *J* = 7.15 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 165.40 (C=O), 144.59 (C_q), 142.18 (C_q), 138.01 (C_q), 129.58 (2 x CH), 128.54 (2 x CH), 128.51 (2 x CH), 128.46 (2 x CH), 125.87 (CH), 84.13 (2 x C_q), 74.95 (CH), 61.37 (CH_2), 37.31 (CH_2), 36.64 (CH_2), 29.83 (C_q), 27.53 (CH_2), 25.49 (2 x CH_3), 25.09 (2 x CH_3), 21.75 (CH_3), 17.14 (CH_3), 14.01 (CH_3).

Major diastereomer: **Appearance** yellow oil; **Rf** 0.2 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.79 – 7.72 (m, 2H), 7.36 – 7.07 (m, 7H), 4.26 (s, 1H), 4.00 (qd, *J* = 7.17, 1.46 Hz, 2H), 2.73 – 2.58 (m, 2H), 2.44 (s, 3H), 2.16 – 1.96 (m, 2H), 1.87 – 1.61 (m, 2H), 1.41 (s, 3H), 1.22 (s, 6H), 1.18 (s, 6H), 1.07 (q, *J* = 7.15 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 166.42 (C=O), 144.54 (C_q), 142.99 (C_q), 138.58 (C_q), 129.49 (2 x CH), 128.58 (2 x CH), 128.40 (2 x CH), 128.36 (2 x CH), 125.72 (CH), 83.86 (2 x C_q), 74.95 (CH), 61.54 (CH_2), 36.88 (CH_2), 34.90 (CH_2), 29.83 (C_q), 28.41 (CH_2), 24.94 (2 x CH_3), 24.82 (2 x CH_3), 21.75 (CH_3), 18.79 (CH_3), 13.86 (CH_3).

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.47; **FT-IR (cm^{-1}, neat)** 2977, 2930, 2860, 1741, 1598, 1495, 1464, 1370, 1317, 1265, 1248, 1141, 1083, 1028, 966, 910, 852, 814, 749, 699, 663, 610, 578, 552, 512, 491, 472, 437, 422, 412; **HRMS (ESI)** m/z calculated for $C_{28}H_{40}O_6BS$ $[M+H]^+$: 515.2620, found: 515.2633.

4,4,5,5-tetraethyl-2-((2*R*,3*S*)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (105)



Chemical Formula: $C_{36}H_{49}BO_4S$
Molecular Weight: 588,65

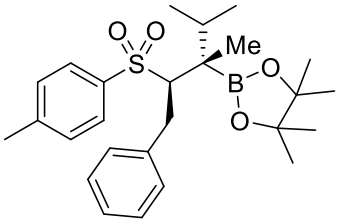
The reaction was performed according to **General Procedure D** with 4,4,5,5-tetraethyl-2-(prop-1-en-2-yl)-1,3,2-dioxaborolane (**103**) (448 mg, 0.9 mmol), diisopropylamine (0.13 mL, 0.9 mmol), *n*-BuLi (2.5 M in hexanes, 0.36 mL, 0.9 mmol), benzyl bromide (0.15 mL, 1.3 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two separable isomers of **105** (423 mg, 80%, dr 32:68). Dr was determined on crude product by quantitative NMR analysis.

Minor diastereomer: **Appearance** yellow oil; **Rf** 0.64 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.46 – 7.40 (m, 2H), 7.34 – 7.14 (m, 4H), 7.04 – 6.95 (m, 6H), 6.92 – 6.85 (m, 2H), 3.86 (dd, *J* = 8.70, 3.85 Hz, 1H), 3.23 – 3.02 (m, 2H), 2.66 (dddd, *J* = 23.18, 13.62, 9.63, 5.85 Hz, 2H), 2.30 (s, 3H), 2.18 – 1.96 (m, 2H), 1.92 – 1.56 (m, 10H), 1.09 (s, 3H), 0.99 – 0.87 (m, 12H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.33 (C_q), 143.06 (C_q), 139.11 (C_q), 138.89 (C_q), 129.08 (2 x CH), 129.00 (2 x CH), 128.60 (2 x CH), 128.33 (2 x CH), 128.11 (2 x CH), 127.94 (2 x CH), 125.98 (CH), 125.60 (CH), 88.81 (2 x C_q), 73.54 (CH), 37.31 (CH_2), 33.74 (CH_2), 31.48 (CH_2), 27.99 (CH_2), 25.86 (2 x CH_2), 25.43 (2 x CH_2), 21.54 (CH_3), 21.08 (CH_3), 9.31 (2 x CH_3), 8.58 (2 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomer: **Appearance** yellow oil; **Rf** 0.57 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.40 – 7.35 (m, 2H), 7.32 – 7.12 (m, 4H), 7.10 – 7.04 (m, 2H), 7.04 – 6.95 (m, 4H), 6.91 – 6.84 (m, 2H), 3.88 (dd, *J* = 9.11, 4.17 Hz, 1H), 3.20 – 2.97 (m, 2H), 2.53 – 2.42 (m, 2H), 2.30 (s, 3H), 1.93 – 1.56 (m, 10H), 1.55 – 1.33 (m, 2H), 1.28 (s, 3H), 0.99 – 0.85 (m, 12H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.88 (C_q), 142.29 (C_q), 139.27 (C_q), 138.37 (C_q), 129.25 (2 x CH), 129.05 (2 x CH), 128.49 (2 x CH), 128.41 (2 x CH), 128.18 (2 x CH), 127.81 (2 x CH), 126.13 (CH), 125.85 (CH), 89.07 (2 x C_q), 71.91 (CH), 38.22 (CH_2), 36.86 (CH_2), 29.89 (CH_2), 27.30 (CH_2), 25.89 (2 x CH_2), 25.27 (2 x CH_2), 21.55 (CH_3), 17.92 (CH_3), 9.43 (2 x CH_3), 8.52 (2 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.01; **FT-IR (cm^{-1}, neat)** 3027, 2972, 2939, 2883, 1598, 1490, 1457, 1352, 1290, 1244, 1175, 1140, 1110, 1026, 916, 810, 734, 690, 565, 511; **HRMS (ESI)** m/z calculated for $C_{36}H_{50}O_4BS$ $[M+H]^+$: 589.3513, found: 589.3517.

2-((2*R*,3*R*)-3,4-dimethyl-1-phenyl-2-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53)



Chemical Formula: $C_{26}H_{37}BO_4S$
Molecular Weight: 456.45

The reaction was performed according to **General Procedure D** with 2-(2,3-dimethyl-1-tosylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**26**) (365 mg, 1.0 mmol), diisopropylamine (0.14 mL, 1.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), benzyl bromide (0.15 mL, 1.3 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two separable isomers of **53** (423 mg, 71%, dr 80:20). Dr was determined on crude product by quantitative NMR analysis.

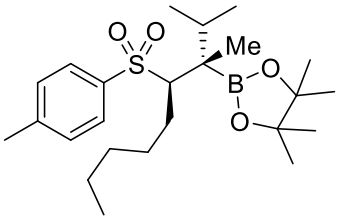
Minor diastereomer: **Appearance** colorless oil; **Rf** 0.3 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.63 – 7.56 (m, 2H), 7.33 – 7.19 (m, 7H), 4.45 (dd, *J* = 9.86, 4.44 Hz, 1H), 3.54 – 3.38 (m, 2H), 2.59 (s, 3H), 2.02 (h, *J* = 6.89 Hz, 1H), 1.70 (s, 6H), 1.68 (s, 9H), 1.39 (d, *J* = 6.88 Hz, 3H), 1.35 (d, *J* = 6.83 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.46 (C_q), 139.97 (C_q), 137.77 (C_q), 129.47 (2 x CH), 128.86 (2 x CH), 128.06 (2 x CH), 127.59 (2 x CH), 126.16 (CH), 83.84 (2 x C_q), 71.91 (CH), 35.16 (CH), 29.51 (CH_2), 26.43 (2 x CH_3), 25.49 (2 x CH_3), 21.51 (CH_3), 19.67 (CH_3), 18.67 (CH_3), 17.63 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.3 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.39 – 7.33 (m, 2H), 7.04 – 6.98 (m, 3H), 6.98 – 6.92 (m, 4H), 3.94 (dd, *J* = 9.15, 2.11 Hz, 1H), 3.26 (dd, *J* = 16.38, 9.14 Hz, 1H), 3.04 (dd, *J* = 16.39, 2.09 Hz, 1H), 2.48 (hept, *J* = 6.80 Hz, 1H), 2.27 (s, 3H), 1.31 (s, 3H), 1.28 (s, 6H), 1.26 (s, 6H), 1.18 (d, *J* = 6.75 Hz, 3H), 0.94 (d, *J* = 6.89 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.26 (C_q), 139.37 (C_q), 139.30 (C_q), 129.08 (2 x CH), 128.71 (2 x CH), 128.04 (2 x CH), 128.00 (2 x CH), 125.76 (CH), 83.79 (2 x C_q), 72.07 (CH), 35.15 (CH_2), 32.38 (CH), 25.41 (2 x CH_3), 25.27 (2 x CH_3), 21.52 (CH_3), 20.31 (CH_3), 19.19 (CH_3), 17.36 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.16; **FT-IR (cm^{-1}, neat)** 2976, 2930, 1598, 1494, 1454, 1366, 1289, 1243, 1209, 1134, 1082, 1048, 965, 887, 848, 816, 771, 744,

703, 667, 634, 616, 573, 553, 533, 510, 473, 409; **HRMS (ESI)** m/z calculated for $C_{26}H_{38}O_4BS$ $[M+H]^+$: 457.2566, found: 457.2578.

2-((3*R*,4*R*)-2,3-dimethyl-4-tosylnonan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (52)



Chemical Formula: $C_{24}H_{41}BO_4S$
Molecular Weight: 436.46

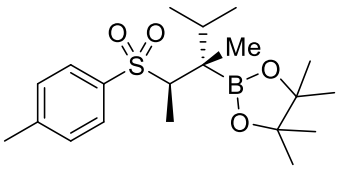
The reaction was performed according to **General Procedure D** with 2-(2,3-dimethyl-1-tosylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**26**) (186 mg, 0.5 mmol), diisopropylamine (0.07 mL, 0.5 mmol), *n*-BuLi (2.5 M in hexanes, 0.2 mL, 0.5 mmol), n-iodopentane (0.08 mL, 0.6 mmol) and THF (7 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two separable isomers of **52** (163 mg, 74%, dr 90:10). Dr was determined on crude product by quantitative NMR analysis.

Minor diastereomer: **Appearance** colorless oil; **Rf** 0.43 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.93 – 7.86 (m, 2H), 7.35 – 7.27 (m, 2H), 3.65 (dd, *J* = 10.13, 2.15 Hz, 1H), 2.43 (s, 3H), 1.99 (dtd, *J* = 14.77, 10.00, 4.54 Hz, 1H), 1.67 – 1.52 (m, 3H), 1.37 (s, 6H), 1.35 (s, 6H), 1.22 (s, 3H), 1.15 – 0.83 (m, 5H), 1.02 (d, *J* = 6.87 Hz, 3H), 0.92 (d, *J* = 6.88 Hz, 3H), 0.71 (t, *J* = 7.02 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.59, 141.03, 129.56, 127.95, 83.72, 70.86, 35.12, 31.82, 27.70, 26.39, 25.59, 23.60, 22.36, 21.69, 19.59, 18.79, 17.45, 13.94. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.70.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.38 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.80 – 7.74 (m, 2H), 7.34 – 7.28 (m, 2H), 3.26 (dd, *J* = 6.91, 1.68 Hz, 1H), 2.43 (hept, *J* = 6.90 Hz, 1H), 2.42 (s, 3H), 1.91 (dddd, *J* = 16.10, 11.73, 6.88, 4.32 Hz, 1H), 1.51 – 1.34 (m, 1H), 1.25 (s, 6H), 1.24 (s, 9H), 1.19 – 0.79 (m, 5H), 1.09 (d, *J* = 6.73 Hz, 3H), 0.90 (d, *J* = 6.93 Hz, 3H), 0.69 (t, *J* = 6.92 Hz, 3H), 0.47 (tdd, *J* = 12.54, 8.46, 4.42 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.94, 139.35, 129.59, 128.61, 83.69, 70.09, 32.90, 31.96, 30.76, 29.73, 25.47, 25.13, 22.39, 21.67, 20.19, 19.51, 16.96, 13.96. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.94.

Mix of diastereomers: **FT-IR (cm^{-1}, neat)** 2931, 2871, 1596, 1463, 1367, 1314, 1284, 1243, 1211, 1137, 1082, 1047, 1015, 966, 893, 854, 818, 777, 705, 667, 612, 568, 537, 484, 466, 448, 422; **HRMS (ESI)** m/z calculated for $C_{24}H_{42}O_4BS$ $[M+H]^+$: 437.2894, found: 437.2891.

2-((3*R*,4*R*)-2,3-dimethyl-4-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51)



Chemical Formula: $C_{20}H_{33}BO_4S$
Molecular Weight: 380.35

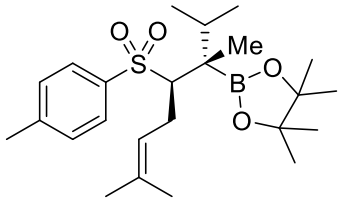
The reaction was performed according to **General Procedure D** with 2-(2,3-dimethyl-1-tosylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**26**) (367 mg, 1.0 mmol), diisopropylamine (0.14 mL, 1.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), methyl iodide (0.1 mL, 1.6 mmol) and THF (7 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two separable isomers of **51** (305 mg, 80%, dr 85:15). Dr was determined on crude product by quantitative NMR analysis.

Minor diastereomer: **Appearance** colorless oil; **Rf** 0.21 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.84 – 7.78 (m, 2H), 7.36 – 7.29 (m, 2H), 3.55 (q, *J* = 7.03 Hz, 1H), 2.44 (s, 3H), 1.51 (hept, *J* = 6.90 Hz, 1H), 1.39 (s, 6H), 1.36 (s, 6H), 1.25 (s, 3H), 1.14 (d, *J* = 7.04 Hfz, 3H), 0.99 (d, *J* = 6.89 Hz, 3H), 0.87 (d, *J* = 6.82 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.91 (C_q), 138.05 (C_q), 129.72 (2 x CH), 128.46 (2 x CH), 83.78 (2 x C_q), 65.23 (CH), 34.55 (CH), 26.16 (2 x CH_3), 25.58 (2 x CH_3), 21.73 (CH_3), 19.42 (CH_3), 18.69 (CH_3), 16.31 (CH_3), 8.02 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.56.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.2 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ =7.77 – 7.72 (m, 2H), 7.33 – 7.28 (m, 2H), 3.37 (q, *J* = 7.06 Hz, 1H), 2.42 (s, 3H), 2.38 (hept, *J* = 6.90 Hz, 1H), 1.26 (s, 6H), 1.26 (s, 6H), 1.23 (s, 3H), 1.20 (d, *J* = 7.01 Hz, 3H), 1.07 (d, *J* = 6.76 Hz, 3H), 0.85 (d, *J* = 6.89 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.90 (C_q), 138.38 (C_q), 129.63 (2 x CH), 128.40 (2 x CH), 83.62 (2 x C_q), 65.32 (CH), 32.45 (CH), 25.40 (2 x CH_3), 25.36 (2 x CH_3), 21.67 (CH_3), 19.98 (CH_3), 18.25 (CH_3), 15.88 (CH_3), 13.95 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.32.

Mix of diastereomers: **FT-IR (cm^{-1}, neat)** 2976, 2928, 2876, 1596, 1458, 1390, 1371, 1361, 1310, 1286, 1266, 1246, 1210, 1164, 1138, 1109, 1083, 1043, 1020, 964, 917, 883, 849, 827, 800, 769, 720, 701, 666, 607, 569, 555, 529, 485, 465, 439, 426, 414; **HRMS (ESI)** m/z calculated for $C_{20}H_{34}O_4BS$ $[M+H]^+$: 381.2265, found: 381.2265.

4,4,5,5-tetramethyl-2-((3*R*,4*R*)-2,3,7-trimethyl-4-tosyloct-6-en-3-yl)-1,3,2-dioxaborolane (54)



Chemical Formula: $C_{24}H_{39}BO_4S$
Molecular Weight: 434.44

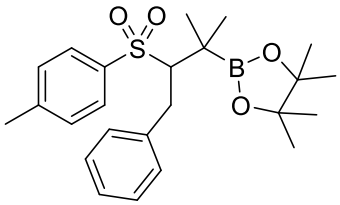
The reaction was performed according to **General Procedure D** with 2-(2,3-dimethyl-1-tosylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**26**) (368 mg, 1.0 mmol), diisopropylamine (0.14 mL, 1.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), 1-bromo-3-methyl-but-2-ene (0.15 mL, 1.2 mmol) and THF (7 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two separable isomers of **54** (313 mg, 72%, dr 83:17). Dr was determined on crude product by quantitative NMR analysis.

Minor diastereomer: **Appearance** colorless oil; **Rf** 0.37 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.79 – 7.69 (m, 2H), 7.30 – 7.21 (m, 2H), 4.53 – 4.40 (m, 1H), 3.65 (dd, *J* = 10.36, 2.58 Hz, 1H), 2.73 (dt, *J* = 15.77, 9.67 Hz, 1H), 2.40 (s, 3H), 2.35 – 2.20 (m, 1H), 1.60 (hept, *J* = 6.90 Hz, 1H), 1.58 (s, 3H), 1.38 (s, 6H), 1.35 (s, 9H), 1.26 (s, 3H), 1.02 (d, *J* = 6.86 Hz, 3H), 0.92 (d, *J* = 6.85 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.26 (C_q), 140.60 (C_q), 133.39 (C_q), 129.08 (2 x CH), 128.27 (2 x CH), 122.08 (CH), 83.71 (2 x C_q), 70.86 (CH), 35.17 (CH), 26.36 (2 x CH_3), 25.78 (CH_2), 25.58 (2 x CH_3), 22.60 (CH_3), 21.65 (CH_3), 19.57 (CH_3), 18.68 (CH_3), 18.04 (CH_3), 17.46 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.75.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.31 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.73 – 7.67 (m, 2H), 7.28 – 7.21 (m, 2H), 4.54 – 4.46 (m, 1H), 3.41 (dd, *J* = 8.25, 2.10 Hz, 1H), 2.70 (dt, *J* = 16.75, 8.13 Hz, 1H), 2.42 (hept, *J* = 6.90 Hz, 1H), 2.39 (s, 3H), 2.30 – 2.17 (m, 1H), 1.39 (s, 3H), 1.32 (s, 3H), 1.26 (s, 6H), 1.24 (s, 6H), 1.23 (s, 3H), 1.13 (d, *J* = 6.72 Hz, 3H), 0.90 (d, *J* = 6.88 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.54 (C_q), 139.63 (C_q), 132.08 (C_q), 129.27 (2 x CH), 128.46 (2 x CH), 123.53 (CH), 83.64 (2 x C_q), 71.22 (CH), 32.44 (CH), 28.37 (CH_2), 25.40 (CH_3), 25.32 (2 x CH_3), 25.24 (2 x CH_3), 21.63 (CH_3), 20.27 (CH_3), 19.05 (CH_3), 18.04 (CH_3), 16.94 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.16.

Mix of diastereomers: **FT-IR (cm^{-1}, neat)** 2978, 2934, 2884, 1596, 1459, 1387, 1372, 1358, 1319, 1297, 1285, 1266, 1249, 1210, 1179, 1166, 1132, 1113, 1082, 1051, 1017, 967, 912, 892, 860, 847, 818, 802, 761, 847, 818, 802, 761, 733, 714, 705, 693, 666, 613, 579, 545, 518, 487, 473, 456, 440; **HRMS (ESI)** m/z calculated for $C_{24}H_{40}O_4BS$ $[M+H]^+$: 435.2732, found: 435.2735.

4,4,5,5-tetramethyl-2-(2-methyl-4-phenyl-3-tosylbutan-2-yl)-1,3,2-dioxaborolane (37)

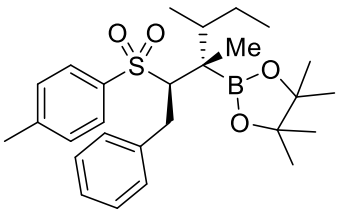


Chemical Formula: $C_{24}H_{33}BO_4S$
Molecular Weight: 428,39

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-(2-methyl-1-tosylpropan-2-yl)-1,3,2-dioxaborolane (**14**) (170 mg, 0.5 mmol), diisopropylamine (0.07 mL, 0.5 mmol), *n*-BuLi (2.5 M in hexanes, 0.2 mL, 0.5 mmol), benzyl bromide (0.1 mL, 0.8 mmol) and THF (7 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane= 15:85, stained in PMA solution) to afford **37** (121 mg, 56%).

Appearance white solid; **Mp** 128 °C; **Rf** 0.3 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.45 – 7.36 (m, 2H), 7.05 – 6.95 (m, 5H), 6.95 – 6.86 (m, 2H), 3.83 (dd, *J* = 8.76, 4.59 Hz, 1H), 3.23 – 3.04 (m, 2H), 2.31 (s, 3H), 1.34 (s, 6H), 1.32 (s, 6H), 1.30 (s, 3H), 1.05 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.08 (C_q), 138.88 (C_q), 138.41 (C_q), 129.32 (2 x CH), 129.11 (2 x CH), 128.16 (2 x CH), 127.92 (2 x CH), 126.16 (CH), 83.63 (2 x C_q), 73.39 (CH), 29.85 (CH_2), 25.19 (2 x CH_3), 24.86 (2 x CH_3), 24.57 (CH_3), 21.58 (CH_3), 18.83 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.40. **FT-IR (cm^{-1}, neat)** 2973, 2924, 2870, 1600, 1495, 1469, 1459, 1389, 1371, 1349, 1294, 1244, 1214, 1100, 1084, 1032, 1007, 966, 885, 851, 833, 813, 799, 749, 712, 700, 681, 666, 653, 634, 573, 557, 534, 513, 504, 490, 464, 404; **HRMS (ESI)** m/z calculated for $C_{24}H_{34}O_4BS$ $[M+H]^+$: 429.2258, found: 429.2265.

2-((2*R*,3*R*,4*S*)-3,4-dimethyl-1-phenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (55)



Chemical Formula: $C_{27}H_{39}BO_4S$
Molecular Weight: 470.48

The reaction was performed according to **General Procedure D** with 2-(2,3-dimethyl-1-tosylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**27**) (200 mg, 0.5 mmol), diisopropylamine (0.07 mL, 0.5 mmol), *n*-BuLi (2.5 M in hexanes, 0.2 mL, 0.5 mmol), benzyl bromide (0.1 mL, 1.6 mmol) and THF (7 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two separable isomers of **55** (185 mg, 75%, dr 71:29). Dr was determined on crude product by quantitative NMR analysis.

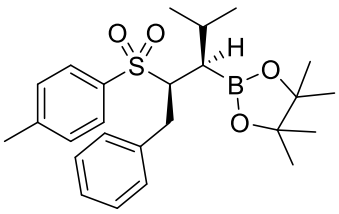
Minor diastereomer: **Appearance** colorless oil; **Rf** 0.5 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.29 – 7.23 (m, 2H), 7.01 – 6.87 (m, 7H), 4.25 – 4.10 (m, 1H), 3.23 – 3.04

(m, 2H), 2.27 (s, 3H), 1.97 – 1.80 (m, 1H), 1.38 (s, 9H), 1.36 (s, 6H), 1.34 – 1.24 (m, 2H), 1.03 (d, *J* = 6.70 Hz, 3H), 0.98 – 0.93 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.82, 140.48, 138.11, 129.89, 129.24, 128.46, 127.97, 126.57, 84.18, 72.39, 43.58, 29.93, 26.83, 26.10, 25.91, 21.93, 17.97, 14.97, 14.28. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.86.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.43 (Et_2O/pentane=15:85); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.39 – 7.32 (m, 2H), 7.06 – 6.93 (m, 7H), 3.99 – 3.91 (m, 1H), 3.34 – 3.15 (m, 1H), 3.14 – 3.01 (m, 1H), 2.27 (s, 3H), 2.16 – 2.03 (m, 1H), 1.92 – 1.75 (m, 1H), 1.33 – 1.24 (m, 15H), 1.21 (t, *J* = 7.05 Hz, 1H), 0.96 (t, *J* = 7.26 Hz, 3H), 0.91 – 0.82 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.31, 139.56, 139.16, 129.09, 128.62, 128.10, 128.00, 125.71, 83.76, 72.24, 39.54, 34.87, 26.79, 25.39, 25.25, 21.52, 17.28, 14.45, 13.05. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.22.

Mix of diastereomers: **FT-IR (cm^{-1}, neat)** 2968, 2927, 2874, 1597, 1455, 1366, 1293, 1244, 1135, 1087, 1024, 965, 896, 850, 813, 740, 699, 664, 570, 517, 454, 405; **HRMS (ESI)** m/z calculated for $C_{27}H_{40}O_4BS$ $[M+H]^+$: 471.2717, found: 471.2735.

4,4,5,5-tetramethyl-2-((2*R*,3*R*)-4-methyl-1-phenyl-2-tosylpentan-3-yl)-1,3,2-dioxaborolane (39)



Chemical Formula: $C_{25}H_{35}BO_4S$
Molecular Weight: 442.42

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-(3-methyl-1-tosylbutan-2-yl)-1,3,2-dioxaborolane (**13**) (336 mg, 1.0 mmol), diisopropylamine (0.14 mL, 1.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), benzyl bromide (0.15 mL, 1.2 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane= 15:85, stained in PMA solution) to afford two inseparable isomers of **39** (315 mg, 75%, dr 22:78). Dr was determined on crude product by quantitative NMR analysis.

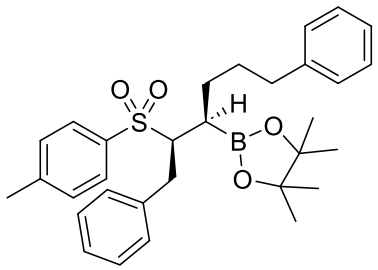
Minor diastereomer: **Appearance** yellow oil; **Rf** 0.37 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.76 – 7.71 (m, 2H), 7.29 – 7.24 (m, 2H), 7.24 – 7.16 (m, 3H), 7.15 – 7.07 (m, 2H), 3.52 – 3.46 (m, 1H), 3.46 – 3.27 (m, 2H), 2.40 (s, 3H), 1.83 – 1.63 (m, 1H), 1.39 – 1.33 (m, 1H), 1.36 (s, 6H), 1.35 (s, 6H), 0.88 (d, *J* = 6.70 Hz, 3H), 0.58 (d, *J* = 6.48 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.13 (C_q), 140.17 (C_q), 135.64 (C_q), 129.69 (2 x CH), 129.20 (2 x CH), 128.91 (2 x CH), 128.33 (2 x CH), 126.18 (CH), 83.60 (2 x C_q), 67.48 (CH), 31.62 (CH_2), 30.95

(CH, broad), 27.09 (CH), 25.49 (2 x CH_3), 25.30 (2 x CH_3), 23.06 (CH_3), 22.12 (CH_3), 21.70 (CH_3).

Major diastereomer: **Appearance** yellow oil; **Rf** 0.37 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.66 – 7.60 (m, 2H), 7.21 – 7.15 (m, 2H), 7.14 – 7.07 (m, 3H), 7.06 – 7.00 (m, 2H), 3.81 – 3.72 (m, 1H), 3.14 – 2.96 (m, 2H), 2.38 (s, 3H), 2.03 (h, *J* = 6.70 Hz, 1H), 1.36 (s, 6H), 1.35 (s, 6H), 1.36 – 1.33 (m, 1H), 0.94 – 0.88 (m, 3H), 0.75 (d, *J* = 6.68 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.78 (C_q), 138.35 (C_q), 137.05 (C_q), 129.45 (2 x CH), 129.18 (2 x CH), 128.65 (2 x CH), 128.31 (2 x CH), 126.33 (CH), 83.67 (2 x C_q), 67.26 (CH), 34.50 (CH_2), 30.95 (CH, broad), 26.50 (CH), 25.72 (2 x CH_3), 25.24 (2 x CH_3), 22.89 (CH_3), 21.66 (CH_3), 20.67 (CH_3).

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.58; **FT-IR (cm^{-1}, neat)** 2965, 2927, 2871, 1598, 1492, 1454, 1376, 1285, 1223, 1139, 1083, 969, 886, 848, 814, 741, 697, 658, 599; **HRMS (ESI)** m/z calculated for $C_{23}H_{35}O_4BSNa$ $[M+Na]^+$: 465.2228, found: 465.2241.

2-((2*R*,3*R*)-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)



Chemical Formula: $C_{31}H_{39}BO_4S$
Molecular Weight: 518,52

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-(5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (**12**) (221 mg, 0.5 mmol), diisopropylamine (0.07 mL, 0.5 mmol), *n*-BuLi (2.5 M in hexanes, 0.2 mL, 0.5 mmol), benzyl bromide (0.08 mL, 1.2 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford two inseparable isomers of **38** (203 mg, 76%, dr 24:76). Dr was determined on crude product by quantitative NMR analysis.

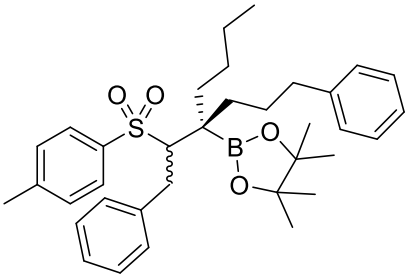
Minor diastereomer: **Appearance** yellow oil; **Rf** 0.3 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.84 – 7.76 (m, 2H), 7.36 – 7.00 (m, 12H), 3.59 (td, *J* = 7.30, 6.85, 2.97 Hz, 1H), 3.26 – 3.16 (m, 1H), 3.06 – 2.90 (m, 1H), 2.62 – 2.47 (m, 2H), 2.45 (s, 3H), 1.83 – 1.47 (m, 4H), 1.45 – 1.34 (m, 1H), 1.35 (s, 6H), 1.33 (s, 6H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.20 (C_q), 142.61 (C_q), 138.65 (C_q), 136.25 (C_q), 129.72 (2 x CH), 129.11 (2 x CH), 128.69 (2 x CH), 128.48 (2 x CH), 128.40 (2 x CH), 128.26 (2 x CH), 126.45 (CH), 125.66 (CH), 83.51 (2 x C_q), 68.61 (CH), 35.92 (CH_2), 32.27 (CH_2), 31.52 (CH_2), 26.30 (CH_2), 25.21 (2 x CH_3), 24.95 (2 x CH_3), 23.11 (CH, broad), 21.67 (CH_3).

Major diastereomer: **Appearance** yellow oil; **Rf** 0.3 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.72 – 7.65 (m, 2H), 7.29 – 6.98 (m, 12H), 3.68 – 3.60 (m, 1H), 3.26 – 3.18 (m,

1H), 3.00 (dd, *J* = 14.48, 8.02 Hz, 1H), 2.65 – 2.47 (m, 2H), 2.41 (s, 3H), 1.86 – 1.46 (m, 5H), 1.22 (s, 6H), 1.20 (s, 6H).; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.01 (C_q), 142.61 (C_q), 138.21 (C_q), 136.65 (C_q), 129.58 (2 x CH), 129.26 (2 x CH), 128.63 (2 x CH), 128.45 (2 x CH), 128.40 (2 x CH), 128.26 (2 x CH), 126.45 (CH), 125.63 (CH), 83.60 (C_q), 68.37 (CH), 35.89 (CH_2), 33.62 (CH_2), 31.01 (CH_2), 27.09 (CH_2), 25.18 (2 x CH_3), 24.92 (2 x CH_3), 23.11 (CH, broad), 21.64 (CH_3).

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.65; **FT-IR (cm^{-1}, neat)** 3060, 3026, 2976, 2927, 2860, 1599, 1493, 1452, 1374, 1297, 1214, 1138, 1083, 1026, 967, 910, 852, 816, 731, 695, 591; **HRMS (ESI)** m/z calculated for $C_{31}H_{39}O_4BSNa$ $[M+Na]^+$: 541.2540, found: 541.2554.

4,4,5,5-tetramethyl-2-((4*S*)-1-phenyl-4-(2-phenyl-1-tosylethyl)octan-4-yl)-1,3,2-dioxaborolane (50)



Chemical Formula: $C_{35}H_{47}BO_4S$
Molecular Weight: 574.63

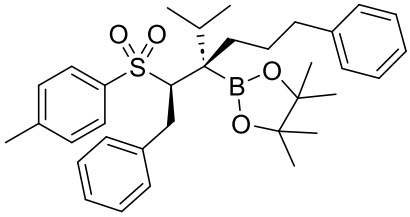
The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-(1-phenyl-4-(tosylmethyl)octan-4-yl)-1,3,2-dioxaborolane (**25**) (321 mg, 0.66 mmol), diisopropylamine (0.1 mL, 0.66 mmol), *n*-BuLi (2.5 M in hexanes, 0.27 mL, 0.66 mmol), benzyl bromide (0.1 mL, 0.8 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford two inseparable isomers of **50** (262 mg, 69%, dr 42:58). Dr was determined on crude product by quantitative NMR analysis.

Minor diastereomer: **Appearance** yellow oil; **Rf** 0.6 (Et_2O/pentane=2:8); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.43 – 7.37 (m, 2H), 7.35 – 7.23 (m, 3H), 7.23 – 7.15 (m, 1H), 7.13 – 7.08 (m, 1H), 7.03 – 6.93 (m, 5H), 6.93 – 6.84 (m, 2H), 4.04 – 3.94 (m, 1H), 3.26 – 3.16 (m, 1H), 3.14 – 3.06 (m, 1H), 2.69 (t, *J* = 7.84 Hz, 2H), 2.30 (s, 3H), 2.14 – 1.94 (m, 2H), 1.93 – 1.44 (m, 4H), 1.47 – 1.32 (m, 2H), 1.36 (s, 6H), 1.34 (s, 6H), 1.30 – 1.14 (m, 2H), 0.86 (t, *J* = 7.15 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 143.47 (C_q), 142.72 (C_q), 139.59 (C_q), 138.40 (C_q), 129.18 (2 x CH), 128.94 (2 x CH), 128.67 (2 x CH), 128.32 (2 x CH), 128.07 (2 x CH), 127.79 (2 x CH), 126.06 (CH), 125.60 (CH), 83.53 (2 x C_q), 72.16 (CH), 37.52 (CH_2), 34.44 (CH_2), 32.57 (CH_2), 30.90 (CH_2), 27.47 (CH_2), 27.10 (CH_2), 25.64 (2 x CH_3), 25.16 (2 x CH_3), 23.73 (CH_2), 21.51 (CH_3), 14.18 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomer: **Appearance** yellow oil; **Rf** 0.6 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.40 (m, 2H), 7.35 – 7.23 (m, 3H), 7.23 – 7.15 (m, 1H), 7.13 – 7.08 (m, 1H), 7.03 – 6.93 (m, 5H), 6.93 – 6.84 (m, 2H), 4.04 – 3.94 (m, 1H), 3.26 – 3.16 (m, 1H), 3.14 – 3.06 (m, 1H), 2.53 (t, *J* = 7.53 Hz, 2H), 2.30 (s, 3H), 2.14 – 1.94 (m, 2H), 1.93 – 1.44 (m, 4H), 1.47 – 1.32 (m, 2H), 1.33 (s, 6H), 1.32 (s, 6H), 1.30 – 1.14 (m, 2H), 0.97 (t, *J* = 7.23 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.82 (C_q), 142.45 (C_q), 139.42 (C_q), 138.62 (C_q), 129.09 (2 x CH), 129.00 (2 x CH), 128.53 (2 x CH), 128.42 (2 x CH), 128.12 (2 x CH), 127.83 (2 x CH), 126.05 (CH), 125.85 (CH), 83.53 (2 x C_q), 72.16 (CH), 37.01 (CH_2), 34.16 (CH_2), 32.23 (CH_2), 31.15 (CH_2), 27.40 (CH_2), 27.22 (CH_2), 25.64 (2 x CH_3), 25.16 (2 x CH_3), 24.17 (CH_2), 21.51 (CH_3), 14.44 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.31; **FT-IR (cm^{-1}, neat)** 3025, 2929, 2865, 1600, 1494, 1454, 1375, 1292, 1244, 1215, 1138, 1082, 1028, 969, 854, 814, 748, 695, 676, 572; **HRMS (ESI)** m/z calculated for $C_{35}H_{47}O_4BSNa$ $[M+Na]^+$: 597.3170, found: 597.3180.

2-((2*R*,3*R*)-3-isopropyl-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56)



Chemical Formula: $C_{34}H_{45}BO_4S$
Molecular Weight: 560,60

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-(2-methyl-6-phenyl-3-(tosylmethyl)hexan-3-yl)-1,3,2-dioxaborolane (**28**) (224 mg, 0.48 mmol), diisopropylamine (0.07 mL, 0.5 mmol), *n*-BuLi (2.5 M in hexanes, 0.2 mL, 0.5 mmol), benzyl bromide (0.1 mL, 0.8 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford two inseparable isomers of **56** (161 mg, 60%, dr 8:92). Dr was determined on crude product by quantitative NMR analysis.

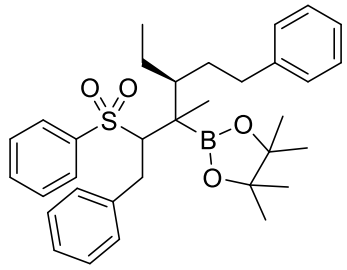
Minor diastereomer (characteristics signals): **Appearance** yellow oil; **Rf** 0.6 (Et_2O/pentane=2:8); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 4.29 (dd, *J* = 10.45, 2.79 Hz, 1H), 2.29 (s, 3H), 1.42 (s, 6H), 1.40 (s, 6H), 1.07 (d, *J* = 6.70 Hz, 3H), 1.04 (d, *J* = 6.85 Hz, 4H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 143.37, 142.44, 139.94, 138.04, 128.97, 128.80, 128.61, 128.31, 127.97, 127.65, 125.97, 125.61, 83.91, 71.35, 37.71, 32.00, 31.21, 29.71, 27.56, 26.28, 25.33, 21.42, 19.55, 18.75. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomer: **Appearance** yellow oil; **Rf** 0.6 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 8.22 Hz, 2H), 7.28 (d, *J* = 7.15 Hz, 2H), 7.23 – 7.17 (m, 3H), 7.02 –

6.87 (m, 7H), 4.20 – 4.12 (m, 1H), 3.32 (dd, *J* = 15.67, 10.35 Hz, 1H), 3.15 – 3.06 (m, 1H), 2.63 (t, *J* = 7.30 Hz, 2H), 2.52 – 2.41 (m, 1H), 2.27 (s, 3H), 2.16 – 1.86 (m, 2H), 1.86 – 1.70 (m, 2H), 1.33 (s, 6H), 1.31 (s, 6H), 1.25 (d, *J* = 6.85 Hz, 3H), 1.20 (d, *J* = 6.85 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.64 (2 x C_q), 140.07 (C_q), 138.75 (C_q), 128.94 (2 x CH), 128.83 (2 x CH), 128.55 (2 x CH), 128.33 (2 x CH), 127.96 (2 x CH), 127.74 (2 x CH), 125.87 (CH), 125.71 (CH), 83.54 (2 x C_q), 71.65 (CH), 37.32 (CH_2), 34.10 (CH_2), 33.71 (CH_2), 31.14 (CH), 27.84 (CH_2), 25.53 (2 x CH_3), 25.23 (2 x CH_3), 21.41 (CH_3), 20.82 (CH_3), 20.71 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.26; **FT-IR (cm^{-1}, neat)** 3026, 2972, 1600, 1493, 1453, 1375, 1293, 1251, 1212, 1136, 1082, 1033, 968, 909, 853, 814, 732, 696, 665, 565; **HRMS (ESI)** m/z calculated for $C_{34}H_{45}O_4BSNa$ $[M+Na]^+$: 583.3011, found: 583.3024.

2-((4*S*)-4-ethyl-3-methyl-1,6-diphenyl-2-(phenylsulfonyl)hexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (93)



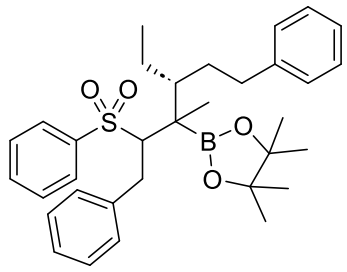
Chemical Formula: $C_{33}H_{43}BO_4S$
Molecular Weight: 546,57

The reaction was performed according to **General Procedure D** with 2-((3*S*)-3-ethyl-2-methyl-5-phenyl-1-(phenylsulfonyl) pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**35**) (407 mg, 0.9 mmol), diisopropylamine (0.14 mL, 1.1 mmol), *n*-BuLi (2.5M in hexanes, 0.4 mL, 1.1 mmol), benzyl bromide (0.13 mL, 1.1 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford four inseparable isomers of **93** (325 mg, 67%, dr nd). Dr was not possible to determine on the crude product by quantitative NMR analysis due to superimposed signals.

Mix of diastereomer (characteristic signals): **Appearance** colorless oil; **Rf** 0.4 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 4.23 (dd, *J* = 10.68, 3.62 Hz, 1H), 4.17 (dd, *J* = 11.00, 3.32 Hz, 1H), 4.00 (dd, *J* = 8.91, 2.27 Hz, 1H), 3.93 (dd, *J* = 8.17, 2.75 Hz, 1H), 1.10 (t, *J* = 7.37 Hz, 3H), 1.09 (t, *J* = 7.40 Hz, 3H), 1.01 (t, *J* = 7.50 Hz, 3H), 0.88 (t, *J* = 7.26 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 143.72, 143.21, 142.98, 142.78, 142.70, 142.68, 142.33, 142.28, 139.56, 139.07, 137.48, 137.42, 133.24, 132.64, 132.53, 131.90, 131.86, 129.44, 129.39, 129.24, 128.71, 128.68, 128.63, 128.60, 128.58, 128.54, 128.50, 128.47, 128.46, 128.43, 128.39, 128.32, 128.32, 128.28, 128.16, 128.16, 128.14, 128.03, 127.93, 127.61, 127.51, 127.49, 127.49, 126.37, 126.34, 126.11, 126.02, 125.90, 125.82, 125.77, 125.70, 84.05, 83.91, 71.73, 71.51, 48.02, 47.15, 45.02, 44.61, 38.34, 36.52, 36.20, 36.00, 35.73, 35.60, 34.69, 34.00, 29.63, 29.56, 26.85, 26.06, 26.03, 25.50, 25.43, 25.42, 25.38,

25.30, 25.27, 18.06, 18.01, 17.57, 17.42, 17.08, 15.03, 14.48, 13.62; **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.80; **FT-IR (cm^{-1}, neat)** 3061, 3026, 2972, 2930, 2873, 1770, 1603, 1585, 1496, 1447, 1389, 1371, 1349, 1298, 1237, 1210, 1138, 1083, 1030, 999, 967, 946, 854, 741, 723, 688, 643, 591, 518, 495, 458, 422, 413; **HRMS (ESI)** m/z calculated for $C_{33}H_{44}O_4BS$ $[M+H]^+$: 547.3047, found: 547.3047.

2-((4*R*)-4-ethyl-3-methyl-1,6-diphenyl-2-(phenylsulfonyl)hexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (106)

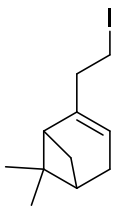


Chemical Formula: $C_{33}H_{43}BO_4S$
Molecular Weight: 546,57

The reaction was performed according to **General Procedure D** with 2-((3*R*)-3-ethyl-2-methyl-5-phenyl-1-(phenylsulfonyl) pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**36**) (192 mg, 0.4 mmol), diisopropylamine (0.06 mL, 0.4 mmol), *n*-BuLi (2.5 M in hexanes, 0.17 mL, 0.4 mmol), benzyl bromide (0.06 mL, 0.5 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford four inseparable isomers of **106** (152 mg, 67%, dr nd). Dr was not possible to determine on the crude product by quantitative NMR analysis due to superimposed signals.

Mix of diastereomers (characteristic signals): **Appearance** colorless oil; **Rf** 0.4 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 4.22 (dd, *J* = 10.67, 3.58 Hz, 1H), 4.16 (dd, *J* = 10.97, 3.29 Hz, 1H), 4.00 (dd, *J* = 8.90, 2.26 Hz, 1H), 3.92 (dd, *J* = 8.17, 2.70 Hz, 1H), 1.15 – 1.05 (m, 3H), 1.09 (t, *J* = 7.40 Hz, 3H), 1.00 (t, *J* = 7.63 Hz, 3H), 0.88 (t, *J* = 7.29 Hz, 3H). Physical and spectral data are in accordance with **RA-169**.

(1*R*)-(-)-Nopol iodide (107)



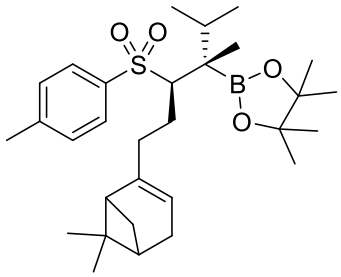
Chemical Formula: $C_{11}H_{17}I$
Molecular Weight: 276,16

Intermediate **107** was prepared similarly to a reported procedure[83].

To a solution of PPh_3 (7.88 g, 30.1 mmol), imidazole (3.6 g, 52.9 mmol) and (1*R*)-(-)-nopol (4.0 g, 24.1 mmol) in dry DCM (100 mL) was added iodine (9.2 g, 36.1 mmol) at 0 °C: The reaction was stirred for 30 min at this temperature and after complete consumption of starting material, the reaction mixture was treated with sat. aq. $K_2S_2O_8$ soln. and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford **107** (4.11 g, 62%).

Appearance colorless liquid; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.35 – 5.25 (m, 1H), 3.22 – 3.04 (m, 2H), 2.54 (ddq, *J* = 7.83, 6.34, 1.41 Hz, 2H), 2.37 (dt, *J* = 8.57, 5.62 Hz, 1H), 2.31 – 2.12 (m, 2H), 2.12 – 2.04 (m, 1H), 1.99 (td, *J* = 5.57, 1.56 Hz, 1H), 1.27 (s, 3H), 1.18 (d, *J* = 8.57 Hz, 1H), 0.84 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 146.88, 118.83, 45.46, 41.60, 40.82, 38.26, 31.89, 31.43, 26.40, 21.51, 3.79. Physical and spectral data are in accordance with literature data[84].

2-((3*R*,4*R*)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)



Chemical Formula: $C_{30}H_{47}BO_4S$
Molecular Weight: 514.57

The reaction was performed according to **General Procedure D** with 2-(2,3-dimethyl-1-tosylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**26**) (185 mg, 0.5 mmol), diisopropylamine (0.07 mL, 0.5 mmol), *n*-BuLi (2.5 M in hexanes, 0.2 mL, 0.5 mmol), (1*R*)-(-)-nopol iodide (**107**) (195 mg, 0.7 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford two separable pairs of isomers of **83** (93 mg, 36%, dr 10:10:39:41). Dr was determined on crude product by quantitative NMR analysis.

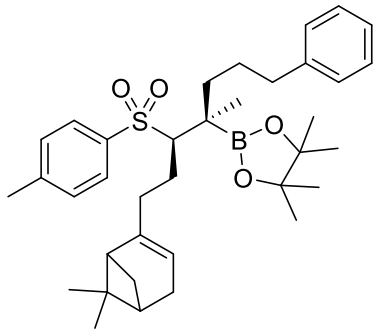
Minor diastereomers: **Dr** 1:1; **Appearance** colorless oil; **Rf** 0.55 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.92 – 7.86 (m, 4H), 7.33 – 7.28 (m, 4H), 5.07 – 5.03 (m, 1H), 4.93 – 4.89 (m, 1H), 3.64 – 3.56 (m, 2H), 2.43 (s, 6H), 2.37 – 2.23 (m, 2H), 2.23 – 1.95 (m, 8H), 1.90 – 1.54 (m, 8H), 1.55 – 1.43 (m, 2H), 1.37 (s, 12H), 1.35 (s, 12H), 1.27 – 1.20 (m, 12H), 1.07 – 1.00 (m, 8H), 0.93 (t, *J* = 6.32 Hz, 6H), 0.75 (d, *J* = 9.89 Hz, 6H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 147.90, 147.49, 143.52, 140.99, 140.84, 129.68, 129.64, 128.04, 116.68, 116.32, 83.74, 71.34, 71.21, 45.86, 45.68, 40.94, 40.84, 38.09, 38.05, 35.79, 35.67, 35.22, 35.17, 31.80, 31.73, 31.34, 31.31, 26.46, 26.41, 26.38, 25.62, 22.11, 21.87, 21.71, 21.41, 21.34, 19.61, 18.95, 18.85, 17.53, 17.45. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomers: **Dr** 1.1; **Appearance** colorless oil; **Rf** 0.45 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.82 – 7.73 (m, 4H), 7.35 – 7.27 (m, 4H), 4.98 – 4.92 (m, 1H), 4.87 – 4.82 (m, 1H), 3.25 (t, *J* = 5.02 Hz, 2H), 2.51 – 2.36 (m, 2H), 2.43 (s, 3H), 2.42 (s, 3H), 2.28 – 1.89 (m, 12H), 1.88 – 1.63 (m, 3H), 1.61 – 1.43 (m, 3H), 1.28 (s, 3H), 1.26 (s, 3H), 1.25 (s, 12H), 1.24 (s, 6H), 1.23 (s, 6H), 1.21 (s, 3H), 1.19 (s, 3H), 1.13 – 1.01 (m, 2H), 1.11 (d, *J* = 3.04 Hz, 3H), 1.09 (d, *J* = 2.89 Hz, 3H), 0.91 (s, 3H), 0.90 (s, 3H), 0.67 (s, 6H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 147.57, 147.48, 143.96, 143.94, 139.19, 139.16, 129.73, 129.65, 128.81,

128.69, 115.95, 115.53, 83.76, 83.73, 69.76, 69.44, 45.99, 45.59, 40.98, 40.88, 37.89, 37.86, 36.85, 36.79, 32.99, 32.85, 31.55, 31.50, 31.34, 31.32, 28.23, 28.16, 26.41, 26.37, 25.61, 25.57, 25.11, 21.68, 21.67, 21.16, 21.11, 20.20, 20.19, 19.57, 19.41, 16.93, 16.90. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.01; **FT-IR (cm^{-1}, neat)** 2973, 2923, 1596, 1459, 1366, 1306, 1291, 1212, 1136, 1083, 962, 891, 850, 817, 706, 668, 614, 550, 524, 471; **HRMS (ESI)** m/z calculated for $C_{30}H_{48}O_4BS$ $[M+H]^+$: 515.3361, found: 515.3361.

2-((3*R*,4*S*)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82)



Chemical Formula: $C_{36}H_{51}BO_4S$
Molecular Weight: 590.67

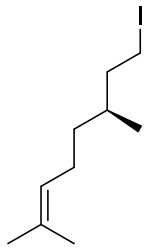
The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-[1-methyl-4-phenyl-1-(p-tolylsulfonylmethyl)butyl]-1,3,2-dioxaborolane (**16**) (427 mg, 1.0 mmol), diisopropylamine (0.14 mL, 1.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), (1*R*)-(-)-nopol iodide (**107**) (344 mg, 1.2 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford two separable pairs of isomers of **82** (341 mg, 60%, dr 24:24:26:26). Dr was determined on crude product by quantitative NMR analysis.

Minor diastereomers: **Dr** 1:1; **Appearance** colorless oil; **Rf** 0.43 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.81 (dd, *J* = 9.97, 8.29 Hz, 4H), 7.31 (dd, *J* = 8.37, 3.50 Hz, 4H), 7.27 (d, *J* = 7.30 Hz, 4H), 7.24 – 7.13 (m, 6H), 4.95 – 4.90 (m, 1H), 4.74 – 4.70 (m, 1H), 3.26 (t, *J* = 7.38 Hz, 1H), 3.26 (t, *J* = 7.53 Hz, 1H), 2.67 (ddd, *J* = 14.91, 9.82, 5.48 Hz, 2H), 2.57 (dq, *J* = 13.39, 5.78 Hz, 2H), 2.44 (s, 3H), 2.43 (s, 3H), 2.26 (ddt, *J* = 11.41, 8.52, 5.63 Hz, 2H), 2.21 – 1.86 (m, 12H), 1.79 – 1.53 (m, 10H), 1.37 (t, *J* = 15.83 Hz, 2H), 1.29 (s, 6H), 1.29 (s, 6H), 1.27 (s, 6H), 1.27 (s, 6H), 1.22 (s, 6H), 1.10 (s, 3H), 1.07 (s, 3H), 1.02 (d, *J* = 8.52 Hz, 1H), 0.99 (d, *J* = 8.52 Hz, 1H), 0.71 (s, 3H), 0.69 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 147.41, 146.99, 143.95, 143.92, 143.31, 143.30, 139.52, 139.24, 129.71, 129.65, 128.57, 128.46, 128.42, 128.30, 125.59, 116.78, 116.19, 83.52, 83.48, 71.75, 71.69, 45.77, 45.29, 40.88, 40.80, 37.98, 37.93, 37.15, 36.81, 36.59, 34.16, 34.05, 31.65, 31.63, 31.30, 31.29, 28.06, 27.97, 26.41, 26.36, 25.10, 25.10, 25.06, 25.06, 24.54, 24.16, 21.70, 21.27, 21.13, 19.79, 19.57. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomers: **Dr** 1.1; **Appearance** colorless oil; **Rf** 0.36 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.88 – 7.79 (m, 4H), 7.35 – 7.22 (m, 8H), 7.22 – 7.10 (m, 6H), 4.99 – 4.94 (m, 1H), 4.78 – 4.73 (m, 1H), 3.38 – 3.29 (m, 2H), 2.57 (t, *J* = 7.30 Hz, 4H), 2.43 (s, 6H), 2.31 – 2.24 (m, 2H), 2.22 – 1.90 (m, 8H), 1.87 – 1.72 (m, 4H), 1.71 – 1.32 (m, 12H), 1.33 (s, 12H), 1.32 (s, 12H), 1.24 (s, 3H), 1.24 (s, 3H), 1.16 (s, 3H), 1.15 (s, 3H), 1.03 (d, *J* = 8.47 Hz, 1H), 1.02 (d, *J* = 8.46 Hz, 1H), 0.75 (s, 3H), 0.73 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 147.49, 147.01, 143.87, 143.84, 142.29, 142.26, 139.94, 139.64, 129.69, 129.64, 128.49, 128.47, 128.44, 128.17, 125.89, 116.90, 116.42, 83.69, 83.68, 71.43, 71.22, 45.76, 45.40, 40.86, 40.77, 38.05, 38.00, 37.72, 37.69, 36.90, 36.34, 36.03, 31.73, 31.69, 31.30, 31.27, 27.32, 27.23, 26.45, 26.39, 25.71, 25.69, 25.35, 25.33, 22.08, 21.84, 21.69, 21.37, 21.24, 17.22, 17.16. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.30; **FT-IR (cm^{-1}, neat)** 2974, 2919, 1599, 1459, 1371, 1292, 1212, 1139, 1026, 963, 851, 813, 745, 676, 571, 513, 469; **HRMS (ESI)** m/z calculated for $C_{36}H_{52}O_4BS$ $[M+H]^+$: 591.3678, found: 591.3674.

(*S*)-(+)-citronellyl iodide (108)



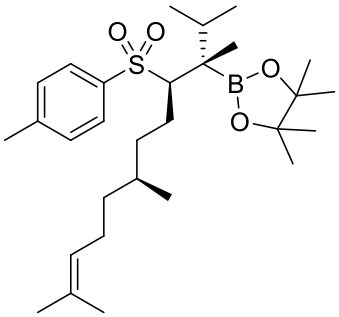
Chemical Formula: $C_{10}H_{19}I$
Molecular Weight: 266,17

Intermediate **108** was prepared to a reported procedure[85].

To a solution of KI (3.58 g, 21.6 mmol) in acetone (25 mL) was added (*S*)-(+)-citronellyl bromide (1.97 g, 9.0 mmol) and was stirred at room temperature overnight, protected from light. The reaction mixture was treated with water and extracted with pentane (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to obtain **108** (2.29 g, 96%).

Appearance colorless liquid; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.13 – 5.04 (m, 1H), 3.30 – 3.11 (m, 2H), 2.09 – 1.80 (m, 3H), 1.76 – 1.46 (m, 2H), 1.69 (t, *J* = 1.37 Hz, 3H), 1.60 (d, *J* = 1.30 Hz, 3H), 1.41 – 1.26 (m, 1H), 1.26 – 1.08 (m, 1H), 0.89 (d, *J* = 6.50 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 131.60, 124.59, 41.04, 36.45, 33.70, 25.86, 25.45, 18.79, 17.82, 5.30 . Physical and spectral data are in accordance with literature data[86].

4,4,5,5-tetramethyl-2-((3*R*,4*R*,7*S*)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (81)



Chemical Formula: $C_{29}H_{49}BO_4S$
Molecular Weight: 504.58

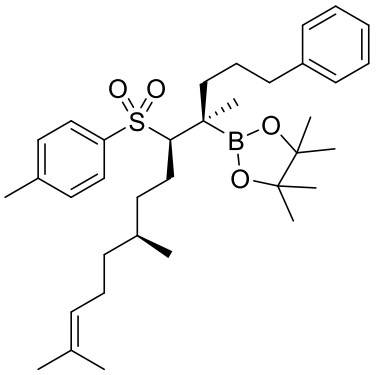
The reaction was performed according to **General Procedure D** with 2-(2,3-dimethyl-1-tosylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**26**) (192 mg, 0.5 mmol), diisopropylamine (0.07 mL, 0.5 mmol), *n*-BuLi (2.5 M in hexanes, 0.2 mL, 0.5 mmol), (*S*)-(+)-citronellyl iodide (**108**) (221 mg, 0.8 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford two separable pairs of isomers of **81** (182 mg, 69%, dr nd). Dr was not possible to determine on the crude product by quantitative NMR analysis due to superimposed signals.

Minor diastereomers (characteristic signals): **Appearance** colorless oil; **Rf** 0.52 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 8.22 Hz, 4H), 7.30 (d, *J* = 8.07 Hz, 4H), 5.06 – 4.95 (m, 2H), 3.63 – 3.56 (m, 2H), 2.42 (s, 6H), 1.95 (d, *J* = 36.68 Hz, 2H), 1.80 (s, 4H), 1.70 -1.51 (m, 4H), 1.67 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H), 1.54 (s, 3H), 1.37 (s, 12H), 1.35 (s, 12H), 1.25 – 0.80 (m, 9H), 1.23 (s, 6H), 1.03 (s, 3H), 1.02 (s, 3H), 0.93 (s, 3H), 0.91 (s, 3H), 0.75 (d, *J* = 19.73 Hz, 3H), 0.73 (d, *J* = 19.63 Hz, 3H), 0.66 (s, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.62, 141.04, 141.00, 131.25, 131.22, 129.59, 129.57, 128.01, 128.00, 124.88, 83.72, 71.67, 71.54, 36.93, 36.86, 35.46, 35.38, 35.22, 35.18, 32.98, 32.93, 29.86, 26.39, 25.85, 25.84, 25.62, 25.46, 21.70, 21.17, 21.09, 19.60, 19.42, 19.24, 18.86, 17.74, 17.71, 17.48, 17.47. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomers (characteristic signals): **Appearance** colorless oil; **Rf** 0.44 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.80 – 7.74 (m, 4H), 7.34 – 7.27 (m, 4H), 5.02 – 4.95 (m, 2H), 3.29 – 3.21 (m, 2H), 2.51 – 2.38 (m, 2H), 2.43 (s, 3H), 2.41 (s, 3H), 2.04 – 1.63 (m, 6H), 1.68 (s, 3H), 1.65 (s, 3H), 1.60 – 1.50 (m, 1H), 1.57 (s, 3H), 1.55 (s, 3H), 1.45 – 1.32 (m, 1H), 1.26 (s, 12H), 1.25 (s, 18H), 1.23 – 0.74 (m, 8H), 1.10 (d, *J* = 6.85 Hz, 3H), 1.10 (d, *J* = 6.85 Hz, 3H), 0.92 (s, 3H), 0.90 (s, 3H), 0.68 (d, *J* = 5.94 Hz, 3H), 0.58 (d, J = 6.39 Hz, 3H), 0.54 – 0.42 (m, 1H), 0.32 – 0.20 (m, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.34, 144.32, 139.71, 139.70, 131.71, 131.54, 130.01, 129.98, 129.16, 129.10, 128.03, 125.27, 125.21, 84.07, 70.90, 70.69, 37.86, 37.79, 37.36, 33.68, 33.28, 33.23, 33.14, 28.98, 28.74, 26.25, 26.21, 26.04, 25.99, 25.76, 25.53, 25.52, 22.07, 22.05, 20.60, 19.87, 19.84, 19.75, 19.20, 18.15, 18.12, 17.34, 17.29. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.35; **FT-IR (cm^{-1}, neat)** 2961, 2924, 1596, 1456, 1367, 1288, 1208, 1135, 1082, 1046, 965, 849, 810, 708, 669, 617, 544, 515, 472; **HRMS (ESI)** m/z calculated for $C_{29}H_{50}O_4BS$ $[M+H]^+$: 505.3522, found: 505.3517.

4,4,5,5-tetramethyl-2-((4*S*,5*R*,8*S*)-4,8,12-trimethyl-1-phenyl-5-tosyltridec-11-en-4-yl)-1,3,2-dioxaborolane (80)



Chemical Formula: $C_{35}H_{53}BO_4S$
Molecular Weight: 580.67

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-[1-methyl-4-phenyl-1-(p-tolylsulfonylmethyl)butyl]-1,3,2-dioxaborolane (**16**) (412 mg, 0.9 mmol), diisopropylamine (0.14 mL, 1.1 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.1 mmol), (*S*)-(+)-citronellyl iodide (**108**) (343 mg, 1.3 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford two separable pairs of isomers of **80** (315 mg, 58%, dr nd). Dr was not possible to determine on the crude product by quantitative NMR analysis due to superimposed signals.

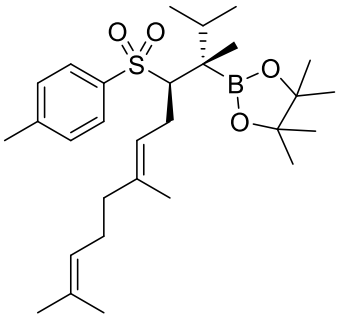
Minor diastereomers (characteristic signals): **Appearance** colorless oil; **Rf** 0.54 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.83 – 7.78 (m, 4H), 7.33 – 7.25 (m, 8H), 7.24 – 7.15 (m, 6H), 4.99 (q, *J* = 7.15 Hz, 2H), 3.25 (t, *J* = 6.24 Hz, 1H), 3.24 (d, *J* = 12.63 Hz, 1H), 2.75 – 2.63 (m, 2H), 2.63 – 2.52 (m, 2H), 2.42 (s, 6H), 2.03 – 1.51 (m, 16H), 1.68 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H), 1.55 (s, 3H), 1.30 (s, 12H), 1.28 (s, 12H), 1.18 – 0.71 (m, 9H), 1.06 (s, 6H), 0.68 (d, *J* = 6.46 Hz, 3H), 0.68 (d, *J* = 6.48 Hz, 3H), 0.60 – 0.49 (m, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.90, 143.39, 139.38, 139.29, 131.23, 131.19, 129.64, 129.63, 128.59, 128.41, 128.40, 128.30, 125.58, 124.84, 124.82, 83.47, 72.50, 72.40, 37.23, 37.11, 37.07, 37.00, 36.68, 33.77, 33.73, 32.79, 32.62, 28.02, 27.99, 25.84, 25.81, 25.51, 25.45, 25.11, 25.09, 23.77, 23.63, 21.68, 19.79, 19.49, 19.07, 17.73, 17.72. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomers (characteristic signals): **Appearance** colorless oil; **Rf** 0.49 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.87 – 7.77 (m, 4H), 7.34 – 7.19 (m, 8H), 7.22 – 7.08 (m, 6H), 5.07 – 4.94 (m, 2H), 3.31 (t, *J* = 7.21 Hz, 1H), 3.30 (t, *J* = 7.30 Hz, 1H), 2.60 – 2.52 (m, 4H), 2.42 (s, 6H), 2.03 – 0.65 (m, 26H), 1.68 (s, 3H), 1.67 (s, 3H), 1.57 (s, 3H), 1.55 (s, 3H), 1.33 (s, 12H), 1.31 (s, 12H), 1.26 (s, 3H), 1.16 (s, 3H), 0.72 (d, *J* = 6.60 Hz, 3H), 0.69 (d, *J* = 6.67 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.83, 142.34, 139.81, 139.71, 131.26, 131.24, 129.64, 128.52, 128.46, 128.17, 125.91, 124.85, 83.71, 71.83, 71.68, 37.76,

36.94, 36.71, 36.31, 36.16, 32.74, 32.68, 29.85, 27.36, 25.86, 25.85, 25.70, 25.52, 25.39, 21.70, 21.26, 19.45, 19.19, 17.76, 17.21. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.55; **FT-IR (cm^{-1}, neat)** 2922, 2859, 1599, 1456, 1371, 1293, 1139, 1083, 1026, 965, 852, 818, 744, 679, 572, 512; **HRMS (ESI)** m/z calculated for $C_{35}H_{54}O_4BS$ $[M+H]^+$: 581.3833, found: 581.3830.

4,4,5,5-tetramethyl-2-((3*R*,4*R*,*E*)-2,3,7,11-tetramethyl-4-tosyldodeca-6,10-dien-3-yl)-1,3,2-dioxaborolane (79)



Chemical Formula: $C_{29}H_{47}BO_4S$
Molecular Weight: 502.56

The reaction was performed according to **General Procedure D** with 2-(2,3-dimethyl-1-tosylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**26**) (366 mg, 1.0 mmol), diisopropylamine (0.14 mL, 1.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), geranyl bromide (277 mg, 1.3 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford two separable isomers of **79** (341 mg, 68%, dr 22:78). Dr was determined on crude product by quantitative NMR analysis.

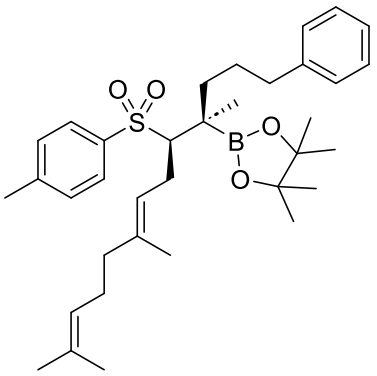
Minor diastereomer (characteristic peaks): **Appearance** colorless oil; **Rf** 0.53 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.80 – 7.74 (m, 2H), 4.99 – 4.90 (m, 1H), 4.56 – 4.46 (m, 1H), 3.67 (dd, *J* = 10.10, 2.52 Hz, 1H), 2.39 (s, 3H), 1.03 (d, *J* = 6.84 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.39 (CH_q), 140.56 (CH_q), 136.94 (CH_q), 131.43 (CH_q), 129.22 (2 x CH), 128.23 (2 x CH), 124.29 (CH), 121.40 (CH), 83.73 (2 x CH_q), 71.02 (CH), 39.55 (CH_2), 35.21 (CH), 29.84 (CH_2), 26.37 (CH_2), 26.15 (2 x CH_3), 25.77 (2 x CH_3), 25.61 (CH_3), 22.50 (CH_3), 19.58 (CH_3), 18.77 (CH_3), 17.75 (CH_3), 17.46 (CH_3), 16.64 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.47 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ =7.70 (d, *J* = 8.37 Hz, 2H), 7.23 (d, *J* = 8.07 Hz, 2H), 4.94 (tt, *J* = 7.01, 1.37 Hz, 1H), 4.54 – 4.47 (m, 1H), 3.42 (dd, *J* = 7.91, 1.83 Hz, 1H), 2.72 (dt, *J* = 16.44, 7.84 Hz, 1H), 2.43 (hept, *J* = 6.90 Hz, 1H), 2.37 (s, 3H), 2.28 – 2.18 (m, 1H), 1.75 (q, *J* = 7.46 Hz, 2H), 1.68 – 1.52 (m. 2H), 1.65 – 1.62 (m, 3H), 1.54 (s, 3H), 1.38 (s, 3H), 1.25 (s, 6H), 1.25 (s, 3H), 1.23 (s, 6H), 1.14 (d, *J* = 6.70 Hz, 3H), 0.90 (d, *J* = 7.00 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.59 (C_q), 139.52 (C_q), 135.64 (C_q), 131.33 (C_q), 129.31 (2 x CH), 128.43 (2 x CH), 124.26

(CH), 123.14 (CH), 83.62 (2 x C_q), 71.03 (CH), 39.34 (CH_2), 32.53 (CH), 28.44 (CH_2), 26.44 (CH_2), 25.75 (2 x CH_3), 25.27 (2 x CH_3), 25.20 (CH_3), 21.59 (CH_3), 20.26 (CH_3), 19.15 (CH_3), 17.71 (CH_3), 16.95 (CH_3), 16.48 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.63; **FT-IR (cm^{-1}, neat)** 2972, 2922, 2361, 1595, 1446, 1369, 1291, 1212, 1137, 1085, 1050, 967, 850, 822, 705, 668, 619, 544, 517, 471, 415; **HRMS (ESI)** m/z calculated for $C_{29}H_{47}O_4BSNa$ $[M+Na]^+$: 525.3193, found: 525.3180.

4,4,5,5-tetramethyl-2-((4*S*,5*R*,*E*)-4,8,12-trimethyl-1-phenyl-5-tosyltrideca-7,11-dien-4-yl)-1,3,2-dioxaborolane (78)



Chemical Formula: $C_{35}H_{51}BO_4S$
Molecular Weight: 578,66

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-[1-methyl-4-phenyl-1-(p-tolylsulfonylmethyl)butyl]-1,3,2-dioxaborolane (**16**) (206 mg, 0.5 mmol), diisopropylamine (0.07 mL, 0.5 mmol), *n*-BuLi (2.5 M in hexanes, 0.2 mL, 0.5 mmol), geranyl bromide (128 mg, 1.2 mmol) and THF (10 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford two separable isomers of **78** (174 mg, 65%, dr 28:72). Dr was determined on crude product by quantitative NMR analysis.

Minor diastereomer: **Appearance** colorless oil; **Rf** 0.49 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.80 – 7.72 (m, 2H), 7.32 – 7.10 (m, 7H), 4.98 – 4.89 (m, 1H), 4.58 – 4.50 (m, 1H), 3.45 (dd, *J* = 8.22, 3.56 Hz, 1H), 2.78 – 2.51 (m, 3H), 2.40 (s, 3H), 2.35 – 2.24 (m, 1H), 2.13 – 1.91 (m, 2H), 1.86 – 1.37 (m, 6H), 1.65 (s, 3H), 1.53 (s, 3H), 1.48 (s, 3H), 1.31 (s, 6H), 1.29 (s, 6H), 1.06 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.66 (C_q), 143.46 (C_q), 139.51 (C_q), 136.47 (C_q), 131.45 (C_q), 129.35 (2 x CH), 128.61 (2 x CH), 128.33 (2 x CH), 128.31 (2 x CH), 125.57 (CH), 124.25 (CH), 122.06 (CH), 83.41 (2 x C_q), 72.83 (CH), 39.46 (CH_2), 37.28 (CH_2), 33.19 (CH_2), 27.89 (CH_2), 26.22 (CH_2), 25.78 (CH_3), 25.13 (2 x CH_3), 25.01 (2 x CH_3), 24.19 (CH_2), 21.65 (CH_3), 20.48 (CH_3), 17.74 (CH_3), 16.44 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

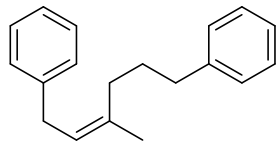
Major diastereomer: **Appearance** colorless oil; **Rf** 0.43 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.78 – 7.74 (m, 2H), 7.29 – 7.23 (m, 4H), 7.20 – 7.11 (m, 3H), 4.99 – 4.92 (m, 1H), 4.56 (t, *J* = 6.62 Hz, 1H), 3.52 – 3.45 (m, 1H), 2.68 (dt, *J* = 16.74, 8.60 Hz, 1H), 2.56

(t, *J* = 7.15 Hz, 2H), 2.40 (s, 3H), 2.36 – 2.27 (m, 1H), 1.90 – 1.59 (m, 5H), 1.57 – 1.35 (m, 3H), 1.66 (s, 3H), 1.54 (s, 3H), 1.53 (s, 3H), 1.33 (s, 6H), 1.33 (s, 6H), 1.22 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.56 (C_q), 142.28 (C_q), 139.76 (C_q), 136.80 (C_q), 131.42 (C_q), 129.29 (2 x CH), 128.48 (2 x CH), 128.40 (2 x CH), 128.23 (2 x CH), 125.86 (CH), 124.23 (CH), 121.44 (CH), 83.65 (2 x C_q), 71.23 (CH), 39.52 (CH_2), 37.97 (CH_2), 36.88 (CH_2), 27.25 (CH_2), 26.69 (C_q, broad), 26.20 (CH_2), 25.75 (CH_3), 25.64 (2 x CH_3), 25.32 (2 x CH_3), 22.65 (CH_2), 21.62 (CH_3), 17.73 (CH_3), 17.59 (CH_3), 16.47 (CH_3).

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.81; **FT-IR (cm^{-1}, neat)** 2929, 2858, 2361, 1738, 1597, 1452, 1370, 1294, 1223, 1141, 1081, 960, 838, 774, 674, 572, 511; **HRMS (ESI)** m/z calculated for $C_{35}H_{51}O_4BSNa$ $[M+Na]^+$: 601.3509, found: 601.3493.

1.4.5 Olefination reactions

(3-methylhex-2-ene-1,6-diyl)dibenzene (57)



Chemical Formula: $C_{19}H_{22}$
Molecular Weight: 250,39

The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-((2*R*,3*S*)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (**40**) (222 mg, 0.4 mmol), TBAF (1.0 M in THF, 1.3 mL, 1.3 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **57** (>98%, *E/Z* 35:65).

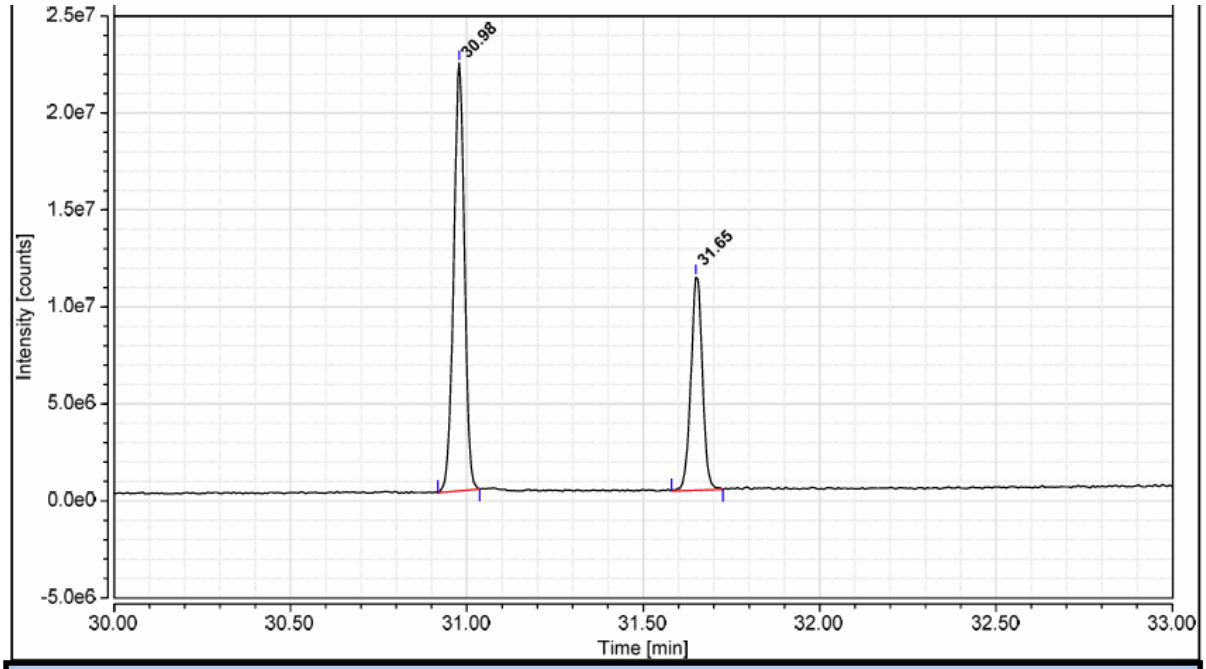
E-olefin*:* **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.35 – 7.22 (m, 4H), 7.24 – 7.12 (m, 6H), 5.37 (tq, *J* = 7.37, 1.41 Hz, 1H), 3.38 (d, *J* = 7.31 Hz, 2H), 2.66 – 2.54 (m, 2H), 2.10 (t, *J* = 7.61 Hz, 2H), 1.83 – 1.74 (m, 2H), 1.73 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.79 (C_q), 141.92 (C_q), 136.12 (C_q), 128.58 (2 x CH), 128.50 (2 x CH), 128.46 (2 x CH), 128.40 (2 x CH), 125.85 (CH), 125.78 (CH), 123.48 (CH), 39.42 (CH_2), 35.69 (CH_2), 34.39 (CH_2), 29.90 (CH_2), 16.25 (CH_3).

Z-olefin: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.33 – 7.23 (m, 4H), 7.22 – 7.12 (m, 6H), 5.40 – 5.31 (m, 1H), 3.32 (d, *J* = 7.37 Hz, 2H), 2.67 – 2.59 (m, 2H), 2.23 – 2.13 (m, 2H), 1.82 – 1.70 (m, 2H), 1.75 (d, *J* = 1.39 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.61 (C_q), 141.94 (C_q), 136.30 (C_q), 128.53 (2 x CH), 128.50 (2 x CH), 128.47 (2 x CH), 128.45 (2 x CH), 125.87 (2 x CH), 124.08 (CH), 36.01 (CH_2), 34.22 (CH_2), 31.66 (CH_2), 29.93 (CH_2), 23.56 (CH_3).

Mix of olefins: **FT-IR (cm^{-1}, neat)** 3025, 2930, 2855, 1603, 1494, 1452, 1377, 1029, 741, 602, 573, 531, 488, 457; **HRMS (EI)** m/z calculated for $C_{19}H_{22}$ $[M]^+$: 250.1720, found: 250.1716.

E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min

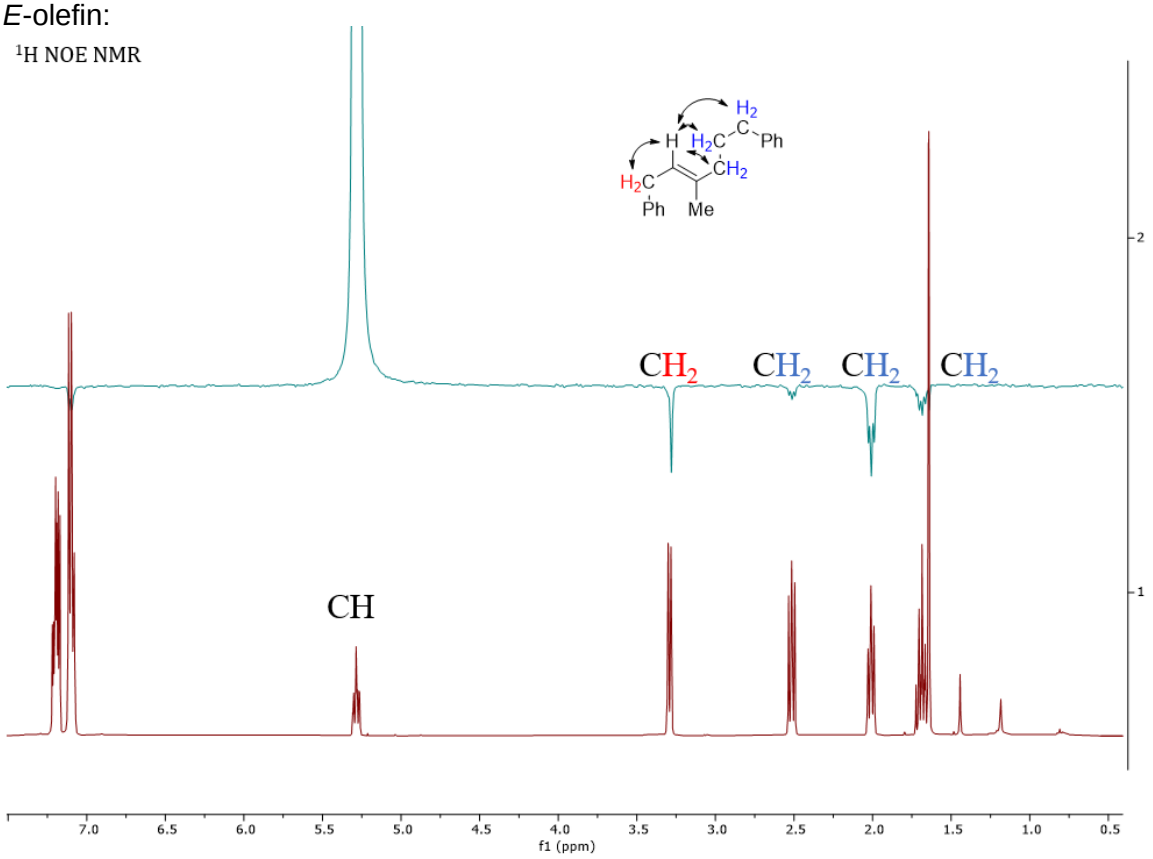


Integration Results

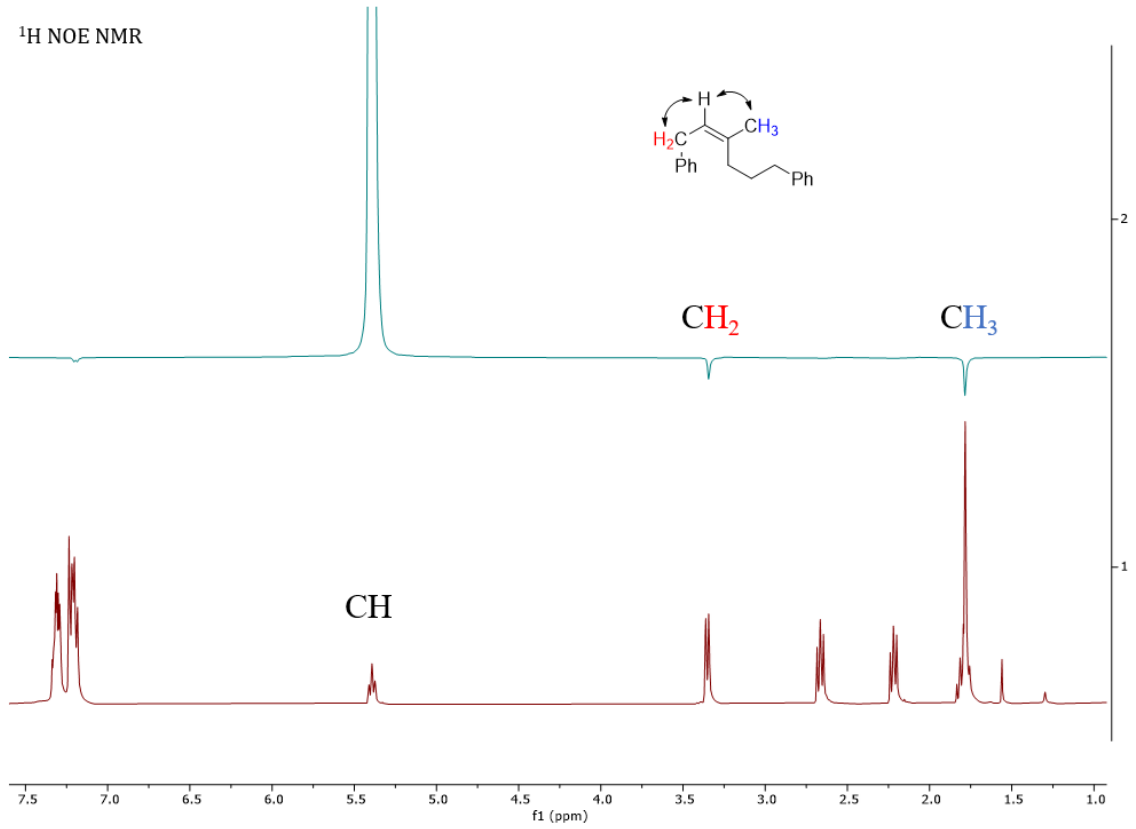
No.	Retention Time min	Rel.Area %	Area counts*min
1	30.978	65.03	775848
2	31.648	34.97	417127

E/Z-determination was assigned via NOE-NMR analysis (diastereomer separated by FCC and treated each with TBAF separately):

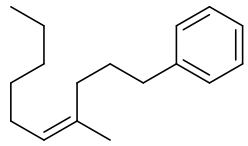
E-olefin:



Z-olefin:



(4-methyldec-4-en-1-yl)benzene (62)



Chemical Formula: $C_{17}H_{26}$
Molecular Weight: 230,40

The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-((4*S*,5*R*)-4-methyl-1-phenyl-5-tosyldecan-4-yl)-1,3,2-dioxaborolane (**44**) (296 mg, 0.6 mmol), TBAF (1.0 M in THF, 1.7 mL, 1.7 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **62** (109 mg, 82%, *E/Z* 36:64). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

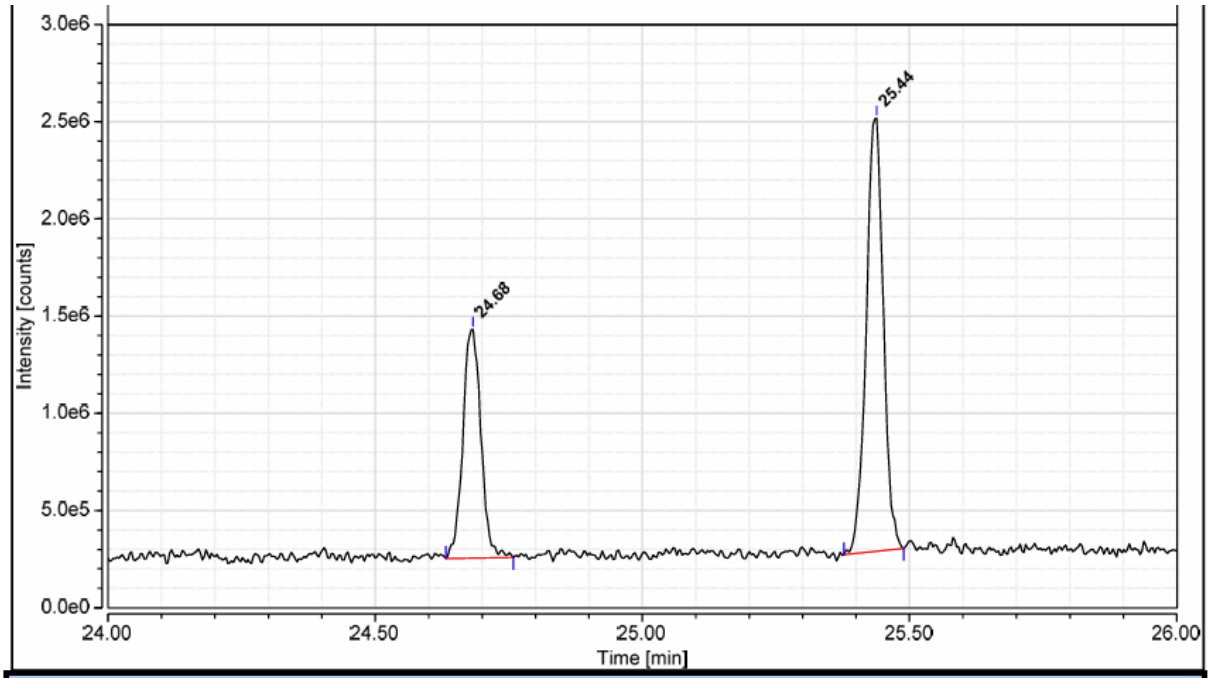
E-olefin*:* **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.80 (C_q), 134.88 (C_q), 128.51 (2 x CH), 128.40 (2 x CH), 126.00 (CH), 125.78 (CH), 36.00 (CH_2), 31.76 (CH_2), 31.62 (CH_2), 29.98 (CH_2), 29.93 (CH_2), 27.93 (CH_2), 23.51 (CH_3), 22.76 (CH_2), 14.25 (CH_3).

Z-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.96 (C_q), 134.63 (C_q), 128.59 (2 x CH), 128.37 (2 x CH), 125.73 (CH), 125.31 (CH), 39.45 (CH_2), 35.65 (CH_2), 31.73 (CH_2), 29.91 (CH_2), 29.73 (CH_2), 28.05 (CH_2), 22.77 (CH_2), 16.02 (CH_3), 14.26 (CH_3).

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.33 – 7.25 (m, 4H), 7.23 – 7.16 (m, 6H), 5.20 – 5.14 (m, 2H), 2.61 (q, *J* = 8.14 Hz, 4H), 2.13 – 1.91 (m, 8H), 1.80 – 1.67 (m, 4H), 1.71 (d, *J* = 1.22 Hz, 3H), 1.62 (s, 3H), 1.40 – 1.24 (m, 12H), 0.91 (t, *J* = 6.85 Hz, 6H); **FT-IR (cm^{-1}, neat)** 3027, 2955, 2925, 2854, 1604, 1496, 1453, 1377, 1085, 1030, 904, 851, 744, 696, 558, 492, 428; **HRMS (EI)** m/z calculated for $C_{17}H_{26}$ $[M]^+$: 230.2028, found: 230.2029.

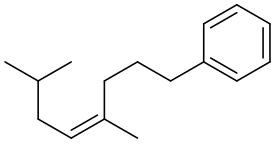
E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results			
No.	Retention Time min	Rel.Area %	Area counts*min
1	24.683	35.75	46172
2	25.438	64.25	82979

(4,7-dimethyloct-4-en-1-yl)benzene (66)



Chemical Formula: $C_{16}H_{24}$
Molecular Weight: 216,37

The reaction was performed according to **General Procedure E** with 2-((4*S*,5*R*)-4,7-dimethyl-1-phenyl-5-tosyloctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**45**) (264 mg, 0.5 mmol), TBAF (1.0 M in THF, 1.6 mL, 1.6 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **66** (102 mg, 89%, *E/Z* 30:70). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

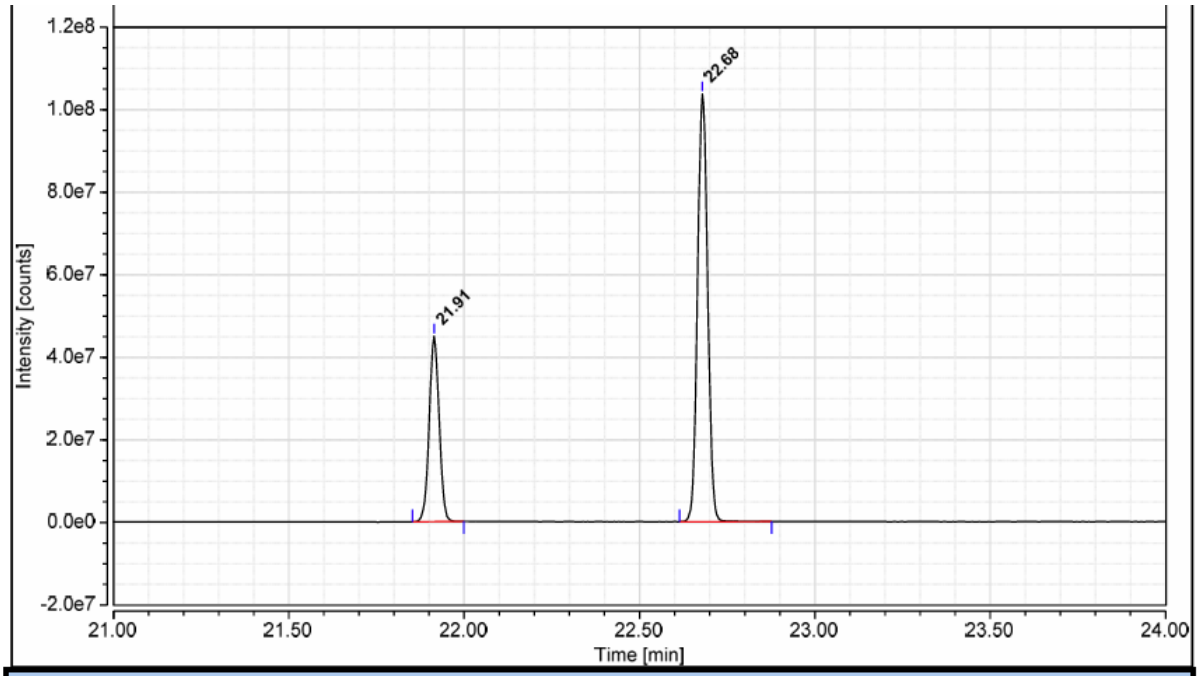
E-olefin*:* **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.82, 135.52, 128.52 (2 x CH), 128.39 (2 x CH), 125.78, 124.68, 39.60, 37.13, 36.05, 31.68, 29.97, 23.59, 22.60 (2 x CH_3).

Z-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.97, 135.33, 128.59 (2 x CH), 128.38 (2 x CH), 125.74, 124.05, 39.60, 37.30, 35.67, 29.99, 29.10, 22.56 (2 x CH_3), 16.17.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.38 – 7.30 (m, 4H), 7.29 – 7.20 (m, 6H), 5.28 – 5.19 (m, 2H), 2.70 – 2.60 (m, 4H), 2.17 – 2.06 (m, 4H), 1.99 – 1.53 (m, 10H), 1.76 (d, *J* = 1.29 Hz, 3H), 1.66 (s, 3H), 0.94 (dd, *J* = 6.61, 5.89 Hz, 12H); **FT-IR (cm^{-1}, neat)** 3063, 3027, 2952, 2927, 2866, 1939, 1666, 1604, 1496, 1453, 1382, 1365, 1167, 1086, 1030, 873, 744, 696, 572, 490, 416; **HRMS (EI)** m/z calculated for $C_{16}H_{24}$ $[M]^+$: 216.1871, found: 216.1873.

E/Z ratio was determined by GC-MS analysis:

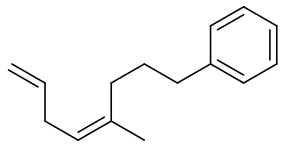
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	21.914	29.84	1481347
2	22.679	70.16	3482525

(4-methylocta-4,7-dien-1-yl)benzene (63)



Chemical Formula: $C_{15}H_{20}$
Molecular Weight: 200,33

The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-((4*S*,5*R*)-4-methyl-1-phenyl-5-tosyloct-7-en-4-yl)-1,3,2-dioxaborolane (**41**) (100 mg, 0.2 mmol), TBAF (1.0 M in THF, 0.6 mL, 0.6 mmol) and THF (3 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **63** (34 mg, 82%, *E/Z* 38:62). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

E-olefin*:* **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.82, 137.59, 136.38, 128.58 (2 x CH), 128.39 (2 x CH), 125.76, 121.80, 114.28, 39.38, 35.66, 32.42, 29.85, 16.03.

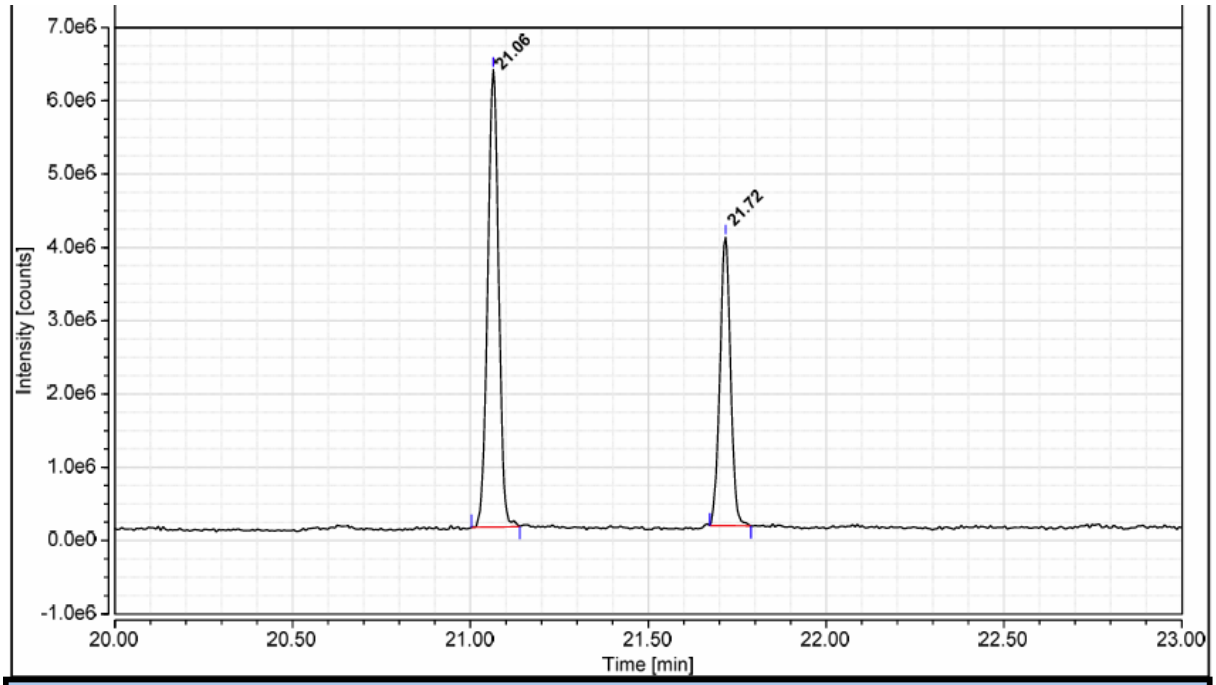
Z-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.67, 137.82, 136.52, 128.51 (2 x CH), 128.41 (2 x CH), 125.83, 122.57, 114.36, 35.96, 32.34, 31.55, 29.87, 23.52.

Mix of olefins: **Appearance** yellow liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.40 – 7.29 (m, 4H), 7.29 – 7.19 (m, 6H), 5.95 – 5.76 (m, 2H), 5.30 – 5.21 (m, 2H), 5.13 – 4.96 (m, 4H), 2.88 – 2.72 (m, 4H), 2.72 – 2.60 (m, 4H), 2.13 (q, *J* = 6.91 Hz, 4H), 1.86 – 1.71 (m, 4H), 1.78 (d, *J* = 1.50 Hz, 3H), 1.68 (d, *J* = 1.34 Hz, 3H); **FT-IR (cm^{-1}, neat)** 3062,

3027, 2931, 2856, 1942, 1802, 1637, 1604, 1496, 1452, 1377, 1143, 1087, 1030, 992, 906, 837, 745, 696, 648, 586, 570, 546, 488, 443, 433, 417, 403; **HRMS (EI)** m/z calculated for $C_{15}H_{20}$ $[M]^+$: 200.1557, found: 200.1560.

E/Z ratio was determined by GC-MS analysis:

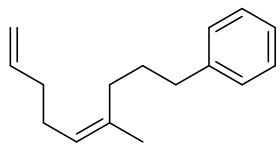
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	21.064	61.70	220711
2	21.717	38.30	137007

(4-methylnona-4,8-dien-1-yl)benzene (65)



Chemical Formula: $C_{16}H_{22}$
Molecular Weight: 214,35

The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-((4*S*,5*R*)-4-methyl-1-phenyl-5-tosylnon-8-en-4-yl)-1,3,2-dioxaborolane (**46**) (131 mg, 0.3 mmol), TBAF (1.0 M in THF, 0.8 mL, 0.8 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **65** (45 mg, 80%, *E/Z* 26:74). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

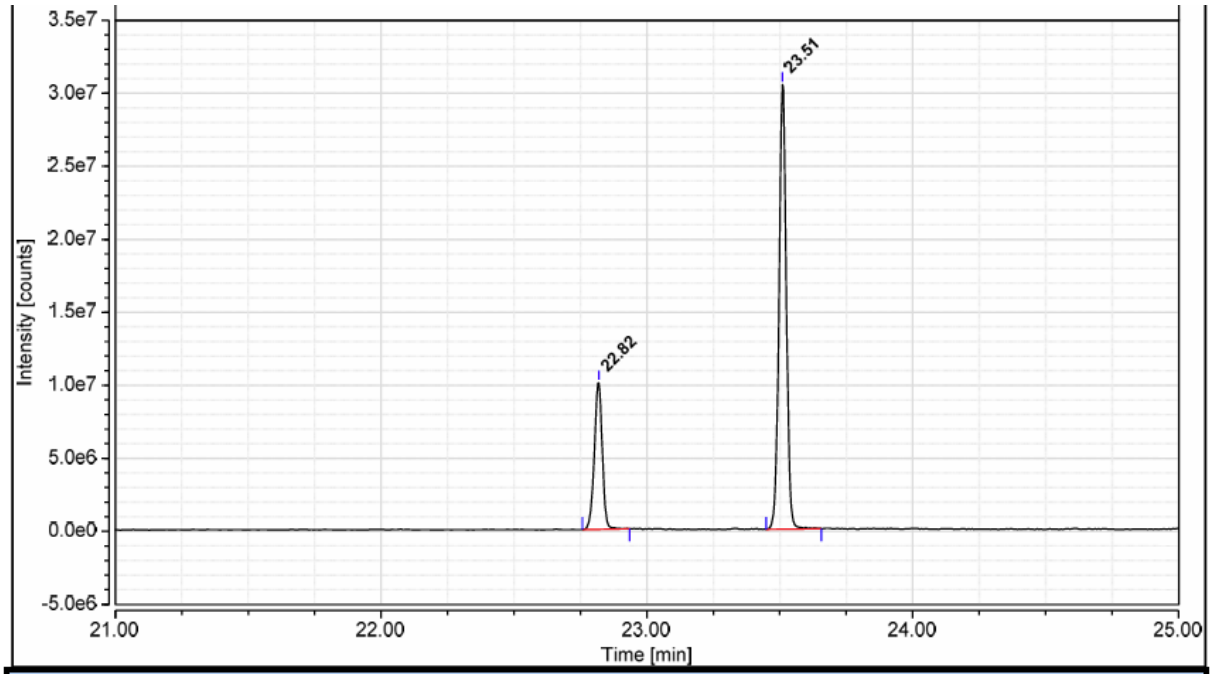
E-olefin*:* **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.73, 138.87, 135.58, 128.50 (2 x CH), 128.41 (2 x CH), 125.81, 124.90, 114.57, 35.97, 34.32, 31.67, 29.91, 27.43, 23.48.

Z-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.91, 138.89, 135.31, 128.59 (2 x CH), 128.38 (2 x CH), 125.74, 124.25, 114.57, 39.38, 35.60, 34.15, 29.85, 27.55, 16.10.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.23 – 7.14 (m, 4H), 7.13 – 7.04 (m, 6H), 5.81 – 5.65 (m, 2H), 5.12 – 5.01 (m, 2H), 4.98 – 4.81 (m, 4H), 2.56 – 2.42 (m, 4H), 2.06 – 1.89 (m, 12H), 1.69 – 1.55 (m, 4H), 1.60 (d, 3H), 1.51 (s, 3H); **FT-IR (cm^{-1}, neat)** 3063, 3026, 2925, 2854, 1943, 1639, 1604, 1496, 1452, 1378, 1086, 1030, 992, 908, 838, 744, 697, 639, 588, 552, 519, 489, 449, 410; **HRMS (EI)** m/z calculated for $C_{16}H_{22}$ $[M]^+$: 214.1716, found: 214.1716.

E/Z ratio was determined by GC-MS analysis:

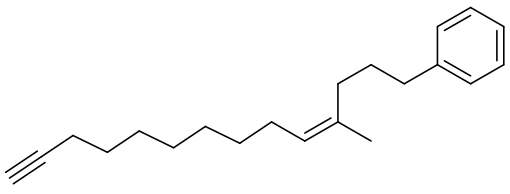
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	22.819	26.23	347092
2	23.510	73.77	976160

(4-methyltetradec-4-en-13-yn-1-yl)benzene (67)



Chemical Formula: $C_{21}H_{30}$
Molecular Weight: 282,47

The reaction was performed according to **General Procedure E** with trimethyl((10*R*,11*S*)-11-methyl-14-phenyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10-tosyltetradec-1-yn-1-yl)silane (**47**) (61 mg, 0.1 mmol), TBAF (1.0 M in THF, 0.3 mL, 0.3 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **67** (23 mg, 85%, *E/Z* 33:67). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

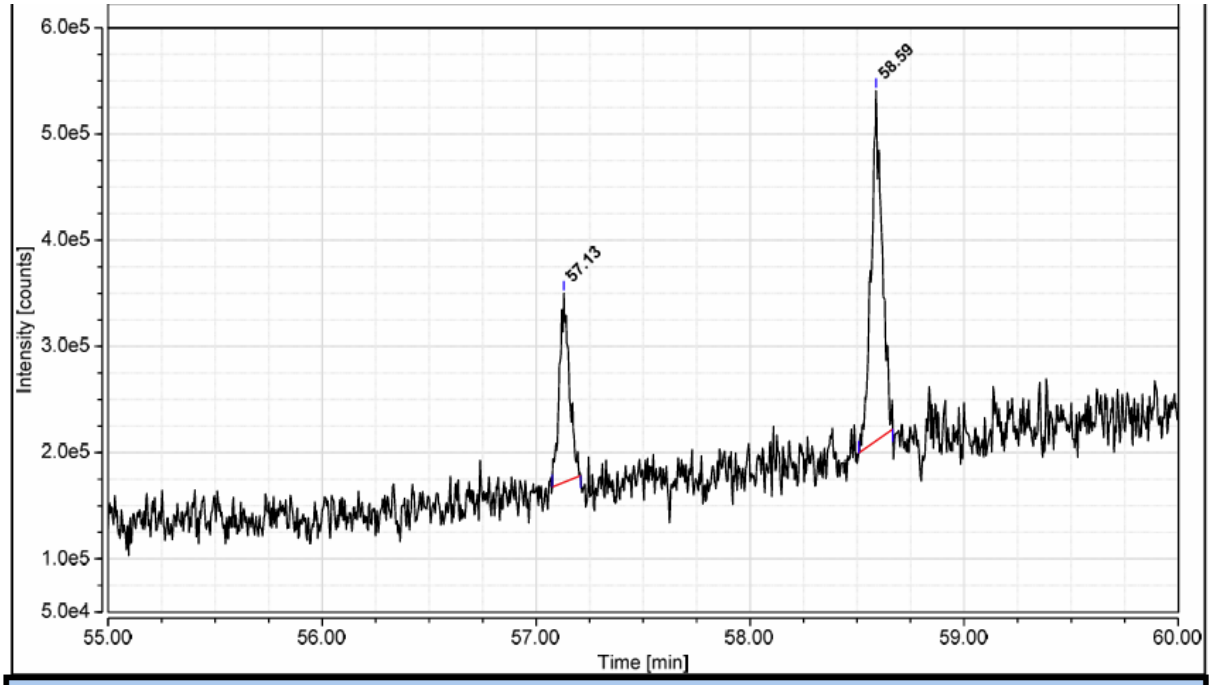
E-olefin*:* **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.76, 134.96, 128.50 (2 x CH), 128.39 (2 x CH), 125.87, 125.78, 84.91, 68.20, 35.98, 31.60, 30.16, 29.95, 29.36, 29.17, 28.89, 28.64, 27.92, 23.50, 18.54.

Z-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.92, 134.72, 128.57 (2 x CH), 128.37 (2 x CH), 125.72, 125.17, 84.91, 68.20, 39.44, 35.64, 29.95, 29.89, 29.30, 29.17, 28.89, 28.64, 28.02, 18.54, 16.03.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.39 – 7.30 (m, 4H), 7.29 – 7.20 (m, 6H), 5.25 – 5.17 (m, 2H), 2.70 – 2.60 (m, 4H), 2.25 (t, *J* = 7.02 Hz, 2H), 2.24 (t, *J* = 6.99 Hz, 2H), 2.17 – 1.95 (m, 10H), 1.88 – 1.71 (m, 4H), 1.76 (d, *J* = 1.47 Hz, 3H), 1.66 (s, 3H), 1.65 – 1.53 (m, 4H), 1.52 – 1.29 (m, 16H); **FT-IR (cm^{-1}, neat)** 3309, 3062, 3027, 2925, 2853, 1604, 1496, 1453, 1377, 1083, 1030, 905, 842, 745, 697, 627, 571, 492, 458, 441, 418, 408; **HRMS (EI)** m/z calculated for $C_{21}H_{30}$ $[M]^+$: 282.2344, found: 282.2342.

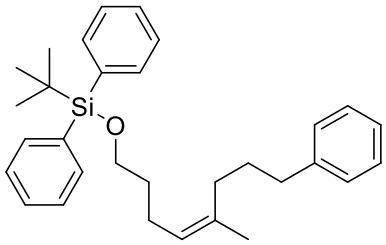
E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-250 °C with 3 °C/min; 250 °C for 5 min



Integration Results			
No.	Retention Time min	Rel.Area %	Area counts*min
1	57.129	33.11	9573
2	58.589	66.89	19341

***tert*-butyl((5-methyl-8-phenyloct-4-en-1-yl)oxy)diphenylsilane (68)**



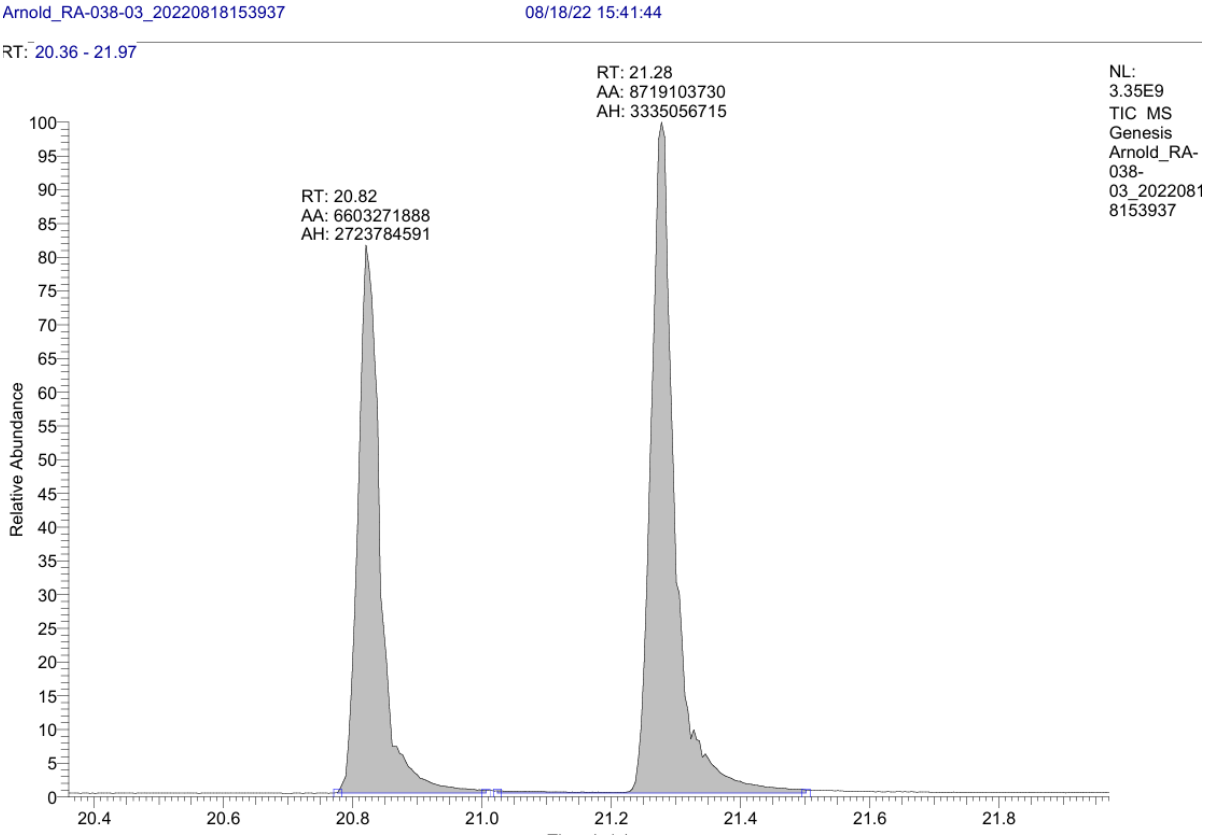
Chemical Formula: $C_{31}H_{40}OSi$
Molecular Weight: 456,74

The reaction was performed according to **General Procedure E** with *tert*-butyl(((4*R*,5*S*)-5-methyl-8-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-tosyloctyl)oxy) diphenylsilane (**48**) (81 mg, 0.1 mmol), MeLi (1.6 M in Et_2O, 0.2 mL, 0.3 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **68** (43 mg, 86%, *E/Z* 43:57). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

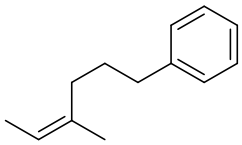
Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.60 – 7.50 (m, 8H), 7.33 – 7.20 (m, 12H), 7.19 – 7.09 (m, 4H), 7.09 – 6.99 (m, 6H), 5.04 – 4.94 (m, 2H), 3.54 (t, *J* = 6.36 Hz, 2H), 3.53 (t, *J* = 6.34 Hz, 2H), 2.49 – 2.39 (m, 4H), 2.02 – 1.83 (m, 8H), 1.64 – 1.38 (m, 8H), 1.55 (d, *J* = 1.35 Hz, 3H), 1.46 (s, 3H), 0.94 (s, 9H), 0.93 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.90, 142.76, 135.73, 135.43, 135.28, 134.28, 129.64, 128.59, 128.49, 128.38, 127.72, 125.78, 125.74, 125.24, 124.48, 117.60, 63.70, 63.59, 39.42, 36.02, 35.68, 33.15, 32.90, 31.66, 29.99, 29.90, 27.04, 27.02, 24.31, 24.29, 23.49, 19.38, 16.03; **FT-IR (cm^{-1}, neat)** 3069, 3026, 2927, 2855, 1954, 1885, 1820, 1710, 1659, 1589, 1496, 1461, 1427, 1389, 1361, 1305, 1253, 1188, 1106, 1029, 1008, 999, 967, 938, 882, 822, 786, 737, 721, 697, 612, 588, 503, 483, 413; **HRMS (EI)** m/z calculated for $C_{27}H_{31}OSi$ $[M\text{-}C_4H_9]^+$: 399.2135, found: 399.2139.

E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 2 min; 50-300 °C with 15 °C/min; 300 °C for 12 min



(4-methylhex-4-en-1-yl)benzene (61)



Chemical Formula: $C_{13}H_{18}$
Molecular Weight: 174,29

The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-((2*R*,3*S*)-3-methyl-6-phenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (**43**) (188 mg, 0.4 mmol), TBAF (1.0 M in THF, 1.2 mL, 1.2 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **61** (59 mg, 82%, *E/Z* 29:71). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

E-olefin*:* **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.79, 135.91, 128.52 (2 x CH), 128.39 (2 x CH), 125.78, 119.39, 35.92, 31.21, 29.67, 23.46, 13.39.

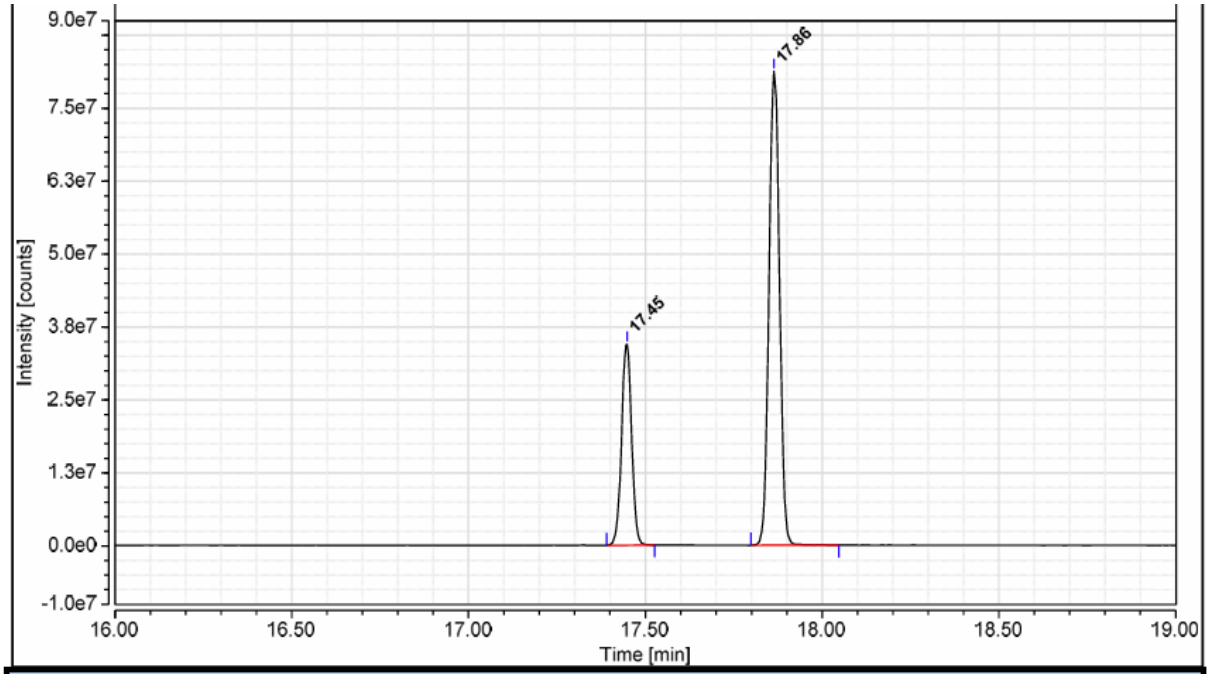
Z-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.92, 135.68, 128.57 (2 x CH), 128.37 (2 x CH), 125.73, 118.71, 39.42, 35.68, 29.86, 15.70, 13.48.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.40 – 7.30 (m, 2H), 7.29 – 7.18 (m, 3H), 5.35 – 5.25 (m, 1H), 2.66 (q, *J* = 8.48 Hz, 2H), 2.19 – 2.05 (m, 2H), 1.86 – 1.72 (m, 3H), 1.70 – 1.56 (m, 5H); **FT-IR (cm^{-1}, neat)** 3062, 3026, 2929, 2857, 1940, 1800, 1670, 1604, 1496, 1452, 1378, 1208, 1147, 1093, 1030, 991,

905, 814, 773, 744, 696, 592, 570, 553, 521, 495, 453, 434; **HRMS (EI)** m/z calculated for $C_{13}H_{18}$ $[M]^+$: 174.1402, found: 174.1403.

E/Z ratio was determined by GC-MS analysis:

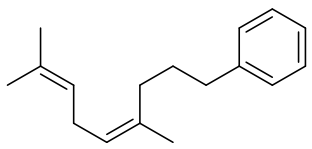
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	17.449	28.83	1132068
2	17.863	71.17	2793969

(4,8-dimethylnona-4,7-dien-1-yl)benzene (64)



Chemical Formula: $C_{17}H_{24}$
Molecular Weight: 228,38

The reaction was performed according to **General Procedure E** with 2-((4*S*,5*R*)-4,8-dimethyl-1-phenyl-5-tosylnon-7-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**42**) (96 mg, 0.2 mmol), TBAF (1.0 M in THF, 0.6 mL, 0.6 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **64** (>98%, *E/Z* 29:71). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

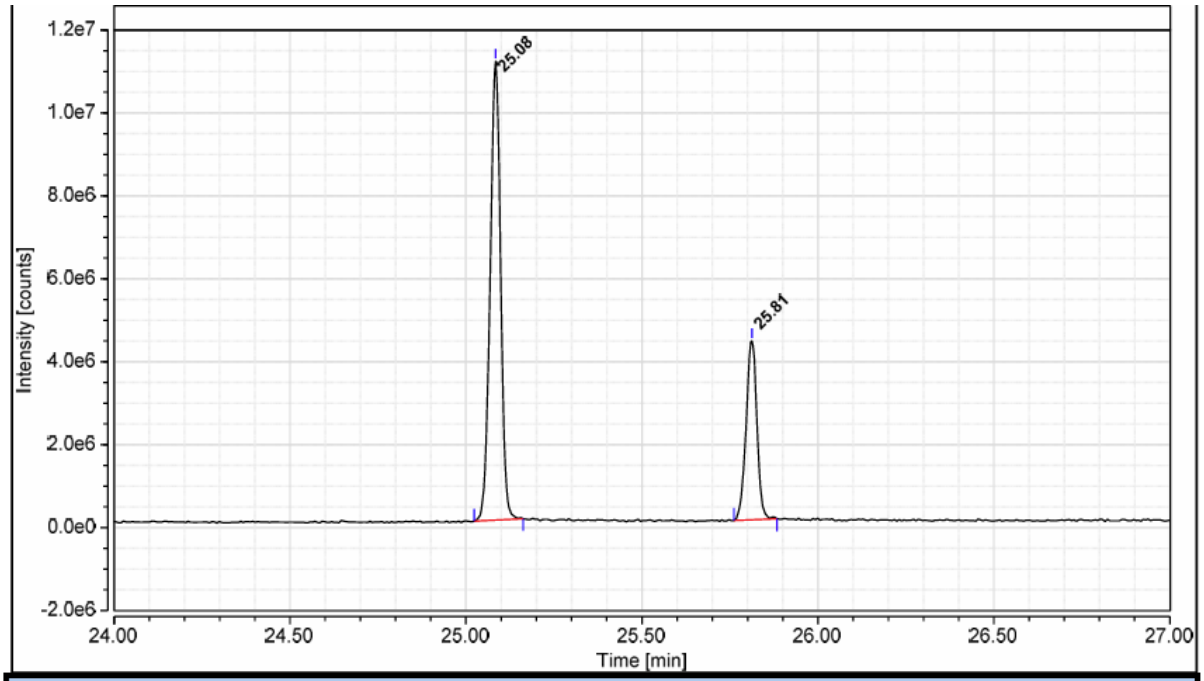
E-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.90, 134.78, 131.48, 128.58 (2 x CH), 128.37 (2 x CH), 125.73, 123.62, 123.49, 39.38, 35.68, 29.87, 27.20, 25.85, 17.85, 16.09.

Z-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.72, 135.12, 131.41, 128.51 (2 x CH), 128.41 (2 x CH), 125.81, 124.27, 123.55, 35.99, 31.64, 29.92, 27.07, 25.85, 23.50, 17.83.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.38 – 7.29 (m, 2H), 7.28 – 7.19 (m, 3H), 5.24 – 5.09 (m, 2H), 2.80 – 2.59 (m, 4H), 2.19 – 2.05 (m, 2H), 1.84 – 1.72 (m, 7H), 1.71 – 1.65 (m, 4H); **FT-IR (cm^{-1}, neat)** 3062, 3027, 2966, 2927, 2855, 1940, 1661, 1604, 1496, 1451, 1376, 1276, 1135, 1103, 1030, 983, 823, 744, 696, 565, 489, 459, 446, 432, 422, 407; **HRMS (EI)** m/z calculated for $C_{17}H_{24}$ $[M]^+$: 228.1872, found: 228.1873.

E/Z ratio was determined by GC-MS analysis:

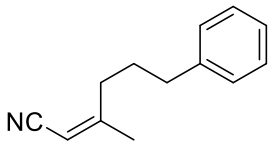
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	25.085	71.26	381343
2	25.812	28.74	153799

3-methyl-6-phenylhex-2-enenitrile (77)



Chemical Formula: $C_{13}H_{15}N$
Molecular Weight: 185,27

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-(2-methyl-5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (**16**) (865 mg, 2.0 mmol), diisopropylamine (0.55 mL, 4.0 mmol), *n*-BuLi (2.5 M in hexanes, 1.6 mL, 2.0 mmol), *p*-tolylsulfonylformonitrile (435 mg, 2.4 mmol) and THF (20 mL). Then, the reaction mixture was directly treated with TBAF (1.0 M in THF, 6.0 mL, 6.0 mmol) according to **General Procedure E**. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford

two inseparable isomers of **77** (217 mg, 60% over two steps, *E/Z* 23:77). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

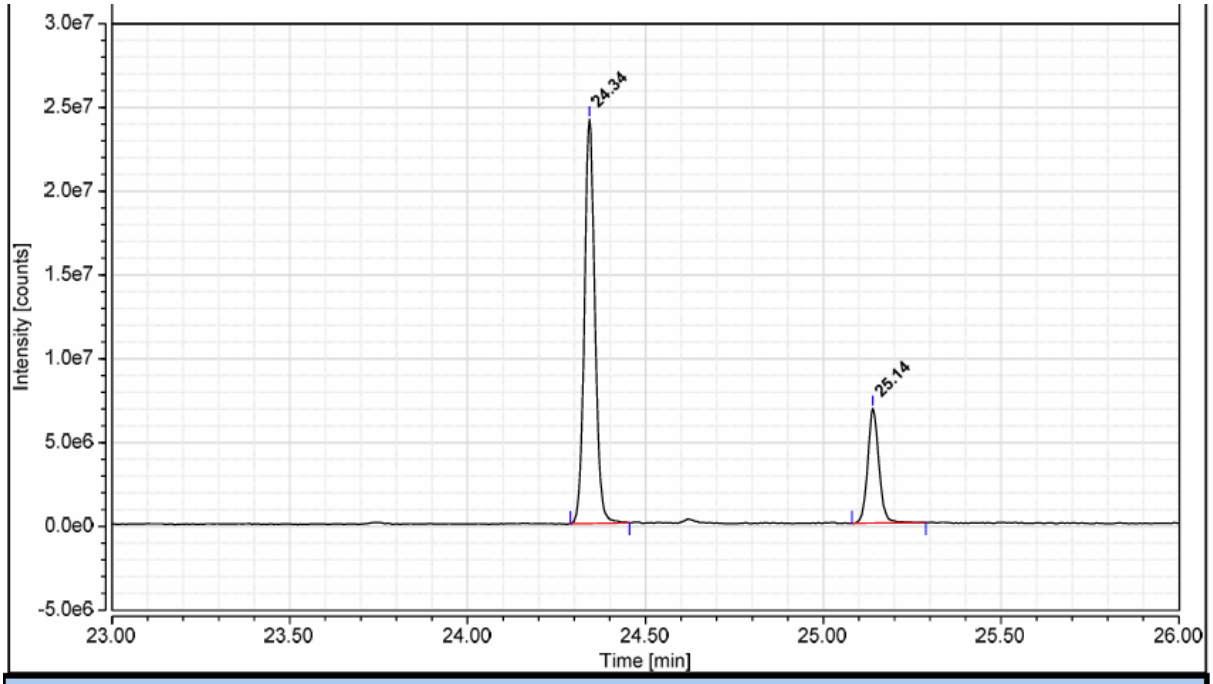
E-olefin*:* **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 165.08, 141.30, 128.58 (2 x CH), 128.45 (2 x CH), 126.22, 117.28, 95.42, 38.07, 35.21, 28.71, 22.84.

Z-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 165.21, 141.52, 128.54 (2 x CH), 128.44 (2 x CH), 126.14, 117.04, 96.03, 36.13, 35.57, 29.44, 22.84.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.40 – 7.30 (m, 4H), 7.30 – 7.19 (m, 6H), 5.20 – 5.14 (m, 2H), 2.78 – 2.63 (m, 4H), 2.57 – 2.46 (m, 2H), 2.31 – 2.22 (m, 2H), 2.10 (d, *J* = 1.04 Hz, 3H), 1.96 (d, *J* = 1.50 Hz, 3H), 1.93 – 1.79 (m, 4H); **FT-IR (cm^{-1}, neat)** 3061, 3027, 2943, 2860, 2216, 1452, 1379, 1351, 1180, 1134, 1084, 1030, 1003, 909, 800, 747, 698, 620, 598, 580, 564, 480, 429, 417, 406; **HRMS (EI)** m/z calculated for $C_{13}H_{15}N$ $[M]^+$: 185.1199, found: 185.1199.

E/Z ratio was determined by GC-MS analysis:

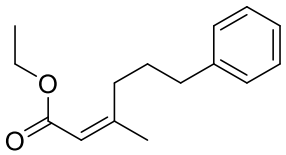
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	24.343	76.76	824619
2	25.139	23.24	249599

ethyl 3-methyl-6-phenylhex-2-enoate (75)



Chemical Formula: $C_{15}H_{20}O_2$
Molecular Weight: 232,32

The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-((4*S*,5*R*)-4-methyl-1-phenyl-5-tosylnon-8-en-4-yl)-1,3,2-dioxaborolane (**49**) (68 mg, 0.1 mmol), TBAF (1.0 M in THF, 0.4 mL, 0.4 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two separable isomers of **75** (25 mg, 81%, *E/Z* 35:65). (grease-impurity in H-NMR!) The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

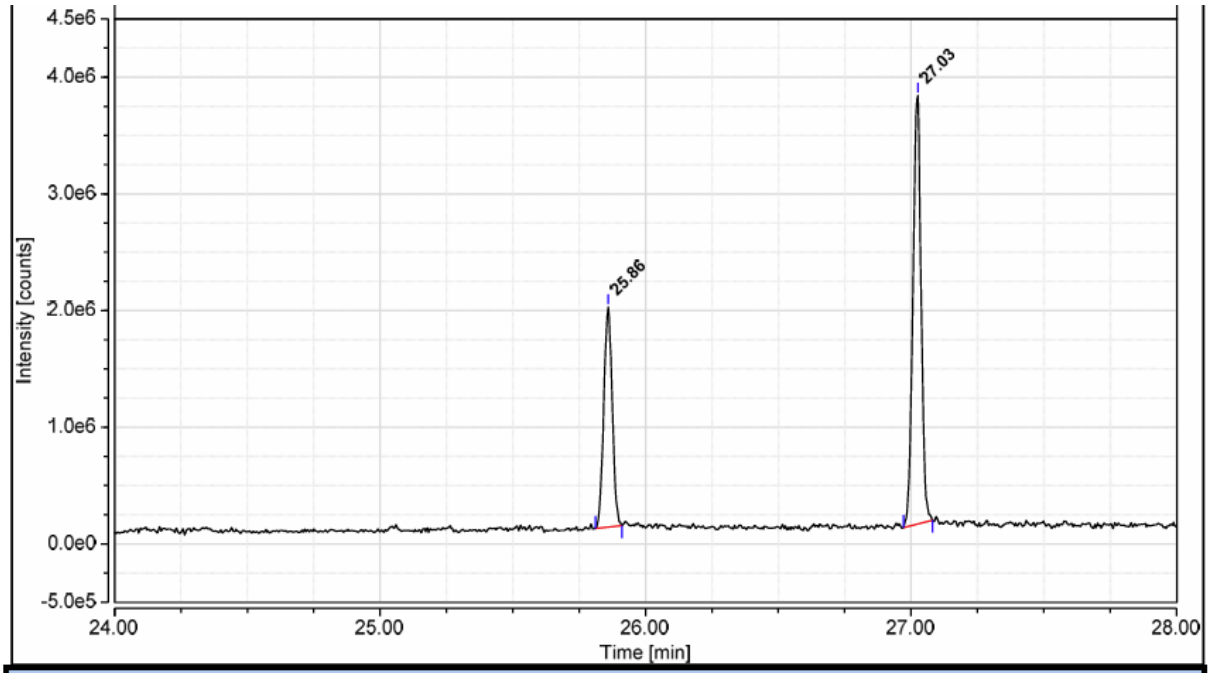
E-olefin*:* **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 166.52, 160.11, 142.45, 128.53 (2 x CH), 128.42 (2 CH), 125.89, 116.59, 59.60, 36.16, 33.36, 30.14, 25.20, 14.47.

Z-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 166.97, 159.74, 141.97, 128.53 (2 x CH), 128.51 (2 x CH), 126.04, 115.95, 59.62, 40.51, 35.47, 29.18, 18.86, 14.47.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.32 – 7.24 (m, 4H), 7.23 – 7.14 (m, 6H), 5.70 – 5.66 (m, 2H), 4.15 (q, *J* = 7.13 Hz, 2H), 4.14 (q, *J* = 7.12 Hz, 2H), 2.74 – 2.58 (m, 4H), 2.22 – 2.14 (m, 4H), 2.16 (d, *J* = 1.32 Hz, 3H), 1.88 (d, *J* = 1.40 Hz, 3H), 1.86 – 1.74 (m, 4H), 1.28 (t, *J* = 7.08 Hz, 3H), 1.27 (t, *J* = 6.72 Hz, 3H); **FT-IR (cm^{-1}, neat)** 2925, 2856, 1712, 1646, 1490, 1450, 1373, 1271, 1219, 1145, 1087, 1037, 965, 861, 742, 698, 580, 486, 413; **HRMS (ESI)** m/z calculated for $C_{15}H_{21}O_2$ $[M+H]^+$: 233.1534, found: 233.1536.

E/Z ratio was determined by GC-MS analysis:

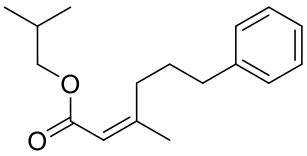
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	25.859	34.91	70110
2	27.026	65.09	130728

isobutyl 3-methyl-6-phenylhex-2-enoate (76)



Chemical Formula: $C_{17}H_{24}O_2$
Molecular Weight: 260,38

The reaction was performed according to **General Procedure D** with 4,4,5,5-tetramethyl-2-(2-methyl-5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (**16**) (438 mg, 1.0 mmol), diisopropylamine (0.28 mL, 2.0 mmol), *n*-BuLi (2.5 M in hexanes, 0.8 mL, 2.0 mmol, 1.0 eq.), isobutyl chloroformate (1.3 mL, 10.0 mmol) and THF (10 mL). Then, the reaction mixture was directly treated with TBAF (1.0 M in THF, 14.0 mL, 14.0 mmol) according to **General Procedure E**. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **76** (187 mg, 73% over two steps, *E/Z* 25:75). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

E-olefin*:* **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 166.62, 160.00, 142.43, 128.51 (2 x CH), 128.41 (2 x CH), 125.87, 116.59, 74.07, 36.15, 33.38, 30.15, 27.91, 25.18, 19.33, 19.05.

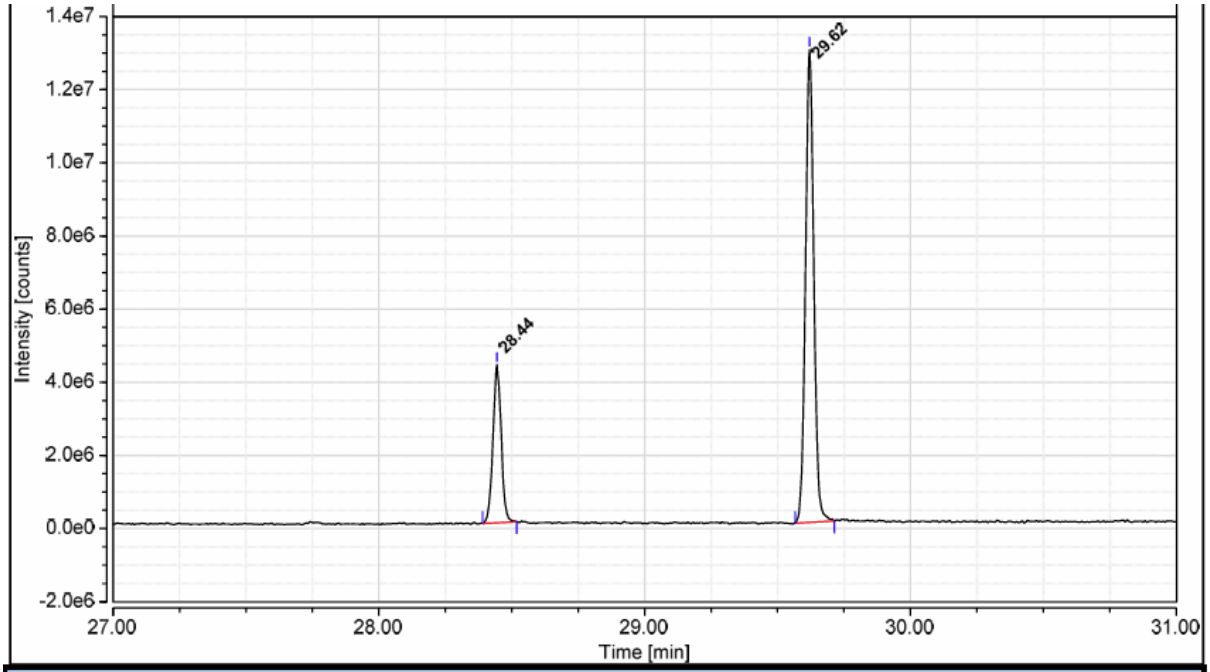
Z-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 167.07, 159.60, 141.96, 128.52 (2 x CH), 128.51 (2 x CH), 126.03, 115.98, 69.95, 40.52, 35.49, 29.19, 27.91, 19.33 (2 x CH_3), 18.88.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.40 – 7.31 (m, 4H), 7.30 – 7.21 (m, 6H), 5.79 – 5.73 (m, 2H), 4.02 – 3.92 (m, 4H), 2.82 – 2.65 (m, 6H), 2.30 – 2.19 (m, 6H), 2.12 – 1.79 (m, 8H), 1.04 (s, 3H), 1.03 (s, 3H), 1.02

(s, 3H), 1.01 (s, 3H); **FT-IR (cm^{-1}, neat)** 3062, 3027, 2959, 2936, 2873, 1743, 1712, 1646, 1604, 1496, 1453, 1379, 1254, 1220, 1148, 1083, 1060, 1012, 971, 907, 854, 792, 746, 697, 586, 491, 459, 433, 418, 403; **HRMS (ESI)** m/z calculated for $C_{17}H_{25}O_2$ $[M+H]^+$: 261.1850, found: 261.1849.

E/Z ratio was determined by GC-MS analysis:

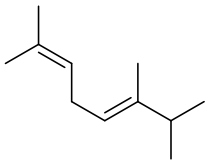
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	28.444	24.86	155664
2	29.621	75.14	470516

2,6,7-trimethylocta-2,5-diene (73)



Chemical Formula: $C_{11}H_{20}$
Molecular Weight: 152,28

The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-((3*R*,4*R*)-2,3,7-trimethyl-4-tosyloct-6-en-3-yl)-1,3,2-dioxaborolane (**54**) (108 mg, 0.25 mmol), TBAF (1.0 M in THF, 0.75 mL, 0.75 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **73** (34 mg, 90%, *E/Z* 83:17). The *E/Z* configuration was assigned based on the NOESY-NMR results of **70**.

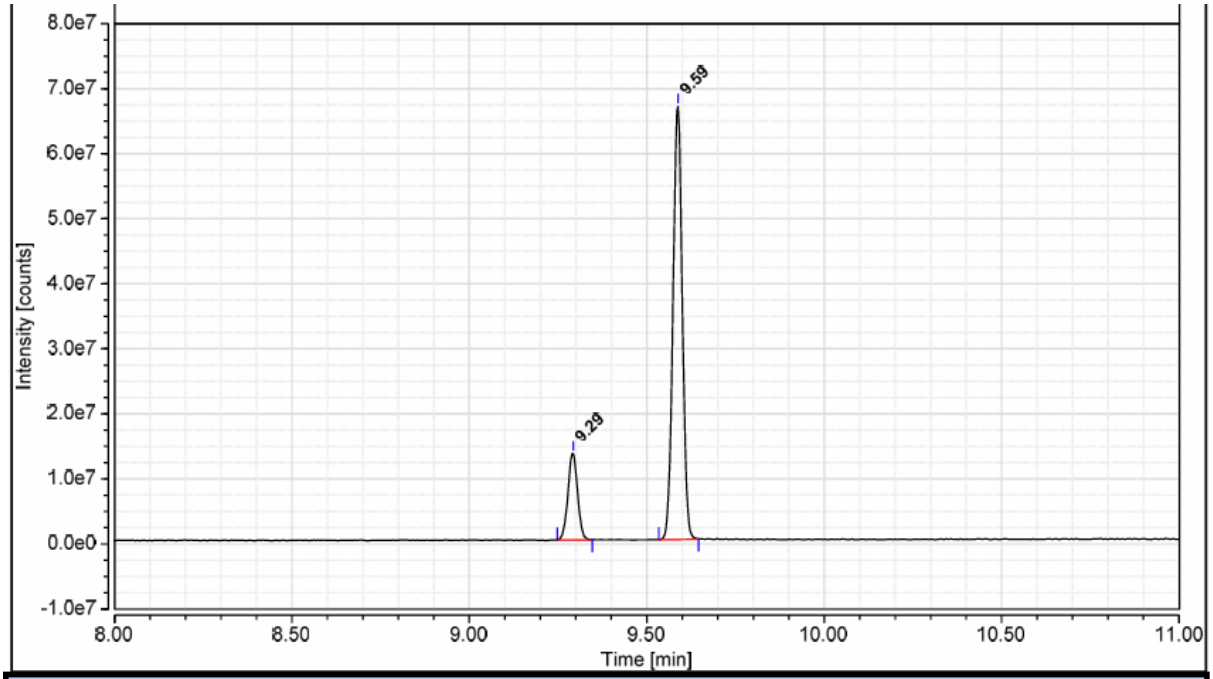
Z-olefin (characteristic signals)*:* **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.67, 122.57, 28.65, 26.47, 20.98 (2 x CH_3), 18.16, 17.80.

E-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.92, 131.34, 123.76, 120.93, 36.85, 27.05, 25.86, 21.60 (2 x CH_3), 17.85, 13.56.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.16 – 5.06 (m, 2H), 5.07 – 4.99 (m, 2H), 2.84 (hept, *J* = 6.84 Hz, 1H), 2.74 – 2.63 (m, 4H), 2.22 (hept, *J* = 6.79 Hz, 1H), 1.70 (s, 6H), 1.63 (s, 6H), 1.59 (s, 6H), 1.00 (s, 3H), 0.98 (s, 3H), 0.97 (s, 3H), 0.96 (s, 3H); **FT-IR (cm^{-1}, neat)** 2960, 2925, 2870, 1658, 1449, 1376, 1308, 1143, 1103, 1040, 984, 931, 885, 826, 777,z 580, 539, 511, 500, 471, 445, 432, 410; **HRMS (EI)** m/z calculated for $C_{11}H_{19}$ $[M-H]^+$: 151.1481, found: 151.1481.

E/Z ratio was determined by GC-MS analysis:

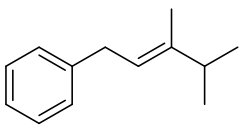
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	9.292	17.02	415485
2	9.588	82.98	2026161

(3,4-dimethylpent-2-en-1-yl)benzene (70)



Chemical Formula: $C_{13}H_{18}$
Molecular Weight: 174,29

The reaction was performed according to **General Procedure E** with 2-((2*R*,3*R*)-3,4-dimethyl-1-phenyl-2-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**53**) (110 mg, 0.2 mmol), TBAF (1.0 M in THF, 0.6 mL, 0.6 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **70** (>98%, *E/Z* 85:15).

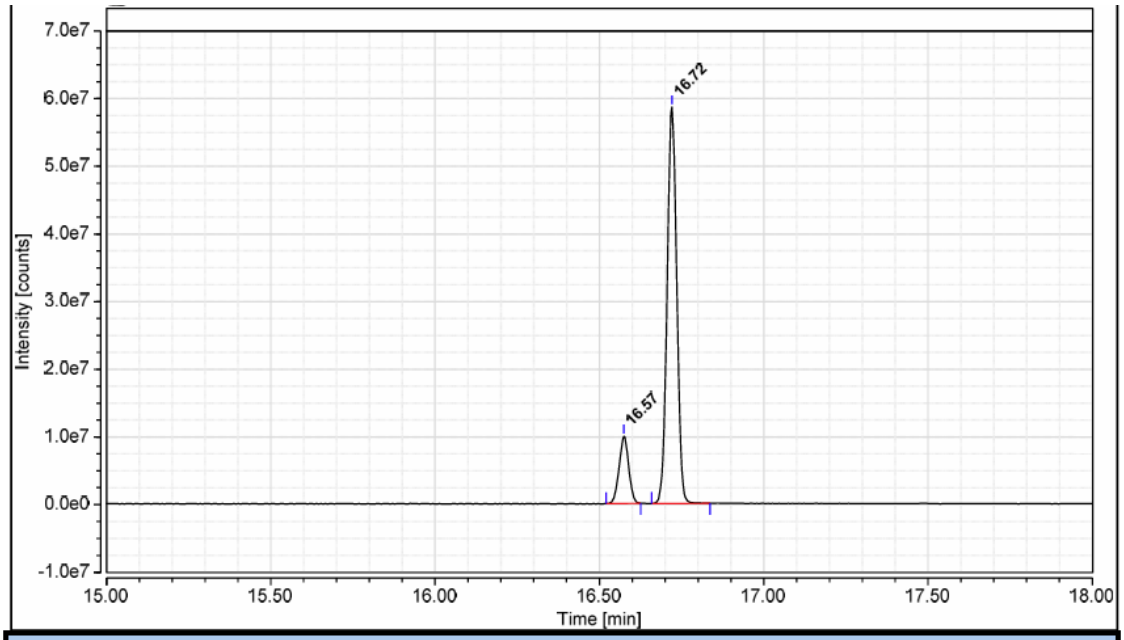
Z-olefin (characteristic signals)*:* **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 141.71, 122.38, 33.64, 28.65, 21.00 (2 x CH_3), 18.21.

E-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.29, 142.08, 128.46 (4 x CH), 125.79, 120.73, 36.96, 34.13, 21.62 (2 x CH_3), 13.71.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.33 – 7.23 (m, 4H), 7.22 – 7.15 (m, 6H), 5.41 – 5.32 (m, 1H), 5.29 – 5.21 (m, 1H), 3.37 (t, *J* = 6.94 Hz, 4H), 2.96 (hept, *J* = 6.87 Hz, 1H), 2.30 (hept, *J* = 6.84 Hz, 1H), 1.71 – 1.67 (m, 3H), 1.67 – 1.65 (m, 3H), 1.04 (s, 3H), 1.03 (s, 3H), 1.02 (s, 3H), 1.01 (s, 3H).; **FT-IR (cm^{-1}, neat)** 3061, 3027, 2959, 2927, 2870, 1659, 1603, 1493, 1452, 1378, 1308, 1079, 1032, 928, 883, 858, 794, 737, 696; **HRMS (EI)** m/z calculated for $C_{13}H_{18}$ $[M]^+$: 174.1404, found: 174.1403.

E/Z ratio was determined by GC-MS analysis:

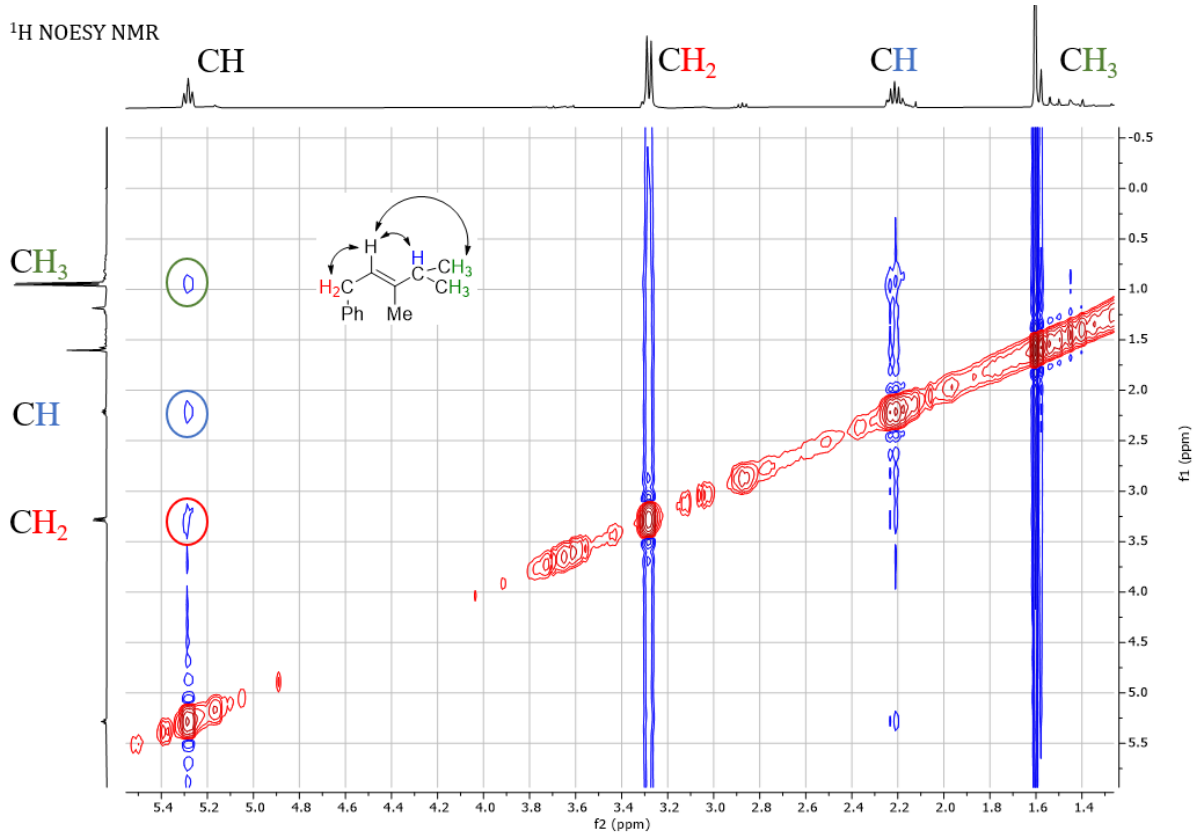
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



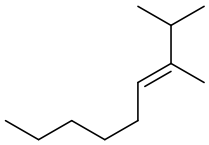
Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	16.574	14.56	336817
2	16.721	85.44	1977136

E/Z-determination was assigned via NOESY-NMR analysis:



2,3-dimethylnon-3-ene (71)



Chemical Formula: $C_{11}H_{22}$
Molecular Weight: 154,30

The reaction was performed according to **General Procedure E** with 2-((3*R*,4*R*)-2,3-dimethyl-4-tosylnonan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**53**) (70 mg, 0.2 mmol), TBAF (1.0 M in THF, 0.6 mL, 0.6 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=15:85, stained in PMA solution) to afford two inseparable isomers of **71** (20mg, 81%, *E/Z* 83:17). The *E/Z* configuration was assigned based on the NOESY-NMR results of **70**.

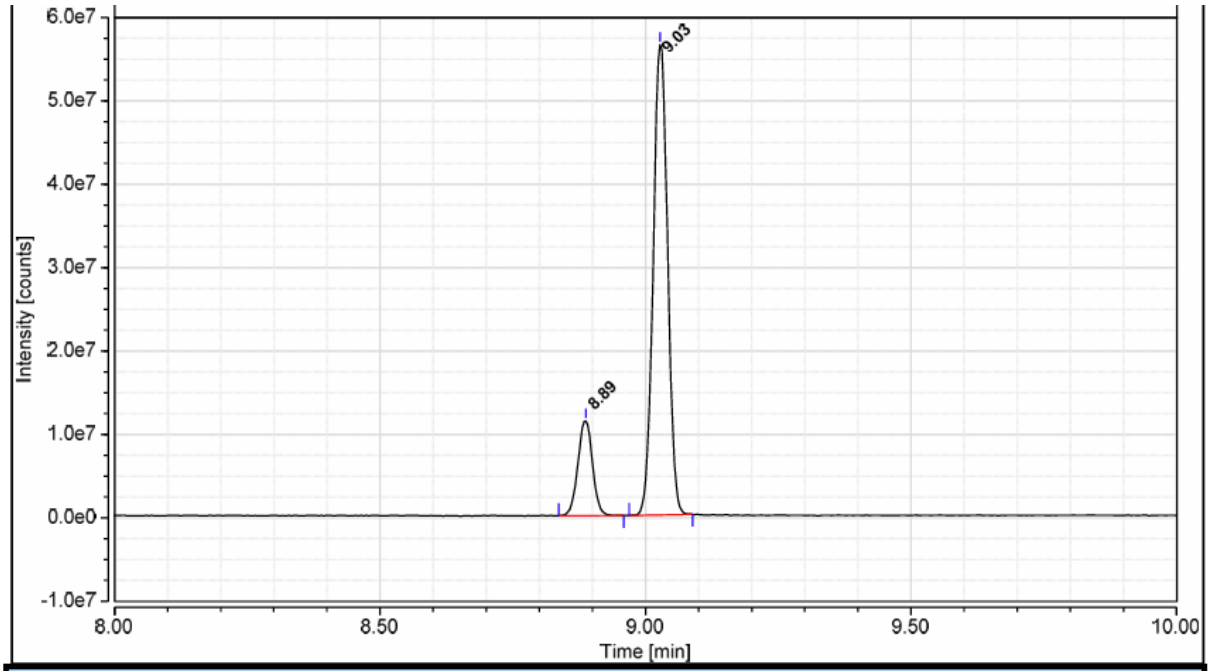
Z-olefin (characteristic signals): **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.04 (t, J = 6.6 Hz, 1H), 2.81 (hept, J = 6.9 Hz, 1H), 1.59 (q, J = 1.4 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.51, 124.28, 30.05, 28.56, 27.31, 21.02, 18.13.

E-olefin: **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.14 (t, J = 7.0 Hz, 1H), 2.21 (hept, J = 6.8 Hz, 1H), 1.96 (q, J = 6.8 Hz, 2H), 1.56 (d, J = 1.4 Hz, 3H), 1.43 – 1.20 (m, 6H), 0.99 (s, 3H), 0.97 (s, 3H), 0.89 (t, J = 6.8 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.79 (C_q), 122.44 (CH), 36.90 (CH), 31.76 (CH_2), 29.76 (CH_2), 27.88 (CH_2), 22.79 (CH_2), 21.67 (2 x CH_3), 14.26 (CH_3), 13.46 (CH_3).

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=15:85); **FT-IR (cm^{-1}, neat)** 2957, 2923, 2855, 1736, 1461, 1377, 1262, 1085, 854, 808, 724; **HRMS (EI)** m/z calculated for $C_{11}H_{21}$ $[M-H]^+$: 153.1638, found: 153.1638.

E/Z ratio was determined by GC-MS analysis:

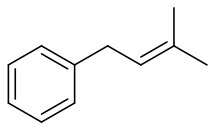
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	8.888	17.06	365292
2	9.027	82.94	1775788

(3-methylbut-2-en-1-yl)benzene (58)

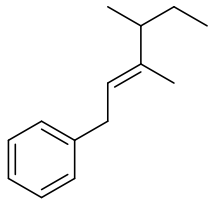


Chemical Formula: $C_{11}H_{14}$
Molecular Weight: 146,23

The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-(2-methyl-4-phenyl-3-tosylbutan-2-yl)-1,3,2-dioxaborolane (**37**) (85 mg, 0.2 mmol), TBAF (1.0 M in THF, 0.6 mL, 0.6 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **58** (27 mg, 93%).

Appearance colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.39 – 7.30 (m, 2H), 7.29 – 7.20 (m, 3H), 5.44 – 5.36 (m, 1H), 3.41 (d, *J* = 7.34 Hz, 2H), 1.82 (t, *J* = 1.34 Hz, 3H), 1.79 (d, *J* = 1.33 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 141.98, 132.65, 128.49 (2 x CH), 128.45 (2 x CH), 125.83, 123.34, 34.52, 25.90, 17.96. Physical and spectral data are in accordance with literature data[87].

(3,4-dimethylhex-2-en-1-yl)benzene (72a)



Chemical Formula: $C_{14}H_{20}$
Molecular Weight: 188,31

The reaction was performed according to **General Procedure E** with 2-((2*R*,3*R*,4*S*)-3,4-dimethyl-1-phenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**55**) (184 mg, 0.4 mmol), TBAF (1.0 M in THF, 1.2 mL, 1.2 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **72a** (67 mg, 91%, *E/Z* 77:23).

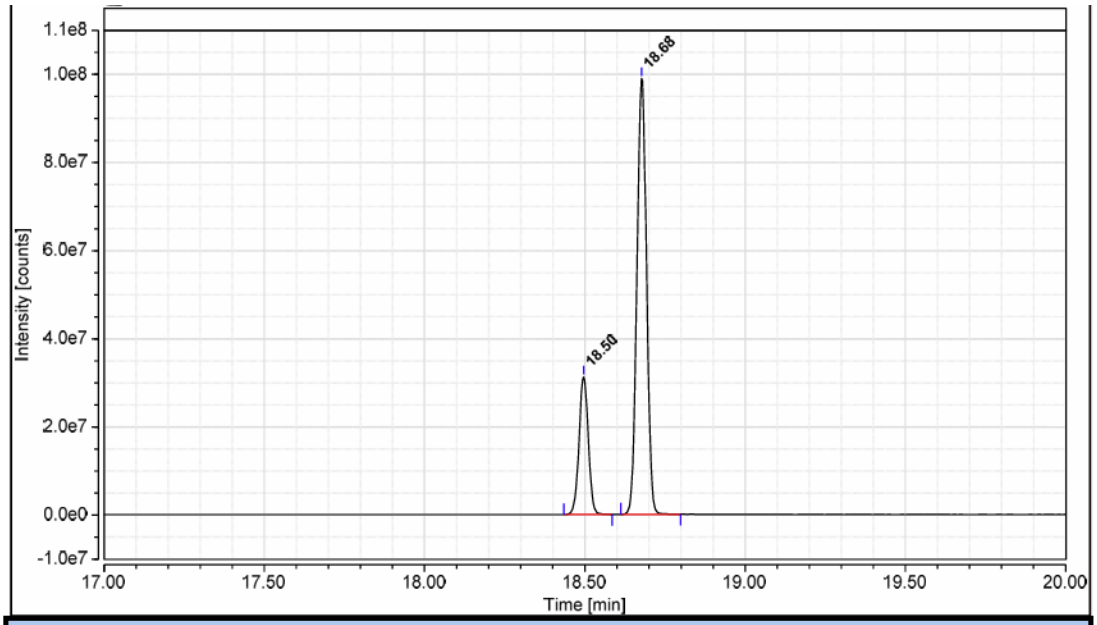
Z-olefin*:* **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.17, 140.16, 128.52 (2 x CH), 128.47 (2 x CH), 125.80, 123.91, 35.89, 33.75, 27.80, 19.25, 18.16, 12.53.

E-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.11, 140.54, 128.47 (2 x CH), 128.44 (2 x CH), 125.77, 122.54, 44.73, 34.13, 27.89, 19.62, 12.63, 12.34.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.34 – 7.24 (m, 4H), 7.24 – 7.14 (m, 6H), 5.41 – 5.29 (m, 2H), 3.50 – 3.30 (m, 4H), 2.68 (h, *J* = 7.06 Hz, 1H), 2.05 (h, *J* = 6.99 Hz, 1H), 1.63 (s, 6H), 1.51 – 1.19 (m, 4H), 1.05 – 0.98 (m, 6H), 0.90 – 0.78 (m, 6H); **FT-IR (cm^{-1}, neat)** 3027, 2959, 2925, 2871, 1603, 1493, 1453, 1375, 1321, 1091, 1029, 1002, 952, 898, 869, 791, 736, 696, 594, 553, 531, 456; **HRMS (EI)** m/z calculated for $C_{14}H_{20}$ $[M]^+$: 188.1561, found: 188.1560.

E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min

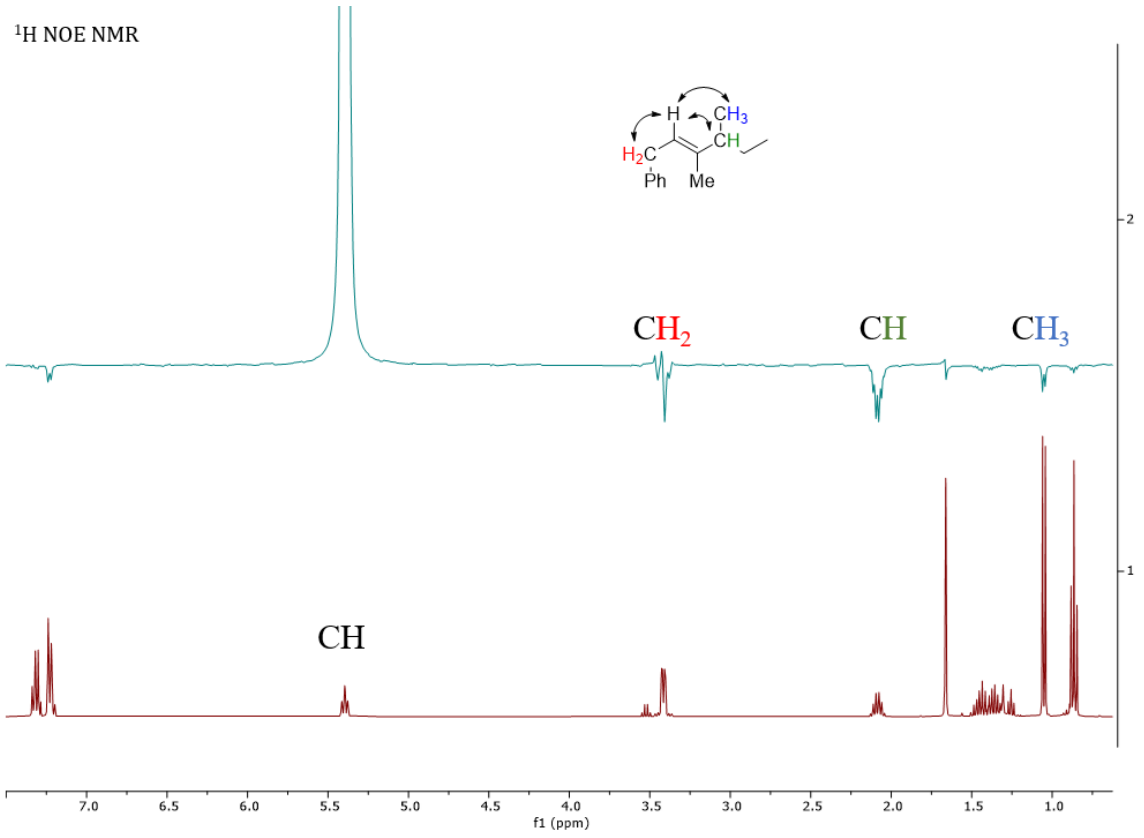


Integration Results

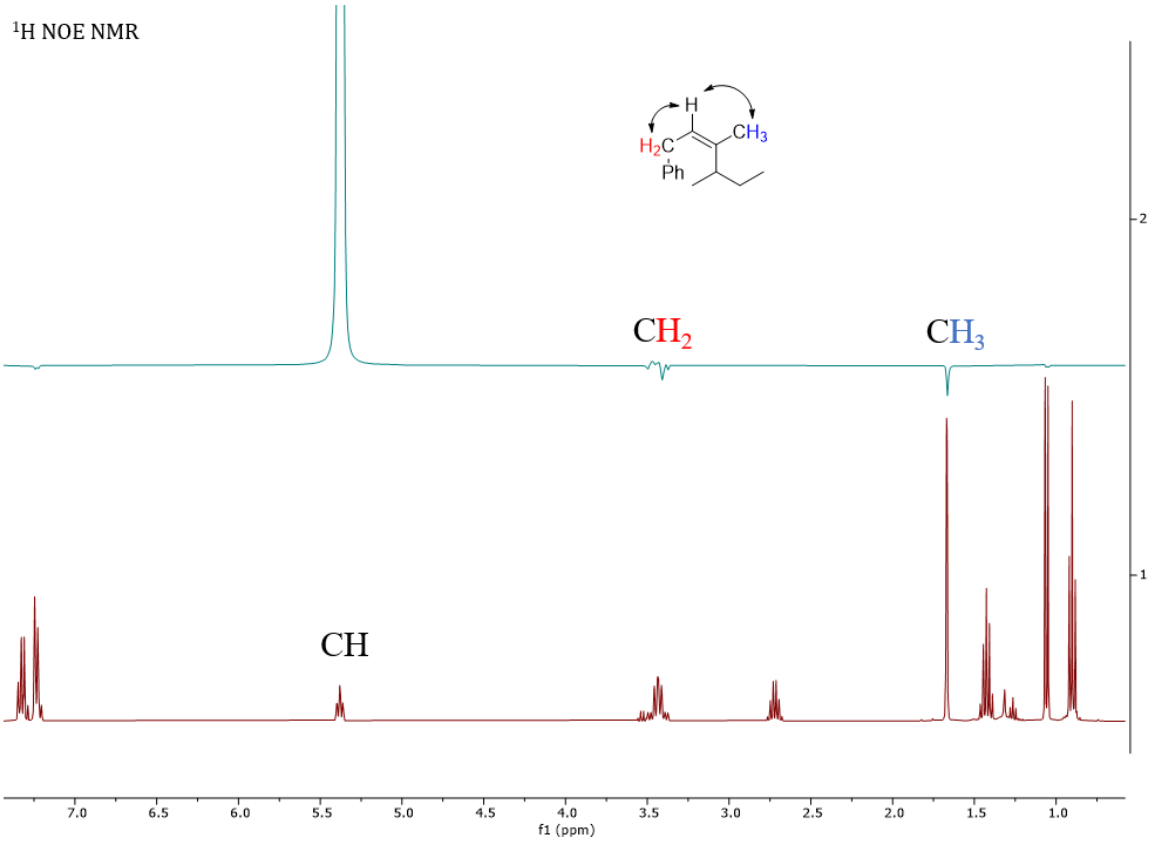
No.	Retention Time min	Rel.Area %	Area counts*min
1	18.496	23.42	1050969
2	18.676	76.58	3437236

E/Z-determination was assigned via NOE-NMR analysis:

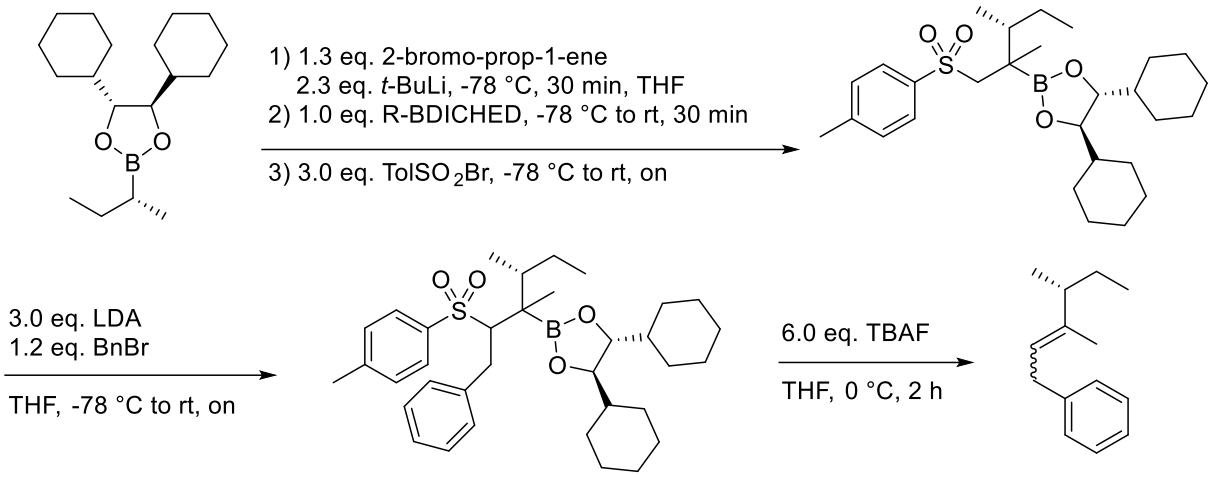
E-olefin:



Z-olefin:



(*R*)-(3,4-dimethylhex-2-en-1-yl)benzene (72b)



In a dry round bottom flask was placed 2-bromo-prop-1-ene (349 mg, 2.9 mmol) in dry THF (7 mL). At -78 °C was added slowly *t*-BuLi (1.7 M in pentane, 2.7 mL, 4.6 mmol) and stirred for 30 min. Then, (4*R*,5*R*)-2-((*R*)-sec-butyl)-4,5-dicyclohexyl-1,3,2-dioxaborolane (**90**) (588 mg, 2.0 mmol) dissolved in dry THF (1 mL) was added to the reaction mixture, stirred for 30 min at -78 °C, warmed up to room temperature, stirred for 5 minutes and then cooled again down to -78 °C. Tosyl bromide (1.43 g, 6.0 mmol) dissolved in dry THF (3 mL) was added, the reaction mixture was stirred 1 h at -78 °C and then warmed up to room temperature overnight.

The next day, the reaction mixture was cooled down to -78 °C, LDA solution (1.0 M in THF; 6.0 mL, 6.0 mmol) was added and stirred for 1 h at this temperature. Then, benzyl bromide (0.3 mL, 2.4 mmol) was added and the reaction mixture was stirred overnight allowing to reach rt. The reaction mixture was cooled down to 0 °C, TBAF (1.0 M in THF, 12.0 mL, 12.0 mmol) was added slowly and after 2 h stirring at 0 °C, the reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford two inseparable isomers of **72b** (131 mg, 35% over three steps, one pot, *E/Z* 12:88). The *E/Z* configuration was assigned based on the NOE-NMR results of **72a**.

E-olefin*:* **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.17, 140.16, 128.52, 128.47, 125.80, 123.91, 35.89, 33.75, 27.80, 19.25, 18.16, 12.53.

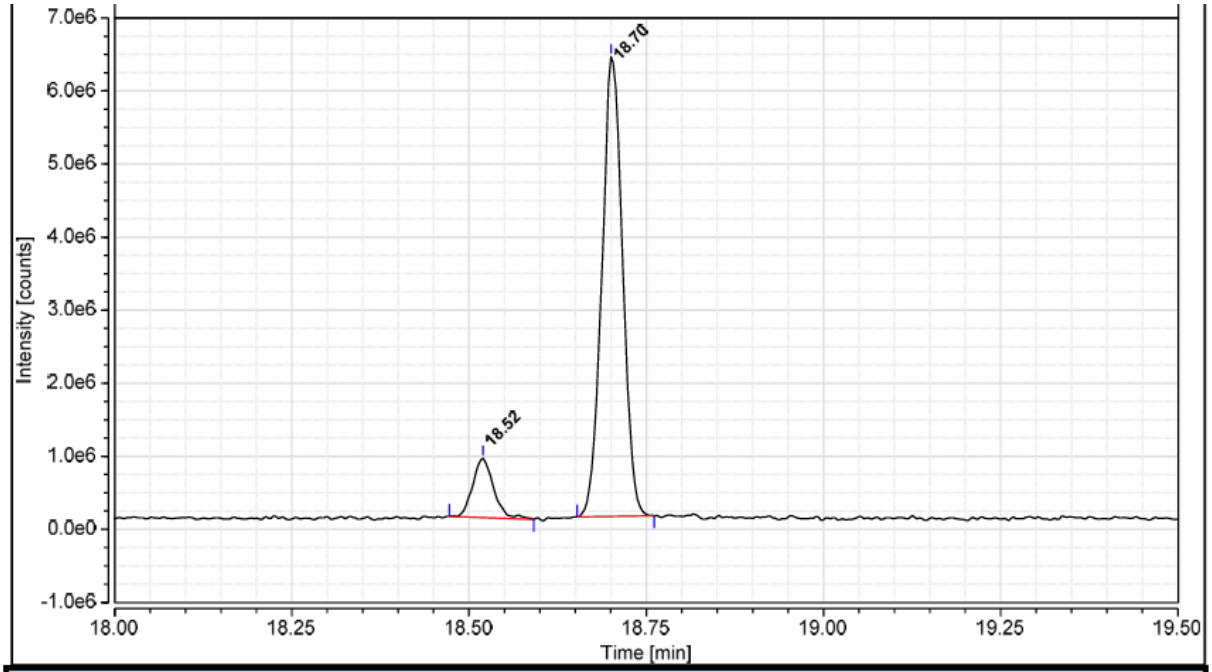
Z-olefin: **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.11, 140.54, 128.47 (2 x CH), 128.44 (2 x CH), 125.77, 122.54, 44.73, 34.13, 27.89, 19.62, 12.63, 12.34.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.32 – 7.24 (m, 4H), 7.23 – 7.14 (m, 6H), 5.40 – 5.32 (m, 2H), 3.38 (d, *J* = 7.23 Hz, 4H), 2.67 (h, *J* = 7.07 Hz, 1H), 2.05 (h, *J* = 6.93 Hz, 1H), 1.62 (s, 6H), 1.50 – 1.19 (m, 4H),

1.01 (d, *J* = 6.87 Hz, 6H), 0.83 (t, *J* = 7.39 Hz, 6H). Physical and spectral data are in accordance with **72a**.

E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min

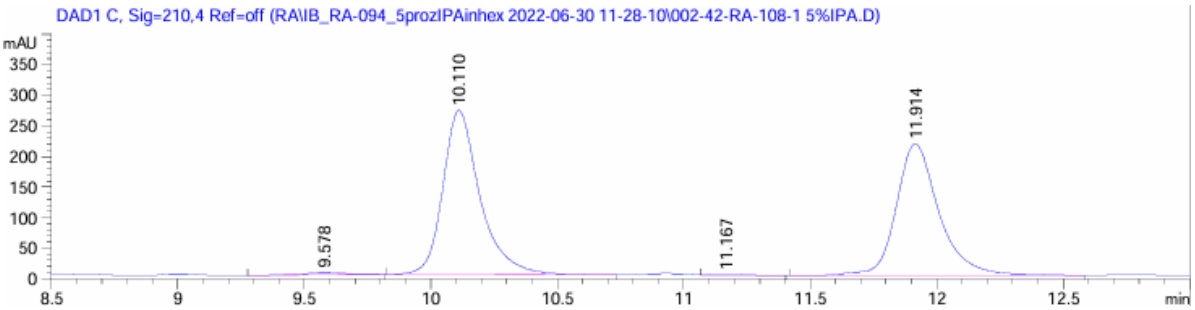


Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	18.520	11.54	27837
2	18.700	88.46	213344

EE 97% for *E*-olefin (1. & 2.) & 98% for *Z*-olefin (3. & 4.); was determined by chiral HPLC analysis:

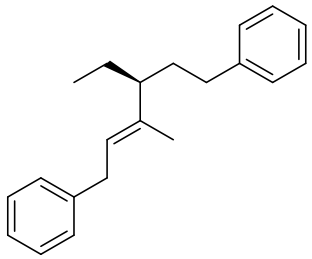
CHIRALPAK IB-3, hexane/IPA 95:5, 0.75 mL min^{-1}, λ = 210 nm



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.578	BB	0.1411	42.06852	3.98601	0.7886
2	10.110	BB	0.1523	2740.65161	268.00009	51.3765
3	11.167	VB	0.1234	17.52695	1.81898	0.3286
4	11.914	BB	0.1763	2534.19849	215.35797	47.5063
Totals :				5334.44557	489.16305	

(*S*)-(4-ethyl-3-methylhex-2-ene-1,6-diyl)dibenzene (94)



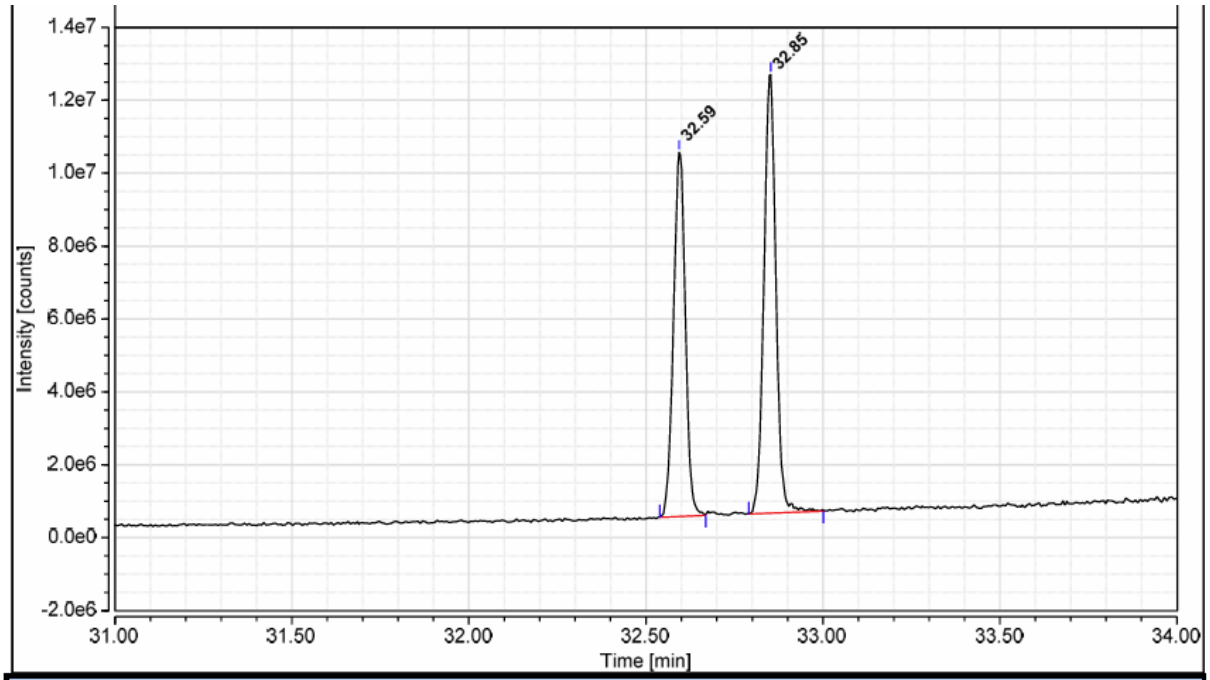
Chemical Formula: $C_{21}H_{26}$
Molecular Weight: 278,44

The reaction was performed according to **General Procedure E** with 2-((4*S*)-4-ethyl-3-methyl-1,6-diphenyl-2-(phenylsulfonyl) hexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**93**) (73 mg, 0.1 mmol), TBAF (1.0 M in THF, 0.4 mL, 0.4 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **94** (30 mg, 83%, *E/Z* 55:45). The *E/Z* configuration was assigned based on the NOE-NMR results of **72a**.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.36 – 7.12 (m, 20H), 5.55 – 5.47 (m, 1H), 5.45 – 5.37 (m, 1H), 3.44 (d, *J* = 7.28 Hz, 2H), 3.37 (d, *J* = 7.23 Hz, 2H), 2.67 – 2.42 (m, 5H), 2.02 – 1.90 (m, 1H), 1.82 – 1.23 (m, 8H), 1.66 (d, *J* = 1.37 Hz, 3H), 1.63 (d, *J* = 1.30 Hz, 3H), 0.86 (t, *J* = 7.40 Hz, 3H), 0.83 (t, *J* = 7.37 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.19, 143.05, 142.17, 142.02, 137.56, 137.50, 128.56, 128.53, 128.49, 128.47, 128.43, 128.36, 126.47, 125.83, 125.76, 125.66, 125.36, 50.71, 41.42, 35.49, 35.37, 34.24, 34.20, 33.95, 26.45, 26.42, 18.14, 12.37, 12.33, 11.79; **FT-IR (cm^{-1}, neat)** 3060, 3025, 2926, 2864, 1600, 1492, 1449, 1375, 1216, 1069, 1028, 901, 744, 598, 527, 494, 452; **HRMS (EI)** m/z calculated for $C_{21}H_{26}$ $[M]^+$: 278.2030, found: 278.2029.

E/Z ratio was determined by GC-MS analysis:

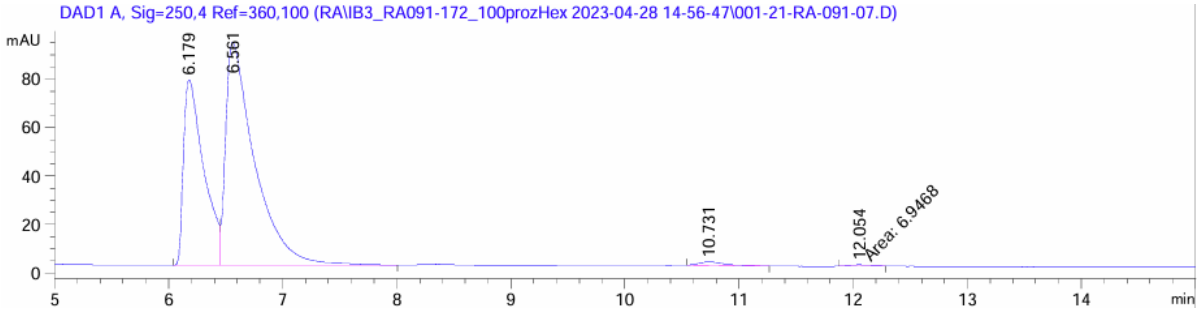
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results			
No.	Retention Time min	Rel.Area %	Area counts*min
1	32.594	45.06	388550
2	32.852	54.94	473668

EE 96% for *E*-olefin (1. & 3.) & 99% for *Z*-olefin (2. & 4.); was determined by chiral HPLC analysis:

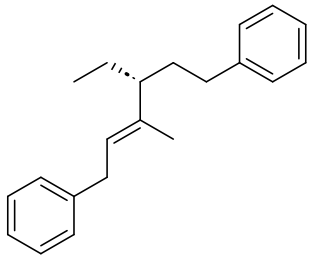
CHIRALPAK IB-3, hexane 100%, 1.0 mL min^{-1}, λ = 250 nm



Signal 1: DAD1 A, Sig=250,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.179	BV	0.1802	938.93030	76.47947	36.3447
2	6.561	VB	0.2532	1616.75415	91.91542	62.5823
3	10.731	BB	0.1799	20.77155	1.43465	0.8040
4	12.054	MM	0.2054	6.94680	5.63733e-1	0.2689
Totals :				2583.40280	170.39327	

(*R*)-(4-ethyl-3-methylhex-2-ene-1,6-diyl)dibenzene (109)



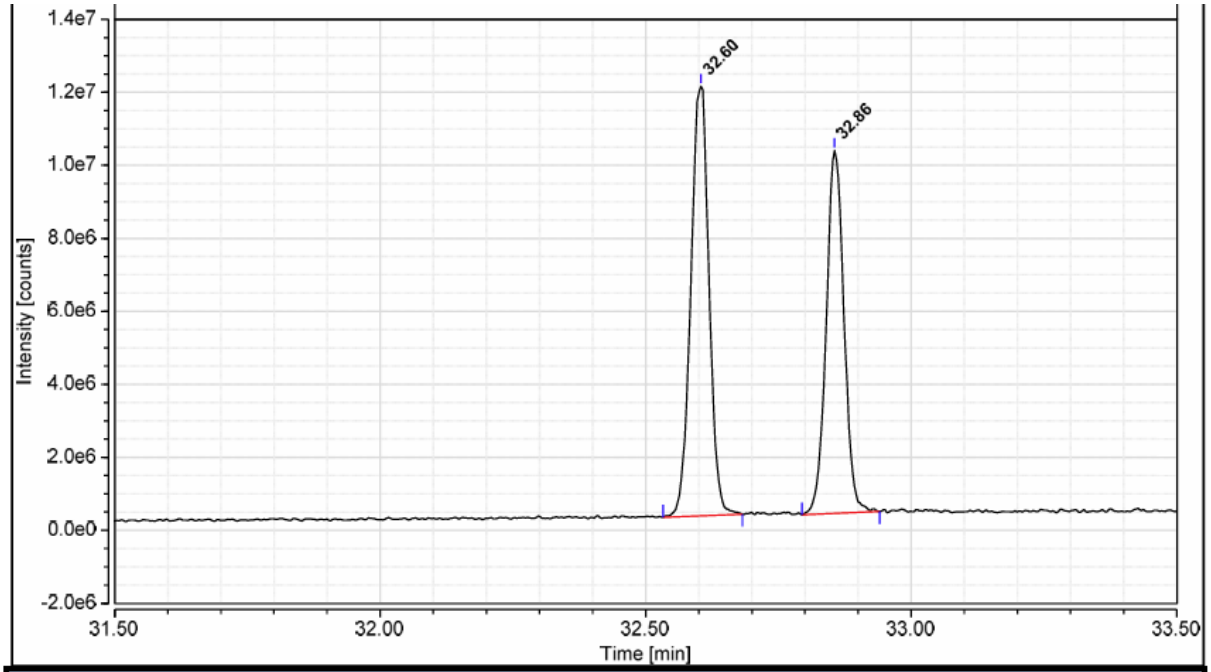
Chemical Formula: $C_{21}H_{26}$
Molecular Weight: 278,44

The reaction was performed according to **General Procedure E** with 2-((4*R*)-4-ethyl-3-methyl-1,6-diphenyl-2-(phenylsulfonyl) hexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**106**) (151 mg, 0.3 mmol), TBAF (1.0 M in THF, 0.8 mL, 0.8 mmol) and THF (8 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **109** (70 mg, 91%, *E/Z* 55:45). The *E/Z* configuration was assigned based on the NOE-NMR results of **72a**.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.35 – 7.14 (m, 20H), 5.56 – 5.47 (m, 1H), 5.46 – 5.37 (m, 1H), 3.45 (d, *J* = 7.29 Hz, 2H), 3.38 (d, *J* = 7.23 Hz, 2H), 2.70 – 2.42 (m, 5H), 2.04 – 1.90 (m, 1H), 1.85 – 1.19 (m, 8H), 1.67 (d, *J* = 1.37 Hz, 3H), 1.64 (d, *J* = 1.25 Hz, 3H), 0.87 (t, *J* = 7.40 Hz, 3H), 0.83 (t, *J* = 7.38 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.19, 143.05, 142.16, 137.56, 137.49, 128.56, 128.53, 128.49, 128.47, 128.43, 128.36, 126.47, 125.83, 125.76, 125.66, 125.36, 50.70, 41.42, 35.49, 35.37, 34.24, 34.20, 33.95, 26.45, 26.43, 18.14, 12.37, 12.34, 11.79. Physical and spectral data are in accordance with **94**.

E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min

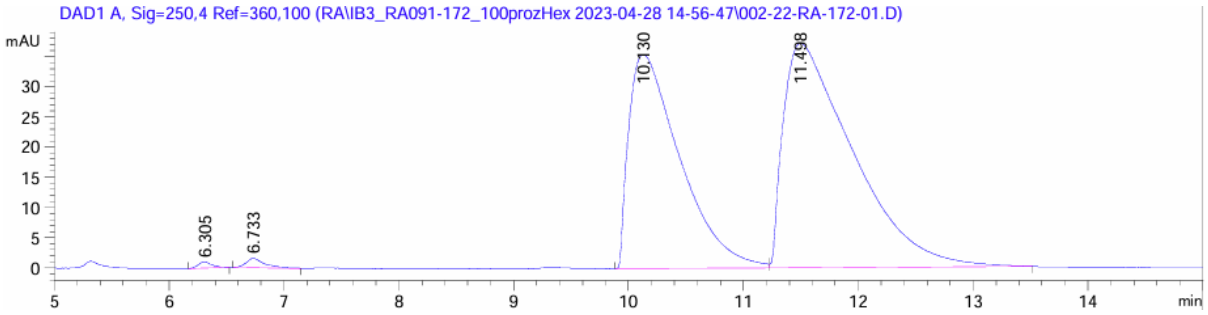


Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	32.604	54.74	466990
2	32.856	45.26	386150

EE 98% for *E*-olefin (1. & 3.) & 98% for *Z*-olefin (2. & 4.); was determined by chiral HPLC analysis:

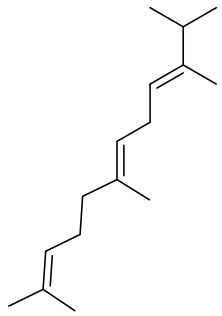
CHIRALPAK IB-3, hexane 100%, 1.0 mL min^{-1}, λ = 250 nm



Signal 1: DAD1 A, Sig=250,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.305	BB	0.1158	8.47144	1.01049	0.3153
2	6.733	BB	0.1454	17.11731	1.54348	0.6371
3	10.130	BV	0.4374	1098.02075	35.45079	40.8694
4	11.498	VB	0.5802	1563.04736	37.20351	58.1782
Totals :				2686.65686	75.20827	

(6*E*,9*E*)-2,6,10,11-tetramethyldodeca-2,6,9-triene (85)



Chemical Formula: $C_{16}H_{28}$
Molecular Weight: 220,40

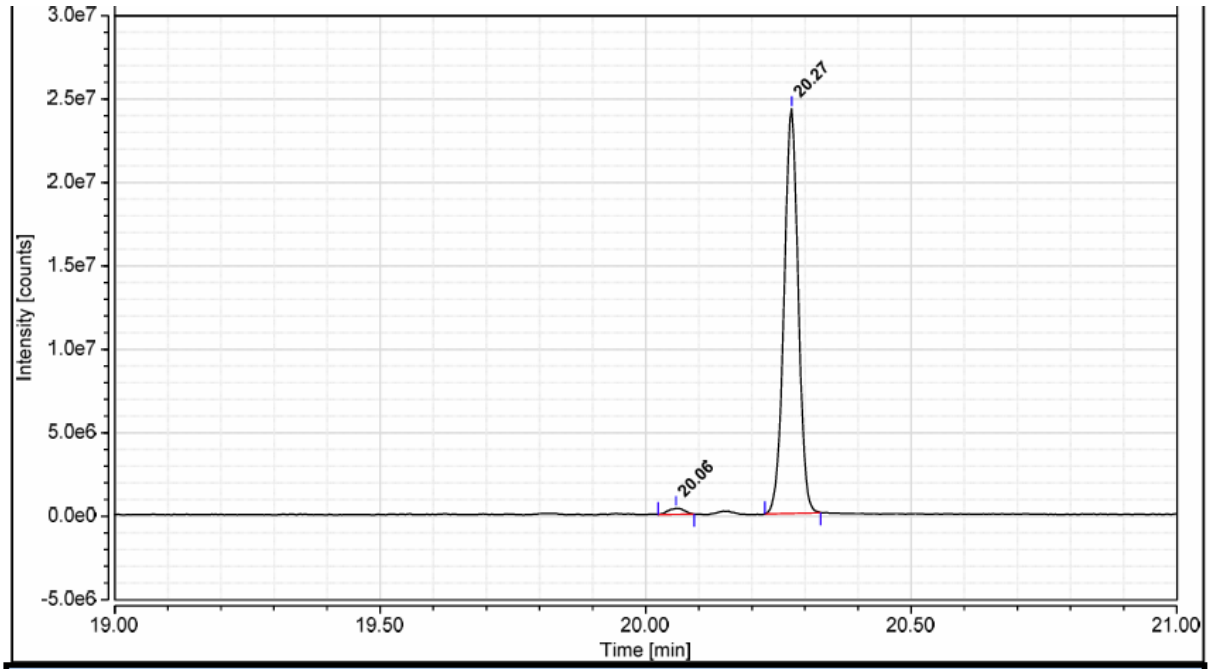
The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-((3*R*,4*R*,*E*)-2,3,7,11-tetramethyl-4-tosyldodeca-6,10-dien-3-yl)-1,3,2-dioxaborolane (**79**) (69 mg, 0.1 mmol), TBAF (1.0 M in THF, 0.4 mL, 0.4 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (100% hexane, stained in PMA solution) to afford single isomer of **85** (25 mg, 83%, *E/Z* 98:2). The *E/Z* configuration was assigned based on the NOESY-NMR results of **70**.

Appearance colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.16 – 5.07 (m, 3H), 2.68 (t, *J* = 7.05 Hz, 2H), 2.30 – 2.15 (m, 1H), 2.13 – 2.03 (m, 2H), 2.03 – 1.94 (m, 2H), 1.72 – 1.66 (m, 3H), 1.64 – 1.57 (m, 9H), 1.02 – 0.99 (m, 3H), 0.98 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.91 (C_q), 134.93 (C_q), 131.44 (C_q), 124.53 (CH), 123.63 (CH), 120.99 (CH), 39.86 (CH_2), 36.85 (CH), 26.93 (CH_2), 26.87 (CH_2), 25.85 (CH_3), 21.61 (2 x CH_3), 17.84 (CH_3), 16.20 (CH_3), 13.57 (CH_3); **FT-IR (cm^{-1}, neat)** 2959, 2922,

2856, 1453, 1377, 1097, 929, 886, 832, 727, 540, 427; **HRMS (EI)** m/z calculated for $C_{16}H_{28}$ $[M]^+$: 220.2185, found: 220.2186.

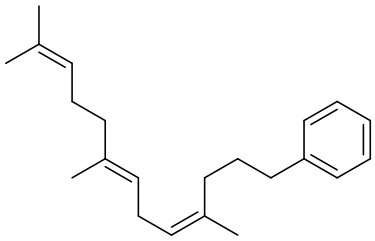
E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results			
No.	Retention Time min	Rel.Area %	Area counts*min
1	20.057	1.68	12860
2	20.275	98.32	750443

((4*Z*,7*E*)-4,8,12-trimethyltrideca-4,7,11-trien-1-yl)benzene (84)



Chemical Formula: $C_{22}H_{32}$
Molecular Weight: 296,50

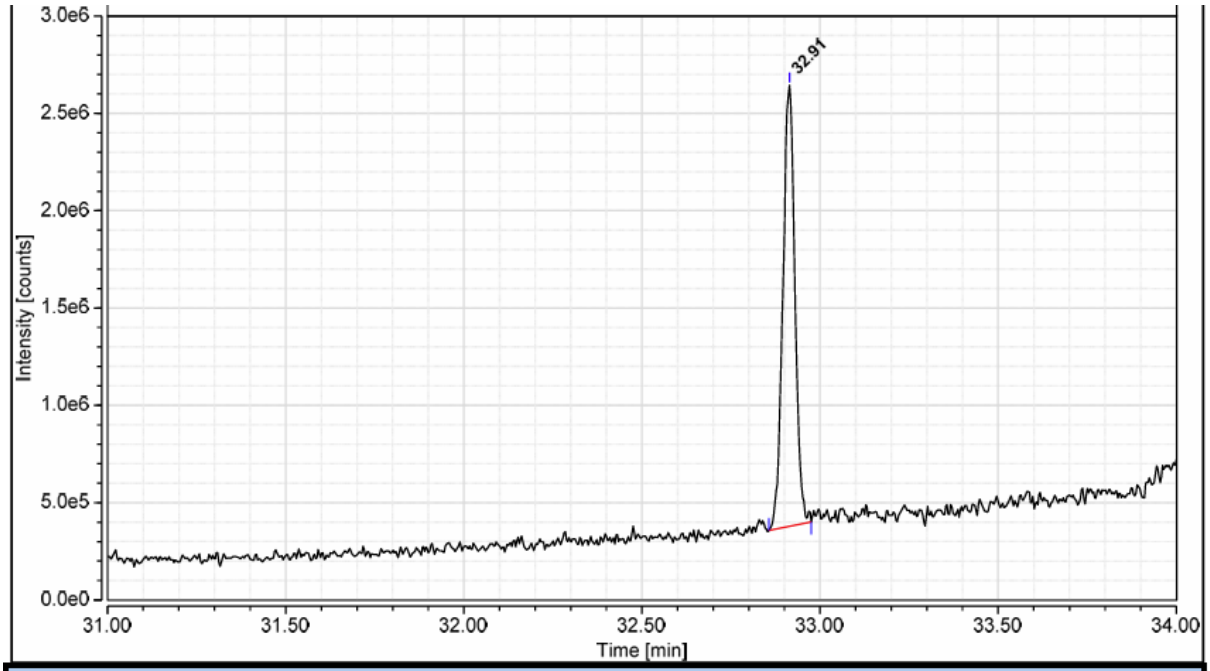
The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-((4*S*,5*R*,*E*)-4,8,12-trimethyl-1-phenyl-5-tosyltrideca-7,11-dien-4-yl)-1,3,2-dioxaborolane (**78)** (66 mg, 0.1 mmol), TBAF (1.0 M in THF, 0.4 mL, 0.4 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford single isomer of **84** (31 mg, 92%, *E/Z* 1:>99). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

Appearance colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.33 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 5.18 – 5.04 (m, 3H), 2.73 – 2.55 (m, 4H), 2.14 – 2.02 (m, 4H), 2.02 – 1.93 (m, 2H), 1.79 – 1.65 (m, 8H), 1.64 – 1.58 (m, 6H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.74 (C_q), 135.11 (C_q), 135.05 (C_q), 131.49 (C_q), 128.52 (2 x CH), 128.42 (2 x CH), 125.81 (CH), 124.49 (CH), 124.35 (CH), 123.39 (CH), 39.85 (CH_2), 36.00 (CH_2), 31.66 (CH_2),

29.91 (CH_2), 26.96 (CH_2), 26.88 (CH_2), 25.84 (CH_3), 23.51 (CH_3), 17.84 (CH_3), 16.21 (CH_3); **FT-IR (cm^{-1}, neat)** 3026, 2923, 2855, 1601, 1492, 1446, 1378, 1087, 1034, 932, 828, 741, 697, 563, 445; **HRMS (EI)** m/z calculated for $C_{22}H_{32}$ $[M]^+$: 296.2499, found: 296.2499.

E/Z ratio was determined by GC-MS analysis:

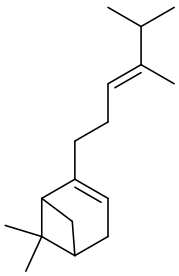
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	32.914	100.00	88836

(*E*)-2-(4,5-dimethylhex-3-en-1-yl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (89)



Chemical Formula: $C_{17}H_{28}$
Molecular Weight: 232,41

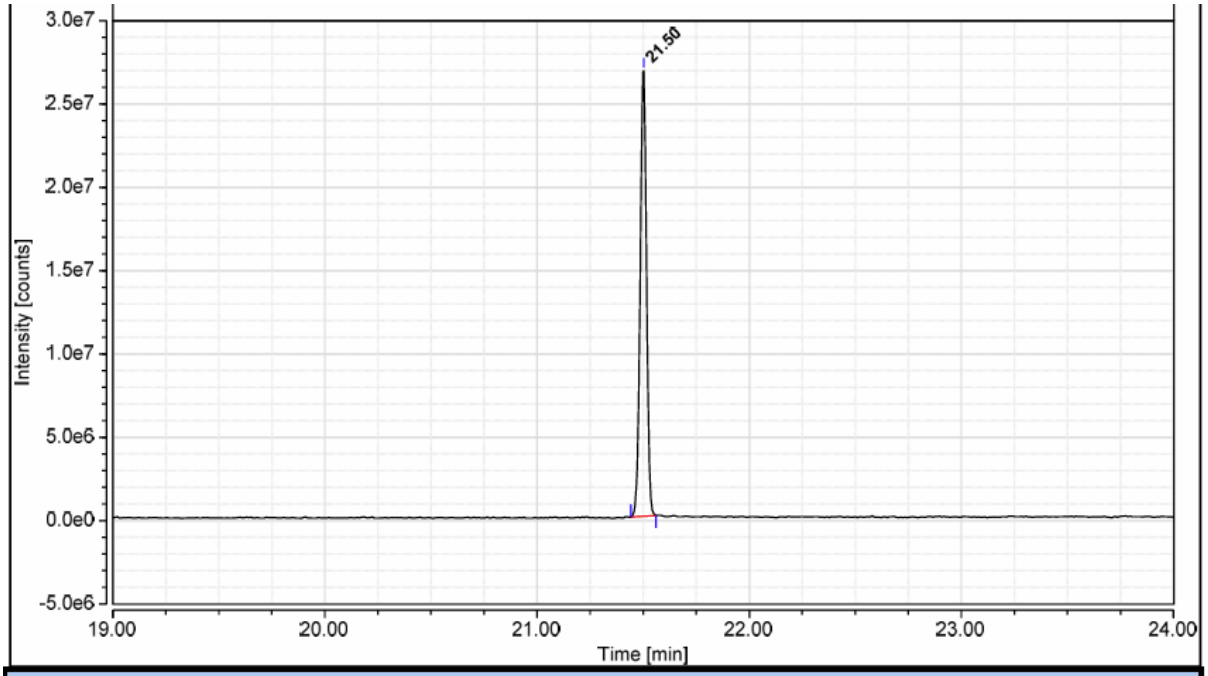
The reaction was performed according to **General Procedure E** with 2-((3*R*,4*R*)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**83**) (57 mg, 0.1 mmol), TBAF (1.0 M in THF, 0.3 mL, 0.3 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford one isomers of **89** (21 mg, 82%, *E/Z* >99:1). The *E/Z* configuration was assigned based on the NOESY-NMR results of **70**.

Appearance colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); $[\propto]_D^{25}$= -31.1° (c=1.6 g/100 mL $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.21 – 5.16 (m, 1H), 5.16 – 5.09 (m, 1H), 2.34 (dt, *J* = 8.41, 5.59 Hz, 1H), 2.30 – 2.12 (m, 3H), 2.11 – 1.91 (m, 6H), 1.56 (s, 3H), 1.27 (s, 3H), 1.14 (d, *J* = 8.46 Hz, 1H), 0.98 (s, 3H), 0.96 (s, 3H), 0.83 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ =

148.56, 140.81, 122.14, 115.91, 46.00, 41.05, 38.09, 37.22, 36.84, 31.81, 31.45, 29.87, 26.54, 25.83, 21.63 (2 x CH_3), 21.35, 13.56; **FT-IR (cm^{-1}, neat)** 2956, 2914, 2877, 2833, 1465, 1380, 1364, 1307, 1264, 1203, 1098, 1083, 1044, 957, 886, 848, 800, 787, 539, 428; **HRMS (EI)** m/z calculated for $C_{17}H_{28}$ $[M]^+$: 232.2190, found: 232.2186.

E/Z ratio was determined by GC-MS analysis:

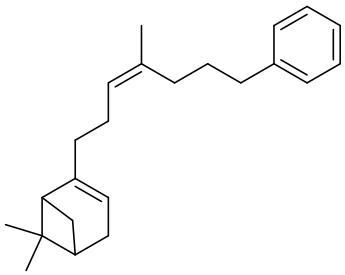
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	21.503	100.00	922201

6,6-dimethyl-2-(4-methyl-7-phenylhept-3-en-1-yl)bicyclo[3.1.1]hept-2-ene (88)



Chemical Formula: $C_{23}H_{32}$
Molecular Weight: 308,51

***Z*-88**:

The reaction was performed according to **General Procedure E** with 2-((3*R*,4*S*)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**82**) (45 mg, 0.1 mmol), TBAF (1.0 M in THF, 0.3 mL, 0.3 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford single isomer of ***Z*-88** (21 mg, 89%, *E/Z* 6:94). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

***Z*-88**: $[\propto]_D^{25}$= -21.3° (c=1.6 g/100 mL $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.32 – 7.25 (m, 2H), 7.23 – 7.14 (m, 3H), 5.22 – 5.11 (m, 2H), 2.67 – 2.58 (m, 2H), 2.46 – 1.91 (m, 10H), 1.70

– 1.67 (m, 3H), 1.51 – 1.20 (m, 2H), 1.27 (s, 3H), 1.15 (d, *J* = 8.44 Hz, 1H), 0.92 (t, *J* = 7.20 Hz, 1H), 0.83 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 148.45, 142.75, 134.98, 128.51 (2 x CH), 128.41 (2 x CH), 125.80, 125.59, 115.91, 45.96, 41.04, 38.10, 37.46, 35.94, 31.80, 31.62, 31.42, 29.87, 26.54, 25.86, 23.50, 21.35.

***E*-88**:

The reaction was performed according to **General Procedure E** with 2-((3*R*,4*R*)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**82**) (29 mg, 0.1 mmol), TBAF (1.0 M in THF, 0.3 mL, 0.3 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford single isomer of ***E*-88** (13 mg, 86%, *E/Z* >99:1). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

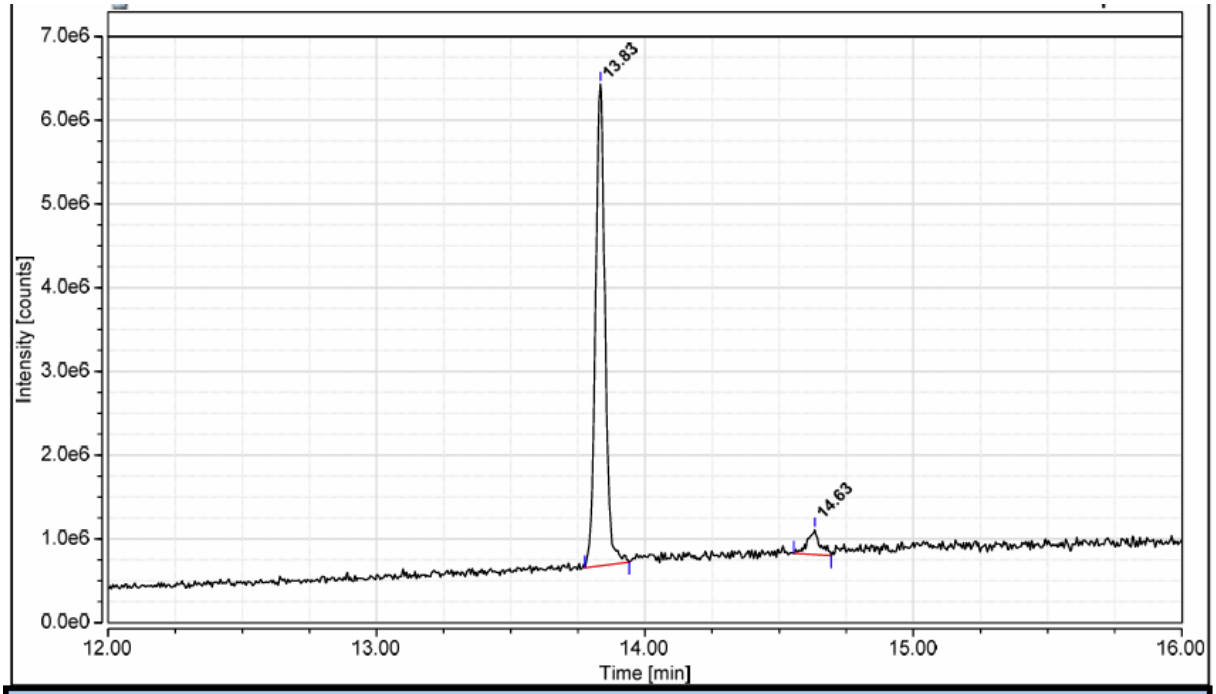
E*-88:* $[\propto]_D^{25}$= -16.5° (c=1.1 g/100 mL $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.32 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 5.22 – 5.17 (m, 1H), 5.17 – 5.10 (m, 1H), 2.61 – 2.54 (m, 2H), 2.35 (dt, *J* = 8.43, 5.58 Hz, 1H), 2.30 – 1.93 (m, 8H), 1.78 – 1.66 (m, 2H), 1.60 (d, *J* = 1.32 Hz, 3H), 1.40 – 1.20 (m, 1H), 1.27 (s, 3H), 1.15 (d, *J* = 8.45 Hz, 1H), 1.05 – 0.75 (m, 1H), 0.83 (s, 3H);**^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 148.47, 142.95, 134.69, 128.60 (2 x CH), 128.37 (2 x CH), 125.72, 125.00, 115.95, 45.98, 41.05, 39.36, 38.10, 37.23, 35.57, 31.80, 31.44, 29.80, 26.54, 25.99, 21.35, 16.07.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **FT-IR (cm^{-1}, neat)** 3026, 2917, 1601, 1492, 1449, 1371, 1263, 1211, 1087, 1034, 955, 882, 838, 792, 741, 696, 566, 485; **HRMS (EI)** m/z calculated for $C_{23}H_{32}$ $[M]^+$: 308.2497, found: 308.2499.

E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-220 °C with 30 °C/min; 220-250 °C with 4 °C/min; 250 °C for 3 min

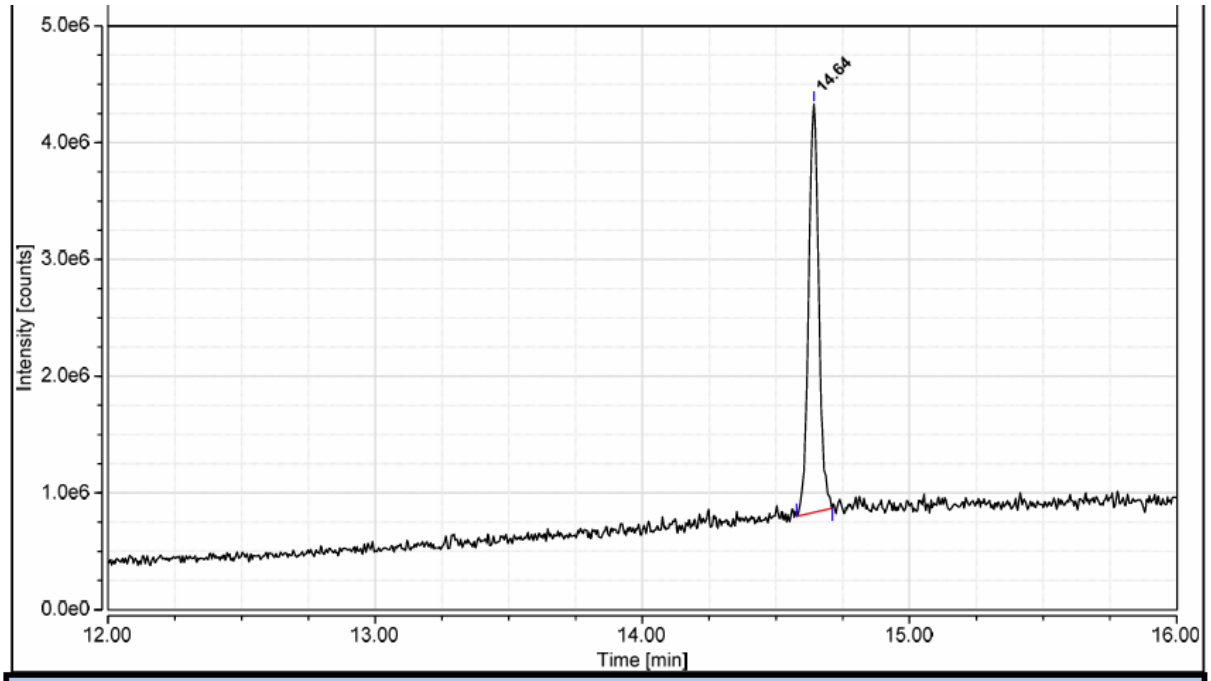
***Z*-88**:



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	13.833	93.66	237057
2	14.633	6.34	16041

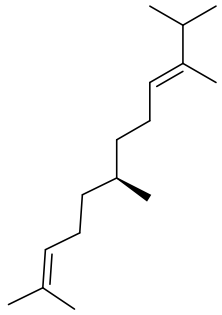
***E*-88**:



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	14.643	100.00	154395

(*S,E*)-2,6,10,11-tetramethyldodeca-2,9-diene (87)



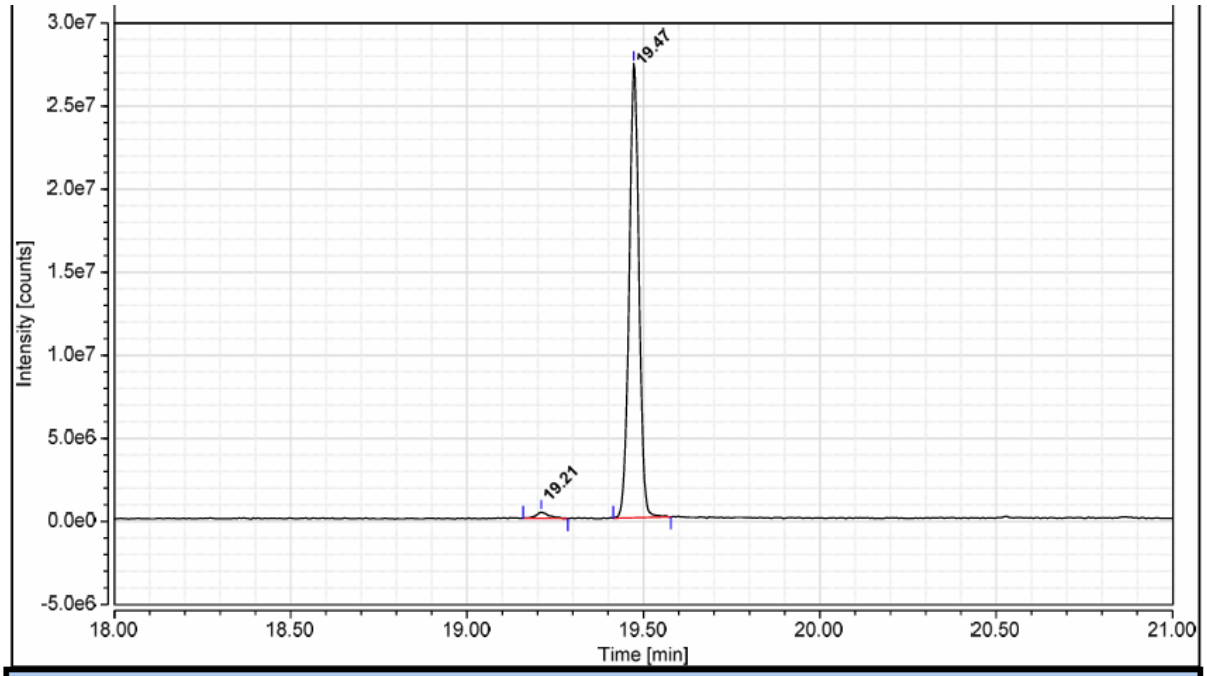
Chemical Formula: $C_{16}H_{30}$
Molecular Weight: 222,42

The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-((3*R*,4*R*,7*S*)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (**81**) (40 mg, 0.1 mmol), TBAF (1.0 M in THF, 0.3 mL, 0.3 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford single isomer of **87** (15 mg, 85%, *E/Z* 98:2). The *E/Z* configuration was assigned based on the NOESY-NMR results of **70**.

Appearance colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); $[\propto]_D^{25}$= +7.1° (c=0.8 g/100 mL $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.16 – 5.06 (m, 2H), 2.21 (p, *J* = 6.84 Hz, 1H), 2.08 – 1.86 (m, 3H), 1.68 (s, 3H), 1.61 (s, 3H), 1.56 (s, 3H), 1.48 – 1.07 (m, 6H), 0.98 (s, 3H), 0.97 (s, 3H), 0.88 (d, *J* = 6.39 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.66, 131.12, 125.22, 122.53, 37.21 (2 x), 36.88, 32.25, 25.88, 25.72, 25.41, 21.66 (2 x), 19.74, 17.78, 13.46; **FT-IR (cm^{-1}, neat)** 2958, 2917, 2859, 1662, 1455, 1377, 1308, 1240, 1085, 1049, 981, 937, 834, 740, 540, 443, 429, 417; **HRMS (EI)** m/z calculated for $C_{16}H_{30}$ $[M]^+$: 222.2346, found: 222.2342.

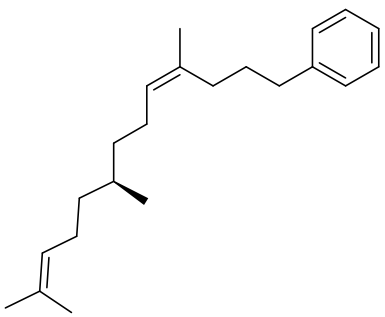
E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results			
No.	Retention Time min	Rel.Area %	Area counts*min
1	19.210	1.85	16585
2	19.472	98.15	881462

(*S*)-(4,8,12-trimethyltrideca-4,11-dien-1-yl)benzene (86)



Chemical Formula: $C_{22}H_{34}$
Molecular Weight: 298,51

***Z*-86**:

The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-((4*S*,5*R*,8*S*)-4,8,12-trimethyl-1-phenyl-5-tosyltridec-11-en-4-yl)-1,3,2-dioxaborolane (**80**) (35 mg, 0.1 mmol), TBAF (1.0 M in THF, 0.3 mL, 0.3 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford single isomer of ***Z*-86** (15 mg, 83%, *E/Z* 3:97). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

***Z*-86**: $[\propto]_D^{25}$= +1.4° (c=0.9 g/100 mL $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.33 – 7.24 (m, 2H), 7.23 – 7.15 (m, 3H), 5.18 – 5.07 (m, 2H), 2.66 – 2.56 (m, 2H), 2.13 – 1.84 (m, 6H), 1.77 – 1.64 (m, 2H), 1.69 (s, 6H), 1.61 (s, 3H), 1.48 – 1.24 (m, 3H), 1.21 – 1.05 (m, 2H), 0.86 (d, *J* = 6.42 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.77 (C_q), 134.78 (C_q), 131.13 (C_q), 128.51 (2 x CH), 128.40 (2 x CH), 126.08 (CH), 125.79 (CH), 125.20 (CH), 37.46 (CH_2), 37.19 (CH_2), 35.99 (CH_2), 32.30 (CH), 31.61 (CH_2), 29.97 (CH_2), 25.88 (CH_3), 25.72 (CH_2), 25.47 (CH_2), 23.51 (CH_3), 19.67 (CH_3), 17.79 (CH_3).

***E*-86**:

The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-((4*R*,5*R*,8*S*)-4,8,12-trimethyl-1-phenyl-5-tosyltridec-11-en-4-yl)-1,3,2-dioxaborolane (**80**) (26 mg, 0.1 mmol), TBAF (1.0 M in THF, 0.3 mL, 0.3 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford single isomer of ***E*-86** (11 mg, 82%, *E/Z* >99:1). The *E/Z* configuration was assigned based on the NOE-NMR results of **57**.

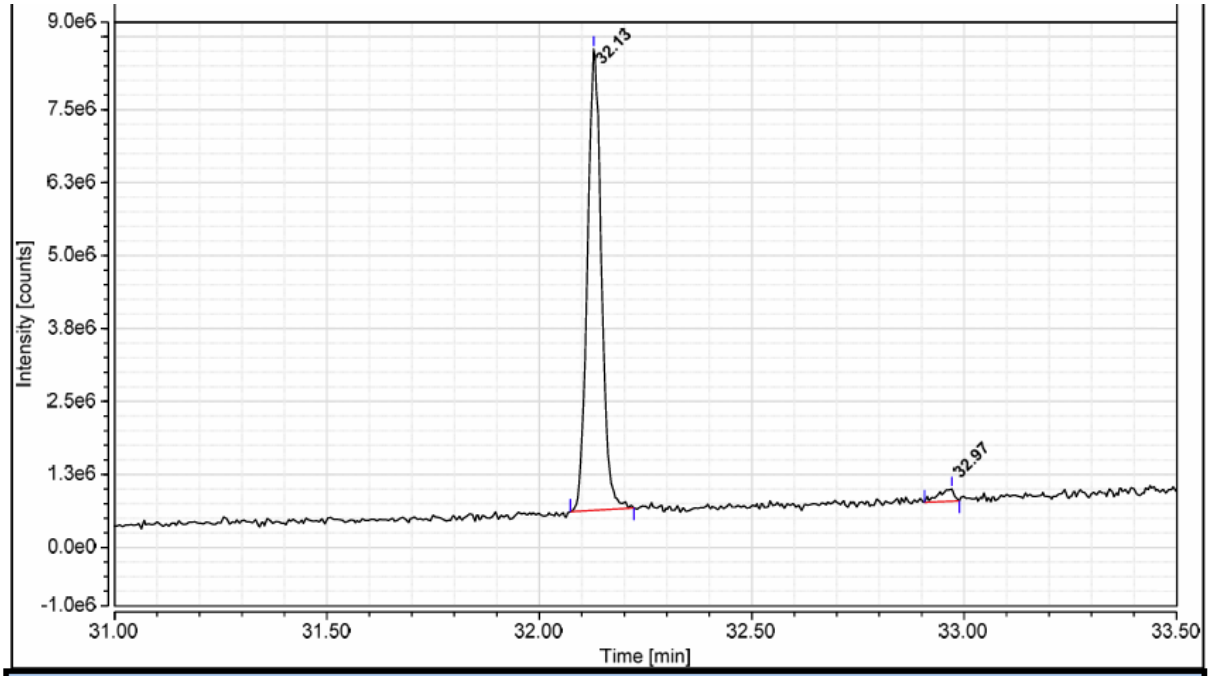
E*-86:* $[\propto]_D^{25}$= +2.7° (c=1.6 g/100 mL $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.33 – 7.24 (m, 2H), 7.24 – 7.13 (m, 3H), 5.18 – 5.06 (m, 2H), 2.62 – 2.53 (m, 2H), 2.12 – 1.86 (m, 5H), 1.79 – 1.65 (m, 2H), 1.68 (d, *J* = 1.38 Hz, 3H), 1.60 (d, *J* = 1.35 Hz, 6H), 1.50 – 1.28 (m, 2H), 1.22 – 1.07 (m, 2H), 0.88 (d, *J* = 6.44 Hz, 3H);**^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.94 (C_q), 134.51 (C_q), 131.14 (C_q), 128.59 (2 x CH), 128.37 (2 x CH), 125.73 (CH), 125.38 (CH), 125.19 (CH), 39.44 (CH_2), 37.20 (2 x CH_2), 35.65 (CH_2), 32.24 (CH), 29.90 (CH_2), 25.87 (CH_3), 25.72 (CH_2), 25.59 (CH_2), 19.68 (CH_3), 17.78 (CH_3), 16.01 (CH_3).

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **FT-IR (cm^{-1}, neat)** 3025, 2918, 2853, 1492, 1449, 1377, 1084, 1028, 982, 830, 741, 697, 567, 489, 445; **HRMS (EI)** m/z calculated for $C_{22}H_{34}$ $[M]^+$: 298.2659, found: 298.2655.

E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min

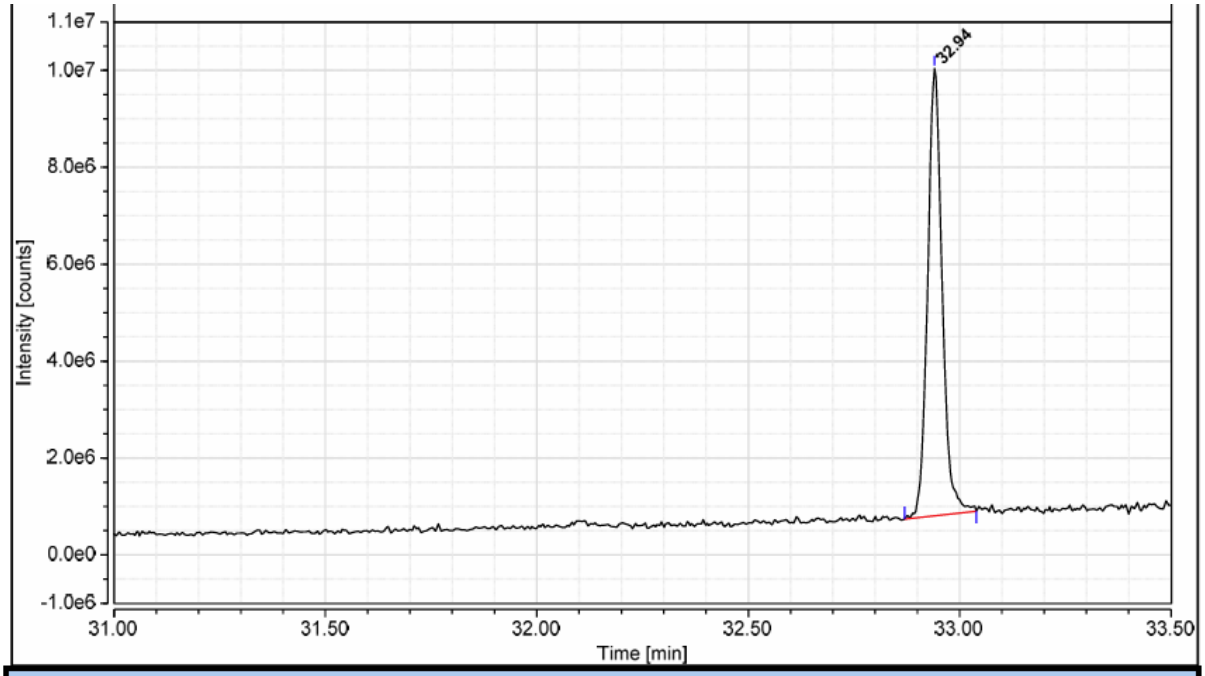
***Z*-86**:



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	32.128	97.05	301827
2	32.971	2.95	9172

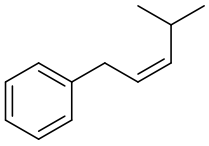
***E*-86**:



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	32.941	100.00	368957

(*Z*)-(4-methylpent-2-en-1-yl)benzene (60)



Chemical Formula: $C_{12}H_{16}$
Molecular Weight: 160,26

The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-((2*R*,3*R*)-4-methyl-1-phenyl-2-tosylpentan-3-yl)-1,3,2-dioxaborolane (**39**) (263 mg, 0.6 mmol), TBAF (1.0 M in THF, 1.8 mL, 1.8 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **60** (77 mg, 81%, *E*/*Z* 32:68).

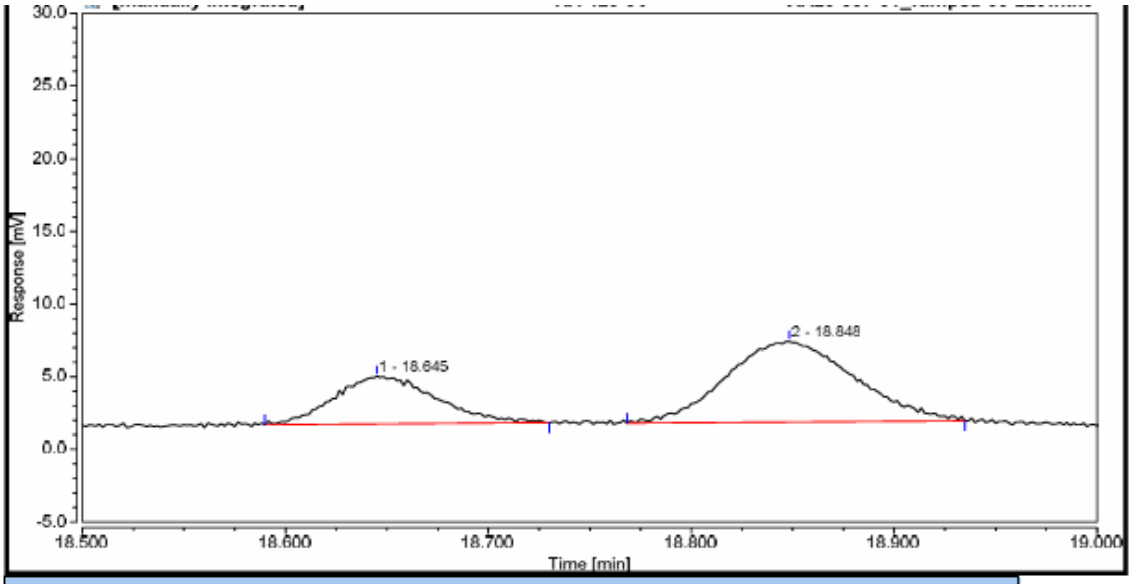
E-olefin (characteristic signals)*:* **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.35 (d, J = 5.1 Hz, 2H), 2.39 – 2.25 (m, 1H), 1.03 (s, 3H), 1.02 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 141.34 (C_q), 139.35 (CH), 128.61 (2 x CH), 128.46 (2 x CH), 125.98 (CH), 125.84 (CH), 39.14 (CH_2), 31.13 (CH), 22.71 (2 x CH_3).

Z-olefin: **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.34 – 7.29 (m, 2H), 7.25 – 7.19 (m, 3H), 5.58 – 5.32 (m, 2H), 3.45 (d, J = 7.2 Hz, 2H), 2.84 – 2.71 (m, 1H), 1.05 (s, 3H), 1.03 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 141.39 (C_q), 138.57 (CH), 128.54 (2 x CH), 128.47 (2 x CH), 125.96 (CH), 125.69 (CH), 33.75 (CH_2), 26.65 (CH), 23.33 (2 x CH_3).

Mix of olefins: **Appearance** yellowish liquid; **Rf** 1.0 (Et_2O/pentane=1:99); **FT-IR (cm^{-1}, neat)** 3061, 3027, 2957, 2925, 2868, 1657, 1602, 1494, 1456, 1362, 1304, 1169, 1101, 1073, 1030, 969, 821, 734, 695, 570; **HRMS (EI)** m/z calculated for $C_{12}H_{16}$ $[M]^+$: 160.1247, found: 160.1246.

E/Z ratio was determined by GC analysis:

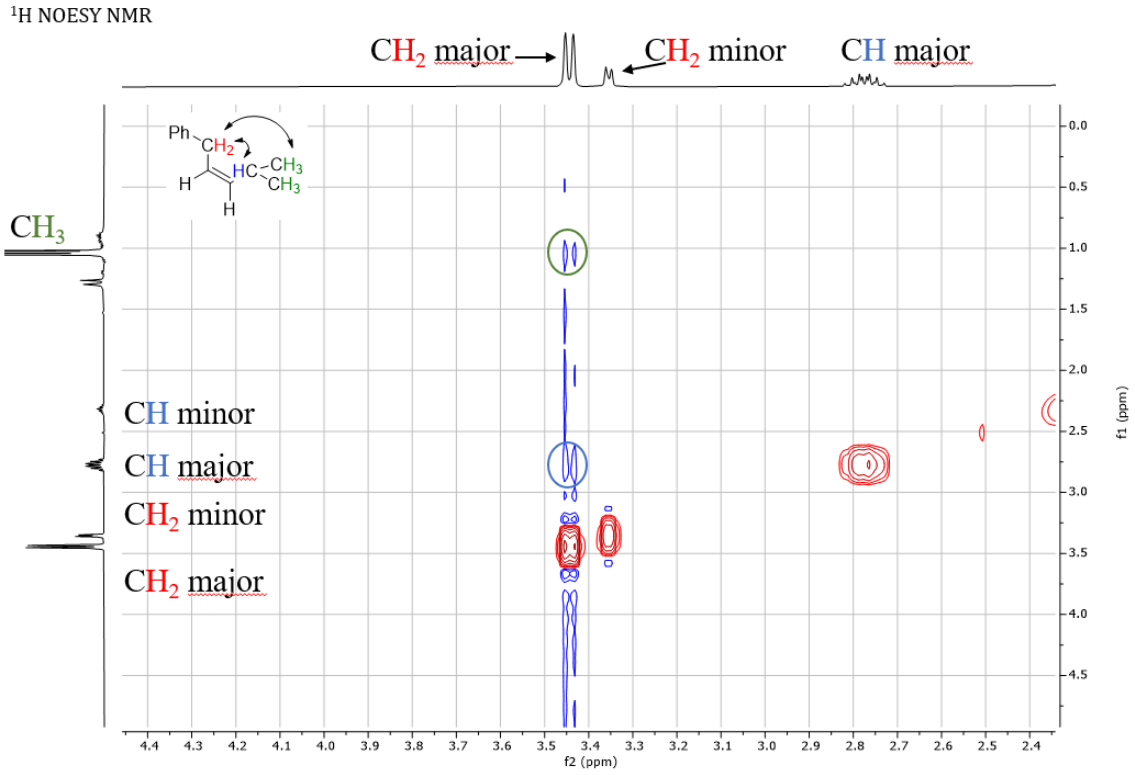
Temperature program: 50 °C for 1 min; 50-220 °C with 5 °C/min; 220 °C for 10 min



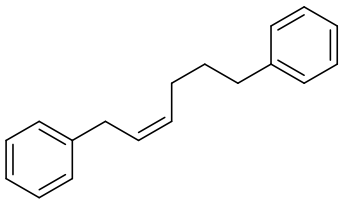
Integration Results

No.	Peak Name	Retention Time min	Area mV*min	Height mV	Relative Area %	Relative Height %
1		18.645	0.191	3.283	32.00	37.12
2		18.848	0.407	5.561	68.00	62.88
Total:			**0.598**	**8.844**	**100.00**	**100.00**

E/Z-determination was assigned via NOESY-NMR analysis: (The correlation signal between CH major and CH_3 major is present, but not visible in the following spectra due to the magnification!)



(*Z*)-hex-2-ene-1,6-diyldibenzene (59)



Chemical Formula: $C_{18}H_{20}$
Molecular Weight: 236,36

The reaction was performed according to **General Procedure E** with 2-((2*R*,3*R*)-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**38**) (183 mg, 0.4 mmol), TBAF (1.0 M in THF, 1.2 mL, 1.2 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **59** (>98%, *E/Z* 32:68). The compound is reported in the literature[88] and the *E/Z* assignment was made by comparison with the reported compound.

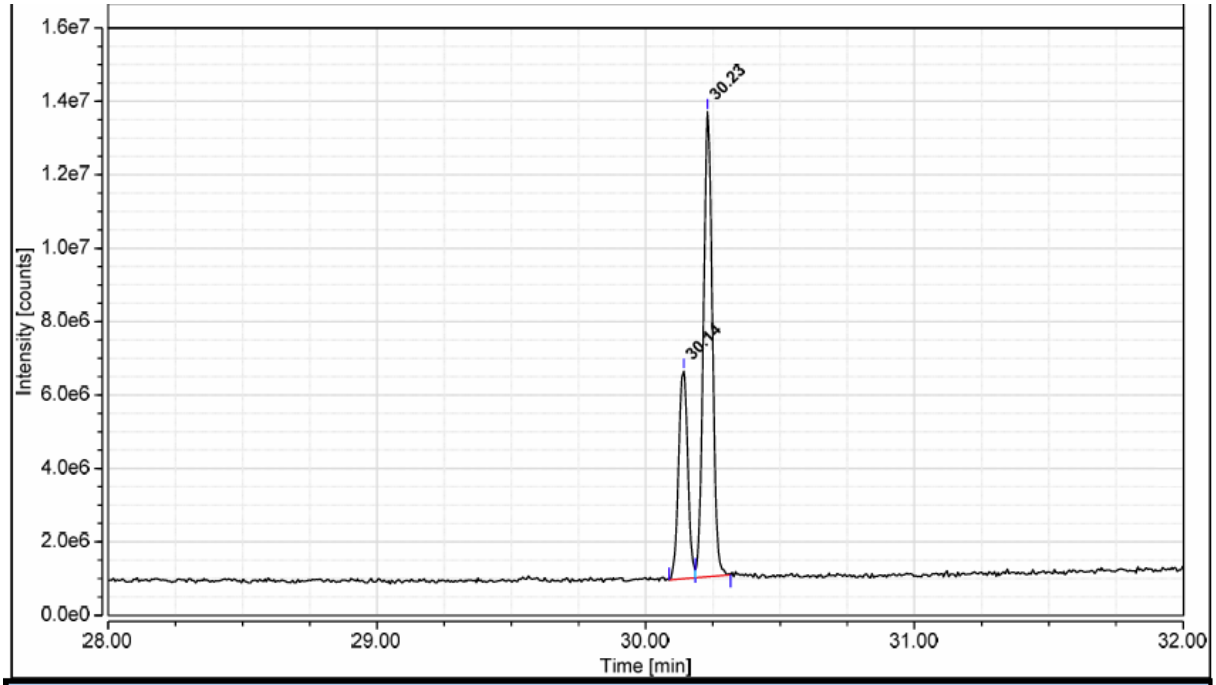
E-olefin (characteristic signals)*:* **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 3.34 (d, J = 5.6 Hz, 2H), 2.11 – 2.04 (m, 2H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 143.13 (C_q), 141.61 (C_q), 131.91 (CH), 129.81 (CH), 128.83 (4 x CH), 128.70 (2 x CH), 128.60 (2 x CH), 126.22 (CH), 125.99 (CH), 39.42 (CH_2), 35.74 (CH_2), 32.46 (CH_2), 31.76 (CH_2).

Z-olefin: **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 7.31 – 7.24 (m, 4H), 7.22 – 7.14 (m, 6H), 5.66 – 5.49 (m, 2H), 3.38 (d, J = 6.2 Hz, 2H), 2.71 – 2.57 (m, 2H), 2.26 – 2.16 (m, 2H), 1.79 – 1.64 (m, 2H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 143.03 (C_q), 141.75 (C_q), 130.76 (CH), 128.97 (CH), 128.83 (2 x CH), 128.76 (2 x CH), 128.72 (2 x CH), 128.64 (2 x CH), 126.18 (CH), 126.04 (CH), 35.87 (CH_2), 33.88 (CH_2), 31.91 (CH_2), 27.25 (CH_2).

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:9); **FT-IR (cm^{-1}, neat)** 3060, 3025, 2925, 2854, 2360, 1945, 1871, 1803, 1653, 1601, 1493, 1450, 1331, 1176, 1068, 1028, 966, 906, 825, 741, 694, 570; **HRMS (EI)** m/z calculated for $C_{18}H_{20}$ $[M]^+$: 236.1560, found: 236.1560.

E/Z ratio was determined by GC-MS analysis:

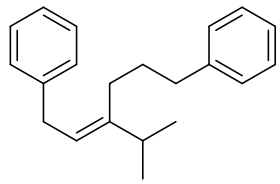
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	30.141	31.57	225733
2	30.230	68.43	489365

(*E*)-(3-isopropylhex-2-ene-1,6-diyl)dibenzene (74)



Chemical Formula: $C_{21}H_{26}$
Molecular Weight: 278,44

The reaction was performed according to **General Procedure E** with 2-((2*R*,3*R*)-3-isopropyl-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**56**) (101 mg, 0.2 mmol), TBAF (1.0 M in THF, 0.6 mL, 0.6 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **74** (47 mg, 94%, *E/Z* 94:6).

E-olefin: **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.31 – 7.25 (m, 4H), 7.22 – 7.14 (m, 6H), 5.35 (t, J = 7.2 Hz, 1H), 3.33 (d, J = 7.3 Hz, 2H), 2.65 (t, J = 7.7 Hz, 2H), 2.29 (hept, J = 6.8 Hz, 1H), 2.20 – 2.13 (m, 2H), 1.80 – 1.69 (m, 2H), 1.03 (s, 3H), 1.02 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 146.65 (C_q), 142.57 (C_q), 142.09 (C_q), 128.53 (2 x CH), 128.46 (4 x CH), 128.43 (2 x CH),

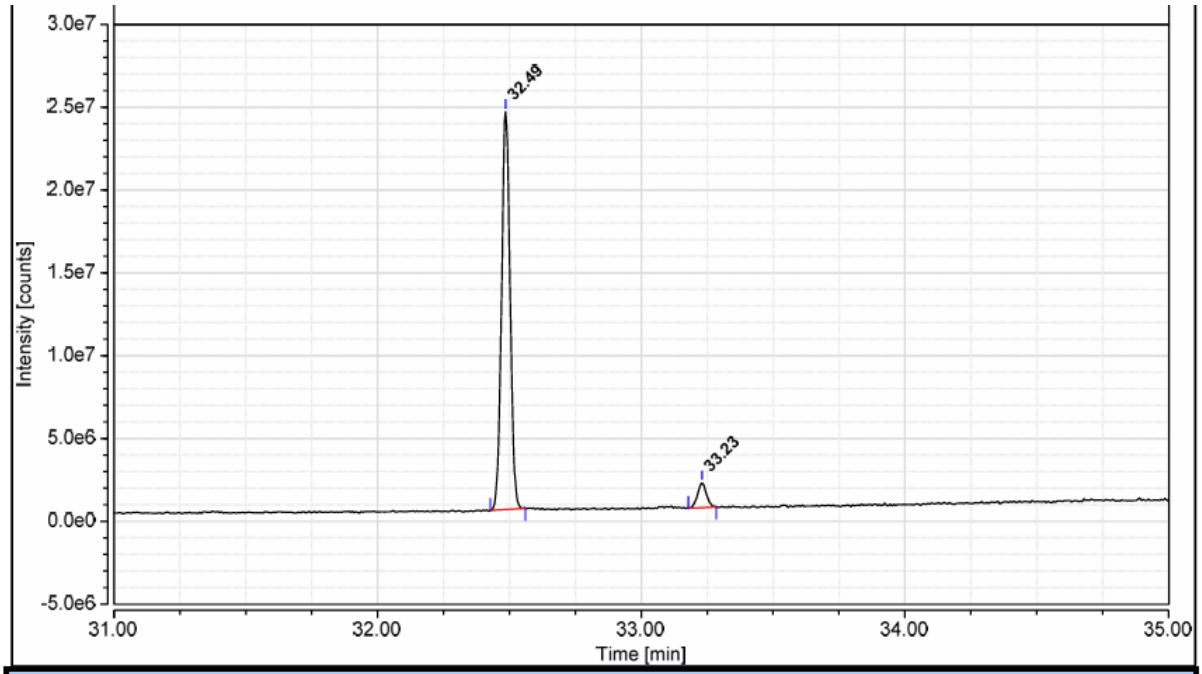
125.86 (CH), 125.83 (CH), 121.11 (CH), 36.45 (CH_2), 34.57 (CH), 33.97 (CH_2), 31.36 (CH_2), 29.51 (CH_2), 22.40 (2 x CH_3).

Z-olefin (characteristic signals) *:* **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 5.26 (t, J = 7.4 Hz, 1H), 3.42 (d, J = 7.3 Hz, 2H), 2.97 (hept, J = 7.1 Hz, 1H), 2.09 – 2.00 (m, 2H), 1.04 (s, 3H), 1.02 (s, 3H).**^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 145.13, 142.85, 128.40, 125.78, 121.81, 36.24, 33.67, 31.26, 31.02, 29.14, 21.37.

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:9); **FT-IR (cm^{-1}, neat)** 3060, 3026, 2955, 2864, 1943, 1867, 1801, 1741, 1655, 1601, 1493, 1454, 1379, 1359, 1261, 1178, 1074, 1028, 936, 903, 867, 800, 738, 695, 644, 567; **HRMS (EI)** m/z calculated for $C_{21}H_{26}$ $[M]^+$: 278.2029, found: 278.2033.

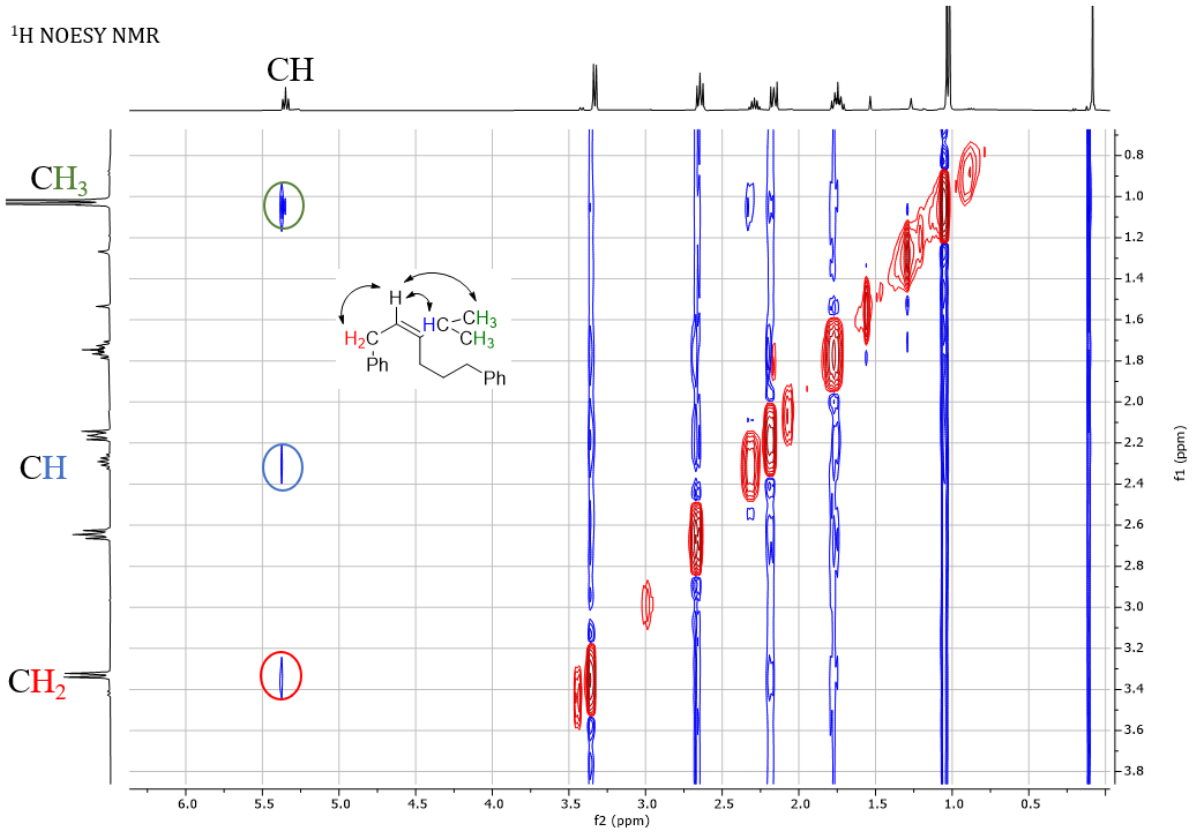
E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min

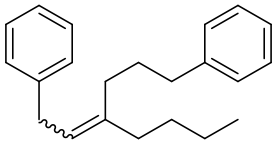


Integration Results			
No.	Retention Time min	Rel.Area %	Area counts*min
1	32.486	93.87	898812
2	33.230	6.13	58650

E/Z-determination was assigned via NOESY-NMR analysis:



(3-butylhex-2-ene-1,6-diyl)dibenzene (69)



Chemical Formula: $C_{22}H_{28}$
Molecular Weight: 292.47

The reaction was performed according to **General Procedure E** with 4,4,5,5-tetramethyl-2-((4*S*)-1-phenyl-4-(2-phenyl-1-tosylethyl)-octan-4-yl)-1,3,2-dioxaborolane (**50**) (131 mg, 0.2 mmol), TBAF (1.0 M in THF, 0.7 mL, 0.7 mmol) and THF (5 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford two inseparable isomers of **69** (54 mg, 81%, *E/Z* 55:45).

Minor olefin (characteristic signals)*:* **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.39 (d, J = 7.2 Hz, 2H), 2.65 – 2.57 (m, 2H), 0.92 (t, J = 7.1 Hz, 3H).

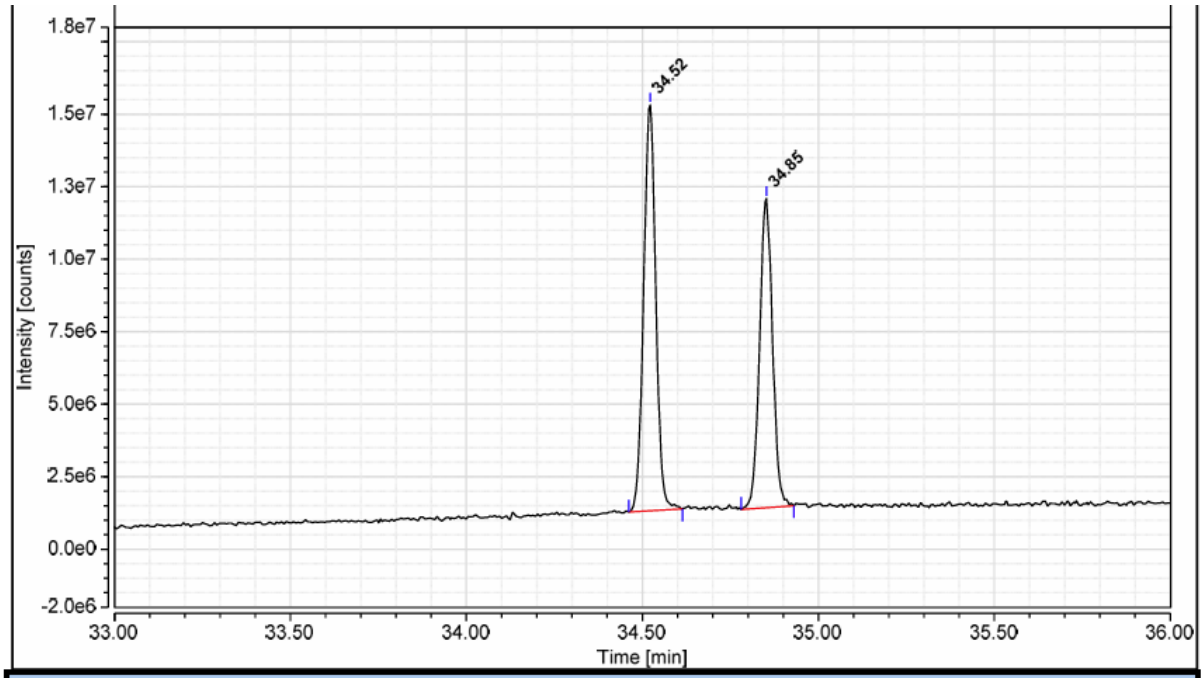
Major olefin: **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.32 – 7.25 (m, 4H), 7.22 – 7.15 (m, 6H), 5.38 – 5.32 (m, 1H), 3.34 (d, J = 7.2 Hz, 2H), 2.68 – 2.60 (m, 2H), 2.21 – 2.01 (m, 4H), 1.81 – 1.70 (m, 2H), 1.45 – 1.25 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H).

Mix of olefins: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:9); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 142.82, 142.62, 142.04, 142.02, 140.60, 140.53, 128.57, 128.53, 128.49, 128.47, 128.43, 128.40, 125.85, 125.83, 125.77, 123.50, 123.39, 36.76, 36.72, 36.18, 35.86, 34.14, 34.09, 30.91, 30.60, 30.36, 30.20, 30.06, 29.97, 23.05, 22.69, 14.21, 14.17. **FT-IR (cm^{-1}, neat)**

3060, 3026, 2926, 2857, 1941, 1867, 1800, 1714, 1658, 1602, 1493, 1452, 1378, 1156, 1074, 1028, 903, 737, 695, 571; **HRMS (EI)** m/z calculated for $C_{22}H_{28}$ $[M]^+$: 292.2186, found: 292.2191.

E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	34.522	55.18	561167
2	34.852	44.82	455870

1.4.6 NMR spectra

All measured NMR spectra are supplied in the appendix.

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Chapter 2

Modified Julia olefination with α-haloboronic esters

Draft in preparation

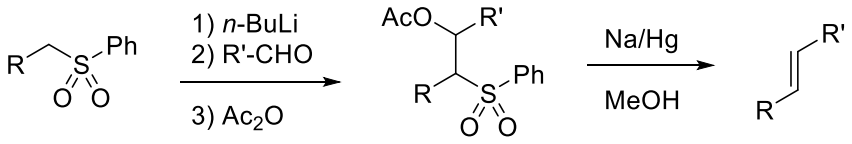
2. Olefination reactions with sulfones

2.1 Introduction

Alkenes, respectively, olefins have a carbon – carbon double bond and are among the most common compounds in chemistry. They can be found in natural products, in pharmaceutically relevant compounds, and in industrial products as substrates for raw materials, fine chemicals and polymer synthesis. The production of alkenes in an efficient, selective, and cost-effective manner has been a major challenge in organic synthesis.[1–3] The methods initially used were based on thermal elimination, but this had major disadvantages such as a lack of selectivity.[4] Since then, various methods based on different strategies have been developed to overcome these problems. Metal catalysed reactions such as cross-coupling reactions[2], olefin metathesis[5], semi hydrogenation of alkynes[6] or reactions starting from aldehydes or ketones, including also various name reactions such as the Wittig[7], Peterson[8], Horner-Wadsworth-Emmons[3,9], Tebbe[3], or Julia olefination[10] to name a few. The latter method, Julia olefination, is a powerful method that can be used to selectively produce *E* or *Z* olefins, depending on the protocol used.[10] As the method investigated in this chapter is related to Julia olefination, it is discussed in more detail below.

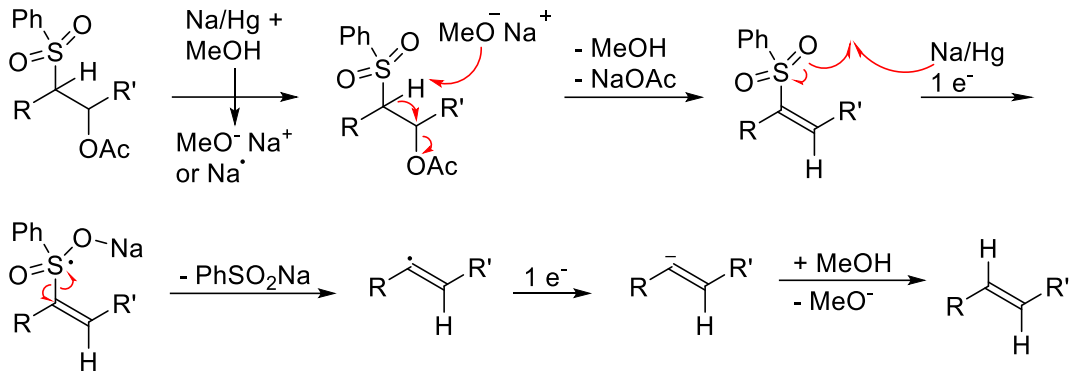
2.1.1 Julia-Lythgoe olefination

In 1973, Marc Julia discovered a multistep synthesis to form olefins, later known as the Julia-Lythgoe olefination (**Scheme 2-1**).[11]



Scheme 2-1 Original method for the Julia olefination.[12]

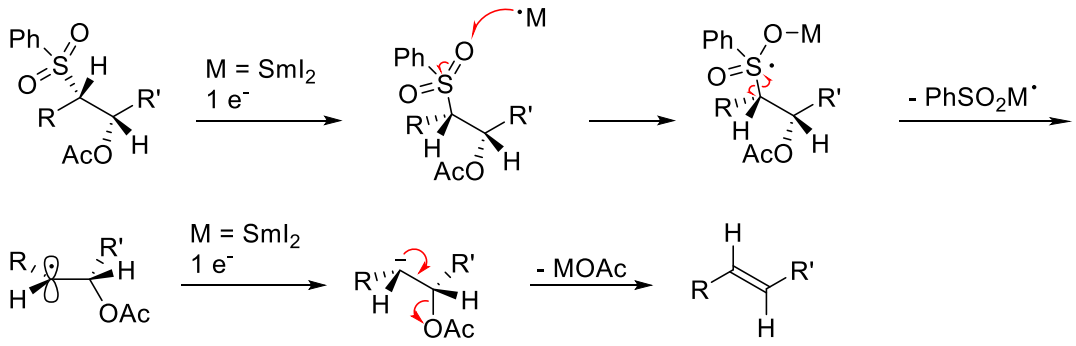
In this approach, the sulfone is first deprotonated and reacted then with an aldehyde. The resulting alcoholate reacts further with acetic anhydride to form the stable β-acetoxy sulfone as a mixture of diastereomers. Treatment of this intermediate with sodium/mercury amalgam affords the desired alkene with a good stereocontrol in favour of the *E* isomer.[12] The reaction mechanism is proposed to proceed as described in **Scheme 2-2**.[12]



Scheme 2-2 Proposed reaction mechanism for the reductive elimination when Na/Hg is used.[12]

First, sodium methoxide is produced, which can remove a proton atom and eliminate an acetoxy group. Then, the vinyl phenyl sulfone is reduced to obtain the vinyl radical, which is later further reduced to the vinyl anion. The vinyl anion is protonated by the solvent to give the resulting olefin. Deuteration experiments with deuterated methanol have supported the assumption that the proton originates from the solvent. Since the vinyl radical can isomerise and thus the more stable radical can be formed, a possible explanation for the formation of the more stable *E*-olefin was also found.[12]

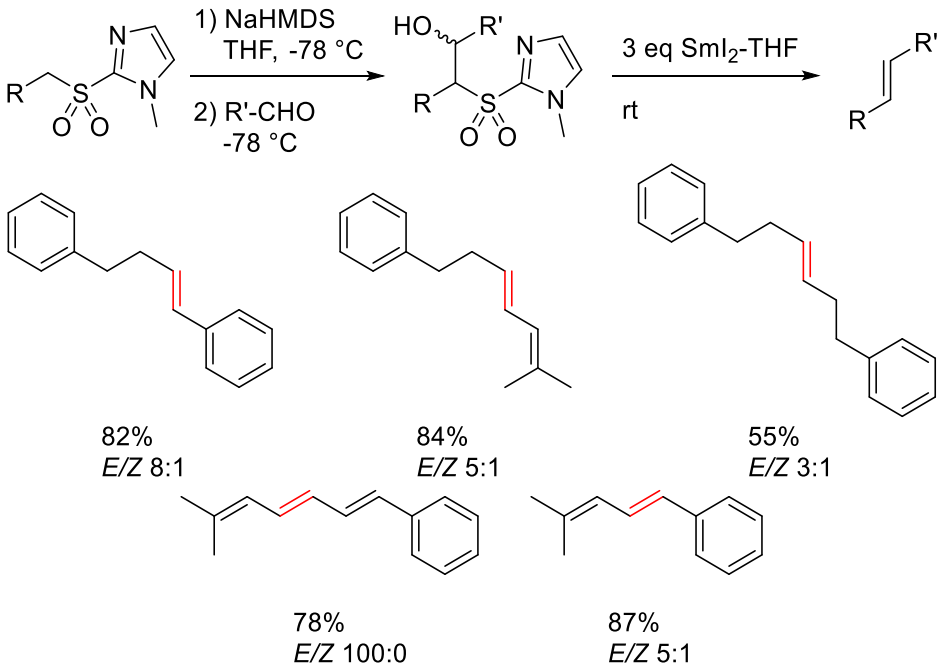
Since the reductive elimination with Na/Hg is a relatively harsh process not suitable for sensitive substrates, a milder reductive elimination method was developed.[12] With samarium iodide a better and especially milder reducing agent was discovered and used roughly at the same time by the groups of Keck[12], Markó[13] and Fukumoto[14]. While the protocols of Fukumoto[14] and Markó[13] used a combination of samarium iodide and hexamethylphosphoramide (HMPA) as an additive to obtain olefins with *E*-selectivity, the protocol of Keck[12] showed improvements when *N,N'*-dimethylpropylene urea (DMPU) was used as an additive instead of HMPA. With DMPU, good yields were obtained and especially the reaction time could be reduced from five days to 35 minutes, compared to the reaction without additive. HMPA let also to shorter reaction times (10 minutes) but lacked in selectivity giving *E/Z* ratios of roughly 1:1. In addition, Keck proposed the reaction mechanism depicted in **Scheme 2-3**.[12]



Scheme 2-3 Proposed reaction mechanism for the reductive elimination with SmI_2.[12]

According to this mechanism, first the benzenesulfonyl moiety is released giving a radical. Then, the radical is reduced to the anion and subsequently the acetyl group is eliminated to form the olefin. Since in the first step diastereomers are formed and both are used for the reductive elimination, both give according to this mechanism the same radical. Like in the first proposed mechanism, selectivity of the olefin is achieved due to isomerization of the radical to the most stable configuration. Deuteration experiments were also carried out, but here no deuterium incorporation was possible, leading to the assumption that the protons originate from the starting sulfone, thus strengthening the mechanism for samarium iodides, which is different from the one for sodium-mercury amalgam.[12]

Another important change on the protocol of the Julia olefination was made in 1990 by Kende (**Scheme 2-4**).[15]



Scheme 2-4 Optimized protocol for Julia olefination by Kende.[15]

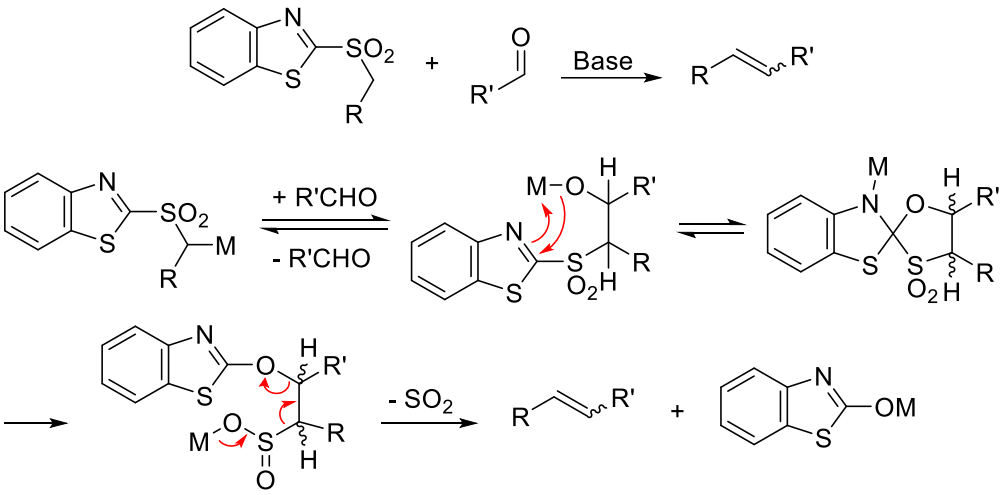
Kende altered the moiety attached to the sulfone from phenyl to methyl imidazole. This small but effective change simplified the protocol by one step, avoiding the functionalisation of the alcohol and allowing the beta-hydroxyl sulfone to be used directly for the reductive elimination step. With this modification, Kende obtained olefins with a yield of 55-87 % and an *E/Z* ratio of up to 8:1.[15]

2.1.2 Modified Julia olefination / Julia-Kocienski olefination

To date, many modifications have been made to the protocol and since the optimisation of Sylvestre A. Julia in 1991[16], the reaction is also known as the modified Julia olefination. Later, after the input of Philip Kocienski[17], this reaction became the Julia-Kocienski olefination.[18] The modification of S. Julia will be discussed first, followed by the modification of P. Kocienski, and by other relevant modifications such as the effect of changing the sulfonyl residue or preparing new products such as methylenation, functionalized enol ethers or alkenyl halides. Finally, the preparation of alkenes from alcohols instead of aldehydes or ketones using the modified Julia olefination is described.

Modifications by S. Julia

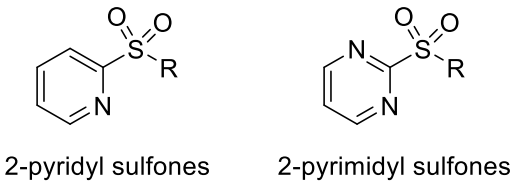
In 1991, Julia presented a modified protocol for the Julia olefination (**Scheme 2-5**).[16,17]



Scheme 2-5 Modified Julia olefination by S. Julia.[17]

By changing the moiety attached to the sulfone to a benzothiazol-2-yl sulfone (BT), a one-pot protocol was established to obtain the olefin. In the first step the BT-sulfone is treated with a base, eg LDA, which results in a metalated intermediate. This intermediate reacts with the aldehyde and undergoes a Smiles rearrangement, where it initially forms a spirocyclic intermediate which, after opening this spirocycle and releasing sulfur dioxide, reacts further to form the desired olefin.[16,17] Julia reported that in addition to the desired olefin, self-condensation products were obtained to an extent depending on the aldehyde or ketone used. By using allyl- or benzyl-BT sulfones or Barbier-conditions, the self-condensation could be reduced and more of the desired olefins were obtained.[16] The stereoselectivity of the olefin obtained by this method is strongly depending on the reaction conditions. A study by Kocienski in 1998[17] showed that when using BT sulfones, varying the solvent and counterion of the base led to different results in terms of yield and *E/Z* ratio. Depending on the choice, the *E*- or the

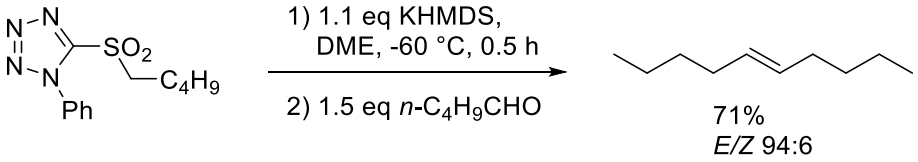
Z-olefin could be favoured, but only in special cases a high selectivity was achieved.[17] In 1993, Julia modified the method further and showed that the reaction can be run as well with 2-pyridiyl or 2-pyrimidyl sulfones (**Scheme 2-6**).[17–20] However, the reaction did not show a significant increase in selectivity.[17]



Scheme 2-6 Further modifications of heterocyclic-sulfones by Julia.[17–20]

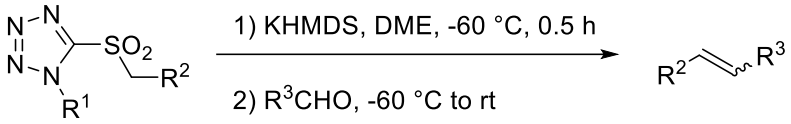
Modifications by P. Kocienski.

In 1998, Kocienski published an optimized method of Julia olefination and a study comparing 1-phenyl-1*H*-tetrazol-5-yl sulfones (PT) with BT-sulfones (**Scheme 2-7**).[17]



Scheme 2-7 Optimized method for Julia olefination by Kocienski using 1-phenyl-1*H*-tetrazol-5-yl sulfones.[17]

In this study, BT- and PT-sulfones were tested with four different aldehydes under specified conditions. The influence of the solvent (toluene, Et_2O, THF, DME) and the counterion of the base (K, Na, Li) on the reaction were investigated. With potassium as the counterion and DME as the solvent, for all aldehydes the best stereoselectivity was obtained when PT-sulfones were used. Compared to the BT sulfones, not only higher yields and *E*-selectivity were achieved with the PT-sulfones, but self-condensation was also lower, which was attributed to the higher steric hindrance of the PT-sulfones.[17] A year later, Kocienski published an extension of this protocol (**Scheme 2-8**).[21]

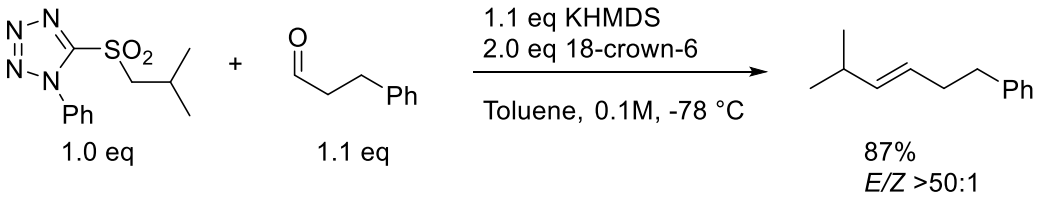


Entry	R^1	R^2	R^3	Yield	*E/Z*
1	Ph	*n*-C_4H_9	*c*-C_5H_{11}	75%	99:1
2		*n*-C_4H_9	Ph	48%	>99:1
3		Ph	*n*-C_9H_{19}	70%	29:71
4		$H_2C{=}CH_2$	*n*-C_9H_{19}	39%	67:33
5	*t*-Bu	*n*-C_4H_9	*c*-C_5H_{11}	88%	89:11
6		*n*-C_4H_9	Ph	80%	79:21
7		Ph	*n*-C_9H_{19}	95%	<1:99
8		$H_2C{=}CH_2$	*n*-C_9H_{19}	60%	4:96

Scheme 2-8 Comparison of 1-*tert*-Butyl-1*H*-tetrazol-5-yl sulfones with 1-Phenyl-1*H*-tetrazol-5-yl sulfones.[21]

By changing R^1 from phenyl to *tert*-butyl, Kocienski could increase the stability of the sulfone, which let to different results. Having an alkyl residue on the 1-*tert*-Butyl-1*H*-tetrazol-5-yl sulfones gave higher yields, but lower *E*-selectivity as when the phenyl analogue was used. For stabilised residues like phenyl or alkenyl, not only higher yields were obtained with 1-*tert*-Butyl-1*H*-tetrazol-5-yl sulfones, also high *Z*-selectivity was achieved.[21]

In 2011, Pospíšil developed a new protocol that increases *E*-selectivity with the help of chelating agents (**Scheme 2-9**).[22]

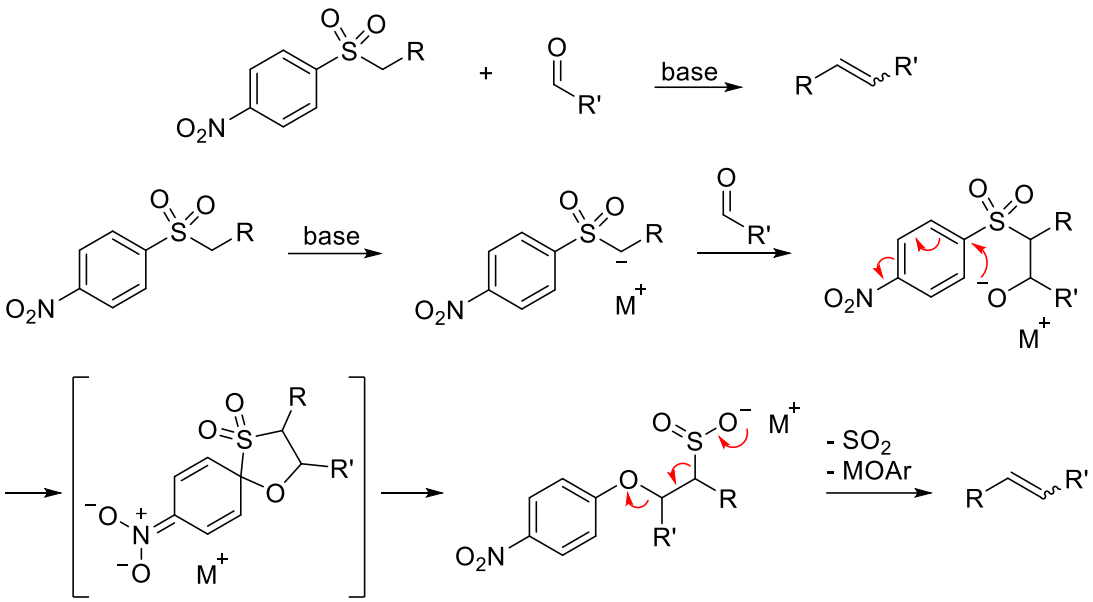


Scheme 2-9 Pospíšil's Julia-Olefination protocol for enhanced *E*-selectivity.[22]

In most cases, the stereoselectivity of Julia olefination has increased *E*-selectivity or, as shown by Kocienski[21], can also favour Z-selectivity under selected conditions. Since no clear trend for the stereoselectivity of Julia olefinations is available, Pospíšil wanted to solve this with the help of chelating agents. These should act like the solvent or the counterion of the base and thus decisively influence the stereoselectivity of the olefin. Pospíšil's work showed that in the case of LiHMDS as the base, DMPU or HMPA have a positive impact and can enrich the *E*-stereoselectivity. The best results were achieved with crown ethers such as the 18-crown-6, which allows an *E/Z* ratio of >50:1 as shown in **Scheme 2-9**. However, attempts to develop a generalised procedure failed and no clear trend has yet been identified.[22]

Modification of sulfonyl residues

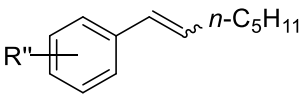
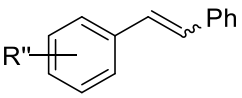
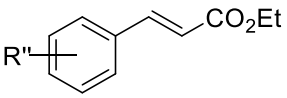
Over time, further promising adjustments were made to the moiety attached to the sulfone. In 2006, Zhu presented a new protocol with 4-nitrophenyl sulfones (**Scheme 2-10**).[23]



Scheme 2-10 Modified Julia olefination with 4-nitrophenyl sulfones.[23]

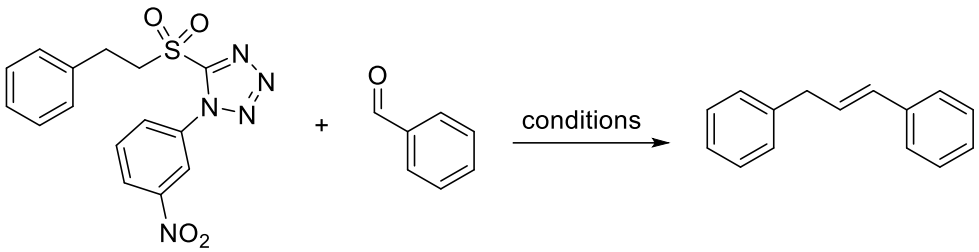
With this protocol, the 4-nitrophenyl sulfone is first deprotonated using a base. After addition to the aldehyde, a spirocycle is formed, which then undergoes a Smiles rearrangement. Then, sulfur dioxide is eliminated and the desired olefin formed.[23] Zhu presented a mild version of the Julia olefination, as in addition to the typical conditions such as KHMDS, crown ether and low temperature, the reaction can now also be run at room temperature and with sodium hydride as a base. The disadvantage of this method when using sodium hydride was the limitation to aromatic aldehydes. Aliphatic aldehydes were tested, as well as aromatic ketones, but neither gave the desired olefin and instead only self-condensation products were obtained.[23]

Table 2-1 Selected results from Zhu with 4-nitrophenyl sulfones.[23]

R''			
4-Cl	68% *E*/*Z* 80:20	78% *E*/*Z* 54:46	50% *E*/*Z* >99:1
4-Br	81% *E*/*Z* 82:18	47% *E*/*Z* 56:44	49% *E*/*Z* >99:1
4-NO_2	64% *E*/*Z* 75:25	97% *E*/*Z* 70:30	41% *E*/*Z* >99:1
4-OMe	78% *E*/*Z* 81:19	78% *E*/*Z* 53:47	40% *E*/*Z* >99:1

With sodium hydride as a base, Zhu presented 26 examples of olefins with yields of 43-97% and an *E/Z* ratio of up to >99:1 (selected examples shown in column 1 and 2, **Table 2-1**). Beside unstabilized (R = aliphatic) and semi-stabilized (R = phenyl) 4-nitrophenyl sulfones, Zhu also used fully-stabilized (R=CO_2Et) 4-nitrophenyl sulfone substrates for the Julia-olefination. For fully-stabilized 4-nitrophenyl sulfones a weaker base (Cs_2CO_3) was used for deprotonation and sometimes higher reaction temperatures (entry 1 and 4, column 3, **Table 2-1**). This led to moderate yields, but fortunately to a high *E*-stereoselectivity.[23]

In 2009, Kan implemented the nitrophenyl group onto tetrazoles and published a modified method for Julia-Kocienski olefination (**Scheme 2-11**).[24]

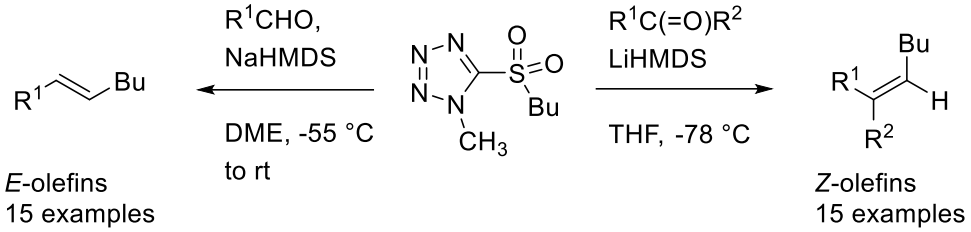


Entry	Conditions	Yield	*E/Z*
1	LiHMDS, THF, -78 °C	76%	23:1
2	Cs_2CO_3, MeCN, 0 °C	41%	9:1
3	DBU, MeCN, 0 °C	50%	10:1
4	DBU, LiCl, MeCN, 0 °C	86%	7:1
5	DBU, NaI, MeCN, 0 °C	77%	27:1

Scheme 2-11 Modified Julia-Kocienski olefination with meta-nitrophenyl tetrazole sulfones by Kan.[24]

With all applied conditions *E*-stereoselectivity was achieved. Beside the classical approach to deprotonate with a metal-HMDS base, with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) Kan found another suitable and well working base which in combination with LiCl or NaI gave even higher yields or *E*-stereoselectivity. More importantly, with DBU-conditions a mild method was found which has a wide functional group tolerance. Kan also used these conditions on an example involving alcohols protected as silyl ethers and achieved higher yields than when using LiHMDS.[24]

Another notable modification of the tetrazole unit was introduced by Ando in 2019[25] by using 1-methyl-1*H*-tetrazol-5-yl sulfones with aldehydes and later in 2020[26] with ketones (**Scheme 2-12**).



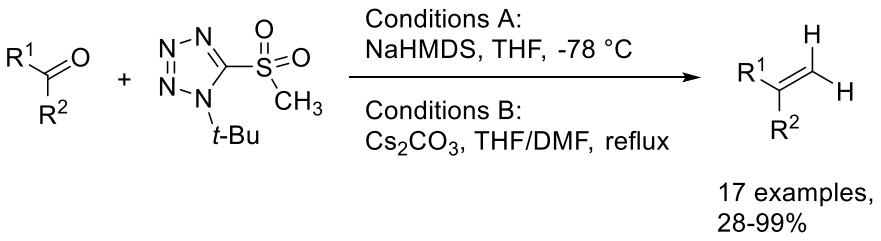
Scheme 2-12 Ando's modified protocols for the Julia-Kocienski olefination on aldehydes[25] and ketones[26].

In the experiments with the aldehydes, Ando compared the 1-methyl-1*H*-tetrazol-5-yl sulfones (MT) with the phenyl (PT) and *tert*-butyl analogues (TBT). Higher yields and equally good stereoselectivity were achieved with MT sulfones as with PT or TBT sulfones. Also different metal-HMDS bases were tested, showing that the stereoselective outcome of the olefin from MT sulfones are less influenced by the counterion of the base.[25]

For the experiments with the ketones, seven different moieties attached to the tetrazole were investigated. With the optimized conditions, the 1-methyl-1*H*-tetrazol-5-yl sulfones were used for a scope with ketones that gave trisubstituted olefins with mostly *Z*-stereoselectivity.[26]

Methylenation

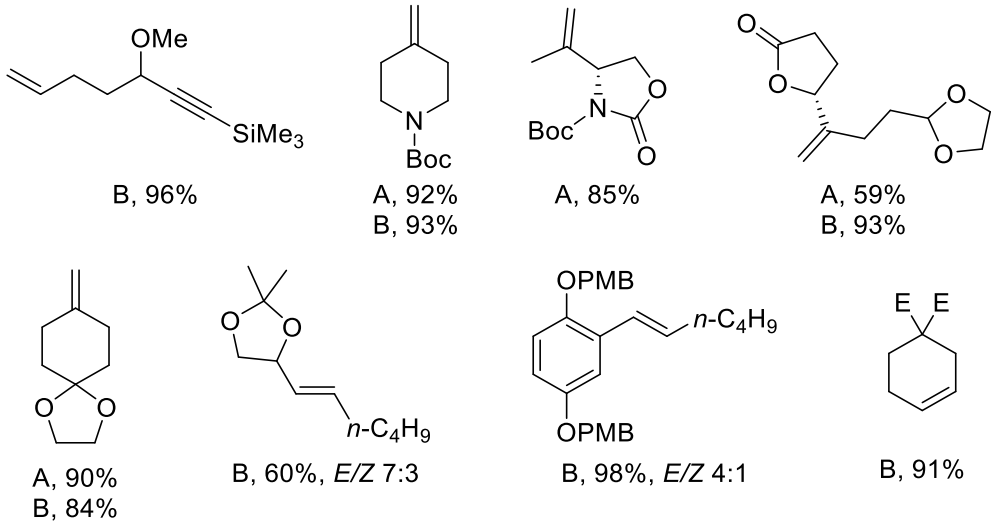
In 2005, Aïssa published improved Julia-Kocienski conditions for the methylenation of aldehydes and ketones (**Scheme 2-13**).[27]



Scheme 2-13 Methylenation of aldehydes and ketones by the protocols of Aïssa.[27]

Aïssa developed two different conditions for the methylenation of aldehydes and ketones. With conditions A the deprotonation was made by NaHMDS in THF and at low temperatures. In contrast with conditions B, Cs_2CO_3 was used in a solvent mixture of THF and DMF at reflux temperature. With those conditions Aïssa was able to prepare 17 terminal olefins in moderate to high yields. Conditions B were also applied to prepare 1,2-disubstituted olefins giving good yields with *E*-stereoselectivity. Interestingly, intramolecular olefinations could also be achieved

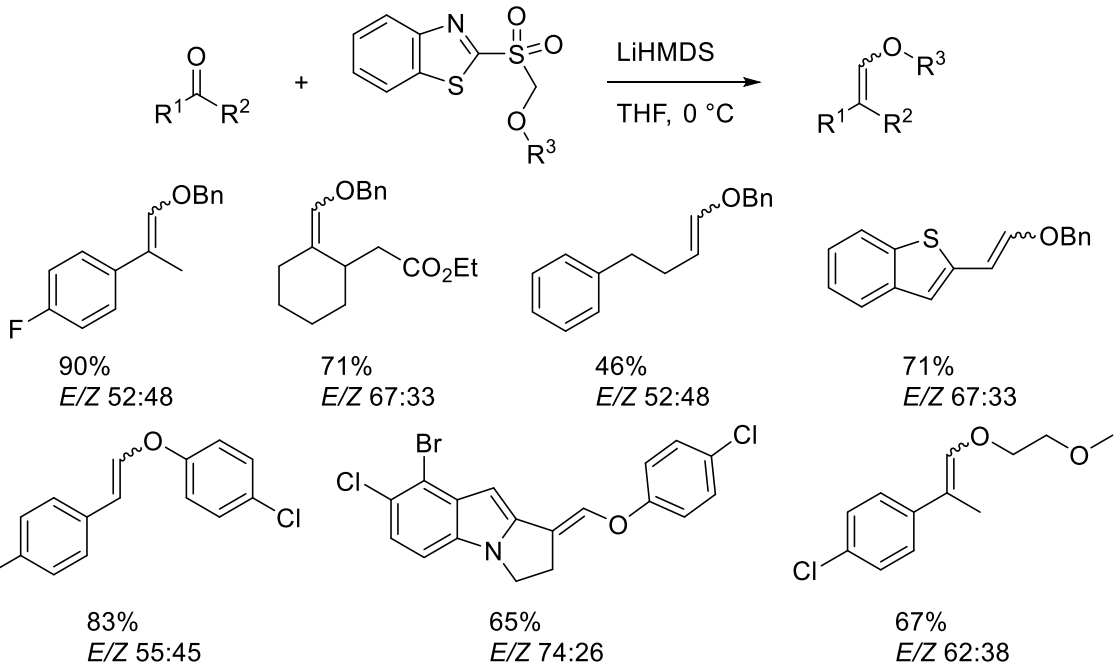
under conditions B, whereas these experiments failed under conditions A. Some selected results are shown in **Scheme 2-14**.[27]



Scheme 2-14 Selected results of Aïssa.[27]

Preparation of enol ethers

In 2003, Berthelette presented a new protocol for the synthesis of vinyl ethers using the Julia olefination (**Scheme 2-15**).[28]

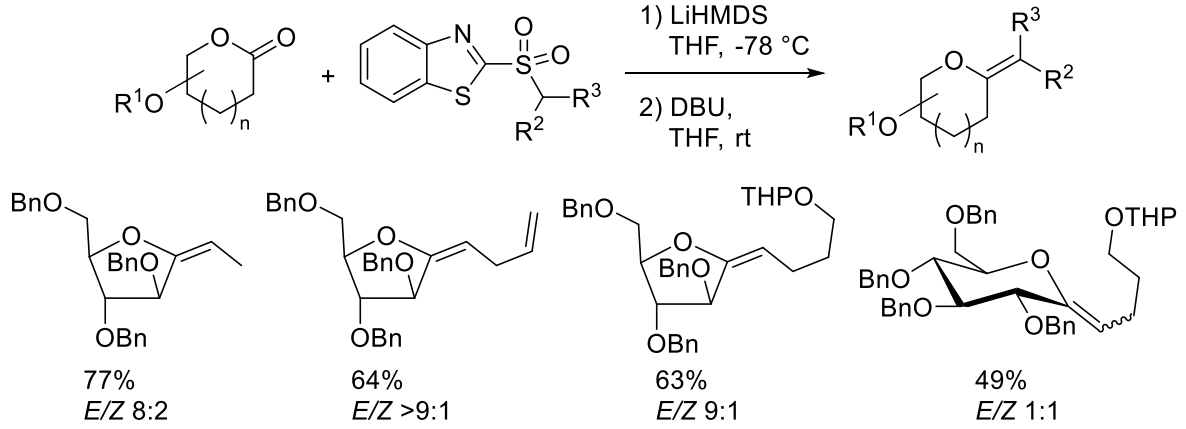


Scheme 2-15 Berthelette's method for vinyl ethers using Julia olefination.[28]

Using BT-sulfones, Berthelette prepared 21 vinyl ethers in 46-90% yield. Despite the good functional group tolerance and moderate to good yields, the method lacks in stereoselectivity.

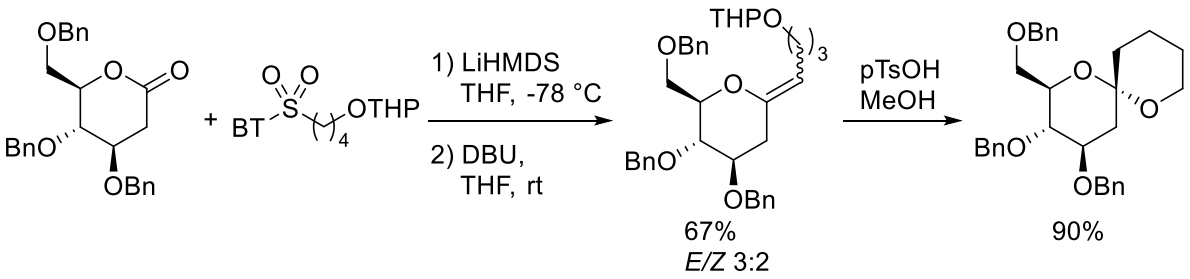
Mostly *E/Z* ratios of about 1:1 were achieved, and rarely increased *E*-stereoselectivities of up to 74:26 were observed.[28]

In 2008, Gueyrard expanded the scope of the synthesis of enol ethers by using lactones as starting materials (**Scheme 2-16**).[29]



Scheme 2-16 Synthesis of exo-glycals by Gueyrard.[29]

Gueyrard showed by using sugar-derived lactones that the stereoselectivity can be increased in favour of the *E*-olefin. Especially when using 5-membered rings, good yields were obtained with 60-77% and with *E*-stereoselectivity of up to >9:1. The 6-membered analogues, on the other hand, gave lower yields and only few to no stereoselectivity.[29] Nevertheless, Gueyrard showed shortly afterwards that these exo-glycals can be used to form spirocycles as single diastereomers, as shown in **Scheme 2-17**.[30]

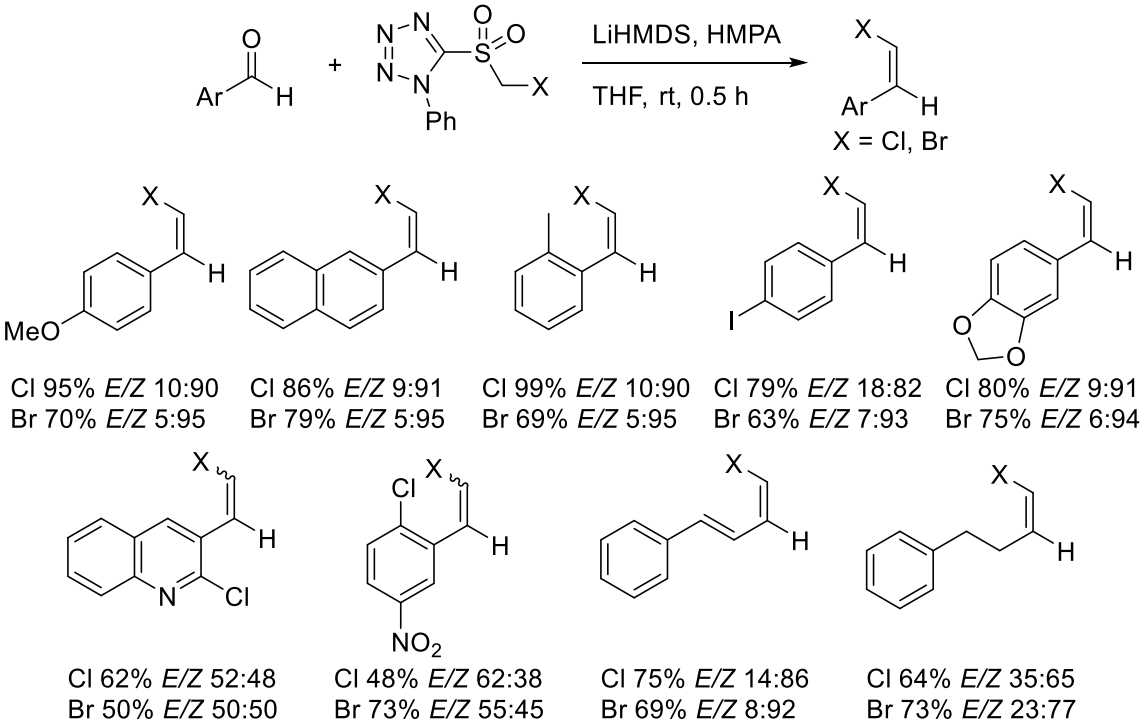


Scheme 2-17 Synthesis of enol ether and transformation to the spirocycle by Gueyrard.[30]

Treating the exo-glycals with *para*-toluenesulfonic acid (pTsOH) in methanol resulted in formation of spirocyclic intermediates. Under this acidic conditions, Gueyrard observed the thermodynamic more stable product as a single diastereomer in high yields.[30]

Preparation of alkenyl halides

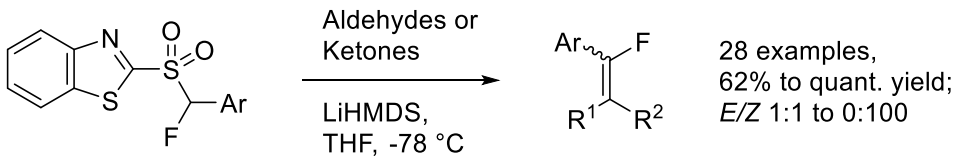
In 2006, Berthelette developed a new method to prepare alkenyl halides via Julia olefination (**Scheme 2-18**).[31]



Scheme 2-18 Preparation of alkenyl halides via Julia olefination by Berthelette.[31]

For the preparation of alkenyl halides, Berthelette chose 1-phenyl-1H-tetrazol-5-yl sulfones (PT), as they are known to achieve better *E/Z* stereoselectivities.[17] The search for the right reaction conditions has shown that the effect of the additive is of decisive importance. When $MgBr_2$-Et_2O is used as an additive, Berthelette obtained alkenyl chlorides with 69% yield and *E*-stereoselectivity of up to 94:6. In order to achieve *Z*-stereoselectivity, HMPA showed to be the additive of choice. As shown in **Scheme 2-18**, alkenyl bromides and chlorides could be prepared, with the chlorides achieving higher yields but slightly lower stereoselectivity than the bromide analogues.[31]

Also in 2006, Zajc published a method for the preparation of alkenyl fluorides (**Scheme 2-19**).[32]



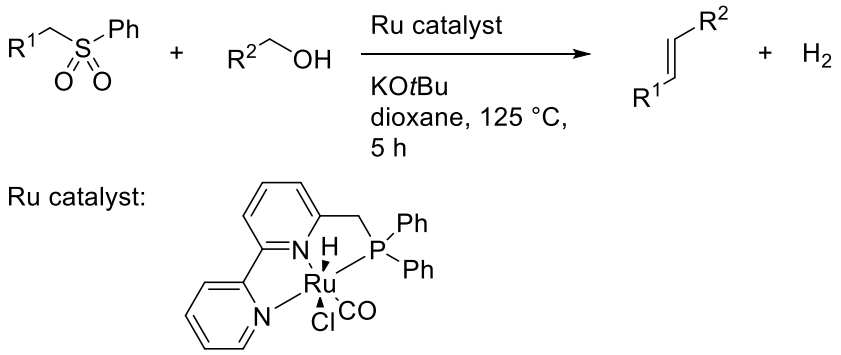
Scheme 2-19 Alkenyl fluoride preparation by Zajc.[32]

Via heterogenous fluorination four different fluorinated BT-sulfones were prepared and used for the preparation of alkenyl fluorides. High yields were obtained with moderate

stereoselectivity. Zajc also showed that PT-sulfones can be used for this reaction sequence and similarly deliver high yields.[32]

Alcohol as starting material

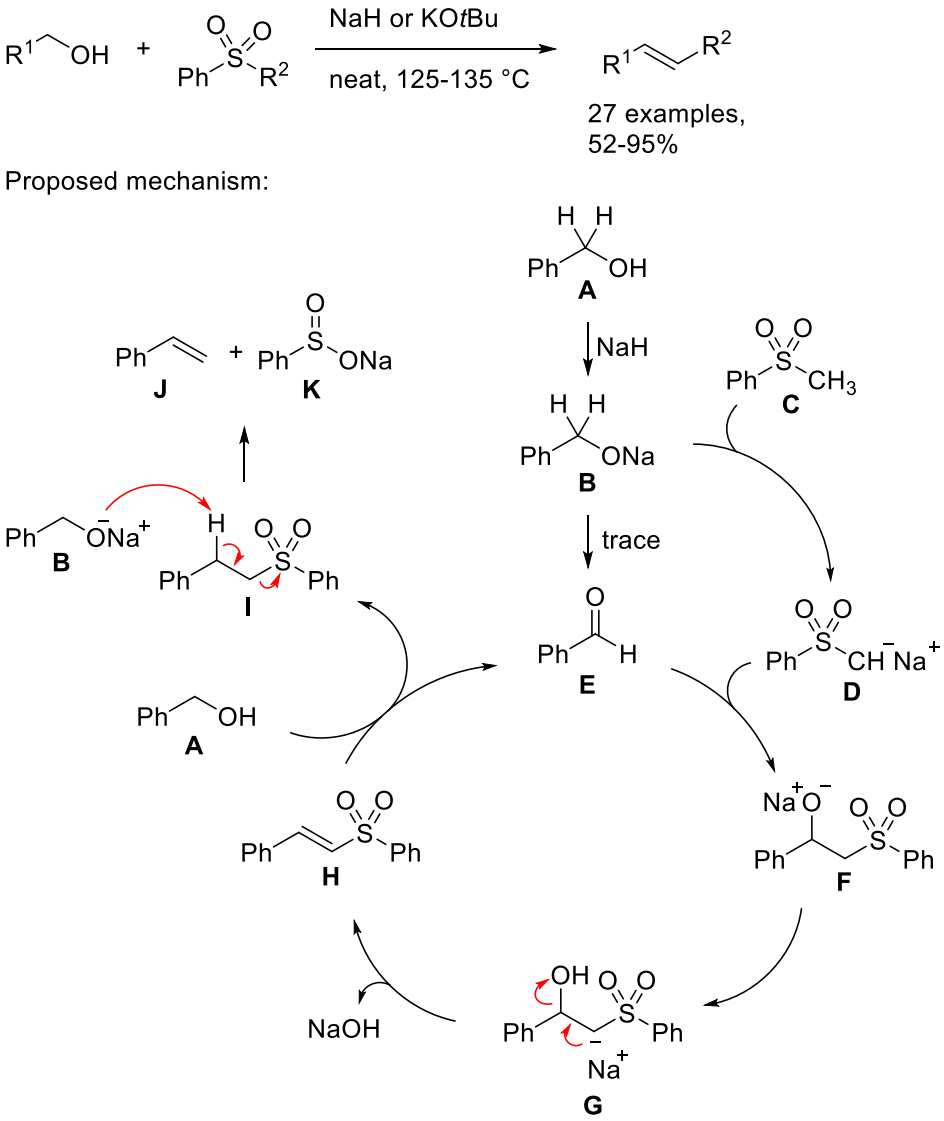
In 2014, Milstein presented a new Julia olefination reaction that is based on alcohols instead of aldehydes or ketones, as was previously the case (**Scheme 2-20**).[33]



Scheme 2-20 Milstein's protocol for olefination reaction with alcohols.[33]

The catalytic olefination reaction follows a simple protocol in which all compounds are mixed and heated for 5 hours. A small catalyst screening revealed that the ruthenium pincer complex shown in **Scheme 2-20** worked best, and the following scope gave *E*-olefins in 35-72% yield. When dimethyl sulfone was used as the sulfone source, methylenation was also possible to make with the developed reaction protocol. However, the release of hydrogen as a side product caused unwanted hydrogenation and formation of more side products. However, Milstein found a way to make positive use of this drawback. By switching from an open to a closed system and pressurising the reaction mixture with a 2.5 bar H_2-atmosphere, Milstein was also able to prepare alkanes from alcohols directly in a one-pot system.[33]

In 2015, Kang presented an alternative method to prepare olefins from alcohols using bases to promote the reaction instead of metals (**Scheme 2-21**).[34]



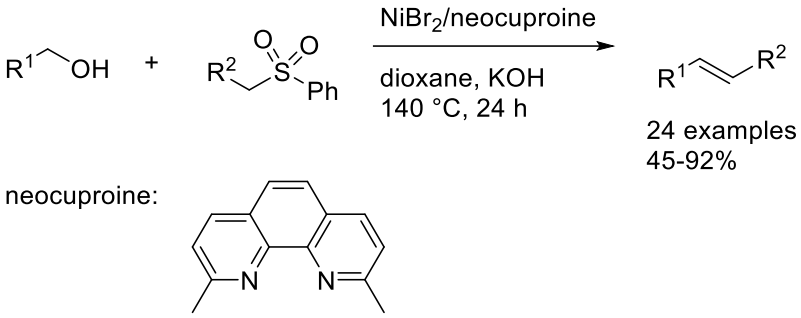
Scheme 2-21 Kang's protocol for preparing olefins starting from alcohols with proposed mechanism.[34]

First, the alcohol **A** is proposed to undergo thermal dehydrogenation to form traces of benzaldehyde **E**, which reacts further with sulfone sodium salt **D** to intermediate **F**. Hydride transfer leads to sulfone salt **G** and elimination of sodium hydroxide results in formation of vinyl sulfone **H**. After the hydride transfer to **H**, sulfone **I** reacts with sodium alcoholate **B** to the desired styrene **J** and benzyl sulfinate **K**.[34]

With this method the reaction is run in neat conditions with sodium hydride or potassium *tert*-butoxide as the base. Catalysing the reaction with a base led to a cleaner reaction, as on the one hand no hydrogen is formed, which can hydrogenate the product, and on the other hand unreacted alcohol can easily be recycled and reused. Depending on the chosen sulfone,

methylenation products or olefins in strictly *E*-stereoselectivity are obtained in yields of 52 to 95%.[34]

In 2019, Maji presented a combination of above described methods. By using base metal-catalysis, alcohols were transformed to olefins (**Scheme 2-22**).[35]

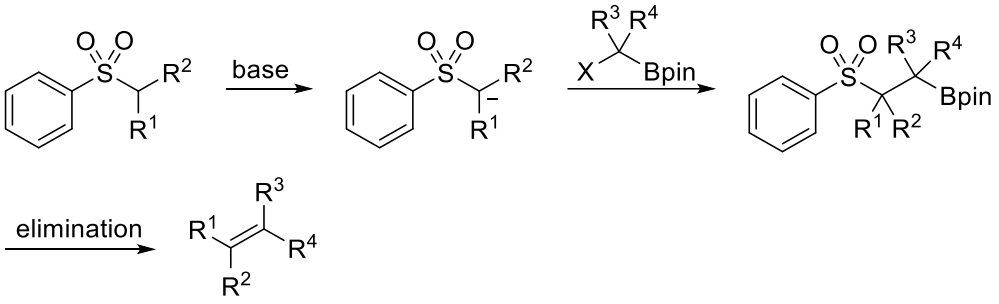


Scheme 2-22 Base metal-catalysed olefination reaction by Maji.[35]

The combination of metal-base catalysis enabled Maji to use non-precious metals such as nickel rather than noble-metals such as ruthenium or platinum.[35] As with Milstein's method[33], a special ligand system had to be used to achieve good yields. Eight different ligands were tested, and neocuproine shown in **Scheme 2-22** proved to be the most suitable. With this protocol, Maji was able to synthesize 24 examples with yields from 45-92% and complete *E*-stereoselectivity.[35]

2.2 Aim of the project

As already shown in the introduction, the sulfone precursor used in Julia olefination is first deprotonated and then used for addition to the aldehydes or ketones.[10,18] However, sulfones can also be used for alkylation reactions in which they are first deprotonated and the sulfonic anion can then react with an electrophile.[36] Various electrophiles can be used for these reactions, but to our knowledge this has not yet been attempted with α-chloroalkyl boronic esters.



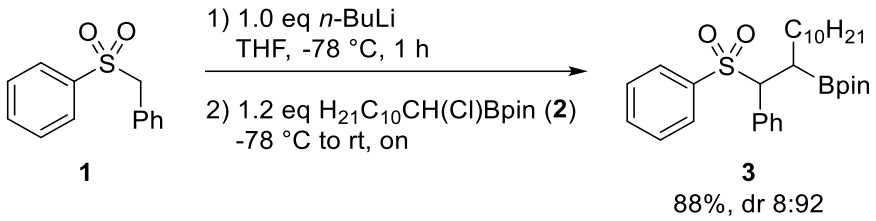
Scheme 2-23 New approach using α-chloroalkyl boronic esters for the synthesis of olefins.

The aim of the project is to develop a new protocol for the use of α-chloroalkyl boronic esters for the reaction with sulfones, as depicted in **Scheme 2-23**. As in the Julia olefination, the sulfone is deprotonated with a base in the first step. Then α-chloroalkyl boronic ester is added and the boronic ester intermediate (corresponds to three-component coupling product of first chapter) should be prepared. The subsequent elimination should lead to the formation of the desired olefin and complete the protocol for the new olefination reaction.

2.3 Results & Discussion

2.3.1 Method development for coupling reaction

The first experiment was started under the reported conditions[36] for alkylation reactions for sulfones (**Scheme 2-24**).

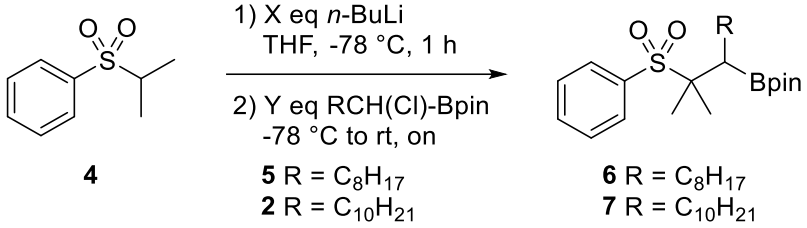


1 **3**
88%, dr 8:92

Scheme 2-24 New approach for synthesis of three-component coupling products.

Benzyl phenyl sulfone **1** was dissolved in dry THF and deprotonated with *n*-BuLi at -78 °C. After one hour, α-chloroalkyl boronic ester **2** was added and the reaction mixture was slowly warmed up to room temperature overnight. After acidic work-up with saturated aqueous NH_4Cl solution and purification of the crude product by flash column chromatography, **3** was obtained in 88% yield and dr of 8:92.

Fortunately, the desired product could already be obtained in high yield and with surprisingly high selectivity with the first set of parameters. However, in order to better understand the reaction, a secondary sulfone, isopropyl phenyl sulfone **4**, was selected for further testing of the reaction conditions, as it does not lead to diastereomers (**Scheme 2-25**).



4

5 R = C_8H_{17}
2 R = $C_{10}H_{21}$

6 R = C_8H_{17}
7 R = $C_{10}H_{21}$

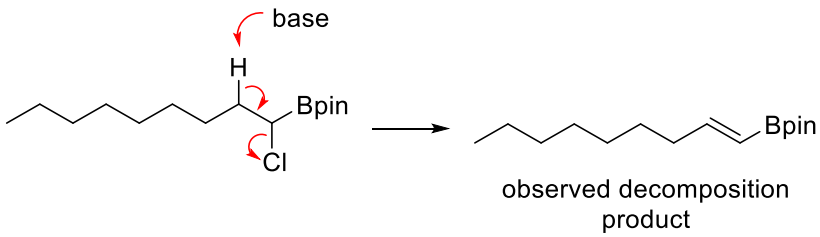
Scheme 2-25 Optimization reactions with isopropyl phenyl sulfone **4**.

First, the influence of the ratio between the sulfone and the α-chloroalkyl boronic ester was investigated and the results are shown in **Table 2-2**.

Table 2-2 Results of optimization reactions with isopropyl phenyl sulfone **4**.

Nr.	Sulfone (**4**) [eq]	*n*-BuLi [eq]	R-Bpin [eq]	Yield (isolated)
1	1.0	1.0	1.2, **2**	62%, **7**
2	1.0	1.0	1.5, **2**	67%, **7**
3	1.2	1.2	1.0, **5**	44%, **6**
4	1.5	1.5	1.0, **5**	0%, **6**

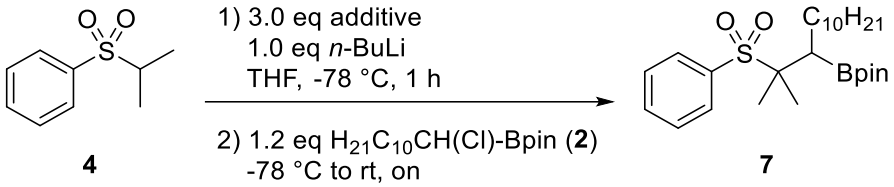
Using the firstly set conditions on isopropyl phenyl sulfone **4** the desired product **7** was obtained in 66% yield (**Table 2-2**, entry 1). Since the yield was considerably lower than that of the starting reaction, a deuteration experiment was performed with the sulfone **4** to see whether the reaction time was long enough to completely deprotonate the sulfone. After deprotonation with *n*-BuLi, the reaction mixture was treated with excess D_2O. Experiments showed that less than 30 minutes are required to fully deprotonate sulfone **4** which is also supported by the literature.[37,38] To increase the yield, the amount of the α-chloroalkyl boronic ester **2** was increased to 1.5 equivalents, but this had a small effect on the yield (**Table 2-2**, entry 2). Reversing the ratio in favour of the sulfone had a big influence on the reaction. Using 1.2 equivalents sulfone **4** gave 44% of desired product **6**, and when 1.5 equivalents were used, no desired product was observed at all (**Table 2-2**, entry 3-4). TLC analysis revealed the formation of a mixture of non-polar compounds when the ratios were in favour of the sulfone, and NMR analysis showed that the main product is the decomposition product of the α-chloroalkyl boronic ester shown in **Scheme 2-26**.



Scheme 2-26 Decomposition of α-chloroalkyl boronic ester.

Accordingly, the original ratio was retained, and the effect of possible additives was investigated next.

Additive with chelating effects



Scheme 2-27 Optimized reaction protocol with additives.

The first class of additives investigated were additives with chelating properties. Improvements were expected especially for sterically hindered sulfones and the results are shown in **Table 2-3**.

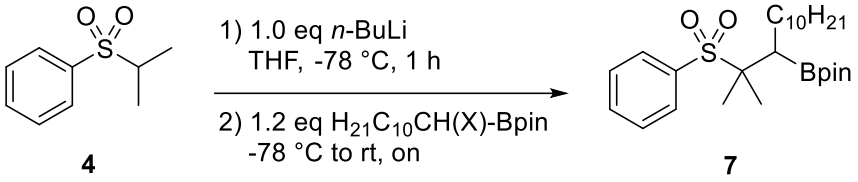
Table 2-3 Results for reactions with chelating additives.

Nr.	Sulfone (**4**) [eq]	*n*-BuLi [eq]	R-Bpin (**2**) [eq]	Additive	Yield (isolated)
1	1.0	1.0	1.2	none	62%
2	1.0	1.0	1.2	HMPA	66%
3	1.0	1.0	1.2	DMPU	49%
4	1.0	1.0	1.2	TMEDA	43%
5	1.0	1.0	1.2	(-)-sparteine	55%

Running the reaction with additives had moderate effects on the yield. HMPA (**Table 2-3**, entry 2) delivered a slightly higher yield as in the reaction without additive. DMPU, TMEDA and (-)-sparteine addition, on the other hand, produced lower yields and are therefore no option (**Table 2-3**, entry 3-5). Since HMPA delivered a slightly higher yield, respectively did not lower the yield like the other additives, it could be of interest for reactions with sterically hindered sulfones.

Source of halogen

The influence of the halogen type in α-haloboronic acid esters was then investigated (**Scheme 2-28**).



4 **7**

Scheme 2-28 Influence of different halogen types.

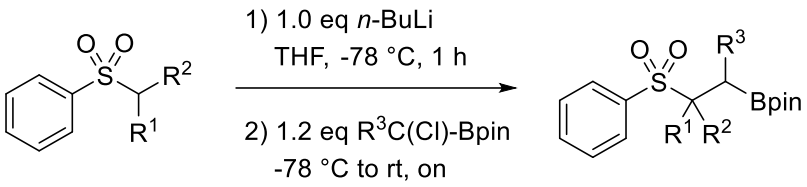
Three different α-haloboronic esters were synthesized and tested. Results are shown in **Table 2-4**.

Table 2-4 Comparison of halogen types.

Nr.	Sulfone (**4**) [eq]	*n*-BuLi [eq]	X	Yield (isolated)
1	1.0	1.0	Cl	62%
2	1.0	1.0	Br	62%
3	1.0	1.0	I	78%

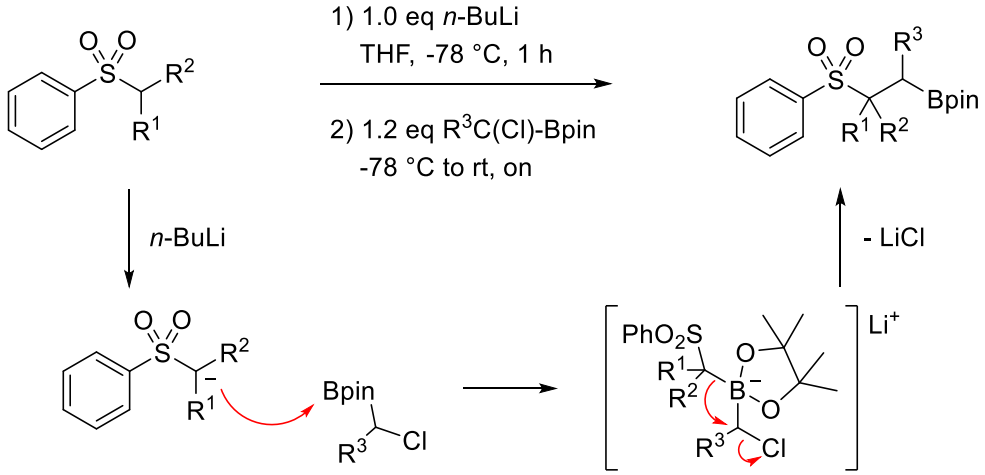
Using α-bromoalkyl boronic esters for the reaction with sulfone **RA-182** delivered 62% as when the reaction is run with α-chloroalkyl boronic esters (**Table 2-4**, entry 2). Changing the halogen type to iodine led to an increased yield of 78% (**Table 2-4**, entry 3). The influence of the halogen source has so far proved to be the most influential and therefore iodide compounds can be used for more demanding reactions.

Optimized method and proposed mechanism



Scheme 2-29 Final reaction conditions after all optimization attempts.

Optimization experiments have shown that the initially chosen reaction conditions are the most suitable. The sulfone is first deprotonated with equimolar amounts of *n*-BuLi at -78 °C and then, 1.2 equivalents of α-chloroalkyl boronic ester is added to the reaction mixture, which is slowly warmed up to room temperature overnight. However, the reaction with sterically demanding substrates can be supported by the addition of HMPA or by using α-iodoalkyl boronic esters instead of α-chloroalkyl boronic esters. The proposed reaction mechanism is shown in **Scheme 2-30**.

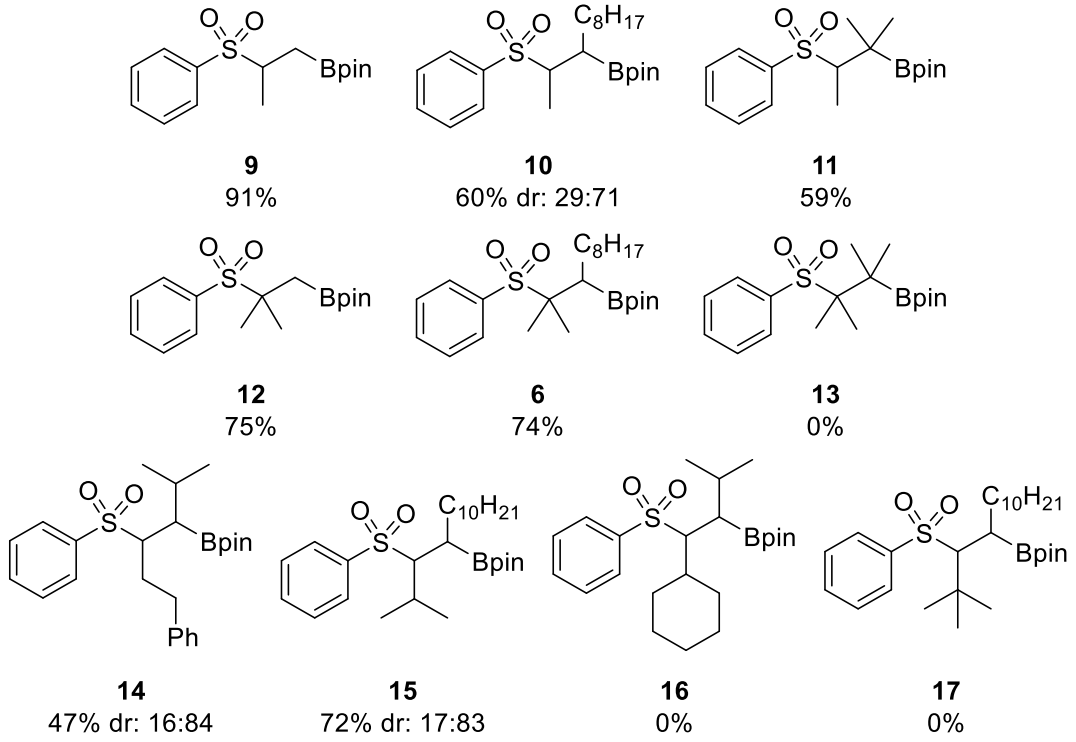


Scheme 2-30 Proposed mechanism.

After deprotonation in the first step, the sulfone anion is expected to attack onto the boronic ester forming an intermediate shown in **Scheme 2-30**. Followed by a ionic [1,2]-metallate shift, the chloride is released and the desired compound formed.

Reactivity study

With the developed method a small reactivity study was made and results are depicted in **Scheme 2-31**.



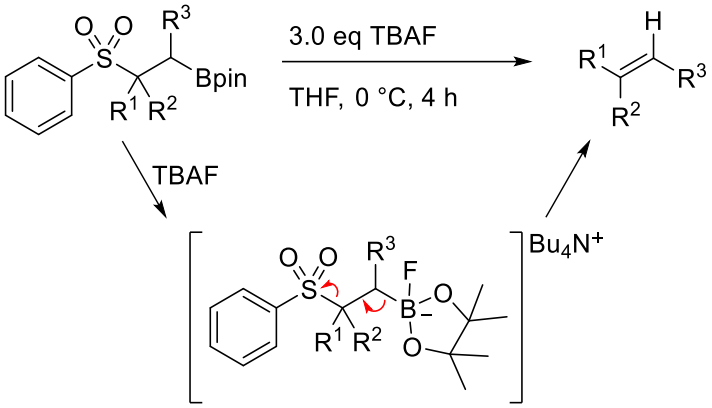
Scheme 2-31 Reactivity study.

In the first row the primary ethyl phenyl sulfone **8** was used. Using unsubstituted α-chloro boronic ester, **9** is obtained in 91% yield. Increasing the substitution on the α-chloro boronic ester led to lower yields, but the trisubstituted product **11** could still be obtained with 59% yield. In the case of secondary phenyl sulfones like isopropyl phenyl sulfone **4**, bis-substituted and tri-substituted products were obtained such as **12** at 75% and **6** at 74%. Tetra-substituted products like **13** on the other hand were not formed, most probably due to steric hindrance. As shown in the last row, it was possible to synthesise products with a secondary alkyl group such as **14** or **15**, resulting in yields of 47% and 72%, respectively. However, when two secondary side chains as in **16** were involved, no product was observed. Similarly, when a tertiary group was present as for **17**, no product formation was observed.

2.3.2 Olefination reaction

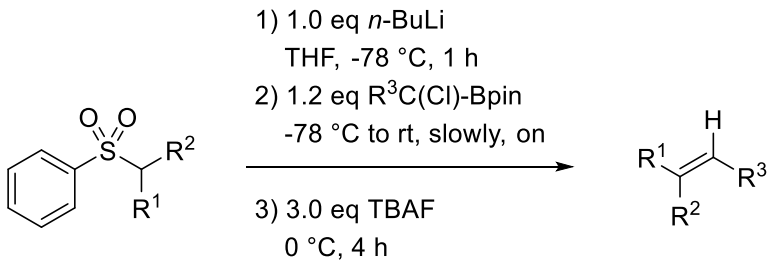
Method development & proposed mechanism

To complete the olefination, the intermediates formed during the addition of the phenyl sulfonyl anion to the α-chloroalkyl boronic ester had to undergo an elimination process. Since this step was already successfully developed in Chapter 1, TBAF was used accordingly for the elimination reaction and the used protocol is shown in **Scheme 2-32**.



Scheme 2-32 Elimination reaction with TBAF and proposed mechanism.

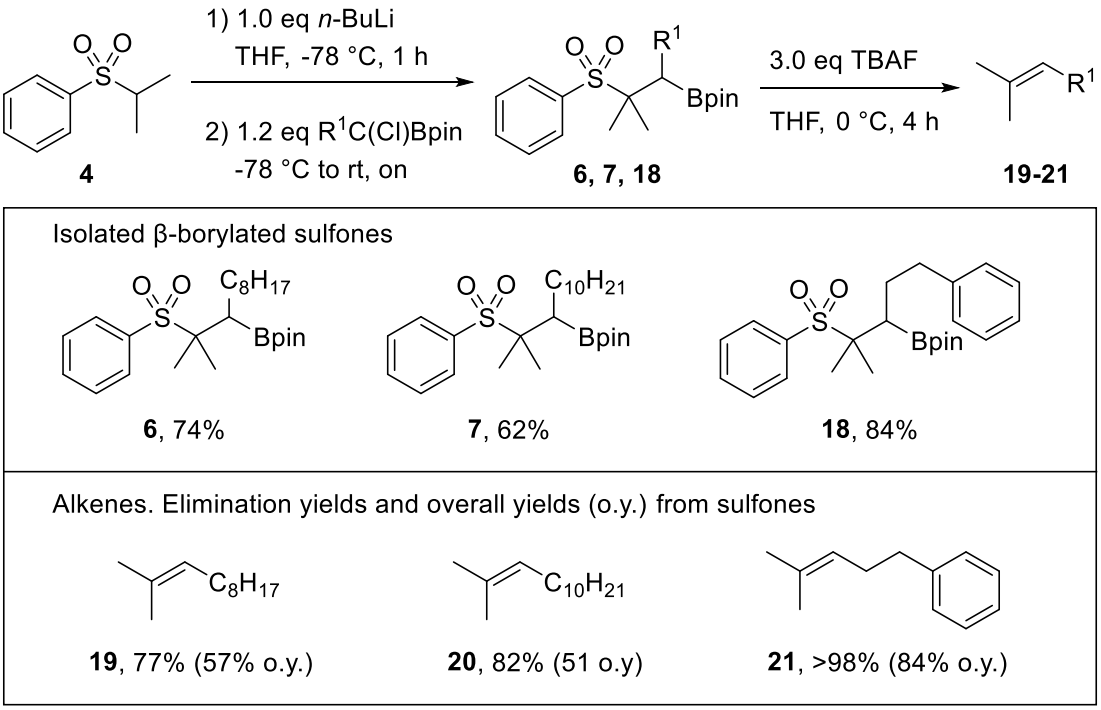
Addition of TBAF to the bench-stable boronic ester intermediate in THF results in formation of unstable fluoroboron-ate complex. The carbon-boronic bond is cleaved under extrusion of benzenesulfinate anion and the desired olefin is formed. The whole olefination process can be performed as a two-step protocol involving isolation of the intermediate β-borylated sulfone or alternatively as a one-pot process according to **Scheme 2-33** by adding TBAF directly to the formed borylated sulfone intermediate. The one-pot method has major advantages over the step-by-step protocol by reducing the quantity of solvent used and the number of purifications. Moreover, it was found that the large difference of polarities between apolar alkene products and polar by-products facilitates the final purification process. In addition, higher yields are achieved as no product is lost during purification of the labile borylated sulfone intermediates.



Scheme 2-33 One-pot protocol for the olefination reaction.

Trisubstituted olefins from isopropyl phenyl sulfone 4

Starting from the β-borylated sulfones **6**, **7** and **18** treatment with 3 equivalents of TBAF in THF over 4 hours gave the corresponding trisubstituted alkenes **19**-**21** in high yields (**Scheme 2-34**). The overall olefination process yields (o.y.) starting from the sulfones are given in parenthesis and they range from 51 to 84% yield.

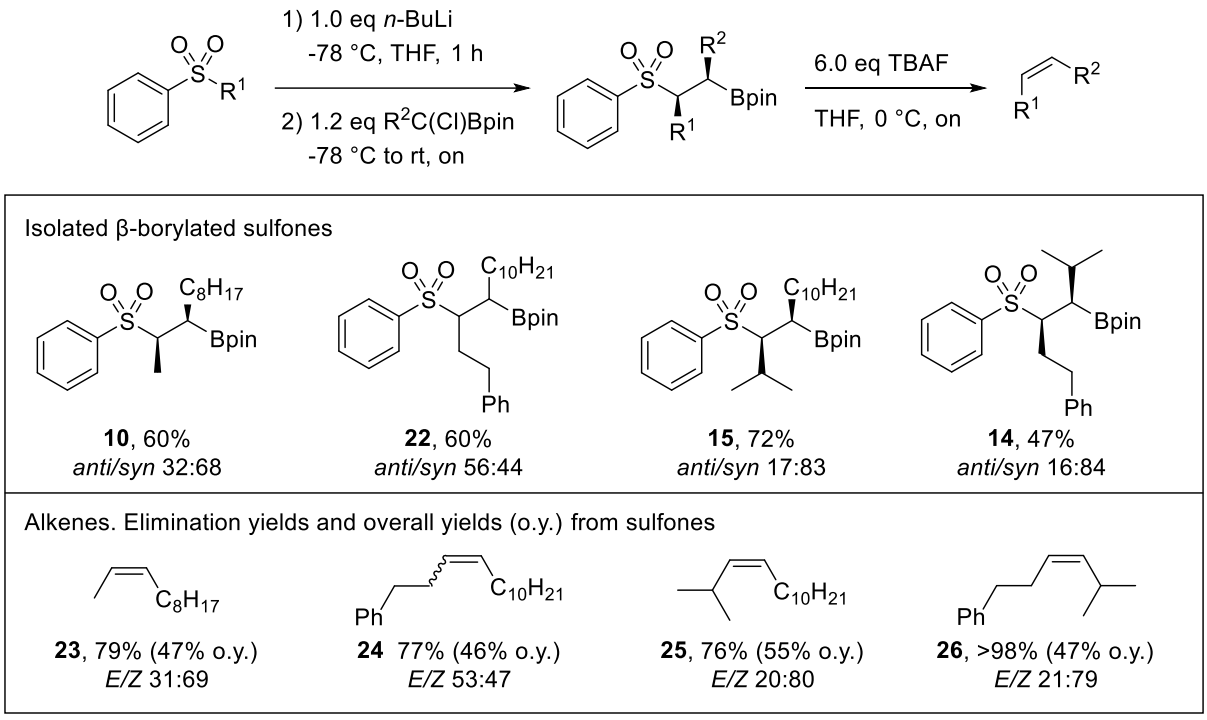


Scheme 2-34 Scope of trisubstituted olefins from isopropyl phenyl sulfone **4**.

1,2-Disubstituted olefins from alkyl phenyl sulfones

The preparation of 1,2-disubstituted alkenes was investigated next and results are shown in **Scheme 2-35**. The reaction involving primary alkyl substituents at the α-position of the sulfone and the boronic ester provided the products **10** and **22** in fair yields but low stereoselectivities. After treatment with TBAF, the corresponding alkenes **23** and **24** were obtained in 79 and 77%, respectively. As anticipated, the diastereomeric ratio of the intermediate β-borylated sulfone determine the *E/Z* ratio of the alkenes pointing towards a stereospecific elimination process. Interesting, when one of the α-substituent was a secondary group, regardless of whether it originates from the sulfone group or the α-haloboronic ester, a good diastereoselectivity was achieved and the β-borylated sulfones **15** and **14** in favour of the *syn* diastereomer. Upon treatment with TBAF, these two β-borylated sulfones afforded the *Z*-alkenes **25** and **26** in good yields and matching diastereomeric ratios. The *E/Z* configuration of the alkenes was determined by NMR-NOESY experiments in combination with the comparison of identical or similar reported structures in the literature[17,22,39–41]. Based on these results and the observation

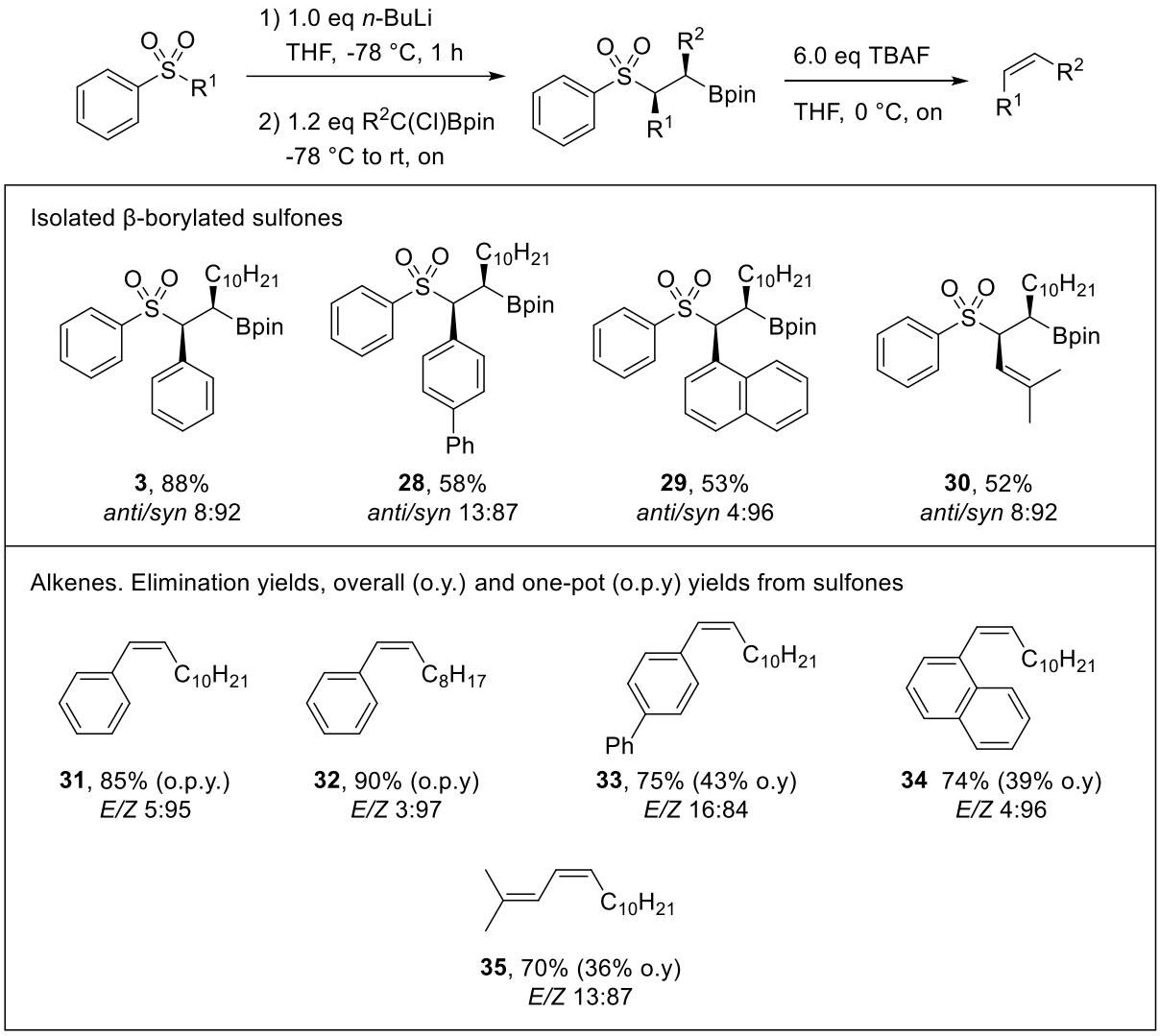
from Chapter 1 that β-borylated sulfones follow an anti-elimination mechanism, the obtained borylated sulfones were assigned to the *syn*- or *anti*-diastereomer.



Scheme 2-35 Stereochemical outcome.

Conjugated 1,2-disubstituted olefins from benzyl and allyl sulfones

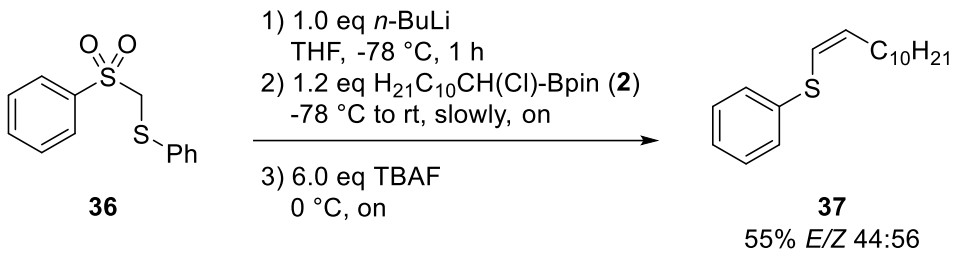
Formation of conjugated alkenes from benzylic and allylic sulfones was investigate next and results are presented in **Scheme 2-36**. The formation of the β-borylated sulfones **3** and **28**-**30** proceeded in all cases with an excellent level of stereocontrol (syn/anti 87:13 to 96:4) in moderate to good yields. The TBAF promoted elimination afforded the corresponding alkene in good to excellent yields with a remarkable *Z* selectivity. The highest yields were obtained for **31** (85%) and **32** (90%) using a one-pot procedure, i.e. by treating the reaction mixture resulting from the alkylation process directly with TBAF. the one-pot method, where **32** was obtained in 90% yield and with a *Z*-selectivity of 97:3. The β-borylated sulfones **28** and **29** afforded as expected the *Z*-alkenes **33** and **34** upon treatment with TBAF. In addition to the benzyl sulfones, prenyl phenyl sulfone **27** gave the β-borylated sulfones **30** with a good stereocontrol. The level of stereocontrol was preserved during the elimination process and the *Z*-configurated diene **35** was obtained with a good stereocontrol (Z/E 87:13) in 70%.



Scheme 2-36 Scope of 1,2-substituted olefin starting from benzylic and allylic phenyl sulfones.

The results obtained for conjugated alkene are particularly promising. With the developed method high yields were obtained in the stepwise and one-pot protocol leading to high *Z*-selectivity. This is particularly interesting because the thermodynamically unfavourable *Z*-styrene-type olefins are not easy accessible via classical olefination processes. A possible method for preparing *Z*-styrene-type olefins is the modified Wittig-type reaction[42] in which semi-stabilised ylides react with *N*-sulfonyl imines. Furthermore, the preparation can also be based on iron-catalysed reductive coupling[2] of alkyl halides with terminal arylalkynes or via molybdenum-catalysed cross-metathesis reactions[43]. Semi-hydrogenation reactions can also lead to *Z*-styrene-type olefins. Instead of the classical use of Lindlar catalyst, which often results in isomerisation and over-reduction, this can be achieved with copper-salts in combination with silane.[44] Although the modified classical approaches lead to olefins with good *Z*-selectivity, the modified Wittig approach produces a stoichiometric phosphine oxide waste, and the other approaches mentioned rely on metal catalysts and complicated ligand systems, which makes them unfavourable compared to the method developed here.[2,42–44]

Heteroatom substituted olefin

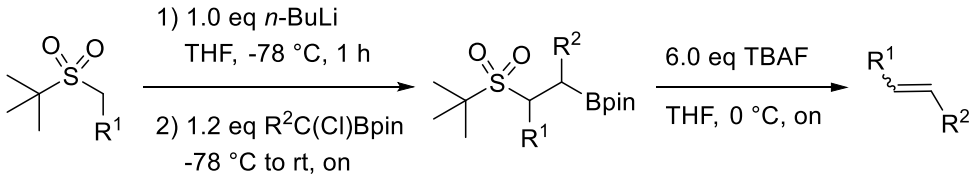


Scheme 2-37 Synthesis of heteroatom substituted olefin.

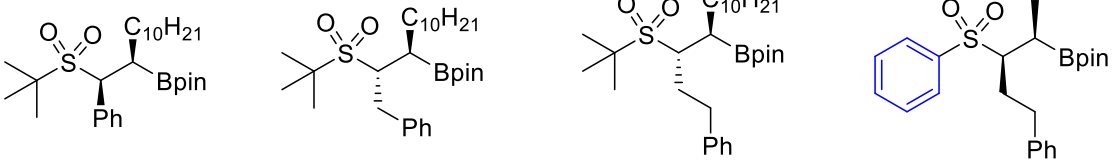
The reaction with the sulfone **36** was initially carried out stepwise, but the intermediate β-borylated sulfone decomposed during purification. Therefore, the reaction was repeated using the one-pot method and the olefin **37** was obtained in 55 % yield as an E/Z mixture.

Olefination with *tert*-butyl sulfone

With the aim of increasing the stereocontrol of the olefination process, we decided to investigate the effect of the nature of the sulfone on the olefination process. For this purpose, the bulky *tert*-butyl sulfones were chosen since they are known to be excellent substrates for base promoted alkylation reaction.[38] The results are shown in **Scheme 2-38** and compared with the results obtained with the corresponding phenyl sulfones (in blue).

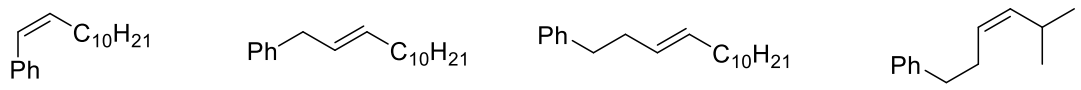


Isolated β-borylated sulfones



38, 89% *anti/syn* 4:96	**39**, 69% *anti/syn* 83:17	**40**, 61% *anti/syn* 56:46	missing
3, 88% *anti/syn* 8:92	missing	**22**, 60% *anti/syn* 56:44	**14**, 47% anti/syn 16:84

Alkenes. Elimination yields, overall (o.y.) and one-pot (o.p.y) yields from sulfones



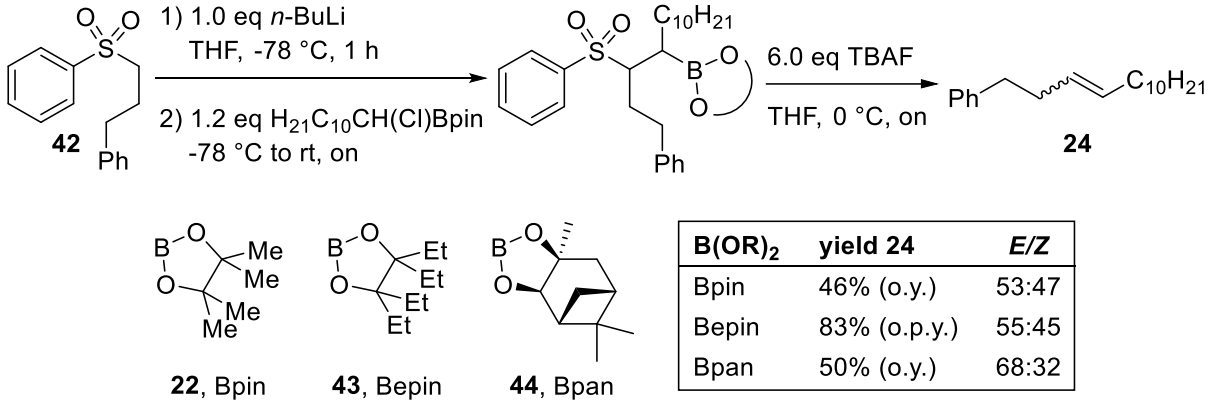
31	**41**	**24**	**26**
81% (o.p.y), *E/Z* 3:97	81% (56% o.y), *E/Z* 86:14	72% (44% o.y), *E/Z* 74:26	58% (o.p.y), *E/Z* 21:79
85% (o.p.y), *E/Z* 5:95	missing	75% (o.p.y.), *E/Z* 75:25	>98% (47% o.y), *E/Z* 21:79
		77% (46% o.y), *E/Z* 53:47	

Scheme 2-38 Olefination with *tert*-butyl sulfones (black) compared with olefination with phenyl sulfone (blue).

Reaction with benzyl *tert*-butyl sulfone afforded the β-borylated sulfone **38** in high yield and stereoselectivity comparable to those obtained with the corresponding phenyl sulfone. Interestingly, reaction between *tert*-butyl alkyl sulfones and α-chloro boronic esters bearing both a primary alkyl substituent at the α-position afforded alkenes **41** and **24** with moderate stereocontrol to in favour of the *E*-isomer. However, a discrepancy in for the diastereomeric ratio of the β-borylated sulfone **40** will have to be confirmed. When the α-chloro boronic ester has a secondary alkyl substituent at the α-position, the olefination with the *tert*-butyl sulfones gave results in line with those obtained with the phenyl sulfone, i.e. the alkene **26** is obtained with a moderate diastereocontrol in favour of the *Z* isomer. Overall, slightly higher diastereoselectivities could be achieved with *tert*-butyl sulfones compared to phenyl sulfones, particularly for 1,2-disubstituted alkenes bearing primary substituents.

Influence of the boronic ester moiety

In addition to boronic acid pinacol ester (Bpin), pinanediol ester (Bpan), and 3,4-hexane-3,4-diol ("ethyl-pinacol") (Bepin)[45,46] were tested for the preparation of the 1,2-disubsituted alkene **24**, the most challenging in term of stereocontrol and results are shown in **Scheme 2-39**.



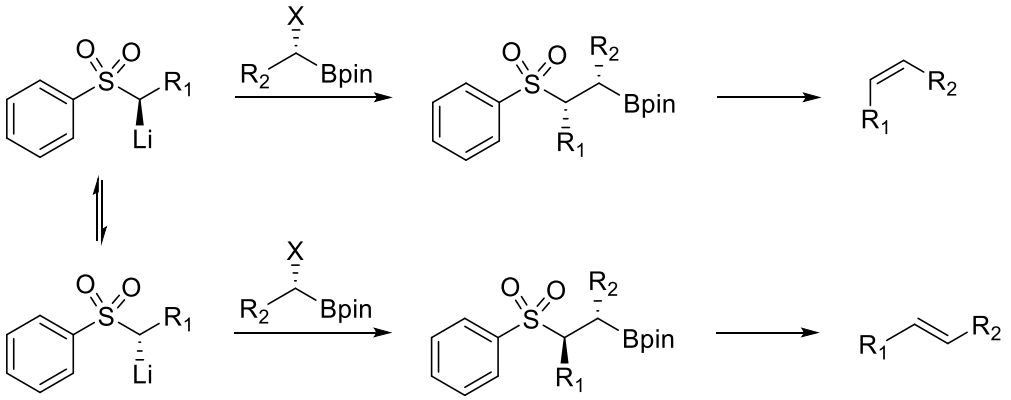
$B(OR)_2$	yield 24	*E/Z*
Bpin	46% (o.y.)	53:47
Bepin	83% (o.p.y.)	55:45
Bpan	50% (o.y.)	68:32

Scheme 2-39 Comparison of different boronic esters.

With the boronic acid pinacol ester, **24** was obtained in the stepwise protocol in 46% overall yield as a 53:47 *E/Z* mixture. The slightly bulkier Bepin ester was used, the intermediate β-borylated sulfone was not isolated and the alkene **24** was obtained in good yield (83%) without noticeable effect on the stereoselectivity compare to the Bpin derivative. The olefination reaction with Bpan gave the intermediate **44** in 67% yield. Due to superimposed signals, no information for the diastereomer ratio was obtained via NMR-analysis. However, the subsequent elimination reaction afforded **24** in 50% overall yield. In this case, the diastereoselectivity was improved to reach an *E/Z* ratio of 68:32.

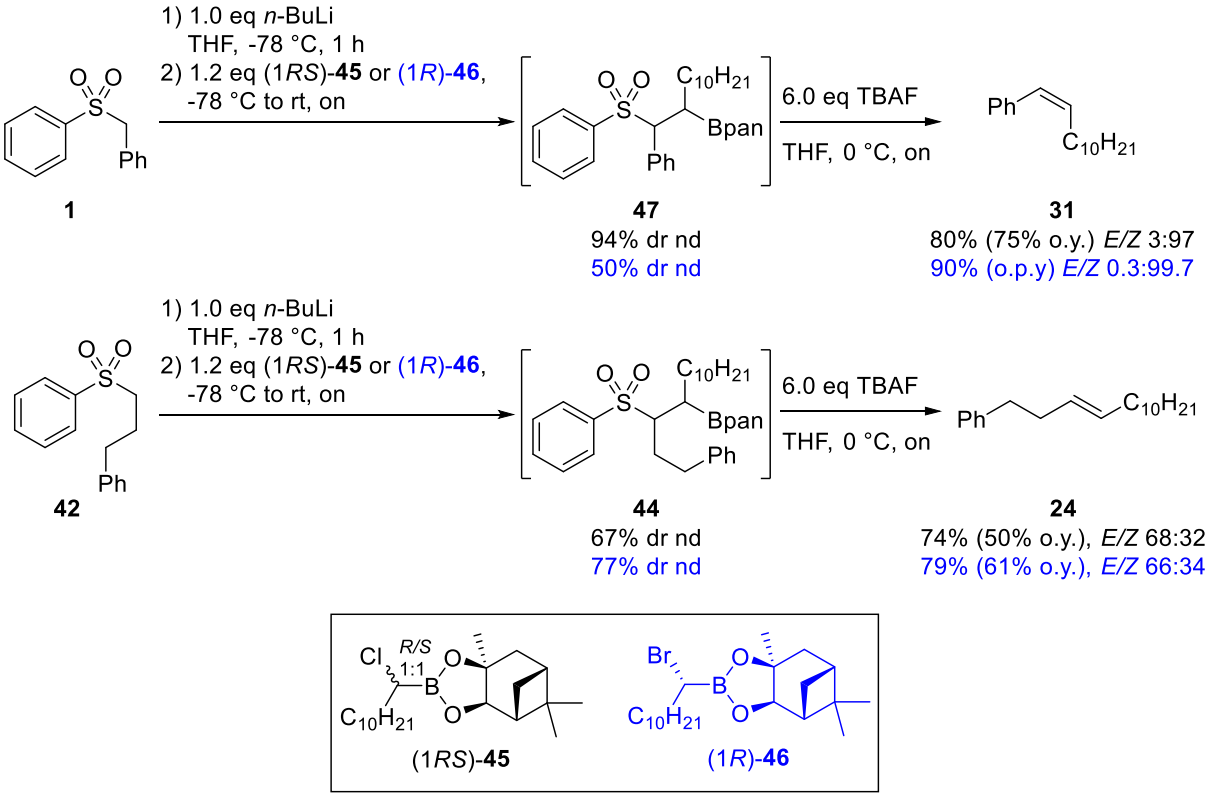
Stereochemical outcome of reaction involving optically pure α-haloalkyl boronic esters

Next, the influence of the absolute stereochemistry of the α-haloalkyl boronic esters was investigated (**Scheme 2-40**). Under our reaction conditions, the lithiated sulfones are formed in racemic form, they are known to be configurationally stable at very low temperature and to react with electrophiles with retention of configuration.[47,48] Therefore, if epimerization of the lithiated sulfone is slower than the alkylation process, a kinetic resolution could take place, this would lead to a slower reaction and a decrease of stereocontrol as the reaction proceed to finally if one reaches 100% conversion a 1:1 mixture of diastereomer. This possibility is very hypothetical due to the rapid epimerization of lithiated phenyl sulfones at –78 °C. If the epimerization process of the lithiated sulfones is faster than the alkylation process, the results starting from a racemic or from the enantiopure α-haloalkyl boronic ester should be identical.



Scheme 2-40 Epimerization of lithiated sulfones.

Since the preparation of enantiopure α-haloboronic pinacol esters is not trivial,[49] we decided to look at the easily available optically pure pinanediol boronic esters. The diastereomerically pure (1*R*)-1-bromoundecyl pinanediol boronic ester (1*R*)-**46** is easily available via a highly diastereoselective Matteson reaction with lithiated dibromomethane. The 1:1 diastereomeric mixture (1*R/S*)-1-chloroundecyl boronic ester (1*R/S*)-**45** could be prepared by transesterification of racemic 1-chloroundecyl pinacol boronic ester with (+)-pinanediol according to Brown procedure.[50] Olefination reactions with sulfones **1** and **42** were investigated and results are presented in **Scheme 2-41**.



Scheme 2-41 Influence of the enantiopurity of α -haloalkyl boronic esters.

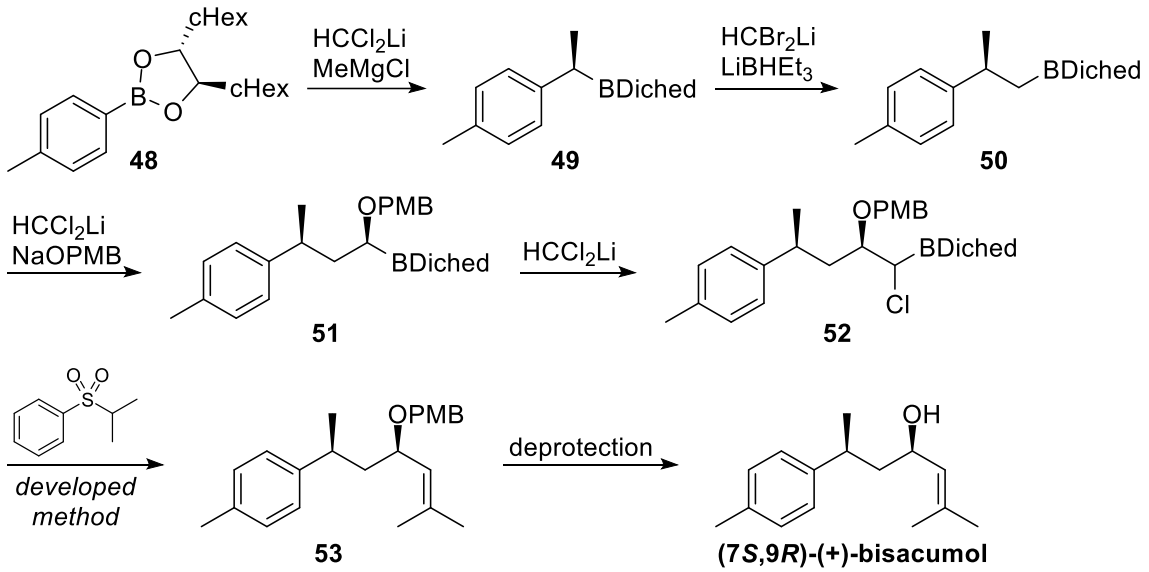
The reaction with the benzyl sulfone **1** gave the (*Z*)-alkene **31** with high stereocontrol with both (1*R*)-**46** and (1*RS*)-**45**, far from 1:1 mixture of diastereomer expected if the alkylation reaction was faster than the epimerization of the lithiated sulfone. However, the moderate yield obtained with (1*R*)-**46** makes this analysis partly questionable. The reaction was repeated with the alkyl sulfone **42**, in that case, yields were good and very similar level of stereocontrol were observed indicated clearly that epimerization of the lithiated sulfone is much faster than the alkylation reaction. Interestingly, the pinanediol boronic ester provided for this example a better stereocontrol (*E/Z* 1:2) than pinacol ester (*E/Z* 1:1).

2.4 Conclusion & Outlook

An olefination reaction was successfully developed, which makes it possible to use α-haloalkyl boronic acid esters as starting materials. The sulfones are coupled under basic condition with α-haloalkyl boronic esters leading to the formation of β-borylated sulfones. These intermediates can be isolated or directly treated with TBAF to provide the desired alkenes. Overall, 27 coupling products with yields of 47 to 91% and 14 olefins with yields of 55% to quantitative were obtained. In most cases, *Z*-alkenes are preferentially formed. A particularly high *Z* stereoselectivity was achieved for arene substituted alkenes, contrasting nicely with most available method such a Wittig and Julia-type olefinations. Indeed, only a few methods for preparing *E*-olefins are known to date[2,42–44], especially without the help of noble metals or expensive catalysts . The extension of the reaction scope should enable a better understanding of the selectivity of the reaction. In particular, the variation in the size of the substituents on the phenyl sulfone should provide information about the change between *E*- and Z-selectivity.

In general, since α-haloboronic acid esters are used as starting materials, introduction of enantioenriched sidechains is simplified drastically. Using Matteson homologation reactions[51,52], enantioenriched compounds can be easily prepared and further modified using this newly developed method.

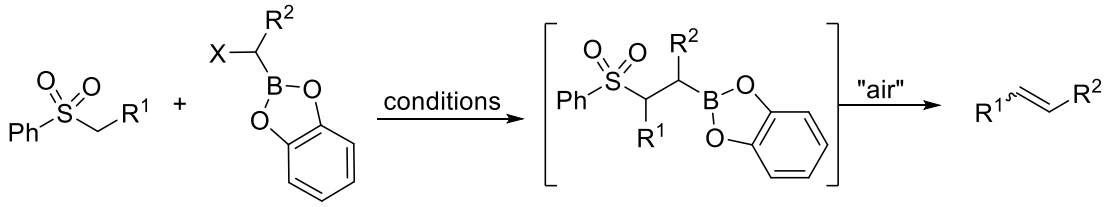
The method is also very promising for the synthesis of natural products. By combining this olefination reaction with well-established asymmetric reaction involving organoboranes, it should enable the preparation of chiral alkenes in a very straightforward method. A possible application of this strategy would be the synthesis of (7*S*,9*R*)-(+)-bisacumol[53] shown in **Scheme 2-42**.



Scheme 2-42 Proposed total synthesis of (7*S*,9*R*)-(+)-bisacumol, using Matteson homologation reactions and the developed modified Julia olefination reaction.

Starting with dicyclohexylethane-1,2-diol *p*-tolylboronic ester (p-TolBDiched) **48**, a series of Matteson reactions according to Kazmaier work[54] is expected to provide the α-chloro boronic ester **52**. Olefination of **52** with isopropyl phenyl sulfone should provide after deprotection the naturally occurring (+)-bisacumol.

The development of even milder reaction conditions for the elimination step that should facilitate a one-pot process is thought. To achieve this, the use of *B*-α-haloalkylcatecholborane[55] should be examined. Indeed, B-alkylcatecholboranes are known to be excellent radical precursor under initiation with oxygen or peroxide and very efficient chain reactions have been developed using sulfonyl radicals intermediates suitable to sustain the chain processes.[56–58] Using this approach, the intermediate β-borylated sulfones ate expected to undergo a facile radical chain fragmentation process (**Scheme 2-43**).



Scheme 2-43 Proposed method for α-halogen catecholboranes.

2.5 Experimental section

2.5.1 General information

Techniques

All reactions requiring anhydrous conditions were performed in heat-gun, oven or flame dried glassware under an argon atmosphere. An ice bath was used to obtain a temperature of 0 °C. To obtain a temperature of –78 °C, a bath of acetone was cooled with dry ice or in case of light reactions ethanol/dry ice was used instead. To obtain a temperature of -100 °C, a bath of liquid nitrogen and ethanol was used. Silica gel 60 Å (40–63 µm) from Sigma Aldrich or Macherey Nagel and 60 Å (15-40 µm) from Macherey Nagel was used for flash column chromatography. Thin layer chromatography (TLC) was performed on Silicycle silica gel 60 F_{254} plates, visualization under UV light (254 nm) and/or by dipping in a solution of $(NH_4)_2MoO_4$ (15.0 g), $Ce(SO_4)_2$ (0.5 g), H_2O (90 mL), conc. H_2SO_4 (10 mL); or $KMnO_4$ (3 g), K_2CO_3 (20 g) and NaOH 5% (3 mL) in H_2O (300 mL) and subsequent heating. Anhydrous sodium sulfate was used as drying reagent.

Deactivated silica gel for the purification of bicyclic amines:

The abovementioned silica gel was suspended in in Et_2O and 20w% of HMDS, then filtered, washed with Et_2O and dried on HV overnight. Deactivated TLC plates: silica plates are dipped in 7M NH_3 in MeOH and then dried.

Materials

Commercial reagents were used without further purification unless otherwise stated. Dry solvents for reactions were filtered over columns of dried alumina under a positive pressure of argon. Solvents for extractions (Et_2O, Heptanes, *n*-pentane, CH_2Cl_2, EtOAc) and flash column chromatography were of technical grade and distilled prior to use. Commercial dry DMF was used without further purification.

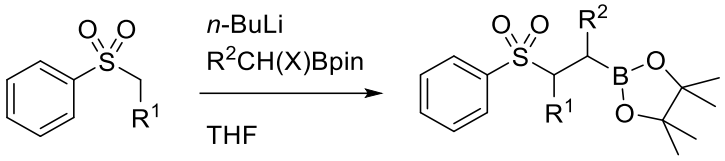
Instrumentation

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance IIIHD-300 spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C at room temperature (24-25°C) unless otherwise stated. Some ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance IIIHD-400 or a Bruker Avance II-400 spectrometer (^1H: 400 MHz; ^{13}C: 75 MHz). Chemical shifts (δ) are reported in parts per million (ppm) using the residual solvent or $Si(CH_3)_4$ (δ = 0.00 for ^1H NMR spectra) as an internal standard. Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), and br (broad). Coupling constant (J) is reported in Hz. In ^{13}C-NMR spectra, the peak positions are reported on one decimal unless the difference in chemical shift between two signals is small and required two decimals. Infrared spectra were recorded on a Jasco FT-

IR-460 plus spectrometer equipped with a Specac MKII Golden Gate Single Reflection Diamond ATR system and are reported in wave numbers (cm^{-1}). At maximum, the ten most prominent peaks are reported. Chrial GC spectra were recorded on a Thermo fisher Trace GC Ultra spectrometer fitted with a Restek Rt-bDEXm capillary column (30m, 0.25mmID, 0.25µm df); gas carrier: He 1.2 mL/min; injector: 220 °C split mode. Chiral HPLC spectra were recorded on an Agilent Technologies 1260 Infinity. Low resolution mass spectra were recorded on a Waters Micromass Autospec Q mass spectrometer in EI mode at 70 eV or were taken from GC-MS analyses performed on a Thermofisher GC-MS (quadrupole mass analyzer using EI mode at 70 eV) fitted with a Macherey-Nagel Optima delta-3-0.25 µm capillary column (20 m, 0.25 mm); gas carrier: He 1.4 mL/min; injector: 220 °C split mode. HRMS analyses and accurate mass determinations were performed on a Thermo Scientific LTQ Orbitrap XL mass spectrometer using ESI mode or a Thermo Scientific Trace 1310 Q Exactive GC mass spectrometer using EI mode fitted with a Macherey-Nagel Optima delta-3-0.25 µm capillary column (20 m, 0.25 mm); gas carrier: He 1.0 mL/min; injector: 200 °C split mode. Melting points were measured on a Büchi B-545 apparatus and are corrected. Syringe filters with polytetrafluoroethylene membrane were used with a pore size of 0.45 µm (or 5 µm) from Machery-Nagel (CHROMAFIL®Xtra PTFE 0.45). Medium pressure liquid chromatography (MPLC) was performed with a CombiFlash® Rf+ system from Teledyne Isco using RediSep® single-use normal phase columns.

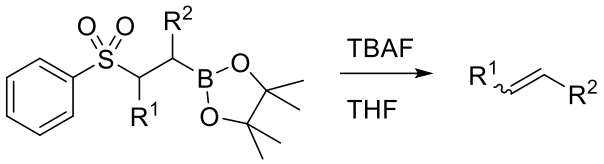
2.5.2 General Procedures

General Procedure A: coupling reaction



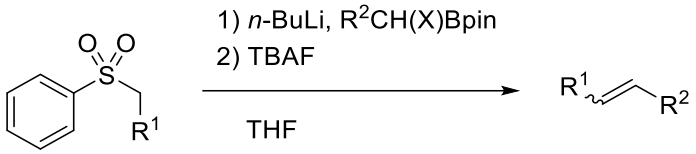
To a solution of sulfone (1.0 mmol) in dry THF (4 mL) was added *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) at -78 °C and stirred for 1 h. Then, Matteson compound (1.2 mmol) dissolved in dry THF (1 mL) was added to the reaction mixture and the solution was slowly warmed up to room temperature overnight (cooling bath not replaced). Then, the reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel.

General Procedure B: olefination reaction



To a solution of boronic ester (1.0 mmol) in dry THF (5 mL) was added TBAF (1.0 M in THF, 6.0 mL, 6.0 mmol) at 0 °C and stirred overnight. The reaction mixture was treated with aq. 1 M NaOH soln. and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel.

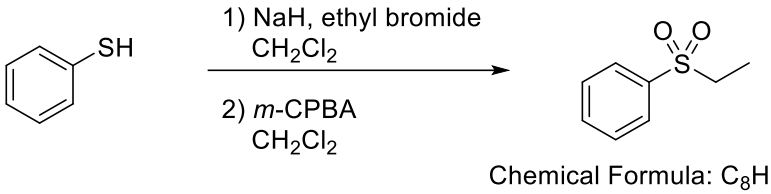
General Procedure C: Coupling and olefination reaction one-pot



To a solution of sulfone (1.0 mmol) in dry THF (4.0 mL) was added *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) at -78 °C and stirred for 1 h. Then, Matteson compound (1.2 mmol) dissolved in dry THF (1 mL) was added to the reaction mixture and the solution was slowly warmed up to room temperature overnight (cooling bath not replaced). Then, the reaction mixture was cooled down to 0 °C, TBAF (1.0 M in THF, 6.0 mL, 6.0 mmol) was added slowly and stirred overnight. The reaction mixture was treated with aq. 1 M NaOH soln. and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel.

2.5.3 Sulfone synthesis

(Ethylsulfonyl)benzene (8)



Chemical Formula: $C_8H_{10}O_2S$
Molecular Weight: 170.23

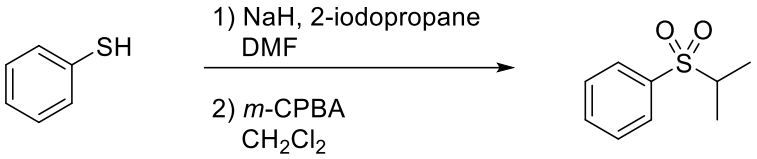
Intermediate **8** was prepared by an adapted reported procedure[59,60].

To a solution of thiophenol (5.0 mL, 49.0 mmol) in dry DMF (200 mL) was added portionwise NaH (90%, 1.58 g, 59.4 mmol) at 0 °C. After stirring for 30 min, ethyl bromide (5.5 mL, 73.5 mmol) was added, continued to stir for 5 min at 0 °C and then warmed up to 100 °C. After 3 h, the reaction mixture was cooled down to room temperature, treated carefully with water and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

The crude product was dissolved in DCM (320 mL) and cooled down to 0 °C. To the reaction mixture was added slowly a solution of *m*-CPBA (70%, 26.6 g, 108 mmol) in DCM (180 mL) and stirred overnight. The reaction mixture was treated with sat. aq. $NaHCO_3$ soln. and extracted with DCM (3 ×). The combined organic phases were washed with water (3 ×), with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **8** (7.66 g, 92%).

Appearance white solid; **Rf** 0.2 (Et_2O/pentane=3:7); **Mp** 35–40 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.93 – 7.82 (m, 2H), 7.67 – 7.60 (m, 1H), 7.59 – 7.51 (m, 2H), 3.09 (q, J = 7.4 Hz, 2H), 1.24 (t, J = 7.4 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 138.54 (C_q), 133.74 (CH), 129.31 (2 x CH), 128.22 (2 x CH), 50.62 (CH_2), 7.48 (CH_3); **FT-IR (cm^{-1}, neat)** 2979, 2333, 1793, 1690, 1577, 1446, 1408, 1298, 1139, 1078, 773, 727, 687, 580, 518, 435; **HRMS (ESI)** m/z calculated for $C_8H_{10}O_2SNa$ $[M+Na]^+$: 193.0294, found: 193.0291.

(Isopropylsulfonyl)benzene (4)



Chemical Formula: $C_9H_{12}O_2S$
Molecular Weight: 184.25

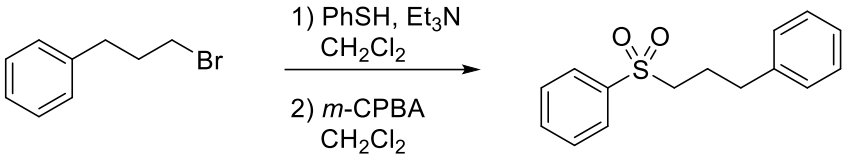
Intermediate **4** was prepared by an adapted reported procedure[59,60].

To a solution of thiophenol (4.0 mL, 39.2 mmol) in dry DMF (170 mL) was added portionwise NaH (90%, 1.26 g, 47.4 mmol) at 0 °C. After stirring for 30 min, 2-iodopropane (6.0 mL, 60.0 mmol) was added, continued to stir for 5 min at 0 °C and then warmed up to 100 °C. After 3 h, the reaction mixture was cooled down to room temperature, treated carefully with water and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

The crude product was dissolved in DCM (300 mL) and cooled down to 0 °C. To the reaction mixture was added slowly a solution of *m*-CPBA (70%, 21.4 g, 86.6 mmol) in DCM (110 mL) and stirred overnight. The reaction mixture was treated with sat. aq. $NaHCO_3$ soln. and extracted with DCM (3 ×). The combined organic phases were washed with water (3 ×), with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **4** (5.47 g, 76%).

Appearance colourless liquid; **Rf** 0.2 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.90 – 7.84 (m, 2H), 7.64 (ddt, J = 8.3, 6.5, 1.4 Hz, 1H), 7.55 (ddt, J = 8.3, 6.5, 1.3 Hz, 2H), 3.18 (hept, J = 6.9 Hz, 1H), 1.29 (s, 3H), 1.26 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 137.06 (C_q), 133.71 (CH), 129.15 (2 x CH), 129.12 (2 x CH), 55.63 (CH), 15.79 (2 x CH_3); **FT-IR (cm^{-1}, neat)** 3064, 2979, 2937, 2875, 2321, 1726, 1581, 1448, 1387, 1296, 1263, 1137, 1081, 1053, 1003, 935, 876, 763, 727, 689, 661, 575, 533, 447; **HRMS (ESI)** m/z calculated for $C_9H_{12}O_2SNa$ $[M+Na]^+$: 207.0450, found: 207.0449.

((3-phenylpropyl)sulfonyl)benzene (42)



Chemical Formula: $C_{15}H_{16}O_2S$
Molecular Weight: 260.35

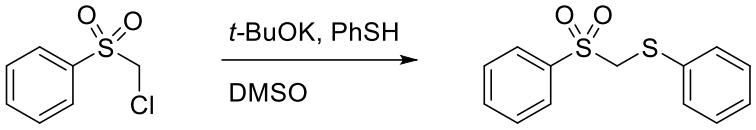
Intermediate **42** was prepared by an adapted reported procedure[61,62].

To a solution of thiophenol (7.0 mL, 68.6 mmol) and 3-bromopropylbenzol (9.2 mL, 60.5 mmol) in DCM (200 mL) was added Et_3N (10.0 mL, 72.0 mmol) at 0 °C and was stirred for 2 h. Then, the reaction mixture was treated with water and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

To the dissolved crude product in DCM (400 mL) was added a solution of *m*-CPBA (70%, 32.5 g, 132 mmol) in DCM (200 mL) at 0 °C and was stirred overnight. The reaction mixture was treated with sat. aq. $NaHCO_3$ soln. and extracted with DCM (3 ×). The combined organic phases were washed with water (3 ×) and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via flash column chromatography on silica gel (Et_2O/pentane=4:6) to afford **42** (7.12 g, 46%).

Appearance white solid; **Rf** 0.3 (Et_2O/pentane=4:6); **Mp** 82–84 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.93 – 7.82 (m, 2H), 7.70 – 7.58 (m, 1H), 7.59 – 7.51 (m, 2H), 7.29 – 7.15 (m, 3H), 7.12 – 7.06 (m, 2H), 3.13 – 3.01 (m, 2H), 2.69 (t, J = 7.5 Hz, 2H), 2.12 – 1.96 (m, 2H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 139.95 (C_q), 139.20 (C_q), 133.78 (CH), 129.39 (2 x CH), 128.71 (2 x CH), 128.47 (2 x CH), 128.14 (2 x CH), 126.53 (CH), 55.52 (CH_2), 34.18 (CH_2), 24.29 (CH_2); **FT-IR (cm^{-1}, neat)** 3057, 3026, 2939, 2862, 2360, 2083, 1692, 1566, 1550, 1516, 1484, 1448, 1402, 1359, 1288, 1211, 1186, 1140, 1078, 1022, 997, 908, 876, 792, 742, 692; **HRMS (ESI)** m/z calculated for $C_{15}H_{16}O_2SNa$ $[M+Na]^+$: 283.0763, found: 283.0757.

phenyl((phenylsulfonyl)methyl)sulfane (36)



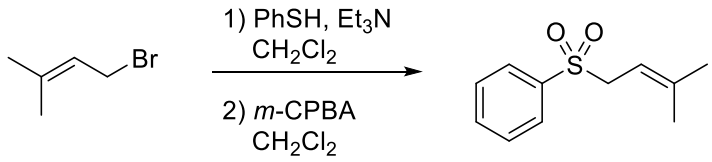
Chemical Formula: $C_{13}H_{12}O_2S_2$
Molecular Weight: 264.36

Intermediate **36** was prepared by a reported procedure[63].

To a solution of chloromethylsulfonylbenzene (8.03 g, 42.2 mmol) in dry DMSO (25 mL) was added thiophenol (8.1 mL, 79.0 mmo). At 0 °C, a solution of potassium *tert*-butoxide (8.83 g, 79 mmol) in dry DMSO (50 mL) was added slowly to the reaction mixture and stirred at room temperature overnight. The reaction mixture was diluted with EtOAc and was washed with water (3 ×) and aq. 0.5 M NaOH soln., each. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford **36** (10.1 g, 79% yield, 87% purity, impurity is thiophenol).

Appearance white solid; **Rf** 0.3 (Et_2O/pentane=2:8); **Mp** 53–58 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.96 – 7.91 (m, 2H), 7.68 – 7.61 (m, 1H), 7.56 – 7.49 (m, 2H), 7.41 – 7.34 (m, 2H), 7.29 – 7.22 (m, 3H), 4.37 (s, 2H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 137.73 (C_q), 134.13 (CH), 132.94 (C_q), 131.63 (2 x CH), 129.28 (2 x CH), 129.19 (2 x CH), 129.04 (2 x CH), 128.22 (CH), 59.78 (CH_2); **FT-IR (cm^{-1}, neat)** 3059, 3000, 2941, 2360, 1894, 1772, 1690, 1579, 1477, 1442, 1374, 1302, 1141, 1079, 1021, 995, 928, 866, 831, 799, 766, 738, 715, 684, 578; **HRMS (ESI)** m/z calculated for $C_{13}H_{12}O_2S_2Na$ $[M+Na]^+$: 287.0171, found: 287.0174.

((3-methylbut-2-en-1-yl)sulfonyl)benzene (27)



Chemical Formula: $C_{11}H_{14}O_2S$
Molecular Weight: 210.29

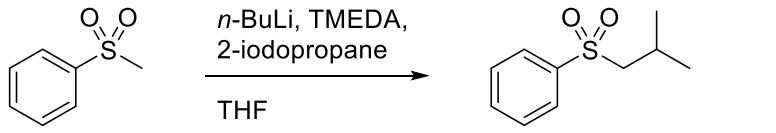
Intermediate **27** was prepared by an adapted reported procedure[59,62,64].

To a solution of thiophenol (4.5 mL, 44.0 mmol) and 1-bromo-3-methyl-but-2-ene (4.7 mL, 40.0 mmol) in DCM (100 mL) was added Et_3N (4.7 mL, 48.0 mmol) at 0 °C and was stirred for 2 h. Then, the reaction mixture was treated with water and extracted with DCM (3 ×). The combined organic phases were washed with brine and dried over Na_2SO_4.

To the dried organic phase was added a solution of *m*-CPBA (70%, 21.7 g, 88.0 mmol) in DCM (200 mL) at 0 °C and was stirred overnight. The reaction mixture was treated with sat. aq. $NaHCO_3$ soln. and extracted with DCM (3 ×). The combined organic phases were washed with water (3 ×) and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via flash column chromatography on silica gel (Et_2O/pentane=4:6) to afford **27** (6.20 g, 74%).

Appearance white solid; **Rf** 0.2 (Et_2O/pentane=2:8); **Mp** 53–55 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.89 – 7.83 (m, 2H), 7.69 – 7.57 (m, 1H), 7.58 – 7.49 (m, 2H), 5.18 (ddq, J = 9.4, 6.5, 1.4 Hz, 1H), 3.78 (d, J = 8.0 Hz, 2H), 1.71 (s, 3H), 1.31 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.08 (C_q), 138.85 (C_q), 133.64 (CH), 129.10 (2 x CH), 128.61 (2 x CH), 110.55 (CH), 56.32 (CH_2), 25.95 (CH_3), 17.85 (CH_3); **FT-IR (cm^{-1}, neat)** 2979, 2911, 2360, 2337, 1713, 1539, 1513, 1442, 1380, 1348, 1296, 1245, 1129, 1081, 1019, 903, 851, 774, 740, 687, 569; **HRMS (ESI)** m/z calculated for $C_{11}H_{14}O_2SNa$ $[M+Na]^+$: 233.0607, found: 233.0609.

(isobutylsulfonyl)benzene (54)



Chemical Formula: $C_{10}H_{14}O_2S$
Molecular Weight: 198.28

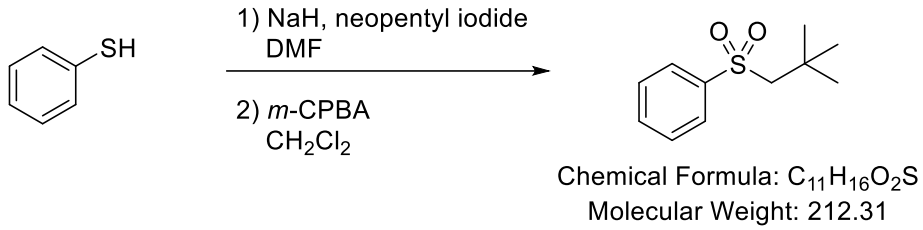
Intermediate **54** was prepared by a reported procedure[36].

To a solution TMEDA (24 mL, 140 mmol) in dry THF (200 mL) was added a solution of methylphenylsulfone (6.25 g, 40.0 mmol) in dry THF (25 mL) at -78 °C. *n*-BuLi (2.5 M in hexanes, 16.8 mL, 42.0 mmol) was added slowly to the reaction mixture and was stirred for 15 min at -78 °C. Then, 2-iodopropane (4.4 mL, 44.0 mmol) was added and the reaction mixture was stirred overnight whilst warming up to room temperature. The reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with Et_2O (3 ×). The combined organic phases were washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=25:75, stained in PMA solution) to afford **54** (5.76 g, 73%).

Appearance colourless oil; **Rf** 0.3 (Et_2O/pentane=25:75); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.94 – 7.88 (m, 2H), 7.68 – 7.61 (m, 1H), 7.60 – 7.52 (m, 2H), 2.99 (d, J = 6.4 Hz, 2H), 2.22 (dh, J = 13.3, 6.6 Hz, 1H), 1.06 (s, 3H), 1.04 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.33 (C_q), 133.66 (CH), 129.39 (2 x CH), 127.95 (2 x CH), 64.10 (CH_2), 24.22 (CH), 22.86 (2 x CH_3); **FT-IR (cm^{-1}, neat)** 2962, 2932, 2875, 2360, 1700, 1583, 1539, 1512, 1466, 1447, 1403, 1372,

1343, 1299, 1257, 1210, 1143, 1083, 1024, 1000, 930, 856, 824, 780, 738, 718, 687, 616, 593, 567; **HRMS (ESI)** m/z calculated for $C_{10}H_{14}O_2SNa$ $[M+Na]^+$: 221.0607, found: 221.0610.

(neopentylsulfonyl)benzene (55)



Chemical Formula: $C_{11}H_{16}O_2S$
Molecular Weight: 212.31

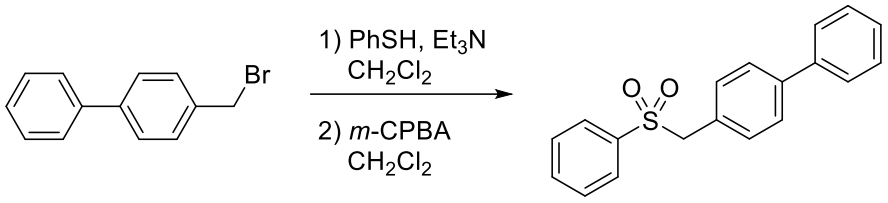
Intermediate **55** was prepared by an adapted reported procedure[59,65].

To a solution of thiophenol (3.5 mL, 34.3 mmol) in dry DMF (30 mL) was added NaH (90%, 1.18 g, 46.0 mmol) portionwise at 0 °C and was stirred for 45 min. Then, neopentyl iodide (8.14 g, 41.1 mmol) was added, the reaction mixture was heated up to 90 °C and stirred overnight. The reaction mixture was treated with water and extracted with DCM (3 ×). The combined organic phases were washed with water and brine, and dried over Na_2SO_4.

The organic phase was cooled to 0 °C, and a solution of *m*-CPBA (70%, 18.8 g, 76.1 mmol) in DCM (100 mL) was added. After stirring for 5 h, the reaction mixture was treated with sat. aq. $NaHCO_3$ soln. and extracted with DCM (3 ×). The combined organic phases were washed with water (3 ×) and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **55** (3.21 g, 44%).

Appearance colourless oil; **Rf** 0.2 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.67 – 7.56 (m, 2H), 7.54 – 7.42 (m, 3H), 2.83 (d, J = 13.6 Hz, 1H), 2.53 (d, J = 13.6 Hz, 1H), 1.19 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 145.46 (C_q), 130.82 (CH), 129.34 (2 x CH), 123.94 (2 x CH), 73.83 (CH_2), 32.02 (C_q), 29.88 (3 x CH_3); **FT-IR (cm^{-1}, neat)** 3057, 2957, 2897, 2867, 2598, 1713, 1574, 1473, 1443, 1385, 1367, 1243, 1184, 1131, 1084, 1070, 1044, 1021, 996, 912, 839, 812, 748, 705, 689, 675, 647; **HRMS (ESI)** m/z calculated for $C_{11}H_{16}OSNa$ $[M+Na-O]^+$: 219.0814, found: 219.0813.

4-((phenylsulfonyl)methyl)-1,1'-biphenyl (56)



Chemical Formula: $C_{19}H_{16}O_2S$
Molecular Weight: 308.40

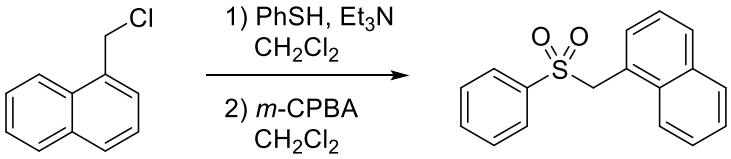
Intermediate **56** was prepared by an adapted reported procedure[59,62].

To a solution of thiophenol (2.4 mL, 23.5 mmol) and 1-(bromomethyl)-4-phenyl-benzene (3.4 mL, 20.0 mmol) in DCM (100 mL) was added Et_3N (3.4 mL, 24.0 mmol) at 0 °C and stirred for 2 h. The reaction mixture was treated with water and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

The obtained crude product was redissolved in DCM (150 mL) and a solution of *m*-CPBA (70%, 10.9 g, 44.1 mmol) in DCM (80 mL) was added at 0 °C and stirred for 2 h. The reaction mixture was treated with sat. aq. $NaHCO_3$ soln. and extracted with DCM (3 ×). The combined organic phase was washed with water (3 ×) and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=6:4, stained in PMA solution) to afford **56** (3.79 g, 61%).

Appearance white solid; **Rf** 0.5 (Et_2O/pentane=6:4); **Mp** 202 – 206 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.73 – 7.30 (m, 12H), 7.21 – 7.11 (m, 2H), 4.35 (s, 2H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 141.74 (C_q), 140.31 (C_q), 138.10 (C_q), 133.88 (CH), 131.36 (2 x CH), 129.07 (2 x CH), 128.98 (2 x CH), 128.79 (2 x CH), 127.80 (CH), 127.37 (2 x CH), 127.19 (2 x CH), 127.10 (C_q), 62.73 (CH_2); **FT-IR (cm^{-1}, neat)** 3055, 2980, 2905, 1478, 1447, 1403, 1301, 1280, 1146, 1078, 1048, 933, 889, 841, 824, 763, 734, 687, 612; **HRMS (ESI)** m/z calculated for $C_{19}H_{16}O_2SNa$ $[M+Na]^+$: 331.0763, found: 331.0761.

1-((phenylsulfonyl)methyl)naphthalene (57)



Chemical Formula: $C_{17}H_{14}O_2S$
Molecular Weight: 282.36

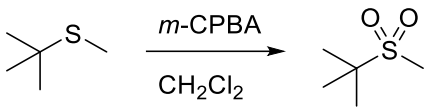
Intermediate **57** was prepared by an adapted reported procedure[59,62].

To a solution of thiophenol (2.4 mL, 23.5 mmol) and 1-(chloromethyl)naphthalene (3.0 mL, 20.0 mmol) in DCM (100 mL) was added Et_3N (3.4 mL, 24.0 mmol) at 0 °C and stirred for 2 h. The reaction mixture was treated with water and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

The obtained crude product was redissolved in DCM (220 mL) and a solution of *m*-CPBA (70%, 10.9 g, 44.2 mmol) in DCM (80 mL) was added at 0 °C and stirred for 2 h. The reaction mixture was treated with sat. aq. $NaHCO_3$ soln. and extracted with DCM (3 ×). The combined organic phases were washed water (3 ×) and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=6:4, stained in PMA solution) to afford **57** (3.18 g, 56%).

Appearance beige solid; **Rf** 0.5 (Et_2O/pentane=1:1); **Mp** 91 – 93 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.88 – 7.75 (m, 3H), 7.66 – 7.57 (m, 2H), 7.56 – 7.46 (m, 1H), 7.43 (ddd, J = 7.6, 5.4, 1.7 Hz, 2H), 7.39 – 7.31 (m, 3H), 7.21 (dd, J = 7.1, 1.2 Hz, 1H), 4.83 (s, 2H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 138.08 (C_q), 133.82 (C_q), 133.80 (CH), 132.18 (C_q), 130.72 (CH), 129.88 (CH), 128.97 (2 x CH), 128.79 (2 x CH), 128.77 (CH), 126.74 (CH), 126.06 (CH), 125.15 (CH), 124.60 (C_q), 123.66 (CH), 59.98 (CH_2); **FT-IR (cm^{-1}, neat)** 3038, 3004, 2973, 2928, 1442, 1405, 1357, 1307, 1150, 1129, 1082, 1033, 1018, 1007, 975, 883, 864, 805, 775, 739, 686, 637; **HRMS (ESI)** m/z calculated for $C_{17}H_{14}O_2SNa$ $[M+Na]^+$: 305.0607, found: 305.0600.

2-methyl-2-(methylsulfonyl)propane (58)



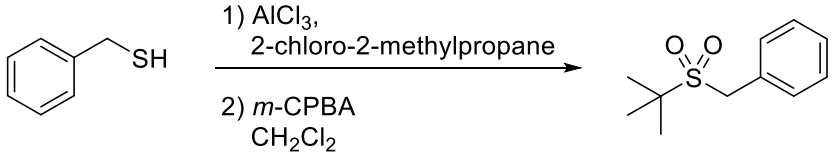
Chemical Formula: $C_5H_{12}O_2S$
Molecular Weight: 136.21

Intermediate **58** was prepared by an adapted reported procedure[59].

To a solution of *tert*-butyl methyl sulfide (5.49 g, 52.7 mmol) in DCM (200 mL) was added a solution of *m*-CPBA (77%, 24.9 g, 110.9 mmol) in DCM (50 mL) at 0 °C and stirred overnight. The reaction mixture was treated with sat. aq. $NaHCO_3$ soln. and extracted with DCM (3 ×). The combined organic phases were washed with water (3 ×) and brine, dried over Na_2SO_4 and concentrated under reduced pressure. No further purification was performed and the obtained crude **58** (>98%) was used as such for further reactions.

Appearance colourless crystals; **Rf** 0.2 (Et_2O/pentane=3:7); **Mp** 70–73 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 2.79 (s, 3H), 1.40 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 58.73 (C_q), 34.23 (CH_3), 23.48 (3 x CH_3); **FT-IR (cm^{-1}, neat)** 3027, 2984, 2938, 2879, 1471, 1403, 1367, 1321, 1276, 1198, 1107, 1038, 952, 807, 755, 604; **HRMS (ESI)** m/z calculated for $C_5H_{12}O_2SNa$ $[M+Na]^+$: 159.0450, found: 159.0449.

((*tert*-butylsulfonyl)methyl)benzene (59)



Chemical Formula: $C_{11}H_{16}O_2S$
Molecular Weight: 212.31

Intermediate **59** was prepared by an adapted reported procedure[59,66].

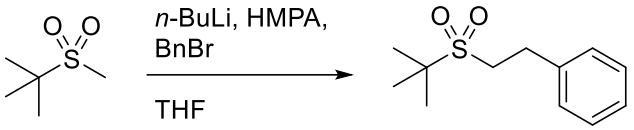
To a solution of $AlCl_3$ (240 mg, 1.8 mmol) in 2-chloro-2-methylpropane (300 mL) was added slowly phenylmethanethiol (4.2 mL, 35.8 mmol) at room temperature and was stirred for 30 min (->HCl-gas evolution! The gases produced were removed by washing in gas wash bottles (NaOH & Bleach).). Then, the reaction mixture was treated with water and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

The crude product was redissolved in DCM (200 mL) and a solution of *m*-CPBA (77%, 18.5 g, 83.0 mmol) in DCM (50 mL) was added at 0 °C and stirred overnight. The reaction mixture was

treated with sat. aq. $NaHCO_3$ soln. and extracted with DCM (3 ×). The combined organic phases were washed water (3 ×) and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:1, stained in PMA solution) to afford **59** (7.15 g, 94%).

Appearance white solid; **Rf** 0.2 (Et_2O/pentane=3:7); **Mp** 119–121 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.48 – 7.32 (m, 5H), 4.20 (s, 2H), 1.43 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 131.32 (CH), 128.85 (4 x CH), 127.38 (C_q), 60.10 (C_q), 52.94 (CH_2), 23.92 (3 x CH_3); **FT-IR (cm^{-1}, neat)** 2974, 2943, 2907, 2877, 1694, 1603, 1571, 1491, 1461, 1403, 1365, 1281, 1200, 1154, 1110, 1030, 1015, 940, 829, 769, 716, 698, 660, 564; **HRMS (ESI)** m/z calculated for $C_{11}H_{16}O_2SNa$ $[M+Na]^+$: 235.0763, found: 235.0763.

(2-(*tert*-butylsulfonyl)ethyl)benzene (60)



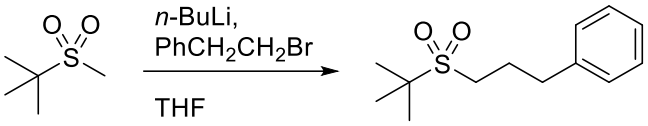
Chemical Formula: $C_{12}H_{18}O_2S$
Molecular Weight: 226.33

Intermediate **60** was prepared by an adapted reported procedure[67].

To a solution of *tert*-butylmethylsulfone **58** (659 mg, 4.8 mmol) in dry THF (30 mL) was added at -78 °C slowly *n*-BuLi (2.5 M in hexanes, 2.0 mL, 5.0 mmol) and after 15 min of stirring at -78 °C HMPA (1.5 mL, 8.5 mmol). The reaction mixture was continued to stir at this temperature for 15 min, benzyl bromide (1.2 mL, 10.1 mmol) was added and the reaction mixture was stirred overnight. The reaction mixture was treated with aq. 1M HCl soln. and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **60** (796 mg, 73%).

Appearance white solid; **Rf** 0.2 (Et_2O/pentane=3:7); **Mp** 103–105 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.37 – 7.22 (m, 5H), 3.27 – 3.07 (m, 4H), 1.43 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 138.48 (C_q), 128.97 (2 x CH), 128.64 (2 x CH), 127.03 (CH), 59.15 (C_q), 47.37 (CH_2), 26.62 (CH_2), 23.54 (3 x CH_3); **FT-IR (cm^{-1}, neat)** 3060, 3028, 2976, 2939, 2876, 1951, 1874, 1810, 1752, 1602, 1493, 1469, 1453, 1403, 1367, 1327, 1282, 1254, 1202, 1105, 1071, 1028, 1006, 944, 910, 806, 763, 734, 696, 661, 572; **HRMS (ESI)** m/z calculated for $C_{12}H_{18}O_2SNa$ $[M+Na]^+$: 249.0920, found: 249.0914.

(3-(*tert*-butylsulfonyl)propyl)benzene (61)



Chemical Formula: $C_{13}H_{20}O_2S$
Molecular Weight: 240.36

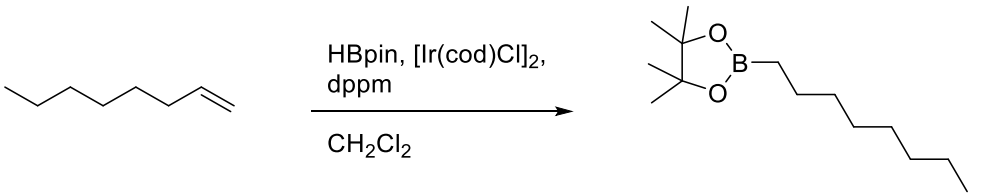
Intermediate **61** was prepared by an adapted reported procedure[67].

To a solution of *tert*-butylmethylsulfone **58** (1.36 g, 10.0 mmol) in dry THF (55 mL) was added *n*-BuLi (2.5 M in hexanes, 4.0 mL, 10.0 mmol) at -78 °C and was stirred for 30 min. A solution of 2-bromoethylbenzene (2.7 mL, 20.0 mmol) in dry THF (5 mL) was added and stirred overnight. The reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **61** (1.75 g, 73%).

Appearance white solid; **Rf** 0.2 (Et_2O/pentane=3:7); **Mp** 58 – 60 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.35 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 2.95 – 2.84 (m, 2H), 2.81 (t, J = 7.5 Hz, 2H), 2.31 – 2.19 (m, 2H), 1.39 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.30 (C_q), 128.71 (2 x CH), 128.58 (2 x CH), 126.49 (CH), 59.09 (C_q), 44.80 (CH_2), 34.66 (CH_2), 23.56 (3 x CH_3), 22.33 (CH_2); **FT-IR (cm^{-1}, neat)** 3027, 2979, 2938, 2872, 1603, 1457, 1401, 1366, 1278, 1202, 1110, 1011, 942, 911, 804, 747, 699, 659, 584; **HRMS (ESI)** m/z calculated for $C_{13}H_{20}O_2SNa$ $[M+Na]^+$: 263.1076, found: 263.1071.

2.5.4 Matteson product synthesis

4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (62)



Chemical Formula: $C_{14}H_{29}BO_2$
Molecular Weight: 240.19

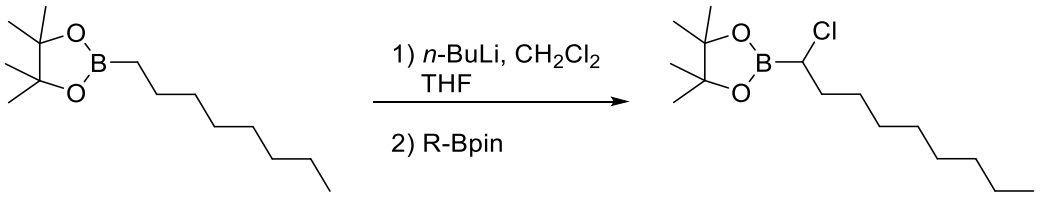
Intermediate **62** was prepared by an adapted reported procedure[68].

In a glovebox, $[Ir(cod)Cl]_2$ (665 mg, 1.0 mmol, 1.5mol%) and dppm (696 mg, 1.8 mmol, 3.0 mol%) were placed in a round bottom flask. Then, pinacolborane (11.0 mL, 75.8 mmol), 1-octene (9.5 mL, 60.5 mmol) and dry DCM (125 mL) were added to the reaction mixture and

stirred at room temperature overnight. The reaction mixture was treated with water and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:99, stained in PMA solution) to afford **62** (14.1 g, 97%).

Appearance colourless liquid; **Rf** 0.3 (Et_2O/pentane=1:99); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 1.37 (p, J = 7.5 Hz, 2H), 1.21 (s, 12H), 1.32 – 1.11 (m, 10H), 0.89 – 0.78 (m, 3H), 0.73 (t, J = 7.7 Hz, 2H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 82.89 (2 x C_q), 32.55 (CH_2), 32.01 (CH_2), 29.49 (CH_2), 29.37 (CH_2), 24.90 (4 x CH_3), 24.11 (CH_2), 22.79 (CH_2), 14.21 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ =34.15; **FT-IR (cm^{-1}, neat)** 2924, 2856, 1462, 1371, 1316, 1217, 1145, 968, 847, 723, 673; **HRMS (ESI)** m/z calculated for $C_{14}H_{30}O_2B$ $[M+H]^+$: 241.2333, found: 241.2337.

2-(1-chlorononyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)



Chemical Formula: $C_{15}H_{30}BClO_2$
Molecular Weight: 288.66

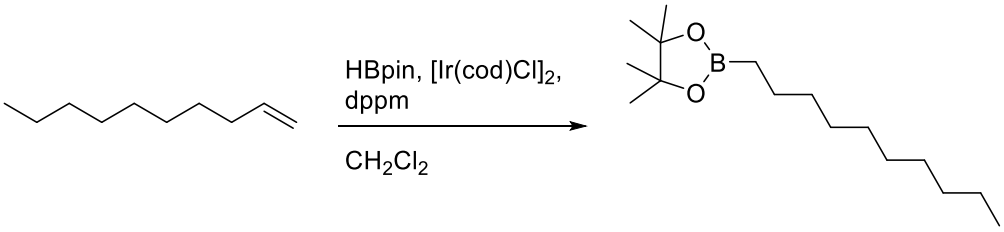
Intermediate **5** was prepared by an adapted reported procedure[69].

In a dry round bottom flask were placed dry THF (30 mL) and dry DCM (1.7 mL, 25.3 mmol). The solvent mixture was cooled down to -100 °C (liquid nitrogen/ethanol bath, internal thermometer for temperature control) and *n*-BuLi (2.5 M in hexanes, 7.5 mL, 18.9 mmol) was added slowly (addition speed is adjusted to the temperature, should not exceed -100 °C). After 20 min of stirring, 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (**62**) (4.34 g, 18.1 mmol) was added and the reaction mixture was slowly warmed up to room temperature overnight. The reaction mixture was diluted with DCM, washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **5** (>98 %).

Appearance colorless liquid; **Rf** 1.0 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 3.40 (dd, J = 8.0, 6.8 Hz, 1H), 1.88 – 1.71 (m, 2H), 1.53 – 1.17 (m, 12H), 1.28 (s, 12H), 0.96 – 0.79 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 84.46 (2 x C_q), 34.20 (CH_2), 31.97 (CH_2), 29.54 (CH_2), 29.32 (CH_2), 29.23 (CH_2), 27.41 (CH_2), 24.73 (2 x CH_3), 24.70 (2 x CH_3), 22.80 (CH_2), 14.23

(CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ =31.41; **FT-IR (cm^{-1}, neat)** 2978, 2925, 2855, 1463, 1414, 1378, 1340, 1269, 1214, 1141, 1008, 967, 885, 847, 722, 675, 653, 578; **HRMS (EI)** m/z calculated for $C_{15}H_{30}O_2BCl$ [M]: 288.2022, found: 288.2027.

2-decyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (63)



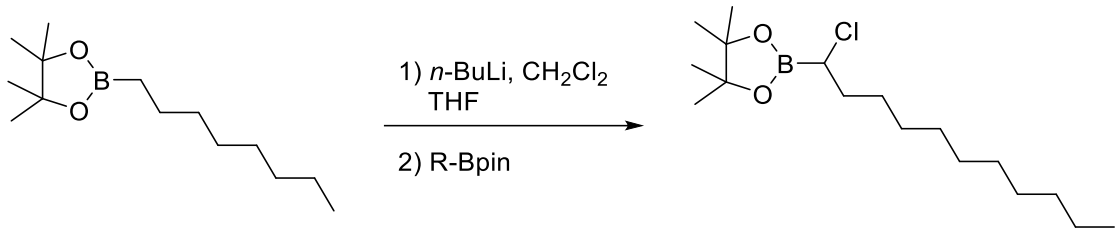
Chemical Formula: $C_{16}H_{33}BO_2$
Molecular Weight: 268.25

Intermediate **63** was prepared by an adapted reported procedure[68].

In a glovebox, $[Ir(cod)Cl]_2$ (595 mg, 0.9 mmol, 1.1 mol%) and dppm (649 mg, 1.7 mmol, 2.1 mol%) were placed in a round bottom flask. Then, pinacolborane (11.7 mL, 80.7 mmol), 1-decene (94%, 12.1 g, 80.7 mmol) and dry DCM (150 mL) were added to the reaction mixture and stirred at room temperature overnight. The reaction mixture was treated with water and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford **63** (20.9 g, 97%).

Appearance yellow liquid; **Rf** 0.8 (Et_2O/pentane=1:9); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 1.39 (p, J = 8.2 Hz, 2H), 1.35 – 1.15 (m, 14H), 1.24 (s, 12H), 0.92 – 0.82 (m, 3H), 0.76 (t, J = 7.7 Hz, 2H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 82.96 (2 x C_q), 32.59 (CH_2), 32.08 (CH_2), 29.78 (CH_2), 29.74 (CH_2), 29.57 (CH_2), 29.50 (CH_2), 24.96 (4 x CH_3), 24.16 (CH_2), 22.84 (CH_2), 14.26 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ =34.10; **FT-IR (cm^{-1}, neat)** 2978, 2923, 2854, 1463, 1372, 1316, 1269, 1237, 1215, 1145, 968, 879, 846, 757, 721, 673, 577; **HRMS (EI)** m/z calculated for $C_{16}H_{33}O_2B$ [M]: 253.2333, found: 253.2338.

2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2)



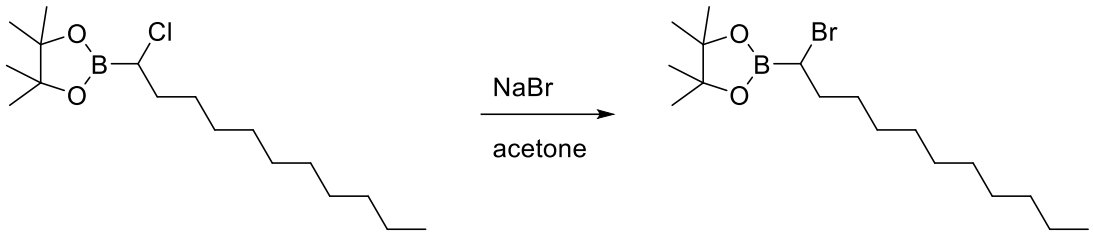
Chemical Formula: $C_{17}H_{34}BClO_2$
Molecular Weight: 316.72

Intermediate **2** was prepared by an adapted reported procedure[69].

In a dry round bottom flask were placed dry THF (60 mL) and dry DCM (3.6 mL, 56.3 mmol). The solvent mixture was cooled down to -100 °C (liquid nitrogen/ethanol bath, internal thermometer for temperature control) and *n*-BuLi (2.5 M in hexanes, 16.9 mL, 42.2 mmol) was added slowly (addition speed is adjusted to the temperature, should not exceed -100 °C). After 20 min of stirring, 2-decyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**63**) (10.8 g, 40.2 mmol) was added and the reaction mixture was slowly warmed up to room temperature overnight. The reaction mixture was diluted with DCM, washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **2** (11.4 g, 90%).

Appearance colorless liquid; **Rf** 1.0 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 3.40 (dd, J = 8.0, 6.8 Hz, 1H), 1.88 – 1.74 (m, 2H), 1.55 – 1.13 (m, 16H), 1.28 (s, 12H), 0.92 – 0.82 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 84.47 (2 x C_q), 34.20 (CH_2), 32.04 (CH_2), 29.72 (CH_2), 29.67 (CH_2), 29.58 (CH_2), 29.47 (CH_2), 29.24 (CH_2), 27.42 (CH_2), 24.74 (2 x CH_3), 24.71 (2 x CH_3), 22.82 (CH_2), 14.25 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ =31.43; **FT-IR (cm^{-1}, neat)** 2924, 2854, 1463, 1414, 1378, 1340, 1269, 1214, 1141, 967, 848, 722, 675, 653, 579; **HRMS (ESI)** m/z calculated for $C_{17}H_{34}O_2BClNa$ $[M+Na]^+$: 339.2233, found: 339.2228.

2-(1-bromoundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (64)



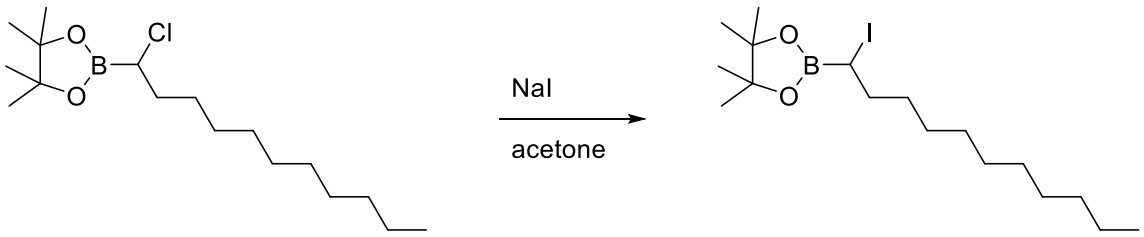
Chemical Formula: $C_{17}H_{34}BBrO_2$
Molecular Weight: 361.17

Intermediate **64** was prepared by an adapted reported procedure[70].

To a solution of 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) (684 mg, 2.2 mmol) in acetone (40 mL) was added NaBr (1.24 g, 12 mmol) and the reaction mixture was refluxed overnight. Then, the reaction mixture was treated with water and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude **64** (743 mg, 95%) was used without further purification.

Appearance yellow liquid; **Rf** 1.0 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 3.31 (t, J = 7.9 Hz, 1H), 1.88 (q, J = 7.4 Hz, 2H), 1.68 – 1.14 (m, 16H), 1.28 (s, 12H), 0.95 – 0.82 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 84.30 (2 x Cq), 34.25 (CH_2), 32.05 (CH_2), 29.72 (CH_2), 29.66 (CH_2), 29.57 (CH_2), 29.47 (CH_2), 29.15 (CH_2), 28.89 (CH_2), 24.67 (2 x CH_3), 24.54 (2 x CH_3), 22.82 (CH_2), 14.26 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ =31.19; **FT-IR (cm^{-1}, neat)** 2924, 2854, 1715, 1642, 1460, 1415, 1378, 1339, 1268, 1215, 1142, 967, 848, 722, 674, 578; **HRMS (EI)** m/z calculated for $C_{17}H_{34}O_2B$ [M-Br]$^+$: 281.2646, found: 281.2652.

2-(1-iodoundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (65)



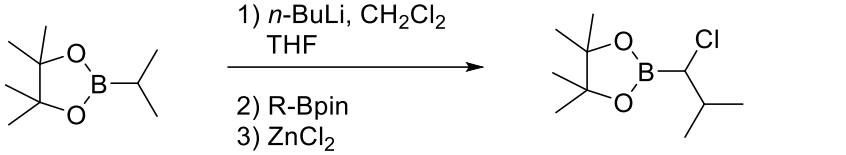
Chemical Formula: $C_{17}H_{34}BIO_2$
Molecular Weight: 408.17

Intermediate **65** was prepared by an adapted reported procedure[70].

To a solution of 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) (1.36 mg, 4.3 mmol) in acetone (10 mL) was added NaI (1.67 g, 11.1 mmol) and the reaction mixture was stirred overnight at room temperature. Then, the reaction mixture was treated with water and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude **65** (>98%) was used without further purification.

Appearance yellow liquid; **Rf** 1.0 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 3.20 (t, J = 8.2 Hz, 1H), 1.96 – 1.73 (m, 2H), 1.50 – 1.07 (m, 16H), 1.27 (s, 6H), 1.26 (s, 6H), 0.92 – 0.82 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 84.03 (2 x C_q), 35.01 (CH_2), 32.05 (CH_2), 31.39 (CH_2), 29.71 (CH_2), 29.66 (CH_2), 29.55 (CH_2), 29.47 (CH_2), 28.96 (CH_2), 24.53 (2 x CH_3), 24.35 (2 x CH_3), 22.82 (CH_2), 14.26 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 31.76; **FT-IR (cm^{-1}, neat)** 2976, 2923, 2853, 1462, 1407, 1374, 1333, 1266, 1215, 1142, 1009, 966, 846, 758, 722, 673, 604, 577; **HRMS (EI)** m/z calculated for $C_{17}H_{34}O_2B$ [M-I]$^+$: 281.2646, found: 281.2651.

2-(1-chloro-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (66)



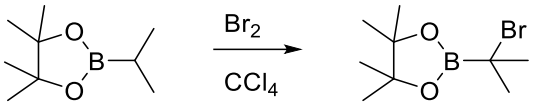
Chemical Formula: $C_{10}H_{20}BClO_2$
Molecular Weight: 218.53

Intermediate **66** was prepared by an adapted reported procedure[69].

In a dry round bottom flask were placed dry THF (25 mL) and dry DCM (1.8 mL, 27.3 mmol). The solvent mixture was cooled down to -100 °C (liquid nitrogen/ethanol bath, internal thermometer for temperature control) and *n*-BuLi (2.5 M in hexanes, 8.2 mL, 20.5 mmol) was added slowly (addition speed is adjusted to the temperature, should not exceed -100 °C). After 20 min of stirring, 2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.32 g, 19.5 mmol) was added and another 20 min was stirred at -100 °C. Then, $ZnCl_2$ (5.05 g, 37.1 mmol) was added in one shot and the reaction mixture was slowly warmed up to room temperature overnight. The reaction mixture was diluted with DCM, washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **66** (2.31 g, 54%).

Appearance colorless liquid; **Rf** 1.0 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 3.24 (d, J = 6.8 Hz, 1H), 2.08 (hept, J = 6.7 Hz, 1H), 1.28 (s, 12H), 1.04 (d, J = 6.7 Hz, 3H), 1.01 (d, J = 6.7 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 84.42 (2 x C_q), 32.06 (CH), 24.74 (2 x CH_3), 24.73 (2 x CH_3), 20.56 (CH_3), 20.06 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 31.23; **FT-IR (cm^{-1}, neat)** 2976, 2933, 2873, 1465, 1411, 1373, 1335, 1273, 1215, 1166, 1140, 1070, 1004, 970, 887, 847, 811, 757, 726, 660, 578; **HRMS (ESI)** m/z calculated for $C_{10}H_{20}O_2BClNa$ $[M+Na]^+$: 241.1137, found: 241.1136.

2-(2-bromopropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (67)



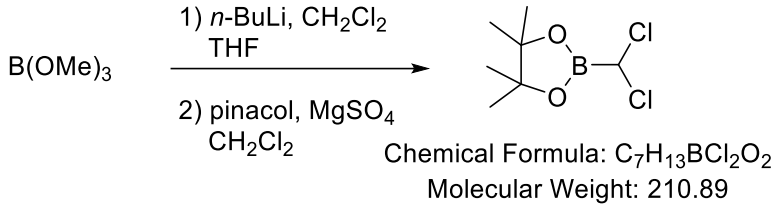
Chemical Formula: $C_9H_{18}BBrO_2$
Molecular Weight: 248.96

Intermediate **67** was prepared by an adapted reported procedure[71].

To a solution of 2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10.0 mL, 50.0 mmol) in dry CCl_4 (50 mL) was added Br_2 (3.1 mL, 60.0 mmol) and was stirred for 4 h at room temperature. The reaction mixture was treated with sat. aq. $Na_2S_2O_3$ soln. and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude **67** (11.7 g, 94%) was used without further purification.

Appearance brown liquid; **Rf** 0.1 (Et_2O/pentane=1:1 **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 1.75 (s, 6H), 1.27 (s, 12H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 84.33 (2 x C_q), 30.39 (2 x CH_3), 24.52 (4 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 31.29; **FT-IR (cm^{-1}, neat)** 2979, 1463, 1362, 1328, 1273, 1214, 1166, 1138, 1087, 1006, 967, 923, 853, 823 668, 594; **HRMS (EI)** m/z calculated for $C_9H_{18}O_2B$ $[M-Br]^+$: 169.1394, found: 169.1397.

2-(dichloromethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (68)



Chemical Formula: $C_7H_{13}BCl_2O_2$
Molecular Weight: 210.89

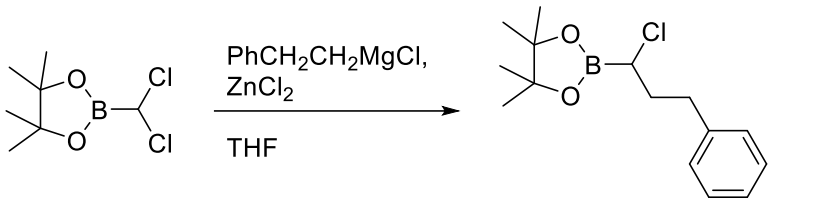
Intermediate **68** was prepared by a reported procedure[72].

In a dry round bottom flask were placed dry THF (100 mL) and dry DCM (5.0 mL, 78.0 mmol). The solvent mixture was cooled down to -100 °C (liquid nitrogen/ethanol bath, internal thermometer for temperature control) and *n*-BuLi (2.5 M in hexanes, 25.5 mL, 63.4 mmol) was added slowly (addition speed is adjusted to the temperature, should not exceed -100 °C). After 20 min of stirring, $B(OMe)_3$ (7.6 mL, 66.8 mmol) was added and the reaction mixture was slowly warmed up to room temperature overnight. Then, the reaction mixture was treated with aq. HCl soln. (6 M, 20 mL), stirred for 2.5 h and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was redissolved in DCM (50 mL) and used for the second step.

To the dissolved crude product was added pinacol (8.12 g, 68.7 mmol) and anhydrous $MgSO_4$ (2-3 tablespoons) and the reaction mixture was stirred at room temperature for 72 h. Then, the reaction mixture was filtered over cotton and concentrated under reduced pressure. Vacuum distillation (b.p. 60 °C at 1 mbar) of the crude product afforded **68** (7.66 g, 56%).

Appearance colorless liquid; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.34 (s, 1H), 1.33 (s, 12H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 85.94 (2 x C_q), 24.58 (4 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 29.03. Physical and spectral data are in accordance with literature data[72].

2-(1-chloro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (69)



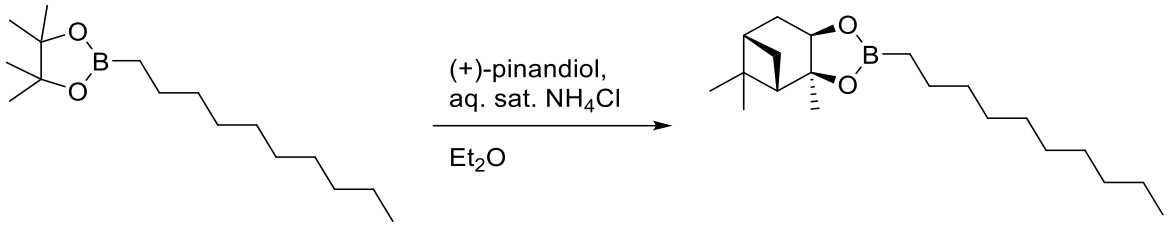
Chemical Formula: $C_{15}H_{22}BClO_2$
Molecular Weight: 280.60

Intermediate **69** was prepared by an adapted reported procedure[69,73].

To a solution of 2-(dichloromethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**68**) (4.21 g, 20.0 mmol) in dry THF (70 mL) was added slowly phenethylmagnesium chloride solution (1.0 M in THF, 30.0 mL, 30.0 mL) at -78 °C. After 20 min of stirring, $ZnCl_2$ (1.33 g, 10.0 mmol) was added in one shot and then, the reaction mixture was slowly warmed up to room temperature overnight. The reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford **69** (4.63 g, 82%).

Appearance colorless liquid; **Rf** 0.8 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.34 – 7.24 (m, 2H), 7.24 – 7.13 (m, 3H), 3.41 (dd, J = 7.9, 6.9 Hz, 1H), 2.92 – 2.67 (m, 2H), 2.20 – 2.02 (m, 2H), 1.28 (s, 12H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 141.26 (C_q), 128.79 (2 x CH), 128.57 (2 x CH), 126.15 (CH), 84.61 (2 x C_q), 35.84 (CH_2), 33.46 (CH_2), 24.77 (2 x CH_3), 24.75 (2 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 31.23; **FT-IR (cm^{-1}, neat)** 3062, 3027, 2978, 2932, 2864, 1603, 1494, 1451, 1413, 1378, 1342, 1269, 1237, 1212, 1139, 1237, 1212, 1139, 1977, 1028, 1005, 967, 898, 874, 847, 774, 747, 698, 677, 656, 574; **HRMS (ESI)** m/z calculated for $C_{15}H_{22}O_2BClNa$ $[M+Na]^+$: 303.1294, found: 303.1291.

(3a*S*,4*S*,6*S*,7a*R*)-2-decyl-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2] dioxaborole (70)



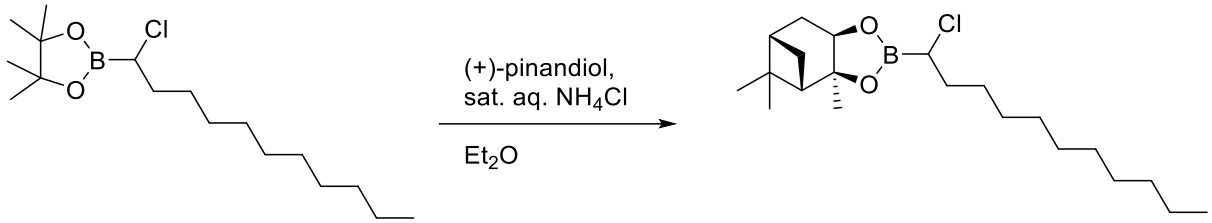
Chemical Formula: $C_{20}H_{37}BO_2$
Molecular Weight: 320.32

Intermediate **70** was prepared by an adapted reported procedure[74].

To a solution of 2-decyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**63**) (2.62 g, 9.3 mmol) and (+)-pinandiol (1.97 g, 11.5 mmol) in Et_2O (40 mL) was added sat. aq. NH_4Cl soln. (4 mL) and then, the reaction mixture was stirred at room temperature overnight. The reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with pentane (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford **70** (>98%).

Appearance colorless oil; **Rf** 1.0 (Et_2O/pentane=1:9); $[\propto]_D^{25}$= +20.1° (c=0.846 g/100 mL $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 4.24 (dd, J = 8.7, 2.0 Hz, 1H), 2.33 (ddt, J = 14.4, 8.8, 2.4 Hz, 1H), 2.21 (dtd, J = 10.9, 6.1, 2.2 Hz, 1H), 2.04 (dd, J = 6.1, 5.0 Hz, 1H), 1.96 – 1.77 (m, 2H), 1.47 – 1.35 (m, 2H), 1.37 (s, 3H), 1.35 – 1.18 (m, 14H), 1.28 (s, 3H), 1.12 (d, J = 10.8 Hz, 1H), 0.92 – 0.82 (m, 3H), 0.91 – 0.72 (m, 2H), 0.84 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 85.38 (C_q), 77.67 (CH), 51.44 (CH), 39.69 (CH), 38.25 (C_q), 35.72 (CH_2), 32.62 (CH_2), 32.08 (CH_2), 29.78 (CH_2), 29.73 (CH_2), 29.57 (CH_2), 29.49 (CH_2), 28.84 (CH_3), 27.23 (CH_3), 26.62 (CH_2), 24.30 (CH_2), 24.14 (CH_3), 22.83 (CH_2), 14.26 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.63; **FT-IR (cm^{-1}, neat)** 2920, 2854, 1459, 1375, 1281, 1233, 1121, 1077, 1052, 1028, 990, 941, 899, 837, 756, 721, 660, 626, 601; **HRMS (EI)** m/z calculated for $C_{20}H_{37}O_2B$ [M]: 320.2881, found: 320.2887.

(3a*S*,4*S*,6*S*,7a*R*)-2-(1-chloroundecyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (1*R/S*-45)



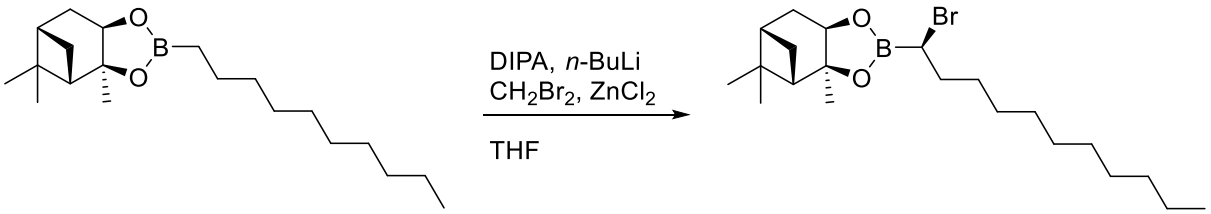
Chemical Formula: $C_{21}H_{38}BClO_2$
Molecular Weight: 368.79

Intermediate **1*R/S*-45** was prepared by an adapted reported procedure[74].

To a solution of 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) (3.16 g, 9.5 mmol) and (+)-pinandiol (2.0 g, 11.7 mmol) in Et_2O (40 mL) was added sat. aq. NH_4Cl soln. (4 mL) and then, the reaction mixture was stirred at room temperature overnight. The reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with pentane (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford **1*R/S*-45** (>98%).

Appearance colorless oil; **Rf** 1.0 (Et_2O/pentane=1:9); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 4.36 (dd, J = 8.8, 1.9 Hz, 1H), 3.46 (ddd, J = 8.1, 6.7, 3.2 Hz, 1H), 2.43 – 2.17 (m, 2H), 2.09 (dd, J = 6.1, 4.8 Hz, 1H), 1.96 – 1.78 (m, 4H), 1.57 – 1.13 (m, 17H), 1.41 (s, 3H), 1.29 (s, 3H), 0.93 – 0.82 (m, 3H), 0.84 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) (characteristic signals, mixture of stereoolefins 1:1) δ = 86.82 (C_q), 86.81 (C_q), 78.63 (CH), 78.61 (CH), 51.31 (CH), 39.50 (CH), 38.36 (C_q), 35.45 (CH_2), 35.43 (CH_2), 34.36 (CH_2), 32.04 (CH_2), 29.72 (CH_2), 29.67 (CH_2), 29.58 (CH_2), 29.47 (CH_2), 29.23 (CH_2), 28.59 (CH_3), 27.45 (CH_2), 27.15 (CH_3), 26.49 (CH_2), 24.10 (CH_3), 22.82 (CH_2), 14.25 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 31.07; **FT-IR (cm^{-1}, neat)** 2921, 2854, 1459, 1377, 1343, 1285, 1242, 1156, 1120, 1077, 1054, 1026, 989, 940, 829, 755, 722, 665, 601; **HRMS (EI)** m/z calculated for $C_{21}H_{38}O_2BCl$ [M]: 368.2648, found: 368.2654.

(3a*S*,4*S*,6*S*,7a*R*)-2-((*R*)-1-bromoundecyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (1*R*-46)



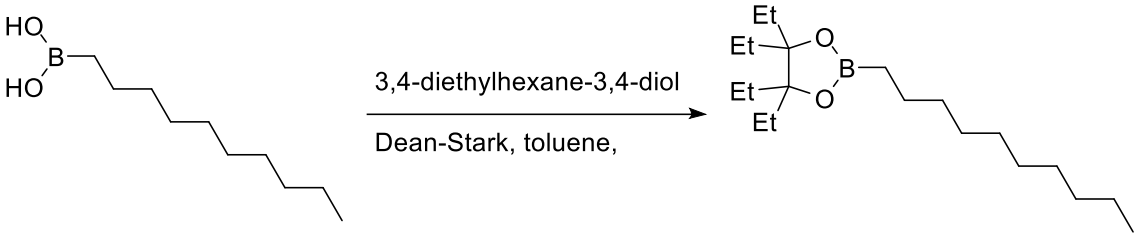
Chemical Formula: $C_{21}H_{38}BBrO_2$
Molecular Weight: 413.25

Intermediate **1*R*-46** was prepared by an adapted reported procedure[69].

In a dry round bottom flask were placed dry THF (5 mL) and dry DIPA (1.45 mL, 10.3 mmol) and cooled down to -78 °C. Then, *n*-BuLi (2.5 M in hexanes, 4.0 mL, 10.0 mmol) was added slowly and the reaction mixture was stirred first 15 min at -78 °C and then, another 15 min at room temperature to complete the LDA formation. In a second dry round bottom flask were placed dry THF (20 mL) and dry CH_2Br_2 (1.8 mL, 26.4 mmol). The solvent mixture was cooled down to -100 °C (liquid nitrogen/ethanol bath, internal thermometer for temperature control) and the freshly prepared LDA solution was added slowly (addition speed is adjusted to the temperature, should not exceed -100 °C). After 20 min of stirring, (3a*S*,4*S*,6*S*,7a*R*)-2-decyl-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2] dioxaborole (**70**) (2.79 g, 8.7 mmol) was added and another 20 min stirred at -100 °C. Then, $ZnCl_2$ (2.69 g, 19.7 mmol) was added in one shot and the reaction mixture was slowly warmed up to room temperature overnight. The reaction mixture was diluted with DCM, washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford **1*R*-46** (2.41 g, 60%).

Appearance yellow liquid; **Rf** 1.0 (Et_2O/pentane=2:8); $[\propto]_{\boldsymbol{D}}^{\mathbf{25}}$= +21.4° (c=0.848 g/100 mL $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 4.36 (dd, J = 8.8, 1.9 Hz, 1H), 3.37 (t, J = 7.8 Hz, 1H), 2.43 – 2.17 (m, 2H), 2.09 (dd, J = 6.1, 4.9 Hz, 1H), 1.98 – 1.79 (m, 4H), 1.56 – 1.17 (m, 17H), 1.40 (s, 3H), 1.29 (s, 3H), 0.87 (t, J = 6.6 Hz, 3H), 0.84 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 86.61 (C_q), 78.54 (CH), 51.41 (CH), 39.48 (CH), 38.45 (C_q), 35.47 (CH_2), 34.38 (CH_2), 32.05 (CH_2), 29.72 (CH_2), 29.68 (CH_2), 29.57 (CH_2), 29.47 (CH_2), 29.16 (CH_2), 28.89 (CH_2), 28.55 (CH_3), 27.16 (CH_3), 26.45 (CH_2), 24.13 (CH_3), 22.82 (CH_2), 14.26 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 30.65; **FT-IR (cm^{-1}, neat)** 2921, 2853, 1495, 1375, 1341, 1284, 1240, 1124, 1076, 1026, 989, 940, 845, 752, 722, 664, 598; **HRMS (EI)** m/z calculated for $C_{21}H_{38}O_2BBr$ [M]: 412.2143, found: 412.2154.

2-decyl-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (71)



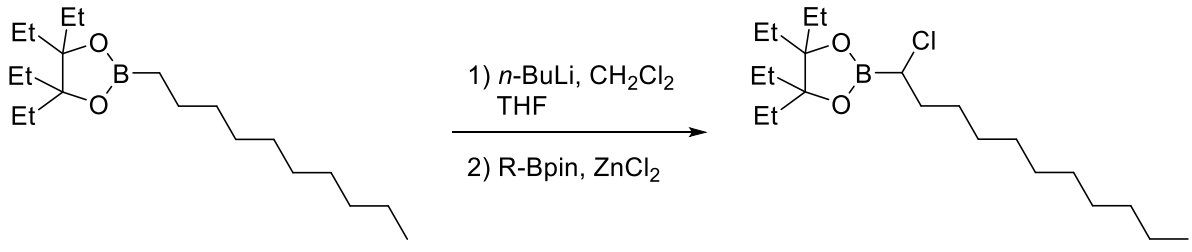
Chemical Formula: $C_{20}H_{41}BO_2$
Molecular Weight: 324.36

Intermediate **71** was prepared by an adapted reported procedure[75].

In a round bottom flask connected to a Dean-Stark trap was placed decylboronic acid (1.92 g, 10.3 mmol), 3,4-diethylhexane-3,4-diol (1.80 g, 10.3 mmol), toluene (40 mL) and was refluxed overnight. The reaction mixture was concentrated under reduced pressure and the crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:98, stained in PMA solution) to afford **71** (1.45 g, 43%).

Appearance colorless oil; **Rf** 1.0 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 1.77 – 1.53 (m, 8H), 1.47 – 1.19 (m, 16H), 0.90 (t, J = 7.5 Hz, 12H), 0.92 – 0.82 (m, 3H), 0.76 (t, J = 7.6 Hz, 2H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 87.97 (2 x C_q), 32.62 (CH_2), 32.09 (CH_2), 29.80 (CH_2), 29.78 (CH_2), 29.62 (CH_2), 29.51 (CH_2), 26.51 (4 x CH_2), 24.38 (CH_2), 22.85 (CH_2), 14.26 (CH_3), 8.95 (4 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.56; **FT-IR (cm^{-1}, neat)** 2923, 2854, 1460, 1378, 1349, 1285, 1236, 1112, 1037, 971, 927, 857, 759, 724, 669; **HRMS (ESI)** m/z calculated for $C_{20}H_{42}O_2B$ $[M+H]^+$: 325.3272, found: 325.3271.

2-(1-chloroundecyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (72)



Chemical Formula: $C_{21}H_{42}BClO_2$
Molecular Weight: 372.83

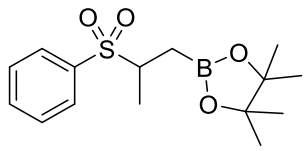
Intermediate **72** was prepared by an adapted reported procedure[69].

In a dry round bottom flask were placed dry THF (30 mL) and dry DCM (0.4 mL, 6.3 mmol). The solvent mixture was cooled down to -100 °C (liquid nitrogen/ethanol bath, internal thermometer for temperature control) and *n*-BuLi (2.5 M in hexanes, 1.7 mL, 4.3 mmol) was added slowly (addition speed is adjusted to the temperature, should not exceed -100 °C). After 20 min of stirring, 2-decyl-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (**71**) (1.31 g, 4.1 mmol) was added and another 20 min was stirred at -100 °C. Then, $ZnCl_2$ (1.16 g, 8.5 mmol) was added in one shot and the reaction mixture was slowly warmed up to room temperature overnight. The reaction mixture was diluted with DCM, washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:98, stained in PMA solution) to afford **72** (1.38 g, 91%).

Appearance colorless oil; **Rf** 1.0 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 3.41 (dd, J = 8.1, 6.8 Hz, 1H), 1.87 – 1.59 (m, 10H), 1.54 – 1.18 (m, 16H), 0.98 – 0.87 (m, 12H), 0.94 – 0.82 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 89.49 (C_q), 34.40 (CH_2), 32.06 (CH_2), 29.73 (CH_2), 29.69 (CH_2), 29.63 (CH_2), 29.48 (CH_2), 29.28 (CH_2), 27.46 (CH_2), 26.31 (2 x CH_2), 26.26 (2 x CH_2), 22.83 (CH_2), 14.26 (CH_3), 8.87 (2 x CH_3), 8.83 (2 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 31.00; **FT-IR (cm^{-1}, neat)** 2925, 2854, 1460, 1384, 1358, 1314, 1289, 1176, 1111, 1069, 971, 922, 856, 761, 722, 672, 649; **HRMS (ESI)** m/z calculated for $C_{21}H_{42}O_2BClNa$ $[M+Na]^+$: 395.2859, found: 395.2860.

2.5.5 Coupling reaction

4,4,5,5-tetramethyl-2-(2-(phenylsulfonyl)propyl)-1,3,2-dioxaborolane (9)



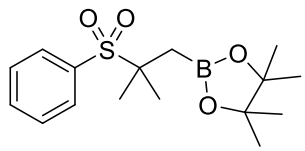
Chemical Formula: $C_{15}H_{23}BO_4S$
Molecular Weight: 310.21

The reaction was performed according to **General Procedure A** with (ethylsulfonyl)benzene (**8**) (193 mg, 1.1 mmol), 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxa-borolane (295 mg, 1.3 mmol), *n*-BuLi (2.5 M in hexanes, 0.45 mL, 1.1 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=4:6, stained in PMA solution) to afford **9** (321 mg, 91%).

Appearance colorless oil; **Rf** 0.5 (Et_2O/pentane=4:6); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.82 – 7.75 (m, 2H), 7.60 – 7.51 (m, 1H), 7.51 – 7.40 (m, 2H), 3.30 – 3.13 (m, 1H), 1.38 (dd, J = 15.8, 4.0 Hz, 1H), 1.19 (d, J = 6.8 Hz, 3H), 1.14 (s, 12H), 0.86 (dd, J = 15.8, 11.0 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 136.69 (C_q), 133.44 (CH), 129.13 (2 x CH), 128.90 (2 x CH), 83.66 (2 x C_q), 57.12 (CH), 24.83 (2 x CH_3), 24.53 (2 x CH_3), 15.54 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not

detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.95; **FT-IR (cm^{-1}, neat)** 2980, 2933, 1447, 1362, 1334, 1299, 1254, 1212, 1140, 1083, 1032, 1009, 969, 904, 875, 842, 767, 729, 687, 629; **HRMS (ESI)** m/z calculated for $C_{15}H_{23}O_4BSNa$ $[M+Na]^+$: 333.1302, found: 333.1298.

4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)propyl)-1,3,2-dioxaborolane (12)

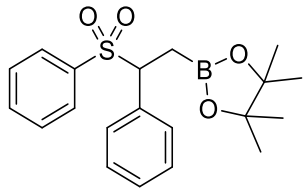


Chemical Formula: $C_{16}H_{25}BO_4S$
Molecular Weight: 324.24

The reaction was performed according to **General Procedure A** with (isopropylsulfonyl)benzene (**4**) (180 mg, 1.0 mmol), 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (299 mg, 1.4 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=35:65, stained in PMA solution) to afford **12** (238 mg, 75%).

Appearance colorless oil; **Rf** 0.3 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.90 – 7.80 (m, 2H), 7.64 – 7.56 (m, 1H), 7.54 – 7.45 (m, 2H), 1.39 (s, 6H), 1.20 (s, 2H), 1.19 (s, 12H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 135.16 (C_q), 133.42 (CH), 130.80 (2 x CH), 128.67 (2 x CH), 83.58 (2 x C_q), 62.08 (C_q), 24.83 (4 x CH_3), 22.17 (2 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.66; **FT-IR (cm^{-1}, neat)** 2979, 2934, 1467, 1445, 1353, 1291, 1217, 1144, 1120, 1074, 967, 913, 889, 847, 788, 760, 726, 691, 630, 575; **HRMS (ESI)** m/z calculated for $C_{16}H_{25}O_4BSNa$ $[M+Na]^+$: 347.1459, found: 347.1457.

4,4,5,5-tetramethyl-2-(2-phenyl-2-(phenylsulfonyl)ethyl)-1,3,2-dioxaborolane (73)



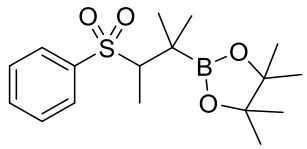
Chemical Formula: $C_{20}H_{25}BO_4S$
Molecular Weight: 372.29

The reaction was performed according to **General Procedure A** with benzenesulfonylmethylbenzene (239 mg, 1.0 mmol), 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaboro-lane (288 mg, 1.3 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=4:6, stained in PMA solution) to afford **73** (256 mg, 67%).

Appearance colorless oil; **Rf** 0.3 (Et_2O/pentane=4:6); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.57 – 7.45 (m, 3H), 7.34 (dd, J = 8.5, 7.1 Hz, 2H), 7.25 – 7.12 (m, 3H), 7.11 – 7.05 (m, 2H), 4.34 (dd, J = 11.4, 5.4 Hz, 1H), 1.80 (dd, J = 15.4, 5.3 Hz, 1H), 1.67 (dd, J = 15.4, 11.4 Hz, 1H), 1.01 (s, 6H), 0.93 (s, 6H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 136.85 (C_q), 133.82 (C_q), 133.43 (CH), 129.83 (2 x CH), 129.36 (2 x CH), 128.60 (CH), 128.55 (2 x CH), 128.12 (2 x CH), 83.70 (2 x C_q), 67.62 (CH), 24.66 (2 x CH_3), 24.29 (2 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B

nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.77; **FT-IR (cm^{-1}, neat)** 2979, 1581, 1449, 1364, 1335, 1301, 1236, 1134,1079, 1021, 999, 965, 884, 846, 823, 764, 732, 714, 693, 627, 561; **HRMS (ESI)** m/z calculated for $C_{20}H_{25}O_4BSNa$ $[M+Na]^+$: 395.1459, found: 395.1452.

4,4,5,5-tetramethyl-2-(2-methyl-3-(phenylsulfonyl)butan-2-yl)-1,3,2-dioxaborolane (11)

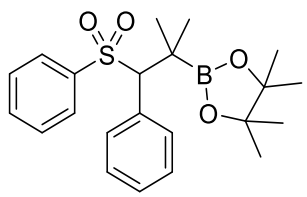


Chemical Formula: $C_{17}H_{27}BO_4S$
Molecular Weight: 338.27

The reaction was performed according to **General Procedure A** with (ethylsulfonyl)benzene (**8**) (172 mg, 1.0 mmol), 2-(2-bromopropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**67**) (312 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=4:6, stained in PMA solution) to afford **11** (200 mg, 59%).

Appearance colorless oil; **Rf** 0.6 (Et_2O/pentane=4:6); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.94 – 7.84 (m, 2H), 7.65 – 7.45 (m, 3H), 3.40 (q, J = 7.1 Hz, 1H), 1.33 (s, 6H), 1.30 (s, 6H), 1.18 (s, 3H), 1.13 (d, J = 7.1 Hz, 3H), 0.95 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.29 (C_q), 133.20 (CH), 129.04 (2 x CH), 128.36 (2 x CH), 83.57 (2 x C_q), 66.10 (CH), 24.98 (2 x CH_3), 24.90 (2 x CH_3), 23.66 (CH_3), 18.09 (CH_3), 7.87 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.88; **FT-IR (cm^{-1}, neat)** 2977, 2930, 1474, 1449, 1366, 1320, 1298, 1257, 1203, 1136, 1062, 1002, 967, 917, 876, 845, 772, 717, 695, 665, 630, 581; **HRMS (ESI)** m/z calculated for $C_{17}H_{27}O_4BSNa$ $[M+Na]^+$: 361.1615, found: 361.1610.

4,4,5,5-tetramethyl-2-(2-methyl-1-phenyl-1-(phenylsulfonyl)propan-2-yl)-1,3,2-dioxaborolane (74)



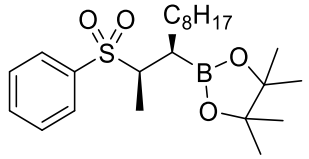
Chemical Formula: $C_{22}H_{29}BO_4S$
Molecular Weight: 400.34

The reaction was performed according to **General Procedure A** with benzenesulfonylmethylbenzene (236 mg, 1.0 mmol), 2-(2-bromopropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**67**) (324 mg, 1.3 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=4:6, stained in PMA solution) to afford **74** (245 mg, 60%).

Appearance colorless oil; **Rf** 0.7 (Et_2O/pentane=4:6); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.54 – 7.42 (m, 3H), 7.38 – 7.17 (m, 7H), 4.35 (s, 1H), 1.49 (s, 3H), 1.35 (s, 6H), 1.33 (s, 6H), 0.72 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.21 (C_q), 133.05 (CH), 131.75 (C_q), 128.62 (CH),

128.42 (CH), 128.34 (CH), 127.98 (CH), 83.88 (2 x C_q), 77.10 (CH), 25.04 (2 x CH_3), 24.98 (2 x CH_3), 24.52 (CH_3), 19.93 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.72; **FT-IR (cm^{-1}, neat)** 2920, 2852, 1581, 1491, 1445, 1410, 1286, 1261, 1200, 1149, 1121, 1078, 1027, 999, 920, 882, 792, 754, 729, 686, 597; **HRMS (ESI)** m/z calculated for $C_{22}H_{29}O_4BSNa$ $[M+Na]^+$: 423.1772, found: 423.1762.

4,4,5,5-tetramethyl-2-((2*R*,3*R*)-2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (10)



Chemical Formula: $C_{23}H_{39}BO_4S$
Molecular Weight: 422.43

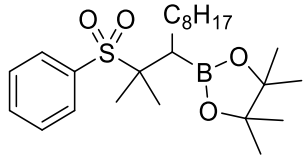
The reaction was performed according to **General Procedure A** with (ethylsulfonyl)benzene (**8**) (163 mg, 1.0 mmol), 2-(1-chlorononyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**) (356 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=4:6, stained in PMA solution) to afford two separable diastereomers of **10** (241 mg, 60%, dr 32:68). Dr was determined on crude product by quantitative NMR analysis.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.47 (Et_2O/pentane=3:7); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.91 – 7.86 (m, 2H), 7.65 – 7.58 (m, 1H), 7.54 (dd, J = 8.3, 6.8 Hz, 2H), 3.30 (p, J = 7.1 Hz, 1H), 1.60 – 1.49 (m, 1H), 1.46 – 1.10 (m, 14H), 1.29 (s, 6H), 1.28 (s, 6H), 1.23 (d, J = 7.5 Hz, 3H), 0.92 – 0.81 (m, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 138.07 (C_q), 133.44 (CH), 129.26 (2 x CH), 129.07 (2 x CH), 83.69 (2 x C_q), 61.83 (CH), 31.97 (CH_2), 29.93 (CH_2), 29.54 (CH_2), 29.33 (CH_2), 28.98 (CH_2), 26.92 (CH_2), 25.24 (2 x CH_3), 25.08 (2 x CH_3), 22.80 (CH_2), 14.22 (CH_3), 12.71 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Minor diastereomer: **Appearance** colorless oil; **Rf** 0.53 (Et_2O/pentane=3:7); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.94 – 7.89 (m, 2H), 7.65 – 7.58 (m, 1H), 7.58 – 7.51 (m, 2H), 3.19 – 3.09 (m, 1H), 1.65 – 1.49 (m, 2H), 1.46 – 1.12 (m, 13H), 1.41 (d, J = 7.1 Hz, 3H), 1.29 (s, 6H), 1.28 (s, 6H), 0.86 (t, J = 6.9 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 138.47 (C_q), 133.41 (CH), 129.12 (2 x CH), 129.10 (2 x CH), 83.54 (2 x C_q), 62.67 (CH), 31.95 (CH_2), 29.60 (CH_2), 29.51 (CH_2), 29.39 (CH_2), 29.33 (CH_2), 29.00 (CH_2), 25.13 (2 x CH_3), 25.05 (2 x CH_3), 22.80 (CH_2), 14.23 (CH_3), 11.02 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.91; **FT-IR (cm^{-1}, neat)** 2925, 2854, 1450, 1375, 1304, 1213, 1141, 1084, 1024, 968, 901, 853, 765, 729, 691, 632, 586; **HRMS (ESI)** m/z calculated for $C_{23}H_{39}O_4BSNa$ $[M+Na]^+$: 445.2554, found: 445.2568.

4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (6)

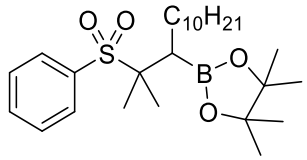


Chemical Formula: $C_{24}H_{41}BO_4S$
Molecular Weight: 436.46

The reaction was performed according to **General Procedure A** with (isopropylsulfonyl)benzene (**4**) (205 mg, 1.1 mmol), 2-(1-chlorononyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**) (359 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.45 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **6** (361 mg, 74%).

Appearance colorless oil; **Rf** 0.6 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.98 – 7.89 (m, 2H), 7.66 – 7.58 (m, 1H), 7.53 (t, J = 7.4 Hz, 2H), 1.68 – 1.36 (m, 2H), 1.41 (s, 3H), 1.35 – 1.02 (m, 13H), 1.31 (s, 3H), 1.30 (s, 12H), 0.86 (t, J = 6.5 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 136.12 (C_q), 133.39 (CH), 130.83 (2 x CH), 128.75 (2 x CH), 83.51 (2 x C_q), 66.02 (C_q), 31.98 (CH_2), 29.99 (CH_2), 29.67 (CH_2), 29.57 (CH_2), 29.34 (CH_2), 26.93 (CH_2), 25.40 (2 x CH_3), 25.31 (2 x CH_3), 22.82 (CH_2), 21.33 (CH_3), 20.20 (CH_3), 14.24 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 30.90; **FT-IR (cm^{-1}, neat)** 2925, 2854, 1463, 1372, 1326, 1295, 1236, 1214, 1138, 1075, 967, 845, 759, 726, 691, 628, 580; **HRMS (ESI)** m/z calculated for $C_{24}H_{41}O_4BSNa$ $[M+Na]^+$: 459.2711, found: 459.2726.

4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)tridecan-3-yl)-1,3,2-dioxaborolane (7)



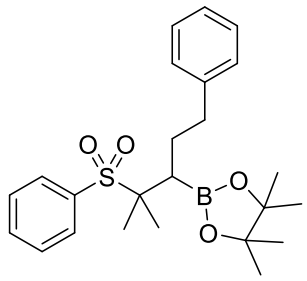
Chemical Formula: $C_{26}H_{45}BO_4S$
Molecular Weight: 464.51

The reaction was performed according to **General Procedure A** with (isopropylsulfonyl)benzene (**4**) (193 mg, 1.1 mmol), 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) (380 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford **7** (301 mg, 62%). (**GPA** with **64**: 62%), (**GPA** with **65**: 78%)

Appearance colorless oil; **Rf** 0.6 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.95 – 7.86 (m, 2H), 7.63 – 7.54 (m, 1H), 7.49 (dd, J = 8.2, 6.6 Hz, 2H), 1.65 – 1.05 (m, 19H), 1.38 (s, 3H), 1.28 (s, 3H), 1.27 (s, 12H), 0.89 – 0.78 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 135.99 (C_q), 133.31 (CH), 130.70 (2 x CH), 128.64 (2 x CH), 83.38 (2 x C_q), 65.88 (C_q), 31.93 (CH_2), 29.86 (CH_2), 29.59 (CH_2), 29.55 (2 x CH_2), 29.49 (CH_2), 29.36 (CH_2), 26.81 (CH_2), 25.29 (CH_3), 25.20 (CH_3), 22.70 (CH_2), 21.28 (CH_3), 20.01 (CH_3), 14.15 (CH_3). Due to coupling to the

quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.65; **FT-IR (cm^{-1}, neat)** 2924, 2854, 1463, 1373, 1325, 1295, 1214, 1138, 1075, 968, 913, 876, 846, 760, 727, 691, 628, 580; **HRMS (ESI)** m/z calculated for $C_{26}H_{45}O_4BSNa$ $[M+Na]^+$: 487.3024, found: 487.3013.

4,4,5,5-tetramethyl-2-(4-methyl-1-phenyl-4-(phenylsulfonyl)pentan-3-yl)-1,3,2-dioxaborolane (18)

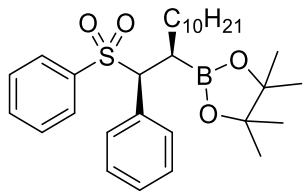


Chemical Formula: $C_{24}H_{33}BO_4S$
Molecular Weight: 428.39

The reaction was performed according to **General Procedure A** with (isopropylsulfonyl)benzene (**4**) (185 mg, 1.0 mmol), 2-(1-chloro-3-phenylpropyl)-4,4,5,5-tetra-methyl-1,3,2-dioxaborolane (**69**) (341 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **18** (358 mg, 84%).

Appearance colorless oil; **Rf** 0.7 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.88 – 7.79 (m, 2H), 7.66 – 7.54 (m, 1H), 7.48 (dd, J = 8.3, 6.9 Hz, 2H), 7.30 – 7.22 (m, 2H), 7.22 – 7.11 (m, 3H), 2.67 (ddd, J = 14.8, 10.5, 4.8 Hz, 1H), 2.39 (ddd, J = 13.5, 10.1, 7.0 Hz, 1H), 2.04 – 1.90 (m, 1H), 1.87 – 1.69 (m, 1H), 1.40 (s, 3H), 1.35 (s, 12H), 1.31 (s, 3H), 1.01 – 0.80 (m, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.20 (C_q), 135.87 (C_q), 133.37 (CH), 130.77 (2 x CH), 128.76 (2 x CH), 128.63 (2 x CH), 128.50 (2 x CH), 126.04 (CH), 83.72 (2 x C_q), 65.72 (C_q), 35.83 (CH_2), 29.23 (CH_2), 25.45 (2 x CH_3), 25.41 (2 x CH_3), 20.96 (CH_3), 20.64 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected. **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 30.68; **FT-IR (cm^{-1}, neat)** 2978, 2935, 1735, 1603, 1450, 1369, 1326, 1291, 1218, 1137, 1074, 1026, 997, 965, 877, 845, 754, 726, 693, 628, 580, 561; **HRMS (ESI)** m/z calculated for $C_{24}H_{34}O_4BS$ $[M+H]^+$: 429.2265, found: 429.2259.

4,4,5,5-tetramethyl-2-((1*S*,2*R*)-1-phenyl-1-(phenylsulfonyl)dodecan-2-yl)-1,3,2-dioxaborolane (3)



Chemical Formula: $C_{30}H_{45}BO_4S$
Molecular Weight: 512.56

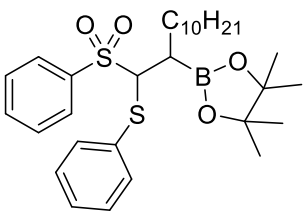
The reaction was performed according to **General Procedure A** with benzenesulfonylmethylbenzene (219 mg, 0.9 mmol), 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaboro-lane (**2**) (388 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford two inseparable diastereomers of **3** (424 mg, 88%, dr 8:92). Dr was determined on crude product by quantitative NMR analysis.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.5 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.52 – 7.43 (m, 1H), 7.42 – 7.35 (m, 2H), 7.33 – 7.24 (m, 2H), 7.24 – 6.99 (m, 3H), 6.97 – 6.87 (m, 2H), 4.31 (d, J = 12.6 Hz, 1H), 1.91 (m, 1H), 1.38 (s, 6H), 1.36 (s, 6H), 1.33 – 0.94 (m, 18H), 0.86 – 0.78 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 137.27 (C_q), 133.27 (CH), 132.63 (C_q), 130.36 (2 x CH), 129.32 (2 x CH), 128.38 (CH), 128.36 (2 x CH), 128.11 (2 x CH), 83.77 (2 x C_q), 73.91 (CH), 31.89 (CH_2), 29.55 (CH_2), 29.49 (CH_2), 29.42 (CH_2), 29.31 (2 x CH_2), 29.15 (CH_2), 28.12 (CH_2), 25.40 (2 x CH_3), 25.31 (2 x CH_3), 22.68 (CH_2), 14.14 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Minor diastereomer (characteristic signals): **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 4.20 (d, *J* = 11.4 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 138.72, 134.95, 132.90, 130.42, 128.78, 128.30, 128.00, 83.35, 72.74, 31.95, 30.01, 29.73, 29.64, 29.61, 29.22, 24.47, 24.40, 22.72, 14.17.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.26; **FT-IR (cm^{-1}, neat)** 2924, 2853, 1451, 1377, 1308, 1256, 1211, 1141, 1082, 1029, 1003, 967, 915, 853, 802, 758, 723, 692, 592, 567; **HRMS (ESI)** m/z calculated for $C_{30}H_{45}O_4BSNa$ $[M+Na]^+$: 535.3024, found: 535.3012.

4,4,5,5-tetramethyl-2-(1-(phenylsulfonyl)-1-(phenylthio)dodecan-2-yl)-1,3,2-dioxaborolane (75)



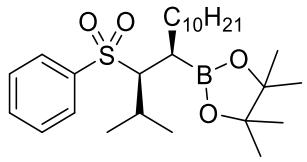
Chemical Formula: $C_{30}H_{45}BO_4S_2$
Molecular Weight: 544.62

The reaction was performed according to **General Procedure A** with phenyl((phenylsulfonyl)methyl)sulfane (**36**) (257 mg, 1.0 mmol), 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaboro-lane (**2**) (382 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in

PMA solution) to afford two inseparable diastereomers of **75** (263 mg, 50%, dr 44:56). Dr was determined on crude product by quantitative NMR analysis.

Mix of diastereomers: **Appearance** colorless oil; **Rf** 0.5 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 1H NMR (300 MHz, CDCl3) δ 7.97 – 7.88 (m, 2H), 7.87 – 7.78 (m, 2H), 7.58 – 7.47 (m, 2H), 7.47 – 7.35 (m, 4H), 7.30 – 7.06 (m, 10H), 4.53 (d, J = 8.3 Hz, 1H), 4.39 (d, J = 5.7 Hz, 1H), 2.06 – 1.82 (m, 4H), 1.80 – 1.01 (m, 56H), 1.17 (d, J = 6.8 Hz, 2H), 0.93 – 0.84 (m, 6H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 138.23 (C_q), 137.49 (C_q), 134.78 (C_q), 134.32 (C_q), 133.61 (CH), 133.44 (CH), 131.88 (2 x CH), 131.64 (2 x CH), 129.95 (2 x CH), 129.40 (2 x CH), 128.89 (4 x CH), 128.68 (2 x CH), 128.66 (2 x CH), 127.71 (CH), 127.63 (CH), 83.96 (2 x C_q), 83.89 (2 x C_q), 76.39 (CH), 76.33 (CH), 31.94 (CH_2), 29.74 (CH_2), 29.63 (CH_2), 29.61 (CH_2), 29.58 (CH_2), 29.51 (CH_2), 29.47 (CH_2), 29.38 (CH_2), 29.30 (CH_2), 28.93 (CH_2), 28.74 (CH_2), 28.11 (CH_2), 25.14 (2 x CH_3), 25.10 (2 x CH_3), 25.02 (2 x CH_3), 24.89 (2 x CH_3), 24.61 (CH), 24.57 (CH), 22.72 (CH_2), 14.17 (2 x CH_3). **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.24 ; **FT-IR (cm^{-1}, neat)** 2923, 2853, 1444, 1373, 1309, 1214, 1140, 1081, 1023, 966, 849, 740, 687, 628, 581; **HRMS (ESI)** m/z calculated for $C_{33}H_{41}O_4BSNa$ $[M+Na]^+$: 567.2711, found: 567.2731.

4,4,5,5-tetramethyl-2-((3*S*,4*R*)-2-methyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (15)



Chemical Formula: $C_{27}H_{47}BO_4S$
Molecular Weight: 478.54

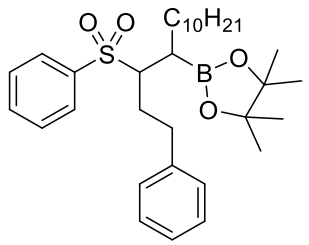
The reaction was performed according to **General Procedure A** with (isobutylsulfonyl)benzene (**54**) (181 mg, 0.9 mmol), 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaboro-lane (**2**) (390 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford two separable diastereomers of **15** (313 mg, 72%, dr 17:83). Dr was determined on crude product by quantitative NMR analysis.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.58 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.93 – 7.86 (m, 2H), 7.61 – 7.43 (m, 3H), 3.26 (dd, J = 6.5, 4.0 Hz, 1H), 2.37 – 2.10 (m, 1H), 1.60 – 1.17 (m, 19H), 1.26 (s, 6H), 1.25 (s, 6H), 1.14 (d, J = 7.9 Hz, 3H), 0.94 (d, J = 7.2 Hz, 3H), 0.89 – 0.79 (m, 3H).**^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.83 (C_q), 133.10 (CH), 128.94 (2 x CH), 128.48 (2 x CH), 83.49 (2 x C_q), 72.19 (CH), 31.94 (CH_2), 29.80 (CH_2), 29.63 (CH_2), 29.59 (CH_2), 29.53 (CH_2), 29.38 (CH_2), 29.17 (CH_2), 28.40 (CH_2), 27.65 (CH), 25.34 (2 x CH_3), 25.03 (2 x CH_3), 22.72 (CH_2), 21.44 (CH_3), 19.45 (CH_3), 14.16 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Minor diastereomer: **Appearance** colorless oil; **Rf** 0.68 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.99 – 7.89 (m, 2H), 7.66 – 7.44 (m, 3H), 3.29 (dd, J = 6.5, 4.1 Hz, 1H), 2.30 (pd, J = 7.0, 4.1 Hz, 1H), 1.64 – 1.12 (m, 19H), 1.29 (s, 6H), 1.28 (s, 6H), 1.07 (d, J = 7.0 Hz, 3H), 0.96 (d, J = 7.0 Hz, 3H), 0.92 – 0.81 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.92 (C_q), 133.17 (CH), 129.04 (2 x CH), 128.63 (2 x CH), 83.60 (2 x C_q), 72.32 (CH), 32.05 (CH_2), 29.93 (CH_2), 29.74 (CH_2), 29.71 (CH_2), 29.65 (CH_2), 29.50 (CH_2), 29.29 (CH_2), 28.53 (CH_2), 27.76 (CH), 25.44 (2 x CH_3), 25.14 (2 x CH_3), 22.83 (CH_2), 21.58 (CH_3), 19.52 (CH_3), 14.26 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.62; **FT-IR (cm^{-1}, neat)** 2924, 2854, 1464, 1373, 1301, 1254, 1213, 1140, 1082, 966, 851, 826, 753, 719, 689, 666, 595; **HRMS (ESI)** m/z calculated for $C_{27}H_{47}O_4BSNa$ $[M+Na]^+$: 501.3180, found: 501.3169.

4,4,5,5-tetramethyl-2-(1-phenyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (22)



Chemical Formula: $C_{32}H_{49}BO_4S$
Molecular Weight: 540.61

The reaction was performed according to **General Procedure A** with ((3-phenylpropyl)sulfonyl)benzene (**42**) (253 mg, 1.0 mmol), 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaboro-lane (**2**) (368 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford two separable diastereomers of **22** (316 mg, 60%, dr 44:56). Dr was determined on crude product by quantitative NMR analysis.

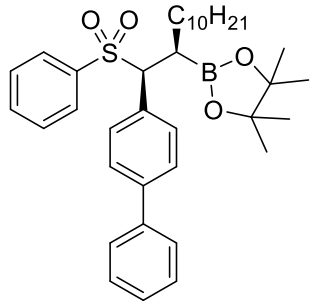
Major diastereomer: **Appearance** colorless oil; **Rf** 0.48 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.97 – 7.83 (m, 2H), 7.68 – 7.49 (m, 3H), 7.32 – 7.03 (m, 5H), 3.37 – 3.28 (m, 1H), 2.78 – 2.51 (m, 2H), 2.22 – 1.88 (m, 2H), 1.64 – 0.99 (m, 19H), 1.26 (s, 6H), 1.25 (s, 6H), 0.88 (t, J = 6.5 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 141.31 (C_q), 139.22 (C_q), 133.49 (CH), 129.22 (2 x CH), 128.95 (2 x CH), 128.58 (2 x CH), 128.45 (2 x CH), 126.24 (CH), 83.75 (2 x C_q), 66.13 (CH), 33.93 (CH_2), 32.06 (CH_2), 29.90 (CH_2), 29.75 (CH_2), 29.71 (CH_2), 29.64 (CH_2), 29.50 (CH_2), 29.43 (CH_2), 29.09 (CH_2), 26.39 (CH_2), 25.27 (2 x CH_3), 24.98 (2 x CH_3), 22.83 (CH_2), 14.26 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Minor diastereomer: **Appearance** colorless oil; **Rf** 0.57 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.90 (d, J = 7.5 Hz, 2H), 7.67 – 7.48 (m, 3H), 7.26 (t, J = 7.3 Hz, 2H), 7.21 –

7.07 (m, 3H), 3.19 – 3.08 (m, 1H), 2.83 – 2.66 (m, 2H), 2.40 – 2.06 (m, 2H), 1.77 – 0.94 (m, 19H), 1.30 (s, 6H), 1.29 (s, 6H), 0.89 (t, J = 6.6 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 141.19 (C_q), 139.24 (C_q), 133.34 (CH), 129.12 (2 x CH), 128.83 (2 x CH), 128.75 (2 x CH), 128.50 (2 x CH), 126.17 (CH), 83.47 (2 x C_q), 65.72 (CH), 34.41 (CH_2), 32.03 (CH_2), 29.69 (CH_2), 29.66 (CH_2), 29.50 (2 x CH_2), 29.45 (CH_2), 29.12 (CH_2), 27.93 (CH_2), 27.87 (CH_2), 25.04 (4 x CH_3), 22.80 (CH_2), 14.24 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.06; **FT-IR (cm^{-1}, neat)** 2924, 2853, 1451, 1374, 1303, 1140, 1083, 1029, 967, 910, 851, 728, 693, 633, 591; **HRMS (ESI)** m/z calculated for $C_{32}H_{49}O_4BSNa$ $[M+Na]^+$: 563.3337, found: 563.3326.

2-((1S,2R)-1-([1,1'-biphenyl]-4-yl)-1-(phenylsulfonyl)dodecan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28)



Chemical Formula: $C_{36}H_{49}BO_4S$
Molecular Weight: 588.65

The reaction was performed according to **General Procedure A** with 4-((phenylsulfonyl)methyl)-1,1'-biphenyl (**56**) (290 mg, 0.9 mmol), 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaboro-lane (**2**) (378 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford two inseparable diastereomers of **28** (319 mg, 58%, dr 13:87). Dr was determined on crude product by quantitative NMR analysis.

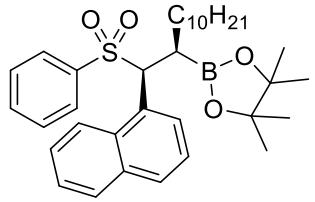
Major diastereomer: **Appearance** colorless oil; **Rf** 0.5 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.60 – 7.53 (m, 2H), 7.52 – 7.39 (m, 7H), 7.38 – 7.29 (m, 3H), 7.01 (d, J = 8.1 Hz, 2H), 4.39 (d, J = 12.5 Hz, 1H), 2.02 – 1.88 (m, 1H), 1.53 – 0.98 (m, 18H), 1.42 (s, 6H), 1.40 (s, 6H), 0.88 – 0.80 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 141.14 (C_q), 140.42 (C_q), 137.37 (C_q), 133.40 (CH), 131.73 (C_q), 130.86 (2 x CH), 129.53 (2 x CH), 128.94 (2 x CH), 128.51 (2 x CH), 127.66 (CH), 127.09 (2 x CH), 126.80 (2 x CH), 83.92 (2 x C_q), 73.78 (CH), 32.00 (CH_2), 29.67 (CH_2), 29.63 (CH_2), 29.56 (CH_2), 29.43 (2 x CH_2), 29.29 (CH_2), 28.28 (CH_2), 25.51 (2 x CH_3), 25.42 (2 x CH_3), 22.78 (CH_2), 14.23 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Minor diastereomer (characteristic signals): **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.13 (d, J = 8.0 Hz, 2H), 4.27 (d, J = 11.2 Hz, 1H), 2.49 – 2.28 (m, 2H), 0.89 (s, 6H), 0.85 (s, 6H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.56 (C_q), 138.82 (C_q), 134.02 (C_q), 130.93 (2 x CH), 128.99 (2 x CH),

128.46 (2 x CH), 126.73 (2 x CH), 83.53 (2 x C_q), 72.58 (CH), 32.06 (CH_2), 29.76 (CH_2), 29.72 (CH_2), 29.51 (CH_2), 29.34 (CH_2), 24.56 (2 x CH_3), 24.52 (2 x CH_3), 22.83 (CH_2), 14.27 (CH_3).

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.11; **FT-IR (cm^{-1}, neat)** 2923, 2852, 1484, 1450, 1377, 1306, 1256, 1211, 1141, 1082, 1004, 967, 848, 757, 723, 691, 669, 595; **HRMS (ESI)** m/z calculated for $C_{36}H_{50}O_4BS$ $[M+H]^+$: 589.3517, found: 589.3514.

4,4,5,5-tetramethyl-2-((1*S*,2*R*)-1-(naphthalen-1-yl)-1-(phenylsulfonyl)dodecan-2-yl)-1,3,2-dioxaborolane (29)



Chemical Formula: $C_{34}H_{47}BO_4S$
Molecular Weight: 562.62

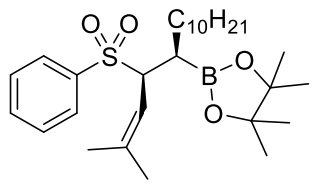
The reaction was performed according to **General Procedure A** with 1-((phenylsulfonyl)methyl)naphthalene (**57**) (291 mg, 1.0 mmol), 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaboro-lane (**2**) (394 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford two inseparable diastereomers of **29** (308 mg, 53%, dr 4:96). Dr was determined on crude product by quantitative NMR analysis.

Major diastereomer: **Appearance** yellow oil; **Rf** 0.5 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.81 – 7.64 (m, 3H), 7.50 – 7.21 (m, 7H), 7.19 – 7.05 (m, 2H), 5.36 (d, J = 12.2 Hz, 1H), 2.15 – 2.00 (m, 1H), 1.44 (s, 6H), 1.42 (s, 6H), 1.33 – 0.92 (m, 18H), 0.85 (t, J = 6.8 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 137.15 (C_q), 133.54 (C_q), 133.17 (CH), 133.02 (C_q), 129.45 (2 x CH), 129.03 (CH), 128.77 (CH), 128.74 (C_q), 128.26 (2 x CH), 127.66 (CH), 126.23 (CH), 125.42 (CH), 124.98 (CH), 122.59 (CH), 83.92 (2 x C_q), 67.09 (CH), 31.95 (CH_2), 29.58 (CH_2), 29.51 (CH_2), 29.43 (CH_2), 29.35 (CH_2), 29.30 (CH_2), 29.03 (CH_2), 28.19 (CH_2), 25.52 (2 x CH_3), 25.44 (2 x CH_3), 22.75 (CH_2), 14.20 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Minor diastereomer (characteristic signals): **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.25 (d, *J* = 11.2 Hz, 1H).

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.95; **FT-IR (cm^{-1}, neat)** 2923, 2852, 1512, 1450, 1376, 1305, 1211, 1141, 1082, 1025, 1002, 967, 848, 806, 777, 753, 724, 687, 668, 640, 591; **HRMS (ESI)** m/z calculated for $C_{34}H_{47}O_4BSNa$ $[M+Na]^+$: 585.3180, found: 585.3175.

4,4,5,5-tetramethyl-2-((4*S*,5*R*)-2-methyl-4-(phenylsulfonyl)pentadec-2-en-5-yl)-1,3,2-dioxaborolane (30)



Chemical Formula: $C_{28}H_{47}BO_4S$
Molecular Weight: 490.55

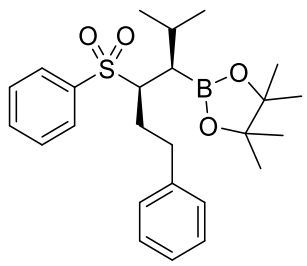
The reaction was performed according to **General Procedure A** with ((3-methylbut-2-en-1-yl)sulfonyl)benzene (**27**) (200 mg, 1.0 mmol), 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaboro-lane (**2**) (381 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford two inseparable diastereomers of **30** (241 mg, 52%, dr 8:92). Dr was determined on crude product by quantitative NMR analysis.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.6 (Et_2O/pentane=3:7); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.82 – 7.77 (m, 2H), 7.62 – 7.52 (m, 1H), 7.52 – 7.44 (m, 2H), 4.92 (dp, J = 10.6, 1.5 Hz, 1H), 4.00 – 3.90 (m, 1H), 1.66 (d, J = 1.4 Hz, 3H), 1.56 – 1.45 (m, 2H), 1.38 – 1.15 (m, 17H), 1.31 (s, 6H), 1.30 (s, 6H), 1.13 (d, J = 1.4 Hz, 3H), 0.86 (t, J = 6.8 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 140.94 (C_q), 138.61 (C_q), 133.18 (CH), 129.41 (2 x CH), 128.69 (2 x CH), 117.88 (CH), 83.65 (2 x C_q), 66.69 (CH), 32.04 (CH_2), 29.90 (CH_2), 29.72 (CH_2), 29.66 (CH_2), 29.59 (CH_2), 29.47 (CH_2), 28.73 (CH_2), 28.18 (CH_2), 25.92 (CH_3), 25.26 (2 x CH_3), 25.22 (2 x CH_3), 22.81 (CH_2), 18.03 (CH_3), 14.23 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Minor diastereomer (characteristic signals): **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 5.25 (dt, J = 11.1, 1.7 Hz, 1H), 3.85 (dd, J = 10.8, 6.5 Hz, 1H), 1.63 (d, J = 1.4 Hz, 3H), 1.16 (d, J = 1.4 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 141.17 (C_q), 139.11 (C_q), 133.10 (CH), 129.24 (2 x CH), 128.64 (2 x CH), 117.38 (CH), 83.52 (2 x C_q), 67.10 (CH), 29.21 (CH_2), 26.09 (CH_3), 25.04 (2 x CH_3), 25.00 (2 x CH_3), 18.06 (CH_3).

Mix of diastereomers: **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 33.07; **FT-IR (cm^{-1}, neat)** 2924, 2854, 1449, 1376, 1301, 1141, 1083, 968, 853, 750, 721, 688, 638, 592; **HRMS (ESI)** m/z calculated for $C_{28}H_{47}O_4BSNa$ $[M+Na]^+$: 513.3180, found: 513.3172.

4,4,5,5-tetramethyl-2-((3*R*,4*R*)-2-methyl-6-phenyl-4-(phenylsulfonyl)hexan-3-yl)-1,3,2-dioxaborolane (14)



Chemical Formula: $C_{25}H_{35}BO_4S$
Molecular Weight: 442.42

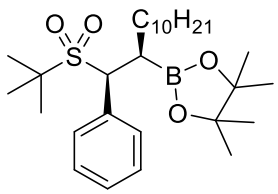
The reaction was performed according to **General Procedure A** with ((3-phenylpropyl)sulfonyl)benzene (**42**) (269 mg, 1.0 mmol), 2-(1-chloro-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**66**) (301 mg, 1.4 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford two inseparable diastereomers of **14** (214 mg, 47%, dr 16:84). Dr was determined on crude product by quantitative NMR analysis.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.5 (Et_2O/pentane=3:7); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.97 – 7.90 (m, 2H), 7.66 – 7.59 (m, 1H), 7.58 – 7.50 (m, 2H), 7.33 – 7.09 (m, 3H), 7.05 – 6.97 (m, 2H), 3.43 (ddd, J = 9.3, 6.1, 5.0 Hz, 1H), 2.72 (ddd, J = 13.8, 10.1, 6.0 Hz, 1H), 2.61 (ddd, J = 13.8, 10.0, 6.5 Hz, 1H), 2.09 – 1.88 (m, 3H), 1.44 (dd, J = 9.3, 5.4 Hz, 1H), 1.36 (s, 6H), 1.35 (s, 6H), 0.99 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.7 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 141.30 (C_q), 139.39 (C_q), 133.44 (CH), 129.16 (2 x CH), 128.96 (2 x CH), 128.55 (2 x CH), 128.39 (2 x CH), 126.17 (CH), 83.75 (2 x C_q), 65.14 (CH), 32.96 (CH_2), 29.41 (CH_2), 26.58 (CH), 25.72 (2 x CH_3), 25.32 (2 x CH_3), 23.23 (CH_3), 20.25 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Minor diastereomer (characteristic signals): **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.14 (dt, J = 8.7, 3.0 Hz, 1H), 2.96 – 2.81 (m, 2H), 2.56 – 2.44 (m, 1H), 2.19 – 2.09 (m, 1H), 1.70 – 1.59 (m, 1H), 1.30 (s, 6H), 1.28 (s, 6H), 0.82 (d, J = 6.7 Hz, 3H), 0.39 (d, J = 6.5 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 141.57 (C_q), 138.93 (C_q), 133.40 (CH), 128.93 (2 x CH), 83.54 (2 x C_q), 64.05 (CH), 34.85 (CH_2), 28.08 (CH_2), 27.30 (CH), 25.42 (2 x CH_3), 25.19 (2 x CH_3), 22.74 (CH_3), 21.77 (CH_3).

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 32.41; **FT-IR (cm^{-1}, neat)** 2968, 2871, 1602, 1449, 1375, 1300, 1215, 1139, 1083, 1027, 999, 969, 877, 848, 806, 750, 727, 692, 594, 576, 555; **HRMS (ESI)** m/z calculated for $C_{25}H_{35}O_4BSNa$ $[M+Na]^+$: 465.2241, found: 465.2235.

2-((1*S*,2*R*)-1-(*tert*-butylsulfonyl)-1-phenyldodecan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)



Chemical Formula: $C_{28}H_{49}BO_4S$
Molecular Weight: 492.57

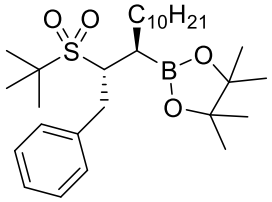
The reaction was performed according to **General Procedure A** with ((*tert*-butylsulfonyl)methyl)benzene (**59**) (208 mg, 1.0 mmol), 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) (372 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford two inseparable diastereomers of **38** (428 mg, 89%, dr 4:96). Dr was determined on crude product by quantitative NMR analysis.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.6 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.42 (d, J = 6.7 Hz, 2H), 7.28 (d, J = 5.1 Hz, 3H), 4.51 (d, J = 12.0 Hz, 1H), 1.93 – 1.78 (m, 1H), 1.72 – 0.46 (m, 27H), 1.28 (s, 6H), 1.27 (s, 6H), 0.87 – 0.75 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 135.12 (C_q), 130.28 (2 x CH), 128.37 (2 x CH), 128.27 (CH), 83.31 (2 x C_q), 65.82 (CH), 61.40 (C_q), 31.85 (CH_2), 29.49 (CH_2), 29.46 (CH_2), 29.38 (CH_2), 29.25 (CH_2), 29.23 (CH_2), 28.48 (CH_2), 27.90 (CH_2), 25.19 (4 x CH_3), 24.20 (3 x CH_3), 22.63 (CH_2), 14.08 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Minor diastereomer (characteristic signals): **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 4.38 (d, J = 9.8 Hz, 1H).**^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 135.77 (C_q), 130.63 (CH), 128.59 (CH), 83.24 (2 x C_q), 66.37 (CH), 62.61 (C_q), 24.10 (CH_3).

Mix of diastereomers: **^{11}B NMR** (96 MHz, $CDCl_3$) δ = 33.49; **FT-IR (cm^{-1}, neat)** 2925, 2854, 1459, 1376, 1320, 1285, 1213, 1143, 1112, 1007, 968, 914, 855, 788, 731, 698, 635, 588, 555; **HRMS (ESI)** m/z calculated for $C_{28}H_{49}O_4BSNa$ $[M+Na]^+$: 515.3337, found: 515.3326.

2-((2*S*,3*R*)-2-(*tert*-butylsulfonyl)-1-phenyltridecan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39)



Chemical Formula: $C_{29}H_{51}BO_4S$
Molecular Weight: 506.59

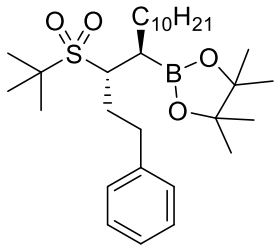
The reaction was performed according to **General Procedure A** with (2-(*tert*-butylsulfonyl)ethyl)benzene (**60**) (215 mg, 1.0 mmol), 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) (428 mg, 1.4 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford two inseparable diastereomers of **39** (332 mg, 69%, dr 17:83). Dr was determined on crude product by quantitative NMR analysis.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.4 (Et_2O/pentane=3:7); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 1H NMR (400 MHz, CDCl3) δ 7.35 – 7.16 (m, 5H), 3.81 (ddd, J = 8.4, 5.1, 3.1 Hz, 1H), 3.33 (dd, J = 15.1, 5.0 Hz, 1H), 3.19 (dd, J = 14.9, 8.7 Hz, 1H), 1.81 – 1.68 (m, 1H), 1.65 – 1.43 (m, 2H), 1.37 (s, 9H), 1.34 – 1.08 (m, 16H), 1.22 (s, 12H), 0.88 (td, J = 6.9, 1.8 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 139.46 (C_q), 129.34 (2 x CH), 128.70 (2 x CH), 126.65 (CH), 83.29 (2 x C_q), 61.37 (CH), 61.19 (C_q), 33.85 (CH_2), 32.07 (CH_2), 30.00 (CH_2), 29.93 (CH_2), 29.75 (2 x CH_2), 29.65 (CH_2), 29.52 (CH_2), 26.41 (CH_2), 25.14 (2 x CH_3), 24.82 (2 x CH_3), 24.29 (3 x CH_3), 22.83 (CH_2), 14.25 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the aliphatic quaternary carbon atom bearing the Bpin was not detected.

Minor diastereomer (characteristic signals): **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.71 (ddd, J = 8.4, 5.3, 2.8 Hz, 1H), 3.29 (dd, J = 15.9, 5.2 Hz, 1H), 3.19 (dd, J = 14.9, 8.7 Hz, 1H), 1.33 (s, 9H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 139.43 (C_q), 129.46 (2 x CH), 128.64 (2 x CH), 126.70 (CH), 83.46 (2 x C_q), 61.16 (CH), 60.78 (C_q), 35.76 (CH_2), 32.05 (CH_2), 29.73 (2 x CH_2), 29.69 (CH_2), 29.57 (CH_2), 29.48 (CH_2), 29.01 (CH_2), 28.20 (CH_2), 24.92 (2 x CH_3), 23.73 (3 x CH_3).

Mix of diastereomers: **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 33.26; **FT-IR (cm^{-1}, neat)** 2924, 2853, 1603, 1459, 1374, 1321, 1283, 1212, 1144, 1108, 1025, 970, 917, 856, 802, 754, 698, 577; **HRMS (ESI)** m/z calculated for $C_{29}H_{51}O_4BSNa$ $[M+Na]^+$: 529.3493, found: 529.3487.

2-((3*S*,4*R*)-3-(*tert*-butylsulfonyl)-1-phenyltetradecan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (40)



Chemical Formula: $C_{30}H_{53}BO_4S$
Molecular Weight: 520.62

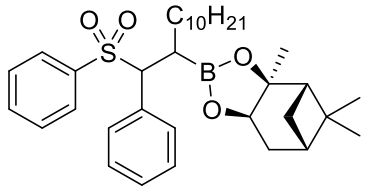
The reaction was performed according to **General Procedure A** with (3-(*tert*-butylsulfonyl)propyl)benzene (**61)** (237 mg, 1.0 mmol), 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) (399 mg, 1.3 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford two inseparable diastereomers of **40** (314 mg, 61%, dr 46:54). Dr was determined on crude product by quantitative NMR analysis.

Major diastereomer: **Appearance** colorless oil; **Rf** 0.5 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.39 – 7.22 (m, 5H), 3.51 (dt, J = 5.5, 3.4 Hz, 1H), 2.92 – 2.66 (m, 2H), 2.39 – 2.15 (m, 2H), 1.77 – 1.57 (m, 2H), 1.56 – 1.11 (m, 17H), 1.38 (s, 9H), 1.30 (s, 6H), 1.29 (s, 6H), 0.94 (t, J = 6.8 Hz, 3H).

Minor diastereomer (characteristic signals): **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 1.40 (s, 9H).

Mix of diastereomers: **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 141.47 (C_q), 141.12 (C_q), 128.80 (2 x CH), 128.59 (CH), 128.57 (CH), 126.30 (CH), 126.28 (CH), 83.53 (2 x C_q), 83.27 (2 x C_q), 60.99 (C_q), 60.87 (C_q), 58.68 (CH), 58.44 (CH), 34.46 (CH_2), 33.92 (CH_2), 32.04 (CH_2), 31.06 (CH_2), 30.09 (CH_2), 29.97 (CH_2), 29.84 (CH_2), 29.74 (CH_2), 29.72 (CH_2), 29.70 (CH_2), 29.63 (CH_2), 29.47 (CH_2), 29.44 (CH_2), 29.24 (CH_2), 27.65 (CH_2), 26.70 (CH_2), 25.27 (2 x CH_3), 25.15 (2 x CH_3), 24.80 (2 x CH_3), 24.72 (2 x CH_3), 24.25 (3 x CH_3), 23.94 (3 x CH_3), 22.80 (2 x CH_2), 14.23 (2 x CH_3); **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 33.82; **FT-IR (cm^{-1}, neat)** 2924, 2853, 1734, 1458, 1374, 1322, 1281, 1213, 1144, 1108, 1010, 968, 853, 802, 747, 699, 578; **HRMS (ESI)** m/z calculated for $C_{30}H_{53}O_4BSNa$ $[M+Na]^+$: 543.3650, found: 543.3646.

(3a*S*,4*S*,6*S*,7a*R*)-3a,5,5-trimethyl-2-(1-phenyl-1-(phenylsulfonyl)dodecan-2-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (47)

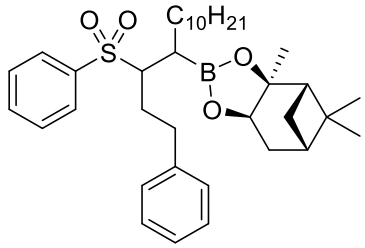


Chemical Formula: $C_{34}H_{49}BO_4S$
Molecular Weight: 564.63

The reaction was performed according to **General Procedure A** with benzenesulfonylmethylbenzene (221 mg, 1.0 mmol), (3a*S*,4*S*,6*S*,7a*R*)-2-(1-chloroundecyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (**1*R*/*S*-45**) (484 mg, 1.3 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford two inseparable diastereomers of **47** (503 mg, 94%). (**GPA** with **1*R*-46**: 50%) Structure assigned from olefin due to complicity of NMR spectra!

Mix of diastereomers (characteristic signals): **Appearance** colorless oil; **Rf** 0.6 (Et_2O/pentane= 3:7); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.52 – 7.43 (m, 1H), 7.43 – 7.36 (m, 2H), 7.29 (t, J = 7.7 Hz, 2H), 7.24 – 7.18 (m, 1H), 7.14 (t, J = 7.3 Hz, 2H), 6.97 – 6.87 (m, 2H), 4.51 – 4.44 (m, 1H), 4.38 – 4.28 (m, 1H), 2.48 – 2.35 (m, 1H), 2.27 – 2.16 (m, 1H), 2.14 (q, J = 5.5 Hz, 1H), 2.04 – 1.87 (m, 3H), 1.57 – 1.52 (m, 3H), 1.52 – 1.44 (m, 1H), 1.34 – 0.97 (m, 18H), 1.33 – 1.28 (m, 3H), 0.88 (s, 3H), 0.84 (t, J = 7.0 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 137.32, 137.13, 133.29, 132.68, 132.64, 130.39, 130.32, 129.43, 129.30, 128.44, 128.40, 128.38, 128.15, 128.13, 86.24, 86.11, 78.03, 77.86, 74.20, 74.15, 51.75, 51.57, 39.75, 39.71, 38.56, 38.50, 35.60, 35.55, 31.90, 29.54, 29.51, 29.49, 29.42, 29.40, 29.31, 29.28, 29.26, 29.14, 29.07, 28.36, 28.31, 28.30, 28.25, 27.25, 27.23, 26.31, 26.15, 24.25, 24.21, 22.69, 14.14.**^{11}B NMR** (96 MHz, $CDCl_3$) δ = 34.12; **FT-IR (cm^{-1}, neat)** 2921, 2854, 1450, 1384, 1338, 1303, 1237, 1146, 1080, 1026, 923, 888, 804, 755, 720, 692, 591, 569; **HRMS (ESI)** m/z calculated for $C_{34}H_{49}O_4BSNa$ $[M+Na]^+$: 587.3337, found: 587.3333.

(3a*S*,4*S*,6*S*,7a*R*)-3a,5,5-trimethyl-2-(1-phenyl-3-(phenylsulfonyl)tetradecan-4-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (44)



Chemical Formula: $C_{36}H_{53}BO_4S$
Molecular Weight: 592.69

The reaction was performed according to **General Procedure A** with ((3-phenylpropyl)sulfonyl)benzene (**42**) (260 mg, 1.0 mmol), (3a*S*,4*S*,6*S*,7a*R*)-2-(1-chloroundecyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d] [1,3,2] dioxaborole (**1*R*/*S*-45**) (478 mg, 1.3 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford two inseparable diastereomers of **44** (396 mg, 67%). (**GPA** with **1*R*-46**: 77%) Structure assigned from olefin due to complicity of NMR spectra!

Mix of diastereomers (characteristic signals): **Appearance** colorless oil; **Rf** 0.6 (Et_2O/pentane= 3:7); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.96 – 7.86 (m, 2H), 7.67 – 7.58 (m, 1H), 7.58 – 7.48 (m, 2H), 7.31 – 7.01 (m, 5H), 4.38 – 4.28 (m, 1H), 3.33 (q, J = 5.8 Hz, 1H), 2.80 – 2.54 (m, 2H), 2.43 – 1.79 (m, 7H), 1.68 – 1.07 (m, 26H), 0.95 – 0.79 (m, 6H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 141.18, 139.18, 133.47, 129.19, 129.13, 128.92, 128.85, 128.72, 128.56, 128.52, 128.44, 126.23, 86.19, 78.01, 77.91, 66.29, 51.46, 39.65, 38.35, 35.57, 33.92, 32.04, 29.87, 29.72, 29.68, 29.67, 29.59, 29.51, 29.48, 29.45, 29.18, 28.48, 27.22, 26.62, 26.60, 24.16, 22.81, 14.24.**^{11}B NMR** (128 MHz, $CDCl_3$) δ = 33.35; **FT-IR (cm^{-1}, neat)** 2921, 2853, 1450, 1374, 1299, 1236, 1141, 1080, 1026, 993, 939, 887, 829, 750, 726, 693, 593; **HRMS (ESI)** m/z calculated for $C_{36}H_{53}O_4BSNa$ $[M+Na]^+$: 615.3650, found: 615.3643.

2.5.6 Olefination reaction

(*Z*)-undec-2-ene (23)



Chemical Formula: $C_{11}H_{22}$
Molecular Weight: 154.30

The reaction was performed according to **General Procedure B** with 4,4,5,5-tetramethyl-2-((2*R*,3*R*)-2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (**10**) (230 mg, 0.5 mmol), TBAF (1.0 M in THF, 3.3 mL, 3.3 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford two inseparable olefins of **23** (66 mg, 79%, *E/Z* 31:69). The compound is reported in the literature[40] and *E/Z* assignment was made by comparison with the reported compound.

E-olefin: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=3:7); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 5.50 – 5.33 (m, 2H), 2.03 (qd, J = 6.7, 1.4 Hz, 2H), 1.62 – 1.57 (m, 3H), 1.41 – 1.15 (m, 12H), 0.94 – 0.81 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 131.08 (CH), 123.73 (CH), 32.07

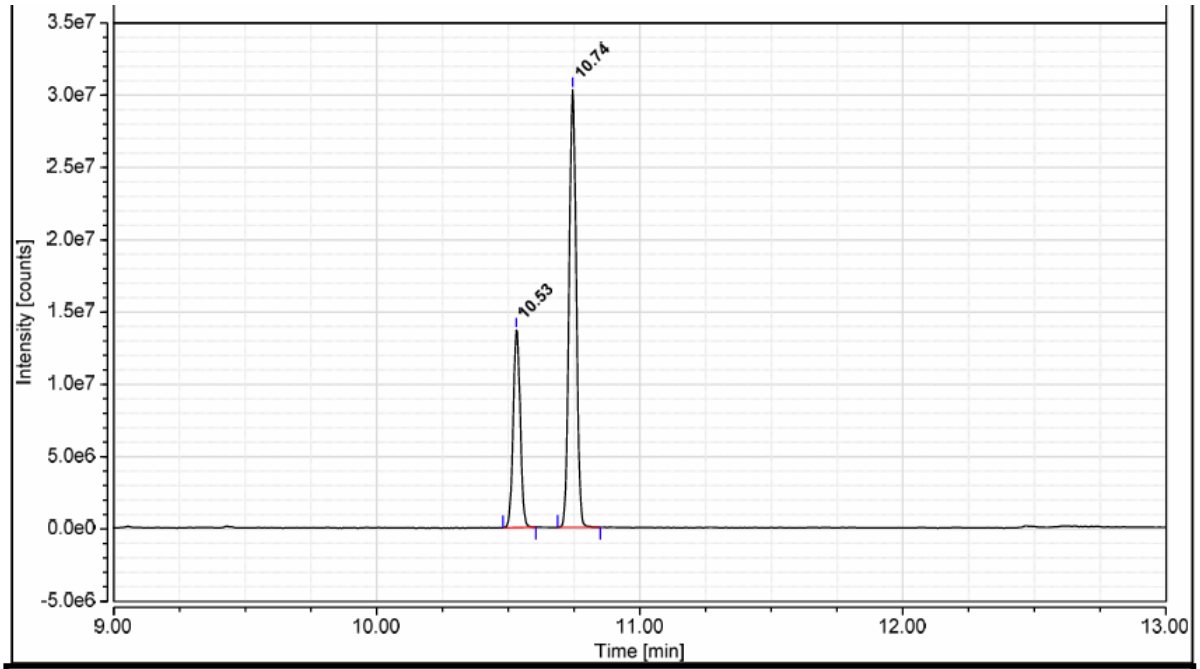
(CH_2), 29.74 (CH_2), 29.69 (CH_2), 29.48 (2 x CH_2), 27.01 (CH_2), 22.84 (CH_2), 14.26 (CH_3), 12.89 (CH_3).

Z-olefin (characteristic signals): **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 1.99 – 1.91 (m, 2H), 1.66 – 1.62 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 131.86 (CH), 124.66 (CH), 32.78 (CH_2), 29.80 (CH_2), 29.67 (CH_2), 29.38 (CH_2), 18.07 (CH_3).

Mix of olefins: **FT-IR (cm^{-1}, neat)** 2923, 2853, 1739, 1513, 1461, 1375, 1343, 1313, 1250, 1164, 1110, 1025, 967, 723, 698; **HRMS (EI)** m/z calculated for $C_{11}H_{22}$ [M]: 154.1722, found: 154.1719.

E/Z ratio was determined by GC-MS analysis:

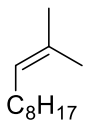
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	10.531	30.63	424448
2	10.745	69.37	961278

2-methylundec-2-ene (19)

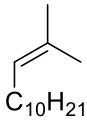


Chemical Formula: $C_{12}H_{24}$
Molecular Weight: 168.32

The reaction was performed according to **General Procedure B** with 4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (**6**) (84 mg, 0.2 mmol), TBAF (1.0 M in THF, 1.2 mL, 1.2 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford **19** (25 mg, 77%).

Appearance colorless liquid; **Rf** 1.0 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.17 – 5.06 (m, 1H), 1.96 (q, J = 6.7 Hz, 2H), 1.69 (d, J = 1.4 Hz, 3H), 1.60 (d, J = 1.4 Hz, 3H), 1.36 – 1.21 (m, 12H), 0.93 – 0.83 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 131.25 (C_q), 125.13 (CH), 32.08 (CH_2), 30.07 (CH_2), 29.73 (CH_2), 29.53 (CH_2), 29.50 (CH_2), 28.22 (CH_2), 25.87 (CH_3), 22.84 (CH_2), 17.80 (CH_3), 14.27 (CH_3); **FT-IR (cm^{-1}, neat)** 2920, 2852, 1739, 1511, 1460, 1375, 1253, 1215, 1162, 1023, 969, 903, 807, 758, 724; **HRMS (EI)** m/z calculated for $C_{12}H_{24}$ [M]: 168.1878, found: 168.1875.

2-methyltridec-2-ene (20)

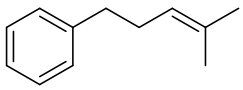


Chemical Formula: $C_{14}H_{28}$
Molecular Weight: 196.38

The reaction was performed according to **General Procedure B** with 4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)tridecan-3-yl)-1,3,2-dioxaborolane (**7**) (316 mg, 0.7 mmol), TBAF (1.0 M in THF, 2.0 mL, 2.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford **20** (110 mg, 82%).

Appearance colorless liquid; **Rf** 1.0 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.18 – 5.06 (m, 1H), 1.96 (q, J = 6.7 Hz, 2H), 1.69 (d, J = 1.4 Hz, 3H), 1.60 (d, J = 1.4 Hz, 3H), 1.38 – 1.17 (m, 16H), 0.94 – 0.83 (m, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 131.24 (C_q), 125.14 (CH), 32.09 (CH_2), 30.08 (CH_2), 29.84 (CH_2), 29.82 (CH_2), 29.77 (CH_2), 29.54 (CH_2), 29.52 (CH_2), 28.22 (CH_2), 25.87 (CH_3), 22.86 (CH_2), 17.80 (CH_3), 14.27 (CH_3); **FT-IR (cm^{-1}, neat)** 2955, 2922, 2853, 1460, 1376, 1310, 1260, 1148, 1119, 1059, 972, 897, 834, 765, 722, 672, 584; **HRMS (EI)** m/z calculated for $C_{14}H_{28}$ [M]: 196.2191, found: 196.2188.

(4-methylpent-3-en-1-yl)benzene (21)



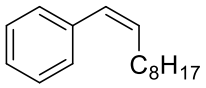
Chemical Formula: $C_{12}H_{16}$
Molecular Weight: 160.26

The reaction was performed according to **General Procedure B** with 4,4,5,5-tetramethyl-2-(4-methyl-1-phenyl-4-(phenylsulfonyl) pentan-3-yl)-1,3,2-dioxaborolane (**18**) (303 mg, 0.7 mmol), TBAF (1.0 M in THF, 2.5 mL, 2.5 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford **21** (>98%).

Appearance colorless oil; **Rf** 1.0 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.34 – 7.12 (m, 5H), 5.18 (tp, J = 7.1, 1.5 Hz, 1H), 2.63 (dd, J = 9.1, 6.7 Hz, 2H), 2.29 (q, J = 7.6 Hz, 2H), 1.69 (d, J = 1.4 Hz, 3H), 1.57 (d, J = 1.4 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.57 (C_q), 132.29 (C_q), 128.59 (2 x CH), 128.36 (2 x CH), 125.80 (CH), 123.88 (CH), 36.30 (CH_2), 30.21 (CH_2), 25.83 (CH_3), 17.79 (CH_3); **FT-IR (cm^{-1}, neat)** 3061, 3027, 2967, 2921, 2855, 1940,

1675, 1603, 1494, 1449, 1377, 1156, 1133, 1106, 1074, 1028, 983, 906, 824, 743, 591, 567; **HRMS (EI)** m/z calculated for $C_{12}H_{16}$ [M]: 160.1252, found: 160.1250.

(*Z*)-dec-1-en-1-ylbenzene (32)



Chemical Formula: $C_{16}H_{24}$
Molecular Weight: 216.37

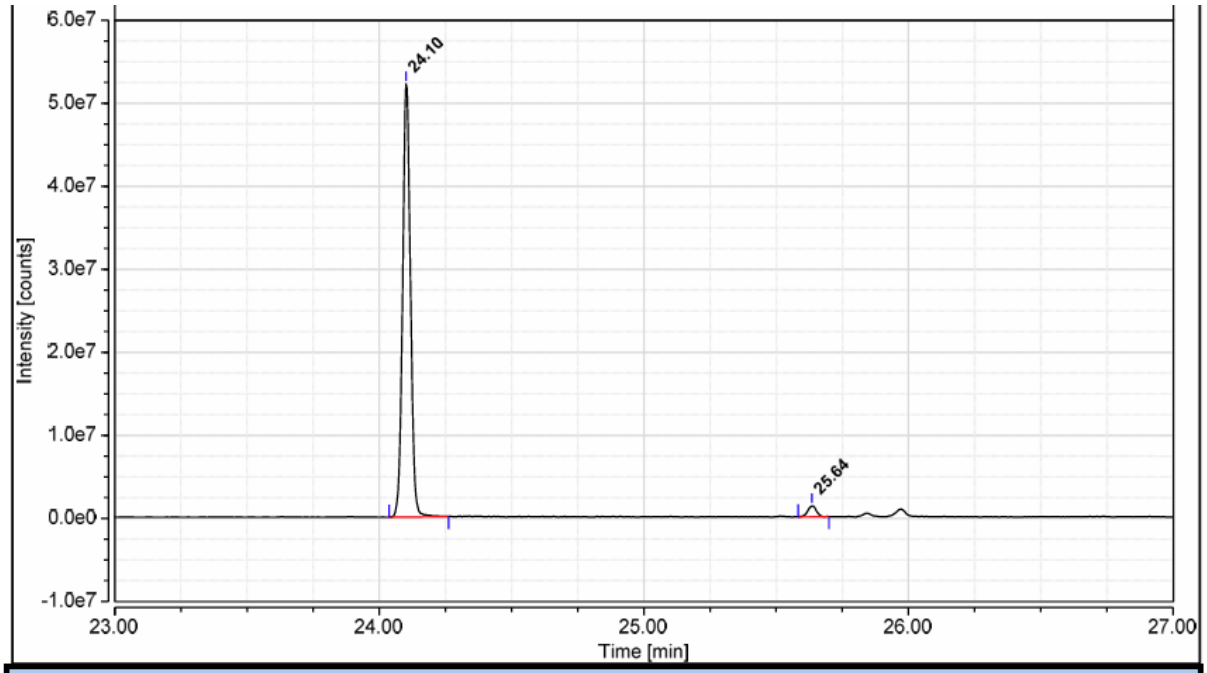
The reaction was performed according to **General Procedure C** with benzenesulfonylmethylbenzene (225 mg, 1.0 mmol), 2-(1-chlorononyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**) (353 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), dry THF (5.0 mL) and TBAF (1.0 M in THF, 6.0 mL, 6.0 mmol). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8 and 1% Et_3N, stained in PMA solution) to afford two inseparable olefins of **32** (188 mg, 90% , *E/Z* 3:97). The *E/Z* assignment was made by comparison with a reported similar compound[39] (shorter alkyl chain C_7H_{15}).

Z-olefin: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=2:8); **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 7.39 – 7.26 (m, 4H), 7.26 – 7.18 (m, 1H), 6.42 (dt, J = 11.7, 1.9 Hz, 1H), 5.70 (dt, J = 11.6, 7.3 Hz, 1H), 2.35 (qd, J = 7.3, 1.9 Hz, 2H), 1.52 – 1.43 (m, 2H), 1.40 – 1.23 (m, 10H), 0.97 – 0.84 (m, 3H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 138.33 (C_q), 133.76 (CH), 129.17 (2 x CH), 128.99 (CH), 128.52 (2 x CH), 126.83 (CH), 32.36 (CH_2), 30.45 (CH_2), 29.94 (CH_2), 29.84 (CH_2), 29.76 (CH_2), 29.12 (CH_2), 23.15 (CH_2), 14.34 (CH_3).

E-olefin (characteristic signals): **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 6.27 (dt, J = 15.8, 6.8 Hz, 1H), 2.26 – 2.20 (m, 2H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 138.50 (C_q), 131.78 (CH), 130.02 (CH), 128.88 (2 x CH), 127.14 (CH), 126.28 (2 x CH), 33.51 (CH_2), 32.01 (CH_2), 25.07 (CH_3).

Mix of olefins: **FT-IR (cm^{-1}, neat)** 3023, 2922, 2852, 1491, 1456, 1373, 1309, 1070, 1023, 961, 909, 738, 692, 612, 495; **HRMS (EI)** m/z calculated for $C_{16}H_{24}$ [M]: 216.1873, found: 216.1875.

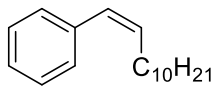
E/Z ratio was determined by GC-MS analysis:
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	24.101	97.31	1792358
2	25.635	2.69	49641

(*Z*)-dodec-1-en-1-ylbenzene (31)



Chemical Formula: $C_{18}H_{28}$
Molecular Weight: 244.42

The reaction was performed according to **General Procedure C** with benzenesulfonyl methylbenzene (227 mg, 1.0 mmol), 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) (380 mg, 1.2 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), dry THF (5.0 mL) and TBAF (1.0 M in THF, 6.0 mL, 6.0 mmol). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8 and 1% Et_3N, stained in PMA solution) to afford two inseparable olefins of **31** (204 mg, 85% , *E/Z* 5:95). The *E/Z* assignment was made by comparison with a reported similar compound[39] (shorter alkyl chain C_7H_{15}).

(**GPB** with **1*R/S*-45**: 80%, *E/Z* 3:97), (**GPC** with **1*R*-46**: 90%, *E/Z* 0.3:99.7), (**GPC** with **59**: 81%, *E/Z* 3:97)

Z-olefin: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane= 2:8); **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 7.38 – 7.27 (m, 4H), 7.25 – 7.18 (m, 1H), 6.42 (dt, J = 11.6, 1.9 Hz, 1H), 5.70 (dt, J = 11.6, 7.3 Hz, 1H), 2.34 (qd, J = 7.3, 1.9 Hz, 2H), 1.53 – 1.41 (m, 2H), 1.41 – 1.22 (m, 14H), 0.91 (t, J = 6.8 Hz, 3H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 138.33 (C_q), 133.76 (CH), 129.16 (2 x CH), 128.99 (CH), 128.52 (2 x CH), 126.83 (CH), 32.40 (CH_2), 30.45 (CH_2), 30.09 (2 x CH_2), 29.98 (CH_2), 29.84 (CH_2), 29.82 (CH_2), 29.12 (CH_2), 23.17 (CH_2), 14.35 (CH_3).

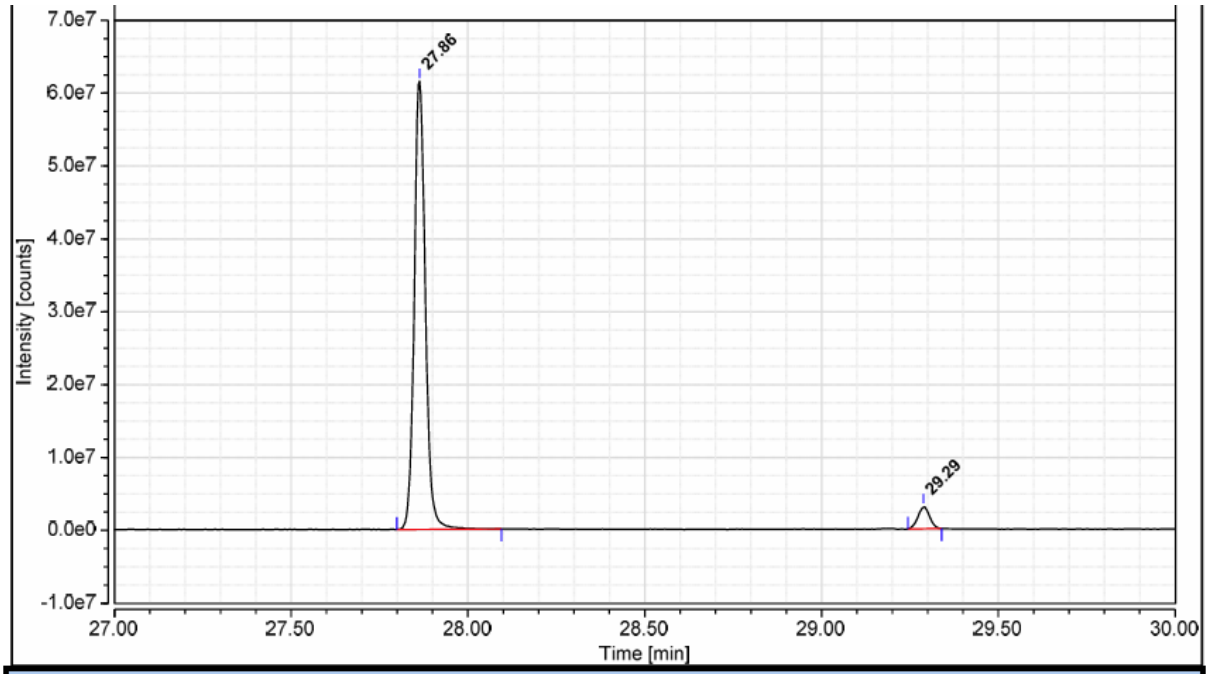
E-olefin (characteristic signals): **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 6.27 (dt, *J* = 15.8, 6.8 Hz, 1H), 2.27 – 2.19 (m, 2H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 138.50 (C_q), 131.78 (CH), 130.02 (CH), 128.87 (2 x CH), 127.14 (CH), 126.28 (2 x CH), 33.50 (CH_2), 30.12 (CH_2), 30.01 (CH_2), 29.87 (CH_2), 29.73 (CH_2).

Mix of olefins: **FT-IR (cm^{-1}, neat)** 2922, 282, 1493, 1461, 1374, 1073, 1027, 962, 912, 766, 695; **HRMS (EI)** m/z calculated for $C_{18}H_{28}$ [M]: 244.2186, found: 244.2190.

E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min

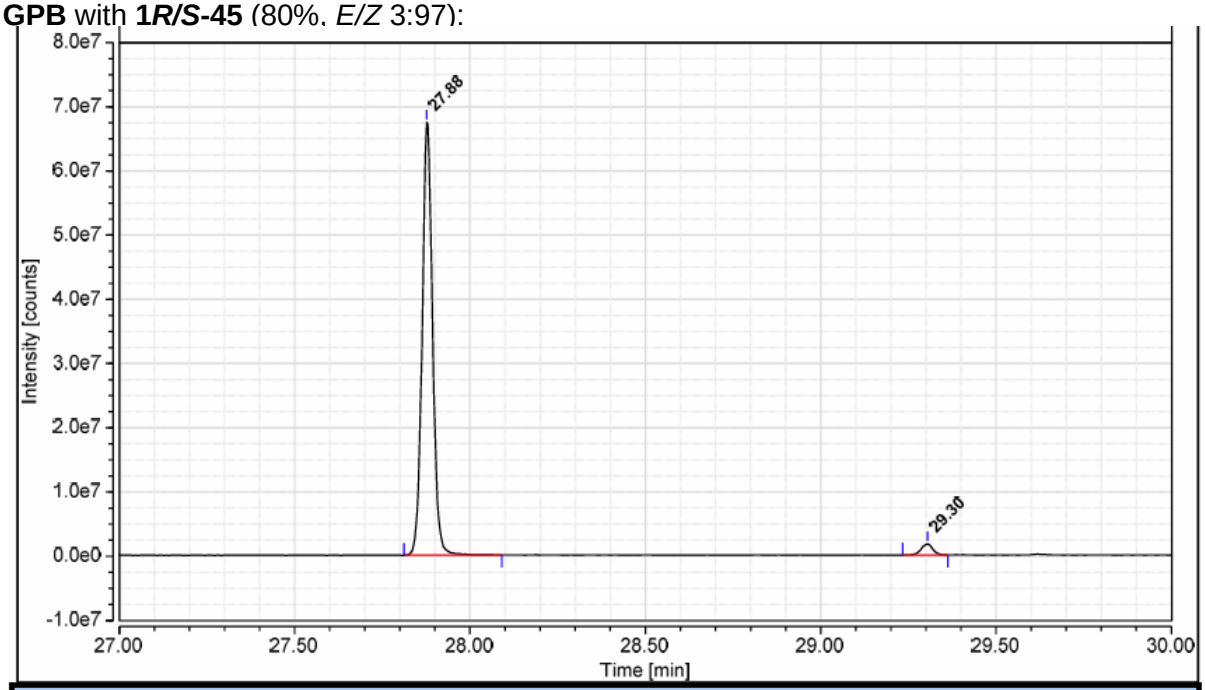
GPC (85% , *E/Z* 5:95):



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	27.863	95.17	2249925
2	29.288	4.83	114140

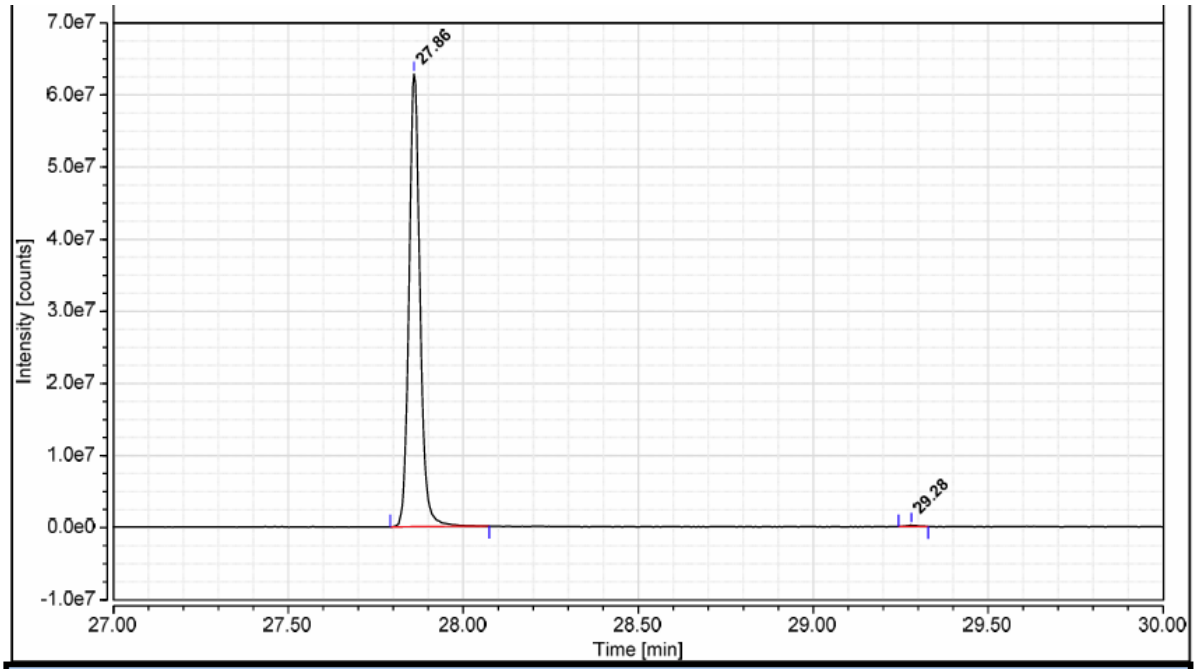
GPB with **1*R/S*-45** (80%, *E/Z* 3:97):



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	27.876	97.12	2320026
2	29.305	2.88	68901

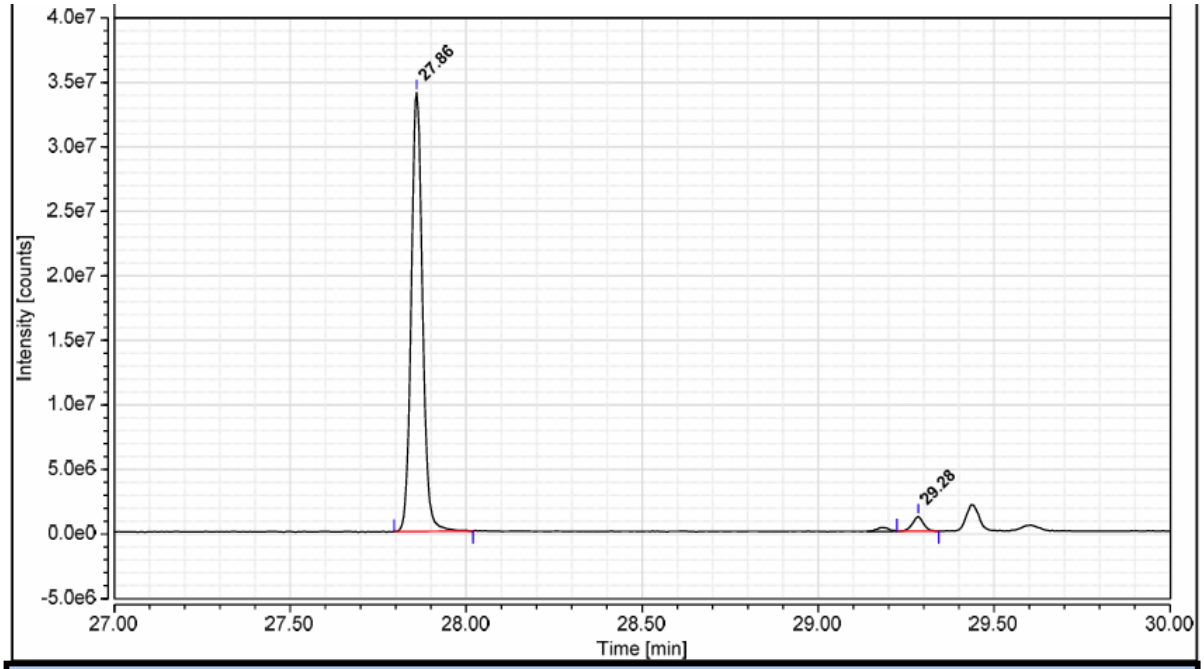
GPC with **1*R*-46** (90%, *E/Z* 0.3:99.7):



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	27.859	99.67	2285604
2	29.281	0.33	7556

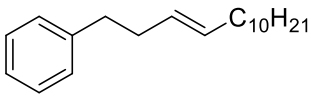
GPC with **59**: (81%, *E/Z* 3:97)



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	27.860	96.83	1263004
2	29.285	3.17	41345

(*E*)-tetradec-3-en-1-ylbenzene (24)



Chemical Formula: $C_{20}H_{32}$
Molecular Weight: 272.48

The reaction was performed according to **General Procedure B** with 4,4,5,5-tetramethyl-2-(1-phenyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (**22**) (370 mg, 0.7 mmol), TBAF (1.0 M in THF, 4.1 mL, 4.1 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9, stained in PMA solution) to afford two inseparable olefins of **24** (143 mg, 77%, *E/Z* 53:47). The *E/Z* assignment was made by comparison with a reported similar compound[39] (shorter alkyl chain C_7H_{15}).

(**GPB** with **1*R/S*-45**: 74%, *E/Z* 68:32), (**GPB** with **1*R*-46**: 90%, *E/Z* 66:34), (**GPB** with **40**: 72%, *E/Z* 74:26), (**GPC** with **61**: 75%, *E/Z* 75:25), (**GPC** with **72**: 83%, *E/Z* 55:45)

E-olefin: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=1:9); **^{1}H-NMR** (300 MHz, CD_2Cl_2) δ = 7.31 – 7.23 (m, 2H), 7.23 – 7.13 (m, 3H), 5.45 (td, J = 3.6, 1.7 Hz, 2H), 2.67 (t, J = 7.7 Hz, 2H), 2.42 – 2.23 (m, 2H), 2.04 – 1.91 (m, 2H), 1.39 – 1.20 (m, 16H), 0.96 – 0.85 (m, 3H); **^{13}C-NMR** (75 MHz, CD_2Cl_2) δ = 142.76 (C_q), 131.62 (CH), 129.70 (CH), 128.87 (2 x CH), 128.57 (2 x CH), 126.03 (CH), 36.54 (CH_2), 34.94 (CH_2), 32.99 (CH_2), 32.37 (CH_2), 30.09 (2 x CH_2), 30.02 (CH_2), 29.97 (CH_2), 29.80 (CH_2), 29.57 (CH_2), 23.14 (CH_2), 14.32 (CH_3).

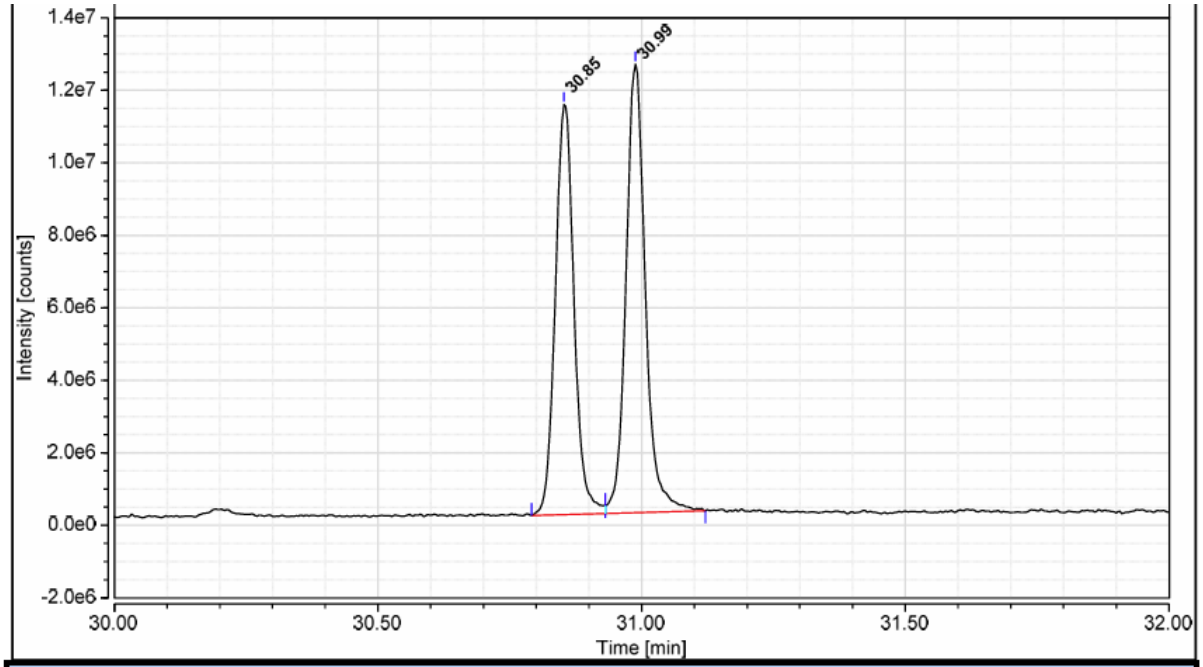
Z-olefin (characteristic signals): **^{1}H-NMR** (300 MHz, CD_2Cl_2) δ = 5.42 – 5.37 (m, 2H), 2.72 – 2.60 (m, 3H).; **^{13}C-NMR** (75 MHz, CD_2Cl_2) δ = 142.73 (C_q), 131.14 (CH), 129.01 (CH), 128.85 (2 x CH), 128.60 (2 x CH), 126.10 (CH), 36.40 (CH_2), 30.14 (CH_2), 29.74 (CH_2), 29.61 (CH_2), 27.64 (CH_2).

Mix of olefins: **FT-IR (cm^{-1}, neat)** 3026, 2921, 2852, 1738, 1603, 1495, 1456, 1375, 1076, 1029, 966, 903, 741, 722, 696, 570; **HRMS (EI)** m/z calculated for $C_{20}H_{32}$ [M]: 272.2499, found: 272.2502.

E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min

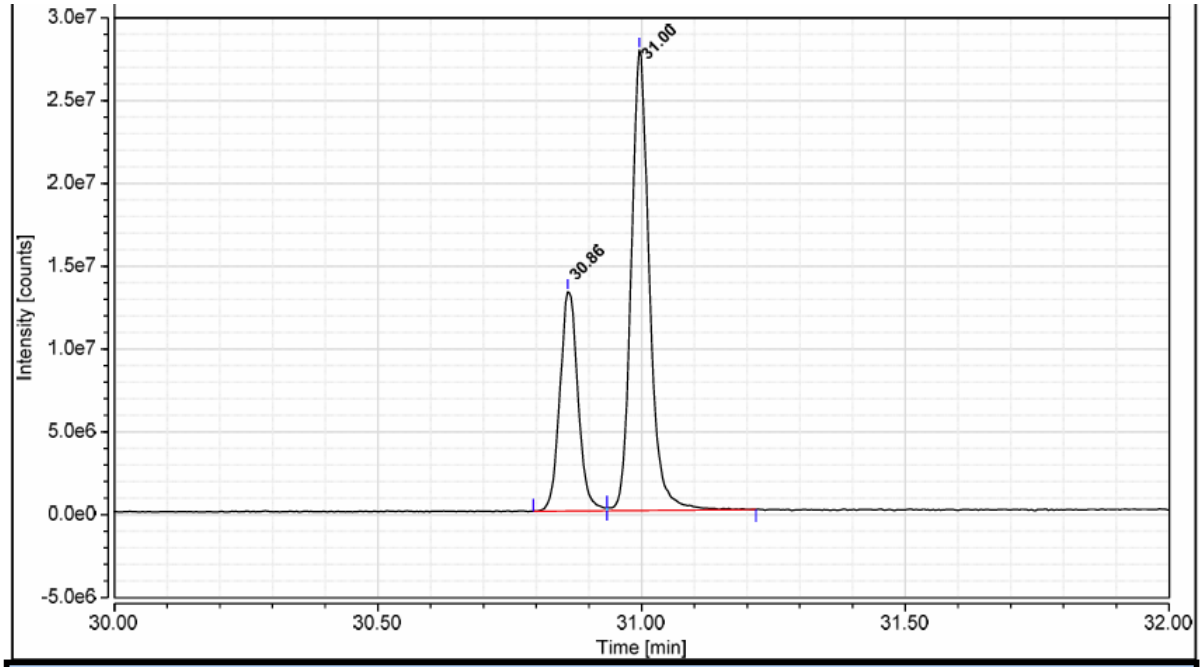
GPB (77%, *E/Z* 53:47):



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	30.852	46.89	464980
2	30.989	53.11	526695

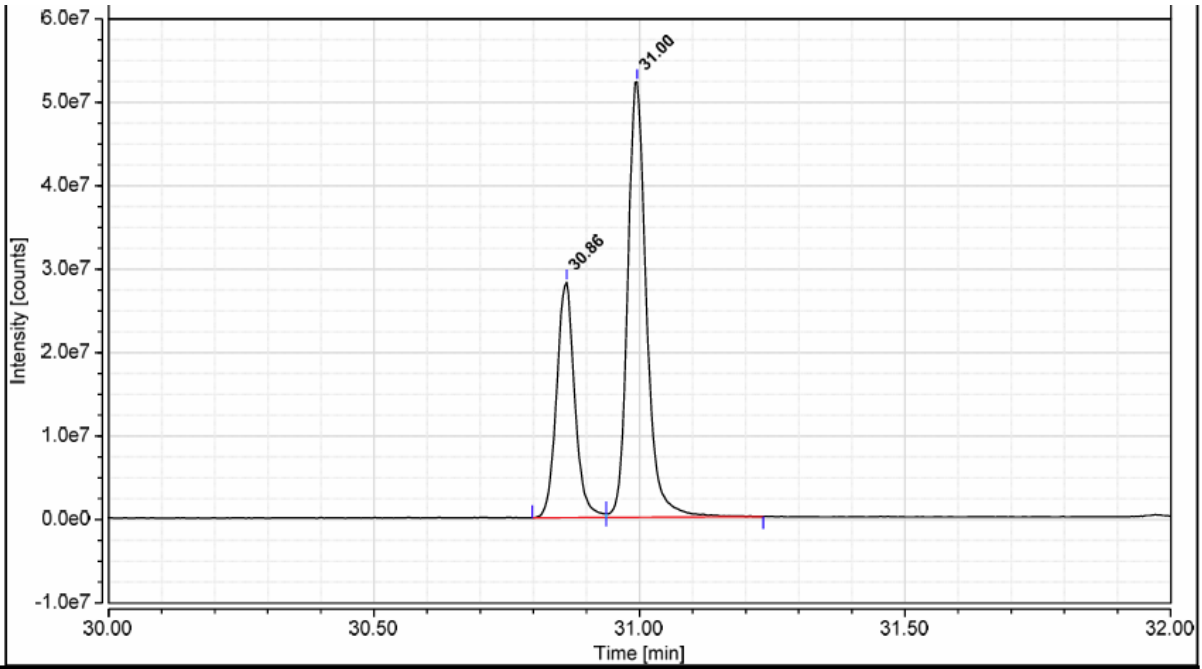
GPB with **1*R/S*-45** (74%, *E/Z* 68:32):



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	30.859	32.08	527222
2	30.996	67.92	1115983

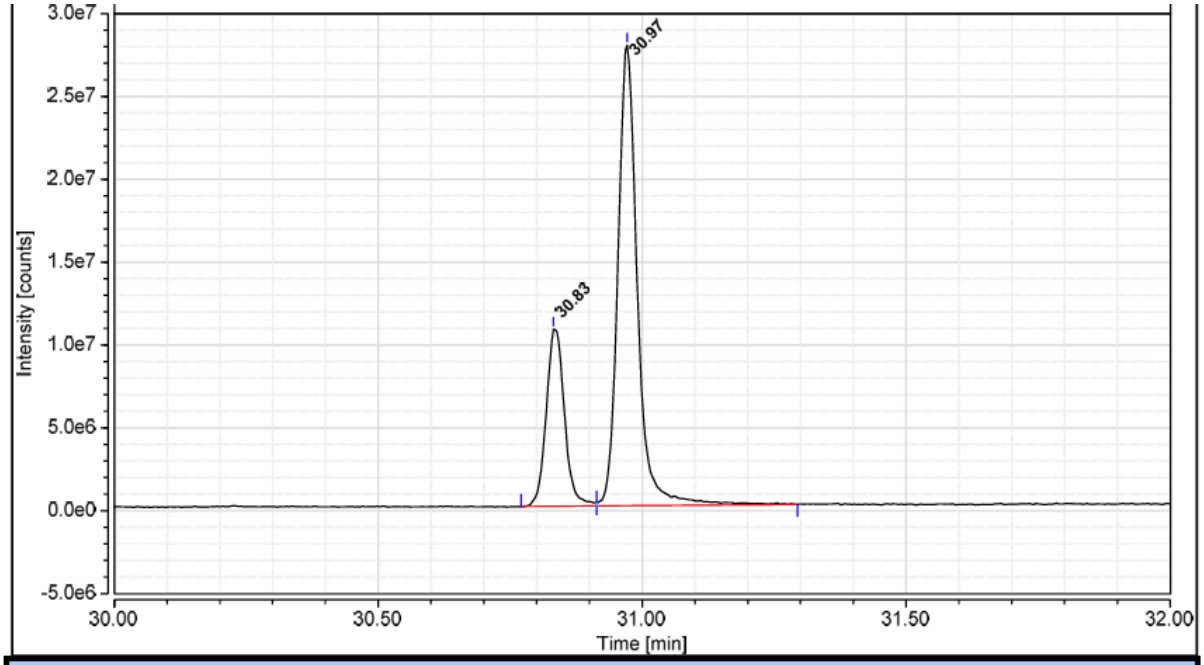
GPB with **1*R*-46** (90%, *E/Z* 66:34):



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	30.863	34.22	1113798
2	30.995	65.78	2141041

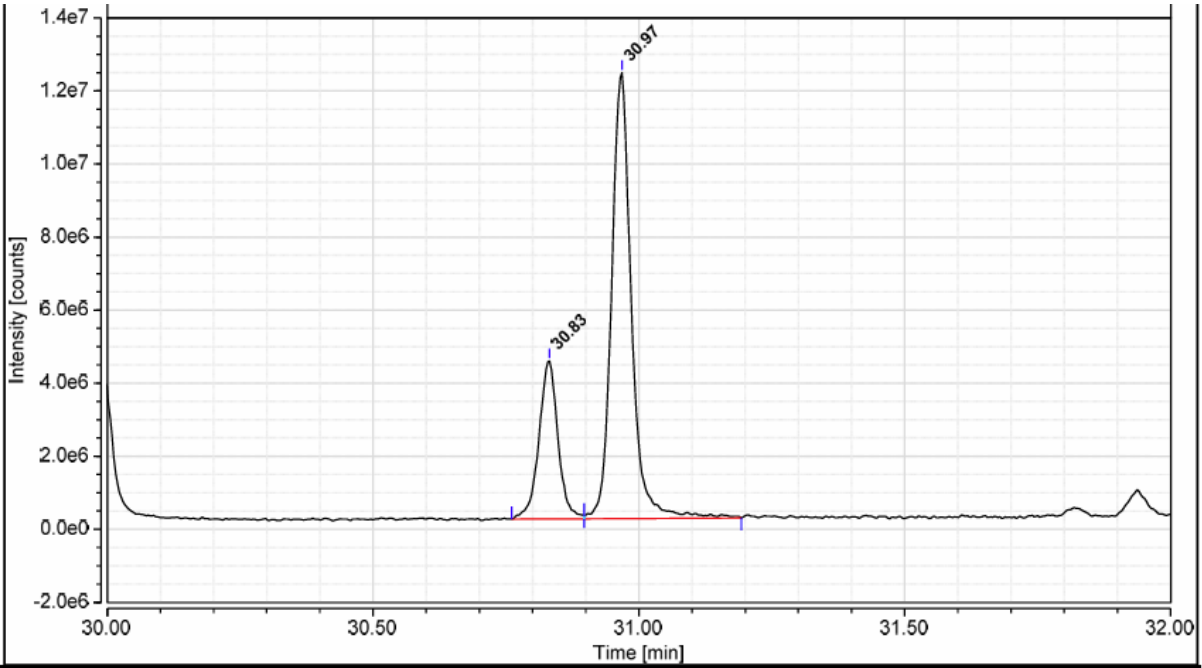
GPB with **40** (72%, *E/Z* 74:26):



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	30.832	26.42	428607
2	30.972	73.58	1193660

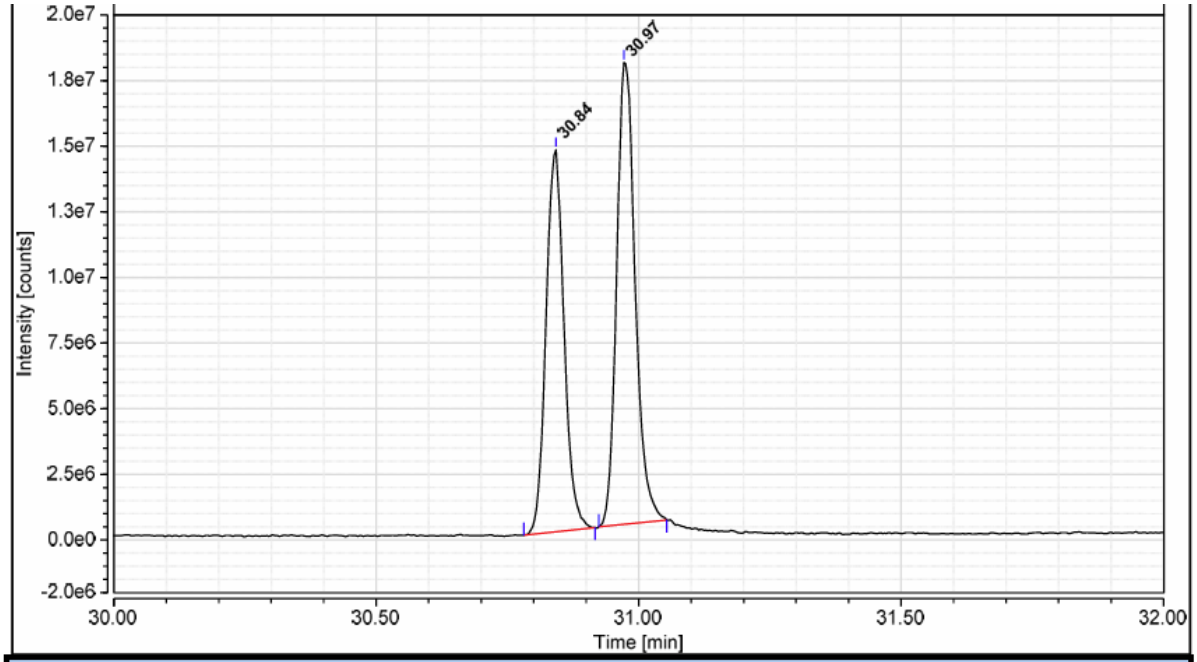
GPC with **61** (75%, *E/Z* 75:25):



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	30.832	25.33	179070
2	30.968	74.67	527810

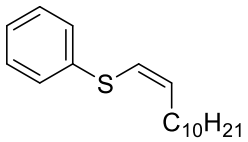
GPC with **72** (83%, *E/Z* 55:45):



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	30.842	44.60	578408
2	30.972	55.40	718571

(*Z*)-dodec-1-en-1-yl(phenyl)sulfane (37)



Chemical Formula: $C_{18}H_{28}S$
Molecular Weight: 276.48

The reaction was performed according to **General Procedure C** with phenyl((phenylsulfonyl)methyl)sulfane (**36**) (308 mg, 1.0 mmol), 2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) (414 mg, 1.4 mmol), *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol), dry THF (5.0 mL) and TBAF (1.0 M in THF, 6.0 mL, 6.0 mmol). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8 and 1% Et_3N, stained in PMA solution) to afford two inseparable olefins of **37** (154 mg, 55% , *E/Z* 44:56). The *E/Z* configuration was assigned based on the results of **32**.

Z-olefin: **Appearance** yellow liquid; **Rf** 1.0 (Et_2O/pentane=2:8); **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 7.38 – 7.26 (m, 4H), 7.23 – 7.16 (m, 1H), 6.16 (dt, J = 23.3, 1.3 Hz, 1H), 5.86 (dt, J = 9.2, 7.3 Hz, 1H), 2.25 (qd, J = 7.2, 1.4 Hz, 2H), 1.51 – 1.39 (m, 2H), 1.39 – 1.24 (m, 14H), 0.89 (t, J = 6.7 Hz, 3H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 137.04 (C_q), 134.35 (CH), 129.37 (2 x CH), 128.97 (2 x CH), 126.46 (CH), 122.66 (CH), 32.36 (CH_2), 30.06 (2 x CH_2), 29.90 (CH_2), 29.78 (CH_2), 29.65 (CH_2), 29.52 (CH_2), 29.44 (CH_2), 23.13 (CH_2), 14.31 (CH_3).

E-olefin (characteristic signals): **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 6.19 (dt, *J* = 17.6, 1.3 Hz, 1H), 6.02 (dt, *J* = 14.9, 6.9 Hz, 1H), 2.18 (qd, *J* = 7.0, 1.2 Hz, 2H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ =

138.63 (CH), 137.27 (C_q), 129.33 (2 x CH), 128.54 (2 x CH), 126.33 (CH), 122.66 (CH), 33.47 (CH_2), 29.87 (CH_2), 29.54 (CH_2), 25.04 (CH_3).

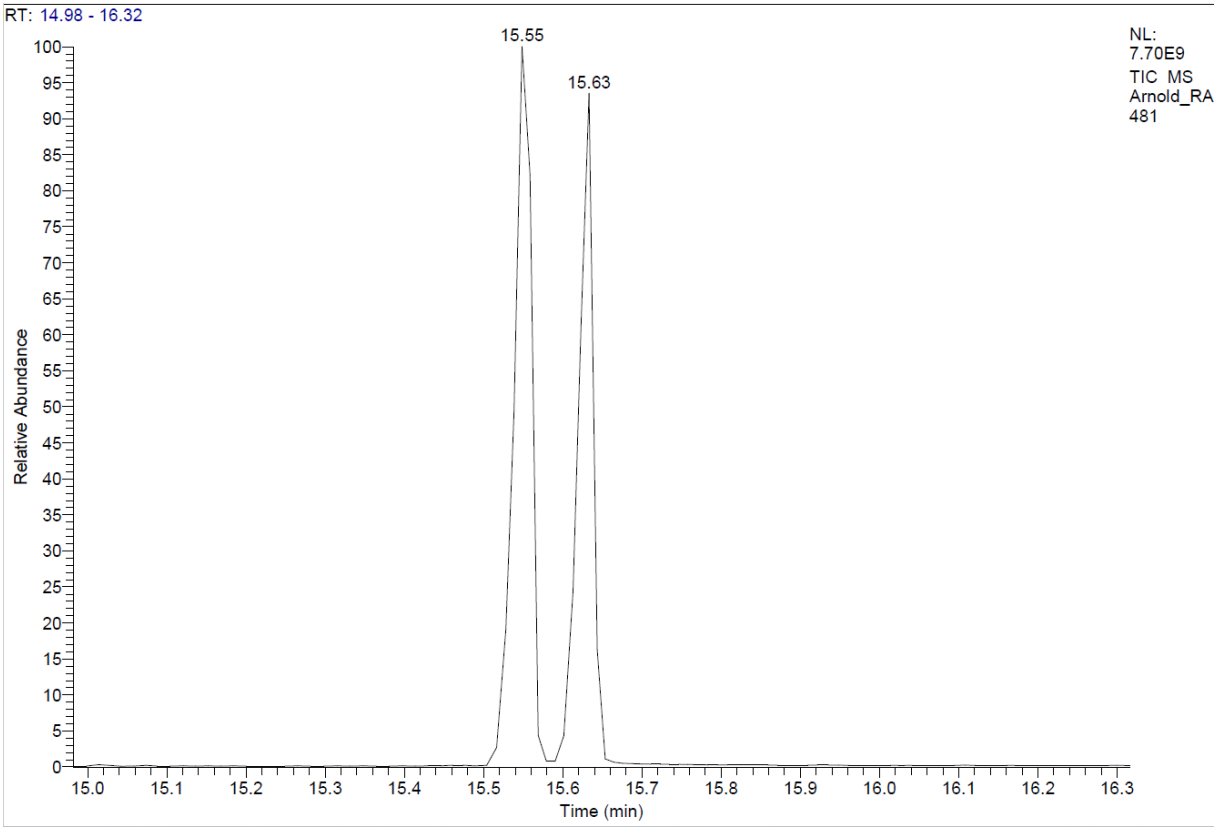
Mix of olefins: **FT-IR (cm^{-1}, neat)** 2922, 2852, 1583, 1462, 1442, 1373, 1318, 1145, 1090, 1023, 948, 898, 847, 735, 688, 577; **HRMS (EI)** m/z calculated for $C_{18}H_{28}$ [M]: 276.1906, found: 276.1910.

E/Z ratio was determined by GC-MS analysis:

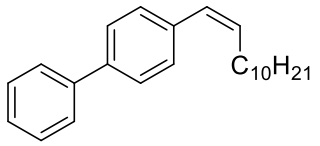
Temperature program: 50 °C for 2 min; 50-300 °C with 15 °C/min; 300 °C for 12 min

PEAK LIST
Arnold_RA-481.raw
RT: 0.00 - 30.01
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
15.55	15.47	15.58	12266100565	56.03	7695019500	51.67
15.63	15.59	15.68	9625061590	43.97	7197126700	48.33



(*Z*)-4-(dodec-1-en-1-yl)-1,1'-biphenyl (33)



Chemical Formula: $C_{24}H_{32}$
Molecular Weight: 320.52

The reaction was performed according to **General Procedure B** with 2-((1*S*,2*R*)-1-([1,1'-biphenyl]-4-yl)-1-(phenylsulfonyl)dodecan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**28**) (276 mg, 0.5 mmol), TBAF (1.0 M in THF, 3.0 mL, 3.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9 and 1% Et_3N, stained in PMA solution) to afford two inseparable olefins of **33** (112 mg, 75%, *E/Z* 16:84). The *E/Z* assignment was made by comparison with a reported similar compound[76] (shorter alkyl chain C_9H_{19}).

Z-olefin: **Appearance** white wax; **Rf** 1.0 (Et_2O/pentane=1:9); **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 7.70 – 7.55 (m, 4H), 7.53 – 7.32 (m, 5H), 6.49 (dt, J = 11.6, 2.0 Hz, 1H), 5.76 (dt, J = 11.6, 7.2 Hz, 1H), 2.43 (qd, J = 7.4, 1.9 Hz, 2H), 1.53 (p, J = 7.2 Hz, 2H), 1.45 – 1.26 (m, 14H), 0.99 – 0.90 (m, 3H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 141.24 (C_q), 139.53 (C_q), 137.48 (C_q), 134.09 (CH), 129.70 (2 x CH), 129.26 (2 x CH), 128.63 (CH), 127.69 (CH), 127.33 (2 x CH), 127.16 (2 x CH), 32.45 (CH_2), 30.52 (CH_2), 30.16 (2 x CH_2), 30.05 (CH_2), 29.91 (CH_2), 29.88 (CH_2), 29.33 (CH_2), 23.22 (CH_2), 14.41 (CH_3).

E-olefin (characteristic signals): **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 6.35 (dt, J = 15.9, 6.7 Hz, 1H), 2.28 (q, J = 7.2 Hz, 2H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 139.83 (C_q), 137.65 (C_q), 132.05 (CH), 129.64 (CH), 129.23 (2 x CH), 127.63 (CH), 127.52 (2 x CH), 127.22 (2 x CH), 126.79 (CH), 33.64 (CH_2), 30.18 (CH_2), 30.08 (CH_2), 29.94 (CH_2), 29.81 (CH_2).

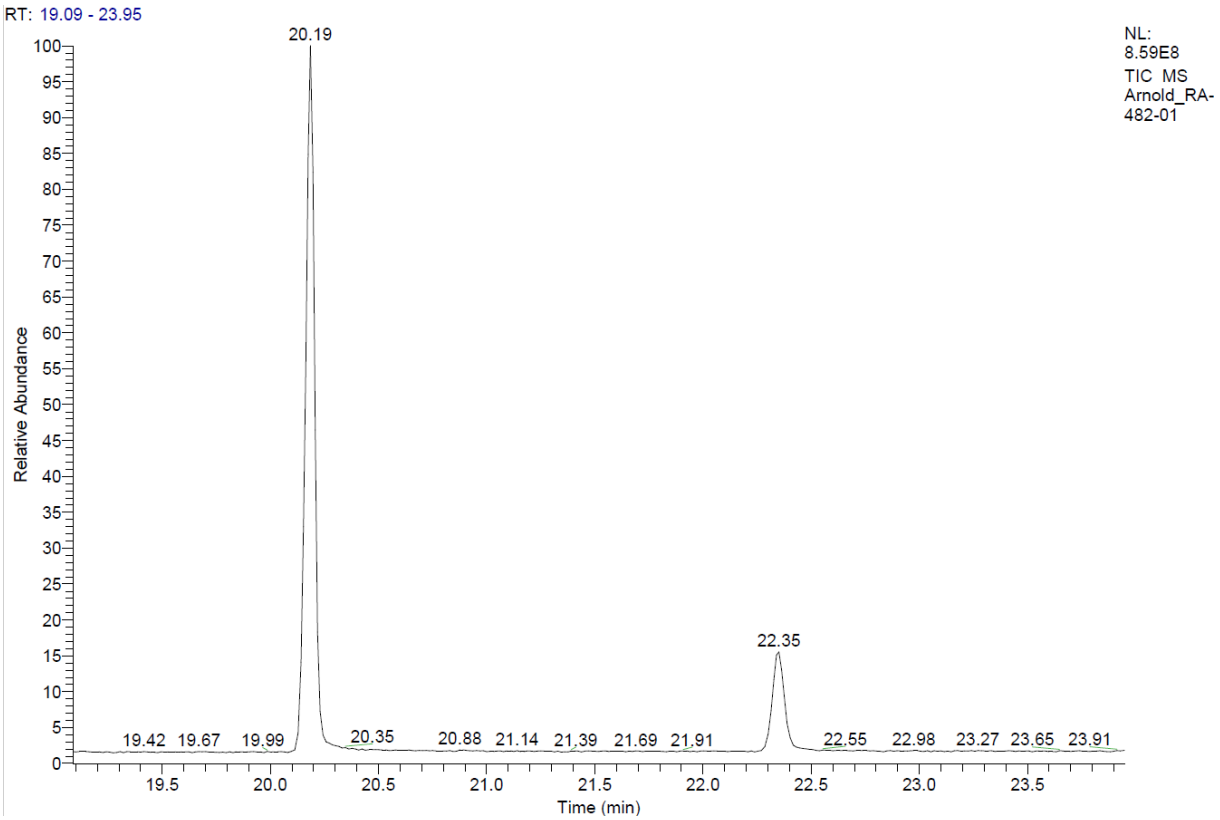
Mix of olefins: **FT-IR (cm^{-1}, neat)** 3055, 3033, 3003, 2955, 2917, 2848, 1483, 1464, 1421, 1400, 1381, 1342, 1266, 1158, 1129, 1073, 1039, 1004, 963, 908, 846, 770, 736, 677, 635; **HRMS (EI)** m/z calculated for $C_{24}H_{32}$ [M]: 320.2499, found: 320.2500.

E/Z ratio was determined by GC-MS analysis:

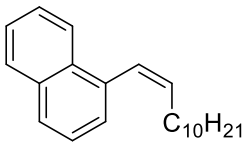
Temperature program: 50 °C for 2 min; 50-300 °C with 15 °C/min; 300 °C for 12 min

PEAK LIST
Arnold_RA-482-01.raw
RT: 18.78 - 24.20
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
20.19	20.03	20.49	2682985282	83.71	850322252.1	87.56
22.35	22.18	22.54	522058946.1	16.29	120859773.1	12.44



(*Z*)-1-(dodec-1-en-1-yl)naphthalene (34)



Chemical Formula: $C_{22}H_{30}$
Molecular Weight: 294.48

The reaction was performed according to **General Procedure B** with 4,4,5,5-tetramethyl-2-((1*S*,2*R*)-1-(naphthalen-1-yl)-1-(phenylsulfonyl)dodecan-2-yl)-1,3,2-dioxaborolane (**29**) (361 mg, 0.6 mmol), TBAF (1.0 M in THF, 4.0 mL, 4.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8 and 1% Et_3N, stained in PMA solution) to afford two inseparable olefins of **34** (139 mg, 74%, *E/Z* 4:96). The *E/Z* assignment was made by comparison with a reported similar compound[76] (shorter alkyl chain C_9H_{19}).

Z-olefin: **Appearance** yellow liquid; **Rf** 1.0 (Et_2O/pentane=2:8); **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 8.06 – 7.97 (m, 1H), 7.91 – 7.72 (m, 2H), 7.49 (ddt, J = 12.8, 8.3, 5.7 Hz, 3H), 7.36 (dt, J = 7.1, 1.2 Hz, 1H), 6.89 (d, J = 11.5 Hz, 1H), 5.97 (dt, J = 11.4, 7.4 Hz, 1H), 2.16 (qd, J = 7.4, 1.7 Hz, 2H), 1.42 (p, J = 7.2 Hz, 2H), 1.36 – 1.15 (m, 14H), 0.89 (t, J = 7.0 Hz, 3H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 135.40 (C_q), 135.19 (CH), 134.03 (C_q), 132.40 (C_q), 128.67 (CH), 127.42 (CH), 127.12 (CH), 126.80 (CH), 126.14 (CH), 126.10 (CH), 125.66 (CH), 125.44 (CH), 32.36 (CH_2), 30.19 (CH_2), 30.03 (2 x CH_2), 29.88 (CH_2), 29.77 (CH_2), 29.68 (CH_2), 29.06 (CH_2), 23.13 (CH_2), 14.33 (CH_3).

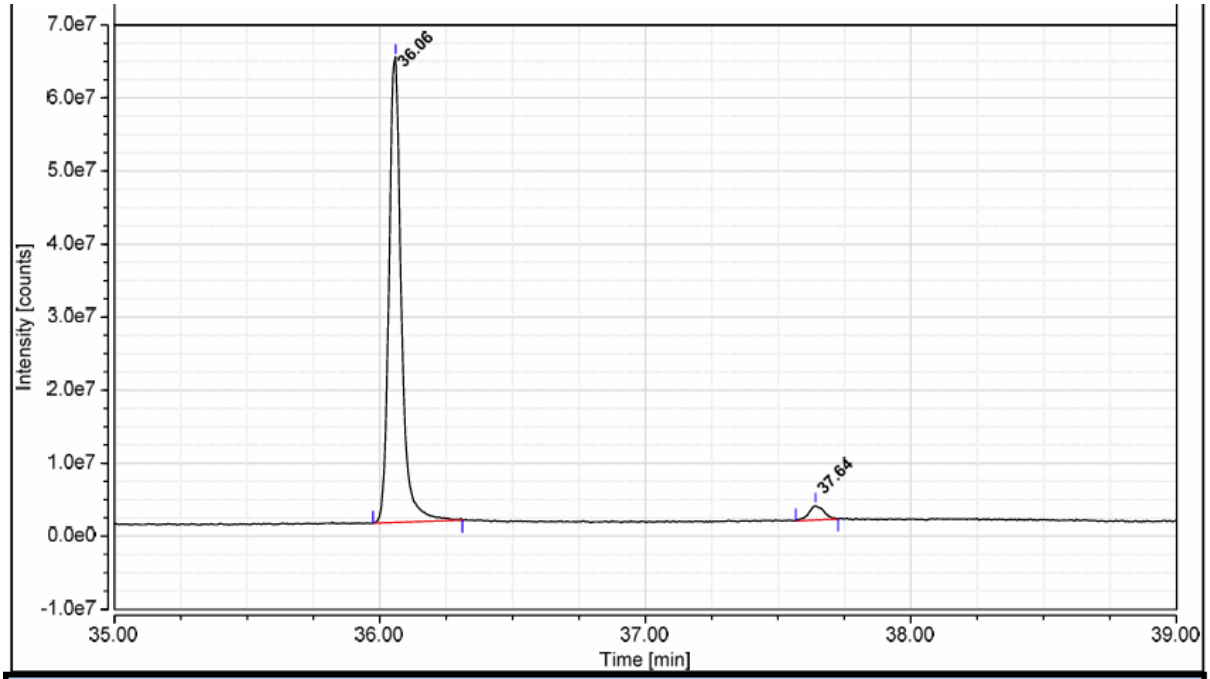
E-olefins (ratio 1:1, characteristic signals): **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 7.14 (d, *J* = 15.5 Hz, 1H), 6.60 – 6.55 (m, 1H), 6.29 (dt, *J* = 15.5, 6.9 Hz, 1H), 5.79 (dt, *J* = 11.6, 7.3 Hz, 1H),

2.44 (qd, *J* = 7.4, 1.9 Hz, 1H), 2.36 (qd, *J* = 7.1, 1.6 Hz, 1H), 1.62 – 1.47 (m, 2H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 136.23, 135.91, 135.14, 134.33, 134.12, 133.85, 132.61, 131.57, 129.00, 128.81, 128.28, 127.92, 127.90, 127.73, 127.71, 127.52, 126.44, 126.18, 126.06, 126.04, 124.30, 123.82, 33.88, 32.40, 30.45, 30.13, 30.11, 30.08, 30.07, 29.96, 29.82, 29.79, 29.74, 29.22, 24.51, 22.32.

Mix of olefins: **FT-IR (cm^{-1}, neat)** 3005, 2921, 2851, 1505, 1461, 1380, 1343, 1262, 1159, 1012, 964, 862, 800, 778, 720, 662, 617; **HRMS (EI)** m/z calculated for $C_{22}H_{30}$ [M]: 294.2342, found: 294.2344.

E/Z ratio was determined by GC-MS analysis:

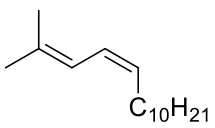
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	36.060	96.40	3439389
2	37.641	3.60	128458

(*Z*)-2-methylpentadeca-2,4-diene (35)



Chemical Formula: $C_{16}H_{30}$
Molecular Weight: 222.42

The reaction was performed according to **General Procedure B** with 4,4,5,5-tetramethyl-2-((4*S*,5*R*)-2-methyl-4-(phenylsulfonyl)-pentadec-2-en-5-yl)-1,3,2-dioxaborolane (**30**) (215 mg, 0.4 mmol), TBAF (1.0 M in THF, 3.0 mL, 3.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:9 and 1% Et_3N, stained in PMA solution) to afford two inseparable

olefins of **35** (68 mg, 70%, *E/Z* 13:87). The *E/Z* assignment was made by comparison with a reported similar compound[77] (shorter alkyl chain C_8H_{17}).

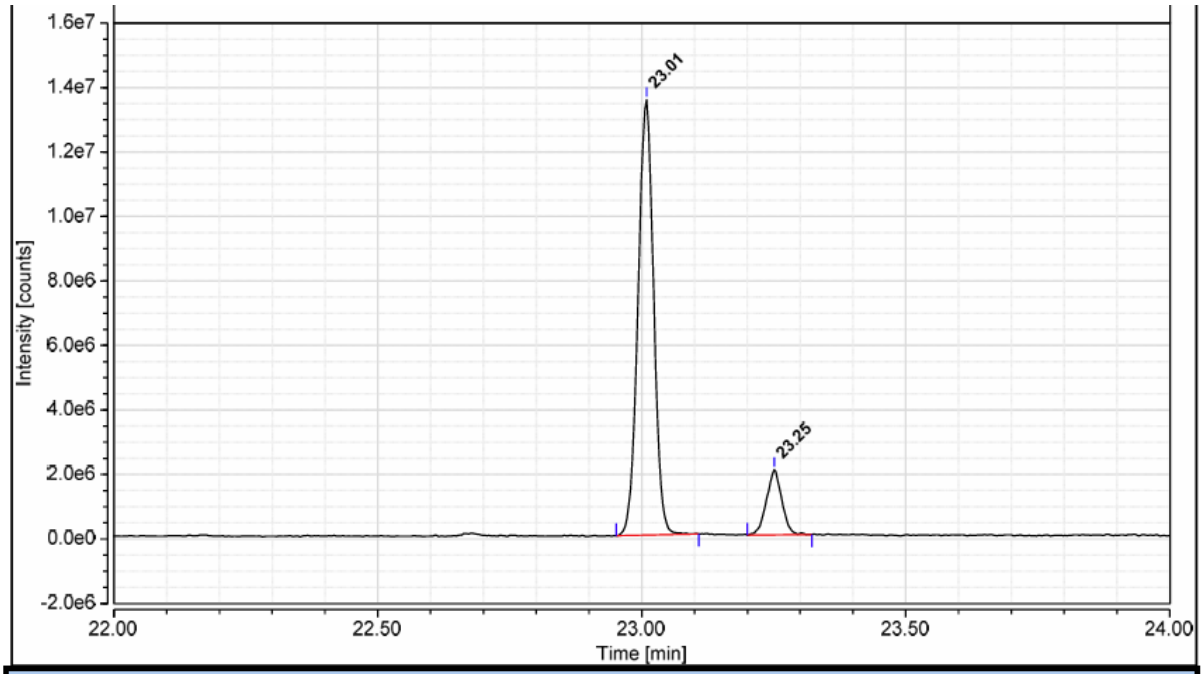
Z-olefin: **Appearance** yellow liquid; **Rf** 1.0 (Et_2O/pentane=3:7); **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 6.20 – 6.03 (m, 2H), 5.37 – 5.27 (m, 1H), 2.15 (qd, J = 7.3, 1.5 Hz, 2H), 1.80 (s, 3H), 1.74 (s, 3H), 1.42 – 1.19 (m, 16H), 0.92 – 0.85 (m, 3H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 135.11 (C_q), 130.02 (CH), 125.02 (CH), 120.81 (CH), 32.37 (CH_2), 30.24 (CH_2), 30.08 (2 x CH_2), 29.98 (CH_2), 29.79 (CH_2), 29.77 (CH_2), 27.92 (CH_2), 26.40 (CH_3), 23.14 (CH_2), 18.16 (CH_3), 14.31 (CH_3).

E-olefin (characteristic signals): **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 6.26 – 6.20 (m, 1H), 5.77 (dq, *J* = 10.9, 1.3 Hz, 1H), 5.54 (dt, *J* = 14.7, 7.0 Hz, 1H), 2.07 (q, *J* = 7.2 Hz, 2H), 1.73 (s, 3H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 132.87 (C_q), 132.48 (CH), 127.13 (CH), 125.56 (CH), 33.30 (CH_2), 30.14 (CH_2), 30.11 (CH_2), 29.69 (CH_2), 25.99 (CH_2), 24.49 (CH_3), 22.31 (CH_3), 18.29 (CH_3).

Mix of olefins: **FT-IR (cm^{-1}, neat)** 2922, 2853, 1704, 1632, 1462, 1373, 1304, 1257, 1147, 1046, 968, 883, 821, 776, 722; **HRMS (EI)** m/z calculated for $C_{16}H_{30}$ [M]: 222.2348, found: 222.2347.

E/Z ratio was determined by GC-MS analysis:

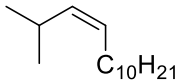
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	23.009	87.15	463446
2	23.251	12.85	68309

(*Z*)-2-methyltetradec-3-ene (25)



Chemical Formula: $C_{15}H_{30}$
Molecular Weight: 210.41

The reaction was performed according to **General Procedure B** with 4,4,5,5-tetramethyl-2-((3*S*,4*R*)-2-methyl-3-(phenylsulfonyl) tetradecan-4-yl)-1,3,2-dioxaborolane (**15**) (259 mg, 0.5 mmol), TBAF (1.0 M in THF, 3.3 mL, 3.3 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8 and 1% Et_3N, stained in PMA solution) to afford two inseparable olefins of **25** (87 mg, 76%, *E/Z* 20:80). The *E/Z* assignment was made by comparison with a reported similar compound[78] (shorter alkyl chain C_8H_{17}).

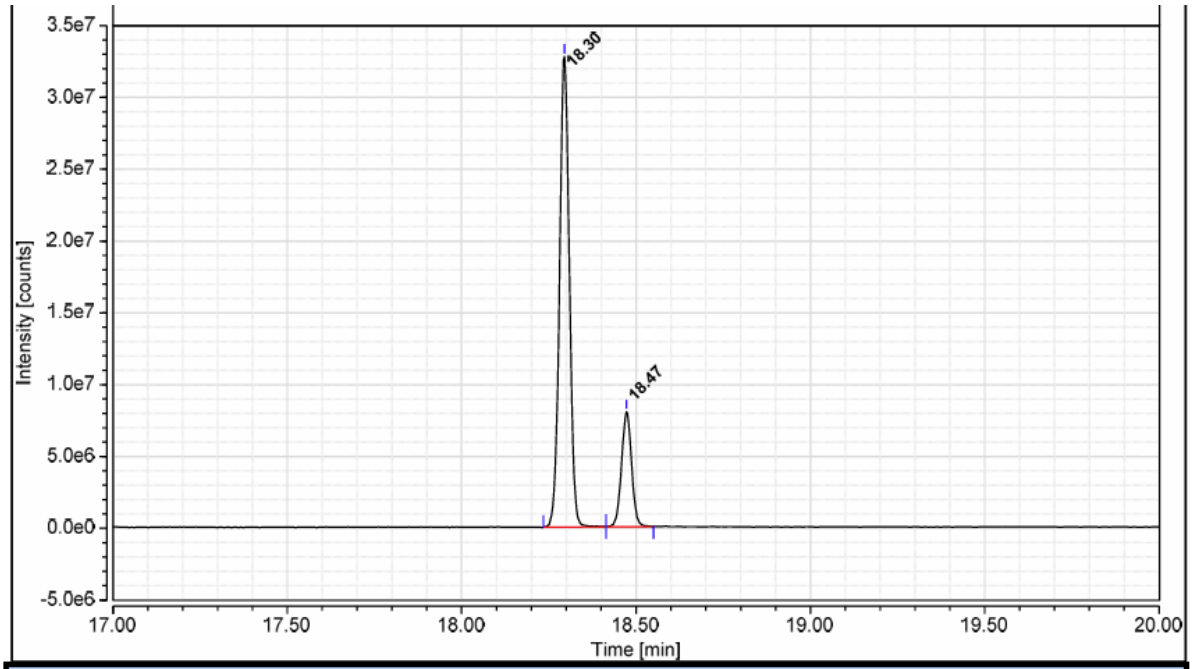
Z-olefin: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=2:8); **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 5.29 – 5.12 (m, 2H), 2.60 (dp, *J* = 8.7, 6.6 Hz, 1H), 2.03 (td, *J* = 6.9, 5.7 Hz, 2H), 1.48 – 1.21 (m, 16H), 0.94 (s, 3H), 0.93 (s, 3H), 0.91 – 0.86 (m, 3H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 137.80 (CH), 127.98 (CH), 32.38 (CH_2), 30.40 (CH_2), 30.11 (CH_2), 30.09 (CH_2), 30.00 (CH_2), 29.81 (CH_2), 29.77 (CH_2), 27.73 (CH_2), 26.86 (CH), 23.42 (2 x CH_3), 23.15 (CH_2), 14.32 (CH_3).

E-olefin (characteristic signals): **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 5.36 (td, *J* = 3.7, 1.8 Hz, 2H), 2.29 – 2.15 (m, 1H), 1.99 – 1.91 (m, 2H), 0.97 (s, 3H), 0.95 (s, 3H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 137.89 (CH), 127.74 (CH), 33.00 (CH_2), 31.49 (CH), 30.17 (CH_2), 29.98 (CH_2), 29.60 (CH_2), 22.92 (CH_3).

Mix of olefins: **FT-IR (cm^{-1}, neat)** 2998, 2956, 2922, 2854, 1462, 1376, 1302, 1160, 1102, 968, 738; **HRMS (EI)** m/z calculated for $C_{15}H_{30}$ [M]: 210.2342, found: 210.2343.

E/Z ratio was determined by GC-MS analysis:

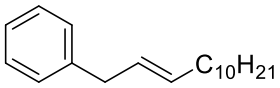
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	18.295	79.81	1067546
2	18.472	20.19	270106

(*E*)-tridec-2-en-1-ylbenzene (41)



Chemical Formula: $C_{19}H_{30}$
Molecular Weight: 258.45

The reaction was performed according to **General Procedure B** with 2-((2*S*,3*R*)-2-(*tert*-butylsulfonyl)-1-phenyltridecan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**39**) (278 mg, 0.5 mmol), TBAF (1.0 M in THF, 3.3 mL, 3.3 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8 and 1% Et_3N, stained in PMA solution) to afford two inseparable olefins of **41** (115 mg, 81%, *E/Z* 86:14). The *E/Z* assignment was made by comparison with a reported similar compound[39] (shorter alkyl chain C_7H_{15}).

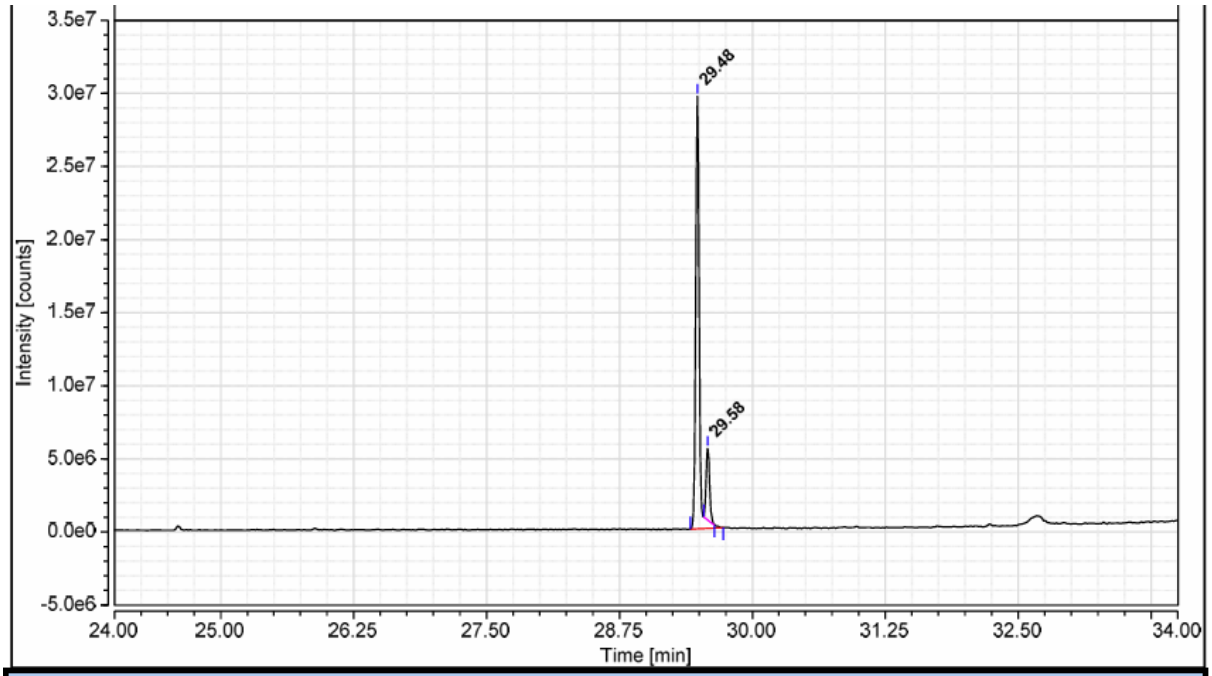
E-olefin: **Appearance** colorless liquid; **Rf** 1.0 (Et_2O/pentane=2:8); **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 7.32 – 7.23 (m, 2H), 7.23 – 7.13 (m, 3H), 5.64 – 5.47 (m, 2H), 3.33 (d, J = 5.3 Hz, 2H), 2.08 – 1.98 (m, 2H), 1.46 – 1.20 (m, 16H), 0.94 – 0.86 (m, 3H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 141.74 (C_q), 132.56 (CH), 129.18 (CH), 128.84 (2 x CH), 128.69 (2 x CH), 126.20 (CH), 39.44 (CH_2), 32.94 (CH_2), 32.38 (CH_2), 30.09 (CH_2), 30.07 (CH_2), 29.96 (CH_2), 29.95 (CH_2), 29.80 (CH_2), 29.64 (CH_2), 23.14 (CH_2), 14.32 (CH_3).

Z-olefin (characteristic signals): **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ = 3.41 (d, *J* = 5.8 Hz, 2H), 2.21 – 2.13 (m, 2H); **^{13}C-NMR** (101 MHz, CD_2Cl_2) δ = 141.88 (C_q), 131.39 (CH), 128.75 (2 x CH), 128.42 (CH), 126.16 (CH), 33.88 (CH_2), 30.16 (CH_2), 30.00 (CH_2), 27.67 (CH_2).

Mix of olefins: **FT-IR (cm^{-1}, neat)** 3027, 2922, 2852, 1738, 1603, 1493, 1457, 1374, 1308, 1159, 1122, 1072, 1030, 967, 914, 736, 696, 580; **HRMS (EI)** m/z calculated for $C_{19}H_{30}$ [M]: 258.2342, found: 258.2346.

E/Z ratio was determined by GC-MS analysis:

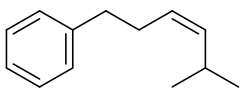
Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	29.482	86.25	1159904
2	29.580	13.75	184989

(*Z*)-(5-methylhex-3-en-1-yl)benzene (26)



Chemical Formula: $C_{13}H_{18}$
Molecular Weight: 174.29

The reaction was performed according to **General Procedure B** with 4,4,5,5-tetramethyl-2-((3*R*,4*R*)-2-methyl-6-phenyl-4-(phenylsulfonyl)hexan-3-yl)-1,3,2-dioxaborolane (**14**) (203 mg, 0.5 mmol), TBAF (1.0 M in THF, 3.0 mL, 3.0 mmol) and dry THF (5.0 mL). The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8 and 1% Et_3N, stained in PMA solution) to afford two inseparable olefins of **26** (>98%, *E/Z* 21:79). (**GPC** with **61**: 58%, *E/Z* 21:79) The compound is reported in the literature[41] and *E/Z* assignment was made by comparison with the reported compound.

Z-olefin: **Appearance** yellow liquid; **Rf** 1.0 (Et_2O/pentane=2:8); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.32 – 7.23 (m, 2H), 7.23 – 7.15 (m, 3H), 5.42 – 5.17 (m, 2H), 2.66 (dd, J = 8.8, 6.7 Hz, 2H), 2.54 (dhept, J = 8.8, 6.5 Hz, 1H), 2.36 (dtd, J = 8.7, 7.1, 1.2 Hz, 2H), 0.89 (s, 3H), 0.87 (s, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ = 142.29 (C_q), 138.41 (CH), 128.62 (2 x CH), 128.38 (2 x CH), 126.39 (CH), 125.90 (CH), 36.38 (CH_2), 29.45 (CH_2), 26.67 (CH), 23.24 (2 x CH_3).

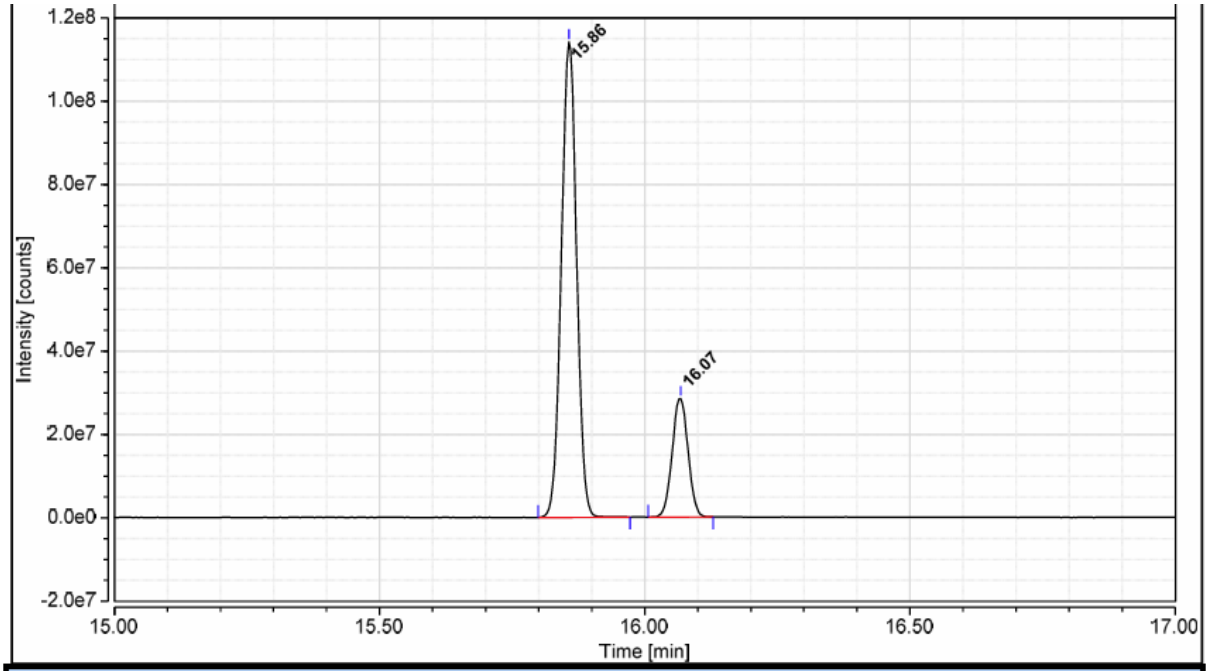
E-olefin (characteristic signals): **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 2.32 – 2.26 (m, 2H), 2.26 – 2.17 (m, 1H), 0.96 (s, 3H), 0.94 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 142.38 (C_q), 138.44 (CH), 128.65 (2 x CH), 128.34 (2 x CH), 125.81 (CH), 34.59 (CH_2), 31.15 (CH), 22.76 (2 x CH_3).

Mix of olefins: **FT-IR (cm^{-1}, neat)** 3063, 3027, 3000, 2955, 2928, 2865, 2797, 1724, 1603, 1495, 1457, 1376, 1302, 1266, 1178, 1080, 1029, 970, 932, 902, 733, 969, 580; **HRMS (EI)** m/z calculated for $C_{13}H_{18}$ [M]: 174.1403, found: 174.1405.

E/Z ratio was determined by GC-MS analysis:

Temperature program: 50 °C for 1 min; 50-250 °C with 6 °C/min; 250 °C for 5 min

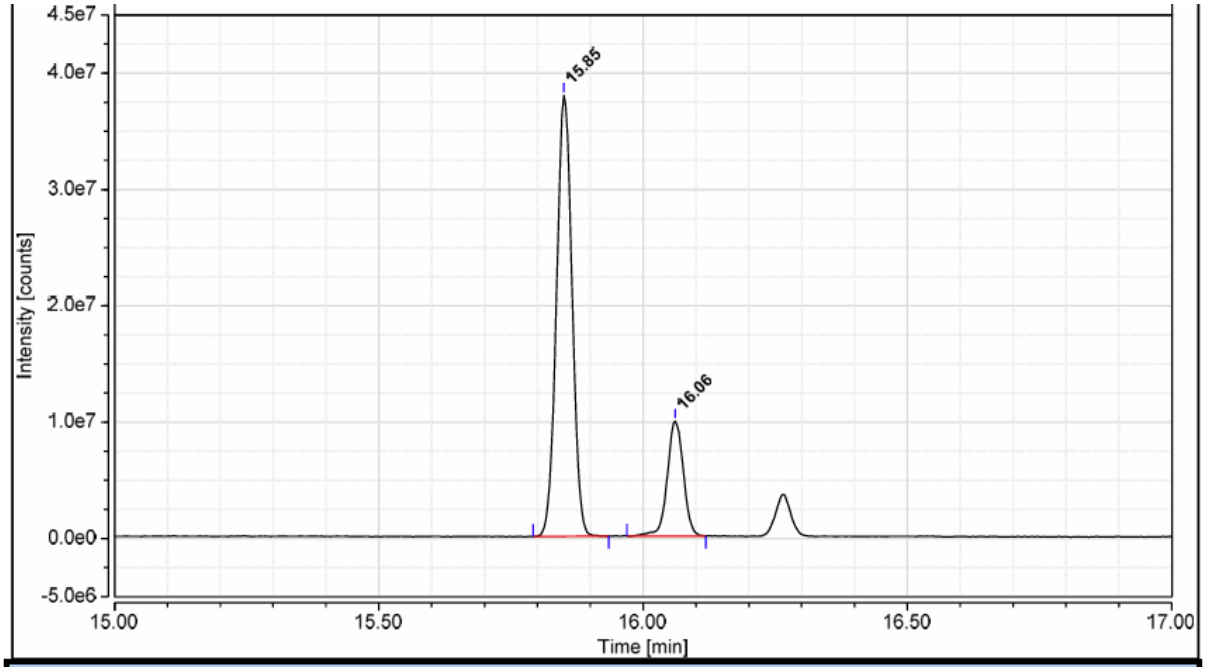
GPB (>98%, *E/Z* 21:79):



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	15.857	79.38	3813997
2	16.068	20.62	990745

GPC with **61** (58%, *E/Z* 21:79):



Integration Results

No.	Retention Time min	Rel.Area %	Area counts*min
1	15.850	78.69	1296990
2	16.061	21.31	351209

2.5.7 NMR spectra

All measured NMR spectra are supplied in the appendix

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Chapter 3

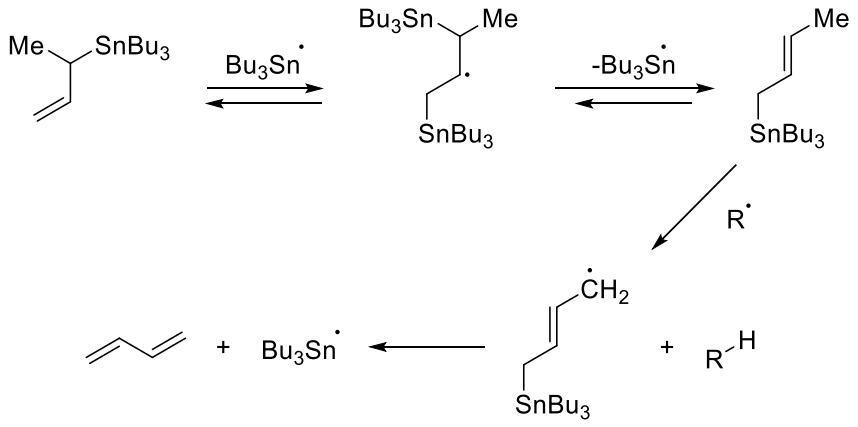
Radical reactions on allyl sulfones

Unpublished results

3. Radical reactions on allyl sulfones

3.1 Introduction

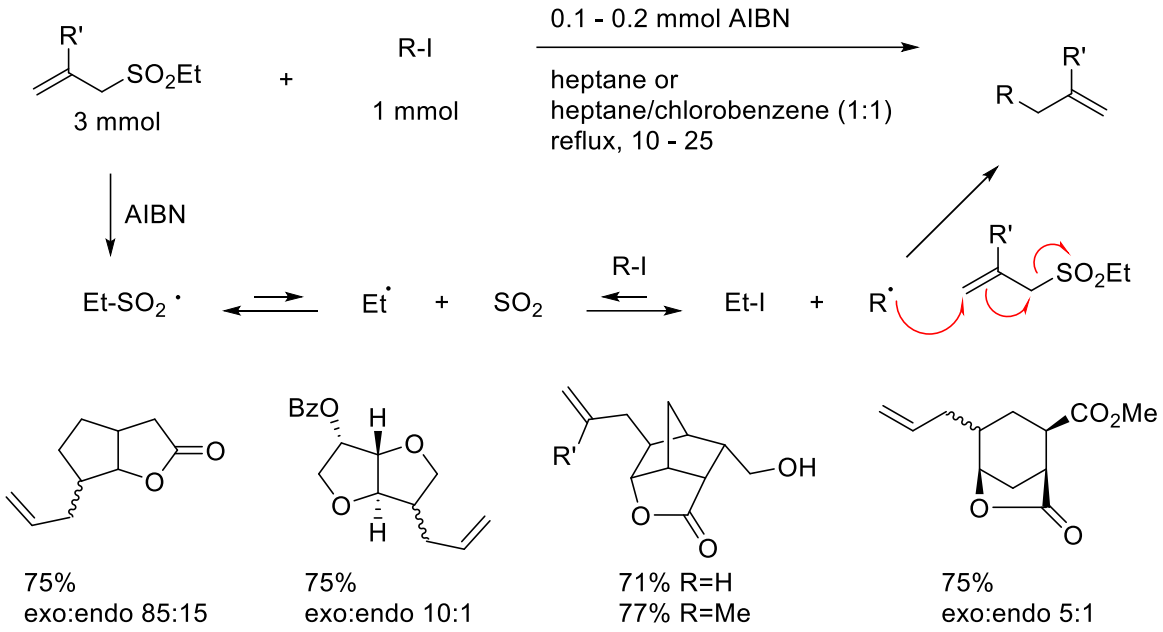
Radical allylation reactions is a well-known process and is commonly performed with allyltin reagents.[1] With allylstannanes high yielding and efficient reactions can be made and also numerous applications underline the importance of this method.[2,3] Nevertheless, using allylstannanes as precursor for radical allylation reactions showed not only advantages. As a major disadvantage of using tin-reagents shows up the toxicity[4] of those compounds as well as the difficulty of eliminating tin-residues from the reaction mixture afterwards.[5] Latter argument is particularly important when the wanted compound has to be used for biological testing.[6] Those two arguments makes the use of allylstannanes not attractive for industrial applications.[4] Furthermore, allylstannanes showed limitations depending on their substitution pattern.[2] Whilst the beta substituted allyl compounds can be run smoothly and without any further problems, α-substituted allyl compounds isomerize quickly into the thermodynamically more stable γ-substituted isomer which is way less reactive or even favours H-abstraction like shown in **Scheme 3-1**.[2,7]



Scheme 3-1 Isomerization of α-allylstannanes to γ-allylstannanes and the H-abstraction side reaction.[2,7]

The use of allyl sulfones for allylation reactions instead of allyl stannanes does not prevent isomerisation, but reduces the toxicity of the reagent.[8] In addition, the synthesis of such allyl sulfone precursors is much simpler and various routes for their preparation are known.[9–11] Therefore, tin-free radical reactions on allyl sulfones were investigated.

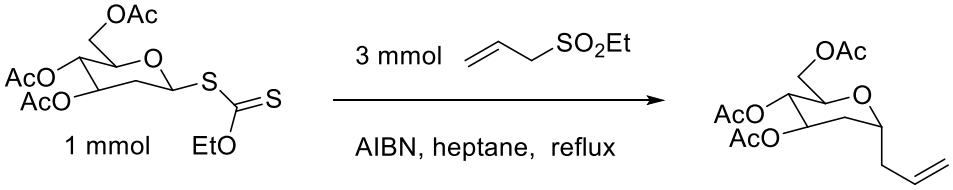
In 1997, Zard developed a new protocol for the tin-free radical allylation reaction of iodides (**Scheme 3-2**).[6]



Scheme 3-2 Zard's tin-free radical allylation method on iodides.[6]

In this method, an alkyl iodide reacts with an allyl ethyl sulfone in the presence of (2,2-azabisisobutyronitrile (AIBN) which is used as a radical initiator. AIBN forms with allyl ethyl sulfone the sulfonyl radical, which is in an equilibrium with sulfur dioxide and an ethyl radical. Although the fragmentation to the ethyl radical is unfavourable, it is of crucial importance, since only the ethyl radical is able to abstract the iodine from R-I, whiles the sulfonyl radical is not.[6,12] The alkyl radical formed can then attack the allyl ethyl sulfone to form the desired product, while cleaving off the ethyl sulfonyl radical and allowing the chain reaction to continue. With this method a wide variety of functional groups can be tolerated and results in high yield like shown in **Scheme 3-2**. Beside the good yield and functional group tolerance, also the purification could be simplified, since the formed side products (SO_2, EtI) are volatile.[6]

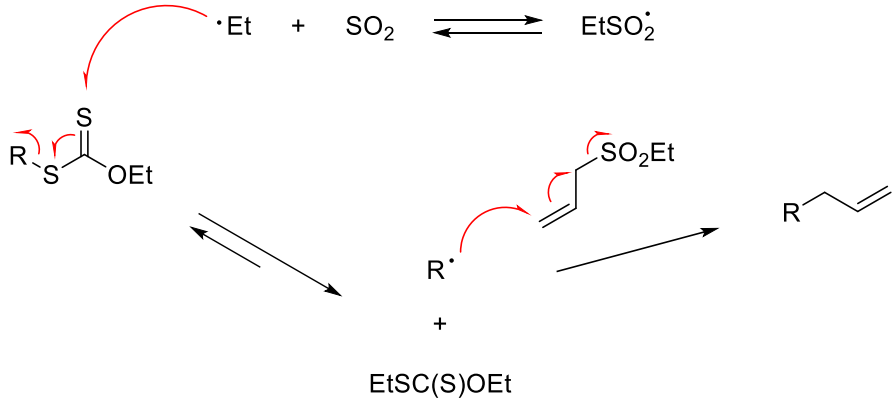
In 1998, Zard published a new method, where he expanded the scope from iodides to dithiocarbonates (xanthates, **Scheme 3-3**).[13]



Scheme 3-3 Radical allylation reaction with xanthates.[13]

Iodides are not widely present in natural compounds, but highly reactive with ethyl radicals.[6] Bromides and chlorides showed to be more stable than iodides, but on the other hand less

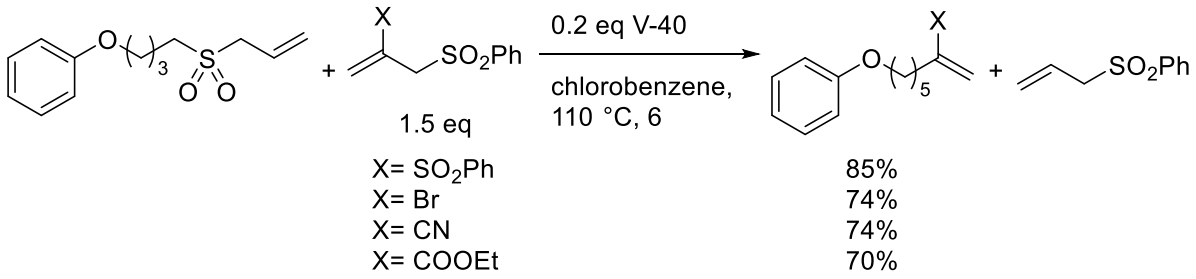
reactive with ethyl radicals. With xanthates, Zard found an good alternative to iodides, which showed good reactivity towards ethyl radicals but also are more stable.[13]



Scheme 3-4 Radical allylation reaction of a xanthate with an allyl ethyl sulfone.[13]

Like with iodides, in the first step the formed ethyl radical attacks the starting material and forms an alkyl radical and ethyl xanthate (**Scheme 3-4**). The alkyl radical in turn reacts with the allyl ethyl sulfone and forms the desired product with cleavage of the ethanesulfonyl radical.[13]

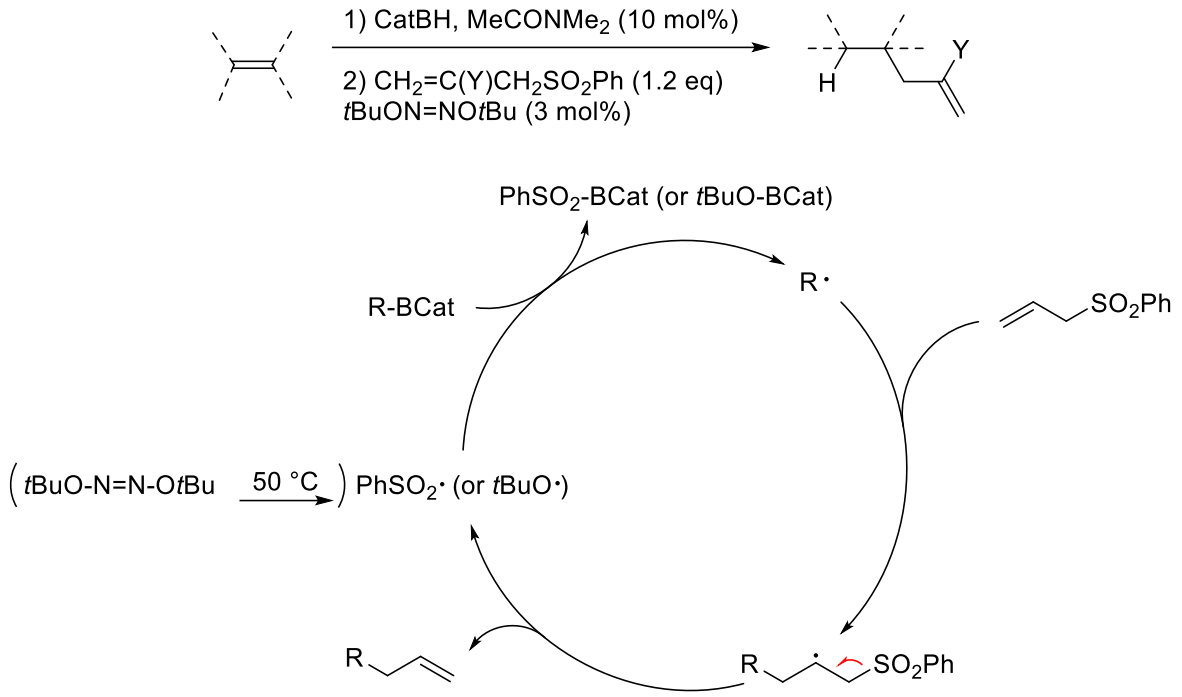
In 2002, Kim reported an allylation method with alkyl allyl sulfones as radical precursors (**Scheme 3-5**).[14]



Scheme 3-5 Kim's allylation method for β-substituted allyl sulfones.[14]

With this method in the first step 1,1'-azobis(cyclohexane-1-carbonitrile) (V-40) reacts with the unsubstituted allyl sulfone forming a primary alkyl radical with cleavage of sulfur dioxide. The primary alkyl radical then attacks the substituted allyl sulfone present in excess, forming the desired product under formation of a benzenesulfonyl radical.[14] Compared to Zard's method where ethanesulfonyl radicals are formed and fragment to ethyl radicals and sulfur dioxide, the benzenesulfonyl radicals lack the possibility to fragment as easily to phenyl radicals and sulfur dioxide.[13,15,16] The benzenesulfonyl radical attacks the allylsulfone radical precursor to sustain the chain process.[14]

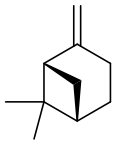
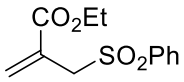
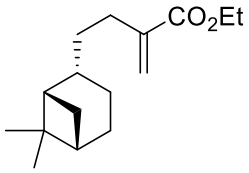
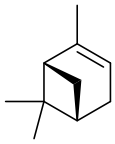
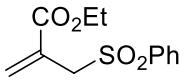
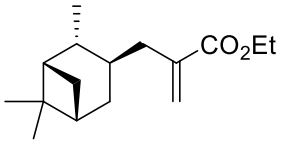
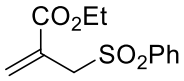
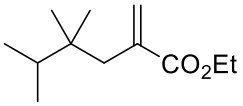
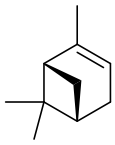
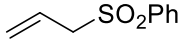
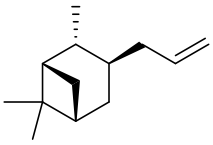
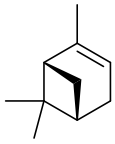
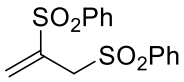
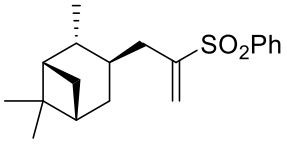
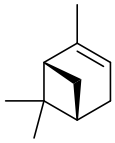
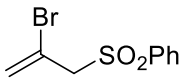
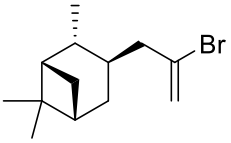
In 2003, our research group reported a new allylation method based on *B*-alkylcatecholboranes (**Scheme 3-6**).[17]



Scheme 3-6 Renaud's radical allylation of B-alkylcatecholboranes.[17]

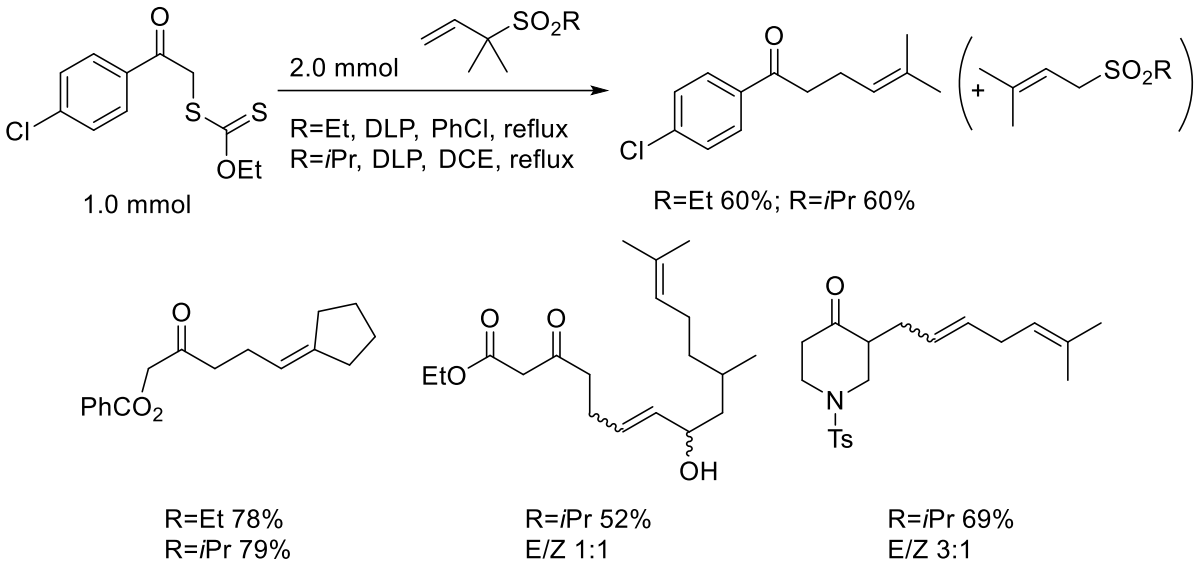
In the first step the alkene undergoes a hydroboration reaction forming an *B*-alkylcatecholborane.[17] The latter are found to be versatile radical precursors for carbon-carbon bond formation. Starting from *B*-alkylcatecholborane not only an allylation method was developed, but also methods for conjugate addition to enones or activated alkenes like vinyl sulfones.[18] The allylation reaction is initiated with di-*tert*-butyl hyponitrite (DTBHN). DTBHN forms alkoxyl radicals that react promptly with *B*-alkylcatecholboranes to form alkyl radicals.[19] The formed alkyl radicals can attack the allyl phenyl sulfone, which results in the formation of desired allylated product and a benzenesulfonyl radical that sustains the chain reaction.[17]

Table 3-1 Radical hydroallylation products made by method shown in **Scheme 3-6**.[17]

Alkene	Allyl sulfone	Product	Yield
			62%, dr 90:10
			89%, dr 96:4
			65%
			52%, dr 95:5
			89%, dr 96:4
			58%, dr 96:4

With Renaud's one-pot hydroallylation method not only good to high yields could be achieved, also pleasing diastereomeric ratios were obtained (**Table 3-1**). Interestingly, only 1.2 equivalents of the allylsulfone trap had to be used, which is significantly less than in the methods of Zard or Kim and is probably due to the high reactivity of the benzene sulfonyl radicals towards the *B*-alkylcatecholborane and thus to the possibility of efficient propagation of the reaction.[13,14,17]

In 2008, Zard optimized his radical allylation method and expanded the scope with α-branched allyl sulfones (**Scheme 3-7**).[7]

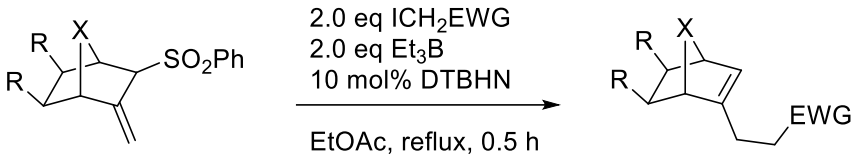


Scheme 3-7 Radical allylation reaction with α-branched allyl sulfones.[7]

With the initial protocol the radical allylation with α-branched allyl sulfones was possible but low yielding. The major problem of this protocol showed to be the isomerization of the allyl sulfone. The problem could be reduced by simply increasing the reaction temperature, for which the solvent had to be changed from dichloroethane (DCE) to chlorobenzene, resulting in an increase in yield to 60% overall. With this small adjustment, higher yields could be achieved while using less radical initiator. In order to use more sensitive allyl sulfone, the protocol was further optimized. Changing the residue on the sulfonyl group from ethyl to isopropyl facilitates α-scission and the release of sulfur dioxide at lower reaction temperatures, which in turn allowed DCE to be used as a solvent. With the adjusted protocol, comparable results were achieved when using the ethyl precursor in chlorobenzene as when using the isopropyl precursor in DCE.[7]

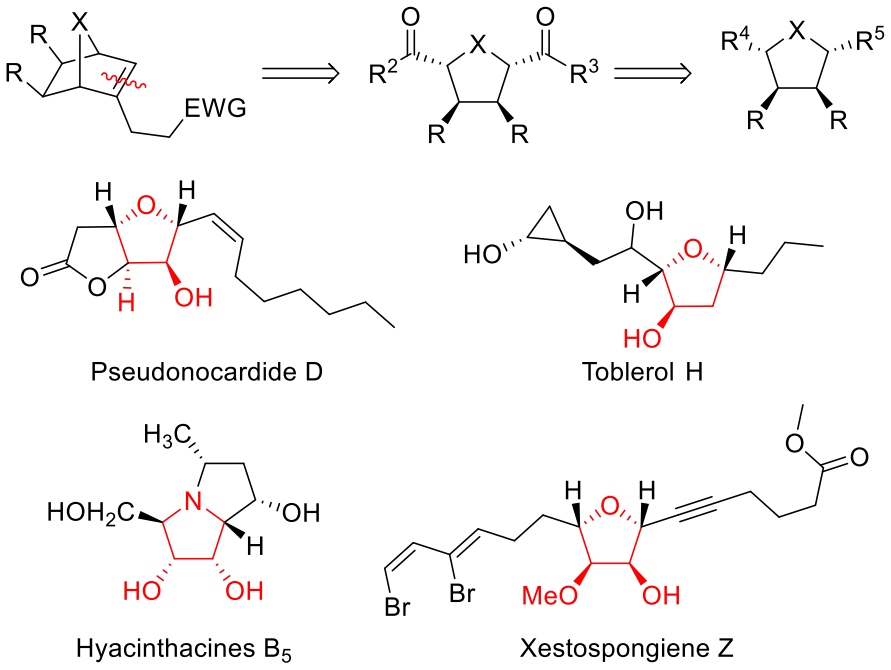
3.2 Aim of the project

The aim of this project is to perform allylation reaction with more complex α,β-disubstituted bicyclic allylic sulfones that are easily available via cycloaddition reactions and highly interesting for application in natural product synthesis (**Scheme 3-8**). Based on the literature precedent described above, it was clear that isomerization of the allylic sulfone could be a major side reaction. However, the very high reactivity of the starting exo-methylene moiety and the fast trapping of the benzenesulfonyl radical by triethylborane is expected to favour the desired reaction.



Scheme 3-8 Aim of project.

The product resulting from these allylations are particularly interesting for a variety of natural product syntheses. Indeed, oxidative opening the bicyclic compounds by ozonolysis afford polysubstituted cyclopentane (X = CH_2), tetrahydrofurans (X = O), and pyrrolidines (X = NR) with a well-defined substitution pattern. These core structures are present in many natural compounds as shown in **Scheme 3-9**.[20–23]



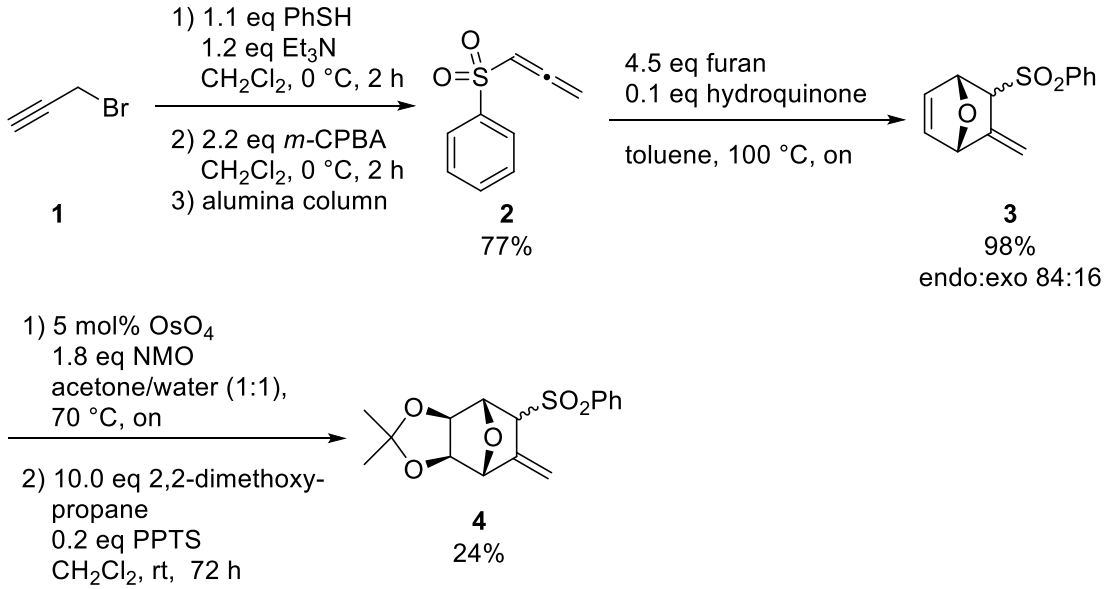
Scheme 3-9 Natural compounds with related core structure.[20–23]

3.3 Results and discussion

Different routes were tried for the radical reactions on bicyclic allylic sulfones, and the following subchapters are divided into triethylborane mediated reactions and photoredox approaches.

3.3.1 Triethylborane mediated reactions

Synthesis of bicyclic allylic sulfone 4

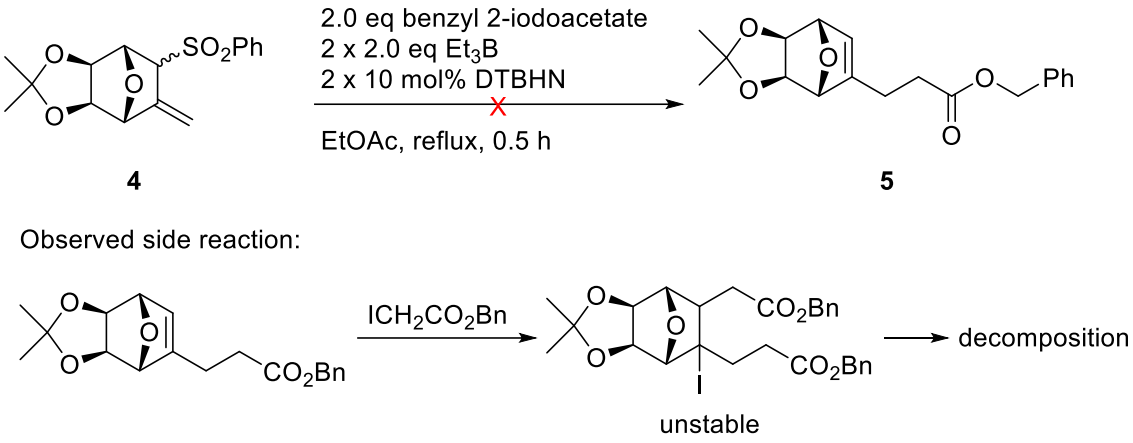


Scheme 3-10 Synthesis of bicyclic allylic sulfone **4**.

The synthesis of **4** started with the preparation of allene **2**. Allene **2** was synthesized in three steps, starting with the addition of propargyl bromide to thiophenol. Then, the formed propargylic thioether was oxidized to the sulfone with *meta*-chloroperbenzoic acid (*m*-CPBA) and in the last step, the alkyne sulfone was purified and isomerized on a basic alumina column to yield **2** in 77% yield with 87% purity. Impurity showed to be non-isomerized propargyl sulfone which could be recovered in the next step and used again for the isomerization step. Having the allenyl sulfone **2** in hand, a Diels-Alder reaction with furan and hydroquinone was made to obtain **3** in 98% yield (endo:exo 84:16). Finally, **3** was treated with osmium tetroxide and NMO, and the diol formed was protected with 2,2-dimethoxypropane (DMP) to give **4** in an overall yield of 24%. The low yield for the two steps is due to the messy work-up after diol formation. This could be avoided in later reactions by concentrating the reaction mixture before extraction.

Radical reaction attempts with bicyclic allylic sulfone 4

The radical reactions of the allylic sulfone **4** with benzyl 2-iodoacetate was run in the presence of triethylborane and DTBHN as an initiator (**Scheme 3-11**).

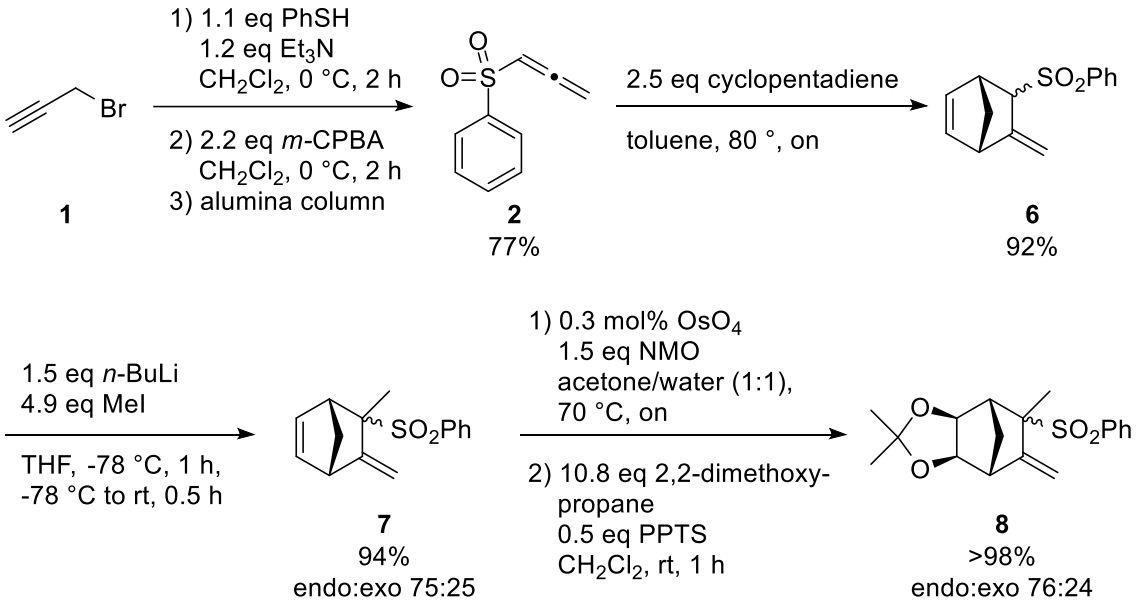


Scheme 3-11 First radical reaction attempt.

The reaction was followed by TLC and rapid formation of new spots was observed. Starting allylic sulfone **4** was partly consumed, and the newly formed spots started to change again. Further initiation did not lead to complete consumption of the starting allylic sulfone **4** and initially formed spots faded. After purification of the reaction mixture, the starting allylic sulfone **4** was recovered and a mixture of inseparable products was formed. NMR analysis of the product mixture indicated that the reaction did not stop after the first addition and the initially formed product reacts further. When repeating the reaction, it was tried to stop the reaction before the initial product **5** could react further, but all attempts to isolate **5** failed. Then various parameters such as the solvent (DCE), the addition of bases (Cs_2CO_3) or the type of initiator (Bu_6Sn_2) were changed, but the result always remained the same and no allylation product **5** could be isolated. A closer look at the NMR of the product mixture indicated that the radical addition happens twice. First, the desired product **5** is formed, and with the newly formed double bond in the bicyclic ring systems, a competing system to the starting allyl phenyl sulfone is present in the reaction mixture which seems to be more reactive. The second radical reaction proceeds on the newly formed double bond to yield a tertiary iodide which is unstable and degrades. Purification yielded clearly violet-coloured fractions, which supports this hypothesis. Therefore, no further experiments were performed on allylic sulfone **4** and our study was continued with bicyclic sulfone **8**.

Synthesis of bicyclic allylic sulfone 8

We hypothesized that introducing a substituent on the bicycle at position α to the sulfone should allow to prevent a second radical addition to the desired allylated product. For that purpose, the methylated bicyclic sulfone **8** was prepared.

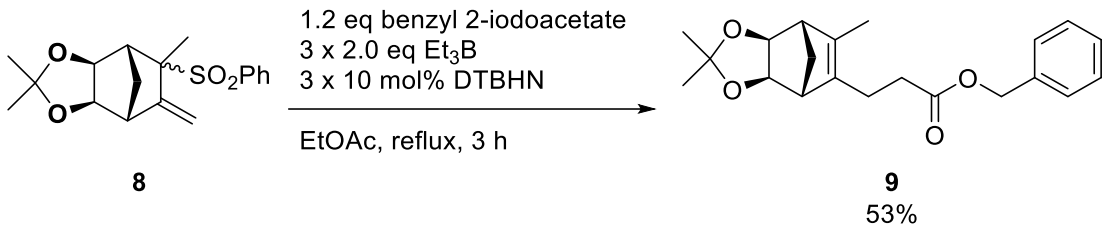


Scheme 3-12 Synthesis of bicyclic allylic sulfone **8**.

The same strategy as described for sulfone **4** was employed. In order to avoid a possible β-fragmentation in the final step, we decided to switch to the cyclopentadiene adduct to avoid the presence of the alkoxy group β to the sulfone.

2 was synthesized according to the procedure used for **4** and used for the Diels-Alder reaction with cyclopentadiene to obtain **6** in 92% yield. Then, **6** was deprotonated with *n*-BuLi und methylated with methyl iodide at -78 °C to obtain **7** in 94% yield (endo:exo 75:25). The dihydroxylation of **7** was again made with osmium tetroxide and NMO as well as the protection with DMP to obtain **8** in quantitative yield (endo:exo 76:24). Like already mentioned before, by adjusting the work-up procedure of the dihydroxylation step the yield could successfully be increased. With **8** in hand, the second series of radical reactions could be started.

Radical reaction attempts with bicyclic allylic sulfone 8



8 **9** 53%

Scheme 3-13 Radical reaction attempt on **8**.

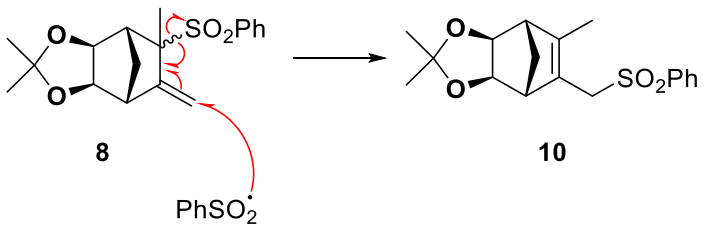
First, the reaction conditions used for **4** were applied to **8**. After two initiations with triethyl borane and DTBHN, TLC showed that still some **8** was left in the reaction mixture and the reaction was initiated a third time. The reaction was cleaner than the one with **4** and the desired allylated ester **9** was isolated in 53% yield.

Based on this result, a short optimization of the solvent was carried out. The results of the optimization are depicted in **Table 3-2**.

Table 3-2 Solvent optimization of radical reaction on **8**.

Nr.	Temp. [°C]	Solvent	Addition of DTBHN and Et_3B	Yield (isolated)
1	80	EtOAc	3x	53% (61% brsm)
2	55	DCE	3x	38%
3	80	DCE	2x	55% (65% brsm)
4	80	ACN	2x	50%
5	80	C_6H_5Cl	2x	30%
6	80	TFT	2x	40%

Five solvents were tested, whereby the firstly used solvent ethyl acetate showed to be already a good choice. The reaction in DCE gave a slightly better yield using only two initiations (**Table 3-2**, entry 3). The reaction was also run in DCE at 55 °C in order to test milder conditions, but this led to a lower yield (**Table 3-2**, entry 2). During the solvent screening, competing isomerization of the starting bicyclic allylic sulfone **8** was observed (**Scheme 3-14**).

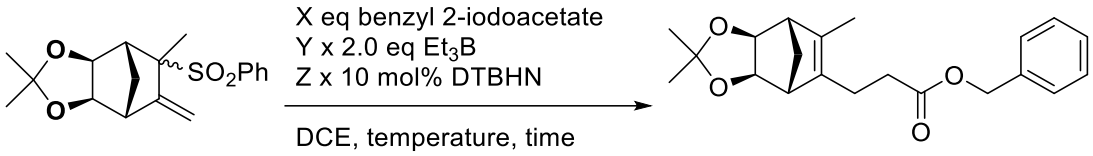


8 **10**

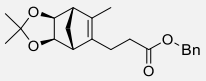
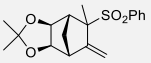
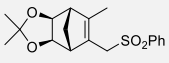
Scheme 3-14 Isomerization reaction of bicyclic allylic sulfone **8**.

Further optimization were run to decrease the amount of isomerized allylic sulfone **8** and results are shown in **Table 3-3**.

Table 3-3 Further optimizations in order to decrease the amount of isomerization.



8 **9**

Nr.	Time [h]	Temp. [°C]	ICH_2 EWG [eq]	Et_3B [eq]	Add. of DTBHN	Yield		
						9 	**8** 	**10** 
1	2	80	1.2	2.0 x 2	2x	50%	7%	42%
2	2	80	1.2	4.0	2x	49%	17%	34%
3	2	80	2.0	4.0	2x	40%	13%	38%
4	2	80	2.0	4.0 (Et_2Zn)	2x	Failed, no reaction and no isomerization		
5	2	55	2.0	4.0	2x	22%	36%	41%
6	1	120	2.0	4.0	None	17%	49%	25%
7	1	120	2.0	4.0	1x 20 mol%	15%	27%	16%

Under the optimized conditions of **Table 3-2** (entry 3), the amount of isomerized allylic sulfone **10** reached 42% (**Table 3-3**, entry 1). By adding twice DTBHN, but all triethylborane at once at the beginning of the reaction, the amount of isomerized allylic sulfone **10** could be decreased but no improvement in yield was obtained (**Table 3-3**, entry 2). Increasing the amount of benzyl 2-iodoacetate decreased the amount of isomerized allylic sulfone **10** but as well the allylated ester **9** (**Table 3-3**, entry 3). Then, the source of ethyl radicals was changed by adding diethyl zinc solution instead of triethylborane solution which shut down the reaction completely (**Table 3-3**, entry 4). Raising or lowering the temperature did not led to any improvement. At lower temperature, the yield dropped and the amount of isomerized allylic sulfone **10** remained the same (**Table 3-3**, entry 5). At higher temperature, the reaction was performed without radical initiator which also led to isomerized allylic sulfone **10** (**Table 3-3**, entry 6). The second attempt at higher temperature was performed with *tert*-butoxy 2-ethylhexyl carbonate, a radical initiator

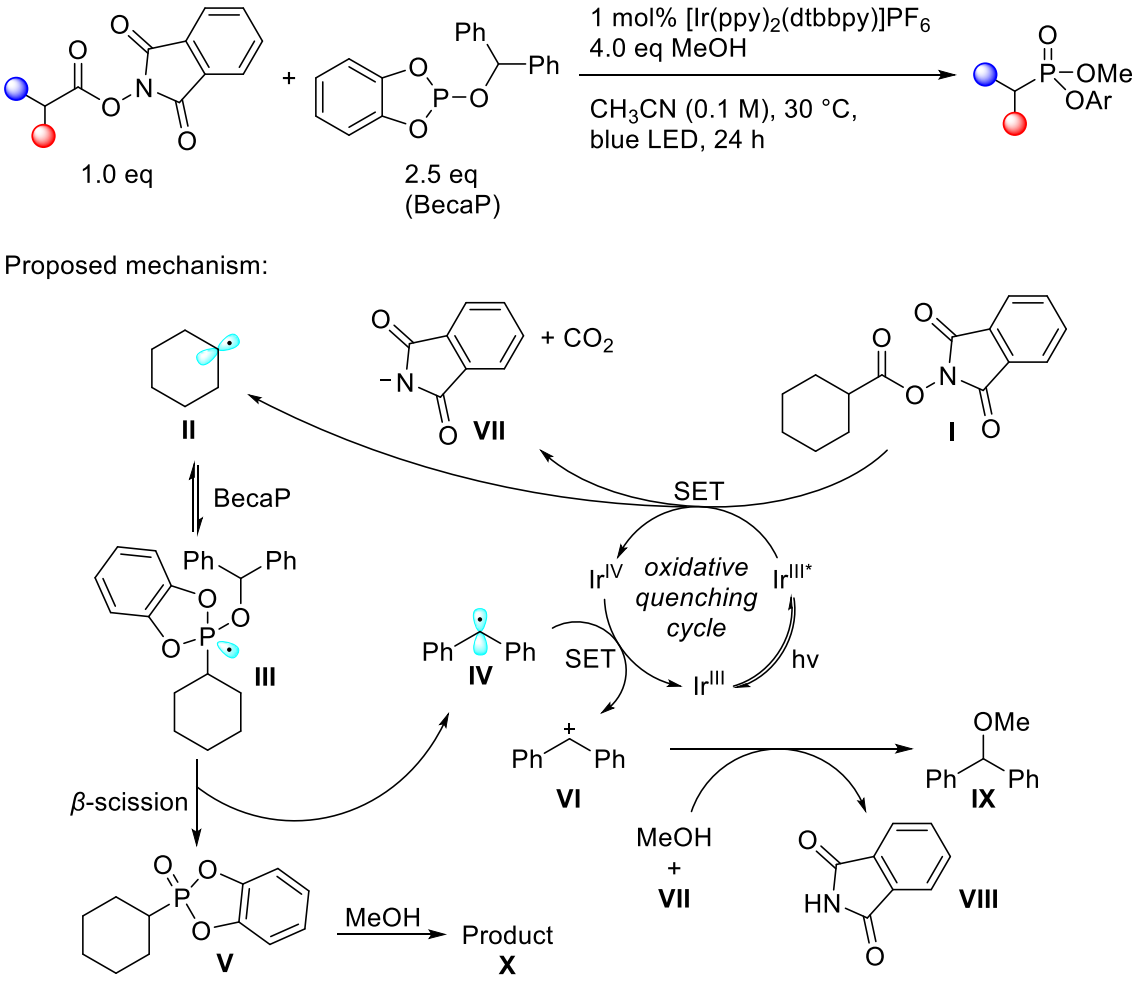
with longer half-life time than DTBHN at 120 °C, but this led to no improvement in formation of product **9** (**Table 3-3**, entry 7).

Despite all our optimization efforts, the yield of the reaction involving **8** could not be improved. To overcome this limitation, other sulfones were prepared and tested.

3.3.2 Photoredox approaches

In order to prevent isomerization, a competing α-scission of the sulfonyl radical was examined next. Zard showed that ethyl or isopropyl sulfonyl radicals undergo α-scission at elevated temperatures, forming ethyl radicals or isopropyl radicals and sulfur dioxide.[6,7] Through α-scission, the alkyl sulfonyl radical was expected to decompose preventing isomerization of the starting allylic sulfone. Inspired by the isopropanesulfonyl radical, which leads to a secondary alkyl radical, allyl sulfones containing secondary and tertiary alkyl groups were investigated.

In 2023, Aggarwal published a new method for the convergent deboronative and decarboxylative phosphonylation reaction based on photoredox chemistry (**Scheme 3-15**).[24]



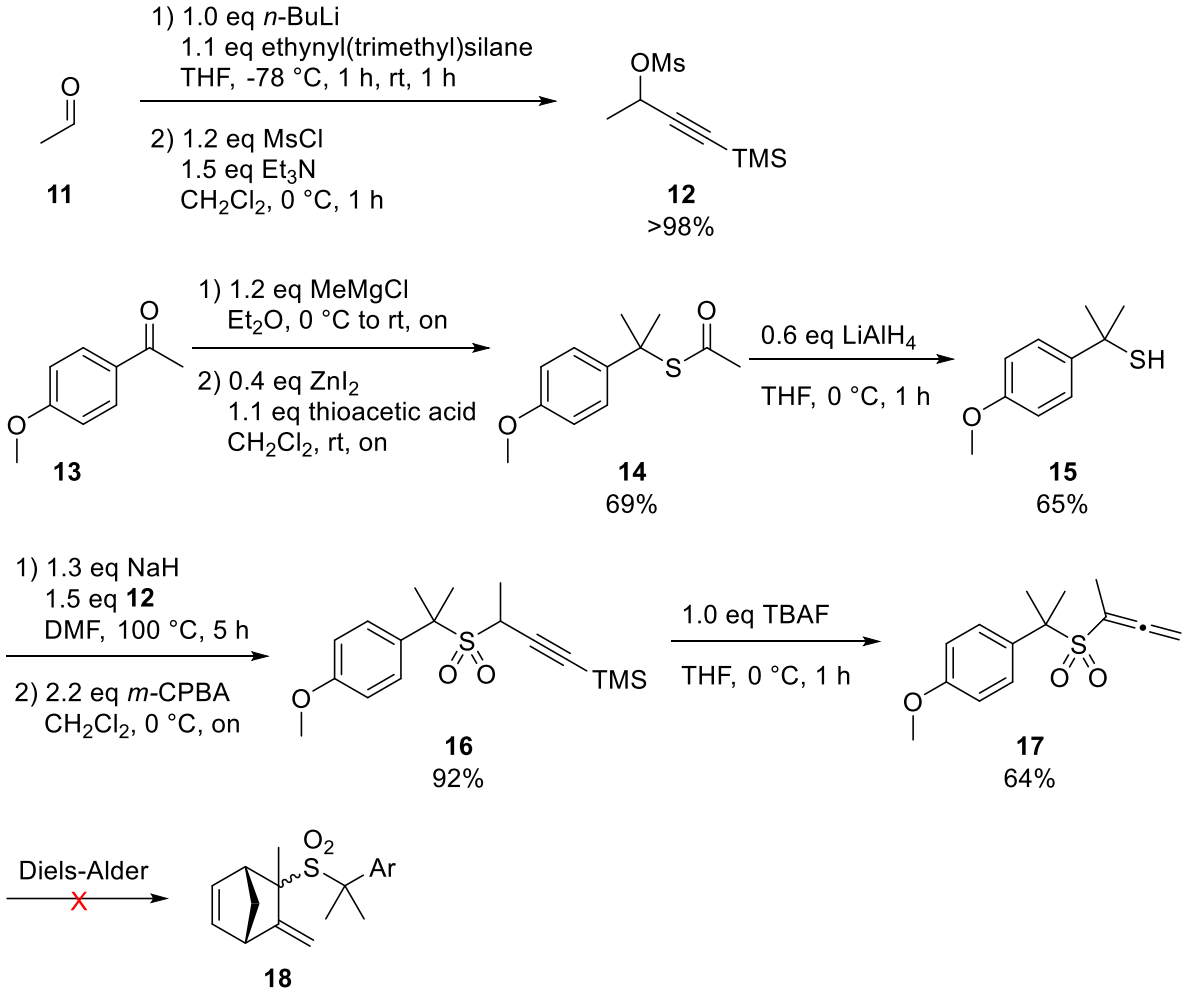
Scheme 3-15 Deboronative and decarboxylative phosphonylation reaction and proposed mechanism by Aggarwal.[24]

With this protocol, first **I** is reduced by the exited iridium catalyst forming phthalimide anion **VII**, CO_2 and alkyl radical **II**. Alkyl radical **II** adds to BecaP forming intermediate **III** whereby **V** and benzhydryl radical **IV** are released after β-scission. While **V** reacts further with methanol to form the desired product **X**, the benzhydryl radical **IV** is oxidised by the iridium catalyst to form **VI** and the regenerated iridium(III) catalyst ready to be used for the next reaction cycle. Lastly,

VI is trapped by methanol to form **IX**, and proton transfer allows the formation of phthalimide **VIII**.[24]

Based on this method, it was planned to use allyl sulfones containing secondary and tertiary alkyl groups. After radical addition to the sulfone, secondary or tertiary sulfonyl radicals were to be formed and, after sulfur dioxide fragmentation, the formed secondary, respectively tertiary radical is expected to be oxidized to the corresponding cation regenerating the Ir(III) catalyst.

Synthesis of allenyl sulfone 17

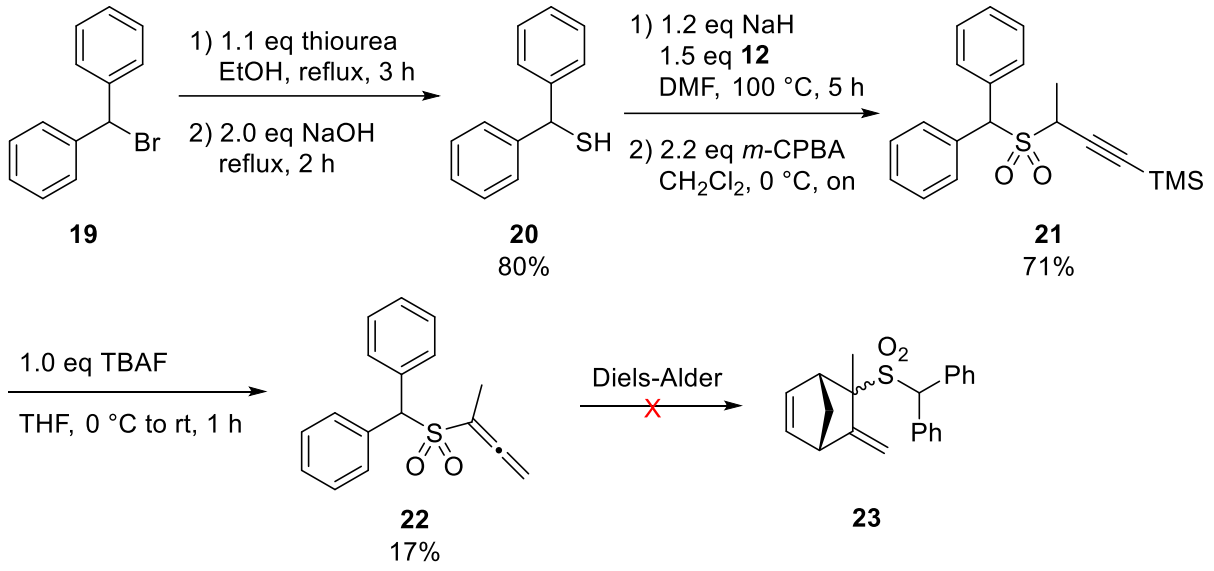


Scheme 3-16 Synthesis of allenyl sulfone **17**.

In the first step ethynyl(trimethyl)silane was deprotonated and reacted with acetaldehyde **11** forming an alcohol, which was mesylated afterwards to obtain **12** in quantitative yield over two steps. Then, 1-(4-methoxyphenyl)ethenone **13** was treated with methyl magnesium chloride forming an alcohol. The prepared alcohol was treated with zinc iodide and thioacetic acid to obtain thioester **14** in 69% yield over two steps. Reduction of **14** with lithium aluminium hydride

gave thiol **15** in 65% yield. Then, thiol **15** was deprotonated with sodium hydride and coupled with the propargylic mesylate **12** to form a thioether which was treated with *m*-CPBA to obtain sulfone **16** in 92% yield over two steps. In the last step, **16** was reacted with TBAF solution whereby the alkyne was deprotected first and directly isomerized afterwards to the sulfonyl allene **17** in 64%. **17** was used for Diels-Alder reactions with cyclopentadiene. Unfortunately, all attempts failed and no bicyclic allylic sulfone **18** could be prepared.

Synthesis of allenyl sulfone 22

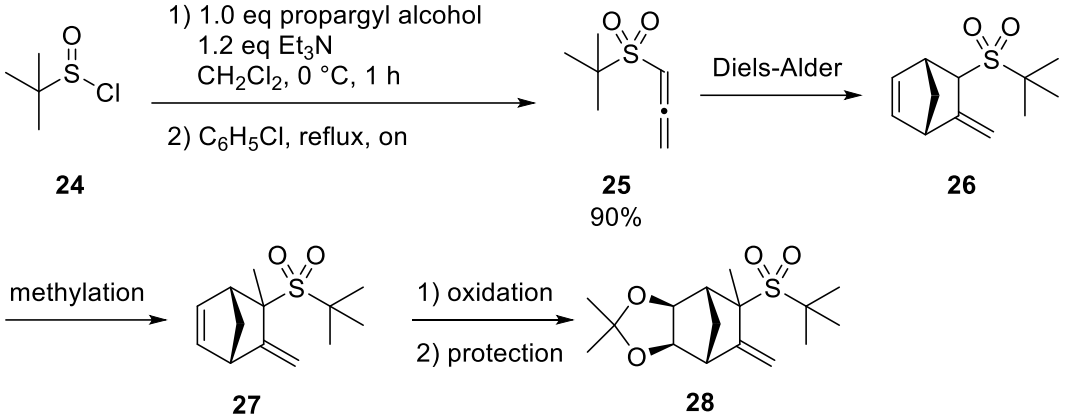


Scheme 3-17 Synthesis of allenyl sulfone **22**.

The bis-benzylic bromide **19** was converted to thiol **20** in 80% yield. Then, **20** was deprotonated with sodium hydride and coupled with the propargylic mesylate **12** to obtain a thioether, which was then oxidized with *m*-CPBA to obtain sulfone **21** in 71% yield over two steps. Propargylic sulfone **21** was treated with TBAF solution to produce the isomerized allenyl sulfone **22** in 17% yield. Unfortunately, all attempts to use **22** for Diels-Alder reactions with cyclopentadiene failed.

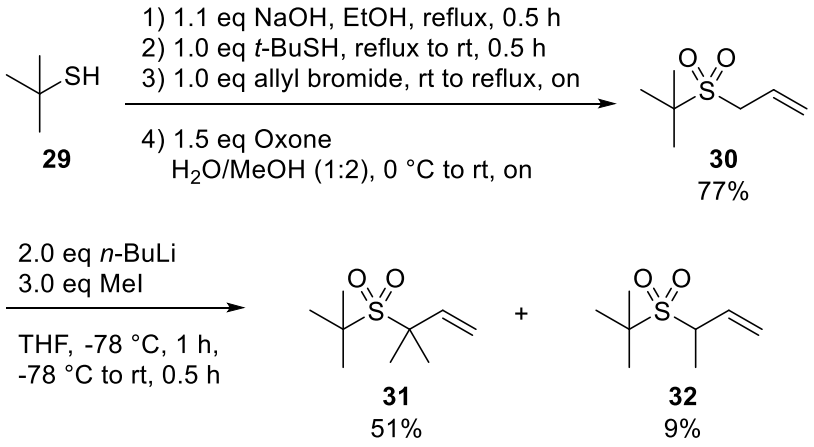
Synthesis of allenyl sulfone 25 and model system 31

Since the use of methylated allenyl sulfones **17** and **22** failed to undergo Diels-Alder reactions with cyclopentadiene, we decided to investigate a route involving the *tert*-butyl sulfone **27**. Its synthesis via methylation of the known **26**[25] was proposed (**Scheme 3-18**).



Scheme 3-18 Proposed synthesis for **28**.

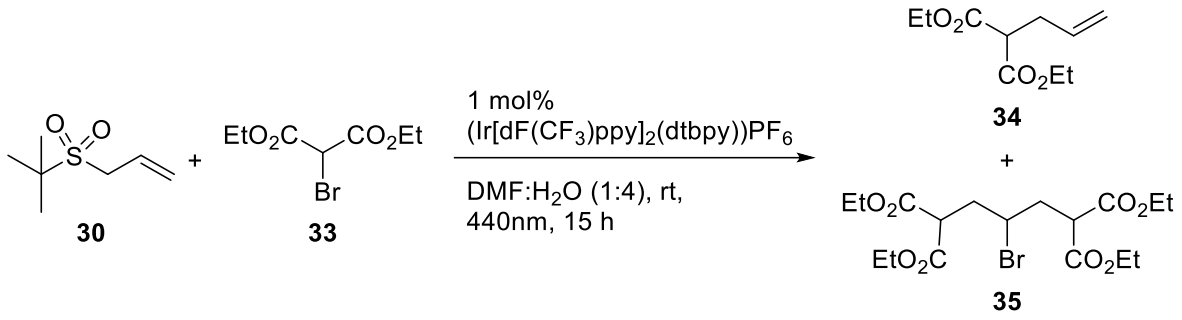
Starting from 2-methylpropane-2-sulfinyl chloride **24**, **25** was synthesized in two steps with 90% yield overall. Conversion of **25** to **26** is reported in the literature[25] but was not performed since we decided to focus first on the model system **31** (**Scheme 3-19**).



Scheme 3-19 Synthesis of model system **31**.

The allyl sulfone **30** was prepared according to literature[26] from tert-butyl mercaptan **29** in 77% yield. Methylation of **30** afforded the desired model substrate **31** in 51% together with the monomethylated **32** (9%).

Allylation reactions with allyl sulfone 30



Scheme 3-20 Radical photoredox catalysis reactions on **30**.

With the conditions of Stephenson[27], the first radical photoredox catalysis reactions were performed on *tert*-butyl allyl sulfone **30** (**Scheme 3-20**) and results are shown in **Table 3-4**.

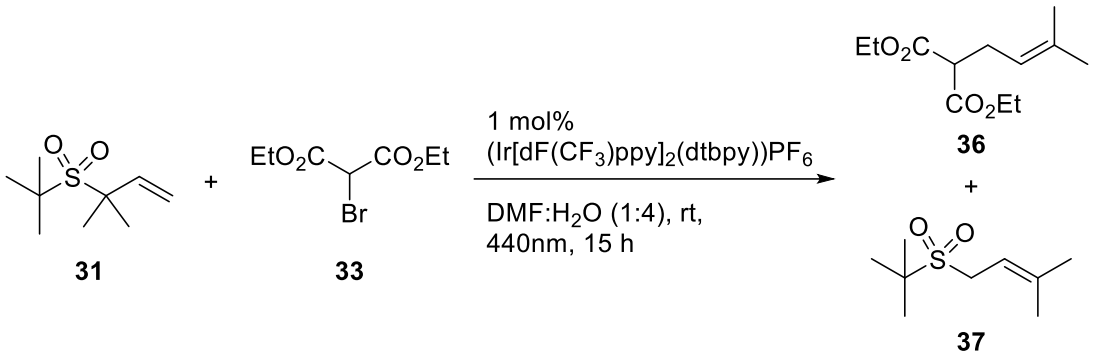
Table 3-4 Results of first radical photoredox catalysis reactions.

Nr.	Temp.	**30** [eq.]	**33** [eq.]	NMR-Yield	
				34	**35**
1	Rt	1	2	0%	80%
2	80 °C	1	2	0%	56%
3	Rt	2	1	18%	29%
4	Rt	3	1	23%	15%
5	Rt	5	1	39%	9%

When 2 equivalents of diehyl bromomalonate **33** relative to the allyl sulfone **30** were used, a smoothly reaction was observed leading to **35** in 80% yield (**Table 3-4**, entry 1). This indicates that the first addition is very productive and works as anticipated. However, the allylation reaction is followed by an efficient ATRA process leading to the bromide **35** of the double addition. When running the reaction with an excess of the alkene, formation of the allylated product **34** started to be observed, but even with a 5-fold excess of the double addition could not be avoided (**Table 3-4**, entry 3-5).

These experiments demonstrate clearly the photoredox catalyzed reaction is proceeding efficiently. However, with the non-methylated allyl sulfone **30**, it was not possible to check if sulfone isomerization is suppressed or not since isomerization in this case is a degenerated process. Therefore, allylation with the 1,1-dimethyl allyl sulfone **31** was examined next.

Allylation reactions with allyl sulfone 31



Scheme 3-21 Radical photoredox catalysis reactions on **31**.

Results from the radical photoredox catalysis reactions with sulfone **31** are shown in **Table 3-5**.

Table 3-5 Results of radical photoredox catalysis reaction on **31**.

Nr.	Temp.	Time [h]	M [mol/L]	**31** [eq.]	**33** [eq]	NMR-Yield		
						36	**37**	**31**
1	Rt	15	0.3	1	2	0%	0%	0%
2	Rt	15	0.3	2	1	0%	96%	0%
3	Rt	1	0.3	1	2	0%	27%	0%
4	Rt	1	0.3	1	1.2	0%	33%	0%
5	90 °C	1	0.3	1	1.2	0%	9%	0%
6	90 °C	1	0.03	1	1.2	6%	12%	0%
7	90 °C	1	0.3*	1	1.2	18%	12%	21%

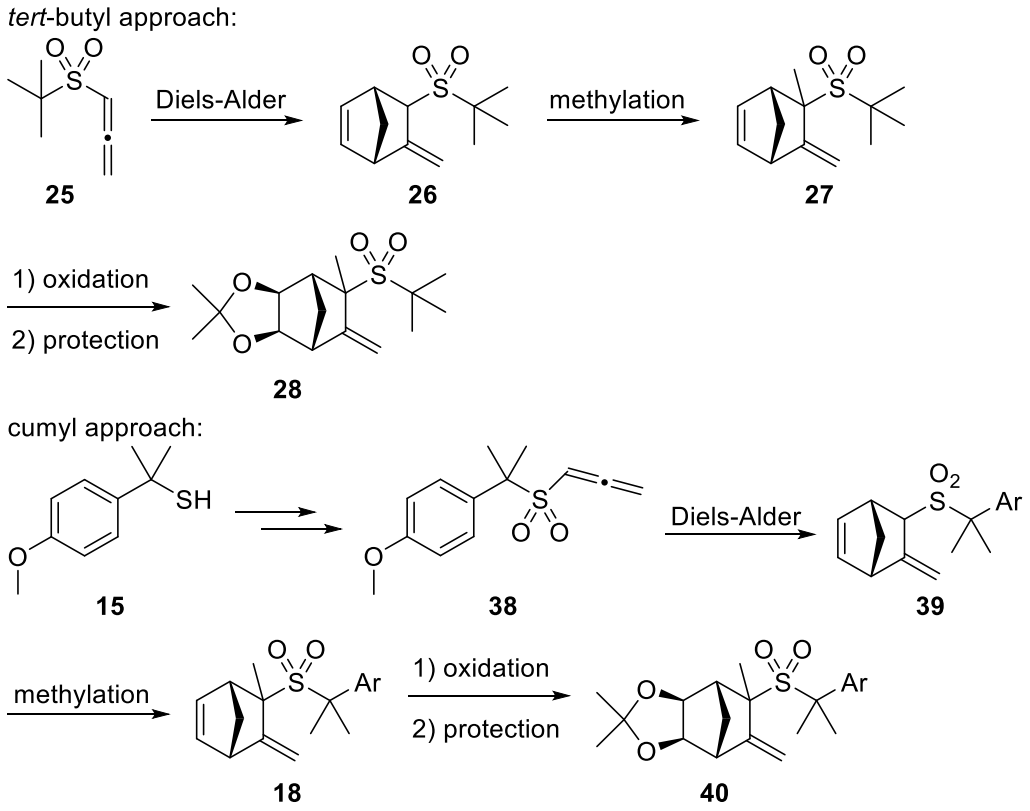
*only DMF as solvent

With an excess of the bromomalonate **33** (**Table 3-5**, entry 1) no product, allyl sulfone or isomerized allyl sulfone were detected. When using an excess of the alkene **31** (**Table 3-5**, entry 2) only isomerized allyl sulfone **37** was obtained and no product **36**. Reducing the reaction time from 15 h to 1 h, reduced as well the formation of isomerized allyl sulfone **37**, but still no desired product **36** was observed (**Table 3-5**, entry 3). Changing the reaction temperature showed to be effective and desired product **36** was obtained when the reaction in addition was run in more dilute conditions (**Table 3-5**, entry 5-6). Running the reaction in DMF only (**Table 3-5**, entry 7) delivered the best results with 18% desired product **36** and 12% isomerized allyl sulfone **37**. The experiments made showed that the photoredox reactions are efficient but further adjustments have to be made to fully avoid isomerization of the sulfone.

3.4 Conclusion & outlook

Two different approaches were tested. In the first approach, triethylborane was used as an initiator and chain transfer reagent. Two bicyclic allylic sulfones **4** and **8** were successfully synthesized in 6, or respectively 7 steps. Radical reactions with **8** demonstrated the importance of the substituent at the α to the sulfonyl group to avoid double radical addition. The radical reaction with **8** gave promising yields of up to 53%, accompanied by isomerised allylic sulfone **10**.

In the second approach, photoredox catalysis was tested. Two allenyl sulfones **17** and **22** were successfully prepared. Both allenyl sulfones were used for Diels-Alder reactions with cyclopentadiene, but in both cases no product was obtained. This demonstrates that it is important to follow the reaction sequence used for the synthesis of **8** by introducing the methyl group after the Diels-Alder reaction via a sulfone alkylation reaction. Allylation reactions with the model substrates **30** and **31** were performed and yielded promising results demonstrating the efficiency of the photoredox reactions. Although the isomerisation of the allyl sulfone could not be completely avoided, the photoredox results of the model substrate are promising for the planned photoredox reactions with the bicyclic allyl sulfones **28** and **40** shown in **Scheme 3-22**.



Scheme 3-22 Proposed synthesis for bicyclic allylic sulfones **28** and **40**.

3.5 Experimental section

3.5.1 General information

Techniques

All reactions requiring anhydrous conditions were performed in heat-gun, oven or flame dried glassware under an argon atmosphere. An ice bath was used to obtain a temperature of 0 °C. To obtain a temperature of –78 °C, a bath of acetone was cooled with dry ice or in case of light reactions ethanol/dry ice was used instead. Silica gel 60 Å (40–63 µm) from Sigma Aldrich or Macherey Nagel and 60 Å (15-40 µm) from Macherey Nagel was used for flash column chromatography. Thin layer chromatography (TLC) was performed on Silicycle silica gel 60 F_{254} plates, visualization under UV light (254 nm) and/or by dipping in a solution of $(NH_4)_2MoO_4$ (15.0 g), $Ce(SO_4)_2$ (0.5 g), H_2O (90 mL), conc. H_2SO_4 (10 mL); or $KMnO_4$ (3 g), K_2CO_3 (20 g) and NaOH 5% (3 mL) in H_2O (300 mL) and subsequent heating. Anhydrous sodium sulfate was used as drying reagent.

Deactivated silica gel for the purification of bicyclic amines:

The abovementioned silica gel was suspended in in Et_2O and 20w% of HMDS, then filtered, washed with Et_2O and dried on HV overnight. Deactivated TLC plates: silica plates are dipped in 7M NH_3 in MeOH and then dried.

Materials

Commercial reagents were used without further purification unless otherwise stated. Dry solvents for reactions were filtered over columns of dried alumina under a positive pressure of argon. Solvents for extractions (Et_2O, Heptanes, *n*-pentane, CH_2Cl_2, EtOAc) and flash column chromatography were of technical grade and distilled prior to use. Commercial dry DMF was used without further purification.

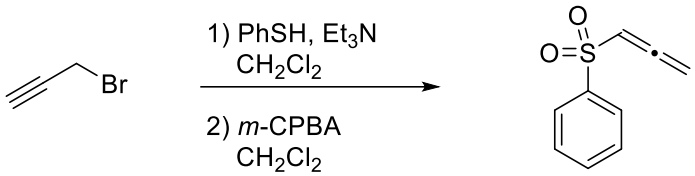
Instrumentation

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance IIIHD-300 spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C at room temperature (24-25°C) unless otherwise stated. Some ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance IIIHD-400 or a Bruker Avance II-400 spectrometer (^1H: 400 MHz; ^{13}C: 75 MHz). Chemical shifts (δ) are reported in parts per million (ppm) using the residual solvent or $Si(CH_3)_4$ (δ = 0.00 for ^1H NMR spectra) as an internal standard. Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), and br (broad). Coupling constant (J) is reported in Hz. In ^{13}C-NMR spectra, the peak positions are reported on one decimal unless the difference in chemical shift between two signals is small and required two decimals. Infrared spectra were recorded on a Jasco FT-IR-460 plus spectrometer equipped with a Specac MKII Golden Gate Single Reflection

Diamond ATR system and are reported in wave numbers (cm^{-1}). At maximum, the ten most prominent peaks are reported. Chrial GC spectra were recorded on a Thermo fisher Trace GC Ultra spectrometer fitted with a Restek Rt-bDEXm capillary column (30m, 0.25mmID, 0.25µm df); gas carrier: He 1.2 mL/min; injector: 220 °C split mode. Chiral HPLC spectra were recorded on an Agilent Technologies 1260 Infinity. Low resolution mass spectra were recorded on a Waters Micromass Autospec Q mass spectrometer in EI mode at 70 eV or were taken from GC-MS analyses performed on a Thermofisher GC-MS (quadrupole mass analyzer using EI mode at 70 eV) fitted with a Macherey-Nagel Optima delta-3-0.25 µm capillary column (20 m, 0.25 mm); gas carrier: He 1.4 mL/min; injector: 220 °C split mode. HRMS analyses and accurate mass determinations were performed on a Thermo Scientific LTQ Orbitrap XL mass spectrometer using ESI mode. Melting points were measured on a Büchi B-545 apparatus and are corrected. Syringe filters with polytetrafluoroethylene membrane were used with a pore size of 0.45 µm (or 5 µm) from Machery-Nagel (CHROMAFIL®Xtra PTFE 0.45). Medium pressure liquid chromatography (MPLC) was performed with a CombiFlash® Rf+ system from Teledyne Isco using RediSep® single-use normal phase columns.

3.5.2 Synthesis of bicyclic allylic sulfone 4

propa-1,2-dienylsulfonylbenzene (2)



Chemical Formula: $C_9H_8O_2S$
Molecular Weight: 180.22

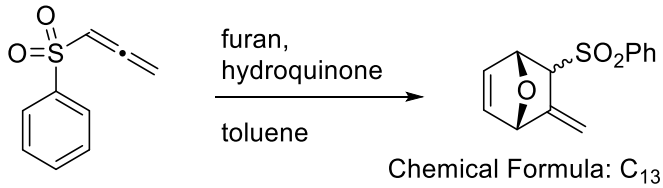
Intermediate **2** was prepared by an adapted reported procedure[28–31].

To a solution of propargyl bromide (80 wt%, 1.7 mL, 15.3 mmol) and PhSH (1.7 mL, 16.8 mmol) in DCM (10 mL) was added Et_3N (2.5 mL, 18.3 mmol) at 0 °C and was stirred for 2 h. Then, the reaction mixture was diluted with water and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

The crude product was dissolved in DCM (30 mL) and cooled down to 0 °C. *m*-CPBA (77%, 7.53 g, 33.6 mmol) dissolved in DCM (90 mL) was added slowly and stirred for 2 h. The reaction mixture was treated with sat. aq. $Na_2S_2O_3$ soln. and sat. aq. $NaHCO_3$ soln. and extracted with DCM (3 ×). The combined organic phases were washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on basic alox (DCM 100%) to afford **2** (2.43 g, 77% yield, 87% purity). Impurity is not isomerized (prop-2-yn-1-ylsulfonyl)benzene.

Appearance yellow oil; **Rf** 0.6 (DCM 100%); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.94 – 7.88 (m, 2H), 7.66 – 7.50 (m, 3H), 6.24 (t, J = 6.3 Hz, 1H), 5.44 (d, J = 6.4 Hz, 2H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 209.55, 141.32, 133.71, 129.34 (2 x CH), 127.72 (2 x CH), 101.09, 84.26. Physical and spectral data are in accordance with literature data[28–30].

(1*R*,4*S*)-5-methylene-6-(phenylsulfonyl)-7-oxabicyclo[2.2.1]hept-2-ene (3)



Chemical Formula: $C_{13}H_{12}O_3S$
Molecular Weight: 248.30

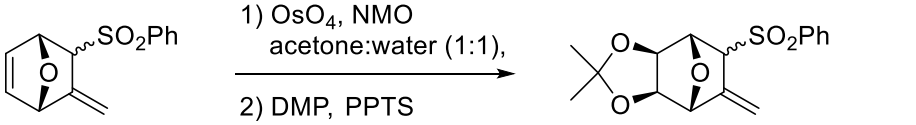
Intermediate **3** was prepared by a reported procedure[32].

In a seal tube were placed propa-1,2-dienylsulfonylbenzene (**2**) (87%, 722 mg, 3.5 mmol), furan (1.15 mL, 15.9 mmol), hydroquinone (43 mg, 0.4 mmol) and toluene (10 mL), and stirred at 100 °C overnight. The reaction mixture was concentrated under reduced pressure and the crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:1, stained in PMA solution) to afford **3** (846 mg, 98%, endo/exo 84:16).

Endo isomer: **Appearance** yellow oil; **Rf** 0.34 (Et_2O/pentane=1:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.91 – 7.78 (m, 2H), 7.68 – 7.60 (m, 1H), 7.58 – 7.46 (m, 2H), 6.44 (dd, J = 5.8, 1.9 Hz, 1H), 6.36 (dd, J = 5.8, 1.6 Hz, 1H), 5.27 (d, J = 1.2 Hz, 1H), 5.27 (d, J = 0.8 Hz, 1H), 5.05 (dd, J = 1.9, 1.0 Hz, 1H), 4.94 (dd, J = 3.8, 1.5 Hz, 1H), 4.29 (dt, J = 4.2, 2.2 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 139.07, 138.55, 135.13, 134.02, 132.97, 129.29, 128.27, 110.23, 83.91, 79.14, 66.40.

Exo isomer: **Appearance** yellow oil; **Rf** 0.29 (Et_2O/pentane=1:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.91 – 7.85 (m, 2H), 7.69 – 7.57 (m, 1H), 7.55 – 7.47 (m, 2H), 6.49 (dd, J = 5.7, 1.7 Hz, 1H), 6.37 (dd, J = 5.7, 1.8 Hz, 1H), 5.50 – 5.43 (m, 1H), 5.40 – 5.36 (m, 1H), 5.34 (dt, J = 1.8, 0.8 Hz, 1H), 4.91 – 4.84 (m, 1H), 3.62 (t, J = 1.8 Hz, 1H), **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 138.23, 138.07, 137.61, 134.48, 133.90, 129.88, 128.81, 111.78, 81.97, 80.74, 67.74.Physical and spectral data are in accordance with literature data[32].

(3a*R*,4*R*,7*R*,7a*R*)-2,2-dimethyl-5-methylene-6-(phenylsulfonyl)hexahydro-4,7-epoxybenzo[d][1,3]dioxole (4)



Chemical Formula: $C_{16}H_{18}O_5S$
Molecular Weight: 322.38

Intermediate **4** was prepared by an adapted reported procedure[33].

To a solution of (1*R*,4*S*)-5-methylene-6-(phenylsulfonyl)-7-oxabicyclo[2.2.1]hept-2-ene (**3**) (9.51 g, 38.3 mmol) and NMO (8.08 g, 69.0 mmol) in acetone:water (45 mL : 45 mL) was added OsO_4 (2.5 wt% in *t*-BuOH, 2.0 mL, 0.2 mmol) and the reaction mixture was stirred at 70 °C overnight. Then, the reaction mixture was treated with 5% aq. $Na_2S_2O_3$ soln., stirred for 30 min and extracted with ethyl acetate (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

To the redissolved crude product in DCM (220 mL) was added DMP (47 mL, 384 mmol) and PPTS (1.94 g, 7.7 mmol) and the reaction mixture was stirred at room temperature for 72 h. The reaction mixture was treated with sat. aq. $NaHCO_3$ soln. and extracted with DCM (3 ×).

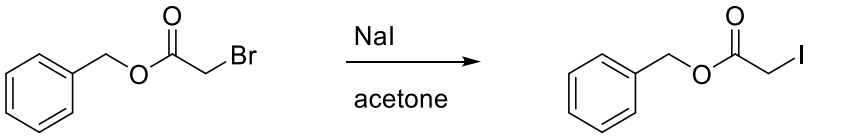
The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:1, stained in PMA solution) to afford **4** (2.94 g, 24%).

Endo isomer: **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.86 – 7.82 (m, 2H), 7.66 – 7.61 (m, 1H), 7.54 – 7.49 (m, 2H), 5.69 (dd, J = 1.8, 1.2 Hz, 1H), 5.44 – 5.42 (m, 1H), 4.81 – 4.76 (m, 1H), 4.44 – 4.41 (m, 1H), 4.29 (d, J = 5.5 Hz, 1H), 4.25 – 4.22 (m, 1H), 3.60 (q, J = 1.5 Hz, 1H), 1.39 (s, 3H), 1.23 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 137.73 (C_q), 137.28 (C_q), 134.17 (CH), 129.95 (2 x CH), 128.97 (2 x CH), 114.83 (CH_2), 112.95 (C_q), 82.94 (CH), 82.20 (CH), 81.70 (CH), 81.33 (CH), 67.24 (CH), 25.79 (CH_3), 25.14 (CH_3).

Exo isomer (characteristic signals): **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 4.71 – 4.70 (m, 1H), 4.70 – 4.68 (m, 1H), 4.61 (d, J = 1.1 Hz, 1H), 4.56 (d, J = 5.4 Hz, 1H), 4.40 (d, J = 5.4 Hz, 1H).

Mix of isomers: **Appearance** white solid; **Rf** 0.5 (Et_2O/pentane=1:1); **Mp** 175 - 180 °C; **FT-IR (cm^{-1}, neat)** 2991, 2959, 2939, 1445, 1377, 1308, 1272, 1197, 1146, 1066, 1024, 998, 966, 932, 906, 859, 822, 765, 727, 691, 642, 608; **HRMS (ESI)** m/z calculated for $C_{16}H_{18}O_5SNa$ $[M+Na]^+$: 345.0767, found: 345.0759.

benzyl 2-iodoacetate (41)



Chemical Formula: $C_9H_9IO_2$
Molecular Weight: 276.07

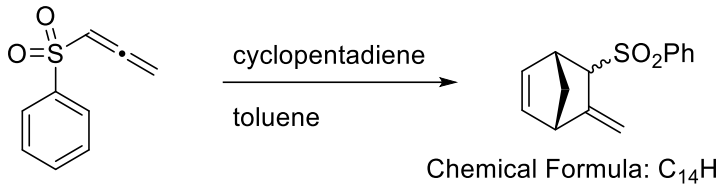
Intermediate **41** was prepared by an adapted reported procedure[34].

To a solution of benzyl 2-bromoacetate (23.0 g, 101 mmol) in acetone (150 mL) was added NaI (17.4 g, 116 mmol) and stirred at room temperature overnight. The reaction mixture was diluted with water, treated with 5% aq. $Na_2S_2O_3$ soln. and extracted with pentane (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to afford **41** (24.2 g, 87%).

Appearance yellow oil; **Rf** 0.7 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.46 – 7.28 (m, 5H), 5.18 (s, 2H), 3.74 (s, 2H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 168.66 (C_q), 135.23 (C_q), 128.73 (2 x CH), 128.61 (CH), 128.41 (2 x CH), 67.87 (CH_2), -5.39 (CH_2). Physical and spectral data are in accordance with literature data.[34]

3.5.3 Synthesis of bicyclic allylic sulfone 8

(1*R*,4*S*)-5-methylene-6-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (6)



Chemical Formula: $C_{14}H_{14}O_2S$
Molecular Weight: 246.32

Intermediate **6** was prepared by a reported procedure[35–37].

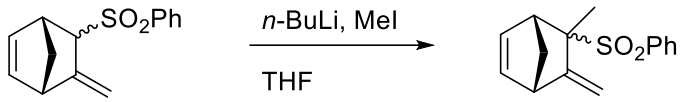
In a seal tube were placed propa-1,2-dienylsulfonylbenzene (**2**) (87%, 5.22 g, 25.2 mmol), cyclopenta-1,3-diene (4.85 g, 73.4 mmol) and toluene (90 mL), and stirred at 80 °C overnight. The reaction mixture was concentrated under reduced pressure and the crude product purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **6** (5.70 g, 92%).

Endo isomer: **Appearance** yellow oil; **Rf** 0.6 (Et_2O/pentane=1:1); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.93 – 7.82 (m, 2H), 7.72 – 7.48 (m, 3H), 6.12 (dd, J = 5.6, 3.2 Hz, 1H), 6.05 (dd, J = 5.5, 2.7 Hz, 1H), 5.31 (d, J = 2.0 Hz, 1H), 5.24 (dd, J = 2.6, 1.0 Hz, 1H), 4.19 (q, J = 2.4 Hz, 1H), 3.31 – 3.26 (m, 1H), 3.07 – 2.99 (m, 1H), 1.63 (dt, J = 8.7, 1.8 Hz, 1H), 1.48 – 1.40 (m, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 143.28 (C_q), 139.58 (C_q), 135.19 (CH), 133.68 (CH), 133.18 (CH), 129.08 (2 x CH), 128.80 (2 x CH), 110.10 (CH_2), 69.09 (CH), 52.39 (CH), 49.92 (CH_2), 45.56 (CH).

Exo isomer: **Appearance** yellow oil; **Rf** 0.7 (Et_2O/pentane=1:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.96 – 7.90 (m, 2H), 7.70 – 7.63 (m, 1H), 7.61 – 7.53 (m, 2H), 6.28 (dd, J = 5.5, 3.0 Hz, 1H), 6.10 (dd, J = 5.5, 3.1 Hz, 1H), 5.27 (d, J = 1.4 Hz, 1H), 5.11 (d, J = 1.7 Hz, 1H), 3.50 (q, J = 2.0 Hz, 1H), 3.30 – 3.26 (m, 1H), 3.19 – 3.15 (m, 1H), 2.07 – 1.99 (m, 1H), 1.51 (dq, J = 9.1, 1.8 Hz, 1H), **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 142.98 (C_q), 140.09 (CH), 139.24 (C_q), 135.74 (CH), 133.78 (CH), 129.28 (2 x CH), 129.06 (2 x CH), 111.30 (CH_2), 67.62 (CH), 50.83 (CH), 46.45 (CH_2), 45.92 (CH).

Physical and spectral data are in accordance with literature data[37,38].

(1*S*,4*R*)-5-methyl-6-methylene-5-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (7)



Chemical Formula: $C_{15}H_{16}O_2S$
Molecular Weight: 260.35

Intermediate **7** was prepared by an adapted reported procedure[38].

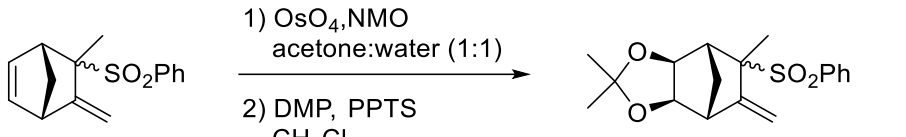
To a solution of (1*R*,4*S*)-5-methylene-6-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (**6**) (1.21 g, 4.9 mmol) in dry THF (25 mL) was added slowly *n*-BuLi (2.5 M in hexanes, 3.0 mL, 7.5 mmol) at -78 °C and stirred for 1 h. Then, MeI (1.5 mL, 24.1 mmol) was added and the reaction mixture was warmed up to room temperature. The reaction mixture was treated with aq. 1 M NaOH soln. and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **7** (1.21 g, 94%, endo:exo 75:25).

Endo isomer: **Appearance** yellow oil; **Rf** 0.4 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.90 – 7.79 (m, 2H), 7.59 (ddt, J = 8.3, 6.7, 1.3 Hz, 1H), 7.51 – 7.43 (m, 2H), 6.19 (dd, J = 5.6, 2.8 Hz, 1H), 5.95 (dd, J = 5.6, 3.2 Hz, 1H), 5.39 (s, 1H), 5.26 (d, J = 1.0 Hz, 1H), 3.30 – 3.21 (m, 1H), 2.85 – 2.76 (m, 1H), 1.75 – 1.67 (m, 1H), 1.71 (s, 3H), 1.61 (dt, J = 9.0, 1.7 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 149.47 (C_q), 138.97 (C_q), 136.40 (CH), 134.95 (CH), 133.37 (CH), 130.13 (2 x CH), 128.49 (2 x CH), 109.95 (CH_2), 73.01 (C_q), 52.42 (CH), 51.55 (CH), 49.32 (CH_2), 24.67 (CH_3).

Exo isomer: **Appearance** yellow oil; **Rf** 0.5 (Et_2O/pentane=3:7); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.94 – 7.88 (m, 2H), 7.64 (ddt, J = 8.4, 6.5, 1.4 Hz, 1H), 7.58 – 7.51 (m, 2H), 6.28 (dd, J = 5.5, 3.1 Hz, 1H), 6.07 (dd, J = 5.4, 3.2 Hz, 1H), 5.32 – 5.27 (m, 1H), 5.16 (s, 1H), 3.35 – 3.29 (m, 1H), 3.10 – 3.05 (m, 1H), 2.58 – 2.52 (m, 1H), 1.52 (dt, J = 9.0, 1.6 Hz, 1H), 1.38 (s, 3H), **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 148.78 (C_q), 139.83 (CH), 137.68 (C_q), 135.90 (CH), 133.62 (CH), 130.47 (2 x CH), 128.82 (2 x CH), 110.85 (CH_2), 72.48 (C_q), 51.82 (CH), 50.42 (CH), 48.01 (CH_2), 24.24 (CH_3).

Physical and spectral data are in accordance with literature data[38].

(3a*S*,4*R*,7*R*,7a*R*)-2,2,5-trimethyl-6-methylene-5-(phenylsulfonyl)hexahydro-4,7-methanobenzo[d][1,3]dioxole (8)



Chemical Formula: $C_{18}H_{22}O_4S$
Molecular Weight: 334.43

Intermediate **8** was prepared by an adapted reported procedure[33].

To a solution of ((1*S*,4*R*)-5-methyl-6-methylene-5-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (**7**) (986 mg, 3.8 mmol) and NMO (658 mg, 5.6 mmol) in acetone:water (10 mL : 1 mL) was added OsO_4 (2.5 wt% in *t*-BuOH, 0.12 mL, 0.01 mmol) and the reaction mixture was stirred at 70 °C overnight. Then, the reaction mixture was concentrated under reduced pressure, diluted with water, treated with aq. 1 M HCl soln. and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

To the redissolved crude product in DCM (50 mL) was added DMP (5.0 mL, 40.8 mmol) and PPTS (430 mg, 1.7 mmol) and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was treated with sat. aq. $NaHCO_3$ soln. and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=1:1, stained in PMA solution) to afford **8** (>98%, endo:exo 76:24).

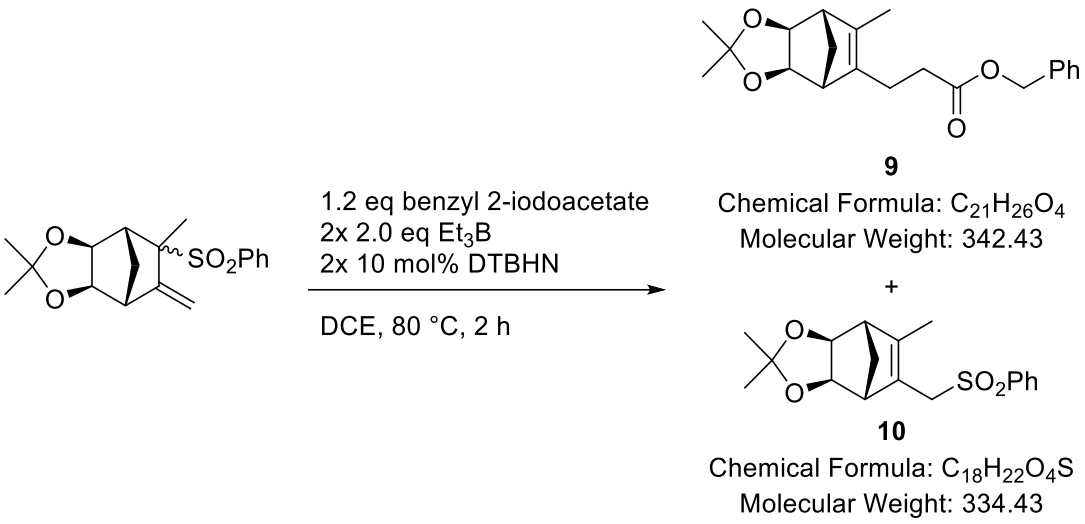
Endo isomer: **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.99 – 7.90 (m, 2H), 7.72 – 7.63 (m, 1H), 7.59 (dd, J = 8.4, 6.9 Hz, 2H), 5.47 (dt, J = 6.7, 3.4 Hz, 1H), 5.39 (s, 1H), 5.34 (s, 1H), 4.43 (dt, J = 5.2, 1.3 Hz, 1H), 2.87 (s, 1H), 2.25 (d, J = 2.0 Hz, 1H), 2.00 (dt, J = 11.0, 1.5 Hz, 1H), 1.51 – 1.44 (m, 1H), 1.48 (s, 3H), 1.46 (s, 3H), 1.37 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 146.64 (C_q), 137.94 (C_q), 133.92 (CH), 130.08 (2 x CH), 129.17 (2 x CH), 112.61 (CH_2), 109.65 (C_q), 79.61 (CH), 77.93 (CH), 70.81 (C_q), 51.85 (CH), 50.58 (CH), 31.02 (CH_2), 25.44 (2 x CH_3), 24.58 (CH_3).

Exo isomer: **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.92 – 7.87 (m, 2H), 7.72 – 7.63 (m, 1H), 7.58 – 7.49 (m, 2H), 5.45 (s, 1H), 5.40 (s, 1H), 4.34 (dt, J = 5.3, 1.3 Hz, 1H), 4.11 – 4.08 (m, 1H), 2.85 (s, 1H), 2.49 (s, 1H), 2.37 (dp, J = 11.0, 1.7 Hz, 1H), 1.75 (dt, J = 11.0, 1.4 Hz, 1H), 1.47 (s, 3H), 1.43 (s, 3H), 1.24 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 147.04 (C_q), 137.18 (C_q), 133.91 (CH), 130.50 (2 x CH), 129.07 (2 x CH), 113.87 (CH_2), 110.14 (C_q), 81.38 (CH), 78.31 (CH), 69.73 (C_q), 51.00 (CH), 48.26 (CH), 30.02 (CH_2), 25.42 (CH_3), 24.38 (CH_3), 20.40 (CH_3).

Mix of isomers: **Appearance** white solid; **Rf** 0.5 (Et_2O/pentane=1:1); **Mp** 135 - 140 °C; **FT-IR (cm^{-1}, neat)** 2987, 2937, 2360, 1711, 1656, 1583, 1448, 1378, 1301, 1263, 1208, 1135, 1075,

1049, 999, 912, 855, 830, 807, 748, 688, 668, 610, 559; **HRMS (ESI)** m/z calculated for $C_{18}H_{23}O_4S$ $[M+H]^+$: 335.1312, found: 335.1310.

benzyl 3-((3a*R*,4*R*,7*S*,7a*S*)-2,2,6-trimethyl-3a,4,7,7a-tetrahydro-4,7-methanobenzo[d][1,3]dioxol-5-yl)propanoate (9)



To a solution of benzyl 2-iodoacetate (**41**) (175 mg, 0.6 mmol) and (3a*S*,4*R*,7*R*,7a*R*)-2,2,5-trimethyl-6-methylene-5-(phenylsulfonyl)hexahydro-4,7-methano-benzo[d][1,3]dioxole (**8**) (172 mg, 0.5 mmol) in dry DCE (4.0 mL) were added Et_3B solution (1.0 M in hexanes, 1.0 mL) and DTBHN (9 mg, 0.05 mmol). The reaction mixture was put in a preheated oil bath at 80 °C and stirred for 1 h. Then, again Et_3B solution (1.0 M in hexanes, 1.0 mL) and DTBHN (9 mg, 0.05 mmol) were added and stirred for another hour at this temperature. The reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (Et_2O/pentane=2:8 to 1:1, stained in PMA solution) to afford **9** (88 mg, 50%) and as a side product **10** (73 mg, 42%).

Appearance colorless oil; **Rf** 0.4 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 1H NMR (300 MHz, CDCl3) δ 7.43 – 7.31 (m, 5H), 5.10 (s, 2H), 4.20 – 4.11 (m, 2H), 2.57 – 2.54 (m, 1H), 2.49 – 2.45 (m, 1H), 2.44 – 2.37 (m, 3H), 2.33 – 2.19 (m, 1H), 1.84 (dt, J = 8.9, 1.6 Hz, 1H), 1.61 – 1.52 (m, 1H), 1.58 (s, 3H), 1.46 (s, 3H), 1.31 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 172.98 (C_q), 138.58 (C_q), 138.49 (C_q), 136.04 (C_q), 128.72 (2 x CH), 128.51 (2 x CH), 128.44 (CH), 113.24 (C_q), 81.60 (CH), 80.92 (CH), 66.48 (CH_2), 50.94 (CH), 48.30 (CH), 40.96 (CH_2), 33.06 (CH_2), 26.23 (CH_3), 24.54 (CH_3), 22.89 (CH_2), 12.77 (CH_3); **FT-IR (cm^{-1}, neat)** 2972, 2930, 1734, 1497, 1450, 1375, 1297, 1260, 1203, 1158, 1056, 1027, 965, 914, 856, 822, 748, 696, 580; **HRMS (ESI)** m/z calculated for $C_{21}H_{27}O_4$ $[M+H]^+$: 343.1904, found: 343.1901.

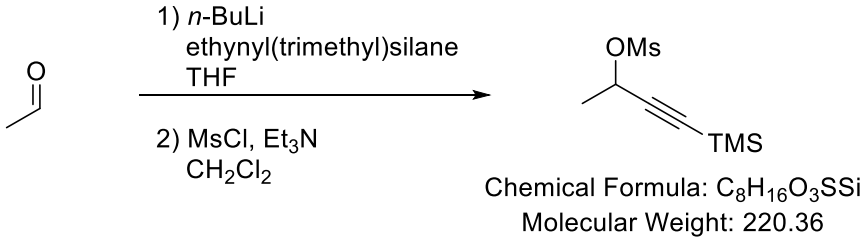
(3a*S*,4*S*,7*R*,7a*R*)-2,2,5-trimethyl-6-((phenylsulfonyl)methyl)-3a,4,7,7a-tetrahydro-4,7-methanobenzo[d][1,3]dioxole (10)

Side product from synthesis of benzyl 3-((3a*R*,4*R*,7*S*,7a*S*)-2,2,6-trimethyl-3a,4,7,7a-tetrahydro-4,7-methanobenzo[d][1,3]dioxol-5-yl)propanoate (**9**).

Appearance colorless oil; **Rf** 0.3 (Et_2O/pentane=1:1); **^{1}H-NMR** (300 MHz, CD_2Cl_2) δ = 7.90 – 7.80 (m, 2H), 7.73 – 7.62 (m, 1H), 7.61 – 7.54 (m, 2H), 4.25 (dt, *J* = 5.5, 1.3 Hz, 1H), 4.09 (dt, *J* = 5.7, 1.3 Hz, 1H), 3.87 (d, *J* = 14.1 Hz, 1H), 3.71 (dd, *J* = 14.1, 1.0 Hz, 1H), 2.63 – 2.56 (m, 1H), 2.51 – 2.44 (m, 1H), 1.83 (dt, *J* = 9.1, 1.7 Hz, 1H), 1.64 – 1.53 (m, 1H), 1.40 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H); **^{13}C-NMR** (75 MHz, CD_2Cl_2) δ = 148.89 (C_q), 139.09 (C_q), 134.16 (CH), 129.58 (2 x CH), 128.76 (2 x CH), 128.36 (C_q), 113.74 (C_q), 81.14 (CH), 80.45 (CH), 55.80 (CH_2), 51.72 (CH), 49.56 (CH), 41.57 (CH_2), 26.17 (CH_3), 24.58 (CH_3), 12.95 (CH_3); **FT-IR (cm^{-1}, neat)** 2978, 2946, 2896, 1739, 1649, 1581, 1447, 1404, 1380, 1300, 1261, 1251, 1203, 1165, 1141, 1057, 1025, 972, 925, 868, 840, 775, 753, 727, 682, 577; **HRMS (ESI)** m/z calculated for $C_{18}H_{23}O_4S$ $[M+H]^+$: 335.1312, found: 335.1311.

3.5.4 Synthesis of allenyl sulfone 17

(1-methyl-3-trimethylsilyl-prop-2-ynyl) methanesulfonate (12)



Chemical Formula: $C_8H_{16}O_3SSi$
Molecular Weight: 220.36

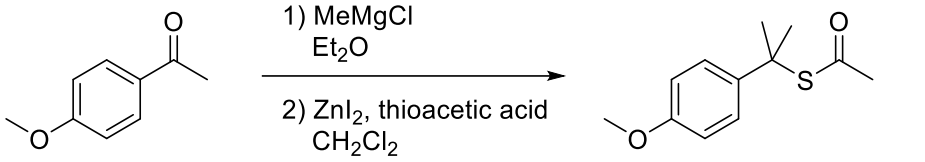
Intermediate **12** was prepared by an adapted reported procedure[39,40].

To a solution of ethynyl(trimetyl)silane (3.01 g, 30.6 mmol) in dry THF (65 mL) was added *n*-BuLi (2.5 M in hexanes, 11.0 mL, 27.5 mmol) at -78 °C and stirred for 1 h. Then, acetaldehyde (73%, 1.69 g, 28.0 mmol) in dry THF (10 mL) was added to the reaction mixture, stirred for 5 min at -78 °C and warmed up to room temperature. The reaction mixture was treated with water and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

To the redissolved crude product in DCM (100 mL) was added Et_3N (5.9 mL, 42.3 mmol) and the reaction mixture was cooled down to 0 °C. MsCl (2.7 mL, 34.9 mmol) was added slowly and the reaction mixture was stirred for 1 h. Then, the reaction mixture was treated with water and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to afford **12** (>98%).

Appearance yellow liquid; **Rf** 0.5 (Et_2O/pentane=1:9); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.25 (q, J = 6.7 Hz, 1H), 3.11 (s, 3H), 1.63 (d, J = 6.7 Hz, 3H), 0.19 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 101.38, 93.81, 68.73, 39.26, 22.62, -0.33 (3 x CH_3); **FT-IR (cm^{-1}, neat)** 2960, 2164, 2024, 1976, 1414, 1357, 1253, 1174, 1126, 1090, 1024, 973, 917, 893, 839, 802, 759, 705, 643, 595, 520; **HRMS (ESI)** m/z calculated for $C_8H_{16}O_3SNaSi$ $[M+Na]^+$: 243.0482, found: 243.0485.

S-(2-(4-methoxyphenyl)propan-2-yl) ethanethioate (14)



Chemical Formula: $C_{12}H_{16}O_2S$
Molecular Weight: 224.32

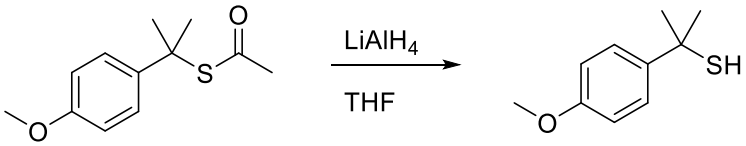
Intermediate **14** was prepared by an adapted reported procedure[41,42].

To a solution of 1-(4-methoxyphenyl)ethenone (15.1 g, 100 mmol) in dry Et_2O (245 mL) was added methylmagnesium chloride solution (3.0 M in THF, 40 mL, 120 mmol) at 0 °C and was stirred overnight. The reaction mixture was treated with sat. aq. NH_4Cl soln. and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

To the redissolved crude product in dry DCM (170 mL) was added ZnI_2 (14.3 g, 44.7 mmol) and thioacetic acid (7.7 mL, 107 mmol) and the reaction mixture was stirred at room temperature overnight. The reaction mixture was treated with sat. aq. $Na_2S_2O_3$ soln. and sat. aq. $NaHCO_3$ soln., and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=5:95, stained in PMA solution) to afford **14** (15.5 g, 69%).

Appearance yellow liquid; **Rf** 0.5 (Et_2O/pentane=5:95); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H), 2.18 (s, 3H), 1.85 (s, 6H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 195.82, 158.41, 137.88, 127.50, 117.61 (2 x CH), 113.46 (2 x CH), 55.34, 52.27, 31.15, 29.00 (2 x CH_3); **FT-IR (cm^{-1}, neat)** 2965, 2926, 2836, 1684, 1607, 1508, 1456, 1356, 1298, 1247, 1181, 1102, 1031, 945, 828, 725, 629, 547, 418; **HRMS (ESI)** m/z calculated for $C_{12}H_{16}O_2SNa$ $[M+Na]^+$: 247.0763, found: 247.0771.

2-(4-methoxyphenyl)propane-2-thiol (15)



Chemical Formula: $C_{10}H_{14}OS$
Molecular Weight: 182.28

Intermediate **15** was prepared by an adapted reported procedure[43].

To a solution of S-(2-(4-methoxyphenyl)propan-2-yl) ethanethioate (**14**) (12.1 g, 54 mmol) in dry THF (300 mL) was added slowly at 0 °C $LiAlH_4$ solution (4.0 M in Et_2O, 8.1 mL, 32.4 mmol) and was stirred at 0 °C for 1 h. The reaction mixture was treated with solid Na_2SO_4 x 10 H_20 and was stirred for 1 h. Then, the reaction mixture was filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:98, stained in PMA solution) to afford **15** (6.41 g, 65%).

Appearance yellow liquid; **Rf** 0.7 (Et_2O/pentane=2:98); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.49 (d, J = 8.9 Hz, 2H), 6.86 (d, J = 8.9 Hz, 2H), 3.81 (s, 3H), 2.23 (s, 1H), 1.82 (s, 6H).; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 158.27, 140.75, 126.70 (2 x CH), 113.58 (2 x CH), 55.42, 45.66, 34.82 (2 x CH_3); **FT-IR (cm^{-1}, neat)** 2962, 2834, 1608, 1508, 1458, 1365, 1298, 1245, 1180, 1132, 1101, 1031, 827, 727, 635, 599, 541; **HRMS (EI)** m/z calculated for $C_{10}H_{14}OS$ $[M]^+$: 182.0760, found: 182.0762.

(3-((2-(4-methoxyphenyl)propan-2-yl)sulfonyl)but-1-yn-1-yl)trimethylsilane (16)



Chemical Formula: $C_{17}H_{26}O_3SSi$
Molecular Weight: 338.54

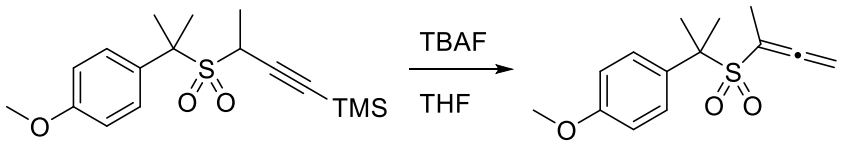
Intermediate **16** was prepared by an adapted reported procedure[44,45].

To a solution of 2-(4-methoxyphenyl)propane-2-thiol (**15**) (936 mg, 5.1 mmol) in dry DMF (21.4 mL) was added NaH (90%, 154 mg, 6.7 mmol) portion wise at 0 °C and was stirred for 30 min. Then, (1-methyl-3-trimethylsilyl-prop-2-ynyl) methanesulfonate (**12**) (1.69 g, 7.7 mmol) was added and the reaction mixture was stirred at 100 °C for 5 h. The reaction mixture was treated slowly with water and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

The redissolved crude product in DCM (30 mL) was cooled down to 0 °C, *m*-CPBA (70%, 2.76 g, 11.2 mmol) dissolved in DCM (22 mL) was added and the reaction mixture was stirred at 0 °C for 1 h. Then, the reaction mixture was treated with sat. aq. $NaHCO_3$ soln. and extracted with DCM (3 ×). The combined organic phases were washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford **16** (7.66 g, 92%).

Appearance yellow liquid; **Rf** 0.6 (Et_2O/pentane=2:8); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 3.39 (q, *J* = 7.2 Hz, 1H), 2.07 (s, 3H), 1.85 (s, 3H), 1.42 (d, *J* = 7.1 Hz, 3H), 0.19 (s, 9H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 159.89 (C_q), 129.63 (2 x CH), 129.19 (C_q), 113.94 (2 x CH), 100.21 (C_q), 93.03 (C_q), 68.23 (C_q), 55.36 (CH_3), 47.68 (CH), 24.46 (CH_3), 24.21 (CH_3), 14.55 (CH_3), -0.34 (3 x CH_3); **FT-IR (cm^{-1}, neat)** 2958, 2839, 1608, 1512, 1456, 1299, 1252, 1186, 1154, 1115, 1096, 1031, 908, 836, 753, 704, 638, 586, 557, 484; **HRMS (ESI)** m/z calculated for $C_{17}H_{26}O_3SNaSi$ $[M+Na]^+$: 361.1264, found: 361.1261.

1-(2-(buta-2,3-dien-2-ylsulfonyl)propan-2-yl)-4-methoxybenzene (17)



Chemical Formula: $C_{14}H_{18}O_3S$
Molecular Weight: 266.36

Intermediate **17** was prepared by an adapted reported procedure[46].

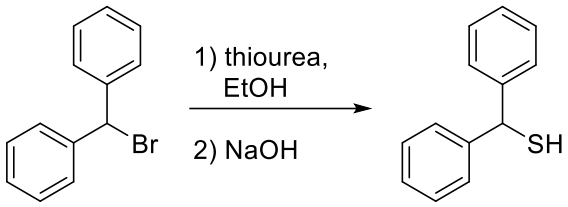
To a solution of (3-((2-(4-methoxyphenyl)propan-2-yl)sulfonyl)but-1-yn-1-yl)trimethylsilane (**16**) (3.16 g, 9.3 mmol) in dry THF (80 mL) was added TBAF solution (1.0 M in THF, 9.5 mL, 9.5 mmol) at 0 °C and was stirred for 1 h. Then, the reaction mixture was treated with water and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=4:6, stained in PMA solution) to afford **17** (1.60 g, 64%).

Appearance brown solid; **Rf** 0.4 (Et_2O/pentane=4:6); **Mp** 57-60 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 9.0 Hz, 2H), 7.46 (d, *J* = 9.0 Hz, 2H), 5.60 (q, *J* = 3.2 Hz, 2H), 4.37 (s, 3H), 2.38 (s, 6H), 2.09 (t, *J* = 3.2 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 210.94 (C_q), 159.73 (C_q), 129.73 (2 x CH), 129.21 (C_q), 113.47 (2 x CH), 103.14 (C_q), 80.81 (CH_2), 67.24 (C_q), 55.27 (CH_3), 22.64 (2 x CH_3), 15.84 (CH_3); **FT-IR (cm^{-1}, neat)** 2987, 2932, 2838, 1608, 1580, 1513,

1462, 1415, 1386, 1365, 1293, 1252, 1187, 1155, 1123, 1082, 1030, 919, 858, 832, 804, 749, 712, 679, 666, 625, 570, 551; **HRMS (ESI)** m/z calculated for $C_{14}H_{18}O_3SNa$ $[M+Na]^+$: 289.0869, found: 289.0866.

3.5.5 Synthesis of allenyl sulfone 22

diphenylmethanethiol (20)



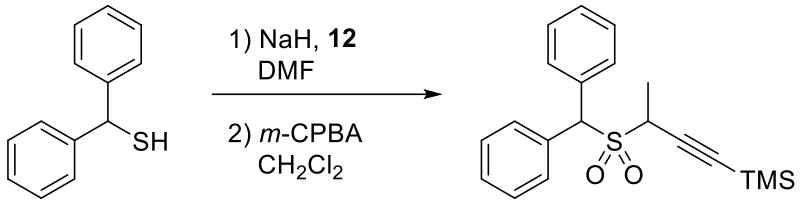
Chemical Formula: $C_{13}H_{12}S$
Molecular Weight: 200.30

Intermediate **20** was prepared by an adapted reported procedure[47].

To a solution of [bromo(phenyl)methyl]benzene (25.2 g, 102 mmol) in EtOH (100 mL) was added thiourea (8.39 g, 110 mmol) and was refluxed for 3 h. Then, NaOH (8.29 g, 20.7 mmol) dissolved in water (20 mL) was added to the reaction mixture and the temperature was kept at reflux temperature for 2 h. The reaction mixture was cooled down to room temperature, treated with aq. 1M HCl soln. and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (DCM/pentane=5:95, stained in PMA solution) to afford **20** (16.4 g, 80%).

Appearance yellow liquid; **Rf** 0.5 (Et_2O/pentane=1:9); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.42 – 7.31 (m, 4H), 7.30 – 7.22 (m, 4H), 7.21 – 7.14 (m, 2H), 5.39 (d, *J* = 5.0 Hz, 1H), 2.22 (d, *J* = 5.0 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.50 (2 x C_q), 128.68 (4 x CH), 127.92 (4 x CH), 127.31 (2 x CH), 47.92 (CH); **FT-IR (cm^{-1}, neat)** 3058, 3025, 2557, 2362, 2165, 1884, 1804, 1592, 1488, 1445, 1333, 1183, 1073, 1026, 914, 840, 745, 692, 620, 573, 502, 467; **HRMS (ESI)** m/z calculated for $C_{13}H_{11}S$ $[M-H]^+$: 199.0587, found: 199.0586.

(3-(benzhydrylsulfonyl)but-1-yn-1-yl)trimethylsilane (21)



Chemical Formula: $C_{20}H_{24}O_2SSi$
Molecular Weight: 356.55

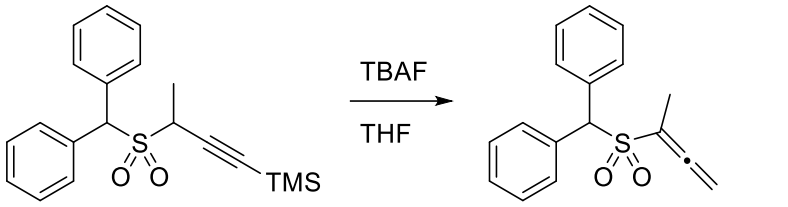
Intermediate **21** was prepared by an adapted reported procedure[44,45].

To a solution of diphenylmethanethiol (**20**) (700 mg, 3.5 mmol) in dry DMF (16 mL) was added NaH (90%, 107 mg, 4.2 mmol) portion wise at 0 °C and was stirred for 30 min. Then, (1-methyl-3-trimethylsilyl-prop-2-ynyl) methanesulfonate (**12**) (1.16 g, 5.3 mmol) was added and the reaction mixture was stirred at 100 °C for 5 h. The reaction mixture was treated slowly with water and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

The redissolved crude product in DCM (20 mL) was cooled down to 0 °C, *m*-CPBA (70%, 1.93 g, 7.8 mmol) dissolved in DCM (16 mL) was added and the reaction mixture was stirred at 0 °C for 1 h. Then, the reaction mixture was treated with sat. aq. $NaHCO_3$ soln. and extracted with DCM (3 ×). The combined organic phases were washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford **21** (888 mg, 71%).

Appearance yellow oil; **Rf** 0.5 (Et_2O/pentane=2:8); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.76 – 7.67 (m, 2H), 7.67 – 7.58 (m, 2H), 7.50 – 7.30 (m, 6H), 5.97 (s, 1H), 3.66 (q, *J* = 7.1 Hz, 1H), 1.52 (d, *J* = 7.1 Hz, 3H), 0.28 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 133.22, 131.55, 130.37 (2 x CH), 130.19 (2 x CH), 129.20 (2 x CH), 129.14, 129.00, 128.97 (2 x CH), 99.26, 93.63, 69.64, 50.24, 12.57, -0.14 (3 x CH_3); **FT-IR (cm^{-1}, neat)** 2959, 2897, 1493, 1448, 1416, 1362, 1314, 1251, 1212, 117, 1130, 1099, 1028, 975, 902, 838, 757, 695, 642, 563, 524, 472; **HRMS (ESI)** m/z calculated for $C_{20}H_{24}O_2SNaSi$ $[M+Na]^+$: 379.1158, found: 379.1152.

((buta-2,3-dien-2-ylsulfonyl)methylene)dibenzene (22)



Chemical Formula: $C_{17}H_{16}O_2S$
Molecular Weight: 284.37

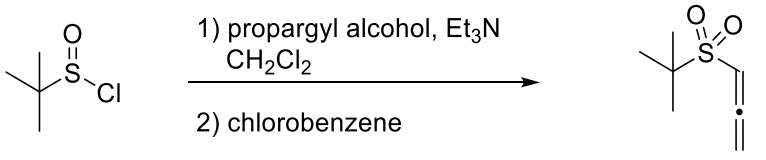
Intermediate **22** was prepared by an adapted reported procedure[46].

To a solution of (3-(benzhydrylsulfonyl)but-1-yn-1-yl)trimethylsilane (**21**) (846 mg, 2.4 mmol) in dry THF (19.4 mL) was added TBAF solution (1.0 M in THF, 2.4 mL, 2.4 mmol) at 0 °C and was stirred for 1 h. Then, the reaction mixture was treated with water and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=3:7, stained in PMA solution) to afford **22** (112 mg, 17%).

Appearance yellow wax; **Rf** 0.3 (Et_2O/pentane=4:6); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.71 – 7.57 (m, 4H), 7.47 – 7.29 (m, 6H), 5.39 (s, 1H), 5.06 (q, *J* = 3.2 Hz, 2H), 1.87 (t, *J* = 3.2 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 210.12, 132.92 (2 x C_q), 130.12 (4 x CH), 128.89 (2 x CH), 128.86 (4 x CH), 105.57, 82.21, 73.96, 14.74; **FT-IR (cm^{-1}, neat)** 2925, 1491, 1446, 1303, 1214, 1136, 1087, 1031, 918, 859, 777, 747, 700, 606, 537; **HRMS (ESI)** m/z calculated for $C_{17}H_{20}O_2SN$ $[M+NH_4]^+$: 302.1209, found: 302.1209.

3.5.6 Synthesis of allenyl sulfone 25

1-(*tert*-butylsulfonyl)propa-1,2-diene (25)



Chemical Formula: $C_7H_{12}O_2S$
Molecular Weight: 160.23

Intermediate **25** was prepared by an adapted reported procedure[25].

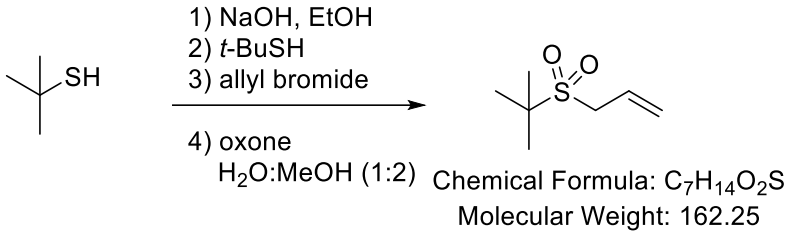
To a solution of Et_3N (1.3 mL, 9.3 mmol) and propargyl alcohol (499 mg, 8.9 mmol) in DCM (25 mL) was added dropwise 2-methylpropane-2-sulfinyl chloride (1.08 g, 7.7 mmol) at 0 °C and stirred for 1 h. Then, the reaction mixture was treated with aq. 1M HCl soln. and sat. aq.

$NaHCO_3$ soln., and extracted with DCM (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

The crude product was dissolved in chlorobenzene (50 mL) and refluxed overnight. The reaction mixture was concentrated under reduced pressure, redissolved in Et_2O, filtered and again concentrated to afford **25** (1.11 g, 90%).

Appearance yellow solid; **Mp** 75 - 80 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 6.07 (t, *J* = 6.3 Hz, 1H), 5.46 (d, *J* = 6.3 Hz, 2H), 1.42 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 212.13 (C_q), 93.33 (CH), 82.82 (CH_2), 60.96 (C_q), 23.53 (3 x CH_3). Physical and spectral data are in accordance with literature data[25].

3-(*tert*-butylsulfonyl)prop-1-ene (30)



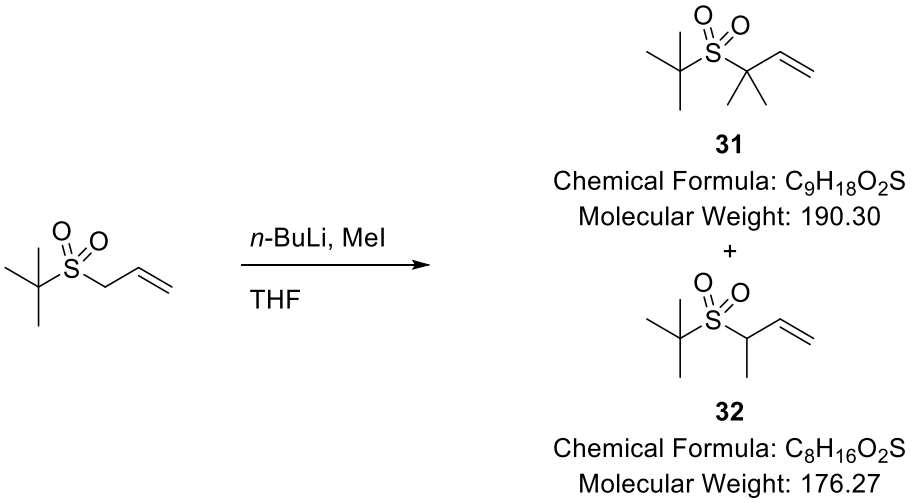
Intermediate **30** was prepared by an adapted reported procedure[26].

NaOH (2.57 g, 64 mmol) was dissolved in EtOH (50 mL) and refluxed for 30 min. Then, the reaction mixture was cooled down to approx. 50 °C, *t*-BuSH (6.8 mL, 60 mol) was added and the reaction mixture was stirred for 30 min whilst cooling down to room temperature. Allyl bromide (5.2 mL, 60 mmol) was added and the reaction mixture was refluxed overnight. The reaction mixture was filtered to remove formed NaBr, the filtrate was treated with aq. 1M HCl soln. and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

The crude product was redissolved in MeOH (200 mL) and cooled down to 0 °C. Oxone (55.5 g, 90 mmol) dissolved in water (100 mL) was added slowly to the reaction mixture and was stirred overnight. Then, the reaction mixture was treated with water and extracted with DCM (3 ×). The combined organic phases were washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure to afford **30** (7.51 g, 77%).

Appearance yellow liquid; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 6.05 – 5.83 (m, 1H), 5.53 – 5.38 (m, 2H), 3.71 (dt, *J* = 7.2, 1.2 Hz, 2H), 1.42 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 124.56, 124.35, 60.07, 51.82, 23.83 (3 x CH_3); **FT-IR (cm^{-1}, neat)** 2981, 2938, 1640, 1469, 1422, 1398, 1368, 1286, 1197, 1111, 1018, 991, 934, 869, 803, 754, 685, 640, 588; **HRMS (ESI)** m/z calculated for $C_7H_{14}O_2SNa$ $[M+Na]^+$: 185.0607, found: 185.0607.

3-(*tert*-butylsulfonyl)-3-methylbut-1-ene (31)



31
Chemical Formula: $C_9H_{18}O_2S$
Molecular Weight: 190.30

+

32
Chemical Formula: $C_8H_{16}O_2S$
Molecular Weight: 176.27

Intermediate **31** was prepared by an adapted reported procedure[48].

To a solution of 3-(*tert*-butylsulfonyl)prop-1-ene (**30**) (3.37 g, 20.7 mmol) in dry THF (45 mL) was added *n*-BuLi (2.5M in hexanes, 16.8 mL, 42.0 mmol) slowly at -78 °C and was stirred for 30 min. Then, MeI (3.8 mL, 61.0 mmol) was added, the reaction mixture was stirred for another 30 min at -78 °C and then was warmed up to room temperature. The reaction mixture was treated with aq. 1M NaOH soln. and extracted with Et_2O (3 ×). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Et_2O/pentane=2:8, stained in PMA solution) to afford **31** (2.02 g, 51%) and as a side product **32** (324 mg, 9%).

Appearance colorless liquid; **Rf** 0.6 (Et_2O/pentane=4:6); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 6.27 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.32 – 5.21 (m, 2H), 1.55 (s, 6H), 1.43 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 139.45, 116.02, 68.50, 65.80, 26.07 (3 x CH_3), 23.06 (2 x CH_3); **FT-IR (cm^{-1}, neat)** 2983, 1468, 1275, 1139, 1092, 1010, 929, 797, 654; **HRMS (ESI)** m/z calculated for $C_8H_{18}O_2SNa$ $[M+Na]^+$: 213.0920, found: 213.0917.

3-(*tert*-butylsulfonyl)but-1-ene (32)

Side product from synthesis of 3-(*tert*-butylsulfonyl)-3-methylbut-1-ene (**31**).

Appearance colorless liquid; **Rf** 0.5 (Et_2O/pentane=4:6); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 6.08 – 5.90 (m, 1H), 5.35 – 5.26 (m, 2H), 3.98 – 3.82 (m, 1H), 1.49 (d, *J* = 7.1 Hz, 3H), 1.43 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 134.93, 119.44, 61.86, 58.84, 24.65 (3 x CH_3), 14.74; **FT-IR (cm^{-1}, neat)** 2982, 1639, 1459, 1281, 1108, 1001, 932, 801, 662; **HRMS (ESI)** m/z calculated for $C_8H_{16}O_2SNa$ $[M+Na]^+$: 199.0763, found: 199.0760.

3.5.7 NMR spectra

All measured NMR spectra are supplied in the appendix.

3.6 References

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Vulcanization of Elemental Sulfur: Structural Characterization of Poly(Sulfur- *Random* -(1,3-Diisopropenylbenzene)). *J. Am. Chem. Soc.* **2023**, *145* (22), 12386–12397. https://doi.org/10.1021/jacs.3c03604.

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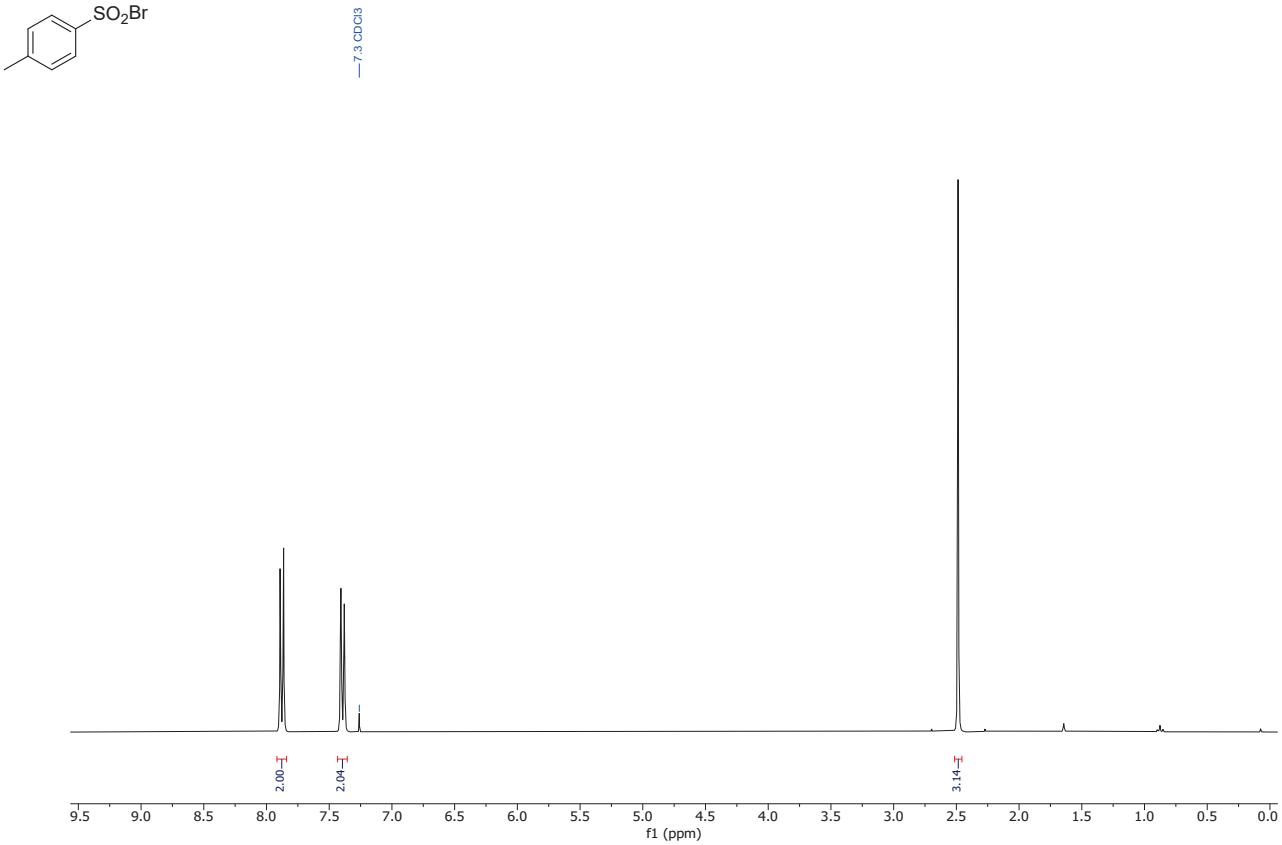
Appendix

Appendix

NMR spectra of Chapter 1

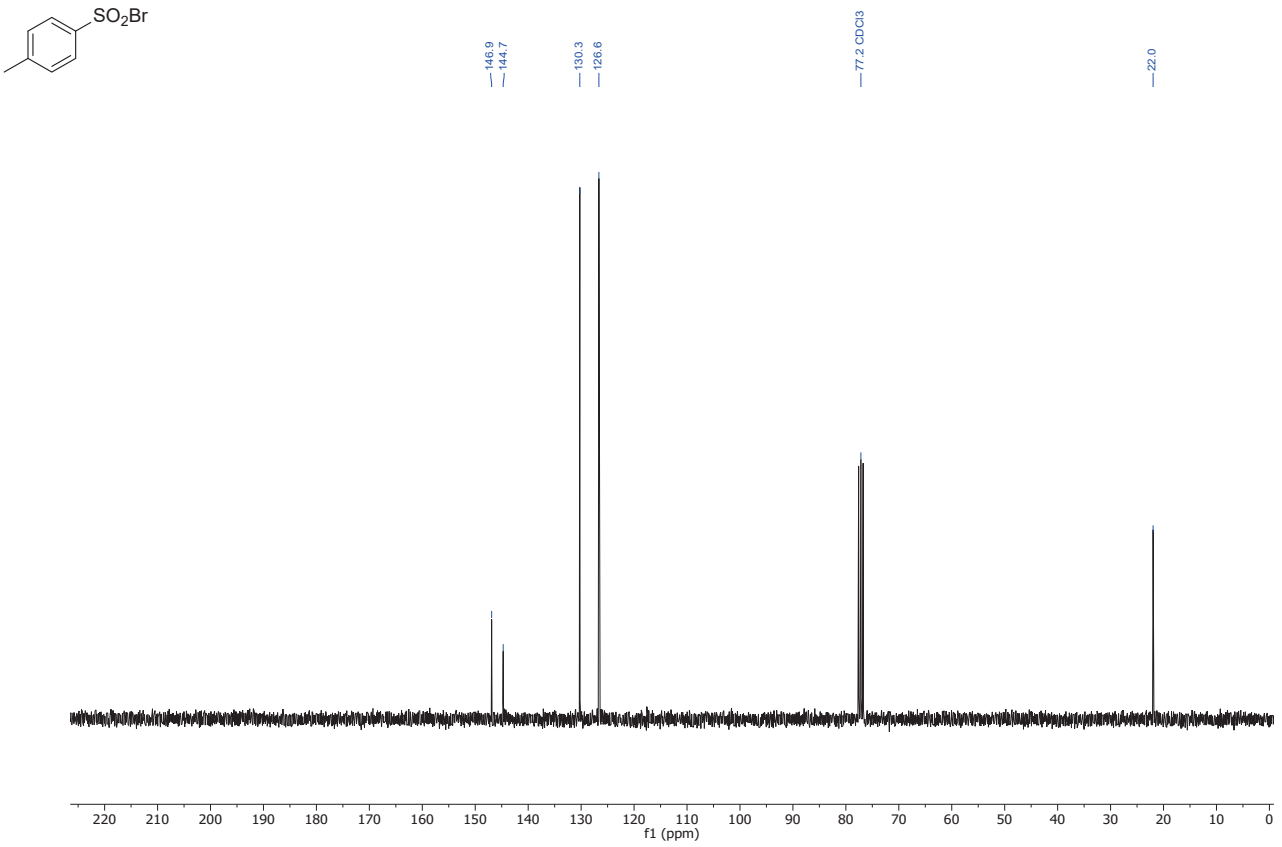
Tosyl bromide (95)

^{1}H NMR (300 MHz, $CDCl_3$)



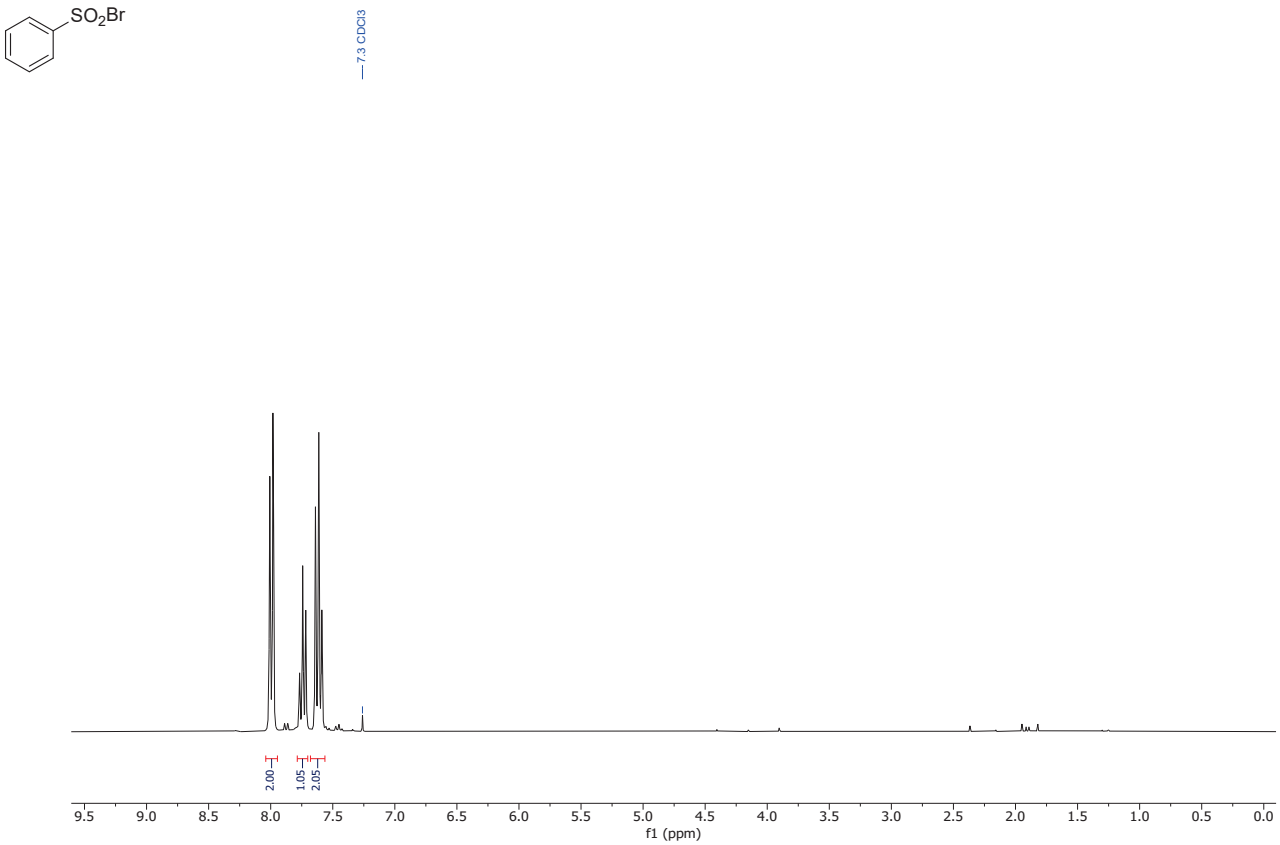
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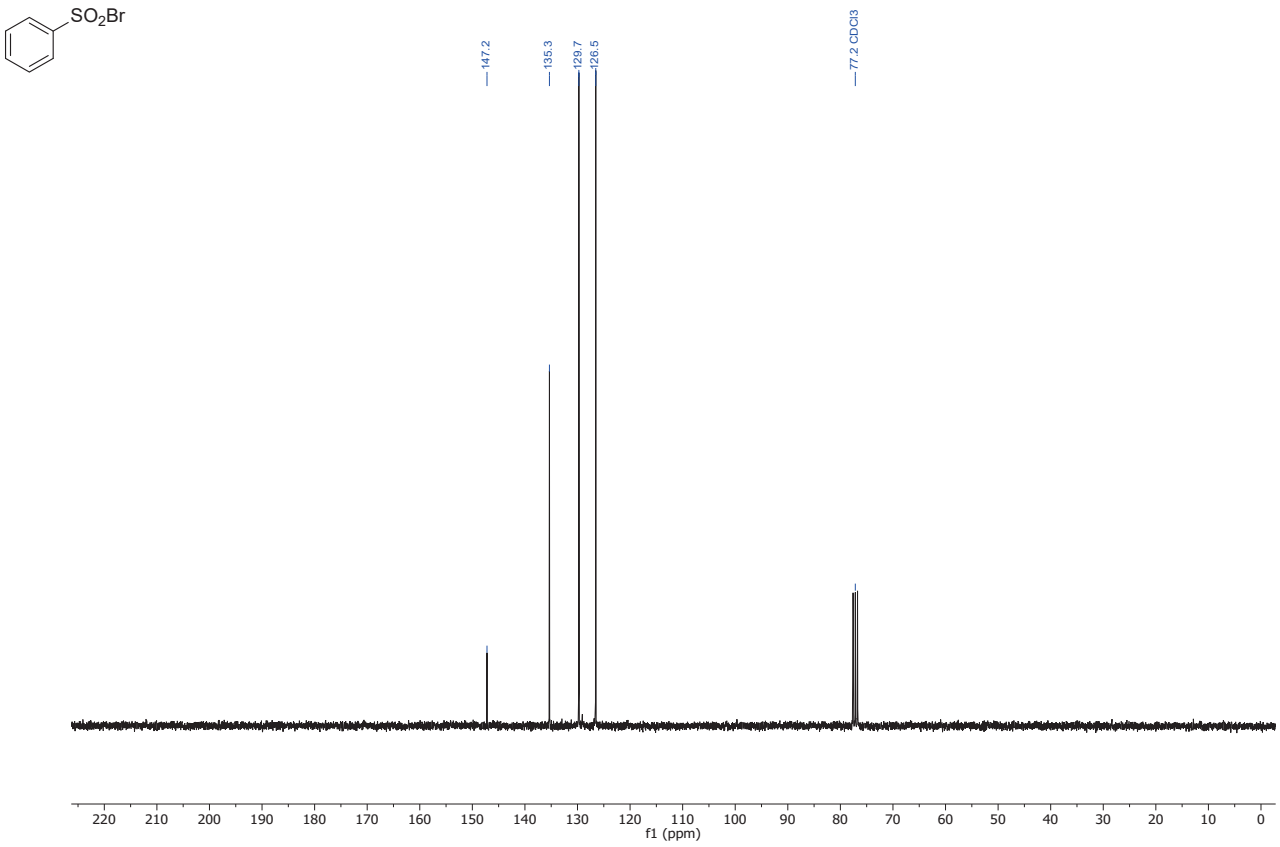
Phenylsulfonyl bromide (96)

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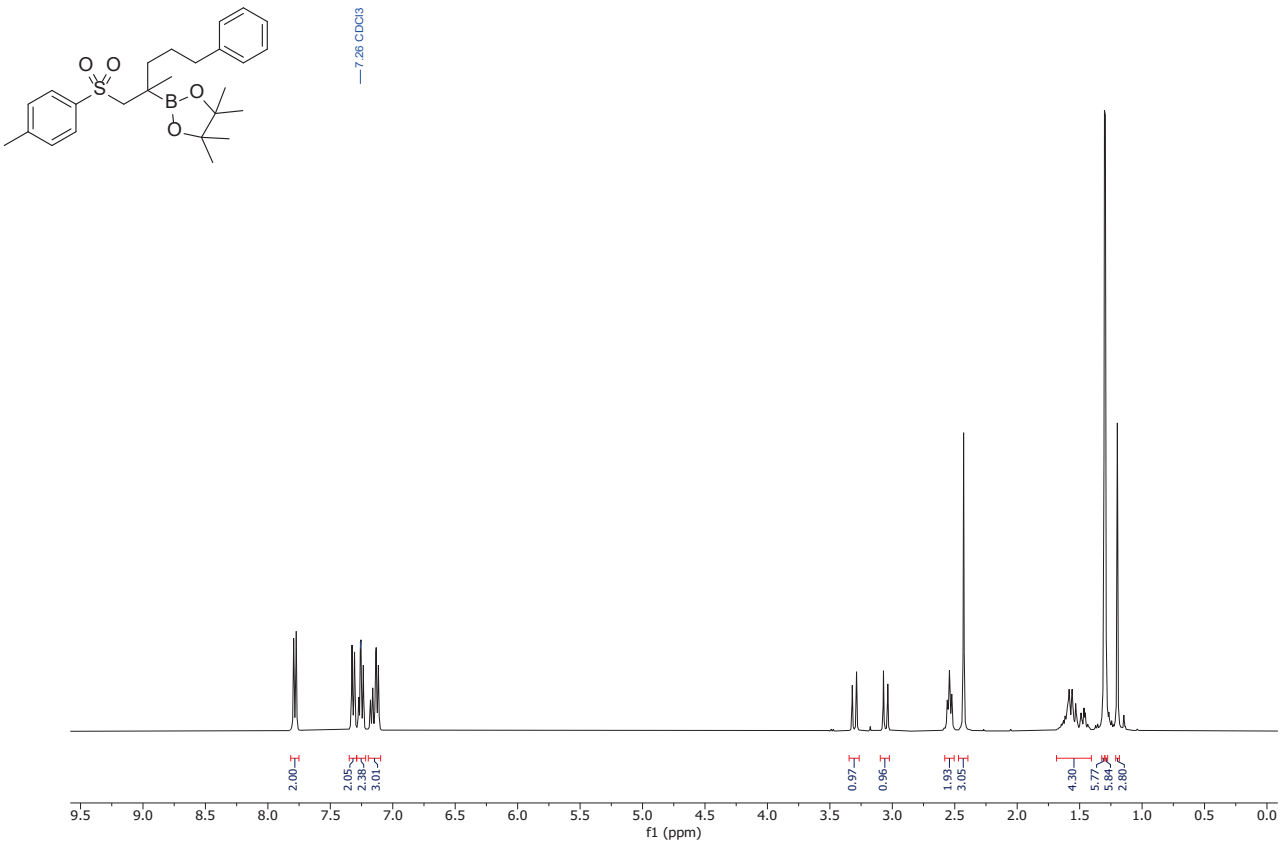
Phenylsulfonyl bromide (96)

^{13}C NMR (75 MHz, $CDCl_3$)



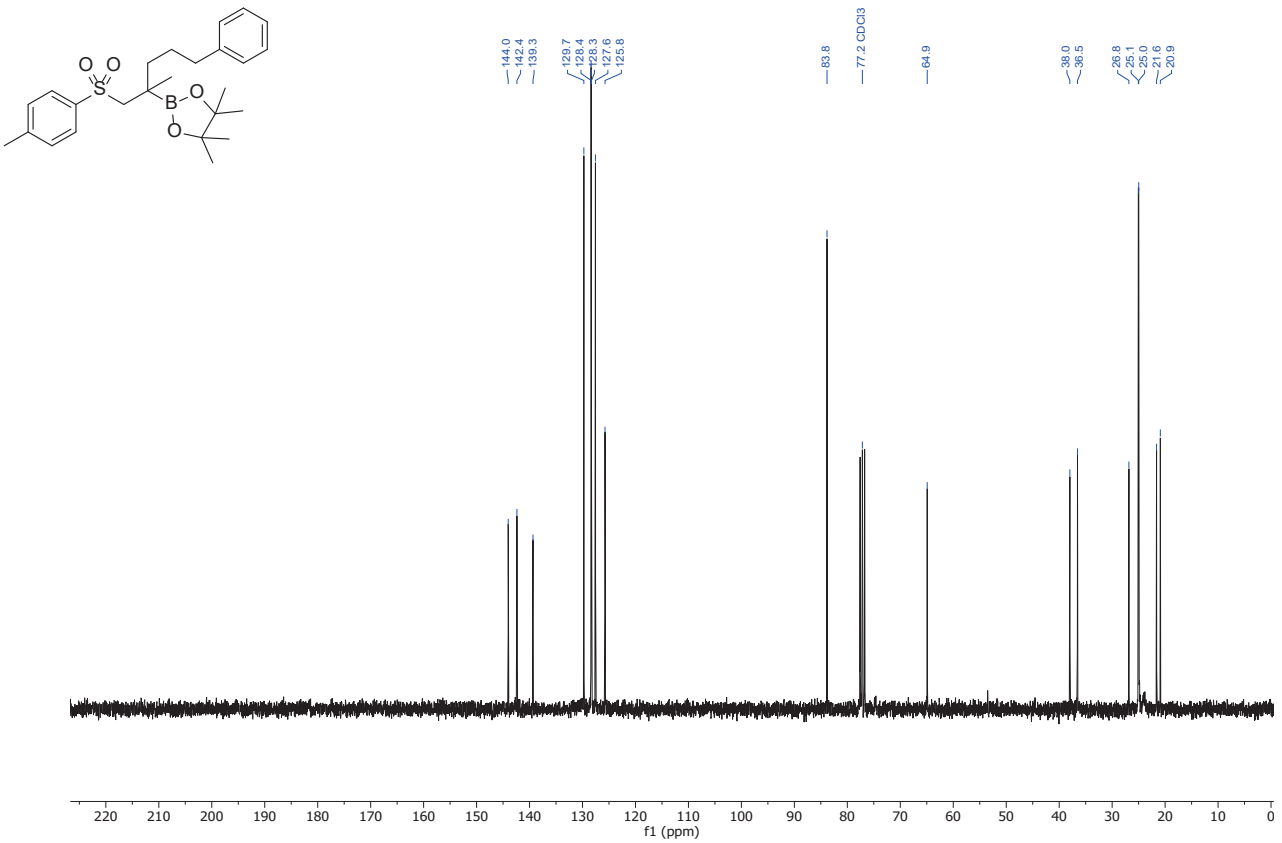
4,4,5,5-tetramethyl-2-(2-methyl-5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (16)

^{1}H NMR (300 MHz, $CDCl_3$)



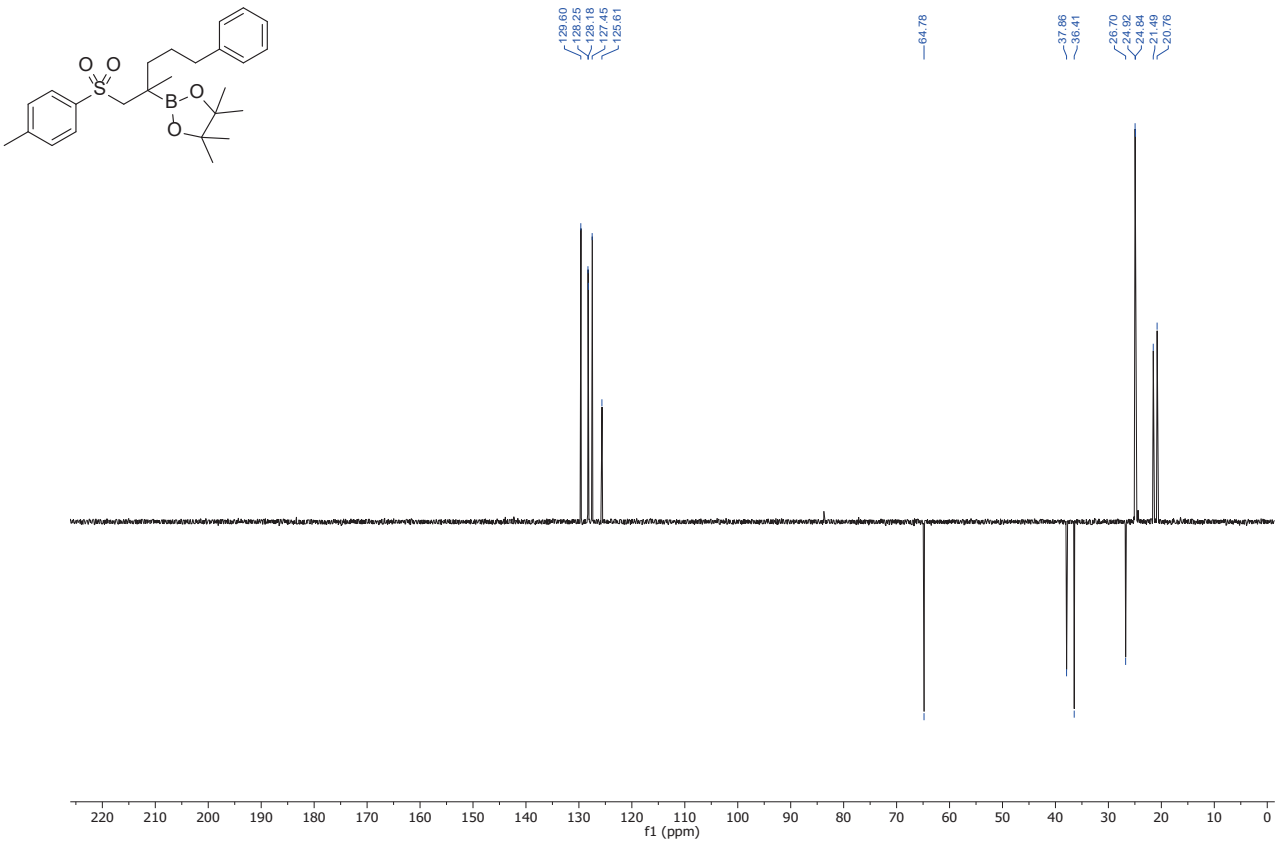
4,4,5,5-tetramethyl-2-(2-methyl-5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (16)

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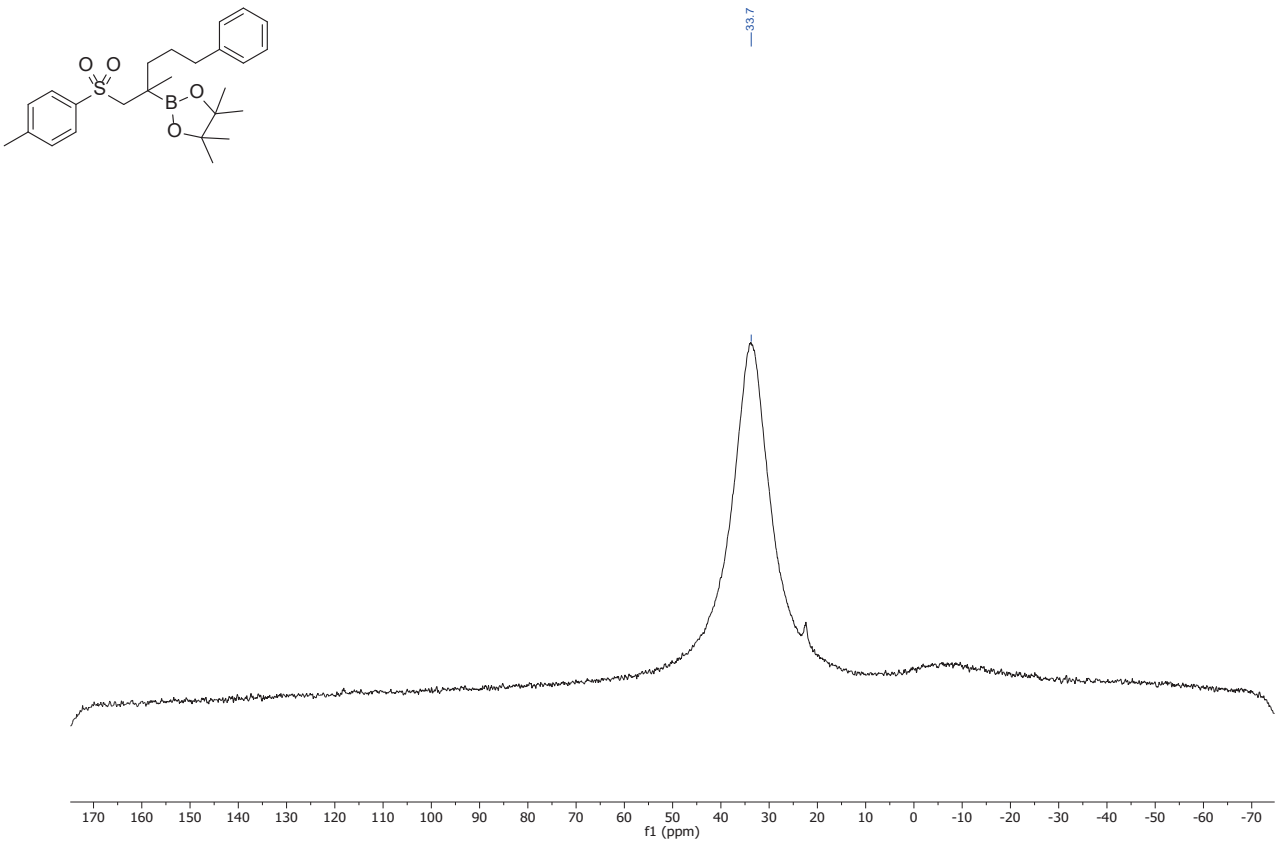
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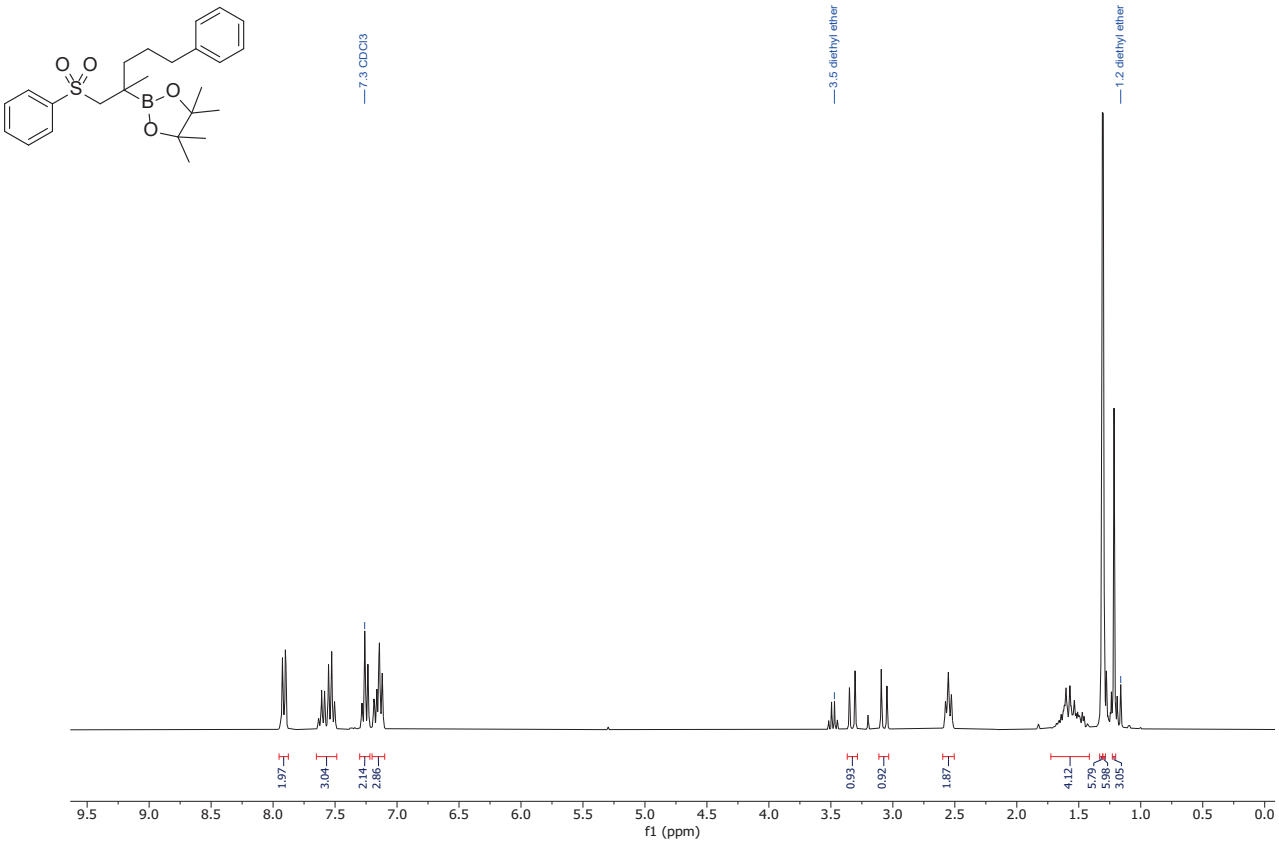
4,4,5,5-tetramethyl-2-(2-methyl-5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (16)

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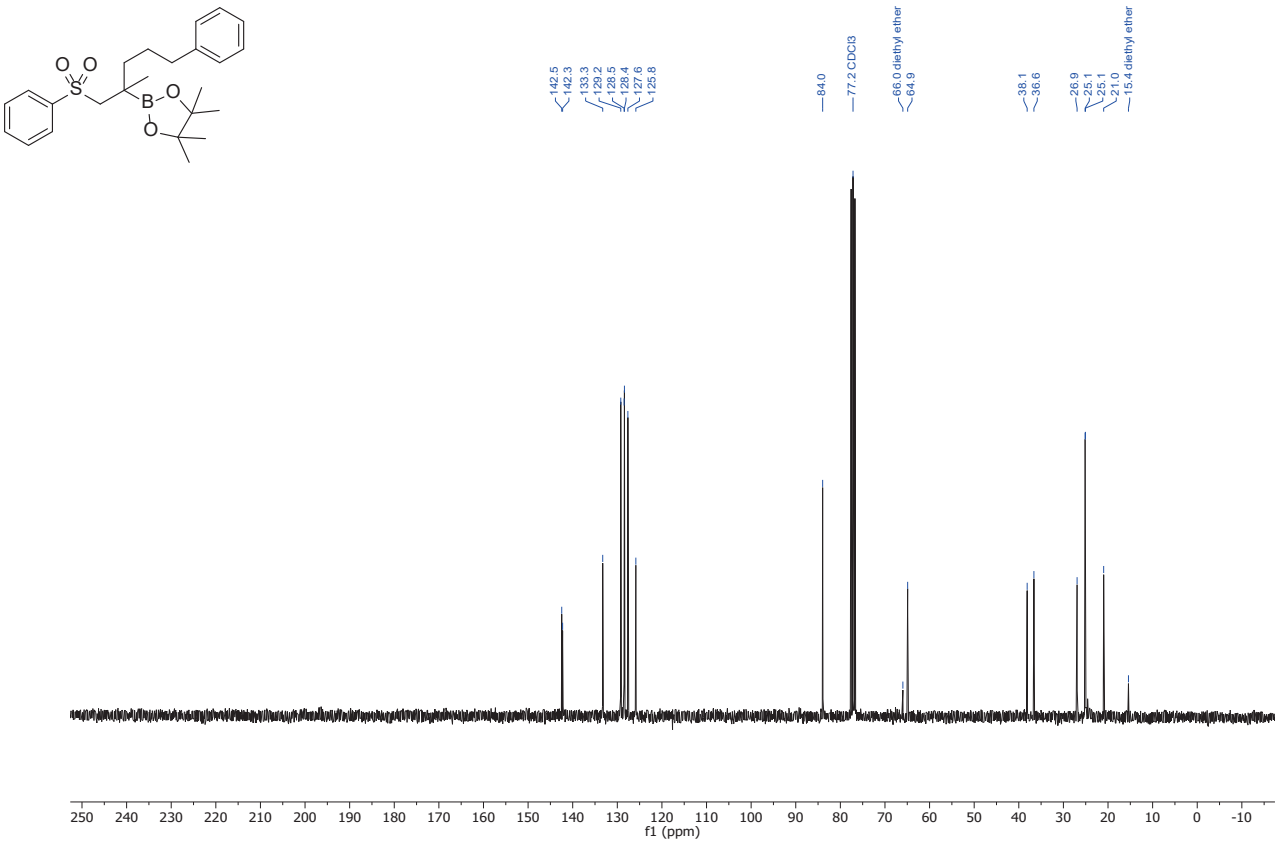
4,4,5,5-tetramethyl-2-(2-methyl-5-phenyl-1-(phenylsulfonyl)pentan-2-yl)-1,3,2-dioxaborolane (22)

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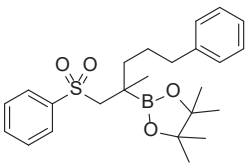
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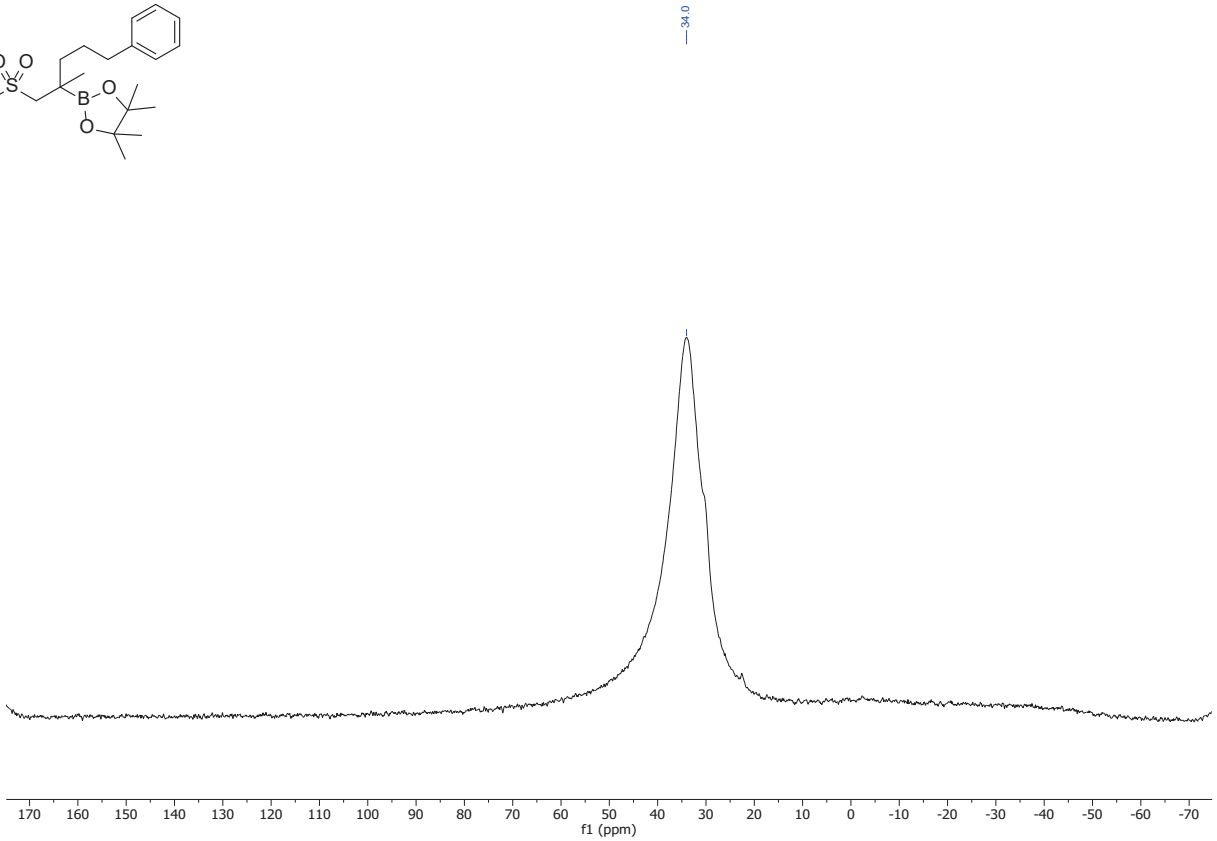
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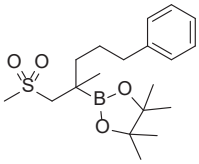
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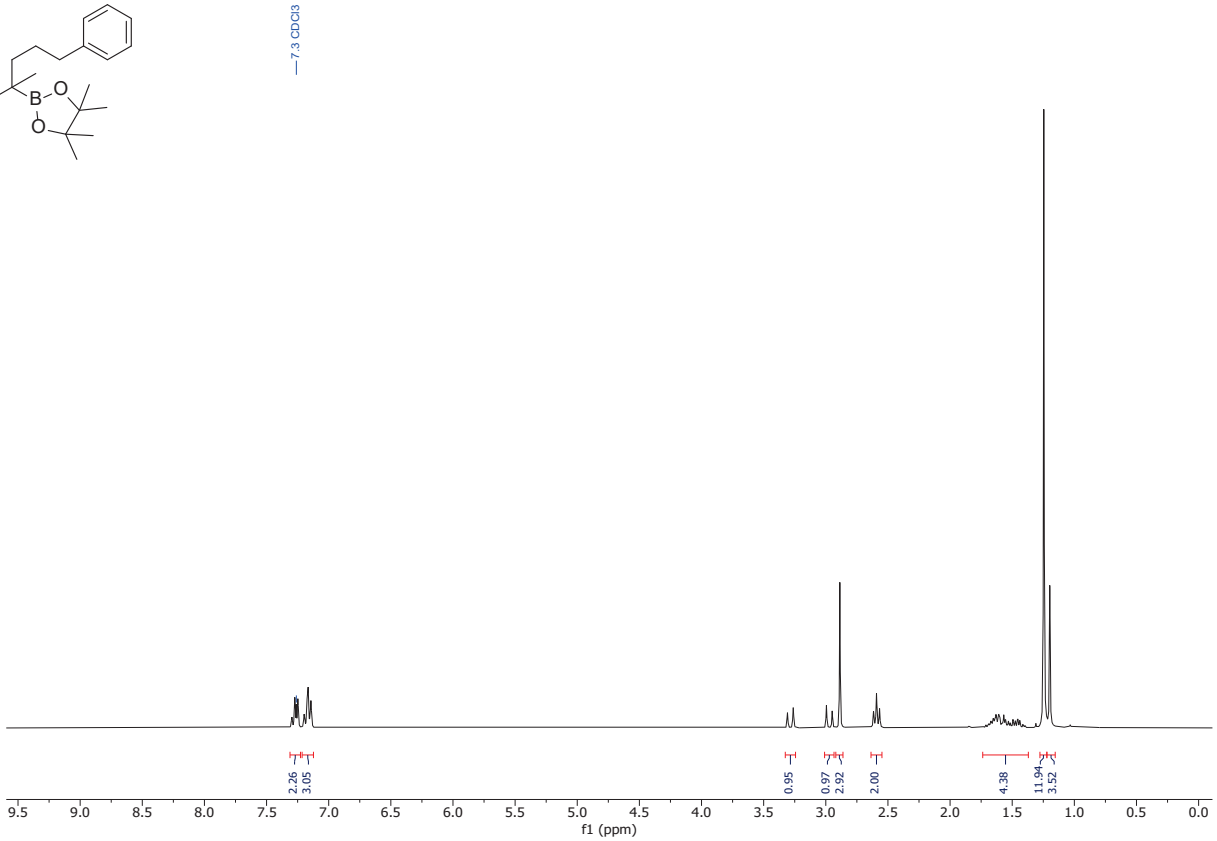




4,4,5,5-tetramethyl-2-(2-methyl-1-(methylsulfonyl)-5-phenylpentan-2-yl)-1,3,2-dioxaborolane (23)

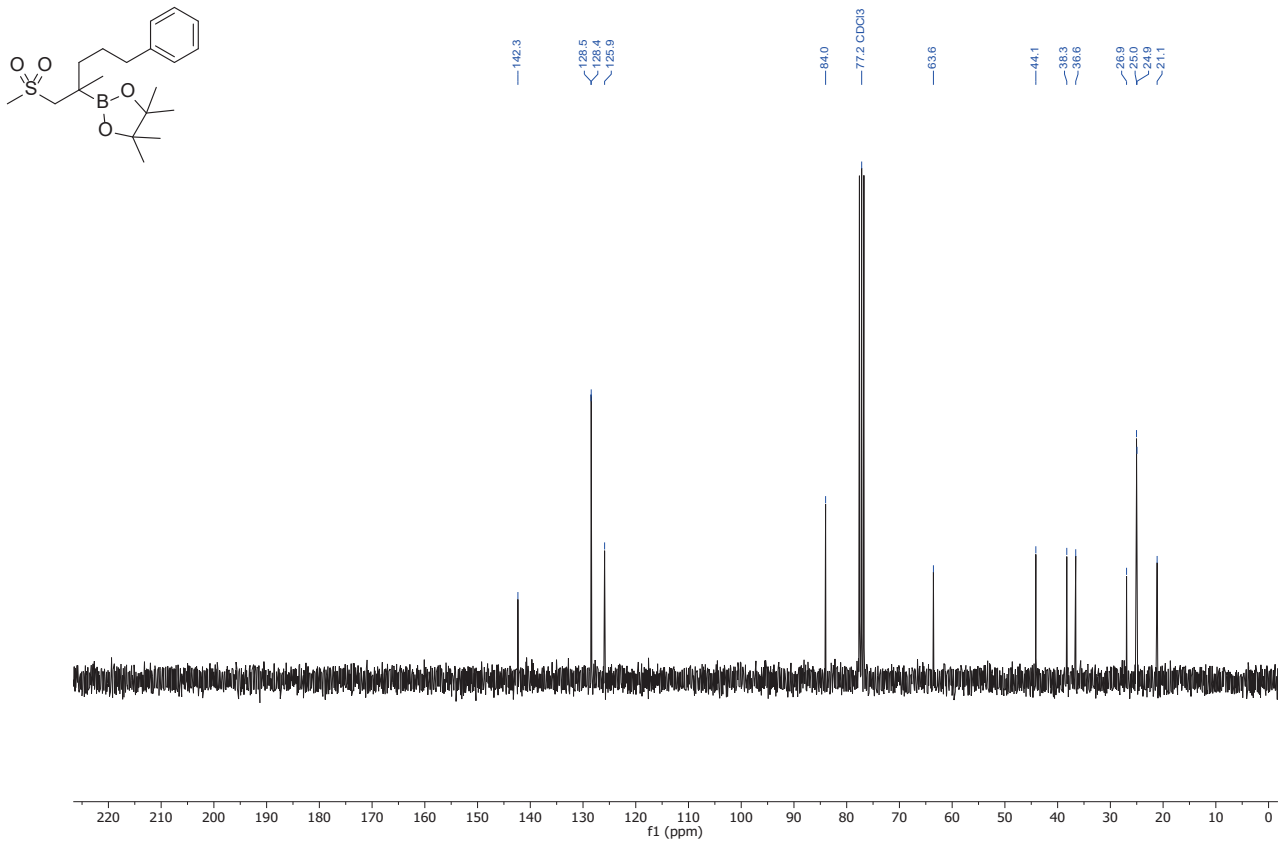
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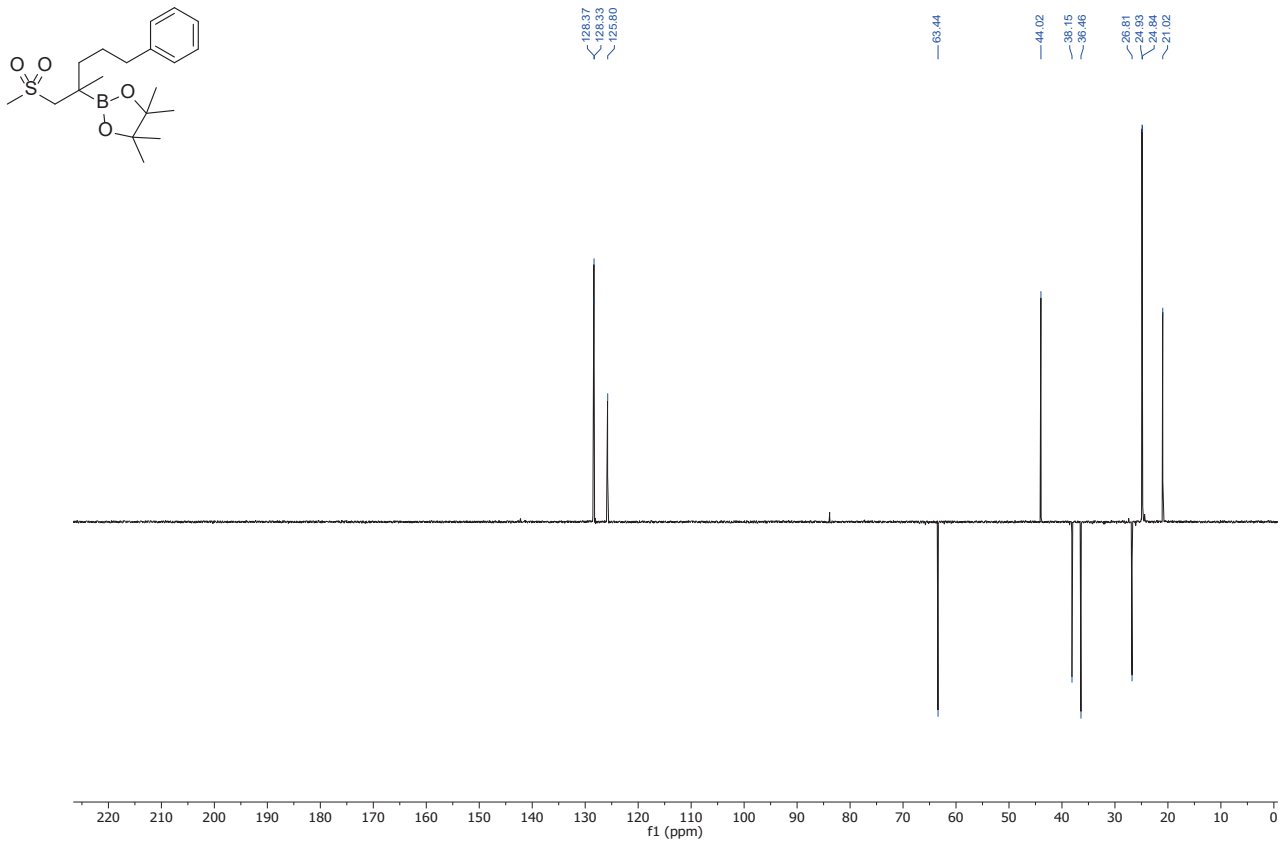
4,4,5,5-tetramethyl-2-(2-methyl-1-(methylsulfonyl)-5-phenylpentan-2-yl)-1,3,2-dioxaborolane (23)

^{13}C NMR (75 MHz, $CDCl_3$)



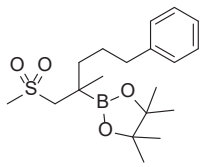
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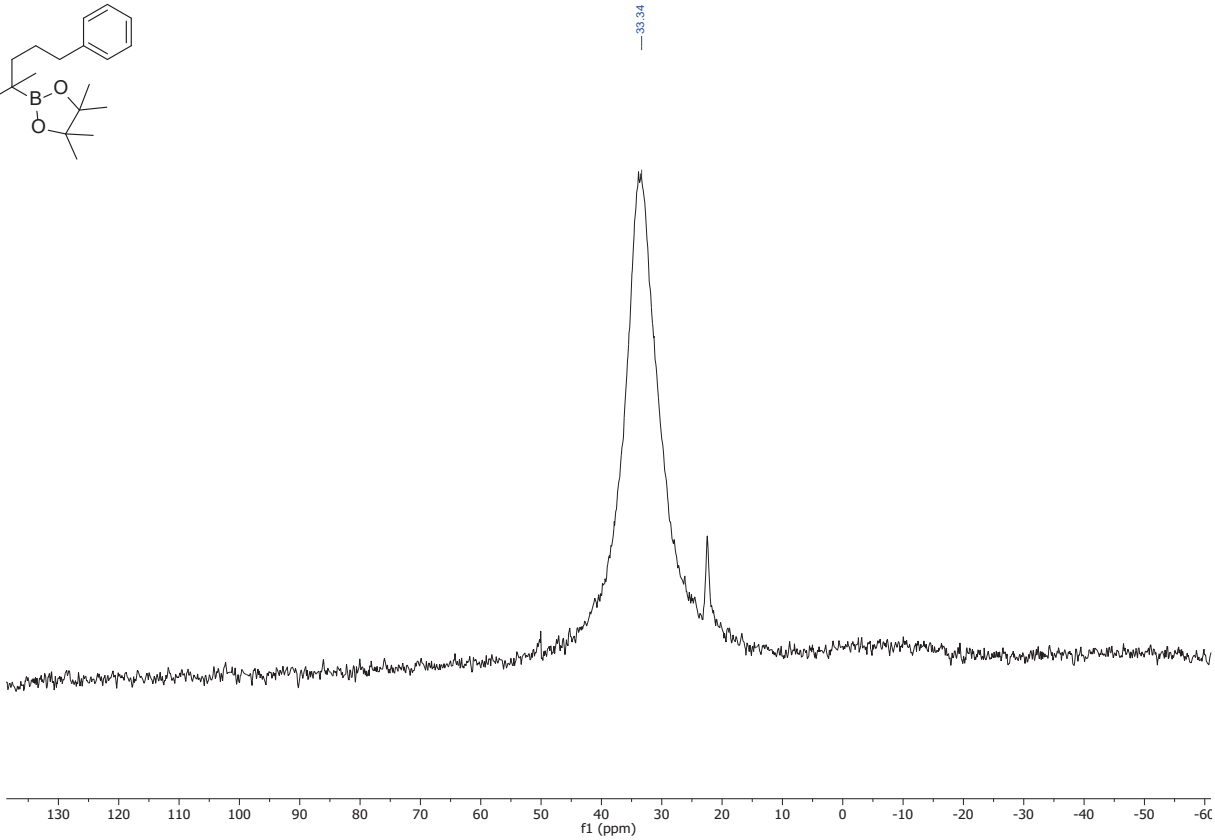
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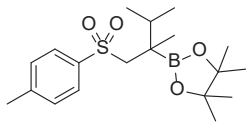
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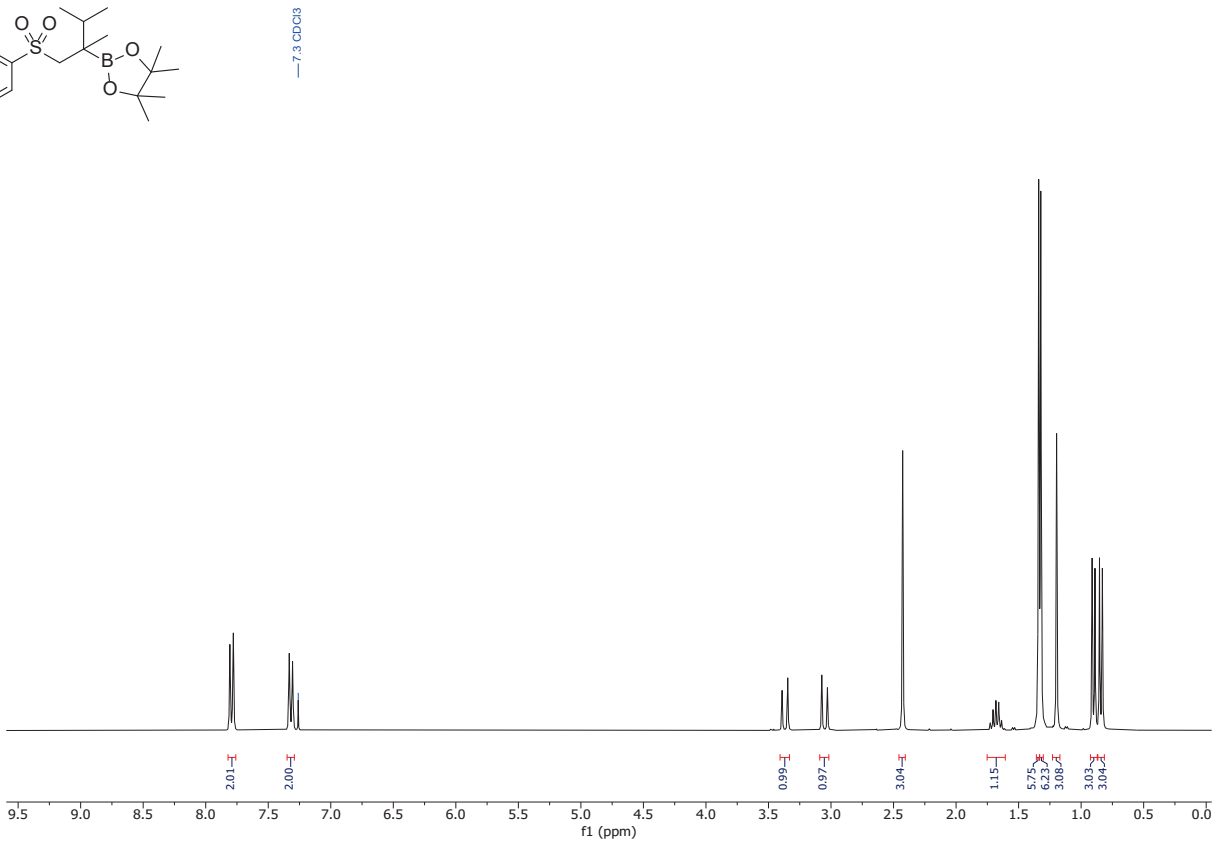




2-(2,3-dimethyl-1-tosylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26)

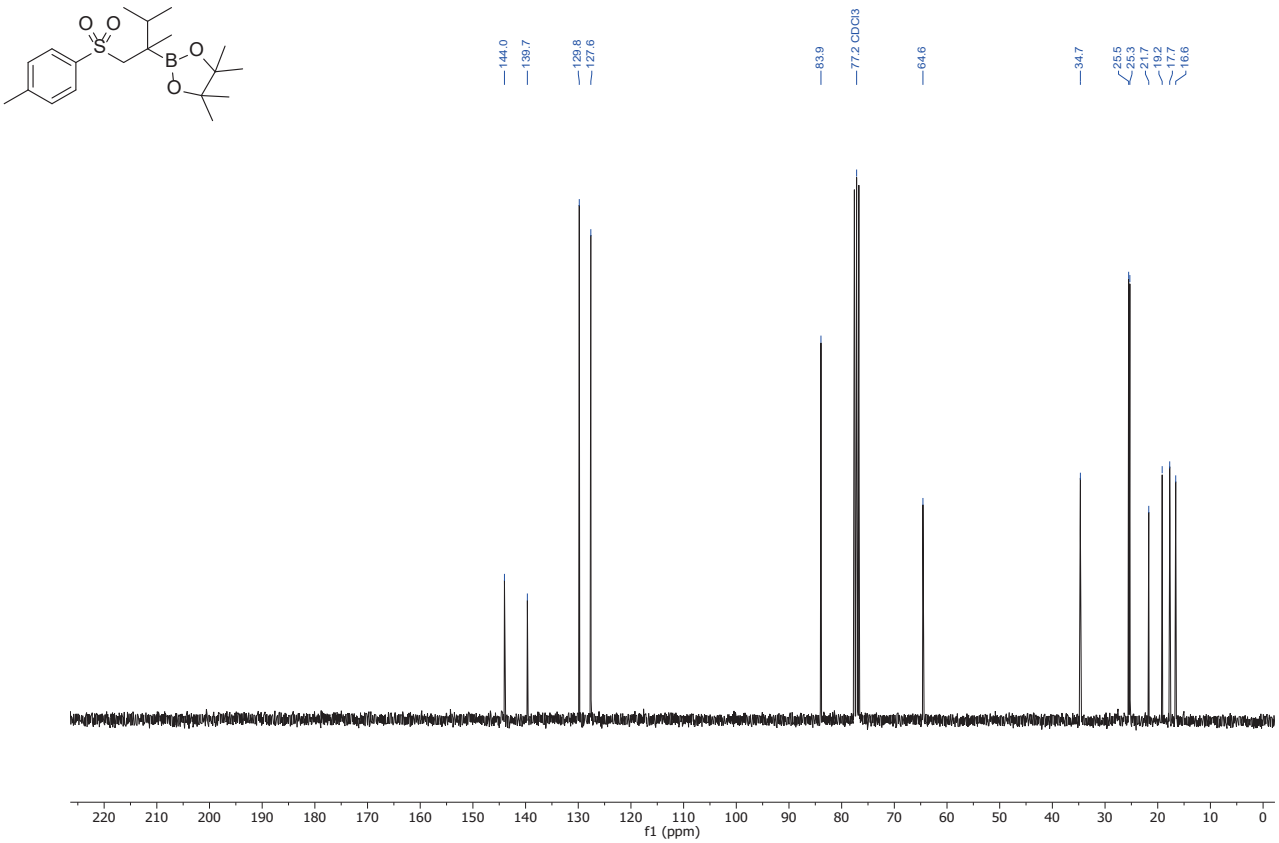
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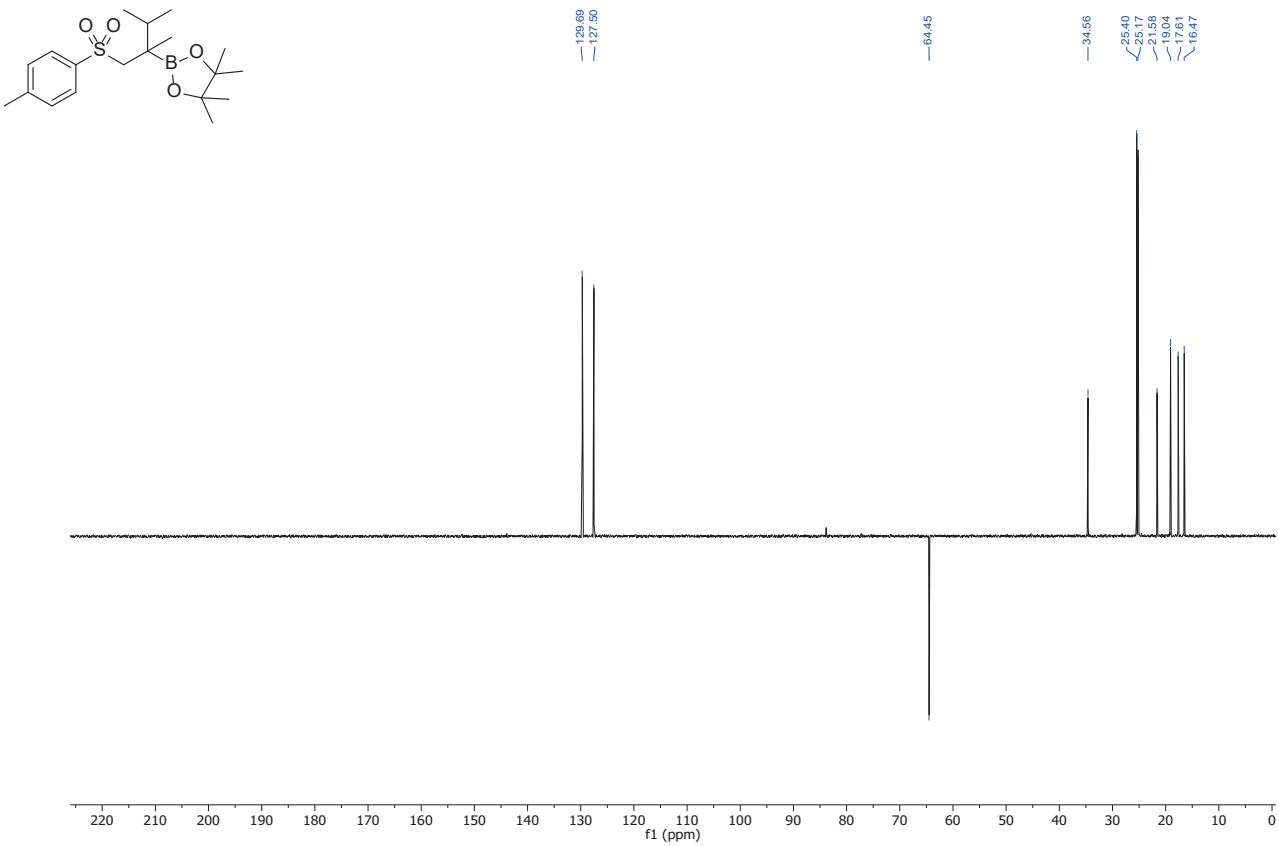
2-(2,3-dimethyl-1-tosylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26)

^{13}C NMR (75 MHz, $CDCl_3$)



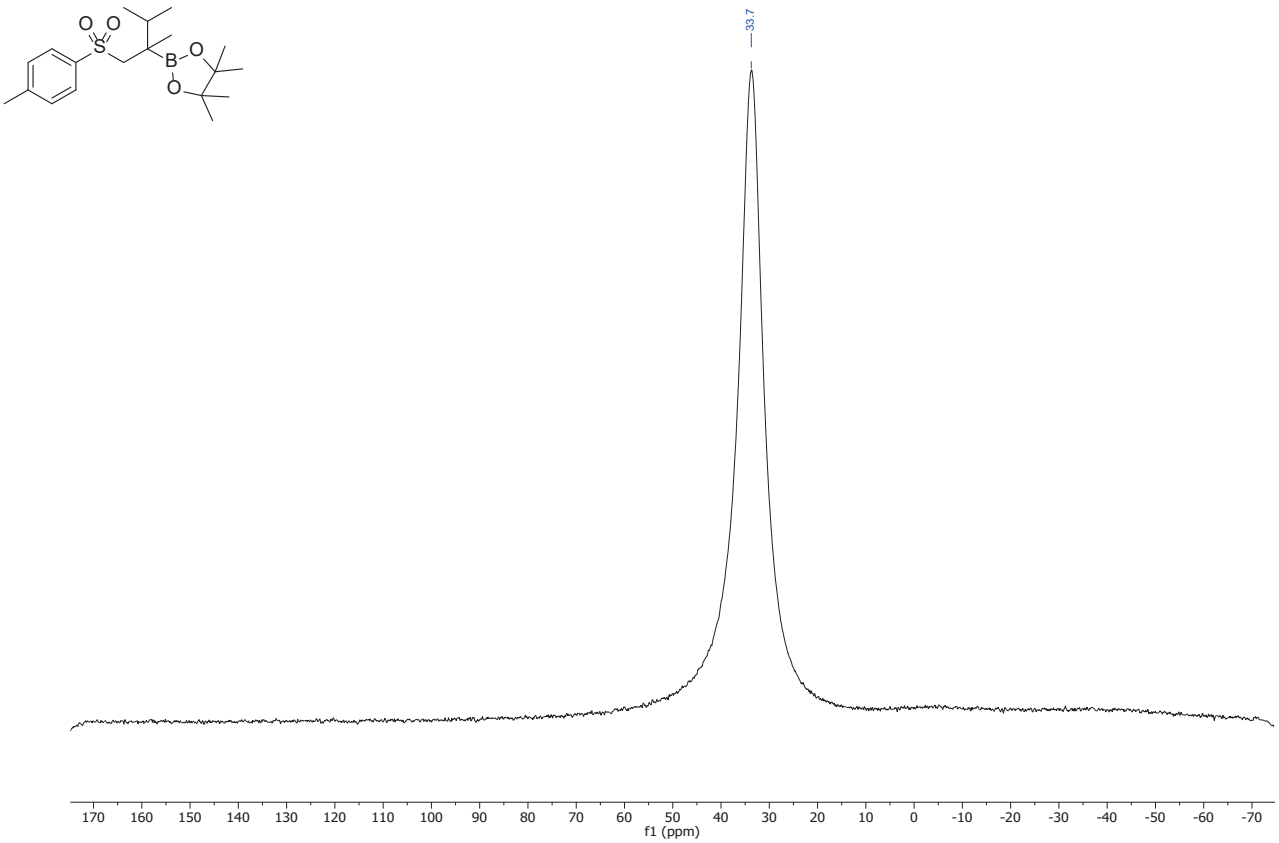
2-(2,3-dimethyl-1-tosylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



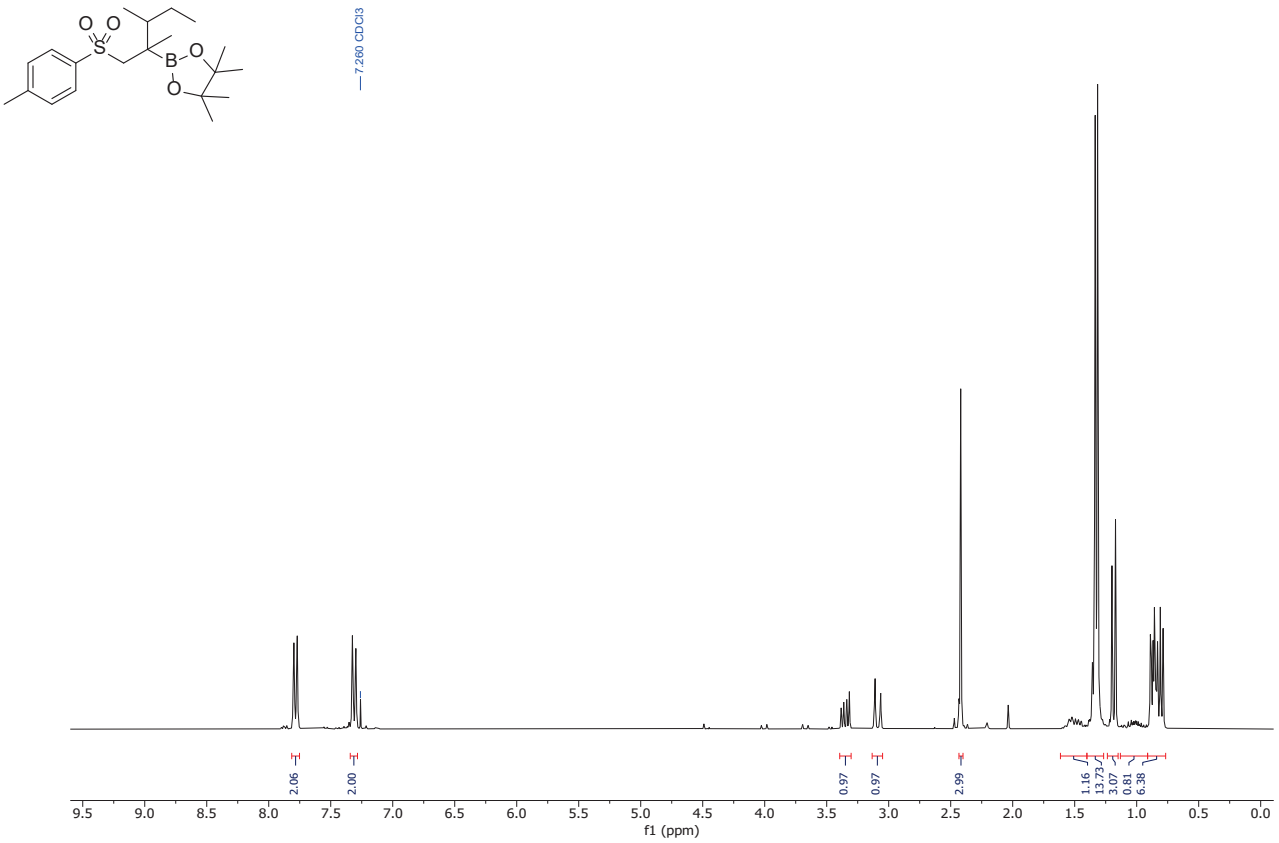
2-(2,3-dimethyl-1-tosylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26)

^{11}B NMR (96 MHz, $CDCl_3$)

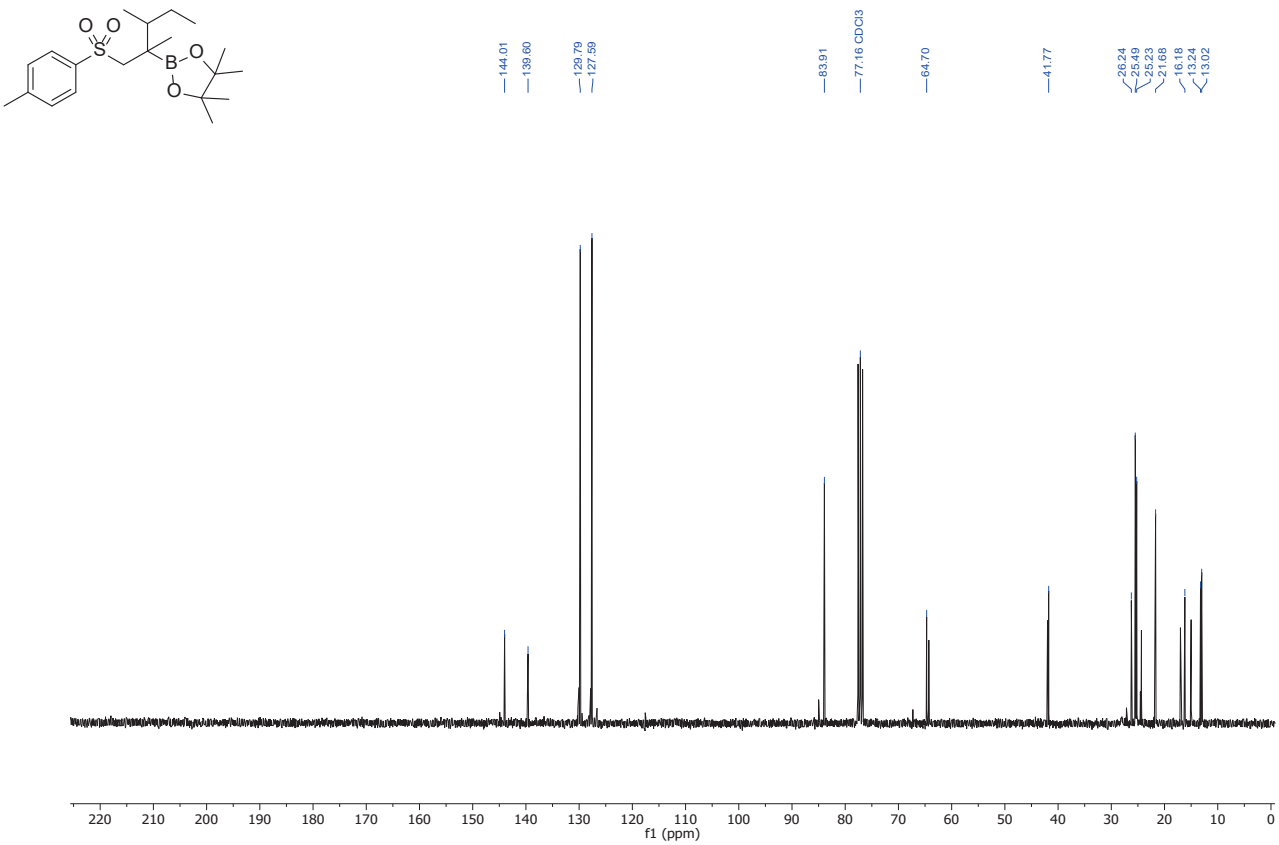


2-(2,3-dimethyl-1-tosylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27)

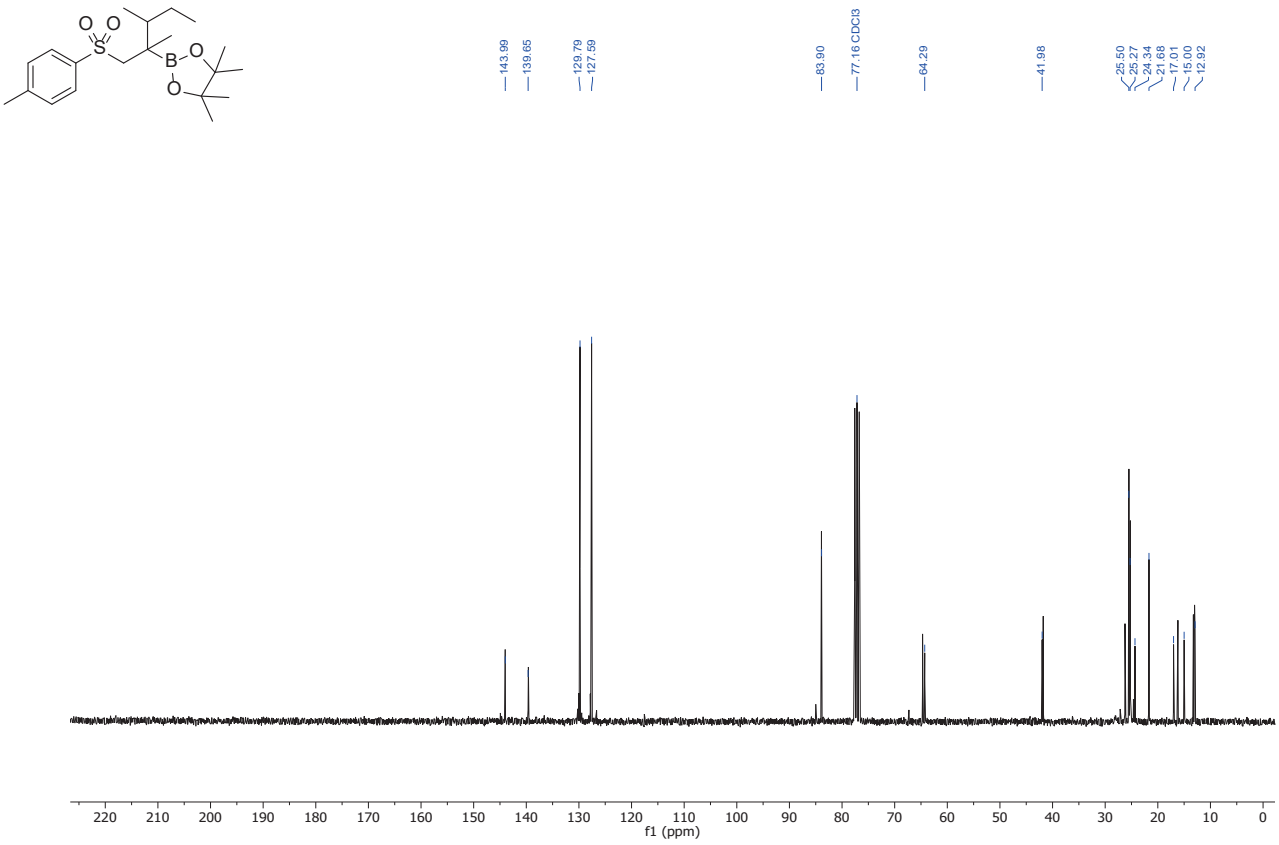
^{1}H NMR (300 MHz, $CDCl_3$)



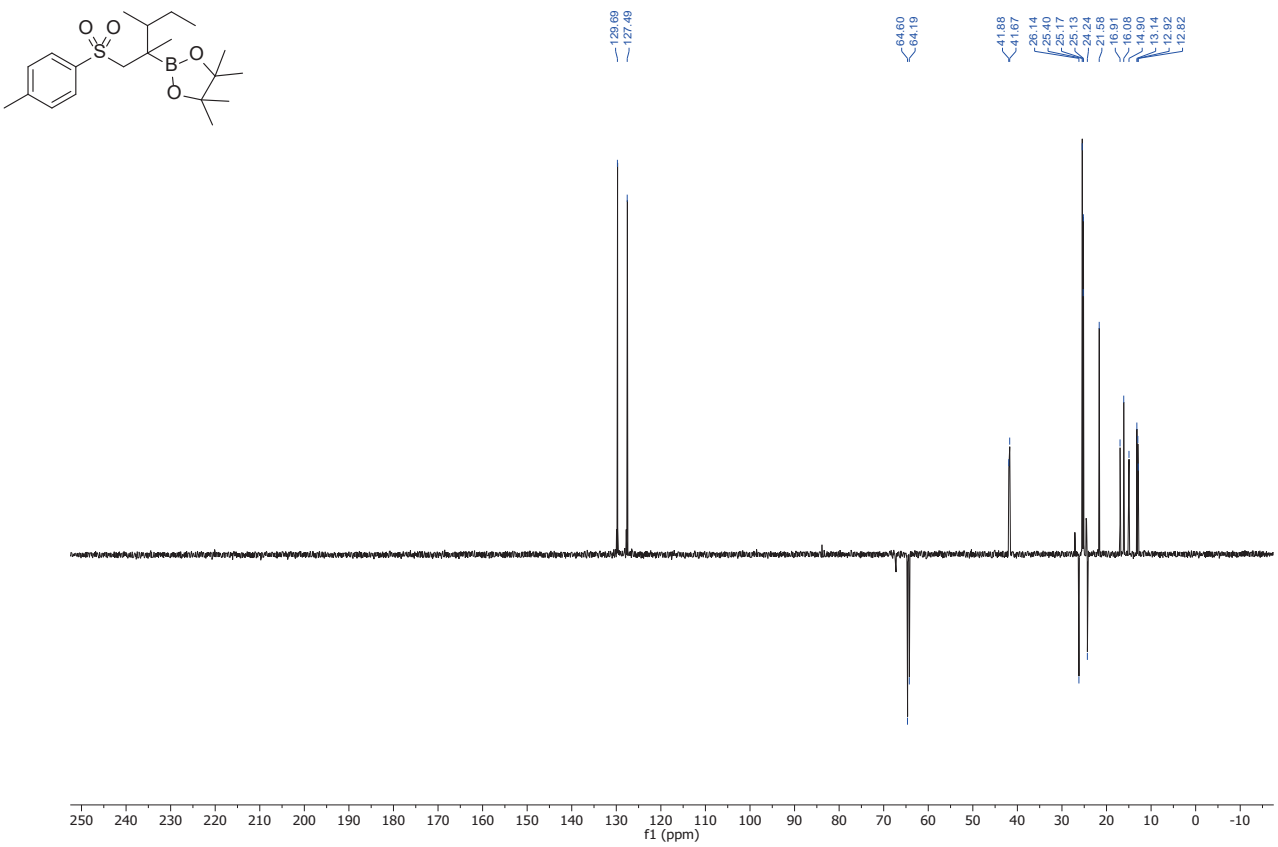
2-(2,3-dimethyl-1-tosylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27) ^{13}C NMR (75 MHz, $CDCl_3$)
Major diastereomer



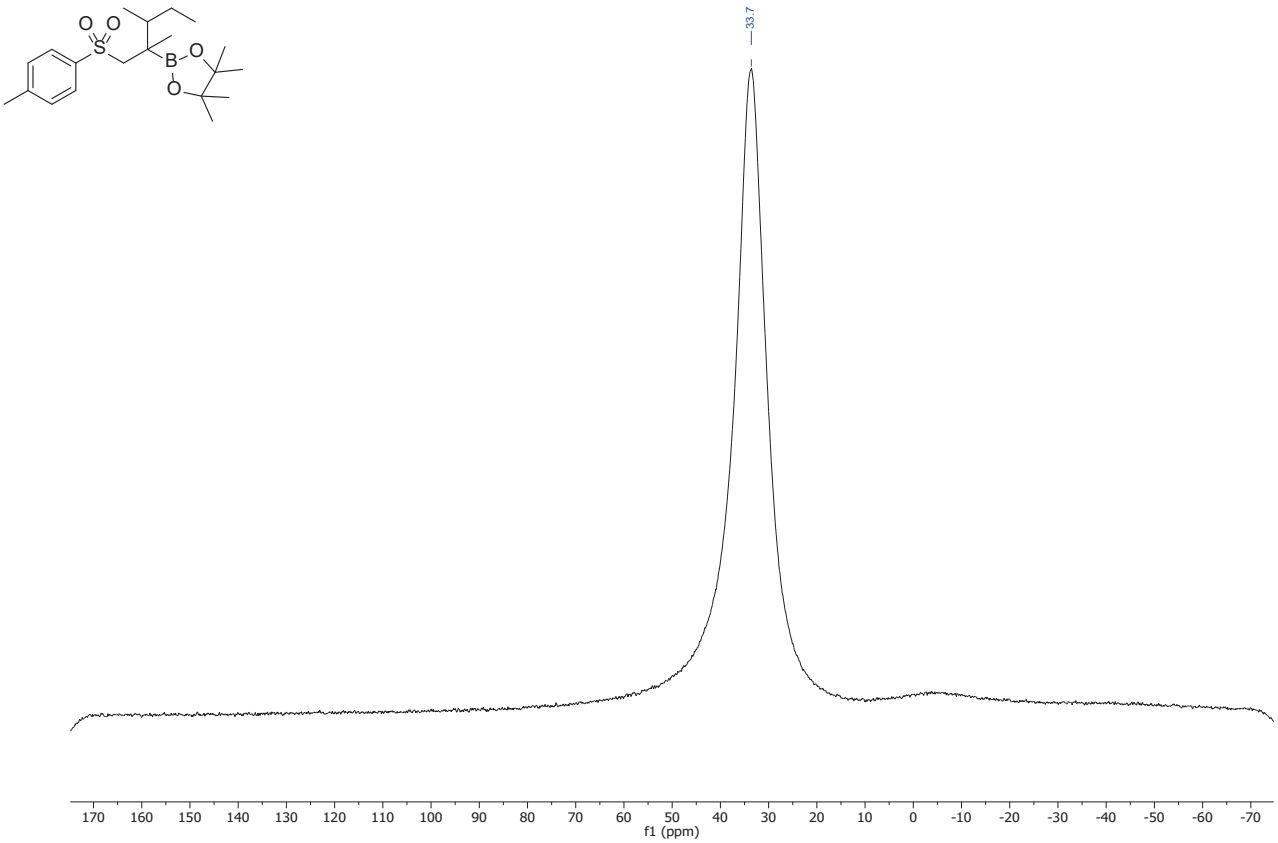
2-(2,3-dimethyl-1-tosylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27) ^{13}C NMR (75 MHz, $CDCl_3$)
Minor diastereomer



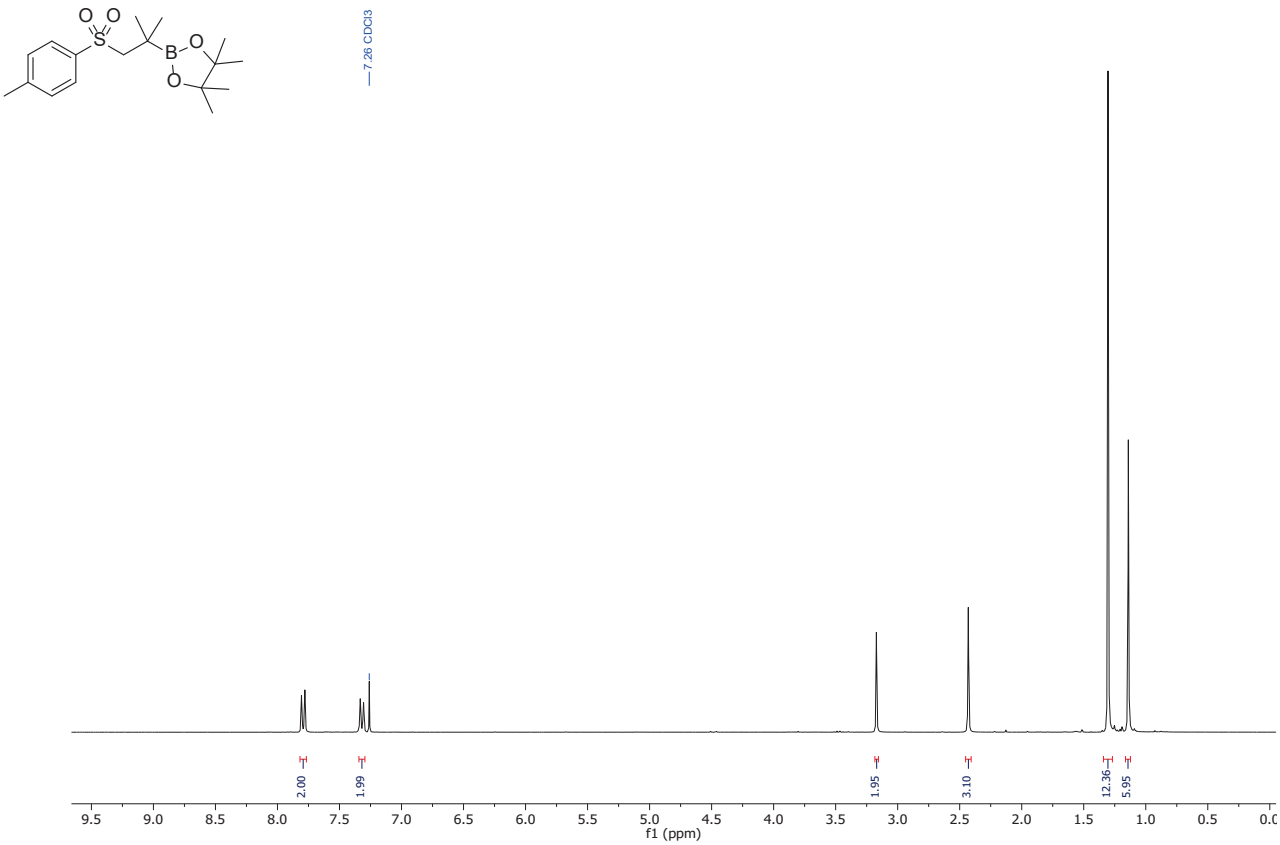
2-(2,3-dimethyl-1-tosylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27) ^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



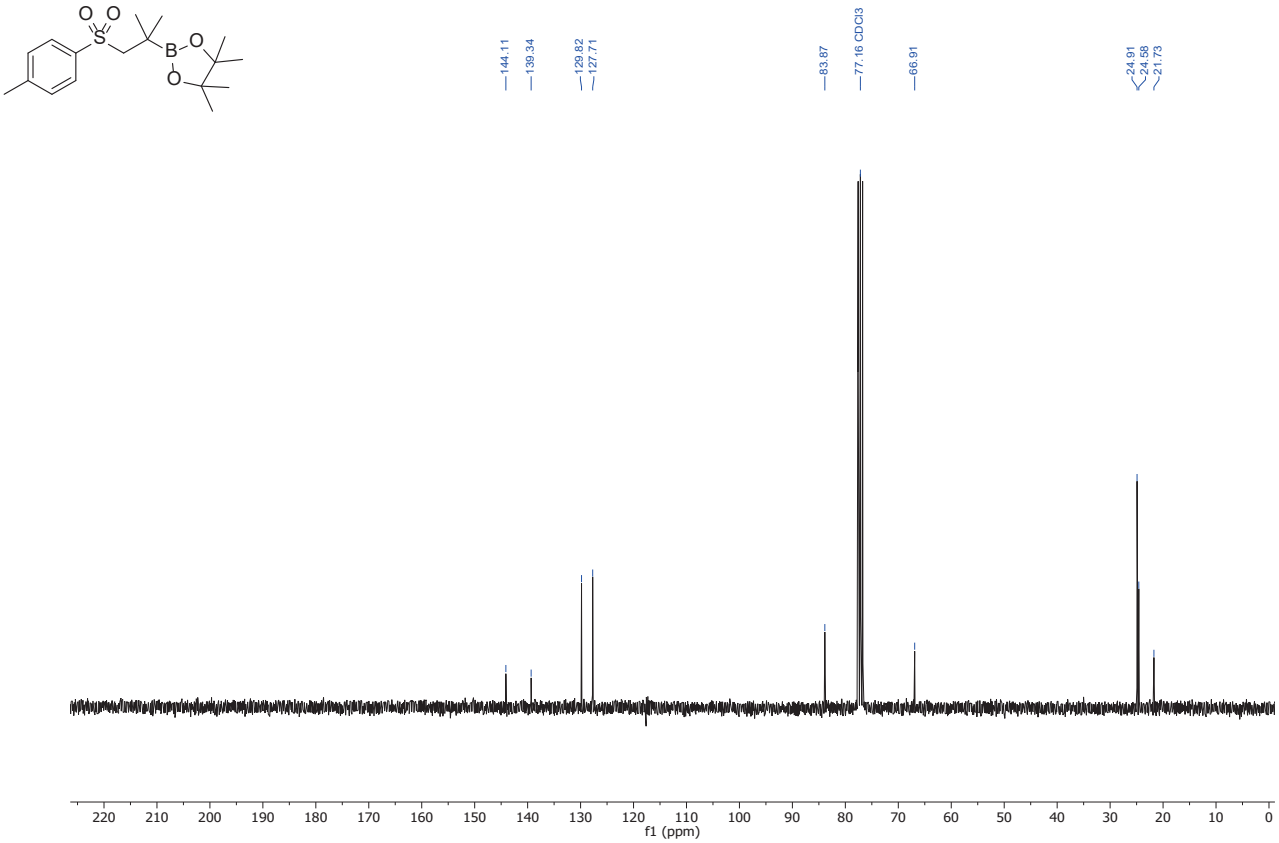
2-(2,3-dimethyl-1-tosylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27) ^{11}B NMR (96 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-(2-methyl-1-tosylpropan-2-yl)-1,3,2-dioxaborolane (14) ^{1}H NMR (300 MHz, $CDCl_3$)

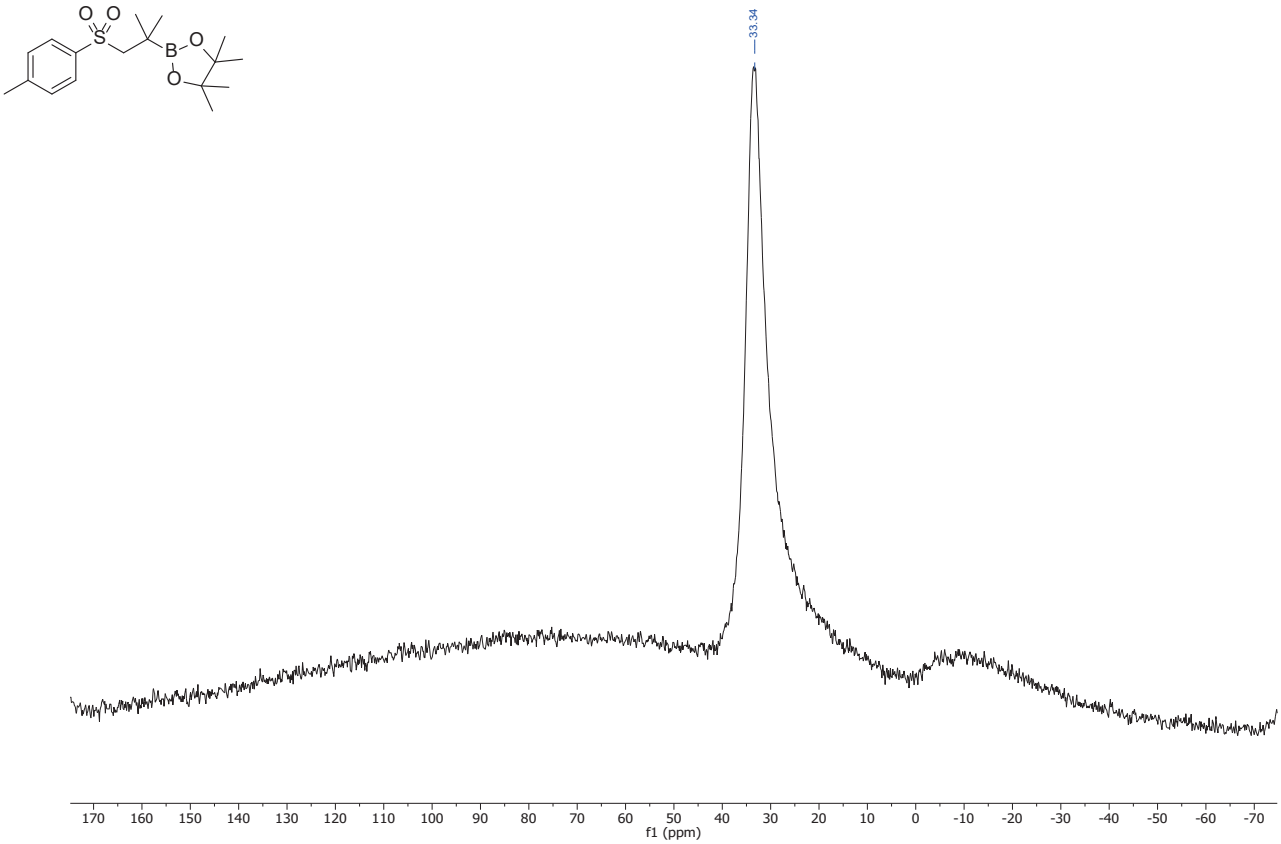


4,4,5,5-tetramethyl-2-(2-methyl-1-tosylpropan-2-yl)-1,3,2-dioxaborolane (14) ^{13}C NMR (75 MHz, $CDCl_3$)



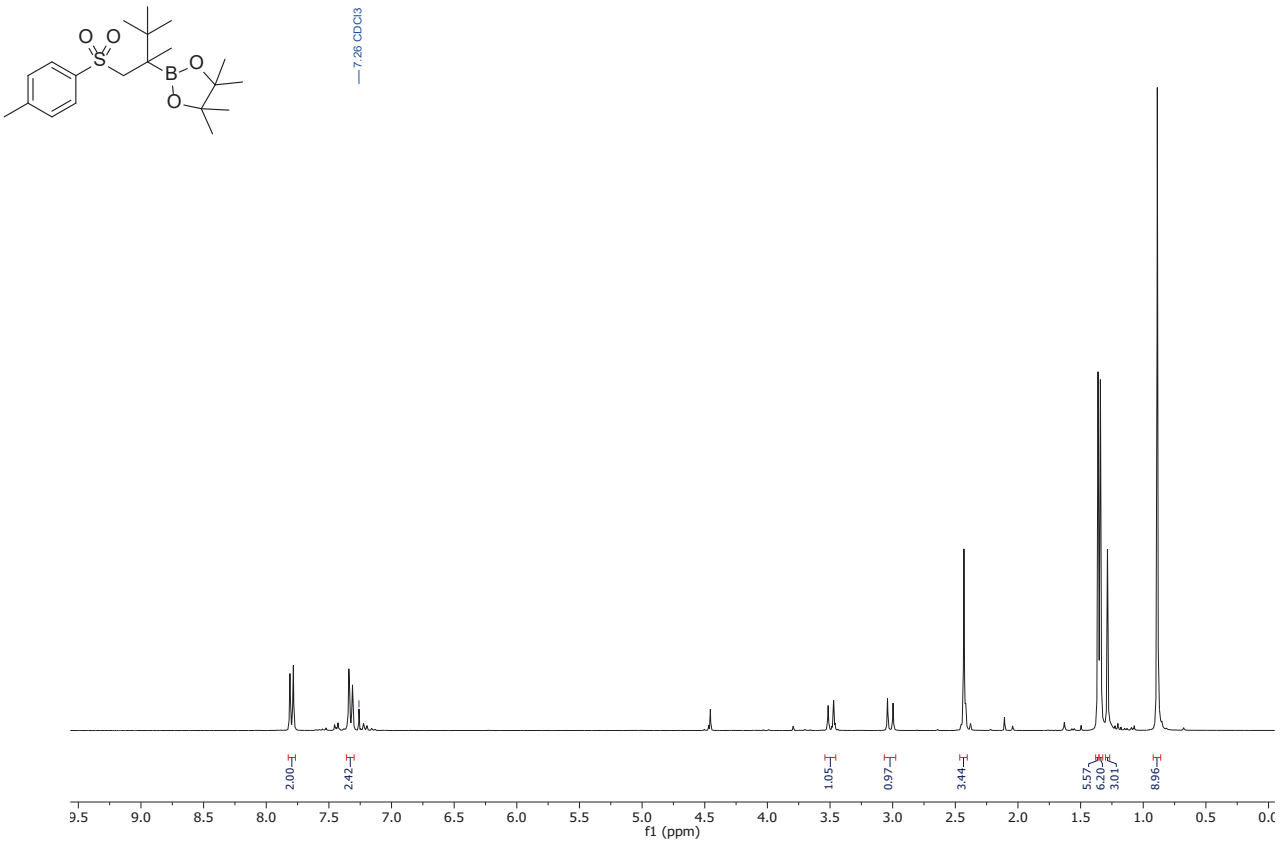
4,4,5,5-tetramethyl-2-(2-methyl-1-tosylpropan-2-yl)-1,3,2-dioxaborolane (14)

^{11}B NMR (96 MHz, $CDCl_3$)

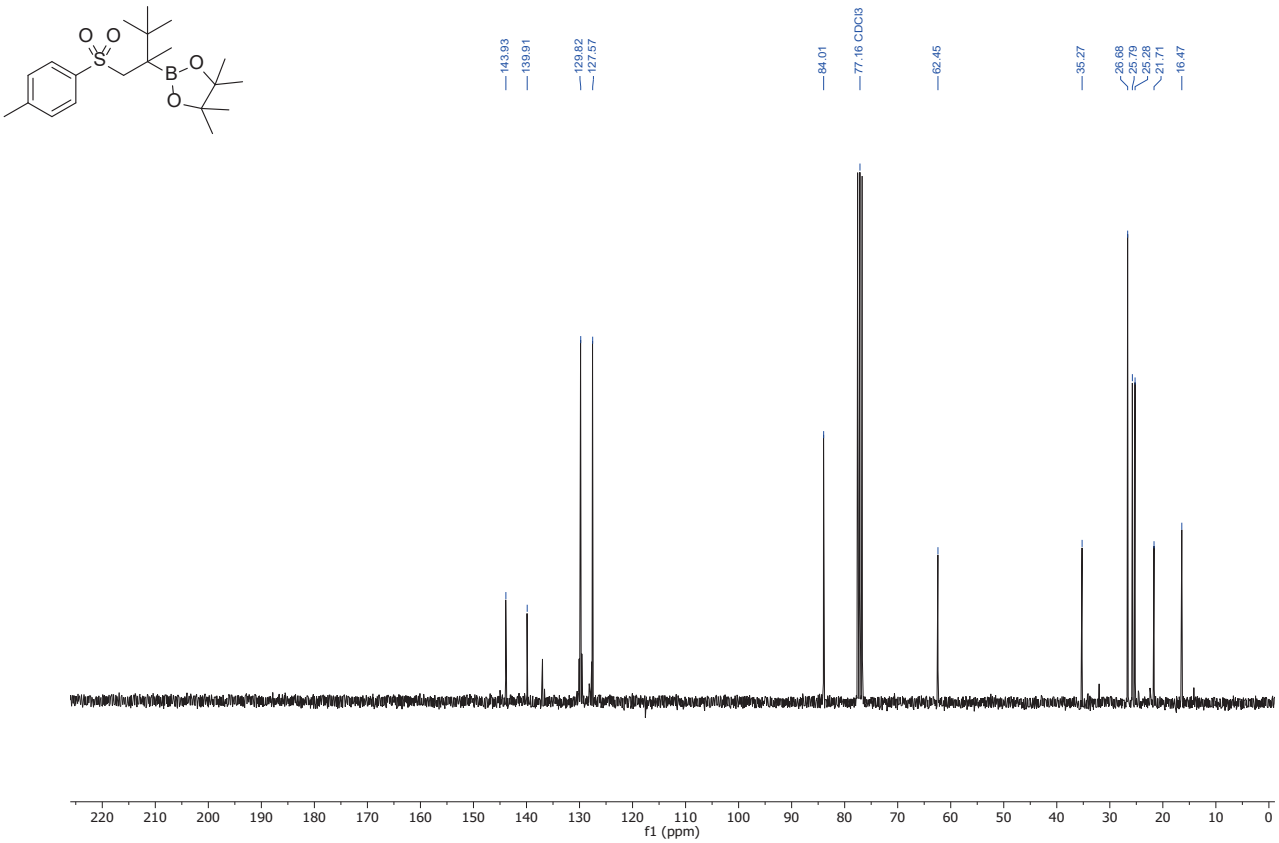


4,4,5,5-tetramethyl-2-(2,3,3-trimethyl-1-tosylbutan-2-yl)-1,3,2-dioxaborolane (34)

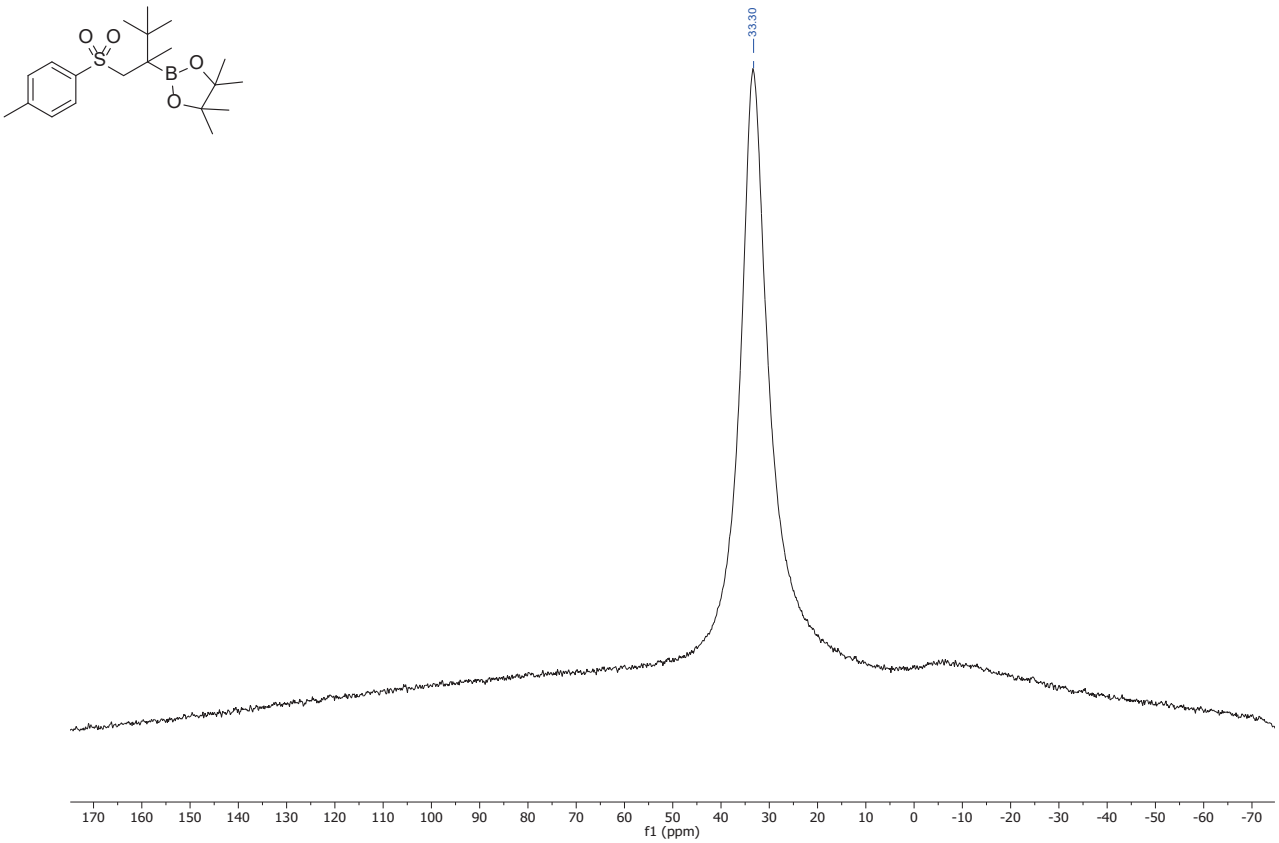
^{1}H NMR (300 MHz, $CDCl_3$)



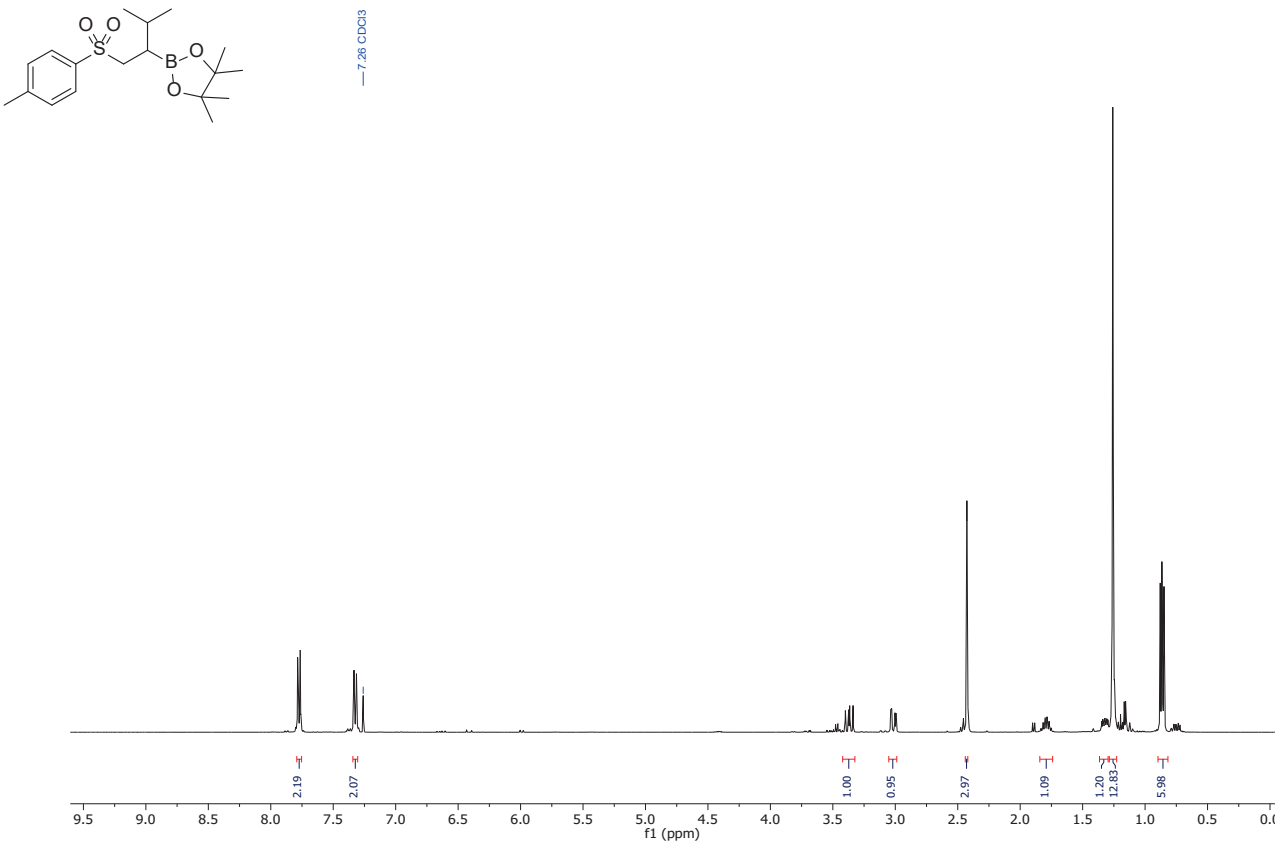
4,4,5,5-tetramethyl-2-(2,3,3-trimethyl-1-tosylbutan-2-yl)-1,3,2-dioxaborolane (34) ^{13}C NMR (75 MHz, $CDCl_3$)



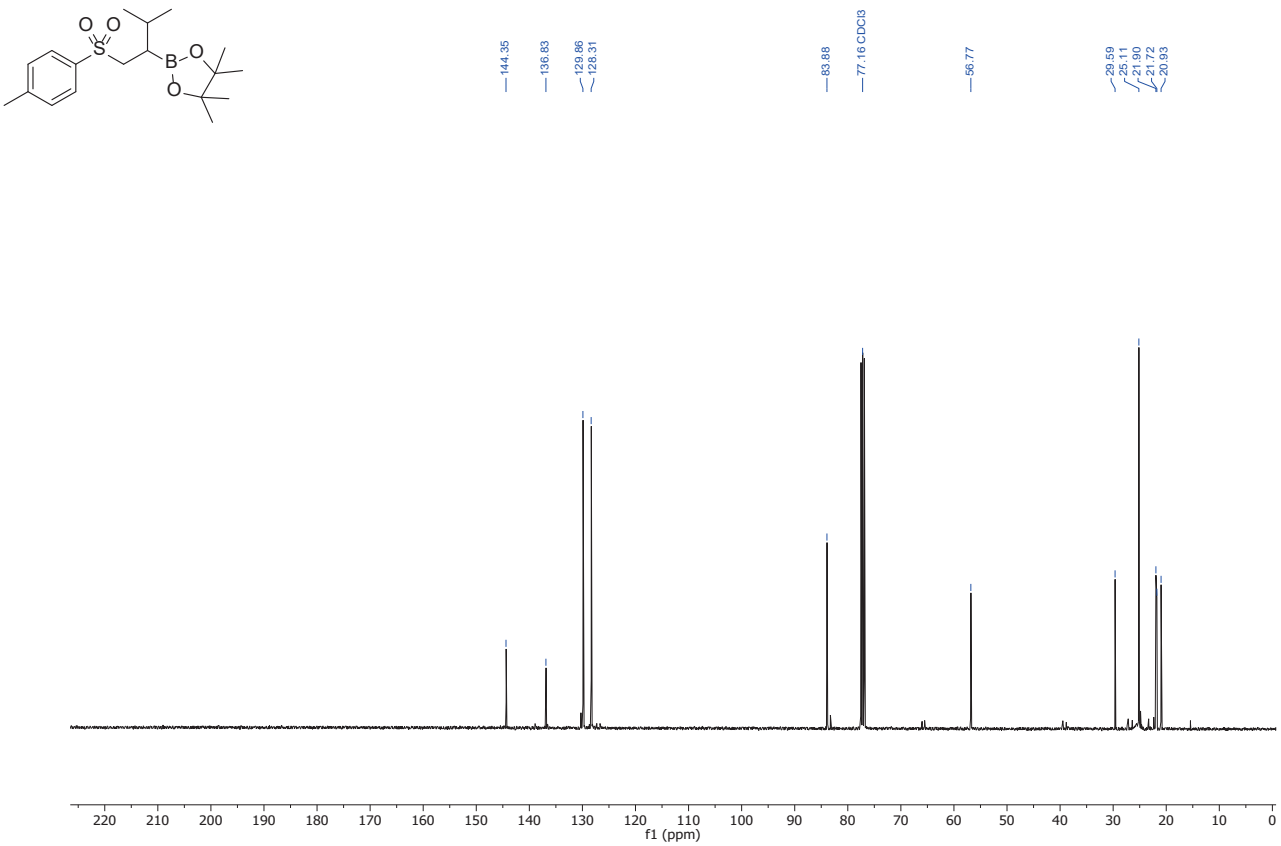
4,4,5,5-tetramethyl-2-(2,3,3-trimethyl-1-tosylbutan-2-yl)-1,3,2-dioxaborolane (34) ^{11}B NMR (96 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-(3-methyl-1-tosylbutan-2-yl)-1,3,2-dioxaborolane (13) ^{1}H NMR (400 MHz, $CDCl_3$)

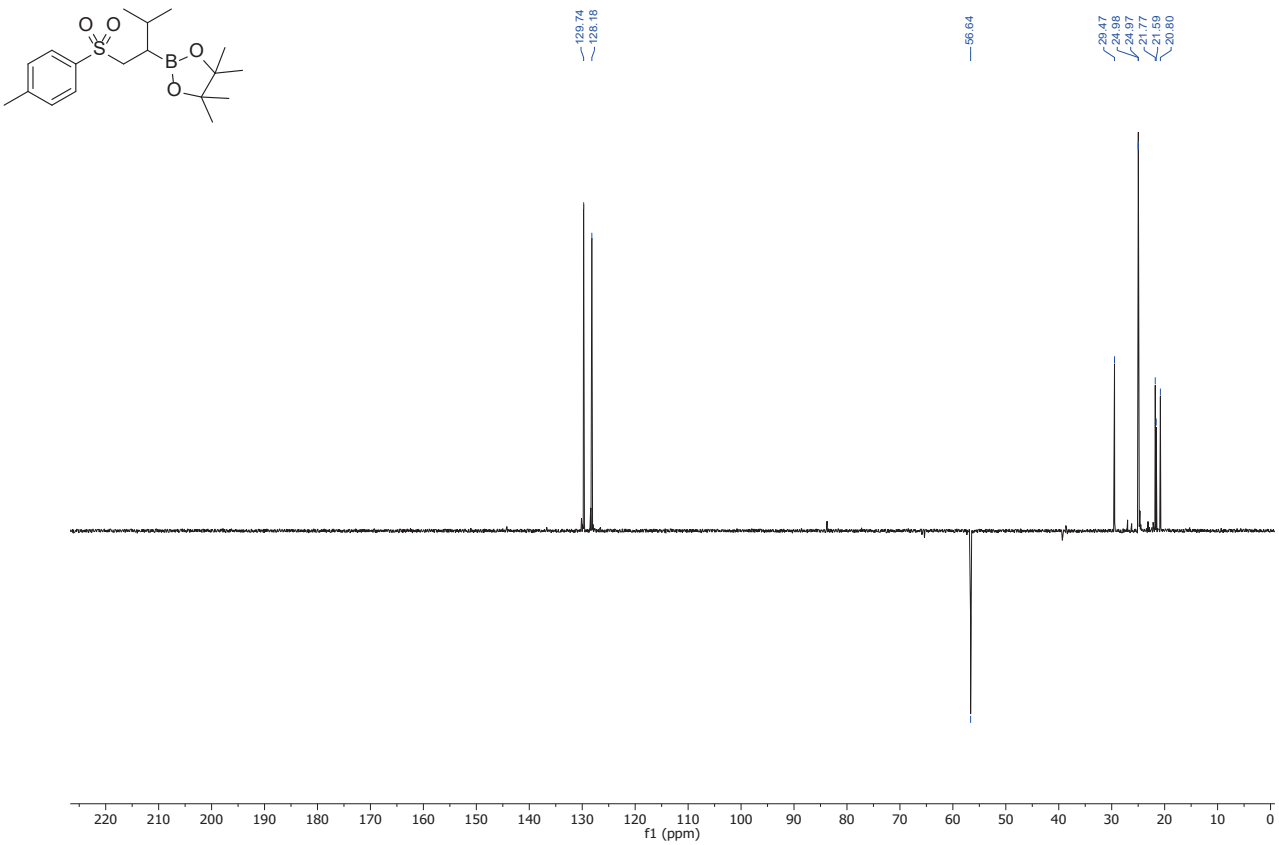


4,4,5,5-tetramethyl-2-(3-methyl-1-tosylbutan-2-yl)-1,3,2-dioxaborolane (13) ^{13}C NMR (101 MHz, $CDCl_3$)



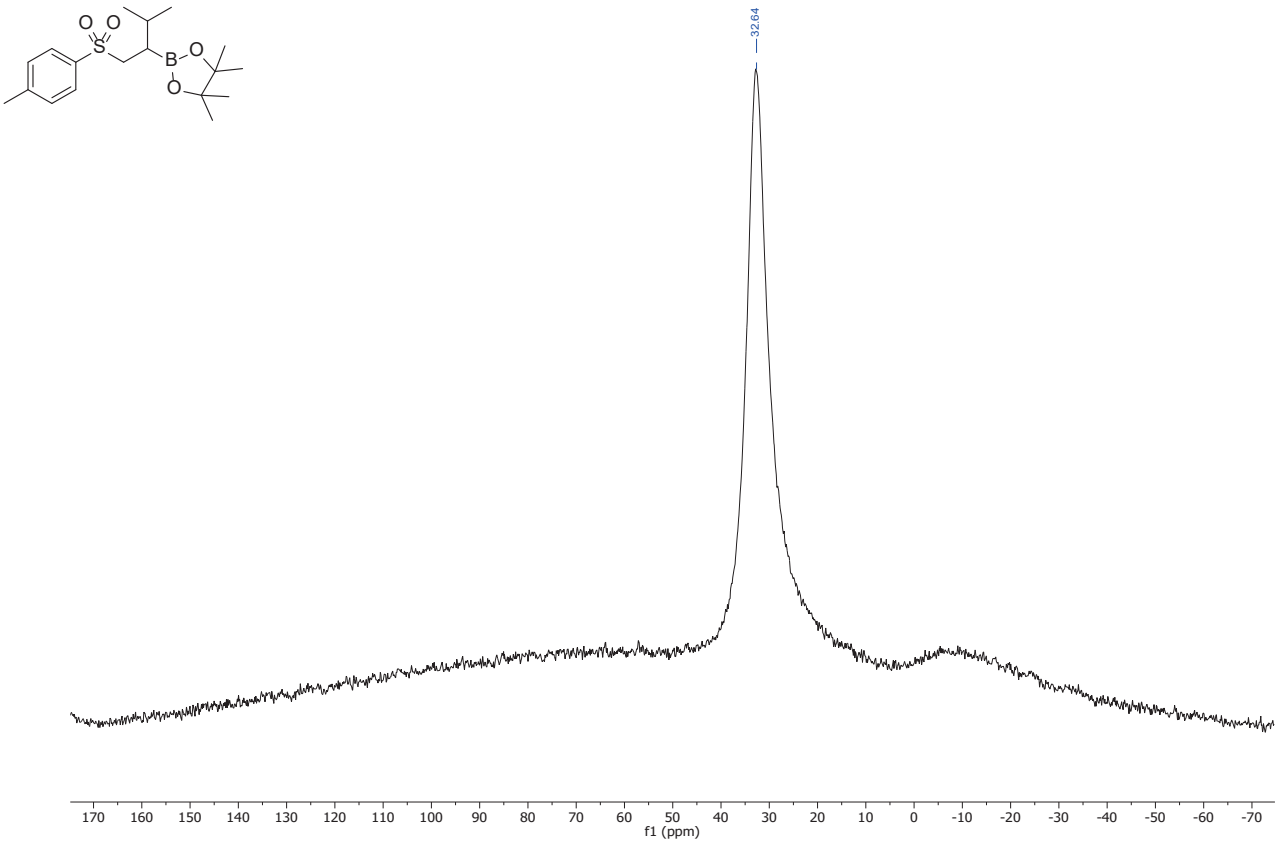
4,4,5,5-tetramethyl-2-(3-methyl-1-tosylbutan-2-yl)-1,3,2-dioxaborolane (13)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)

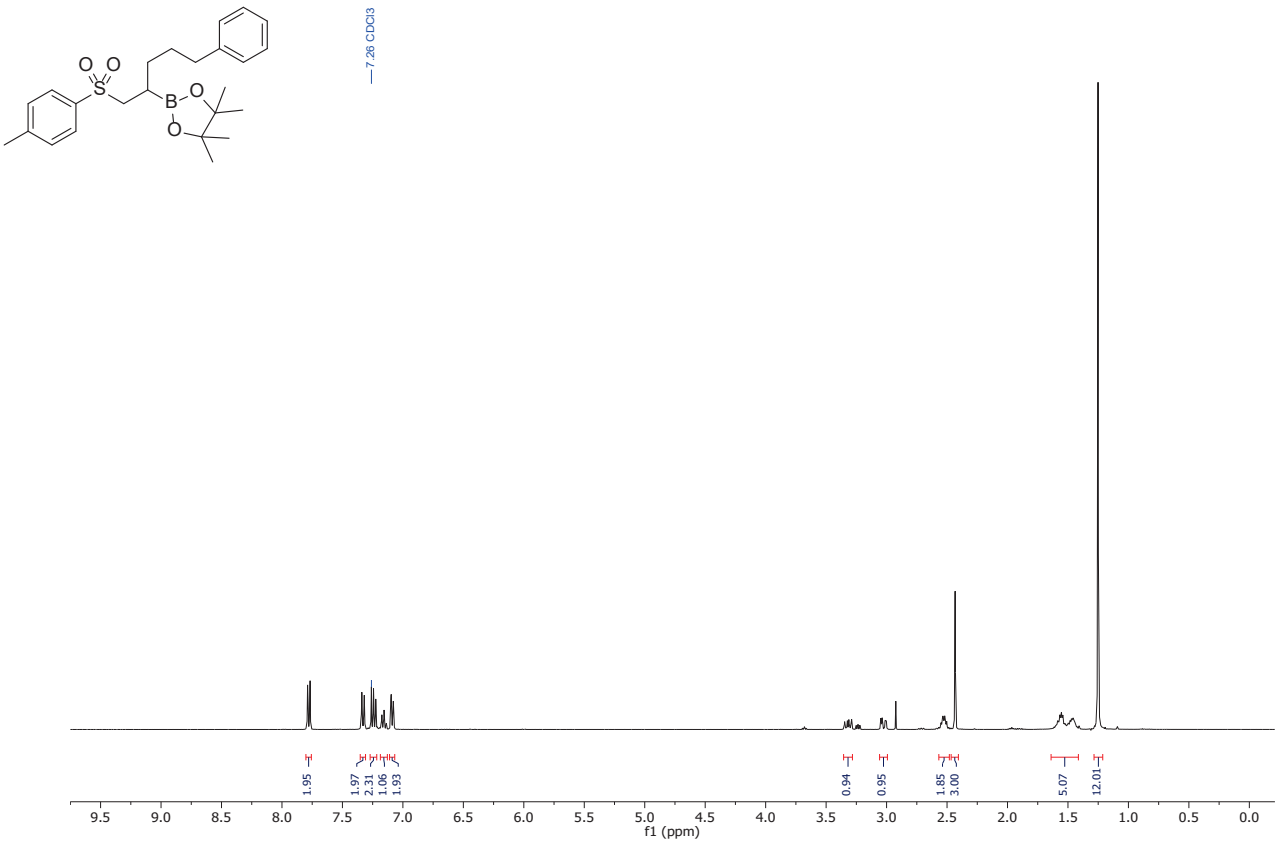


4,4,5,5-tetramethyl-2-(3-methyl-1-tosylbutan-2-yl)-1,3,2-dioxaborolane (13)

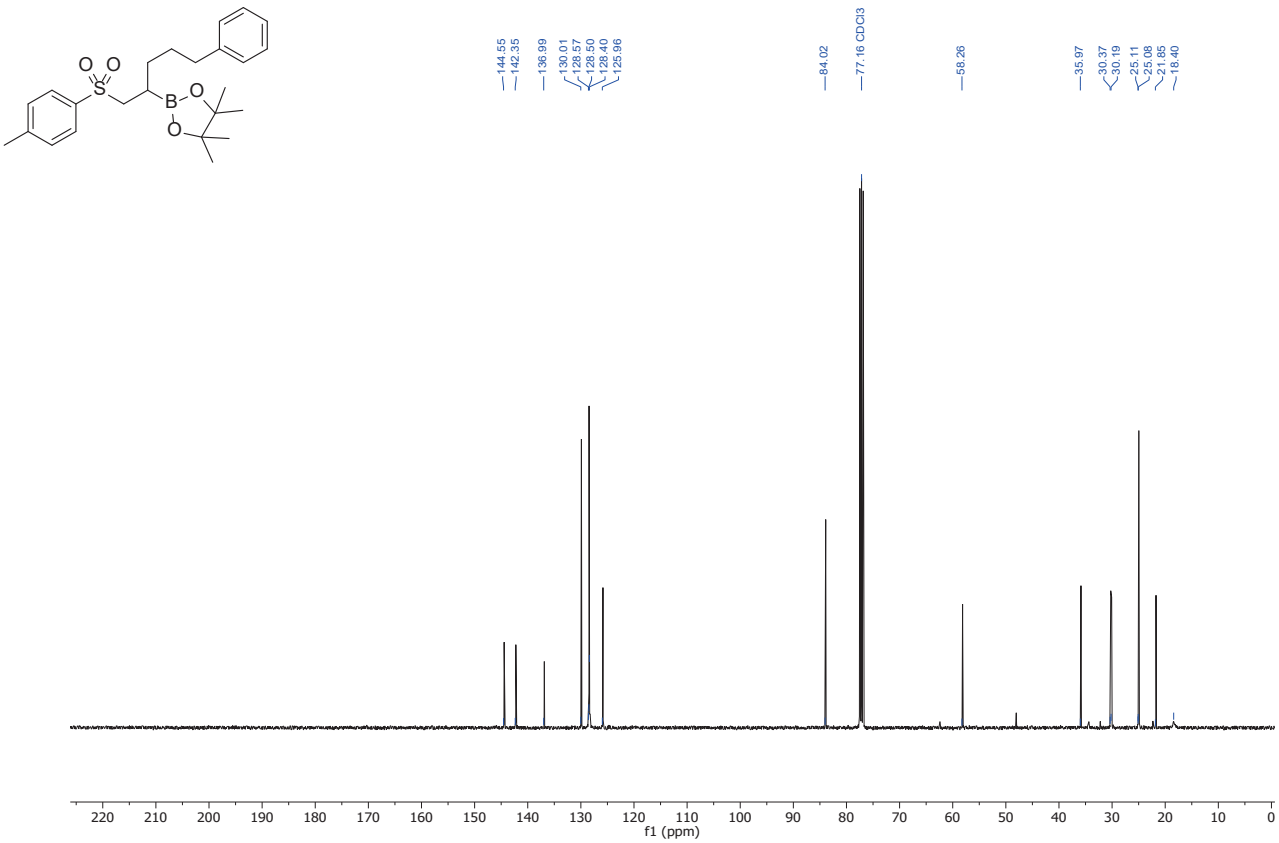
^{11}B NMR (96 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-(5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (12) ^{1}H NMR (400 MHz, $CDCl_3$)

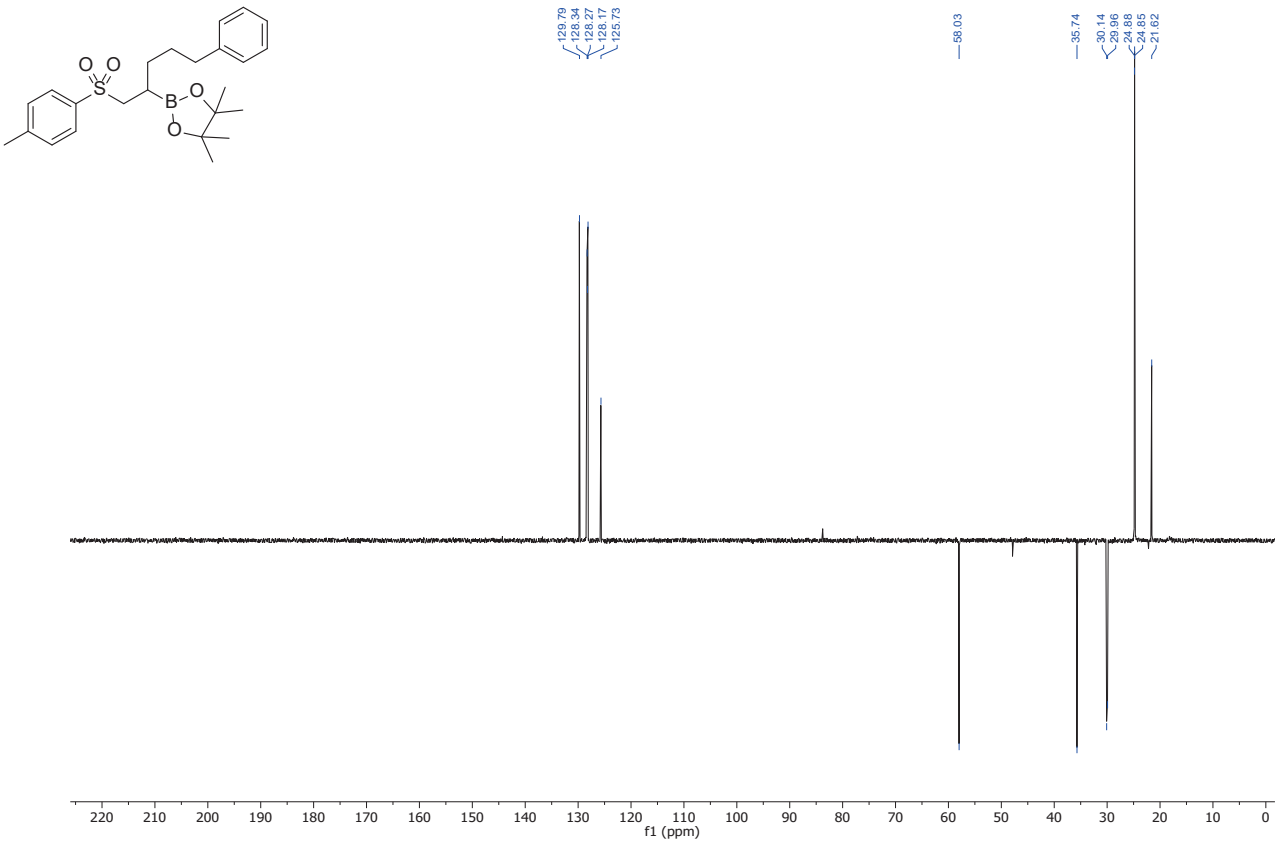


4,4,5,5-tetramethyl-2-(5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (12) ^{13}C NMR (101 MHz, $CDCl_3$)



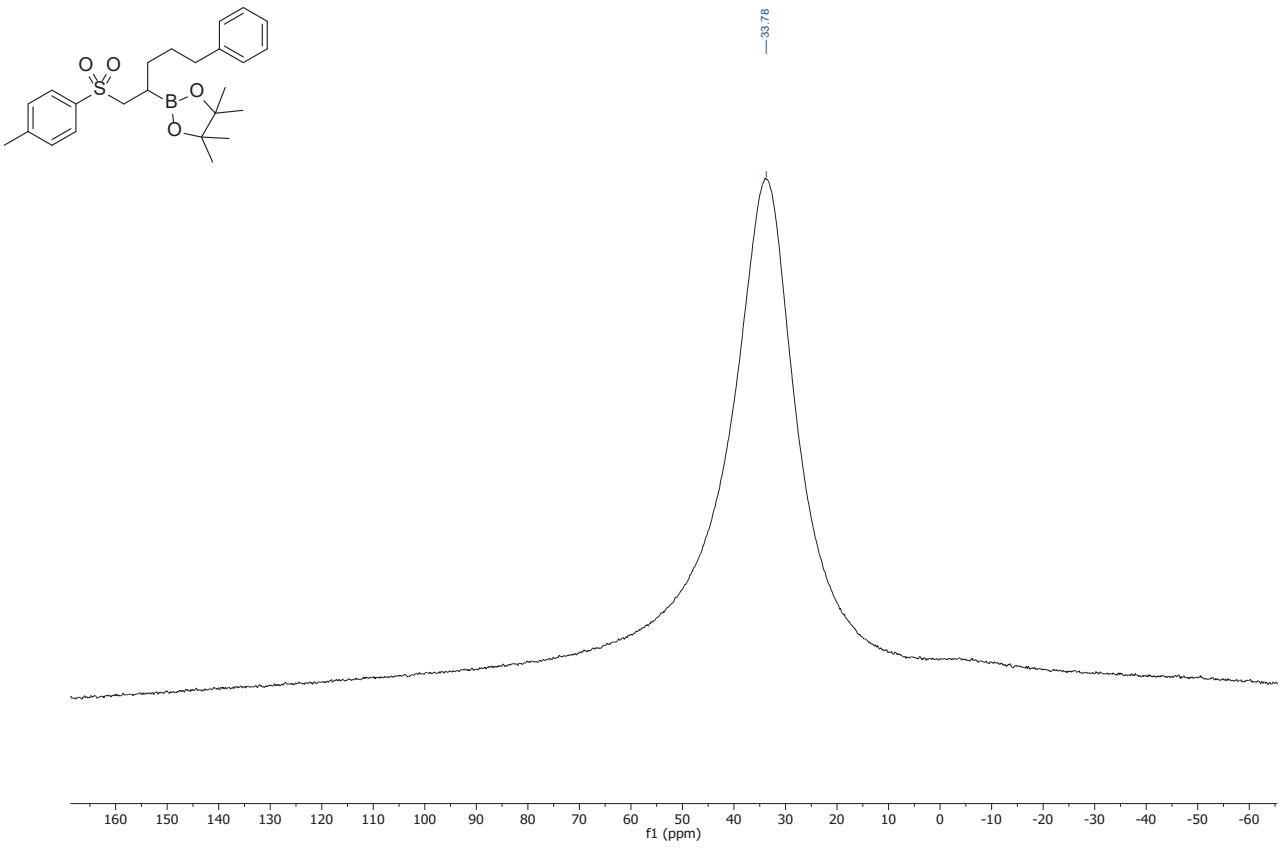
4,4,5,5-tetramethyl-2-(5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (12)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)

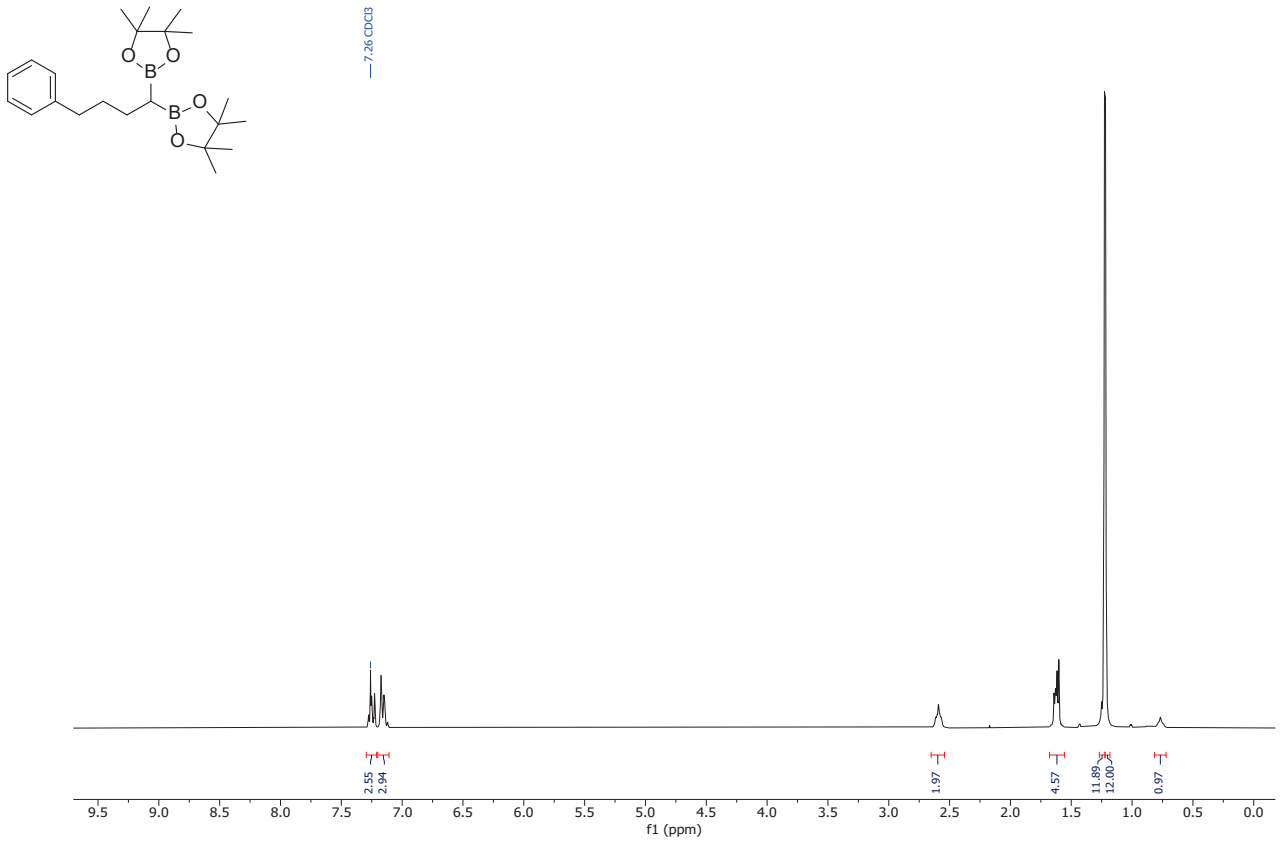


4,4,5,5-tetramethyl-2-(5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (12)

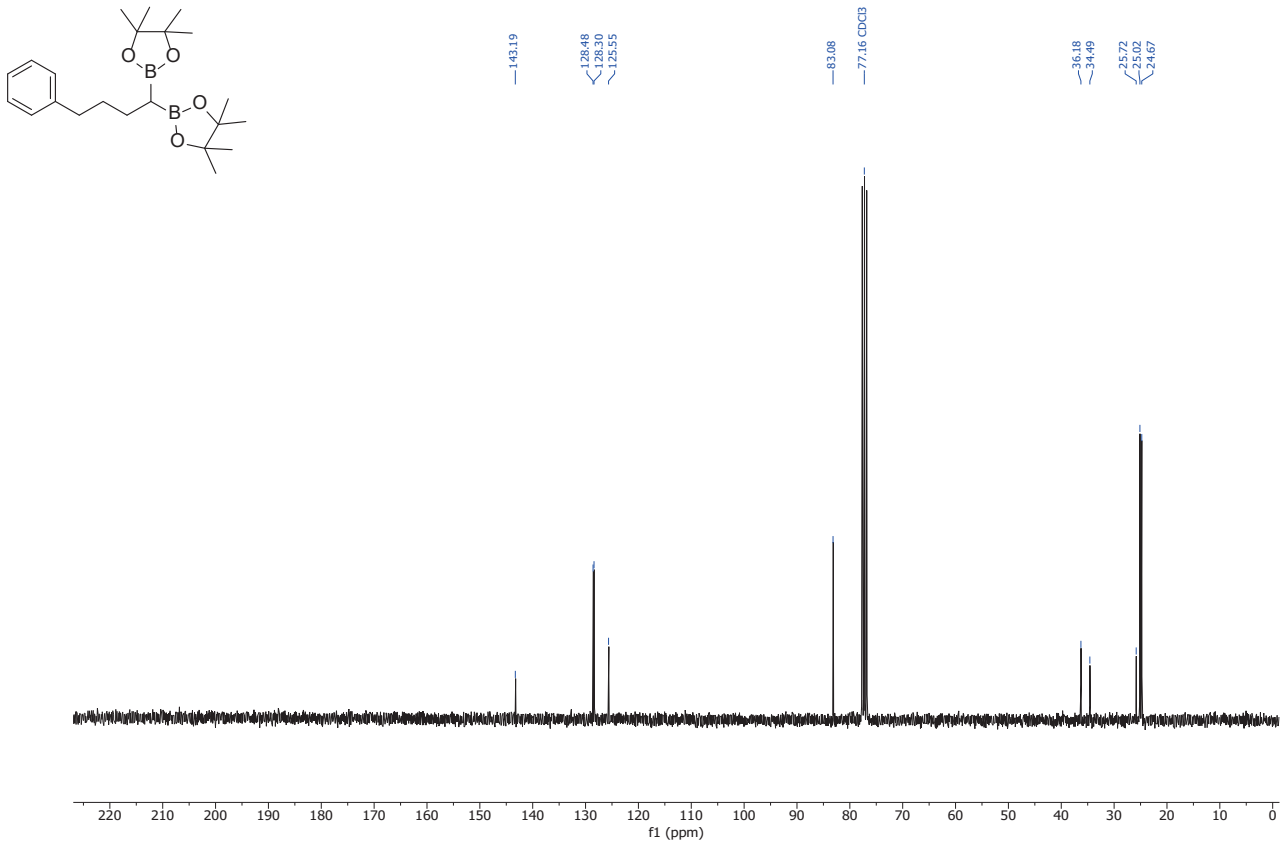
^{11}B NMR (96 MHz, $CDCl_3$)



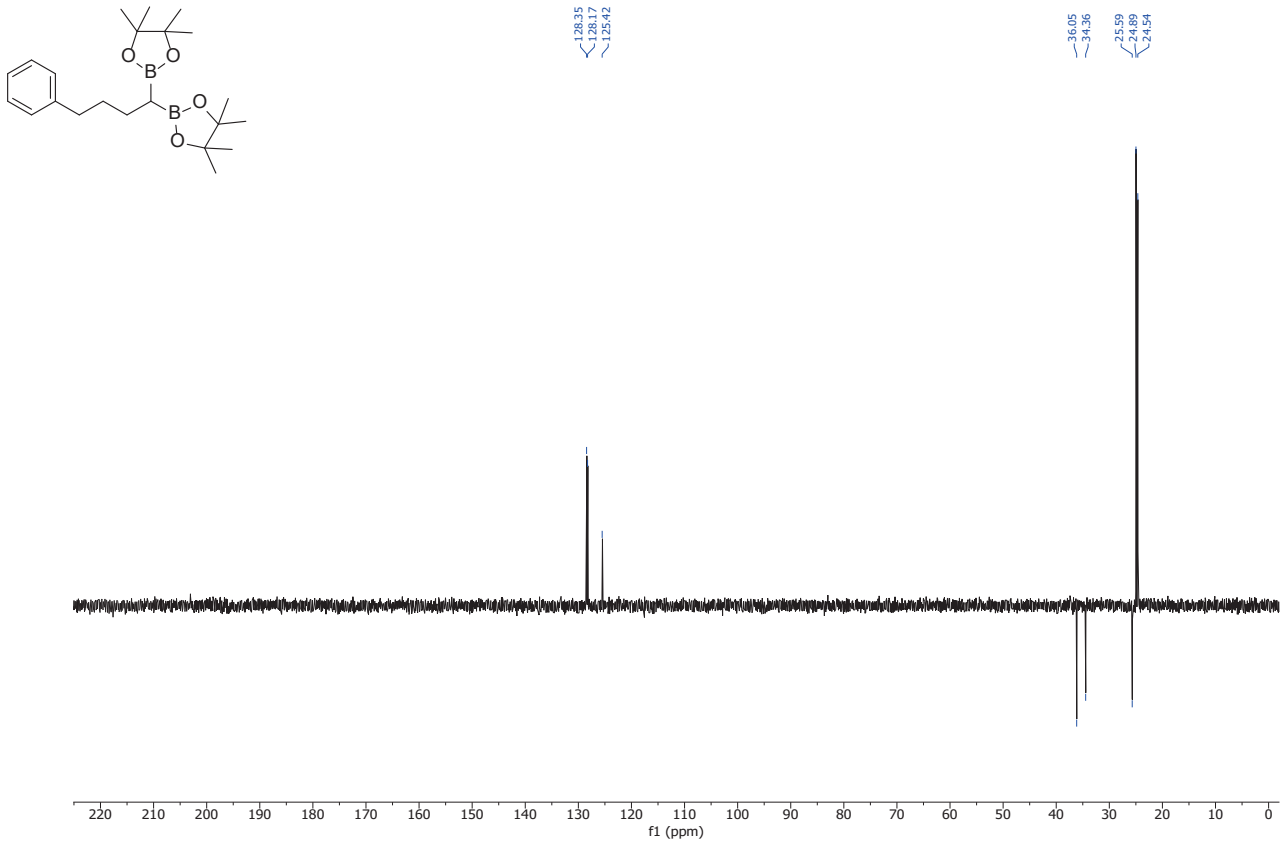
2,2'-(4-phenylbutane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (97) ^{1}H NMR (300 MHz, $CDCl_3$)



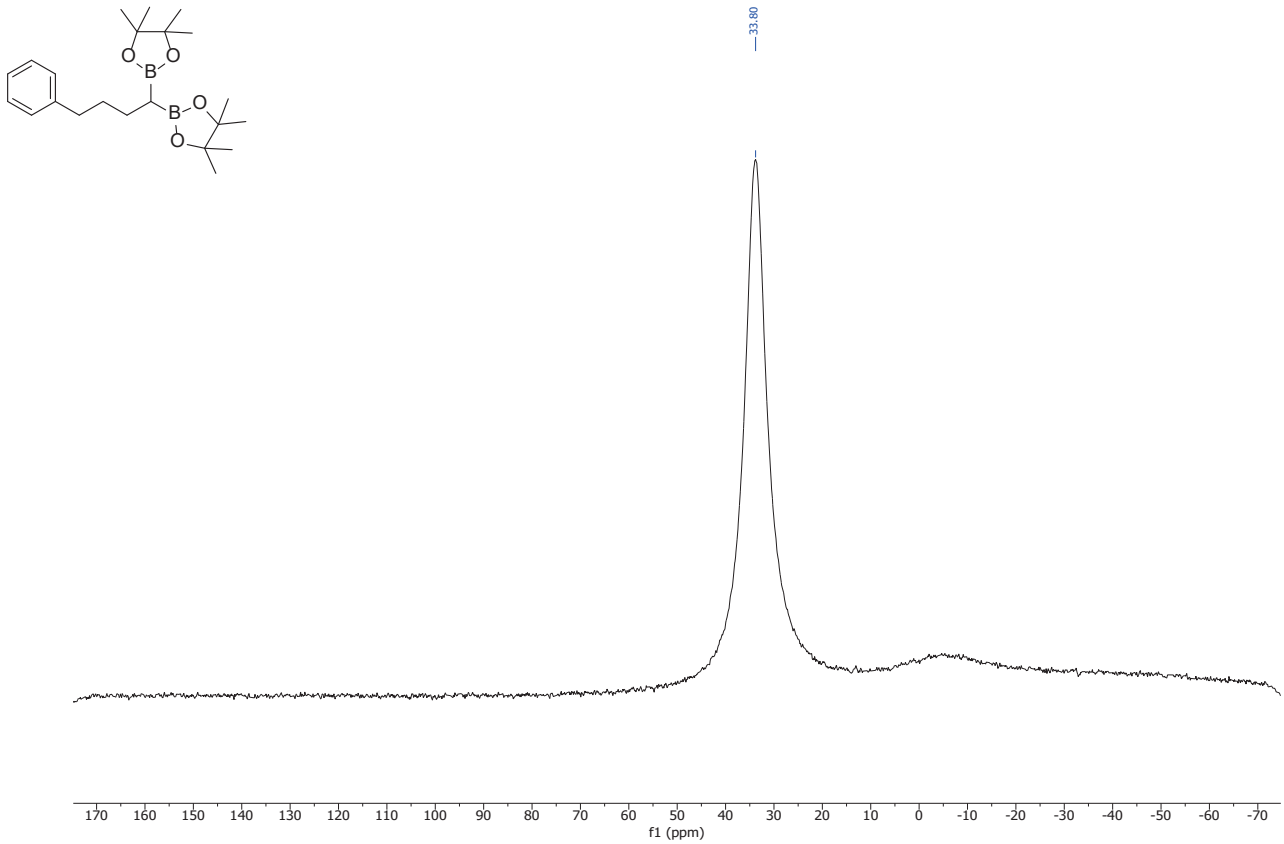
2,2'-(4-phenylbutane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (97) ^{13}C NMR (75 MHz, $CDCl_3$)



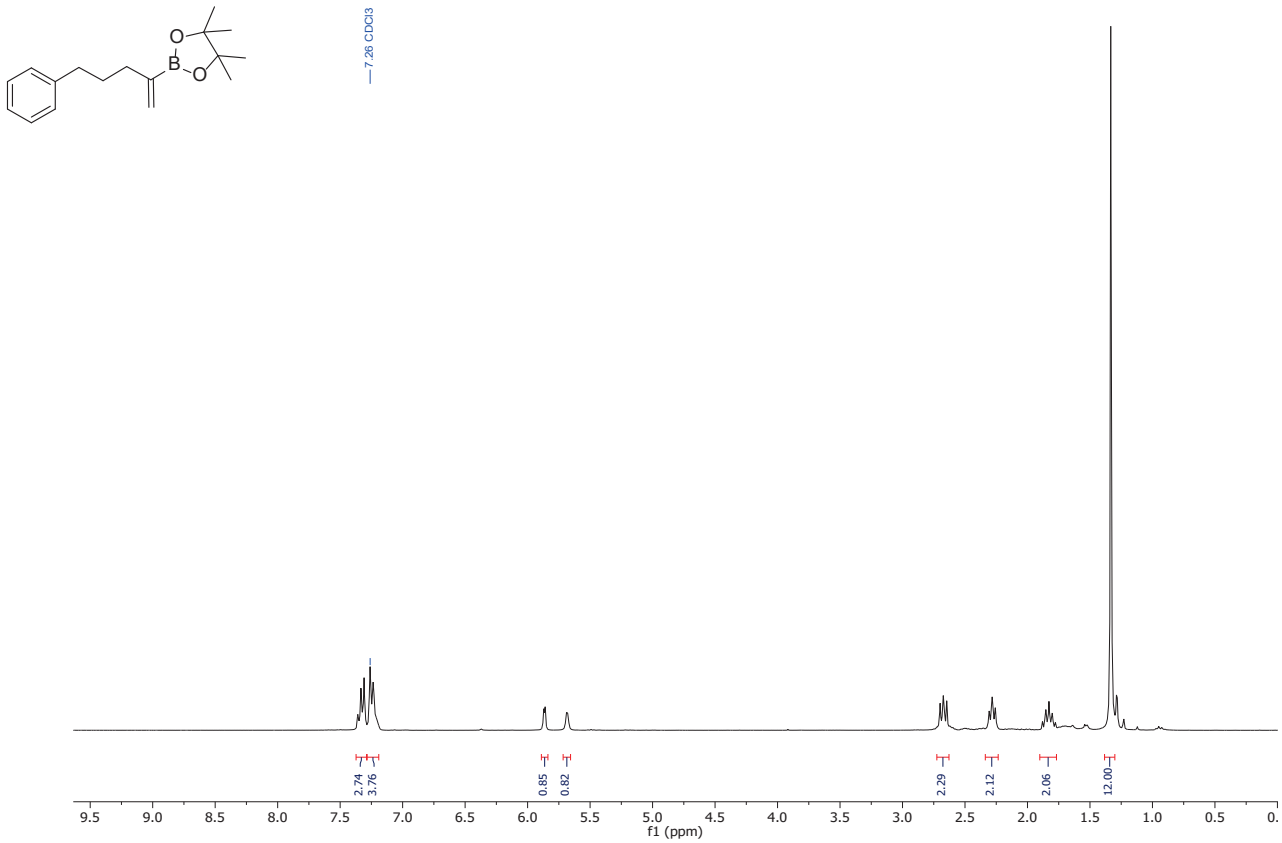
2,2'-(4-phenylbutane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (97) ^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



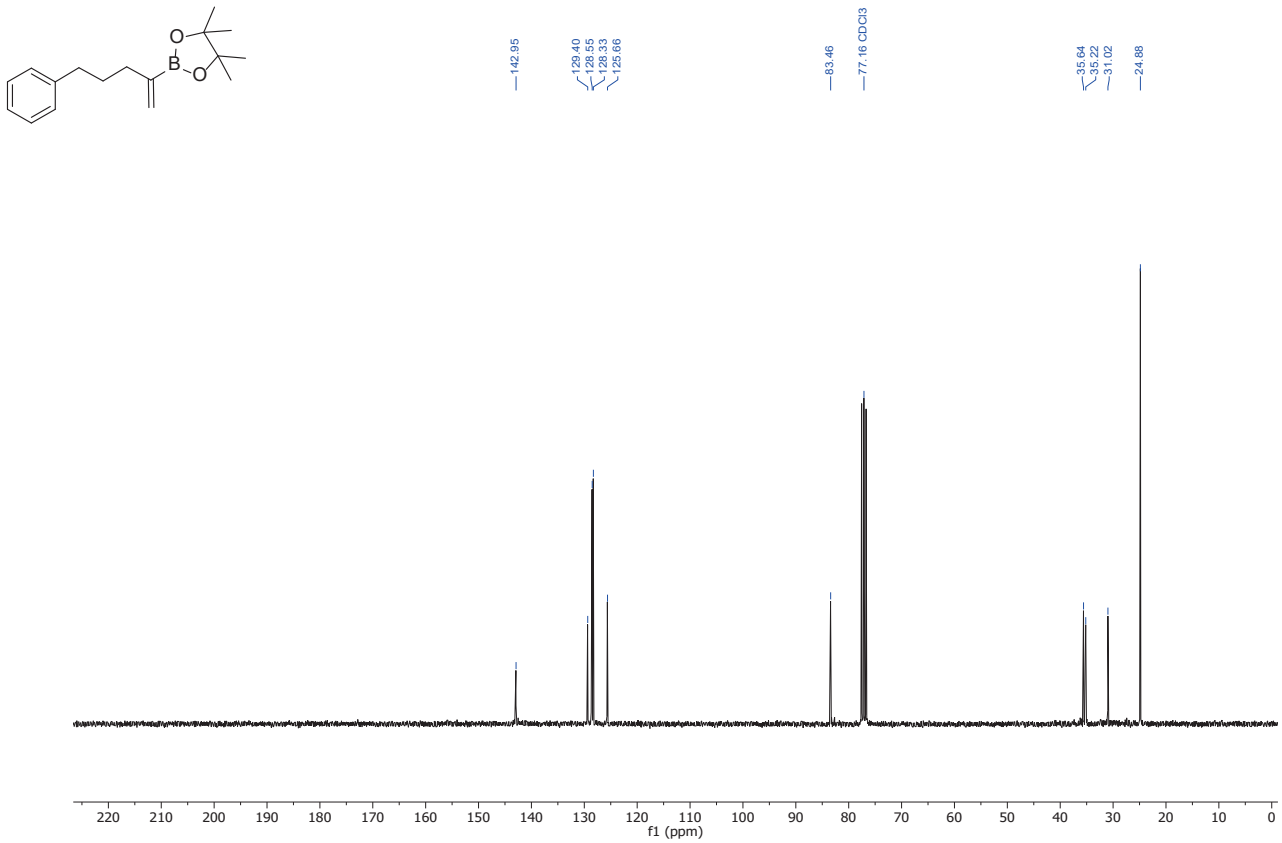
2,2'-(4-phenylbutane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (97) ^{11}B NMR (96 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (98) ^{1}H NMR (300 MHz, $CDCl_3$)

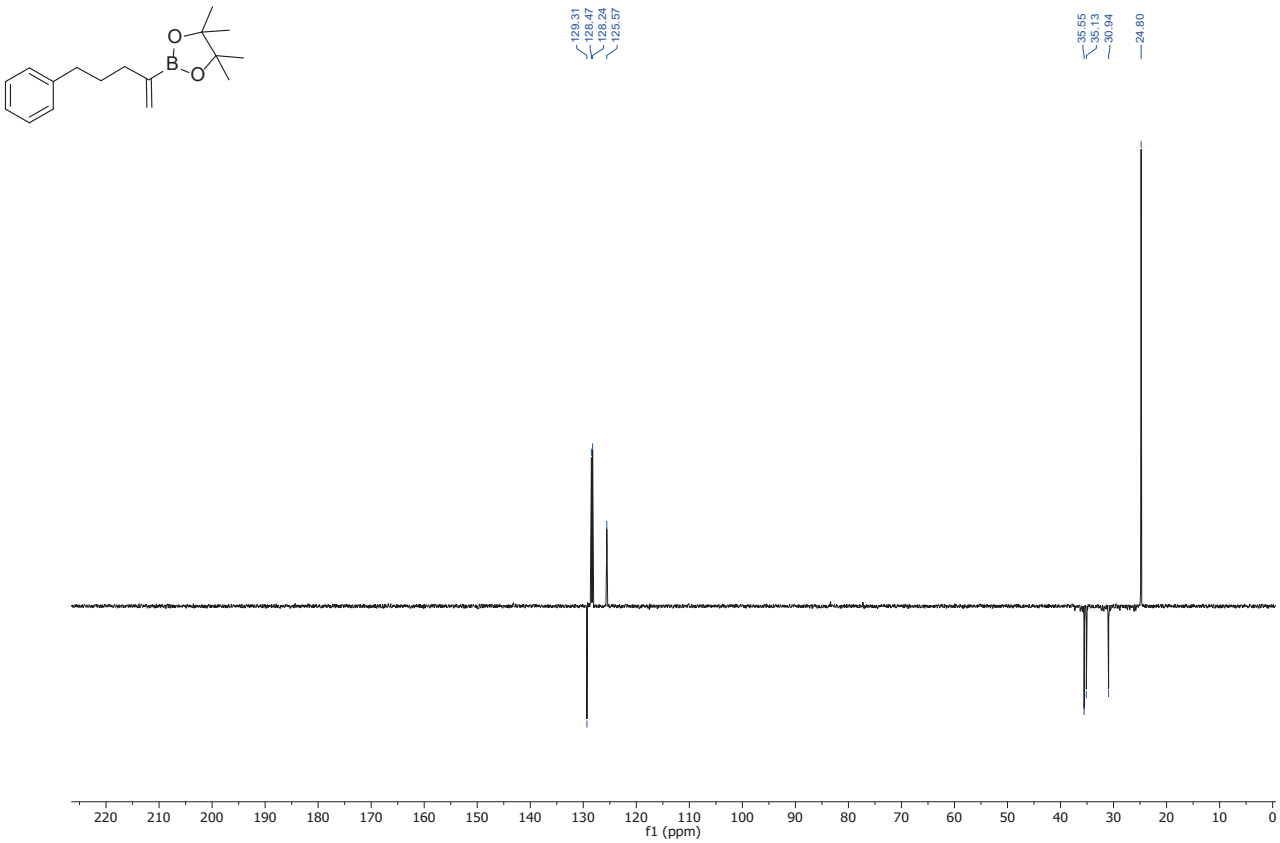


4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (98) ^{13}C NMR (75 MHz, $CDCl_3$)



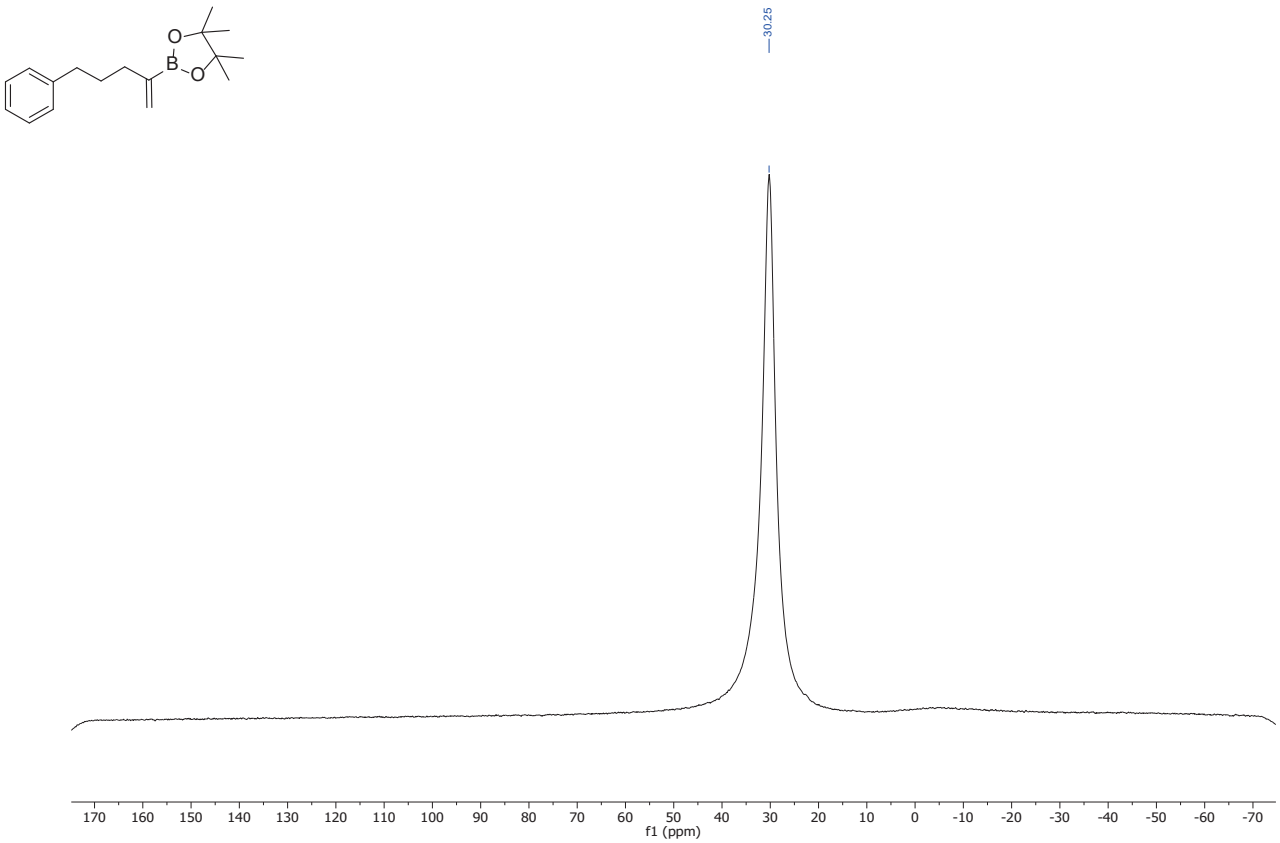
4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (98)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



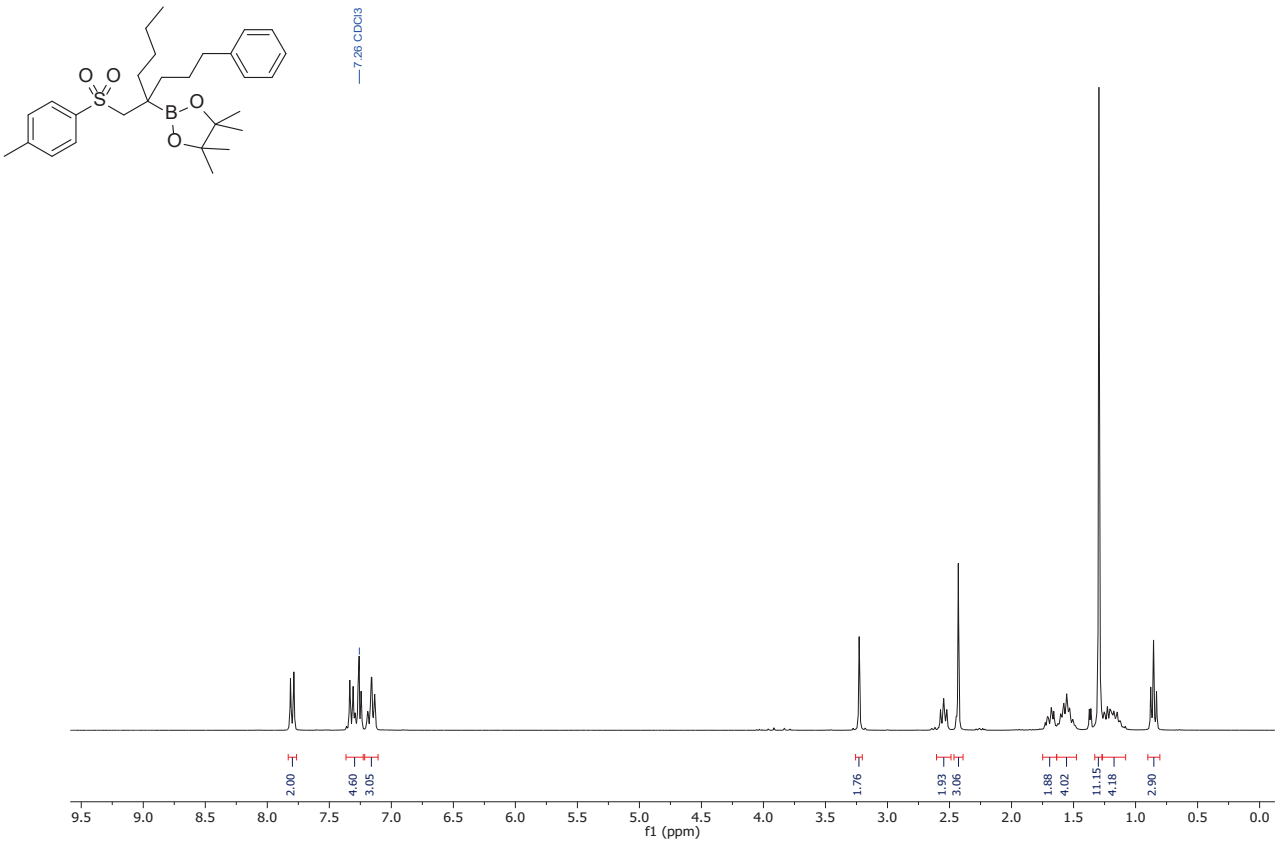
4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (98)

^{11}B NMR (96 MHz, $CDCl_3$)



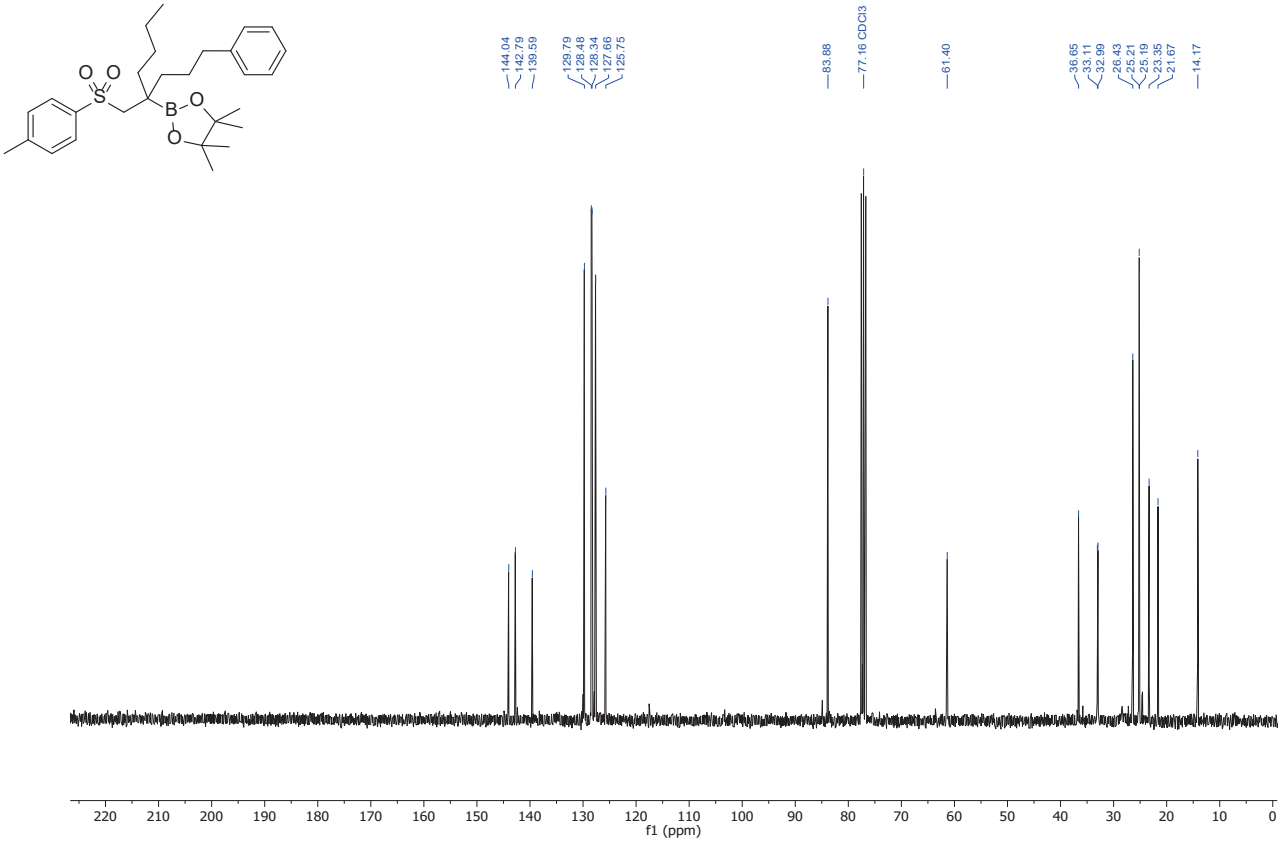
4,4,5,5-tetramethyl-2-(1-phenyl-4-(tosylmethyl)octan-4-yl)-1,3,2-dioxaborolane (25)

^{1}H NMR (300 MHz, $CDCl_3$)



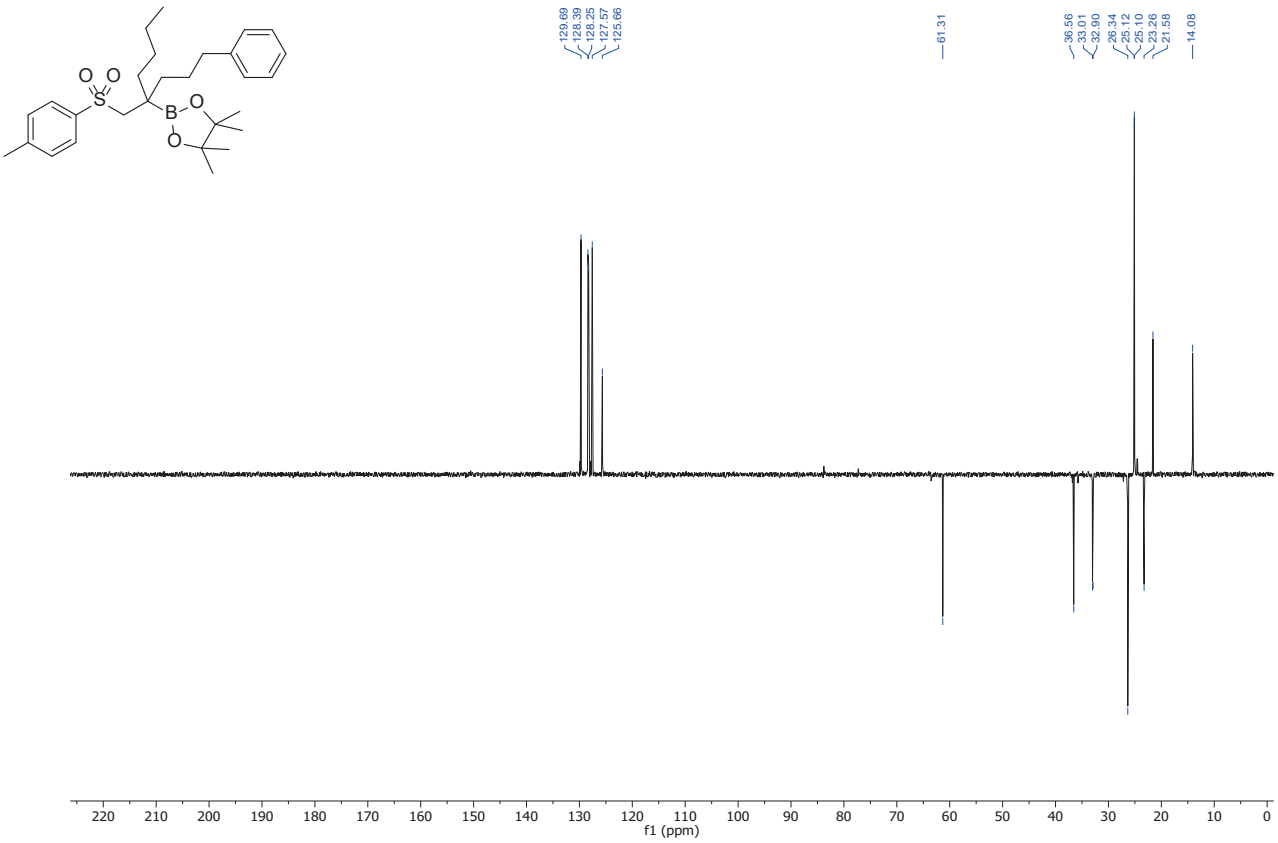
4,4,5,5-tetramethyl-2-(1-phenyl-4-(tosylmethyl)octan-4-yl)-1,3,2-dioxaborolane (25)

^{13}C NMR (75 MHz, $CDCl_3$)



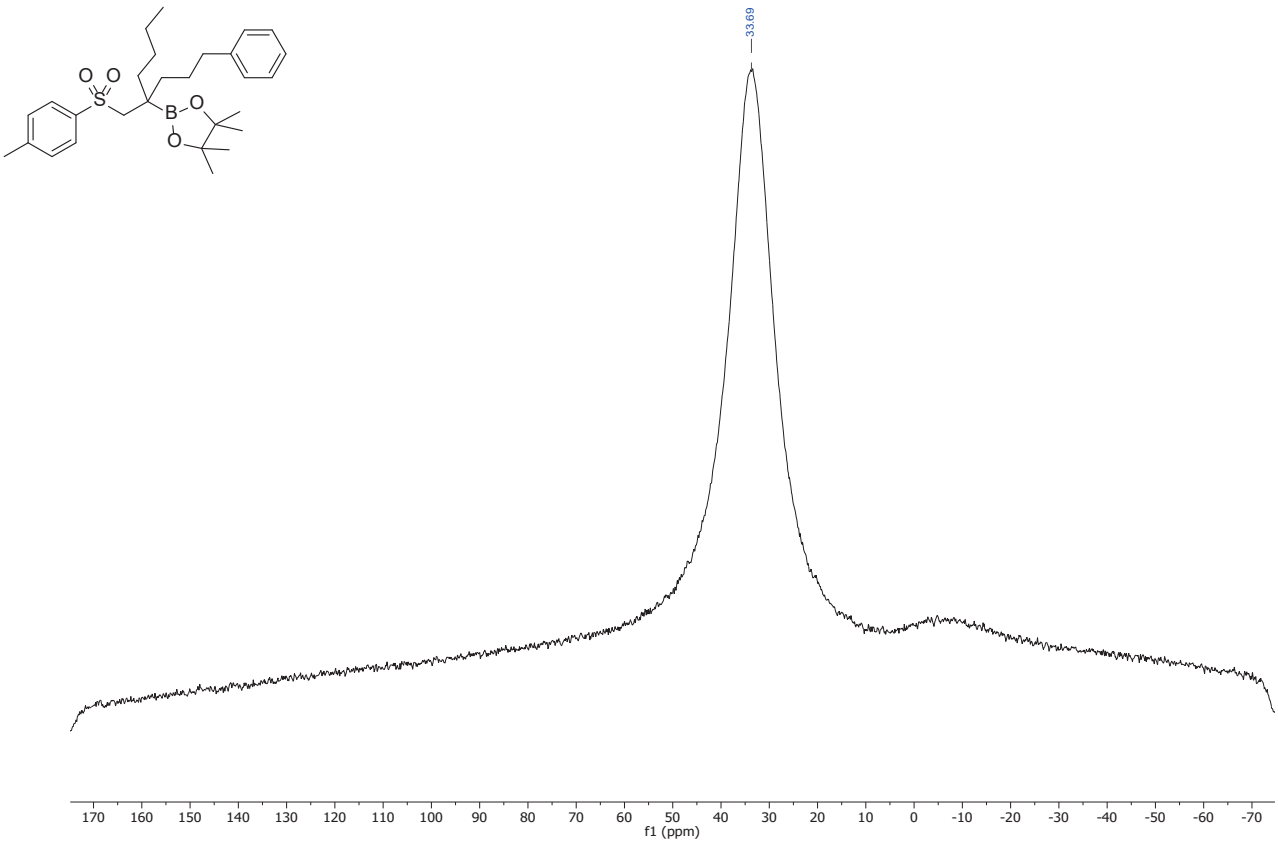
4,4,5,5-tetramethyl-2-(1-phenyl-4-(tosylmethyl)octan-4-yl)-1,3,2-dioxaborolane (25)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



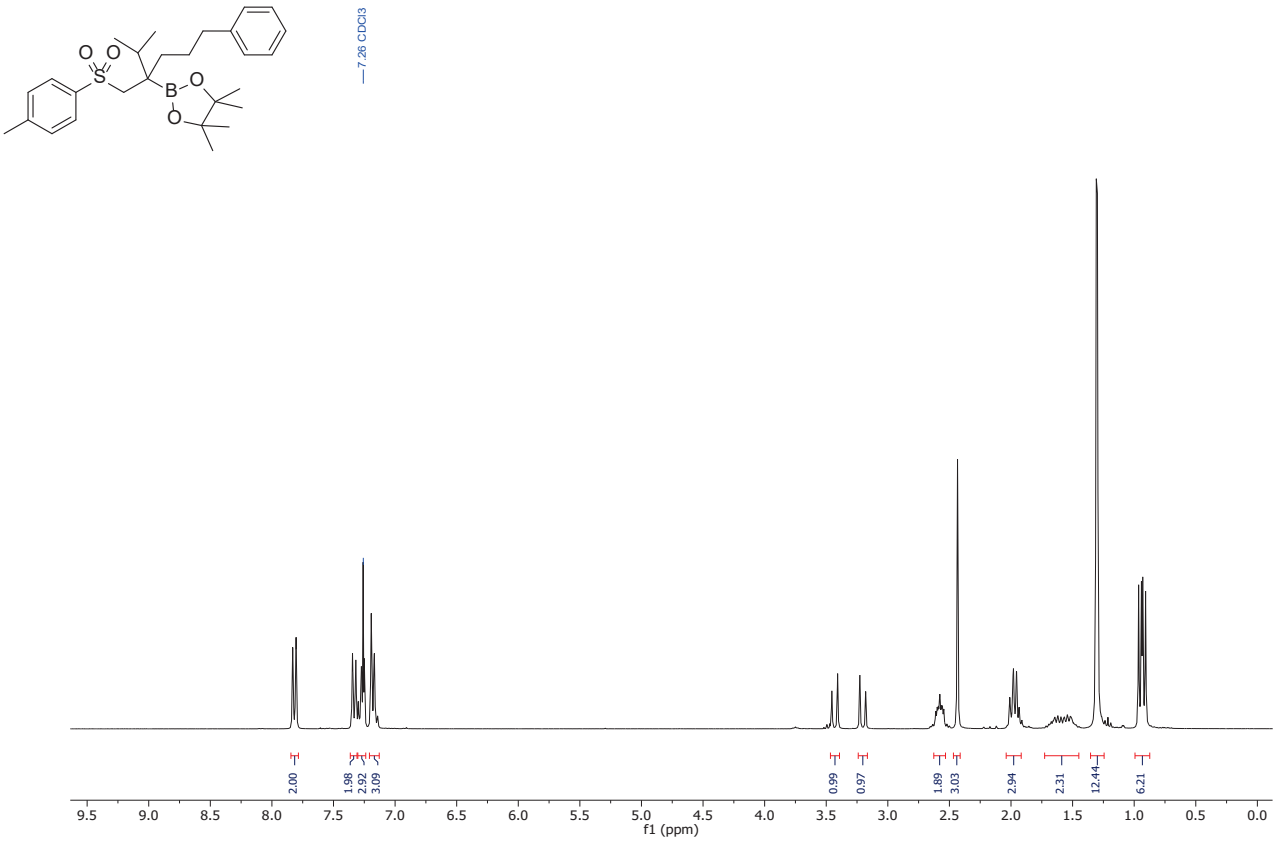
4,4,5,5-tetramethyl-2-(1-phenyl-4-(tosylmethyl)octan-4-yl)-1,3,2-dioxaborolane (25)

^{11}B NMR (96 MHz, $CDCl_3$)



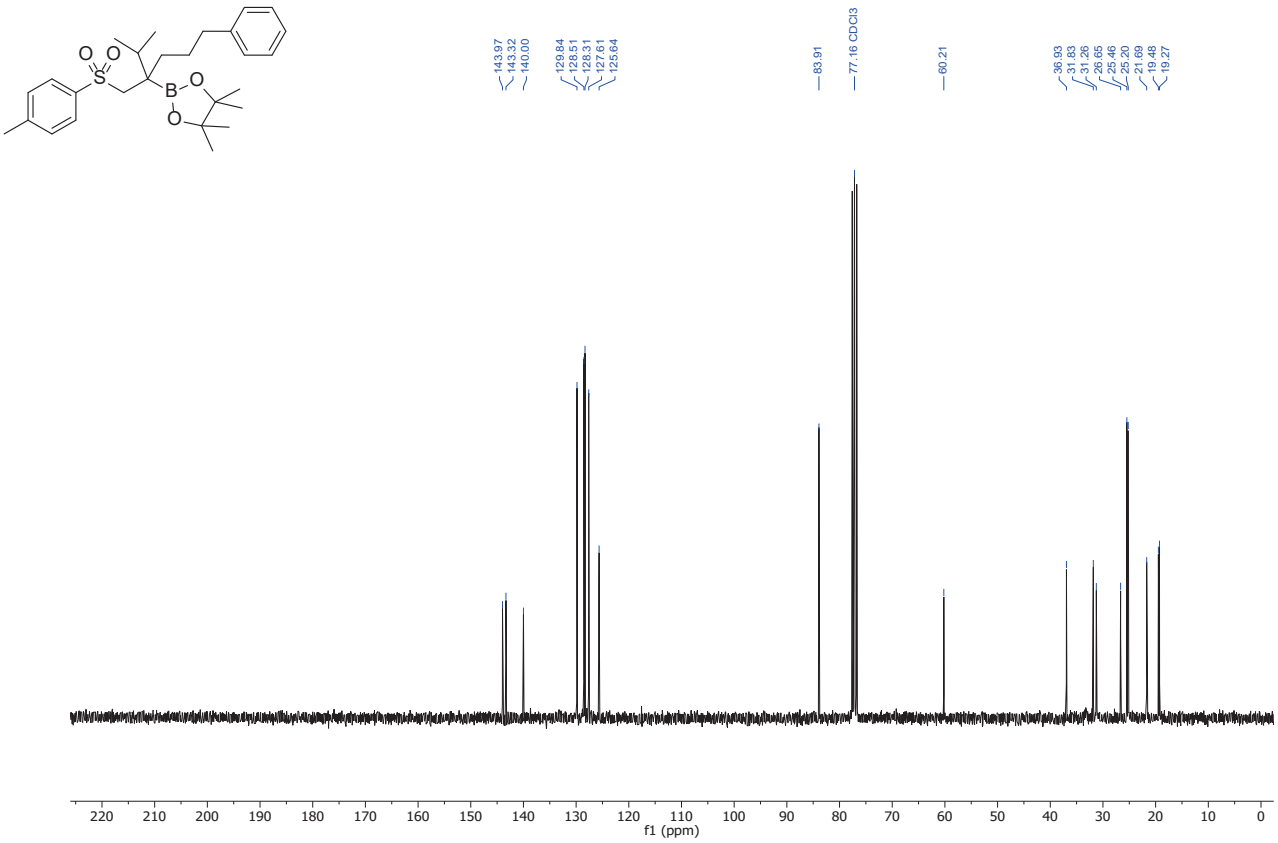
4,4,5,5-tetramethyl-2-(2-methyl-6-phenyl-3-(tosylmethyl)hexan-3-yl)-1,3,2-dioxaborolane (28)

^{1}H NMR (300 MHz, $CDCl_3$)



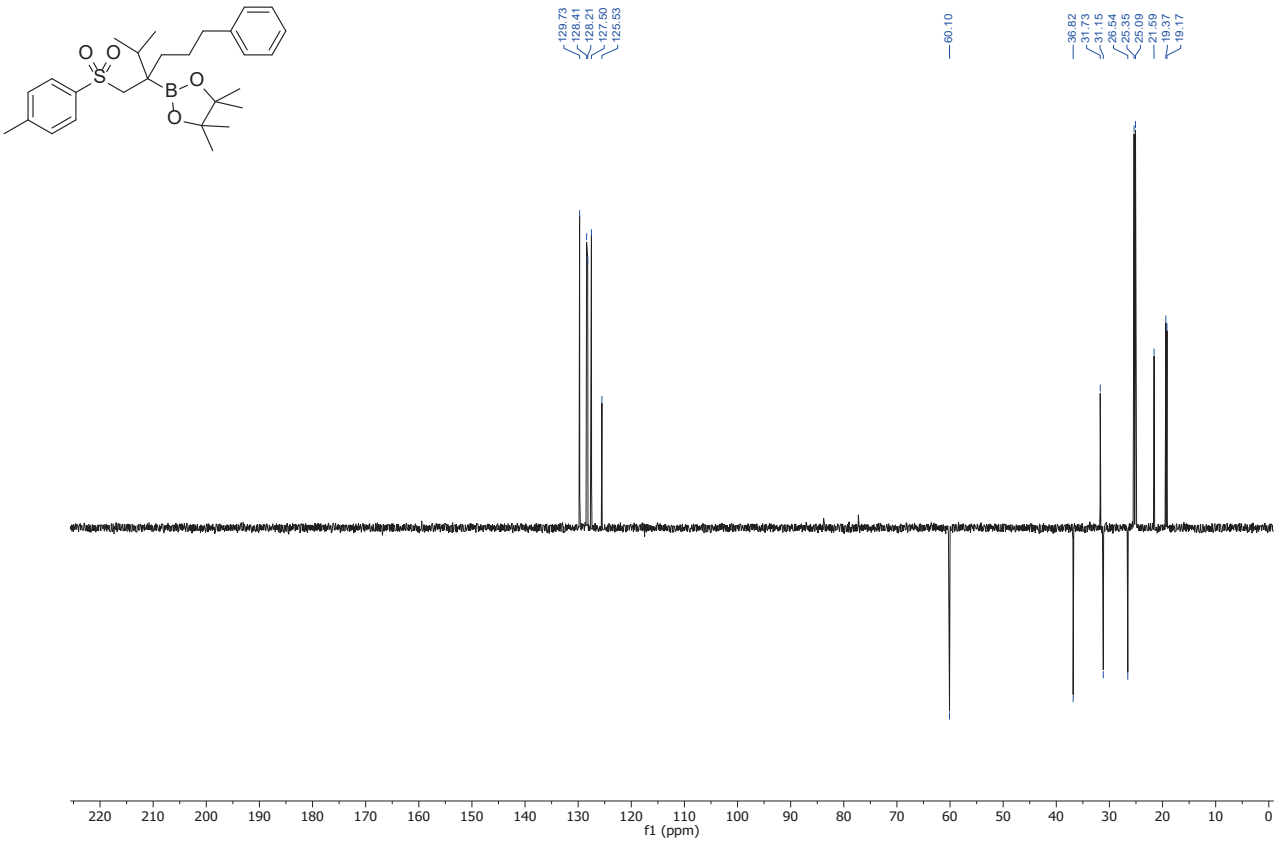
4,4,5,5-tetramethyl-2-(2-methyl-6-phenyl-3-(tosylmethyl)hexan-3-yl)-1,3,2-dioxaborolane (28)

^{13}C NMR (75 MHz, $CDCl_3$)



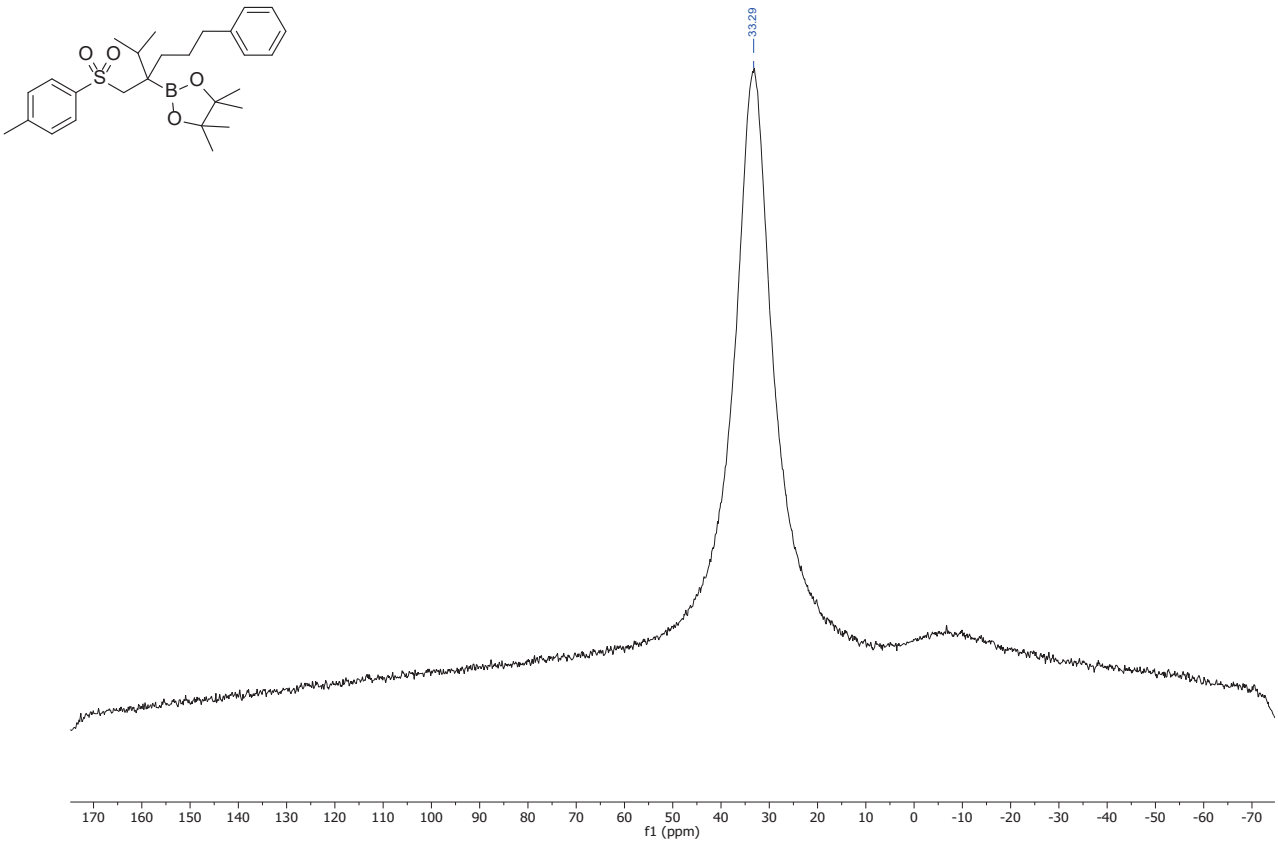
4,4,5,5-tetramethyl-2-(2-methyl-6-phenyl-3-(tosylmethyl)hexan-3-yl)-1,3,2-dioxaborolane (28)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



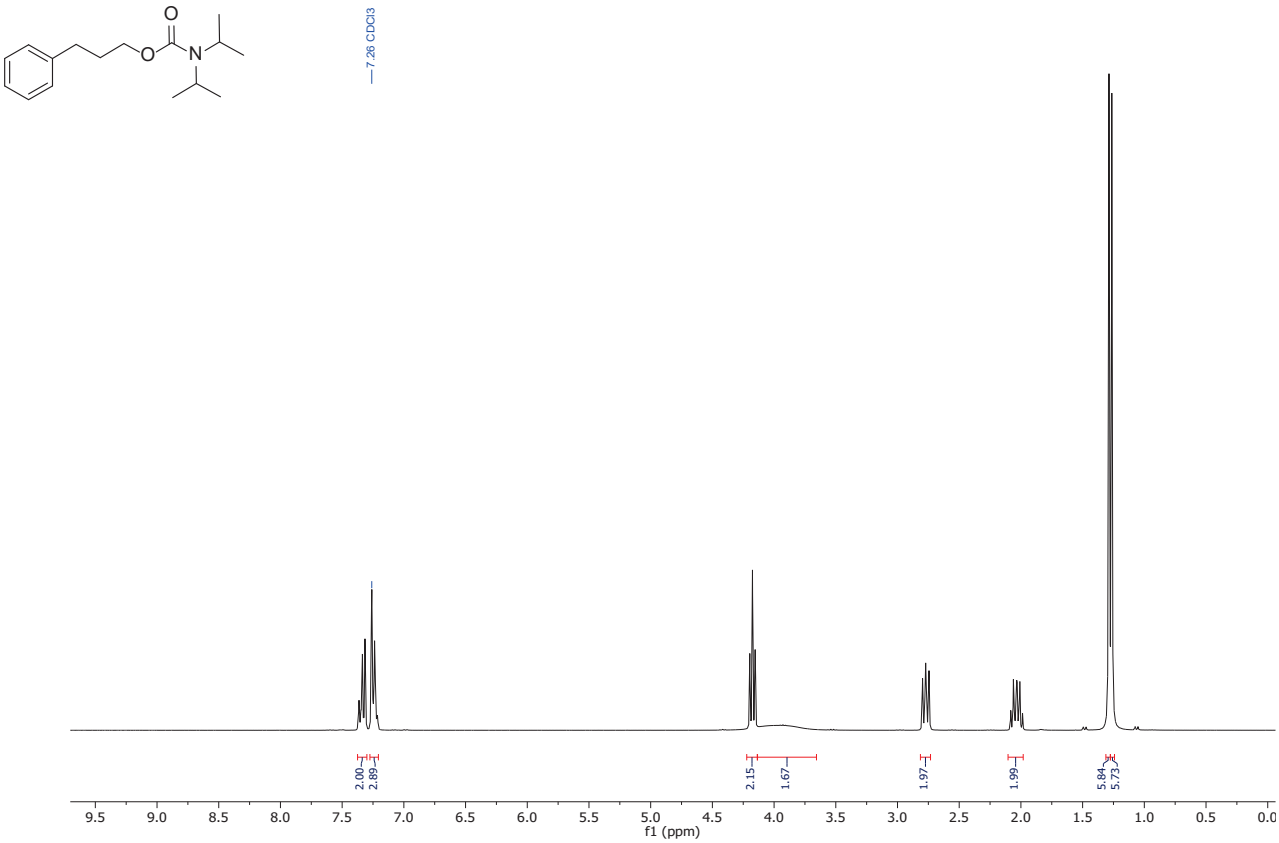
4,4,5,5-tetramethyl-2-(2-methyl-6-phenyl-3-(tosylmethyl)hexan-3-yl)-1,3,2-dioxaborolane (28)

^{11}B NMR (96 MHz, $CDCl_3$)



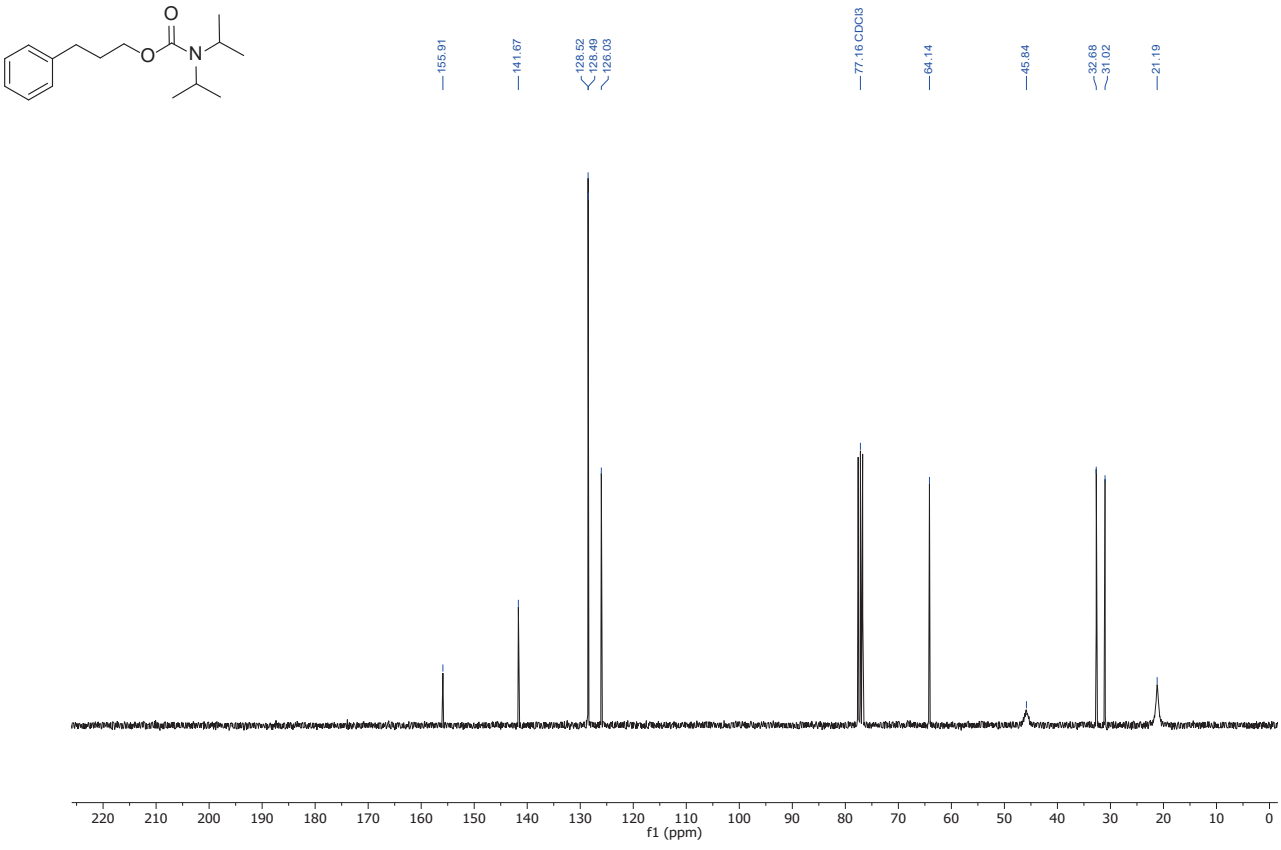
3-phenylpropyl diisopropylcarbamate (91)

^{1}H NMR (300 MHz, $CDCl_3$)

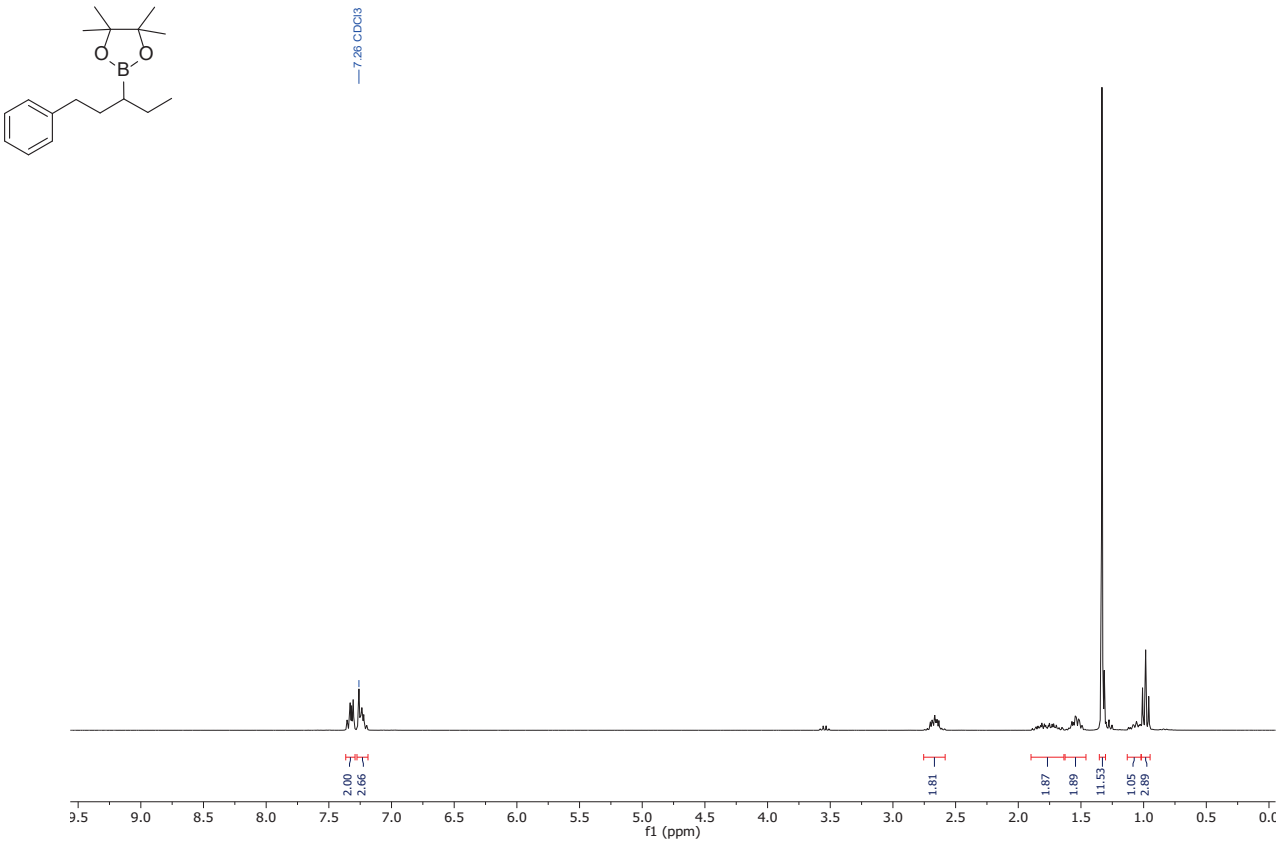


3-phenylpropyl diisopropylcarbamate (91)

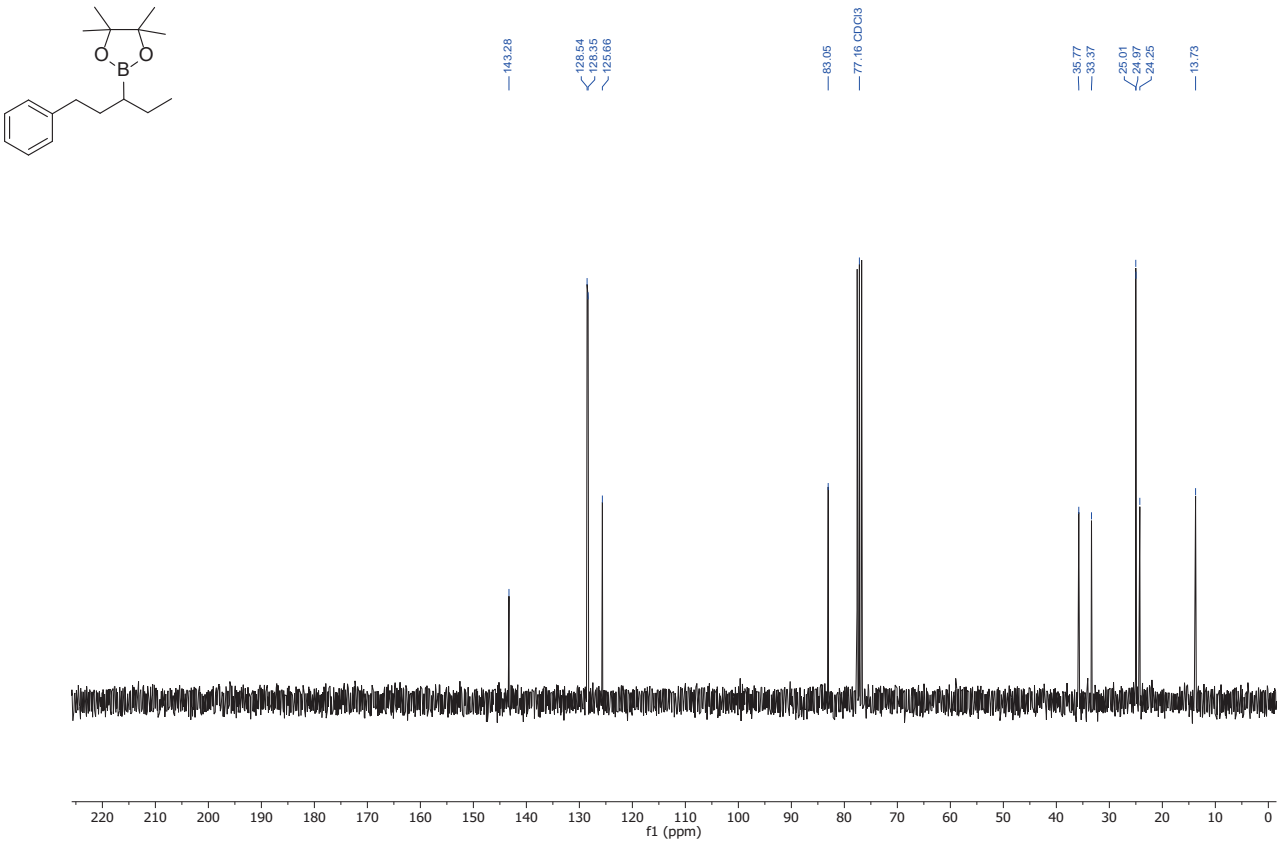
^{13}C NMR (75 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (99) ^{1}H NMR (300 MHz, $CDCl_3$)

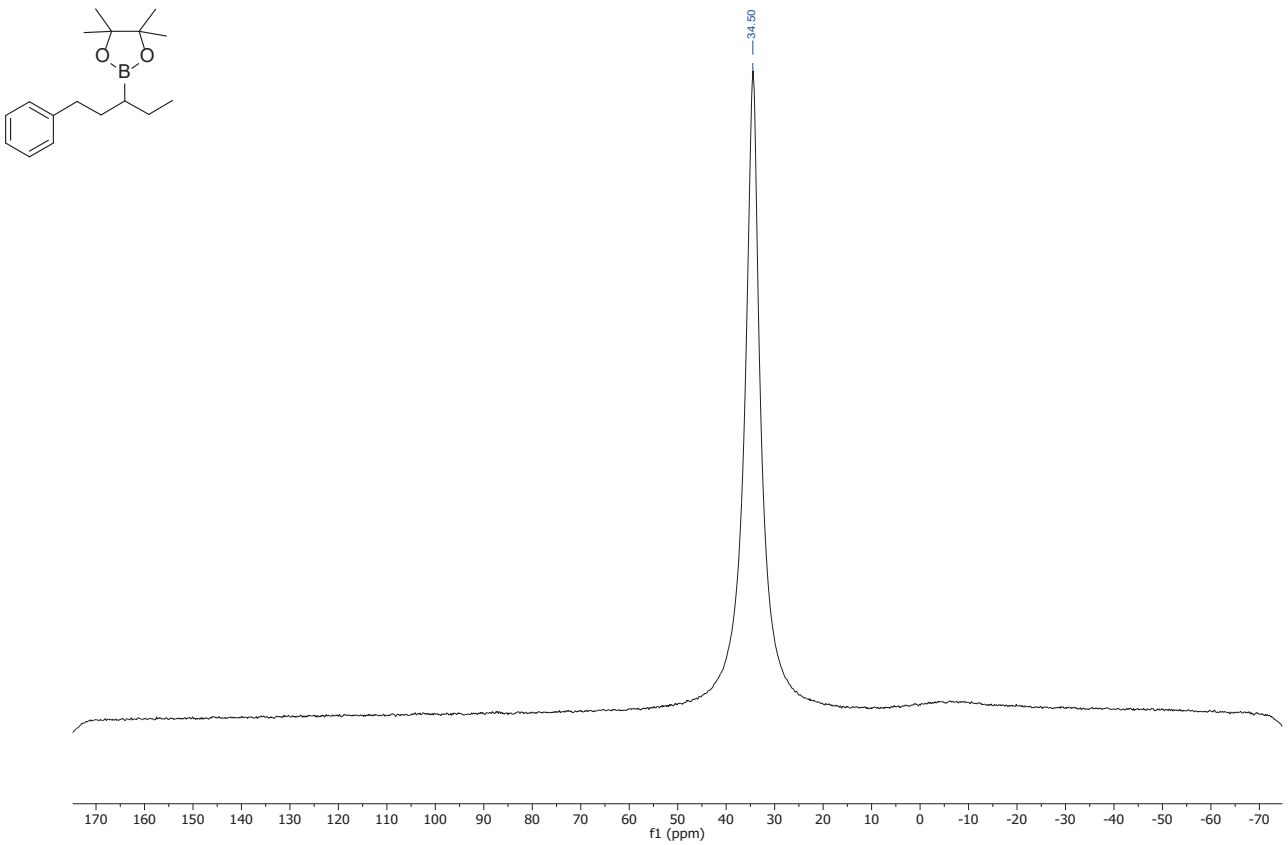


4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (99) ^{13}C NMR (75 MHz, $CDCl_3$)



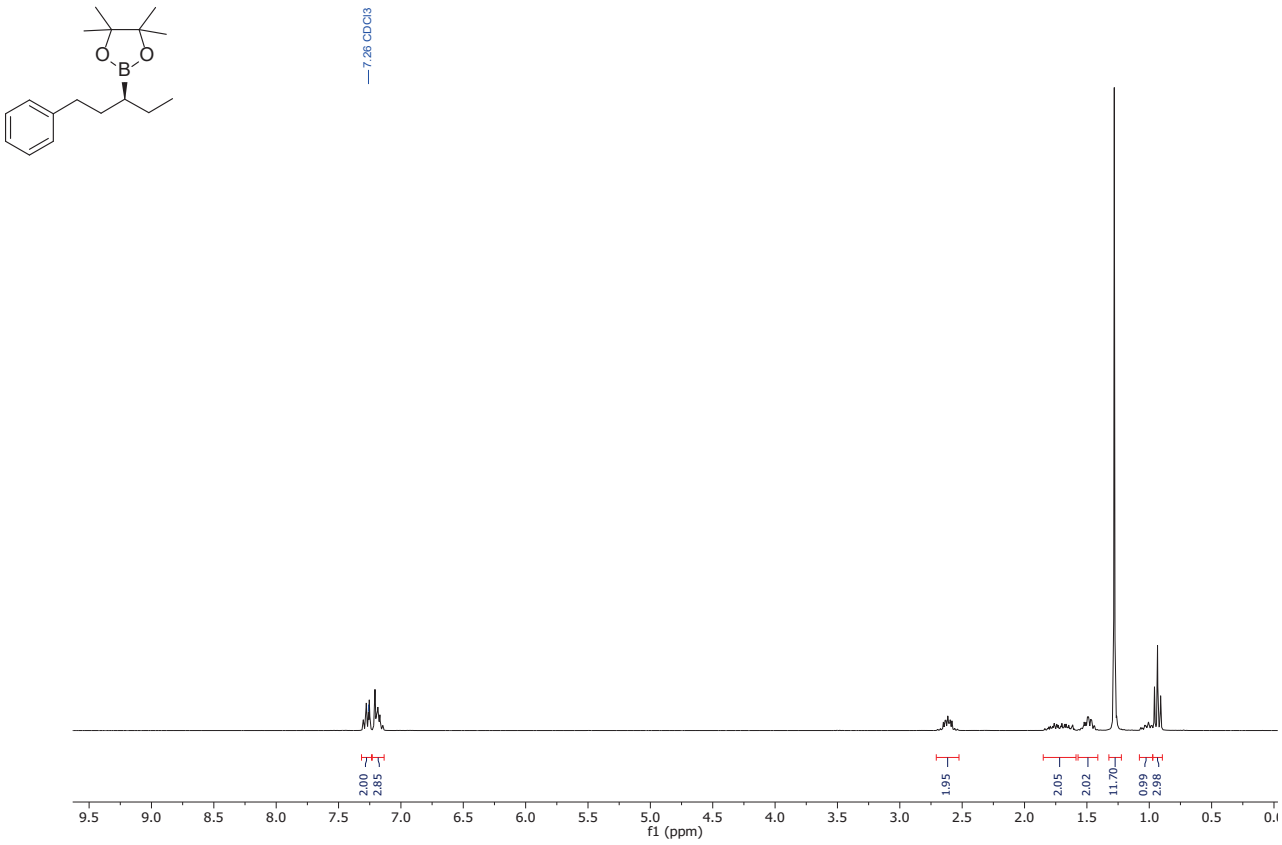
4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (99)

^{11}B NMR (96 MHz, $CDCl_3$)

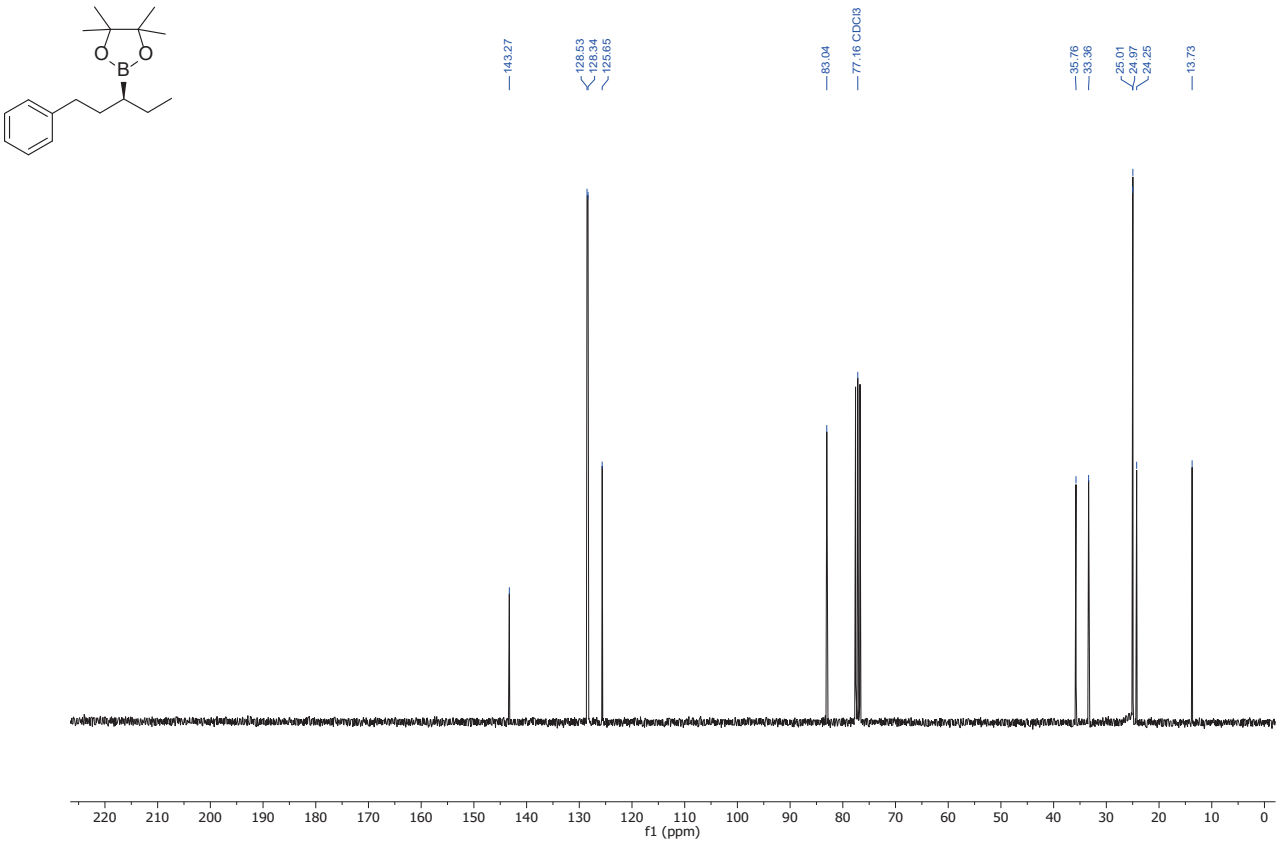


(S)-4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (92)

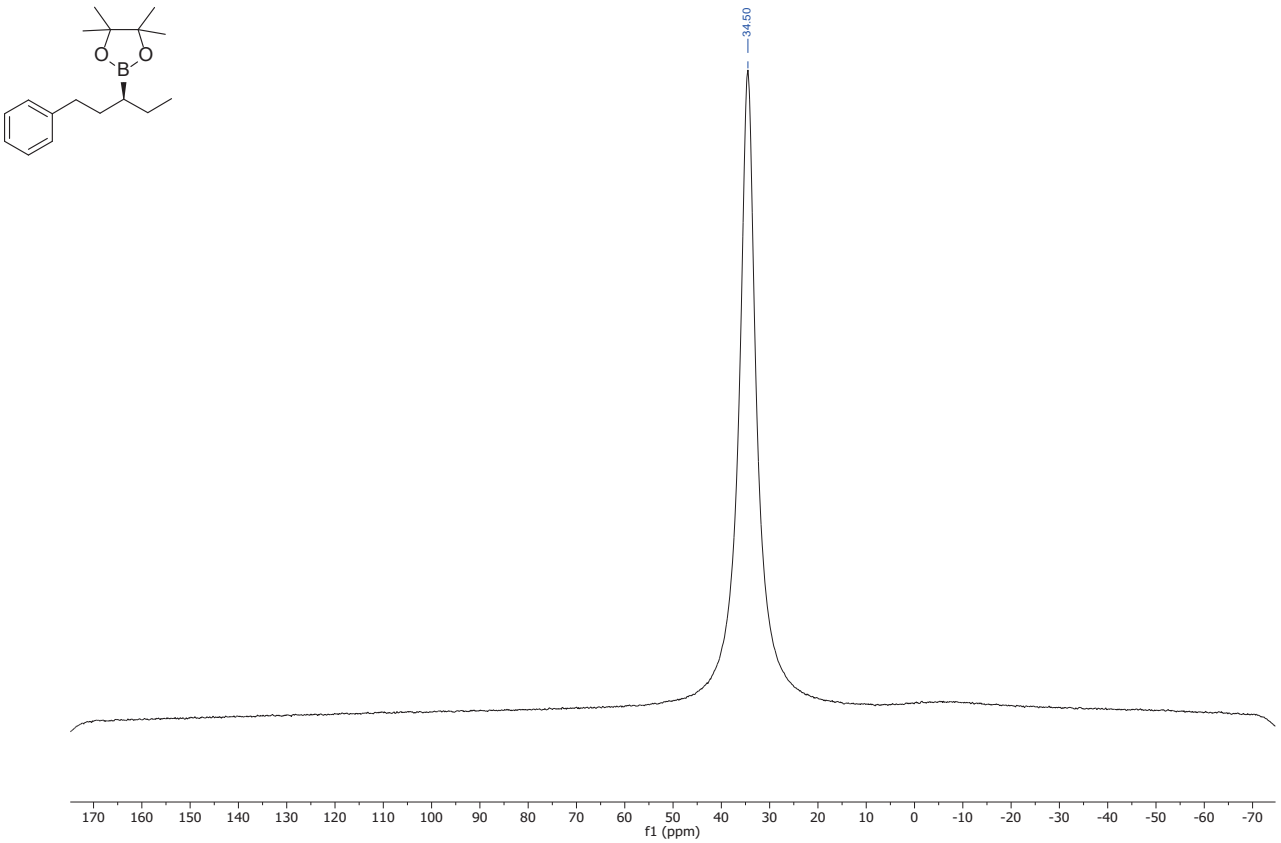
^{1}H NMR (300 MHz, $CDCl_3$)



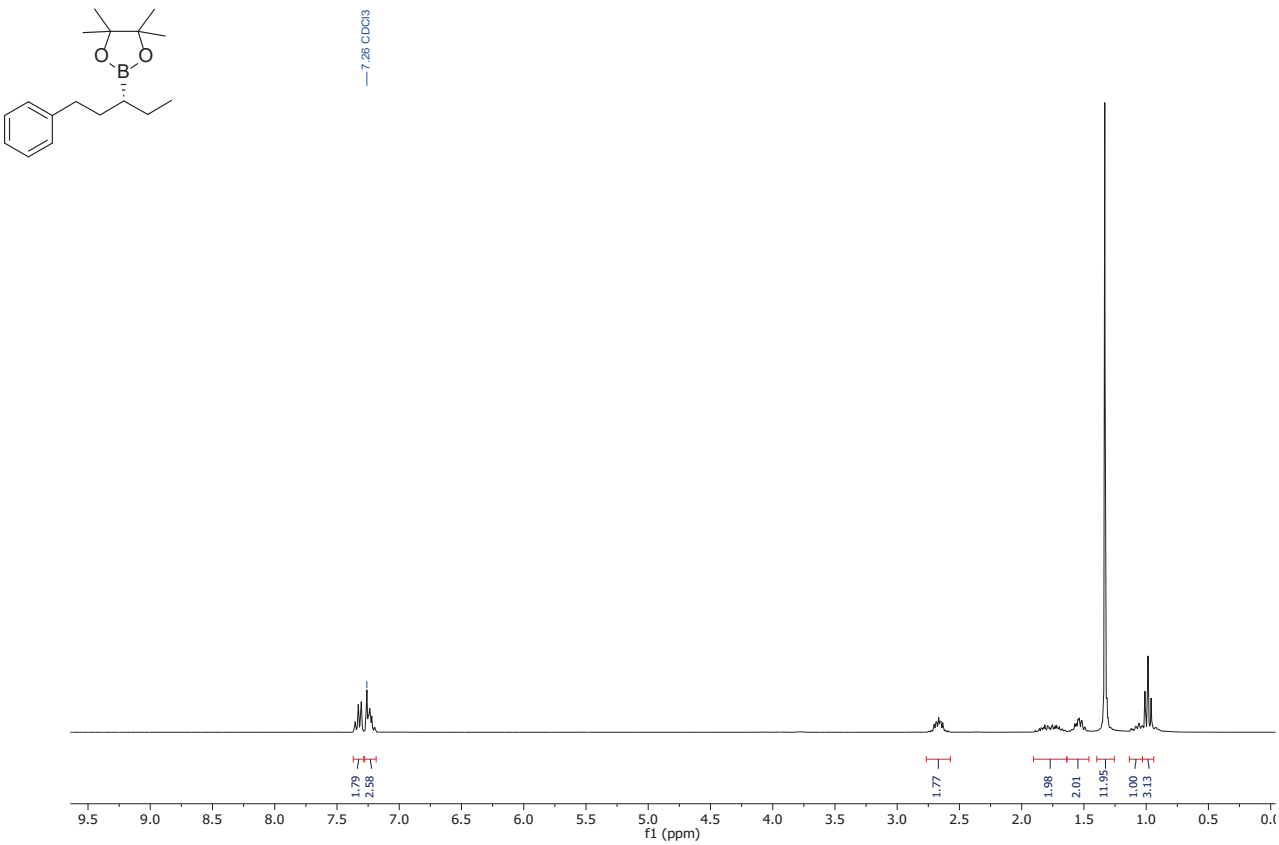
(S)-4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (92) ^{13}C NMR (75 MHz, $CDCl_3$)



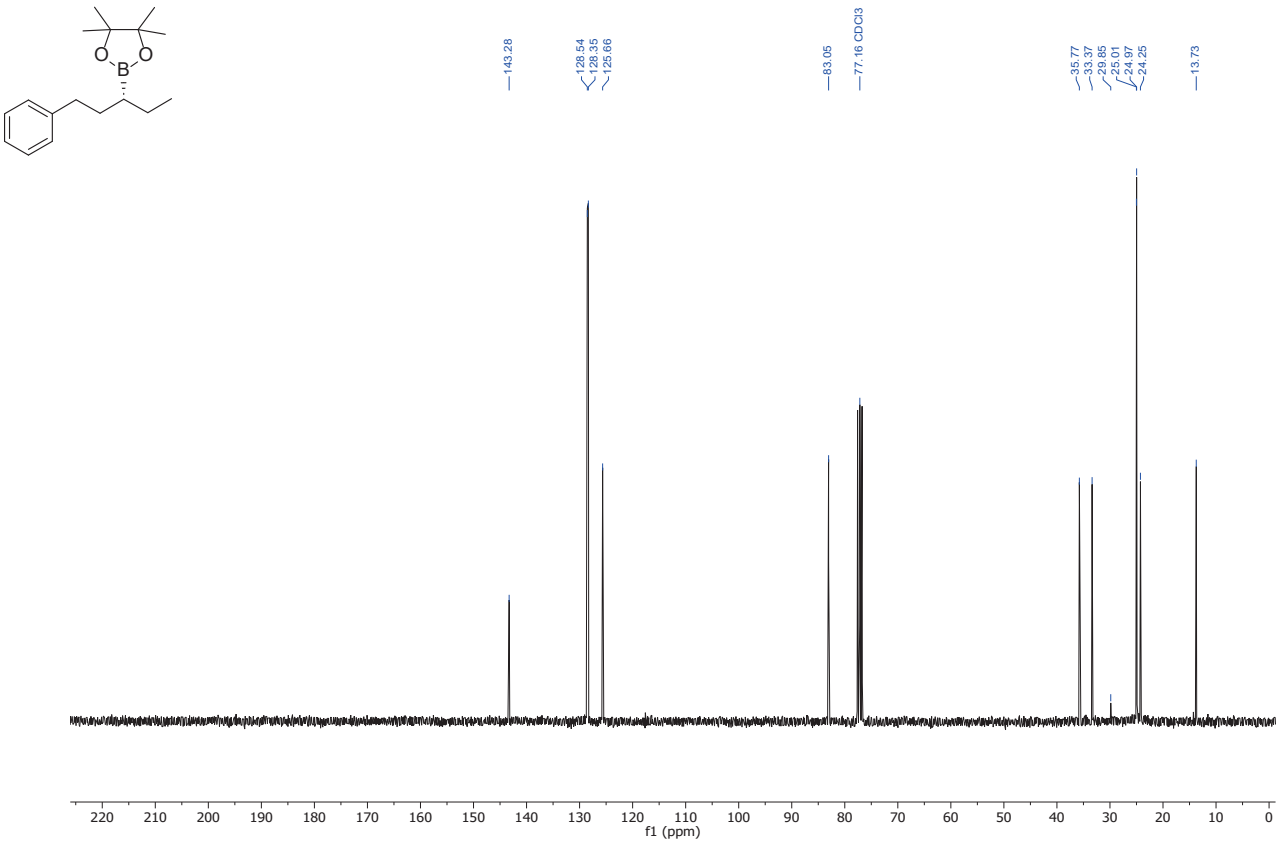
(S)-4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (92) ^{11}B NMR (96 MHz, $CDCl_3$)



(R)-4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (100) ^{1}H NMR (300 MHz, $CDCl_3$)

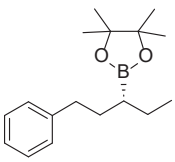


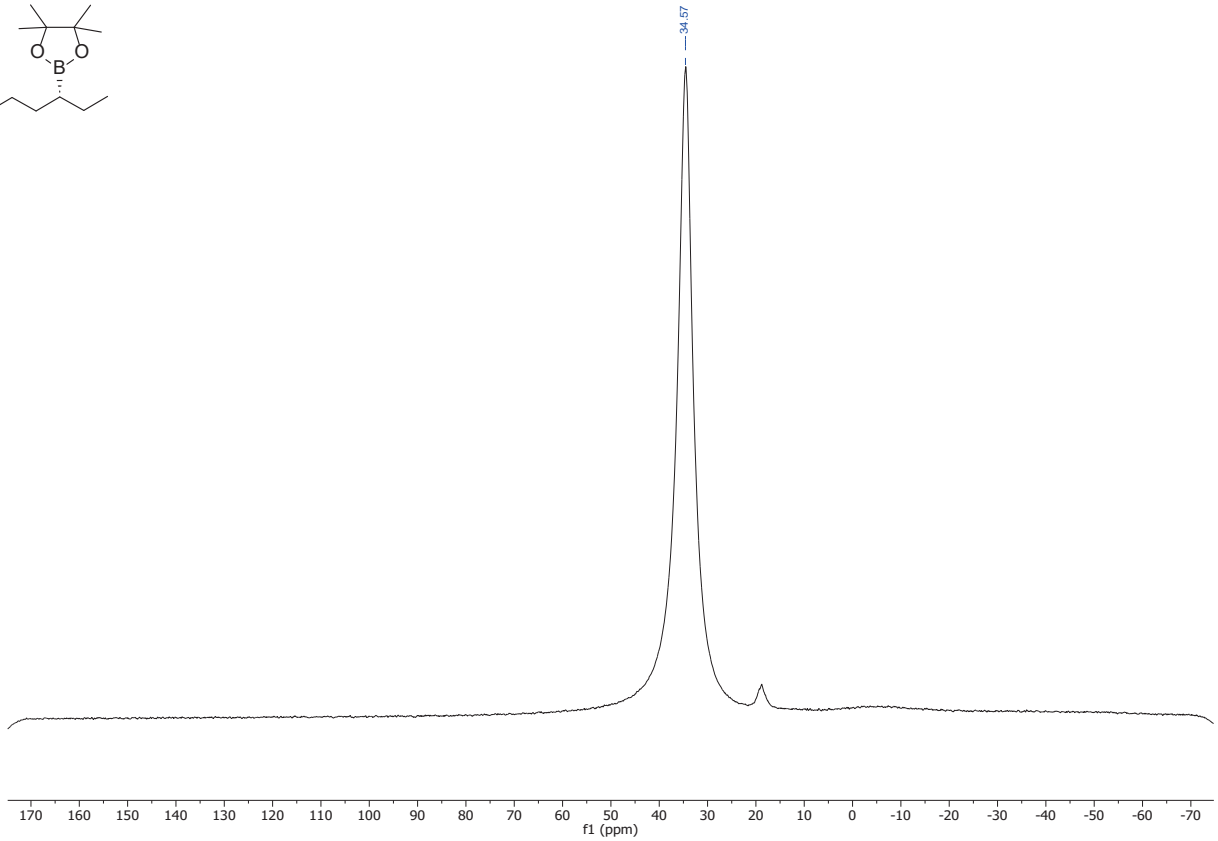
(R)-4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (100) ^{13}C NMR (75 MHz, $CDCl_3$)



(R)-4,4,5,5-tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (100)

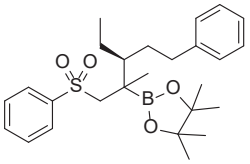
^{11}B NMR (96 MHz, $CDCl_3$)

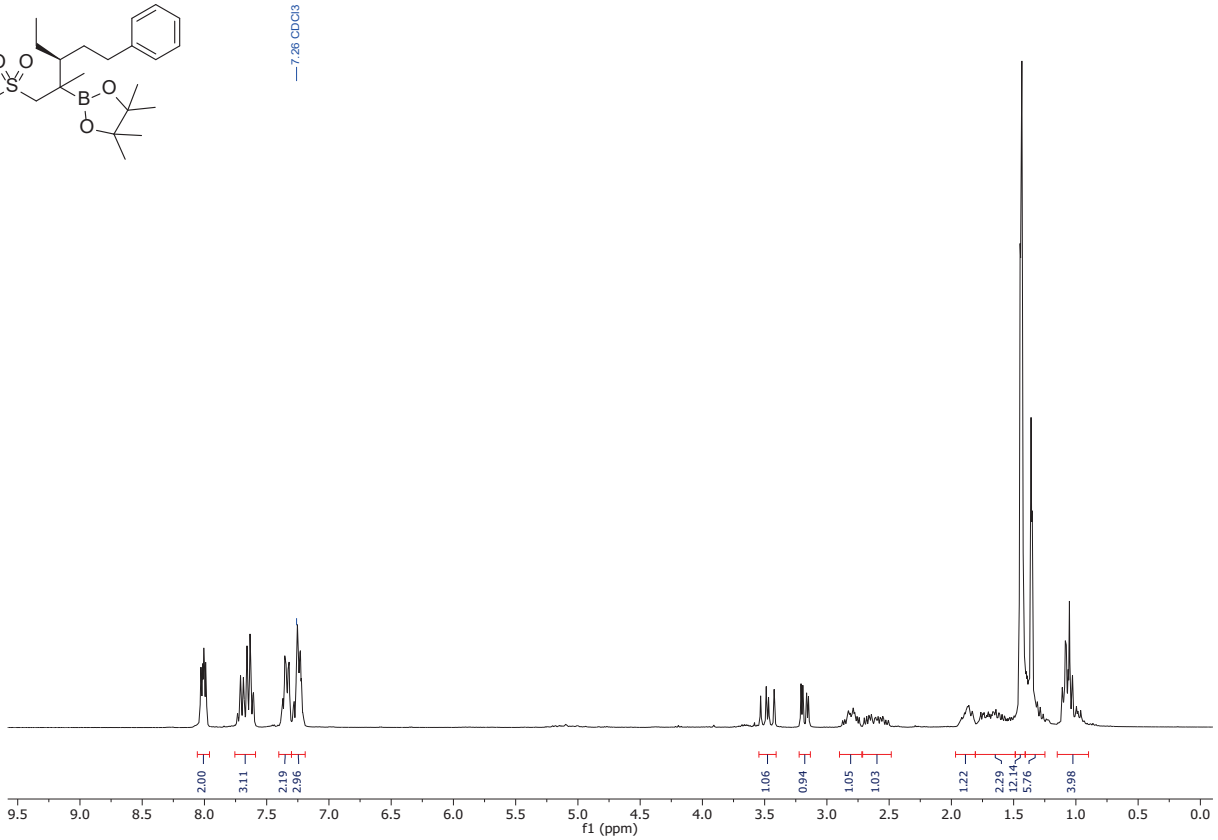




2-((3S)-3-ethyl-2-methyl-5-phenyl-1-(phenylsulfonyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (35)

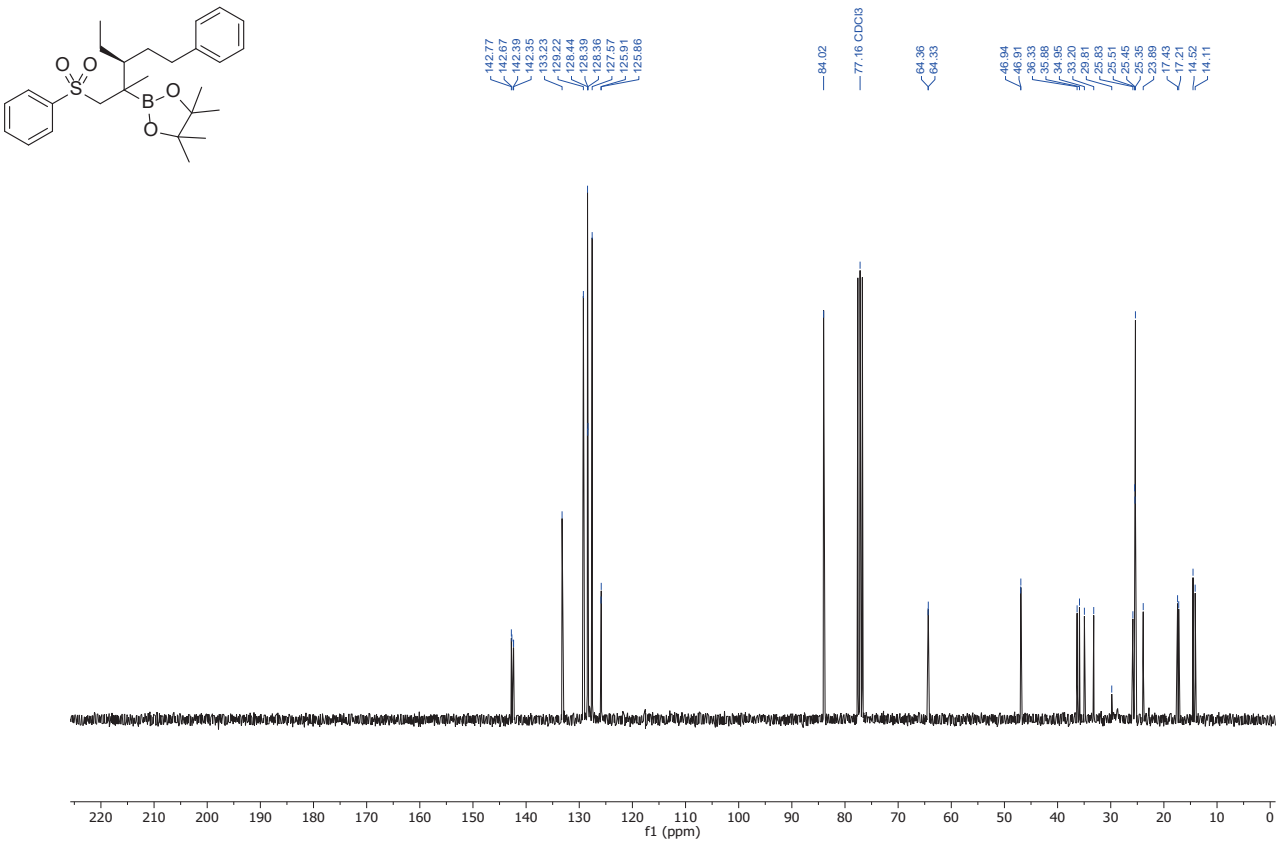
^{1}H NMR (300 MHz, $CDCl_3$)





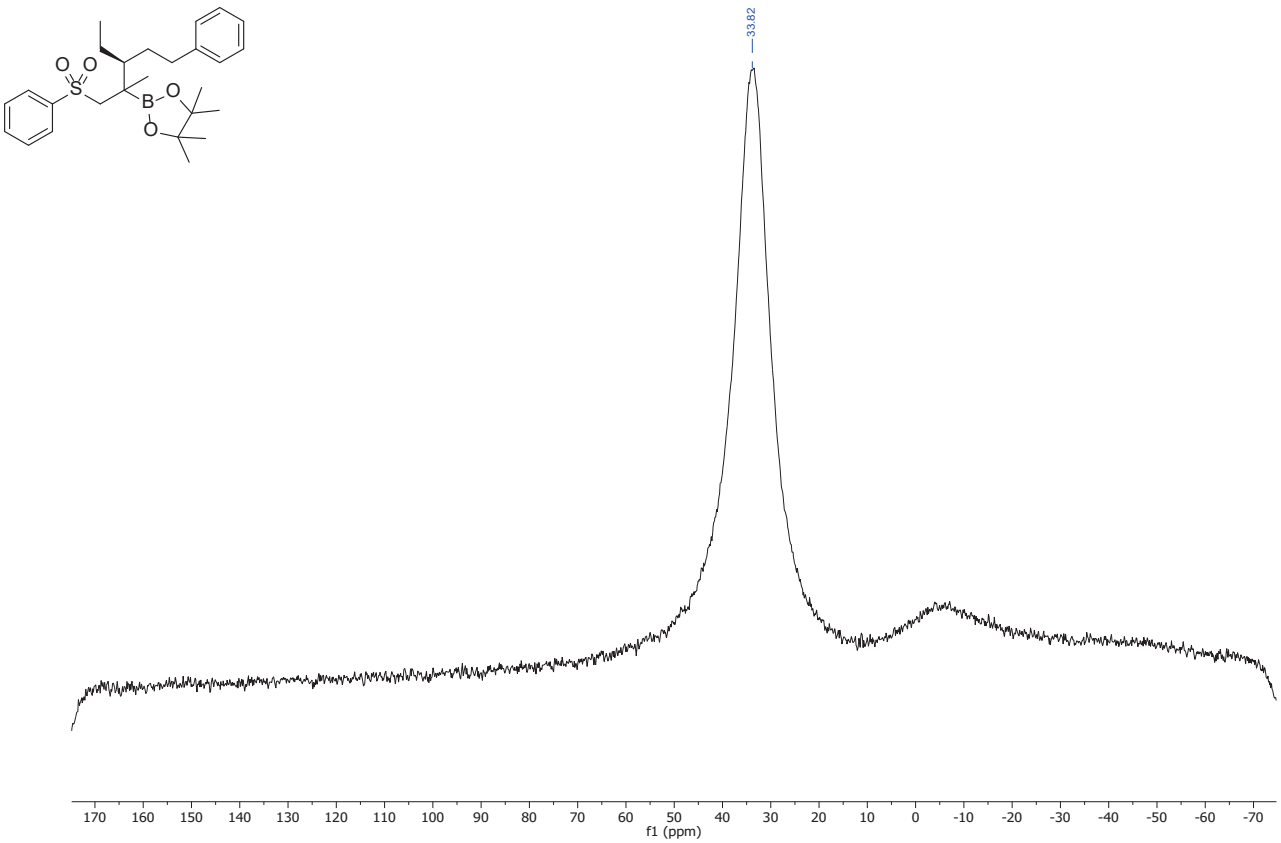
2-((3S)-3-ethyl-2-methyl-5-phenyl-1-(phenylsulfonyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (35)

^{13}C NMR (75 MHz, $CDCl_3$)



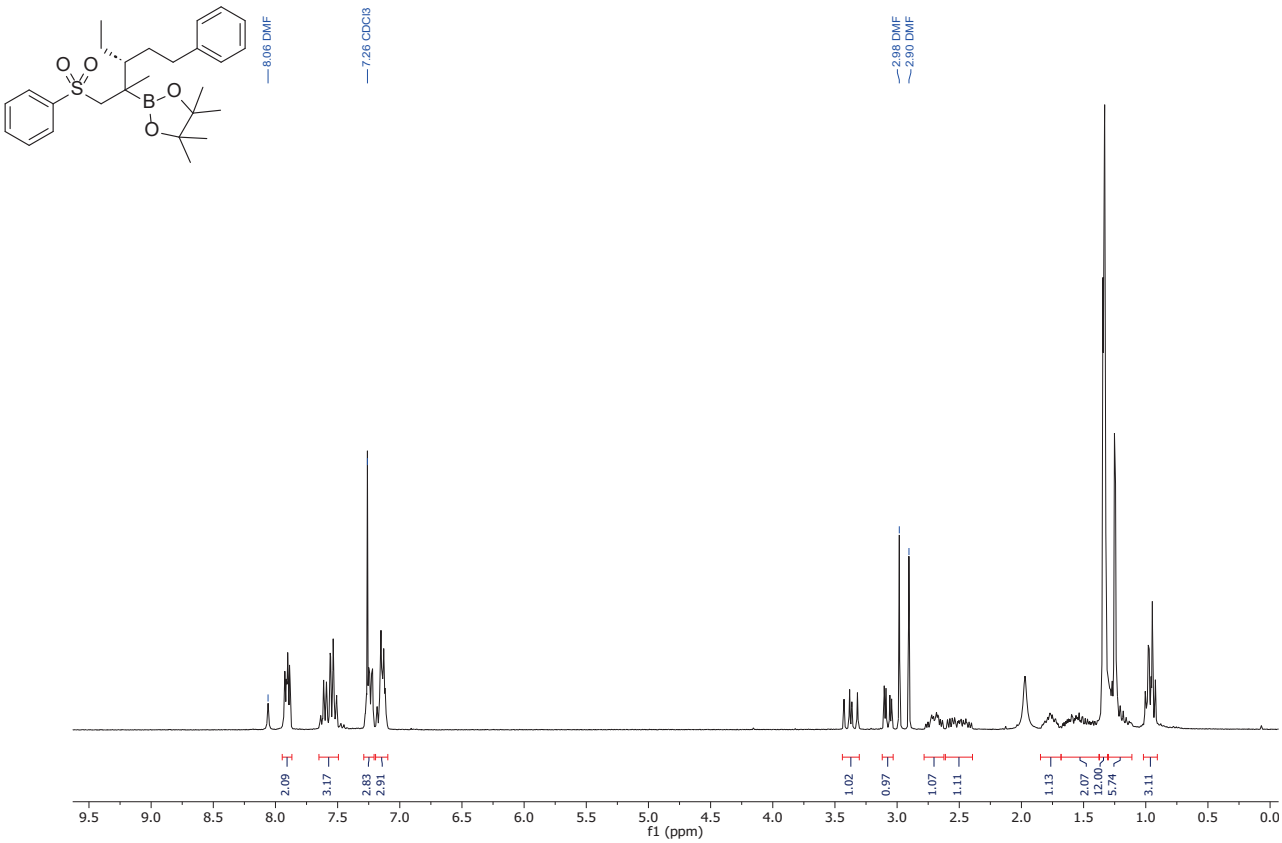
2-((3S)-3-ethyl-2-methyl-5-phenyl-1-(phenylsulfonyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (35)

^{11}B NMR (96 MHz, $CDCl_3$)



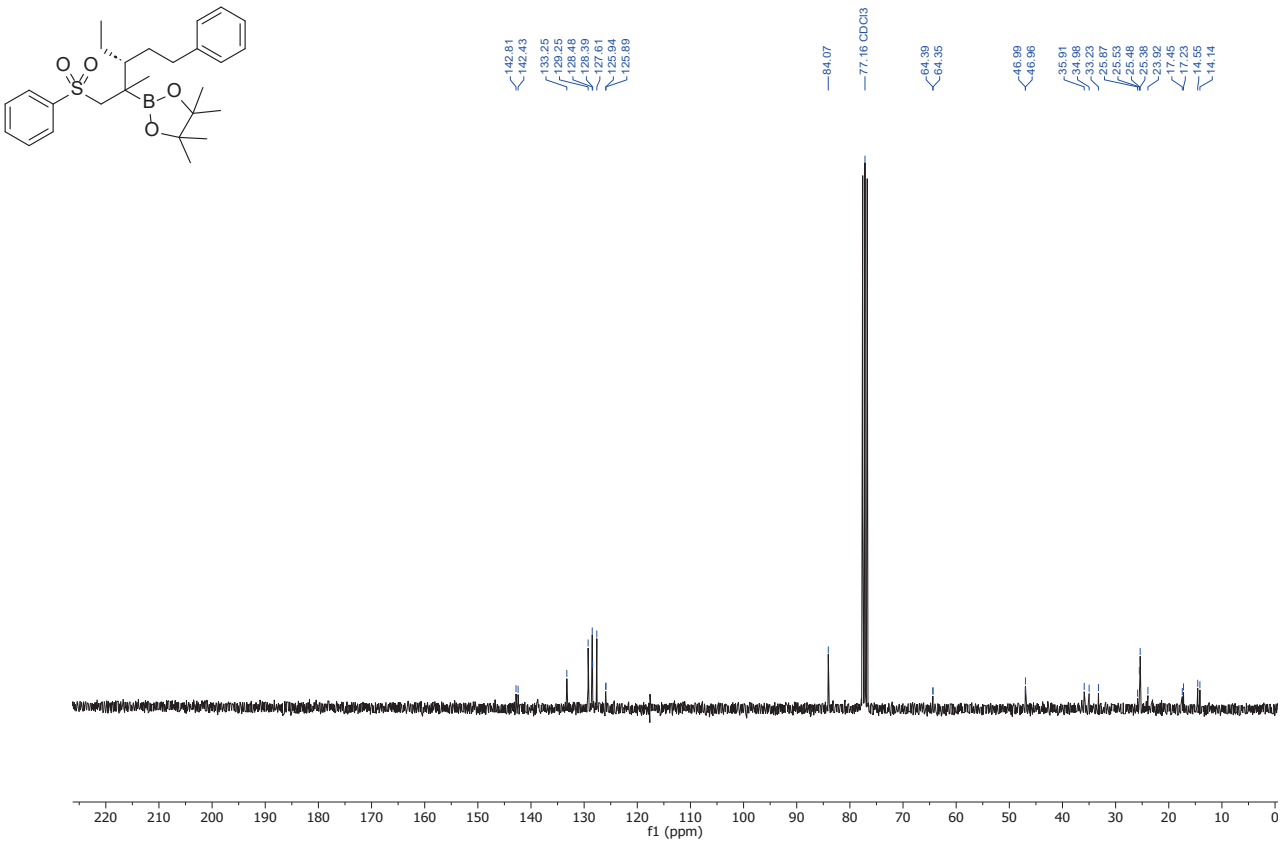
2-((3R)-3-ethyl-2-methyl-5-phenyl-1-(phenylsulfonyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36)

^{1}H NMR (300 MHz, $CDCl_3$)



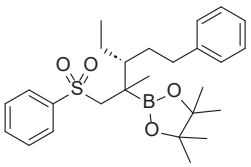
2-((3R)-3-ethyl-2-methyl-5-phenyl-1-(phenylsulfonyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36)

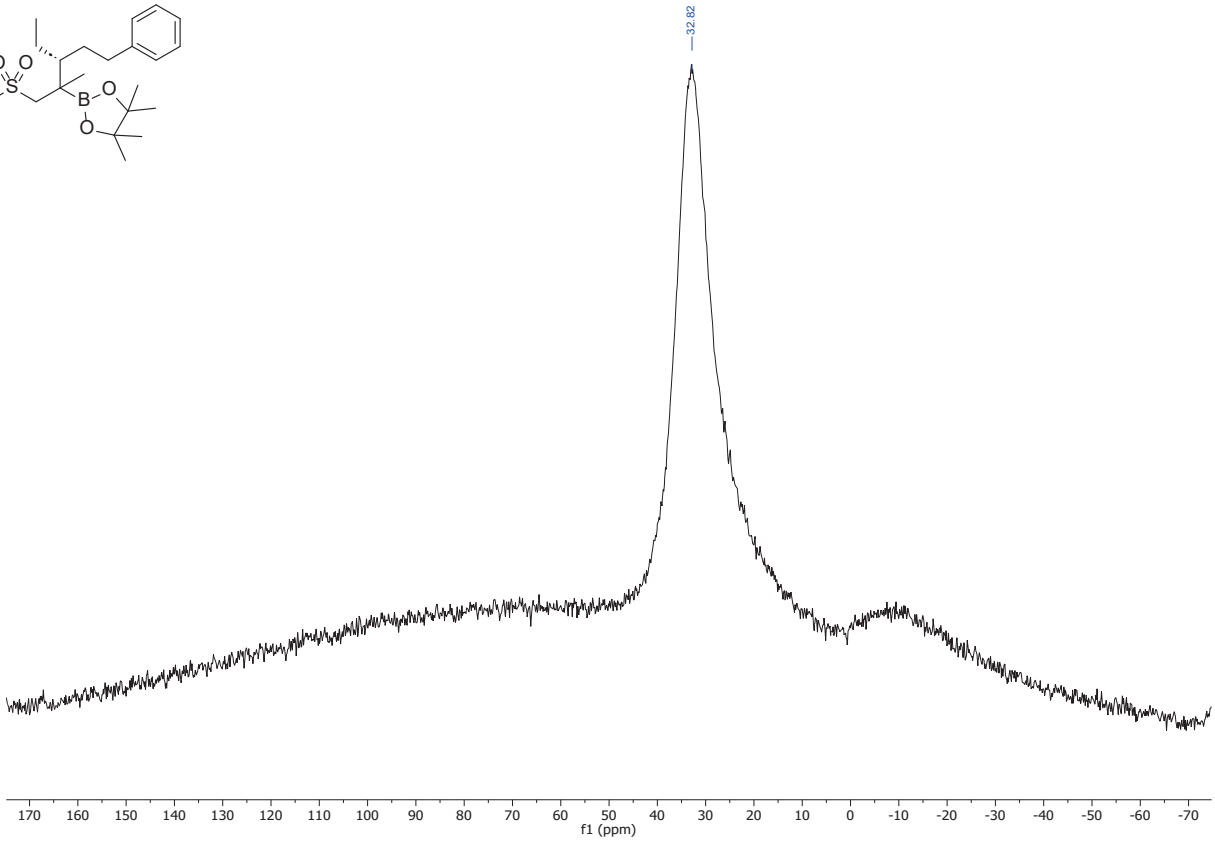
^{13}C NMR (75 MHz, $CDCl_3$)



2-((3R)-3-ethyl-2-methyl-5-phenyl-1-(phenylsulfonyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36)

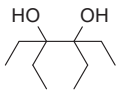
^{11}B NMR (96 MHz, $CDCl_3$)

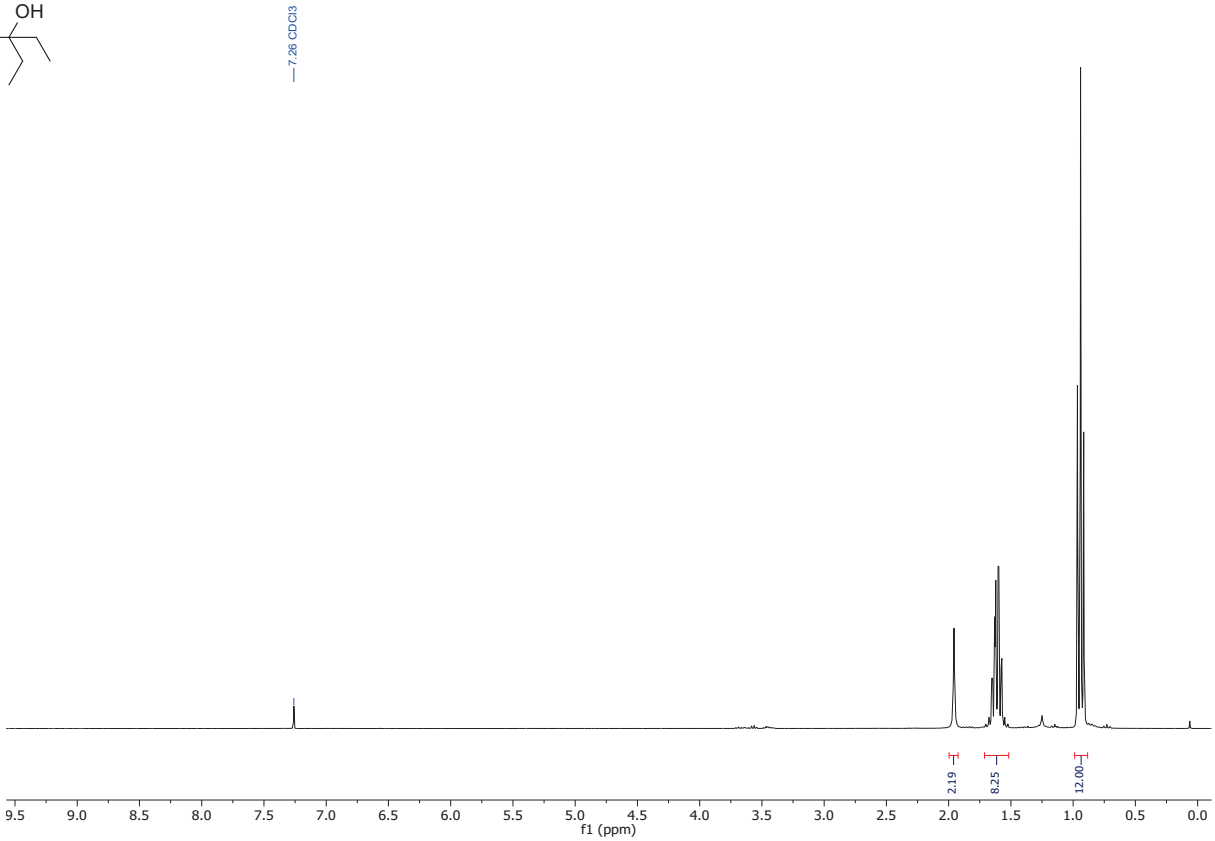




3,4-diethylhexane-3,4-diol (101)

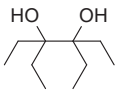
^{1}H NMR (300 MHz, $CDCl_3$)

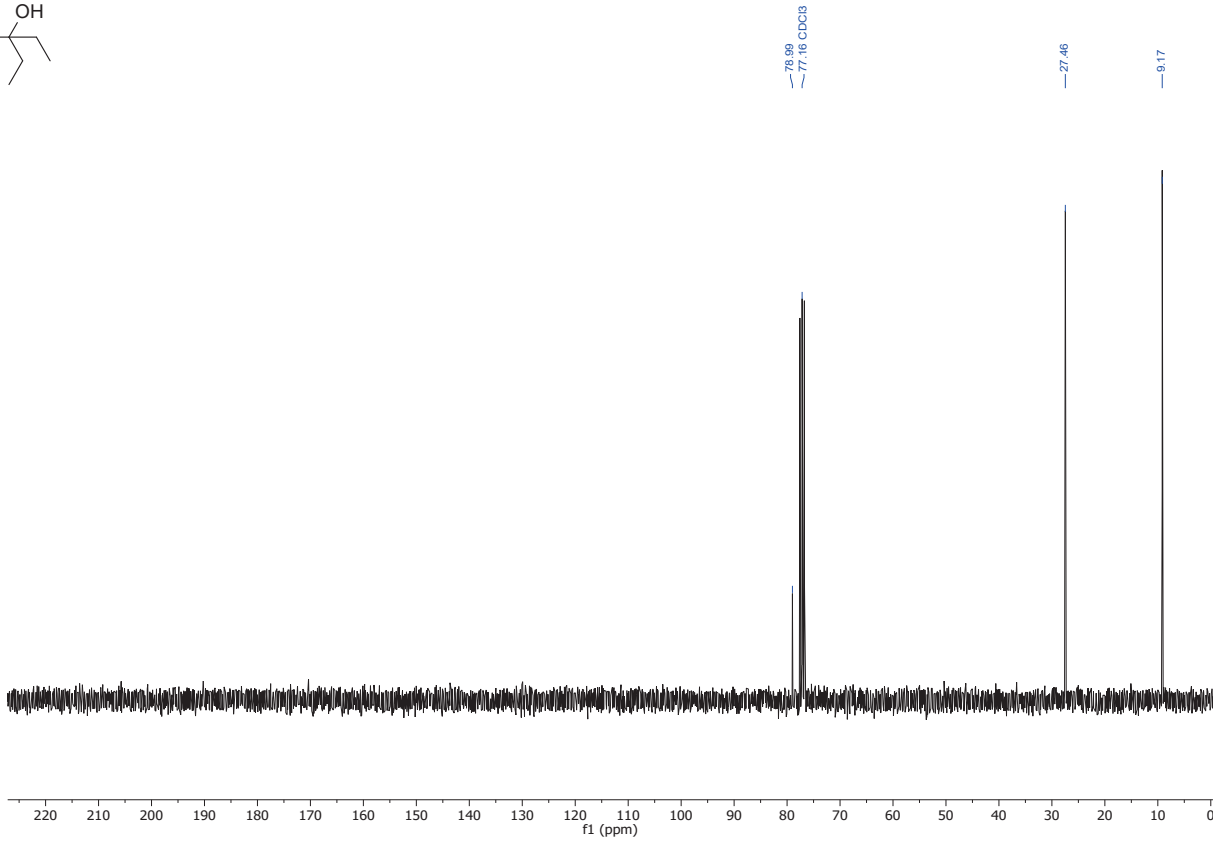




3,4-diethylhexane-3,4-diol (101)

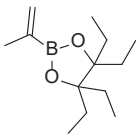
^{13}C NMR (75 MHz, $CDCl_3$)

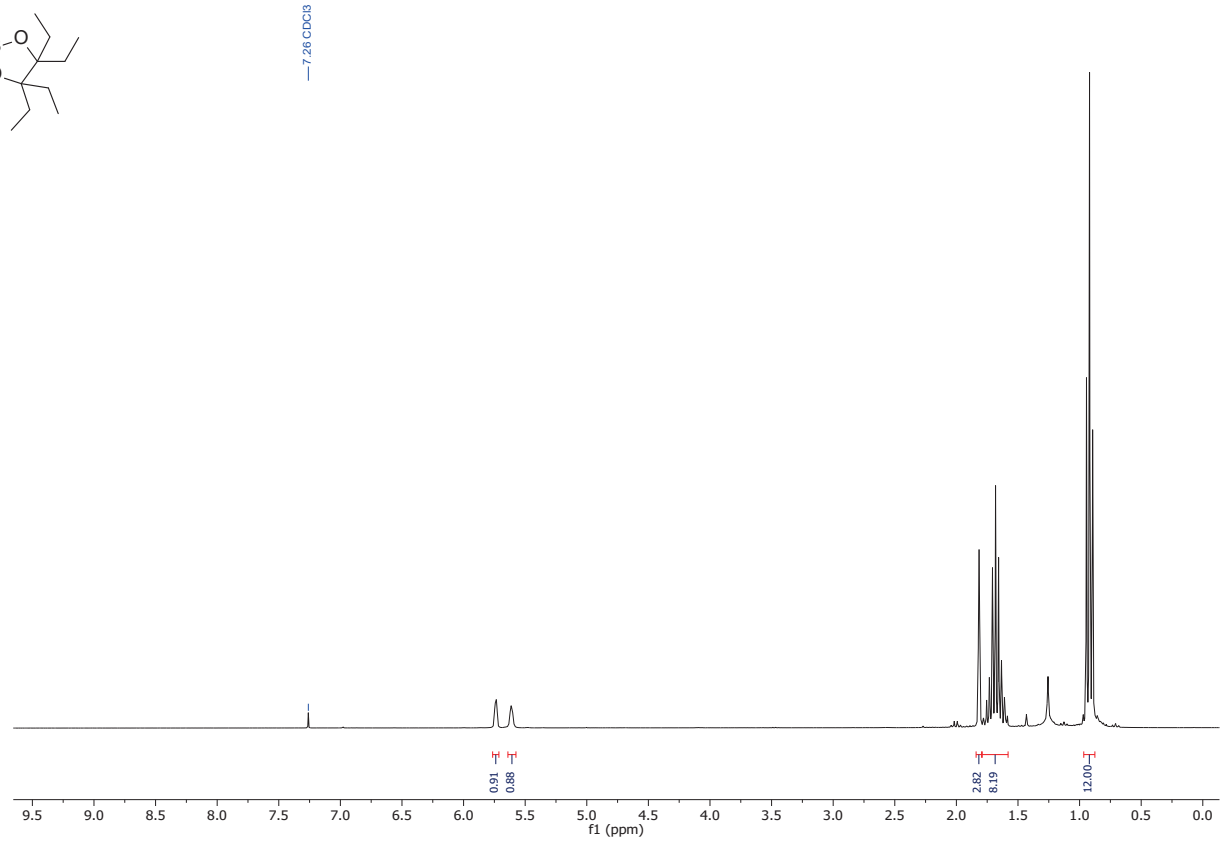




4,4,5,5-tetraethyl-2-(prop-1-en-2-yl)-1,3,2-dioxaborolane (102)

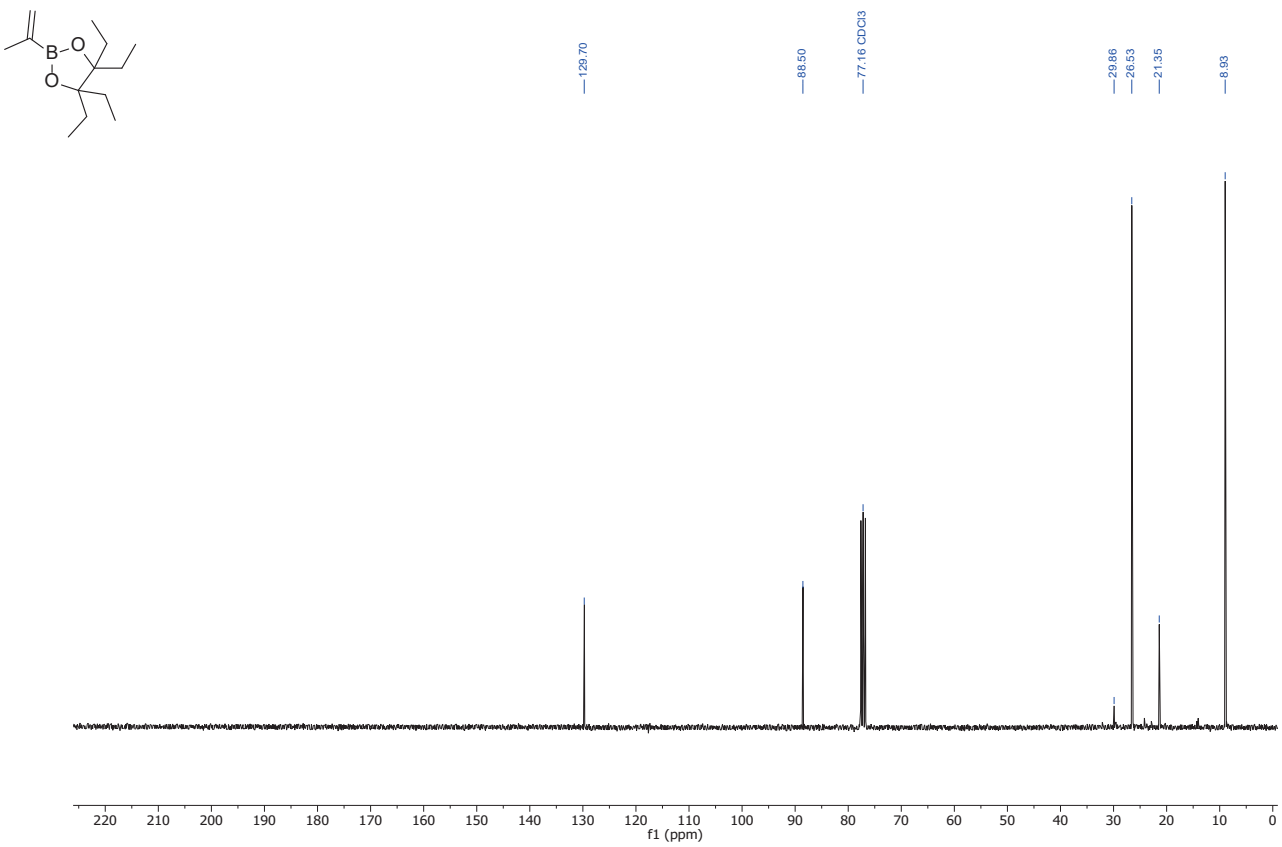
^{1}H NMR (300 MHz, $CDCl_3$)





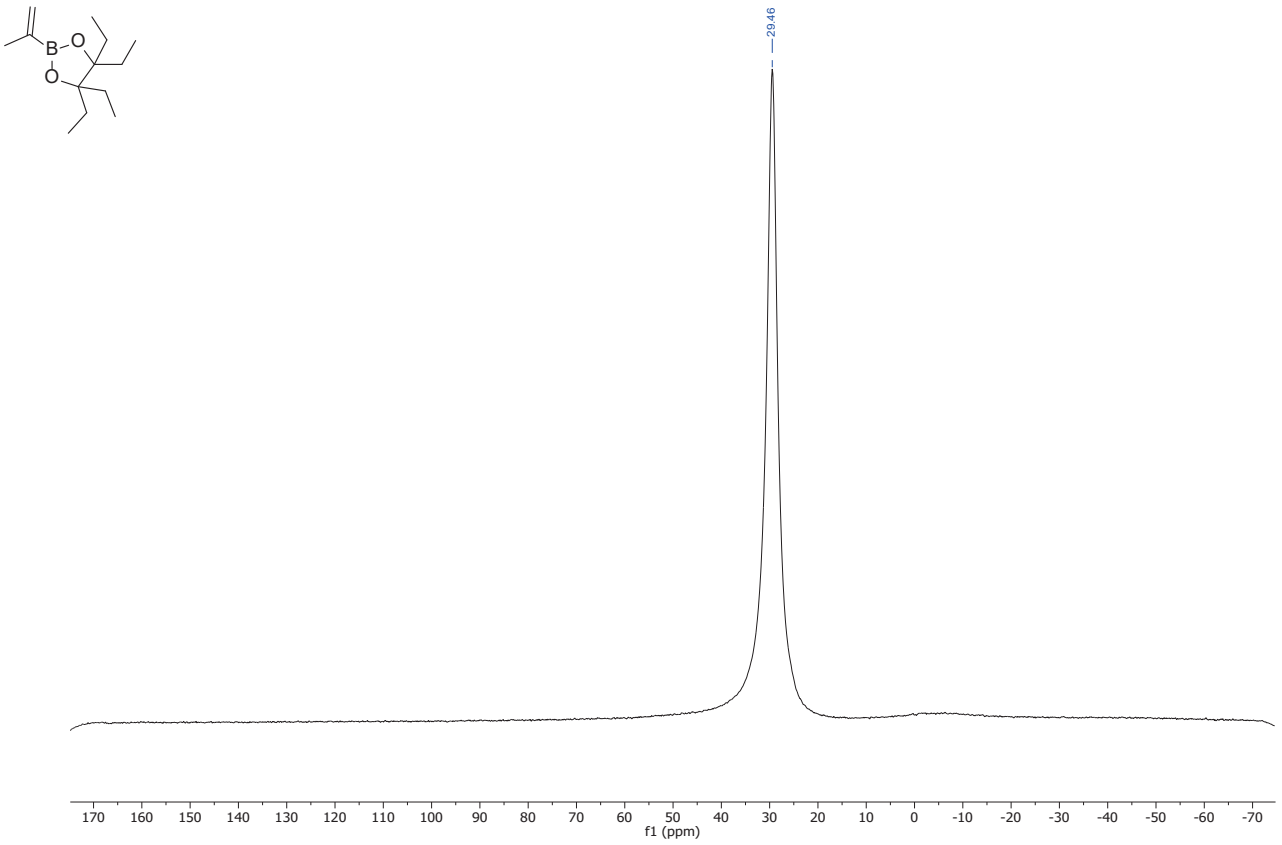
4,4,5,5-tetraethyl-2-(prop-1-en-2-yl)-1,3,2-dioxaborolane (102)

^{13}C NMR (75 MHz, $CDCl_3$)



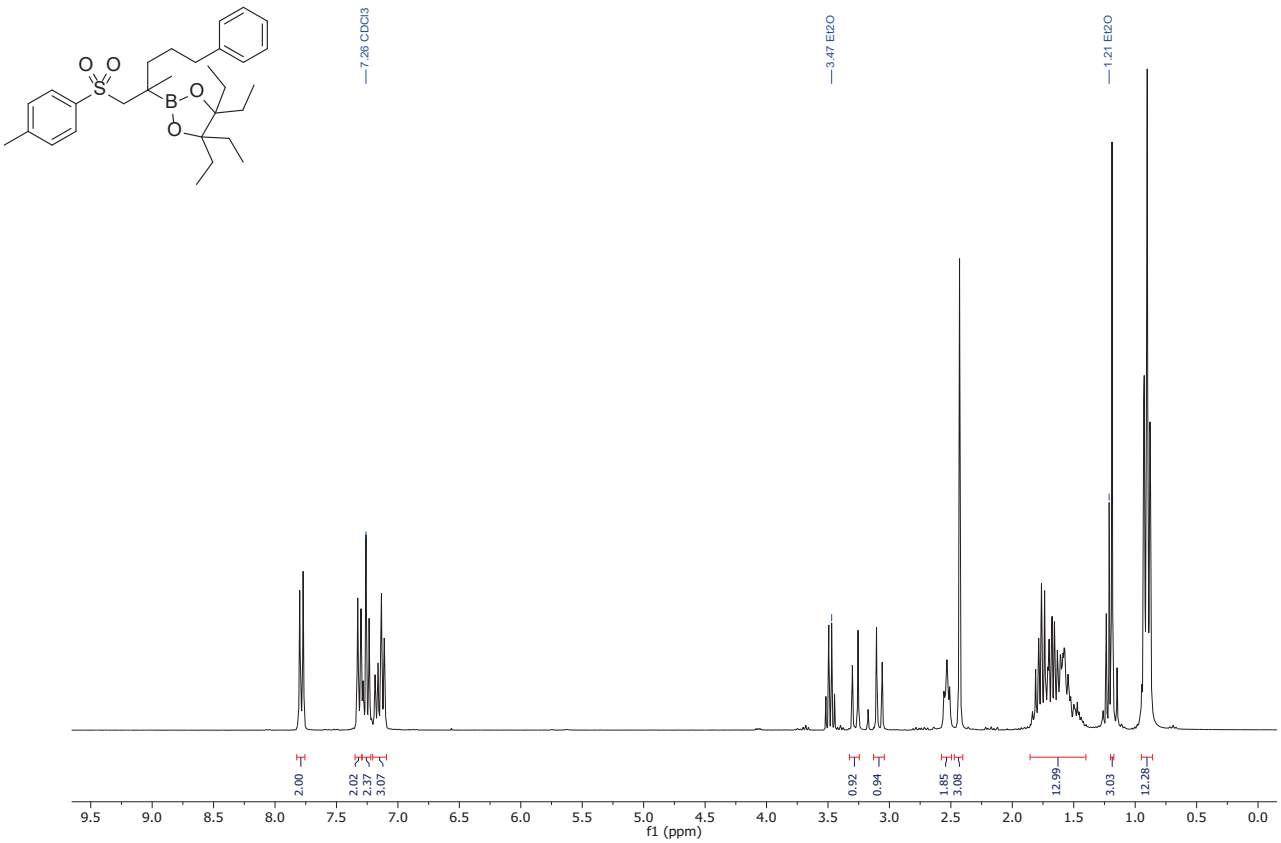
4,4,5,5-tetraethyl-2-(prop-1-en-2-yl)-1,3,2-dioxaborolane (102)

^{11}B NMR (96 MHz, $CDCl_3$)



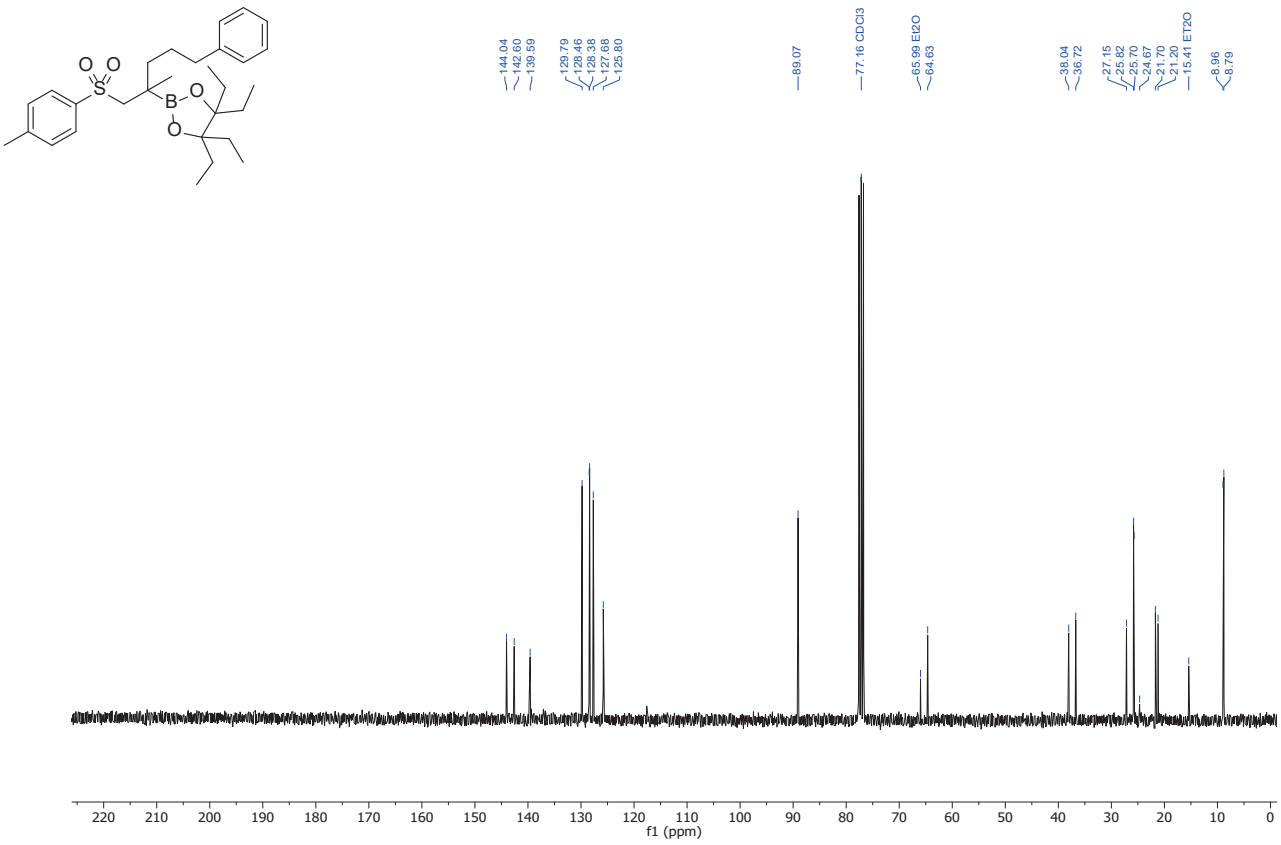
4,4,5,5-tetraethyl-2-(2-methyl-5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (103)

^{1}H NMR (400 MHz, $CDCl_3$)



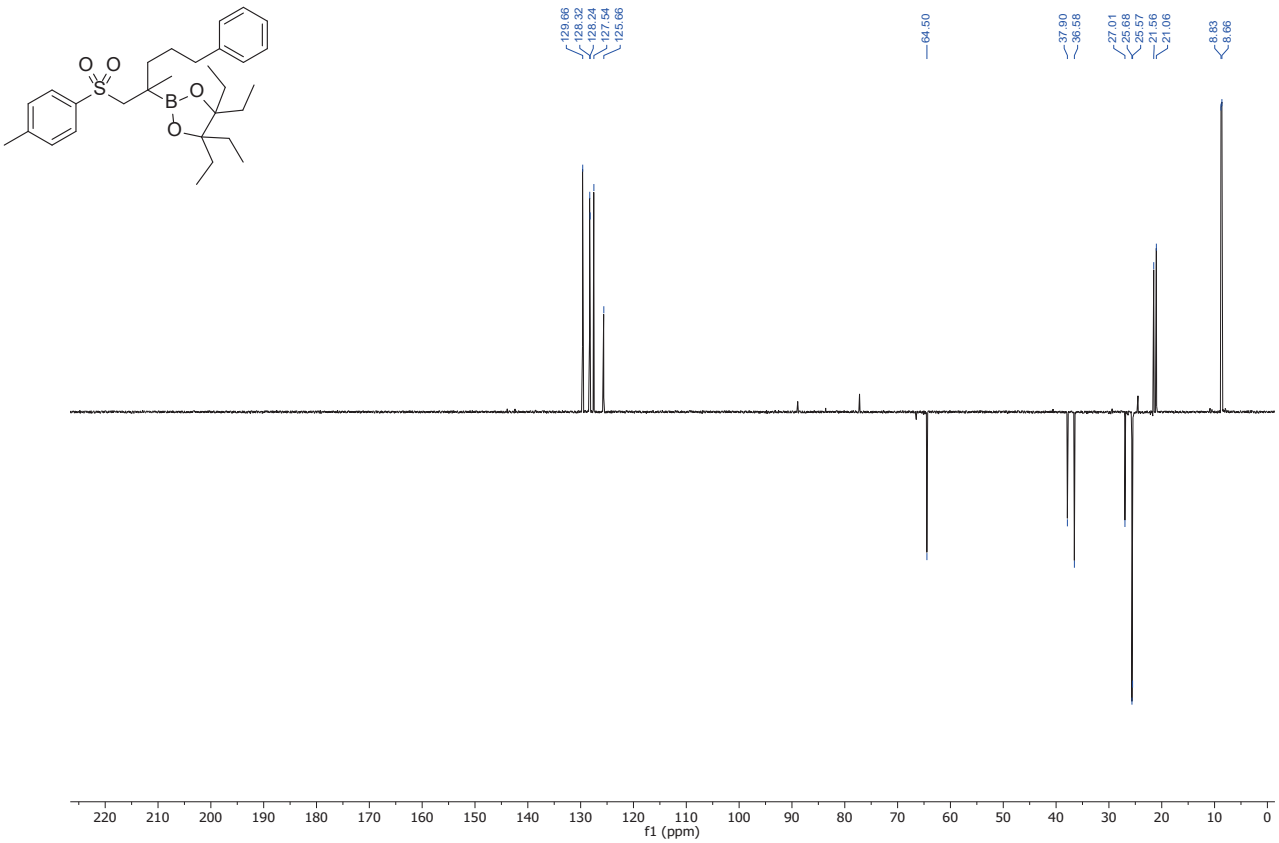
4,4,5,5-tetraethyl-2-(2-methyl-5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (103)

^{13}C NMR (101 MHz, $CDCl_3$)



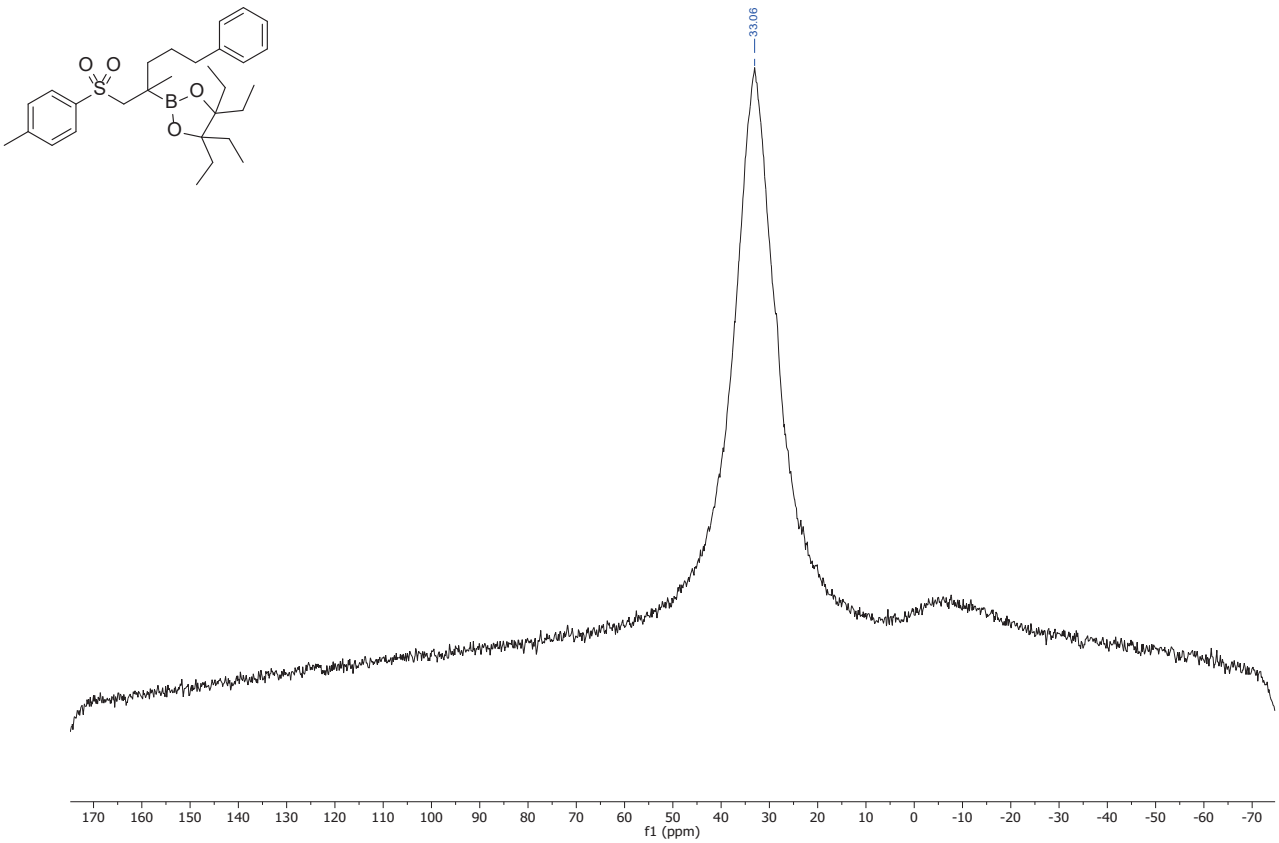
4,4,5,5-tetraethyl-2-(2-methyl-5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (103)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



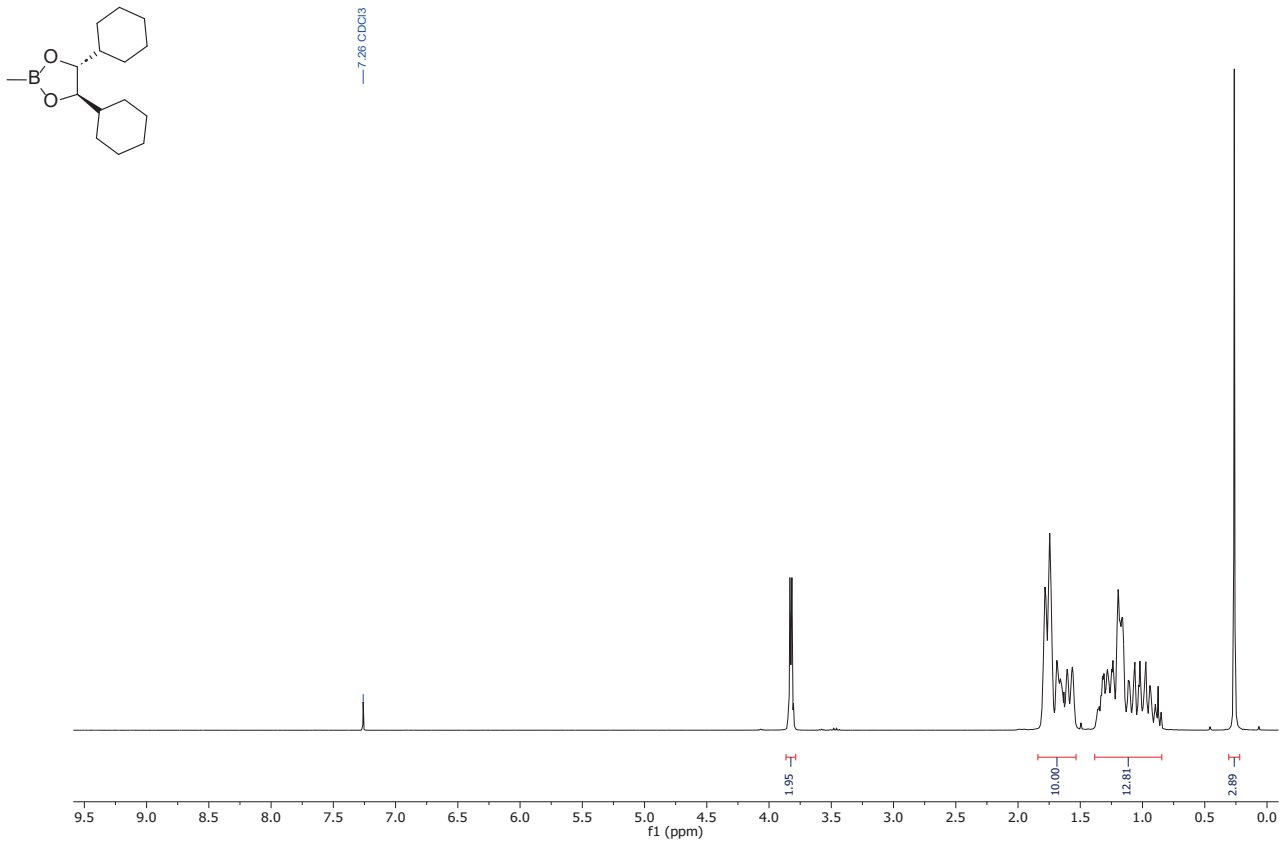
4,4,5,5-tetraethyl-2-(2-methyl-5-phenyl-1-tosylpentan-2-yl)-1,3,2-dioxaborolane (103)

^{11}B NMR (96 MHz, $CDCl_3$)



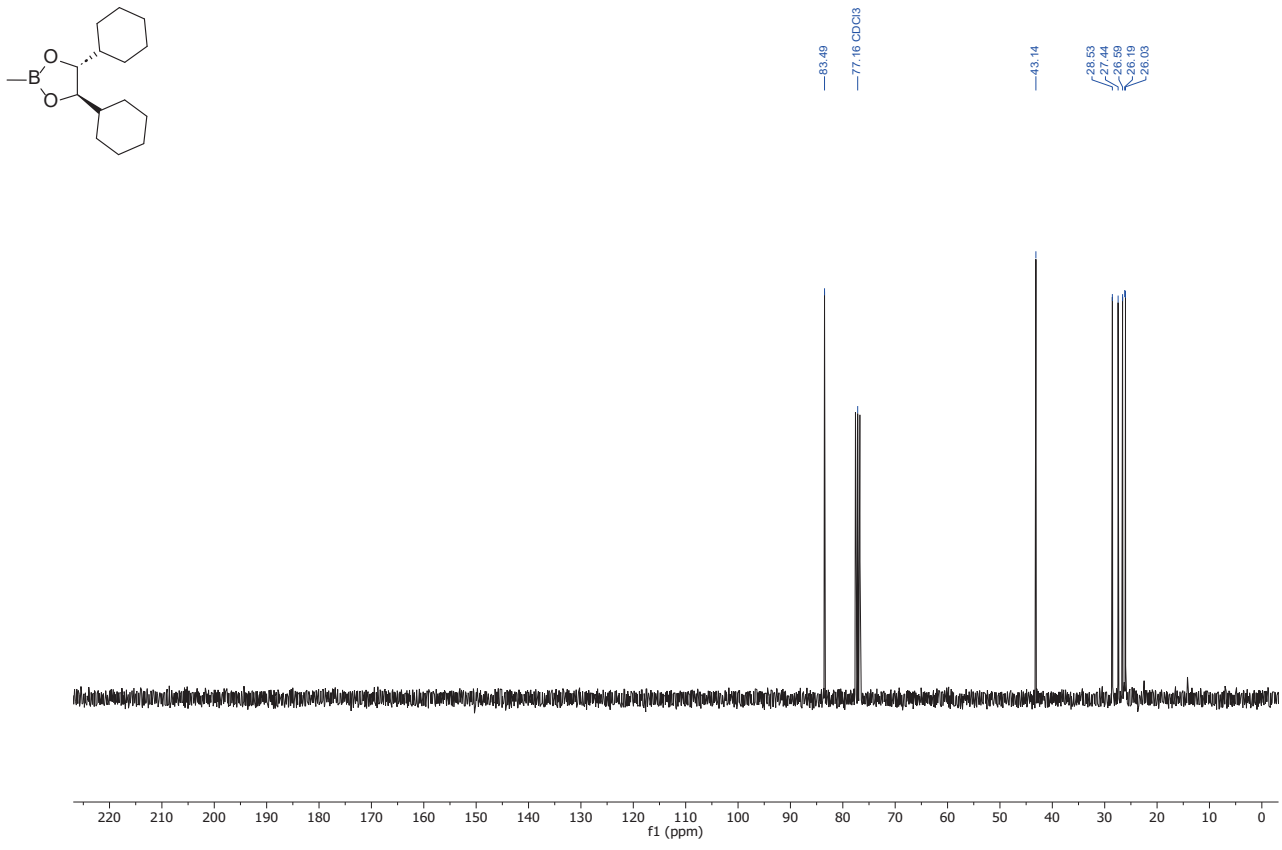
(4R,5R)-4,5-dicyclohexyl-2-methyl-1,3,2-dioxaborolane (104)

^{1}H NMR (300 MHz, $CDCl_3$)



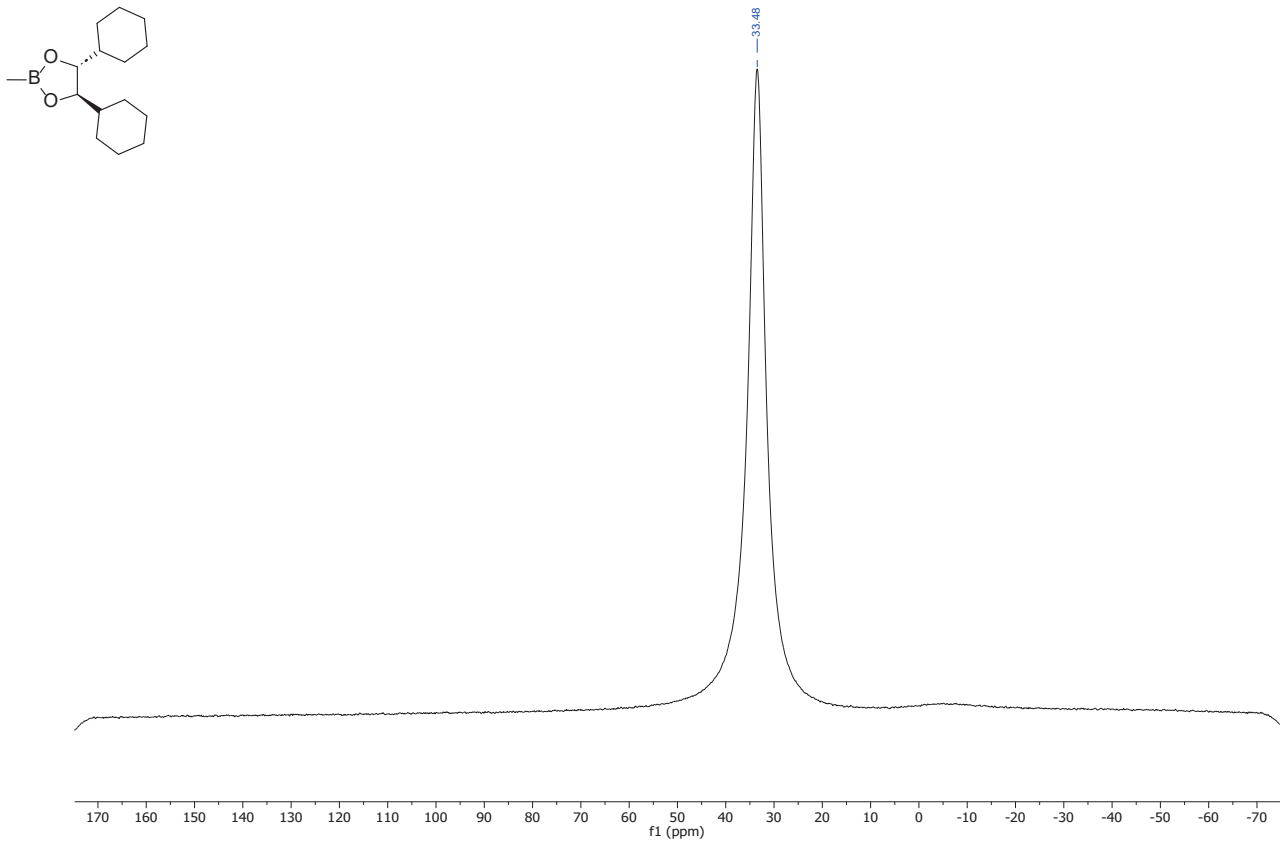
(4R,5R)-4,5-dicyclohexyl-2-methyl-1,3,2-dioxaborolane (104)

^{13}C NMR (75 MHz, $CDCl_3$)



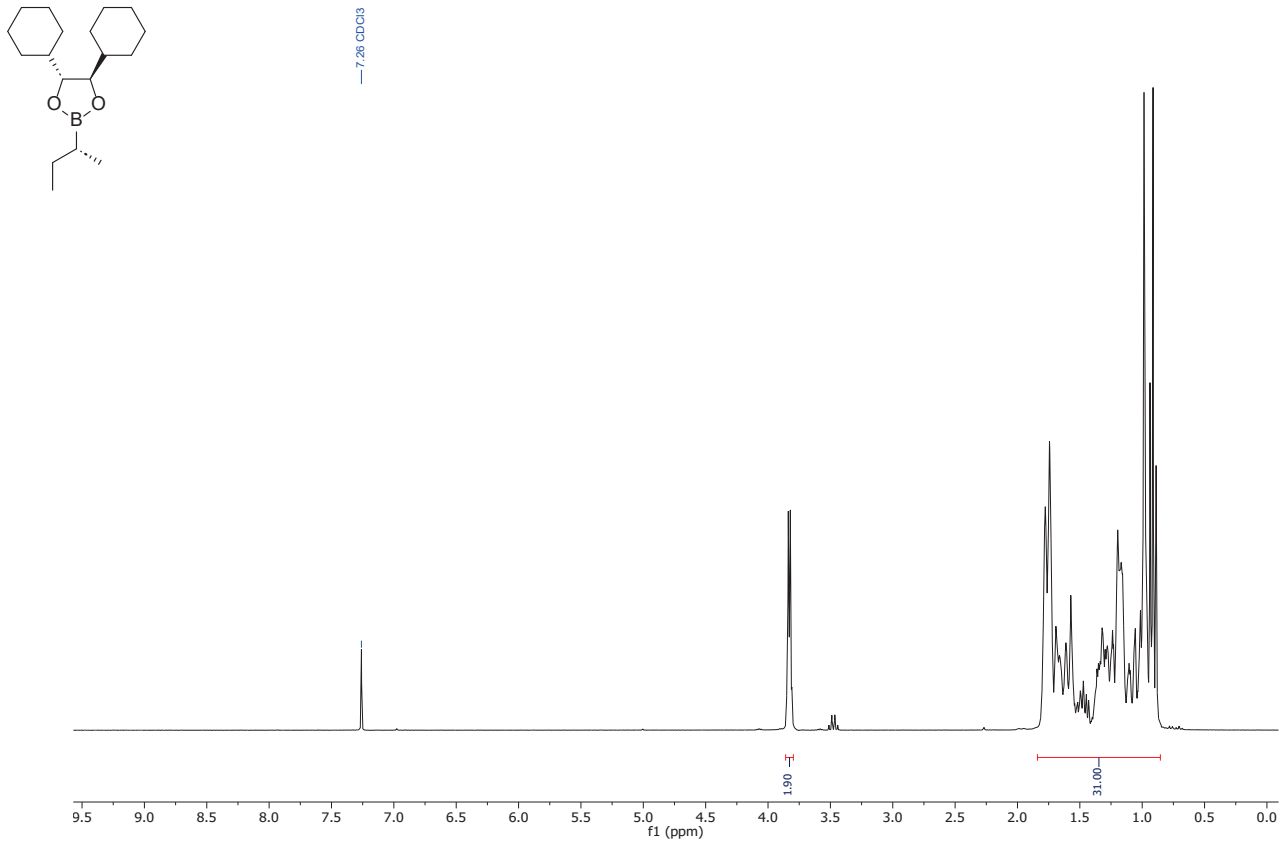
(4R,5R)-4,5-dicyclohexyl-2-methyl-1,3,2-dioxaborolane (104)

^{11}B NMR (96 MHz, $CDCl_3$)



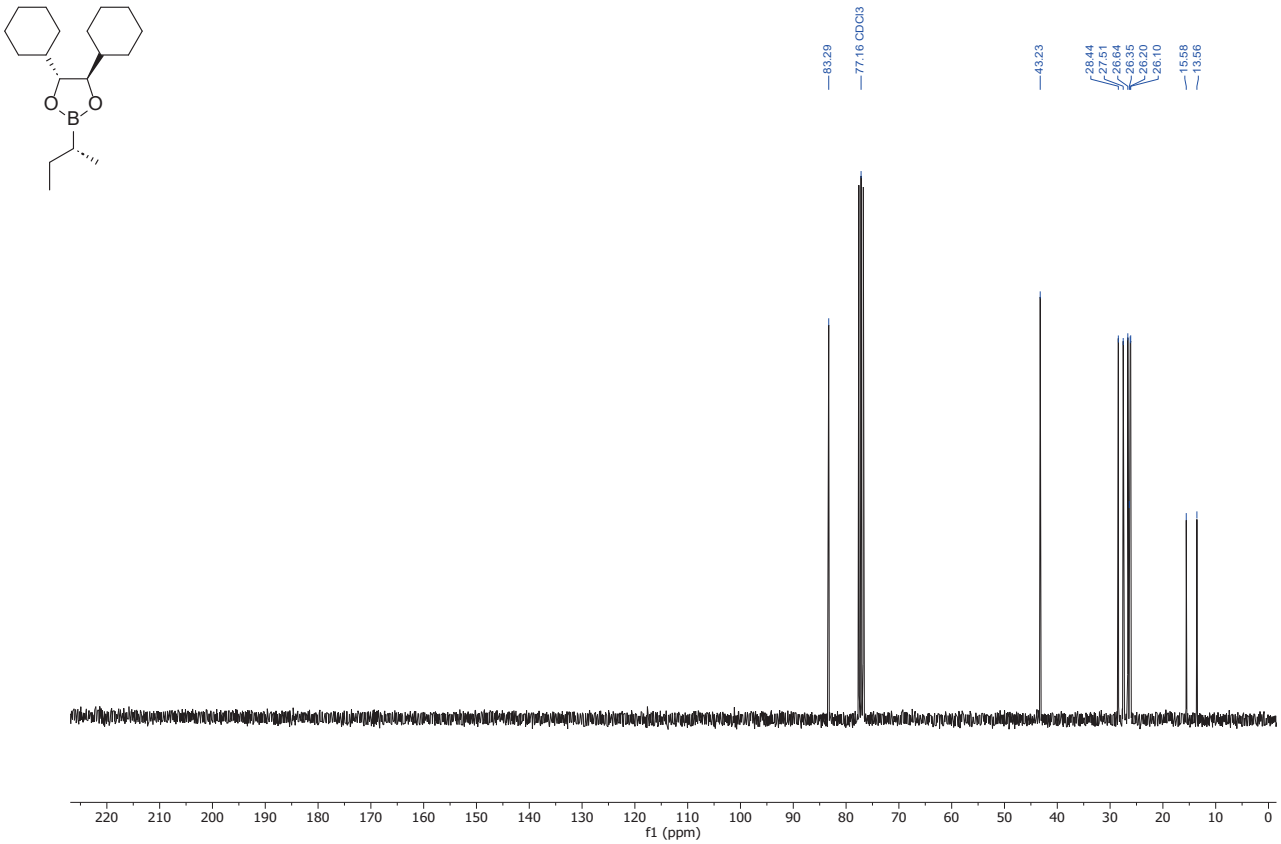
(4R,5R)-2-((R)-sec-butyl)-4,5-dicyclohexyl-1,3,2-dioxaborolane (90)

^{1}H NMR (300 MHz, $CDCl_3$)



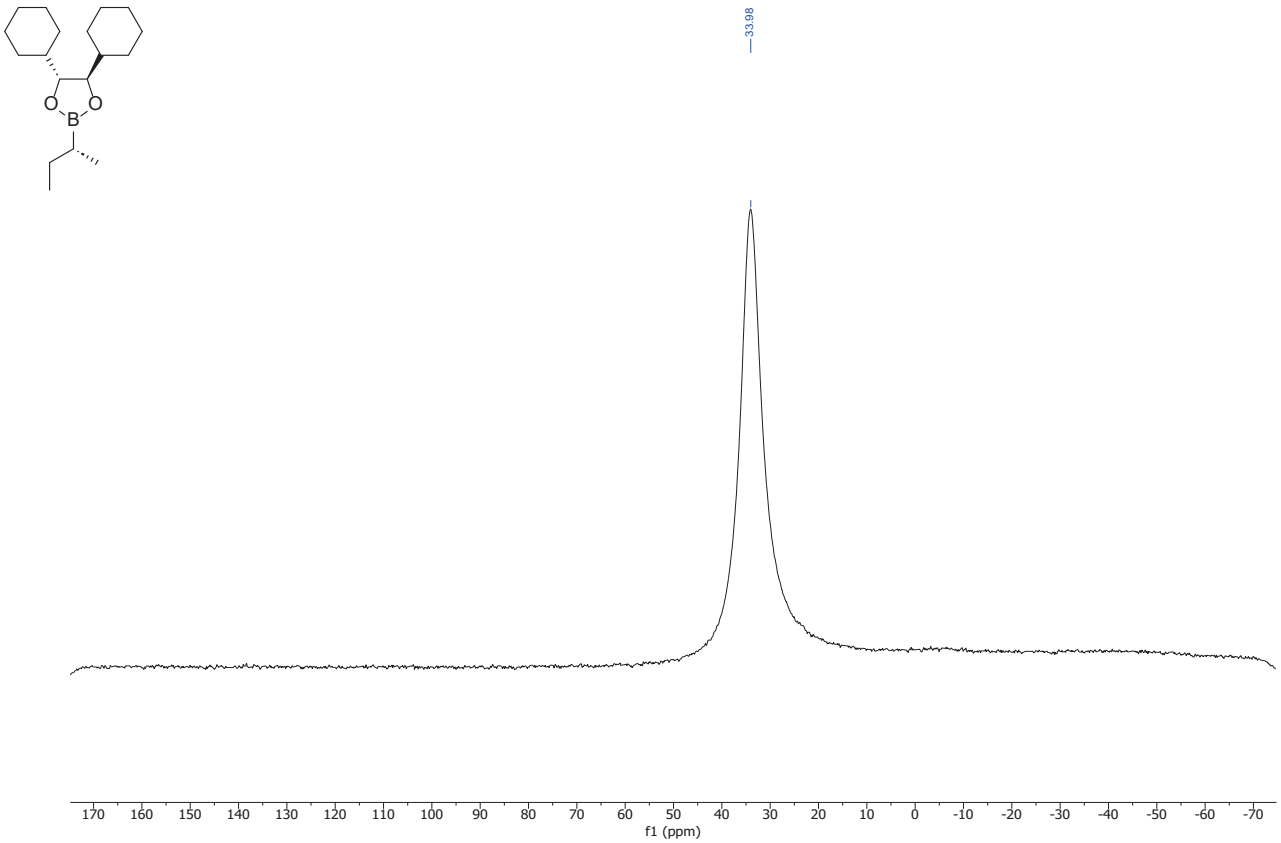
(4R,5R)-2-((R)-sec-butyl)-4,5-dicyclohexyl-1,3,2-dioxaborolane (90)

^{13}C NMR (75 MHz, $CDCl_3$)



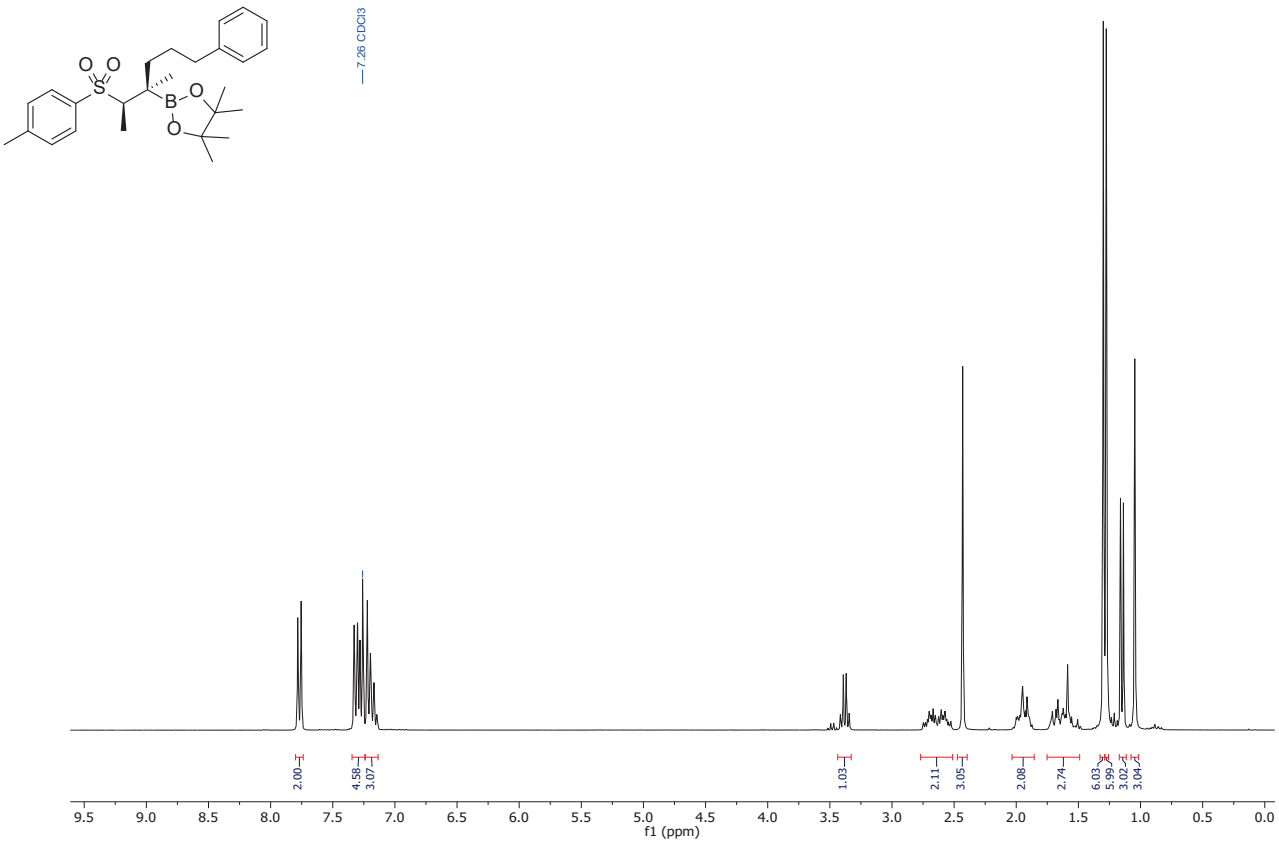
(4R,5R)-2-((R)-sec-butyl)-4,5-dicyclohexyl-1,3,2-dioxaborolane (90)

^{11}B NMR (96 MHz, $CDCl_3$)



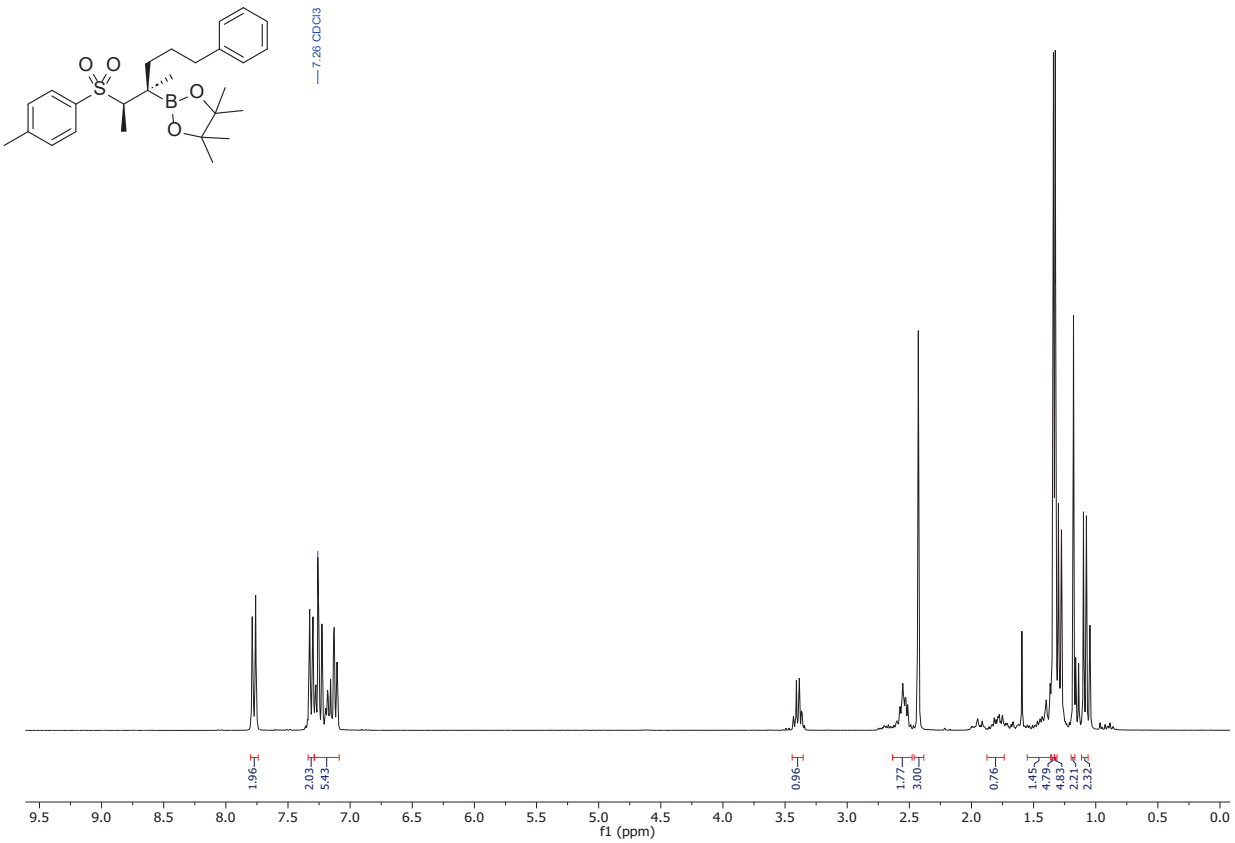
4,4,5,5-tetramethyl-2-((2R,3S)-3-methyl-6-phenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (43)
Major diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



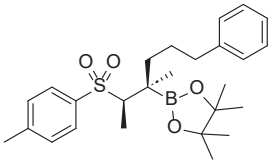
4,4,5,5-tetramethyl-2-((2R,3S)-3-methyl-6-phenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (43)
Minor diastereomer

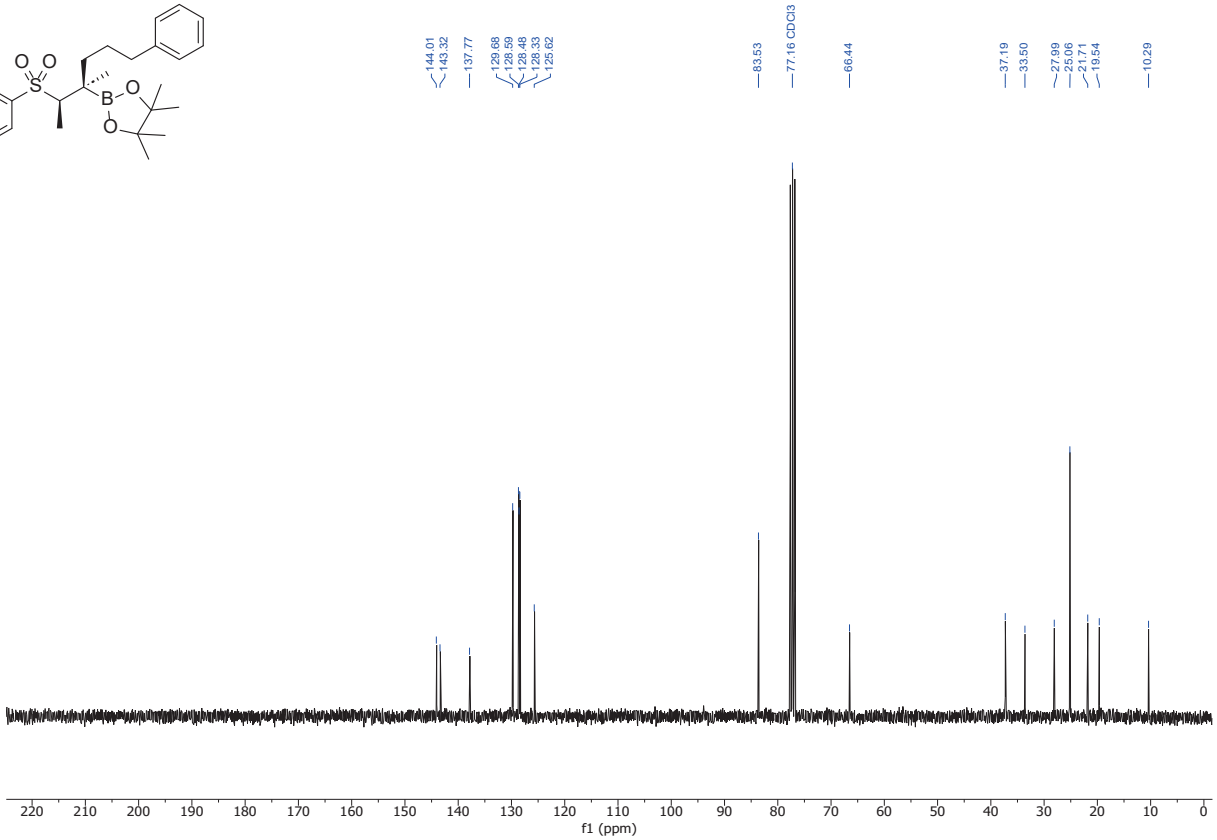
^{1}H NMR (300 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-((2R,3S)-3-methyl-6-phenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (43)
Major diastereomer

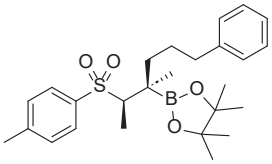
^{13}C NMR (75 MHz, $CDCl_3$)

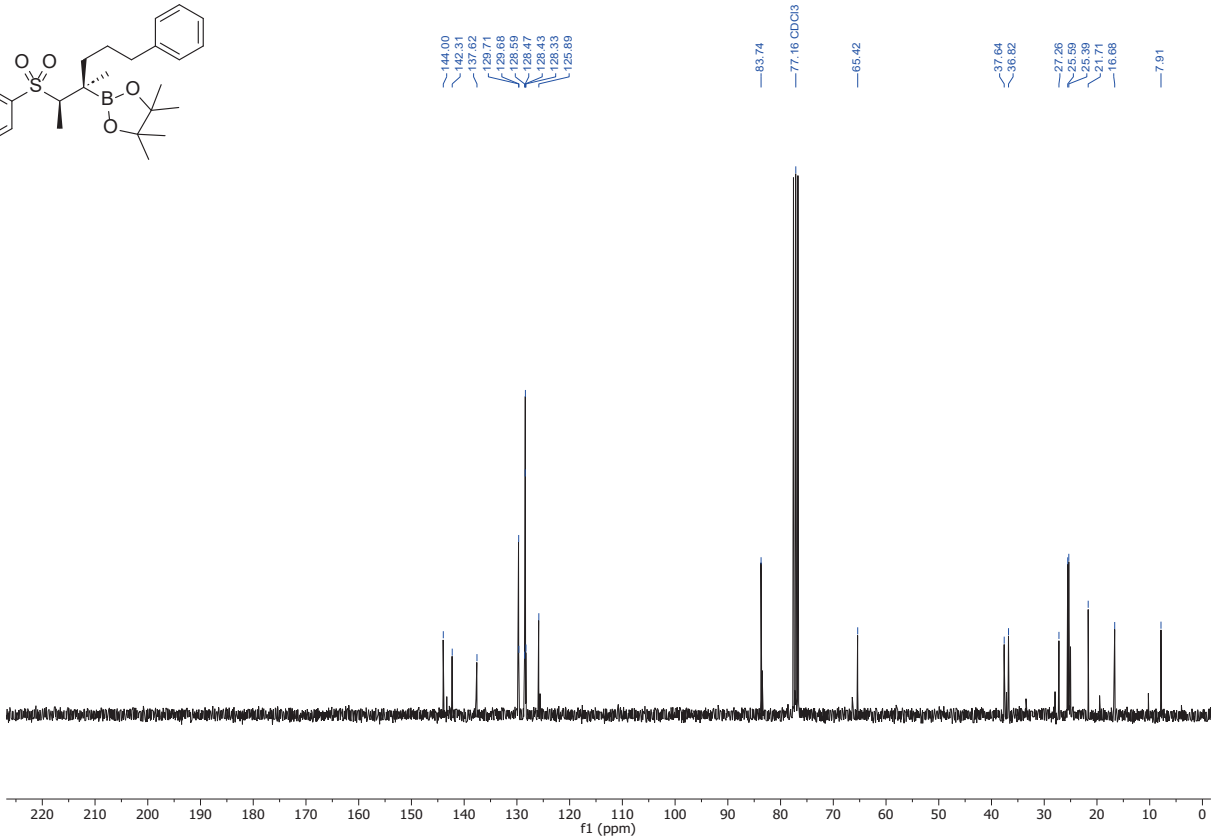




4,4,5,5-tetramethyl-2-((2R,3S)-3-methyl-6-phenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (43)
Minor diastereomer

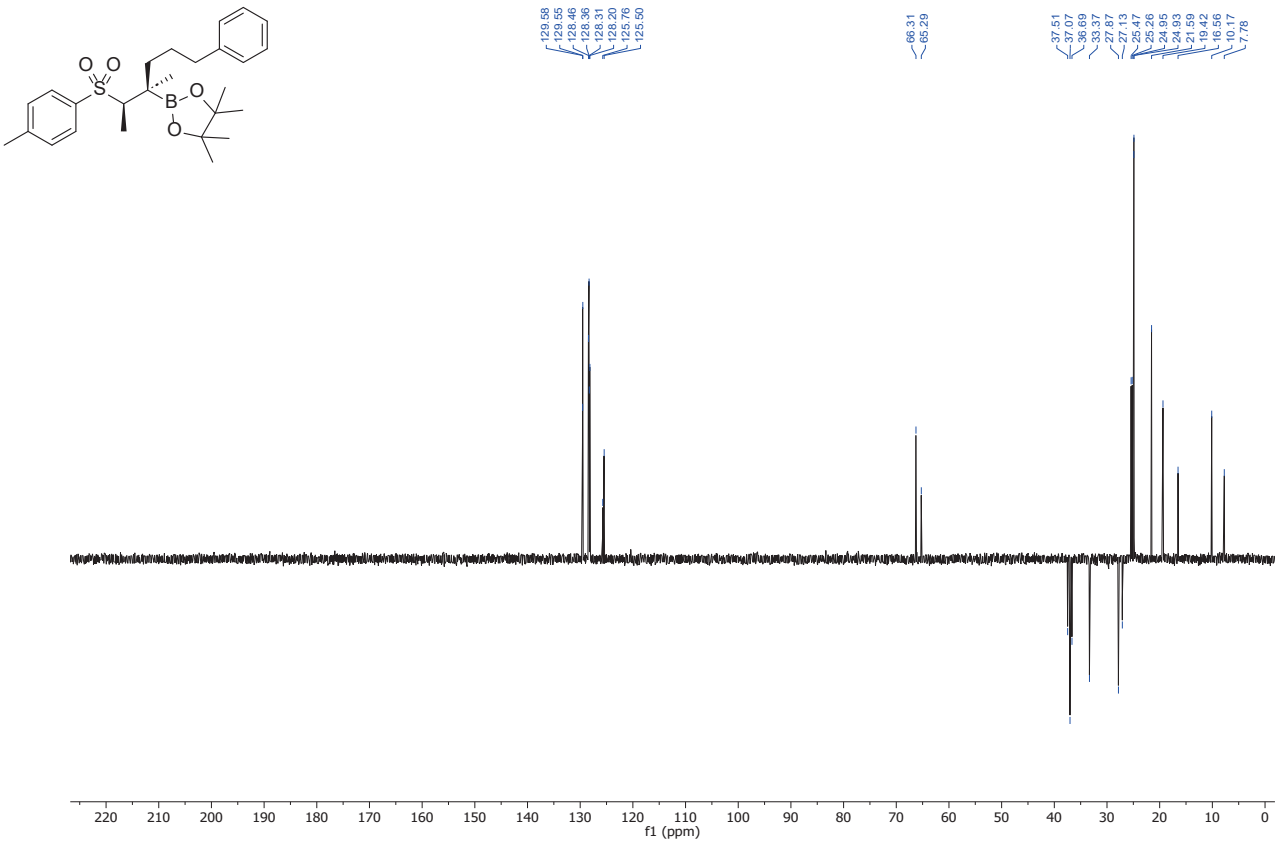
^{13}C NMR (75 MHz, $CDCl_3$)





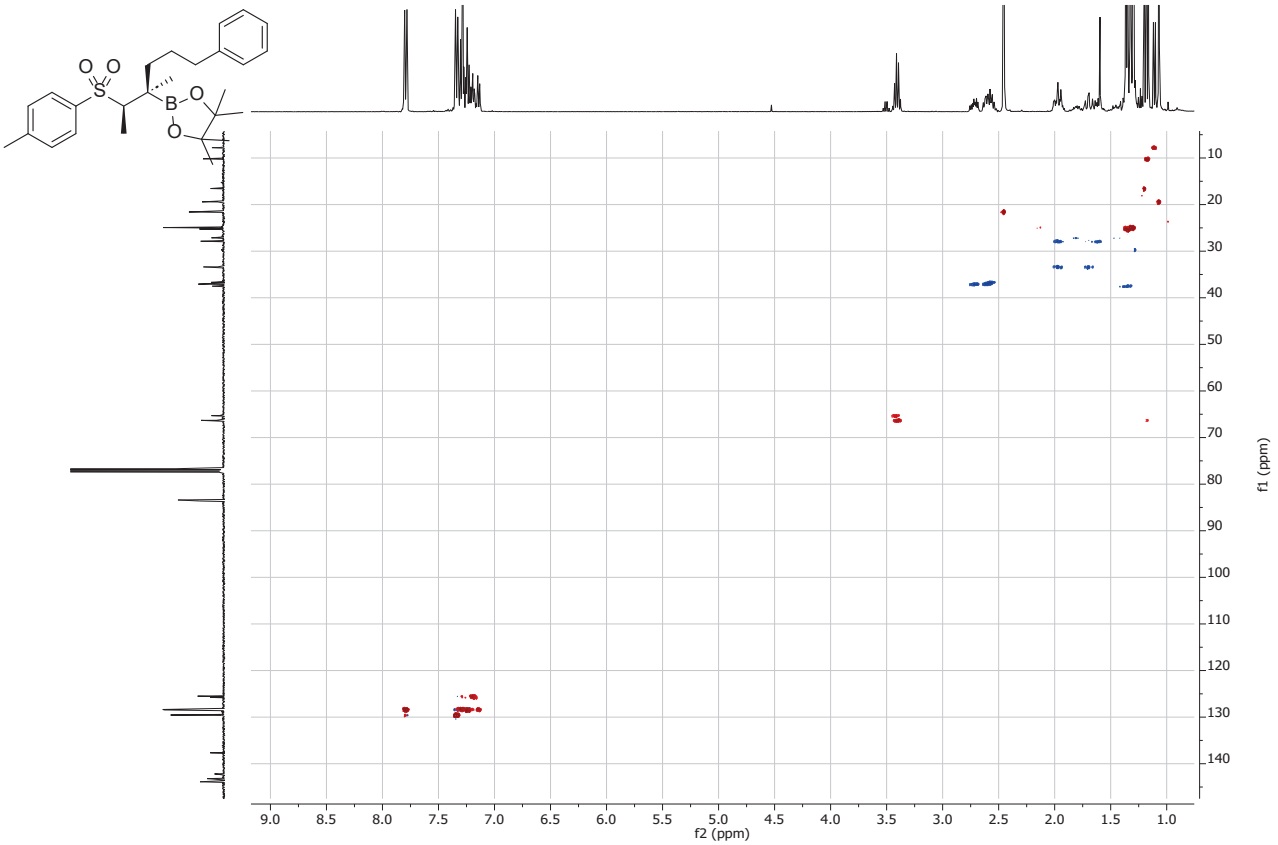
4,4,5,5-tetramethyl-2-((2R,3S)-3-methyl-6-phenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (43)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



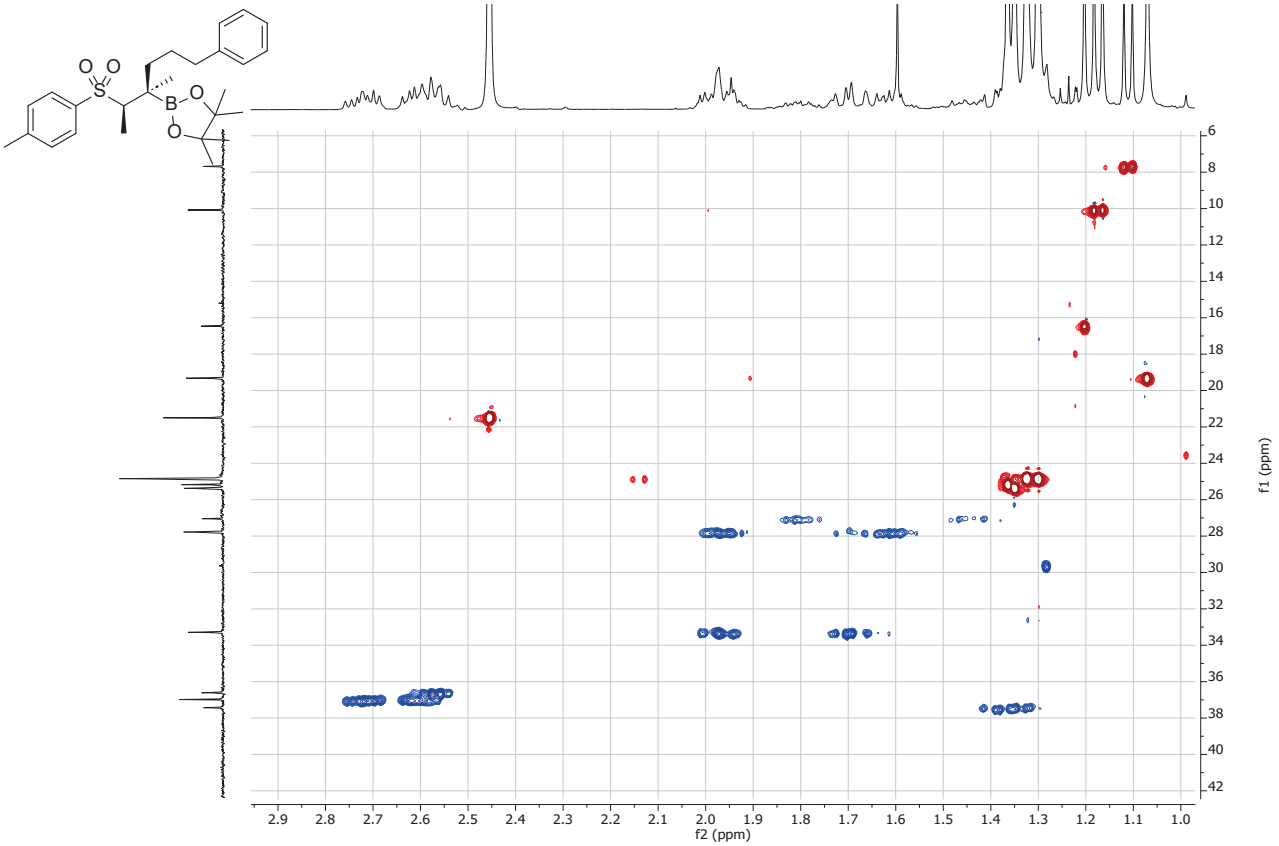
4,4,5,5-tetramethyl-2-((2R,3S)-3-methyl-6-phenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (43)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



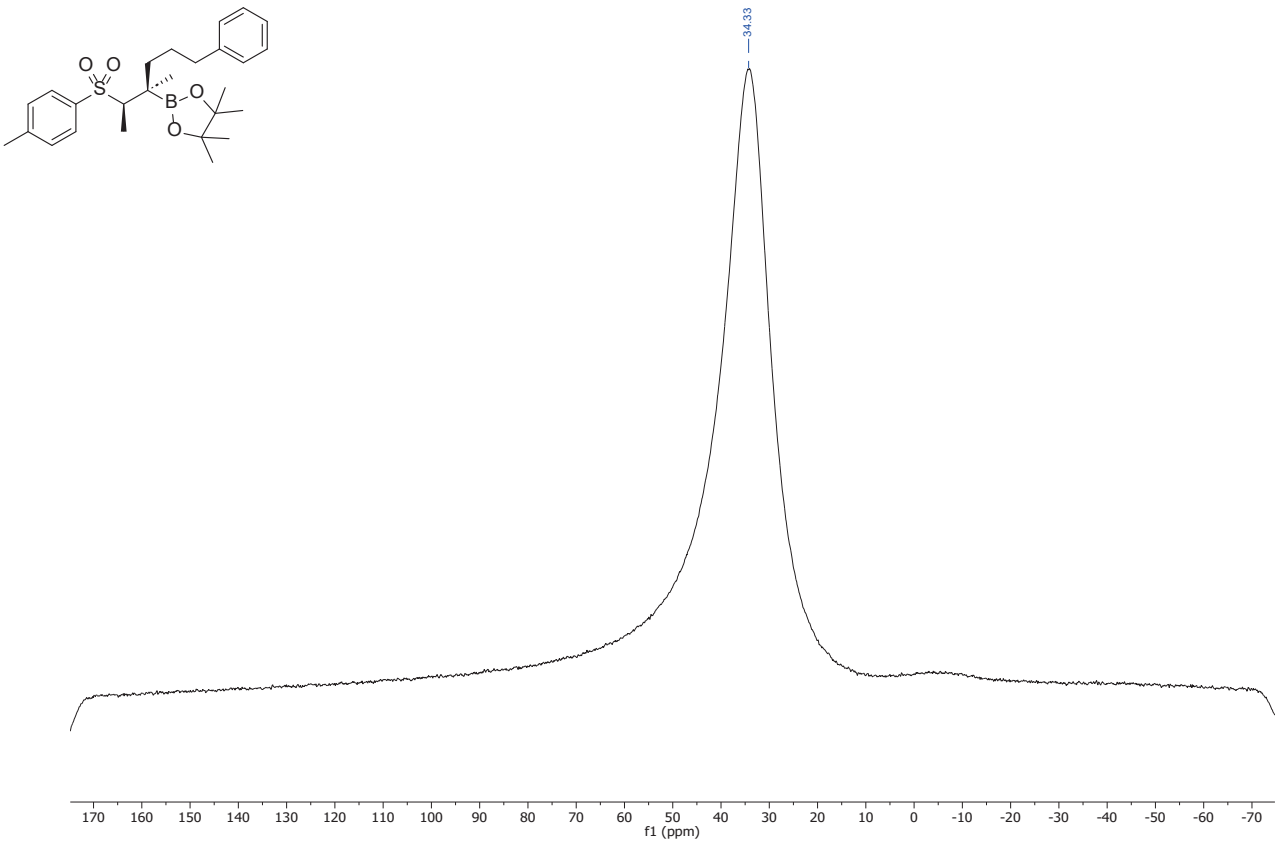
4,4,5,5-tetramethyl-2-((2R,3S)-3-methyl-6-phenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (43)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



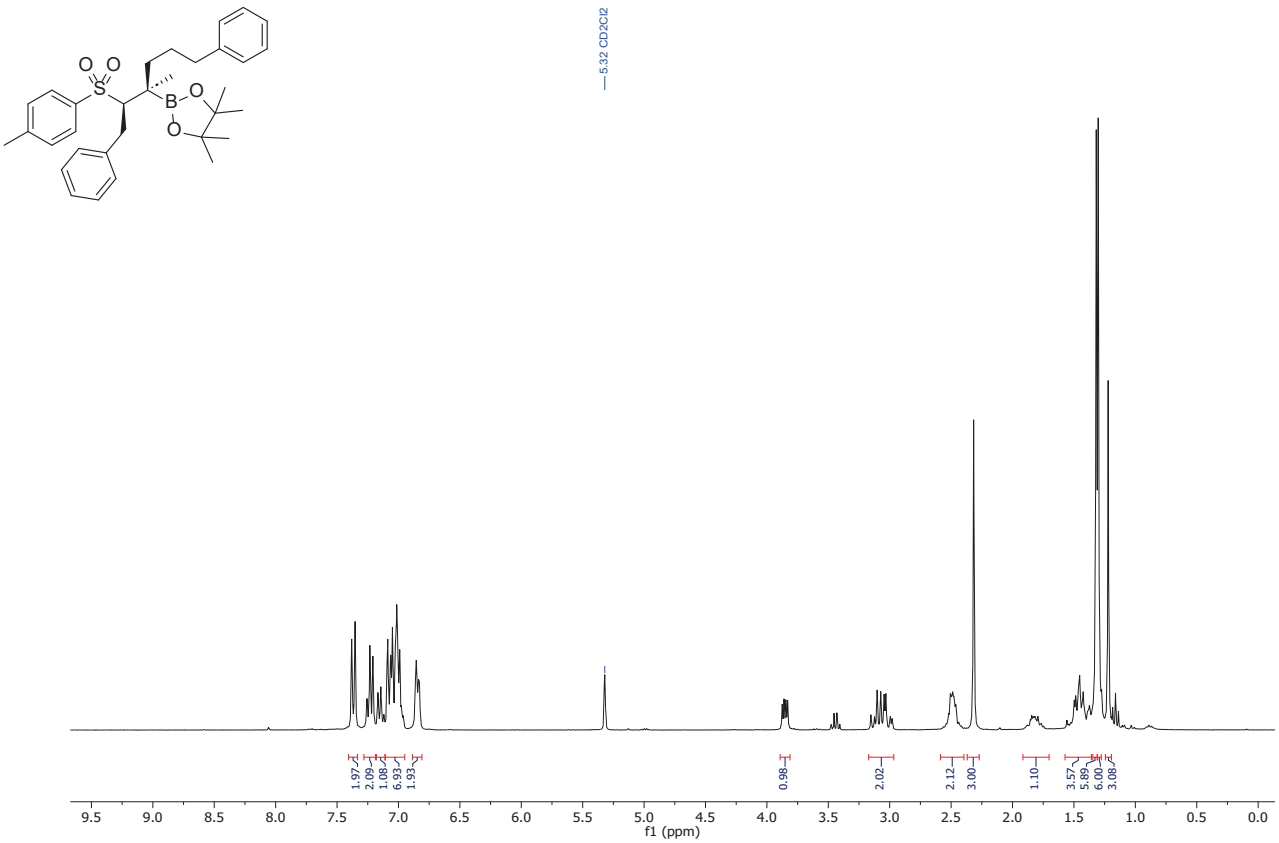
4,4,5,5-tetramethyl-2-((2R,3S)-3-methyl-6-phenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (43)

^{11}B NMR (96 MHz, $CDCl_3$)



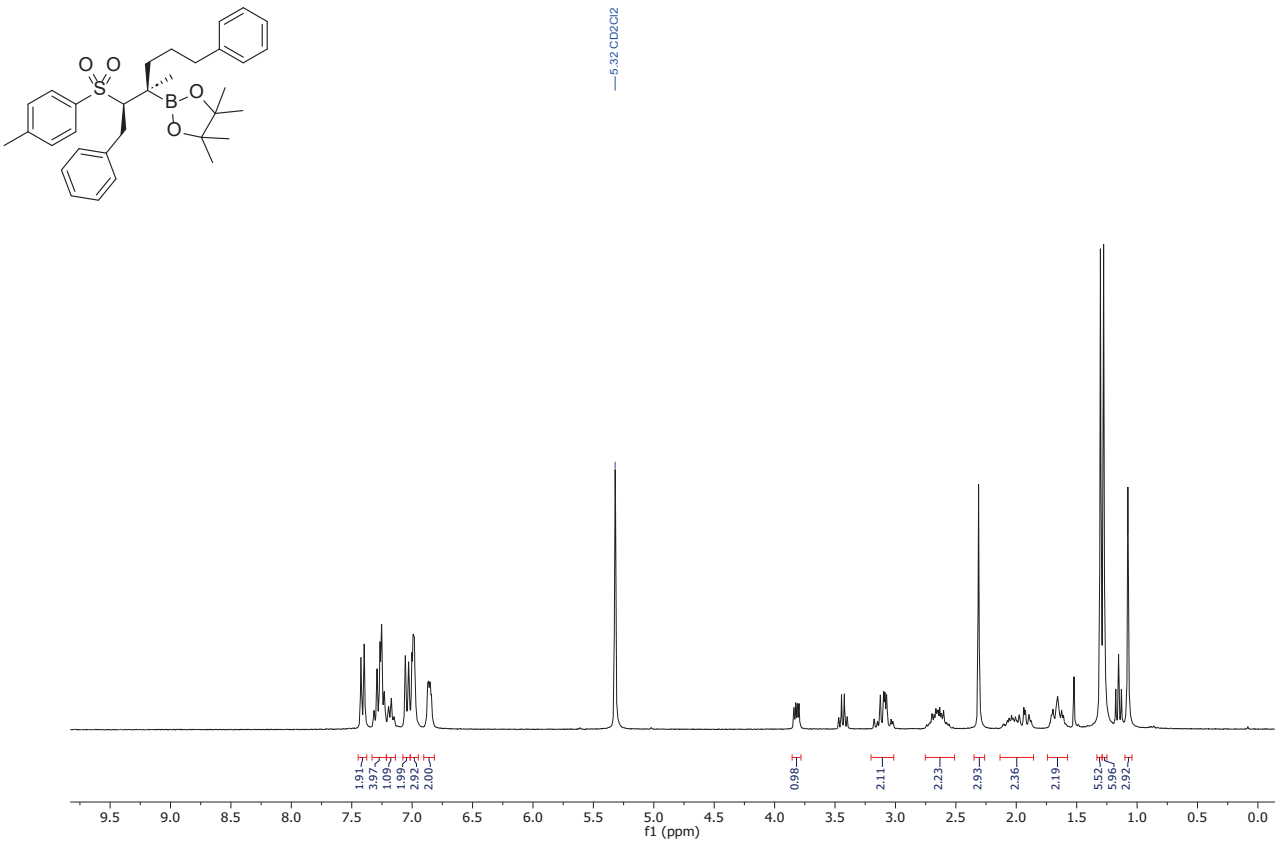
4,4,5,5-tetramethyl-2-((2R,3S)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (40)
Major diastereomer

^{1}H NMR (300 MHz, CD_2Cl_2)



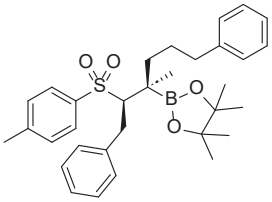
4,4,5,5-tetramethyl-2-((2R,3S)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (40)
Minor diastereomer

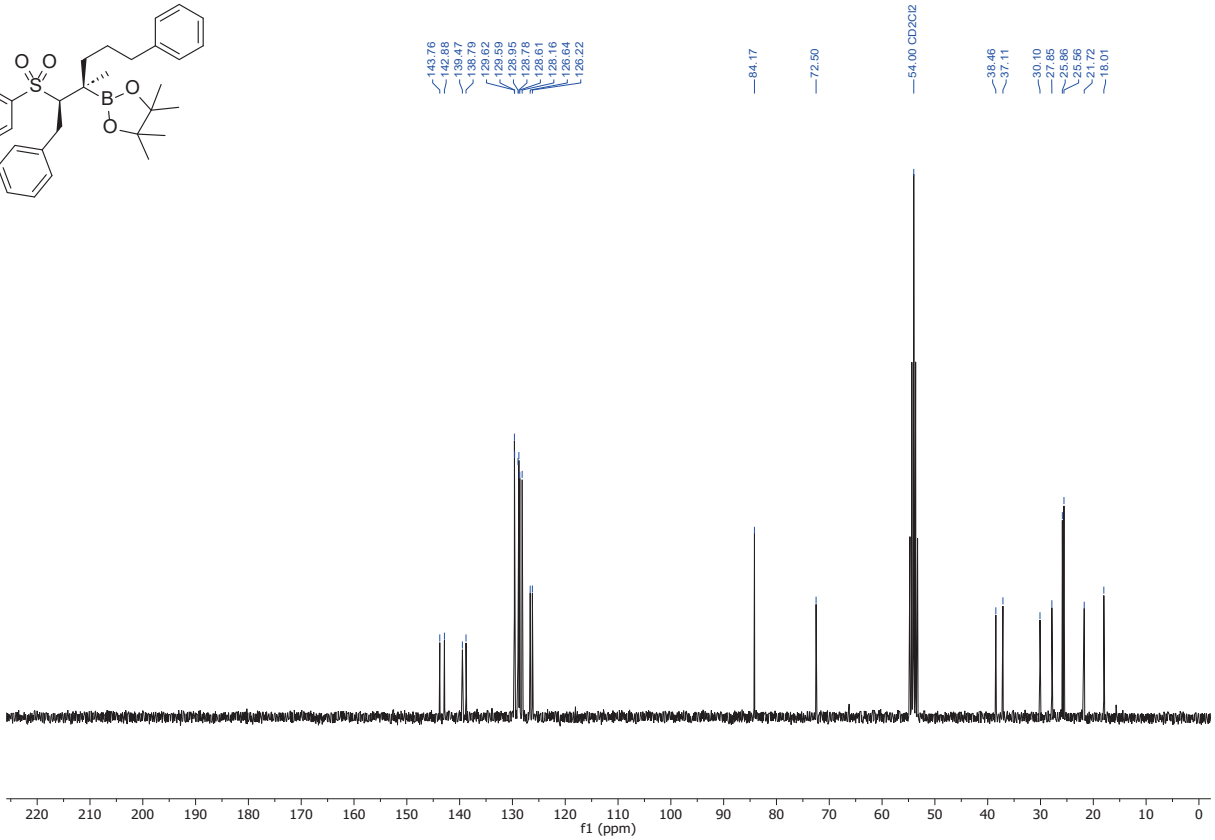
^{1}H NMR (300 MHz, CD_2Cl_2)



4,4,5,5-tetramethyl-2-((2R,3S)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (40)
Major diastereomer

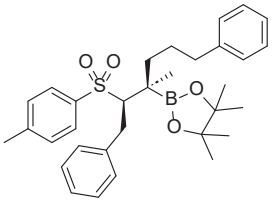
^{13}C NMR (75 MHz, CD_2Cl_2)

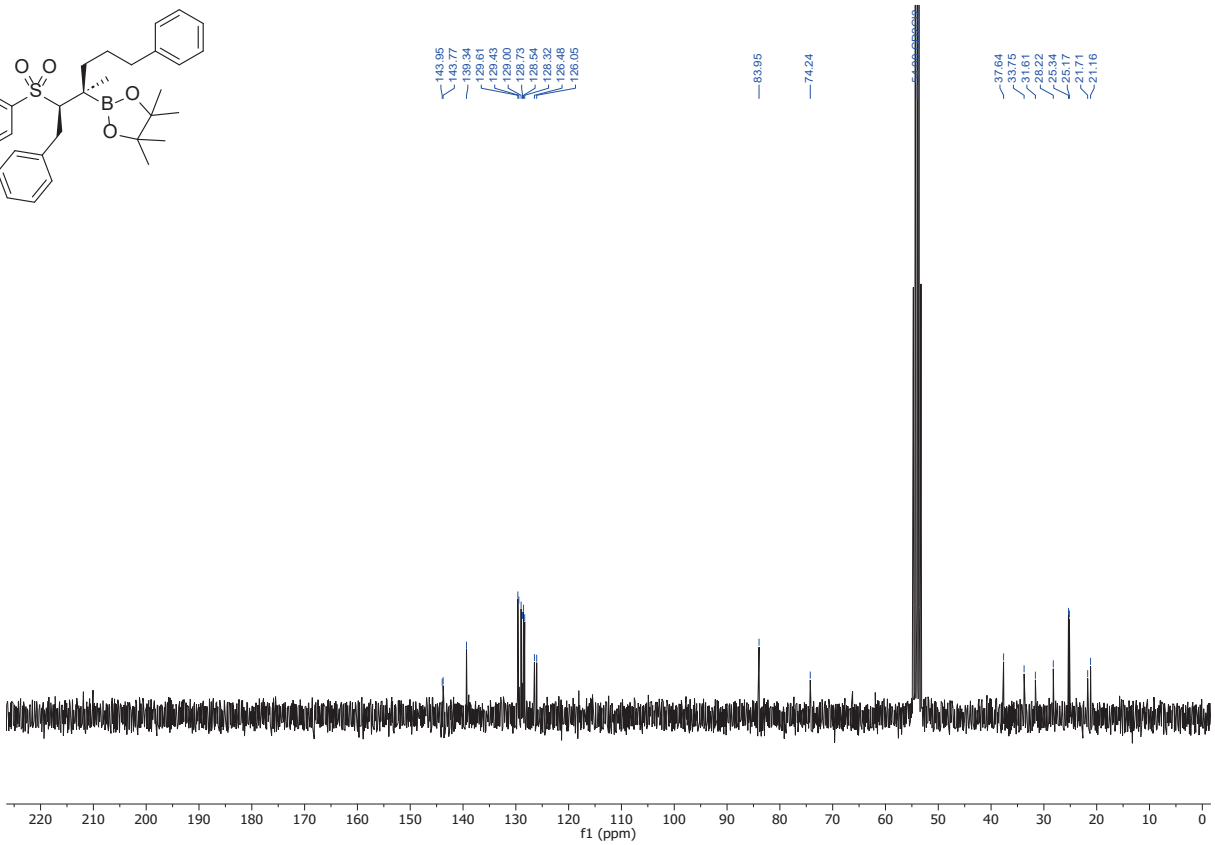




4,4,5,5-tetramethyl-2-((2R,3S)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (40)
Minor diastereomer

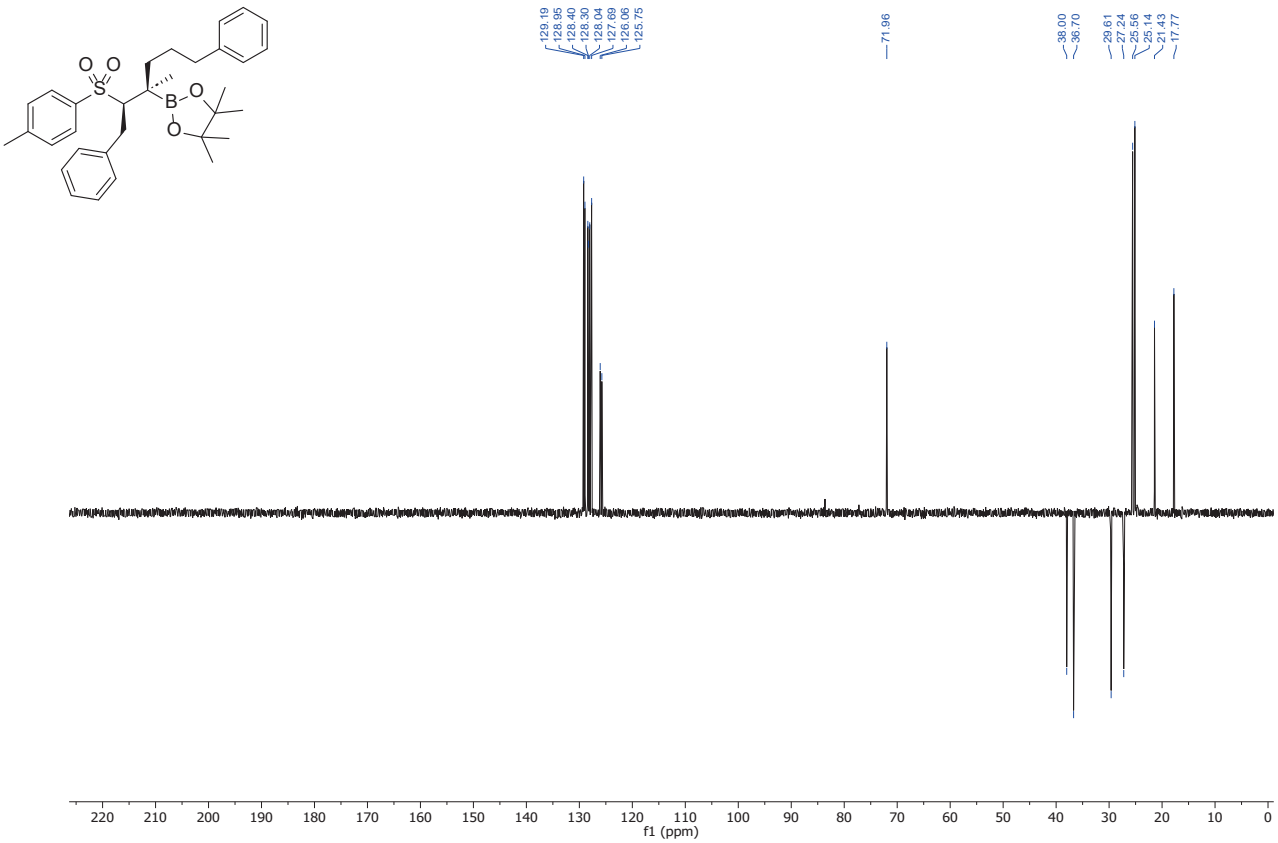
^{13}C NMR (75 MHz, CD_2Cl_2)





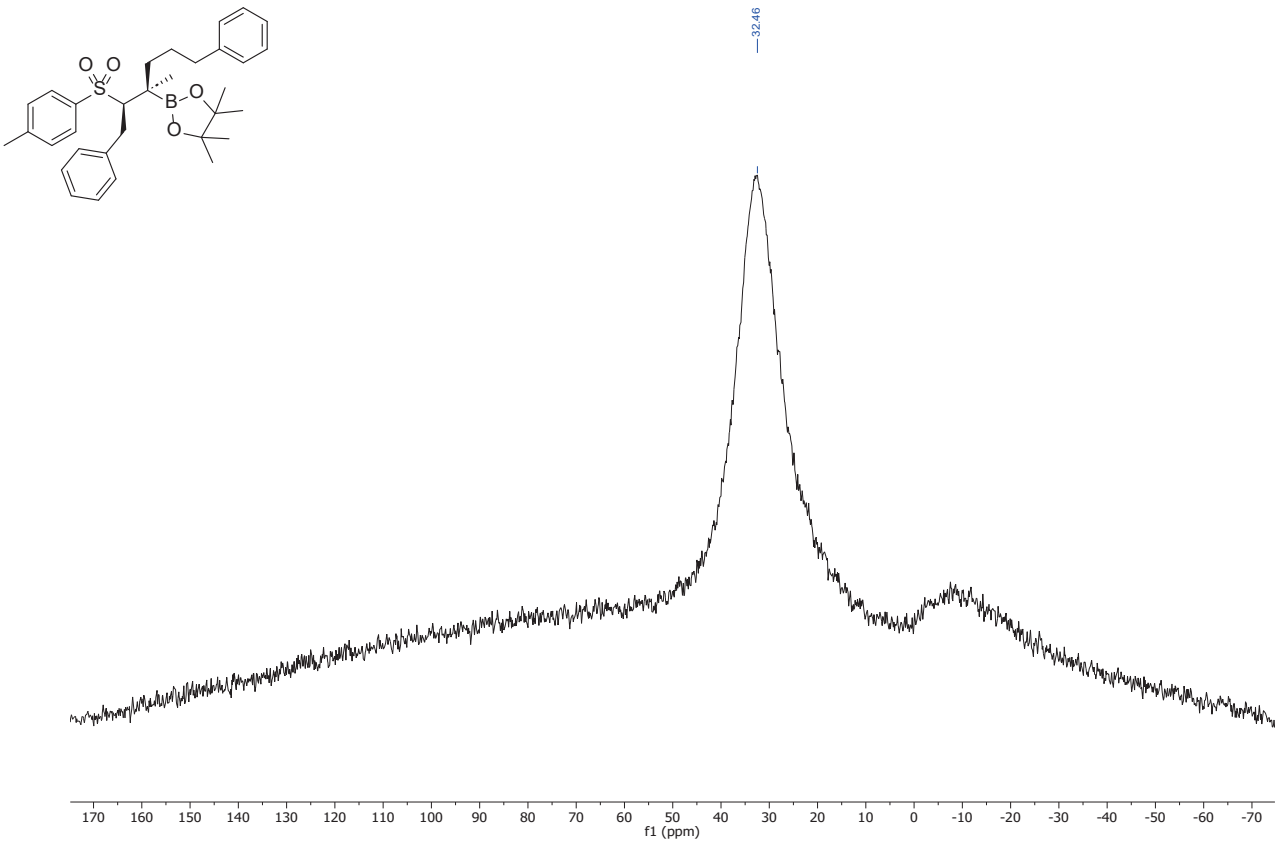
4,4,5,5-tetramethyl-2-((2R,3S)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (40)
Major diastereomer

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-((2R,3S)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (40)

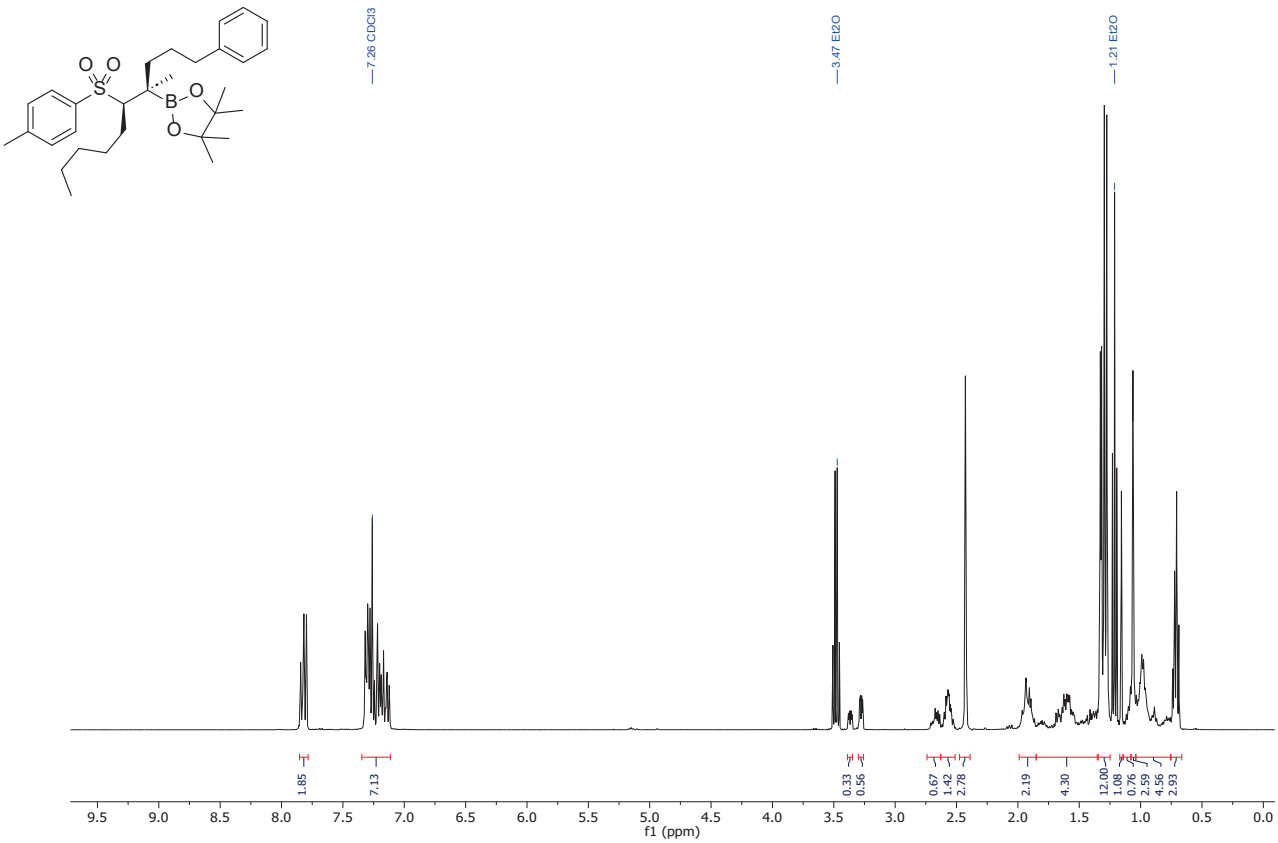
^{11}B NMR (96 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyldecan-4-yl)-1,3,2-dioxaborolane (44)

Mix of diastereomer

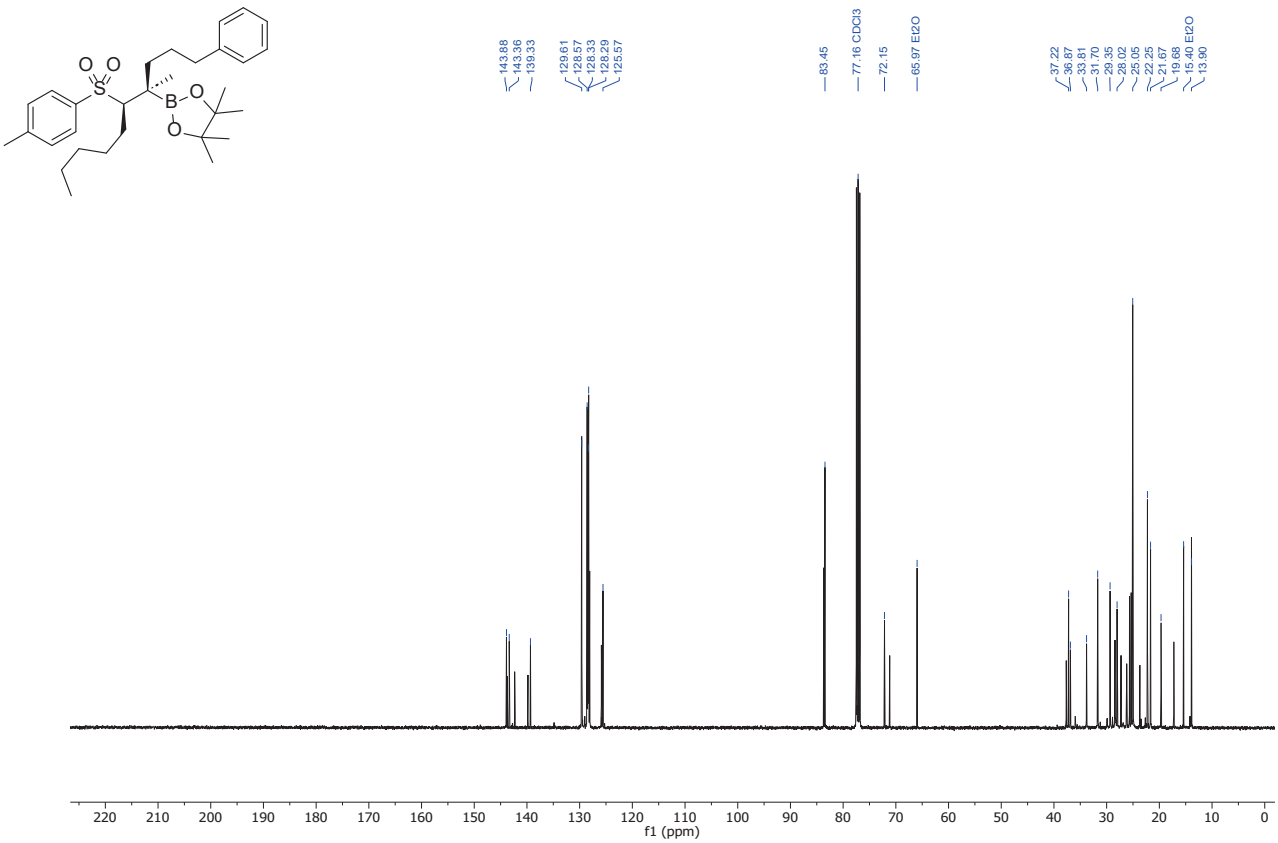
^{1}H NMR (300 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyldecan-4-yl)-1,3,2-dioxaborolane (44)

Major diastereomer

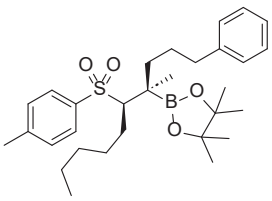
^{13}C NMR (75 MHz, $CDCl_3$)

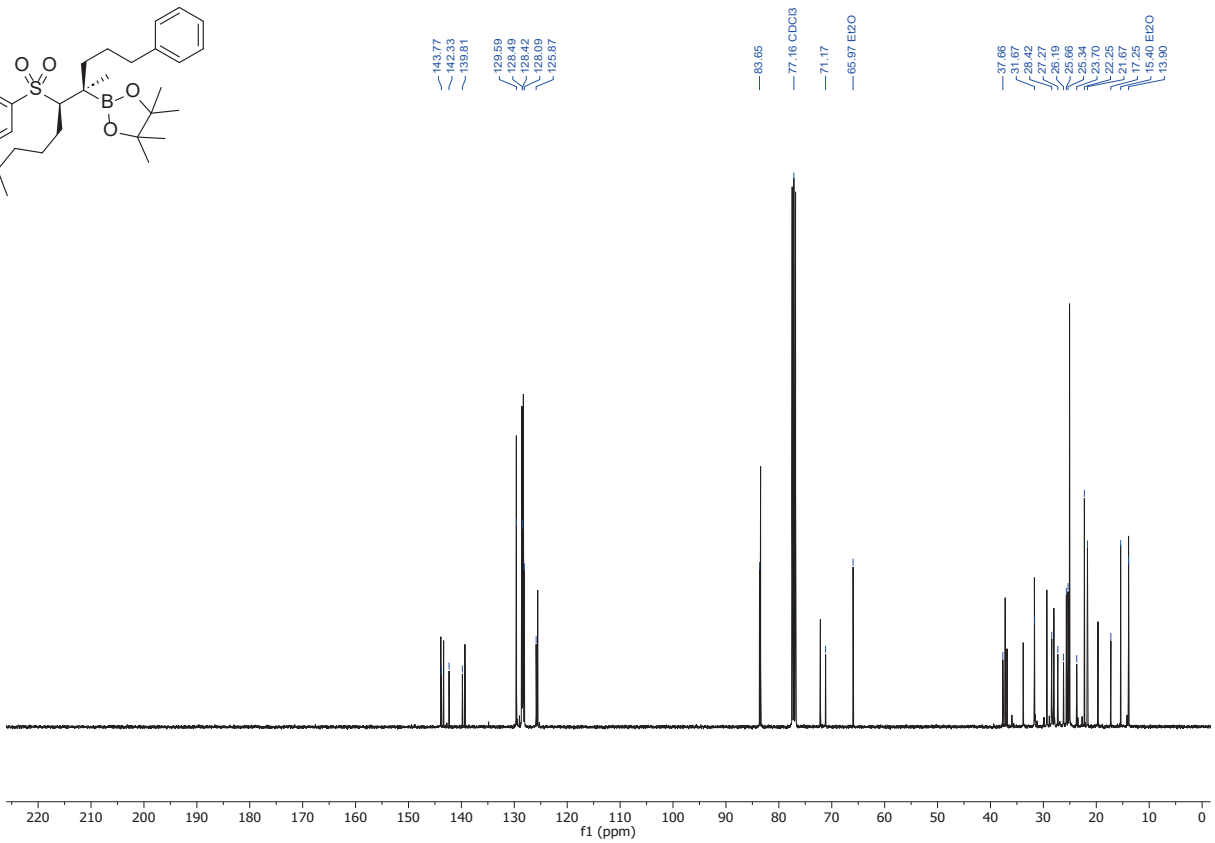


4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyldecan-4-yl)-1,3,2-dioxaborolane (44)

Minor diastereomer

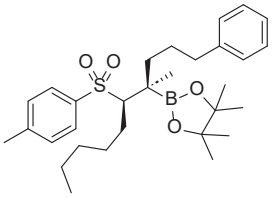
^{13}C NMR (75 MHz, $CDCl_3$)

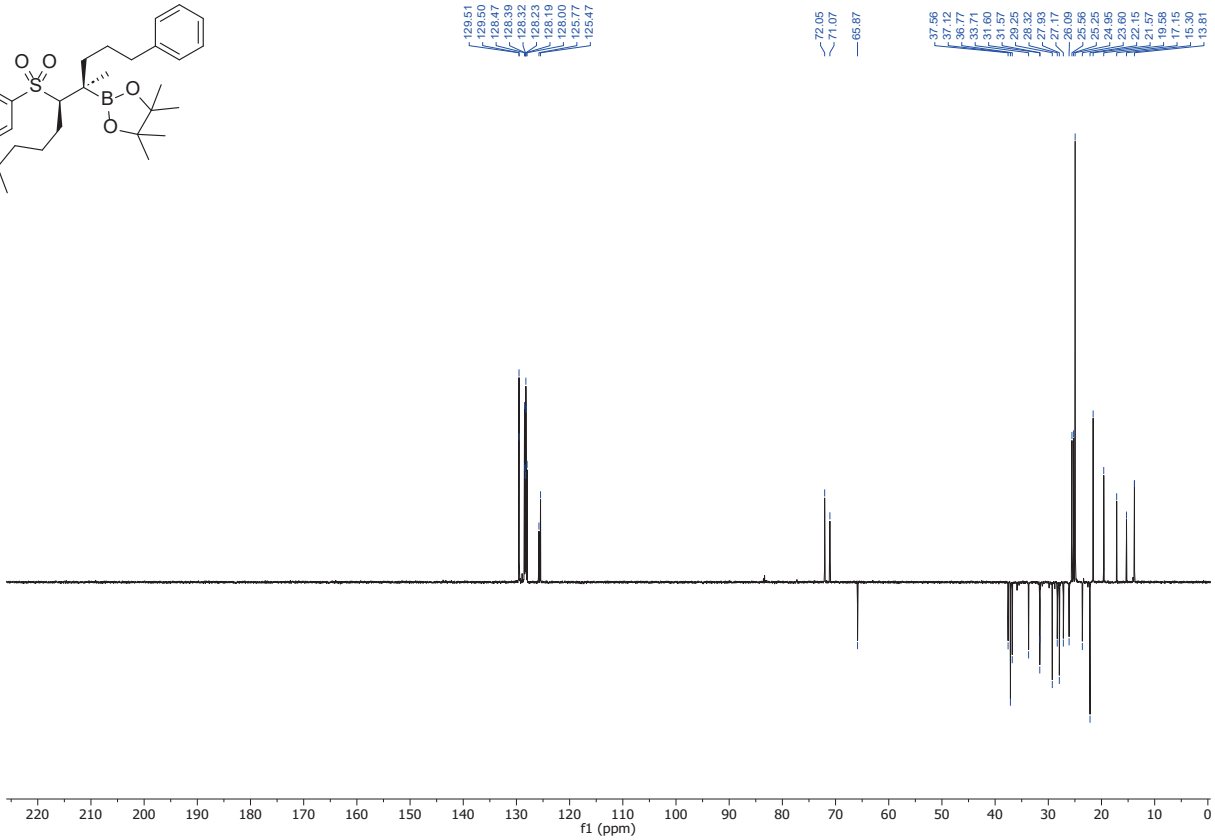




4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyldecan-4-yl)-1,3,2-dioxaborolane (44)

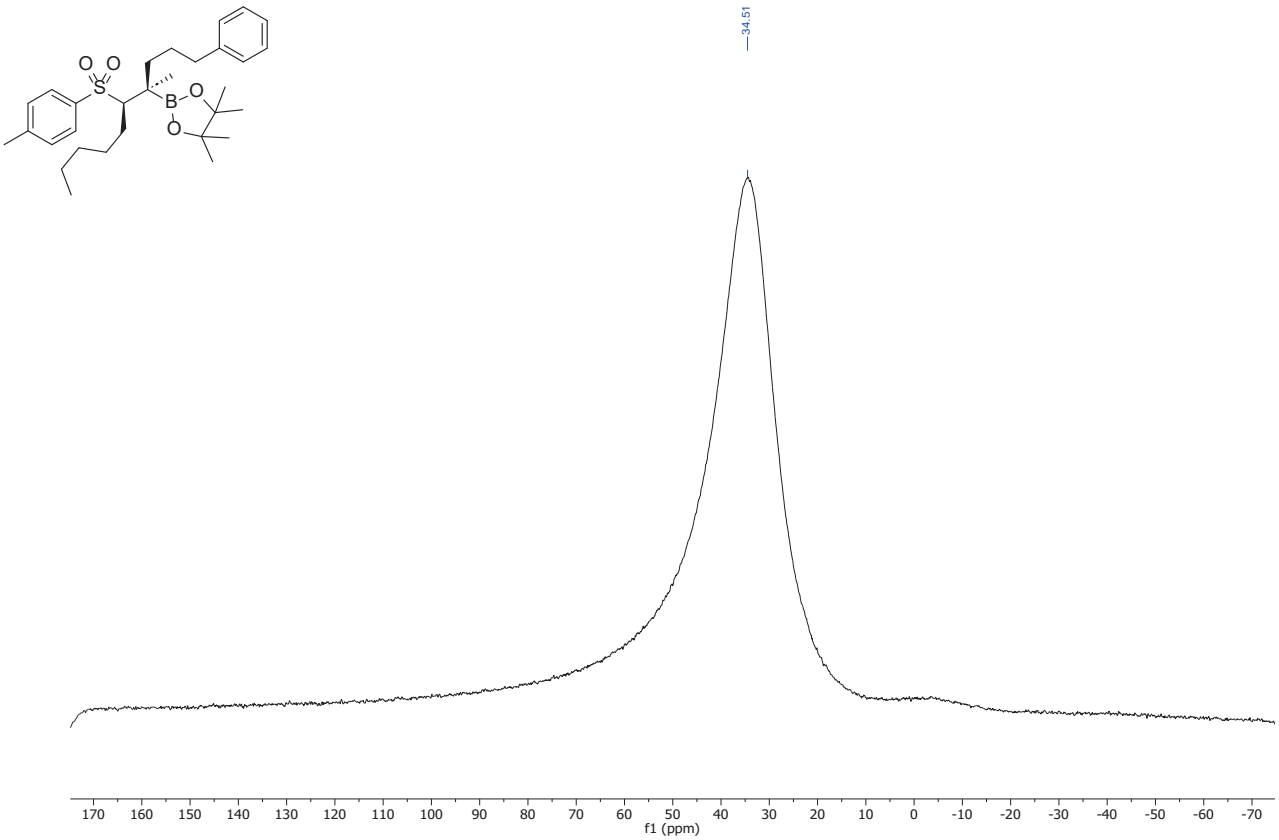
^{13}C NMR Dept-135 (100 MHz, $CDCl_3$)





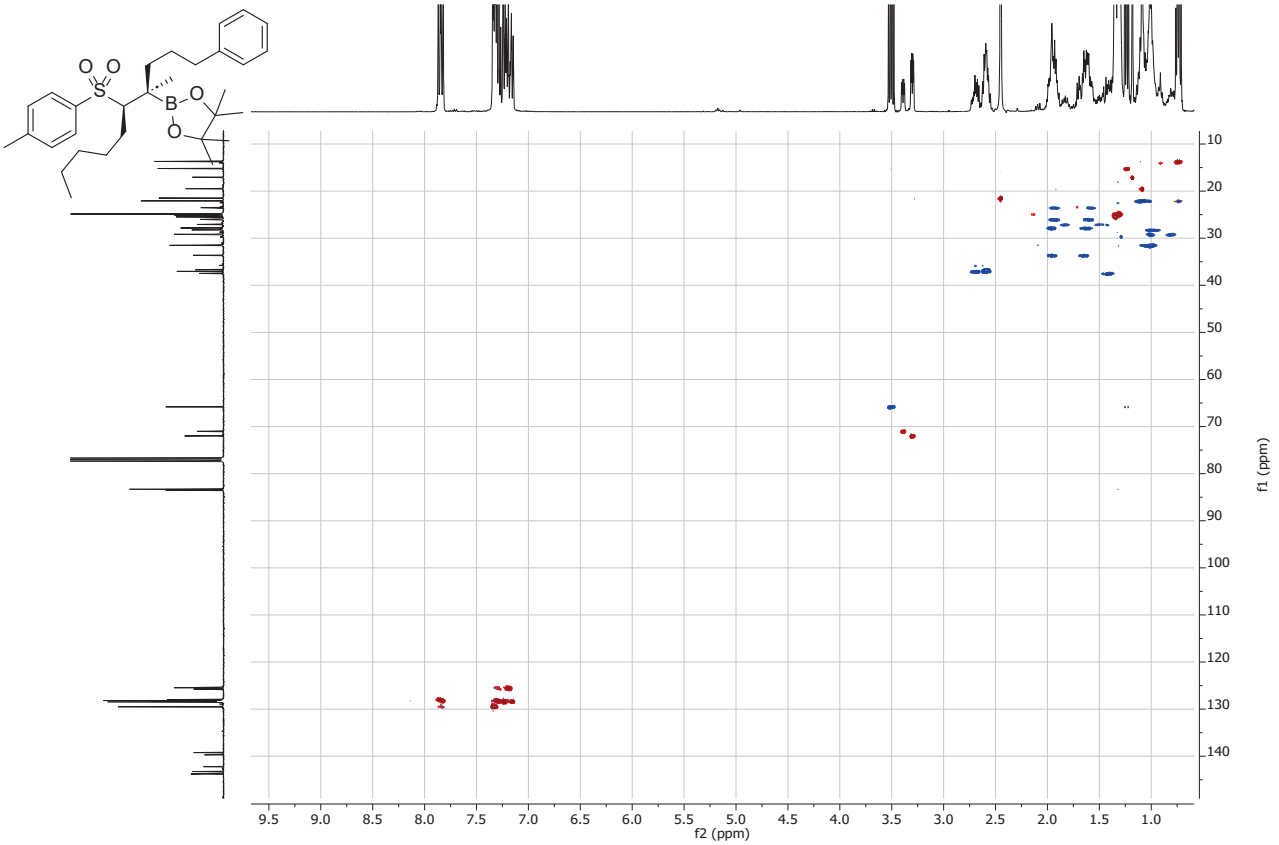
4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyldecan-4-yl)-1,3,2-dioxaborolane (44)

^{11}B NMR (96 MHz, $CDCl_3$)



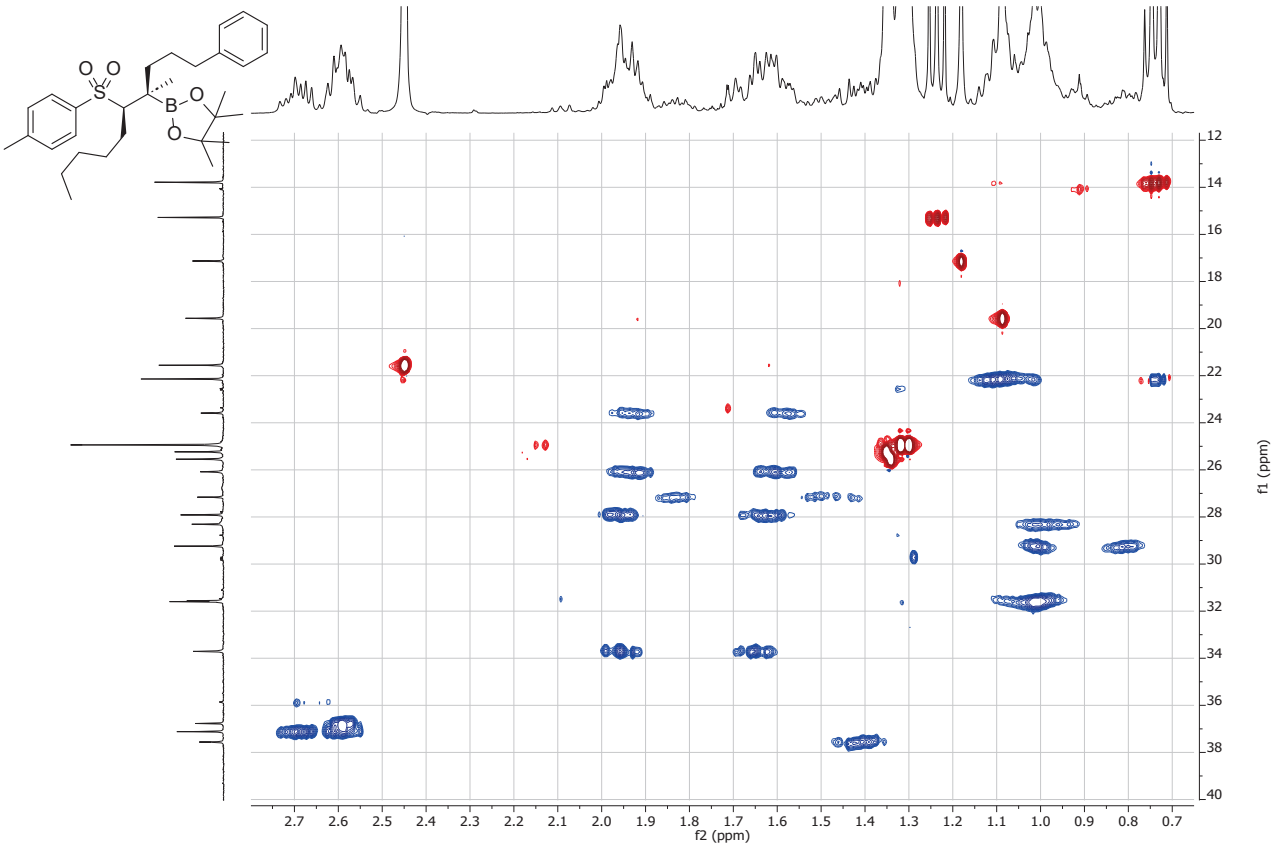
4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyldecan-4-yl)-1,3,2-dioxaborolane (44)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



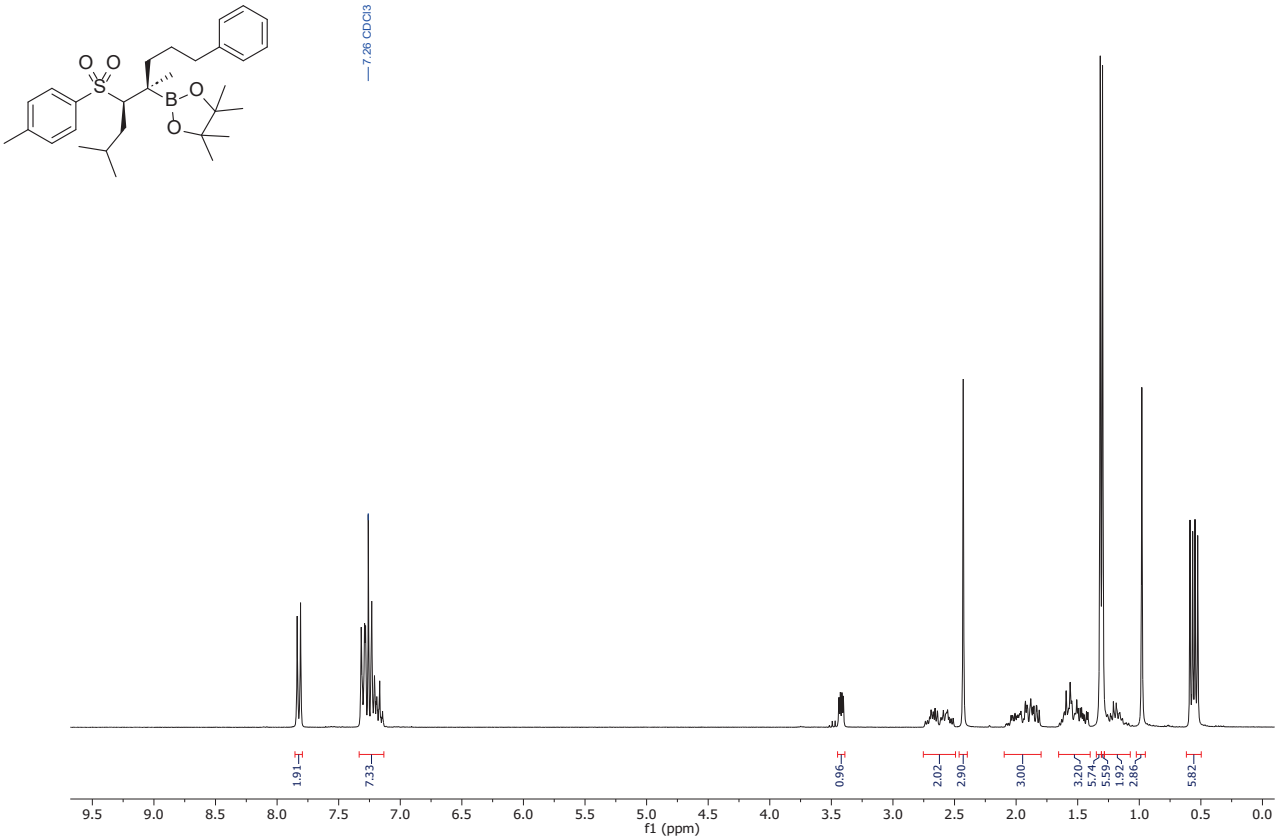
4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyldecan-4-yl)-1,3,2-dioxaborolane (44)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



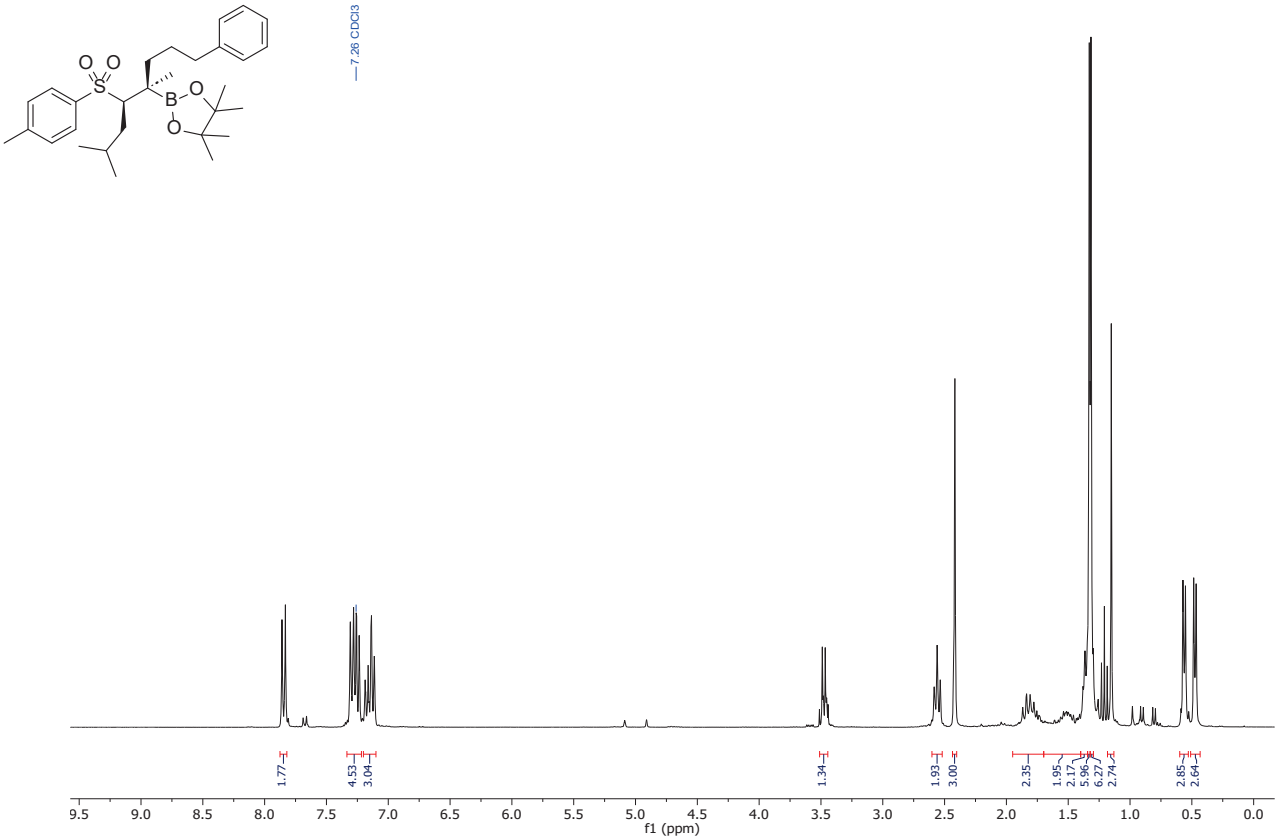
2-((4S,5R)-4,7-dimethyl-1-phenyl-5-tosyloctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (45)
Major diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



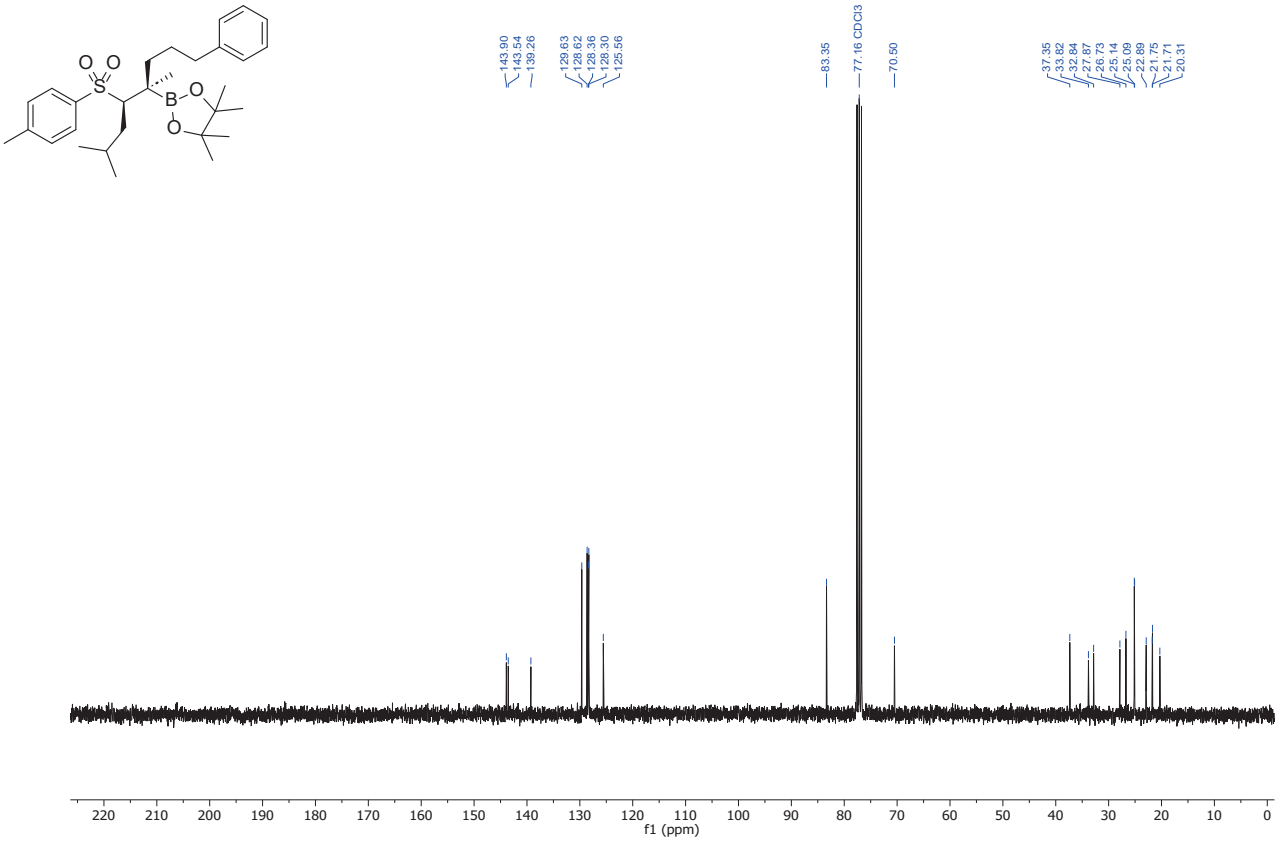
2-((4S,5R)-4,7-dimethyl-1-phenyl-5-tosyloctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (45)
Minor diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



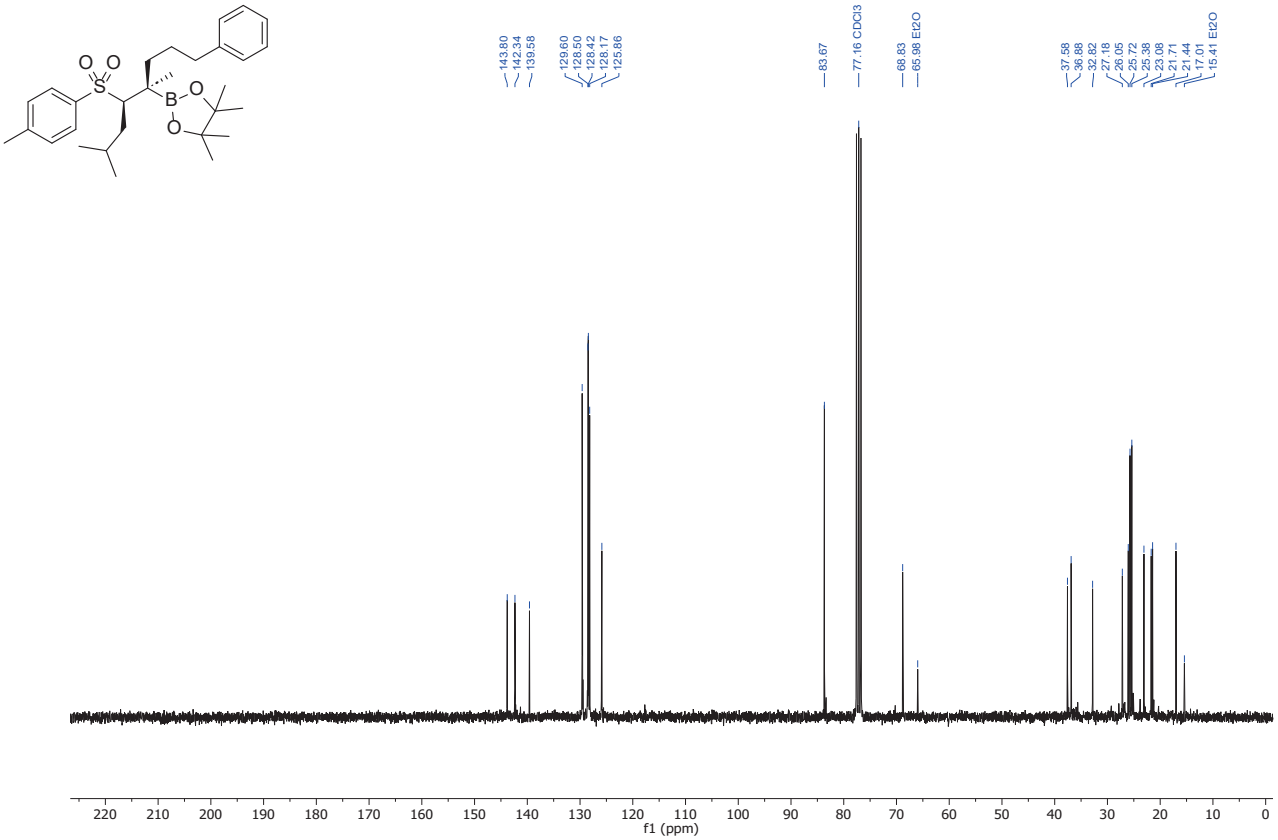
2-((4S,5R)-4,7-dimethyl-1-phenyl-5-tosyloctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (45)
Major diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



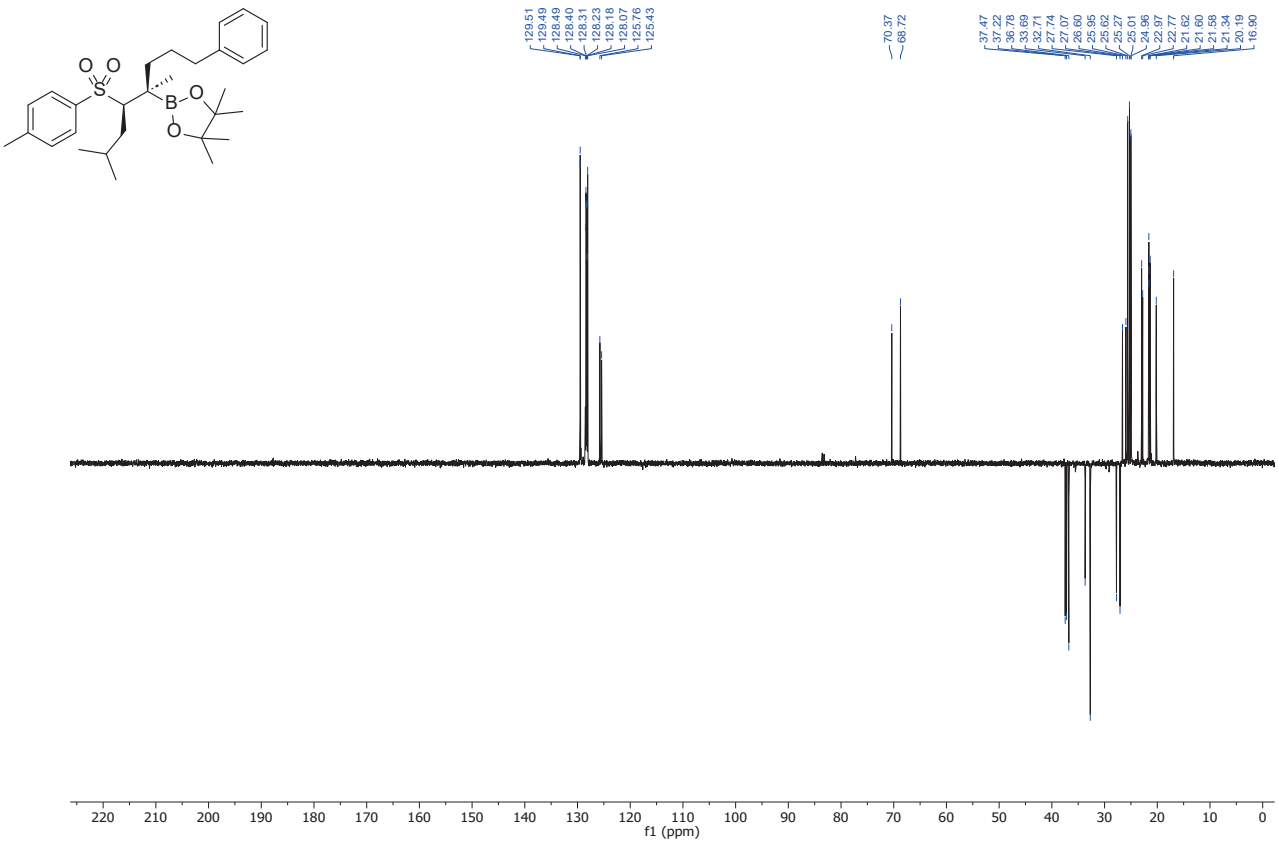
2-((4S,5R)-4,7-dimethyl-1-phenyl-5-tosyloctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (45)
Minor diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



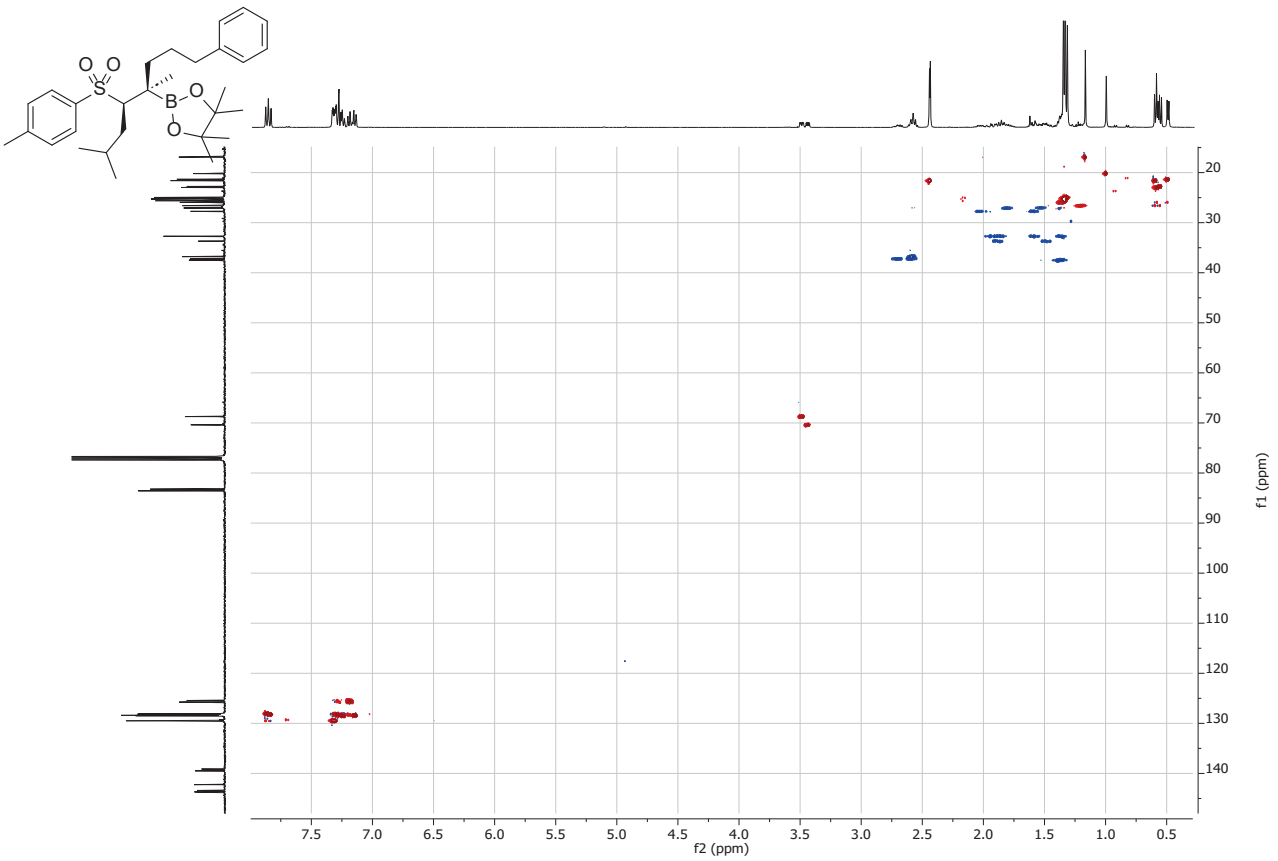
2-((4S,5R)-4,7-dimethyl-1-phenyl-5-tosyloctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (45)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



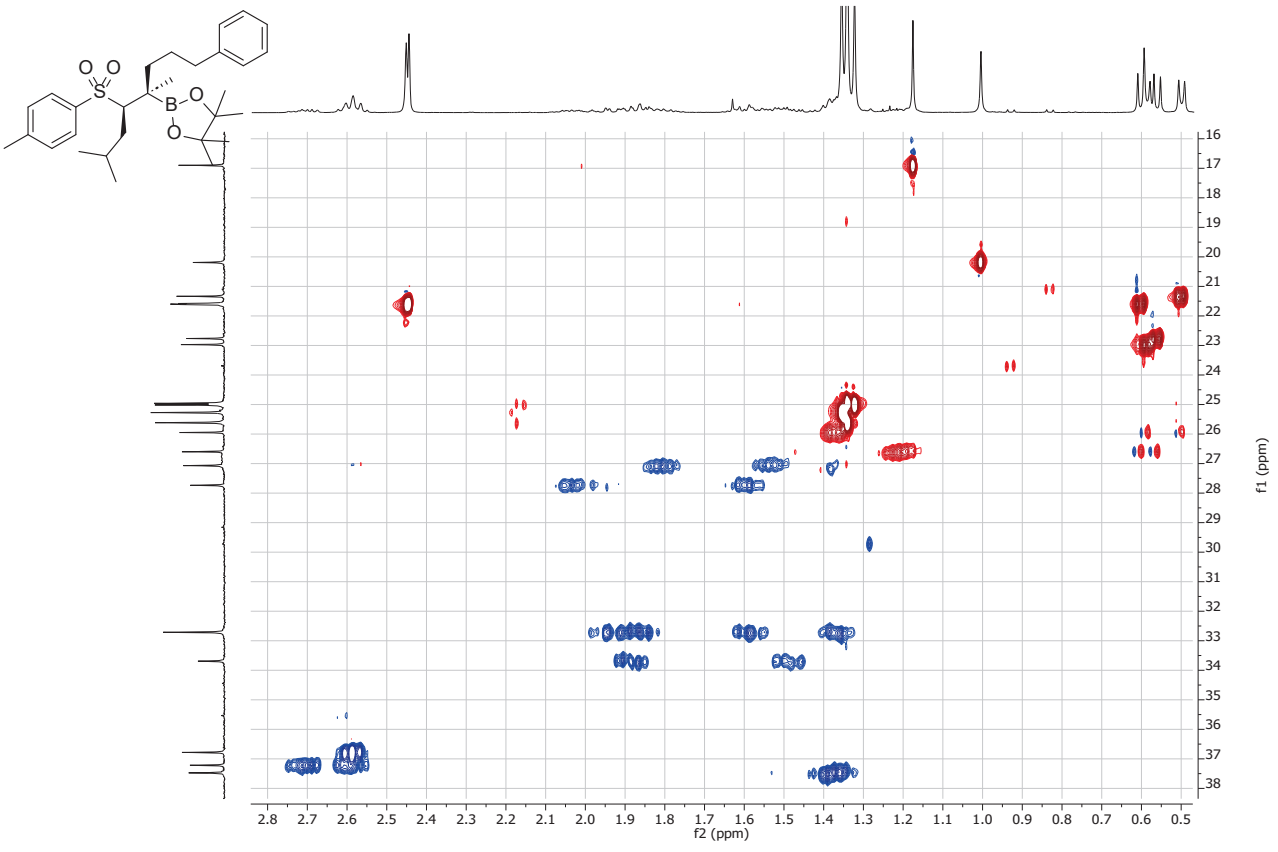
2-((4S,5R)-4,7-dimethyl-1-phenyl-5-tosyloctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (45)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



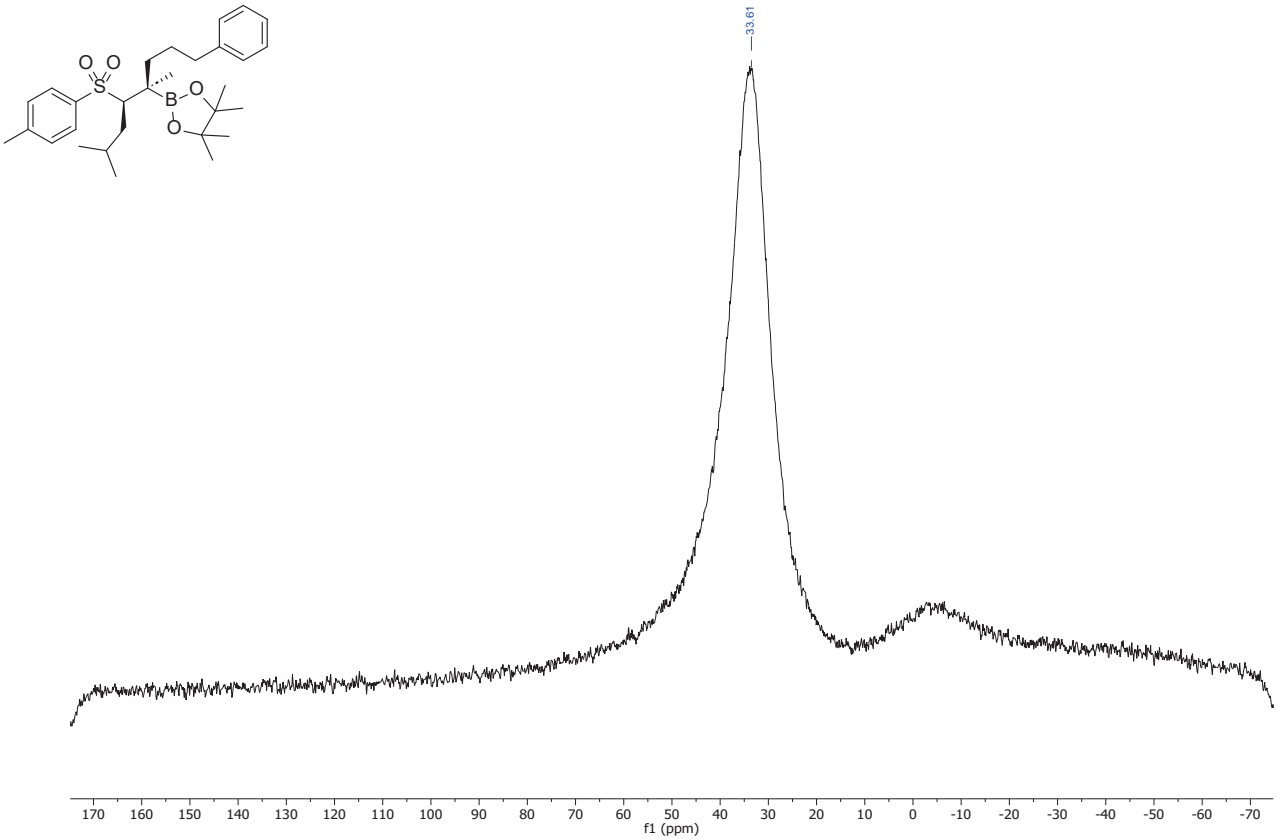
2-((4S,5R)-4,7-dimethyl-1-phenyl-5-tosyloctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (45)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



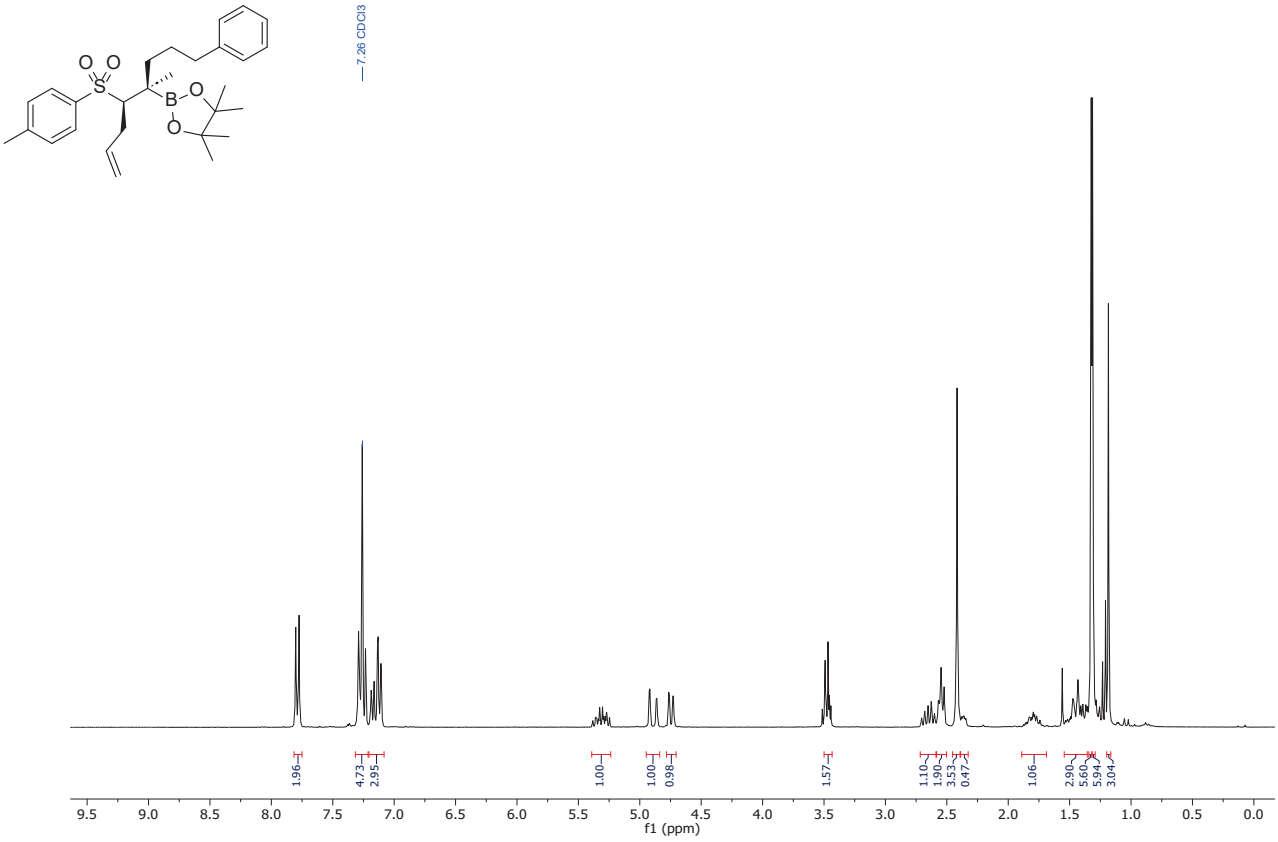
2-((4S,5R)-4,7-dimethyl-1-phenyl-5-tosyloctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (45)

^{11}B NMR (96 MHz, $CDCl_3$)



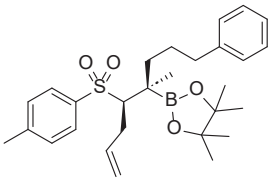
4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyloct-7-en-4-yl)-1,3,2-dioxaborolane (41)
Major diastereomer

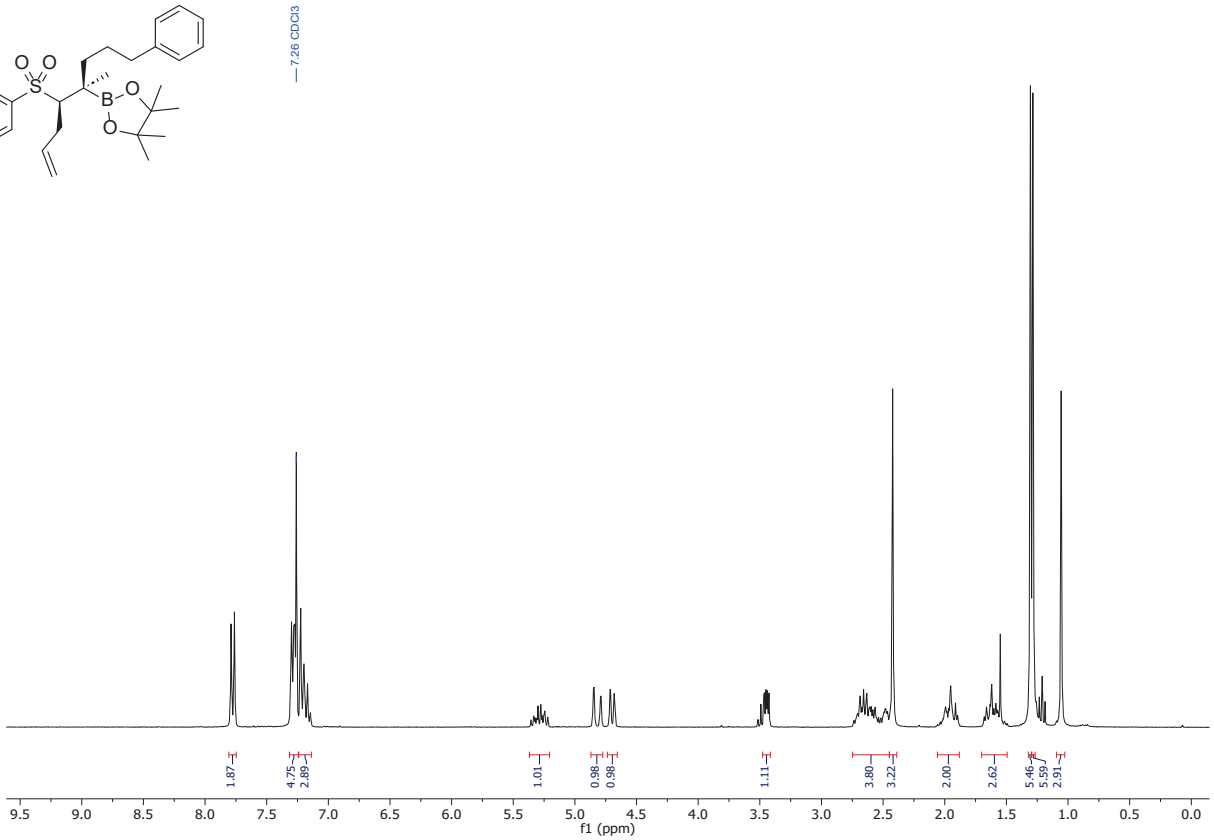
^{1}H NMR (300 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyloct-7-en-4-yl)-1,3,2-dioxaborolane (41)
Minor diastereomer

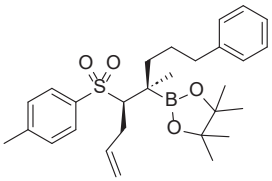
^{1}H NMR (300 MHz, $CDCl_3$)

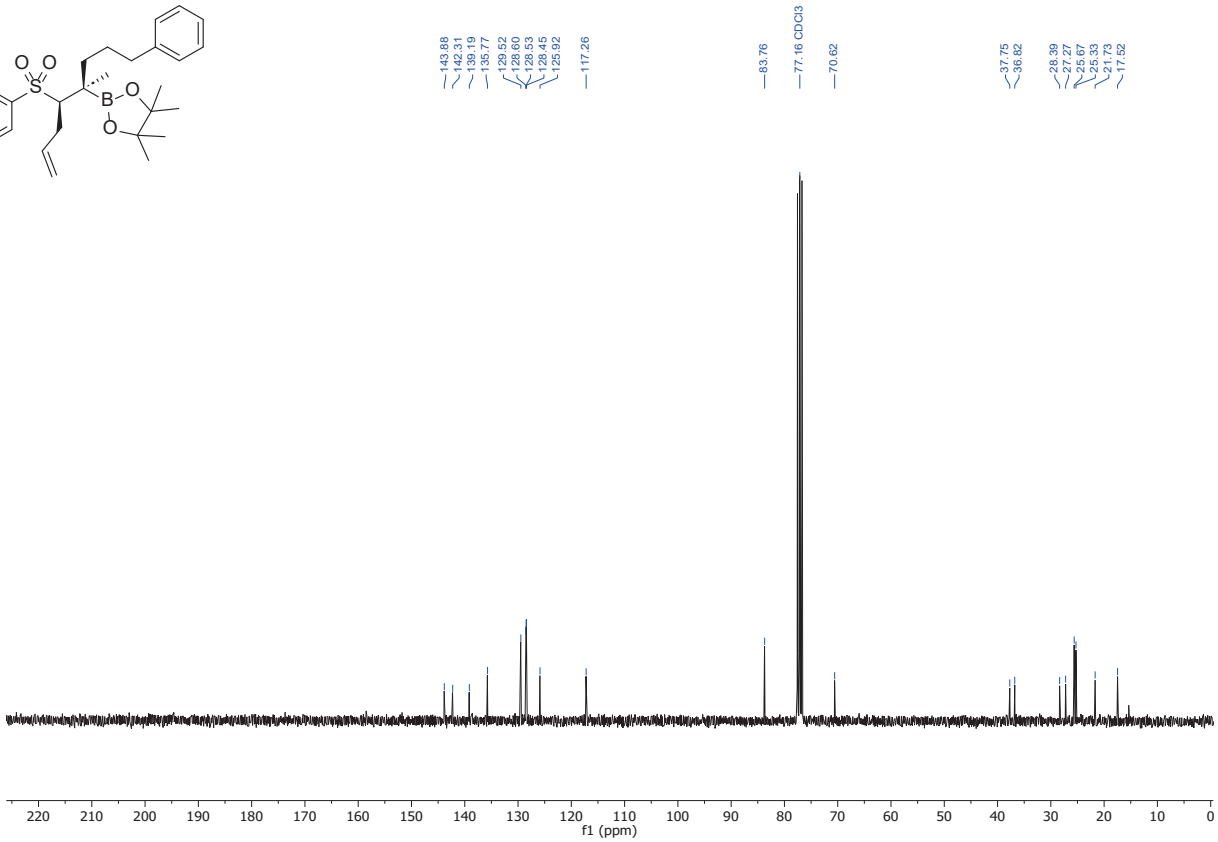




4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyloct-7-en-4-yl)-1,3,2-dioxaborolane (41)
Major diastereomer

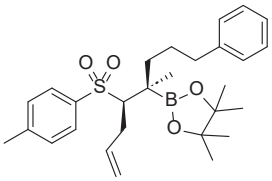
^{13}C NMR (75 MHz, $CDCl_3$)

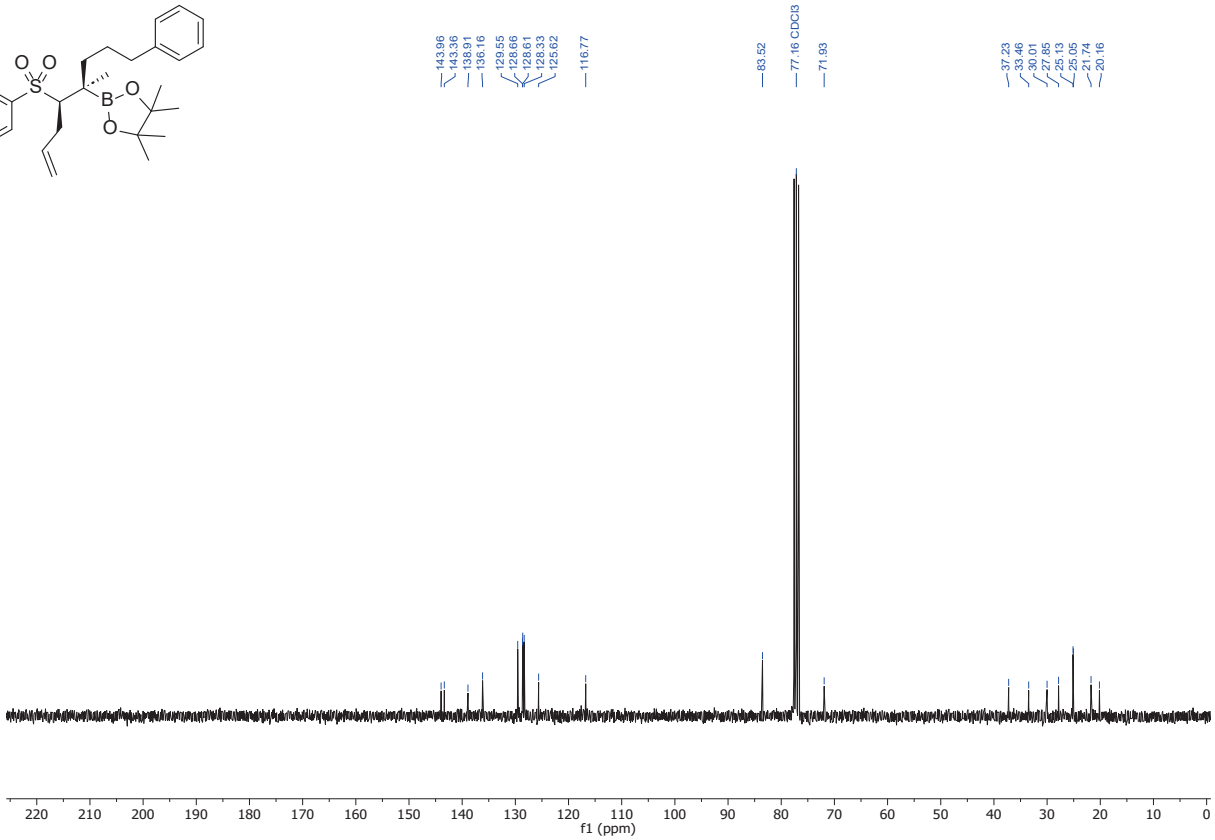




4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyloct-7-en-4-yl)-1,3,2-dioxaborolane (41)
Minor diastereomer

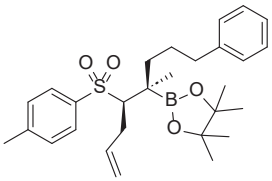
^{13}C NMR (75 MHz, $CDCl_3$)

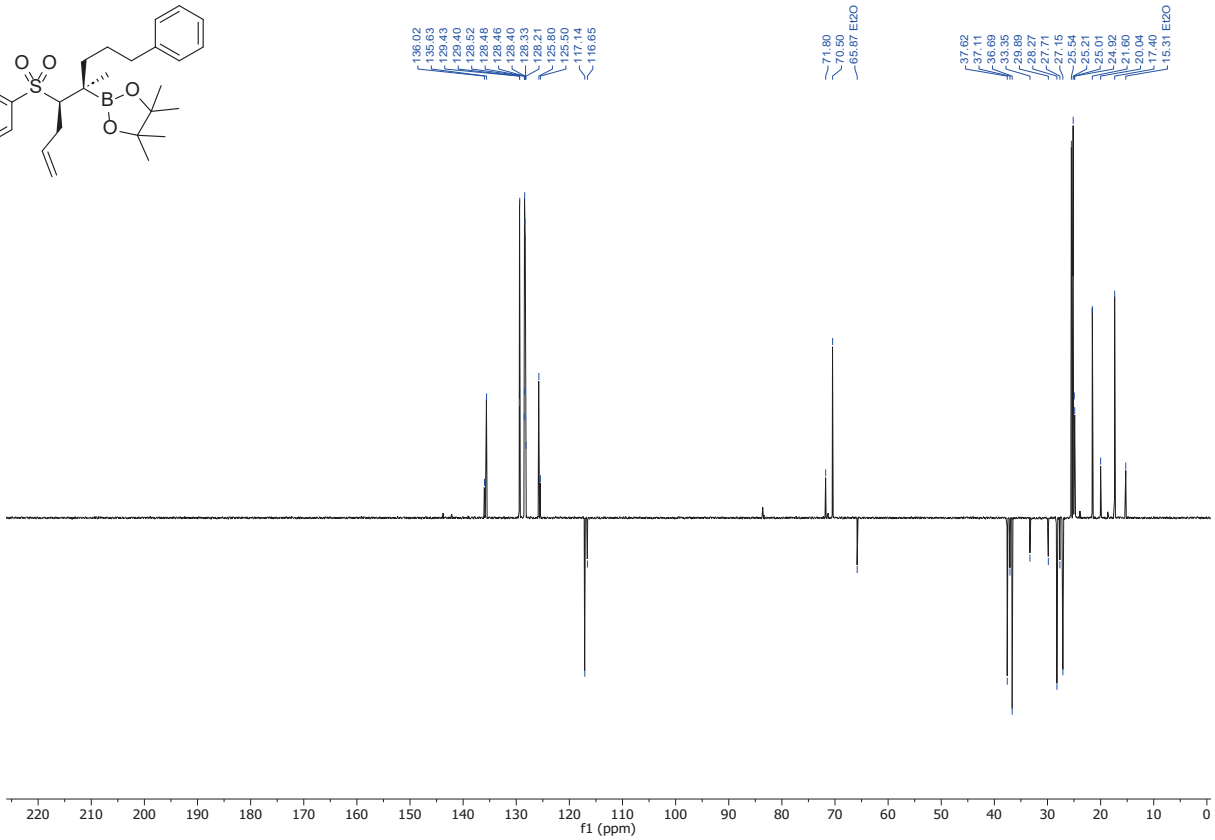




4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyloct-7-en-4-yl)-1,3,2-dioxaborolane (41)

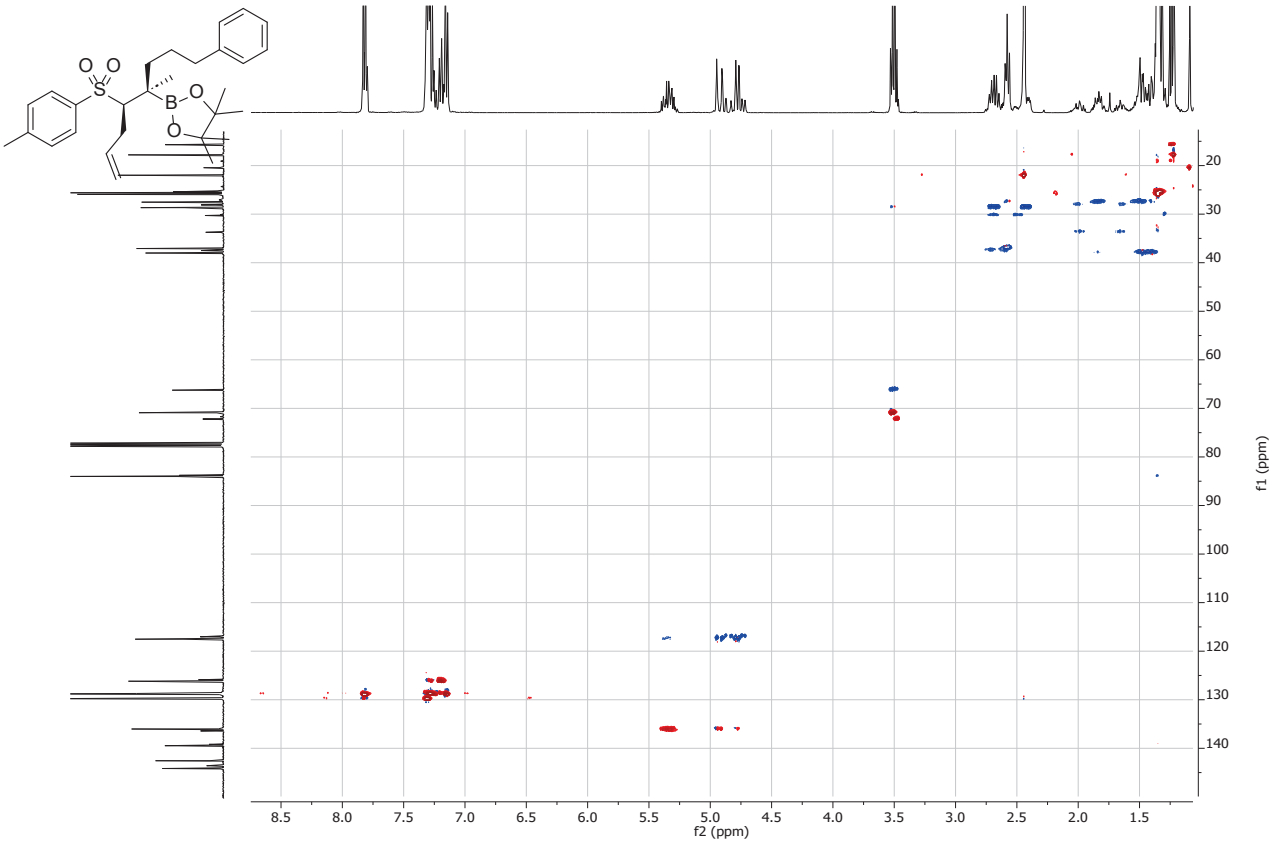
^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)





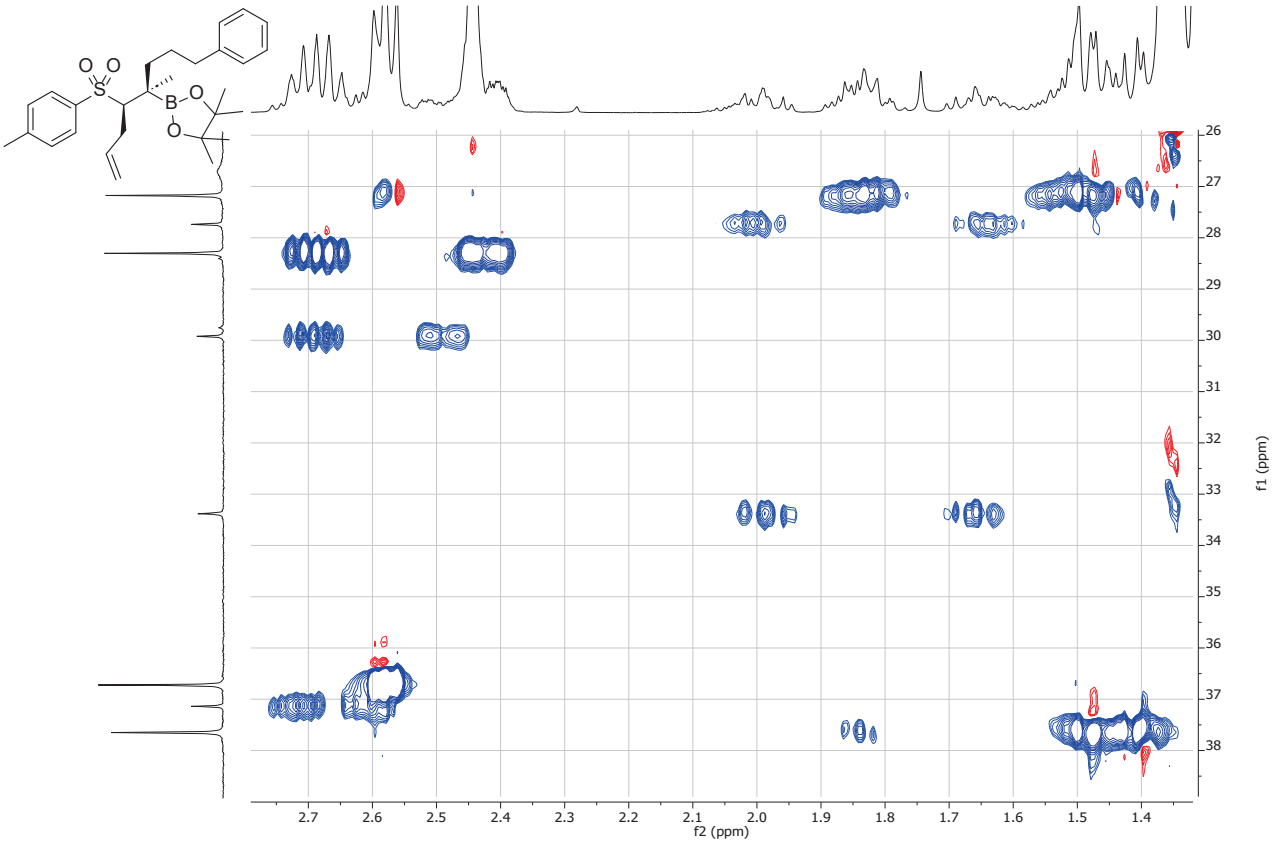
4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyloct-7-en-4-yl)-1,3,2-dioxaborolane (41)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



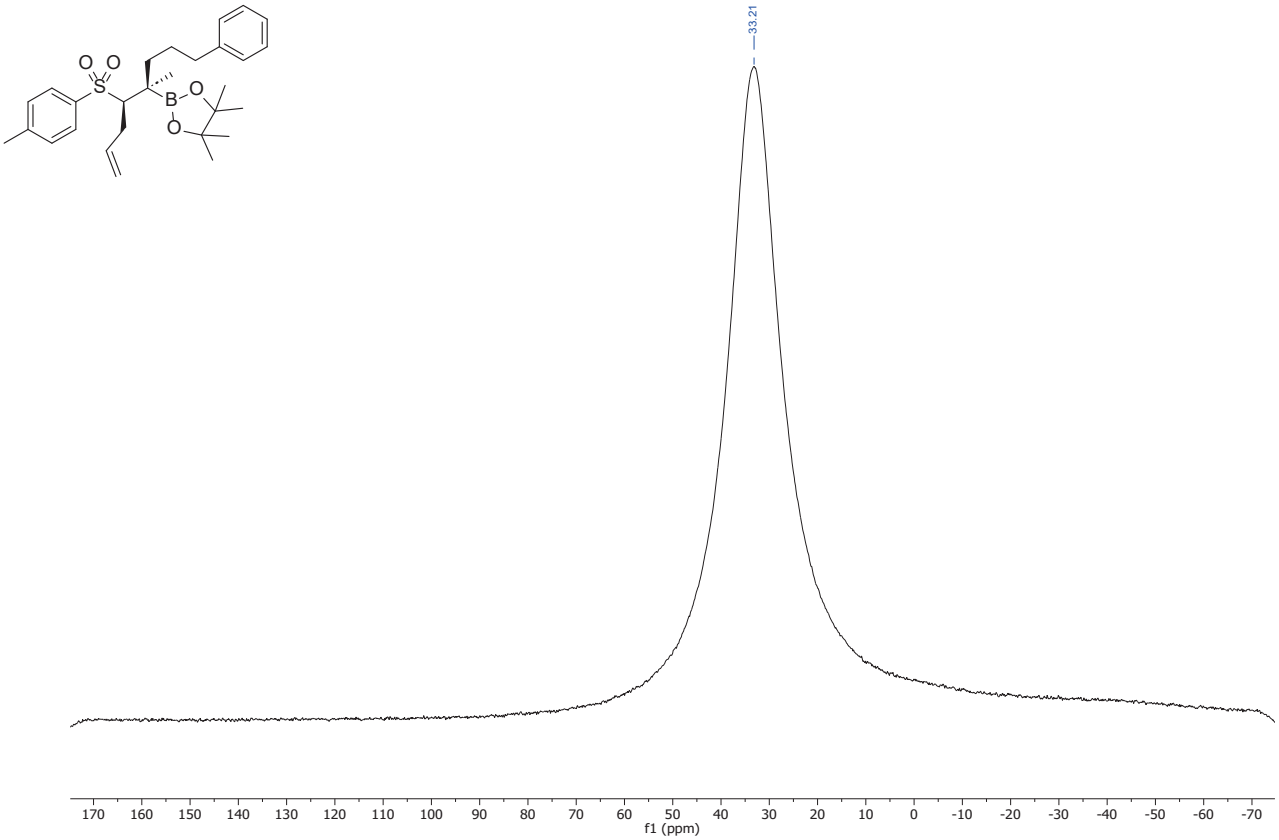
4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyloct-7-en-4-yl)-1,3,2-dioxaborolane (41)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



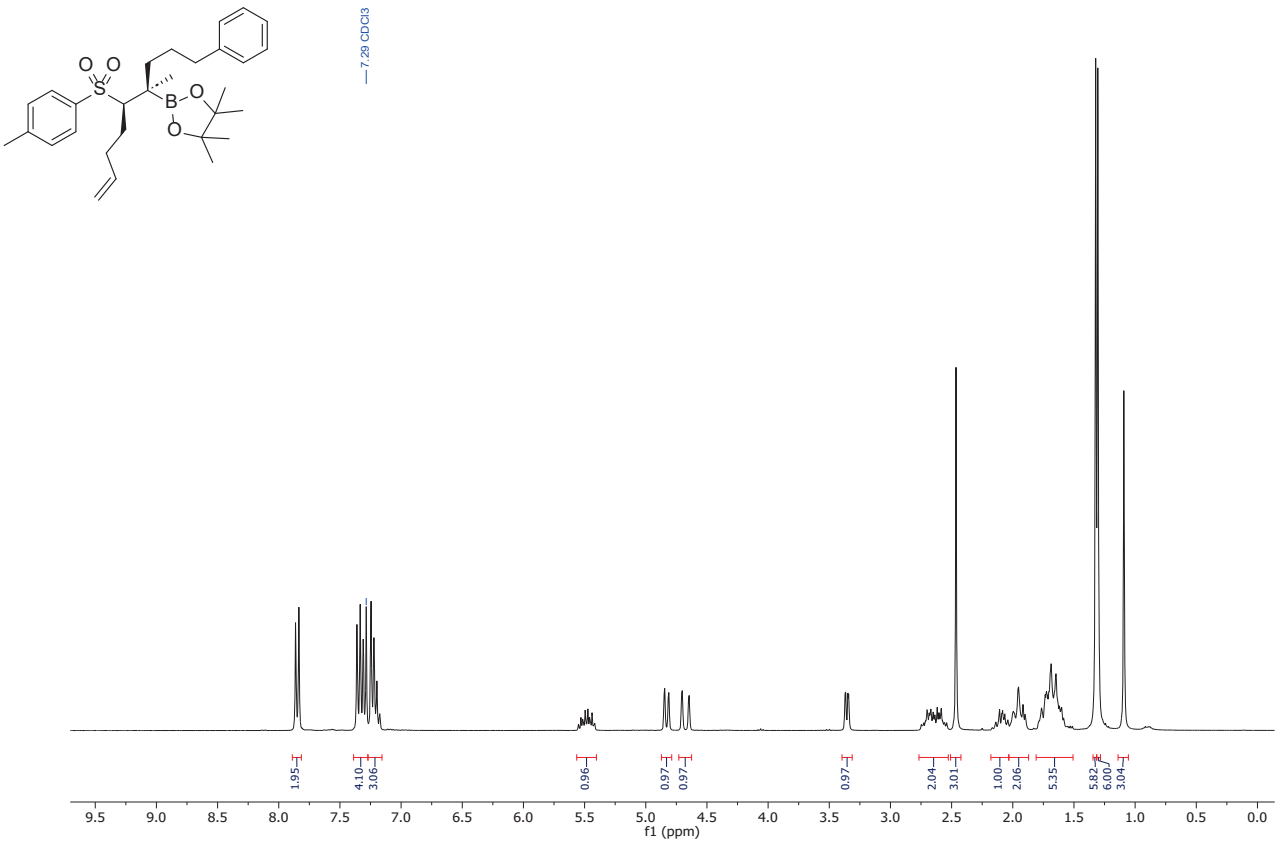
4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosyloct-7-en-4-yl)-1,3,2-dioxaborolane (41)

^{11}B NMR (96 MHz, $CDCl_3$)



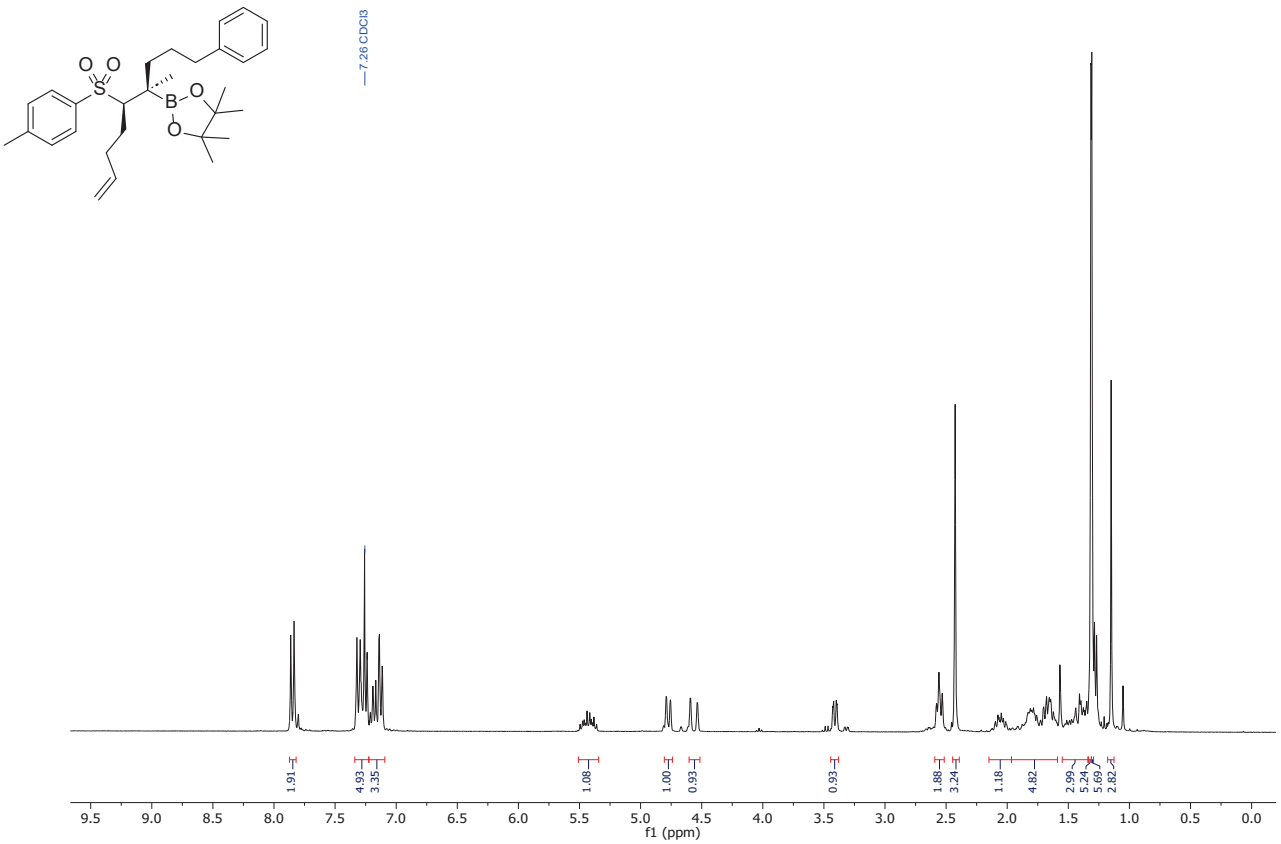
4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosylnon-8-en-4-yl)-1,3,2-dioxaborolane (46)
Major diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



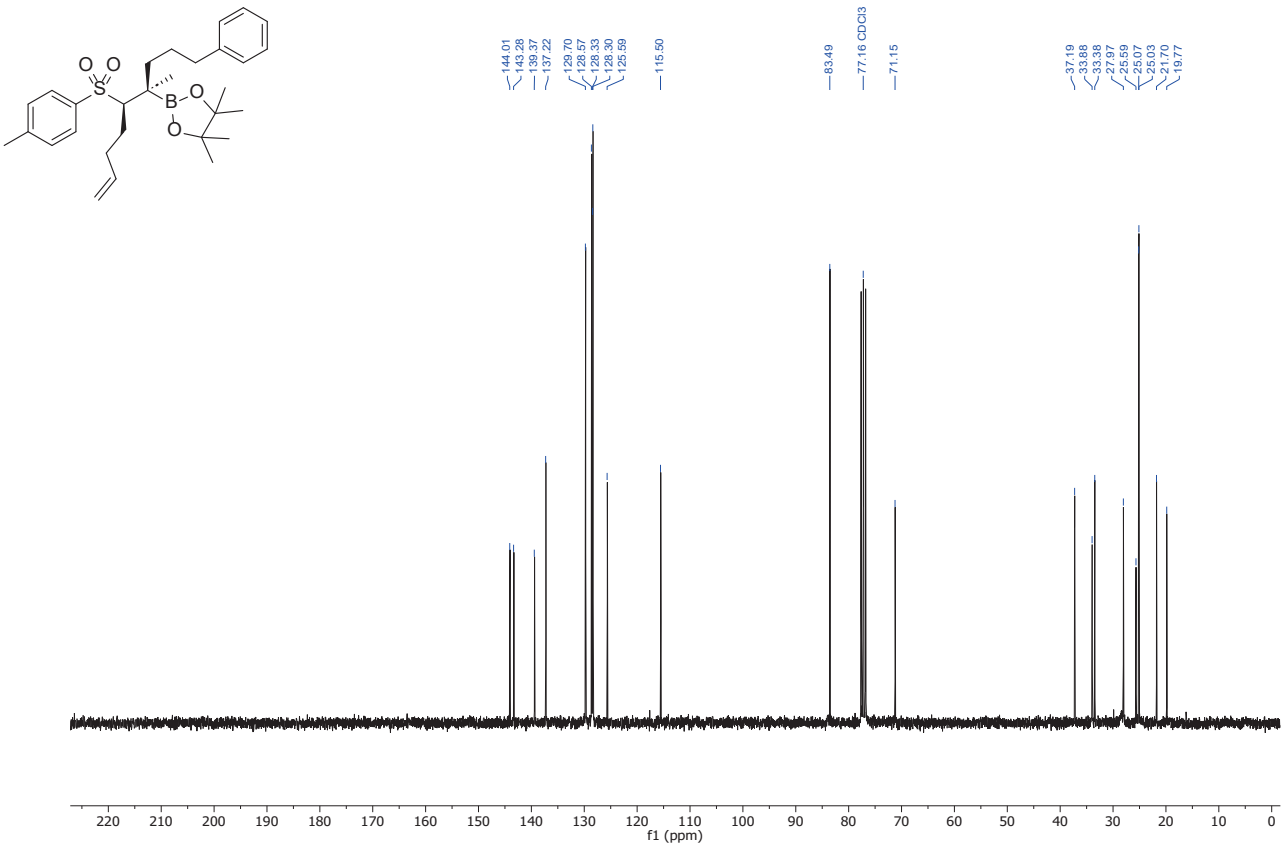
4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosylnon-8-en-4-yl)-1,3,2-dioxaborolane (46)
Minor diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



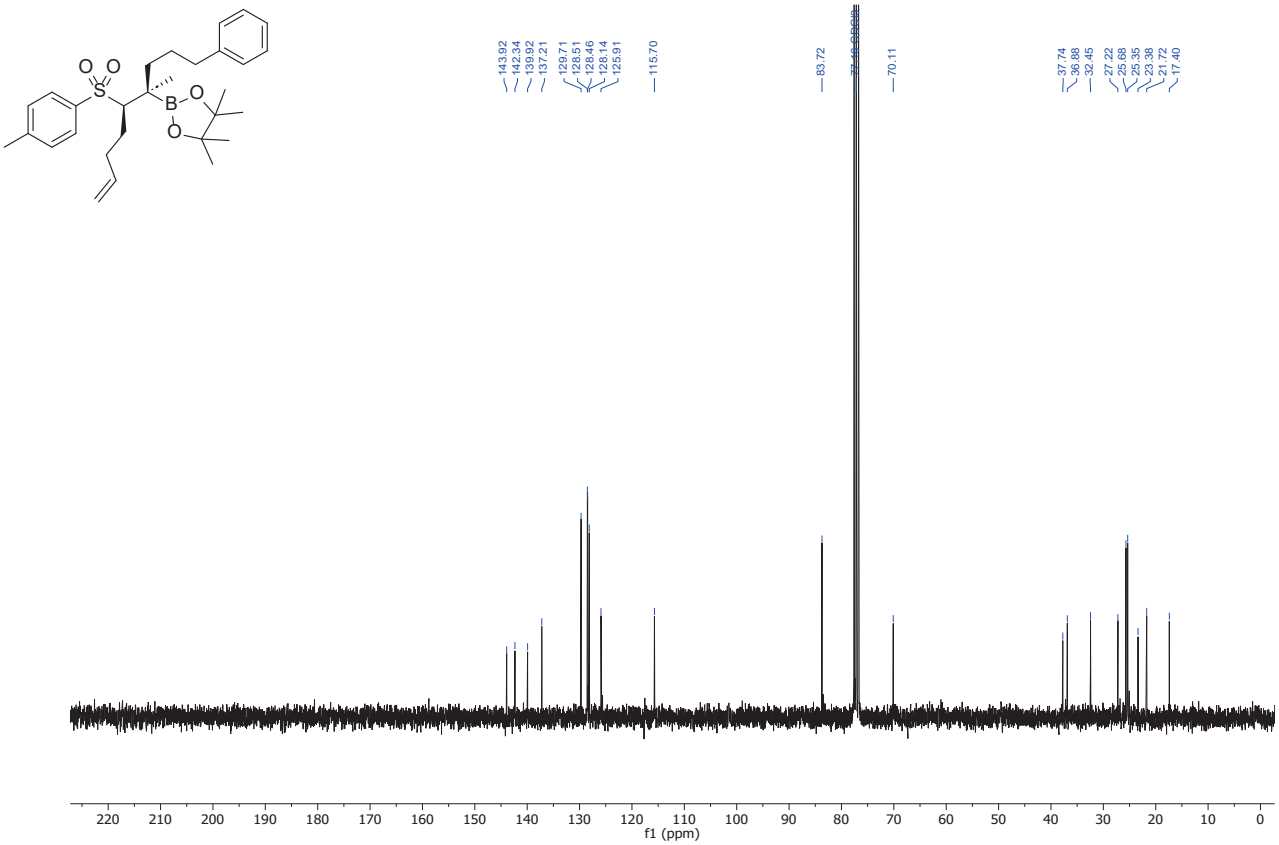
4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosylnon-8-en-4-yl)-1,3,2-dioxaborolane (46)
Major diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



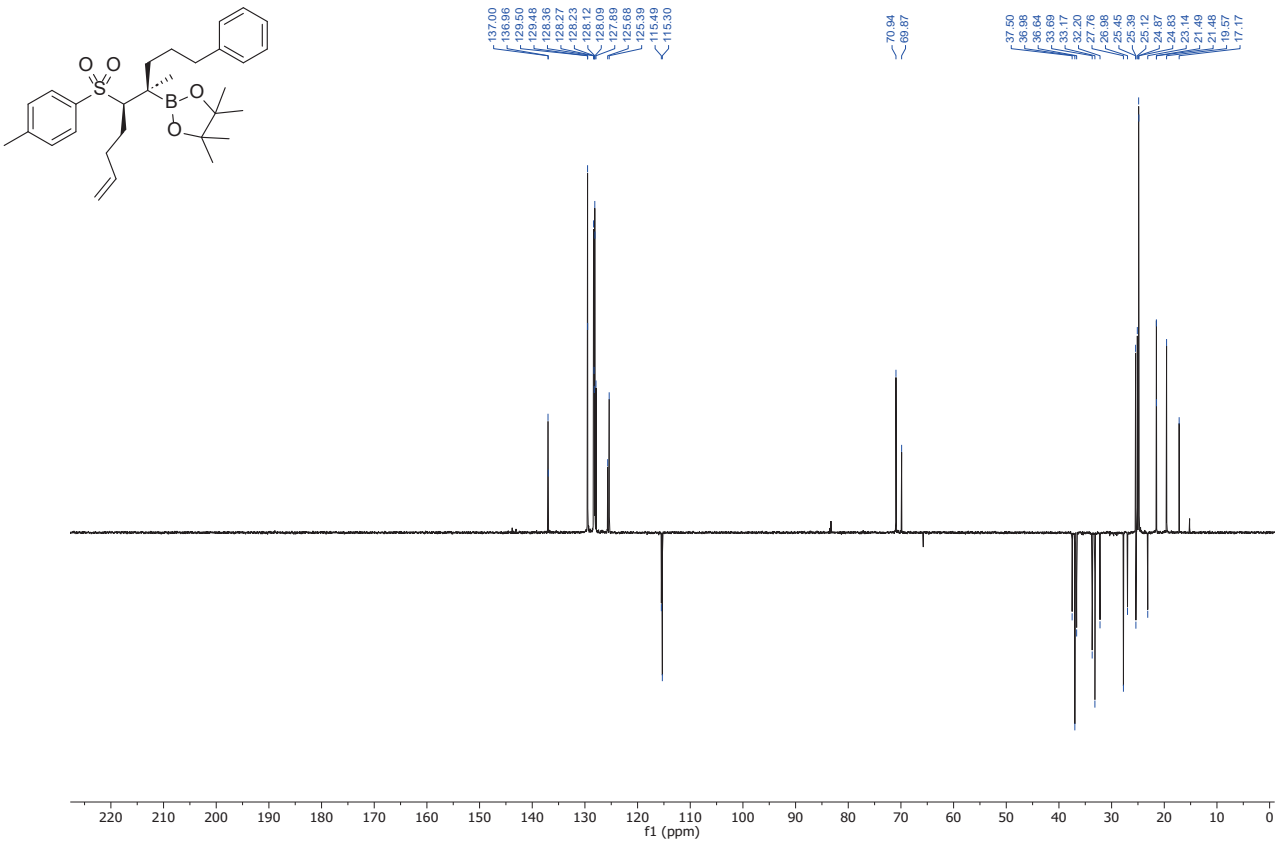
4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosylnon-8-en-4-yl)-1,3,2-dioxaborolane (46)
Minor diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



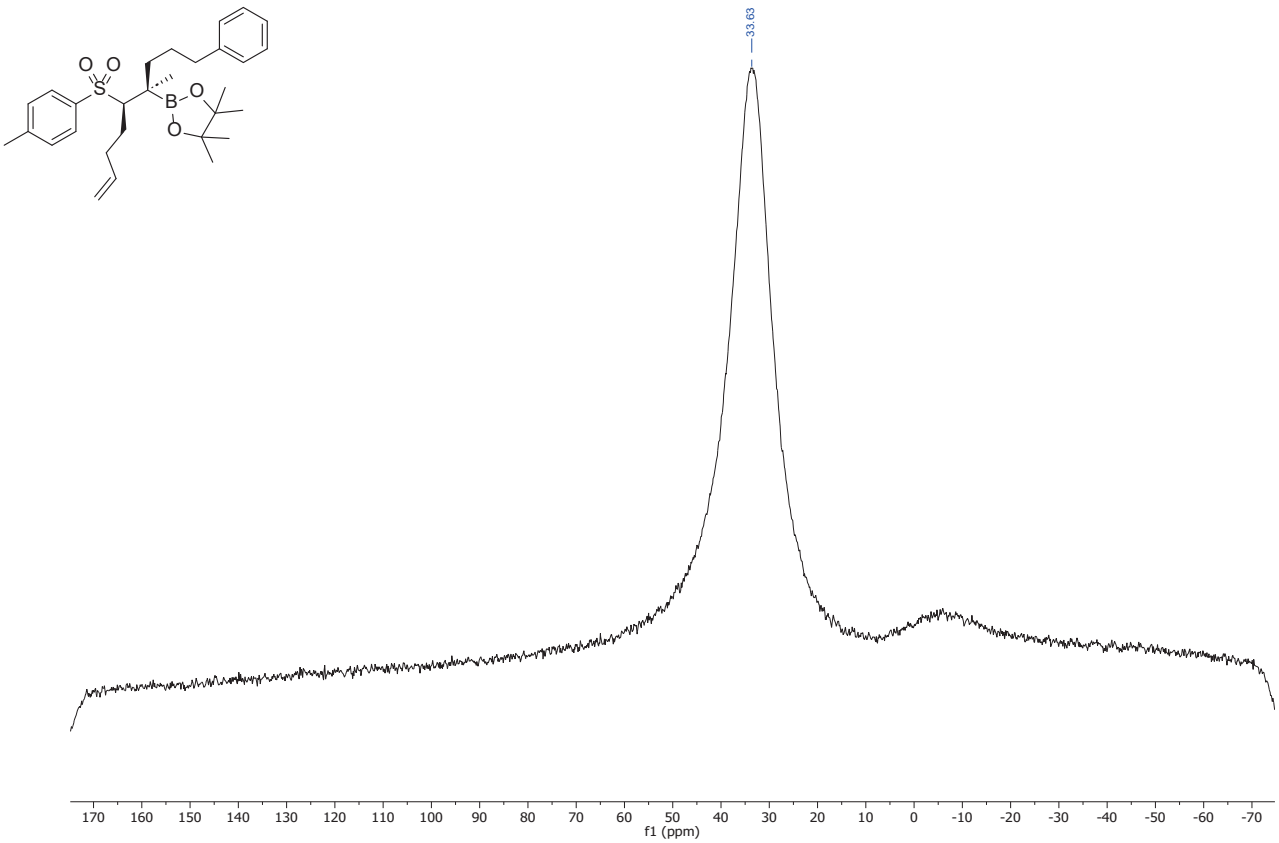
4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosylnon-8-en-4-yl)-1,3,2-dioxaborolane (46)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



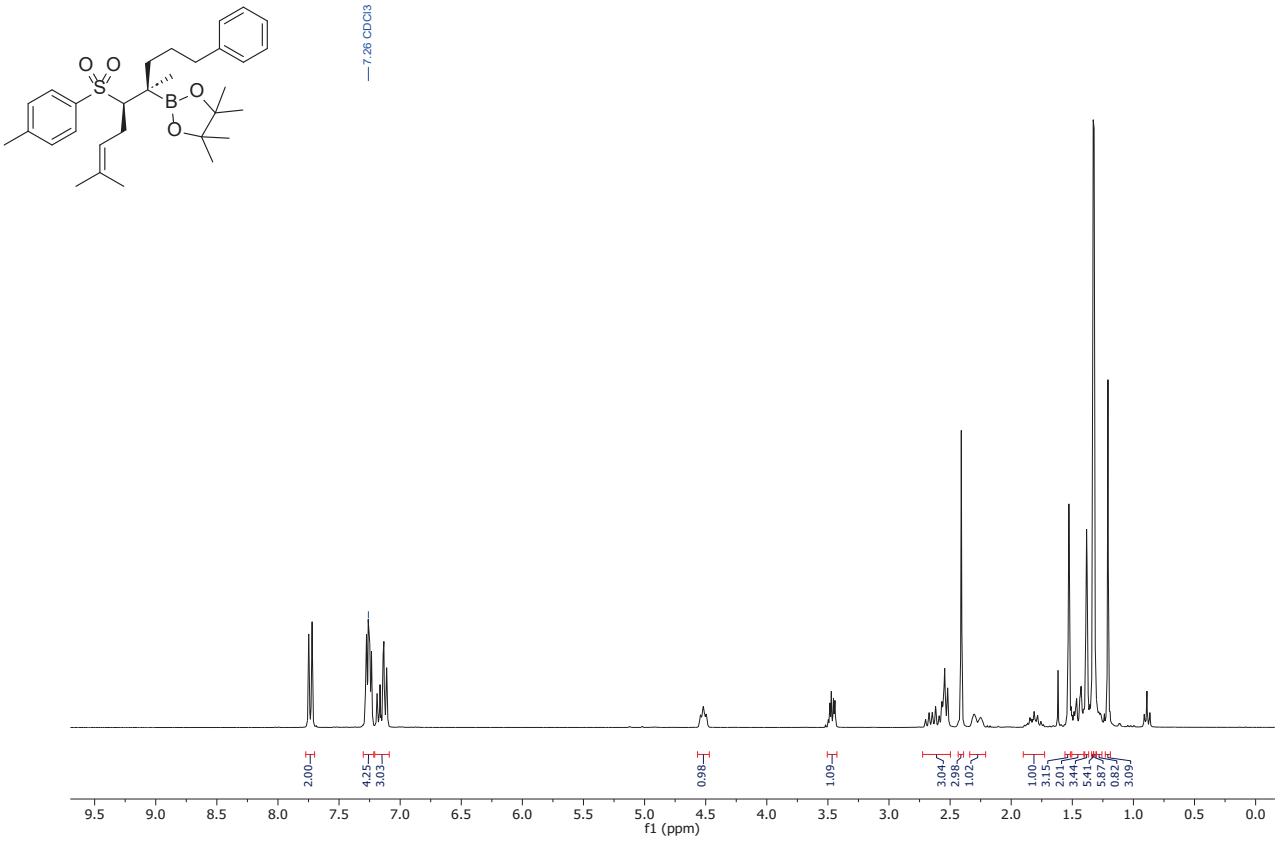
4,4,5,5-tetramethyl-2-((4S,5R)-4-methyl-1-phenyl-5-tosylnon-8-en-4-yl)-1,3,2-dioxaborolane (46)

^{11}B NMR (96 MHz, $CDCl_3$)



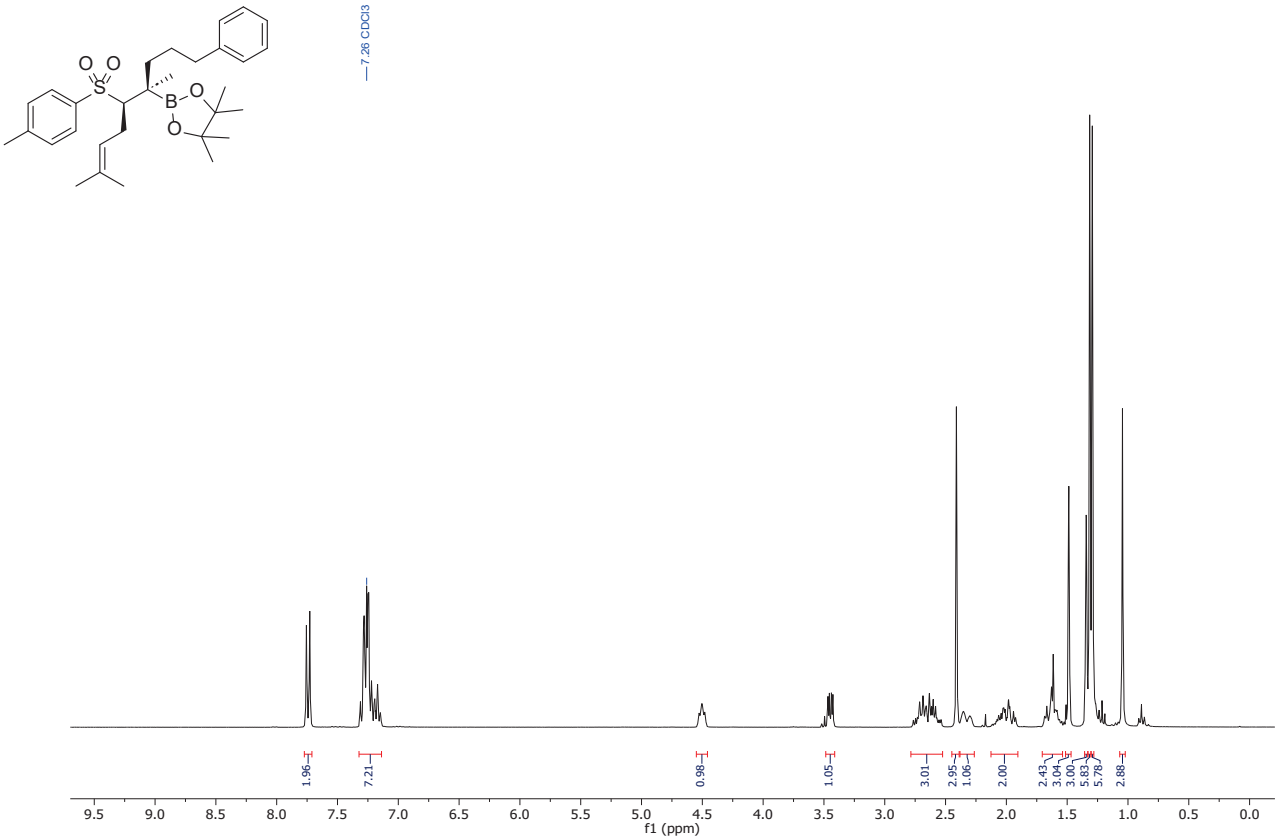
2-((4S,5R)-4,8-dimethyl-1-phenyl-5-tosylnon-7-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (42)
Major diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



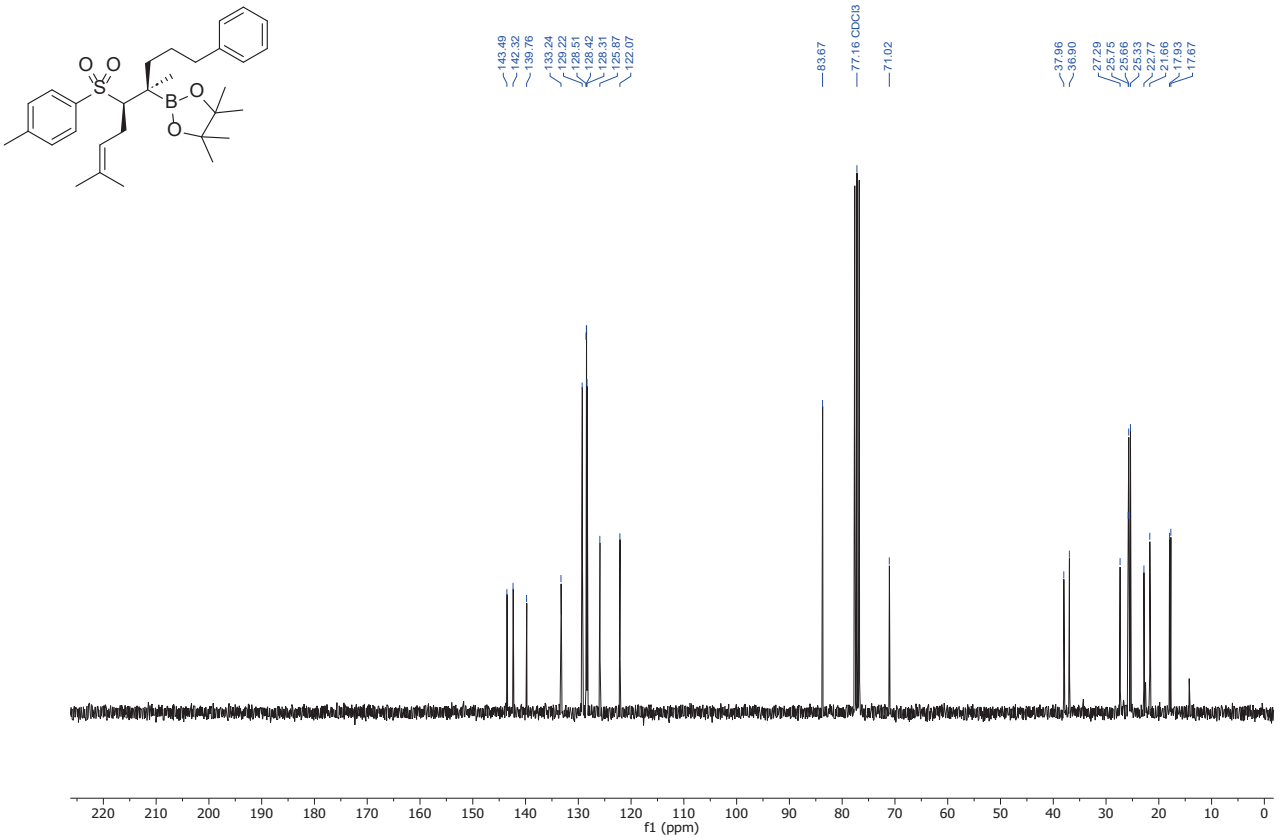
2-((4S,5R)-4,8-dimethyl-1-phenyl-5-tosylnon-7-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (42)
Minor diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



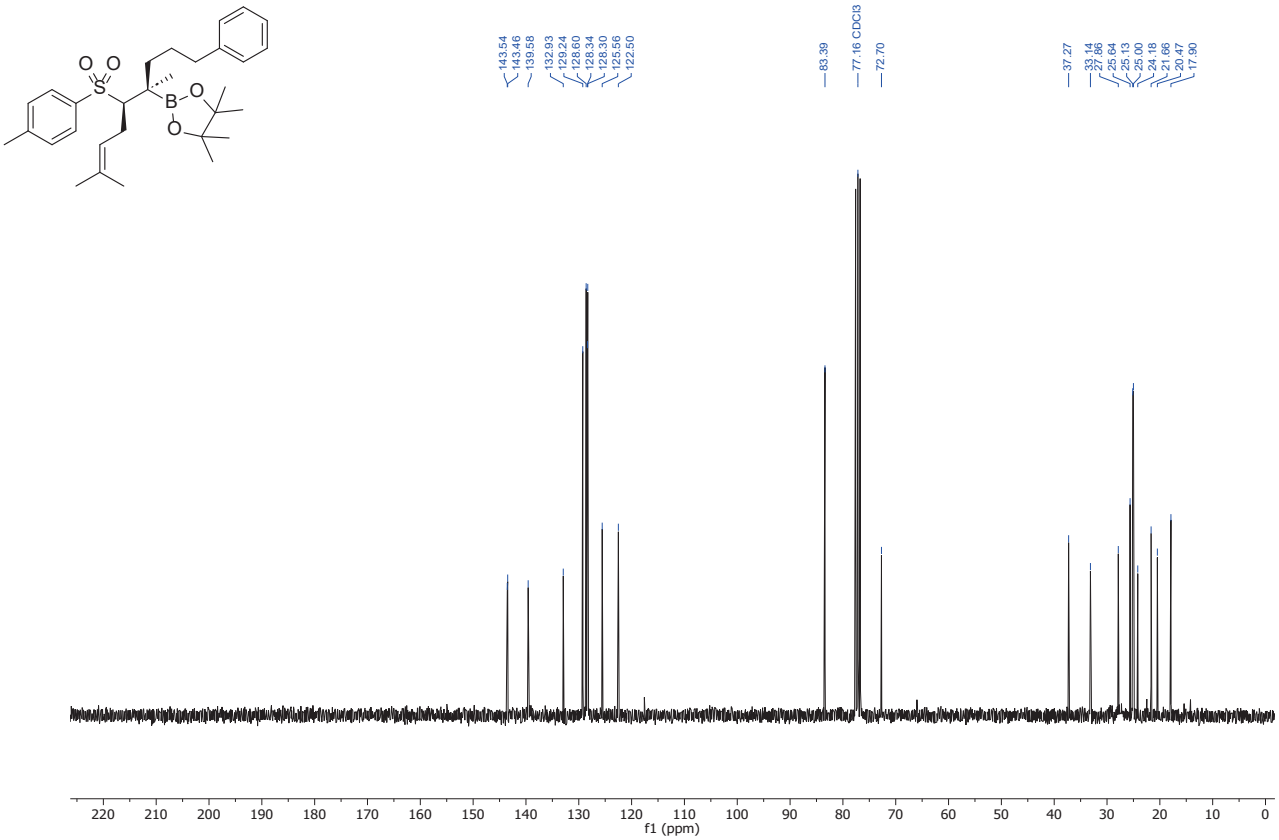
2-((4S,5R)-4,8-dimethyl-1-phenyl-5-tosylnon-7-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (42)
Major diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



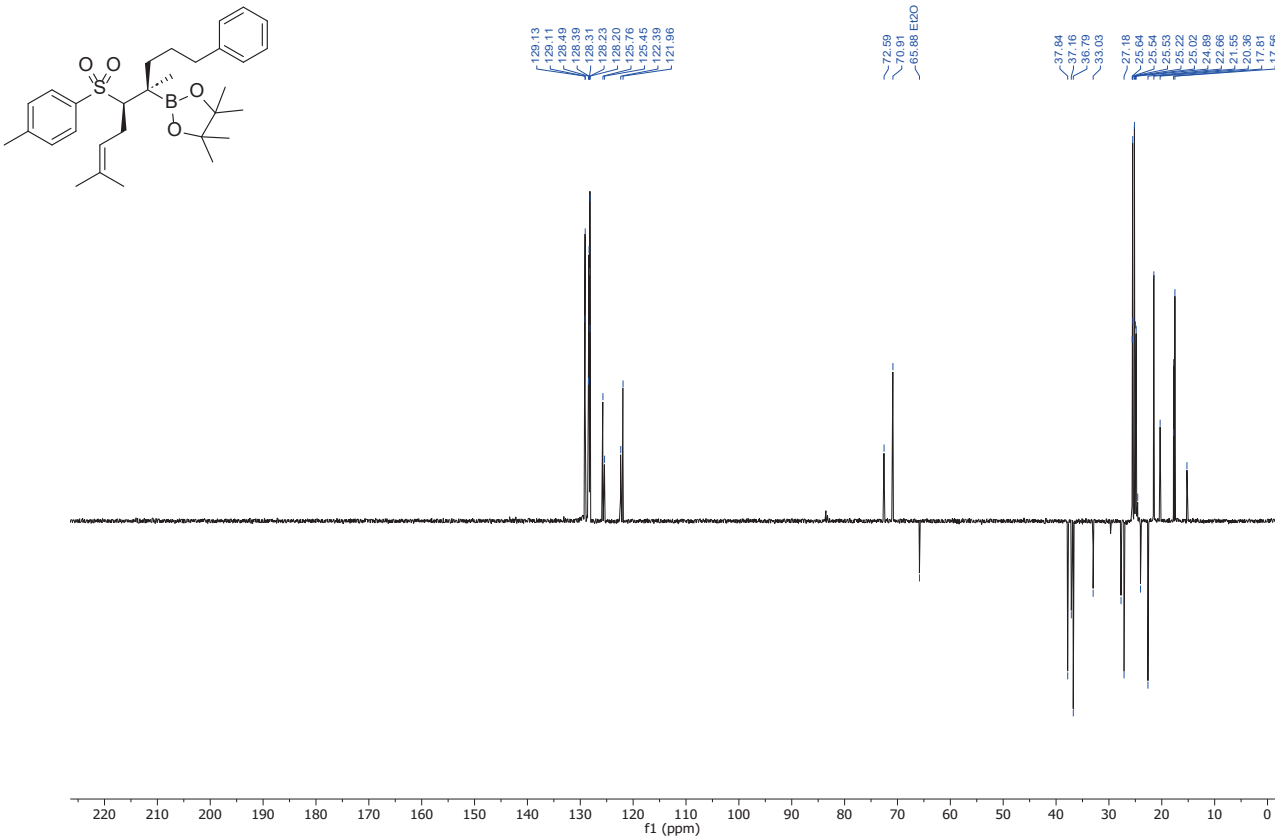
2-((4S,5R)-4,8-dimethyl-1-phenyl-5-tosylnon-7-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (42)
Minor diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



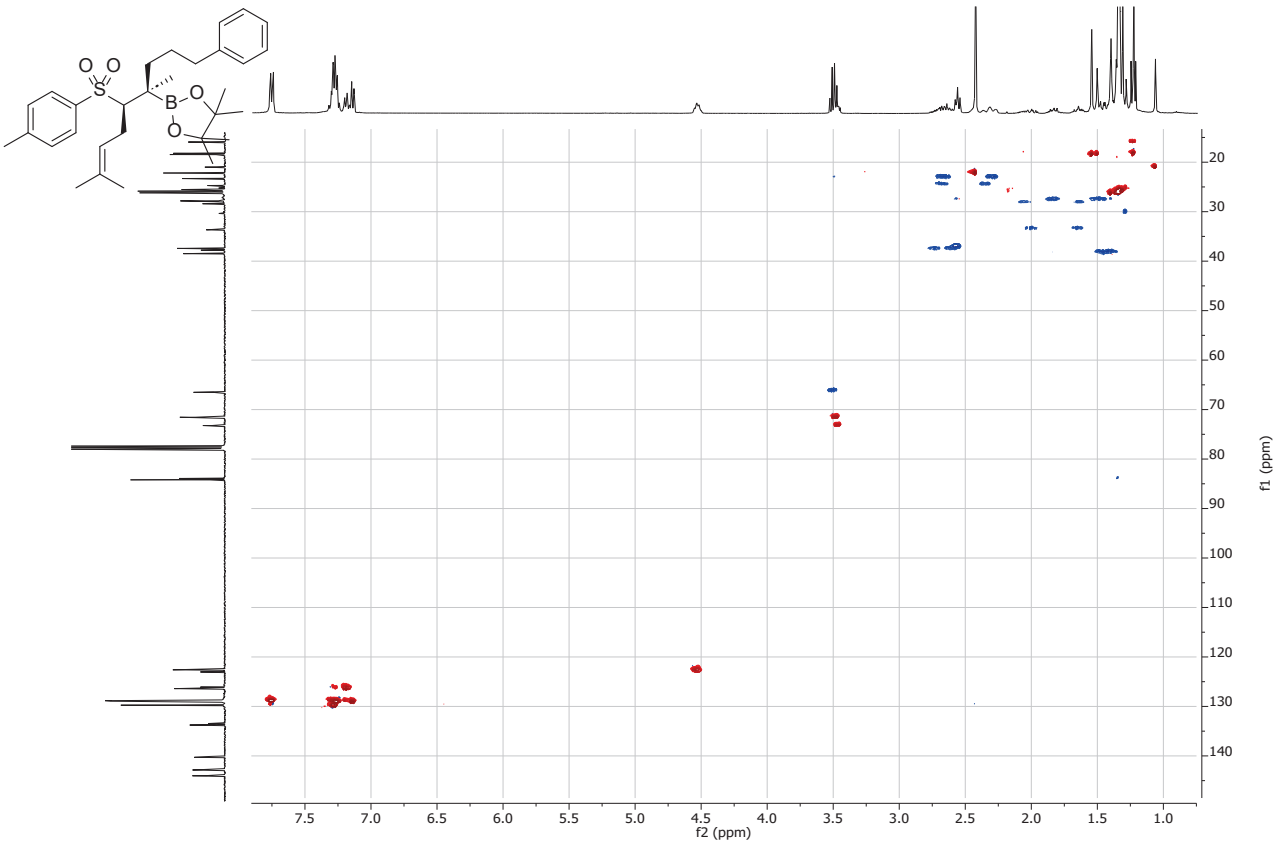
2-((4S,5R)-4,8-dimethyl-1-phenyl-5-tosylnon-7-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (42)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



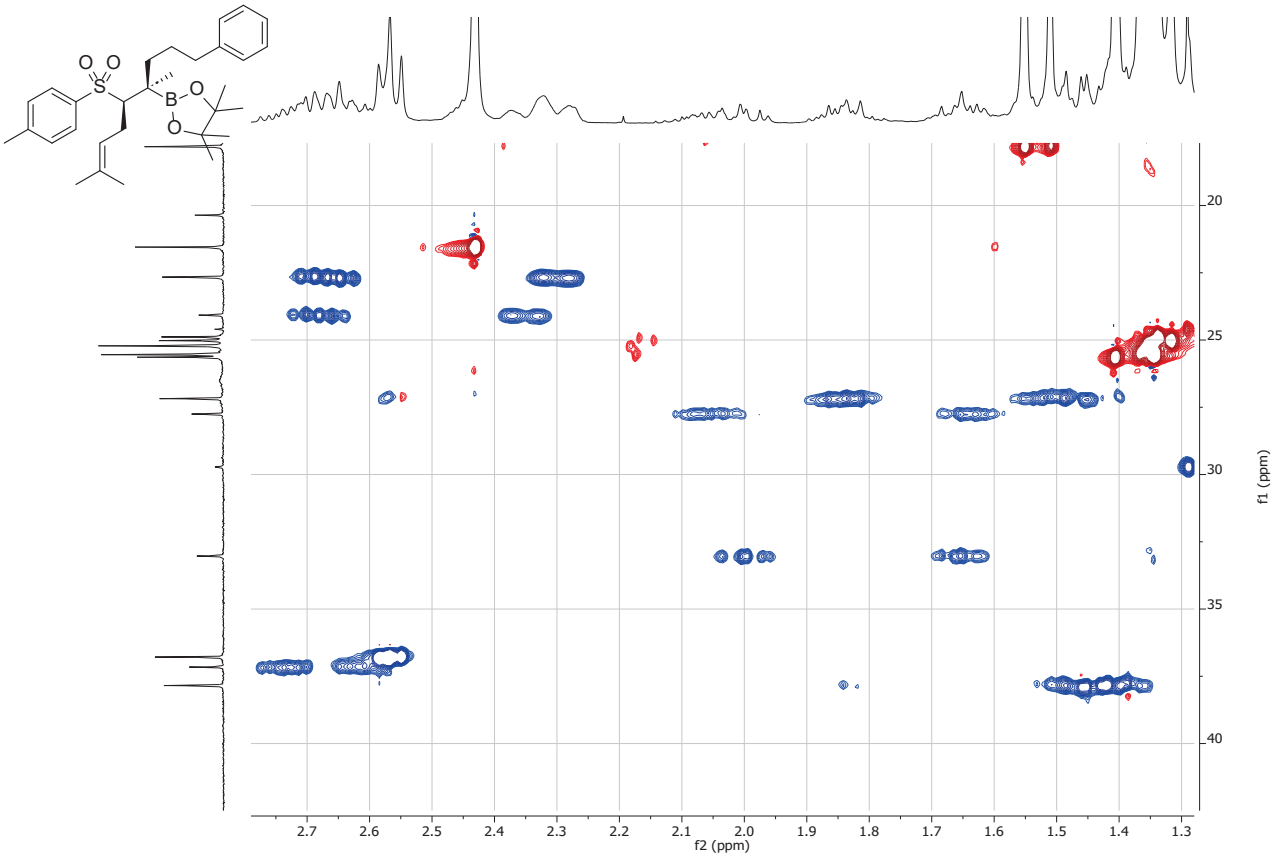
2-((4S,5R)-4,8-dimethyl-1-phenyl-5-tosylnon-7-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (42)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



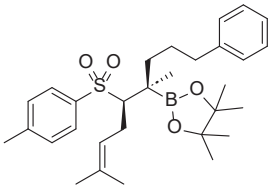
2-((4S,5R)-4,8-dimethyl-1-phenyl-5-tosylnon-7-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (42)

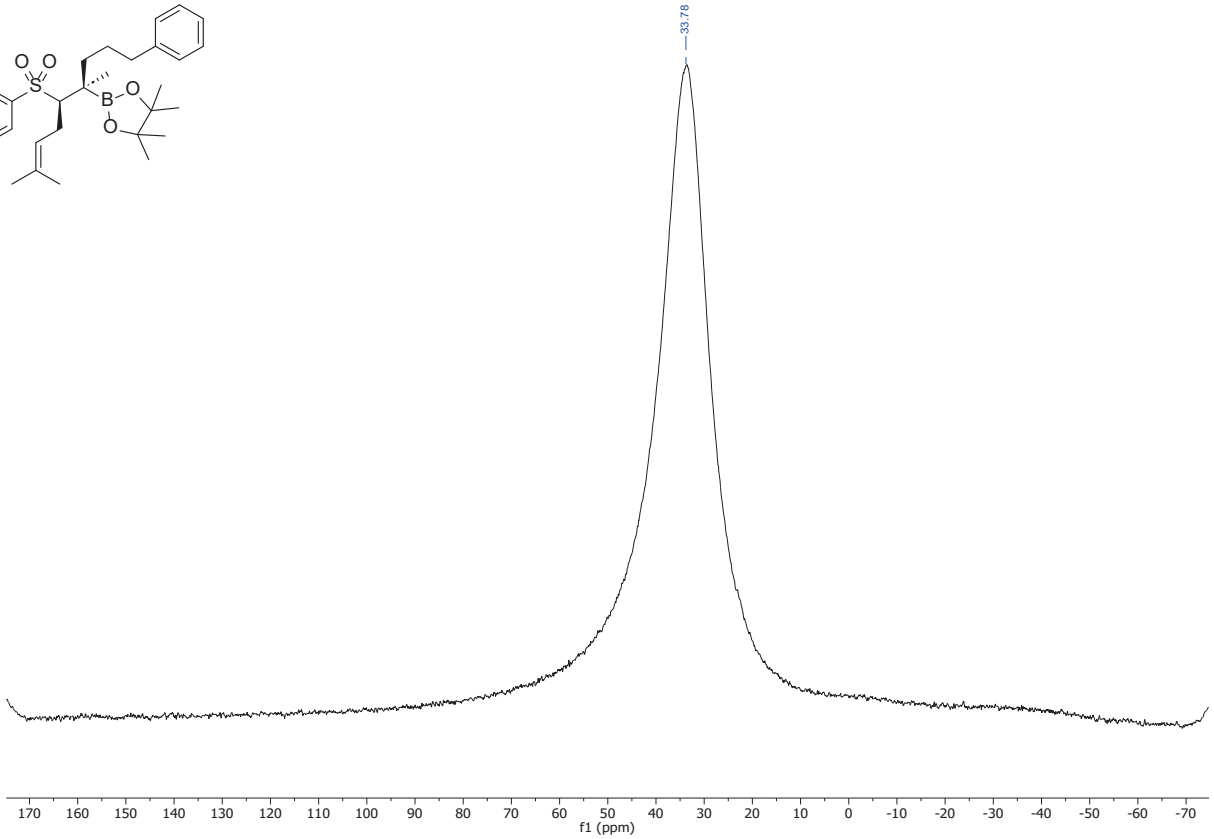
^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



2-((4S,5R)-4,8-dimethyl-1-phenyl-5-tosylnon-7-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (42)

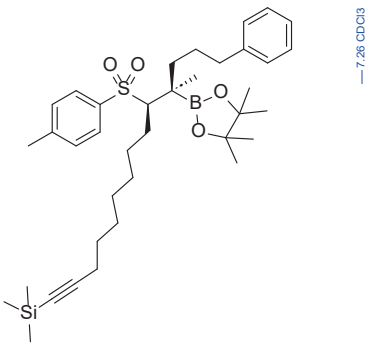
^{11}B NMR (96 MHz, $CDCl_3$)

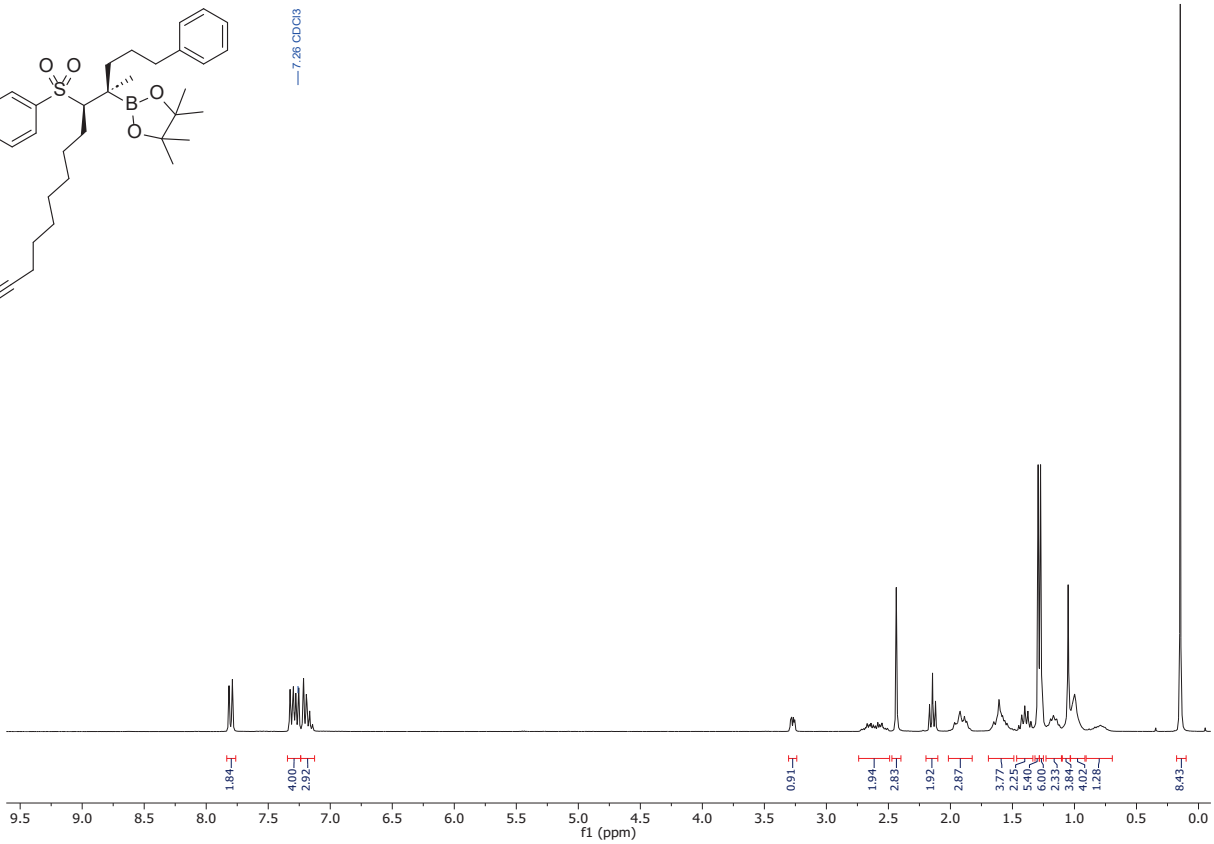




trimethyl((10R,11S)-11-methyl-14-phenyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10-tosyltetradec-1-yn-1-yl)silane (47)
Major diastereomer

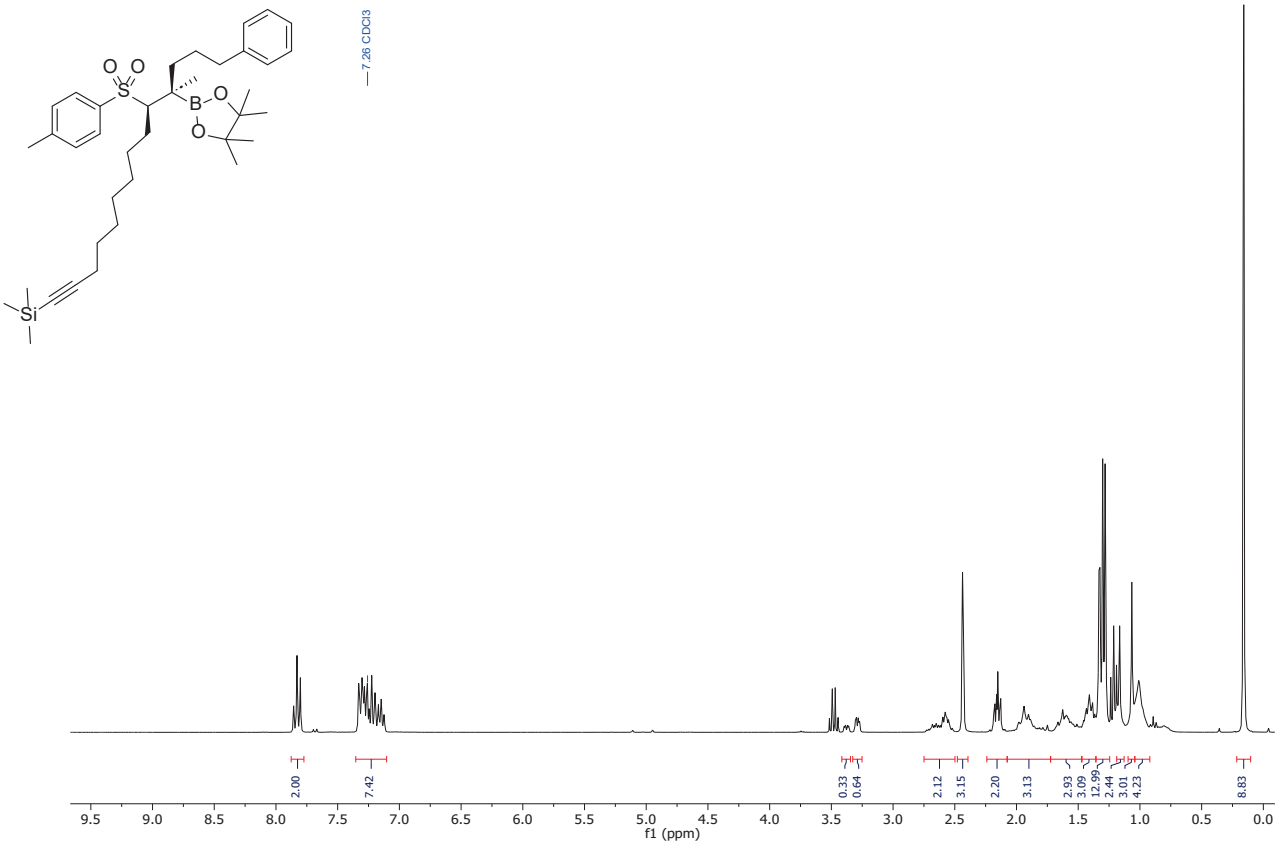
^{1}H NMR (300 MHz, $CDCl_3$)





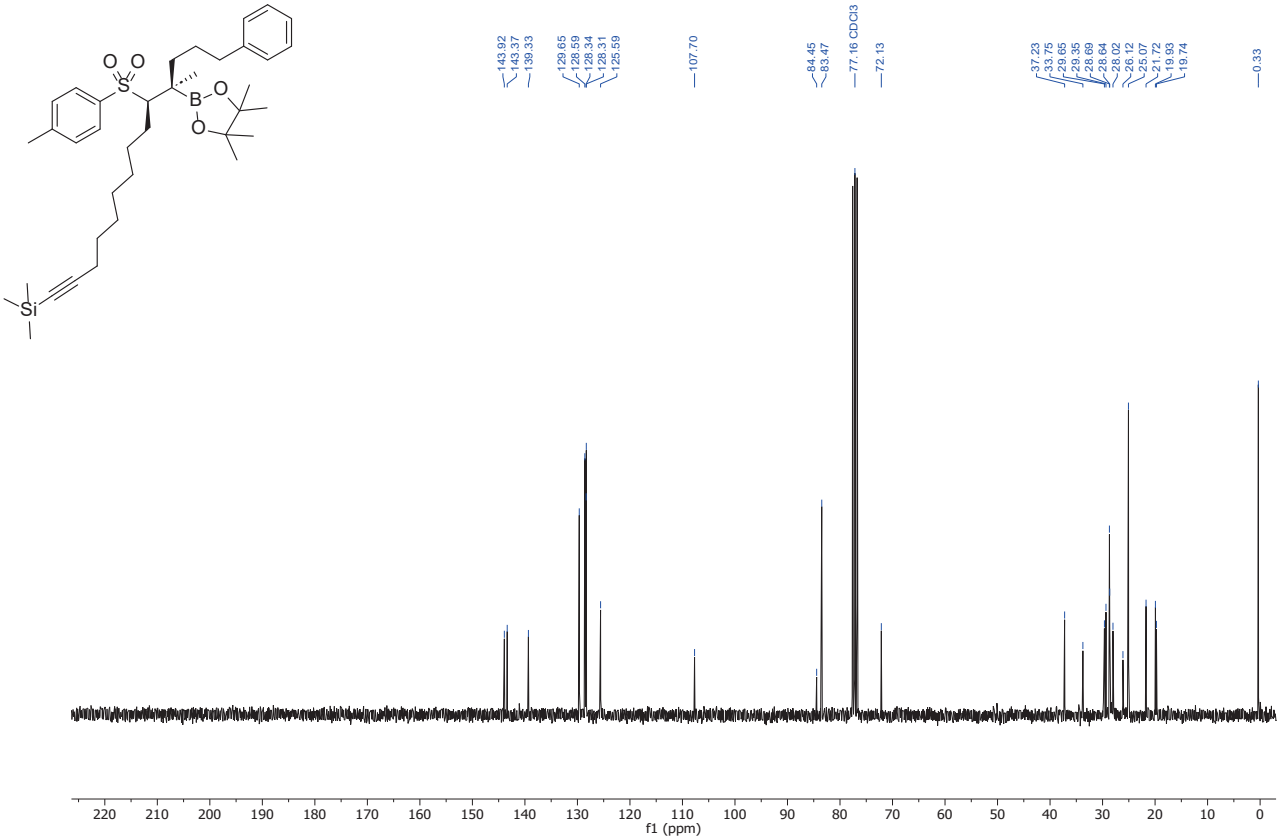
trimethyl((10R,11S)-11-methyl-14-phenyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10-tosyltetradec-1-yn-1-yl)silane (47)
Mix of diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



trimethyl((10R,11S)-11-methyl-14-phenyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10-tosyltetradec-1-yn-1-yl)silane (47)
Major diastereomer

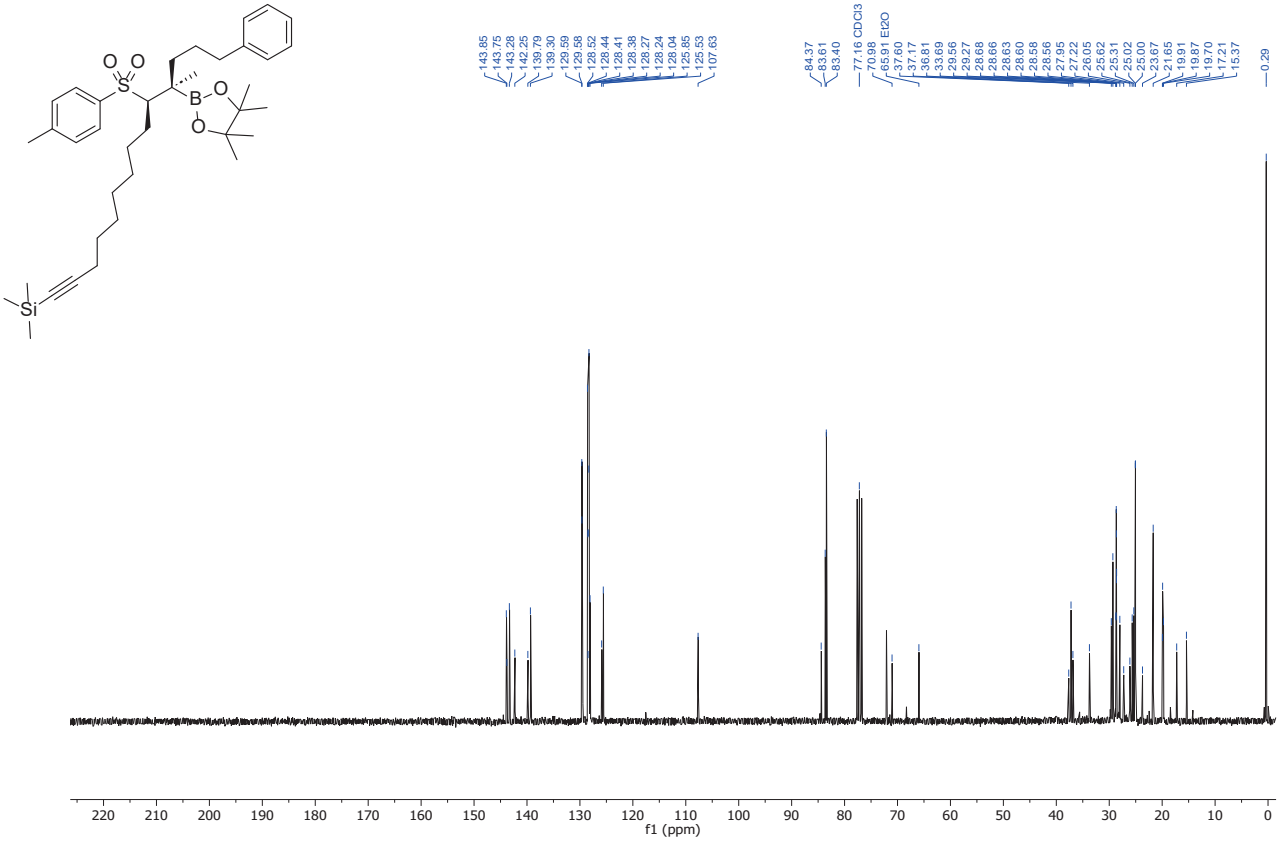
^{13}C NMR (75 MHz, $CDCl_3$)



trimethyl((10R,11S)-11-methyl-14-phenyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10-tosyltetradec-1-yn-1-yl)silane (47)

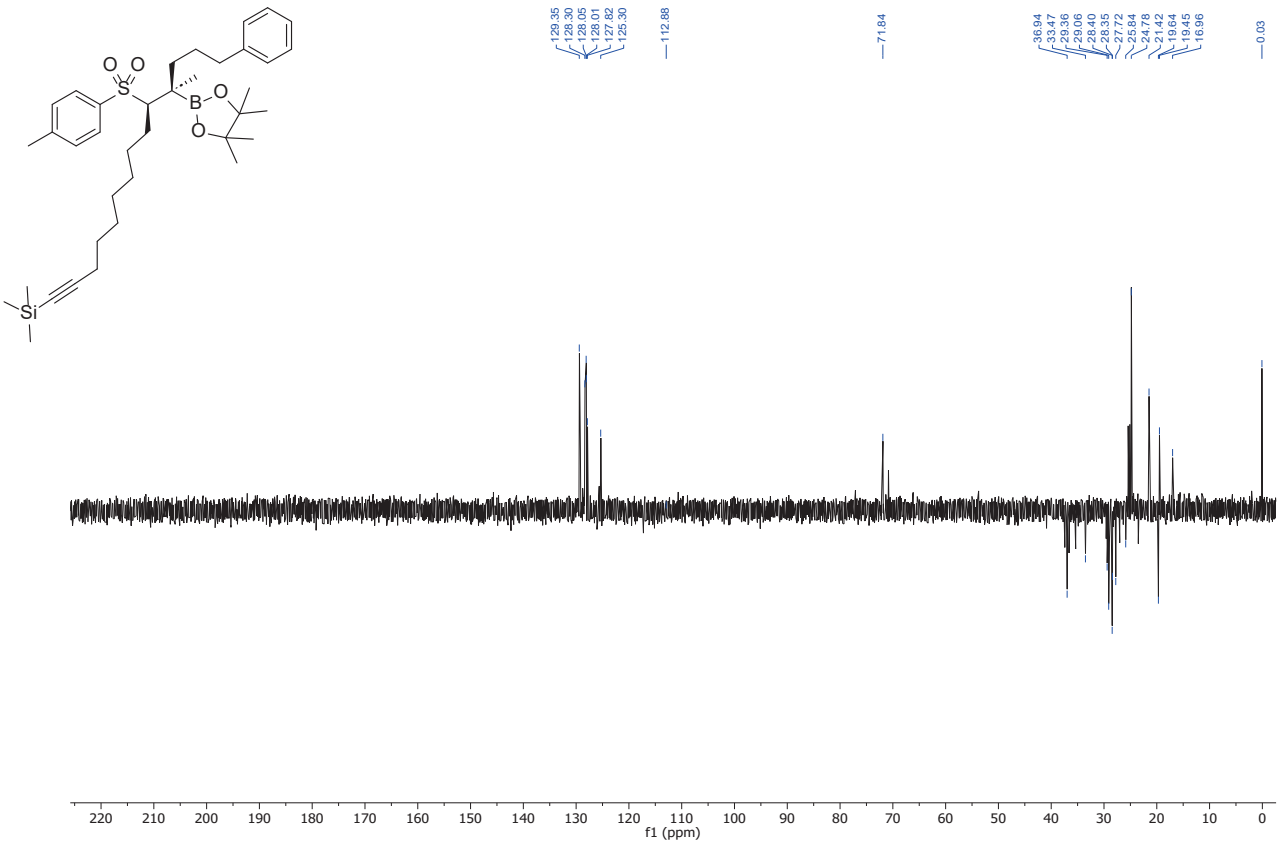
Mix of diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



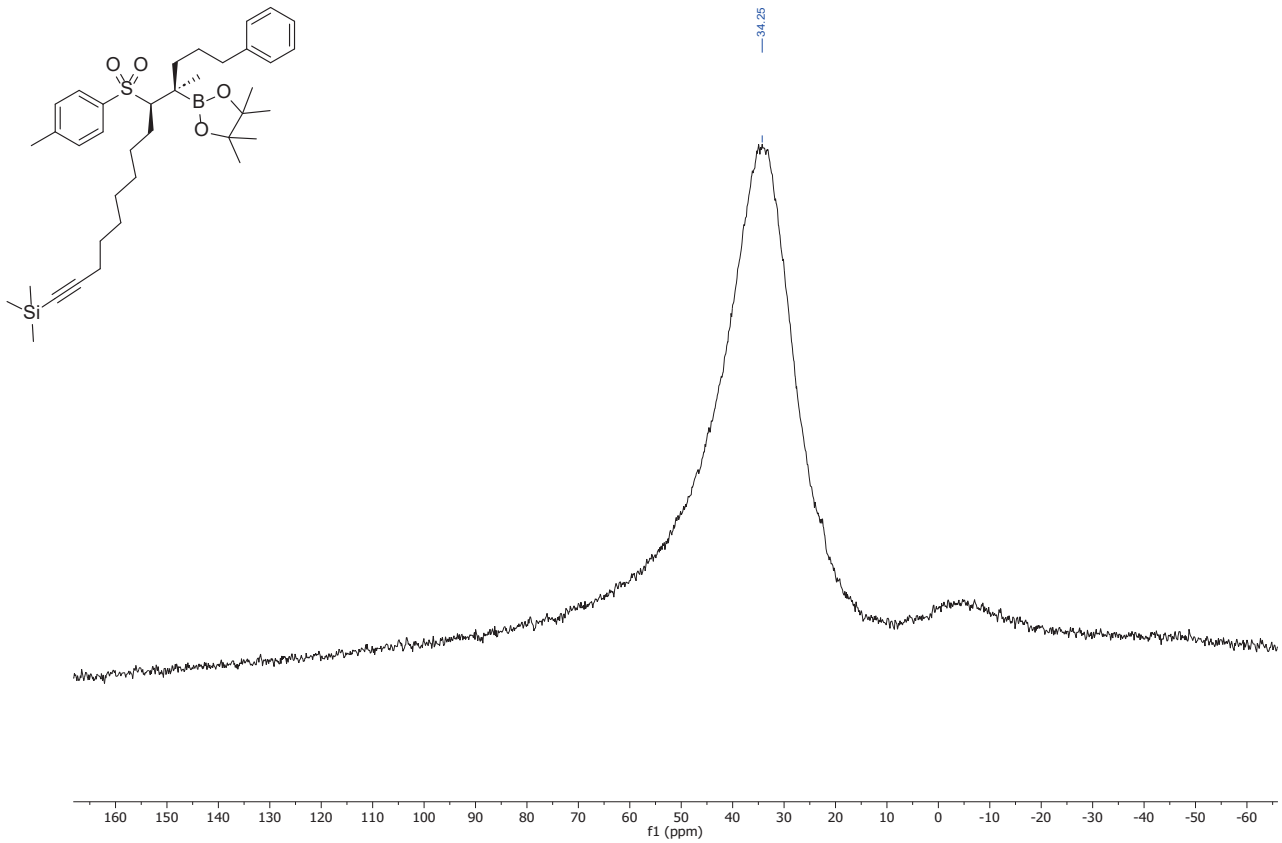
trimethyl((10R,11S)-11-methyl-14-phenyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10-tosyltetradec-1-yn-1-yl)silane (47)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



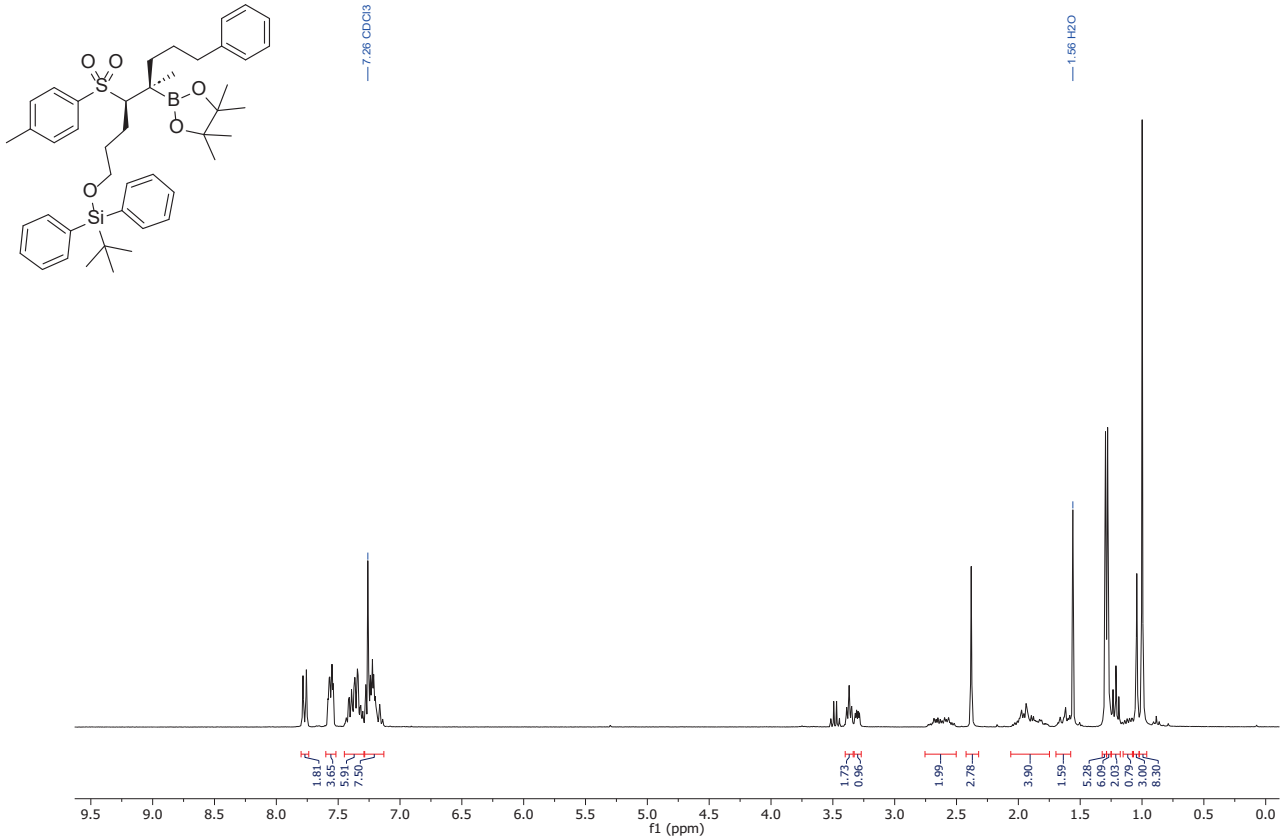
trimethyl((10R,11S)-11-methyl-14-phenyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10-tosyltetradec-1-yn-1-yl)silane (47)

^{11}B NMR (96 MHz, $CDCl_3$)



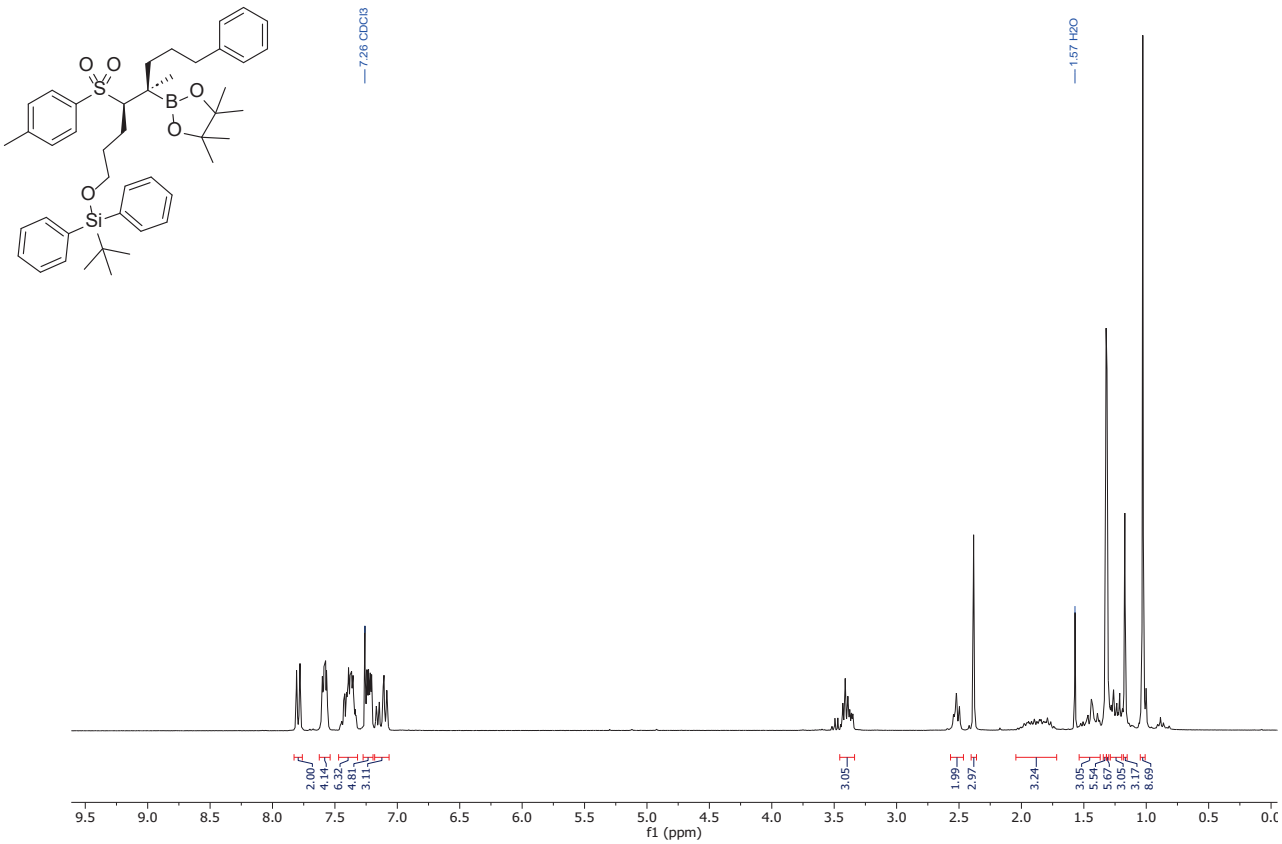
tert-butyl(((4R,5S)-5-methyl-8-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-tosyloctyl)oxy)diphenylsilane (48)
First diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



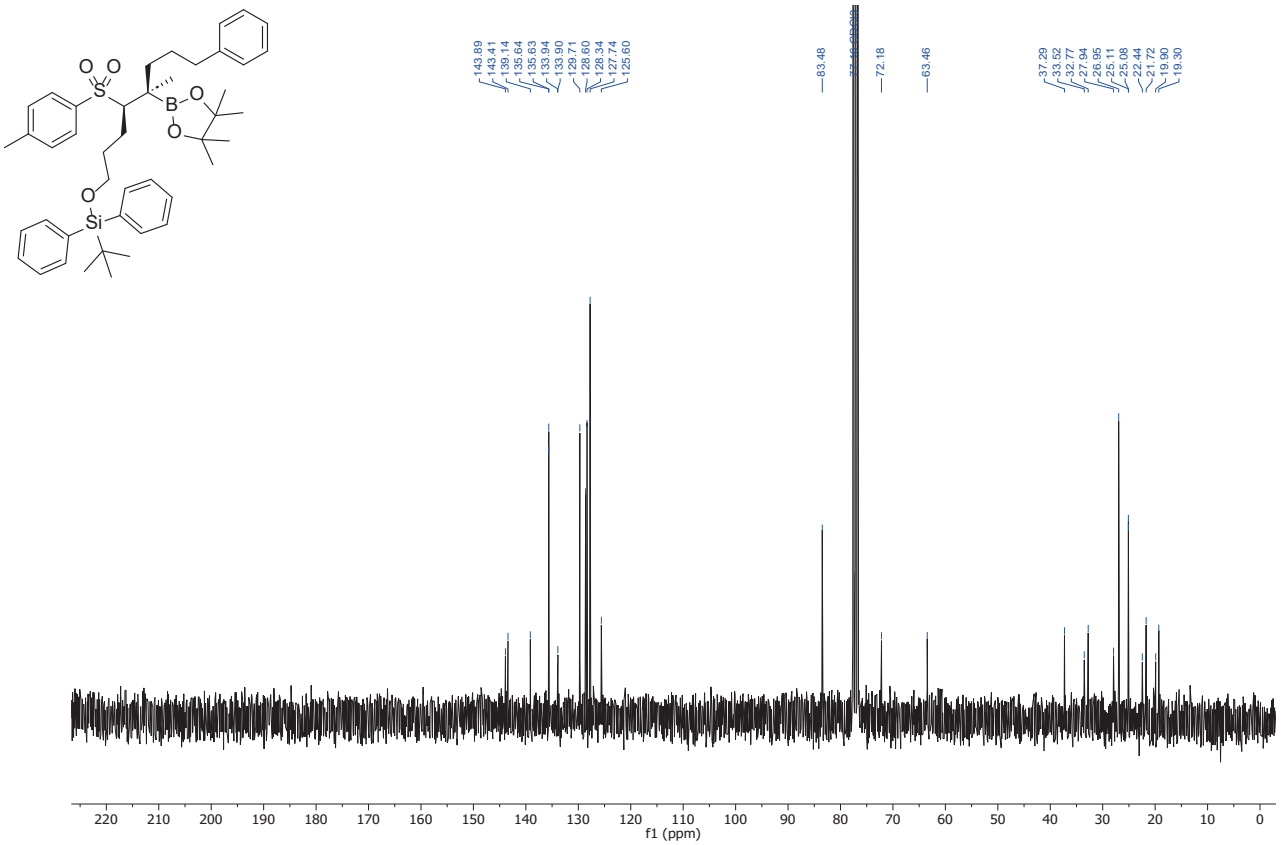
tert-butyl(((4R,5S)-5-methyl-8-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-tosyloctyl)oxy)diphenylsilane (48)
Second diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



tert-butyl(((4R,5S)-5-methyl-8-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-tosyloctyl)oxy)diphenylsilane (48)
First diastereomer

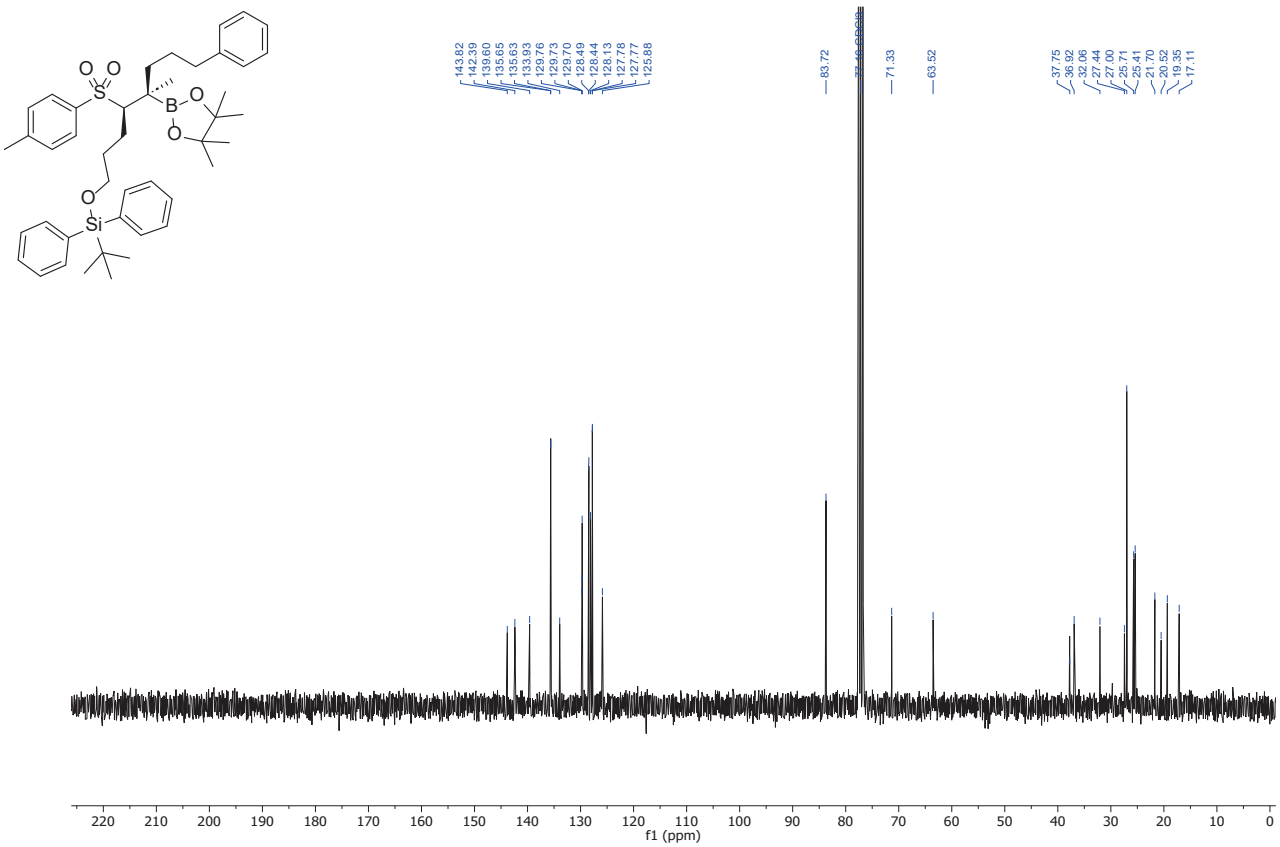
^{13}C NMR (75 MHz, $CDCl_3$)



tert-butyl(((4R,5S)-5-methyl-8-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-tosyloctyl)oxy)diphenylsilane (48)

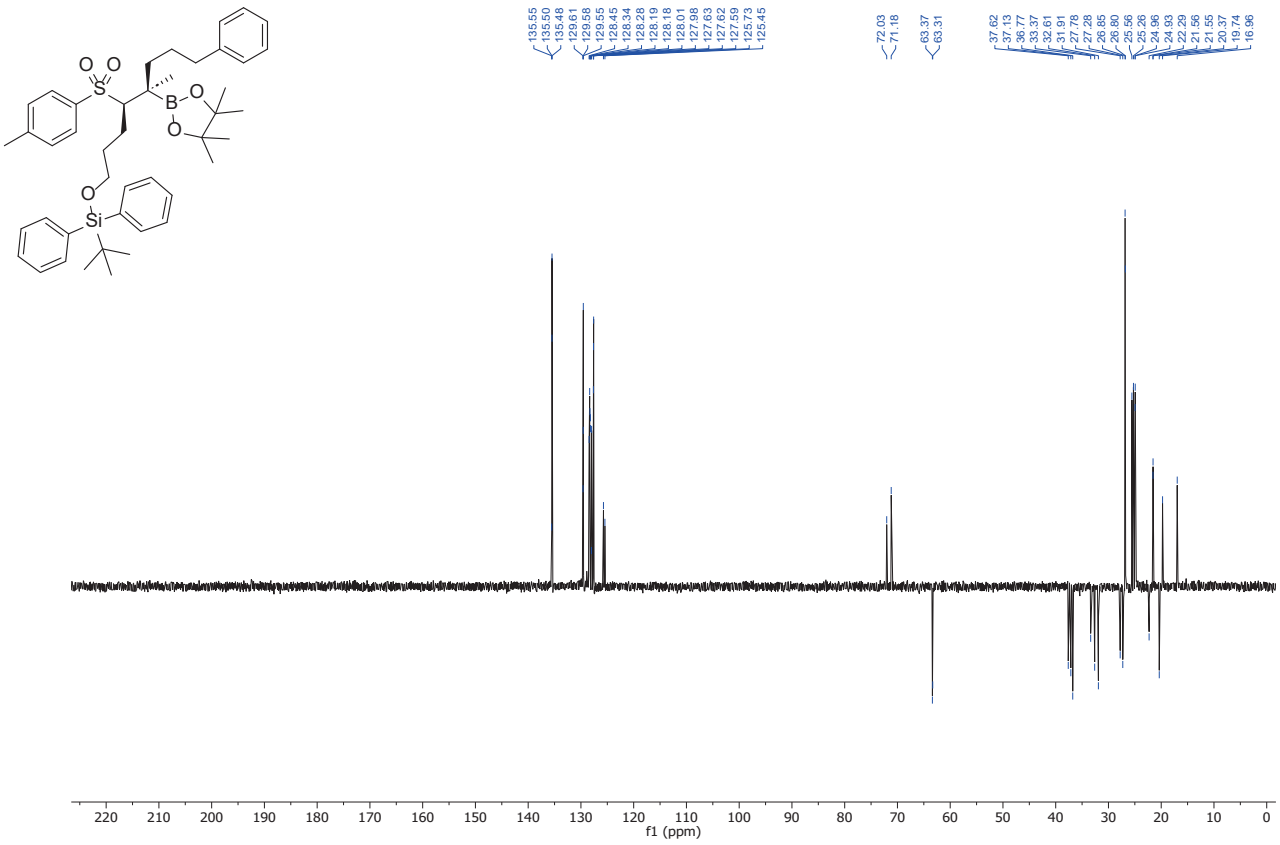
Second diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



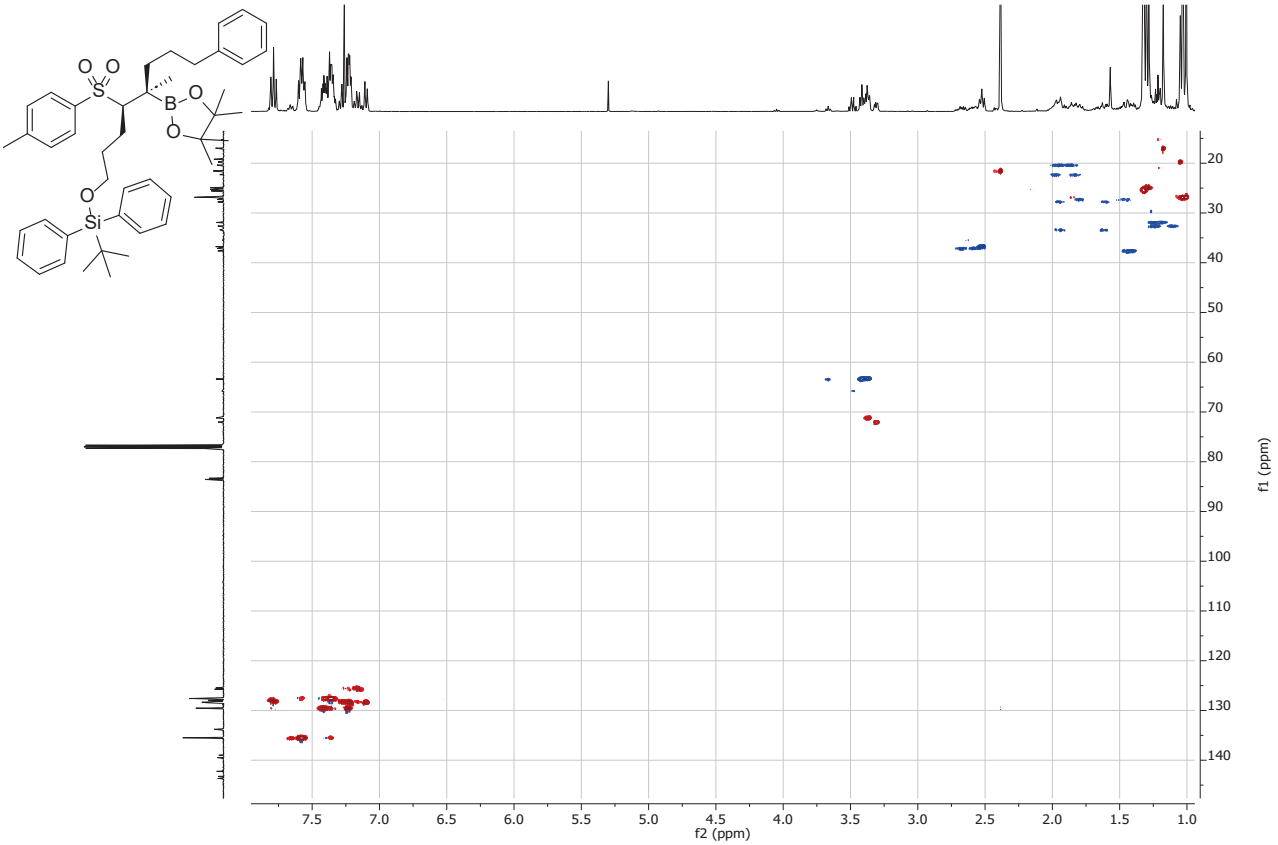
tert-butyl(((4R,5S)-5-methyl-8-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-tosyloctyl)oxy)diphenylsilane (48)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



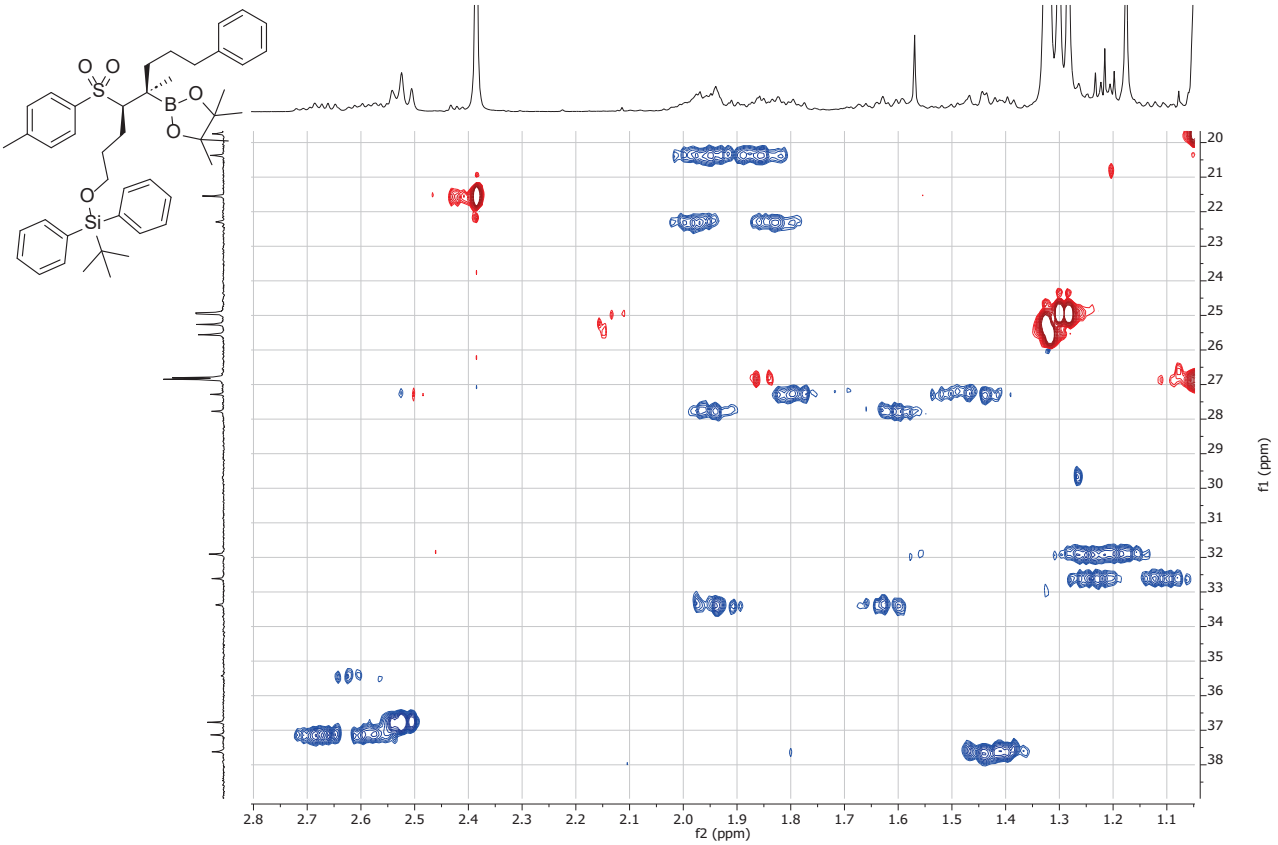
tert-butyl(((4R,5S)-5-methyl-8-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-tosyloctyl)oxy)diphenylsilane (48)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



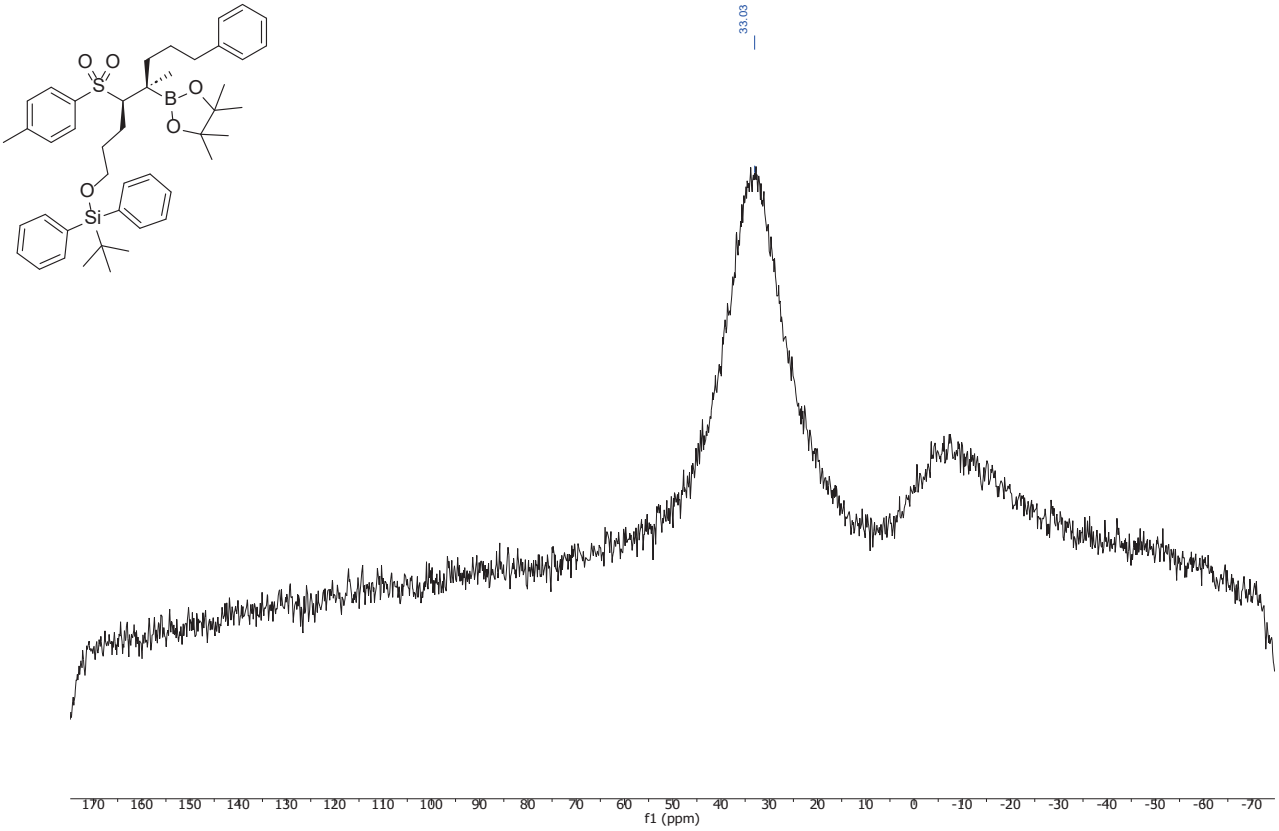
tert-butyl(((4R,5S)-5-methyl-8-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-tosyloctyl)oxy)diphenylsilane (48)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



tert-butyl(((4R,5S)-5-methyl-8-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-tosyloctyl)oxy)diphenylsilane (48)

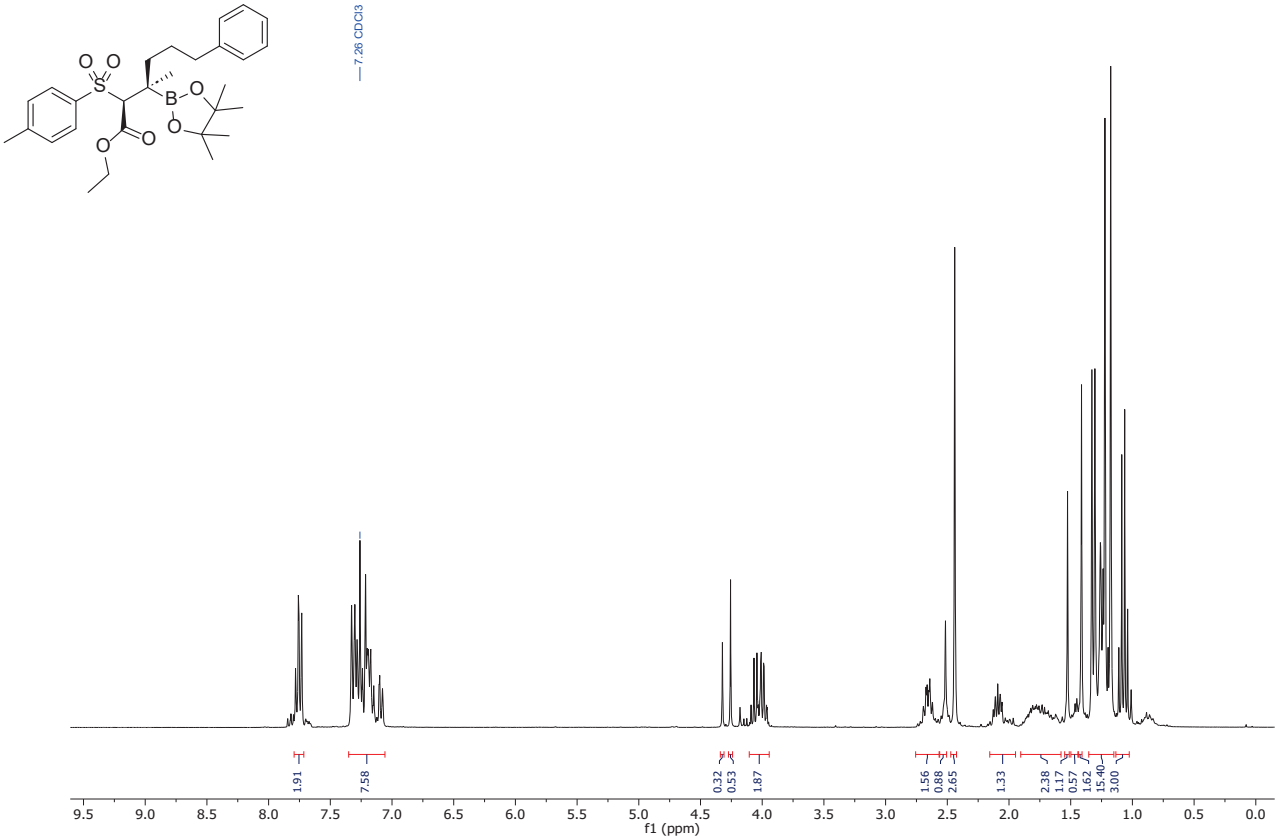
^{11}B NMR (96 MHz, $CDCl_3$)



ethyl (2S,3S)-3-methyl-6-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-tosylhexanoate (49)

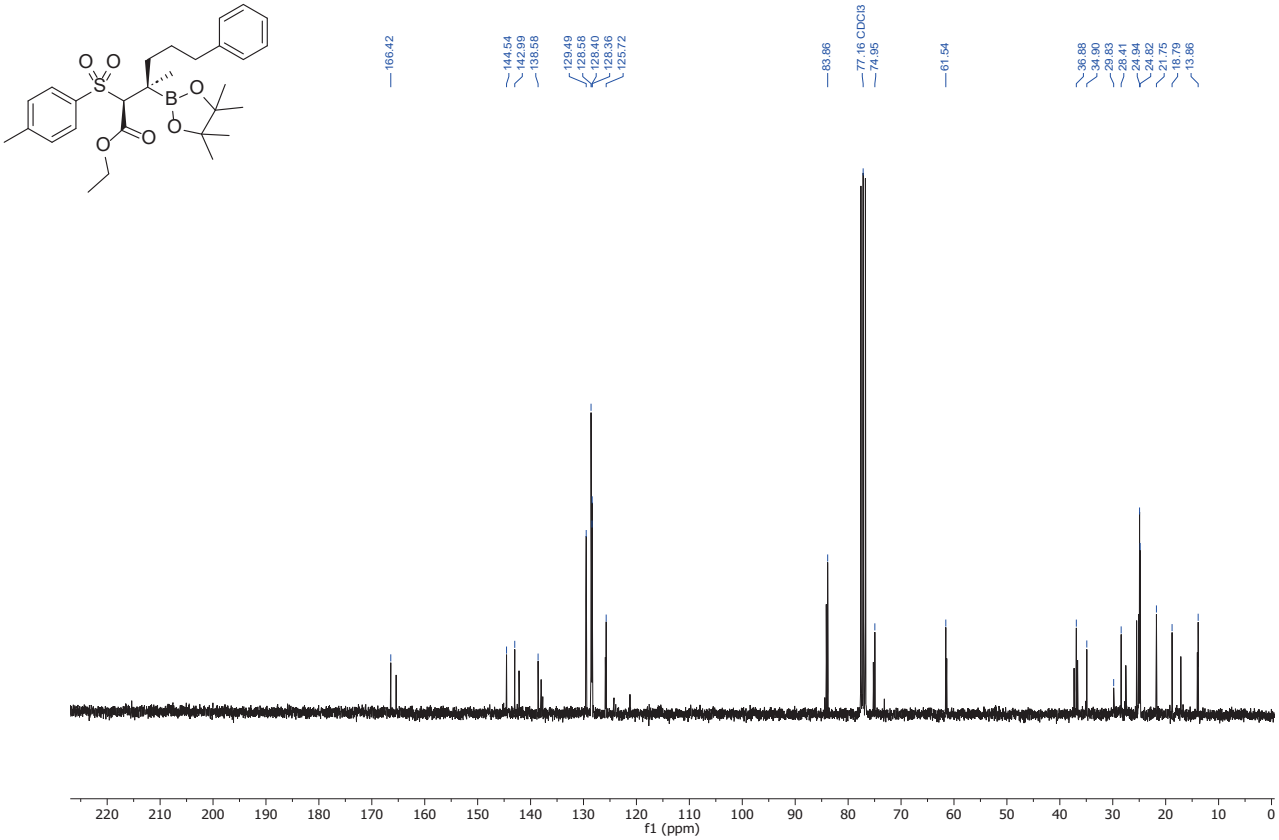
Mix of diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



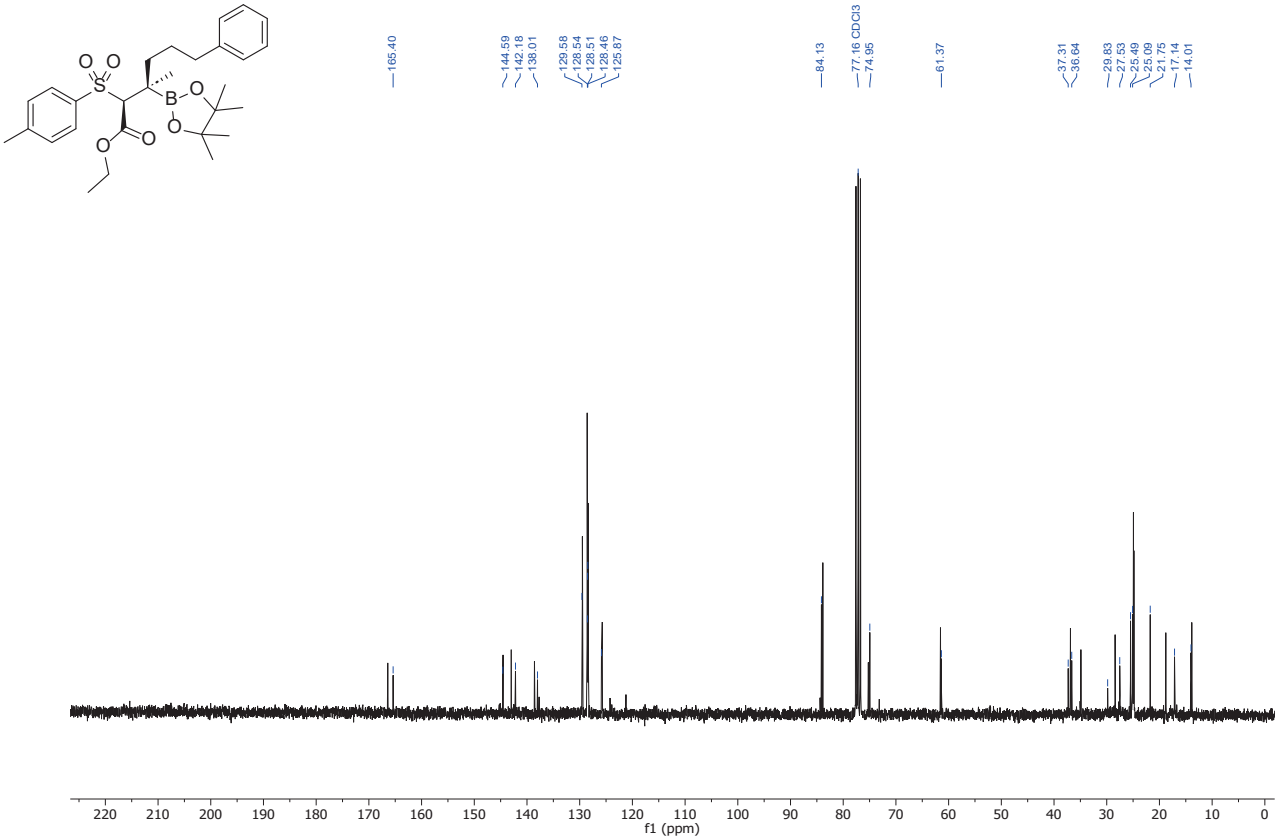
ethyl (2S,3S)-3-methyl-6-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-tosylhexanoate (49)
Major diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



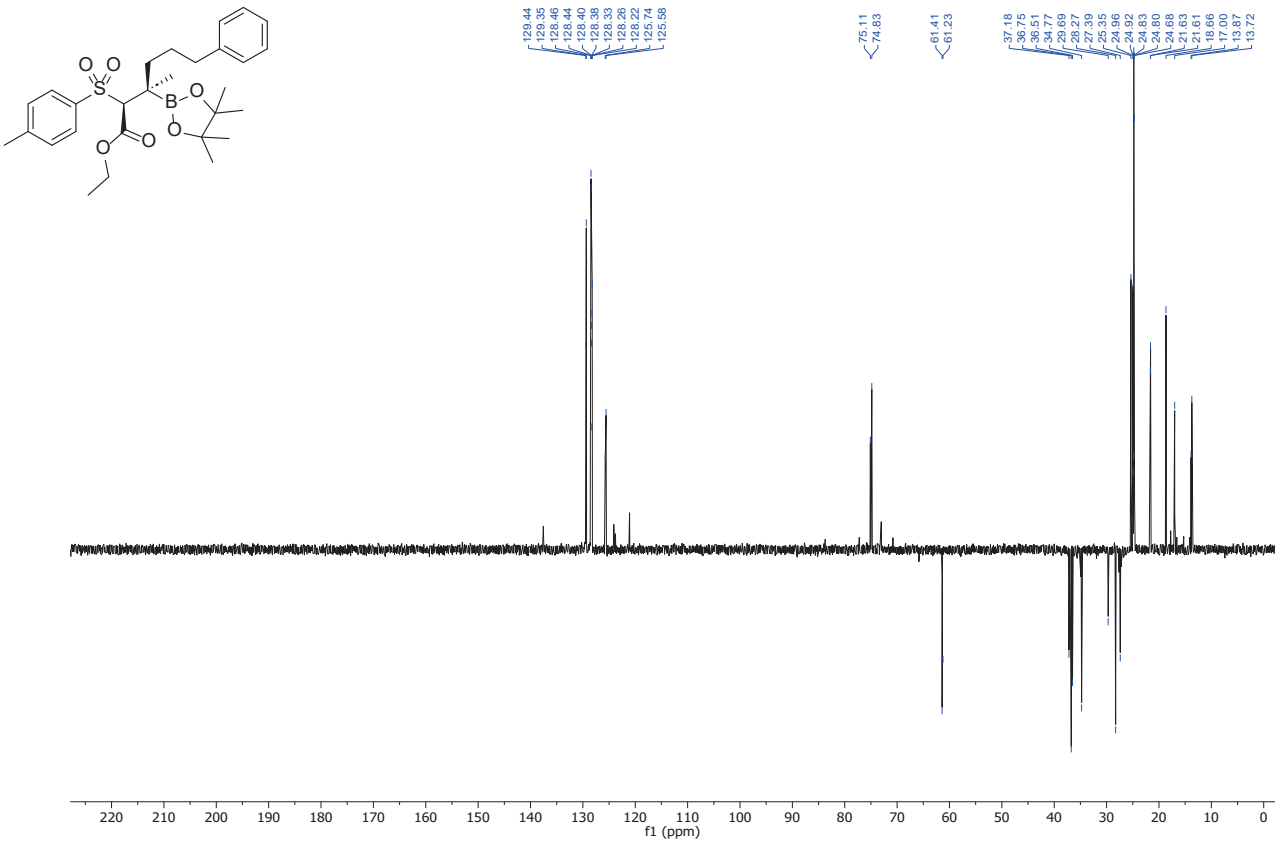
ethyl (2S,3S)-3-methyl-6-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-tosylhexanoate (49)
Minor diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



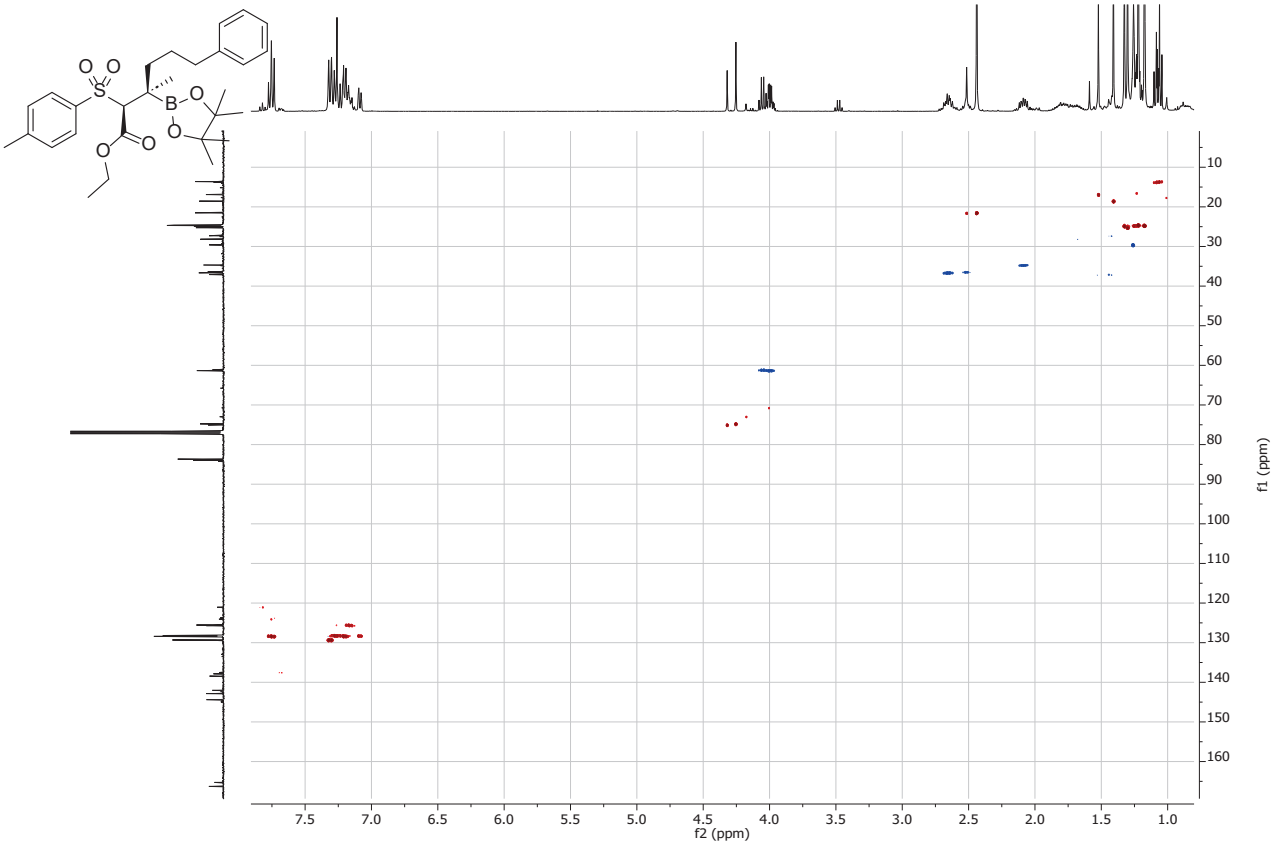
ethyl (2S,3S)-3-methyl-6-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-tosylhexanoate (49)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



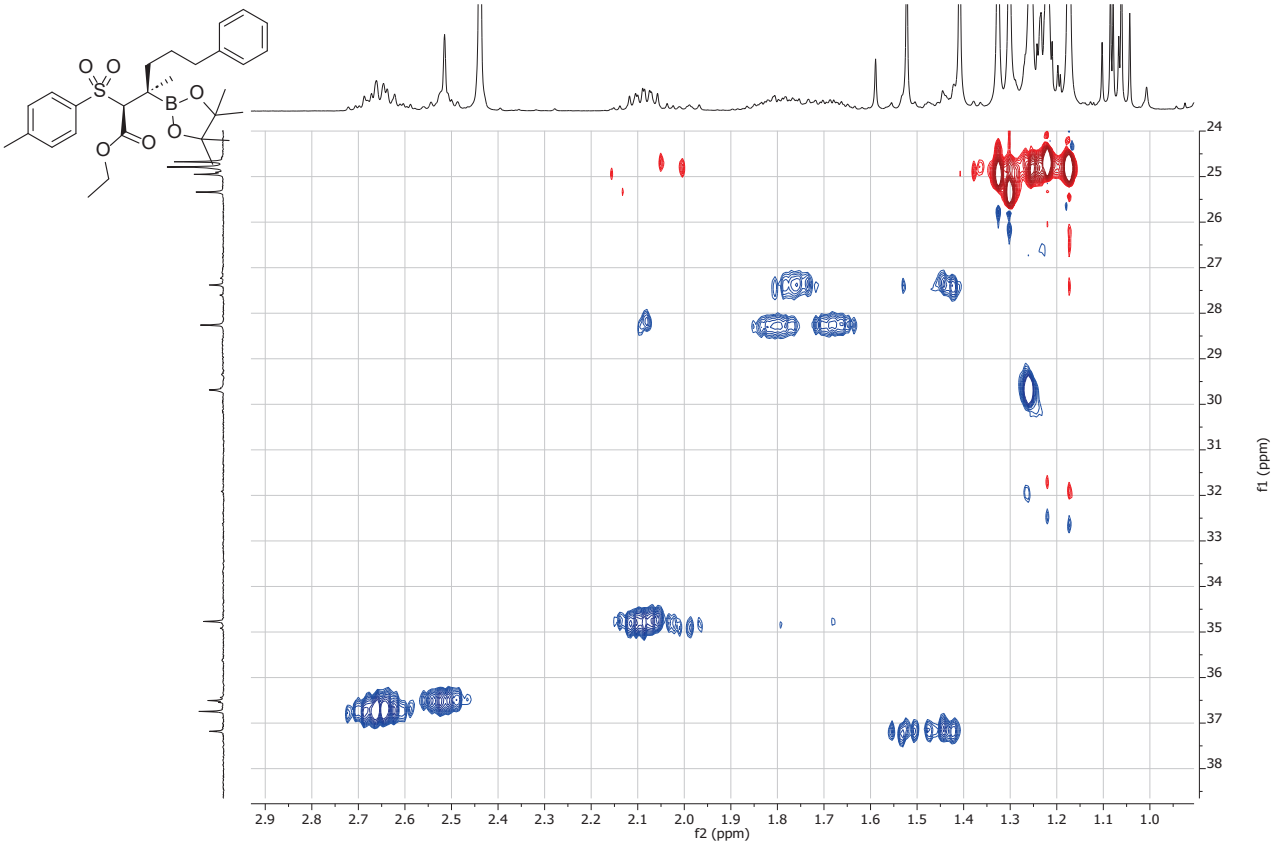
ethyl (2S,3S)-3-methyl-6-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-tosylhexanoate (49)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



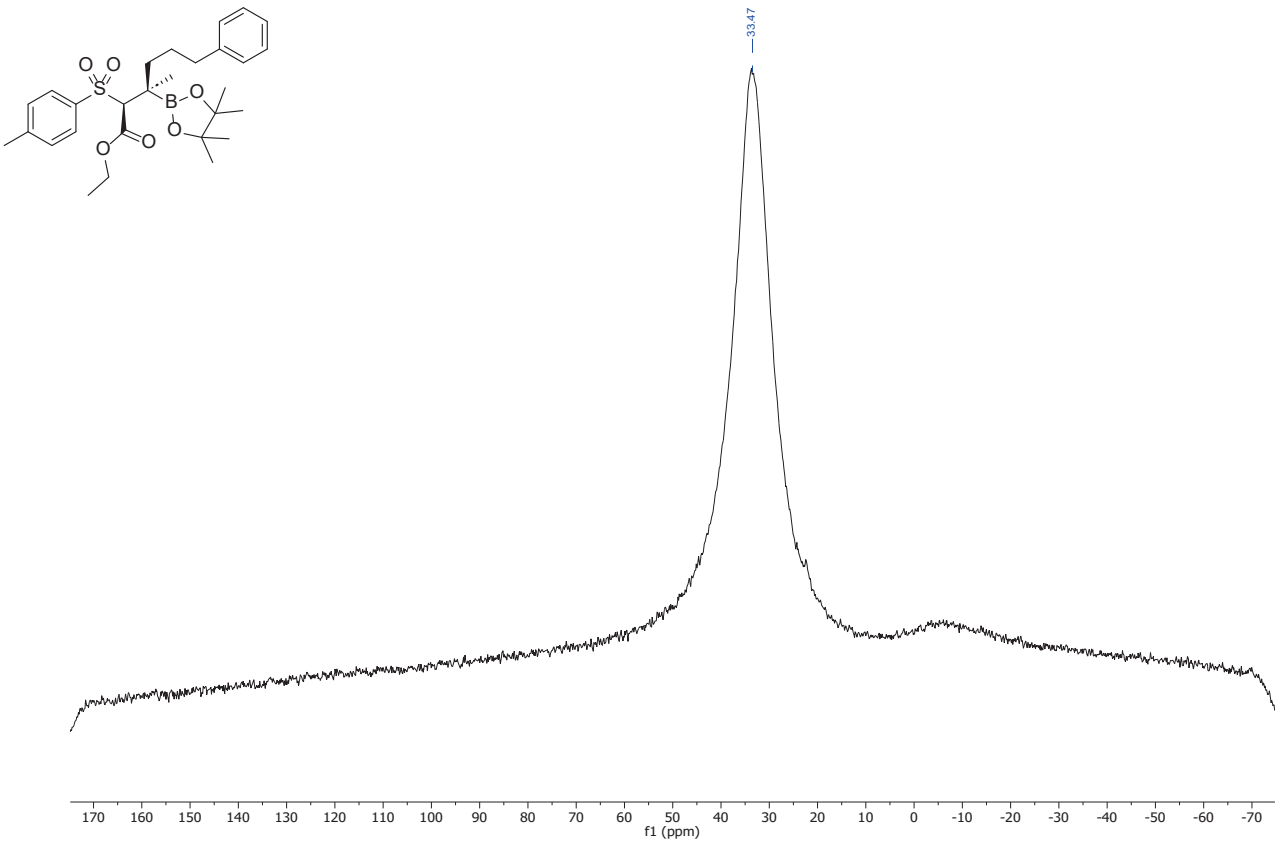
ethyl (2S,3S)-3-methyl-6-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-tosylhexanoate (49)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



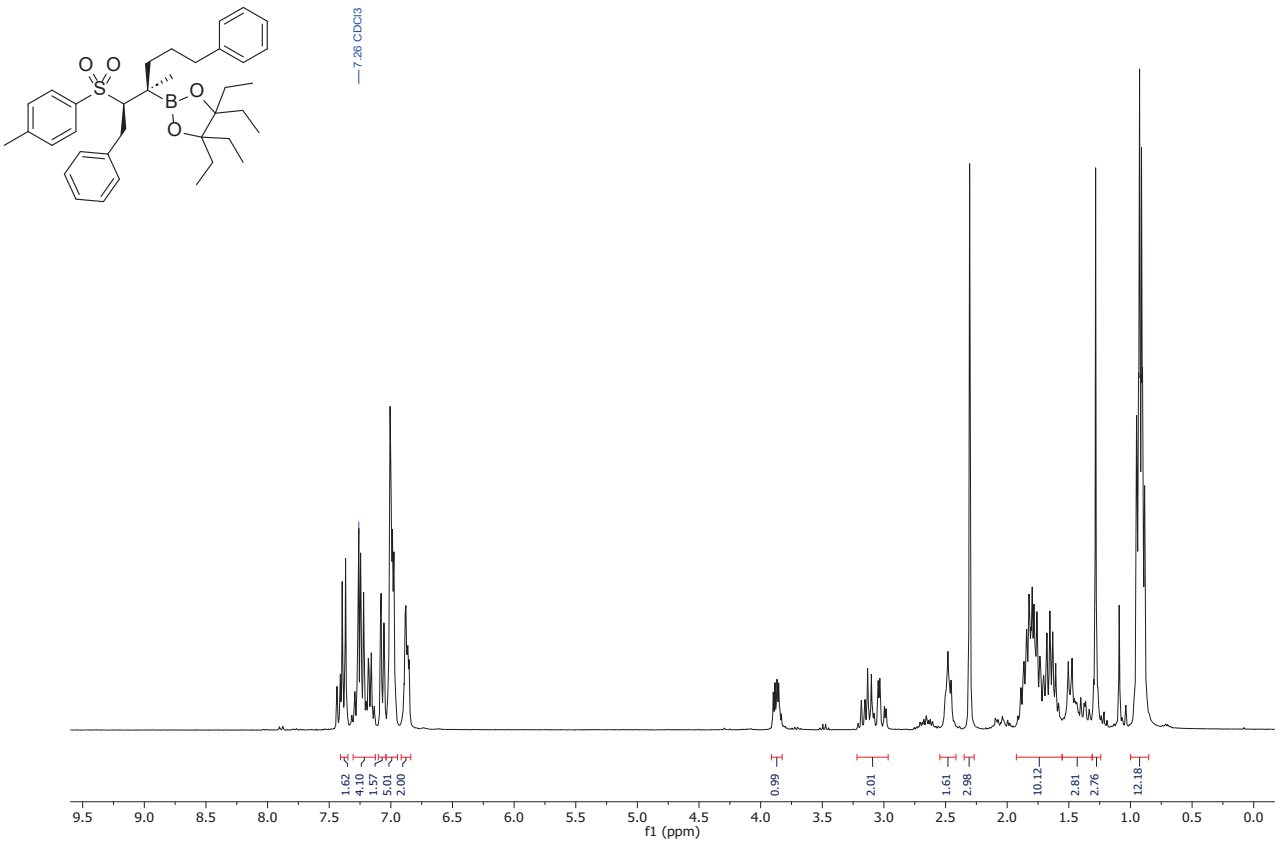
ethyl (2S,3S)-3-methyl-6-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-tosylhexanoate (49)

^{11}B NMR (96 MHz, $CDCl_3$)



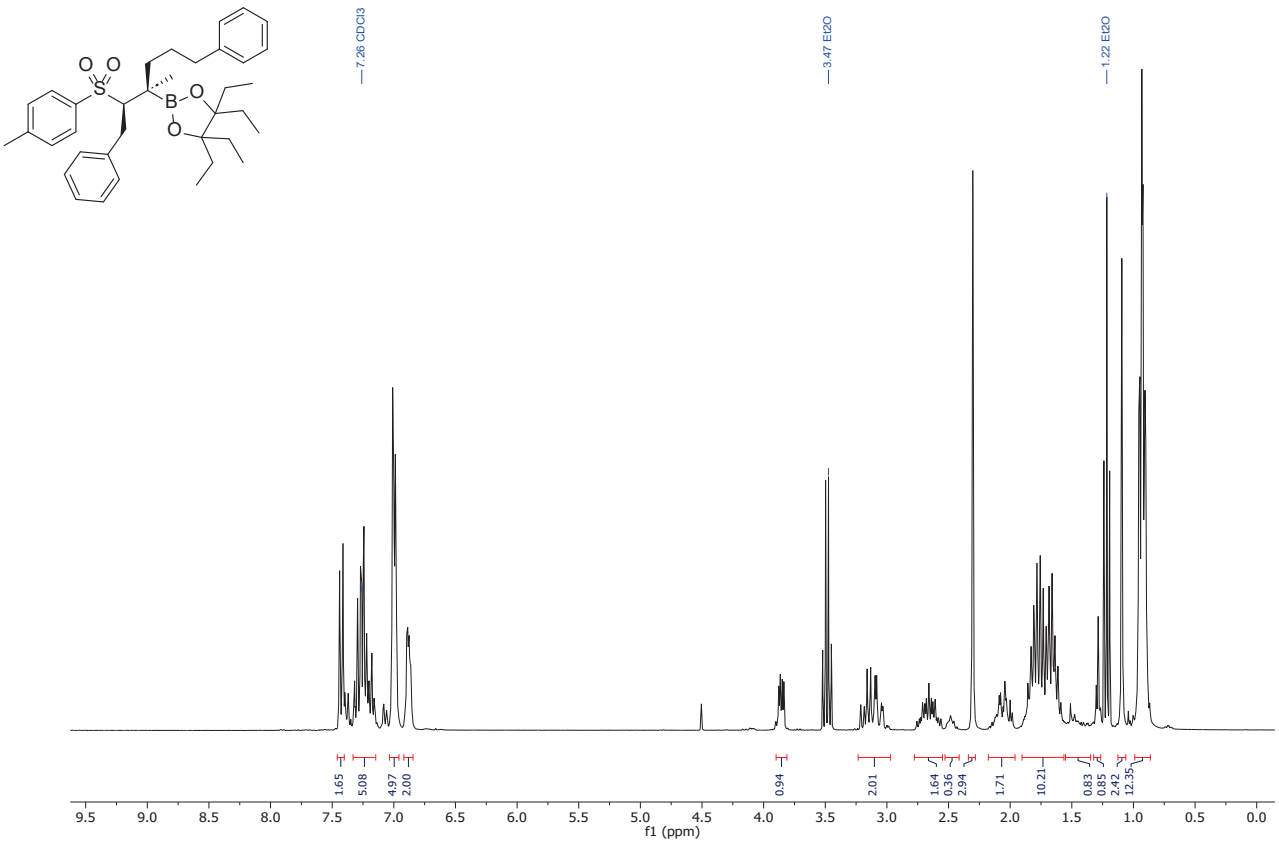
4,4,5,5-tetraethyl-2-((2R,3S)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (105)
Major diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



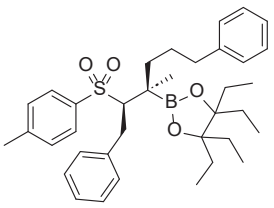
4,4,5,5-tetraethyl-2-((2R,3S)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (105)
Minor diastereomer

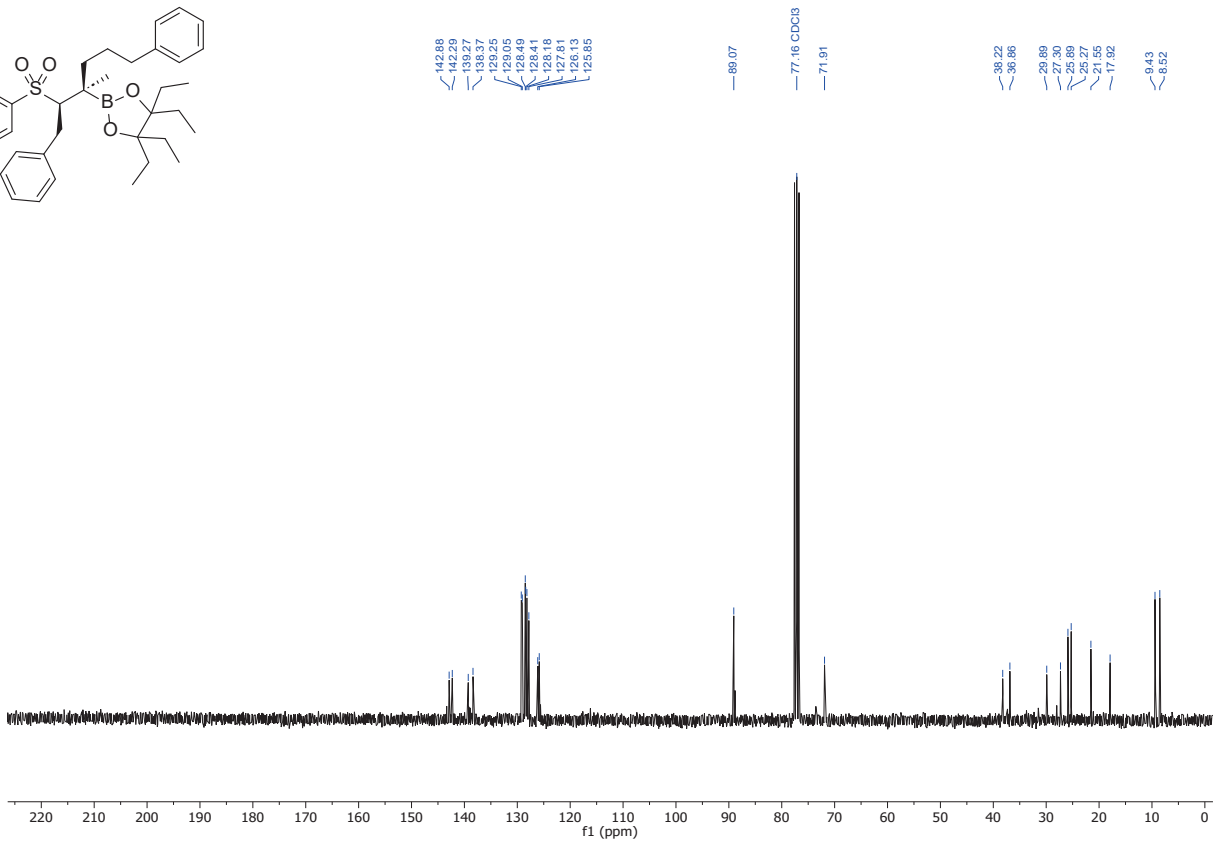
^{1}H NMR (300 MHz, $CDCl_3$)



4,4,5,5-tetraethyl-2-((2R,3S)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (105)
Major diastereomer

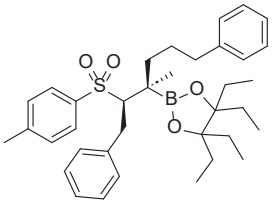
^{13}C NMR (75 MHz, $CDCl_3$)

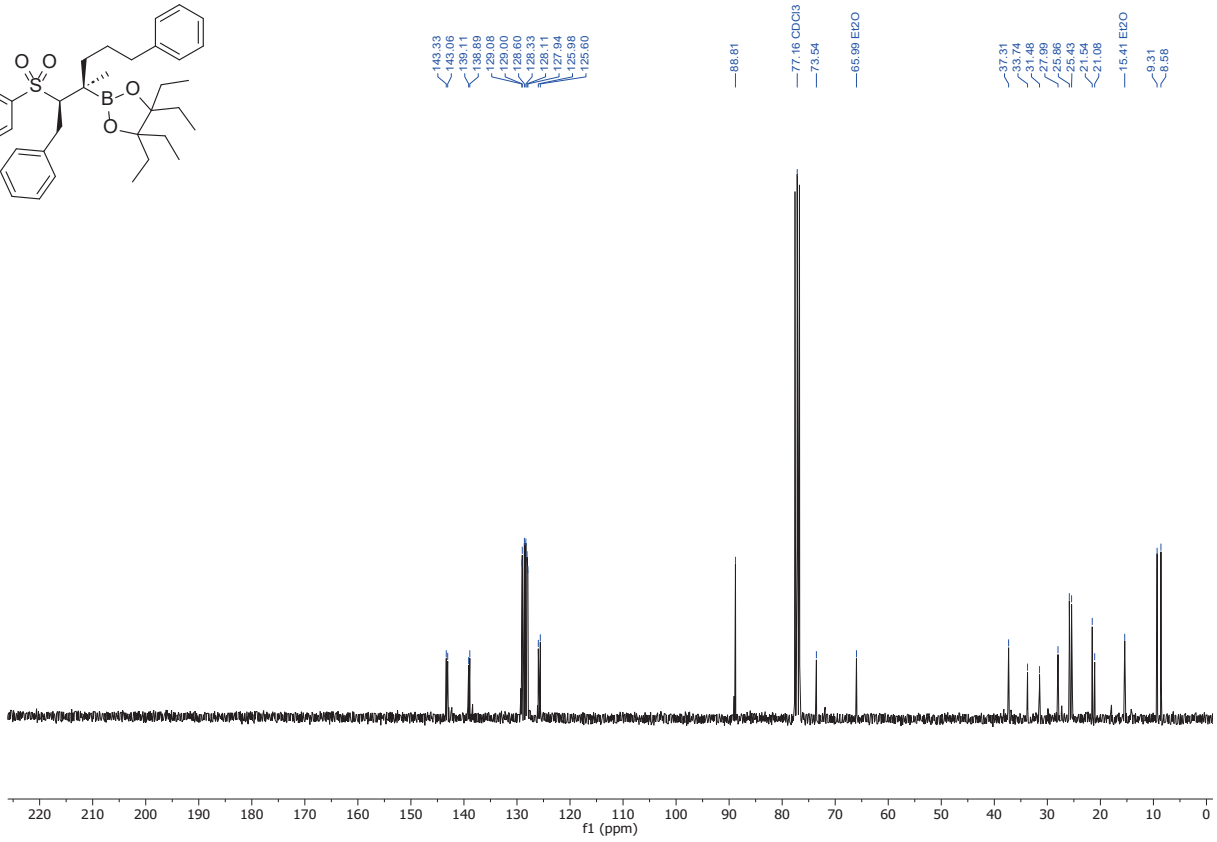




4,4,5,5-tetraethyl-2-((2R,3S)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (105)
Minor diastereomer

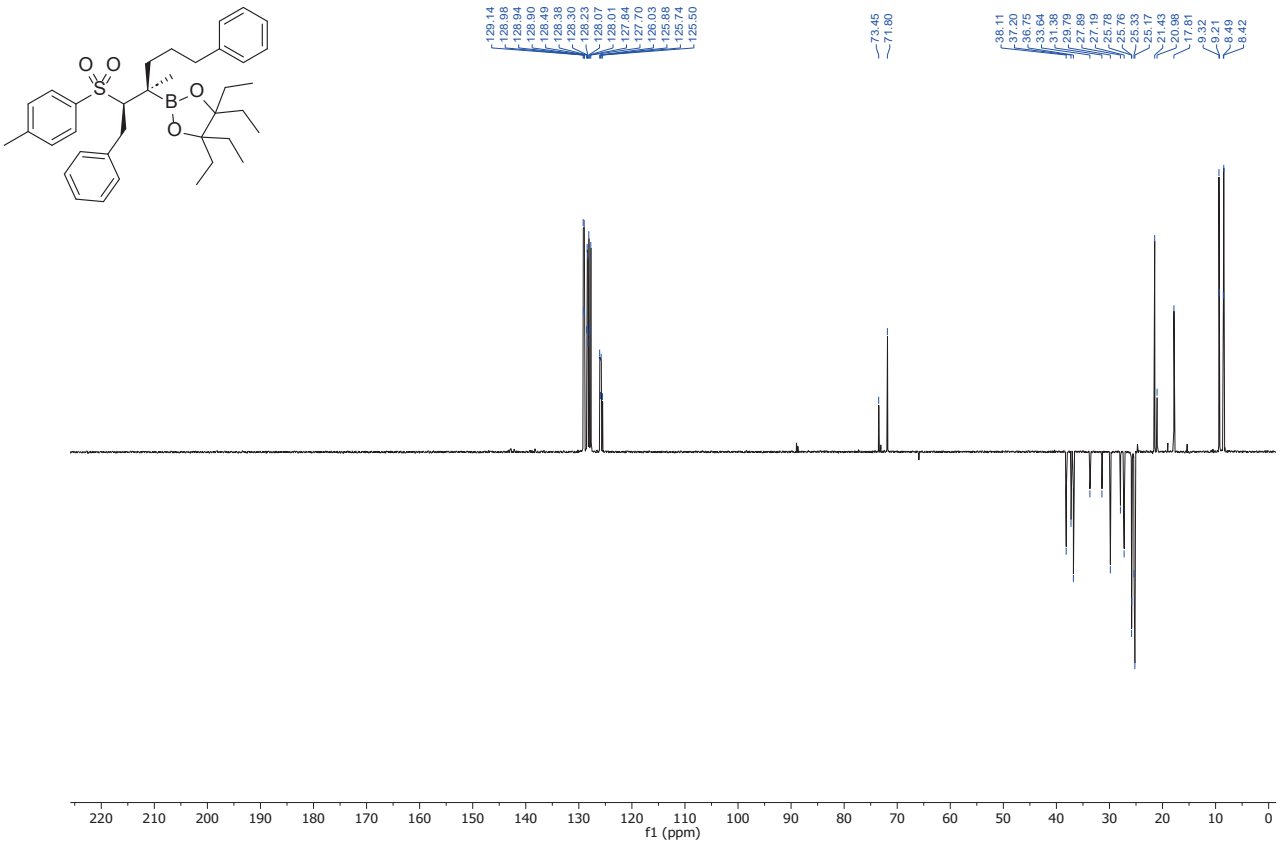
^{13}C NMR (75 MHz, $CDCl_3$)





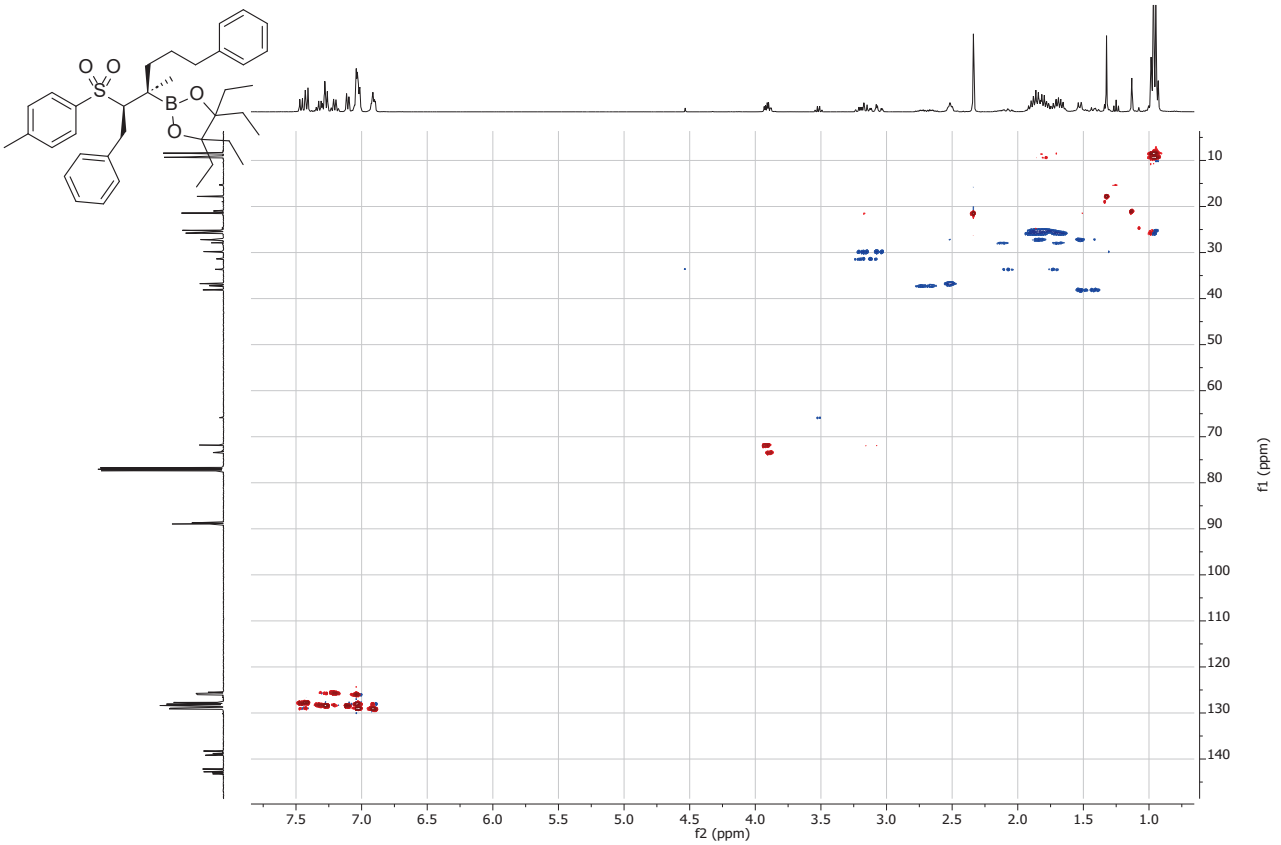
4,4,5,5-tetraethyl-2-((2R,3S)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (105)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



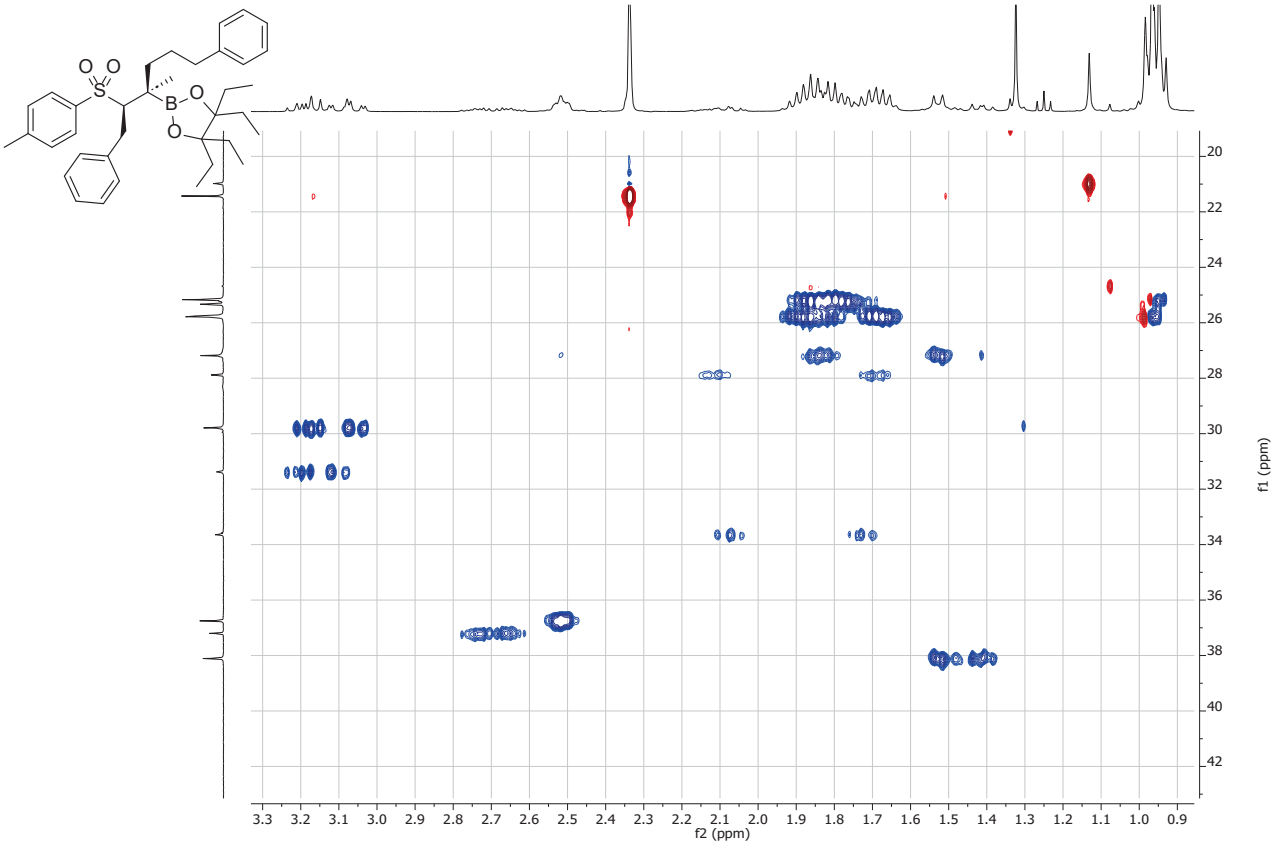
4,4,5,5-tetraethyl-2-((2R,3S)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (105)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



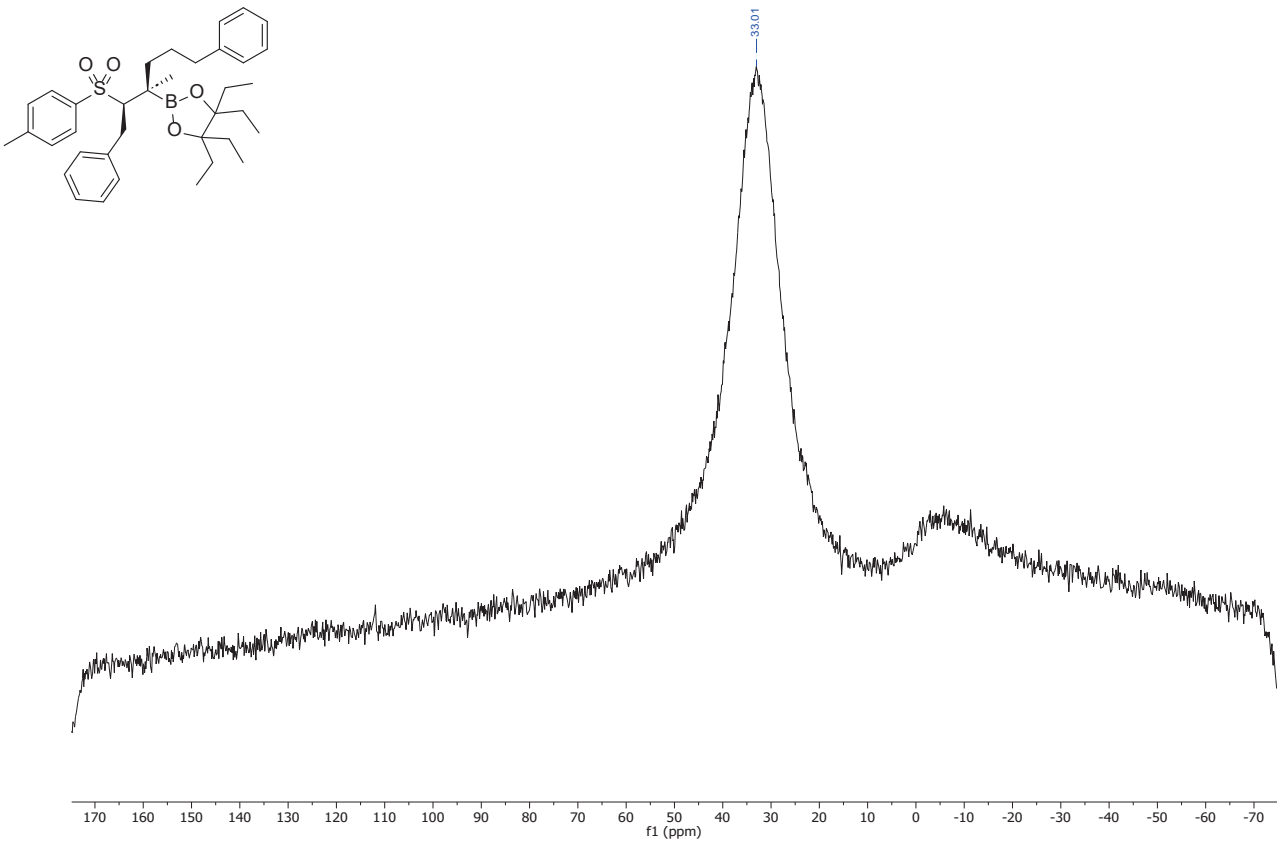
4,4,5,5-tetraethyl-2-((2R,3S)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (105)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



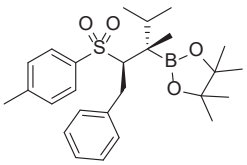
4,4,5,5-tetraethyl-2-((2R,3S)-3-methyl-1,6-diphenyl-2-tosylhexan-3-yl)-1,3,2-dioxaborolane (105)

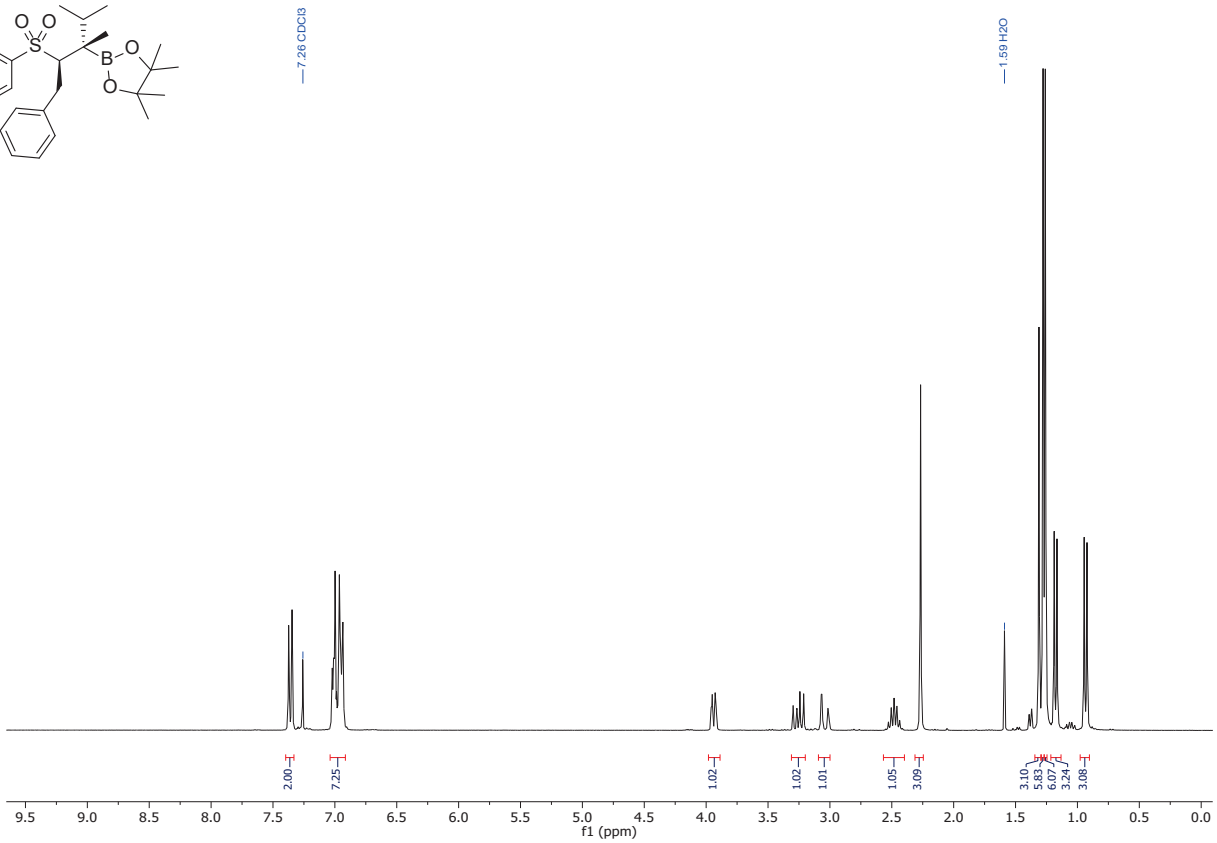
^{11}B NMR (96 MHz, $CDCl_3$)



2-((2R,3R)-3,4-dimethyl-1-phenyl-2-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53)
Major diastereomer

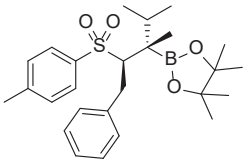
^{1}H NMR (300 MHz, $CDCl_3$)

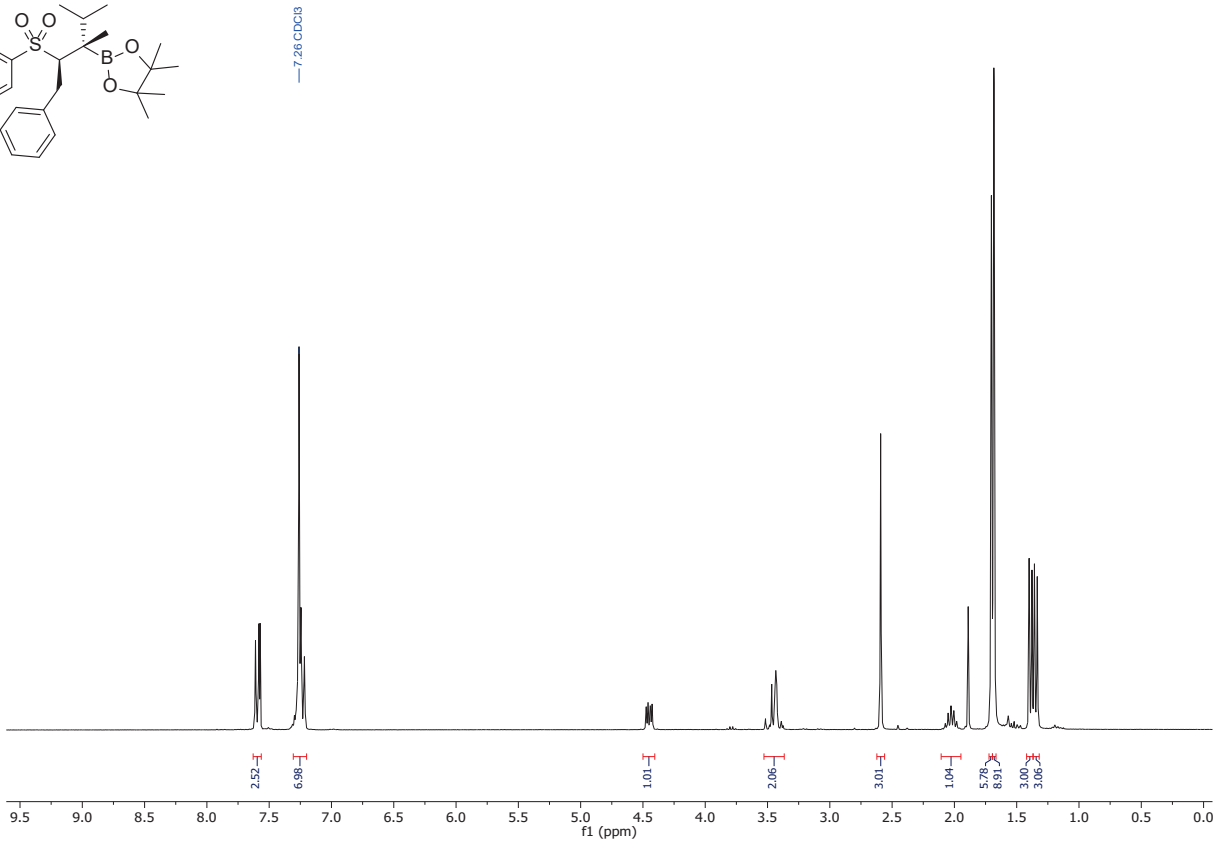




2-((2R,3R)-3,4-dimethyl-1-phenyl-2-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53)
Minor diastereomer

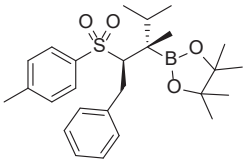
^{1}H NMR (300 MHz, $CDCl_3$)

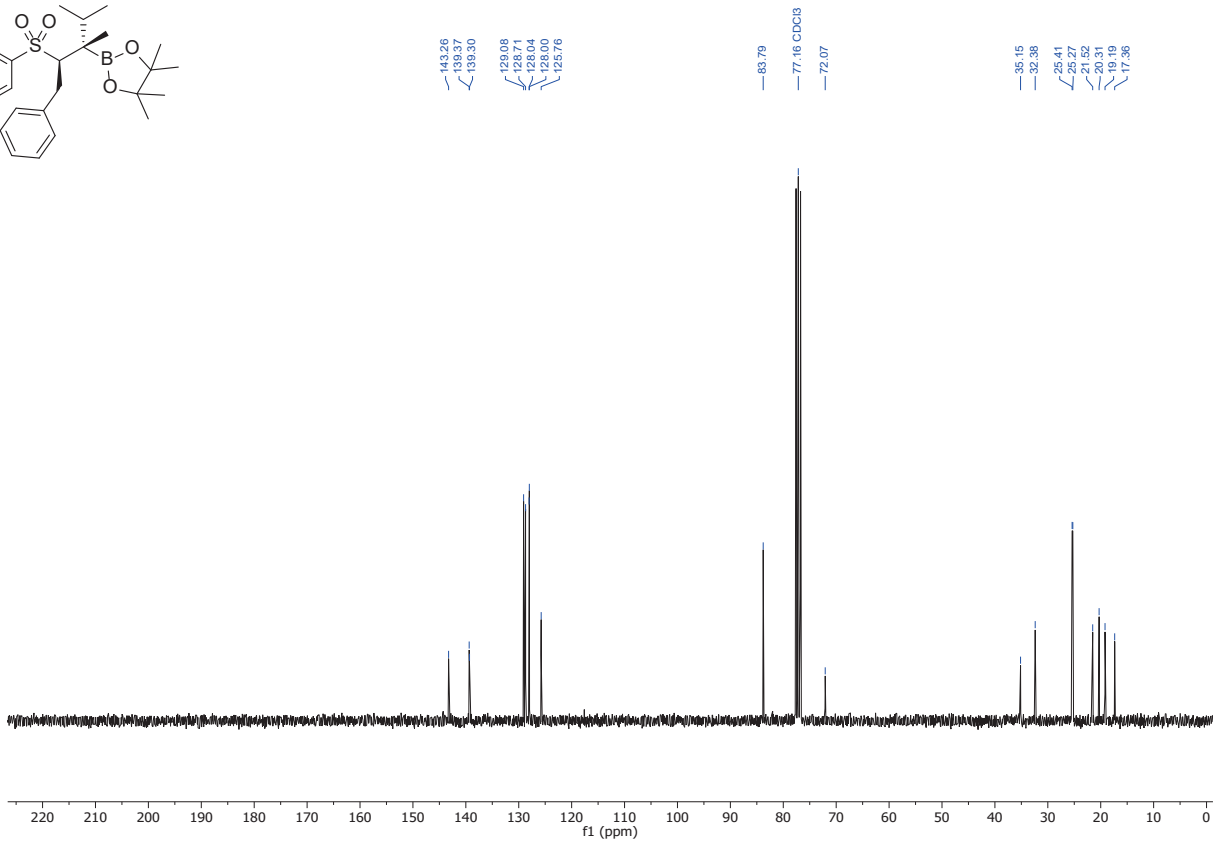




2-((2R,3R)-3,4-dimethyl-1-phenyl-2-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53)
Major diastereomer

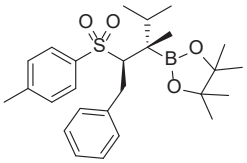
^{13}C NMR (75 MHz, $CDCl_3$)

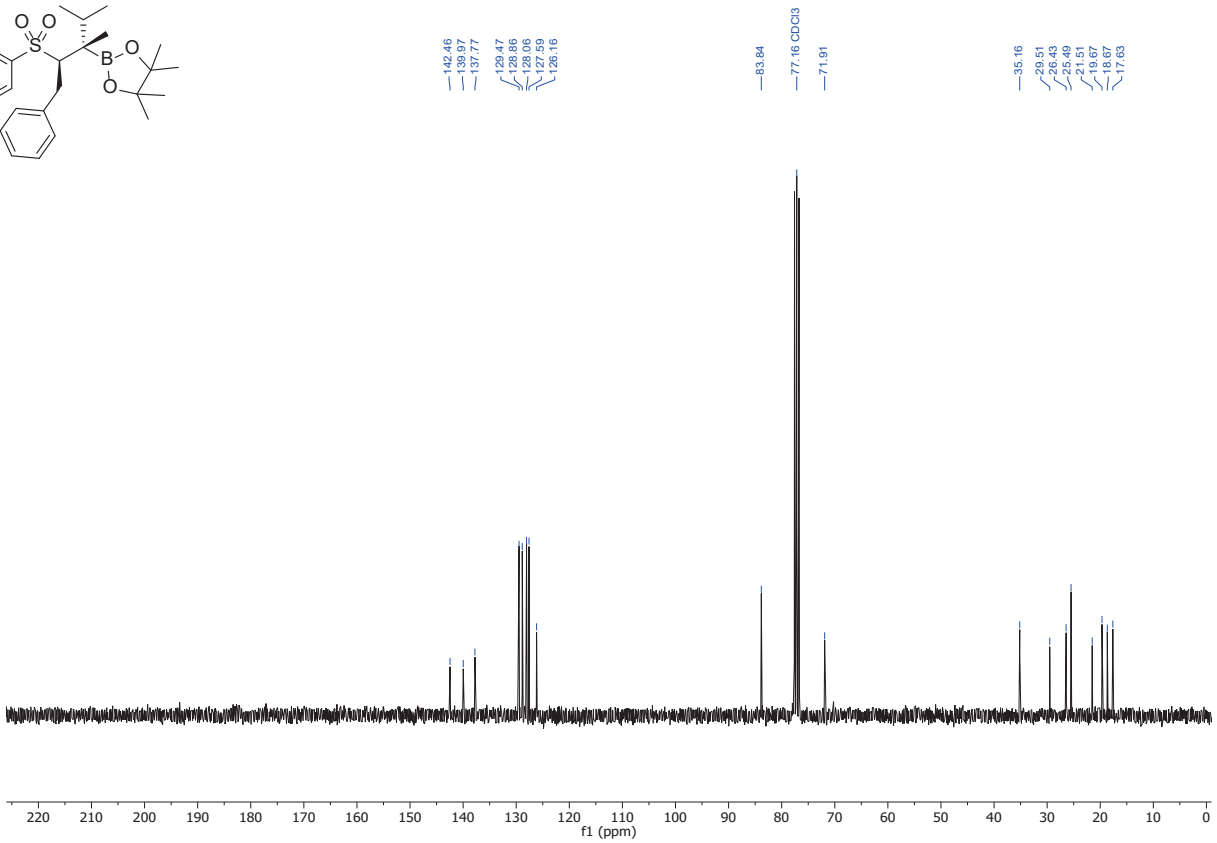




2-((2R,3R)-3,4-dimethyl-1-phenyl-2-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53)
Minor diastereomer

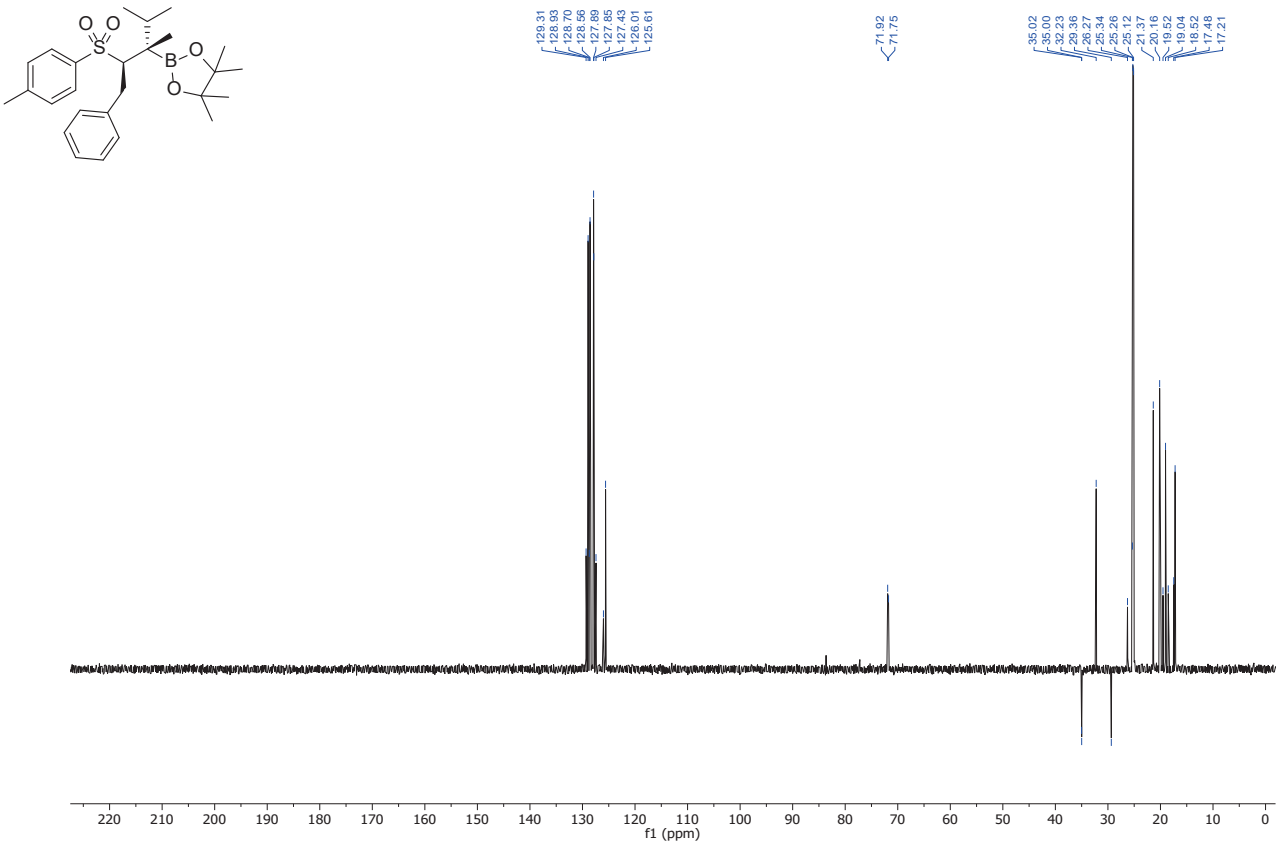
^{13}C NMR (75 MHz, $CDCl_3$)





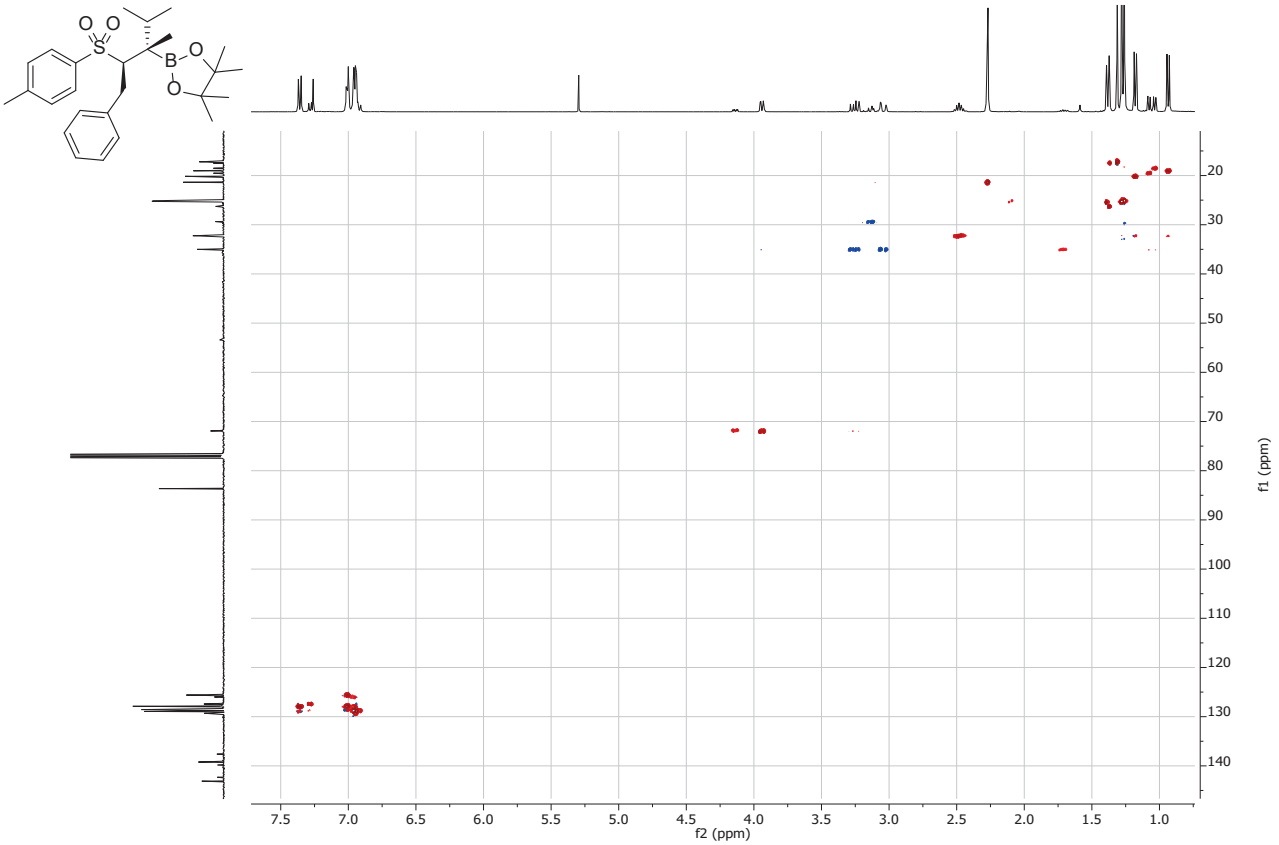
2-((2R,3R)-3,4-dimethyl-1-phenyl-2-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



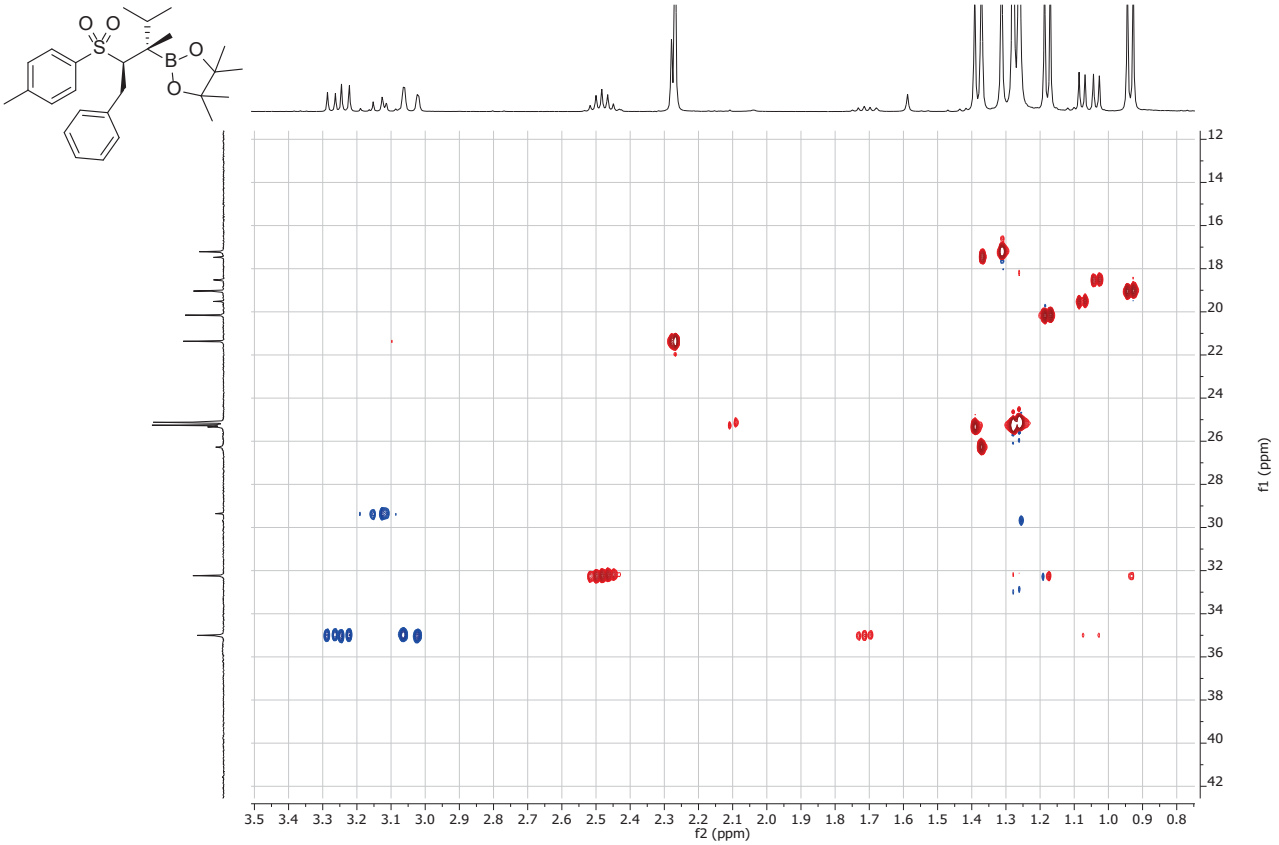
2-((2R,3R)-3,4-dimethyl-1-phenyl-2-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



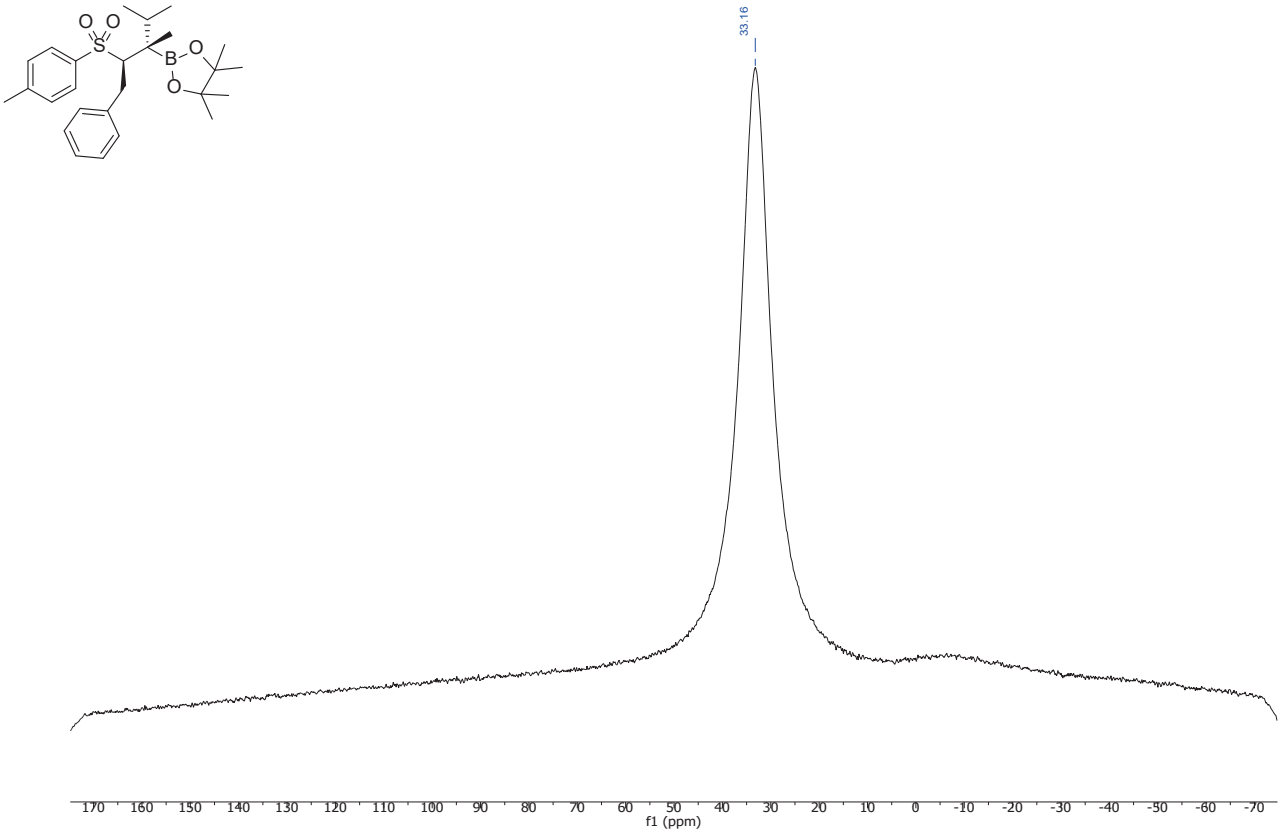
2-((2R,3R)-3,4-dimethyl-1-phenyl-2-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



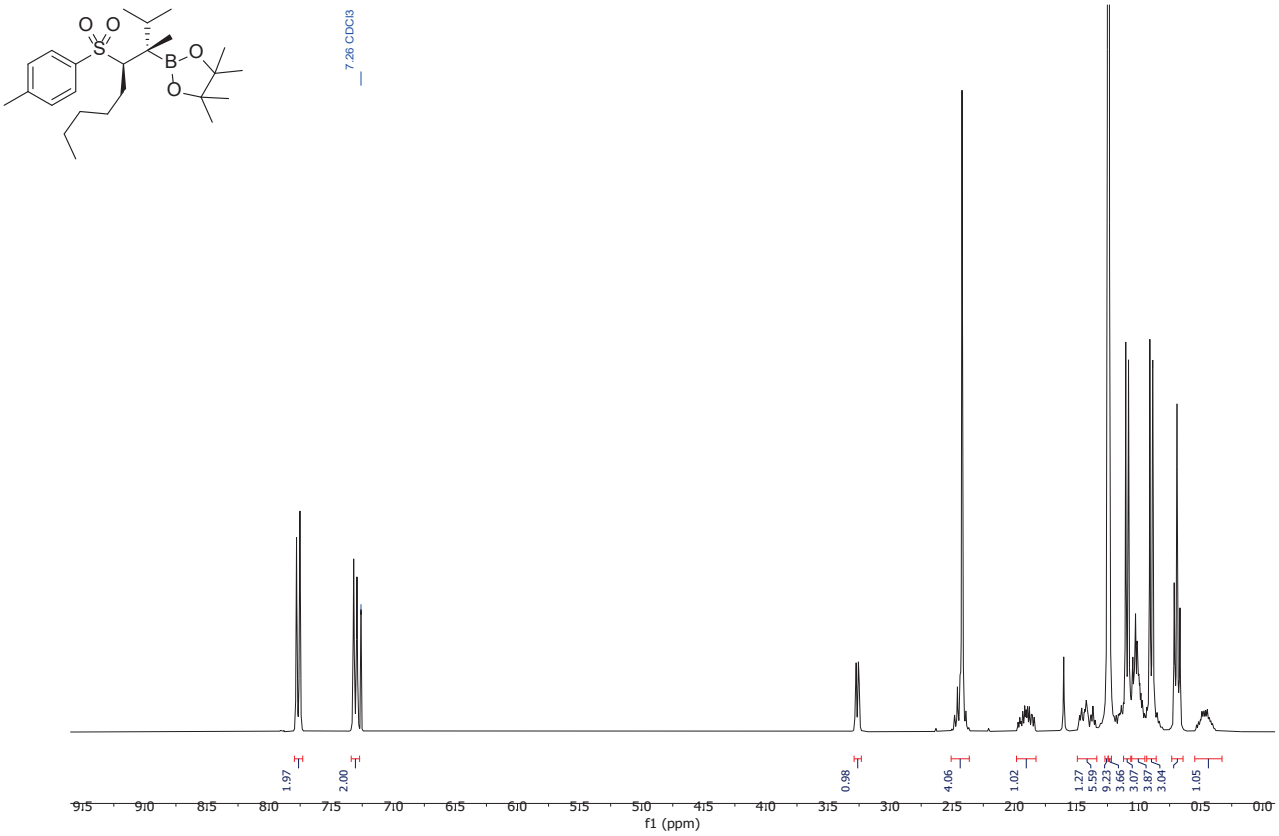
2-((2R,3R)-3,4-dimethyl-1-phenyl-2-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53)

^{11}B NMR (96 MHz, $CDCl_3$)



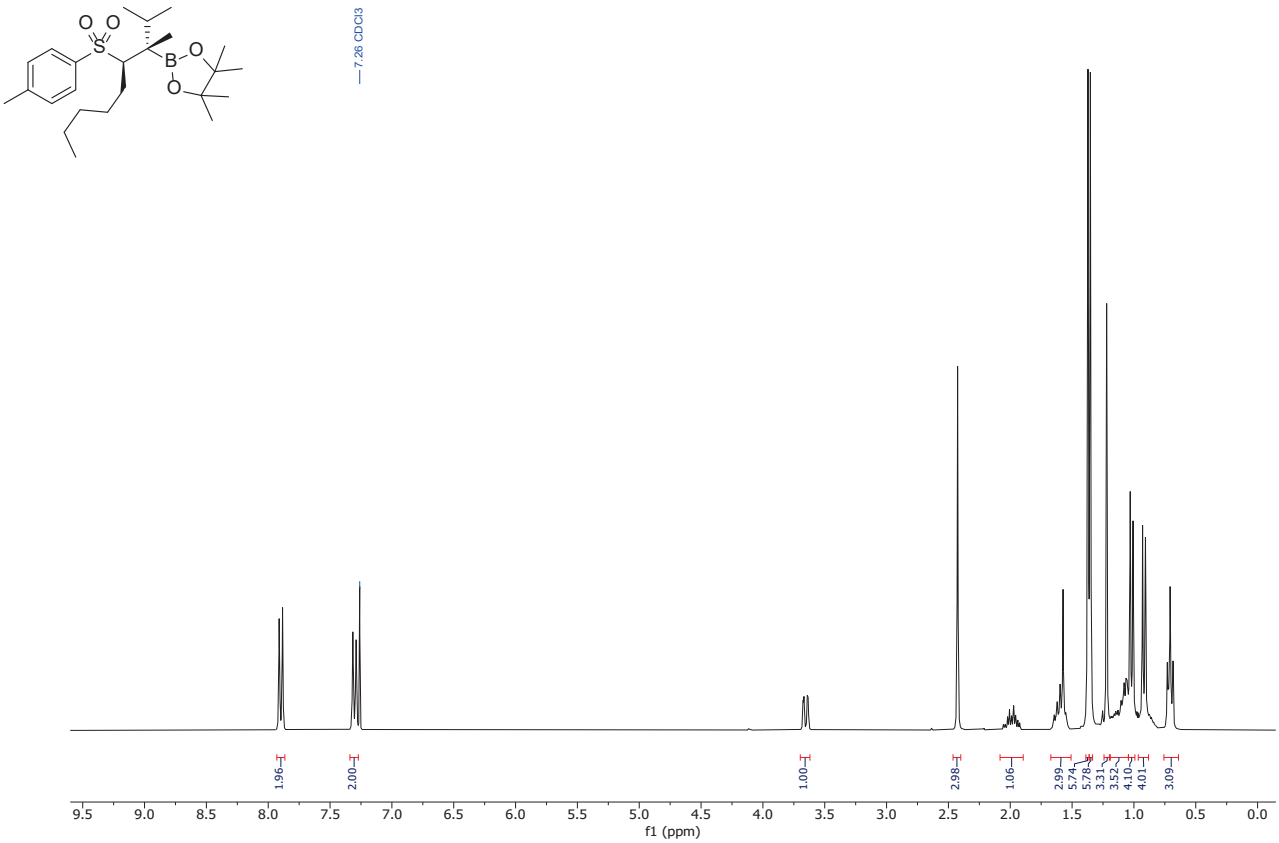
^{1}H NMR (300 MHz, $CDCl_3$)

2-((3R,4R)-2,3-dimethyl-4-tosylnonan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (52)
Major diastereomer



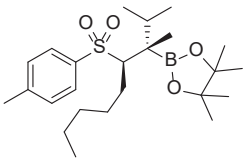
^{1}H NMR (300 MHz, $CDCl_3$)

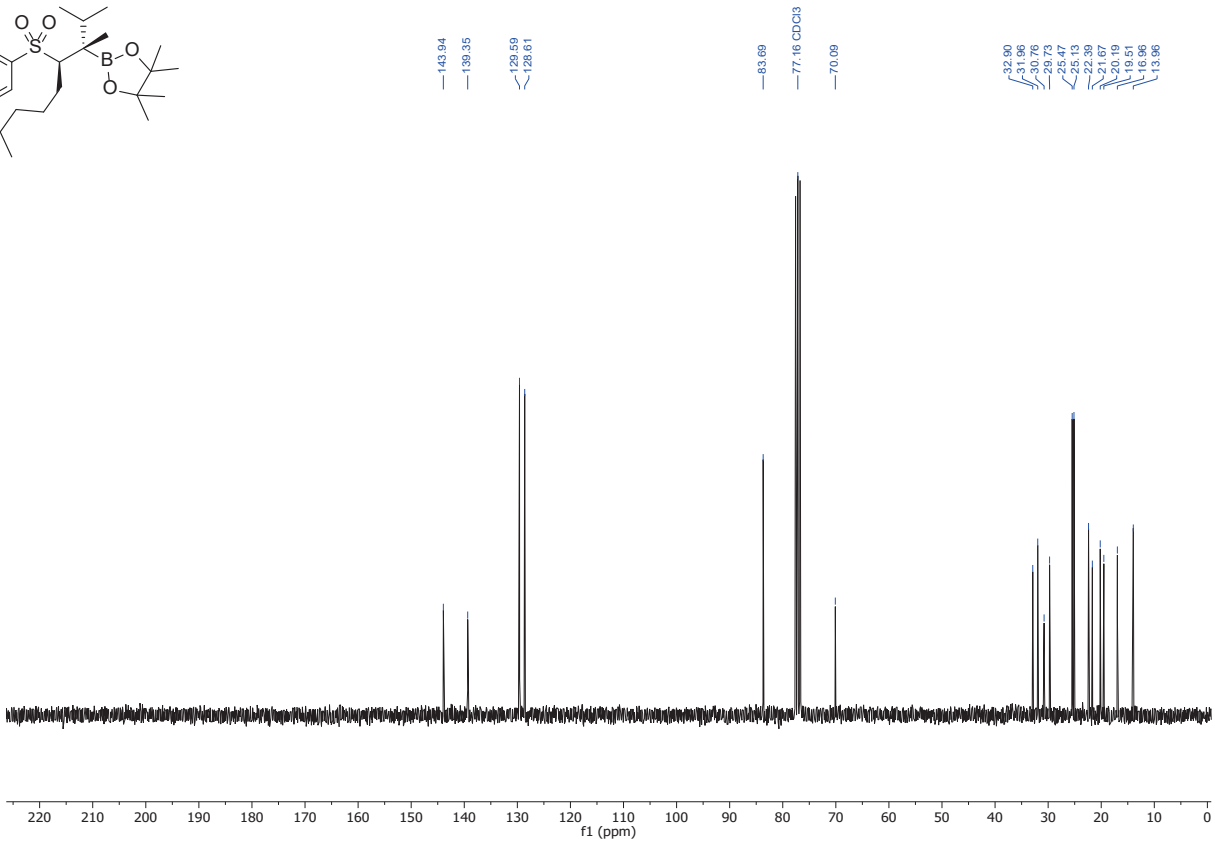
2-((3R,4R)-2,3-dimethyl-4-tosylnonan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (52)
Minor diastereomer



^{13}C NMR (75 MHz, $CDCl_3$)

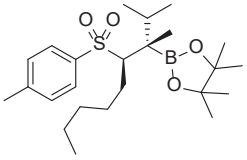
2-((3R,4R)-2,3-dimethyl-4-tosylnonan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (52)
Major diastereomer

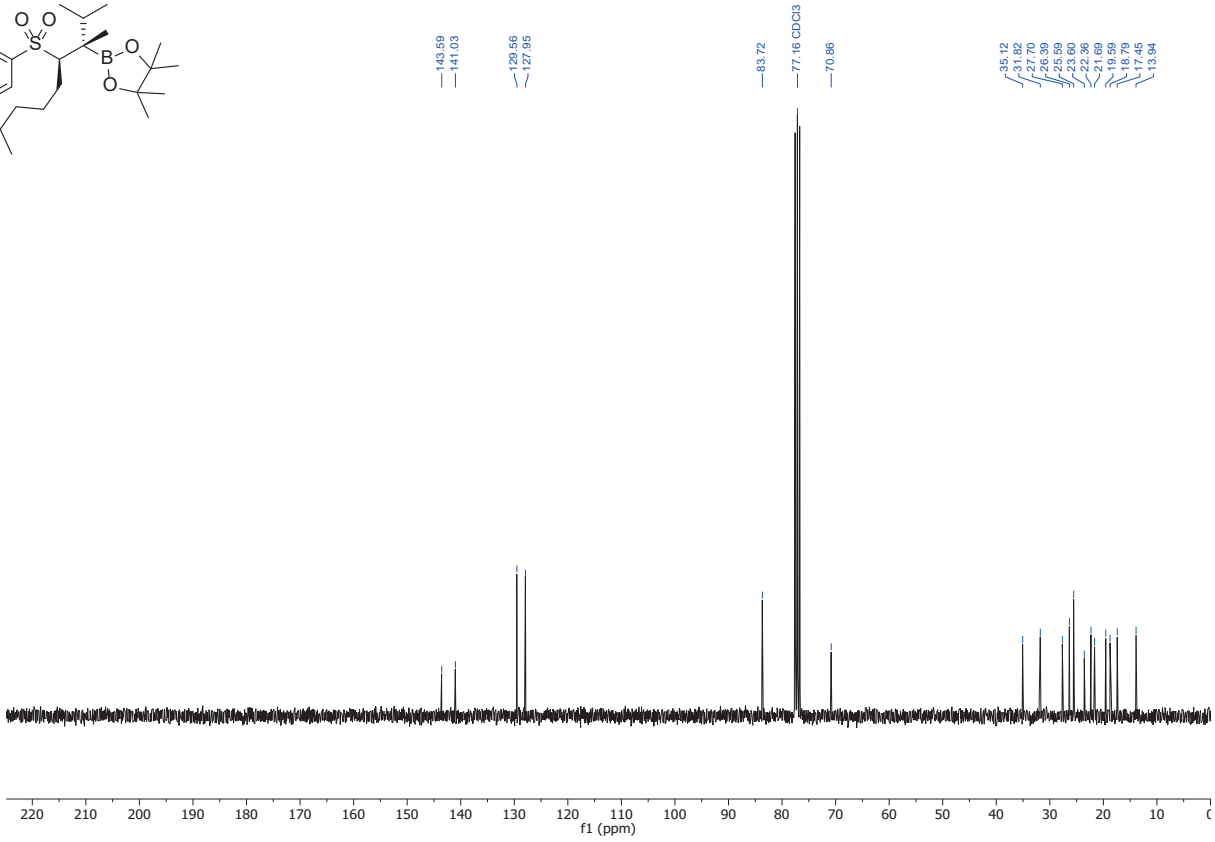




^{13}C NMR (75 MHz, $CDCl_3$)

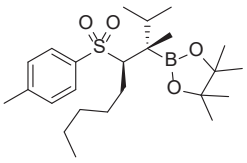
2-((3R,4R)-2,3-dimethyl-4-tosylnonan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (52)
Minor diastereomer

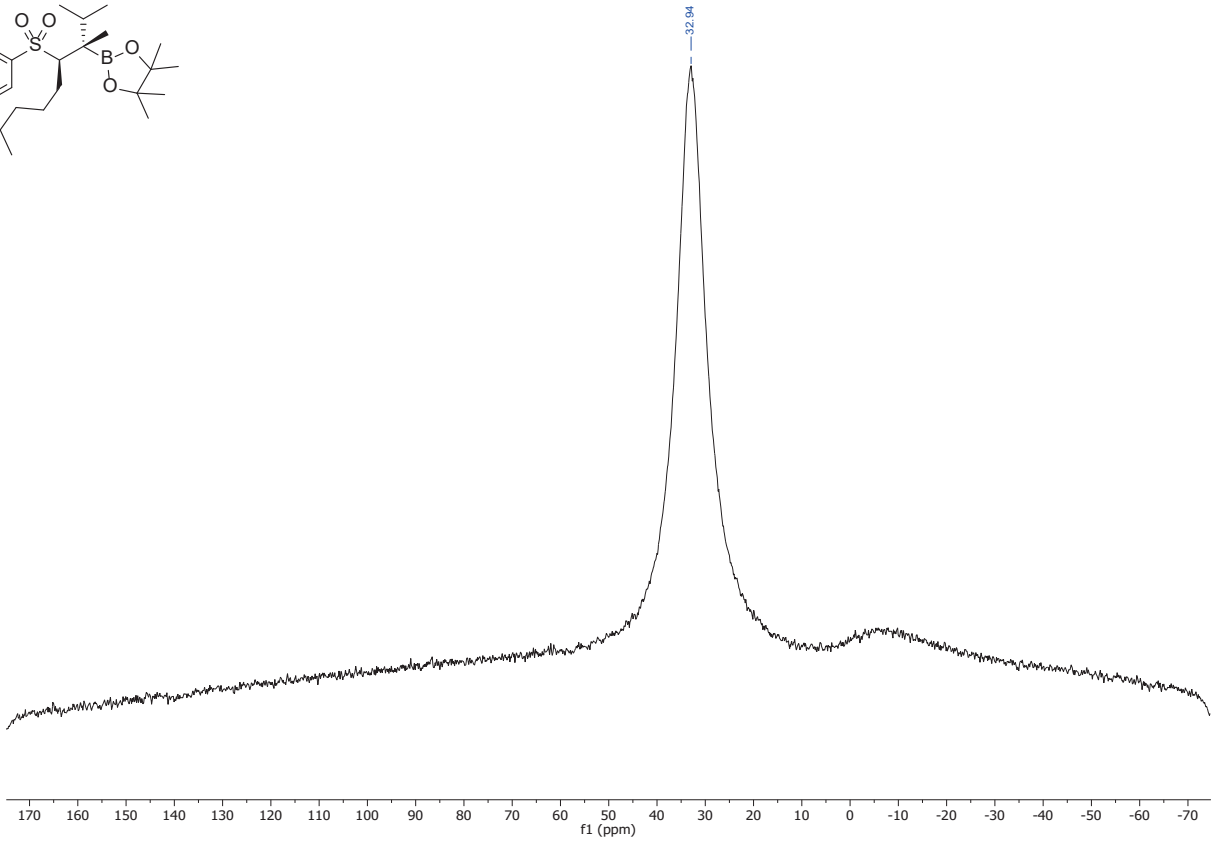




^{11}B NMR (96 MHz, $CDCl_3$)

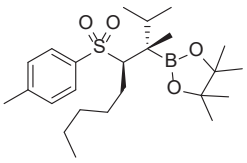
2-((3R,4R)-2,3-dimethyl-4-tosylnonan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (52)
Major diastereomer

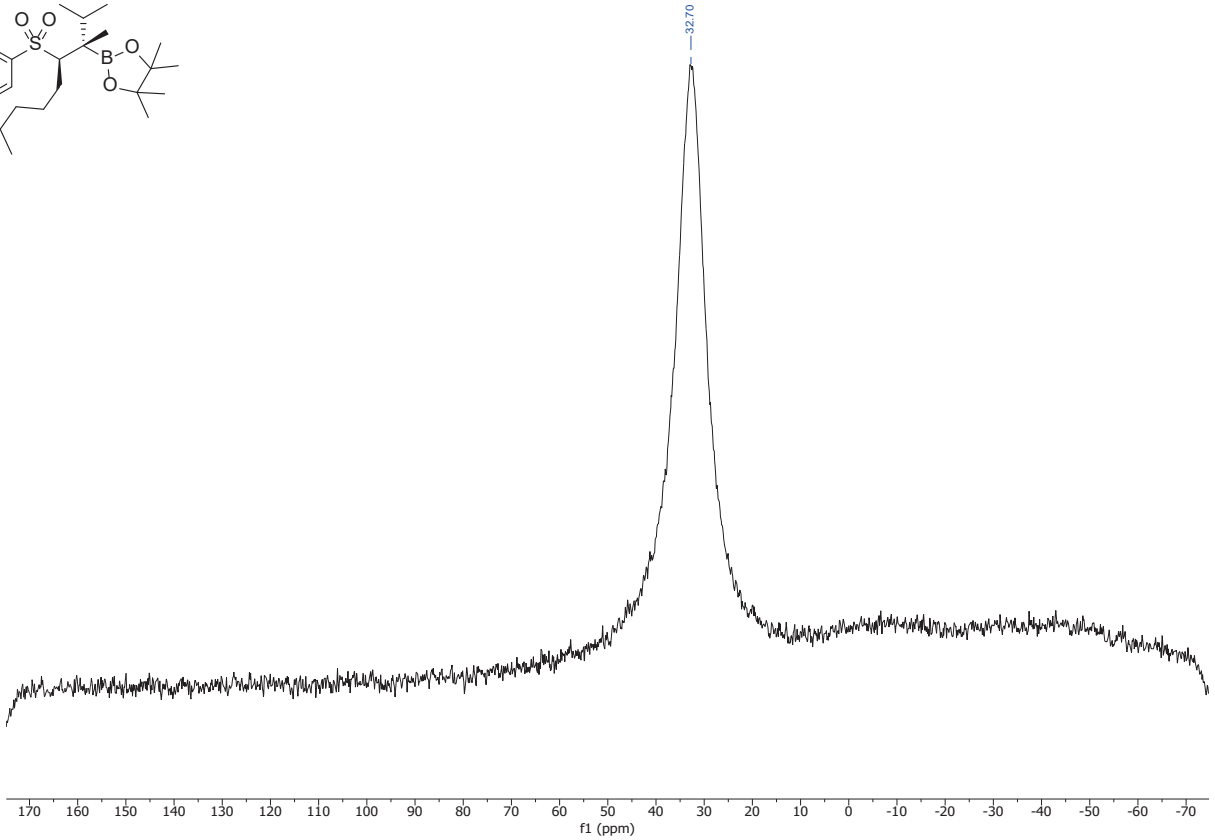




^{11}B NMR (96 MHz, $CDCl_3$)

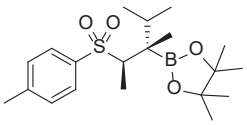
2-((3R,4R)-2,3-dimethyl-4-tosylnonan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (52)
Minor diastereomer

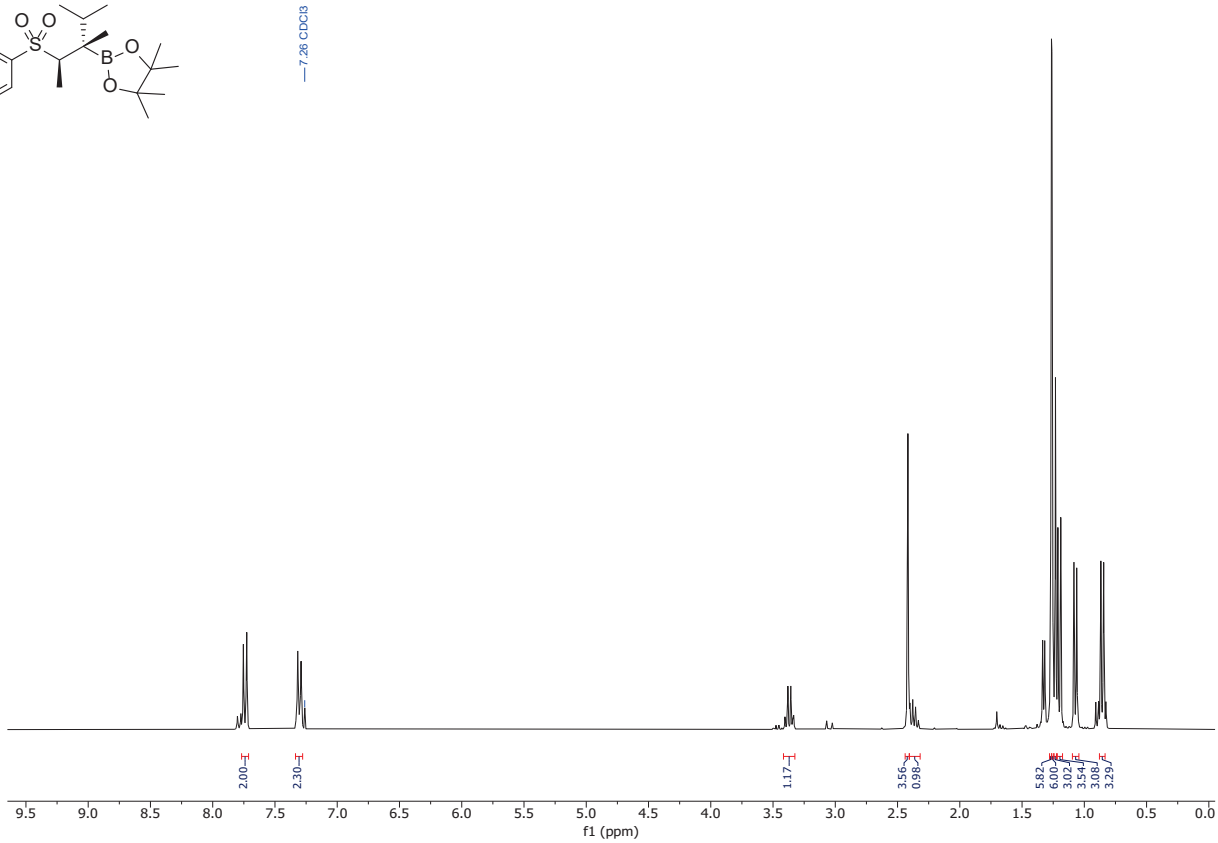




^{1}H NMR (300 MHz, $CDCl_3$)

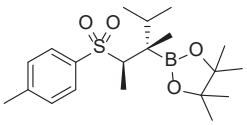
2-((3R,4R)-2,3-dimethyl-4-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51)
Major diastereomer

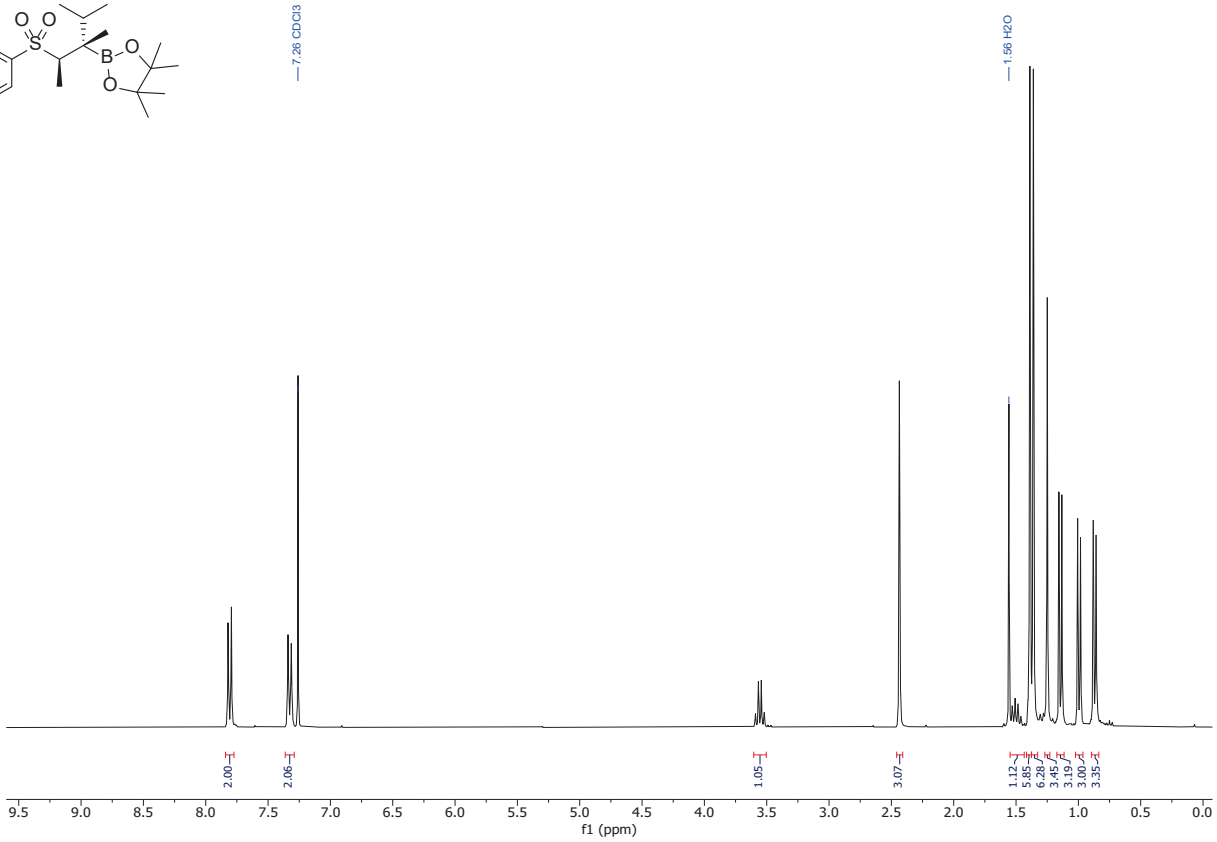




^{1}H NMR (300 MHz, $CDCl_3$)

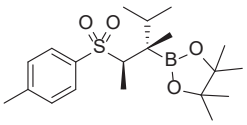
2-((3R,4R)-2,3-dimethyl-4-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51)
Minor diastereomer

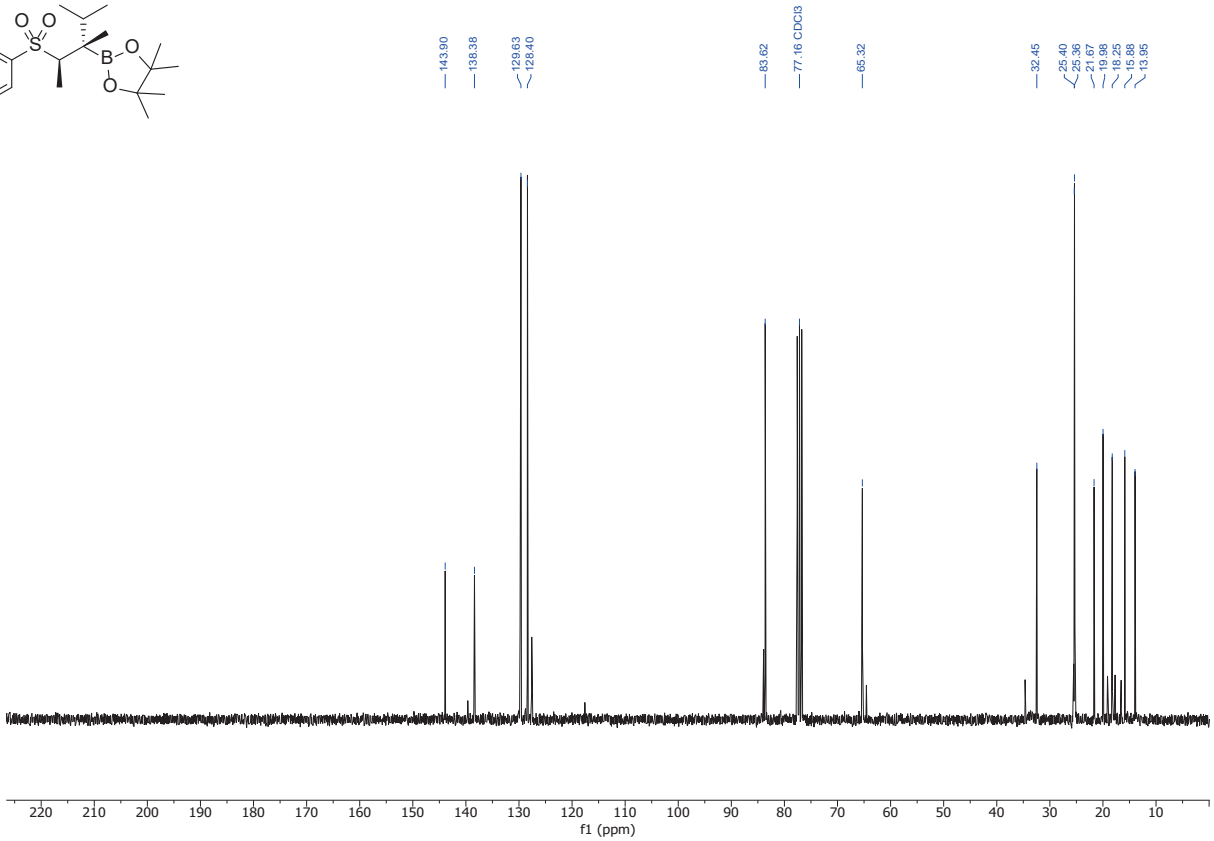




^{13}C NMR (75 MHz, $CDCl_3$)

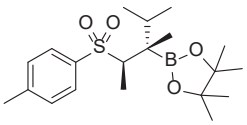
2-((3R,4R)-2,3-dimethyl-4-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51)
Major diastereomer

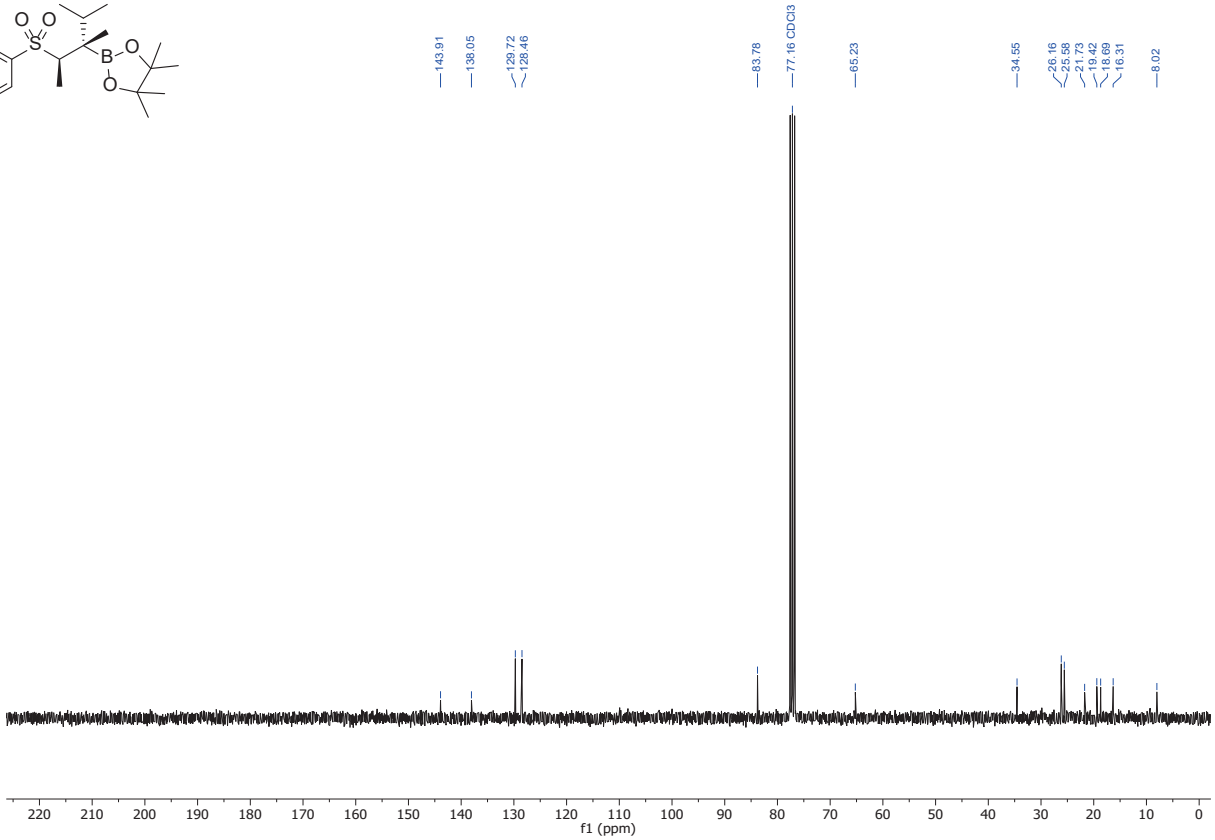




^{13}C NMR (75 MHz, $CDCl_3$)

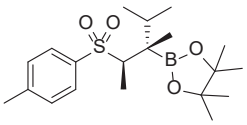
2-((3R,4R)-2,3-dimethyl-4-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51)
Minor diastereomer

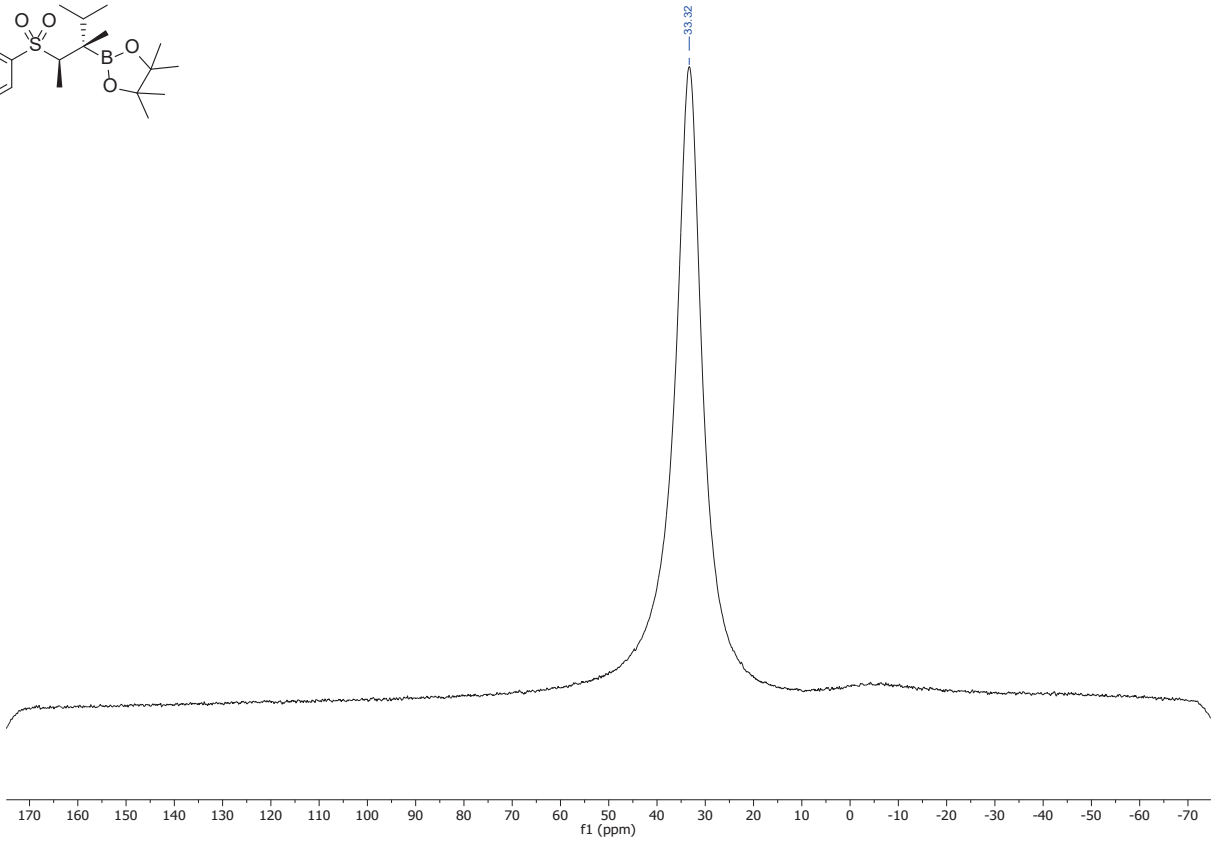




^{11}B NMR (96 MHz, $CDCl_3$)

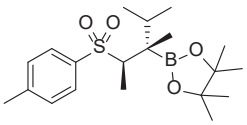
2-((3R,4R)-2,3-dimethyl-4-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51)
Major diastereomer

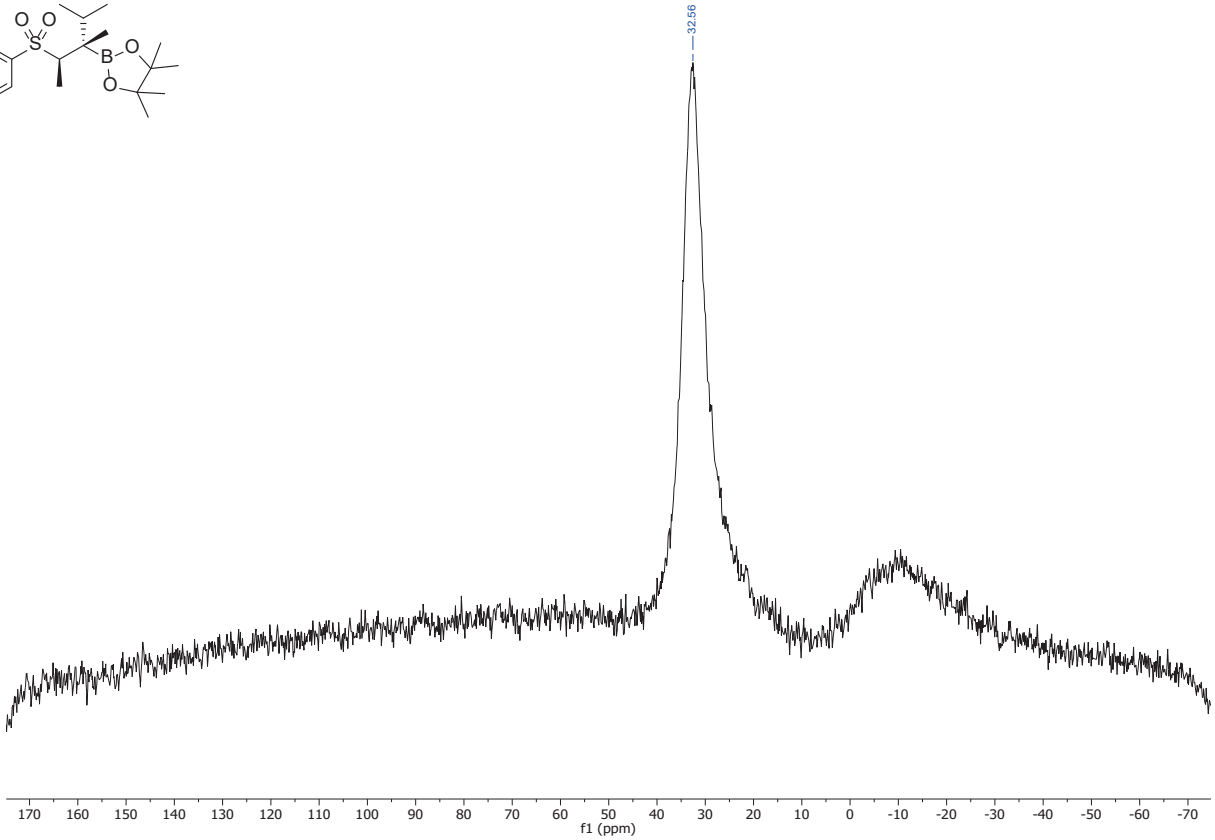




^{11}B NMR (96 MHz, $CDCl_3$)

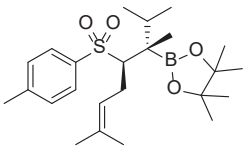
2-((3R,4R)-2,3-dimethyl-4-tosylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51)
Minor diastereomer

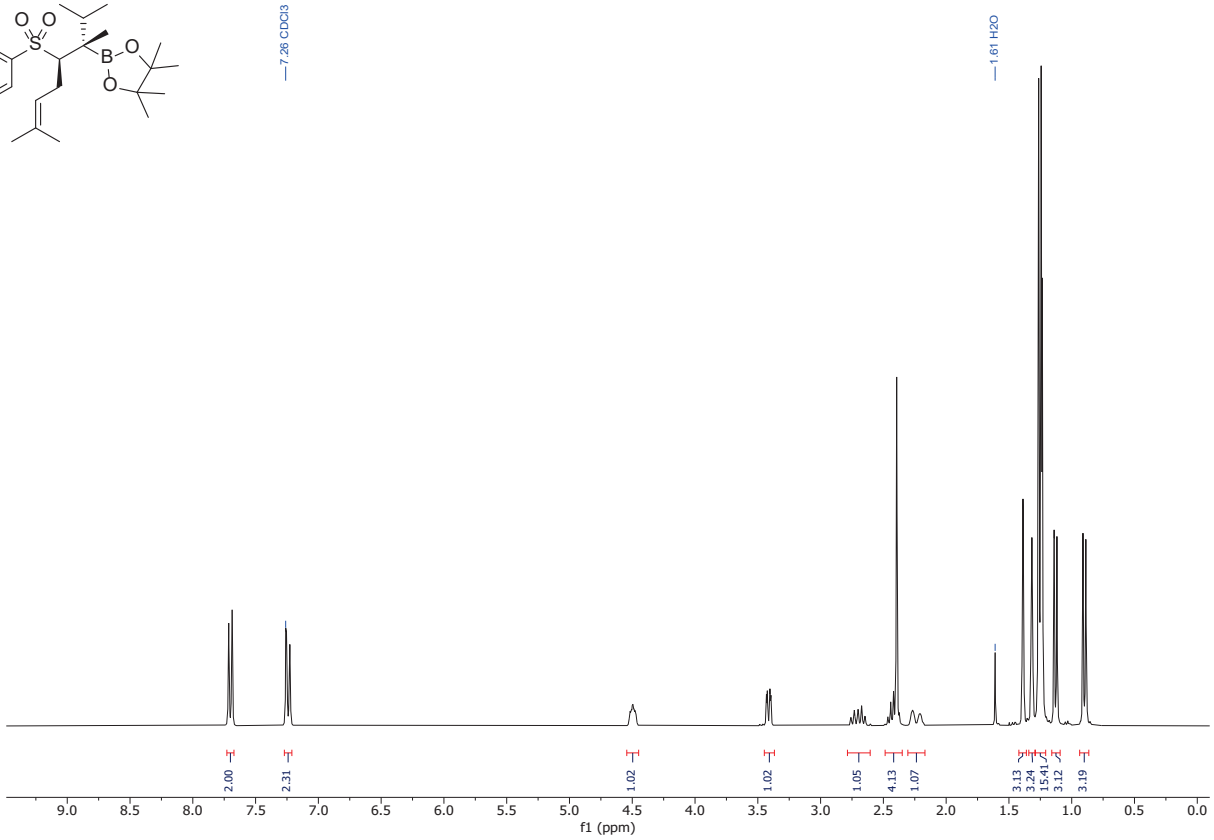




4,4,5,5-tetramethyl-2-((3R,4R)-2,3,7-trimethyl-4-tosyloct-6-en-3-yl)-1,3,2-dioxaborolane (54)
Major diastereomer

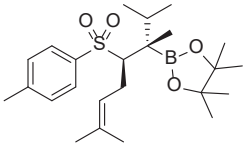
^{1}H NMR (300 MHz, $CDCl_3$)

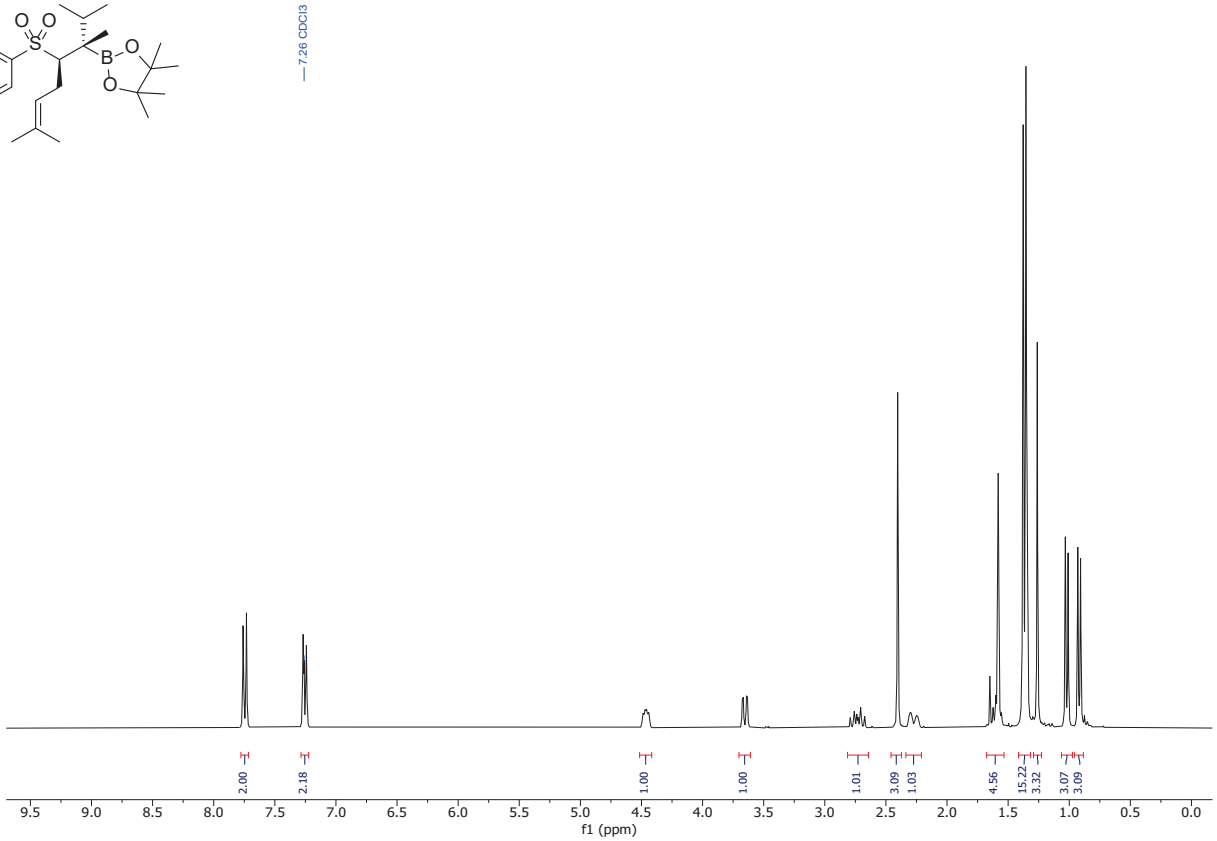




4,4,5,5-tetramethyl-2-((3R,4R)-2,3,7-trimethyl-4-tosyloct-6-en-3-yl)-1,3,2-dioxaborolane (54)
Minor diastereomer

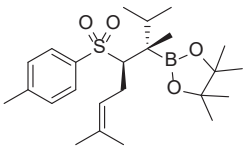
^{1}H NMR (300 MHz, $CDCl_3$)

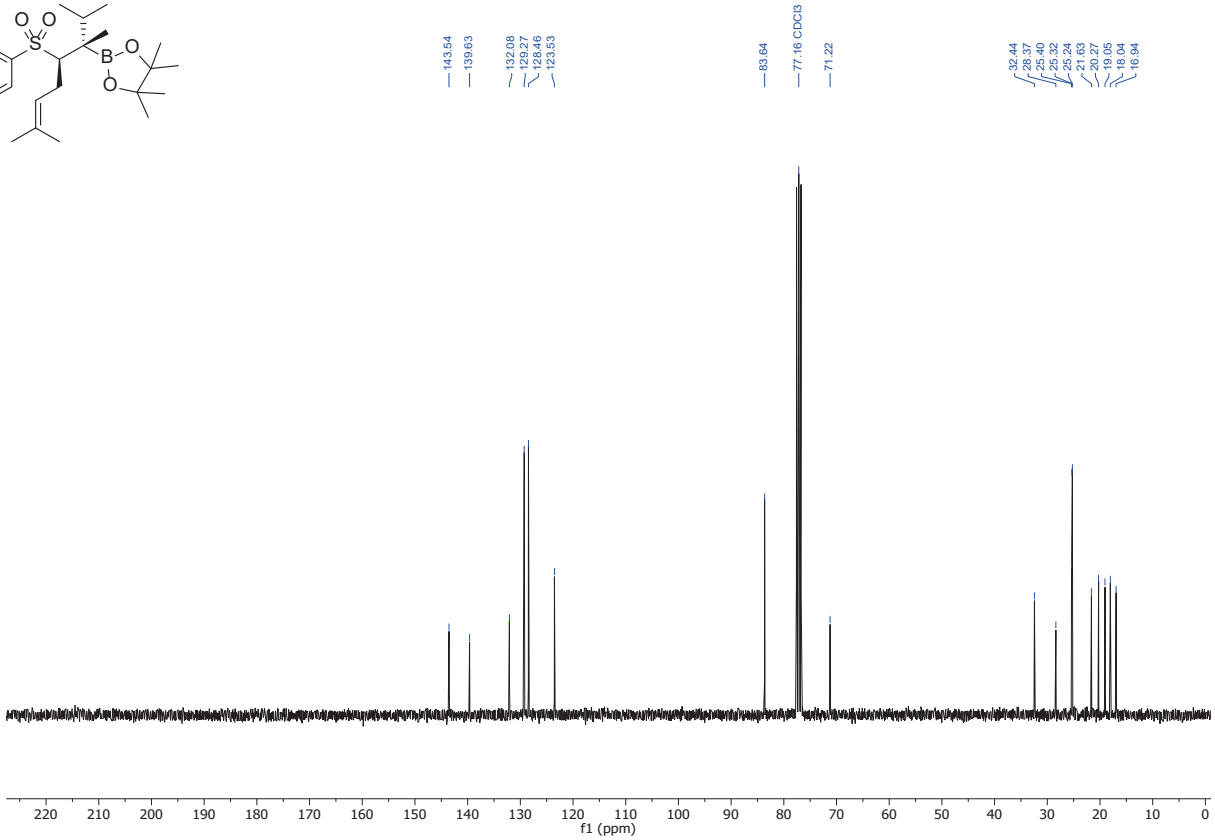




4,4,5,5-tetramethyl-2-((3R,4R)-2,3,7-trimethyl-4-tosyloct-6-en-3-yl)-1,3,2-dioxaborolane (54)
Major diastereomer

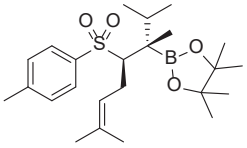
^{13}C NMR (75 MHz, $CDCl_3$)

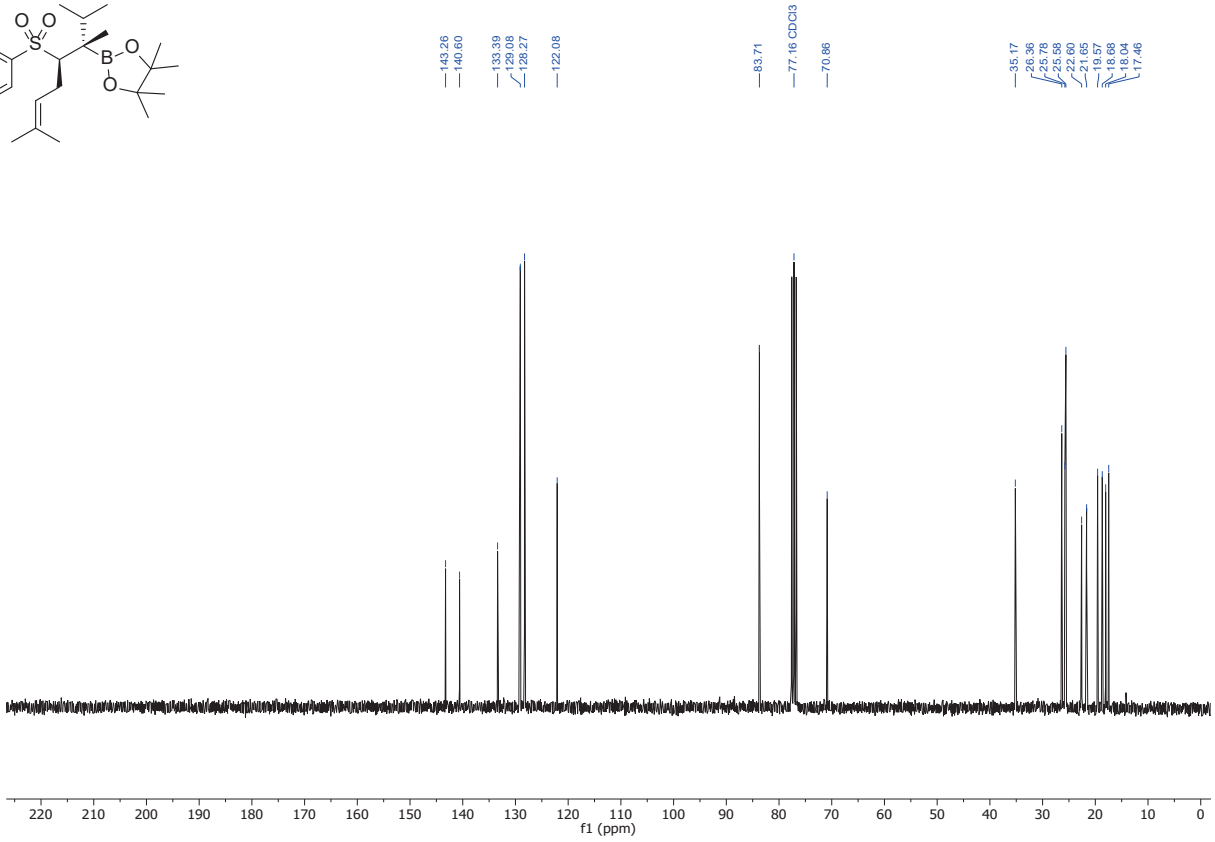




4,4,5,5-tetramethyl-2-((3R,4R)-2,3,7-trimethyl-4-tosyloct-6-en-3-yl)-1,3,2-dioxaborolane (54)
Minor diastereomer

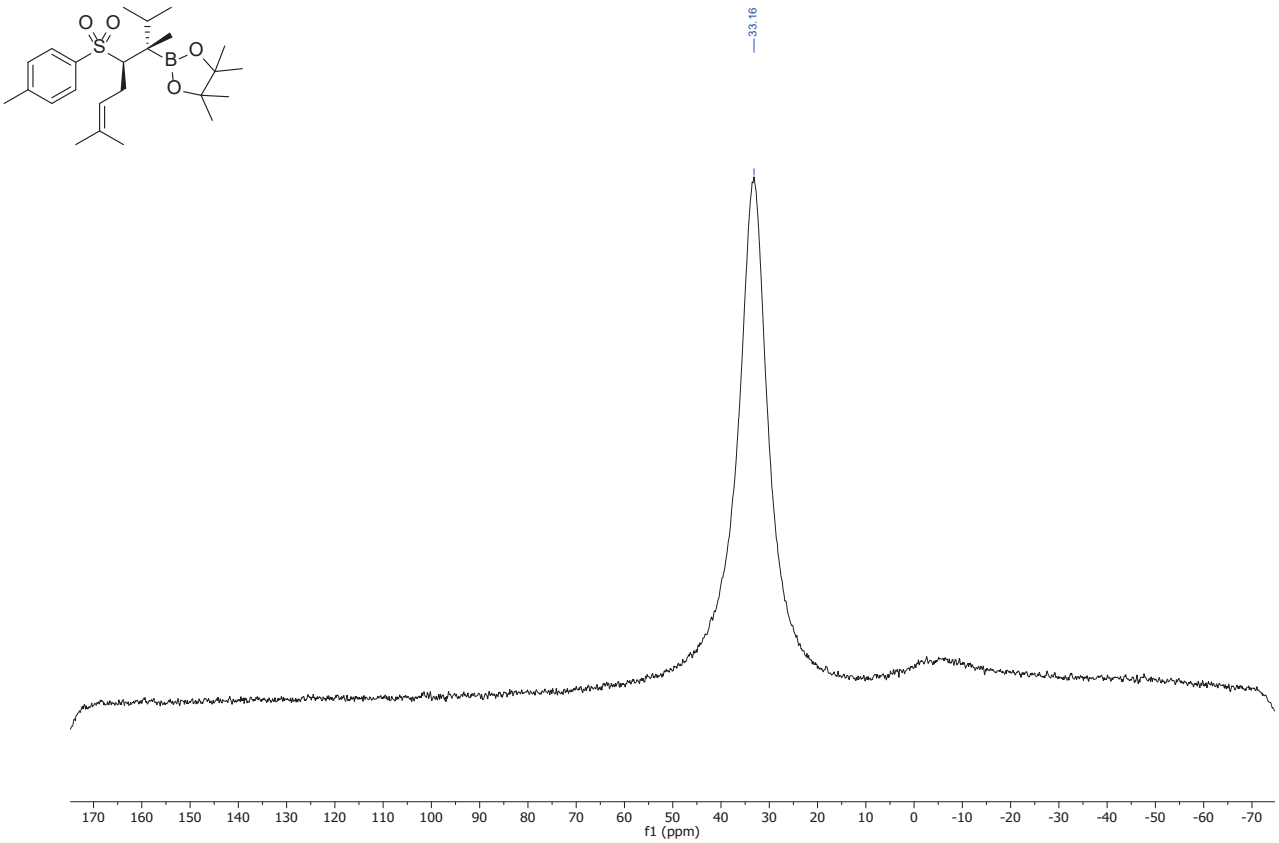
^{13}C NMR (75 MHz, $CDCl_3$)





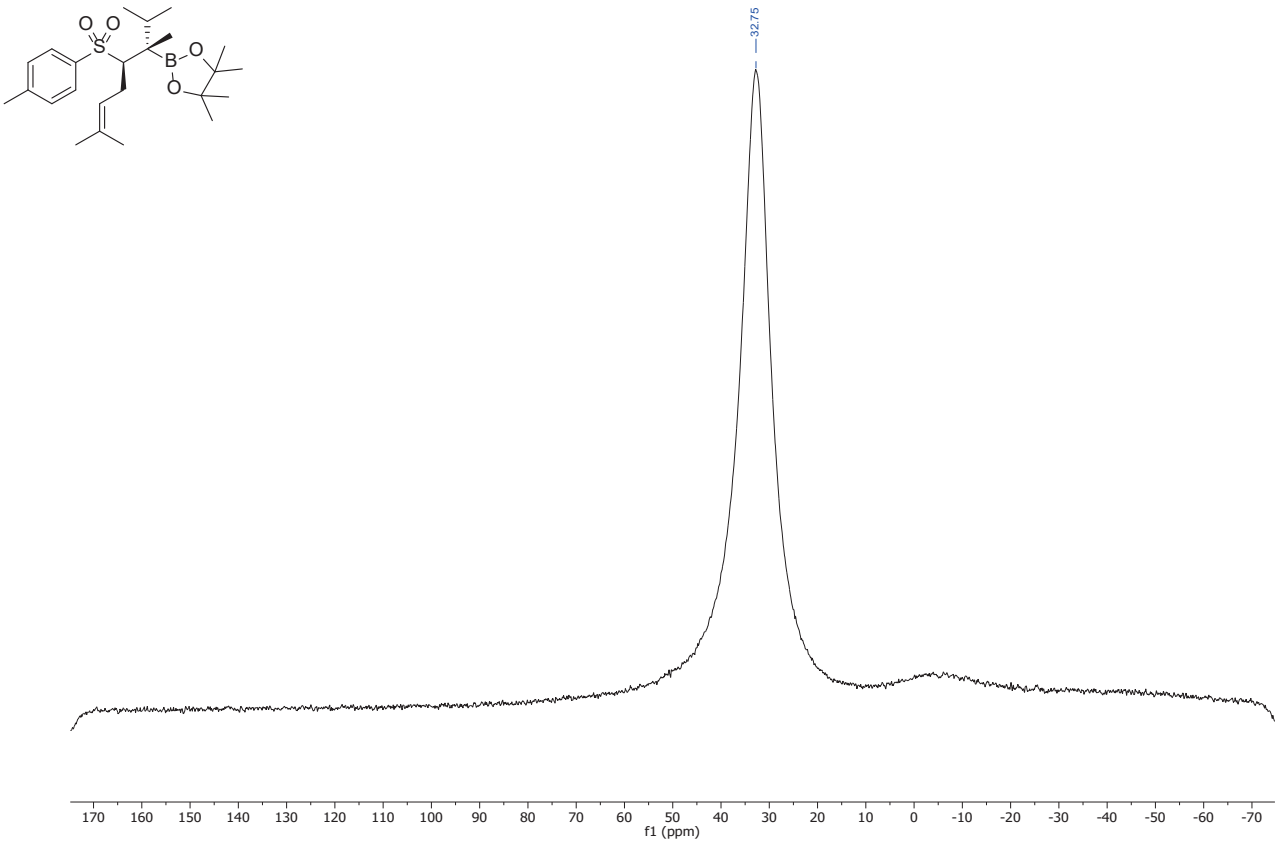
4,4,5,5-tetramethyl-2-((3R,4R)-2,3,7-trimethyl-4-tosyloct-6-en-3-yl)-1,3,2-dioxaborolane (54)
Major diastereomer

^{11}B NMR (96 MHz, $CDCl_3$)



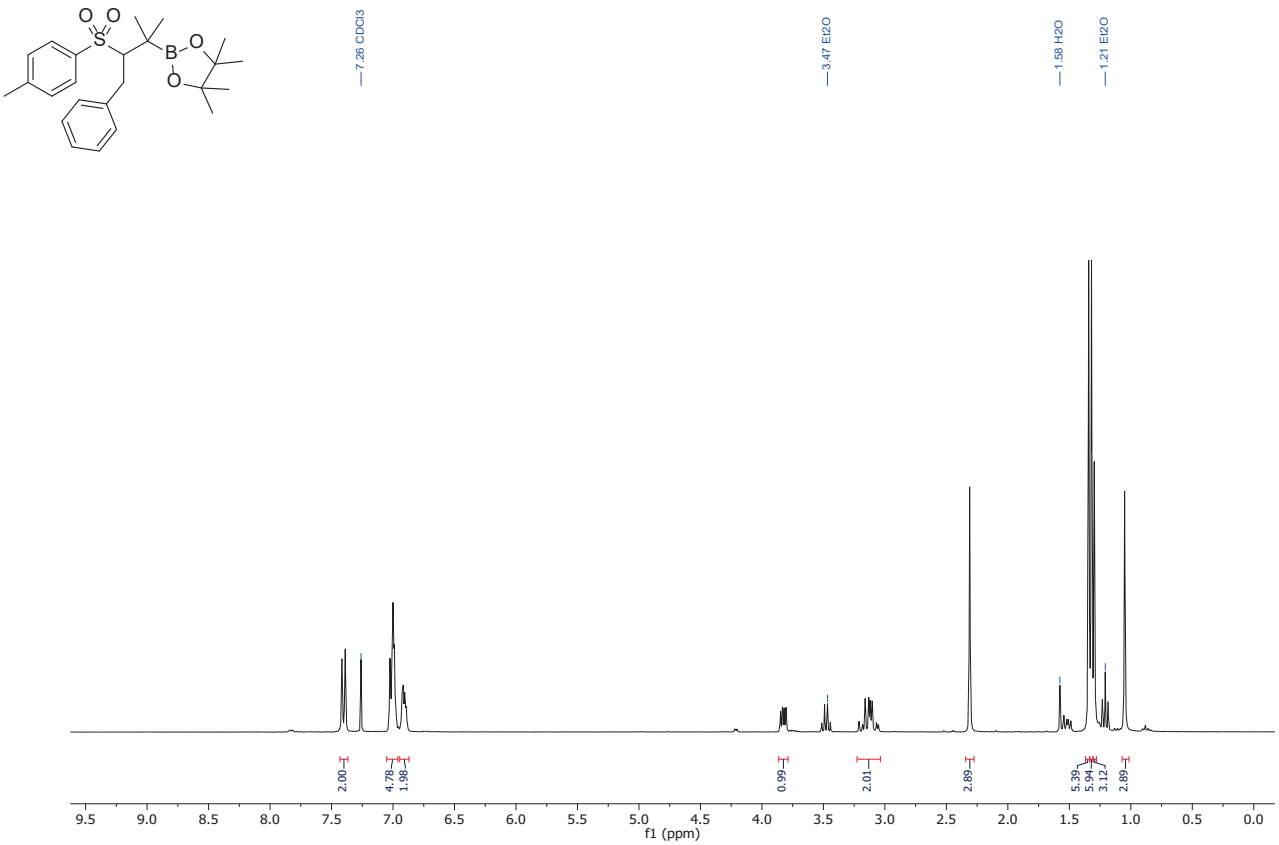
4,4,5,5-tetramethyl-2-((3R,4R)-2,3,7-trimethyl-4-tosyloct-6-en-3-yl)-1,3,2-dioxaborolane (54)
Minor diastereomer

^{11}B NMR (96 MHz, $CDCl_3$)



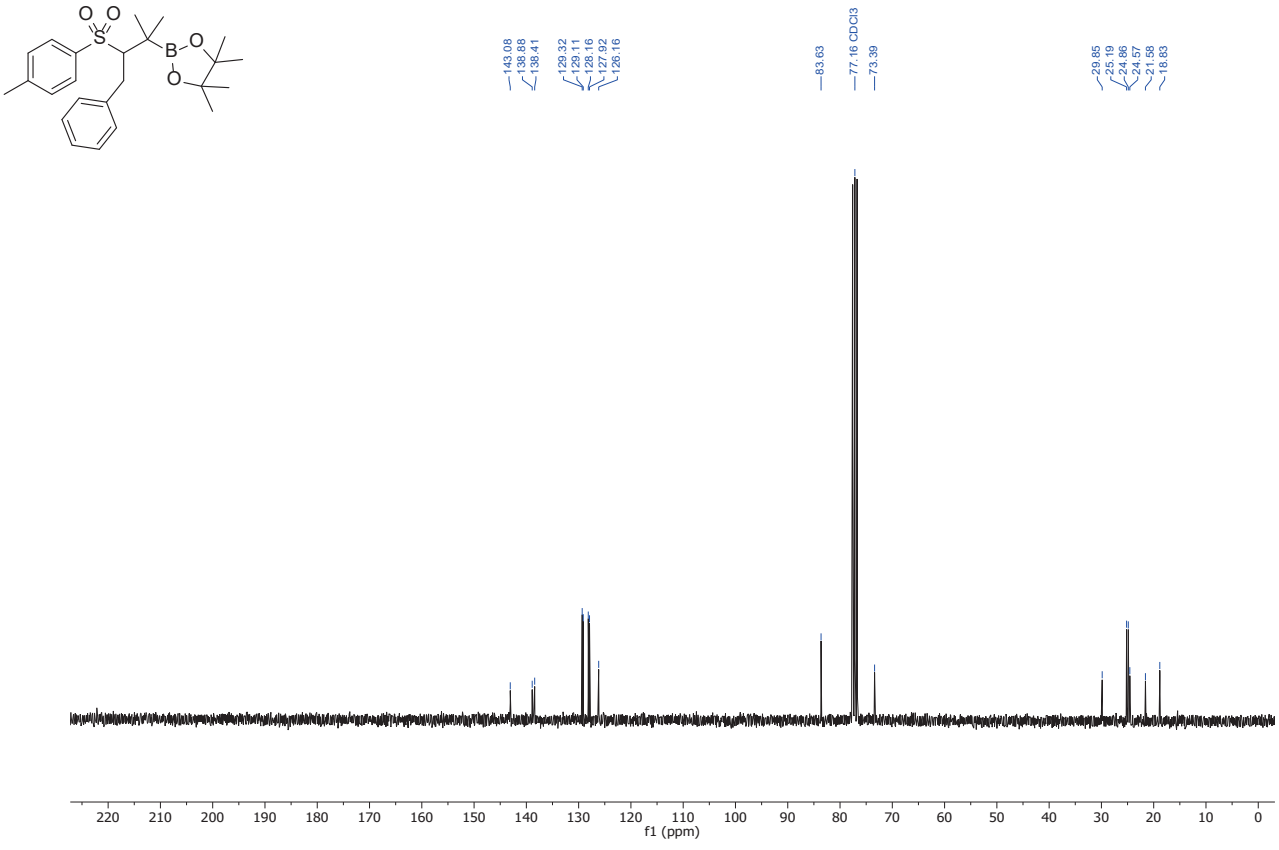
4,4,5,5-tetramethyl-2-(2-methyl-4-phenyl-3-tosylbutan-2-yl)-1,3,2-dioxaborolane (37)

^{1}H NMR (300 MHz, $CDCl_3$)



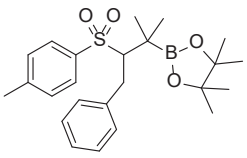
4,4,5,5-tetramethyl-2-(2-methyl-4-phenyl-3-tosylbutan-2-yl)-1,3,2-dioxaborolane (37)

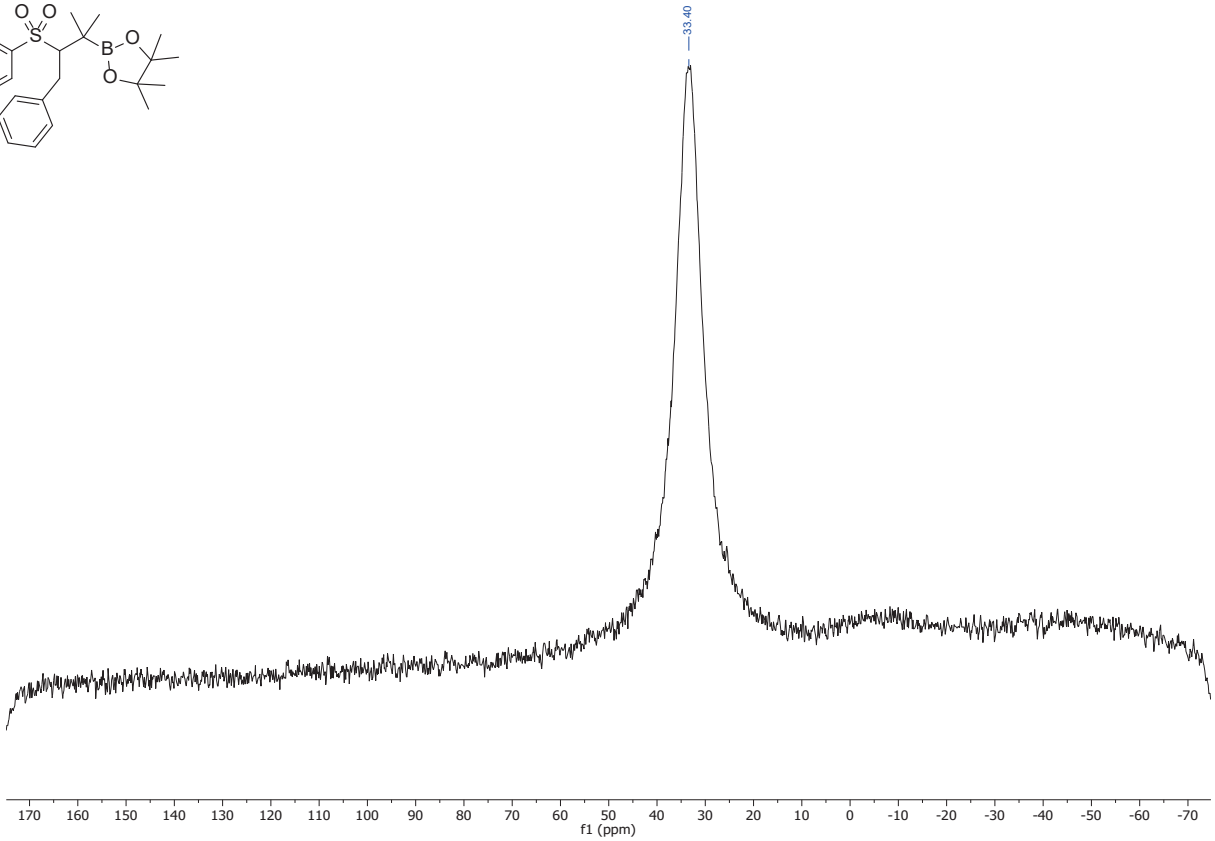
^{13}C NMR (75 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-(2-methyl-4-phenyl-3-tosylbutan-2-yl)-1,3,2-dioxaborolane (37)

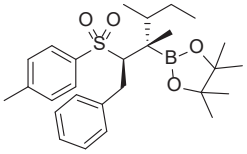
^{11}B NMR (96 MHz, $CDCl_3$)

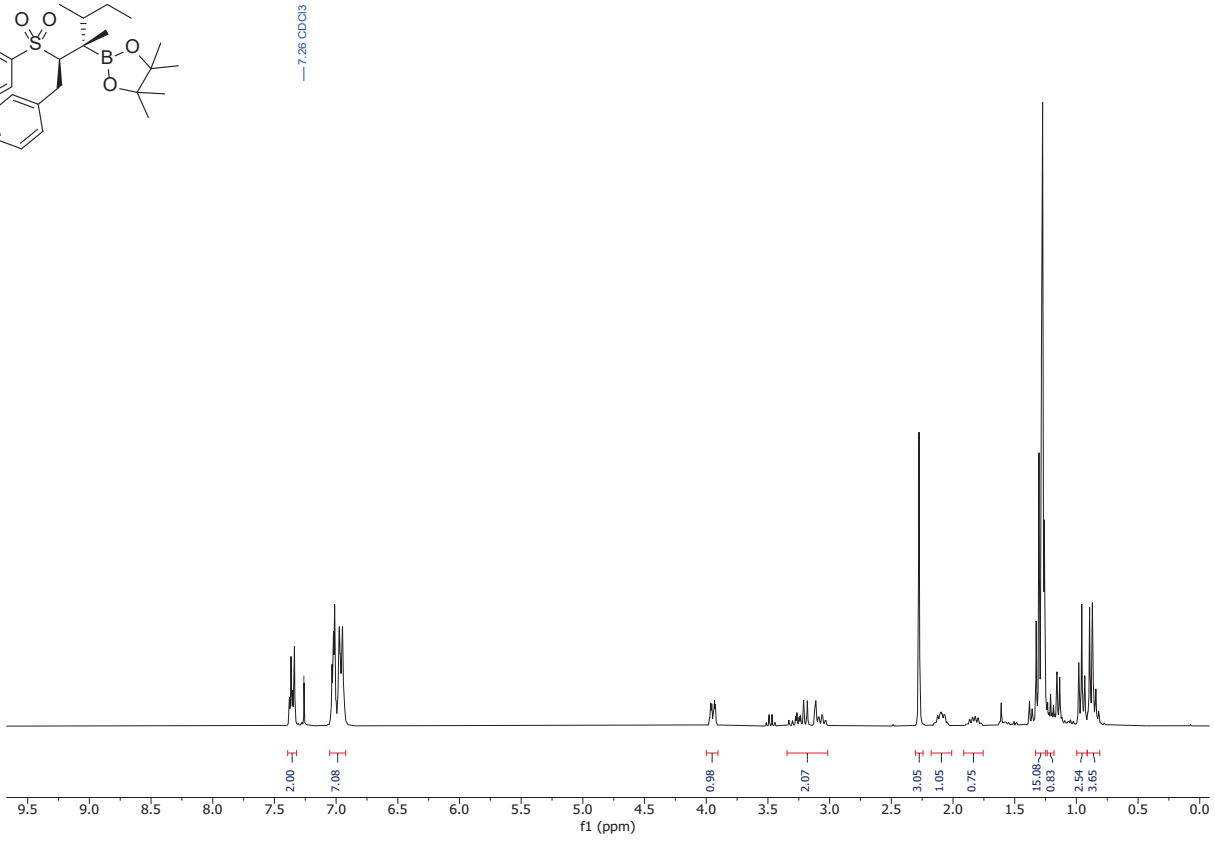




2-((2R,3R,4R)-3,4-dimethyl-1-phenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (55)
Major diastereomer

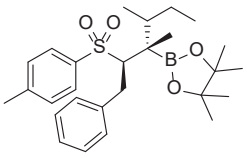
^{1}H NMR (300 MHz, $CDCl_3$)

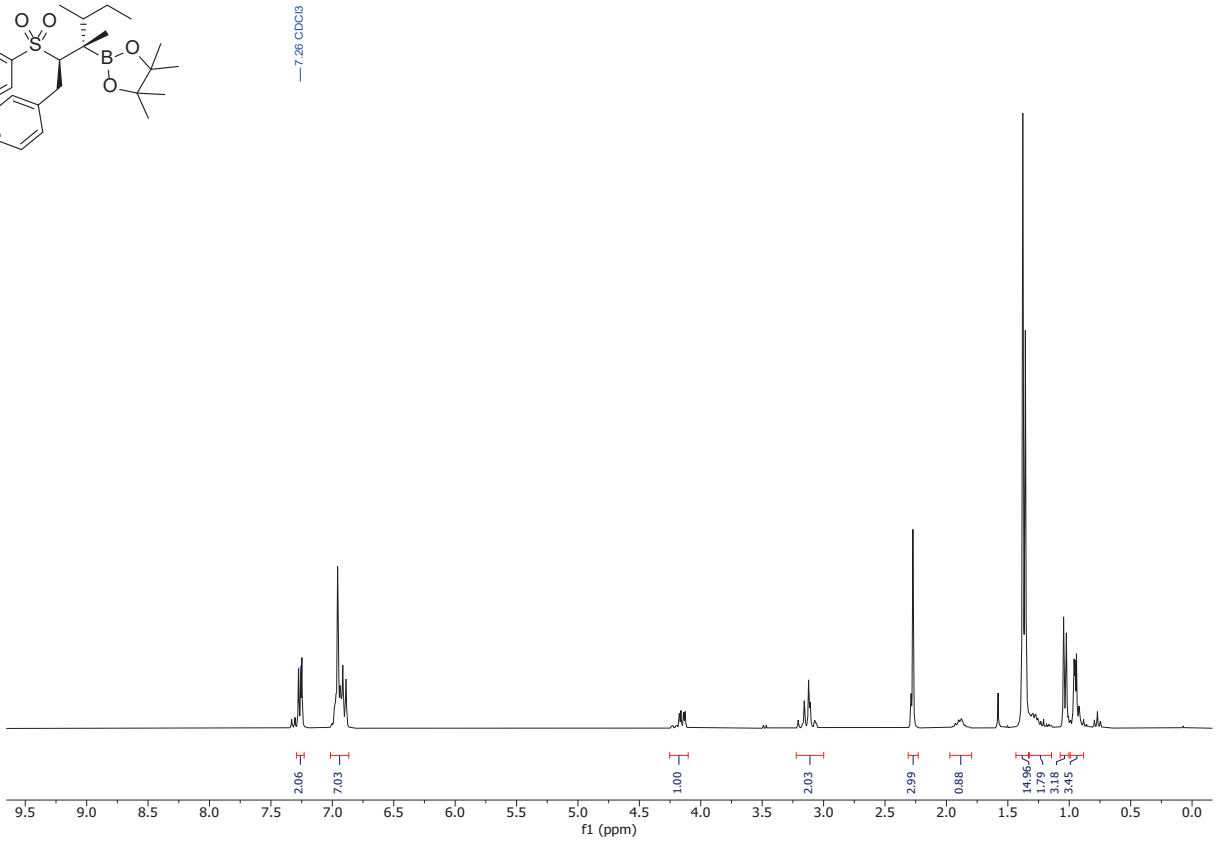




2-((2R,3R,4R)-3,4-dimethyl-1-phenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (55)
Minor diastereomer

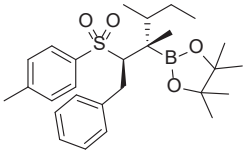
^{1}H NMR (300 MHz, $CDCl_3$)

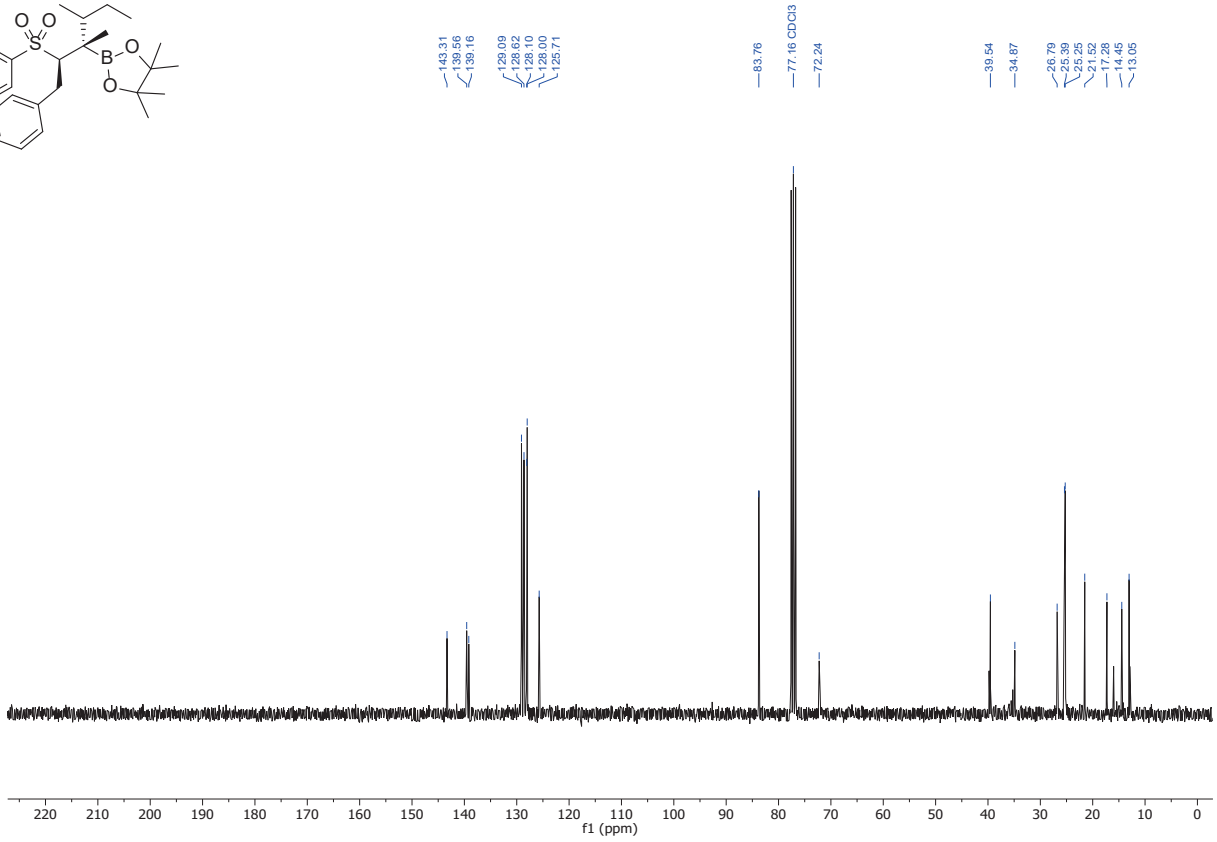




2-((2R,3R,4R)-3,4-dimethyl-1-phenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (55)
Major diastereomer

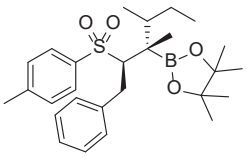
^{13}C NMR (75 MHz, $CDCl_3$)

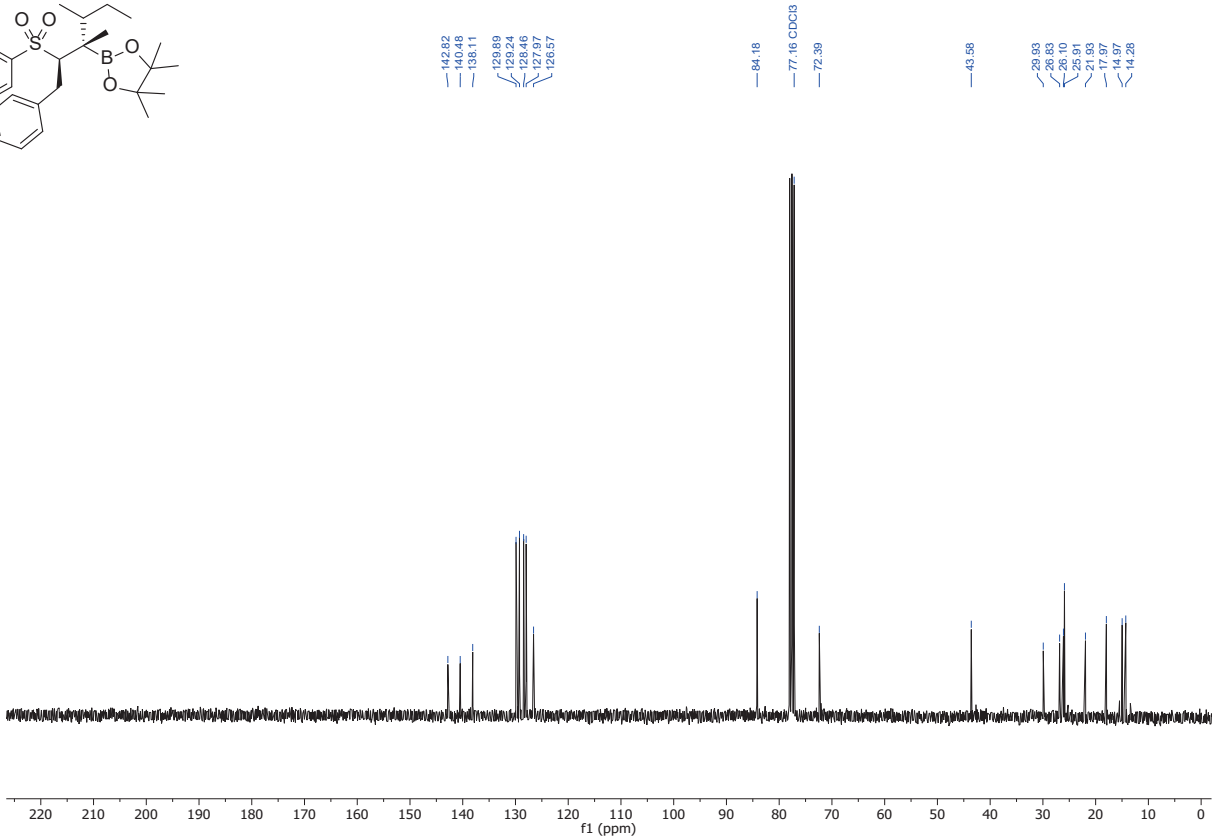




2-((2R,3R,4R)-3,4-dimethyl-1-phenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (55)
Minor diastereomer

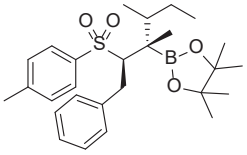
^{13}C NMR (75 MHz, $CDCl_3$)

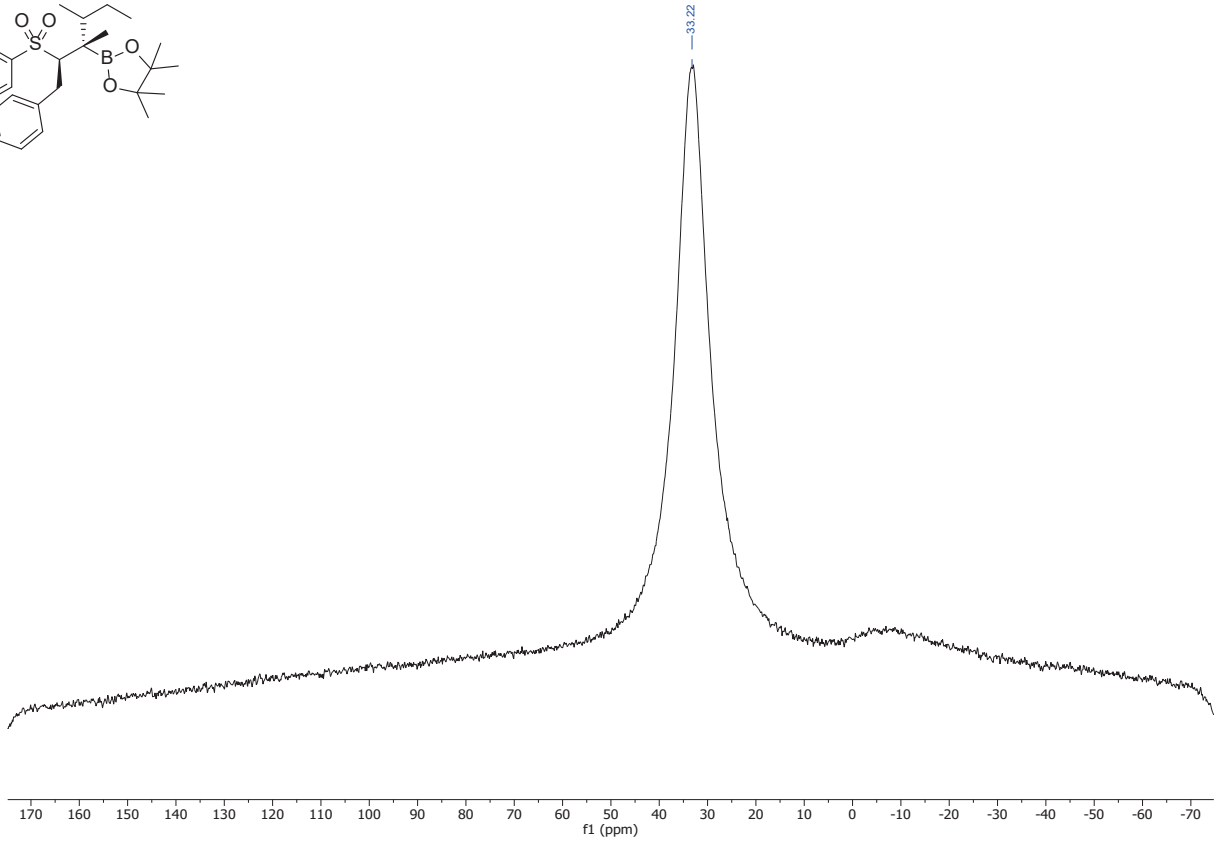




2-((2R,3R,4R)-3,4-dimethyl-1-phenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (55)
Major diastereomer

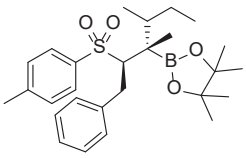
^{11}B NMR (96 MHz, $CDCl_3$)

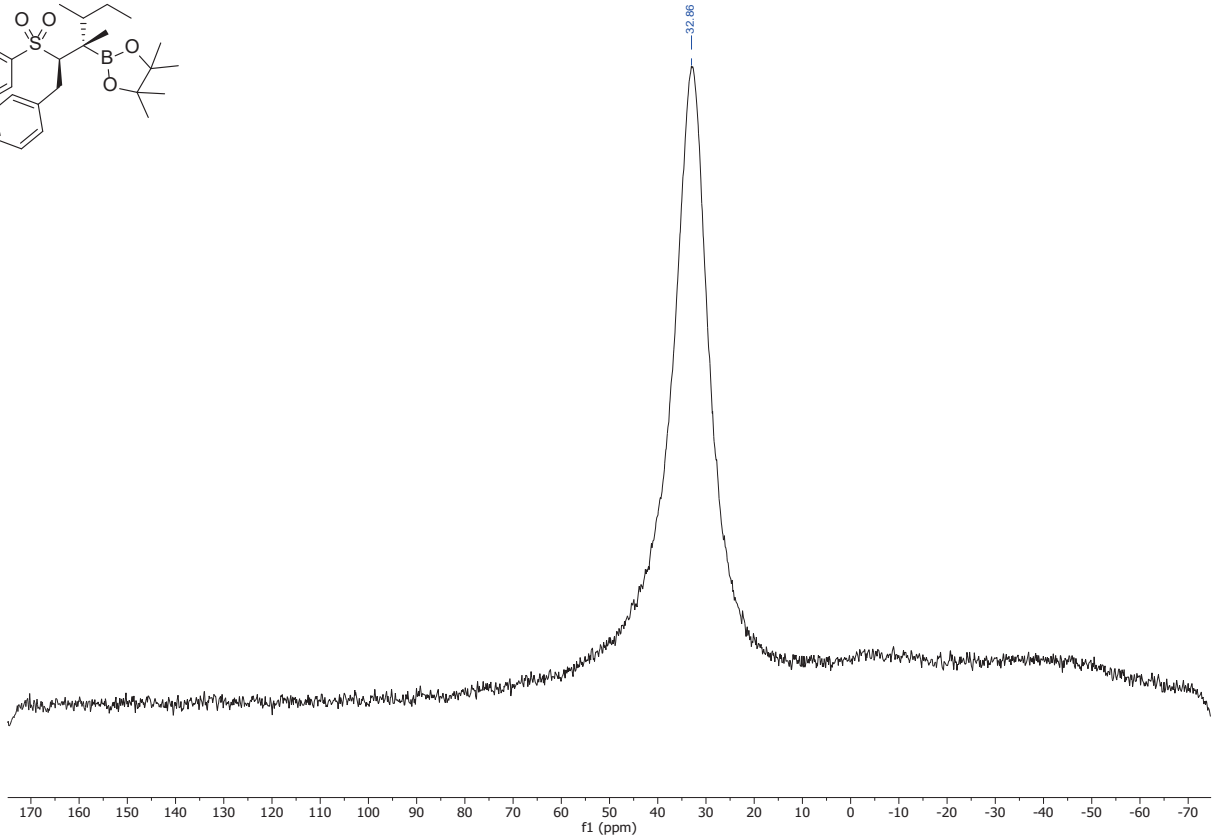




2-((2R,3R,4R)-3,4-dimethyl-1-phenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (55)
Minor diastereomer

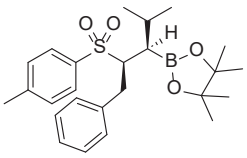
^{11}B NMR (96 MHz, $CDCl_3$)

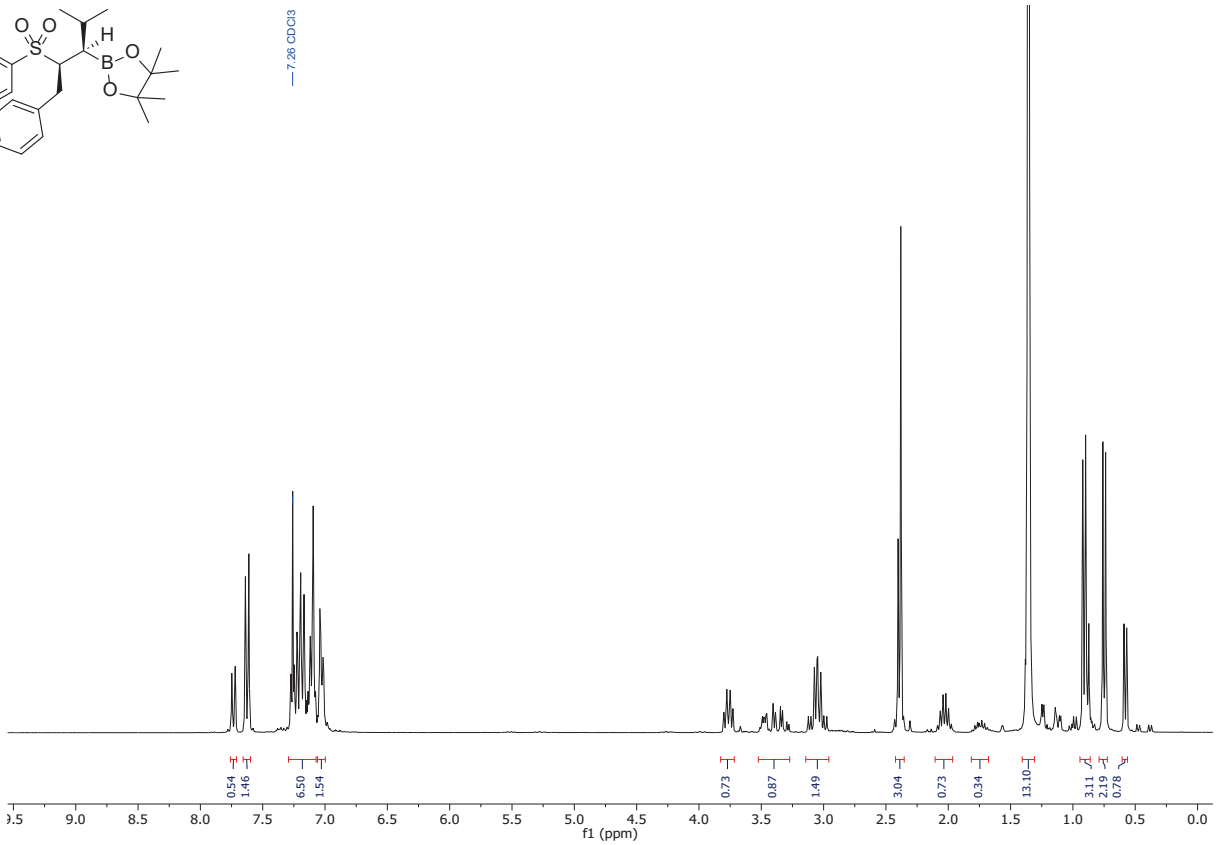




4,4,5,5-tetramethyl-2-((2R,3R)-4-methyl-1-phenyl-2-tosylpentan-3-yl)-1,3,2-dioxaborolane (39)

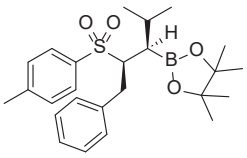
^{1}H NMR (300 MHz, $CDCl_3$)

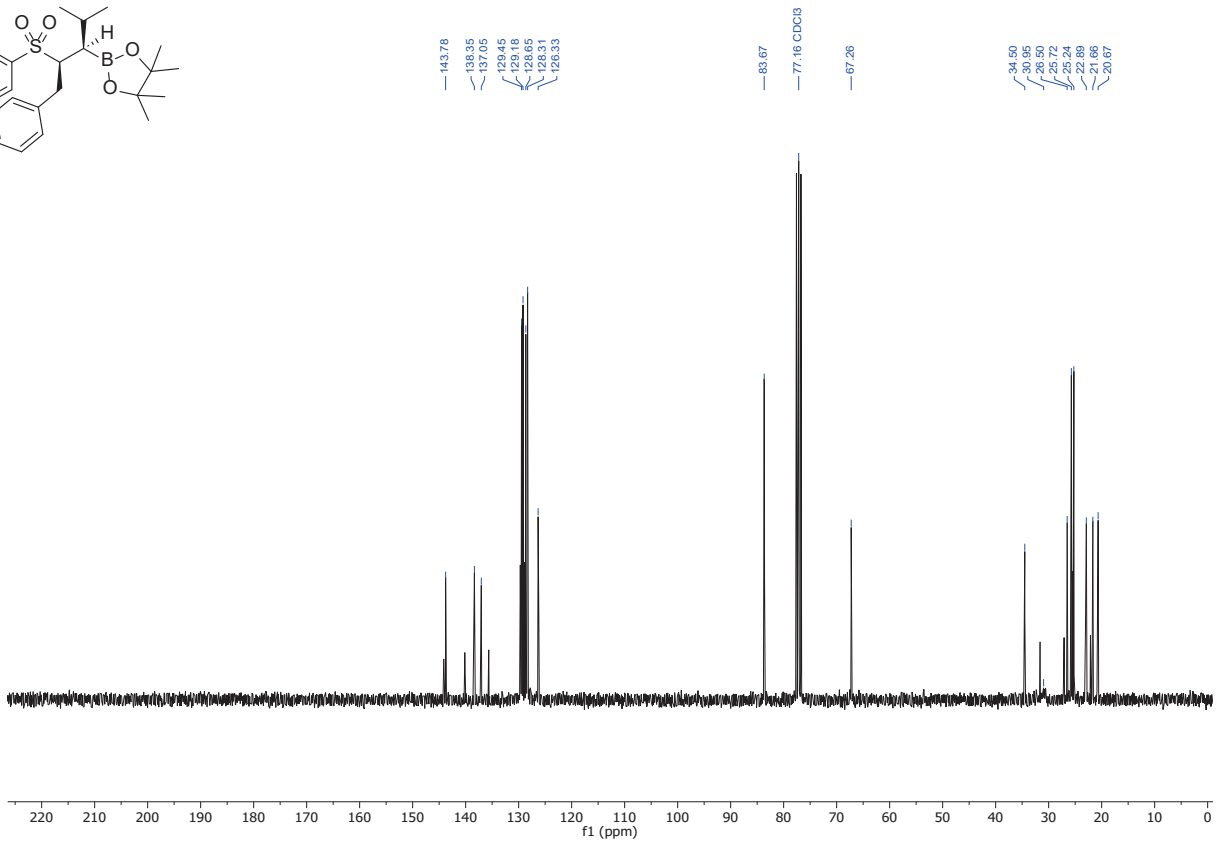




4,4,5,5-tetramethyl-2-((2R,3R)-4-methyl-1-phenyl-2-tosylpentan-3-yl)-1,3,2-dioxaborolane (39)
Major diastereomer

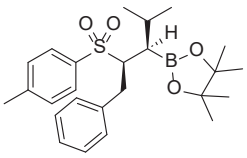
^{13}C NMR (75 MHz, $CDCl_3$)

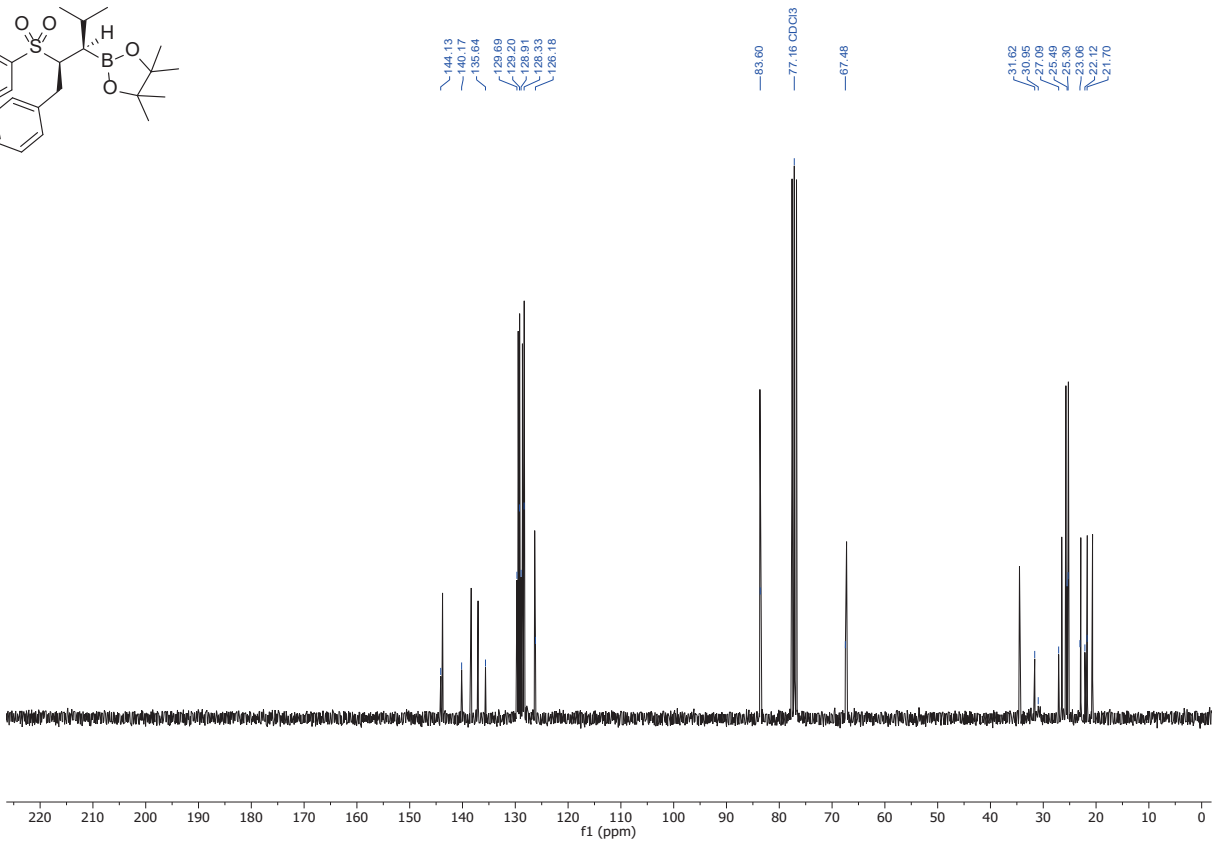




4,4,5,5-tetramethyl-2-((2R,3R)-4-methyl-1-phenyl-2-tosylpentan-3-yl)-1,3,2-dioxaborolane (39)
Minor diastereomer

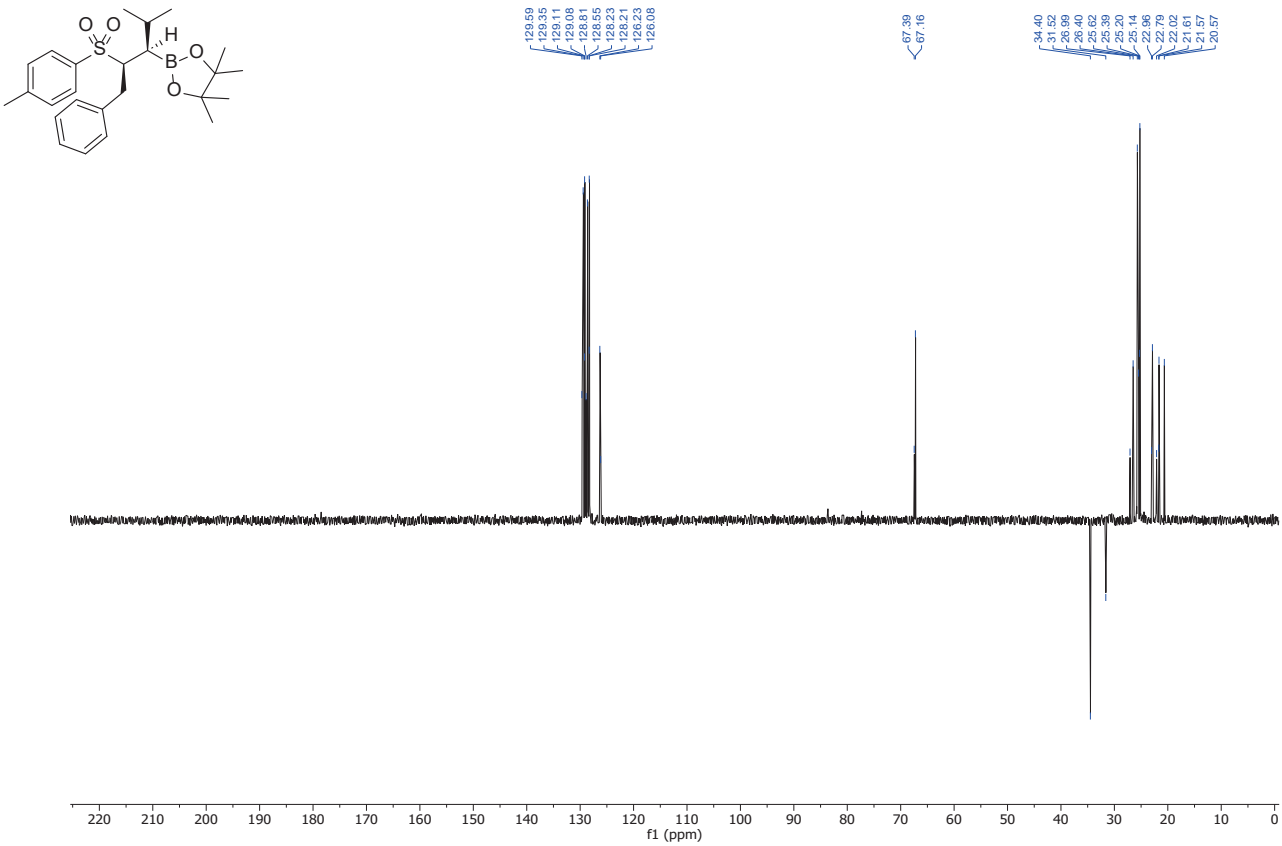
^{13}C NMR (75 MHz, $CDCl_3$)





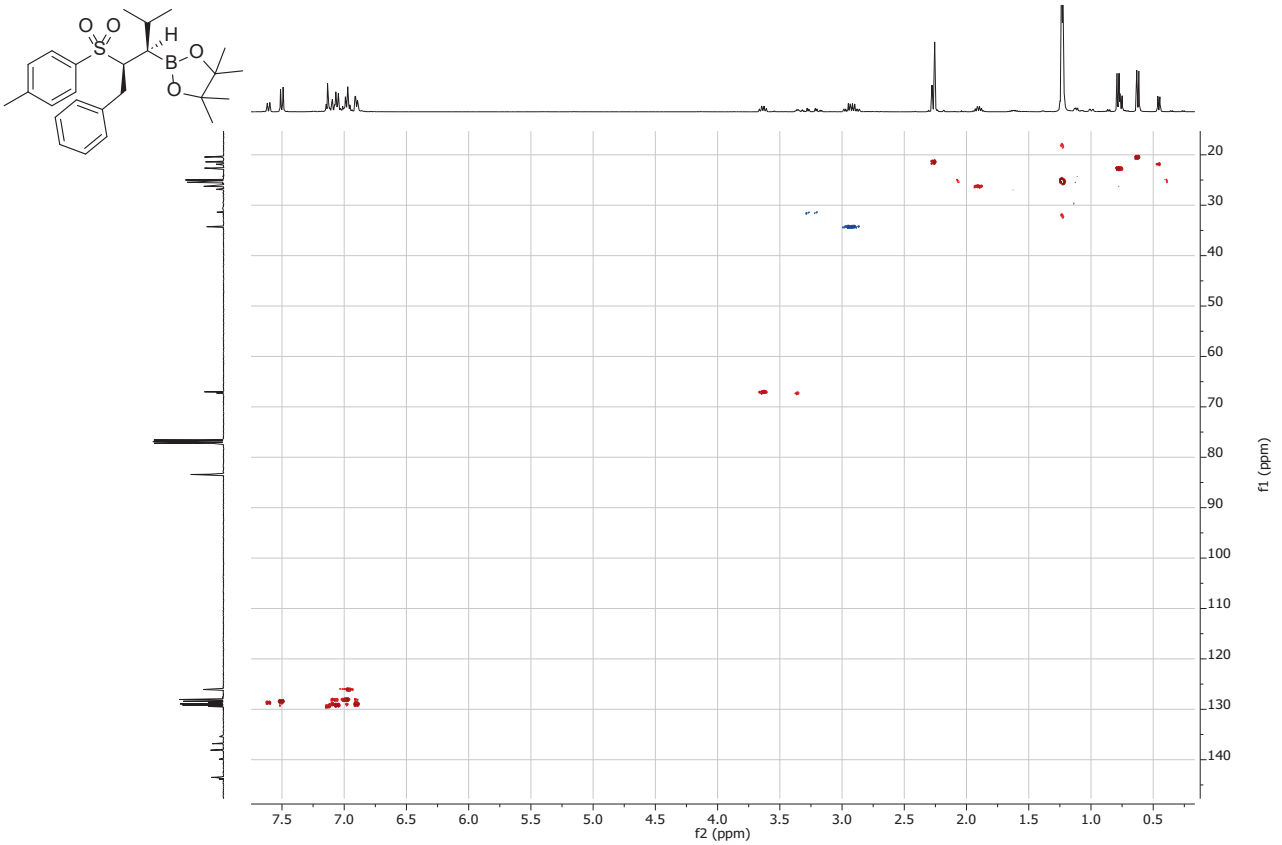
4,4,5,5-tetramethyl-2-((2R,3R)-4-methyl-1-phenyl-2-tosylpentan-3-yl)-1,3,2-dioxaborolane (39)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



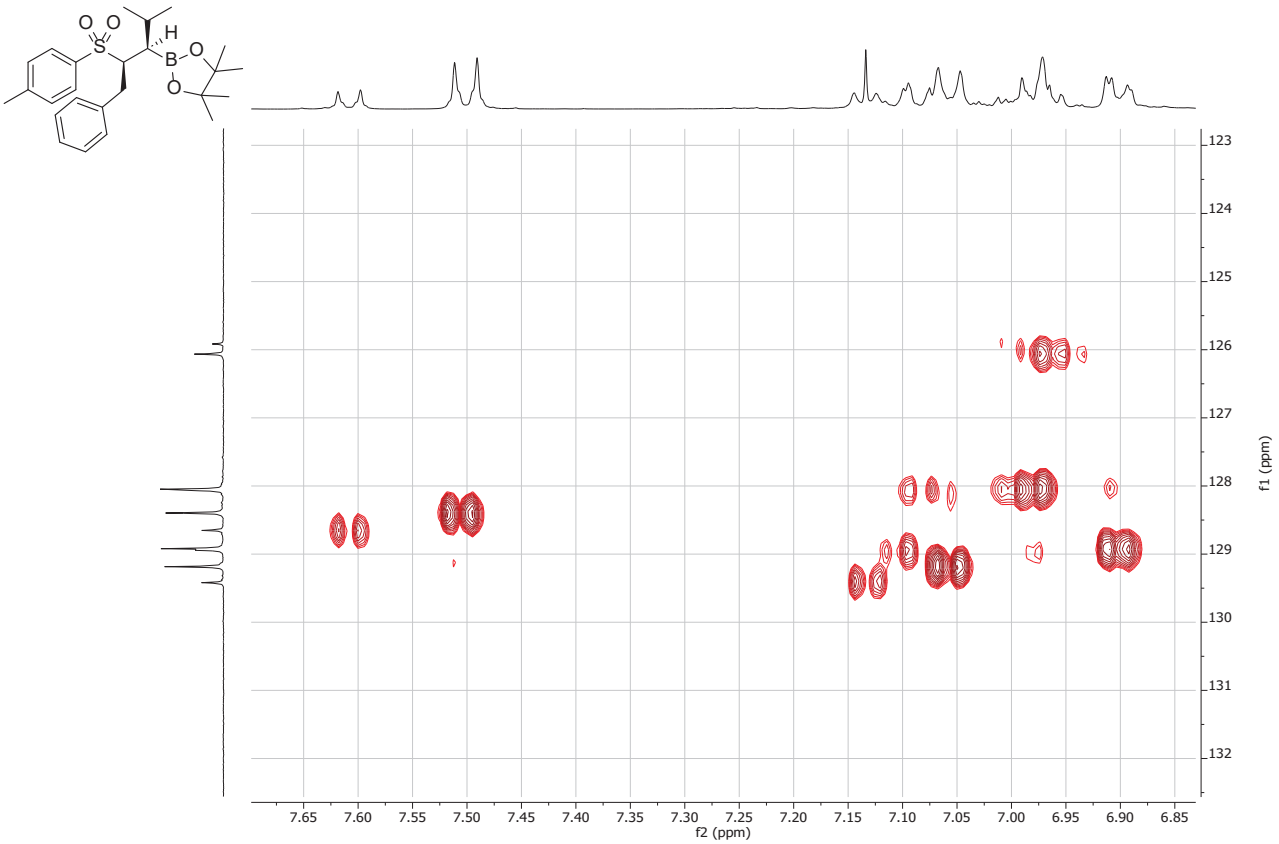
4,4,5,5-tetramethyl-2-((2R,3R)-4-methyl-1-phenyl-2-tosylpentan-3-yl)-1,3,2-dioxaborolane (39)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



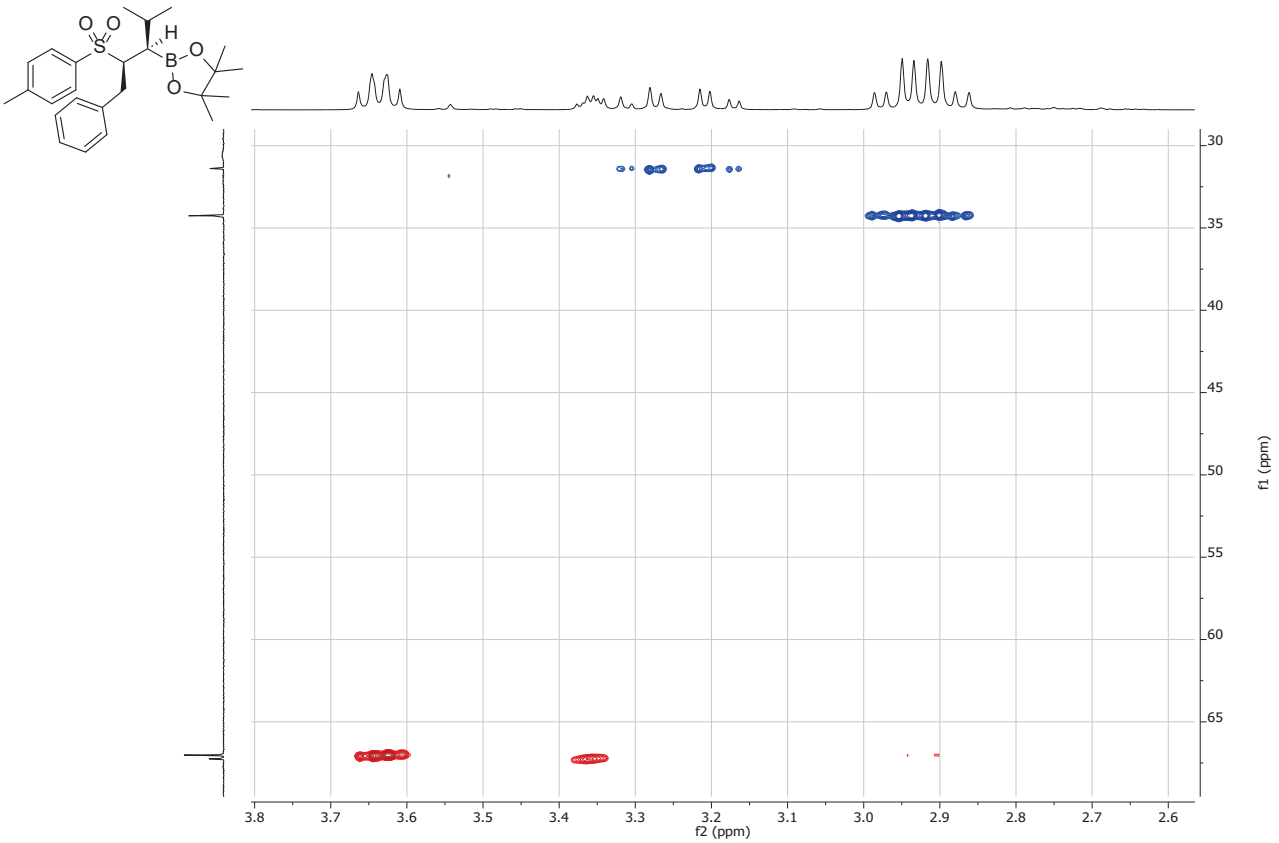
4,4,5,5-tetramethyl-2-((2R,3R)-4-methyl-1-phenyl-2-tosylpentan-3-yl)-1,3,2-dioxaborolane (39)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



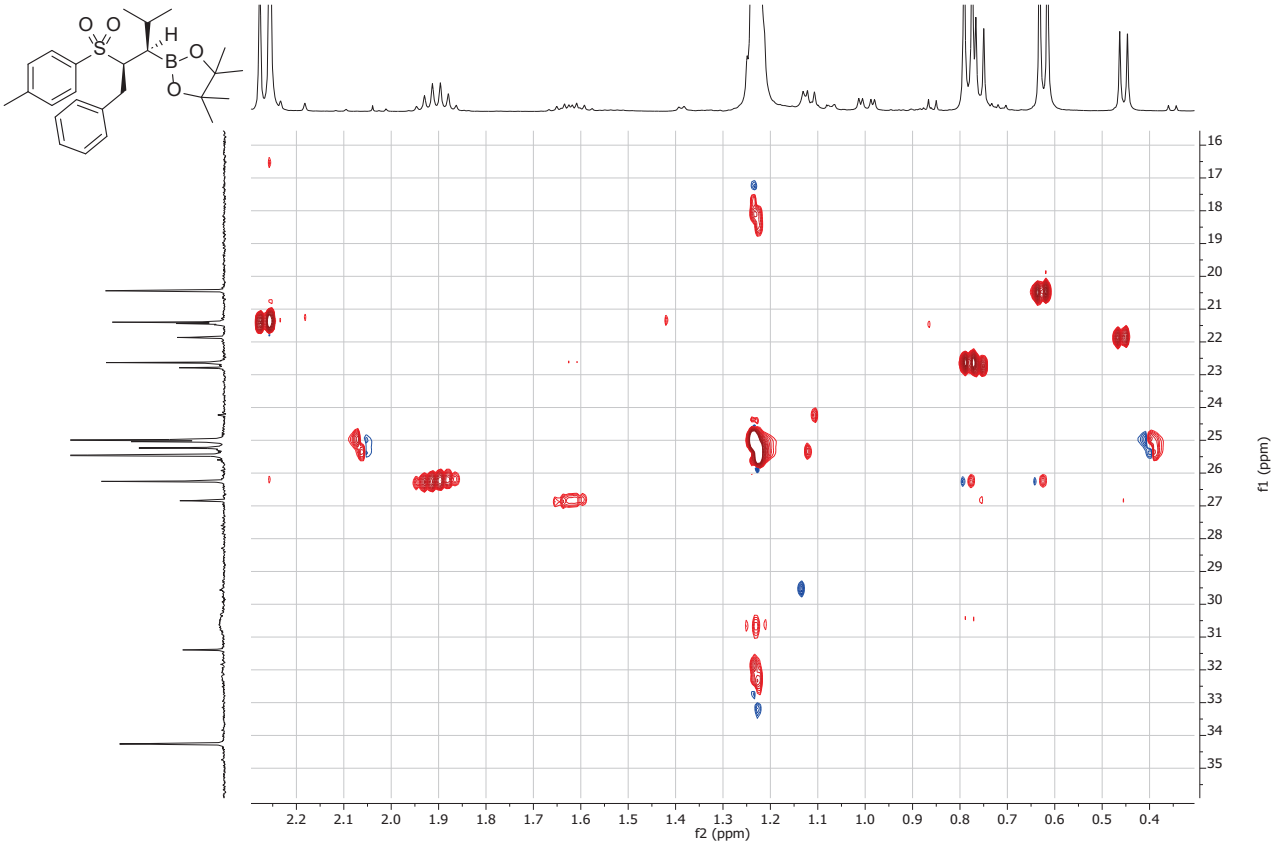
4,4,5,5-tetramethyl-2-((2R,3R)-4-methyl-1-phenyl-2-tosylpentan-3-yl)-1,3,2-dioxaborolane (39)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



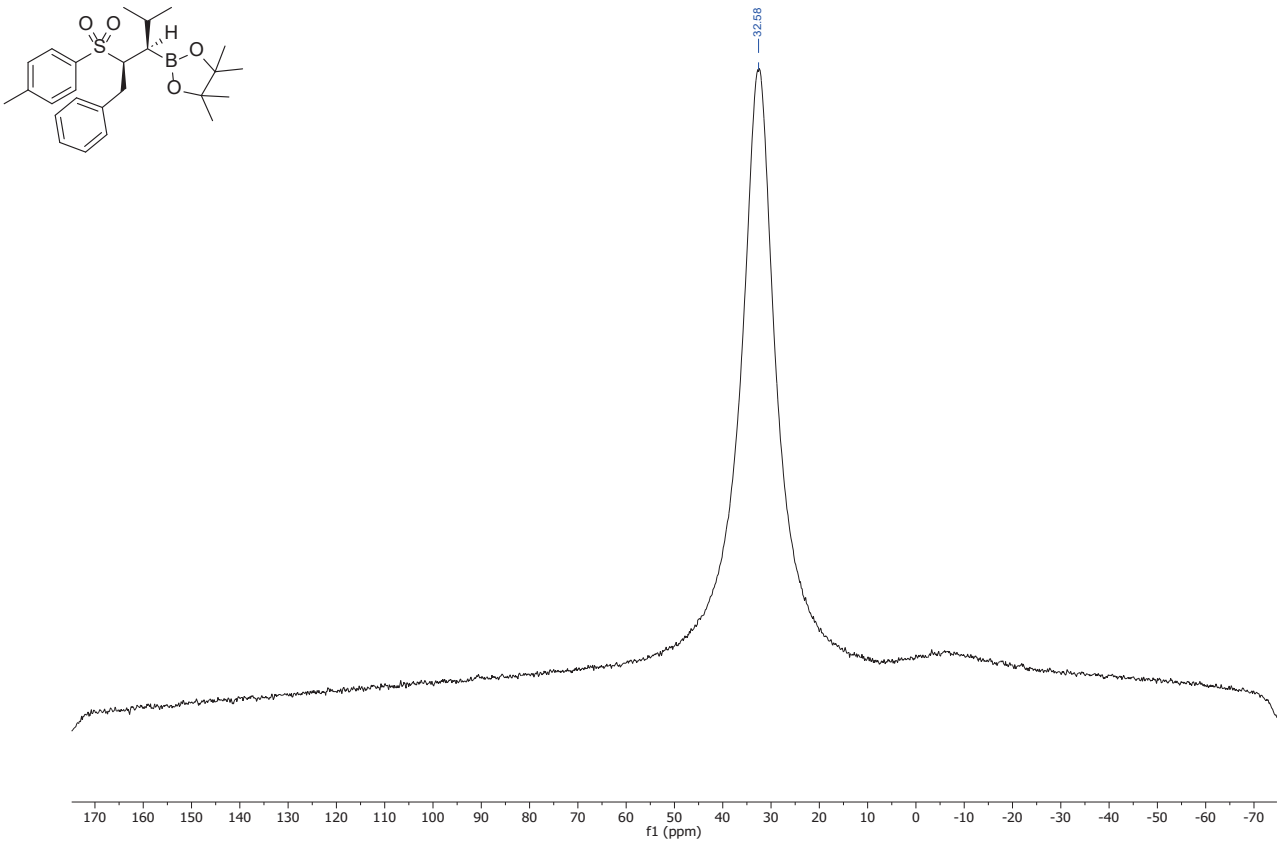
4,4,5,5-tetramethyl-2-((2R,3R)-4-methyl-1-phenyl-2-tosylpentan-3-yl)-1,3,2-dioxaborolane (39)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



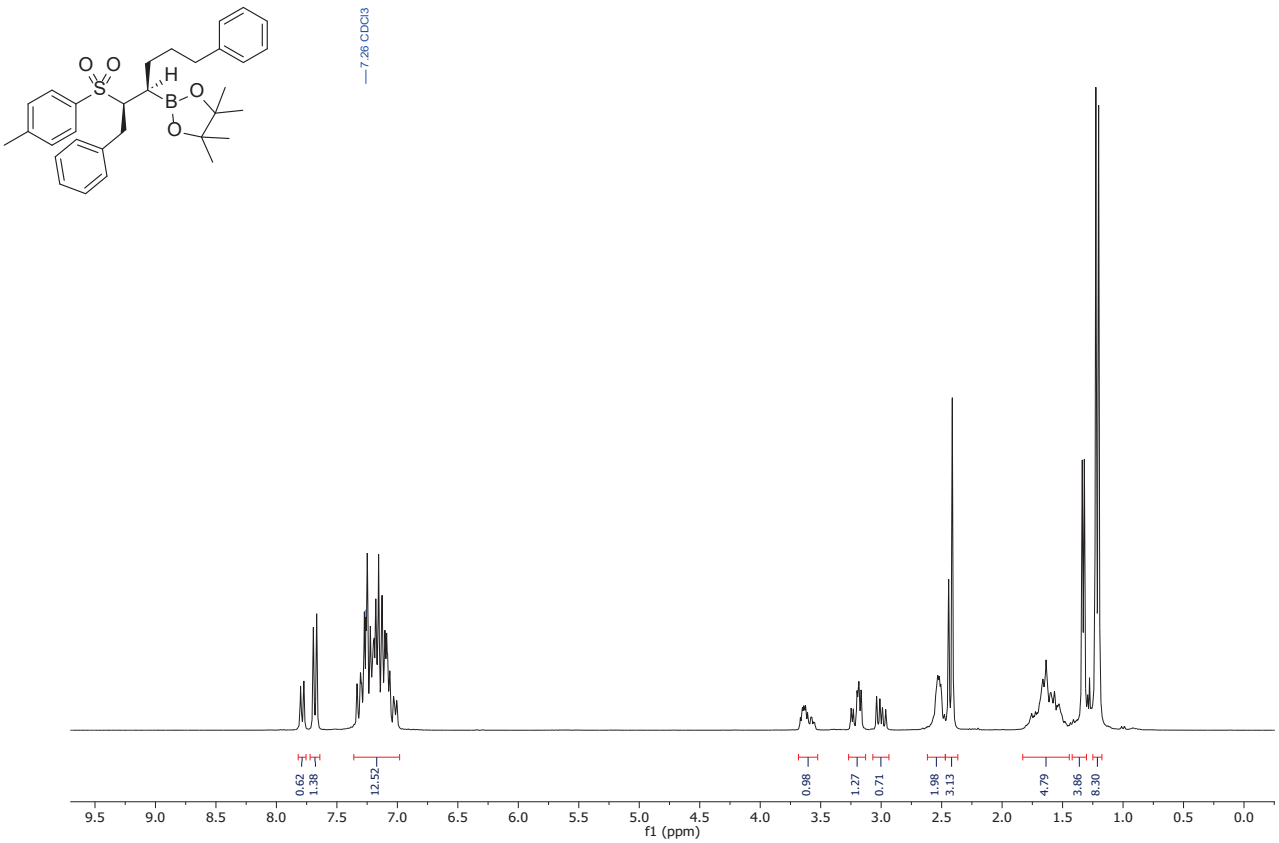
4,4,5,5-tetramethyl-2-((2R,3R)-4-methyl-1-phenyl-2-tosylpentan-3-yl)-1,3,2-dioxaborolane (39)

^{11}B NMR (96 MHz, $CDCl_3$)



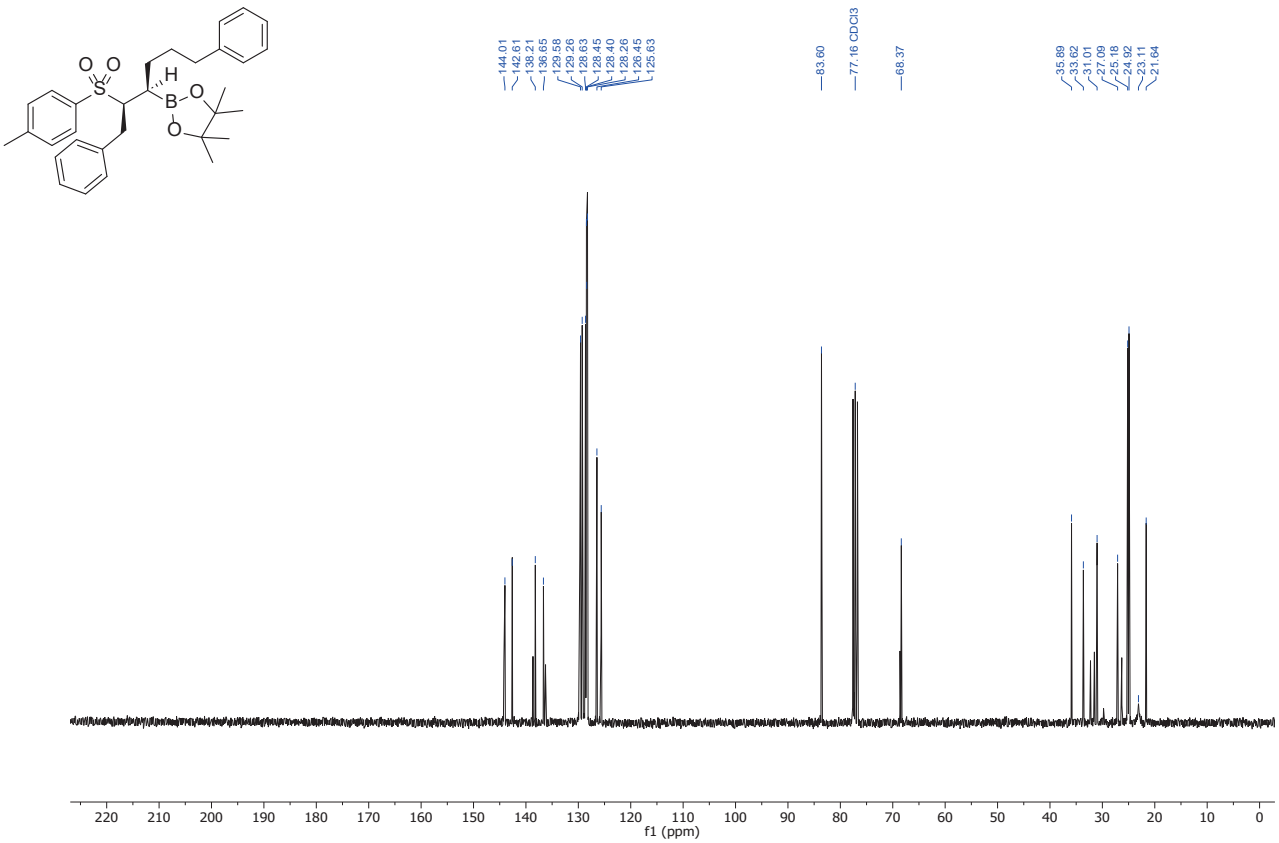
^{1}H NMR (300 MHz, $CDCl_3$)

2-((2R,3R)-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)



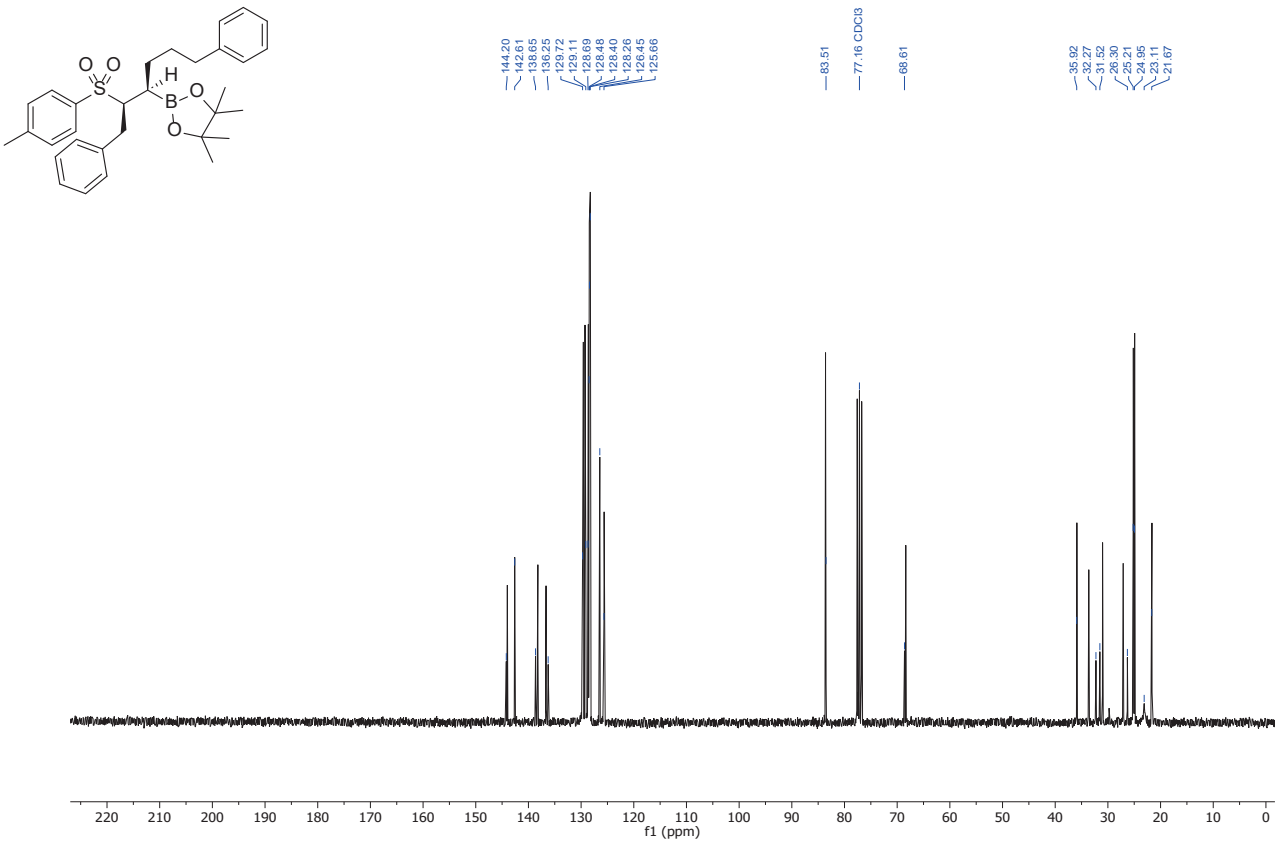
^{13}C NMR (75 MHz, $CDCl_3$)

2-((2R,3R)-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)
Major diastereomer



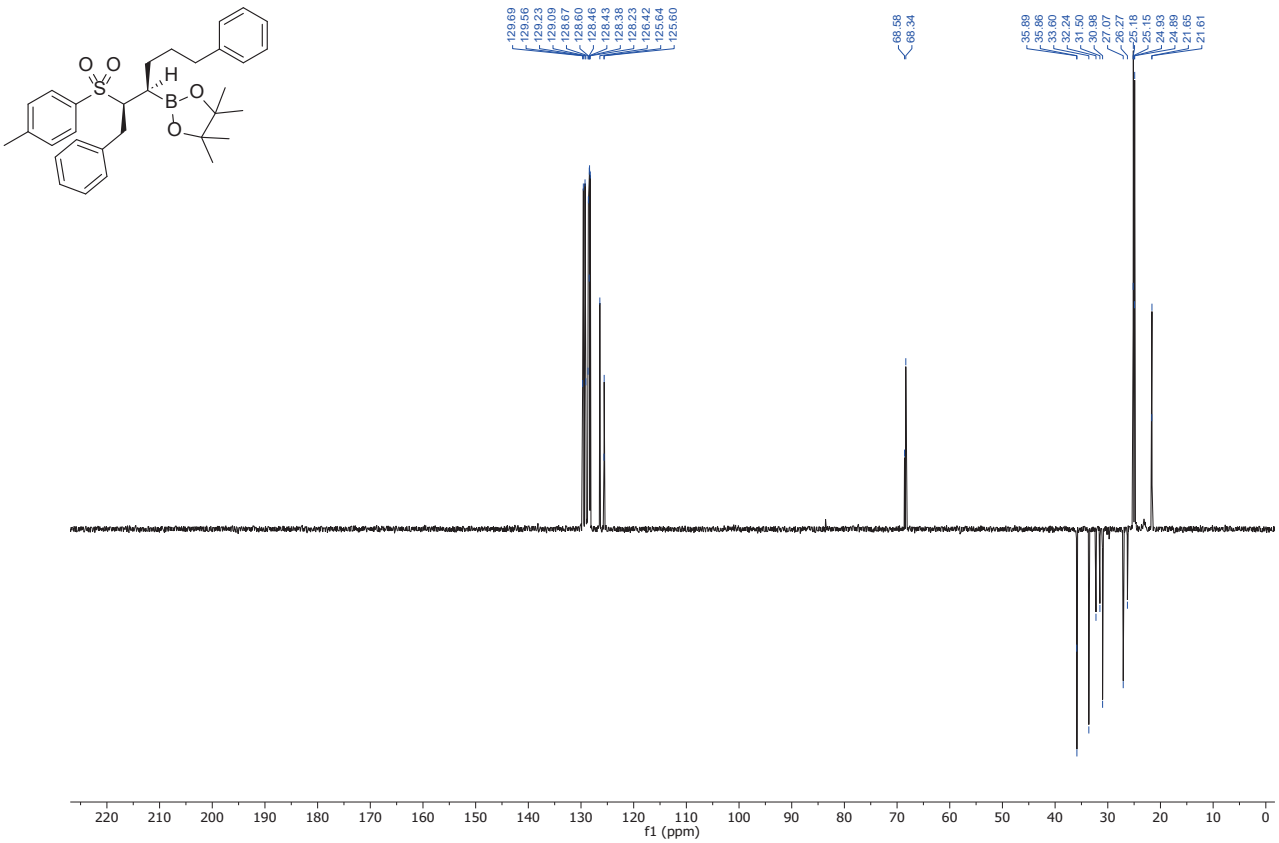
2-((2R,3R)-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)
Minor diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



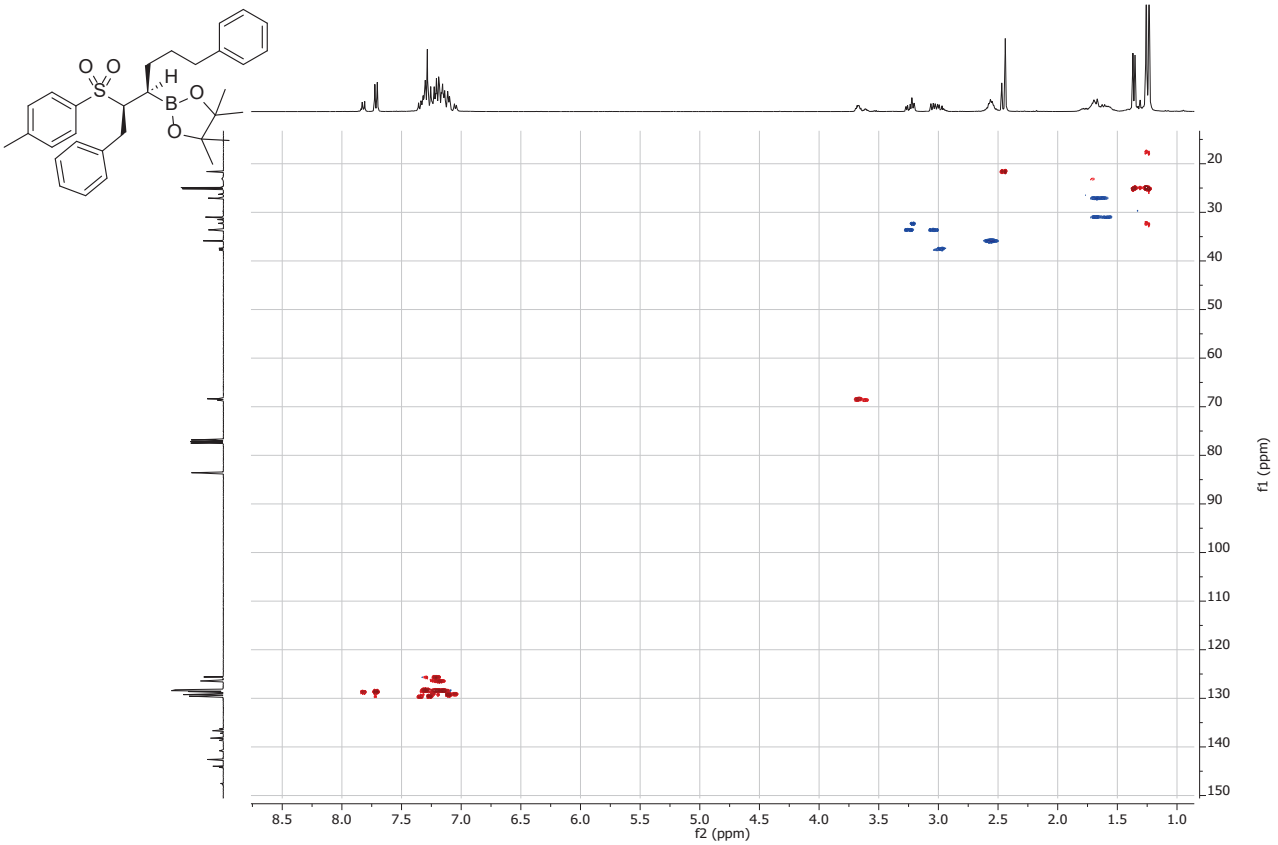
2-((2R,3R)-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



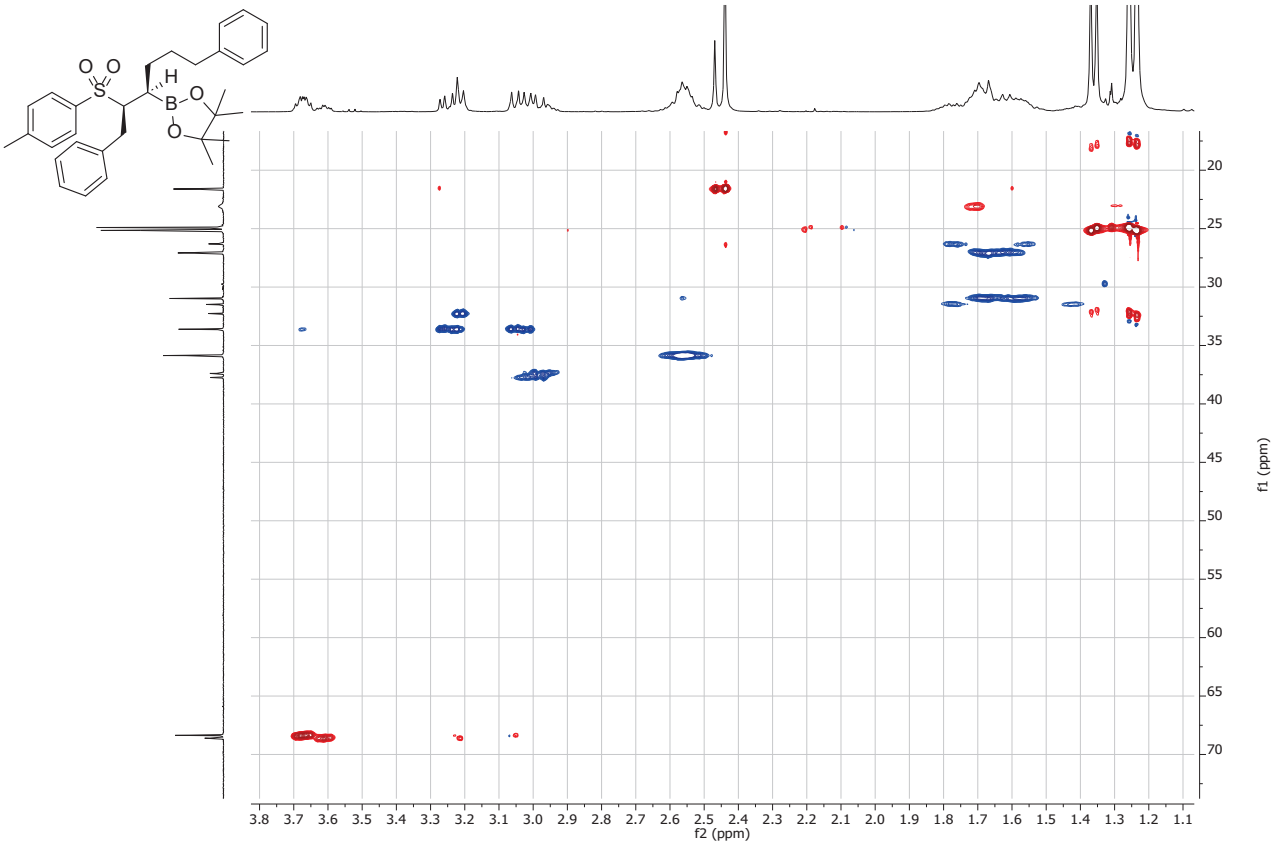
2-((2R,3R)-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



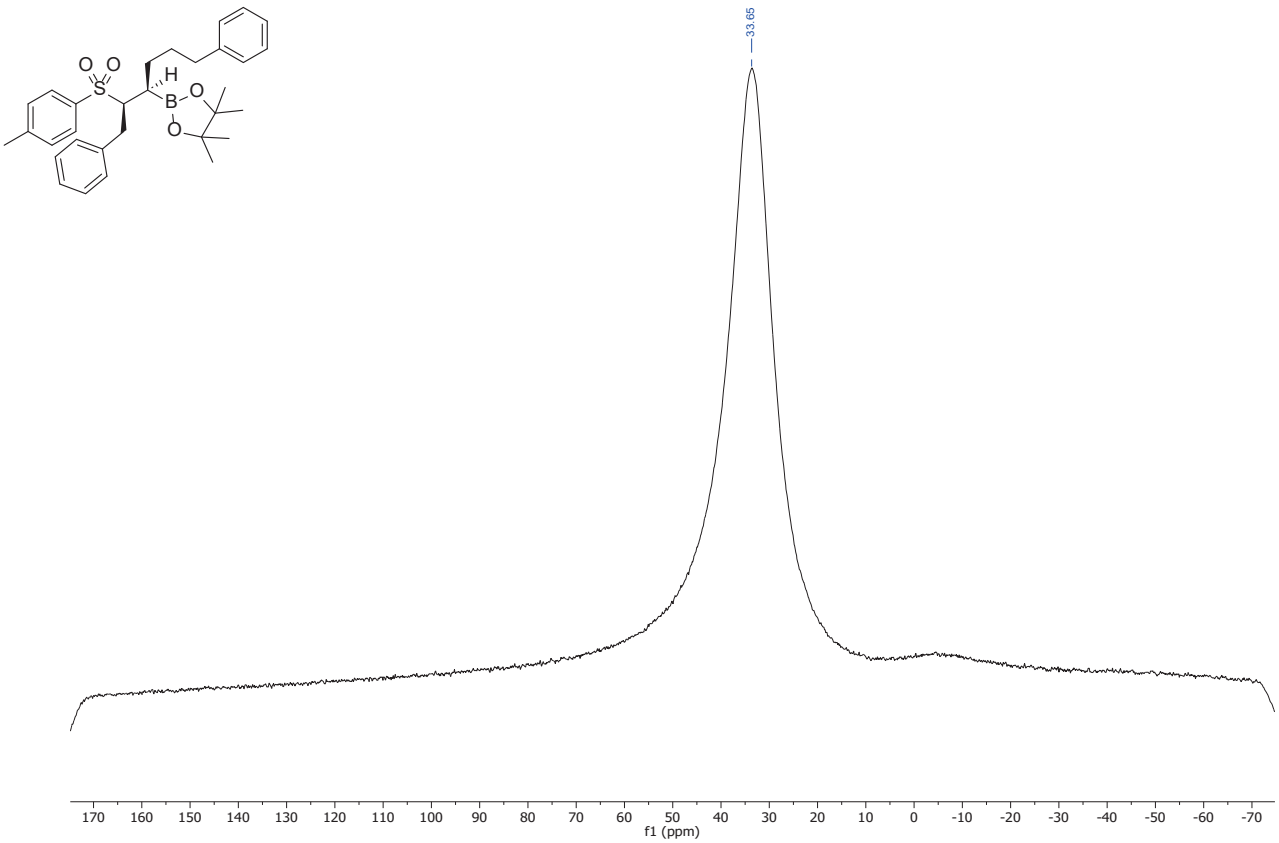
2-((2R,3R)-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



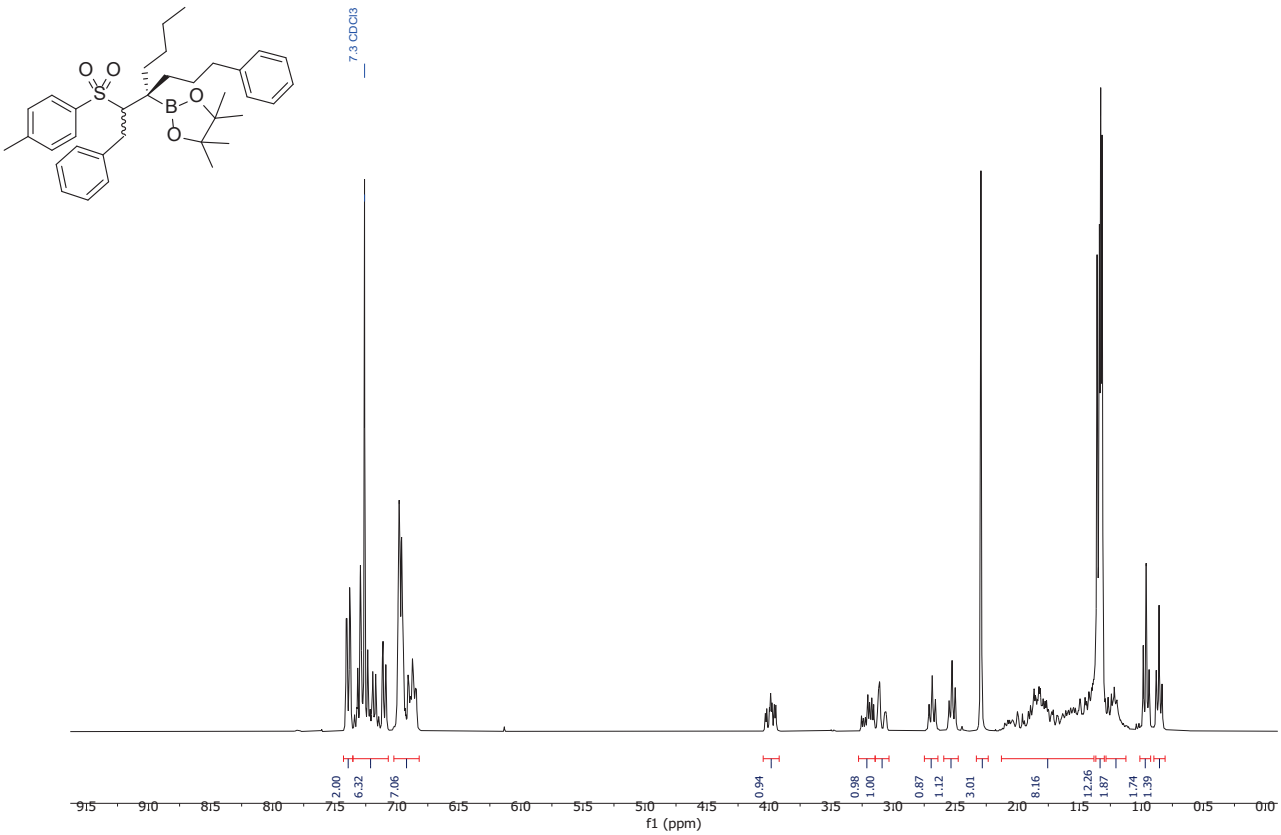
2-((2R,3R)-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)

^{11}B NMR (96 MHz, $CDCl_3$)



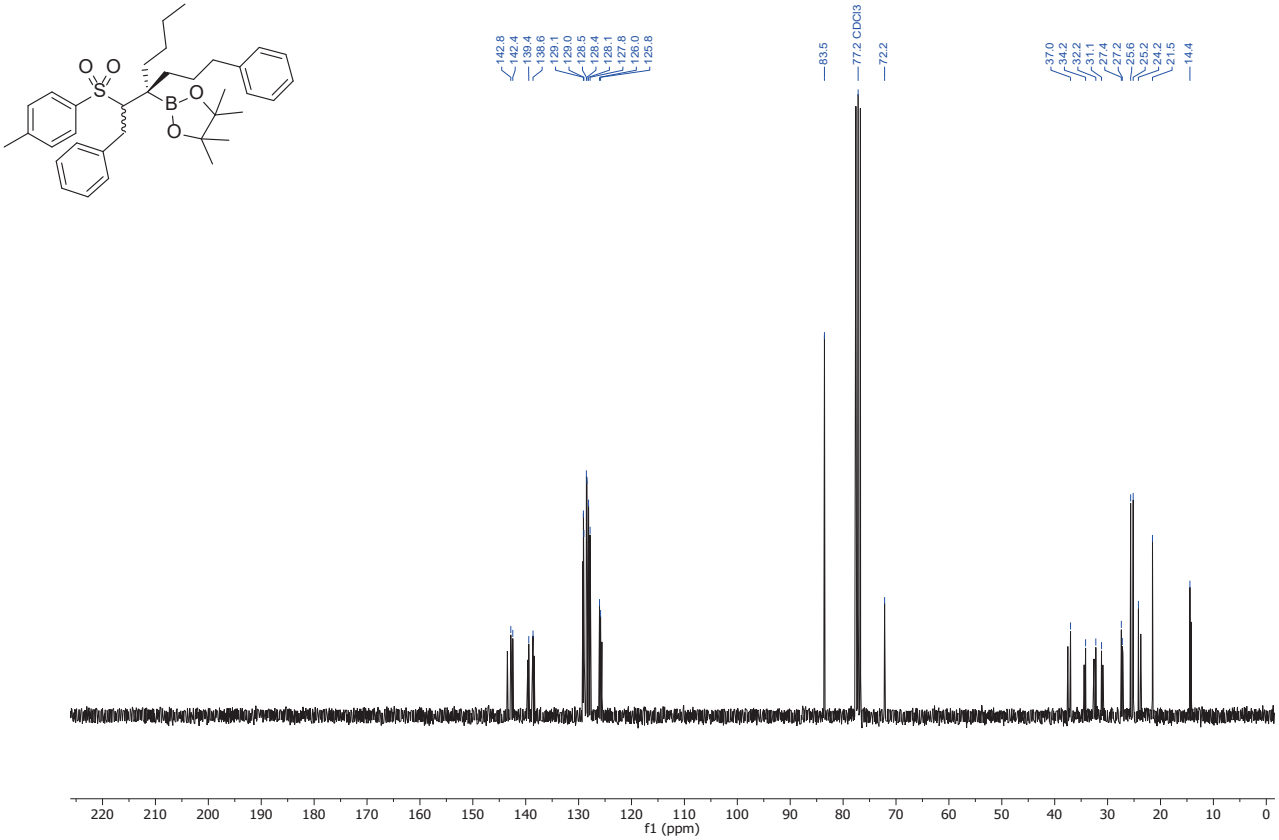
4,4,5,5-tetramethyl-2-((S)-1-phenyl-4-(2-phenyl-1-tosylethyl)octan-4-yl)-1,3,2-dioxaborolane (50)

^{1}H NMR (400 MHz, $CDCl_3$)



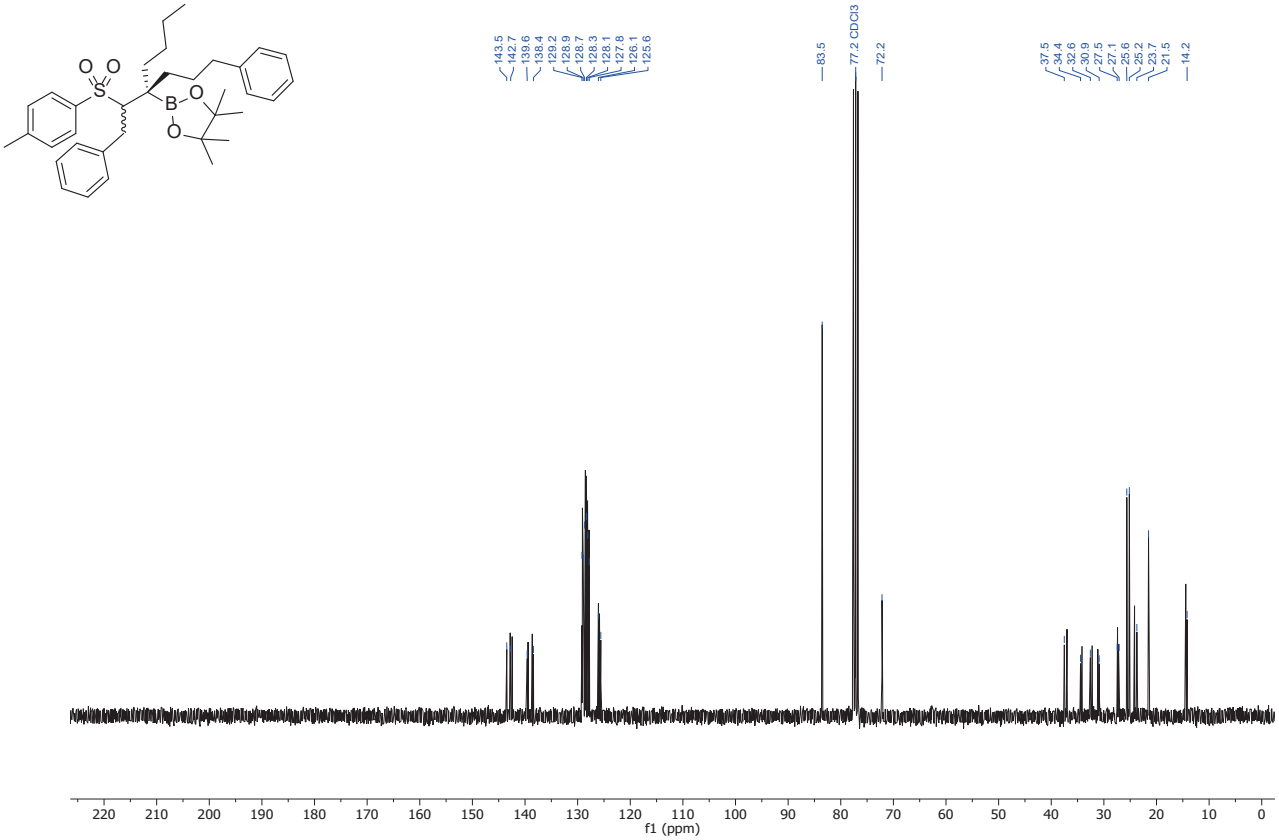
4,4,5,5-tetramethyl-2-((S)-1-phenyl-4-(2-phenyl-1-tosylethyl)octan-4-yl)-1,3,2-dioxaborolane (50)
Major diastereomer

^{13}C NMR (101 MHz, $CDCl_3$)



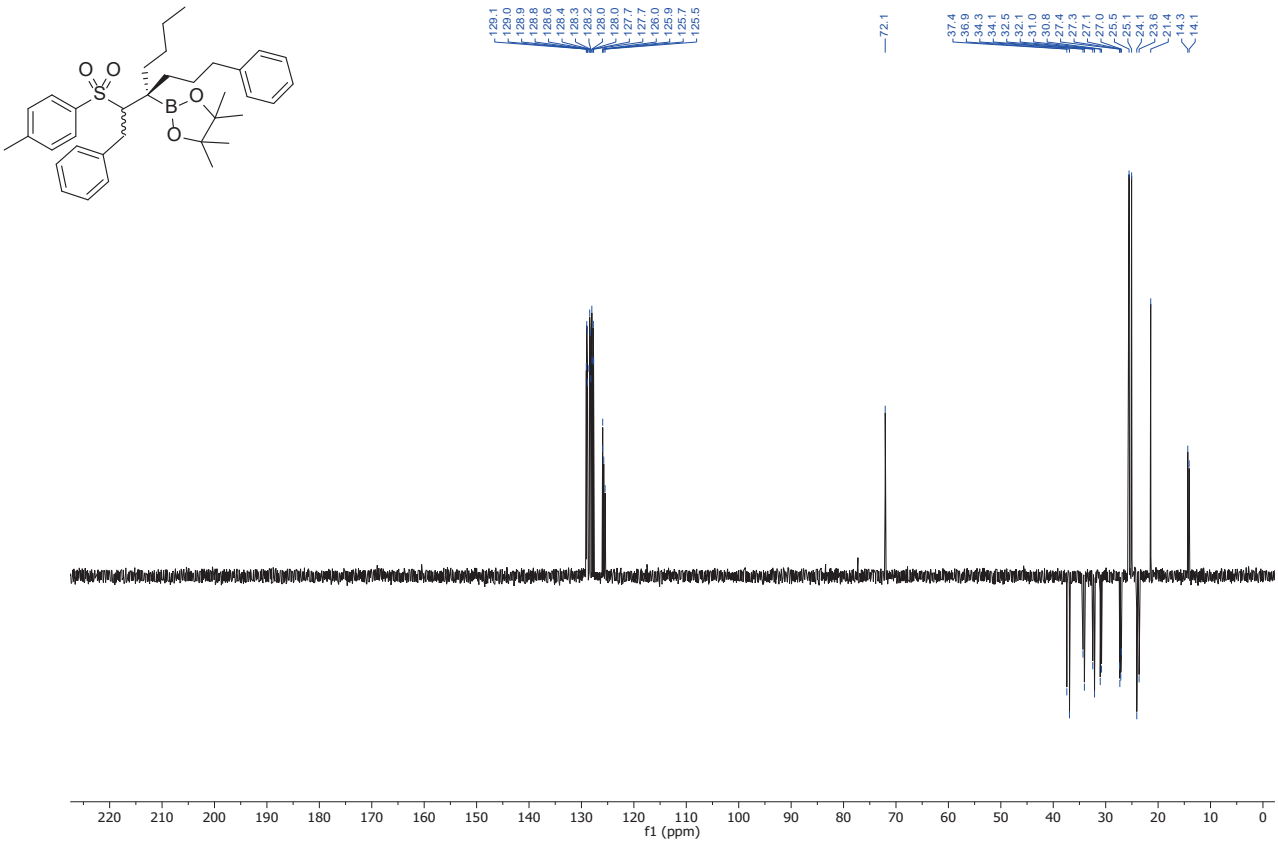
4,4,5,5-tetramethyl-2-((S)-1-phenyl-4-(2-phenyl-1-tosylethyl)octan-4-yl)-1,3,2-dioxaborolane (50)
Minor diastereomer

^{13}C NMR (101 MHz, $CDCl_3$)



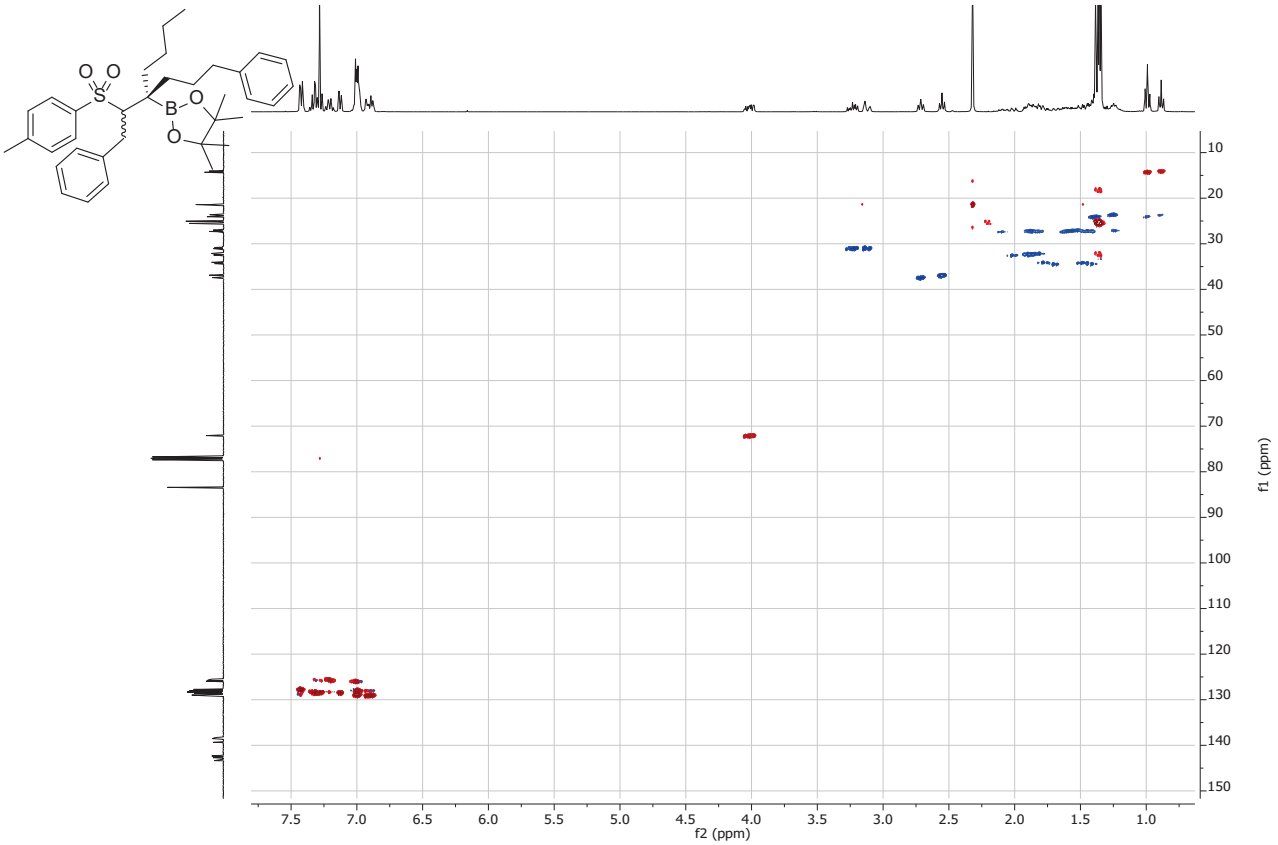
4,4,5,5-tetramethyl-2-((S)-1-phenyl-4-(2-phenyl-1-tosylethyl)octan-4-yl)-1,3,2-dioxaborolane (50)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



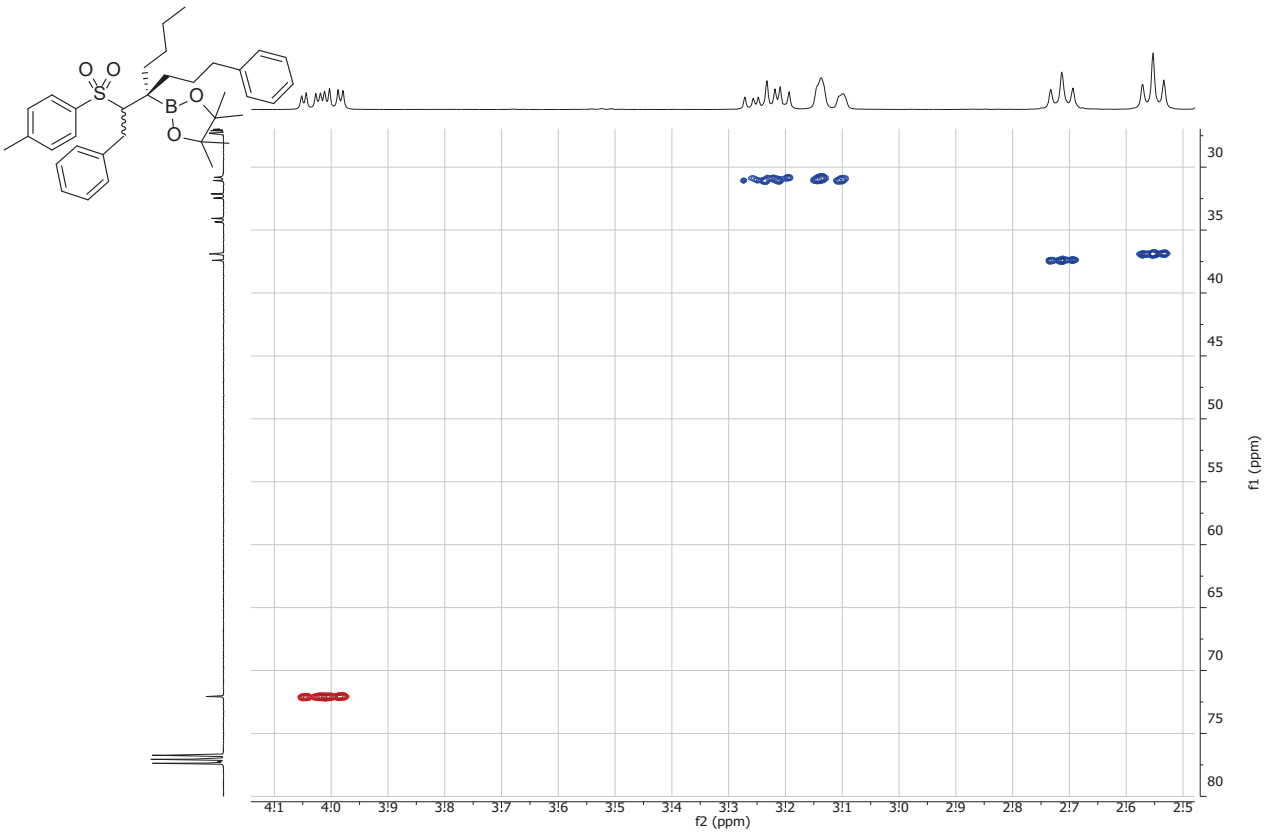
4,4,5,5-tetramethyl-2-((S)-1-phenyl-4-(2-phenyl-1-tosylethyl)octan-4-yl)-1,3,2-dioxaborolane (50)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



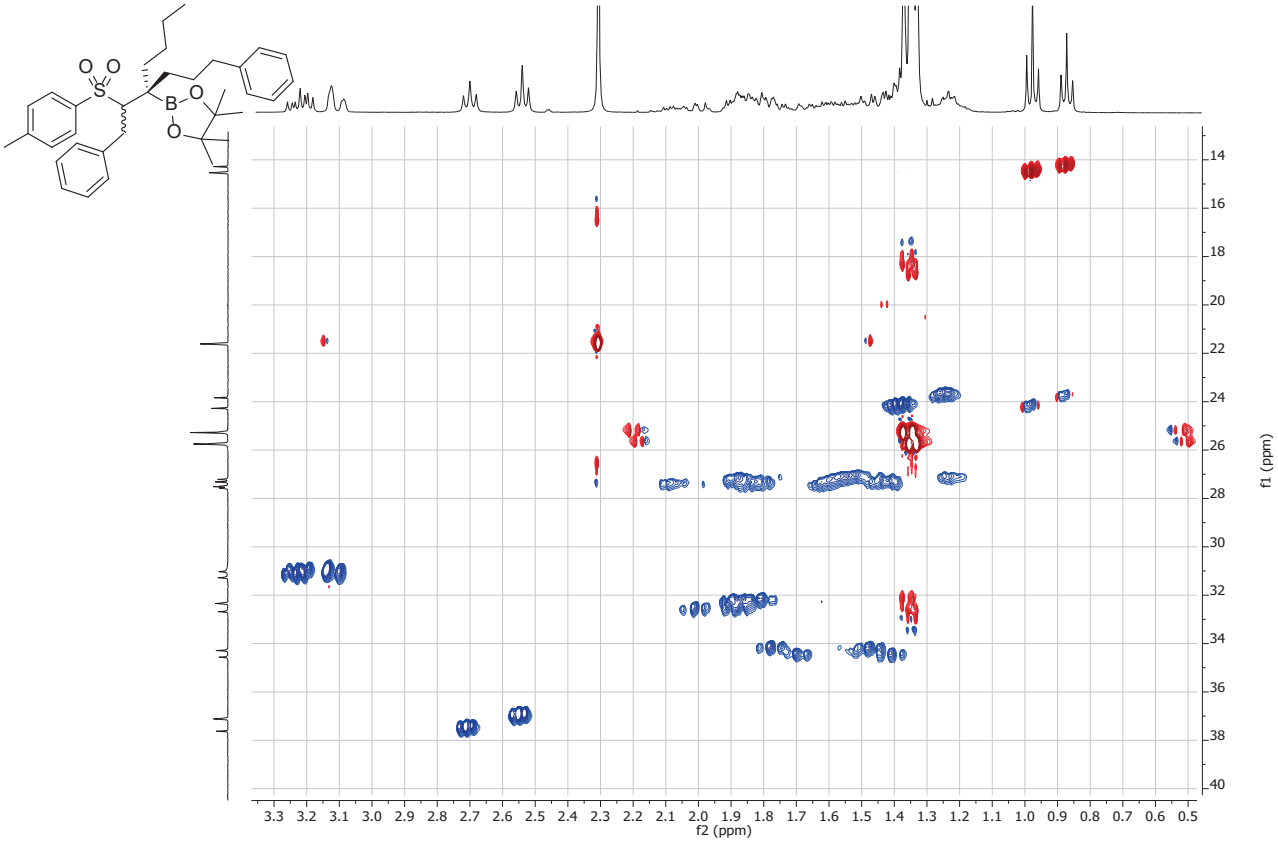
4,4,5,5-tetramethyl-2-((S)-1-phenyl-4-(2-phenyl-1-tosylethyl)octan-4-yl)-1,3,2-dioxaborolane (50)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



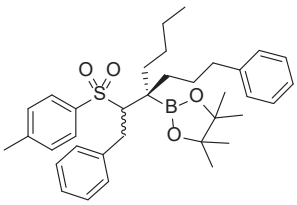
4,4,5,5-tetramethyl-2-((S)-1-phenyl-4-(2-phenyl-1-tosylethyl)octan-4-yl)-1,3,2-dioxaborolane (50)

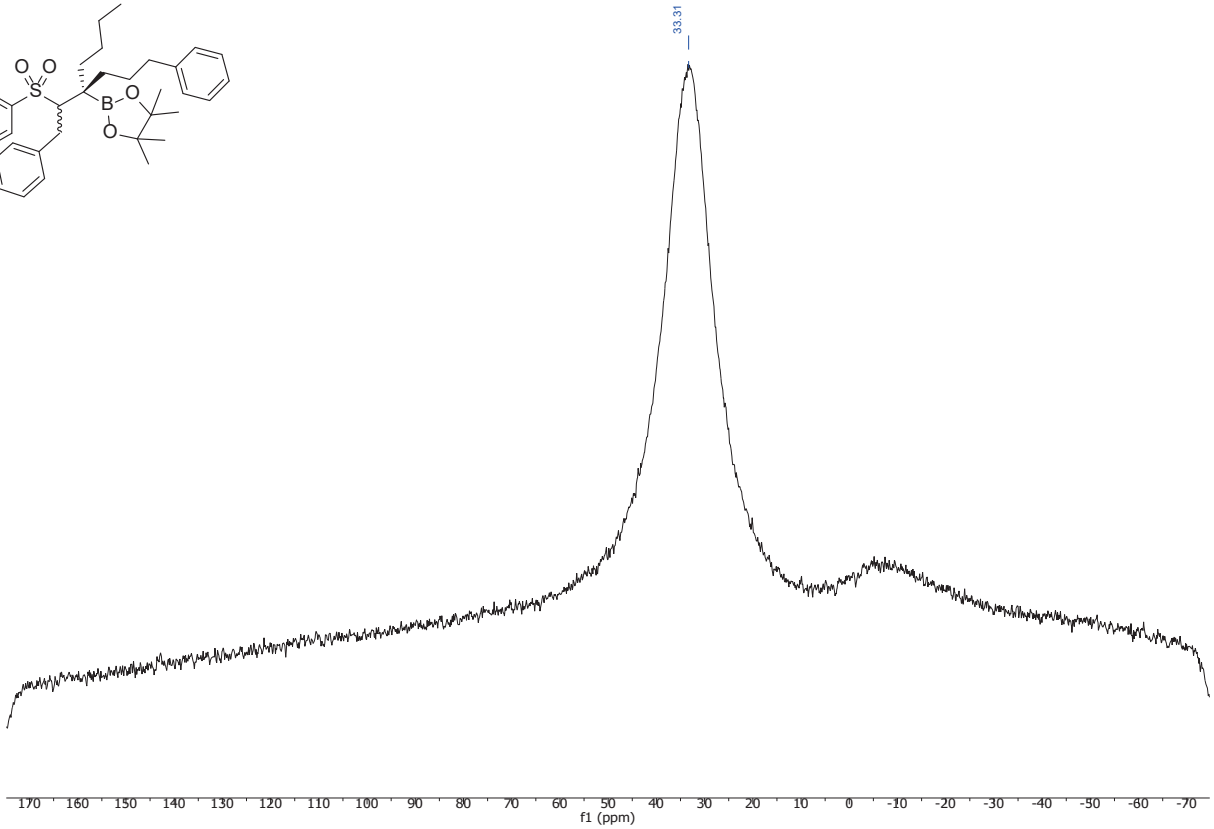
^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-((S)-1-phenyl-4-(2-phenyl-1-tosylethyl)octan-4-yl)-1,3,2-dioxaborolane (50)

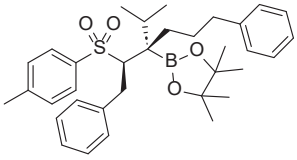
^{11}B NMR (96 MHz, $CDCl_3$)

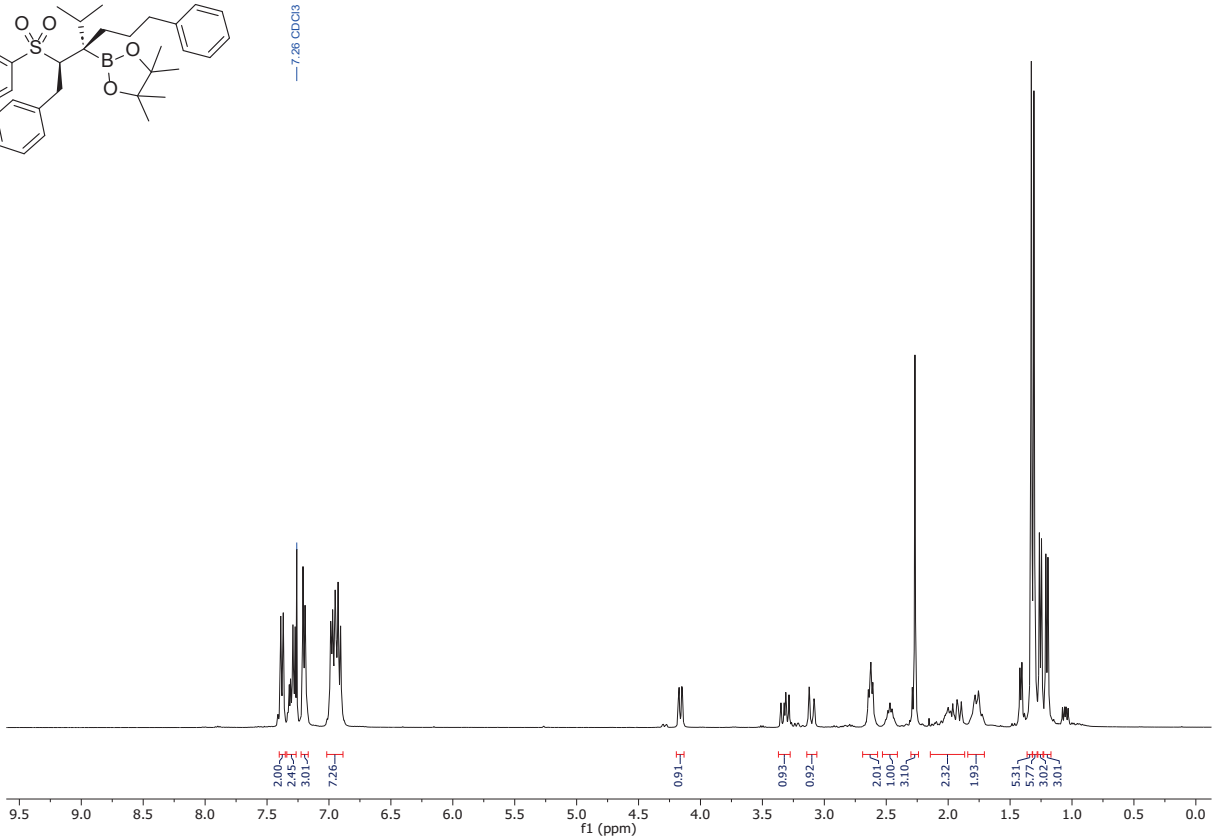




2-((2R,3R)-3-isopropyl-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56)
Major diastereomer

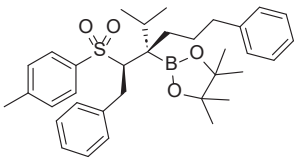
^{1}H NMR (400 MHz, $CDCl_3$)

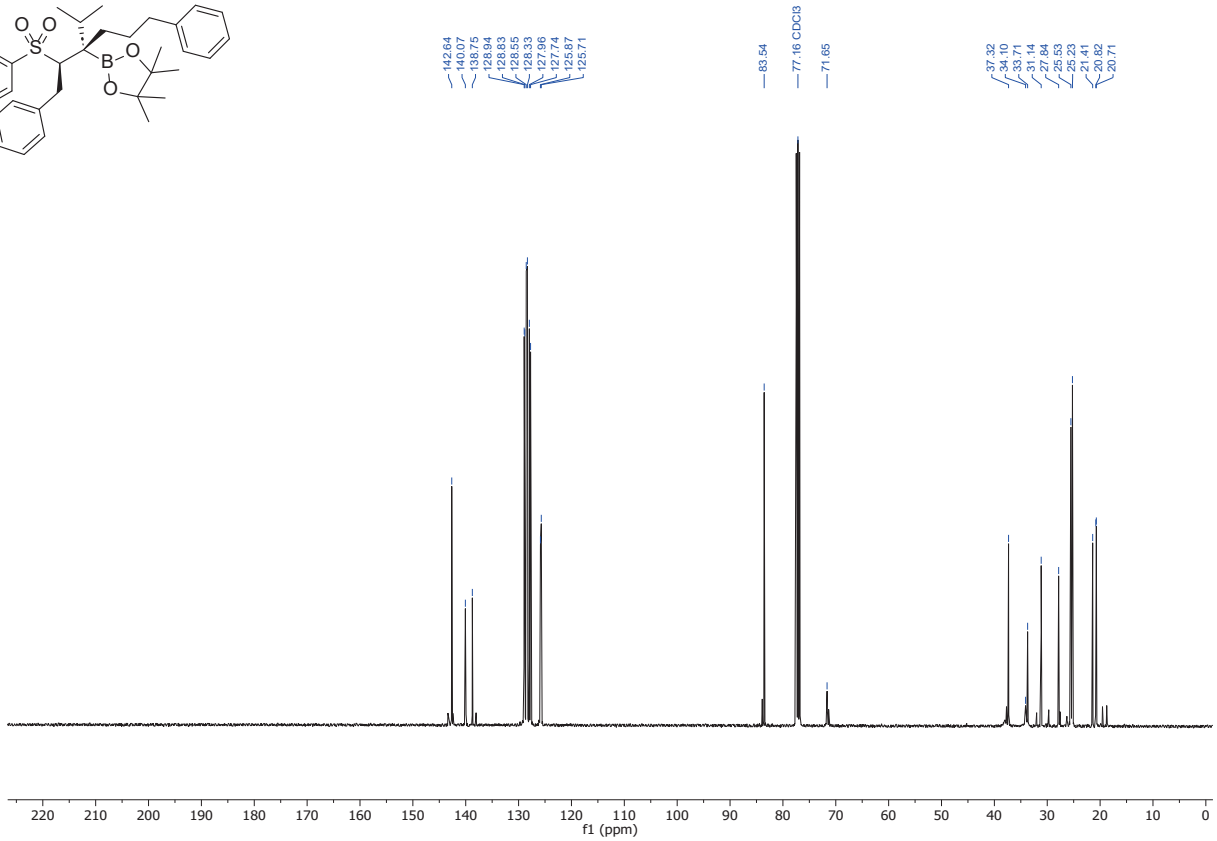




2-((2R,3R)-3-isopropyl-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56)
Major diastereomer

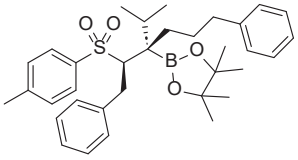
^{13}C NMR (101 MHz, $CDCl_3$)

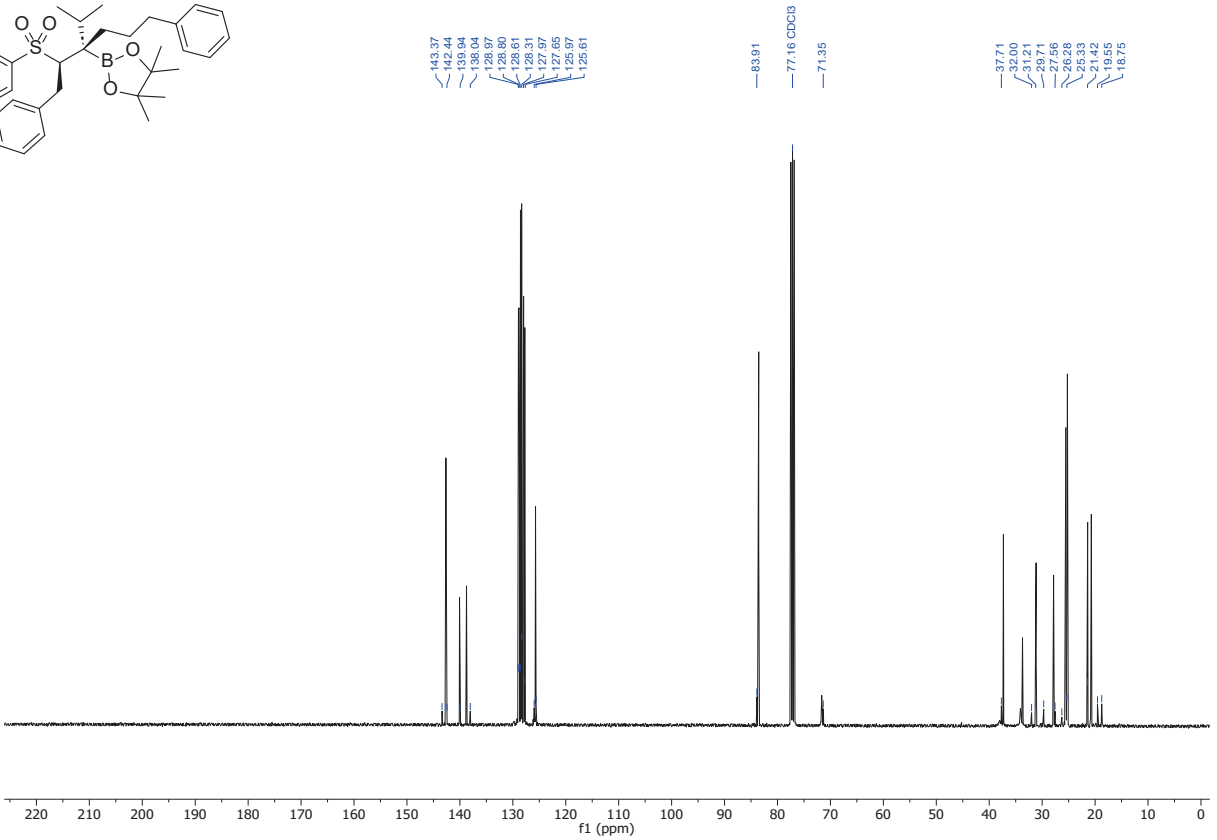




2-((2R,3R)-3-isopropyl-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56)
Minor diastereomer

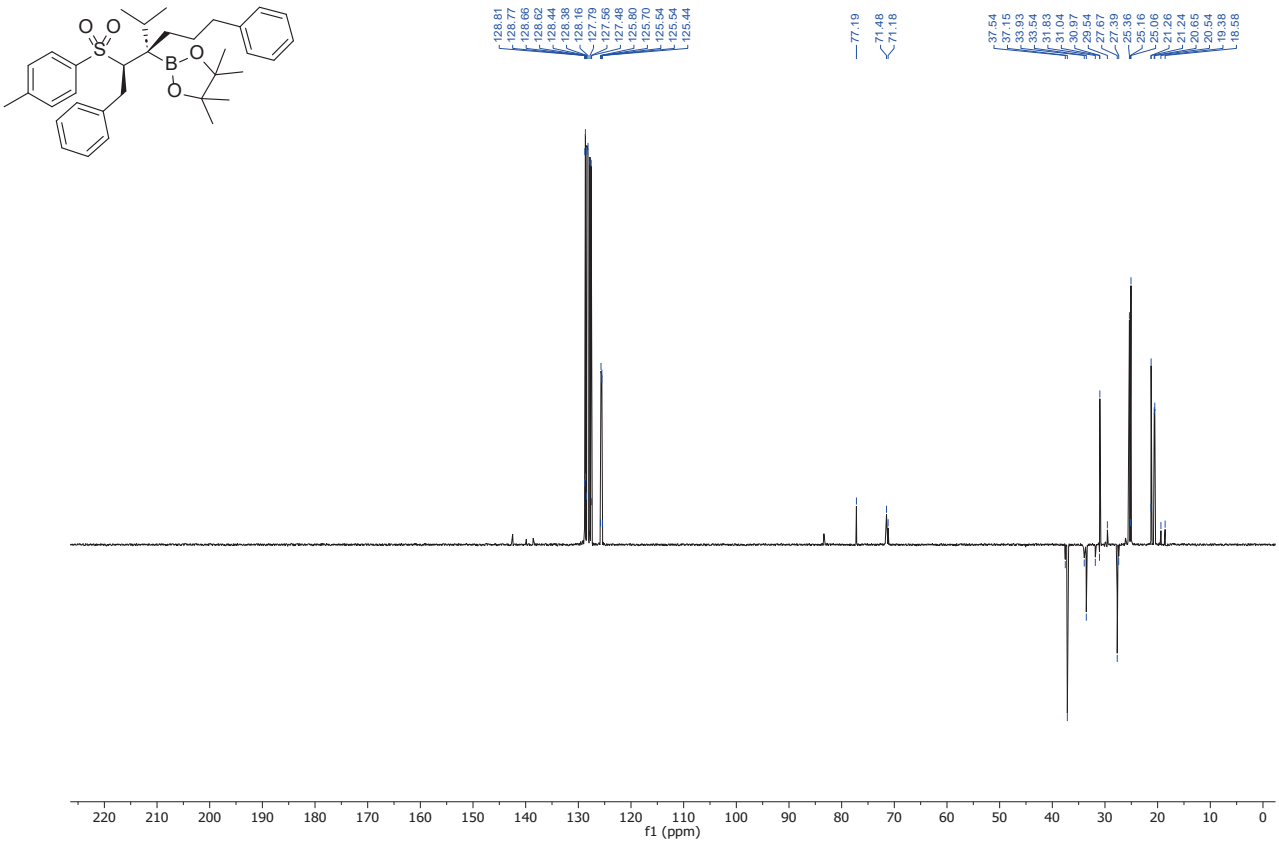
^{13}C NMR (101 MHz, $CDCl_3$)





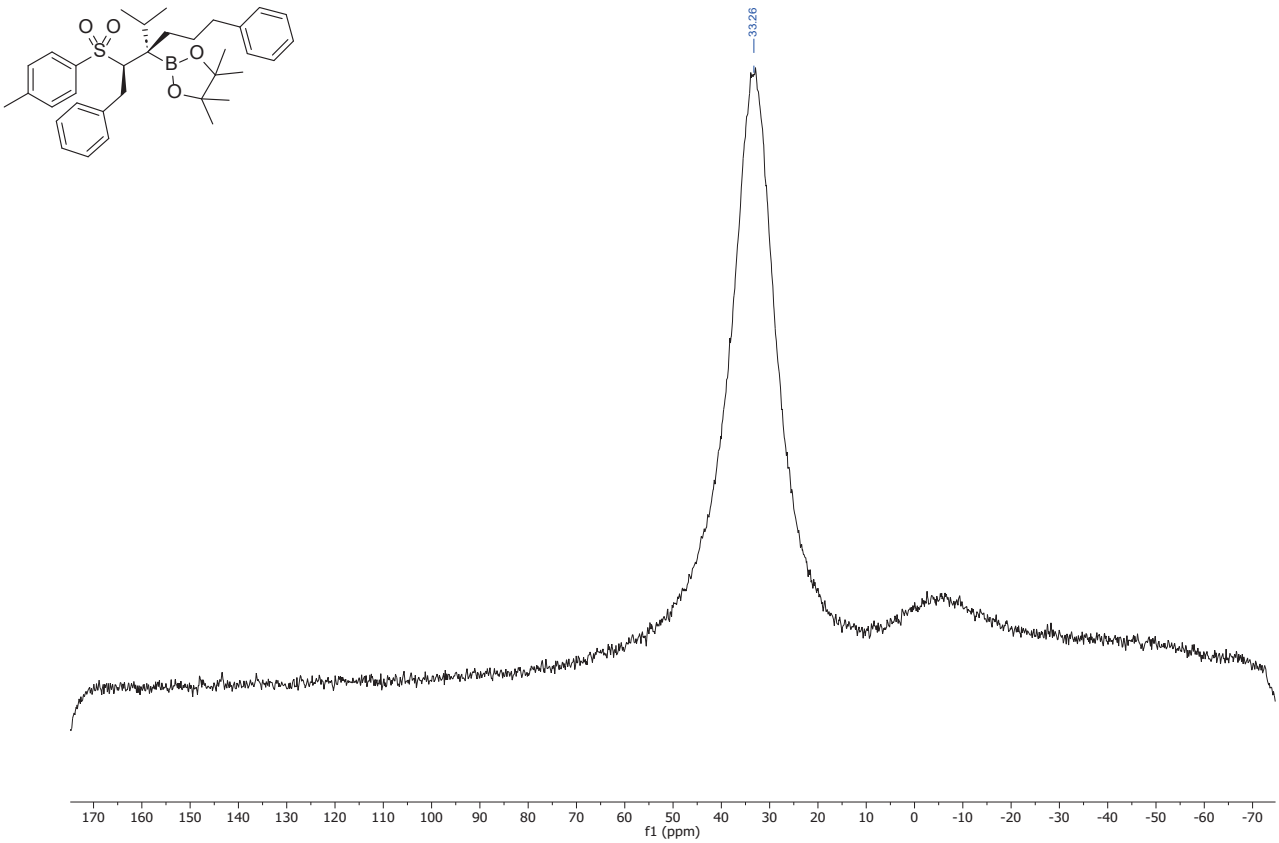
2-((2R,3R)-3-isopropyl-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



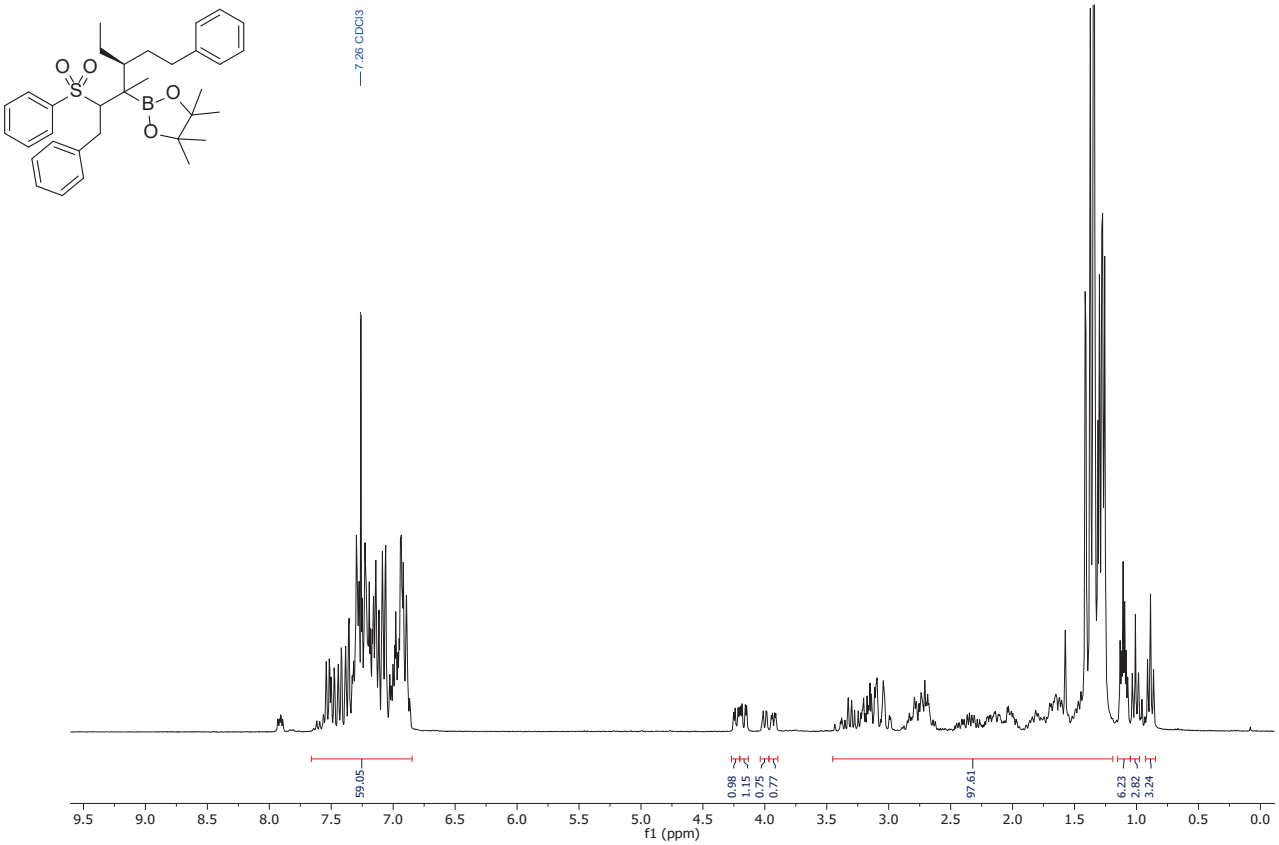
2-((2R,3R)-3-isopropyl-1,6-diphenyl-2-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56)

^{11}B NMR (96 MHz, $CDCl_3$)



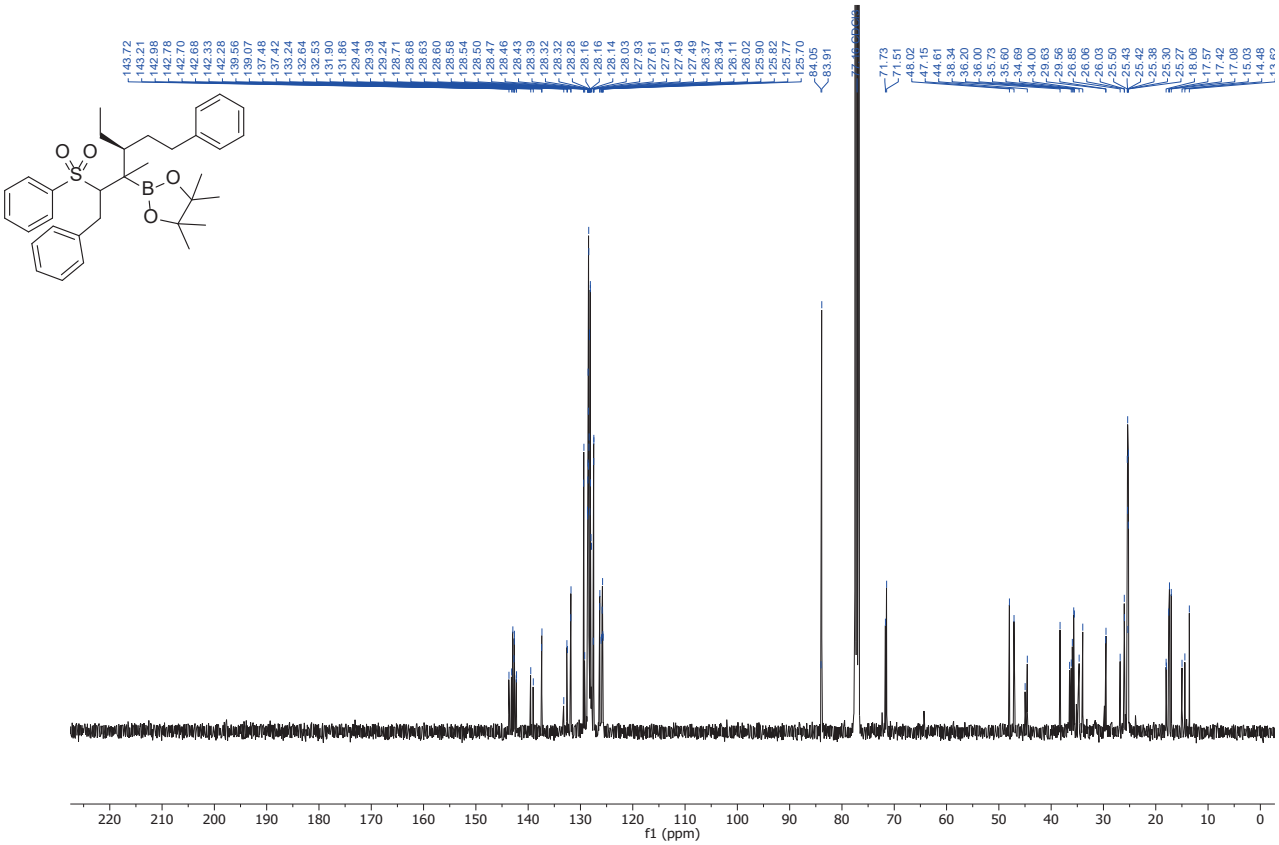
2-((4*S*)-4-ethyl-3-methyl-1,6-diphenyl-2-(phenylsulfonyl)hexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (93)

^{1}H NMR (300 MHz, $CDCl_3$)



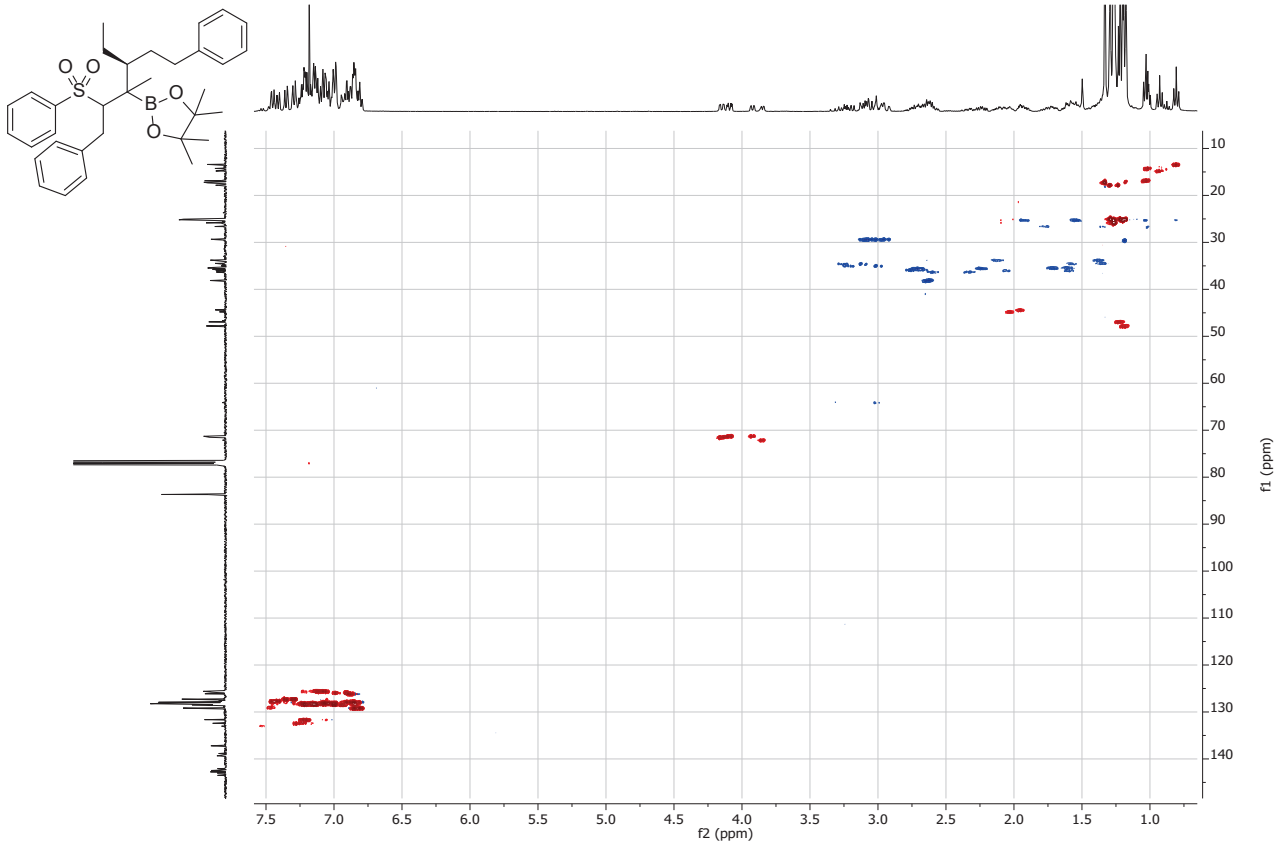
2-((4*S*)-4-ethyl-3-methyl-1,6-diphenyl-2-(phenylsulfonyl)hexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (93)

^{13}C NMR (101 MHz, $CDCl_3$)



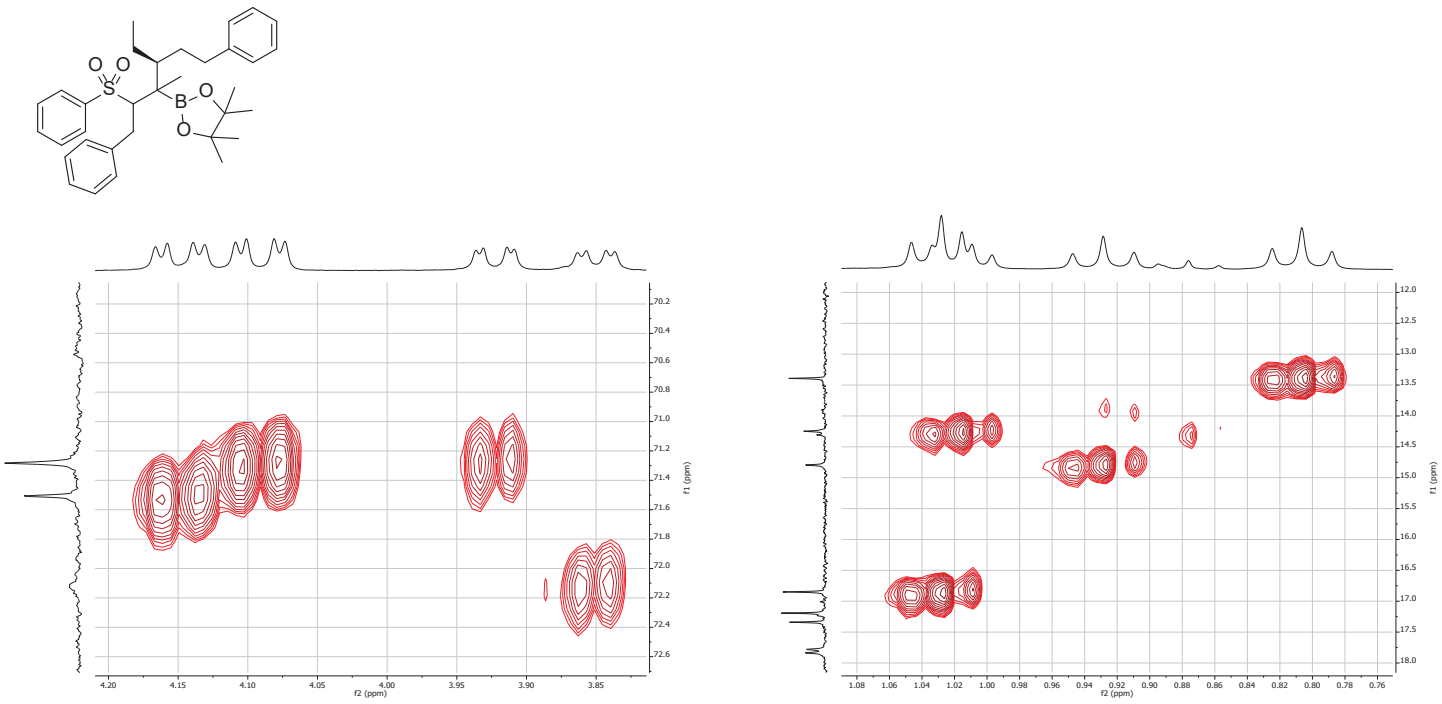
2-((4*S*)-4-ethyl-3-methyl-1,6-diphenyl-2-(phenylsulfonyl)hexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (93)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



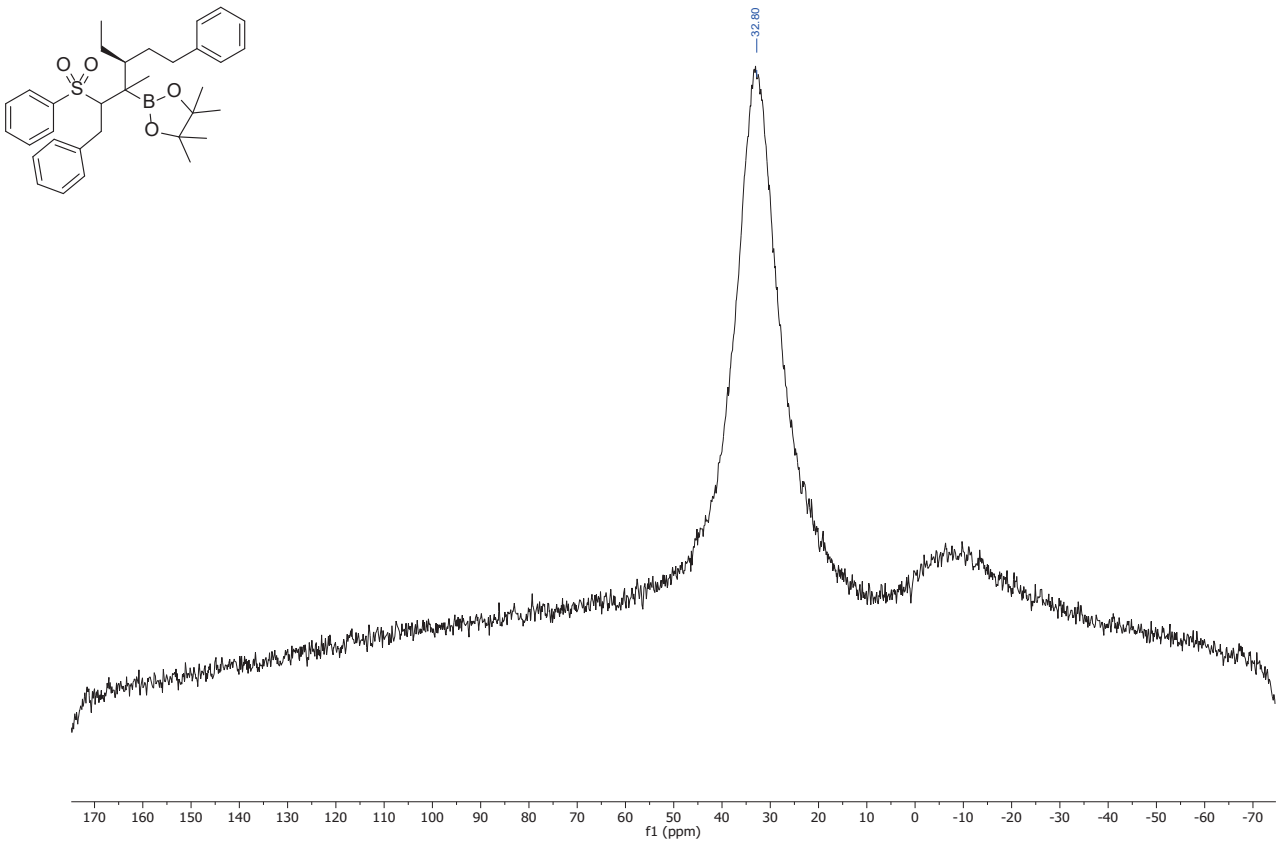
2-((4*S*)-4-ethyl-3-methyl-1,6-diphenyl-2-(phenylsulfonyl)hexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (93)

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



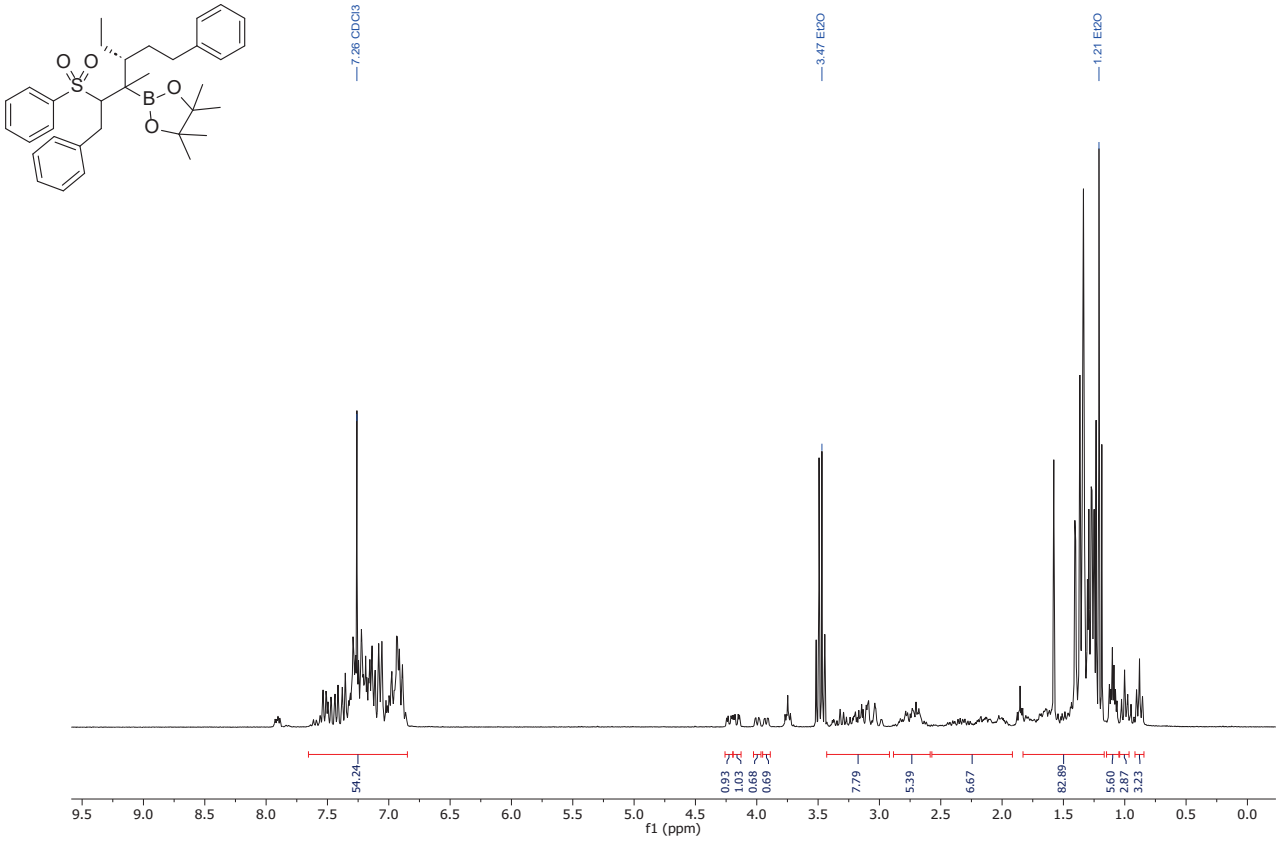
2-((4S)-4-ethyl-3-methyl-1,6-diphenyl-2-(phenylsulfonyl)hexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (93)

^{11}B NMR (96 MHz, $CDCl_3$)



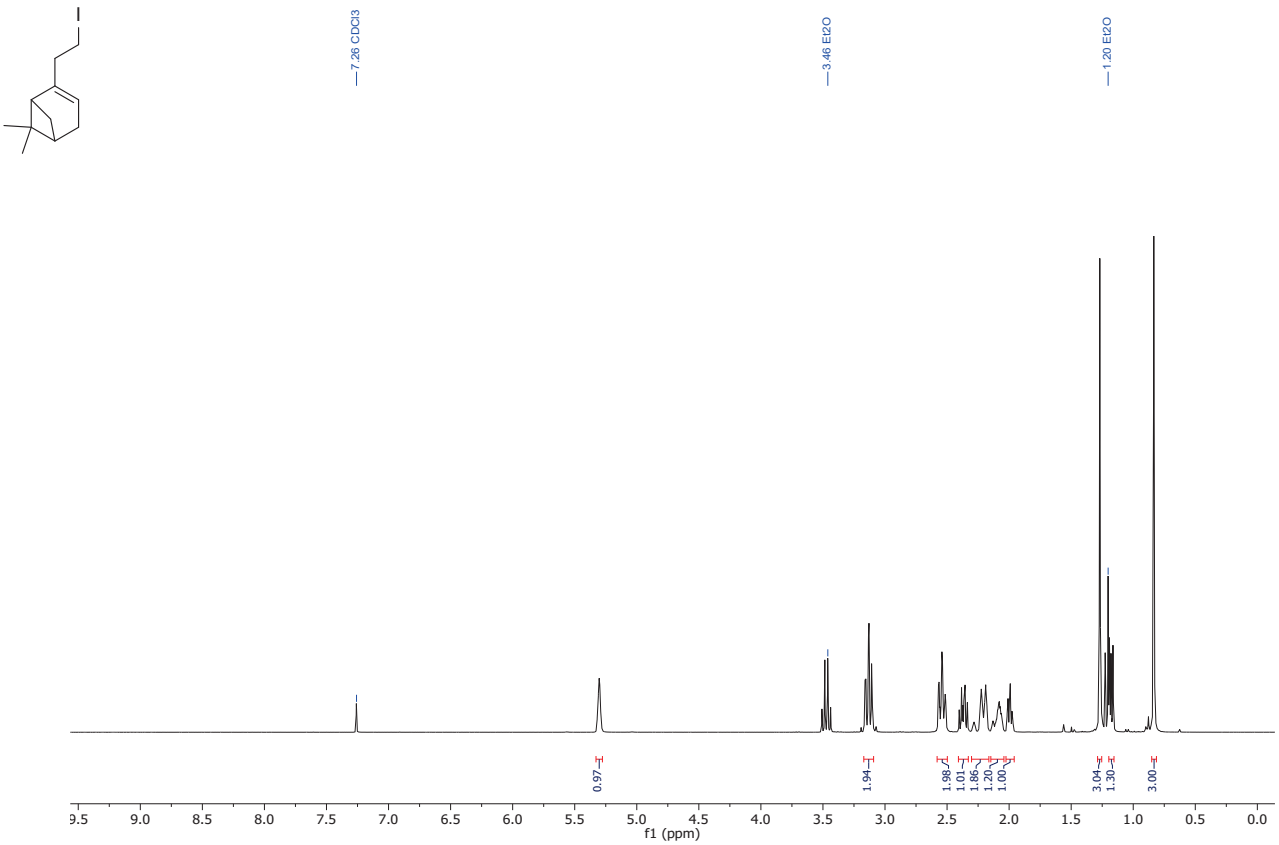
2-((4R)-4-ethyl-3-methyl-1,6-diphenyl-2-(phenylsulfonyl)hexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (106)

^{1}H NMR (300 MHz, $CDCl_3$)



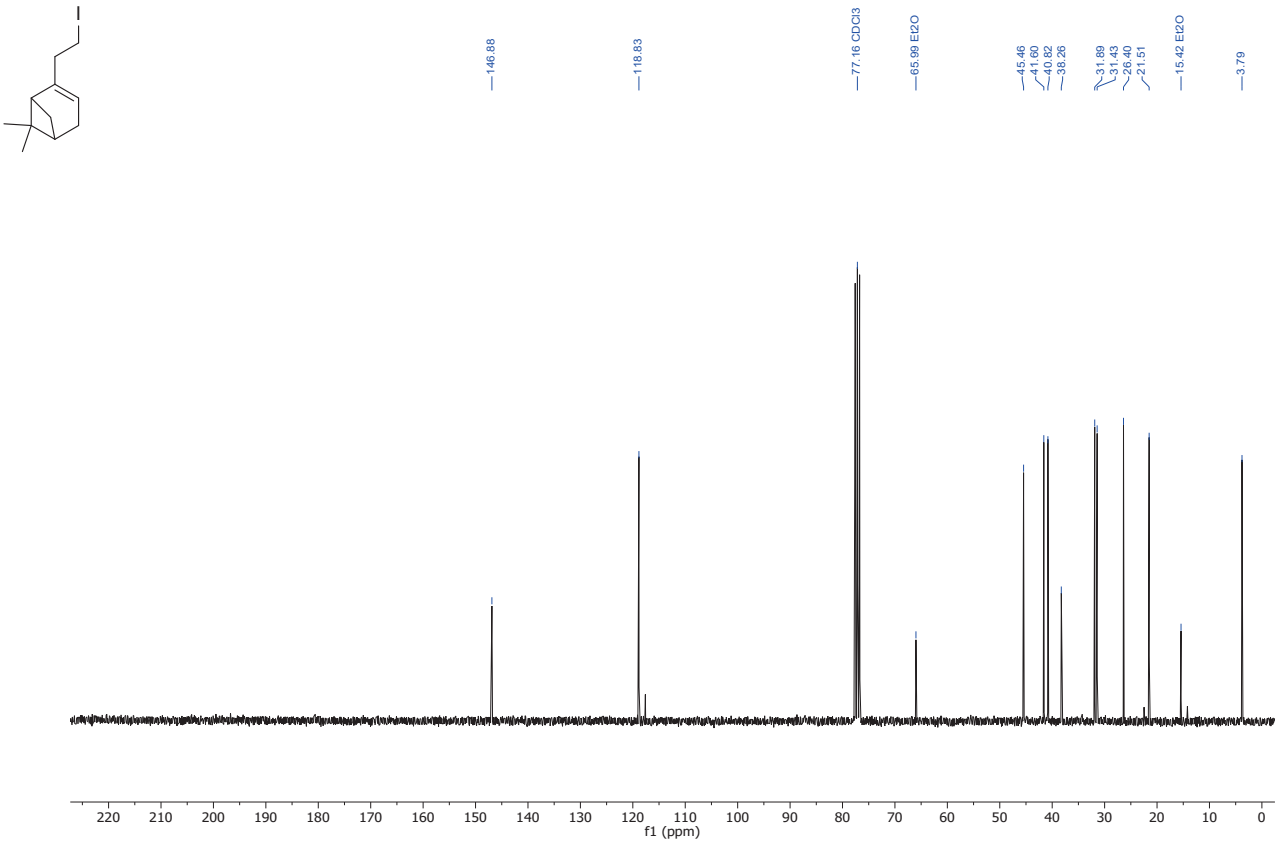
(1*R*)-(-)-Nopol iodide (107)

^{1}H NMR (300 MHz, $CDCl_3$)



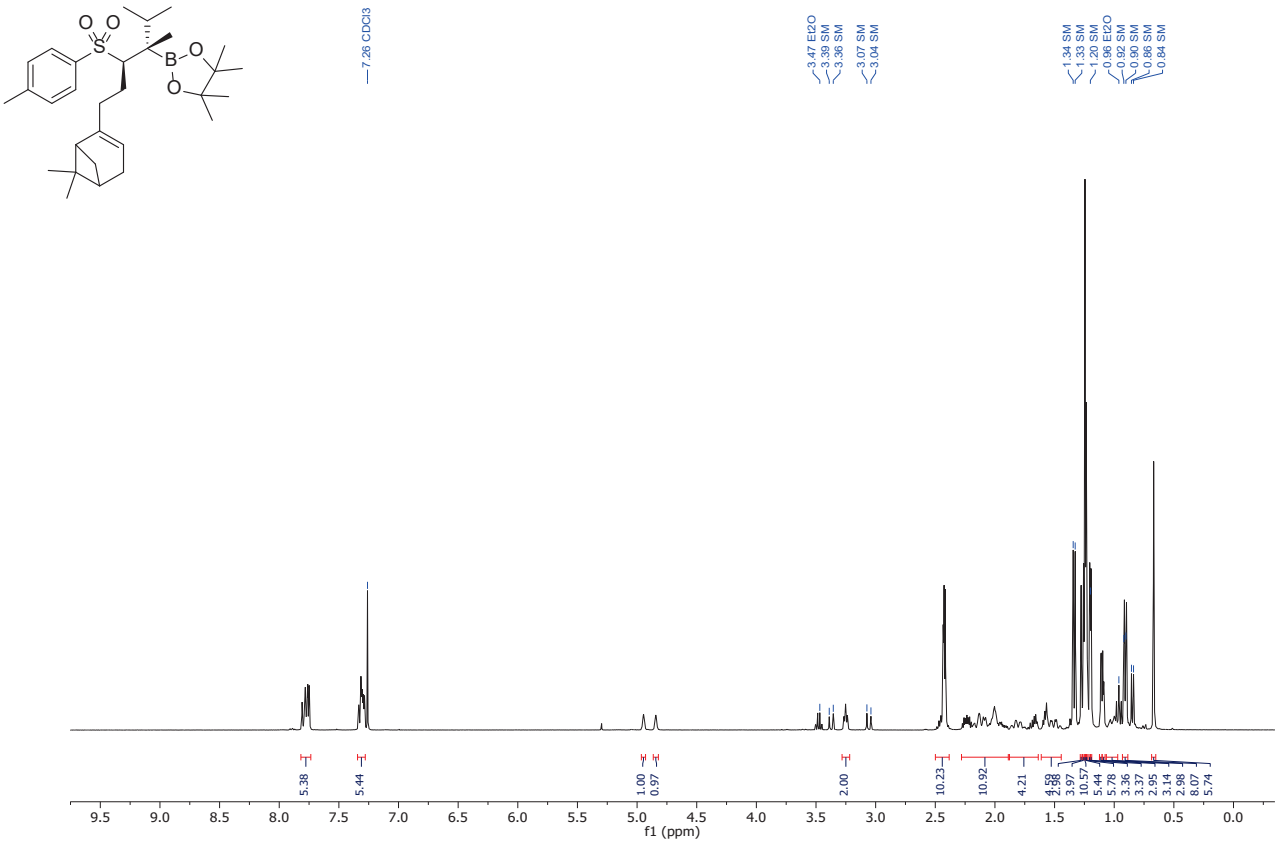
(1*R*)-(-)-Nopol iodide (107)

^{13}C NMR (75 MHz, $CDCl_3$)



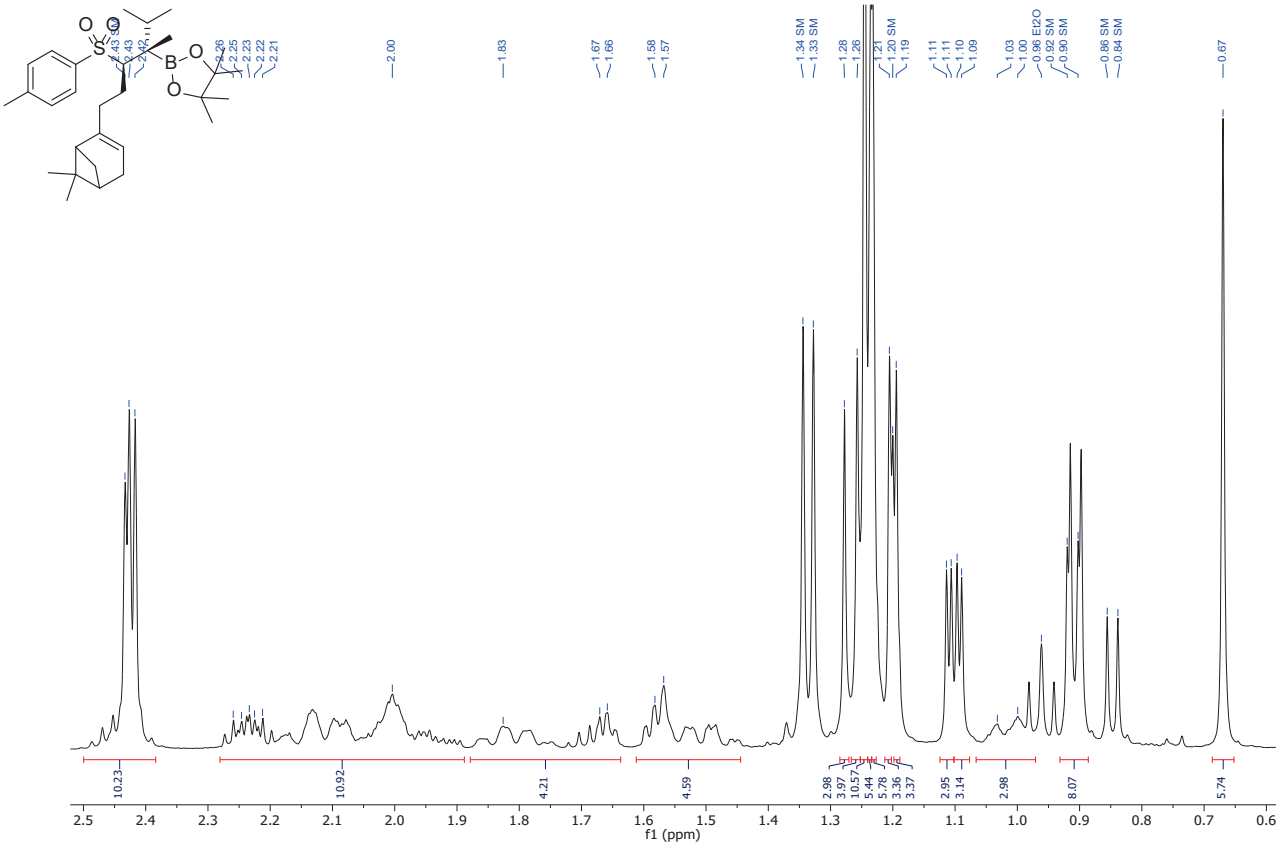
2-((3R,4R)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)

^{1}H NMR (300 MHz, $CDCl_3$)



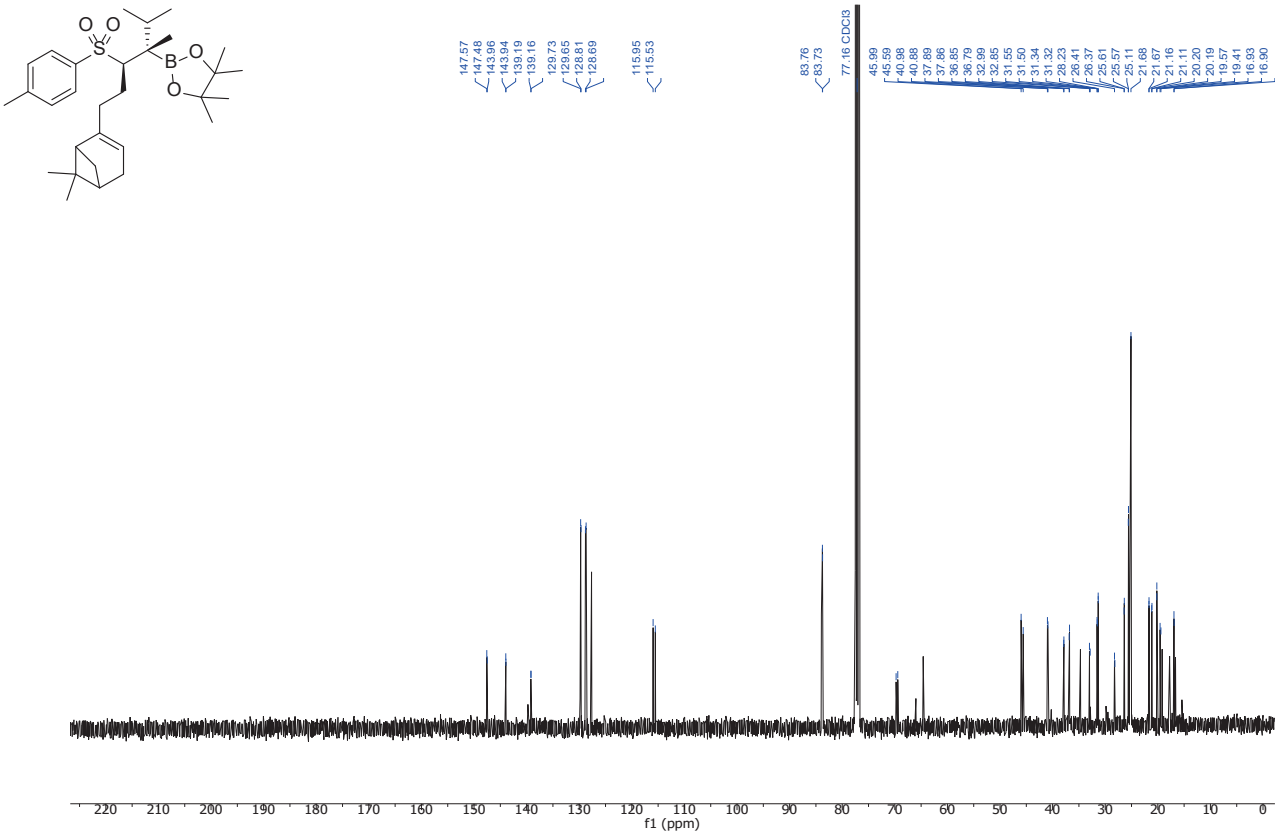
2-((3R,4R)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)

^{1}H NMR (300 MHz, $CDCl_3$)



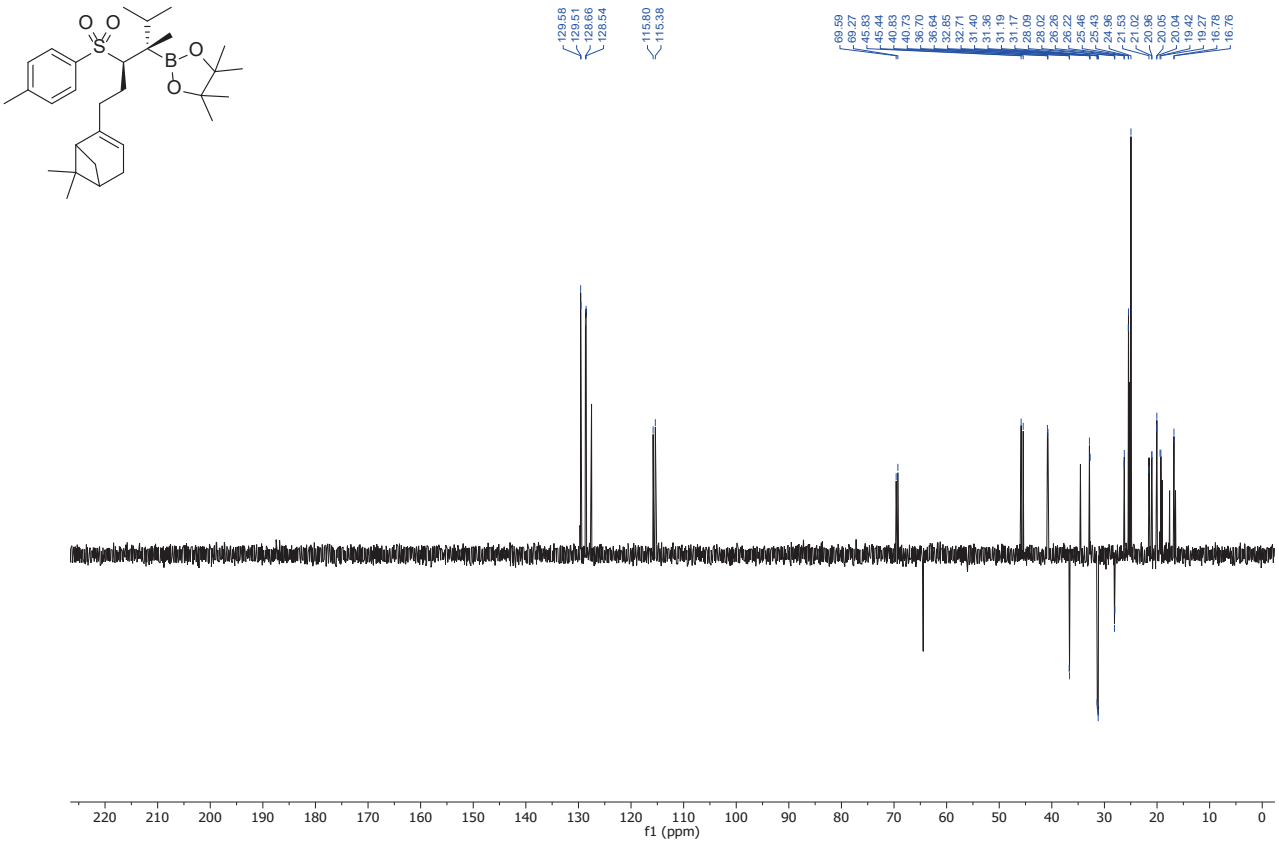
2-((3R,4R)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)
Major diastereomers

^{13}C NMR (75 MHz, $CDCl_3$)



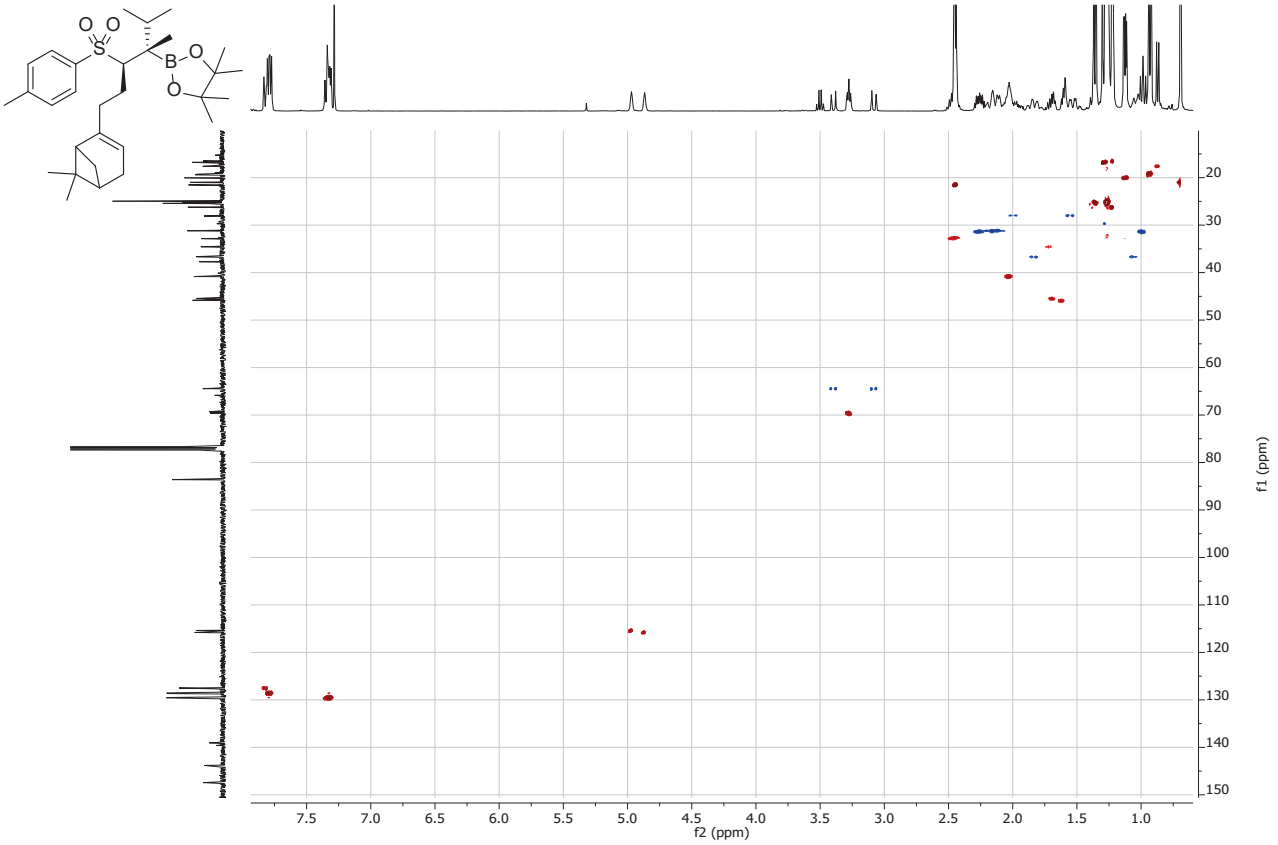
2-((3R,4R)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)
Major diastereomers

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



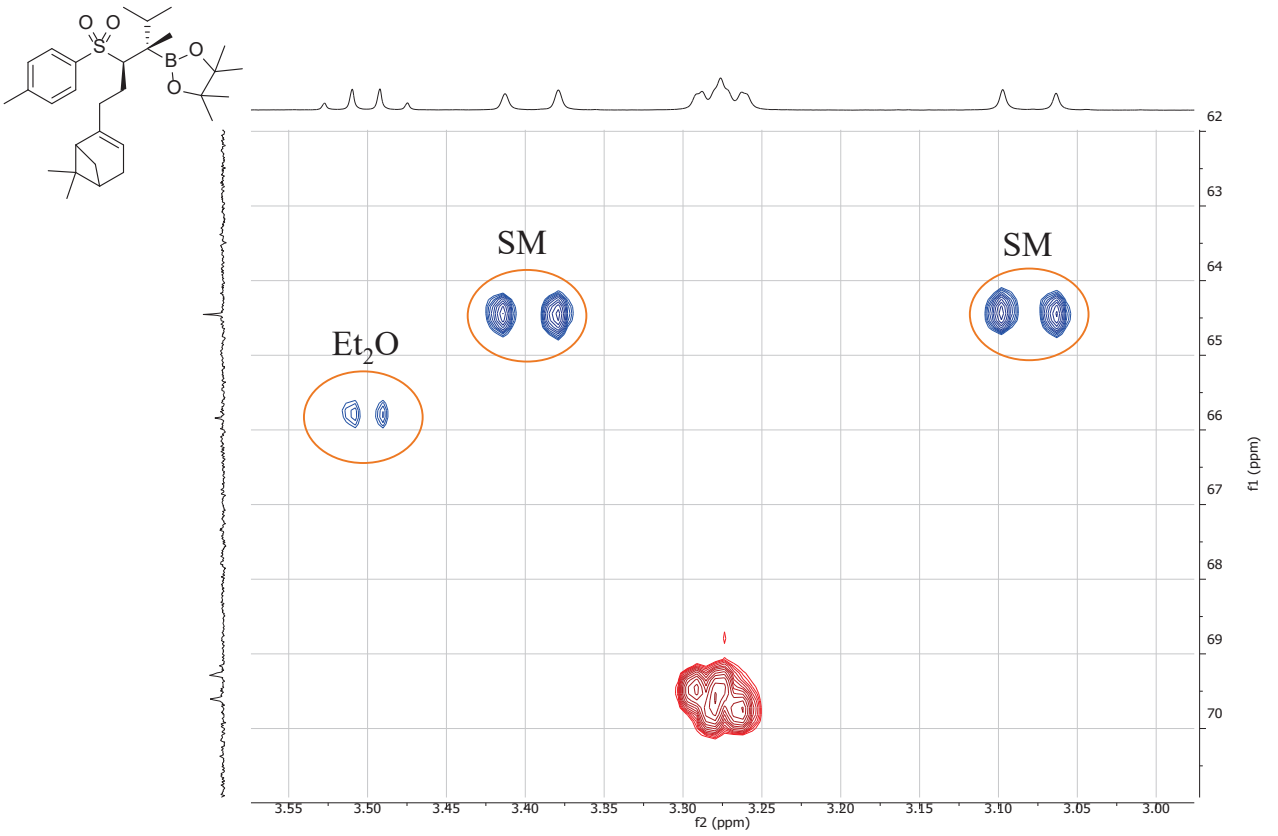
2-((3R,4R)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)
Major diastereomers

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



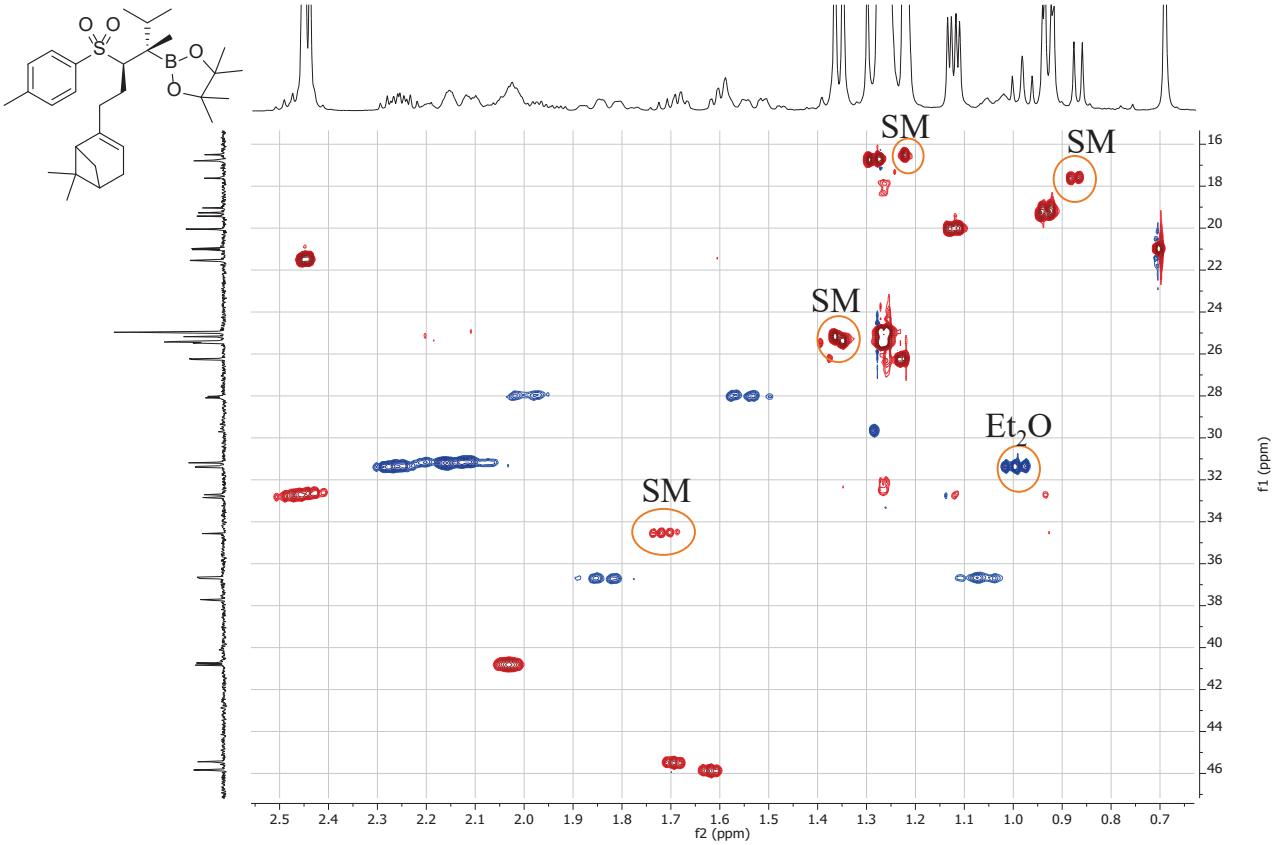
2-((3R,4R)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)
Major diastereomers

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



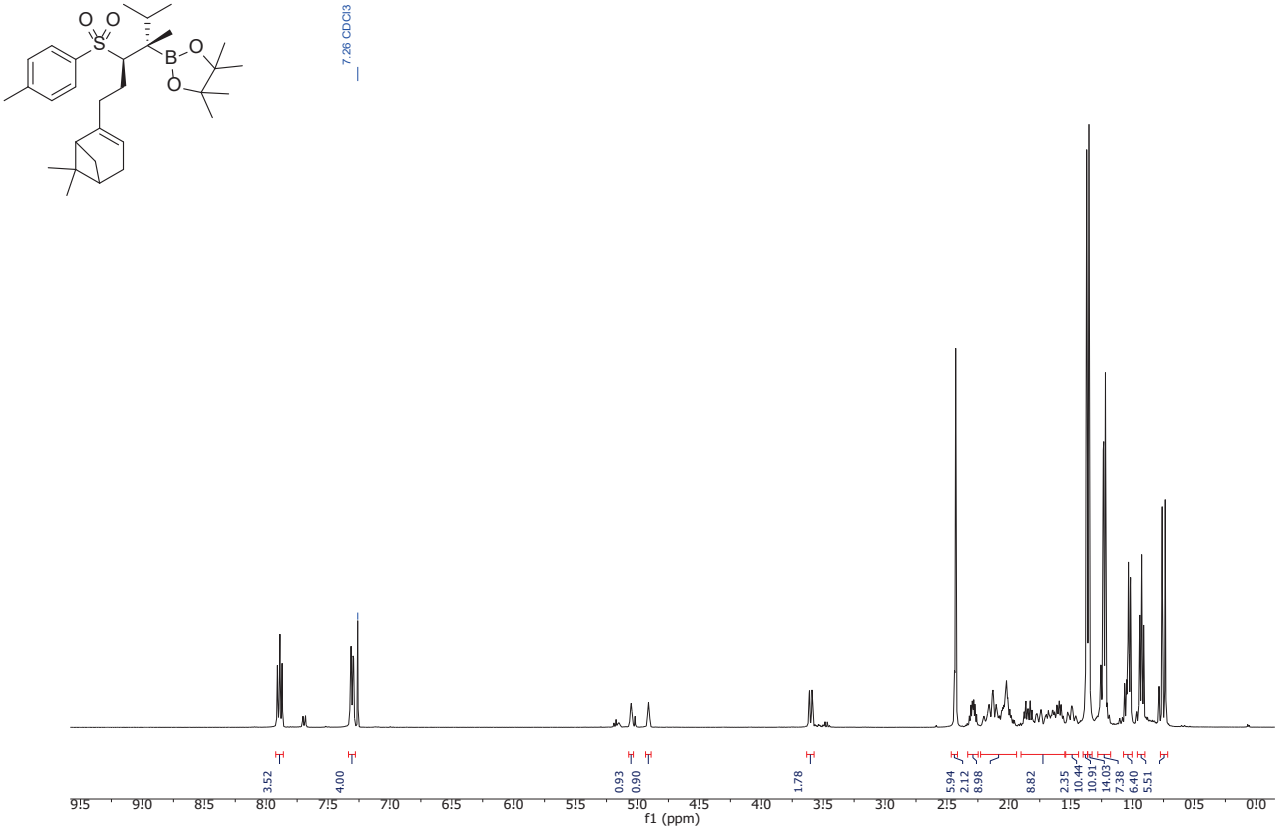
2-((3R,4R)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)
Major diastereomers

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



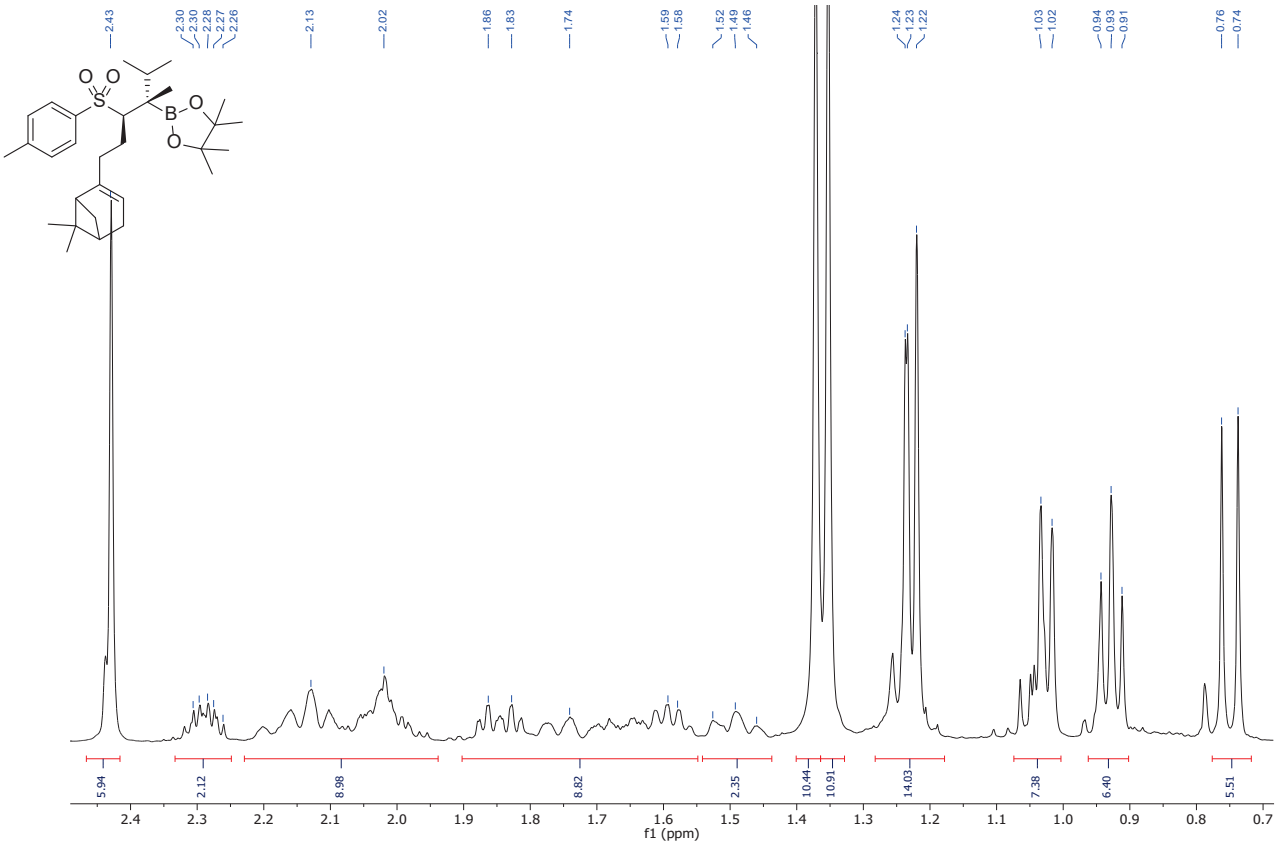
2-((3R,4R)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)
Minor diastereomers

^{1}H NMR (300 MHz, $CDCl_3$)



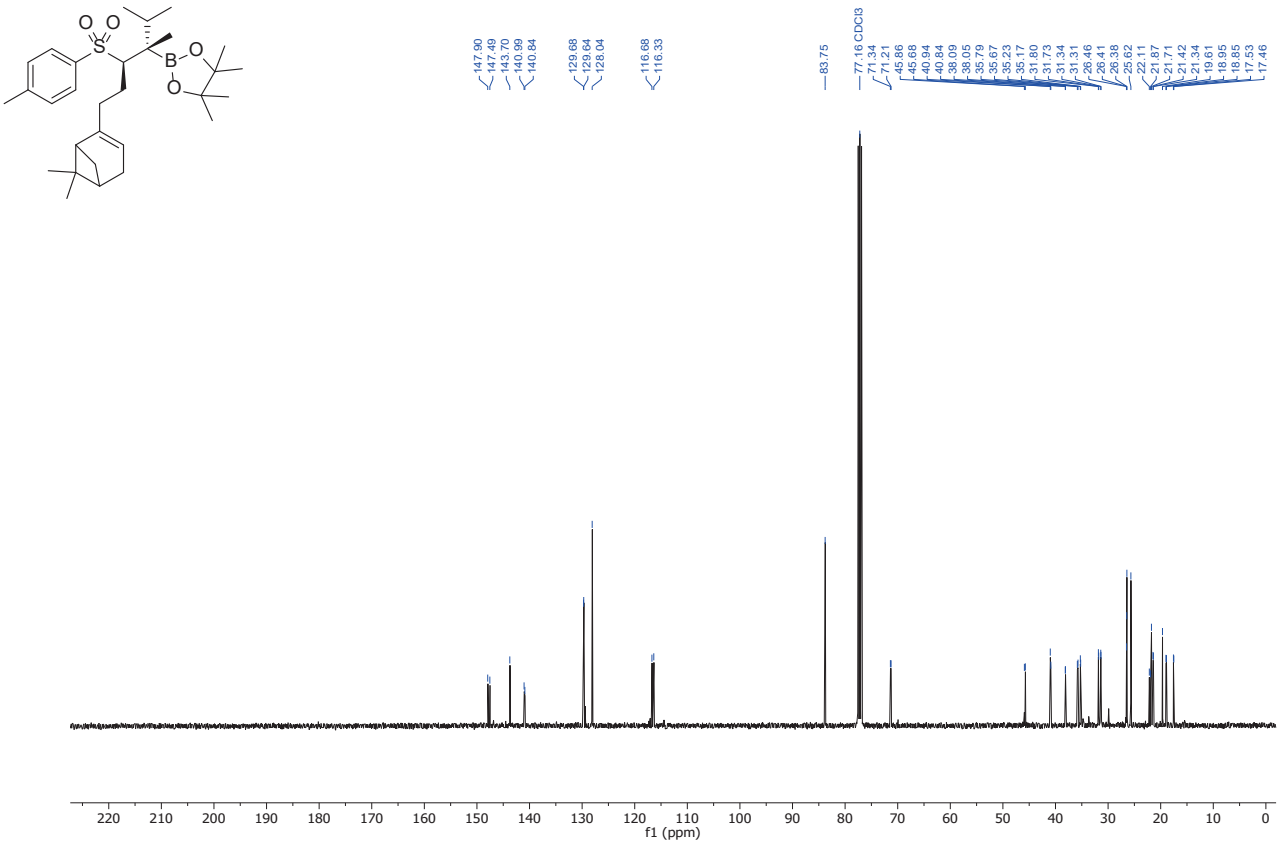
2-((3R,4R)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)
Minor diastereomers

^{1}H NMR (300 MHz, $CDCl_3$)



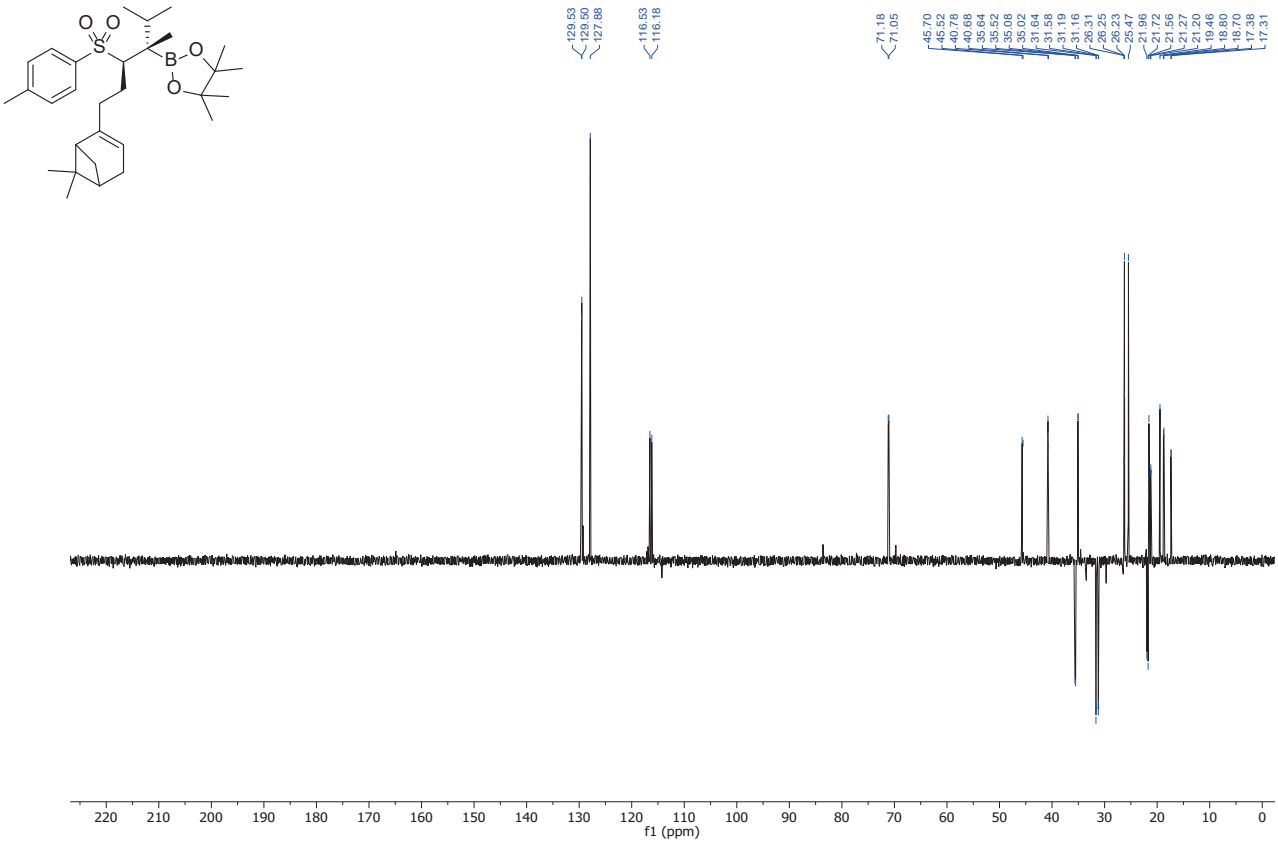
2-((3R,4R)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)
Minor diastereomers

^{13}C NMR (75 MHz, $CDCl_3$)



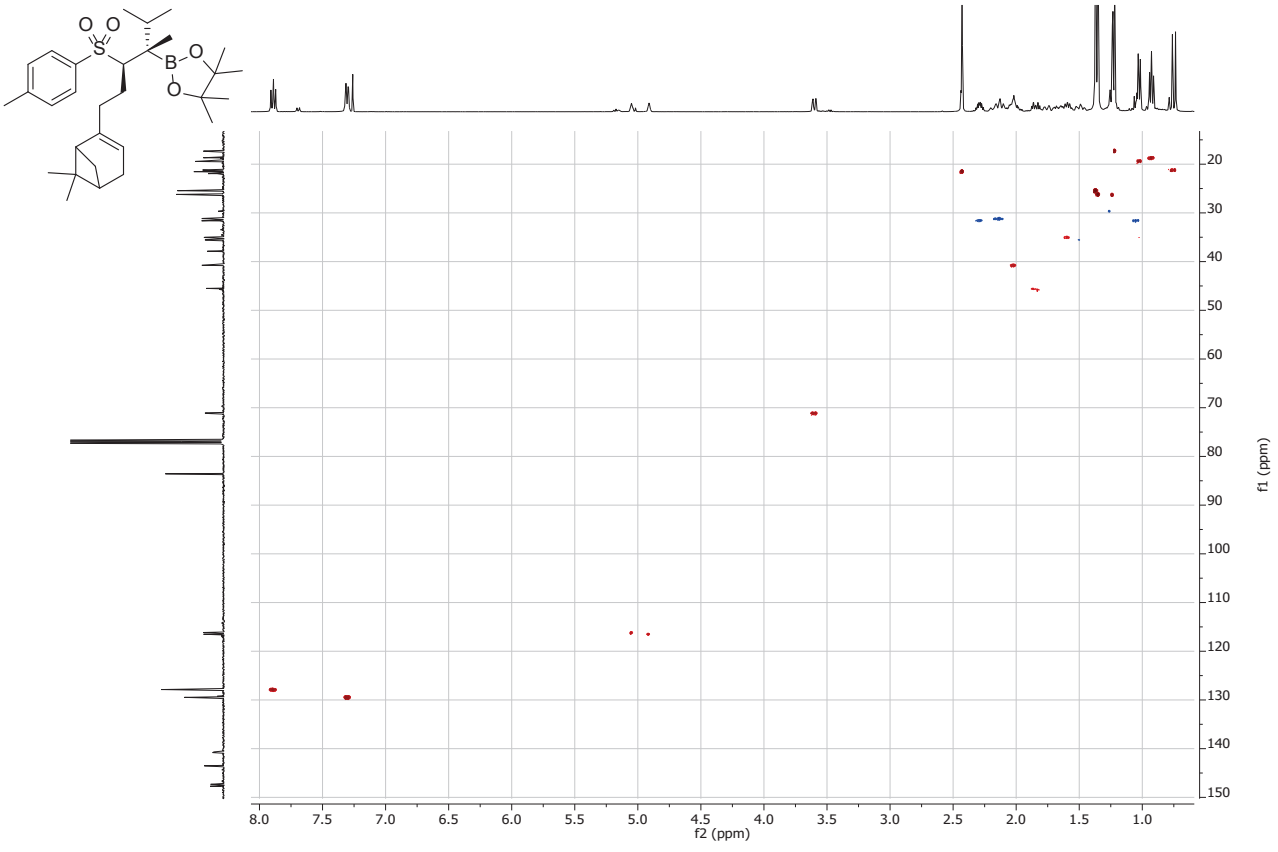
2-((3R,4R)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)
Minor diastereomers

^{13}C NMR Dept-135 (100 MHz, $CDCl_3$)



2-((3R,4R)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)
Minor diastereomers

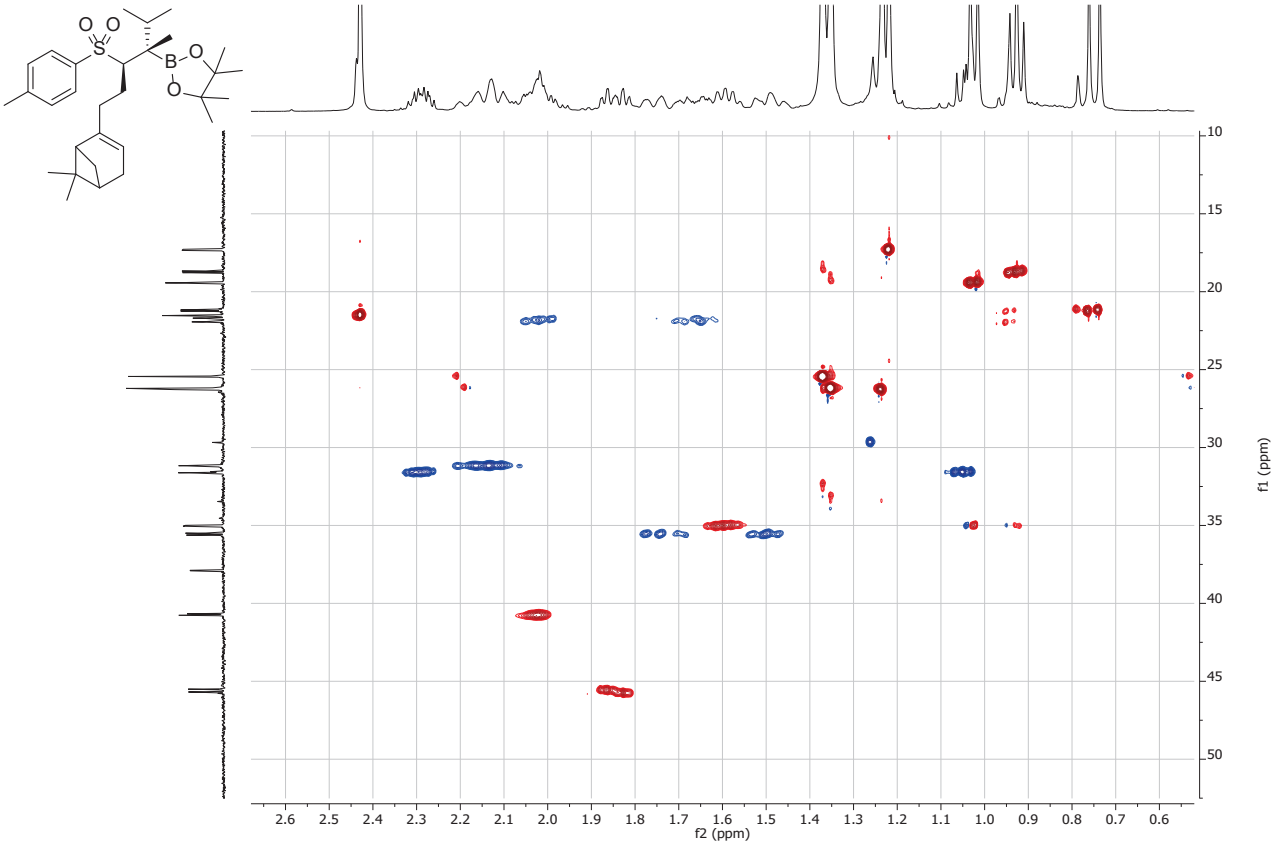
^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



2-((3R,4R)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)

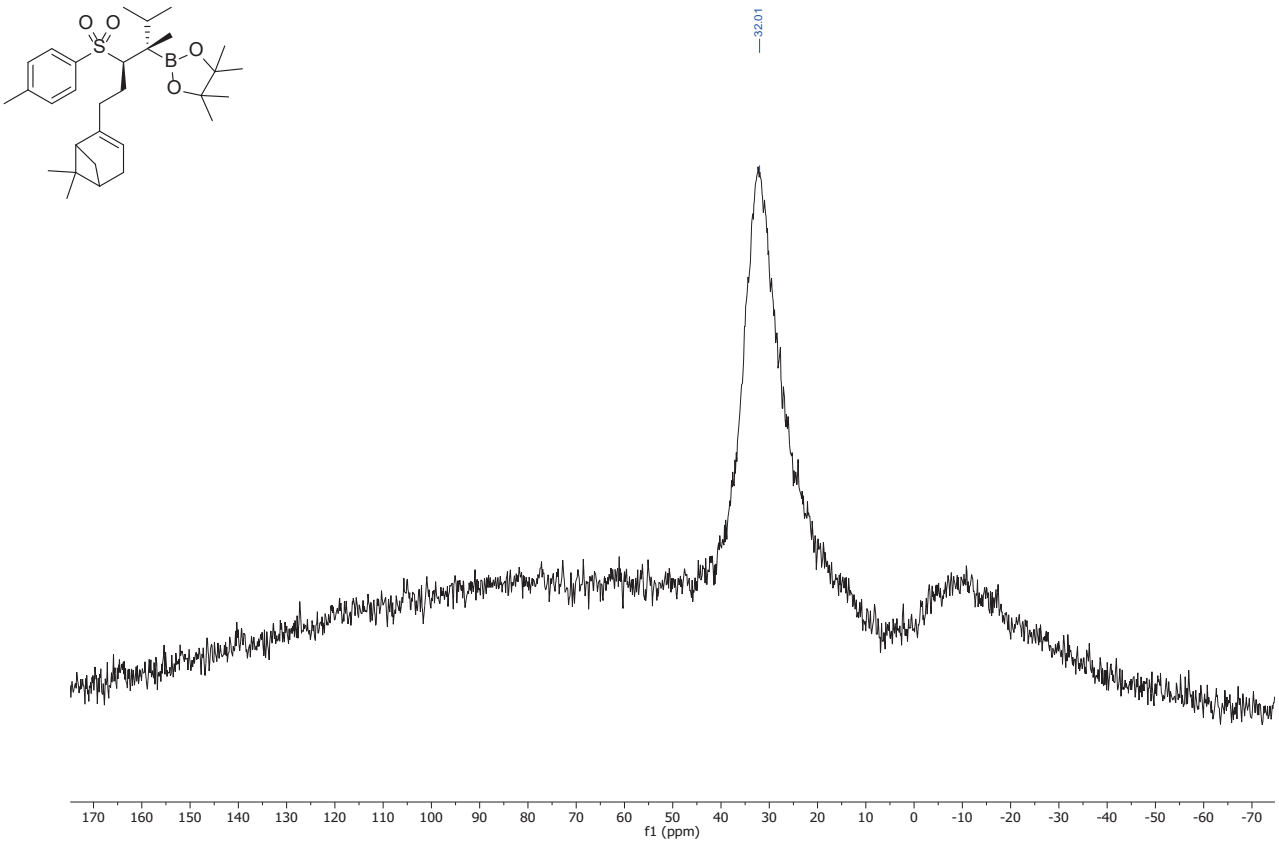
Minor diastereomers

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)

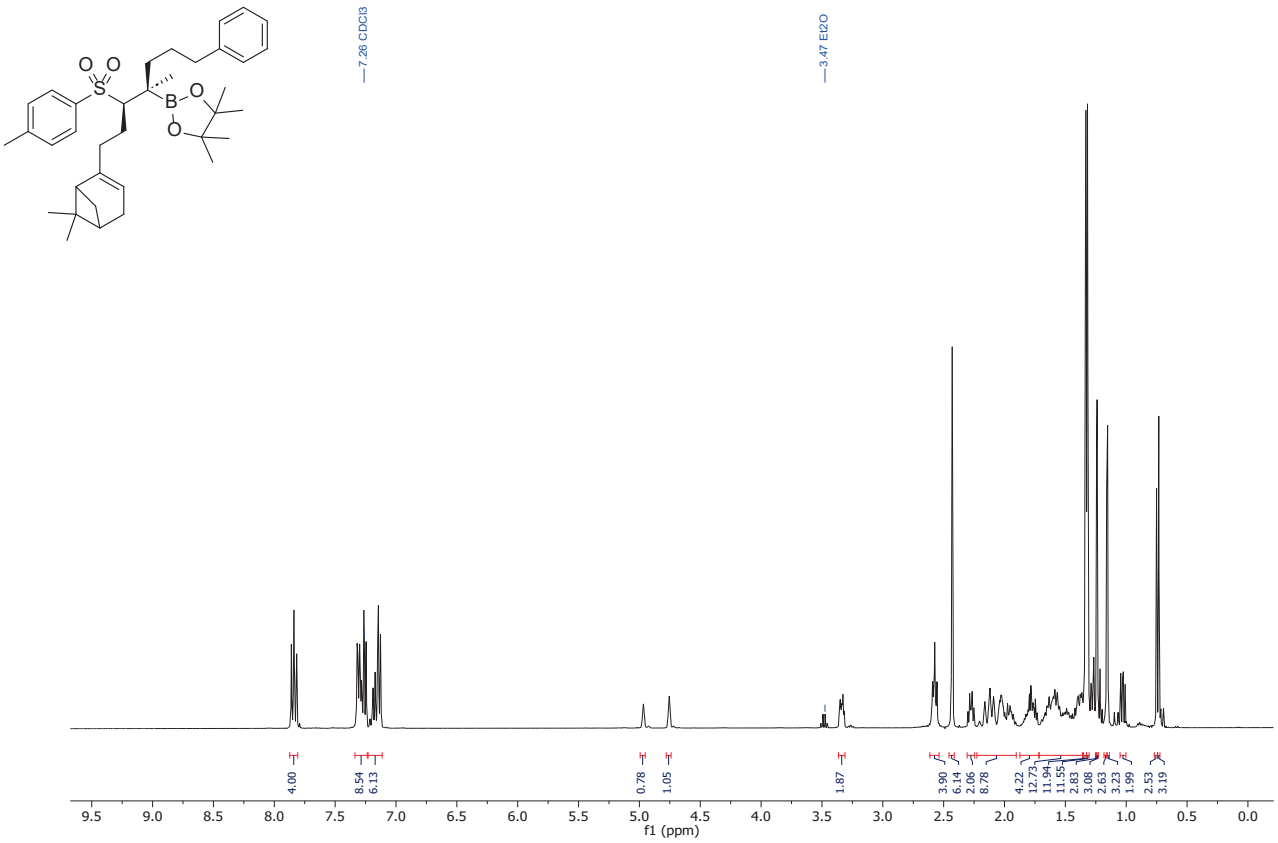


2-((3R,4R)-6-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2,3-dimethyl-4-tosylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83)

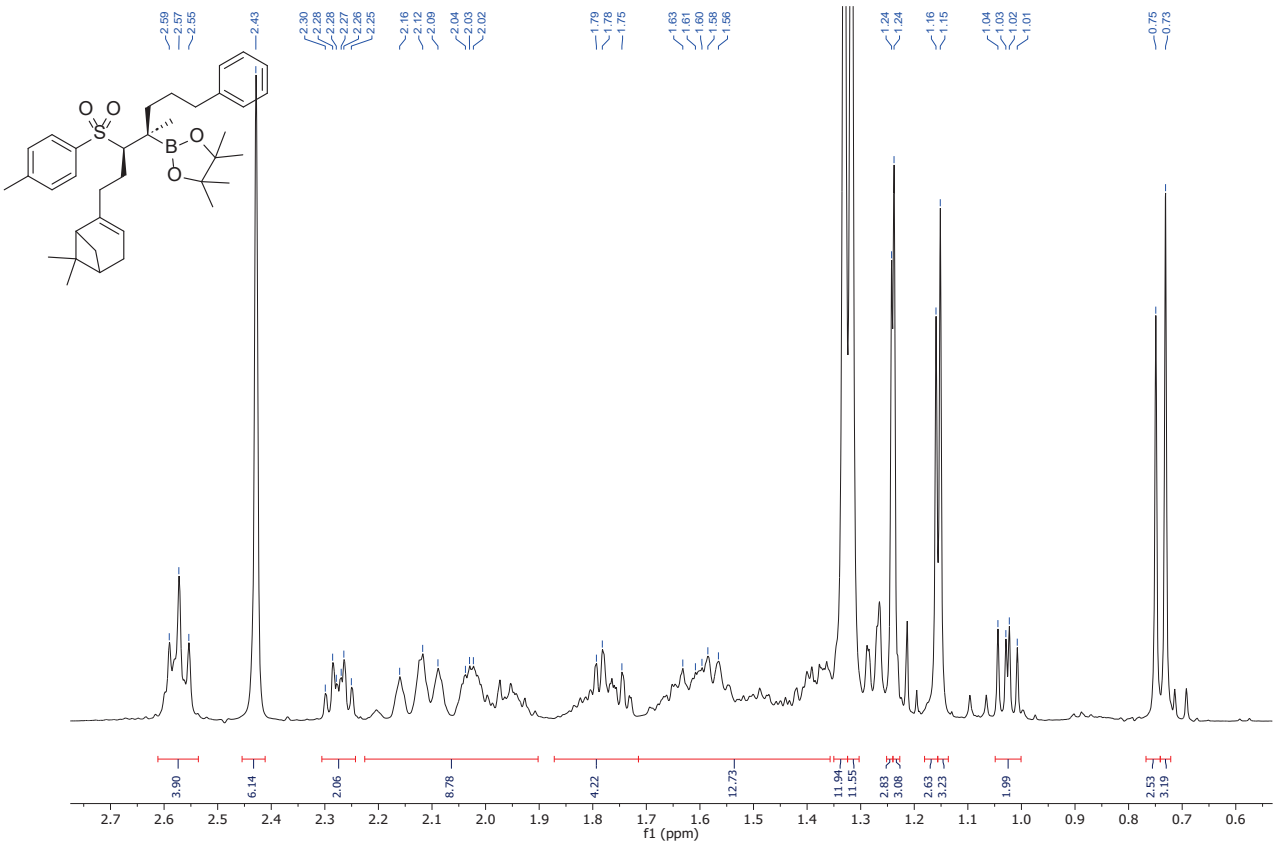
^{11}B NMR (96 MHz, $CDCl_3$)



2-((3R,4S)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82)
Major diastereomers

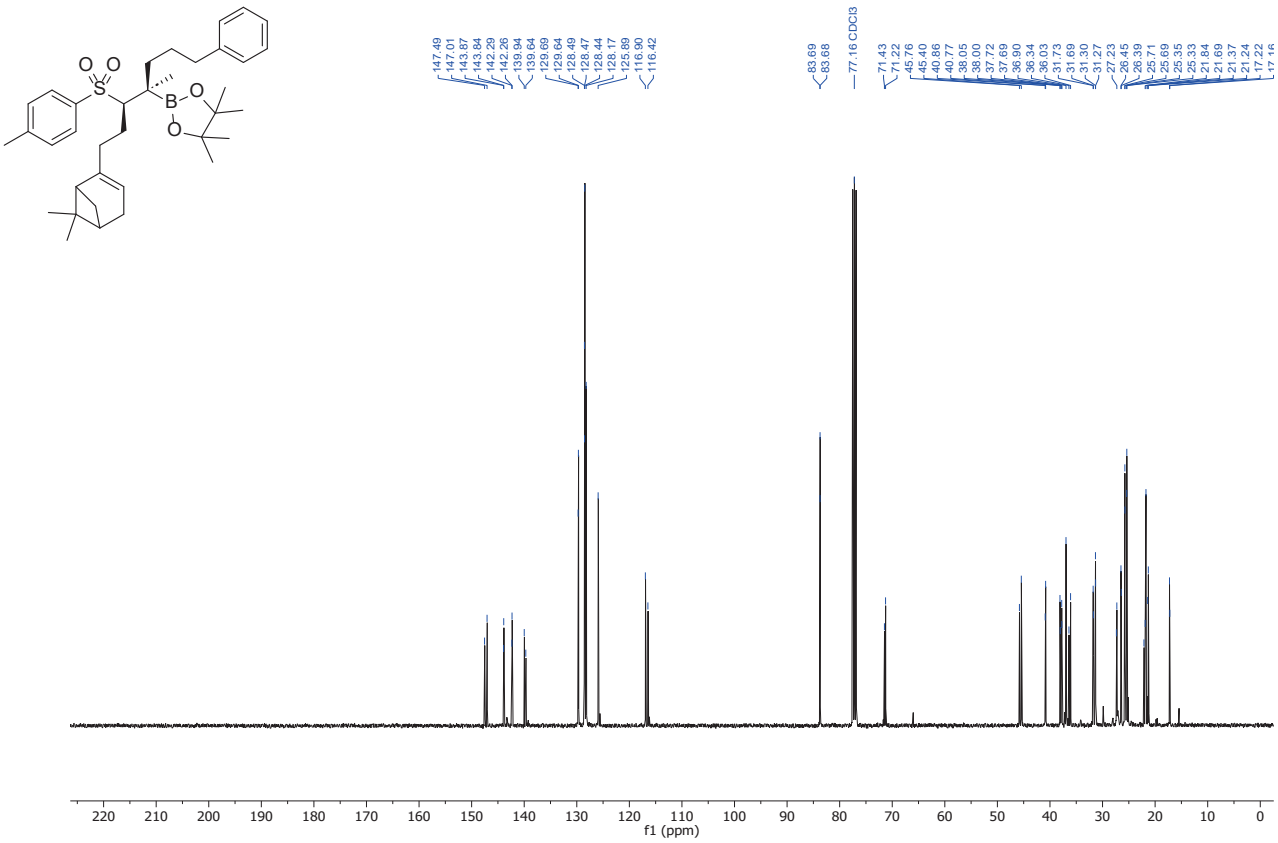


2-((3R,4S)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82)
Major diastereomers



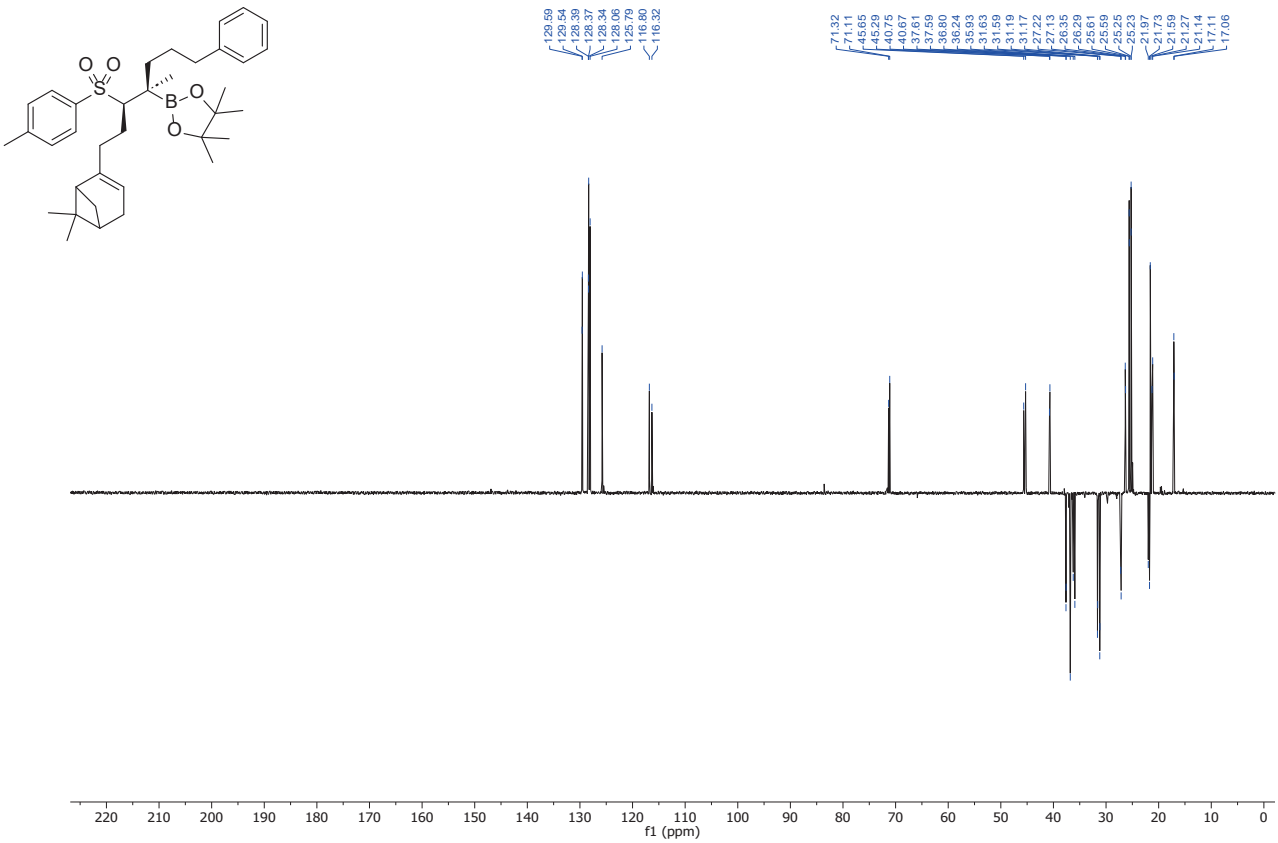
2-((3R,4S)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82)
Major diastereomers

^{13}C NMR (75 MHz, $CDCl_3$)



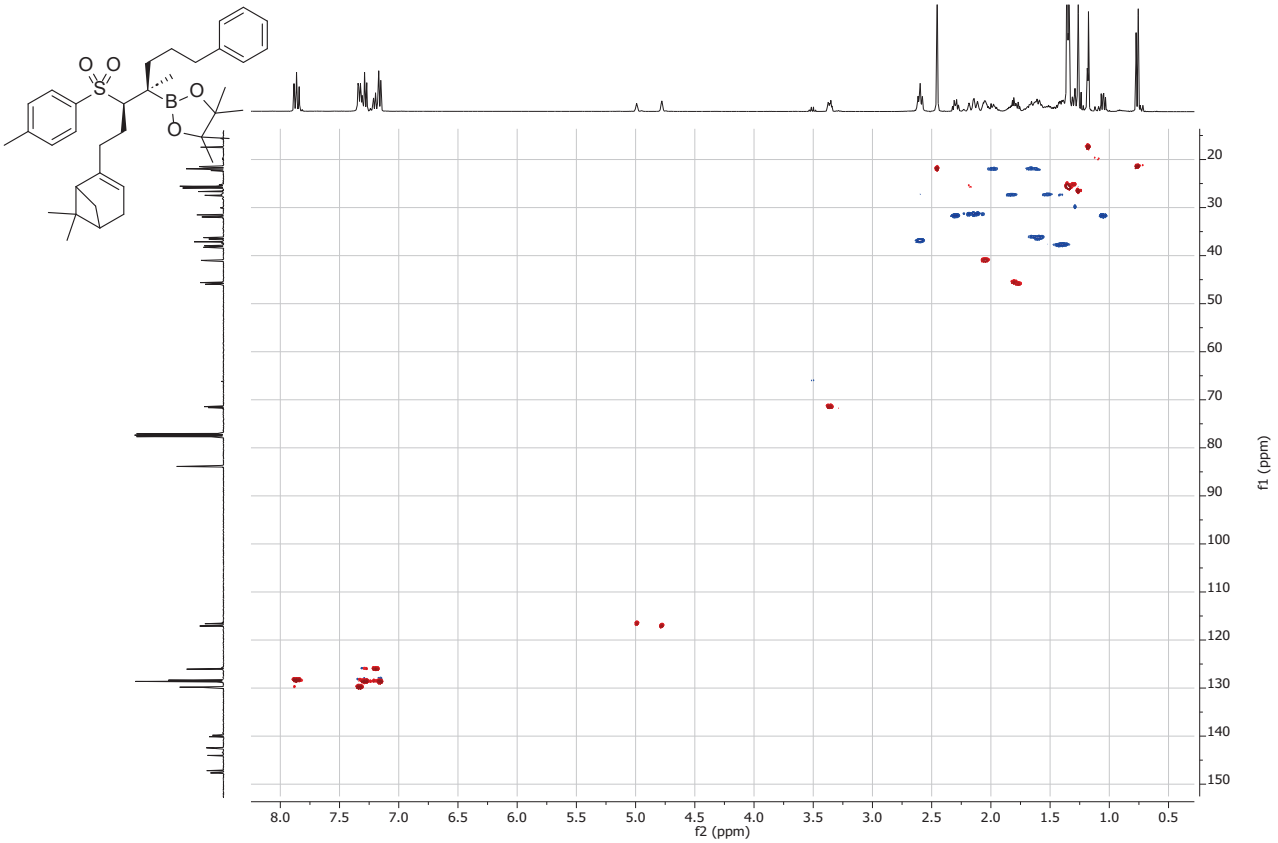
2-((3R,4S)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82)
Major diastereomers

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



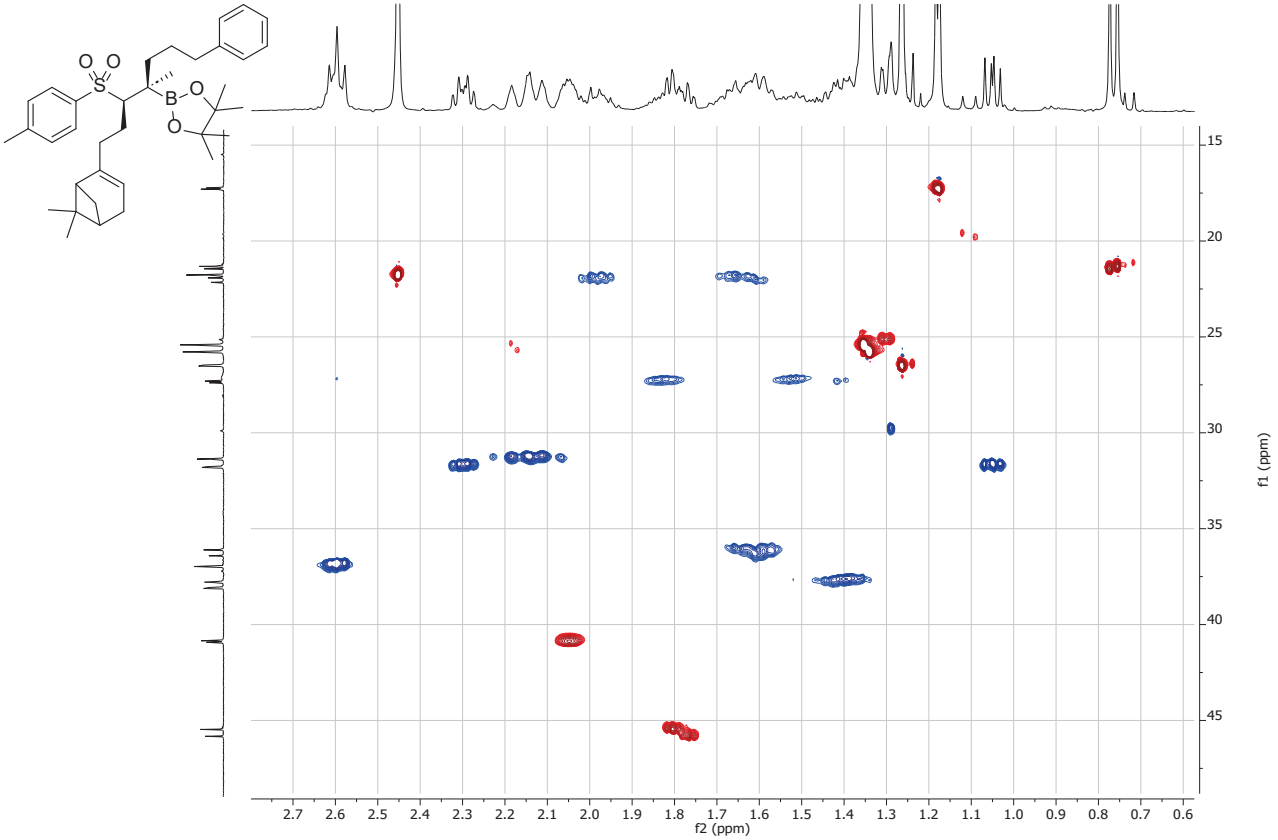
2-((3R,4S)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82)
Major diastereomers

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



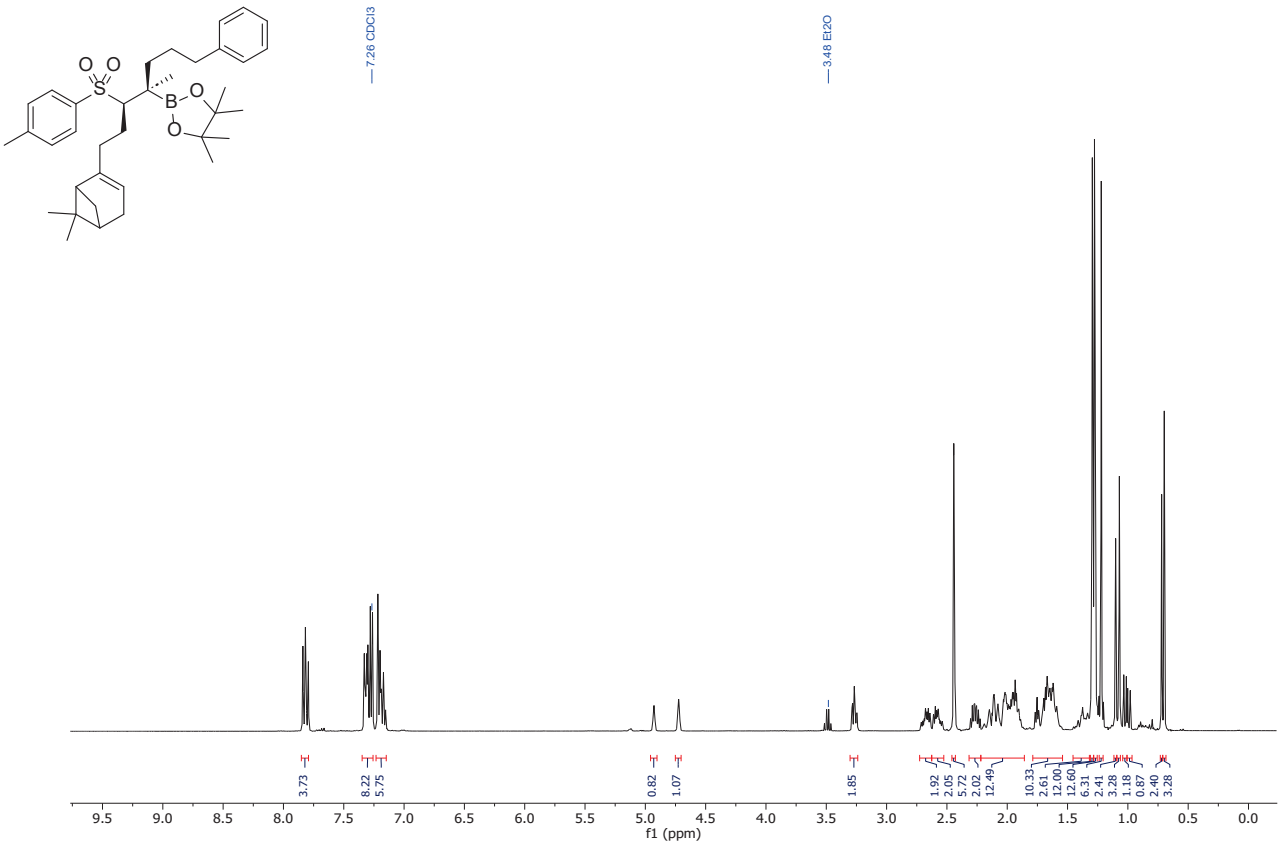
2-((3R,4S)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82)
Major diastereomers

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



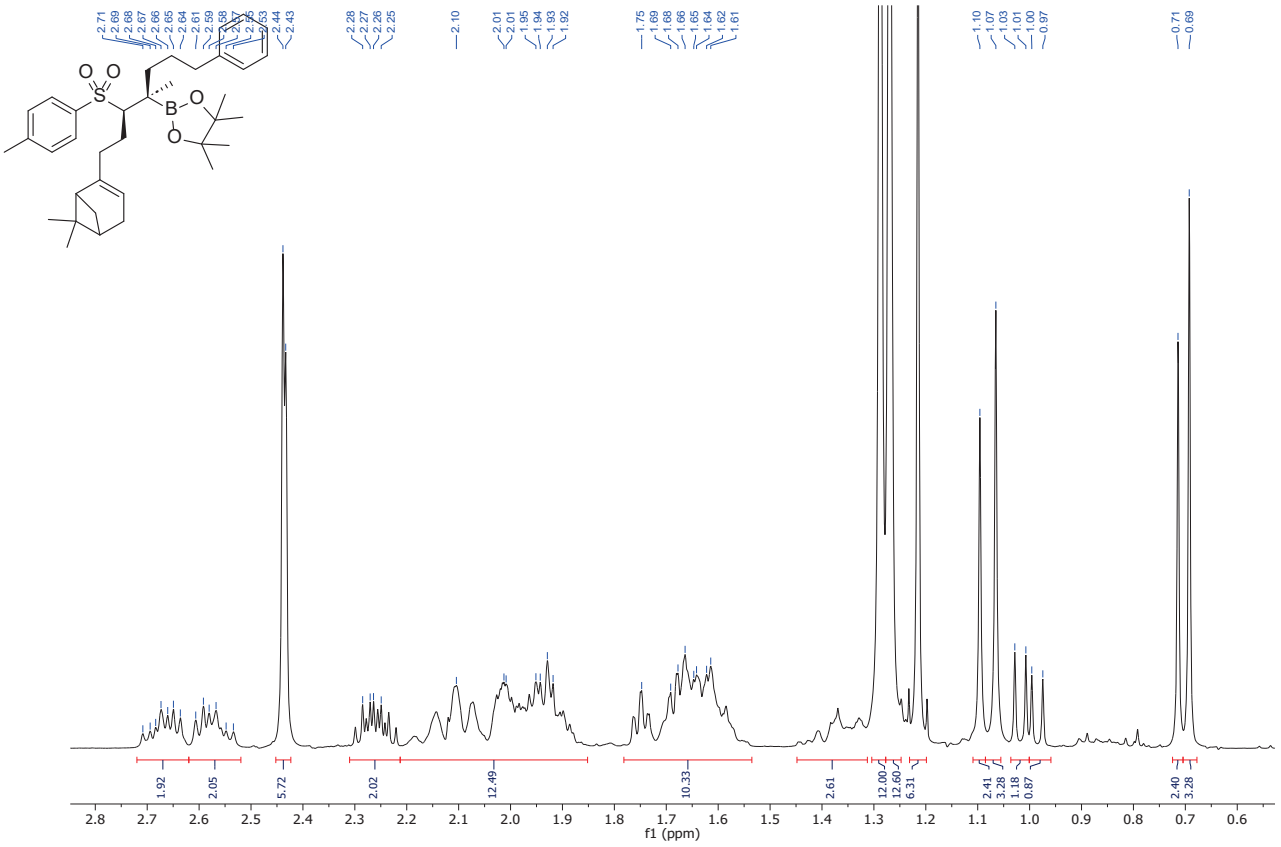
2-((3R,4S)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82)
Minor diastereomers

^{1}H NMR (300 MHz, $CDCl_3$)



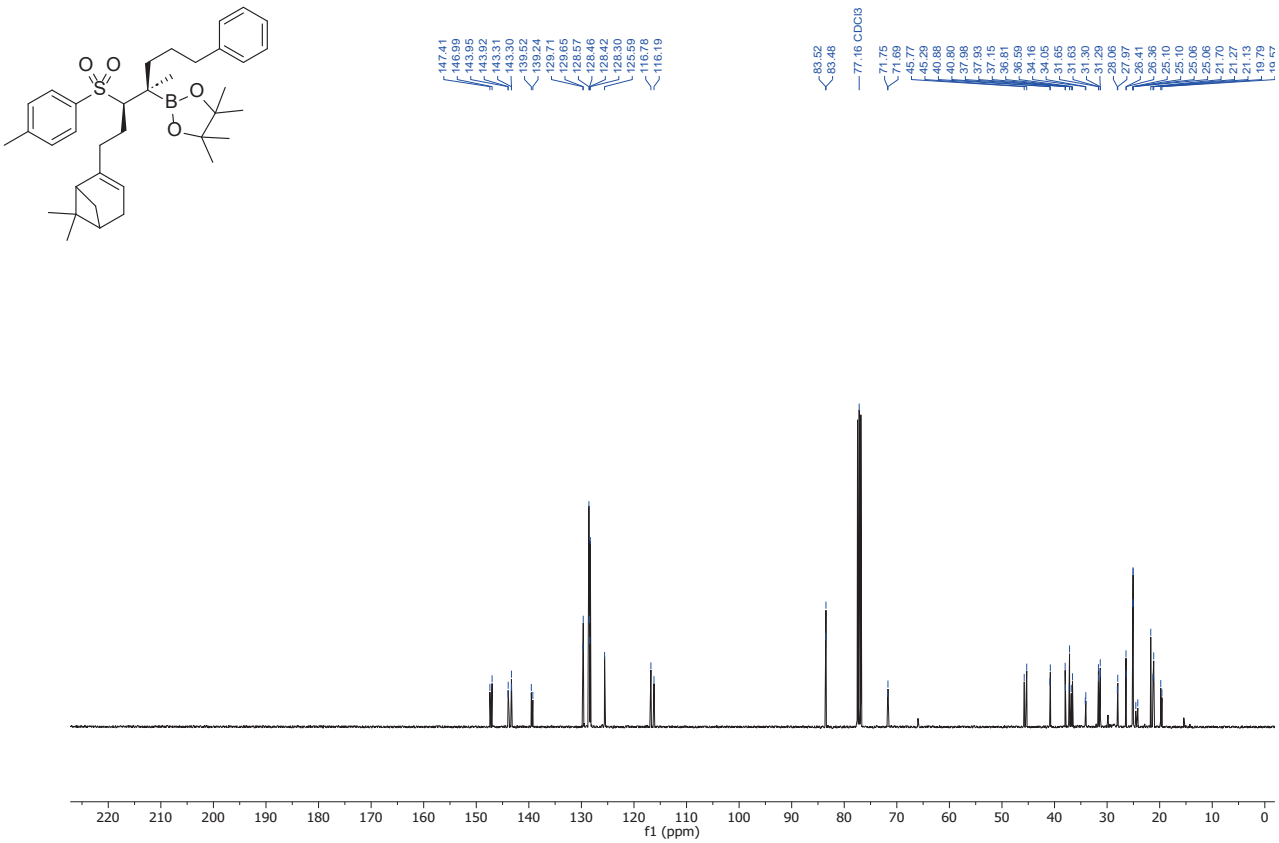
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Minor diastereomers

^{1}H NMR (300 MHz, $CDCl_3$)



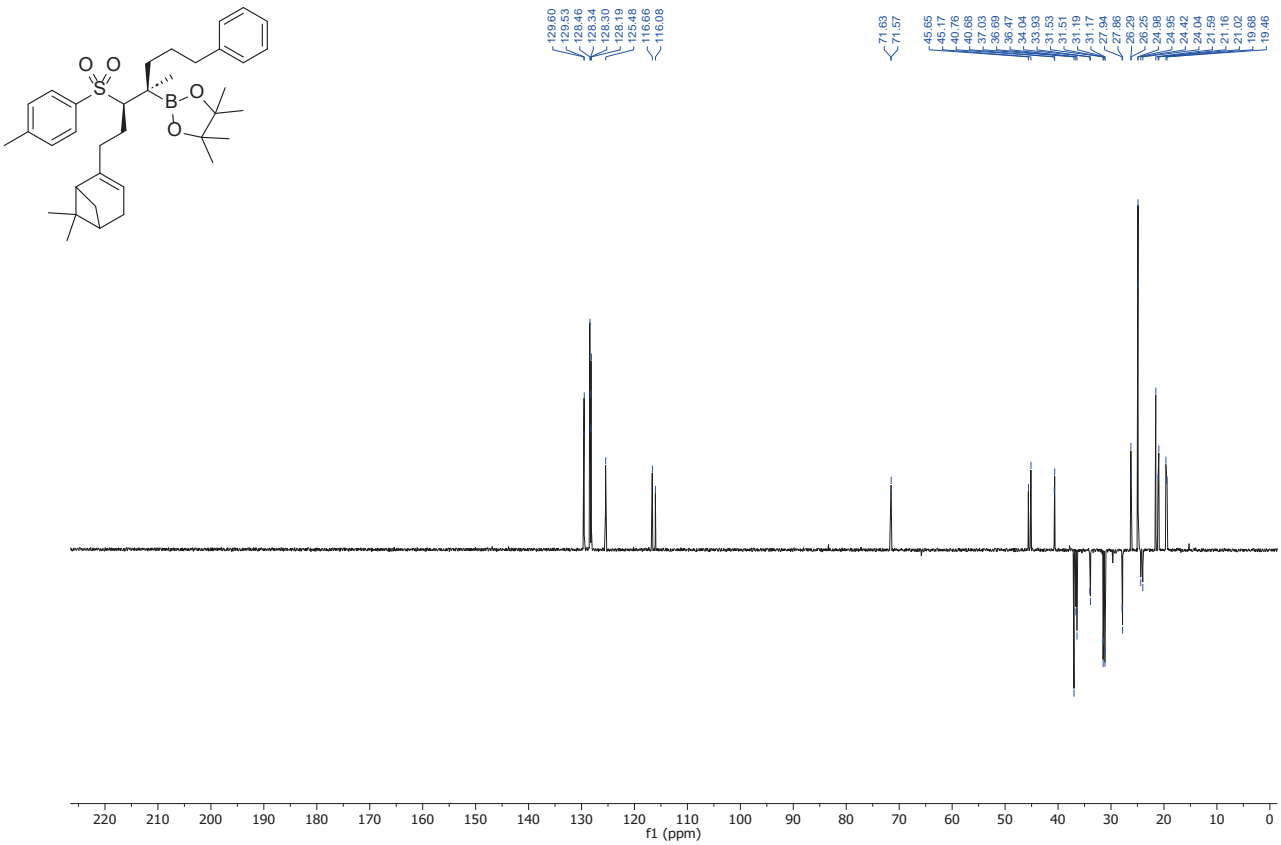
2-((3R,4S)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82)
Minor diastereomers

^{13}C NMR (75 MHz, $CDCl_3$)



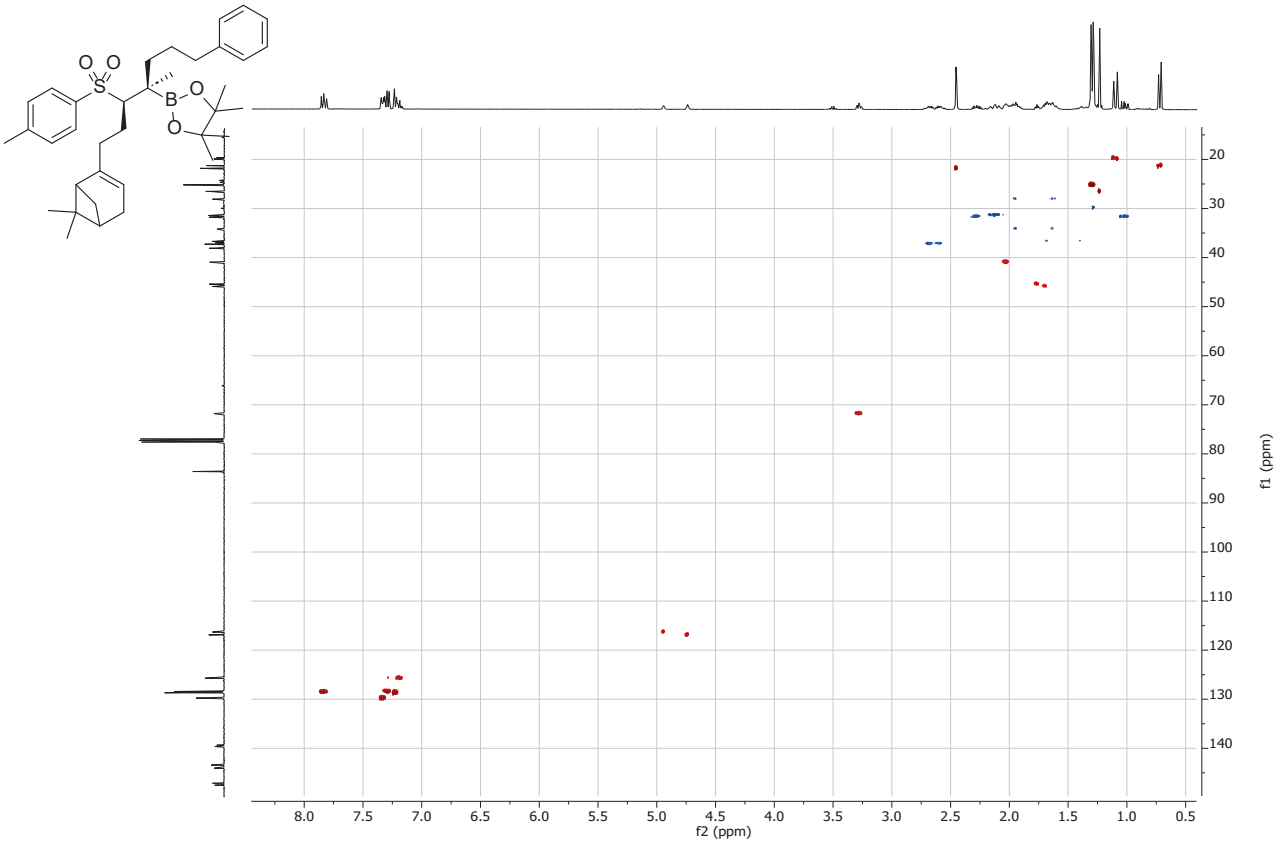
2-((3R,4S)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82)
Minor diastereomers

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



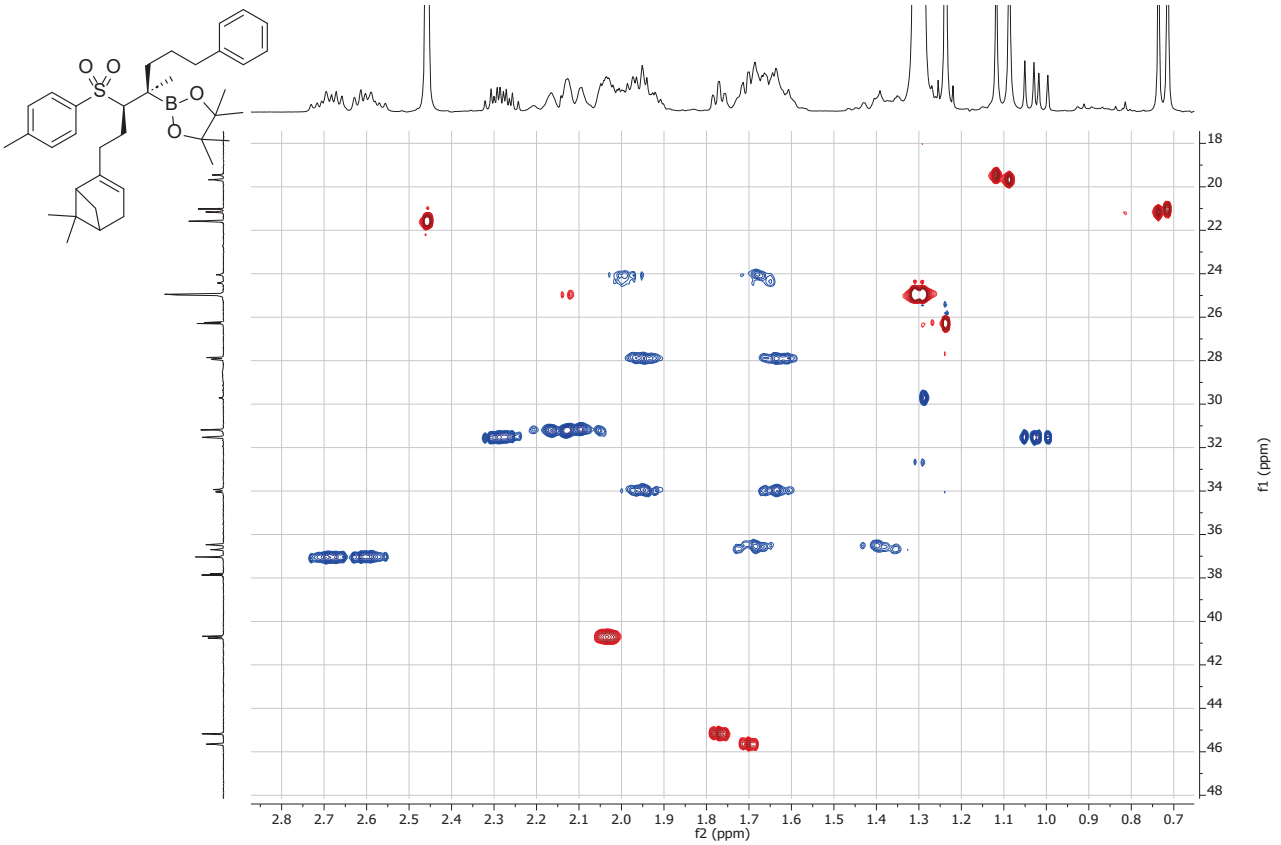
2-((3R,4S)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82)
Minor diastereomers

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



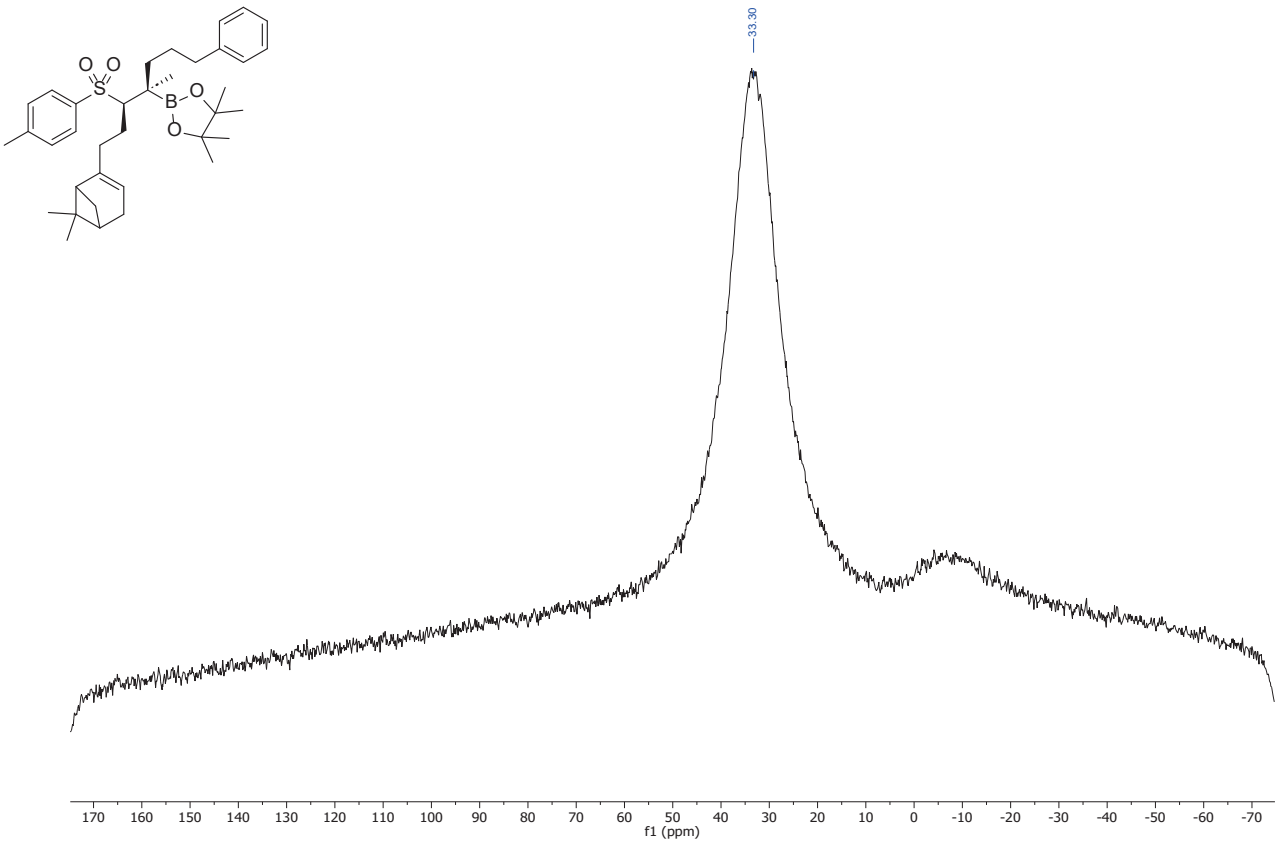
2-((3R,4S)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82)
Minor diastereomers

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



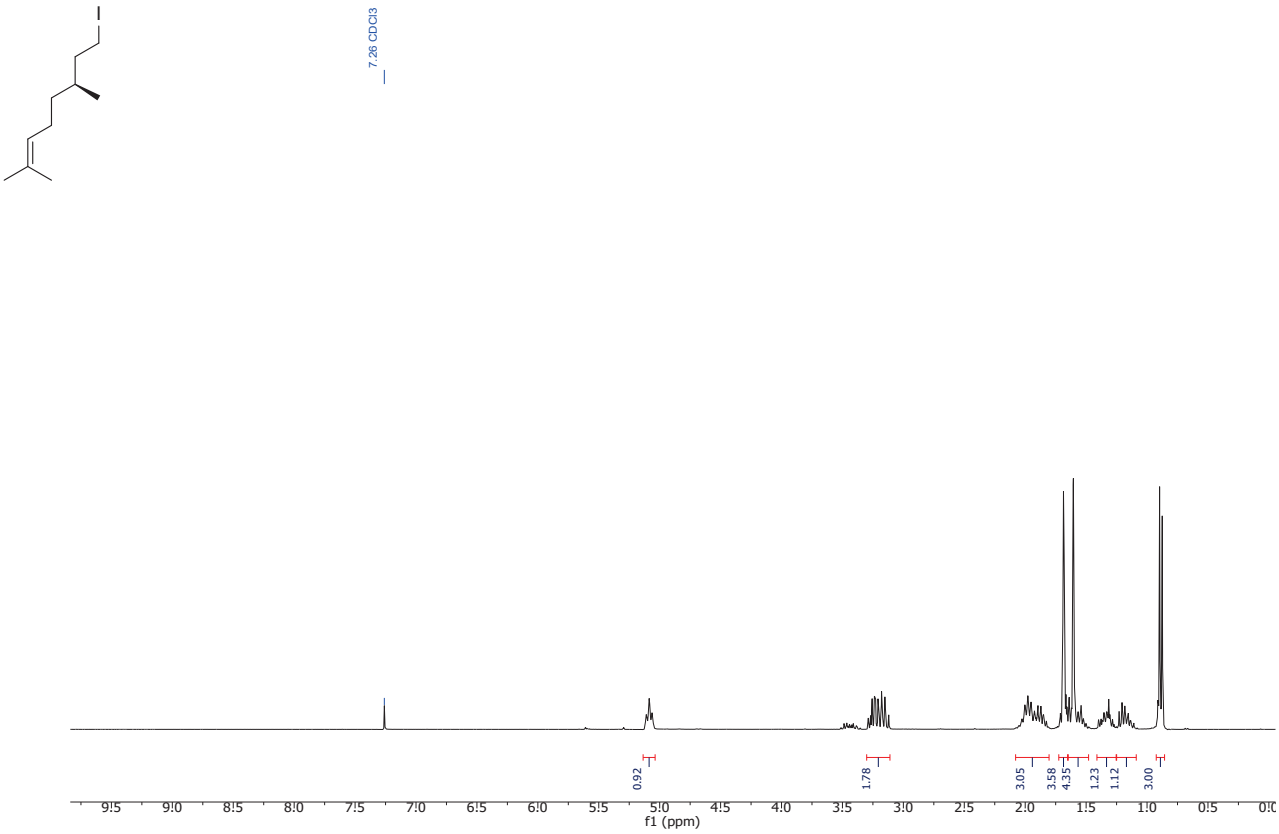
2-((3R,4S)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-7-phenyl-3-tosylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82)

^{11}B NMR (96 MHz, $CDCl_3$)



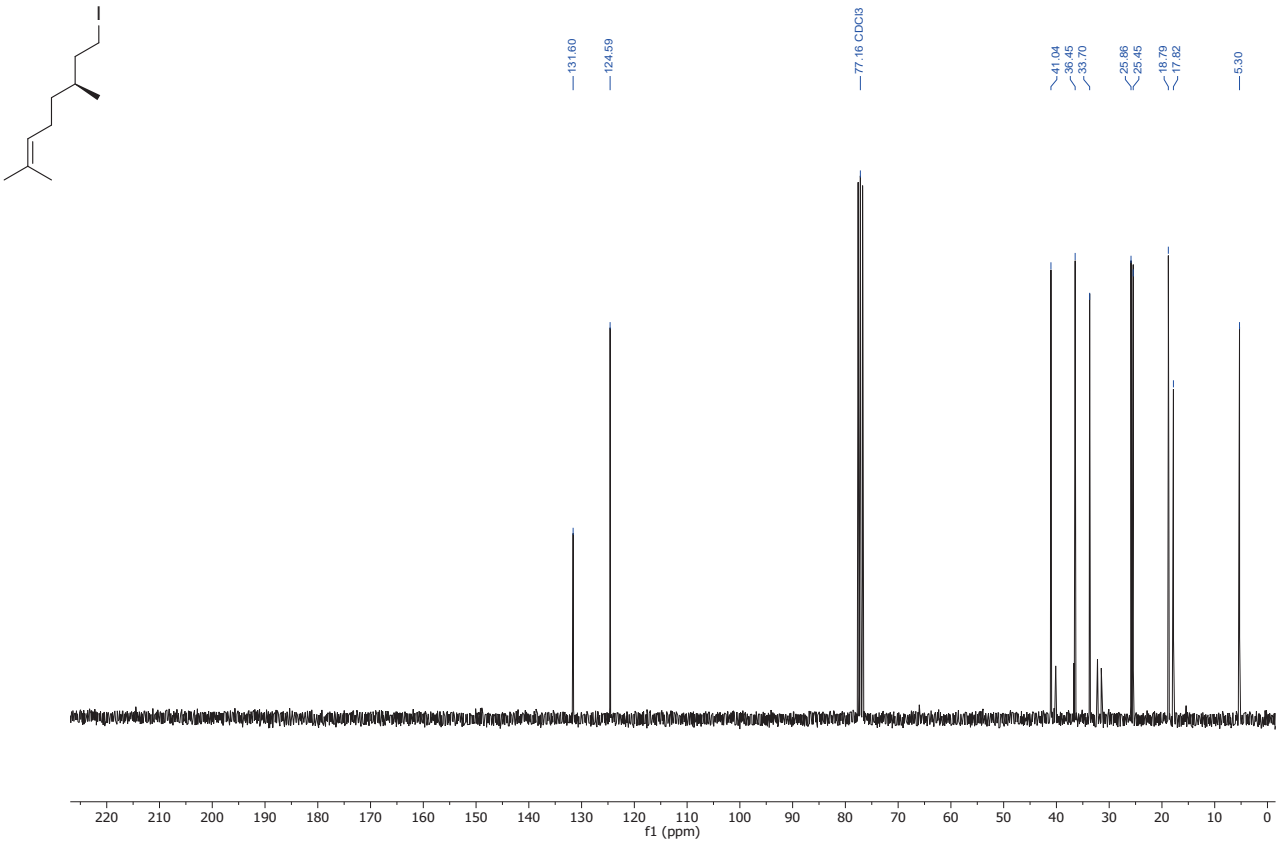
(S)-(+)-citronellyl iodide (108)

^{1}H NMR (300 MHz, $CDCl_3$)



(S)-(+)-citronellyl iodide (108)

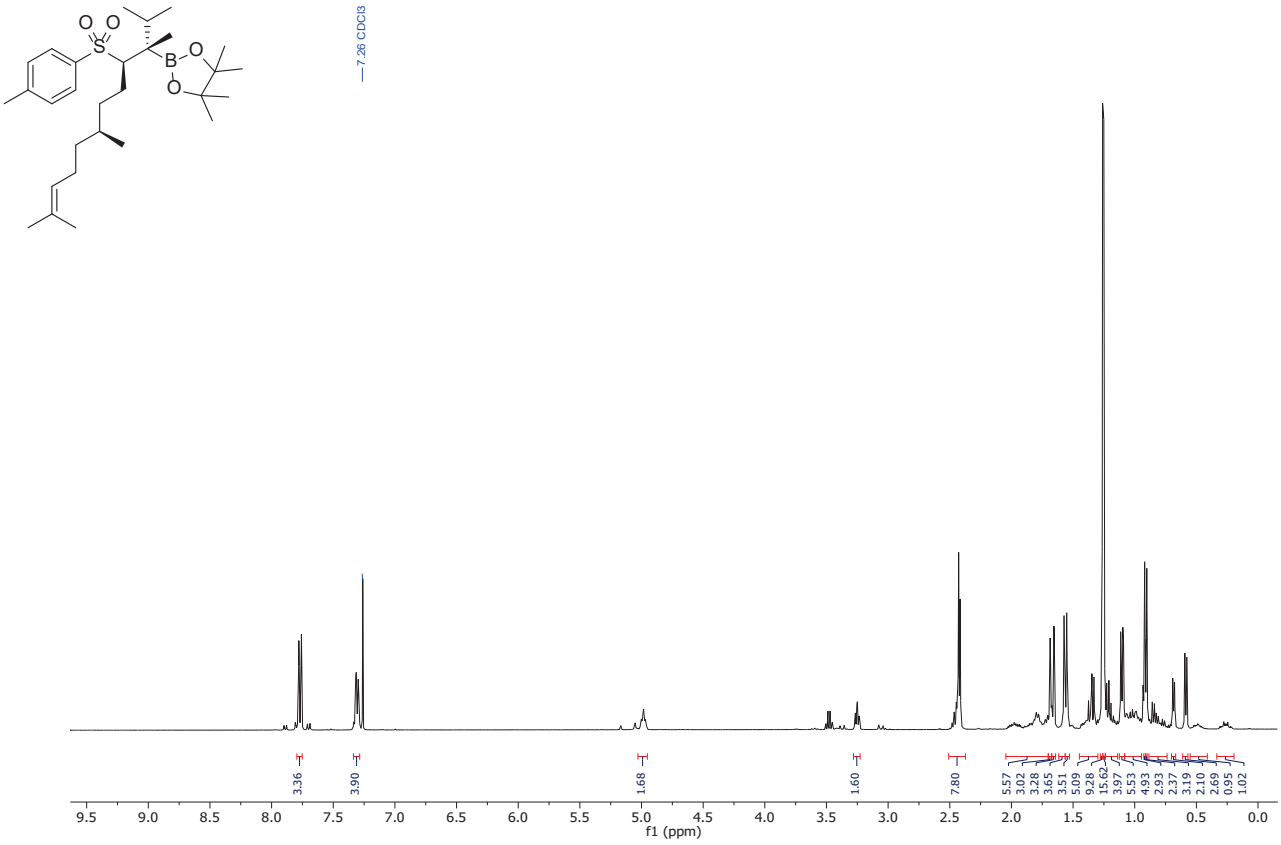
^{13}C NMR (75 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-((3R,4R,7S)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (81)

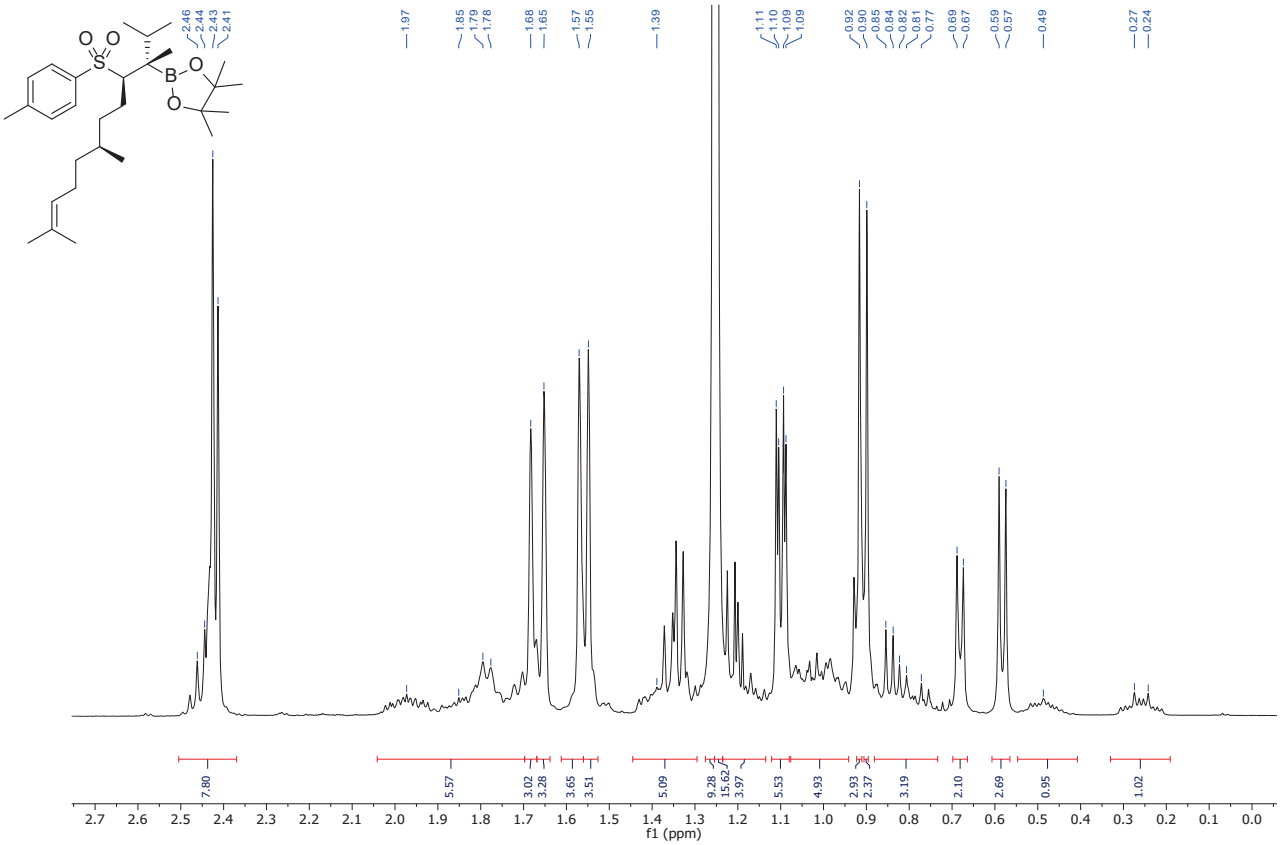
Major diastereomers

^{1}H NMR (300 MHz, $CDCl_3$)



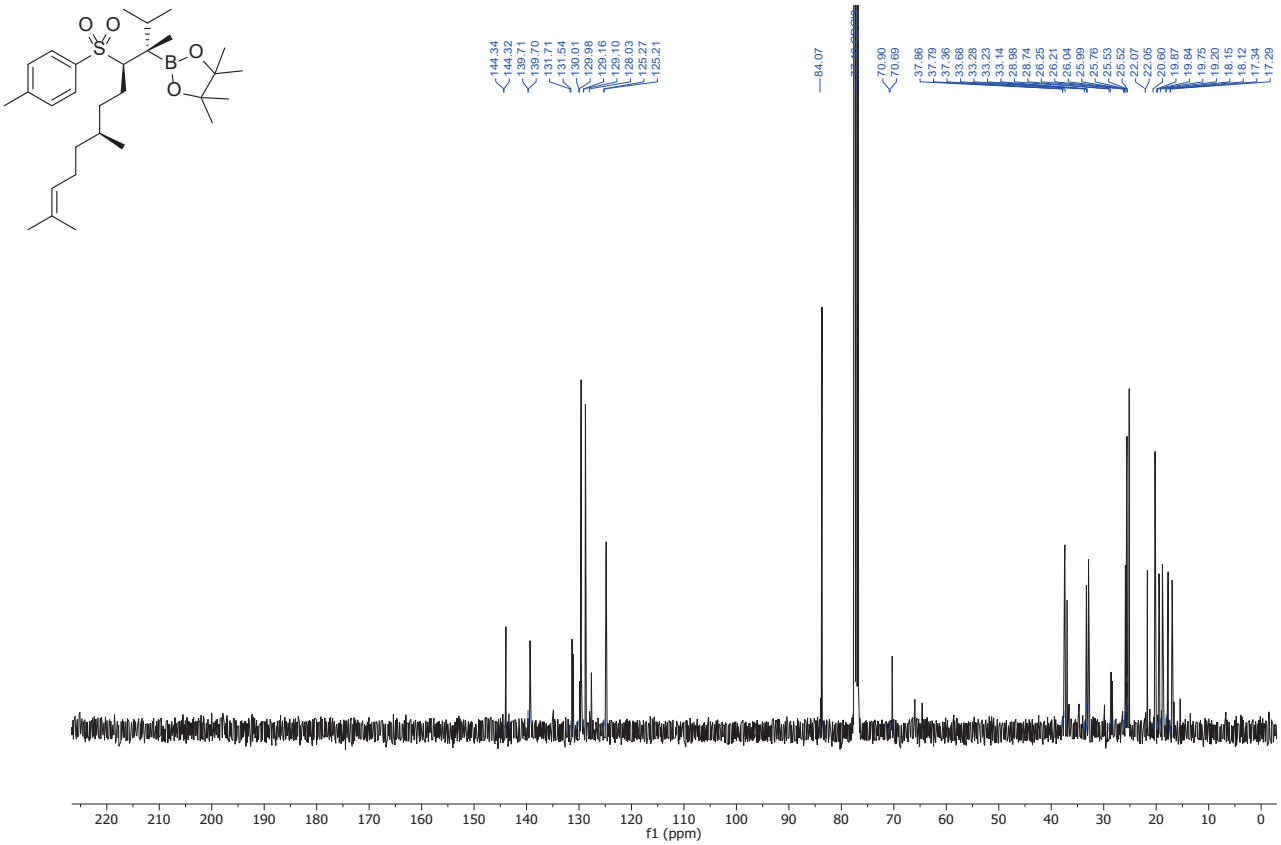
4,4,5,5-tetramethyl-2-((3R,4R,7S)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (81)
Major diastereomers

^{1}H NMR (300 MHz, $CDCl_3$)



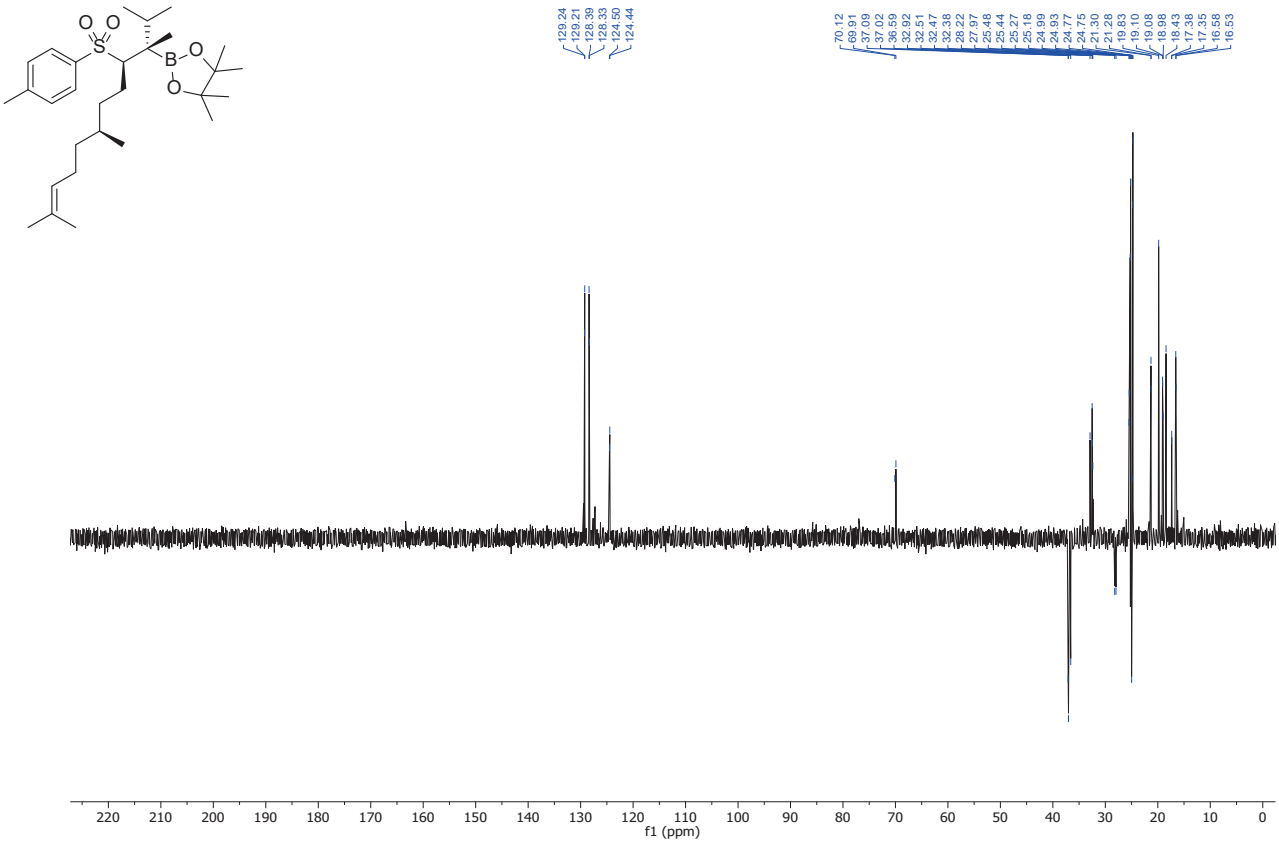
4,4,5,5-tetramethyl-2-((3R,4R,7S)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (81)
Major diastereomers

^{13}C NMR (75 MHz, $CDCl_3$)



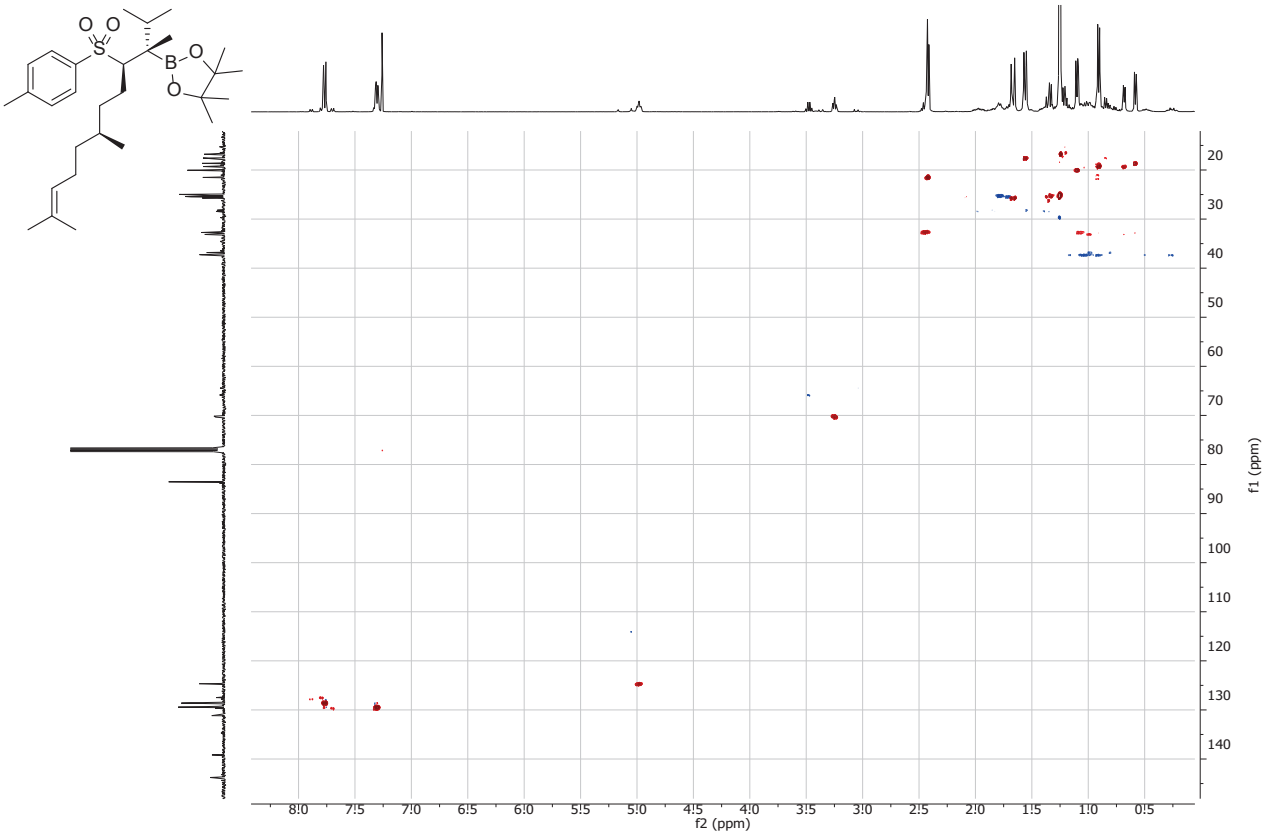
4,4,5,5-tetramethyl-2-((3R,4R,7S)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (81)
Major diastereomers

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



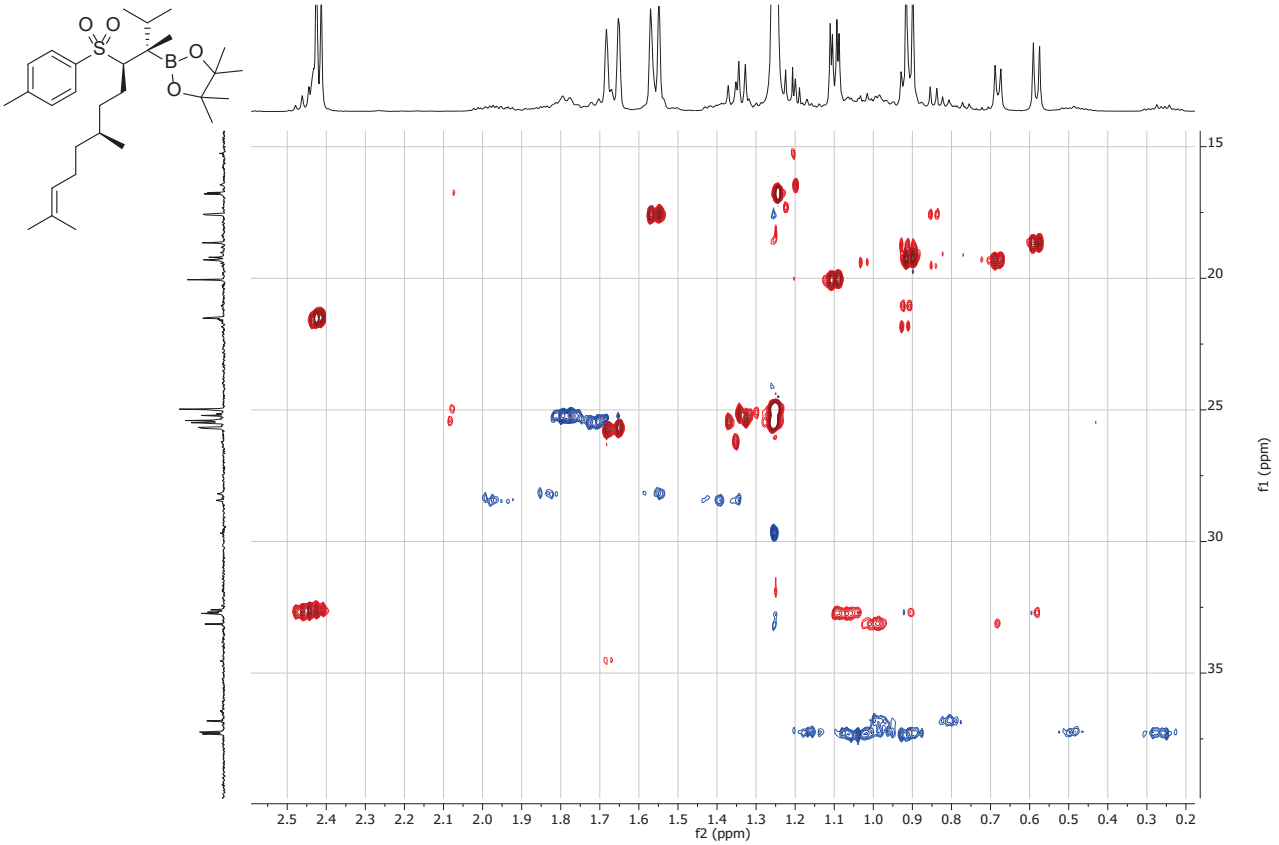
4,4,5,5-tetramethyl-2-((3R,4R,7S)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (81)
Major diastereomers

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



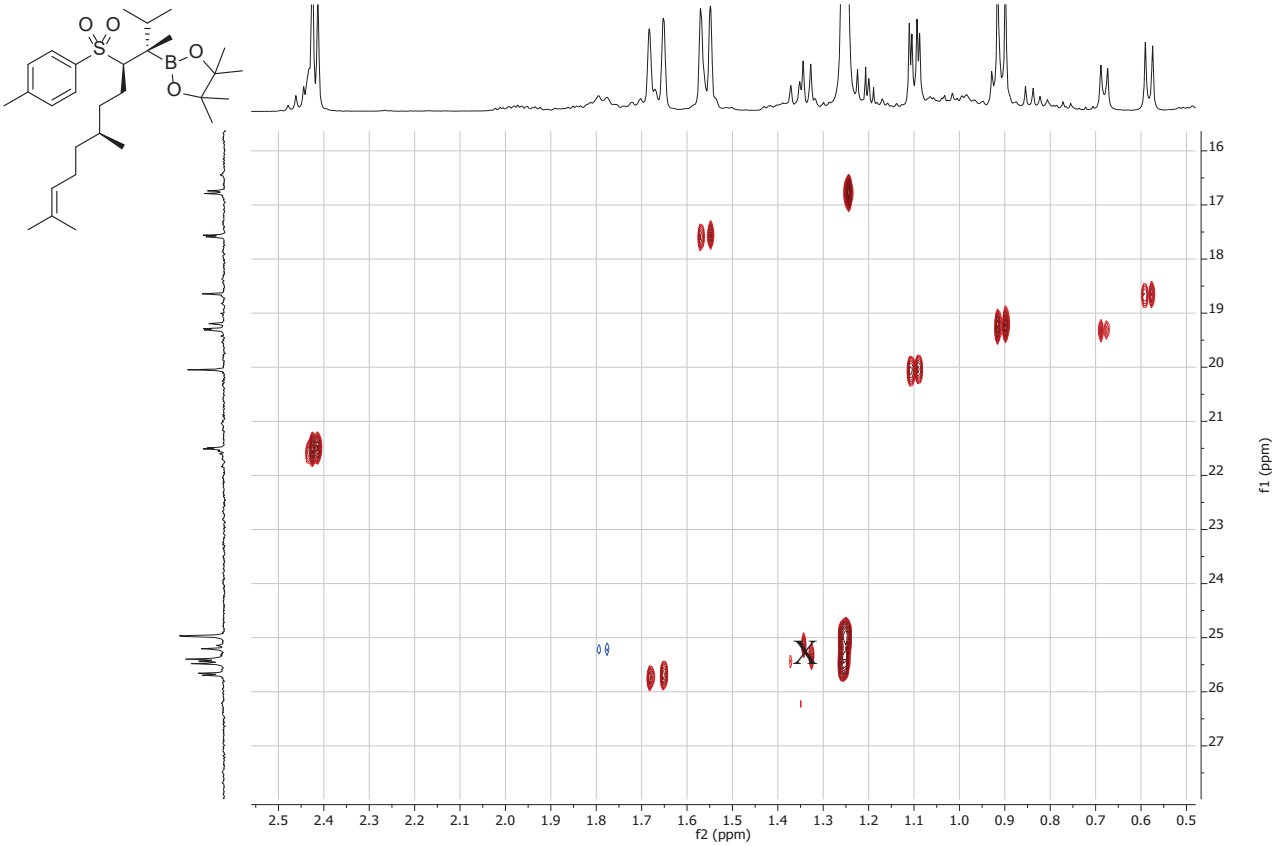
4,4,5,5-tetramethyl-2-((3R,4R,7S)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (81)
Major diastereomers

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-((3R,4R,7S)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (81)
Major diastereomers

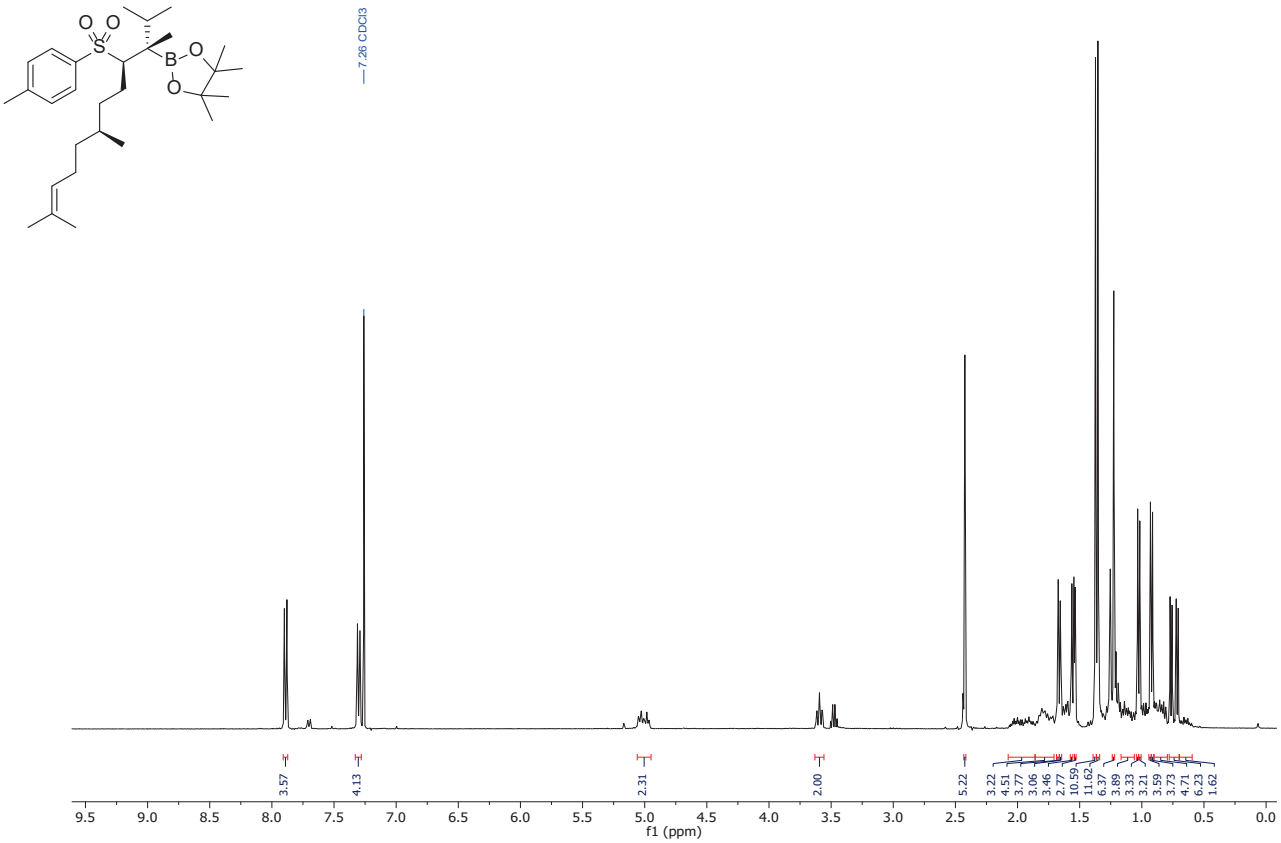
^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-((3R,4R,7S)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (81)

Minor diastereomers

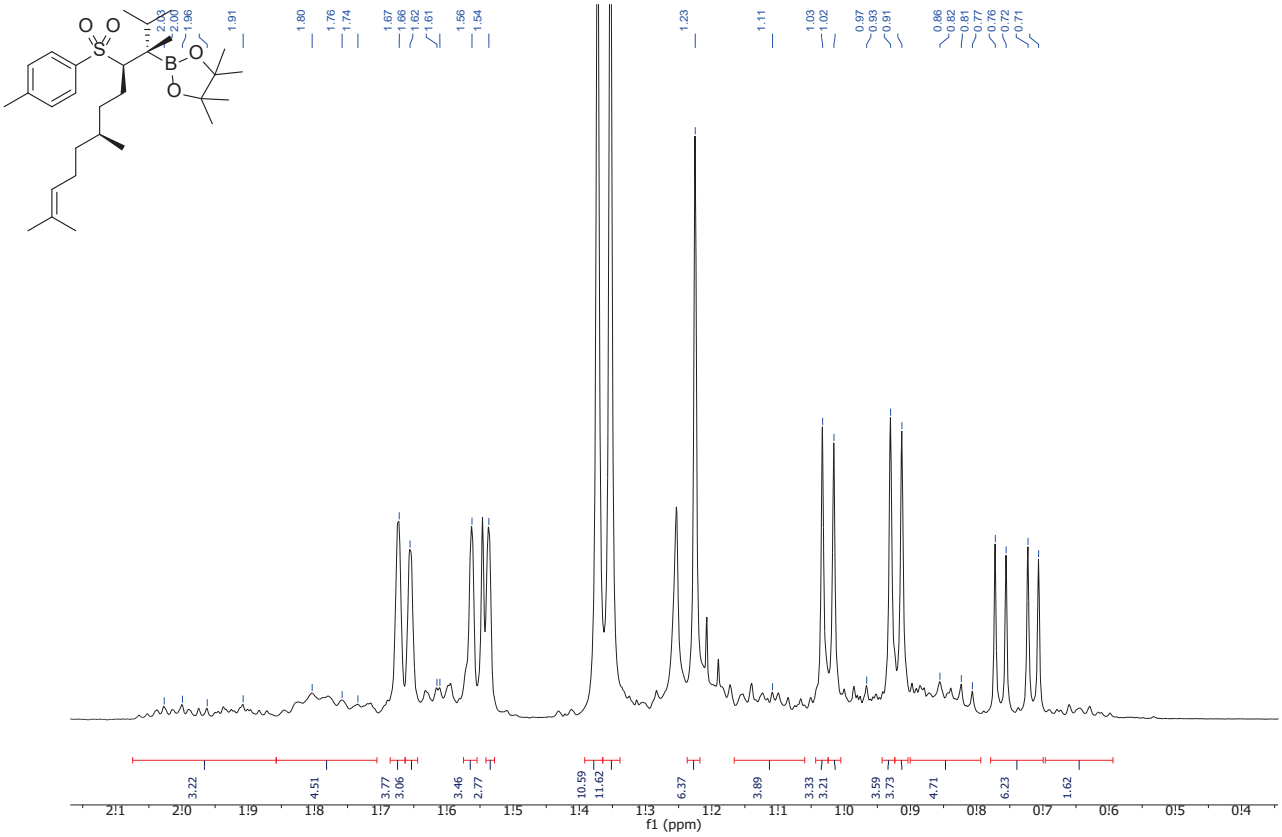
^{1}H NMR (300 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-((3R,4R,7S)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (81)

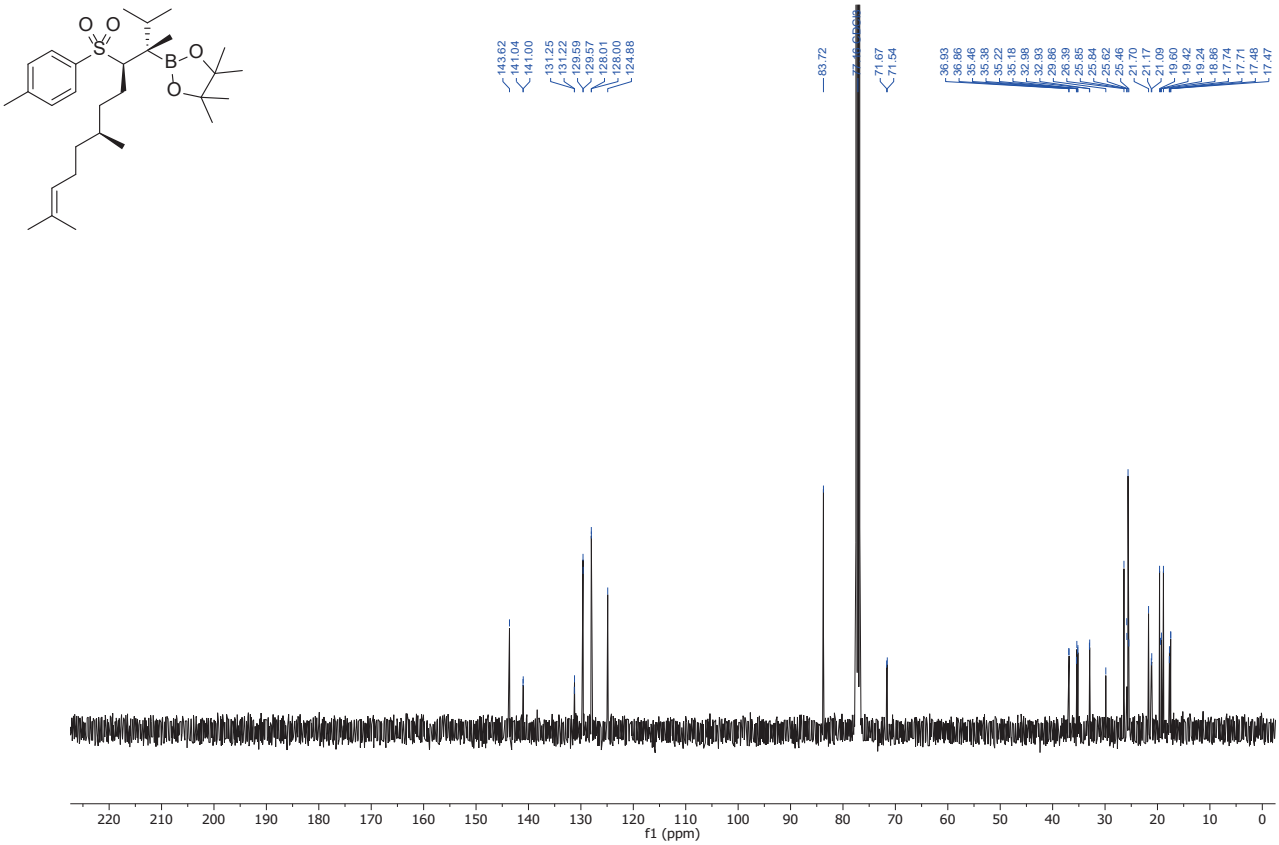
Minor diastereomers

^{1}H NMR (300 MHz, $CDCl_3$)



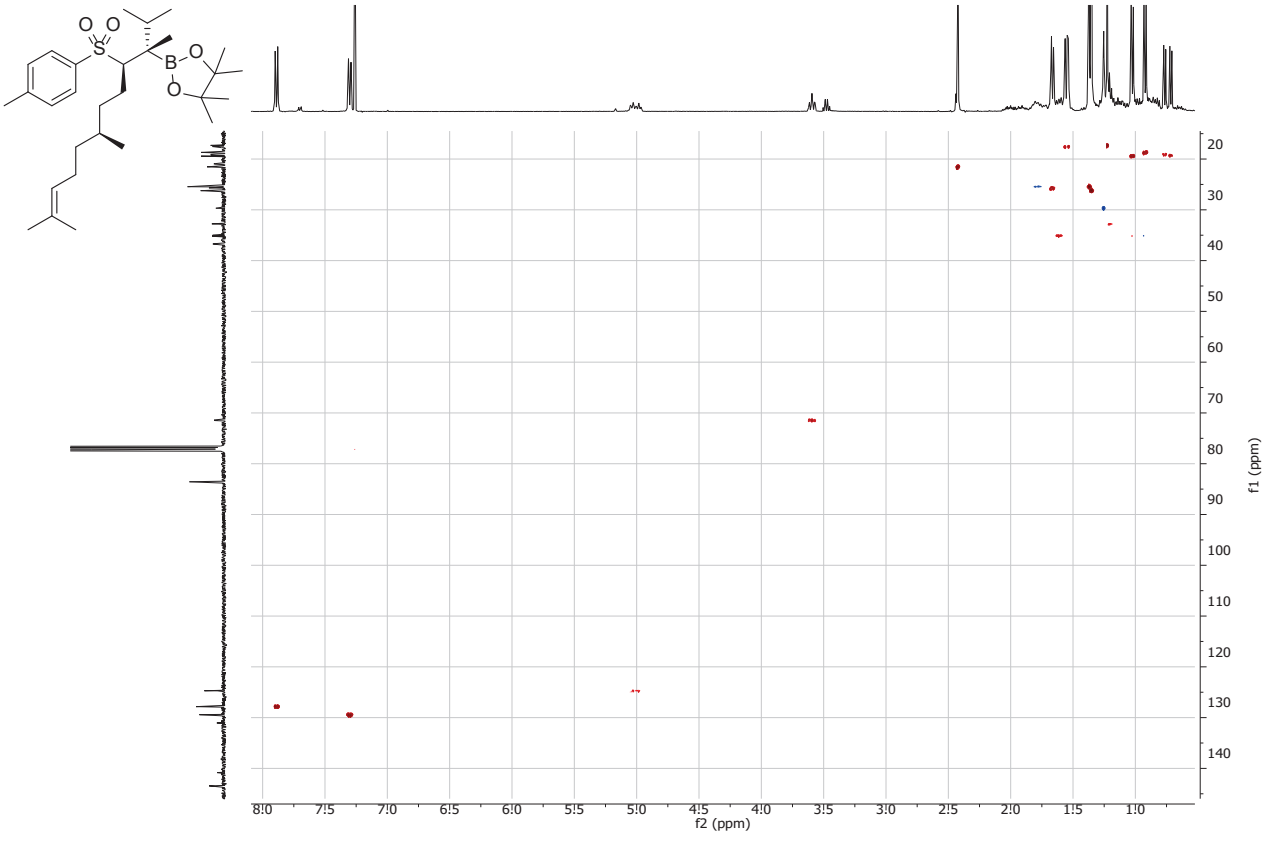
4,4,5,5-tetramethyl-2-((3R,4R,7S)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (81)
Minor diastereomers

^{13}C NMR (75 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-((3R,4R,7S)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (81)
Minor diastereomers

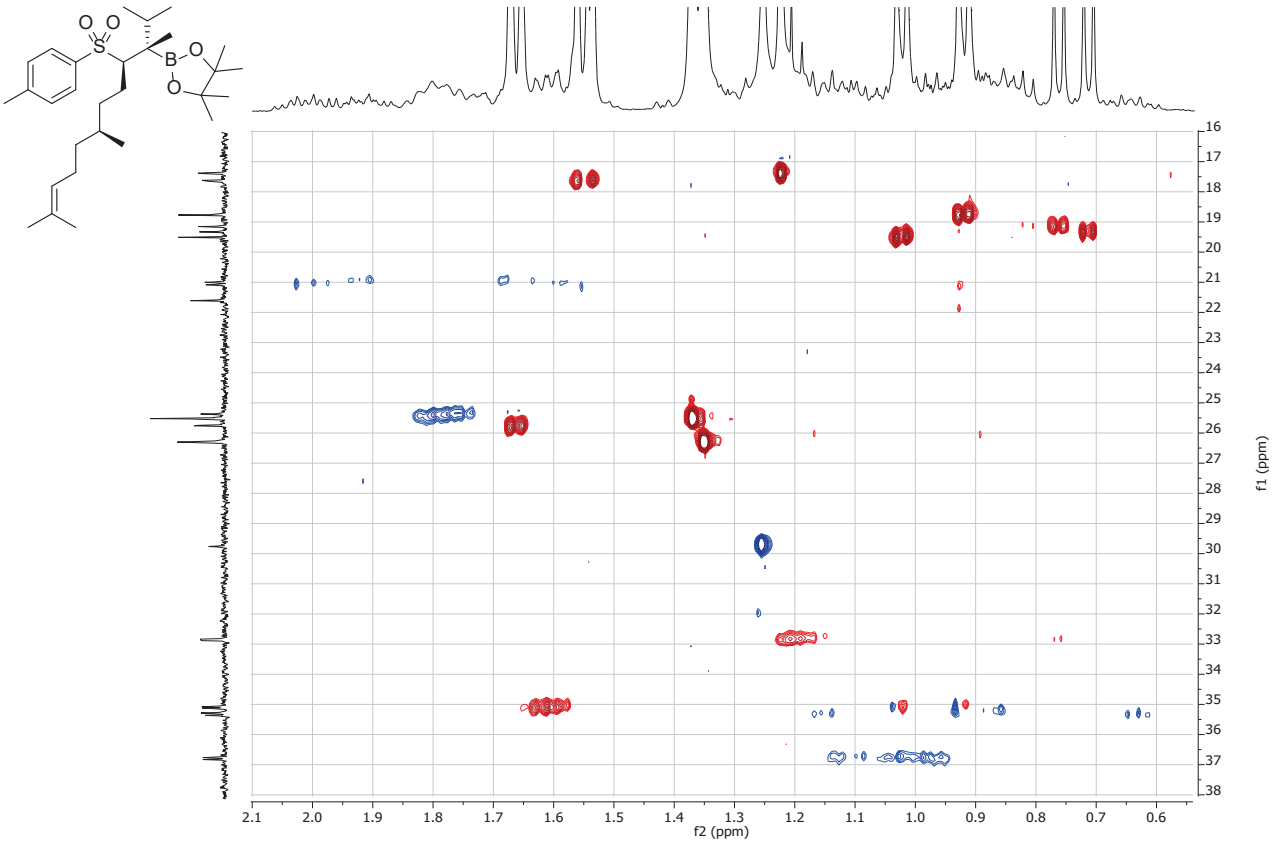
^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-((3R,4R,7S)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (81)

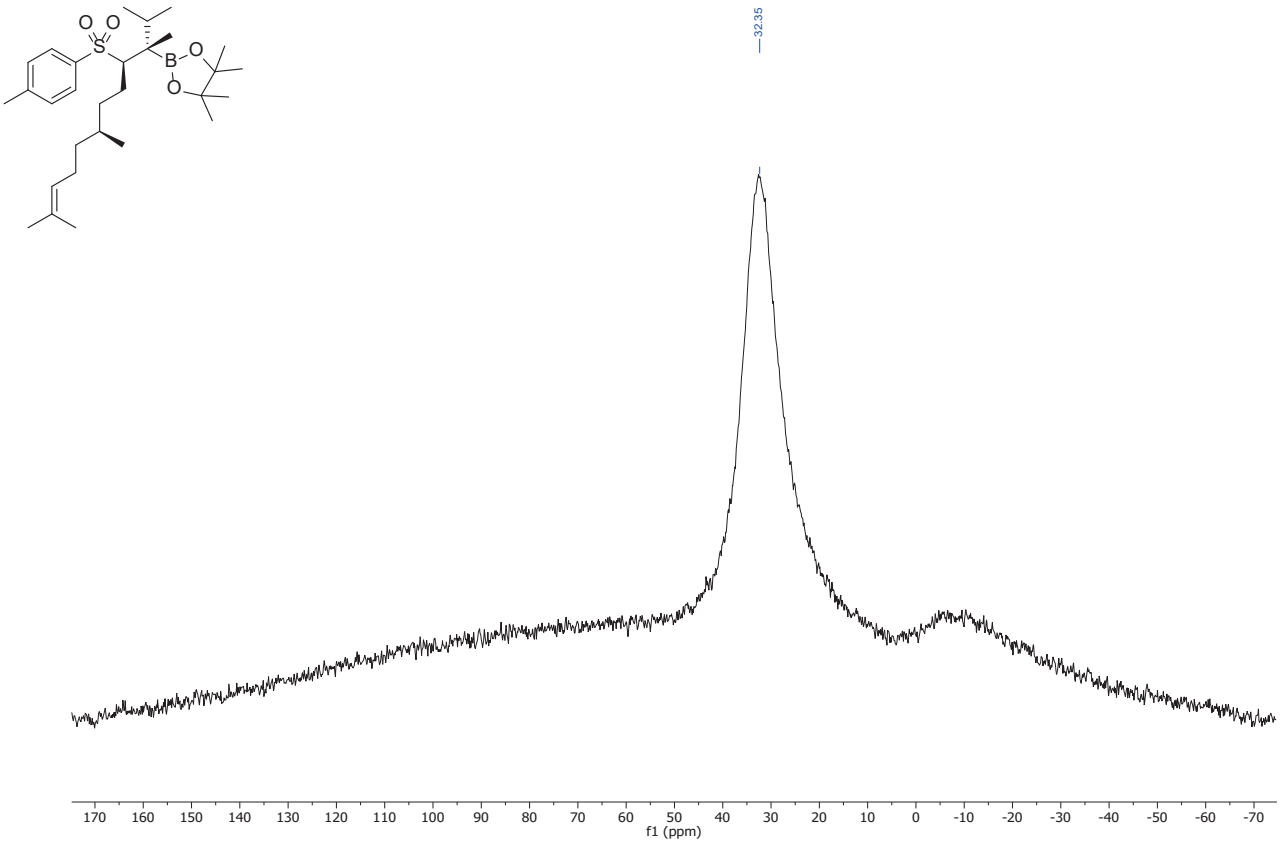
Minor diastereomers

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



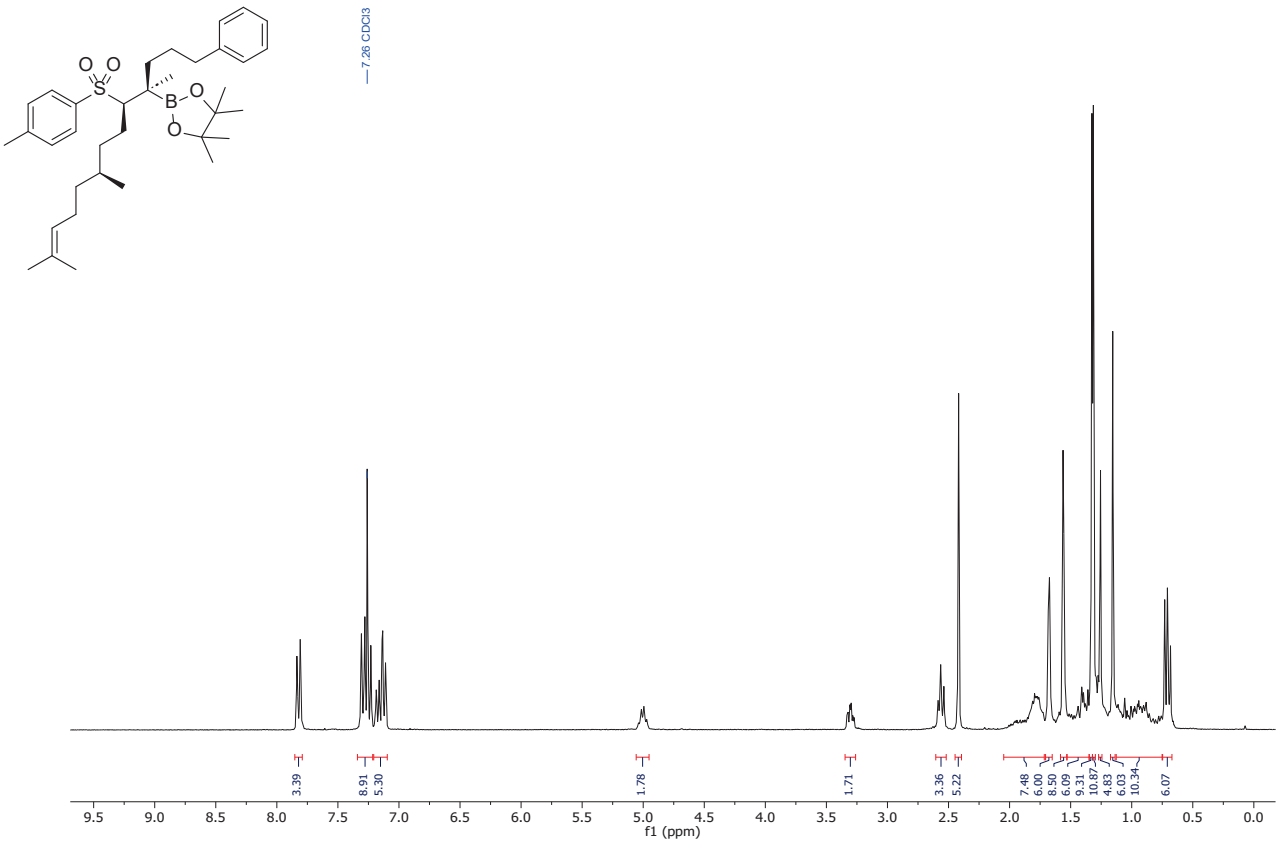
4,4,5,5-tetramethyl-2-((3R,4R,7S)-2,3,7,11-tetramethyl-4-tosyldodec-10-en-3-yl)-1,3,2-dioxaborolane (81)

^{11}B NMR (96 MHz, $CDCl_3$)



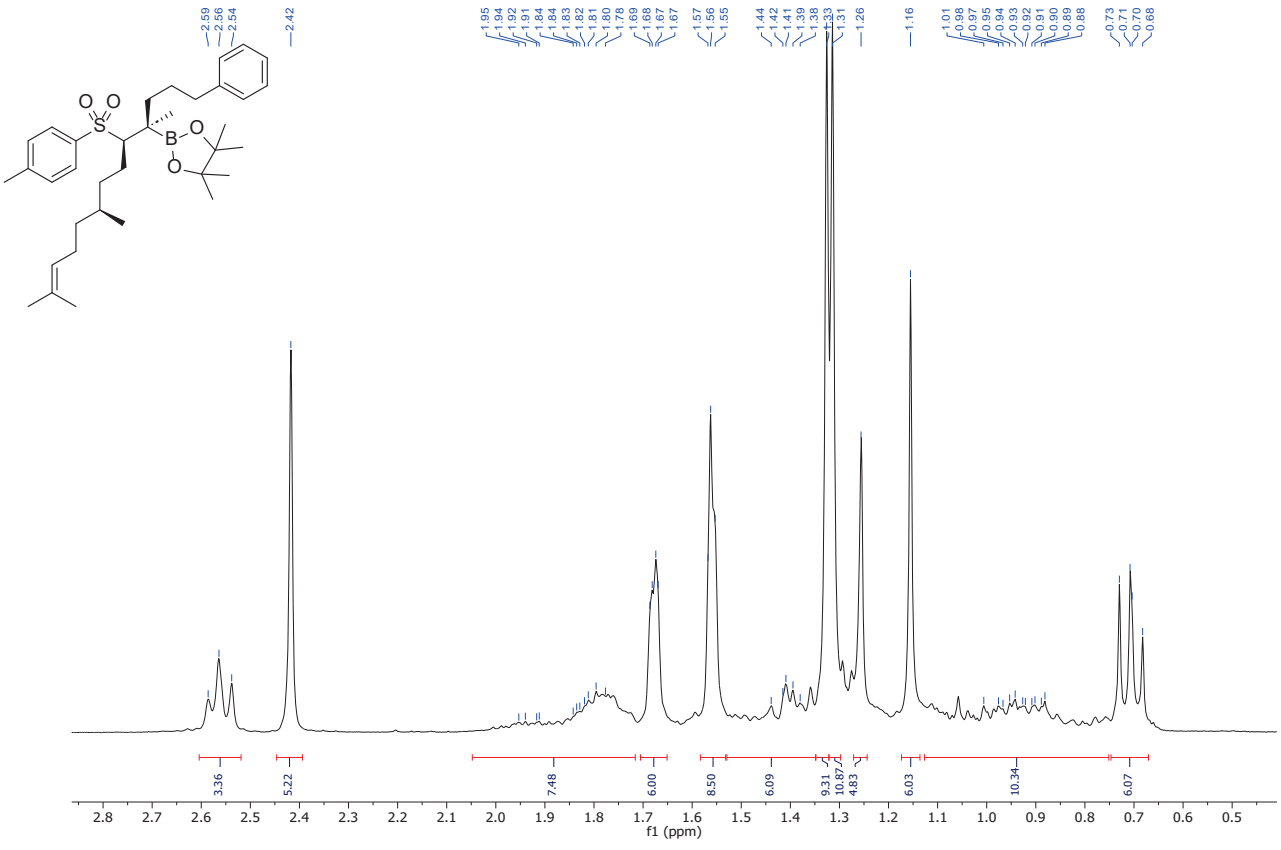
4,4,5,5-tetramethyl-2-((4S,5R,8S)-4,8,12-trimethyl-1-phenyl-5-tosyltridec-11-en-4-yl)-1,3,2-dioxaborolane (80)
Major diastereomers

^{1}H NMR (300 MHz, $CDCl_3$)



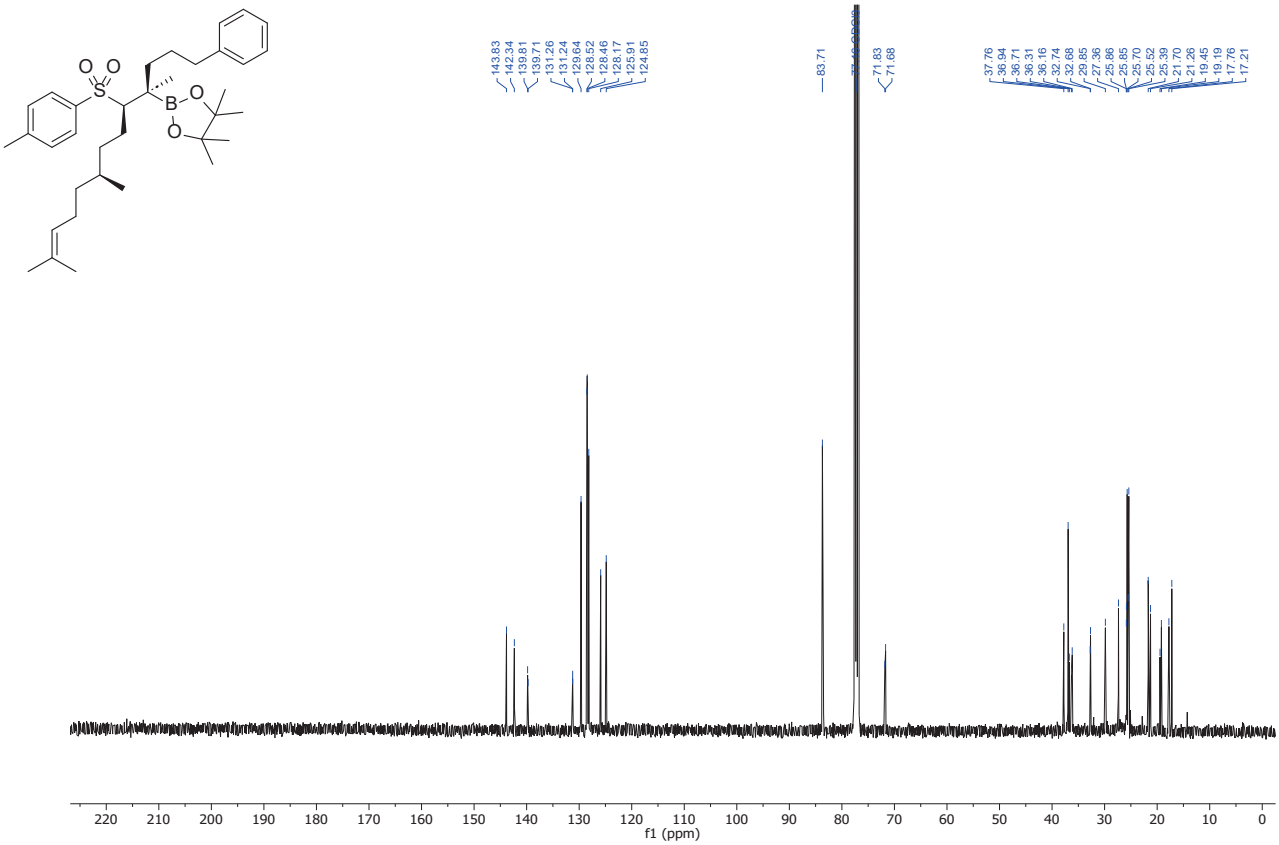
4,4,5,5-tetramethyl-2-((4S,5R,8S)-4,8,12-trimethyl-1-phenyl-5-tosyltridec-11-en-4-yl)-1,3,2-dioxaborolane (80)
Major diastereomers

^{1}H NMR (300 MHz, $CDCl_3$)



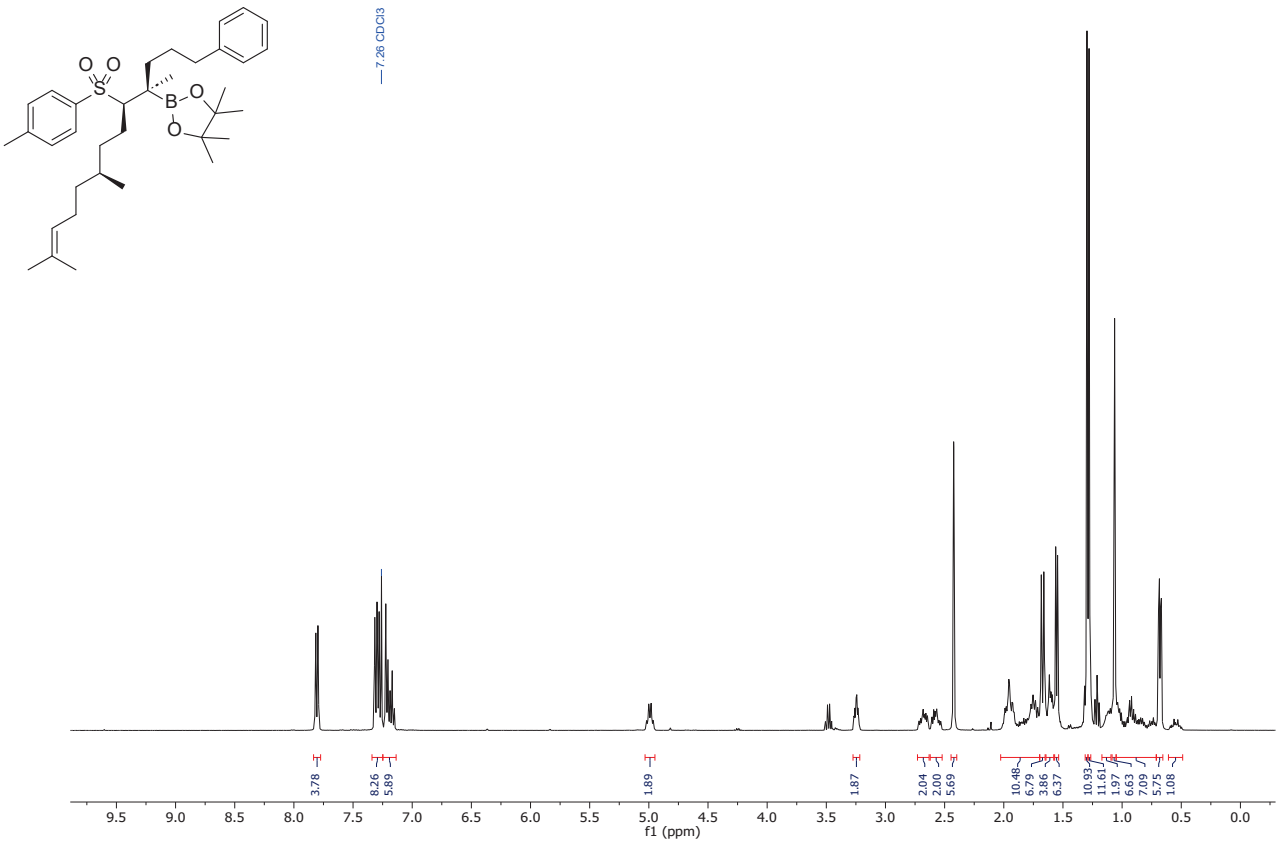
4,4,5,5-tetramethyl-2-((4S,5R,8S)-4,8,12-trimethyl-1-phenyl-5-tosyltridec-11-en-4-yl)-1,3,2-dioxaborolane (80)
Major diastereomers

^{13}C NMR (75 MHz, $CDCl_3$)



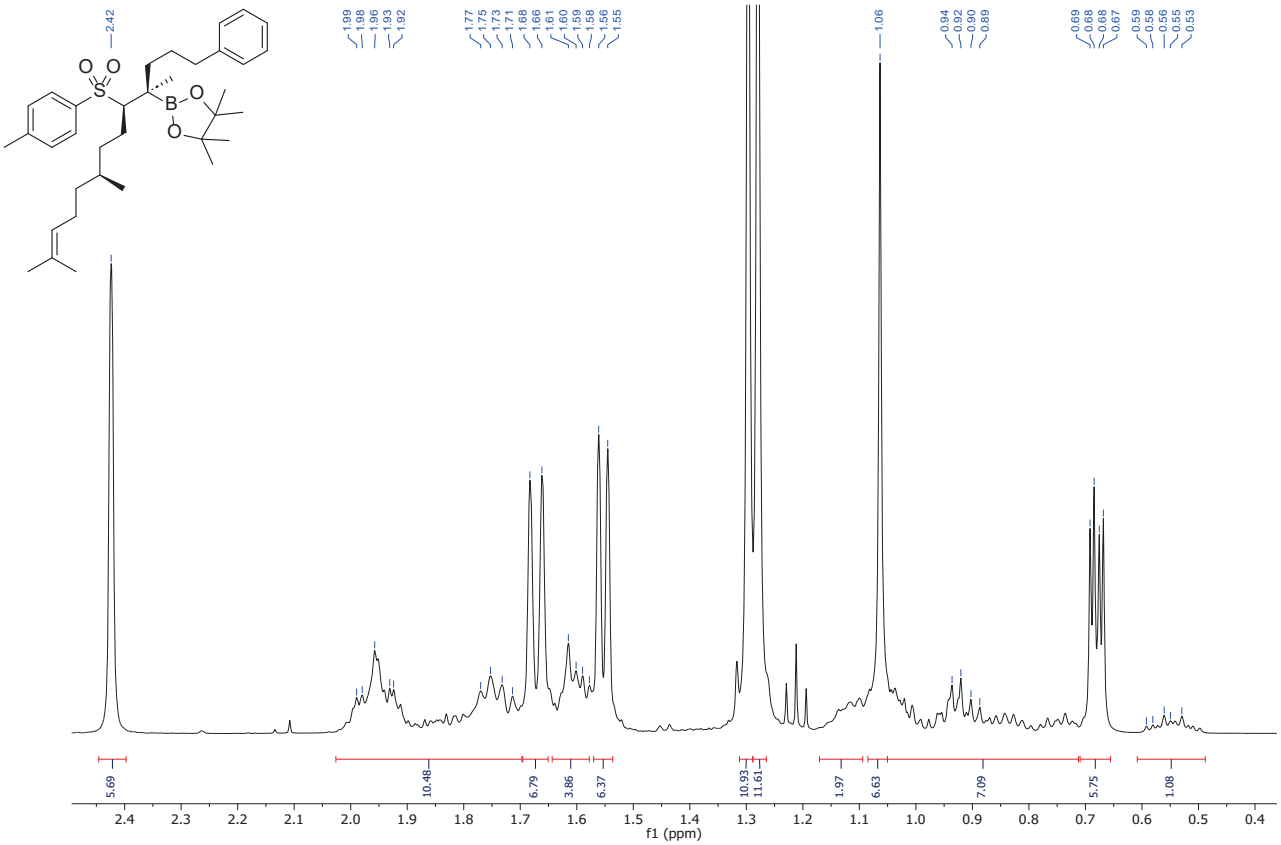
4,4,5,5-tetramethyl-2-((4S,5R,8S)-4,8,12-trimethyl-1-phenyl-5-tosyltridec-11-en-4-yl)-1,3,2-dioxaborolane (80)
Minor diastereomers

^{1}H NMR (300 MHz, $CDCl_3$)



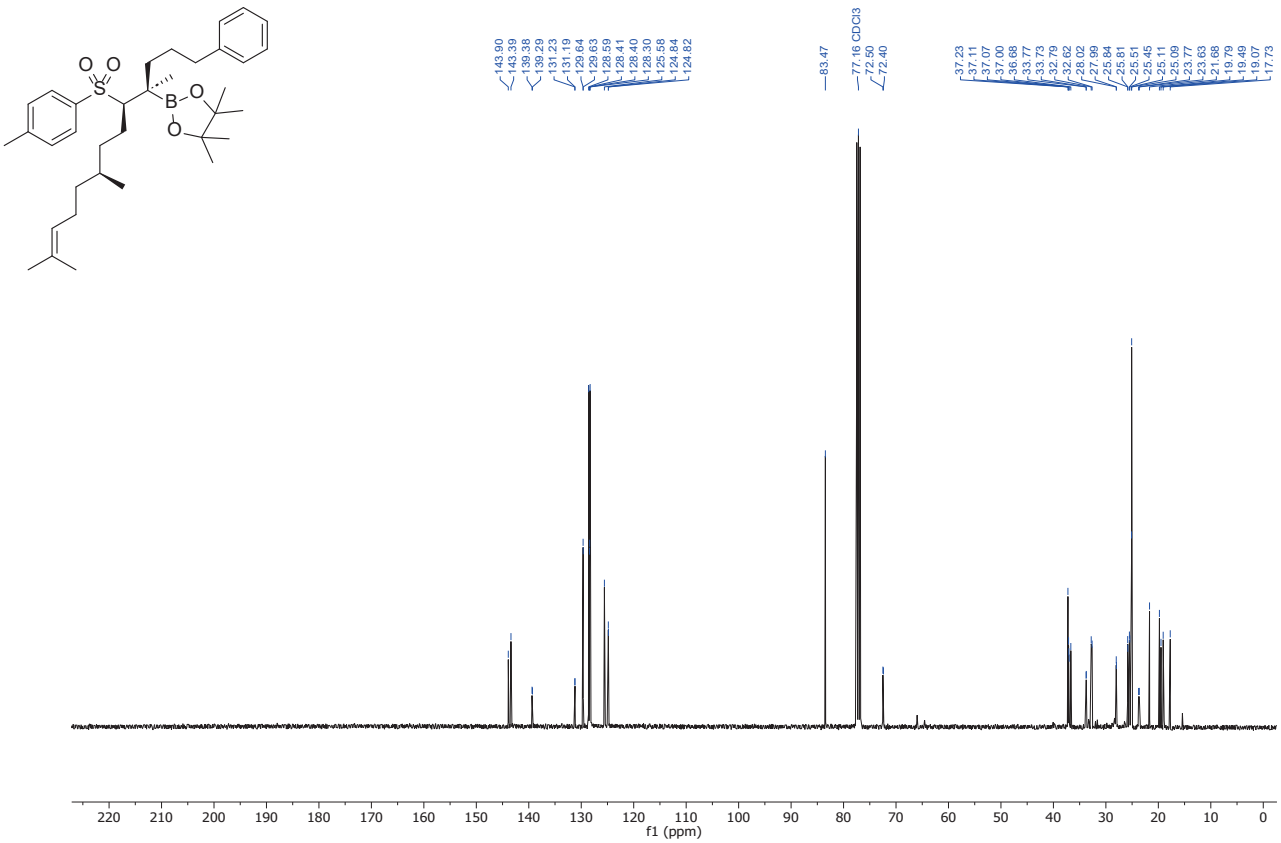
4,4,5,5-tetramethyl-2-((4S,5R,8S)-4,8,12-trimethyl-1-phenyl-5-tosyltridec-11-en-4-yl)-1,3,2-dioxaborolane (80)
Minor diastereomers

^{1}H NMR (300 MHz, $CDCl_3$)



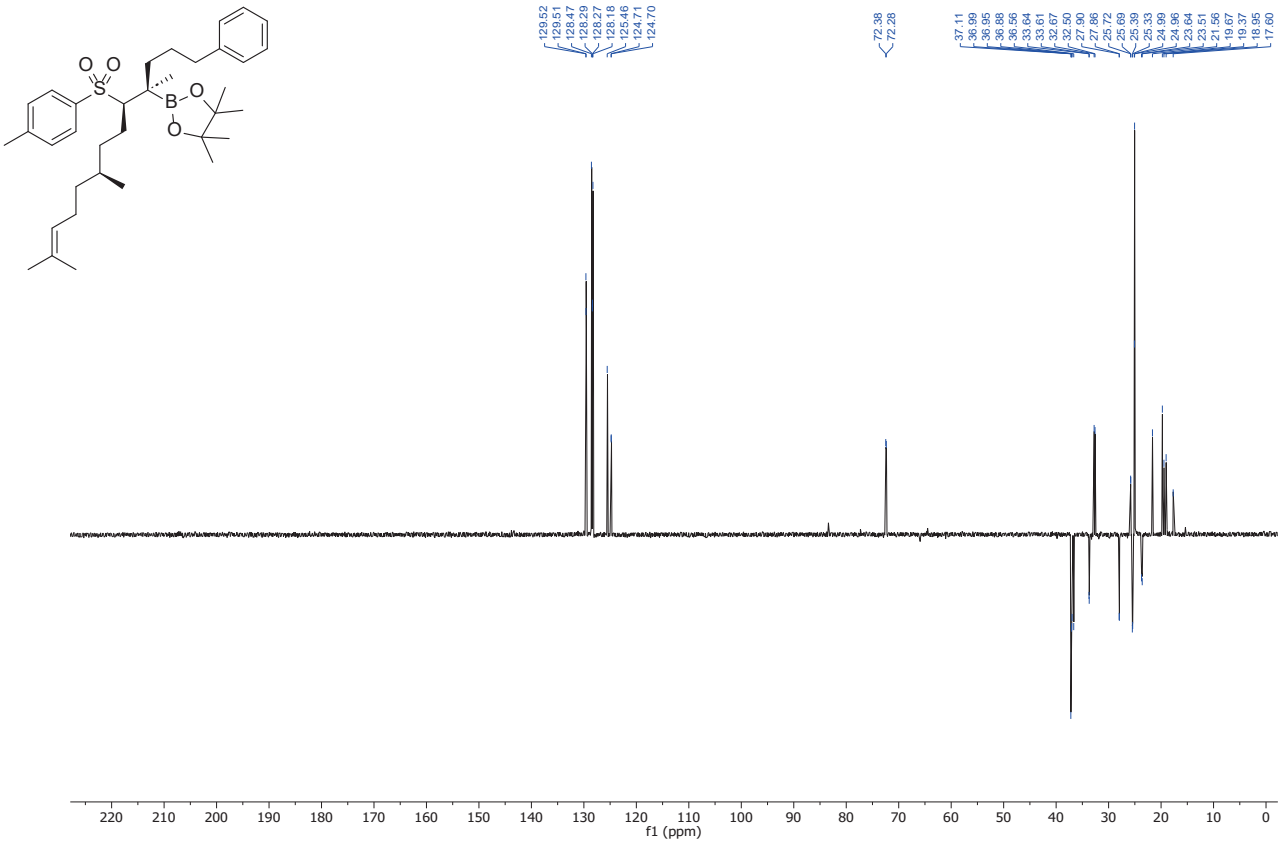
4,4,5,5-tetramethyl-2-((4S,5R,8S)-4,8,12-trimethyl-1-phenyl-5-tosyltridec-11-en-4-yl)-1,3,2-dioxaborolane (80)
Minor diastereomers

^{13}C NMR (75 MHz, $CDCl_3$)



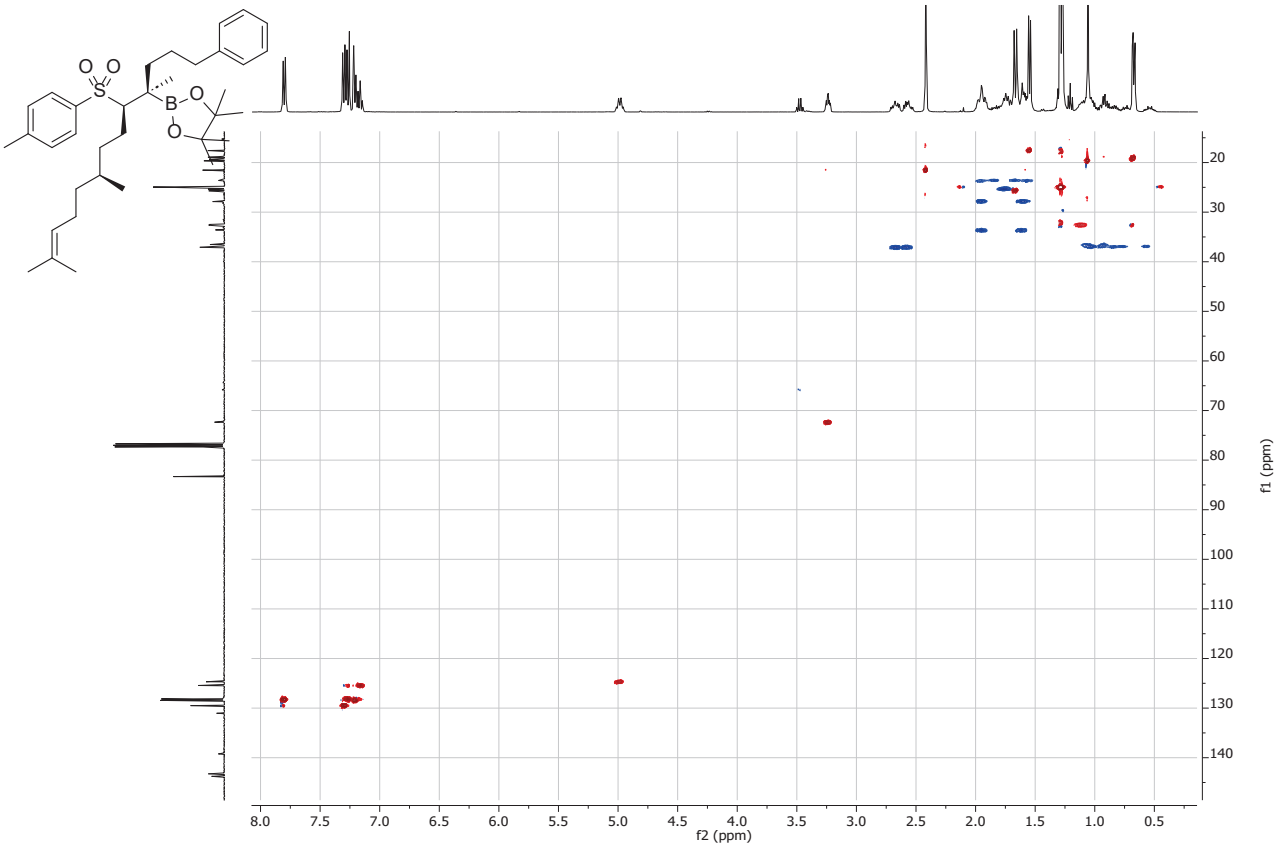
4,4,5,5-tetramethyl-2-((4S,5R,8S)-4,8,12-trimethyl-1-phenyl-5-tosyltridec-11-en-4-yl)-1,3,2-dioxaborolane (80)
Minor diastereomers

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



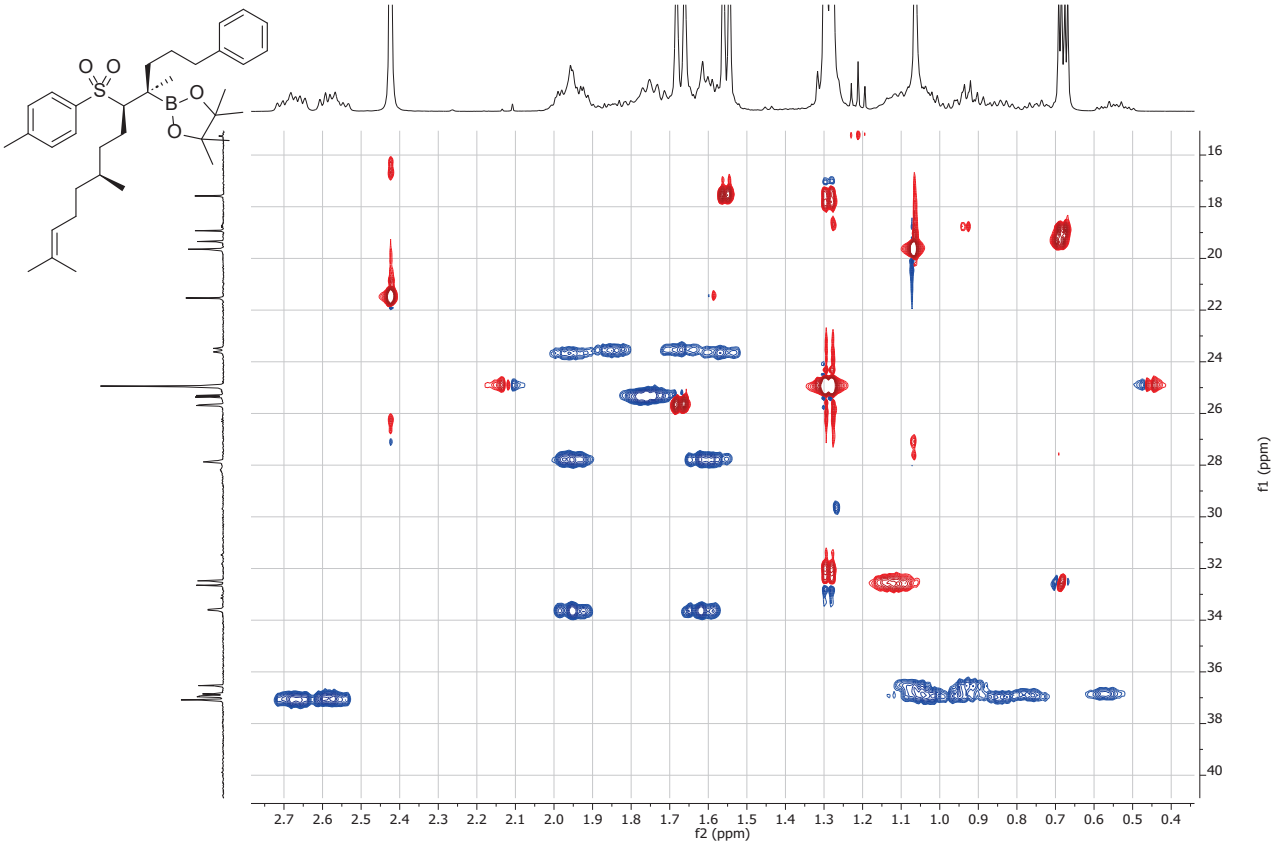
4,4,5,5-tetramethyl-2-((4S,5R,8S)-4,8,12-trimethyl-1-phenyl-5-tosyltridec-11-en-4-yl)-1,3,2-dioxaborolane (80)
Minor diastereomers

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



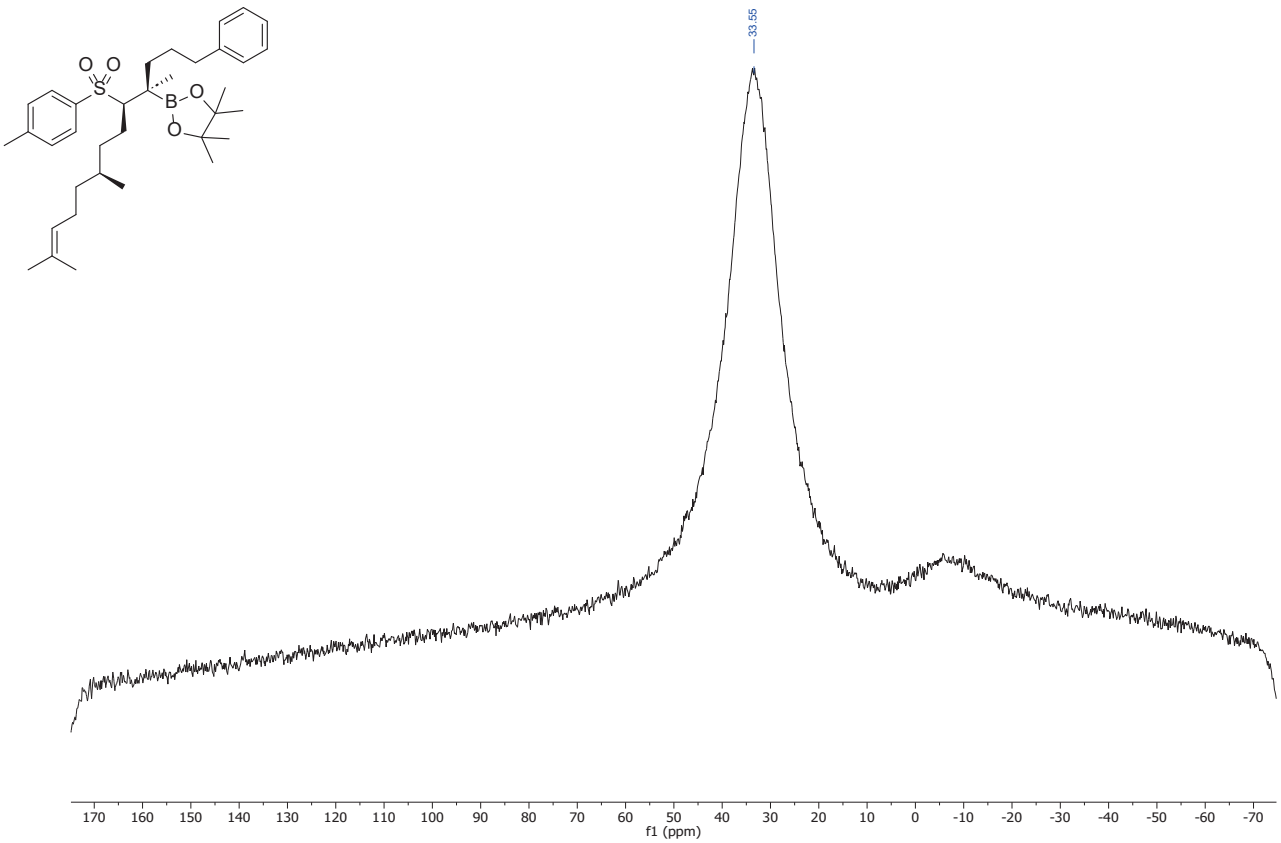
4,4,5,5-tetramethyl-2-((4S,5R,8S)-4,8,12-trimethyl-1-phenyl-5-tosyltridec-11-en-4-yl)-1,3,2-dioxaborolane (80)
Minor diastereomers

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



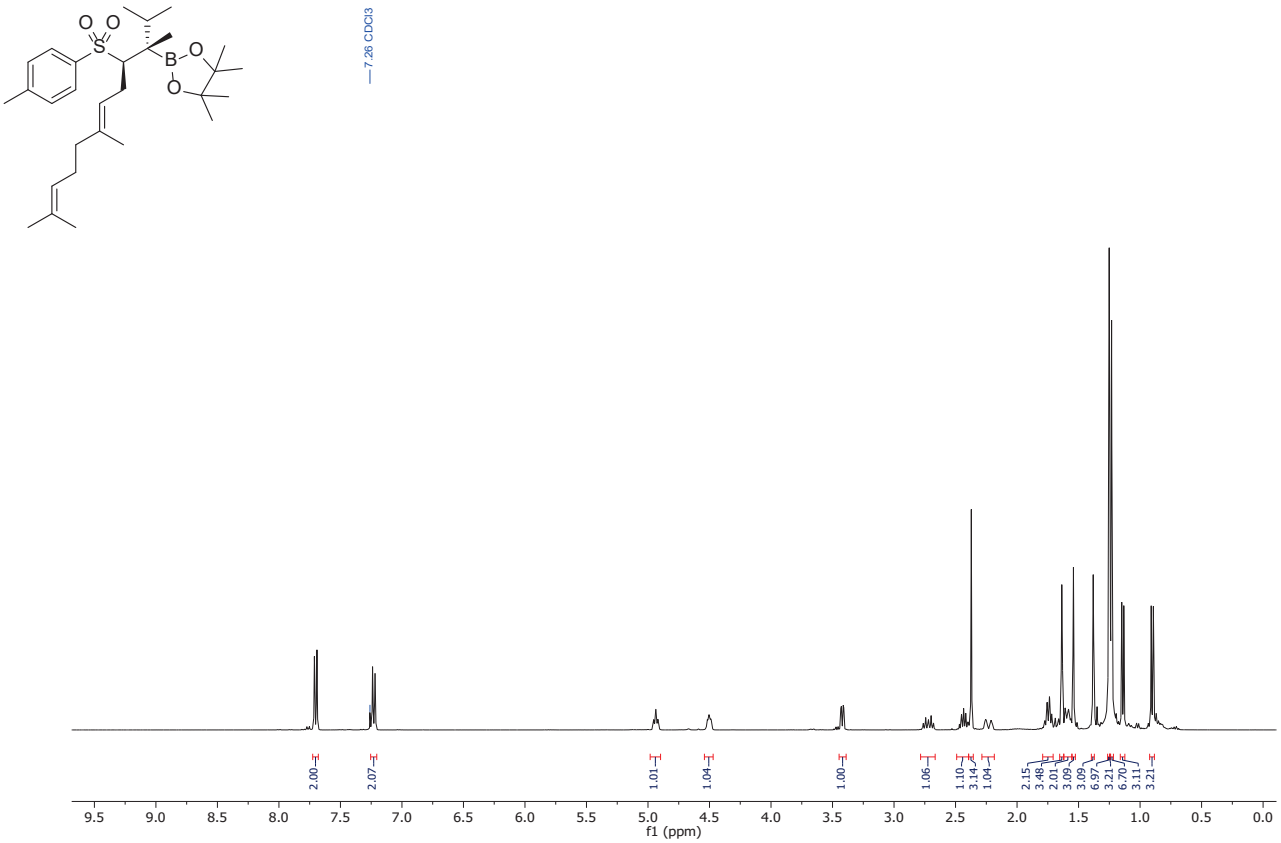
4,4,5,5-tetramethyl-2-((4S,5R,8S)-4,8,12-trimethyl-1-phenyl-5-tosyltridec-11-en-4-yl)-1,3,2-dioxaborolane (80)

^{11}B NMR (96 MHz, $CDCl_3$)



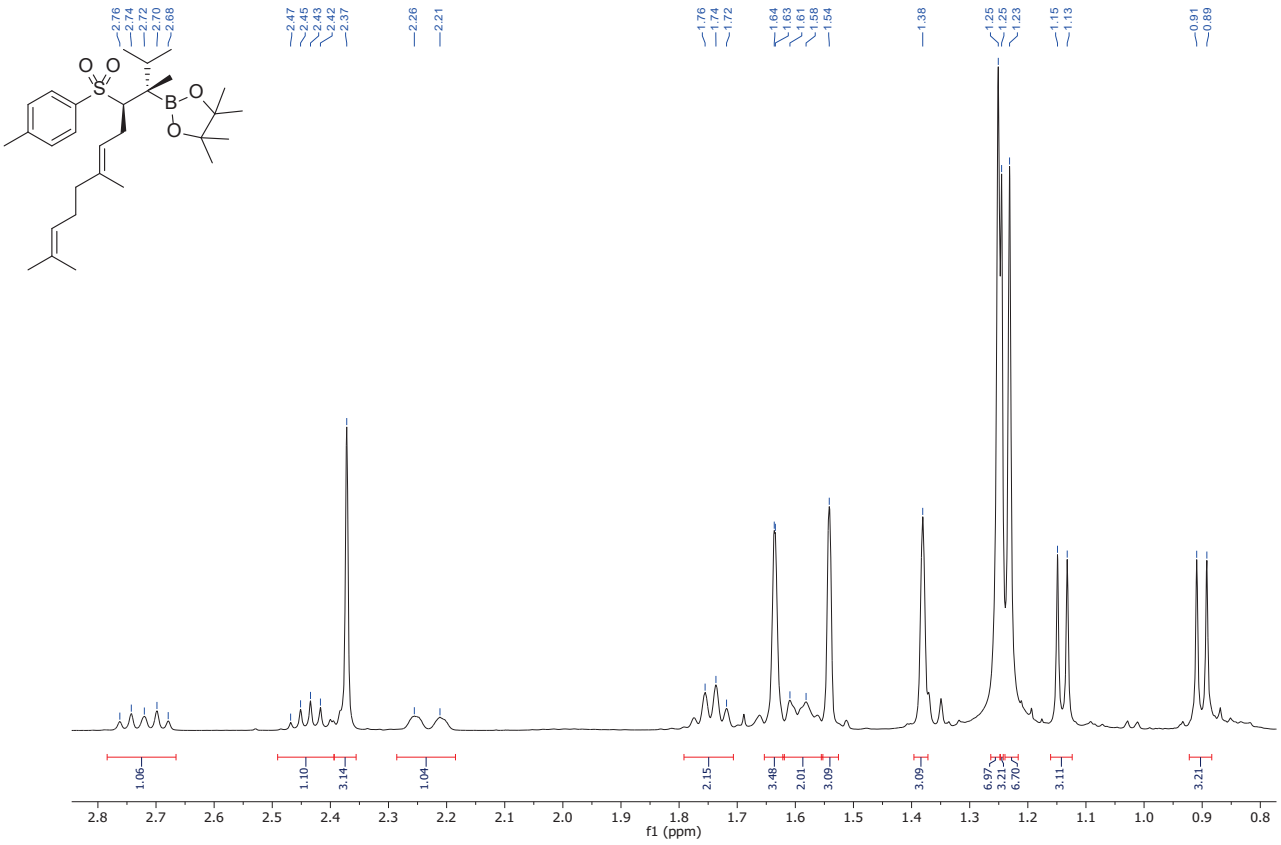
4,4,5,5-tetramethyl-2-((3R,4R,E)-2,3,7,11-tetramethyl-4-tosyldodeca-6,10-dien-3-yl)-1,3,2-dioxaborolane (79)
Major diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



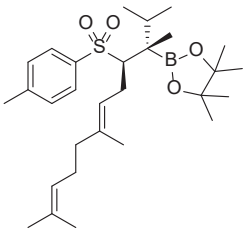
4,4,5,5-tetramethyl-2-((3R,4R,E)-2,3,7,11-tetramethyl-4-tosyldodeca-6,10-dien-3-yl)-1,3,2-dioxaborolane (79)
Major diastereomer

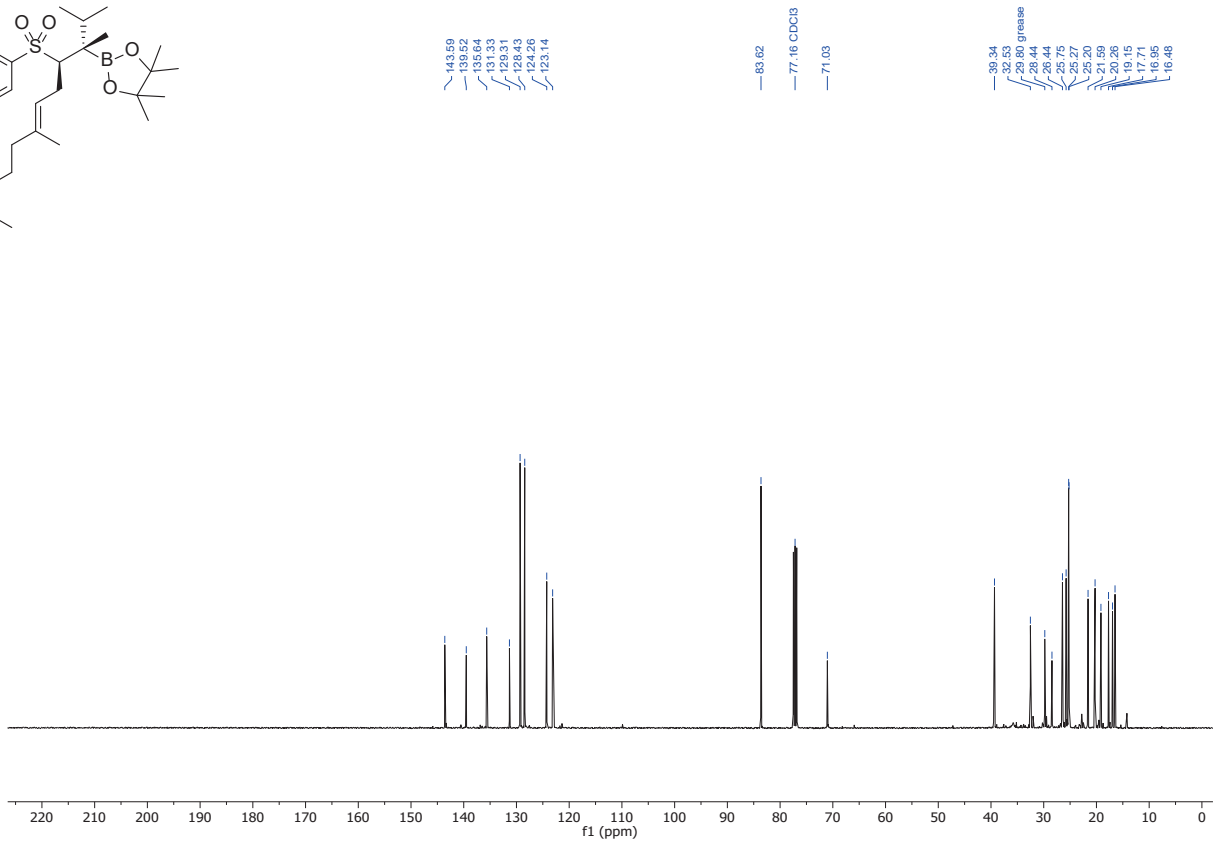
^{1}H NMR (300 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-((3R,4R,E)-2,3,7,11-tetramethyl-4-tosyldodeca-6,10-dien-3-yl)-1,3,2-dioxaborolane (79)
Major diastereomer

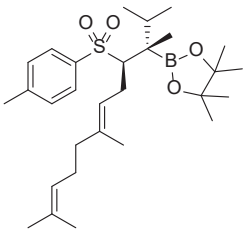
^{13}C NMR (75 MHz, $CDCl_3$)

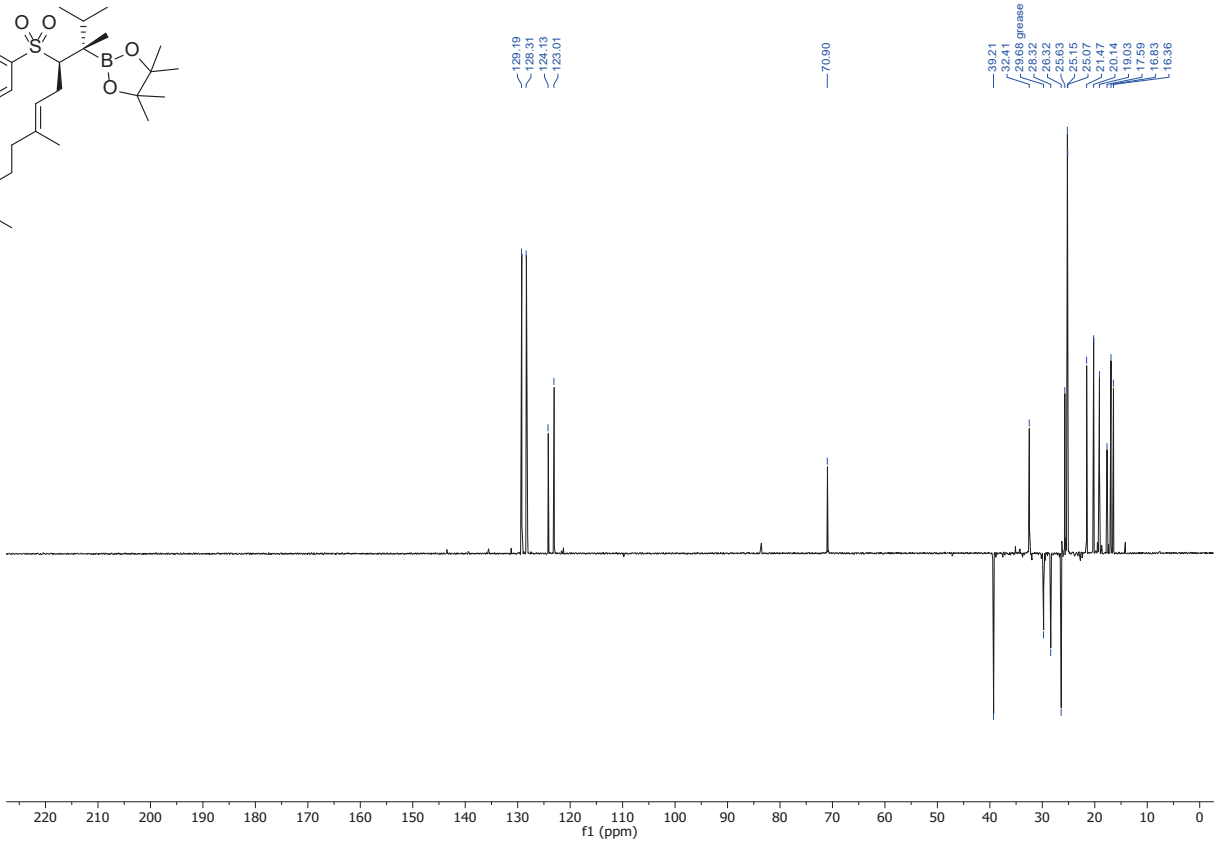




4,4,5,5-tetramethyl-2-((3R,4R,E)-2,3,7,11-tetramethyl-4-tosyldodeca-6,10-dien-3-yl)-1,3,2-dioxaborolane (79)
Major diastereomer

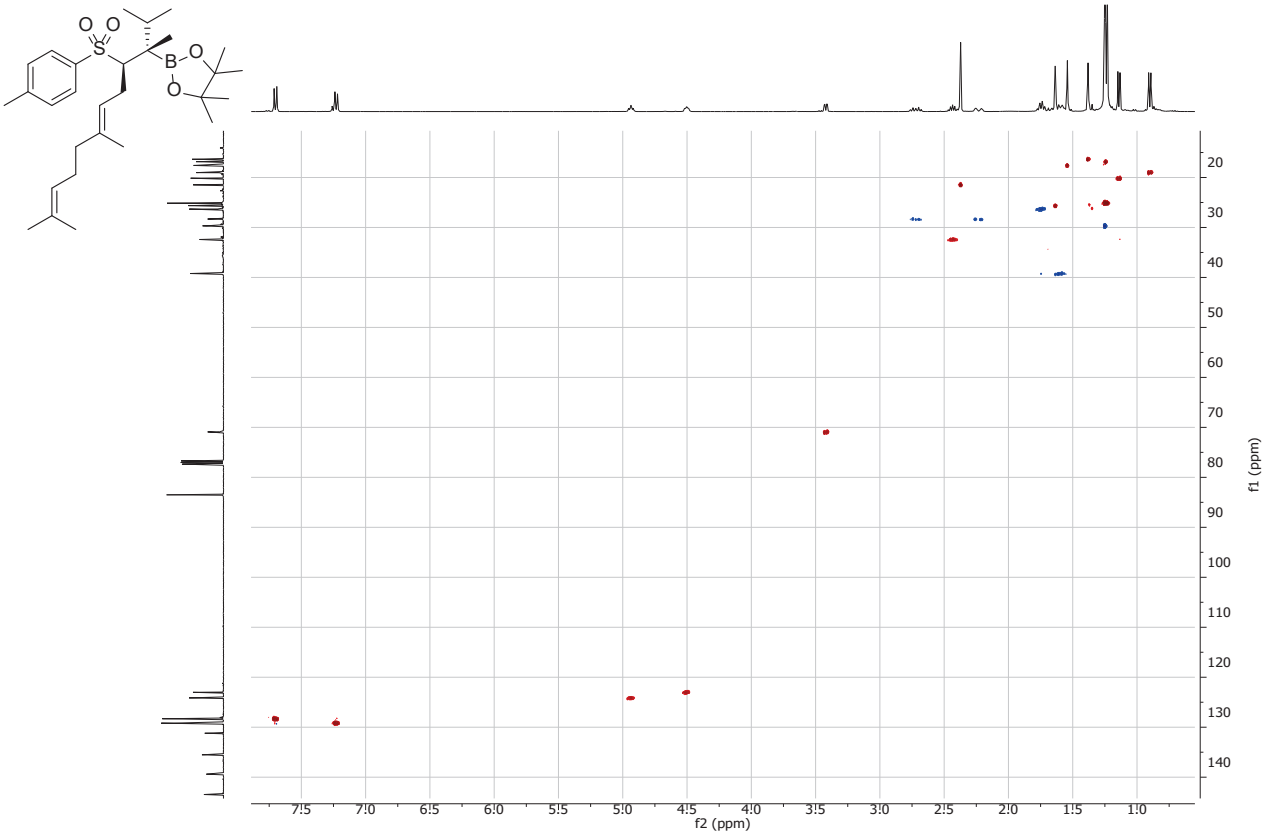
^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)





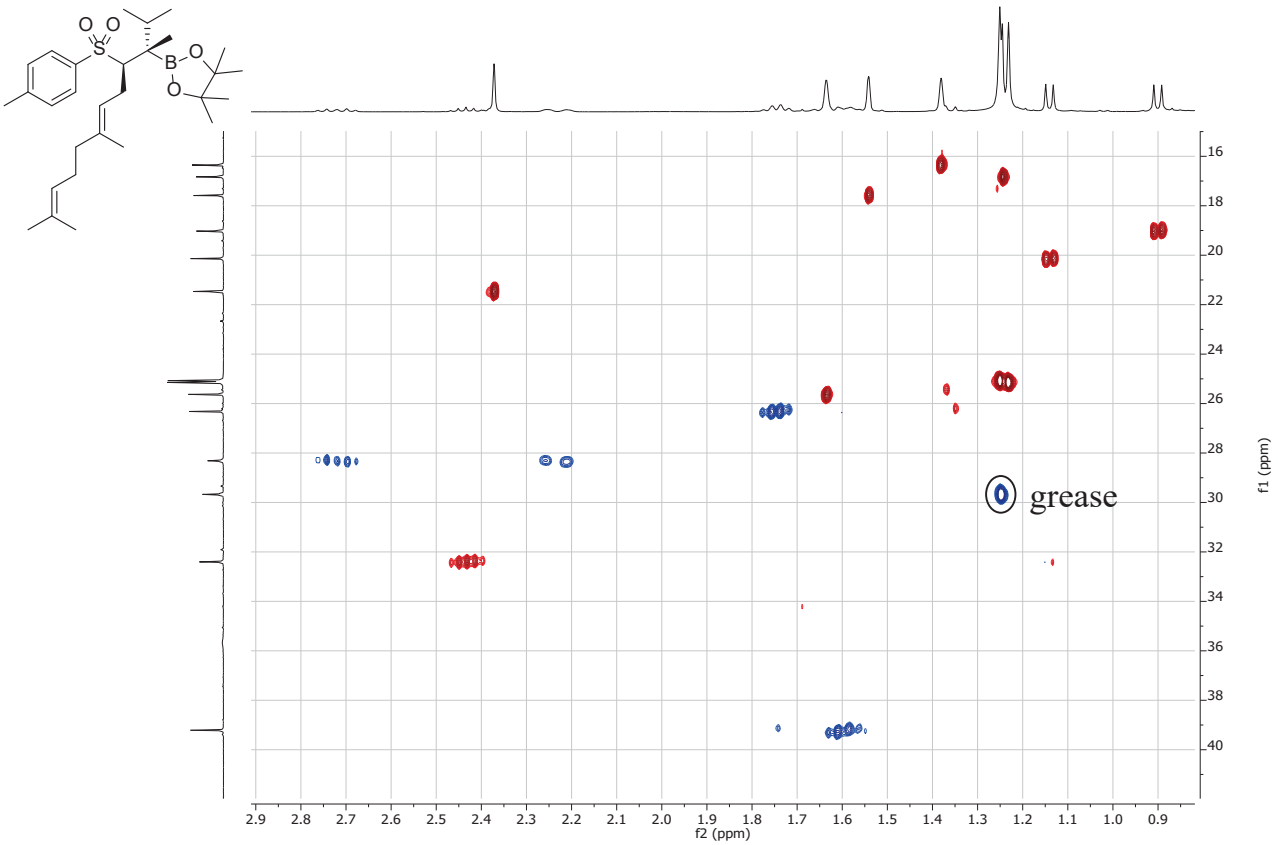
4,4,5,5-tetramethyl-2-((3R,4R,E)-2,3,7,11-tetramethyl-4-tosyldodeca-6,10-dien-3-yl)-1,3,2-dioxaborolane (79)
Major diastereomer

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



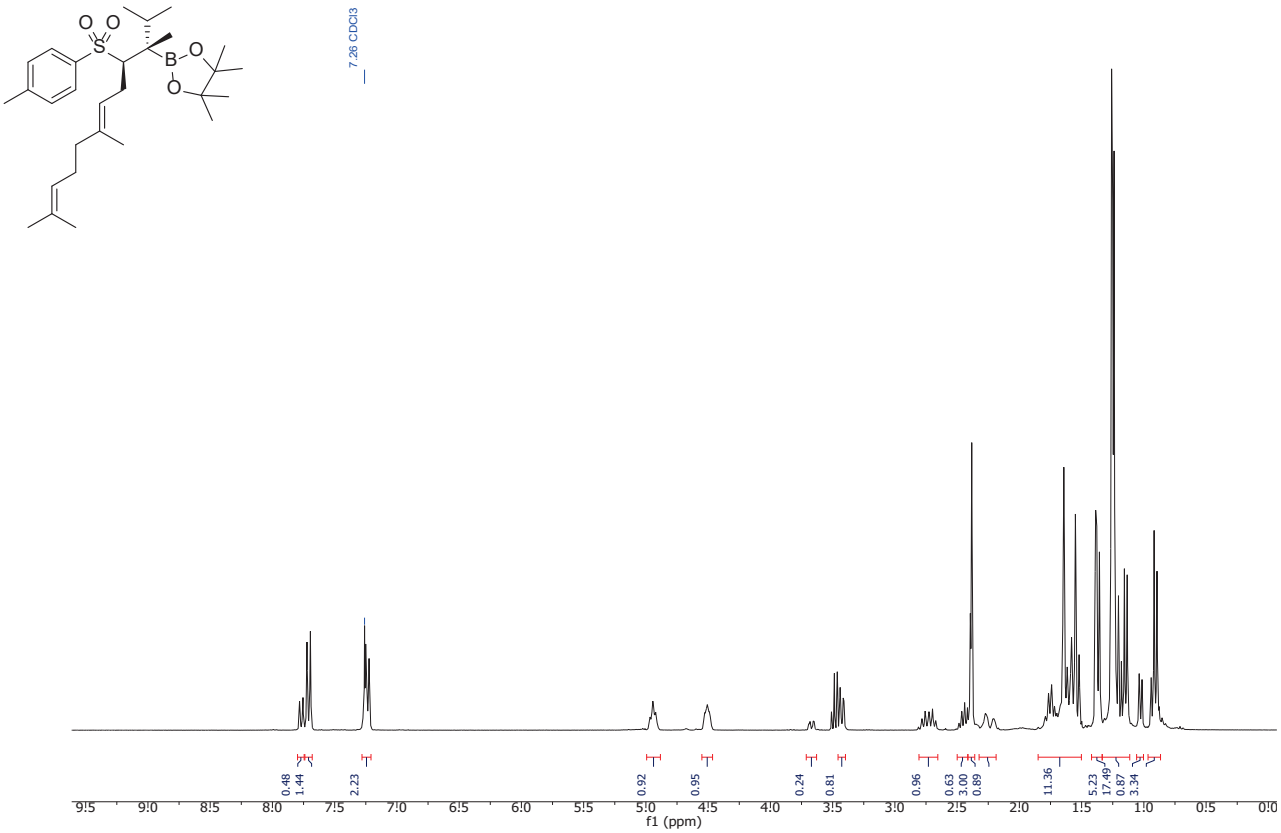
4,4,5,5-tetramethyl-2-((3R,4R,E)-2,3,7,11-tetramethyl-4-tosyldodeca-6,10-dien-3-yl)-1,3,2-dioxaborolane (79)
Major diastereomer

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



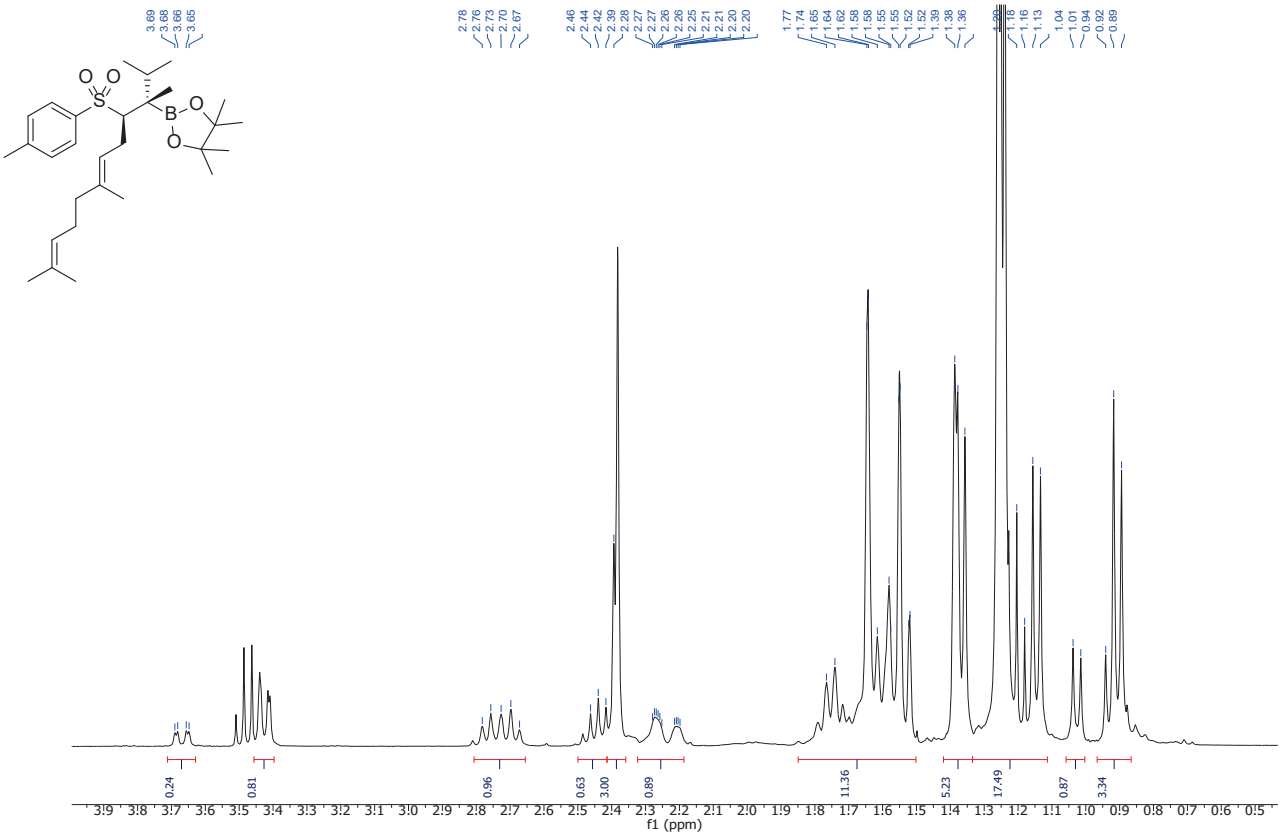
4,4,5,5-tetramethyl-2-((3R,4R,E)-2,3,7,11-tetramethyl-4-tosyldodeca-6,10-dien-3-yl)-1,3,2-dioxaborolane (79)
Minor diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



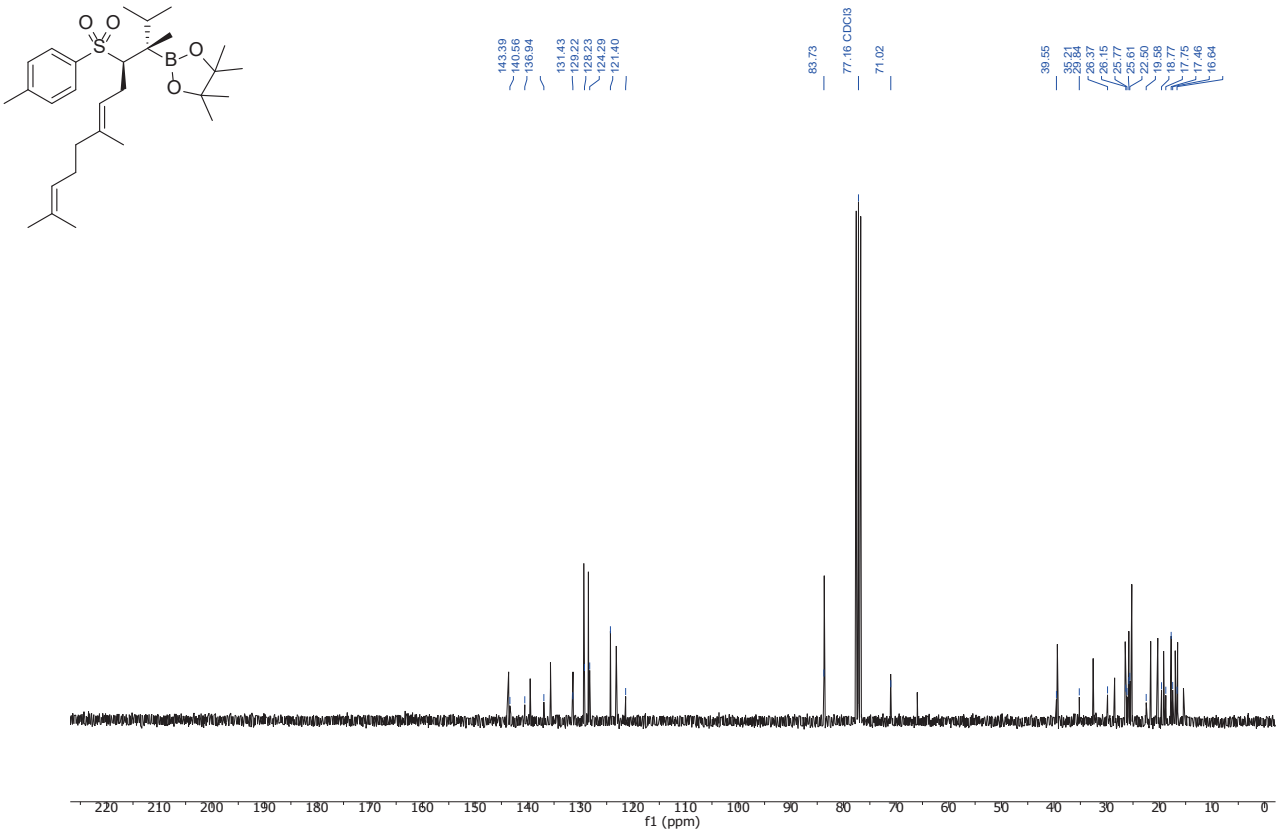
4,4,5,5-tetramethyl-2-((3R,4R,E)-2,3,7,11-tetramethyl-4-tosyldodeca-6,10-dien-3-yl)-1,3,2-dioxaborolane (79)
Minor diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



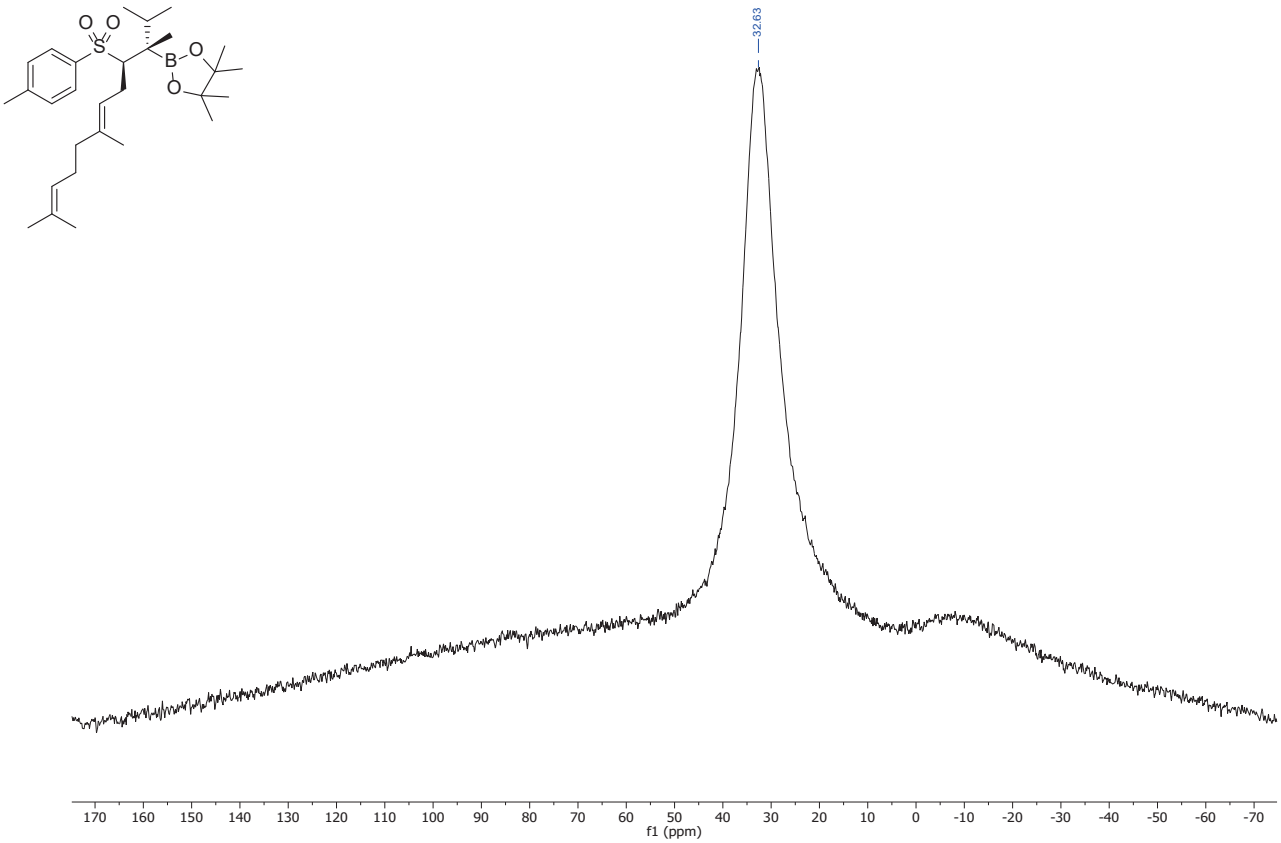
4,4,5,5-tetramethyl-2-((3R,4R,E)-2,3,7,11-tetramethyl-4-tosyldodeca-6,10-dien-3-yl)-1,3,2-dioxaborolane (79)
Minor diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



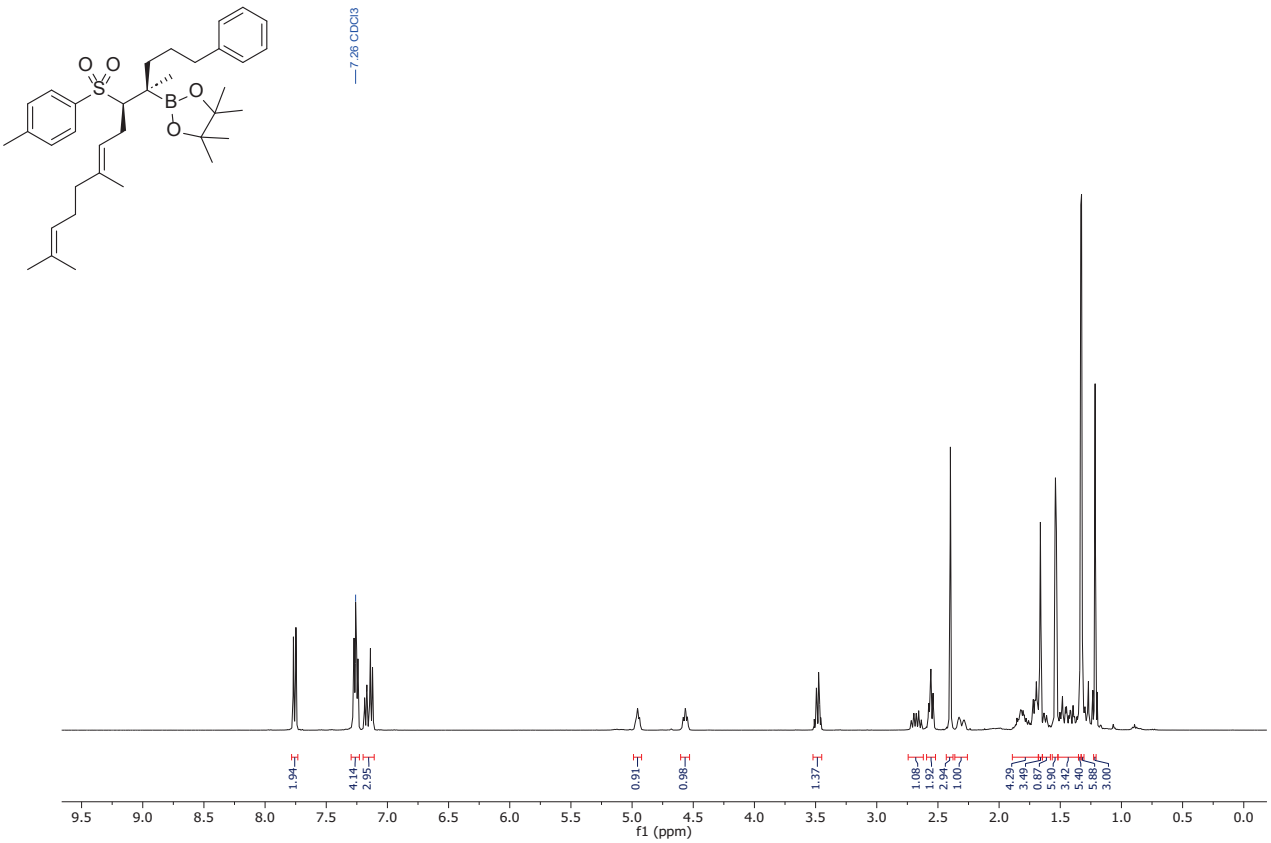
4,4,5,5-tetramethyl-2-((3R,4R,E)-2,3,7,11-tetramethyl-4-tosyldodeca-6,10-dien-3-yl)-1,3,2-dioxaborolane (79)

^{11}B NMR (96 MHz, $CDCl_3$)



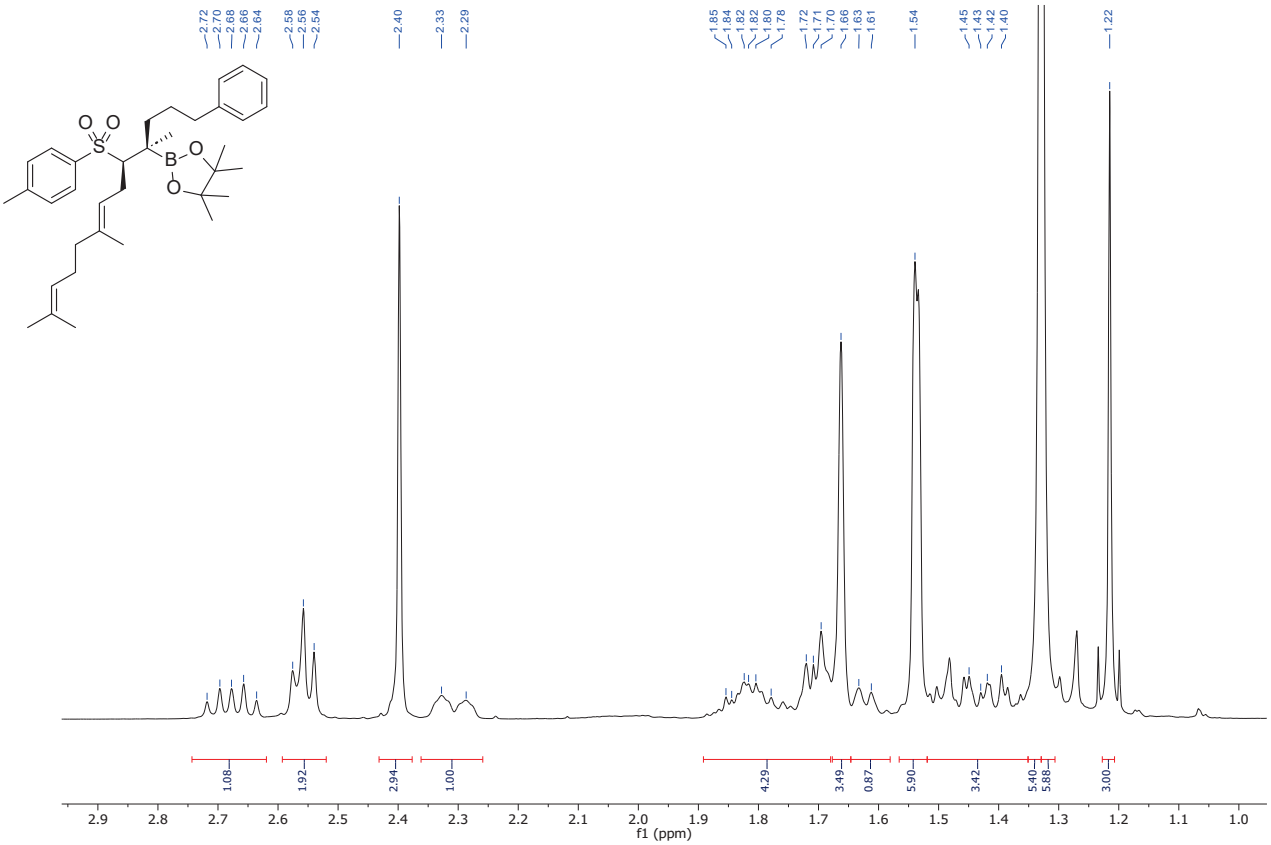
4,4,5,5-tetramethyl-2-((4S,5R,E)-4,8,12-trimethyl-1-phenyl-5-tosyltrideca-7,11-dien-4-yl)-1,3,2-dioxaborolane (78)
Major diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



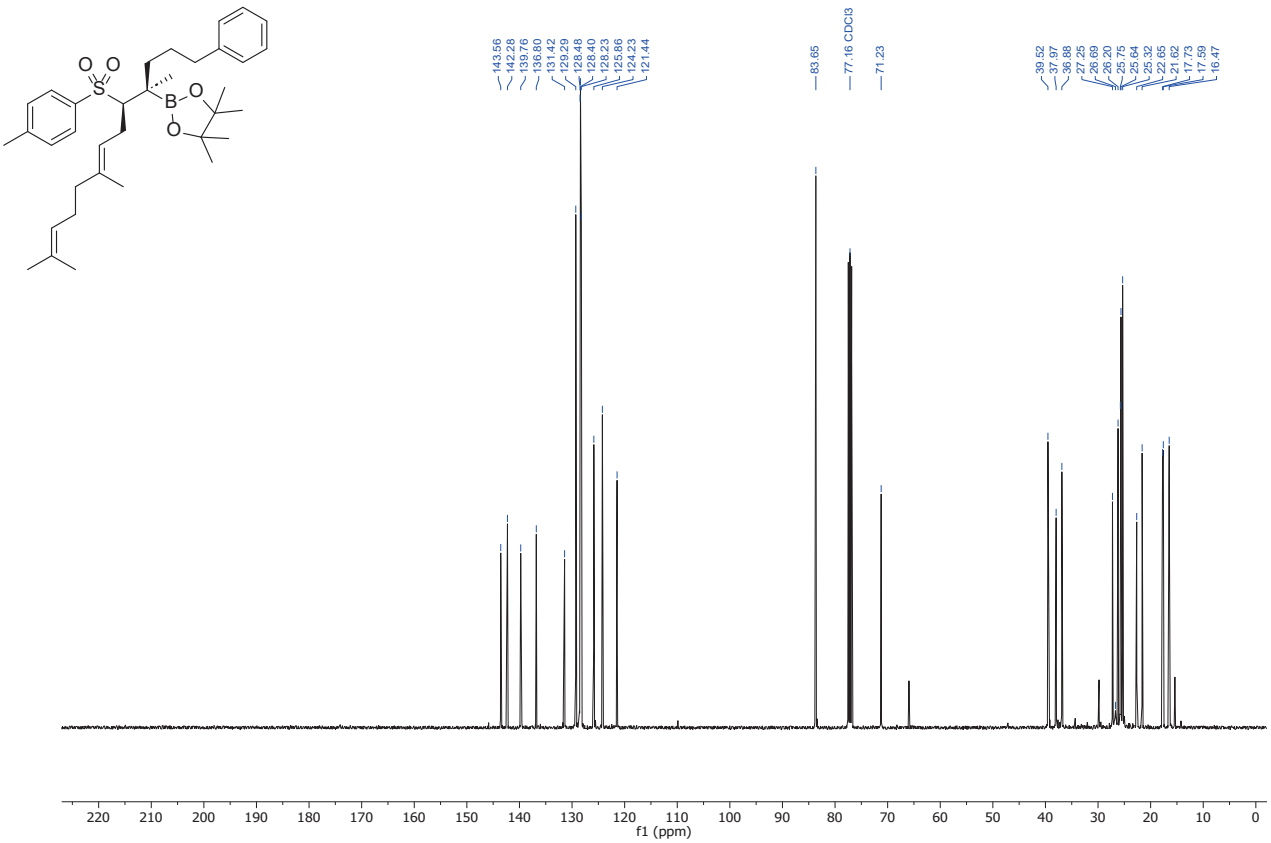
4,4,5,5-tetramethyl-2-((4S,5R,E)-4,8,12-trimethyl-1-phenyl-5-tosyltrideca-7,11-dien-4-yl)-1,3,2-dioxaborolane (78)
Major diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



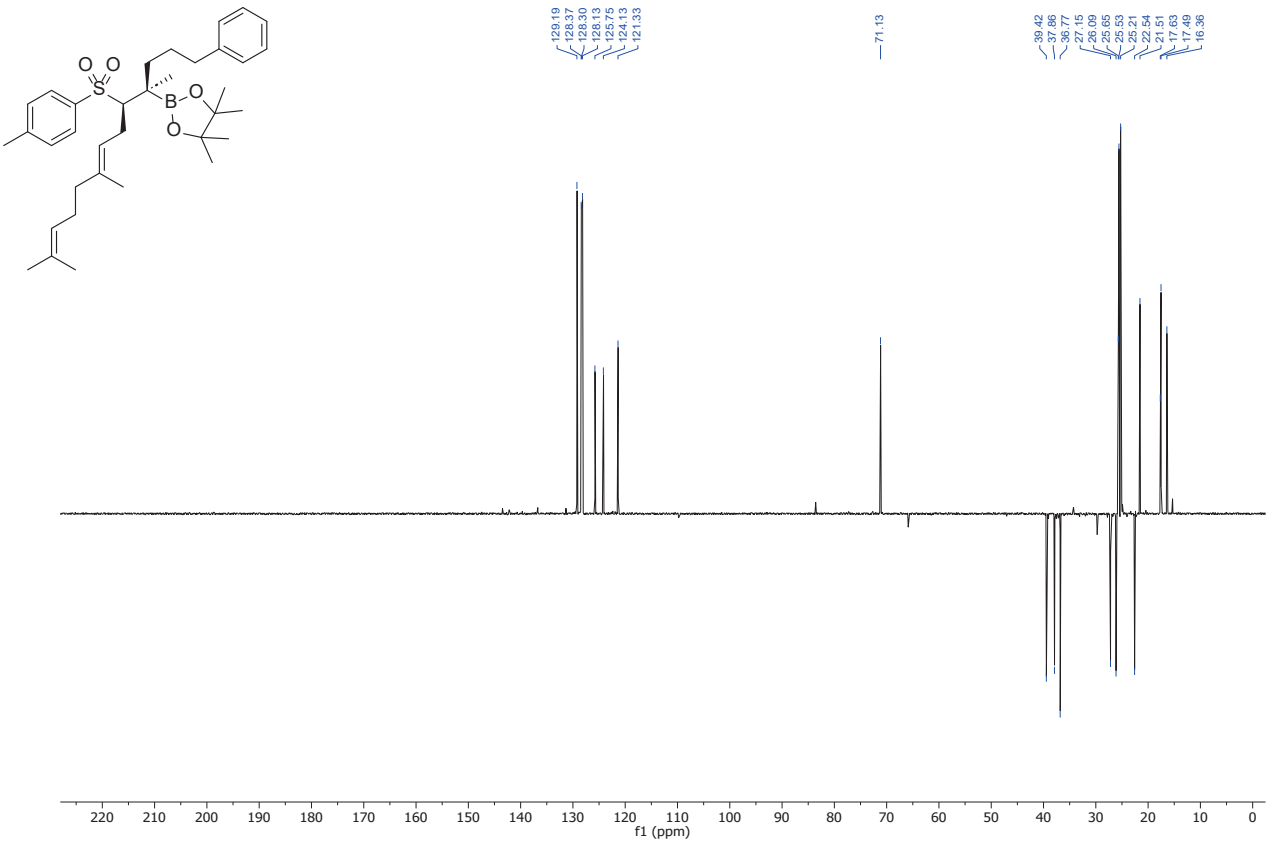
4,4,5,5-tetramethyl-2-((4S,5R,E)-4,8,12-trimethyl-1-phenyl-5-tosyltrideca-7,11-dien-4-yl)-1,3,2-dioxaborolane (78)
Major diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



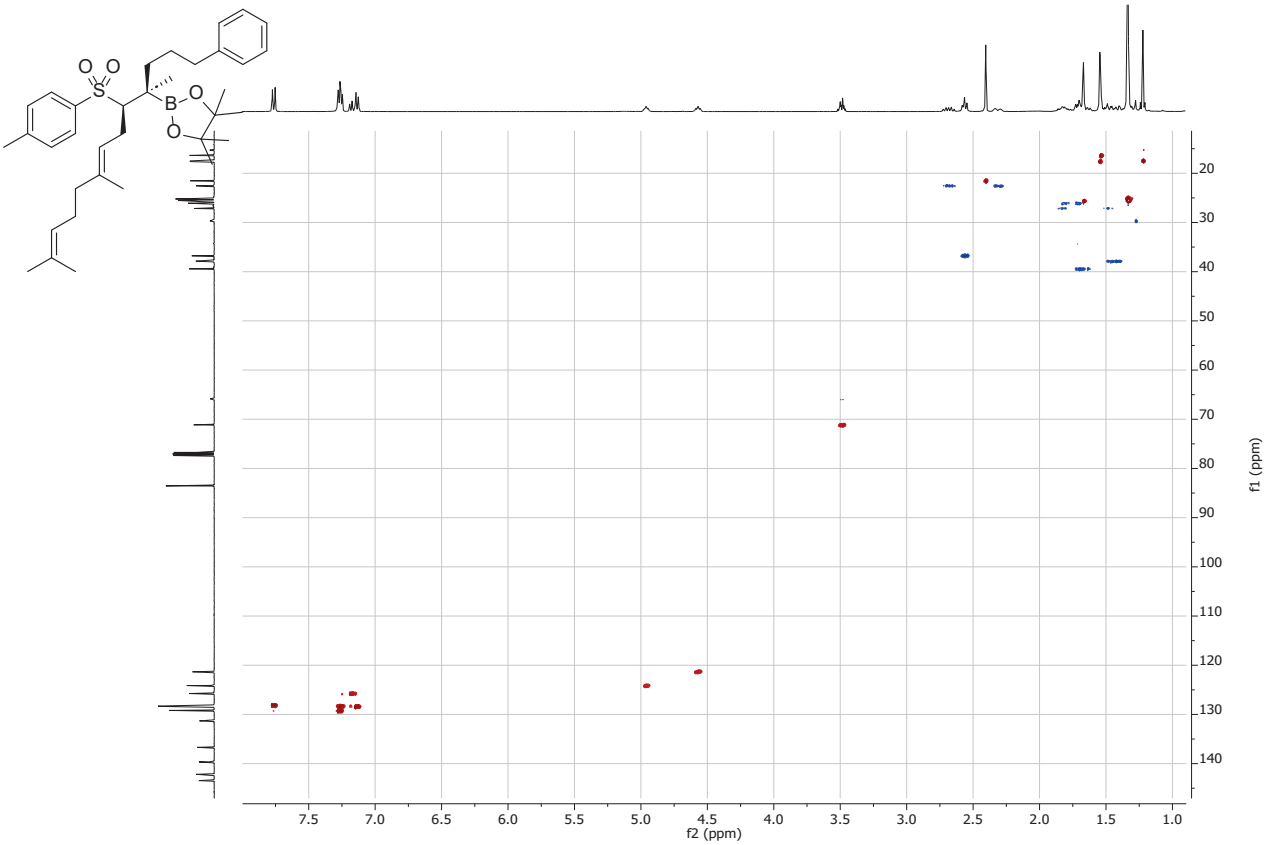
4,4,5,5-tetramethyl-2-((4S,5R,E)-4,8,12-trimethyl-1-phenyl-5-tosyltrideca-7,11-dien-4-yl)-1,3,2-dioxaborolane (78)
Major diastereomer

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



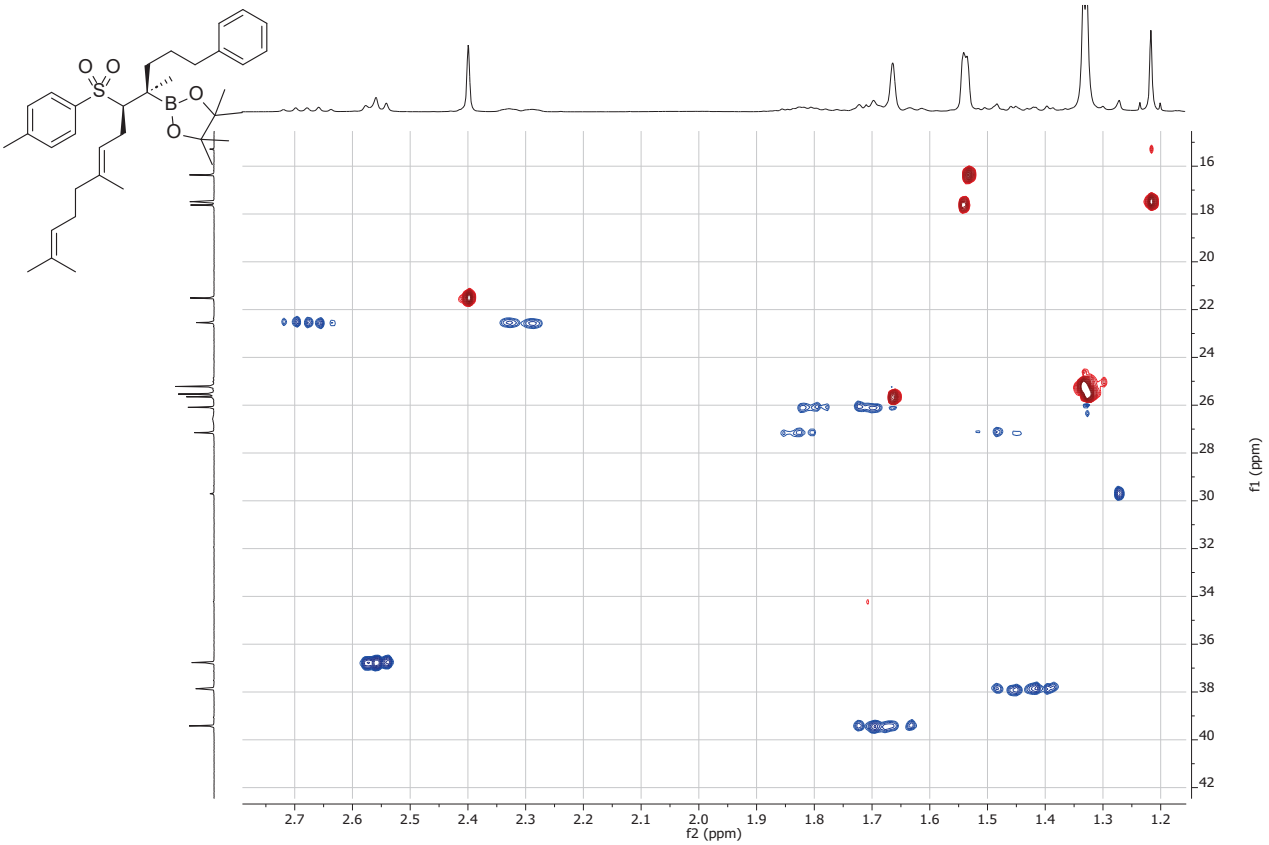
4,4,5,5-tetramethyl-2-((4S,5R,E)-4,8,12-trimethyl-1-phenyl-5-tosyltrideca-7,11-dien-4-yl)-1,3,2-dioxaborolane (78)
Major diastereomer

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



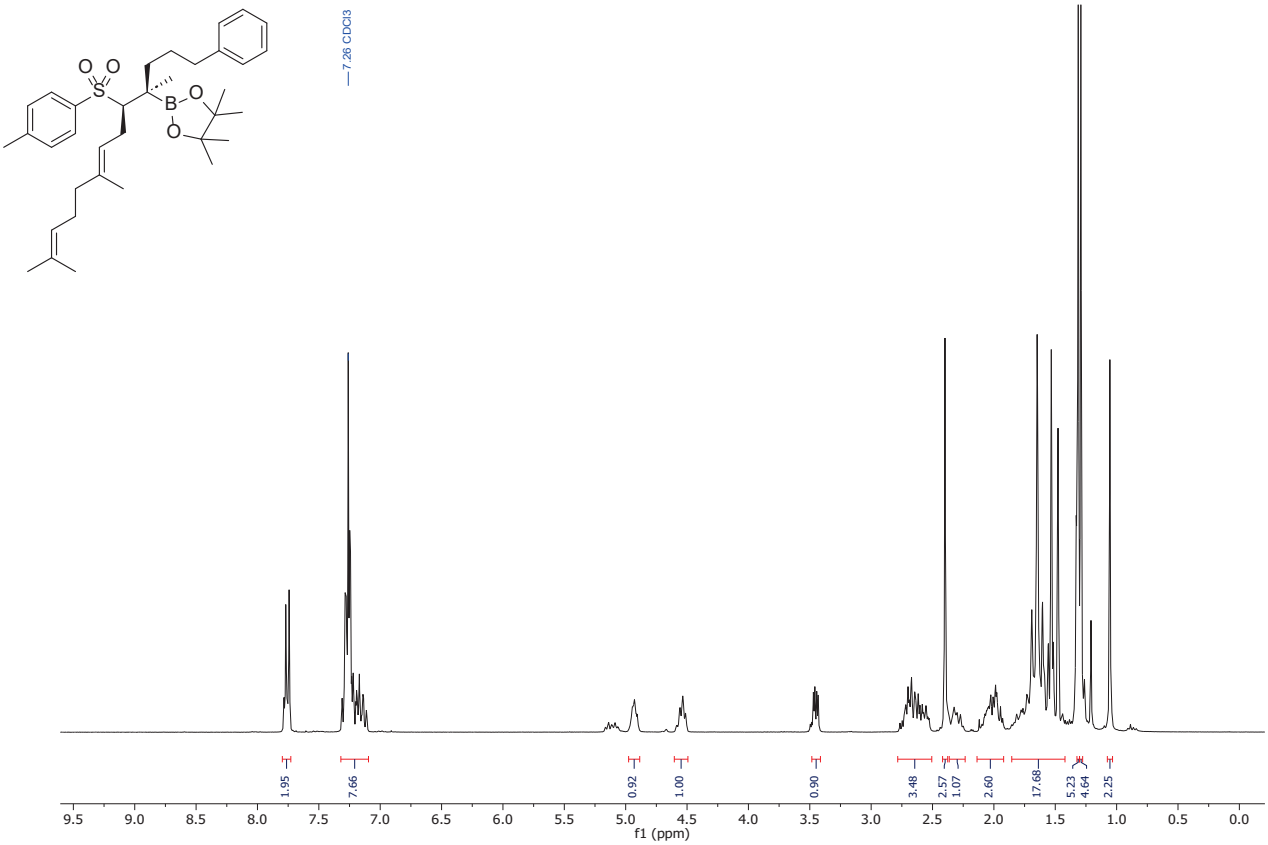
4,4,5,5-tetramethyl-2-((4S,5R,E)-4,8,12-trimethyl-1-phenyl-5-tosyltrideca-7,11-dien-4-yl)-1,3,2-dioxaborolane (78)
Major diastereomer

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



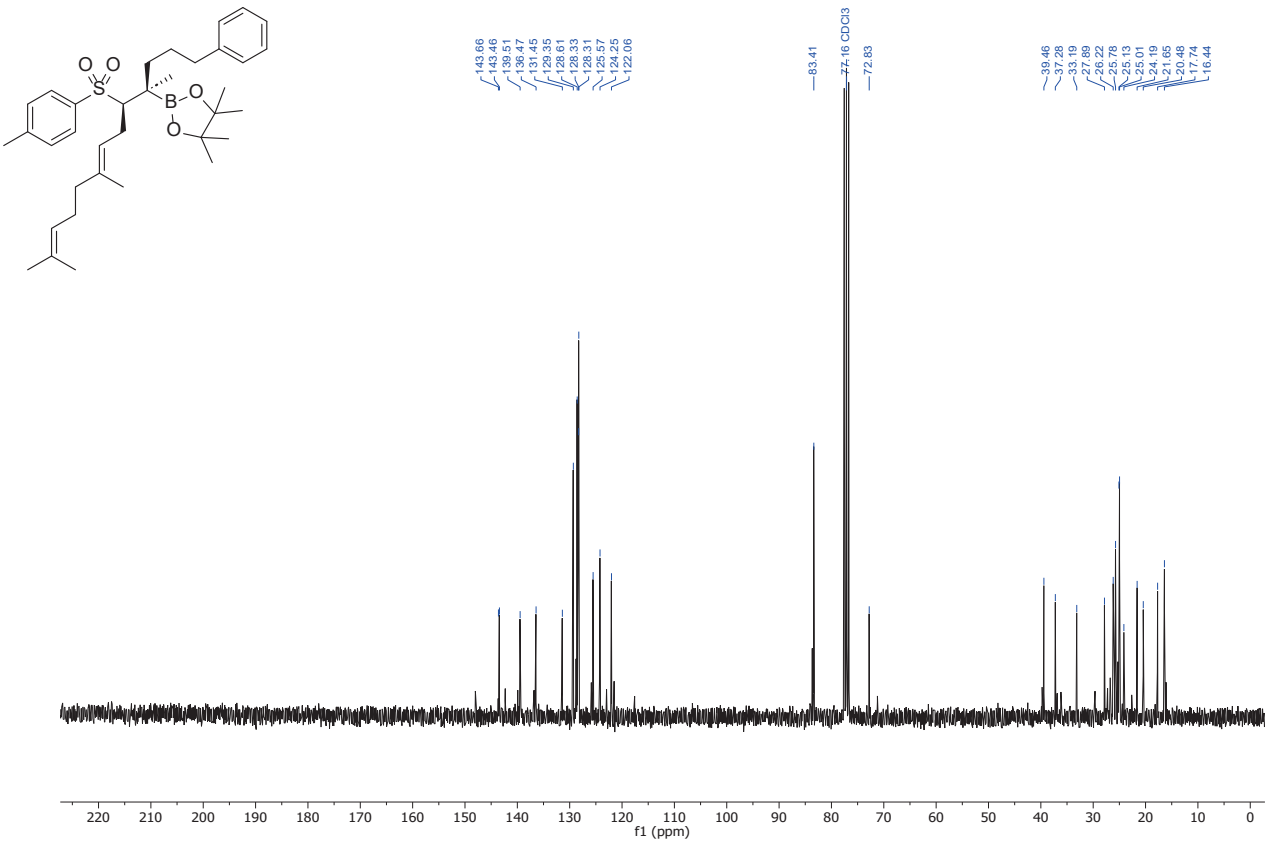
4,4,5,5-tetramethyl-2-((4S,5R,E)-4,8,12-trimethyl-1-phenyl-5-tosyltrideca-7,11-dien-4-yl)-1,3,2-dioxaborolane (78)
Minor diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)



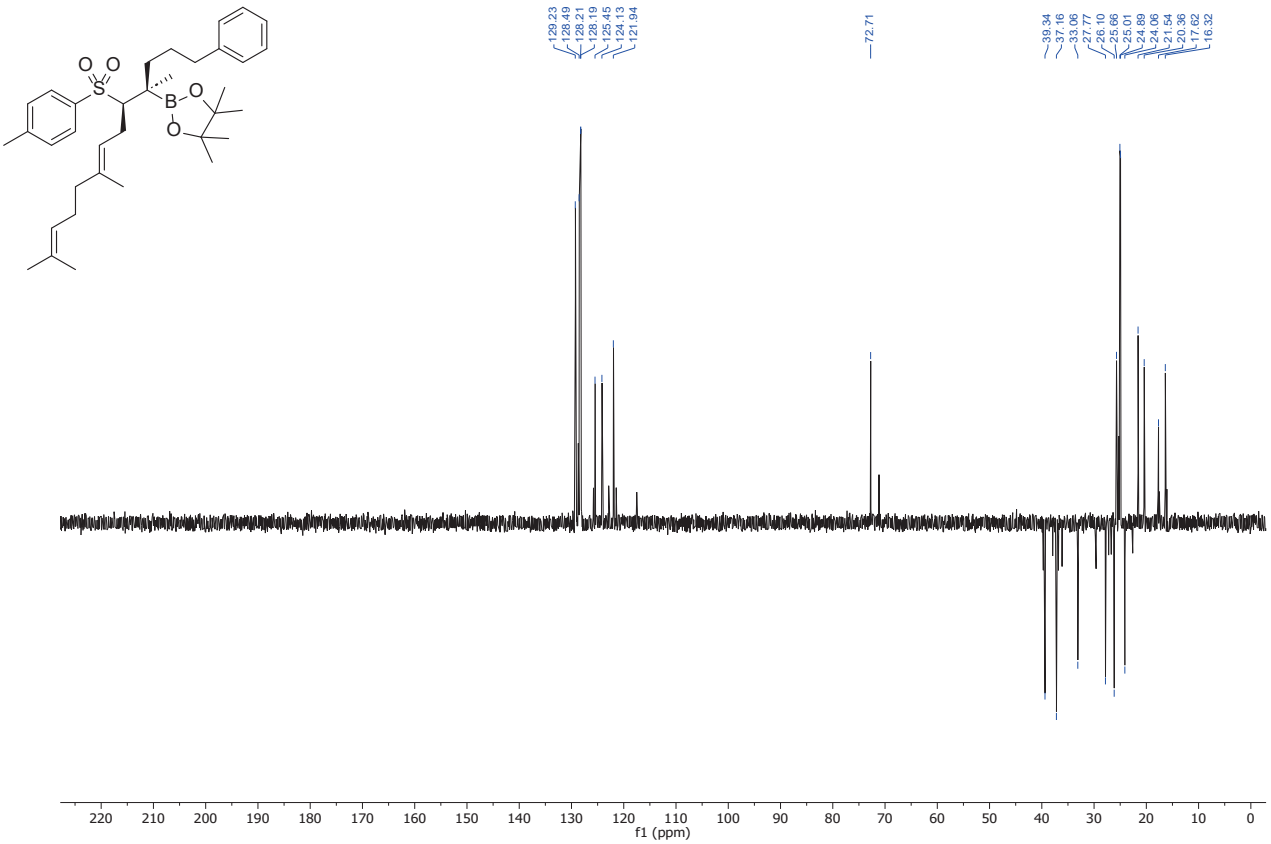
4,4,5,5-tetramethyl-2-((4S,5R,E)-4,8,12-trimethyl-1-phenyl-5-tosyltrideca-7,11-dien-4-yl)-1,3,2-dioxaborolane (78)
Minor diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



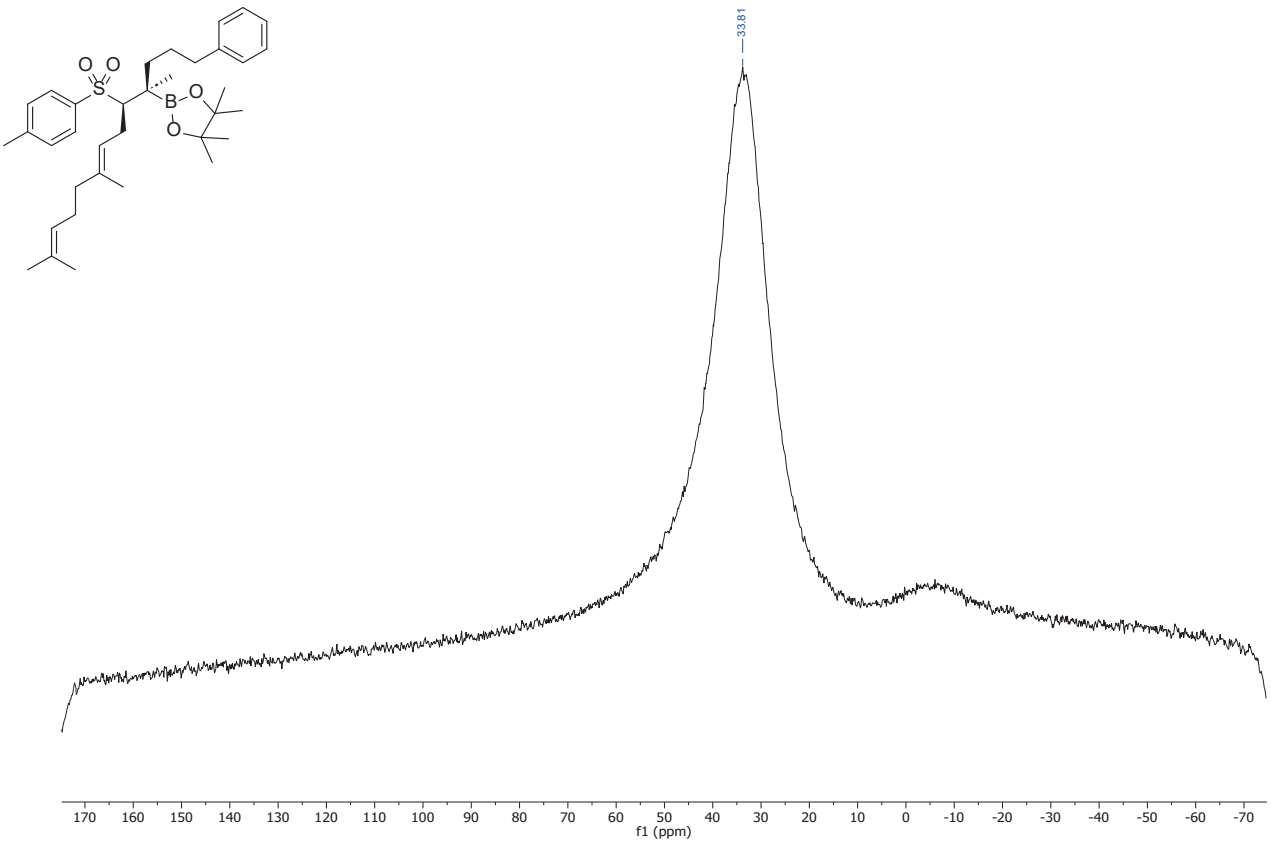
4,4,5,5-tetramethyl-2-((4S,5R,E)-4,8,12-trimethyl-1-phenyl-5-tosyltrideca-7,11-dien-4-yl)-1,3,2-dioxaborolane (78)
Minor diastereomer

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-((4S,5R,E)-4,8,12-trimethyl-1-phenyl-5-tosyltrideca-7,11-dien-4-yl)-1,3,2-dioxaborolane (78)

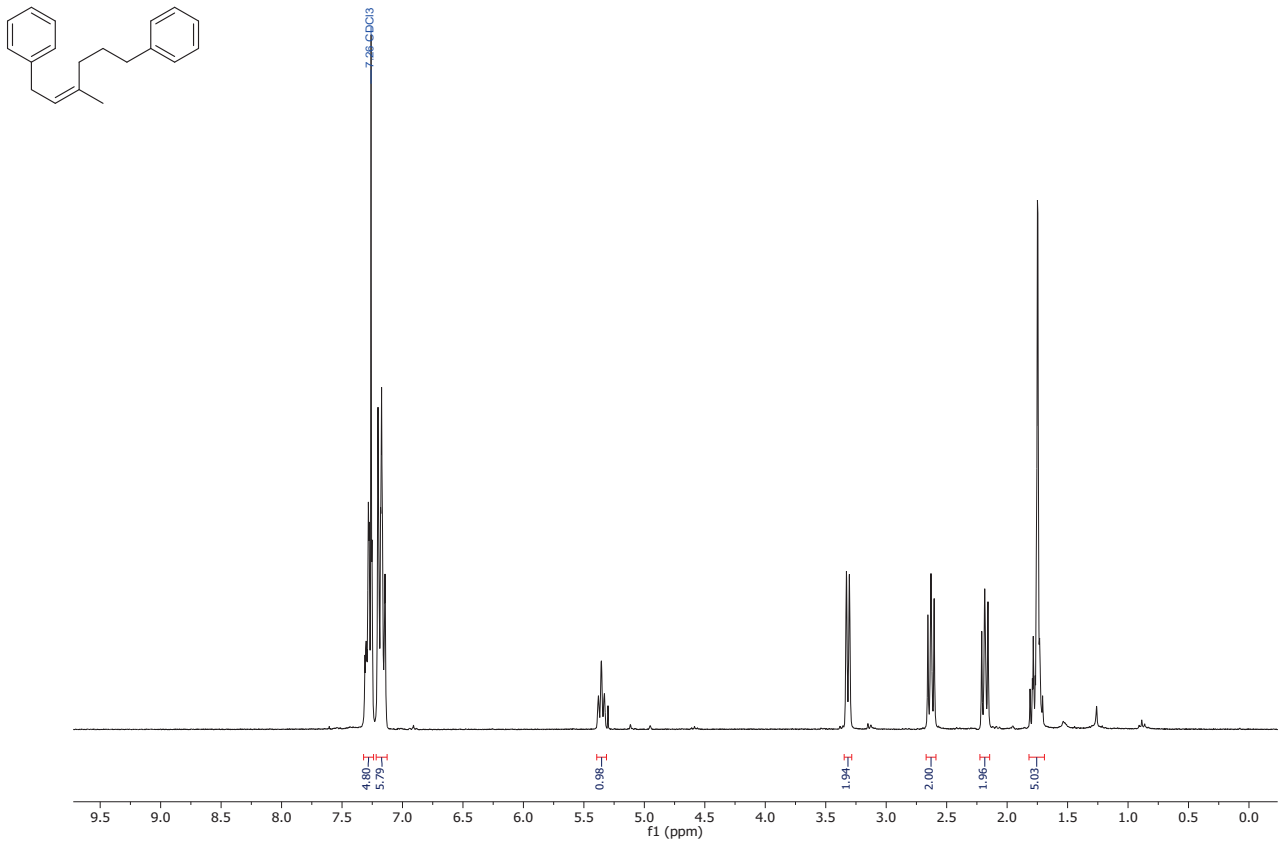
^{11}B NMR (96 MHz, $CDCl_3$)



(3-methylhex-2-ene-1,6-diyl)dibenzene (57)

^{1}H NMR (300 MHz, $CDCl_3$)

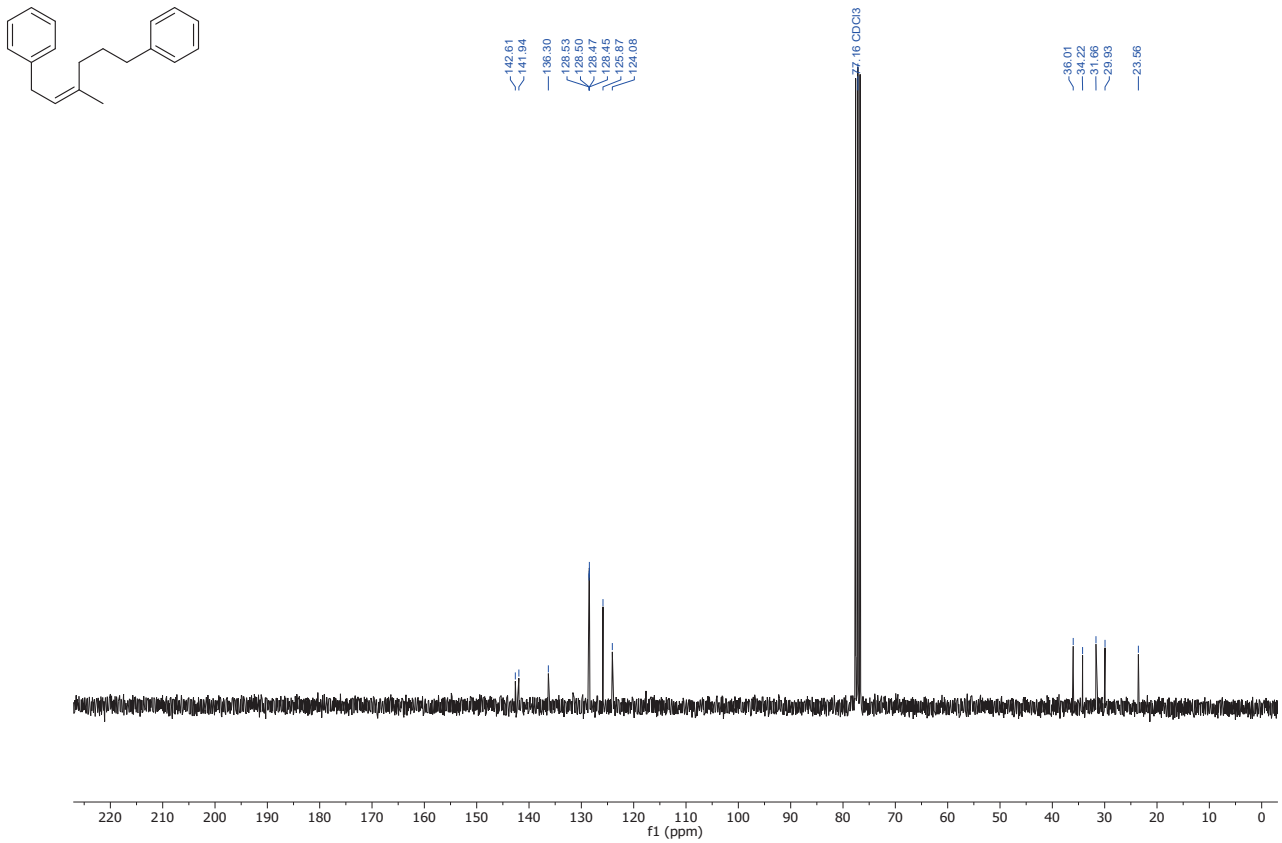
Z-olefin



(3-methylhex-2-ene-1,6-diyl)dibenzene (57)

^{13}C NMR (75 MHz, $CDCl_3$)

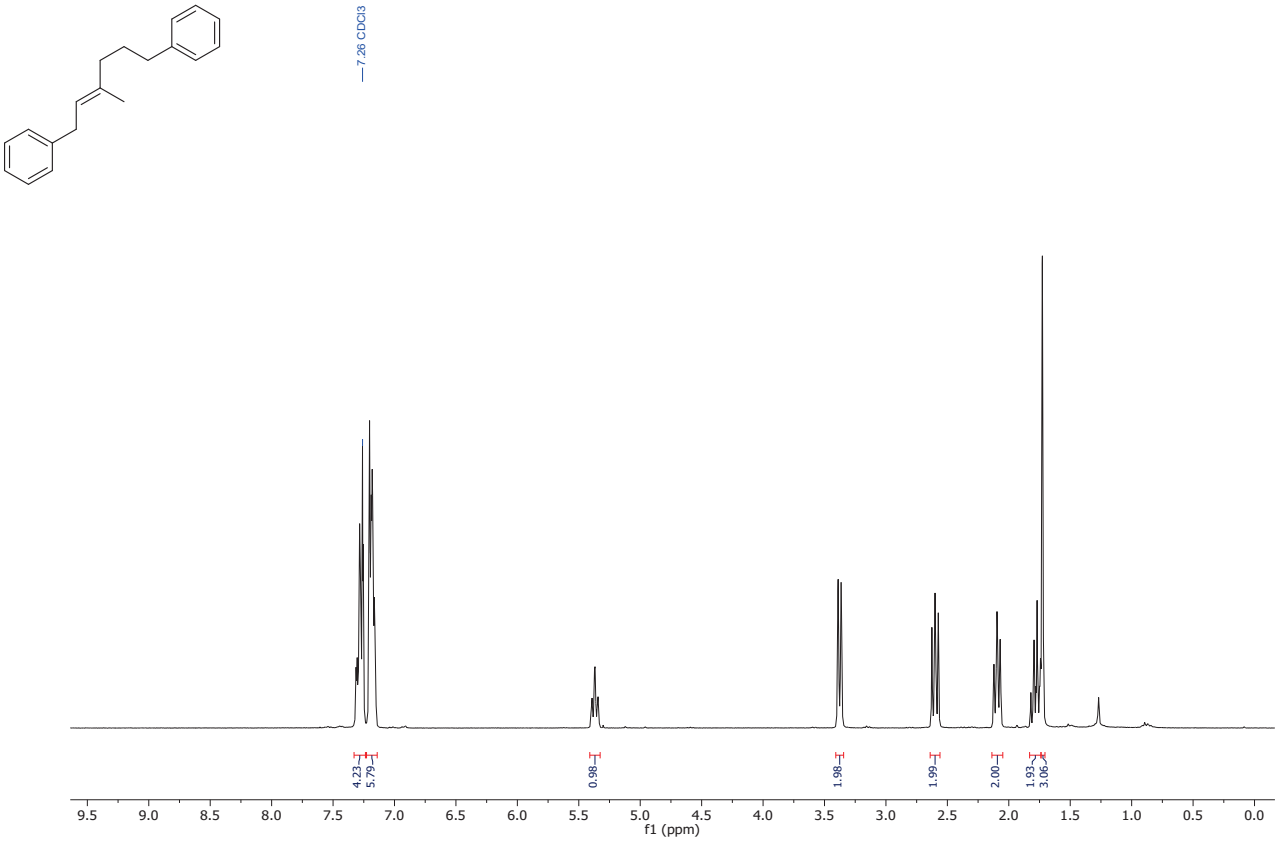
Z-olefin



(3-methylhex-2-ene-1,6-diyl)dibenzene (57)

^{1}H NMR (300 MHz, $CDCl_3$)

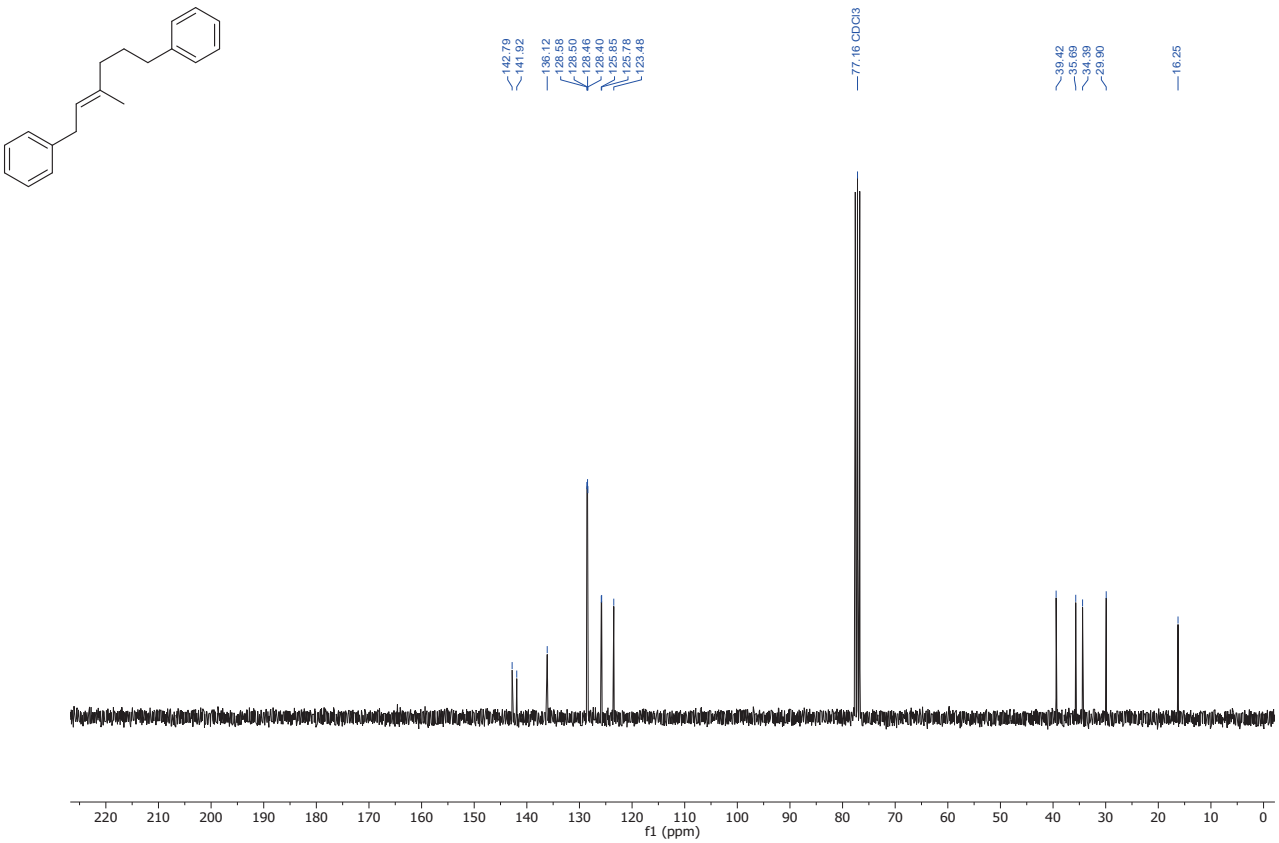
E-olefin



(3-methylhex-2-ene-1,6-diyl)dibenzene (57)

^{13}C NMR (75 MHz, $CDCl_3$)

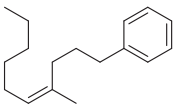
E-olefin

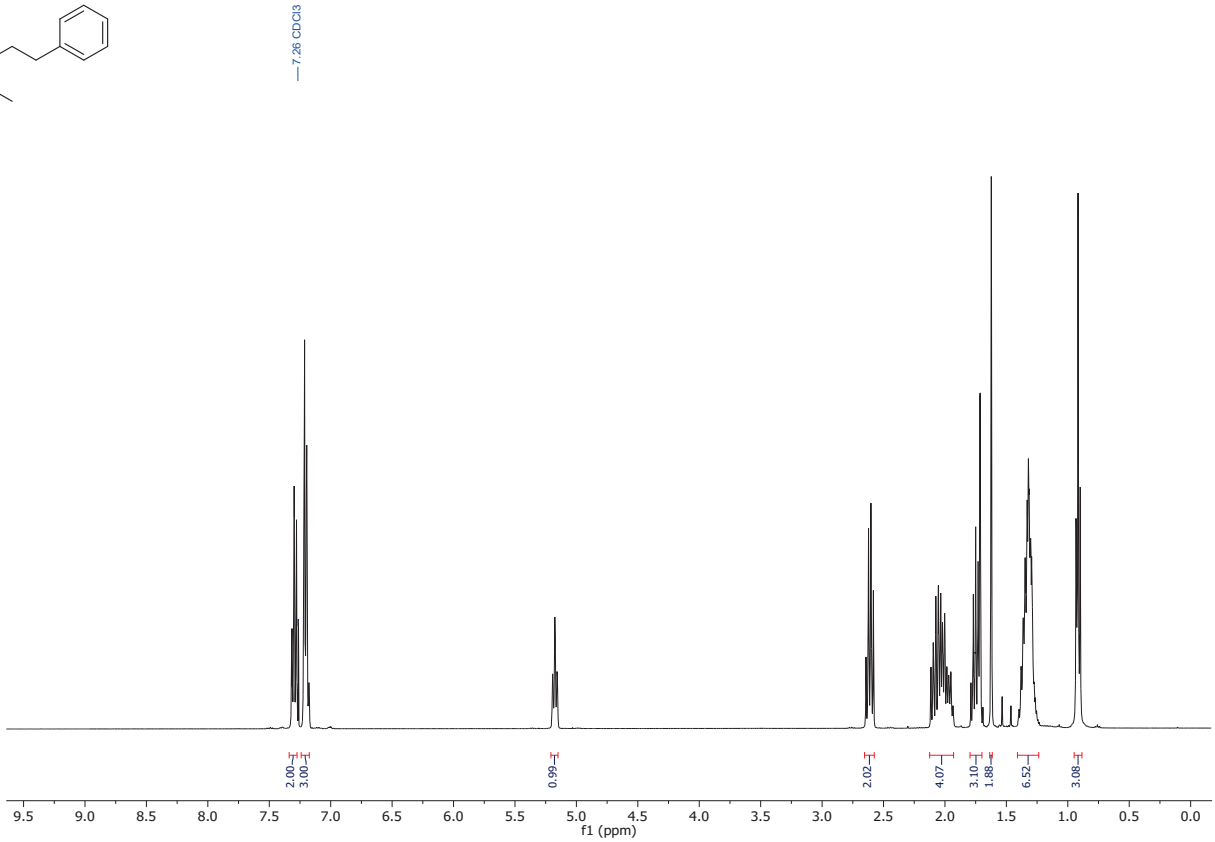


(4-methyldec-4-en-1-yl)benzene (62)

^{1}H NMR (300 MHz, $CDCl_3$)

Mix of olefin

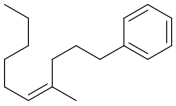


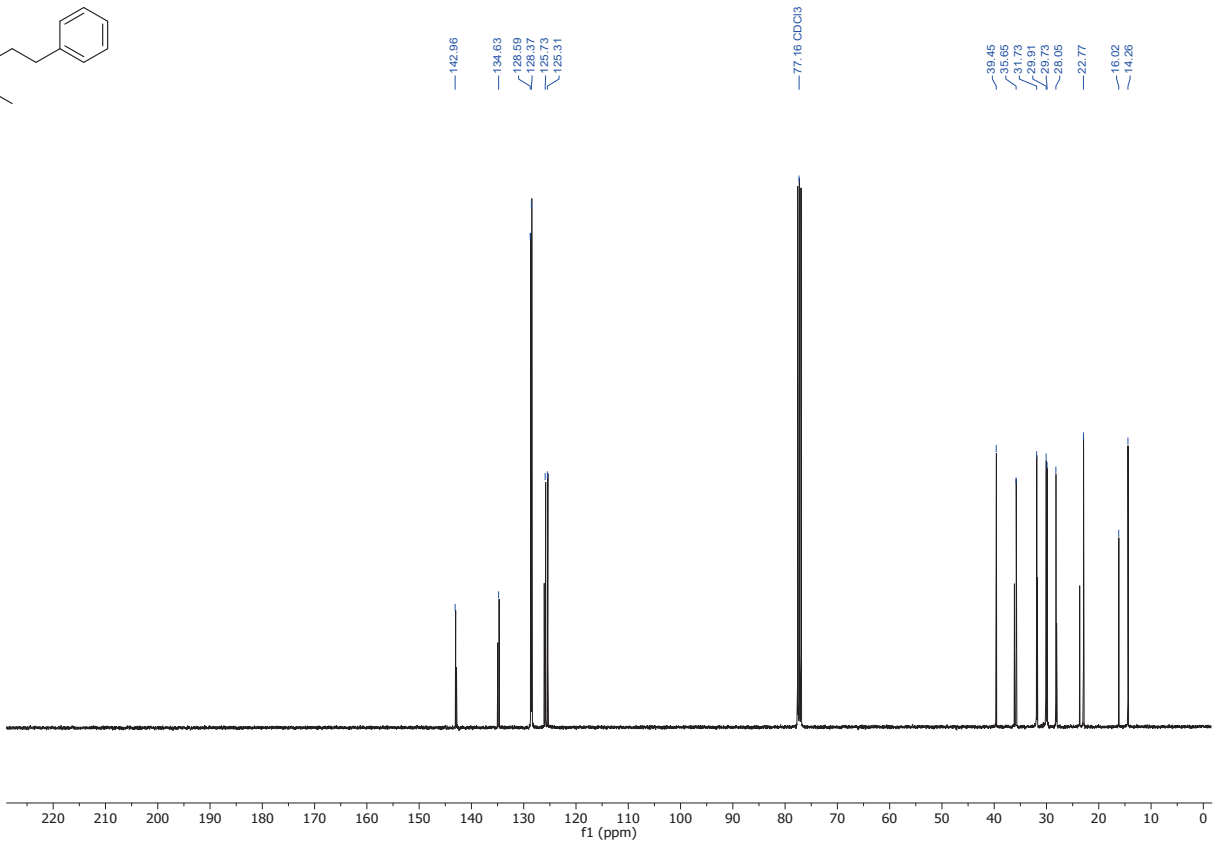


(4-methyldec-4-en-1-yl)benzene (62)

^{13}C NMR (75 MHz, $CDCl_3$)

Z-olefin

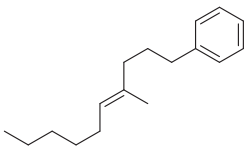


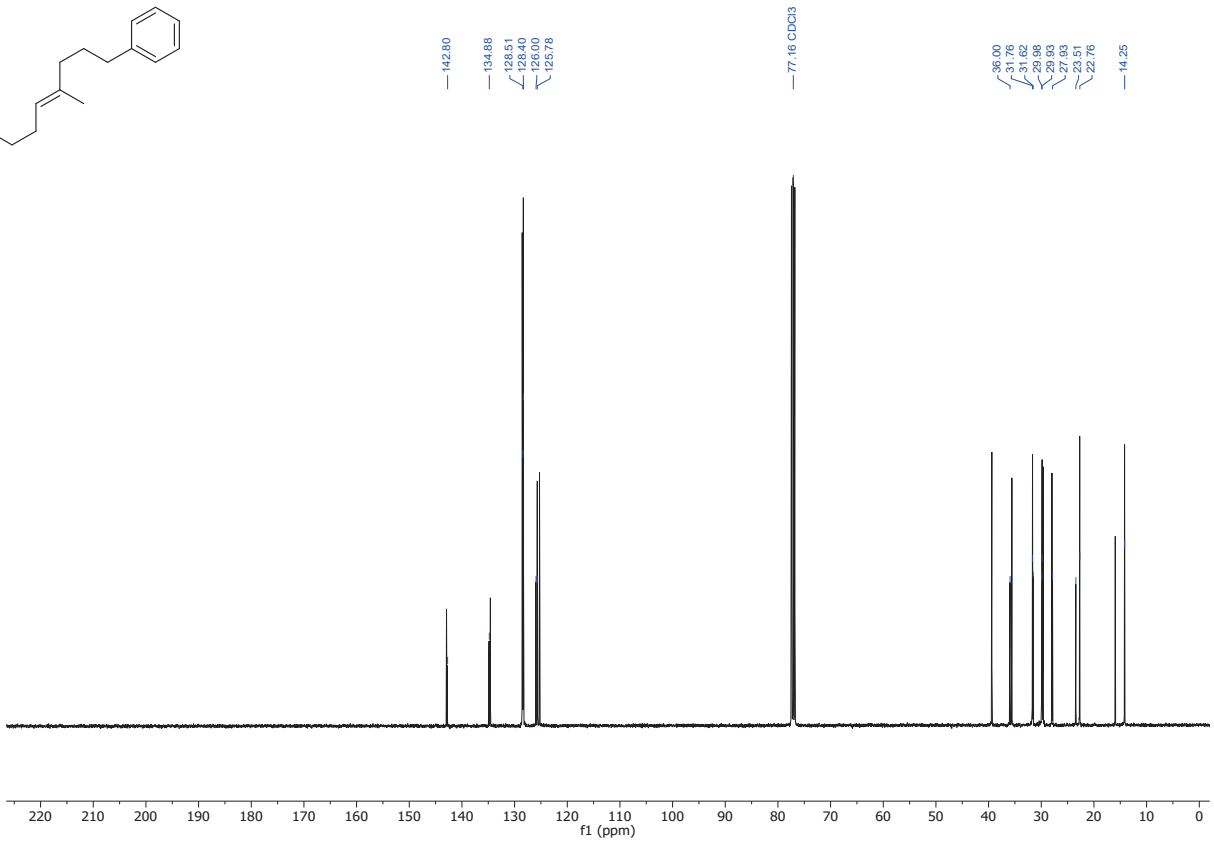


(4-methyldec-4-en-1-yl)benzene (62)

^{13}C NMR (75 MHz, $CDCl_3$)

E-olefin

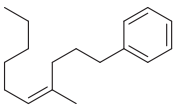


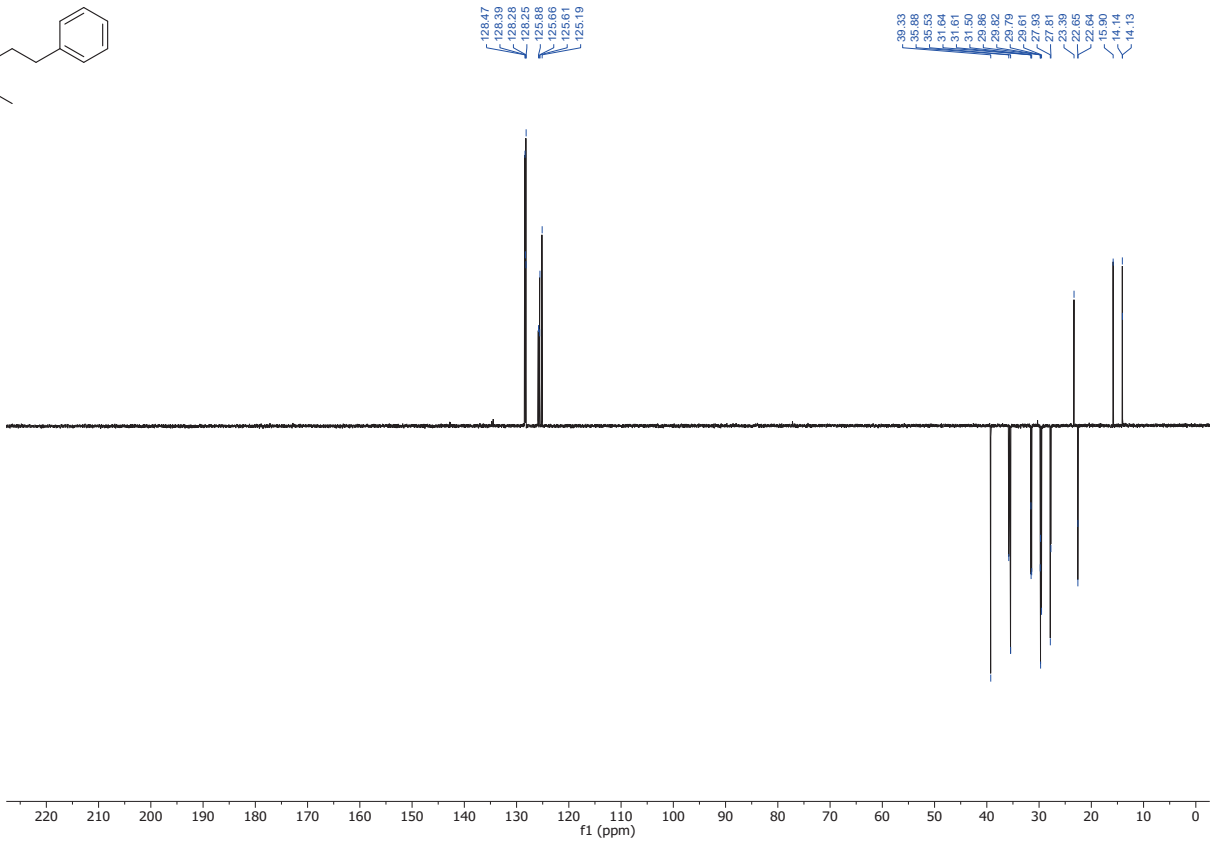


(4-methyldec-4-en-1-yl)benzene (62)

^{13}C NMR Dept-135 (100 MHz, $CDCl_3$)

Mix of olefin

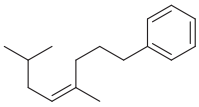


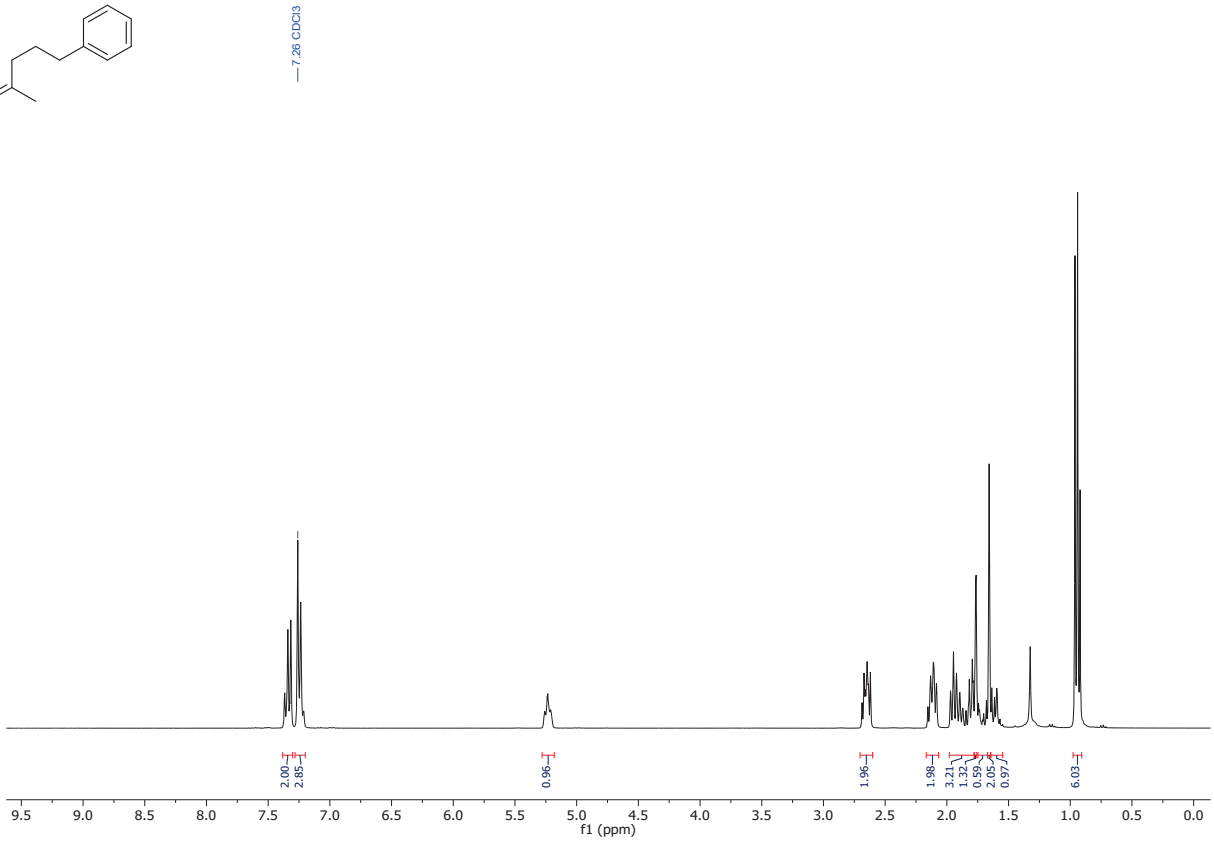


(4,7-dimethyloct-4-en-1-yl)benzene (66)

^{1}H NMR (300 MHz, $CDCl_3$)

Mix of olefin

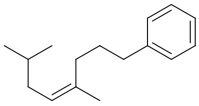


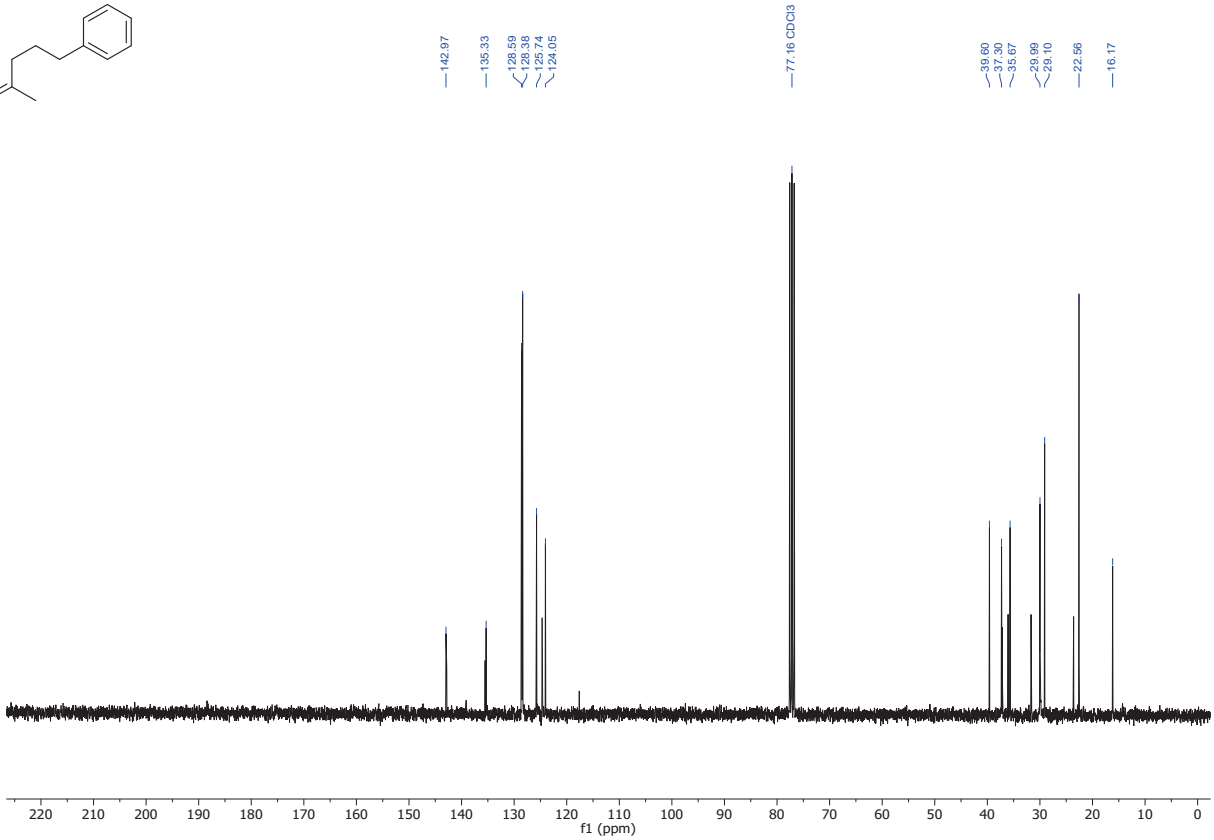


(4,7-dimethyloct-4-en-1-yl)benzene (66)

^{13}C NMR (75 MHz, $CDCl_3$)

Z-olefin

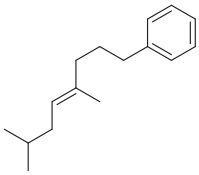


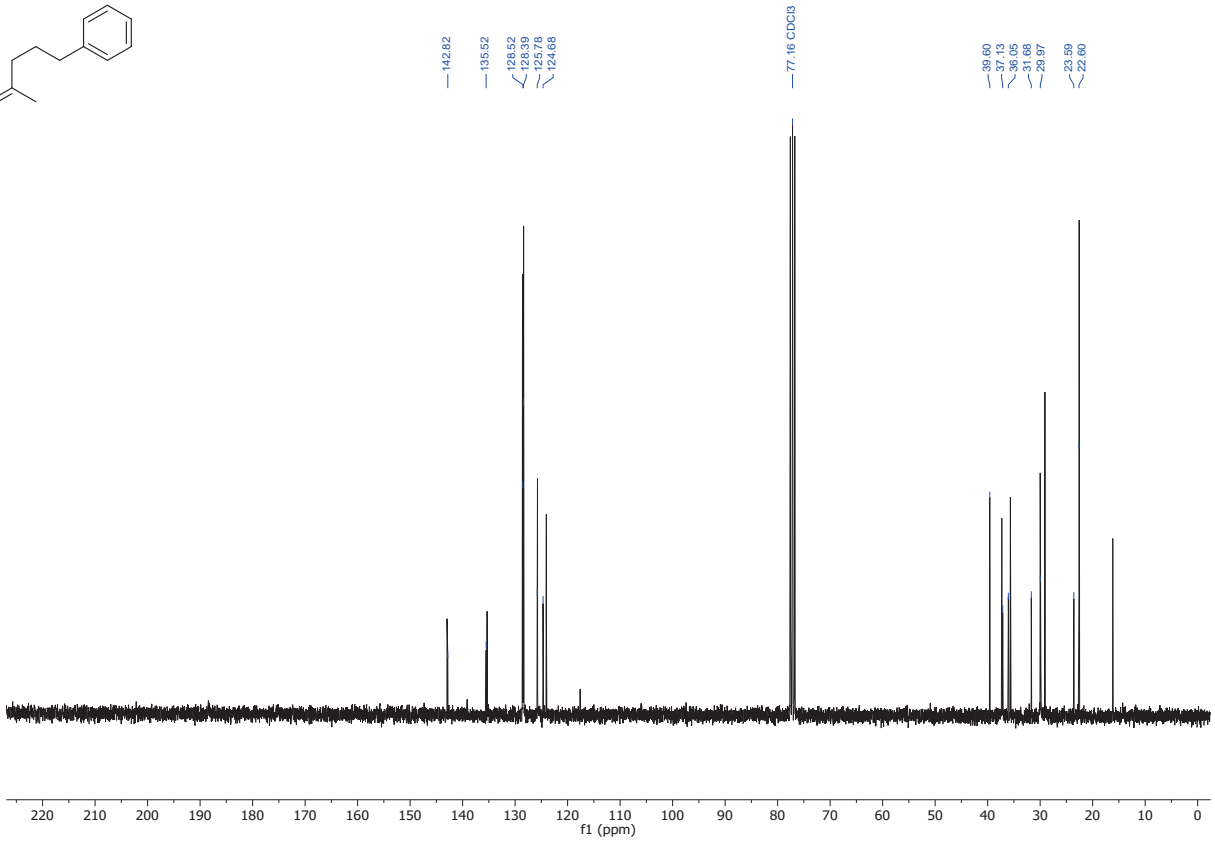


(4,7-dimethyloct-4-en-1-yl)benzene (66)

^{13}C NMR (75 MHz, $CDCl_3$)

E-olefin

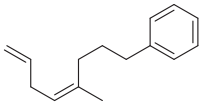


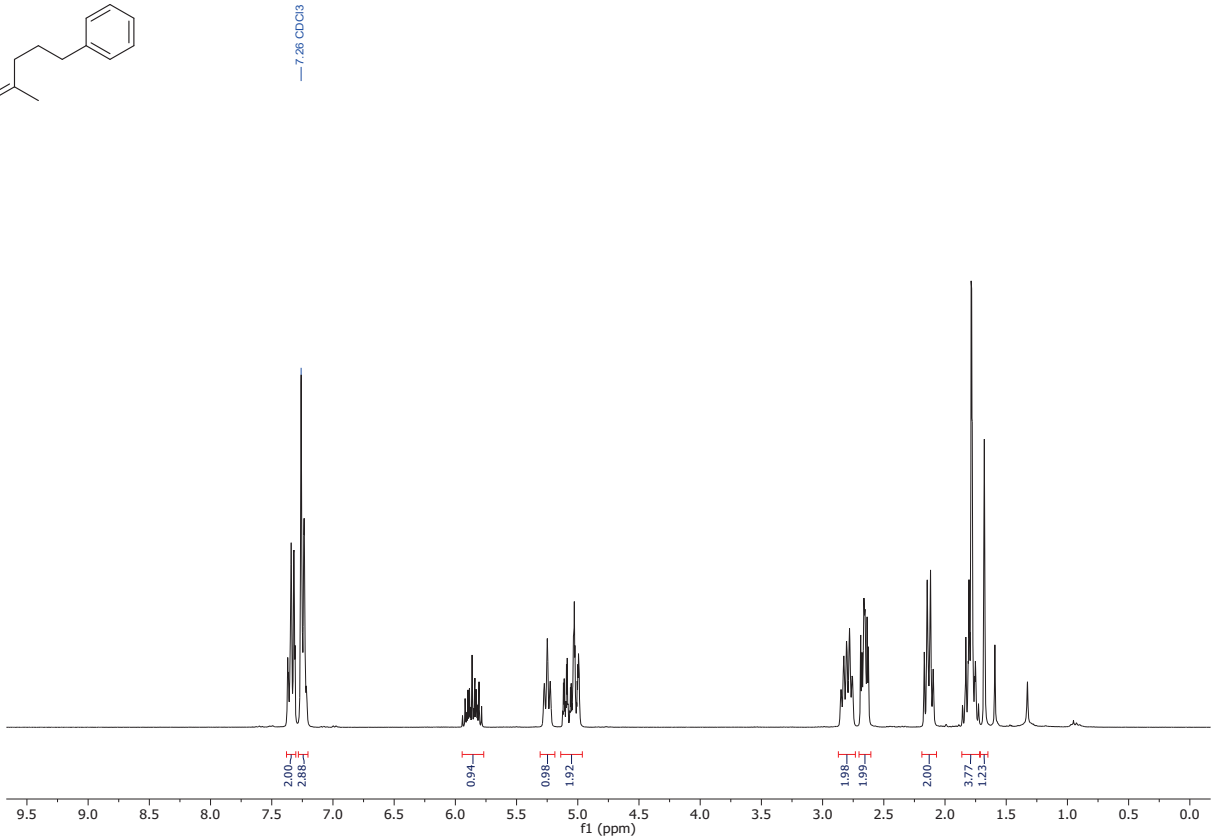


(4-methylocta-4,7-dien-1-yl)benzene (63)

^{1}H NMR (300 MHz, $CDCl_3$)

Mix of olefin

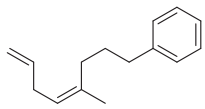


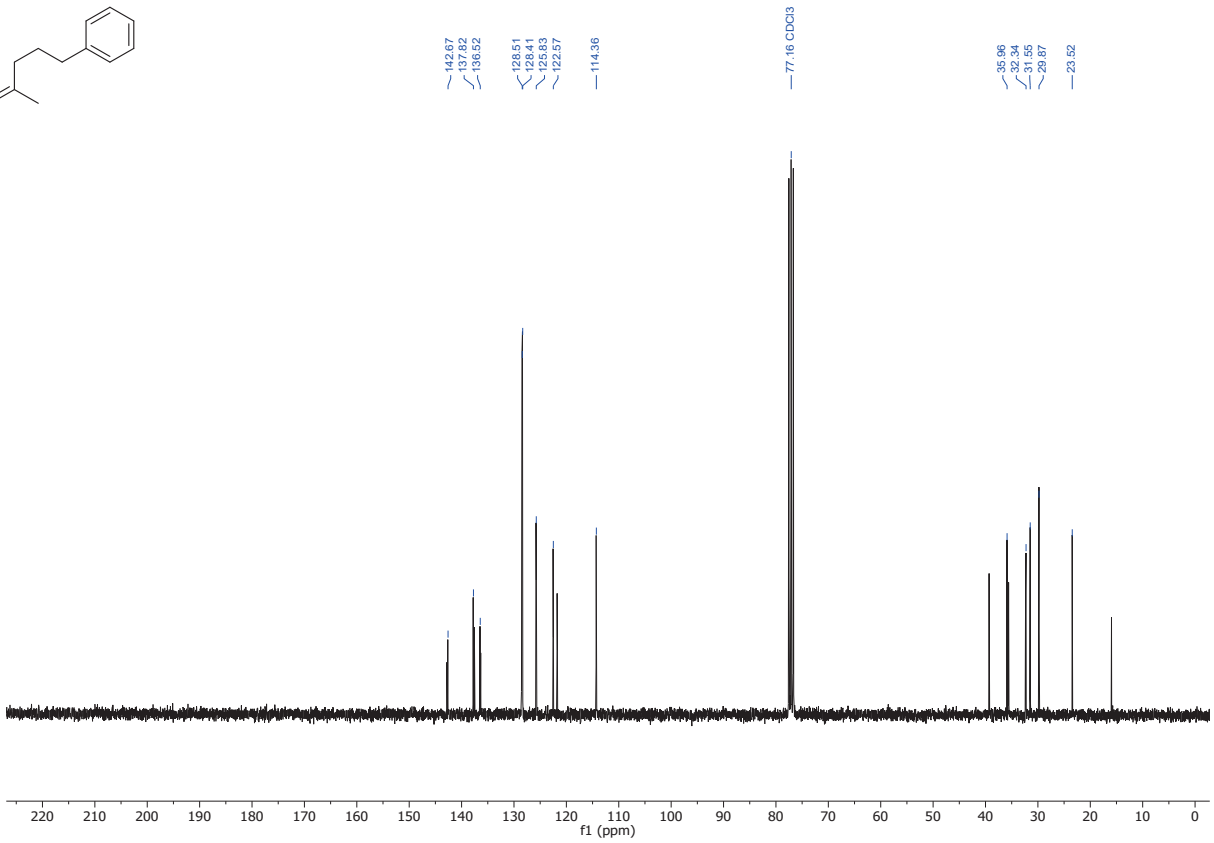


(4-methylocta-4,7-dien-1-yl)benzene (63)

^{13}C NMR (75 MHz, $CDCl_3$)

Z-olefin

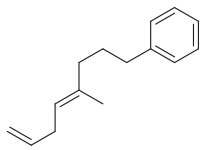


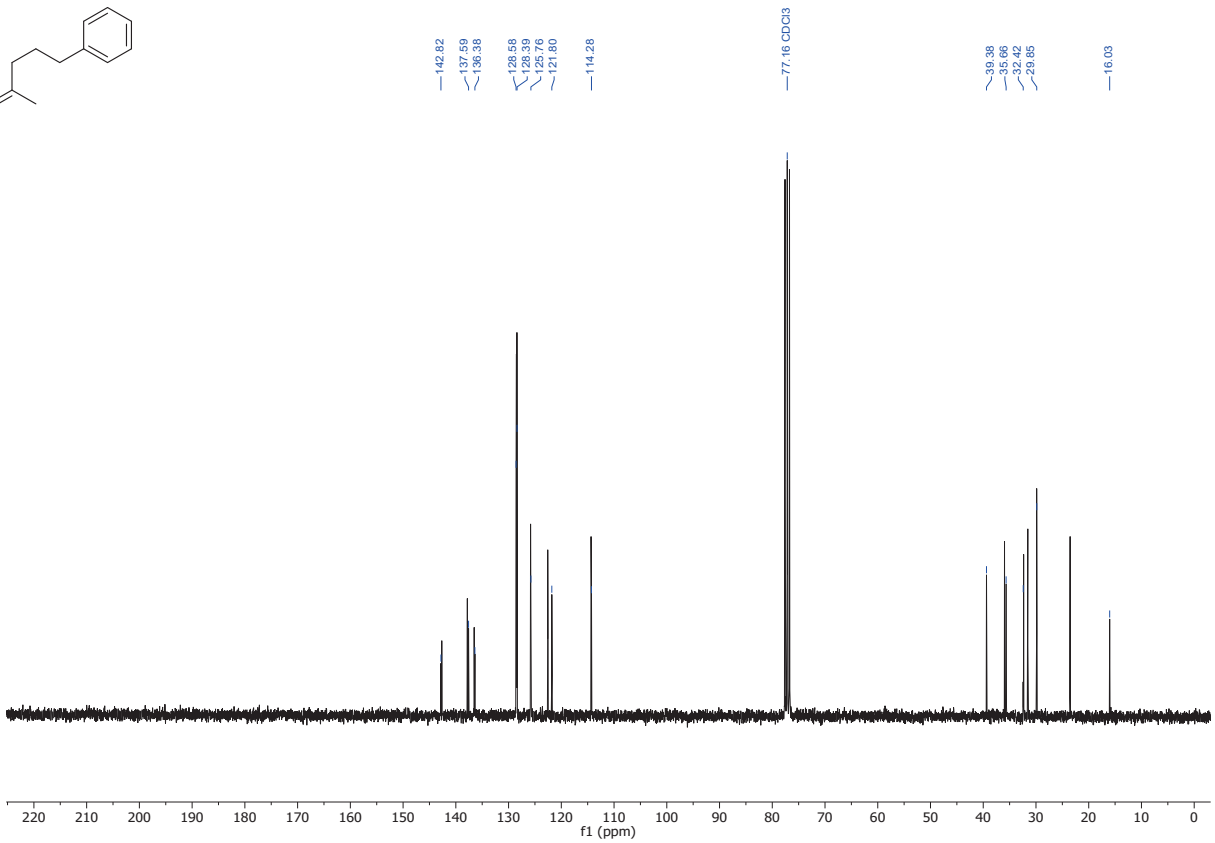


(4-methylocta-4,7-dien-1-yl)benzene (63)

^{13}C NMR (75 MHz, $CDCl_3$)

E-olefin

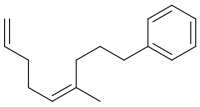


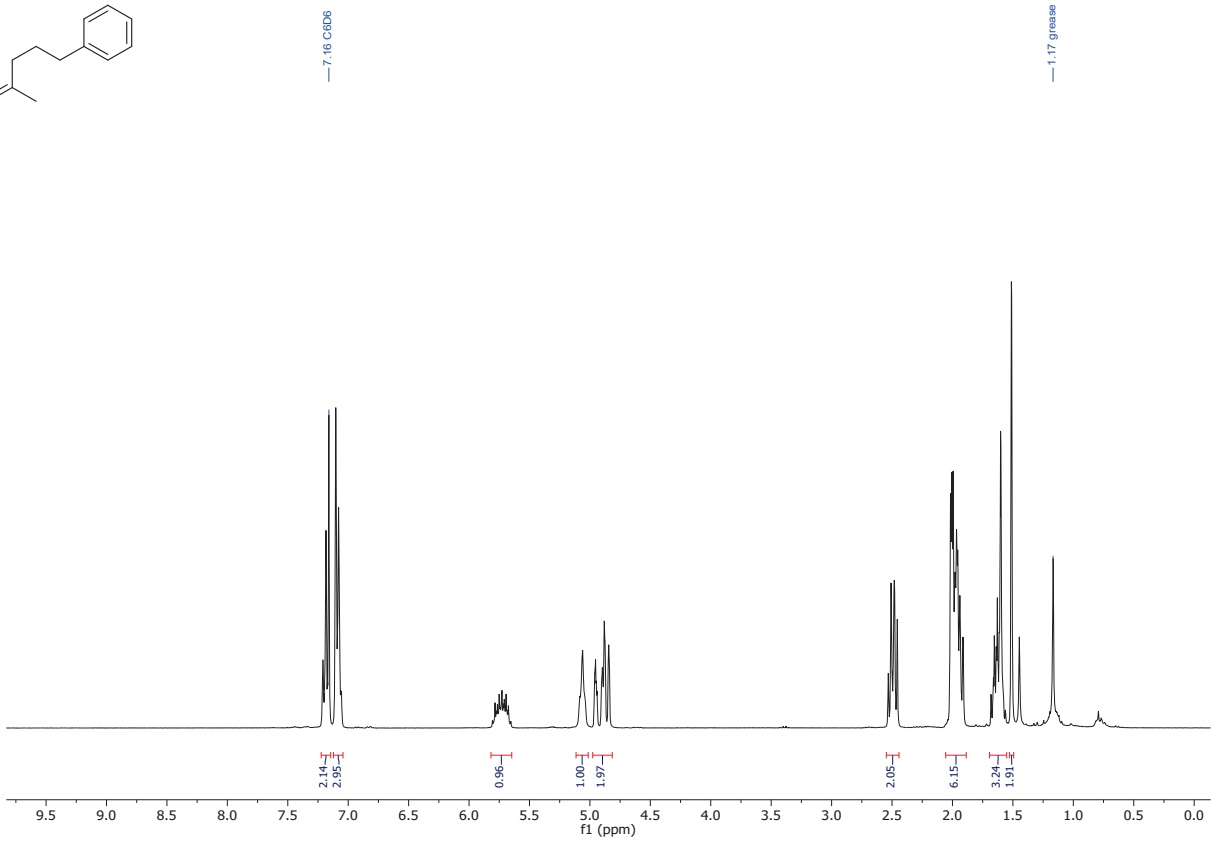


(4-methylnona-4,8-dien-1-yl)benzene (65)

^{1}H NMR (300 MHz, $CDCl_3$)

Mix of olefin

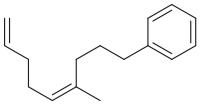


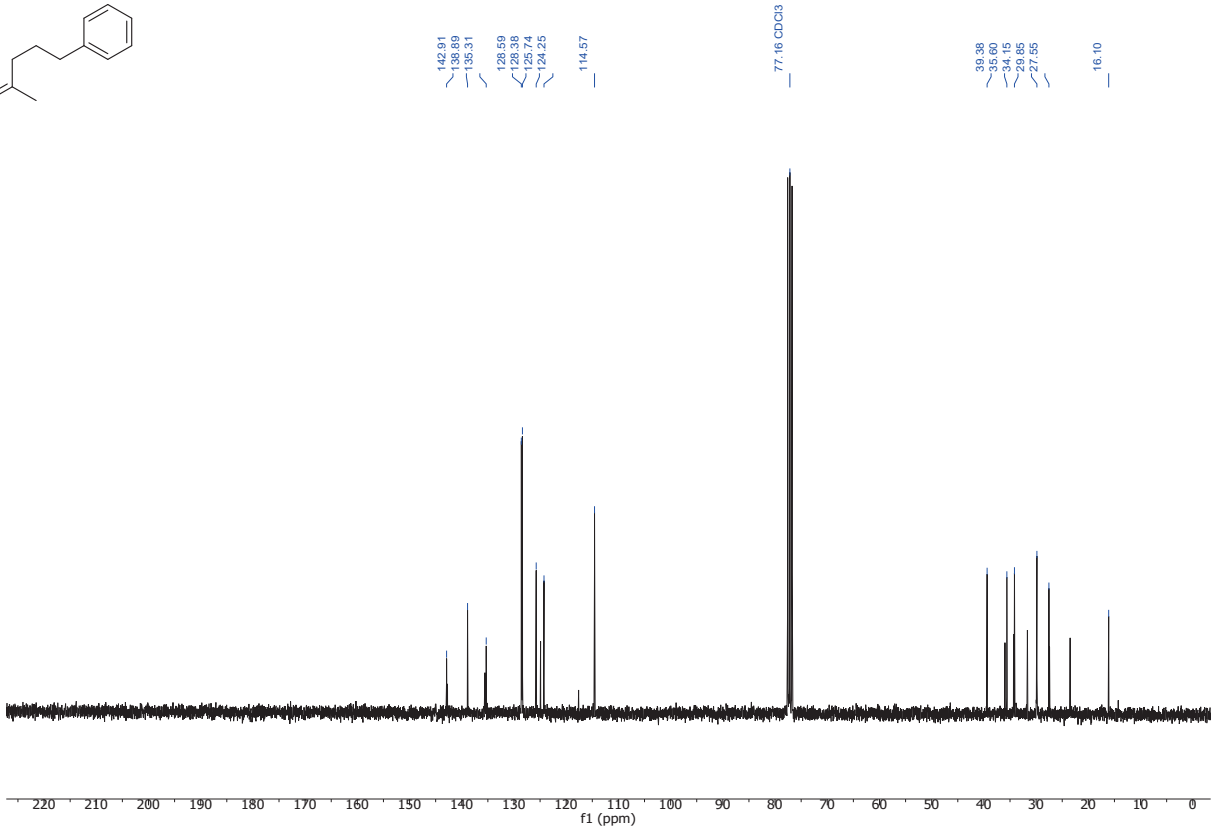


(4-methylnona-4,8-dien-1-yl)benzene (65)

^{13}C NMR (75 MHz, $CDCl_3$)

Z-olefin

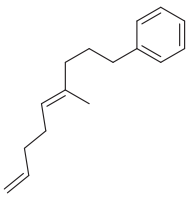


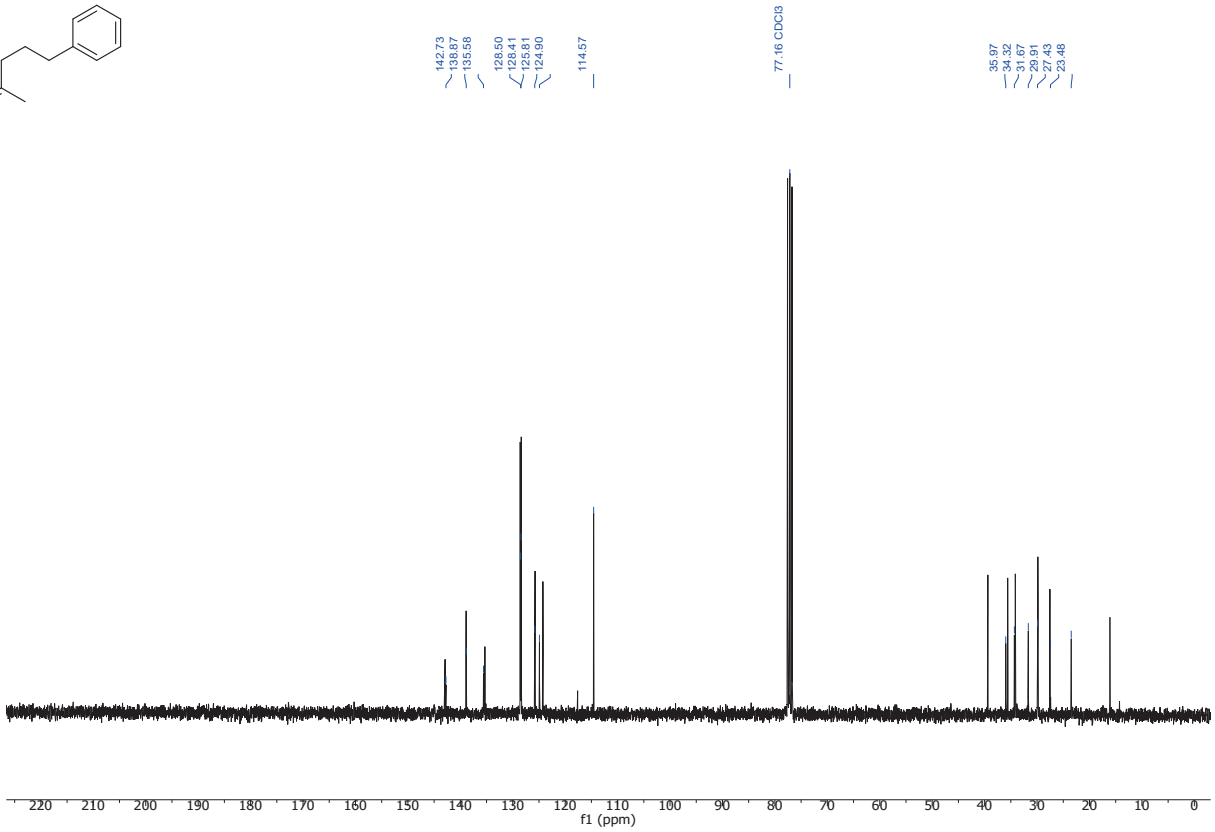


(4-methylnona-4,8-dien-1-yl)benzene (65)

^{13}C NMR (75 MHz, $CDCl_3$)

E-olefin

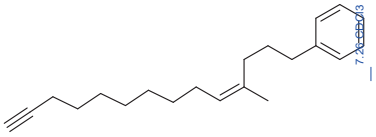


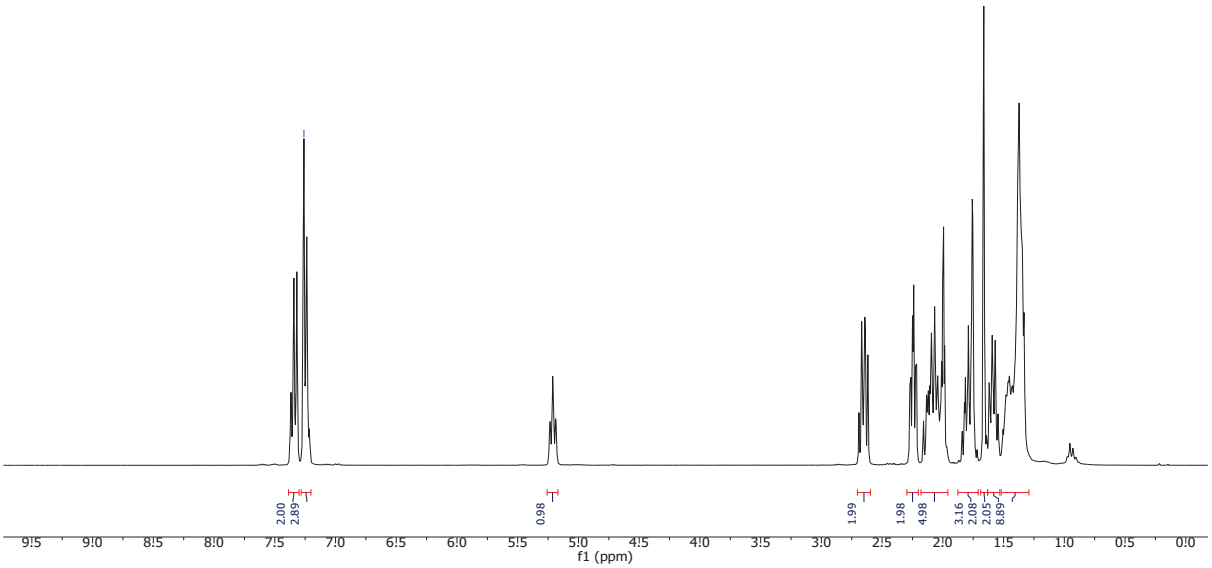


(4-methyltetradec-4-en-13-yn-1-yl)benzene (67)

^{1}H NMR (300 MHz, $CDCl_3$)

Mix of olefin

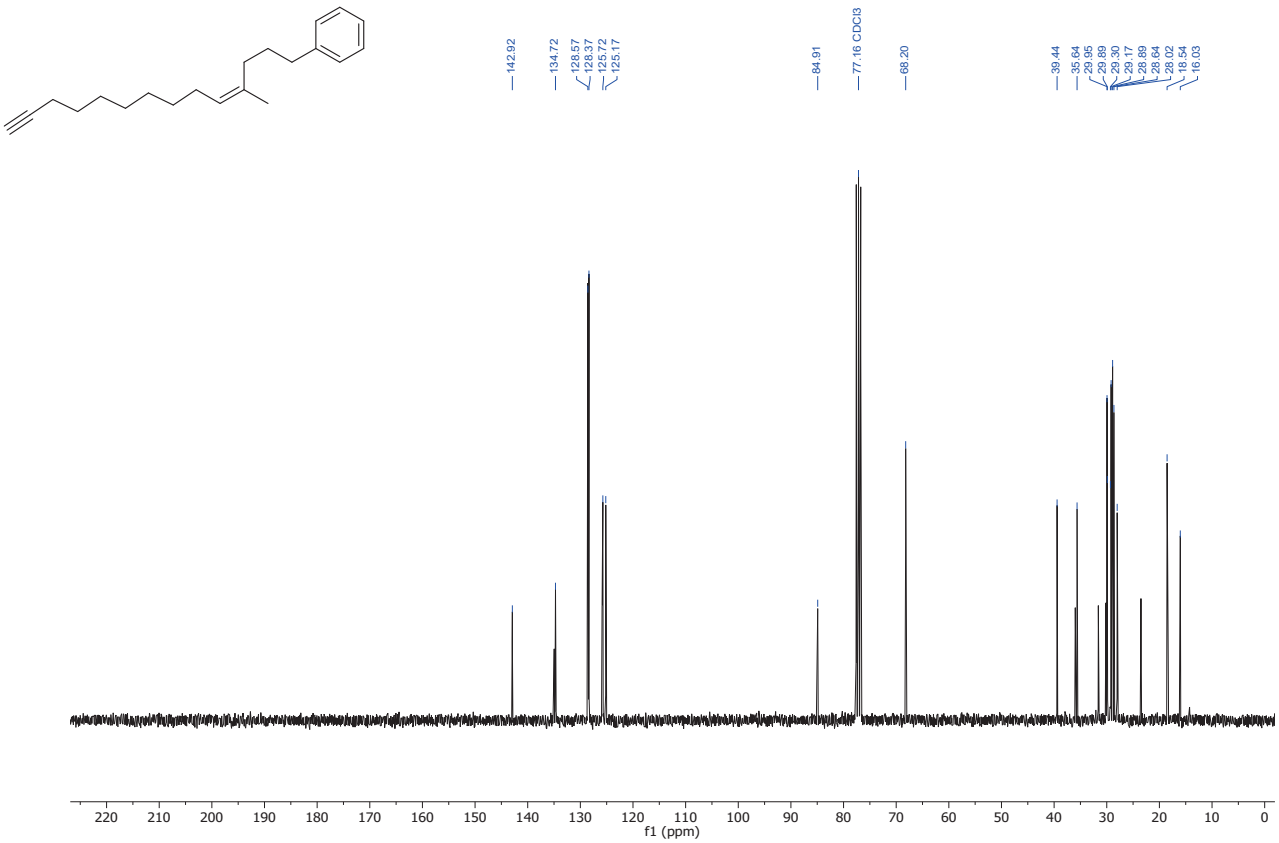




(4-methyltetradec-4-en-13-yn-1-yl)benzene (67)

^{13}C NMR (75 MHz, $CDCl_3$)

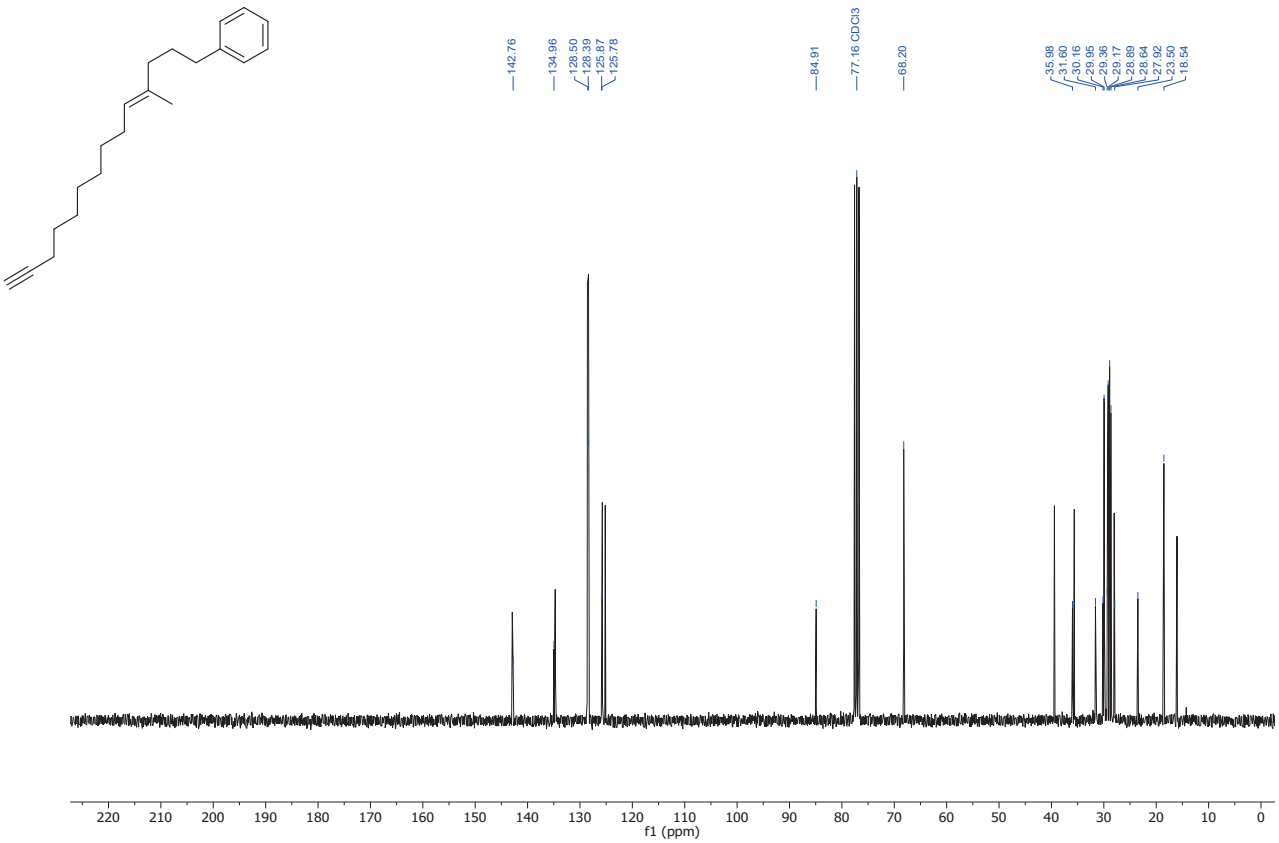
Z-olefin



(4-methyltetradec-4-en-13-yn-1-yl)benzene (67)

^{13}C NMR (75 MHz, $CDCl_3$)

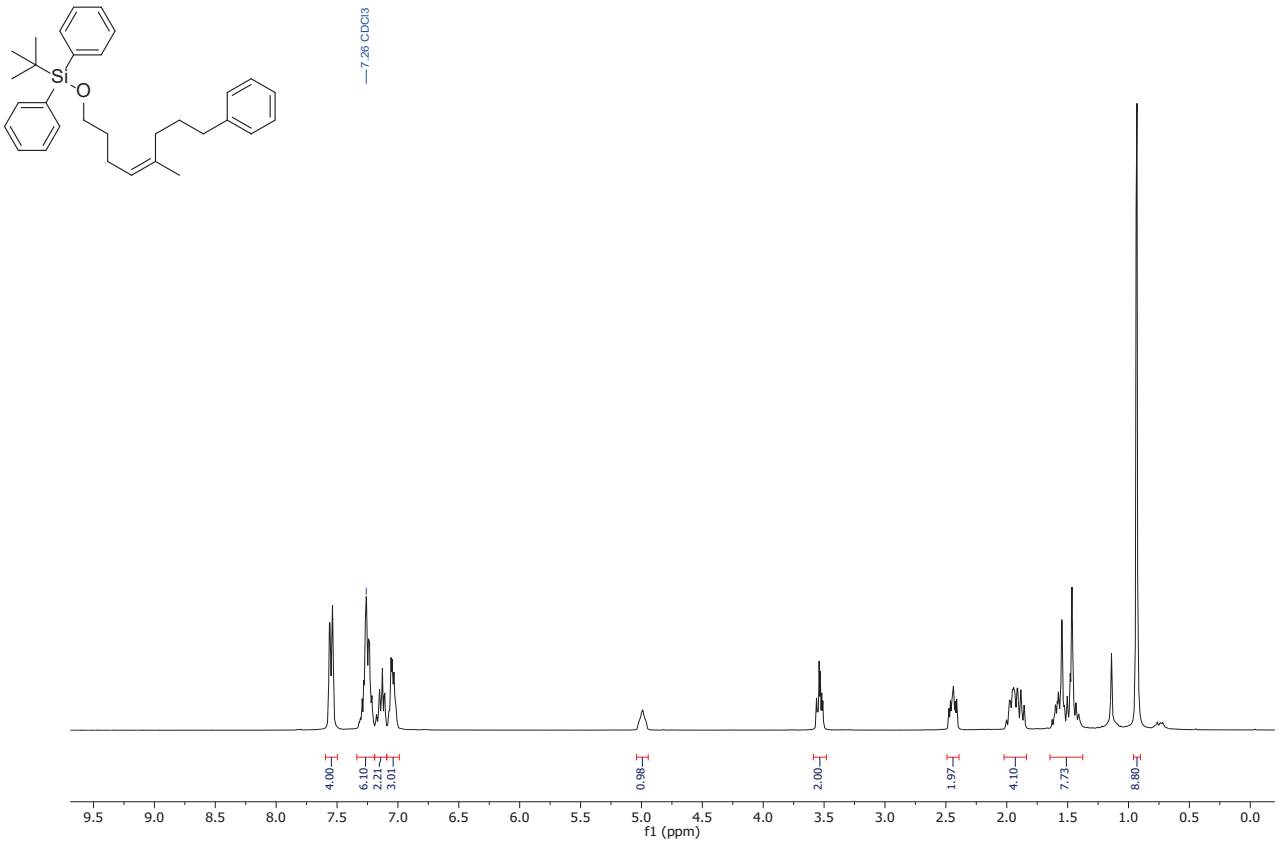
E-olefin



tert-butyl((5-methyl-8-phenyloct-4-en-1-yl)oxy)diphenylsilane (68)

^{1}H NMR (300 MHz, $CDCl_3$)

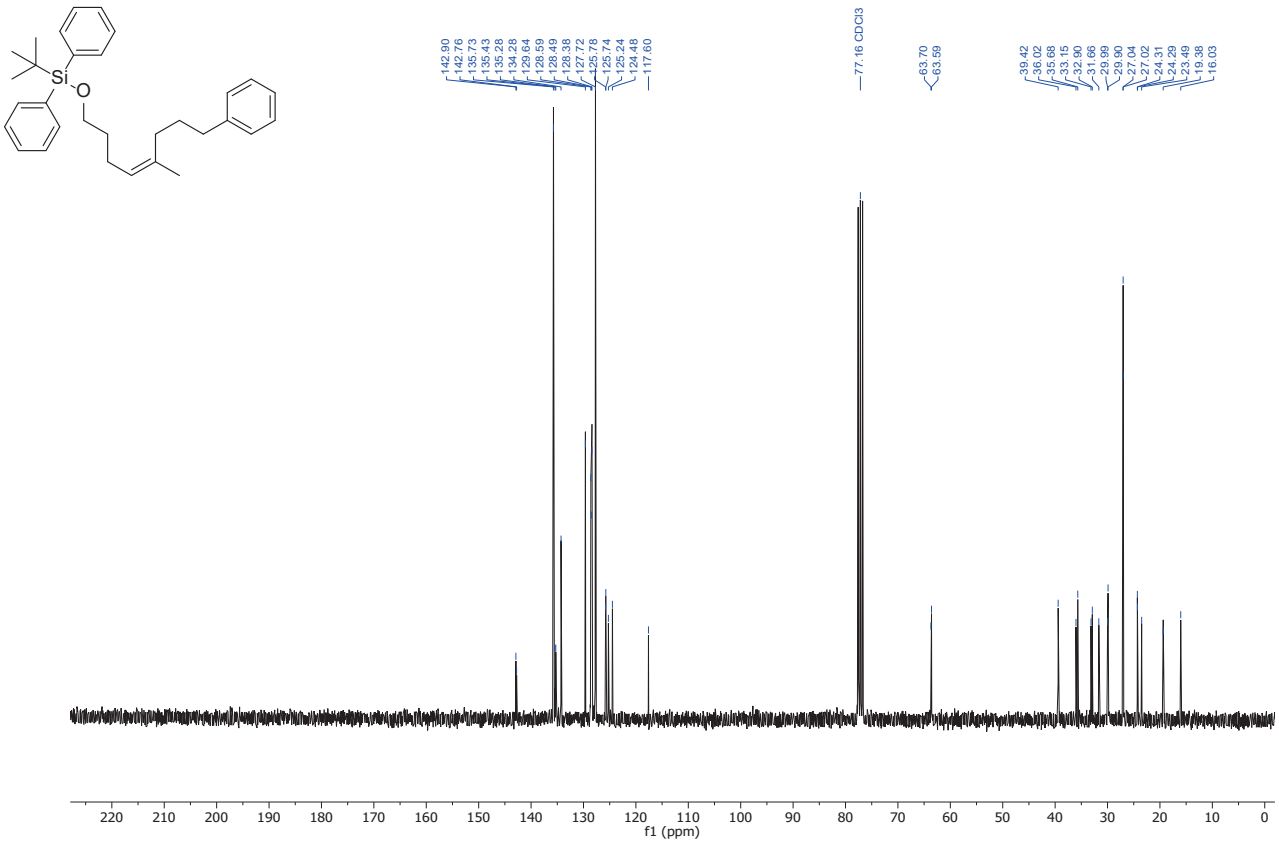
Mix of olefin



tert-butyl((5-methyl-8-phenyloct-4-en-1-yl)oxy)diphenylsilane (68)

^{13}C NMR (75 MHz, $CDCl_3$)

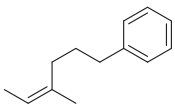
Mix of olefin

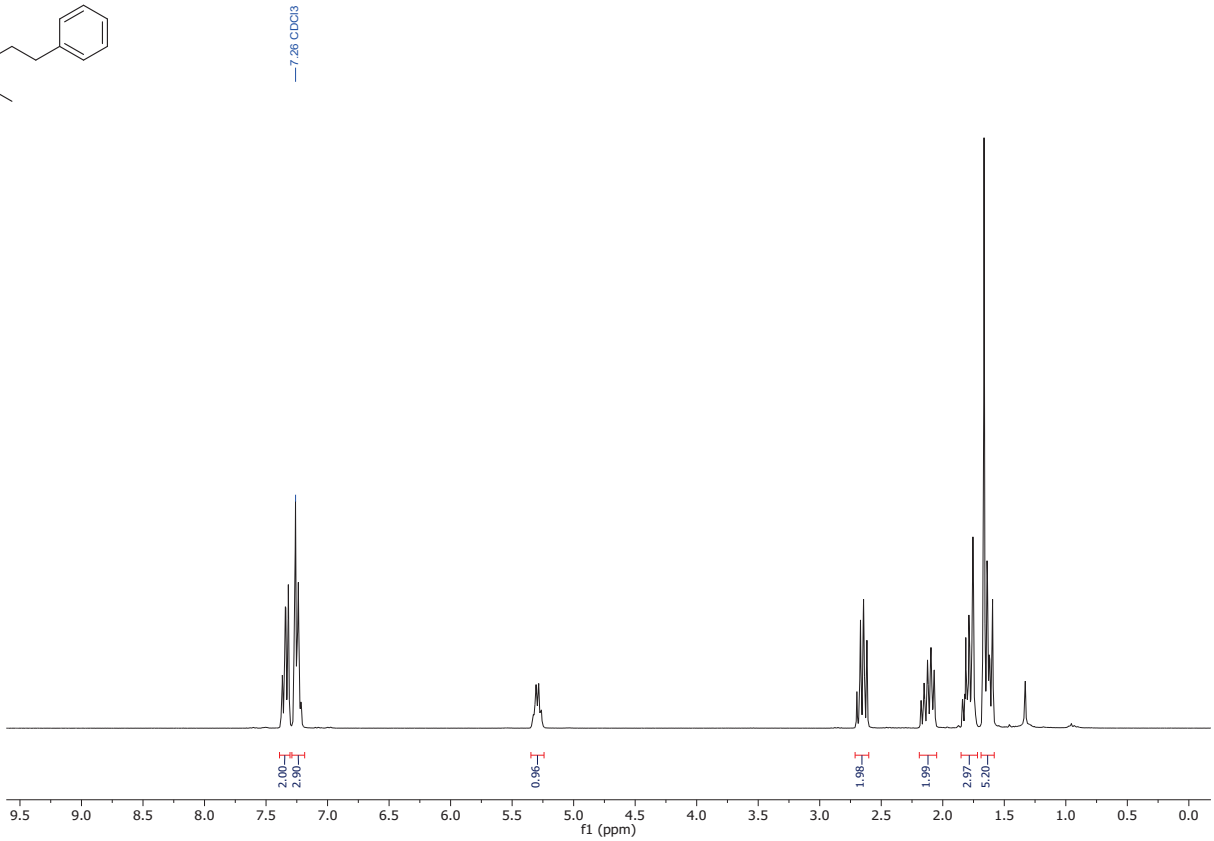


(4-methylhex-4-en-1-yl)benzene (61)

^{1}H NMR (300 MHz, $CDCl_3$)

Mix of olefin

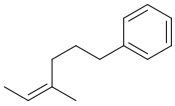


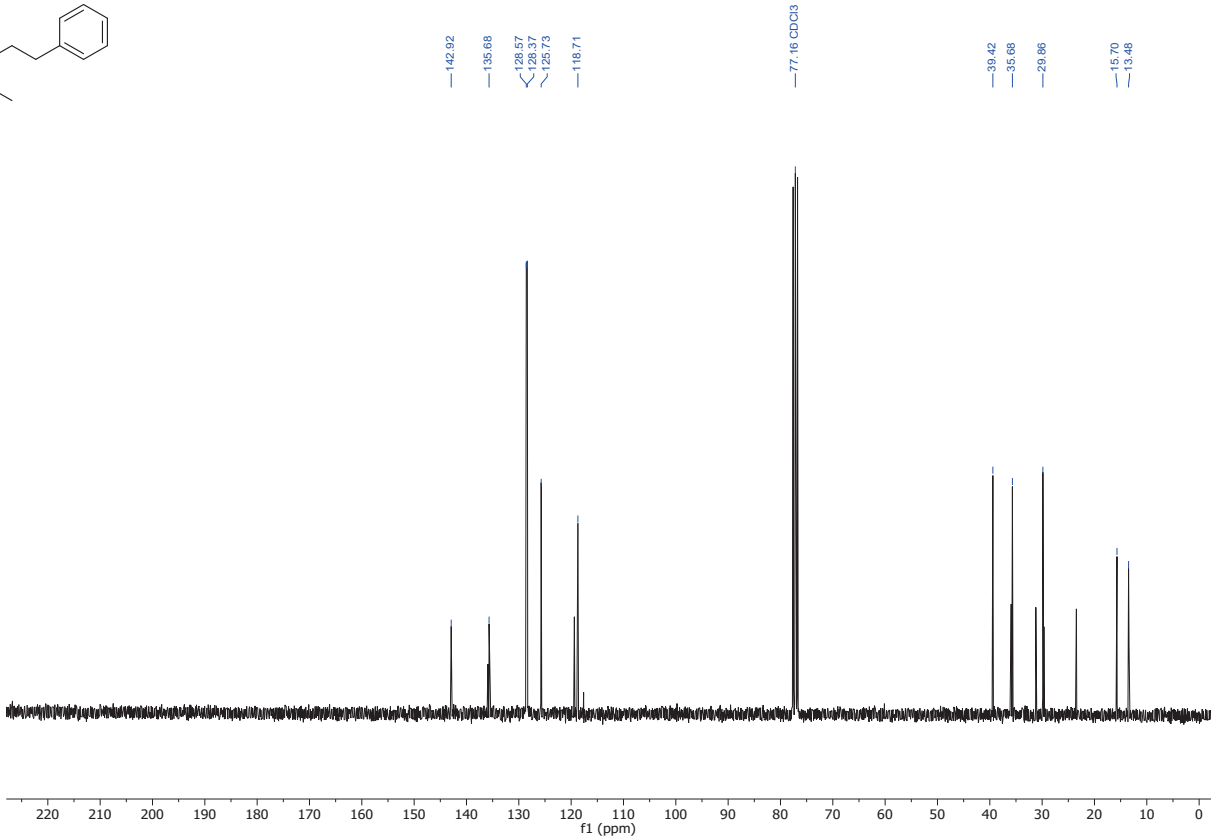


(4-methylhex-4-en-1-yl)benzene (61)

^{13}C NMR (75 MHz, $CDCl_3$)

Z-olefin

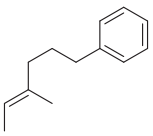


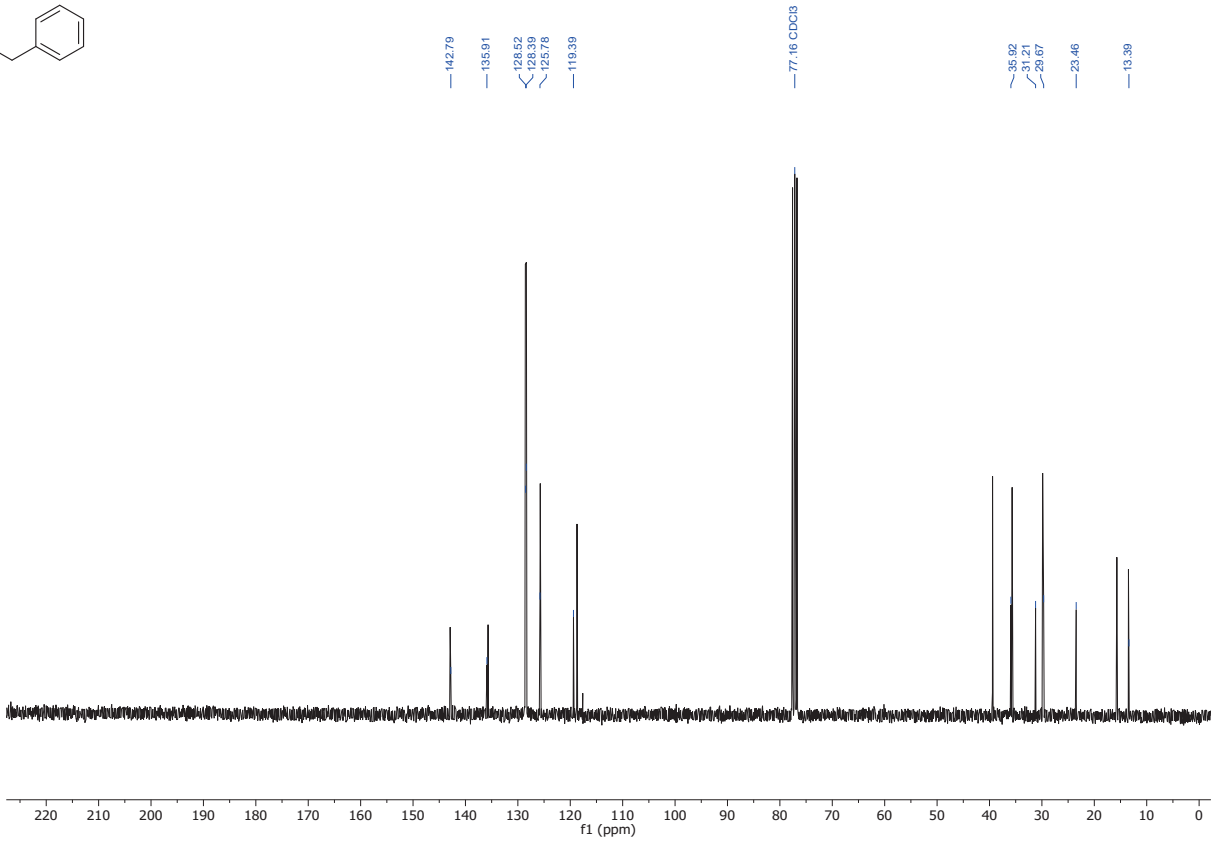


(4-methylhex-4-en-1-yl)benzene (61)

^{13}C NMR (75 MHz, $CDCl_3$)

E-olefin

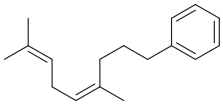


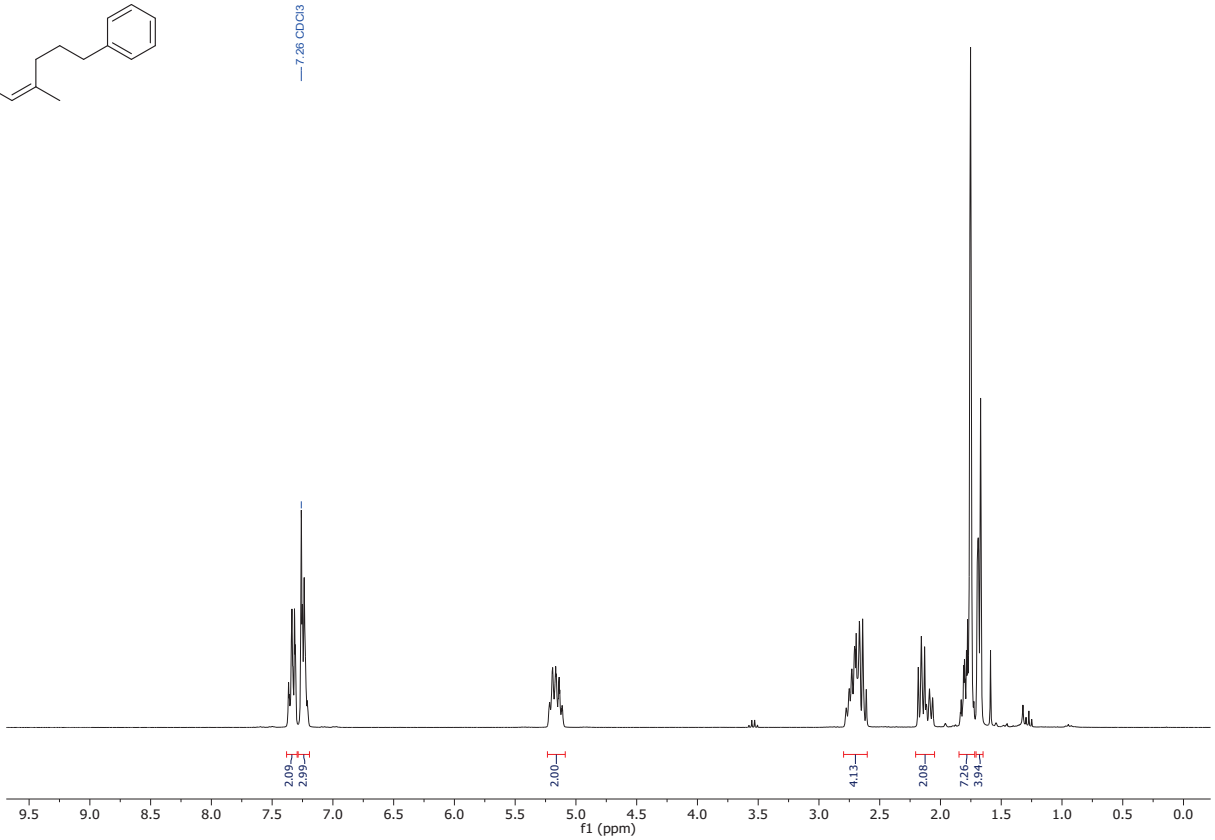


(4,8-dimethylnona-4,7-dien-1-yl)benzene (64)

^{1}H NMR (300 MHz, $CDCl_3$)

Mix of olefin

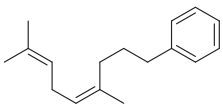


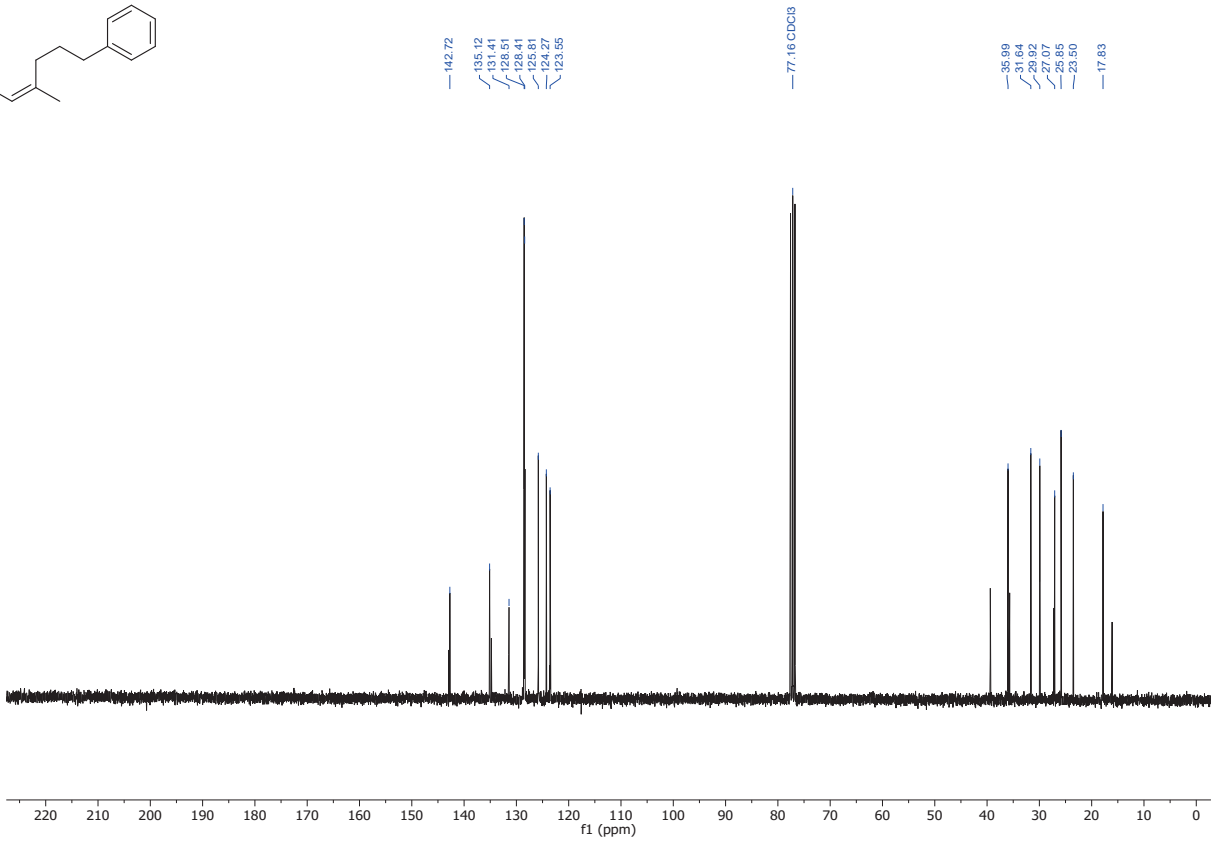


(4,8-dimethylnona-4,7-dien-1-yl)benzene (64)

^{13}C NMR (75 MHz, $CDCl_3$)

Z-olefin

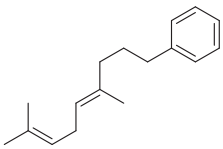


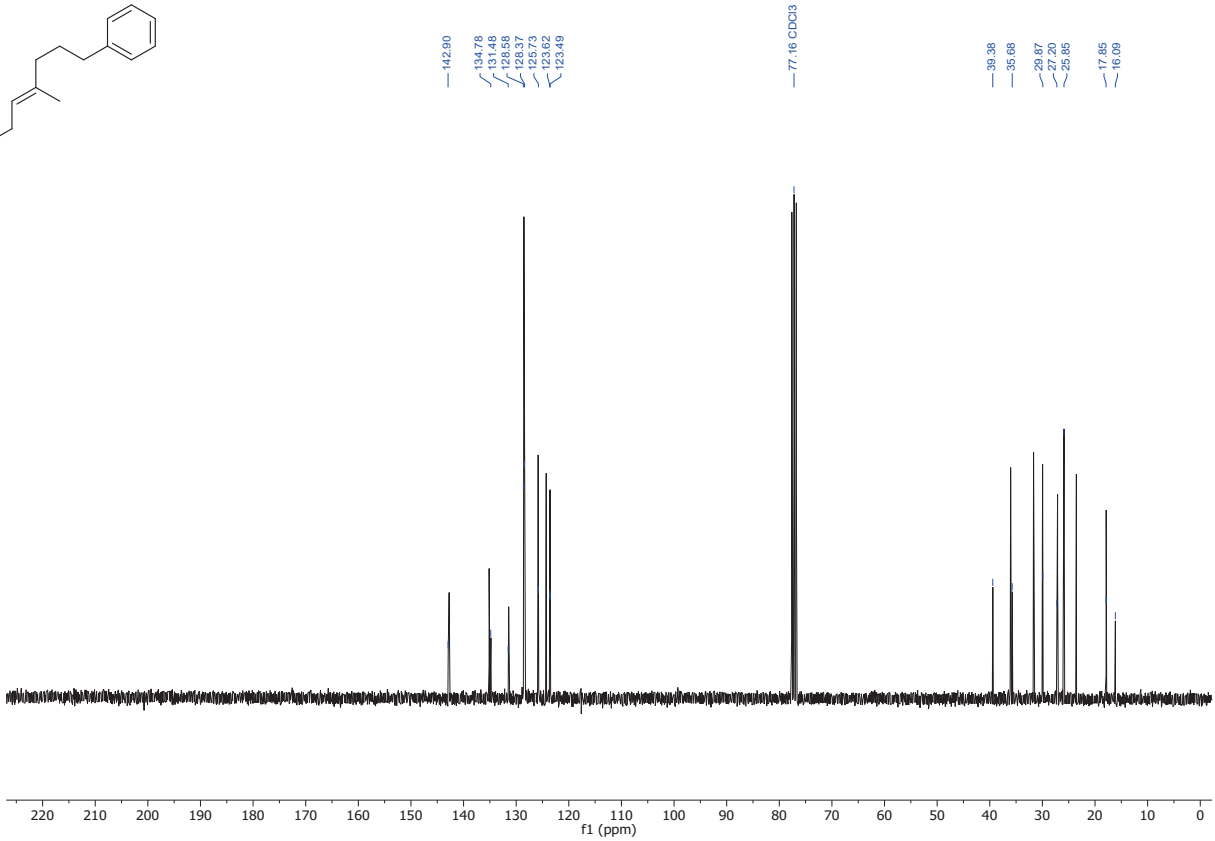


(4,8-dimethylnona-4,7-dien-1-yl)benzene (64)

^{13}C NMR (75 MHz, $CDCl_3$)

E-olefin

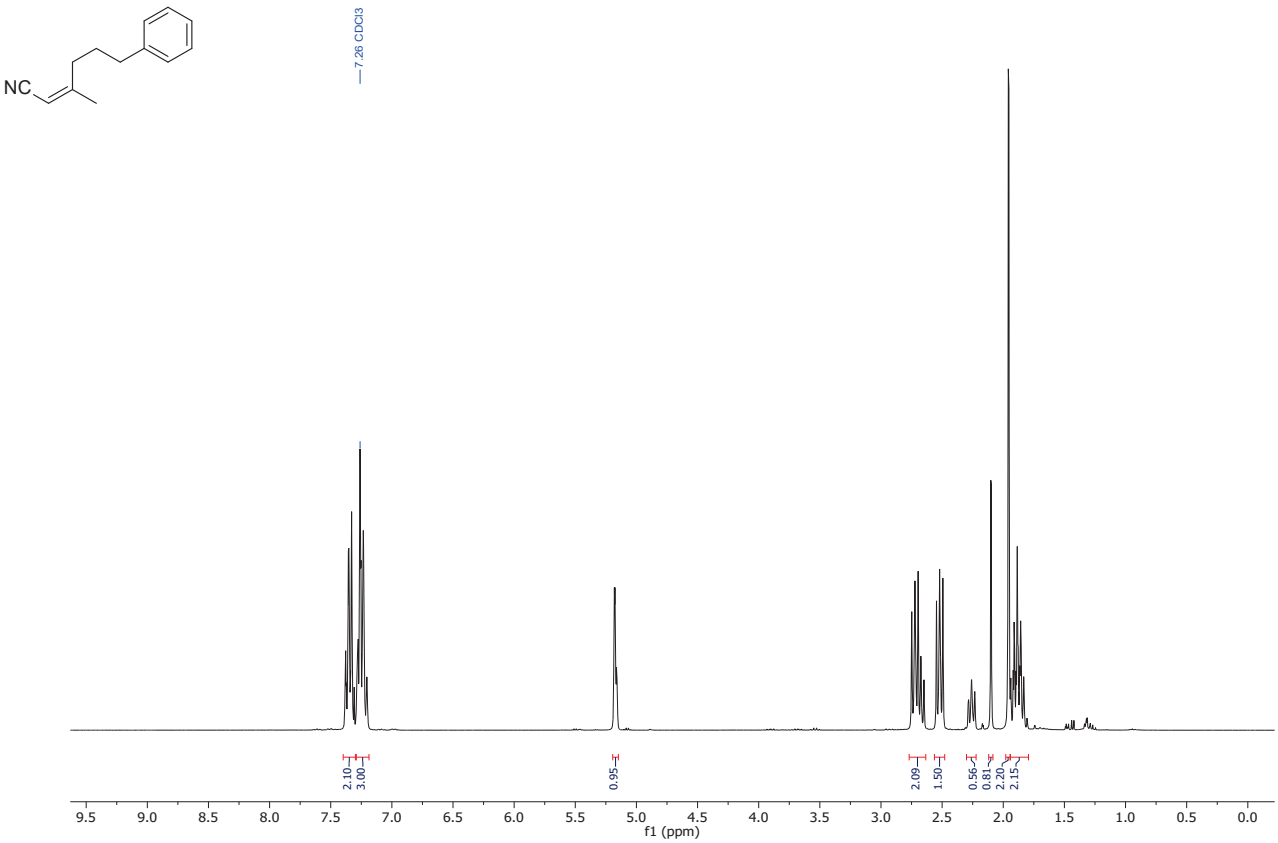




3-methyl-6-phenylhex-2-enenitrile (77)

^{1}H NMR (300 MHz, $CDCl_3$)

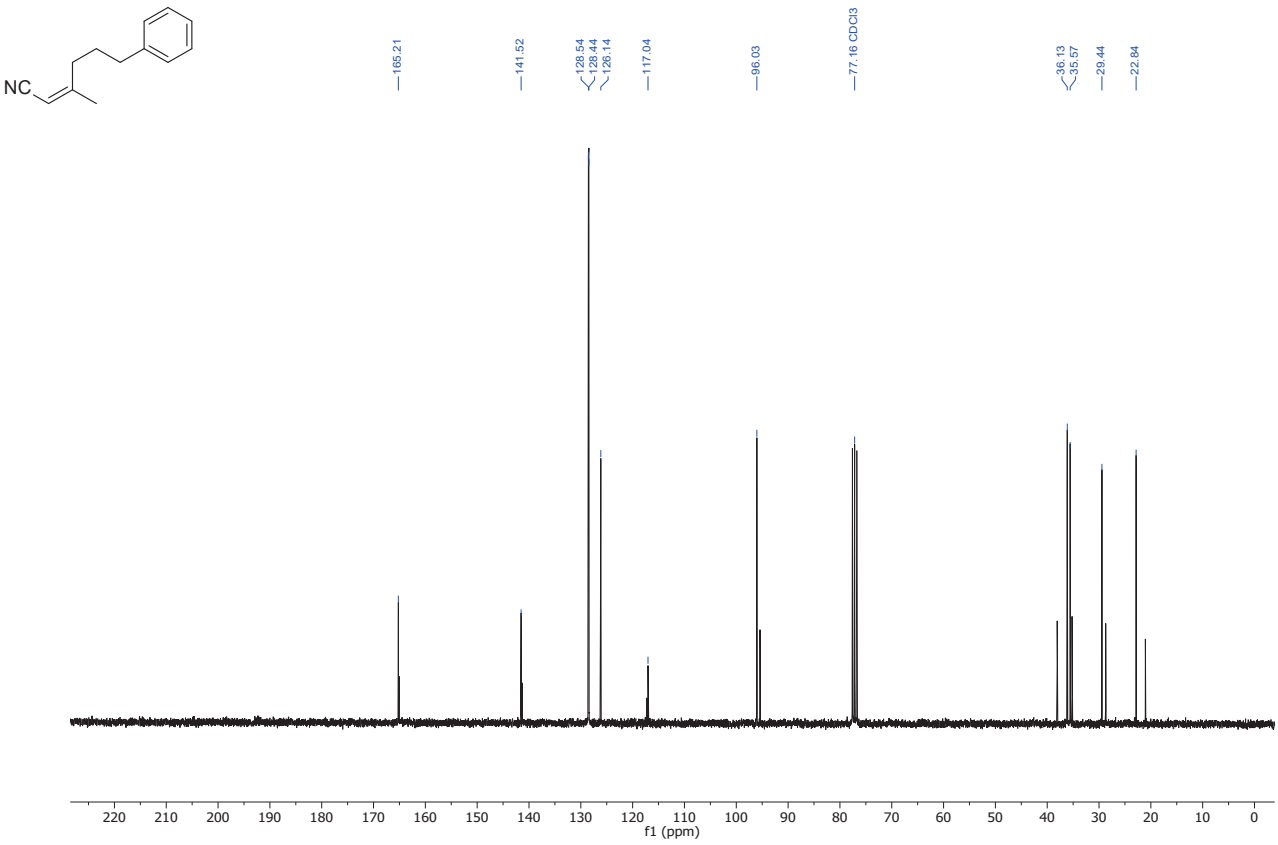
Mix of olefin



3-methyl-6-phenylhex-2-enenitrile (77)

^{13}C NMR (75 MHz, $CDCl_3$)

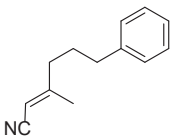
Z-olefin

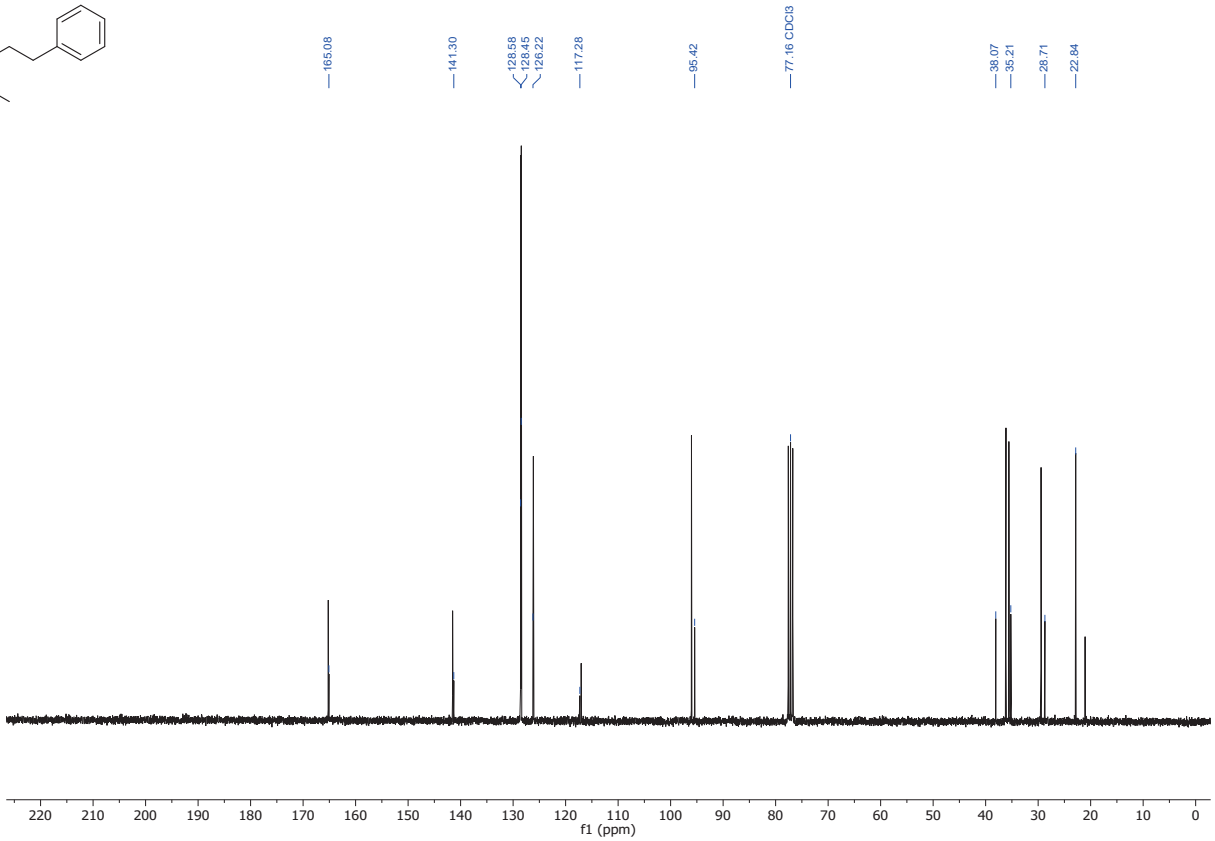


3-methyl-6-phenylhex-2-enenitrile (77)

^{13}C NMR (75 MHz, $CDCl_3$)

E-olefin

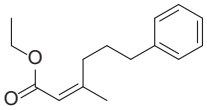


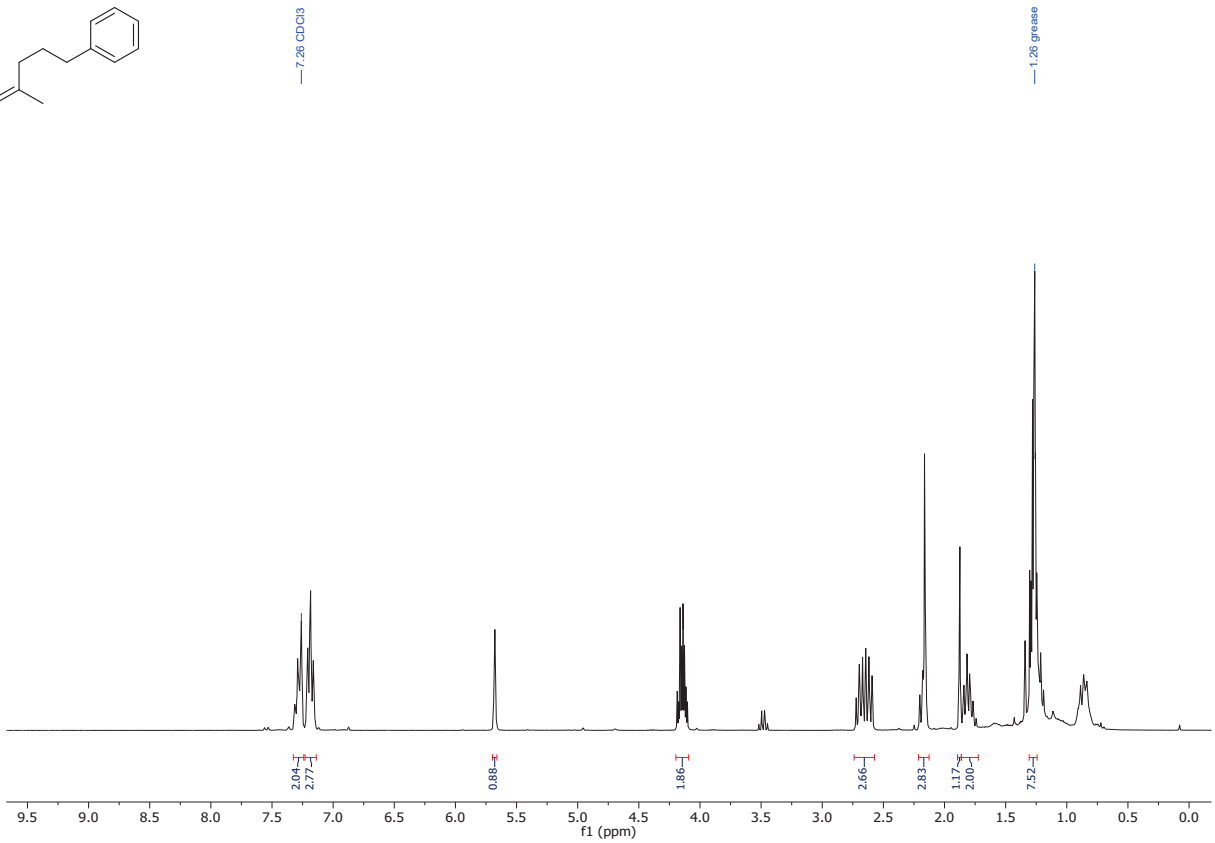


Ethyl 3-methyl-6-phenylhex-2-enoate (75)

^{1}H NMR (300 MHz, $CDCl_3$)

Mix of olefin

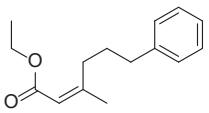


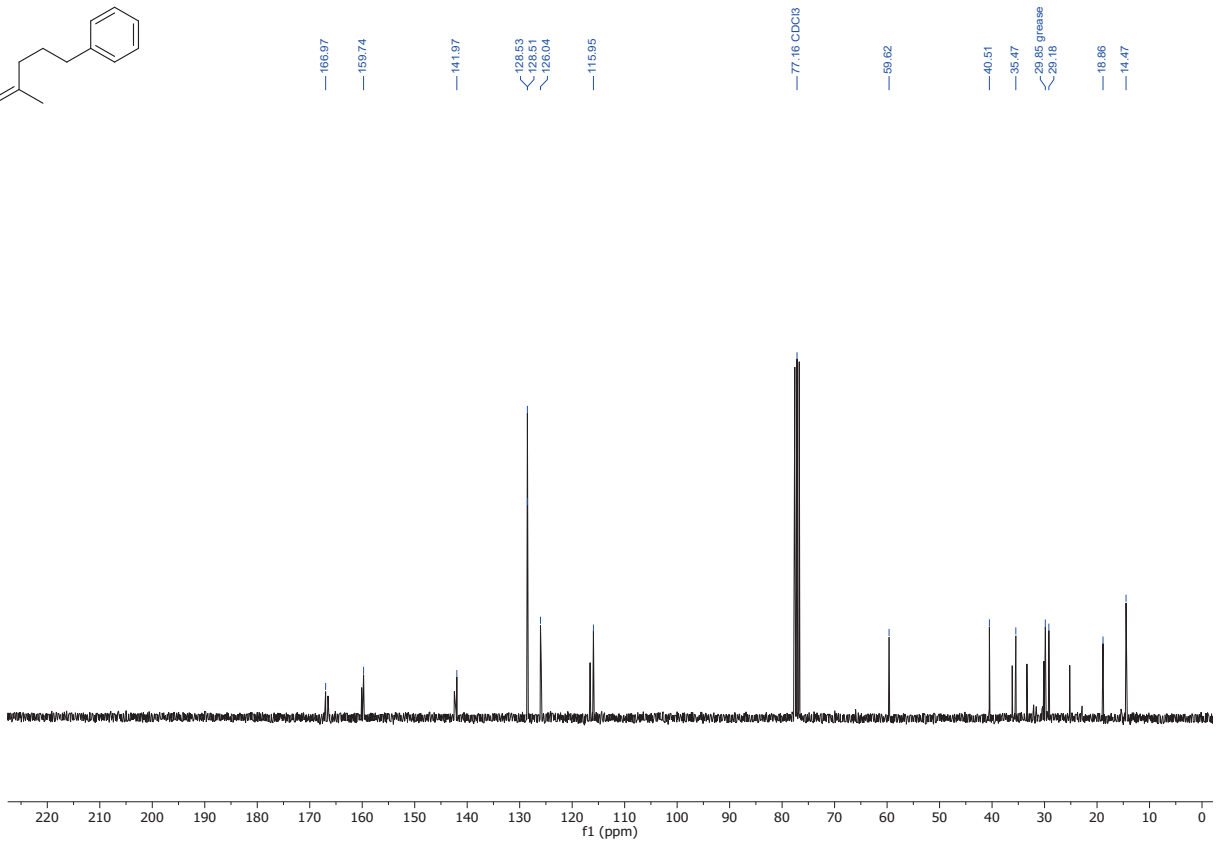


Ethyl 3-methyl-6-phenylhex-2-enoate (75)

^{13}C NMR (75 MHz, $CDCl_3$)

Z-olefin

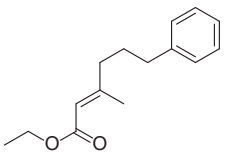


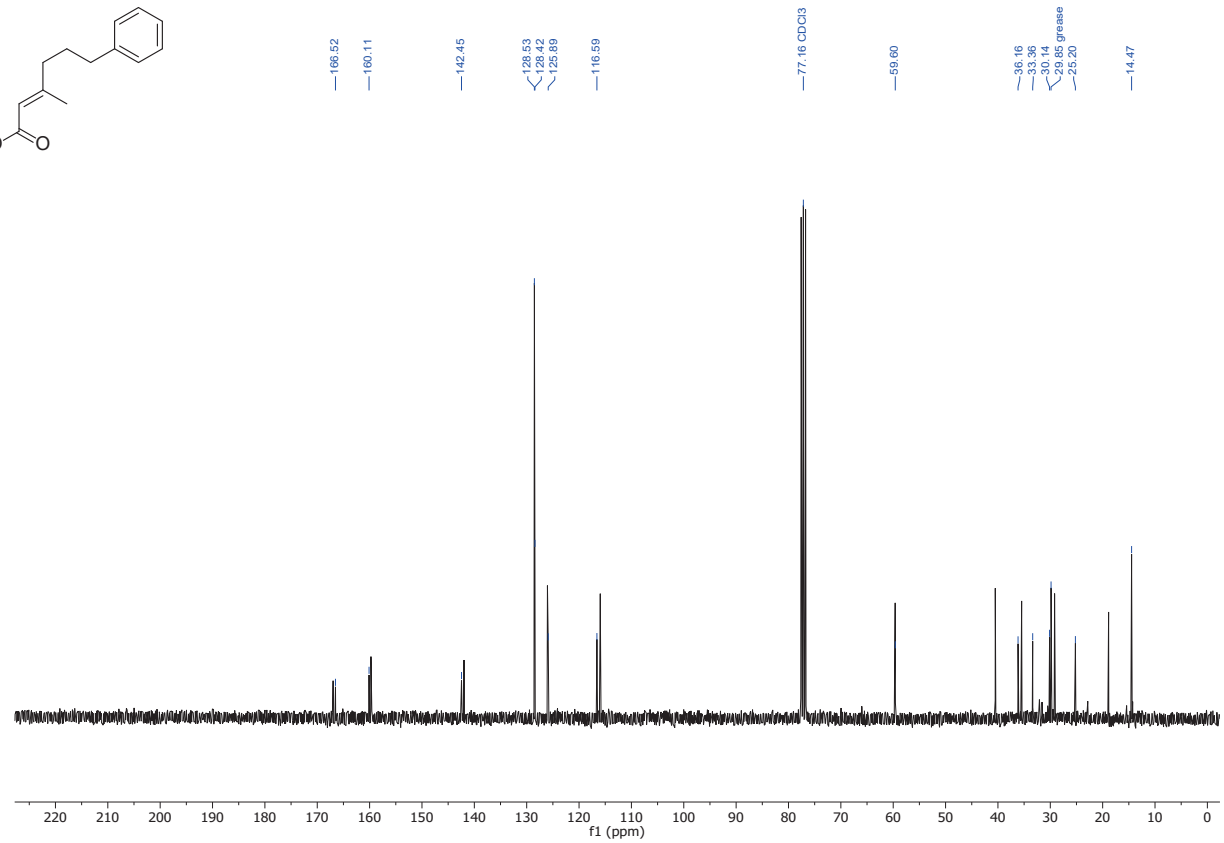


Ethyl 3-methyl-6-phenylhex-2-enoate (75)

^{13}C NMR (75 MHz, $CDCl_3$)

E-olefin

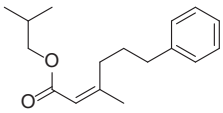


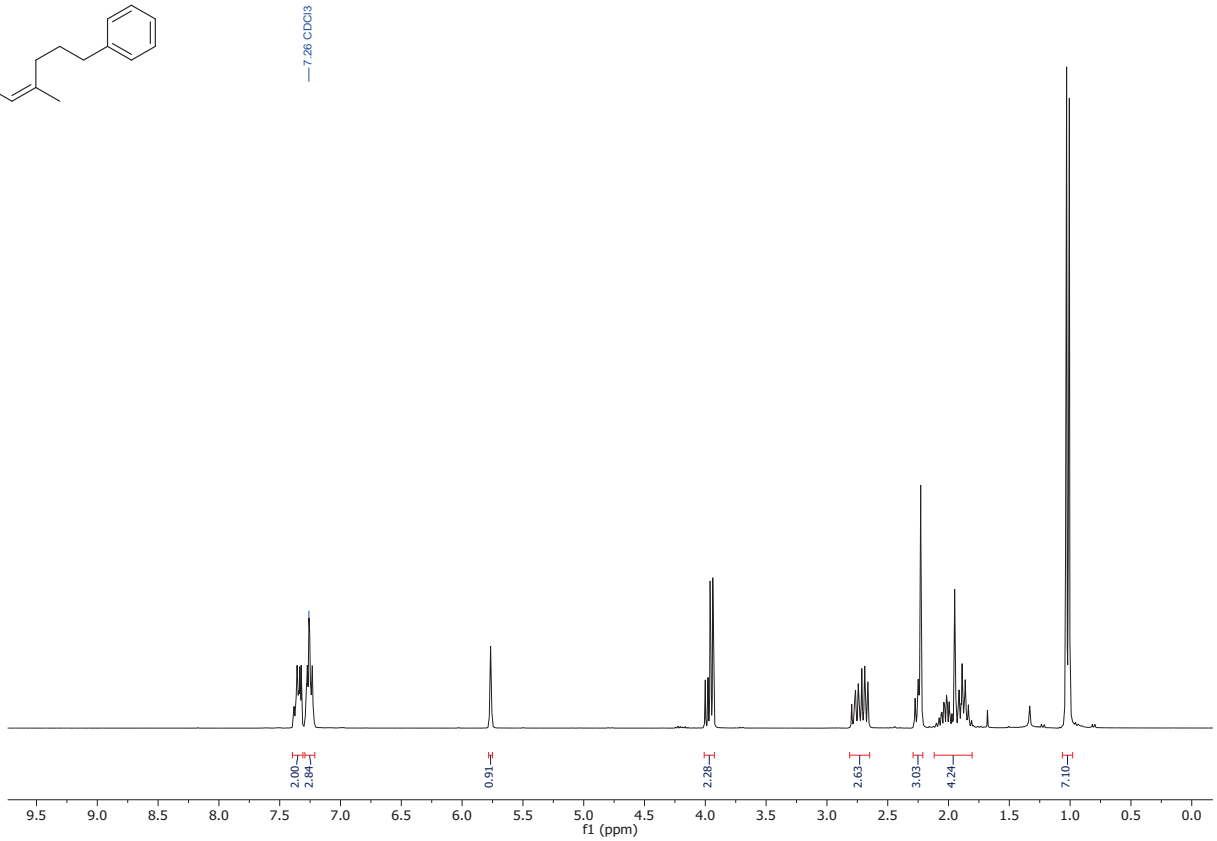


isobutyl 3-methyl-6-phenylhex-2-enoate(76)

^{1}H NMR (300 MHz, $CDCl_3$)

Mix of olefin

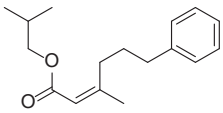


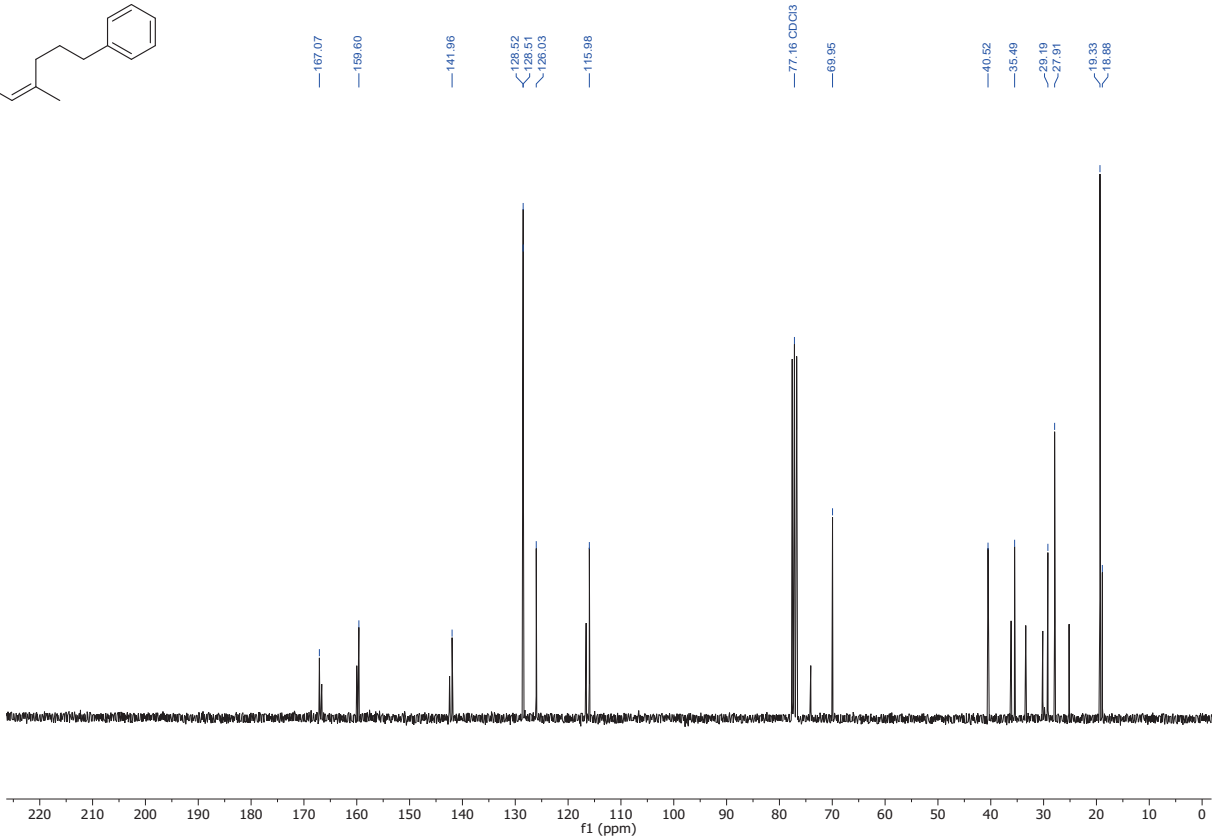


isobutyl 3-methyl-6-phenylhex-2-enoate(76)

^{13}C NMR (75 MHz, $CDCl_3$)

Z-olefin

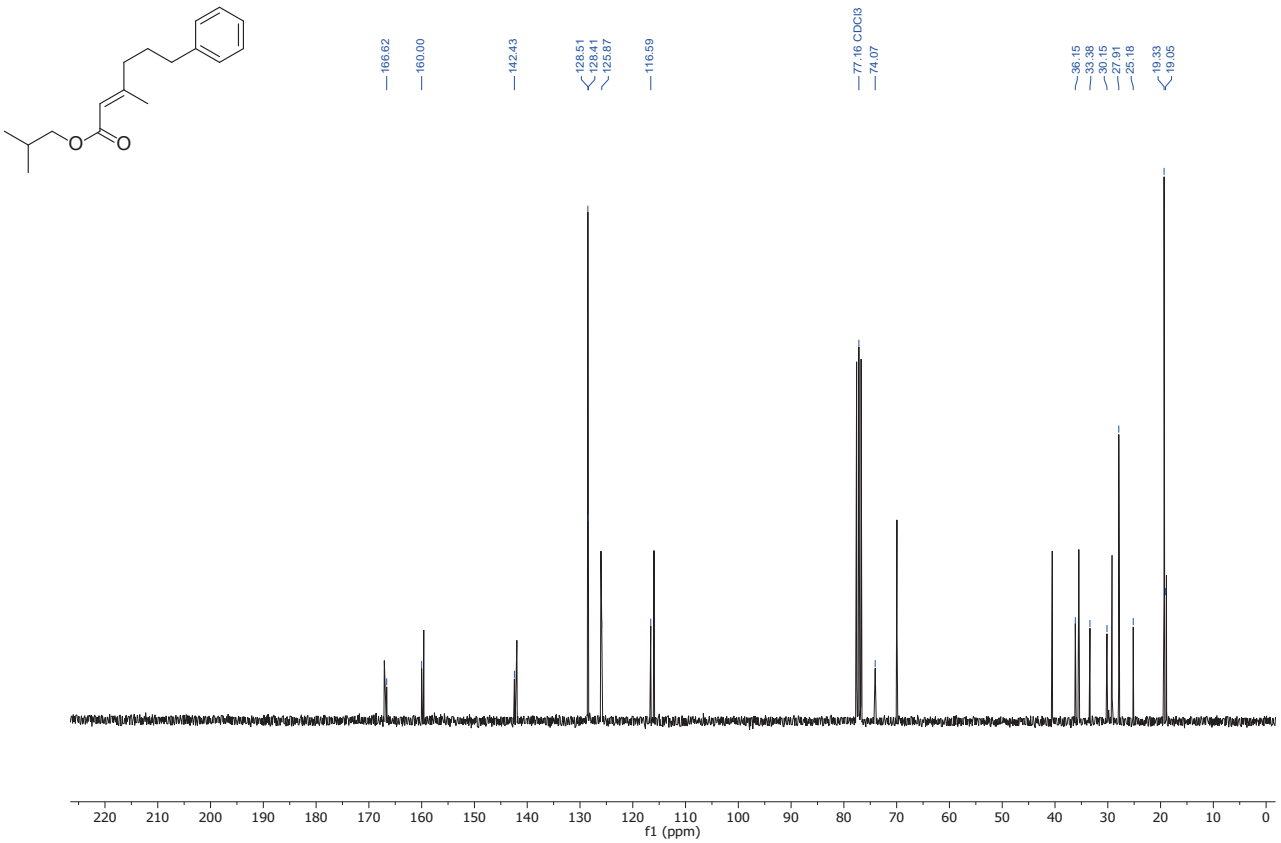




isobutyl 3-methyl-6-phenylhex-2-enoate(76)

^{13}C NMR (75 MHz, $CDCl_3$)

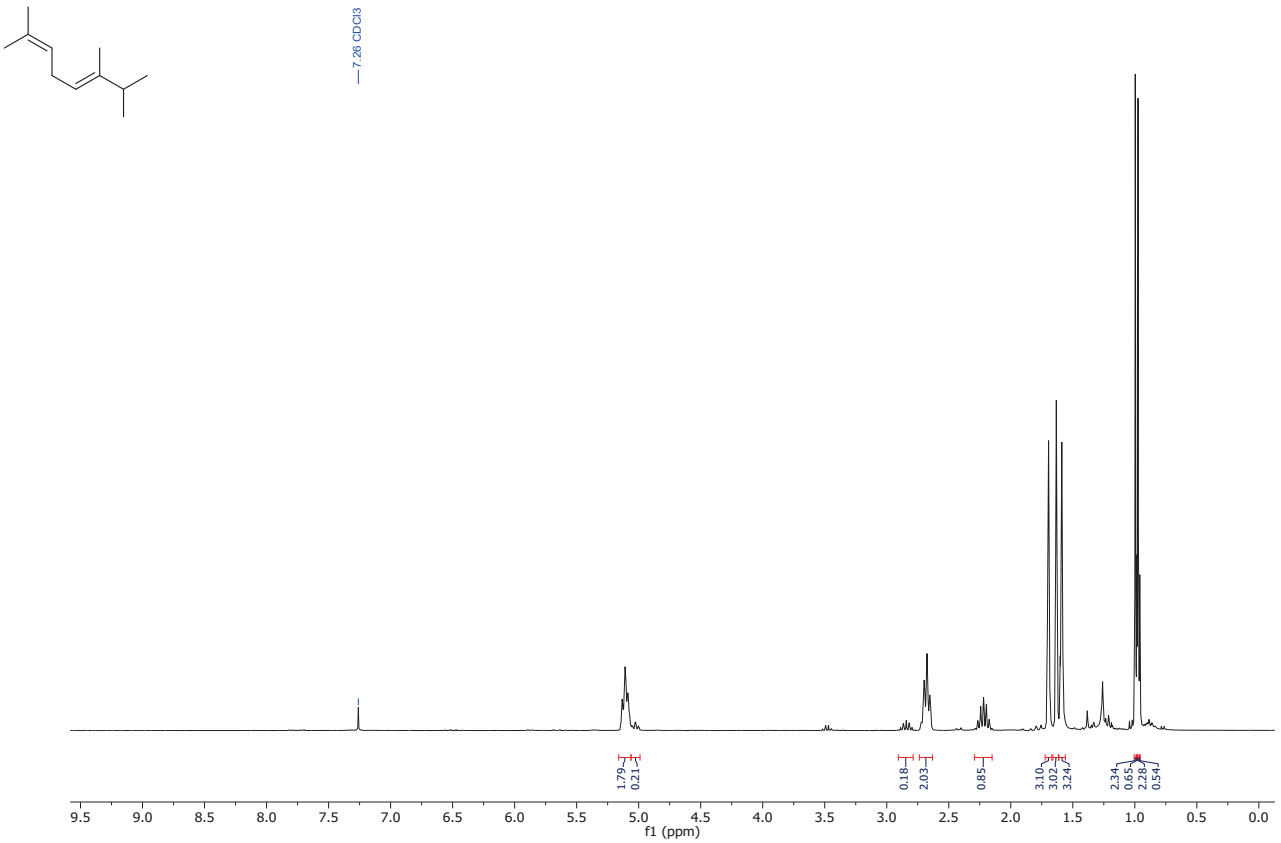
E-olefin



2,6,7-trimethylocta-2,5-diene (73)

^{1}H NMR (300 MHz, $CDCl_3$)

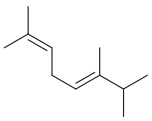
Mix of olefin

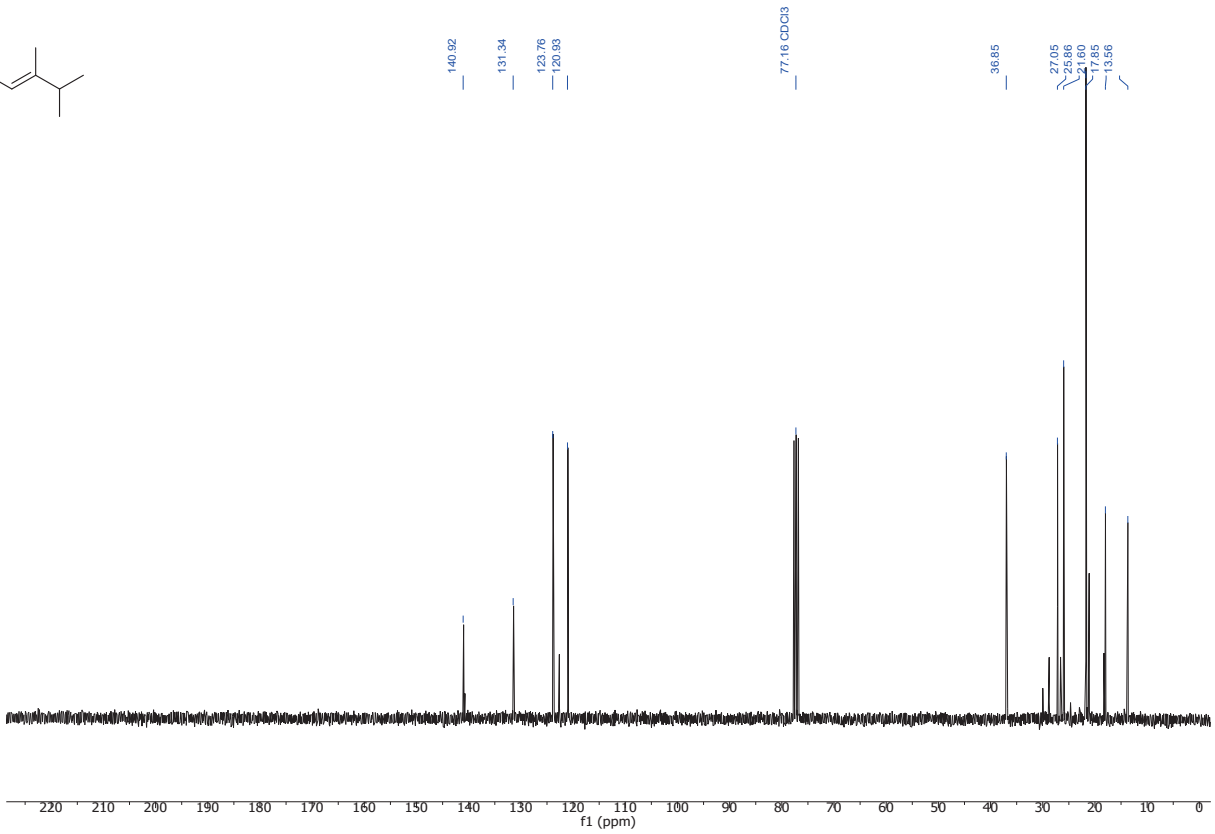


2,6,7-trimethylocta-2,5-diene (73)

^{13}C NMR (75 MHz, $CDCl_3$)

E-olefin

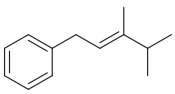


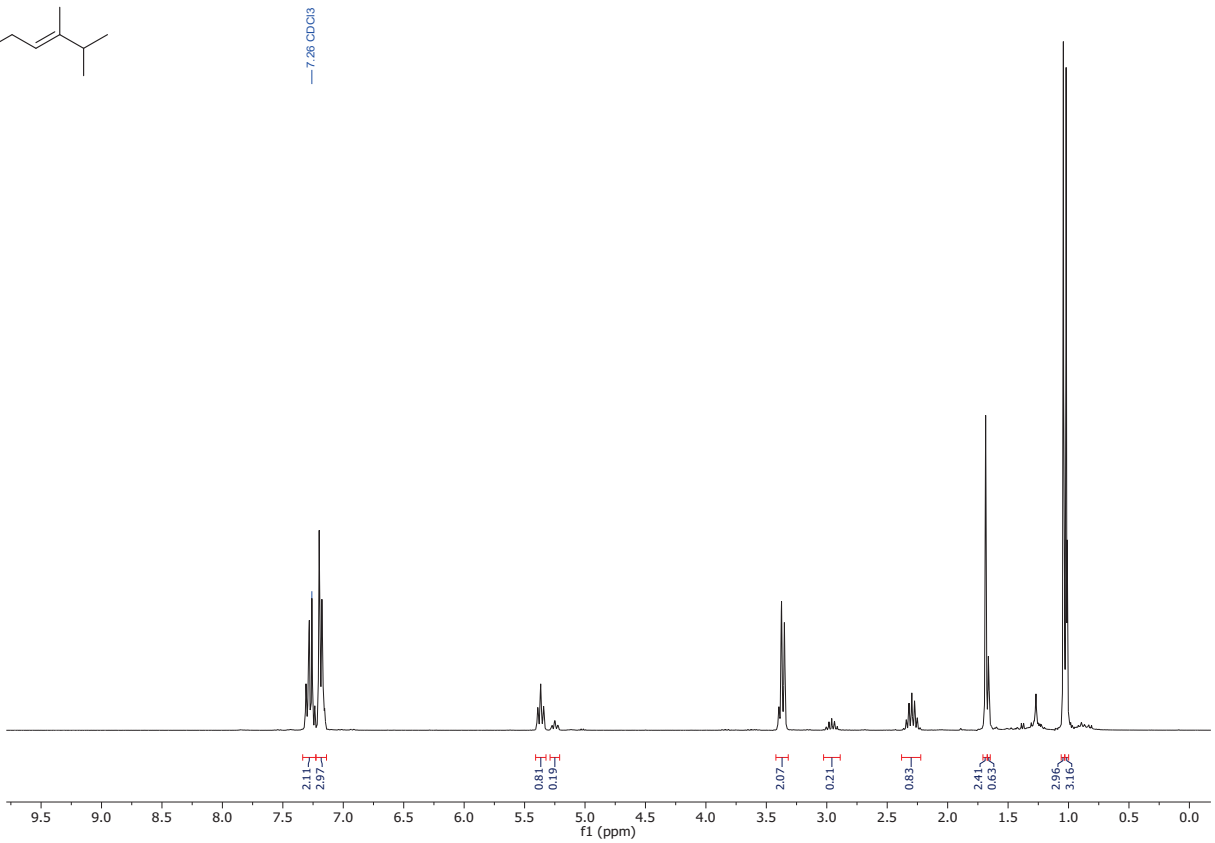


(3,4-dimethylpent-2-en-1-yl)benzene (70)

^{1}H NMR (300 MHz, $CDCl_3$)

Mix of olefin

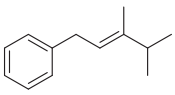


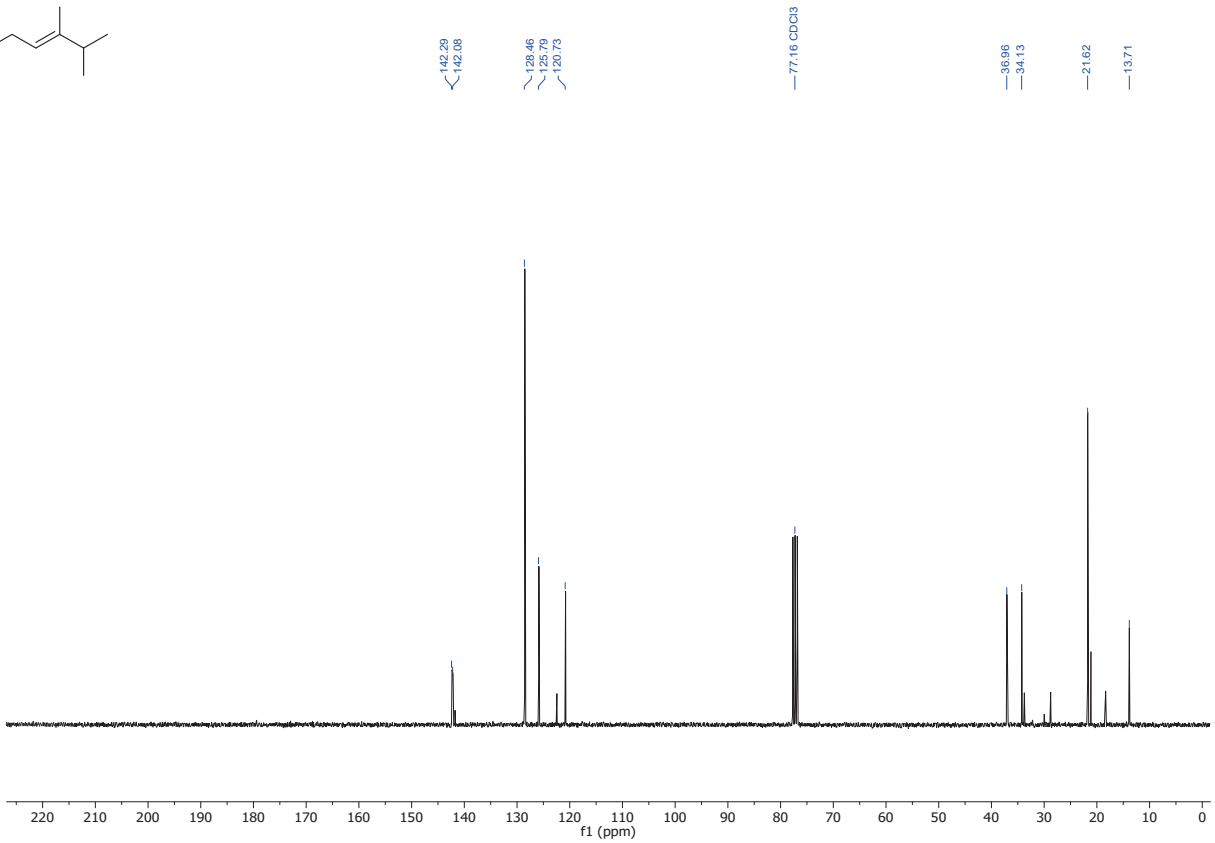


(3,4-dimethylpent-2-en-1-yl)benzene (70)

^{13}C NMR (75 MHz, $CDCl_3$)

E-olefin

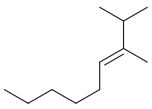


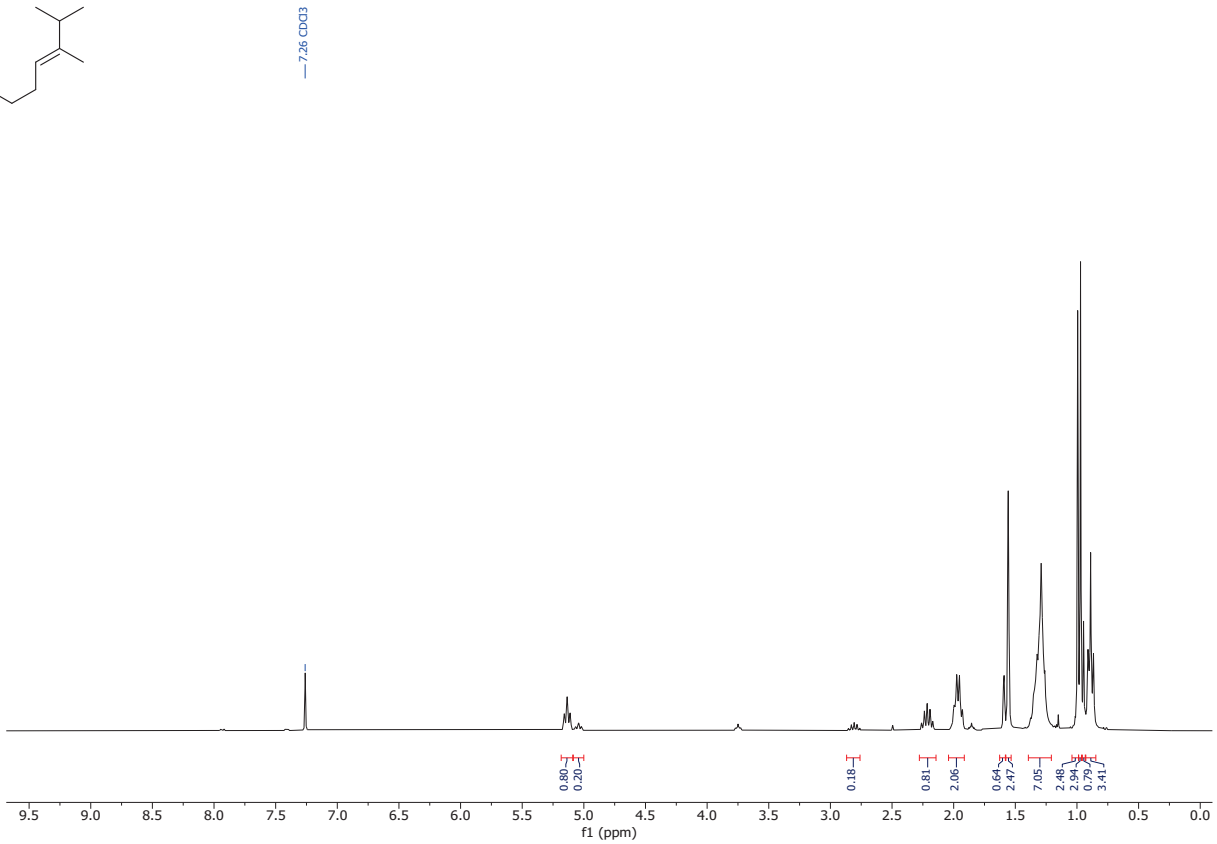


2,3-dimethylnon-3-ene (71)

^{1}H NMR (300 MHz, $CDCl_3$)

Mix of olefin

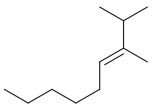


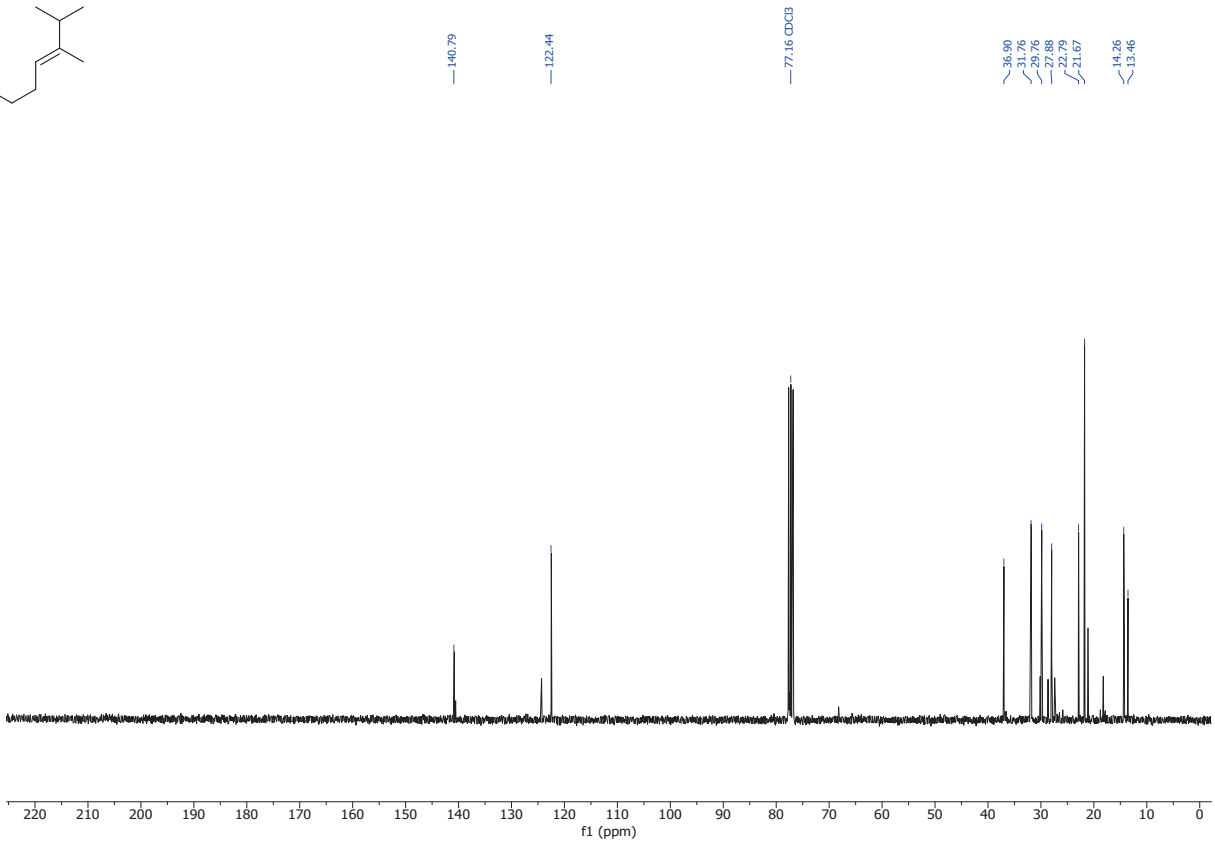


2,3-dimethylnon-3-ene (71)

^{13}C NMR (75 MHz, $CDCl_3$)

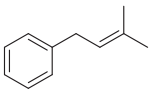
Mix of olefin

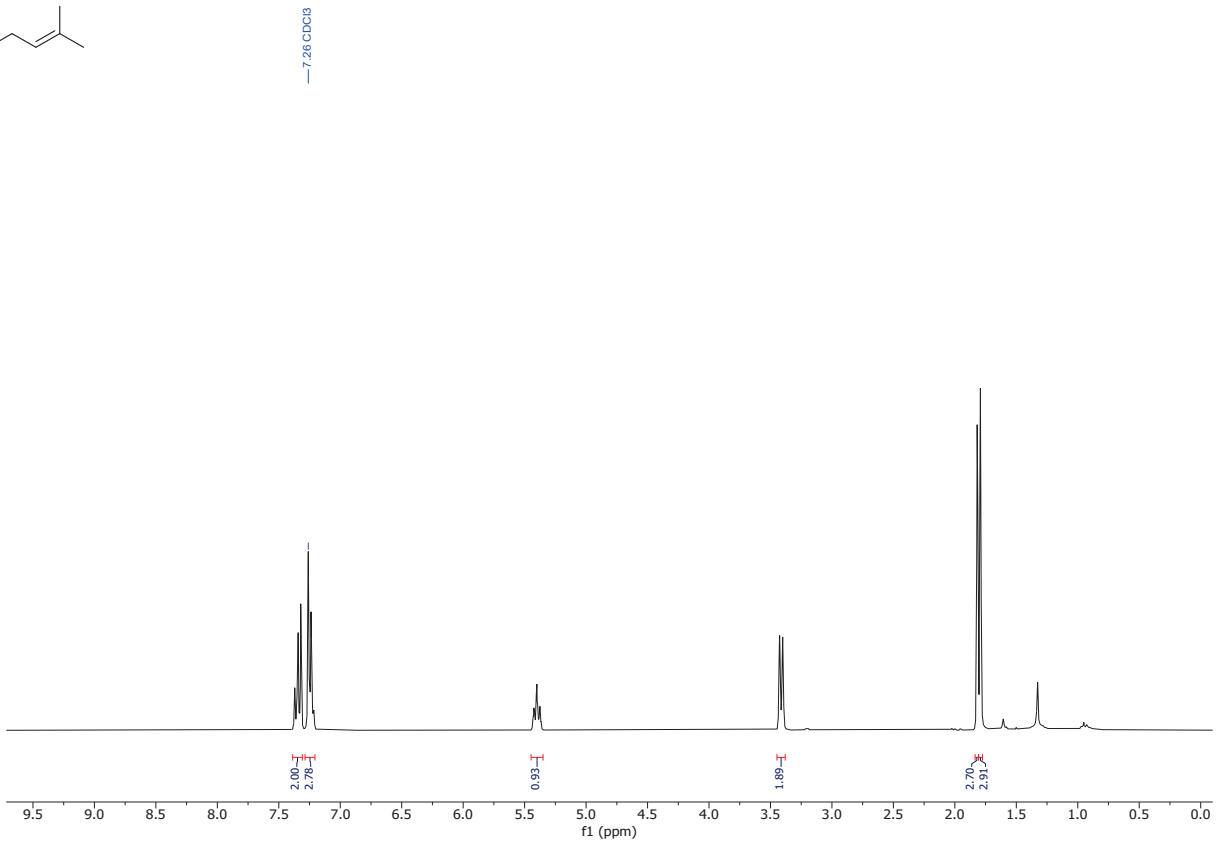




(3-methylbut-2-en-1-yl)benzene (58)

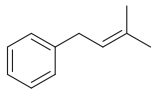
^{1}H NMR (300 MHz, $CDCl_3$)

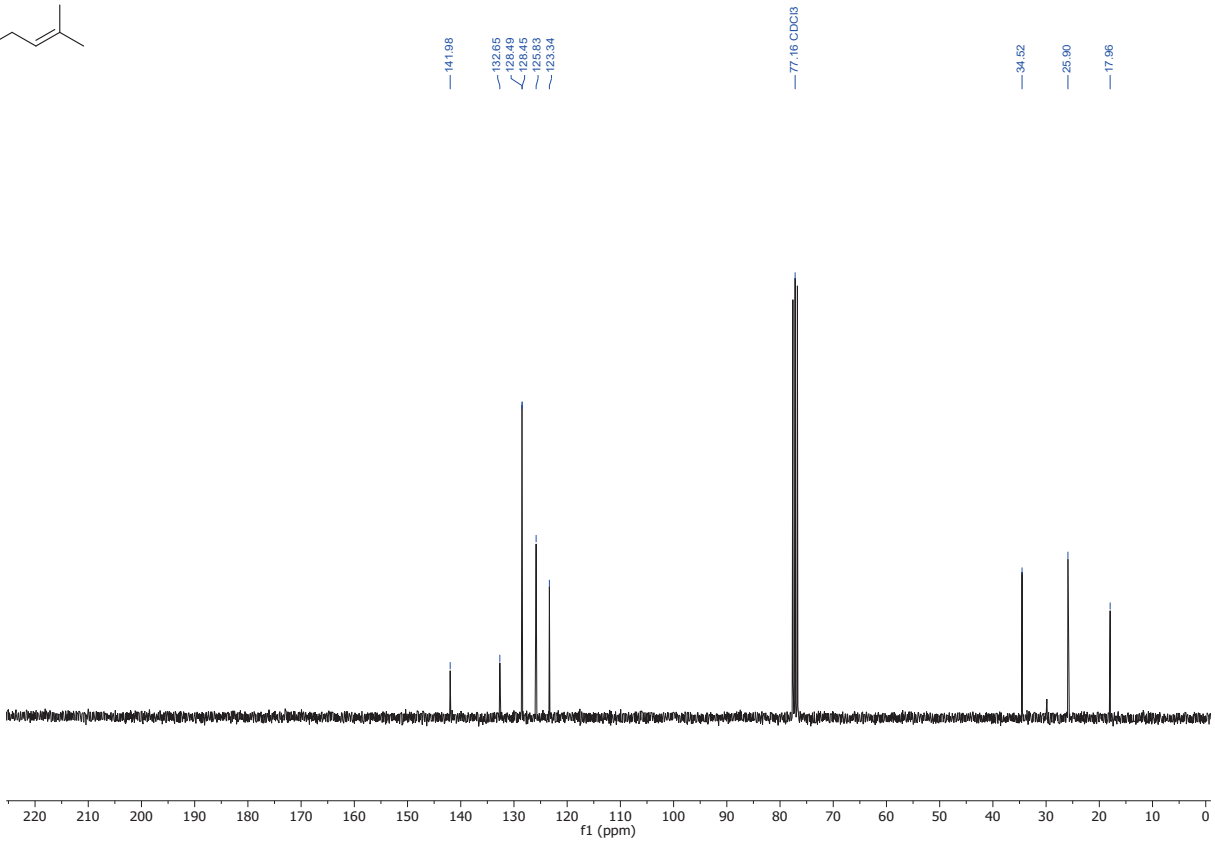




(3-methylbut-2-en-1-yl)benzene (58)

^{13}C NMR (75 MHz, $CDCl_3$)

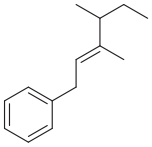


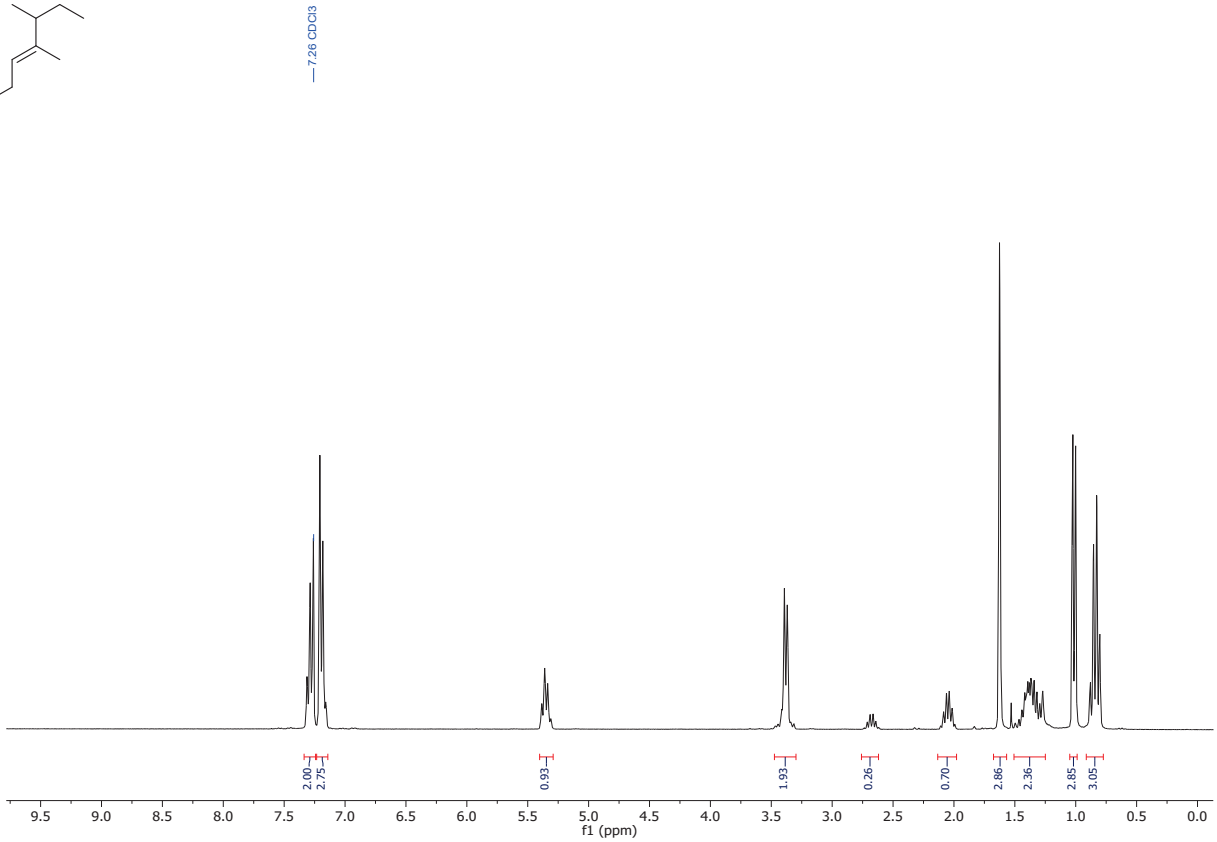


(3,4-dimethylhex-2-en-1-yl)benzene (72a)

^{1}H NMR (300 MHz, $CDCl_3$)

Mix of olefin

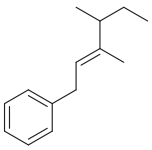


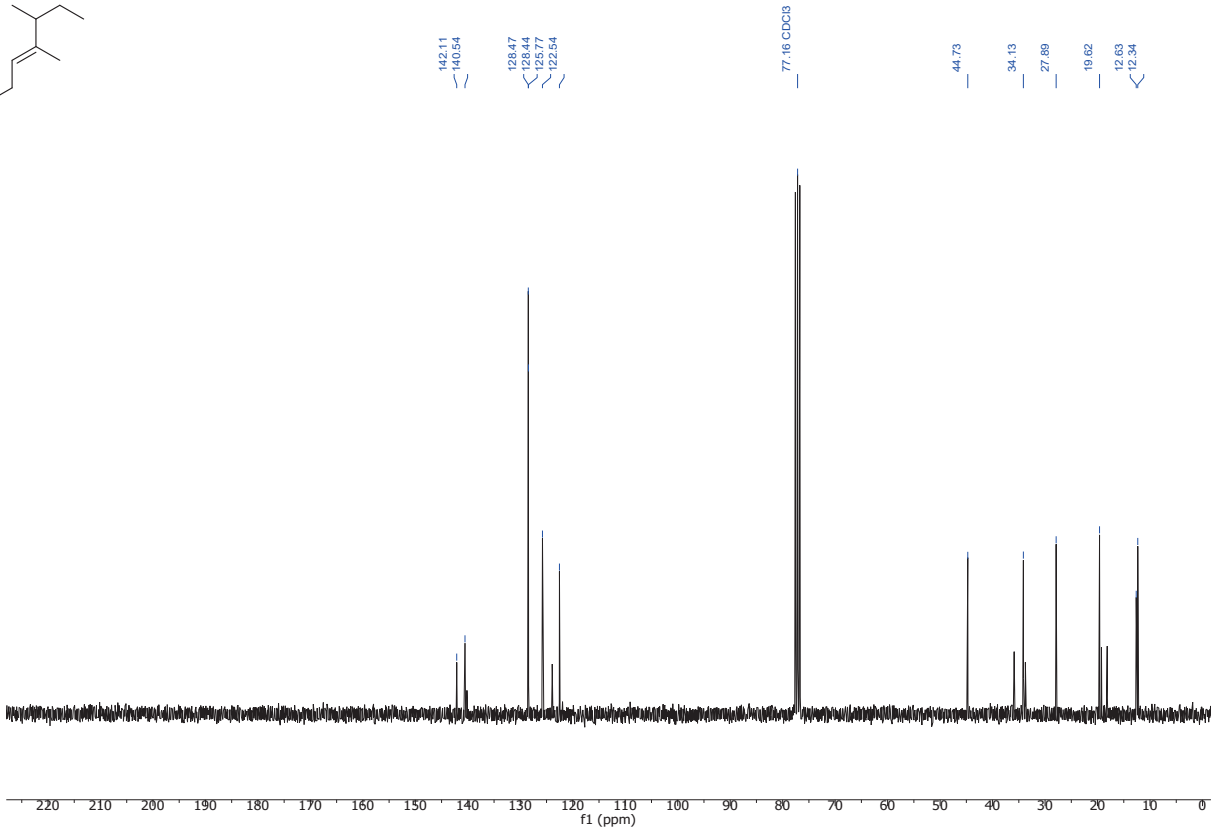


(3,4-dimethylhex-2-en-1-yl)benzene (72a)

^{13}C NMR (75 MHz, $CDCl_3$)

E-olefin

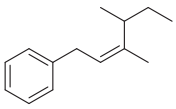


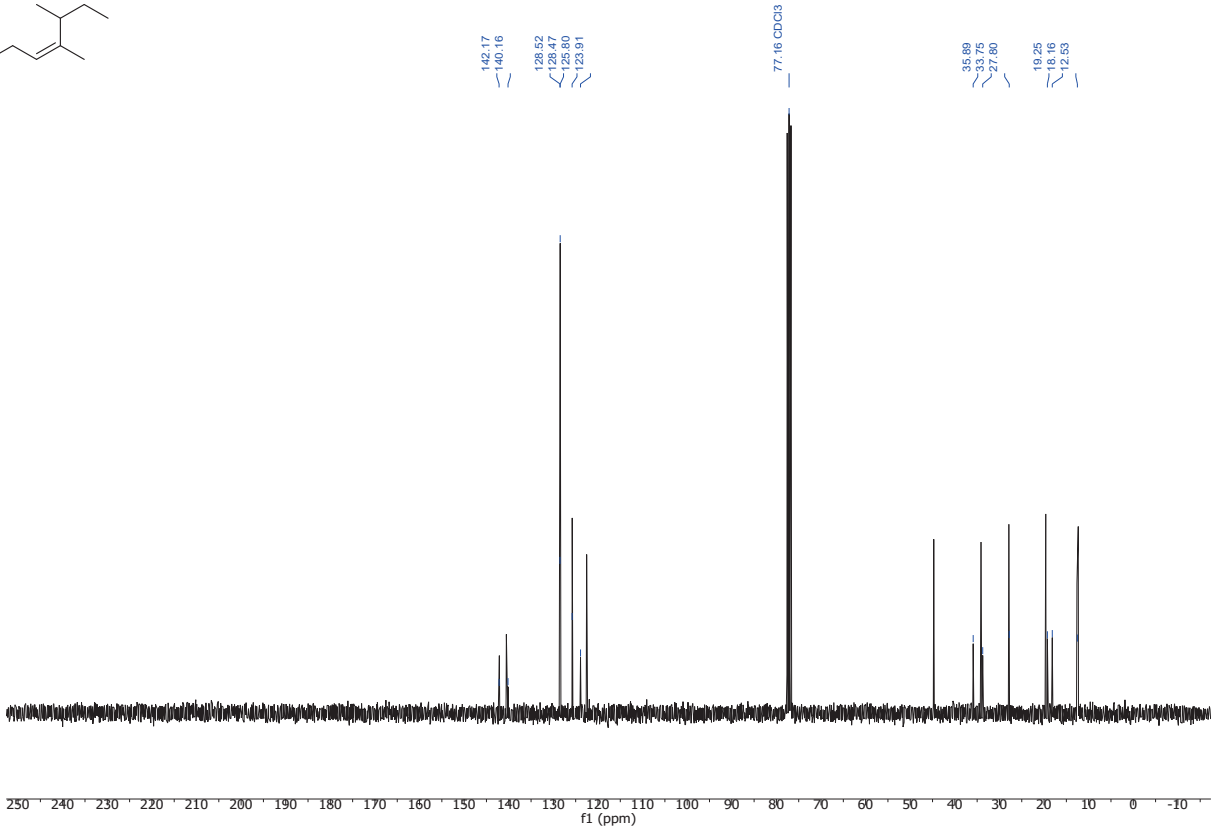


(3,4-dimethylhex-2-en-1-yl)benzene (72a)

^{13}C NMR (75 MHz, $CDCl_3$)

Z-olefin

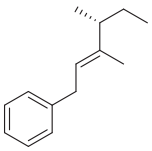


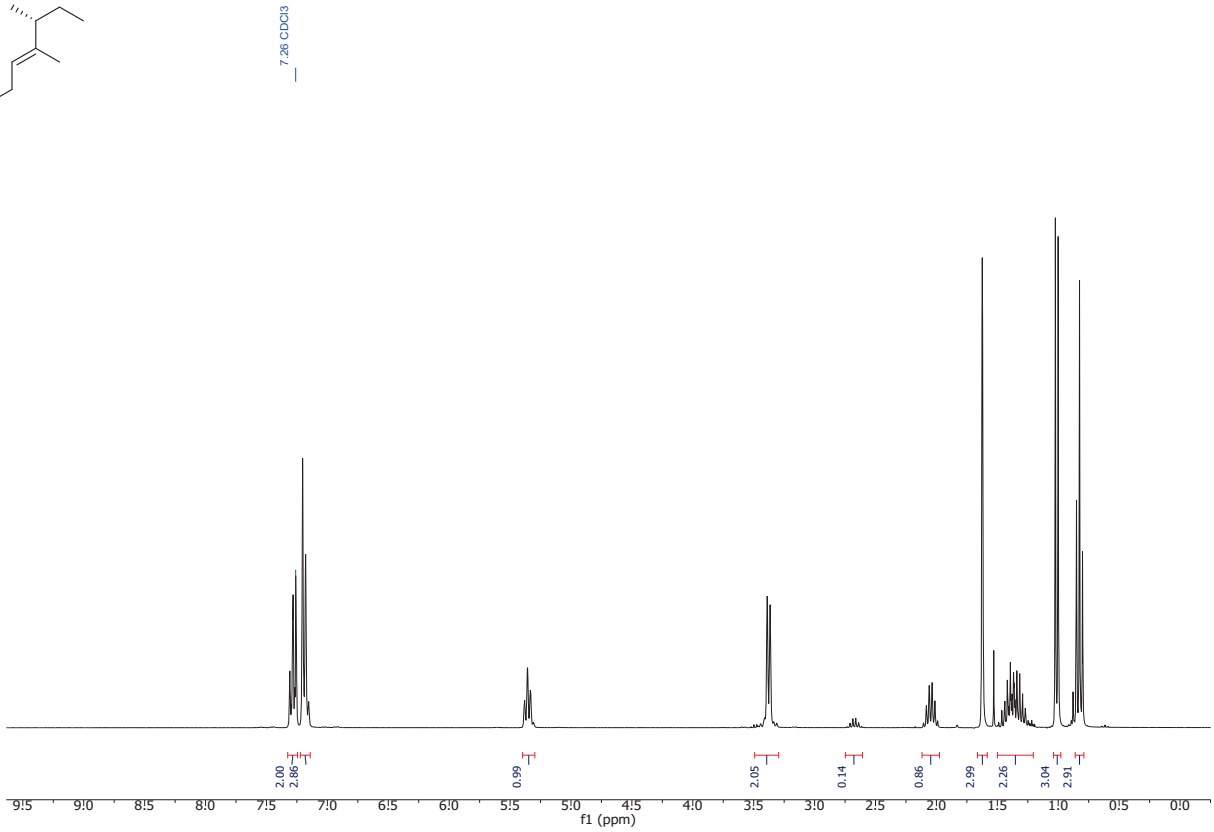


(R)-(3,4-dimethylhex-2-en-1-yl)benzene (72b)

^{1}H NMR (300 MHz, $CDCl_3$)

Mix of olefin

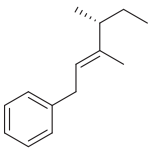


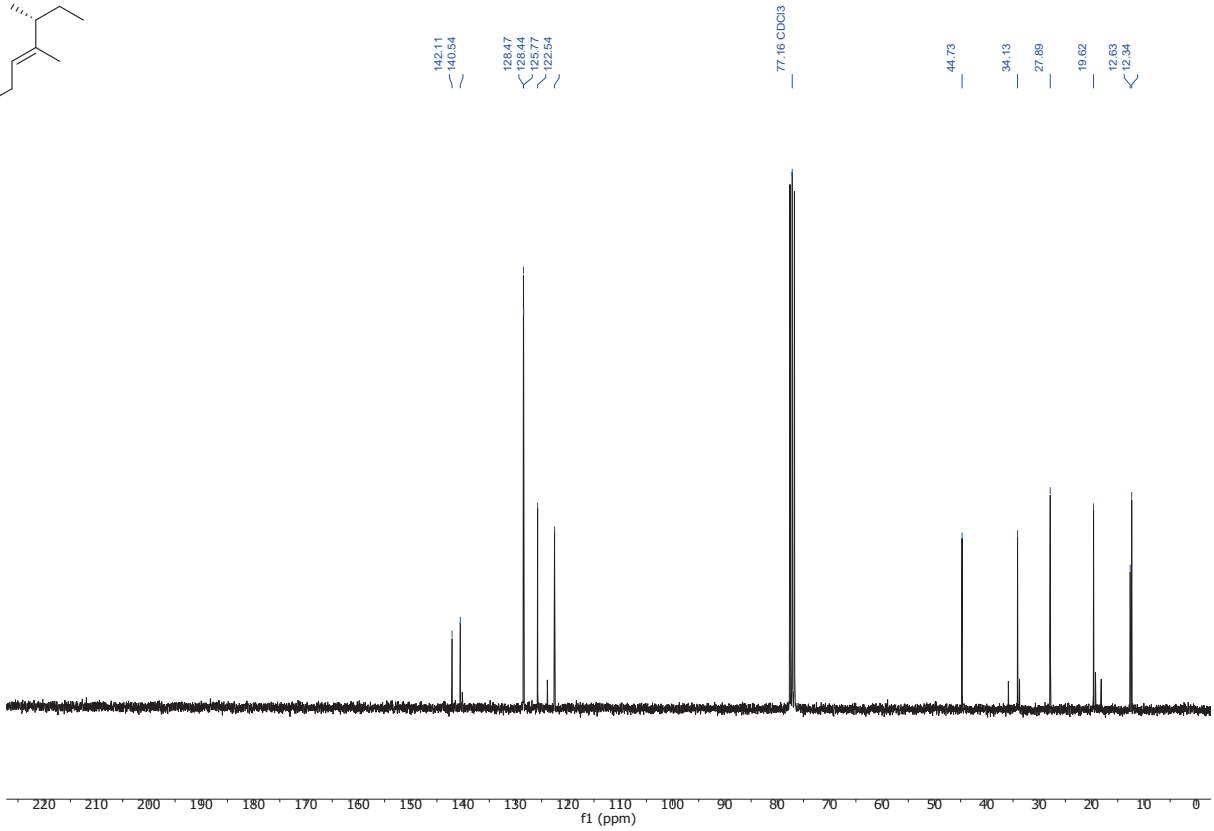


(R)-(3,4-dimethylhex-2-en-1-yl)benzene (72b)

^{13}C NMR (75 MHz, $CDCl_3$)

E-olefin

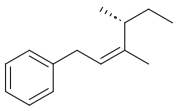


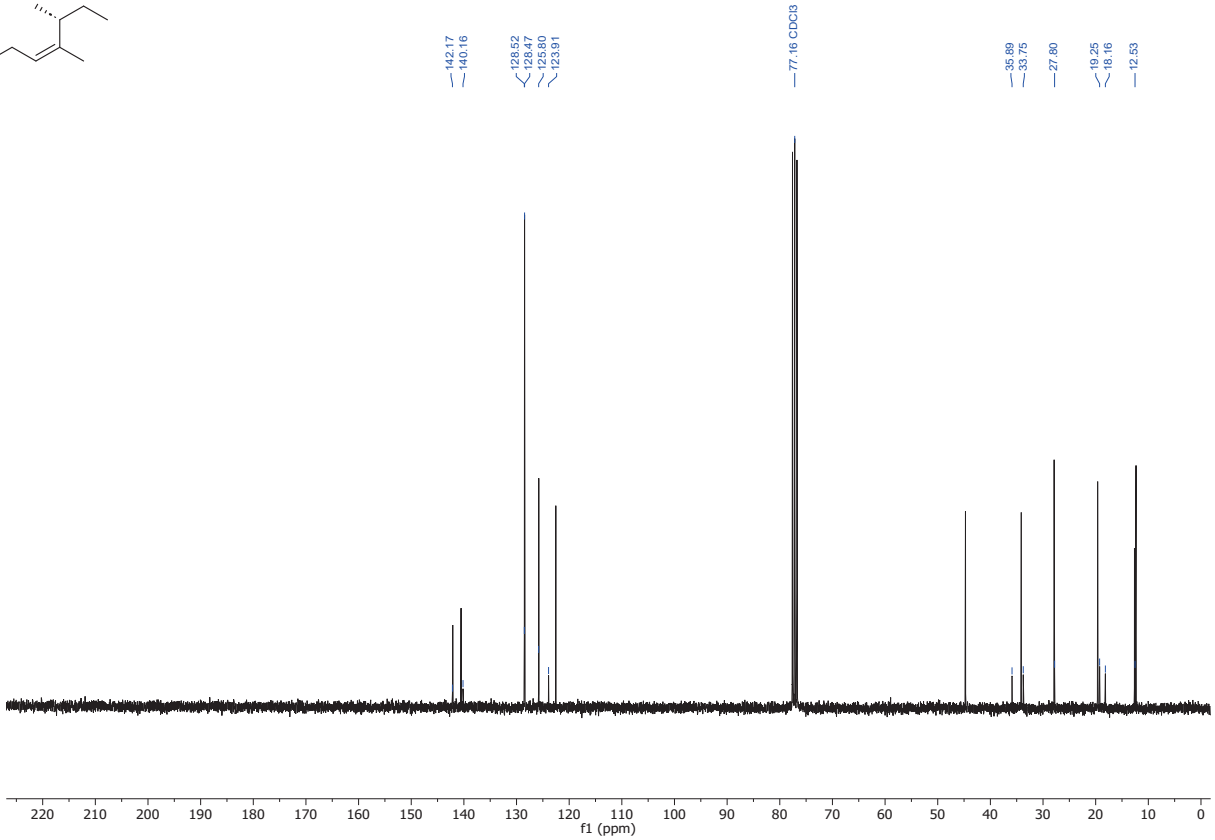


(R)-(3,4-dimethylhex-2-en-1-yl)benzene (72b)

^{13}C NMR (75 MHz, $CDCl_3$)

Z-olefin

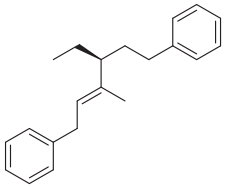


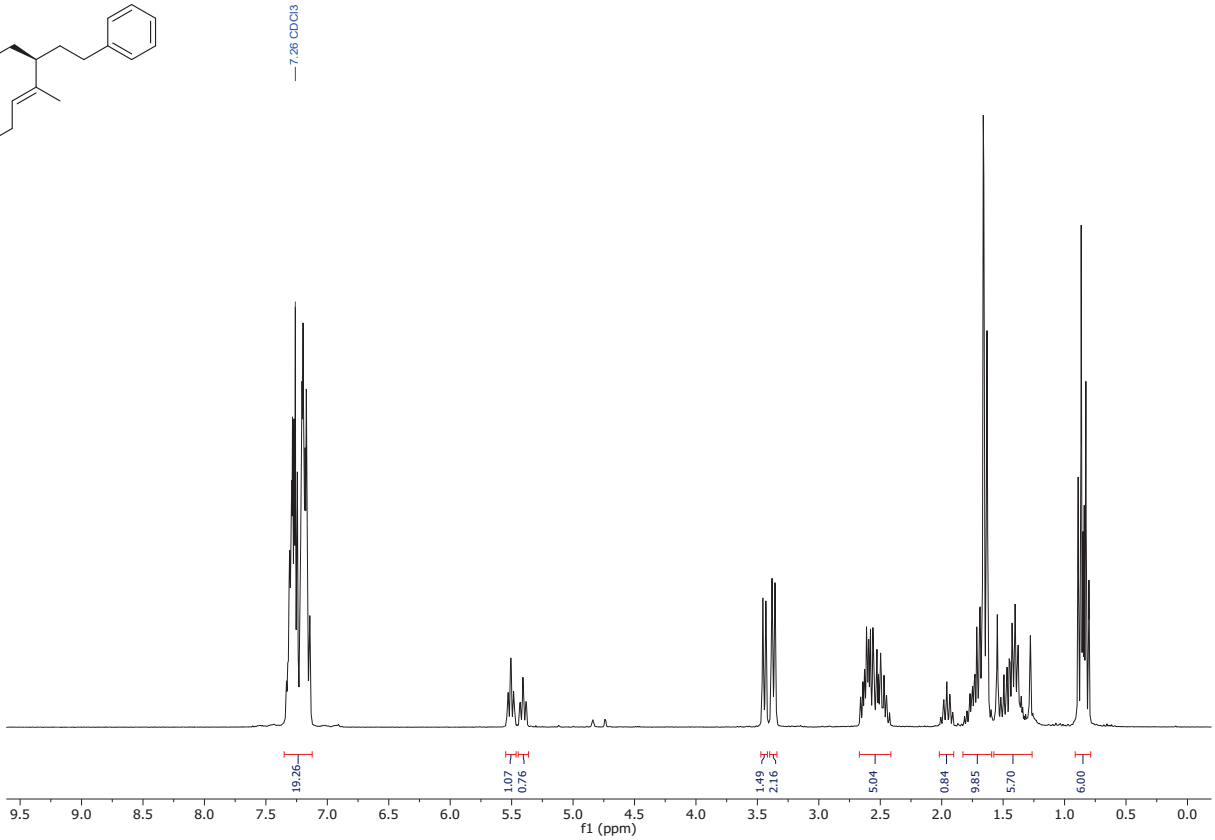


(*S*)-(4-ethyl-3-methylhex-2-ene-1,6-diyl)dibenzene (94)

^{1}H NMR (300 MHz, $CDCl_3$)

Mix of olefin

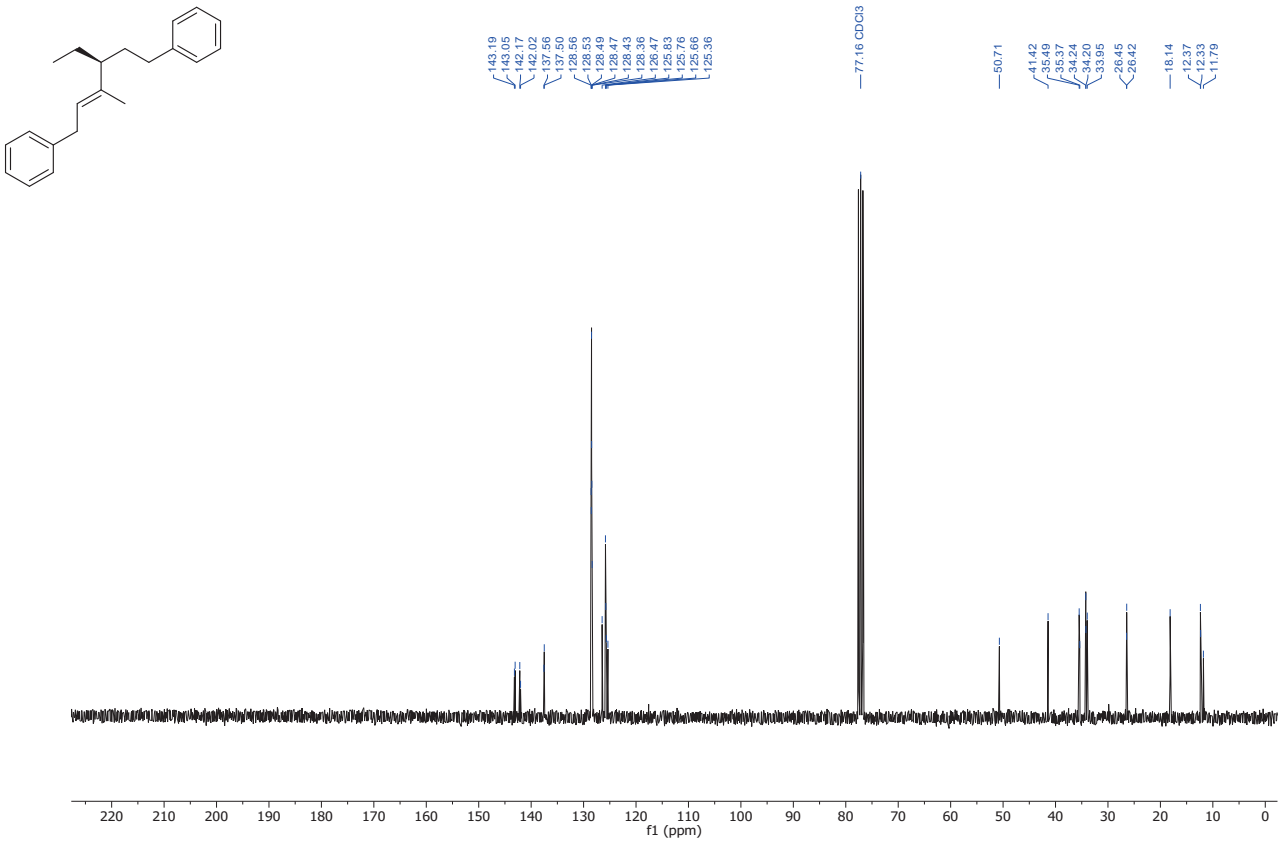




(*S*)-(4-ethyl-3-methylhex-2-ene-1,6-diyl)dibenzene (94)

^{13}C NMR (75 MHz, $CDCl_3$)

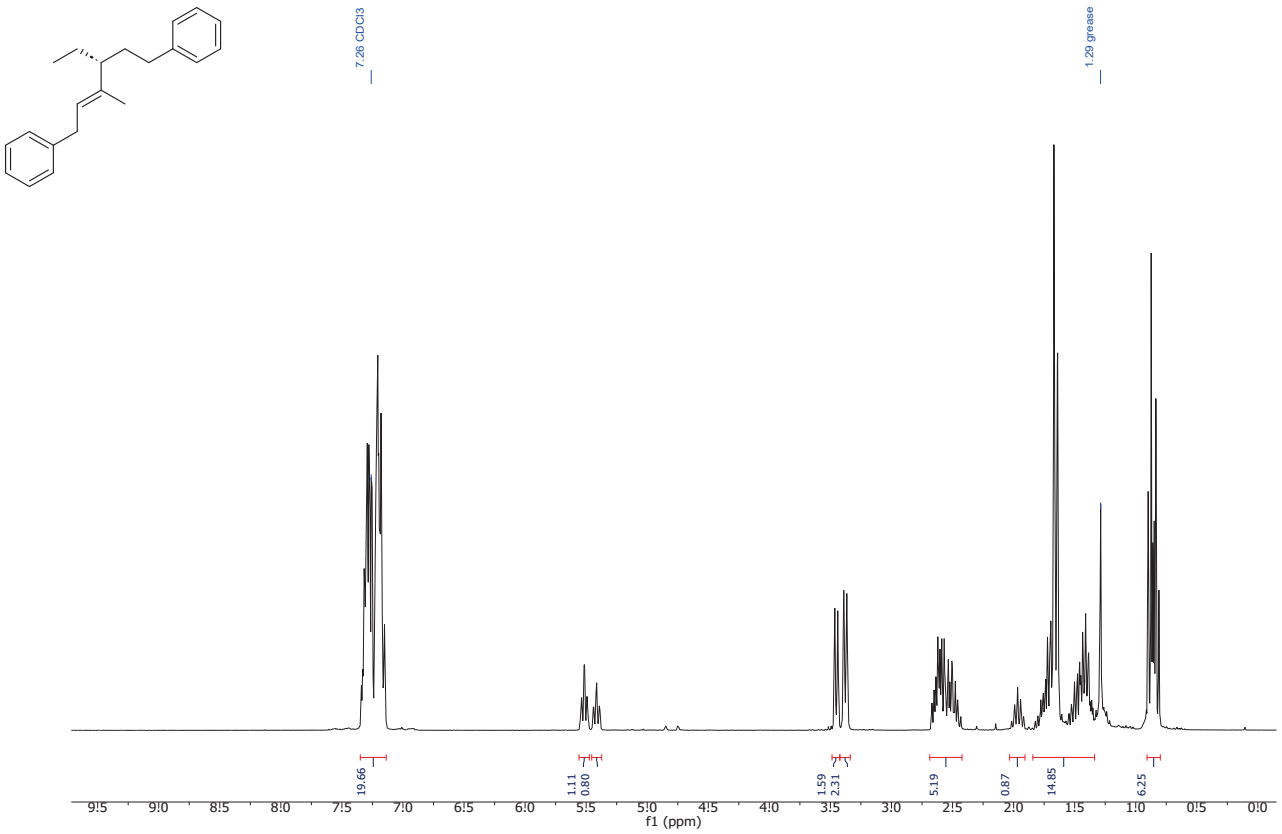
Mix of olefin



(*R*)-(4-ethyl-3-methylhex-2-ene-1,6-diyl)dibenzene (109)

^{1}H NMR (300 MHz, $CDCl_3$)

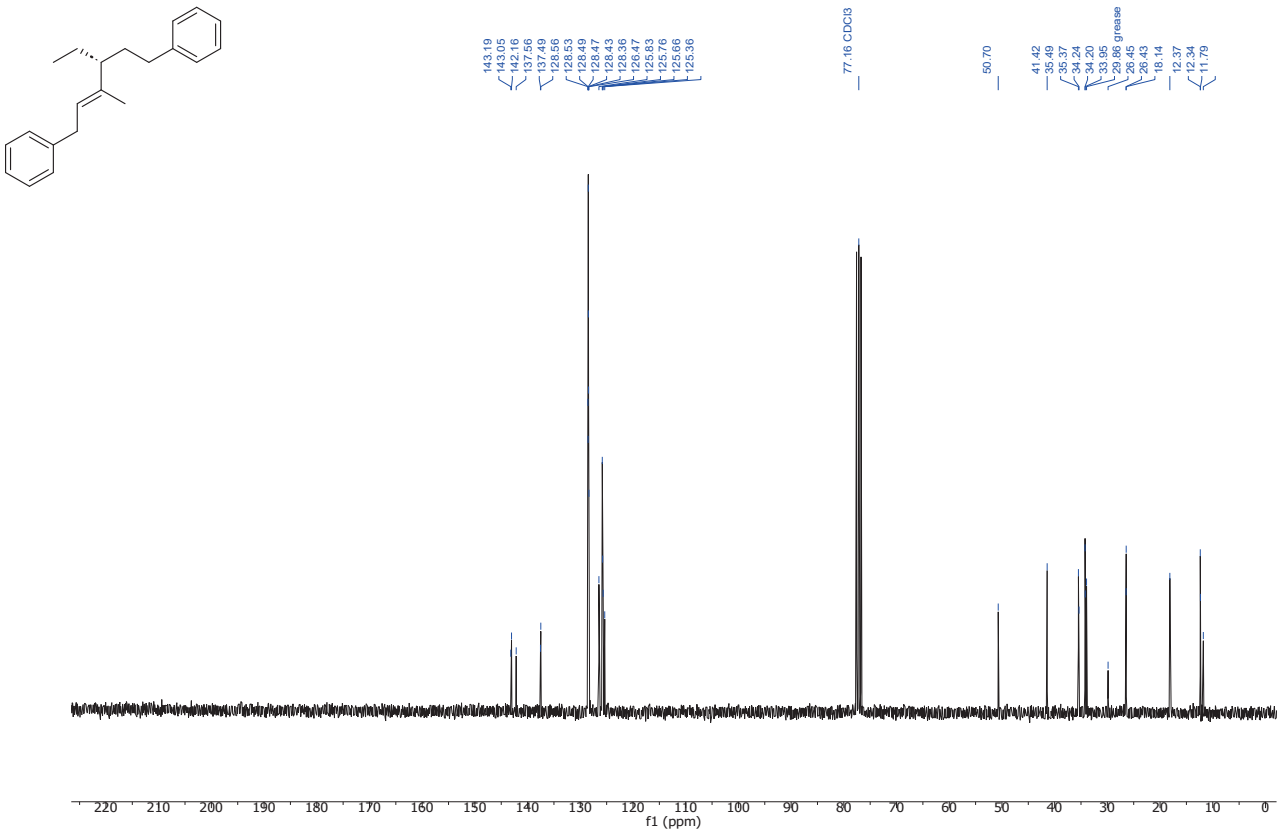
Mix of olefin



(*R*)-(4-ethyl-3-methylhex-2-ene-1,6-diyl)dibenzene (109)

^{13}C NMR (75 MHz, $CDCl_3$)

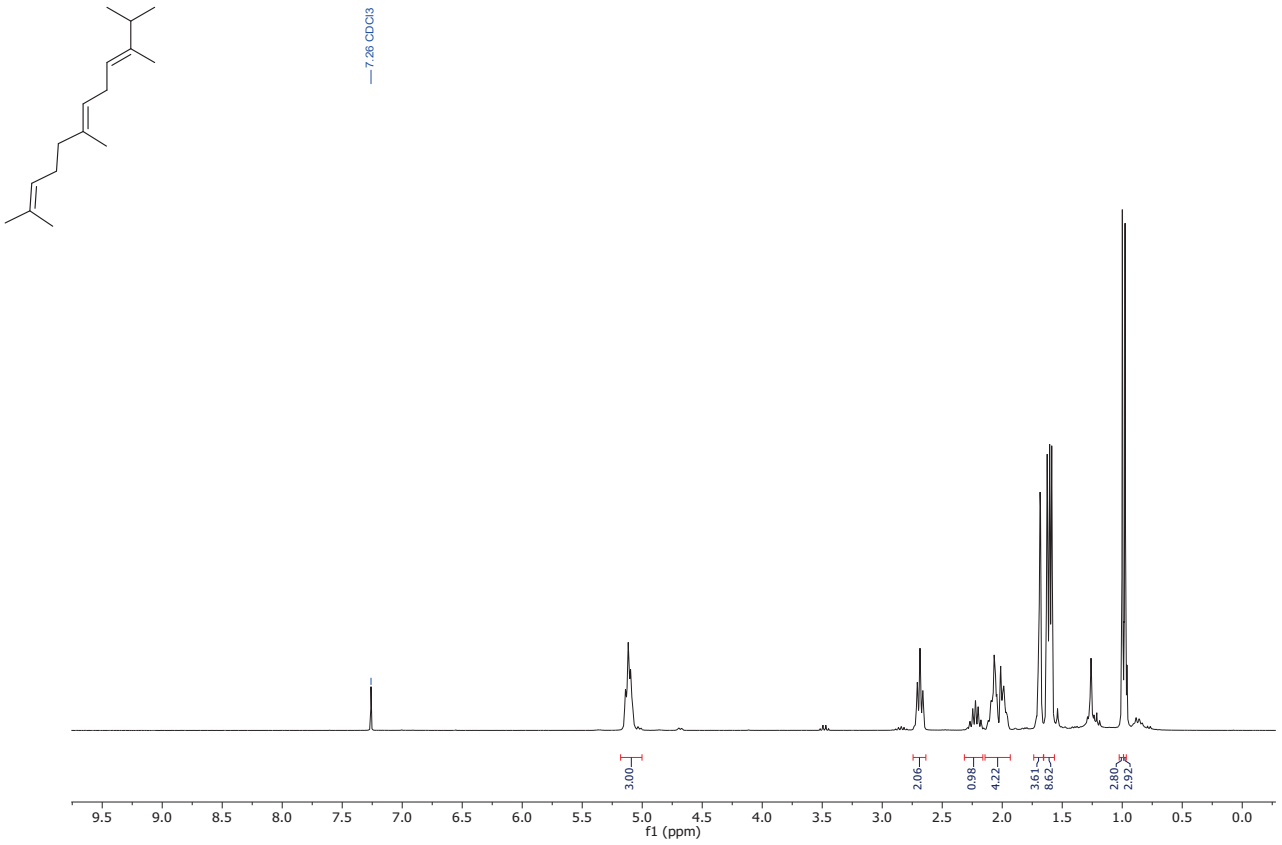
Mix of olefin



(6E,9E)-2,6,10,11-tetramethyldodeca-2,6,9-triene (85)

^{1}H NMR (300 MHz, $CDCl_3$)

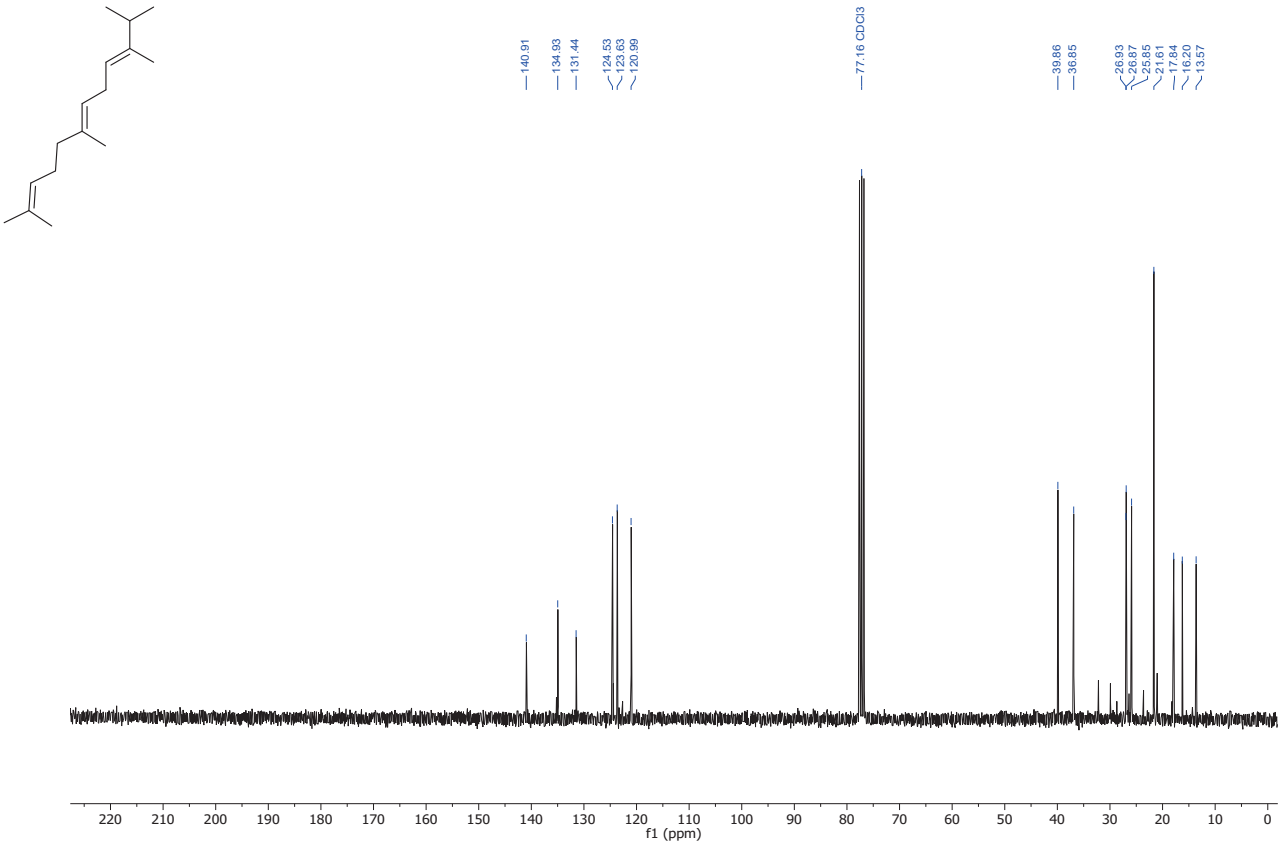
E-olefin



(6E,9E)-2,6,10,11-tetramethyldodeca-2,6,9-triene (85)

^{13}C NMR (75 MHz, $CDCl_3$)

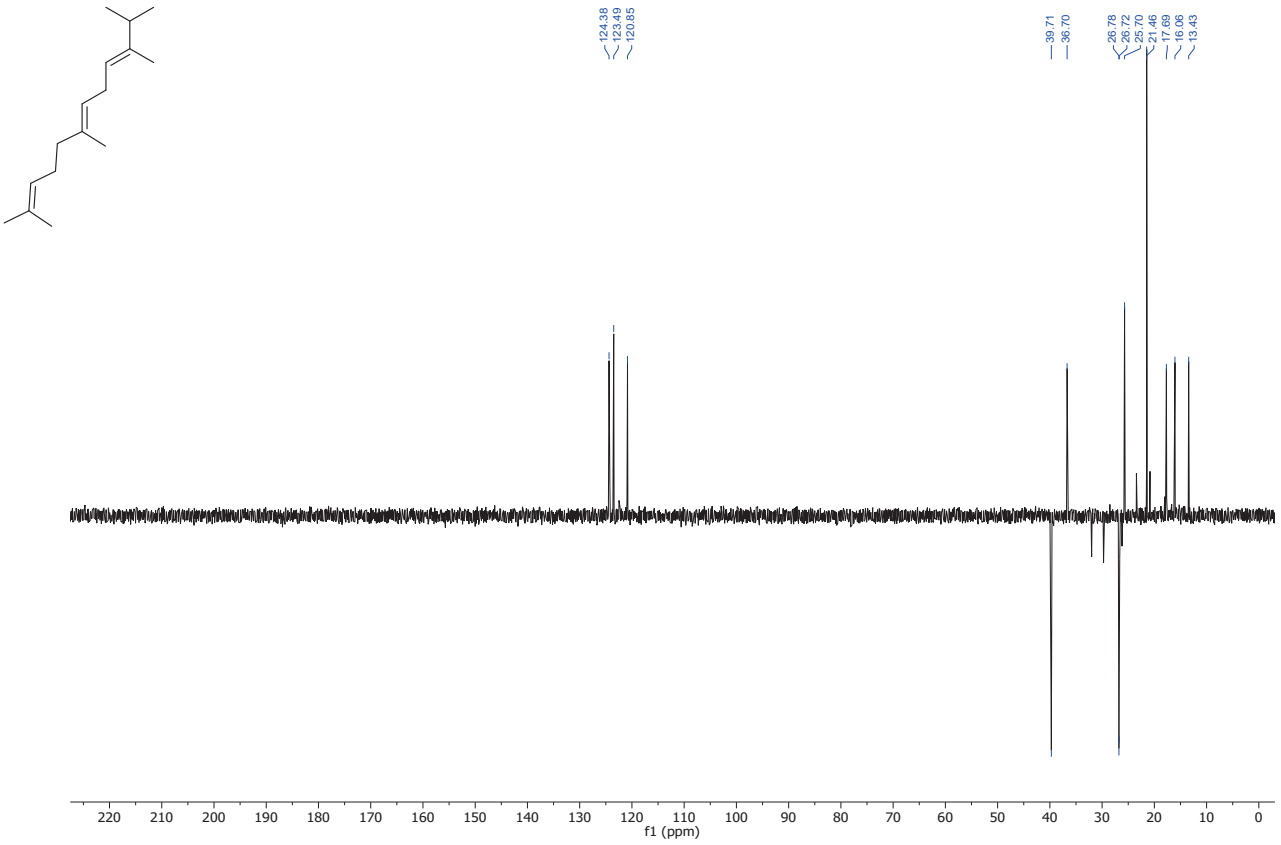
E-olefin



(6E,9E)-2,6,10,11-tetramethyldodeca-2,6,9-triene (85)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

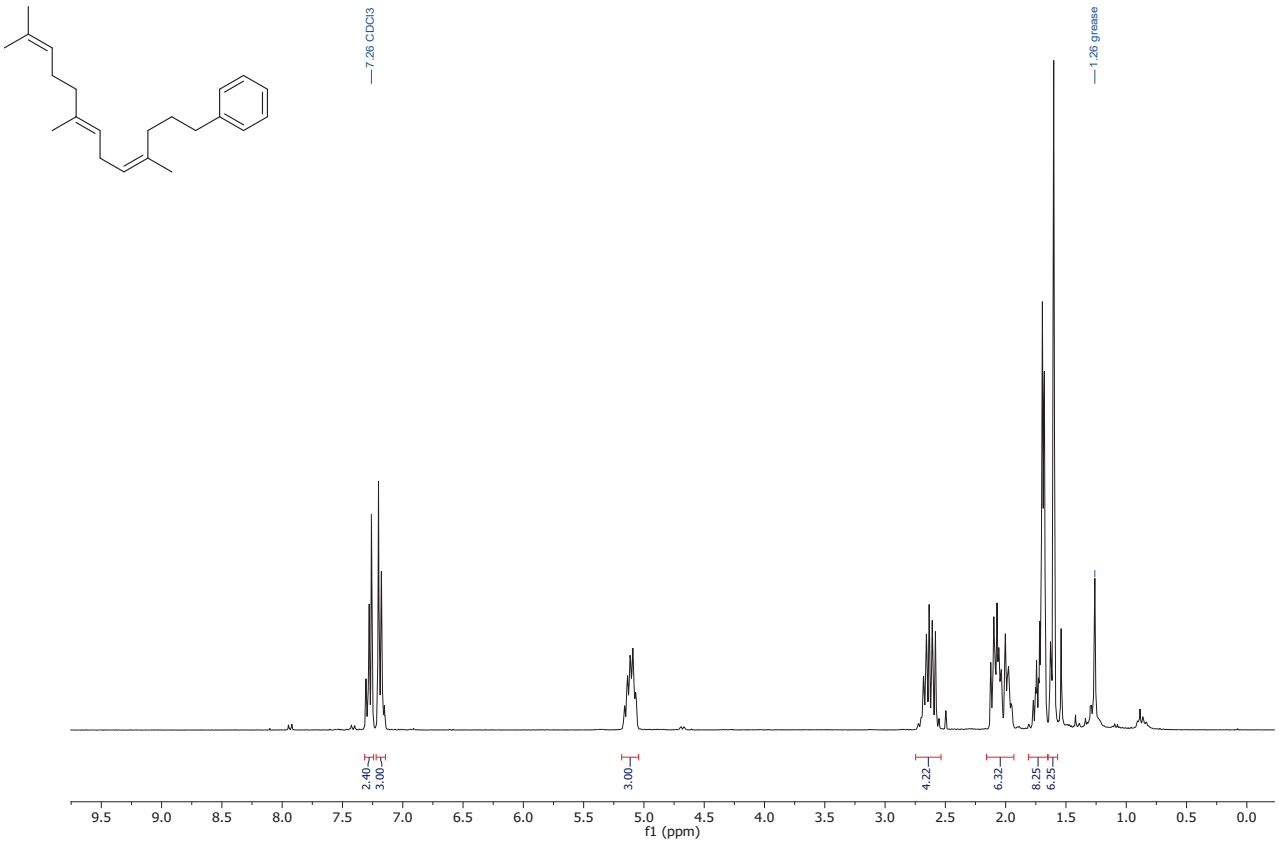
E-olefin



((4Z,7E)-4,8,12-trimethyltrideca-4,7,11-trien-1-yl)benzene (84)

^{1}H NMR (300 MHz, $CDCl_3$)

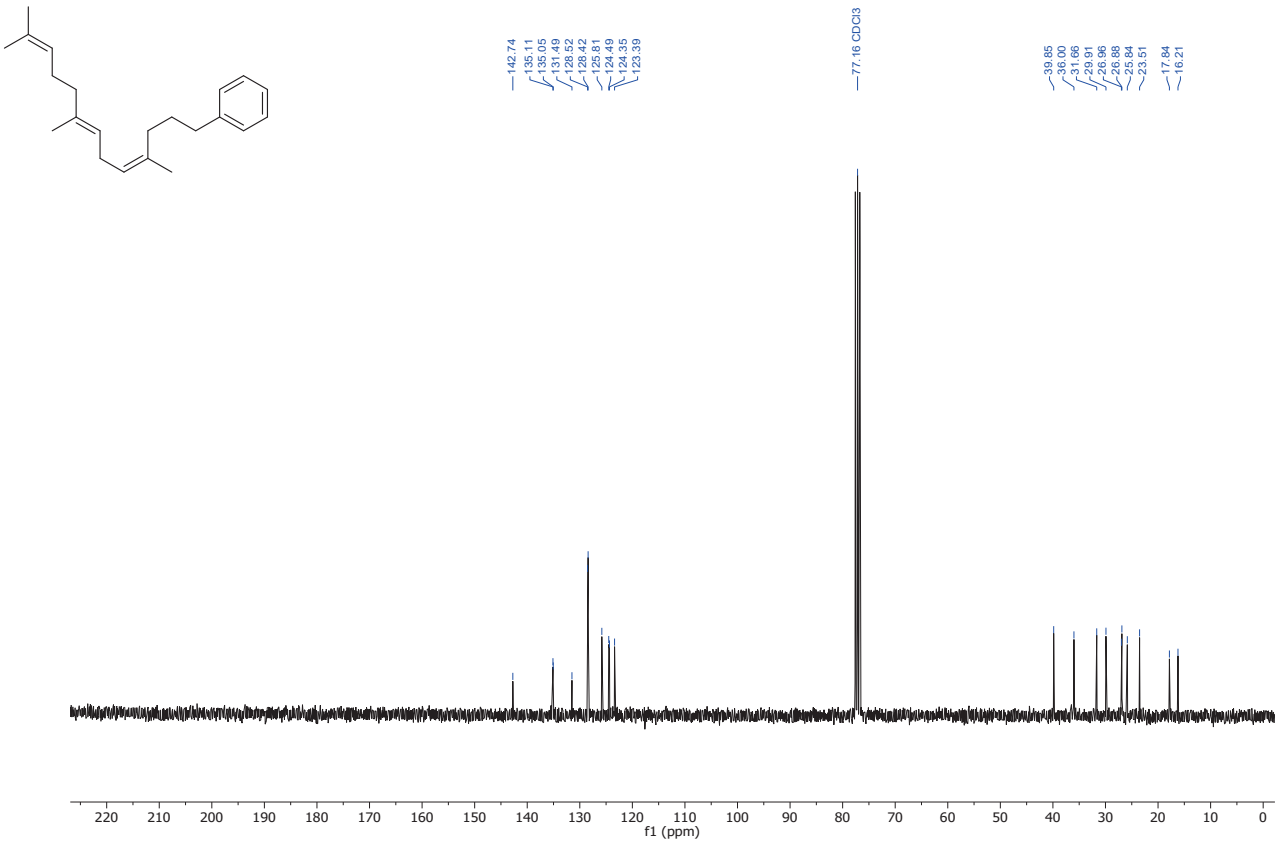
Z-olefin



((4Z,7E)-4,8,12-trimethyltrideca-4,7,11-trien-1-yl)benzene (84)

^{13}C NMR (75 MHz, $CDCl_3$)

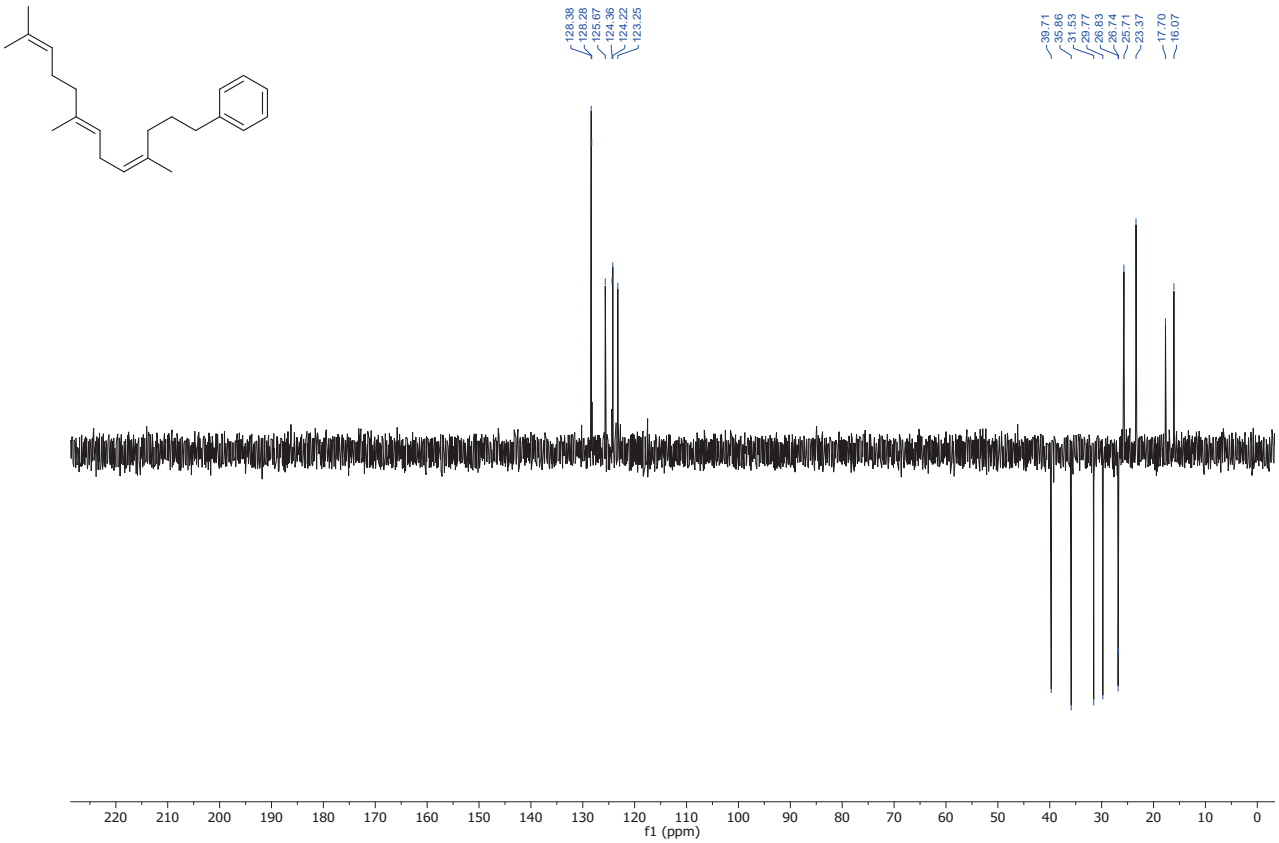
Z-olefin



((4Z,7E)-4,8,12-trimethyltrideca-4,7,11-trien-1-yl)benzene (84)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

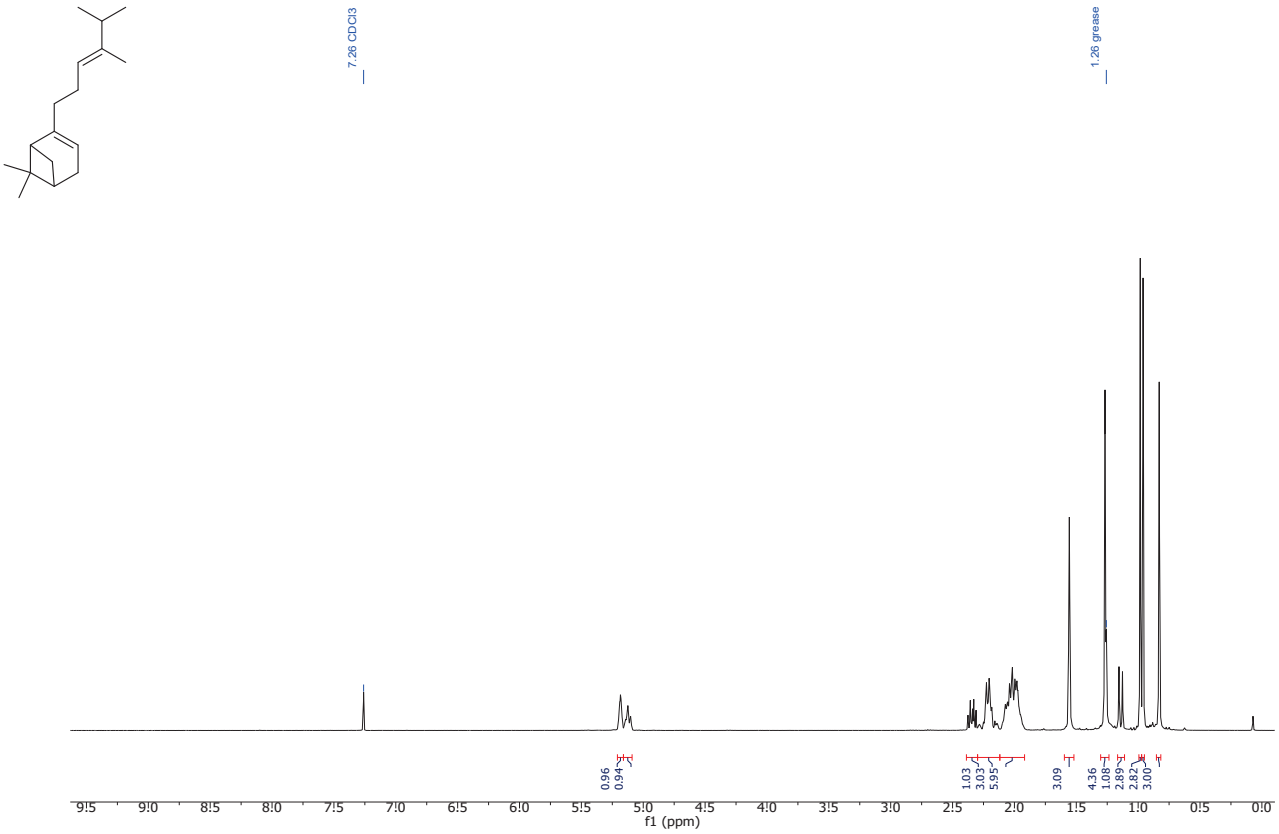
Z-olefin



(E)-2-(4,5-dimethylhex-3-en-1-yl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (89)

^{1}H NMR (300 MHz, $CDCl_3$)

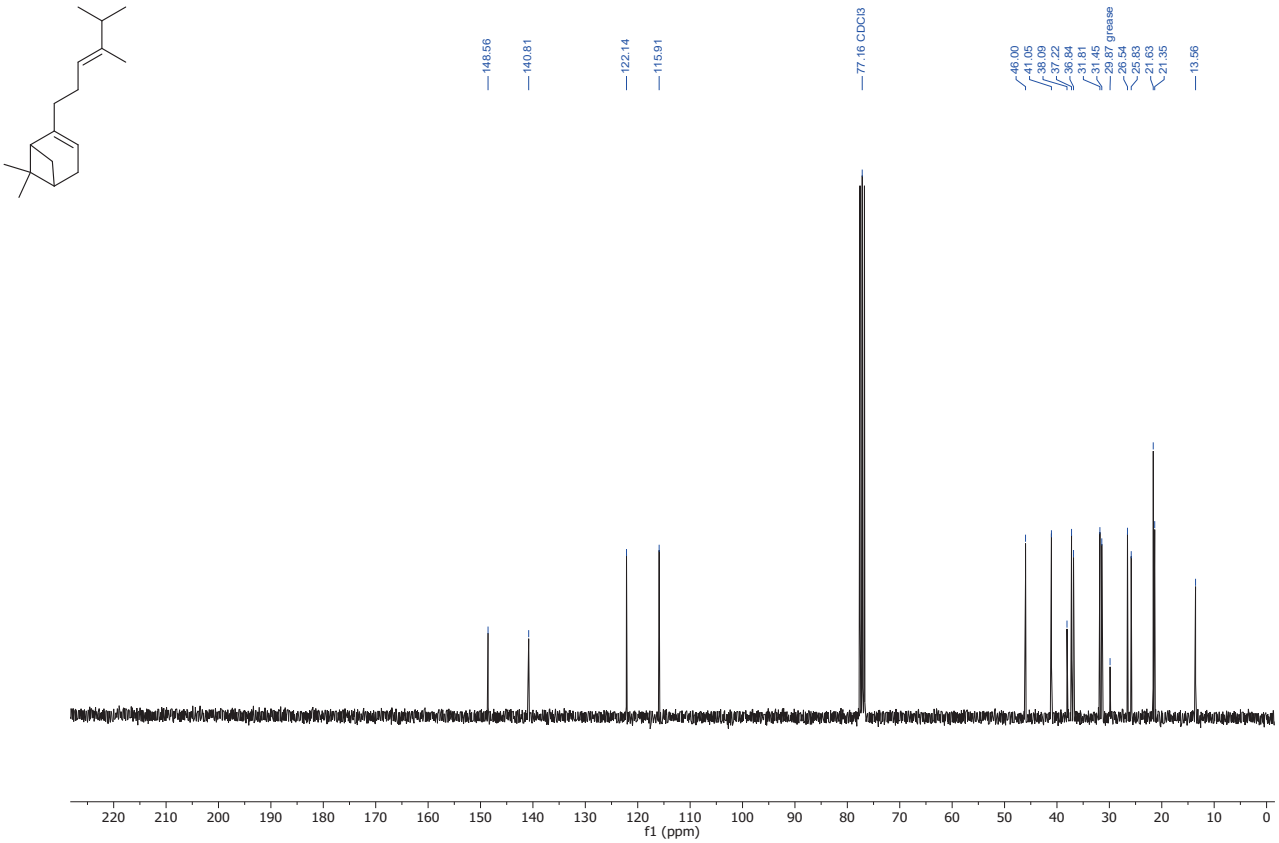
E-olefin



(E)-2-(4,5-dimethylhex-3-en-1-yl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (89)

^{13}C NMR (75 MHz, $CDCl_3$)

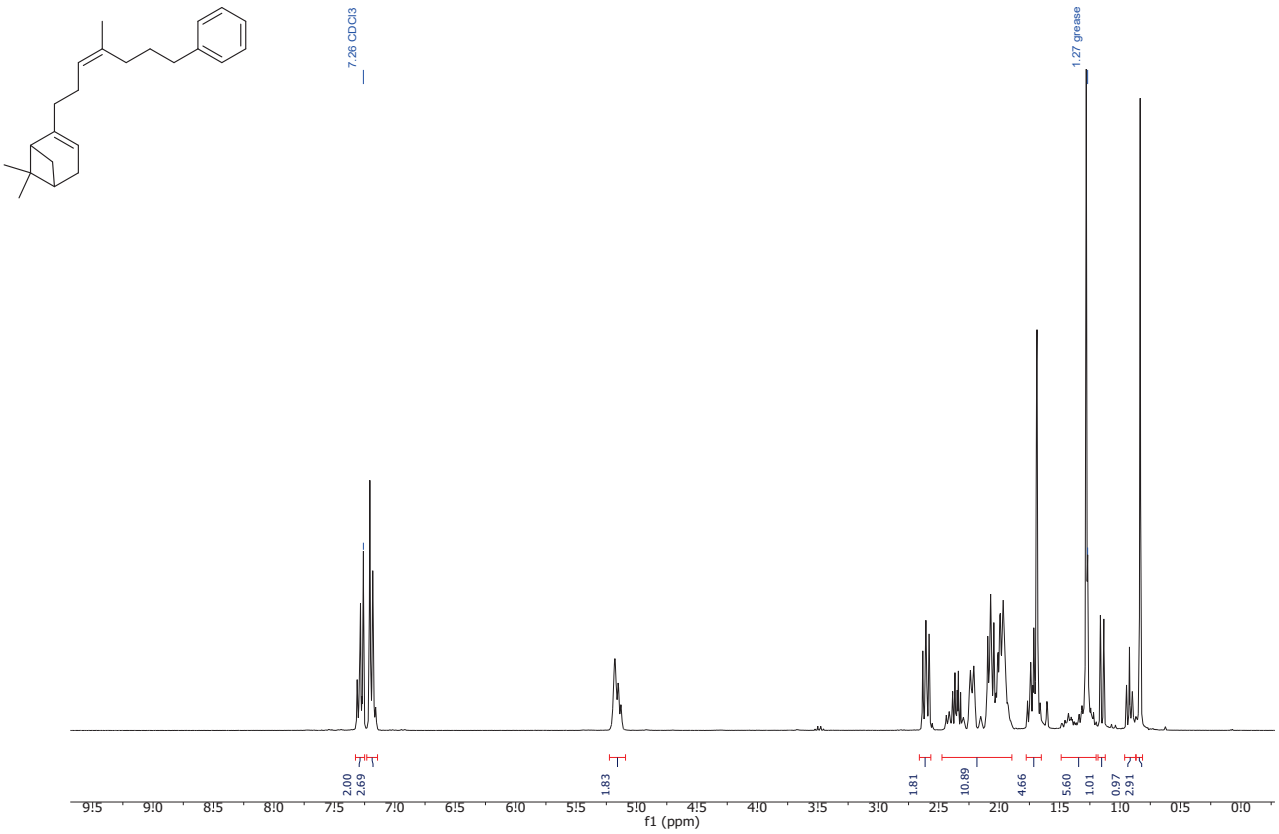
E-olefin



(Z)-6,6-dimethyl-2-(4-methyl-7-phenylhept-3-en-1-yl)bicyclo[3.1.1]hept-2-ene (88)

^{1}H NMR (300 MHz, $CDCl_3$)

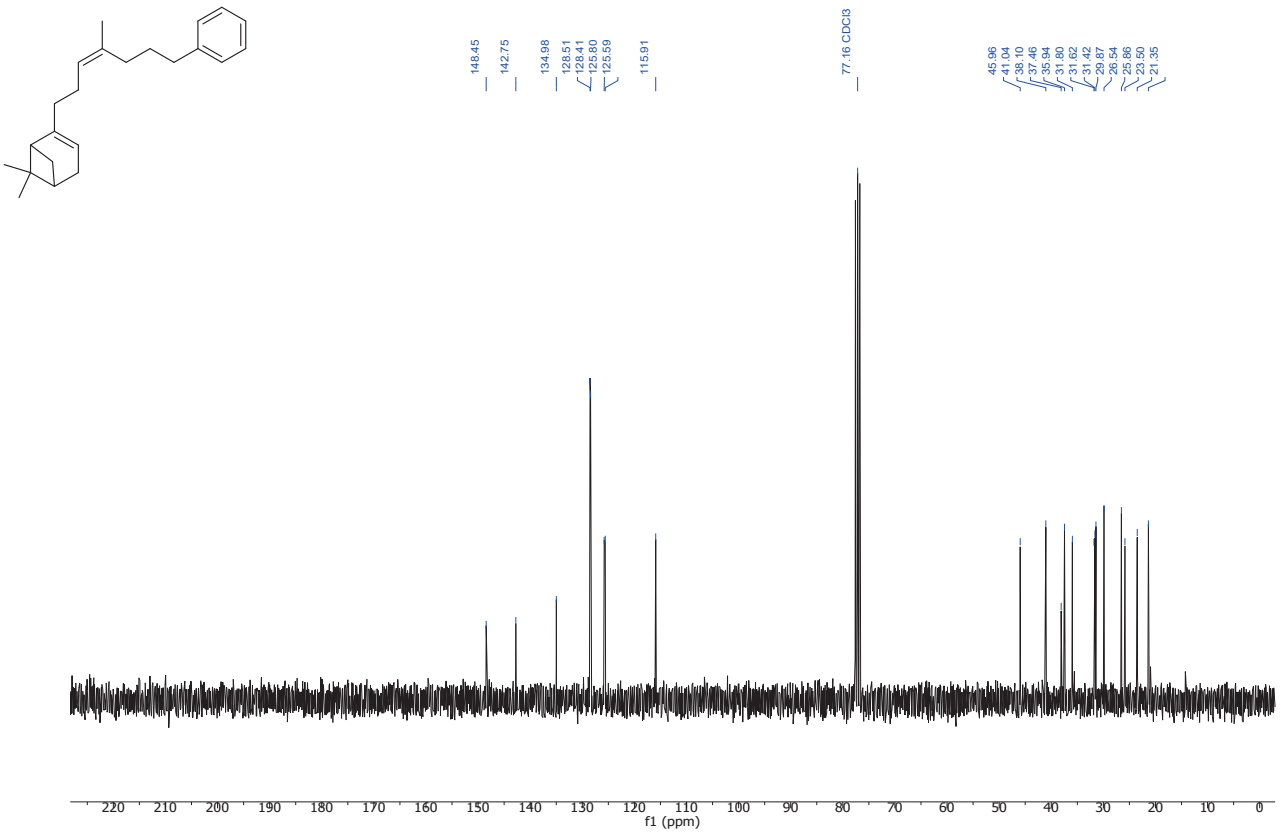
Z-olefin



(Z)-6,6-dimethyl-2-(4-methyl-7-phenylhept-3-en-1-yl)bicyclo[3.1.1]hept-2-ene (88)

^{13}C NMR (75 MHz, $CDCl_3$)

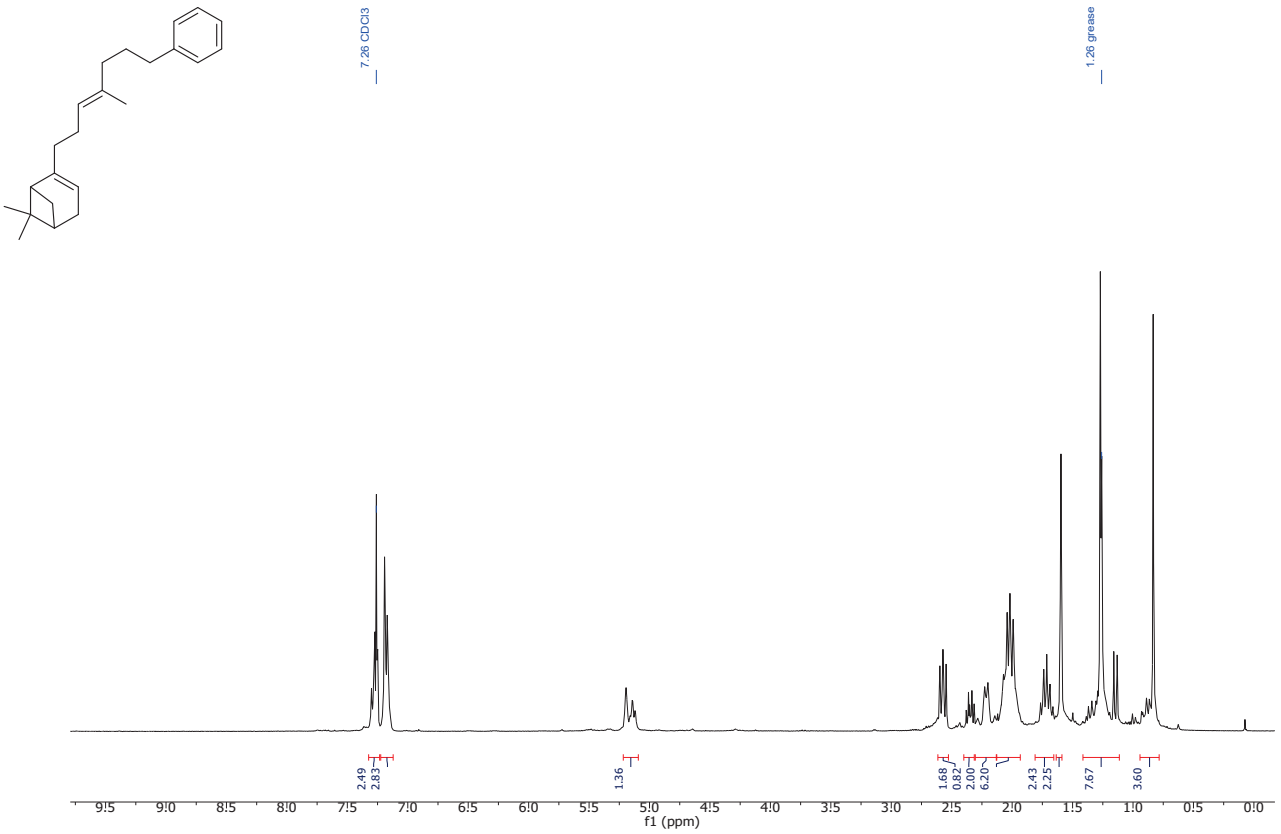
Z-olefin



(Z)-6,6-dimethyl-2-(4-methyl-7-phenylhept-3-en-1-yl)bicyclo[3.1.1]hept-2-ene (88)

^{1}H NMR (300 MHz, $CDCl_3$)

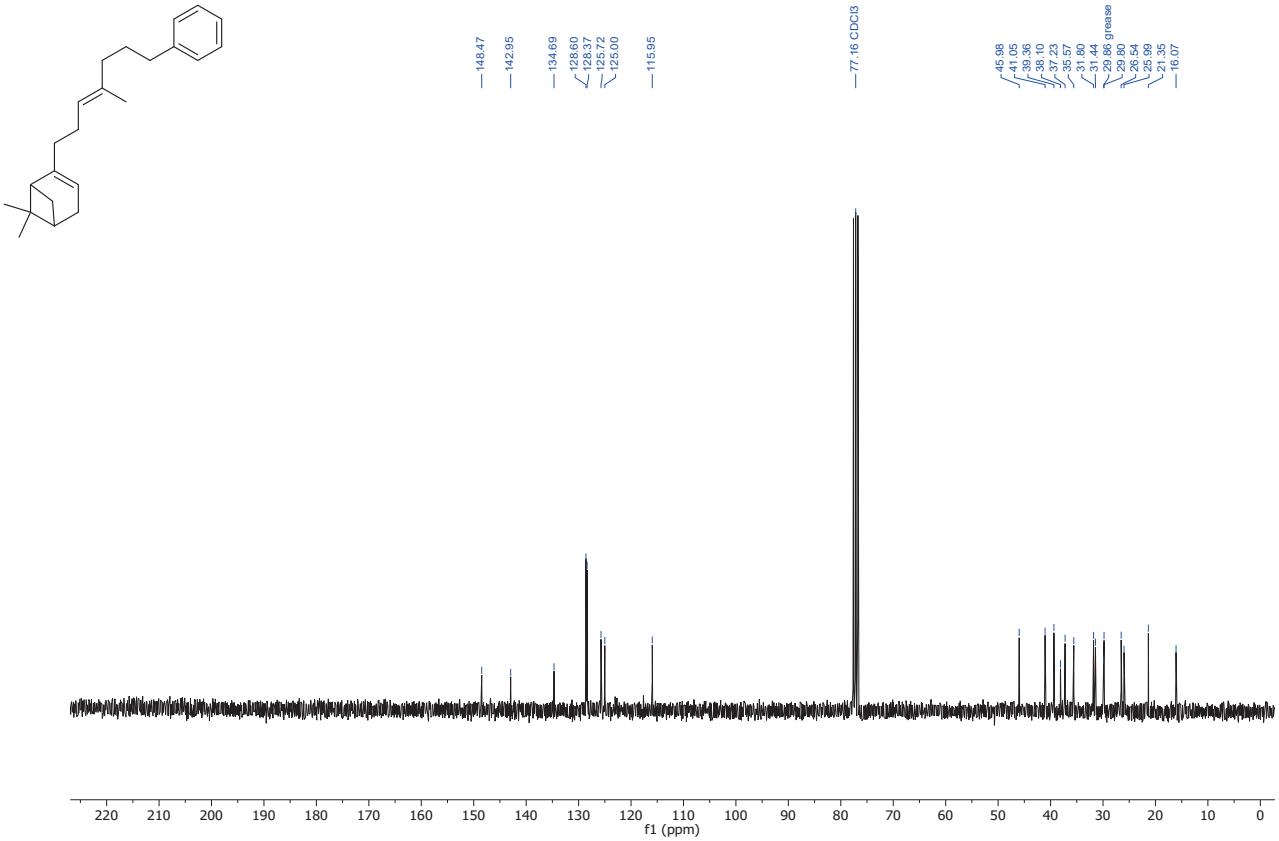
E-olefin



(Z)-6,6-dimethyl-2-(4-methyl-7-phenylhept-3-en-1-yl)bicyclo[3.1.1]hept-2-ene (88)

^{13}C NMR (75 MHz, $CDCl_3$)

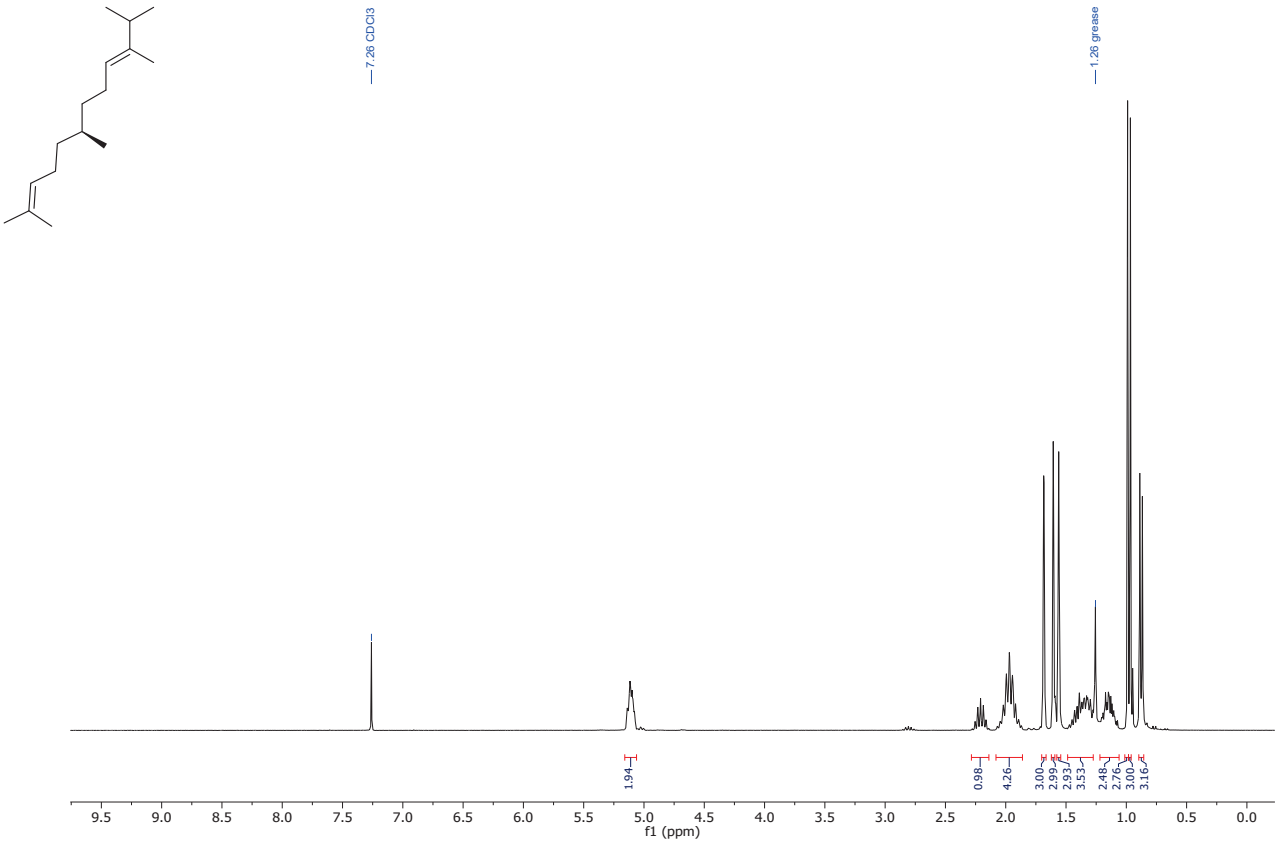
E-olefin



(S,E)-2,6,10,11-tetramethyldodeca-2,9-diene (87)

^{1}H NMR (300 MHz, $CDCl_3$)

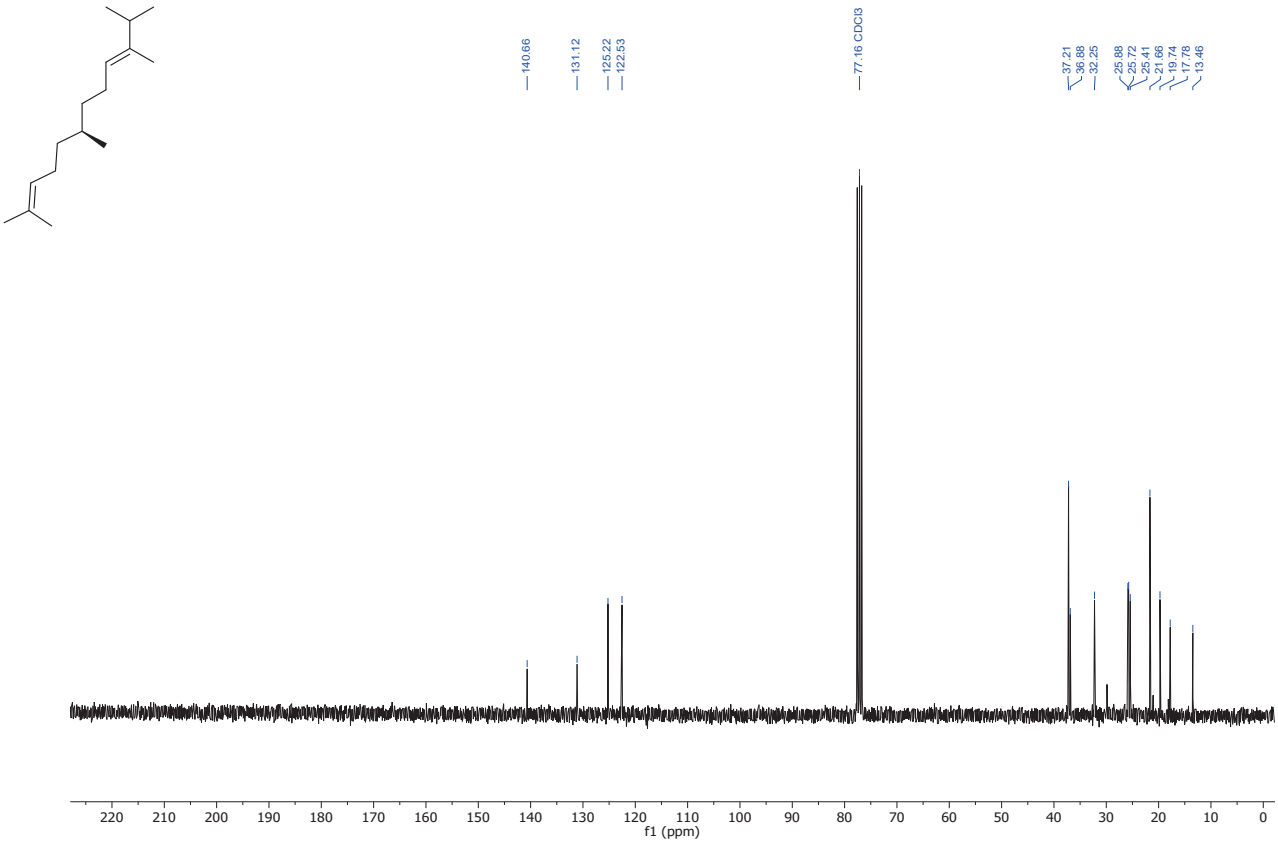
E-olefin



(S,E)-2,6,10,11-tetramethyldodeca-2,9-diene (87)

^{13}C NMR (75 MHz, $CDCl_3$)

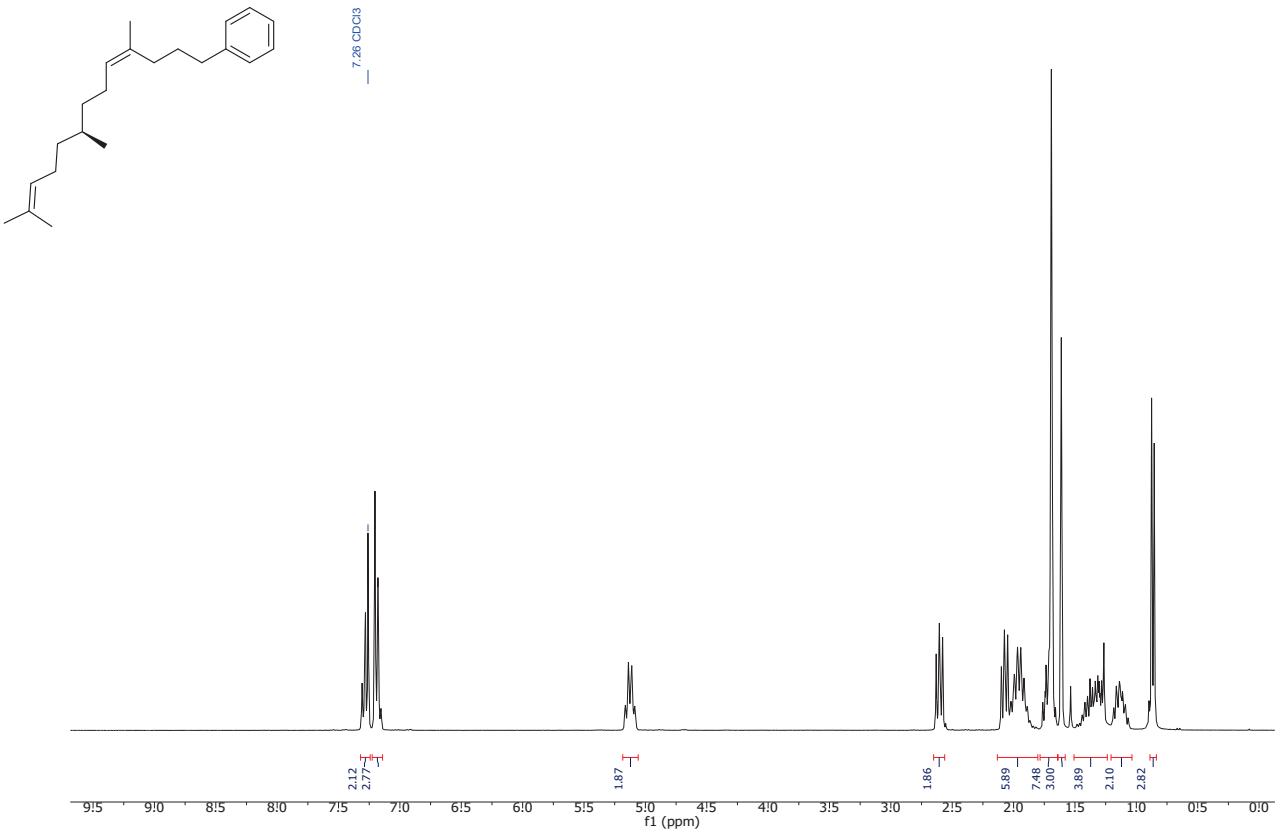
E-olefin



(S,Z)-(4,8,12-trimethyltrideca-4,11-dien-1-yl)benzene (86)

^{1}H NMR (300 MHz, $CDCl_3$)

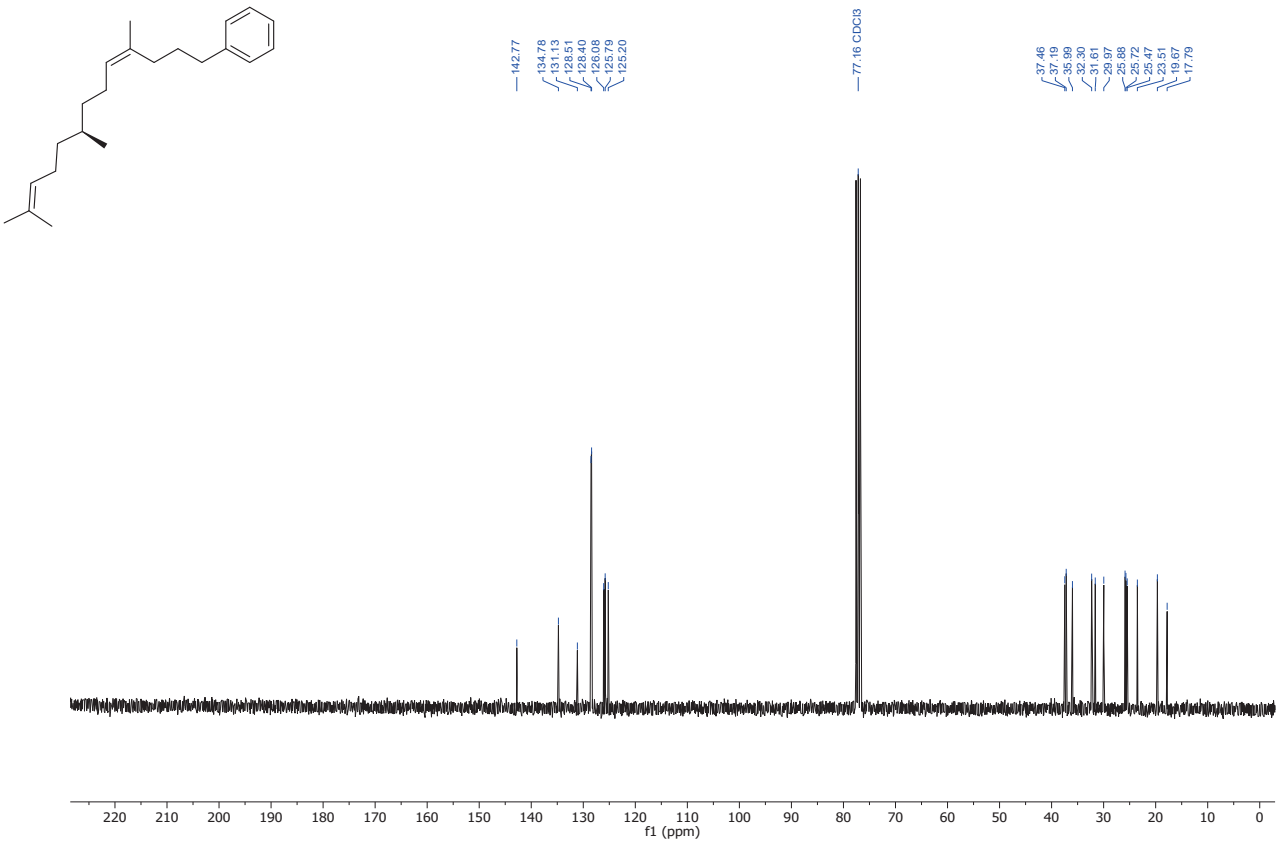
Z-olefin



(S,Z)-(4,8,12-trimethyltrideca-4,11-dien-1-yl)benzene (86)

^{13}C NMR (75 MHz, $CDCl_3$)

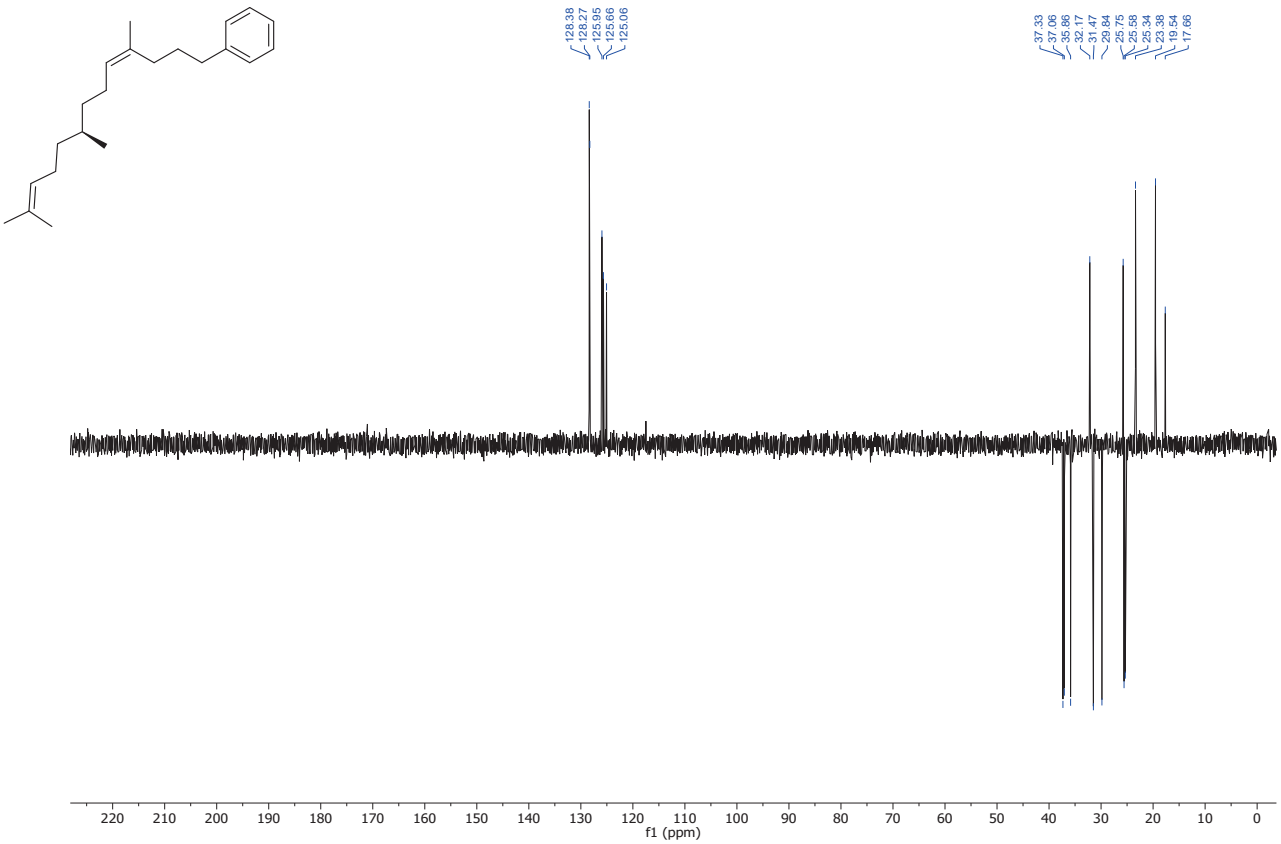
Z-olefin



(S,Z)-(4,8,12-trimethyltrideca-4,11-dien-1-yl)benzene (86)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

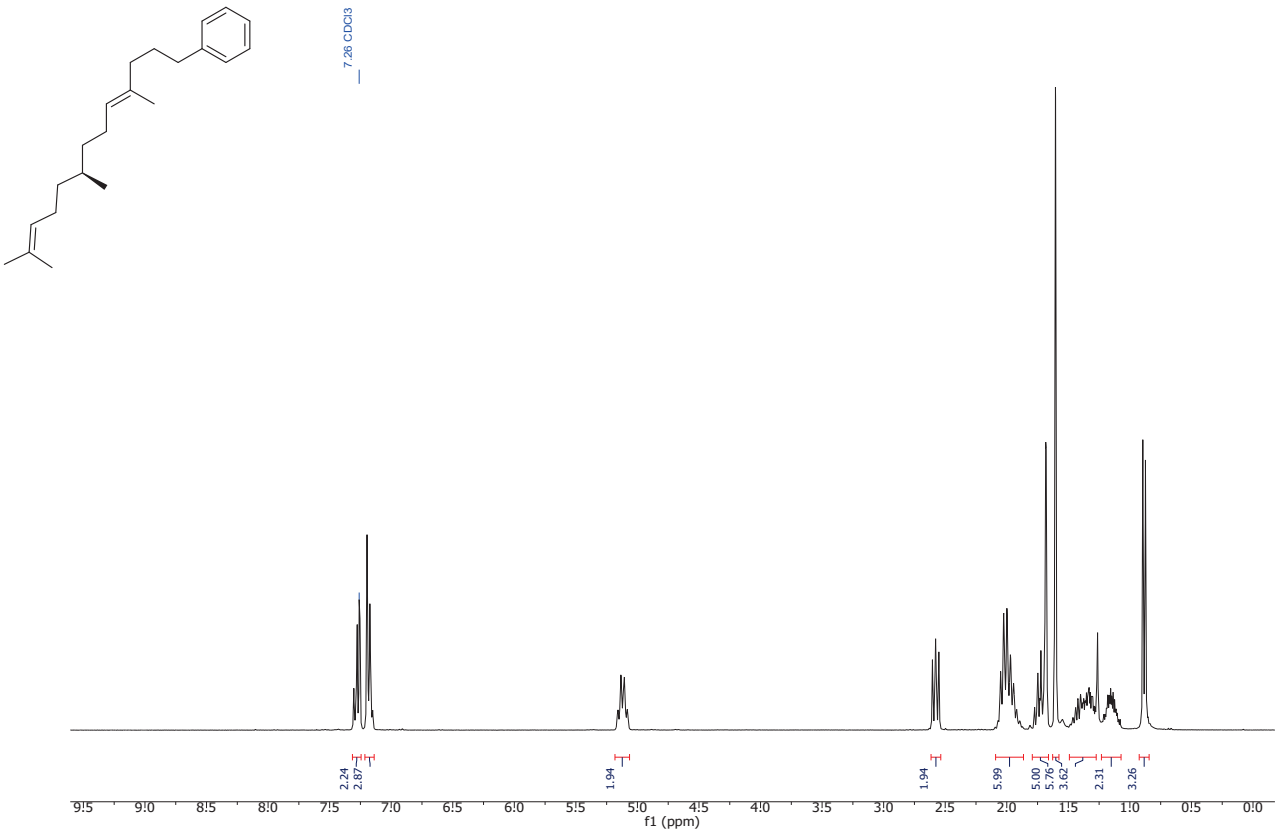
Z-olefin



(S,E)-(4,8,12-trimethyltrideca-4,11-dien-1-yl)benzene (86)

^{1}H NMR (300 MHz, $CDCl_3$)

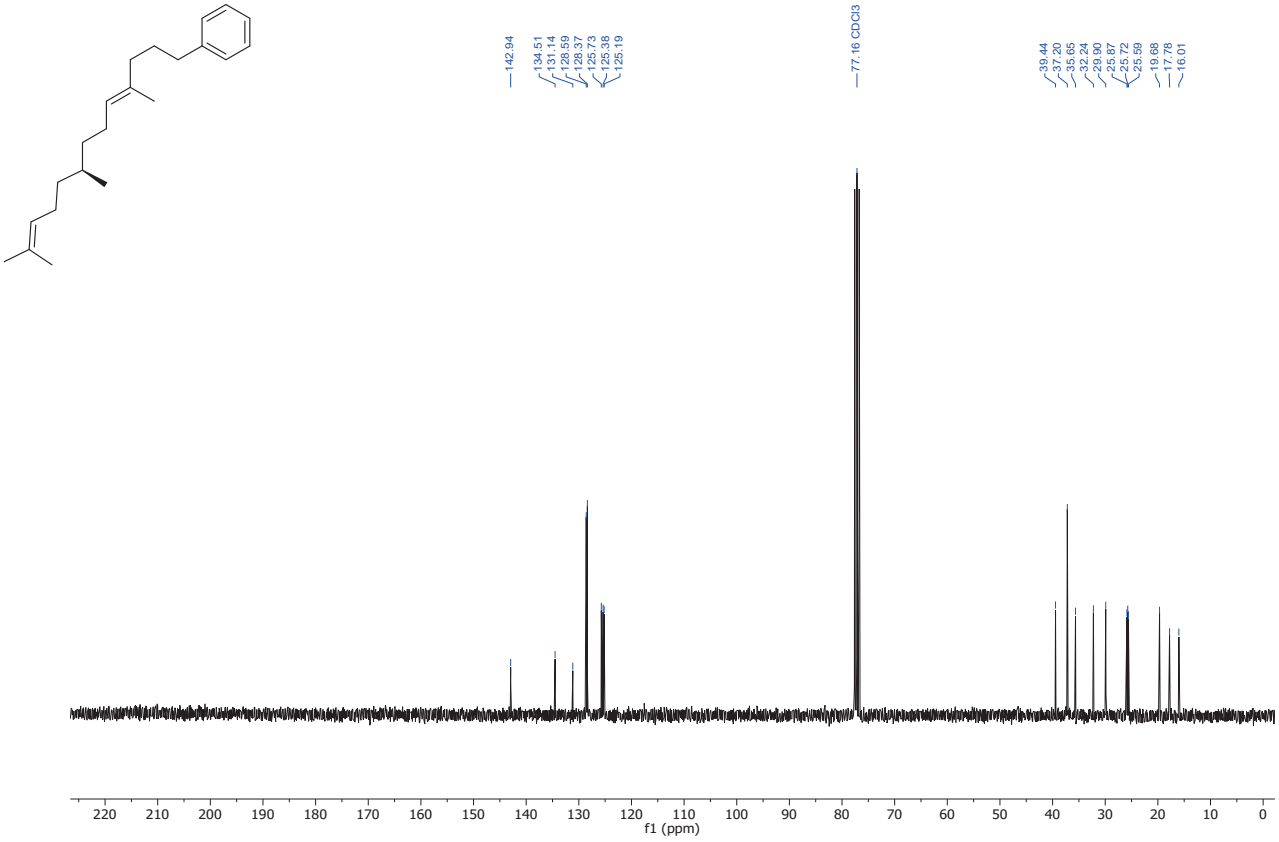
E-olefin



(S,E)-(4,8,12-trimethyltrideca-4,11-dien-1-yl)benzene (86)

^{13}C NMR (75 MHz, $CDCl_3$)

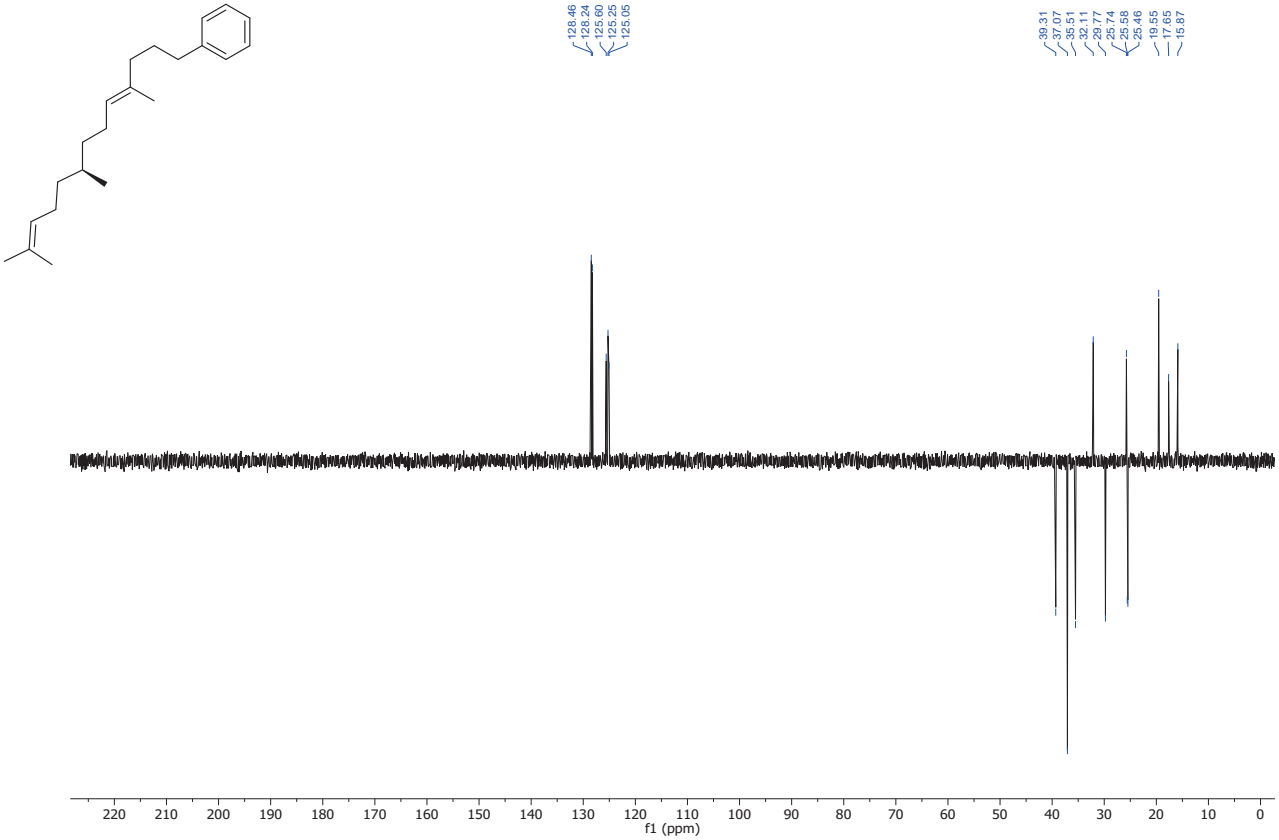
E-olefin



(S,E)-(4,8,12-trimethyltrideca-4,11-dien-1-yl)benzene (86)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

E-olefin

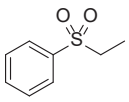


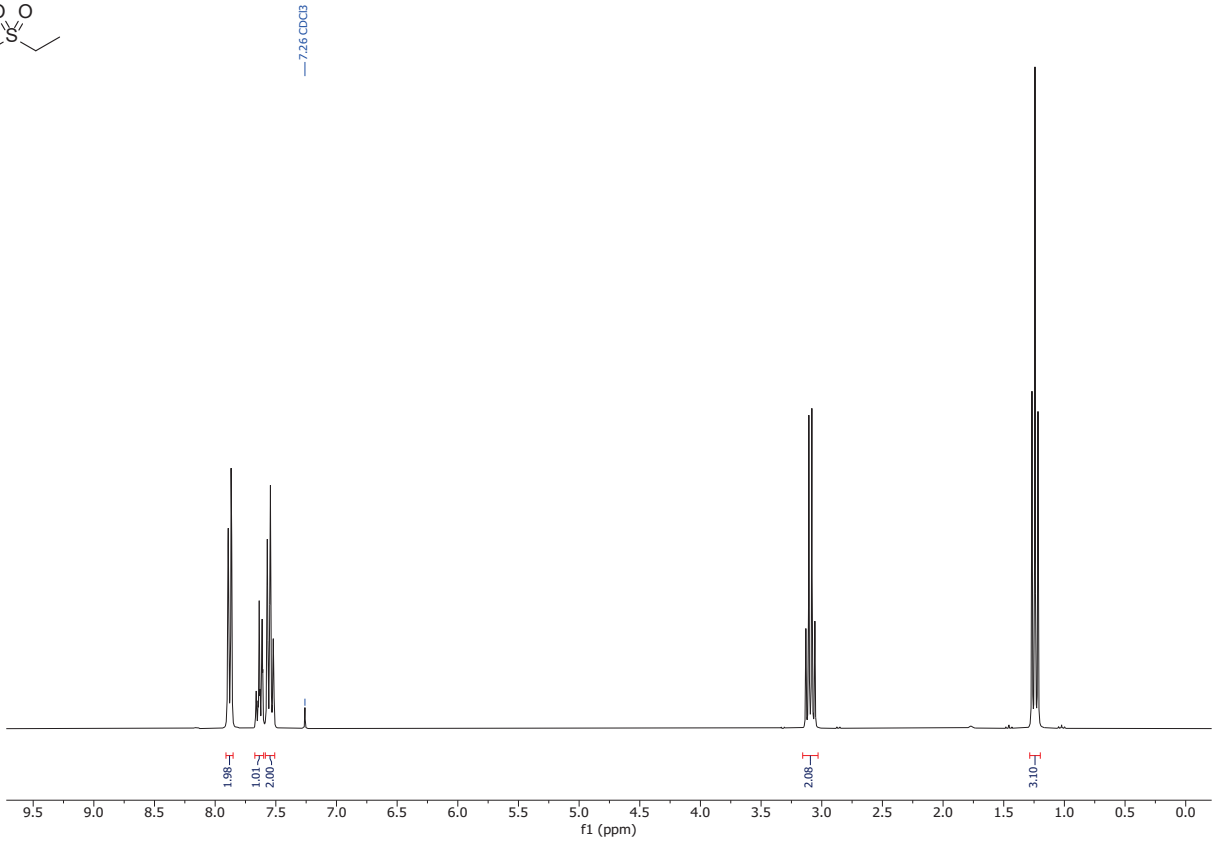
Appendix

NMR spectra of Chapter 2

(Ethylsulfonyl)benzene (8)

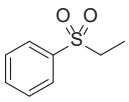
^{1}H NMR (300 MHz, $CDCl_3$)

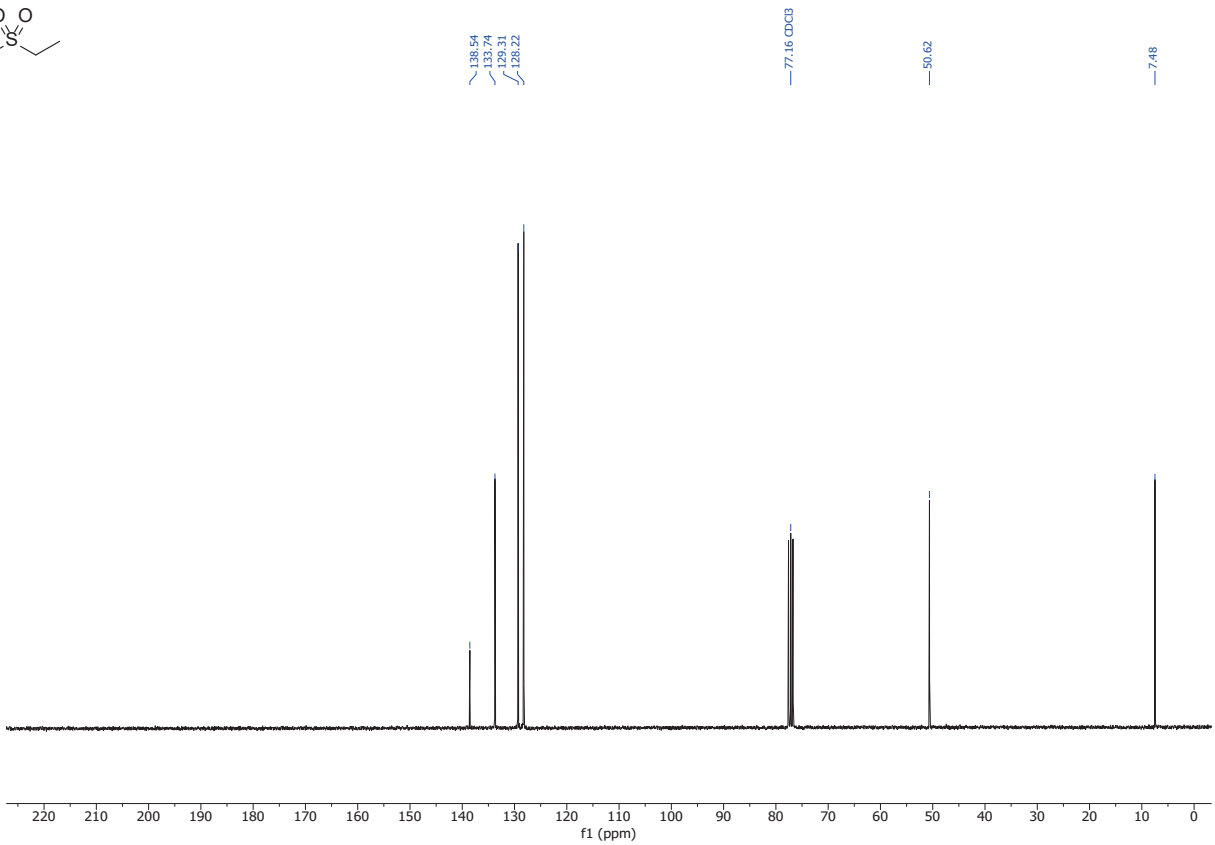




(Ethylsulfonyl)benzene (8)

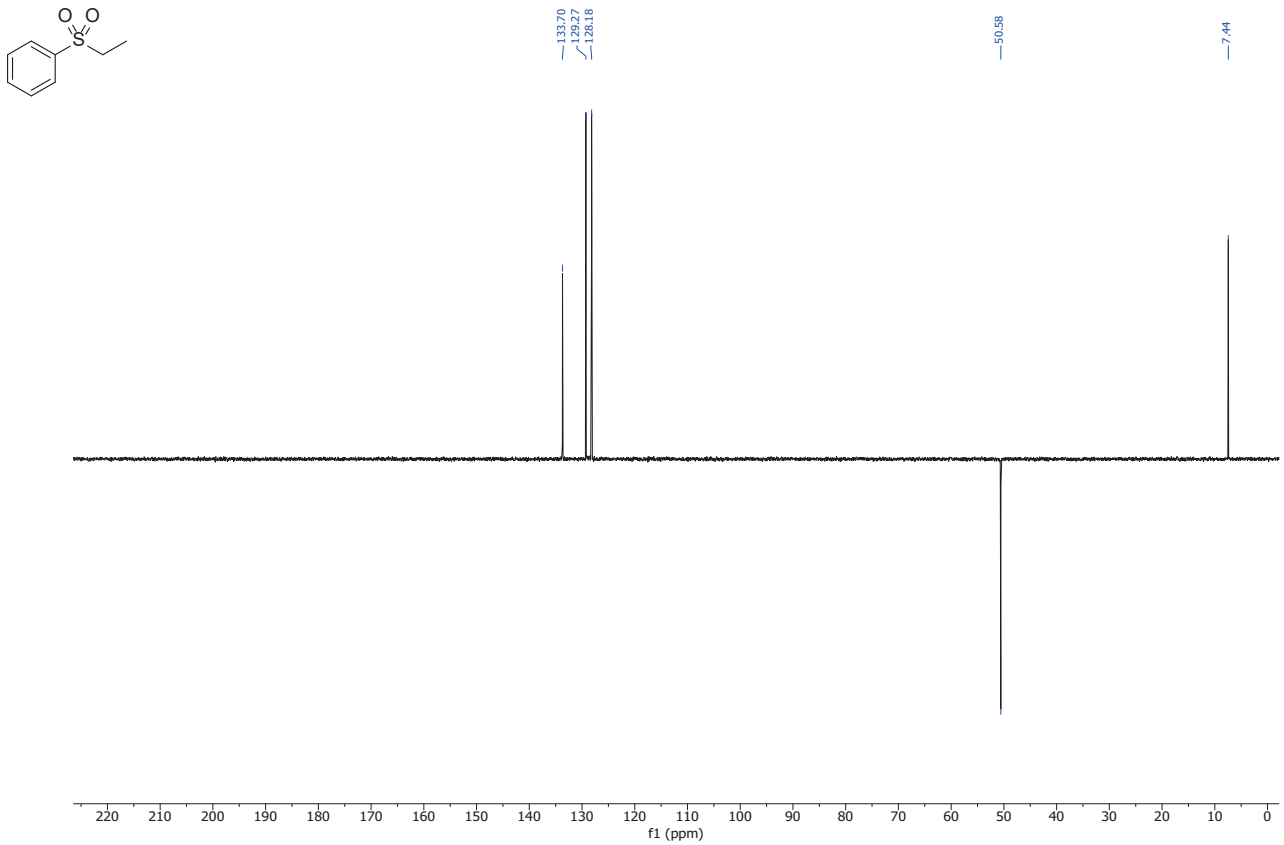
^{13}C NMR (75 MHz, $CDCl_3$)





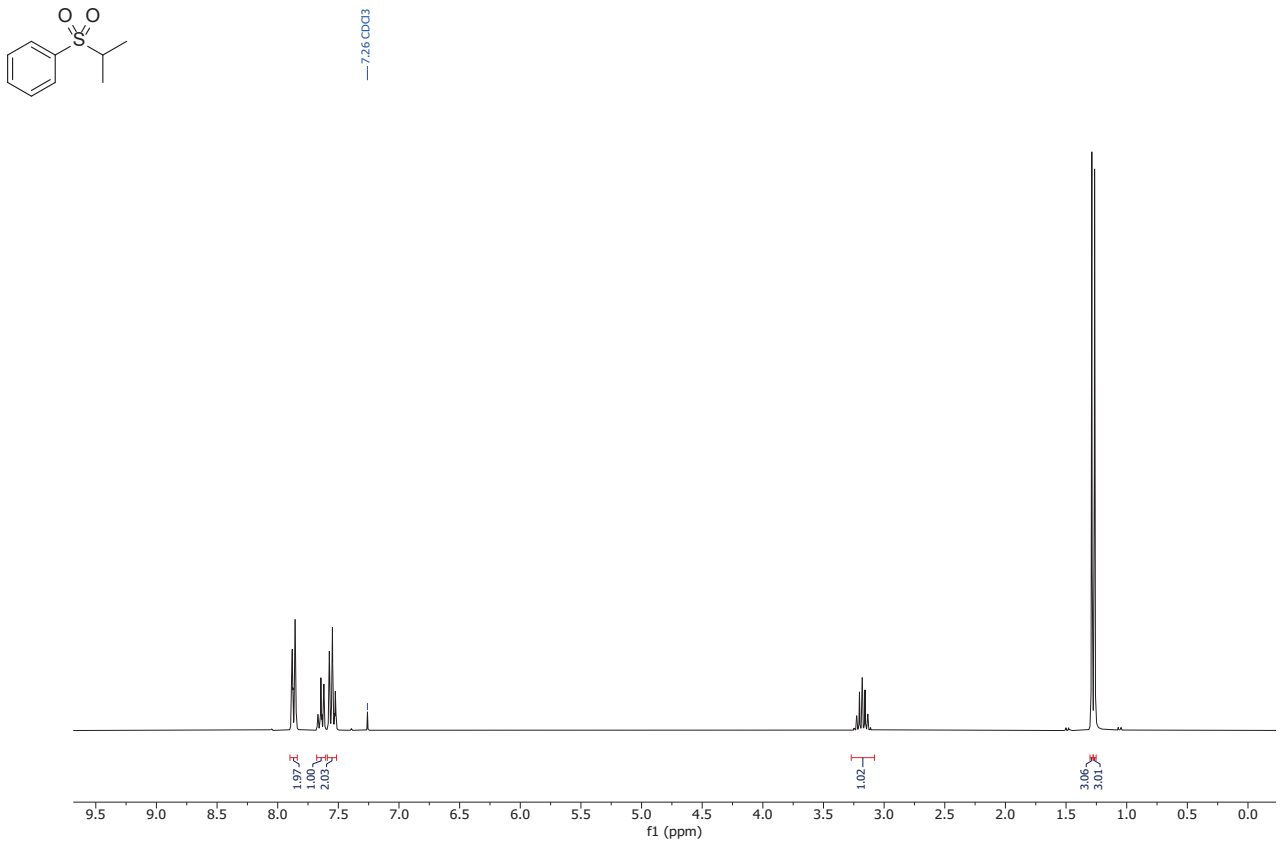
(Ethylsulfonyl)benzene (8)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



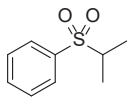
(Isopropylsulfonyl)benzene (4)

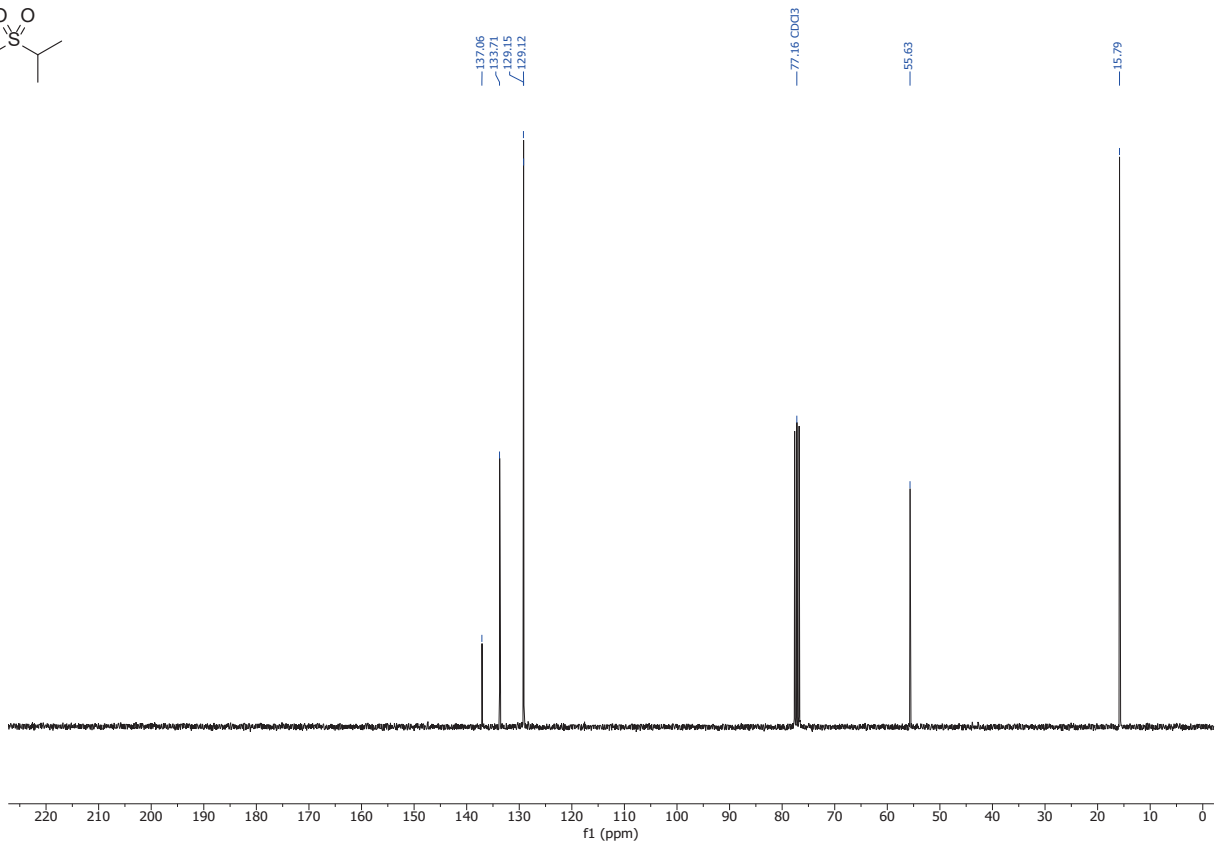
^{1}H NMR (300 MHz, $CDCl_3$)



(Isopropylsulfonyl)benzene (4)

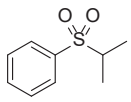
^{13}C NMR (75 MHz, $CDCl_3$)

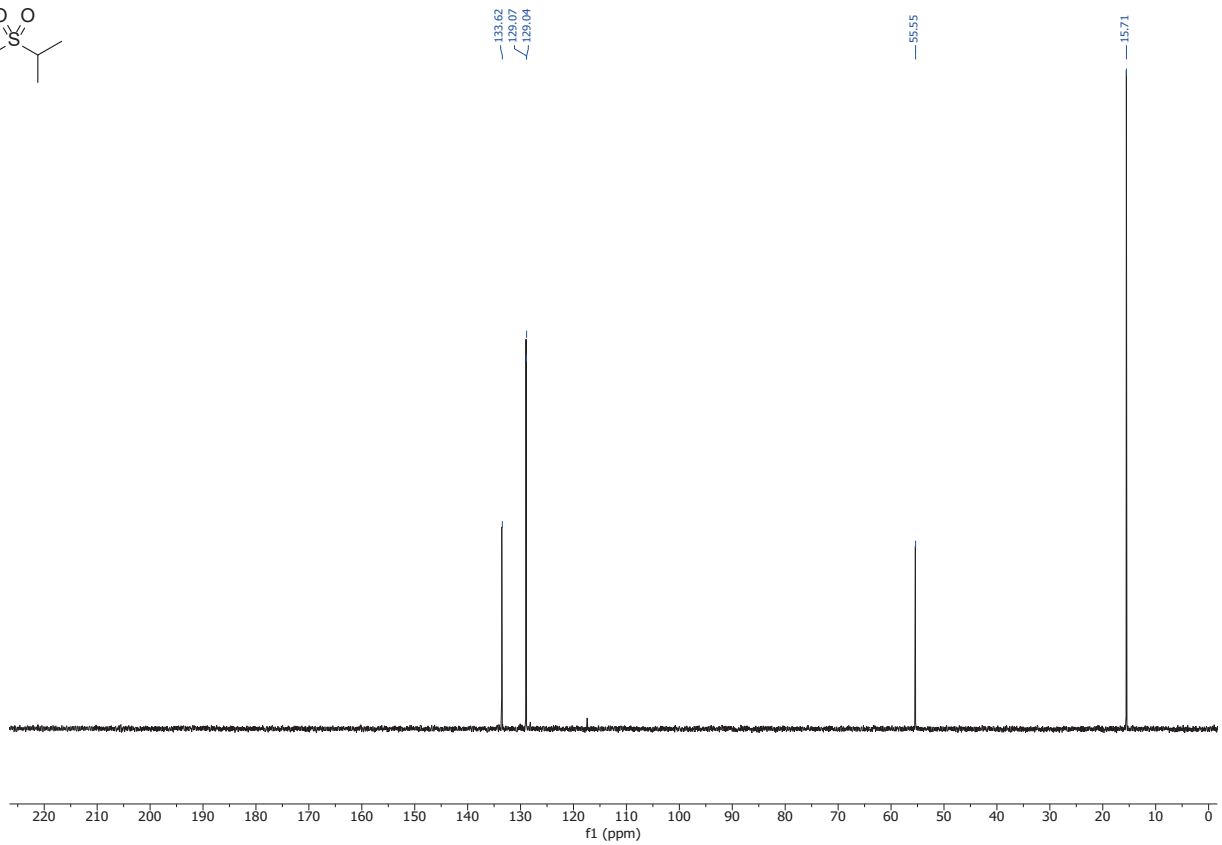




(Isopropylsulfonyl)benzene (4)

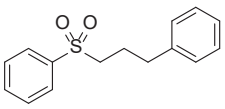
^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

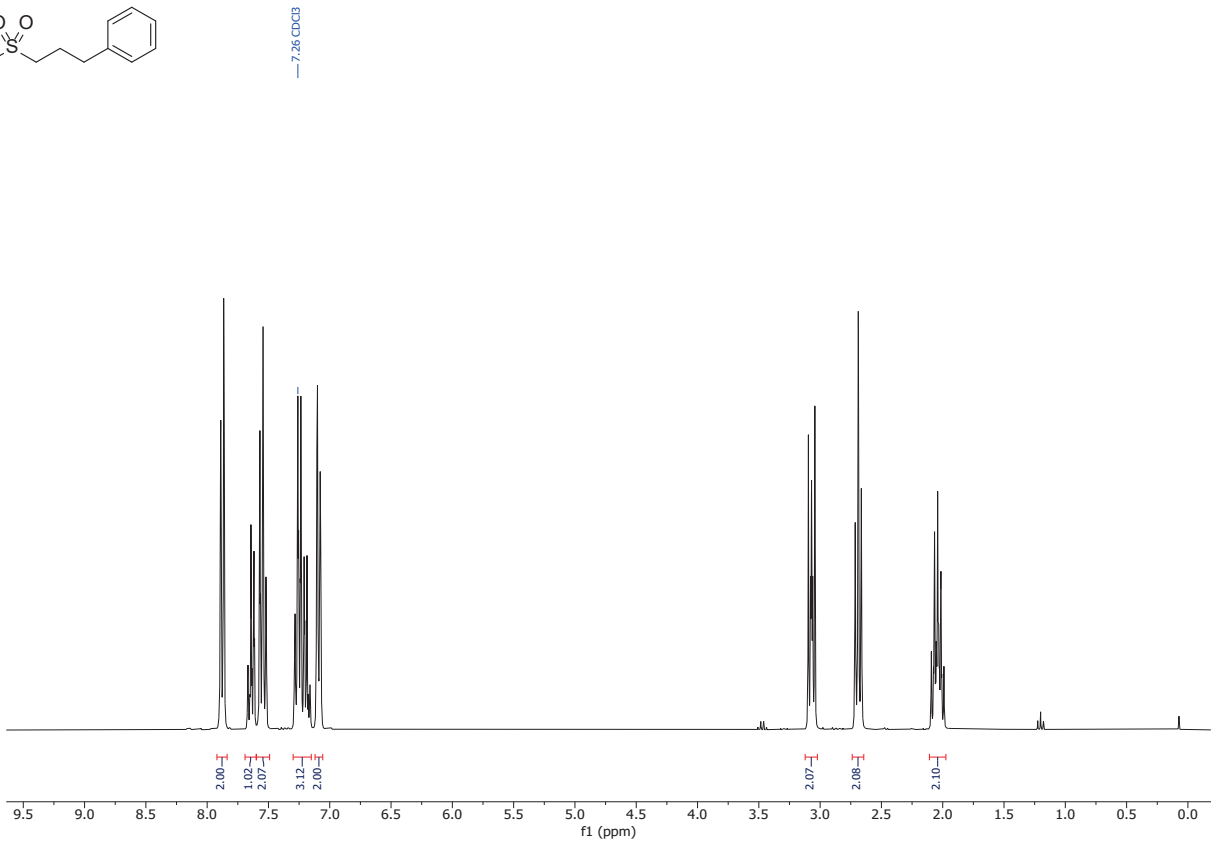




((3-phenylpropyl)sulfonyl)benzene (42)

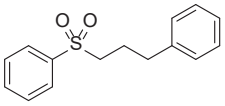
^{1}H NMR (300 MHz, $CDCl_3$)

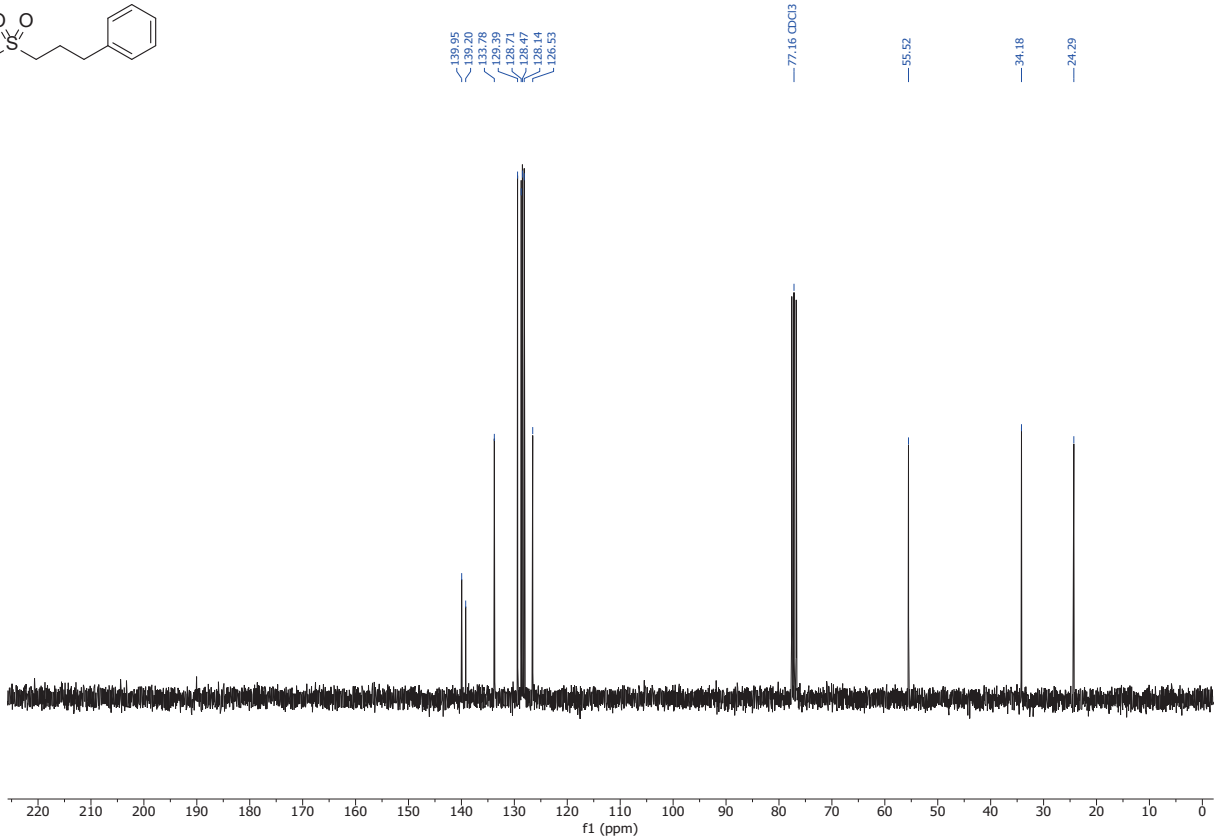




((3-phenylpropyl)sulfonyl)benzene (42)

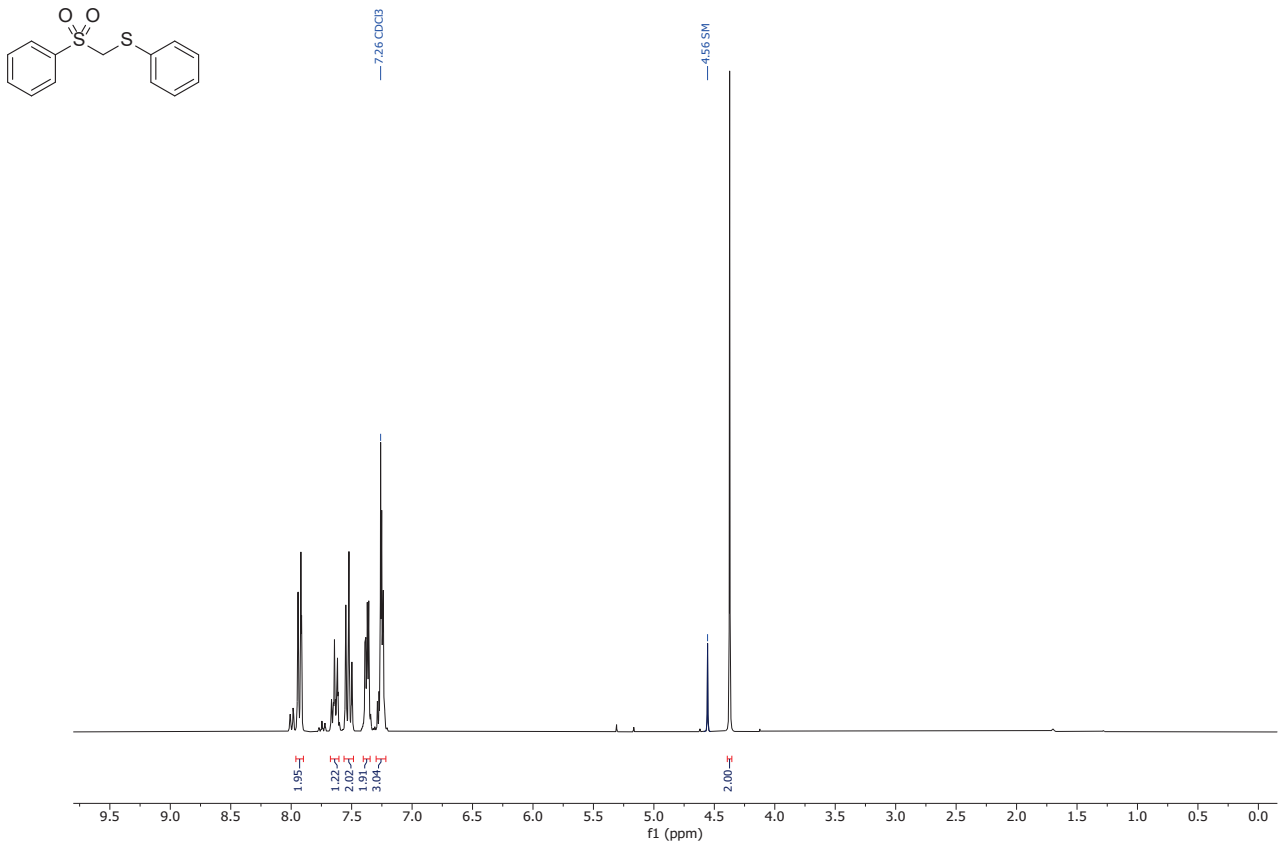
^{13}C NMR (75 MHz, $CDCl_3$)





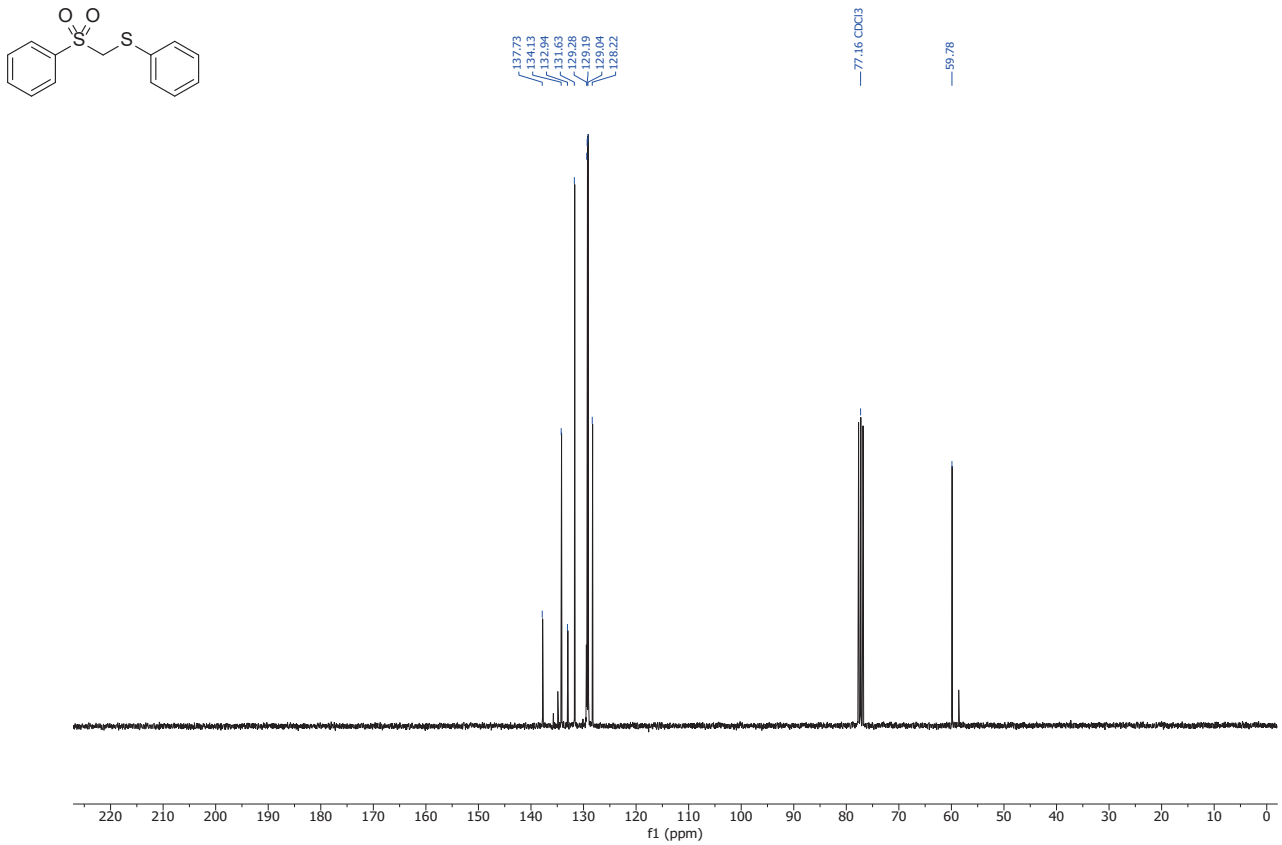
phenyl((phenylsulfonyl)methyl)sulfane (36)

^{1}H NMR (300 MHz, $CDCl_3$)



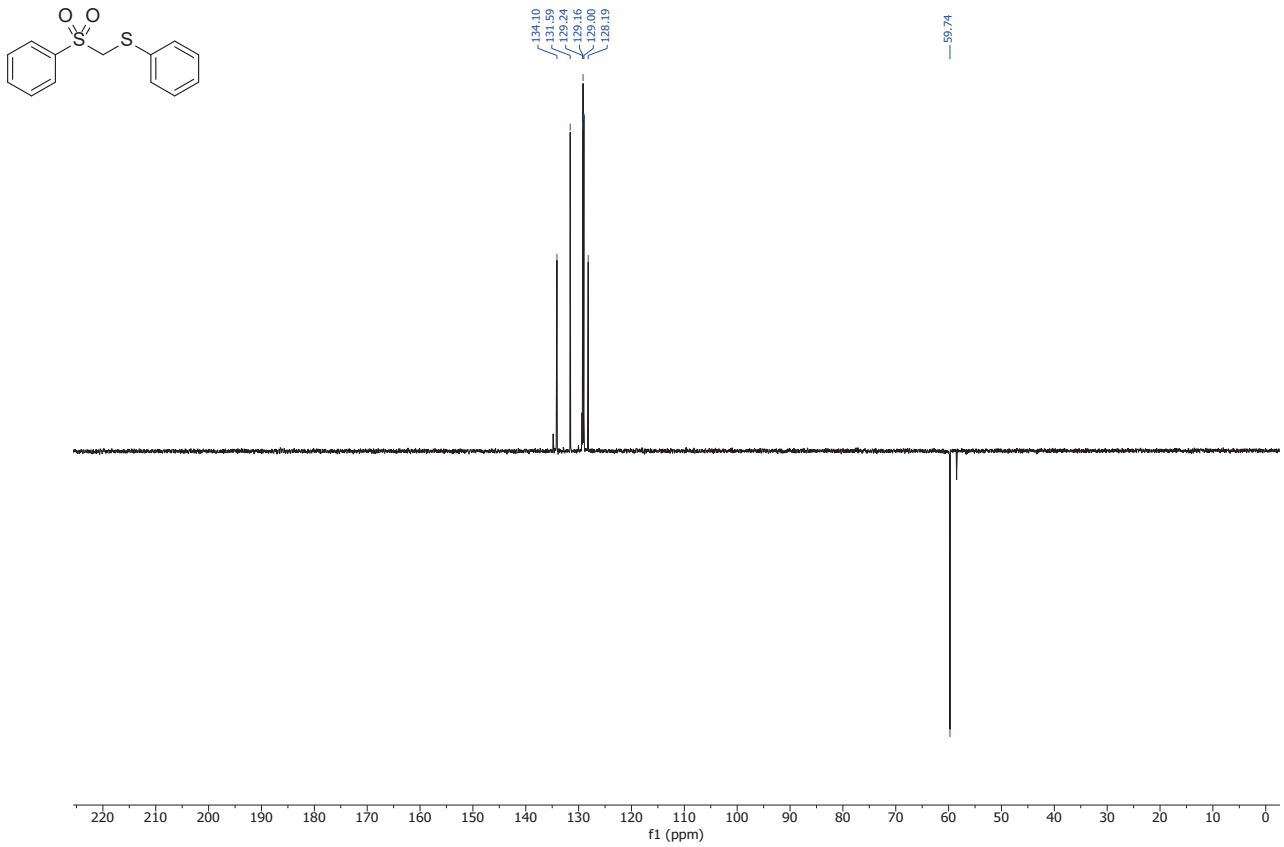
phenyl((phenylsulfonyl)methyl)sulfane (36)

^{13}C NMR (75 MHz, $CDCl_3$)



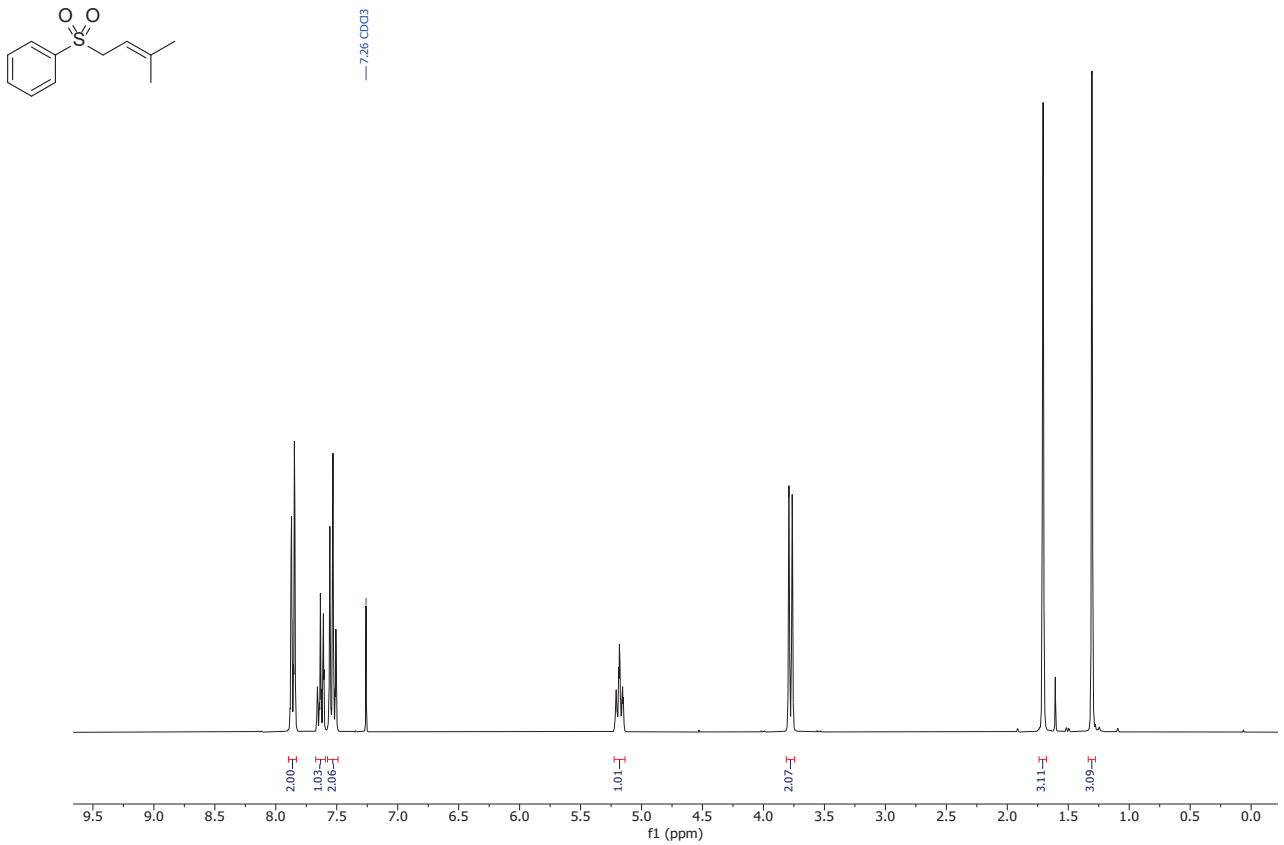
phenyl((phenylsulfonyl)methyl)sulfane (36)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



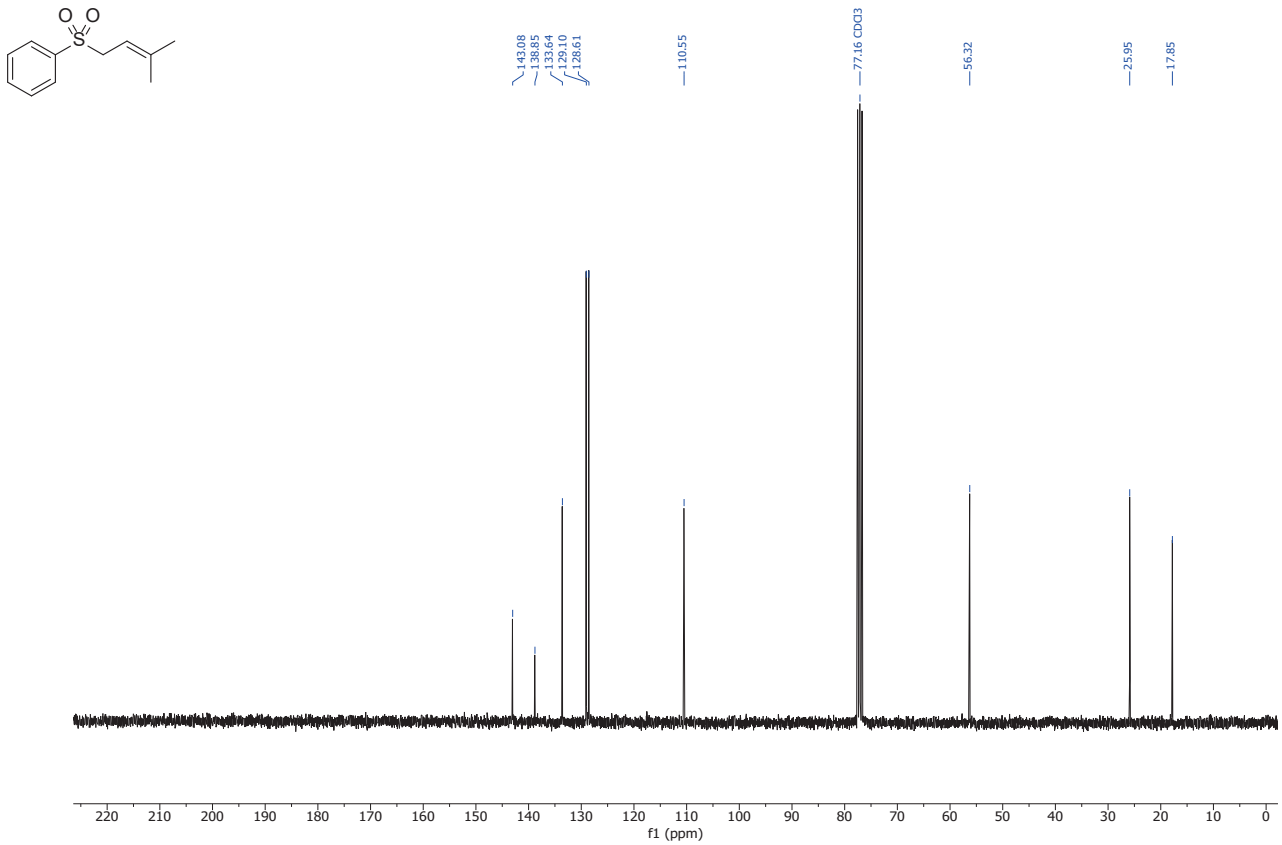
((3-methylbut-2-en-1-yl)sulfonyl)benzene (27)

^{1}H NMR (300 MHz, $CDCl_3$)



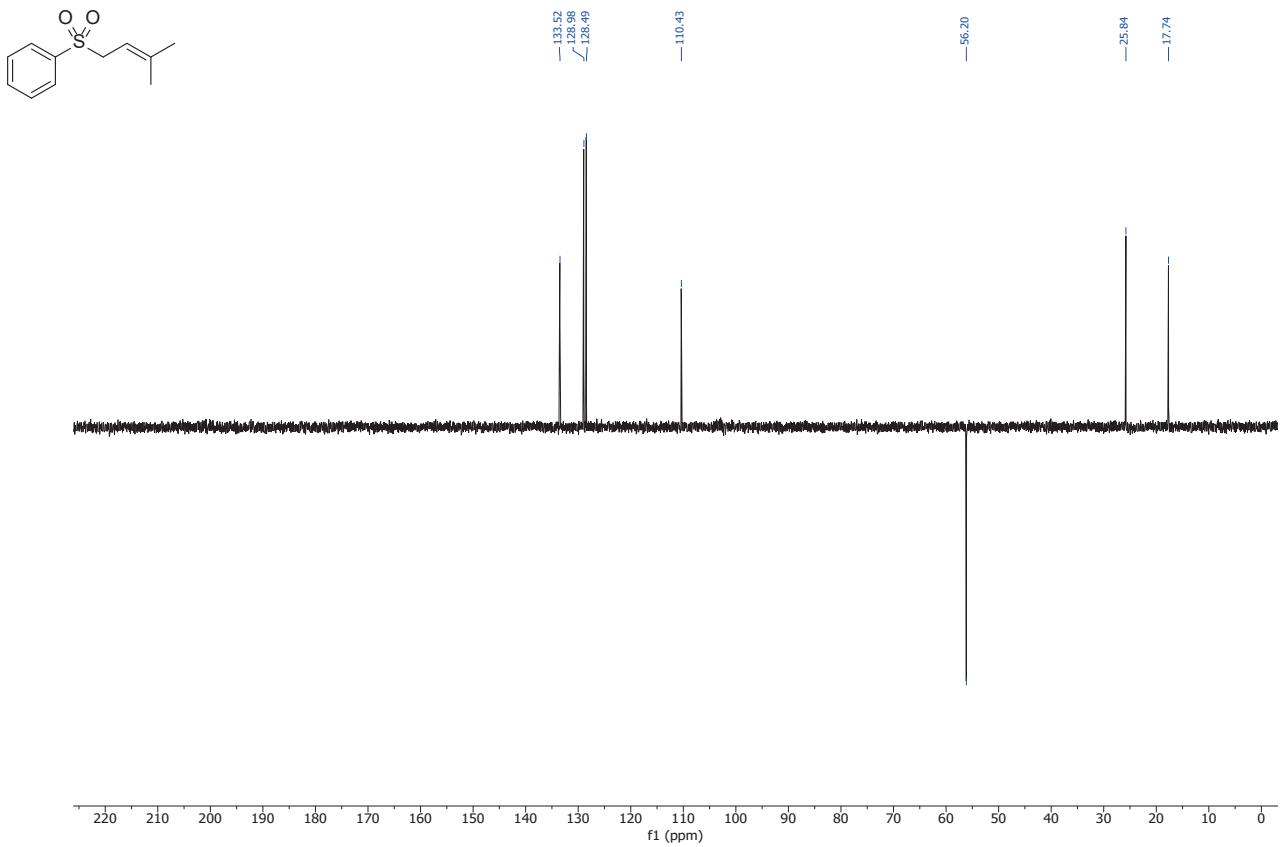
((3-methylbut-2-en-1-yl)sulfonyl)benzene (27)

^{13}C NMR (75 MHz, $CDCl_3$)



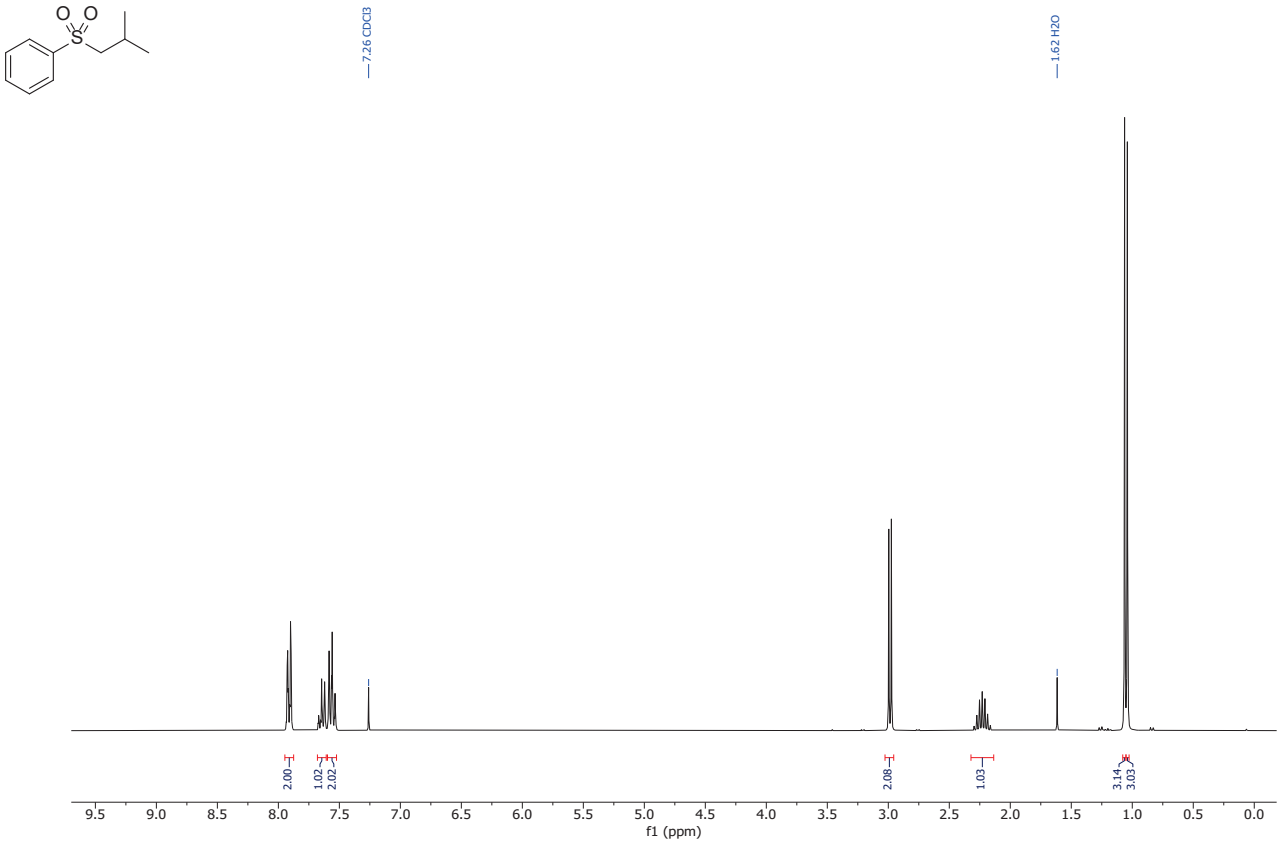
((3-methylbut-2-en-1-yl)sulfonyl)benzene (27)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



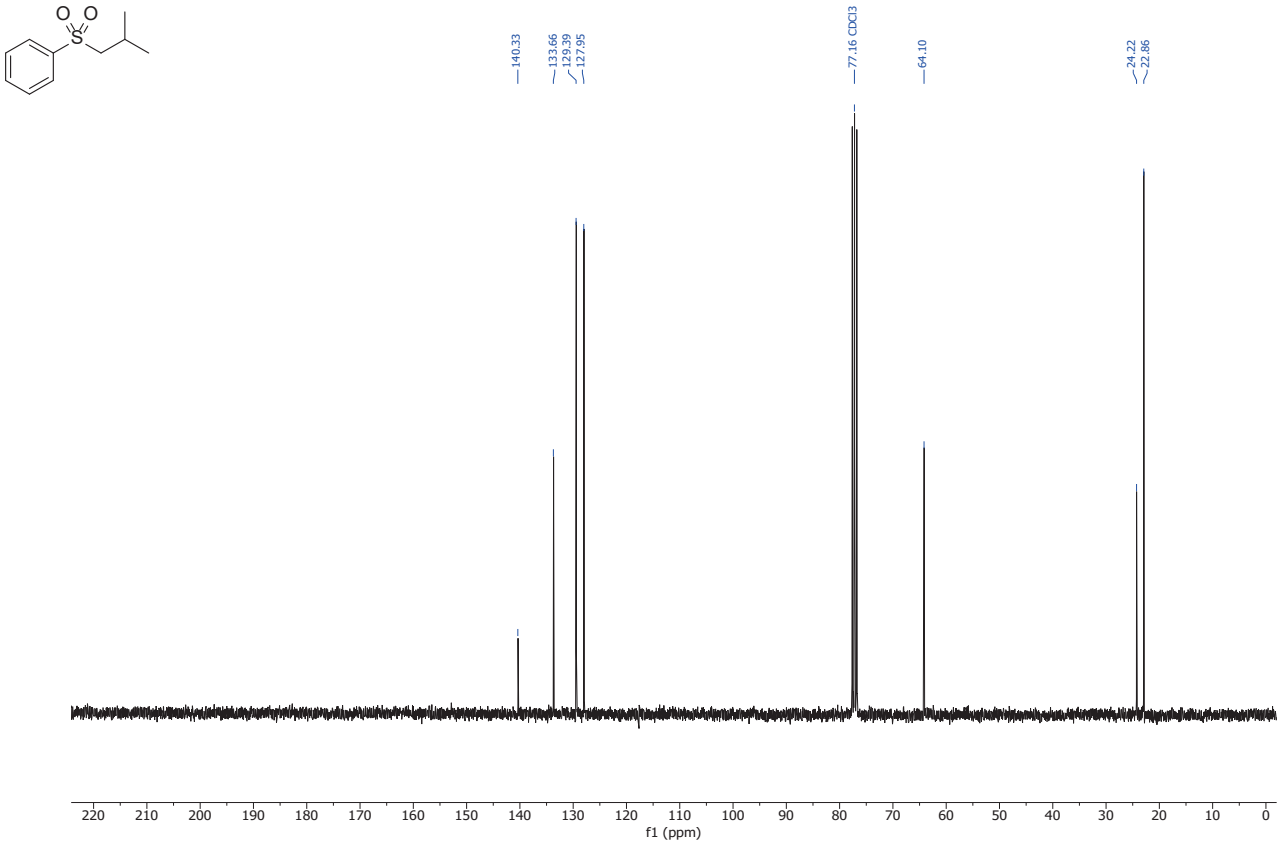
(isobutylsulfonyl)benzene (54)

^{1}H NMR (300 MHz, $CDCl_3$)



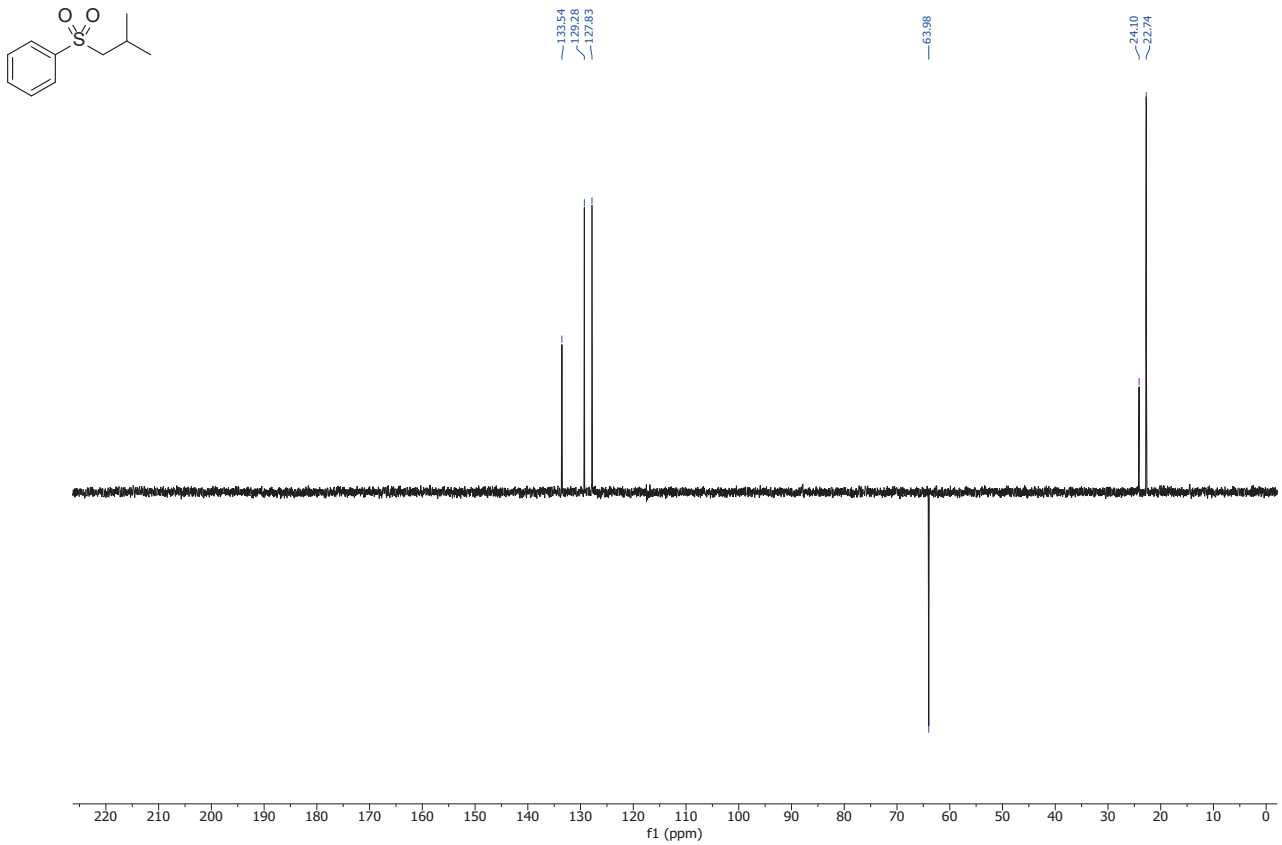
(isobutylsulfonyl)benzene (54)

^{13}C NMR (75 MHz, $CDCl_3$)



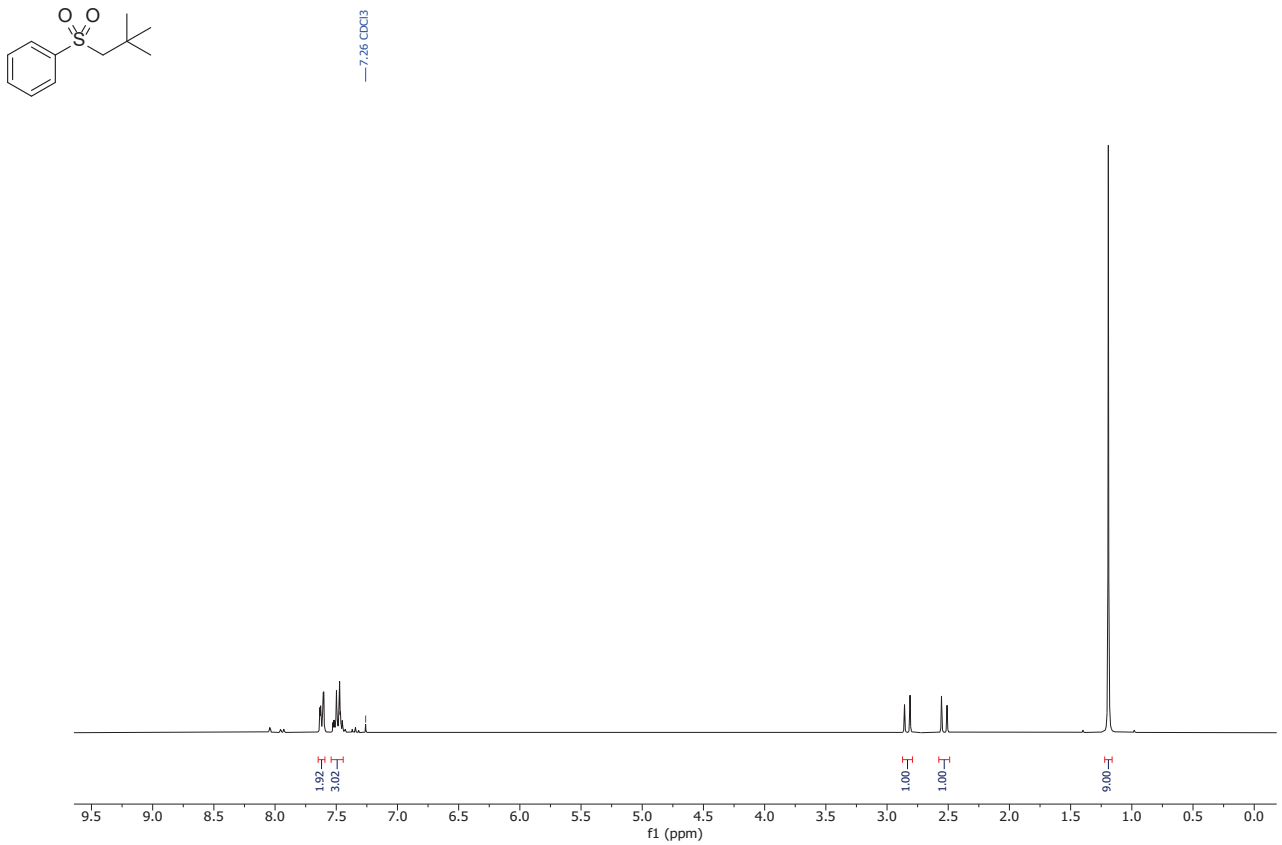
(isobutylsulfonyl)benzene (54)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



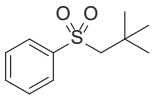
(neopentylsulfonyl)benzene (55)

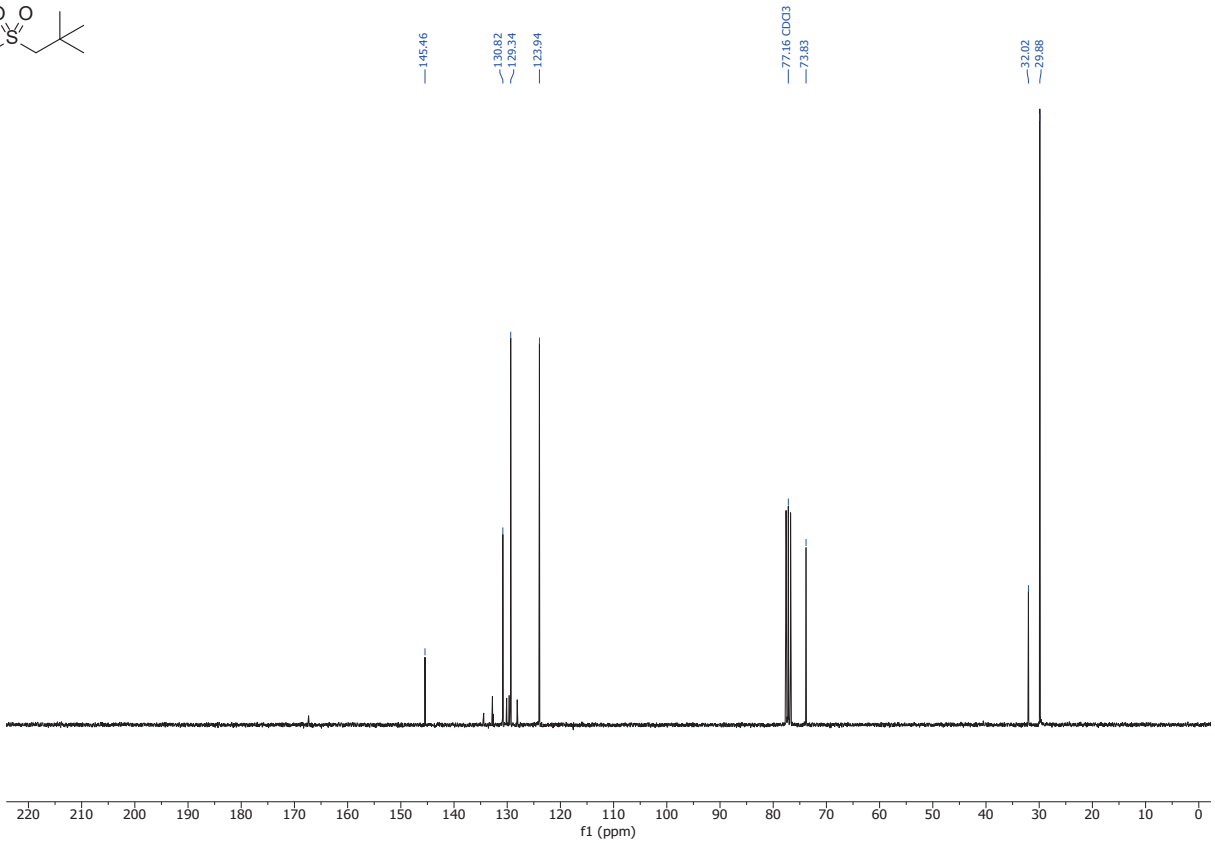
^{1}H NMR (300 MHz, $CDCl_3$)



(neopentylsulfonyl)benzene (55)

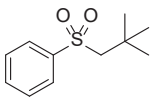
^{13}C NMR (75 MHz, $CDCl_3$)

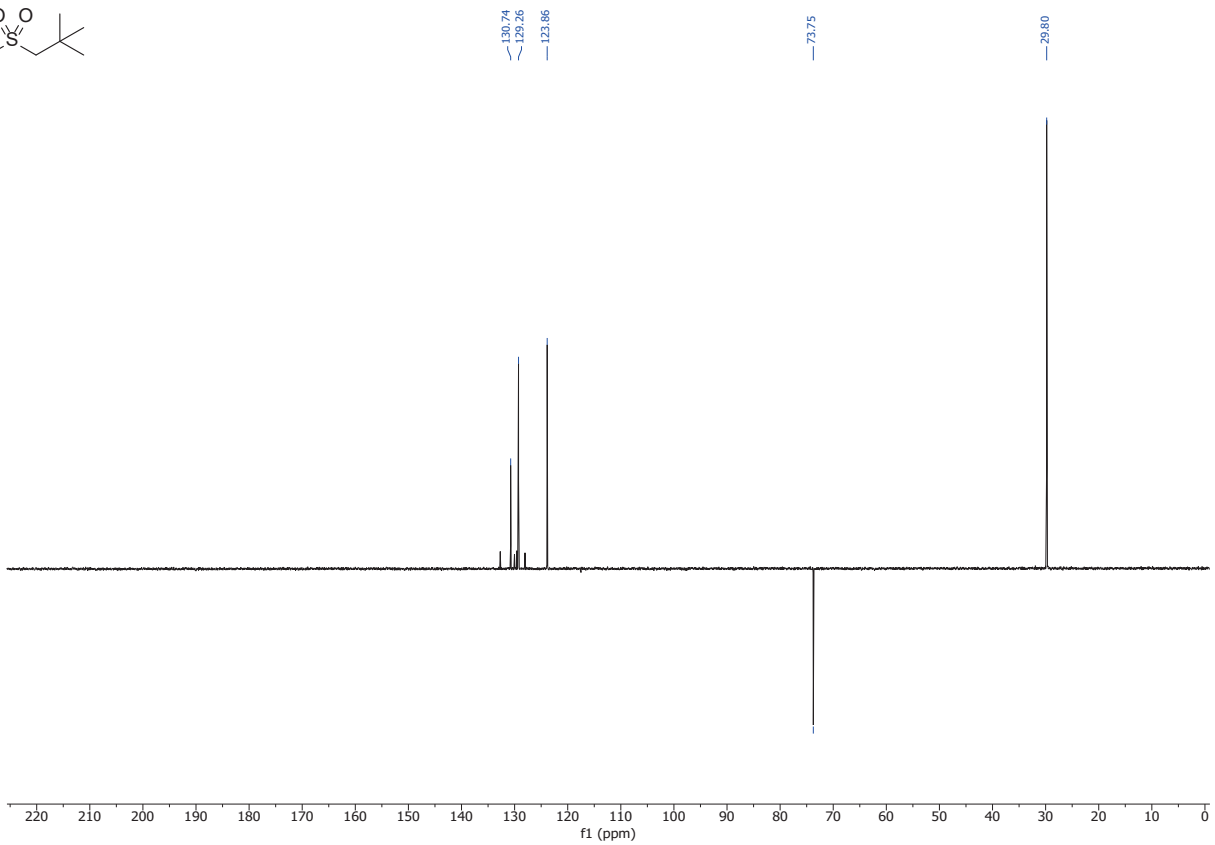




(neopentylsulfonyl)benzene (55)

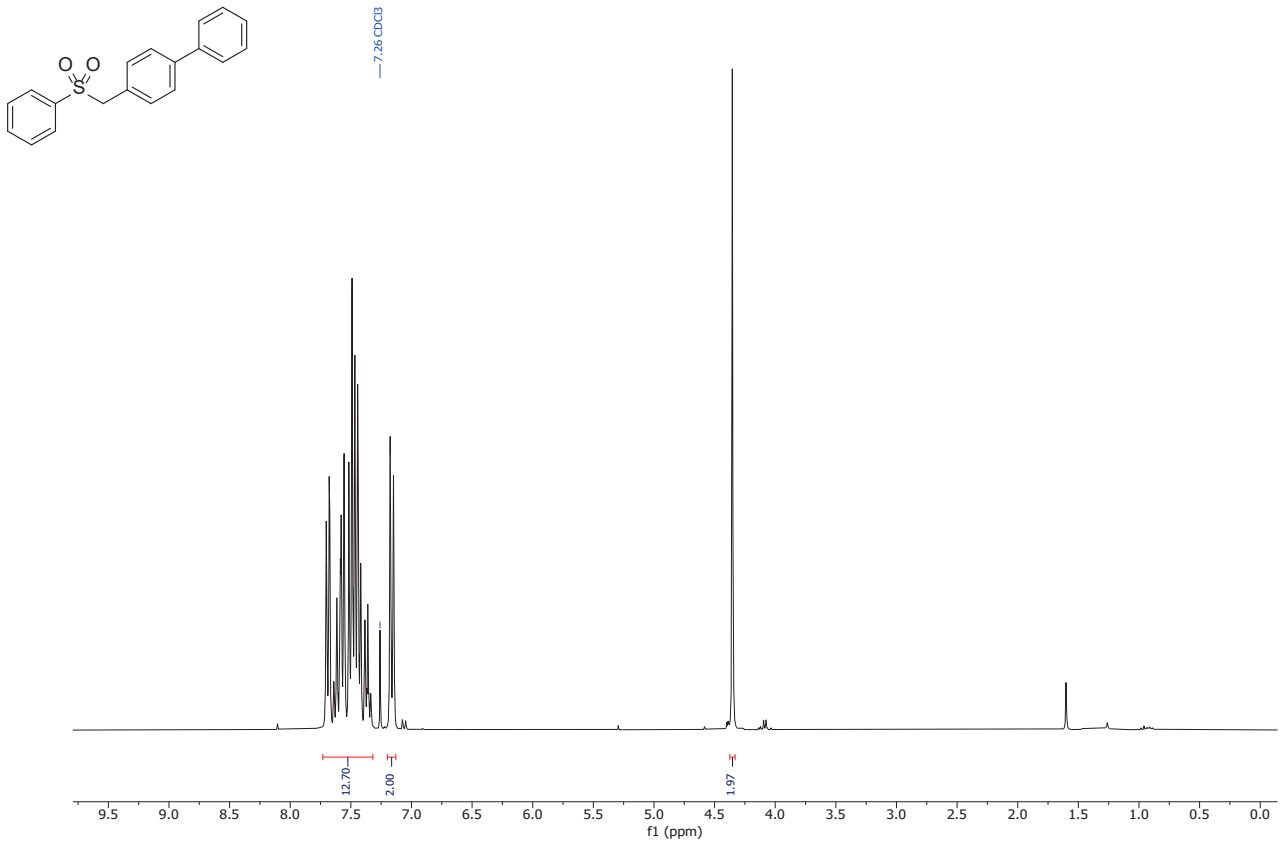
^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)





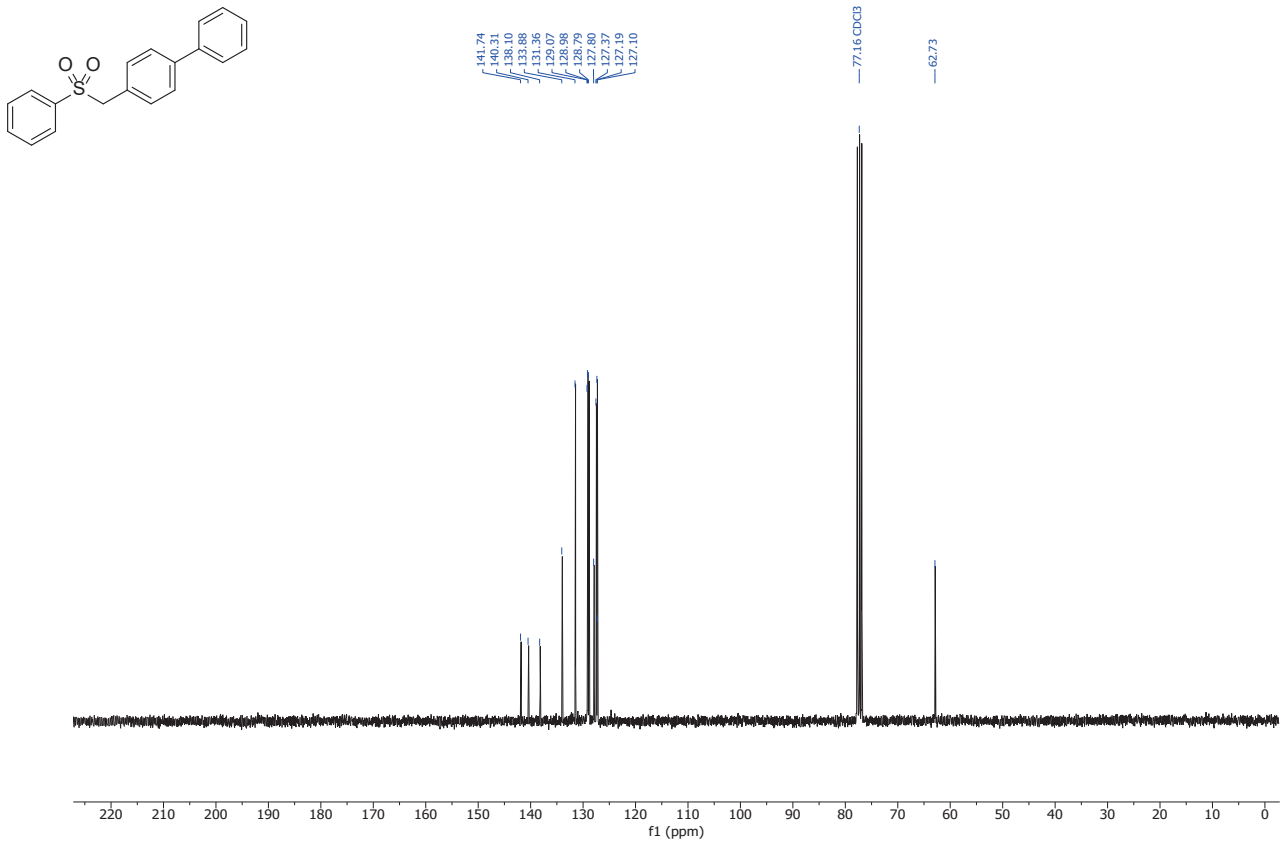
4-((phenylsulfonyl)methyl)-1,1'-biphenyl (56)

^{1}H NMR (300 MHz, $CDCl_3$)



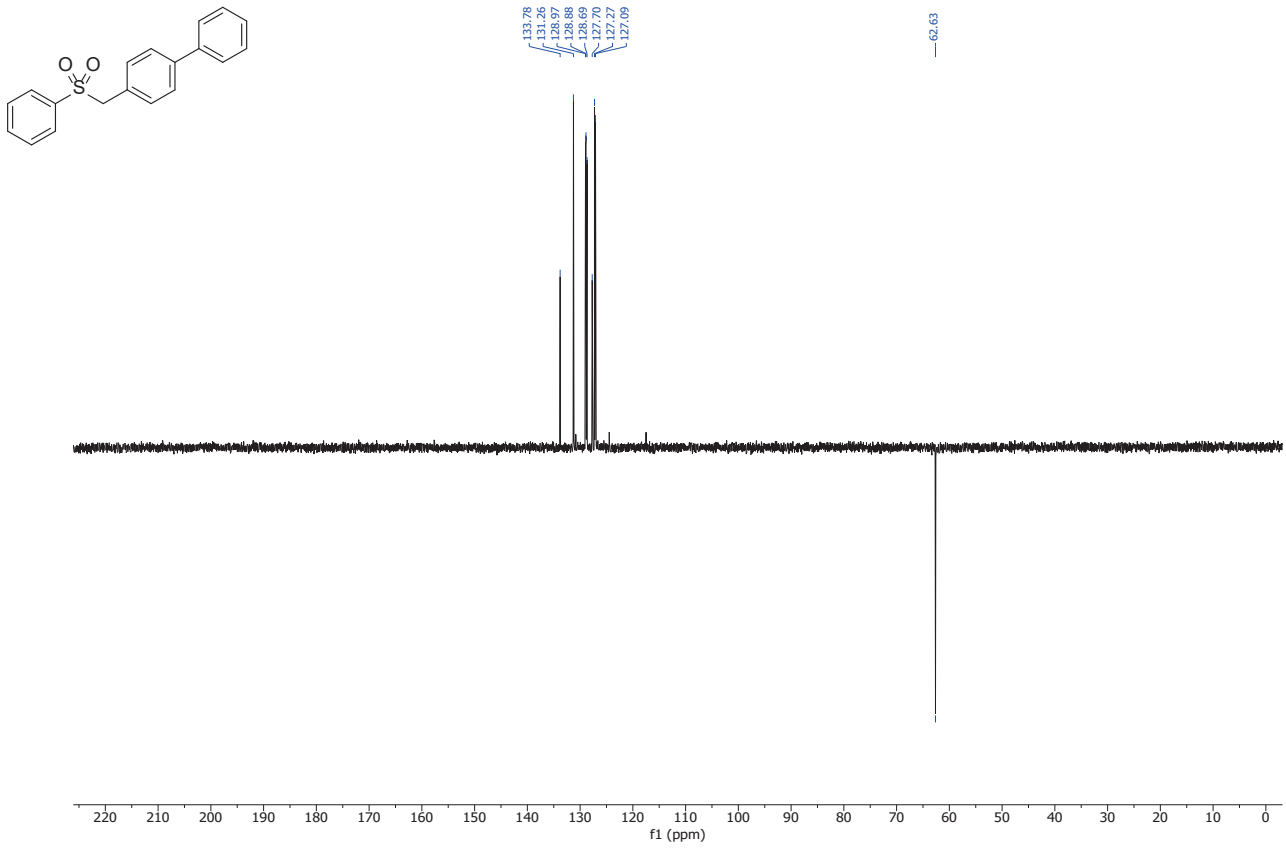
4-((phenylsulfonyl)methyl)-1,1'-biphenyl (56)

^{13}C NMR (75 MHz, $CDCl_3$)



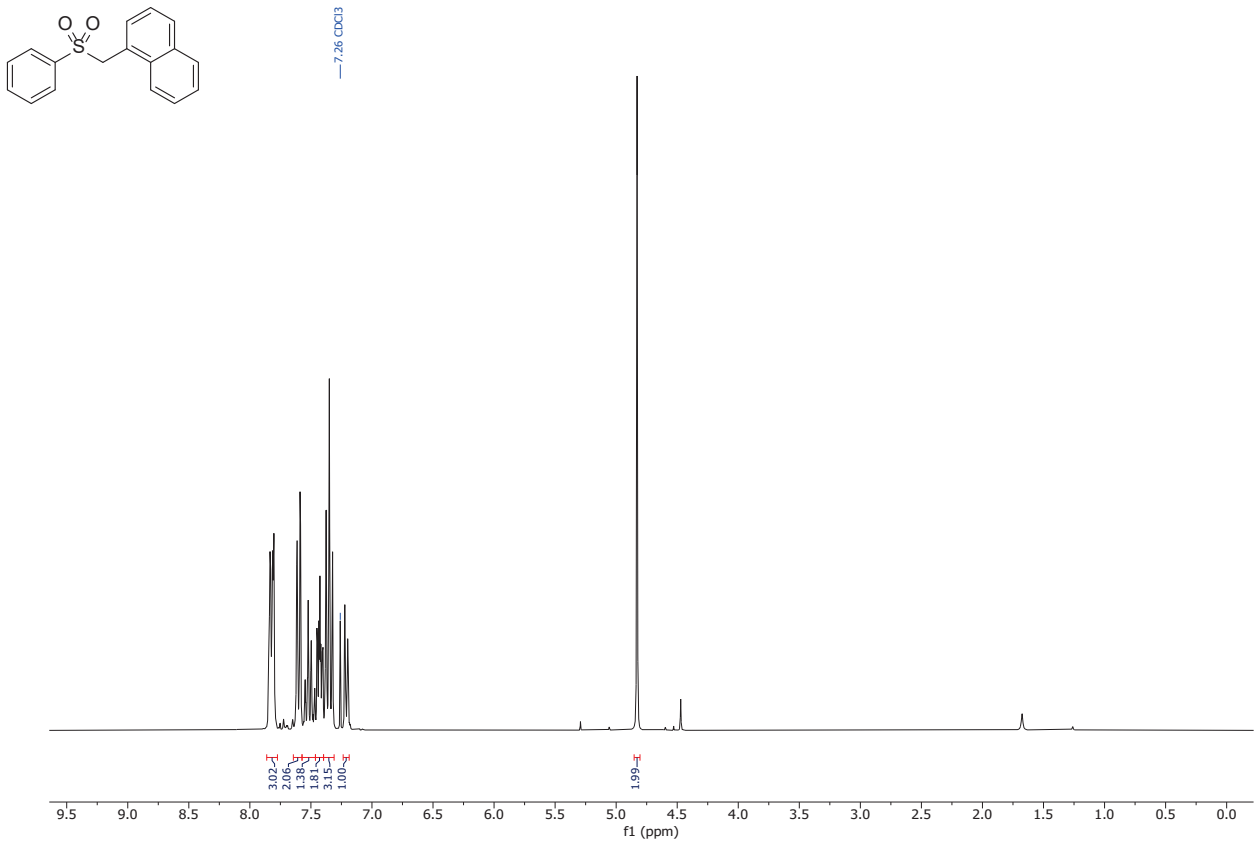
4-((phenylsulfonyl)methyl)-1,1'-biphenyl (56)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



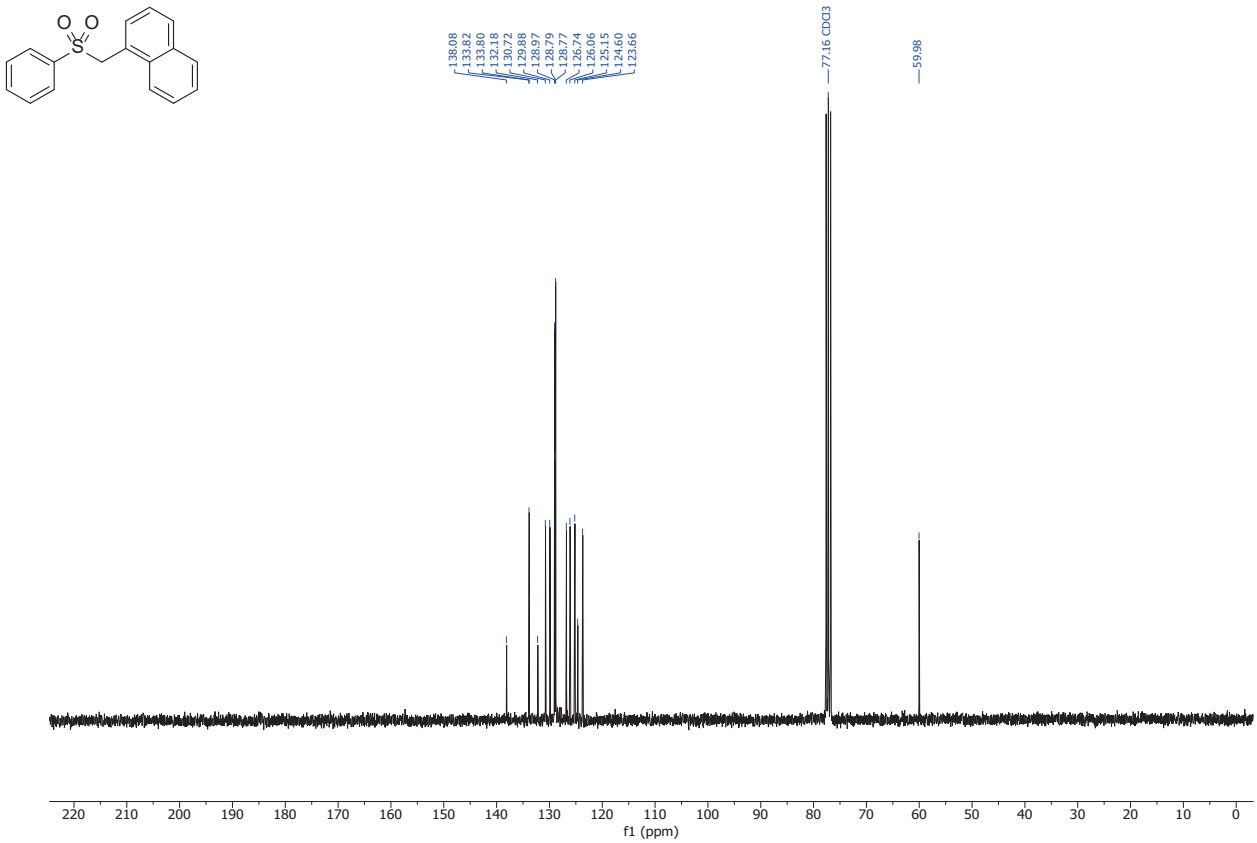
1-((phenylsulfonyl)methyl)naphthalene (57)

^{1}H NMR (300 MHz, $CDCl_3$)



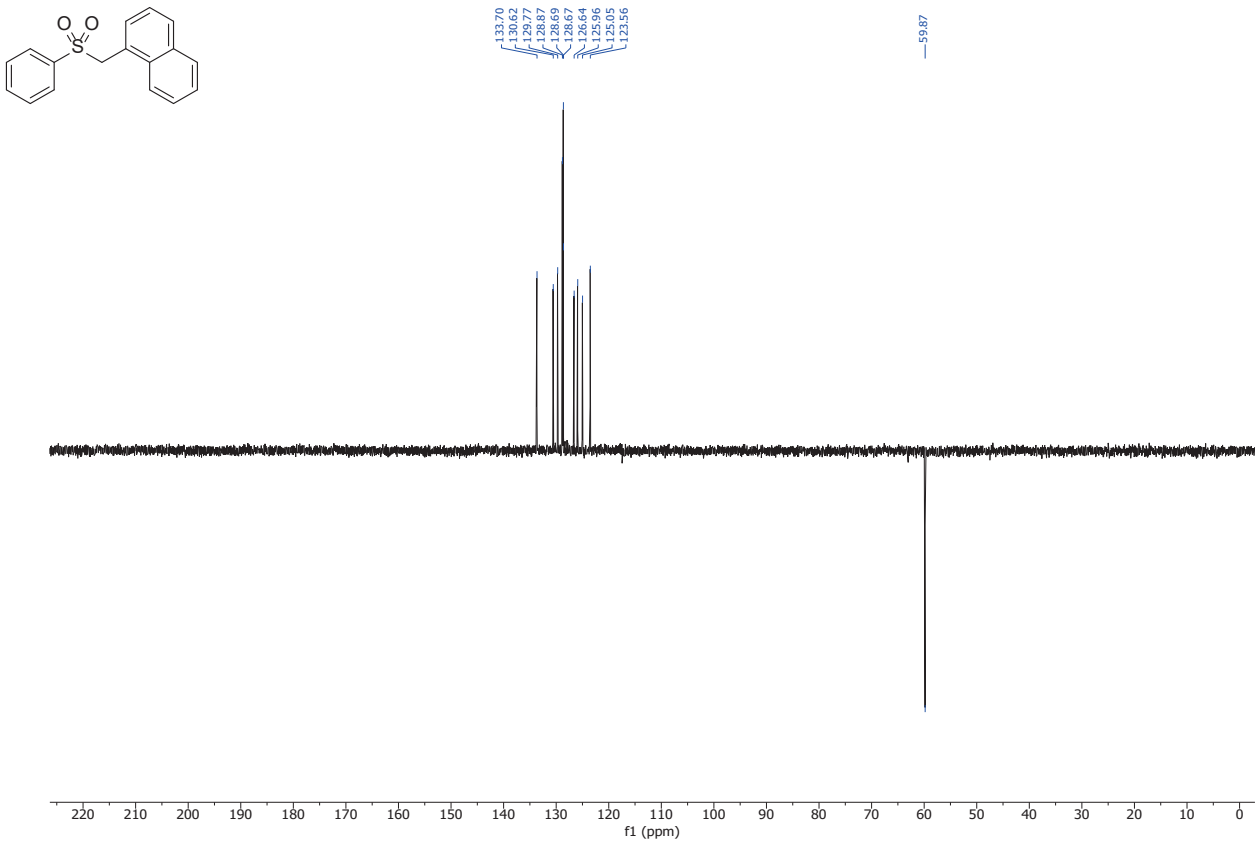
1-((phenylsulfonyl)methyl)naphthalene (57)

^{13}C NMR (75 MHz, $CDCl_3$)



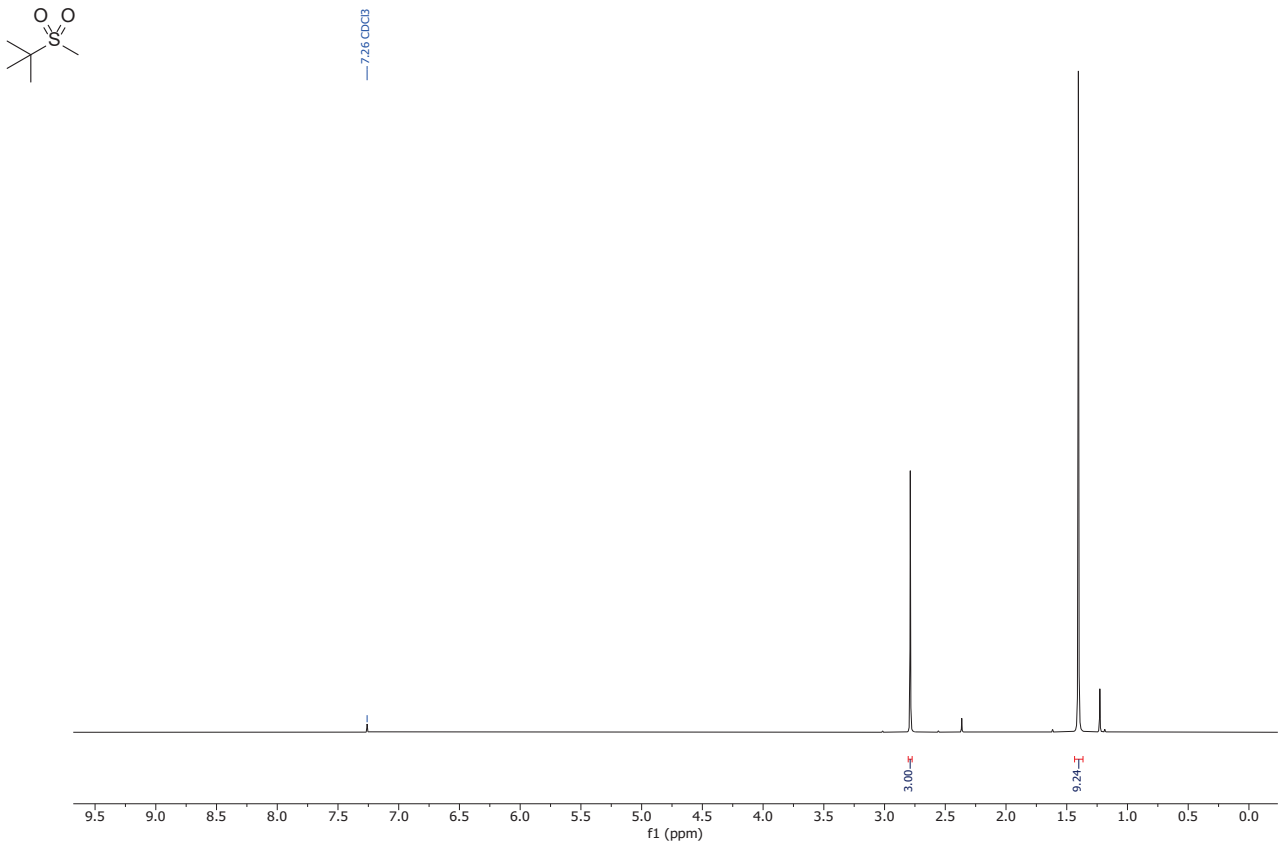
1-((phenylsulfonyl)methyl)naphthalene (57)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



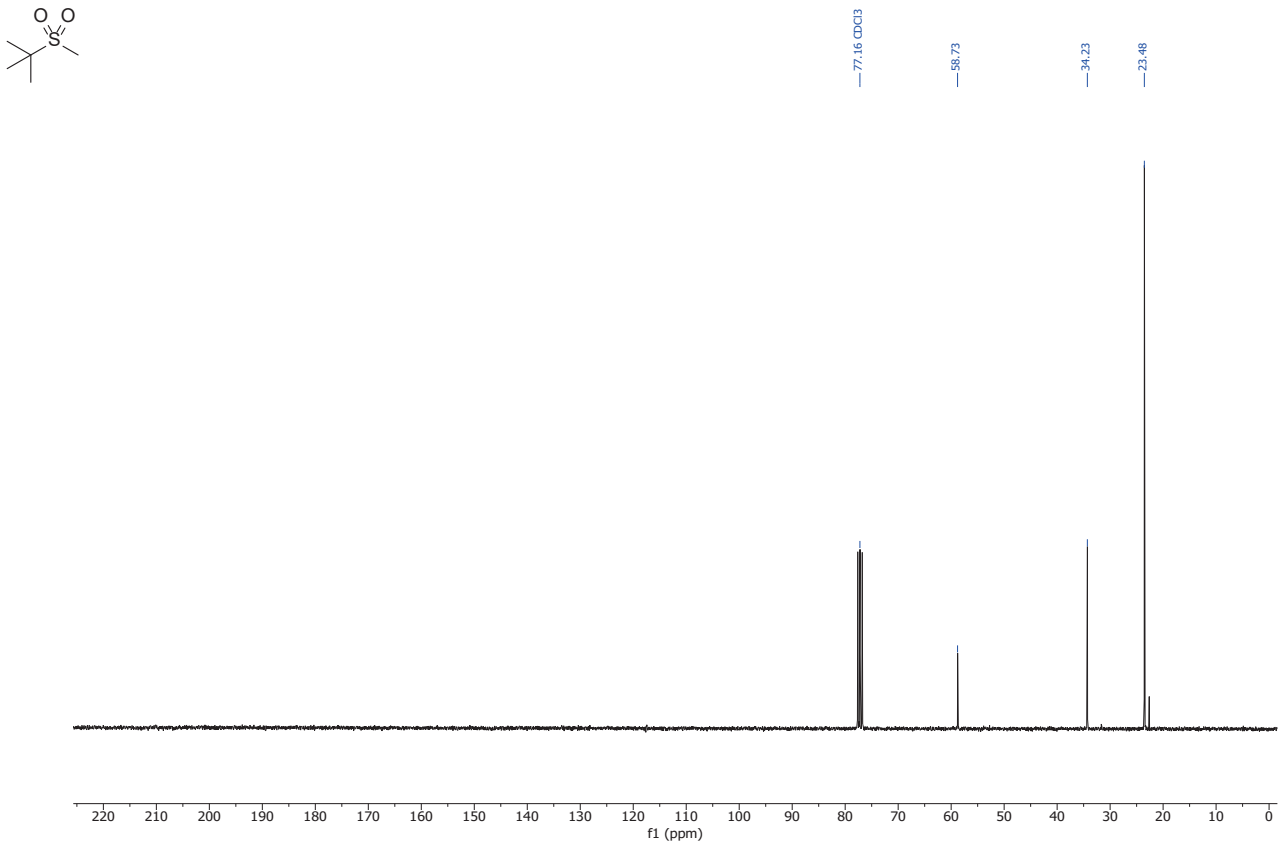
2-methyl-2-(methylsulfonyl)propane (58)

^{1}H NMR (300 MHz, $CDCl_3$)



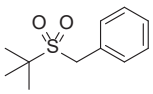
2-methyl-2-(methylsulfonyl)propane (58)

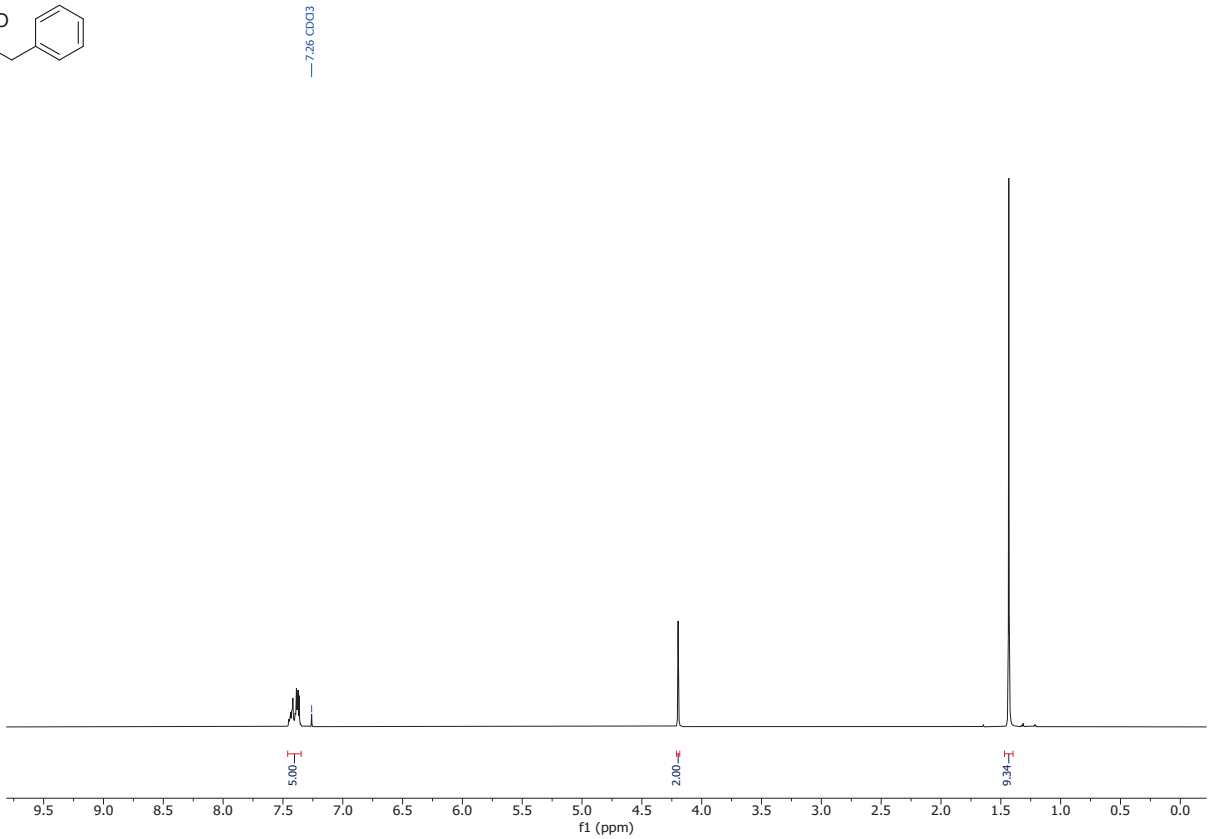
^{13}C NMR (75 MHz, $CDCl_3$)



((tert-butylsulfonyl)methyl)benzene (59)

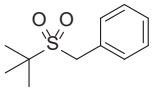
^{1}H NMR (300 MHz, $CDCl_3$)

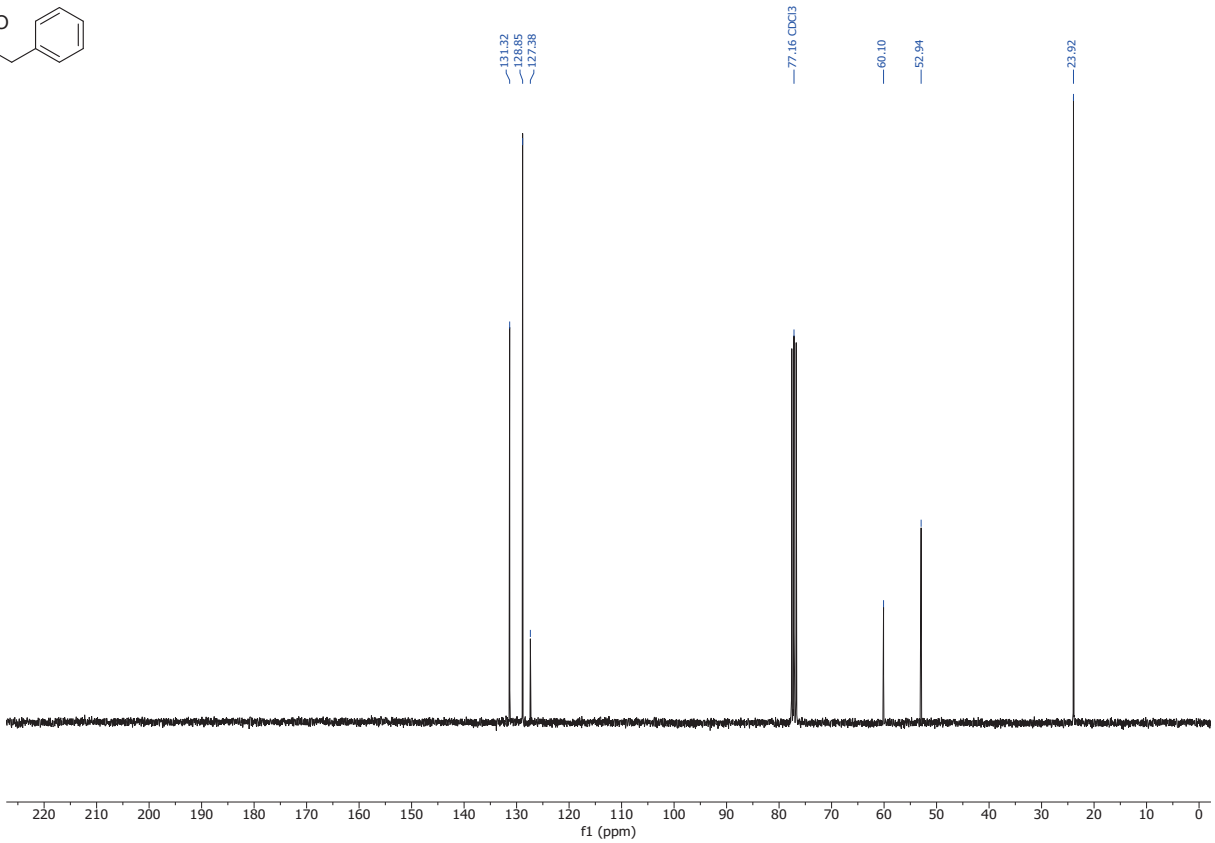




((tert-butylsulfonyl)methyl)benzene (59)

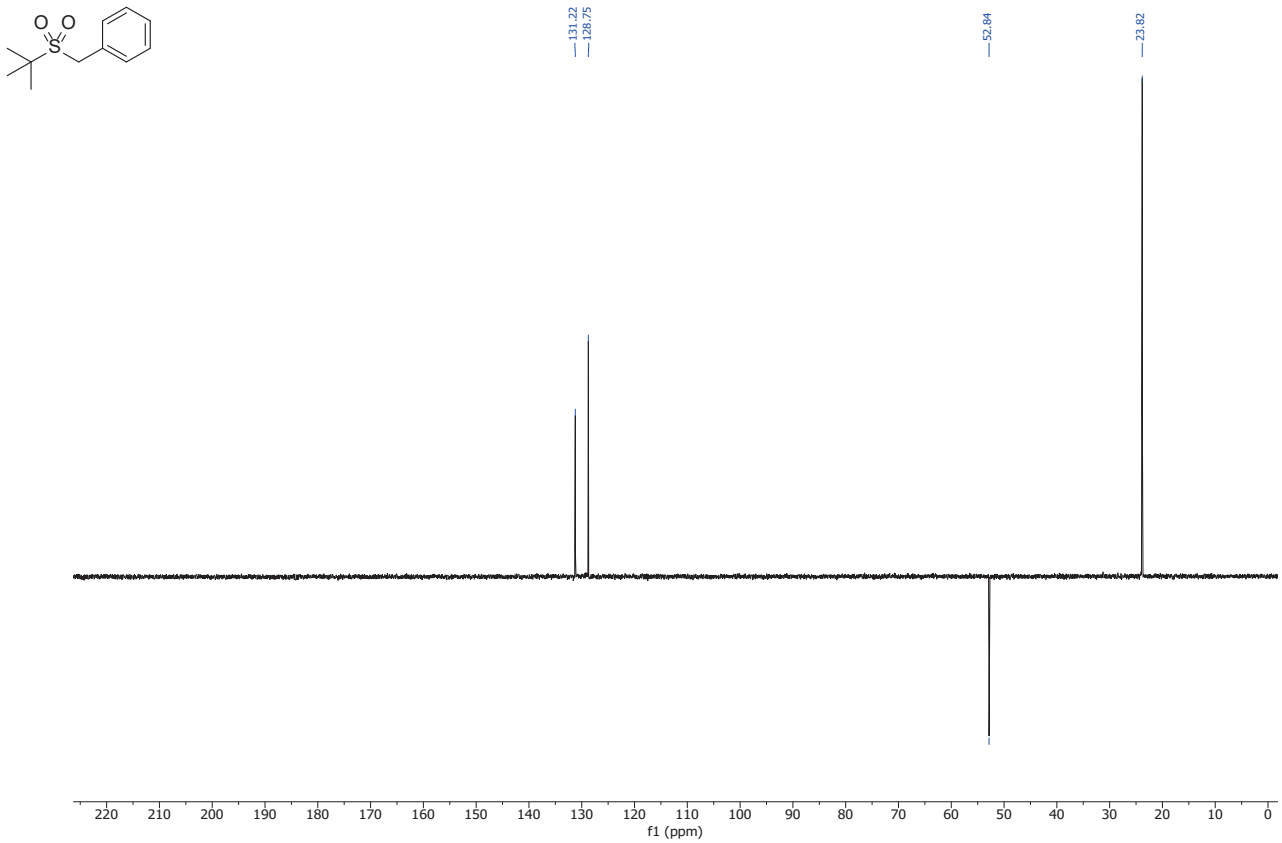
^{13}C NMR (75 MHz, $CDCl_3$)





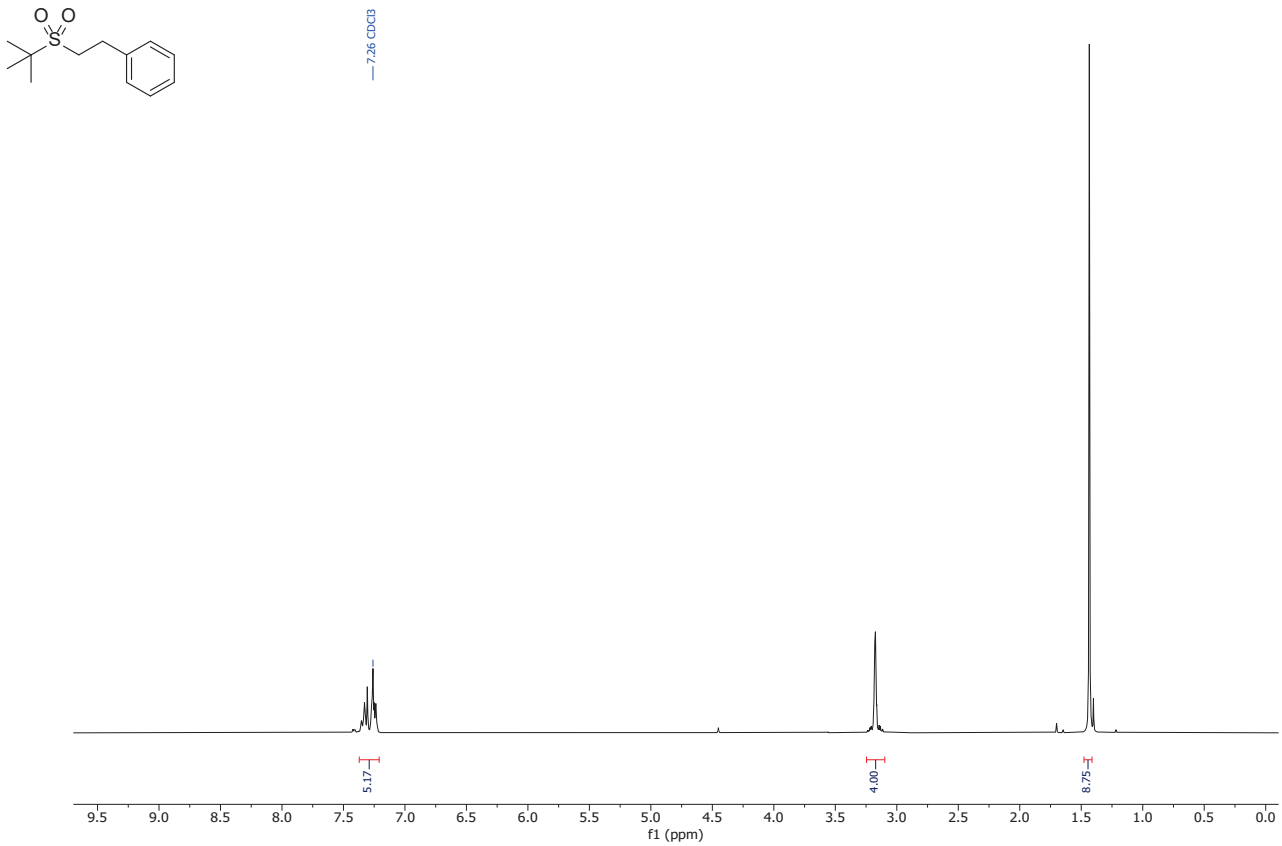
((tert-butylsulfonyl)methyl)benzene (59)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



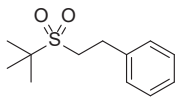
(2-(tert-butylsulfonyl)ethyl)benzene (60)

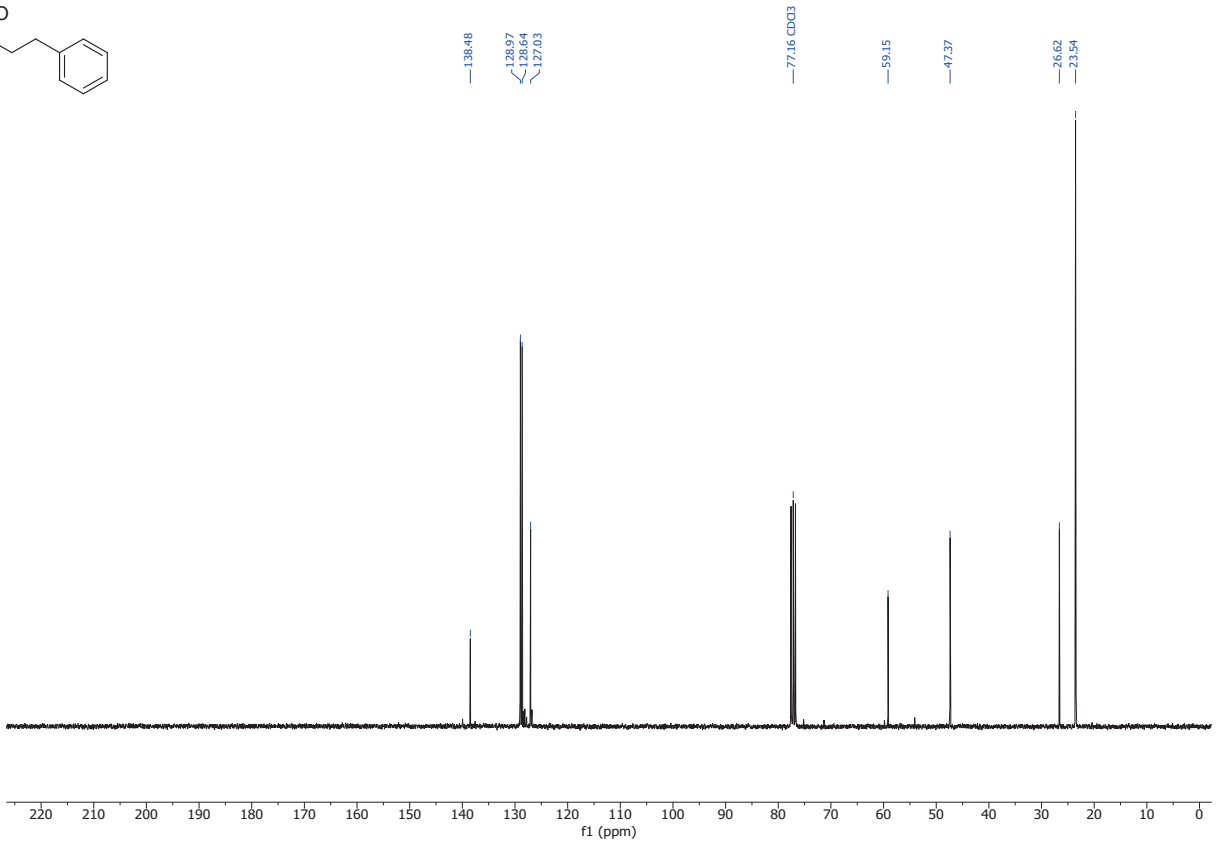
^{1}H NMR (300 MHz, $CDCl_3$)



(2-(tert-butylsulfonyl)ethyl)benzene (60)

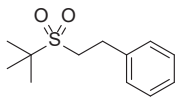
^{13}C NMR (75 MHz, $CDCl_3$)

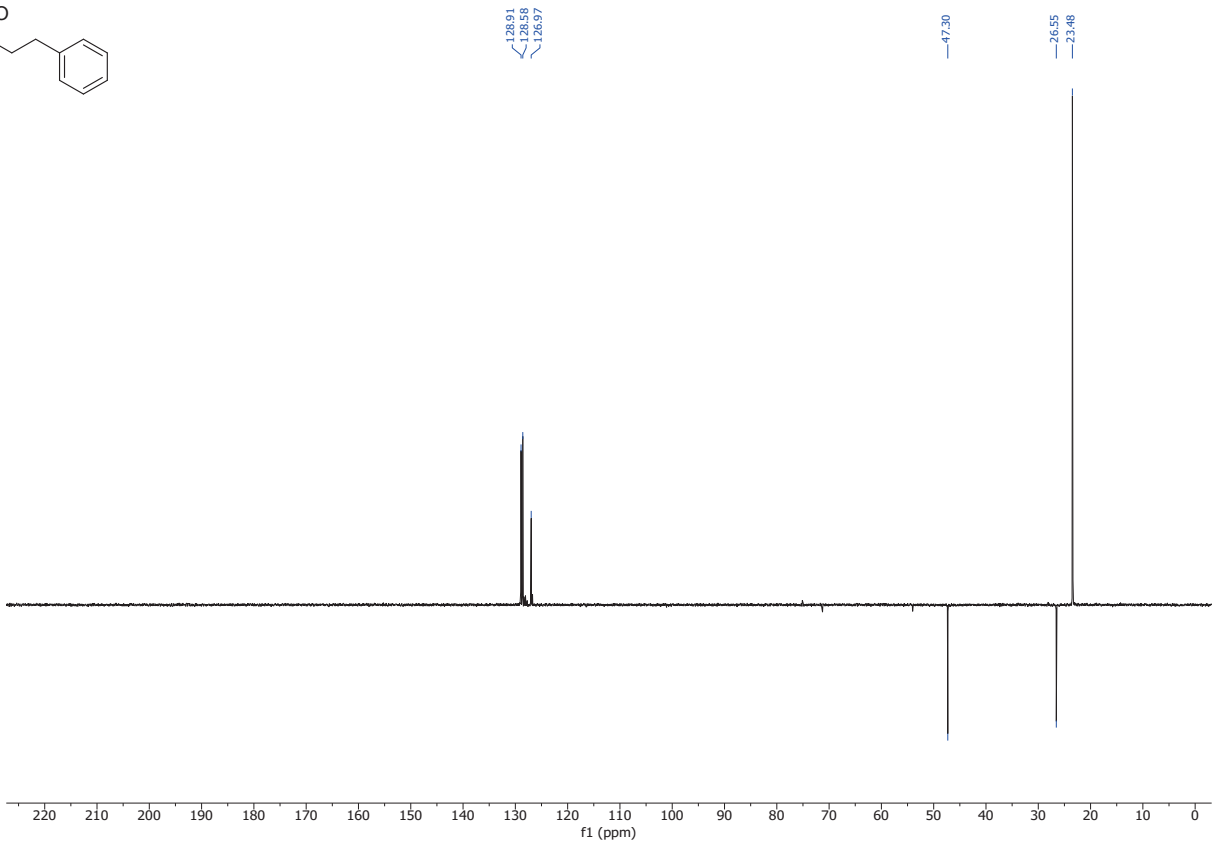




(2-(tert-butylsulfonyl)ethyl)benzene (60)

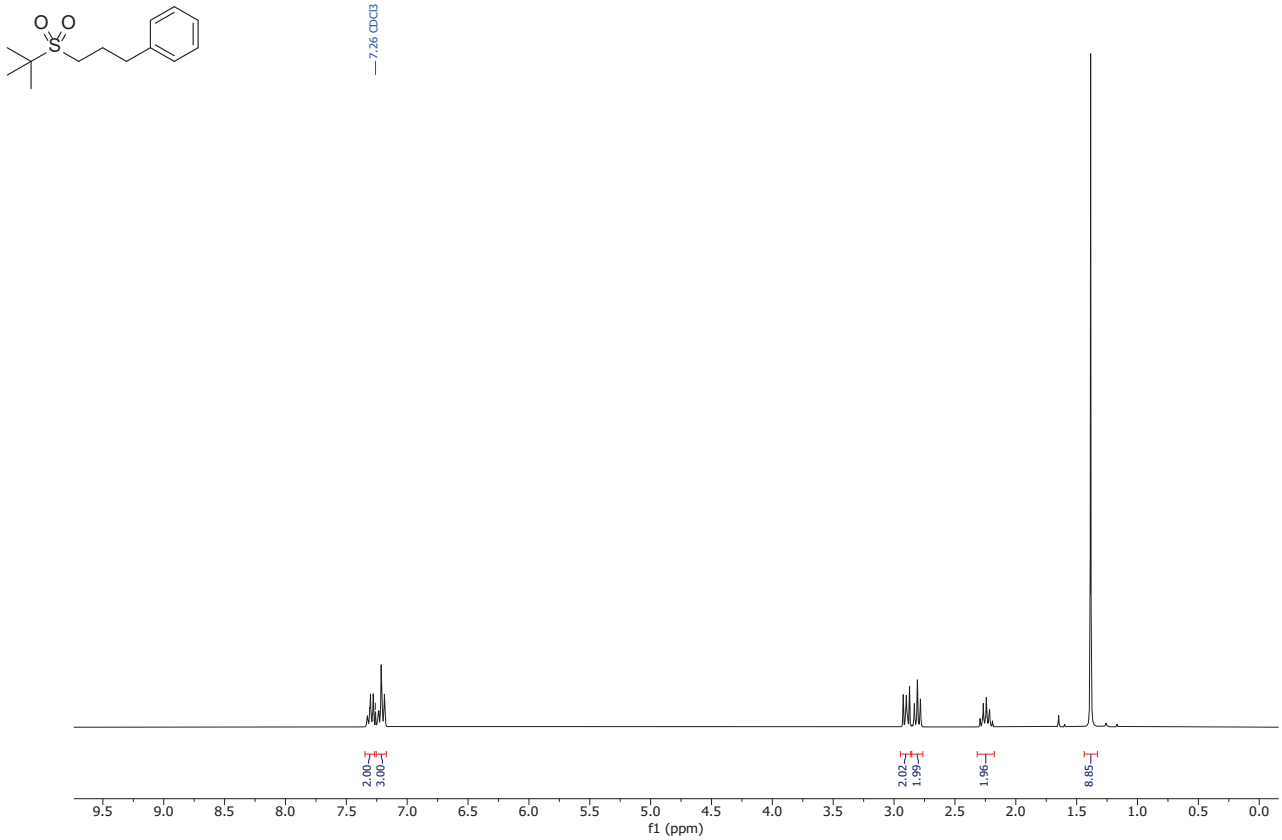
^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)





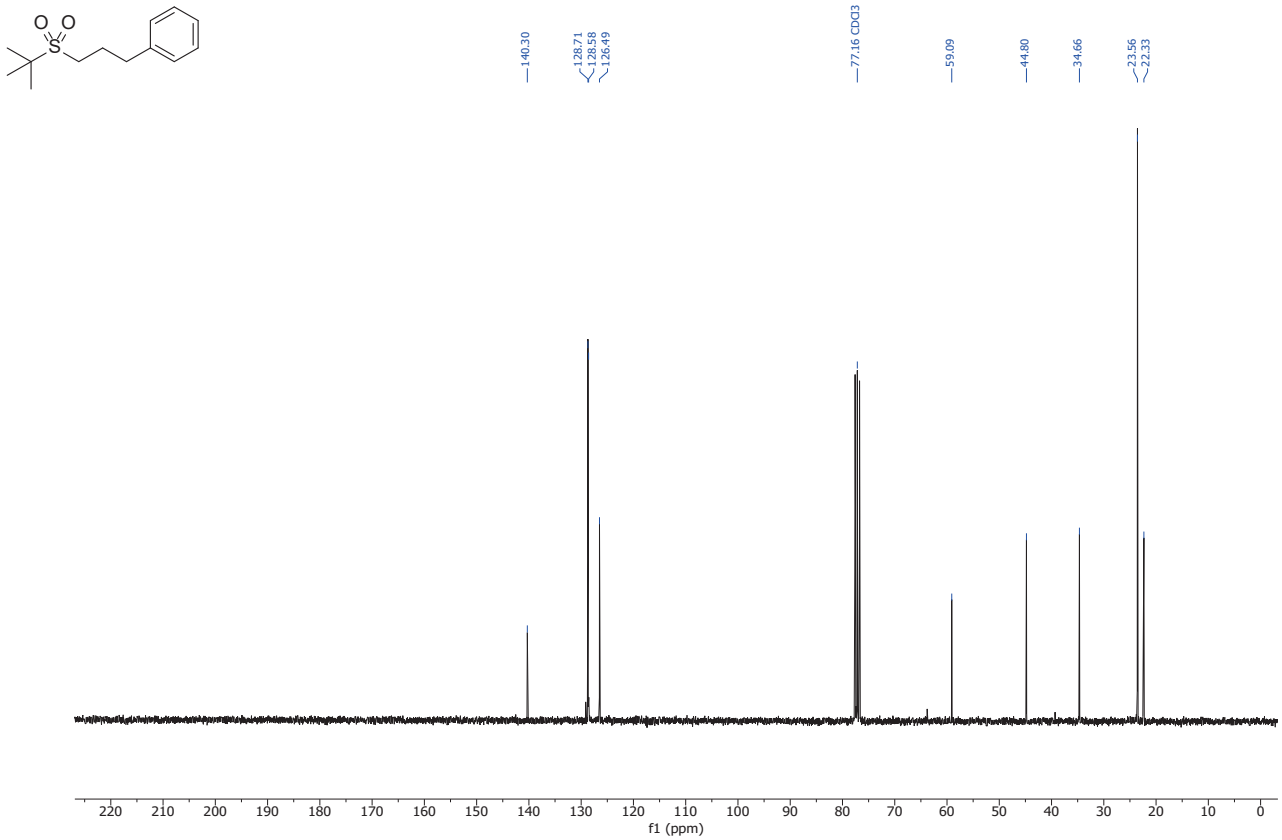
(3-(tert-butylsulfonyl)propyl)benzene (61)

^{1}H NMR (300 MHz, $CDCl_3$)



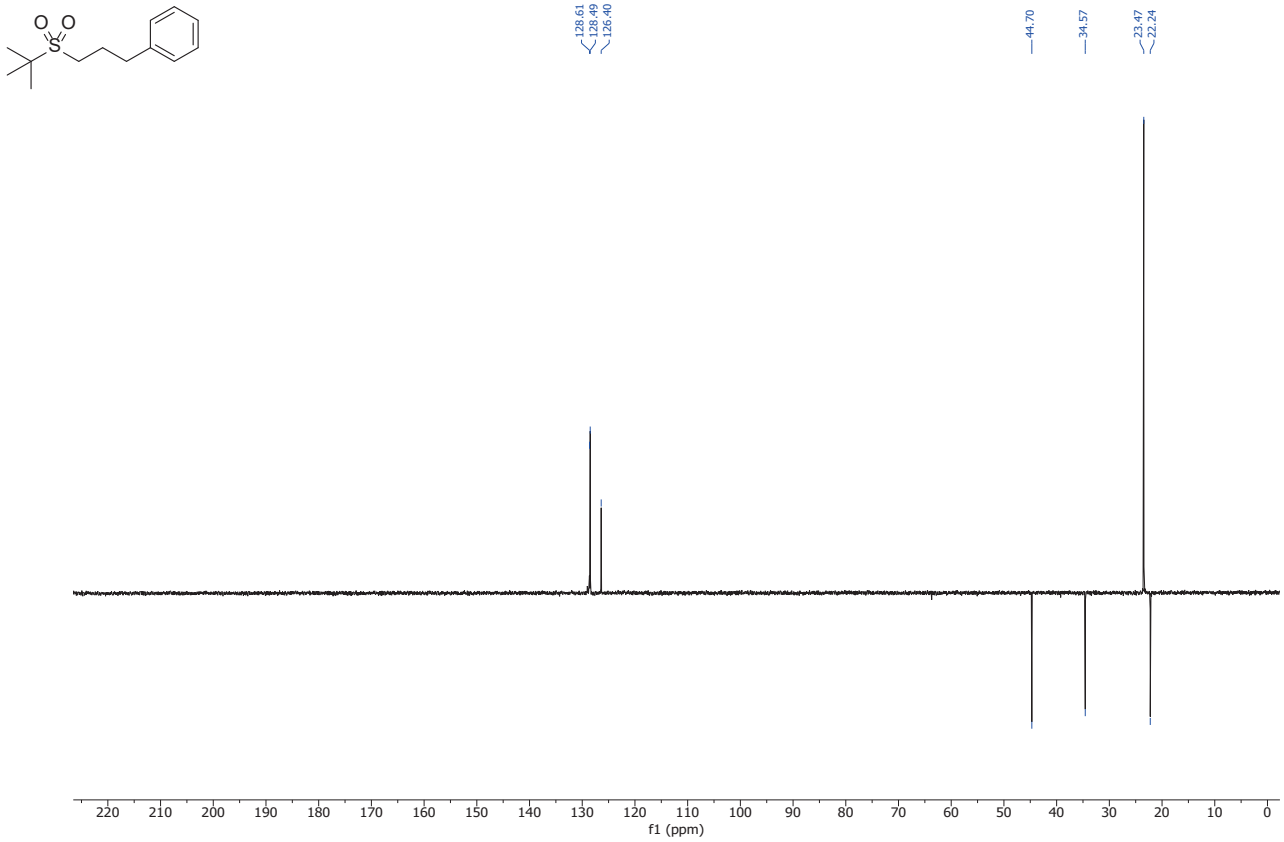
(3-(tert-butylsulfonyl)propyl)benzene (61)

^{13}C NMR (75 MHz, $CDCl_3$)



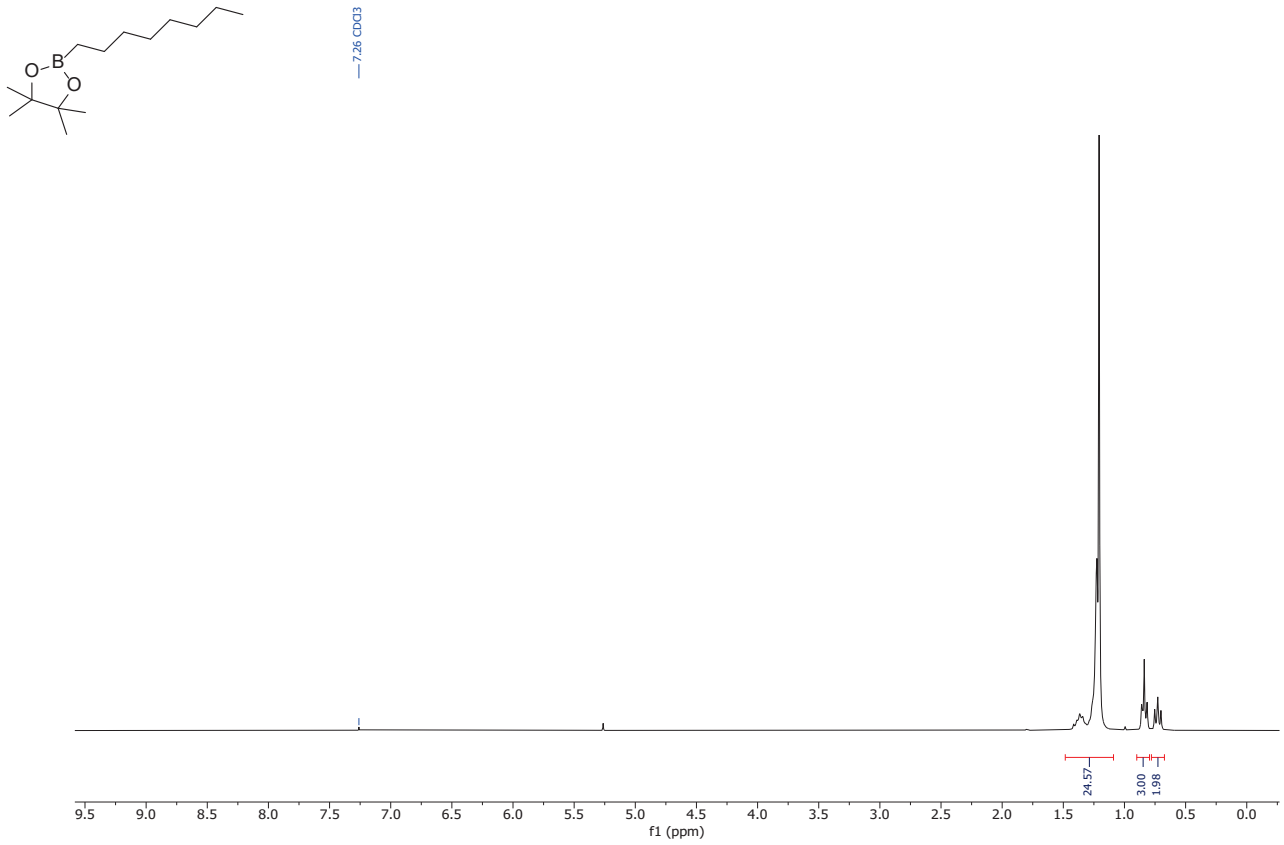
(3-(tert-butylsulfonyl)propyl)benzene (61)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



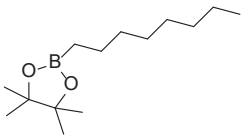
4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (62)

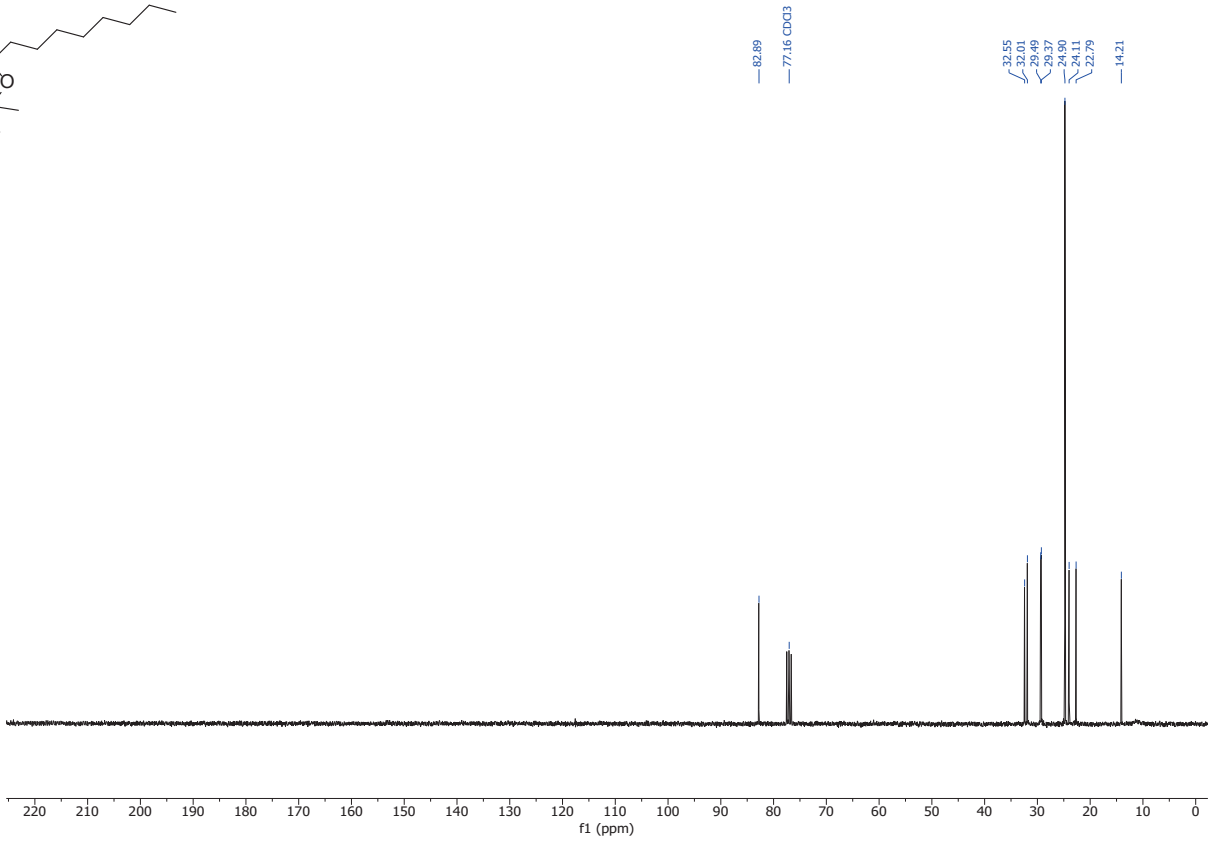
^{1}H NMR (300 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (62)

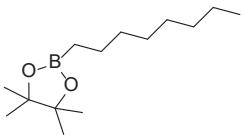
^{13}C NMR (75 MHz, $CDCl_3$)

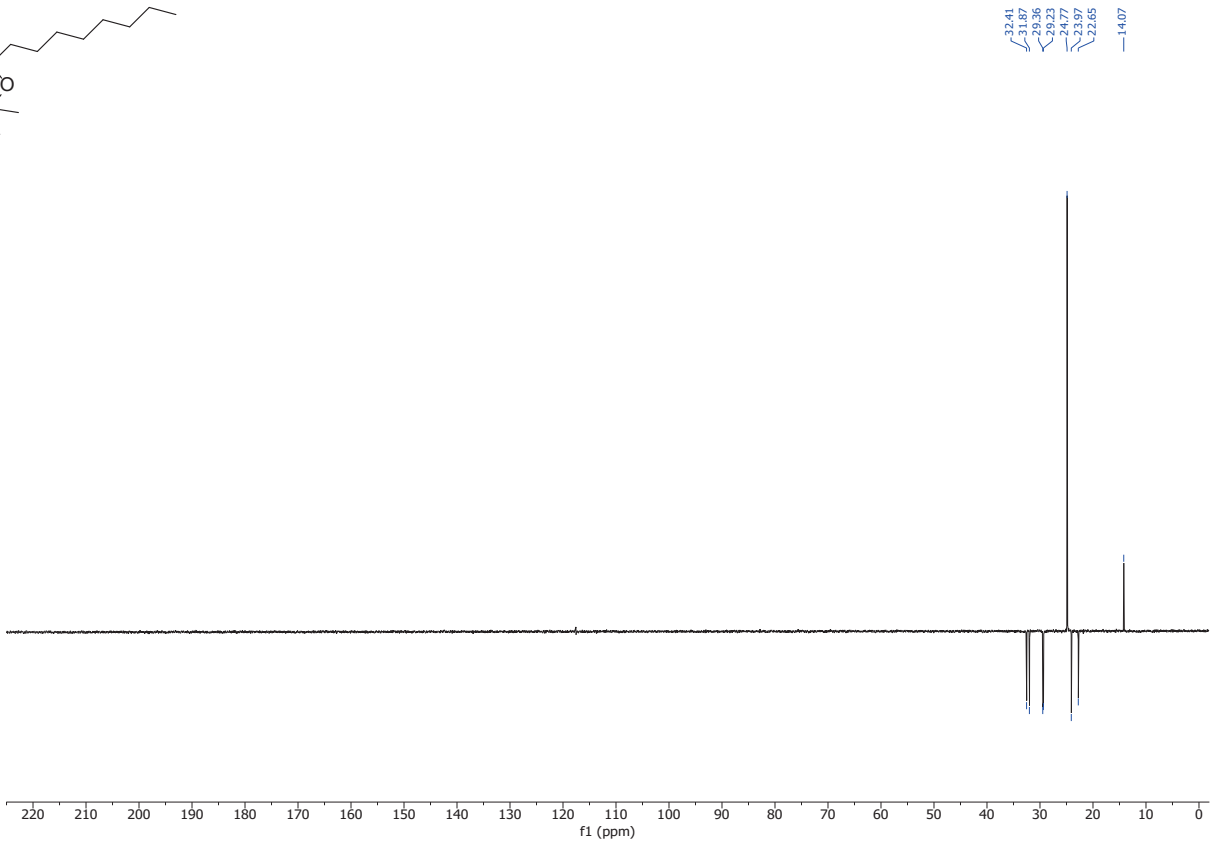




4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (62)

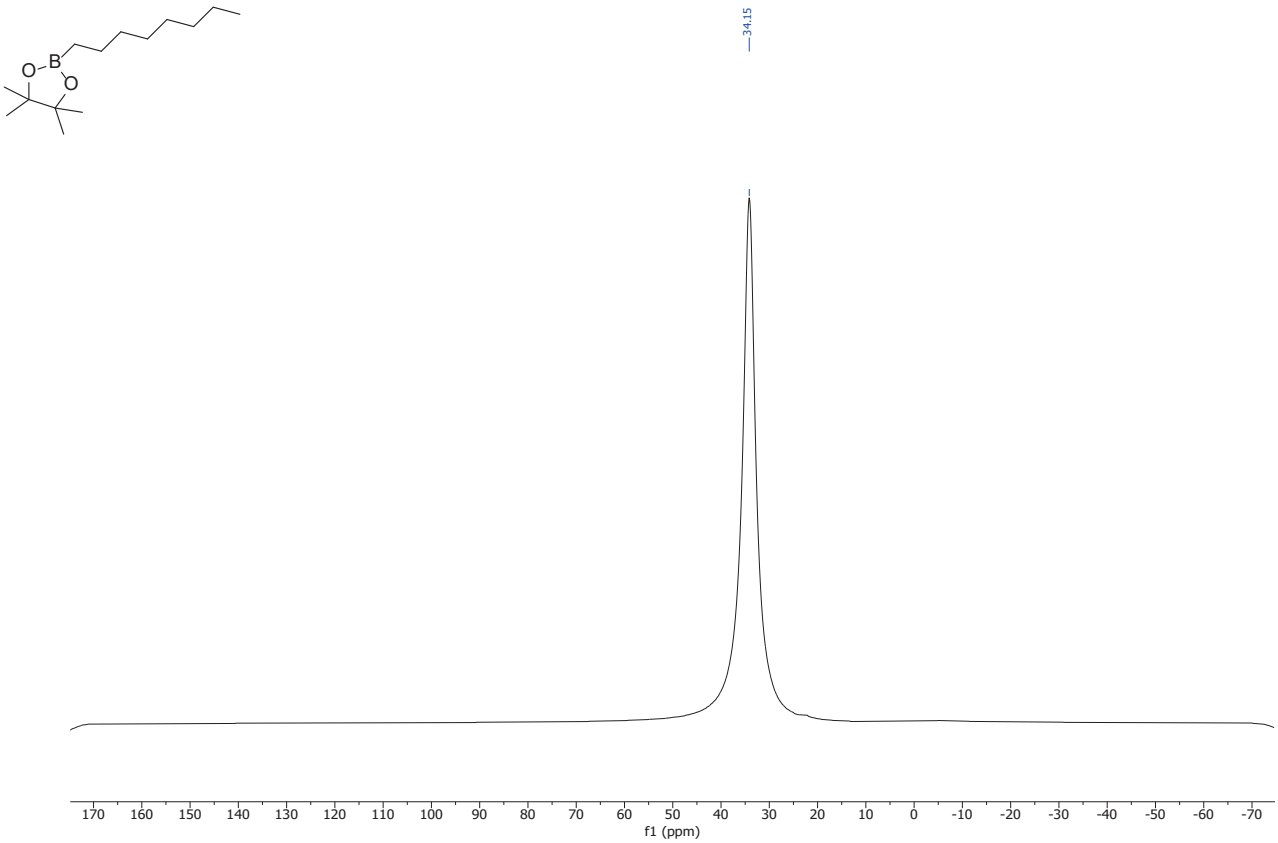
^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)





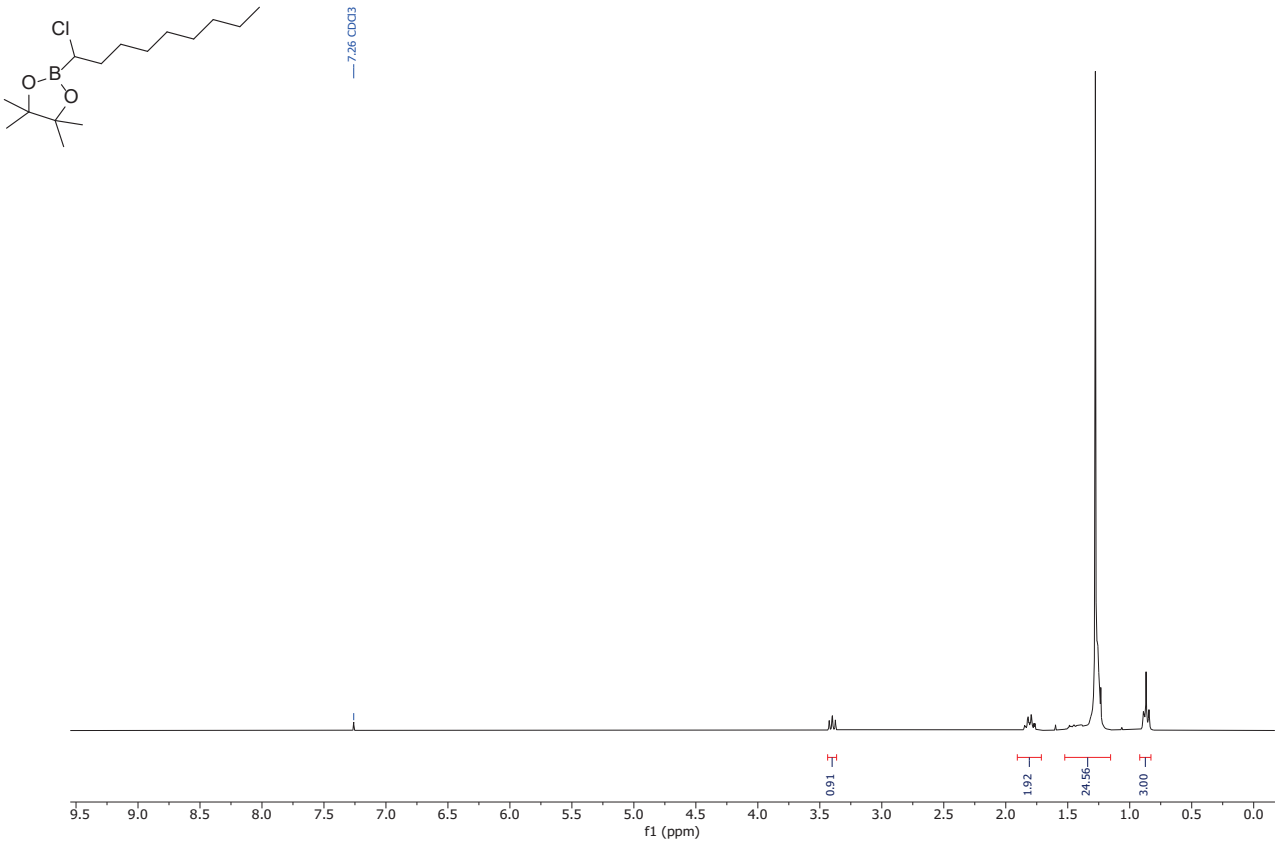
4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (62)

^{11}B NMR (96 MHz, $CDCl_3$)



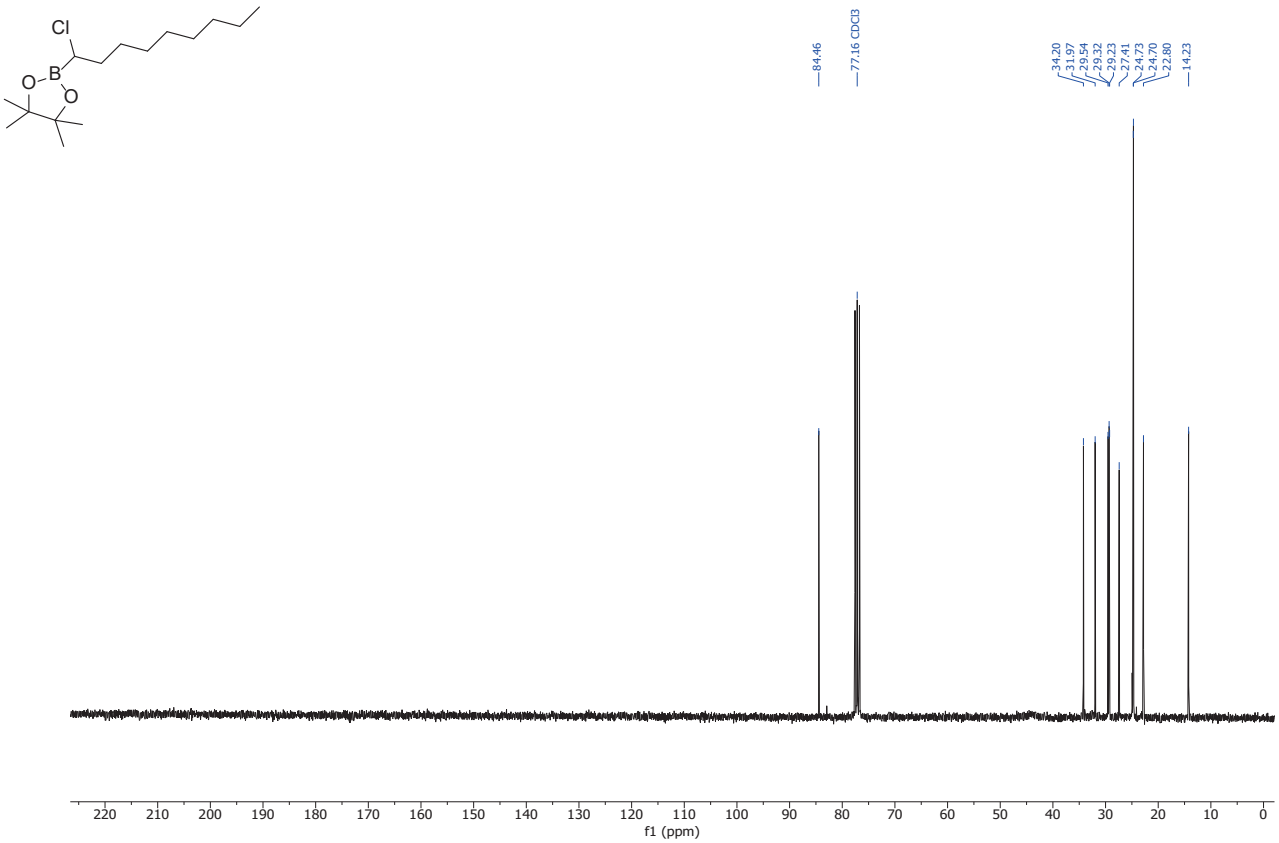
2-(1-chlorononyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)

^{1}H NMR (300 MHz, $CDCl_3$)



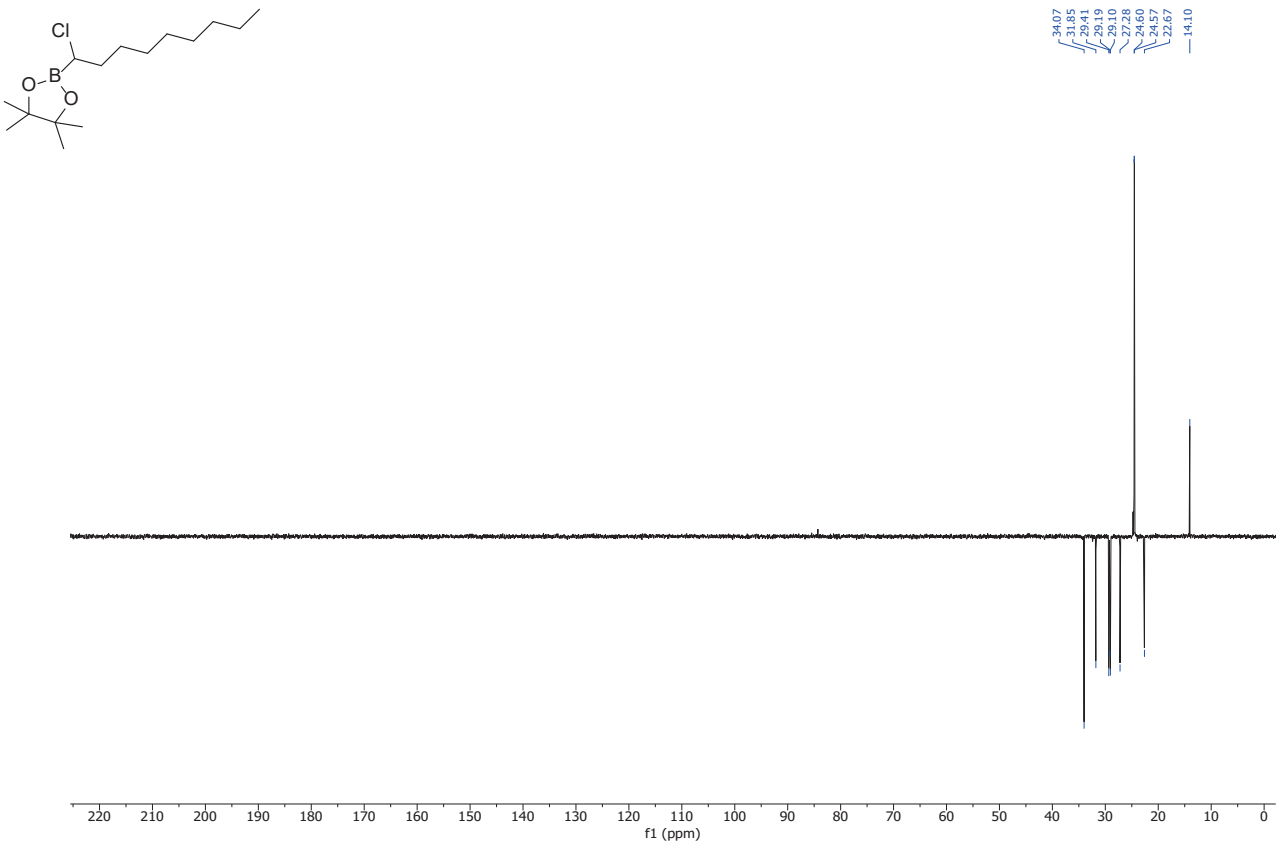
2-(1-chlorononyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)

^{13}C NMR (75 MHz, $CDCl_3$)



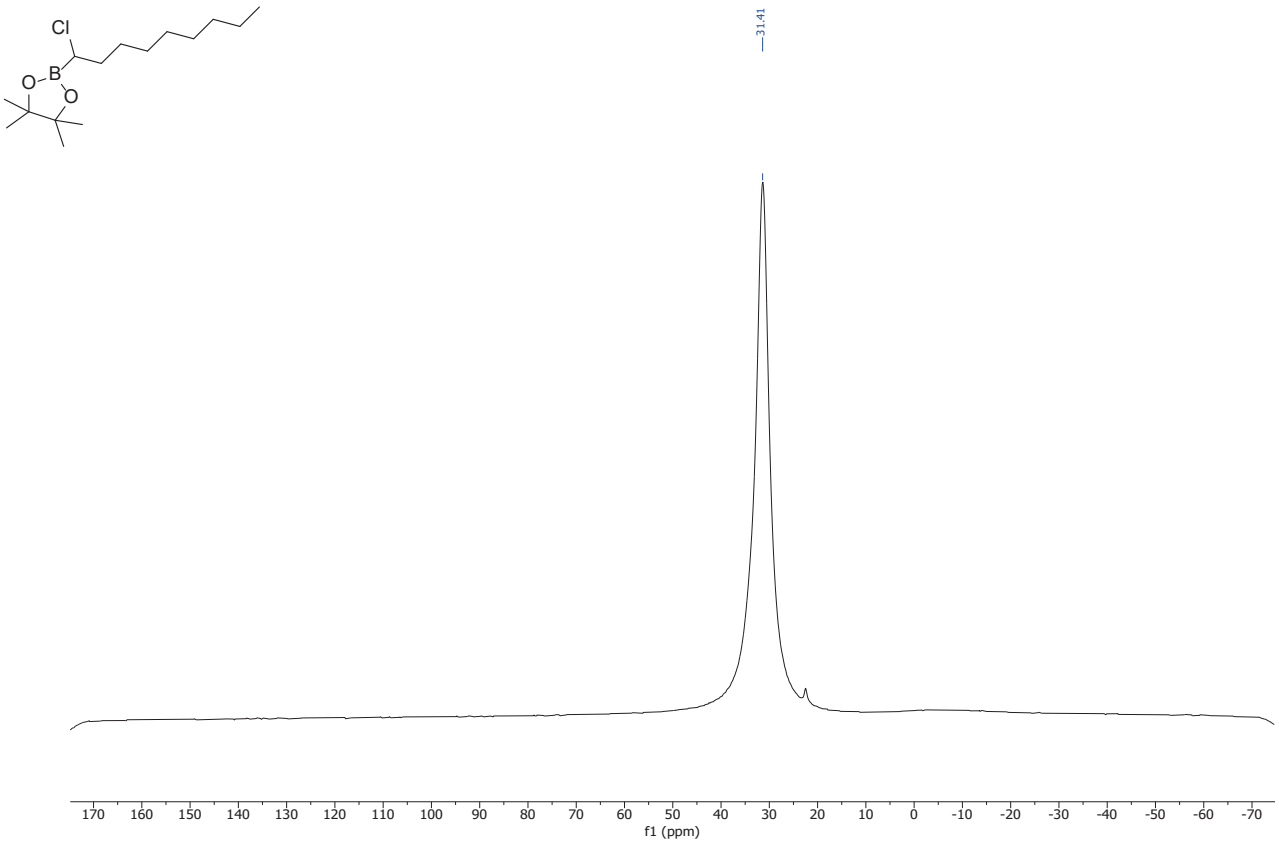
2-(1-chlorononyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



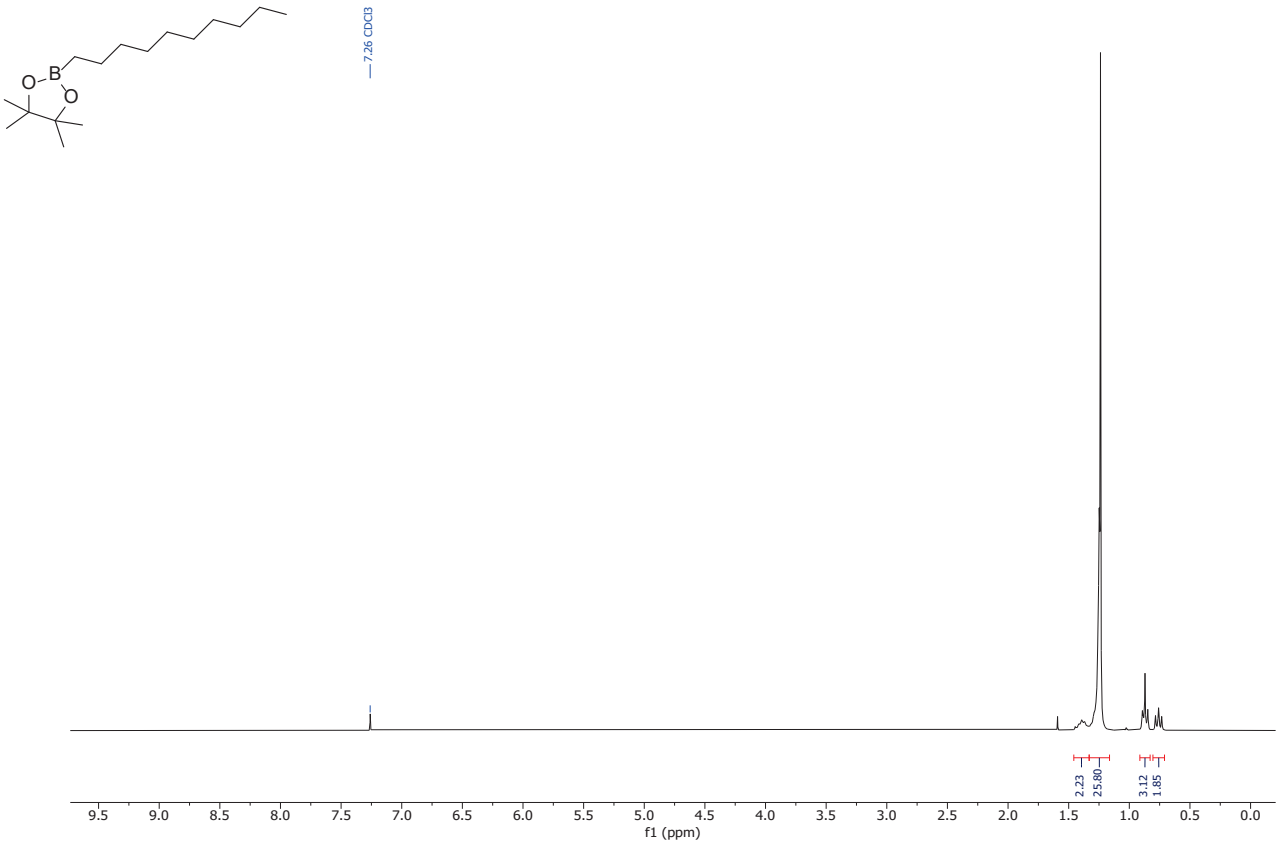
2-(1-chlorononyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)

^{11}B NMR (96 MHz, $CDCl_3$)



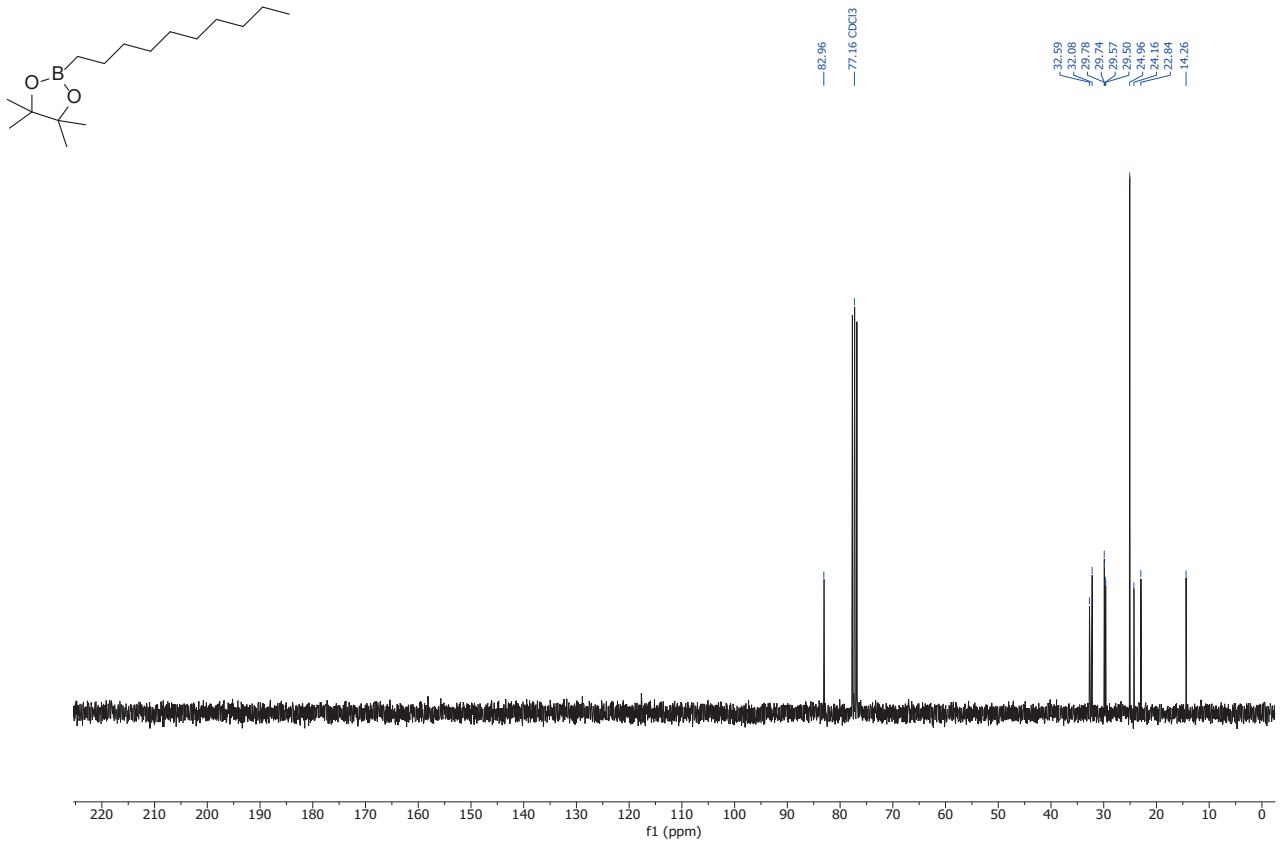
2-decyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (63)

^{1}H NMR (300 MHz, $CDCl_3$)



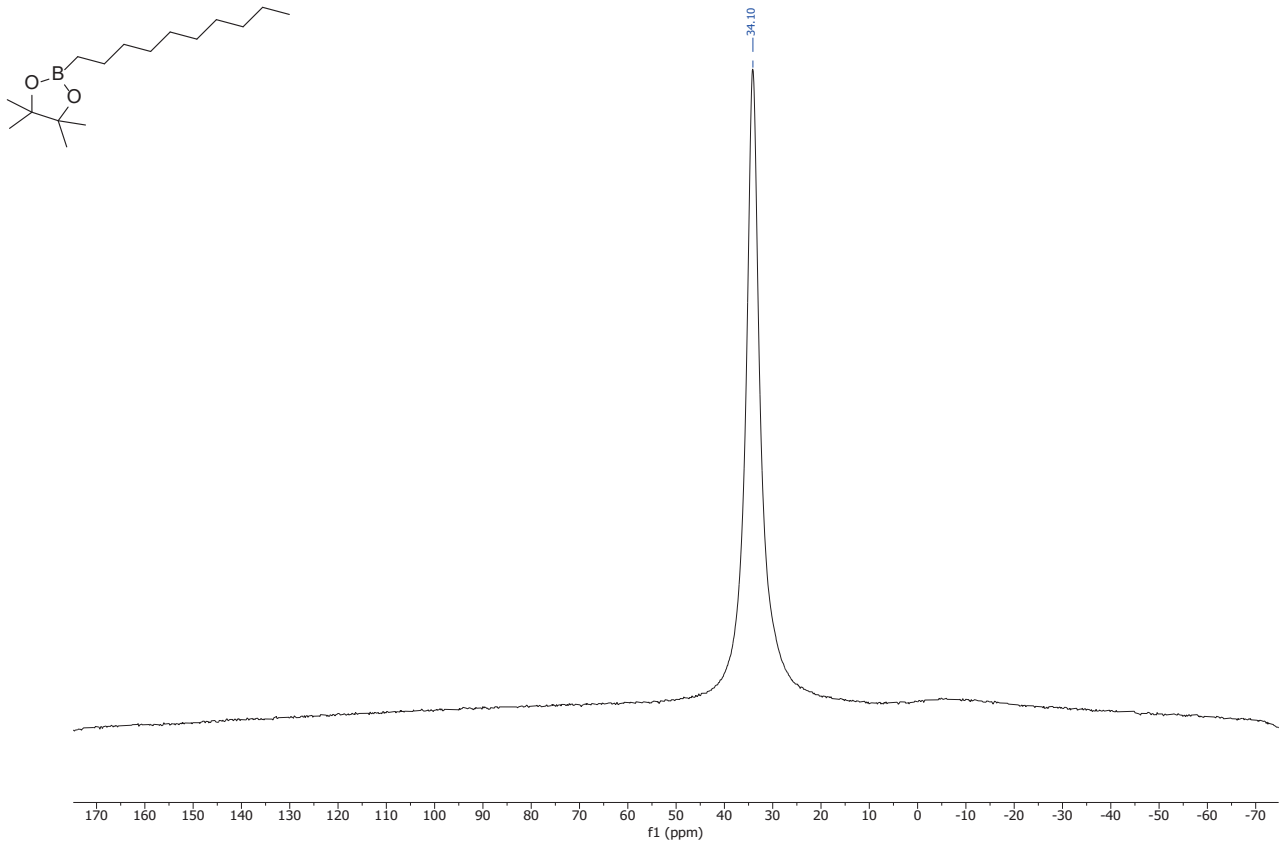
2-decyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (63)

^{13}C NMR (75 MHz, $CDCl_3$)



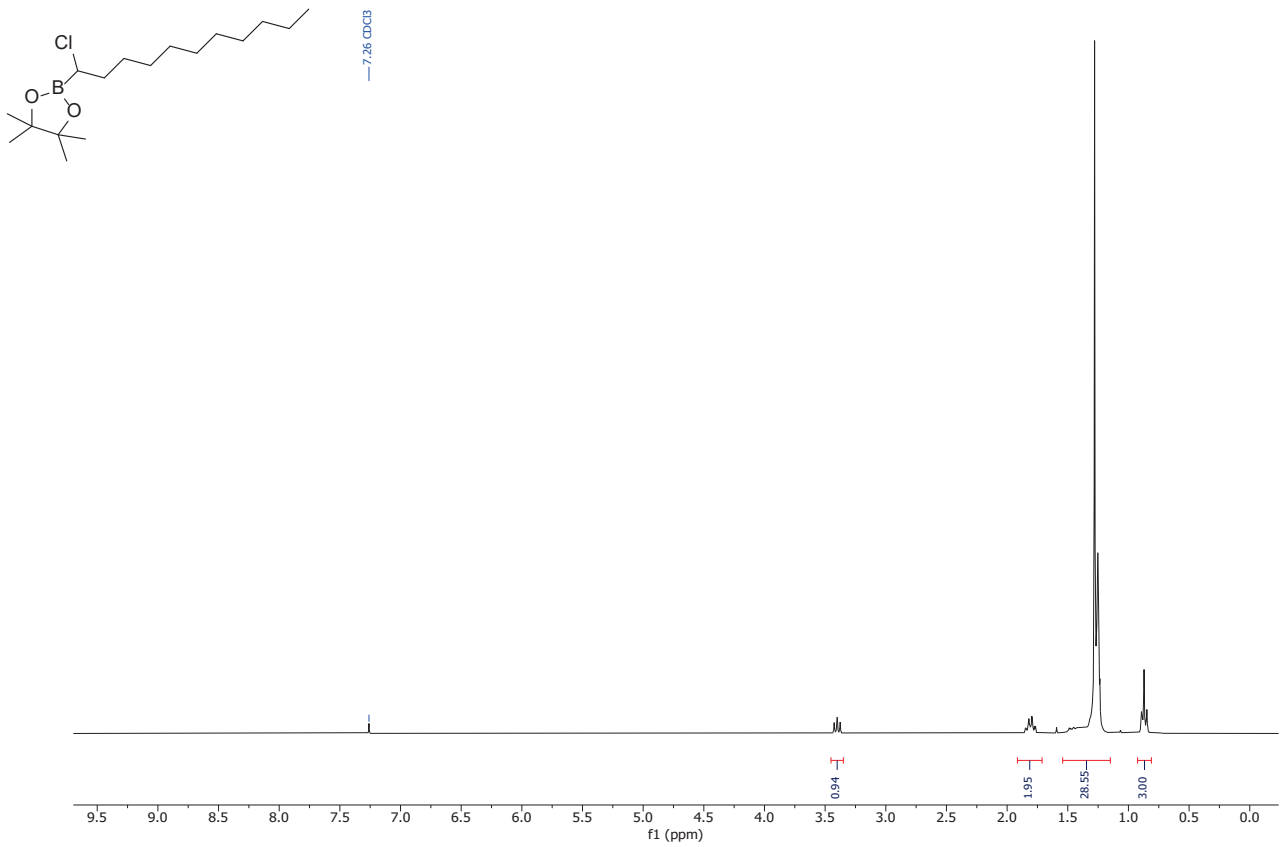
2-decyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (63)

^{11}B NMR (96 MHz, $CDCl_3$)



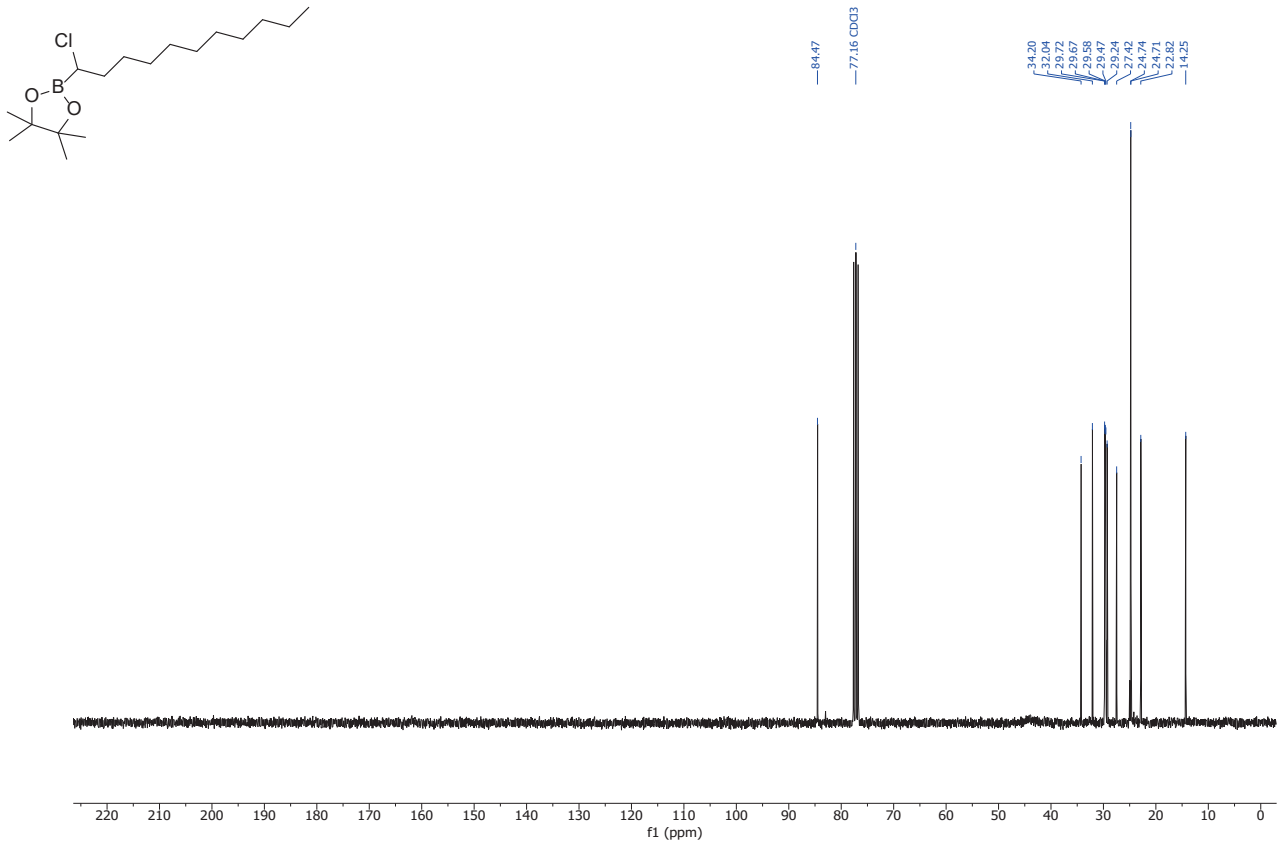
2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2)

^{1}H NMR (300 MHz, $CDCl_3$)



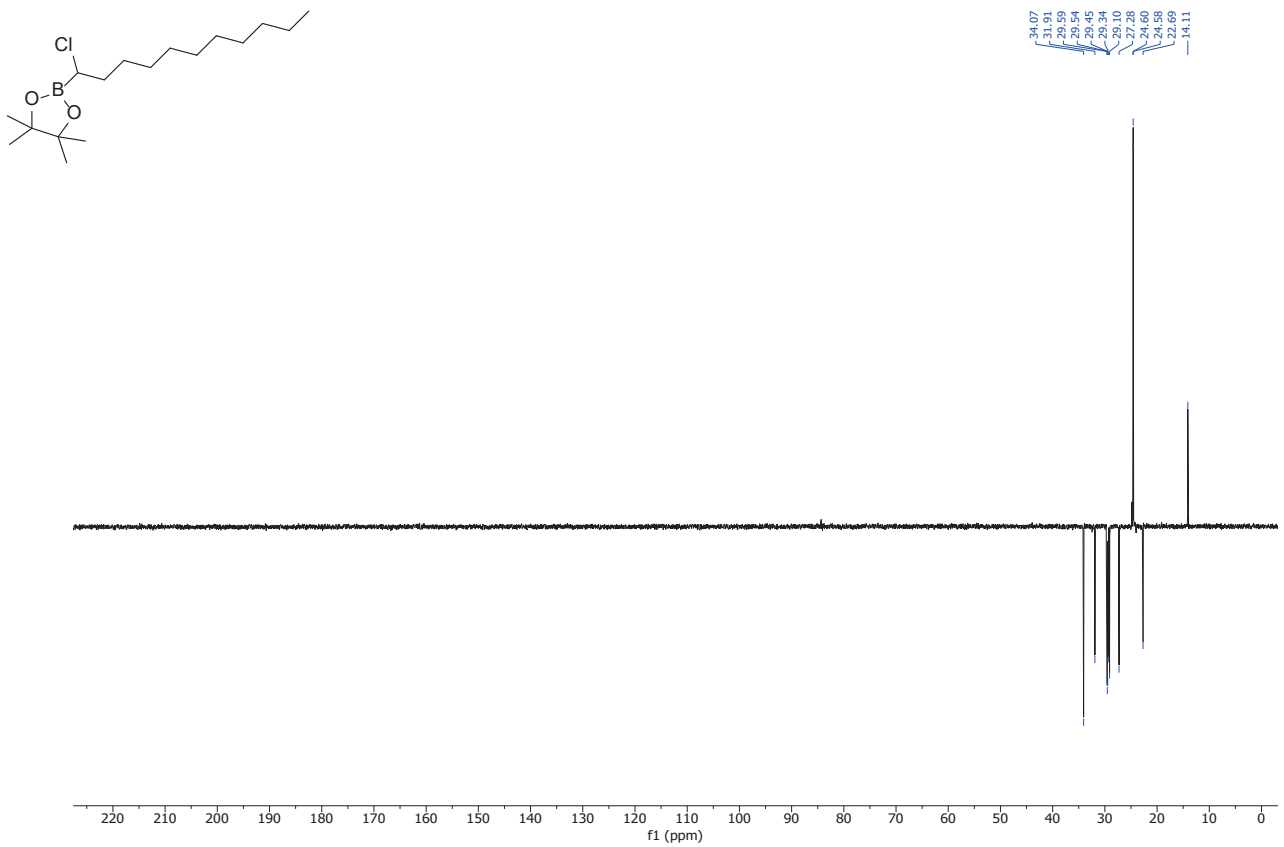
2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2)

^{13}C NMR (75 MHz, $CDCl_3$)



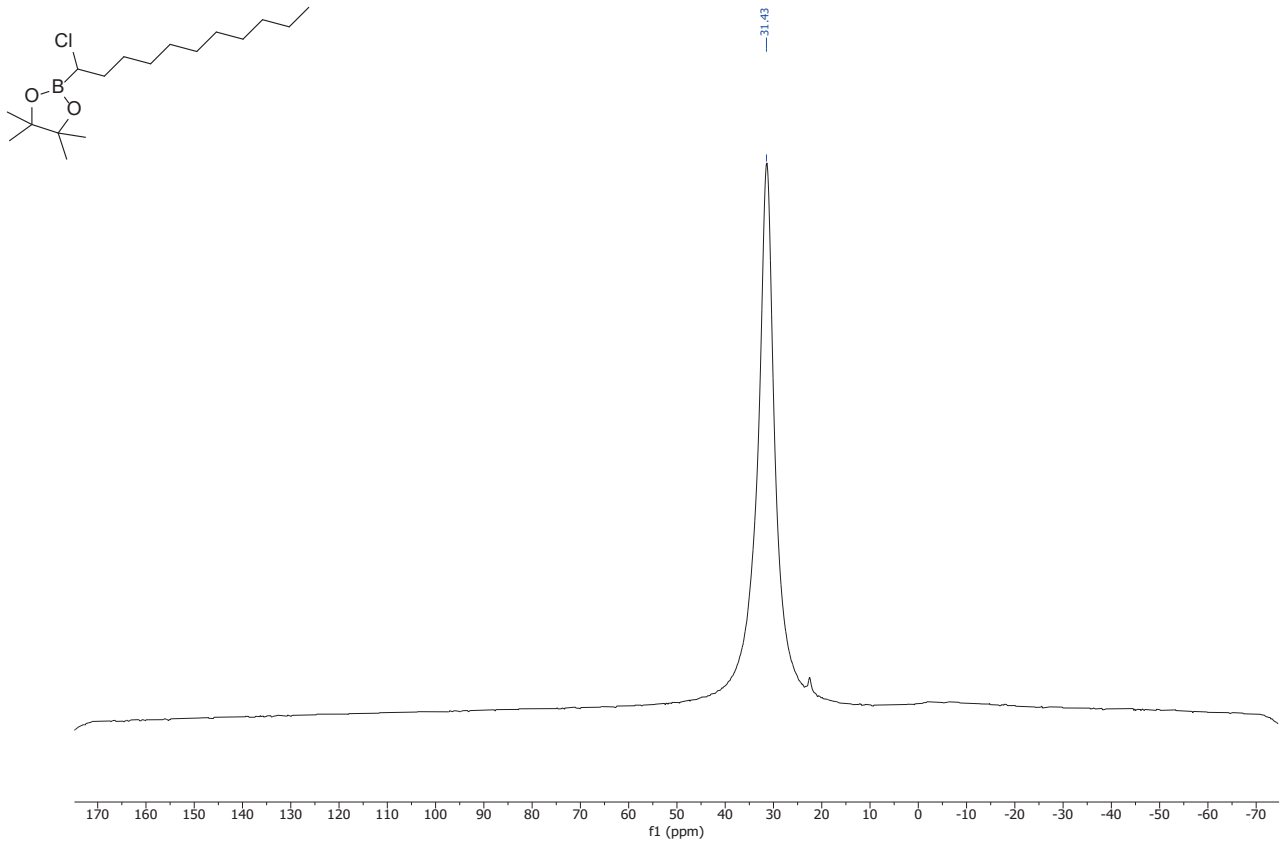
2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



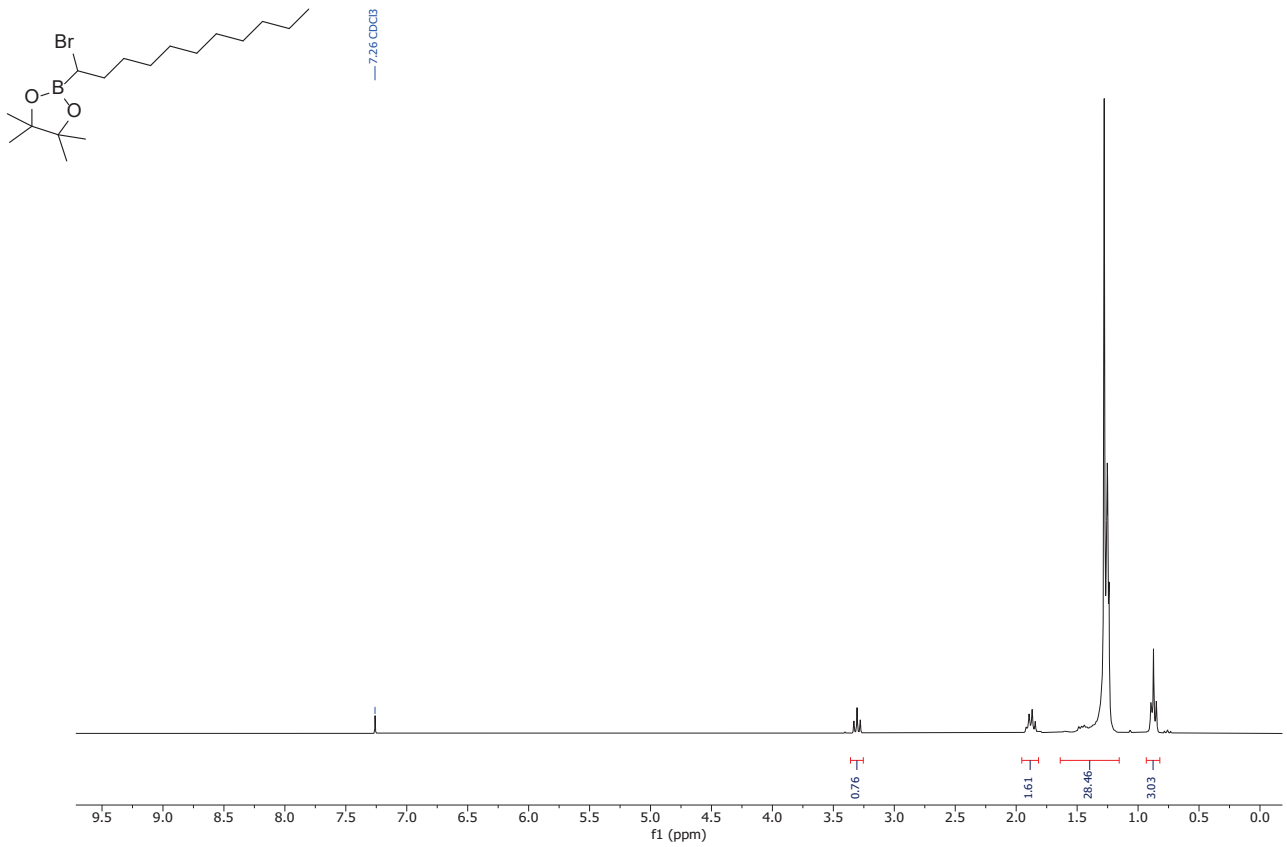
2-(1-chloroundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2)

^{11}B NMR (96 MHz, $CDCl_3$)



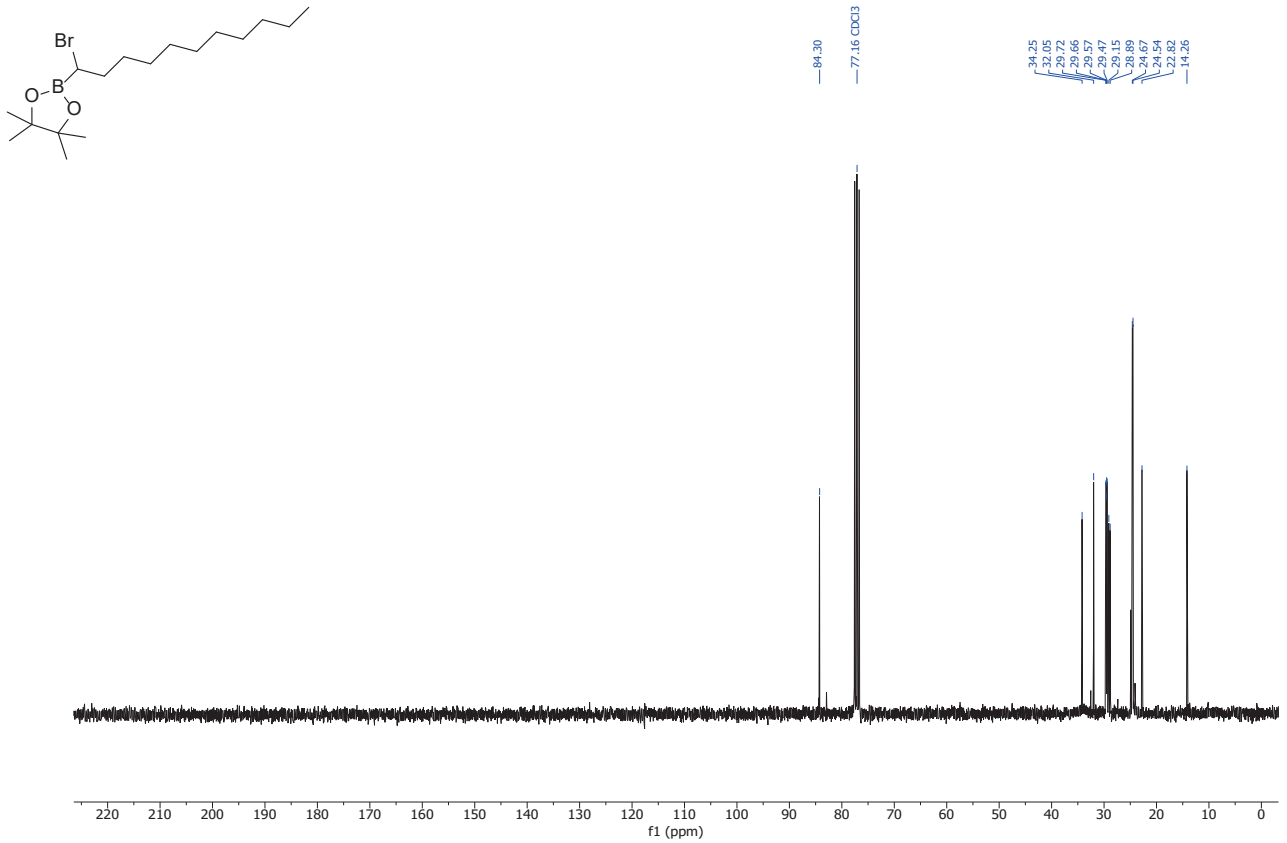
2-(1-bromoundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (64)

^{1}H NMR (300 MHz, $CDCl_3$)



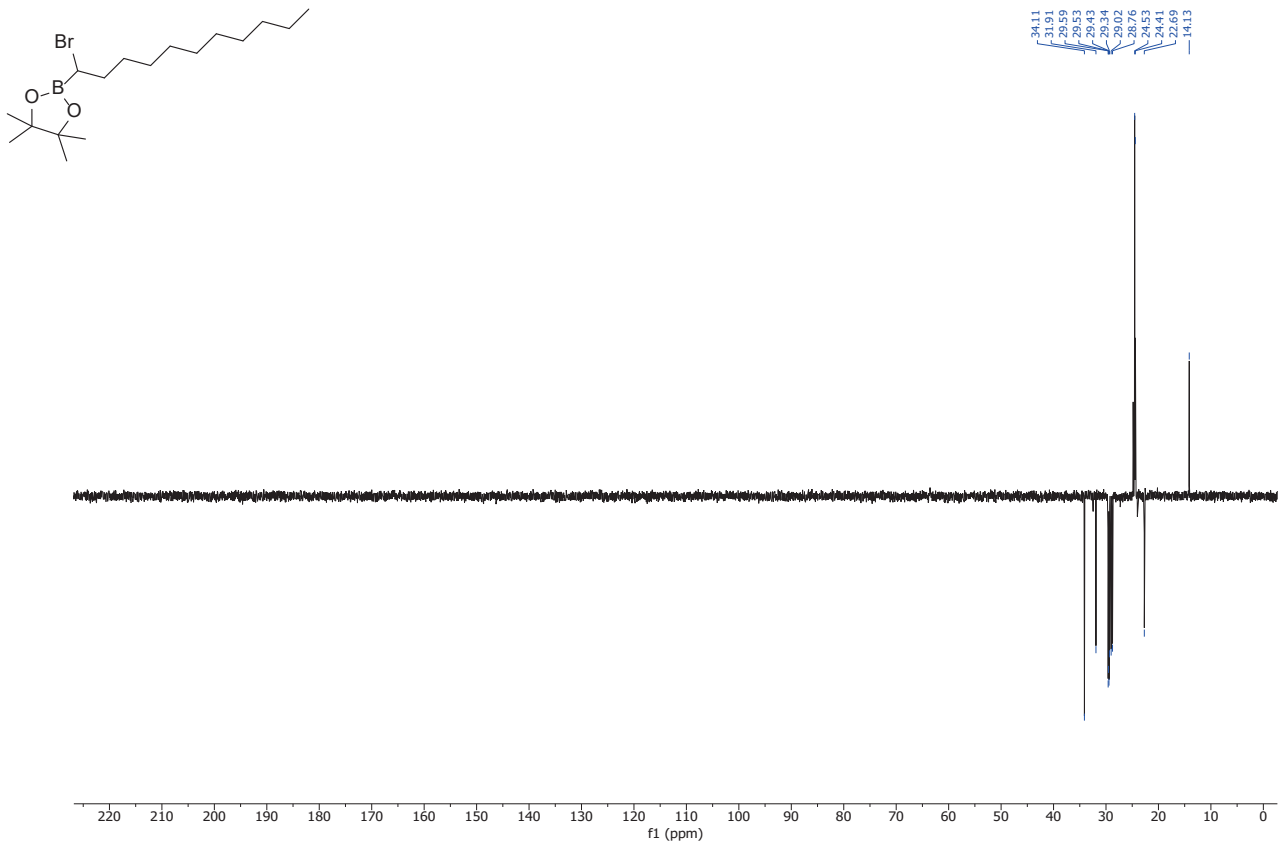
2-(1-bromoundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (64)

^{13}C NMR (75 MHz, $CDCl_3$)



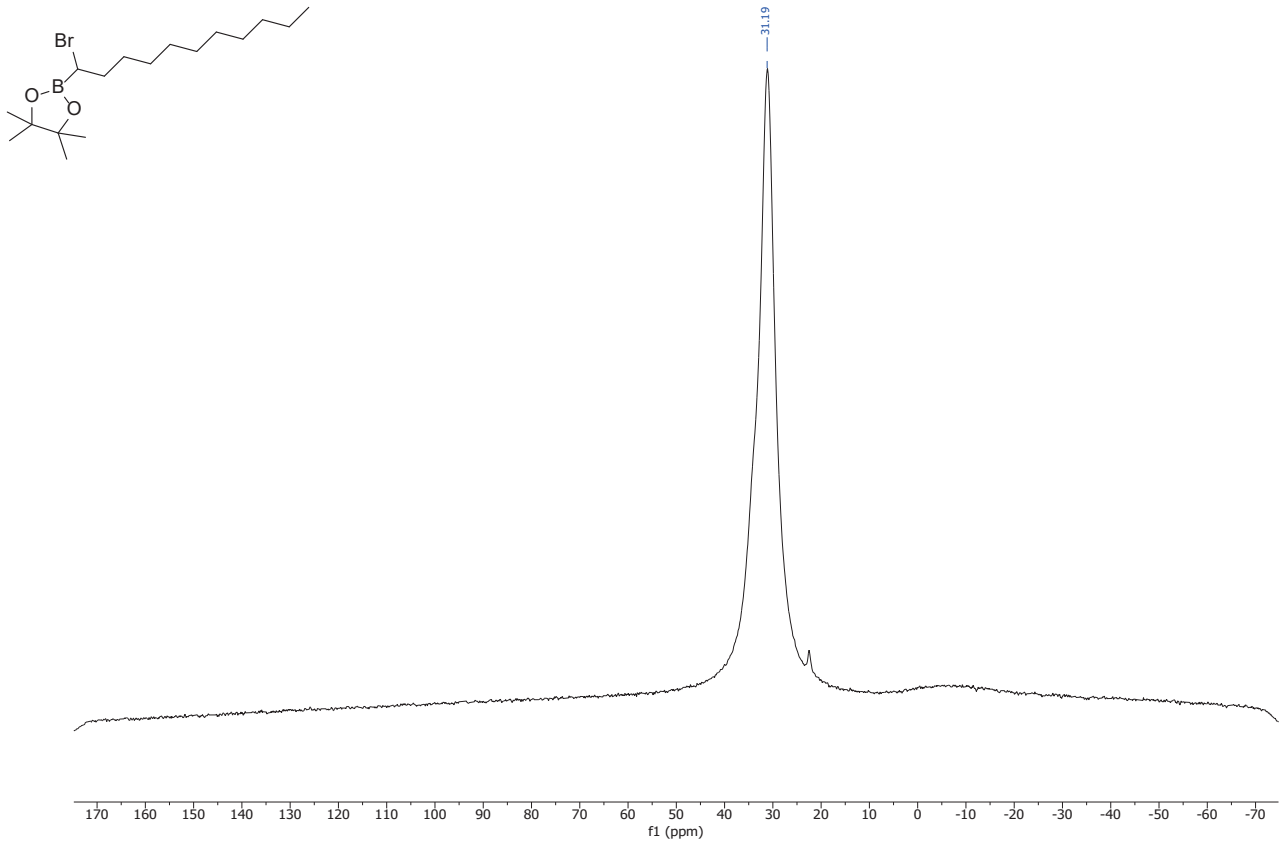
2-(1-bromoundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (64)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



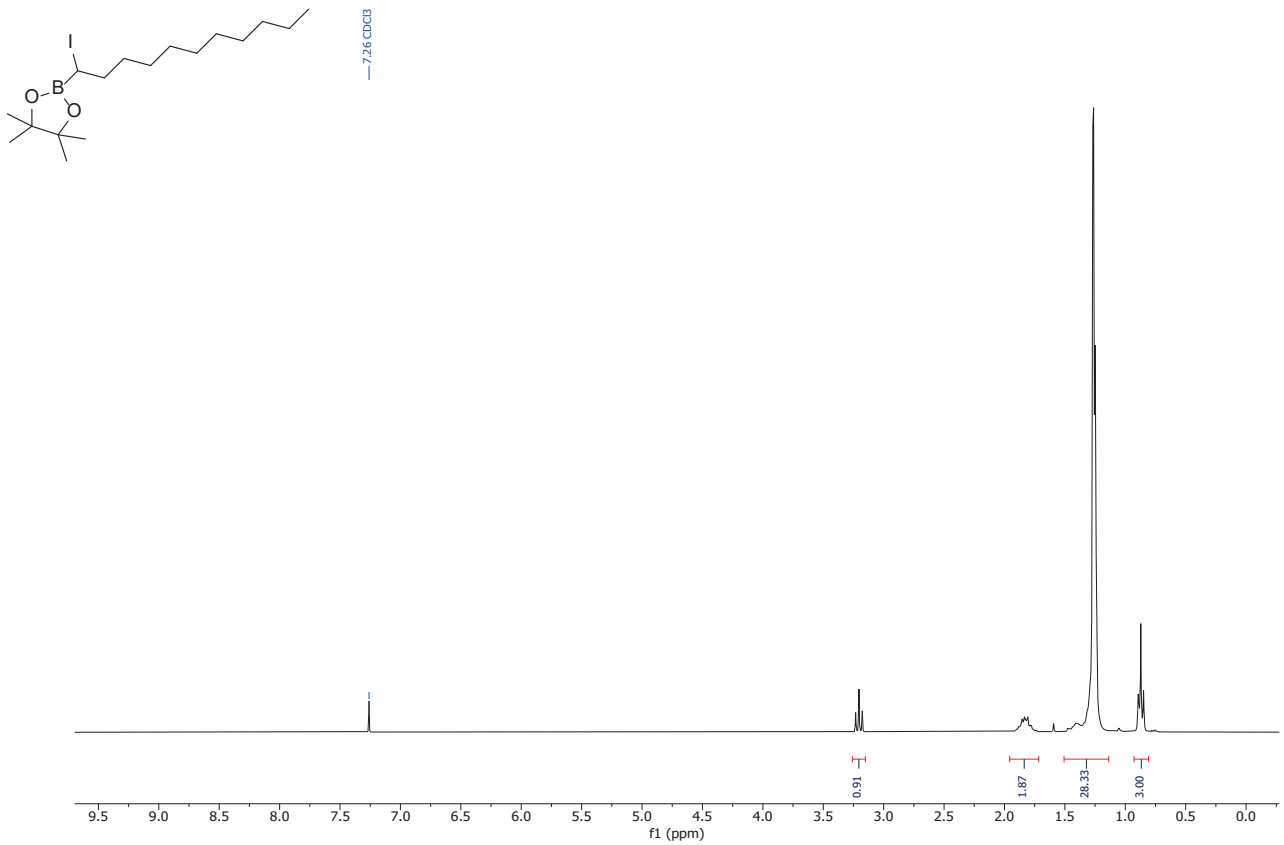
2-(1-bromoundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (64)

^{11}B NMR (96 MHz, $CDCl_3$)



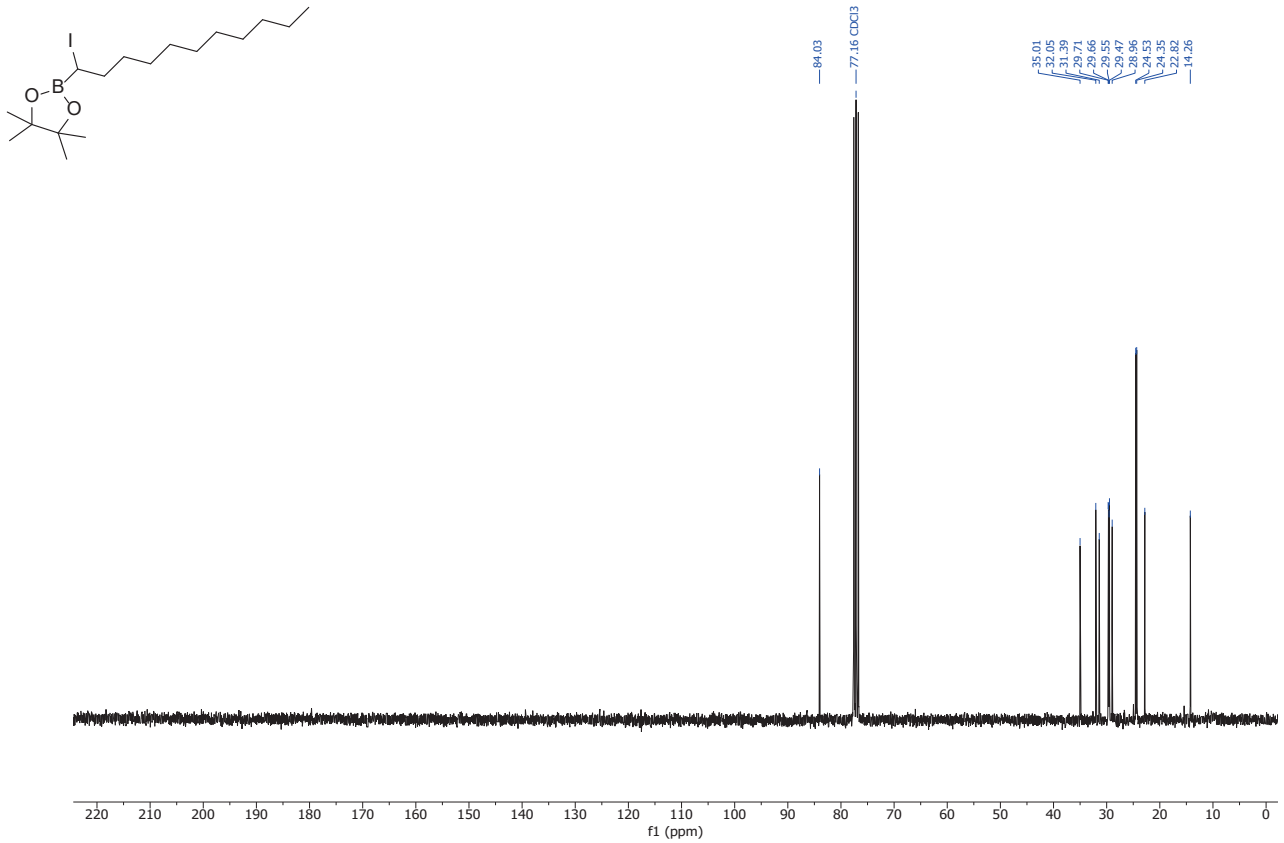
2-(1-iodoundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (65)

^{1}H NMR (300 MHz, $CDCl_3$)



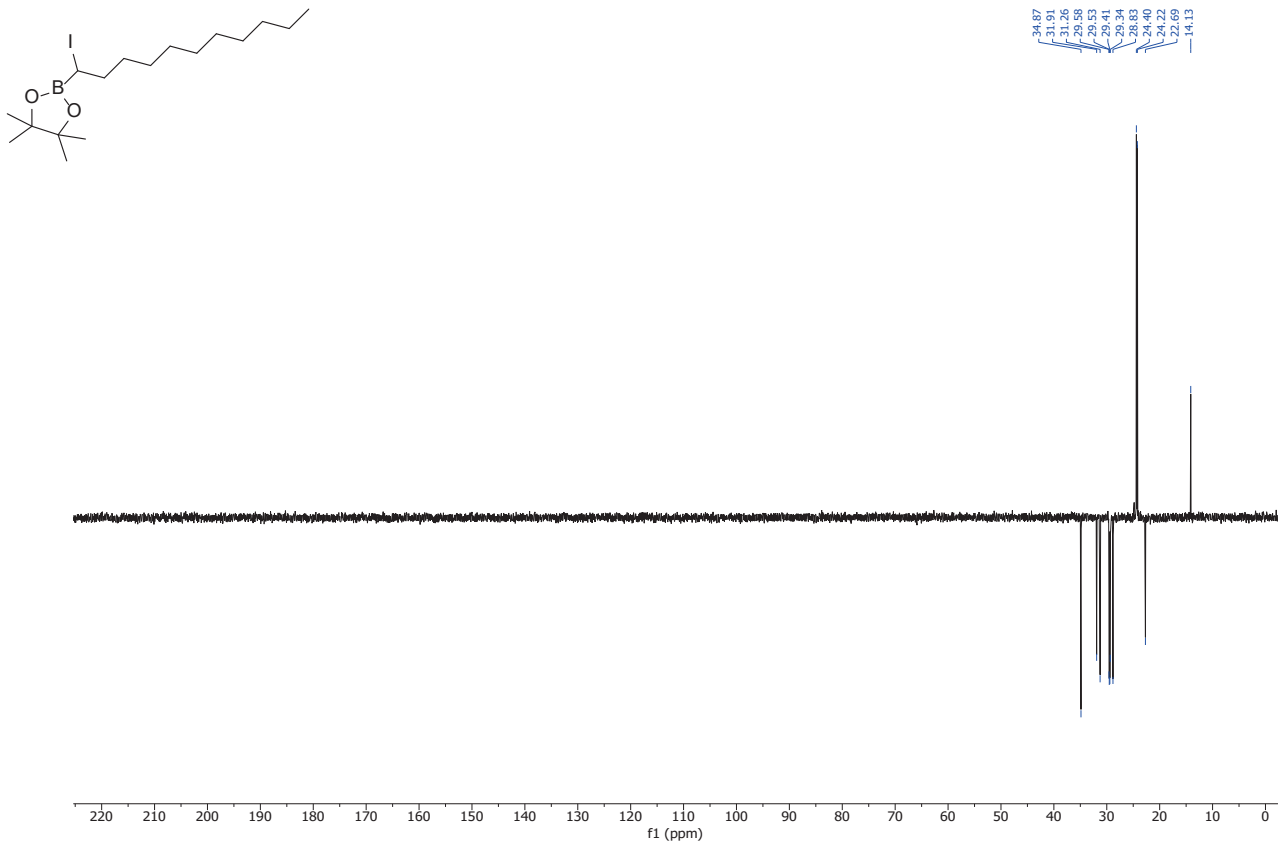
2-(1-iodoundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (65)

^{13}C NMR (75 MHz, $CDCl_3$)



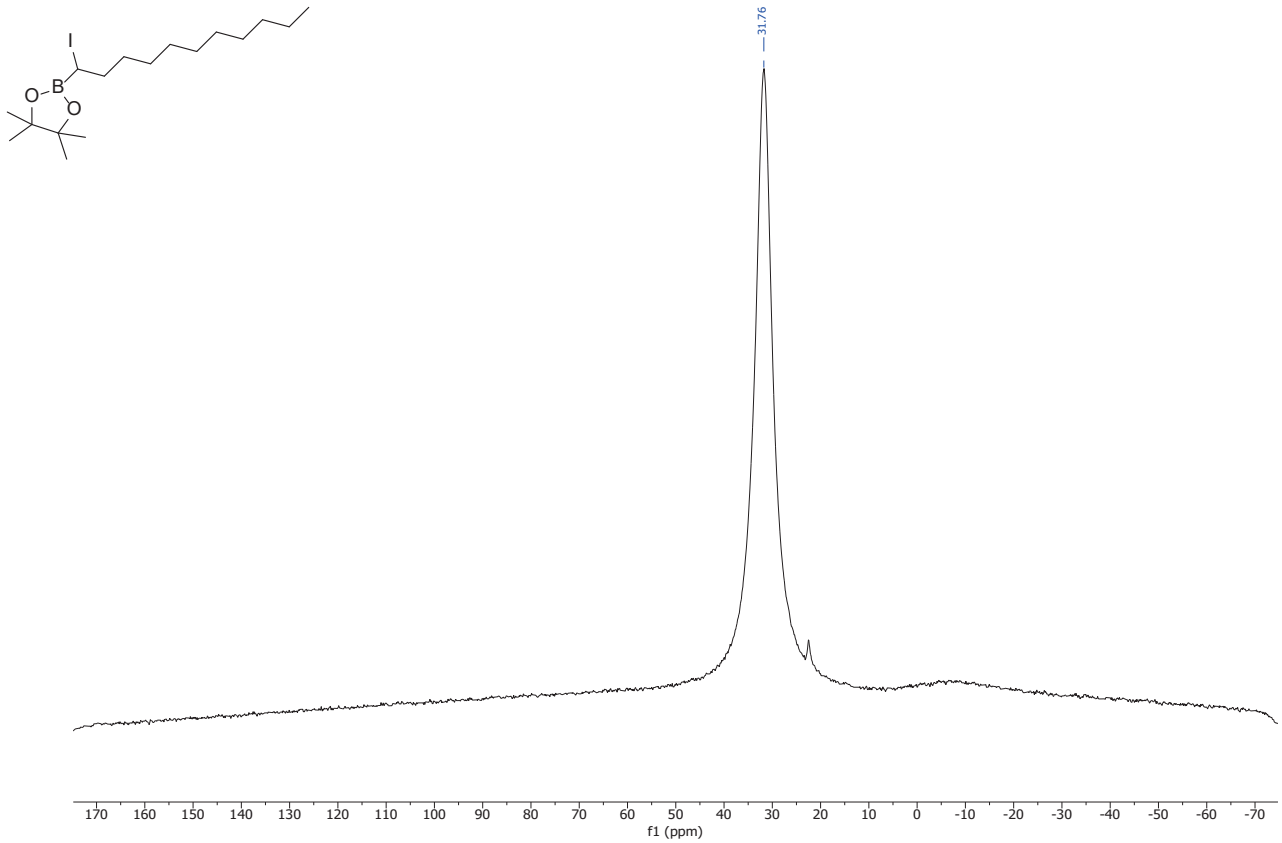
2-(1-iodoundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (65)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

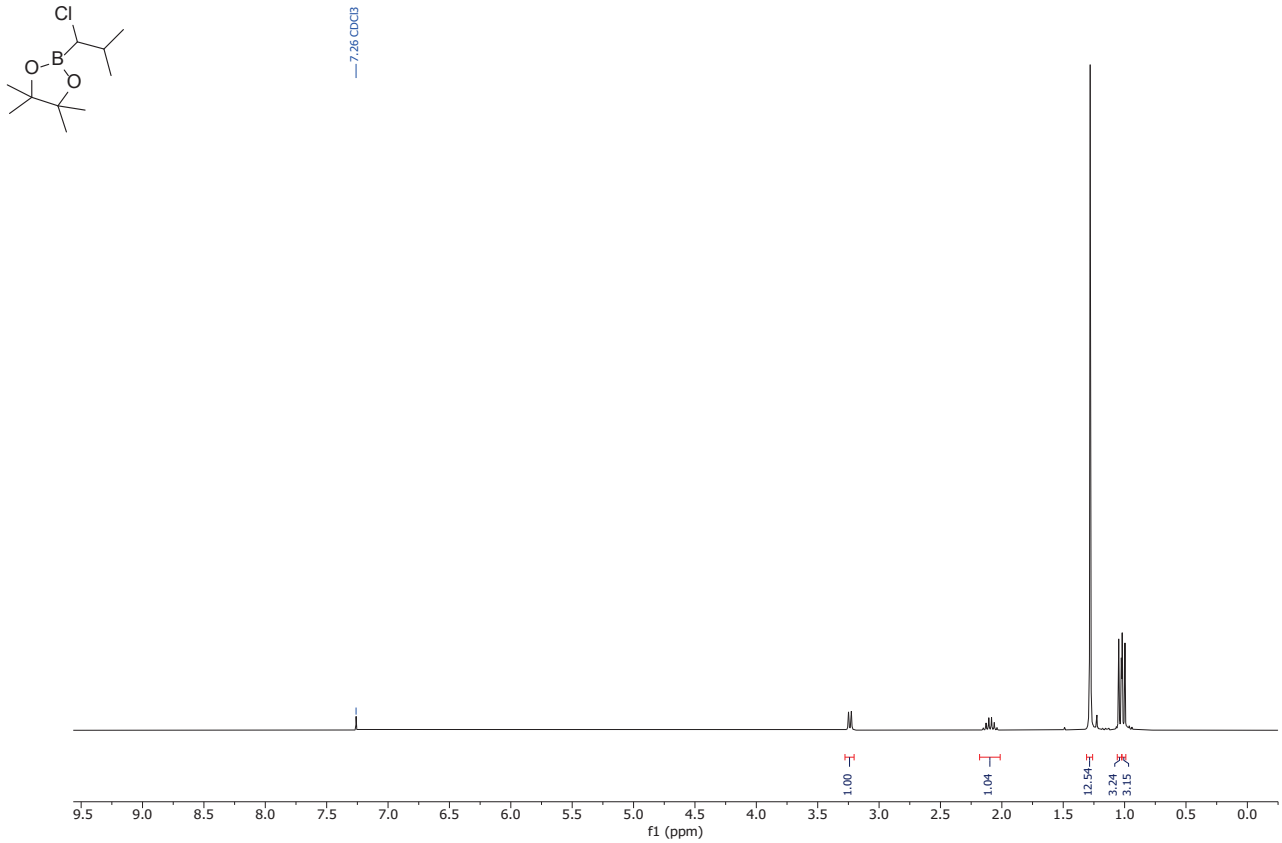


2-(1-iodoundecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (65)

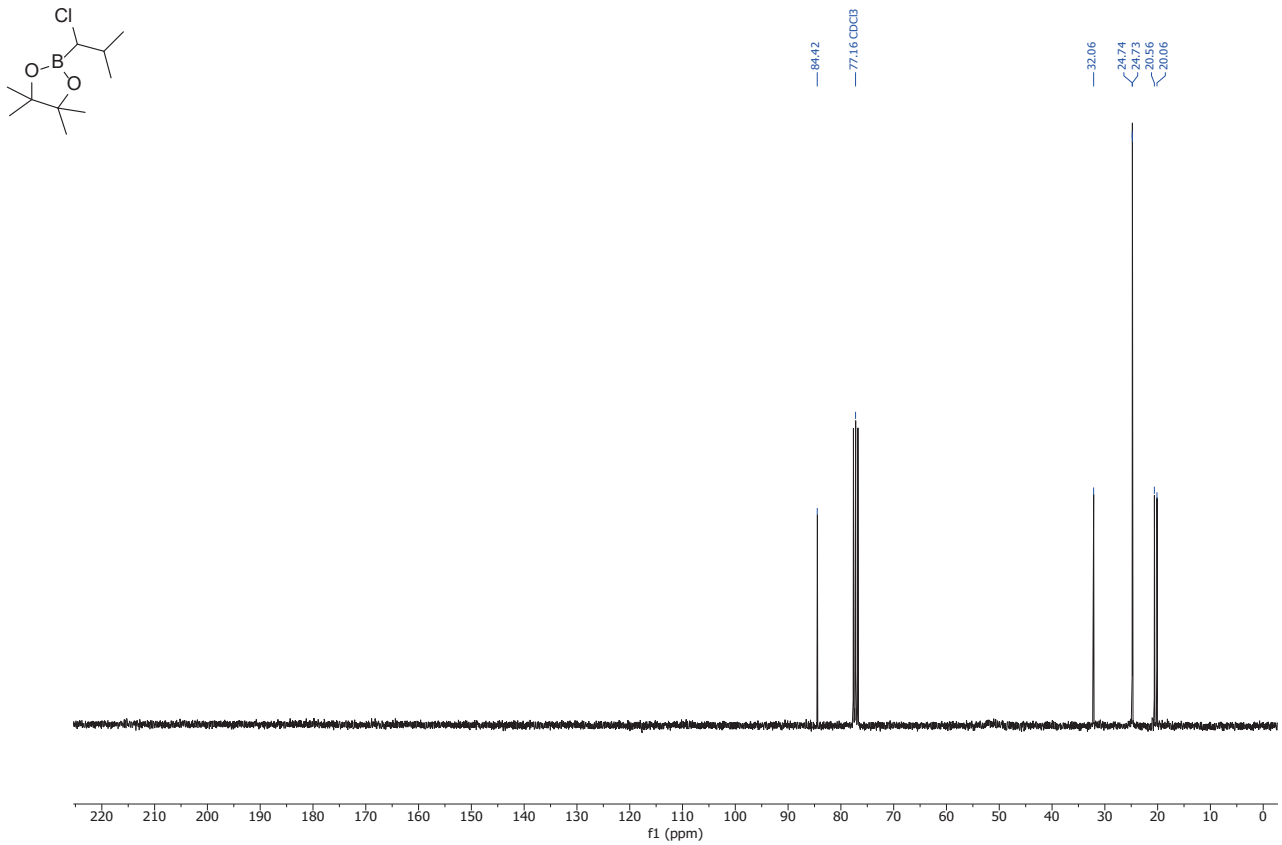
^{11}B NMR (96 MHz, $CDCl_3$)



2-(1-chloro-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (66) ^{1}H NMR (300 MHz, $CDCl_3$)

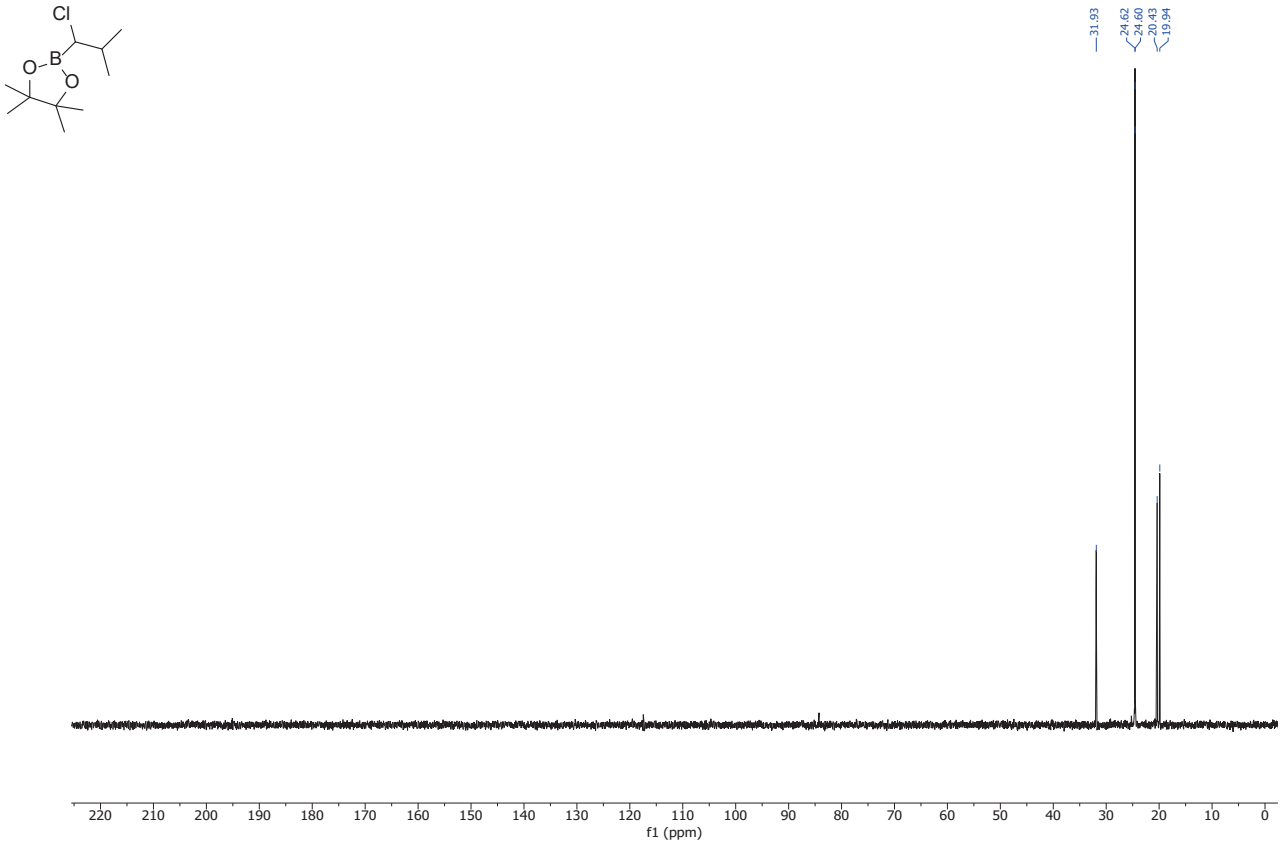


2-(1-chloro-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (66) ^{13}C NMR (75 MHz, $CDCl_3$)



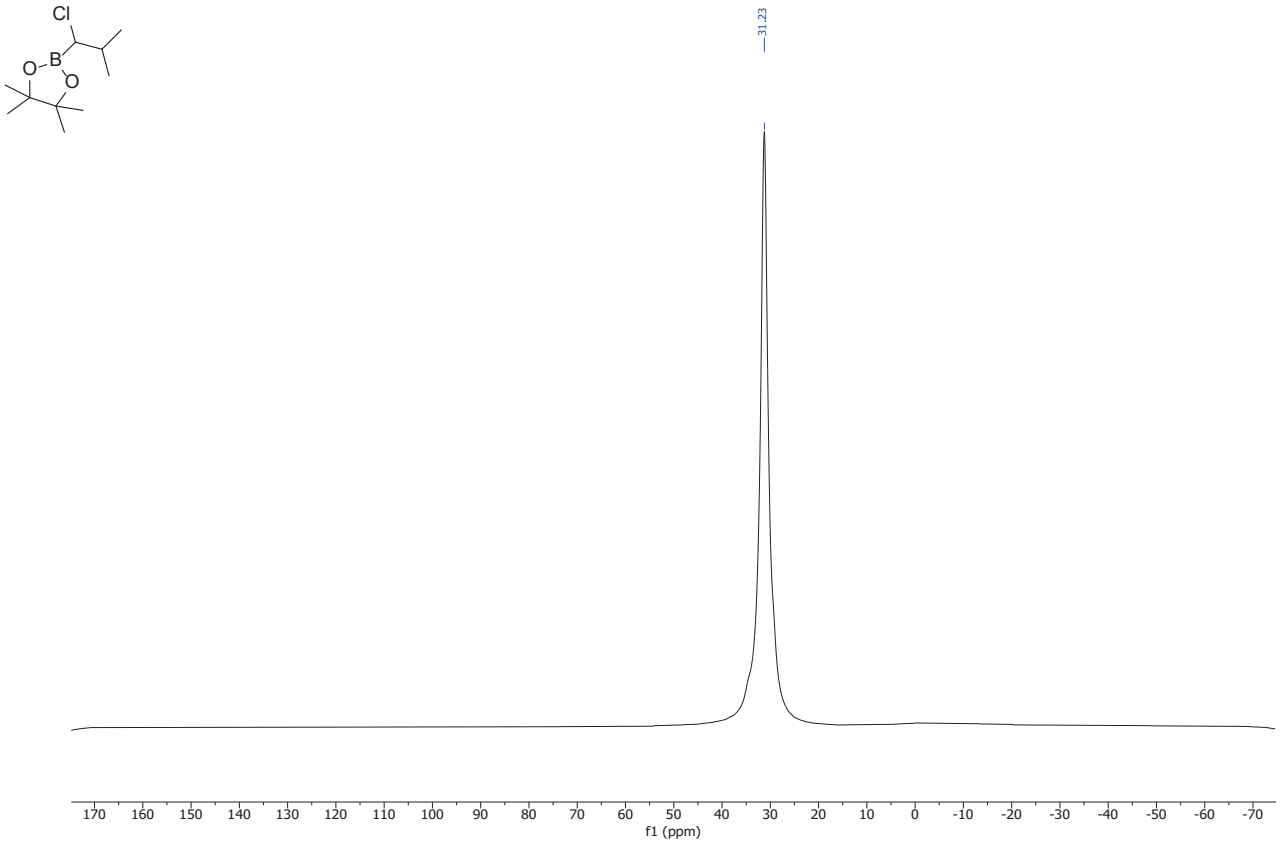
2-(1-chloro-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (66)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

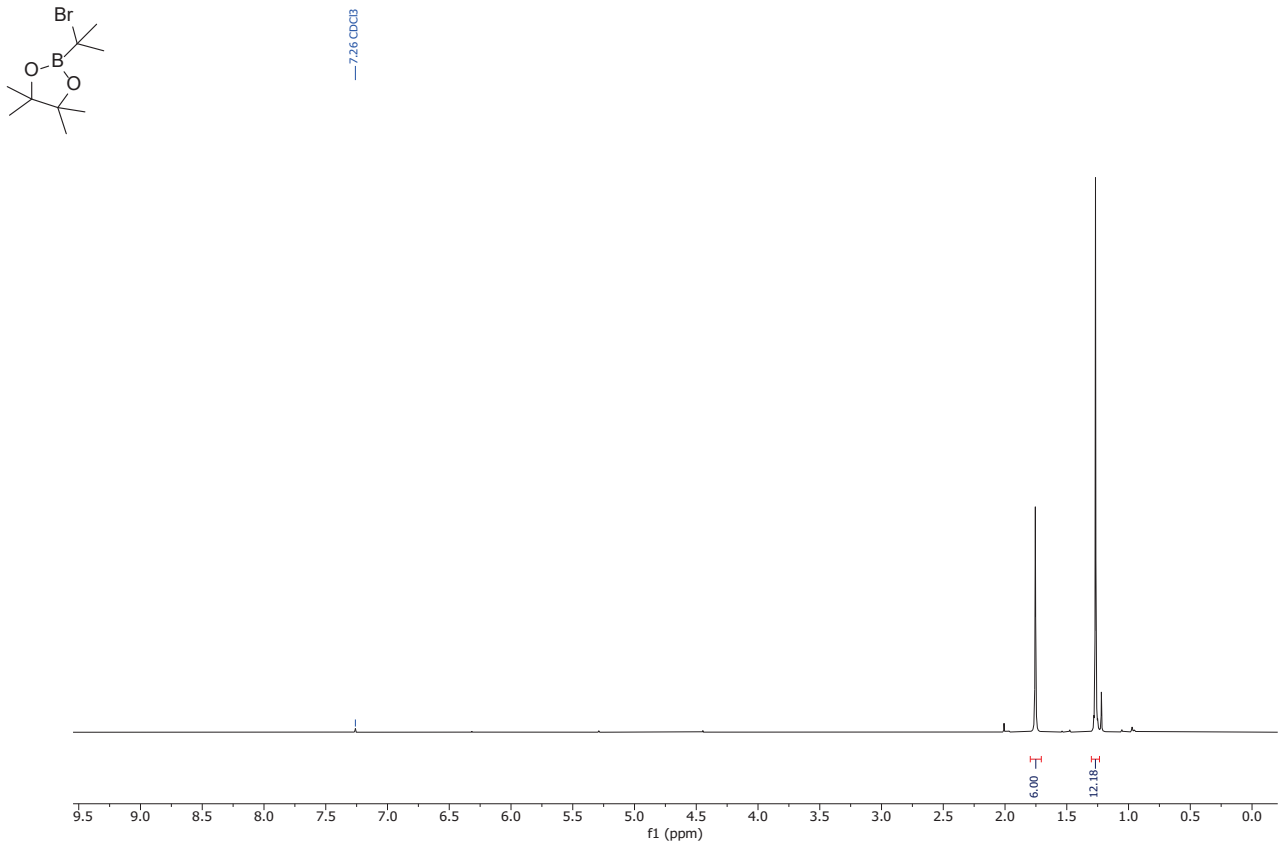


2-(1-chloro-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (66)

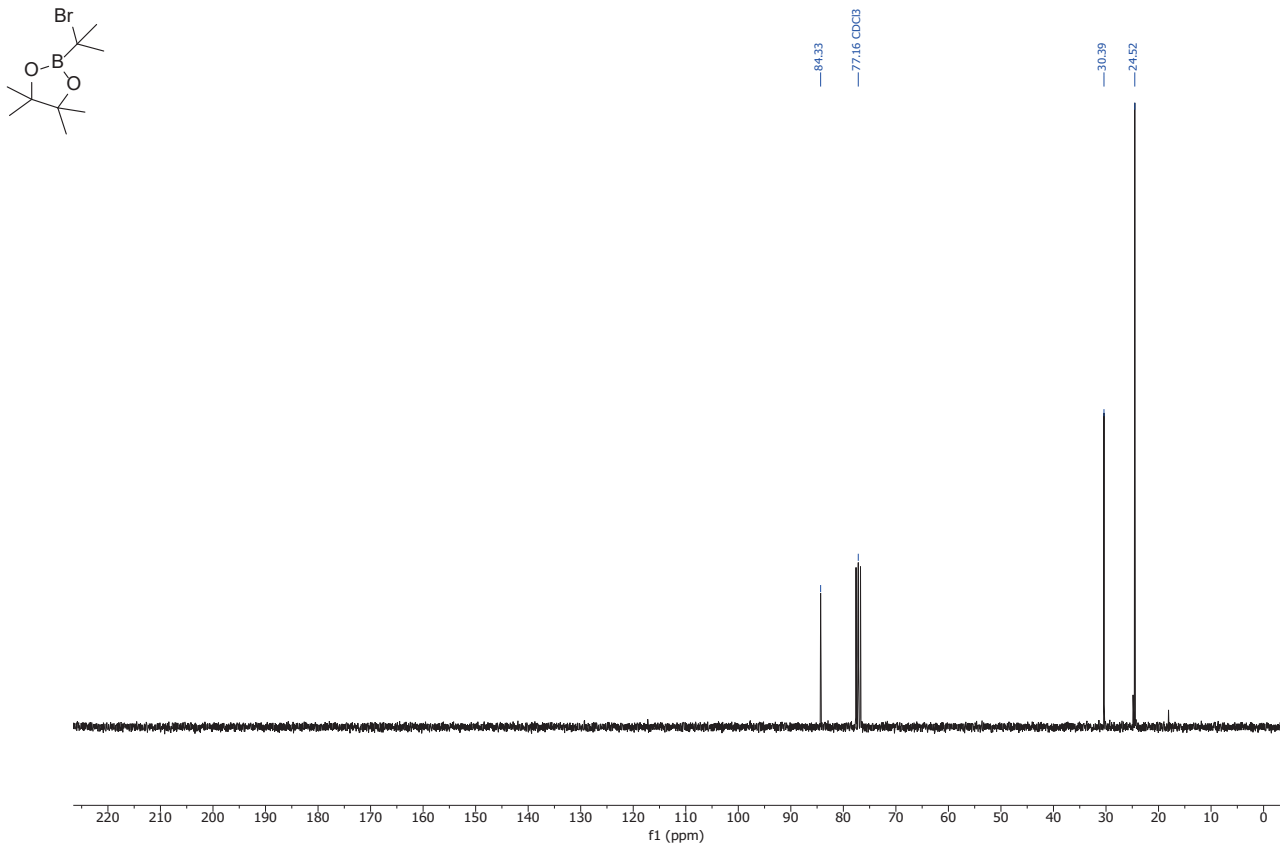
^{11}B NMR (96 MHz, $CDCl_3$)



2-(2-bromopropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (67) ^{1}H NMR (300 MHz, $CDCl_3$)

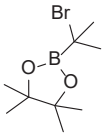


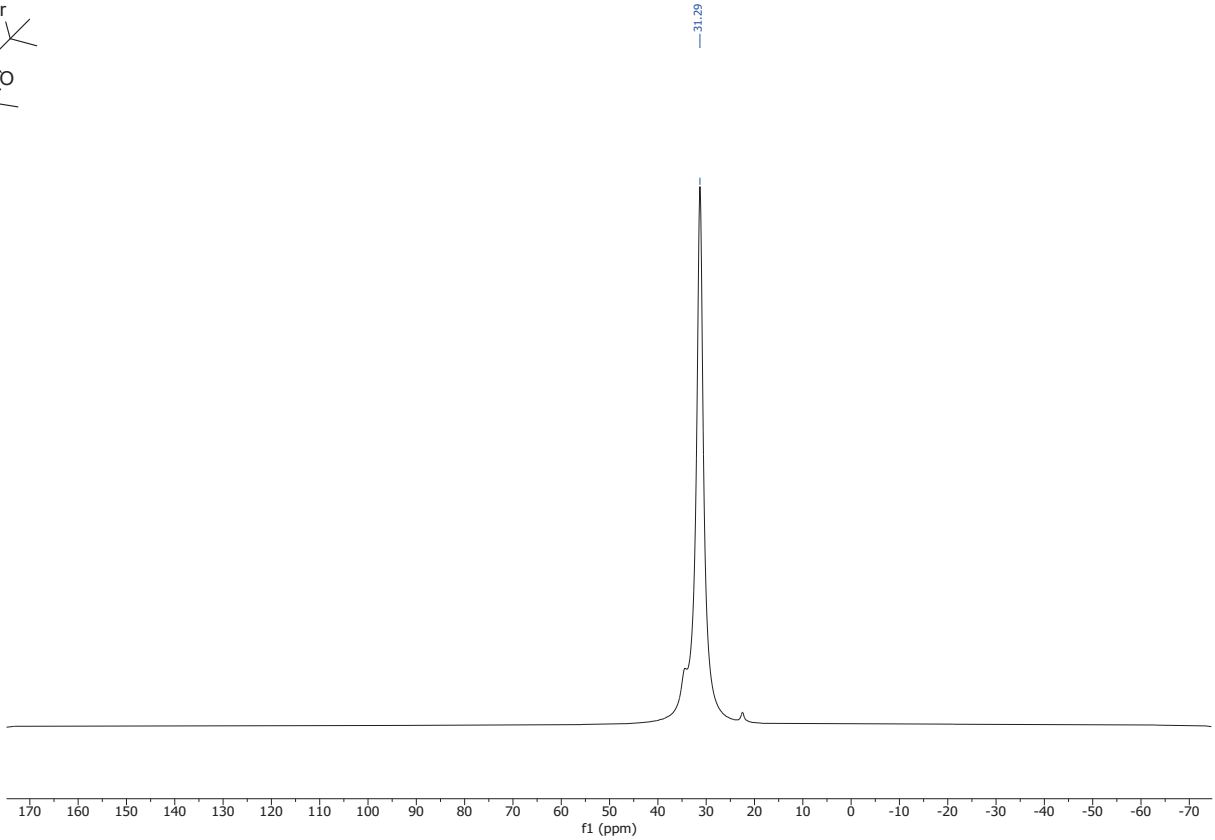
2-(2-bromopropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (67) ^{13}C NMR (75 MHz, $CDCl_3$)



2-(2-bromopropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (67)

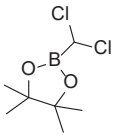
^{11}B NMR (96 MHz, $CDCl_3$)

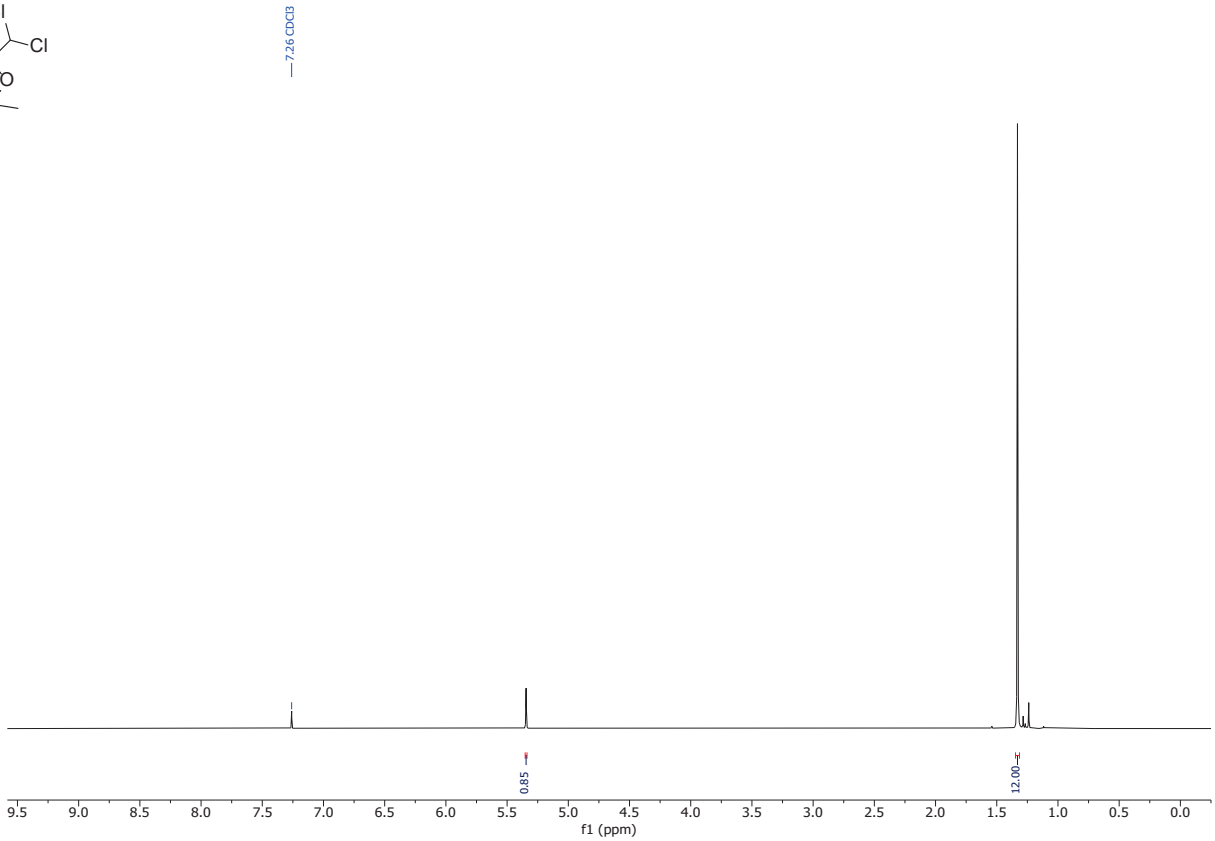




2-(dichloromethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (68)

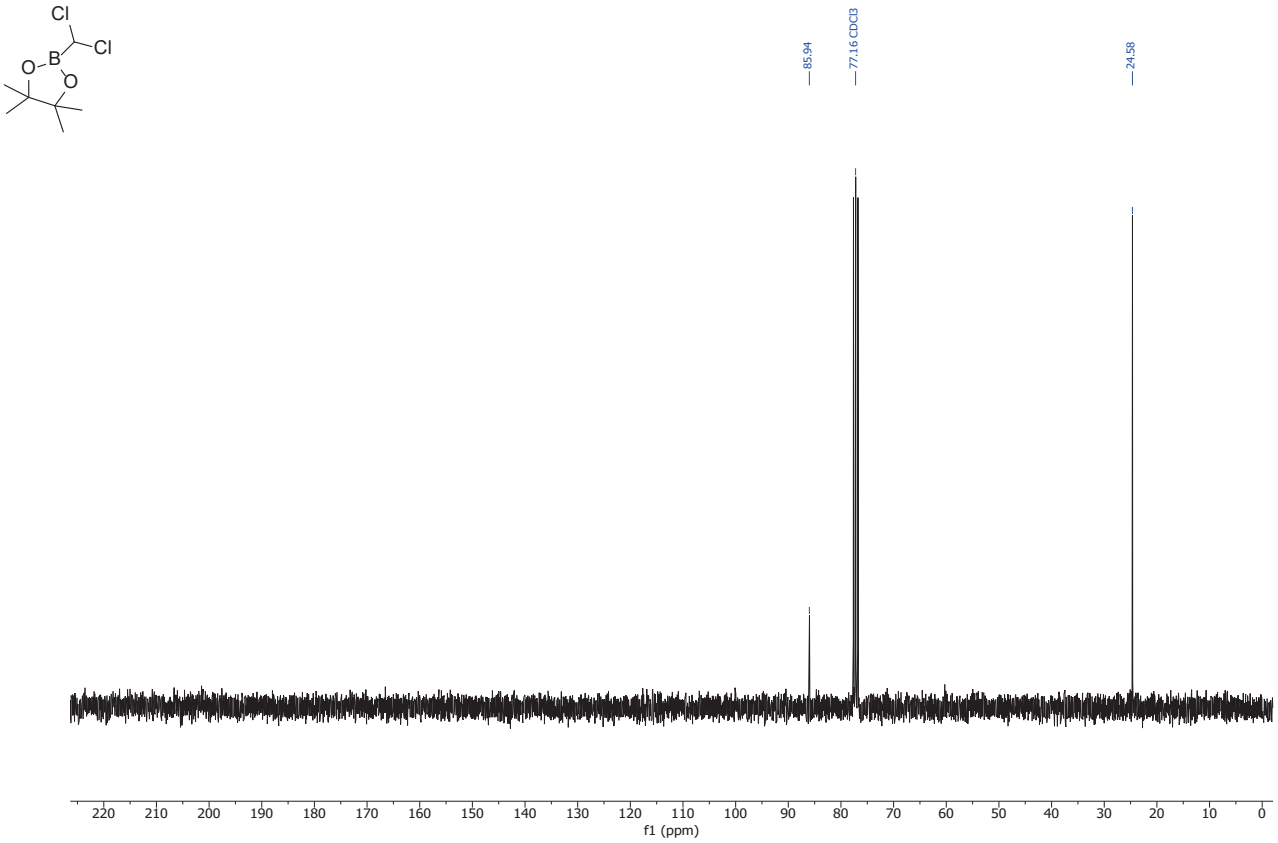
^{1}H NMR (300 MHz, $CDCl_3$)





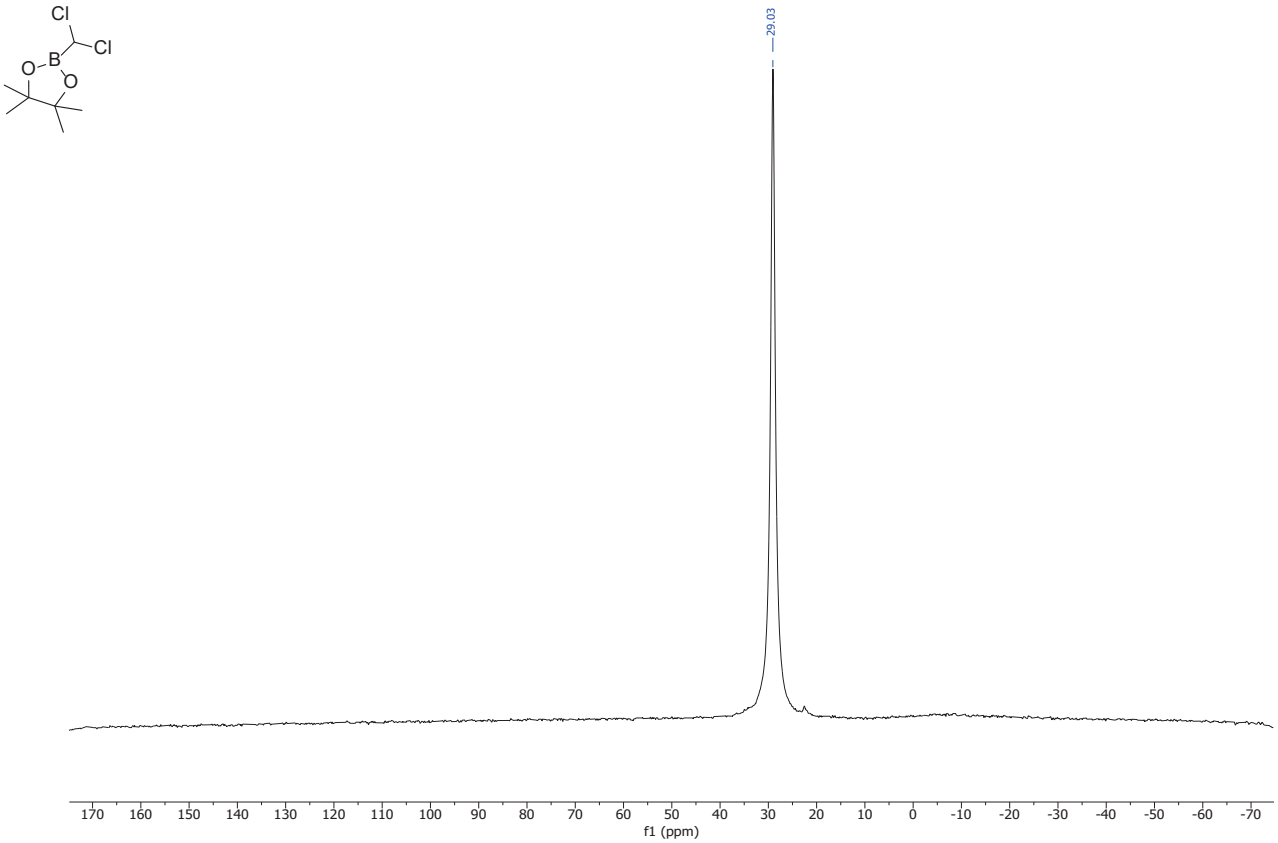
2-(dichloromethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (68)

^{13}C NMR (75 MHz, $CDCl_3$)

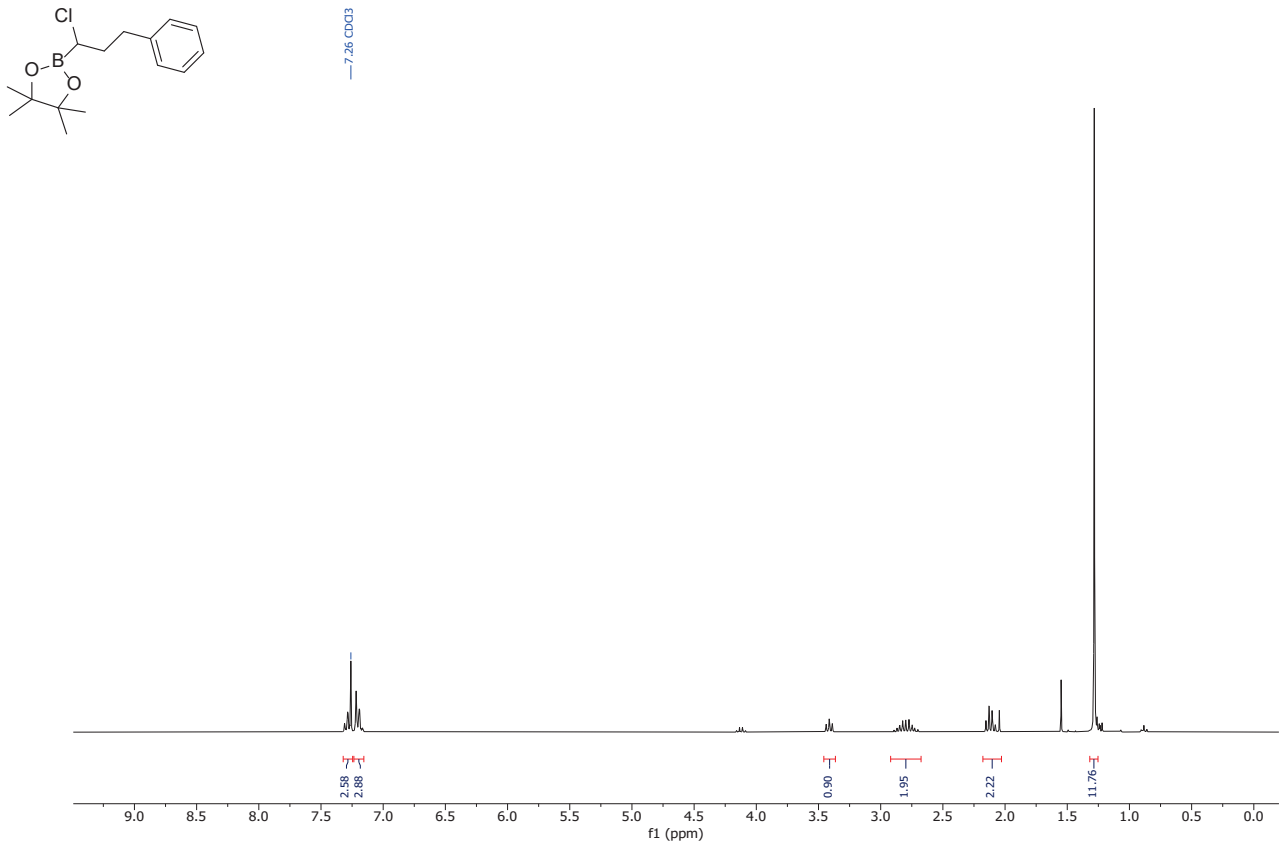


2-(dichloromethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (68)

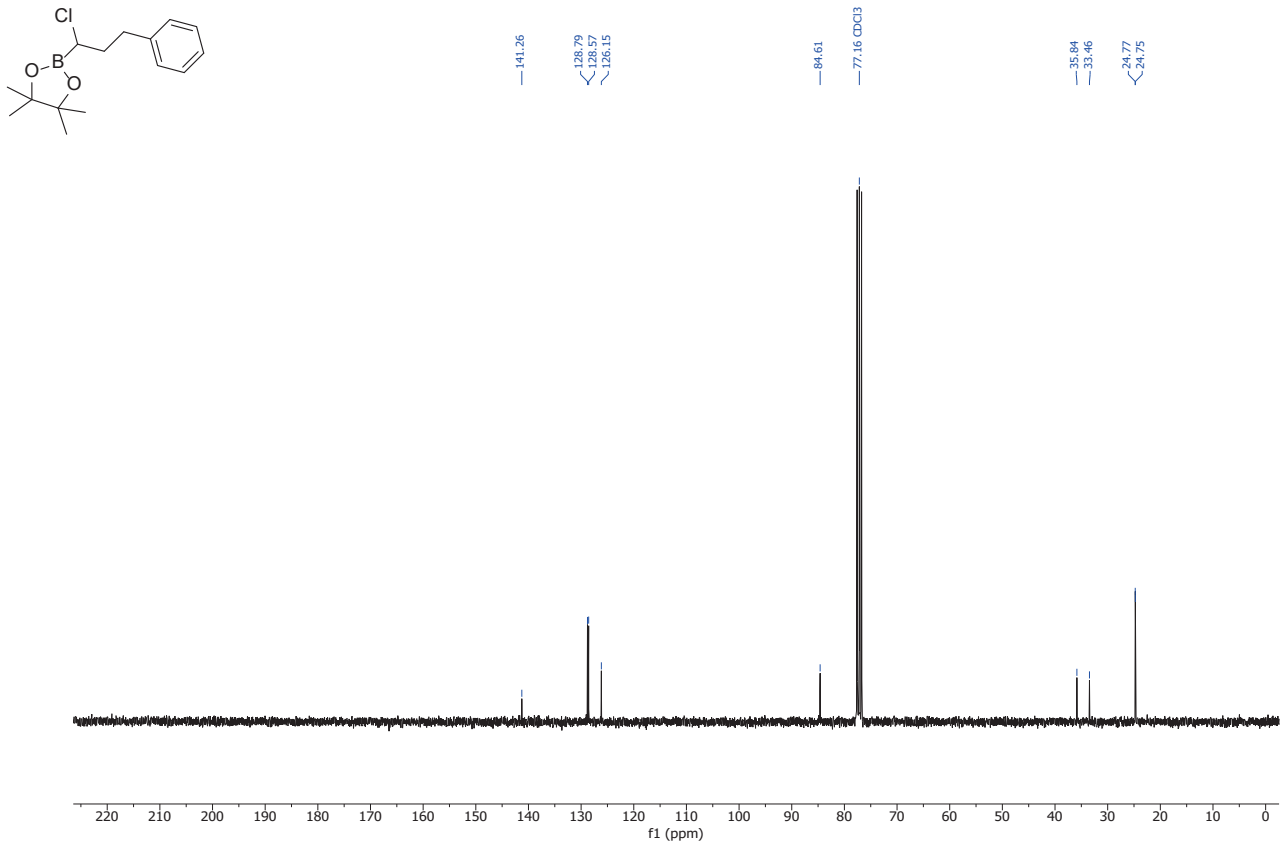
^{11}B NMR (96 MHz, $CDCl_3$)



2-(1-chloro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (69) ^{1}H NMR (300 MHz, $CDCl_3$)

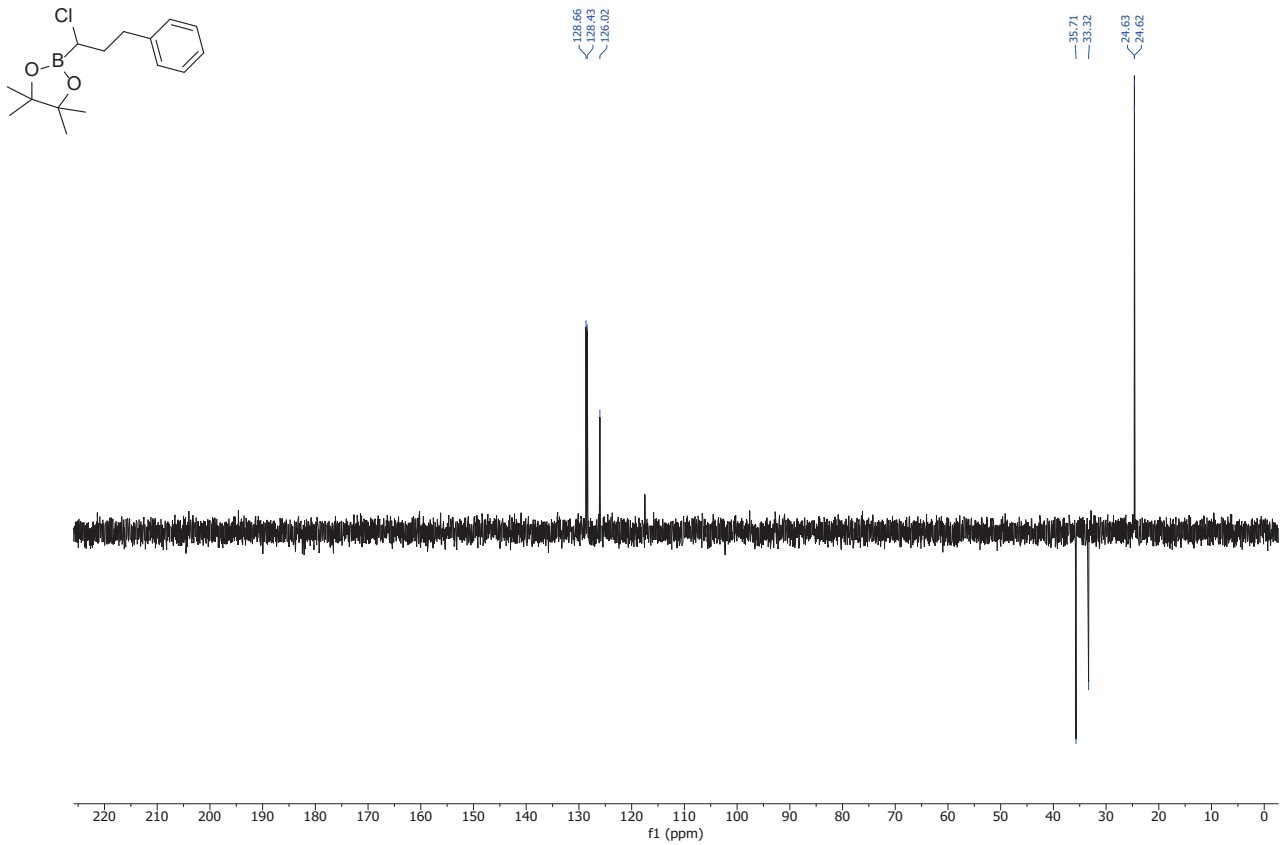


2-(1-chloro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (69) ^{13}C NMR (75 MHz, $CDCl_3$)



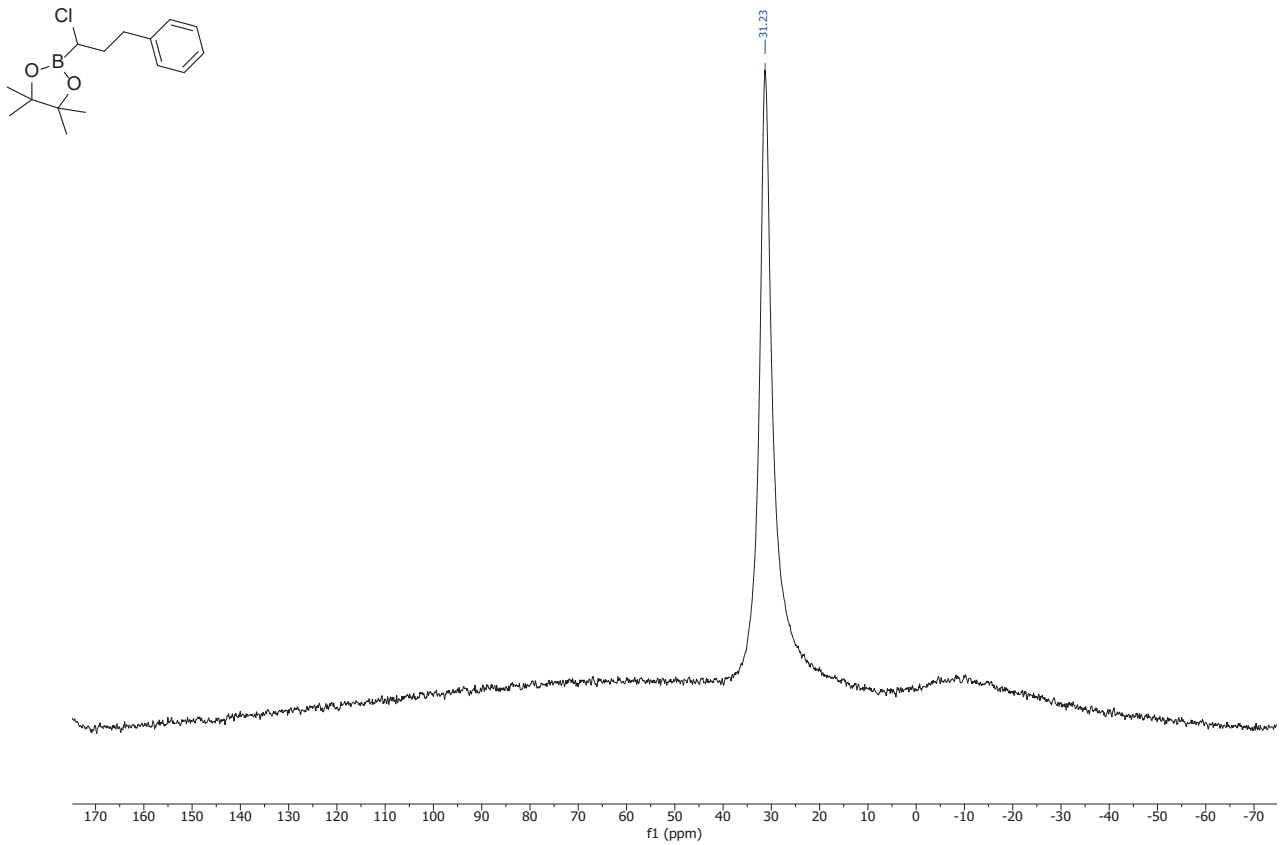
2-(1-chloro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (69)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



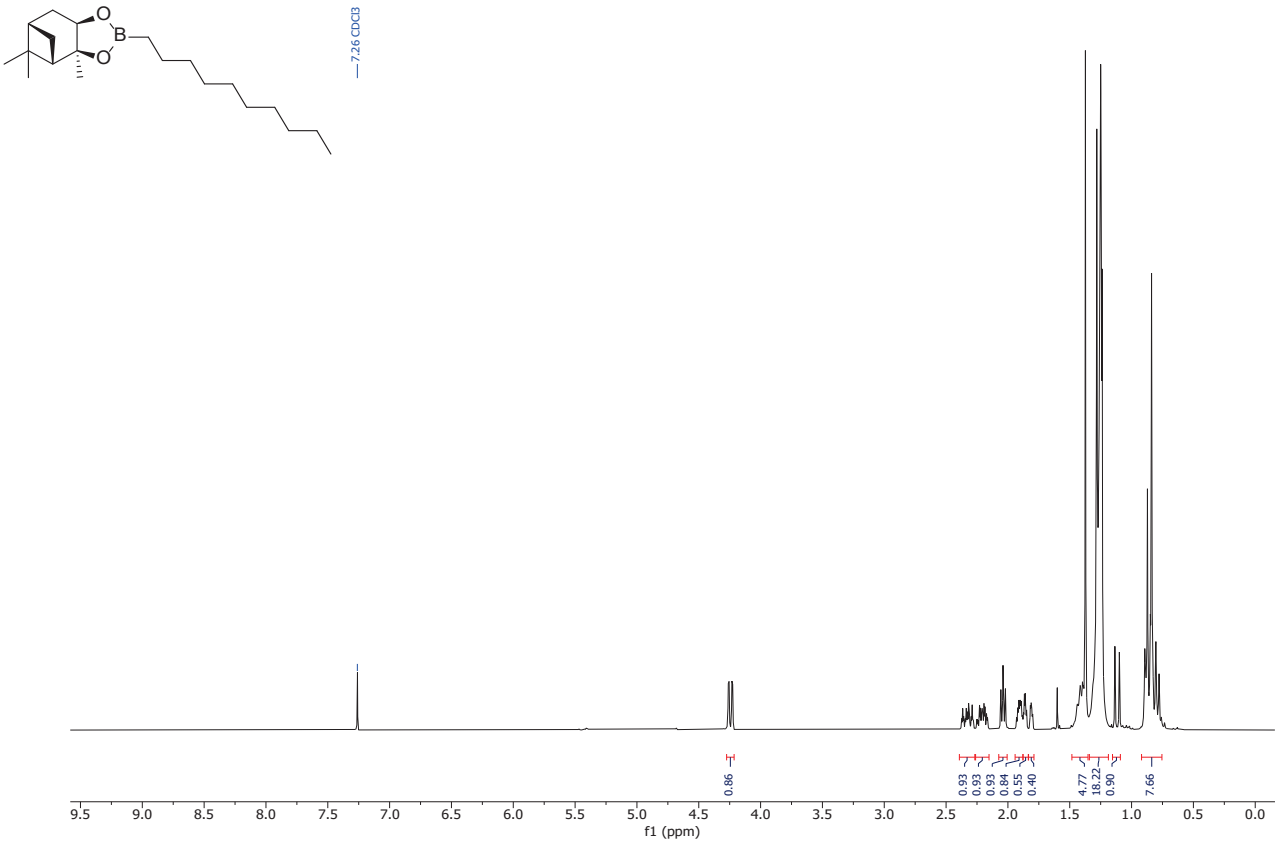
2-(1-chloro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (69)

^{11}B NMR (96 MHz, $CDCl_3$)



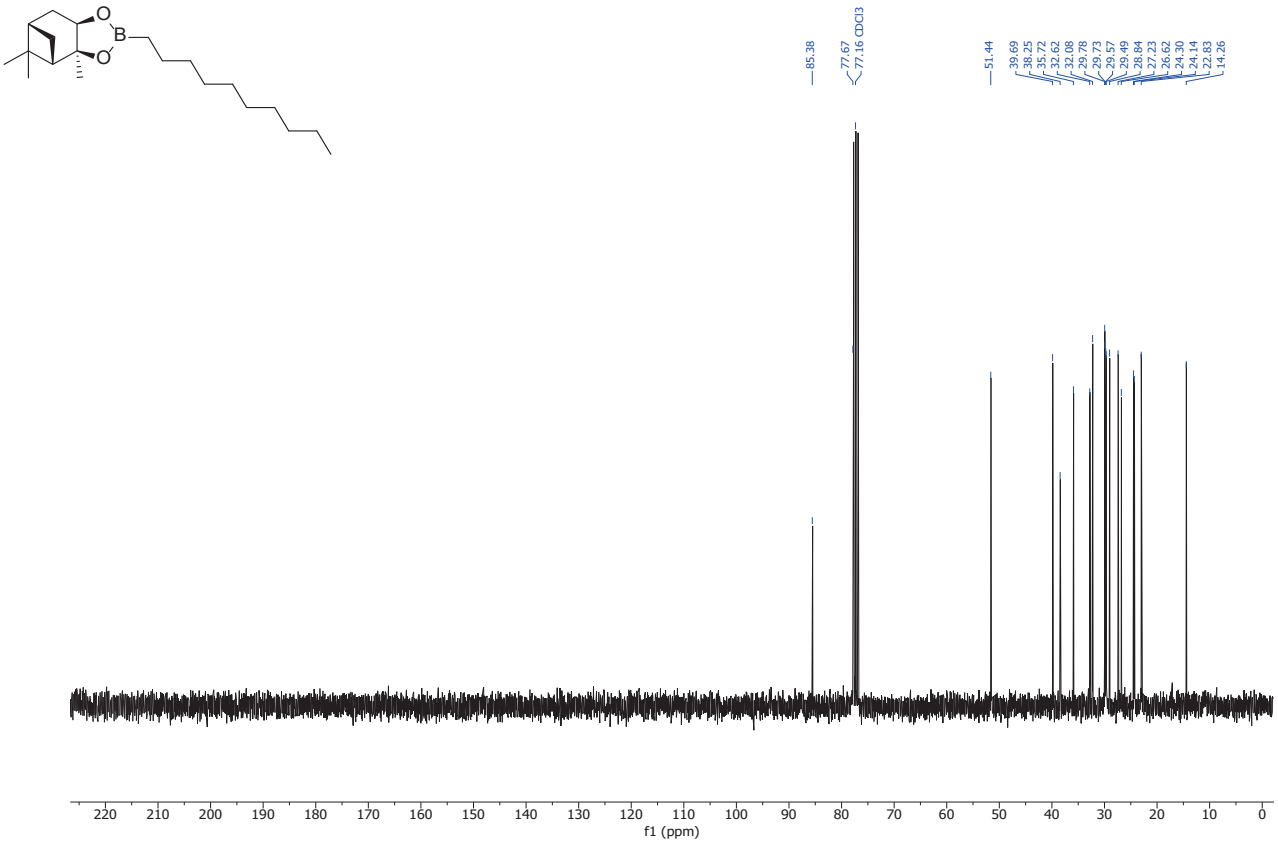
(3aS,4S,6S,7aR)-2-decyl-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2] dioxaborole (70)

^{1}H NMR (300 MHz, $CDCl_3$)



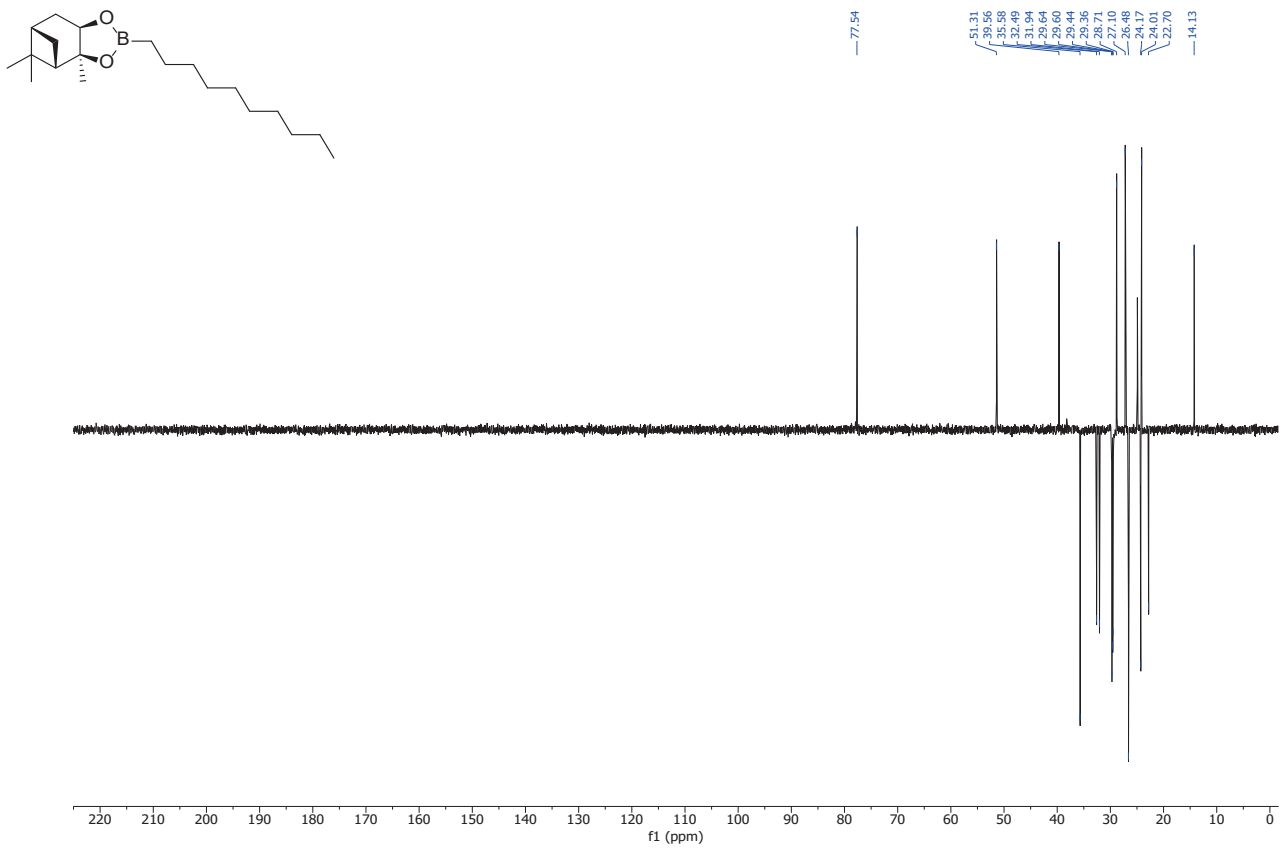
(3aS,4S,6S,7aR)-2-decyl-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2] dioxaborole (70)

^{13}C NMR (75 MHz, $CDCl_3$)



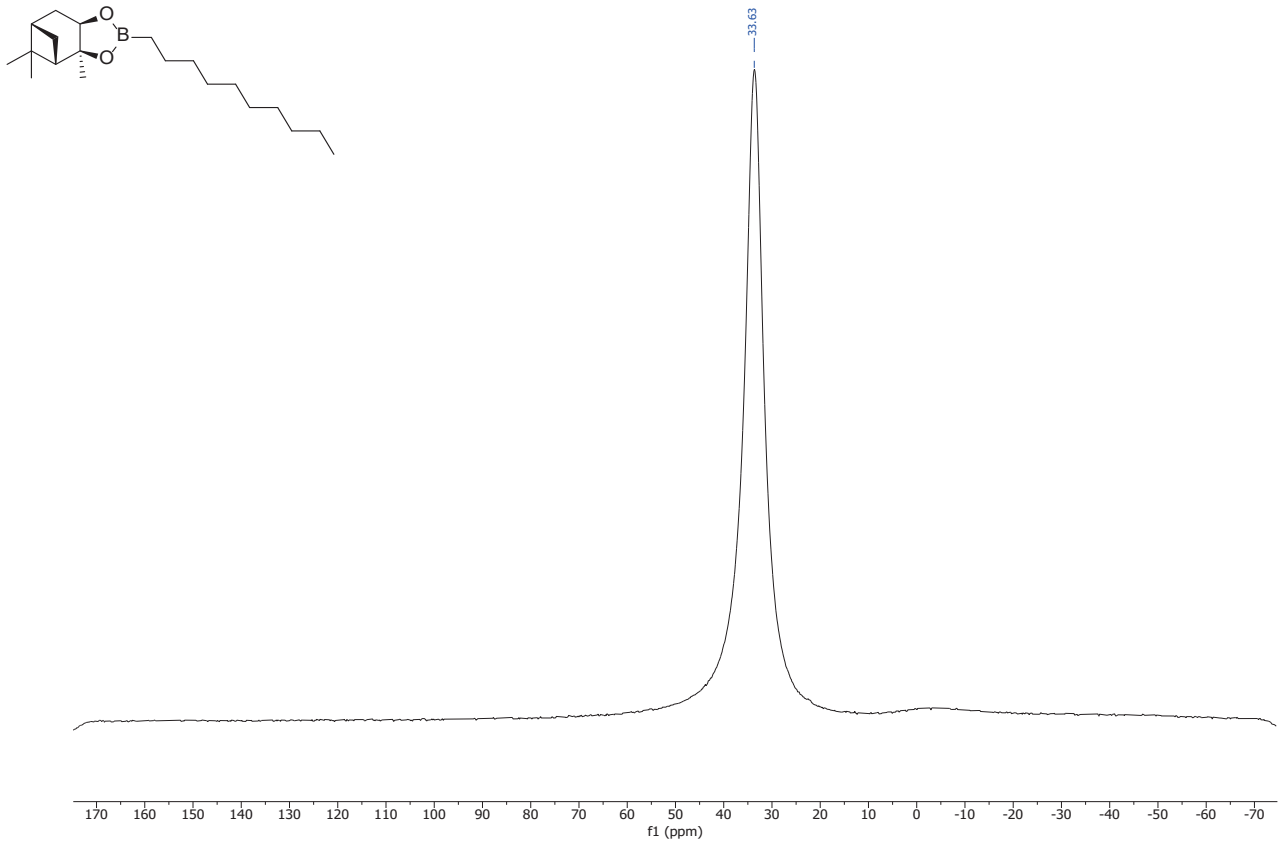
(3aS,4S,6S,7aR)-2-decyl-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2] dioxaborole (70)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



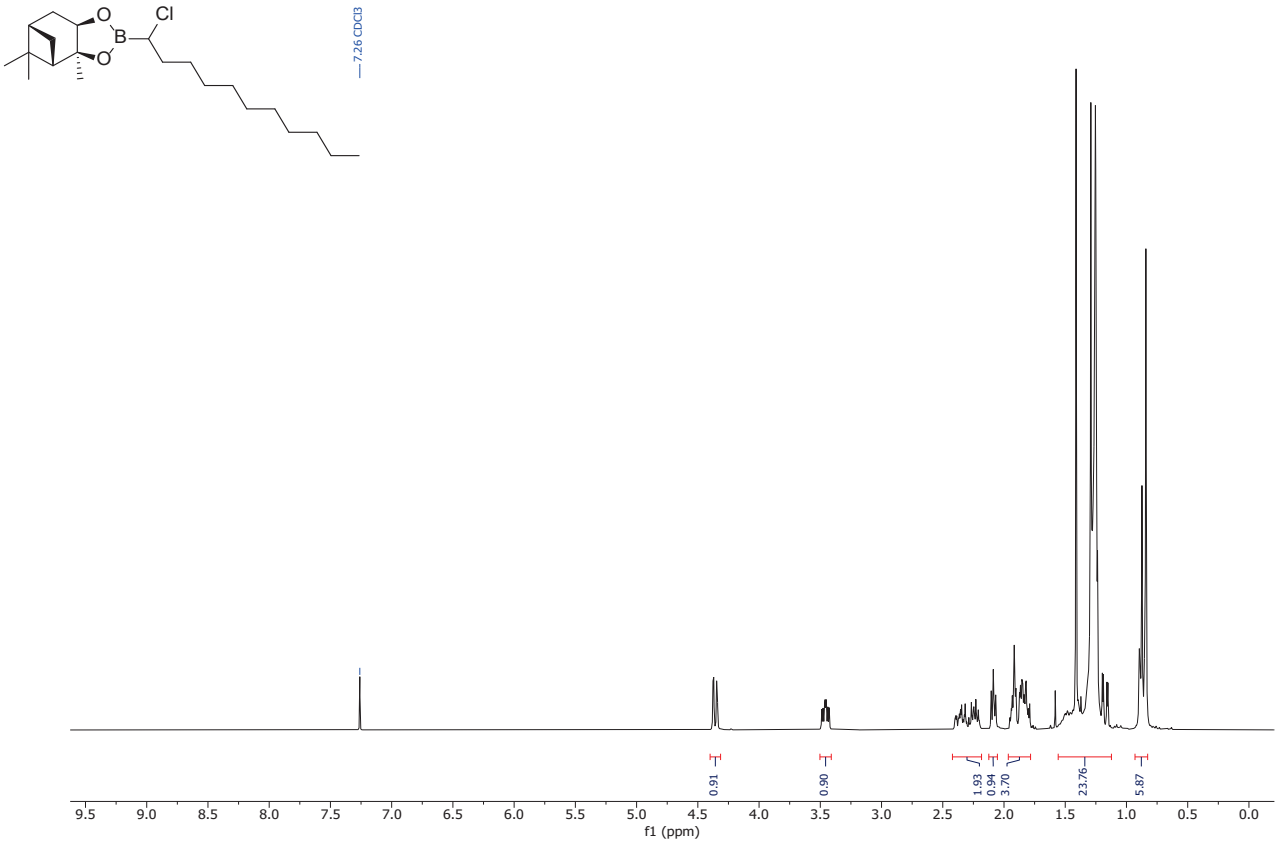
(3aS,4S,6S,7aR)-2-decyl-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2] dioxaborole (70)

^{11}B NMR (96 MHz, $CDCl_3$)



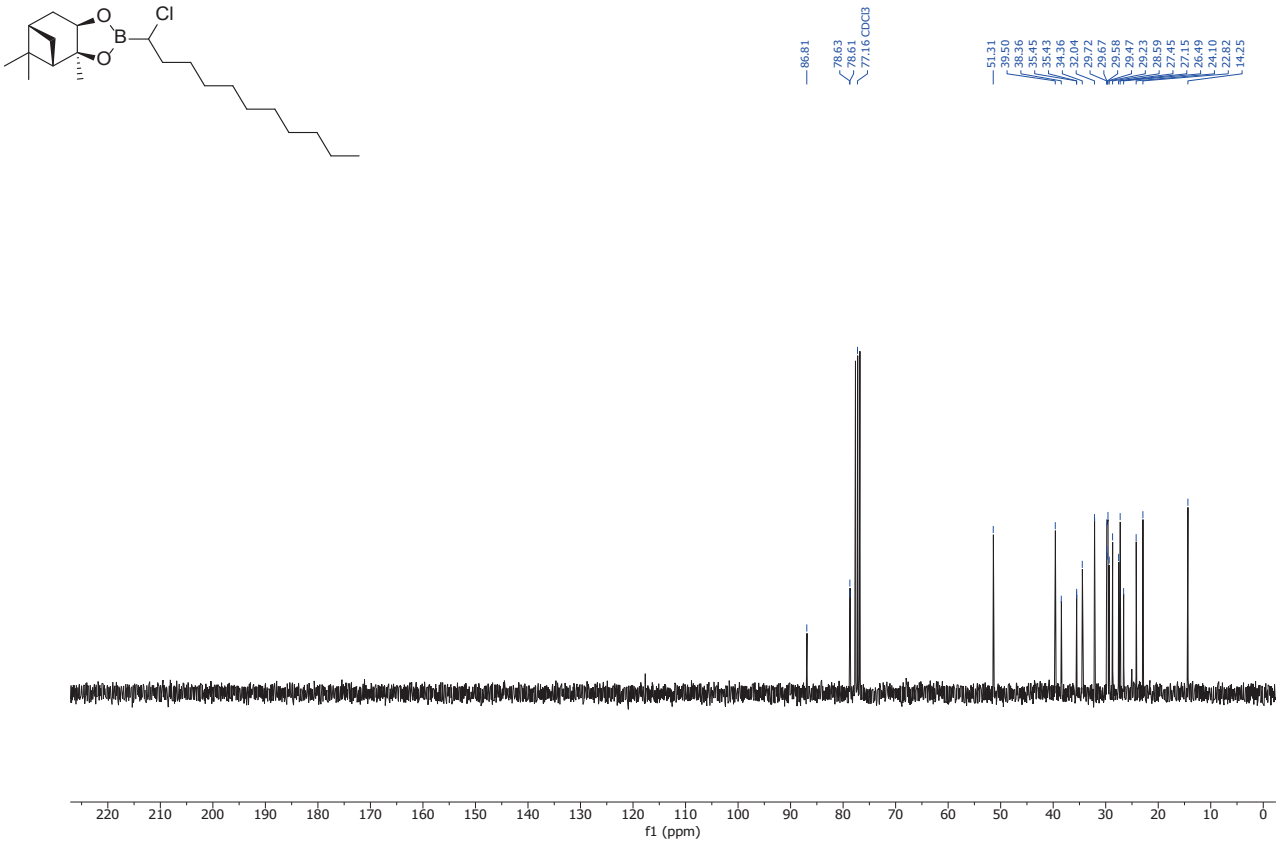
(3aS,4S,6S,7aR)-2-(1-chloroundecyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (1R/S-45)

^{1}H NMR (300 MHz, $CDCl_3$)



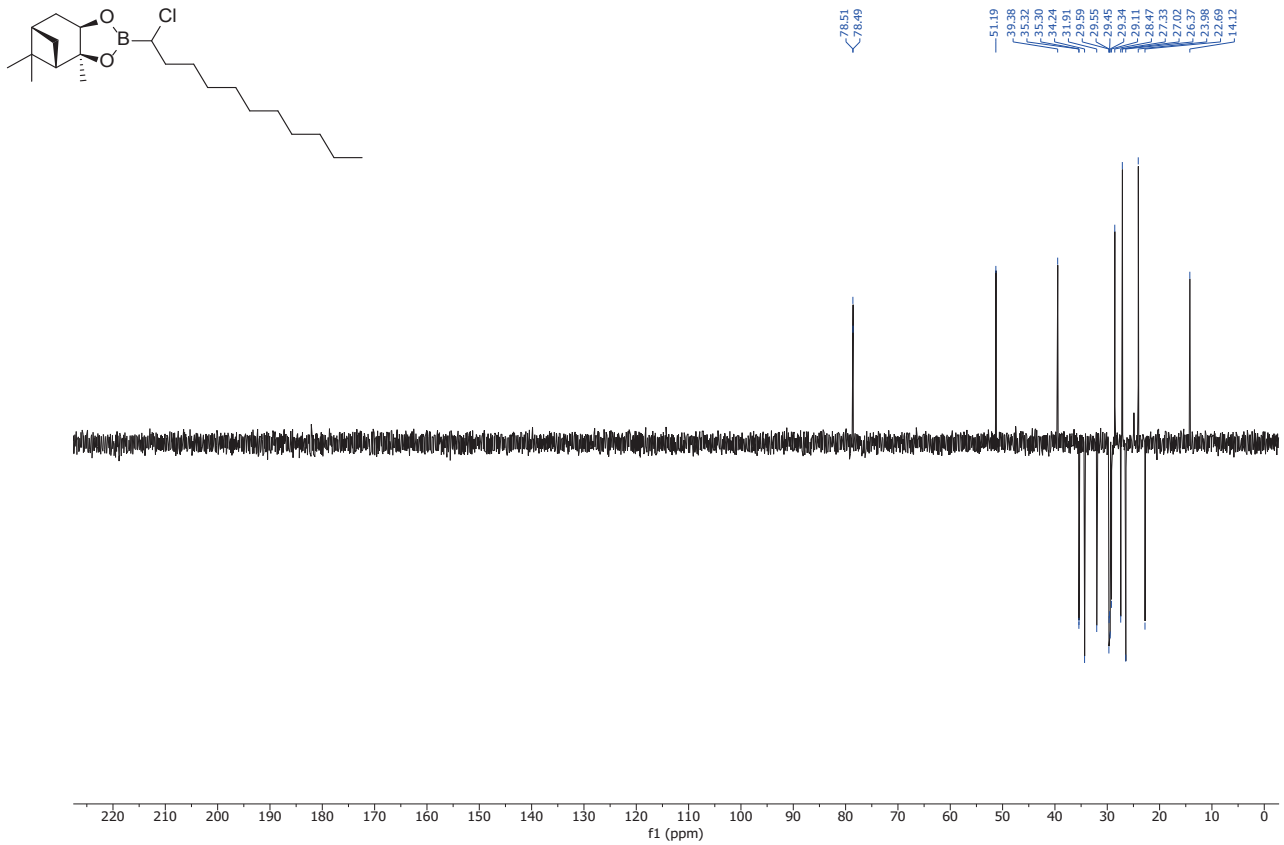
(3aS,4S,6S,7aR)-2-(1-chloroundecyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (1R/S-45)

^{13}C NMR (75 MHz, $CDCl_3$)



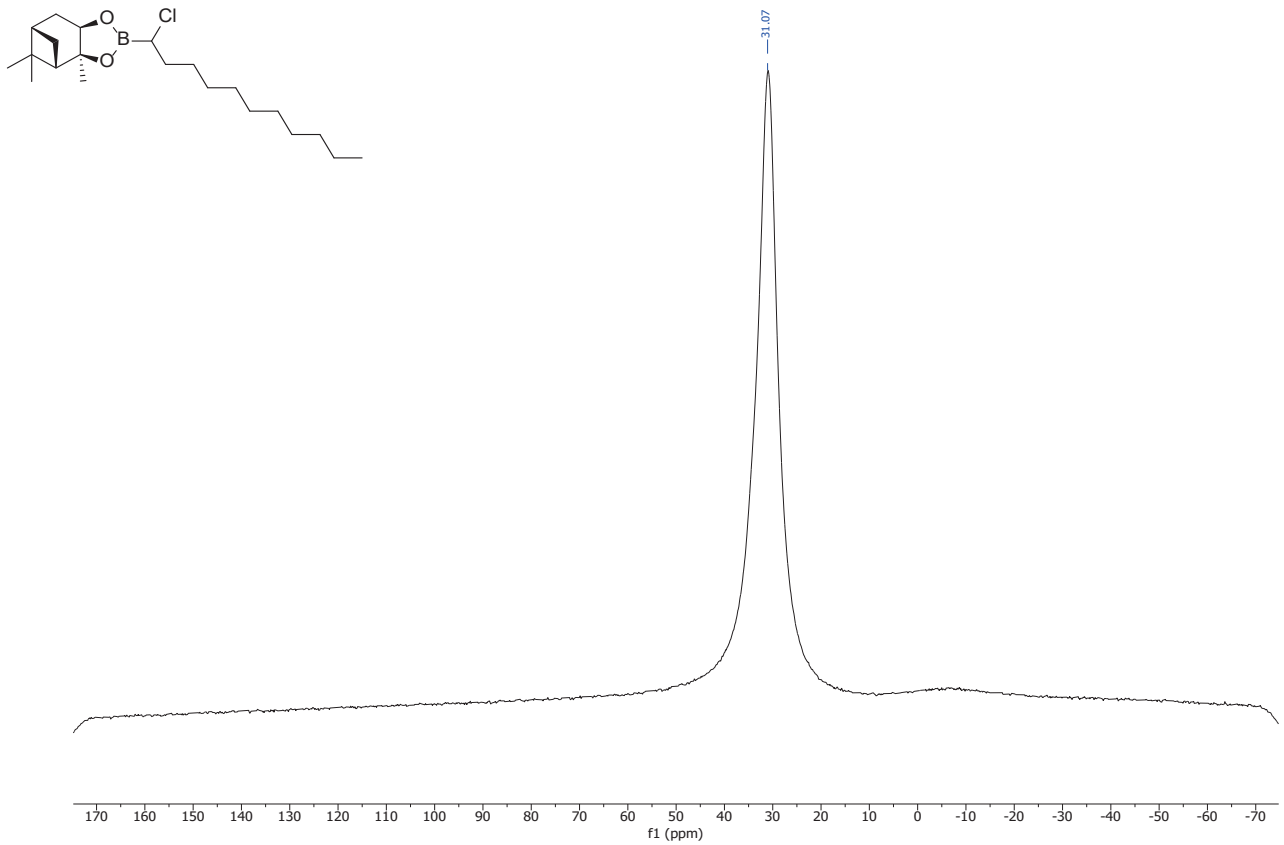
(3aS,4S,6S,7aR)-2-(1-chloroundecyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (1R/S-45)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



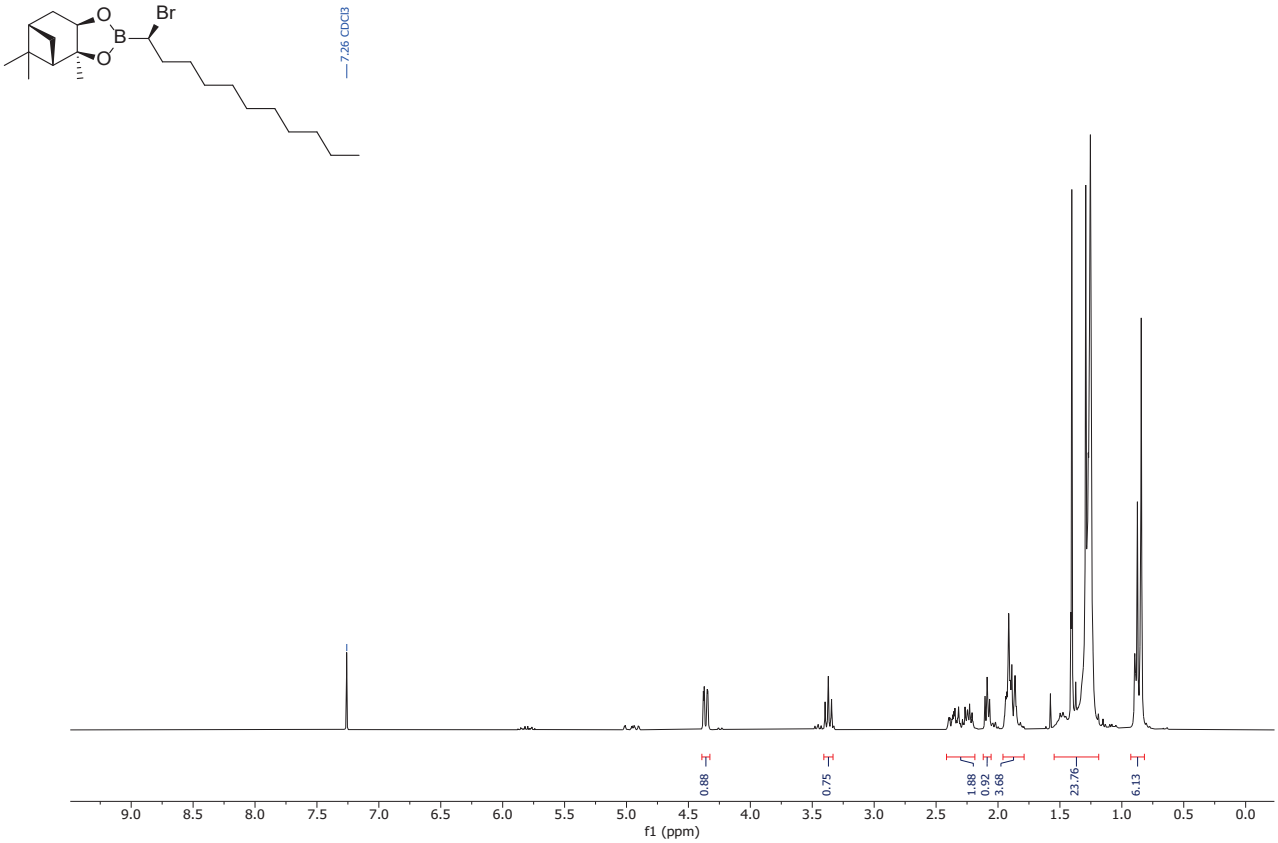
(3aS,4S,6S,7aR)-2-(1-chloroundecyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (1R/S-45)

^{11}B NMR (96 MHz, $CDCl_3$)



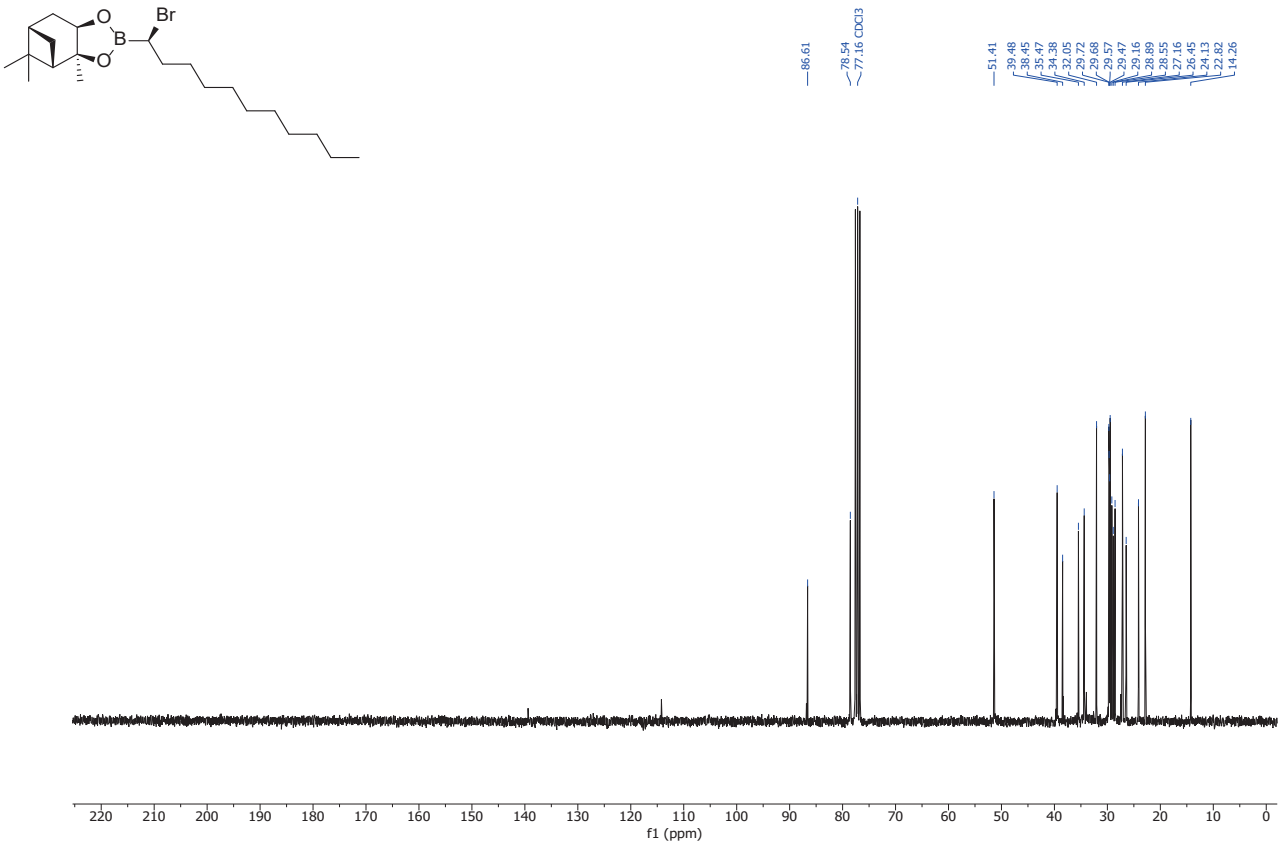
(3aS,4S,6S,7aR)-2-((R)-1-bromoundecyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (1*R*-46)

^{1}H NMR (300 MHz, $CDCl_3$)



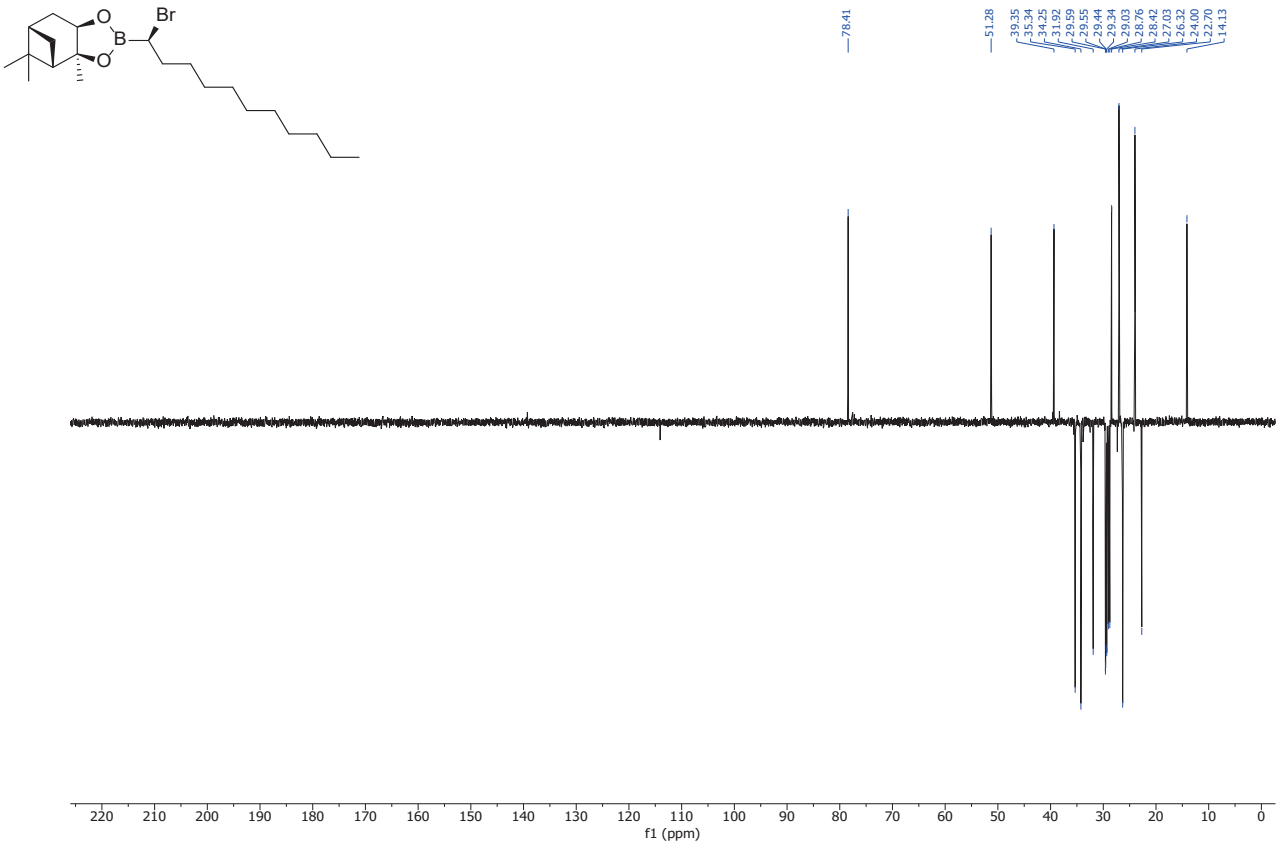
(3aS,4S,6S,7aR)-2-((R)-1-bromoundecyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (1*R*-46)

^{13}C NMR (75 MHz, $CDCl_3$)



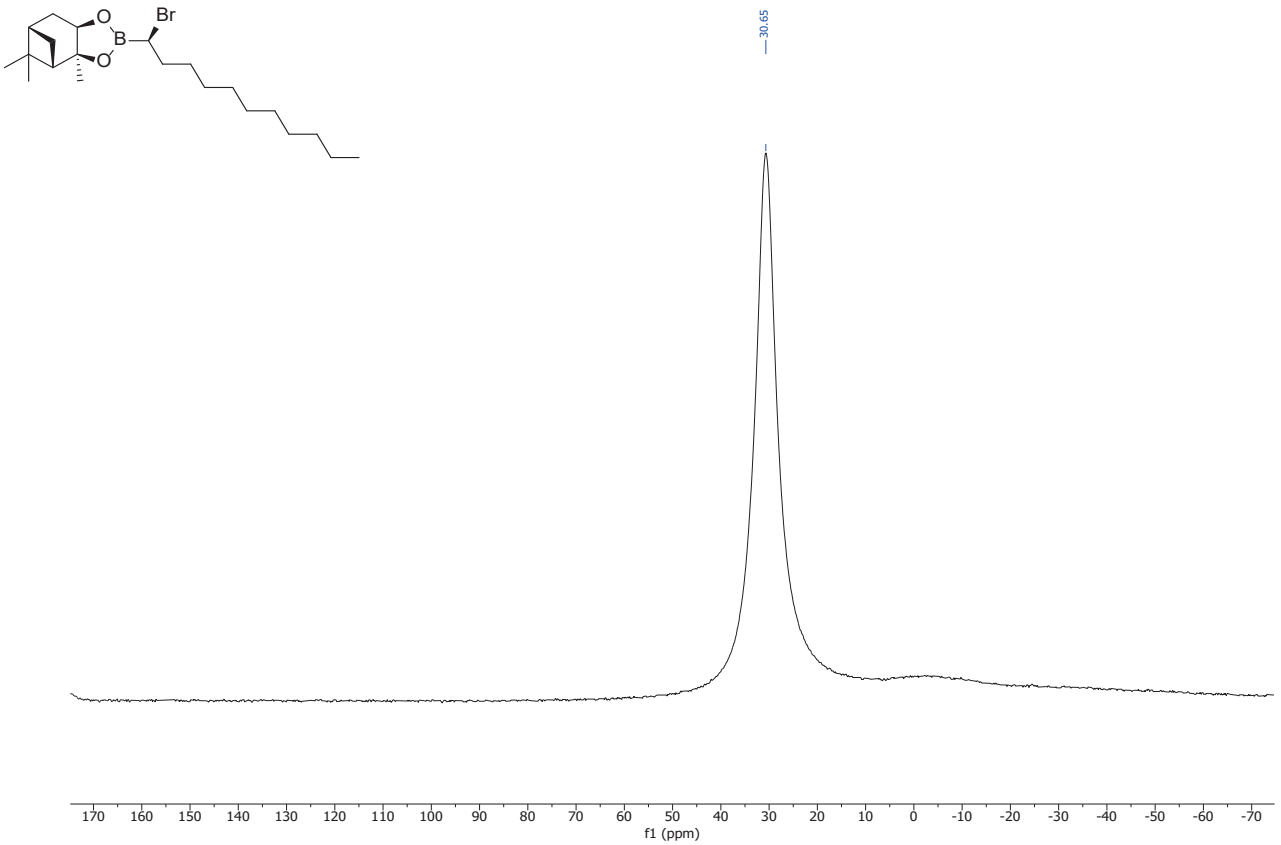
(3aS,4S,6S,7aR)-2-((R)-1-bromoundecyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (1*R*-46)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



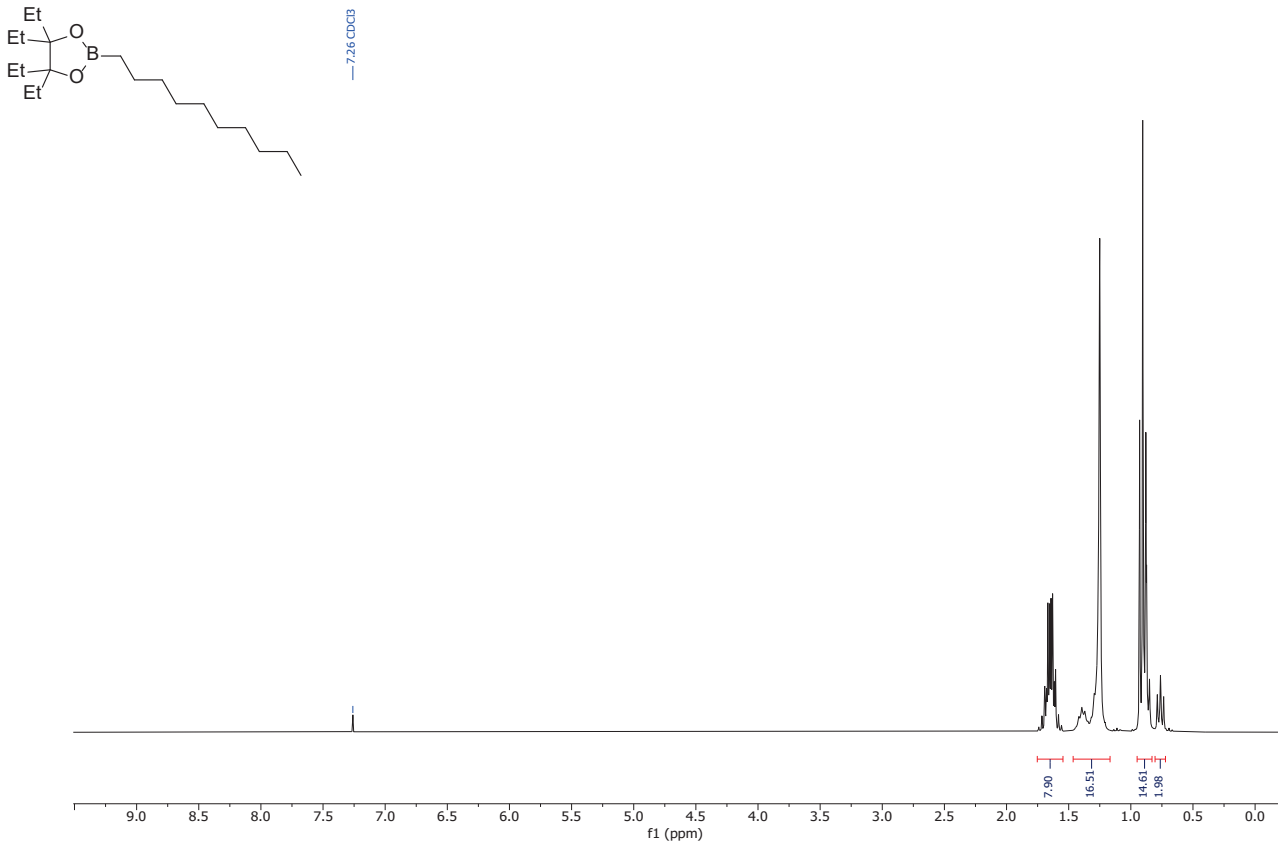
(3aS,4S,6S,7aR)-2-((R)-1-bromoundecyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (1*R*-46)

^{11}B NMR (96 MHz, $CDCl_3$)



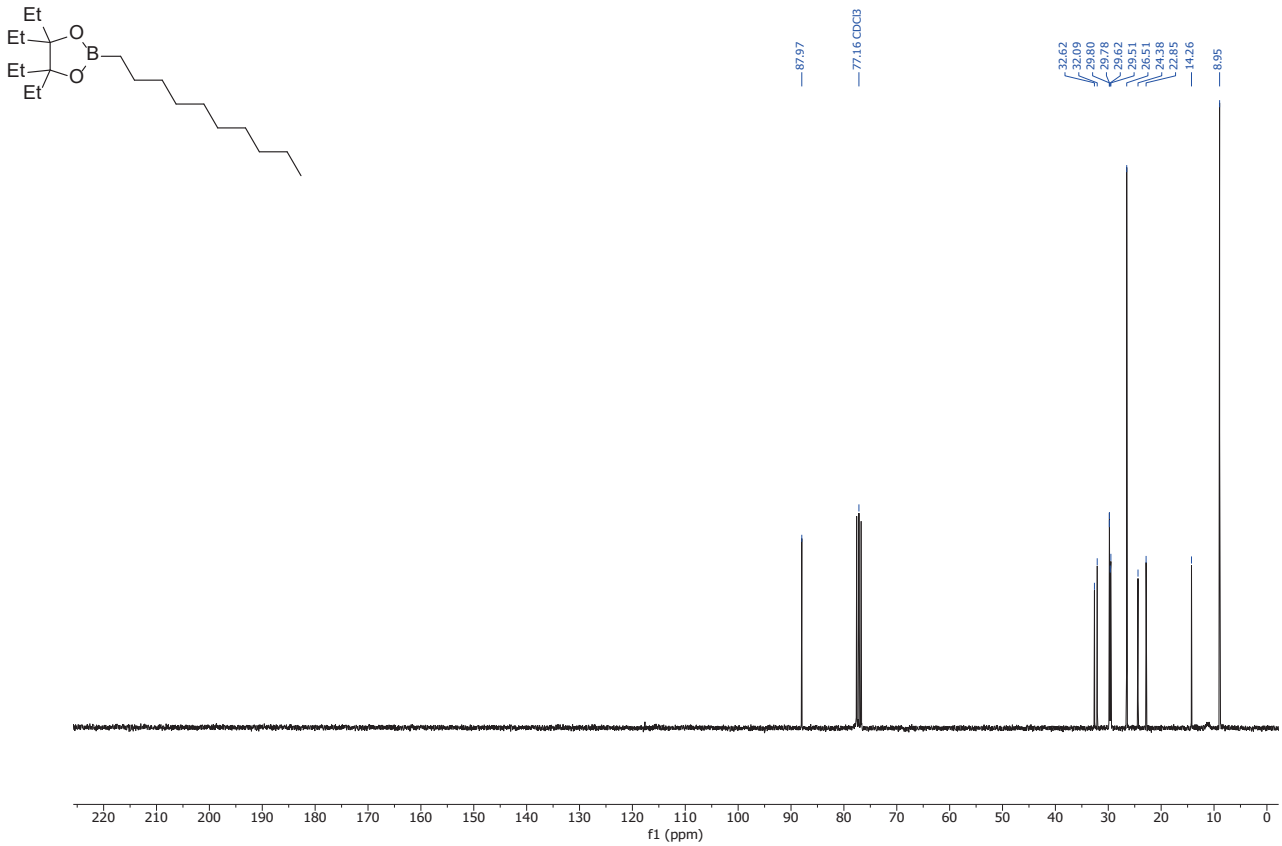
2-decyl-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (71)

^{1}H NMR (300 MHz, $CDCl_3$)



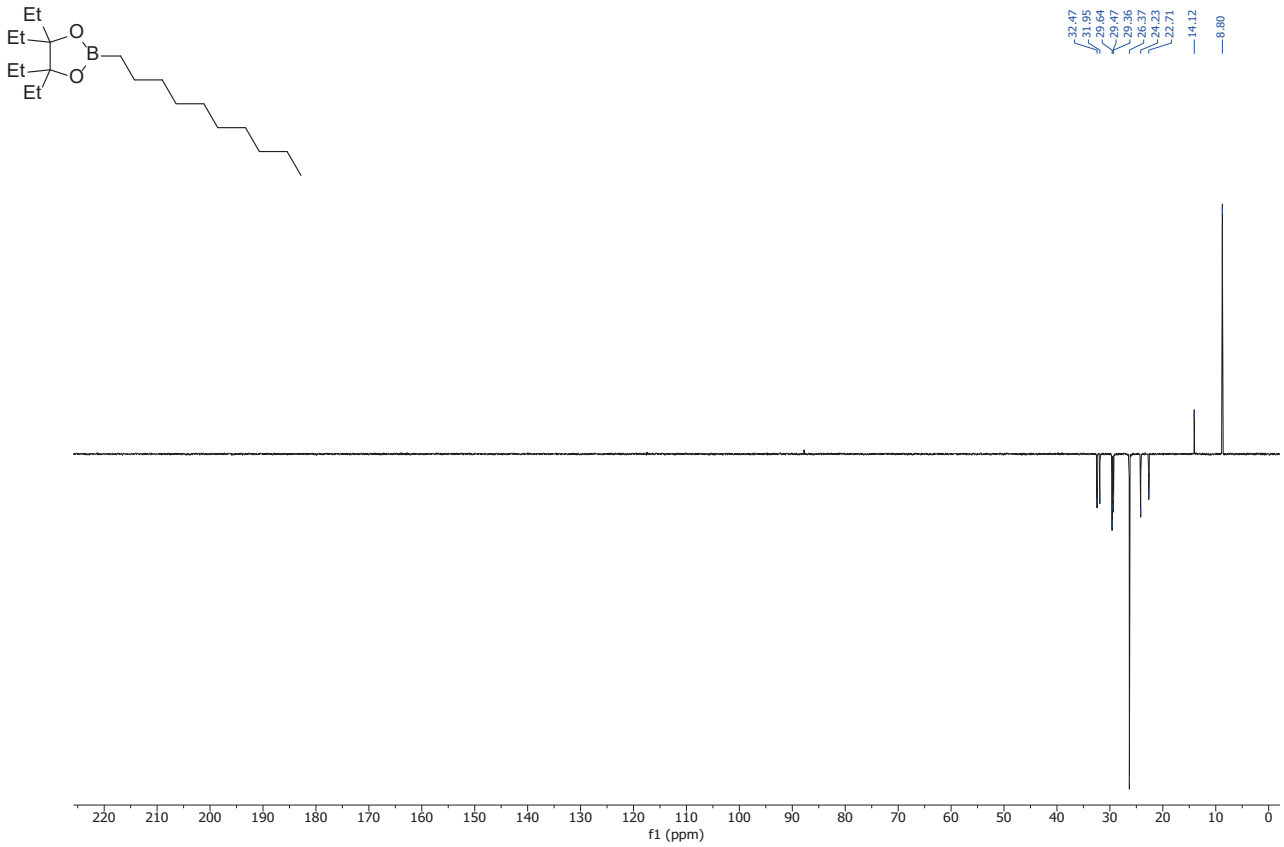
2-decyl-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (71)

^{13}C NMR (75 MHz, $CDCl_3$)



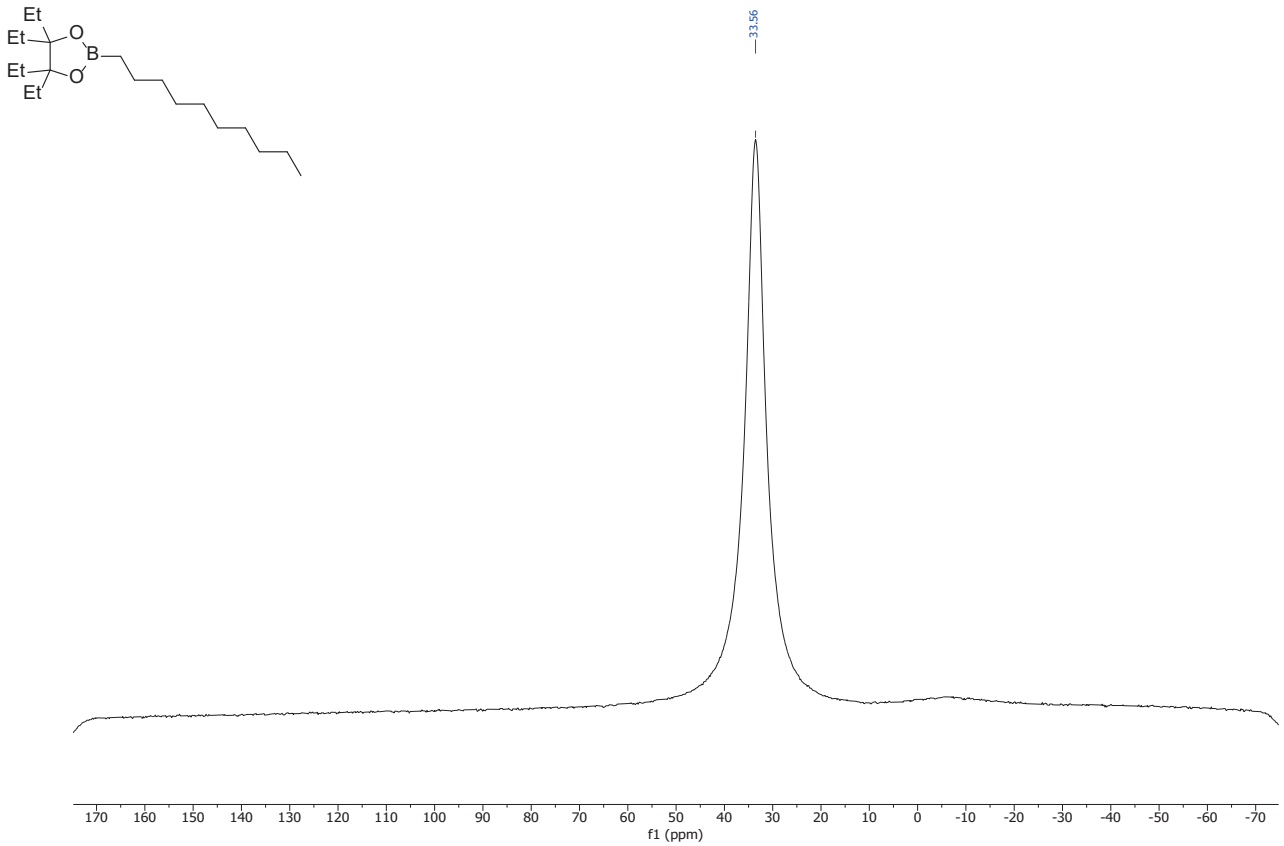
2-decyl-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (71)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



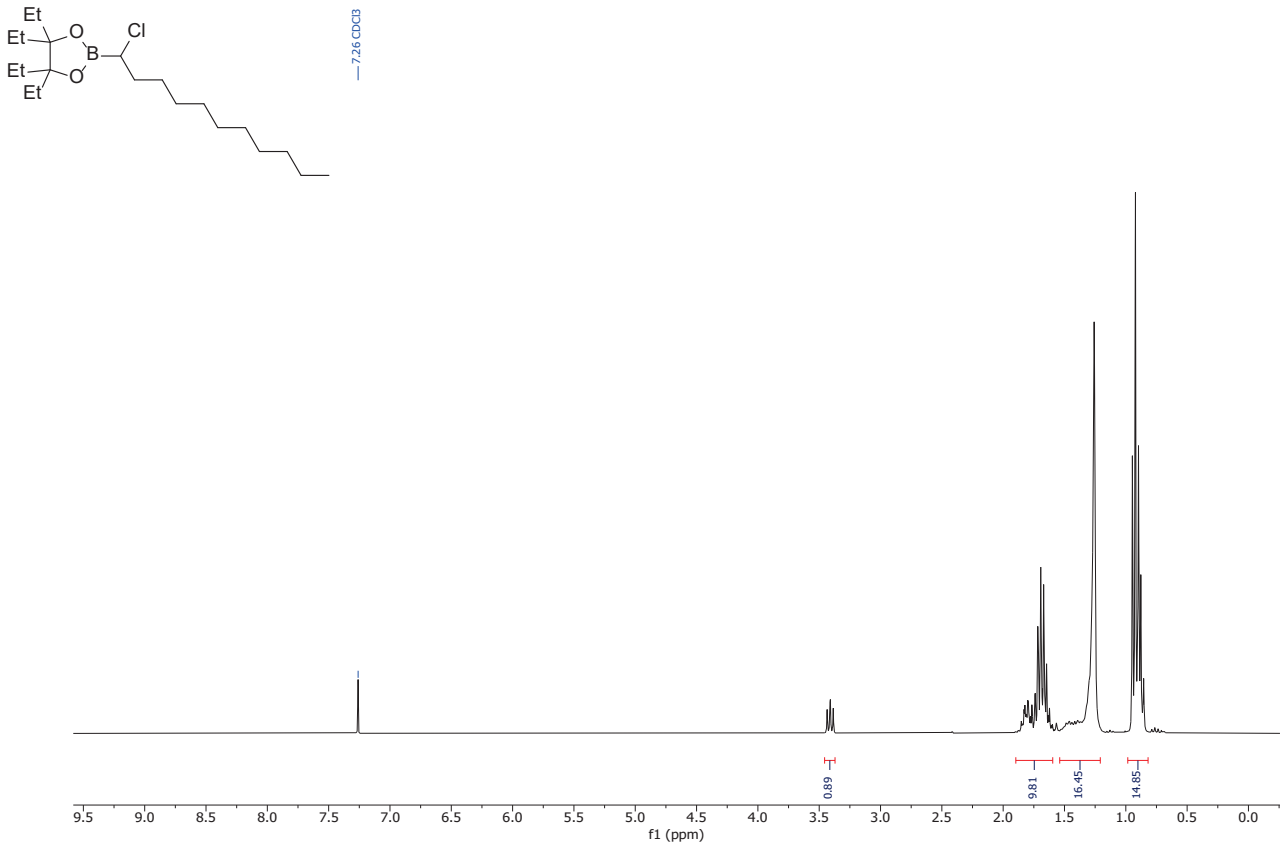
2-decyl-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (71)

^{11}B NMR (96 MHz, $CDCl_3$)



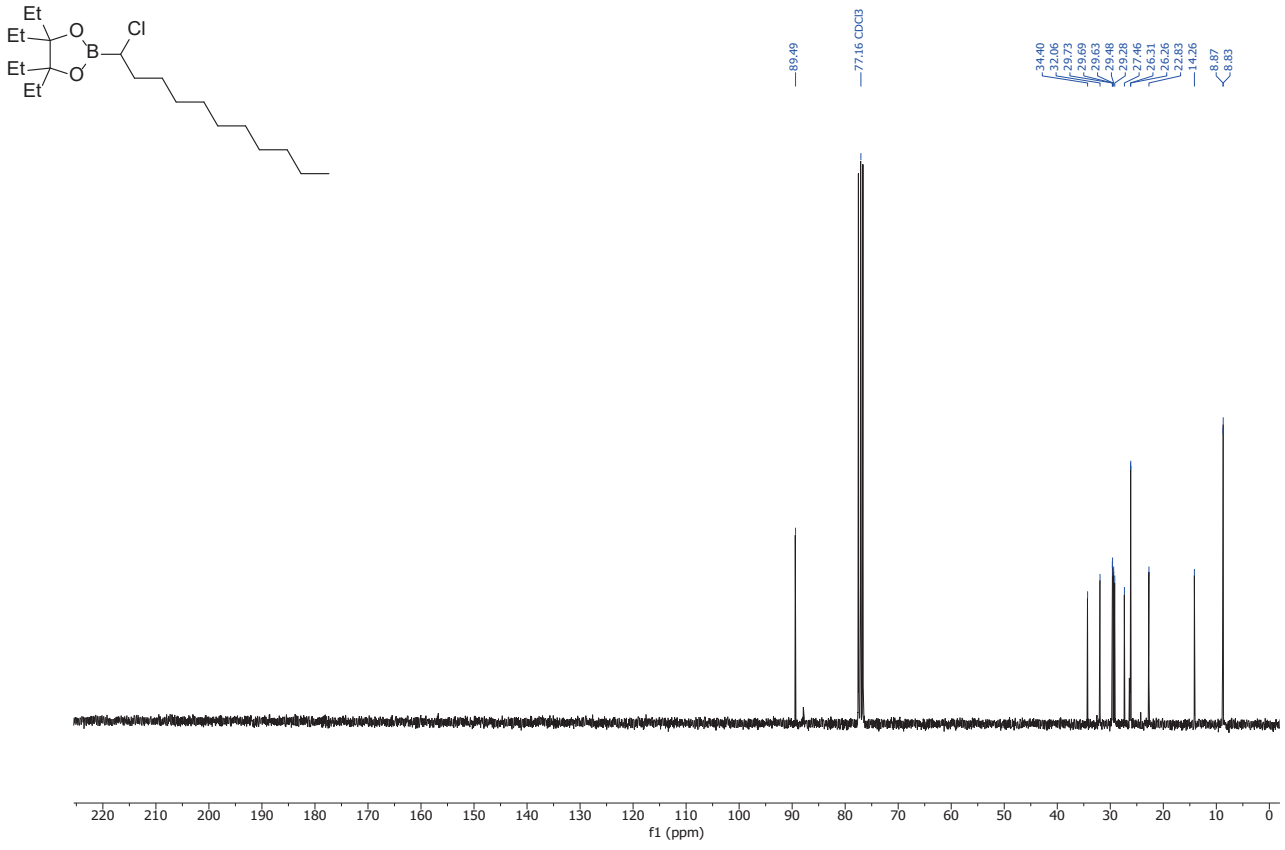
2-(1-chloroundecyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (72)

^{1}H NMR (300 MHz, $CDCl_3$)



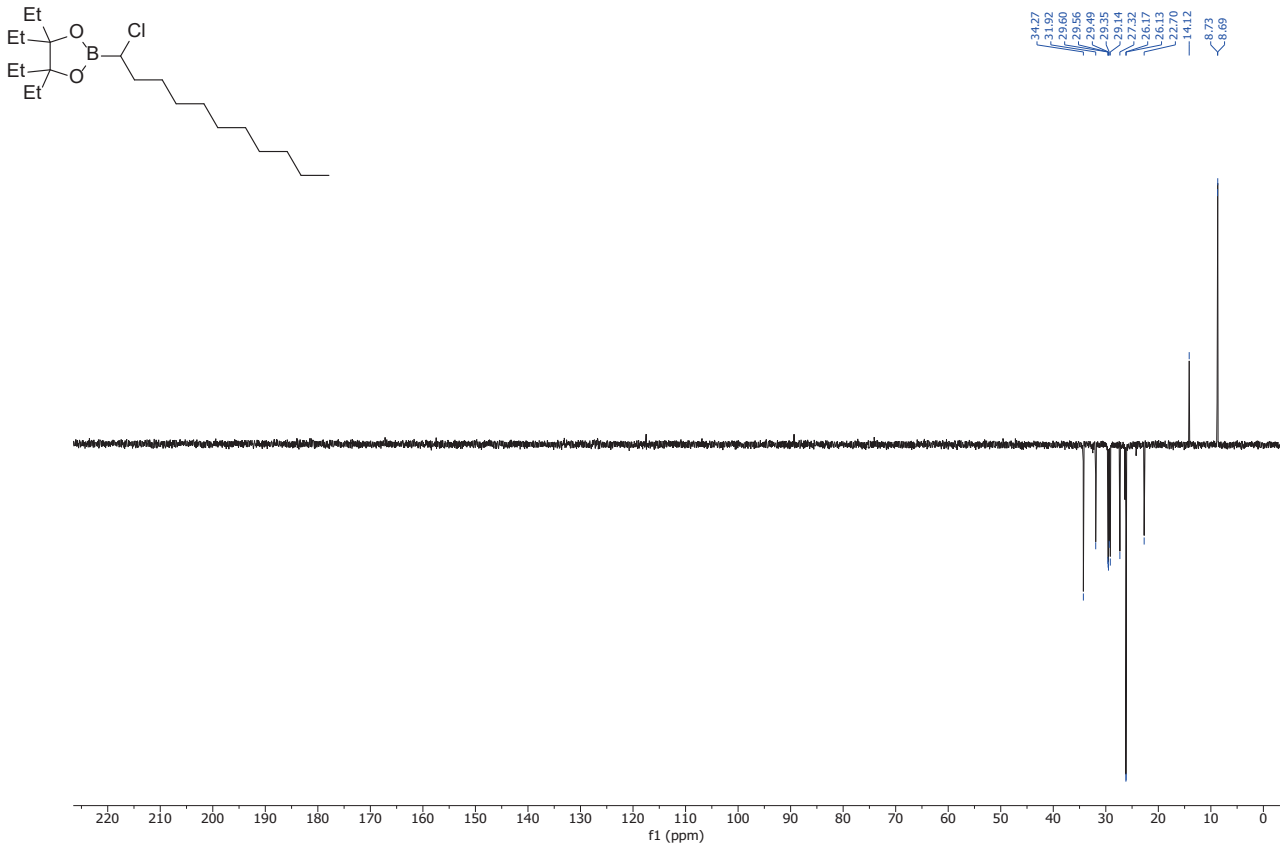
2-(1-chloroundecyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (72)

^{13}C NMR (75 MHz, $CDCl_3$)



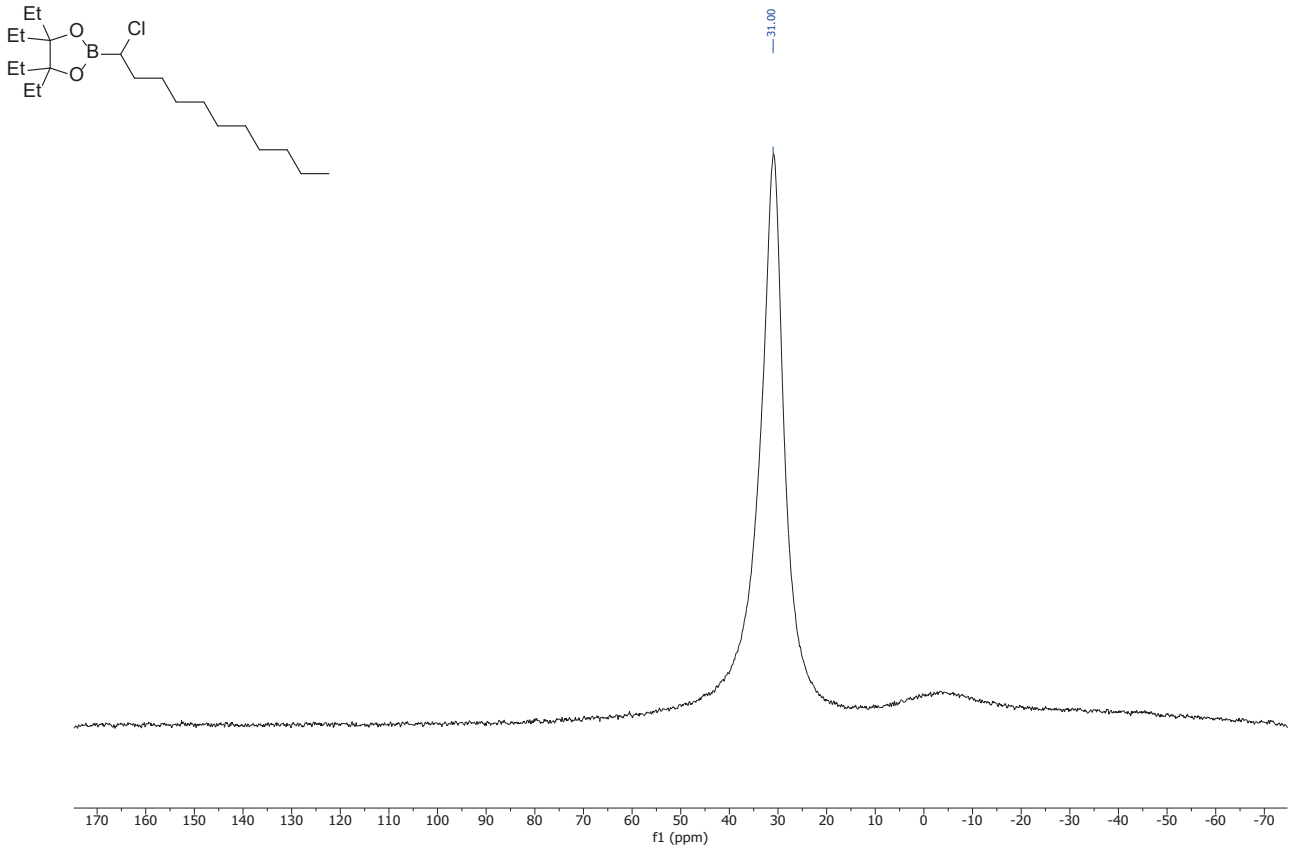
2-(1-chloroundecyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (72)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

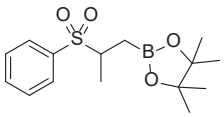


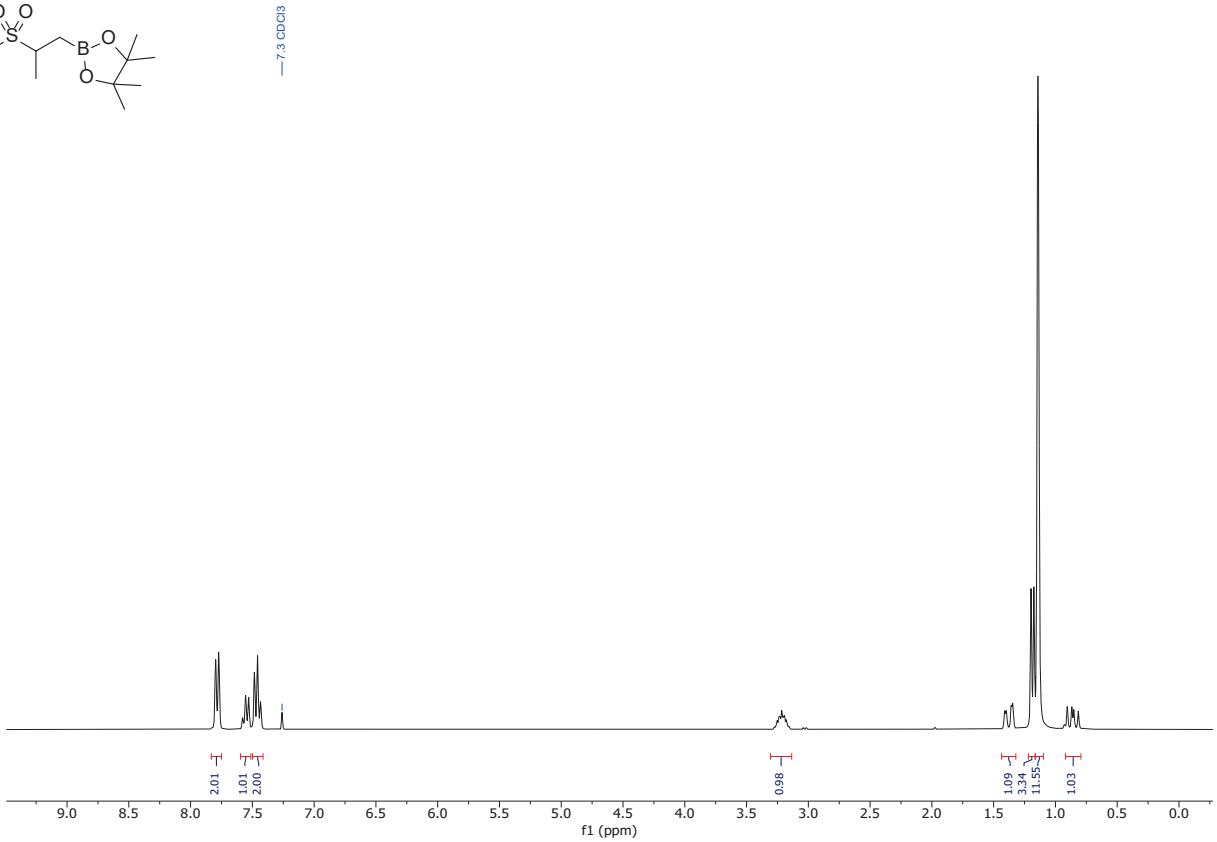
2-(1-chloroundecyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (72)

^{11}B NMR (96 MHz, $CDCl_3$)

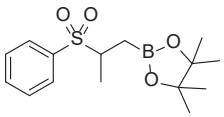


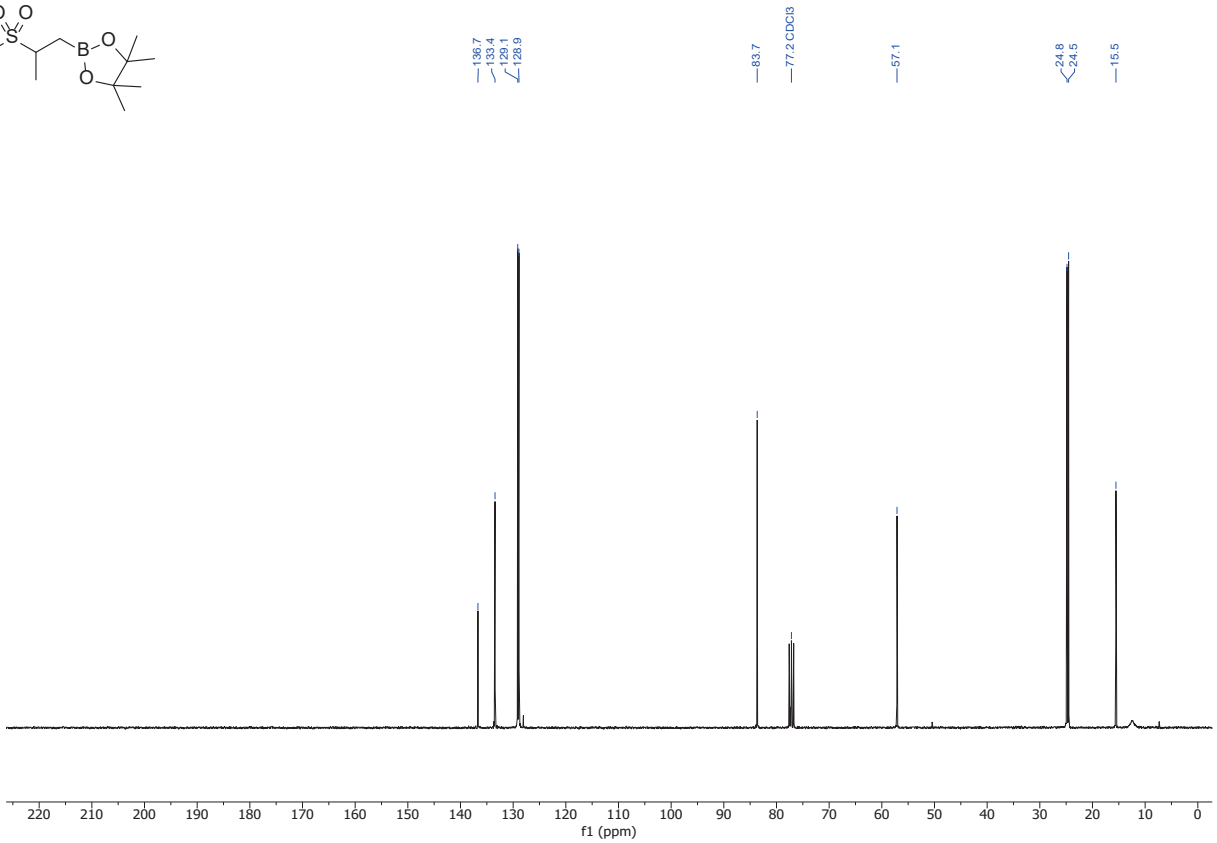
4,4,5,5-tetramethyl-2-(2-(phenylsulfonyl)propyl)-1,3,2-dioxaborolane (9) ^{1}H NMR (300 MHz, $CDCl_3$)





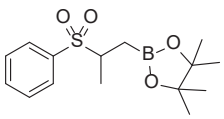
4,4,5,5-tetramethyl-2-(2-(phenylsulfonyl)propyl)-1,3,2-dioxaborolane (9) ^{13}C NMR (75 MHz, $CDCl_3$)

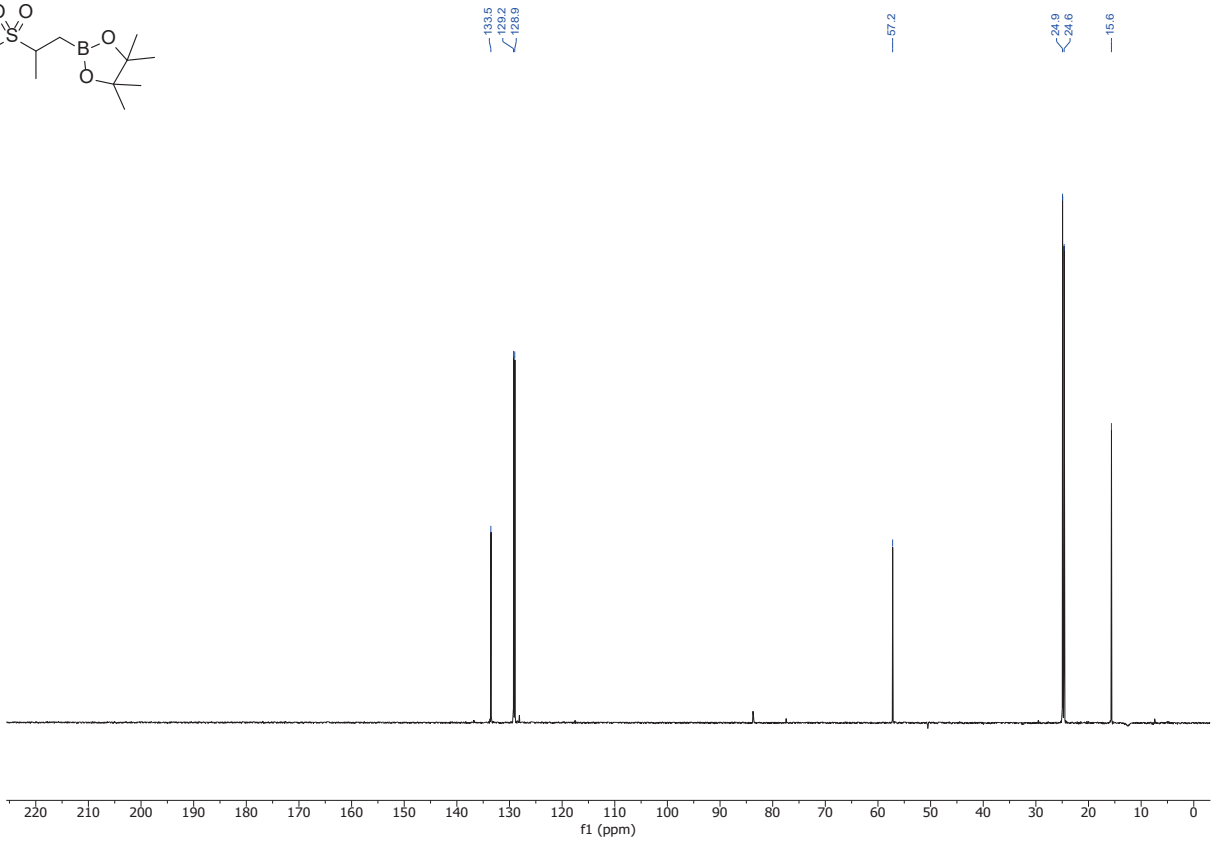




4,4,5,5-tetramethyl-2-(2-(phenylsulfonyl)propyl)-1,3,2-dioxaborolane (9)

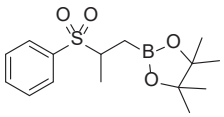
^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

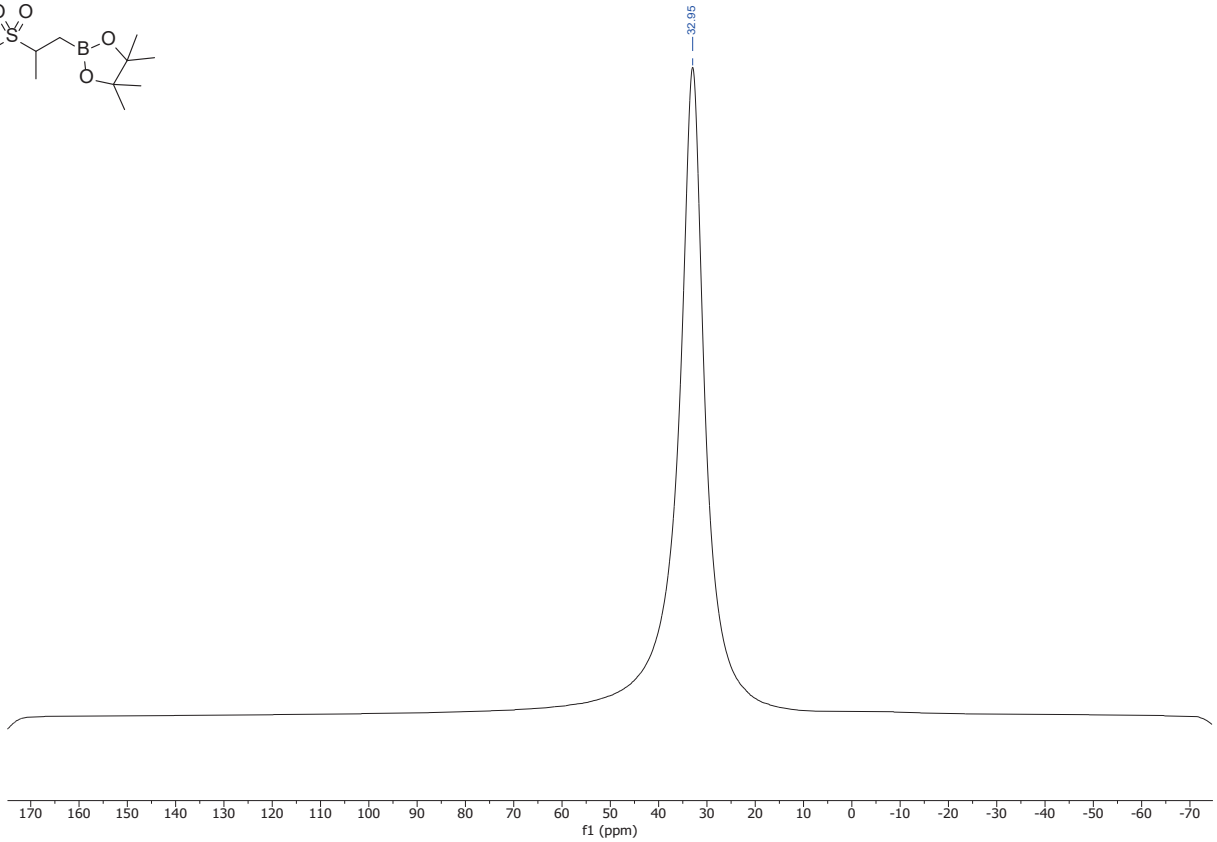




4,4,5,5-tetramethyl-2-(2-(phenylsulfonyl)propyl)-1,3,2-dioxaborolane (9)

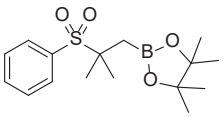
^{11}B NMR (96 MHz, $CDCl_3$)

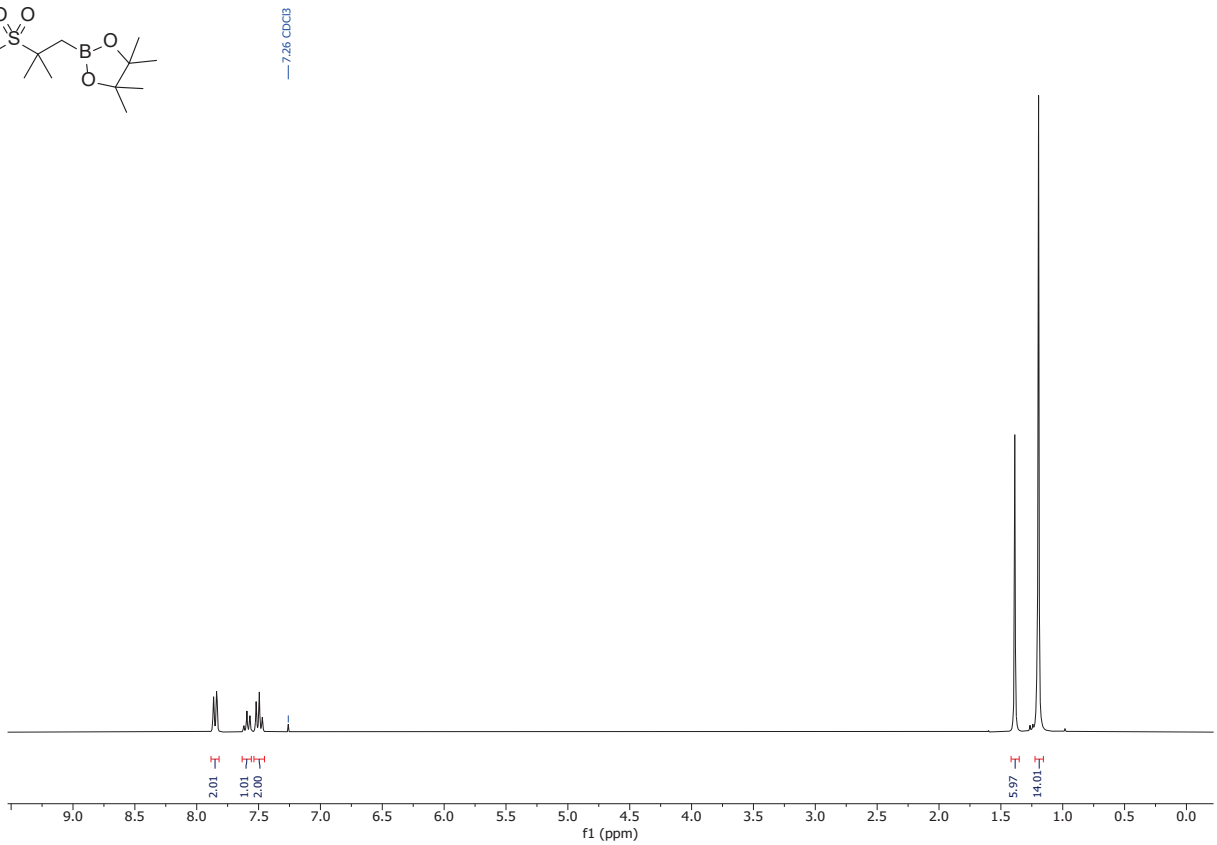




4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)propyl)-1,3,2-dioxaborolane (12)

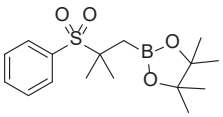
^{1}H NMR (300 MHz, $CDCl_3$)

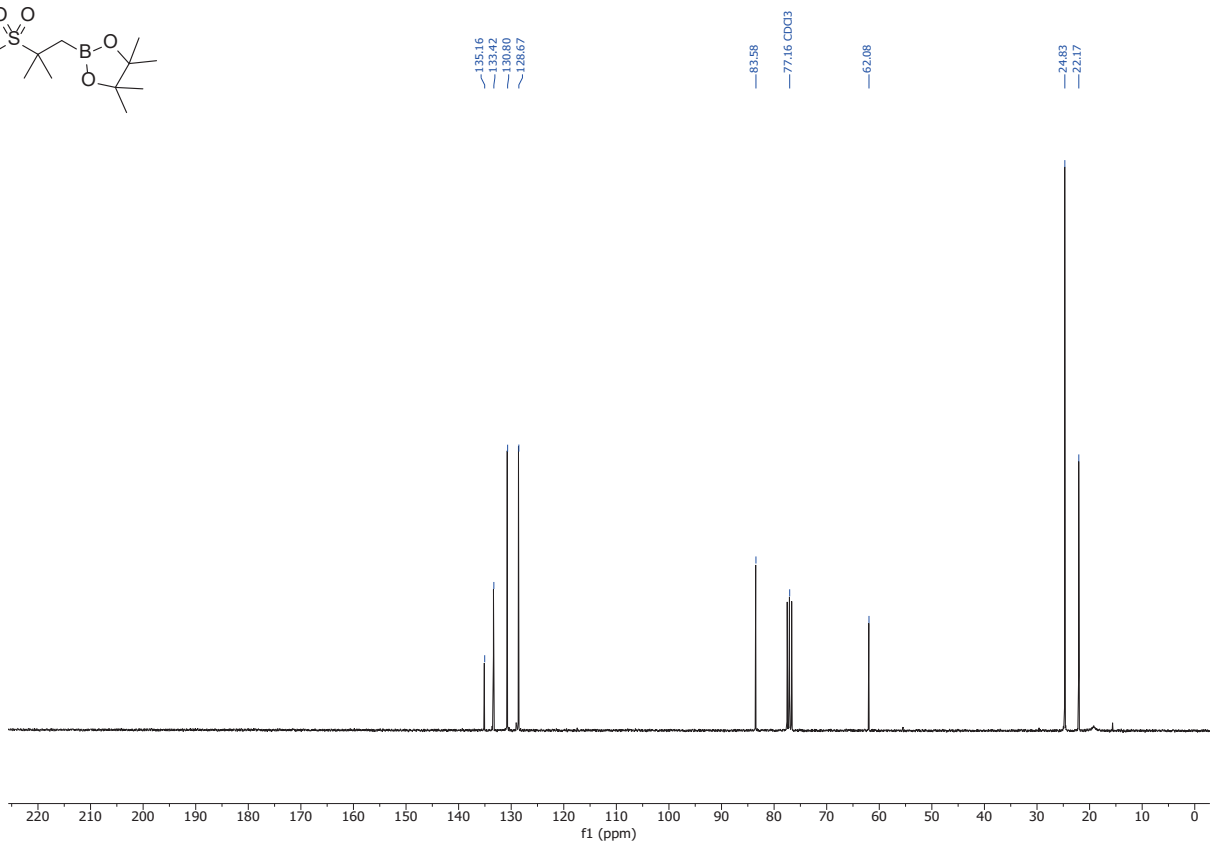




4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)propyl)-1,3,2-dioxaborolane (12)

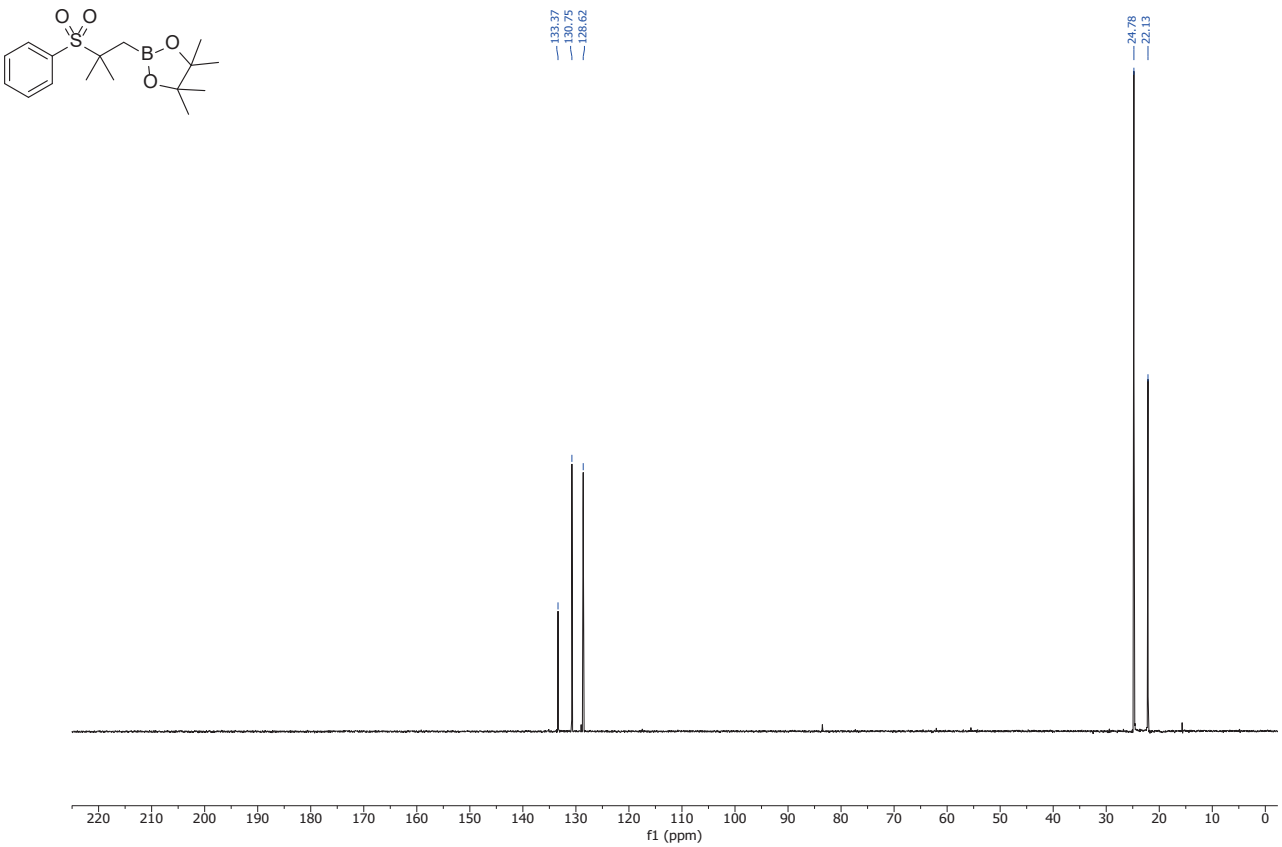
^{13}C NMR (75 MHz, $CDCl_3$)





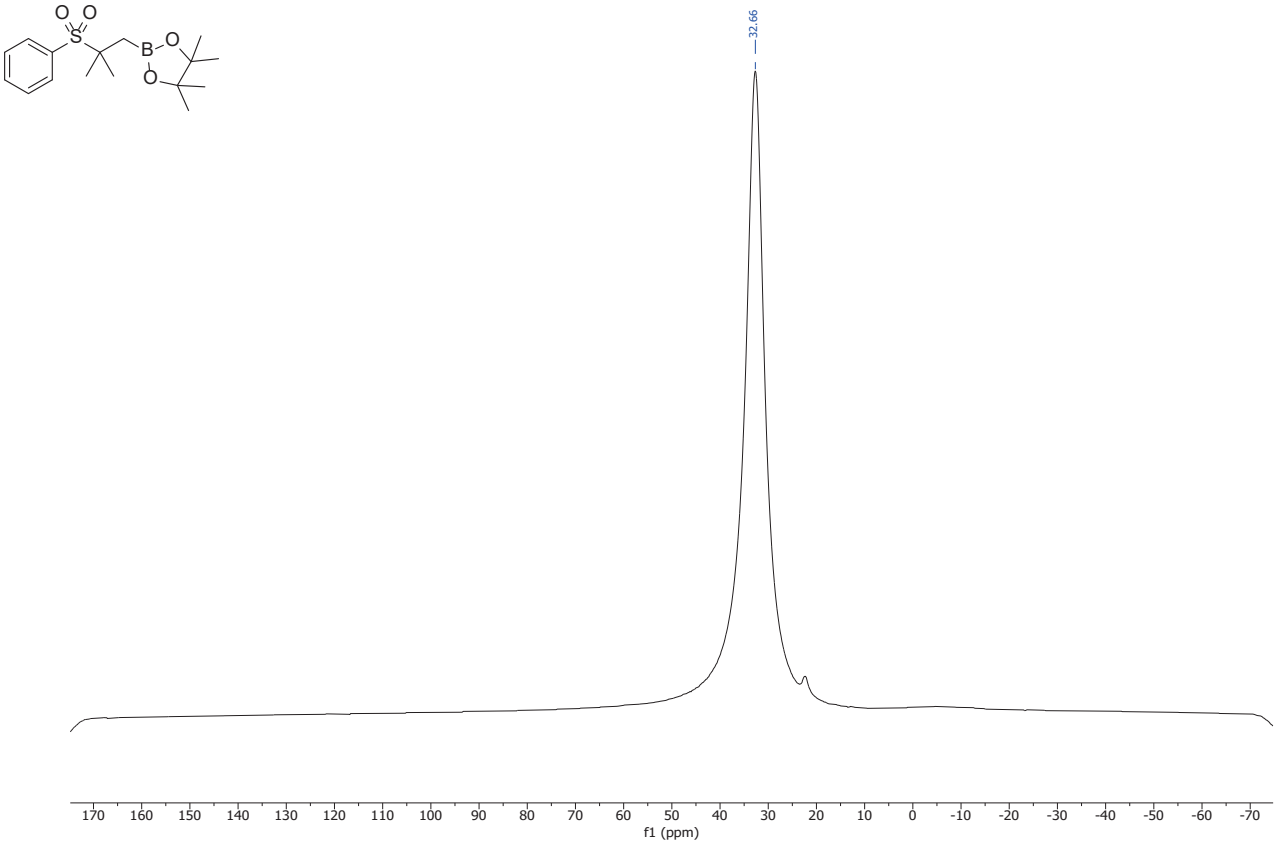
4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)propyl)-1,3,2-dioxaborolane (12)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

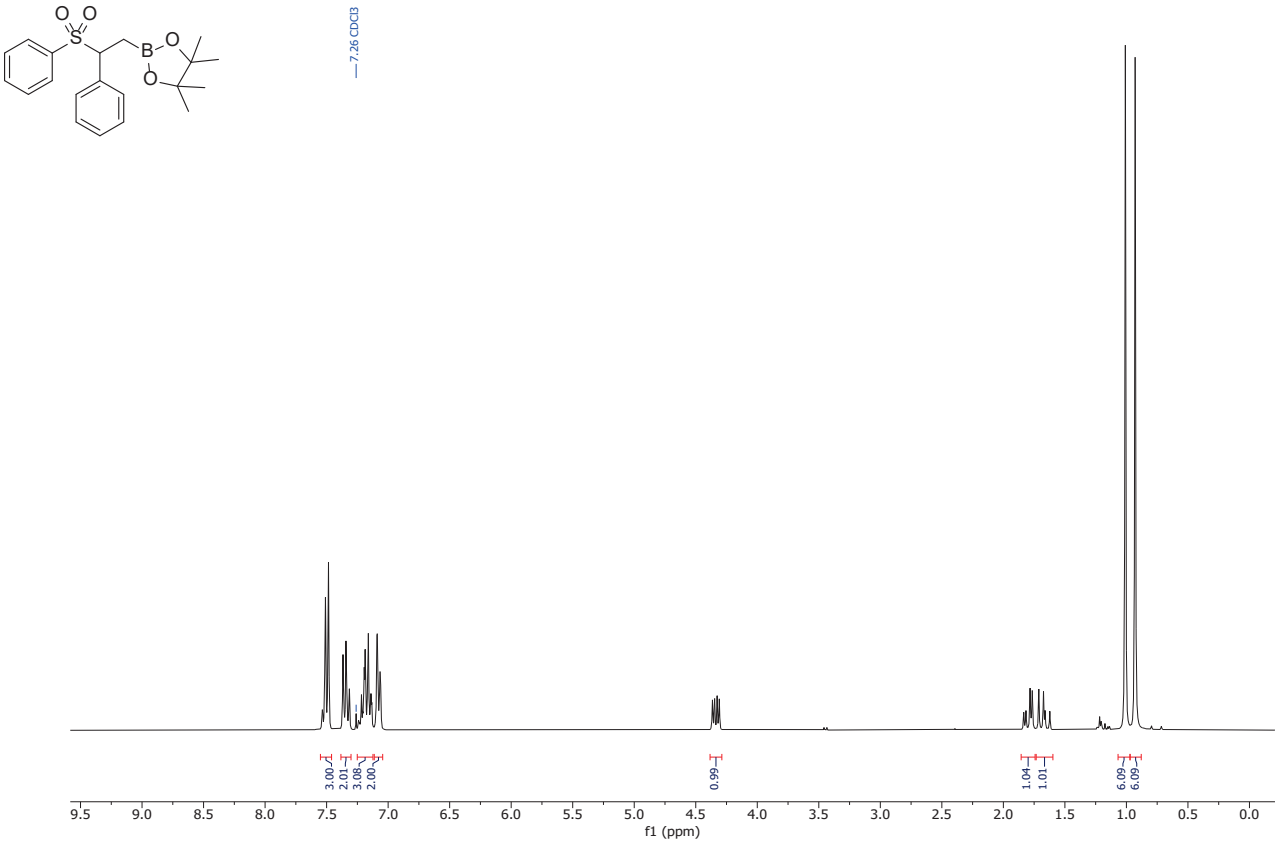


4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)propyl)-1,3,2-dioxaborolane (12)

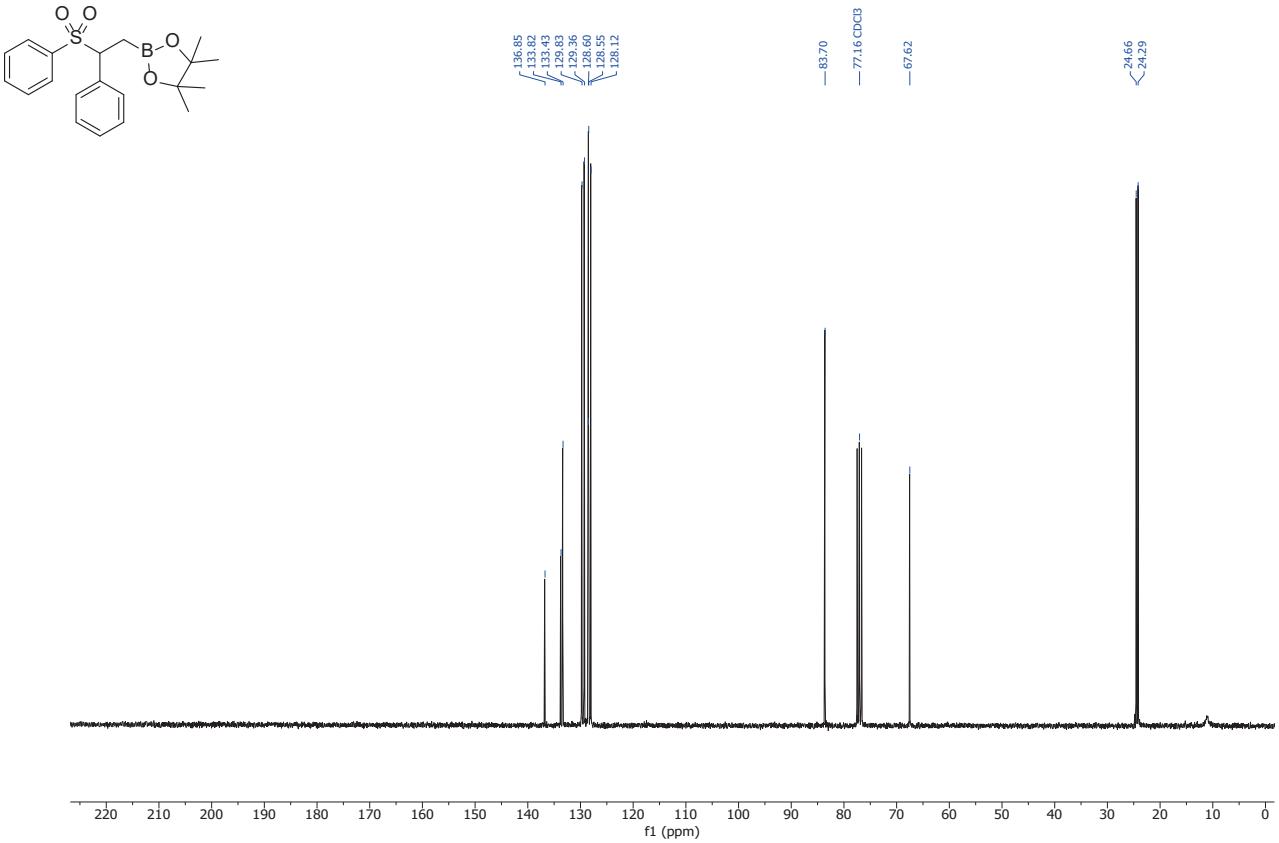
^{11}B NMR (96 MHz, $CDCl_3$)



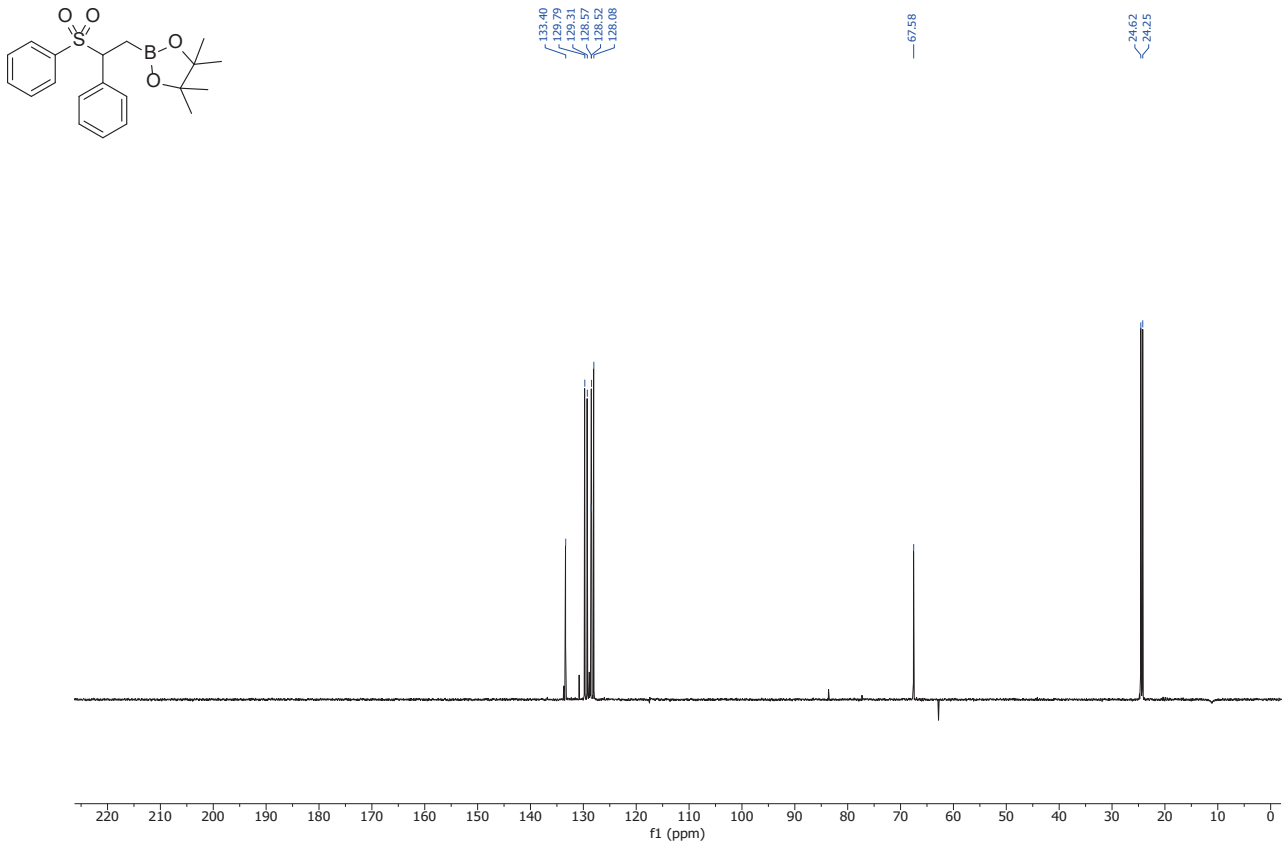
4,4,5,5-tetramethyl-2-(2-phenyl-2-(phenylsulfonyl)ethyl)-1,3,2-dioxaborolane (73) ^{1}H NMR (300 MHz, $CDCl_3$)



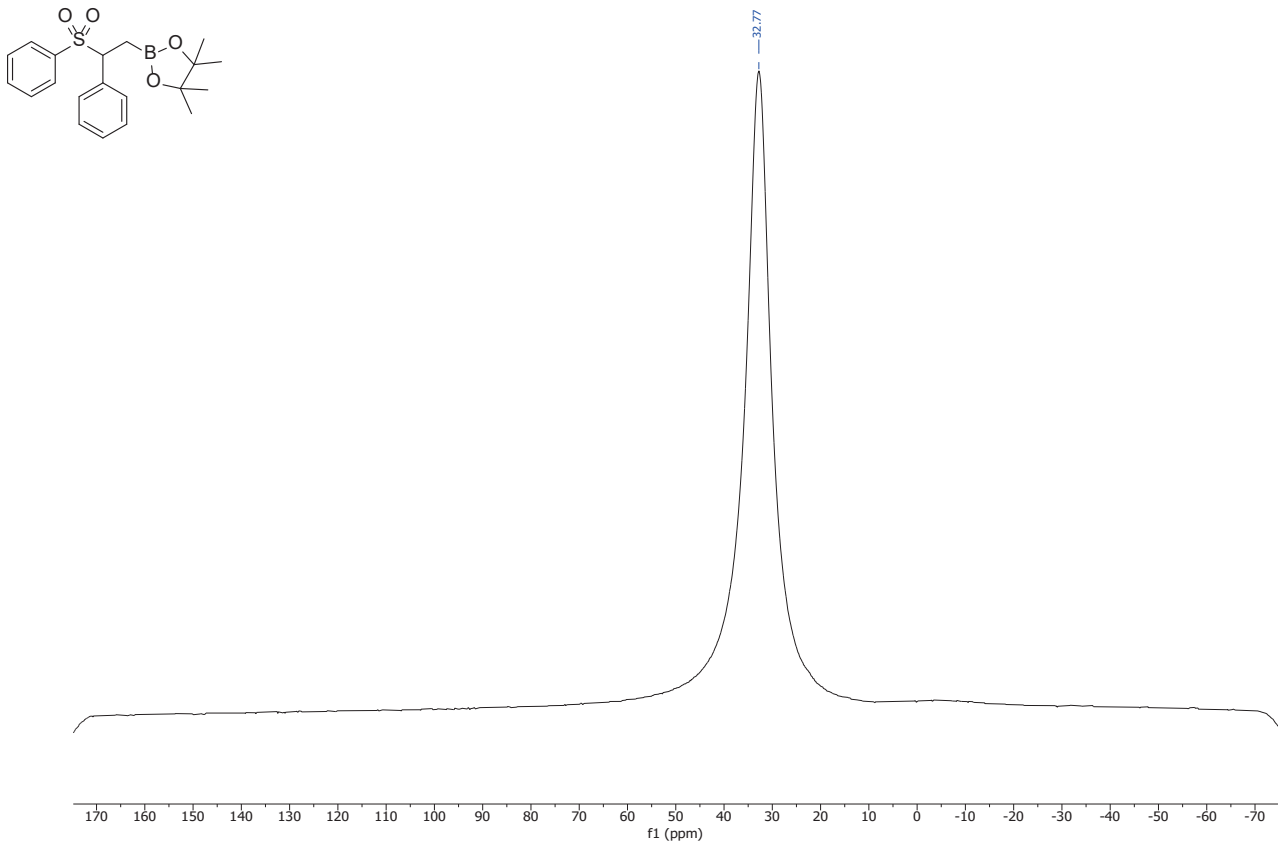
4,4,5,5-tetramethyl-2-(2-phenyl-2-(phenylsulfonyl)ethyl)-1,3,2-dioxaborolane (73) ^{13}C NMR (75 MHz, $CDCl_3$)



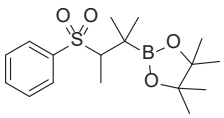
4,4,5,5-tetramethyl-2-(2-phenyl-2-(phenylsulfonyl)ethyl)-1,3,2-dioxaborolane (73) ^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

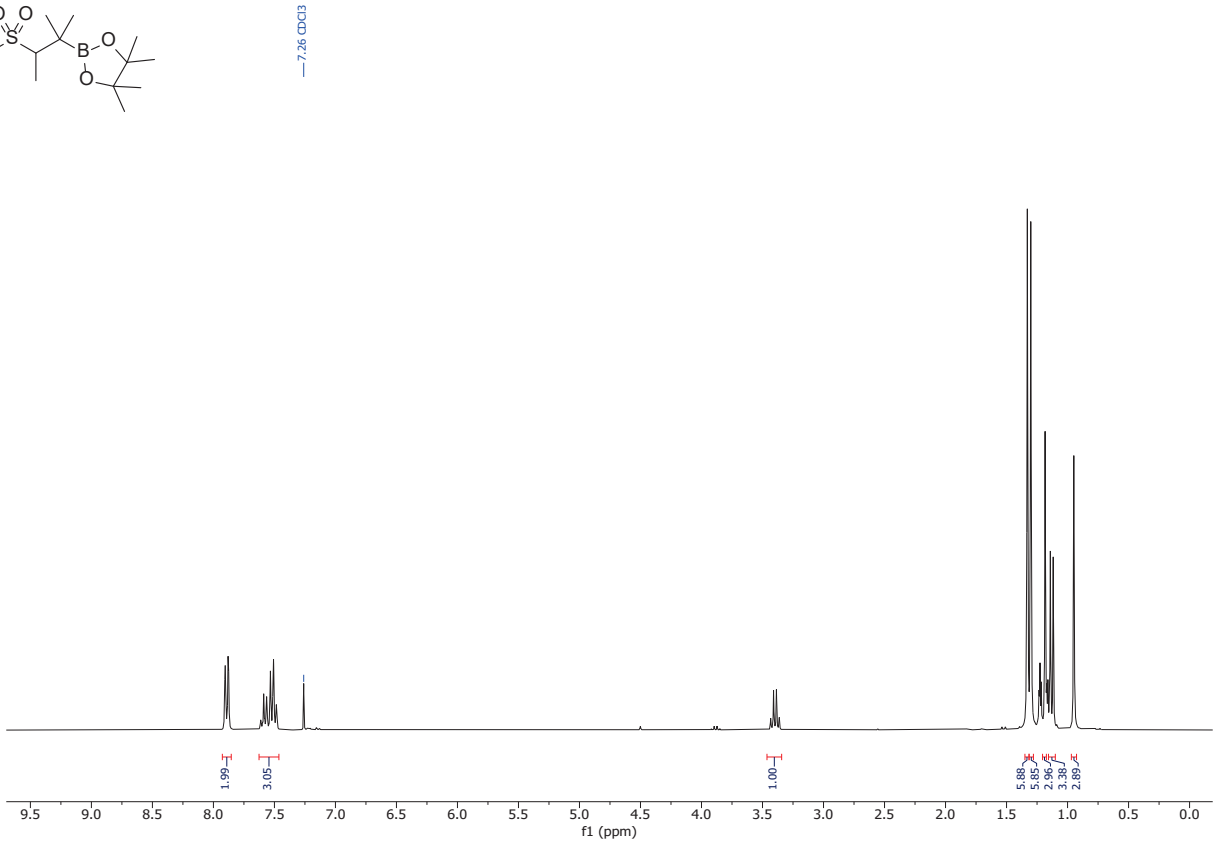


4,4,5,5-tetramethyl-2-(2-phenyl-2-(phenylsulfonyl)ethyl)-1,3,2-dioxaborolane (73) ^{11}B NMR (96 MHz, $CDCl_3$)

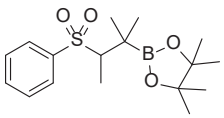


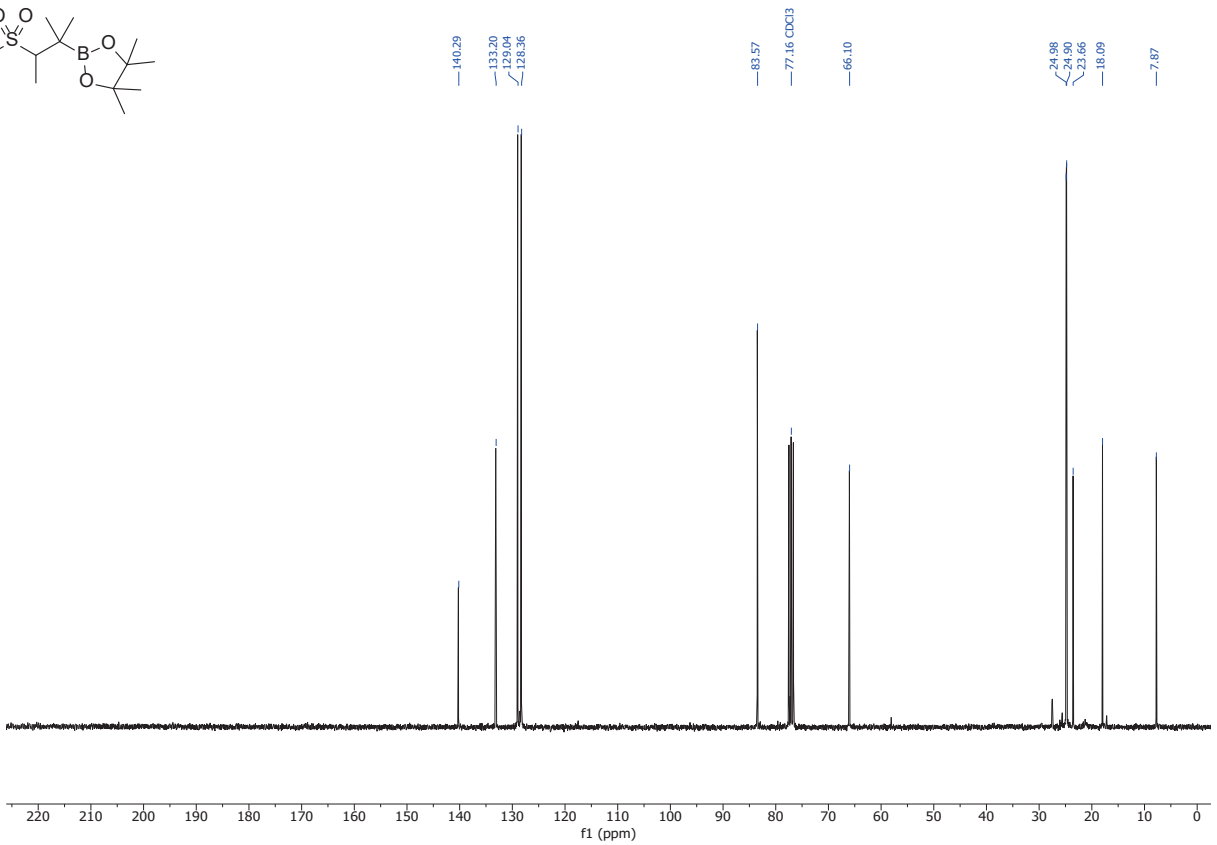
4,4,5,5-tetramethyl-2-(2-methyl-3-(phenylsulfonyl)butan-2-yl)-1,3,2-dioxaborolane (11) ^{1}H NMR (300 MHz, $CDCl_3$)



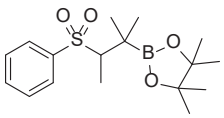


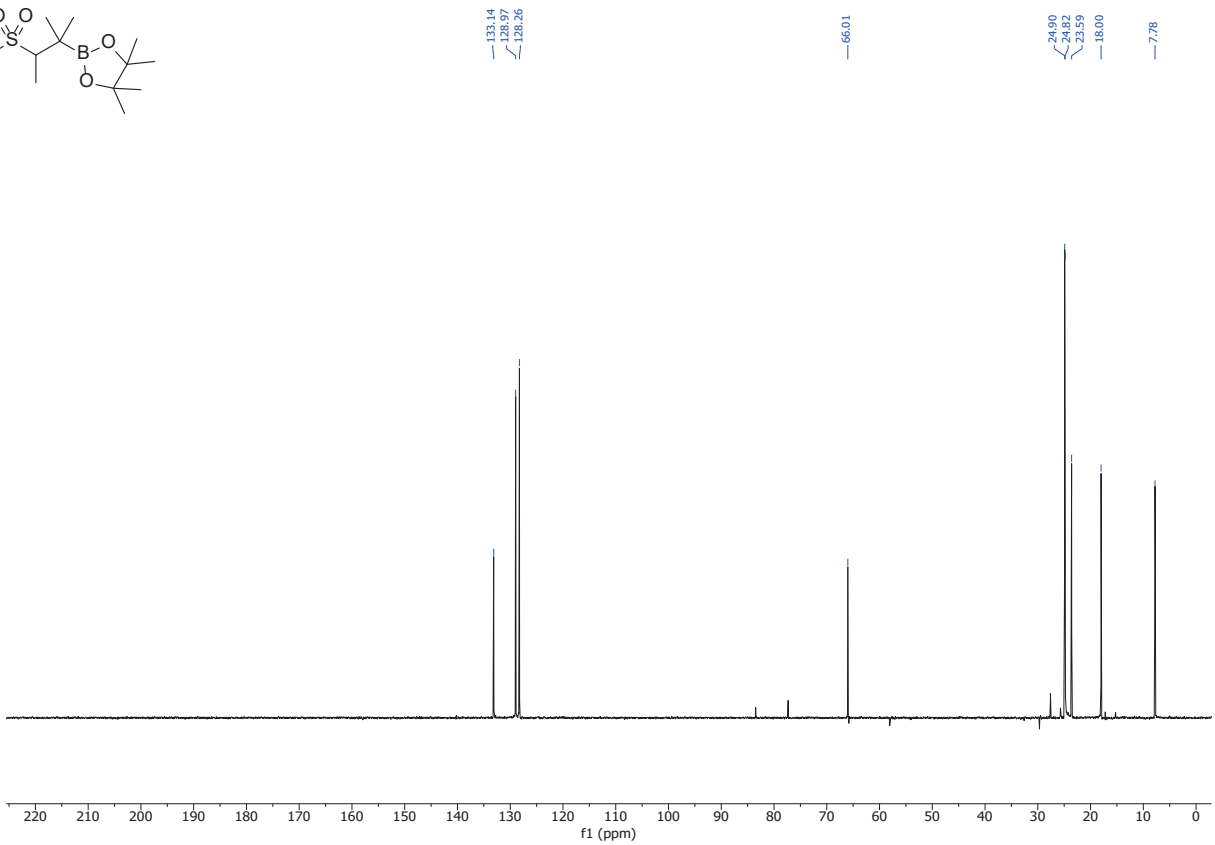
4,4,5,5-tetramethyl-2-(2-methyl-3-(phenylsulfonyl)butan-2-yl)-1,3,2-dioxaborolane (11) ^{13}C NMR (75 MHz, $CDCl_3$)



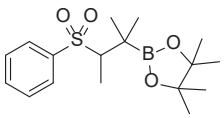


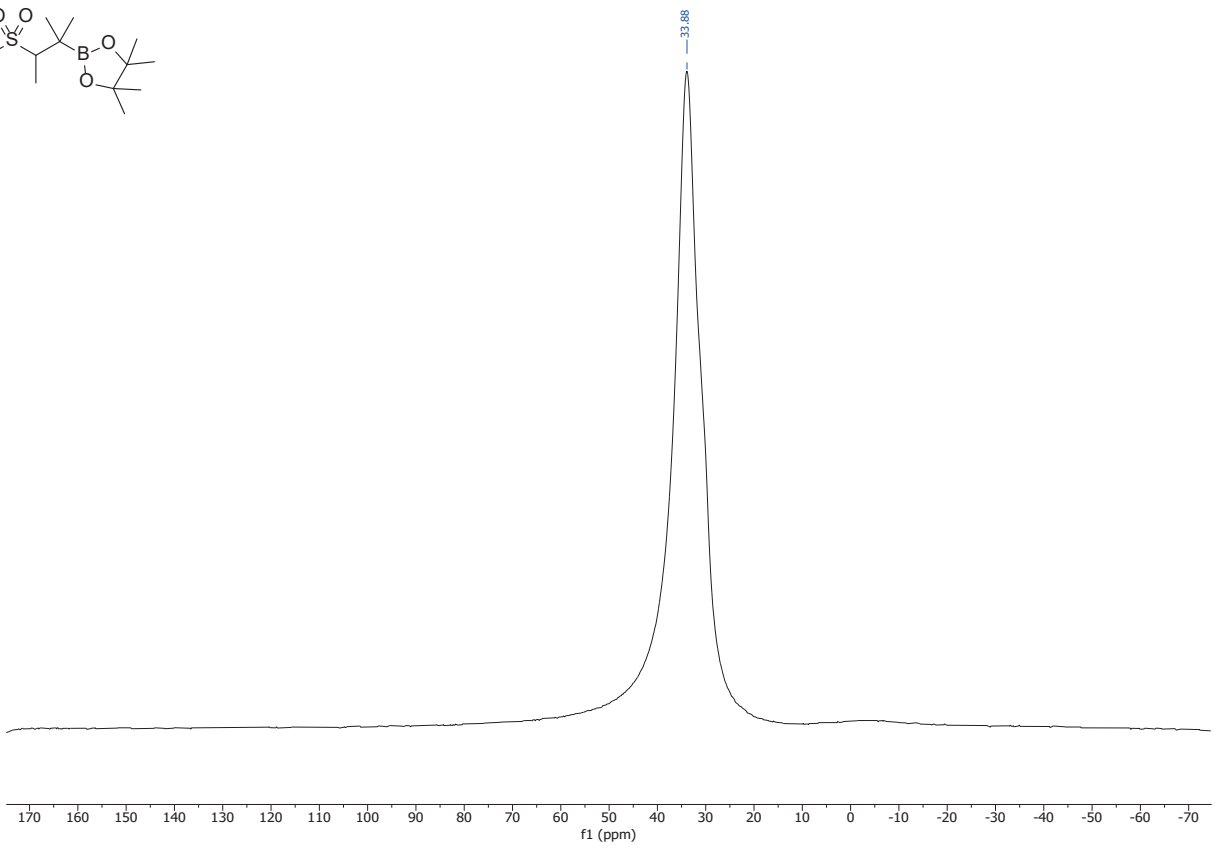
4,4,5,5-tetramethyl-2-(2-methyl-3-(phenylsulfonyl)butan-2-yl)-1,3,2-dioxaborolane (11) ^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)





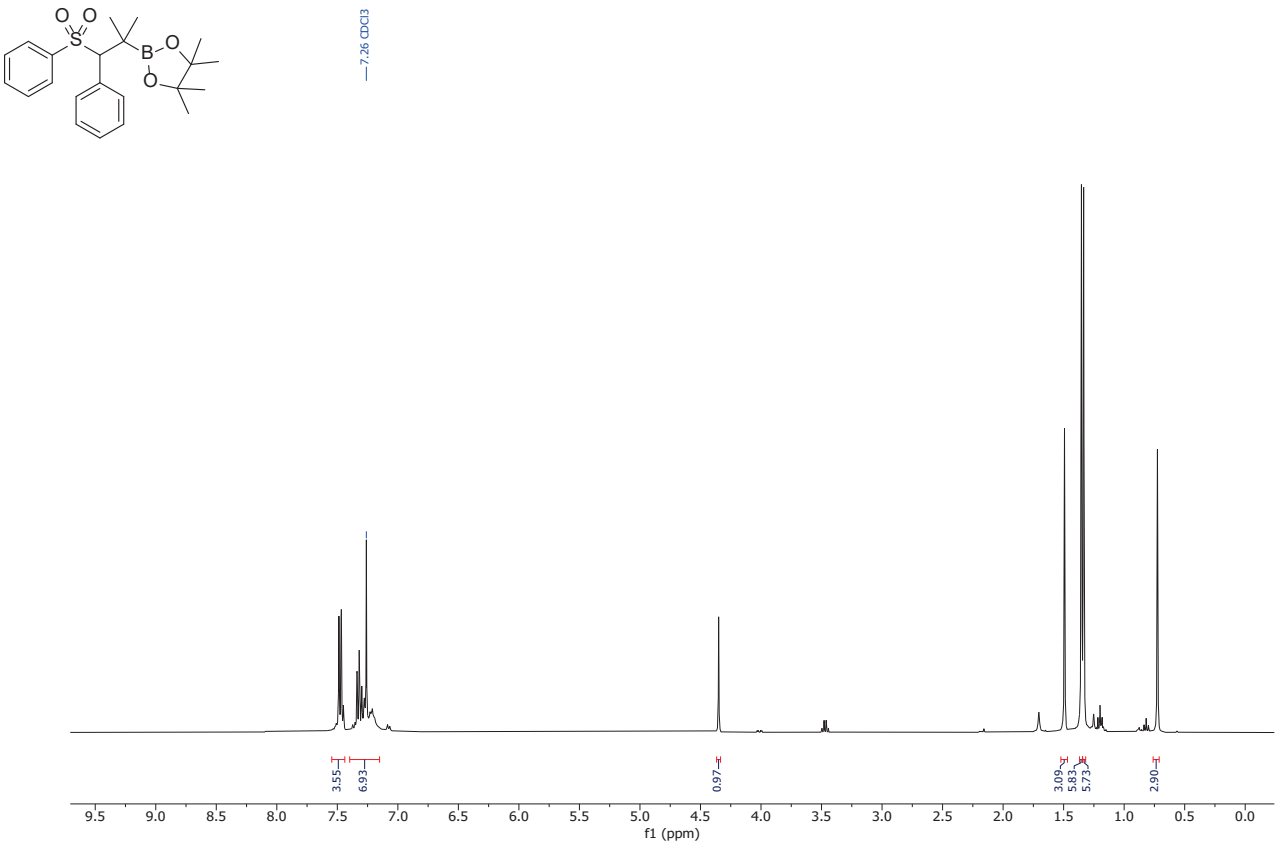
4,4,5,5-tetramethyl-2-(2-methyl-3-(phenylsulfonyl)butan-2-yl)-1,3,2-dioxaborolane (11) ^{11}B NMR (96 MHz, $CDCl_3$)





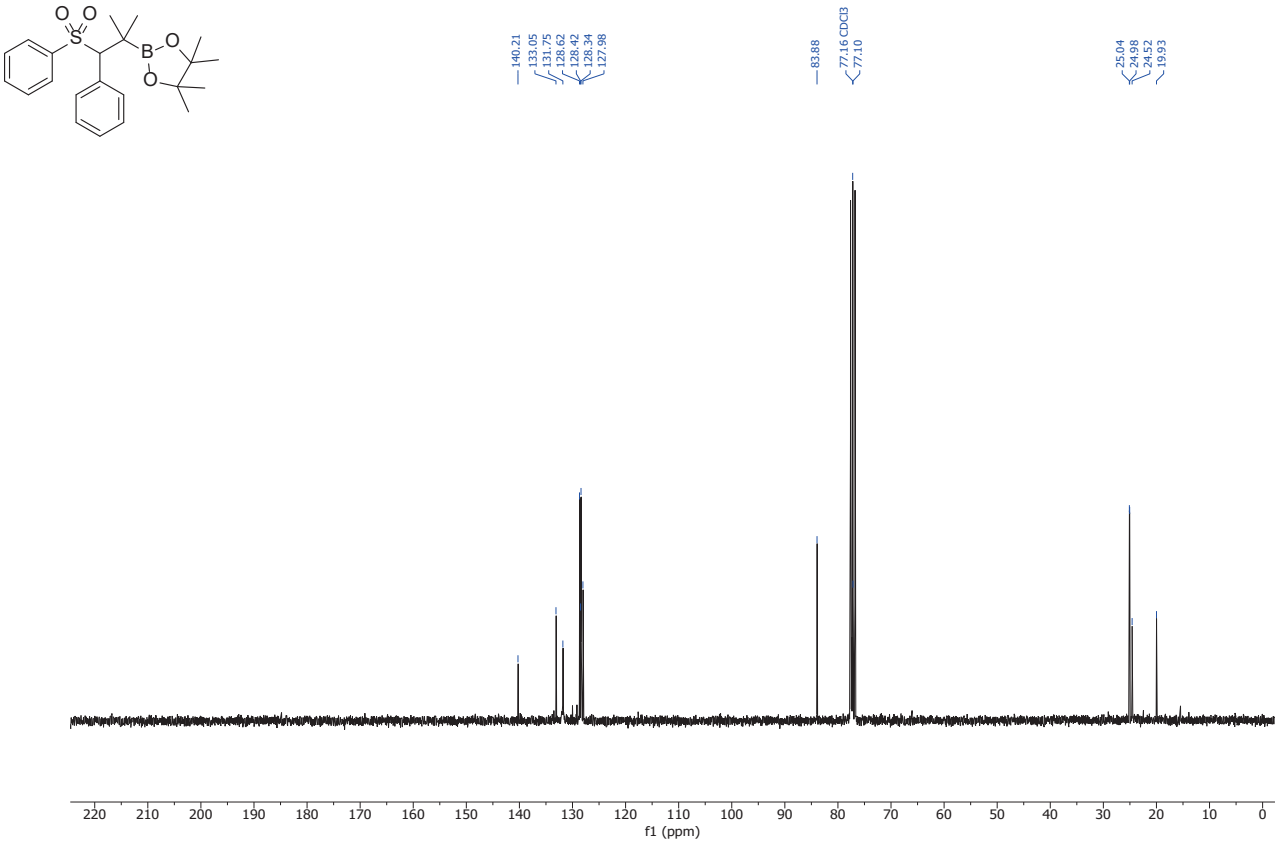
4,4,5,5-tetramethyl-2-(2-methyl-1-phenyl-1-(phenylsulfonyl)propan-2-yl)-1,3,2-dioxaborolane (74)

^{1}H NMR (300 MHz, $CDCl_3$)



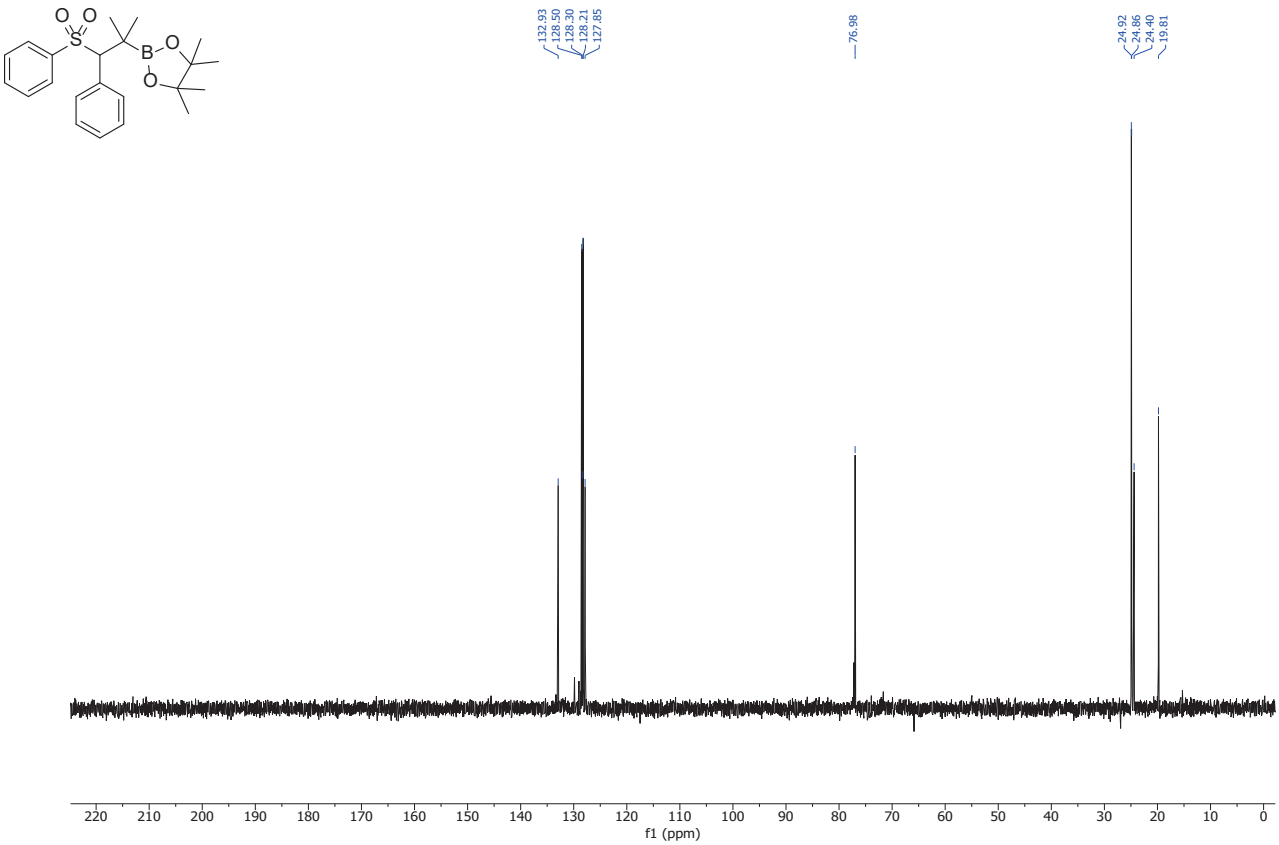
4,4,5,5-tetramethyl-2-(2-methyl-1-phenyl-1-(phenylsulfonyl)propan-2-yl)-1,3,2-dioxaborolane (74)

^{13}C NMR (75 MHz, $CDCl_3$)



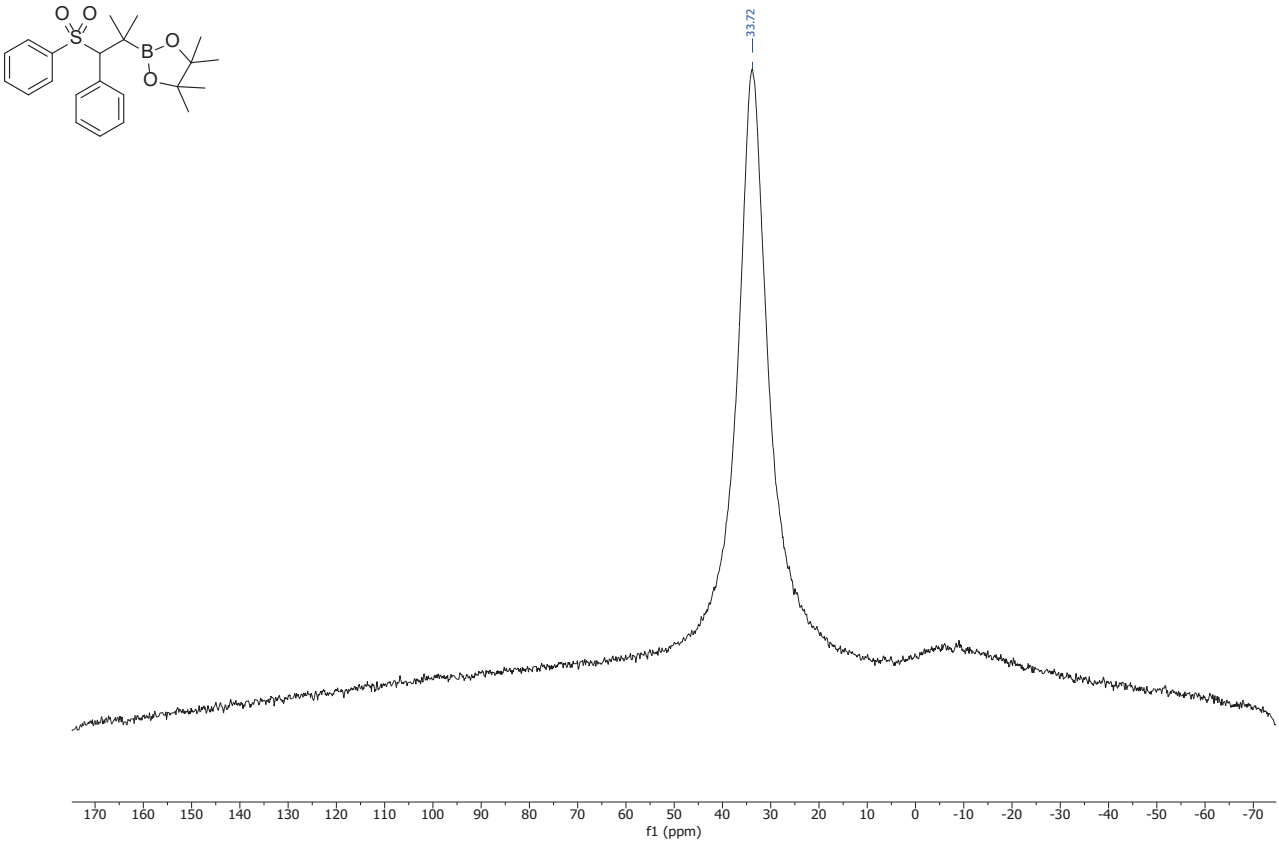
4,4,5,5-tetramethyl-2-(2-methyl-1-phenyl-1-(phenylsulfonyl)propan-2-yl)-1,3,2-dioxaborolane (74)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



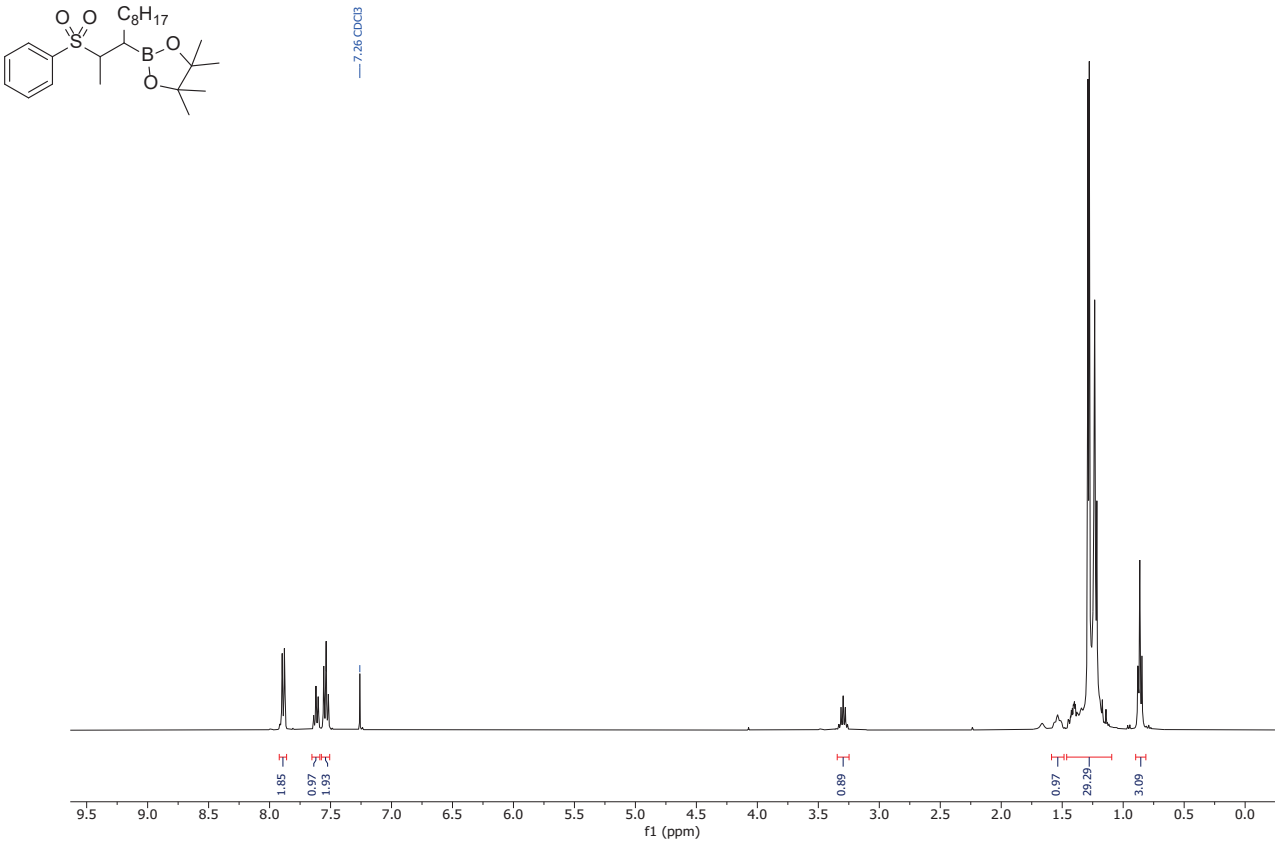
4,4,5,5-tetramethyl-2-(2-methyl-1-phenyl-1-(phenylsulfonyl)propan-2-yl)-1,3,2-dioxaborolane (74)

^{11}B NMR (96 MHz, $CDCl_3$)



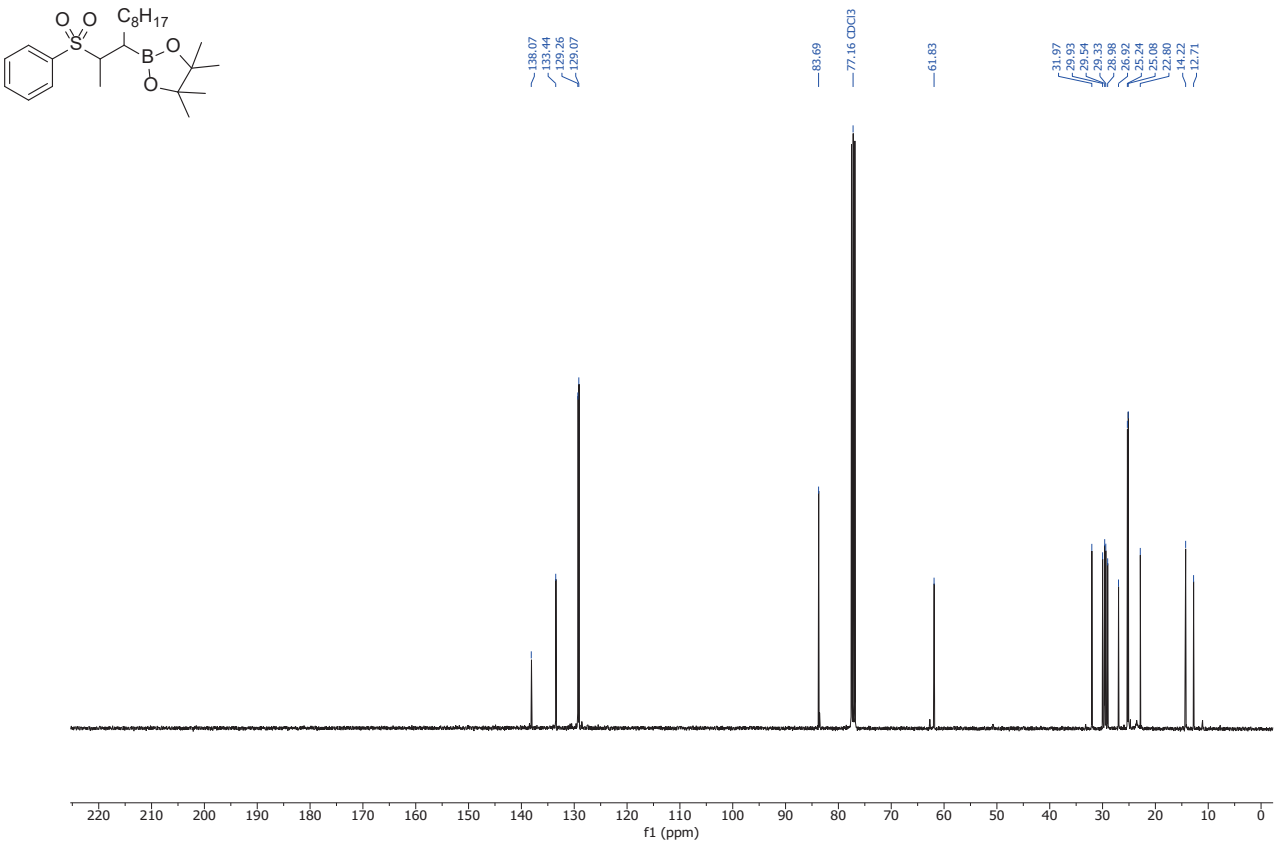
4,4,5,5-tetramethyl-2-(2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (10)
Major diastereomer

^{1}H NMR (400 MHz, $CDCl_3$)



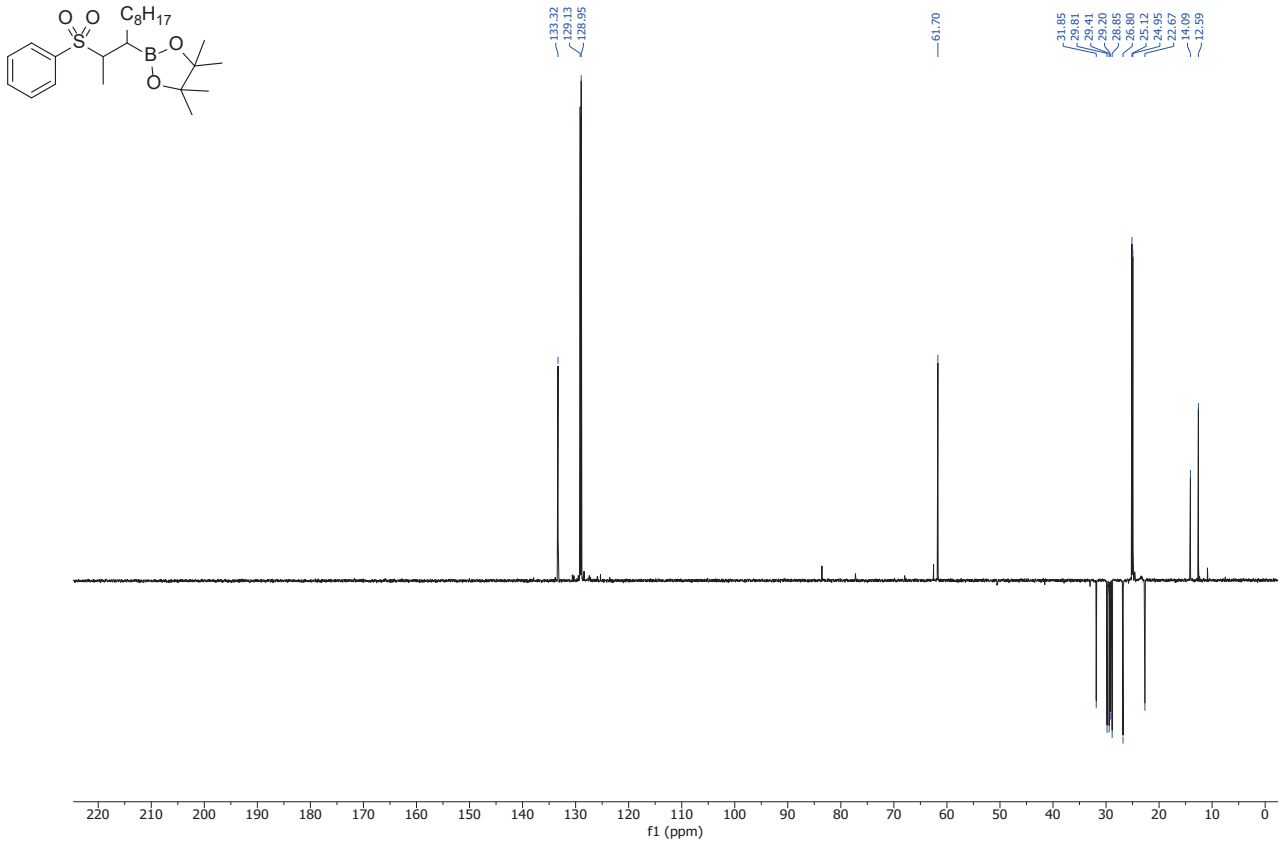
4,4,5,5-tetramethyl-2-(2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (10)
Major diastereomer

^{13}C NMR (101 MHz, $CDCl_3$)



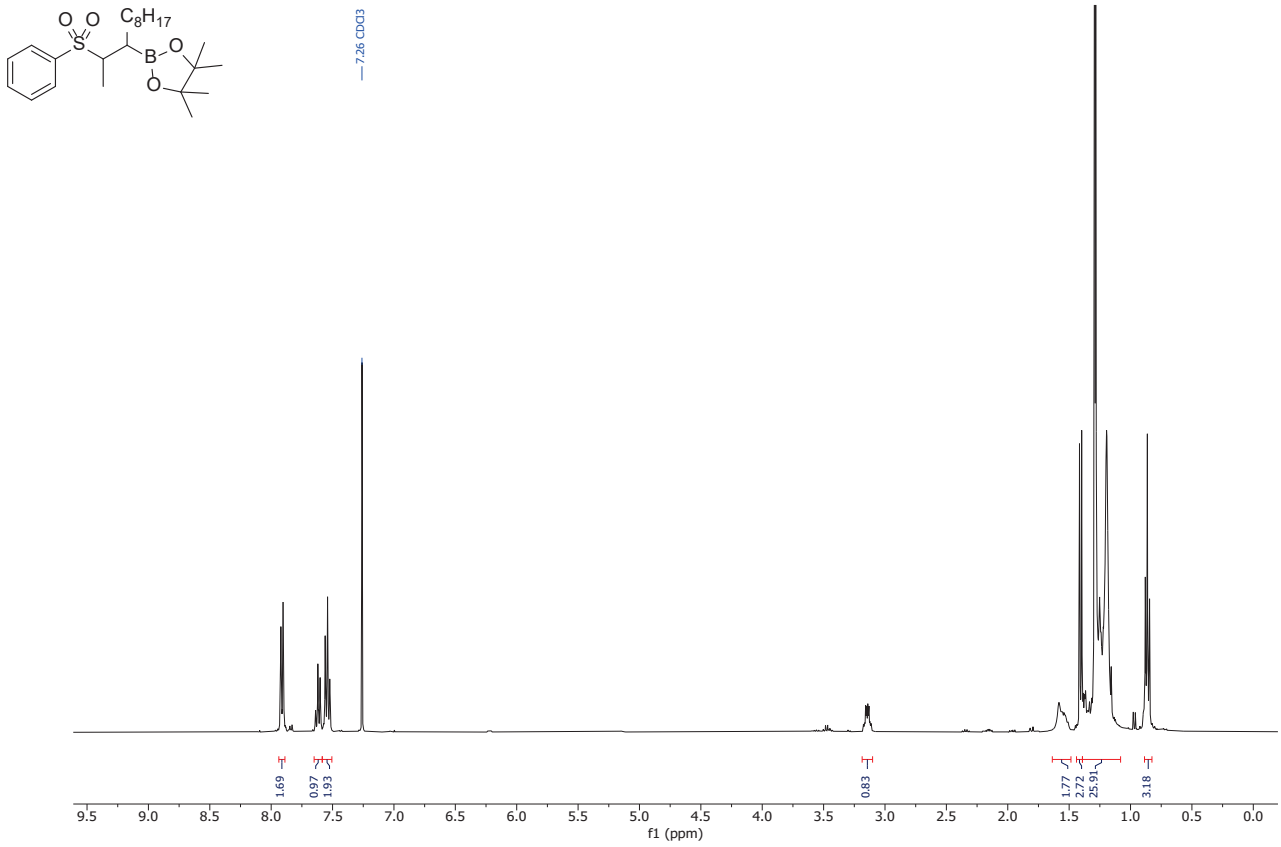
4,4,5,5-tetramethyl-2-(2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (10)
Major diastereomer

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



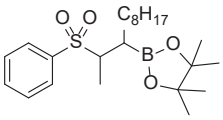
4,4,5,5-tetramethyl-2-(2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (10)
Minor diastereomer

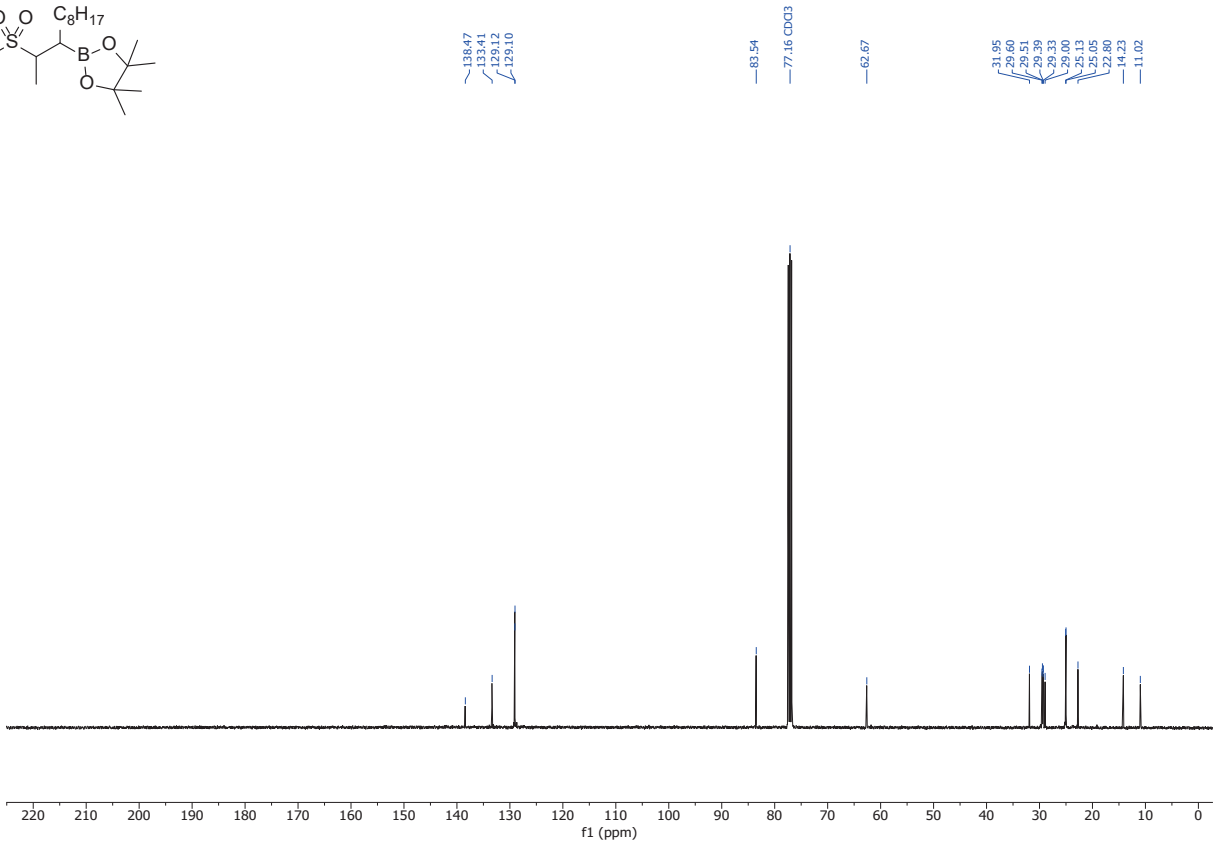
^{1}H NMR (400 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-(2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (10)
Minor diastereomer

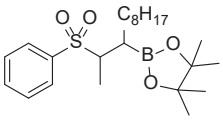
^{13}C NMR (101 MHz, $CDCl_3$)

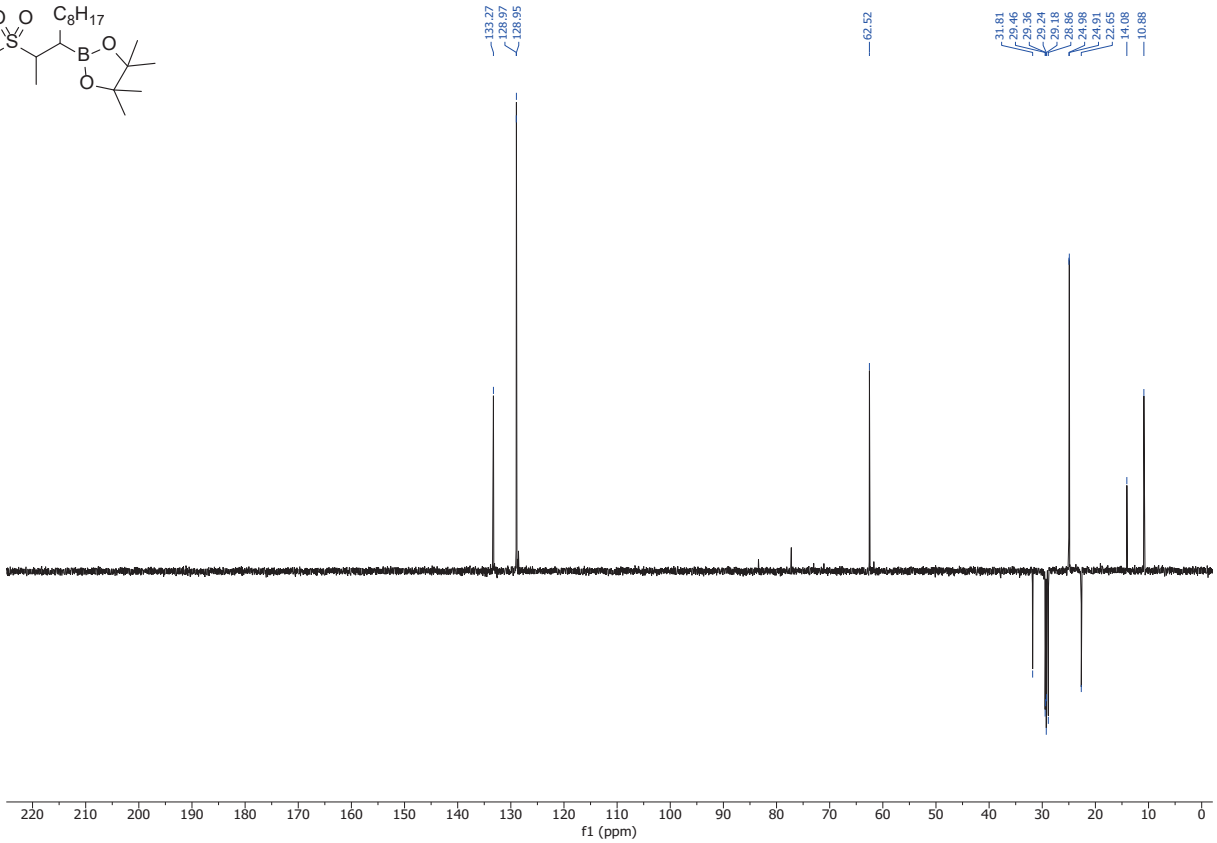




4,4,5,5-tetramethyl-2-(2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (10)
Minor diastereomer

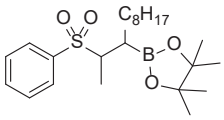
^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)

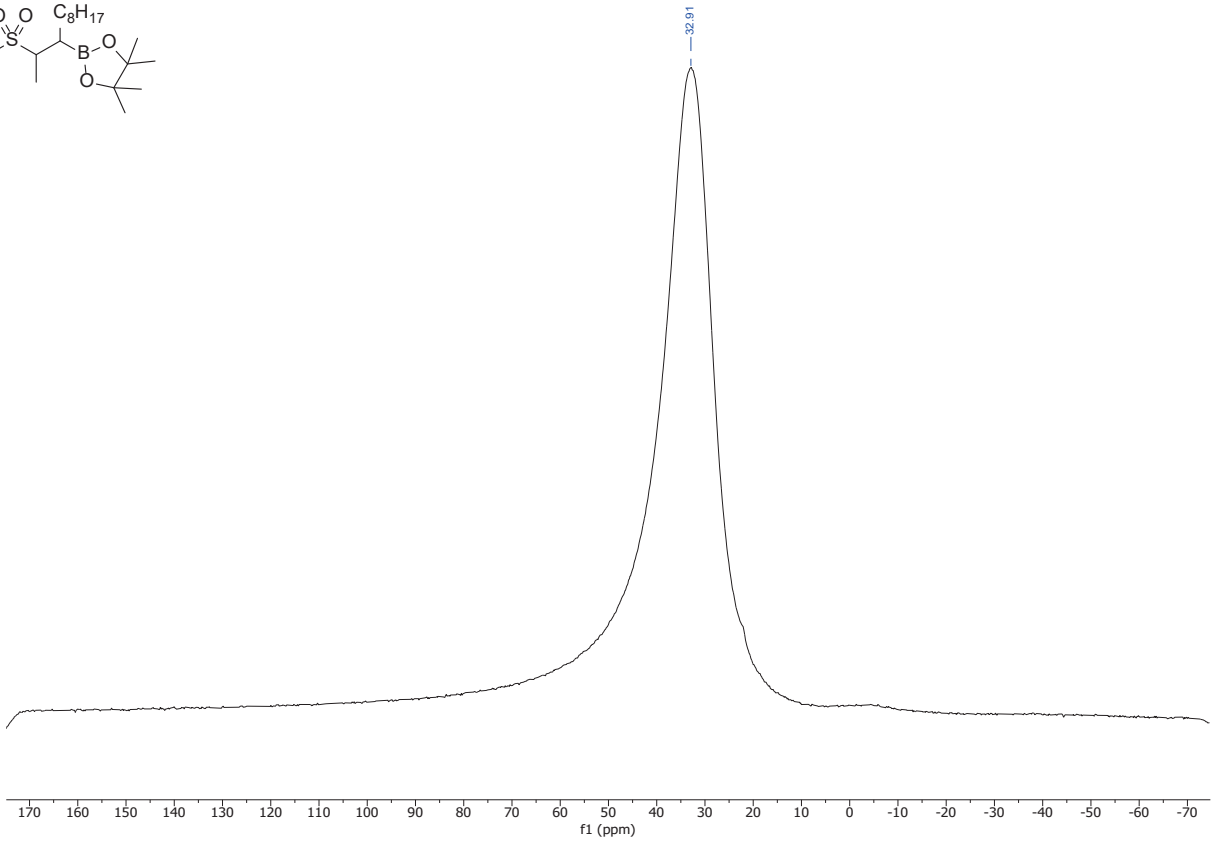




4,4,5,5-tetramethyl-2-(2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (10)
Mix of diastereomer

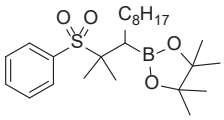
^{11}B NMR (96 MHz, $CDCl_3$)

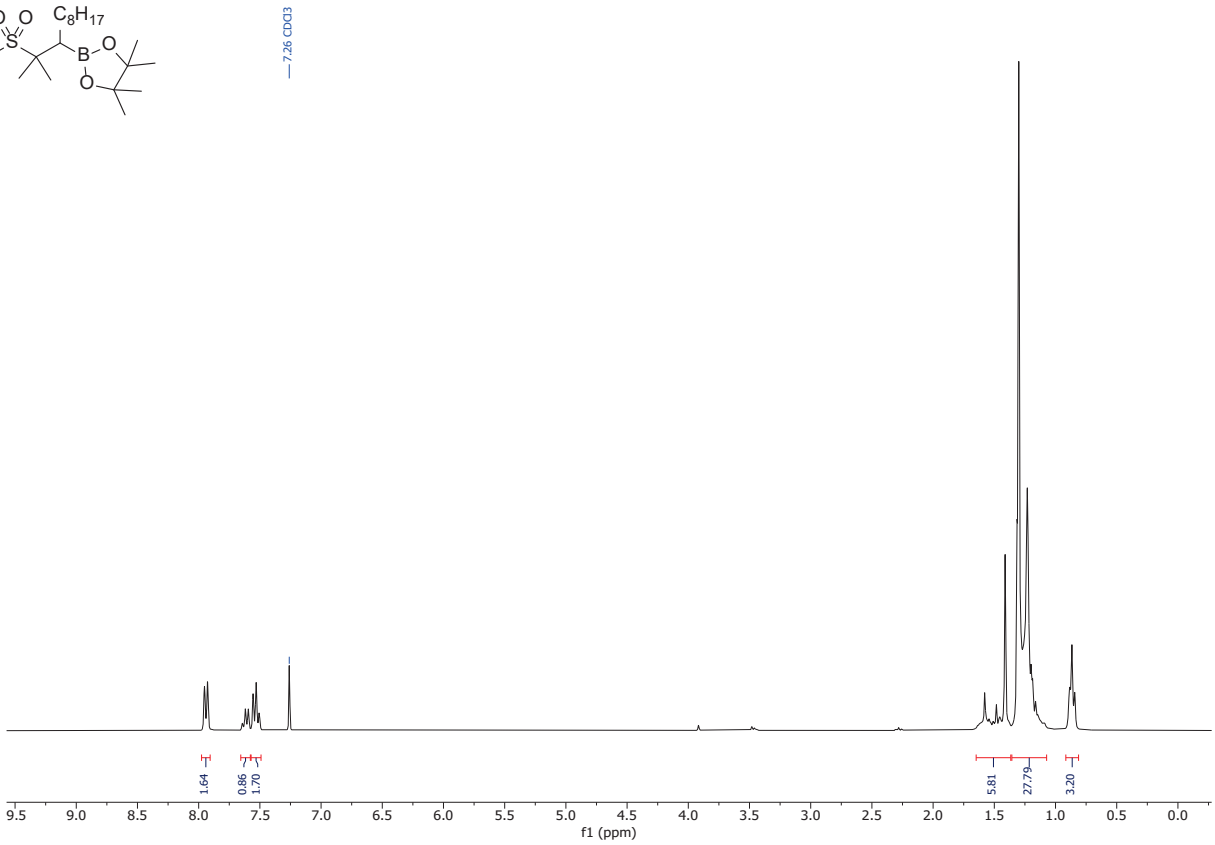




4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (6)

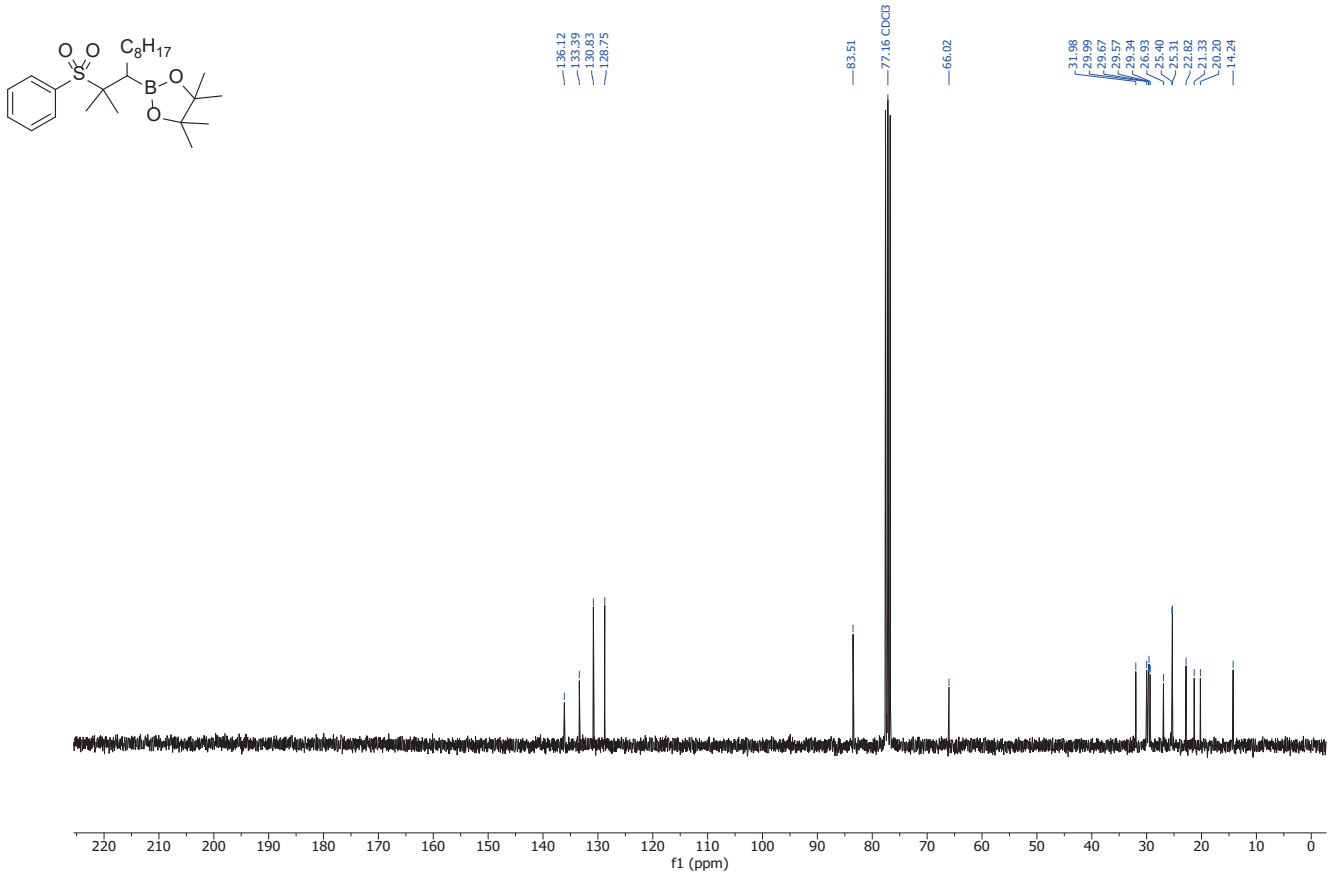
^{1}H NMR (300 MHz, $CDCl_3$)





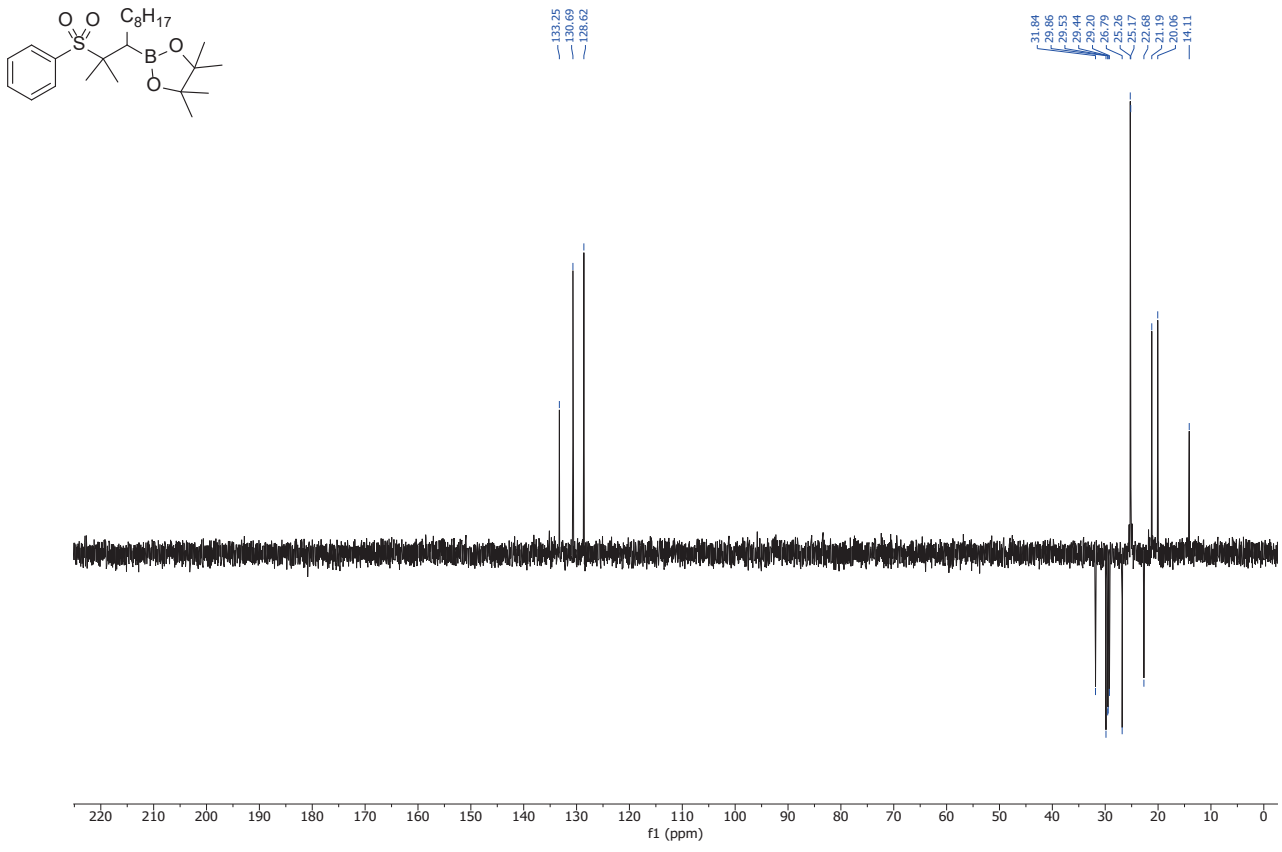
4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (6)

^{13}C NMR (75 MHz, $CDCl_3$)



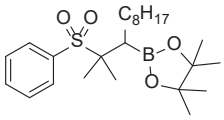
4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (6)

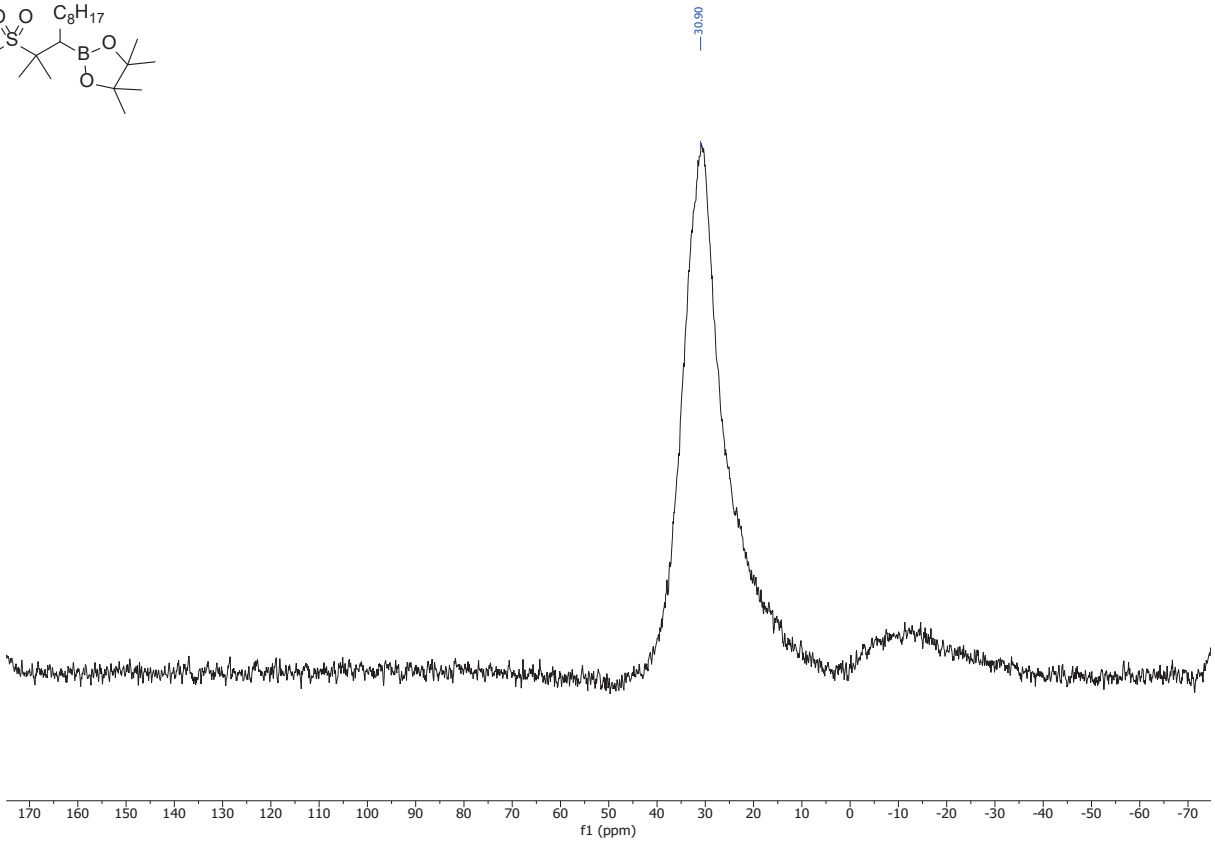
^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)undecan-3-yl)-1,3,2-dioxaborolane (6)

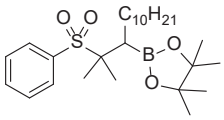
^{11}B NMR (96 MHz, $CDCl_3$)

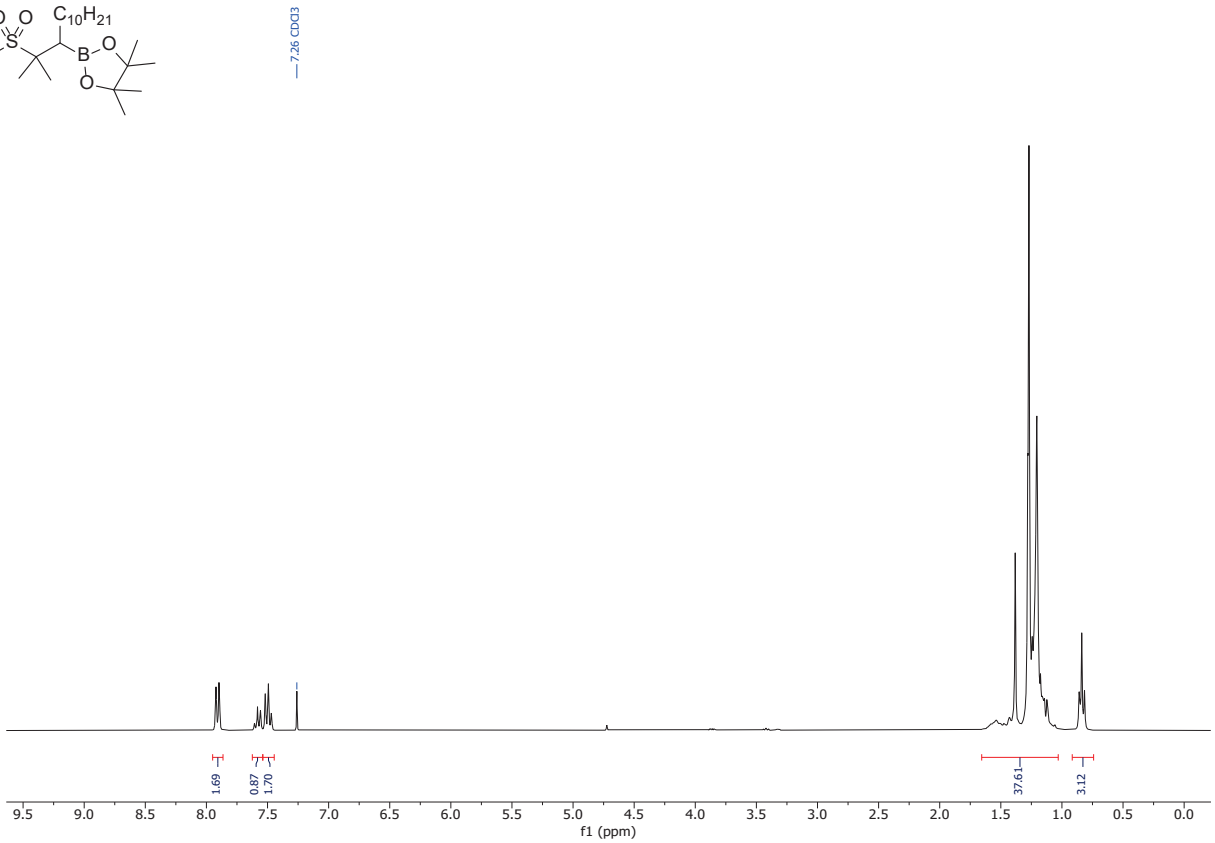




4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)tridecan-3-yl)-1,3,2-dioxaborolane (7)

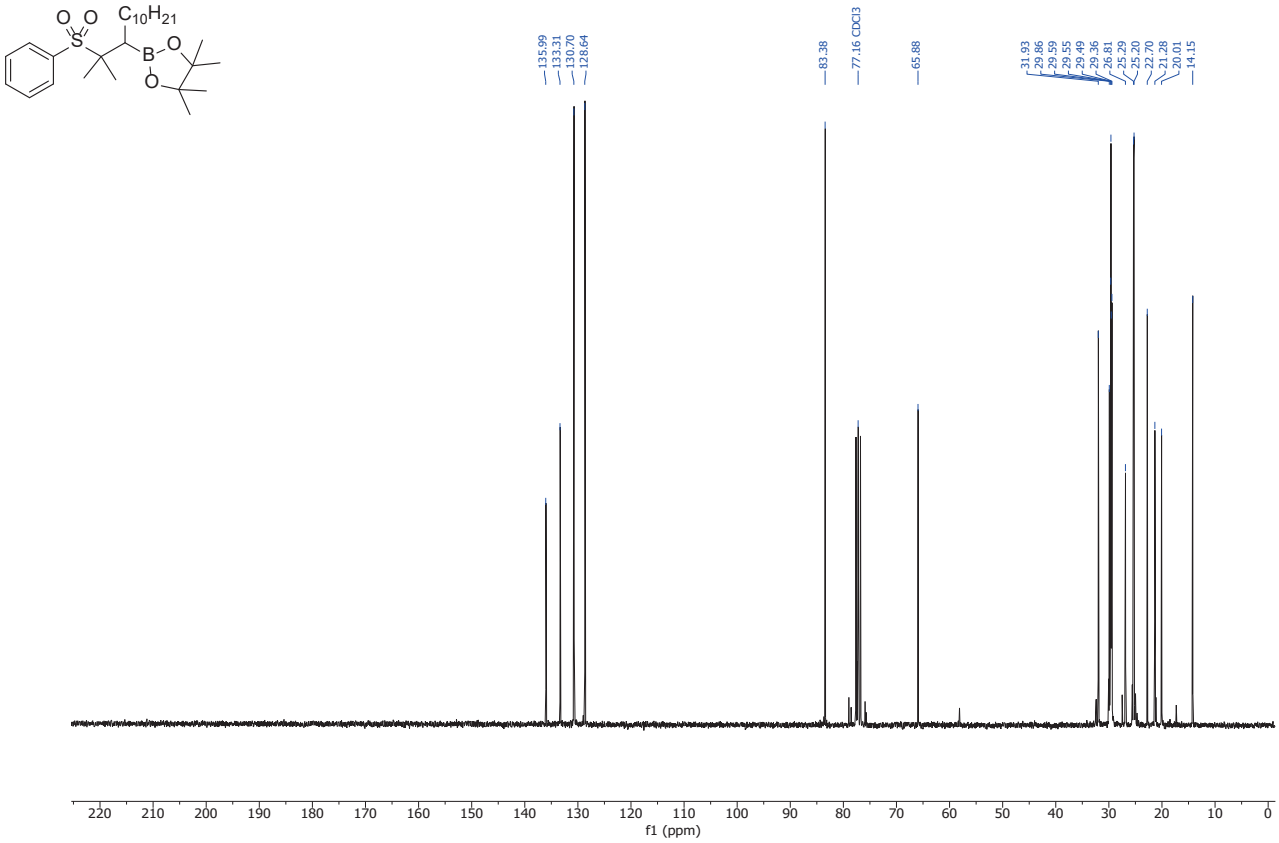
^{1}H NMR (300 MHz, $CDCl_3$)





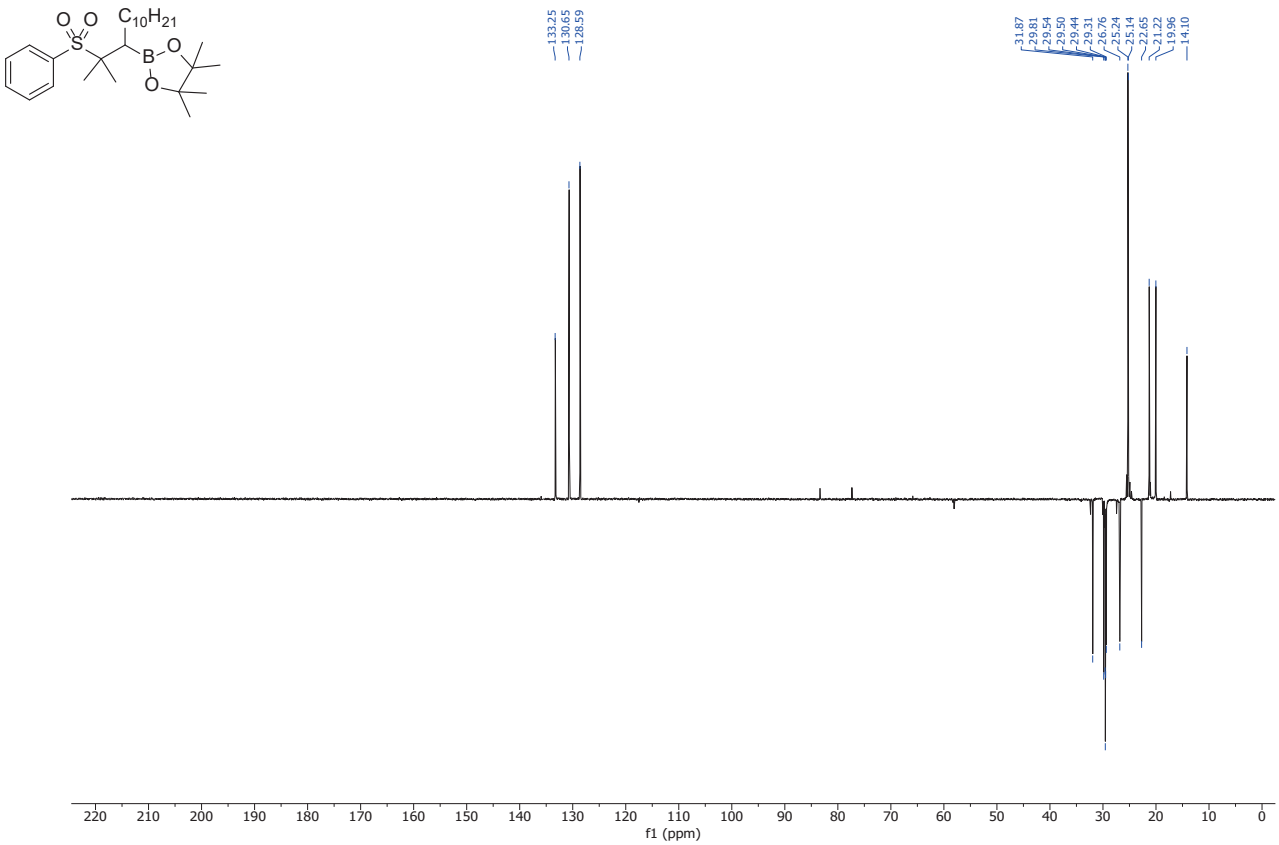
4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)tridecan-3-yl)-1,3,2-dioxaborolane (7)

^{13}C NMR (75 MHz, $CDCl_3$)



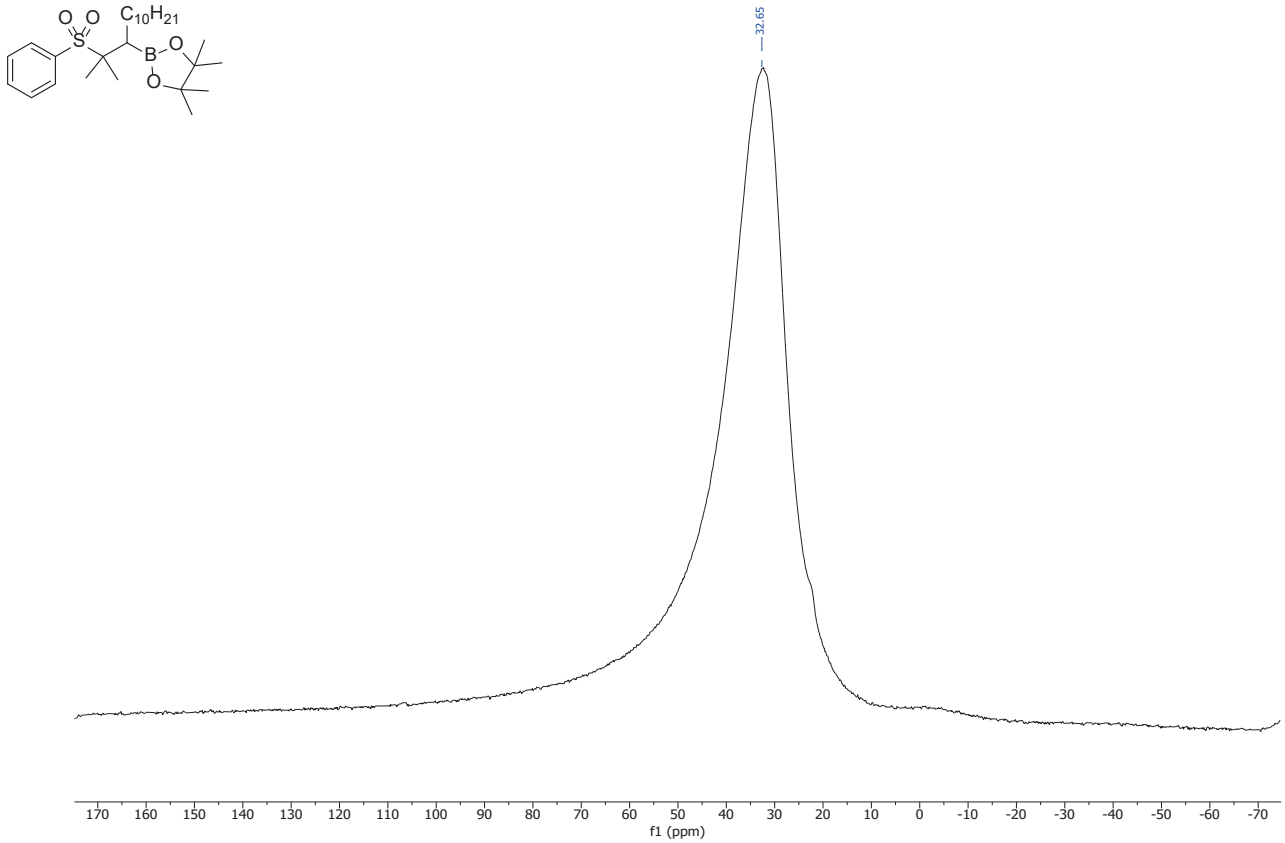
4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)tridecan-3-yl)-1,3,2-dioxaborolane (7)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



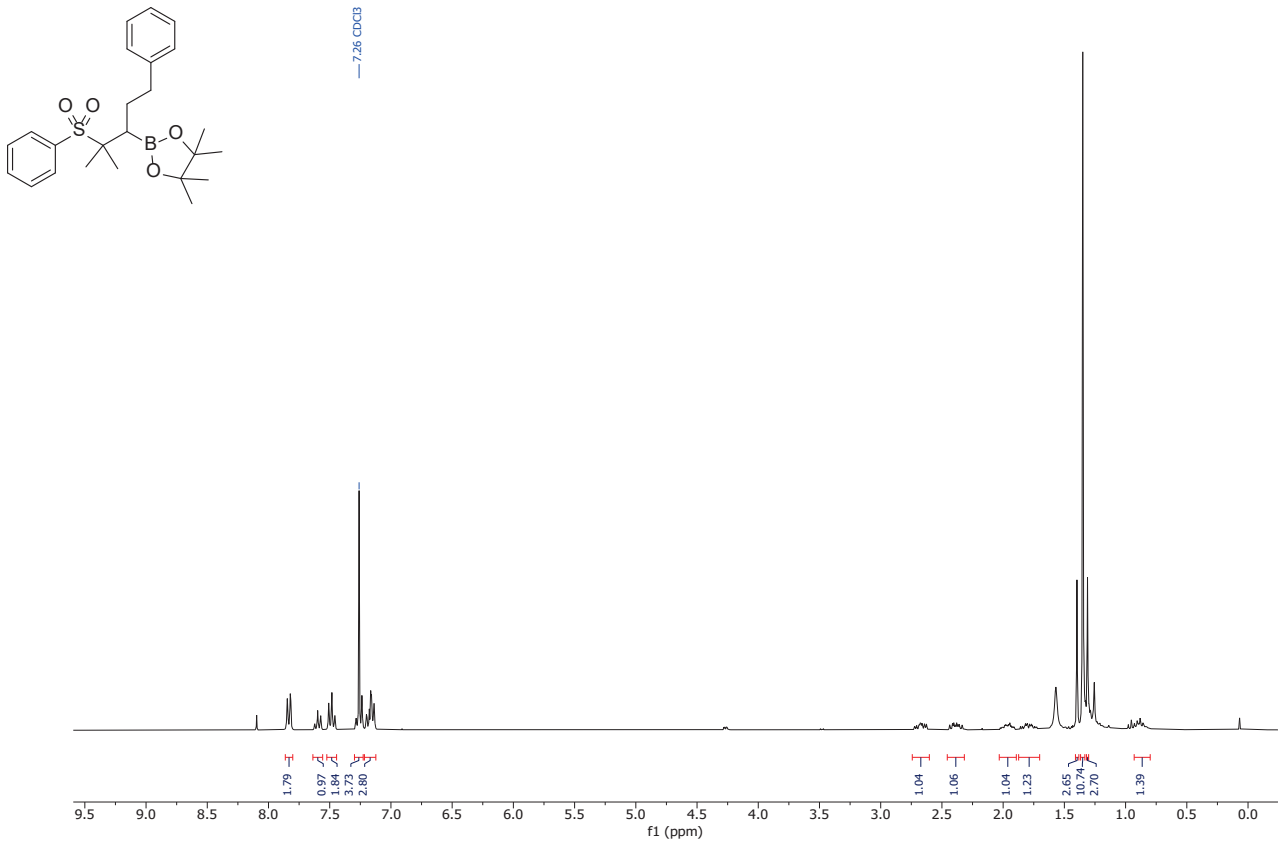
4,4,5,5-tetramethyl-2-(2-methyl-2-(phenylsulfonyl)tridecan-3-yl)-1,3,2-dioxaborolane (7)

^{11}B NMR (96 MHz, $CDCl_3$)



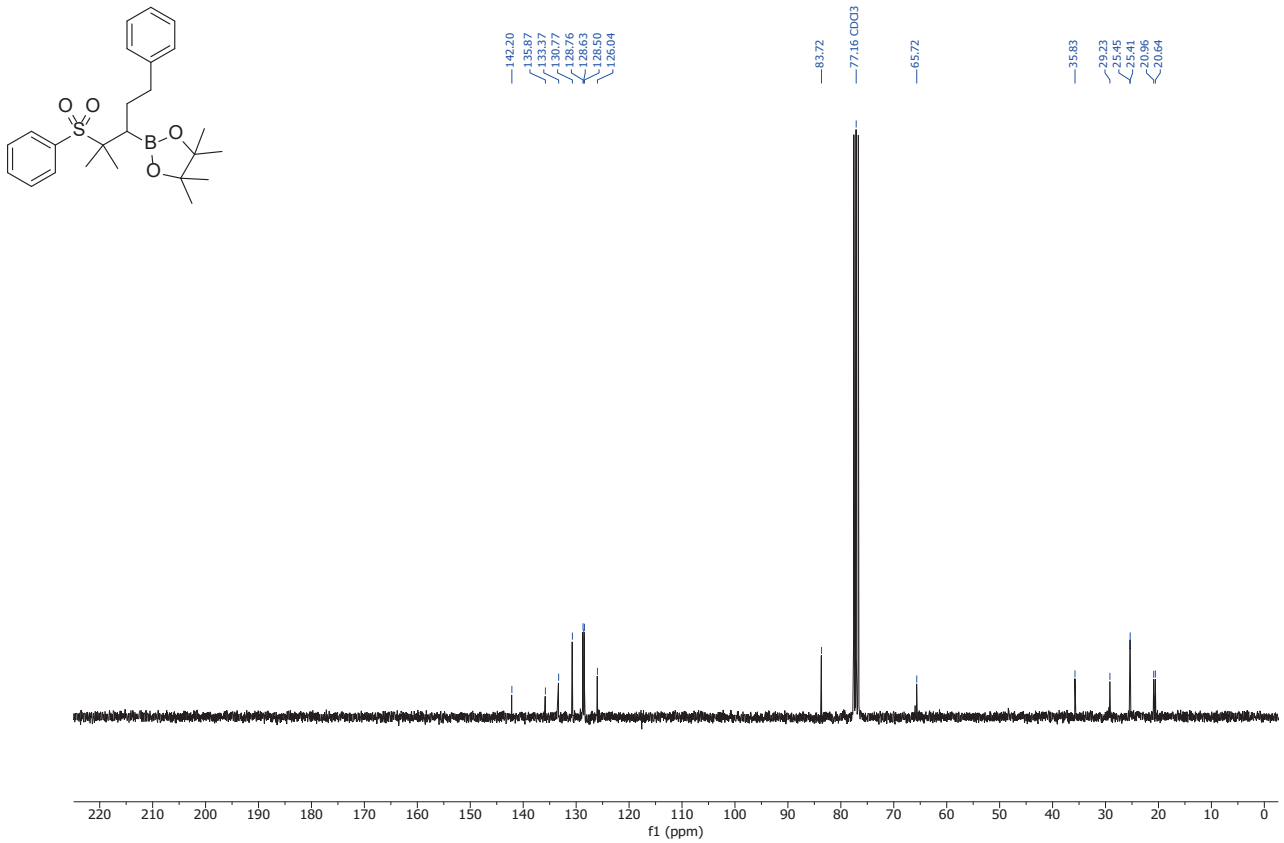
4,4,5,5-tetramethyl-2-(4-methyl-1-phenyl-4-(phenylsulfonyl)pentan-3-yl)-1,3,2-dioxaborolane (18)

^{1}H NMR (300 MHz, $CDCl_3$)



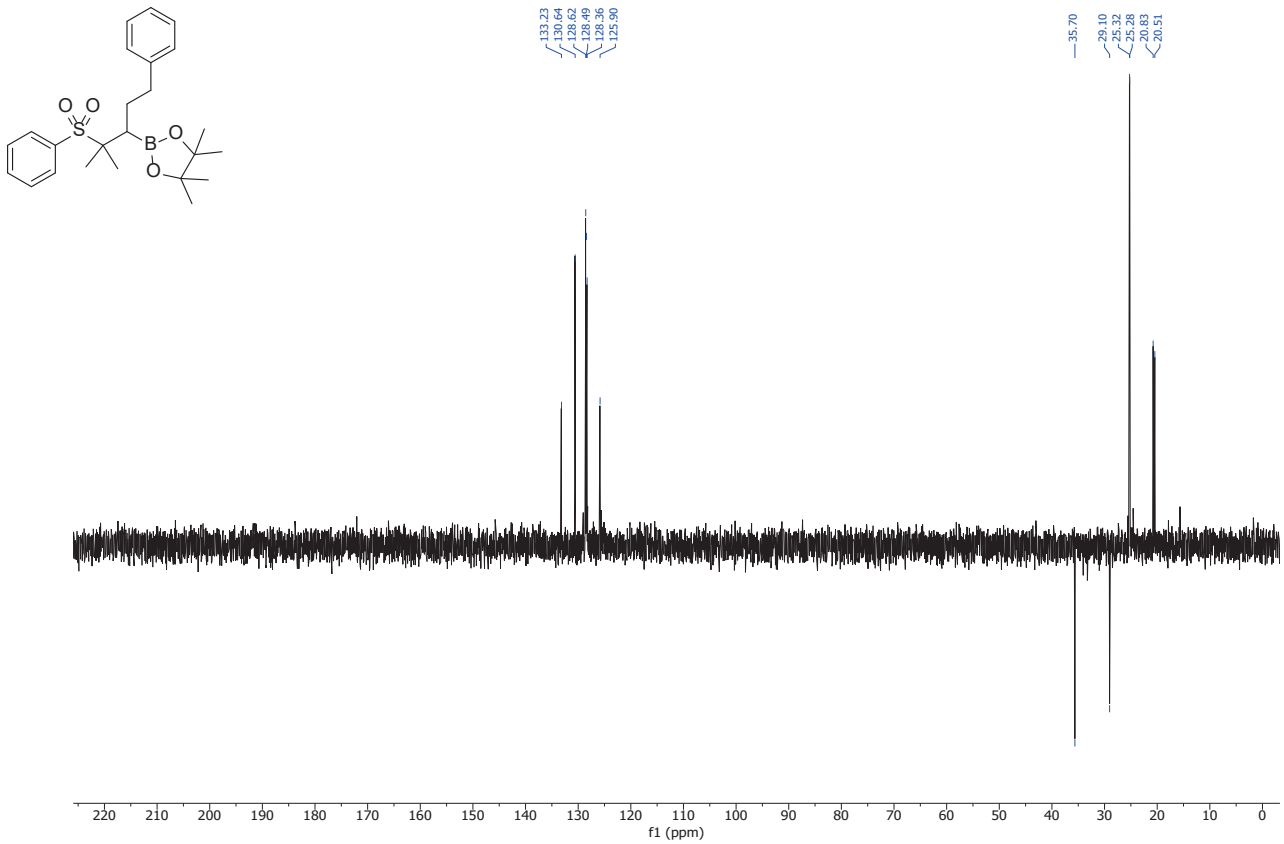
4,4,5,5-tetramethyl-2-(4-methyl-1-phenyl-4-(phenylsulfonyl)pentan-3-yl)-1,3,2-dioxaborolane (18)

^{13}C NMR (75 MHz, $CDCl_3$)



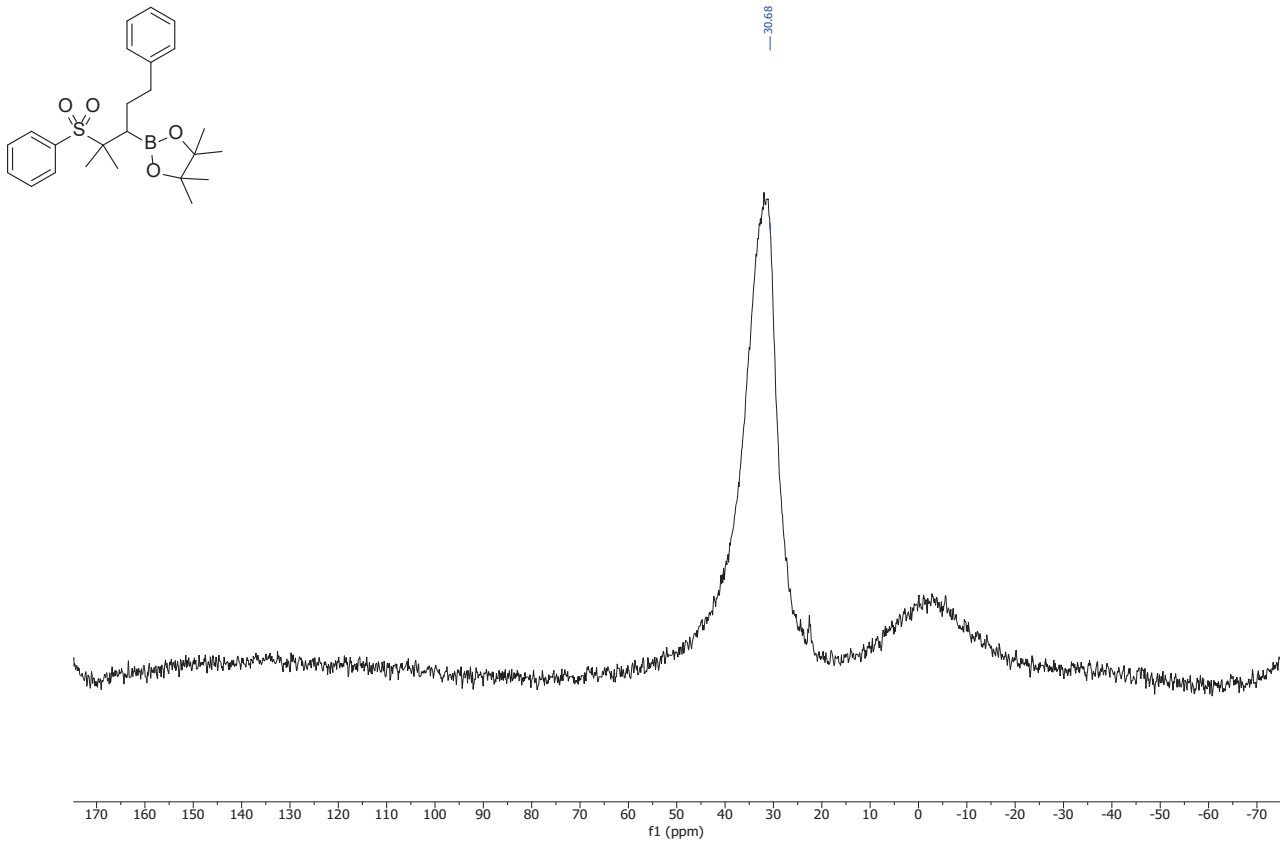
4,4,5,5-tetramethyl-2-(4-methyl-1-phenyl-4-(phenylsulfonyl)pentan-3-yl)-1,3,2-dioxaborolane (18)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



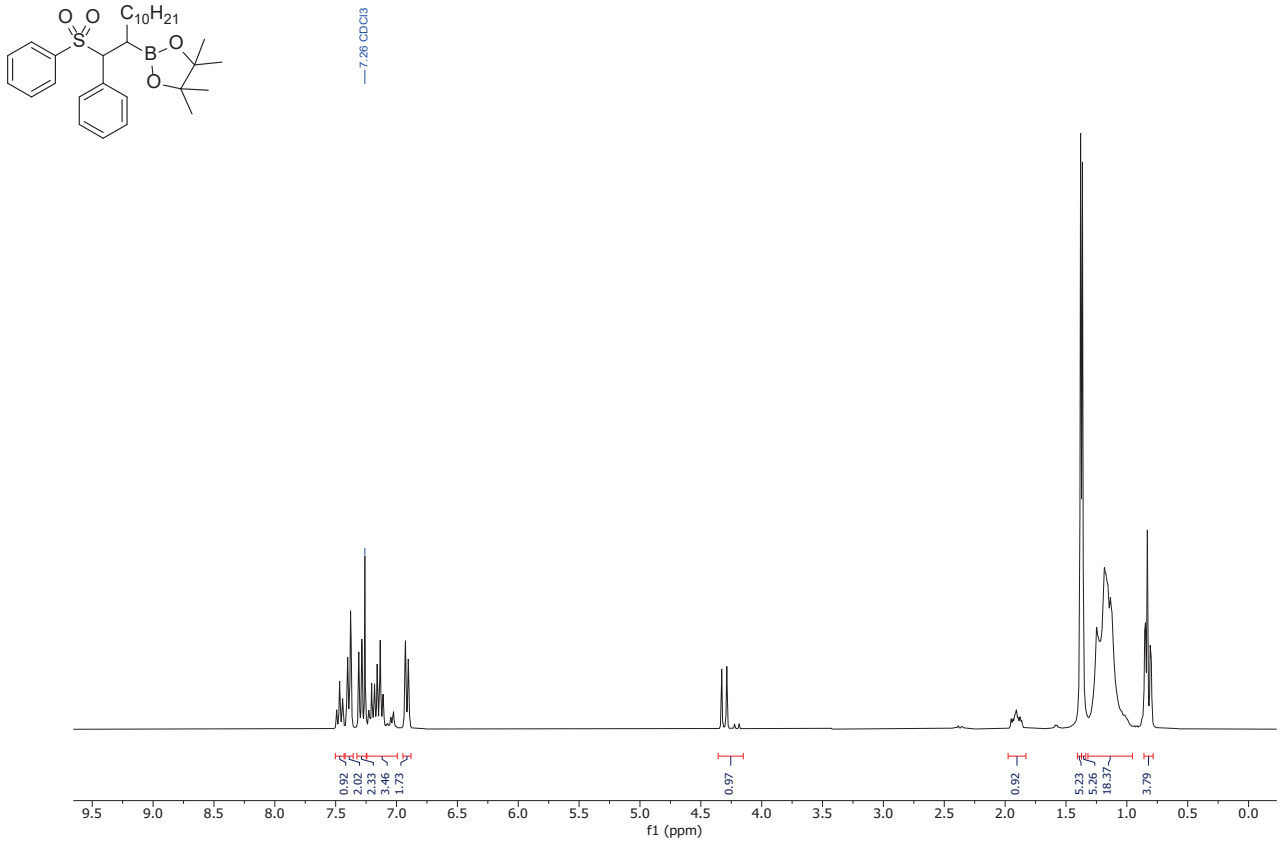
4,4,5,5-tetramethyl-2-(4-methyl-1-phenyl-4-(phenylsulfonyl)pentan-3-yl)-1,3,2-dioxaborolane (18)

^{11}B NMR (96 MHz, $CDCl_3$)

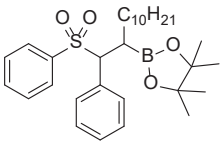


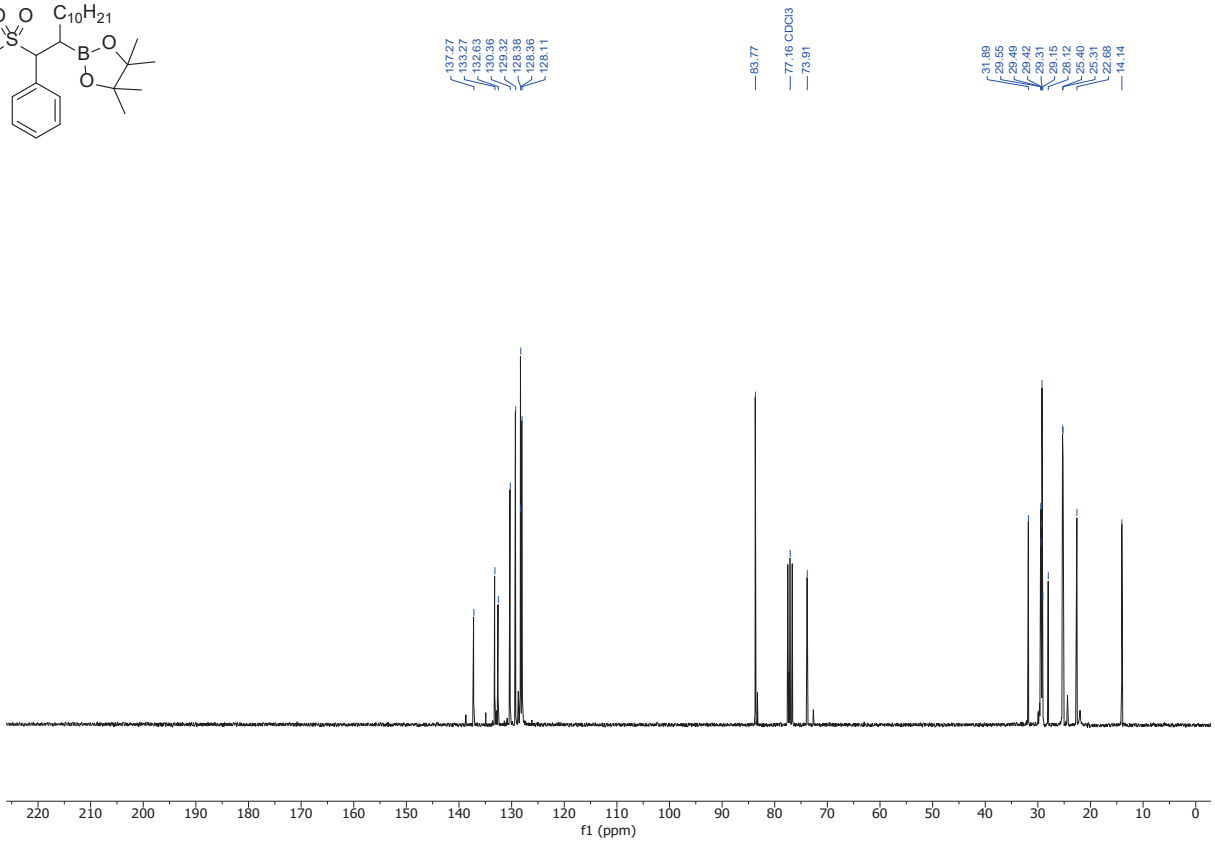
4,4,5,5-tetramethyl-2-(1-phenyl-1-(phenylsulfonyl)dodecan-2-yl)-1,3,2-dioxaborolane (3)
Major diastereomer

^{1}H NMR (300 MHz, $CDCl_3$)

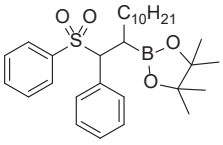


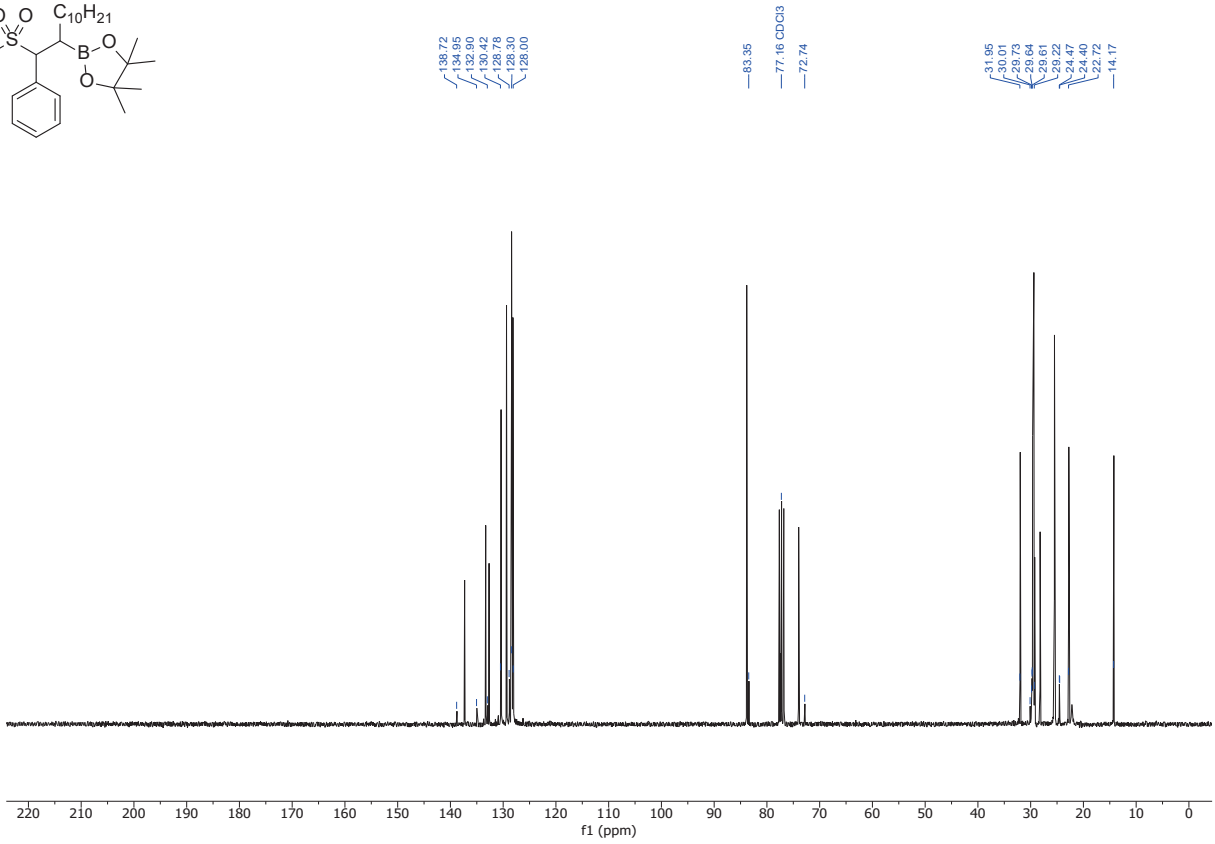
4,4,5,5-tetramethyl-2-(1-phenyl-1-(phenylsulfonyl)dodecan-2-yl)-1,3,2-dioxaborolane (3) ^{13}C NMR (75 MHz, $CDCl_3$)
Major diastereomer





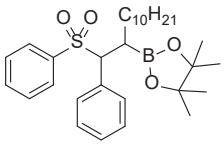
4,4,5,5-tetramethyl-2-(1-phenyl-1-(phenylsulfonyl)dodecan-2-yl)-1,3,2-dioxaborolane (3) ^{13}C NMR (75 MHz, $CDCl_3$)
Minor diastereomer (characteristic signals)

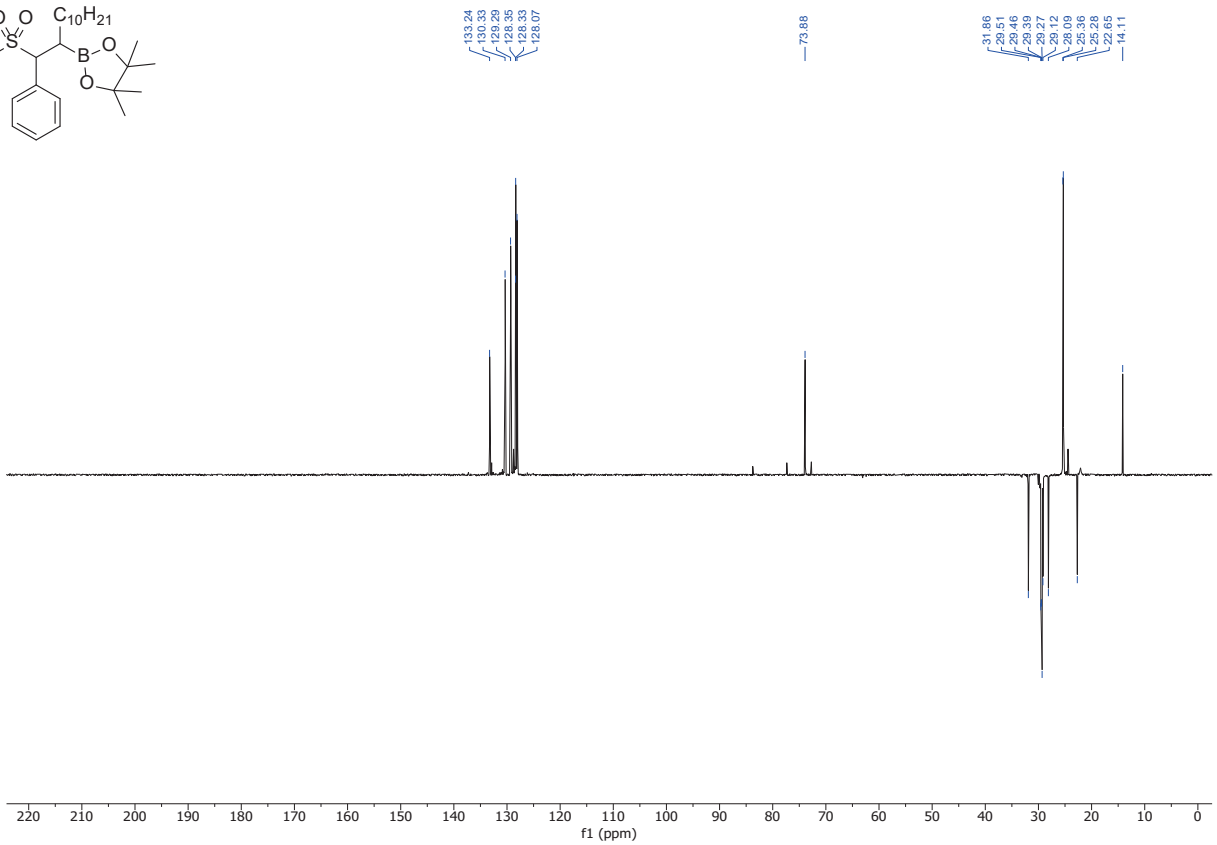




4,4,5,5-tetramethyl-2-(1-phenyl-1-(phenylsulfonyl)dodecan-2-yl)-1,3,2-dioxaborolane (3)
Major diastereomer

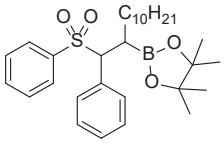
^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

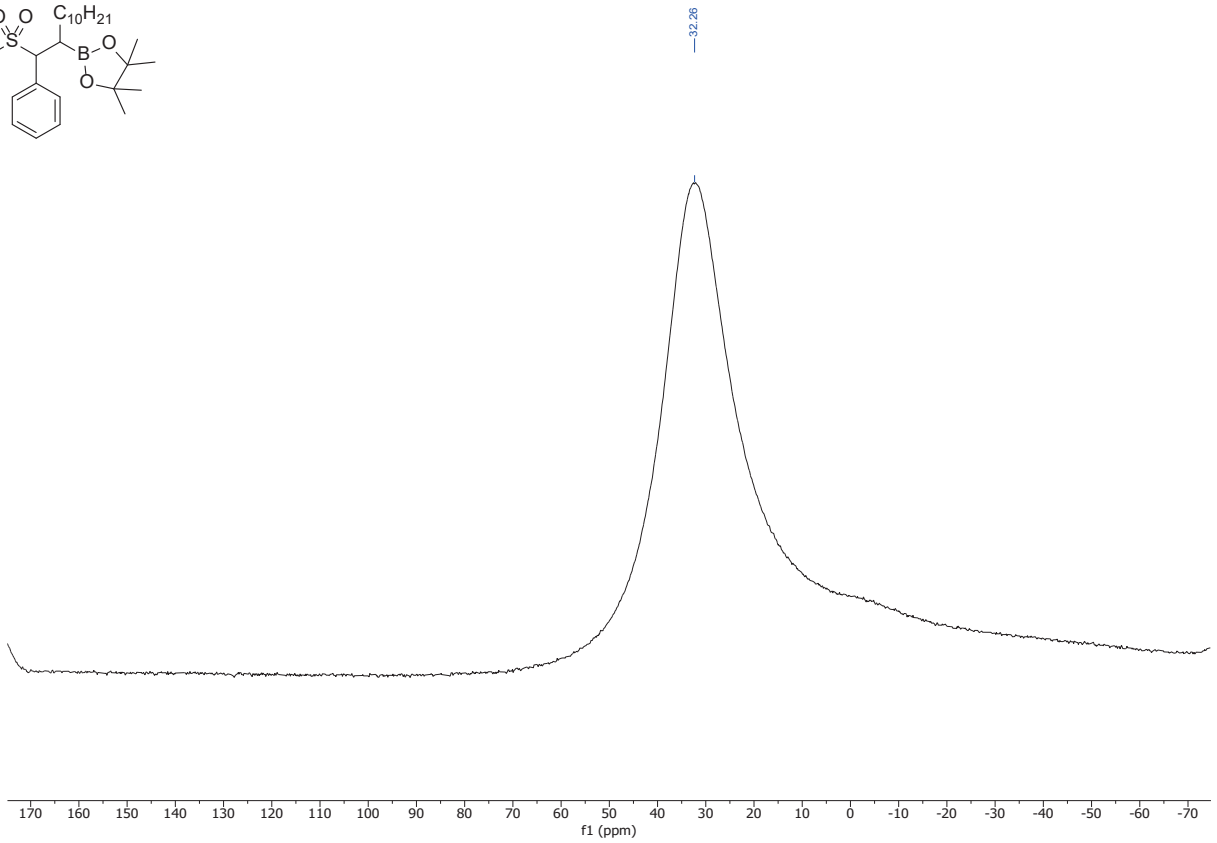




4,4,5,5-tetramethyl-2-(1-phenyl-1-(phenylsulfonyl)dodecan-2-yl)-1,3,2-dioxaborolane (3)
Mix of diastereomer

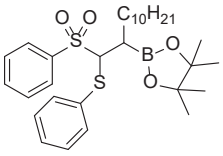
^{11}B NMR (96 MHz, $CDCl_3$)

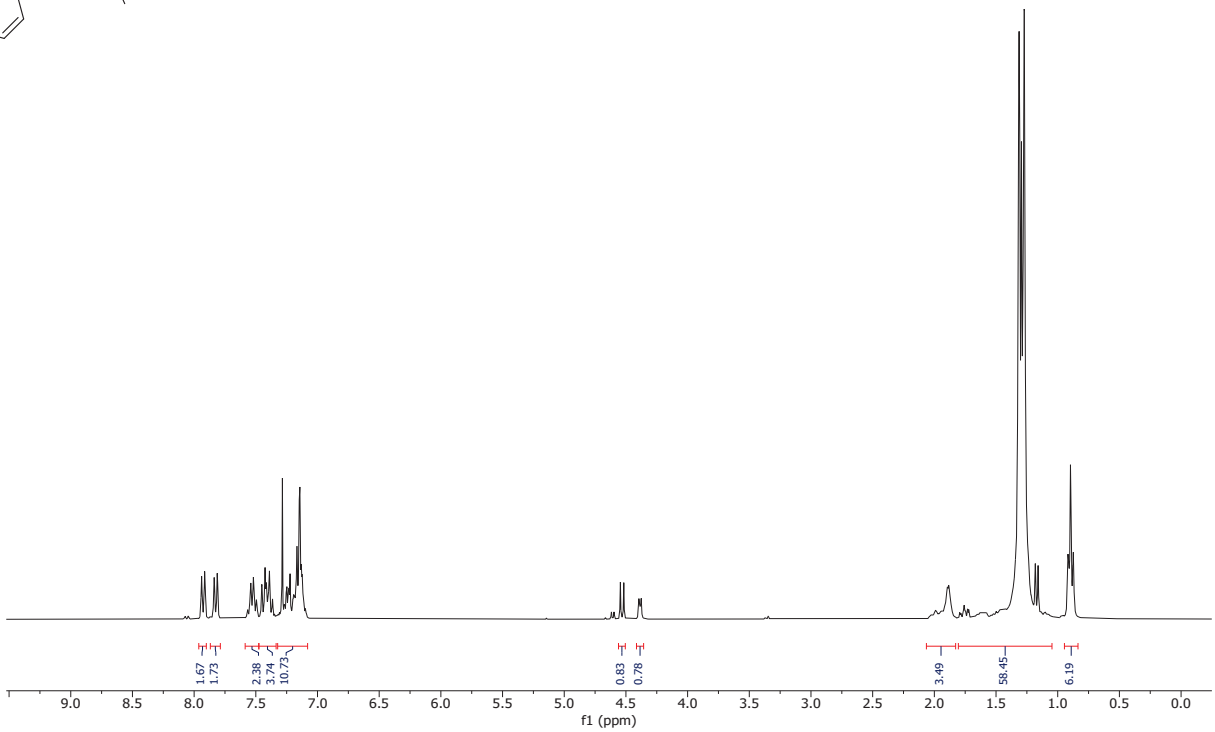




4,4,5,5-tetramethyl-2-(1-(phenylsulfonyl)-1-(phenylthio)dodecan-2-yl)-1,3,2-dioxaborolane (75)
Mix of diastereomers

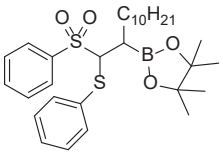
^{1}H NMR (300 MHz, $CDCl_3$)

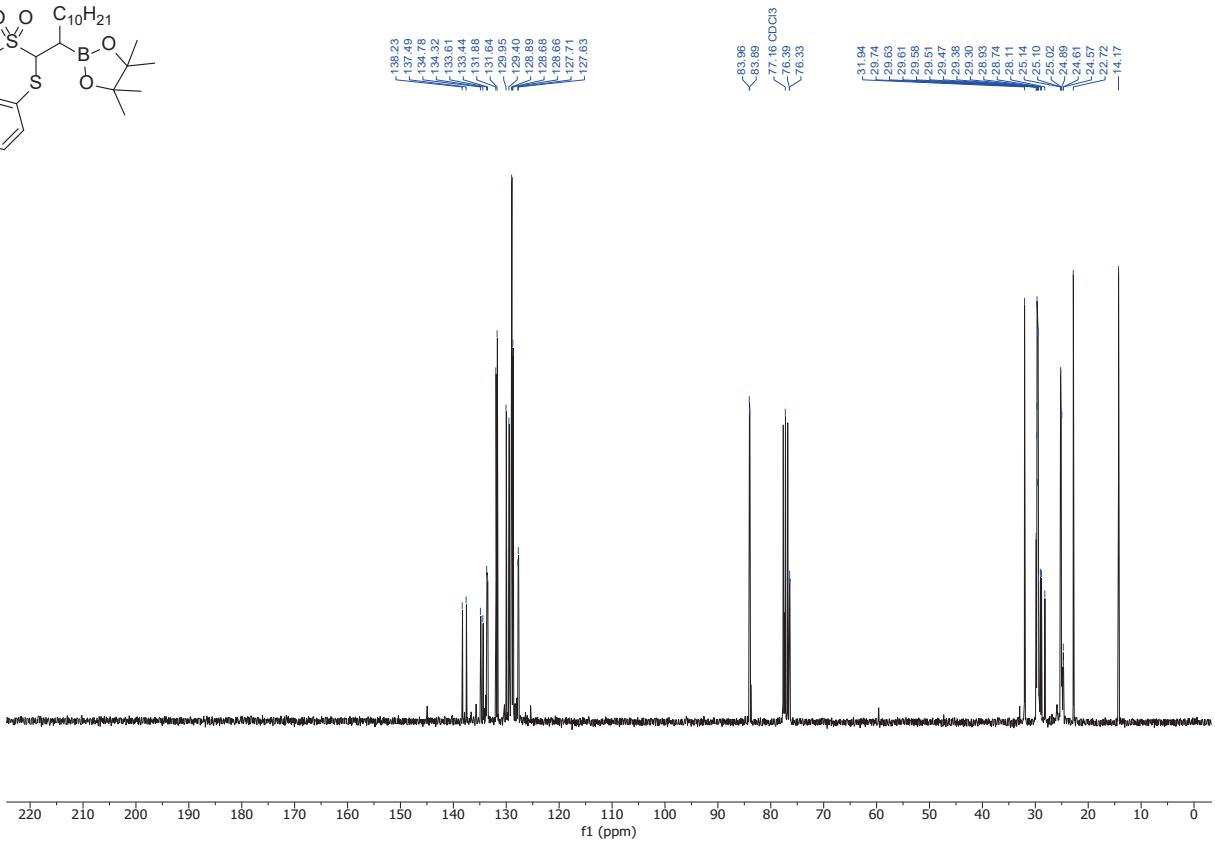




4,4,5,5-tetramethyl-2-(1-(phenylsulfonyl)-1-(phenylthio)dodecan-2-yl)-1,3,2-dioxaborolane (75)
Mix of diastereomers

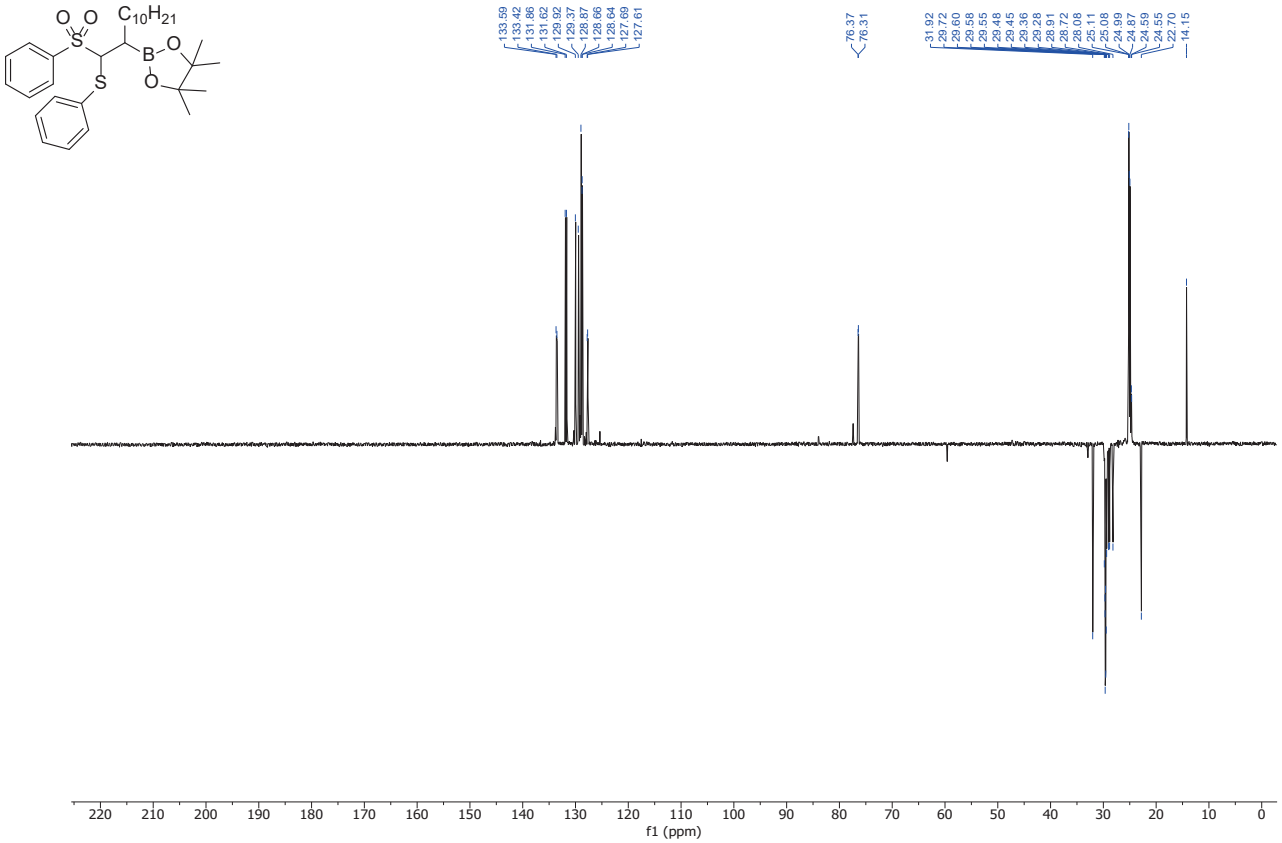
^{13}C NMR (75 MHz, $CDCl_3$)





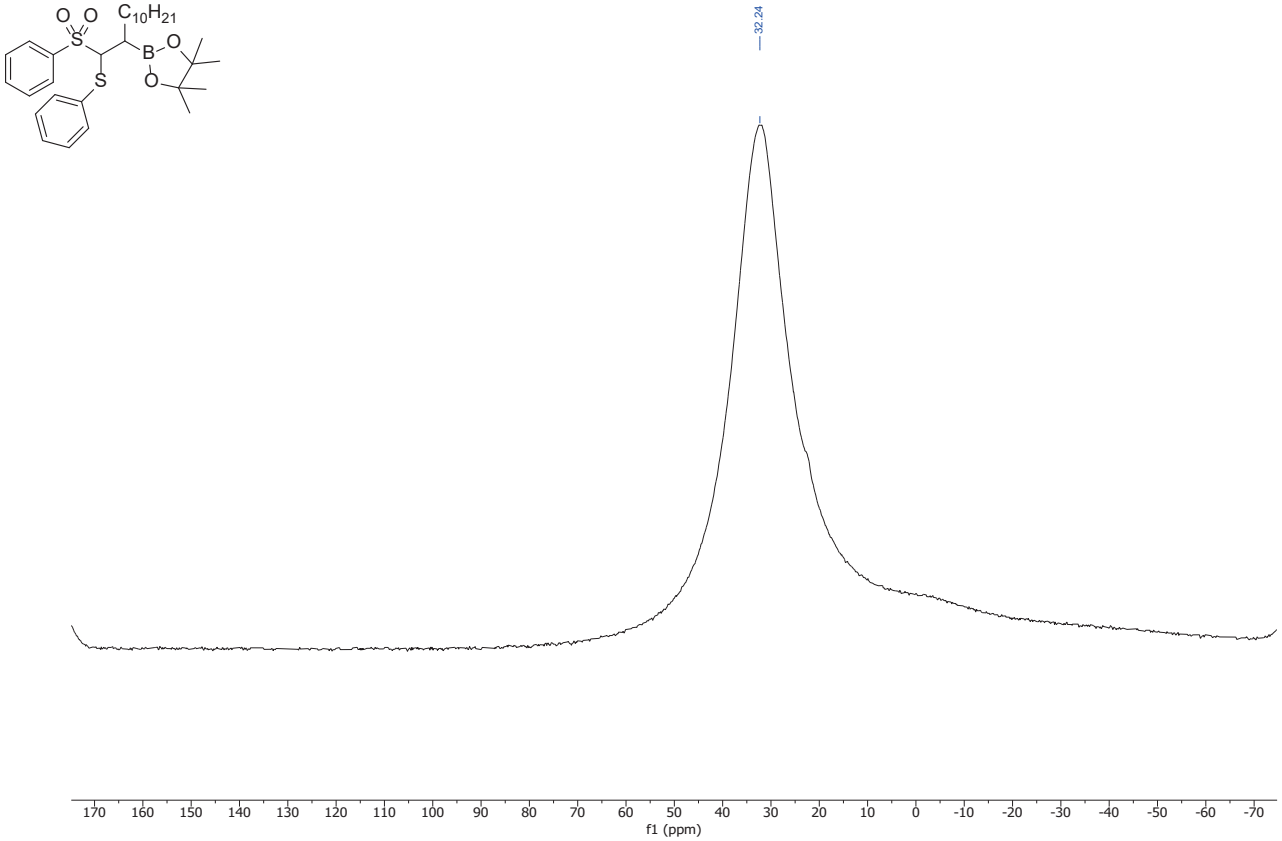
4,4,5,5-tetramethyl-2-(1-(phenylsulfonyl)-1-(phenylthio)dodecan-2-yl)-1,3,2-dioxaborolane (75)
Mix of diastereomers

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



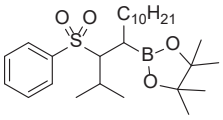
4,4,5,5-tetramethyl-2-(1-(phenylsulfonyl)-1-(phenylthio)dodecan-2-yl)-1,3,2-dioxaborolane (75)
Mix of diastereomers

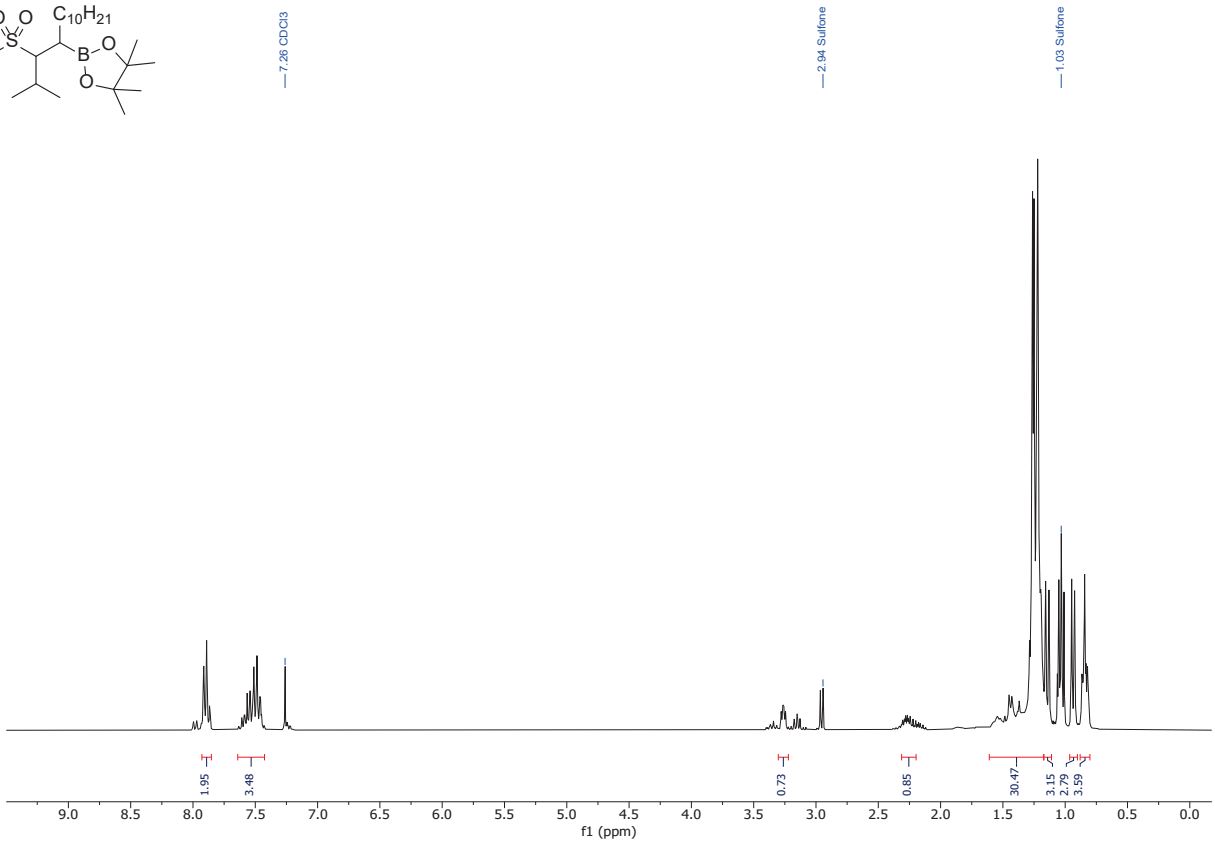
^{11}B NMR (96 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-(2-methyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (15)
Major diastereomer

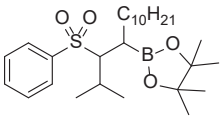
^{1}H NMR (300 MHz, $CDCl_3$)

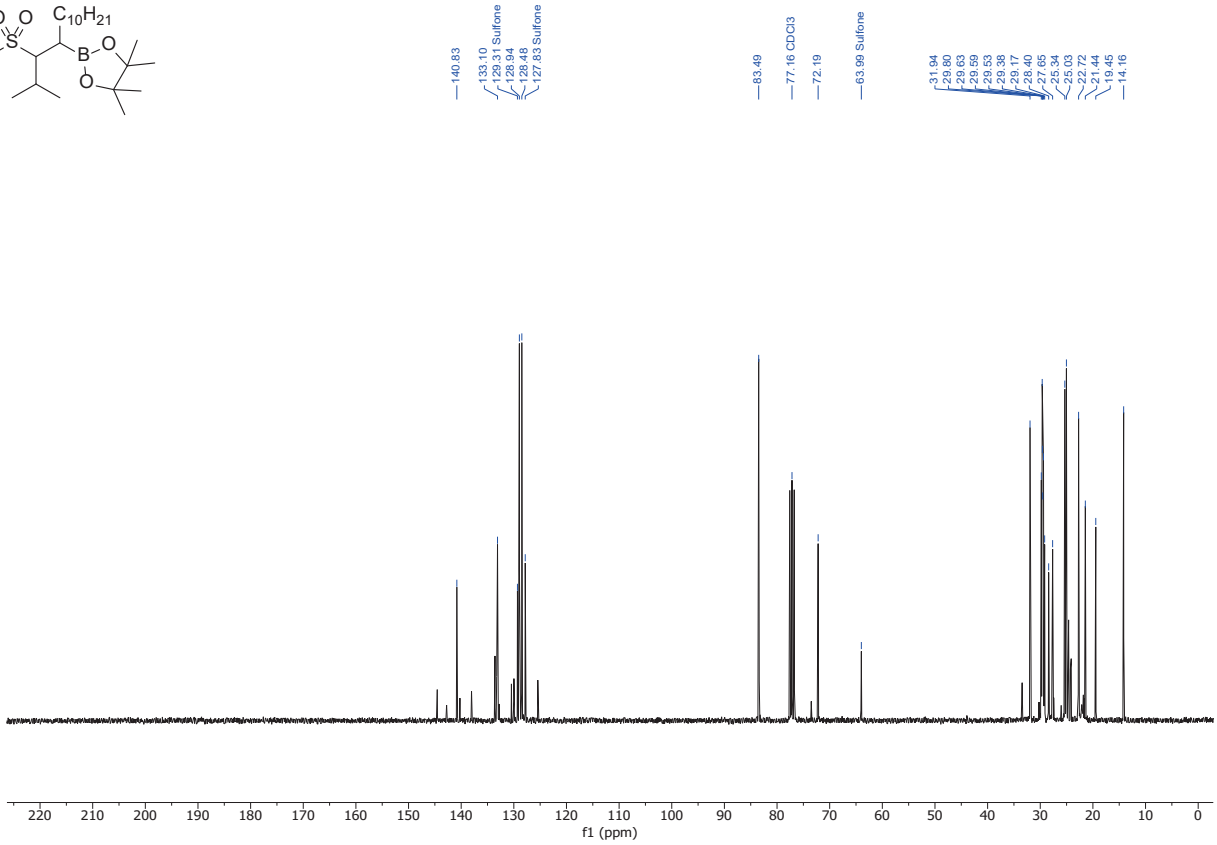




4,4,5,5-tetramethyl-2-(2-methyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (15)
Major diastereomer

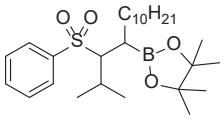
^{13}C NMR (75 MHz, $CDCl_3$)

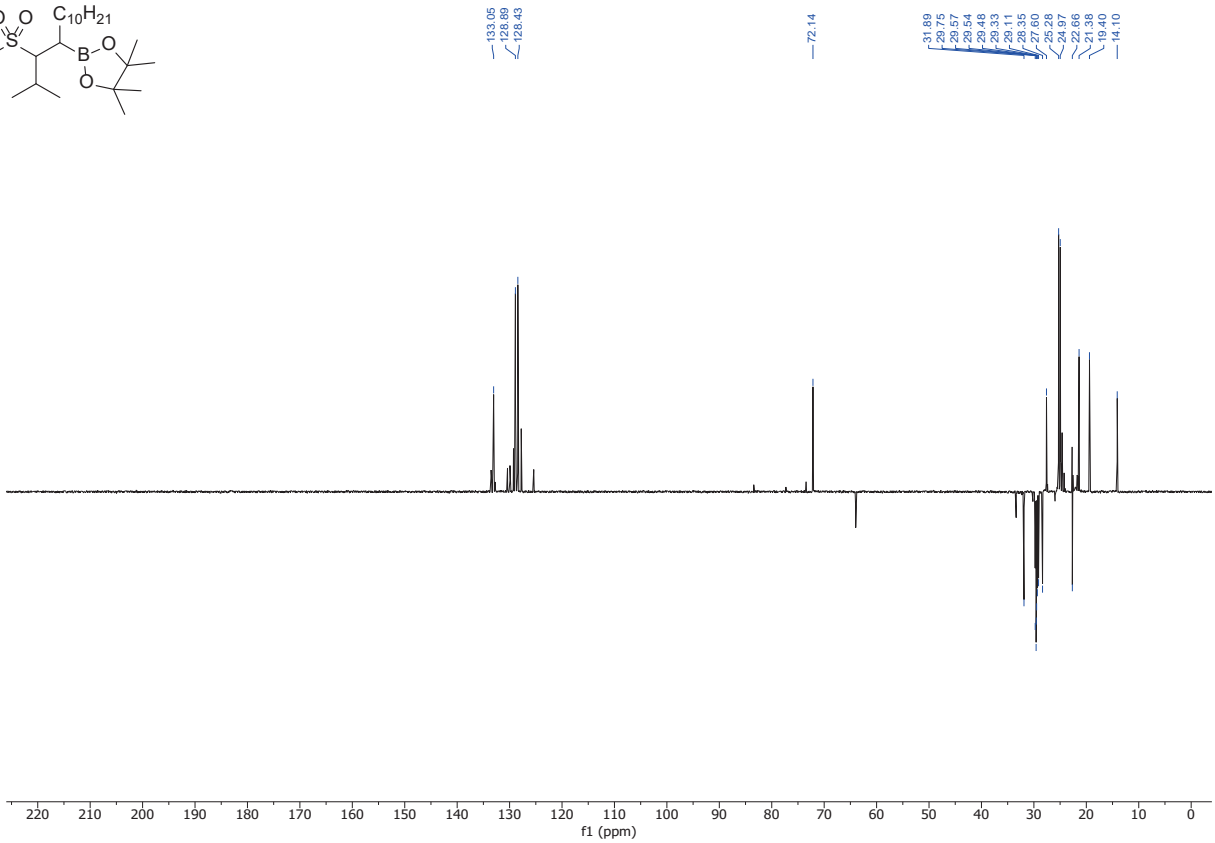




4,4,5,5-tetramethyl-2-(2-methyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (15)
Major diastereomer

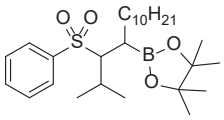
^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

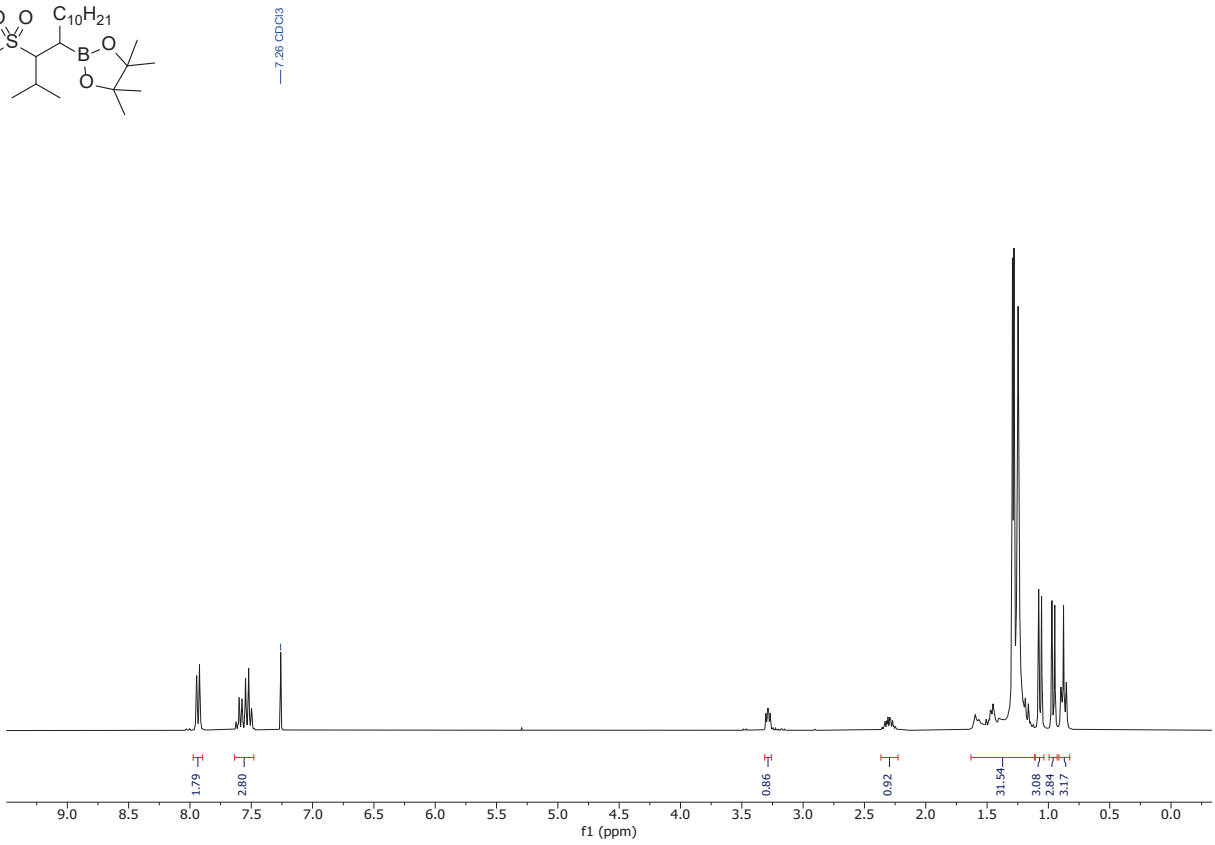




4,4,5,5-tetramethyl-2-(2-methyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (15)
Minor diastereomer

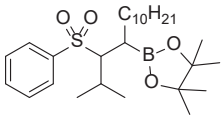
^{1}H NMR (300 MHz, $CDCl_3$)

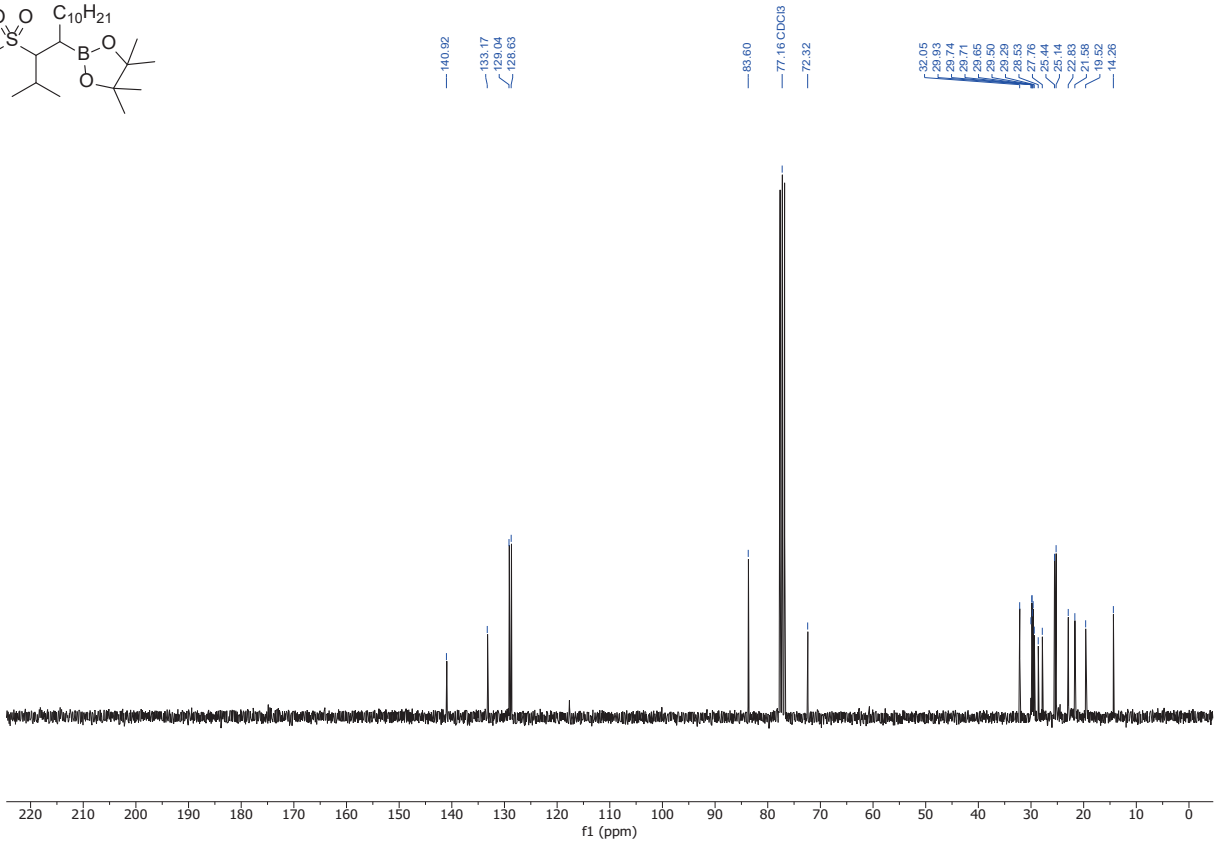




4,4,5,5-tetramethyl-2-(2-methyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (15)
Minor diastereomer

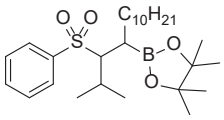
^{13}C NMR (75 MHz, $CDCl_3$)

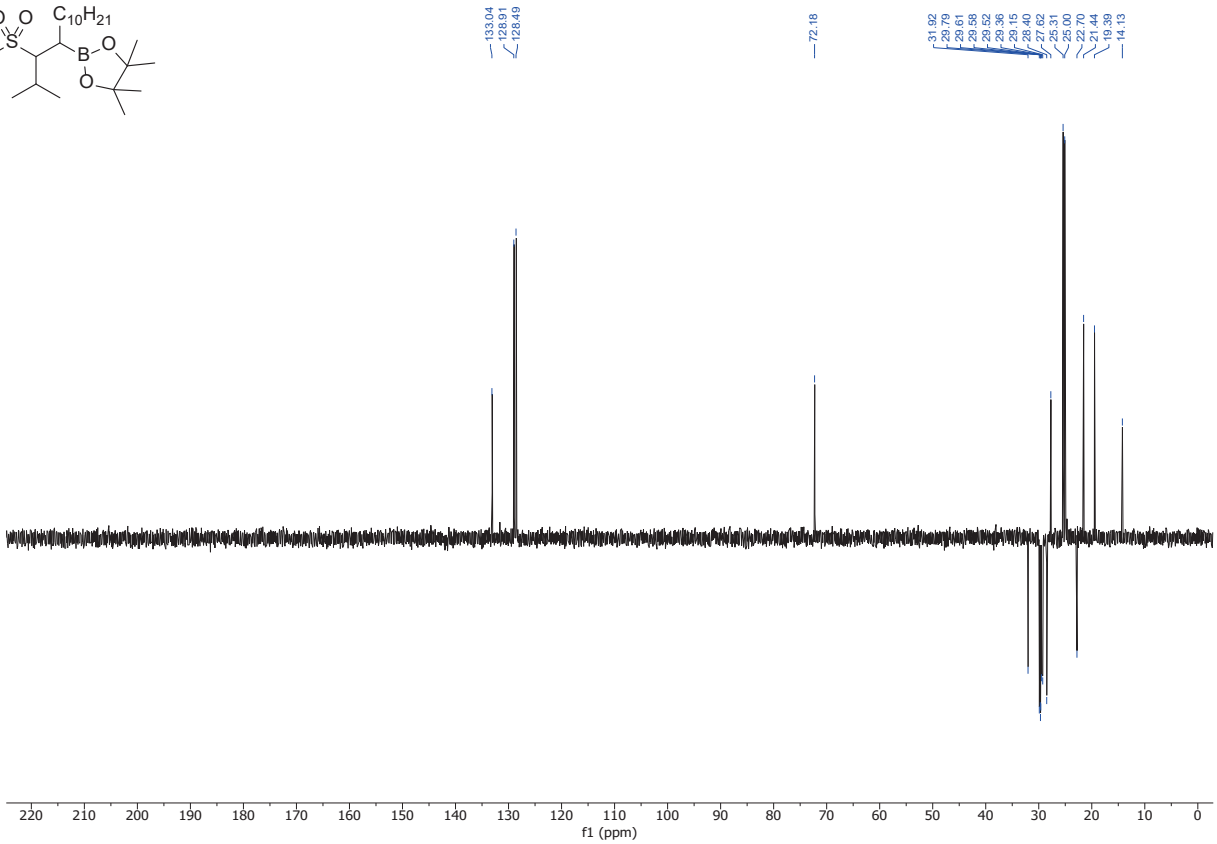




4,4,5,5-tetramethyl-2-(2-methyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (15)
Minor diastereomer

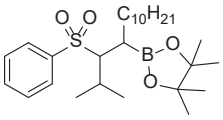
^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

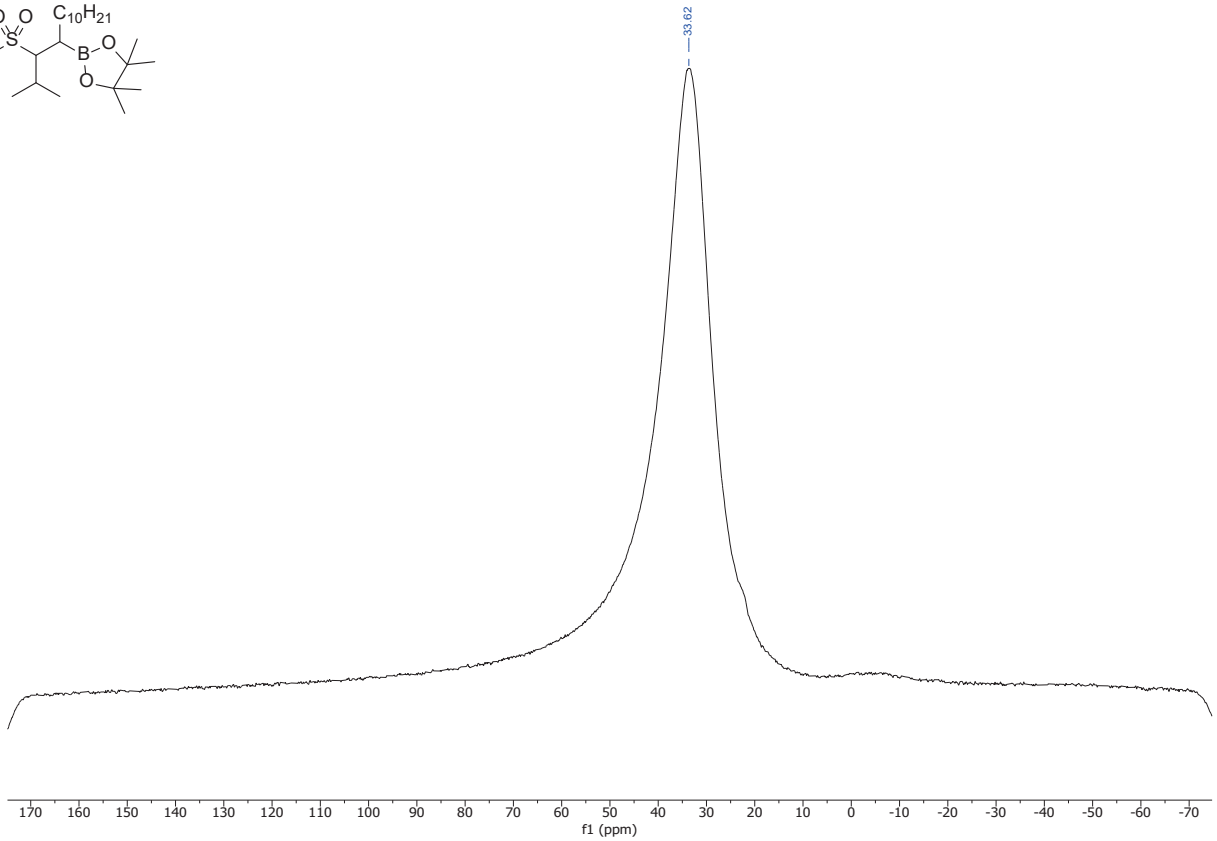




4,4,5,5-tetramethyl-2-(2-methyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (15)
Mix of diastereomer

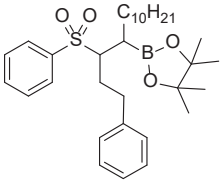
^{11}B NMR (96 MHz, $CDCl_3$)

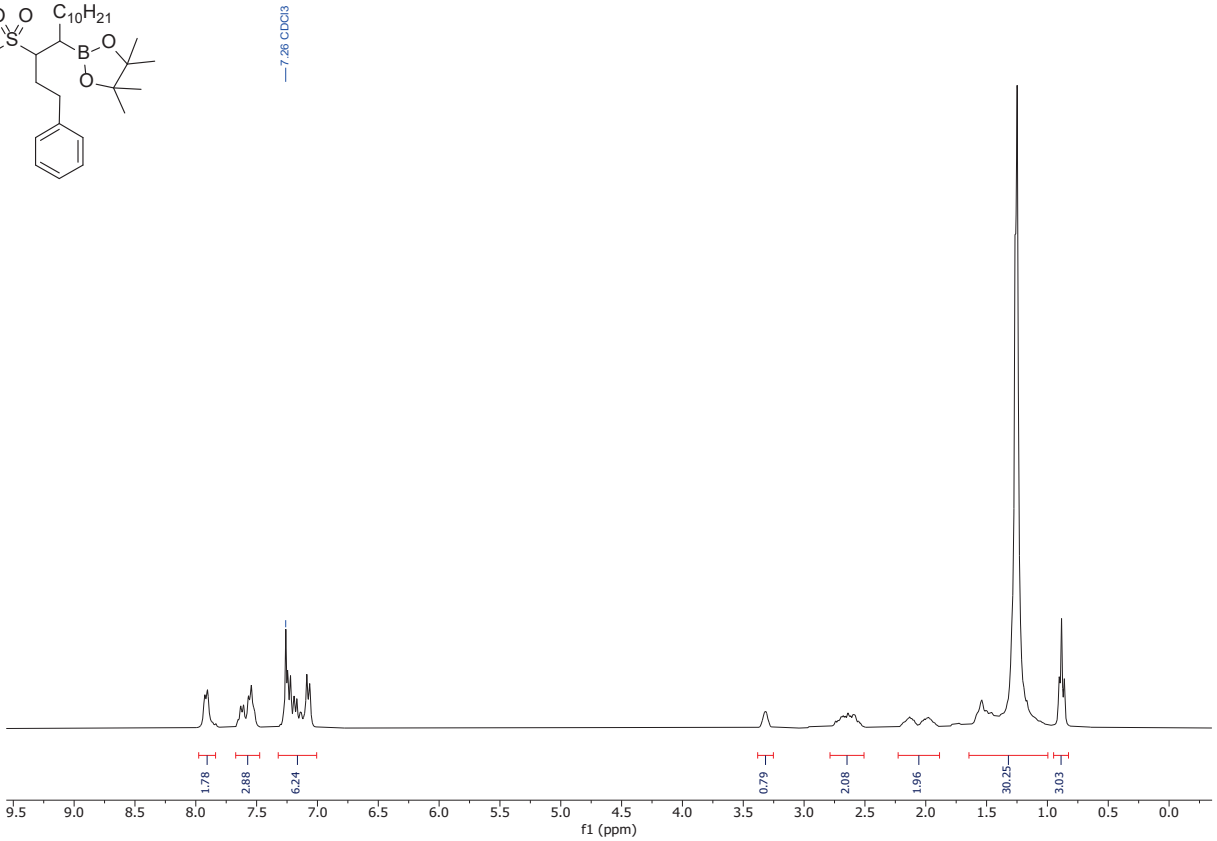




4,4,5,5-tetramethyl-2-(1-phenyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (22)
Major diastereomer

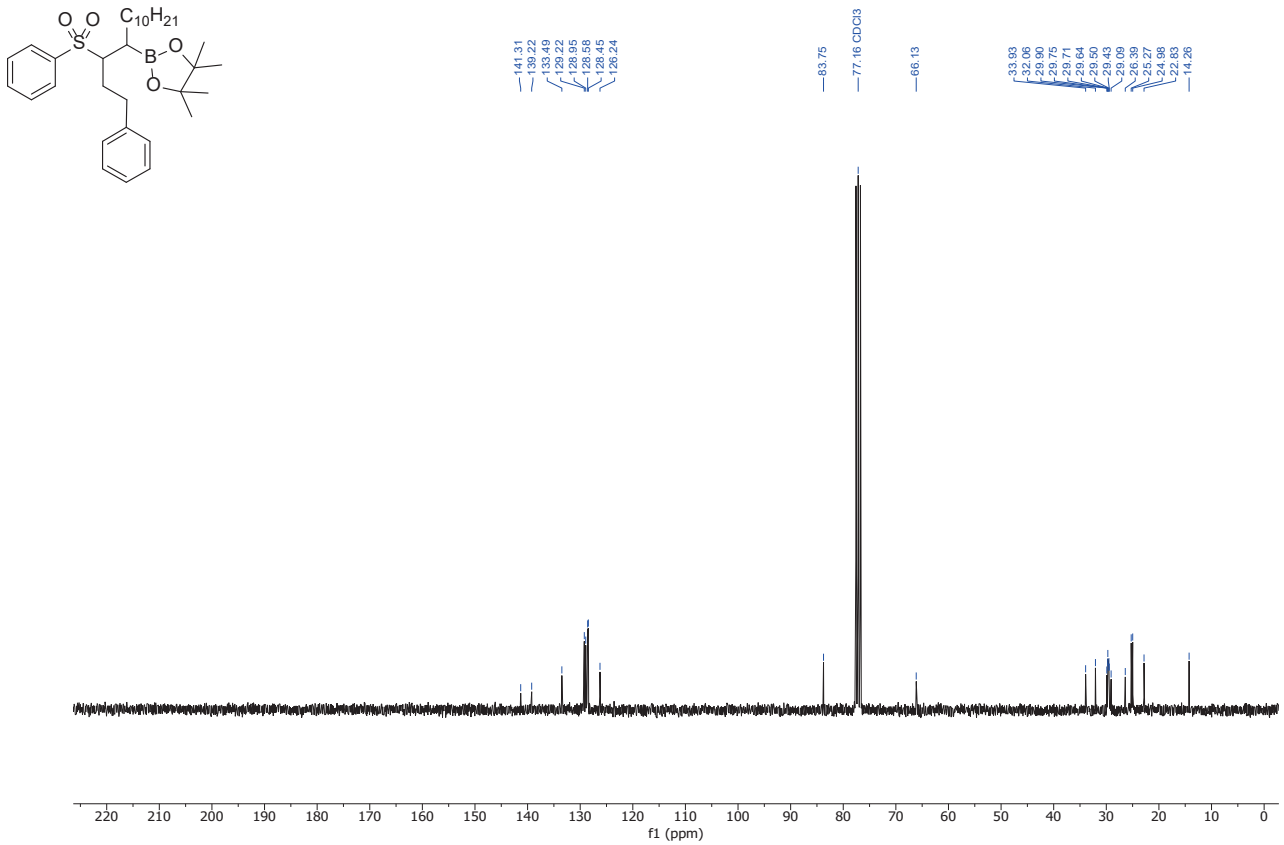
^{1}H NMR (300 MHz, $CDCl_3$)





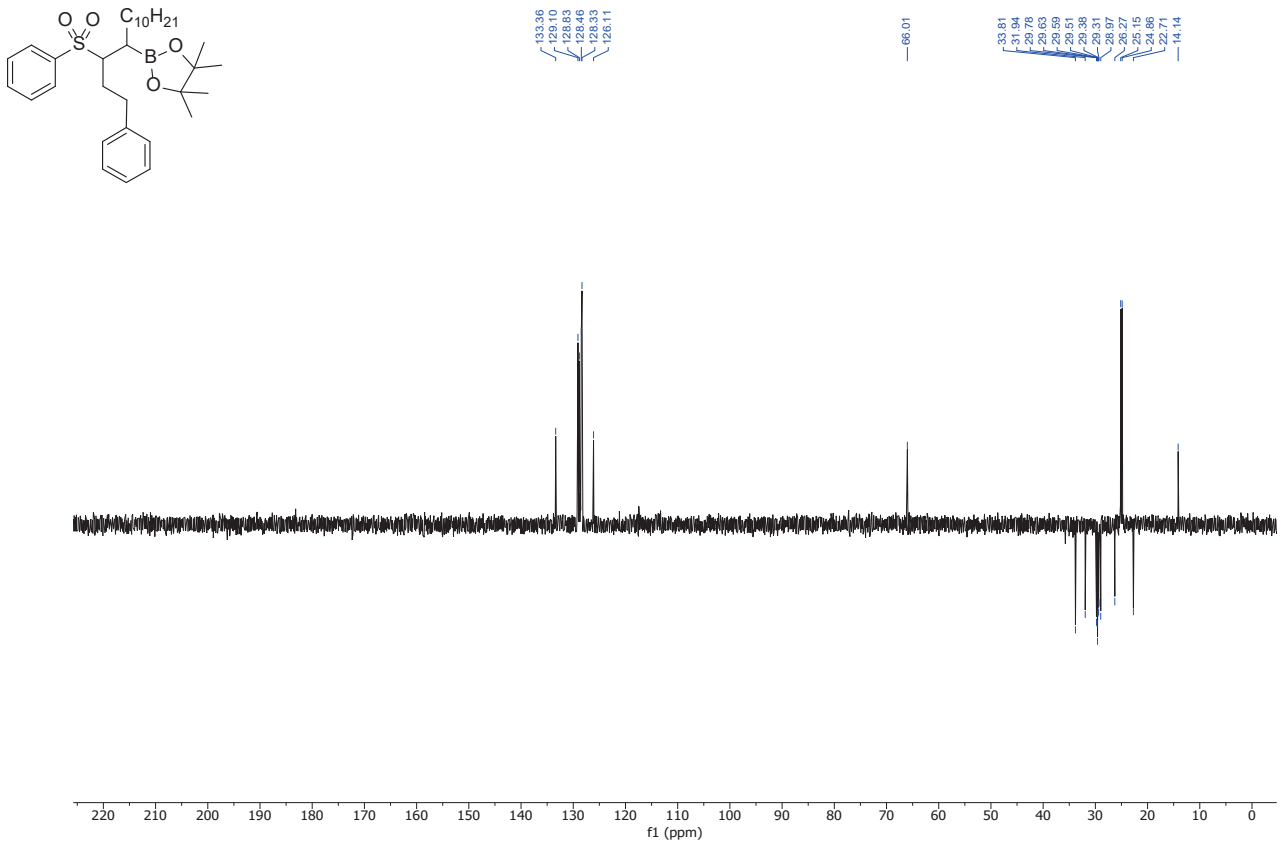
4,4,5,5-tetramethyl-2-(1-phenyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (22)
Major diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



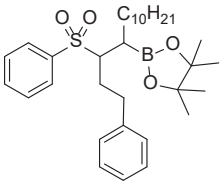
4,4,5,5-tetramethyl-2-(1-phenyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (22)
Major diastereomer

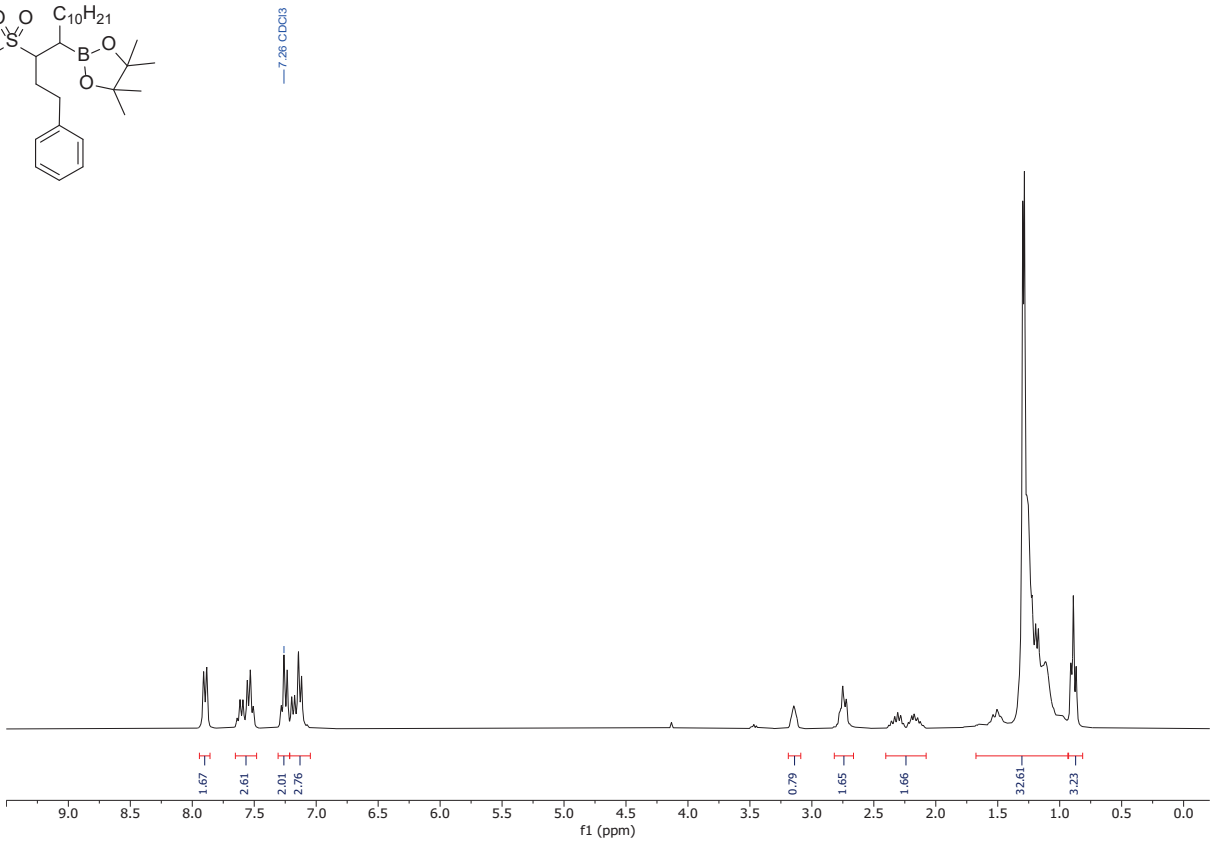
^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-(1-phenyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (22)
Minor diastereomer

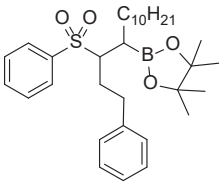
^{1}H NMR (300 MHz, $CDCl_3$)

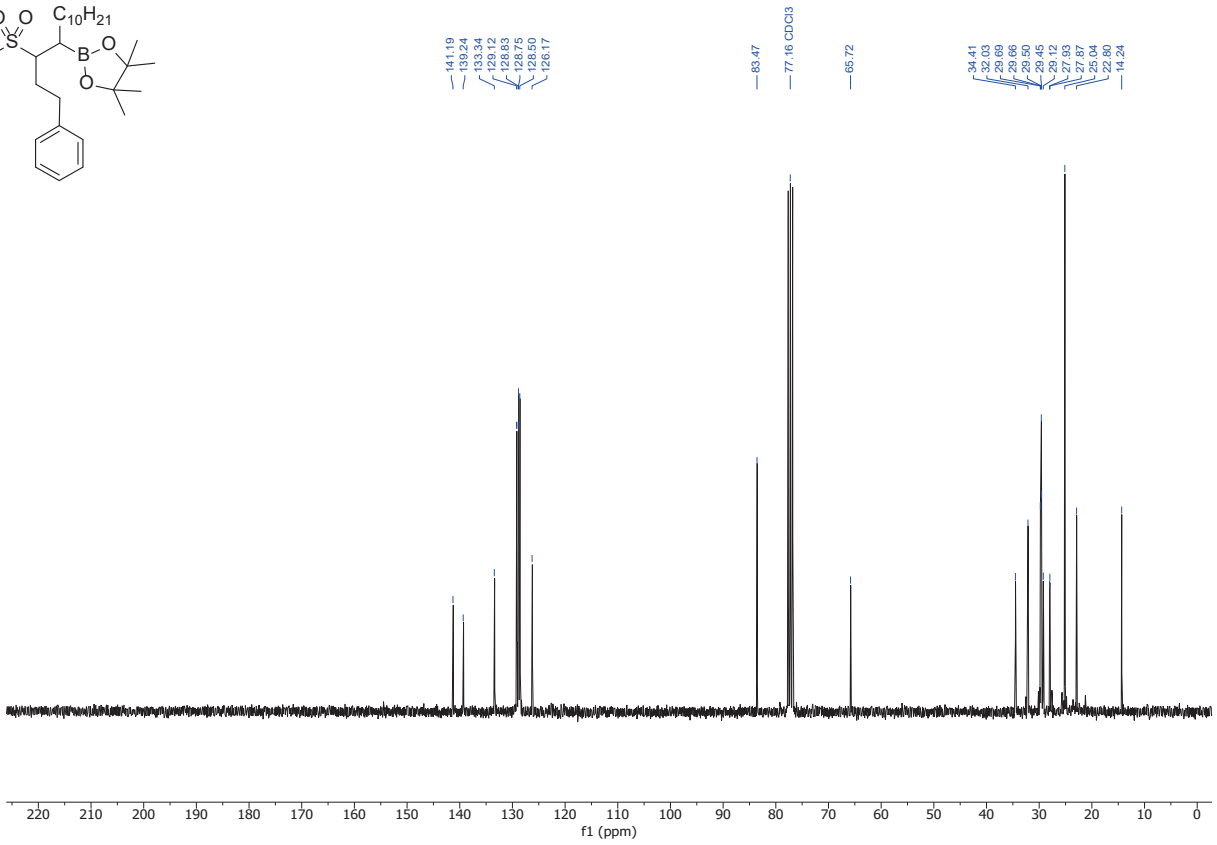




4,4,5,5-tetramethyl-2-(1-phenyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (22)
Minor diastereomer

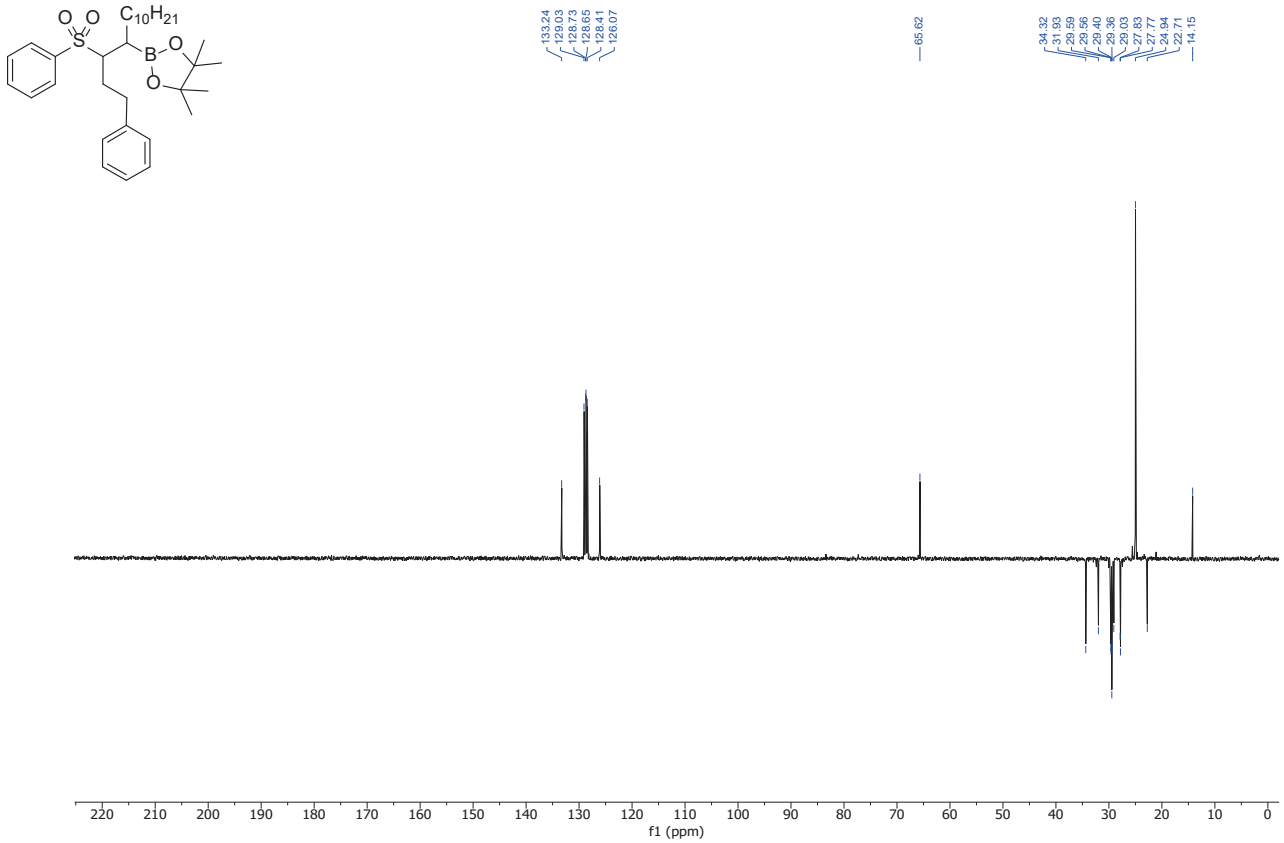
^{13}C NMR (75 MHz, $CDCl_3$)





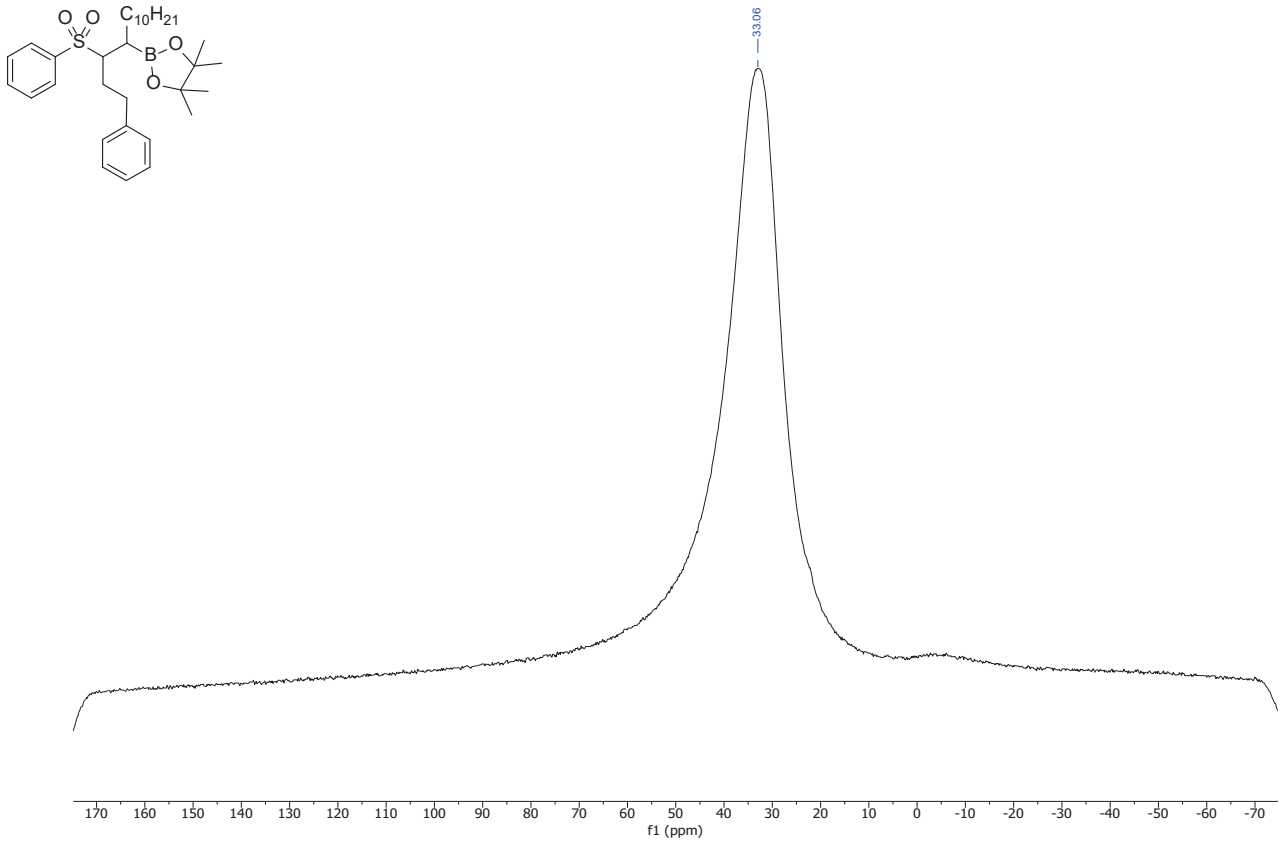
4,4,5,5-tetramethyl-2-(1-phenyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (22)
Minor diastereomer

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



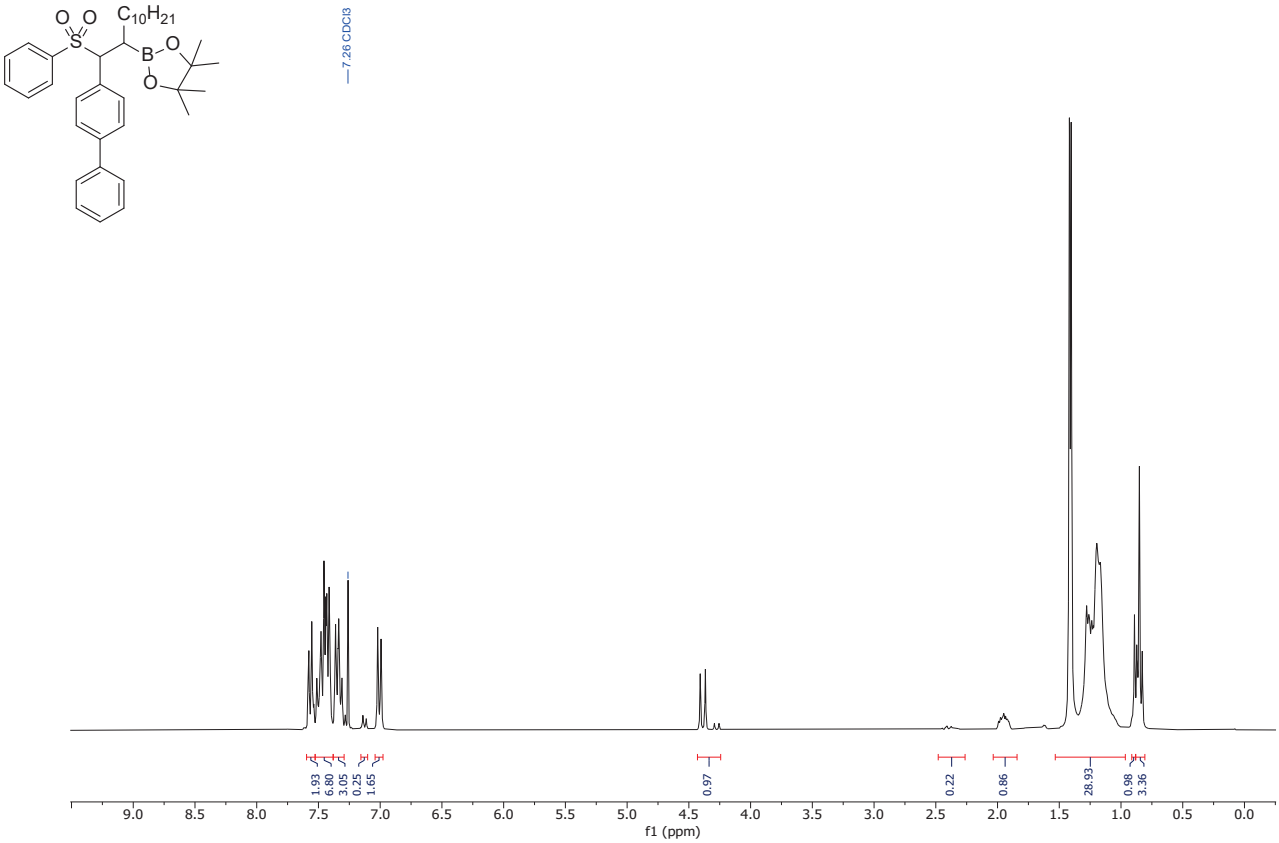
4,4,5,5-tetramethyl-2-(1-phenyl-3-(phenylsulfonyl)tetradecan-4-yl)-1,3,2-dioxaborolane (22)
Mix of diastereomers

^{11}B NMR (96 MHz, $CDCl_3$)



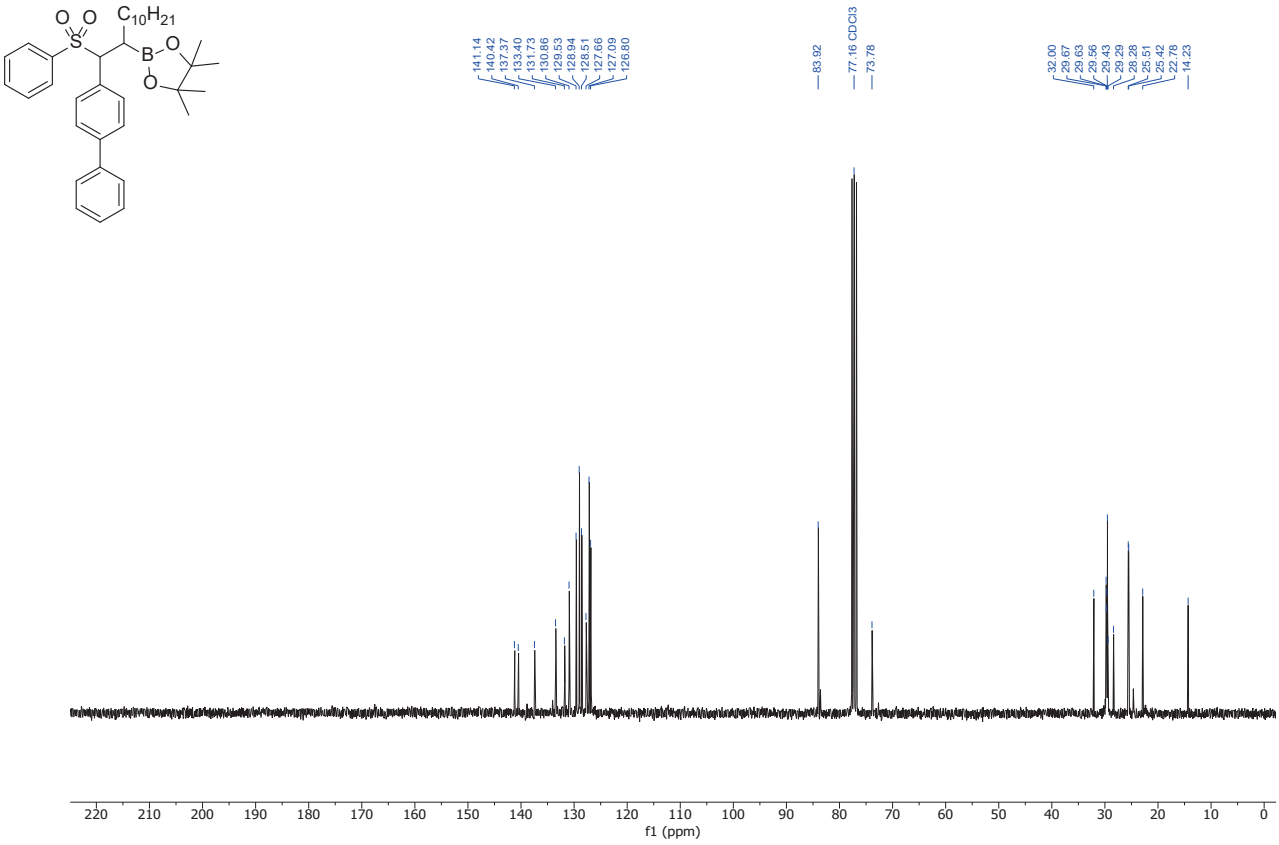
2-(1-([1,1'-biphenyl]-4-yl)-1-(phenylsulfonyl)dodecan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28)
Mix of diastereomers

^{1}H NMR (300 MHz, $CDCl_3$)



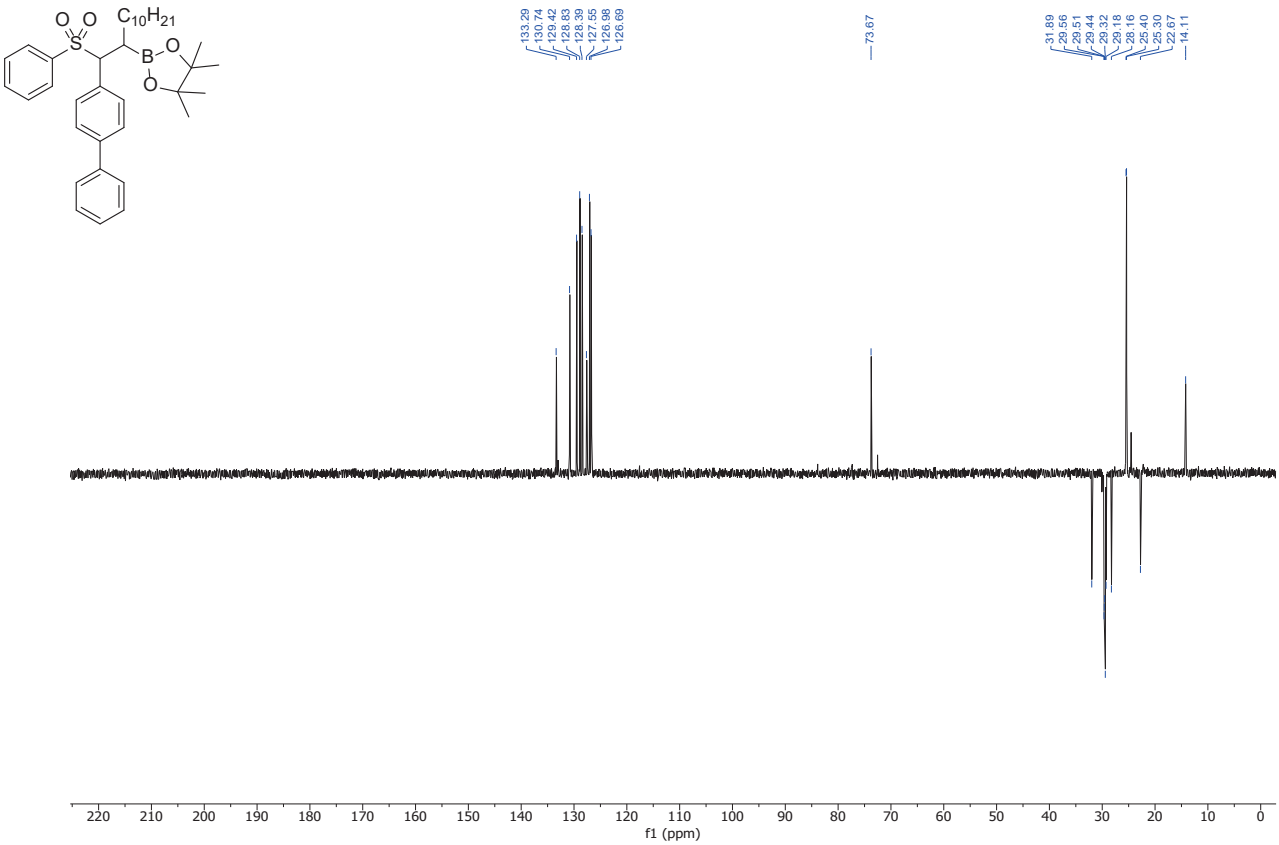
2-(1-([1,1'-biphenyl]-4-yl)-1-(phenylsulfonyl)dodecan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28)
Major diastereomer

^{13}C NMR (75 MHz, $CDCl_3$)



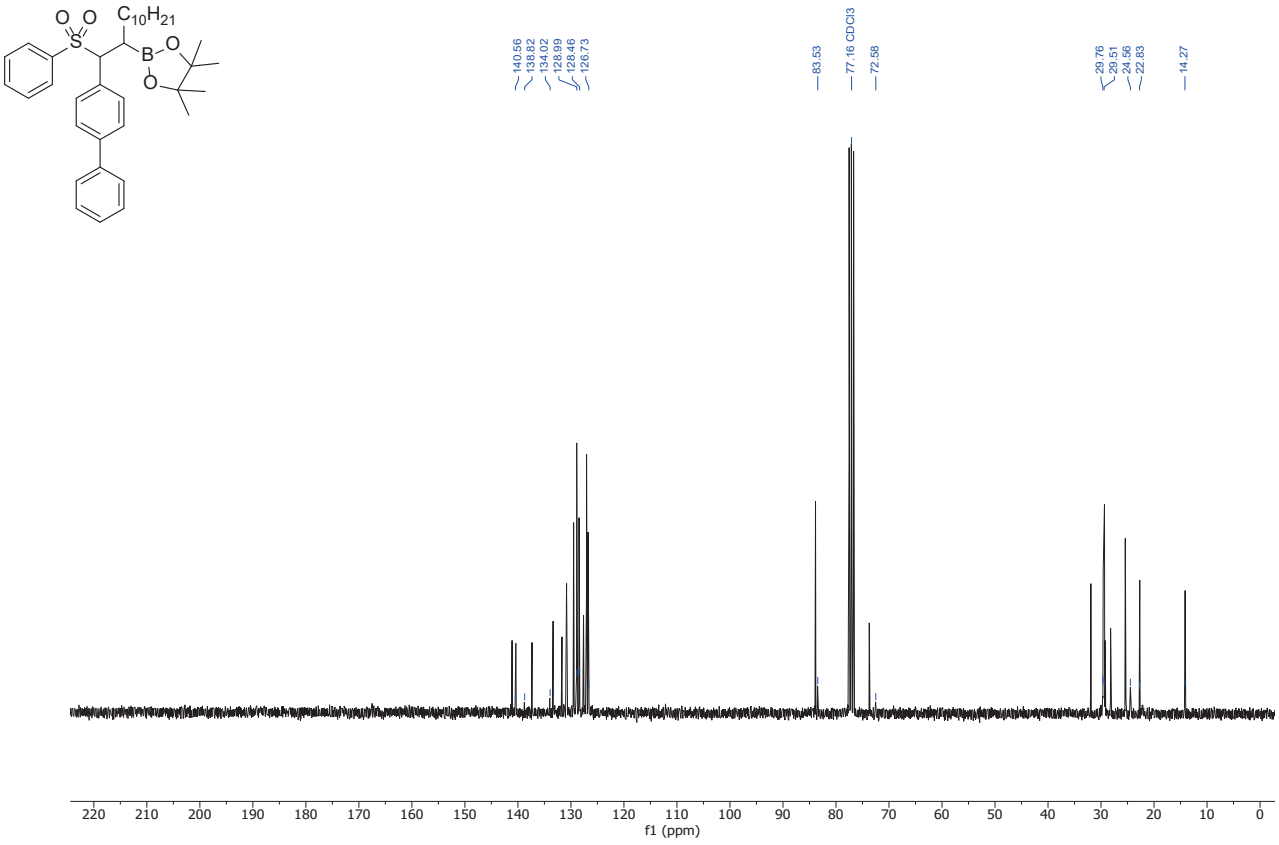
2-(1-([1,1'-biphenyl]-4-yl)-1-(phenylsulfonyl)dodecan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28)
Major diastereomer

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



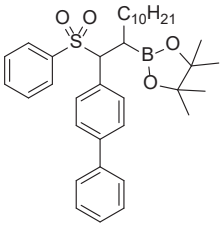
2-(1-([1,1'-biphenyl]-4-yl)-1-(phenylsulfonyl)dodecan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28)
Minor diastereomer

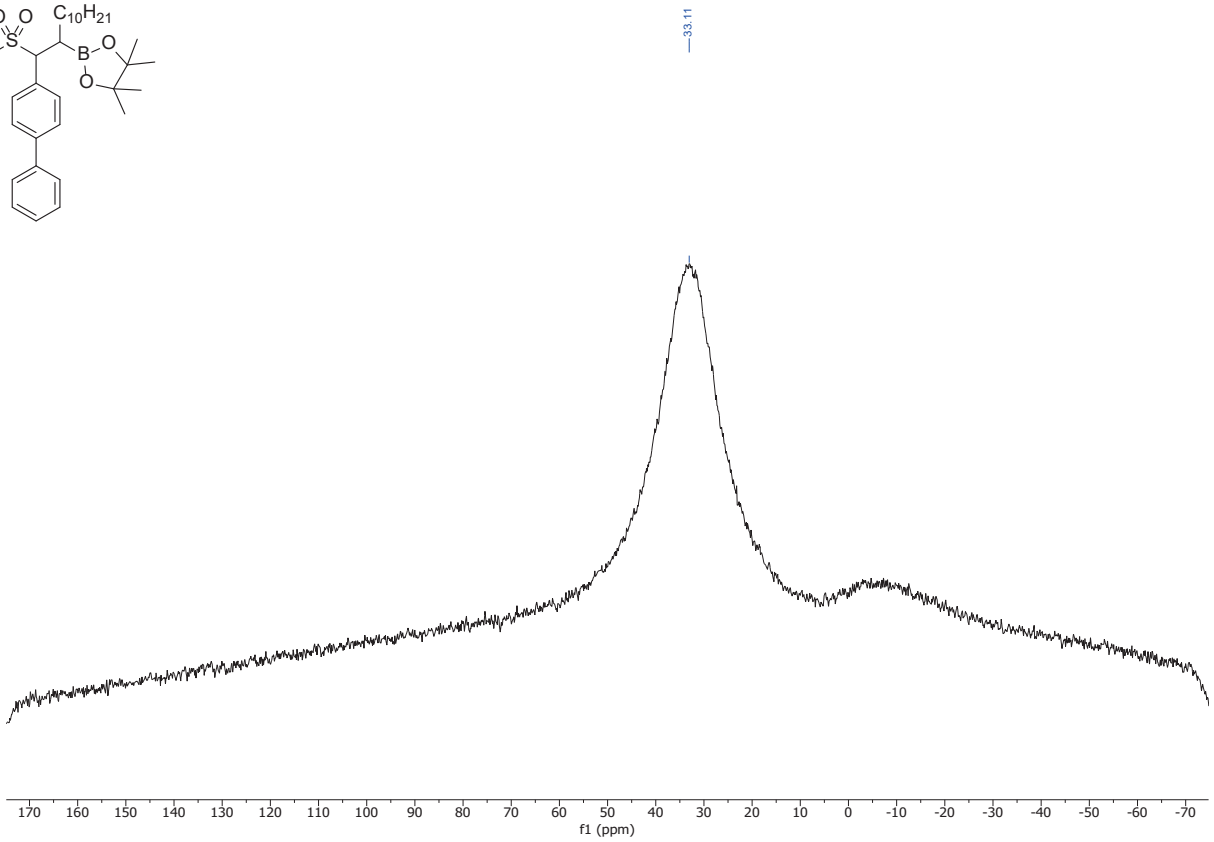
^{13}C NMR (75 MHz, $CDCl_3$)



2-(1-([1,1'-biphenyl]-4-yl)-1-(phenylsulfonyl)dodecan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28)
Mix of diastereomers

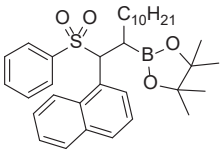
^{11}B NMR (96 MHz, $CDCl_3$)

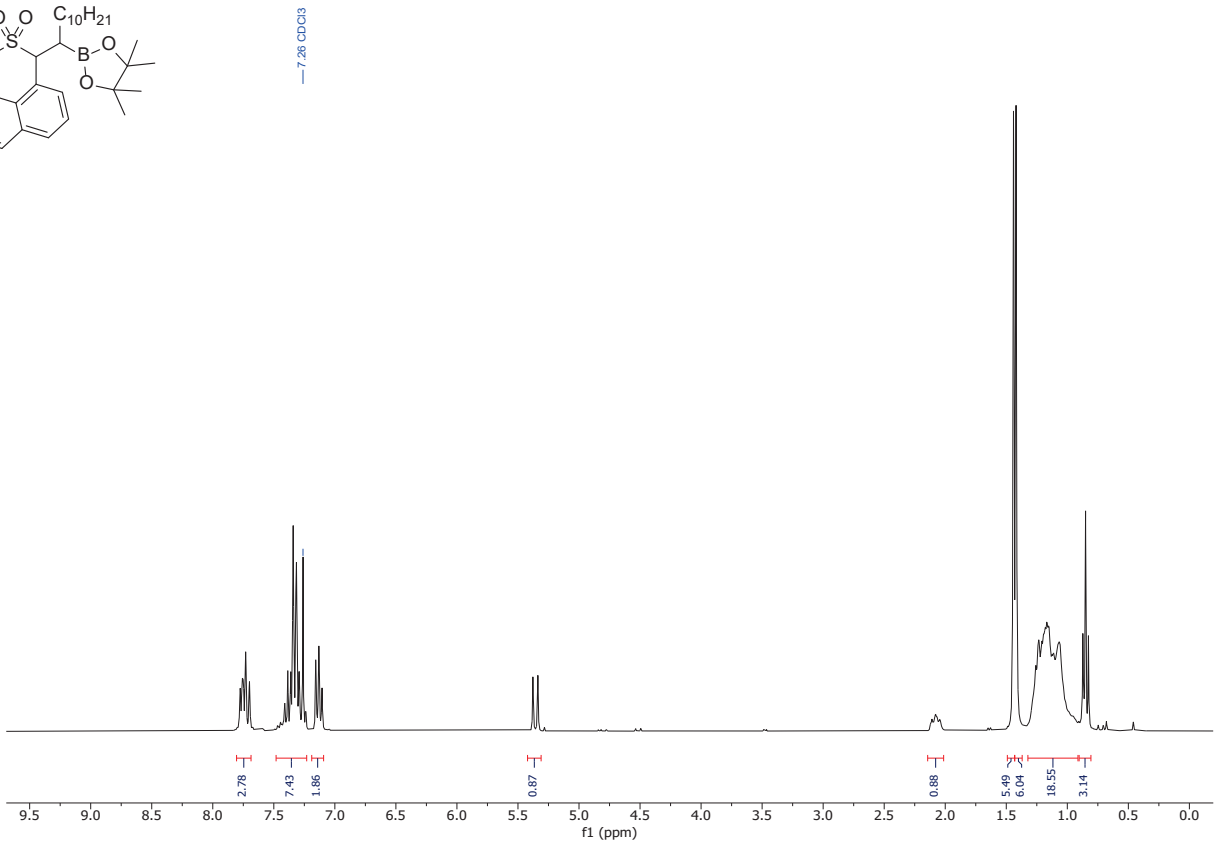




4,4,5,5-tetramethyl-2-(1-(naphthalen-1-yl)-1-(phenylsulfonyl)dodecan-2-yl)-1,3,2-dioxaborolane(29)
Major diastereomer

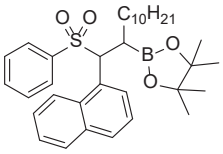
^{1}H NMR (300 MHz, $CDCl_3$)

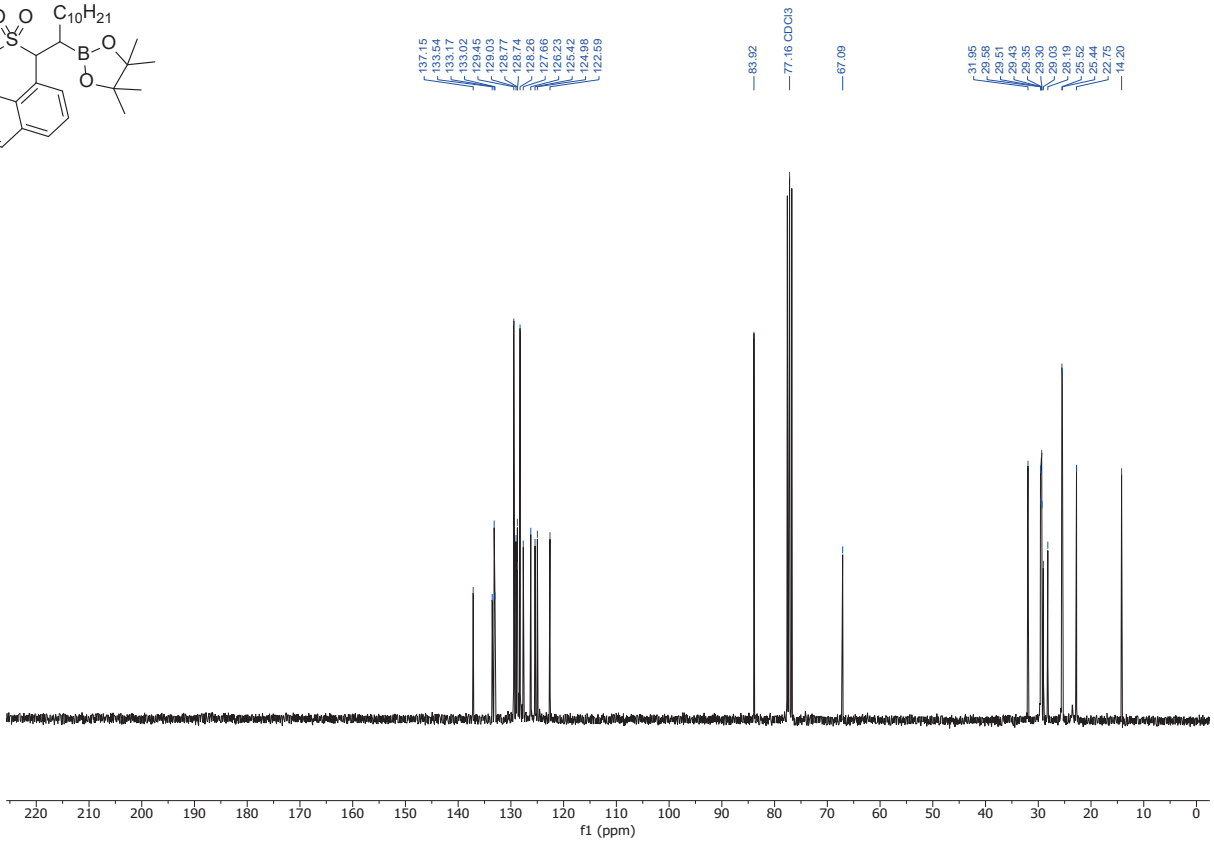




4,4,5,5-tetramethyl-2-(1-(naphthalen-1-yl)-1-(phenylsulfonyl)dodecan-2-yl)-1,3,2-dioxaborolane(29)
Major diastereomer

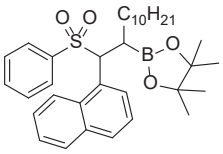
^{13}C NMR (75 MHz, $CDCl_3$)

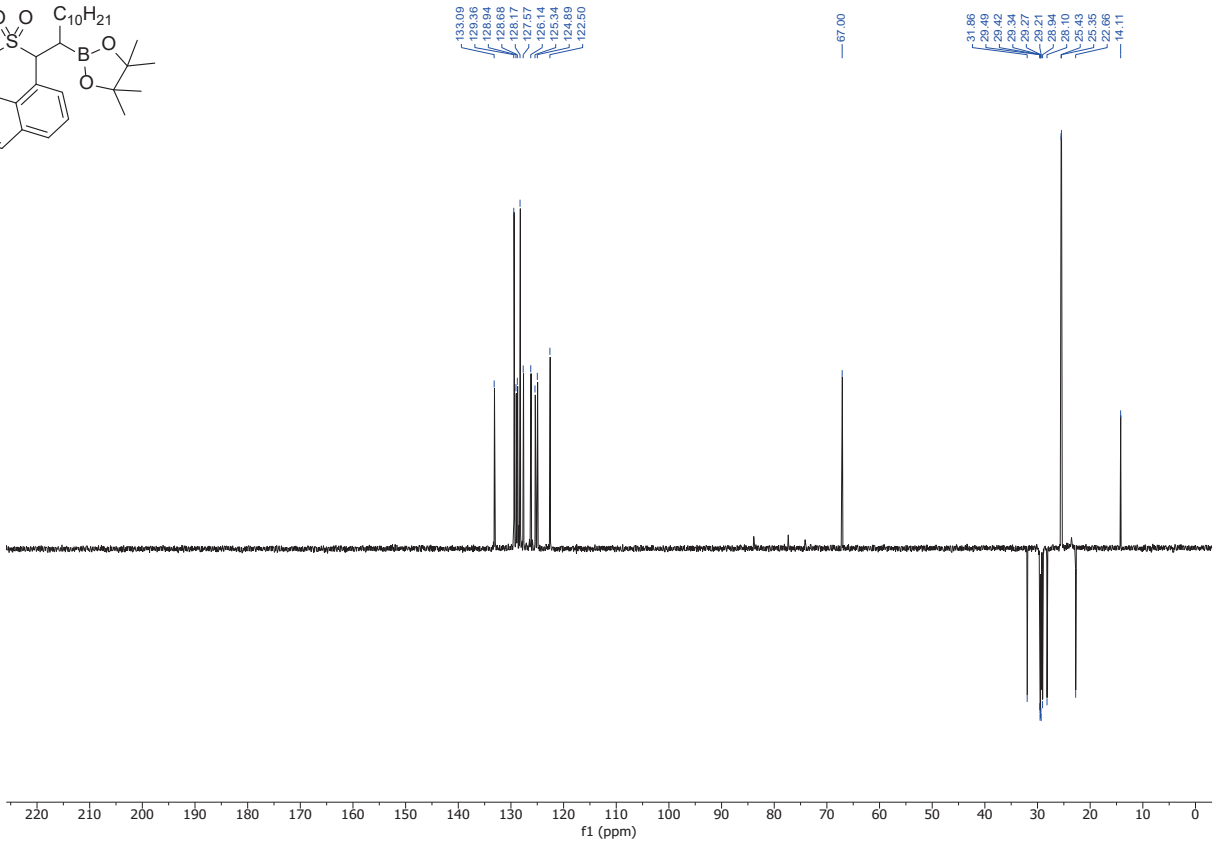




4,4,5,5-tetramethyl-2-(1-(naphthalen-1-yl)-1-(phenylsulfonyl)dodecan-2-yl)-1,3,2-dioxaborolane(29)
Major diastereomer

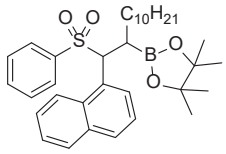
^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

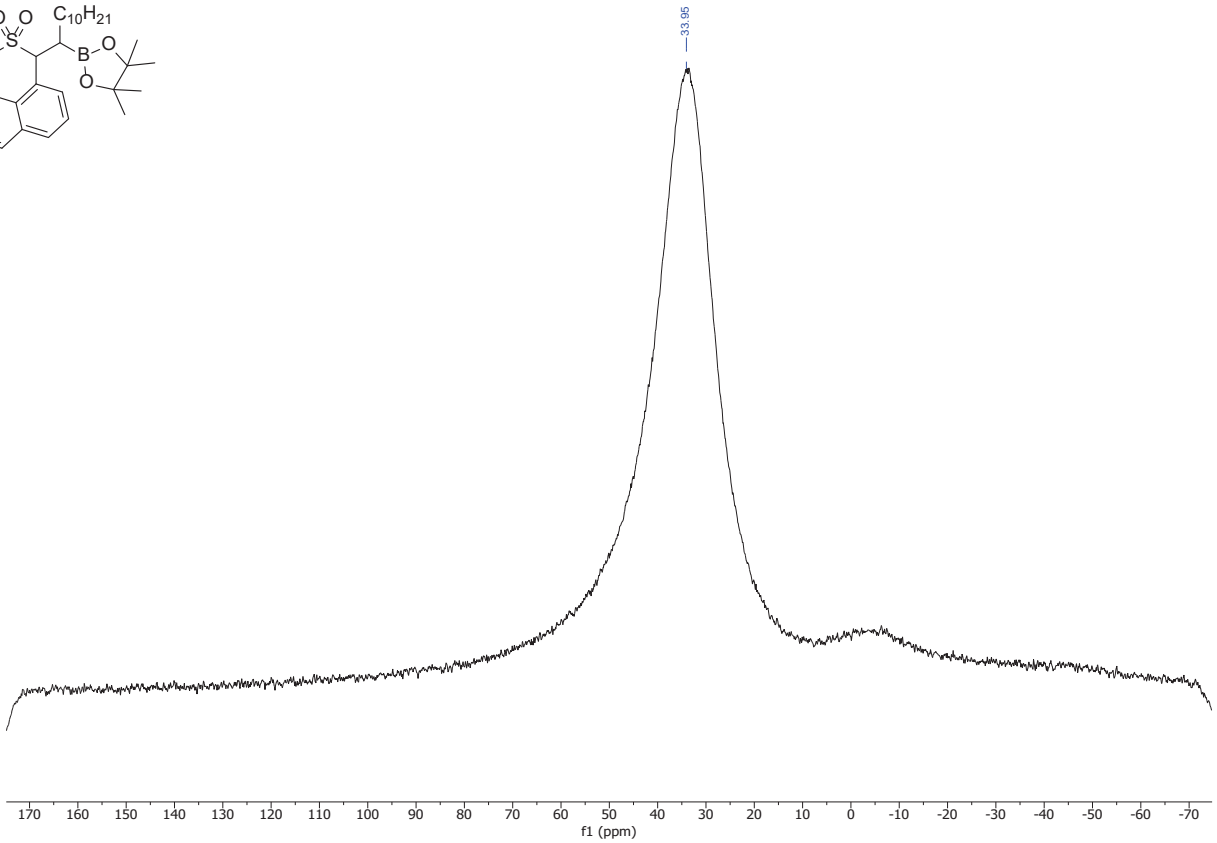




4,4,5,5-tetramethyl-2-(1-(naphthalen-1-yl)-1-(phenylsulfonyl)dodecan-2-yl)-1,3,2-dioxaborolane(29)
Mix of diastereomers

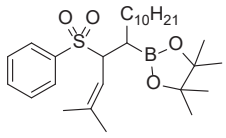
^{11}B NMR (96 MHz, $CDCl_3$)

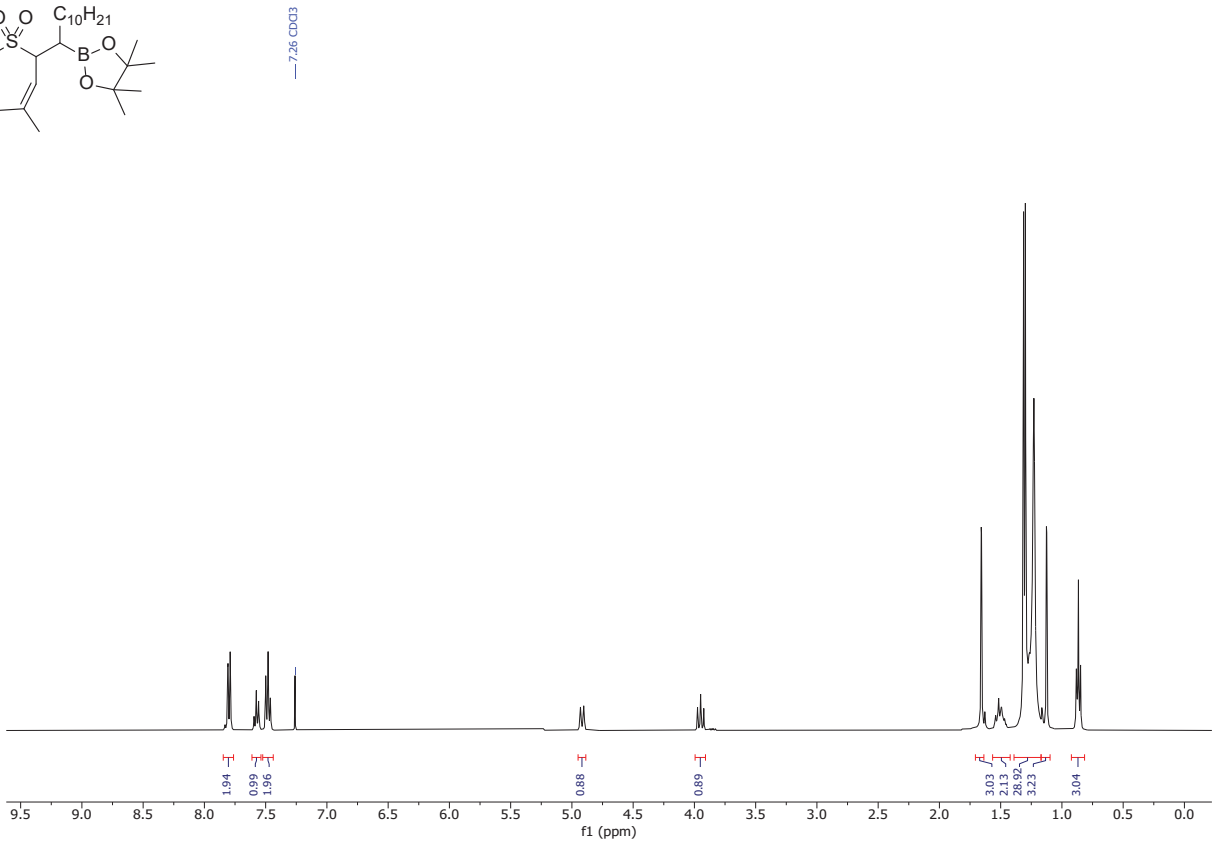




4,4,5,5-tetramethyl-2-(2-methyl-4-(phenylsulfonyl)pentadec-2-en-5-yl)-1,3,2-dioxaborolane (30)
Major diastereomer

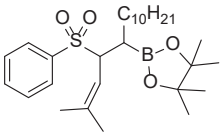
^{1}H NMR (400 MHz, $CDCl_3$)

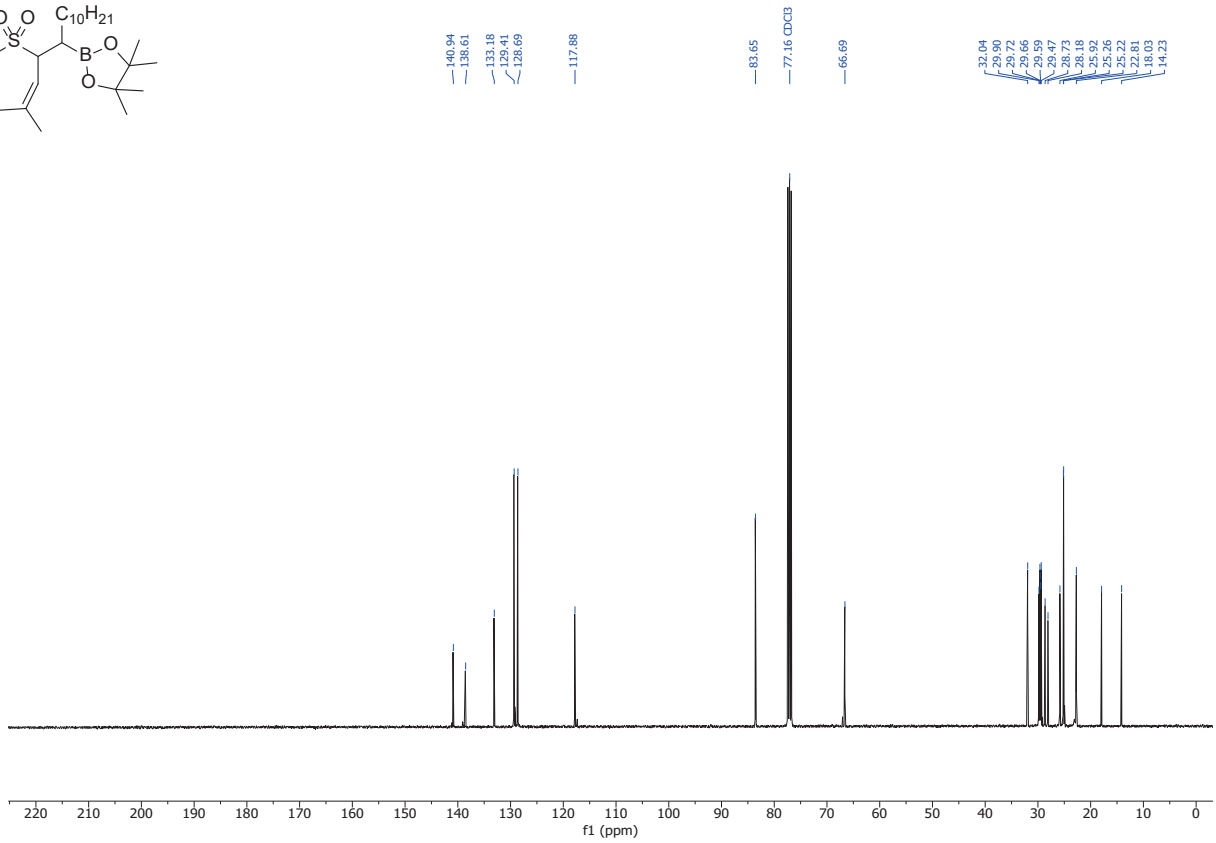




4,4,5,5-tetramethyl-2-(2-methyl-4-(phenylsulfonyl)pentadec-2-en-5-yl)-1,3,2-dioxaborolane (30)
Major diastereomer

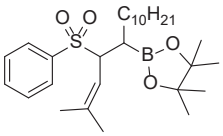
^{13}C NMR (101 MHz, $CDCl_3$)

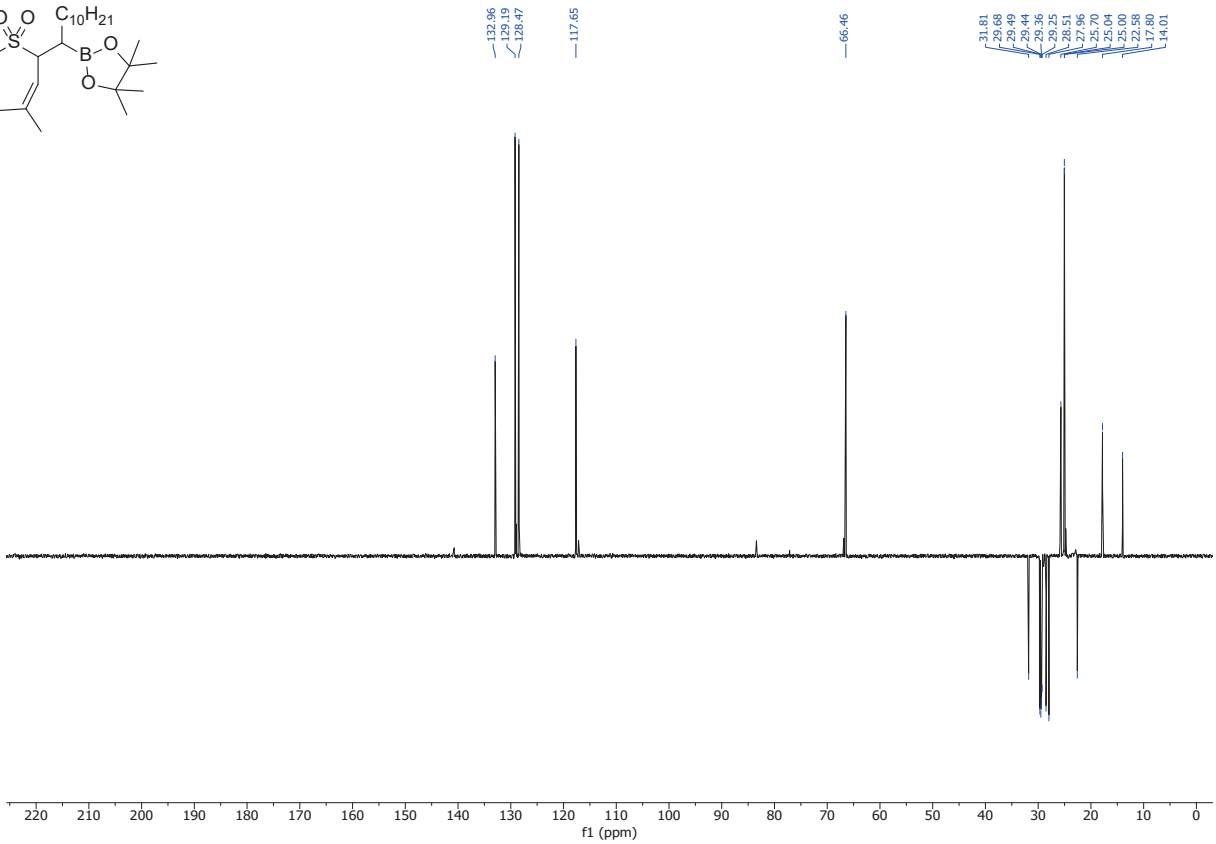




4,4,5,5-tetramethyl-2-(2-methyl-4-(phenylsulfonyl)pentadec-2-en-5-yl)-1,3,2-dioxaborolane (30)
Major diastereomer

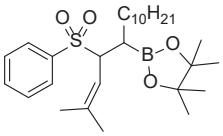
^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)

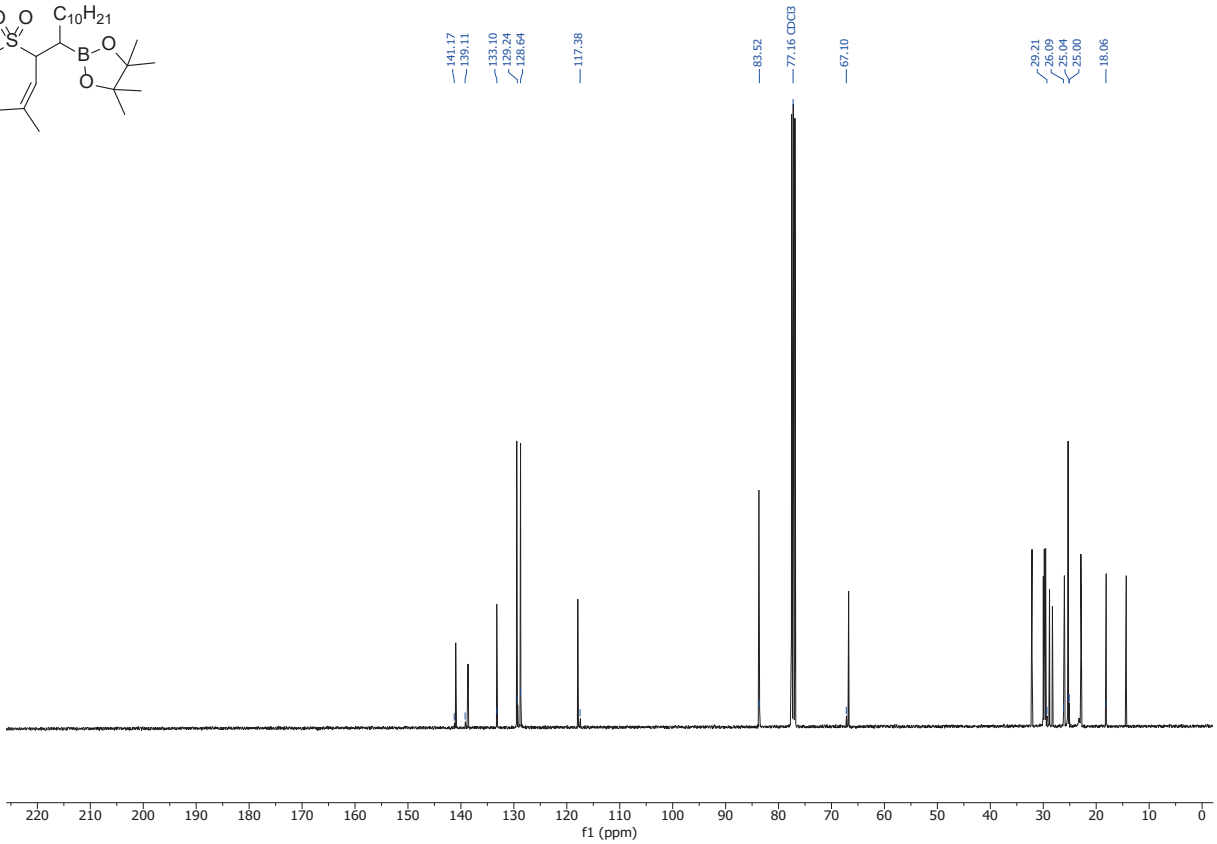




4,4,5,5-tetramethyl-2-(2-methyl-4-(phenylsulfonyl)pentadec-2-en-5-yl)-1,3,2-dioxaborolane (30)
Minor diastereomer

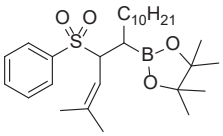
^{13}C NMR (101 MHz, $CDCl_3$)

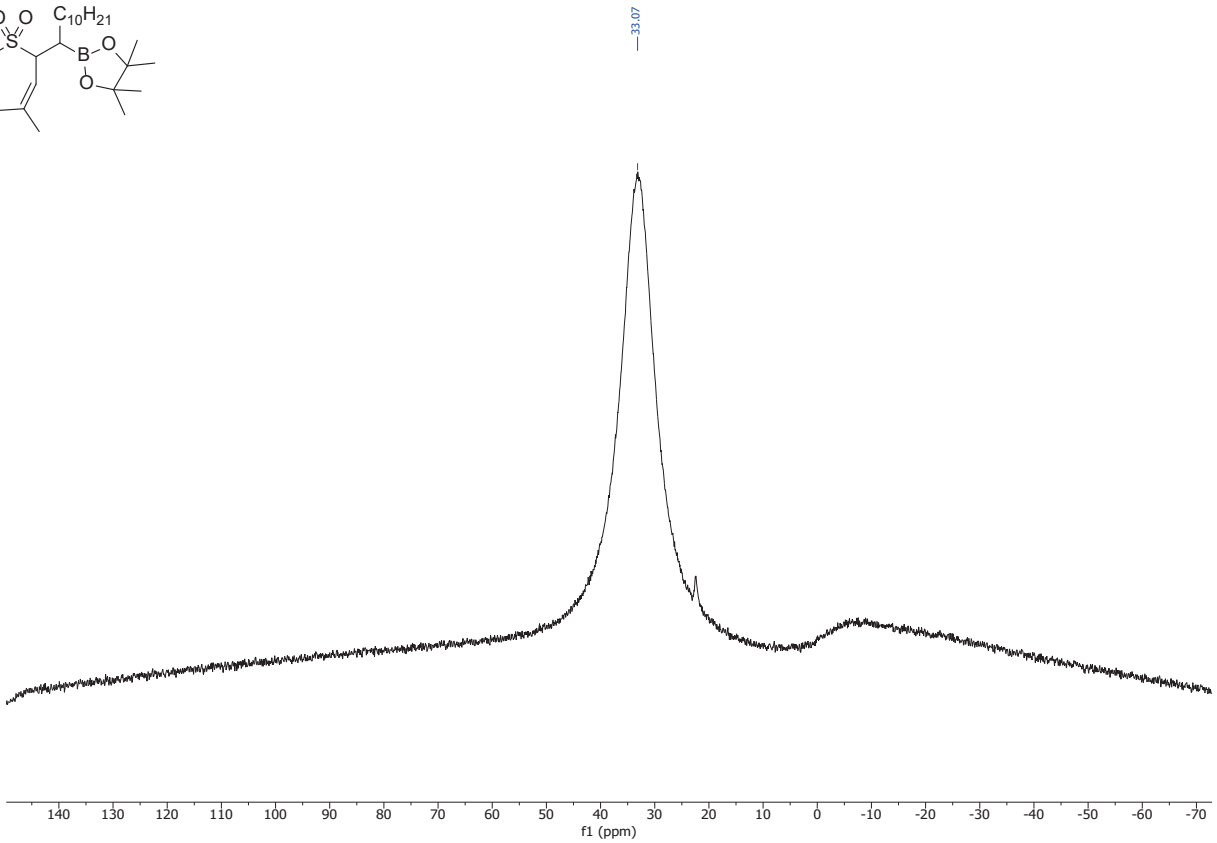




4,4,5,5-tetramethyl-2-(2-methyl-4-(phenylsulfonyl)pentadec-2-en-5-yl)-1,3,2-dioxaborolane (30)
Mix of diastereomers

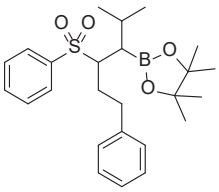
^{11}B NMR (128 MHz, $CDCl_3$)

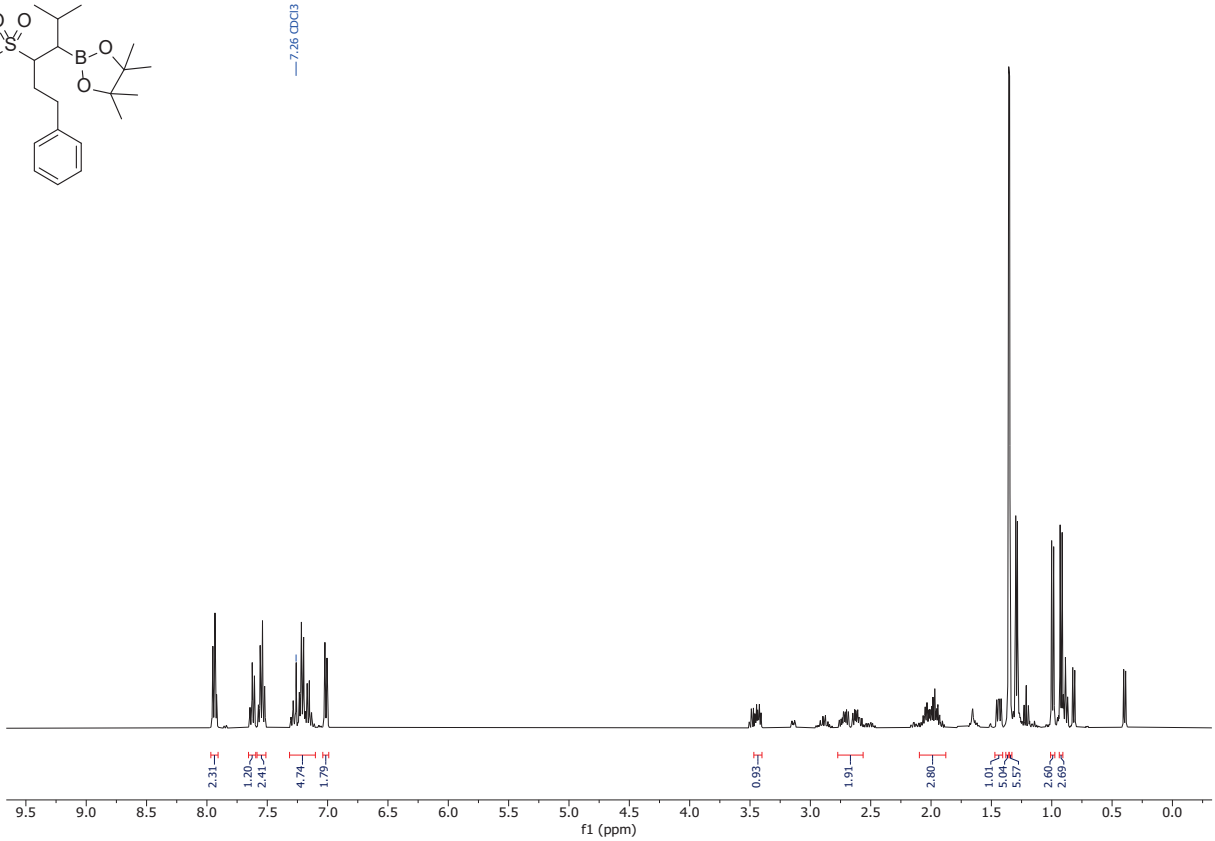




4,4,5,5-tetramethyl-2-(2-methyl-6-phenyl-4-(phenylsulfonyl)hexan-3-yl)-1,3,2-dioxaborolane (14)
Major diastereomer

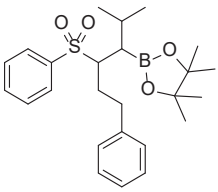
^{1}H NMR (400 MHz, $CDCl_3$)

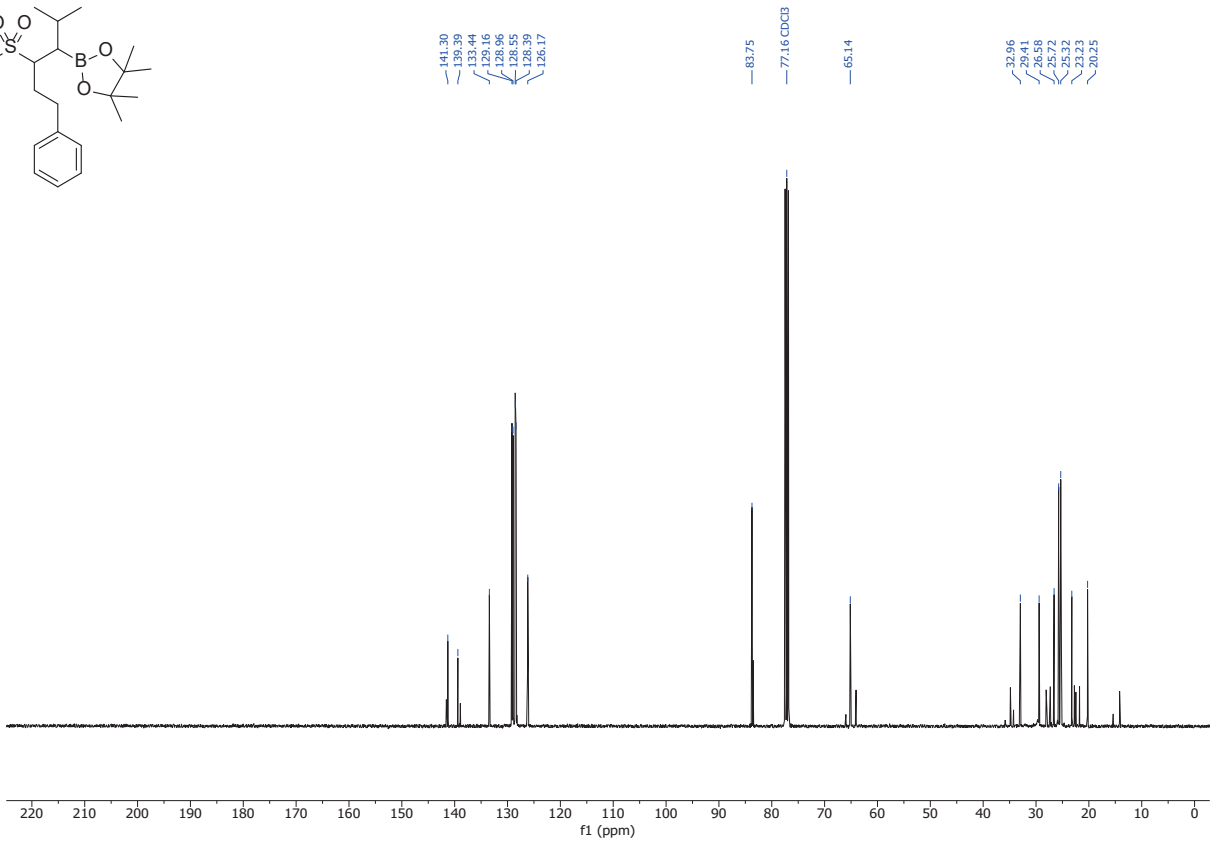




4,4,5,5-tetramethyl-2-(2-methyl-6-phenyl-4-(phenylsulfonyl)hexan-3-yl)-1,3,2-dioxaborolane (14)
Major diastereomer

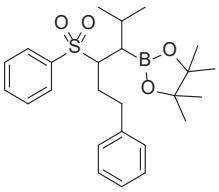
^{13}C NMR (101 MHz, $CDCl_3$)

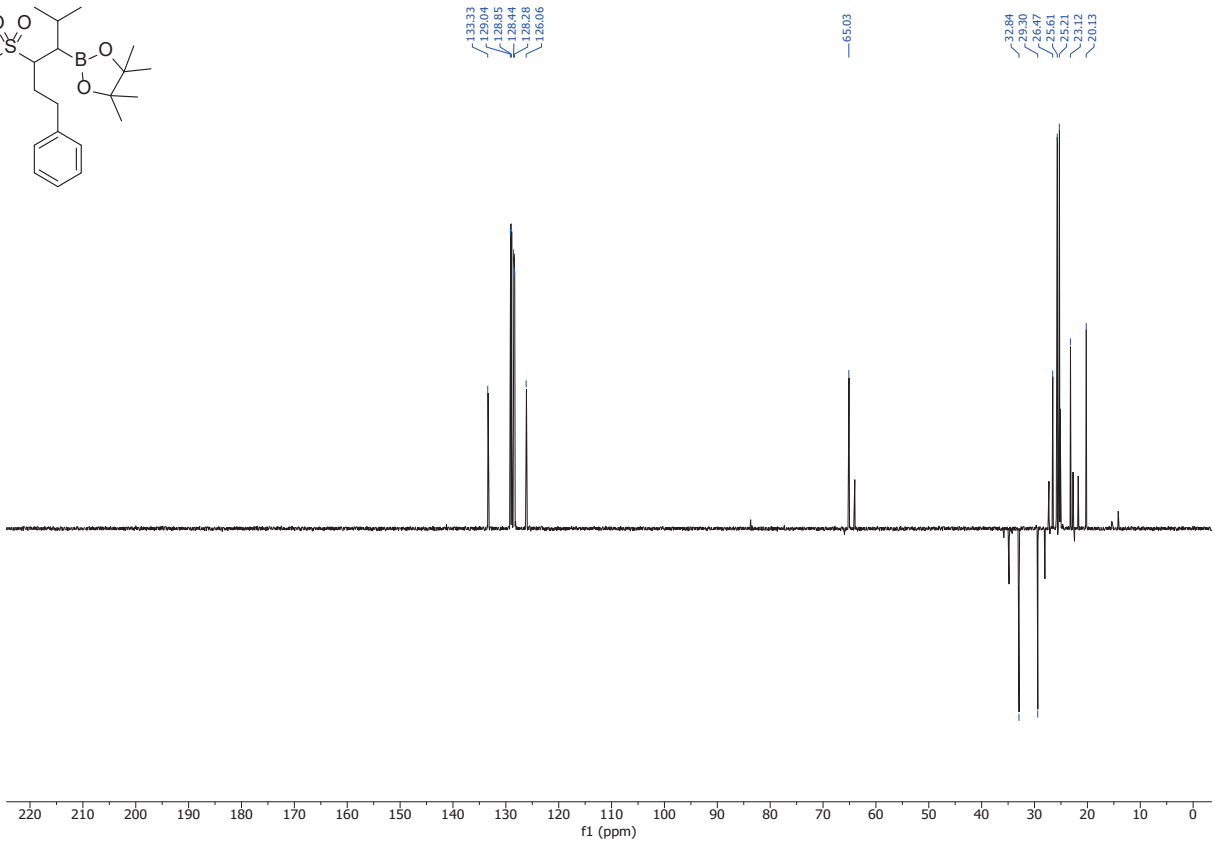




4,4,5,5-tetramethyl-2-(2-methyl-6-phenyl-4-(phenylsulfonyl)hexan-3-yl)-1,3,2-dioxaborolane (14)
Major diastereomer

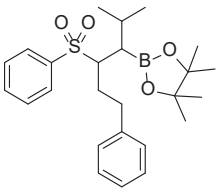
^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)

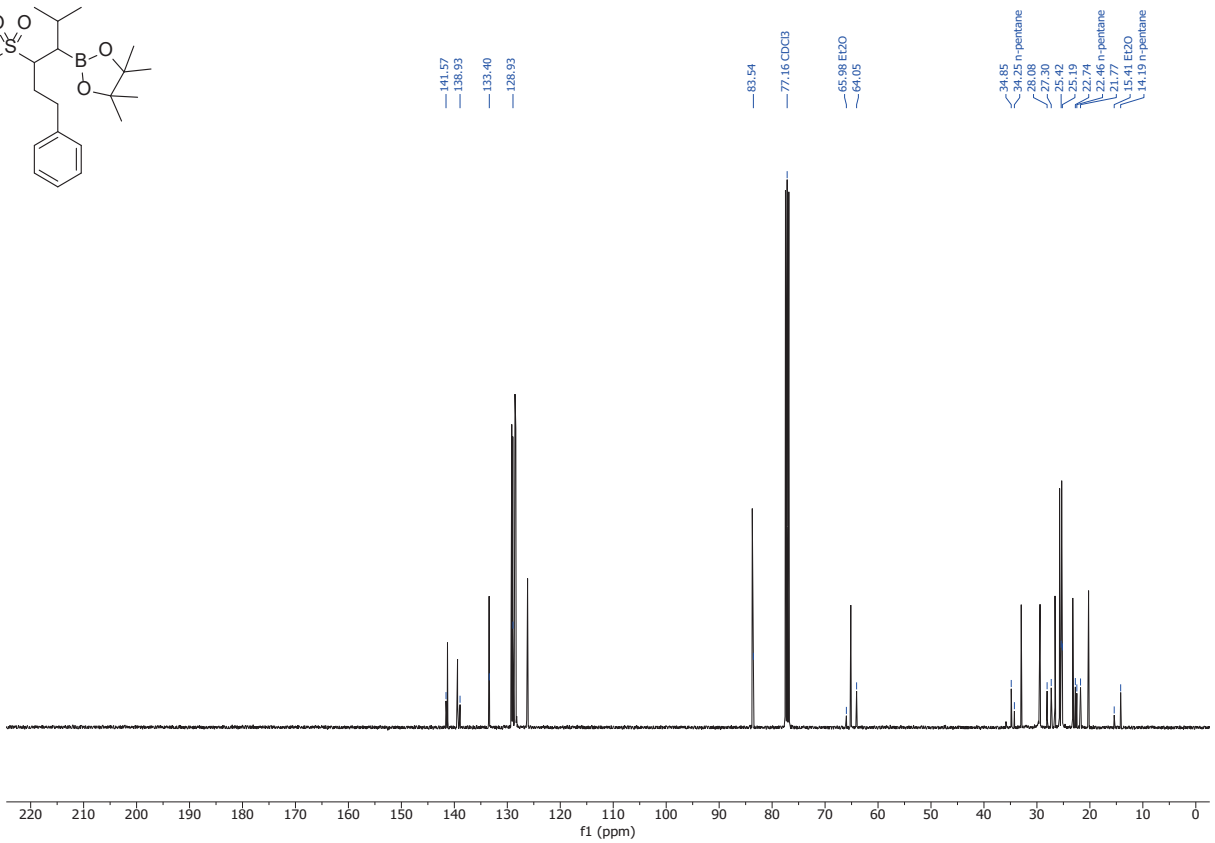




4,4,5,5-tetramethyl-2-(2-methyl-6-phenyl-4-(phenylsulfonyl)hexan-3-yl)-1,3,2-dioxaborolane (14)
Minor diastereomer

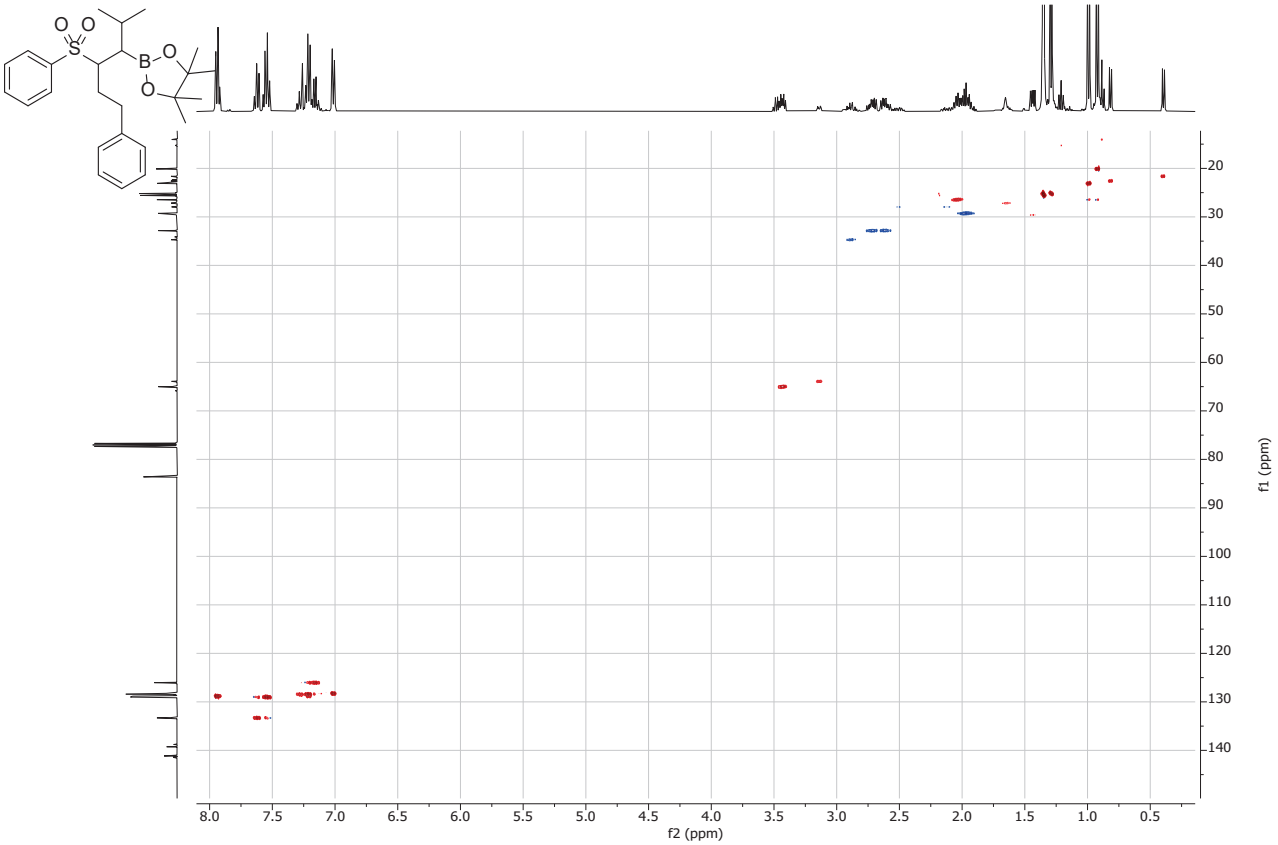
^{13}C NMR (101 MHz, $CDCl_3$)





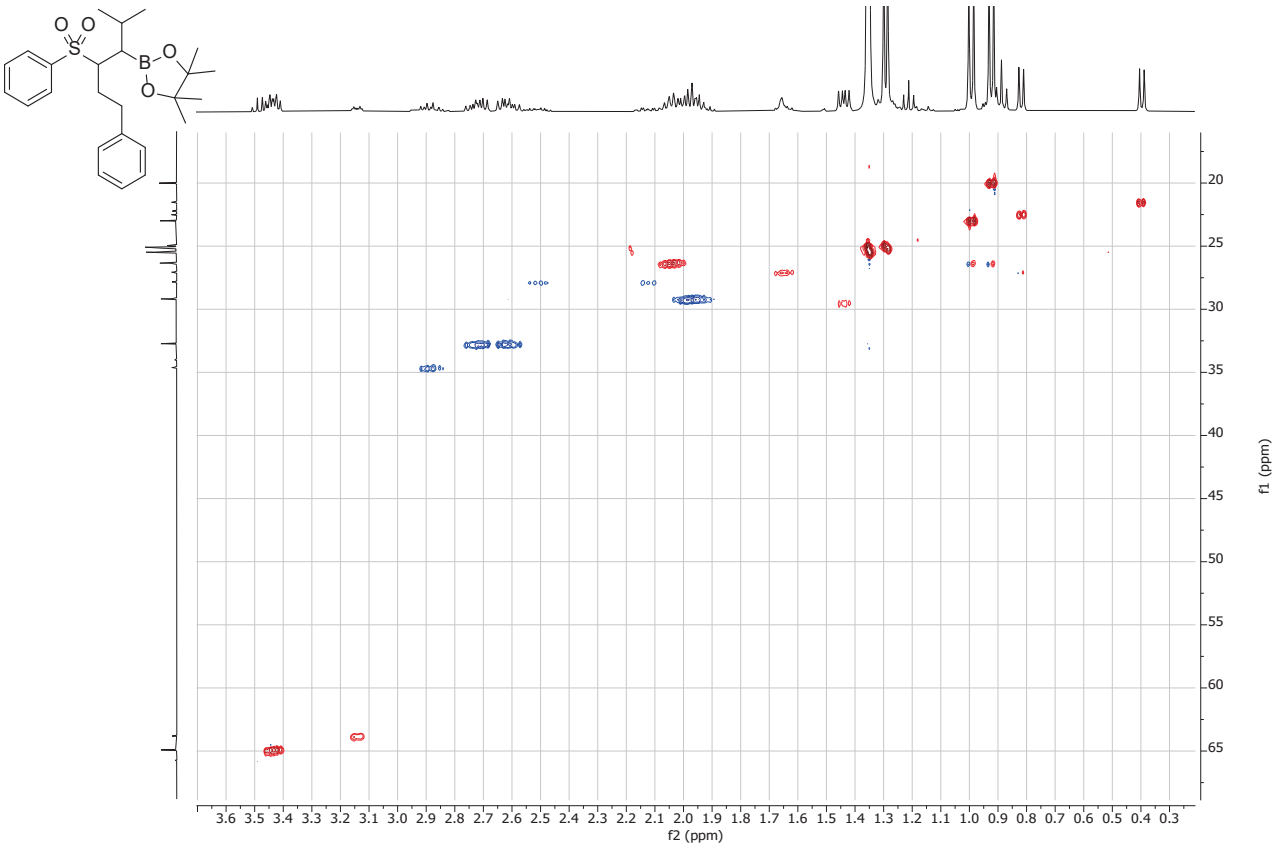
4,4,5,5-tetramethyl-2-(2-methyl-6-phenyl-4-(phenylsulfonyl)hexan-3-yl)-1,3,2-dioxaborolane (14)
Minor diastereomer

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



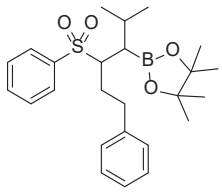
4,4,5,5-tetramethyl-2-(2-methyl-6-phenyl-4-(phenylsulfonyl)hexan-3-yl)-1,3,2-dioxaborolane (14)
Minor diastereomer

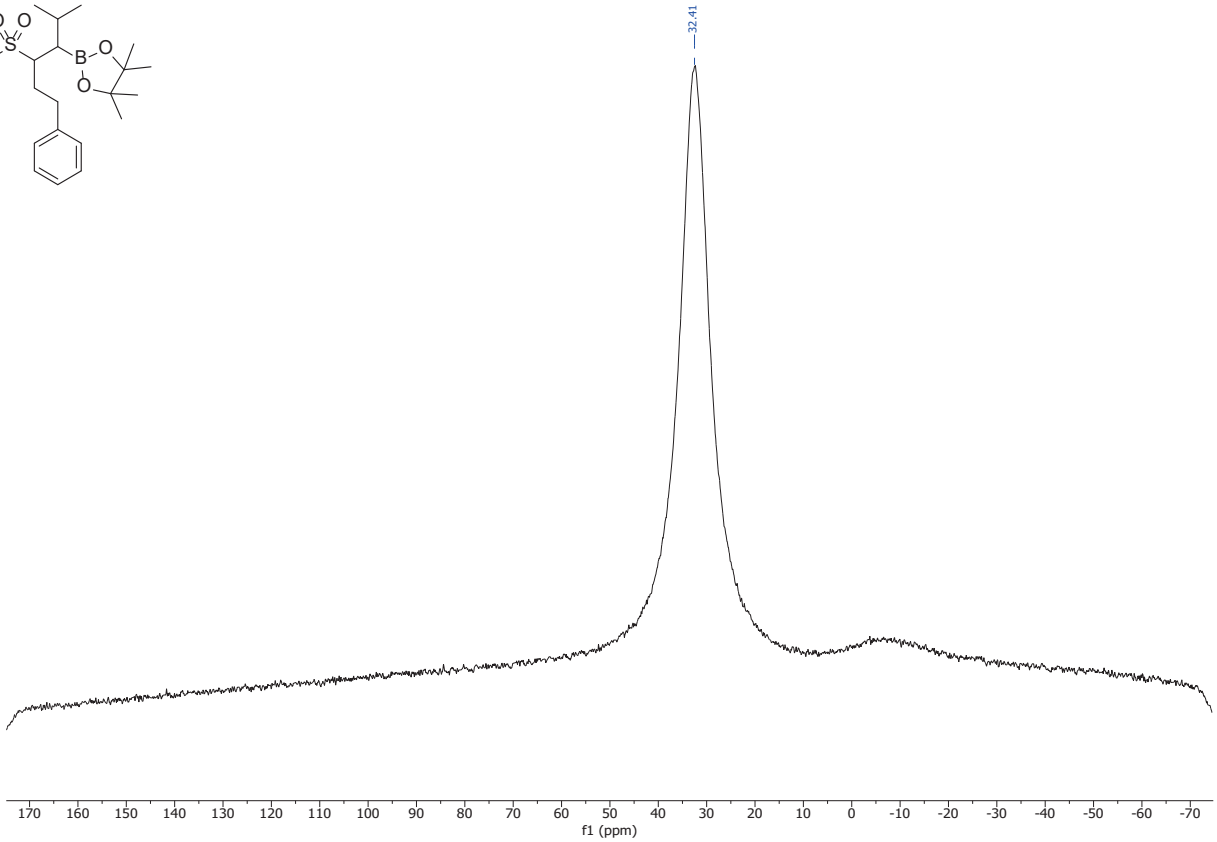
^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-(2-methyl-6-phenyl-4-(phenylsulfonyl)hexan-3-yl)-1,3,2-dioxaborolane (14)
Mix of diastereomers

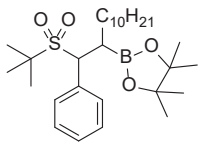
^{11}B NMR (96 MHz, $CDCl_3$)

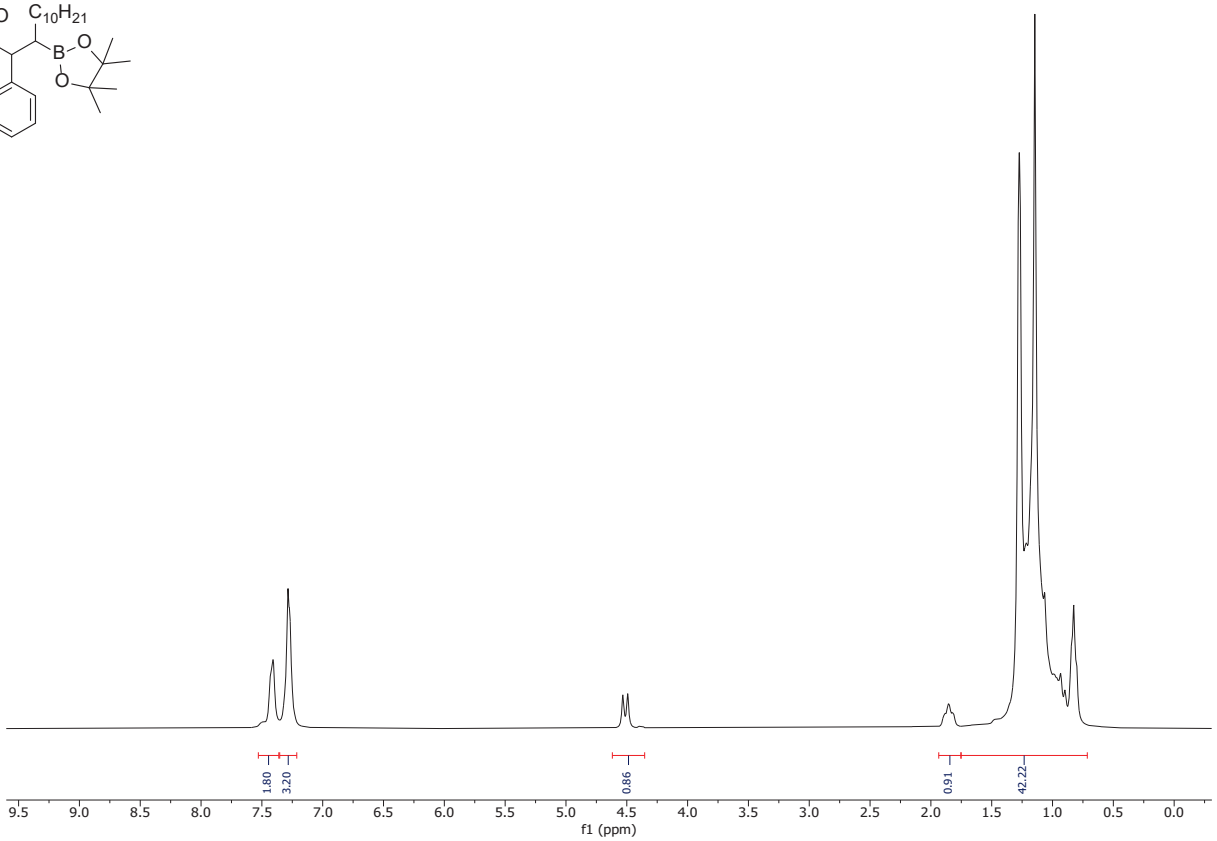




2-(1-(tert-butylsulfonyl)-1-phenyldodecan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)
Major diastereomer

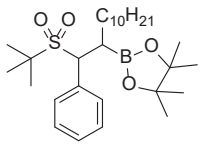
^{1}H NMR (300 MHz, $CDCl_3$)

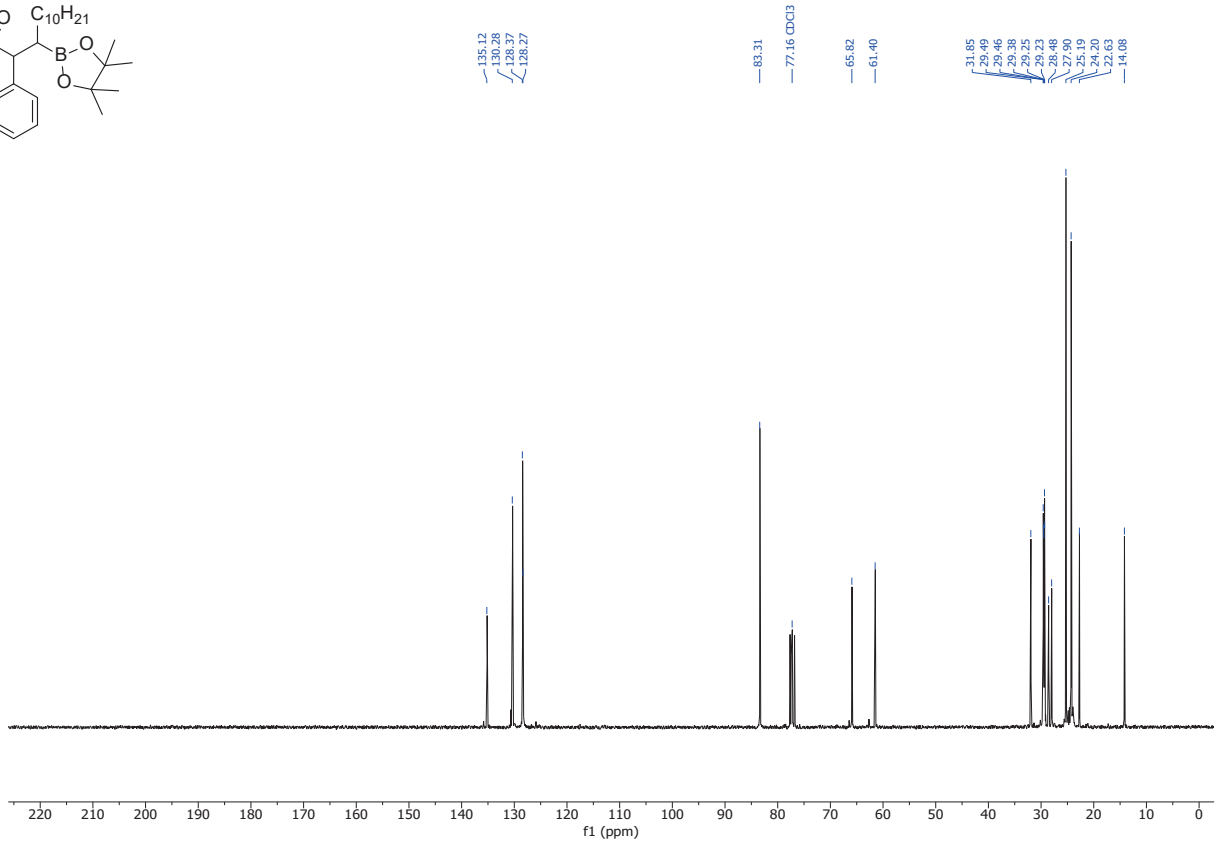




2-(1-(tert-butylsulfonyl)-1-phenyldodecan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)
Major diastereomer

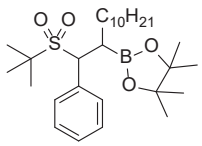
^{13}C NMR (75 MHz, $CDCl_3$)

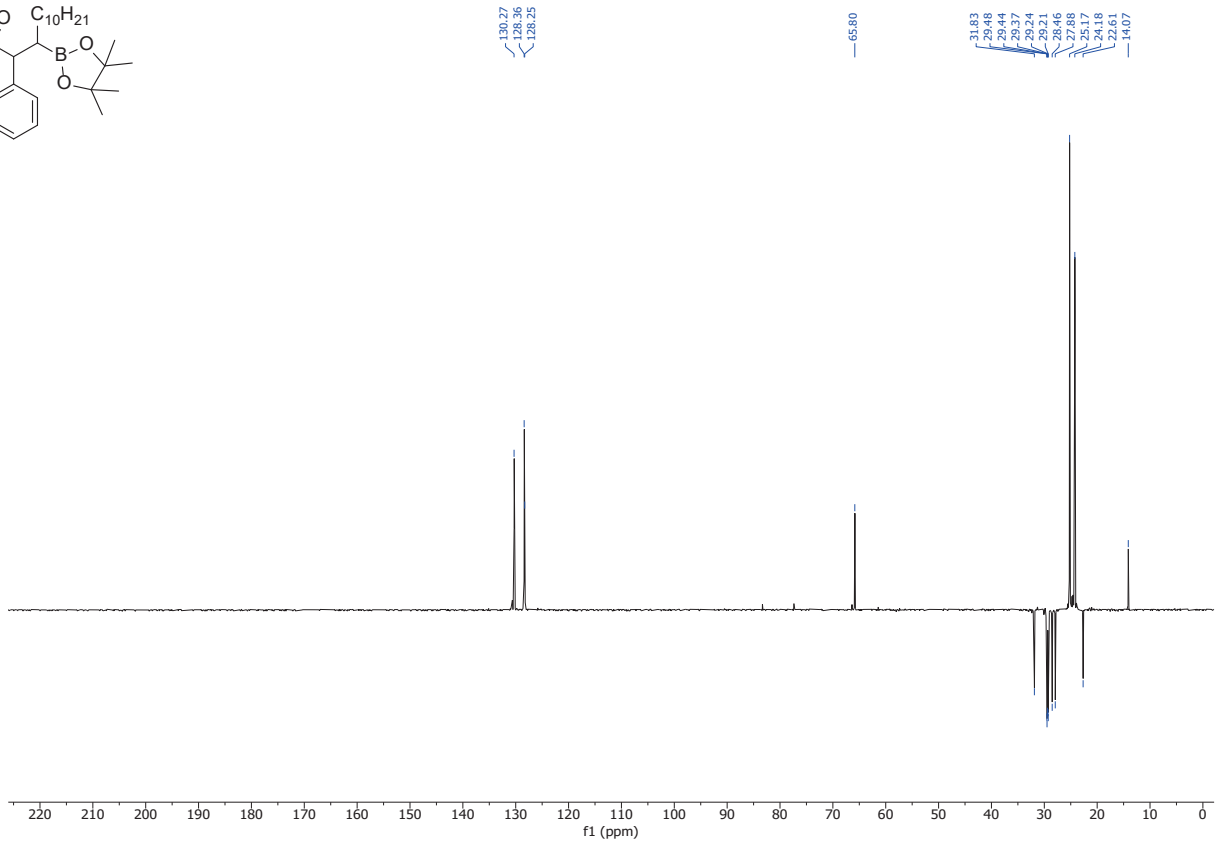




2-(1-(tert-butylsulfonyl)-1-phenyldodecan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)
Major diastereomer

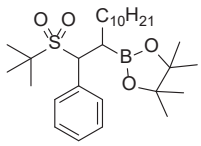
^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

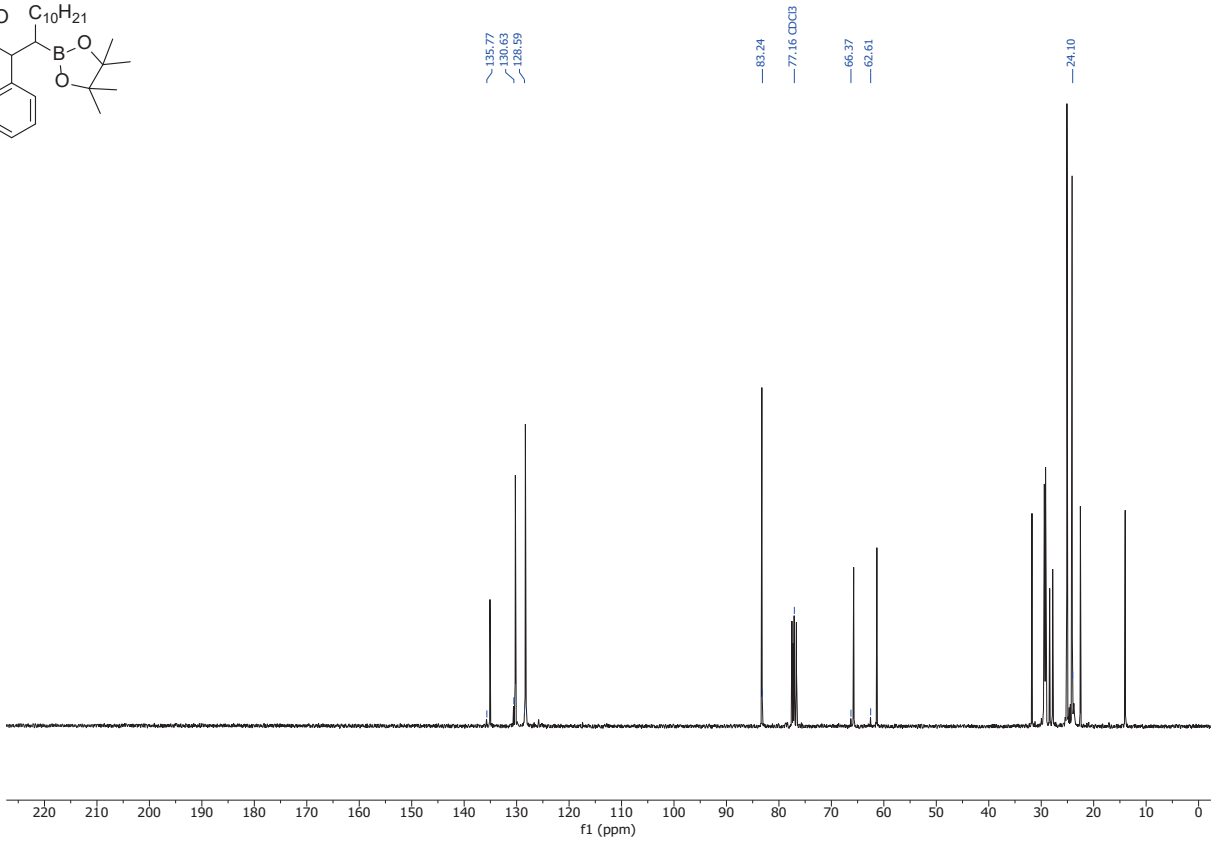




2-(1-(tert-butylsulfonyl)-1-phenyldodecan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)
Minor diastereomer

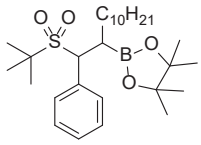
^{13}C NMR (75 MHz, $CDCl_3$)

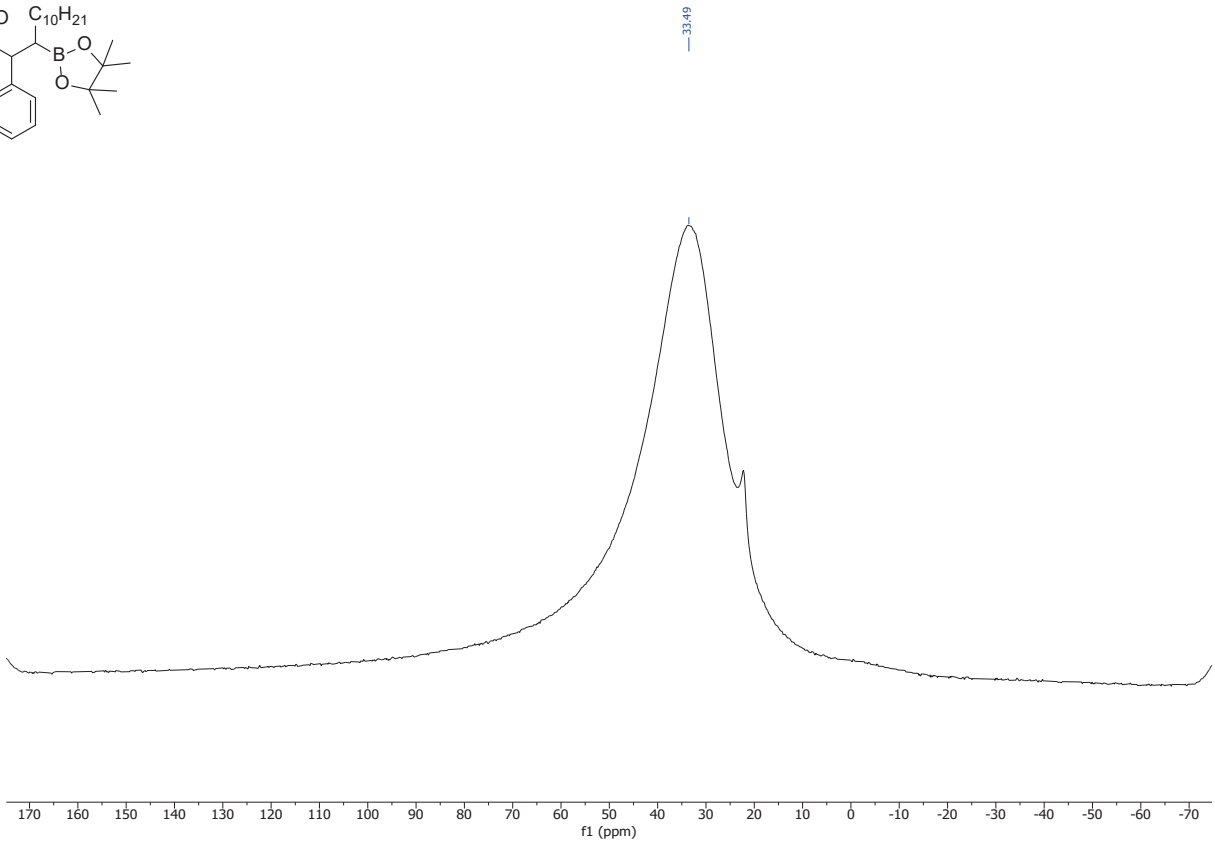




2-(1-(tert-butylsulfonyl)-1-phenyldodecan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)
Mix of diastereomers

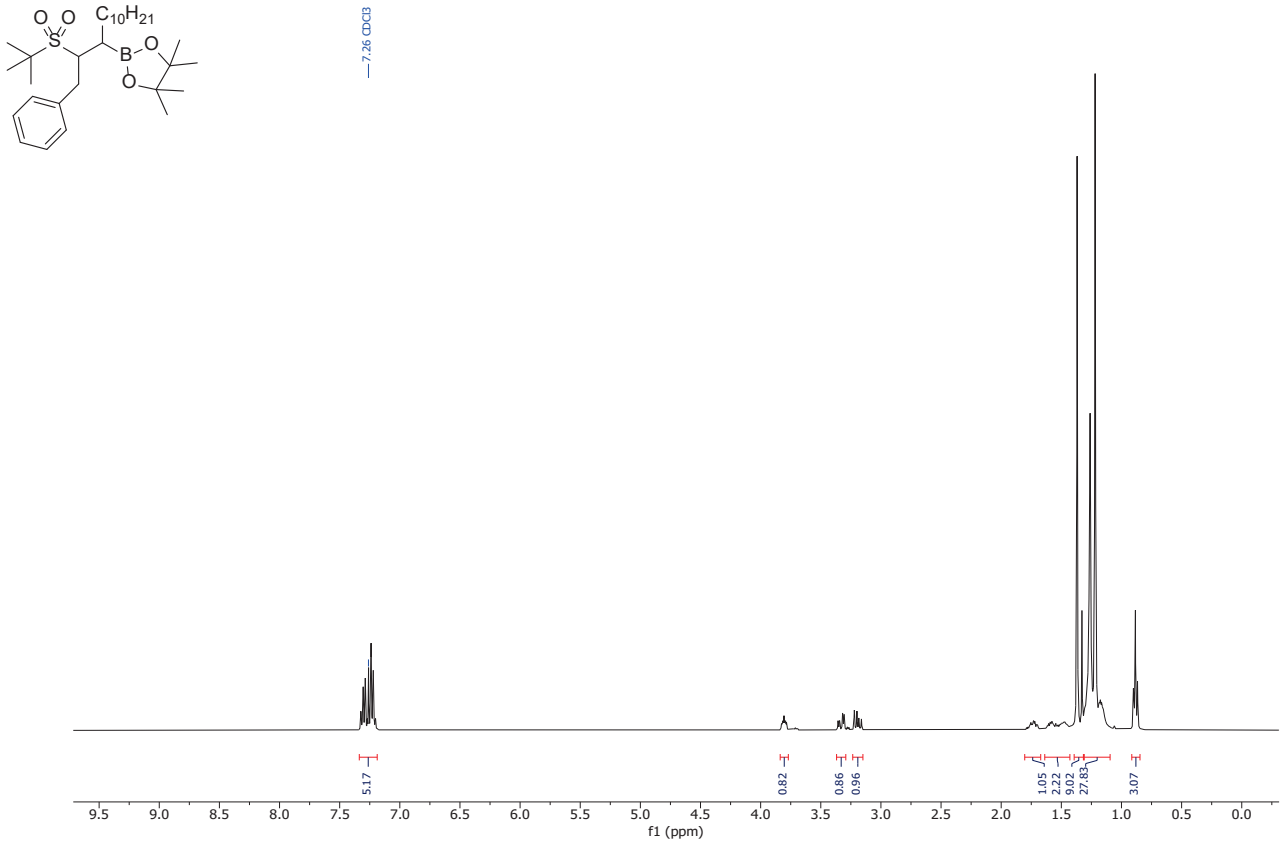
^{11}B NMR (96 MHz, $CDCl_3$)





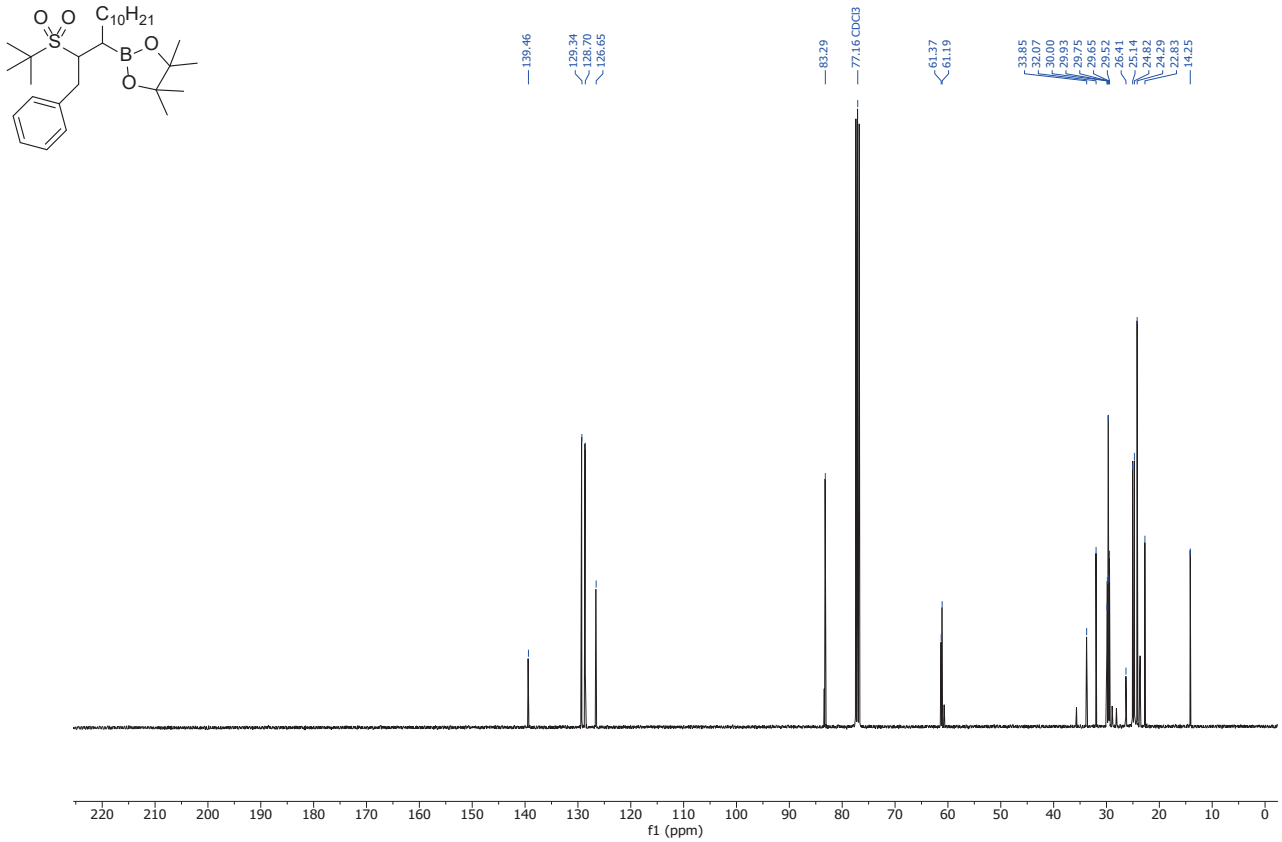
2-(2-(tert-butylsulfonyl)-1-phenyltridecan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39)
Major diastereomer

^{1}H NMR (400 MHz, $CDCl_3$)



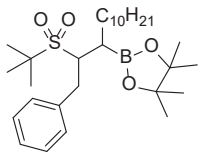
2-(2-(tert-butylsulfonyl)-1-phenyltridecan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39)
Major diastereomer

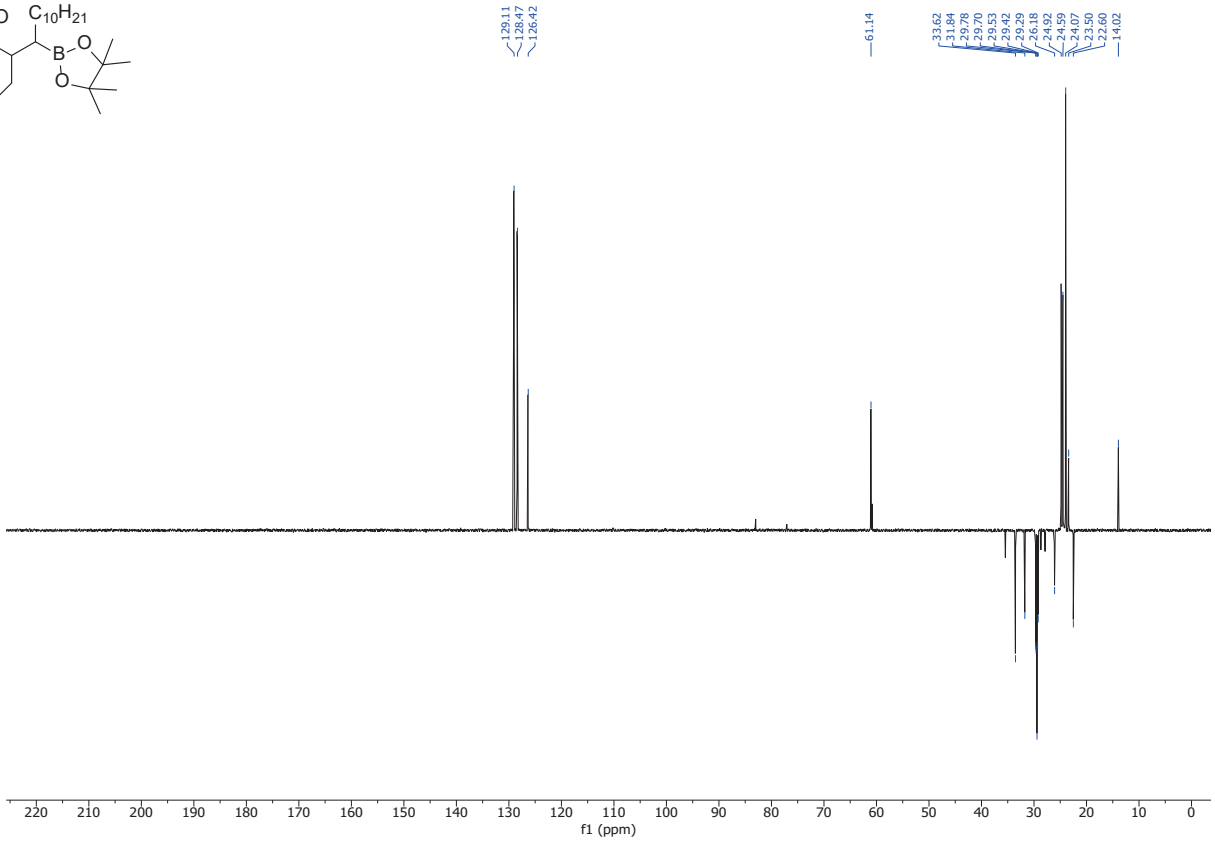
^{13}C NMR (101 MHz, $CDCl_3$)



2-(2-(tert-butylsulfonyl)-1-phenyltridecan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39)
Major diastereomer

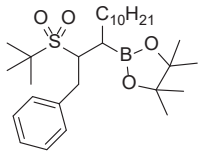
^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)

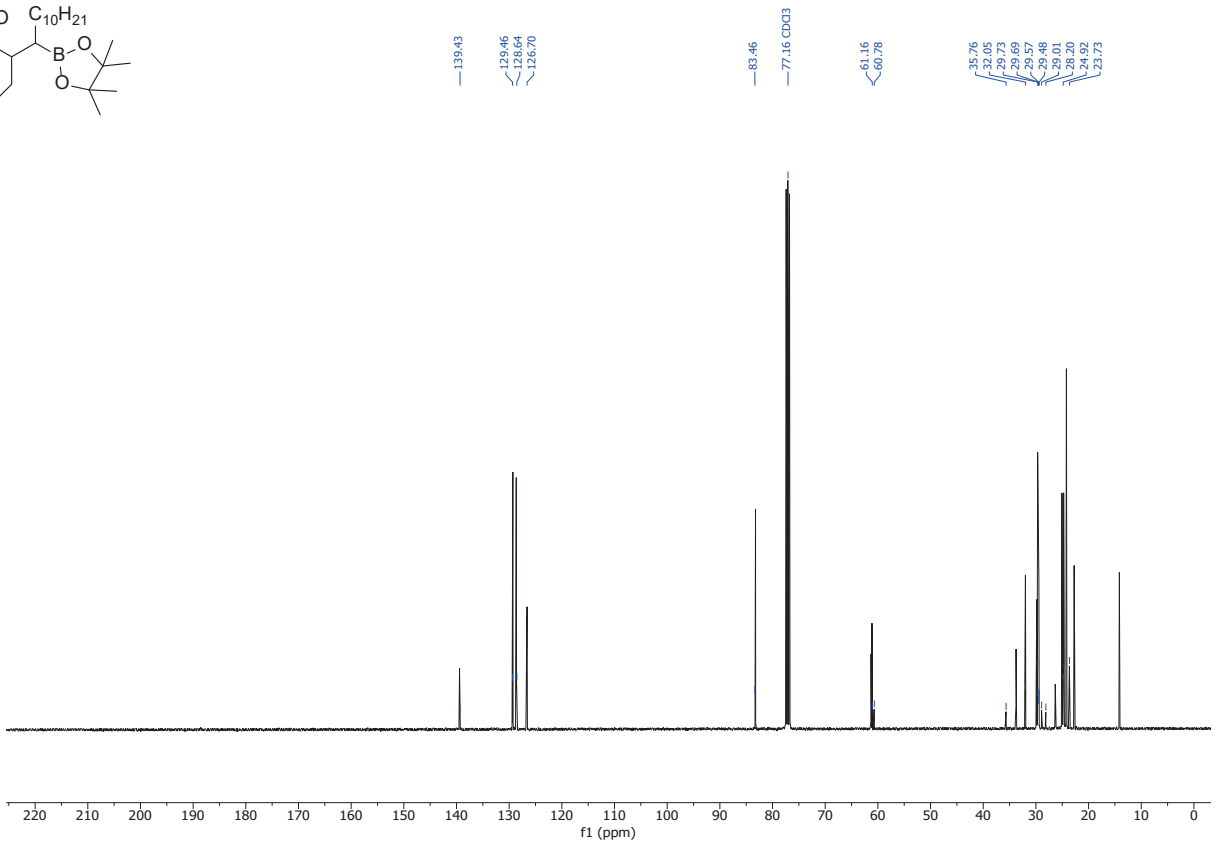




2-(2-(tert-butylsulfonyl)-1-phenyltridecan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39)
Minor diastereomer

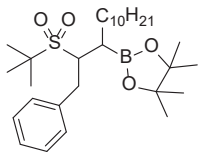
^{13}C NMR (101 MHz, $CDCl_3$)

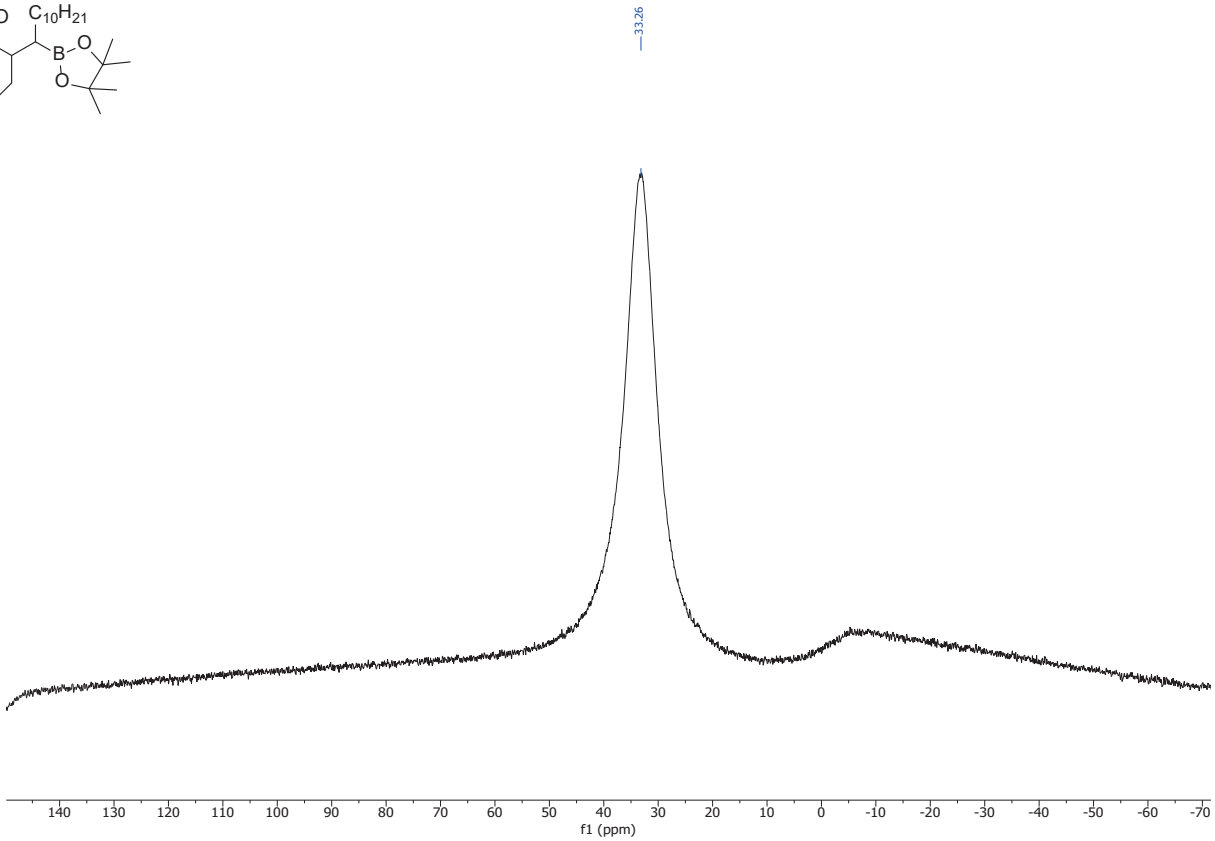




2-(2-(tert-butylsulfonyl)-1-phenyltridecan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39)
Mix of diastereomers

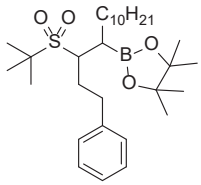
^{11}B NMR (128 MHz, $CDCl_3$)

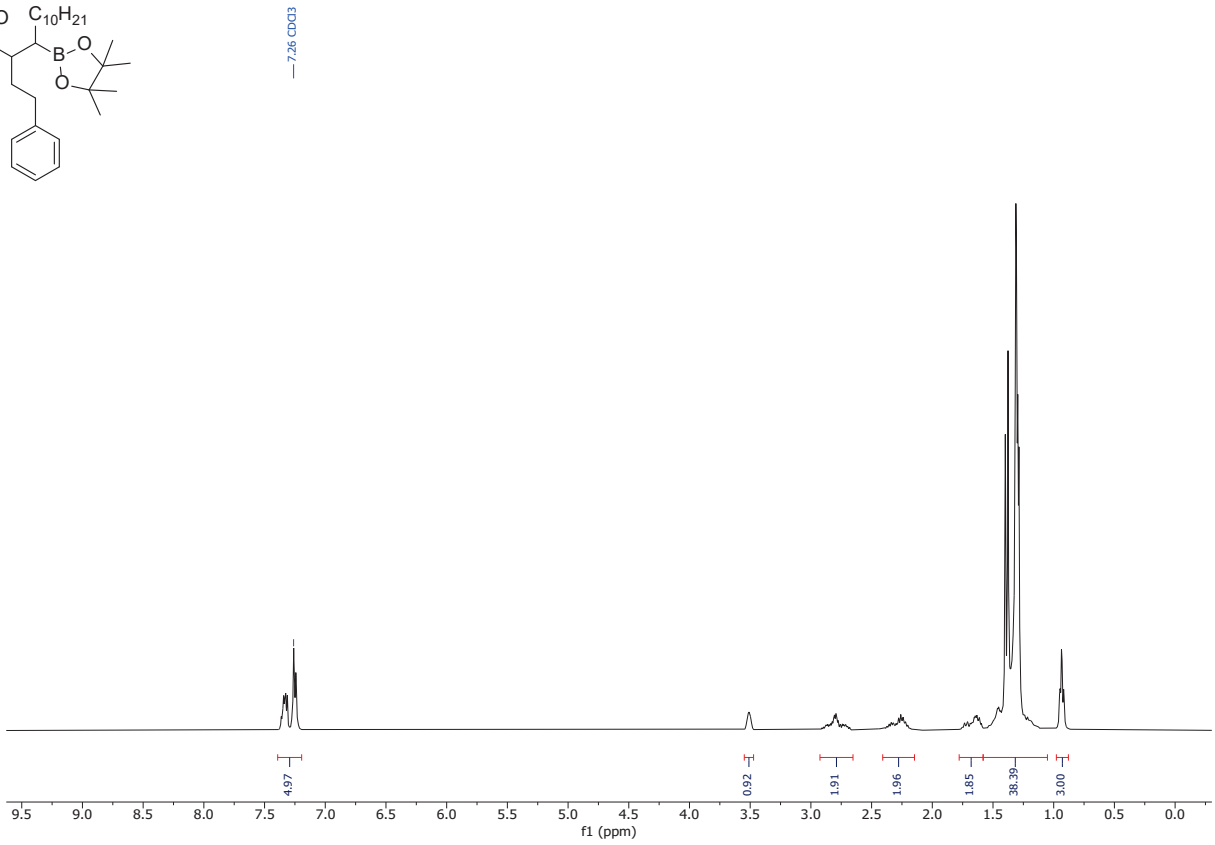




2-(3-(tert-butylsulfonyl)-1-phenyltetradecan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (40)
Mix of diastereomers

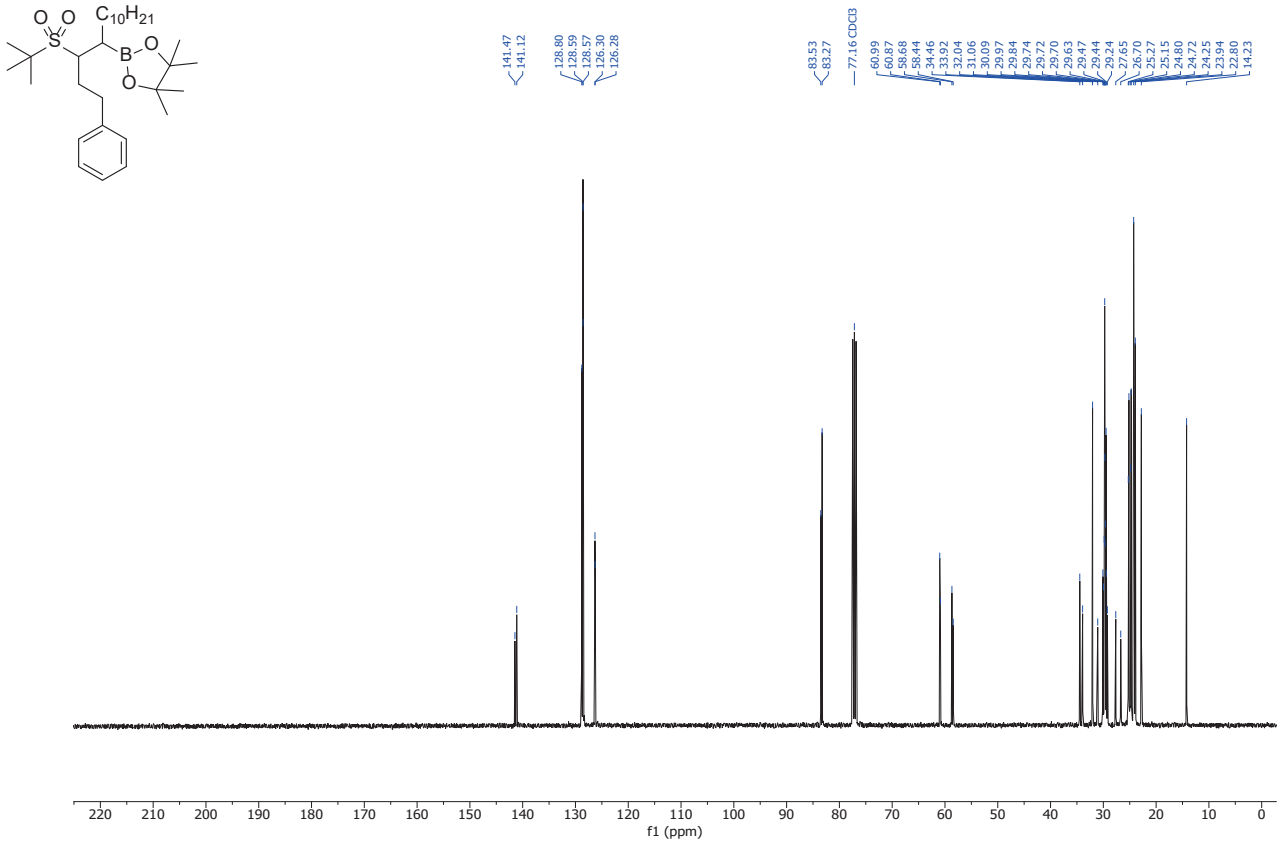
^{1}H NMR (400 MHz, $CDCl_3$)





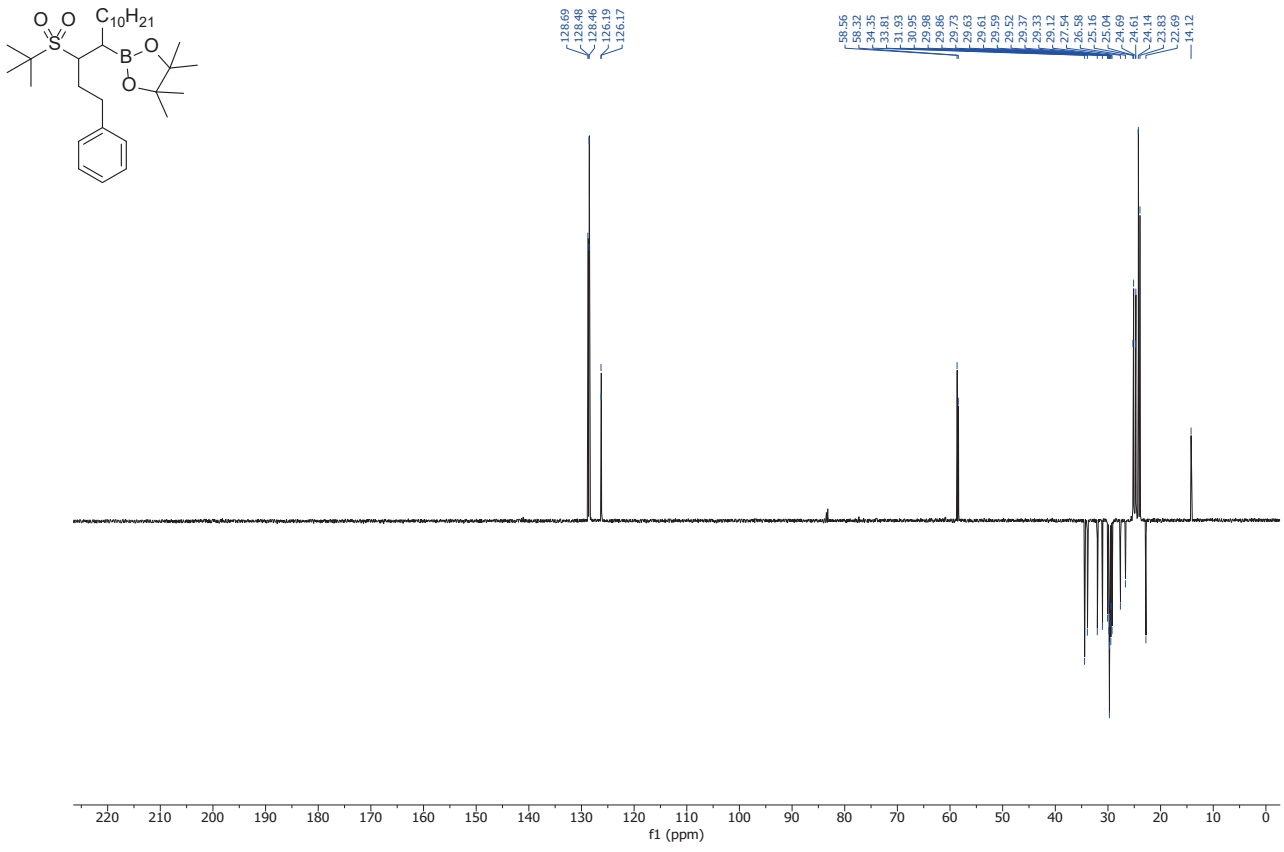
2-(3-(tert-butylsulfonyl)-1-phenyltetradecan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (40)
Mix of diastereomers

^{13}C NMR (101 MHz, $CDCl_3$)



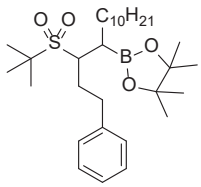
2-(3-(tert-butylsulfonyl)-1-phenyltetradecan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (40)
Mix of diastereomers

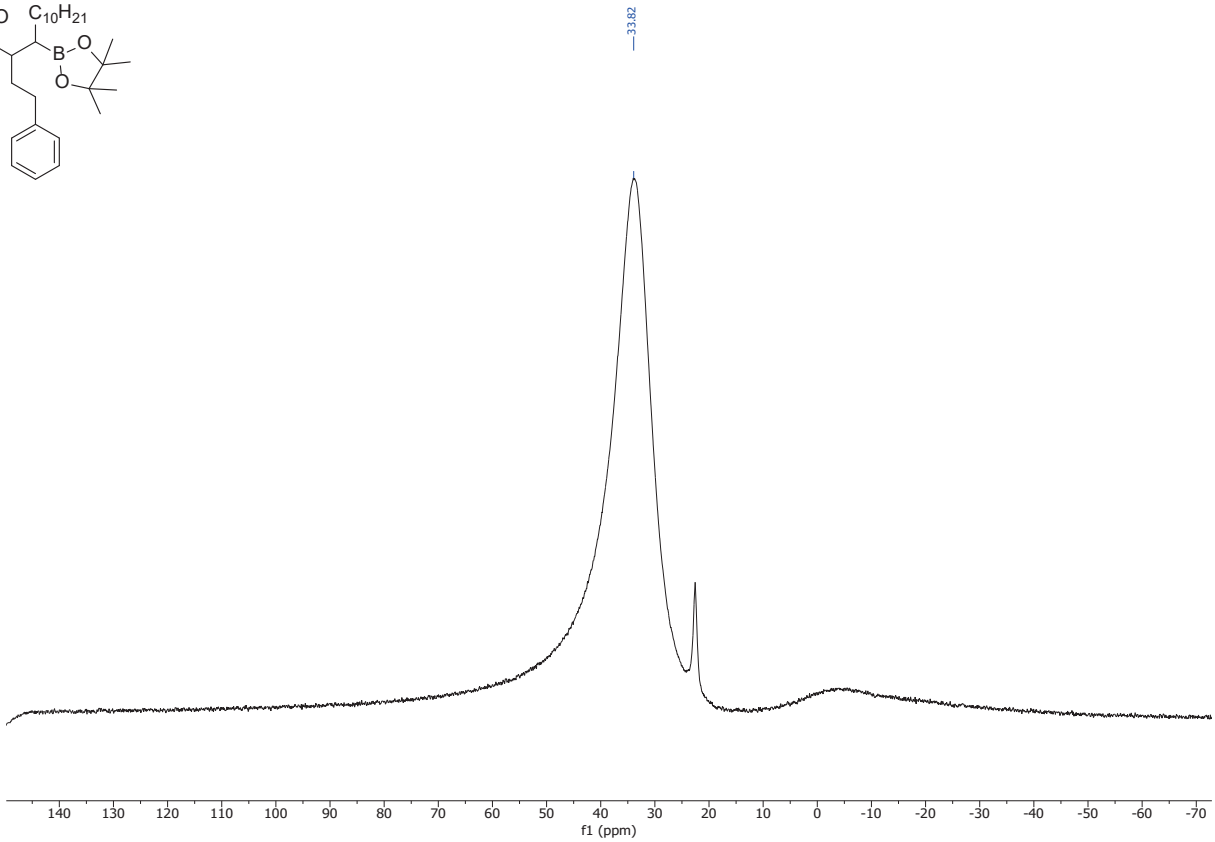
^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



2-(3-(tert-butylsulfonyl)-1-phenyltetradecan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (40)
Mix of diastereomers

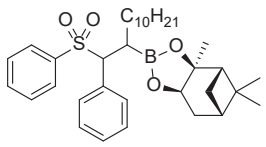
^{11}B NMR (128 MHz, $CDCl_3$)

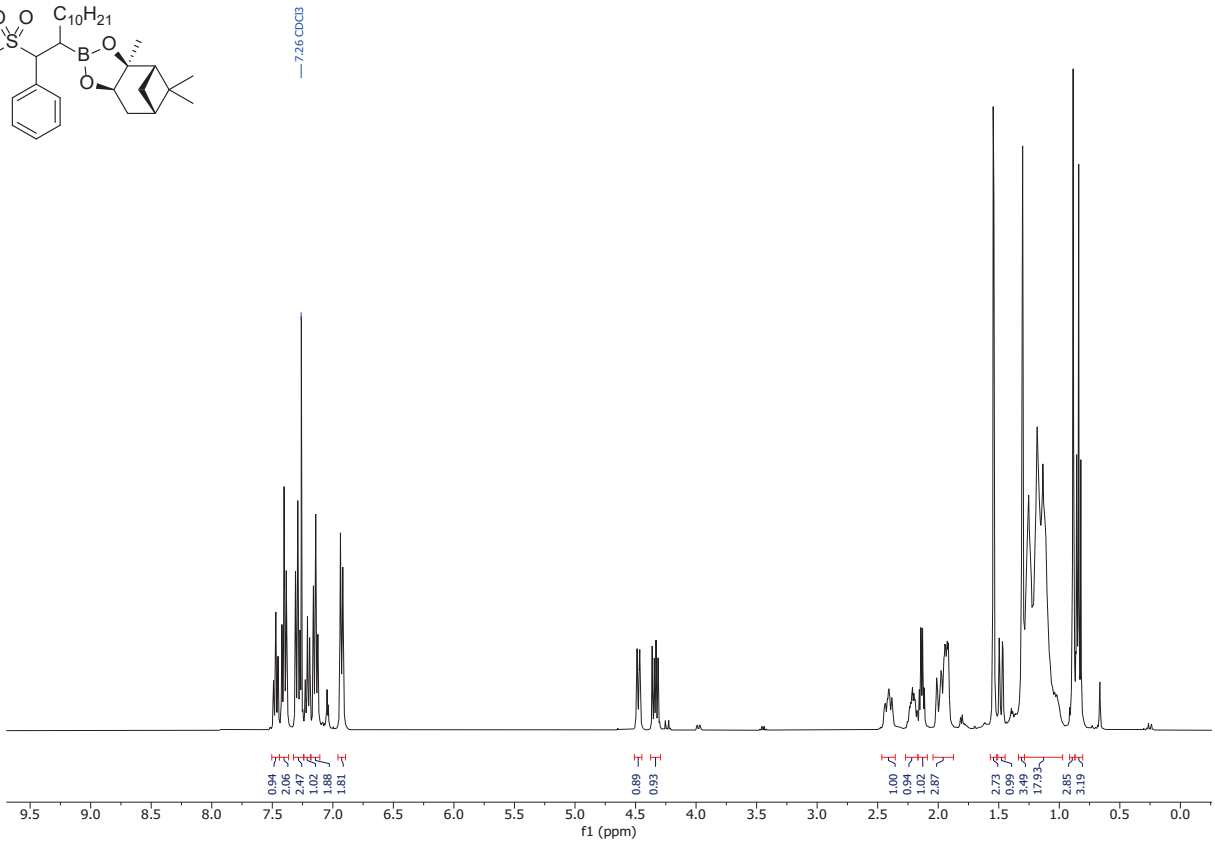




(3aS,4S,6S,7aR)-3a,5,5-trimethyl-2-(1-phenyl-1-(phenylsulfonyl)dodecan-2-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (47)
Mix of diastereomers

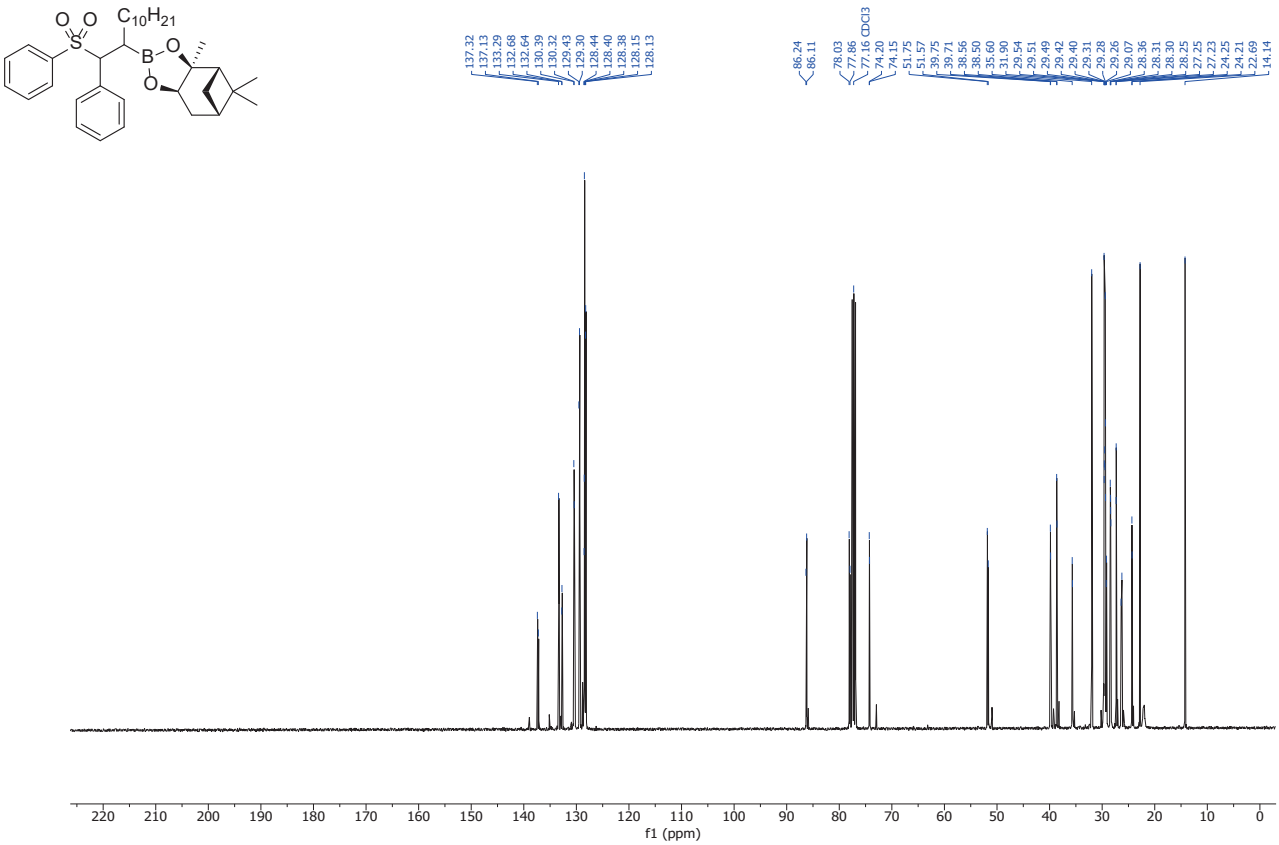
^{1}H NMR (400 MHz, $CDCl_3$)





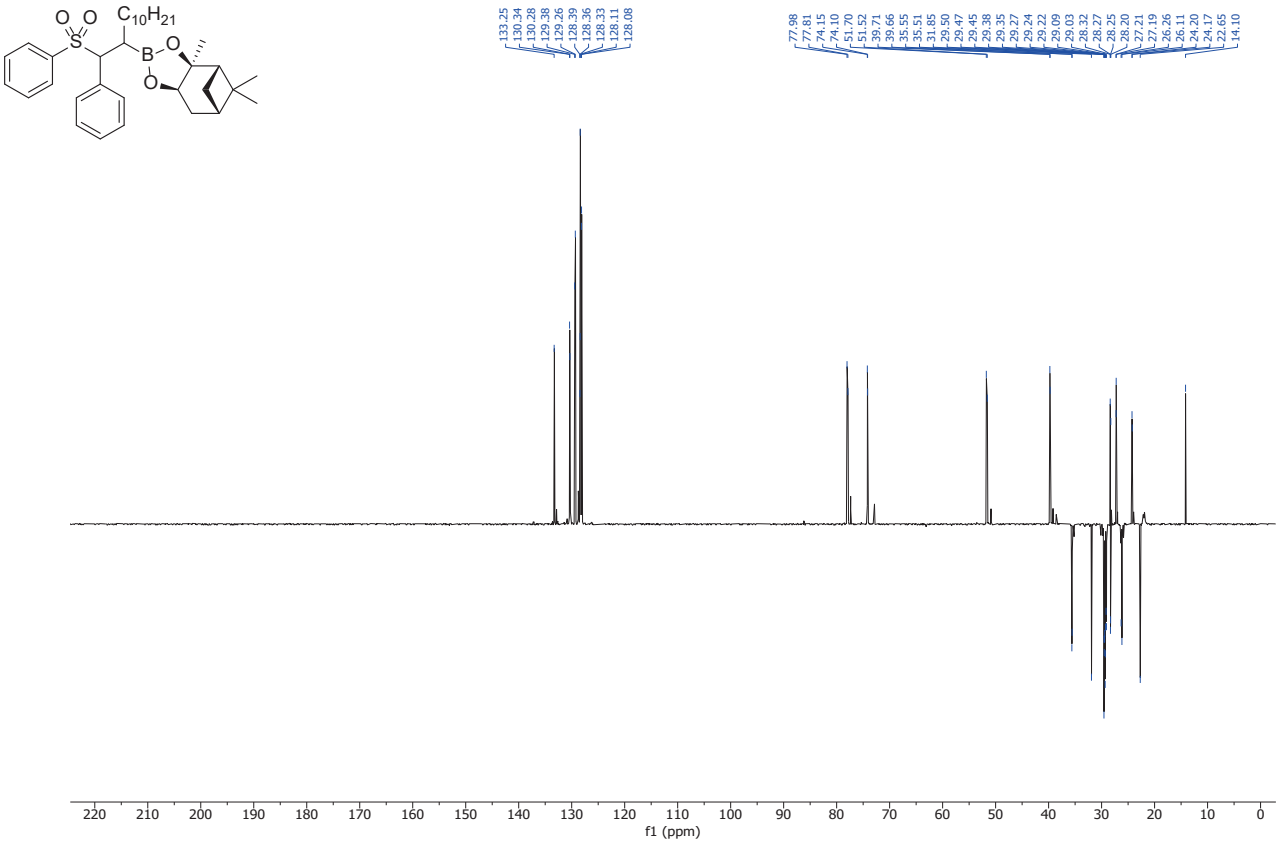
(3aS,4S,6S,7aR)-3a,5,5-trimethyl-2-(1-phenyl-1-(phenylsulfonyl)dodecan-2-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (47)
Mix of diastereomers

^{13}C NMR (101 MHz, $CDCl_3$)



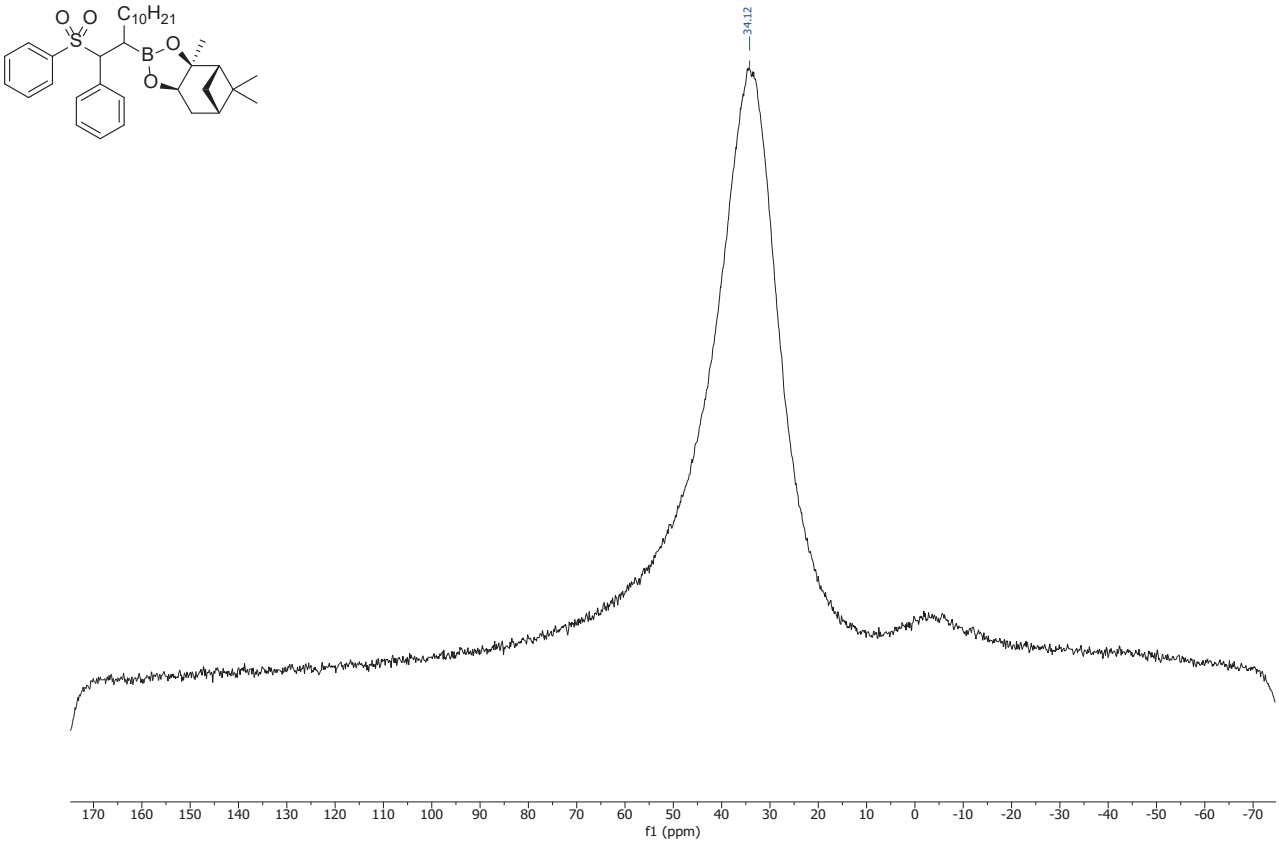
(3aS,4S,6S,7aR)-3a,5,5-trimethyl-2-(1-phenyl-1-(phenylsulfonyl)dodecan-2-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (47)
Mix of diastereomers

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



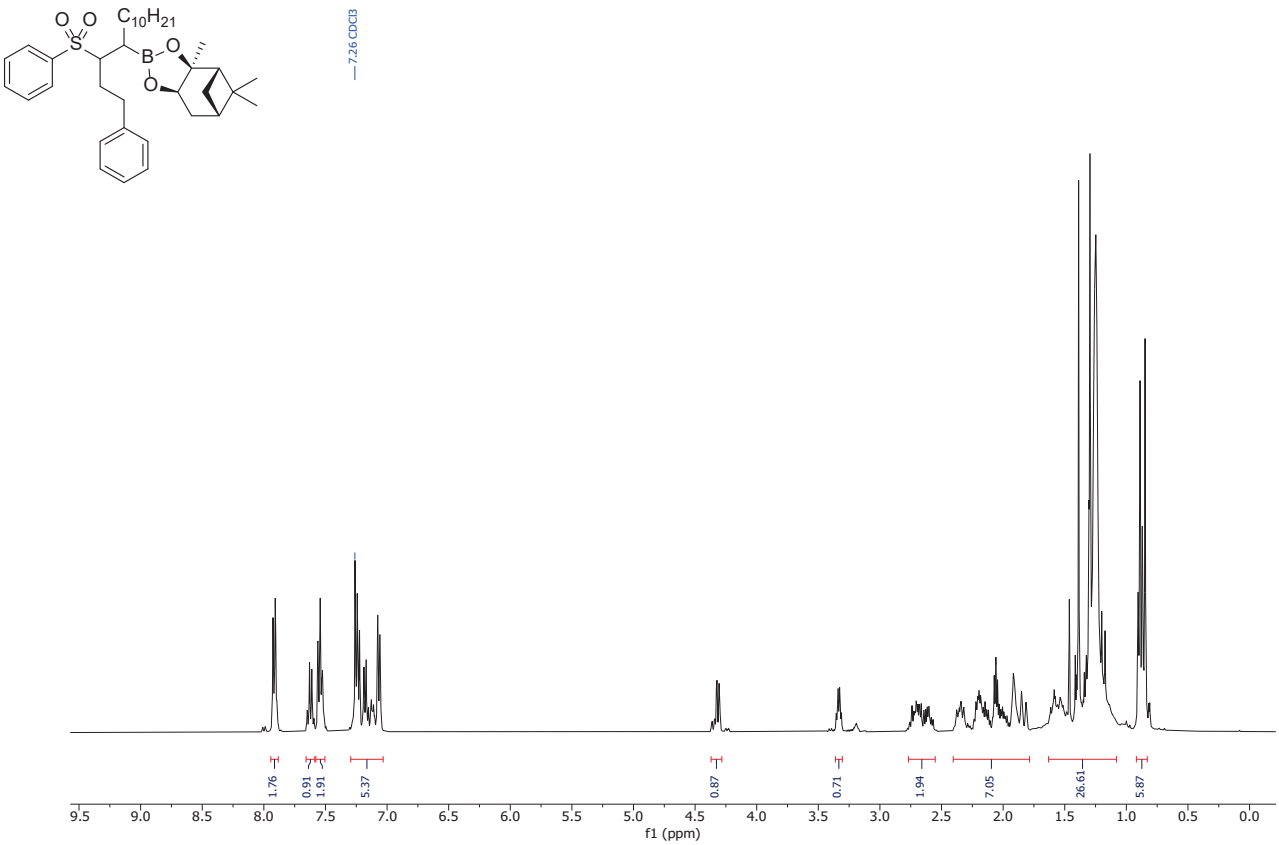
(3aS,4S,6S,7aR)-3a,5,5-trimethyl-2-(1-phenyl-1-(phenylsulfonyl)dodecan-2-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (47)
Mix of diastereomers

^{11}B NMR (96 MHz, $CDCl_3$)



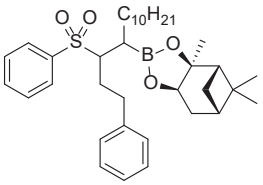
(3aS,4S,6S,7aR)-3a,5,5-trimethyl-2-(1-phenyl-3-(phenylsulfonyl)tetradecan-4-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (44)
Mix of diastereomers

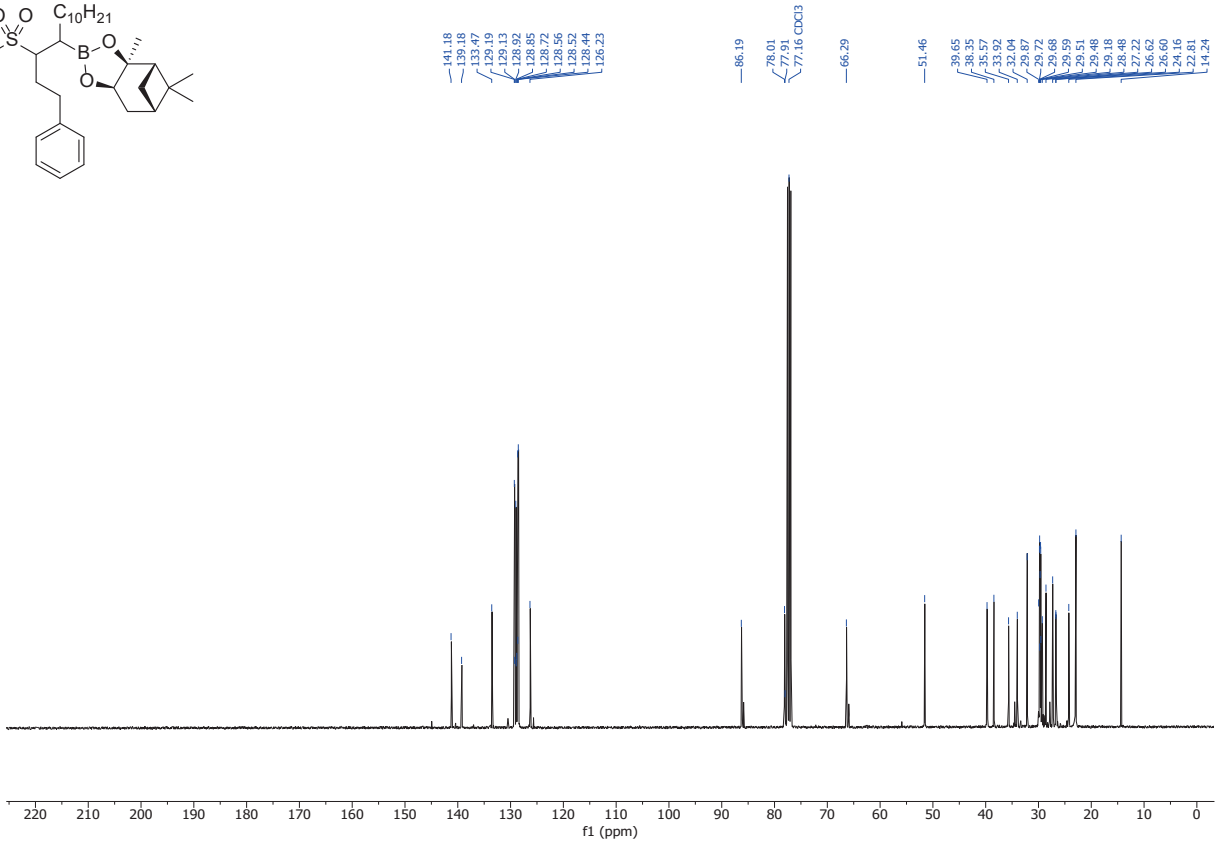
^{1}H NMR (400 MHz, $CDCl_3$)



(3aS,4S,6S,7aR)-3a,5,5-trimethyl-2-(1-phenyl-3-(phenylsulfonyl)tetradecan-4-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (44)
Mix of diastereomers

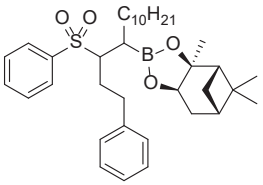
^{13}C NMR (101 MHz, $CDCl_3$)

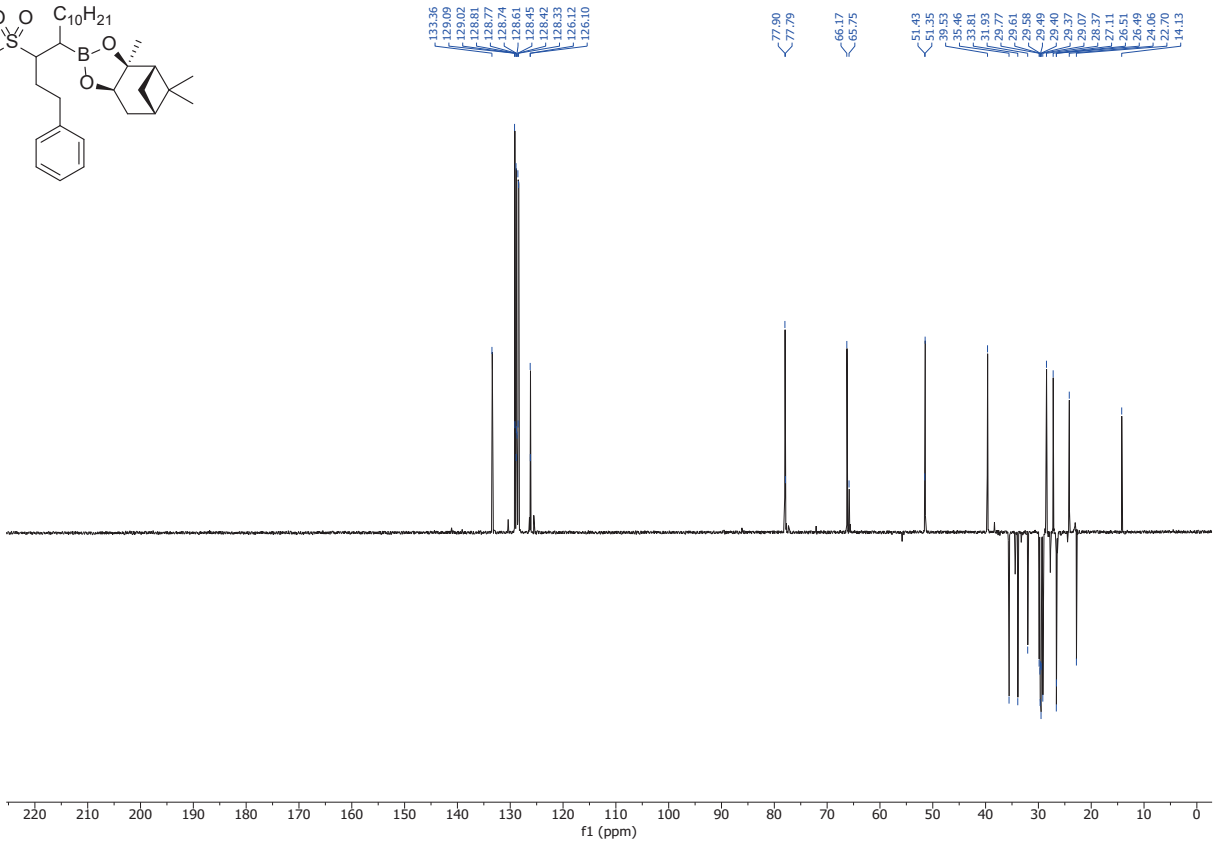




(3aS,4S,6S,7aR)-3a,5,5-trimethyl-2-(1-phenyl-3-(phenylsulfonyl)tetradecan-4-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (44)
Mix of diastereomers

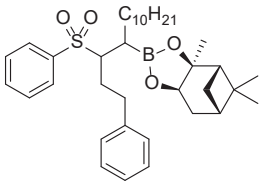
^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)

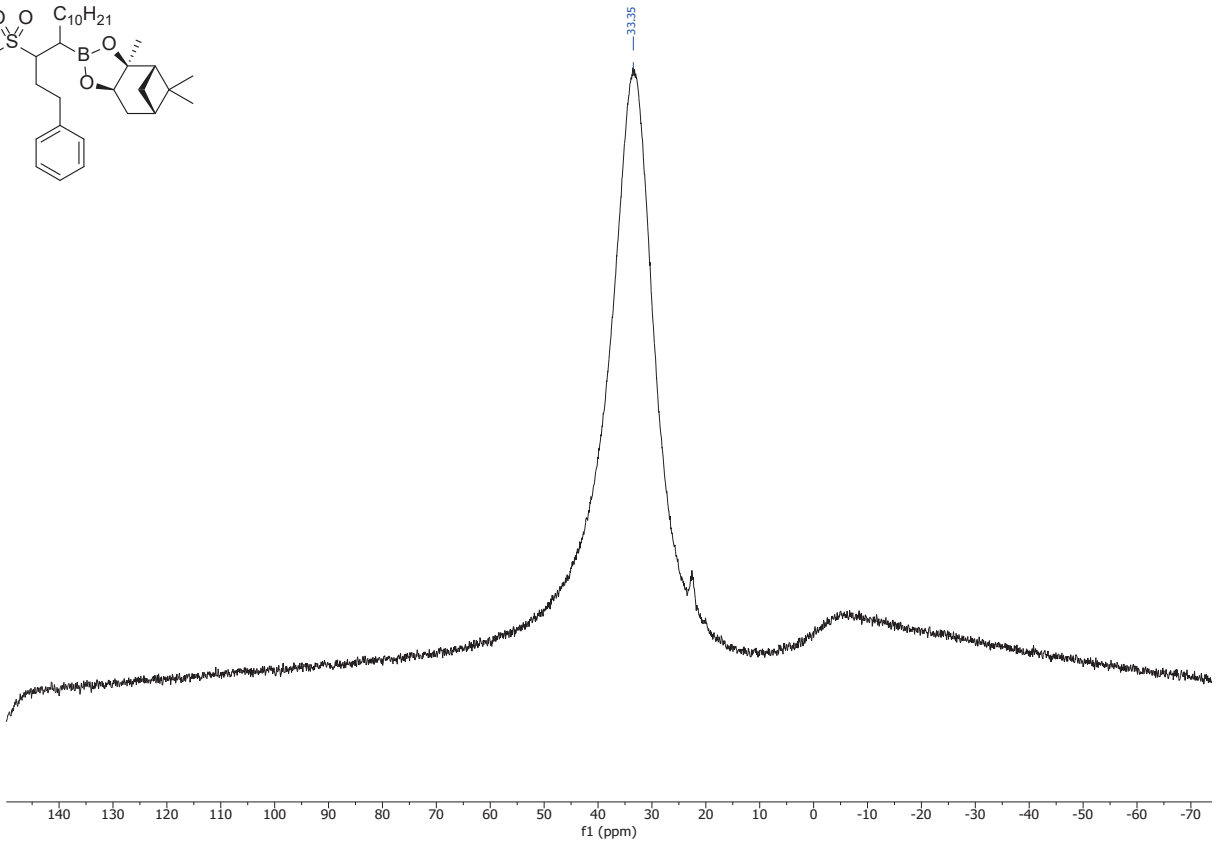




(3aS,4S,6S,7aR)-3a,5,5-trimethyl-2-(1-phenyl-3-(phenylsulfonyl)tetradecan-4-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (44)
Mix of diastereomers

^{11}B NMR (128 MHz, $CDCl_3$)

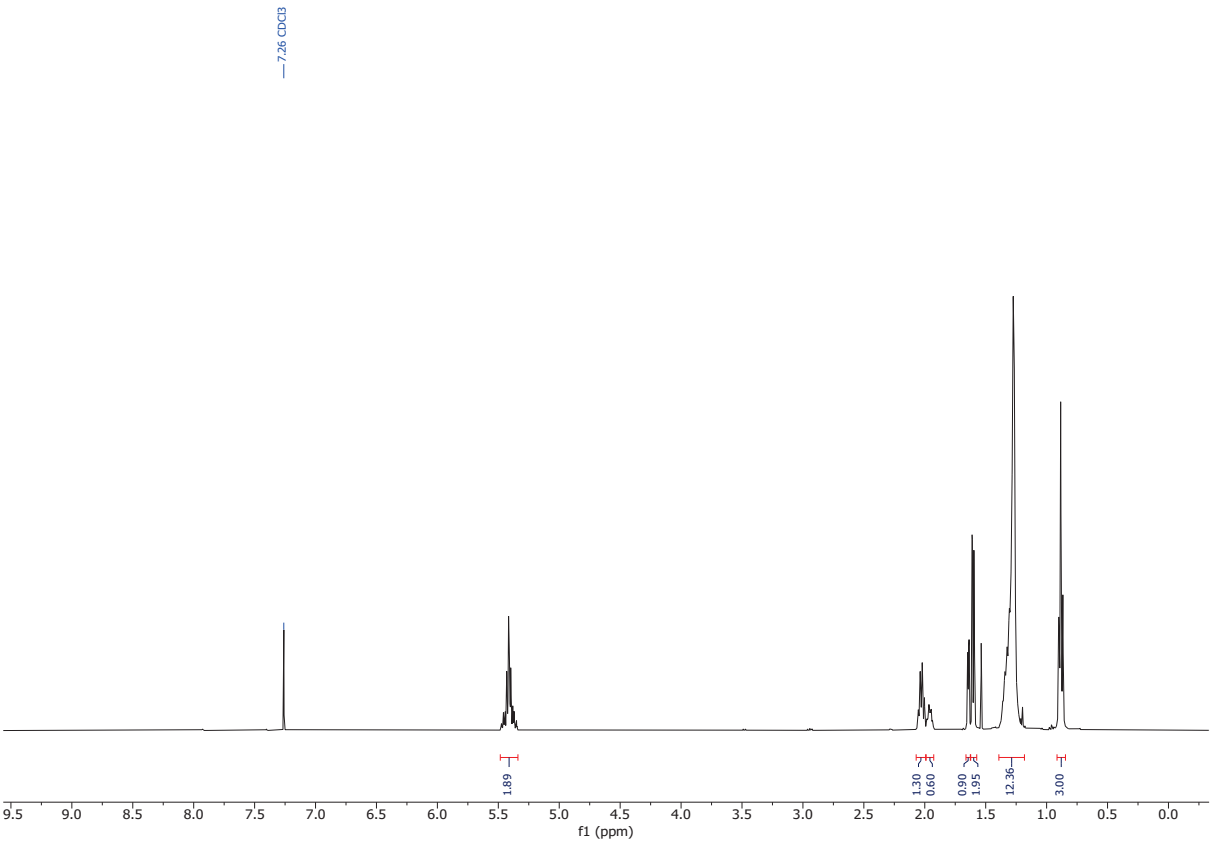




(Z)-undec-2-ene (23)
Mix of diastereomers

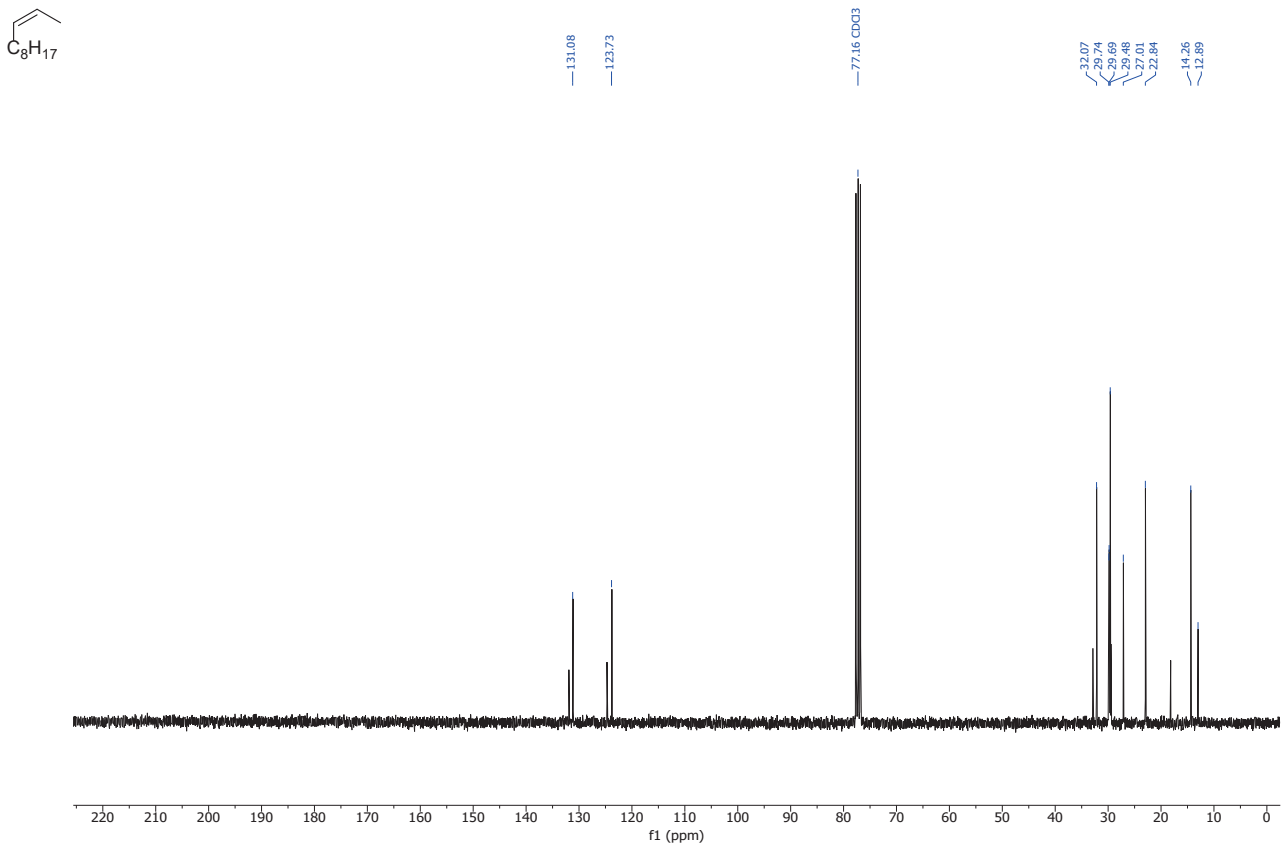
^{1}H NMR (400 MHz, $CDCl_3$)





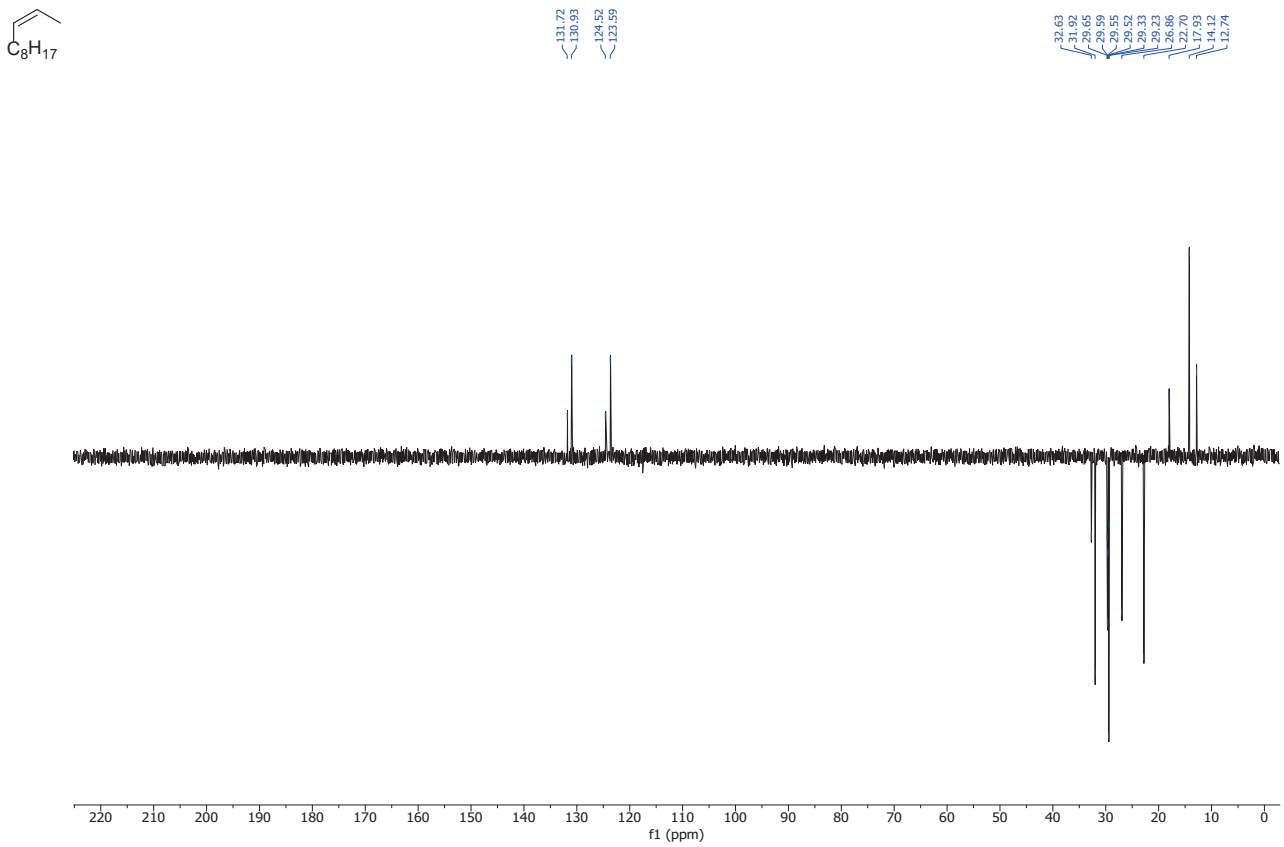
(Z)-undec-2-ene (23)
Major isomer

^{13}C NMR (75 MHz, $CDCl_3$)



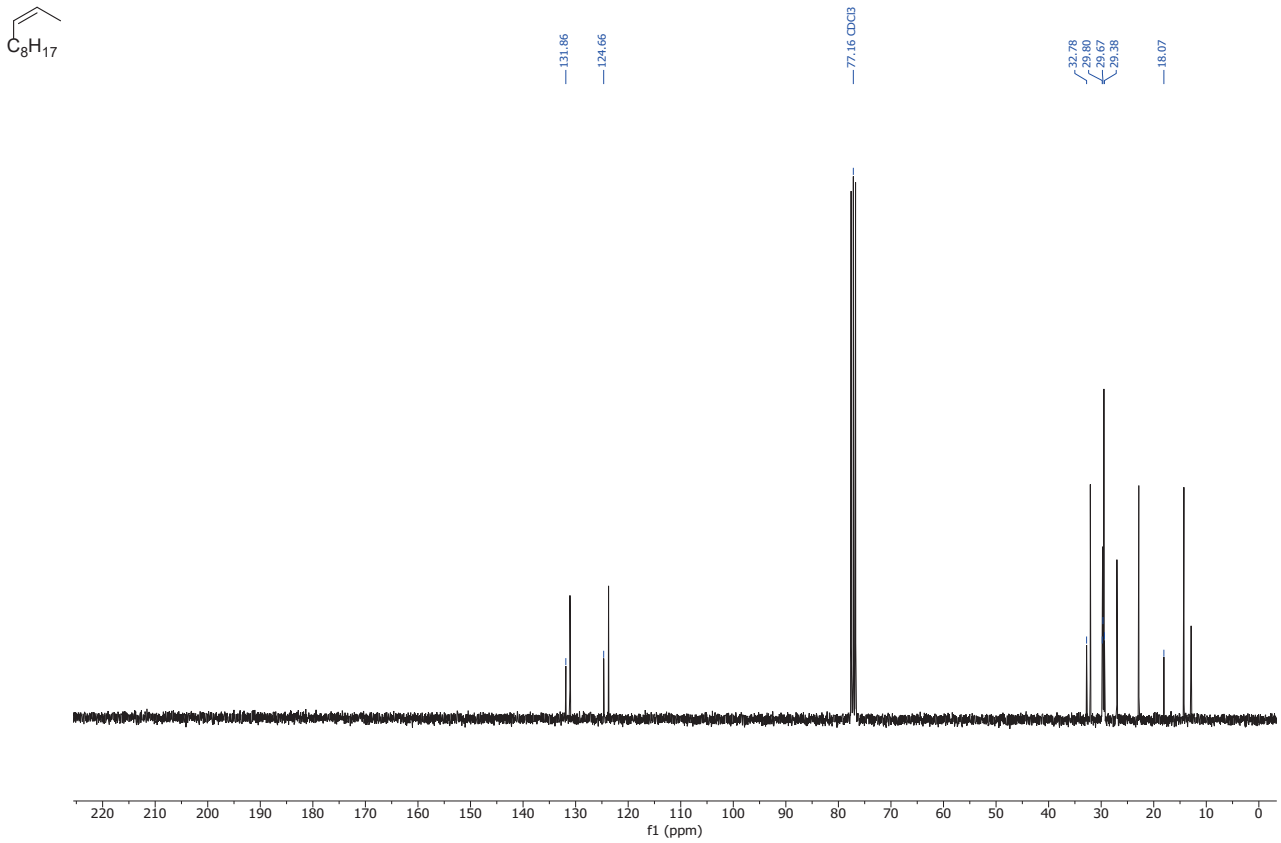
(Z)-undec-2-ene (23)
Mix of isomers

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



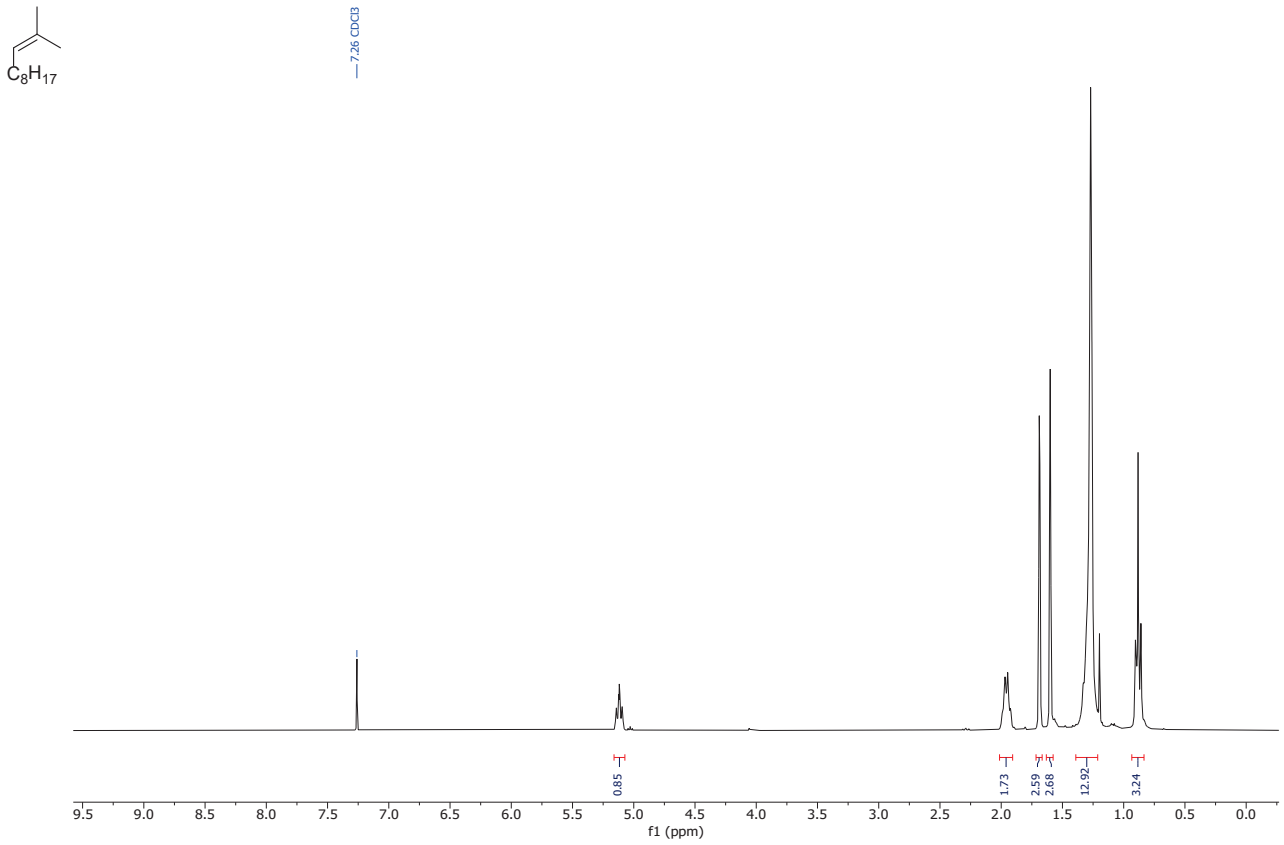
(Z)-undec-2-ene (23)
Minor isomer

^{13}C NMR (75 MHz, $CDCl_3$)



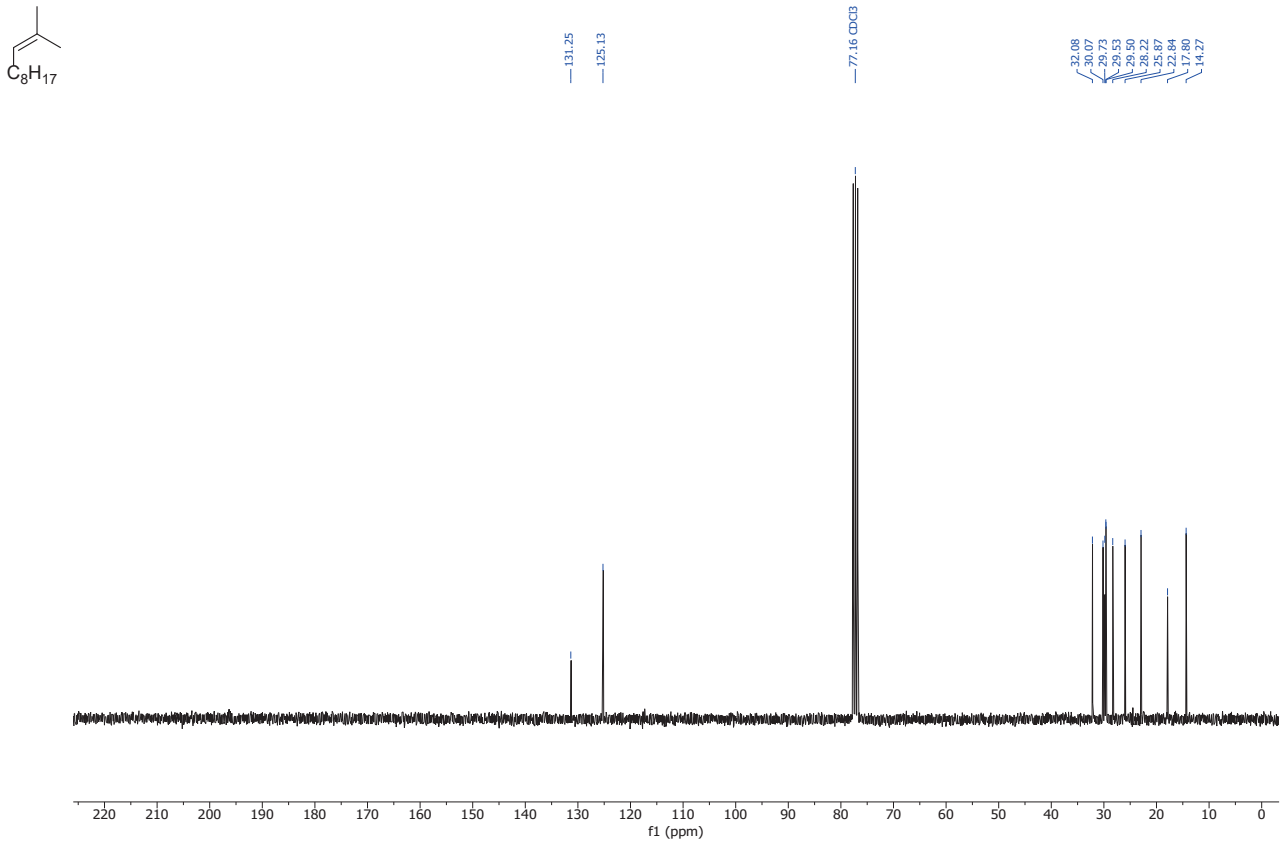
2-methylundec-2-ene (19)

^{1}H NMR (300 MHz, $CDCl_3$)



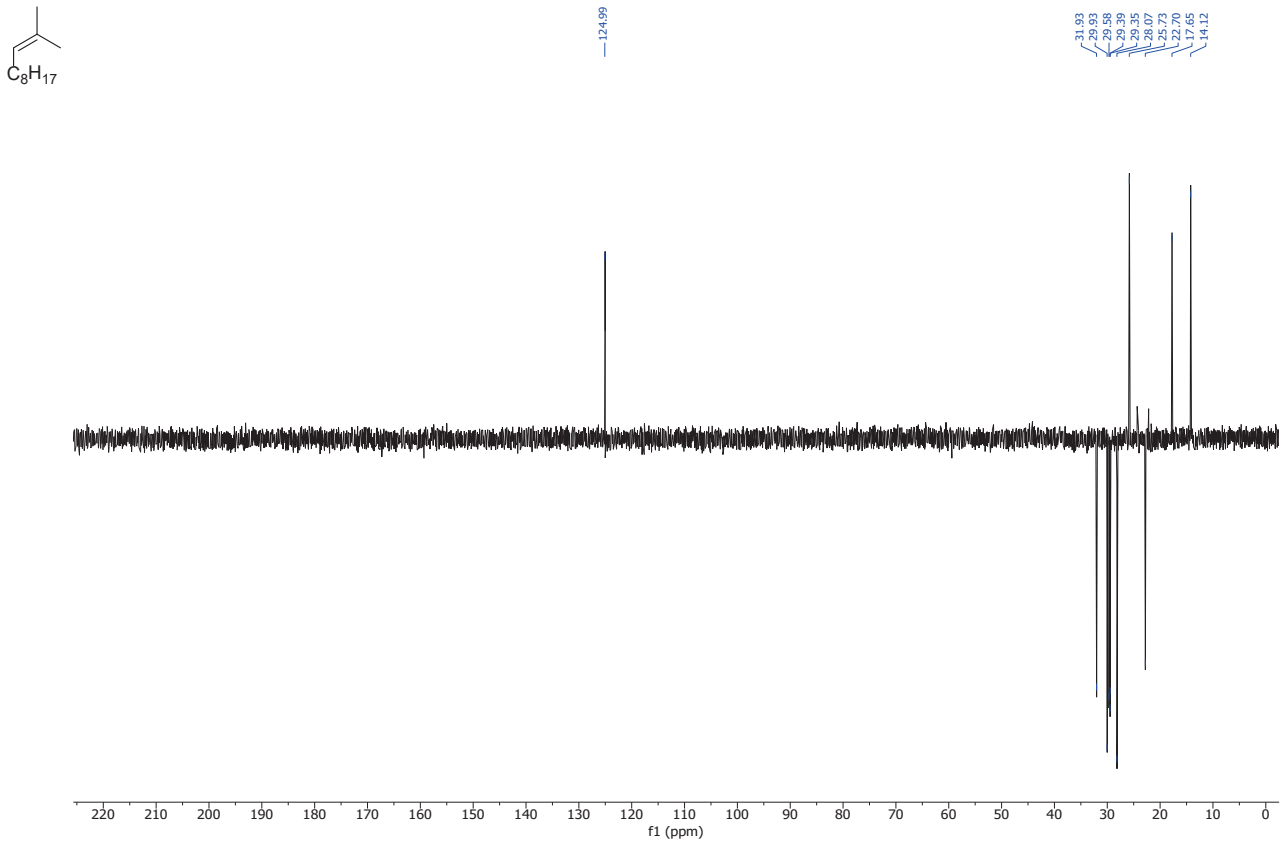
2-methylundec-2-ene (19)

^{13}C NMR (75 MHz, $CDCl_3$)



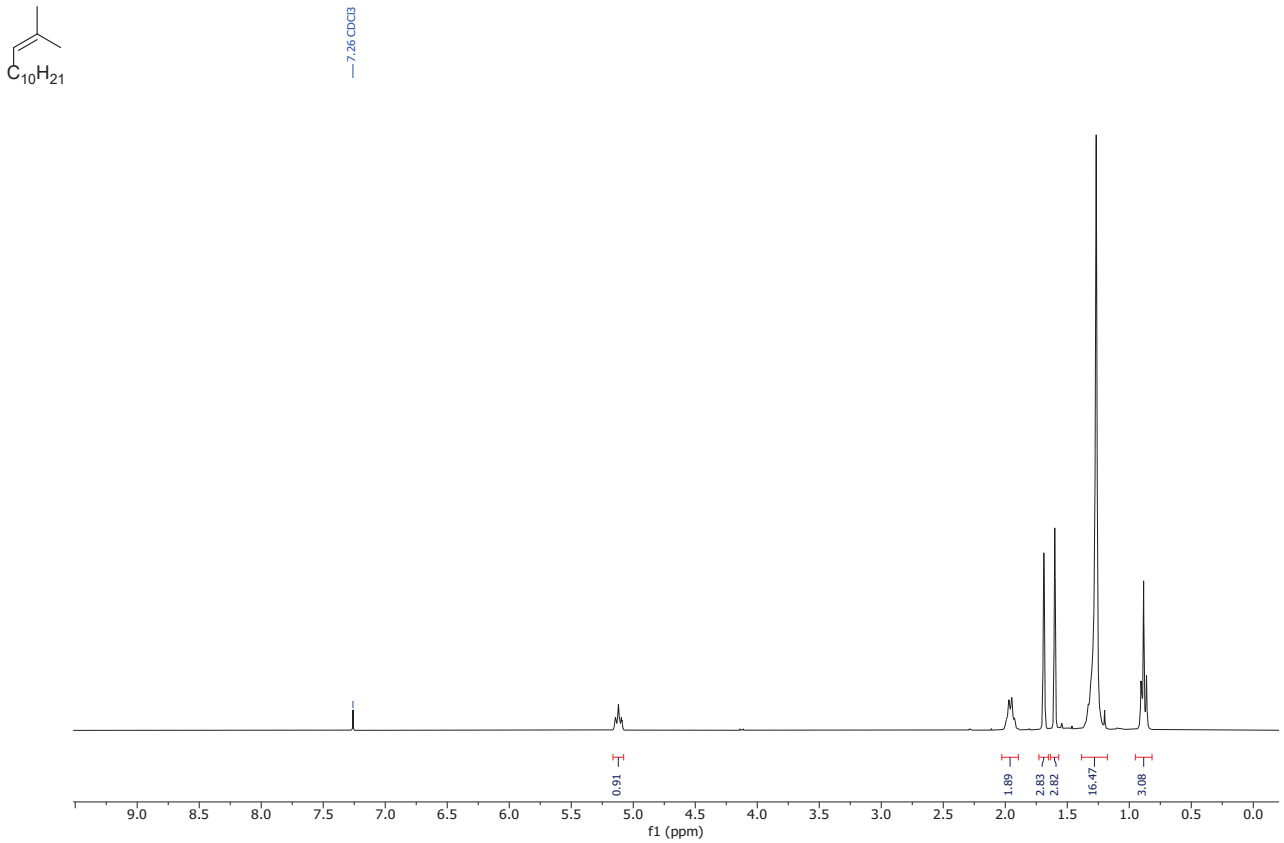
2-methylundec-2-ene (19)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



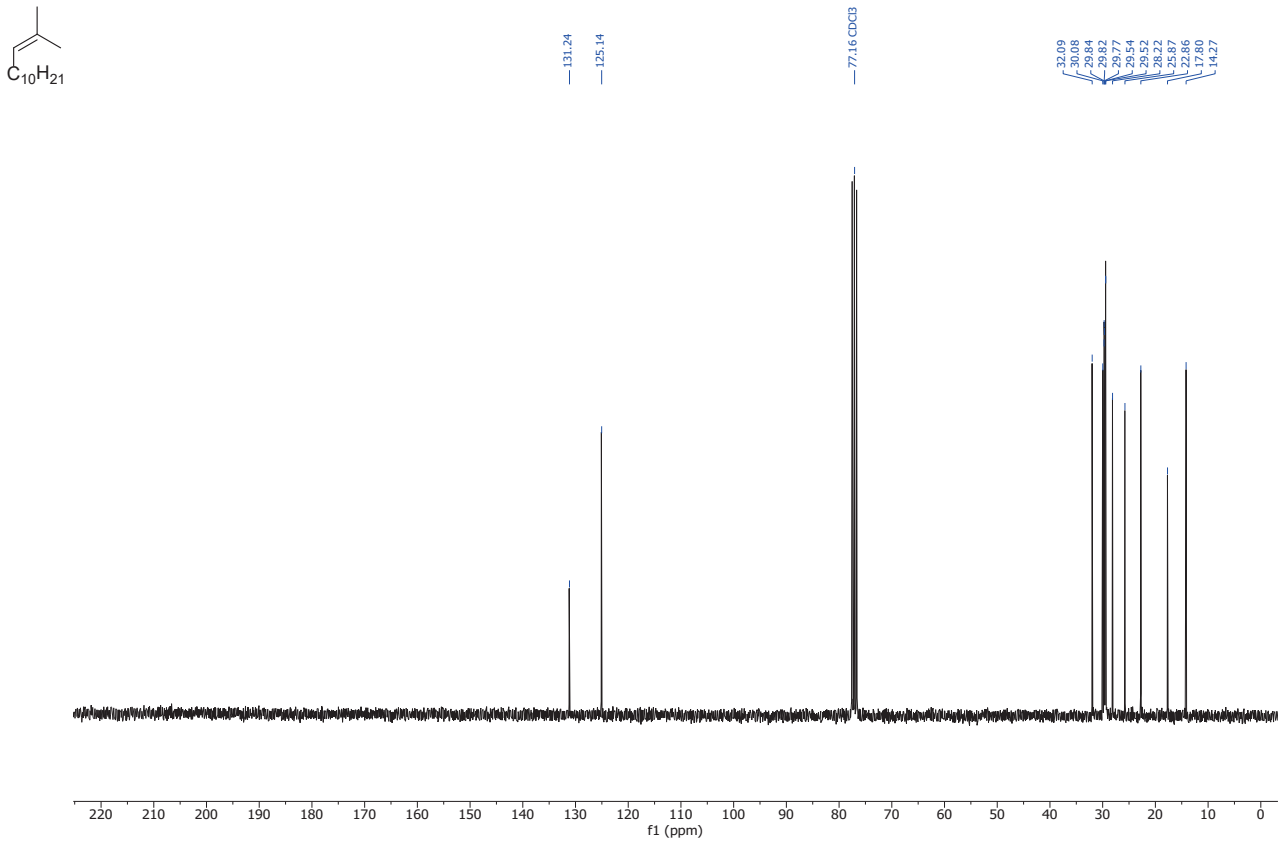
2-methyltridec-2-ene (20)

^{1}H NMR (300 MHz, $CDCl_3$)



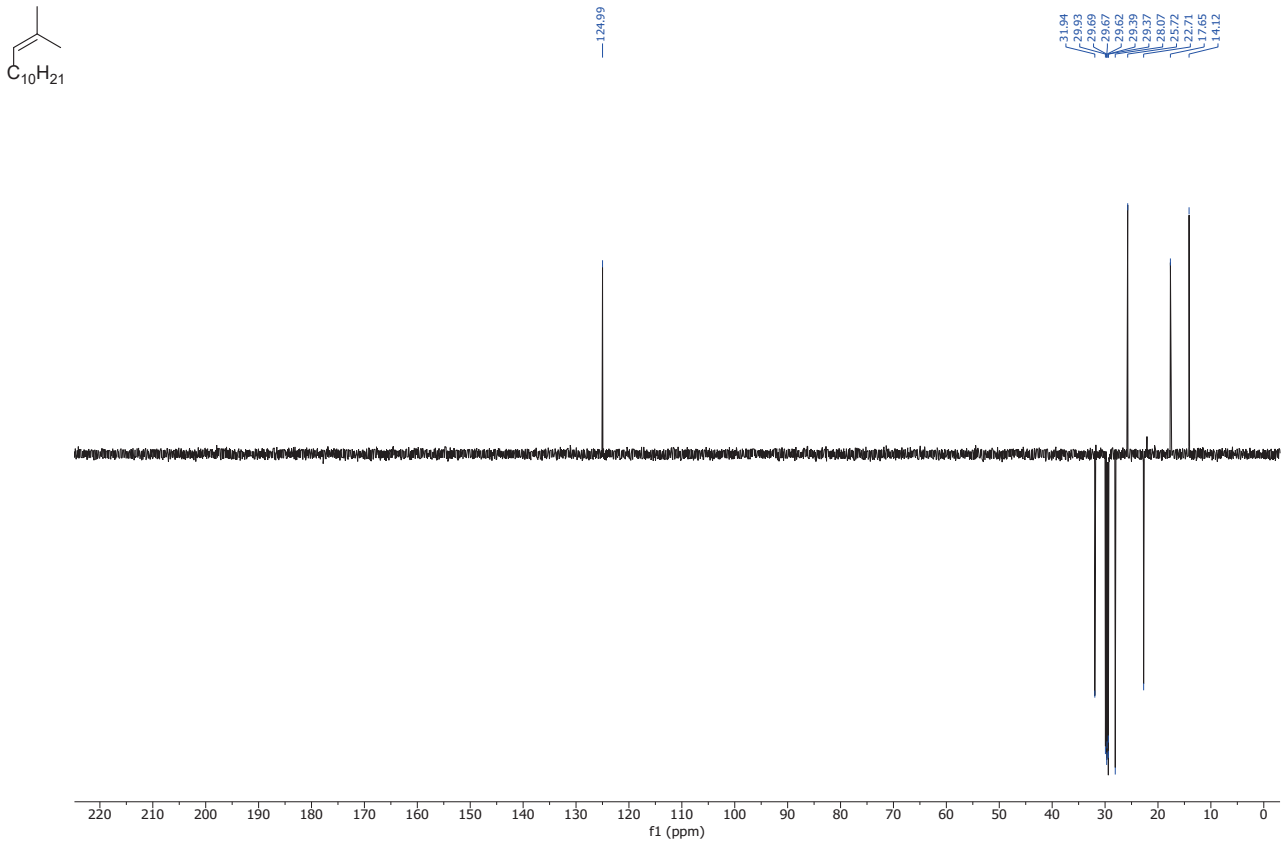
2-methyltridec-2-ene (20)

^{13}C NMR (75 MHz, $CDCl_3$)



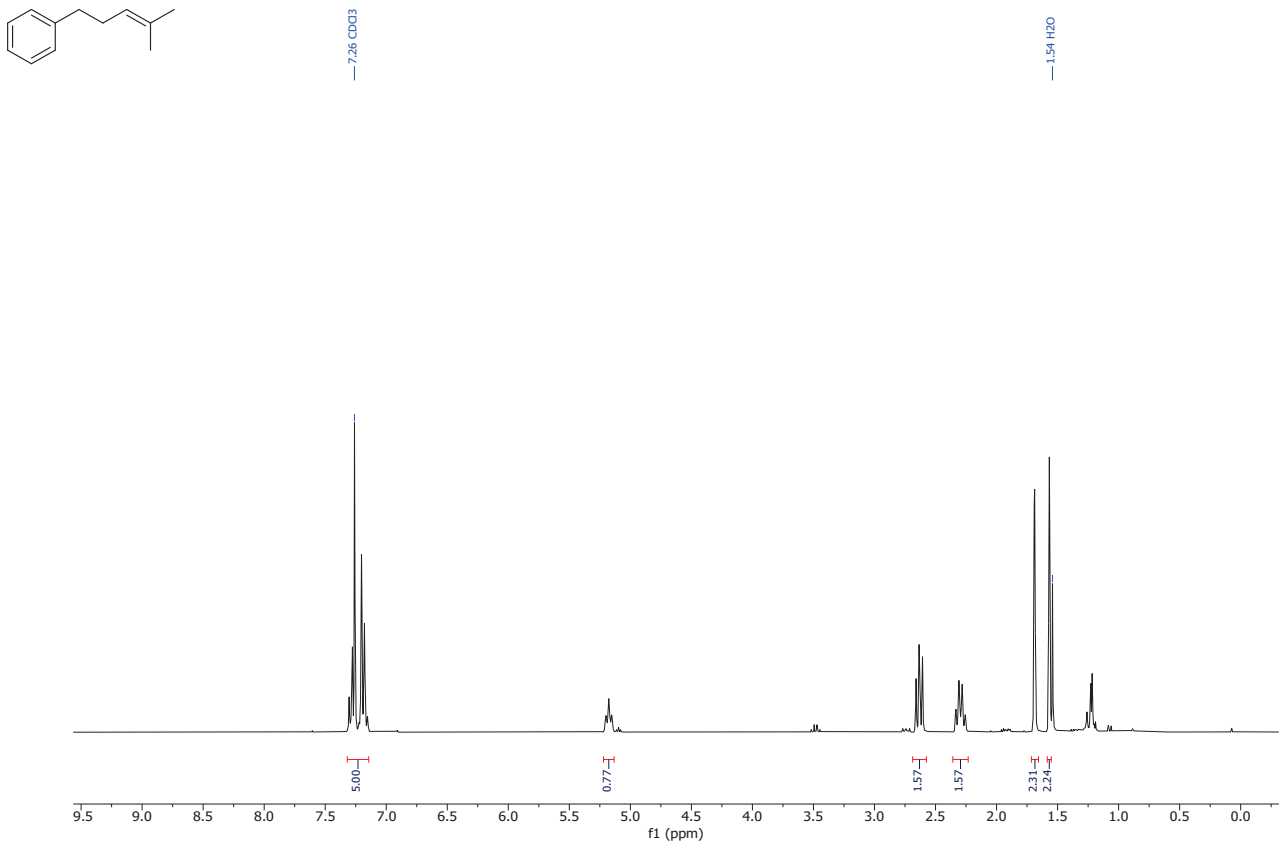
2-methyltridec-2-ene (20)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



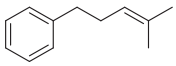
(4-methylpent-3-en-1-yl)benzene (21)

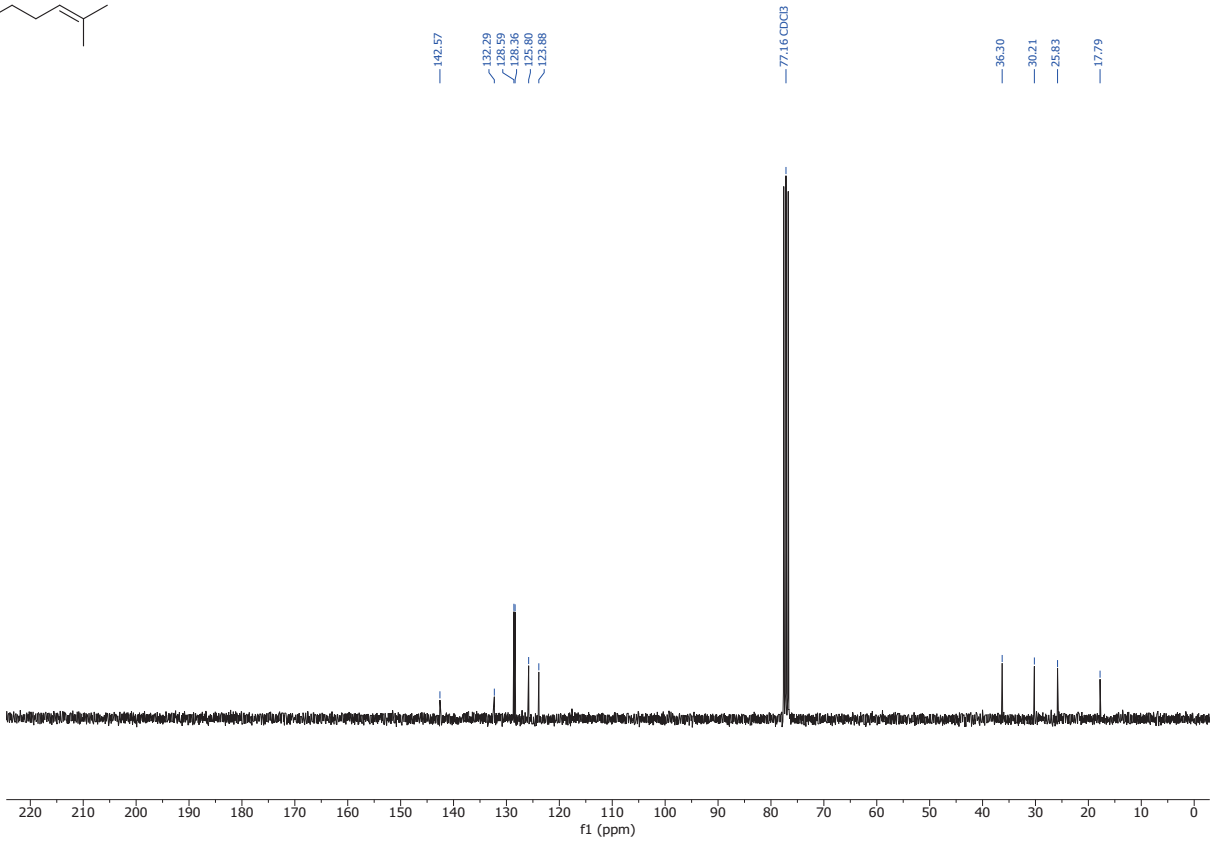
^{1}H NMR (300 MHz, $CDCl_3$)



(4-methylpent-3-en-1-yl)benzene (21)

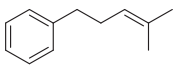
^{13}C NMR (75 MHz, $CDCl_3$)

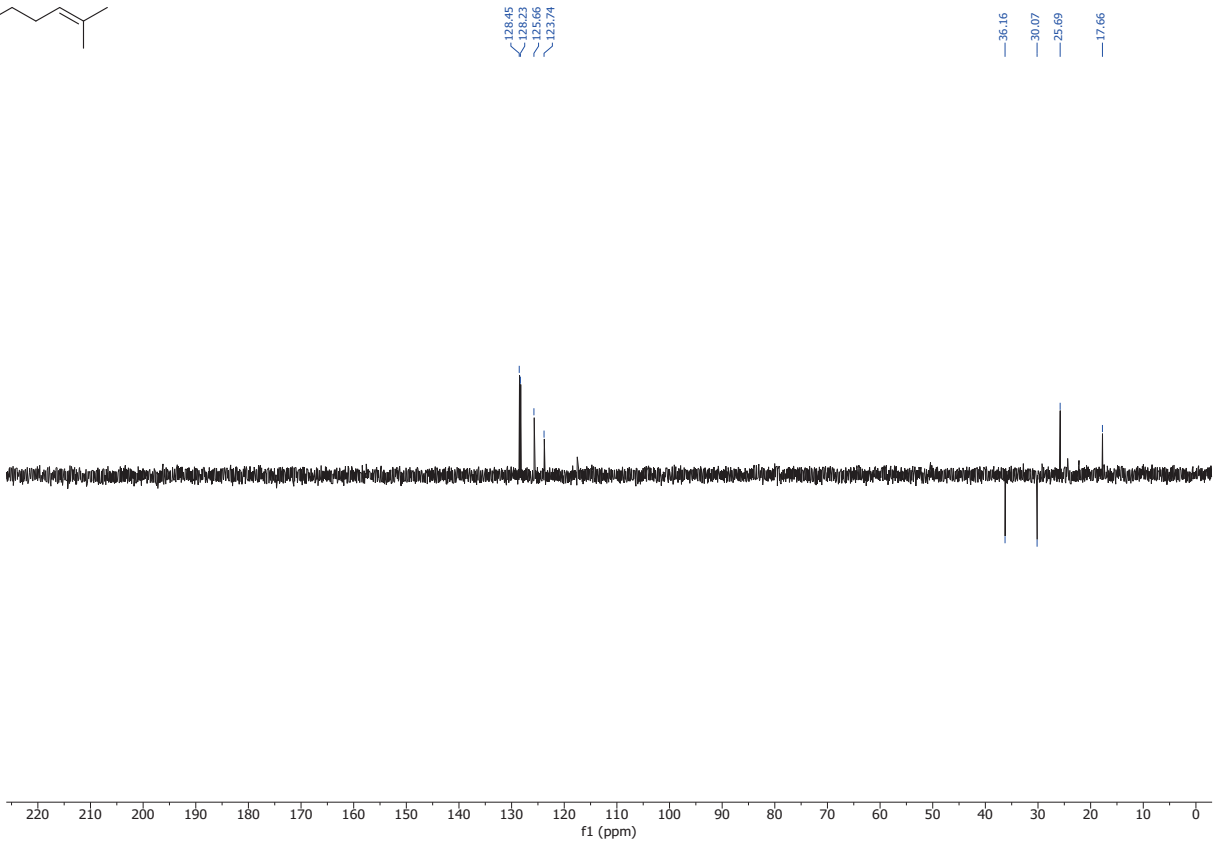




(4-methylpent-3-en-1-yl)benzene (21)

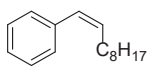
^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

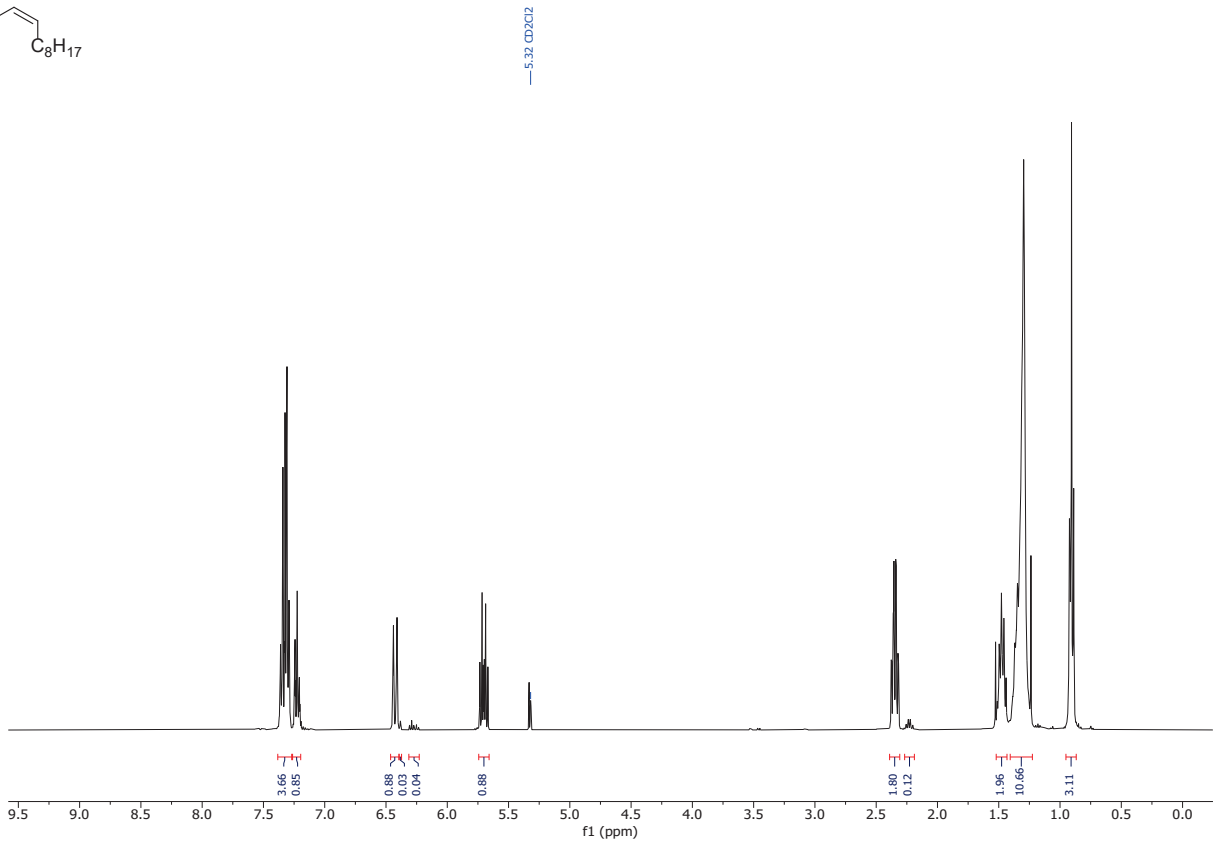




(Z)-dec-1-en-1-ylbenzene (32)
Mix of isomers

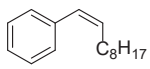
^{1}H NMR (400 MHz, CD_2Cl_2)

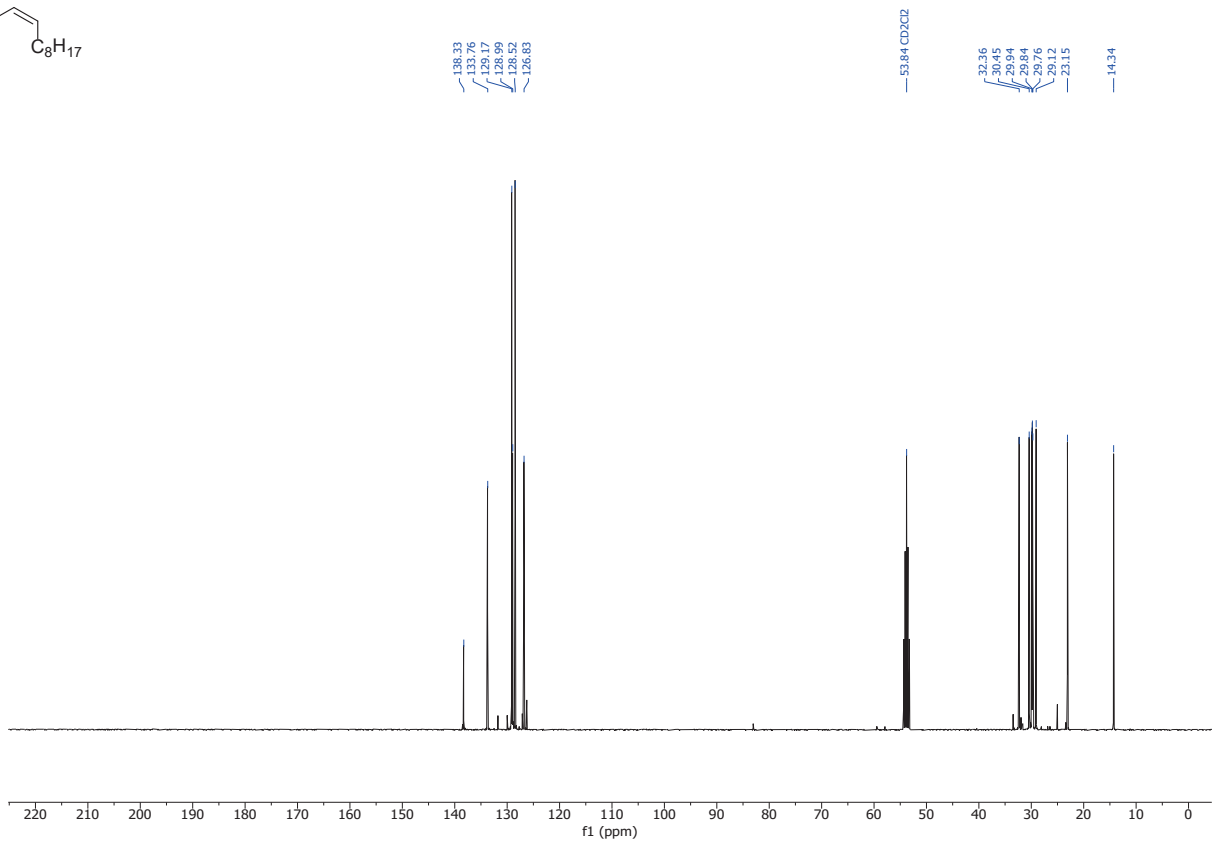




(Z)-dec-1-en-1-ylbenzene (32)
Major isomer

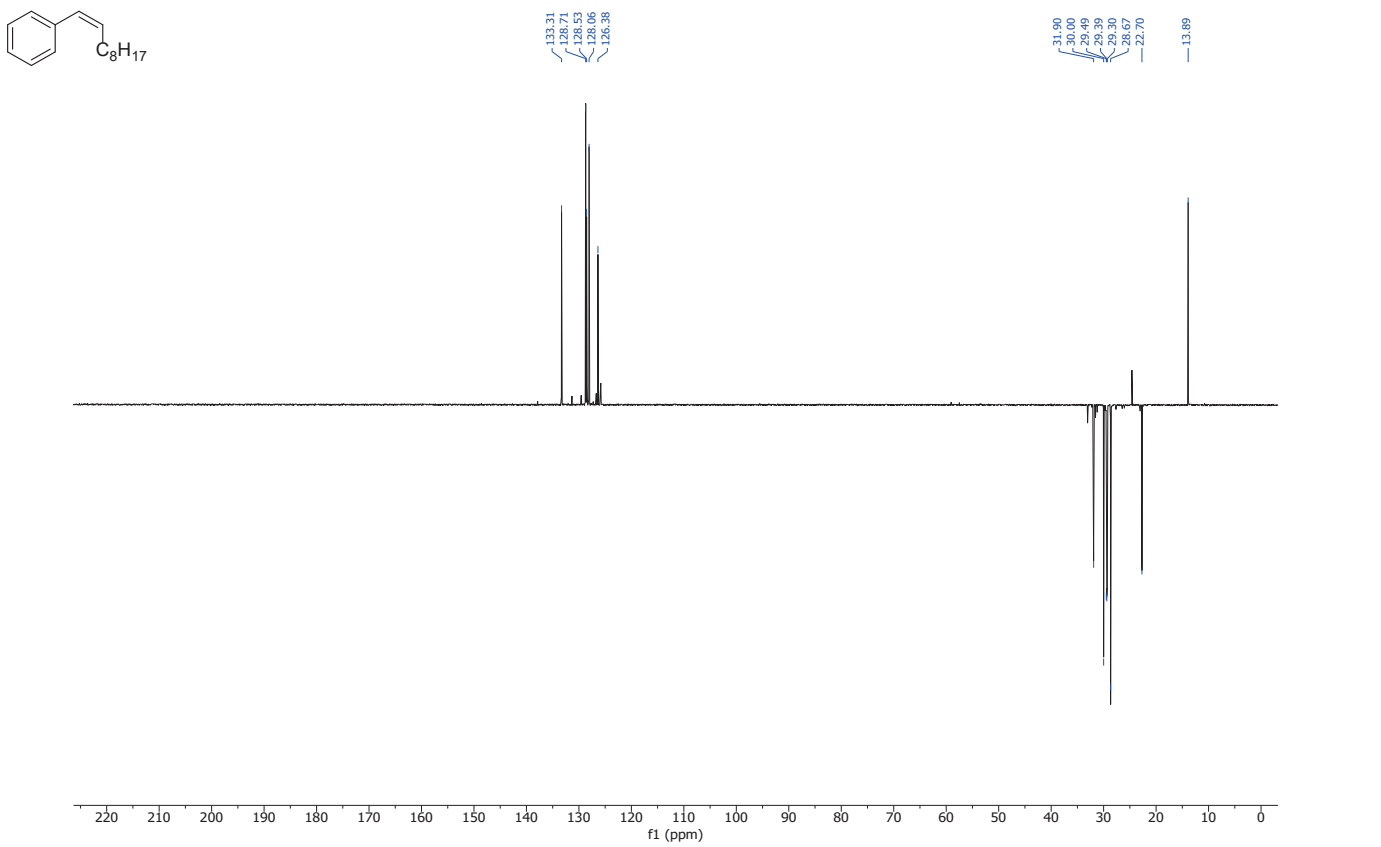
^{13}C NMR (101 MHz, CD_2Cl_2)





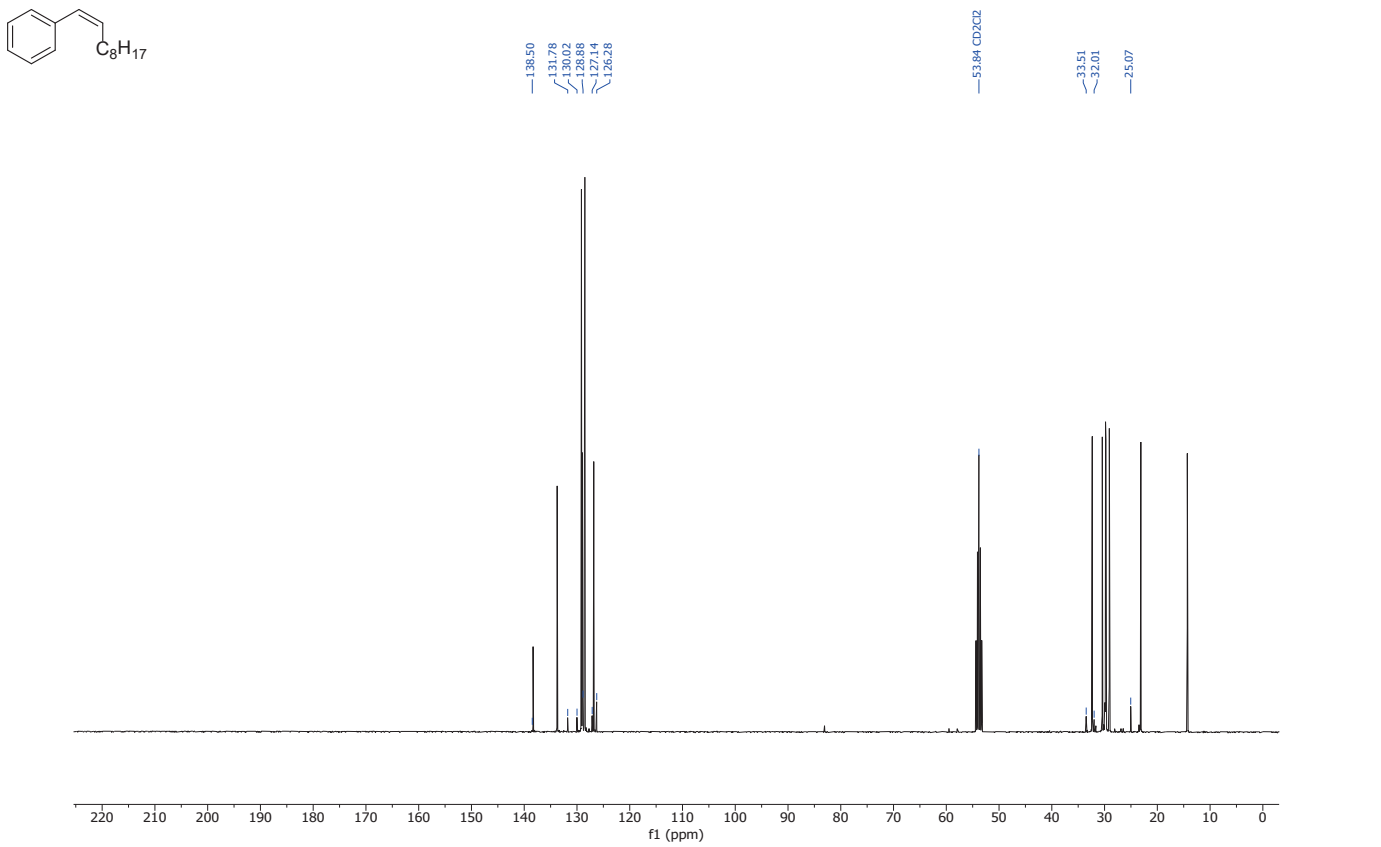
(Z)-dec-1-en-1-ylbenzene (32)
Mix of isomers

^{13}C NMR Dept-135 (101 MHz, CD_2Cl_2)



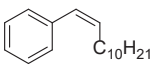
(Z)-dec-1-en-1-ylbenzene (32)
Minor isomer

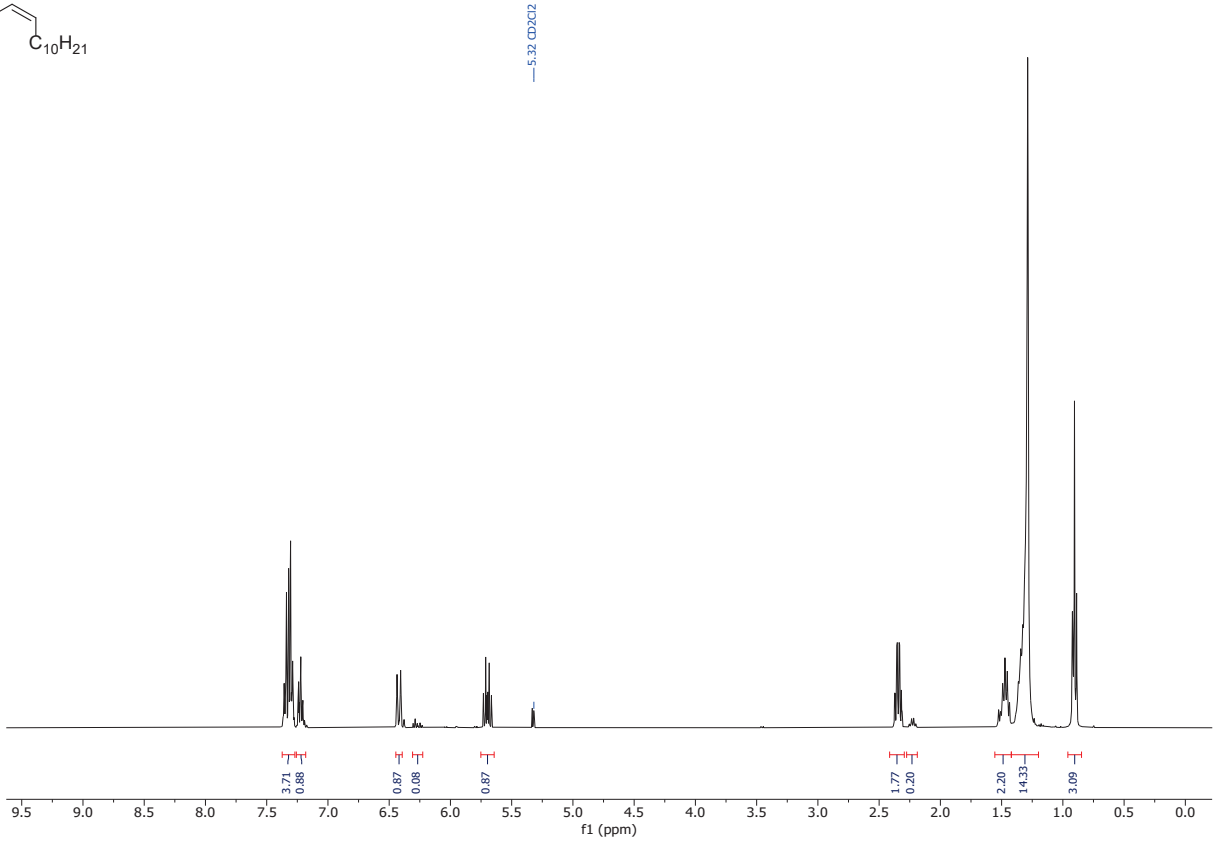
^{13}C NMR (101 MHz, CD_2Cl_2)



(Z)-dodec-1-en-1-ylbenzene (31)
Mix of isomers

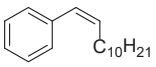
^{1}H NMR (400 MHz, CD_2Cl_2)

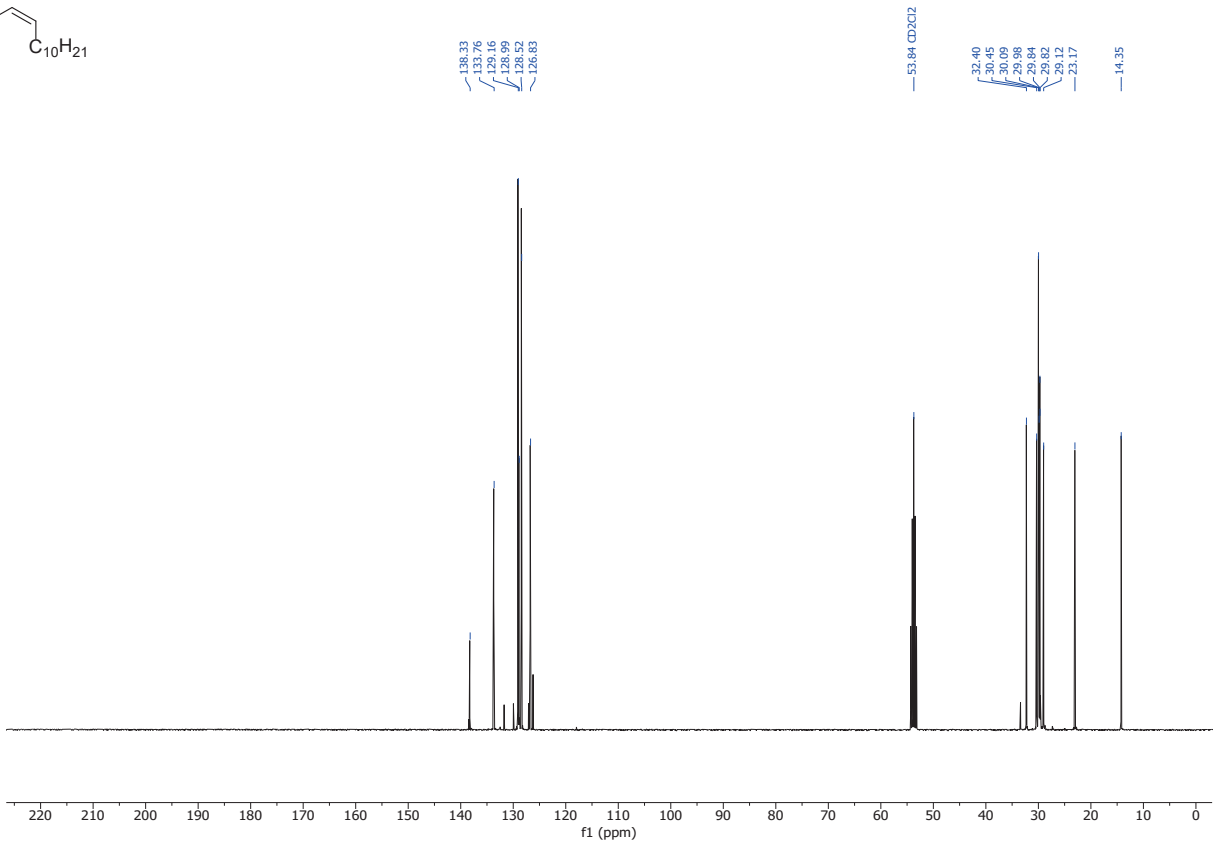




(Z)-dodec-1-en-1-ylbenzene (31)
Major isomer

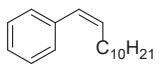
^{13}C NMR (101 MHz, CD_2Cl_2)

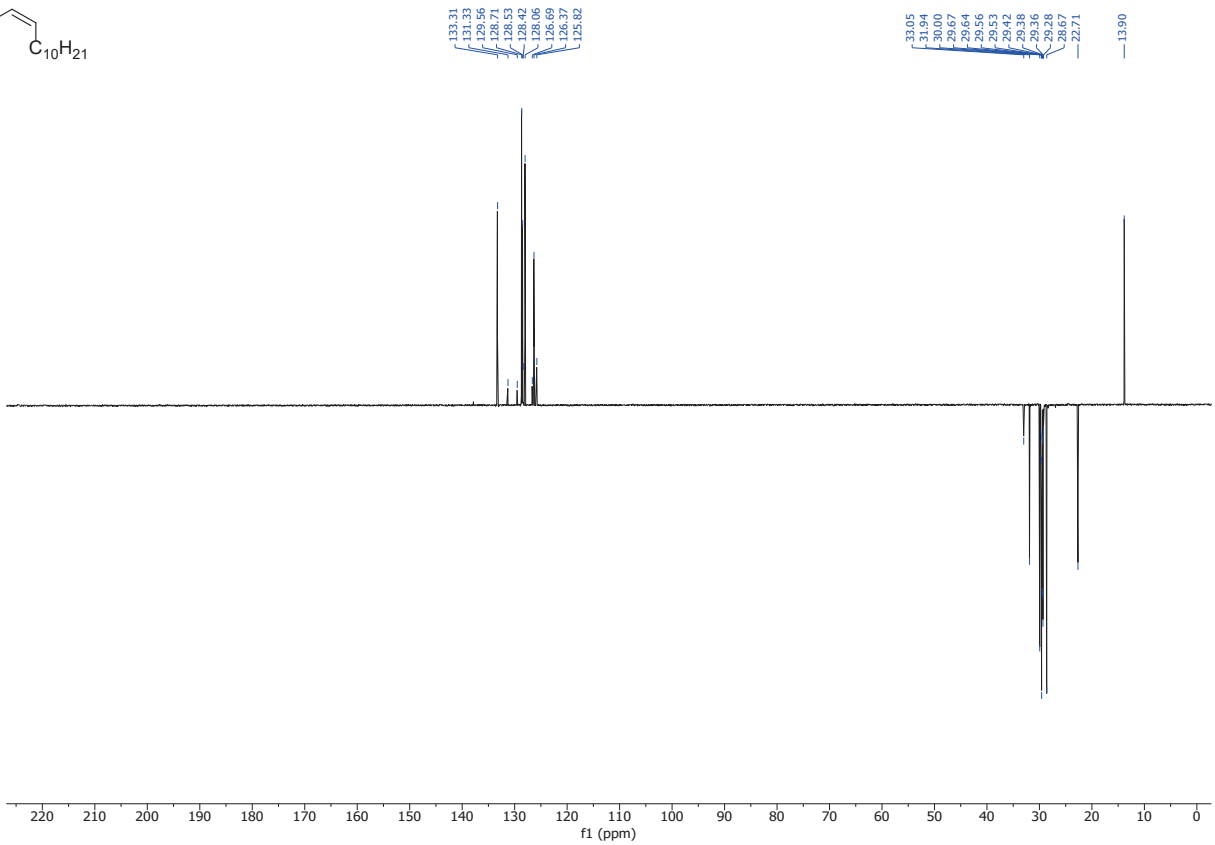




(Z)-dodec-1-en-1-ylbenzene (31)
Mix of isomers

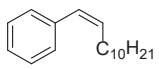
^{13}C NMR Dept-135 (101 MHz, CD_2Cl_2)

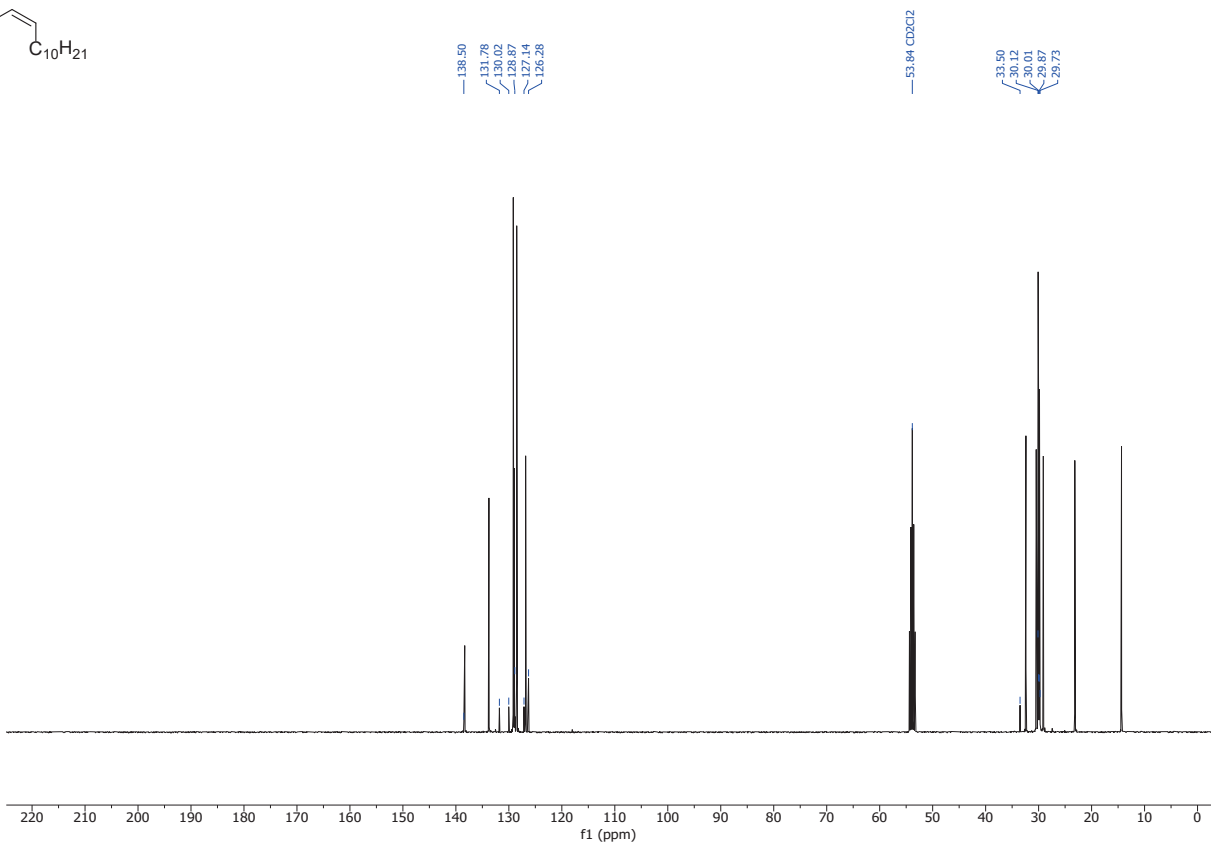




(Z)-dodec-1-en-1-ylbenzene (31)
Minor isomer

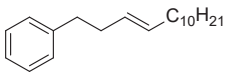
^{13}C NMR (101 MHz, CD_2Cl_2)

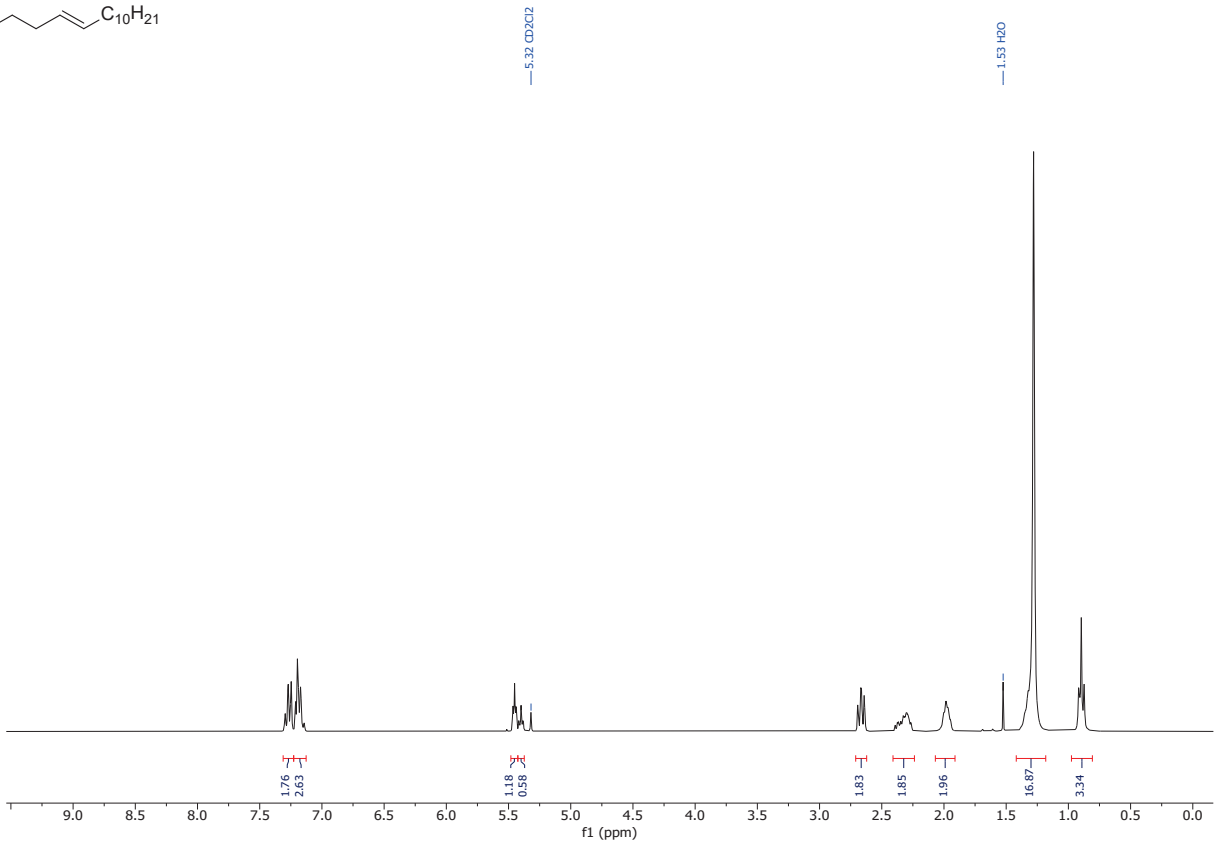




(E)-tetradec-3-en-1-ylbenzene (24)
Mix of isomers

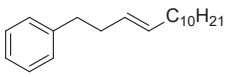
^{1}H NMR (300 MHz, CD_2Cl_2)

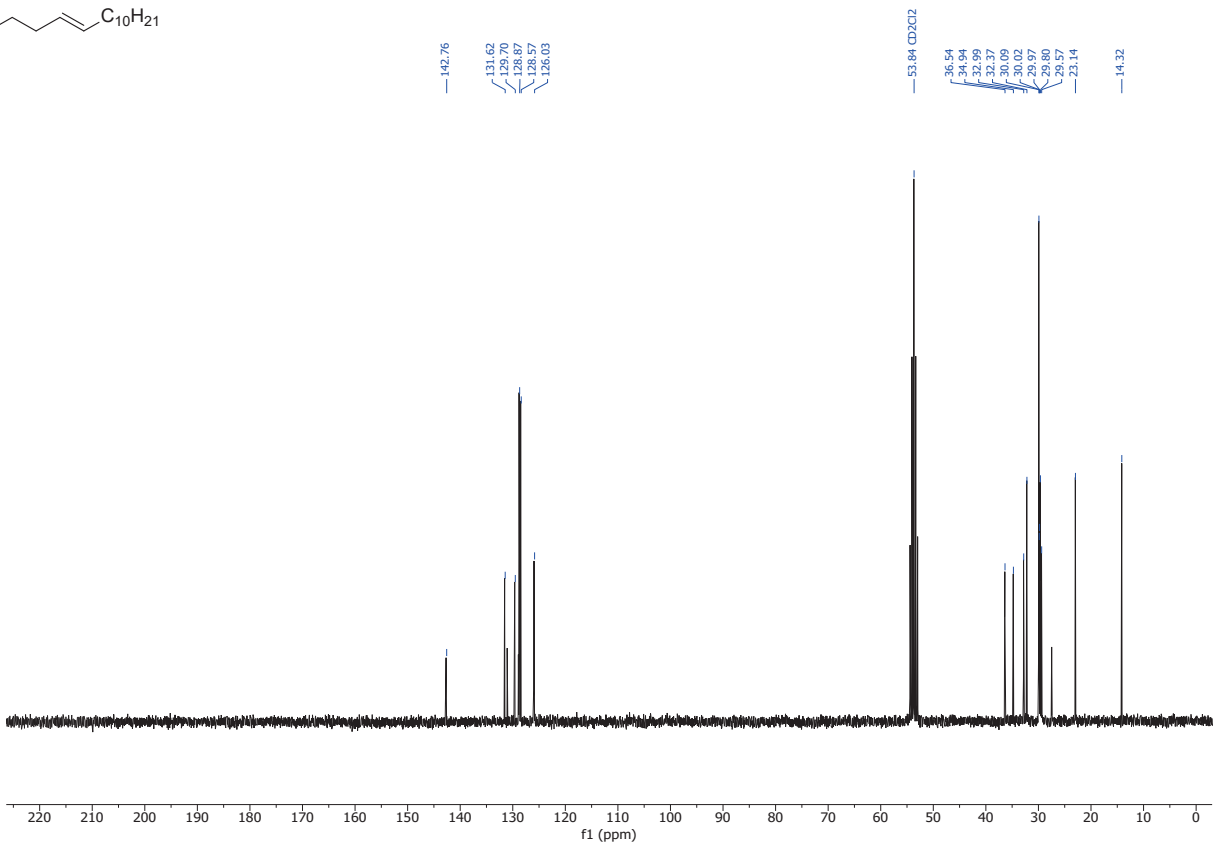




(E)-tetradec-3-en-1-ylbenzene (24)
Major isomer

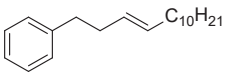
^{13}C NMR (75 MHz, CD_2Cl_2)



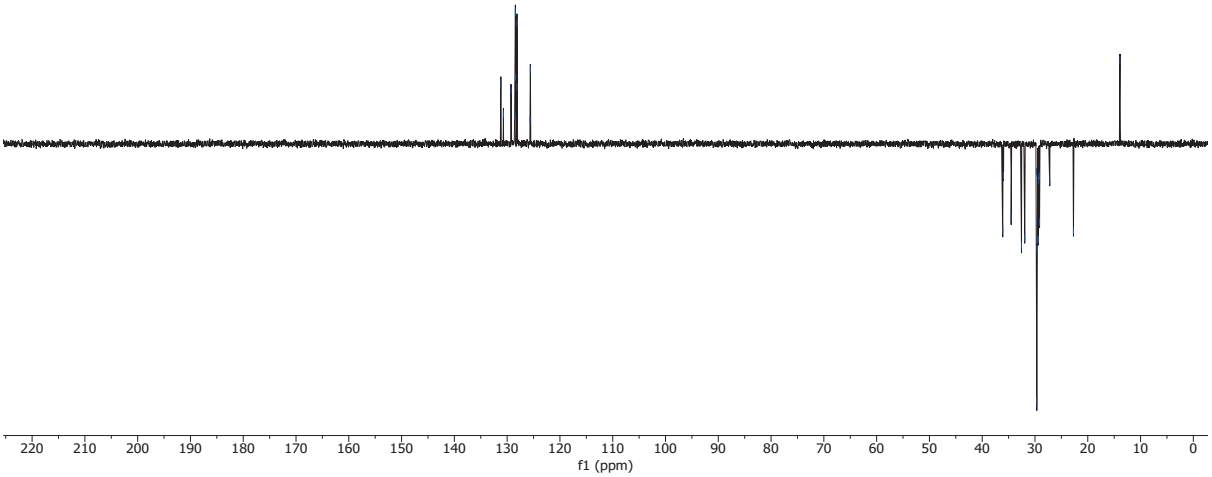


(E)-tetradec-3-en-1-ylbenzene (24)
Mix of isomers

^{13}C NMR Dept-135 (75 MHz, CD_2Cl_2)

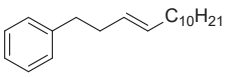




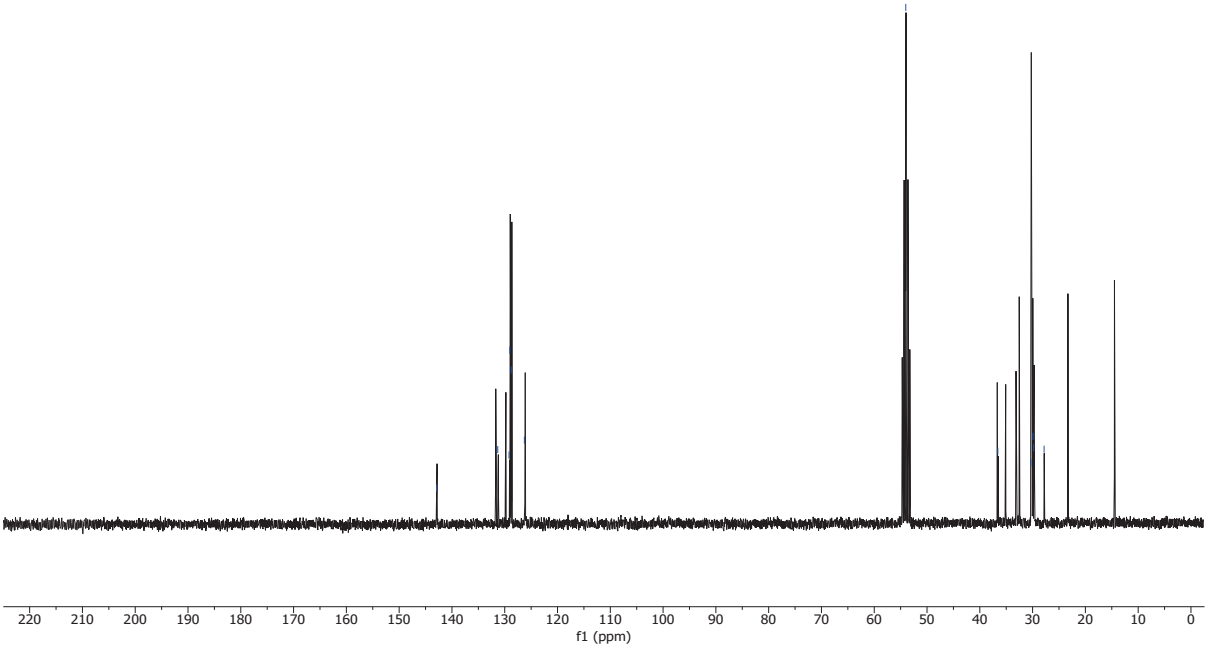


(E)-tetradec-3-en-1-ylbenzene (24)
Minor isomer

^{13}C NMR (75 MHz, CD_2Cl_2)

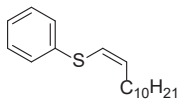


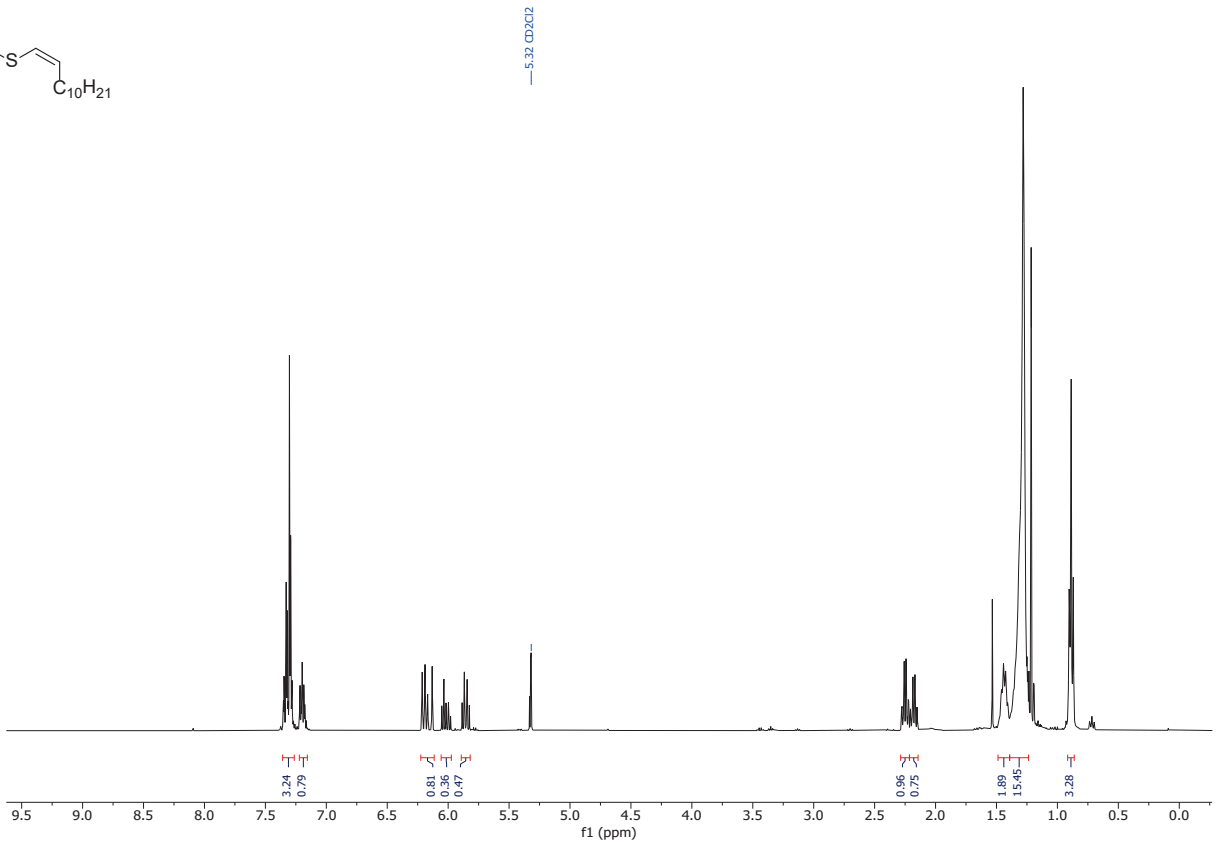




(Z)-tetradec-3-en-1-ylbenzene (37)
Mix of isomers

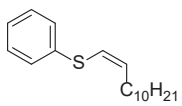
^{1}H NMR (400 MHz, CD_2Cl_2)

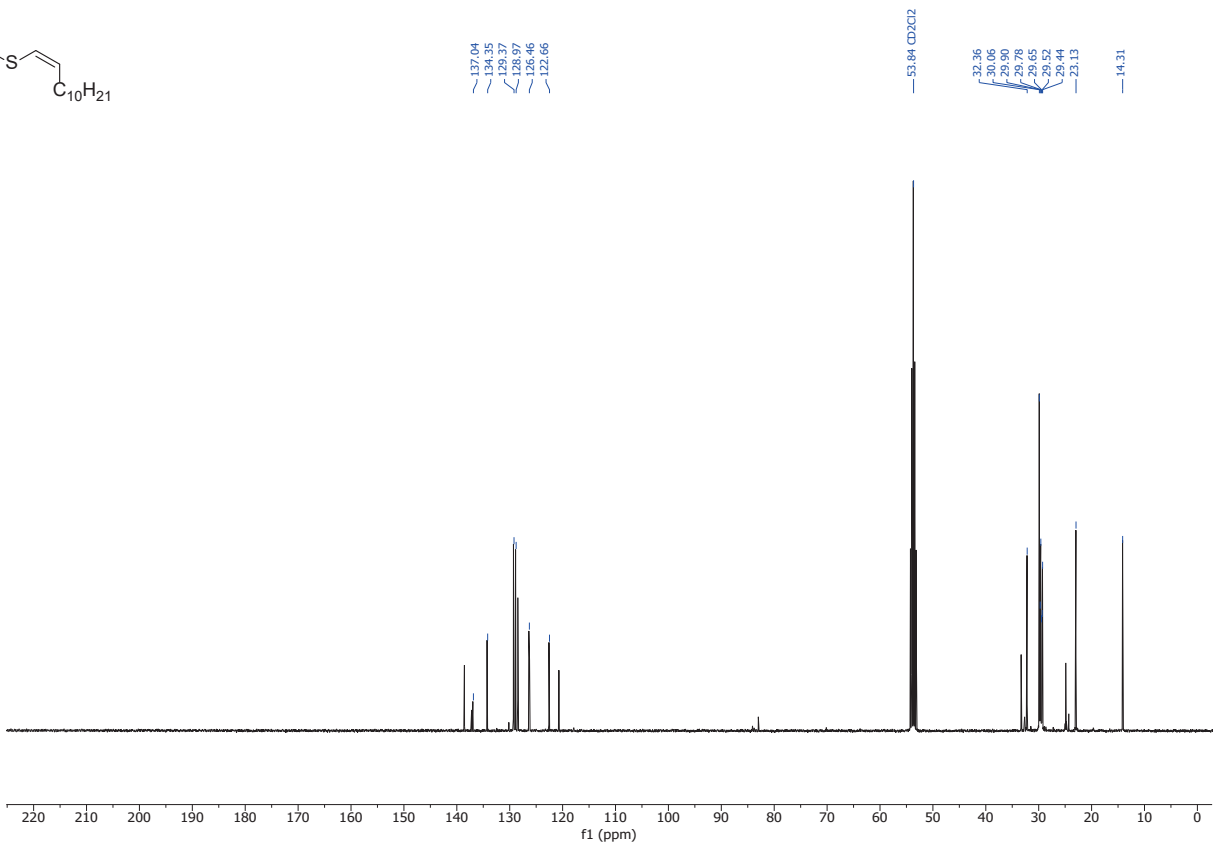




(Z)-tetradec-3-en-1-ylbenzene (37)
Major isomer

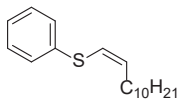
^{13}C NMR (101 MHz, CD_2Cl_2)

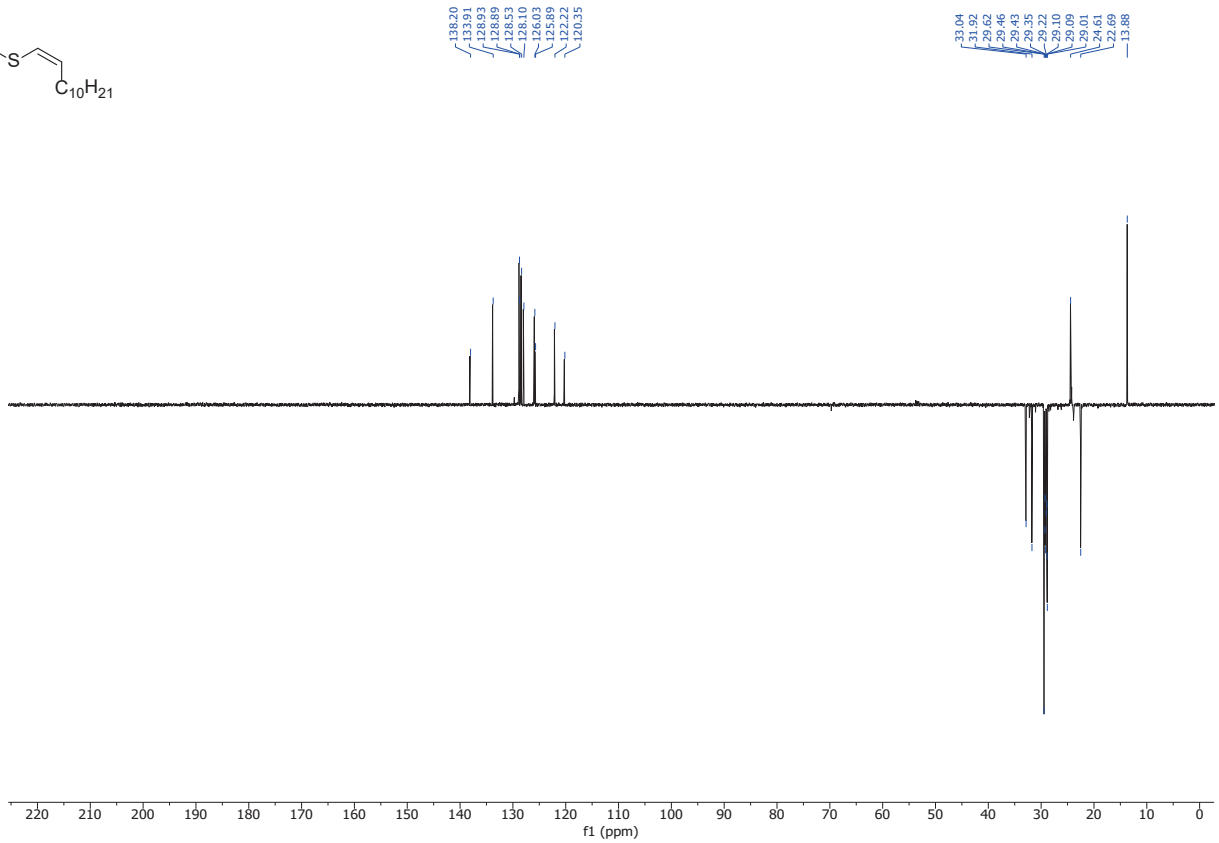




(Z)-tetradec-3-en-1-ylbenzene (37)
Mix of isomers

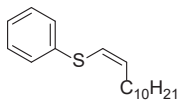
^{13}C NMR Dept-135 (101 MHz, CD_2Cl_2)

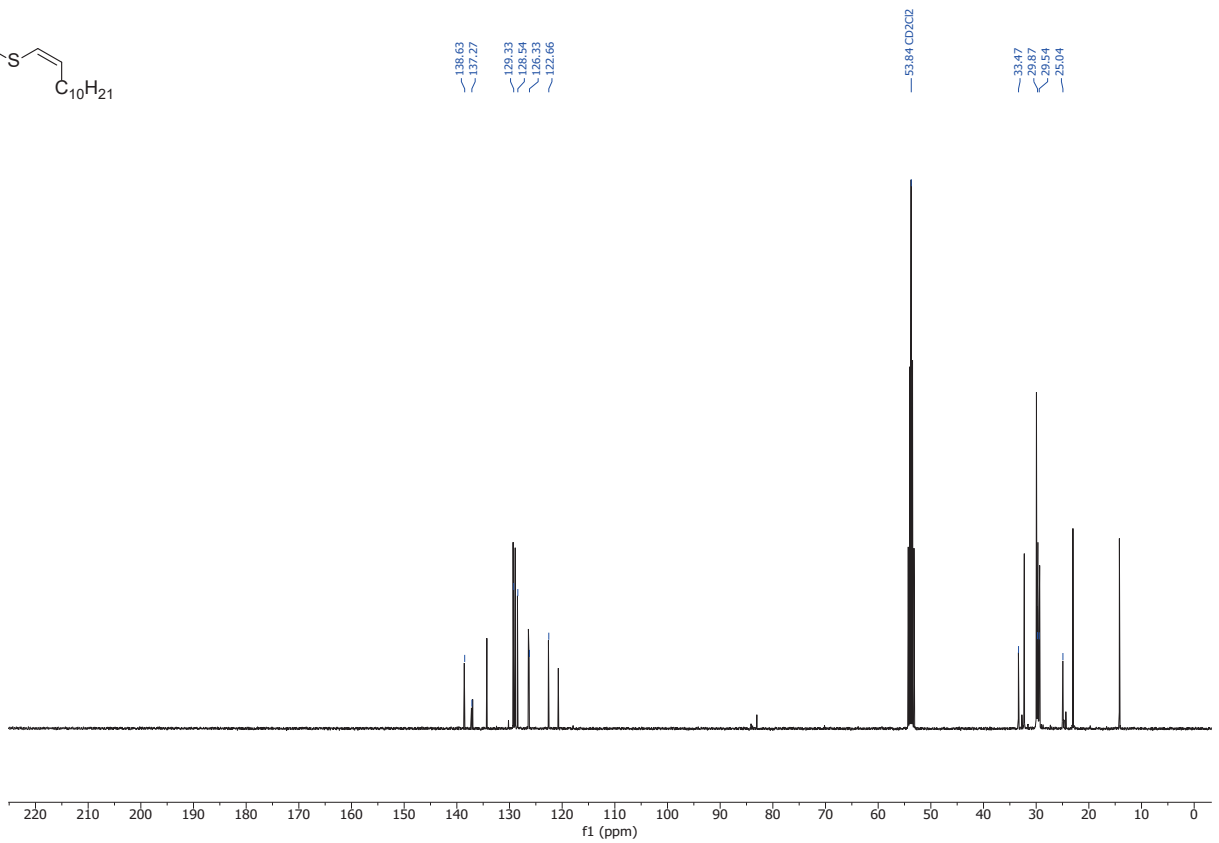




(Z)-tetradec-3-en-1-ylbenzene (37)
Minor isomer

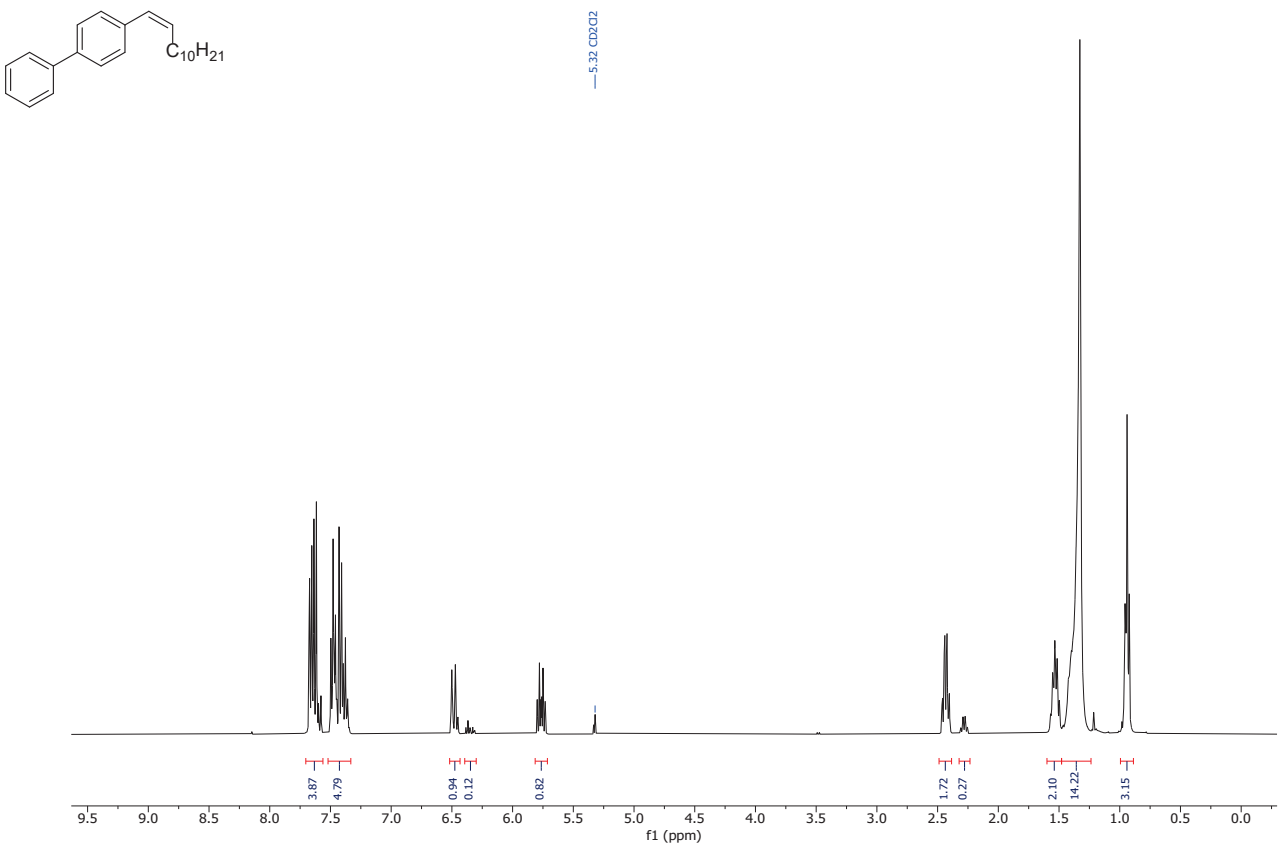
^{13}C NMR (101 MHz, CD_2Cl_2)





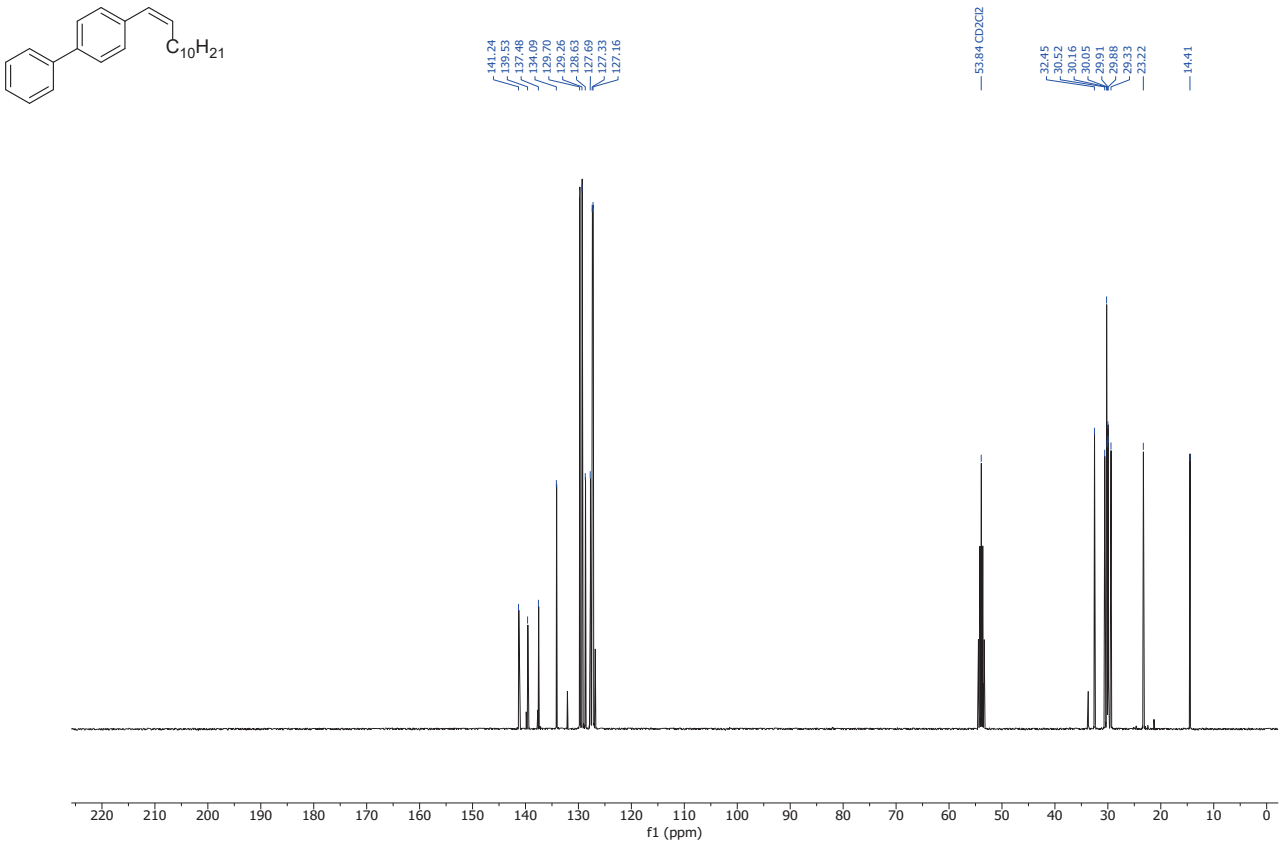
(Z)-4-(dodec-1-en-1-yl)-1,1'-biphenyl (33)
Mix of isomers

^{1}H NMR (400 MHz, CD_2Cl_2)



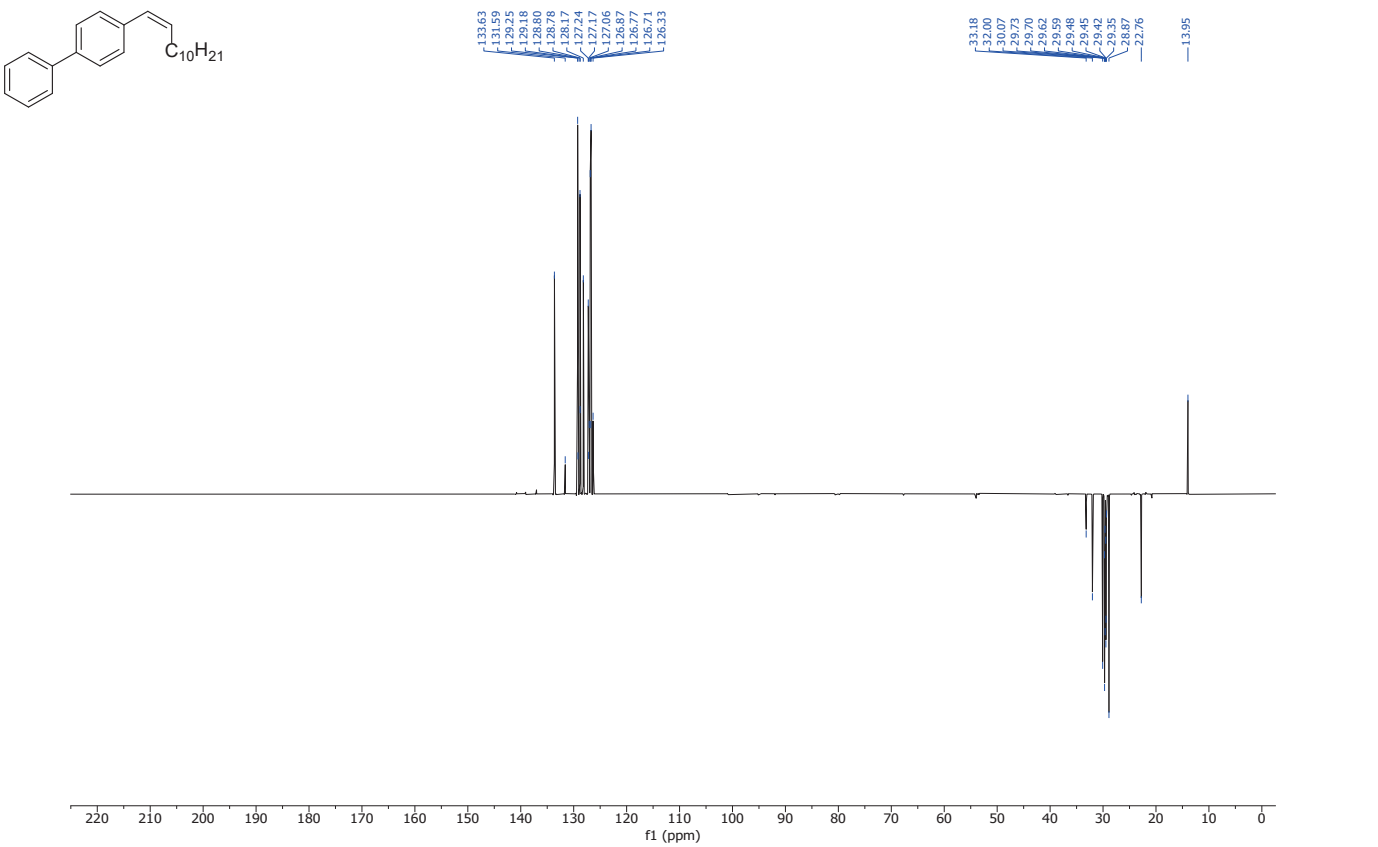
(Z)-4-(dodec-1-en-1-yl)-1,1'-biphenyl (33)
Major isomer

^{13}C NMR (101 MHz, CD_2Cl_2)



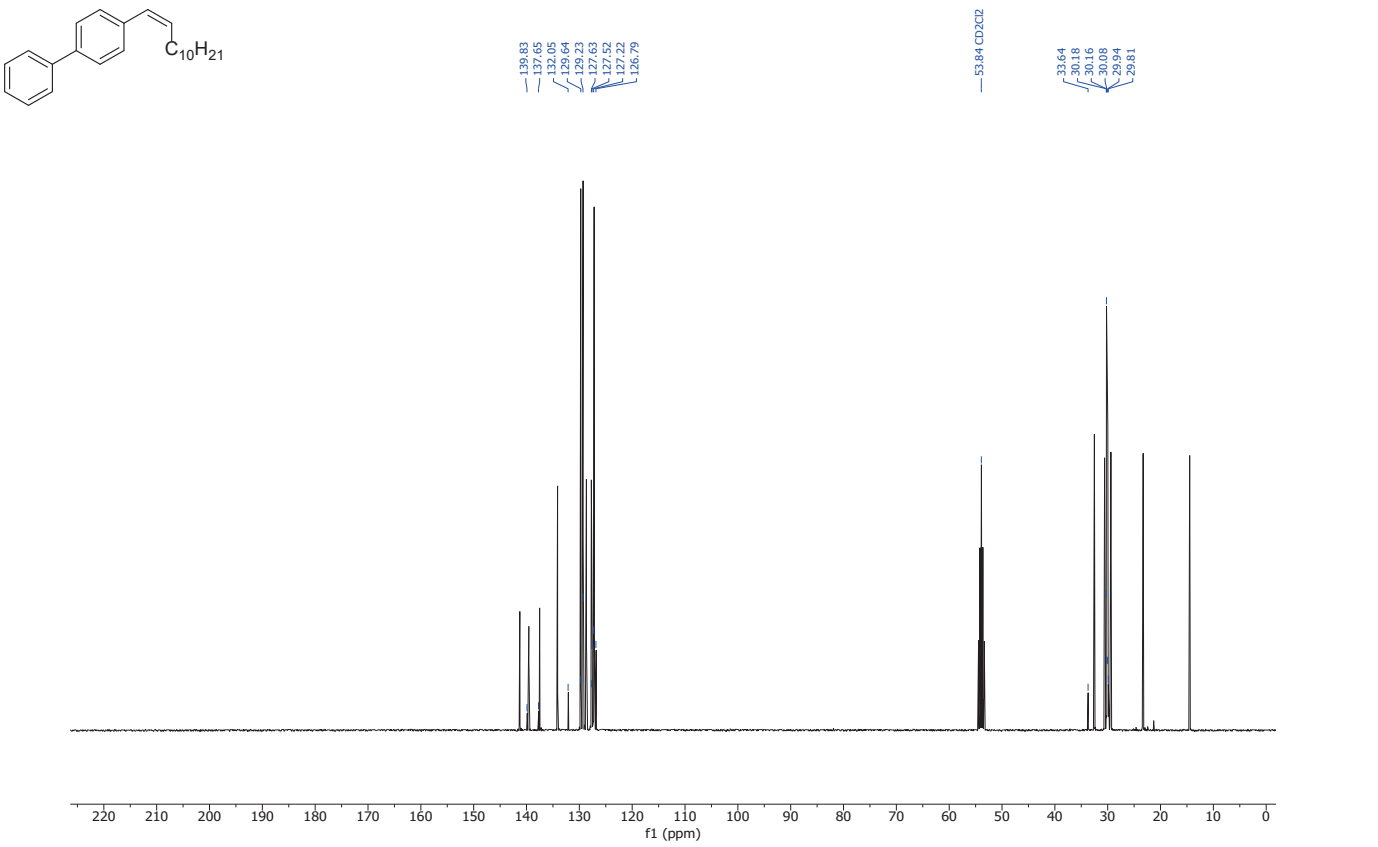
(Z)-4-(dodec-1-en-1-yl)-1,1'-biphenyl (33)
Mix of isomers

^{13}C NMR Dept-135 (101 MHz, CD_2Cl_2)



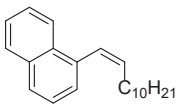
(Z)-4-(dodec-1-en-1-yl)-1,1'-biphenyl (33)
Minor isomer

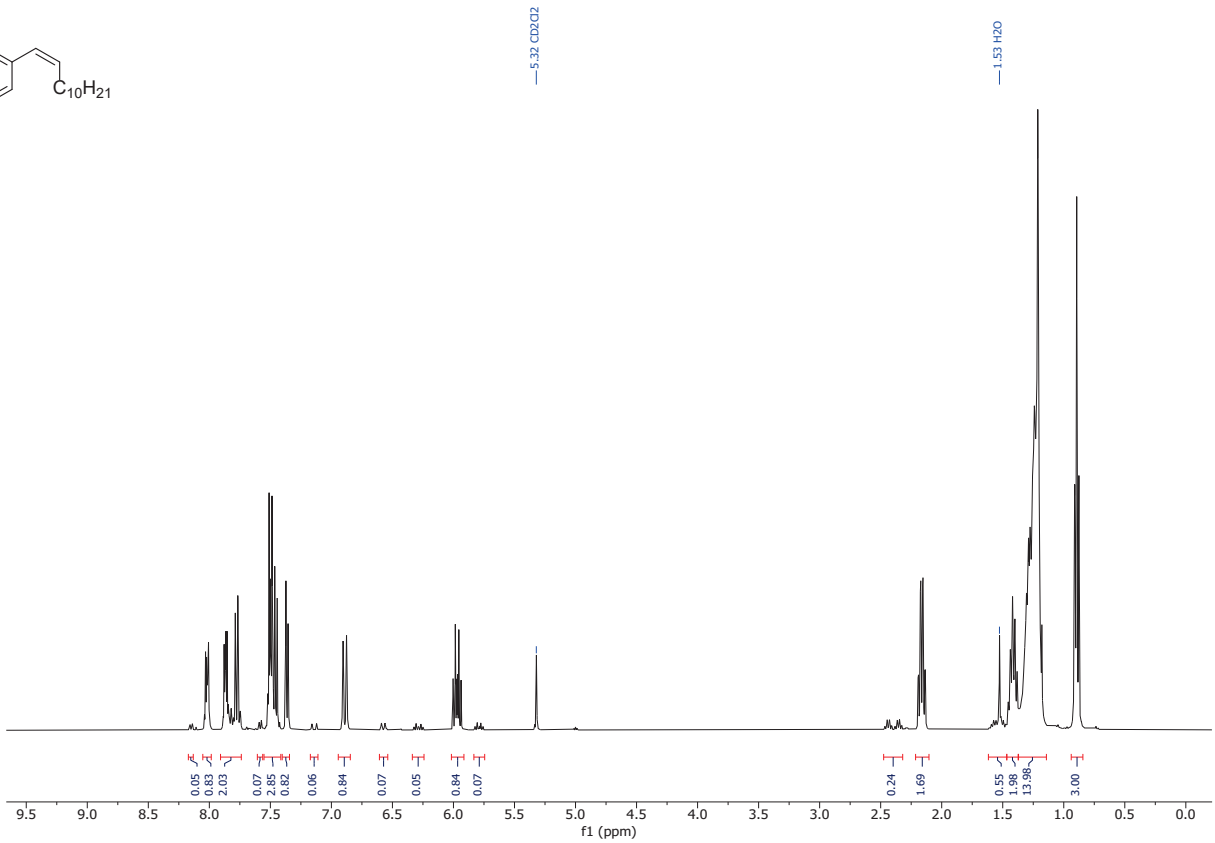
^{13}C NMR (101 MHz, CD_2Cl_2)



(Z)-1-(dodec-1-en-1-yl)naphthalene (34)
Mix of isomers

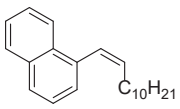
^{1}H NMR (400 MHz, CD_2Cl_2)

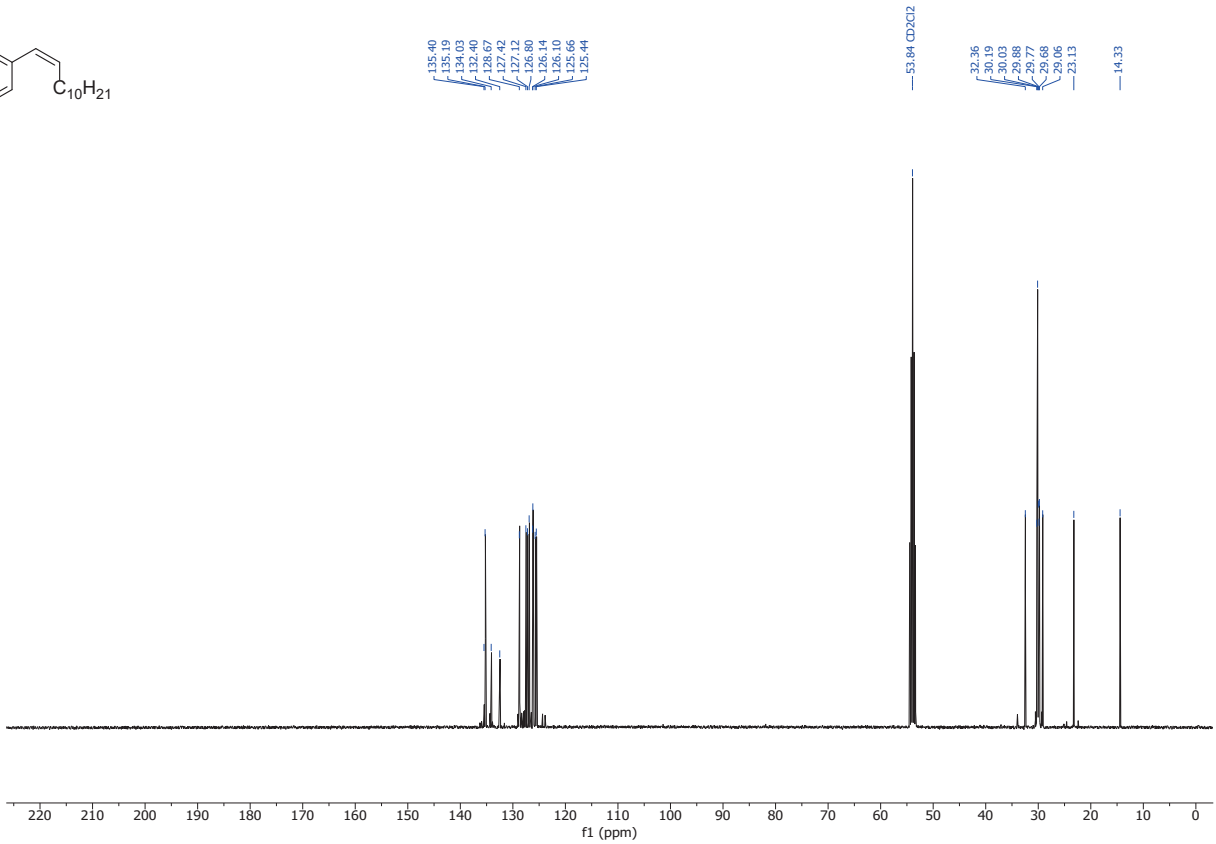




(Z)-1-(dodec-1-en-1-yl)naphthalene (34)
Major isomer

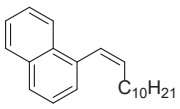
^{13}C NMR (101 MHz, CD_2Cl_2)

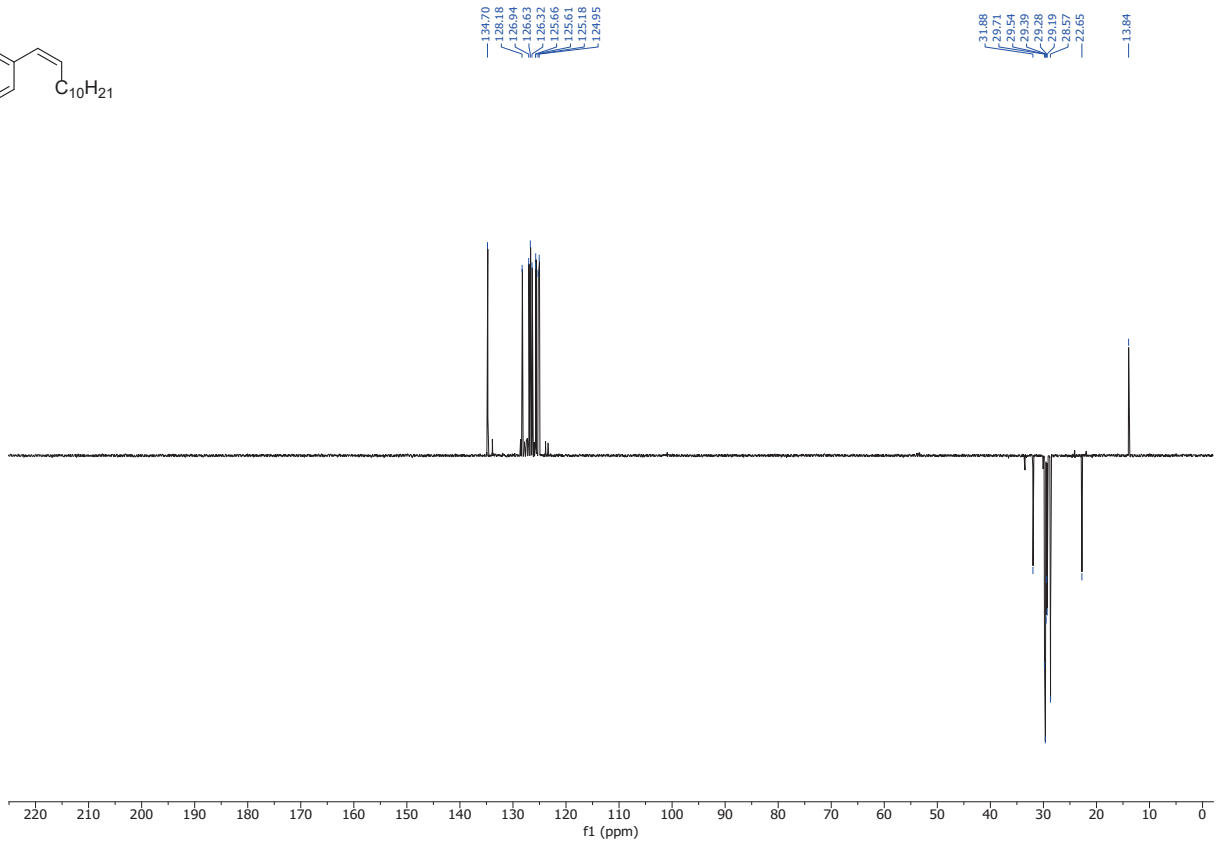




(Z)-1-(dodec-1-en-1-yl)naphthalene (34)
Major isomer

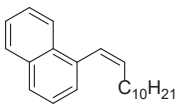
^{13}C NMR Dept-135 (101 MHz, CD_2Cl_2)

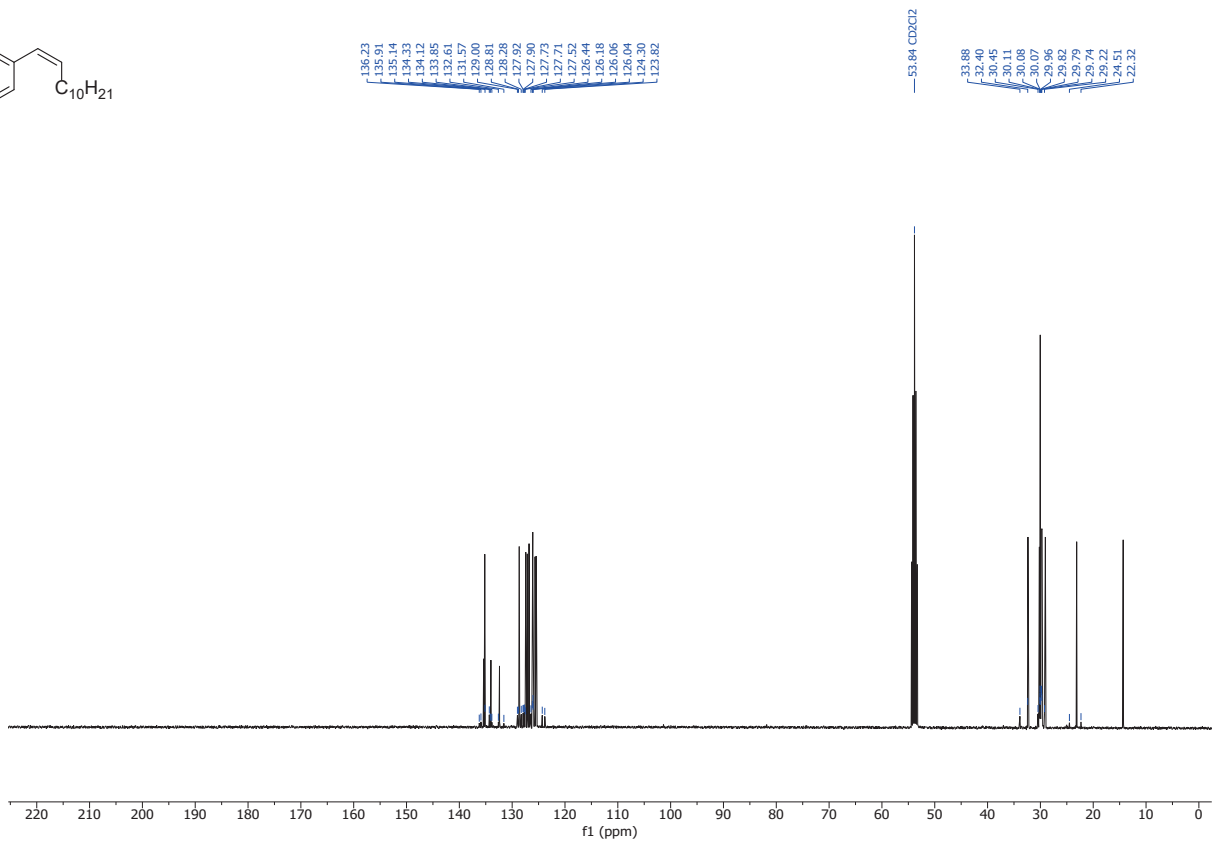




(Z)-1-(dodec-1-en-1-yl)naphthalene (34)
Minor isomer

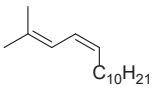
^{13}C NMR (101 MHz, CD_2Cl_2)

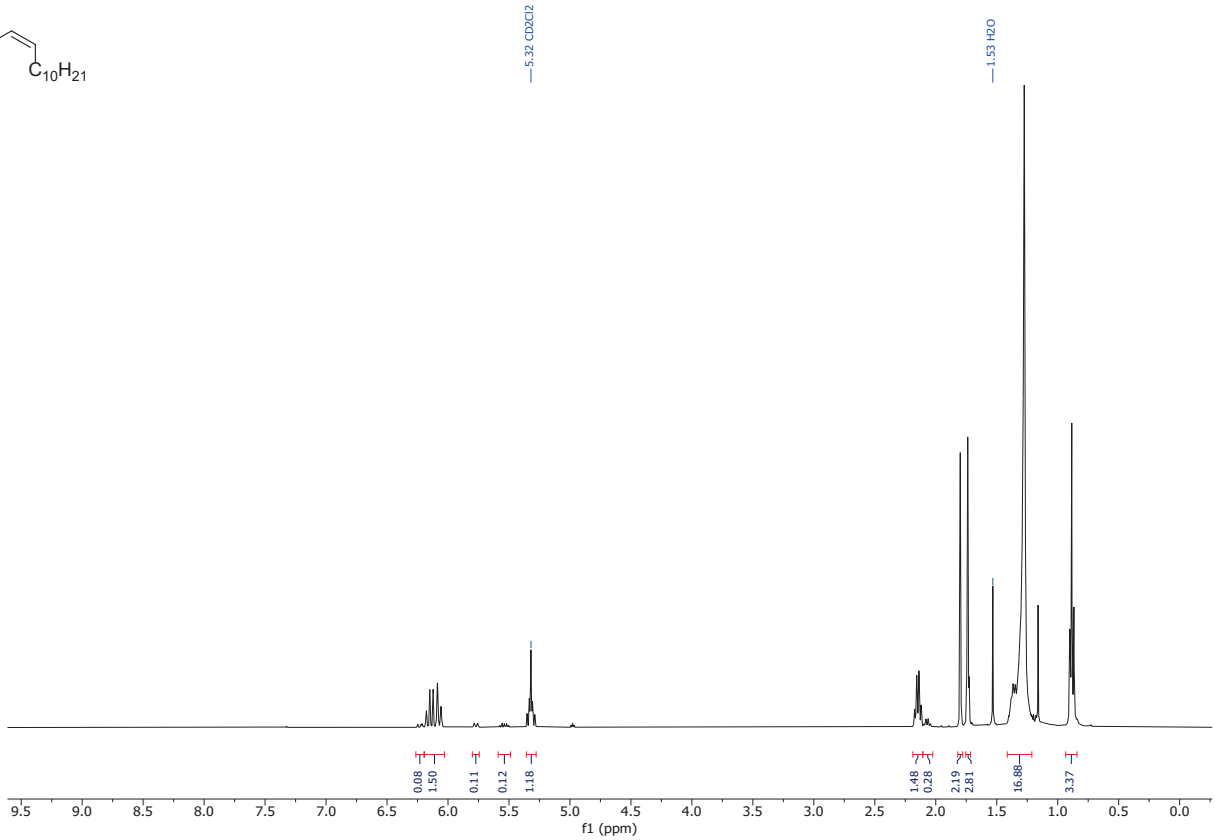




(Z)-2-methylpentadeca-2,4-diene (35)
Mix of isomers

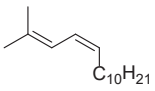
^{1}H NMR (400 MHz, CD_2Cl_2)

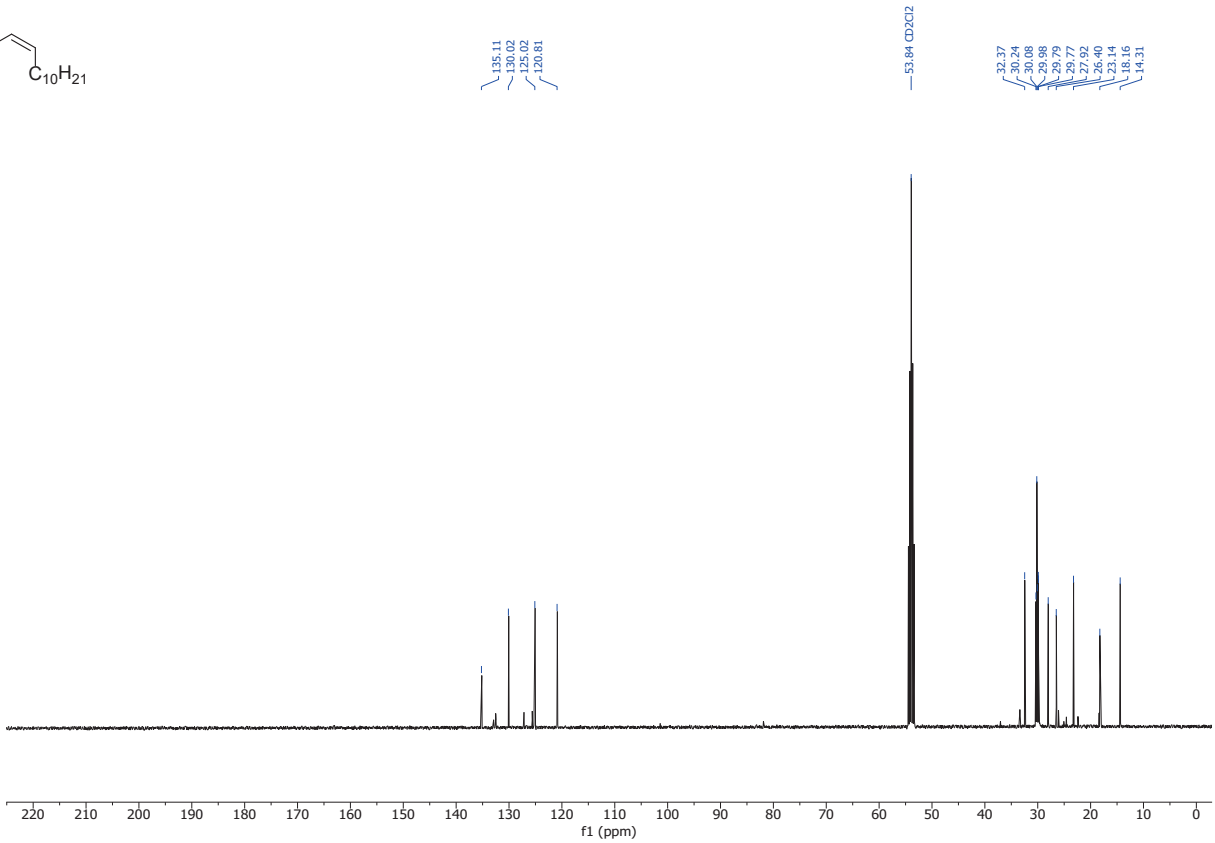




(Z)-2-methylpentadeca-2,4-diene (35)
Major isomer

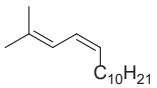
^{13}C NMR (101 MHz, CD_2Cl_2)

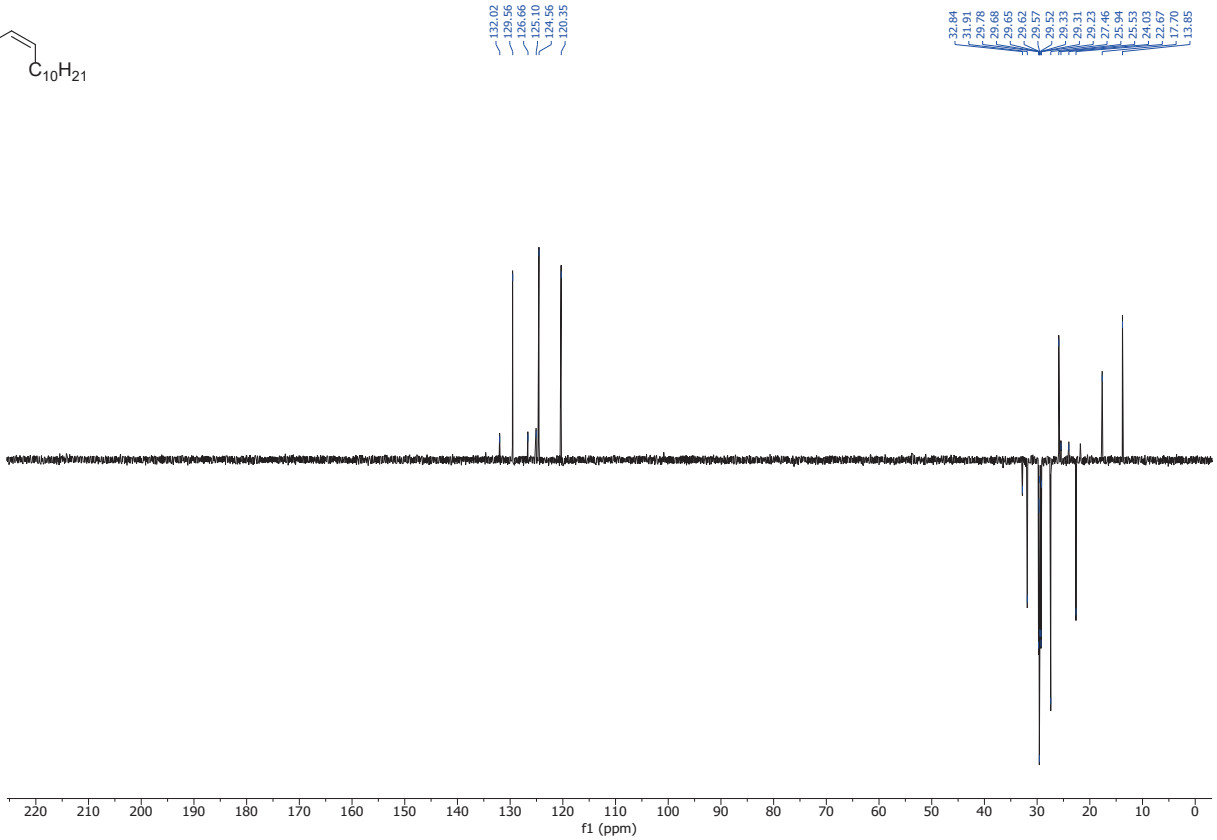




(Z)-2-methylpentadeca-2,4-diene (35)
Mix of isomers

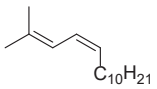
^{13}C NMR Dept-135 (101 MHz, CD_2Cl_2)

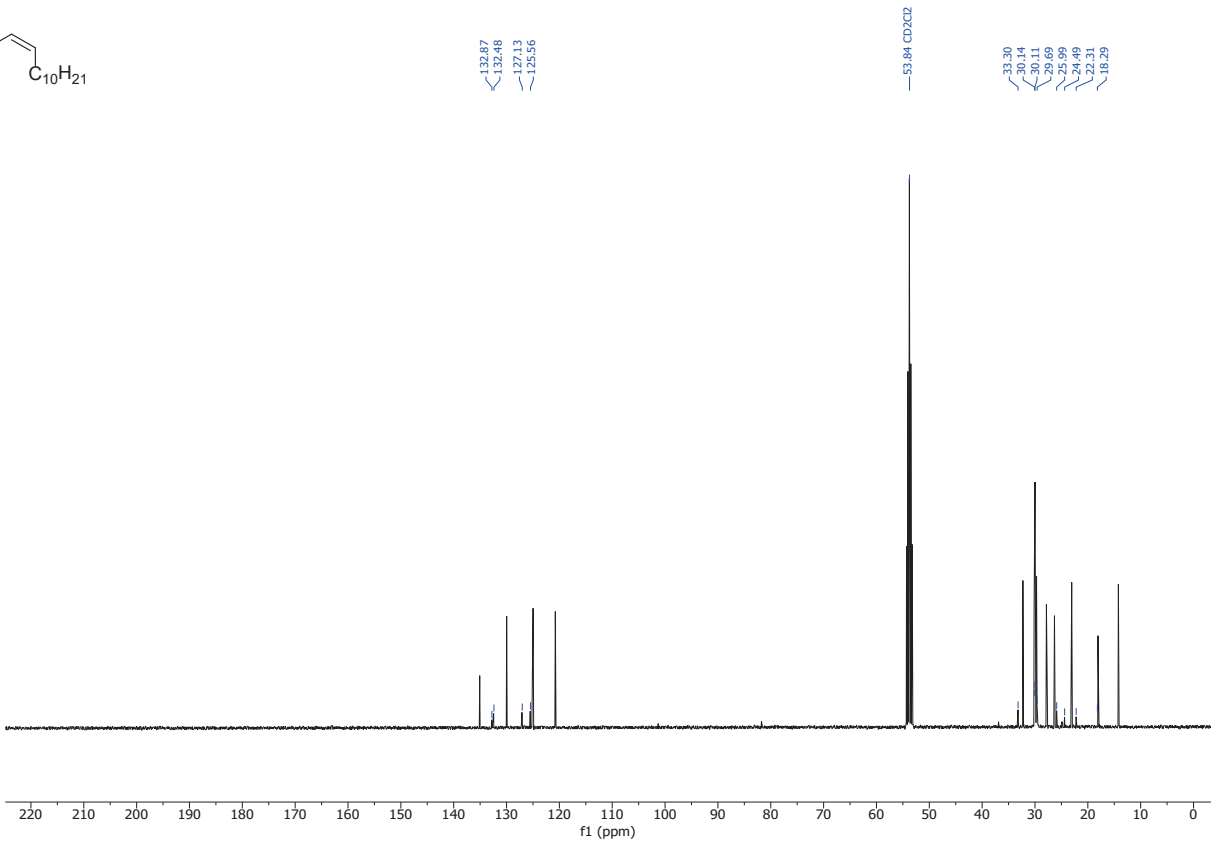




(Z)-2-methylpentadeca-2,4-diene (35)
Minor isomer

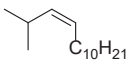
^{13}C NMR (101 MHz, CD_2Cl_2)

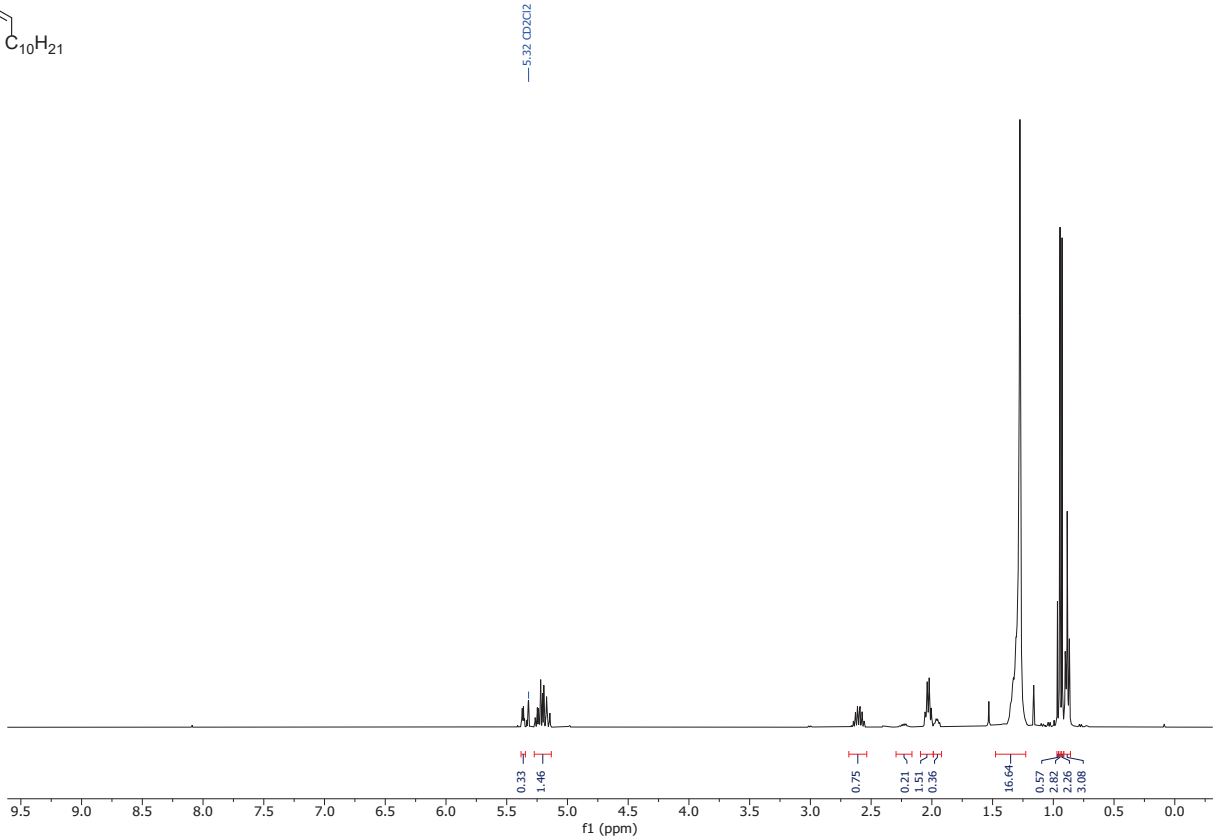




(Z)-2-methyltetradec-3-ene (25)
Mix of isomers

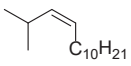
^{1}H NMR (400 MHz, CD_2Cl_2)

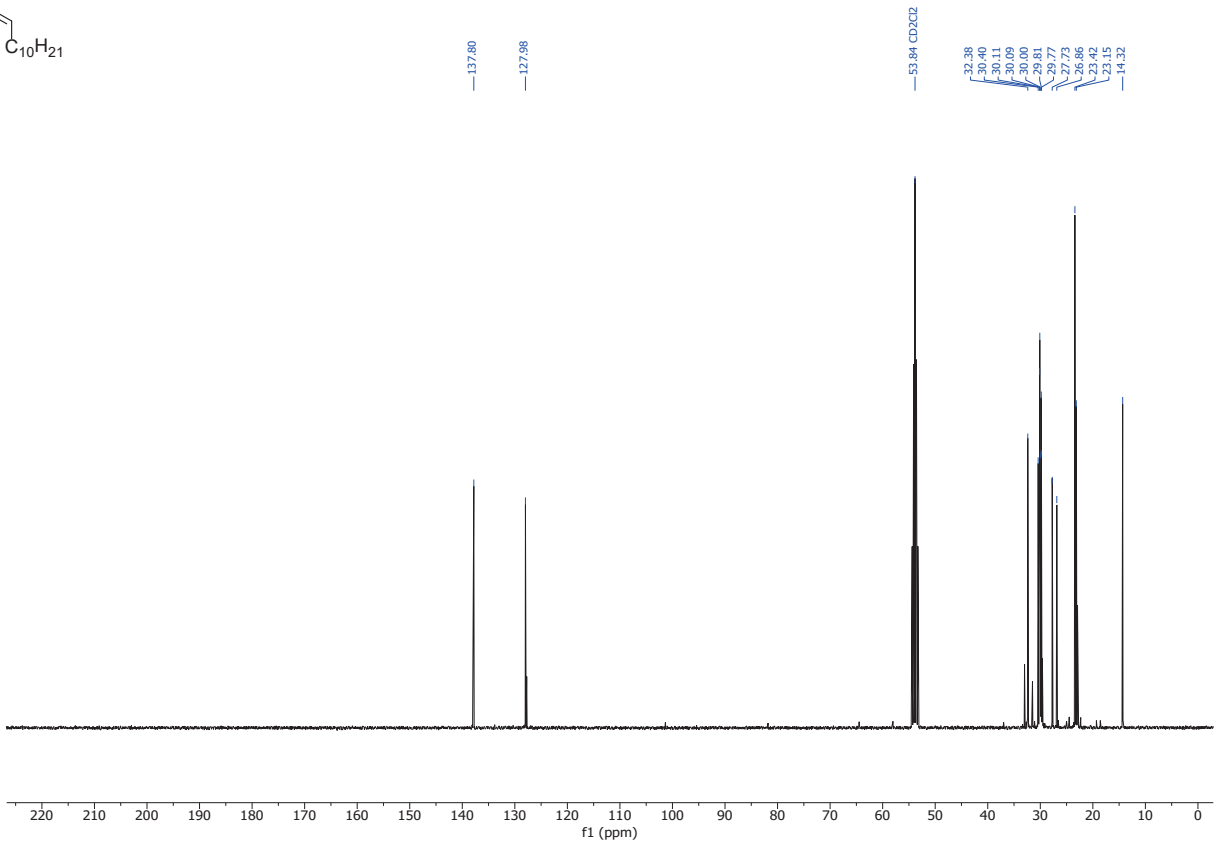




(Z)-2-methyltetradec-3-ene (25)
Major isomer

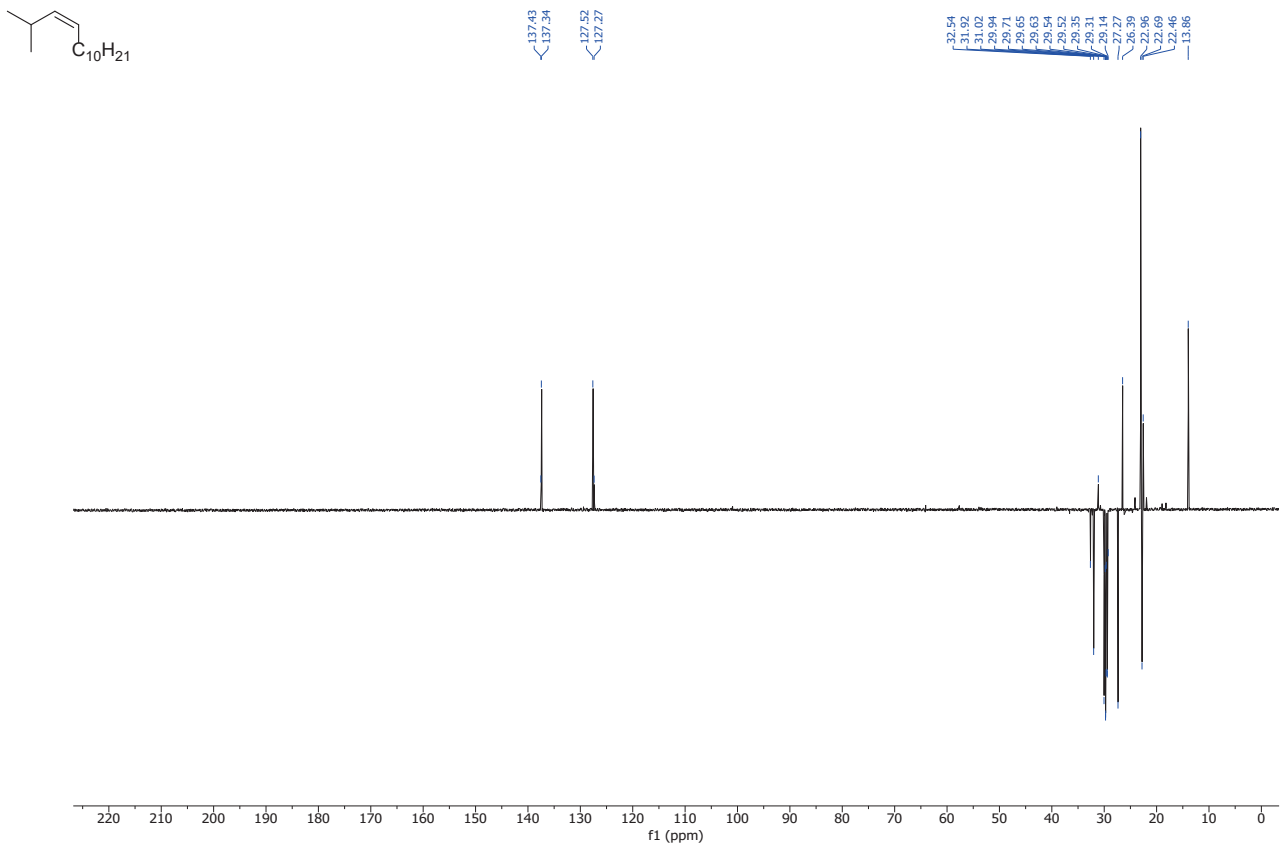
^{13}C NMR (101 MHz, CD_2Cl_2)





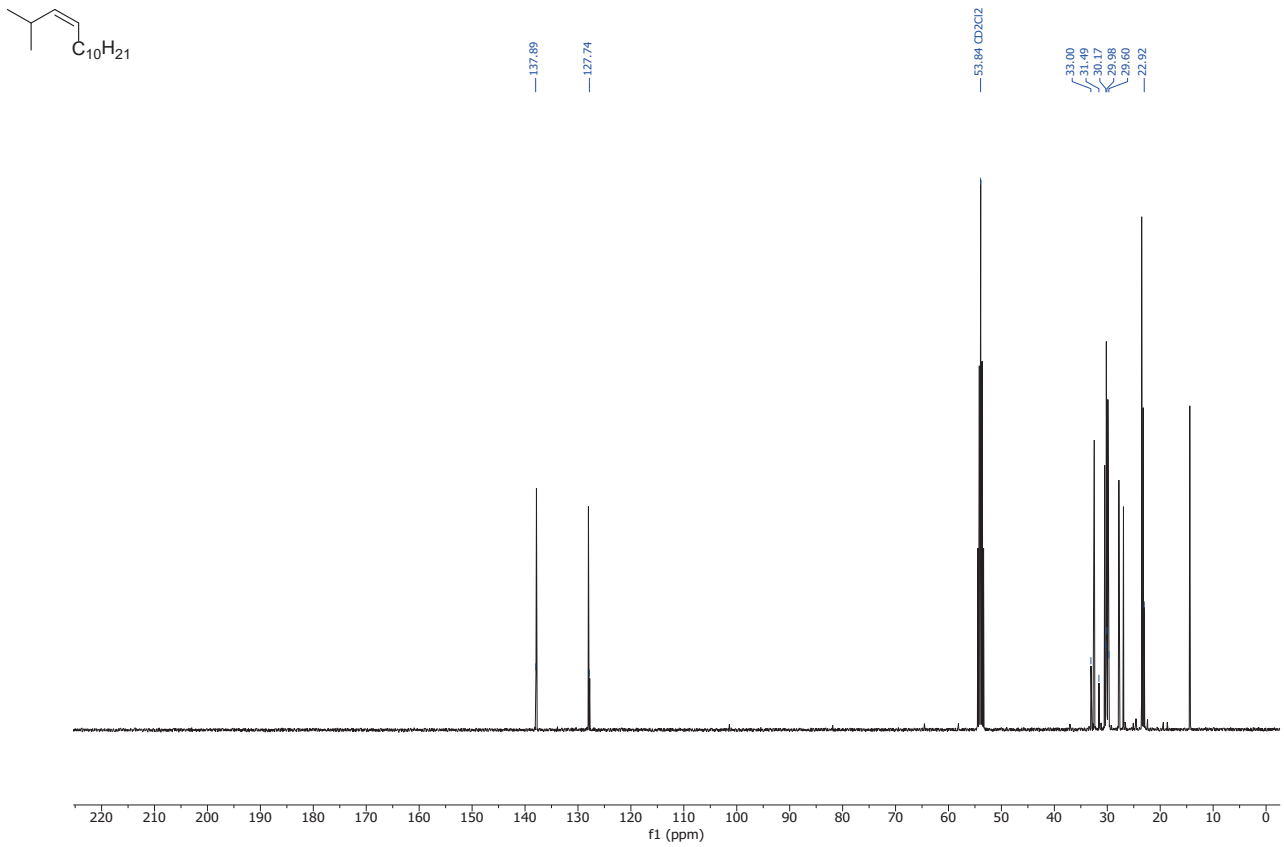
(Z)-2-methyltetradec-3-ene (25)
Mix of isomers

^{13}C NMR Dept-135 (101 MHz, CD_2Cl_2)



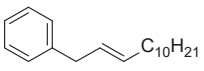
(Z)-2-methyltetradec-3-ene (25)
Minor isomer

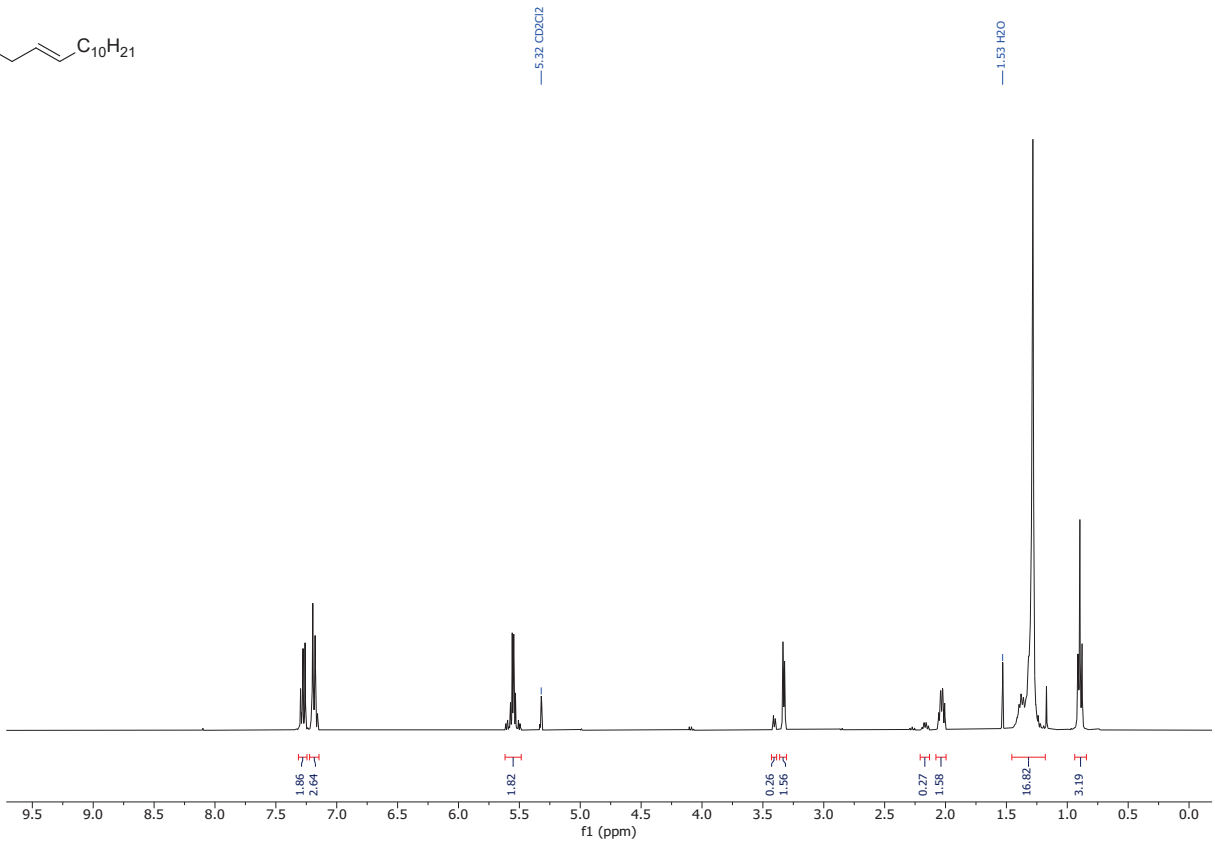
^{13}C NMR (101 MHz, CD_2Cl_2)



(E)-tridec-2-en-1-ylbenzene (41)
Mix of isomers

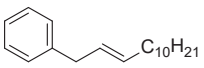
^{1}H NMR (400 MHz, CD_2Cl_2)

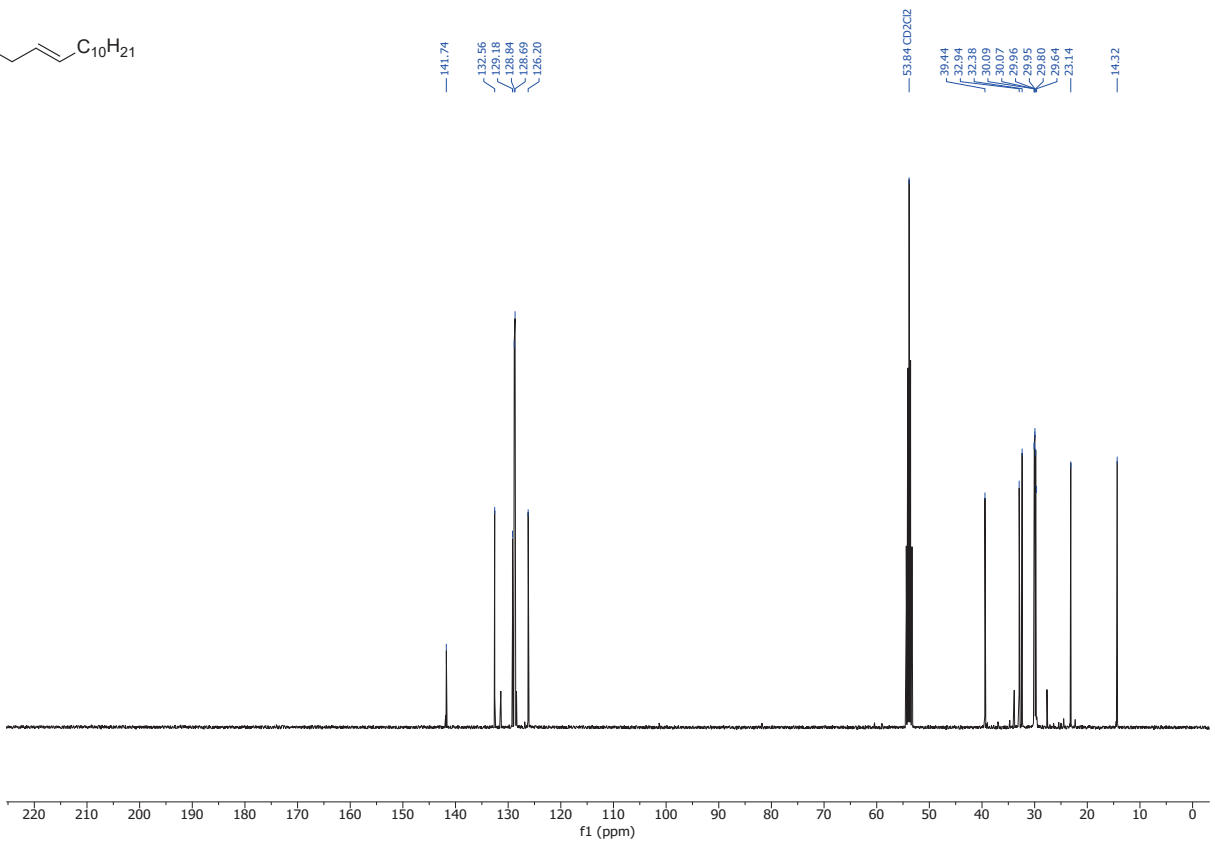




(E)-tridec-2-en-1-ylbenzene (41)
Major isomer

^{13}C NMR (101 MHz, CD_2Cl_2)

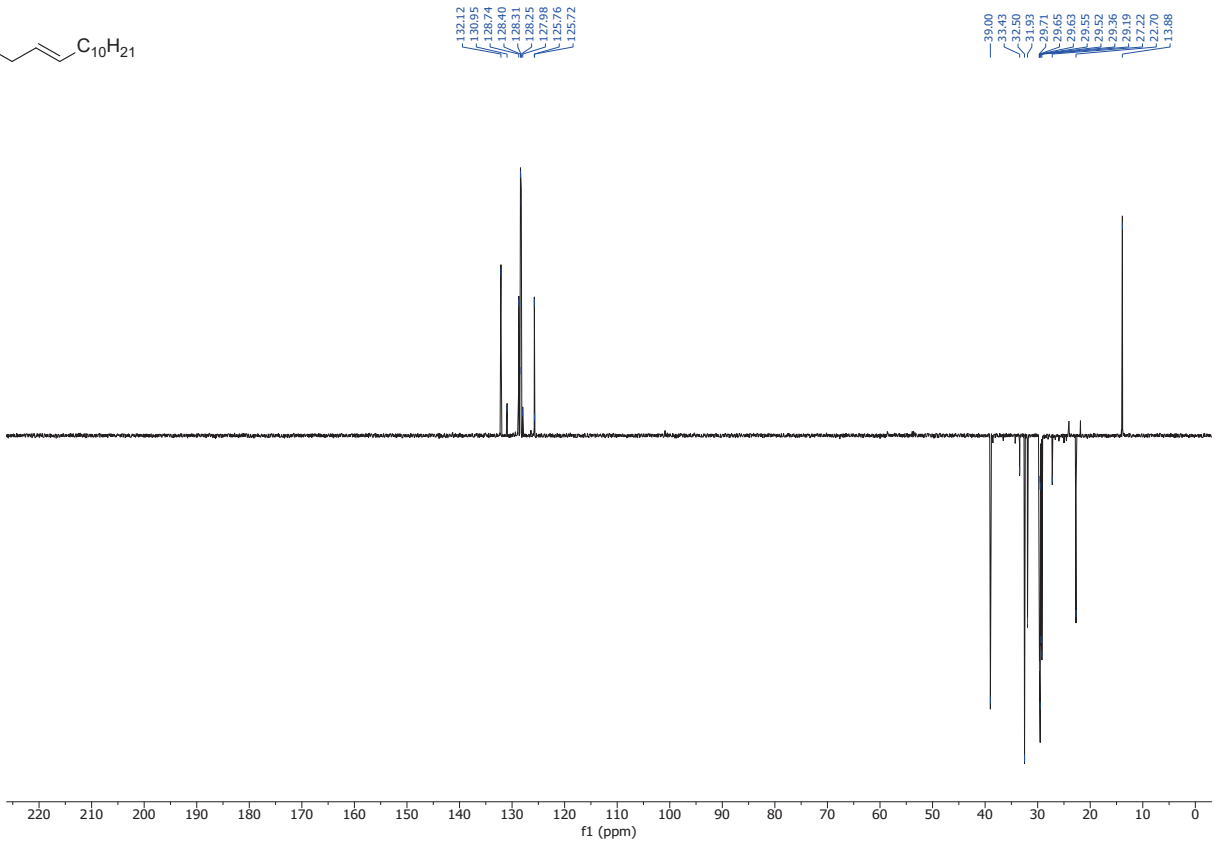




(E)-tridec-2-en-1-ylbenzene (41)
Mix of isomers

^{13}C NMR Dept-135 (101 MHz, CD_2Cl_2)

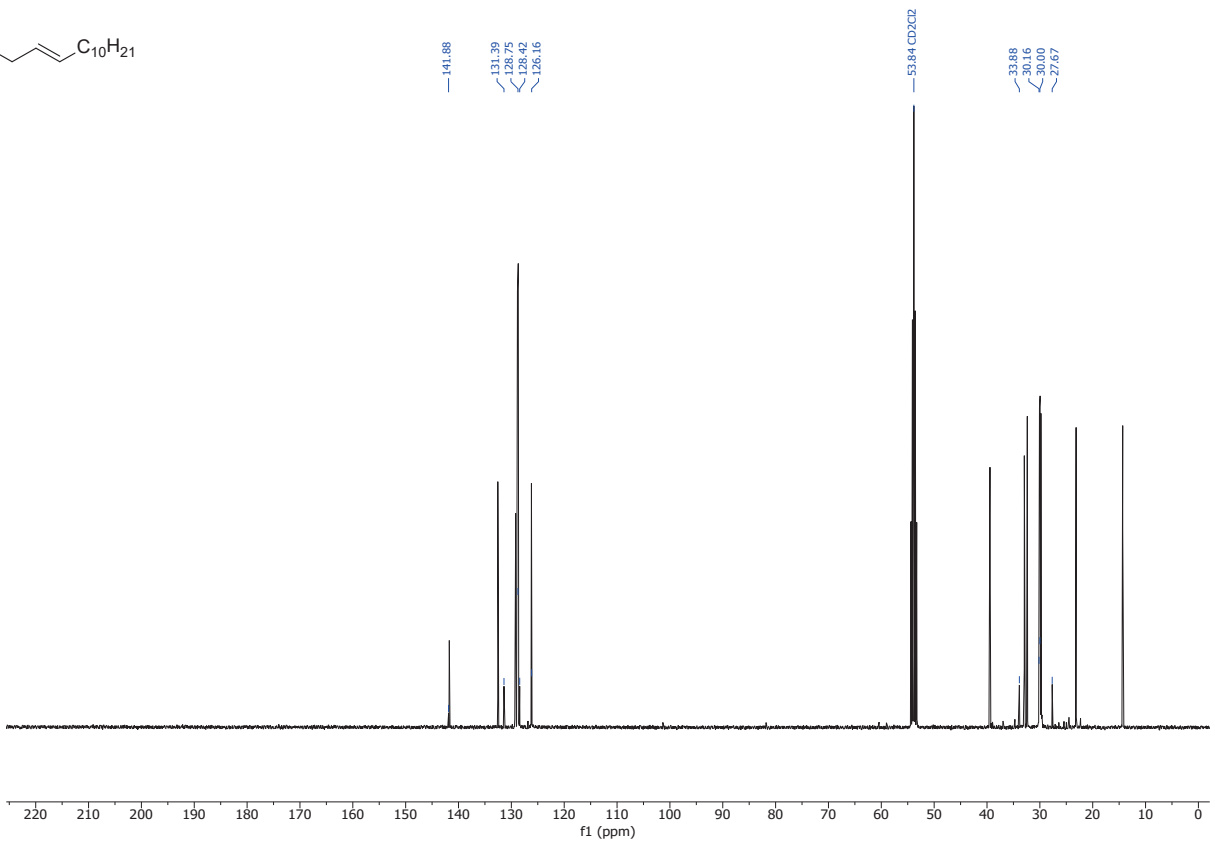




(E)-tridec-2-en-1-ylbenzene (41)
Minor isomer

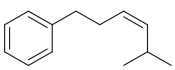
^{13}C NMR (101 MHz, CD_2Cl_2)

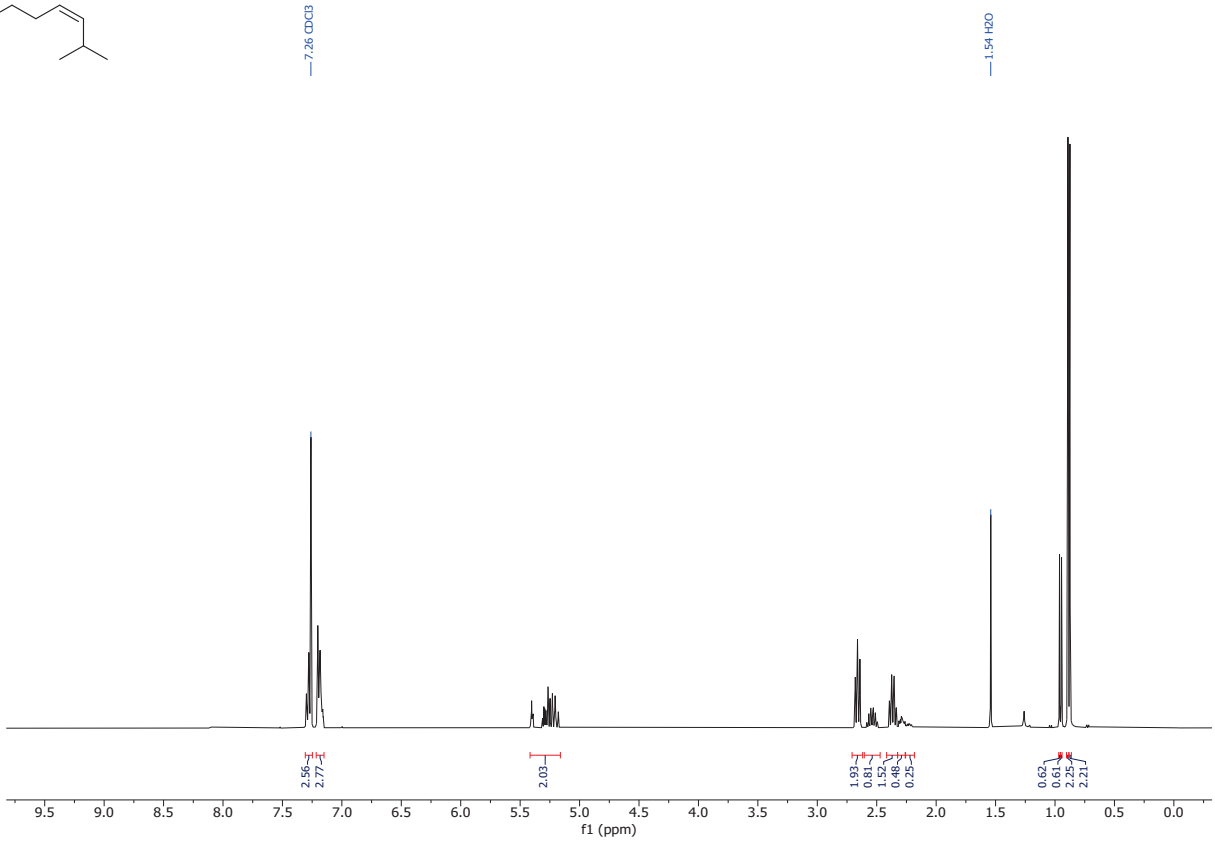




(Z)-(5-methylhex-3-en-1-yl)benzene (26)
Mix of isomers

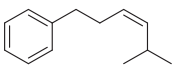
^{1}H NMR (400 MHz, $CDCl_3$)

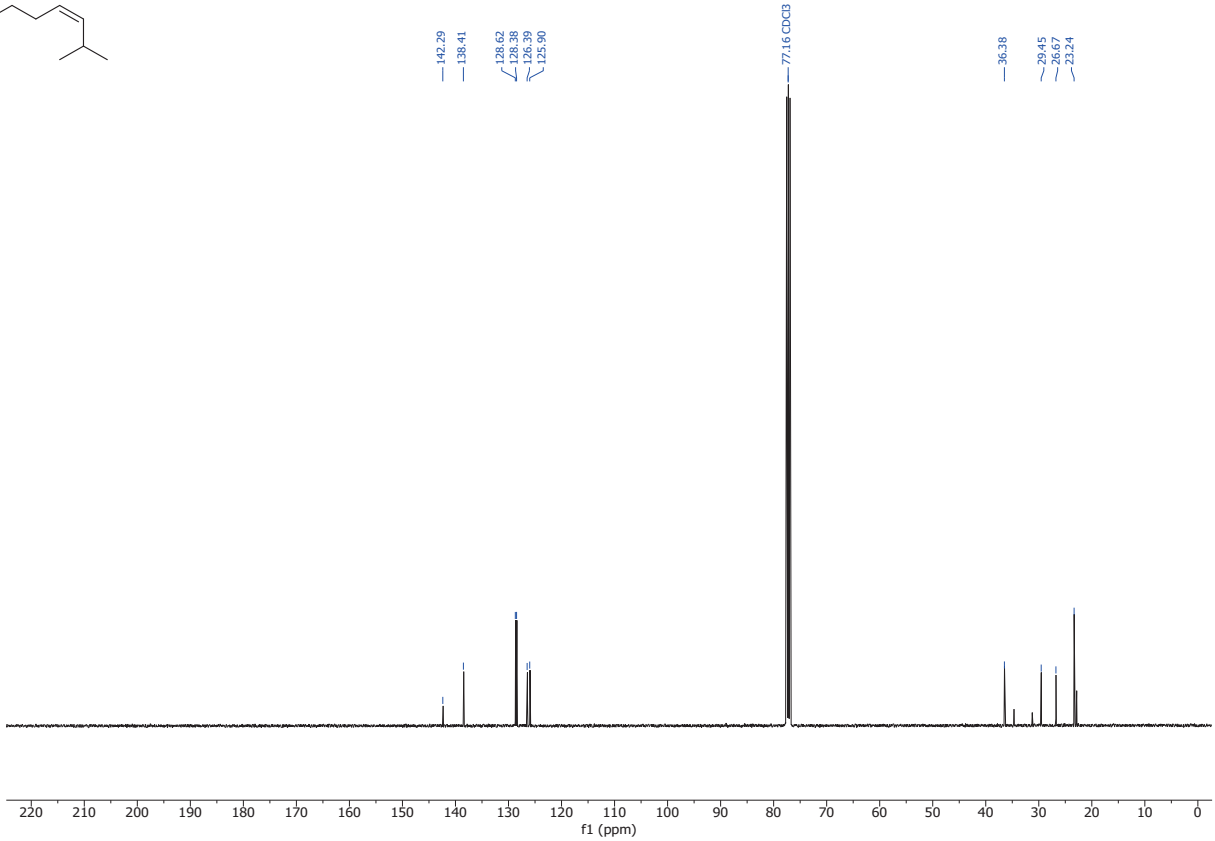




(Z)-(5-methylhex-3-en-1-yl)benzene (26)
Major isomer

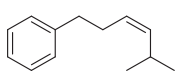
^{13}C NMR (101 MHz, $CDCl_3$)

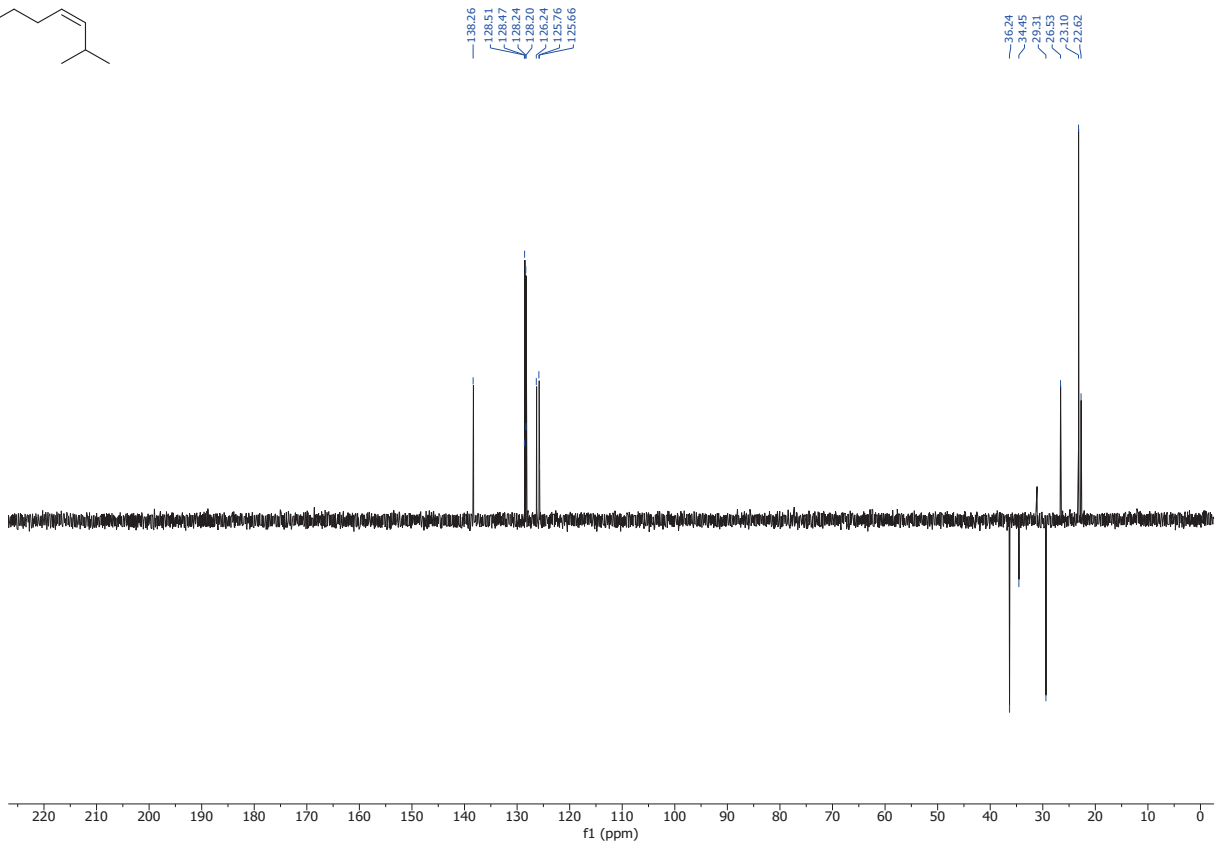




(Z)-(5-methylhex-3-en-1-yl)benzene (26)
Mix of isomers

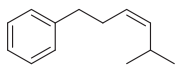
^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)

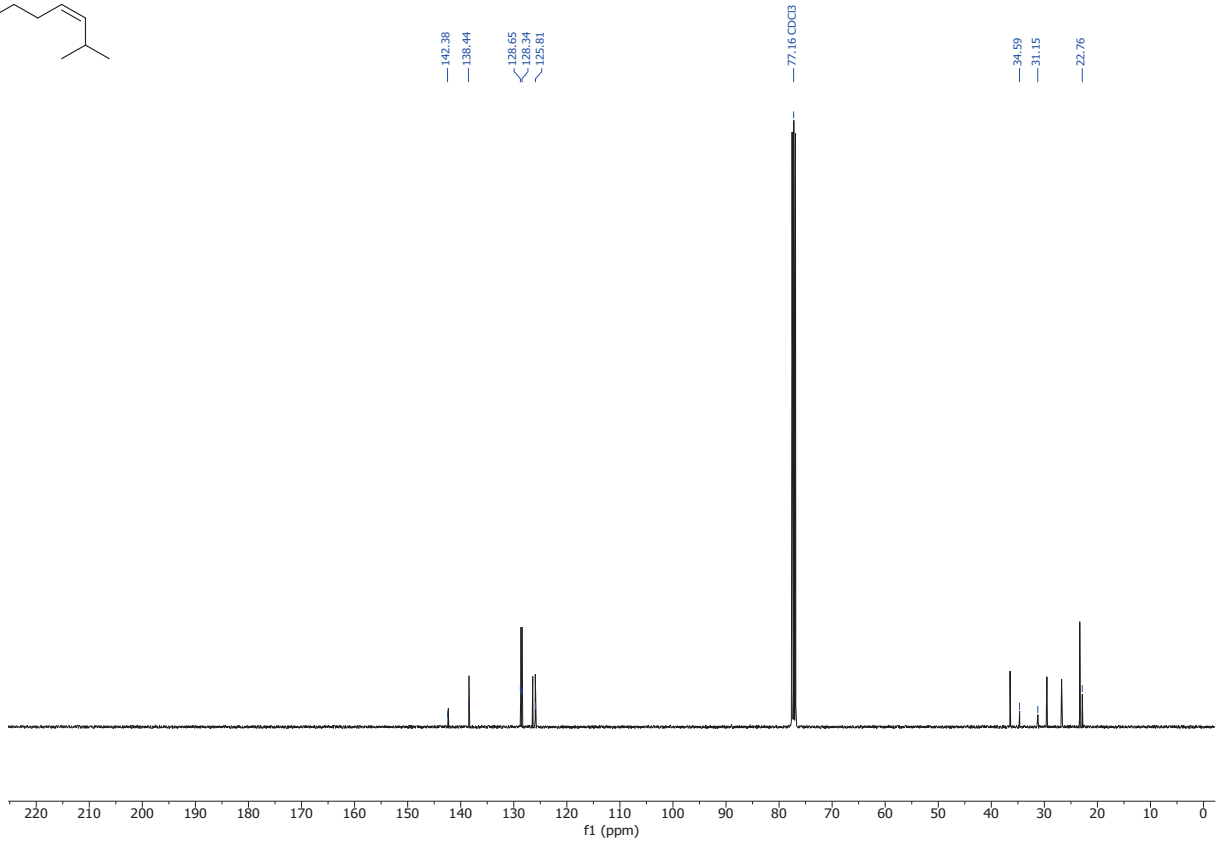




(Z)-(5-methylhex-3-en-1-yl)benzene (26)
Minor isomer

^{13}C NMR (101 MHz, $CDCl_3$)



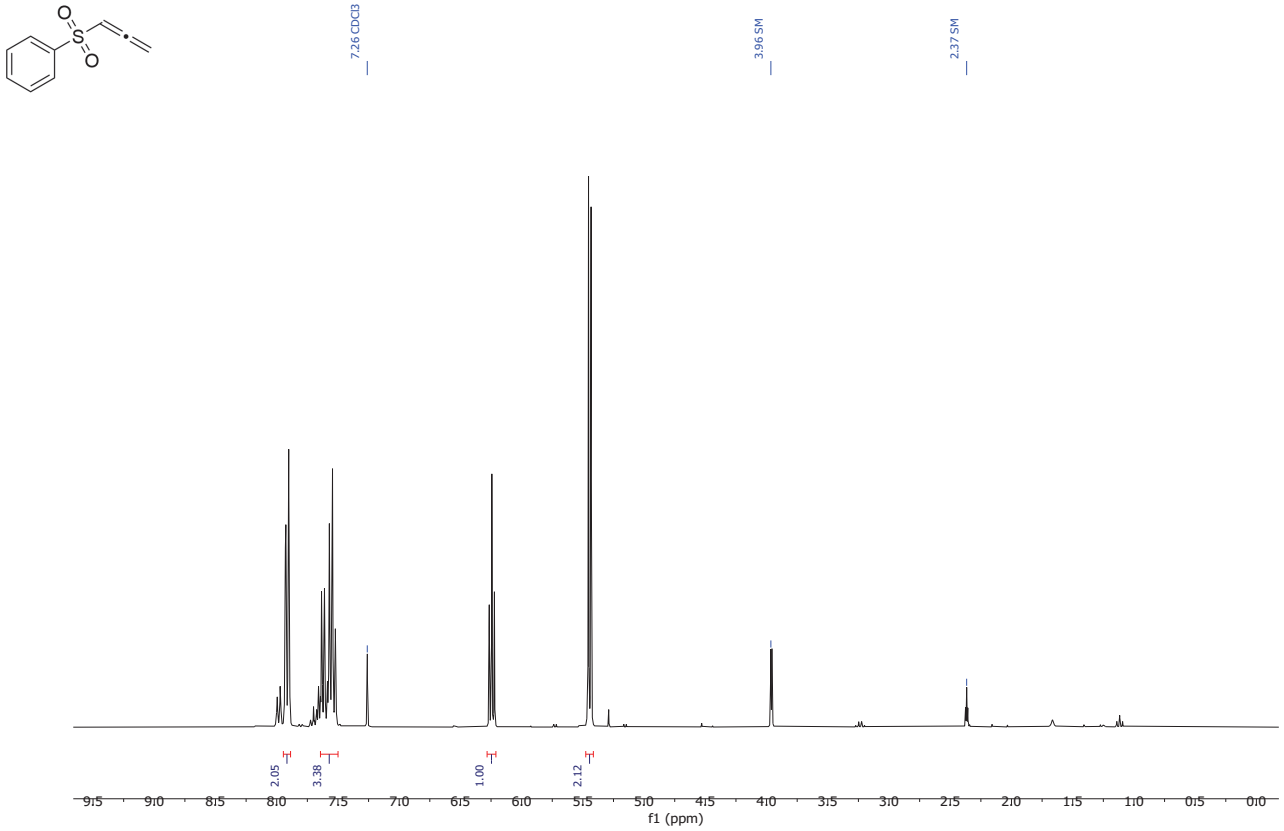


Appendix

NMR spectra of Chapter 3

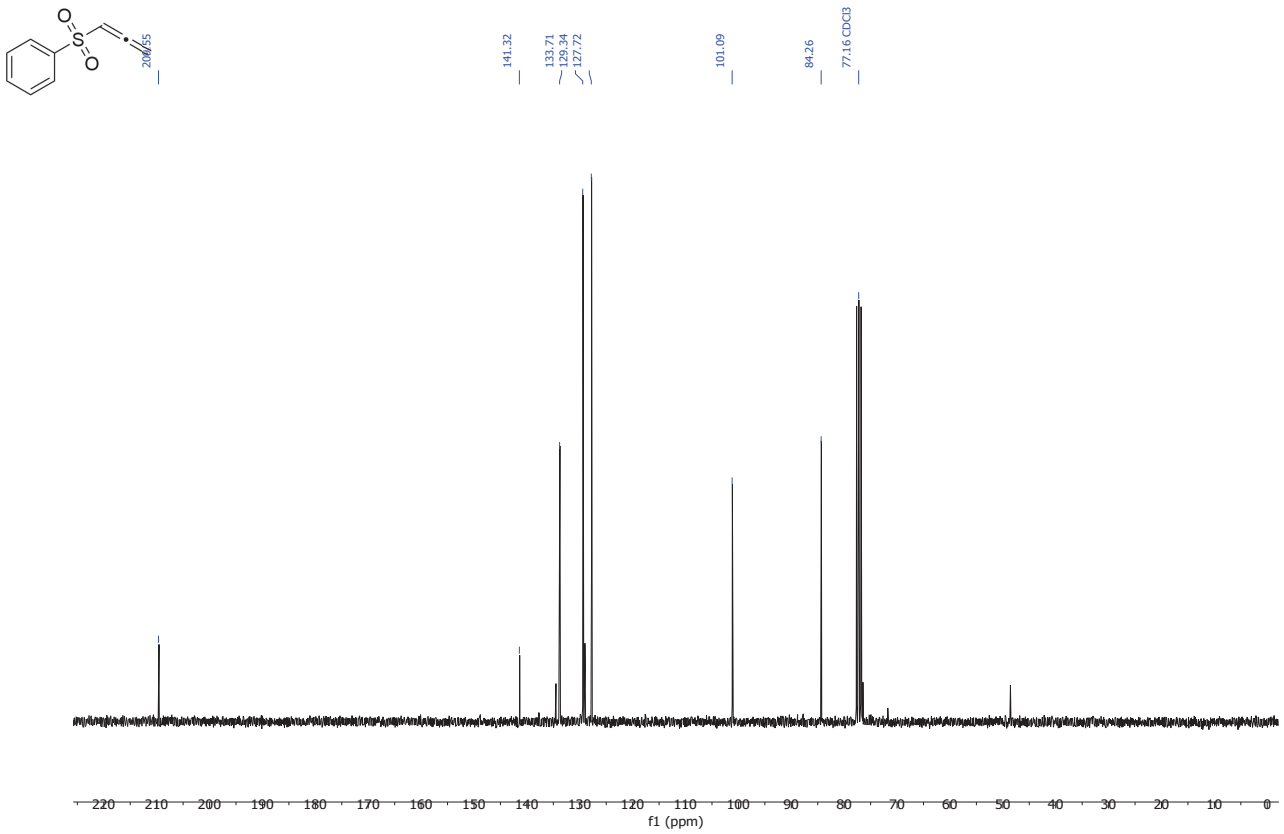
propa-1,2-dienylsulfonylbenzene (2)

^{1}H NMR (300 MHz, $CDCl_3$)

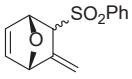


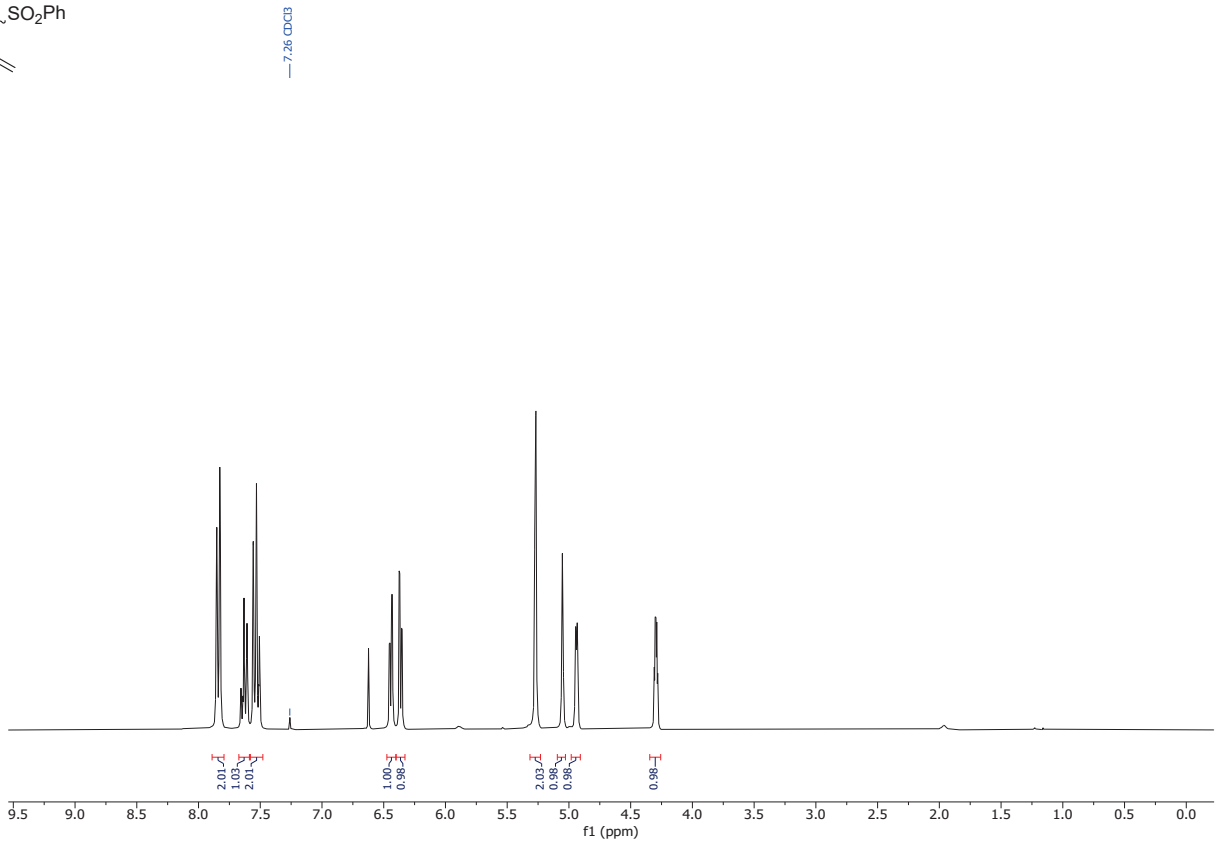
propa-1,2-dienylsulfonylbenzene (2)

^{13}C NMR (75 MHz, $CDCl_3$)

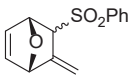


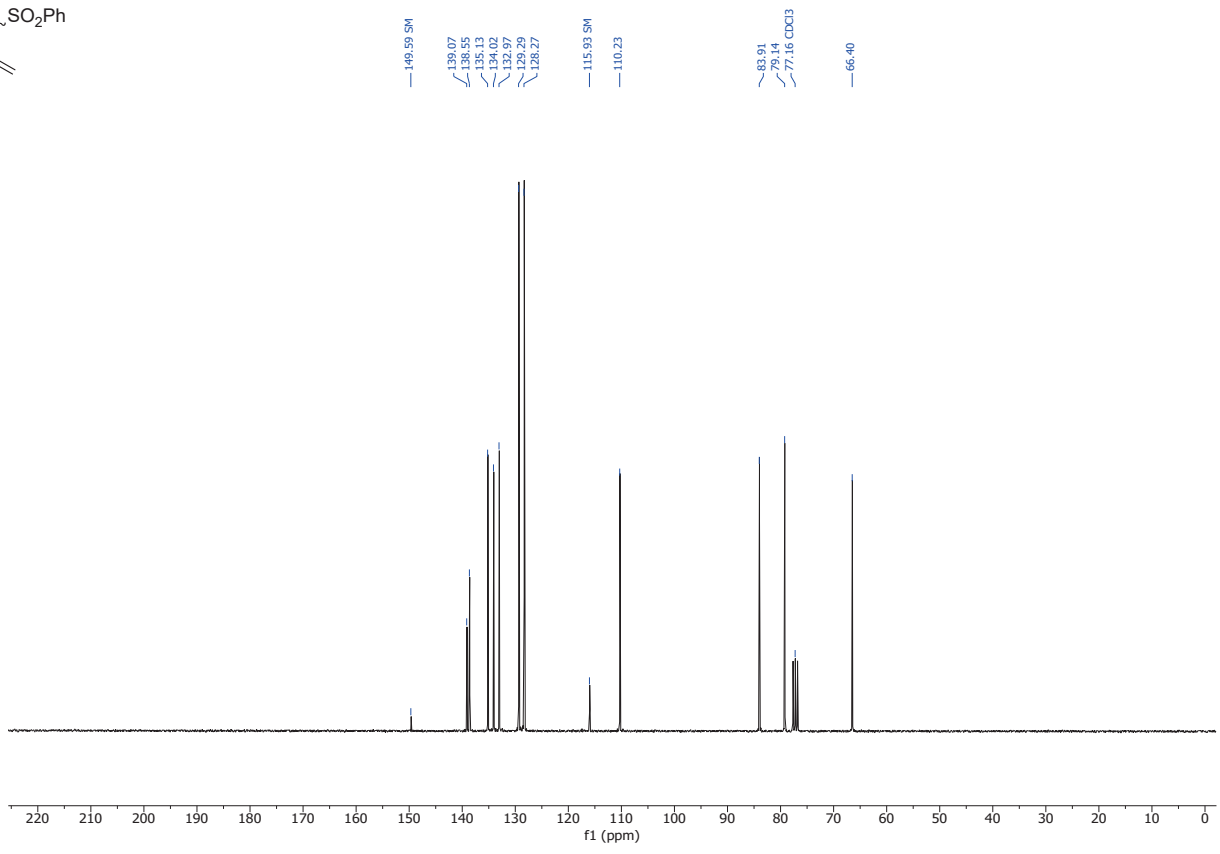
(1R,4*S*)-5-methylene-6-(phenylsulfonyl)-7-oxabicyclo[2.2.1]hept-2-ene (3) ^{1}H NMR (300 MHz, $CDCl_3$)
Endo isomer



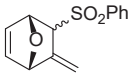


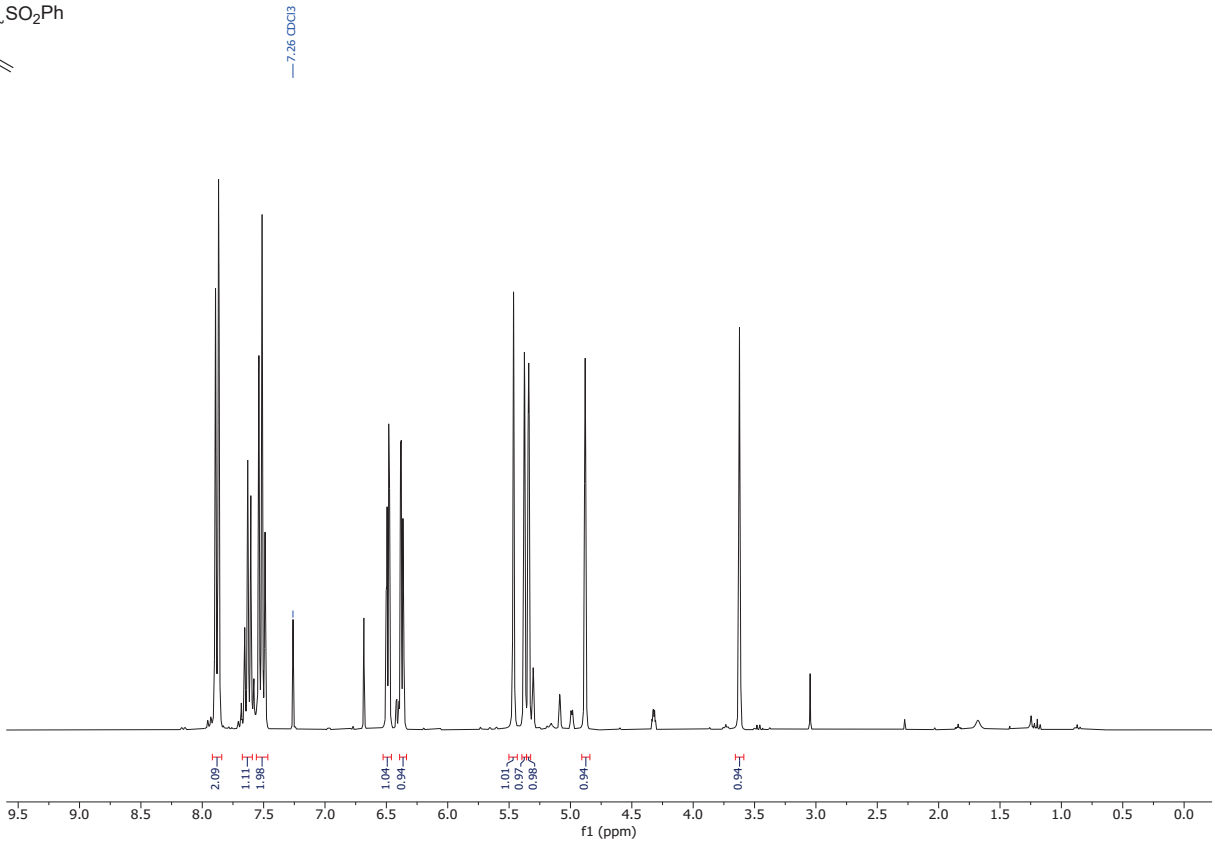
(1R,4*S*)-5-methylene-6-(phenylsulfonyl)-7-oxabicyclo[2.2.1]hept-2-ene (3) ^{13}C NMR (75 MHz, $CDCl_3$)
Endo isomer



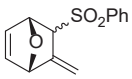


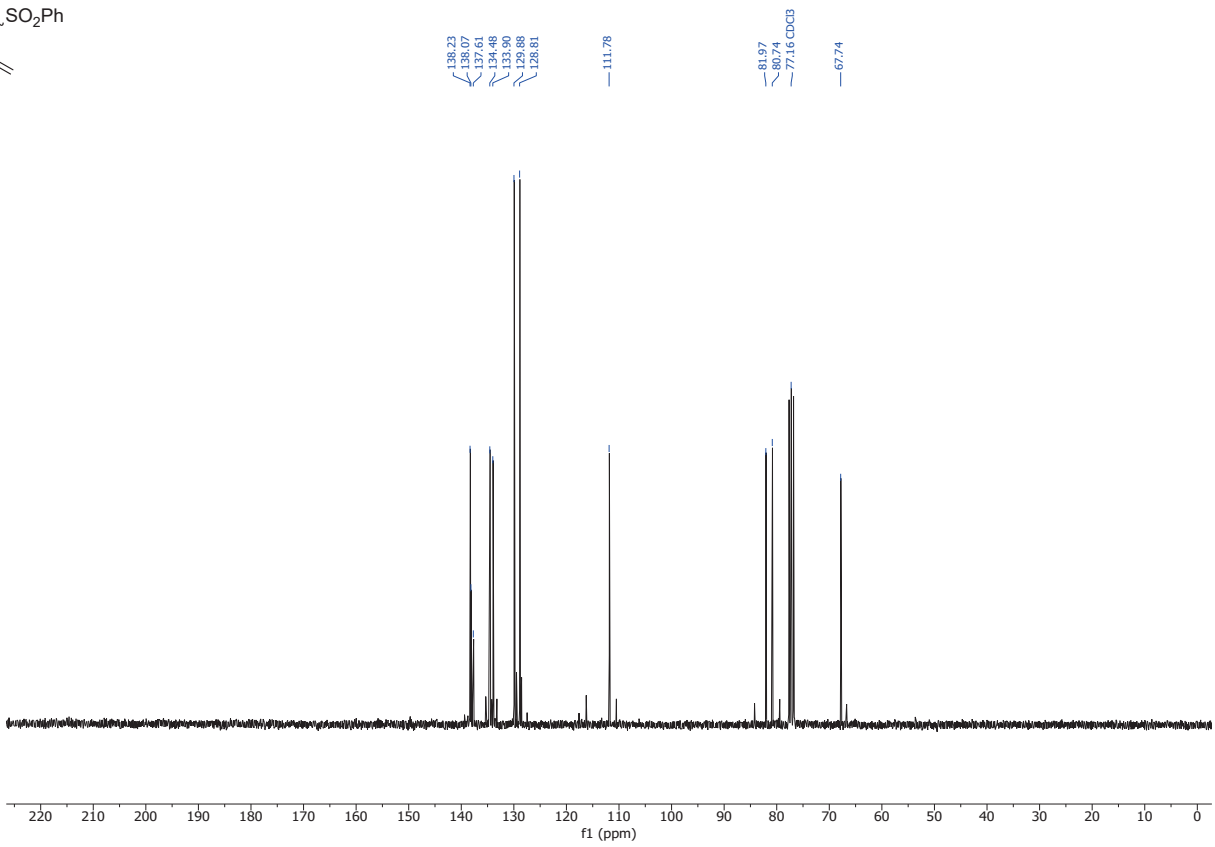
(1R,4*S*)-5-methylene-6-(phenylsulfonyl)-7-oxabicyclo[2.2.1]hept-2-ene (3) ^{1}H NMR (300 MHz, $CDCl_3$)
Exo isomer





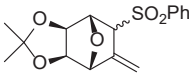
(1R,4*S*)-5-methylene-6-(phenylsulfonyl)-7-oxabicyclo[2.2.1]hept-2-ene (3) ^{13}C NMR (75 MHz, $CDCl_3$)
Exo isomer

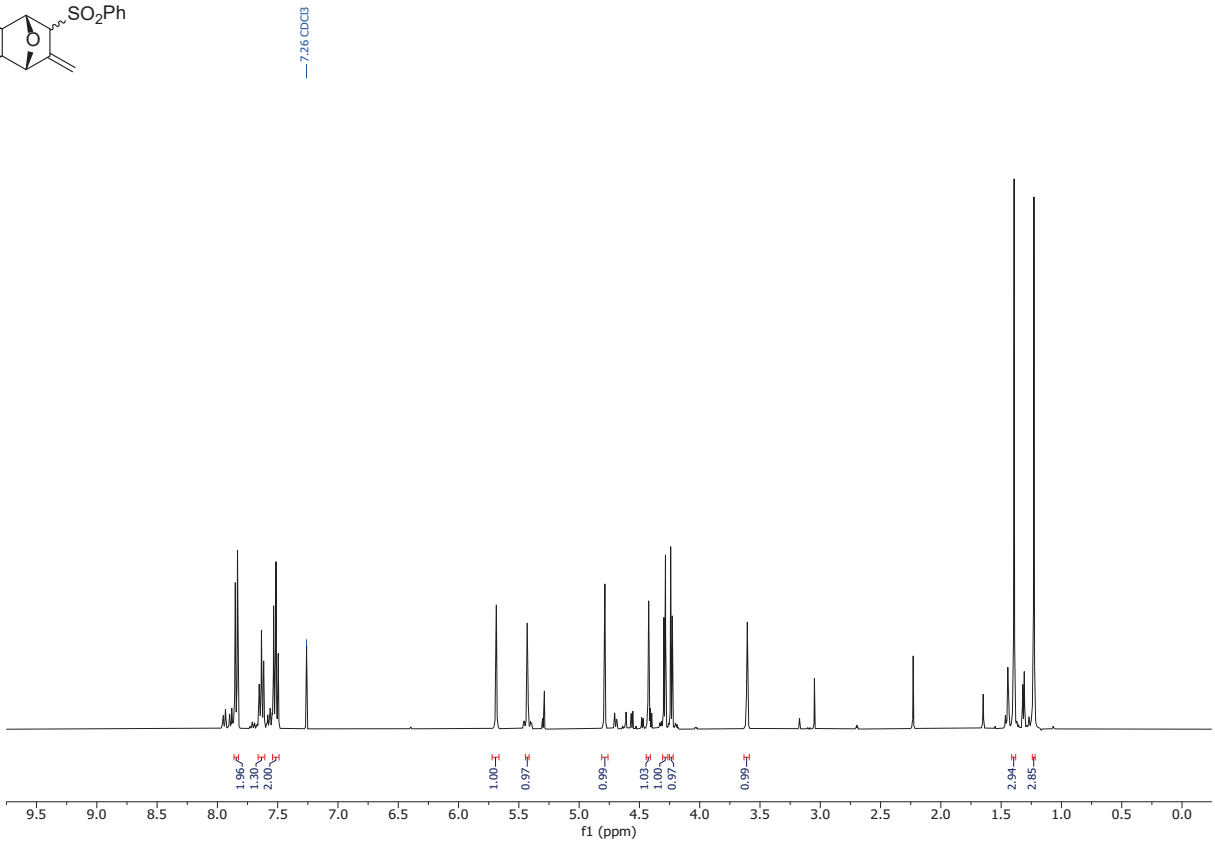




(3aR,4R,7R,7aR)-2,2-dimethyl-5-methylene-6-(phenylsulfonyl)hexahydro-4,7-epoxybenzo[d][1,3]dioxole (4)
Endo isomer

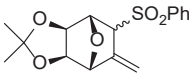
^{1}H NMR (400 MHz, $CDCl_3$)

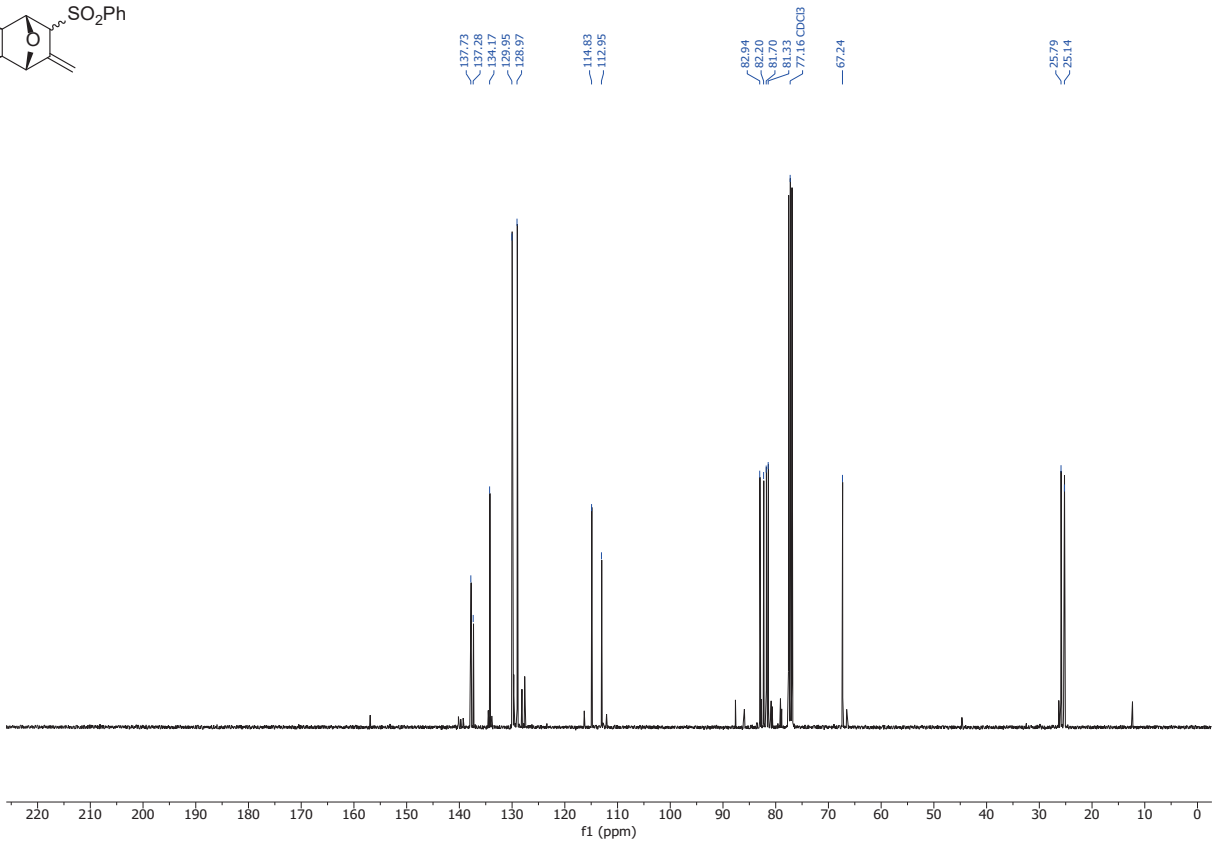




(3aR,4R,7R,7aR)-2,2-dimethyl-5-methylene-6-(phenylsulfonyl)hexahydro-4,7-epoxybenzo[d][1,3]dioxole (4)
Endo isomer

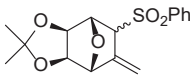
^{13}C NMR (101 MHz, $CDCl_3$)

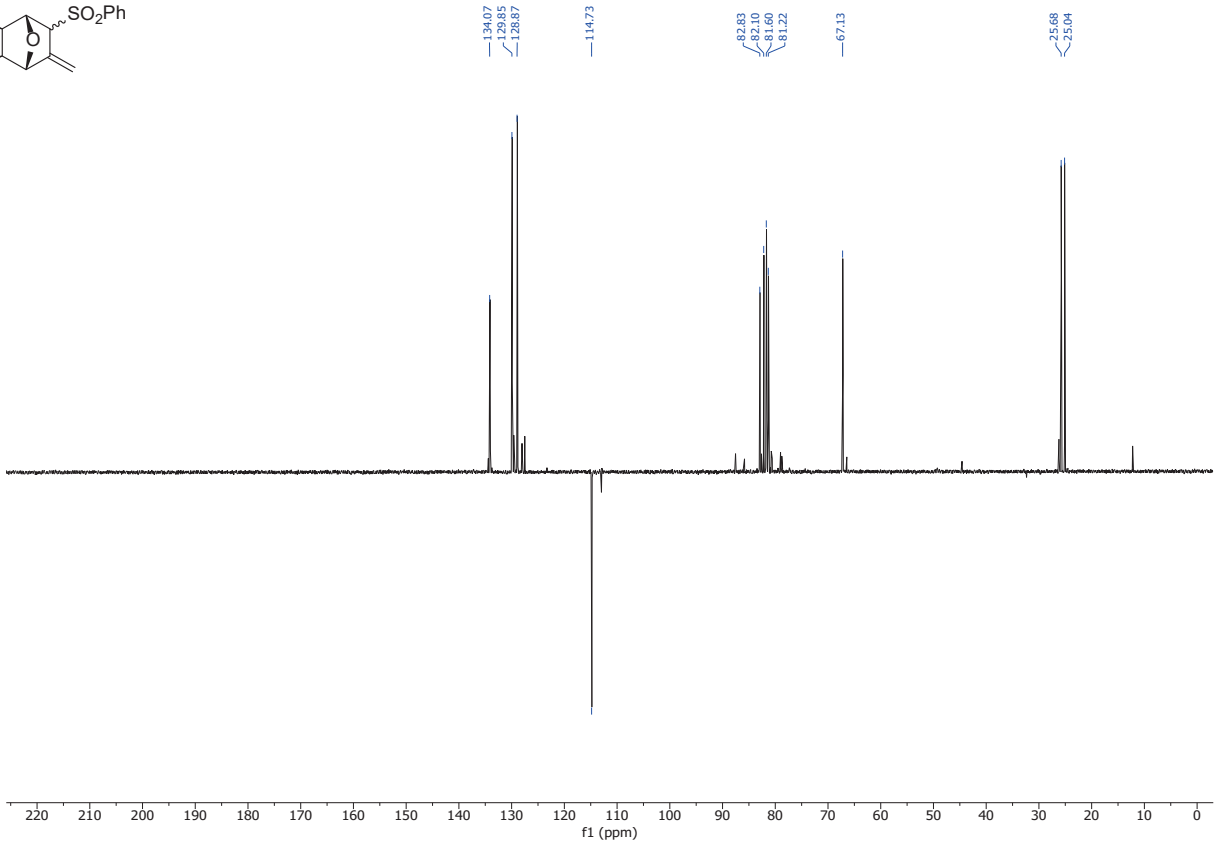




(3aR,4R,7R,7aR)-2,2-dimethyl-5-methylene-6-(phenylsulfonyl)hexahydro-4,7-epoxybenzo [d][1,3]dioxole (4)
Endo isomer

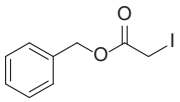
^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)

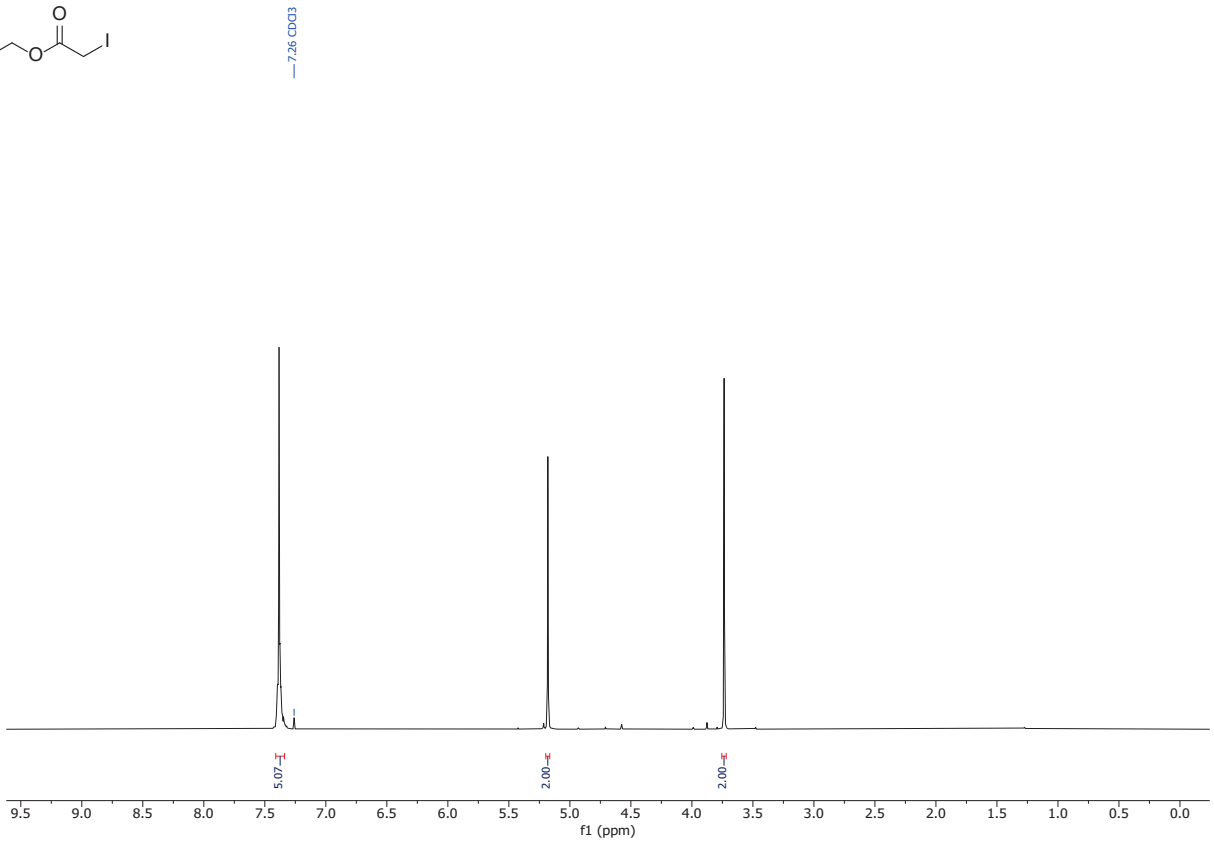




benzyl 2-iodoacetate (41)

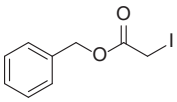
^{1}H NMR (300 MHz, $CDCl_3$)

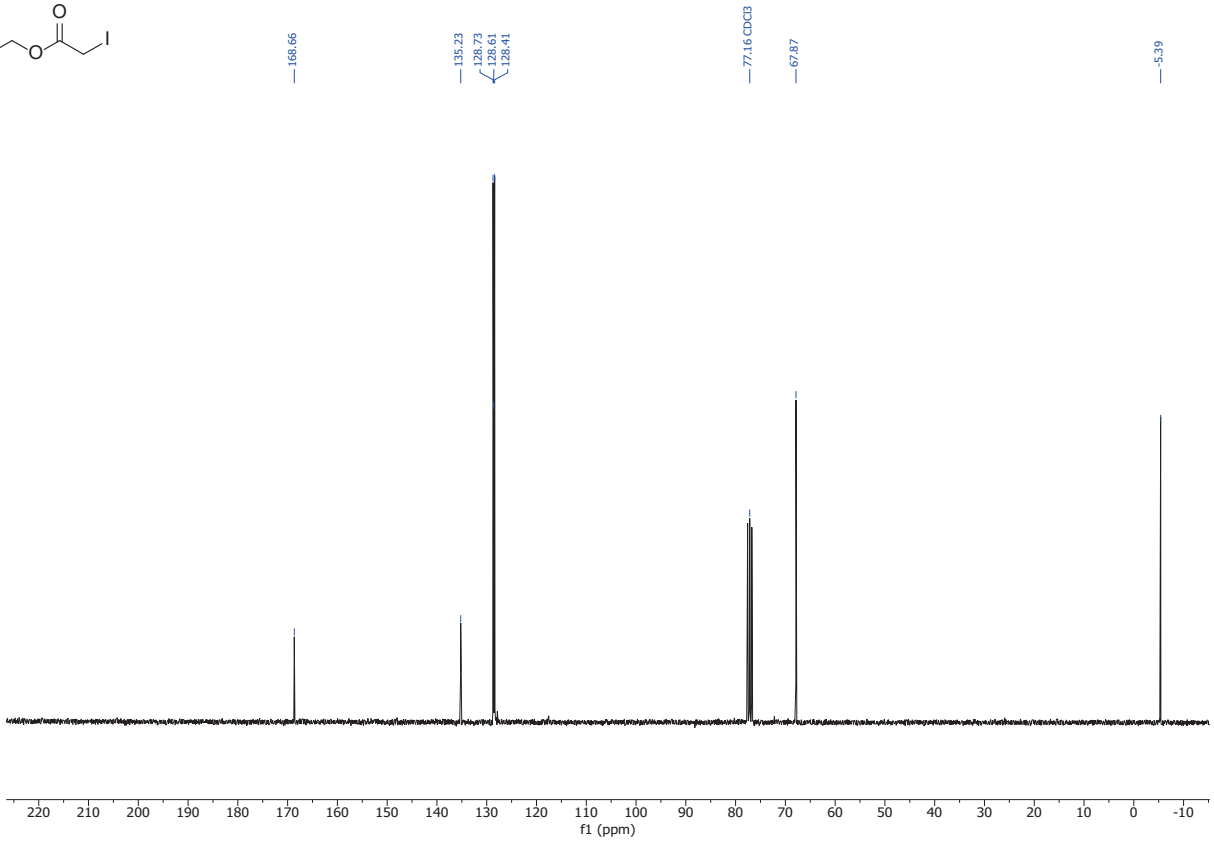




benzyl 2-iodoacetate (41)

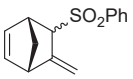
^{13}C NMR (75 MHz, $CDCl_3$)

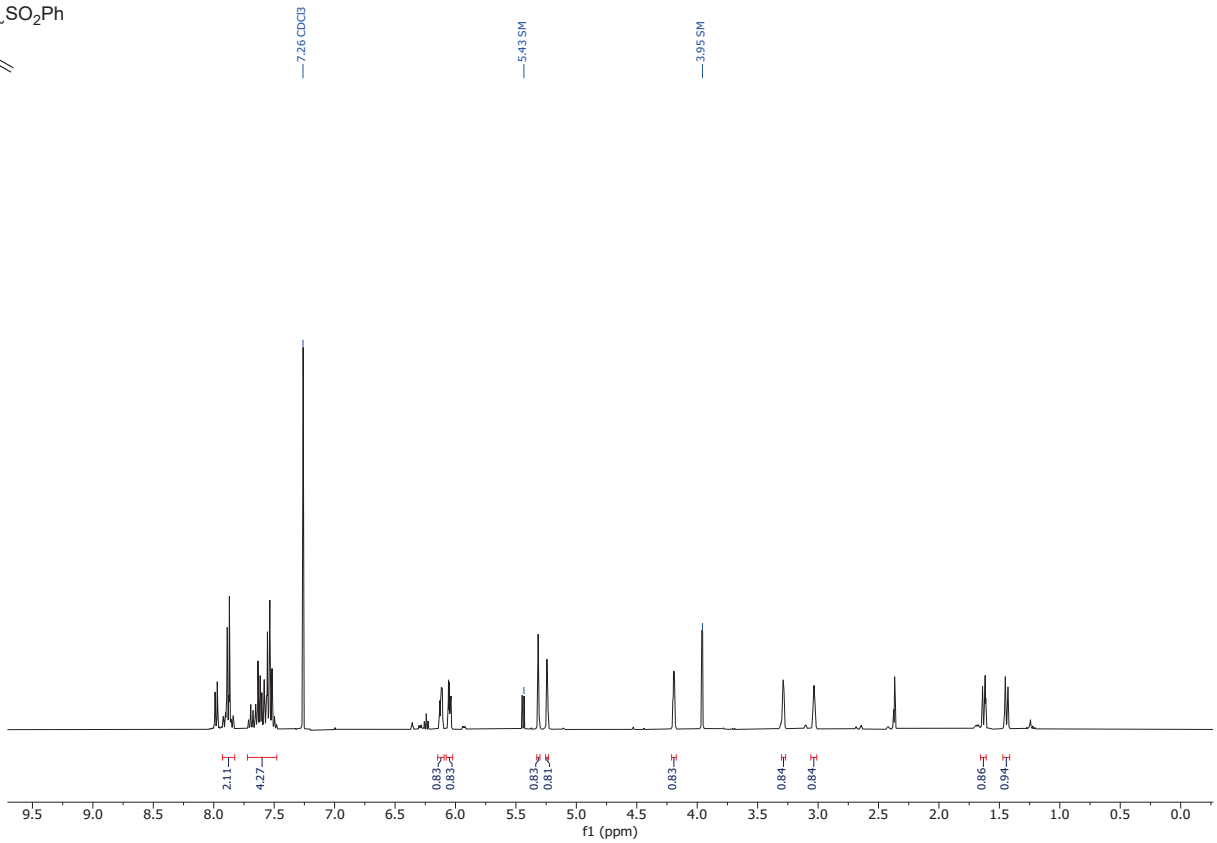




(1R,4S)-5-methylene-6-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (6)
Endo isomer

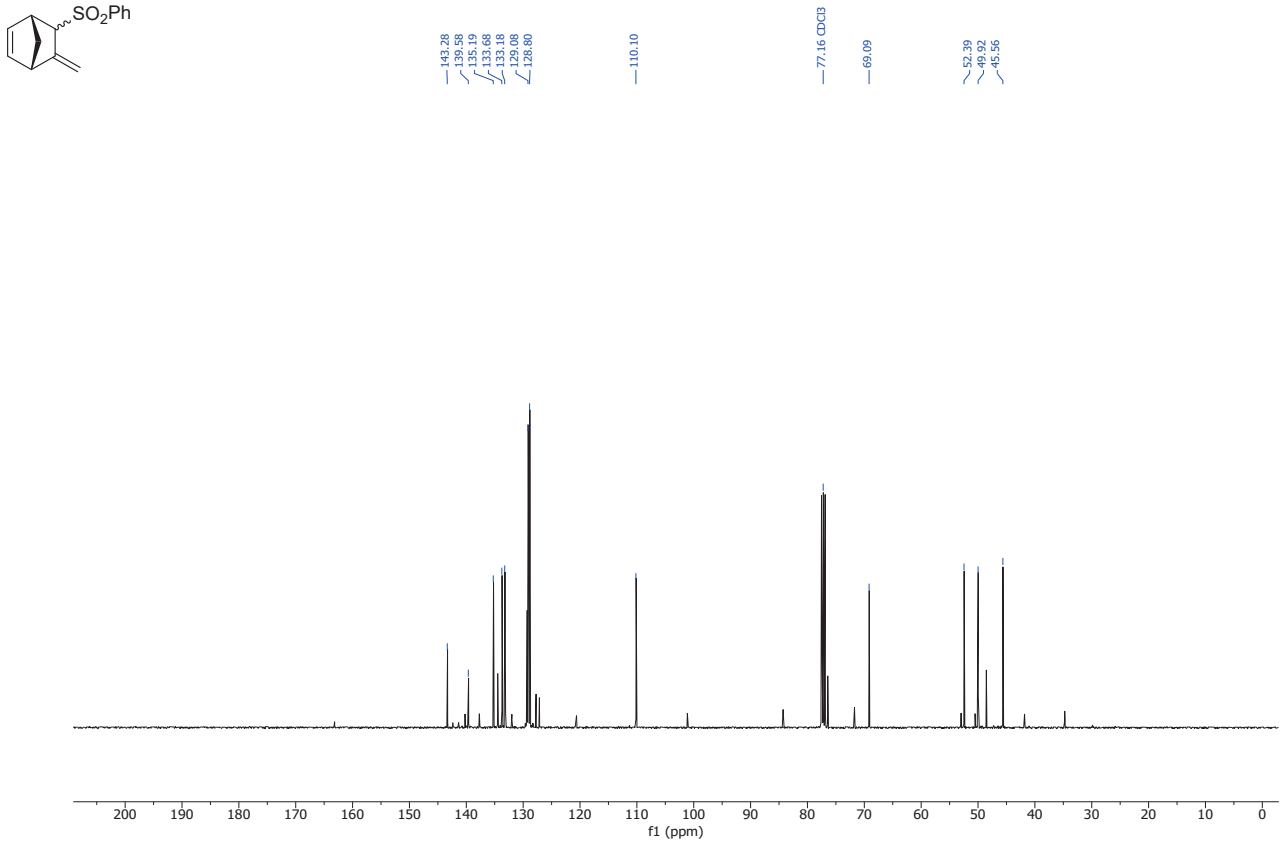
^{1}H NMR (400 MHz, $CDCl_3$)





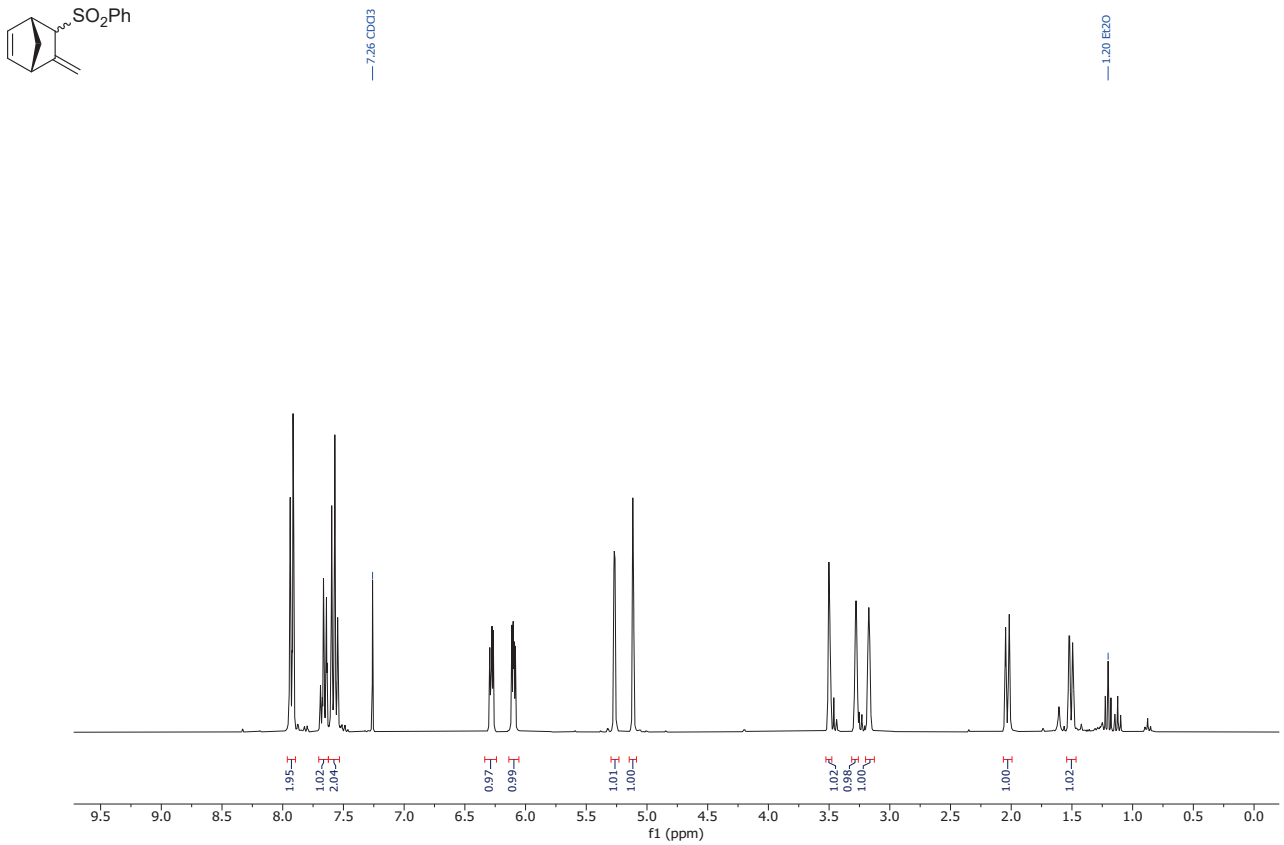
(1R,4*S*)-5-methylene-6-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (6)
Endo isomer

^{13}C NMR (101 MHz, $CDCl_3$)



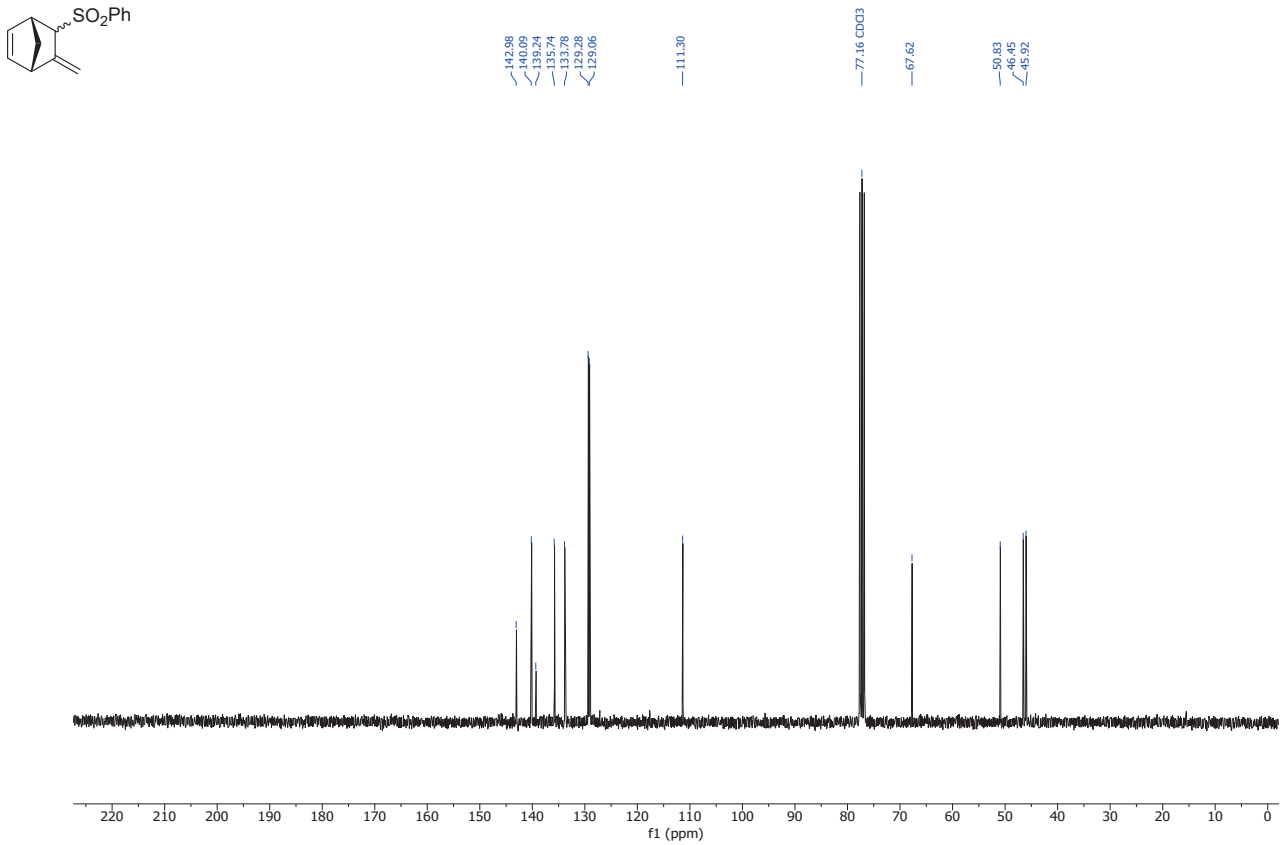
(1R,4*S*)-5-methylene-6-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (6)
Exo isomer

^{1}H NMR (300 MHz, $CDCl_3$)



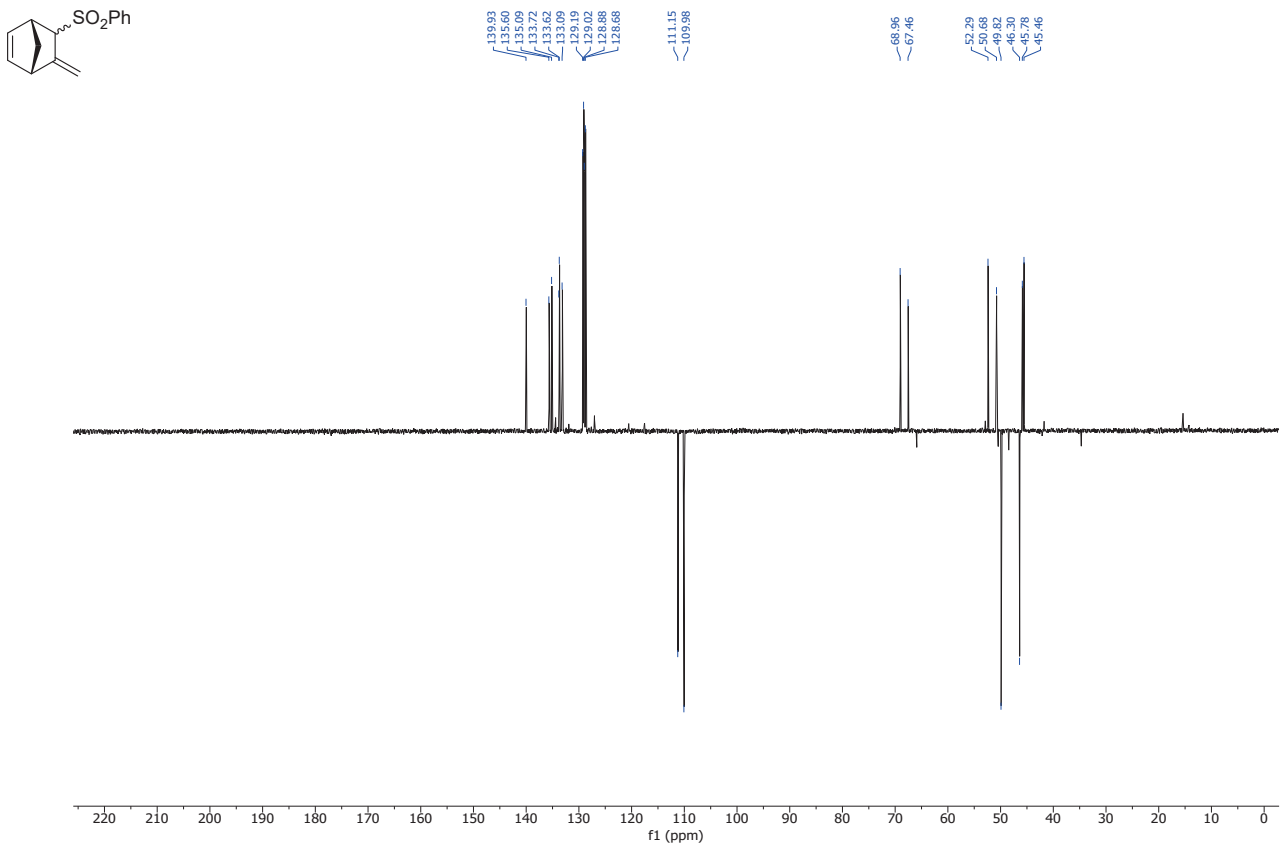
(1R,4*S*)-5-methylene-6-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (6)
Exo isomer

^{13}C NMR (75 MHz, $CDCl_3$)

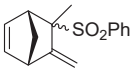


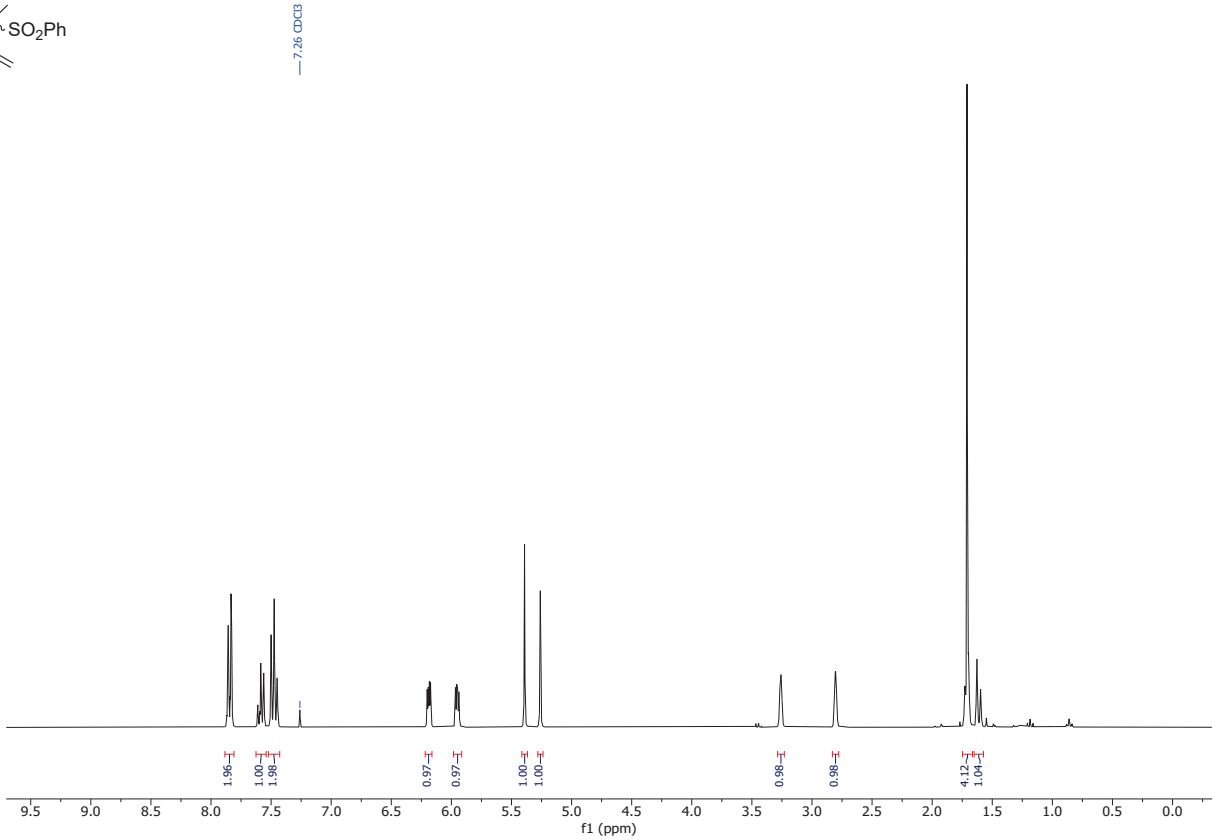
(1R,4*S*)-5-methylene-6-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (6)
Mix of isomers

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)

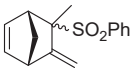


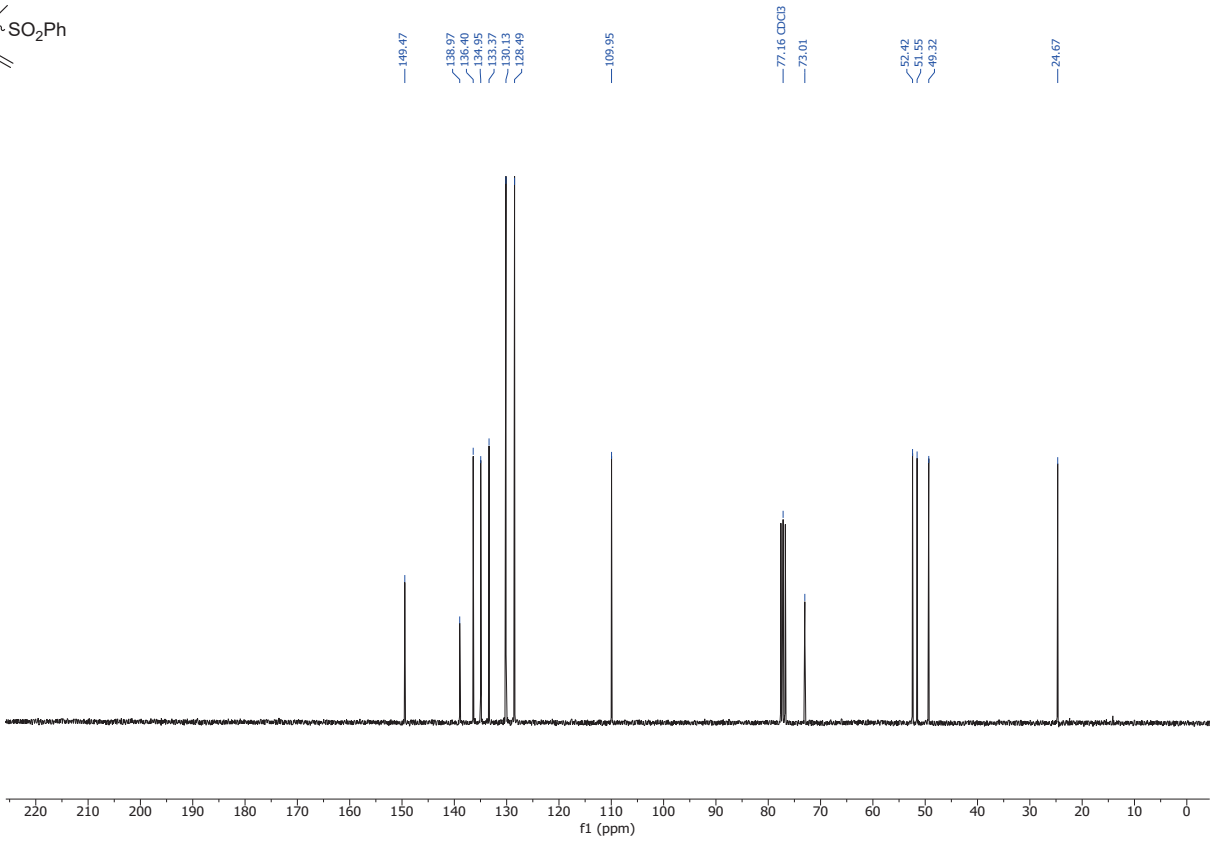
(1S,4R)-5-methyl-6-methylene-5-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (7) ^{1}H NMR (300 MHz, $CDCl_3$)
Endo isomer





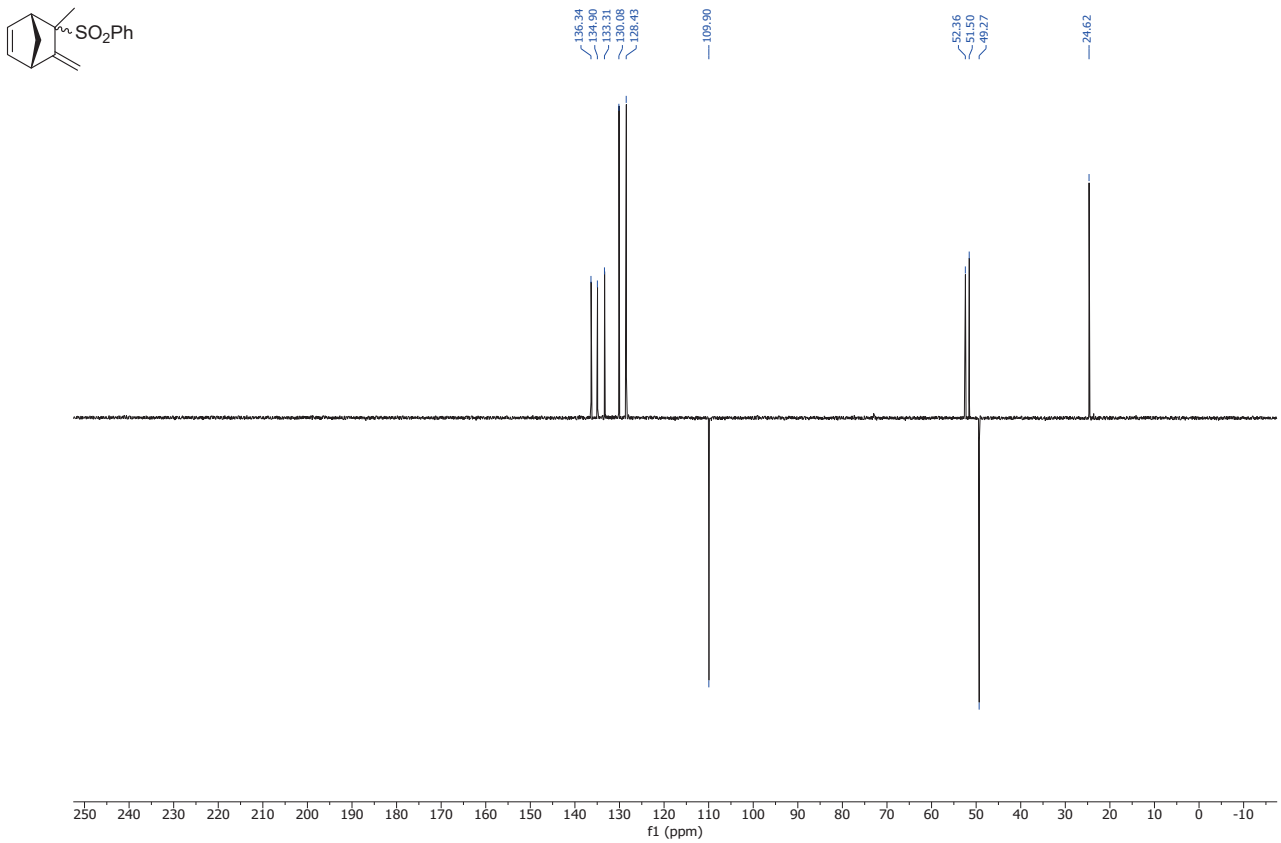
(1S,4R)-5-methyl-6-methylene-5-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (7) ^{13}C NMR (75 MHz, $CDCl_3$)
Endo isomer





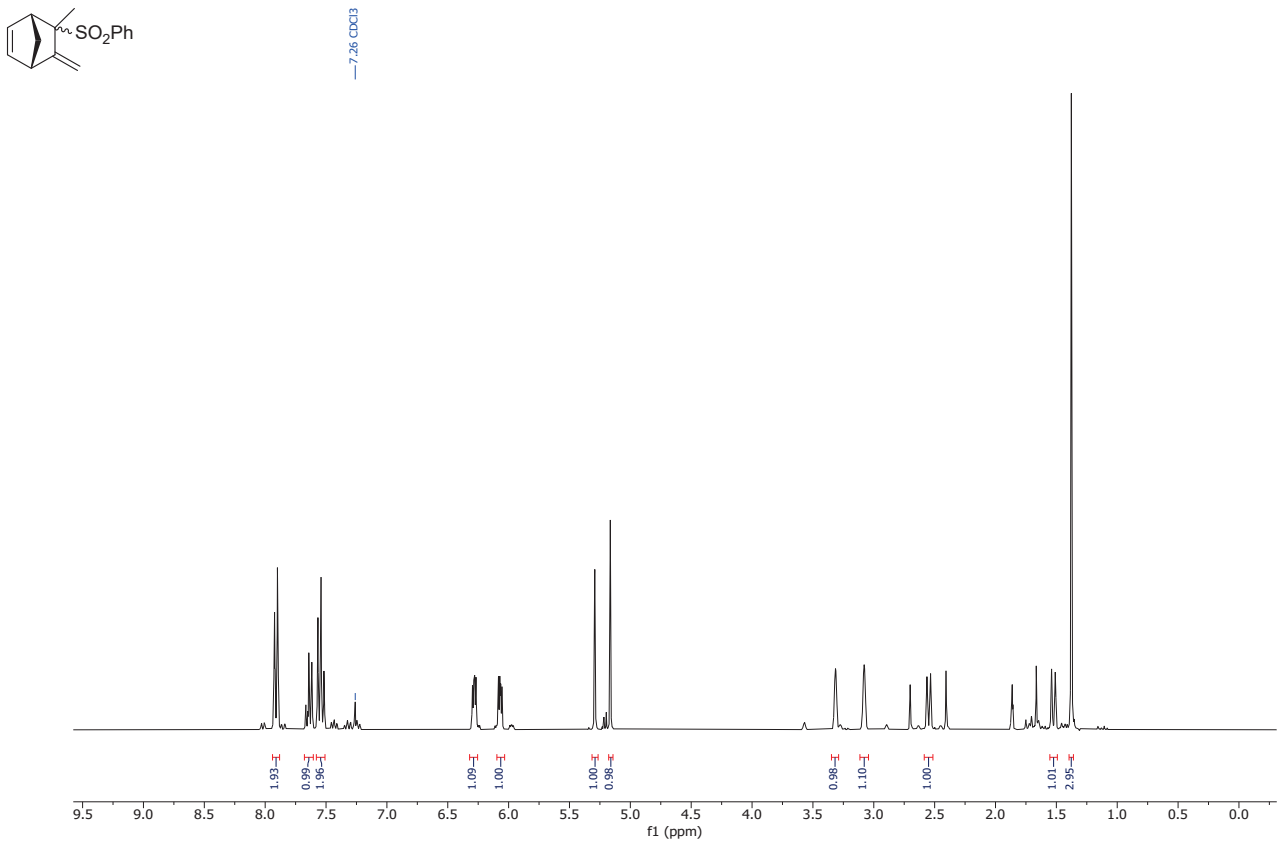
(1S,4R)-5-methyl-6-methylene-5-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (7)
Endo isomer

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



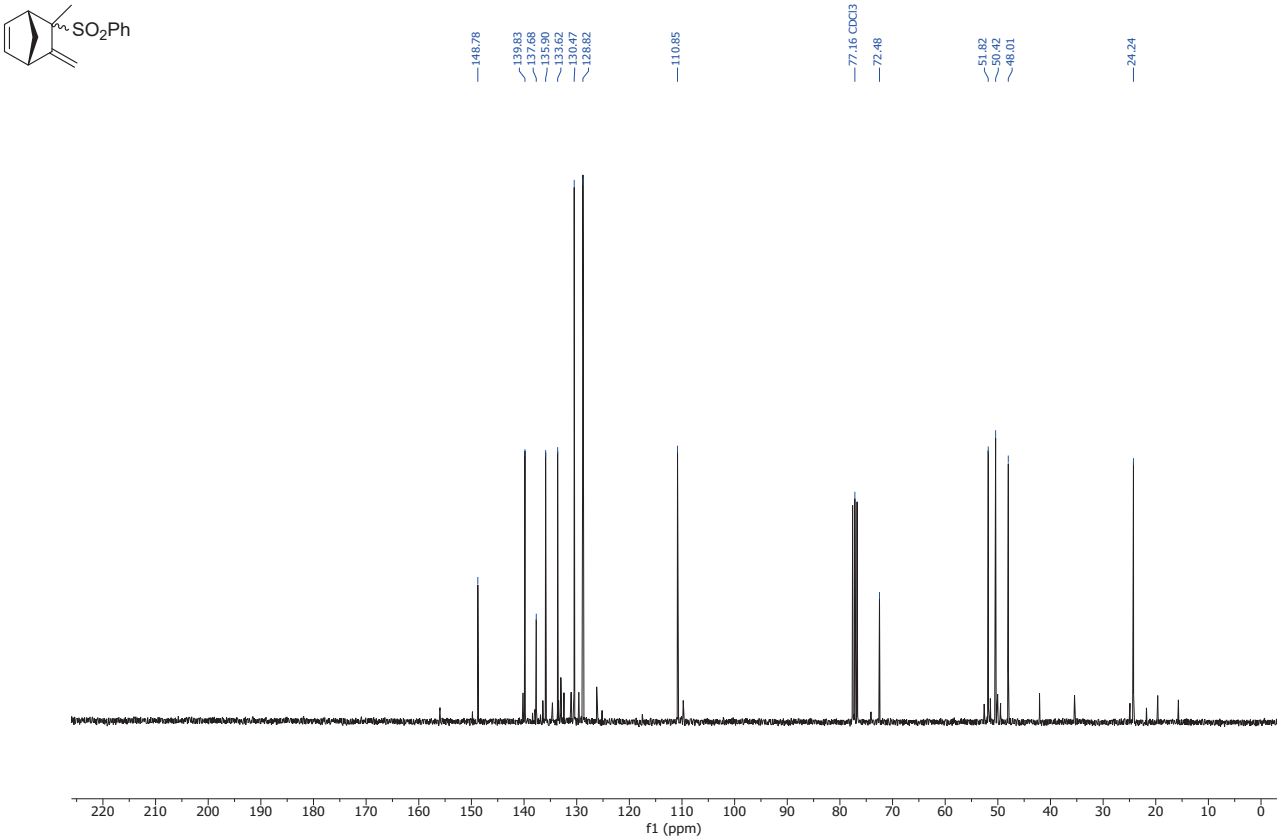
(1S,4R)-5-methyl-6-methylene-5-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (7)
Exo isomer

^{1}H NMR (300 MHz, $CDCl_3$)



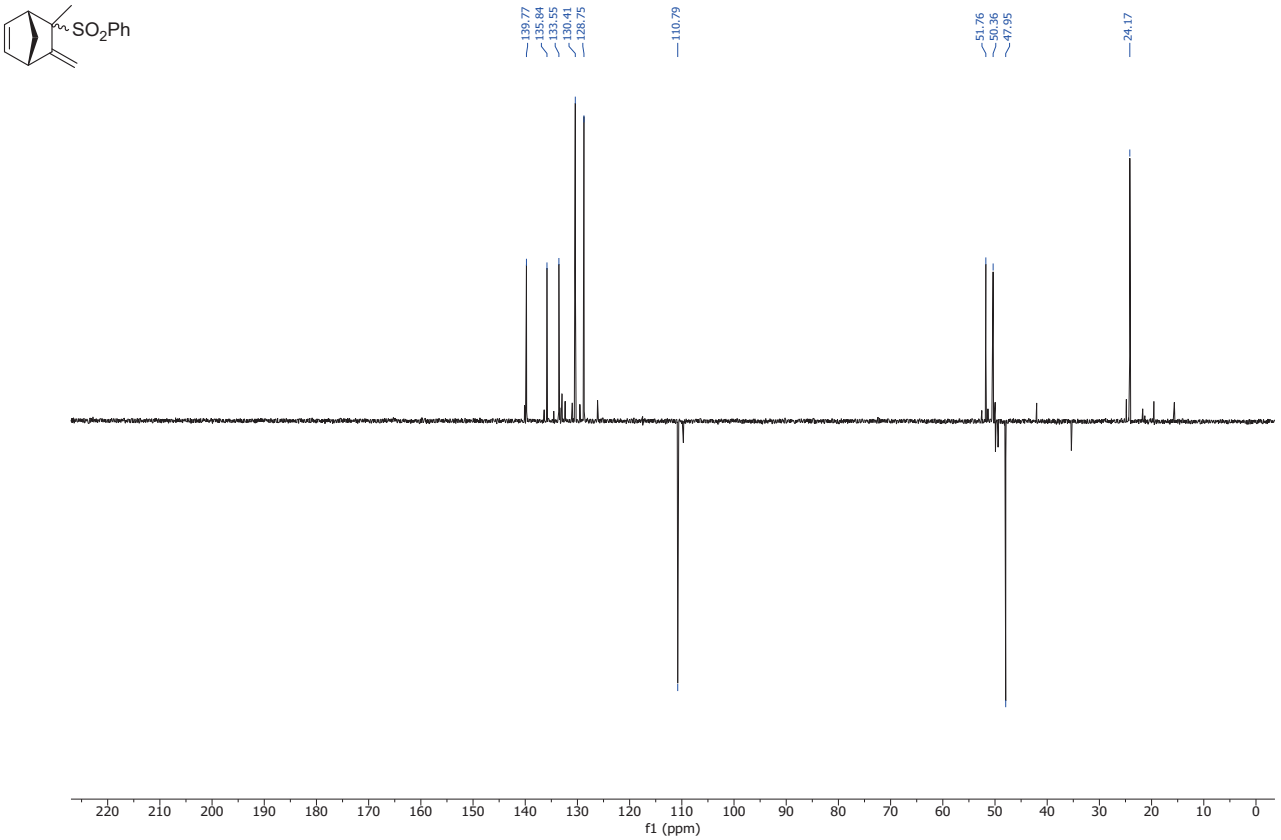
(1S,4R)-5-methyl-6-methylene-5-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (7)
Exo isomer

^{13}C NMR (75 MHz, $CDCl_3$)



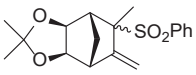
(1S,4R)-5-methyl-6-methylene-5-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (7)
Exo isomer

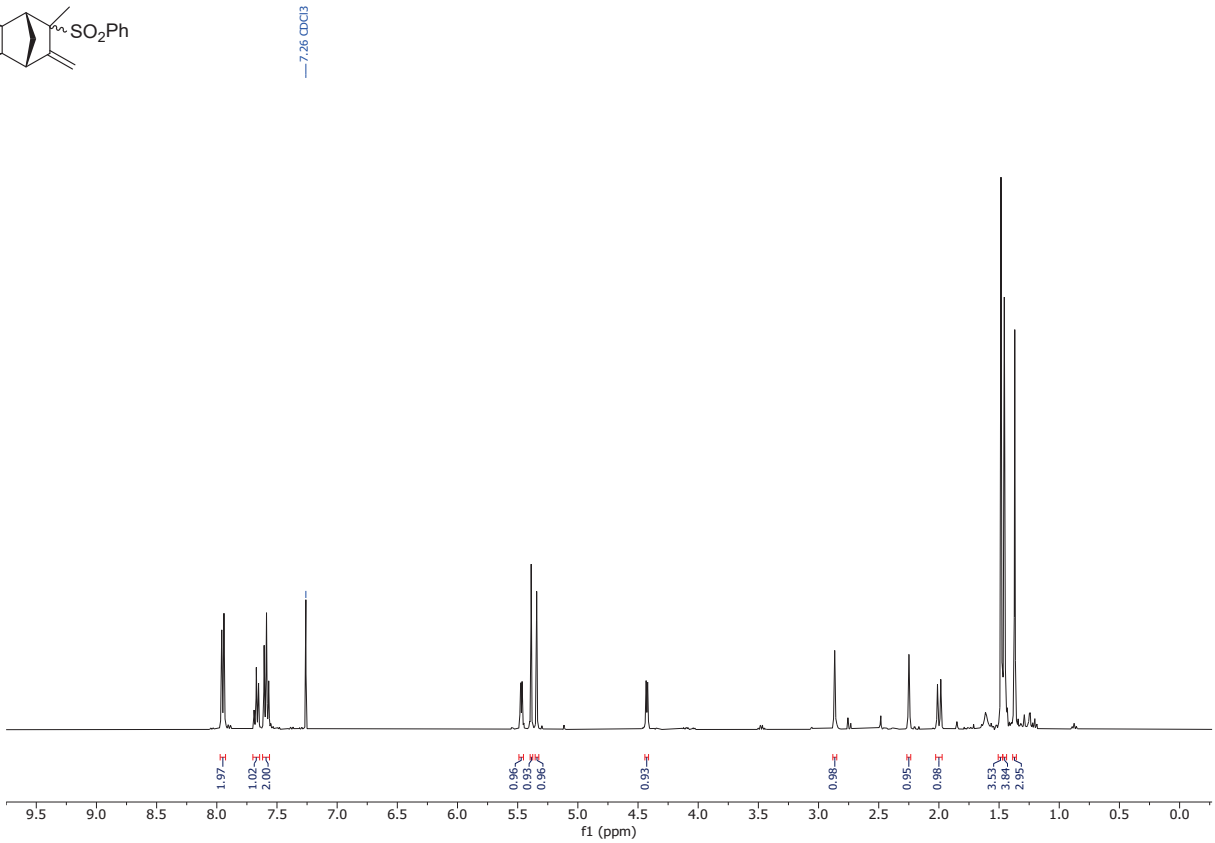
^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



(3aS,4R,7R,7aR)-2,2,5-trimethyl-6-methylene-5-(phenylsulfonyl)hexahydro-4,7-methanobenzo[d][1,3]dioxole (8)
Endo isomer

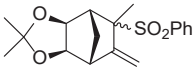
^{1}H NMR (400 MHz, $CDCl_3$)

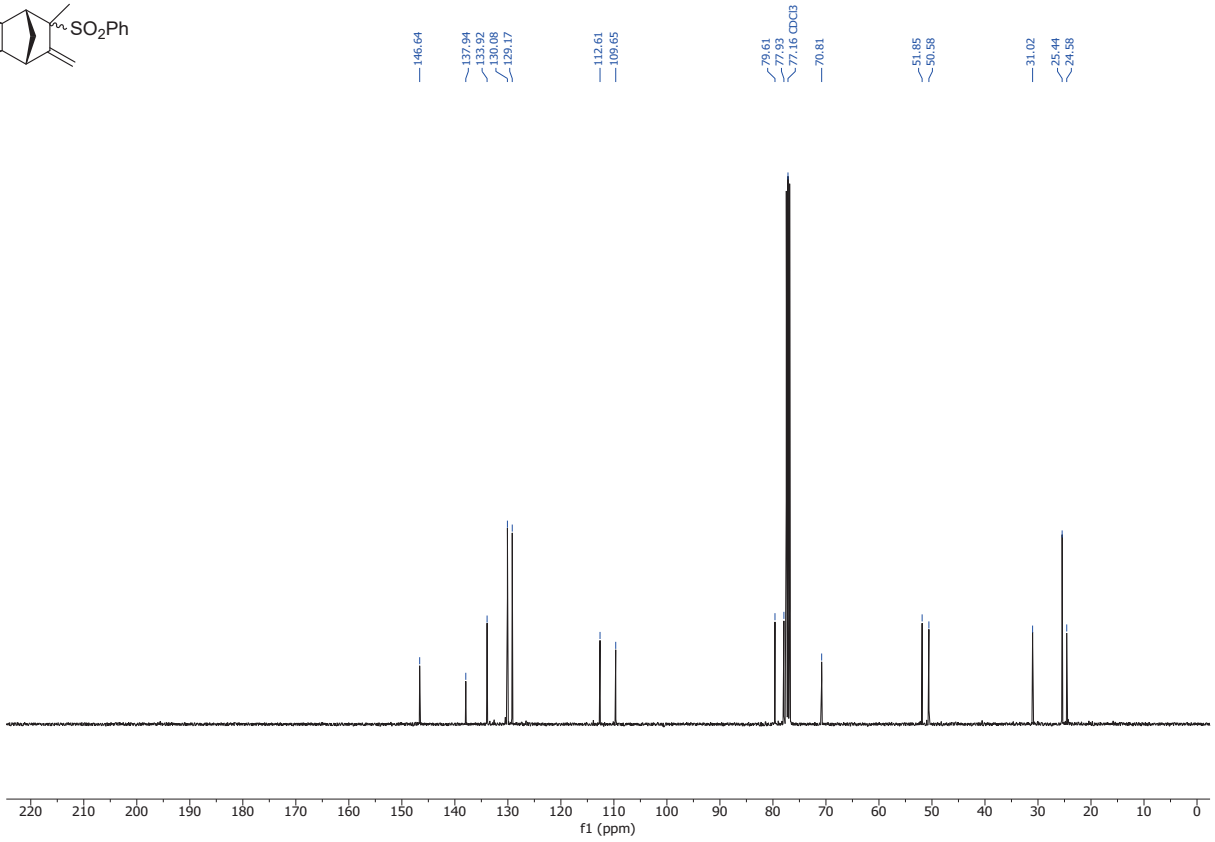




(3aS,4R,7R,7aR)-2,2,5-trimethyl-6-methylene-5-(phenylsulfonyl)hexahydro-4,7-methanobenzo[d][1,3]dioxole (8)
Endo isomer

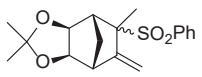
^{13}C NMR (101 MHz, $CDCl_3$)

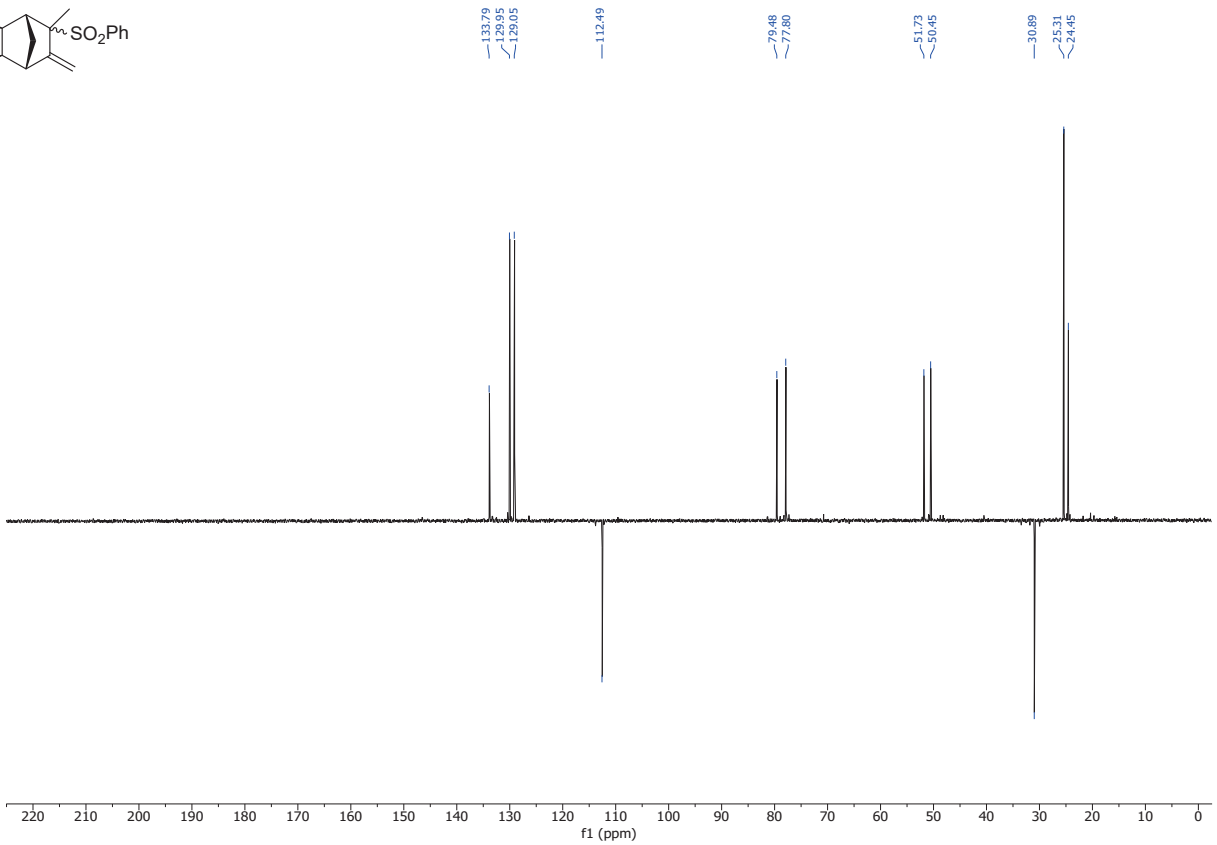




(3aS,4R,7R,7aR)-2,2,5-trimethyl-6-methylene-5-(phenylsulfonyl)hexahydro-4,7-methanobenzo[d][1,3]dioxole (8)
Endo isomer

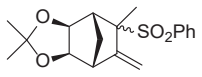
^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)

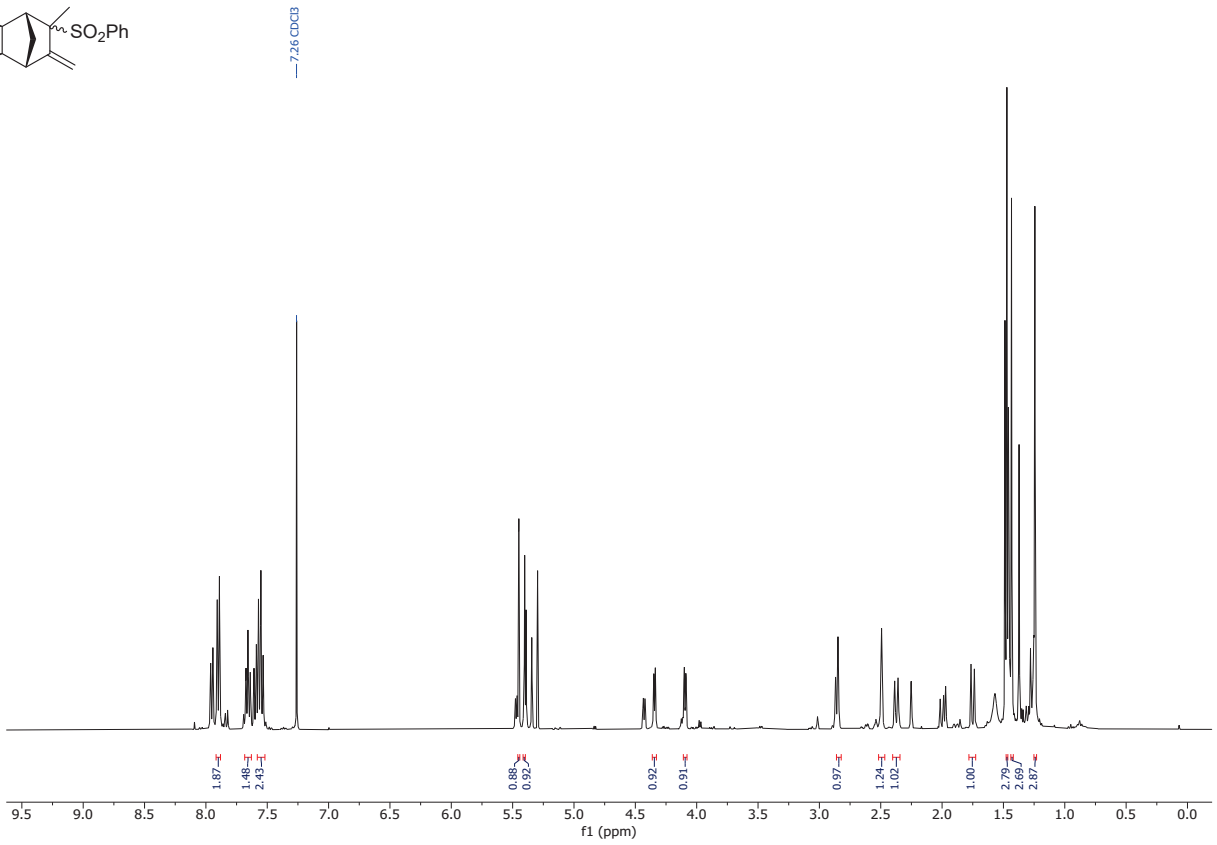




(3aS,4R,7R,7aR)-2,2,5-trimethyl-6-methylene-5-(phenylsulfonyl)hexahydro-4,7-methanobenzo[d][1,3]dioxole (8)
Exo isomer

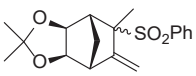
^{1}H NMR (400 MHz, $CDCl_3$)

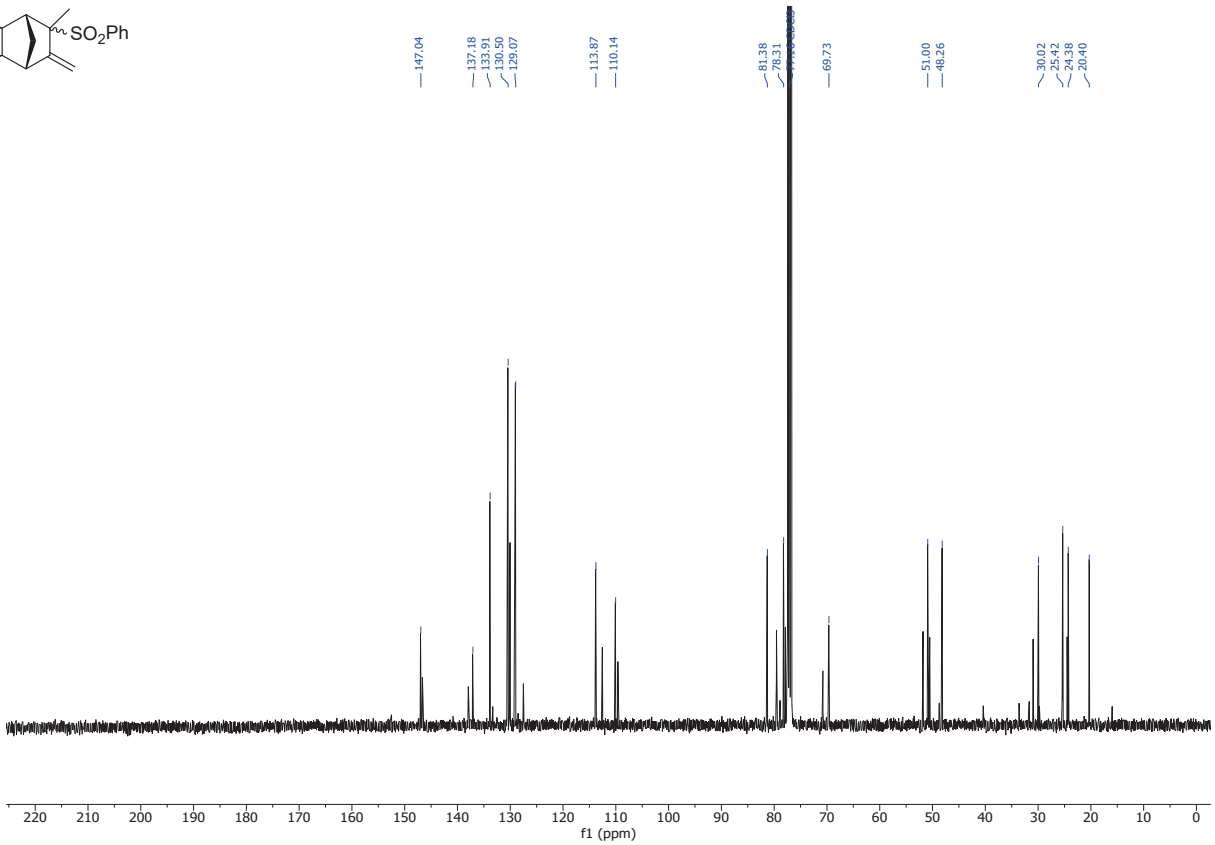




(3aS,4R,7R,7aR)-2,2,5-trimethyl-6-methylene-5-(phenylsulfonyl)hexahydro-4,7-methanobenzo[d][1,3]dioxole (8)
Exo isomer

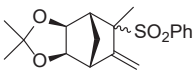
^{13}C NMR (101 MHz, $CDCl_3$)

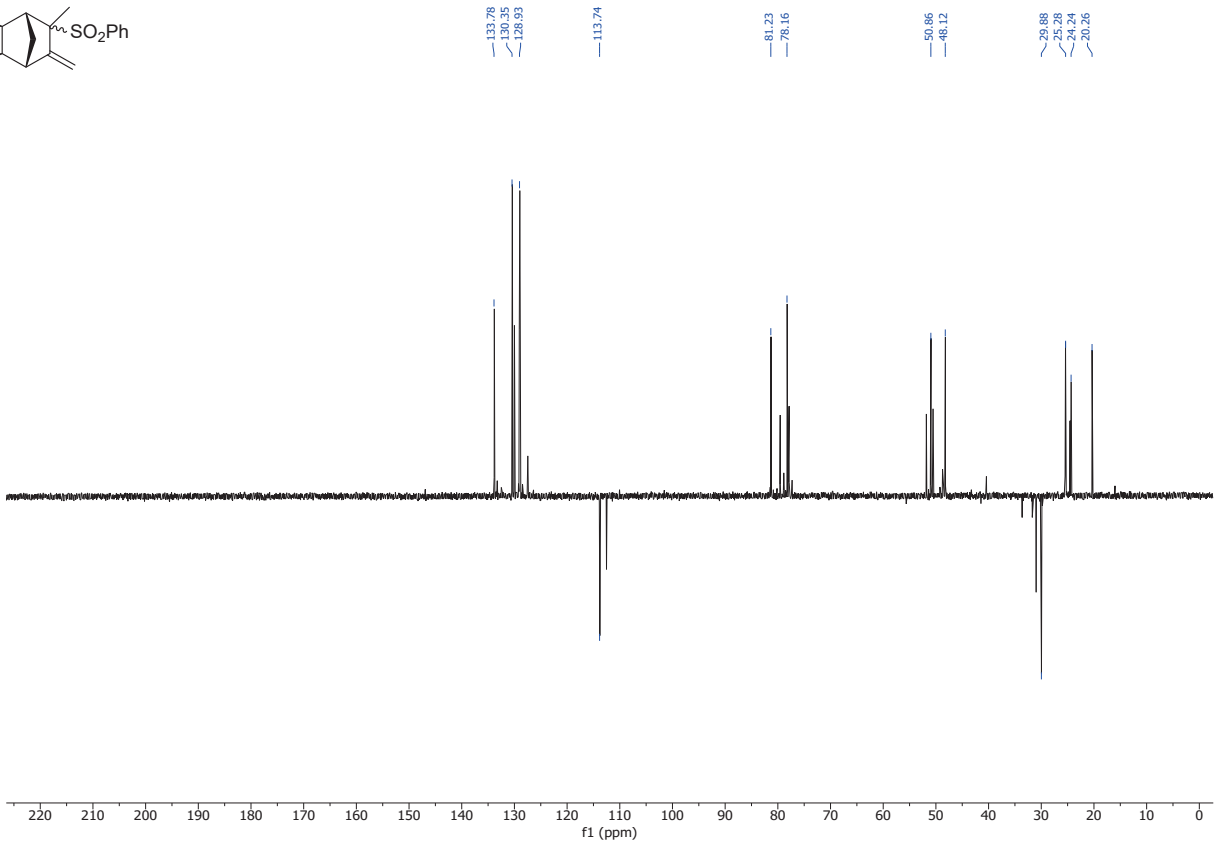




(3aS,4R,7R,7aR)-2,2,5-trimethyl-6-methylene-5-(phenylsulfonyl)hexahydro-4,7-methanobenzo[d][1,3]dioxole (8)
Exo isomer

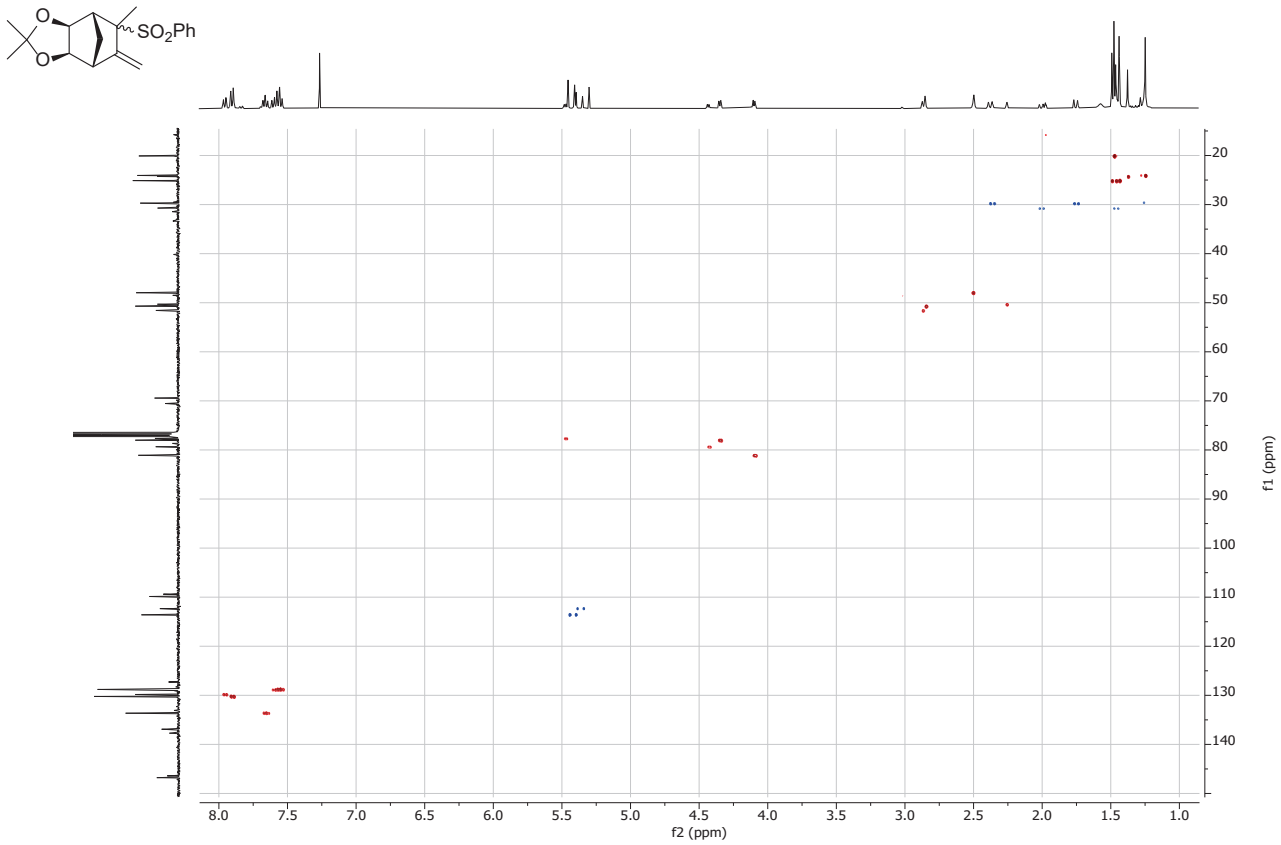
^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)





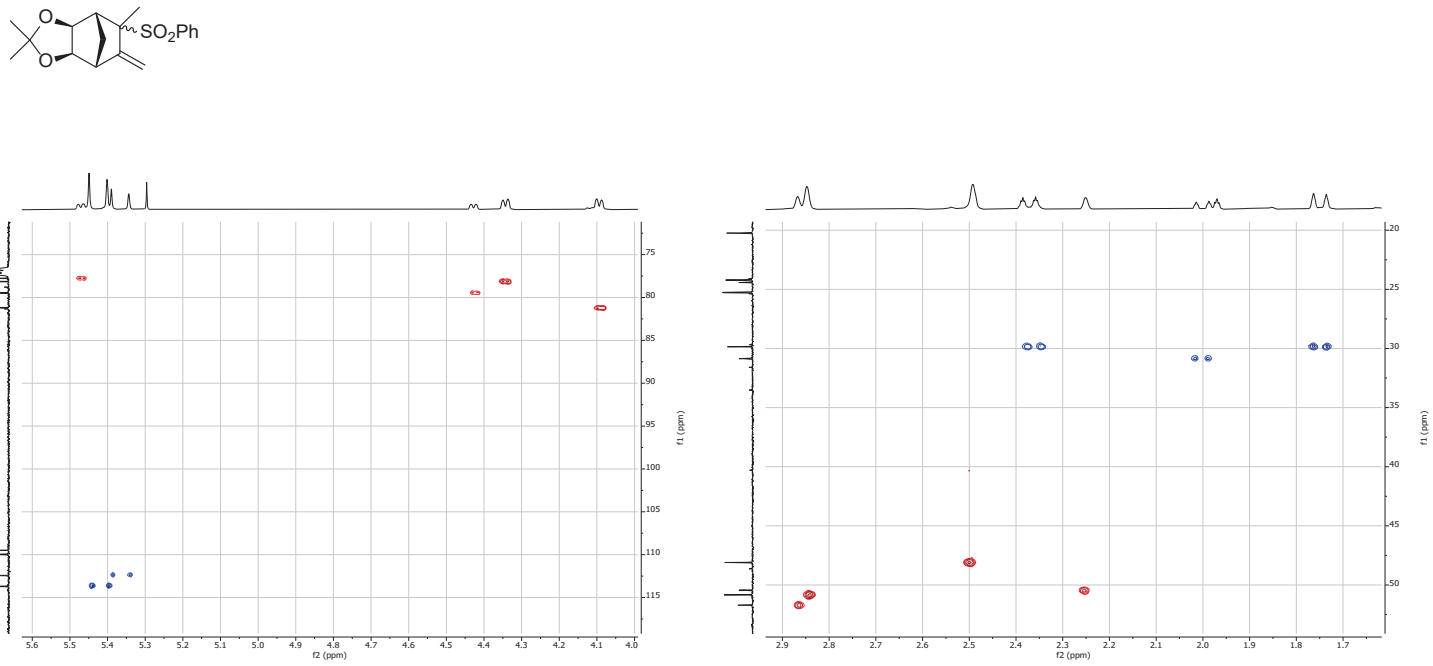
(3aS,4R,7R,7aR)-2,2,5-trimethyl-6-methylene-5-(phenylsulfonyl)hexahydro-4,7-methanobenzo[d][1,3]dioxole (8)
Exo isomer

^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



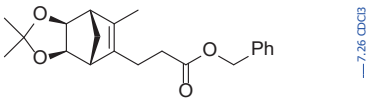
(3aS,4R,7R,7aR)-2,2,5-trimethyl-6-methylene-5-(phenylsulfonyl)hexahydro-4,7-methanobenzo[d][1,3]dioxole (8)
Exo isomer

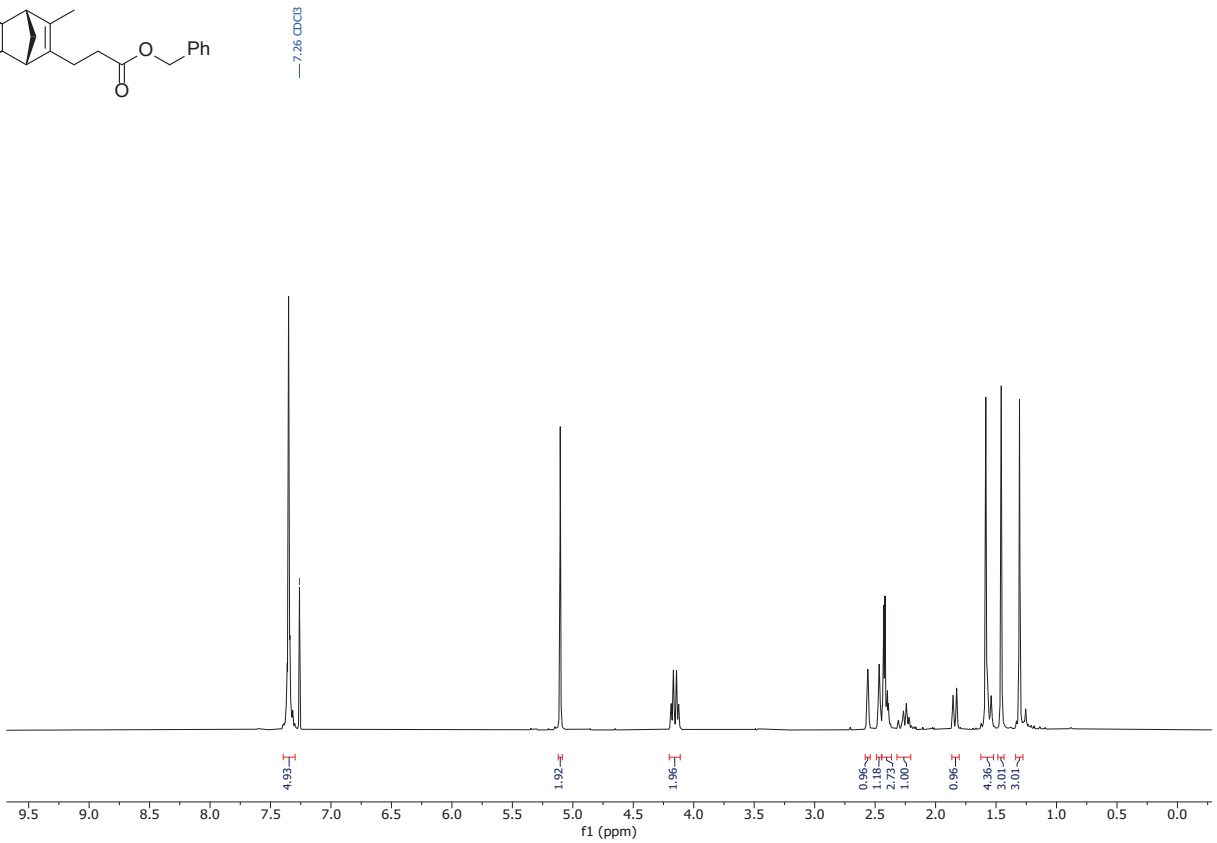
^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



benzyl 3-((3aR,4R,7S,7aS)-2,2,6-trimethyl-3a,4,7,7a-tetrahydro-4,7-methanobenzo[d][1,3]dioxol-5-yl)propanoate (9)

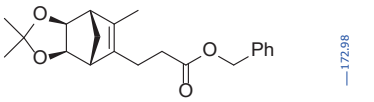
^{1}H NMR (300 MHz, $CDCl_3$)

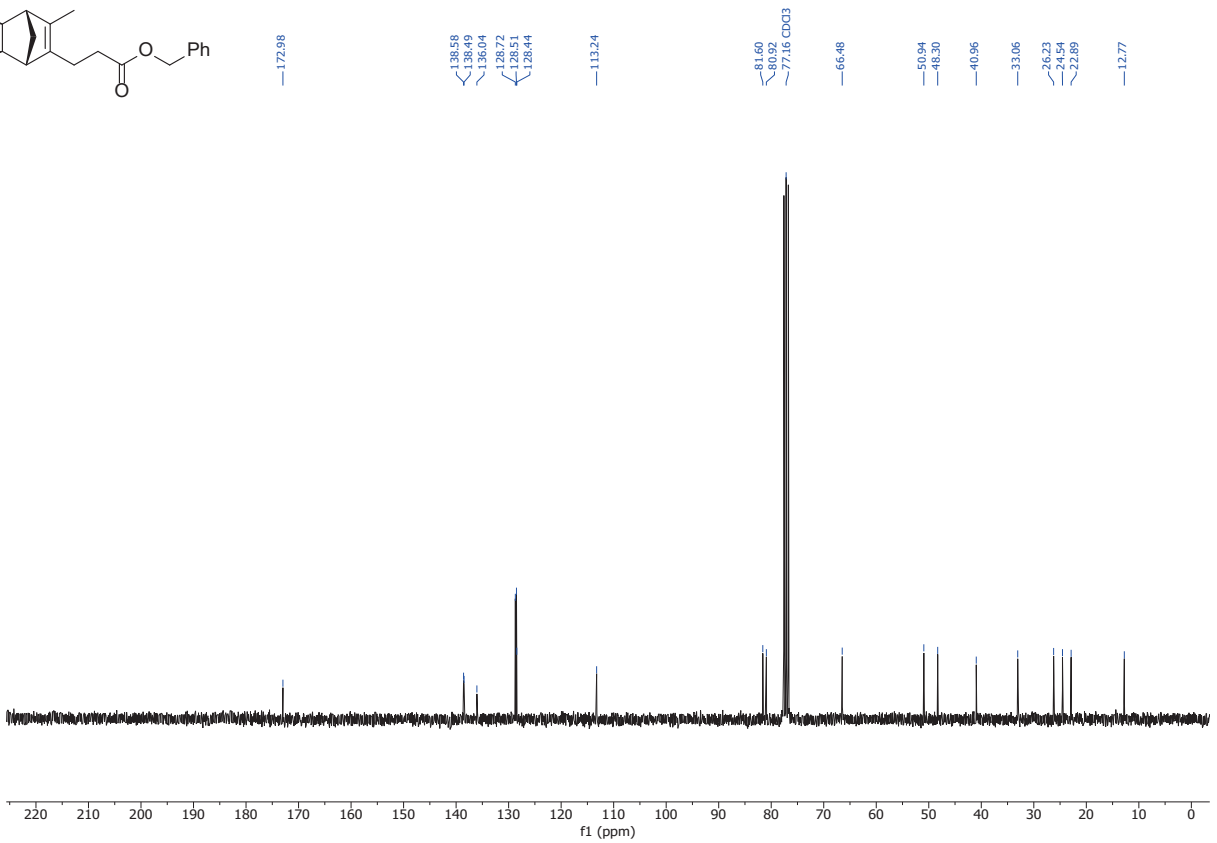




benzyl 3-((3aR,4R,7S,7aS)-2,2,6-trimethyl-3a,4,7,7a-tetrahydro-4,7-methanobenzo[d][1,3]dioxol-5-yl)propanoate (9)

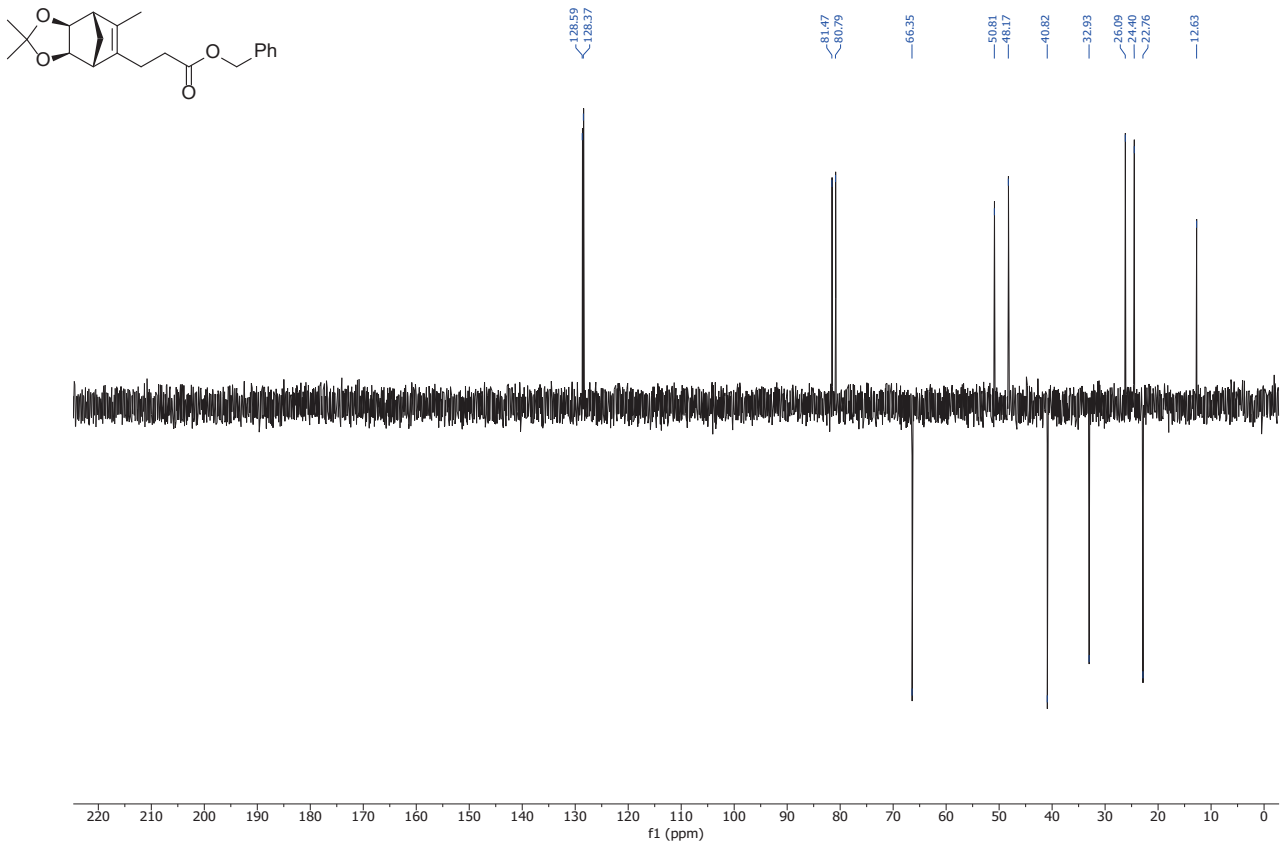
^{13}C NMR (75 MHz, $CDCl_3$)





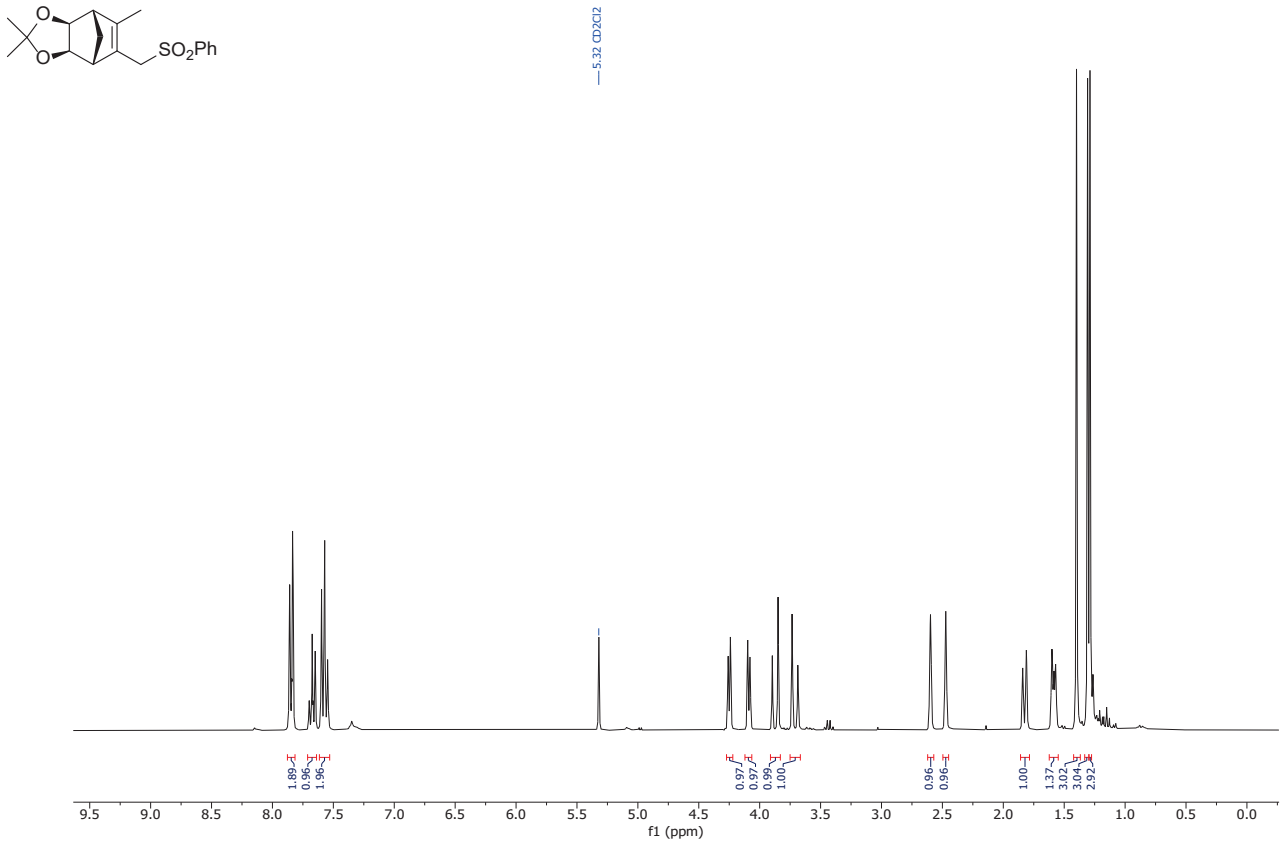
benzyl 3-((3aR,4R,7S,7aS)-2,2,6-trimethyl-3a,4,7,7a-tetrahydro-4,7-methanobenzo[d][1,3]dioxol-5-yl)propanoate (9)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



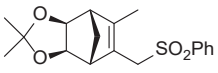
(3aS,4S,7R,7aR)-2,2,5-trimethyl-6-((phenylsulfonyl)methyl)-3a,4,7,7a-tetrahydro-4,7-methanobenzo[d][1,3]dioxole (10)

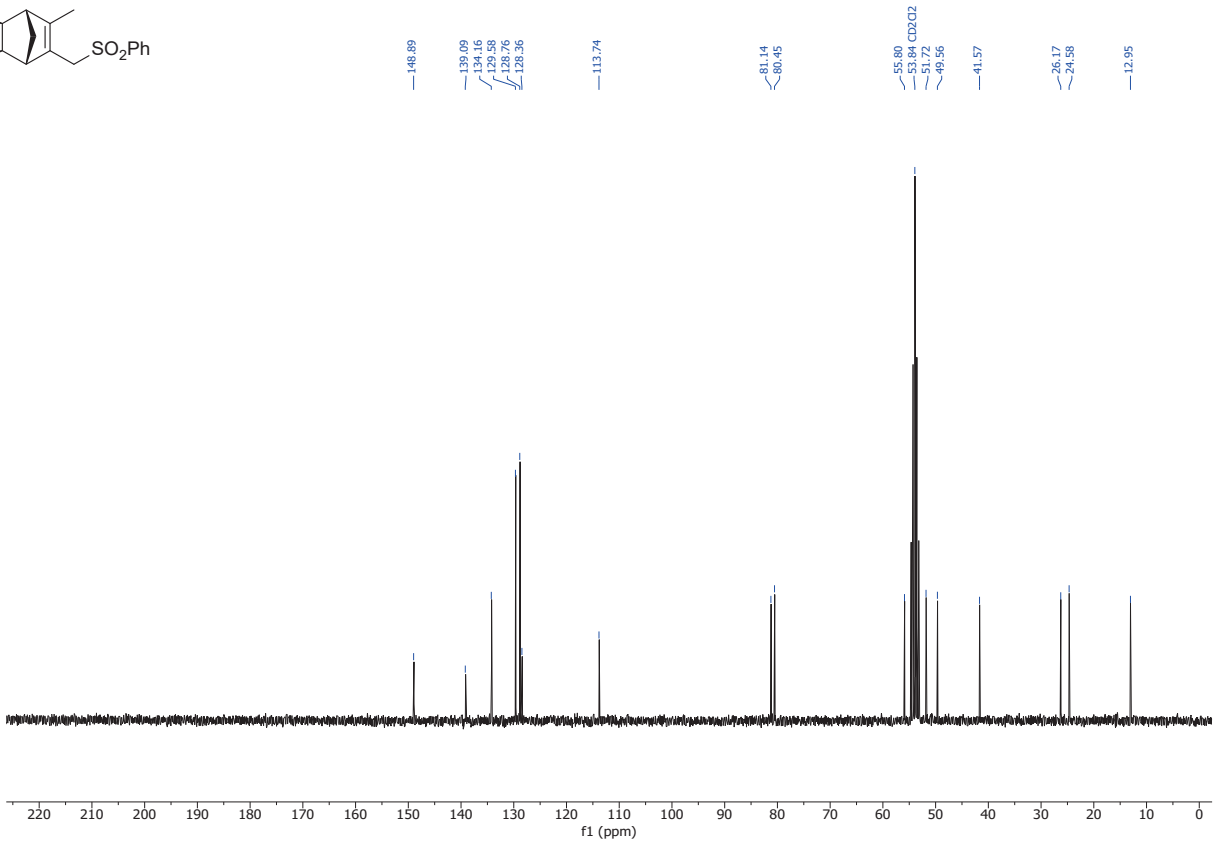
^{1}H NMR (300 MHz, CD_2Cl_2)



(3aS,4S,7R,7aR)-2,2,5-trimethyl-6-((phenylsulfonyl)methyl)-3a,4,7,7a-tetrahydro-4,7-methanobenzo[d][1,3]dioxole (10)

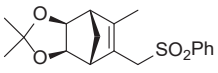
^{13}C NMR (75 MHz, CD_2Cl_2)

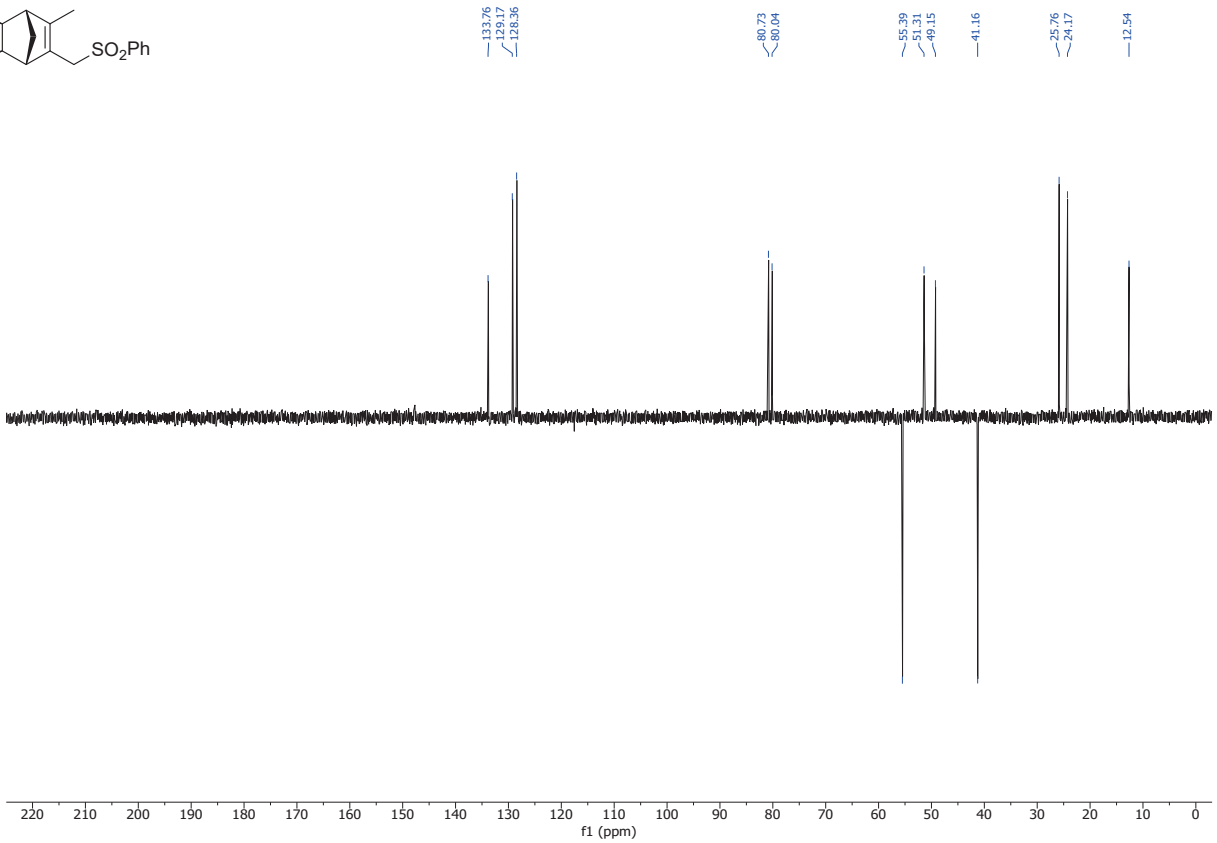




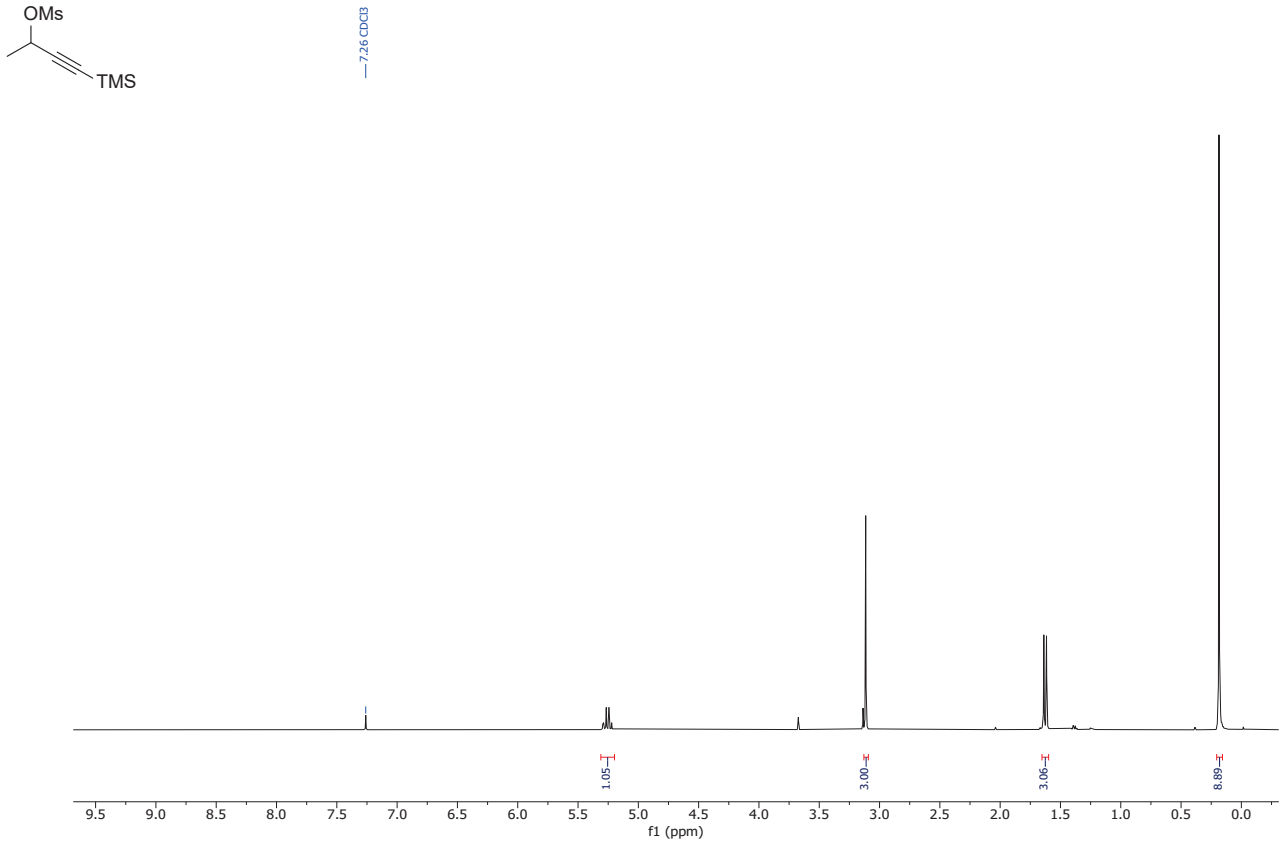
(3aS,4S,7R,7aR)-2,2,5-trimethyl-6-((phenylsulfonyl)methyl)-3a,4,7,7a-tetrahydro-4,7-methanobenzo[d][1,3]dioxole (10)

^{13}C NMR Dept-135 (75 MHz, CD_2Cl_2)

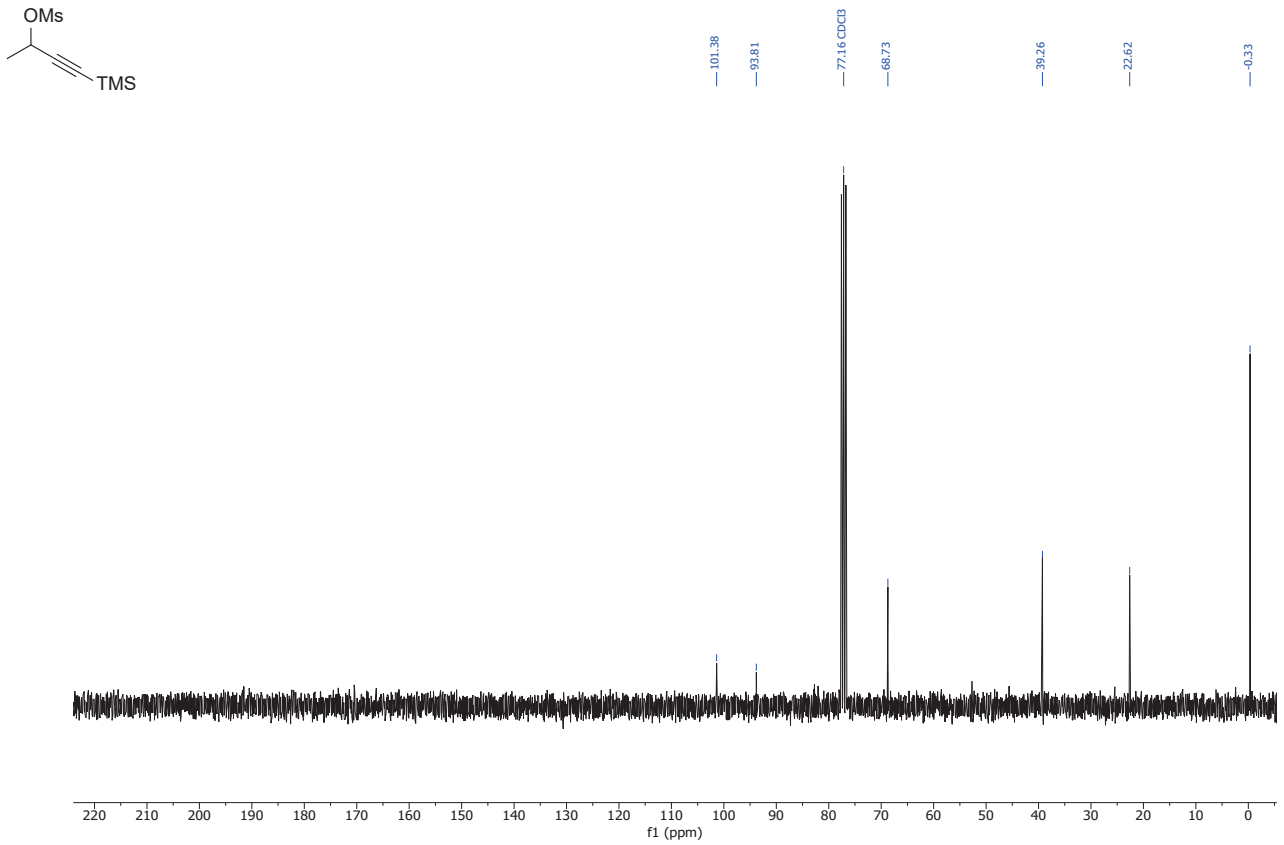




(1-methyl-3-trimethylsilyl-prop-2-ynyl) methanesulfonate (12) ^{1}H NMR (300 MHz, $CDCl_3$)

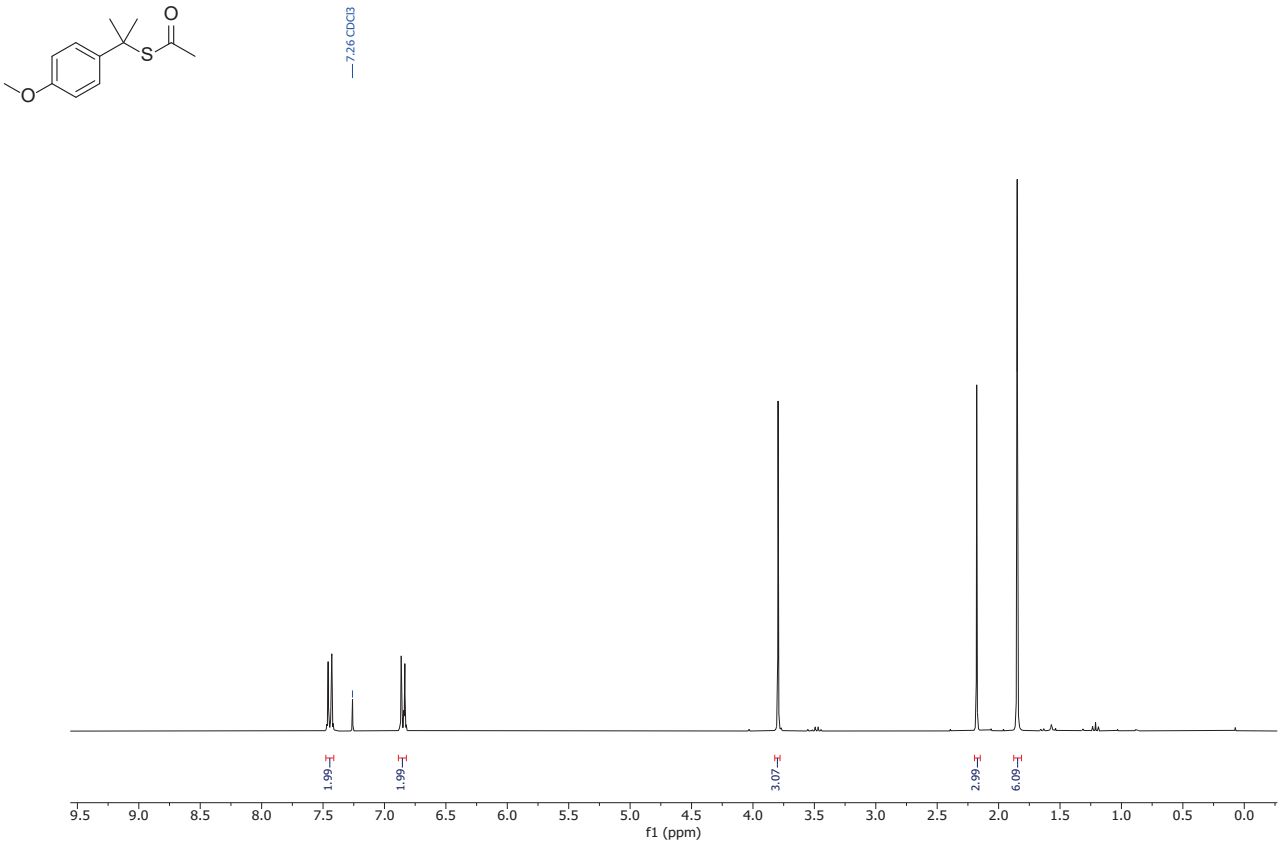


(1-methyl-3-trimethylsilyl-prop-2-ynyl) methanesulfonate (12) ^{13}C NMR (75 MHz, $CDCl_3$)



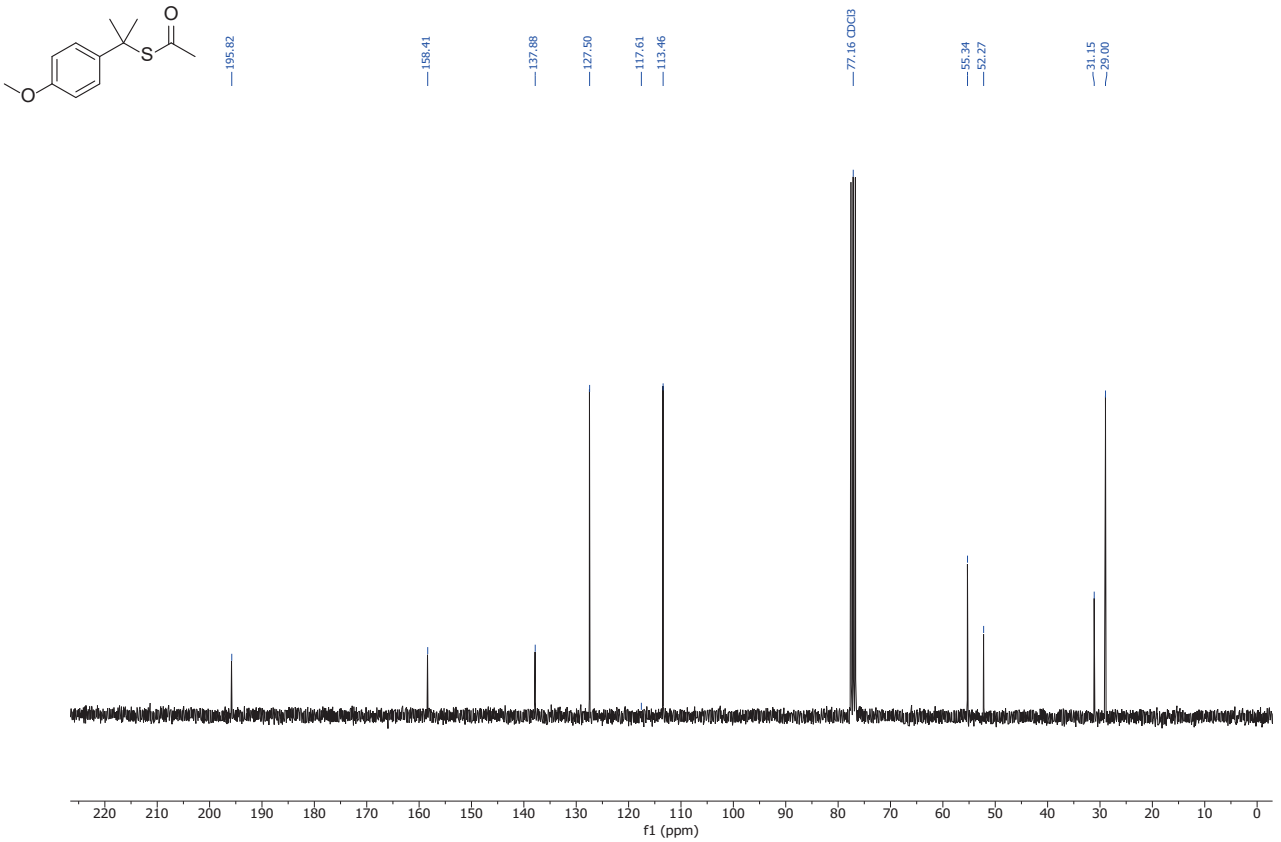
S-(2-(4-methoxyphenyl)propan-2-yl) ethanethioate (14)

^{1}H NMR (300 MHz, $CDCl_3$)



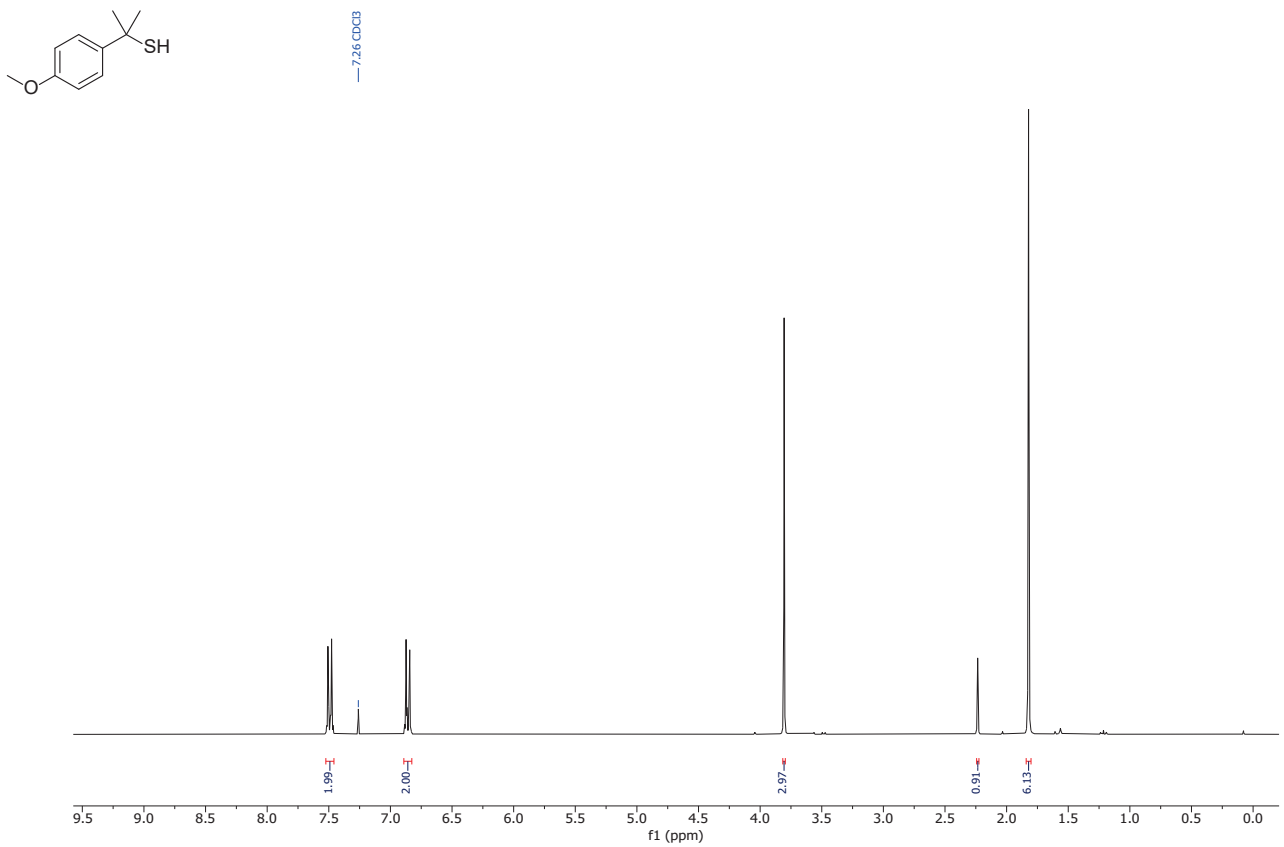
S-(2-(4-methoxyphenyl)propan-2-yl) ethanethioate (14)

^{13}C NMR (75 MHz, $CDCl_3$)



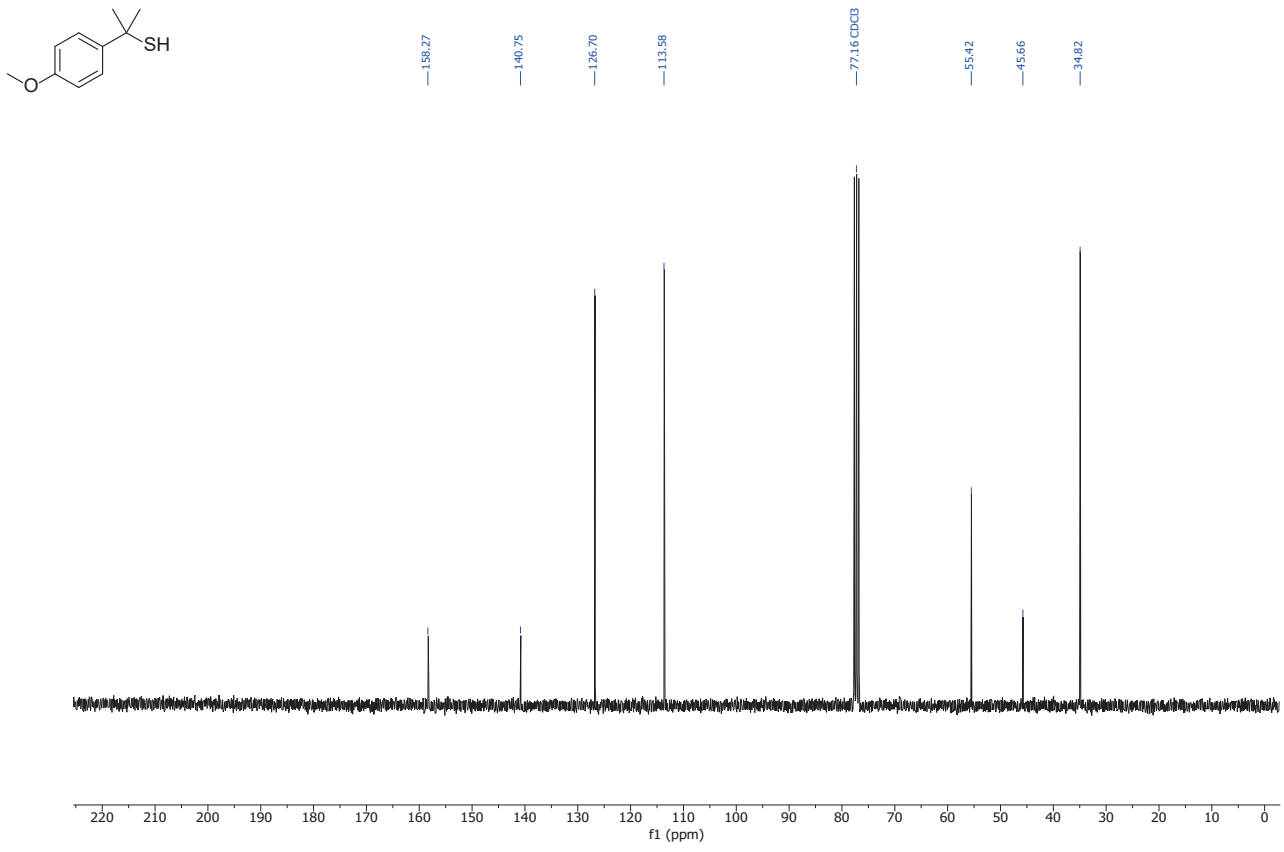
2-(4-methoxyphenyl)propane-2-thiol (15)

^{1}H NMR (300 MHz, $CDCl_3$)

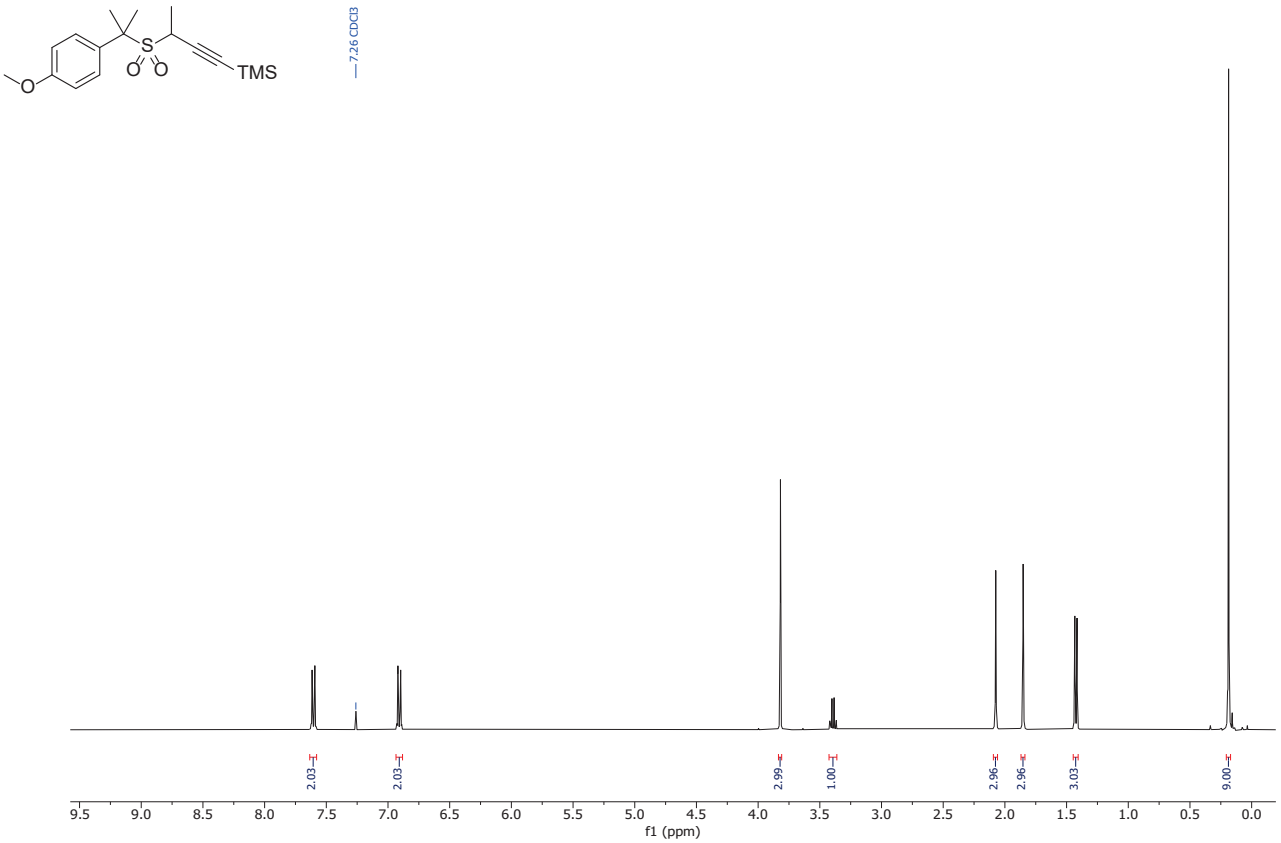


2-(4-methoxyphenyl)propane-2-thiol (15)

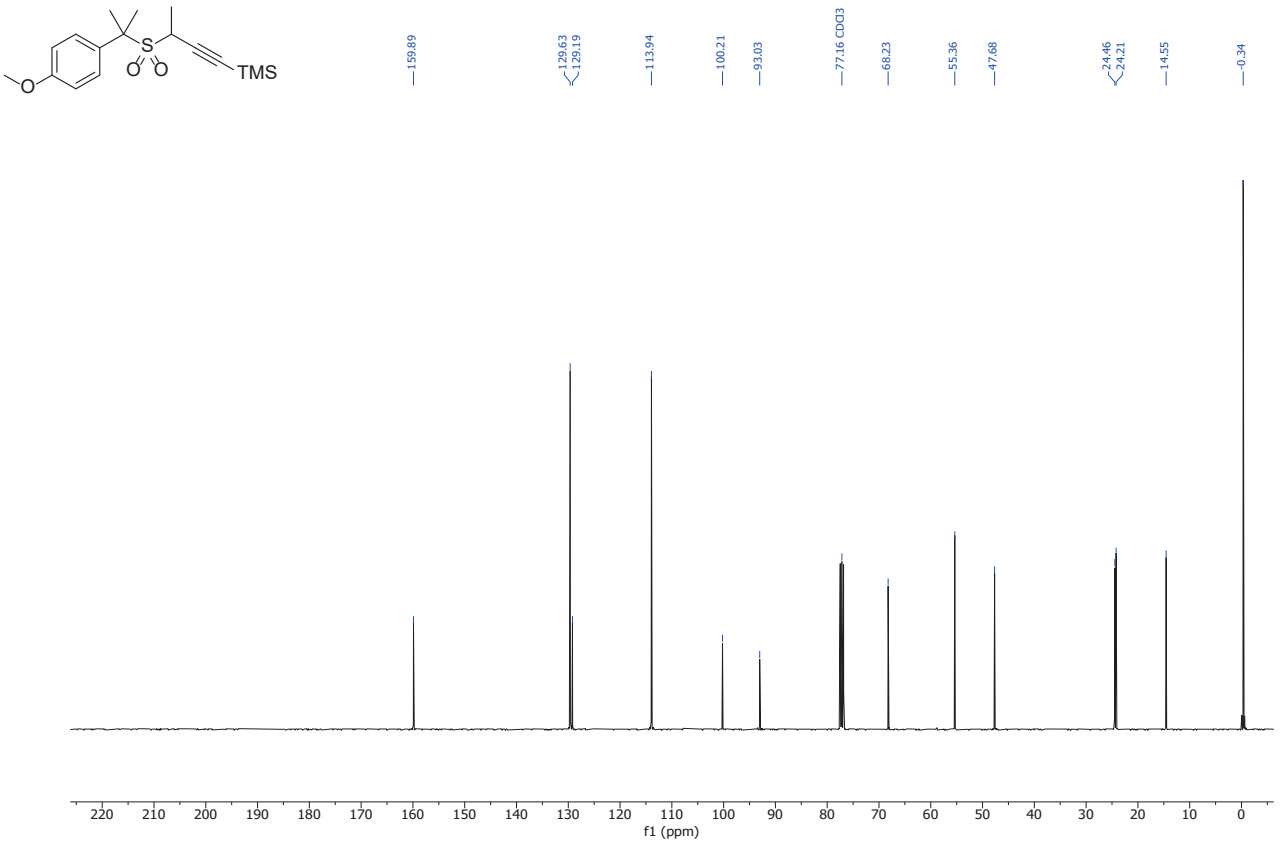
^{13}C NMR (75 MHz, $CDCl_3$)



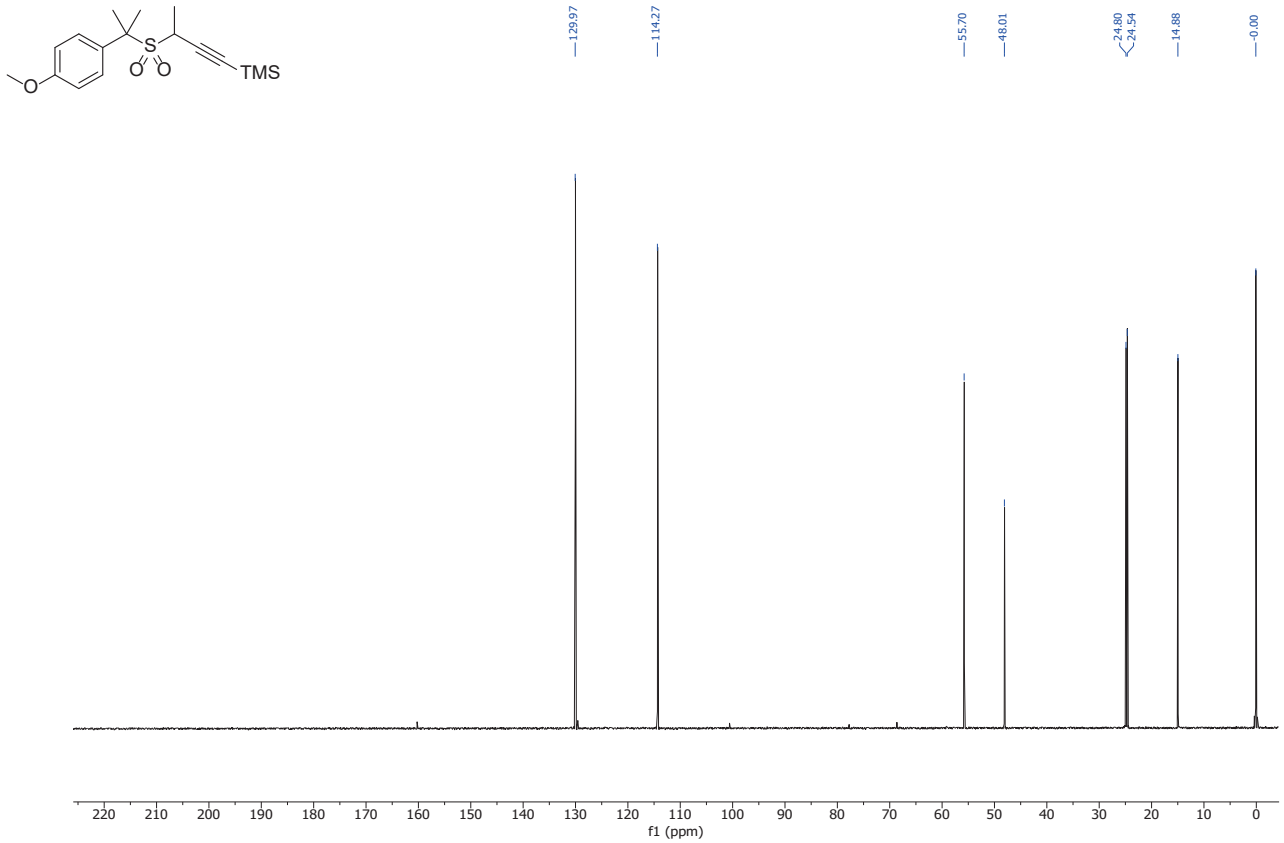
(3-((2-(4-methoxyphenyl)propan-2-yl)sulfonyl)but-1-yn-1-yl)trimethylsilane (16) ^{1}H NMR (400 MHz, $CDCl_3$)



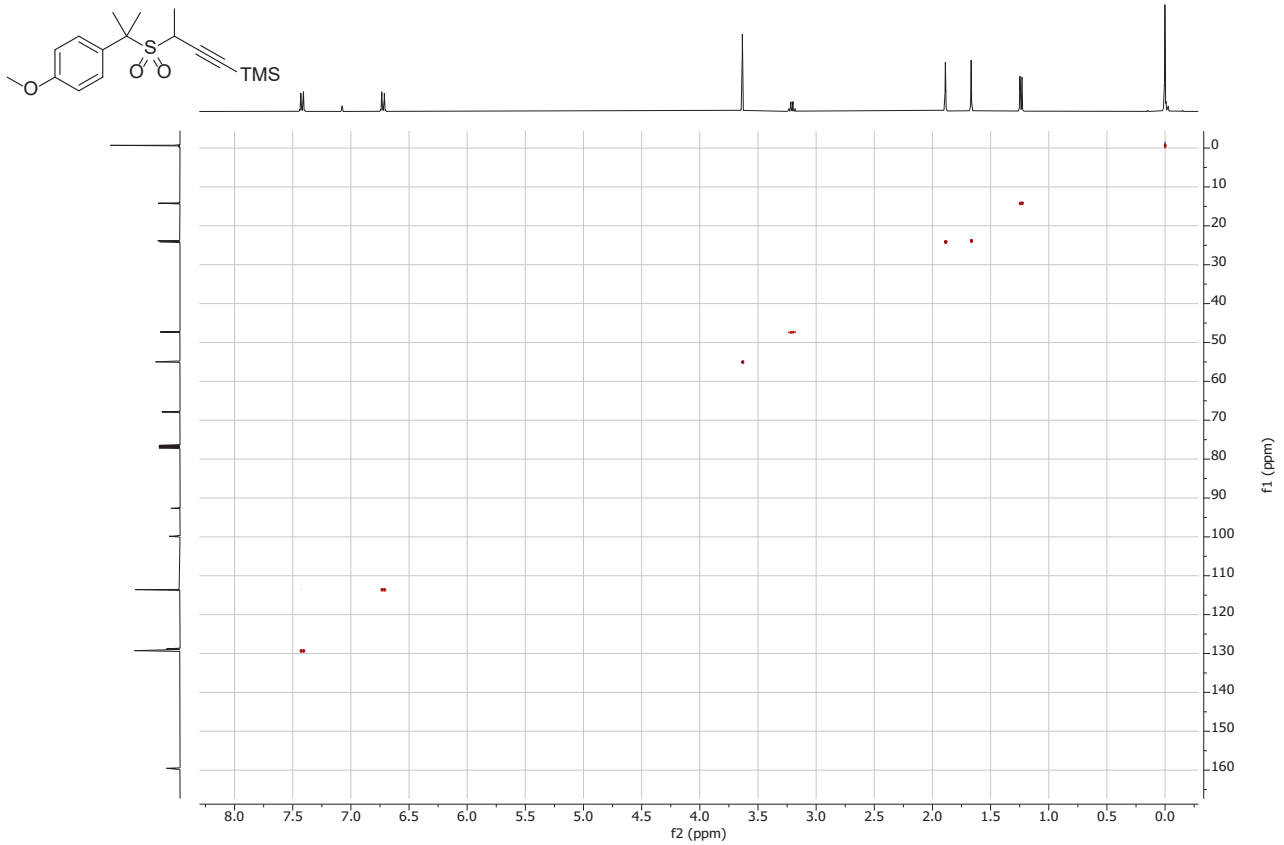
(3-((2-(4-methoxyphenyl)propan-2-yl)sulfonyl)but-1-yn-1-yl)trimethylsilane (16) ^{13}C NMR (101 MHz, $CDCl_3$)



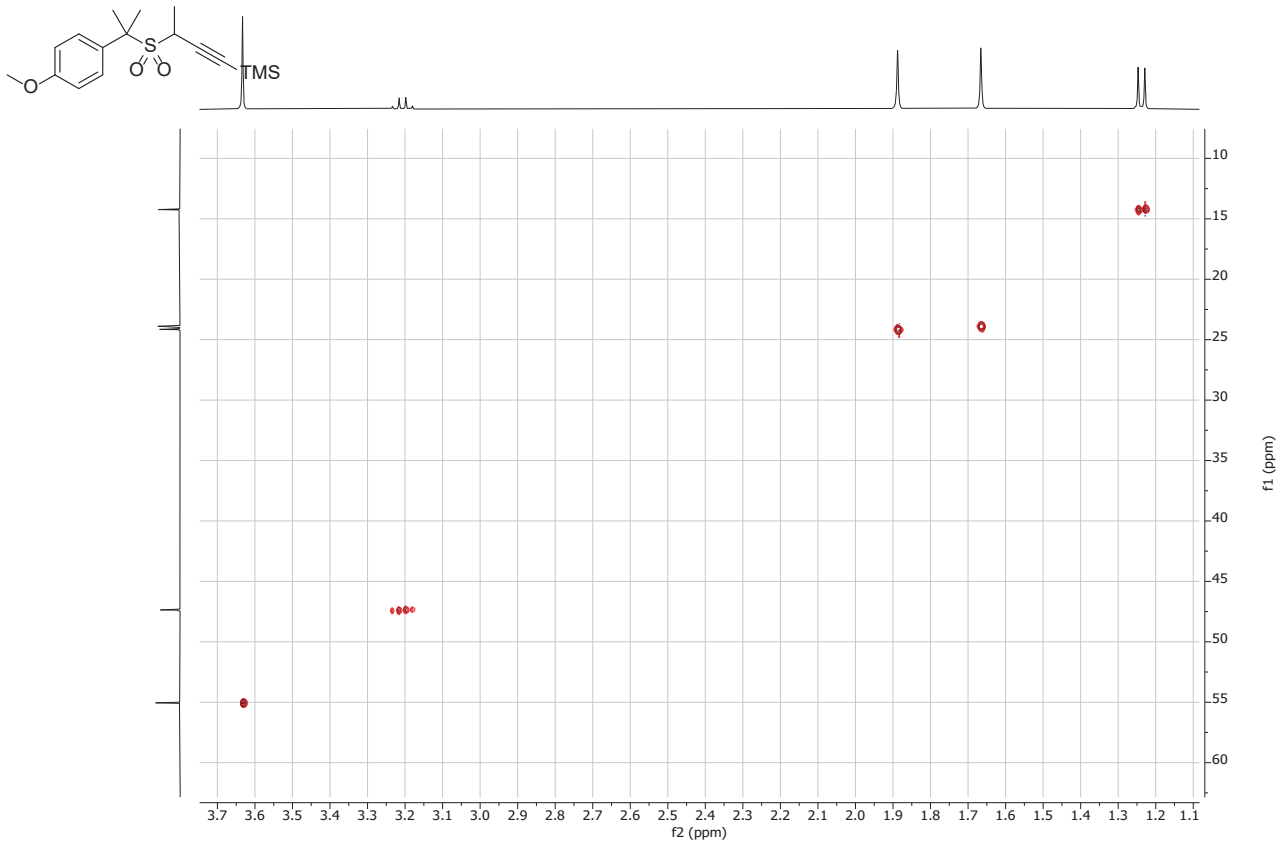
(3-((2-(4-methoxyphenyl)propan-2-yl)sulfonyl)but-1-yn-1-yl)trimethylsilane (16) ^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



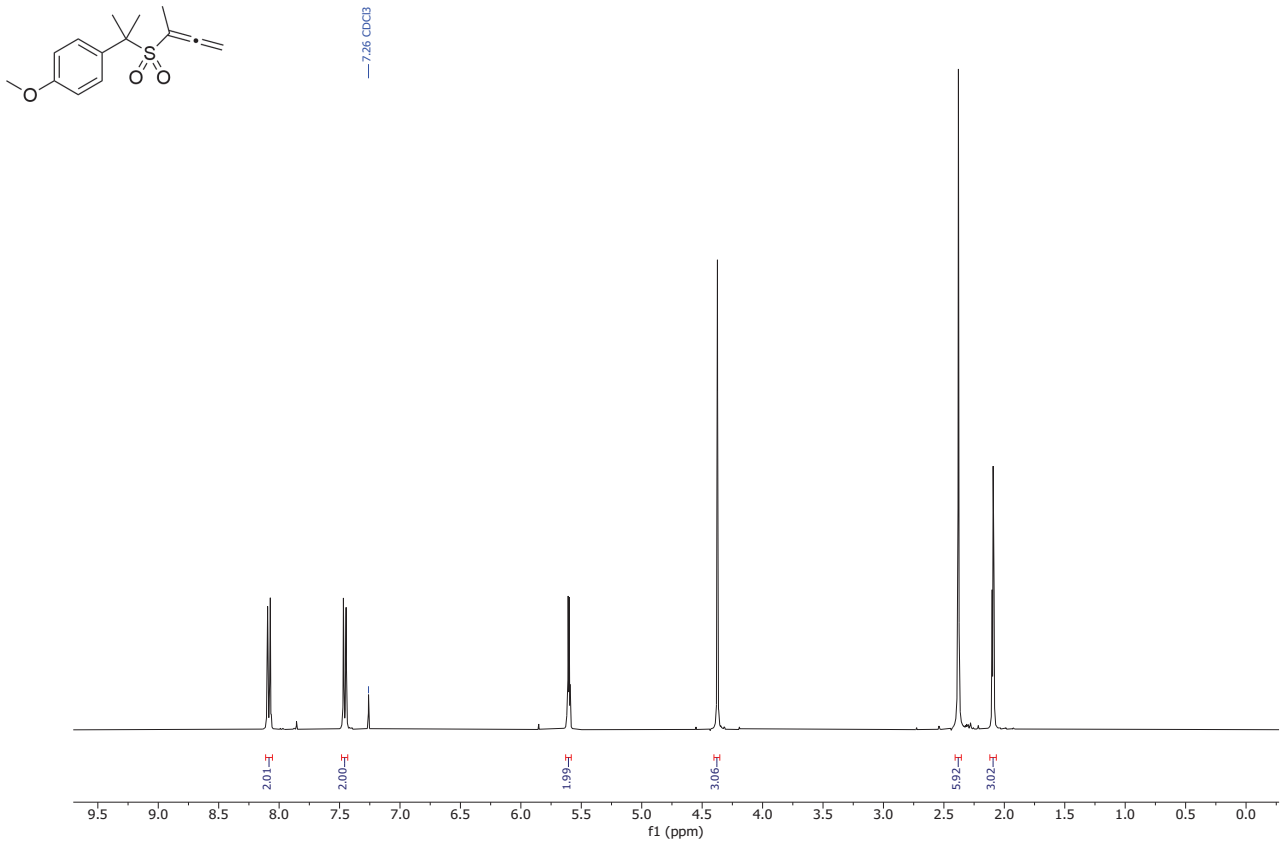
(3-((2-(4-methoxyphenyl)propan-2-yl)sulfonyl)but-1-yn-1-yl)trimethylsilane (16) ^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)



(3-((2-(4-methoxyphenyl)propan-2-yl)sulfonyl)but-1-yn-1-yl)trimethylsilane (16) ^{1}H, ^{13}C - HSQC (400 MHz, $CDCl_3$)

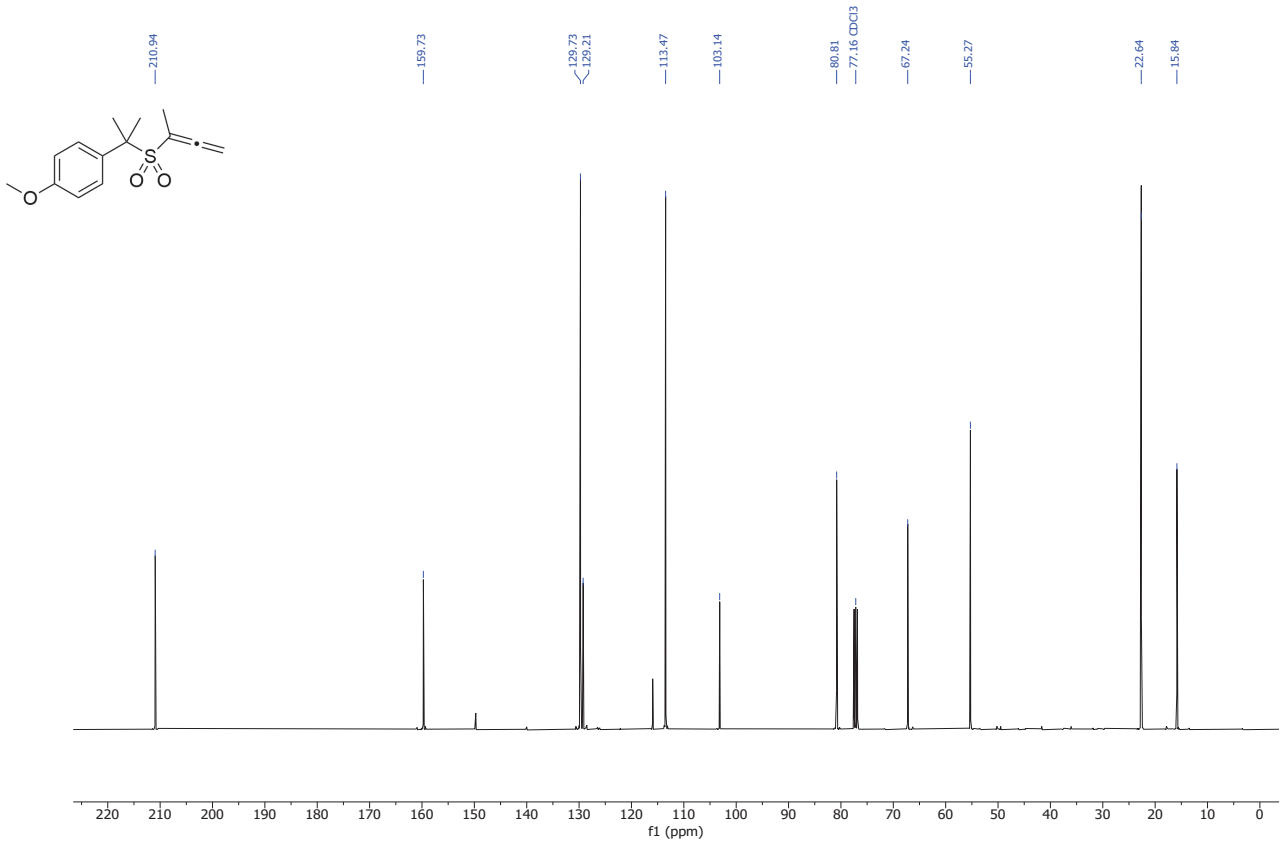


1-(2-(buta-2,3-dien-2-ylsulfonyl)propan-2-yl)-4-methoxybenzene (17) ^{1}H NMR (400 MHz, $CDCl_3$)



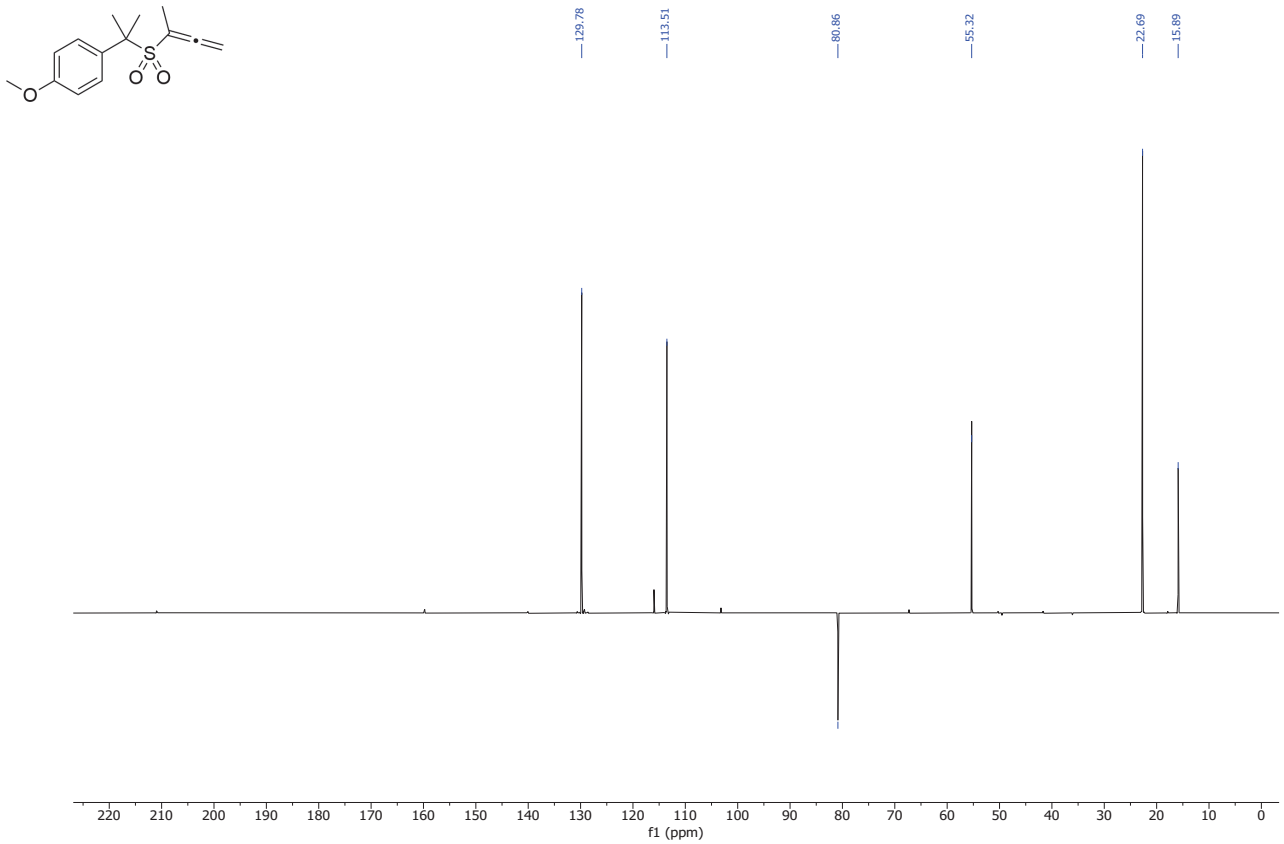
1-(2-(buta-2,3-dien-2-ylsulfonyl)propan-2-yl)-4-methoxybenzene (17)

^{13}C NMR (101 MHz, $CDCl_3$)



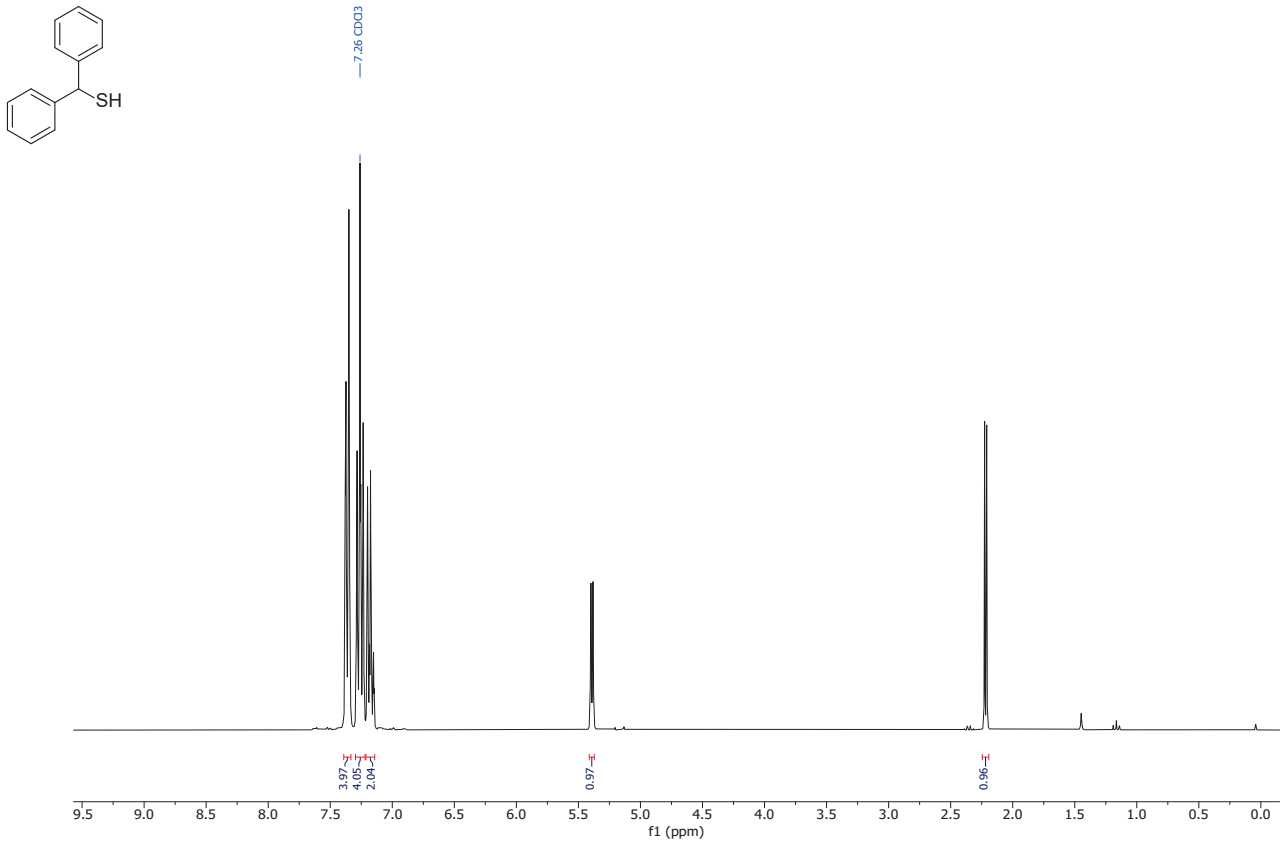
1-(2-(buta-2,3-dien-2-ylsulfonyl)propan-2-yl)-4-methoxybenzene (17)

^{13}C NMR Dept-135 (101 MHz, $CDCl_3$)



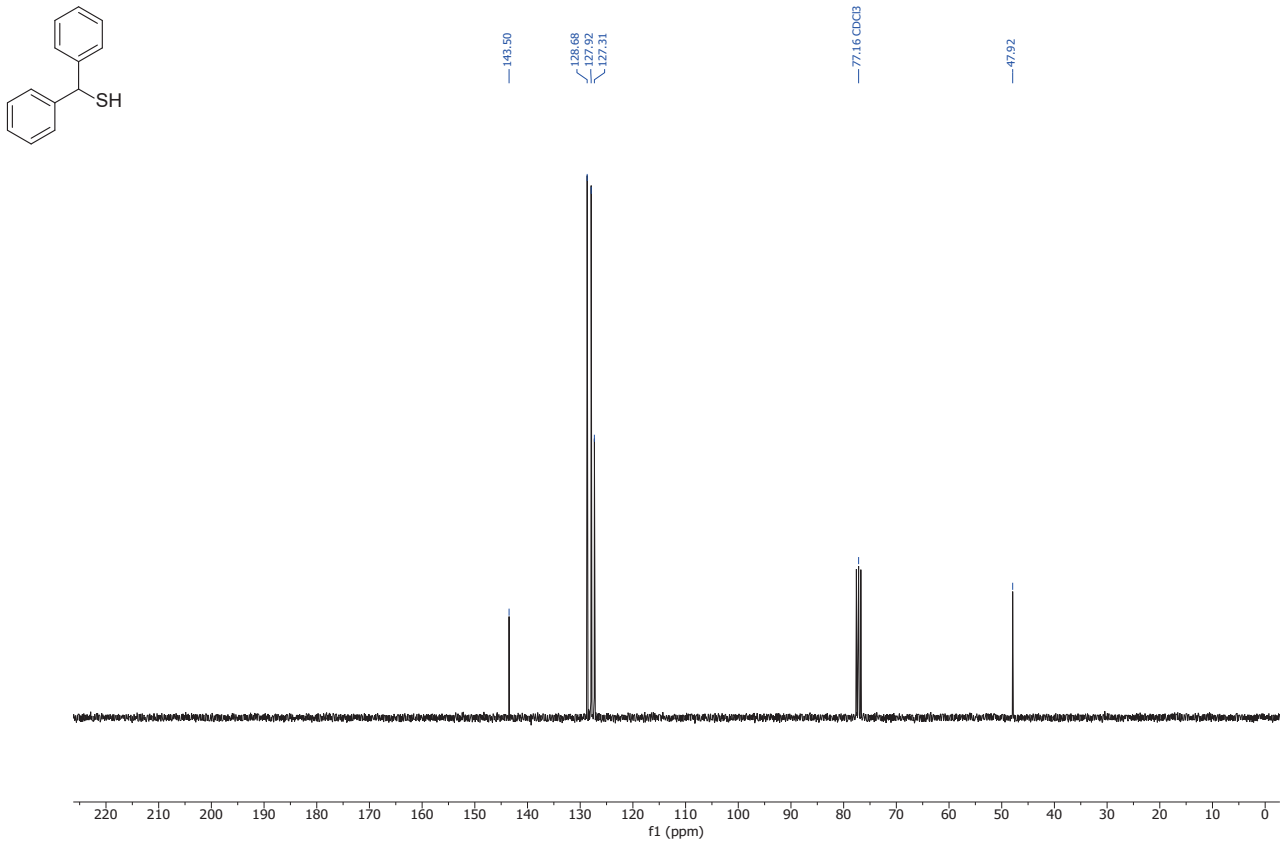
Diphenylmethanethiol (20)

^{1}H NMR (300 MHz, $CDCl_3$)



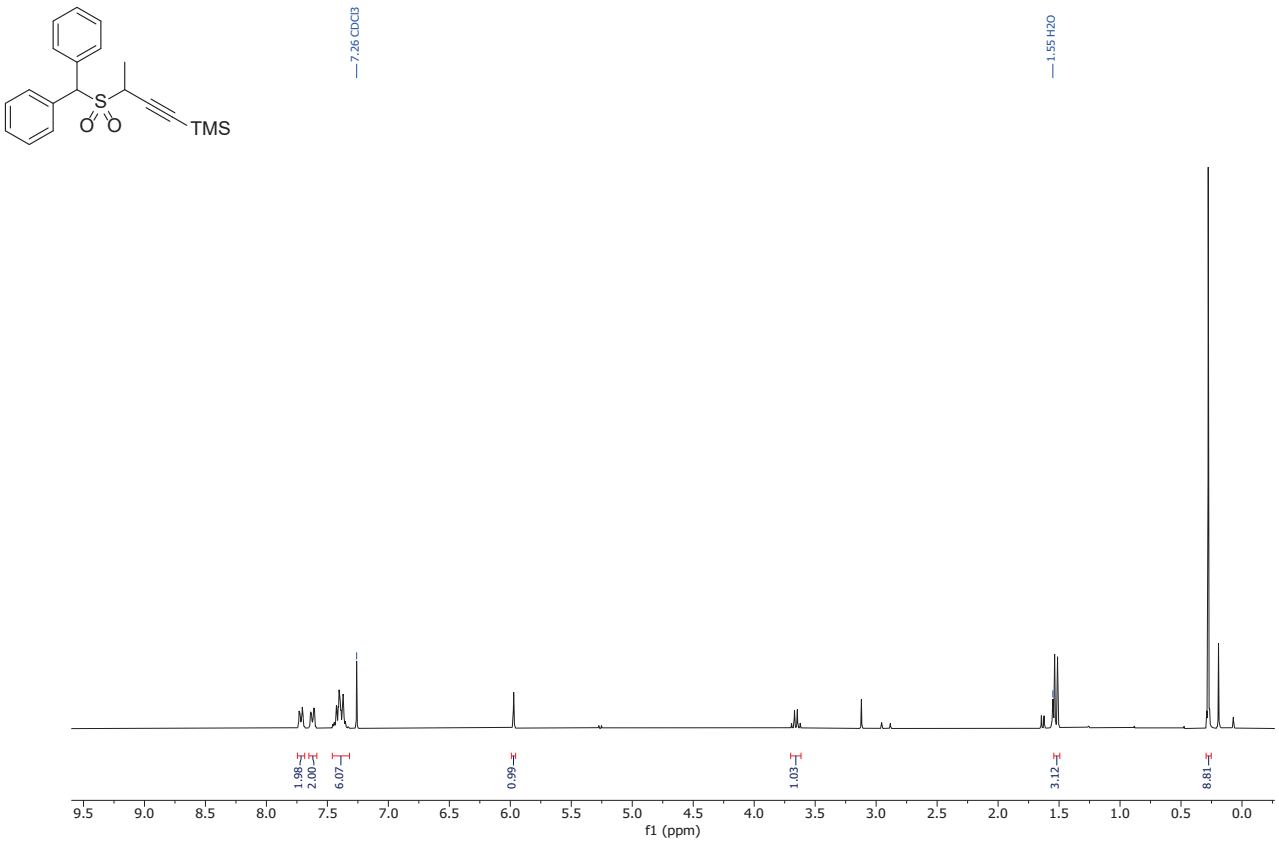
Diphenylmethanethiol (20)

^{13}C NMR (75 MHz, $CDCl_3$)



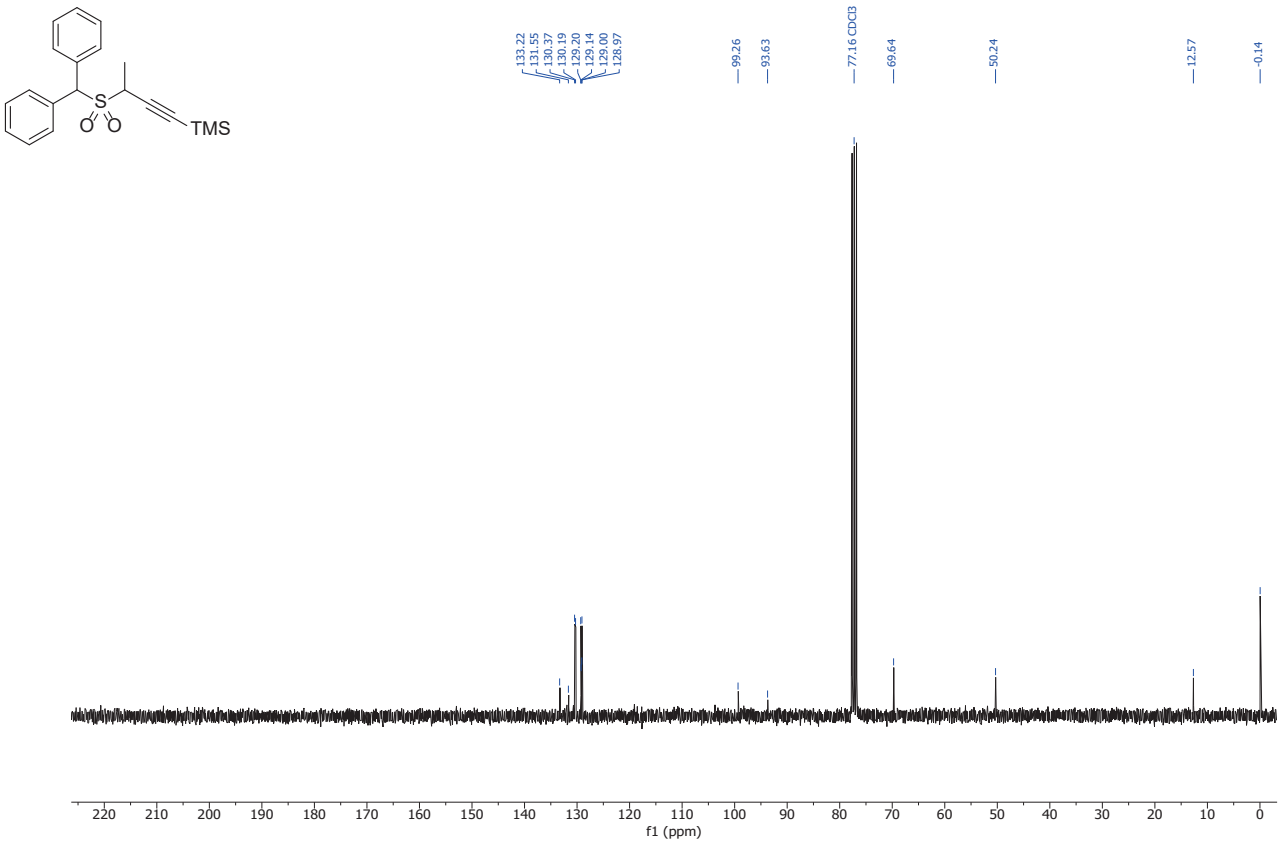
(3-(benzhydrylsulfonyl)but-1-yn-1-yl)trimethylsilane (21)

^{1}H NMR (300 MHz, $CDCl_3$)

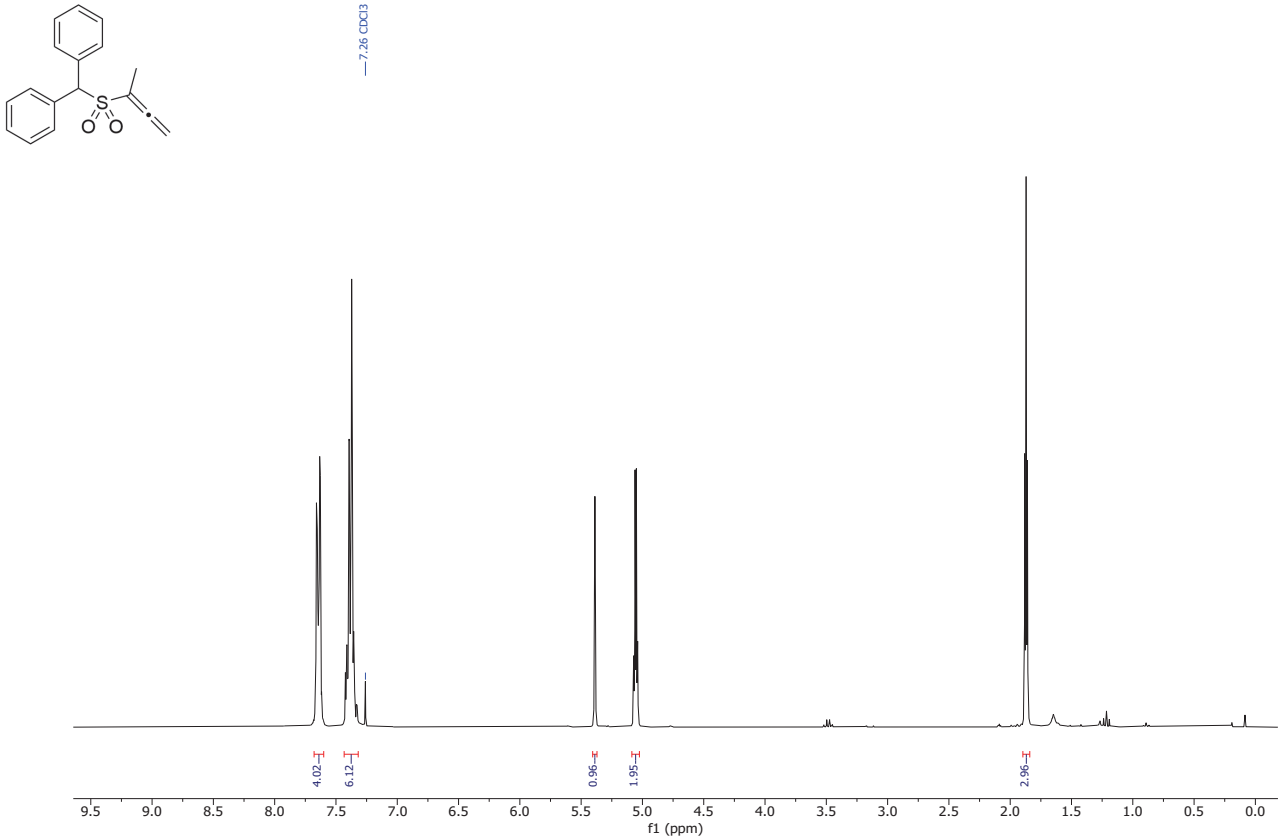


(3-(benzhydrylsulfonyl)but-1-yn-1-yl)trimethylsilane (21)

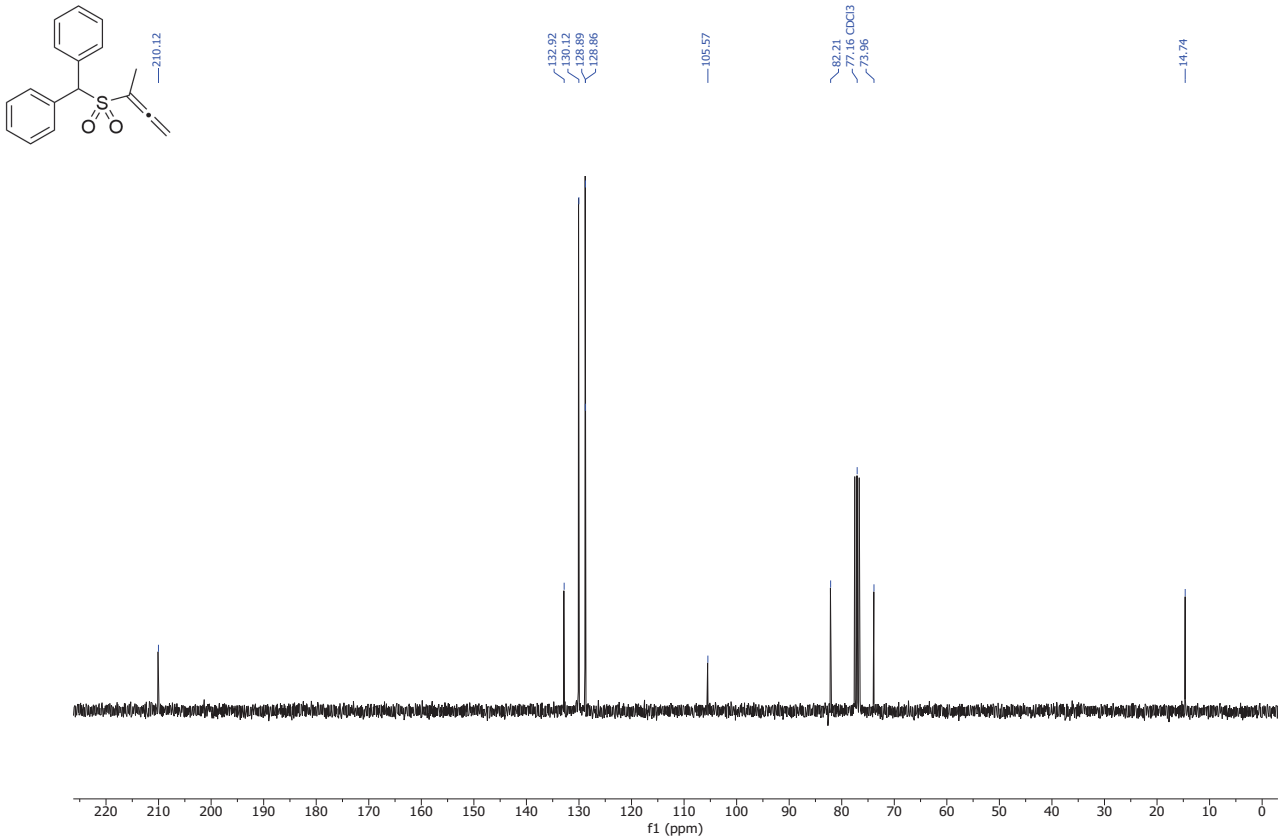
^{13}C NMR (75 MHz, $CDCl_3$)



((buta-2,3-dien-2-ylsulfonyl)methylene)dibenzene (22) ^{1}H NMR (300 MHz, $CDCl_3$)

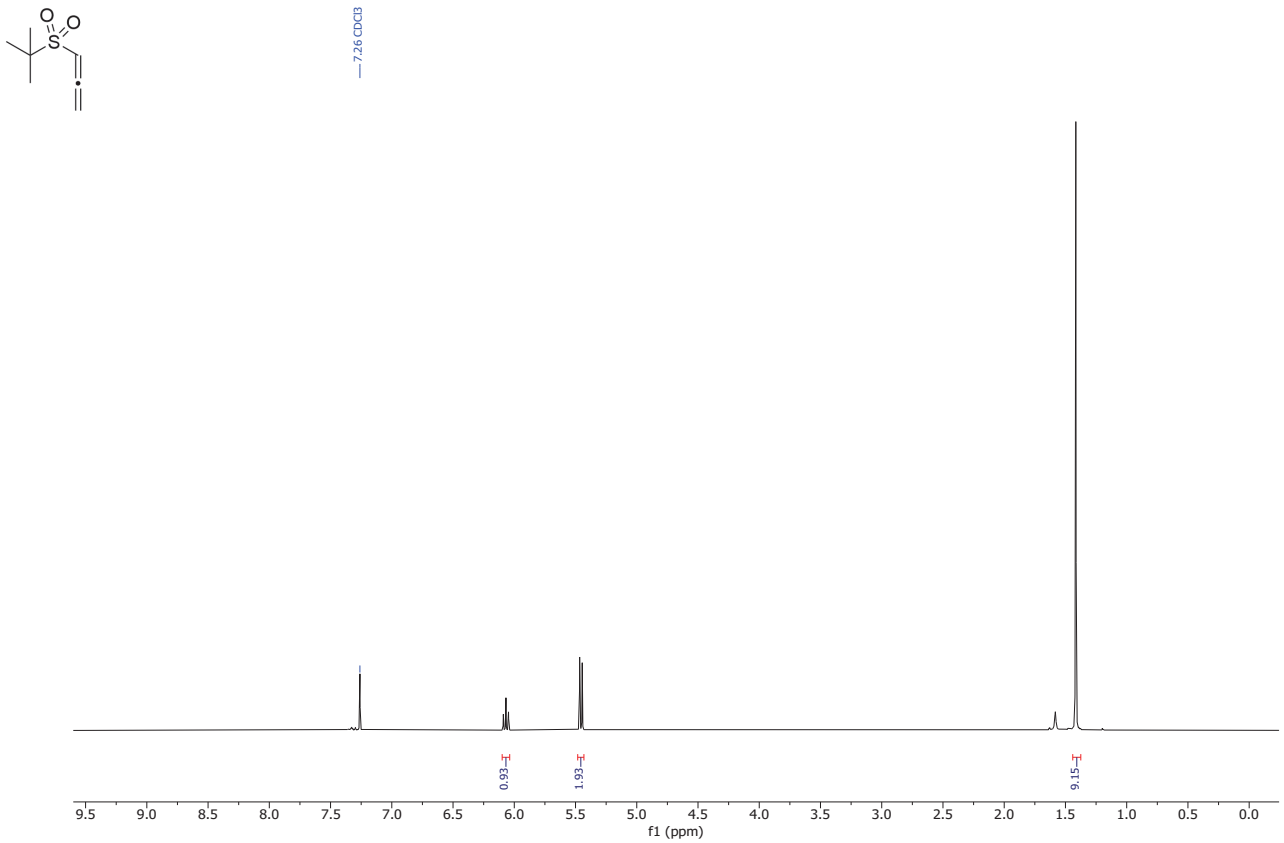


((buta-2,3-dien-2-ylsulfonyl)methylene)dibenzene (22) ^{13}C NMR (75 MHz, $CDCl_3$)



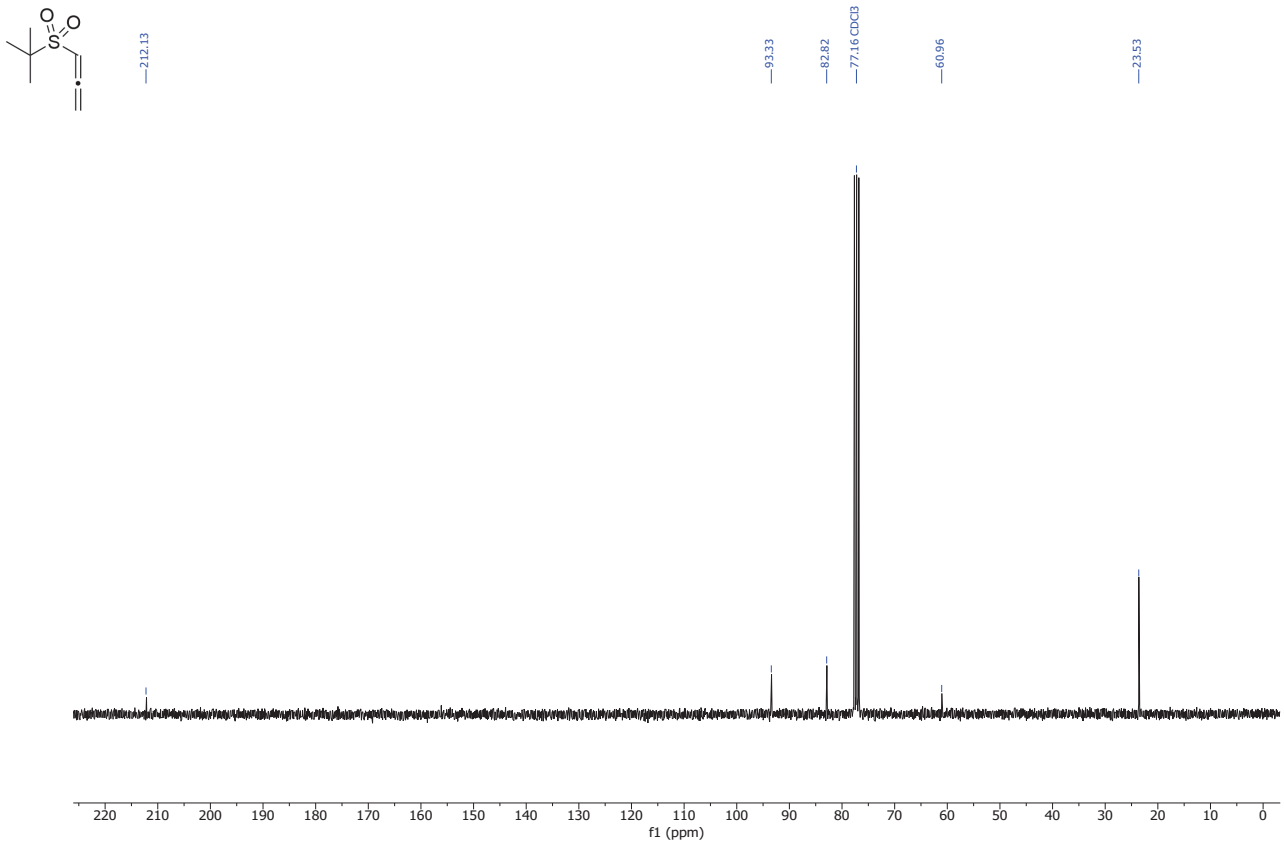
1-(*tert*-butylsulfonyl)propa-1,2-diene (25)

^{1}H NMR (300 MHz, $CDCl_3$)



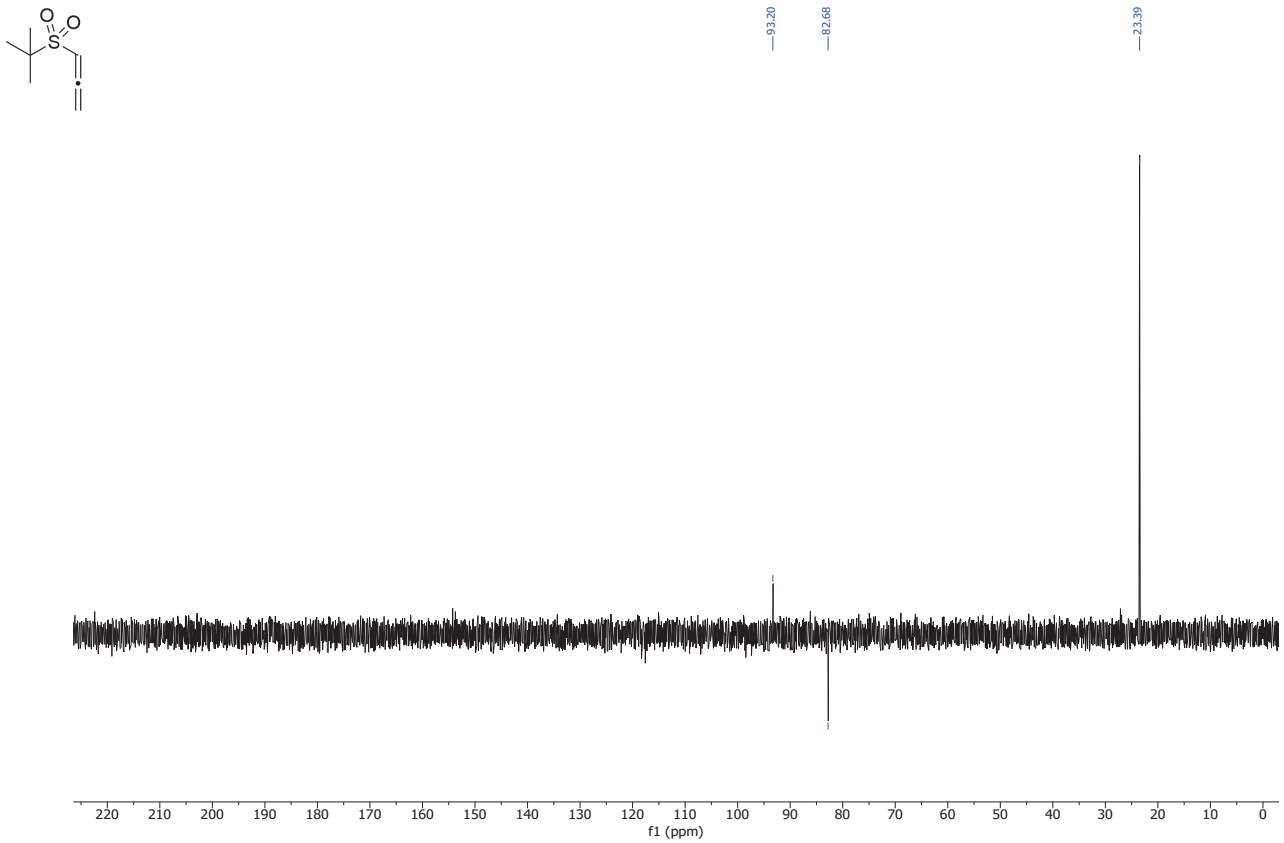
1-(*tert*-butylsulfonyl)propa-1,2-diene (25)

^{13}C NMR (75 MHz, $CDCl_3$)



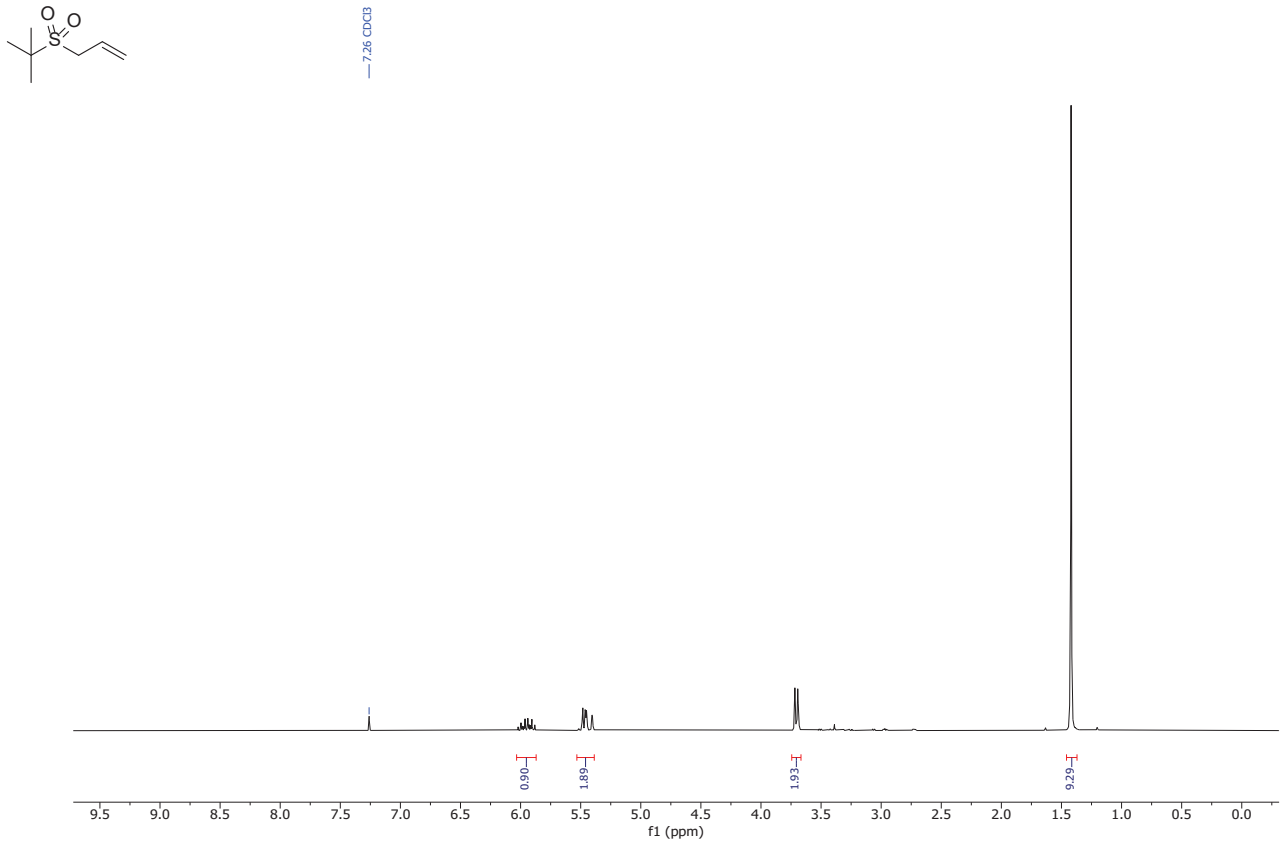
1-(*tert*-butylsulfonyl)propa-1,2-diene (25)

^{13}C NMR Dept-135 (75 MHz, $CDCl_3$)



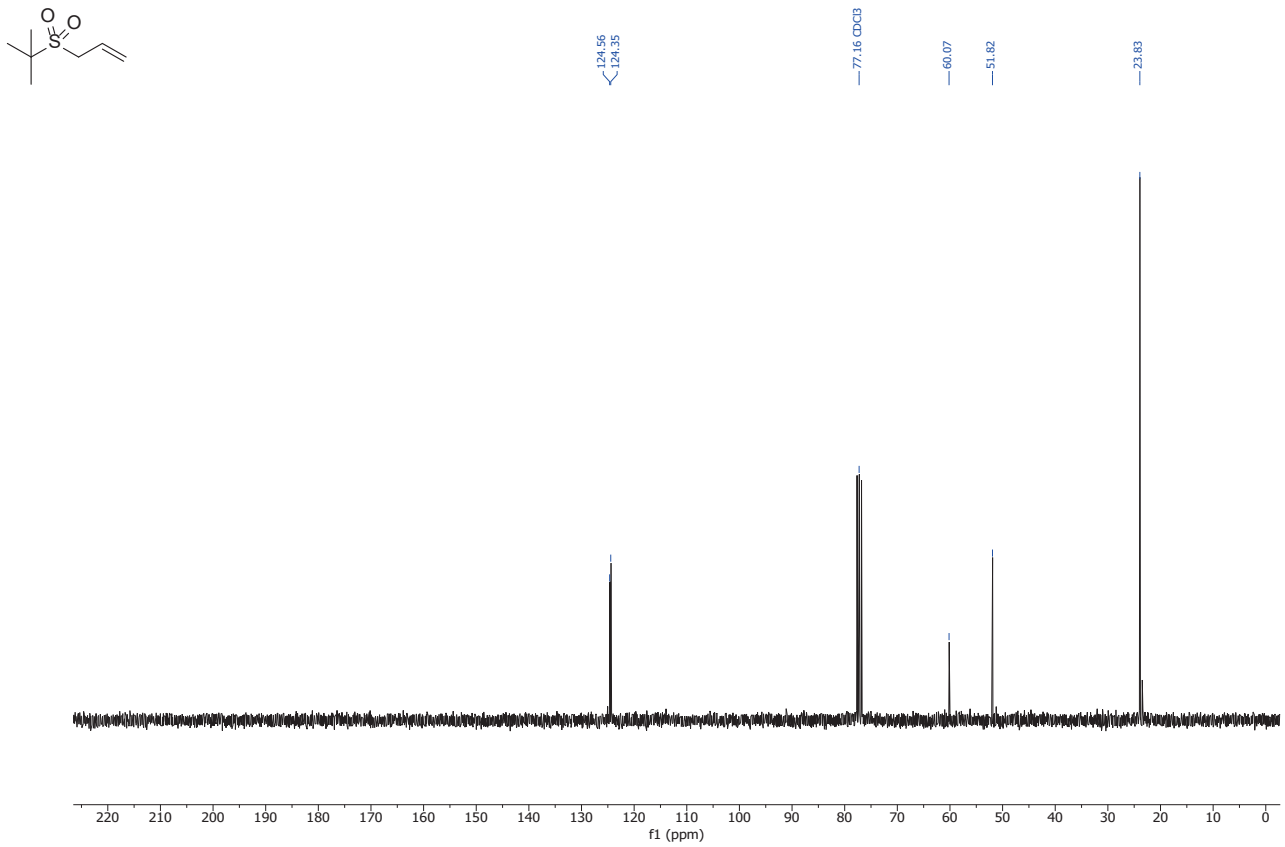
3-(tert-butylsulfonyl)prop-1-ene (30)

^{1}H NMR (300 MHz, $CDCl_3$)



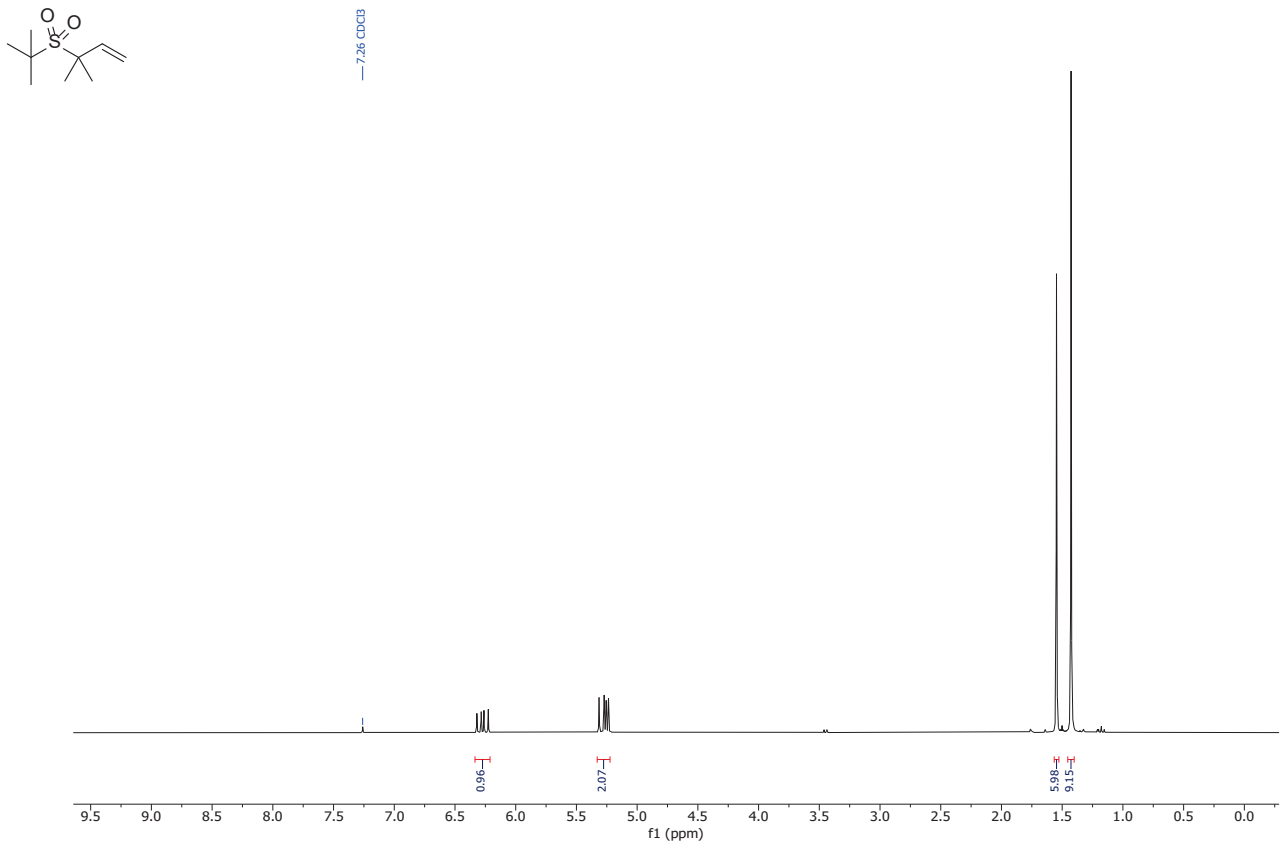
3-(tert-butylsulfonyl)prop-1-ene (30)

^{13}C NMR (75 MHz, $CDCl_3$)



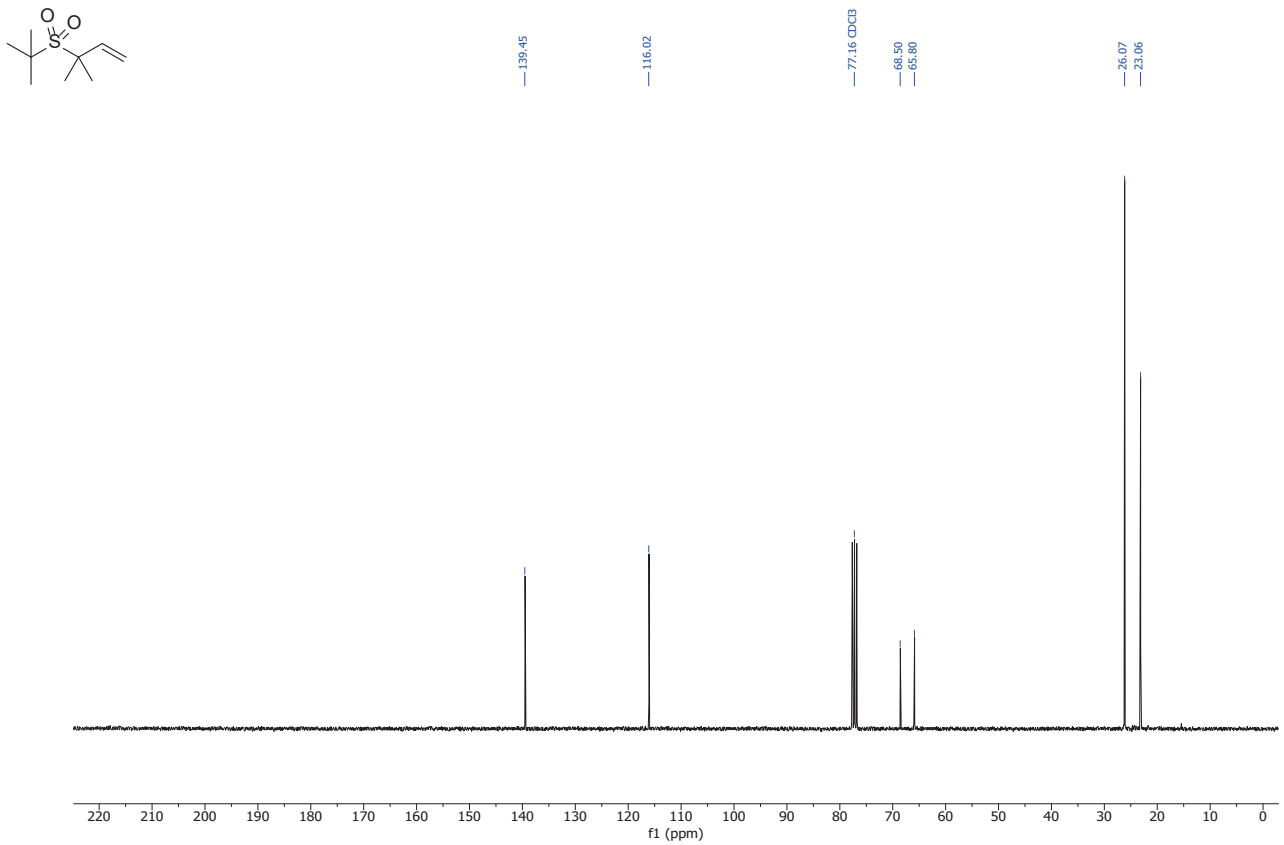
3-(tert-butylsulfonyl)-3-methylbut-1-ene (31)

^{1}H NMR (300 MHz, $CDCl_3$)



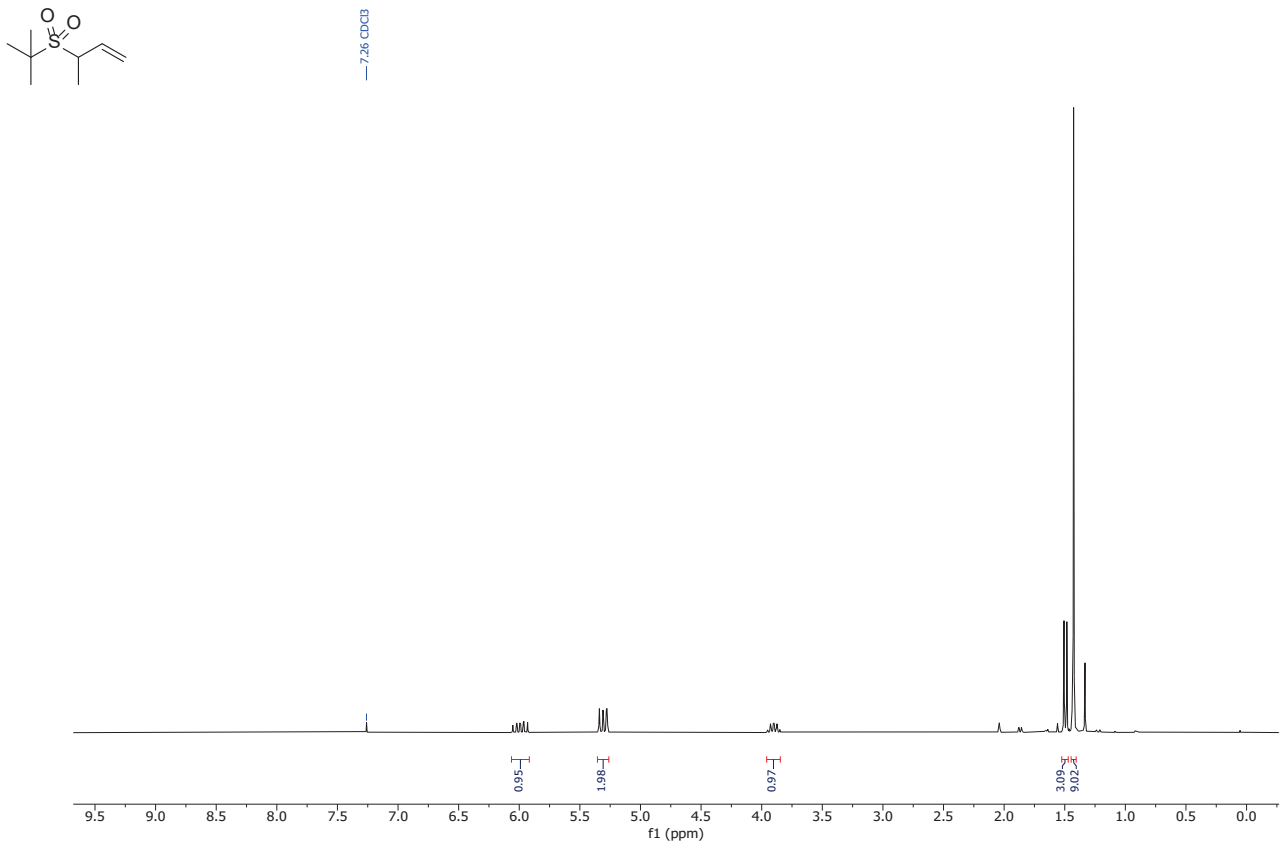
3-(tert-butylsulfonyl)-3-methylbut-1-ene (31)

^{13}C NMR (75 MHz, $CDCl_3$)



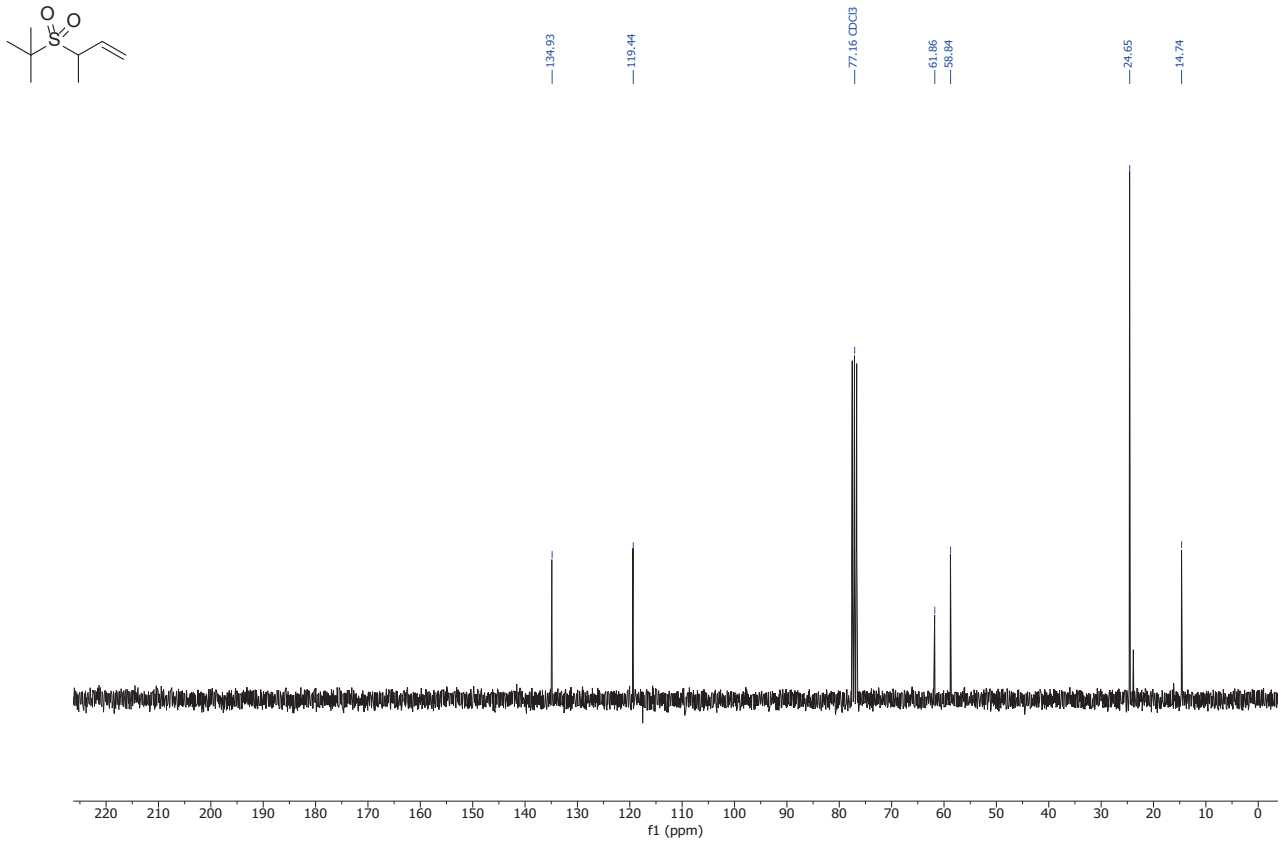
3-(tert-butylsulfonyl)but-1-ene (32)

^{1}H NMR (300 MHz, $CDCl_3$)



3-(tert-butylsulfonyl)but-1-ene (32)

^{13}C NMR (75 MHz, $CDCl_3$)



Declaration of consent

on the basis of Article 18 of the PromR Phil.-nat. 19

Name/First Name: Arnold, Remo

Registration Number: 15-557-267

Study program: Chemistry and Molecular Sciences

Bachelor ☐ Master ☐ Dissertation ☑

Title of the thesis: Sulfone mediated olefination & allylation reactions

Supervisor: Prof. Dr. Philippe Renaud

I declare herewith that this thesis is my own work and that I have not used any sources other than those stated. I have indicated the adoption of quotations as well as thoughts taken from other authors as such in the thesis. I am aware that the Senate pursuant to Article 36 paragraph 1 litera r of the University Act of September 5th, 1996 and Article 69 of the University Statute of June 7th, 2011 is authorized to revoke the doctoral degree awarded on the basis of this thesis.
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