Application of alpha-boryl radicals in ATRA reactions

Inaugural dissertation
of the Faculty of Science,
University of Bern

presented by

Gaetano Geraci

from Italy

Supervisor of the doctoral thesis:
Prof. Dr. Philippe Renaud

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Bern, 05.07.2024

The Dean
Prof. Dr. Marco Herwegh

Ever tried. Ever failed. No matter. Try Again. Fail again. Fail better."
- Samuel Beckett -
Cchiu longa è a pinsata, cchiu rossa è a minchiata."
- Anonymous -

Acknowledgements

First of all, I would like to thank **Prof. Philippe Renaud** for giving me the opportunity to realize a PhD in his group under his supervision. I started this adventure during the pandemic but I could feel your support and help, especially since I was coming from a different university. I enjoyed and learned a lot from your passion for science and I always appreciated our discussions inside and outside the lab. However, you still did not succeed in motivating me trying skiing, maybe it will come in the future but right now it is still a big no!

I would like to thank **Dr. Xavier Bugaut** and **Prof. Dmitry Katayev** for having accepted to evaluate my manuscript.

A big *merci* to **Dr. Fabrice Dénès** for his support and help during these three and a half years! It took a while for us to know each other, sometimes it was hard to understand each other, but I am particularly thankful to you because thanks to our conversations I grew up not only as a chemist, but also as a man. For sure, I will talk about you to my future kids.

Special thanks as well to our collaborators in Prof. Christoforos Kokotos group at the University of Athens. They hosted me for two weeks and made me feel like at home! I am especially indebted to **Chara Batsika** for her guidance and interesting discussion about the project but, most importantly, for having introduced me to the Greek culture. Our good time in the lab will be unforgettable.

Cheers to former and present members of the Renaud Group. I am particularly grateful to **Dr. Dace Cirule** and **Dr. Lars Gnägi** for having introduced me to the lab and for their help in the initial stage of my PhD. **Dr. Elena Hofstetter** for her support, her friendship and for being constantly beside me since 2021. **Dr. Ravi Kumar** for being a mentor to me, for his assistance in good and bad moments and for dealing with my everyday crisis with calm and with (a lot of) patience.

During my PhD, I had the chance to supervise two apprentices, **Leo** and **Zoe**. Thanks for all the work and effort you put into my project and for always being polite, punctual and efficient. I have learned a lot from you as well and I am looking forward to seeing what you are going to become. I just hope that you will not forget this crazy Italian guy speaking a questionable Swiss German who taught you how to do column chromatographies.

A big *merci viu mau* to all the different people of DCPB who are constantly there to assist us in our work. Starting from the *Ausgabe team* (Michel, Dani, Simon and Marco), the *NMR team*

Ilche and Martina), the *HRMS team* (Claudia and Andrea), the *Werkstatt* and the *Renés* for IT support. Thanks to our group secretary **Fränzi** and the department secretaries **Beatrice** and **Sandra** as well.

Thanks to other PhD Students of the department with whom I had the chance to work with during this time. I am very proud to have founded the PhD Coalition together with **Kaila**, **Sarah**, **Laurianne**, **Sophia**, **Aline**, **Isabelle**, **Marianna** (just to cite a few) and I hope that it will continue growing in the future. Thanks as well to other groups members: **Etienne**, **Luca**, **Keir**, **Jan** and the whole **Katayev group** for the fruitful discussions we had.

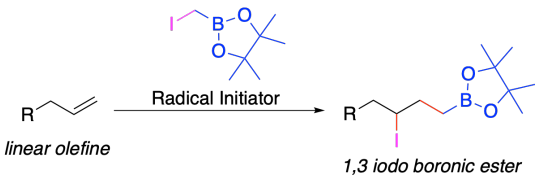
I cannot mention the community of *youngSCS* which I have joined in 2023 and where I am currently the vice-president of. I had the chance to interact with very talented chemists who have a big motivation in sharing their passion in chemistry. A big thank you to **Désirée**, **Tara**, **Ghewa**, **Konstantina**, **Magdalena**, **Chrysanthi** and **Patrick** (again just to cite a few) for what you taught me during this time. I am looking forward for our future work together!

Last but not least, my friends and my family. You dealt with my emotions, you supported me and you were always standing next to me during the bad moments. I would like to cite two persons: **Valeria**, perché mi sopporti e supporti dal 2010 e senza cui non potrei più vivere and **Phuong Trinh**, une soeur désormais, une inspiration et une personne à qui je dois beaucoup pour m'avoir accepté ouvertement quand on s'est connu à l'uni en 2015 (oui ça fait bientôt 10 ans). A big *grazie* to my family for their assistance towards the years and for always supporting my decisions. Grazie a mia sorella **Sara** perché è sempre stata vicino a me durante le tempeste e il bel tempo.

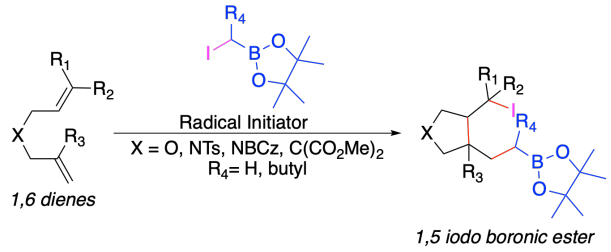
Questa tesi è dedicata ai miei nonni **Caterina e Francesco** e **Gaetano e Rosaria** perché è grazie a voi che sono arrivato a questo punto. Mi avete insegnato a vivere con spirito critico e aperto e un pezzo di voi sarà per sempre dentro di me. Spero di avervi reso orgoglioso, soprattutto tu nonno Francesco che mi guardi da lassù.

Abstract

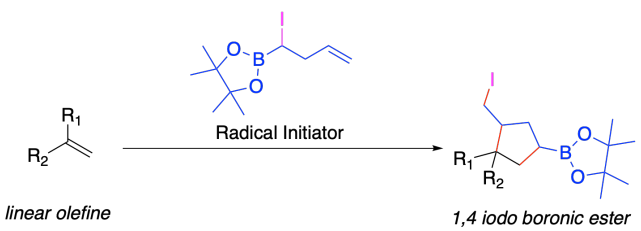
The common thread of this thesis is the application of alpha-boryl radicals in different ATRA (Atom Transfer Radical Addition) reactions. They were generated by using various types of initiators, but the most reliable and efficient was Et_3B/DTBHN. The first part of the thesis is devoted to the application of alpha-boryl radicals in intermolecular ATRA reactions which delivered 1,3-iodo boronic esters as final products. The optimization of the conditions and a small scope on different linear olefines will be presented.



The observed yields being moderate, we then decided to study the reaction on dienes, with the aim of better understanding the last step of the ATRA reaction, the Iodine Atom transfer. The choice of this unsaturated system was not random: when the alpha-boryl radical is added, they undergo 5-*exo*-trig cyclization and deliver 1,5-iodo boronic esters as products. We speculated that the relative position of iodine and boronic ester being different, the compounds would be more stable on silica than the parent 1,3-iodo boronic esters. This cascade reaction was renamed ATRAC (Atom Transfer Radical Addition and Cyclization). The synthesis and the reaction of different dienes with different radical precursor together with some investigations about the reactivity of alpha-boryl radicals will be detailed.



Based on the knowledge acquired from the ATRAC project, a new annulation reaction using secondary alpha-boryl radicals was investigated. The scope and the limitations of the reaction will be presented. This new annulation reaction was renamed ATRAn (Atom Transfer Radical Annulation).



List of Abbreviations and Symbols

α_D	optical rotation
δ	chemical shift (ppm)
AIBN	2,2'-Azobis(2-Methylpropionitrile)
Alox	aluminium oxide
aq.	aqueous
ATRA	Atom Transfer Radical Addition
ATRAC	Atom Transfer Radical Addition and Cyclization
ATRAn	Atom Transfer Radical Addition and Annulation
BDE	Bond Dissociation Energy
c	concentration
cat.	catalytic
calcd.	calculated
Cbz	Benzyl chloroformate
conc.	concentrated
COSY	Correlated Spectroscopy (2D NMR experiment)
dan	1,8-diaminonaphthalene
DAT	Deuterium atom transfer
DCE	dichloroethane
DCM	dichloromethane
DEPT	Distortionless Enhancement by Polarization Transfer (1D NMR experiment)
DIPEA	Diisopropylethylamine
DLP	dilauroyl peroxide
DMF	dimethylformamide
dmg	dimethylglyoximato
DMSO	dimethylsulfoxide
DTBHN	di-*tert*-butylhyponitrite
dr	diastereomeric ratio
EDG	Electron Donating Group
ee	enantiomeric excess
equiv.	equivalents
er	enantiomeric ratio
ESI	Electron spray ionization
EWG	Electron Withdrawing Group
FC	Flash Chromatography
hν	light irradiation
HAT	Hydrogen Atom Transfer
HMBC	Heteronuclear Multiple Bond Correlation (2D NMR experiment)
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)

k	absolute rate constant
m/z	mass to charge ratio
Mp	melting point
nep	neopentylglycolato
NMR	Nuclear Magnetic Resonance
NOESY	Nuclear Overhauser Enhancement Spectroscopy (2D NMR experiment)
PC	photocatalyst
BPin	pinacol boronic ester
ppm	parts per million
pyr	pyridine
R	rest (or substituent)
rt	room temperature
RP-HPLC	Reversed Phase - High Performance Liquid Chromatography
RSE	Radical Stabilisation Energy
quant.	quantitative
TEA	triethylamine
TBC	4-*tert*-butylcatechol
TBAF	tetrabutylammonium fluoride
TBME	*tert*-butylmethyl ether
THF	tetrahydrofuran
TLC	Thin Layer Chromatography
TMEDA	*N,N,N',N'*-Tetramethylethylenediamine
Ts	Tosyl
sat.	saturated
SET	Single Electron Transfer
sol.	solution
UV	ultra-violet
XAT	Halogen (X) Atom Transfer

Contents

1 α-Boryl radicals: synthesis and applications

This chapter presents a general introduction to the reactivity of α-boryl radicals. It will also include some methods used to generate these species and some examples of application, particularly in ATRA reactions. The structure of this chapter follows a review from Masarwa and co.[1] published in 2020.

1.1 Introduction

Although most frequently underestimated, boron (from the arab word *Burāq* - flash) has emerged as an important element in chemistry. It was first isolated in 1808 by French chemists Joseph-Louis Gay-Lussac and Louis-Jacques Thenard. Over the years, boron containing compounds have been employed for different uses. Amorphous boron is used in fireworks to obtain a nice green flame, in the borosilicate glass synthesis or to develop new resistent materials.[2] In the field of medicinal chemistry, they have emerged, among others, as new agents for cancer treatment.[3] In organic chemistry, organoboron compounds are today employed in various reactions. Among them it is worth to cite the palladium catalyzed Suzuki cross coupling,[4] which allows the formation of a new carbon bond between an alkenyl or aryl halide and a boronic ester.

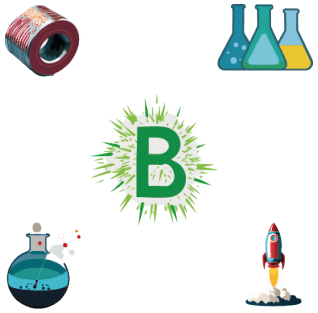


Figure 1.1: Examples of items where boron containing compounds are found.

The electronic configuration of boron is $1s^2\ 2s^2\ 2p^1$, meaning that it possesses 2 empty *p* orbitals. For this reason, a lot of boron based compounds are also used in organic chemistry as Lewis acids. In the context of radical chemistry, boron containing compounds are extremely versatile: the generation of new radicals can, for instance, occur via *in situ* transesterification of a pinacol boronic ester to a catechol borane which is now able to react in a radical chain process and be converted into a new alkyl radical, ready to be further functionalized.[5] But radicals can be generate at the α position as well with respect to the boron atom, giving rise to a new species whose reactivity is now influenced by the boron moiety. These radicals are called **α-boryl radicals** and have gained in interest as building blocks for useful transformations.[1]

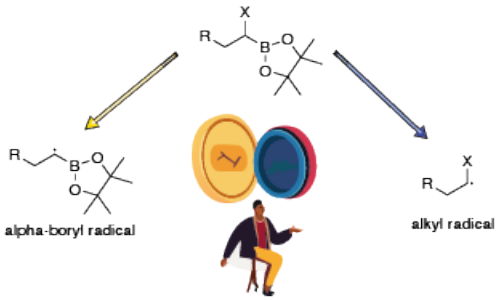


Figure 1.2: The dual nature of a pinacol boronic ester: one piece, two possibilities.

1.2 α-Boryl radicals: a new powerful synthetic tool?

1.2.1 Properties of α-boryl radicals

According to some literature reports and calculations, α-boryl radicals are more stable than a secondary alkyl ($\approx$ 14.5 kcal/mol).[1] Analogously, they can be compared to the methyl radical of toluene: the α-boryl radical arising from the H-atom abstraction of Et_3B will be more stable.[6] This increased stabilization arises from the hyperconjugation of the radical with the adjacent empty *p* orbital of the boron atom. Since there are a variety of organoboron compounds used in chemistry, the boron atom can be bound to different substituents, having thus an impact on the stabilization of the α-boryl radical. As shown in Table 1.1, the α-borane radical is more stable than an α-boronate radical, because the lone pairs on the oxygen atoms are also in conjugation with the empty *p* orbital of boron.[7] However, in comparison to an α-ester radical, the RSE is lower.[8]

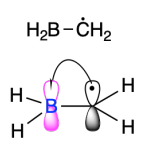
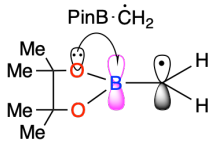
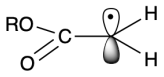
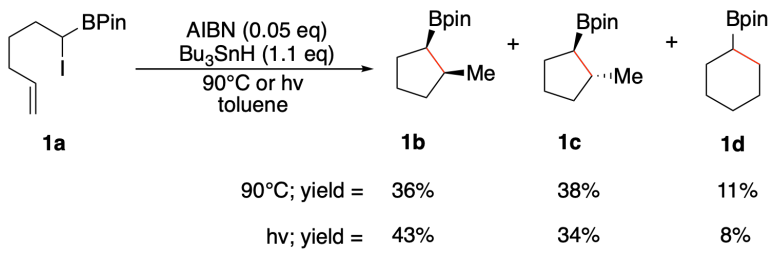
Radical			
RSE [Kcal/mol]	-10.4	-6.7	-5.0

Table 1.1: Comparaison of the RSE of different α-boryl radicals with an α-ester radical.

1.2.2 Preparation of α-boryl radicals

AIBN (with stannates or with TTMSS) as radical initiator

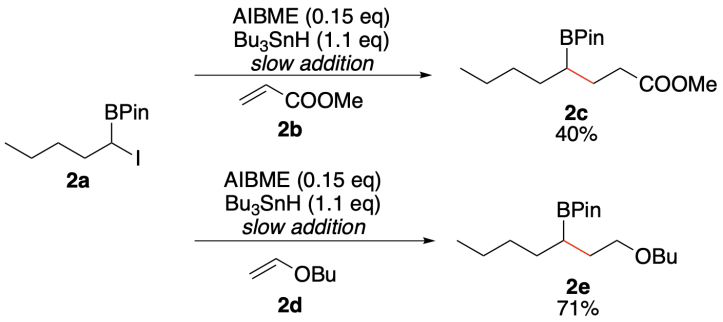
One of the first reports about generation of α-boryl-radicals was published in 1995 by Carboni and co.[9] The radical was generated via iodine atom abstraction performed by $Bu_3Sn\bullet$, formed after AIBN or light initiation. It then underwent a radical cyclisation which delivered a mixture of three products: two diasteroisomers of the cyclopentane (**1b** and **1c**) and one cyclohexane (**1d**). This was due to the lack in selectivity of this cyclization in absence of a Thorpe-Ingold effect at elevated temperatures.[10]



Scheme 1.1: Radical cyclization of a secondary α-boryl radical to a linear olefin. Isolated yields.

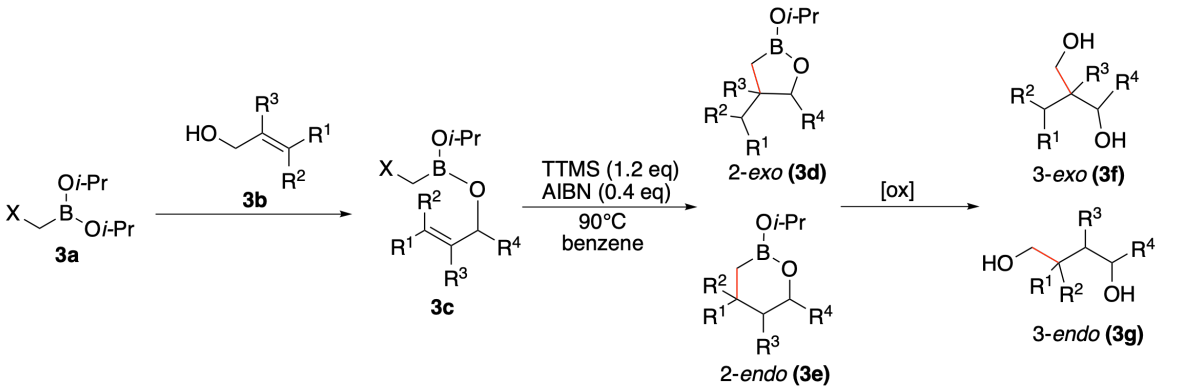
The following year, the Batey group reported the intermolecular addition of a secondary α-boryl radical, generated from α-iodoalkyl boronic esters, using Bu_3SnH on different olefins.

Interestingly, better yields were observed when electron-rich olefin **2b** was used. The addition on electron-poor olefins proved to be more difficult due to the oligomerization of the trap and the reduction of the radical precursor. To increase the yield, the reaction was thus performed using slow addition of the reducing agent. In a competition reaction experiment between the radical and **2b** and **2d** present in the same pot, the addition on **2d** occurred preferentially and the desired product **2c** was not observed.[11] This supports the hypothesis of the electrophilic tendency of the α-boryl radical.

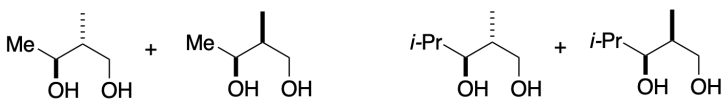


Scheme 1.2: Intermolecular addition of a secondary α-boryl radical to a different activated olefins. Isolated yields.

Some years later, the same group reported an interesting reaction involving, again, secondary α-boryl radicals, which underwent a 5-*exo* or 6-*endo* cyclization to form boracyles **3d** and **3e**. These were efficiently oxidized using trimethylamine-*N*-oxide, delivering the desired 1,3-diols as final products. Notably, diastereoselectivity was good and the reaction could be performed using propargyl alcohols too.[12]



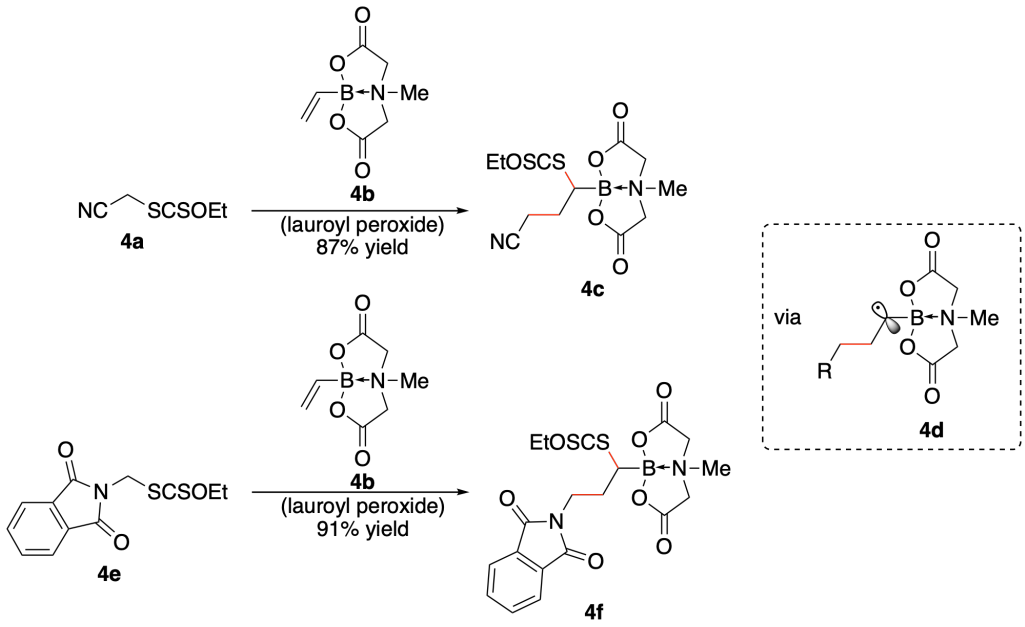
Selected examples:



Scheme 1.3: 1,3-diol synthesis using boracycles as reaction intermediates. Isolated yields.

DLP as radical initiator

DLP (Luperox ©) is a cheap, commercially available and easy to handle initiator which is increasingly used in radical chemistry. Its 10h half-time temperature is 60°C in benzene. However, one of his drawbacks is related to the amount of side-products generated after initiation, which may render the purification problematic.[13] In 2015, the Zard group employed DLP to generate α-boryl radicals after addition of a carbon center radical to vinyl MIDA boronates. Upon generation of **4d**, the radical was not stabilized because the *p* orbital of boron was occupied by the lone pair of the nitrogen atom, and it was thus more reactive towards the xanthation reaction. As a result, highly functionalized MIDA boronates could be synthesized and then treated to yield post-functionalized products. The reaction works with different electrophilic or nucleophilic sources of radicals (**4a** and **4e**). This example is interesting because it clearly shows the importance of the empty *p* orbital of boron atom in stabilizing α-boryl radical.[14] Recent studies showed, however, that **4d** can be depicted as a stabilized radical (RSE: $\sim$-4.6 kcal/mol) and this effect comes from σ_{B-N} hyperconjugation.[15]



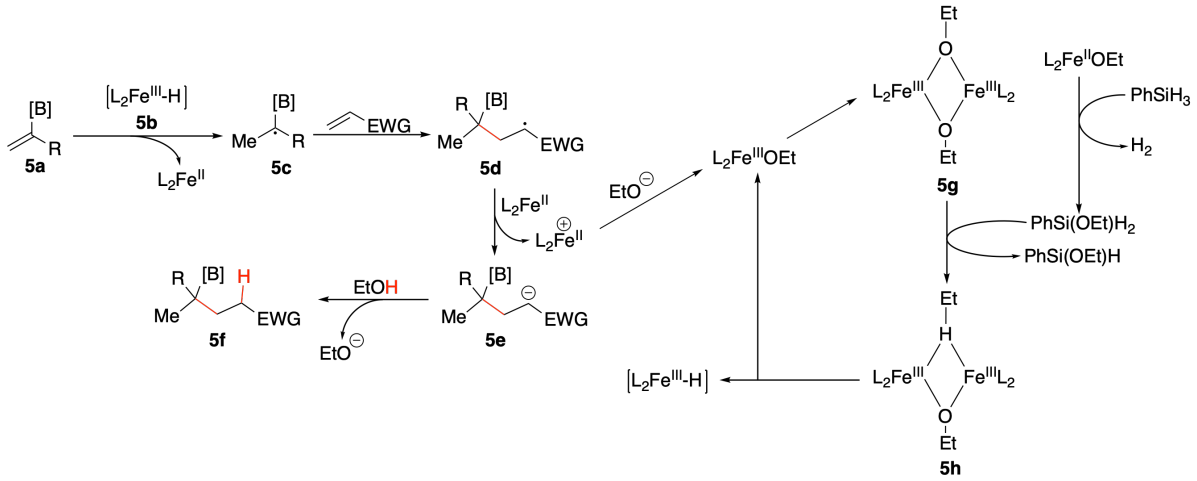
Scheme 1.4: Generation of α-boryl radicals on vinyl MIDA boronates using DLP as initiator. Isolated yields.

DLP was employed to generate α-boryl radicals used in ATRA reactions: these examples will be treated in a separate paragraph.

Metal-mediated reactions

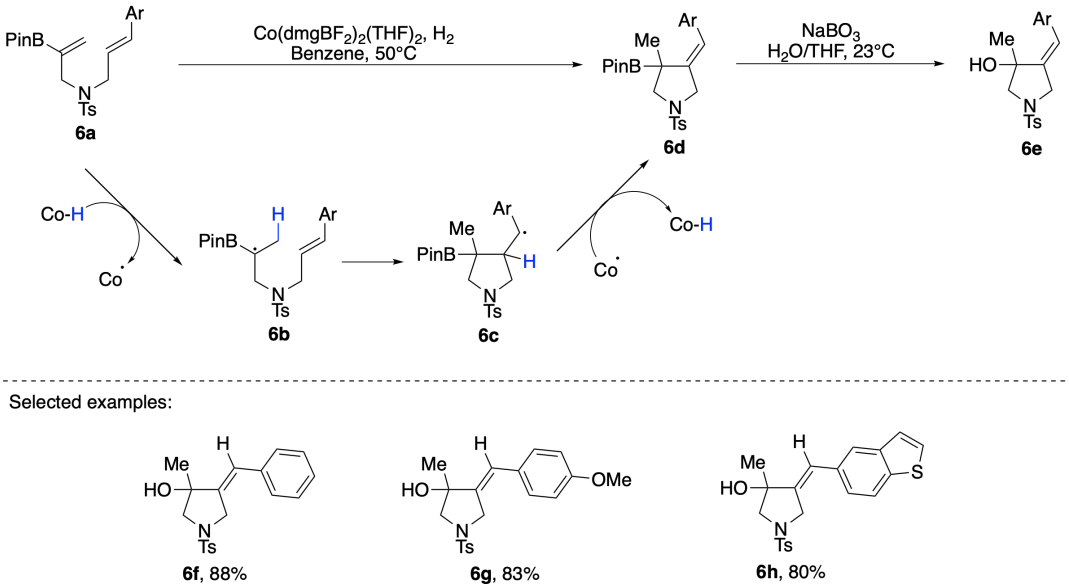
One of the first reports where α-boryl radicals were generated using a metal complex was published by Baran and co. in 2017.[16] In this work, they performed the anti-Markovnikov hydrofunctionalization of different olefins using $Fe(acac)_3/PhSiH_3$ system.[17] The reaction worked

as well when vinyl pinacol or 1,8-diaminonaphthalene boronic esters or MIDA boronates were employed. As shown in Scheme 1.5, the tertiary α-boryl radical **5c** was generated after addition of the active species **5b** to a vinyl boronic ester **5a**. This complex originated from the bridged intermediates **5h** and **5g**, which were formed after reaction of $Fe(acac)_3$ with another *in situ* generated specie, $PhSi(OEt)H_2$. The newly formed radical added to an electron deficient olefin to form intermediate **5d**. The radical was then reduced to a stabilized carbanion which gets protonated by the solvent to deliver the desired hydroborylated compound.



Scheme 1.5: Generation of α-boryl radicals upon addition of a hydride complex on a vinyl boronic ester.

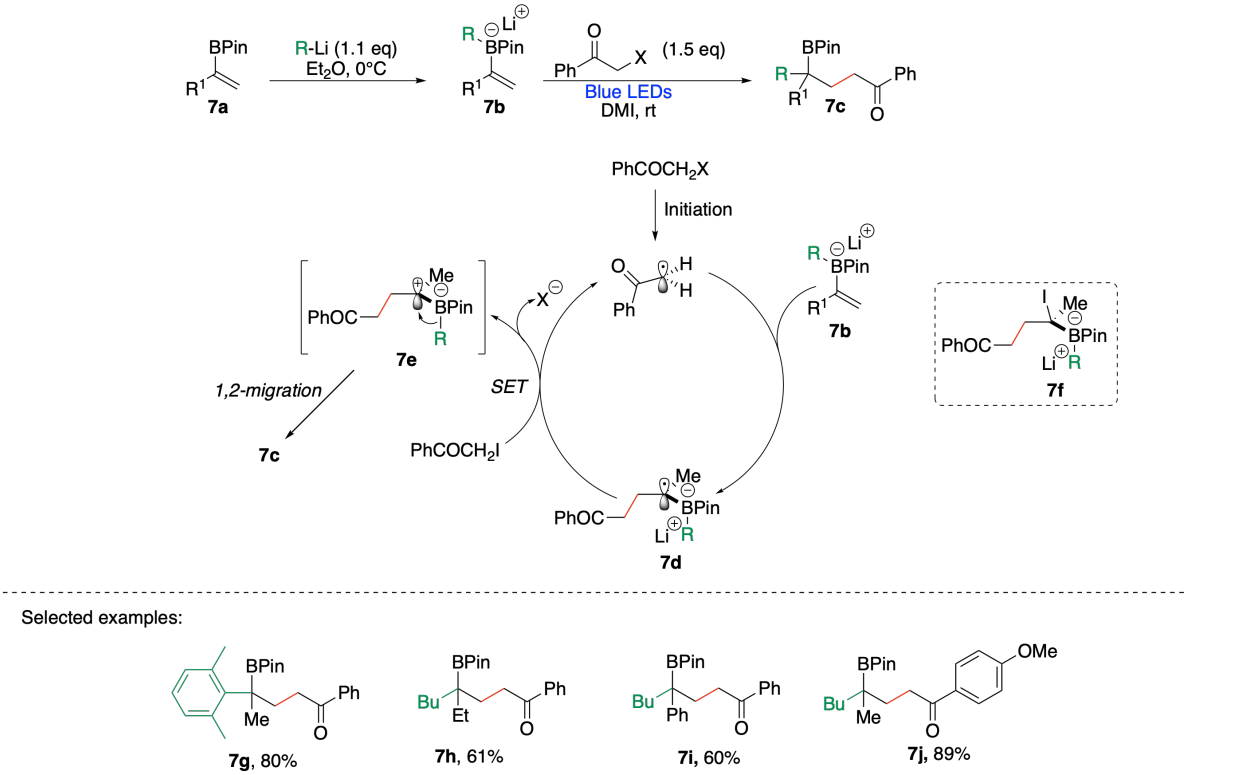
In 2021, Norton and co. reported an α-boryl radical triggered addition-cyclisation cascade strategy to synthesize functionalized pyrrolidines (Scheme 1.6). α-boryl radical **6b** formed after addition of a hydride coming from an *in situ* generated cobalt complex and undergoes fast cyclisation to form the secondary stabilized radical **6c**. β-hydride elimination regenerates the active species and compound **6d**, which is then further oxidized using sodium perborate to deliver the desired tertiary alcohol as final product. No isomerisation, hydrogenation, or cyclohydrogenation side reactions have been observed. This method proved to be quite generic and can be used as well for the synthesis substituted tetrahydrofuran rings.[18]



Scheme 1.6: Tertiary α-boryl radical generation using a cobalt hydride complex, followed by cyclization to obtain complex pyrrolidine scaffolds. Isolated yields.

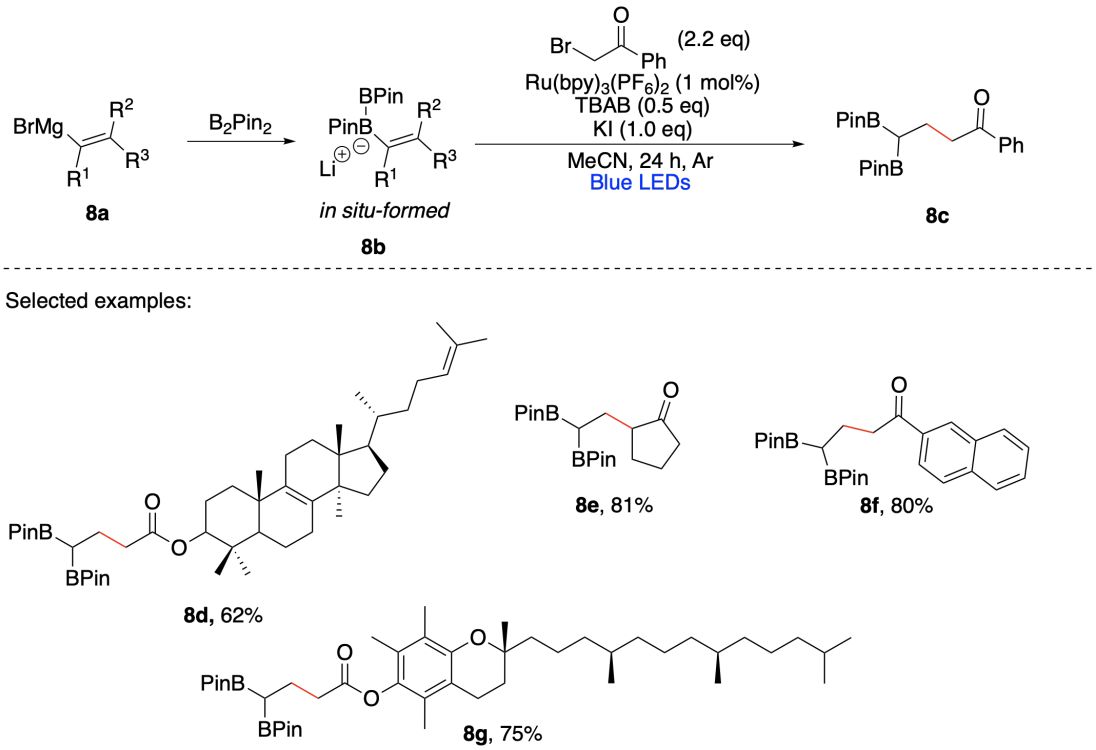
Visible light mediated reactions

The new photoredox chemistry tool has been recently employed in combination with the generation of α-boryl radicals. The advantage of this method is the formation of new radicals in selective positions by using mild conditions. The first example was reported by Aggarwal and co. in 2017. They described the 1,2-metallate rearrangement of vinyl boronates using a Ru photocatalyst. Two different reactions were merged together: the well-known Matteson homologation,[19] typical reaction of boronate complexes, and the addition of a radical on an unsaturated system. In the presence of light, the newly formed radical **7d** underwent a SET to form a carbocation, which was subjected to 1,2-metallate shift (Scheme 1.7). The mechanism was recently revised by the group and most probably involves the formation of an iodine atom transfer intermediate **7f**.[20] The scope of the reaction is quite broad and general and furnished a variety of γ-carbonyl boronic esters.[21] An enantioselective version of the reaction was reported by the same group in 2018.[22] Another version of the reaction involving the same reactive species but using Et_3B/DTBHN for the second step (and not photoredox catalysis) was reported by Renaud and co. in 2018.[23]



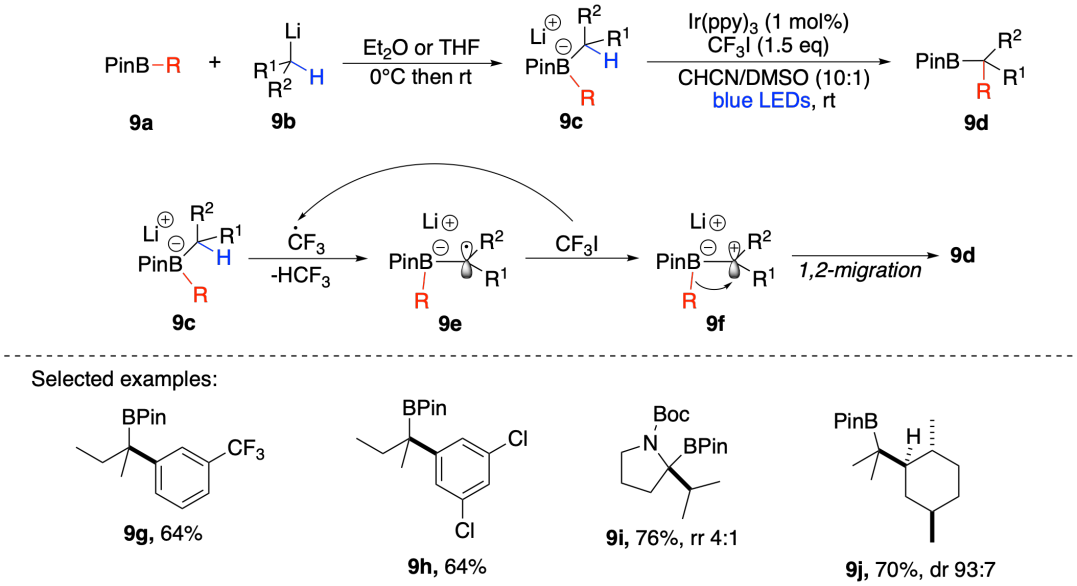
Scheme 1.7: Generation of α-boryl radicals under photoredox conditions and application in 1,2-metallate shift reaction. Isolated yields.

The same chemistry was used by Shi and co. to synthesize various *gem*-bis(boryl)alkanes. The key intermediate was generated by the reaction of a vinyl Grignard with B_2Pin_2 and it underwent radical addition and SET, followed by pinacol boronic ester migration to form the desired compound in good to moderate yields[24] (Scheme 1.8).



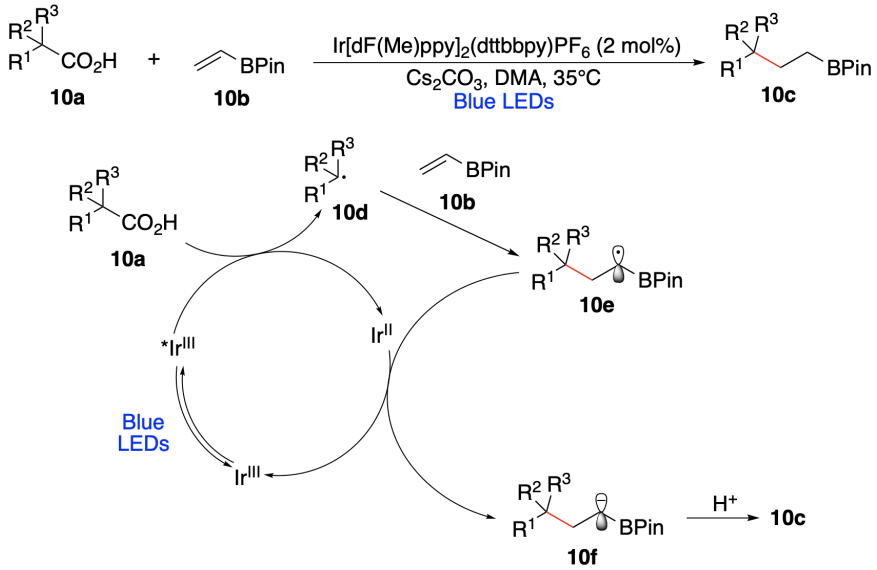
Scheme 1.8: Generation of α-boryl radicals under photoredox conditions and application in 1,2-metallate shift reaction - synthesis of gem-bis(boryl)alkanes. Isolated yields.

Studer and co. reported a very similar reaction starting from pinacol boronic esters. Their strategy had a major advantage: a broader scope could be envisioned since a lot of pinacol boronic esters are commercially available. The first version of the reaction was reported in 2017 and involved a radical-polar crossover reactions of vinylboronate complexes.[25] Some years later, the group updated the reaction conditions, as shown in Scheme 1.9. The α-boryl radical was generated via H-atom abstraction of the ate-complex **9c** and the reactive species was a trifluoromethyl radical. The radical **9e** was then oxidized by CF_3I to form carbocation **9f** which undergoes 1,2-metallate shift.[26] In a nutschell, CF_3I replaced the more dangerous Et_3B.



Scheme 1.9: Generation of α-boryl radicals under photoredox conditions and application in 1,2-metallate shift reaction - use of CF_3I as oxidant. Isolated yields.

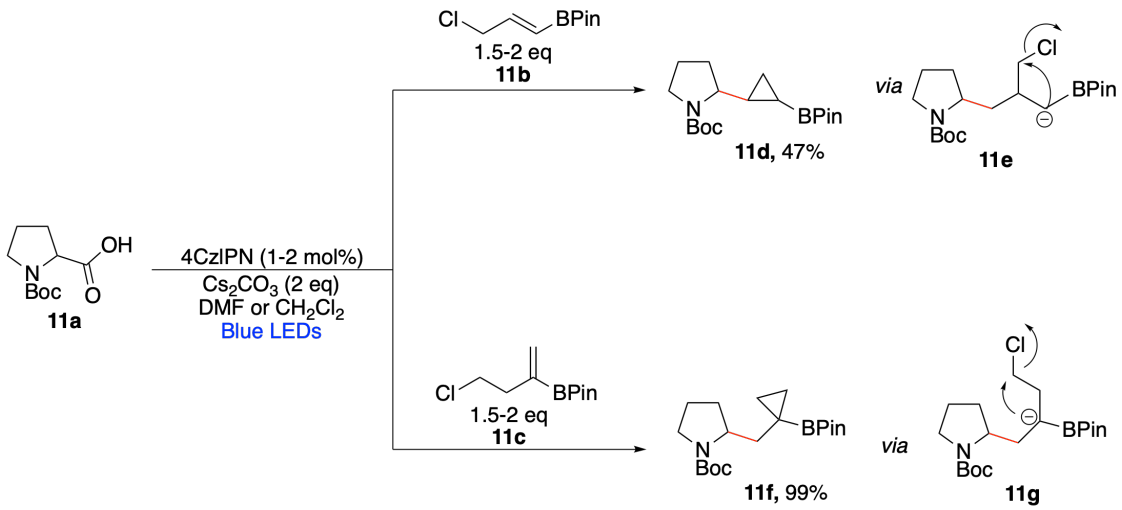
Apart from application to 1,2-metallate shift, the photoredox reaction conditions can be applied to generate α-boryl radical which can be reduced and trapped by an electrophile. In 2018, Aggarwal and co. reported the addition of different radicals to vinyl pinacol boronic ester under photoredox conditions. The reaction intermediate was a secondary α-boryl radical **10e** which was reduced to carbanion **10f** by the photocatalyst and then protonated to form the hydroborylalkylated adduct (Scheme 1.10).[27]



Scheme 1.10: Hydroborylalkylation reaction via photoredox generation of an α-boryl radical, reduction and trapping by a proton.

The same strategy was used by the group to develop a new cyclopropanation reaction: the

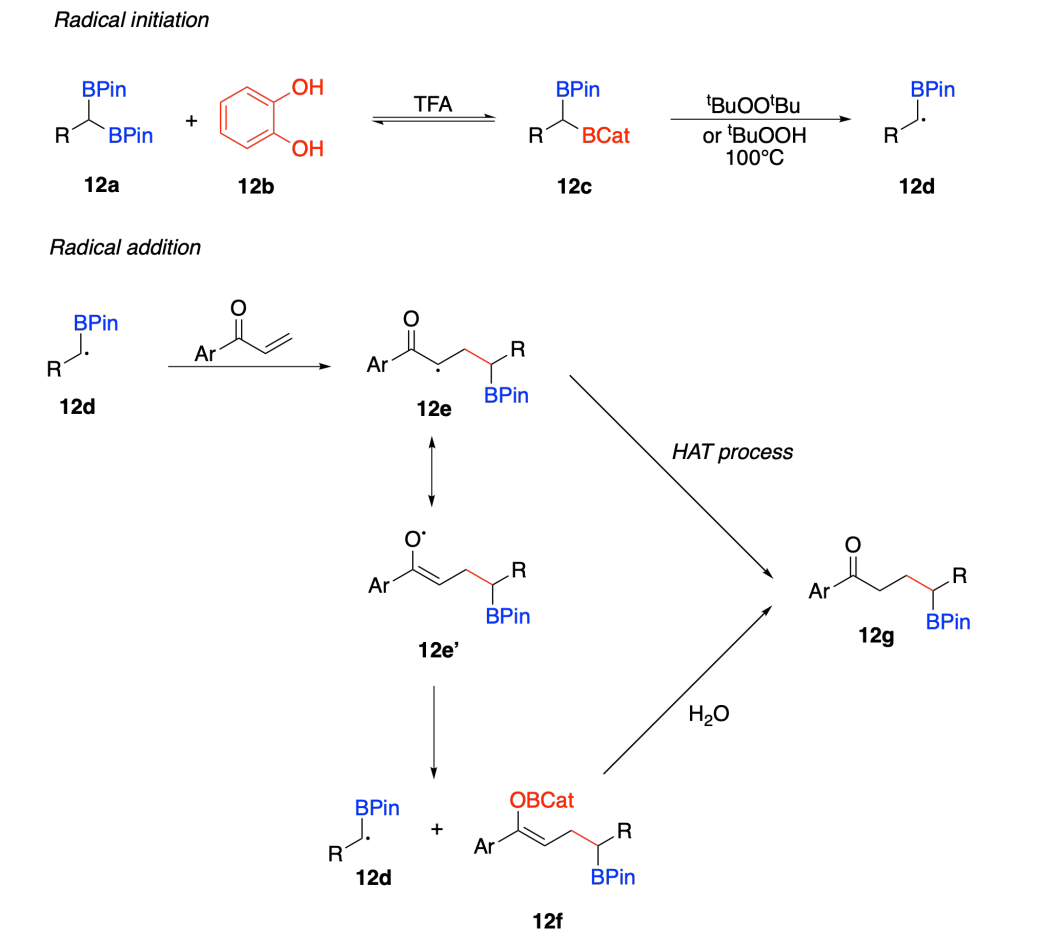
carbanion intermediates **11e** or **11g** undergo 1,3-elimination to yield a highly functionalized boracyclopropane (Scheme 1.11).[28]



Scheme 1.11: Synthesis of borocyclopropanes via 1,3-elimination from in-situ reduced secondary or tertiary α-boryl radicals. Isolated yields.

Miscellanous

An interesting example of α-boryl radical preparation was reported by Wang and co. in 2021 via radical alkylative deborylation of *gem*-diborylalkane.[29] As depicted in scheme 1.12, their work exploited the chemistry previously described in our group[29] and thus uses catechol to transesterify one half of the molecule to form catechol borane **12c**. Upon interaction with an alkoxy radical, this moiety is substituted to form the desired α-boryl radical **12d**. This is employed to perform conjugate addition on various enones. Two plausible mechanisms are described: after addition of the radical on the Michael acceptor, **12e** can be reduced via HAT process from a hydrogen atom donor to deliver **12g** as desired product or form **12e'** which, upon interaction with intermediate **12c**, forms the boron enolate **12f** and a new α-boryl radical **12d**. **12f** is then hydrolyzed with water to deliver the desired compound **12g**.

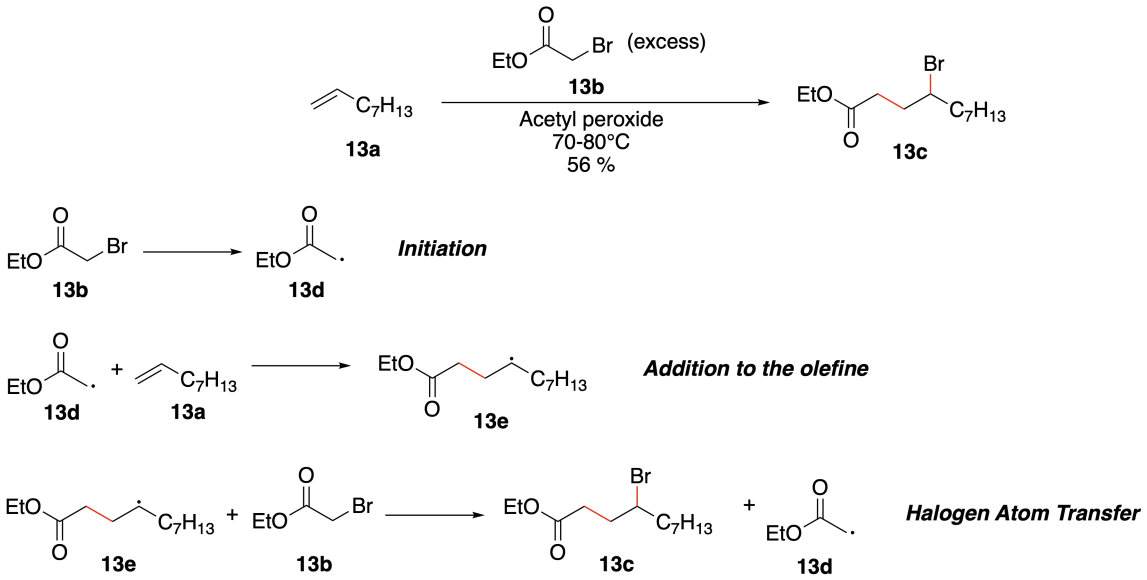


Scheme 1.12: α-boryl radicals generation via radical alkylative deborylation and addition of enones. Isolated yields.

1.3 Application of α-boryl radicals in ATRA and related reactions

1.3.1 ATRA reactions

The pioneer of Atom Transfer Radical Addition reactions is Morris S. Kharasch who, in 1945, published the very first paper on this topic where he described the radical addition of carbon tetrachloride and chloroform on olefins.[30] His discovery had a huge impact, particularly in the field of polymer chemistry and for the synthesis of new plastics, needed during the period after the Second World War. It is important to mention that, based on Kharasch's reports, Atom-Transfer Radical Polymerization was developed and is one of the most used methods to synthesize size-specific polymers today.[31,32] But what are the peculiarities of this reaction? To illustrate them, an example published in 1948 is described in Scheme 1.13.[33]



Scheme 1.13: Typical reaction mechanism of an ATRA reaction.

The first step is the **initiation**, in which the radical **13d** is generated from radical precursor **13b**. This will **add on the unsaturated system 13a** and form the secondary radical **13e**. To close the chain process, **13e** will now under **Halogen Atom Transfer** from radical precursor **13b** to form the desired product **13c** and a new radical **13d** which will sustain the chain. Three important features of this reactions are worth to mention:

1. The final product will bear two new functional groups and can be further functionalized by using other reactions.

2. The conditions are mild and the temperature of the reactions can be chosen as a function of the initiator.

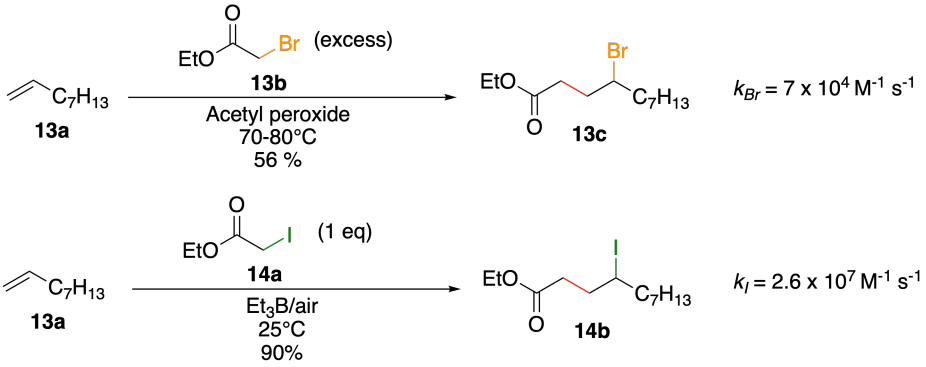
3. The reaction is completely atom-economic and side-products are originated by recombination of the radicals at the end of the chain process. As a reminder, the atom-economic or atom efficiency/percentage is a measurement of the conversion efficiency of a reaction

and tracks the amount of atoms transferred from the reactant to the product.[34]

Two important effects contribute to the correct progression of the reaction and have to be considered to design efficient ATRA processes:

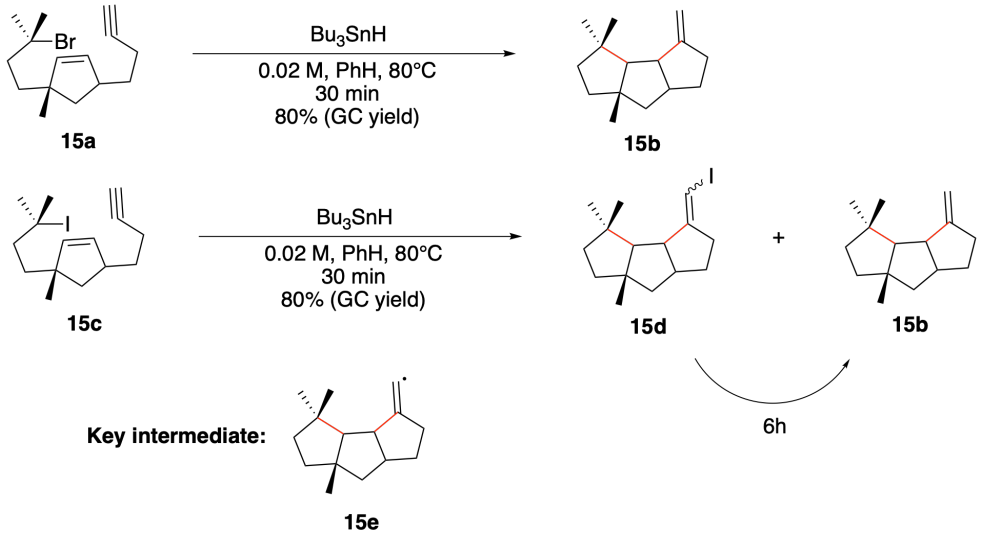
1. *Thermodynamic effect*: the reaction is exothermic due to the formation of two new σ bonds from a π system. Moreover, **13e** must be less stable than **13d** so that the Halogen Atom Transfer can take place.

2. *Kinetic effect*: the faster the rate of halogen atom transfer, the more efficient the chain process. To illustrate this concept, let's compare the reactions in Scheme 1.14. The synthesis of **13c** was previously detailed in Scheme 1.13 and reported by Kharasch and co. In the nineties, Baciocchi and co.[35] reported the same reaction using ethyl iodoacetate **14a** and a different initiator. The yield of this reaction nearly doubled and the reason is because the iodine atom transfer reaction is faster than the bromine atom transfer. Curran and co. determined the rate constants of the aforementioned reactions[36] and the values are in accordance with the experimental results.



Scheme 1.14: Comparaison between two ATRA reactions using different radical precursors to illustrate the kinetic effect. Isolated yields.

When talking about Atom Transfer Radical Addition reactions, the work of Dennis Curran has to be cited as well, since he and his group made huge efforts in studying the iodine atom transfer processes, particularly in annulation reactions.[37] But why did he get interested in this particular topic? During the total synthesis of *capnellene*,[38] a potentially chemotherapeutic agent found in a soft coral, they employed a radical annulation strategy to build the main core of the natural product (Scheme 1.15). When bromide **15a** was employed, the reaction worked well, giving 80% yield of the desired compound **15b** in 30 minutes under *n*-Bu_3SnH conditions. However, when iodide **15c** was employed, the yield surprisingly dropped off 20% using the previous conditions. Interestingly, when the mixture was left under longer reaction time, the obtained yield of **15b** was the same as the first reaction using the bromide. After several mechanistic study, they discovered that when **15c** was used, the intermediate **15e** underwent iodine atom transfer to form **15d**, which was then reduced to the desired compound **15b**. This proved that the iodine atom transfer reaction from **15c** to vinyl radical **15e** was surprisingly faster than reduction with *n*-Bu_3SnH.



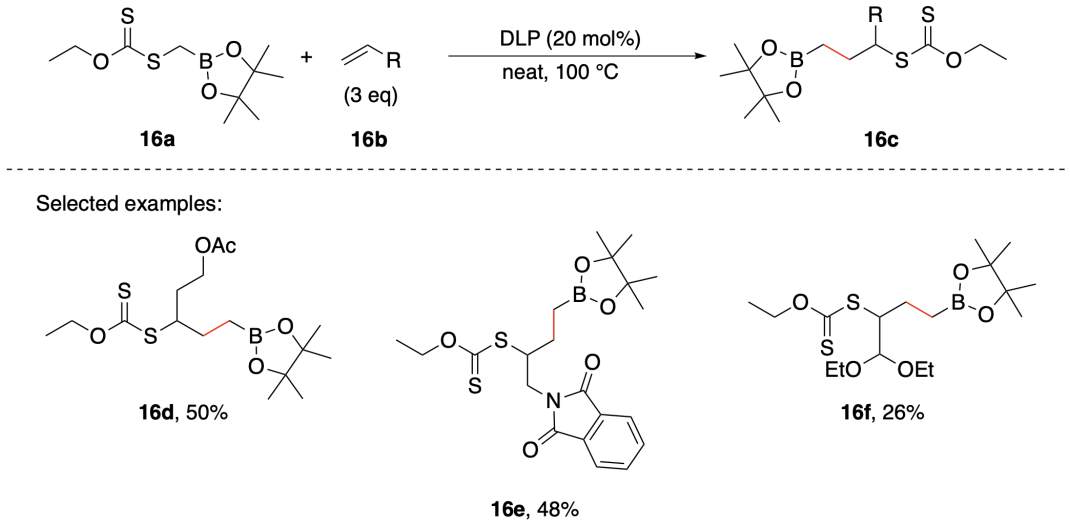
Scheme 1.15: Key step of the total synthesis of *capnellene*.

The group started to investigate these annulation reactions in more details using different simpler systems[39] and better elucidated the mechanism of the reaction. It was a Kharasch type addition reaction and the iodine atom transfer is very fast due to the formation of a new σ bond at the expanse of a π bond. Other similar reactions were later investigated by Curran and co., particularly in the development of new annulation reactions.[37]

Kharasch and Curran's seminal works on ATRA reactions have gained more and more importance in the field of radical chemistry and today different reactions have been reported using various conditions. Worth to mention are some works published by Renaud and co. on radical carboazidation[40] and ATRA reactions using DTBHN as initiator[41] or employed for the post-functionalization of natural products.[42] An ATRA reaction under photoredox catalysis conditions was reported by Stephenson and co. in 2011.[43] Recently, the use of ascorbic acid[44] or sodium ascorbate,[45] under irradiation, as an initiation method for ATRA reactions has been employed. Lastly, transition metal catalysts have been developed to perform ATRA reactions and they are notably based on copper.[46,47]

1.3.2 Merging α-boryl radicals and ATRA reactions: synthesis of 1,3-xanthopinacol boronic esters

The very first example where α-boryl radicals were used in ATRA reactions was published by Zard and co. in 2019. Radical precursor **16a** (Scheme 1.17) was employed to perform ATRA reactions on different olefins using thermal initiation (DLP, 100°C) to yield the desired bisfunctionalized compounds in moderate yields.[48] The results can be explained by a not efficient chain process and by the formation of oligomers as by-products. It was important to perform the reaction neatly probably to accelerate the xanthate group transfer step, which sustains the chain.

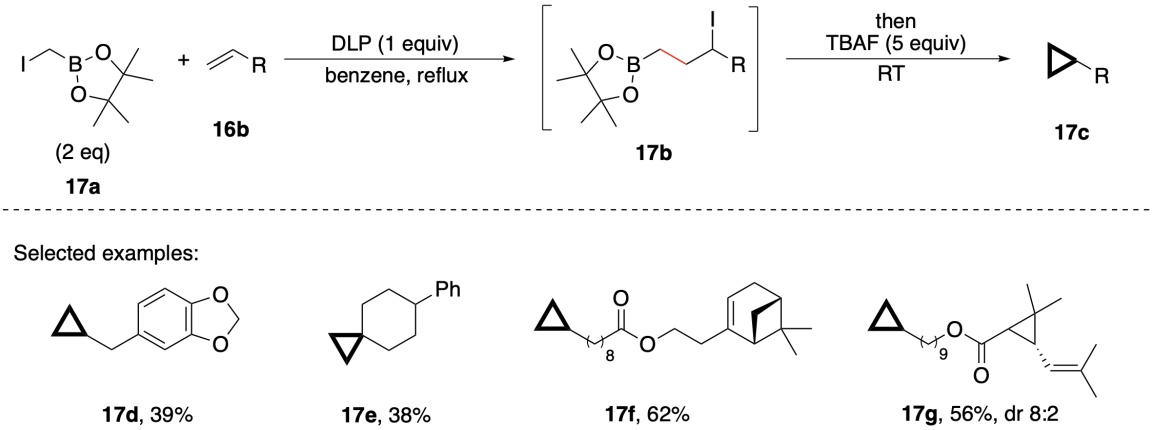


Scheme 1.16: Synthesis of 1,3-xanthopinacol boronic esters via ATRA process. Isolated yields.

1.3.3 Merging α-boryl radicals and ATRA reactions: cyclopropanation reactions

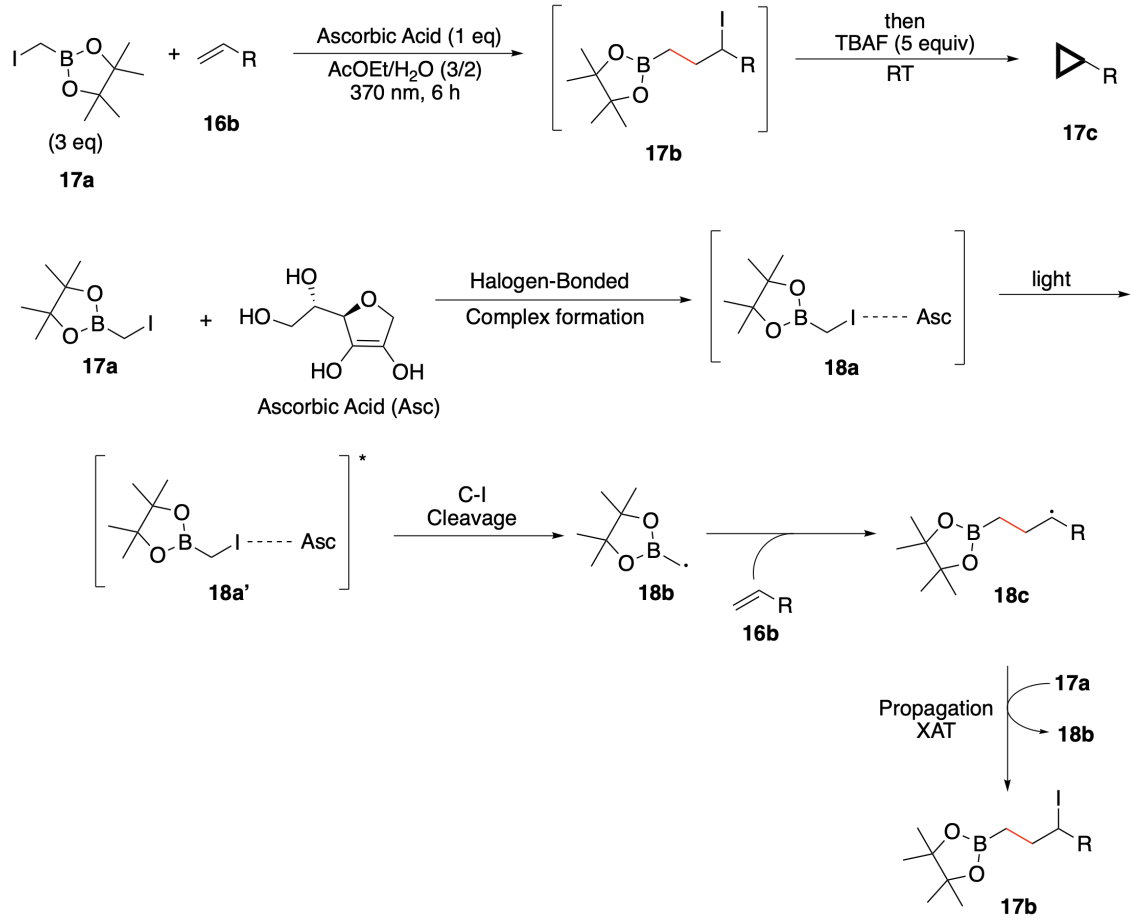
α-Boryl radicals have been increasingly used in combination with the development of new cyclopropanation reactions. Classical organic chemistry methodologies include the use of very highly reactive chemicals which might be incompatible with different substrates, especially in late stage functionalization of natural compounds. In addition to that, the reaction intermediates are difficult to prepare and quite unstable because of their high reactivity. As an example, the Simmons-Smith reaction, one of the most used cyclopropanation strategies, requires the use of an organozinc carbenoid which is prepared by the reaction between diiodomethane and a zinc-copper couple.[49] Several reports have been recently published about the development of new mild conditions for cyclopropanation of olefins,[50–54] and a few of them utilized the addition of 1-haloalkylboronates on unsaturated systems.

Renaud and co. reported the one-pot metal-free cyclopropanation of linear olefins from 1,3-iodo pinacol boronic esters intermediates **17c**, generated after ATRA reaction using iodomethyl pinacol boronic ester **17a** as radical precursor. The isolation of the intermediates being complicated due to important yield losses during column chromatography purification, the crude mixtures were treated *in situ* with TBAF so that 1,3-elimination could take place and deliver the desired cyclopropane **17d** as final compound (Scheme 1.17).[55] Interestingly, the method is selective for terminal olefins, as shown in examples **17f** and **17g**.



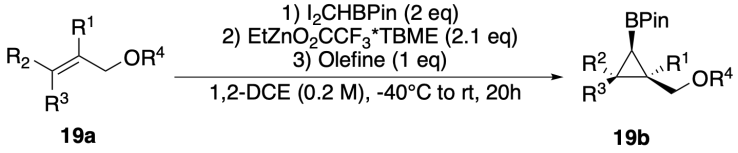
Scheme 1.17: Synthesis of cyclopropanes via elimination of 1,3-iodopinacol boronic ester intermediates - DLP initiation. Isolated yields.

In 2024, Kokotos and Renaud and co. reported the same cyclopropanation reaction using ascorbic acid under photoredox conditions (Scheme 1.18).The key α-boryl radical is generated after the cleavage of the C-I bond of the halogen-bonded complex **18a** between **17a** and ascorbic acid. The cleavage occurs exclusively upon irradiation (370 nm light). Once the radical is formed, it adds to the unsaturated system, forming intermediate **18c** which can now abstract an iodine atom from **17a** to form the 1,3-iodo pinacol boronic ester intermediate **17b** and another α-boryl radical **18b**, which will sustain the chain.[45]



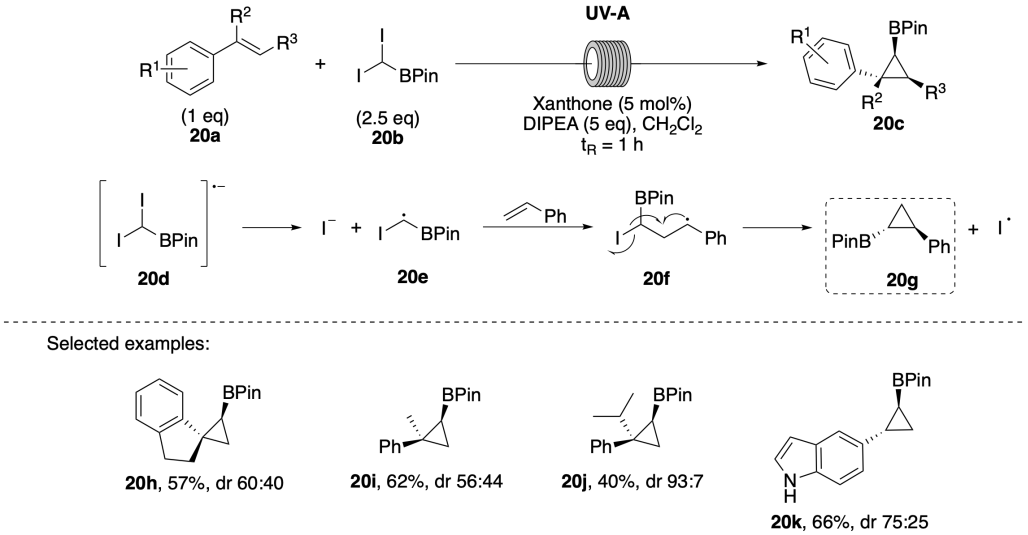
Scheme 1.18: Synthesis of cyclopropanes via elimination of 1,3-iodopinacol boronic ester intermediates - photoredox initiation.

1-Haloalkylboronates have been employed as well for the synthesis of borocyclopropanes, a pattern which was previously accessed via several reaction steps. Indeed, vinyl boronates are required as starting materials, on which the cyclopropane moiety is introduced via a Simmons-Smith reaction or by using a diazo compound. In 2017, Charette and co. first reported their direct synthesis starting from alkenes using a novel boromethylzinc carbenoid (Scheme 1.19). After having developed a new scalable synthesis of the key precursor diiodomethyl pinacol boronic ester, the method proved to work on different olefins with excellent diastereoselectivities, particularly when 1,2-disubstituted olefins were used, thanks to the allylic ether oxygen of the substrate. The reaction worked on styrenes as well, although an erosion of the selectivity was observed. Mechanistically, it works analogously to the Simmons-Smith reaction, namely the desired carbenoid is first synthesized and then it adds to the unsaturated system via a concerted mechanism.[56]



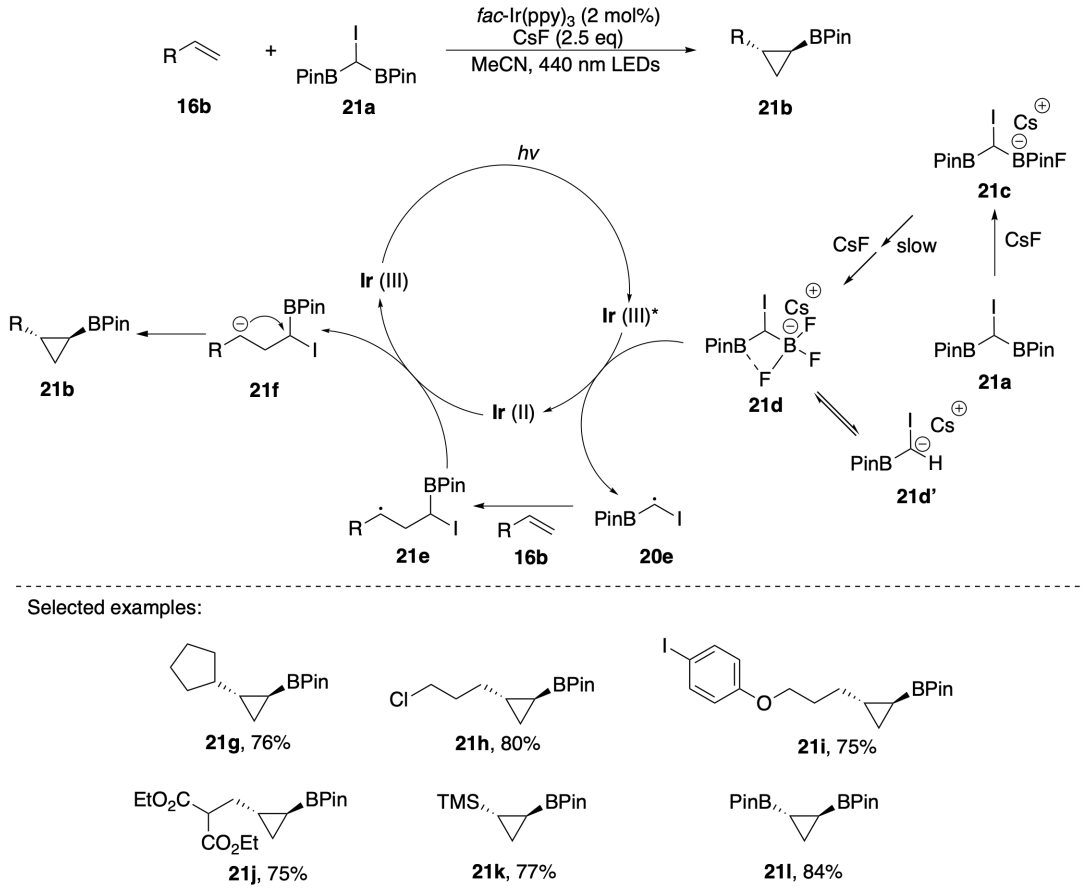
Scheme 1.19: First report on direct borocyclopropanation of olefins.

Shortly after this report, Takai and co. reported the same cyclopropanation reaction using diiodomethyl pinacol boronic ester promoted by $CrCl_2$ and TMEDA, still requiring, however, the use of transition metal carbenoide as well as very toxic and pyroforic reagents.[57]
An important milestone for the development of the borocyclopropanation reactions was the use of photoredox catalysis. Based on the seminal work of Suero and co. on the development of new metal-free cyclopropanation reactions on styrenes[58] or Micheal acceptors,[59] Charette and co. developed new photoredox conditions for borocyclopropanation of styrenes using diiodomethyl pinacol boronic under UV light irradiation in a continuous flow reactor. The use of xanthone as organic photosensitizer greatly impacted the efficiency of the reaction by reducing the residence time from 3h to 1h, delivering 78% of yield of the desired product. Interestingly, the same reaction in batch resulted in a yield of 58% after 18h and no conversion was observed after 1h reaction time. Pleasingly, the reaction was efficient on a broad range of styrene derivatives. Mechanistically, long-lived triplet excited state of xanthone is accessed after UV-A irradiation. This transient species can be reduced by Hünig's base (DIPEA) or oxidized by diiodomethyl pinacol boronic ester **20d** (Scheme 1.20), although experimental evidences support the first pathway. In both cases, however, a radical anion is formed and will fragment to form an iodomethyl pinacol ester radical which will add on the styrene to form intermediate **20f**. After radical 3-*exo*-tet process, the desired borylated cyclopropane **20g** and an iodine radical are formed, which can be quenched by DIPEA.[60]



Scheme 1.20: Photoredox borylcyclopropanation of styrenes under flow conditions. Isolated yields.

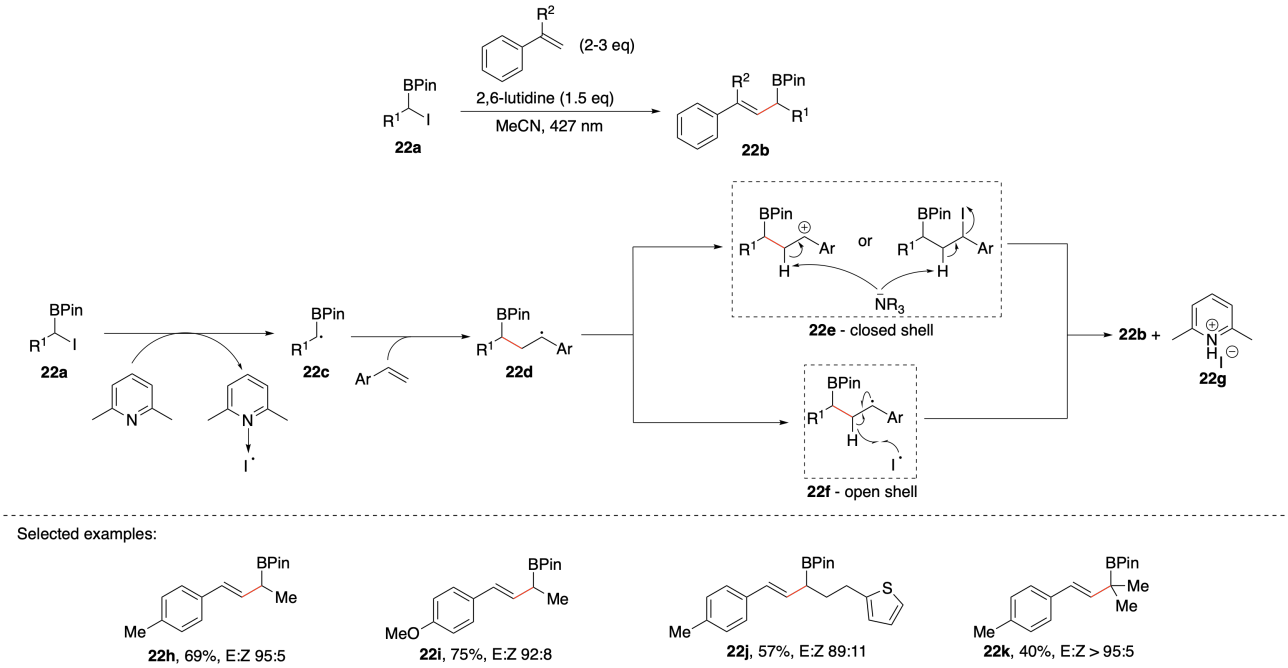
A modified version of the reaction, restricted to styrenes, was reported in 2023 by the same group for the synthesis of *gem*-borosilylcyclopropanes. In this case, the reaction could be performed in batch and it delivered the desired compounds with yields up to 96%.[61] Recently, the borylcylopropanation using (diborylmethyl)iodide was reported by Marder and co., expanding the scope to unactivated olefins as well. The reaction requires the use of *fac*-Ir(ppy)$_3$ as photocatalyst and a fluoride source (CsF) as base. It is compatible with a variety of different alkenes, tolerant to functional groups such as amides, halides, alcohols and esters, and was selective towards terminal olefins. However, it did not work on styrene derivatives. Concerning the mechanism of the reaction, the group proposed a tentative mechanism for this transformation. They rapidly understood that CsF was playing a huge role in the mechanism, in particular, for the formation of mixed species **21d** (Scheme 1.21). This will undergo reductive quenching by the excited iridium photocatalyst and the desired iodomethylpinacol boronic ester radical **20e** is generated. This adds onto the unsaturated system to deliver intermediate **21e**, which undergoes SET from the reduced iridium catalyst to deliver carbanion **21f**. The product **21b** is then generated from ionic 3-*exo*-tet cyclisation of intermediate **21f**. An alternative to this mechanism would be the formation of 1,1,3-diboryliodo intermediate via an ATRA process, followed by ionic cyclisation triggered by CsF.[62]



Scheme 1.21: General borylcyclopropanation reaction on unactivated alkenes using photoredox catalysis. Isolated yields.

1.3.4 Other uses of α-iodoalkyl boronic esters derivatives

Very recently, Molloy and co. reported the addition of α-boryl radicals on styrenes: as a result, E-allylic boronic esters can be obtained. As shown in Scheme 1.22, the protocol is transition metal free and uses 2,6-lutidine to form the Electron Donor-Acceptor (EDA) complex, responsible for the formation of the α-boryl radical. The radical **22c** adds to the unsaturated system and a new benzylic radical is formed. This radical can undergo two different mechanisms to form the final compound. In the so-called *closed shell* assumption (**22e**), the radical is oxidized to carbocation and lutidine acts as a base to remove a proton and then forms a double bond. The base is as well required in the scenario where the ATRA product is formed *in situ* because it is allows for the elimination reaction. Another possibility is the formation of the new double bond in the so-called *open shell* mechanism (**22f**). In this case, an iodine radical abstracts the hydrogen α to the benzylic radical and, after recombination, the new double bond is installed. The authors supports the *closed shell* mechanism and they studied the whole process using various experiments. Last but not least, they were able to develop a way to access Z-allylic boronic esters by adding an Ir catalyst to the mixture which acts as a sensitizer, enabling selective energy transfer.[63]

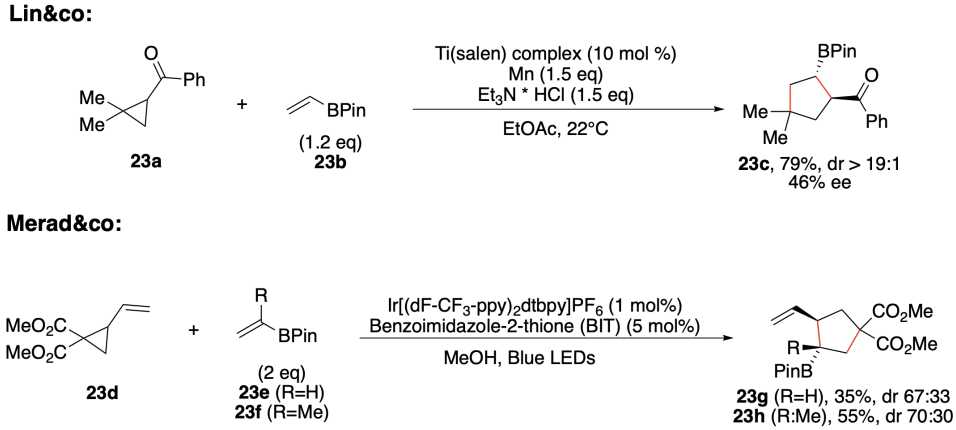


Scheme 1.22: Addition of α-boryl radicals on styrenes and formation of E-allylic boronic esters. Isolated yields.

1.3.5 Annulation reactions involving α-boryl radicals

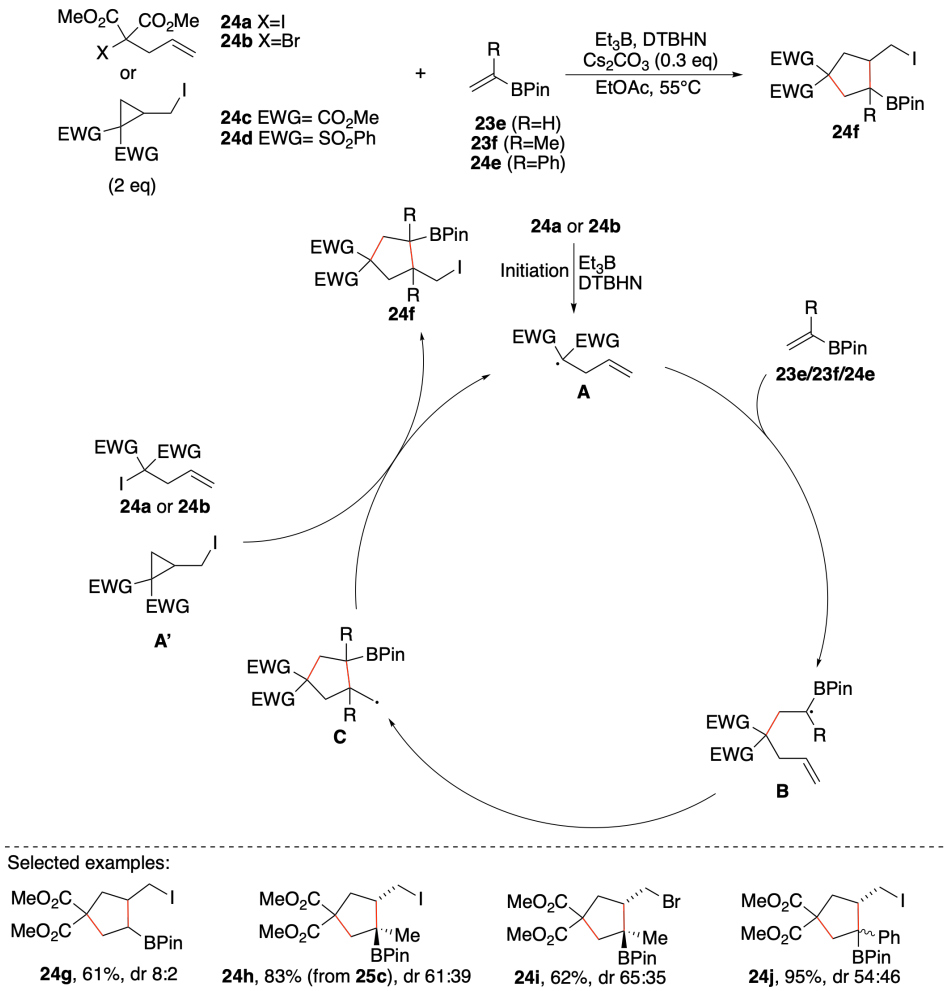
The use of α-boryl radicals can be expanded to the synthesis of 5-member rings through annulation reactions. The most used strategy is the addition of a radical on a boron containing radical trap (namely vinyl boronate derivatives) and subsequent intramolecular cyclization to

deliver the desired borylcyclopentane. Previous reports include the work of Lin and co.[64] and Merad and co.[65] where cyclopropyl ketones (via Ti-catalyzed radical redox relay reaction) and isothiouronyl radical cations were respectively added on vinyl pinacol boronic ester to deliver the desired five-member ring (Scheme 1.23).

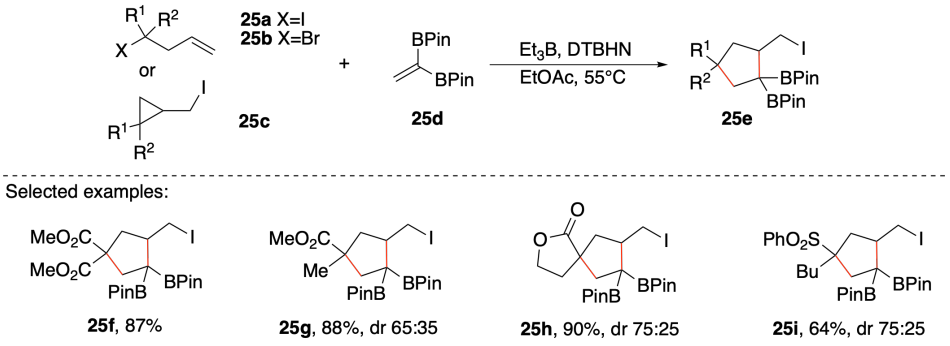


Scheme 1.23: Previous literature on the formation of borylated cyclopentane via annulation reaction. Isolated yields.

Recently, our group published the first example of annulation reaction using α-boryl radical which follows an ATRA mechanism. As shown in Scheme 1.24, two different types of radical precursors **24a**/**24b** or **24c**/**24d** can be employed for the reaction. After Et_3B/DTBHN initiation, the first radical **B** is formed and adds on the vinyl pinacol boronic ester derivative **23e**, **23f** or **24e** to form the alpha boryl radical **B**, which undergoes annulation to deliver intermediate **C**. After the iodine atom transfer takes place, final product **24f** is delivered, together with radical **A** which will be engaged in another addition/annulation reaction.[66] The same reaction can be performed using 1,1-diborylethene **25d** (Scheme 1.25) as radical trap: after addition of a radical on the unsaturated system, a new α-boryl radical is formed and engaged in the annulation reaction to deliver iodo-*gem*-diborylated cyclopentanes as desired compounds.[67]



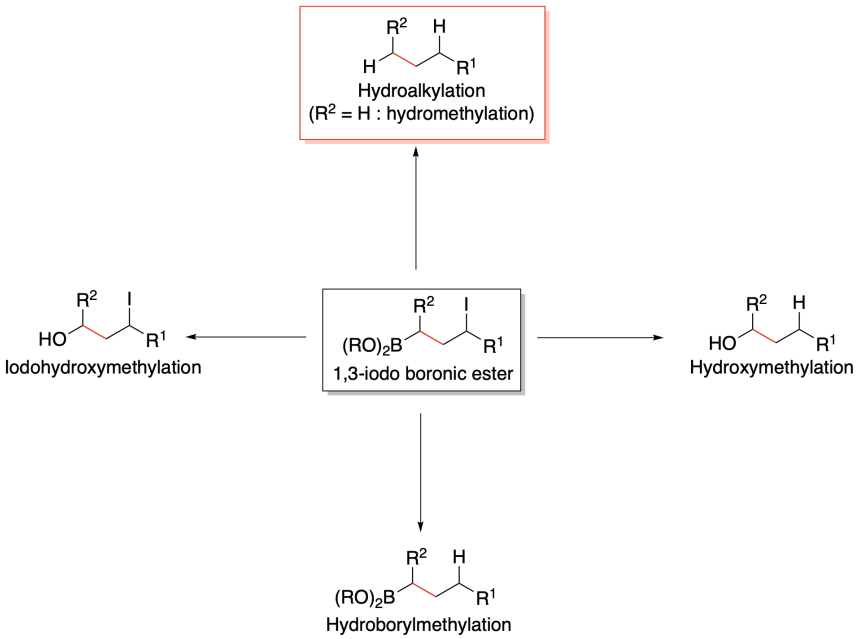
Scheme 1.24: Borylated cyclopentanes via Atom Transfer Radical [3+2] Annulation. Isolated yields.



Scheme 1.25: *gem*-Diborylated cyclopentanes via Atom Transfer Radical [3+2] Annulation. Isolated yields.

1.4 Hydromethylation of alkenes

In 2019, our group published a two-step cyclopropanation strategy where the ATRA intermediates 1,3-iodo boronic esters were treated *in situ* with TBAF to deliver the desired cyclopropanes as final products.[55] Let's now focus on the intermediate of the cyclopropanation sequence: after the ATRA reaction, a new C-C bond is formed selectively and using mild conditions. Although a variety of different reactions can be applied to functionalize olefins (hydrogenation, dihydroxylation, addition, cycloadditions), the formation of simple C-C bonds is difficult and foresees the use of metal complexes. This reaction is called **carbometallation** and usually consists in the addition of an organometallic reagent on a π-system to form two new σ bonds, a C-C and a C-Metal ones, which can further react with an electrophile or with another olefin, like in the case of Ziegler-Natta polymerization.[68] Although the carbometallation of alkynes is a well-controlled, predictable and widely-used process in organometallic chemistry, the reaction on alkenes still presents some drawbacks, namely the lack of regio-, stereo- and enantioselectivity of the addition of the organometallic species on the unsaturated system. Moreover, the stability of the new saturated intermediate being low, it is hard to perform further reactions and extend its utility for new transformations.[69] In contrast to carbometallation, our method will enable us to form new C-C bonds using mild conditions and in a regioselective fashion: the addition of α-boryl radicals on terminal olefins will only occur on the less-substituted side of the olefin (*anti*-Markovnikov addition). Besides that, the 1,3-iodo boronic esters have a great potential in terms of other post-functionalizations. It is, in fact, possible to access different compounds from this common intermediate by means of previously reported reactions (Scheme 1.26). The iodine atom can be selectively reduced using radical chemistry (Et_3B, H_3PO_2/Et_3N or TTMS/AIBN). The pinacol boronic ester moiety can be easily oxidized using sodium borate or transformed into a radical active species and then functionalized using different radical traps. This last reaction was the object of a previous study performed in our group.[5] The boronic ester can be transesterified *in situ* using MeOBCat to a catechol borane which, upon reaction with an α-alkoxy radical, will form a new alkyl radical which can be functionalized using a radical trap or reduced in the presence of an H-atom donor (TBC). The complete reduction of 1,3-iodoboronic esters was considered an interesting transformation, allowing possible **hydromethylation** and **hydroalkylation** of the starting olefin. Moreover, due to the regioselective addition of the α-boryl radical on the double bond, a new protocol for *anti*-Markovnikov hydromethylation can be envisioned.

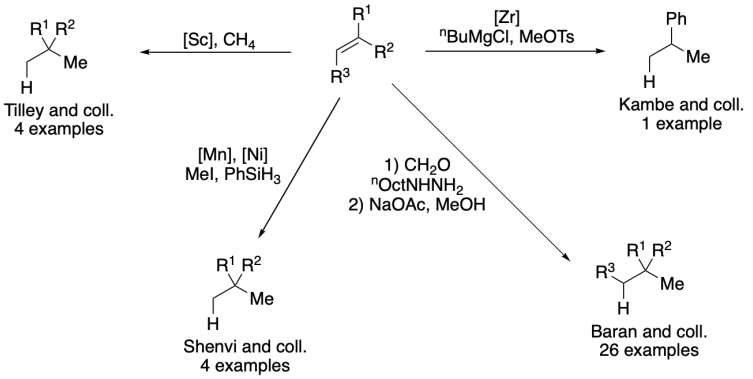


Scheme 1.26: Possible post-functionalizations of 1,3-iodo boronic esters.

Are there any reports in the literature concerning the hydromethylation of olefins? To the best of our knowledge, there are only 4 methods to perform direct Markovnikov hydromethylation (Scheme 1.27). The very first example was reported by Kambe and co.[70] and it involved the use of a zirconium metal complex and MeOTs as methylating agent. Later, Tilley and co. reported other examples of hydromethylation of unactivated olefins using a scandium metal complex.[71,72] However, in both cases, the scope of the reaction was not broad and included just few examples.

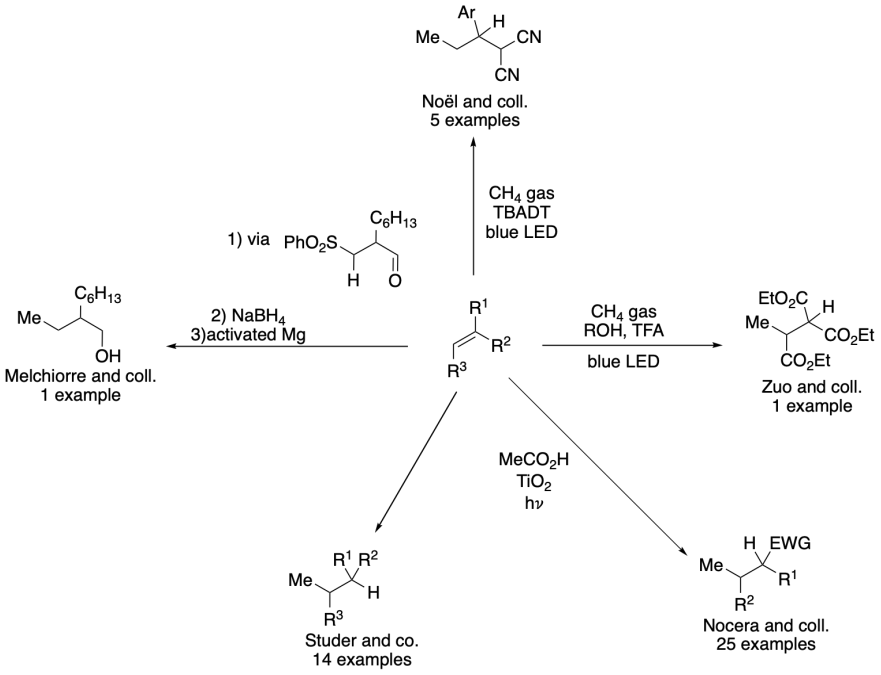
A general method was published by Baran and co. in 2015 and it utilised an iron complex to form a hydrazone intermediate which was then treated to deliver the hydromethylated compound.[73] Although the scope was broader and more sensible towards various functional groups, setting the stage for possible late stage functionalization of natural products, it had as some important limitations as well. For example, styrenes gave poor yields owing to the homodimerization by-products and sterically hindered olefins reacted worse, giving rise to an increased amount of reduced by-products. Moreover, the purification step was quite difficult because of the similar polarity of the desired product with other side products.

In 2019, the Shenvi group reported 4 examples of hydromethylation of alkenes where manganese and nickel metal complexes were involved in metal hydride hydrogen atom transfer (MHAT) catalysis and nickel-catalysis to form quaternary carbon centers.[74]



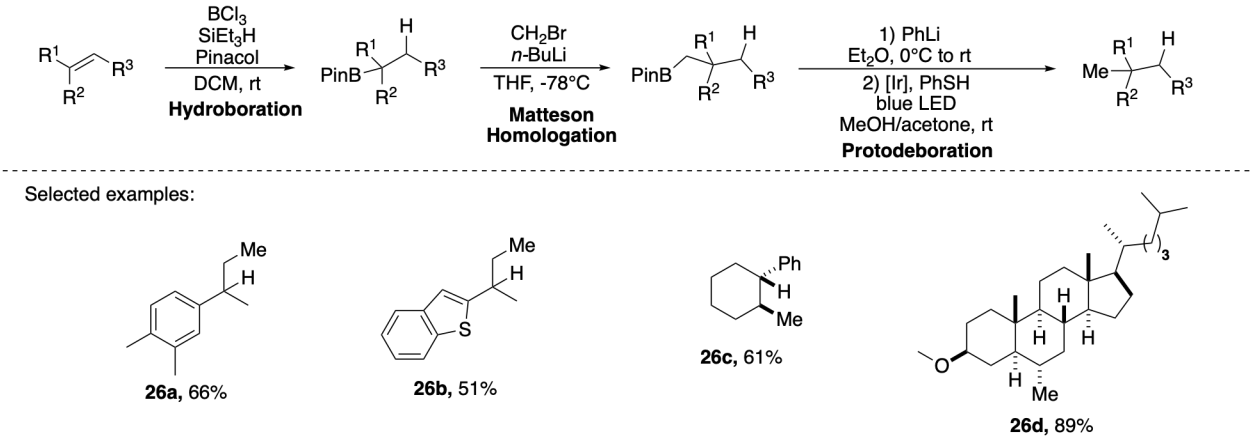
Scheme 1.27: Examples of Markovnikov hydromethylation of olefins.

The range of reactions for *anti*-Markvnikov hydromethylation is also quite limited. (Scheme 1.28). Melchiorre and co. reported an example of *anti*-Markovnikov hydromethylation in which, after the enantionselective addition of an α-sulfone radical on an enamine was performed, the sulfone moiety was reduced under harsh conditions (magnesium metal) to deliver the fully reduced compound.[75] Other examples involve the use of cheap and sustainable methyl group sources such as methane[76,77] or acetic acid[78] under photoredox catalysis conditions.



Scheme 1.28: Examples of *anti*-Markovnikov hydromethylation of olefins.

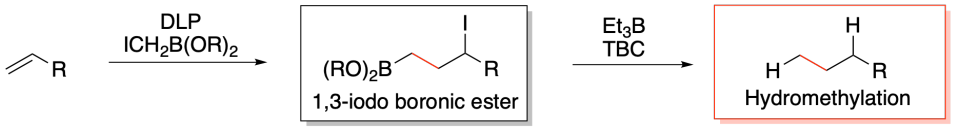
To the best of our knowledge, the only general reported procedure for *anti*-Markovnikov hydromethylation was published in 2019 by Studer and co. in 2019.[79] In their 3-step approach, an olefin is hydroborated to form the desired pinacol boronic ester **A** (Scheme 1.29) which is then engaged to a 1,2-metallated shift reaction (Matteson homologation) to introduce a new carbon atom and form intermediate **B**. The BPin moiety is then removed by protodeboronation using photoredox conditions and thiophenol as hydrogen-atom donor to form the desired *anti*-Markovnikov methylated compound **C**.



Scheme 1.29: *Anti*-Markovnikov hydromethylation of linear olefins reported by Studer and co. Isolated yields.

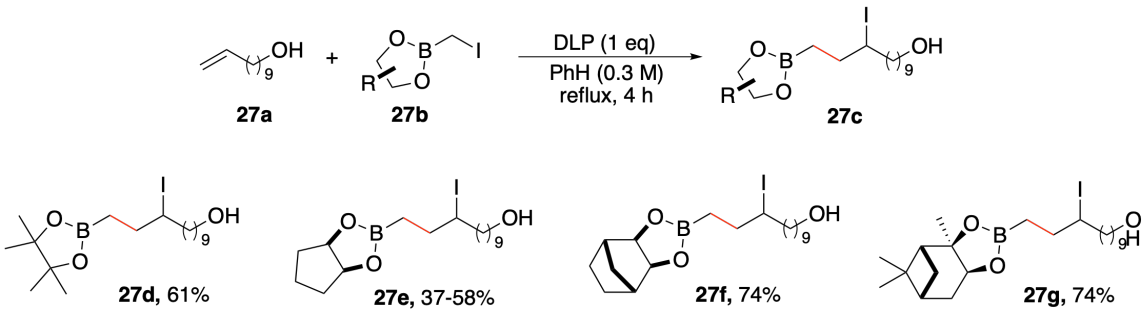
1.5 Previous results: on a new *anti*-Markovnikov hydromethylation strategy

Dr. Tappin and Dr. André-Joyaux, two former PhD students of the group, gathered all the knowledge acquired from the previously reported cyclopropanation reaction involving 1,3-iodo pinacol boronic esters intermediates and proposed a one-pot, two steps strategy for the *anti*-Markovnikov hydromethylation of unactivated alkenes (Scheme 1.30).

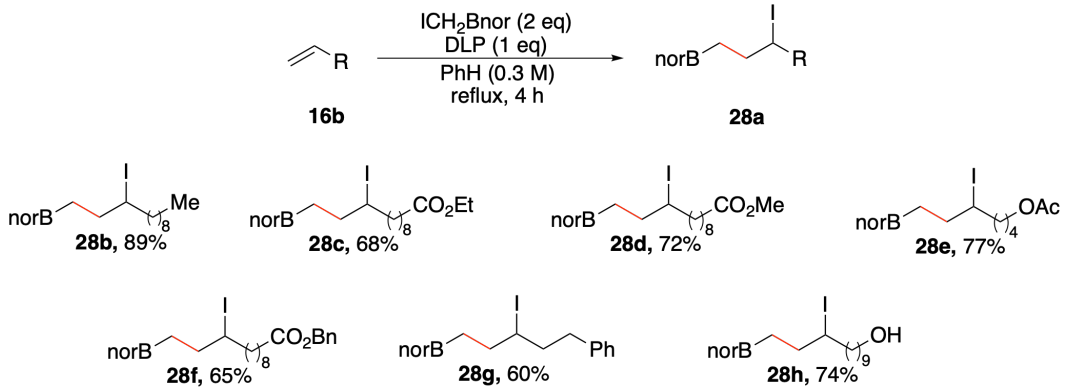


Scheme 1.30: Proposed method for direct *anti*-Markovnikov hydromethylation of unactivated alkenes.

One of the first issue to solve was related to the stability of the 1,3-iodo pinacol boronic esters intermediates. Dr. Tappin realized that these molecules were relatively unstable on silica and, as a result, a yield loss of about 20% was observed after column chromatography purification. He tackled this problem by first studying the transesterification reaction of pinacol boronic esters in presence of other diols. The principle behind this experiment is to find a new boronic ester which is more thermodynamically stable yet still prone to transesterify with TBC. Pleasingly, ***exo,exo*-2,3-norbornanediol boronic esters** can satisfy both requirements. Once the new boronic ester identified, Dr. Tappin synthesized different iodomethyleneboronic esters derivatives, tested them in ATRA reactions to synthesize the desired 1,3-iodo boronic esters and check their stability on silica. As shown in Scheme 1.31, the best results were found with norbornanediol and pinanediol boronic esters (**27f** and **27g**) and the first one was chosen to have easier spectra to analyze. Compared to commercial pinacol boronic ester, the gain is of about 15% yield. He then scoped the method on different unactivated olefins and was able to obtain the desired compounds in good yields (Scheme 1.32).

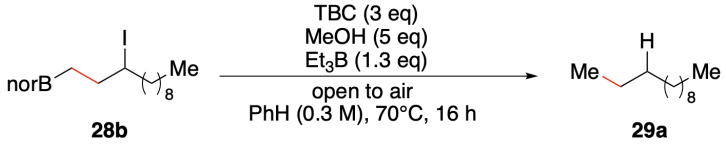


Scheme 1.31: ATRA on undec-10-en-1-ol using different iodomethyleneboronic esters as radical precursors and comparison of the isolated yields after column chromatography. Isolated yields.



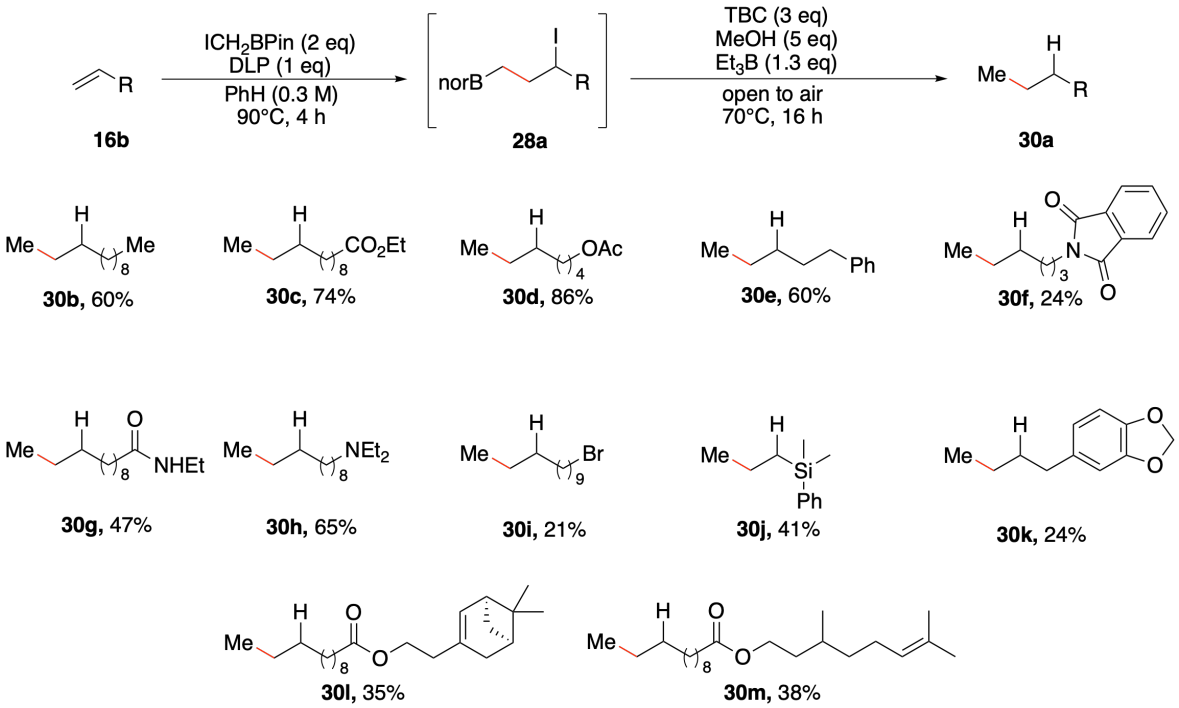
Scheme 1.32: Scope of 1,3-iodonorbornene boronic esters using DLP as radical initiator. Isolated yields.

Once the problem of the stability of the intermediates solved, the focus moved to study the transesterification reaction of norbornene boronic esters (RBnor) to catechol boronic esters (RBCat) using MeOBCat. The following studies were conducted by Dr. Emy André-Joyaux. After several NMR studies, it was showed that the transesterification reaction on alkyl norbornane boronic esters is even more favourable than with the corresponding alkyl pinacol boronic esters derivatives and it occurs at room temperature already. These findings are in accordance with previous works available in the literature.[80,81] The protodeboronation step was then optimized and worked well upon acidic catalysis and using TBC as catechol source. Prolongated reaction times had a positive impact on the outcome of the reaction. The last step to develop the hydromethylation reaction was finding new conditions for the deiodination of 1,3-iodonorbornene boronic esters. Giving the fact that TBC, a very good hydrogen atom donor is needed for the protodeboronation reaction, it was thought to add Et_3B to the mixture and open the system to air with a chance of performing both reactions at the same time. Indeed, the attempt was successfull and the desired hydromethylated compound was obtained in 67% GC yield (Scheme 1.33).



Scheme 1.33: Conditions for one-pot deiodination/protodeboronation sequence.

With the optimized conditions in hand, Dr. Emy André-Joyaux scoped the method and synthesized different methylated compounds starting from commercial olefins and obtained promising initial results (Scheme 1.34). Some of the examples come from natural products bearing an unactivated double bond. Moreover, the protocol is selective to non-substituted double bonds. The DTBHN initiation method for the ATRA reaction can be as used as well and has a big advantage, since all by-products are volatile.



Scheme 1.34: Scope of hydromethylation sequence. GC yields.

1.6 Goal of the work

The initial aim of the work was to optimize the previously reported reaction conditions. In particular, most of obtained yields were determined by GC because the compounds could not be obtained pure due to several impurities coming from the two reaction steps. It was important for us to show that these yields correlated with the corresponding isolated yields. To achieve this purpose, it was critical to optimize the purification step which is challenging for two main reasons:

- The stability of 1,3-iodo boronic esters on silica;
- The separation of the desired hydromethylated compounds from DLP decomposition by-products.

The project was thus structured in a way that the two steps of the hydromethylation sequence, namely the ATRA reaction and the full reduction of the reaction intermediates, could be separately investigated. In the first case, we wanted also to better understand the reactivity of the α-boryl radical and their α-iodoalkyl boronic esters precursors in ATRA reactions, in particular for what concerns the iodine-atom transfer step. Indeed, there are no reports about this topic which can be found in the literature. Moreover, it was still not clear why the ATRA intermediates were unstable: is it due to the relative position of iodine and boronic ester moieties on the molecule or is it due to other side-reactions (namely cyclopropanation) arising upon exposure to acidic conditions or light? The isolation of pure compounds, i.e. not contaminated with products arising from the decomposition of the initiator, was very important for us as well, because we could envisioned to submit them to different post-functionalization reactions which would give access to a library of different derivatives starting from the same olefin via the ATRA intermediates. Last but not least, some reaction parameters also needed to be changed, namely the solvent, as we wanted to switch from the harmful benzene to a more environmental-friendly and safer alternative. To summarize, the goal was to understand how to pass from a proof of concept to a preparative method applicable to a wide range of linear olefins and to get more insights about the reactivity of the α-boryl radical and their α-iodoalkyl boronic esters precursors in ATRA reactions.

References

(1) Kumar, N.; Reddy, R. R.; Eghbarieh, N.; Masarwa, A. *Chem. Commun.* **2020**, *56*, 13–25.

(2) Grams, R. J.; Santos, W. L.; Scorei, I. R.; Abad-García, A.; Rosenblum, C. A.; Bita, A.; Cerecetto, H.; Viñas, C.; Soriano-Ursúa, M. A. *Chemical Reviews* **2024**, *124*, 2441–2511.

(3) Kulkarni, S.; Bhandary, D.; Singh, Y.; Monga, V.; Thareja, S. *Pharmacology & Therapeutics* **2023**, *251*, 108548.

(4) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Letters* **1979**, *20*, 3437–3440.

(5) André-Joyaux, E.; Kuzovlev, A.; Tappin, N. D. C.; Renaud, P. *Angewandte Chemie International Edition* **2020**, *59*, 13859–13864.

(6) Grotewold, J.; Lissi, E. A.; Scaiano, J. C. *J. Chem. Soc. B* **1971**, 1187–1191.

(7) Walton, J. C.; McCarroll, A. J.; Chen, Q.; Carboni, B.; Nziengui, R. *Journal of the American Chemical Society* **2000**, *122*, 5455–5463.

(8) Zipse, H. In *Radicals in Synthesis I*, Gansäuer, A., Ed.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2006, pp 163–189.

(9) Guennouni, N.; Lhermitte, F.; Cochard, S.; Carboni, B. *Tetrahedron* **1995**, *51*, 6999–7018.

(10) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc., Trans.* **1915**, *107*, 1080–1106.

(11) Batey, R. A.; Pedram, B.; Yong, K.; Baquer, G. *Tetrahedron Letters* **1996**, *37*, 6847–6850.

(12) Batey, R. A.; Smil, D. V. *Tetrahedron Letters* **1999**, *40*, 9183–9187.

(13) Fraind, A.; Turncliff, R.; Fox, T.; Sodano, J.; Ryzhkov, L. R. *Journal of Physical Organic Chemistry* **2011**, *24*, 809–820.

(14) Quiclet-Sire, B.; Zard, S. Z. *Journal of the American Chemical Society* **2015**, *137*, 6762–6765.

(15) LaPorte, A. J.; Feldner, J. E.; Spies, J. C.; Maher, T. J.; Burke, M. D. *Angewandte Chemie International Edition* **2023**, *62*, e202309566.

(16) Lo, J. C.; Kim, D.; Pan, C.-M.; Edwards, J. T.; Yabe, Y.; Gui, J.; Qin, T.; Gutiérrez, S.; Giacoboni, J.; Smith, M. W.; Holland, P. L.; Baran, P. S. *Journal of the American Chemical Society* **2017**, *139*, 2484–2503.

(17) Crossley, S. W. M.; Obradors, C.; Martinez, R. M.; Shenvi, R. A. *Chemical Reviews* **2016**, *116*, 8912–9000.

(18) Shi, S.; Salahi, F.; Vibbert, H. B.; Rahman, M.; Snyder, S. A.; Norton, J. R. *Angewandte Chemie International Edition* **2021**, *60*, 22678–22682.

(19) Matteson, D. S.; Mah, R. W. H. *Journal of the American Chemical Society* **1963**, *85*, 2599–2603.

(20) Lewis-Borrell, L.; Sneha, M.; Clark, I. P.; Fasano, V.; Noble, A.; Aggarwal, V. K.; Orr-Ewing, A. J. *Journal of the American Chemical Society* **2021**, *143*, 17191–17199.

(21) Silvi, M.; Sandford, C.; Aggarwal, V. K. *Journal of the American Chemical Society* **2017**, *139*, 5736–5739.

(22) Silvi, M.; Schrof, R.; Noble, A.; Aggarwal, V. K. *Chemistry – A European Journal* **2018**, *24*, 4279–4282.

(23) Tappin, N. D. C.; Gnägi-Lux, M.; Renaud, P. *Chemistry – A European Journal* **2018**, *24*, 11498–11502.

(24) Zhao, B.; Li, Z.; Wu, Y.; Wang, Y.; Qian, J.; Yuan, Y.; Shi, Z. *Angewandte Chemie International Edition* **2019**, *58*, 9448–9452.

(25) Kischkewitz, M.; Okamoto, K.; Mück-Lichtenfeld, C.; Studer, A. *Science* **2017**, *355*, 936–938.

(26) Wang, D.; Mück-Lichtenfeld, C.; Studer, A. *Journal of the American Chemical Society* **2019**, *141*, 14126–14130.

(27) Noble, A.; Mega, R. S.; Pflästerer, D.; Myers, E. L.; Aggarwal, V. K. *Angewandte Chemie International Edition* **2018**, *57*, 2155–2159.

(28) Shu, C.; Mega, R. S.; Andreassen, B. J.; Noble, A.; Aggarwal, V. K. *Angewandte Chemie International Edition* **2018**, *57*, 15430–15434.

(29) Wu, C.; Bao, Z.; Dou, B.; Wang, J. *Chemistry – A European Journal* **2021**, *27*, 2294–2298.

(30) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *Science* **1945**, *102*, 128–128.

(31) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, Publisher: American Chemical Society, 1721–1723.

(32) Wang, J.-S.; Matyjaszewski, K. *Journal of the American Chemical Society* **1995**, *117*, 5614–5615.

(33) Kharasch, M.; Skell, P.; Fisher, P. *Journal of the American Chemical Society* **1948**, *70*, 1055–1059.

(34) Dicks, A. P.; Hent, A., Green chemistry metrics : a guide to determining and evaluating process greenness, 1 online resource (viii, 90 pages) : illustrations vols.; SpringerBriefs in molecular science; Springer: Cham, 2014.

(35) Baciocchi, E.; Muraglia, E. *Tetrahedron Letters* **1994**, *35*, 2763–2766.

(36) Curran, D. P.; Bosch, E.; Kaplan, J.; Newcomb, M. *The Journal of Organic Chemistry* **1989**, *54*, 1826–1831.

(37) Curran, D. P.; Chen, M. H.; Spletzer, E.; Seong, C. M.; Chang, C. T. *Journal of the American Chemical Society* **1989**, *111*, 8872–8878.

(38) Curran, D. P.; Chen, M.-H. *Tetrahedron Letters* **1985**, *26*, 4991–4994.

(39) Curran, D. P.; Chen, M. H.; Kim, D. *Journal of the American Chemical Society* **1986**, *108*, 2489–2490.

(40) Panchaud, P.; Ollivier, C.; Renaud, P.; Zigmantas, S. *The Journal of Organic Chemistry* **2004**, *69*, 2755–2759.

(41) Tappin, N. D. C.; Renaud, P. *Advanced Synthesis & Catalysis* **2021**, *363*, 275–282.

(42) Pruteanu, Elena; Tappin, Nicholas D.C.; Gîrbu, Vladilena; Morarescu, Olga; Dénès, Fabrice; Kulciţki, Veaceslav; Renaud, Philippe *Synthesis* **2021**, *53*, 1247–1261.

(43) Nguyen, J. D.; Tucker, J. W.; Konieczynska, M. D.; Stephenson, C. R. J. *Journal of the American Chemical Society* **2011**, *133*, 4160–4163.

(44) Magagnano, G.; Gualandi, A.; Marchini, M.; Mengozzi, L.; Ceroni, P.; Cozzi, P. G. *Chem. Commun.* **2017**, *53*, 1591–1594.

(45) Rrapi, M.; Batsika, C. S.; Nikitas, N. F.; Tappin, N. D. C.; Triandafillidi, I.; Renaud, P.; Kokotos, C. G. *Chemistry – A European Journal* **2024**, *30*, e202400253.

(46) Yang, Z. Y.; Burton, D. J. *The Journal of Organic Chemistry* **1991**, *56*, 5125–5132.

(47) Metzger, J. O.; Mahler, R. *Angewandte Chemie International Edition in English* **1995**, *34*, 902–904.

(48) Huang, Q.; Michalland, J.; Zard, S. Z. *Angewandte Chemie International Edition* **2019**, *58*, 16936–16942.

(49) Simmons, H. E.; Smith, R. D. *Journal of the American Chemical Society* **1958**, *80*, 5323–5324.

(50) Li, L.; Wang, F.; Ni, C.; Hu, J. *Angewandte Chemie International Edition* **2013**, *52*, 12390–12394.

(51) Phipps, E. J. T.; Rovis, T. *Journal of the American Chemical Society* **2019**, *141*, 6807–6811.

(52) Phelan, J. P.; Lang, S. B.; Compton, J. S.; Kelly, C. B.; Dykstra, R.; Gutierrez, O.; Molander, G. A. *Journal of the American Chemical Society* **2018**, *140*, 8037–8047.

(53) Sakurai, S.; Inagaki, T.; Kodama, T.; Yamanaka, M.; Tobisu, M. *Journal of the American Chemical Society* **2022**, *144*, 1099–1105.

(54) Ni, J.; Xia, X.; Zheng, W.-F.; Wang, Z. *Journal of the American Chemical Society* **2022**, *144*, 7889–7900.

(55) Tappin, N. D. C.; Michalska, W.; Rohrbach, S.; Renaud, P. *Angewandte Chemie International Edition* **2019**, *58*, 14240–14244.

(56) Benoit, G.; Charette, A. B. *Journal of the American Chemical Society* **2017**, *139*, 1364–1367.

(57) Murai, M.; Mizuta, C.; Taniguchi, R.; Takai, K. *Organic Letters* **2017**, *19*, 6104–6107.

(58) Del Hoyo, A. M.; Herraiz, A. G.; Suero, M. G. *Angewandte Chemie International Edition* **2017**, *56*, 1610–1613.

(59) Del Hoyo, A. M.; García Suero, M. *European Journal of Organic Chemistry* **2017**, *2017*, 2122–2125.

(60) Sayes, M.; Benoit, G.; Charette, A. B. *Angewandte Chemie International Edition* **2018**, *57*, 13514–13518.

(61) Thai-Savard, L.; Sayes, M.; Perreault-Dufour, J.; Hong, G.; Wells, L. A.; Kozlowski, M. C.; Charette, A. B. *The Journal of Organic Chemistry* **2023**, *88*, 1515–1521.

(62) Hu, J.; Tang, M.; Wang, J.; Wu, Z.; Friedrich, A.; Marder, T. B. *Angewandte Chemie International Edition* **2023**, *62*, e202305175.

(63) Marotta, A.; Fang, H.; Adams, C. E.; Sun Marcus, K.; Daniliuc, C. G.; Molloy, J. J. *Angewandte Chemie International Edition* **2023**, *62*, e202307540.

(64) Hao, W.; Harenberg, J. H.; Wu, X.; MacMillan, S. N.; Lin, S. *Journal of the American Chemical Society* **2018**, *140*, 3514–3517.

(65) Archer, G.; Cavalère, P.; Médebielle, M.; Merad, J. *Angewandte Chemie International Edition* **2022**, *61*, e202205596.

(66) Cirule, D.; Dénès, F.; Gnägi-Lux, M.; Rohrbach, S.; Renaud, P. *Advanced Synthesis & Catalysis* **2024**, *366*, 1366–1374.

(67) Cirule, D.; Dénès, F.; Renaud, P. *Advanced Synthesis & Catalysis* **2024**, adsc.202400340.

(68) Fisch, A. G. In *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, Ltd: 2019, pp 1–22.

(69) Marek, I. *Beilstein Journal of Organic Chemistry* **2013**, *9*, 234–235.

(70) Terao, J.; Watanabe, T.; Saito, K.; Kambe, N.; Sonoda, N. *Tetrahedron Letters* **1998**, *39*, 9201–9204.

(71) Sadow, A. D.; Tilley, T. D. *Journal of the American Chemical Society* **2003**, *125*, 7971–7977.

(72) Fontaine, F.-G.; Tilley, T. D. *Organometallics* **2005**, *24*, 4340–4342.

(73) Dao, H. T.; Li, C.; Michaudel, Q.; Maxwell, B. D.; Baran, P. S. *Journal of the American Chemical Society* **2015**, *137*, 8046–8049.

(74) Green, S. A.; Huffman, T. R.; McCourt, R. O.; van der Puyl, V.; Shenvi, R. A. *Journal of the American Chemical Society* **2019**, *141*, 7709–7714.

(75) Filippini, G.; Silvi, M.; Melchiorre, P. *Angewandte Chemie International Edition* **2017**, *56*, 4447–4451.

(76) Hu, A.; Guo, J.-J.; Pan, H.; Zuo, Z. *Science* **2018**, *361*, 668–672.

(77) Laudadio, G.; Deng, Y.; Wal, K. v. d.; Ravelli, D.; Nuño, M.; Fagnoni, M.; Guthrie, D.; Sun, Y.; Noël, T. *Science* **2020**, *369*, 92–96.

(78) Zhu, Q.; Nocera, D. G. *Journal of the American Chemical Society* **2020**, *142*, 17913–17918.

(79) Clausen, F.; Kischkewitz, M.; Bergander, K.; Studer, A. *Chem. Sci.* **2019**, *10*, 6210–6214.

(80) Roy, C. D.; Brown, H. C. *Monatshefte für Chemie - Chemical Monthly* **2007**, *138*, 879–887.

(81) Roy, C. D.; Brown, H. C. *Journal of Organometallic Chemistry* **2007**, *692*, 784–790.

2 Synthesis and Isolation of 1,3-iodopinacol boronic esters via intermolecular Atom Transfer Radical Addition of α-boryl radicals

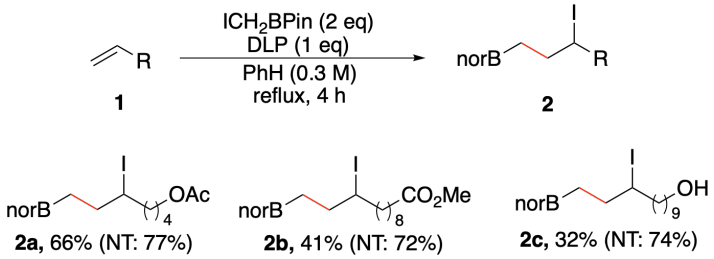
This chapter will include the initial results obtained on Intermolecular Atom Transfer Radical Addition of α-boryl radicals, based on what was previously reported by Dr. Nicholas Tappin and Dr. Emy André-Joyaux. Because of the moderate results obtained and of the willing to study the reactivity of α-boryl radicals in a more systematic way (see Chapter 3), the project was then continued by Dr. Yanis Lazib and Dr. Ruairí McCourt.

2.1 Initial results

Several points still needed to be clarified before performing a full scope of the 1,3-iodonorbornene boronic esters.

- Need of solvent switch because benzene is an harmful solvent.
- Improving purification conditions: a big amount of by-products coming from the thermal decomposition of DLP were always present in the crude mixture and they caused the isolation of the products to be difficult.
- Develop one-pot protocols for the synthesis of more stable post-functionalized compounds originated from a common 1,3-iodonorbornene boronic ester intermediate.

Initially, the previously reported results were tried to be reproduced. However, as shown in Scheme 2.1, the obtained yields are very far to what previously reported. This might be explained by differences in purifying the compounds or executing the reactions. Moreover, DLP initiation proved to give better results than DTBHN initiation.



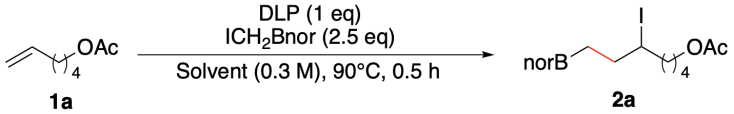
Scheme 2.1: Initial results compared with what previously reported (yield of Dr.Tappin in brackets). Isolated yields.

In order to better understand the ATRA step, to improve the reaction conditions and to obtain better isolated yields, an extensive optimization of the reaction condition was then conducted.

2.2 Optimization of ATRA reaction

2.2.1 Solvent screening

It's well known that benzene is considered as an harmful solvent. In fact, prolonged exposure to benzene can lead to a decrease in red blood cells productions, causing thus anemia diseases.[1] Moreover, it can affect as well the good functioning of the immune system. It was thus necessary to find a better solvent for the atom-transfer reaction step. Table 2.1 summarizes the obtained results:



1a **2a**

Entry	Solvent	Isolated yield
1	Benzene	59%
2	Heptane	53%
3	Cyclohexane	43%
4	Toluene	43%
5	Trifluorotoluene (TFT)	65%
6	Chlorobenzene	54%
7	Ethyl Acetate	55%

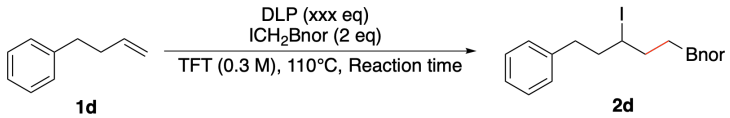
Table 2.1: Solvent screening for the optimization of the ATRA reaction.

Initial experiments were conducted with non-polar solvents such as heptane, cyclohexane and toluene which gave similar results (*Entries 2-4*). Switching to TFT significantly increased the reaction efficiency and up to 65% isolated yield was obtained. Increasing the polarity of the solvent by using chlorobenzene or ethyl acetate as solvents (*Entries 6-7*) did not led to a further improvement in yield. TFT was then used for the round of optimization, which has the aim of looking for the optimum amount of DLP for the reaction.

2.2.2 Optimization of the equivalents of initiator (DLP)

Widely used in industry for his low cost and easiness to handle, Dilauroyl peroxide (DLP) (Luperox ©) is one the most used thermal initiators for radical reactions. As we sought to develop an easy and cheap protocol for ATRA reactions, this was our initiator of choice for initial investigations. It has, as already anticipated before, a major drawback: the crude mixtures are always contaminated by different by-products coming from radical-radical recombination or ionic decomposition which behave similarly to the desired product on column chromatography.[2] Previously, 1 equivalent of DLP was used to perform ATRA reactions. However, other reports present in the literature show that this amount can be reduced.[3] We wanted then to find the optimum amount of initiator to facilitate the purification step, yet having a good yield of the desired

1,3-iodonorbornene boronic ester compound. For this optimization, NMR yields using internal standard were taken to speed up the process. Moreover, we changed substrate from hexenyl acetate to but-3-en-1-ylbenzene **1d** because the calculation of the NMR yield was easier. The reactions were performed like before at refluxing conditions, so, when TFT was used as solvent, the reaction temperature was raised to 110 °C. As shown in table 2.2, 1 eq of DLP gave the best NMR yield (*Entry 1*). However, it was decided to use 0.5 eq of initiator (*Entry 2*) because the yield was still acceptable and we expected less amount of by-products resulting from initiator decomposition and radical-radical recombination. Interestingly, after 0.5h of reaction, a yield of 54% was found, meaning that the ATRA process is very fast (*Entry 3*). Both using less equivalents of initiator (*Entry 4)* or adding it portionwise (*Entry 5 and 6)* did not result in an improved yield.



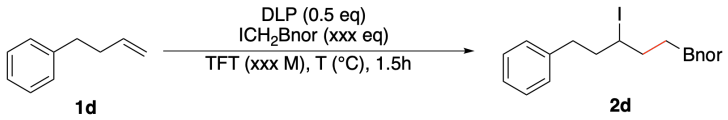
1d **2d**

Entry	DLP (xxx eq)	Reaction time (h)	NMR yield[a]	Amount of **1d**
1	1 eq	1h30	69%	9%
2	0.5 eq	1h30	64%	25%
3	0.5 eq	0.5 h	54%	16%
4	0.2 eq	0.5 h	26%	52%
5	0.2 eq x2 (second addition after 1h30)	2 h	35%	40%
6	0.5 eq (slow addition in three portions over 1h30)	1h30	60%	16%

Table 2.2: Table of optimization of the amount of the equivalents of initiator. [a]1,3,5-trimethoxybenzene used as internal standard

2.2.3 Optimization of other parameters (Radical precursor, temperature and concentration).

To finish with the optimization of the reaction, the following parameters were as well checked (Table 2.3):

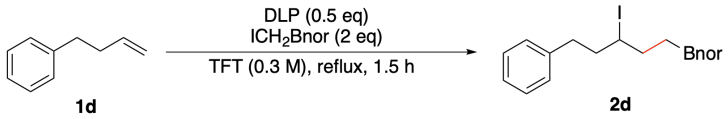


Entry	ICH_2Bnor (xxx eq)	TFT (xxx M)	T (°C)	NMR yield[a]	Amount of **1d**
1	2.5	0.3 M	reflux (110 °C)	60%	34%
2	2	0.3 M	reflux (110 °C)	64%	25%
3	1.5	0.3 M	reflux (110 °C)	57%	14%
4	2	0.06 M	reflux (110 °C)	39%	41%
5	2	0.5 M	reflux (110 °C)	40%	30%
6	2	0.3 M	90 °C	61%	n/d
7	2	0.3 M	100 °C	59%	n/d

Table 2.3: Table of optimization of other reactions parameters. [a]1,3,5-trimethoxybenzene used as internal standard.

1. **The equivalents of radical precursor** ICH_2Bnor were reduced from 2.5 (*Entry 1*) to **2 equivalents** (*Entry 2*), the yield remaining always in the same range. When lower amounts of radical precursor were used (*Entry 3*), the yield of the desired ATRA compound was lower.
2. **The concentration of the reaction mixture** was also checked and **0.3 M** (*Entry 2*) proved to be the right one. Neither less concentrated (0.06 M) (*Entry 4*) nor more concentrated (0.5 M) (*Entry 5*) conditions improved the yield of the reaction.
3. **110 °C** was found to be the best temperature, giving the highest yield. By lower temperatures (*Entry 6 and 7*), slightly decreased yields were found.

At the end of the optimization, the conditions displayed in Scheme 2.2 were found:



Scheme 2.2: Final optimized conditions for ATRA reaction.

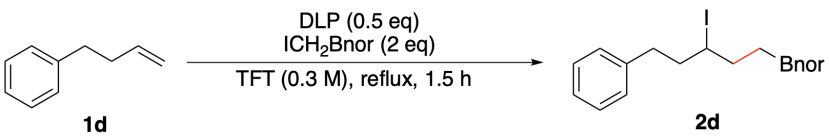
Before starting with the scope, it was important to understand how these compounds can be purified rapidly to minimize yield losses during column chromatography. For this reason, the purification step was as well studied in details.

2.3 Development of a work-up/purification strategy to purify 1,3-iodonorbornene boronic esters

As already mentioned, Dr.Tappin and Dr.André-Joyaux decided to use iodomethylene norbornene boronic ester as radical precursor because the resulting ATRA compounds were more stable and, as a result, the isolated yield was closer to the NMR yield determined by using an internal standard. One of the initial observations made by them is that the choice of the right type of silica is very important. These compounds being unstable under acidic conditions, it is important to choose a silica-gel which is less acidic. Dr.Tappin tried different commercially available sources of SiO_2 and he found that the use of Macherey&Nagel silica led to a minimum yield loss during column chromatography. Sigma-Aldrich silica resulted in complete decomposition of the desired product and Silicycle silica resulted in great product loss. Moreover, he observed a greater yield loss when the purification step was taking too much time. For this reason, it is very important to use the right amount of silica for the column packing to keep the purification step time to 15 minutes, avoiding thus huge yield losses. Specifically, after having identified the right solvent for the flash column chromatography (Rf of the desired product $\sim$0.3), the mass of the crude mixture to engage in the purification step was multiplied by a factor of 0.5 to 0.9, depending the easiness of the separation.

In addition to that, the ATRA compounds are secondary iodides and it is thus critical to perform all manipulations without light to prevent side-reactions such as elimination.

Another important feature to consider when purifying theses compounds is that the excess of the radical precursor ICH_2Bnor interacts badly with the silica, leading to a 'tailing spot' which can be visible on TLC. As a result, the final compounds are always contaminated by 10-20% and another round of purification will be then required. To solve this issue, it was thought to introduce a work-up strategy using a nucleophile with the aim of substituting the I atom of the radical precursor with a -OH or -NH_2 group. This compound is now supposed to be very polar and thus will not be recovered together with the desired apolar 1,3-iodonorbornene boronic esters. Two nucleophiles were then employed in the work-up, both as an aqueous solution which was used to wash the organic phase during the work-up: 1M NaOH and 25% NH_4OH solution. The results can be found in Table 2.4:



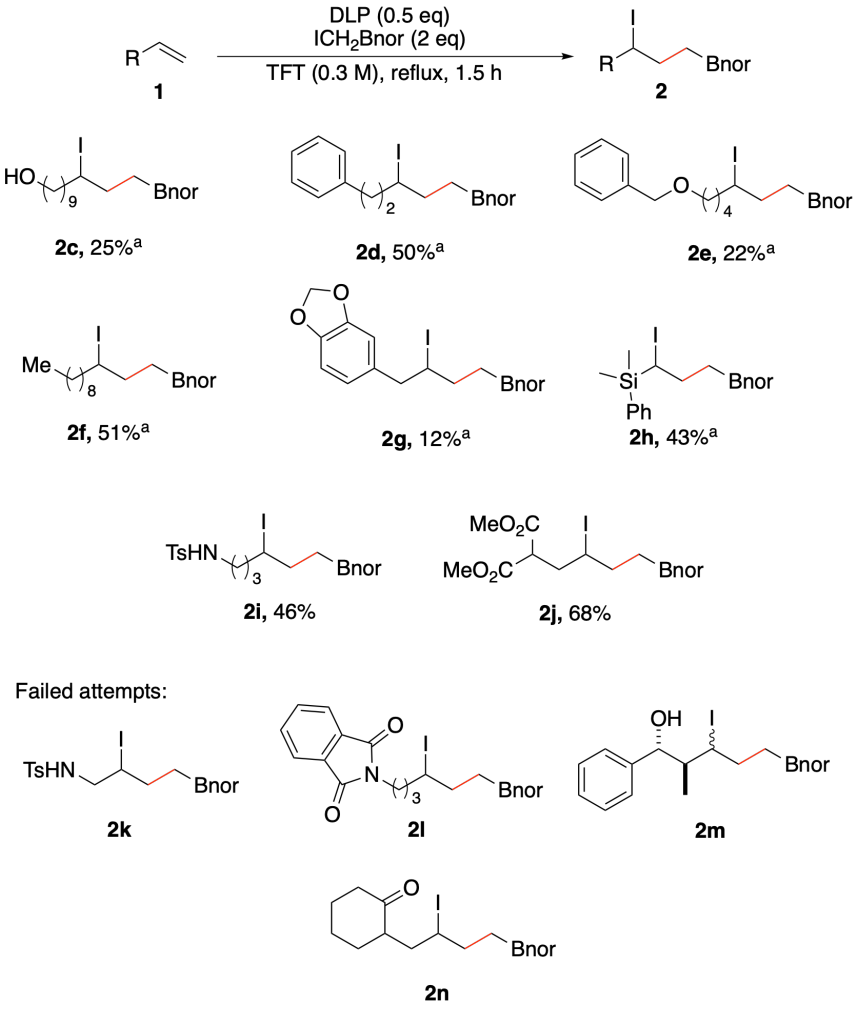
Entry	Work-up	Yield
1	/	55%[a], 50%[b]
2	1M NaOH	50%[b]
3	25% NH_4OH	50%[b]

Table 2.4: Optimization of the work-up procedure to facilitate the purification step. [a] NMR yield using 1,3,5-trimethoxybenzene used as internal standard; [b] isolated yield

The work-up procedure has no impact on the yield of the desired compound and simplifies the purification part. In *Entry 1*, the isolated yield of 50% was found after three FCC purifications, while in *Entry 2 and 3* the purification proceeds smoothly and the desired compound is recovered pure after one round of column chromatography.

2.4 Substrate scope

Based on the previous discussed observations, a substrate scope with the optimized conditions was then performed (Scheme 2.3):



Scheme 2.3: Substrate scope of 1,3-iodonorbornene boronic esters using optimized conditions. Isolated yields. [a]Basic work-up with 1M NaOH performed.

In general, the yields range from moderate to low. Surprisingly, the highest yield was obtained when allyl malonate was used, despite the presence of a very acidic proton (**2j**). Together with yield losses during column chromatography, another possible reason for low yields are intramolecular HAT processes which might take place as in the case of **2e**. It is, however, hard to determine a general tendency of functional group tolerance, as it looks more that the method is very substrate dependant.

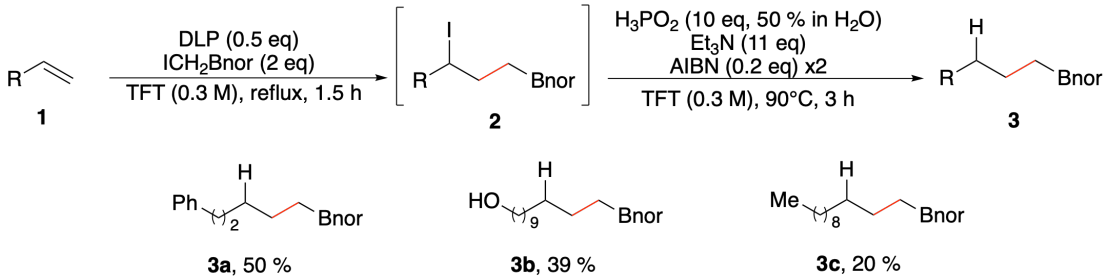
Unsatisfied with these results, we decided to go back to the initial strategy and develop two protocols for in-situ functionalization of the 1,3-iodonorbornene boronic esters intermediates. The advantage of this approach is that the new products will be much more stable on silica,

preventing thus a big loss in isolated yields.

2.5 One-pot ATRA and functionalizations protocols

2.5.1 One-pot ATRA + deiodination (Hydroborylmethylation)

The first post-functionalization that we wanted to implement was the removal of the iodine atom using Barton's deiodination conditions (H_3PO_2, Et_3N, AIBN).[4] These conditions are known to be very mild and are a cheap and safe alternative to the more frequently employed Bu_3SnH/AIBN reduction protocol. In this case, hypophosphorous acid acts as a hydrogen atom donor and thus reducing agent while Et_3N is needed to counterbalance the acidity of the acid and to allow the reaction on acid labile substrates. 1,3-iodonorbornene boronic esters being sensitive to acidic conditions, this was our method of choice. We thus conducted a small scope of ATRA+deiodination reaction (Scheme 2.4). However, disappointing results were as well obtained for this transformation. For this reason, we decided to get rid of the boronic ester moiety via sodium borate oxidation and thus develop a one-pot protocol for iodohydroxymethylation.



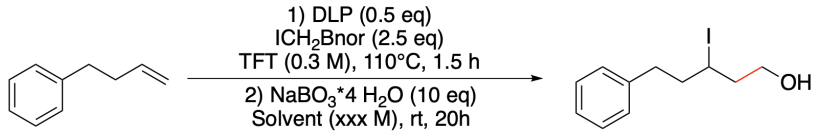
Scheme 2.4: Substrate scope of hydroborylmethylation. Isolated yields.

2.5.2 One-pot ATRA + oxidation (Iodohydroxymethylation)

We then turned our attention to optimize conditions for the synthesis of 1,3-iodoalcohols. We believed that the removal of the boronic ester part could lead to better results since the new products should not be unstable on silica. We thus first optimized the oxidation reaction using sodium perborate, $NaBO_3$. This reagent, dissolved in water, is known to be a source of peroxides which can be used to oxidize boronic esters. It is thus a mild and selective method which is tolerant towards all functional groups.[5]

First, the second step of the ATRA+oxidation sequence was optimized. As shown in Table 2.4, **6a** is not formed when the solvent is TFT:H_2O (*Entry 1)* and this is due to the fact that the mixture is completely heterogeneous. For this reason, it was attempted to add a phase-transfer catalyst to promote the reaction between the two phases. Although the addition of tetrabutylammonium iodide (TBAI) (*Entry 2-3)* or tetrabutylammonium periodate (TBAP) (*Entry 4)* slightly improved the yield of the reaction, we decided to try to perform a solvent switch from TFT to THF:H_2O, which is the solvent reported for this reaction. The yield improved to 47%, meaning that a water-miscible solvent is required for the reaction (*Entry 5)*. In the end, we decided to add directly THF and H_2O after the ATRA reaction (which is performed in TFT) and then continue with the

oxidation step. Pleasingly, the reaction worked well, furnishing 53% of the desired compound (*Entry 6)*. The yield of the ATRA intermediate being 50% (Section 2.4), the oxidation reaction works nearly quantitative.

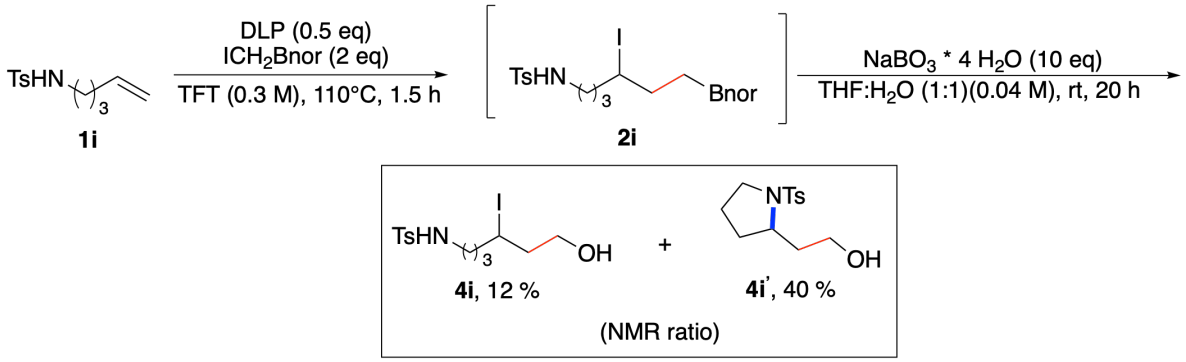


1d **4d**

Entry	Solvent	Additives	Yield	Comments
1	TFT:H_2O (1:1) (0.04 M)	/	Traces	Acidic work-up performed
2	TFT:H_2O (1:1) (0.04 M)	0.2 eq TBAI	23%	Acidic work-up performed
3	TFT:H_2O (1:1) (0.04 M)	0.5 eq TBAI	33%	
4	TFT:H_2O (1:1) (0.04 M)	0.5 eq TBAP	17%	
5	THF:H_2O (1:1) (0.04 M)	/	47%	Solvent switch from TFT to THF:H_2O
6	TFT:THF:H_2O (0.04 M)	/	53%	No evaporation of TFT

Table 2.5: Optimization of oxidation conditions for one-pot ATRA-oxidation protocol. Isolated yields.

A second example of iodohydroxymethylation was performed on 4-methyl-*N*-pent-4-enyl-benzenesulfonamide (Scheme 2.5). Notably, **4i** and **4i'** were recovered as a *mixture* after the ATRA+-oxidation sequence. This pathway, which was not further explored, can represent an easy access to nitrogen containing heterocycles such as tosylpyrrolidines or tosylpiperidines. This core is present in a lot of natural compounds and can thus have an important synthetic interest.



Scheme 2.5: Iodohydroxymethylation of 4-methyl-*N*-pent-4-enyl-benzenesulfonamide. Isolated yield.

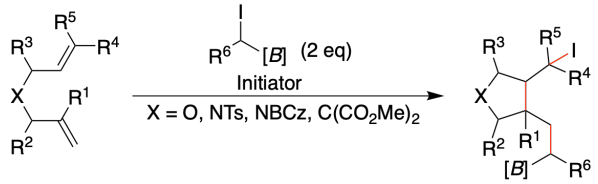
At this point of the research, we decided to stop the Intermolecular Atom Transfer Radical Addition of α-boryl radicals project because we were interested in extensively studying the reactivity of these radicals and, in particular, the Iodine Atom Transfer process when iodomethylenenorbornene boronic ester is used as a radical precursor. This work will represent the core of this PhD Thesis and will be described in Chapter 3.

2.6 Conclusion and Outlook

The attempt to perform intermolecular Atom-Transfer Radical Addition of α-boryl radicals on unactivated olefines was discussed. The work was started by two former PhD Students of the group and had as main goal to develop a new *anti*-Markvonikov hydromethylation (hydroalkylation) strategy. The sequence consisted of two steps: the first one is the synthesis of 1,3-iodonorbornene boronic ester and the second is the complete reduction of this intermediate using Et_3B and TBC.

Due to unsuccessful reproducibility of previously reported results, the ATRA step was studied more carefully and new conditions for this reaction were found. However, the method did not give excellent yields. This might be due to the instability of the final compounds on silica, which leads to yield losses during purification. To facilitate this step, a work-up strategy using 1M NaOH was developed to remove the excess radical precursor in the crude mixture, enabling easier and faster purifications. Since the results were still unsatisfactory, two one-pot ATRA+post-functionalizations protocols were developed. However, the observed yields did not improve.

In order to better understand the ATRA reaction when iodomethylene boronic esters are used as radical precursors, we decided to study a new reaction on a diene. As shown in Scheme 2.6, this system will enable us to end-up with different radicals and thus study the Iodine-Atom Transfer step. This topic will be discussed in Chapter 3.



Scheme 2.6: ATRAc strategy to form 1,5-iodoboronic esters and model to study the Iodine-Atom Transfer Reaction.

The Intermolecular Atom-Transfer Radical Addition project was then continued by Dr.Yanis Lazib who found better reaction conditions using Dicumyl peroxide as radical initiator. He performed a small optimization of the method and a substrate scope of the reaction (including some post-functionalizations). Currently, Dr. Ruairí McCourt is carrying on further studies using photoredox conditions to perform ATRA reaction using bromomethylene boronic esters. We speculated that 1,3-bromomethylene boronic esters are more stable than the corresponding iodides during purification, therefore better yields are expected.

References

(1) Bailer, A. J.; Hoel, D. G. *Environmental Health Perspectives* **1989**, *82*, 177–184.

(2) Fraind, A.; Turncliff, R.; Fox, T.; Sodano, J.; Ryzhkov, L. R. *Journal of Physical Organic Chemistry* **2011**, *24*, 809–820.

(3) Huang, Q.; Michalland, J.; Zard, S. Z. *Angewandte Chemie International Edition* **2019**, *58*, 16936–16942.

(4) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C. *The Journal of Organic Chemistry* **1993**, *58*, 6838–6842.

(5) McKillop, A.; Sanderson, W. R. *Tetrahedron* **1995**, *51*, 6145–6166.

2.7 Experimental Section

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. A liquid Nitrogen/ethanol bath was used to reach a temperature of -100 °C. Macherey-Nagel Silica 60, 0.04–0.063 mm silica gel was always used for flash column chromatography: it proved to be the best one compared to others because the iodoboronic esters were less prone to decomposition. In some specific cases, Macherey-Nagel Silica 60, 0.015-0.04 mm was used to achieve better purification and it will be indicated as **Finer silica**. Thin layer chromatography (TLC) was performed on Macherey-Nagel SIL G/UV254, 0.25 mm analytical plates. Visualization was done 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); or $H_3PMo_{12}O_{40}$ dissolved in 100 mL ethanol and subsequent heating. Anhydrous sodium sulphate was used as drying reagent.

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 and/or stored over 3Å molecular sieves. Solvents for extractions (Et_2O, *n*-pentane, CH_2Cl_2, AcOEt, *n*-heptanes, TBME) and flash column chromatography were of technical grade and distilled prior to use. Commercially available Dilauroyl peroxide (Luperox © LP, Lauroyl peroxide, Sigma Aldrich – 290875) was used as initiator for the radical reactions. Commercial 1,3,5-trimethoxybenzene (0.5 eq) (Sigma-Aldrich, Standard for quantitative NMR, Trace **CERT**© - Art. 74599) was used as external standard for NMR yields.

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 B*ruker Avance IIIHD-400* or a *Bruker Avance II-400 spectrometer 5* (^1H: 400 MHz; ^{13}C: 101 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 constants (*J*) are 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. Due to coupling to the quadrupolar ^{11}B and ^{10}B

nuclei, the carbons linked to boron atoms give a broad signal in ^{13}C NMR, and are generally not detected.

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.

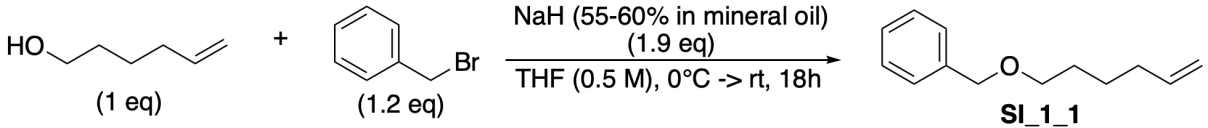
Low resolution mass spectra were recorded on a *Waters Micromass Autospec Q* mass spectrometer in EI mode at 70 eV or were taken from GC-MS analyses performed on a *Finnigan Trace GC-MS* (quadrupole mass analyzer using EI mode at 70 eV) fitted with a Macherey-Nagel Optima delta-3-0.25 μm capillary column (20 m, 0.25 mm); gas carrier: He 1.4 mL/min; injector: 220 °C split mode. GC analyses were performed on a *ThermoFisher Trace GC* ultra, fitted with a chiral Restek Rt®-bDEXm capillary column (20 m, 0.25 mm ID, 0.25 μm), helium as carrier gas (1.2 mL/min), and FID (290 °C base temperature, 35 mL/min H_2, 350 mL/min air); temperature gradients are indicated for each compound.

HRMS analyses and accurate mass determinations were performed on a *Thermo Scientific LTQ Orbitrap XL* mass spectrometer using ESI mode (positive ion mode).

Synthesis

Preparation of radical traps

Hex-5-enoxymethylbenzene (SI_1_1)



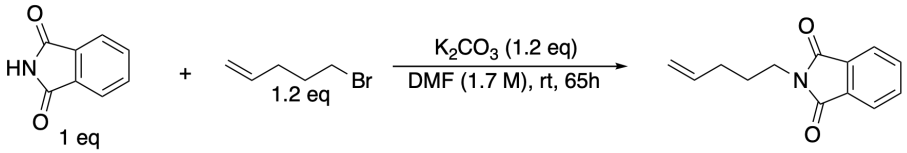
SI_1_1
Chemical Formula: $C_{13}H_{18}O$
Exact Mass: 190.1358

To a suspension of NaH (3.96 g, 55.0 % dispersion in mineral oil, 94.8 mmol) in THF (100 mL) at 0 °C was added dropwise hex-5-en-1-ol (6.00 mL, 49.9 mmol). After 5 min, bromomethylbenzene (7.12 mL, 59.9 mmol) was added dropwise and the reaction mixture allowed to warm to RT. The reaction mixture was stirred at rt for 16h, then quenched by slow addition of MeOH (5 mL) at 0°C, followed by addition of saturated aqueous NH_4Cl (100 mL). The mixture turned from milky light orange to milky yellow (presence of a solid). After filtration over Celite®, the organics were extracted with Et_2O (3 x 50 mL), washed with H_2O (50 mL), brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography (0-2-5% EtOAc:heptane) provided the desired compound **SI_1_1** (5.32 g, 27.9 mmol, yield: 56 %).

Colorless oil; Rf: 0.79 (9:1 heptane:EA); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.34–7.11 (m, 5H), 5.72 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 4.98–4.80 (m, 2H), 4.41 (s, 2H), 3.39 (t, J = 6.4 Hz, 2H), 2.02–1.94 (m, 2H), 1.61–1.49 (m, 2H), 1.46-1.33 (m, 2H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 138.79, 138.75, 128.4 (2x CH), 127.6 (2x CH), 127.5 (CH), 114.6 (CH_2), 72.9 (CH_2), 70.3 (CH_2), 33.6 (CH_2), 29.3 (CH_2), 25.6 (CH_3).

The physical and spectral data are in accordance with literature data:
Florence, G. J.; Fraser, A. L.; Gould, E. R.; King, E. F. B.; Menzies, S. K.; Morris, J. C.; Tulloch, L. B.; Smith, T. K. *ChemMedChem* **2014**, *9* (11), 2548–2556.

2-(Pent-4-en-1-yl)isoindoline-1,3-dione (SI_1_2)



SI_1_2
Chemical Formula: $C_{13}H_{13}NO_2$
Exact Mass: 215.0946

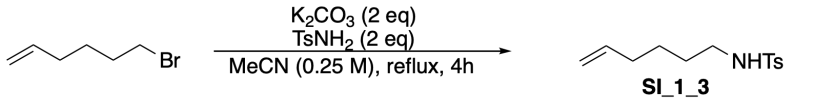
A 100 mL flask was charged with isoindoline-1,3-dione (5.88 g, 40.0 mmol) and N,N-Dimethylformamide (23.5 mL, 1.7 M). K_2CO_3 (6.63 g, 48.0 mmol) was then added portion wise. The

colour of the initial white suspension turned from white to yellow. After 5 minutes, 5-bromopent-1-ene (5.69 mL, 48.0 mmol) was added dropwise and the suspension became more whitish. The reaction mixture was stirred at rt for 65h. It was partitioned between EtOAc (50 mL) and H_2O (50 mL). The phases were separated and the aqueous layer was extracted with EtOAc (3 x 20mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, and concentrated under reduced pressure to afford a yellow oil. Purification by flash column chromatography (0-3-10% EtOAc: heptane) provided the desired product **SI_1_2** (7.98 g, 37.1 mmol, yield: 93 %).

Colorless oil; Rf: 0.34 (9:1 heptane:EA); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.83-7.77 (m, 2H), 7.71-7.65 (m, 2H), 5.76 (ddt, *J* = 16.8, 10.1, 6.5 Hz, 1H), 5.021 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.943 (dq, *J* = 10.1, 1.5 Hz, 1H), 3.69-3.34 (m, 2H), 2.12 – 2.01 (m, 2H), 1.81 – 1.65 (m, 2H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 168.3 (2x Cq), 137.3 (2x Cq), 133.8 (2xCH), 132.1 (CH), 123.1 (2x CH), 115.3 (CH_2), 37.5 (CH_2), 31.0 (CH_2), 27.6 (CH_2).

The physical and spectral data are in accordance with literature data:
Liu, R.; Wei, Z.; Wang, J.; Liu, Y.; Xue, H. *Chemical Communications* **2020**, *56* (37), 5038–5041.

4-Methyl-N-pent-4-enyl-benzenesulfonamide (SI_1_3)



SI_1_3
Chemical Formula: $C_{13}H_{19}NO_2S$
Exact Mass: 253.1136

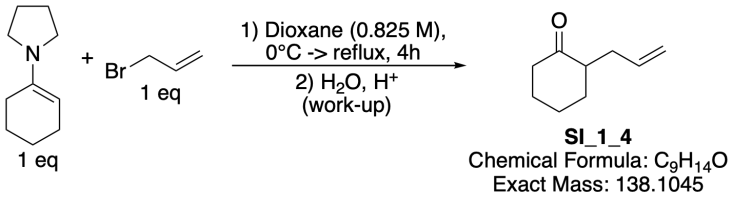
To a solution of 5-bromopent-1-ene (1.42 mL, 12.0 mmol) in acetonitrile (40 mL, 0.3 M) were added K_2CO_3 (3.32 g, 24.0 mmol) and p-toluenesulfonamide (4.11 g, 24.0 mmol). The reaction mixture was heated to reflux for 4 hours. The reaction mixture was filtrated through Celite® and concentrated under reduced pressure to afford a yellow oil. Purification by flash column chromatography (heptane: EA 9:1) provided the desired compound 4-methyl-N-pent-4-enyl-benzenesulfonamide (2.96 g, 12.4 mmol, quant).

Colorless oil; Rf: 0.10 (9:1 heptane:EA); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.77–7.71 (m, 2H), 7.33–7.28 (m, 2H), 5.70 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.03–4.89 (m, 2H), 4.62 (t, *J* = 6.2 Hz, 1H), 2.94 (q, *J* = 6.9 Hz, 2H), 2.42 (s, 3H), 2.04 (dtt, *J* = 7.9, 6.7, 1.4 Hz, 2H), 1.56 (p, *J* = 7.1 Hz, 2H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 143.5 (Cq), 137.4 (CH), 137.1 (Cq), 129.7 (2x CH), 127.1 (2x CH), 115.7 (CH_2), 42.8 (CH_2), 30.8 (CH_2), 28.8 (CH_2), 21.6 (CH_3).

The physical and spectral data are in accordance with literature data:

Della-Felice, F.; Zanini, M.; Jie, X.; Tan, E.; Echavarren, A. M. *Angewandte Chemie* **2021**, *60* (11), 5693–5698.

2-Allylcyclohexanone (SI_1_4)



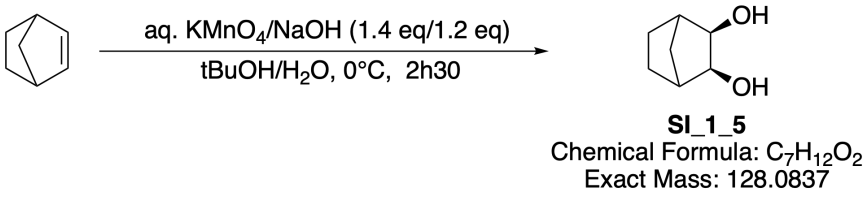
To a stirred solution of 1-(cyclohexen-1-yl)pyrrolidine (4.83 mL, 30.0 mmol) in anhydrous 1,4-dioxane (18 mL) at 0 °C was added dropwise a mixture of 3-bromoprop-1-ene (2.60 mL, 30.0 mmol) in anhydrous 1,4-dioxane (18 mL, 0.825 M). The reaction mixture was refluxed for 4 h. Water (20 mL) was added and the reaction mixture was stirred at reflux for an additional 1 h reflux. The reaction mixture was then concentrated slowly under reduced pressure. The residue was dissolved in EtOAc (40 mL) and treated with 4M HCl (40 mL). The phases were separated, and the aqueous layer was extracted three times with EtOAc (3 x 10 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated to afford a green oil. Purification by flash column chromatography (Heptane:EtOAc 95:5) provided 2-allylcyclohexanone as desired compound (1.5 g, 10.8 mmol, yield: 36 %).

Colourless oil; Rf: 0.4 (9:1 heptane:EA); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 5.86 – 5.66 (m, 1H), 5.08 – 4.92 (m, 2H), 2.53 (dddt, *J* = 14.6, 6.6, 5.4, 1.5 Hz, 1H), 2.43 – 2.23 (m, 3H), 2.17 – 2.00 (m, 2H), 1.96 (ddt, *J* = 14.3, 7.7, 1.2 Hz, 1H), 1.85 (qdd, *J* = 6.5, 3.0, 1.7 Hz, 1H), 1.74 – 1.56 (m, 2H), 1.35 (dddd, *J* = 15.4, 13.1, 8.4, 3.6 Hz, 1H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 212.5 (Cq), 136.5 (CH), 116.2 (CH_2), 50.3 (CH), 42.1 (CH_2), 33.8 (CH_2), 33.4 (CH_2), 27.9 (CH_2), 25.0 (CH_2).

The physical and spectral data are in accordance with literature data:
Özdemirhan, D.; Sarıçelik, Ö. *Tetrahedron: Asymmetry* **2017**, *28* (1), 118–124.

Preparation of radical precursors

(2R,3S)-norbornane-2,3-diol (SI_1_5)

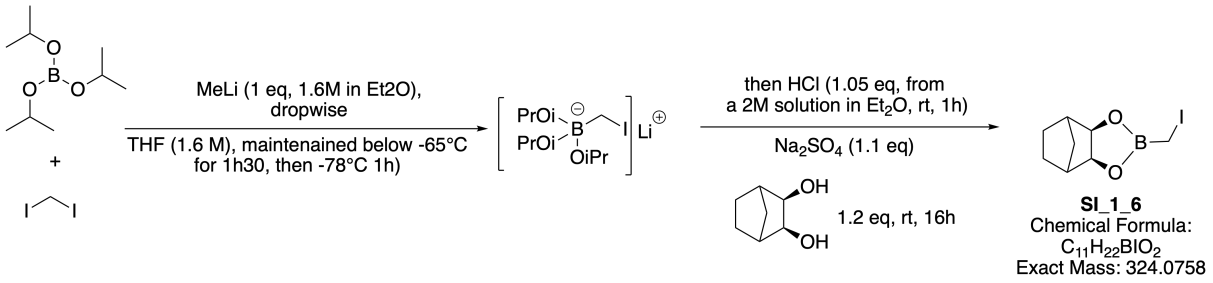


A cold mixture of $KMnO_4$ (24.0 g, 0.15 mmol, 1.4 eq.) and NaOH (5.22 g, 0.13 mmol, 1.2 eq.) in water (500 mL) was added dropwise (over 45 min using a dropping funnel) to a solution of norbornene (10.0 g, 0.11 mmol, 1.0 eq.) in t-BuOH (400 mL) and water (100 mL) at -10 °C (ice-salt bath). After the addition, the reaction mixture was stirred for 1h at the same temperature. It was then quenched with a saturated aqueous solution of sodium metabisulphite ($Na_2S_20_5$) (300 mL) until the solution turned colorless. The resulting mixture was filtered and t-BuOH was evaporated under reduced pressure. The remaining aqueous solution was extracted with EtOAc (6 × 250 mL). The organic layer was then washed with brine (200 mL), dried over anh. Na_2SO_4, filtered and concentrated under reduced pressure to give (2R,3S)-norbornane-2,3-diol (7.48 g, 58.4 mmol, yield: 55 %) which was used for the next step without further purification.

White solid; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 3.69 (d, J = 1.7 Hz, 2H), 2.39 (s, 3H), 2.14 (dq, J = 3.2, 1.6 Hz, 2H), 1.77 (dt, J = 10.4, 2.0 Hz, 1H), 1.55–1.35 (m, 2H), 1.17–0.95 (m, 3H).

The physical and spectral data are in accordance with literature data:
Donohoe, T. J.; Jahanshahi, A.; Tucker, M. J.; Bhatti, F. L.; Roslan, I. A.; Kabeshov, M.; Wrigley, G. *Chemical Communications* **2011**, *47* (20), 5849.

(3aR,7aS)-2-(Iodomethyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole (ICH_2Bnor) (SI_1_6)



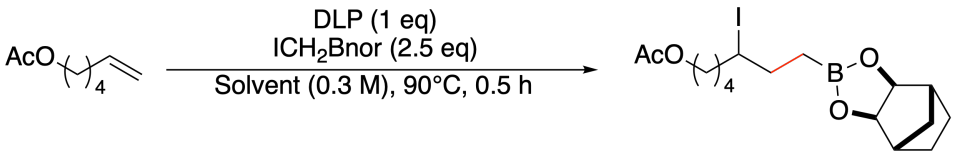
A 250 mL two-neck round-bottom flask, equipped with a 100 mL dropping funnel and a low-temperature thermometer was charged with triisopropyl borate (23.1 mL, 100 mmol) and diiodomethane (8.07 mL, 100 mmol) and dissolved in THF (71 mL) with vigorous stirring. Methyllithium (62.5 mL, 100.0 mmol, 1.6 M) was loaded into the dropping funnel by syringe stepwise. The contents of the flask were cooled to –78 °C with a dry ice/acetone bath and the MeLi solution was added at a steady strip rate to maintain the temperature below –65 °C (addition over ca. 1h). Once the addition was complete, the reaction mixture was stirred at -78 °C for 1 h and the cooling bath was removed. Dry HCl (52.5 mL, 105 mmol, 2.00 M in Et_2O) was added quickly. The reaction mixture was stirred for 1 h at rt, and (2S,3R)-norbornane-2,3-diol (14.7 g, 115 mmol) was added as a solid. The reaction mixture was stirred at rt for 16 h. Most of the volatiles were removed in vacuo (**caution**: MeI is formed as a product of the reaction – perform in a well-ventilated fume-hood). The remaining contents were partitioned between TBME (150 mL) and 0.5 M aq. HCl (150 mL) and stirred for 5 min. The organic phase

was washed with H_2O (150 mL), and the combined aqueous phases were back extracted with TBME (20 mL). The combined organic phases were successively washed with 10% (w/v) aq. $Na_2S_2O_3$ (150 mL), sat. aq. $NaHCO_3$ (2 x 150 mL) dried with sat. aq. NaCl (2 x 150 mL), then dried over Na_2SO_4, filtered, and concentrated in vacuo to afford an orange oil. Purification by vacuum distillation (2.10^{-2} mbar) provided (3aR,7aS)-2-(Iodomethyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole (ICH2Bnor) as desired product (13.7 g, 49.3 mmol, 49 %).

Light yellow oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 4.30 (d, J = 1.4 Hz, 2H), 2.33 (br dq, J = 3.2, 1.6 Hz, 2H), 2.19 (s, 2H), 1.71 (br dp, J = 11.1, 2.0 Hz, 1H), 1.54-1.44 (m, 2H), 1.27-1.20 (m, 1H), 1.07-0.98 (m, 2H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 84.4 (2x CH), 41.0 (2x CH), 30.8 (CH_2), 23.4 (2x CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 32.2. IR (thin film): ν_{max} = 2957, 2873, 1407, 1387, 1367, 1352, 1306, 1280, 1226, 1132, 1093, 1021, 1001 cm^{-1}. HRMS (ESI): Calculated for $C_8H_{13}BIO_3$ $[M+OH]^+$: 295.008; found: 295.014. HRMS (ESI): Calculated for $C_8H_{12}BIO_2$ $[M]^+$: 277.9970; found: 277.9961.

The compound was stored at -20 °C in dark vials under an argon atmosphere. The color of the compound changes from light yellow to dark orange because of slow degradation, which occurs fast at rt and with exposure to light. The degradation product is iodine, and this explains the change in color of the compound. However, this does not seem to have an impact on the radical ATRA reaction yields.

ATRA with DLP: solvent screening



2a
Chemical Formula: $C_{16}H_{26}BIO_4$
Exact Mass: 420.0969

A flame-dried 10 mL one-neck round-bottom flask, equipped with a reflux condenser, was charged with hex-5-enyl acetate (71 mg, 0.5 mmol), lauroyl peroxide (199 mg, 0.5 mmol), ICH_2Bnor (347 mg, 1.25 mmol) and the contents dissolved in the desired solvent (1.7 mL) under a positive nitrogen atmosphere. The reaction mixture was heated at a 90 °C for 30 minutes in a pre-heated oil bath. The cooled reaction mixture was partitioned between TBME (15 mL) and H_2O (10 mL) and the organic phase was successively washed with sat. aq. $Na_2S_2O_3$ (5 mL) and water (10 mL). The combined aqueous phases were back extracted with TBME (5 mL). The combined organic phases were washed with brine (15 mL), then over anhydrous Na_2SO_4, filtered through a short pad of cotton and concentrated under reduced pressure. Purification by

flash column chromatography (Gradient EA:heptane 2-3-5-7-10 %) provided the desired **2a**.

Colourless oil; Rf: 0.18 (heptane:EA 85:15); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 4.20 (d, J = 1.4 Hz, 2H), 4.16-4.07 (m, 1H), 4.07 (t, J = 6.4 Hz, 2H), 2.29-2.22 (m, 2H), 2.05 (s, 3H), 1.98–1.41 (m, 12H), 1.19 (dp, J = 11.0, 1.4 Hz, 1H), 1.09-0.85 (m, 4H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 171.2 (Cq), 83.8 (2x CH), 64.2 (CH_2), 42.7 (CH), 40.9 (CH), 39.8 (CH_2), 35.2 (CH_2), 30.7 (CH_2), 27.8 (CH_2), 26.0 (CH_2), 23.3 (CH_2), 21.0 (CH_3); ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 33.5; IR (thin film): ν_{max} = 2951, 2873, 1736, 1387, 1368, 1225, 1166, 1027 cm^{-1}; HRMS (ESI): Calculated for $C_{16}H_{27}O_4BI$ $[M+H]^+$: 421.1042; found: 421.1038.

General Procedure (NMR yields)

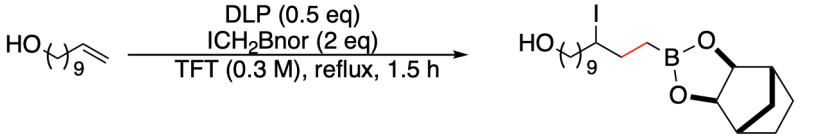
A flame-dried one-neck round bottom flask, equipped with a reflux condenser, was charged with but-3-enylbenzene (66 mg, 0.5 mmol) and the desired quantities of lauroyl peroxide and ICH_2Bnor. TFT (xxx mL, xxx M) was added under a positive nitrogen atmosphere and the reaction mixture was heated at a 110 °C for 1h30 in a pre-heated oil bath. The cooled reaction mixture was concentrated in vacuo. Commercial 1,3,5-trimethoxybenzene (0.5 eq) was used as external standard for the determination of the NMR yields. It was weighted directly into the flask containing the crude mixture and the mixture was then dissolved in 5 mL of $CDCl_3$. To be sure that everything was solubilized, the flask was left $\sim$30 minutes in a sonicator. 0.5 mL of the obtained solution was used for the NMR yield determination.

Substrate scope

Iodohydroborylation

GP1: A flame-dried 5 mL one-neck round bottom flask, equipped with a reflux condenser, was charged with the alkene (1 mmol), lauroyl peroxide (199 mg, 0.5 mmol), ICH_2Bnor (556 mg, 2 mmol) and the contents dissolved in TFT (3.4 mL) under a positive argon atmosphere. The mixture was heated at reflux (110°C) for 1.5 h. The cooled reaction mixture was partitioned between distilled water (15 mL) and TBME (10 mL). The aqueous layer was extracted with TBME (3 x 10 mL). The organic layer was treated with 1M NaOH (to eliminate the remaining unreacted ICH_2Bnor), washed with brine, dried over anhydrous Na_2SO_4, filtered and the solvents was concentrated in vacuo to afford a the crude mixture as an oil. Purification by flash column chromatography delivered the desired compound.

12-((3aR,4S,7R,7aS)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-10-iodododecan-1-ol (2c)

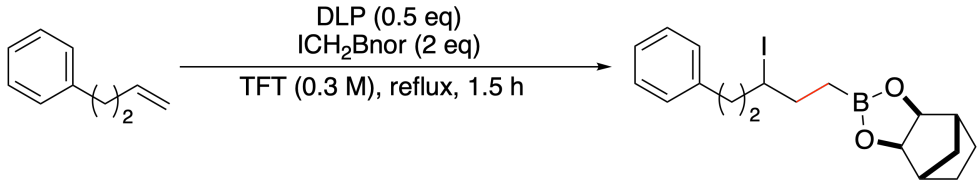


2c
Chemical Formula: $C_{19}H_{34}BIO_3$
Exact Mass: 448.1646

The title compound was prepared following **GP1** with 10-undecen-1-ol (170 mg, 1 mmol). Purification by flash column chromatography (Gradient 5-10-15-20 % EtOAc:heptane) provided the desired product **2c** (114 mg, 0.254 mmol, 25 %).

Light-orange oil; Rf: 0.17 (8:2 heptane:EA); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 4.17 (d, J = 1.4 Hz, 2H), 4.11 (tt, J = 8.7, 4.6 Hz, 1H), 3.60 (app t, J = 6.6 Hz, 1H), 2.28-2.18 (m, 2H), 1.97-0.80 (m, 27H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 83.8 (2x CH), 63.1 (CH_2), 43.8 (CH), 40.9 (CH), 40.4 (CH_2), 32.8 (CH_2), 30.8 (CH_2), 29.57 (CH_2), 29.52 (CH_2) 29.45 (CH_2), 29.37 (CH_2), 25.8 (CH_2), 23.4 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 33.7; IR (thin film): ν_{max} = 3352, 2924, 2853, 1456, 1387, 1371, 1321, 1283, 1224, 1169, 1132, 1027 cm^{-1}. HRMS (ESI): Calculated for $C_{19}H_{35}O_3BI$ $[M+H]^+$: 449.1718; found: 449.1703.

(3aR,4S,7R,7aS)-2-(3-Iodo-5-phenylpentyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole (2d)

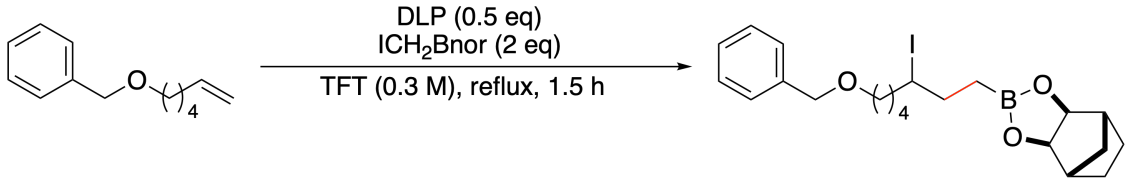


2d
Chemical Formula: $C_{18}H_{24}BIO_2$
Exact Mass: 410.0914

The title compound was prepared following **GP1** with but-3-en-1-yl-benzene (132 mg, 1 mmol). Purification by flash column chromatography (Gradient 0-1-2 % EtOAc:heptane) provided the desired product **2d** (252 mg, 0.504 mmol, 50 %).

Yellow oil; Rf: 0.55 (9:1 heptane:EA); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.24–7.07 (m, 5H), 4.11 (d, *J* = 1.3 Hz, 2H), 4.00 (tt, *J* = 8.8, 4.4 Hz, 1H), 2.81 (ddd, *J* = 14.0, 9.1, 5.1 Hz, 1H), 2.65 (ddd, *J* = 13.7, 9.0, 6.9 Hz, 1H), 2.24-2.02 (m, 3H), 1.98–1.70 (m, 3H), 1.60-1.14 (m, 5H), 1.12-1.06 (m, 1H), 1.04–0.81 (m, 4H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 140.9 (CqAr), 128.5 (2x CHAr), 128.4 (CHAr), 126.1 (2x CHAr), 83.76 (CH), 83.75 (CH), 42.5 (CH), 41.9 (CH_2), 40.9 (CH_2), 35.6 (CH_2), 35.3 (CH_2), 30.7 (CH_2), 23.3 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 33.9; IR (thin film): ν_{max} = 2950, 2922, 2874, 1495, 1454, 1386, 1369, 1321, 1284, 1223, 1132, 1105, 1026, 1002 cm^{-1}; HRMS (ESI): Calculated for $C_{18}H_{25}O_2BI$ $[M+H]^+$: 411.0987; found: 411.0983.

((3aR,4S,7R,7aS)-2-(7-(benzyloxy)-3-iodoheptyl)hexahydro-4,7methanobenzo[d][1,3,2]dioxaborole (2e)



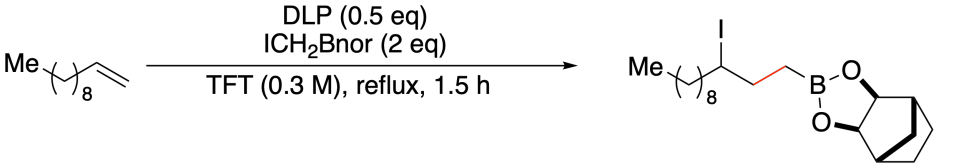
2e
Chemical Formula: $C_{21}H_{30}BIO_3$
Exact Mass: 468.1333

The title compound was prepared following **GP1** with hex-5-enoxymethylbenzene (190 mg, 1 mmol). Purification by flash column chromatography (Gradient 0-2-4-5 % EtOAc:heptane) provided the desired product **2e** (102 mg, 0.218 mmol, 22 %).

Colorless oil; Rf: 0.4 (9:1 heptane:EA); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.30-7.18 (m, 5H), 4.43 (s, 2H), 4.13 (d, *J*= 1.4 Hz, 2H), 4.06 (tt, *J* = 8.8, 4.6 Hz, 1H), 3.40 (t, *J* = 6.0 Hz, 2H), 2.21-2.16 (m,

2H), 1.93-1.33 (m, 12H), 1.21-1.17 (m, 1H), 1.12 (dp, *J* = 11.0 Hz, 1.5 Hz, 1H), 1.00-0.92 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.6 (Cq), 128.5 (2 × CHAr), 127.8 (2x CHAr), 127.7 (CHAr), 83.7 (2x CH), 72.9 (CH_2), 70.1 (CH_2), 43.2 (CH–I), 40.9 (2x CH), 40.1 (CH_2), 35.2 (CH_2), 30.7 (CH_2), 29.0 (CH_2), 26.4 (CH_2), 23.3 (2x CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; **^{11}B NMR** (96 MHz, $CDCl_3$) δ 33.6; IR (thin film): ν_{max} = 3063, 2941, 2870, 1452, 1387, 1369, 1223, 1099, 1026, 732, 697 cm^{-1}. HRMS (ESI): Calculated for $C_{21}H_{31}O_3BI$ $[M+H]^+$: 469.1405; found: 469.1422.

(3aR,4S,7R,7aS)-2-(3-Iodododecyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole (2f)

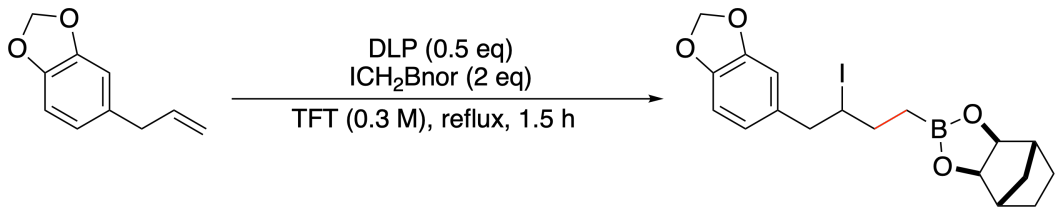


2f
Chemical Formula: $C_{19}H_{34}BIO_2$
Exact Mass: 432.1697

The title compound was prepared following **GP1** with undec-1-ene (154 mg, 1 mmol). Purification by flash column chromatography (Gradient 0-0.5-1-2 % EtOAc:heptane) provided the desired product **2f** (220 mg, 0.508 mmol, 51 %).

Light-orange oil; Rf: 0.27 (92:8 heptane:EA); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.20 (d, J = 1.3 Hz, 2H), 4.123 (tt, J = 8.7, 4.7, Hz, 1H), 2.30–2.18 (m, 2H), 2.00–0.95 (m, 28H), 0.92–0.84 (m, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 83.8 (2x CH), 43.8 (CH), 41.0 (CH), 40.4 (CH_2), 35.4 (CH_2), 31.9 (CH_2), 30.8 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.0 (CH_2), 23.4 (CH_2), 22.8 (CH_2), 14.2 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; **^{11}B NMR** (96 MHz, $CDCl_3$) δ 33.9; IR (thin film): ν_{max} = 2954, 2922, 2873, 2852, 1386, 1370, 1321, 1310, 1283, 1224, 1166, 1132, 1028 cm^{-1}. HRMS (ESI): Calculated for $C_{19}H_{35}O_2BI$ $[M+H]^+$: 455.1589; found: 455.1583.

(3aR,4S,7R,7aS)-2-(4-(benzo[d][1,3]dioxol-5-yl)-3-iodobutyl)hexahydro-4,7-methanobenzo-[d][1,3,2]dioxaborole (2g)

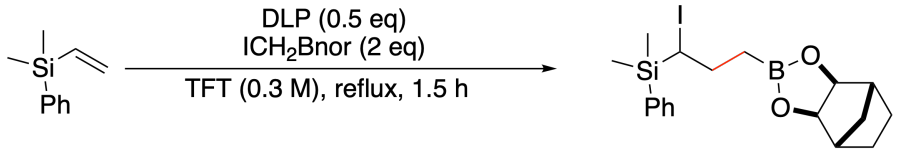


2g
Chemical Formula: $C_{18}H_{22}BIO_4$
Exact Mass: 440.0656

The title compound was prepared following **GP1** with safrole (162 mg, 1 mmol). Purification by flash column chromatography (Gradient 0-0.5-1-2 % EtOAc:heptane) provided the desired product **2g** (51 mg, 0.116 mmol, 12 %).

Colorless oil; Rf: 0.09 (85:15 heptane:EA); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 6.74 (d, J = 7.8 Hz, 1H), 6.70–6.60 (m, 2H), 5.94 (s, 2H), 4.25 (tdd, J = 8.1, 6.7, 4.9 Hz, 1H), 4.19 (d, J = 1.3 Hz, 2H), 3.16 (dd, J = 14.5, 8.0 Hz, 1H), 3.08 (dd, J = 14.4, 6.7 Hz, 1H), 2.28–2.23 (m, 2H), 1.95–1.76 (m, 2H), 1.47–1.36 (m, 3H), 1.18 (dp, J = 11.2, 1.4 Hz, 1H), 1.28–0.84 (m, 4H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 147.6 (Cq), 146.3 (Cq), 133.8 (Cq), 122.1 (CHAr), 109.3 (CHAr), 108.1 (CHAr), 100.9 (CH_2), 83.7 (2x CH), 46.8 (CH_2), 42.5 (CH–I), 40.9 (2x CH), 34.3 (CH_2), 30.7 (CH_2), 23.3 (2x CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) δ 33.65; IR (thin film): ν_{max} = 2952, 2874, 1502, 1488, 1441, 1386, 1369.2, 1244, 1226, 1030, 1002, 926, 809, 765, 730 cm^{-1}. HRMS (ESI): Calculated for $C_{18}H_{25}O_2BI$ $[M+Na]^+$: 463.0550; found: 463.0538.

(3-((3aR,4S,7R,7aS)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-1-iodopropyl)-dimethyl(phenyl)silane (2h)



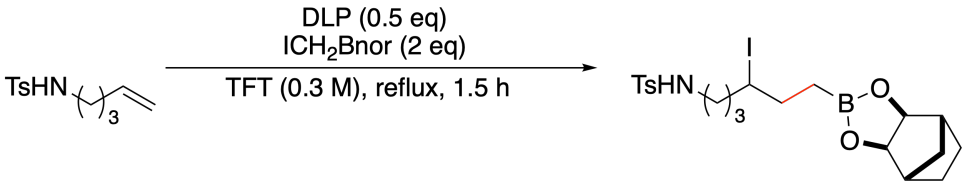
2h
Chemical Formula: $C_{18}H_{26}BIO_2Si$
Exact Mass: 440.0840

The title compound was prepared following **GP1** with dimethyl-phenyl-vinyl-silane (162 mg, 1 mmol). Purification by flash column chromatography (Gradient 0-0.5 % EtOAc:heptane) provided the desired product **2h** (190 mg, 0.432 mmol, 43 %).

Colorless oil; Rf: 0.29 (98:2 heptane:EA); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.43–7.30 (m, 3H), 4.16 (d, J = 1.3 Hz, 2H), 3.36–3.33 (m, 1H), 2.25–2.21 (m, 2H), 1.78–1.63 (m, 2H), 1.52–1.43 (m, 3H), 1.31–1.24 (m, 2H), 1.18–1.12 (m, 2H), 1.06–0.97 (m, 2H), 0.93–0.78 (m, 1H), 0.46 (s, 6H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 136.7 (Cq), 134.3 (2x CHAr), 129.6 (CHAr), 128.0 (2x CHAr), 83.8 (2x CH), 41.0 (2x CH), 30.8 (CH_2), 28.7 (CH_2), 26.8 (CH), 23.5 (2x CH_2), -2.2 (CH_3), -4.1(CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) δ 34.12; IR (thin film): ν_{max} = 3068, 2953, 2874, 2853, 1385, 1370, 1318, 1225, 1112, 1025, 813, 730, 698 cm^{-1}. HRMS (ESI): Calculated for $C_{18}H_{26}O_2BISi$ $[M+Na]^+$: 463.0740; found: 463.0717.

N-(6-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-4-iodohexyl)-

4-methylbenzenesulfonamide (2i)

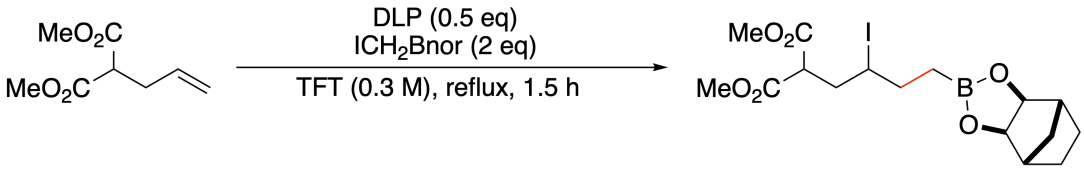


2i
Chemical Formula: $C_{20}H_{29}BINO_4S$
Exact Mass: 517.0955

The title compound was prepared following **GP1** with 4-Methyl-N-pent-4-enyl-benzenesulfonamide (239 mg, 1 mmol). Purification by flash column chromatography (Gradient 10-15-20 % EtOAc:heptane) provided the desired product **2i** (239 mg, 0.462 mmol, 46 %).

Red oil; Rf: 0.18 (98:2 heptane:EA); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.76–7.71 (m, 2H), 7.33–7.24 (m, 2H), 4.50–4.40 (m, 1H), 4.19 (d, J = 1.3 Hz, 2H), 4.02 (tt, J = 8.6, 4.1 Hz, 1H), 3.02–2.88 (m, 2H), 2.43 (s, 3H), 2.28–2.22 (m, 2H), 1.95–1.84 (m, 1H), 1.84–1.42 (m, 8H), 1.25 (dp, J = 11.0, 1.4 Hz, 1H), 1.08–0.77 (m, 4H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 143.5 (Cq), 137.0 (Cq), 129.8 (2x CHAr), 127.1 (2x CHAr), 83.8 (2x CH), 42.4 (CH_2), 41.5 (CH), 40.9 (2x CH), 37.0 (CH_2), 35.3 (CH_2), 30.7 (CH_2), 29.6 (CH_2), 23.3 (2x CH_2), 21.5 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) δ 33.72; IR (thin film): ν_{max} = 3274, 2951, 2874, 1321, 1155, 1092, 1025, 813, 730, 660, 571, 549 cm^{-1}. HRMS (ESI): Calculated for $C_{20}H_{29}O_4BINS$ $[M+Na]^+$: 540.0960; found: 540.0840.

Dimethyl 2-(4-((3aR,4S,7R,7aS)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-2-iodobutyl)malonate (2j)



2j
Chemical Formula: $C_{16}H_{24}BIO_6$
Exact Mass: 450.0711

The title compound was prepared following **GP1** with dimethyl 2-allyl malonate (172 mg, 1 mmol). Purification by flash column chromatography (Gradient 5-10 % EtOAc:heptane) provided the desired product **2j** (307 mg, 0.682 mmol, 68 %).

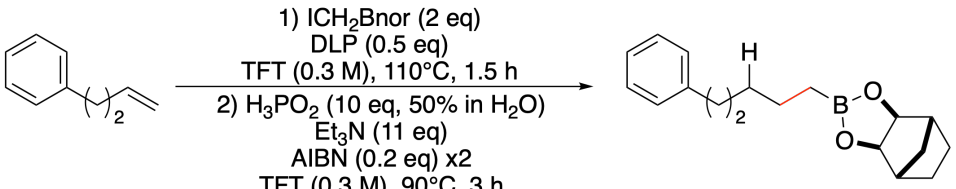
Light-yellow oil; Rf: 0.2 (9:1 heptane:EA); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.18 (d, J = 1.3 Hz, 2H), 4.03 (tdd, J = 10.5, 7.3, 5.0 Hz, 1H), 3.78–3.74 (m, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 2.34–2.29 (m, 2H), 2.26–2.21 (m, 2H), 2.00–1.80 (m, 2H), 1.53–1.43 (m, 3H), 1.17 (dp, J = 11.0, 1.5 Hz,

1H), 1.10– 0.85 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3 (Cq), 169.1 (Cq), 83.9 (CH), 83.8 (CH), 52.9 CH_3), 52.8 (CH_3), 52.3 (CH), 41.0 (2x CH), 39.3 (CH_2), 38.6 (CH), 35.6 (CH_2), 30.8 (CH_2), 23.4 (2x CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.03; IR (thin film): ν_{max} = 2953, 2875, 1733, 1371, 1224, 1198, 1149, 1026, 916, 730 cm^{-1}. HRMS (ESI): Calculated for $C_{16}H_{24}O_6BI$ [M+Na]$^+$: 473.0710; found: 473.0596.

Hydroborylmethylation

GP2: A flame-dried 5 mL one neck round-bottom, equipped with a cold-finder condenser, was charged with the alkene (1.00 mmol), Lauroyl peroxide (199 mg, 0.500 mmol) and ICH_2Bnor (556 mg, 2.00 mmol) under a positive argon atmosphere and the contents were dissolved in TFT (3.4 mL). The mixture was immersed in a pre-heated oil bath and heated at 110 °C for 1h30. Upon completion (TLC monitoring), the cooled reaction flask was charged with hypophosphorous acid (50.0 %, 1.09 mL, 10.0 mmol), Et_3N (1.53 mL, 11.0 mmol, distilled prior to use), and AIBN (33 mg, 0.200 mmol) and the reaction mixture was stirred at 90 °C for 1h30. After partial cooling, a second portion of AIBN (33 mg, 0.200 mmol) was added and the reaction mixture heated at 90 °C for a further 1h30. The reaction mixture was cooled to rt, partitioned between TBME (25 mL) and 2 M aq. HCl (15 mL). The organic phase was washed with 1 M aq. HCl (15 mL), and the combined aqueous phases were back-extracted with TBME (5 mL). The combined organic phases were successively washed with 2 M aq. NaOH (15 mL) and 1 M aq. NaOH (15 mL), sat. aq. $Na_2S_2O_3$ (25 mL), sat. aq. $NaHCO_3$ (25 mL), and brine (25 mL), then dried over Na_2SO_4, filtered, and concentrated in vacuo the crude mixture as an oil. Purification by flash column chromatography delivered the desired compound.

(3aR,4S,7R,7aS)-2-(5-Phenylpentyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole (3a)



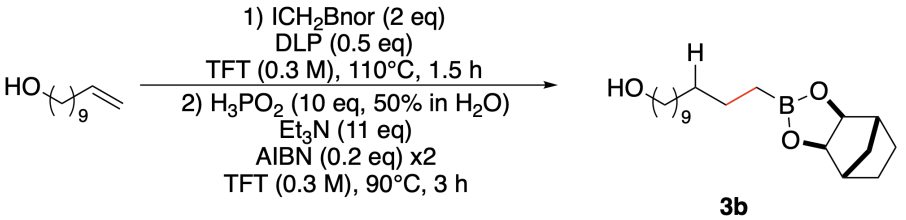
3a
Chemical Formula: $C_{18}H_{25}BO_2$
Exact Mass: 284.1948

The title compound was prepared following **GP2** with but-3-en-1-yl-benzene (134 mg, 1.02 mmol). Purification by flash column chromatography (Gradient 0-0.5-1 % EtOAc:heptane) provided the desired product **3a** (160 mg, 0.495 mmol, 50 %).

Colorless oil; Rf: 0.57 (9:1 heptane:EA); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23–7.16 (m, 2H), 7.12–7.06 (m, 3H), 4.11 (d, J = 1.3 Hz, 2H), 2.64–2.51 (m, 2H), 2.20–2.16 (m, 2H), 1.58–1.51

(m, 2H), 1.48–1.14 (m, 7H), 1.10 (dp, J = 10.9, 1.5 Hz, 1H), 1.00–0.92 (m, 2H), 0.79 (t, J = 7.7 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1 (Cq), 128.6 (2x CHAr), 128.3 (2x CHAr), 125.7 (CHAr), 83.7 (2x CH), 41.1 (2x CH), 36.0 (CH_2), 32.1 (CH_2), 31.2 (CH_2), 30.8 (CH_2), 24.1 (CH_2), 23.5 (2x CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.51; IR (thin film): ν_{max} = 3027, 2929, 2873, 2854, 1734, 1371, 1320, 1223, 1199, 1162, 1029, 1004, 743, 732, 697 cm^{-1}. HRMS (ESI): Calculated for $C_{18}H_{25}O_2B$ [M+Na]$^+$: 307.1840; found: 307.1837.

12-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)dodecan-1-ol (3b)

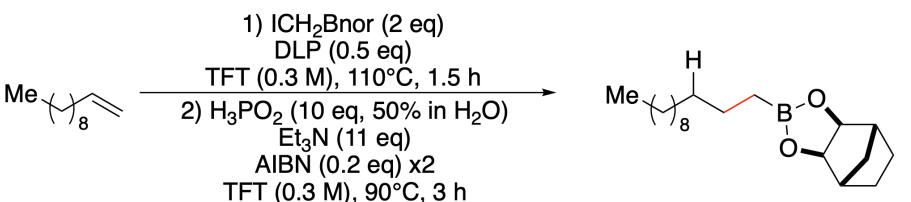


3b
Chemical Formula: $C_{18}H_{25}BO_2$
Exact Mass: 284.1948

The title compound was prepared following **GP2** with undec-10-en-1-ol (168 mg, 0.986 mmol). Purification by flash column chromatography (Gradient 5-10-15 % EtOAc:heptane) provided the desired product **3b** (126 mg, 0.391 mmol, 39 %).

Colorless oil; Rf: 0.34 (9:1 heptane:EA); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.19 (d, J = 1.3 Hz, 2H), 3.63 (t, J = 6.6 Hz, 2H), 2.28–2.23 (m, 2H), 1.62–1.22 (m, 24H), 1.17 (dp, J = 10.9, 1.4 Hz, 1H), 1.08–0.99 (m, 2H), 0.80 (t, J = 7.7 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 83.7 (2x CH), 63.3 (CH_2), 41.0 (2x CH), 33.0 (CH_2), 32.6 (CH_2), 30.8 (CH_2), 29.77 (CH_2), 29.74 (CH_2), 29.71 (CH_2), 29.67 (CH_2), 29.57 (CH_2), 29.55 (CH_2), 25.9 (CH_2), 24.3 (CH_2), 23.5 (2x CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; **^{11}B NMR** (96 MHz, $CDCl_3$) δ 33.91; IR (thin film): ν_{max} = 3383.5, 2922.6, 2852.2, 1457.9, 1373.07, 1321.9, 1222.6, 1028.8, 1002.8, 721.2 cm^{-1}. HRMS (ESI): Calculated for $C_{19}H_{35}O_3B$ [M+Na]$^+$: 345.2500; found: 345.2568.

(3aR,4S,7R,7aS)-2-Dodecylhexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole (3c)



3c
Chemical Formula: $C_{18}H_{25}BO_2$
Exact Mass: 284.1948

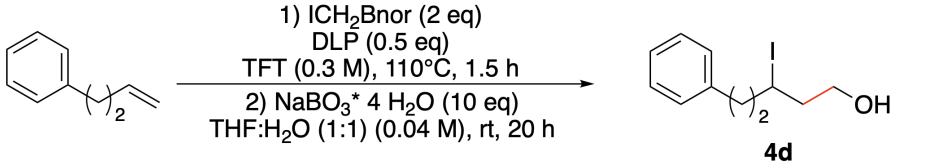
The title compound was prepared following **GP2** with undec-10-en-1-ol (154 mg, 1.00 mmol). Purification by flash column chromatography (15:85 DCM:pentane) provided the desired product **3c** (78 mg, 0.204 mmol, 20 %).

Colorless oil; Rf: 0.4 (85:15 pentane:DCM); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.19 (d, J = 1.3 Hz, 2H), 2.28–2.23 (m, 2H), 1.55–1.44 (m, 3H), 1.44–1.33 (m, 2H), 1.33–1.21 (m, 18H), 1.17 (dp, J = 10.9, 1.5 Hz, 1H), 1.08–0.98 (m, 2H), 0.92–0.84 (m, 3H), 0.80 (dd, J1 = J2 = 7.7 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 83.7 (2x CH), 41.0 (2x CH), 32.6 (CH_2), 32.1 (CH_2), 30.8 (CH_2), 29.83 (CH_2), 29.81 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 24.3 (CH_2), 23.5 (CH_2), 22.8 (CH_2), 14.3 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; **^{11}B NMR** (96 MHz, $CDCl_3$) δ 34.2; IR (thin film): ν_{max} = 2995, 2922, 2874, 2852, 1408, 1383, 1372, 1321, 1220, 1031 cm^{-1}. Thermal Elemental Analysis: Calculated for $C_{19}H_{35}BO_2$: C, 74.51; H, 11.52, N, 0.00; found: C, 75.06; H, 11.48, N, 0.00.

Iodohydroxymethylation

GP3: A flame-dried 5 mL one neck round-bottom, equipped with a cold-finder condenser, was charged with the alkene (1.00 mmol), Lauroyl peroxide (199 mg, 0.500 mmol) and ICH_2Bnor (556 mg, 2.00 mmol) under a positive argon atmosphere and the contents dissolved in TFT (3.4 mL). The reaction mixture was immersed in a pre-heated oil bath and heated at 110 °C for 1h30. The reaction mixture was transferred into a 50 mL flask, where THF (12.5 mL) and water (12.5 mL) were added. $NaBO_3 \cdot 4\ H_2O$ (10 mmol) was then added portion wise. The reaction mixture was stirred at rt for 20h. The reaction mixture was partitioned between EtOAc (20 mL) and water (25 mL). The phases were separated and the aqueous layer phase was extracted with EtOAc (3 x 10 mL). The combined organic phases were washed with $Na_2S_2O_3$ 5% (25 mL) and sat. aq. NaCl (25 mL). The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo to afford the crude mixture as an oil. Purification by flash column chromatography delivered the desired compound.

3-Iodo-5-phenyl-pentan-1-ol (4d)



4d
Chemical Formula: $C_{11}H_{15}IO$
Exact Mass: 290.0168

The title compound was prepared following **GP3** with but-3-en-1-yl-benzene (132 mg, 1.00 mmol). Purification by flash column chromatography (10-15 % EtOAc:heptane) afforded the desired product **4d** (154 mg, 0.531 mmol, 53 %).

Yellow oil; Rf: 0.27 (8:2 heptane:EA); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.36–7.28 (m, 2H), 7.24 (d, *J* = 7.1 Hz, 2H), 4.25 (tt, *J* = 9.5, 4.2 Hz, 1H), 3.93–3.77 (m, 2H), 2.95 (ddd, *J* = 14.2, 9.3, 5.1 Hz, 1H), 2.77 (ddd, *J* = 13.7, 9.3, 6.7 Hz, 1H), 2.42–1.88 (m, 4H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 140.8 (Cq), 128.6 (2x CH), 128.5 (2x CH), 126.2 (CH), 62.5 (CH_2), 42.8 (CH), 42.5 (CH_2), 35.6 (CH_2), 34.7 (CH_2).

The physical and spectral data are in accordance with literature data:
Träff, A. M.; Janjetovic, M.; Ta, L.; Hilmersson, G. *Angewandte Chemie* **2013**, *52* (46), 12073–12076.

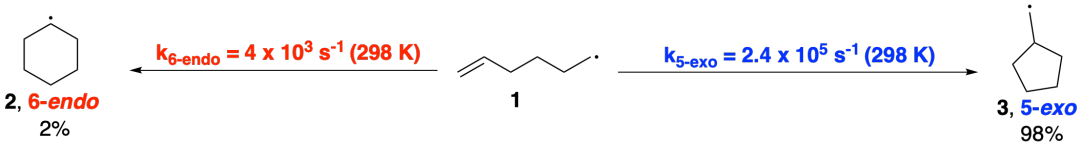
3 Cyclisation reactions involving α-boryl radicals: Atom Transfer Radical Addition and Cyclisation (ATRAC) and Atom Transfer Radical Addition and Annulation (ATRAn)

This first part of this chapter will be dedicated to description of the ATRAC reaction. The optimization of the method, a substrate scope, some post-functionalizations of the obtained products and mechanistic investigations will be detailed. In the second part of the chapter, a new annulation strategy involving α-boryl radicals will be described. A substrate scope and some mechanistic investigations will be discussed. Personal contributions include everything except the scope using photoredox conditions which was part of a collaboration with the research group of Prof. Christoforos Kokotos (National and Kapodistrian University of Athens) and was performed by Ms. Charikleia Batsika.

3.1 Introduction and aim of the project

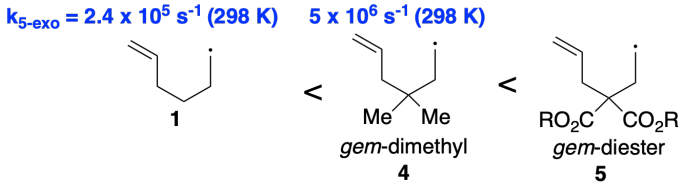
Radical cyclisation reactions have been increasingly used for the synthesis of complex natural products.[1] As a prove of concept, Curran and co. used a radical cyclisation strategy to synthesize the main core of *capnellene*.[2]
But what are the advantages of introducing such a step for the total synthesis of a natural compound? This step is highly sustainable and synthetically powerful, building several new σ-bonds from two or more π-systems. Moreover, these reactions are quite regioselective and can be introduced at the end of the synthesis of a natural compound. Last but not least, stereoselective versions can be achieved by controlling the substituents on the molecule, which have an impact on the different transition states of the reaction. Radical cyclisations can be performed using different conditions e.g reducing conditions, atom-transfer conditions, fragmentation method or persistent radical effect.[3] Moreover, several cyclisation reactions were developed and can be employed for the construction of carbo- or heterocycles of different sizes. Baldwin and co. extensively studied radical cyclisation reactions and came up with different rules which regulate the feasibility of the process.[4]
Several reports in the literature showed that cyclisation reactions can be performed using atom transfer conditions[5–7] and they are often based on a **5-*exo*-trig cyclisation** approach. There are different reasons for this choice:

- The 5-*exo*-trig cyclisation is faster and regioselective (Scheme 3.1) due to stereoelectronic effects which favours the formation of the five-membered ring. The 6-*endo*-trig chair-like transition state is indeed $\approx$ 3 kcal mol^{-1} higher in energy than the corresponding 5-*exo*-trig transition state.[8–10]



Scheme 3.1: 5-*exo*-trig vs 6-*endo*-trig cyclisations.

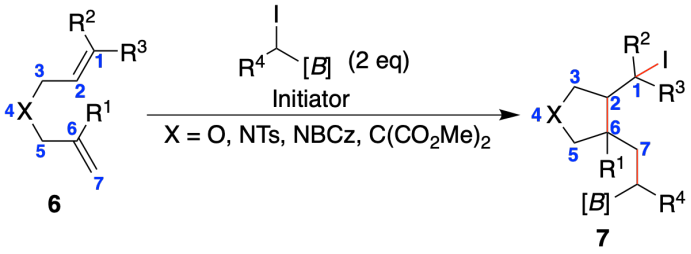
- This ratio can be further improved with the help of a ***gem*-disubstituent effect.**[11–14] As shown in Scheme 3.2, the addition of a *gem*-dimethyl group positively affects the cyclisation rate. This effect can be also explained both referring to the enthalpy and the entropy of the reaction. **3** is more destabilized than **1** due to the increased amount of *gauche* interactions after addition of the dimethyl group, therefore the cyclisation occurs faster because the cyclised product is more stable. Entropy also plays a huge role in the ring formation, since the cyclic product has less degree of freedom than the open chain and thus it will be increased after cyclisation. The addition of a *gem*-diester group accelerates even more the rate of the reaction via **Thorpe-Ingold effect**.[13,15]



Scheme 3.2: Impact of *gem*-disubstituent effect on cyclisation rate.

- Apart from the case of the cyclisation of malonyl derivatives,[16] the reaction is **irreversible**.
- The stereoselectivity of the reaction can be improved by the addition of substituents which causes the 1,3-allylic strains or by performing the reaction at low temperature.[8,10,17]

In this work, we aimed to use the atom transfer radical addition and cyclisation reaction to synthesize a variety different substituted five-membered rings (Scheme 3.3). After addition of the α-boryl radical at position 7, the newly-formed secondary radical at position 6 will undergo fast 5-*exo*-trig radical cyclization to form a new radical at position 1. This radical will be then involved in iodine atom transfer with the radical precursor to form the desired product **3b** and a new α-boryl radical which will sustain the chain. This system will allow us to vary substituents at position 1 and thus study the iodine atom transfer of a primary, secondary and tertiary radical when iodomethylene boronic esters are used as radical precursors. In addition to that, we synthesized different dienes bearing various groups at position 6 to understand the philicity of α-boryl radicals. Last but not least, we attempted the synthesis of different heterocycles using this methodology (pyrrolidines and tetrahydrofurans rings).

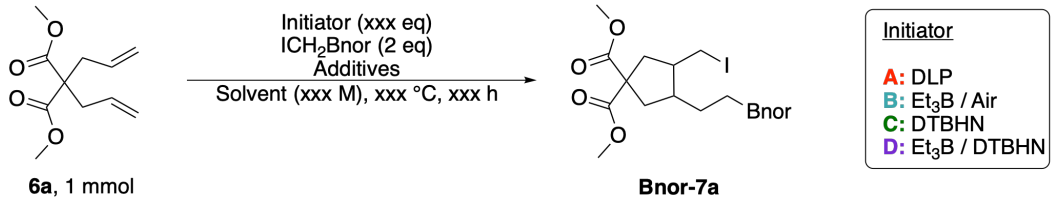


Scheme 3.3: General scheme of ATRAC reaction.

3.2 Optimization of the reaction conditions

3.2.1 Initiator

The substrate of choice for the optimation of the reaction was Dimethyl 2,2-diallylmalonate: it is very easy to synthesize and it bears a *gem*-diester group which will ensure the cyclization to be fast and selective towards the five member ring formation. The results of the optimization are summarized in Table 3.1.



6a, 1 mmol — **Bnor-7a**

Entry	Initiator (xxx eq)	T°	Solvent (xxx M)	Time	Additives	Isolated yield
1	**A** (0.5 eq)	110°C	TFT (0.3 M)	1h30	/	62% (dr 8:2)
2	**B** (0.5 eq)[a]	RT	DCM (0.1 M)	4 h	/	38% (dr 8:2)
3	**B** (1.3 eq)[a]	RT	DCM (0.1 M)	4 h	/	41% (dr 8:2)
4	**C** (0.4 eq)	60°C	TFT (0.25 M)	1h30	/	53% (dr 8:2)
5	**C** (0.4 eq)	80°C	TFT (0.25 M)	1h30	/	57% (dr 8:2)
6	**C** (0.4 eq)	80°C	TFT (2.3 M)	1h30	/	69% (dr 8:2)
7	**C** (0.4 eq)	80°C	TFT (2.3 M)	1h30	Cs_2CO_3 (0.3 eq)	76% (dr 8:2)
8	**D** (0.5 eq/0.2 eq)[a]	55°C	TFT (0.25 M)	1h30	/	53% (dr 8:2)
9	**D** (1 eq/0.2 eq)[a]	55°C	TFT (1.15 M)	1h30	/	60% (dr 8:2)
10	**D** (1.3 eq/0.2 eq)[a]	55°C	TFT (0.25 M)	1h30	/	34% (dr 8:2)
11	**D** (1 eq/0.2 eq)[a]	70°C	TFT (1.15 M)	1h30	/	67% (dr 8:2)
12	**D**(1 eq/0.2 eq)[b]	70°C	TFT (1.15 M)	1h30	/	76% (dr 8:2)
13	**D** (0.5 eq/0.1 eq)[b]	70°C	TFT (2.3 M)	1h30	/	75% (dr 8:2)
14	**D** (0.5 eq/0.1 eq)[b]	70°C	TFT (2.3 M)	1h30	Cs_2CO_3 (0.3 eq)	80% (dr 8:2)

Table 3.1: Optimization of the initiator for the ATRAC reaction on dimethyl 2,2-diallylmalonate **6a**. [a] 1.15 M Et_3B solution in PhH. [b] 1.15 M Et_3B solution in TFT. Isolated yields.

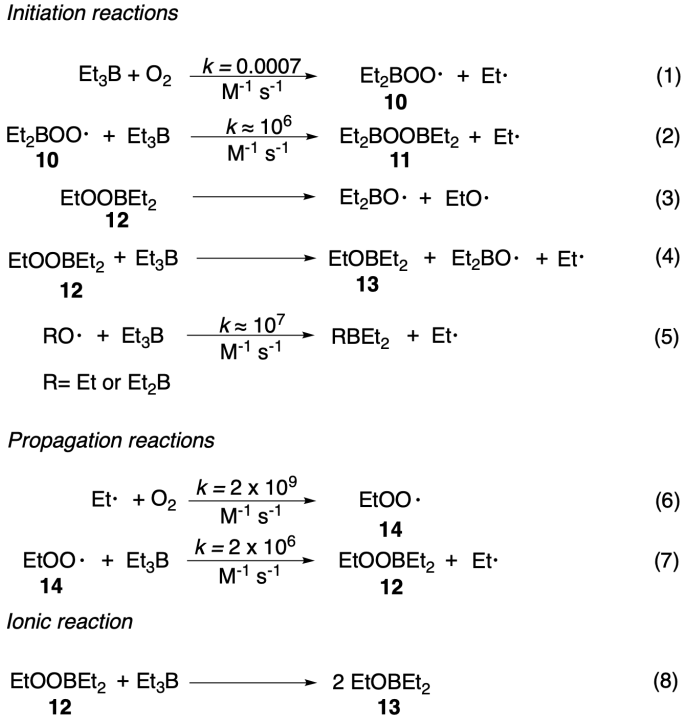
We first started to apply the optimized conditions for Intermolecular ATRA (see chapter 1) for the cyclization. Pleasingly, a yield of 62% was found (Table 3.1, *Entry 1*). However, due to presence of several DLP decomposition by-products which rendered the purification more difficult,[18] we decided to explore other initiation systems.

Therefore, we moved to Et_3B/air as initiator since less by-products will be produced and the purification would then proceed smoother. As reported by Brown et all. in the early sixities,[19] Et_3B can be used in presence of oxygen and utilized as initiation system. This method was exploited several times in our group for different purposes,[20–22] but never in combination with Atom Transfer Radical Addition and Cyclisation reactions. However, the use of Et_3B/air did not deliver better results (Table 3.1, *Entry 2 and 3)*. A big disadvantage of this initiator is the re-

producibility of the reactions because it is hard to measure exactly the amount of air (and thus oxygen) present in the reaction mixture.
Since our group previously reported the use of DTBHN ($t_{1/2}$ = 29 min at 65 °C, neat) in ATRA reactions,[23] it was then tried as well as initiator during the optimization of the ATRAC reaction. In this case, after thermal decomposition at high temperatures (refluxing conditions) of DTBHN, methyl radicals are generated, which can be engaged in the initial iodine atom abstraction process with a molecule of radical precursor. When the reaction was performed at 60°C, a moderate yield of 53% was obtained (Table 3.1, *Entry 4*). Increasing the temperature to 80°C did not have a positive impact on the yield (Table 3.1, *Entry 5*). Increase of the concentration of the reaction mixture to 2.3 M led to an improved yield of 69% (Table 3.1, *Entry 6*). The addition of an heterogeneous base had a positive outcome on the reaction and a yield of 76% was observed (Table 3.1, *Entry 7*). The base might act as HI scavenger and has thus a beneficial impact on the reaction outcome. This was as well observed in previously reported reactions of our group.[24]
Due to the high amount of DTBHN used (0.4 eq) and because of the tedious synthesis of this initiator, we decided to turn our attention to the Et_3B/DTBHN initiation system, where the quantity of DTBHN can be reduced. Initially, the yield of the reaction did not improve neither with substoichiometric (Table 3.1, *Entry 8*) nor with excess equivalents of Et_3B (Table 3.1, *Entry 10*). We then decided to check the yield of the reaction at increased reaction concentration and temperature. Pleasingly, the yield reached 60% (Table 3.1, *Entry 9*) and 67% respectively (Table 3.1, *Entry 11*). Changing the solvent of the Et_3B solution from benzene to trifluorotoluene (TFT) had a beneficial impact on the reaction yield which raised to 76% (Table 3.1, *Entry 12*). The reaction was working even when lower amounts of initiator were used (Table 3.1, *Entry 13*). It is worth to mention that from now on, no additional solvent is added to the reaction mixture but all the reactants are solubilized thanks to the very small amount of solvent coming from the Et_3B solution. We anticipate that very concentrated reaction mixture are needed to favour the iodine atom transfer reactions. Lastly, the yield increased even more with the addition of the heterogeneous base Cs_2CO_3 (Table 3.1, *Entry 14*).

Curran and coworkers[25] elucidated the mechanism of initiation with Et_3B/air: Et_3B reacts in presence of oxygen to form an ethyl radical and diethylborylperoxy radical **10** (Scheme 3.4). This intermediate can further react with another molecule of Et_3B to form **11** via homolytic substitution (Step 2): formally a displacement of an ethyl group occurs to form another ethyl radical. This can now react with a radical precursor to initiate the desired chain reaction or further react with oxygen to form ethylperoxyradical **14** (Step 6). **14** undergoes homolytic substitution with Et_3B (Step 7) providing a new ethyl radical and diethylboron peroxide **12**. It is important to note that step 1 is not fast, even in presence of high concentrations of oxygen, but, on the other hand, the **autoxidation** of Et_3B is a fast process which keeps producing new ethyl radicals which will eventually initiate the desired chain reaction. Interestingly, primary autoxidation product **12** reacts differently in presence of high or low oxygen concentrations. In the first case,

different highly oxidized boronate esters and ultimately borate esters can form through various boryl peroxides; in the second case, ionic oxidation can occur and ethyldiethylborinate **13** will be delivered as product (8). As shown in step (3) or (4), different reactions can led to EtO• which can further react as drawn in (5). Oxygen can be added to the reaction mixture in different ways: by using an amount of air by syringe (and then derive the amount of oxygen) or by opening the reaction mixture using a $CaCl_2$ guard tube, preventing moisture to interact with the reaction mixture and therefore Et_3B. The second method was employed to perform the reaction using this initiation system.
The use of the DTBHN allows the exact control of the amount of oxygen centered radicals reacting with Et_3B. In fact, upon partial thermal decomposition at 60°C, DTBHN delivers 2 molecules of alkoxy radical which will react with Et_3B analogously as shown in Scheme 3.4.

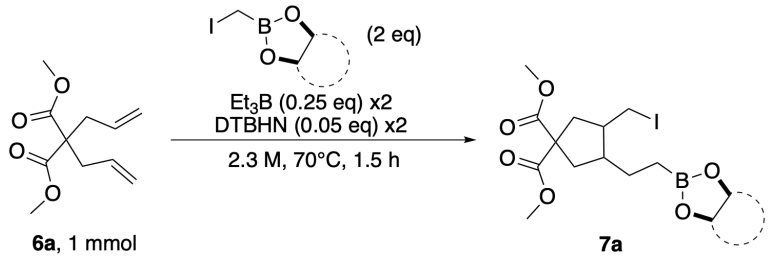


Scheme 3.4: Elementary steps in reactions of Et_3B and oxygen.

3.2.2 Radical precursor

Before starting with the scope of the reaction, we were interested in assessing the stability of these new 1,5-iodoboronic esters compounds over silica and compare it with 1,3-iodoboronic esters. Since the relative position of iodine atom and the boronic ester moiety is different, we were speculating that the compounds were **more stable** and thus **easier to purify.** Together with Dr. Yanis Lazib, we repeated the ATRAC reaction using different radical precursors bearing 4 different types of boronic esters. As shown in Scheme 3.2, the same yields were found when iodomethylenepinacol boronic ester (*Entry 1*) and iodomethylenenorbornene boronic ester were used as radical precursors for the reactions (*Entry 2*). The yield of the reaction is slightly lower

when iodomethylenepinane boronic ester was employed (Table 3.2, *Entry 3*). The best yield was found when iodomethyleneethylpinacol boronic ester was used as radical precursor (Table 3.2, *Entry 5*). Intrigued by the results of Ikawa and co.,[26] we wanted to exploit the unique feature of ethyl pinacol boronic esters whose stability on silica is increased with regards to the commercial pinacol boronic esters analogues. According to their work, these molecules adopt a conformation in which the empty *p* orbital of the boron atom is partially occupied by the C-H bond electrons of the ethyl moiety. As a result, the interaction between boron and the free OH groups of silica is reduced, the compounds are less retained and can migrate better on TLC. At the same time, degradation and yield losses during purification are reduced, as shown as well by our own results. At this point, the stage was set to start the substrate scope of the reaction and our investigation concerning the reactivity of α-boryl radicals.



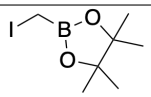
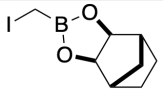
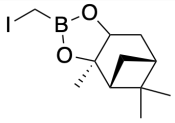
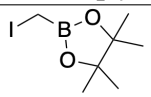
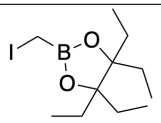
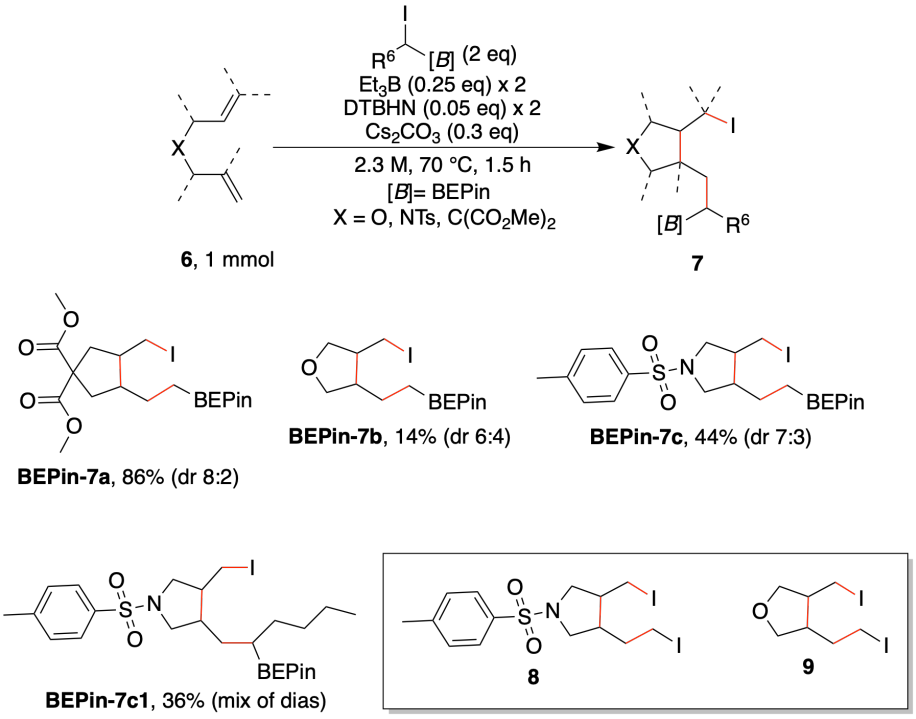
Entry	Radical Precursor	Additives	Isolated yield
1	 = ICH_2Bpin	/	**Bpin-7a** - 76% (dr 8:2)
2	 = ICH_2Bnor	/	**Bnor-7a** - 76% (dr 8:2)
3	 = ICH_2Bpan	/	**Bpan-7a** - 74% (dr 4:4:1:1)
4	 = ICH_2Bpin	0.3 eq Cs_2CO_3	**Bpin-7a** - 80% (dr 8:2)
5	 = ICH_2BEpin	0.3 eq Cs_2CO_3	**BEpin-7a** - 86% (dr 8:2)

Table 3.2: Choice of the radical precursor for the ATRAC reaction on dimethyl 2,2-diallylmalonate **6a**. Isolated yields.

3.3 Scope with ICH_2BEPin as radical precursor

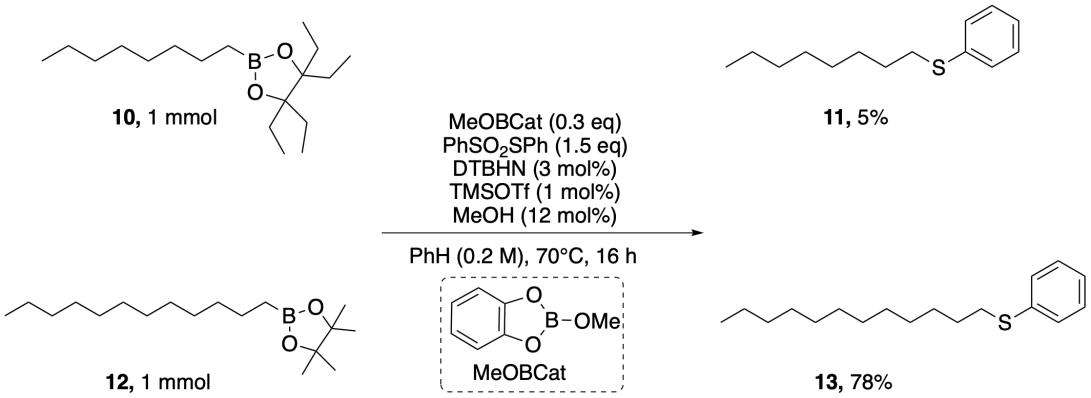
To assess the feasibility of the reaction, we decided to apply the methodology for the synthesis of different carbo- and heterocycles (Scheme 3.5). If the synthesis of cyclopentane **BEPin-7a** proceeded with an excellent yield, the synthesis of tetrahydrofuran **BEPin-7b** or pyrrolidine **BEPin-7c** was more problematic. The main issue was that, besides the desired product, a side-product was as well isolated. We identified that these compounds are the bis-iodinated derivatives **8** (for pyrrolidine) and **9** (for tetrahydrofuran) because of 2 peaks in the 0 - 10 ppm ^{13}C NMR region, accounted as primary iodinated carbon in a diastereomeric form. The synthesis of **8** via a multistep synthesis starting from **BEpin-7c** confirmed the result. It is not clear yet why this compound is generated during the reaction. Concerning **BEPin-7b**, an additional problem is the volatility of the starting diene at 70°C which lowers even more the yield of the reaction. The attempt in using a secondary radical percursor, delivered the desired product **BEPin-7c1** in a moderate yield of 36%.



Scheme 3.5: Substrate scope of ATRAC using $ICH_2$2BEPin as radical precursor. Isolated yields.

Before understanding in more details the mechanism of generation of this side product, we had a look at possible post-functionalizations of the cyclized compounds bearing a BEPin group. Oxidation and deiodination worked smoothly, but, once we wanted to apply the published methodology to perform deboronative functionalization,[27] the ethyl pinacol boronic ester moiety proved to be too stable and less prone to transesterification with MeOBCat (Scheme 3.6). Very low yield (∼5%) were obtained in comparaison to the reaction with pinacol boronic esters **12** (78%)

(Scheme 3.6). It was interesting to discover this huge difference in reactivity of -BPin vs -BEPin in the context of the reaction with MeOBCat: if both moieties are present on the same molecule, one can envision the selective functionalization of the pinacol boronic ester in the presence of a ethyl pinacol boronic ester, which can undergo another type of functionalization in a successive step.



Scheme 3.6: Radical deboronative sulfuration on ethyl pinacol and pinacol boronic esters: comparison of results. Isolated yields.

The use of ICH_2BEPin did not prove to be broad and different problems were encountered. If it is as well taken into account that the synthesis of the radical precursor is quite tedious, it turned out not to be the best radical precursor for the substrate scope of ATRAC reaction. If we now look back at Table 3.2, the second best results were obtained when iodomethylenenorbornene boronic ester (ICH_2Bnor) and iodomethylenepinacol boronic ester (ICH_2Bpin) were used as radical precursors. In conclusion, we selected the ICH_2Bpin as radical precursor due to its easier preparation and availability of starting reagents.

3.4 Scope with ICH_2BPin as radical precursor

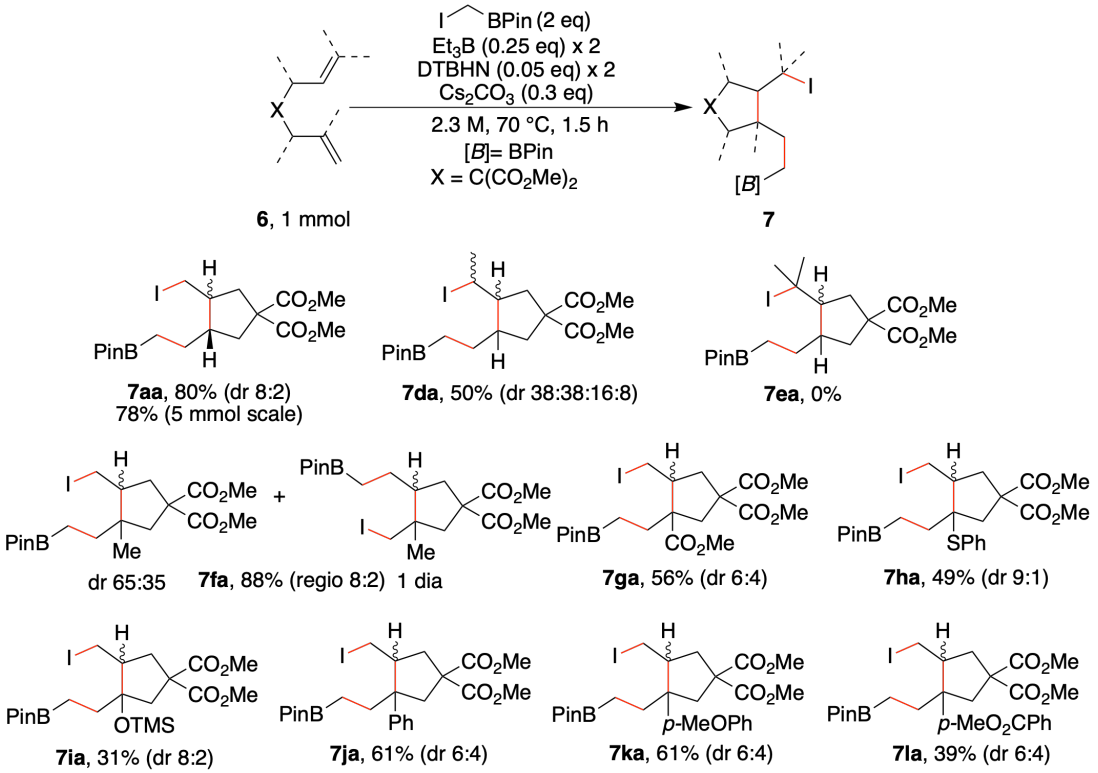
Cyclopentanes and pyrrolidines

A variety of different dienes were synthesized and then tested in ATRAC reaction using ICH_2BPin as radical precursor. Moderate to excellent results were obtained (Scheme 3.7). If compounds **7aa**, **7da** and **7ea** are considered, a substantial difference in yield can be observed and this is due to the fact that the final radical after cyclisation is, respectively, a primary, a secondary and a tertiary one. The results show a tendency where iodine atom transfer is faster and more efficient if performed with a primary radical with regards to a secondary and a tertiary one. Moreover, the yield of **7da** is in the same range with the observed yields of the intermolecular ATRA reaction (discussed in Chapter 2) meaning that this step has a huge impact in the outcome of the reaction. When a tertiary radical is formed at the end of the cyclisation, the iodine atom transfer did not take place efficiently or the desired compound is so unstable that it degrades after light exposure or during the work-up. We attempted to add a base to form the unsaturated compound from **7ea** but we did not recover the desired product after column chromatography purification.

In addition to that, we wanted to assess the philicity of the α-boryl radical, since this is still not fully understood.[28] Another series of dienes was thus synthesized, bearing an internal substituent on one of the double bonds (**7fa** to **7la**). The double bond being now more activated, oligomerization reaction was observed and it had an impact on the final yield. For this reason, 4 equivalents of radical precursor were used to favour the iodine atom transfer step.

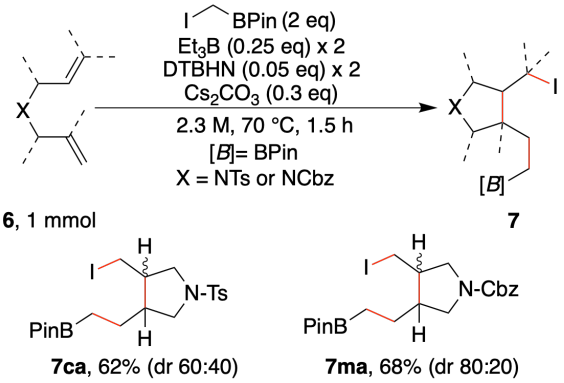
In presence of methyl group bound to one of the two double bonds, the desired **7fa** was recovered with 88% yield. However, two regioisomers were identified because of the similar electron richness of both double bonds on the dienes. When more activating groups were employed, only one regioisomer was formed after cyclization reaction. When -EWG and -EDG groups (**7ga** and **7ha**) were introduced to the double bond, small differences in yield were observed. **7ia** has to be treated separately, since the desired compound was unstable on silica due to the acid labile -OTMS group. Lastly, different phenyl groups were introduced as well on one side of the diene and the ATRAC reaction was then performed. The same yield was found when phenyl (**7ja**) and paramethoxyphenyl groups (**7ka**) were used. However, in the case of paraestergroup (**7la**), the yield dropped to 39% because the competing oligomerization reaction occurs faster and thus led to a more important erosion in yield.

Our results show **a possible tendency of alpha-boryl radicals to be ambiphilic**, reacting well with electron rich and electron poor traps.



Scheme 3.7: ATRAC with ICH_2BPin - synthesis of substituted cyclopentane rings. **7fa** to **7la**: performed with 4 eq. of ICH_2BPin. Isolated yields.

The synthesis of pyrrolidines proceeded smoothly without any significant side-reaction observed (Scheme 3.8).

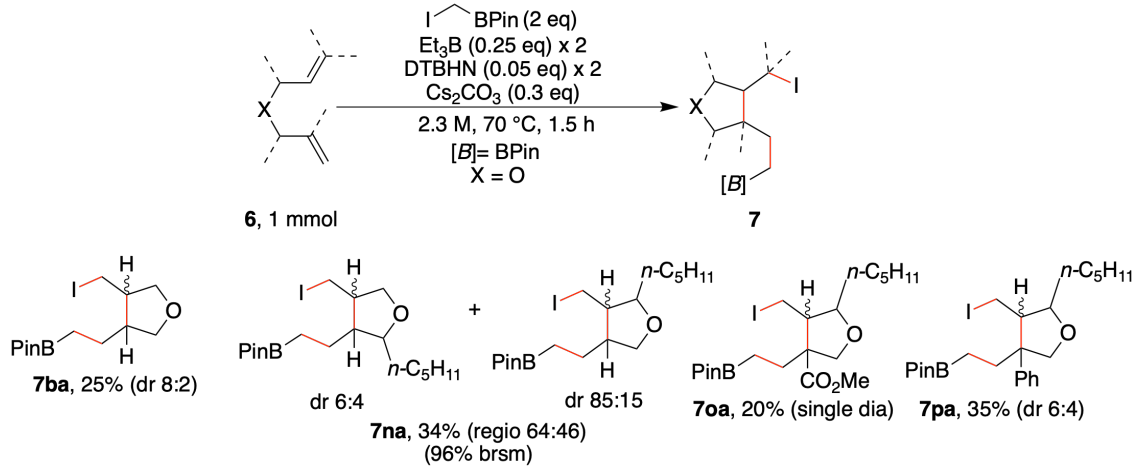


Scheme 3.8: ATRAC with ICH_2BPin - synthesis of substituted pyrrolidines rings. Isolated yields.

Tetrahydrofurans

The synthesis of tetrahydrofurans derivatives was unfortunately more difficult (Scheme 3.9). The yield of the simplest tetrahydrofuran ring **7ba** was low due to the volatility of the starting material. For this reason, the cyclisation was attempted on a diene bearing an alkyl chain. Unfortunately, not only the yield was low (**7na**) but two regioisomers were as well recovered.

We then introduced a substituent on one of the two double bonds of the dienes, as previously done with the cyclopentanes ring serie. However, also in this case, the observed yields were quite low (**7oa** and **7pa**). Besides the possible oligomerization reaction which can take place and erode the yields, other side reactions might impact the desired radical chain reaction. One important prove for that is the very high yield based on recovered starting material for compound **7na** (Scheme 3.9). This clearly speaks for a inefficient chain reaction or, in other words, that iodine atom transfer is slower than another concurrent process. As a result, the chain is killed and the starting diene is recovered after column chromatography.

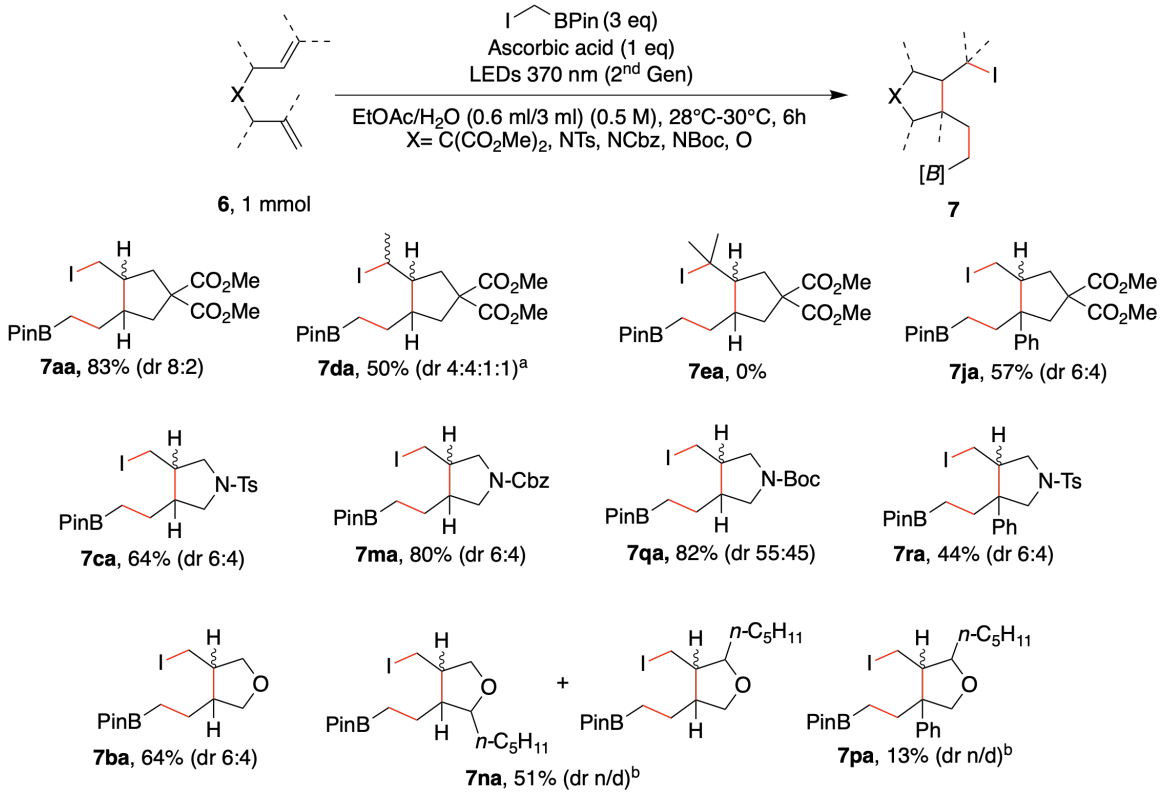


Scheme 3.9: ATRAC with ICH_2BPin - synthesis of substituted tetrahydrofurans. **7oa**-**7pa** performed with 4 eq. of ICH_2BPin.

Before investigating what is the reaction which negatively affects the ATRAC process, we wanted to change initiation conditions: the idea is that by reducing the reaction temperature, the rate of any side reaction will be reduced as well and higher yields of the desired ATRAC product will be expected.

Scope using photoredox conditions

As discussed in the introduction part (Chapter 1, pag.17), Kokotos and Renaud et al. have recently published a method to synthesize 1,3-iodopinacol boronic esters using photoredox conditions.[29] This method appeared particularly interesting because we wanted to attempt the ATRAC reaction using these conditions, expecting that possible side reactions would be reduced or completely suppressed. Indeed, all the reactions were performed at 30°C instead of 70°C, so we were believing that this big difference in temperature might impact the rate of side reactions which interfere with the desired ATRAC process. A collaboration was therefore started and Ms. Charikleia Batsika repeated some reactions using photoredox conditions (Scheme 3.10).

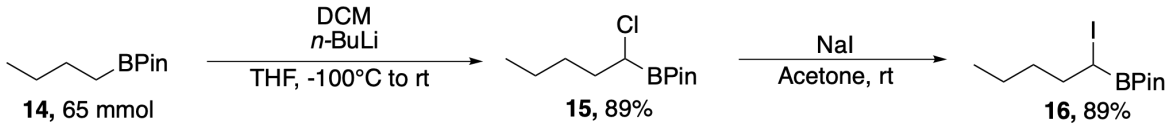


Scheme 3.10: ATRAC with ICH_2BPin - scope using photoredox conditions. [a]30 minutes reaction. [b]0.05 M solution. Isolated yields.

The obtained results are very interesting: if **7aa**, **7da**, **7ea** and **7ja** are considered, the same yields as the Et_3B/DTBHN initiation method were observed. Also in this case, the iodine atom transfer from a primary radical works better than when a secondary or tertiary radical are formed after cyclisation. Concerning the heterocycles, the results were slightly different. The yields for the pyrrolidines **7ca** and **7ma** improved of about 15%-20%. For the tetrahydrofurans ring formation, we were pleased to observe that the desired compound **7ba** was obtained from diallyl ether with 64% yield. However, once substituents decorated the starting diene, either α to the oxygen atom (**7na**) or on one of the two double bonds (**7pa**), the yields dropped to what was previously observed. We concluded that possible side reactions might occur as well at this temperature and have thus an impact on the final yield of the desired ATRAC transformation.

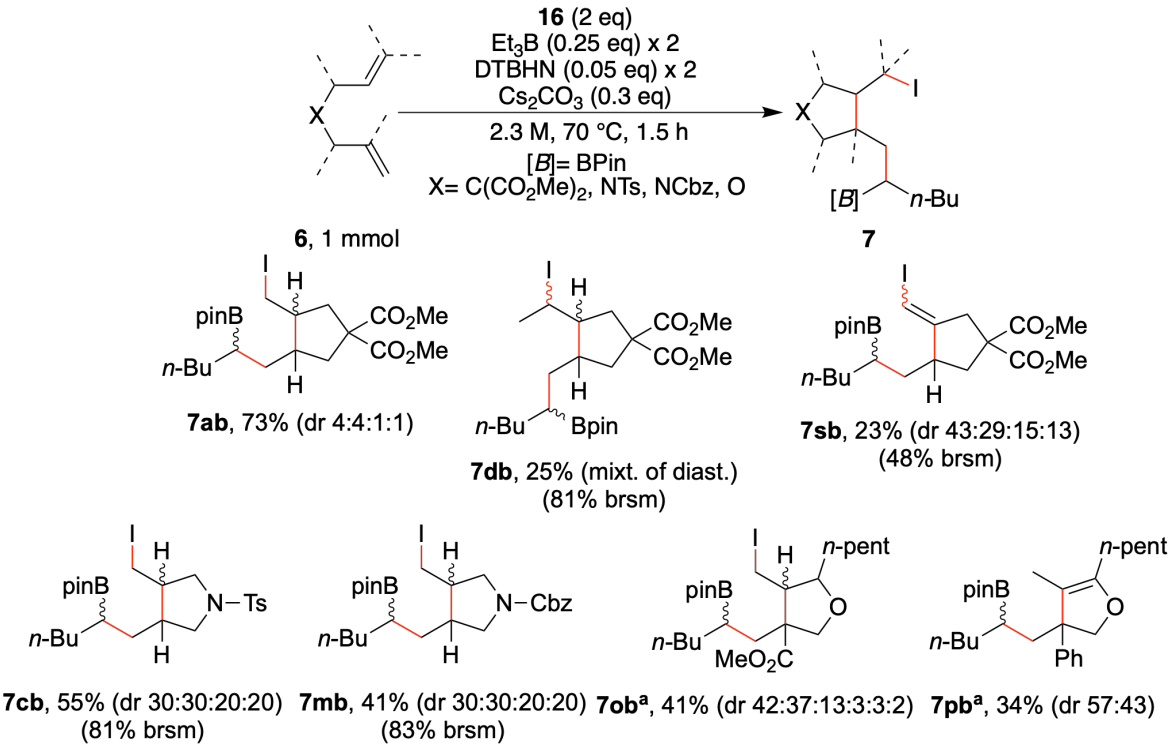
3.5 Substrate scope using a secondary radical precursor

After having performed the scope using a primary radical precursor (ICH_2BPin), the radical cyclisation reactions were repeated using a new radical precursor which delivers a secondary α-boryl radical after the initiation step. The radical precursor can be easily synthesized by Matteson homologation approach starting from the commercial alkyl boronic ester **14**, followed by a Finkelstein reaction delivering the desired radical precursor **16** (Scheme 3.11).



Scheme 3.11: Synthesis of secondary radical precursor **16** for ATRAC reactions. Isolated yields.

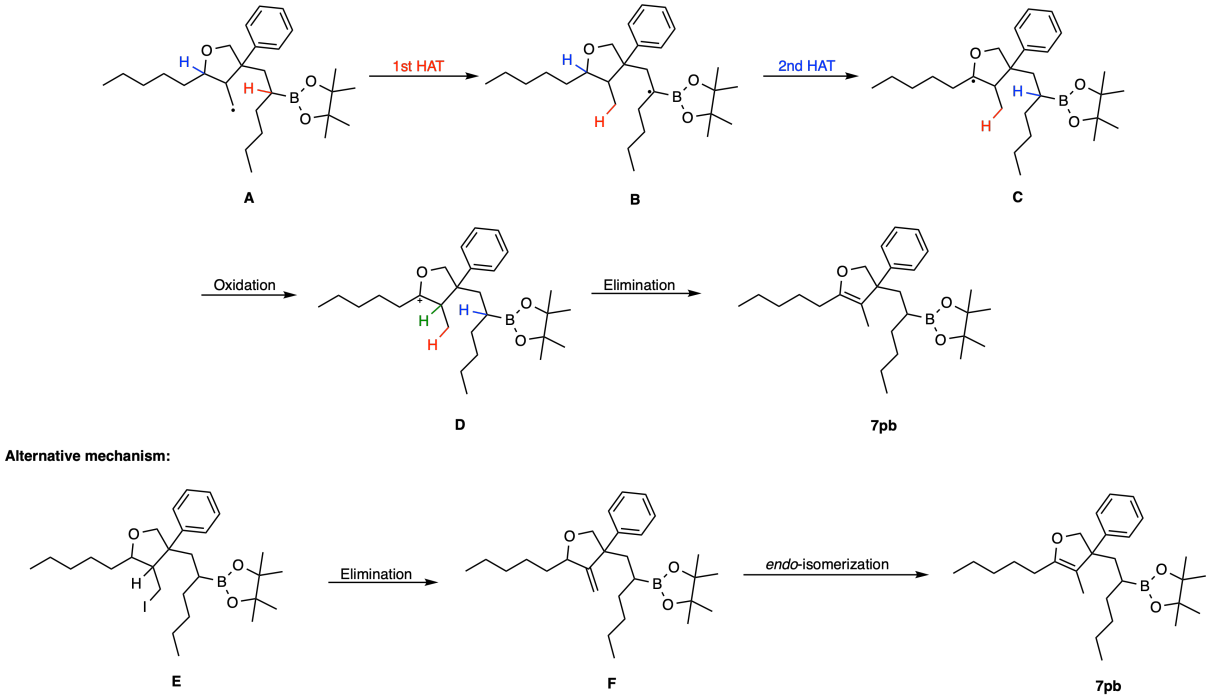
The results of the substrate scope are highlighted in Scheme 3.12. Apart from example **7ab**, the yields are quite low. However, if examples **7db**, **7sb**, and **7cb** are considered, the yields based on recovered starting material are very high. The most interesting examples are, however, the tetrahydrofurans derivatives **7ob** and **7pb**. If **7ob** was synthesized in moderate yield, changing from ester to phenyl group leads to a completely different compound **7pb**.



Scheme 3.12: Substrate scope with secondary radical precursor. [a]4 equivalents of **16** used. Isolated yields.

At this point, we had a first evidence that the concurring reaction which takes place during the ATRAC process is the **intramolecular 1,5-hydrogen atom transfer (1,5-HAT)**. To obtain

7pb, we speculated that two 1,5-HAT processes take place (Scheme 3.13): intermediate **A** is subjected to the first intramolecular 1,5-HAT process to form a tertiary α-boryl radical **B**. This intermediate undergoes the second intramolecular 1,5-HAT reaction to form intermediate **C**, a tertiary alkoxy radical. This radical is then oxidised to the carbocation **D**, which after a endo-elimination process (under Cs_2CO_3 presence) delivers the **7pb**. is now oxidized to a carbocation **D** which is then eliminated during the reaction, presumibly helped by the presence of Cs_2CO_3. An alternative to this mechanism for the synthesis of **7pb** is HI elimination from the ATRAC product **E** and *endo*-isomerization of the resulting unsaturated compound **F** to the more stable tetrasubstituted double bond.

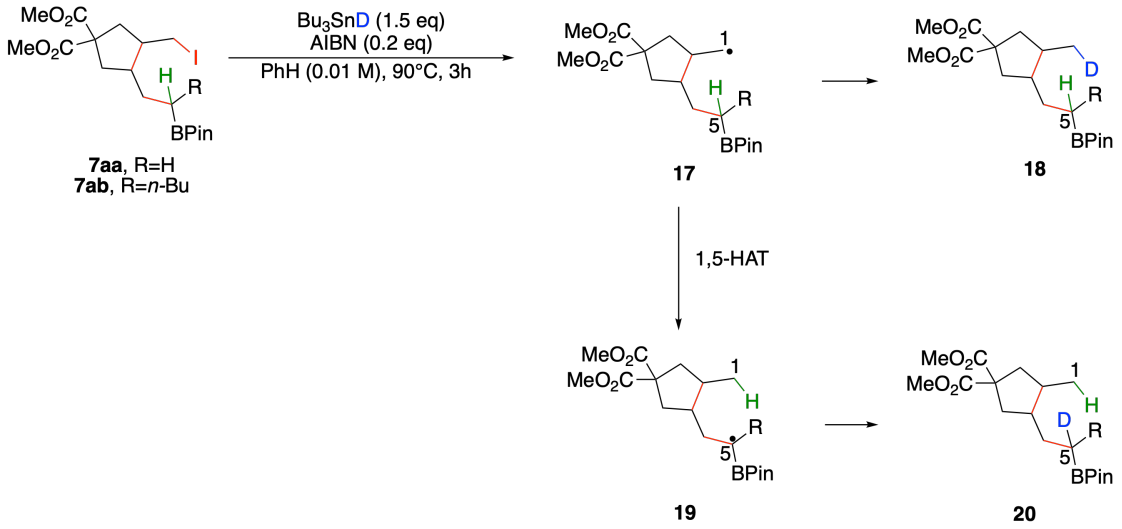


Scheme 3.13: Possible mechanisms for the formation of compound **7pb**.

Going back to scope, when an ester group is introduced on one of the double bond of the diene, the desired ATRAC compound **7ob** was obtained, but not the unsaturated one. We speculated that the transition state which delivers compound **7pb** is more planar than the one delivering **7ob** enabling thus the crucial 1,5-HAT processes which give rise to compound **7pb**. In other words, the phenyl group will be exclusively in an equatorial position because of its high A value ($\sim$3 kcal/mol),[30] allowing the hydrogen atom abstraction process to take place.

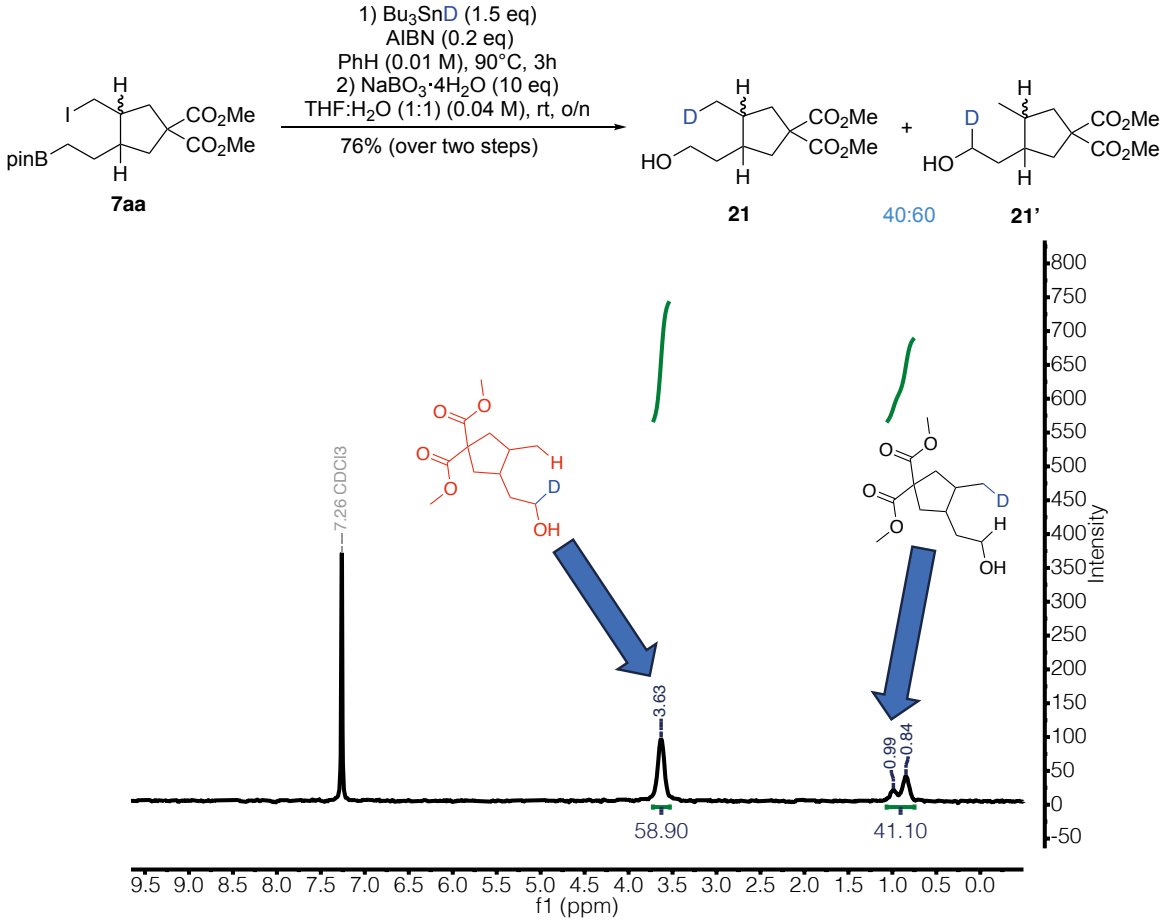
3.6 Mechanistic investigations

At this point of the project, we were interested in performing a final experiment which would prove the presence of 1,5-HAT process during the ATRAC reaction. Our idea was to take two ATRAC products, **7aa** and **7ab** and submit them to $SnBu_3D$/AIBN deuteration conditions. Mechanistically, after iodine atom abstraction, the same final intermediate of ATRAC **17** is reformed and 1,5-HAT process can take place to deliver intermediate **19**. Depending at which position deuterium is integrated, we can now verify if the reaction takes place and evaluate its performance. To verify where deuterium was incorporated, ^{2}H-NMR was measured. However, **18**/**20** was oxidized to the corresponding alcohol because we expected a different shift in the NMR spectra between the 2 deuterium positions 1 and 5.



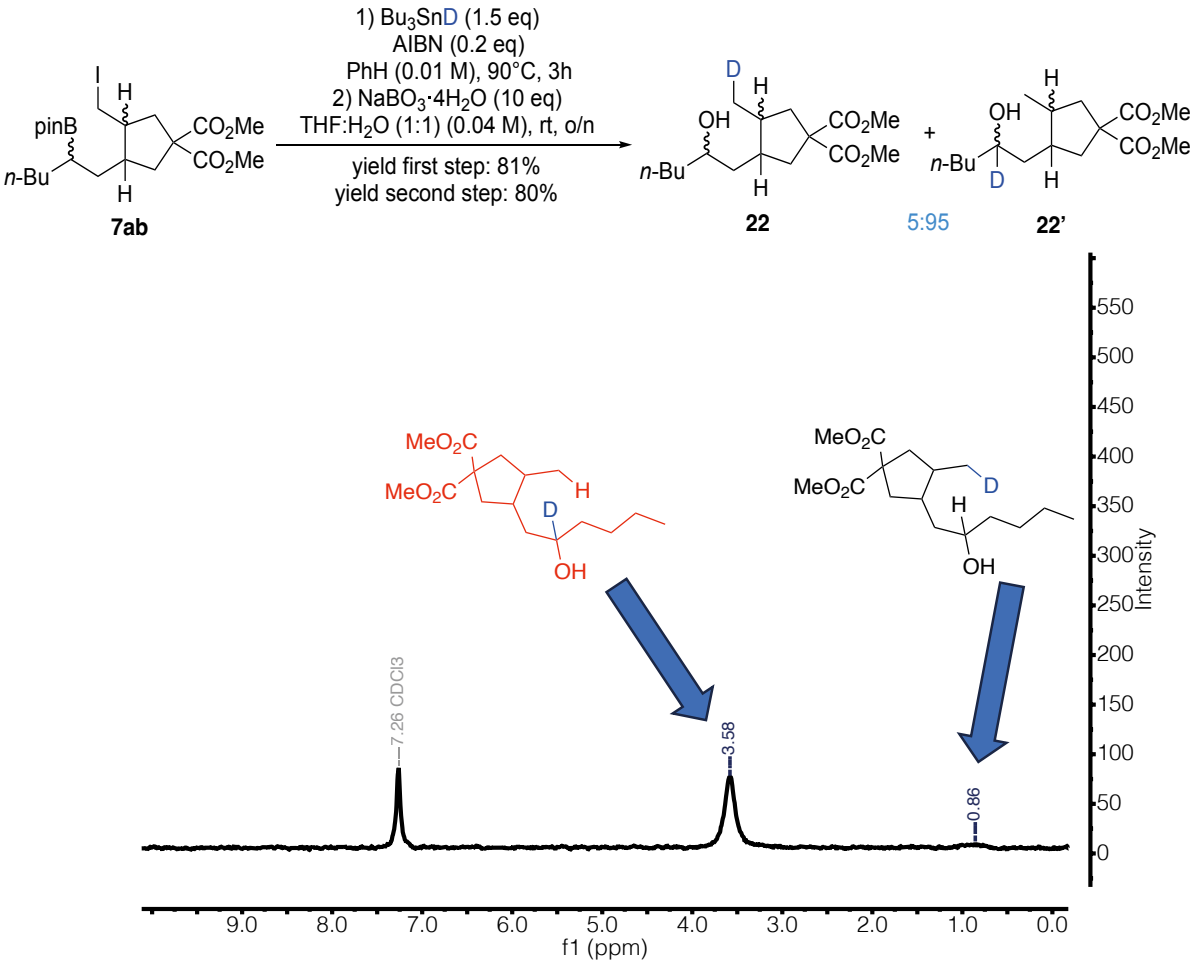
Scheme 3.14: Aim of the deuteration experiment.

For compound **7aa**, the results of the experiment are shown in Scheme 3.15. The spectra shows a ratio of 60:40 between, the major being the compound where deuterium is α to the alcohol group (**21'**).



Scheme 3.15: Deuteration experiment on ATRAC product **7aa**.

The same experiment was performed using **7ab** and the results are shown in Scheme 3.16. In this case, the majority of the mixture contained compound **22'** which arise from 1,5-HAT and subsequent deuteration. This result explains why, when a secondary radical precursor is used for the substrate scope, the yield based on recovered starting material is high. Indeed, the radical chain has to be reinitiated to convert the starting diene into the desired ATRAC product because the 1,5-HAT process is faster and keeps killing the chain.



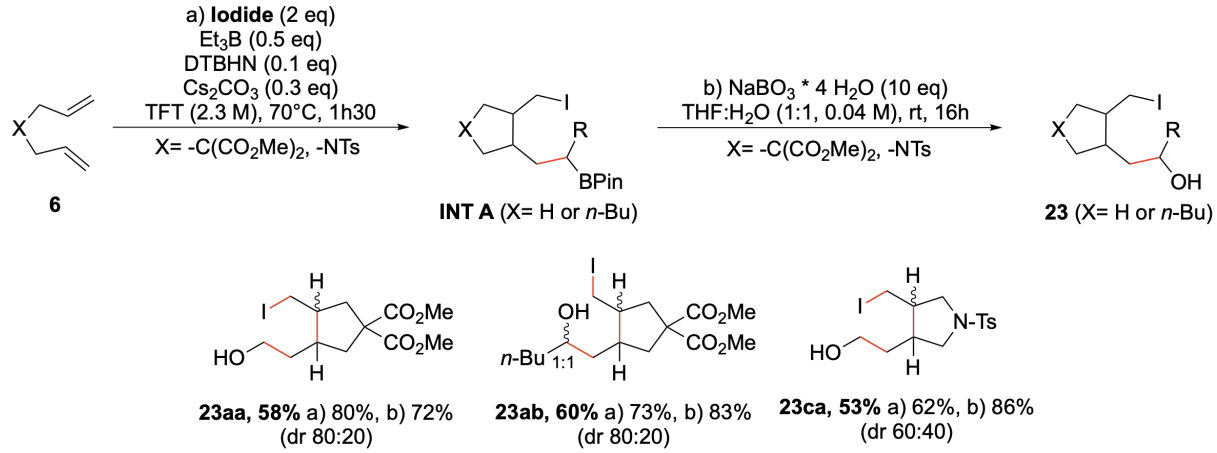
Scheme 3.16: Deuteration experiment on ATRAC product **7ab**.

3.7 Post-functionalizations

To further show the value of the developed synthetic method and of the obtained compounds, we attempted to post-functionalize the ATRAC products using different reactions.

3.7.1 Iodohydroxyalkylation

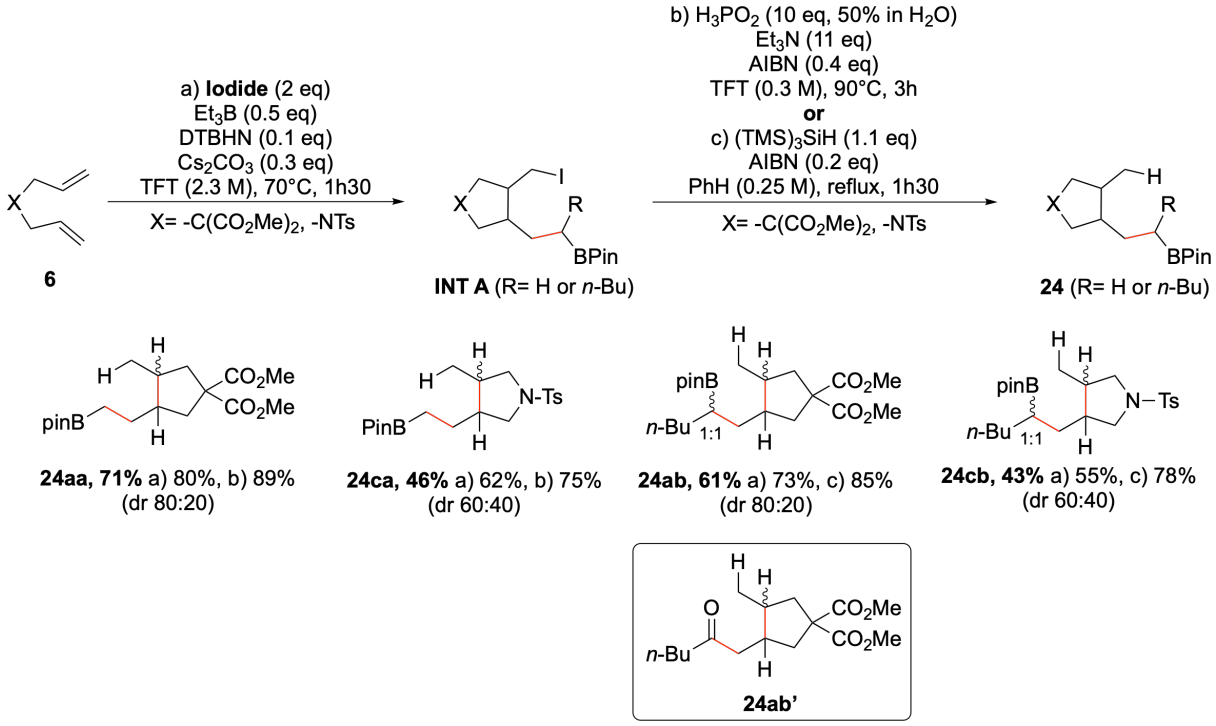
The first transformation attempted was the oxidation of the boronic ester moiety using sodium perborate. The reaction worked well in all the three selected ATRAC compounds, giving high isolated and overall yields (Scheme 3.17).



Scheme 3.17: Scope iodohydroxyalkylation. Isolated yields.

3.7.2 Hydroborylalkylation

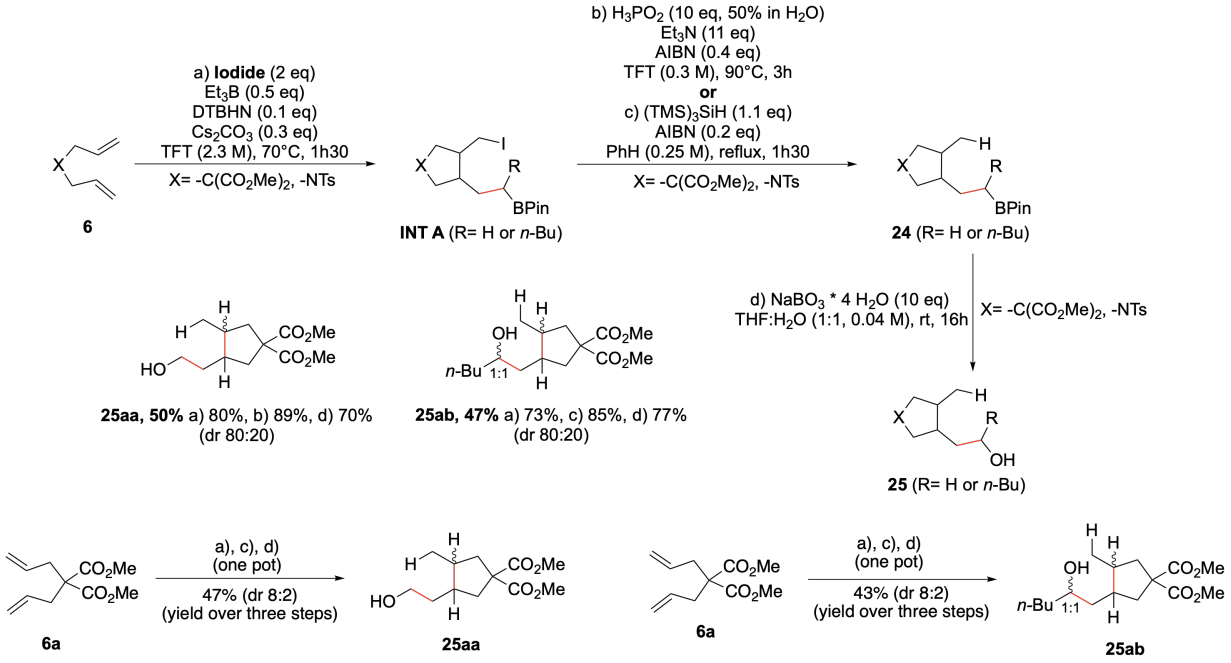
Hydroborylalkylation was performed starting from alkenes **6** by submitting the ATRA products to Barton's deiodination[31] conditions (Scheme 3.18). If the synthesis of **24aa** and **24ca** proceeded smoothly and with excellent yields, when the same reaction conditions were applied for the synthesis of **24ab**, side product **24ab'** was recovered together with the desired compound **24ab**, whose yield was ∼50%. We suspected that this product was formed via a 1,5-HAT mechanism, but no additional studies were conducted to understand the pathway which led to the formation of this compound. To improve the yield of the transformation, the deiodination conditions were changed to TTMS/AIBN, reported by Chatgilialoglu et al.[32] Pleasingly, by using this method, only the reduced compound **24ab** was obtained with 85% yield. These reaction conditions were as well applied to synthesize **24cb** from the corresponding ATRAC intermediate and a yield of 78% was obtained.



Scheme 3.18: Scope hydroborylalkylation. Isolated yields.

3.7.3 Hydroxymethylation

The hydroborylalkylated compounds **24aa** and **24ab** (Scheme 3.18) were submitted to sodium borate oxidation conditions to yield the corresponding oxidized compounds. Formally, it is an hydroxymethylation (or hydroxyalkylation) of starting olefin **6**. The synthesis of **25aa** and **25ab** proceeded smoothly and a yield of 70% and 77% respectively for the oxidation step were observed. It's important to note that every reaction is followed by a work-up and a purification step. However, we wanted to show that three reactions can be performed in one-pot to deliver the desired hydroxymethylated compound. Pleasingly, **25aa** and **25ab** can be synthesized in a one-pot ATRAC, oxidation and deiodination process with a yield of 47% and 43% over three steps respectively. In this case, just one purification was performed at the end of the third step, which is a huge advantage in terms of solvents wastes and time optimization.



Scheme 3.19: Scope hydroxymethylation. Isolated yields.

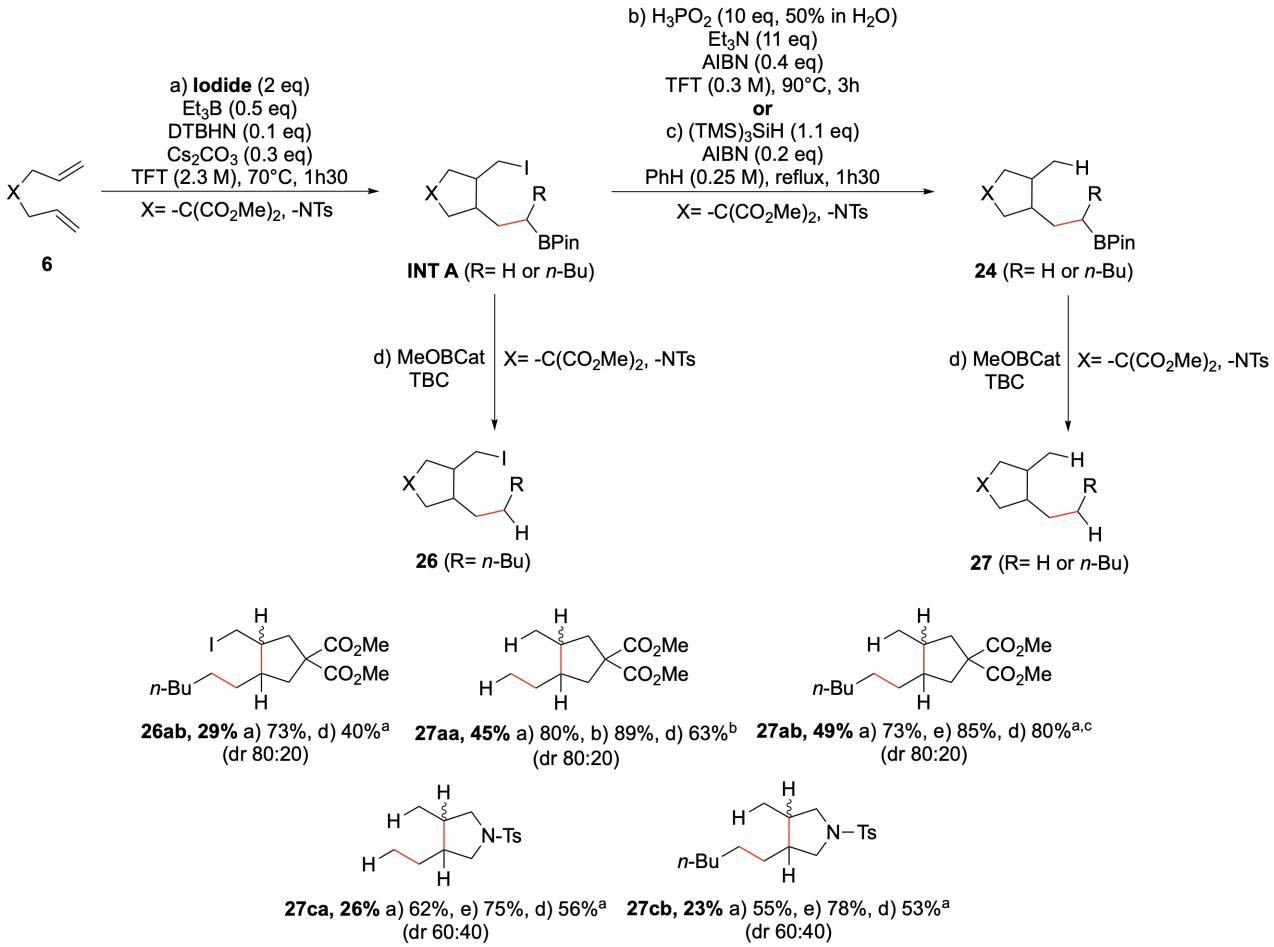
3.7.4 Hydromethylation and hydroalkylation

We wanted as well to valorise the pinacol boronic ester moiety by applying other functionalization reactions apart from oxidation. For this reason, we used the previously reported conditions on radical deboronative functionalization developed in our group[27] and we were particularly interested in the reduction of the boronic ester moiety using TBC/MeOBCat.

Initially, we attempted the direct reduction of **INT A** (Scheme 3.20) using MeOBCat and TBC in the presence of an iodide moiety in the molecule. The reaction worked only with a secondary pinacol boronic ester and delivered compound **26ab** in moderate yield. We suspected that the presence of the iodine moiety might interfere during the radical deboronative reduction step. For this reason, we reduced INT A using the previously described reaction conditions (Chapter 3 - Paragraph 3.7.2) and then submitted the resulting compounds to radical deboronative reduction. The reaction worked well this time but it is important to discuss each example separately. For the synthesis of **27aa**, the initial attempts were unsuccessful and poor yield were found using the before published protocol where 0.3 eq. MeOBCat and 1.5 eq TBC were employed. We speculated that the conformation of the five-membered ring might render the trans-esterification more complicated either due to steric hindrance or because of the coordination of the empty *p* orbital of boron with the oxygen atom of the malonate moiety. To push the transesterification reaction, the quantity of MeOBCat and TBC were increased to 1 eq. and 3 eq. respectively. Pleasingly, the reaction worked well with a yield of 63% and it was finished after 2 hours, instead of 16 hours.

For the synthesis of **27ab**, **27ca** and **27cb**, substoichiometric amounts of MeOBCat and reduced equivalents of TBC, as previously reported, were sufficient to achieve good yields. Notably, for

the synthesis of **27ca**, 0.3 eq. of MeOBCat were sufficient to perform the reaction, supporting our hypothesis that the malonate moiety might hinder the desired radical deboronative chain either because of steric hindrance or for complexation of the boron atom with one oxygen of the malonate group.

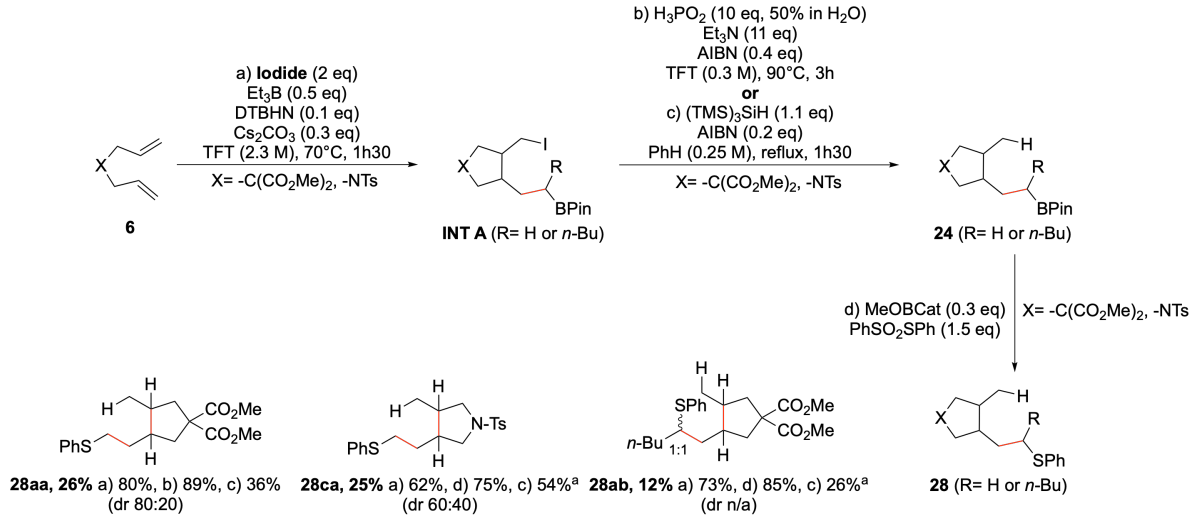


Scheme 3.20: Scope hydroxymethylation and hydroalkylation. Isolated yields. [a]0.3 eq. MeOBCat and 1.5 eq. TBC used; [b]1 eq MeOBCat and 3 eq. TBC used; [c]Yield determined by using an internal standard (1,3,5-trimethoxybenzene) in impure fractions.

3.7.5 Hydrothiolation

Based on the same approach presented for the hydromethylation and hydroalkylation, we attempted the sulfurization reaction of the ATRAC intermediates via a radical deboronative process. Compound **28aa** (Scheme 3.21) was synthesized after ATRAC, reduction and radical deboronative sulfurization and a overall yield of 26% was obtained. Apart from the previously discussed issues concerning the transesterefication with MeOBCat, the sulfurization reaction is known to be quite slow, especially for a primary radical, meaning that possible side reactions can occur during the reaction and thus the impact on the yield is more important. **28ca** was

obtained with moderated yield, showing that the malonate group might impact negatively the transterification step with MeOBCat. Concerning **28ab**, the yield of the reaction was quite low, although the sulfurisation of a secondary radical should work better.

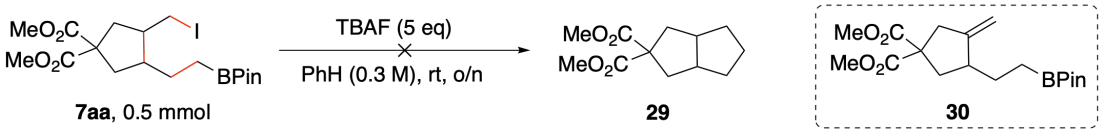


Scheme 3.21: Scope Hydrothiolation. Isolated yields. [a]Yield determinated by using an internal standard (1,3,5-trimethoxybenzene) in impure fractions.

3.7.6 Miscellaneous

A variety of different other reactions were tried on the ATRAC compounds bearing a *gem*-ester group for further post-functionalizations. The purpose was the synthesis of a second ring to access bicyclic structures which are main core of various natural compounds.

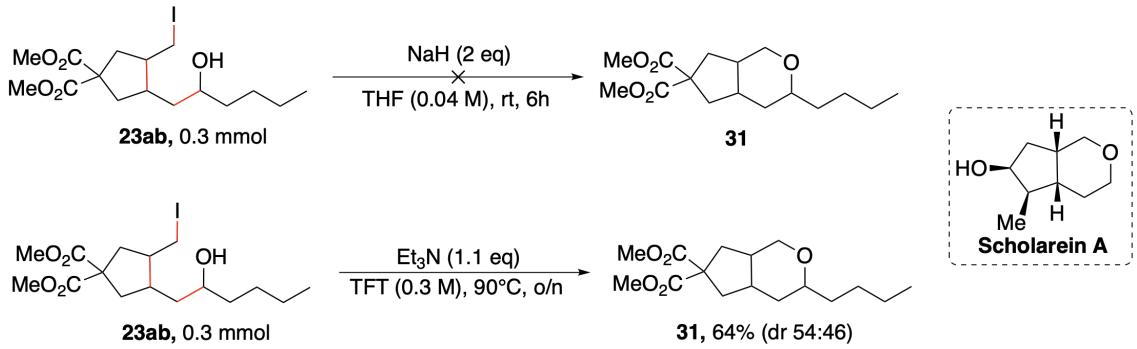
We first attempted to synthesize the octahydropentalene structure (**29**, Scheme 3.22) using TBAF elimination,[33] supposing that ionic 5-*exo*-tet cyclization could take place. Unfortunately, the reaction did not work but traces compound **29** were recovered after column chromatography. We speculated that the fluorine anion coming from TBAF acted as base instead of nucleophile, provoking the elimination reaction. However, **30** attracted our attention for possible derivatization products which might be synthesized: the *exo*-methylene group can in fact be functionalized using various reactions. We attempted the synthesis of **30** using potassium tert-butoxide and DBU as bases to perform the desired E2 elimination. However, the reaction was messy and did not have a positive outcome.



Scheme 3.22: Attempt for the synthesis of octahydropentalene scaffold.

Another interesting scaffold we wanted to access was the byclic 3-butyloctahydrocyclopenta[c]-

pyran (**31**, Scheme 3.23), main core of the iridolactones natural products, such as Scholarein A.[34] First, the deprotonation of alcohol **23ab** was attempted using sodium hydride as base. However, the reaction did not work. While performing the synthesis of **23ab** (Scheme 3.19) via one-pot three steps reaction, after deiodination of the 1,5-iodo alcohol intermediate using Barton's conditions (H_3PO_2/Et_3N/AIBN), **31** (Scheme 3.23) was recovered together with the desired compound. We decided then to try the reaction by using just a small excess of base and with the same solvent and temperature of the deiodination step. Pleasingly, the desired bicyclic compound **31** might be furnished with 64% yield.



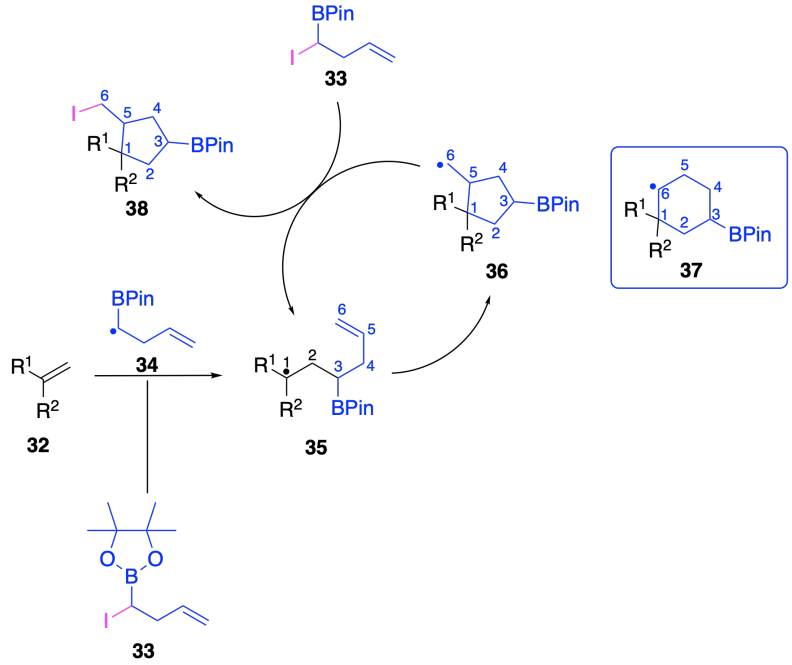
Scheme 3.23: Attempt for the synthesis of butyloctahydrocyclopenta[c]pyran scaffold. Isolated yield.

3.8 On an annulation reaction involving α-boryl radicals: ATRAn (Atom Transfer Radical Addition and Annulation)

At this point of the project, we gained a lot of knowledge about the reactivity of α-boryl radicals, in particular in the understanding of the side-reactions which negatively impact the outcome of the desired ATRAC reaction. However, we still wanted to apply this chemistry to develop new annulation reactions which gave access to interesting building blocks for natural product synthesis.

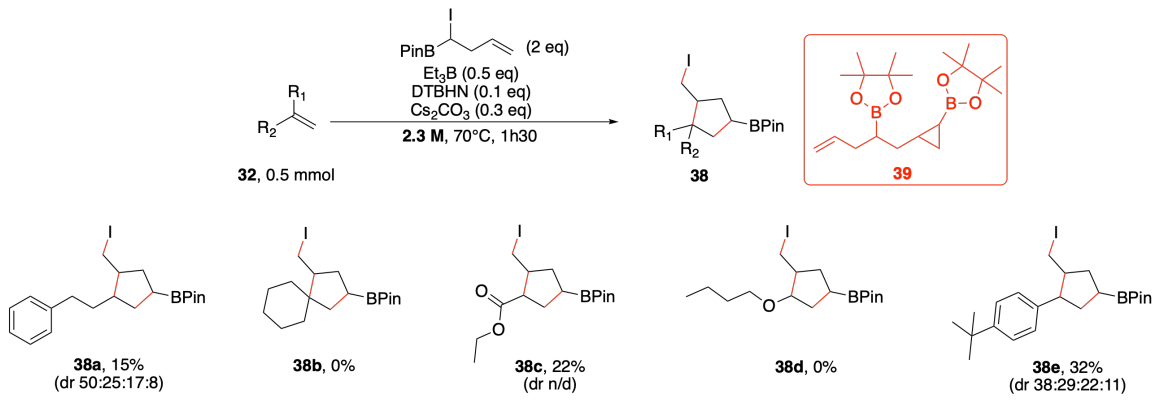
Previously, our group reported the first [3+2]-annulation reaction involving α-boryl radicals.[24,35] In this case, the addition of a radical was done on a vinyl pinacol boronic ester, thus generating the intermediate α-boryl radicals in-situ. This radical could then undergo annulation and formation of the desired borylated cyclopentane. The reaction was extended to 1,1-diborylethene and the desired γ-iodo-*gem*-diborylated cyclopentanes, issued from the addition of α-boryl radicals on this radical trap, was recovered.

For this annulation reaction, the approach was opposite. Our idea was to add a secondary α-boryl radical bearing a double bond **34** (Scheme 3.24) to different commercial linear olefins **32**. The radical can be generated from **33** after initiation with Et_3B/DTBHN. **34** will then add on the olefin to form intermediate **35** which will undergo [3+2]-annulation to deliver **36**. It is important to point out that **37** can theoretically form as well. However, the 6-member ring formation is disfavoured, mainly because the reaction is slower and the transition state is more energetic. **36** will then react with a new molecule of **33** in the deciding iodine-atom transfer reaction step: compound **38** will be formed as desired product and a new radical **34** will sustain the chain. The final products of this annulation reaction will be **1,4-iodo pinacol boronic esters**: the position of iodine and boronic ester moieties being different, we were hoping that particularly the 1,5-HAT reaction would be disfavoured, leading to better yields and a more efficient radical chain process.



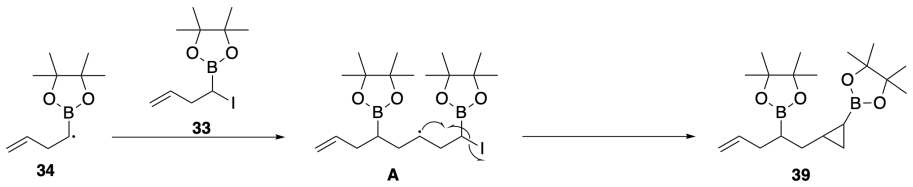
Scheme 3.24: Mechanism of the ATRAn reaction.

First of all, we attempted to use the optimized ATRAC conditions for the neww ATRAn reaction (Scheme 3.25). For this reason, we screened 5 commercial olefins with different characteristics. At this stage, the radical traps were used as such without preliminary purification via distillation or filtration over silica. When an inactivated olefin was employed, desired compound **38a** was recovered with very low yield. When a 1,1-disubstituted olefin was submitted to the reaction conditions, the desired compound **38b** was not formed. We tried activated olefins with strong EWG or EDG groups but, also in this case, the results were not satisfactory: **38c** was recovered with 22% and **38d** was not formed after the reaction. The best yield was found when the synthesis of styrene derivative **38e** was attempted. Beside the low yields, another common point between these examples is the presence of side-product **39** which was always recovered after column chromatography. But why this compound is formed? A plausible mechanism is described in the Scheme 3.26.



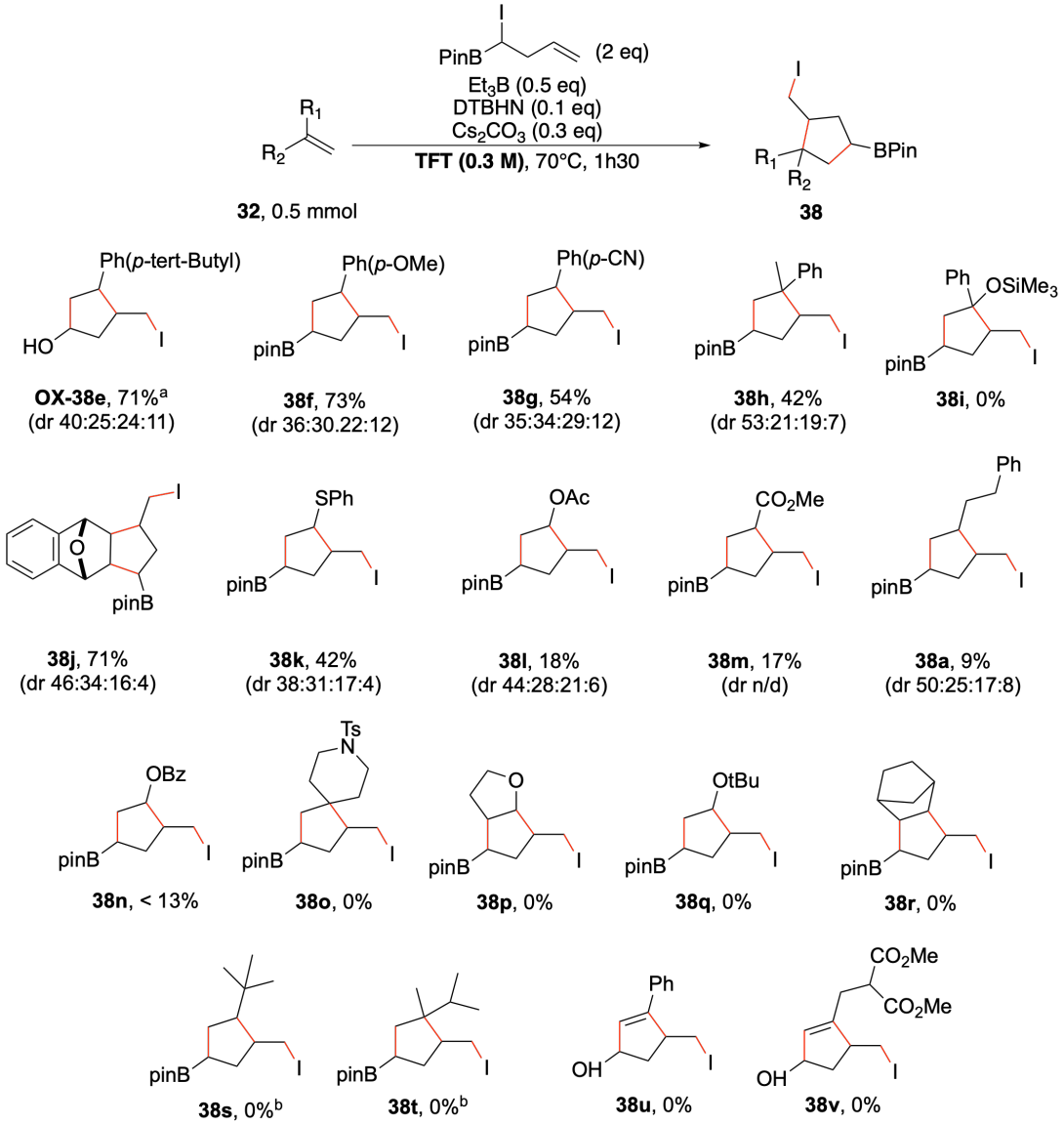
Scheme 3.25: Initial screening of different olefins - ATRAC conditions. Isolated yields.

For the synthesis of the desired 1,4-iodo pinacol boronic ester, α-boryl radical **34** (Scheme 3.26) has to add the olefin to undergo the desired annulation reaction. However, if the addition on the olefin is disfavoured due to polar effects or steric hindrance, radical **34** will add on **33** to form intermediate **A**. This will undergo 1,3-homolytic substitution to deliver compound **39** as a side product of ATRAn reaction.



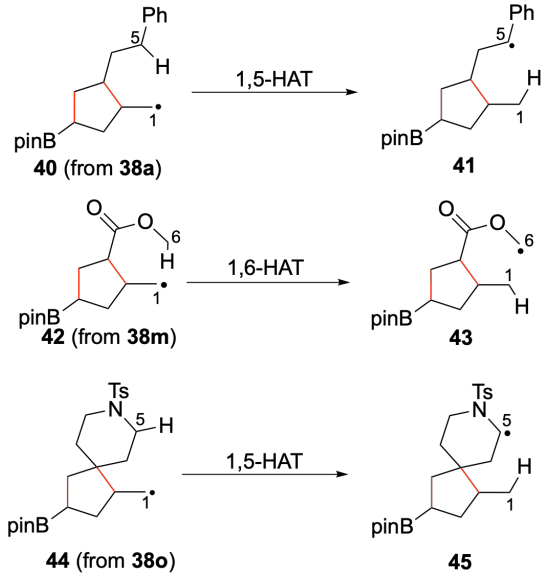
Scheme 3.26: Mechanism of formation of borylcyclopropane side product **39**.

At this point of the project, we tried to optimize the reaction and repeated the examples in Scheme 3.27 under diluted conditions (0.25 M). We speculated that concentrated conditions were not required in this case due to the fact that the oligomerization side-reaction, which can lower the yield of the final compound, is slower. When applying these conditions on a styrene derivative, an increase of yield was observed and compound **OX-38e** was obtained in 71% after oxidation of the boronic ester moiety. The reaction proved to work well on different styrene derivatives (**38f**, **38g**) including 1,1-disubstituted α-methyl styrene **38h**. However, when the substituent was changed from a methyl to a silyl ether, product **38i** was not formed. Other successful examples include epoxynaphathalene **38j** and phenyl vinyl thioether **38k**. Low yields of **38l**, **38m**, **38a** and **38n** or no conversion (**38o**-**38v**) to desired product were obtained when other activated olefins were employed for the annulation reaction.



Scheme 3.27: Substrate scope for ATRAn reaction. Isolated yields. [a]Yield after oxidation of the pinacol boronic ester moiety; [b]Performed in a sealed tube.

Some of the poor observed results can be explained due to possible HAT process taking place intramolecularly which might kill the desired radical chain (1,6-HAT or 1,5-HAT - Scheme 3.28) or instability of the 1,4-iodo boronic ester (**38u** and **38v**). For other examples, we suspect that the addition of the radical with the desired radical trap cannot take place due to polar effects. The general trend of the scope let us hypothesize that the reaction works well when the olefin is neither too electron rich nor electron poor and this might be linked to the ambiphilicity of the generated α-boryl radical. In other words, the radical is neither electrophilic nor nucleophilic enough to add on activated olefins. These results are in accordance with what reported in the ATRAC part (Chapter 3 - Paragraph 3.4).



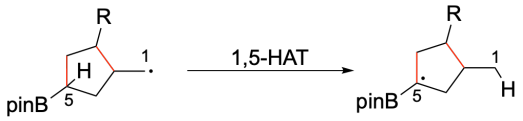
40 (from **38a**) **41**

42 (from **38m**) **43**

44 (from **38o**) **45**

Scheme 3.28: Possible HAT processes which can occur during the annulation reaction.

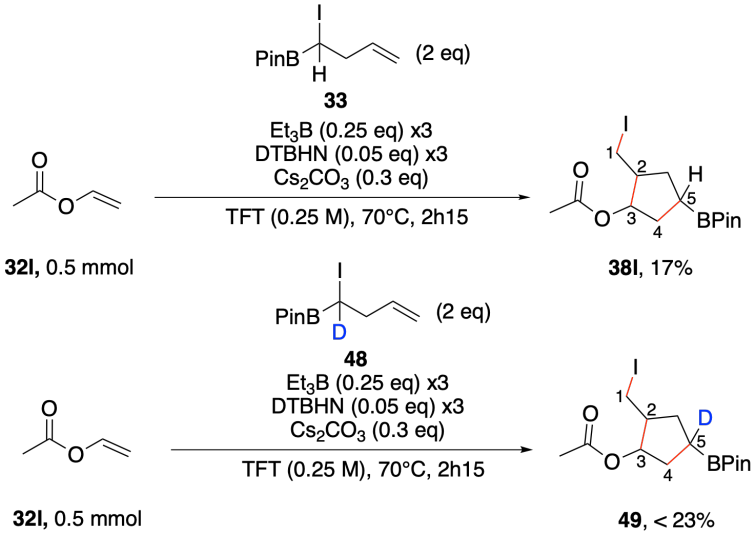
Another 1,5-HAT side reaction which might occur during the cyclisation is showed in Scheme 3.29. In particular, the reaction should be favoured because the new formed radical at position 5 (**47**, Scheme 3.29) is a tertiary α-boryl radical, which is more stabilized than a primary alkyl radical.



46 **47**

Scheme 3.29: 1,5-HAT leading to a tertiary α-boryl radical.

We then decided to perform a simple experiment using **32l** (Scheme 3.30) as radical trap. This trap was chosen because the yield of the annulated compound **38l** was low (17%). The same reaction was repeated using a deuterated radical precursor **48**: we expected that, being the rate of 1,5-HAT faster than 1,5-DAT due isotopic effect,[36] the yield of the reaction would have been higher. However, **38l** and **49** were isolated with similar yields. This proves that the intramolecular 1,5-Hydrogen Atom Transfer reaction showed in Scheme 3.29 is not occuring during the annulation. Moreover, it sustains our hypothesis that polar effects might greatly affect the positive outcome of the ATRAn reaction.



Scheme 3.30: Substrate scope for ATRAn reaction.

3.9 Conclusion

This chapter illustrated our efforts to study the reactivity of α-boryl radicals in a new reaction which combines atom transfer radical addition and cyclisation. The optimization of the method, particularly in the choice of the initiator and radical precursor, was presented. Et_3B/DTBHN initiation proved to be the best initiation system for the reaction, however DTBHN can be used as well as an alternative.

Despite the initial good results with ICH_2BEPin as radical precursor, the more readily availble pinacol boronic ester derivative (ICH_2BPin) was used for the substrate scope. It indeed proved to be the cheapest and most accessible option, delivering good yields and compatibility with further post-functionalization reactions we wanted to perform on the ATRAC products.

A scope of the reaction using a secondary radical precursor was as well presented. The limitations of the reaction were discussed, together with our efforts to explain the obtained results. In particular, intramolecular 1,5-HAT side reaction takes places after the cyclisation reactions which kills the desired radical chain. Indeed, iodine atom transfer, the final step of ATRAC reactions, is slower than 1,5-HAT. For this reason, particularly for the examples using the secondary radical precursor, the yield based on recovered starting material are quite high.

Some ATRAC products were submitted to different post-functionalization reactions to show their synthetic utility. 3 different reactions (oxidation, deiodination and radical deboronative functionalization) were attempted to synthesize new derivatized products. Worth to mention is the effort we made to understand and optimize the radical deboronative reduction of a primary pinacol boronic ester using MeOBCat and TBC, which allowed the synthesis of the fully reduced ATRAC compound in good yield.

Lastly, a new annulation reaction involving α-boryl radicals was described. The scope of the method was presented, although the obtained results were unsatisfactory and good yields were obtained particularly on styrene derivatives. We proved that 1,5-HAT α to the boron is not responsible for the low yields. However, other intramolecular HAT-process can take place on the side chain with many of the examples presented. The unsatifactory results might be explained as well by polar effects influencing the desired radical annulation process.

References

(1) Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chemical Reviews* **1991**, *91*, 1237–1286.

(2) Curran, D. P.; Chen, M.-H. *Tetrahedron Letters* **1985**, *26*, 4991–4994.

(3) Liao, J.; Yang, X.; Ouyang, L.; Lai, Y.; Huang, J.; Luo, R. *Org. Chem. Front.* **2021**, *8*, 1345–1363.

(4) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–736.

(5) Chuang, C.-P. *Synthetic Communications* **1992**, *22*, 3151–3158.

(6) Chuang, C.-P.; Tsai, A.-I.; Tsai, M.-Y. *Tetrahedron* **2013**, *69*, 3293–3301.

(7) Mantrand, N.; Renaud, P. *Tetrahedron* **2008**, *64*, 11860–11864.

(8) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073–3100.

(9) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925–3941.

(10) Spellmeyer, D. C.; Houk, K. N. *The Journal of Organic Chemistry* **1987**, *52*, 959–974.

(11) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc., Trans.* **1915**, *107*, 1080–1106.

(12) Jung, M. E. *Tetrahedron* **1976**, *32*, 3–31.

(13) Jung, M. E.; Piizzi, G. *Chemical Reviews* **2005**, *105*, 1735–1766.

(14) Karaman, R. *Tetrahedron Letters* **2009**, *50*, 6083–6087.

(15) Bachrach, S. M. *The Journal of Organic Chemistry* **2008**, *73*, 2466–2468.

(16) Julia, M. *Accounts of Chemical Research* **1971**, *4*, 386–392.

(17) Hoffmann, R. W. *Chemical Reviews* **1989**, *89*, 1841–1860.

(18) Fraind, A.; Turncliff, R.; Fox, T.; Sodano, J.; Ryzhkov, L. R. *Journal of Physical Organic Chemistry* **2011**, *24*, 809–820.

(19) Brown, H. C.; Rogic, M. M.; Rathke, M. W.; Kabalka, G. W. *Journal of the American Chemical Society* **1967**, *89*, 5709–5710.

(20) Brucelle, F.; Renaud, P. *Organic Letters* **2012**, *14*, 3048–3051.

(21) Povie, G.; Ford, L.; Pozzi, D.; Soulard, V.; Villa, G.; Renaud, P. *Angewandte Chemie International Edition* **2016**, *55*, 11221–11225.

(22) Huang, Q.; Suravarapu, S. R.; Renaud, P. *Chemical Science* **2021**, *12*, 2225–2230.

(23) Tappin, N. D. C.; Renaud, P. *Advanced Synthesis & Catalysis* **2021**, *363*, 275–282.

(24) Cirule, D.; Dénès, F.; Renaud, P. *Advanced Synthesis & Catalysis* **2024**, adsc.202400340.

(25) Curran, D. P.; McFadden, T. R. *Journal of the American Chemical Society* **2016**, *138*, 7741–7752.

(26) Oka, N.; Yamada, T.; Sajiki, H.; Akai, S.; Ikawa, T. *Organic Letters* **2022**, *24*, 3510–3514.

(27) André-Joyaux, E.; Kuzovlev, A.; Tappin, N. D. C.; Renaud, P. *Angewandte Chemie International Edition* **2020**, *59*, 13859–13864.

(28) Batey, R. A.; Pedram, B.; Yong, K.; Baquer, G. *Tetrahedron Letters* **1996**, *37*, 6847–6850.

(29) Rrapi, M.; Batsika, C. S.; Nikitas, N. F.; Tappin, N. D. C.; Triandafillidi, I.; Renaud, P.; Kokotos, C. G. *Chemistry – A European Journal* **2024**, *30*, e202400253.

(30) Hirsch, J. A. In *Topics in Stereochemistry*; John Wiley & Sons, Ltd: 1967, pp 199–222.

(31) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C. *The Journal of Organic Chemistry* **1993**, *58*, 6838–6842.

(32) Chatgilialoglu, C.; Griller, D.; Lesage, M. *The Journal of Organic Chemistry* **1988**, *53*, 3641–3642.

(33) Tappin, N. D. C.; Michalska, W.; Rohrbach, S.; Renaud, P. *Angewandte Chemie International Edition* **2019**, *58*, 14240–14244.

(34) Salam, A.; Ray, S.; Zaid, M. A.; Kumar, D.; Khan, T. *Org. Biomol. Chem.* **2019**, *17*, Publisher: The Royal Society of Chemistry, 6831–6842.

(35) Cirule, D.; Dénès, F.; Gnägi-Lux, M.; Rohrbach, S.; Renaud, P. *Advanced Synthesis & Catalysis* **2024**, *366*, 1366–1374.

(36) Blanc, A.; Bochet, C. G. *Journal of the American Chemical Society* **2004**, *126*, 7174–7175.

3.10 Experimental Section

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. A liquid Nitrogen/ethanol bath was used to reach a temperature of - 100°C. Unless otherwise stated, Macherey-Nagel Silica 60, 0.04–0.063 mm Silica gel was always used for flash column chromatography: it proved to be the best one compared to others because the iodoboronic esters were less prone to decomposition. In some specific cases, Macherey-Nagel Silica 60, 0.015–0.04 mm was used to achieve better separation. Thin layer chromatography (TLC) was performed on Macherey-Nagel SIL G/UV254, 0.25 mm analytical plates. Visualization was done under UV light (254 nm) and/or by dipping into 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); or $H_3PMo_{12}O_{40}$ dissolved in 100 mL ethanol and subsequent heating. Anhydrous sodium sulphate was used as drying reagent.

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 and/or stored over 3Å molecular sieves. Solvents for extractions (Et_2O, *n*-pentane, CH_2Cl_2, AcOEt, heptanes, TBME) and for flash column chromatography were of technical grade and distilled prior to use. Commercially available Dilauroyl peroxide (Luperox © LP, Lauroyl peroxide, Sigma Aldrich – 290875) was used as initiator for the radical reactions. Commercial 1,3,5-trimethoxybenzene (0.5 eq) (Sigma-Aldrich, Standard for quantitative NMR, Trace **CERT**© - Art. 74599) was used as external standard for NMR yields.

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 B*ruker Avance IIIHD-400* or a *Bruker Avance II-400 spectrometer 5* (^1H: 400 MHz; ^{13}C: 101 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) for calibration. Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), and br (broad). Coupling constants (*J*) are 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. Due to coupling to the quadrupolar

^{11}B and ^{10}B nuclei, the carbons linked to boron atoms give a broad signal in ^{13}C NMR, and are generally not detected.

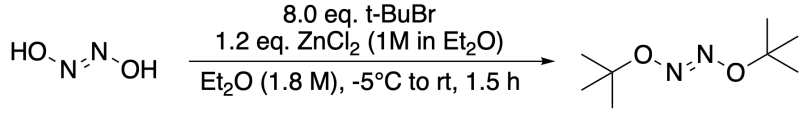
Infrared spectra were recorded on a *Jasco FT−IR−460* plus spectrometer equipped with a *Specac MKII Golden Gate Single Reflection Diamond ATR* system and are reported in wave numbers (cm^{-}1). At maximum, the ten most prominent peaks are reported.

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 *Finnigan Trace 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. GC analyses were performed on a *ThermoFisher Trace GC* ultra, fitted with a chiral Restek Rt®-bDEXm capillary column (20 m, 0.25 mm ID, 0.25 μm), helium as carrier gas (1.2 mL/min), and FID (290 °C base temperature, 35 mL/min H2, 350 mL/min air); temperature Gradients are indicated for each compound.

HRMS analyses and accurate mass determinations were performed on a *Thermo Scientific LTQ Orbitrap XL* mass spectrometer using ESI mode (positive ion mode).

3.10.1 Initiators

Di-tert-butylhyponitrite (DTBHN) (SI_2_1)



SI_2_1
Chemical Formula: $C_8H_{18}N_2O_2$
Exact Mass: 174.1368

In a flame-dried 250 mL two-neck round bottom flask was added a solution of the dry [(E)-sodio-oxyazo]oxysodium (5.95 g, 56.1 mmol) in dry Et_2O (32 mL). Tert-butylbromide (50.4 mL, 449 mmol) was then added and the resulting milky white mixture was cooled to –10 °C (internal temperature) using an ice/NaCl/water bath. Then, zinc chloride (67.4 mL, 67.4 mmol, 1.00 mol/L,) was added dropwise using a dropping funnel at such a rate that the internal temperature did not exceed –5 °C. After complete addition, the mixture was allowed to warm up to rt and stirred for another 1.5 h at rt. The orange solution was filtered carefully and the remaining solid was washed with Et_2O (3 × 20 mL). The resulting yellow solution was transferred into a separatory funnel and water was added. The aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na_2SO_4 and the volatiles were partially removed under reduced pressure (IMPORTANT: bath temperature 20°C, 400 mbar) to afford a yellow solution. Recrystallization from pentane (3 times) at –20 °C afforded di-tert-butylhyponitrite (DTBHN) (2.07 g, 11.9 mmol, 21 %).

In a dry-flame 250 mL two-neck round bottom flask was added a solution of the dry [(E)-sodio-oxyazo]oxysodium (5.95 g, 56.1 mmol) in dry Et_2O (32 mL). Tert-butylbromide (50.4 mL, 449 mmol, 8 eq.) was then added and the resulting milky white mixture was cooled to –10 °C (internal temperature) using an ice/NaCl/water bath. Then, the zinc chloride solution (1.00 mol/L, 67.4 mL, 67.4 mmol, 1.2 eq) was added dropwise using a dropping funnel at such a rate that the internal temperature did not exceed –5 °C. After complete addition, the mixture was allowed to warm up to rt and stirred for another 1.5 h at this temperature. The orange solution was filtered and the remaining solid was washed with Et_2O (3 x20 mL). The resulting yellow solution was transferred into a separatory funnel and water was added. The aqueous layer was extracted with Et_2O (3 x20 mL) and the combined organic layers were washed with brine (50 mL), dried over anh. Na_2SO_4 and the volatiles were partly removed under reduced pressure (bath temperature 20°C, 400 mbar) to afford a yellow solution. Recrystallization from pentane (3 times) at -20°C afforded the desired compound di-tert-butylhyponitrite (DTBHN) (2.07 g, 11.9 mmol, 21 %).

White solid; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 1.39 (s, 18H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 81.2 (Cq), 27.8 (CH_3).

The physical and spectral data are in accordance with literature data:

Boukouvalas, J.; Cren, S.; Renaud, P.; Gnägi, L.; Renaud, P. Di- tert -Butyl hyponitrite. Encyclopedia of Reagents for Organic Synthesis 2021, 1–8.

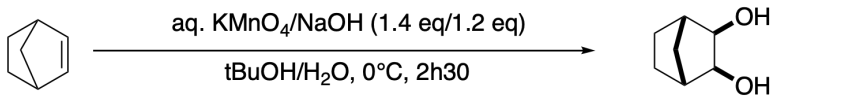
Triethylborane (Et_3B)

1.15 M Et_3B solutions were prepared from pure Et_3B using dry solvents (benzene from SPSS line or Alox © -dried trifluorotoluene). The solvents were degassed through argon bubbling 30 minutes prior to the use for the solution preparation. Et_3B solutions were stored at rt in dessicators and used within periods of 1 to 2 months.

Radical precursors

Synthesis of diols

(1R*,2S*,3R*,4S*)-bicyclo[2.2.1]heptane-2,3-diol (SI_2_2)



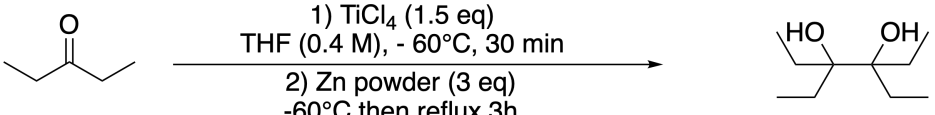
SI_2_2
Chemical Formula: $C_7H_{12}O_2$
Exact Mass: 128.0837

A cold solution of $KMnO_4$ (24.0 g, 0.15 mmol) and NaOH (5.22 g, 0.13 mmol) in water (500 mL) was slowly added dropwise (over 45 min, using a dropping funnel) to a solution of norbornene (10.0 g, 0.11 mmol) in t-BuOH/H_2O (500 mL, 4:1) at –10 °C (ice-NaCl bath). After the end of addition, the reaction mixture was stirred for 1h at –10 °C, then quenched with a saturated aqueous solution of sodium metabisulphite ($Na_2S_20_5$) (300 mL) until the solution turned colourless. The resulting reaction mixture was filtered and t-BuOH was evaporated under reduced pressure. The remaining aqueous solution was extracted with EtOAc (6 × 250 mL). The combined organic phases were then washed with brine (200 mL), dried over anhydrousydrous Na_2SO_4, filtered and concentrated under reduced pressure to give (1R*,2S*,3R*,4S*)-bicyclo[2.2.1]heptane-2,3-diol (7.48 g, 58.4 mmol, 55 %), which was used for the next step without further purification.

White solid; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 3.69 (d, *J* = 1.7 Hz, 2H), 2.39 (s, 3H), 2.14 (dq, *J* = 3.2, 1.6 Hz, 2H), 1.77 (dt, *J* = 10.4, 2.0 Hz, 1H), 1.55–1.35 (m, 2H), 1.17–0.95 (m, 3H).

The physical and spectral data are in accordance with literature data:
Donohoe, T. J.; Jahanshahi, A.; Tucker, M. J.; Bhatti, F. L.; Roslan, I. A.; Kabeshov, M.; Wrigley, G. *Chemical Communications* **2011**, *47* (20), 5849.

3,4-diethylhexane-3,4-diol (SI_2_3)



SI_2_3
Chemical Formula: $C_{10}H_{22}O_2$
Exact Mass: 174.1620

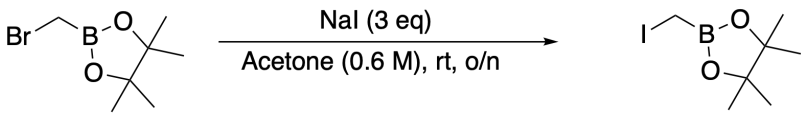
A flame-dried 250 mL 3-neck round-bottom flask, equipped with a reflux condenser, was charged with pentan-3-one (8 mL, 75.5 mmol) and anhydrous THF (164 mL), under an inert argon atmosphere. The resulting solution was cooled to –60 ºC using an acetone/dry ice bath. $TiCl_4$ (13 mL, 119 mmol) was then added slowly via syringe and the mixture was stirred for 30 min at –60 ºC. Zn dust (14.8 g, 227 mmol) was added and the obtained suspension was gently heated up to rt, then refluxed (80 ºC bath temperature, internal temperature 69°C) for 3 h. The reaction mixture was then cooled to 0 ºC and saturated aqueous K_2CO_3 solution (200 mL) was added slowly. The reaction mixture was stirred for 30 min, then filtered through a pad of Celite, which was washed with EtOAc. The filtrate was extracted with EtOAc (3 x 30 mL). The combined organic phases were washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give 3,4-diethylhexane-3,4-diol (3.85 g, 22.1 mmol, 59 %). The latter was used for the next step without further purification.

Colorless oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 1.89 (s, 2H), 1.55 (qd, J = 7.5, 2.0 Hz, 8H), 0.88 (t, J = 7.5 Hz, 12H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 79.0 (2 x Cq), 27.5 (4 x CH_2), 9.2 (4 x CH_3).

The physical and spectral data are in accordance with literature data:
Rubio-Presa, R.; Suárez-Pantiga, S.; Pedrosa, M. R.; Sanz, R. *Advanced Synthesis & Catalysis* **2018**, *360* (11), 2216–2220.

Synthesis of radical precursors

2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (ICH_2BPin) (SI_2_4)



SI_2_4
Chemical Formula: $C_7H_{14}BIO_2$
Exact Mass: 268.0132

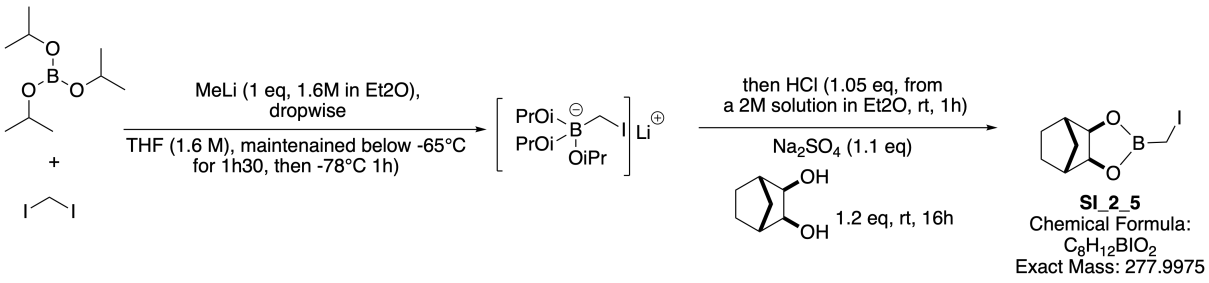
2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10 g, 45.3 mmol) was dissolved in acetone (75 mL, HPLC grade). Then, sodium iodide (20.4 g, 136 mmol) was added, the flask was covered with an aluminium foil to protect the mixture from light, and the mixture was stirred

at rt for 14 h. The crude mixture was partitioned between H_2O (100 mL) and CH_2Cl_2 (50 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL). The organic layers were washed with 5% $Na_2S_2O_3$ (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4, filtered and the solvent concentrated under reduced pressure (flask covered with aluminium foil to protect it from light) to afford 2-(iodomethyl)-4,4,5,5-tetramethyl- 1,3,2-dioxaborolane (10.2 g, 38.1 mmol, 84 %). The latter was used for the next step without further purification.

Light-yellow oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 2.16 (s, 2H), 1.26 (s, 12H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 84.3 (2 x Cq), 24.5 (4 x CH_3); ^{11}**B NMR** (75 MHz, $CDCl_3$) δ 31.7.

The physical and spectral data are in accordance with literature data:
Tappin, N. D. C.; Michalska, W.; Rohrbach, S.; Renaud, P. *Angewandte Chemie* **2019**, *58* (40), 14240–14244.

(3aR*,4S*,7R*,7aS*)-2-(iodomethyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole (ICH_2Bnor) (SI_2_5)



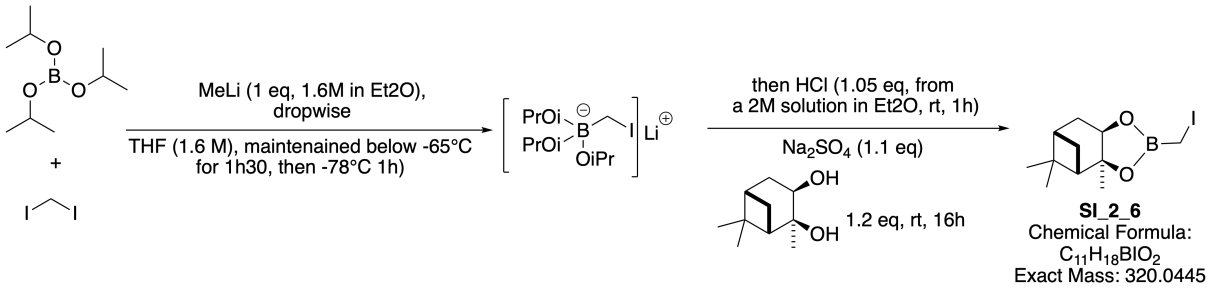
GP1: A two-neck 250 mL round-bottom flask, equipped with a 100 mL dropping funnel and a low-temperature thermometer was charged with triisopropyl borate (23.1 mL, 100 mmol), diiodomethane (8.07 mL, 100 mmol) and THF (71 mL). Methyllithium (62.5 mL, 100.0 mmol, 1.6 M) was loaded into the dropping funnel The reaction mixture was vigorously stirred and cooled to –78 °C,then MeLi was added via the dropping funnel at a such a rate that the temperature did not exceed –65 °C (over ca. 1h). After the end of the addition, the reaction mixture was stirred at –65 °C for 1h and the cold bath was removed. Dry HCl (52.5 mL, 105 mmol, 2.0 M in Et_2O,) was added quickly and the reaction mixture was stirred for additional 1h at rt before (1R*,2S*,3R*,4S*)-bicyclo[2.2.1]heptane-2,3-diol (14.7 g, 115 mmol) was added as a solid. The reaction mixture was stirred at rt for 16 h. Most of the volatiles were removed under reduced pressure (caution: MeI is generated during this reaction. Perform in a well-ventilated fume-hood). The residue was partitioned between TBME (150 mL) and 0.5 M aq. HCl (150 mL) and stirred for 5 min. The organic layer was washed with H_2O (150 mL), and the combined aqueous phases were back extracted with TBME (20 mL). The combined organic phases were successively washed with 10% (w/v) aq. $Na_2S_2O_3$ (150 mL), sat. aq. $NaHCO_3$ (2 x 150 mL), brine (2 x 150 mL), then dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford an orange oil. Purification by distillation (bp = 85°C; $2*10^{-2}$ mbar) provided (3aR*,4S*,7R*,7aS*)-

2-(iodomethyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole as desired product (13.7 g, 49.3 mmol, 49%).

Light yellow oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 4.30 (d, J = 1.4 Hz, 2H), 2.33 (dq, J = 3.2, 1.6 Hz, 2H), 2.19 (s, 2H), 1.71 (dp, J = 11.1, 2.0 Hz, 1H), 1.54–1.44 (m, 2H), 1.27–1.20 (m, 1H), 1.07-0.98 (m, 2H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 84.4 (2 x Cq), 41.0 (2 x CH), 30.8 (CH_2), 23.4 (2 x CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 32.2; IR (neat): ν_{max} = 2957, 2873, 1407, 1387, 1367, 1352, 1306, 1280, 1226, 1132, 1093, 1021, 1001 cm^{-1}; HRMS (ESI): Calculated for $C_8H_{13}BIO_3$ $[M+OH]^+$: 295.008; found: 295.014; HRMS (ESI): Calculated for $C_8H_{12}BIO_2$ $[M]^+$: 277.9970; found: 277.9961.

The compound is stored at -20°C in dark vials under an argon atmosphere. The colour of the compound changes from light yellow to dark orange because of slow degradation, which occurs fast at rt and with exposure to light. The degradation product is iodine, and this explains the change in colour of the compound. However, this does not seem to have an impact on the radical ATRA reaction yields.

(3aR,4R,6R,7aS)-2-(Iodomethyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (ICH_2BPan) (SI_2_6)

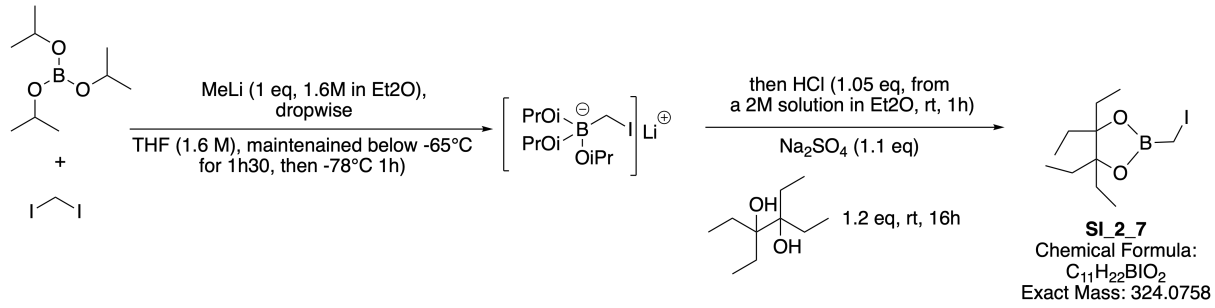


The title compound was prepared following General Procedure **GP1** with commercial α-(–)-pinanediol (6.13 g, 36 mmol). Purification by column chromatography provided (3aR,4R,6R,7aS)-2-(Iodomethyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]- dioxaborole as desired product (7.57 g, 23.6 mmol, 79 %).

Orange oil; Rf: 0.65 (8:2 cyclohexane:EtOAc); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 4.37 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.41-2.23 (m, 2H), 2.21 (s, 2H), 2.08 (app br t, *J* = 5.5 Hz, 1H), 1.97–1.83 (m, 2H), 1.40 (s, 3H), 1.30 (s, 3H), 1.28 (d, *J* = 11.3 Hz, 1H), 0.85 (s, 3H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 86.5 (2 x Cq), 78.5 (CH), 51.4 (CH), 39.3 (CH), 38.4 (Cq), 35.3 (CH_2), 28.3 (CH_3), 27.0 (CH_3), 26.3 (CH_2), 24.0 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 31.3; HRMS (ESI): Calculated

for $C_{11}H_{19}BIO_3$ $[M+OH]^-$: 337.0477; found: 337.0483.

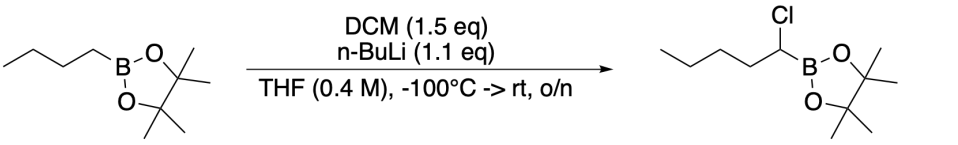
4,4,5,5-tetraethyl-2-(iodomethyl)-1,3,2-dioxaborolane (ICH_2BEPin) (SI_2_7)



The title compound was prepared following General Procedure **GP1** with commercial 3,4-diethylhexane-3,4-diol (1.58 g, 9.06 mmol). Purification by column chromatography provided 4,4,5,5-tetraethyl-2-(iodomethyl)-1,3,2-dioxaborolane as desired product (2.10 g, 6.48 mmol, 79 %).

Dark-yellow oil; Rf: 0.78 (heptanes:EtOAc 8:2); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 2.17 (s, 2H), 1.82–1.56 (m, 8H), 0.92 (t, J = 7.5 Hz, 12H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 89.5 (2 x Cq), 26.1 (4 x CH_2), 8.8 (4 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 31.2; IR (neat): ν_{max} = 2971.8, 2943, 2883, 1405, 1355, 1322, 1283, 1091, 926, 859 cm^{-1}; HRMS (ESI): Calculated for $C_11H_{22}BIO_2$ $[M+H]^+$: 324.0758; found: 324.0752.

2-(1-chloropentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15)



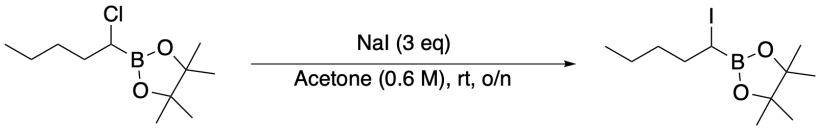
To an oven dried 250 mL two-neck round bottom flask equipped with a stirring bar, CH_2Cl_2 (4.2 mL, 65.6 mmol) and THF (82 mL) were added. The mixture was cooled down to -100 °C using an ethanol/liquid nitrogen bath. Then n-butyllithium (21 mL, 52.5 mmol) was added dropwise at such a rate that the temperature stayed below –90 °C. 2-butyl-4,4,5,5- tetramethyl-1,3,2-dioxaborolane (10 mL, 47.0 mmol) was finally added in one portion by syringe. The reaction mixture was stirred for 18h under inert atmosphere. Then the reaction mixture was allowed to slowly warm to room temperature overnight. After the reaction was complete, CH_2Cl_2 (500 mL) was added to precipitate LiCl and the solution was filtered through a pad of Celite (eluted with CH_2Cl_2) and concentrated under reduced pressure to afford a light brown turbid solution.

This solution was again filtered over a small pad of SiO_2 and the flask washed with Et_2O. After concentration under reduced pressure of the obtained solution, 2-(1-chloropentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was recovered as desired product (9.74 g, 41.9 mmol, 89 %) and was used without further purification.

Light-brown oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 3.41 (t, J = 6.8 Hz, 1H), 1.92–1.72 (m, 1H), 1.28 (s, 17H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 84.5 (2 x Cq), 33.9 (CH_2), 29.6 (CH_2), 24.7 (4 x CH_3), 22.4 (CH_2), 14.1 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 31.4 (s).

The physical and spectral data are in accordance with literature data:
Lou, Y.; Qiu, J.; Yang, K.; Zhang, F.; Wang, C.; Song, Q. *Org. Lett.* **2021**, *23* (12), 4564-4569.

2-(1-iodopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16)



16
Chemical Formula: $C_{11}H_{22}BIO_2$
Exact Mass: 324.0758

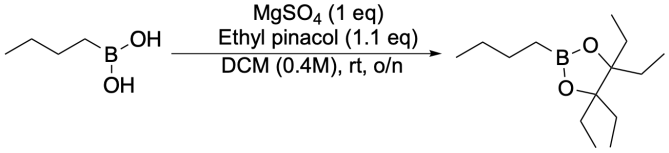
A 100 mL round bottom flask, was charged with 2-(1-chloropentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9.7 g, 41.7 mmol) and acetone (69 mL; HPLC grade). NaI (18.8 g, 125 mmol) was then added and the mixture was stirred overnight at room temperature, protected from light using aluminium foil. The mixture was then partitioned between water (50 mL) and EtOAc (30 mL). The water phase was back-extracted with EtOAc (3 × 20 mL). The organic phase was washed with 5% $Na_2S_2O_3$ (50 mL), brine (50 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford 2-(1-iodopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11.1 g, 34.2 mmol, 84 %). It was used without further purification.

Orange oil; Rf: 0.78 (heptanes:EtOAc 8:2); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 3.21 (t, J = 8.2 Hz, 1H), 1.94-1.74 (m, 2H), 1.48-1.20 (m, 4H), 1.274 (s, 6H), 1.268 (s, 6H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 84.1 (2 x Cq), 34.7 (CH_2), 33.6 (CH_2), 24.5 (2 x CH_3), 24.4 (2 x CH_3), 22.1 (CH_2), 14.1 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 31.8 (s); IR (neat): ν_{max} = 2977, 2928, 2870, 1371, 1331, 1142, 1120, 966, 845, 672 cm^{-1}.

The compound was stored at -20 °C in dark vials under an argon atmosphere. The colour of the compound changes from light yellow to dark orange because of slow degradation, which occurs fast at rt and with exposure to light. The degradation product is iodine, and this explains the change in colour of the compound. However, this does not seem to have an impact on the

radical ATRA reaction yields.

2-butyl-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (SI_2_8)

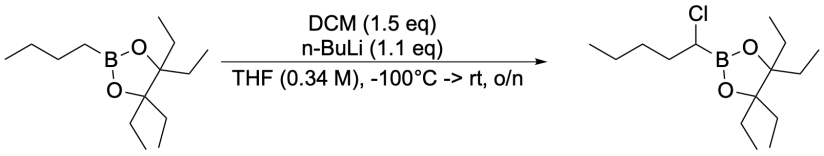


SI_2_8
Chemical Formula: $C_{14}H_{29}BO_2$
Exact Mass: 240.2261

In a 250 mL round-bottom flask, n-butylboronic acid (3.036 g, 28.9 mmol) was dissolved dry DCM (75 mL). Magnesium sulfate (3.669 g, 30.5 mmol) and 3,4-diethylhexane-3,4-diol (5.78 g, 33.2 mmol) were then added. The mixture was stirred for 5 days at room temperature. The mixture was filtered over Celite and eluted with EtOAc. After evaporation of the solvent under reduced pressure, an orange oil was recovered. Purification by flash column chromatography (2% EtOAc:heptanes) provided the desired 2-butyl-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (4.63 g, 19.3 mmol, 65%).

Colorless oil; Rf: 0.55 (95:5 heptanes:EtOAc); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 1.63 (qd, J = 7.5, 3.9 Hz, 8H), 1.43–1.21 (m, 4H), 0.87 (dt, J = 9.2, 7.3 Hz, 14H), 0.78–0.72 (m, 3H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 87.9 (2 x Cq), 26.5 (4 x CH_2), 26.5 (CH_2), 25.6 (CH_2), 14.0 (CH_3), 8.9 (4 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 33.5 (s); IR (neat): ν_{max} = 2969, 2953, 2930, 2883, 2860, 1373, 1347, 1284, 930, 923 cm^{-1}.

2-(1-chloropentyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (SI_2_9)



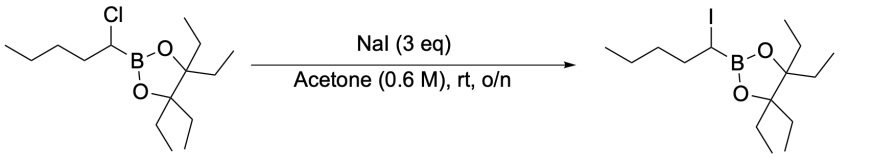
SI_2_9
Chemical Formula: $C_{15}H_{30}BClO_2$
Exact Mass: 288.2027

To an oven-dried 100 mL two-neck round bottom flask, equipped with a stirring bar, CH_2Cl_2 (1 mL, 15.6 mmol) and THF (14 mL) were added by syringe, and the solution was cooled to -100 °C using an ethanol/liquid nitrogen bath. Then n-butyllithium (1.6 M solution in hexane, 4.6 mL, 11.6 mmol) was added dropwise so that the temperature stayed at max. -90 °C. After stirring for 45 min, a solution of corresponding 2-butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.3 mL, 10.8 mmol) in THF (5 mL) was directly added dropwise via syringe. Then the reaction mixture was allowed to slowly warm to room temperature overnight. After the reaction

was completed, DCM (200 mL) was added to precipitate LiCl. The solution was directly filtered through a short pad of Celite (eluted with DCM) and concentrated under reduced pressure to afford a light brown turbid solution, due to the presence of residual LiCl. Purification by flash column chromatography (5% EtOAc:heptanes) provided the desired 2-(1-chloropentyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (1.78 g, 6.18 mmol, 74%).

Colorless oil; Rf: 0.78 (9:1 heptanes:EtOAc); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 3.41 (t, J = 8.2, 6.7 Hz, 1H), 1.81 (dddd, J = 12.5, 9.2, 5.2, 2.7 Hz, 2H), 1.76–1.59 (m, 8H), 1.51-1.23 (m, 4H), 0.98–0.86 (m, 15H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 89.4 (2 x Cq), 33.9 (2 x CH_2), 29.5 (2 x CH_2), 26.2 (4 x CH_2), 22.2 (CH_2), 14.0 (CH_3), 8.7 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 30.7 (s); IR (neat): ν_{max} = 2955, 2934, 2884, 1458, 1386, 1359, 1112, 921 cm^{-1}.

2-(1-iodopentyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (SI_2_10)



SI_2_10
Chemical Formula: $C_{15}H_{30}BIO_2$
Exact Mass: 380.1384

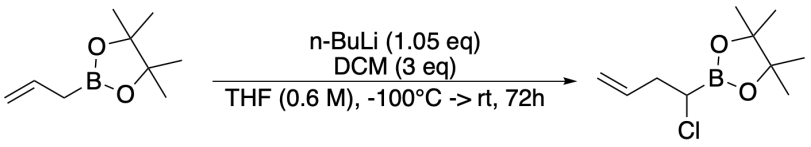
In a 25 mL one-neck round bottom flask, 2-(1-chloropentyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (1.58 g, 5.49 mmol) was dissolved in acetone (9 mL, HPLC grade). NaI (2.47 g, 16.5 mmol) was then added (mixture turned yellow) and the mixture was stirred for 14 h at room temperature, protected from light using aluminium foil. The mixture was partitioned between water (50 mL) and EtOAc (30 mL). The water phase was back-extracted EtOAc (3 x 20 mL). The combined organic phases were successively washed with 5% $Na_2S_2O_3$ (50 mL) and brine (50 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure to deliver 2-(1-iodopentyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (1.94 g, 5.11 mmol, 93%), which was used without further purification.

Light yellow oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 3.41 (t, J = 8.2, 6.7 Hz, 1H), 1.81 (dddd, J = 12.5, 9.2, 5.2, 2.7 Hz, 2H), 1.76–1.59 (m, 8H), 1.51–1.23 (m, 4H), 0.98–0.86 (m, 15H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 89.1 (2 x Cq), 34.8 (CH_2), 33.6 (CH_2), 26.0 (4 x CH_2), 22.1 (CH_2), 14.1 (CH_3), 8.9 (4 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 31.3 (s); IR (neat): ν_{max} = 2965, 2931, 2882, 1457, 1374, 1352, 1287, 1112, 972 cm^{-1}; HRMS (ESI): Calculated for $C_{15}H_{30}BIO_2$ $[M+H]^+$: 380.1384; found: 380.1384.

The compound is stored at –20 °C in dark vials under an argon atmosphere. The colour of

the compound changes from light yellow to dark orange because of slow degradation, which occurs fast at rt and with exposure to light. The degradation product is iodine, and this explains the change in colour of the compound. However, this does not seem to have an impact on the radical ATRA reaction yields.

2-(1-chlorobut-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (SI_2_11)



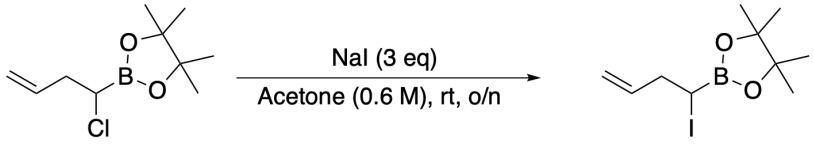
SI_2_11
Chemical Formula: $C_{10}H_{18}BClO_2$
Exact Mass: 216.1088

A flame dried two-neck round bottom flask was charged with DCM (5 mL, 78.3 mmol) and THF (24 mL) and cooled down to –100 °C using an ethanol/liquid nitrogen slush bath. n-butyllithium (11.2 mL, 28 mmol, 2.5 M in hexanes,) was added dropwise, at such a rate that the internal temperature never exceeded –90 °C. After the addition, 2-allyl-4,4,5,5-tetramethyl- 1,3,2-dioxaborolane (5 mL, 26.7 mmol) was added in one portion to the mixture and the contents were allowed to warm up to room temperature and stirring was continued for 16 hours. DCM (500 mL) was added to precipitate LiCl and the solution was filtered over a pad of SiO_2 and eluted with DCM. After concentration under reduced pressure, an orange oil was recovered. Vacuum distillation (bp = 110 °C; 7.3×10^{-10} mbar) provided the desired 2-(1-chlorobut-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.66 g, 21.5 mmol, 81%).

Orange oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 5.84 (ddt, J = 17.0, 10.2, 6.8 Hz, 1H), 5.20–5.06 (m, 2H), 3.44 (t, J = 7.4 Hz, 1H), 2.59 (dtt, J = 7.9, 6.6, 1.3 Hz, 2H), 1.28 (s, 12H); ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 31.2.

The physical and spectral data are in accordance with literature data:
Sun, S.; Martin, R. *Angewandte Chemie* **2018**, *57* (14), 3622–3625.

2-(1-iodobut-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (33)



33
Chemical Formula: $C_{10}H_{18}BIO_2$
Exact Mass: 308.0445

2-(1-chlorobut-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.44 g, 20.5 mmol) was dissolved in acetone (32 mL, HPLC grade). Then, sodium iodide (9.23 g, 61.6 mmol) was added and the

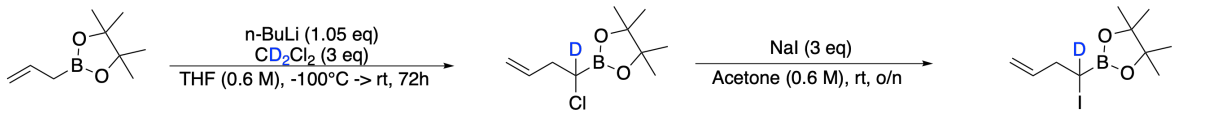
mixture was stirred at rt for 16 h. During the reaction time, the flask was covered with an aluminium foil to protect the reaction mixture from light. The crude reaction mixture was partitioned between H_2O (100 mL) and DCM (50 mL). The water phase was extracted DCM (3 x 30 mL). The organic layers were washed with 5% $Na_2S_2O_3$ (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4, filtered and the solvent concentrated under reduced pressure (flask covered with alu foil to protect it from light) to afford 2-(1-iodobut-3-enyl)-4,4,5,5- tetramethyl-1,3,2-dioxaborolane (5.52 g, 17.9 mmol, 87%) which was not further purified.

Light brown oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 5.75 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.15–5.04 (m, 2H), 3.20 (t, J = 8.3 Hz, 1H), 2.64 (dddd, J = 9.2, 6.6, 3.9, 1.3 Hz, 2H), 1.26 (d, J = 2.7 Hz, 12H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 137.4 (CH), 116.9 (CH_2), 84.0 (2 x Cq), 39.0 (CH_2), 24.2 (4 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 31.6.

The physical and spectral data are in accordance with literature data:
Sun, S.; Martin, R. *Angewandte Chemie* **2018**, *57* (14), 3622–3625.

The compound is stored at -20 °C in dark vials under an argon atmosphere. The colour of the compound changes from light yellow to dark orange because of slow degradation, which occurs fast at rt and with exposure to light. The degradation product is iodine, and this explains the change in colour of the compound. However, this does not seem to have an impact on the radical ATRA reaction yields.

2-(1-deuterio-1-iodo-but-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (48)



INT A: A flame dried two-neck round bottom flask was charged with dry CD_2Cl_2 (3.5 mL, 56 mmol) and THF (36 mL) and cooled to -100 °C using an ethanol/liquid nitrogen slush bath. n-Butyllithium (7.9 mL, 19.8 mmol, 2.5 M in hexanes) was added dropwise, at such a rate that the internal temperature never exceeded –90 °C. After the addition, 2-allyl-4,4,5,5-tetramethyl-1,3,2- dioxaborolane (3.5 mL, 18.7 mmol) was added in one portion to the mixture and the contents were allowed to warm up to room temperature and stirring was continued for 72 hours. DCM (500 mL) was added to precipitate LiCl and the solution was filtered over a pas of SiO_2 and eluted with DCM. After concentration under reduced pressure, an orange oil was recovered. Vacuum distillation (bp = 80 °C, 7.3 × 10^{-1} mbar) provided the desired 2-(1-chloro-1-deuterio-but-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**INT A**) (1.47 g, 6.76 mmol, 36%).

Colorless oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 5.84 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.19–5.06 (m, 2H), 2.58 (d, *J* = 6.4 Hz, 2H), 1.28 (s, 12H); ^{2}**H NMR** (61 MHz, Lock_Off, $CHCl_3$) 3.42; ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 134.9 (CH), 117.8 (CH_2), 84.6 (2 x Cq), 38.4 (CH_2), 24.8 (4 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 31.2; IR (neat): ν_{max} = 2080, 2931, 1365, 1337, 1138, 969, 856, 672, 647 cm^{-1}; HRMS (EI): Calculated for $C_{10}H_{17}DBClO_2$ $[M\text{-}CH_2H_3ClD]^+$: 153.1165; found: 153.1084.

48: INT A (1.45 g, 6.67 mmol) was dissolved in acetone (11 mL, HPLC grade), then sodium iodide (3 g, 20 mmol) was added and the mixture was stirred at rt for 16 h. During the reaction time, the flask was covered with an aluminium foil to protect the mixture from light. The crude mixture was partitioned between H_2O (100 mL) and DCM (50 mL). The water phase was extracted DCM (3 x 20 mL). The combined organic layers were washed with 5% $Na_2S_2O_3$ (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4, filtered and the solvent concentrated under reduced pressure (flask covered with aluminium foil to protect it from light) to afford **48** (2.08 g, 6.76 mmol, quant.) which was used without further purification.

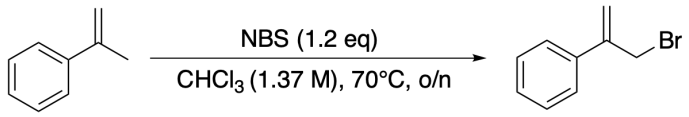
Colorless oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 5.75 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.16–5.04 (m, 2H), 2.64 (d, *J* = 5.5 Hz, 2H), 1.27 (d, *J* = 2.8 Hz, 12H); ^{2}**H NMR** (61 MHz, Lock_Off, $CHCl_3$) 3.2; ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 137.5 (CH), 117.0 (CH_2), 84.2 (2 x Cq), 39.0 (CH_2), 24.4 (4 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 31.6; IR (neat): ν_{max} = 2977, 2929, 1380, 1354, 1328, 1133, 965, 917, 847, 671 cm^{-1}; HRMS (EI): Calculated for $C_{10}H_{17}DBIO_2$ $[M\text{-}CH_3]^+$: 294.0351; found: 294.0272.

The compound is stored at –20 °C in dark vials under an argon atmosphere. The colour of the compound changes from light yellow to dark orange because of slow degradation, which occurs fast at rt and with exposure to light. The degradation product is iodine, and this explains the change in colour of the compound. However, this does not seem to have an impact on the radical ATRA reaction yields.

3.10.2 Synthesis of radical traps

Synthesis of the alkylating chains

1-(bromomethyl)vinylbenzene (SI_2_12)



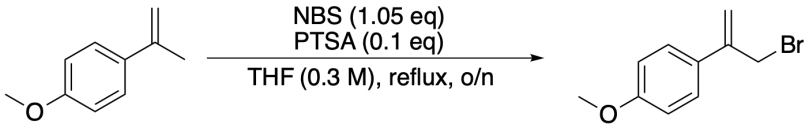
SI_2_12
Chemical Formula: C_9H_9Br
Exact Mass: 195.9888

To a solution of isopropenylbenzene (5.20 mL, 40.0 mmol) in $CHCl_3$ (24 mL) was added *N*-Bromosuccinimide (8.57 g, 48.1 mmol). The mixture was stirred and heated under reflux for 16 h. The reaction mixture was concentrated under reduced pressure and Et_2O (100 mL) was then added. The organic layer was separated and the aqueous phase extracted with Et_2O (3 x 50mL). The combined organic phases were washed with brine (50 mL), dried over Na_2SO_4 and then filtered. After concentration under reduced pressure (max 100 mbar for 5 min), a light yellow oil containing some remaining succinimide was recovered. Purification by flash column chromatography (Gradient 0-2% Et_2O:pentane) delivered 1-(bromomethyl)vinylbenzene (3.46 g, 17.5 mmol, 44

Light brown oil; Rf: 0.46 (100% heptanes); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.55–7.45 (m, 2H), 7.43–7.30 (m, 3H), 5.56 (d, *J* = 0.7 Hz, 1H), 5.50 (q, *J* = 0.8 Hz, 1H), 4.39 (d, *J* = 0.8 Hz, 2H).

The physical and spectral data are in accordance with literature data:
Levin, M. D.; Toste, F. D. *Angewandte Chemie* **2014**, *53* (24), 6211–6215.

1-[1-(bromomethyl)vinyl]-4-methoxy-benzene (SI_2_13)



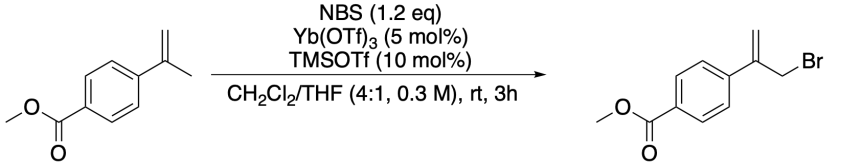
SI_2_13
Chemical Formula: $C_{10}H_{11}BrO$
Exact Mass: 225.9993

An oven dried 100 mL one-neck round-bottom flask was charged with 1-isopropenyl-4-methoxy-benzene (1.48 g, 10.0 mmol) and THF (31 mL). *N*-Bromosuccinimide (1.87 g, 10.5 mmol) and TsOH (80 mg, 0.419 mmol) were then added and the reaction mixture was heated under reflux for 16h. The reaction mixture was cooled down to rt and partitioned between petroleum ether (60 mL) and 100 mL water. The organic layer was washed with H_2O (3 x 30 mL), dried over anhydrous Na_2SO_4, concentrated under reduced pressure to obtain a yellow oil. The compound was used without further purification due to his instability on silica.

^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.48 (s, 1H), 5.40 (s, 1H), 4.37 (s, 2H), 3.83 (s, 3H).

The physical and spectral data are in accordance with literature data:
Farid, U.; Wirth, T. *Angewandte Chemie* **2012**, *51* (14), 3462–3465.

Methyl 4-[1-(bromomethyl)vinyl]benzoate (SI_2_14)



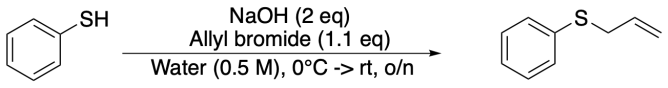
SI_2_14
Chemical Formula: $C_{11}H_{11}BrO_2$
Exact Mass: 253.9942

To a mixture of methyl 4-isopropenylbenzoatederivative (650 mg, 3.69 mmol) and TMSOTf (0.07 mL, 0.387 mmol in dry CH_2Cl_2/THF (4:1, 15 mL) under an nitrogen atmosphere were added NBS (788 mg, 4.43 mmol) and $Yb(OTf)_3$ (114 mg, 0.184 mmol) in one portion. The reaction mixture was stirred for 3h at rt, then concentrated under reduced pressure. The resulting residue was filtered three times with Et_2O, and the combined filtrates were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product mixture containing the desired methyl 4-[1-(bromomethyl)vinyl]benzoate (60%, 946 mg, 2.2 mmol, 60%) was used as such for the next step due to the instability of the molecule on silica.

^{1}**H NMR** (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 5.70–5.57 (m, 2H), 4.40 (d, *J* = 0.8 Hz, 2H), 3.94 (s, 3H).

The physical and spectral data are in accordance with literature data:
Häfliger, J.; Livingstone, K.; Daniliuc, C. G.; Gilmour, R. *Chemical Science* **2021**, *12* (17), 6148–6152.

1-(bromomethyl)vinylsulfanylbenzene (SI_2_17)

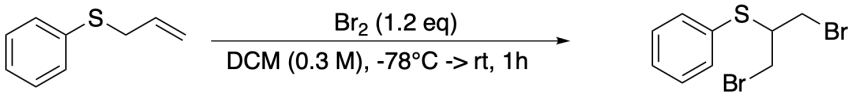


SI_2_15
Chemical Formula: $C_9H_{10}S$
Exact Mass: 150.0503

First step: A 250mL two-neck round bottom flask was charged with benzenethiol (3 mL, 29.4

mmol) and water (55 mL) and cooled down to 0 °C. Sodium hydroxide (2.35 g, 58.8 mmol) was then added portionwise and the reaction mixture was stirred at 0 °C for 10 minutes before allyl bromide (2.8 mL, 32.4 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 14 h. The reaction mixture was poured in a separatory funnel and EtOAc (50 mL) was added. The phase were separated and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure to deliver phenyl thioether **(SI_2_15)** (4.5 g, 30 mmol, quant) which was used for the next step without further purification.

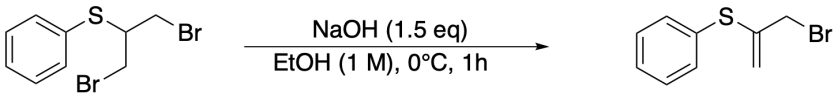
Light yellow oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.41–7.07 (m, 5H), 5.91 (ddt, *J* = 16.9, 10.0, 6.8 Hz, 1H), 5.23–5.05 (m, 2H), 3.58 (dt, *J* = 6.8, 1.2 Hz, 2H).



SI_2_16
Chemical Formula: $C_9H_{10}Br_2S$
Exact Mass: 307.8870

Second step: To a solution of allyl phenyl thioether (3 g, 20 mmol) in dry CH_2Cl_2 (30 mL) at –78 °C was added dropwise a solution of bromine (1.2 mL, 23.4 mmol) in CH_2Cl_2 (15 mL), at such a rate that the temperature did not exceed –78 °C. The reaction mixture was stirred for 30 min at –78 °C and then warmed to rt. The reaction mixture was successively washed with a solution of sat. $NaHSO_3$ (100 mL), 5% $Na_2S_2O_3$ (100 mL) and brine (100 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. After concentration under reduced pressure, [2-bromo-1-(bromomethyl)ethyl]sulfanylbenzene **(SI_2_16)** (5.05 g, 16.3 mmol, 82%) was obtained and used for the next step without further purification.

Colorless oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.56–7.42 (m, 3H), 7.45–7.27 (m, 2H), 3.77 (d, *J* = 5.6 Hz, 4H), 3.60–3.47 (m, 1H); ^{13}**C NMR** (75 MHz, $CDCl_3$) 133.4 (Cq_{Ar}), 132.3 (2 x CH_{Ar}), 129.6 (2 x CH_{Ar}), 128.6 (CH_{Ar}), 51.1 (CH), 34.1 (2 x CH_2).



SI_2_17
Chemical Formula: C_9H_9BrS
Exact Mass: 227.9608

Third step: To a slurry of NaOH (824 mg, 20.6 mmol) in ethanol (8 mL) was added [2-bromo-1-(bromomethyl)ethyl]sulfanylbenzene (4.26 g, 13.27 mmol). The reaction mixture was stirred at 0 °C for 1 h, then diluted with hexane (100 mL), filtered over a pad of Na_2SO_4 and concentrated under reduced pressure to afford a colorless oil. Purification by flash column chromatogra-

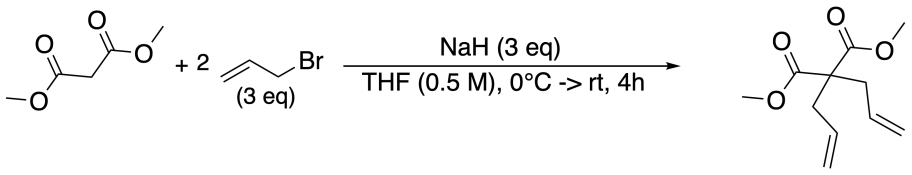
phy (Gradient 0-2 % Et_2O:pentane) delivered 1-(bromomethyl)vinylsulfanylbenzene **(SI_2_17)** (2.71 g, 11.8 mmol, 86%) (contaminated with DCM).

Colorless oil; Rf: 0.62 (100% pentane); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.50–7.44 (m, 2H), 7.40–7.29 (m, 3H), 5.30 (bs, 1H), 5.26 (bs, 1H), 4.03 (d, J = 1.0 Hz, 2H).

The physical and spectral data for the three compounds are in accordance with literature data: Chen, W.; Zhao, X.; Lu, L.; Cohen, T. *Organic Letters* **2006**, *8* (10), 2087–2090.

Radical traps

Dimethyl 2,2-diallylpropanedioate (6a)



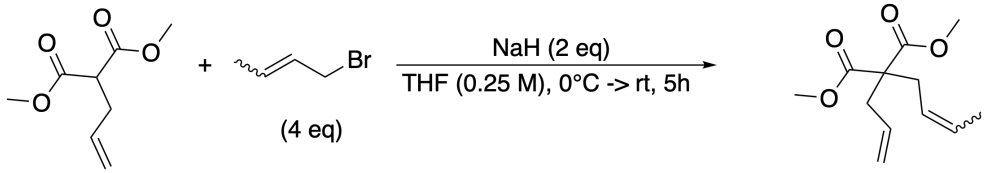
6a
Chemical Formula:
$C_{11}H_{16}O_4$
Exact Mass: 212.1049

To a suspension of NaH (55.0 %, 3.76 g, 90.0 mmol) in THF (40 mL) was slowly added a solution of dimethyl propanedioate (3.96 g, 30.0 mmol) in THF (20 mL) at 0 °C. The reaction was allowed to reach rt and stirred at rt for 30 min. The reaction mixture was then cooled down to 0 °C and allylbromide (7.7 mL, 89.2 mmol) was slowly added. The resulting mixture was allowed to reach rt and stirred at rt for additional 3h. The reaction mixture was carefully quenched with MeOH (5 mL) and a saturated solution of NH_4Cl was then added until complete dissolution of the suspended solid. The solution was transferred in a separatory funnel and phases were separated. The aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (5% EtOAc:heptane) delivered dimethyl 2,2-diallylpropanedioate (4.91 g, 23.1 mmol, 79%).

Colorless oil; Rf: 0.34 (95:5 heptanes:EtOAc); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 5.64 (ddt, J = 17.1, 9.5, 7.4 Hz, 2H), 5.17–5.04 (m, 4H), 3.71 (s, 6H), 2.64 (dt, J = 7.4, 1.1 Hz, 4H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 171.3 (2 x Cq), 132.4 (2 x CH), 119.4 (2 x CH_2), 57.8 (Cq), 52.5 (2 x CH_3), 37.1 (2 x CH_2).

The physical and spectral data for the three compounds are in accordance with literature data: Tappin, N. D. C.; Renaud, P. *Advanced Synthesis & Catalysis* **2020**, *363* (1), 275–282.

Dimethyl 2-allyl-2-(but-2-en-1-yl)malonate (6d)



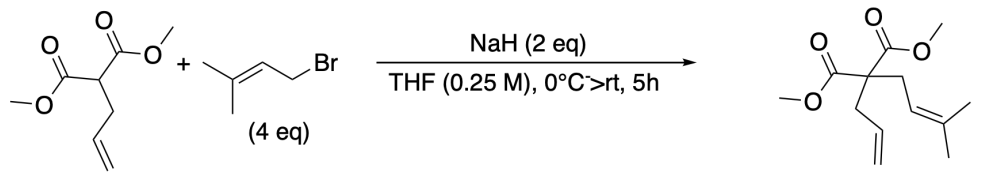
6d
Chemical Formula: $C_{12}H_{18}O_4$
Exact Mass: 226.1205

To a suspension of sodium hydride (2.53 g, 60.4 mmol, 55.0 % in mineral oil) in THF (55 mL) at 0 °C was slowly added a solution of dimethyl 2-allylpropanedioate (4.50 mL, 30.2 mmol) in THF (20 mL). The reaction was allowed to reach rt and stirred for 1h at rt. The reaction mixture was then cooled down to 0°C and crotyl bromide (14.6 mL, 121 mmol) (E:Z = 85:15) was slowly added. The resulting reaction mixture was allowed to reach rt and stirred at this temperature for additional 4h. The reaction mixture was quenched with MeOH (5 mL). Then, saturated solution of NH_4Cl (50 mL) was added and the solution was poured into a separatory funnel. The phases were separated, and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (10% EtOAc:heptanes) delivered dimethyl 2-allyl-2-(but-2-en-1-yl)malonate (5.11 g, 22.6 mmol, 75%).

Yellow oil; Rf: 0.43 (9:1 heptanes:EtOAc); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 5.74–5.41 (m, 2H), 5.31–5.14 (m, 1H), 5.11–5.03 (m, 2H), 3.69 (d, *J* = 1.5 Hz, 6H), 2.68–2.50 (m, 4H), 1.63–1.57 (m, 3H); ^{13}**C NMR** (75 MHz, $CDCl_3$) (E-Isomer) δ 171.5 (2 x Cq), 132.6 (CH), 130.1 (CH), 124.6 (CH), 119.1 (CH_2), 58.0 (Cq), 52.4 (2 x CH_3), 37.0 (CH_2), 35.8 (CH_2), 18.1 (CH_3); ^{13}**C NMR** (75 MHz, $CDCl_3$) (Z-Isomer) δ 171.5 (2 x Cq), 132.6 (CH), 128.1 (CH), 123.5 (CH), 119.2 (CH_2), 57.8 (Cq), 52.5 (2 x CH_3), 37.0 (CH_2), 30.0 (CH_2), 13.1 (CH_3).

The physical and spectral data are in accordance with literature data:
Perch, N. S.; Pei, T.; Widenhoefer, R. A. *Journal of Organic Chemistry* **2000**, *65* (12), 3836–3845.

Dimethyl 2-allyl-2-(3-methylbut-2-en-1-yl)malonate (6e)



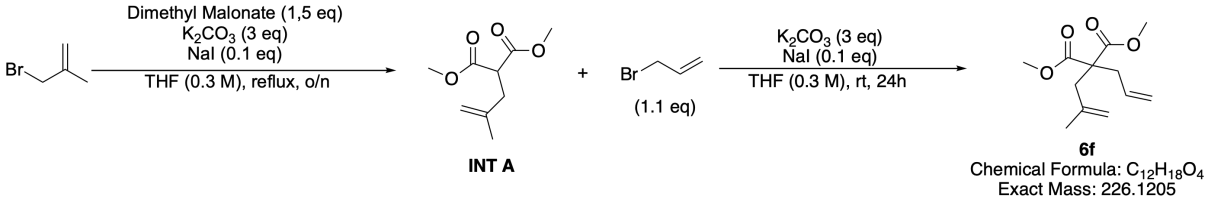
6e
Chemical Formula: $C_{13}H_{20}O_4$
Exact Mass: 240.1362

To a suspension of sodium hydride (2.53 g, 60.4 mmol, 55.0 % in mineral oil) in THF (55 mL) at 0 °C was slowly added a solution of dimethyl 2-allylpropanedioate (4.50 mL, 30.2 mmol) in THF (20 mL). The reaction mixture was allowed to reach rt and stirred at rt for 1h. The reaction mixture was cooled down to 0°C and 1-bromo-3-methyl-but-2-ene (18.0 g, 121 mmol) was slowly added. The resulting reaction mixture was allowed to reach rt and stirred at this temperature for additional 4h. The reaction mixture was quenched with MeOH (5 mL). Then, saturated solution of NH_4Cl (50 mL) was added and the solution was poured into a separatory funnel. The phases were separated, and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (6% EtOAc:heptane) delivered dimethyl 2-allyl-2-(3-methylbut-2-en-1-yl)malonate (4.55 g, 18.9 mmol, 63%).

Yellow oil; Rf: 0.37 (9:1 heptanes:EtOAc); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 5.72–5.52 (m, 1H), 5.11–4.98 (m, 2H), 4.92 (tp, *J* = 7.5, 1.4 Hz, 1H), 3.67 (s, 6H), 2.60-2.55 (m, 4H), 1.66 (s, 3H), 1.57 (s, 3H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 171.6 (2 x Cq), 135.8 (Cq), 132.7 (CH), 119.0 (CH), 117.6 (CH_2), 58.0 (Cq), 52.4 (2 x CH_3), 37.0 (CH_2), 31.2 (CH_2), 26.1 (CH_3), 18.0 (CH_3).

The physical and spectral data for the three compounds are in accordance with literature data: Kerber, W. D.; Gagné, M. R. *Organic Letters* **2005**, *7* (15), 3379–3381.

Dimethyl 2-allyl-2-(2-methylallyl)propanedioate (6f)



First step: A 250 mL two-neck round bottom flask was charged with dipotassium carbonate (8.22 g, 59.5 mmol) and sodium iodide (297 mg, 1.98 mmol) and THF (60 mL). 3-Bromo-2-methyl-prop-1-ene (2.00 mL, 19.8 mmol) and dimethyl propanedioate (3.00 mL, 26.2 mmol) were then added and the mixture was heated under reflux (75 °C) for 14 h. Sat. NH_4Cl (150 mL) and DCM (70 mL) were added to the reaction mixture, which was then poured into a separatory funnel. The phases were separated, and the aqueous layer was extracted with DCM (3 x 50 mL). The combined organic phases were washed with brine (150 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure (100 mbar, bath temperature at 30 °C) to afford a light yellow oil. Purification by flash column chromatography (6% EtOAc:heptane) delivered dimethyl 2-(2-methylallyl)malonate **INT A** (3.18 g, 17.1 mmol, 86%).

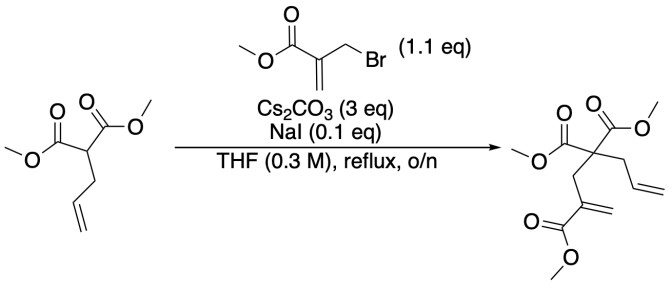
Colorless oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 4.79 (ddp, J = 2.3, 1.5, 0.9 Hz, 1H), 4.72 (dq, J = 2.1, 1.2 Hz, 1H), 3.73 (s, 6H), 2.67–2.58 (m, 2H), 1.78–1.71 (m, 3H). Contain traces solvents (EtOAc).

Second step: Dimethyl 2-(2-methylallyl)propanedioate (1.52 g, 8.52 mmol) and 3-bromo- prop-1-ene (0.760 mL, 8.78 mmol) were added to a suspension of potassium carbonate (3.34 g, 24.2 mmol) and NaI (122 mg, 0.815 mmol) in THF (25 mL). The reaction mixture was heated under reflux for 24 h. The reaction mixture was then quenched with saturated NH_4Cl (100 mL). The phases were separated and the aqueous layer was extracted with DCM (3 x 50 mL). The combined organic phases were washed with brine (1 x 50 mL), dried over Na_2O_4, filtered, and concentrated under reduced pressure to afford a light brown oil. Purification by flash column chromatography (10% EtOAc:heptanes) delivered dimethyl 2-allyl-2-(2-methylallyl)propanedioate (1.36 g, 5.99 mmol, 50%).

Light yellow oil; Rf: 0.6 (8:2 heptanes:EtOAc); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 5.68 (ddt, J = 17.0, 9.4, 7.4 Hz, 1H), 5.15–5.03 (m, 2H), 4.91–4.84 (m, 1H), 4.75 (s, 1H), 3.71 (s, 6H), 2.73–2.62 (m, 4H), 1.65 (s, 3H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 171.7 (2 x Cq), 140.6 (Cq), 132.8 (CH), 119.2 (CH_2), 116.0 (CH_2), 57.5 (Cq), 52.5 (2 x CH_3), 40.5 (CH_2), 37.1 (CH_2), 23.3 (CH_3).

The physical and spectral data for the two compounds are in accordance with literature data: Verendel, J. J.; Li, J.; Quan, X.; Peters, B.; Zhou, T.; Gautun, O. R.; Govender, T.; Andersson, P. G. *Chem. Eur. J.* **2012**, *18* (21), 6507–6513.

Trimethyl hepta-1,6-diene-2,4,4-tricarboxylate (6g)



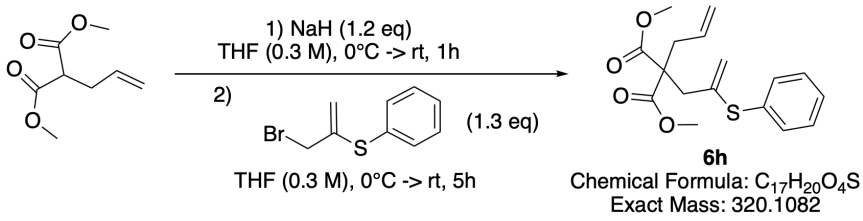
6g
Chemical Formula: $C_{13}H_{18}O_6$
Exact Mass: 270.1103

Dimethyl 2-allylpropanedioate (1.6 mL, 9.95 mmol) and methyl 2-(bromomethyl)prop-2- enoate (1.3 mL, 10.8 mmol) were added to a suspension of cesium carbonate (9.73 g, 29.9 mmol) and NaI (149 mg, 0.995 mmol) in THF (30 mL). The reaction mixture was stirred under reflux for 16h. It was then quenched with saturated NH_4Cl (100 mL). DCM (50 mL) was added, and the phases were separated. The aqueous layer was extracted with DCM (3 x 50 mL). The com-

bined organic phases were washed with brine (1 x 50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a light brown oil. Purification by flash column chromatography (Gradient: 10- 20% EtOAc:heptane) delivered trimethyl hepta-1,6-diene-2,4,4-tricarboxylate (2.28 g, 8.43 mmol, 85%).

Colorless oil; Rf: 0.3 (heptanes:EtOAc 9:1); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 6.27 (d, J = 1.4 Hz, 1H), 5.80–5.61 (m, 2H), 5.17–5.02 (m, 2H), 3.72 (s, 3H), 3.69 (s, 6H), 2.97 (d, J = 1.0 Hz, 2H), 2.59 (dt, J = 7.3, 1.2 Hz, 2H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 171.1 (2 x Cq), 167.5 (Cq), 136.0 (Cq), 132.6 (CH), 129.4 (CH_2), 119.4 (CH_2), 58.0 (Cq), 52.5 (CH_3), 52.1 (2 x CH_3), 37.5 (CH_2), 34.1 (CH_2); IR (neat): ν_{max} = 2953, 1724, 1437, 1285, 1250, 1196, 1150, 963, 924, 817 cm^{-1}; HRMS (ESI): Calculated for $C_{13}H_{19}O_6$ $[M+H]^+$: 271.1184; found: 271.1103.

Dimethyl 2-allyl-2-(2-phenylsulfanylallyl)propanedioate (6h)

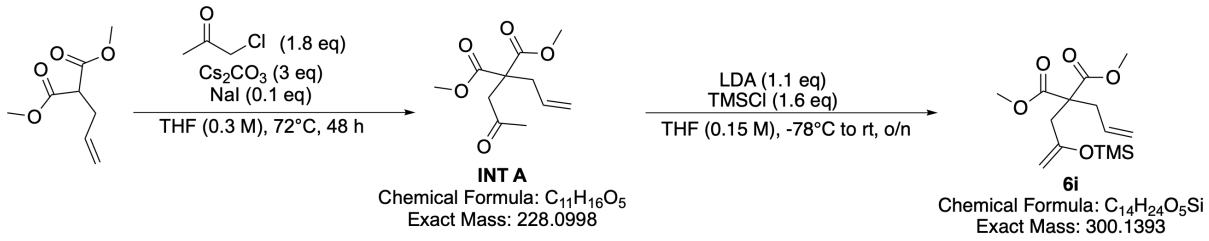


6h
Chemical Formula: $C_{17}H_{20}O_4S$
Exact Mass: 320.1082

To a suspension of sodium hydride (293 mg, 7 mmol, 55–65% dispersion in mineral oil) in dry THF (11 mL) at 0° C was added dropwise a solution of dimethyl 2-allylpropanedioate (0.9 mL, 5.6 mmol) in THF (5 mL). The reaction mixture was then heated at 50 °C and stirred for 1 hour. The reaction mixture ws cooled down to 0 °C and a solution of 1-(bromomethyl)vinylsulfanylbenzene (1.668 g, 7.28 mmol) in THF (5 mL) was then slowly added. The reaction mixture was stirred for 5 h at 0 °C, then carefully quenched with MeOH (2 mL). Saturated NH_4Cl (30 mL) and Et_2O (30 mL) were added. The phases were separated, and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with brine (1 x 100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (Gradient 10% EtOAc:heptane) delivered dimethyl 2-allyl-2-(2-phenylsulfanylallyl)propanedioate (1.59 g, 4.96 mmol, 88%).

Yellow oil; Rf: 0.25 (Heptane:EtOAc 9:1); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.43–7.29 (m, 4H), 5.67 (ddt, J = 17.4, 10.2, 7.3 Hz, 1H), 5.20 (d, J = 0.9 Hz, 1H), 5.15–5.04 (m, 2H), 4.91 (s, 1H), 3.71 (s, 6H), 2.93 (d, J = 0.8 Hz, 2H), 2.81 (dt, J = 7.3, 1.2 Hz, 2H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 171.1 (2 x Cq), 140.6 (Cq_{Ar}), 133.3 (2 x CH_{Ar}), 133.0 (Cq), 132.6 (CH_{Ar}), 129.4 (2 x CH_{Ar}), 128.3 (CH), 119.5 (CH_2), 117.5 (CH_2), 57.8 (Cq), 52.6 (2 x CH_3), 38.5 (CH_2), 36.6 (CH_2); IR (neat): ν_{max} = 2950, 1727, 1440.6, 1291, 1207, 1156, 921, 861, 750, 689 cm^{-1}; HRMS (ESI): Calculated for $C_{17}H_{20}O_4S$ $[M+Na]^+$: 343.1082; found: 343.0968.

Dimethyl 2-allyl-2-(2-((trimethylsilyl)oxy)allyl)malonate (6i)



INT A
Chemical Formula: $C_{11}H_{16}O_5$
Exact Mass: 228.0998

6i
Chemical Formula: $C_{14}H_{24}O_5Si$
Exact Mass: 300.1393

First step: To a suspension of caesium carbonate (16.2 g, 49.7 mmol) and sodium iodide (447 mg, 2.98 mmol) in THF (90 mL) were added 1-chloropropan-2-one (4.5 mL, 54.6 mmol) and dimethyl 2-allylpropanediodate (4.8 mL, 29.8 mmol). The reaction mixture was stirred under reflux (72°C) for 48 h. The reaction mixture was then quenched with saturated NH_4Cl (150 mL) and EtOAc (70 mL) was added. The aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic phases were washed with brine (1 x 100 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a brown oil. Purification by flash column chromatography (20% EtOAc:heptane) delivered dimethyl 2-allyl-2-(2-oxopropyl)malonate **INT A** (4.36 g, 19.1 mmol, 61%), contaminated by an unknown compound. The compound was used as such for the next step.

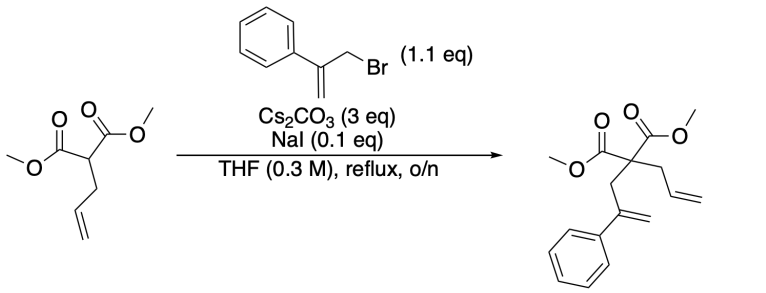
Yellow oil; Rf: 0.27 (heptanes:EtOAc 8:2); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 5.63 (ddt, *J* = 16.7, 10.3, 7.5 Hz, 1H), 5.15–4.99 (m, 2H), 3.73 (s, 6H), 3.11 (s, 2H), 2.77 (dt, *J* = 7.5, 1.2 Hz, 2H), 2.14 (s, 3H).

The physical and spectral data are in accordance with literature data:
Mello, R.; Alcalde-Aragonés, A.; González-Núñez, M. E. *Tetrahedron Letters* **2010**, *51* (32), 4281–4283.

Second step: To a solution of diisopropylamine (0.23 mL, 1.64 mmol) in THF (3 mL) at –78 °C was added dropwise n-BuLi (0.69 mL, 1.79 mmol, 2.6 M in hexanes). The reaction mixture stirred 1 min at -78 °C, then a solution of dimethyl 2-acetonyl-2-allyl-propanedioate (340 mg, 1.49 mmol) in THF (2 mL) was added at -78 °C. The reaction mixture was stirred 15 min at –78 °C and a solution of chloro(trimethyl)silane (0.3 mL, 2.39 mmol) in THF (2 mL) was then added dropwise at -78 °C. The reaction mixture was stirred for 15 min at -78°C, then the cooling bath was removed, and it was stirred overnight to rt. The reaction mixture was quenched with saturated NH_4Cl (50 mL) and Et_2O (50 mL) was added. The aqueous layer was extracted Et_2O (3 x 20 mL). The combined organic phases were washed with brine (1 x 100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to deliver an orange oil. Purification by flash column chromatography (Macherey-Nagel Silica 60, 0.015–0.04 mm, 5% Et_2O:pentane) delivered dimethyl 2-allyl-2-(2-((trimethylsilyl)oxy)allyl)malonate (176 mg, 0.586 mmol, 39%).

Colorless oil; Rf: 0.51 (Pentane:Et_2O 9:1); ^{1}**H NMR** (300 MHz, C_6D_6) δ 5.71 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H); 5.85 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.05-4.84 (m, 2H), 3.96 (d, *J* = 1.2 Hz, 1H), 3.94 (d, *J* = 1.3 Hz, 1H), 3.23 (s, 6H), 2.95 – 2.85 (m, 4H), -0.00 (s, 9H); ^{13}**C NMR** (75 MHz, C_6D_6) δ 171.1 (2 x Cq), 155.4 (Cq), 133.5 (CH), 119.0 (CH_2), 92.9 (CH_2), 56.7 (Cq), 51.9 (2 x CH_3), 39.8 (CH_2), 37.0 (CH_2), -0.2 (3 x CH_3); IR (neat): ν_{max} = 2954, 1736, 1629, 1436, 1211, 1196, 1178, 1011, 693, 529 cm^{-1}; HRMS (ESI): Calculated for $C_{14}H_{24}O_5Si$ $[M+H]^+$: 300.1393; found: 300.1387.

Dimethyl 2-allyl-2-(2-phenylallyl)malonate (6j)



6j
Chemical Formula: $C_{17}H_{20}O_4$
Exact Mass: 288.1362

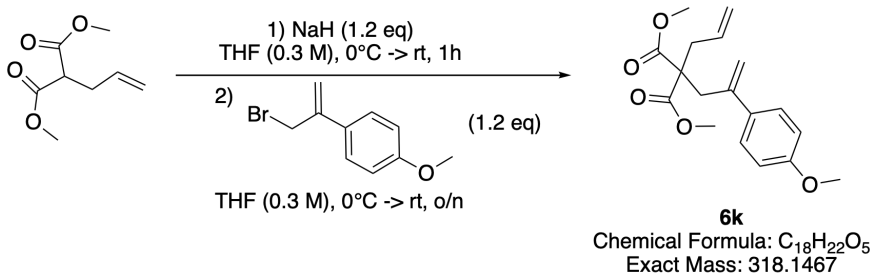
To a solution of 1-(bromomethyl)vinylbenzene (1.48 g, 7.53 mmol) in THF (22 mL) were added successively dimethyl 2-allylpropanedioate (1.1 mL, 6.84 mmol), cesium carbonate (6.69 g, 20.5 mmol) and NaI (103 mg, 0.684 mmol). The reaction mixture was stirred under reflux for 16h. The reaction mixture was quenched with saturated NH_4Cl (50 mL) and DCM (30 mL) was added. The phases were separated and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic phases were washed with brine (1 x 100 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a light brown oil. Purification by flash column chromatography (10% EtOAc:heptane) delivered dimethyl 2-allyl-2-(2-phenylallyl)malonate (1.90 g, 6.59 mmol, 96%).

Yellow oil; Rf: 0.38 (heptanes:EtOAc 9:1); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.37–7.20 (m, 5H), 5.63 (ddt, *J* = 16.8, 10.2, 7.3 Hz, 1H), 5.28 (d, *J* = 1.7 Hz, 1H), 5.17 (dt, *J* = 1.8, 0.9 Hz, 1H), 5.09–4.96 (m, 2H), 3.45 (s, 6H), 3.19 (d, *J* = 0.9 Hz, 2H), 2.61 (dt, *J* = 7.3, 1.2 Hz, 2H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 171.1 (2 x Cq), 144.6 (Cq_{Ar}), 141.7 (Cq), 132.6 (CH_{Ar}), 128.2 (2 x CH_{Ar}), 127.6 (CH), 127.1 (2 x CH_{Ar}), 119.3 (CH), 118.8 (CH_2), 57.6 (Cq), 52.2 (2 x CH_3), 37.6 (CH_2), 36.4 (CH_2).

The physical and spectral data are in accordance with literature data:
Verendel, J. J.; Li, J.; Quan, X.; Peters, B.; Zhou, T.; Gautun, O. R.; Govender, T.; Andersson,

P. G. *Chem. Eur. J.* **2012**, *18* (21), 6507–6513.

Dimethyl 2-allyl-2-[2-(4-methoxyphenyl)allyl]propanedioate (6k)

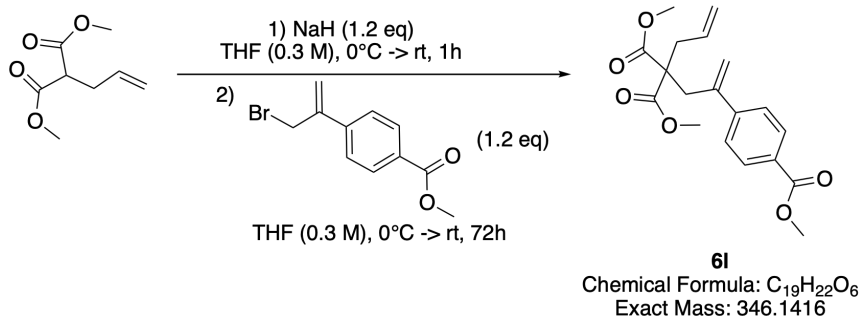


6k
Chemical Formula: $C_{18}H_{22}O_5$
Exact Mass: 318.1467

To a suspension of sodium hydride (228 mg, 5.44 mmol, 55–65% in mineral oil) in THF (4 mL) was slowly added a solution of dimethyl 2-allylpropanedioate (0.730 mL, 4.54 mmol) in THF (5 mL) at 0 °C. The reaction mixture was allowed to reach rt and stirred for 1h at rt. The reaction mixture was then cooled down to 0 °C and a solution of 1-[1-(bromomethyl)vinyl]-4-methoxybenzene **SI_2_13** (2.15 g, 5.67 mmol, 60% purity) in THF (5 mL) was added dropwise. The resulting reaction mixture was allowed to reach rt and stirred at rt for 24 h. The reaction mixture was quenched with MeOH (2 mL), then saturated NH_4Cl (30 mL) and Et_2O (30 mL) were added. The phases were separated, and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with brine (1 x 100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford an orange oil. Purification by flash column chromatography (Gradient 15-30% Et_2O:pentane) delivered dimethyl 2-allyl-2-[2-(4-methoxyphenyl)allyl]propanedioate (707 mg, 2.22 mmol, 49%).

Colorless oil; Rf: 0.33 (Pentane:Et_2O 8:2); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.28–7.17 (m, 2H), 6.87–6.76 (m, 2H), 5.62 (ddt, *J* = 17.4, 10.3, 7.3 Hz, 1H), 5.19 (d, *J* = 1.7 Hz, 1H), 5.11–4.95 (m, 3H), 3.77 (s, 3H), 3.45 (s, 5H), 3.13 (s, 2H), 2.58 (dt, *J* = 7.3, 1.3 Hz, 2H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 171.0 (2 x Cq), 159.1 (Cq_{Ar}), 143.8 (Cq), 133.9 (Cq_{Ar}), 132.6 (2 x CH_{Ar}), 128.0 (2 x CH_{Ar}), 119.1 (CH_2), 117.4 (CH_2), 113.4 (CH), 57.5 (Cq), 55.2 (CH_3), 52.1 (2 x CH_3), 37.5 (CH_2), 36.3 (CH_2); IR (neat): ν_{max} = 2951, 1731, 1606, 1510, 1435, 1287, 1247, 1209, 1198, 1178, 1032, 836 cm^{-1}; HRMS (ESI): Calculated for $C_{18}H_{23}O_5$ $[M+H]^+$: 319.1467; found: 319.1534.

Dimethyl 2-allyl-2-[2-(4-methoxycarbonylphenyl)allyl]propanedioate (6l)

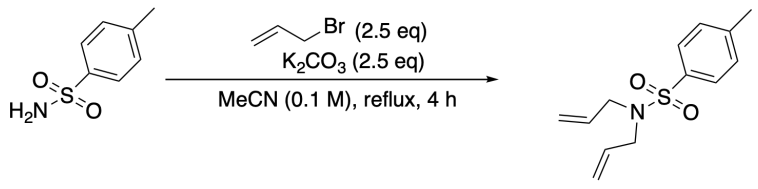


6l
Chemical Formula: $C_{19}H_{22}O_6$
Exact Mass: 346.1416

To a suspension of sodium hydride (103 mg, 2.46 mmol, 55–65% dispersion in mineral oil) in THF (4 mL) was slowly added dimethyl 2-allylpropanedioate (0.330 mL, 2.05 mmol) at 0 °C. The reaction mixture was allowed to reach rt and stirred for 1h at rt. The reaction mixture was cooled down to 0 °C and a solution of methyl 4-[1- (bromomethyl)vinyl]benzoate **SI_2_14** (964 mg, 2.27 mmol, 60% purity) in THF (5 mL) was added dropwise. The resulting reaction mixture was allowed to reach rt and stirred at rt for 24h. The reaction mixture was quenched with MeOH (2 mL), then saturated NH_4Cl (30 mL) and Et_2O (30 mL) were added. The phases were separated, and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with brine (1 x 100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford an orange oil. Purification by flash column chromatography (Gradient 15-30% Et_2O:pentane) delivered the desired Dimethyl 2-allyl-2-[2-(4-methoxycarbonylphenyl)allyl]propanedioate (593 mg, 1.54 mmol, 75%).

Colorless oil; Rf: 0.23 (Pentane:Et_2O 8:2); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.99–7.92 (m, 2H), 7.42–7.33 (m, 2H), 5.59 (ddt, J = 17.4, 10.2, 7.3 Hz, 1H), 5.34 (d, J = 1.4 Hz, 1H), 5.24 (d, J = 1.4 Hz, 1H), 5.12–4.93 (m, 2H), 3.91 (s, 3H), 3.44 (s, 6H), 3.18 (d, J = 0.9 Hz, 2H), 2.61–2.47 (m, 2H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 171.0 (2 x Cq), 167.0 (Cq), 146.3 (Cq_{Ar}), 143.9 (Cq), 132.4 (Cq_{Ar}), 129.6 (2 x CH_{Ar}), 129.3 (CH), 127.1 (2 x CH_{Ar}), 120.5 (CH_2), 119.6 (CH_2), 57.6 (Cq), 52.29 (2 x CH_3), 52.25 (CH_3), 37.4 (CH_2), 36.5 (CH_2); HRMS (ESI): Calculated for $C_{19}H_{22}O_6$ $[M+H]^+$: 346.1416; found: 346.1416.

***N,N*-Diallyl-p-toluenesulfonamide (6c)**



6c
Chemical Formula: $C_{13}H_{17}NO_2S$
Exact Mass: 251.0980

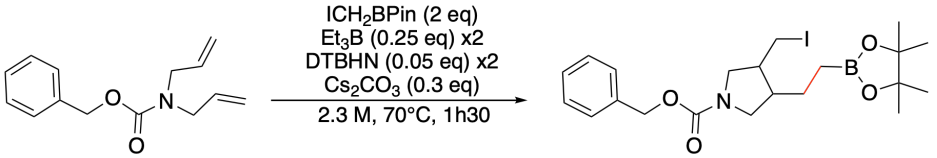
To a solution of 4-methylbenzenesulfonamide (3.44 g, 20.1 mmol) and potassium carbon-

ate (6.94 g, 50.2 mmol) in acetonitrile (220 mL) was added 3-bromoprop-1-ene (4.34 mL, 50.2 mmol). The reaction mixture was heated under reflux for 4 h. The reaction mixture was then filtered through a pad of Celite and the filtrate was concentrated under reduced pressure to afford an orange solution. Purification by flash column chromatography (Gradient 10% EtOAc:heptanes) delivered the desired *N*,*N*-diallyl-p-toluenesulfonamide (4.28 g, 17 mmol, 85%).

Colorless oil; Rf: 0.4 (Heptane:EtOAc 9:1); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.78–7.68 (m, 2H), 7.38–7.26 (m, 2H), 5.64 (ddt, *J* = 17.4, 9.8, 6.3 Hz, 2H), 5.23–5.10 (m, 4H), 3.83 (dt, *J* = 6.2, 1.2 Hz, 4H), 2.45 (s, 3H).

The physical and spectral data are in accordance with literature data:
Terada, Y.; Arisawa, M.; Nishida, A. *Angewandte Chemie* **2004**, *43* (31), 4063–4067.

Benzyl *N*,*N*-diallylcarbamate (6m)



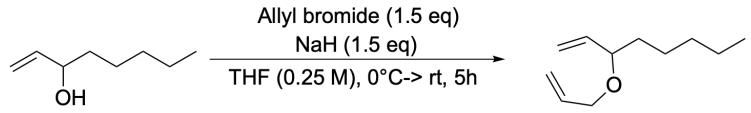
6m
Chemical Formula: $C_{21}H_{31}BINO_4$
Exact Mass: 499.1391

To a solution of *N*-allylprop-2-en-1-amine (1.90 mL, 15.4 mmol) and triethylamine (3.89 mL, 28.0 mmol) in DCM (24.0 mL) at 0°C was added dropwise benzyl carbonochloridate (1.99 mL, 14.0 mmol). The reaction mixture was then allowed to reach rt and stirred for 1h at rt. H_2O (25 mL) was added and the phases were separated. The aqueous layer was extracted DCM (3 x 20 mL). The combined organic phases were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford an orange oil. Purification by flash column chromatography (Gradient 10% EtOAc:heptanes) delivered the desired benzyl *N*,*N*-diallylcarbamate (1.22 g, 5.27 mmol, 38%).

Colorless oil; Rf: 0.39 (Heptane:EtOAc 9:1); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.39–7.28 (m, 5H), 5.77 (d, *J* = 5.8 Hz, 2H), 5.14 (d, *J* = 7.4 Hz, 6H), 3.89 (s, 4H).

The physical and spectral data are in accordance with literature data:
Connolly, T.; Wang, Z.; Walker, M. A.; McDonald, I. M.; Peese, K. M. *Organic Letters* **2014**, *16* (17), 4444–4447.

3-allyloxyoct-1-ene (6n)



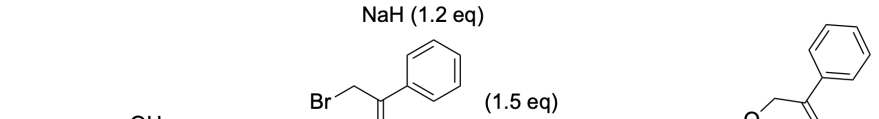
6n
Chemical Formula: $C_{11}H_{20}O$
Exact Mass: 168.1514

To a suspension of NaH (1.12 g, 29.3 mmol, 55–65% dispersion in mineral oil) in THF (50 mL) et 0° C was added dropwise a solution of oct-1-en-3-ol (3 mL, 19.5 mmol) in THF (10 mL). The reaction mixture was stirred for 30 min at rt, then a solution of 3-bromoprop-1-ene (2.5 mL, 28.9 mmol) in THF (10 mL) was added dropwise and the reaction mixture was stirred for 4h at rt. The reaction mixture was quenched with MeOH (2 mL), then saturated NH_4Cl (30 mL) and Et_2O (30 mL) were added. The phases were separated, and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with brine (1 x 100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (2% Et_2O:pentane) delivered the desired 3-allyloxyoct-1-ene (3.29 g, 19.6 mmol, quant).

Colorless oil; Rf: 0.76 (Pentane:Et_2O 96:4); ^{1}**H NMR** δ 5.91 (dddd, *J* = 17.2, 10.3, 6.0, 5.2 Hz, 1H), 5.76–5.58 (m, 1H), 5.31–5.10 (m, 4H), 4.04 (ddt, *J* = 12.8, 5.2, 1.5 Hz, 1H), 3.83 (ddt, *J* = 12.8, 6.0, 1.4 Hz, 1H), 3.67 (q, *J* = 6.8 Hz, 1H), 1.67–1.16 (m, 8H), 0.93–0.83 (m, 3H); ^{13}**C NMR** δ 139.4 (CH), 135.4 (CH), 116.9 (CH_2), 116.7 (CH_2), 80.9 (CH), 69.3 (CH_2), 35.6 (CH_2), 32.0 (CH_2), 25.2 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

The physical and spectral data are in accordance with literature data:
Schmidt, B. and Wildemann, H. *Chem. Eur. J.* **2000**, *18*, 3145–3163.

1-(1-vinylhexoxymethyl)vinylbenzene (6o)



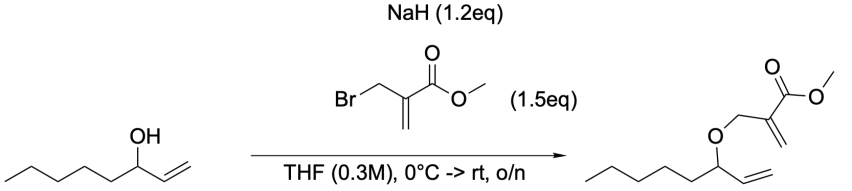
6o
Chemical Formula: $C_{17}H_{24}O$
Exact Mass: 244.1827

To a suspension of NaH (524 mg, 12.5 mmol, 55–65% dispersion in mineral oil) in THF (11 mL) at 0°C was added dropwise a solution of oct-1-en-3-ol (1.60 mL, 10.4 mmol, 1 eq) in THF (11 mL). The reaction mixture was stirred at rt for 1h and a solution of 1-(bromomethyl)vinylbenzene (3.08 g, 15.7 mmol) in THF (11 mL) was then slowly added at 0°C. The reaction mixture was stirred at rt for 72h. The reaction mixture was quenched with MeOH (2 mL), then saturated

NH_4Cl (30 mL) and Et_2O (30 mL) were added. The phases were separated, and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with brine (1 x 100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (Macherey-Nagel Silica 60, 0.015–0.04 mm, 100% pentane) delivered 1-(1-vinylhexoxymethyl)vinylbenzene (2.57 g, 10.5 mmol, quant).

Colorless oil; Rf: 0.64 (Pentane:Et_2O 9:1); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.49–7.43 (m, 2H), 7.26 (m, 3H), 5.79–5.62 (m, 1H), 5.50 (dt, *J* = 1.5, 0.8 Hz, 1H), 5.33 (q, *J* = 1.5 Hz, 1H), 5.25–5.14 (m, 2H), 4.46 (ddd, *J* = 13.0, 1.5, 0.8 Hz, 1H), 4.19 (ddd, *J* = 13.0, 1.3, 0.7 Hz, 1H), 3.74 (ddd, *J* = 7.9, 6.9, 5.9 Hz, 1H), 1.55 (ddd, *J* = 13.0, 9.2, 5.9 Hz, 1H), 1.44 (ddd, *J* = 13.0, 9.2, 5.9 Hz, 1H), 1.34 – 1.14 (m, 6H), 0.89–0.78 (m, 3H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 144.9 (Cq_{Ar}), 139.3 (Cq), 128.4 (2 x CH_{Ar}), 127.8 (CH), 126.3 (2 x CH_{Ar}), 117.1 (CH_2), 114.1 (CH_2), 80.7 (CH), 70.0 (CH_2), 35.6 (CH_2), 31.9 (CH_2), 25.2 (CH_2), 22.7 (CH_2), 14.2 (CH_3); IR (neat): ν_{max} = 2954, 2928, 2857, 1495, 1444, 1420, 1071, 903, 777, 706 cm^{-1}; HRMS (ESI): Calculated for $C_{17}H_{25}O$ $[M+H]^+$: 245.1827; found: 245.1909.

Methyl 2-((oct-1-en-3-yloxy)methyl)acrylate (6p)



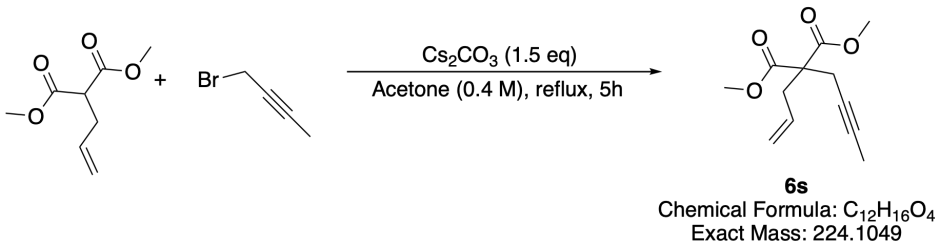
6p
Chemical Formula: $C_{13}H_{22}O_3$
Exact Mass: 226.1569

To a suspension of NaH (262 mg, 6.27 mmol, 55–65% dispersion in mineral oil) in THF (5mL) at 0 °C was added dropwise a solution of oct-1-en-3-ol (0.800 mL, 5.22 mmol) in THF (5mL). The reaction mixture was stirred at rt for 1h, then a solution of methyl 2-(bromomethyl)prop-2-enoate (0.900 mL, 7.49 mmol) in THF (8 mL) was slowly added to the reaction mixture at 0°C. The mixture was stirred for 14 h at rt. The reaction mixture was quenched with MeOH (2 mL), then saturated NH_4Cl (30 mL) and Et_2O (30 mL) were added. The phases were separated, and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with brine (1 x 100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (5% Et2O:pentane) delivered methyl 2-((oct-1-en-3-yloxy)methyl)acrylate (0.522 g, 2.31 mmol, 44%).

Colorless oil; Rf: 0.64 (Pentane:Et_2O 9:1); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 6.34-6.27 (m, 1H), 5.97-5.83 (m, 1H), 5.78–5.60 (m, 1H), 5.26–5.12 (m, 2H), 4.30–4.15 (m, 1H), 4.04 (dt, *J* = 14.3, 1.6 Hz, 1H), 3.76 (s, 3H), 1.70–1.20 (m, 9H), 0.93–0.83 (m, 3H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 166.6 (Cq), 139.1 (CH), 137.8 (Cq), 125.8 (CH_2), 117.1 (CH_2), 81.6 (CH), 66.5 (CH_2),

51.9 (CH_3), 35.5 (CH_2), 31.9 (CH_2), 25.1 (CH_2), 22.8 (CH_2), 14.2 (CH_3); IR (neat): ν_{max} = 2953, 2930, 2856, 1720, 1438, 1278, 1196, 1158, 1088, 925 cm^{-1}; HRMS (ESI): Calculated for $C_{13}H_{22}O$ [M+Na]$^+$: 249.1569; found: 249.1460.

Dimethyl 2-allyl-2-but-2-ynyl-propanedioate (6s)



6s
Chemical Formula: $C_{12}H_{16}O_4$
Exact Mass: 224.1049

A 100 mL two-neck round bottom flask was charged with dicesium carbonate (9.91 g, 30.4 mmol), dimethyl allyl malonate (3.47 g, 20.2 mmol), 1-bromobut-2-yne (2.30 mL, 30.4 mmol) and acetone (50mL, HPLC grade). The mixture was stirred and heated under reflux for 5h. Upon completion, the suspension was filtered over Celite and the filtrate concentrated under reduced pressure to afford a yellow oil. Purification by flash column chromatography (10% EtOAc:heptane) delivered dimethyl 2-allyl- 2-but-2-ynyl-propanedioate (4.42 g, 19.7 mmol, 98%).

Colorless oil; Rf: 0.5 (8:2 heptanes:EtOAc); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 5.62 (ddt, *J* = 17.4, 10.1, 7.5 Hz, 1H), 5.21–5.04 (m, 2H), 3.71 (s, 6H), 2.81–2.67 (m, 4H), 1.74 (t, *J* = 2.6 Hz, 3H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 170.6 (2 x Cq), 132.1 (CH), 119.7 (CH_2), 79.0 (Cq), 73.3 (Cq), 57.4 (Cq), 52.7 (2 x CH_3), 36.7 (CH_2), 23.2 (CH_2), 3.6 (CH_3).

The physical and spectral data are in accordance with literature data:
Zheng, J.; Peters, B. B. C.; Jiang, W.; Suàrez, L. A.; Ahlquist, M. S. G.; Singh, T.; Andersson, P. G. *Chem. Eur. J.* **2024**, *30* (13).

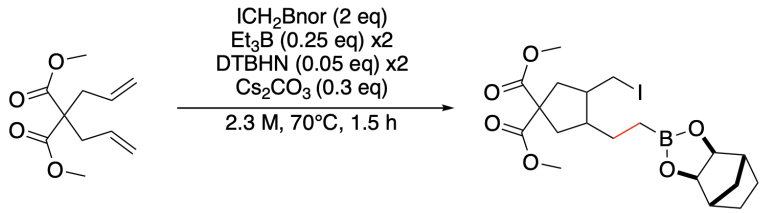
3.10.3 ATRAC products

GP1: A flame-dried 10 mL two neck round-bottom flask, equipped with a cold-finger reflux condenser, was charged with the diene (1.00 mmol), the radical precursor (ICH_2Bxxx) (2.00 mmol) and Cs_2CO_3 (98 mg, 0.3 mmol). Triethylborane (0.217 mL, 0.25 mmol, 1.15 M in TFT) was then added, with the needle immersed in the solution. Next, DTBHN (9 mg, 0.05 mmol) was added, and the contents heated at 70 °C for 45 minutes in a pre-heated oil bath. After having cooled down the reaction mixture, an additional portion of triethylborane (0.217 mL, 0.25 mmol, 1.15 M in TFT) and DTBHN (9 mg, 0.05 mmol) were then added, and the mixture was heated for additional 45 minutes at 70°C. The crude product was filtered over a small pad of neutral

aluminum oxide (2.0 cm) and eluted with EtOAc. After concentration under reduced pressure, the crude mixture was purified by flash column chromatography on silica gel.

GP2: A flame-dried 10 mL two neck round-bottom flask, equipped with a cold-finger reflux condenser, was charged with the diene (1.00 mmol), **ICH_2BPin** (4.00 mmol) and Cs_2CO_3 (98 mg, 0.3 mmol). Triethylborane (0.217 mL, 0.25 mmol, 1.15 M in TFT) was then added, with the needle immersed in the solution. Next, DTBHN (9 mg, 0.05 mmol) was added, and the contents heated at 70 °C for 45 minutes in a pre-heated oil bath. After having cooled down the reaction mixture, an additional portion of triethylborane (0.217 mL, 0.25 mmol, 1.15 M in TFT) and DTBHN (9 mg, 0.05 mmol) were then added, and the mixture was heated for additional 45 minutes at 70°C. The crude product was filtered over a small pad of neutral aluminum oxide (2.0 cm) and eluted with EtOAc. After concentration under reduced pressure, the crude mixture was purified by flash column chromatography on silica gel.

Dimethyl 3-[2-[(6S,7R)-3,5-dioxa-4-boratricyclo[5.2.1.02,6]decan-4-yl]ethyl]-4-(iodomethyl)-cyclopentane-1,1-dicarboxylate (Bnor-7a)



Bnor-7a
Chemical Formula: $C_{19}H_{28}BIO_6$
Exact Mass: 490.1024

Using Followed **GP1** using **6a** (1 mmol) as radical trap and ICH_2Bnor as radical precursor. Purification by flash column chromatography (Gradient 5-10% EtOAc:heptanes) provided the desired **Bnor-7a** (392 mg, 0.8 mmol, 80% - dr 8:2).

Light yellow oil; Rf: 0.17 (9:1 heptanes:EtOAc);

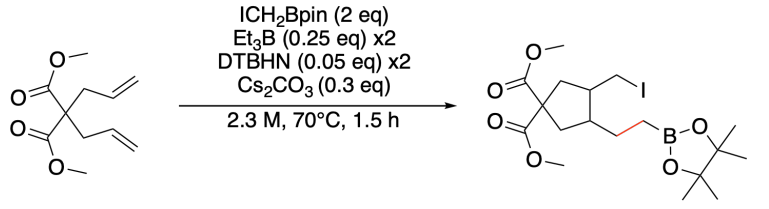
Major diastereomer (Characteristic signals): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.19 (d, J = 1.4 Hz, 2H), 3.720 (s, 3H), 3.716 (s, 3H), 3.26 (dd, J = 9.7, 5.6 Hz, 1H), 3.02 (t, J = 9.9 Hz, 1H), 2.58–2.44 (m, 2H), 2.38 (dd, J = 13.6, 6.8 Hz, 1H), 2.27–2.23 (m, 2H), 2.23–2.15 (m, 1H), 2.09 (dd, J = 13.5, 8.5 Hz, 1H), 2.04–1.95 (m, 1H), 1.53–1.44 (m, 3H), 1.18 (dp, J = 11.0, 1.4 Hz, 1H), 1.08–0.98 (m, 2H), 0.91–0.69 (m, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.2 (Cq), 173.1 (Cq), 83.86 (CH), 83.85 (CH), 58.6 (Cq), 53.0 (2 × CH_3), 45.5 (CH), 45.0 (CH), 41.0 (2 × CH), 40.3 (CH_2), 38.2 (CH_2), 30.8 (CH_2), 23.5 (2 × CH_2), 23.2 (CH_2), 8.0 (CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected.

Minor diastereomer (Characteristic signals):
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.38 (dd, J = 9.9, 3.5 Hz, 1H), 3.10 (dd, J = 9.9, 8.2 Hz, 1H), 2.63

(dd, J = 13.5, 7.4 Hz, 1H), 2.567 (dd, J = 13.8, 7.6 Hz, 1H), 1.89 (dd, J = 13.5, 10.1 Hz, 1H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.0 (Cq), 172.9 (Cq), 84.4 (CH), 83.8 (CH), 57.7 (Cq), 52.91 (CH_3), 52.90 (CH_3), 47.1 (CH), 46.8 (CH), 41.8 (CH_2), 41.0 (2 × CH), 40.5 (CH_2), 27.8 (CH_2), 11.1 (CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected.

Mixture of isomers: ^{11}**B NMR** (128 MHz, $CDCl_3$) 34.0; IR (neat): ν_{max} = 2951, 2875, 1730, 1455, 1434, 1379, 1251, 1061, 1001, 690 cm^{-1}; HRMS (ESI): Calculated for $C_{19}H_{28}BIO_6$ $[M+Na]^+$: 513.1024; found: 513.0908.

Dimethyl 3-(iodomethyl)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentane-1,1-dicarboxylate (Bpin-7a)

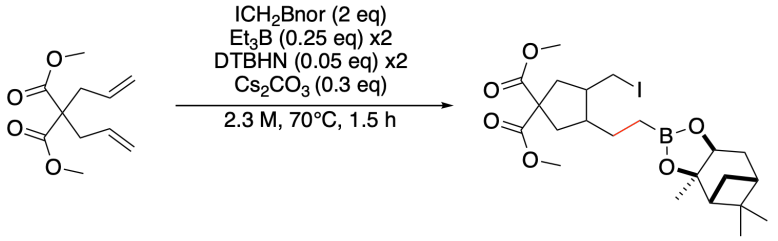


Bpin-7a
Chemical Formula: $C_{18}H_{30}BIO_6$
Exact Mass: 480.1180

Followed **GP1** using **6a** (210 mg, 1 mmol) as radical trap and ICH_2BPin as radical precursor. Purification by flash column chromatography (Gradient 5-10% EtOAc:heptanes) provided the desired **Bpin-7a** (381 mg, 0.794 mmol, 80%, dr = 8:2).

Light yellow oil; Rf: 0.46 (8:2 heptanes:EtOAc); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 3.68 (d, *J* = 1.6 Hz, 6H), 3.38–3.19 (m, 1H), 3.12–2.89 (m, 1H), 2.63–2.39 (m, 2H), 2.34 (dd, *J* = 13.1, 6.4 Hz, 1H), 2.22–2.10 (m, 1H), 2.09–1.80 (m, 1H), 1.74–1.37 (m, 1H), 1.20 (s, 12H), 0.85–0.60 (m, 2H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 173.0 (Cq), 173.0 (Cq), 172.8 (Cq), 83.1 (Cq), 58.4 (Cq), 57.5 (Cq), 52. (CH_3), 47.0 (CH), 46.7 (CH), 45.3 (CH), 44.9 (CH), 41.7 (CH_2), 40.4 (CH_3), 24.9 (CH_3), 24.9 (CH_3), 23.0 (CH_2), 11.1 (CH_2), 8.2 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) 33.9; IR (neat): ν_{max} = 2977, 1731, 1378, 1318, 1251, 1143, 1095, 966, 847, 733 cm^{-1}; HRMS (ESI): Calculated for $C_{18}H_{30}BIO_6$ $[M+H]^+$: 481.1180 ; found: 481.1250.

Dimethyl 3-(iodomethyl)-4-[2-[(1R,2R,6S)-2,9,9-trimethyl-3,5-dioxa-4-boratricyclo[6.1.1.02,6]-decan-4-yl]ethyl]cyclopentane-1,1-dicarboxylate (BPan-7a)

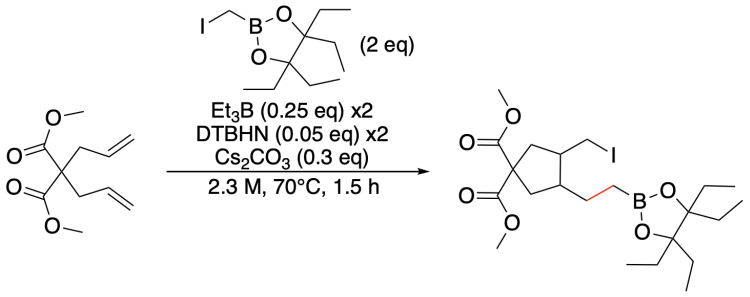


Bpan-7a
Chemical Formula: $C_{22}H_{34}BIO_6$
Exact Mass: 532.1493

Followed **GP1** using **6a** (208 mg, 0.987 mmol) as radical trap and ICH_2BPan as radical precursor. Purification by flash column chromatography (Gradient 5-10% EtOAc:heptanes) provided the desired **BPan-7a** (402 mg, 0.755 mmol, 73%, dr = 4:4:1:1).

Light yellow oil; Rf: 0.44 (8:2 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.22 (dt, J = 8.6, 1.7 Hz, 1H), 3.69 (d, J = 2.0 Hz, 6H), 3.39–3.21 (m, 1H), 3.12–2.94 (m, 1H), 2.66–2.42 (m, 2H), 2.40–2.25 (m, 2H), 2.23–2.13 (m, 2H), 2.11–1.94 (m, 3H), 1.89 (dp, J = 8.7, 2.4 Hz, 1H), 1.80 (ddt, J = 14.6, 3.6, 1.9 Hz, 1H), 1.56–1.46 (m, 1H), 1.35 (s, 3H), 1.24 (d, J = 12.1 Hz, 5H), 1.10–1.00 (m, 1H), 0.92–0.66 (m, 5H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.1 (Cq), 173.0 (Cq), 172.9 (Cq), 172.8 (Cq), 85.6 (Cq), 77.8 (CH), 60.4 (Cq), 58.48 (Cq), 58.47 (Cq), 52.9 (CH_3), 52.8 (CH), 52.8 (CH), 51.4 (CH), 47.1 (CH), 47.1 (CH), 46.8 (CH), 45.4 (CH), 45.4 (CH), 45.0 (CH), 45.0 (CH), 41.7 (CH_2), 40.5 (CH_2), 40.5 (CH_2), 40.4 (CH_2), 40.3 (CH_2), 39.6 (CH), 38.2 (CH_2), 38.1 (CH_2), 35.6 (CH_2), 28.8 (CH_3), 27.8 (CH_3), 27.8 (CH_3), 27.2 (CH_3), 26.6 (CH_2), 24.1 (CH_3), 24.0 (CH_3), 23.3 (CH_2), 23.2 (CH_2), 21.1 (CH_3), 11.1 (CH_2), 8.2 (CH_2), 8.1 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 33.4; IR (neat): ν_{max} = 2917, 2870, 1731, 1434, 1376, 1250, 1197, 1165, 1077, 1030 cm^{-1}; HRMS (ESI): Calculated for $C_{22}H_{34}BIO_6$ $[M+Na]^+$: 555.1391 ; found: 555.1423.

Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate (BEPin-7a)

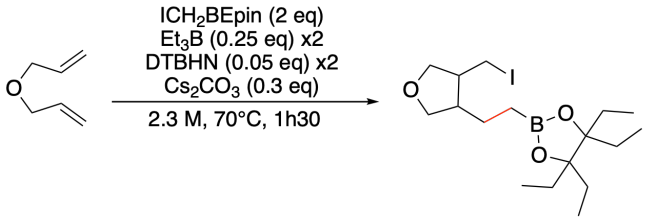


BEpin-7a
Chemical Formula: $C_{22}H_{38}BIO_6$
Exact Mass: 536.1806

Followed **GP1** using **6a** (215 mg, 1.01 mmol) as radical trap and ICH_2BEPin as radical precursor. Purification by flash column chromatography (Gradient 5-10% EtOAc:heptanes) provided the desired **BEpin-7a** (470 mg, 0.876 mmol, 87%, dr = 8:2).

Light yellow oil; Rf: 0.46 (8:2 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.74–3.61 (m, 6H), 3.24 (dd, *J* = 9.6, 5.3 Hz, 1H), 3.09–2.92 (m, 1H), 2.62–2.41 (m, 2H), 2.39–2.28 (m, 1H), 2.24–2.12 (m, 1H), 2.09–1.89 (m, 2H), 1.86 (dd, *J* = 13.4, 10.1 Hz, 1H), 1.60 (qd, *J* = 7.5, 4.5 Hz, 8H), 1.51–1.43 (m, 1H), 1.29–1.14 (m, 1H), 0.86 (t, *J* = 7.5 Hz, 15H), 0.82–0.75 (m, 1H), 0.72–0.64 (m, 1H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.1 (Cq), 173.0 (Cq), 88.1 (Cq), 88.0 (Cq), 58.4 (Cq), 57.6 (Cq), 52.8 (Cq), 52.8 (2 x CH_3), 47.0 (CH), 46.9 (CH), 45.3 (CH), 44.9 (CH), 41.8 (CH_2), 40.5 (CH_2), 40.4 (CH_2), 38.2 (CH_2), 27.8 (CH_2), 26.5 (CH_2), 26.4 (CH_2), 23.2 (CH_2), 11.1 (CH_2), 8.9(CH_3), 8.8 (CH_3), 8.2 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 30.9; IR (neat): ν_{max} = 2973, 2948, 2883, 1732, 1384, 1349, 1250, 1161, 927, 854 cm^{-1}; HRMS (ESI): Calculated for $C_{22}H_{38}BIO_6$ $[M+H]^+$: 537.1806; found: 537.1879.

4,4,5,5-tetraethyl-2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-1,3,2-dioxaborolane (BEpin-7b)



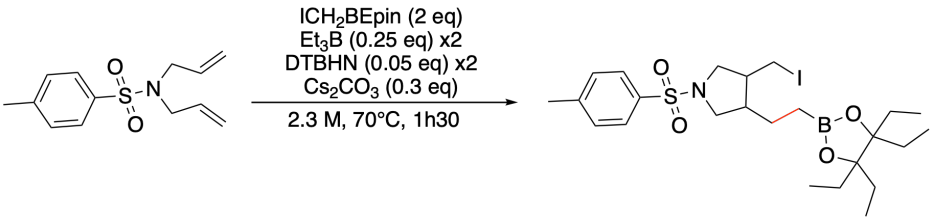
7b
Chemical Formula: $C_{17}H_{32}BIO_3$
Exact Mass: 422.1489

Followed **GP1** using commercial diallyl ether (101 mg, 1.03 mmol) as radical trap and ICH_2BEPin as radical precursor. Purification by flash column chromatography (10% EtOAc:heptanes) pro-

vided the desired **BEpin-7b** (63 mg, 0.149 mmol, 14%, dr = 6:4).

Light yellow oil; Rf: 0.55 (8:2 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.07–3.89 (m, 2H), 3.71 (dd, *J* = 8.8, 5.0 Hz, 1H), 3.59–3.42 (m, 1H), 3.30 (ddt, *J* = 9.7, 5.1, 1.1 Hz, 1H), 3.17–3.02 (m, 1H), 2.68 (dtt, *J* = 11.4, 6.6, 4.9 Hz, 1H), 2.22 (dddd, *J* = 14.5, 9.6, 7.1, 5.8 Hz, 1H), 1.89–1.78 (m, 1H), 1.76–1.50 (m, 9H), 1.50–1.31 (m, 1H), 0.90 (t, *J* = 7.5 Hz, 12H), 0.85–0.69 (m, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 88.4 (Cq), 88.3 (Cq), 74.7 (CH_2), 74.4 (CH_2), 74.1 (CH_2), 72.3 (CH_2), 48.7 (CH), 48.1 (CH), 45.7 (CH), 45.7 (CH), 27.6 (CH_2), 26.5 (CH_2), 21.4 (CH_2), 9.3 (CH_2), 9.0 (CH_3), 5.4 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 33.1; IR (neat): ν_{max} = 2972, 2933, 2882, 2860, 1372, 1349, 1112, 1044, 918, 730 cm^{-1}; HRMS (ESI): Calculated for $C_{17}H_{33}BIO_3$ $[M+H]^+$: 423.1489; found: 423.1562.

3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine (BEpin-7c)

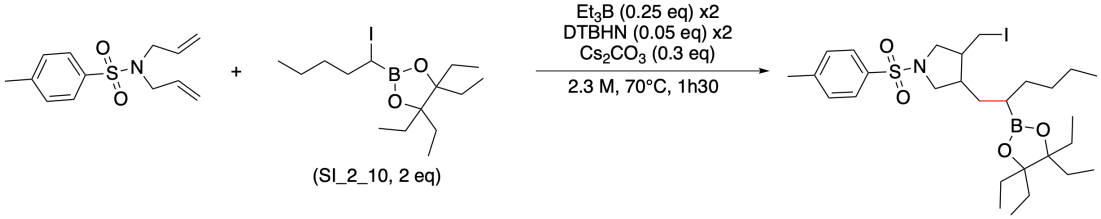


BEPin-7c
Chemical Formula: $C_{24}H_{39}BINO_4S$
Exact Mass: 575.1738

Followed **GP1** using **6c** (259 mg, 1.03 mmol) as radical trap and ICH_2BEPin as radical precursor. Purification by flash column chromatography (10% EtOAc:heptanes) provided the desired **BEpin-7c** (257 mg, 0.447 mmol, 44%, dr = 7:3).

Yellow thick oil; Rf: 0.55 (8:2 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.76–7.66 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.59–3.29 (m, 3H), 3.22–3.08 (m, 1H), 3.07–2.82 (m, 2H), 2.57 (dd, *J* = 11.2, 9.6 Hz, 1H), 2.52–2.39 (m, 4H), 2.07 (dddd, *J* = 13.5, 9.3, 7.6, 6.0 Hz, 1H), 1.93 (dddd, *J* = 10.8, 7.7, 4.6, 2.3 Hz, 1H), 1.80–1.70 (m, 1H), 1.70–1.50 (m, 8H), 1.40 (ddt, *J* = 13.1, 9.5, 6.4 Hz, 1H), 1.20 (qdd, *J* = 15.5, 7.9, 4.6 Hz, 1H), 0.88 (td, *J* = 7.5, 1.3 Hz, 12H), 0.79–0.59 (m, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 143.6 (Cq_{Ar}), 134.0 (Cq_{Ar}), 129.9 (2 x CH_{Ar}), 127.8 (CH_{Ar}), 127.6 (CH_{Ar}), 88.4 (Cq), 54.6 (CH_2), 53.6 (CH_2), 51.1 (CH_2), 49.5 (CH_2), 46.7 (CH), 46.4 (CH), 45.0 (CH), 44.7 (CH), 26.9 (CH_2), 26.5 (CH_2), 21.72 (CH_2), 21.67 (CH_3), 8.9 (CH_3), 7.4 (CH_2), 4.3 (CH_2); ^{11}**B NMR** (128 MHz, $CDCl_3$) 33.2. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; IR (neat): ν_{max} = 2977, 2939, 2881, 1344, 1157, 924, 661, 585, 546 cm^{-1}; HRMS (ESI): Calculated for $C_{24}H_{39}BINO_4S$ $[M+H]^+$: 576.1738; found: 576.1810.

3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine (BEpin-7c1)

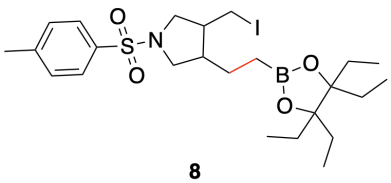


BEpin-7c1
Chemical Formula: $C_{28}H_{47}BINO_4S$
Exact Mass: 631.2364

Followed **GP1** using **6c** (250 mg, 0.995 mmol) as radical trap and **SI_2_10** as radical precursor. Purification by flash column chromatography (5% EtOAc:heptanes) provided the desired **BEpin-7c1** (226 mg, 0.358 mmol, 36%, dr = 39:21:21:19).

Yellow thick oil; Rf: 0.45 (9:1 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.72 (td, *J* = 8.2, 1.6 Hz, 2H), 7.37–7.29 (m, 2H), 3.61–3.42 (m, 1H), 3.37 (ddd, *J* = 9.9, 7.2, 2.4 Hz, 1H), 3.28–3.19 (m, 1H), 3.14–2.64 (m, 3H), 2.51–2.40 (m, 4H), 2.13 (tt, *J* = 6.7, 4.3 Hz, 1H), 1.93–1.74 (m, 1H), 1.60 (dtt, *J* = 13.5, 8.4, 2.7 Hz, 8H), 1.46–1.12 (m, 8H), 0.99–0.74 (m, 17H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 143.6 (Cq_{Ar}), 143.6 (Cq_{Ar}), 143.5 (Cq_{Ar}), 143.5 (Cq_{Ar}), 134.1 (Cq_{Ar}), 134.0 (Cq_{Ar}), 133.7 (Cq_{Ar}), 133.5 (Cq_{Ar}), 129.9 (4 x CH_{Ar}), 127.8 (2 x CH_{Ar}), 127.6 (2 x CH_{Ar}), 88.4 (Cq), 54.5 (CH_2), 54.0 (CH_2), 53.6 (CH_2), 53.3 (CH_2), 51.5 (CH_2), 51.3 (CH_2), 47.1 (CH), 46.6 (CH), 45.6 (CH), 44.7 (CH), 42.1 (CH), 41.9 (CH), 31.9 (CH_2), 31.3 (CH_2), 31.3 (CH_2), 31.2 (CH_2), 31.2 (CH_2), 31.1 (CH_2), 30.6 (CH_2), 29.1 (CH_2), 28.8 (CH_2), 26.2 (CH_2), 26.2 (CH_2), 26.2 (CH_2), 26.2 (CH_2), 23.2 (CH_2), 23.1 (CH_2), 23.1 (CH_2), 21.7 (CH_3), 21.7 (CH_3), 14.2 (CH_3), 14.2 (CH_3), 8.9 (CH_3), 8.9 (CH_3), 8.9 (CH_3), 8.8 (CH_3), 8.8 (CH_3), 8.8 (CH_3), 7.7 (CH_2), 6.9 (CH_2), 4.7 (CH_2), 4.1 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 32.2; IR (neat): ν_{max} = 2924, 2882, 2856, 1346, 1160, 921, 813, 661, 586, 546 cm^{-1}; HRMS (ESI): Calculated for $C_{28}H_{47}BINO_4S$ $[M+Na]^+$: 654.2364; found: 654.2229.

3-(2-iodoethyl)-4-(iodomethyl)-1-(p-tolylsulfonyl)pyrrolidine (8)

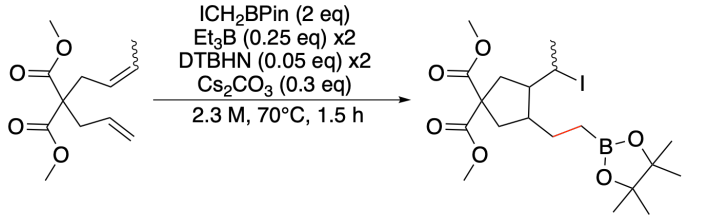


8
Chemical Formula: $C_{24}H_{39}BINO_4S$
Exact Mass: 575.1738

Light yellow oil; Rf: 0.72 (1:1 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.72 (ddd, J =

8.3, 4.5, 2.0 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 3.56–3.31 (m, 2H), 3.22–3.06 (m, 3H), 3.04–2.88 (m, 3H), 2.74 (t, J = 9.9 Hz, 1H), 2.59–2.48 (m, 1H), 2.44 (s, 3H), 2.26 (dtd, J = 16.9, 6.2, 4.7 Hz, 1H), 2.06–1.89 (m, 1H), 1.86–1.75 (m, 1H), 1.65 (ttd, J = 13.3, 5.3, 2.2 Hz, 1H), 1.50–1.40 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0 (Cq_{Ar}), 143.9 (Cq_{Ar}), 133.7 (Cq_{Ar}), 132.3 (Cq_{Ar}), 130.0 (CH_{Ar}), 128.7 (CH_{Ar}), 127.7 (CH_{Ar}), 127.5 (CH_{Ar}), 54.1 (CH_2), 52.8 (CH_2), 52.5 (CH_2), 50.4 (CH_2), 45.9 (CH), 45.2 (CH), 44.6 (CH), 42.9 (CH), 36.4 (CH_2), 30.6 (CH_2), 21.7 (CH_3), 6.6 (CH_2), 2.7 (2 x CH_2), 2.5 (CH_2); IR (neat): ν_{max} = 2923, 1596, 1339, 1154, 1090, 812, 729, 660, 584, 546 cm^{-1}; HRMS (ESI): Calculated for $C_{14}H_{19}I_2NO_2S$ $[M+H]^+$: 519.9226; found: 519.9314.

Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate (7da)

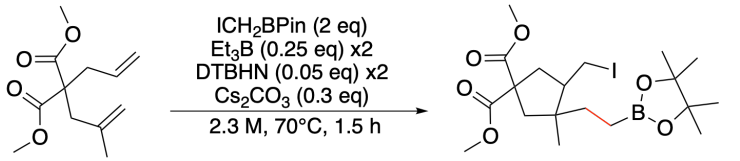


7da
Chemical Formula: $C_{19}H_{32}BIO_6$
Exact Mass: 494.1337

Followed **GP1** using **6d** (228 mg, 1.01 mmol) as radical trap and ICH_2BPin as radical precursor. Purification by flash column chromatography (10% EtOAc:heptanes) provided the desired **7da** (250 mg, 0.506 mmol, 50%, dr = 37:37:16:8 - 5% contaminated by radical precursor).

Yellow thick oil; Rf: 0.38 (8:2 heptanes:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.51–3.98 (m, 1H), 3.77–3.66 (m, 6H), 2.63 (td, *J* = 12.8, 7.2 Hz, 1H), 2.57–2.39 (m, 1H), 2.39–2.23 (m, 1H), 2.21–2.12 (m, 1H), 2.11–2.00 (m, 1H), 1.99–1.80 (m, 3H), 1.79–1.51 (m, 1H), 1.38 (dtd, *J* = 11.8, 8.3, 3.1 Hz, 1H), 1.31–1.16 (m, 13H), 1.13–0.57 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.7 (Cq), 173.4 (Cq), 173.3 (Cq), 173.2 (Cq), 173.2 (Cq), 173.0 (Cq), 172.9 (Cq), 172.8 (Cq), 172.5 (Cq), 172.3 (Cq), 171.8 (Cq), 84.3 (Cq), 84.0 (Cq), 83.2 (Cq), 83.1 (Cq), 83.1 (Cq), 83.0 (Cq), 65.9 (Cq), 59.6 (Cq), 58.9 (Cq), 57.8 (Cq), 57.7 (Cq), 57.5 (Cq), 57.4 (Cq), 55.1 (CH), 54.3 (CH), 53.9 (CH), 53.6 (CH), 53.0 (CH_3), 52.9 (CH_3), 52.9 (CH_3), 52.8 (CH_3), 52.8 (CH_3), 52.8 (CH_3), 52.6 (CH_3), 52.5 (CH_3), 47.6 (CH), 46.2 (CH), 44.1 (CH), 42.0 (CH_2), 41.9 (CH), 40.1 (CH_2), 39.5 (CH_2), 38.7 (CH_2), 38.2 (CH_2), 38.1 (CH_2), 36.8 (CH_2), 36.4 (CH_2), 35.5 (CH_2), 30.5 (CH_2), 30.0 (CH), 29.0 (CH), 28.4 (CH), 28.4 (CH), 28.2 (CH), 28.2 (CH), 27.5 (CH_2), 25.1 (CH_3), 25.0 (CH_3), 25.0 (CH_3), 25.0 (CH_3), 24.9 (CH_3), 24.9 (CH_3), 23.5 (CH_2), 20.8 (CH_2), 20.3 (CH_2) (CH_2), 16.9 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) 33.8; IR (neat): ν_{max} = 2977, 2951, 1732, 1371, 1315, 1249, 966, 846, 732 cm^{-1}; HRMS (ESI): Calculated for $C_{19}H_{33}BIO_4$ $[M+Na]^+$: 517.1337; found: 517.1223.

Dimethyl 4-(iodomethyl)-3-methyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-cyclopentane-1,1-dicarboxylate (7fa)

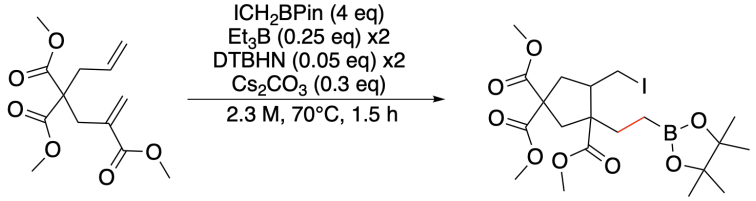


7fa
Chemical Formula: $C_{19}H_{32}BIO_6$
Exact Mass: 494.1337

Followed **GP2** using **6f** (224 mg, 0.990 mmol) as radical trap. Purification by flash column chromatography (10% EtOAc:heptane) provided the desired **7fa** (430 mg, 0.870 mmol, 88%, dr = 8:2 (presence of two regioisomer).

Colorless oil; Rf: 0.41 (8:2 heptanes:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.75–3.65 (m, 6H), 3.32–3.10 (m, 1H), 3.04–2.69 (m, 1H), 2.58–2.37 (m, 1H), 2.33–2.06 (m, 3H), 2.01 (d, J = 14.1 Hz, 1H), 1.67–1.47 (m, 1H), 1.34 (d, J = 5.2 Hz, 1H), 1.28–1.15 (m, 12H), 1.14–0.62 (m, 5H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.3 (Cq), 173.3 (Cq), 173.2 (Cq), 173.1 (Cq), 173.0 (Cq), 83.3 (Cq), 83.2 (Cq), 83.2 (Cq), 57.1 (Cq), 56.8 (Cq), 56.1 (Cq), 53.7 (Cq), 53.6 (Cq), 53.0 (2 x CH), 51.5 (CH_3), 50.6 (CH_3), 47.6 (CH_2), 47.1 (CH_2), 46.1 (Cq), 46.0 (Cq), 45.5 (Cq), 44.9 (CH_2), 41.0 (CH_2), 40.4 (CH_2), 38.5 (CH_2), 35.2 (CH_2), 27.4 (CH_2), 27.3 (CH_3), 25.0 (CH_3), 24.9 (CH_3),23.2 (CH_2), 19.8 (CH_2), 19.0 (CH_3), 6.5 (CH_2), 5.9 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) 34.3; IR (neat): ν_{max} = 2976, 2952, 1731, 1371, 1254, 1199, 1142, 967, 847 cm^{-1}; HRMS (ESI): Calculated for $C_{19}H_{32}BIO_6$ $[M+H]^+$: 495.1337; found: 495.1409.

Trimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1,3-tricarboxylate (7ga)

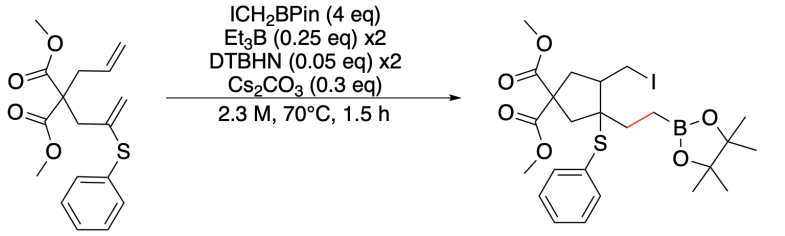


7ga
Chemical Formula: $C_{20}H_{32}BIO_8$
Exact Mass: 538.1235

Followed **GP2** using **6g** (276 mg, 1.02 mmol) as radical trap. Purification by flash column chromatography (10% EtOAc:heptanes) provided the desired **7ga** (312 mg, 0.580 mmol, 56%, dr = 6:4 - 15% contaminated by radical precursor).

Colorless oil; Rf: 0.29 (8:2 heptanes:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.77–3.59 (m, 9H), 3.41 (dd, *J* = 9.8, 3.0 Hz, 1H), 3.07–2.89 (m, 1H), 2.87–2.74 (m, 1H), 2.52 (d, *J* = 14.6 Hz, 1H), 2.42–2.20 (m, 2H), 2.17–2.04 (m, 1H), 1.62 (dd, *J* = 14.0, 4.3 Hz, 1H), 1.49–1.35 (m, 1H), 1.22 (d, *J* = 5.5 Hz, 12H), 1.00–0.80 (m, 1H), 0.69 (dddd, *J* = 22.7, 17.4, 12.5, 4.8 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.3 (Cq), 174.3 (Cq), 173.3 (Cq), 172.5 (Cq), 172.3 (Cq), 172.2 (Cq), 83.4 (Cq), 83.3 (Cq), 58.4 (Cq), 57.2 (Cq), 56.9 (Cq), 56.7 (Cq), 53.2 (CH_3), 53.1 (CH_3), 53.0 (CH_3), 52.3 (CH_3), 52.1 (CH_3), 51.9 (CH_3), 49.3 (CH_3), 42.5 (CH_2), 40.8 (CH_2), 40.7 (CH_2), 40.4 (CH_2), 35.5 (CH_2), 32.0 (CH_2), 31.7 (CH_2), 26.6 (CH_2), 26.4 (CH_2), 26.2 (CH_2), 25.0 (CH_3), 6.1 (CH_2), 5.0 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) 34.2; IR (neat): ν_{max} = 2977, 2951, 1731, 1372, 1324, 1256, 1142, 967, 846, 736 cm^{-1}; HRMS (ESI): Calculated for $C_{20}H_{33}BIO_8$ $[M+H]^+$: 539.1235; found: 539.1311.

Dimethyl 4-(iodomethyl)-3-phenylsulfanyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate (7ha)



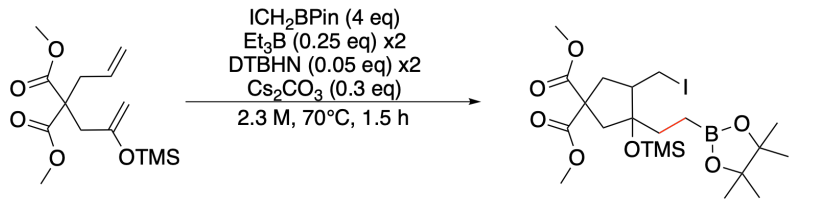
7ha
Chemical Formula: $C_{24}H_{34}BIO_6S$
Exact Mass: 588.1214

Followed **GP2** using **6h** (328 mg, 1.02 mmol) as radical trap. Purification by flash column chromatography (20% Et_2O:pentane) provided the desired **7ha** (295 mg, 0.501 mmol, 49%, dr = 9:1).

Light yellow oil; Rf: 0.29 (8:2 pentane:Et_2O); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52–7.27 (m, 5H), 3.75–3.58 (m, 6H), 3.51–3.33 (m, 1H), 3.00–2.79 (m, 2H), 2.72–2.53 (m, 1H), 2.46–2.30 (m, 2H), 2.17 (dd, *J* = 13.9, 9.4 Hz, 1H), 1.61–1.41 (m, 2H), 1.23 (d, *J* = 5.8 Hz, 12H), 1.19–0.88 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.6 (Cq), 172.1 (Cq), 172.1 (Cq), 137.6 (2 x CH_{Ar}), 130.7 (Cq_{Ar}), 129.4 (CH_{Ar}), 129.0 (2 x CH_{Ar}), 83.2 (Cq), 63.2 (Cq), 56.2 (Cq), 53.1 (CH_3), 52.9 (CH_3), 51.0 (CH), 42.4 (CH_2), 38.9 (CH_2), 26.9 (CH_2), 24.9 (CH_3), 24.8 (CH_3), 5.7 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) 34.0; IR (neat): ν_{max} = 2976, 2950, 1733, 1370, 1320, 1252, 1143, 847, 750, 694 cm^{-1}; HRMS (ESI): Calculated for $C_{24}H_{34}BIO_6S$ $[M+Na]^+$: 611.1214; found: 611.1091.

Dimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-3-trimethyl-

silyloxy-cyclopentane-1,1-dicarboxylate (7ia)

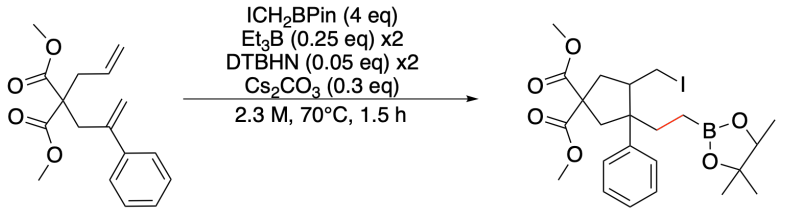


7ia
Chemical Formula: $C_{21}H_{38}BIO_7Si$
Exact Mass: 568.1525

Followed **GP2** using **6i** (223 mg, 0.742 mmol) as radical trap. Purification by flash column chromatography (15% EtOAc:heptane) provided the desired **7ia** (178 mg, 0.232 mmol, 31%, dr = 8:2).

Light yellow oil; Rf: 0.36 (8:2 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, d-Acetone) δ 3.63–3.51 (m, 6H), 3.41–3.20 (m, 1H), 2.98–2.71 (m, 1H), 2.53–2.25 (m, 3H), 1.92 (d, J = 21.3 Hz, 2H), 1.70–1.30 (m, 2H), 1.10 (d, J = 1.7 Hz, 12H), 0.82–0.51 (m, 2H), 0.12—0.06 (m, 9H); ^{13}**C NMR** (101 MHz, d-Acetone) δ 173.5 (Cq), 173.3 (Cq), 173.2 (Cq), 173.0 (Cq), 86.8 (Cq), 84.6 (Cq), 84.1 (Cq), 83.9 (Cq), 83.8 (Cq), 57.2 (Cq), 56.9 (Cq), 55.0 (CH), 53.4 (CH), 53.4, 53.3 (CH_3), 51.4 (CH_3), 48.0 (CH_2), 45.4 (CH_2), 39.7 (CH_2), 37.4 (CH_2), 30.1 (CH_2), 25.5 (CH_3) 8.0 (CH_2), 2.7 (CH_3), 2.6 (CH_3), 2.4 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, d-Acetone) 34.0; IR (neat): ν_{max} = 2977, 2952, 1733, 1372, 1321, 1250, 1143, 967, 869, 753 cm^{-1}; HRMS (ESI): Calculated for $C_{21}H_{38}BIO_7Si$ $[M+Na]^+$: 591.1525; found: 591.1417.

Dimethyl 4-(iodomethyl)-3-phenyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-cyclopentane-1,1-dicarboxylate (7ja)



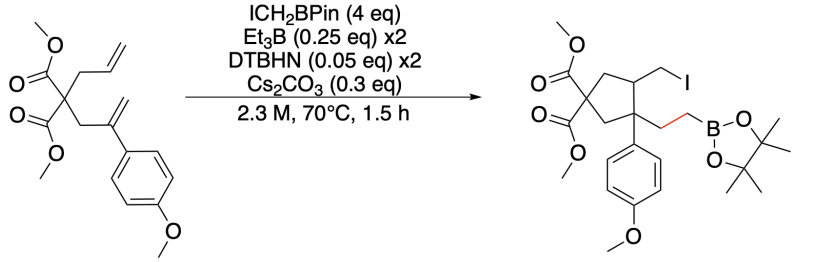
7ja
Chemical Formula: $C_{23}H_{32}BIO_6$
Exact Mass: 542.1337

Followed **GP2** using **6j** (286 mg, 0.992 mmol) as radical trap. Purification by flash column chromatography (15% EtOAc:heptanes) provided the desired **7ja** (337 mg, 0.606 mmol, 61%, dr = 6:4).

White opaque oil; Rf: 0.45 (8:2 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, CD_2Cl_2) δ 1H NMR 7.37–7.27 (m, 3H), 7.27–7.12 (m, 2H), 3.81–3.64 (m, 6H), 3.45–2.91 (m, 2H), 2.90–2.72 (m,

2H), 2.68–2.51 (m, 1H), 2.41–2.29 (m, 1H), 1.90 (td, J = 13.4, 4.3 Hz, 1H), 1.66–1.46 (m, 1H), 1.19 (dd, J = 10.9, 2.2 Hz, 12H), 0.61–0.13 (m, 2H); **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 173.1 (Cq), 172.8 (Cq), 172.7 (Cq), 172.6 (Cq), 144.3 (Cq_{Ar}), 142.5 (Cq_{Ar}), 128.4 (2 x CH_{Ar}), 127.7 (CH_{Ar}), 126.6 (CH_{Ar}), 126.2 (CH_{Ar}), 83.0 (Cq), 82.9 (Cq), 57.5 (Cq), 56.8 (Cq), 56.0 (Cq), 54.3 (Cq), 54.0 (Cq), 53.73 (Cq), 53.66 (CH), 53.45 (Cq), 53.19 (Cq), 53.15 (CH), 53.0 (CH_3), 52.94 (CH_3), 52.92 (CH_3), 52.89 (CH_3), 52.8 (CH_3), 43.5 (CH_2), 40.1 (CH_2), 40.0 (CH_2), 38.9 (CH_2), 34.9 (CH_2), 26.9 (CH_2), 24.7 (CH_3), 24.7 (CH_3), 24.6 (CH_3), 10.1 (CH_2), 7.0 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; **^{11}B NMR** (128 MHz, CD_2Cl_2) 34.0; IR (neat): ν_{max} = 2977, 2950, 2928, 1731, 1370, 1257, 1142, 967, 847, 701 cm^{-1}; HRMS (ESI): Calculated for $C_{24}H_{34}BIO_6$ $[M+H]^+$: 557.1493; found: 557.1561.

Dimethyl 4-(iodomethyl)-3-(4-methoxyphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate (7ka)

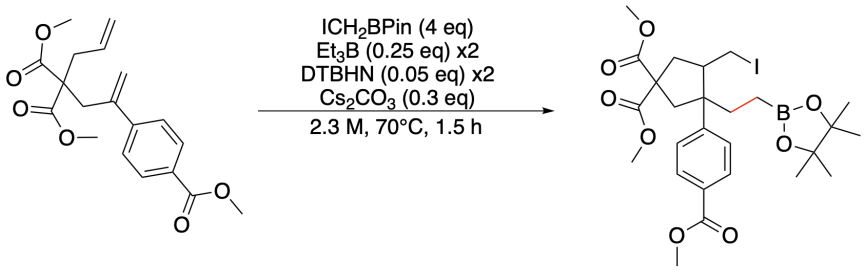


7ka
Chemical Formula: $C_{25}H_{36}BIO_7$
Exact Mass: 586.1599

Followed **GP2** using **6k** (173 mg, 0.543 mmol) as radical trap. Purification by flash column chromatography (20% Et_2O:pentane) provided the desired **7ka** (216 mg, 0.328 mmol, 56%, dr = 1:1 - 11% contaminated by radical precursor).

Light orange opaque oil; Rf: 0.45 (8:2 pentane:Et_2O); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23–7.16 (m, 1H), 7.09–7.01 (m, 1H), 6.87–6.77 (m, 2H), 3.81–3.60 (m, 9H), 3.41–2.90 (m, 2H), 2.89–2.66 (m, 3H), 2.61-2.57 (m, 1H), 2.55–2.48 (m, 1H), 2.40–2.23 (m, 1H), 1.96–1.77 (m, 1H), 1.66–1.44 (m, 1H), 1.19 (dd, J = 7.4, 2.1 Hz, 12H), 0.64–0.20 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4 (Cq), 173.1 (Cq), 173.1 (Cq), 173.0 (Cq), 158.0 (Cq), 136.0 (Cq_{Ar}), 134.2 (Cq_{Ar}), 128.8 (CH_{Ar}), 127.7 (CH_{Ar}), 113.8 (2 x CH_{Ar}), 83.2 (Cq), 83.1 (Cq), 57.5 (Cq), 57.0 (Cq), 55.3 (CH_3), 53.89 (Cq), 53.78 (CH), 53.55 (Cq), 53.4 (CH), 53.2 (CH_3), 53.1 (CH_3), 53.1 (CH_3), 53.1 (CH_3), 43.6 (CH_2), 40.9 (CH_2), 40.2 (CH_2), 39.4 (CH_2), 35.0 (CH_2), 29.8 (CH_2), 27.1 (CH_2), 25.0 (CH_3), 24.9 (CH_3), 10.1 (CH_2), 7.4 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) 33.9; IR (neat): ν_{max} = 2977, 2951, 2930, 1731, 1371, 1324, 1251, 1142, 830, 736 cm^{-1}; HRMS (ESI): Calculated for $C_{25}H_{36}BIO_7$ $[M+H]^+$: 586.1599; found: 587.1670.

Dimethyl 4-(iodomethyl)-3-(4-methoxycarbonylphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate (7la)

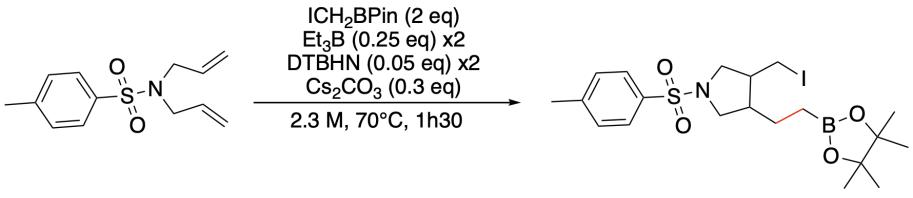


9j
Chemical Formula: $C_{26}H_{36}BIO_8$
Exact Mass: 614.1548

Followed **GP2** using **6l** (164 mg, 0.473 mmol) as radical trap. Purification by flash column chromatography (30% Et_2O:pentane) provided the desired **7la** (143 mg, 0.163 mmol, 56%, dr = 6:4 - 30% contaminated by radical precursor).

Light orange opaque oil; Rf: 0.33 (7:3 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.00–7.91 (m, 2H), 7.37-7.32 (m, 1H), 7.31–7.17 (m, 1H), 3.88 (d, *J* = 0.9 Hz, 3H), 3.78–3.63 (m, 6H), 3.40–2.94 (m, 2H), 2.91–2.70 (m, 2H), 2.61 (dqd, *J* = 14.8, 6.8, 4.6 Hz, 3H), 2.54–2.30 (m, 1H), 1.89 (td, *J* = 12.9, 3.9 Hz, 1H), 1.68–1.45 (m, 1H), 1.17 (dd, *J* = 10.7, 2.3 Hz, 12H), 0.61–0.08 (m, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.2 (Cq), 172.9 (Cq), 172.8 (Cq), 172.7 (Cq), 166.9 (Cq), 149.8 (Cq_{Ar}), 148.0 (Cq_{Ar}), 129.8 (CH_{Ar}), 128.3 (CH_{Ar}), 127.8 (CH_{Ar}), 126.7 (CH_{Ar}), 83.2 (Cq), 83.1 (Cq), 57.4 (Cq), 56.9 (Cq), 56.4 (Cq), 54.7 (Cq), 53.30 (CH), 53.12 (CH_3), 52.93 (CH), 52.93 (CH_3), 52.01 (CH_3), 43.5 (CH_2), 40.2 (CH_2), 40.0 (CH_2), 39.1 (CH_2), 34.8 (CH_2), 27.2 (CH_2), 24.94 (CH_3), 24.86 (CH_3), 9.2 (CH_2), 6.4 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 33.6; IR (neat): ν_{max} = 2977, 1720, 1371, 1322, 1272, 1254, 1141, 1108, 967, 846 cm^{-1}; HRMS (ESI): Calculated for $C_{26}H_{36}BIO_8$ $[M+H]^+$: 615.1548; found: 615.1632.

3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine (7ca)



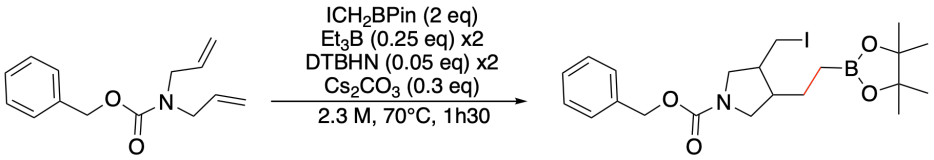
7ca
Chemical Formula: $C_{20}H_{31}BINO_4S$
Exact Mass: 519.1112

Followed **GP1** using **6c** (252 mg, 1 mmol) as radical trap and ICH_2BPin as radical precursor. Purification by flash column chromatography (10% EtOAc:heptane) provided the desired **7ca**

(357 mg, 0.620 mmol, 62%, dr = 6:4).

Light yellow sticky oil; Rf: 0.49 (7:3 heptanes:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (t, J = 8.6 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 3.58–3.40 (m, 1H), 3.40–3.29 (m, 1H), 3.22–3.08 (m, 1H), 3.07–2.81 (m, 2H), 2.56 (dd, J = 11.2, 9.5 Hz, 1H), 2.48 (ddd, J = 10.9, 6.0, 4.4 Hz, 1H), 2.43 (d, J = 2.1 Hz, 3H), 2.09–1.99 (m, 1H), 1.95–1.66 (m, 1H), 1.57–1.35 (m, 1H), 1.22 (s, 12H), 0.77–0.61 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7 (Cq_{Ar}), 143.6 (Cq_{Ar}), 134.0 (Cq_{Ar}), 133.5 (Cq_{Ar}), 129.9 (CH_{Ar}), 129.8 (CH_{Ar}), 127.8 (CH_{Ar}), 127.6 (CH_{Ar}), 83.4 (2 x Cq), 54.6 (CH_2), 53.6 (CH_2), 53.5 (CH_2), 51.1 (CH_2), 46.7 (CH), 46.3 (CH), 45.0 (CH), 44.7 (CH), 26.7 (CH_2), 25.0 (CH_3), 21.7 (CH_3), 21.5 (CH_2), 7.4 (CH_2), 4.3 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) 33.5; IR (neat): ν_{max} = 2976, 2929, 2880, 1341, 1158, 1142, 966, 813, 661, 546 cm^{-1}; HRMS (ESI): Calculated for $C_{20}H_{31}BINO_4S$ $[M+H]^+$: 520.1112; found: 520.1179.

Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine-1-carboxylate (7ma)

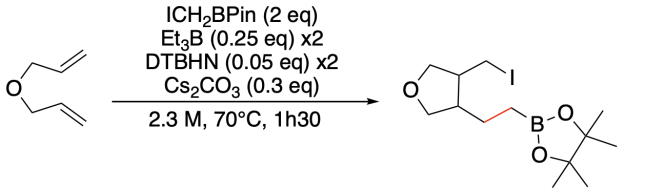


7ma
Chemical Formula: $C_{21}H_{31}BINO_4$
Exact Mass: 499.1391

Followed **GP1** using **6m** (231 mg, 1 mmol) as radical trap and ICH_2BPin as radical precursor. Purification by flash column chromatography (20% EtOAc:heptane) provided the desired **7ma** (338 mg, 0.677 mmol, 68% (80% brsm), dr = 6:4).

Light yellow oil; Rf: 0.31 (8:2 heptanes:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41–7.25 (m, 5H), 5.20–5.04 (m, 2H), 3.83–3.67 (m, 1H), 3.61–3.39 (m, 2H), 3.37–2.99 (m, 3H), 2.62 (dt, J = 10.8, 5.3 Hz, 1H), 2.15 (dq, J = 11.6, 6.3 Hz, 1H), 2.05–1.79 (m, 1H), 1.74–1.46 (m, 1H), 1.41–1.15 (m, 14H), 0.93–0.68 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.8 (Cq_{Ar}), 137.0 (Cq_{Ar}), 137.0 (Cq_{Ar}), 128.6 (CH_{Ar}), 128.1 (CH_{Ar}), 128.0 (CH_{Ar}), 128.0 (CH_{Ar}), 128.0 (CH_{Ar}), 83.3 (2 x Cq), 66.9 (CH_2), 53.3 (CH_2), 52.9 (CH_2), 52.0 (CH_2), 51.8 (CH_2), 51.6 (CH_2), 49.7 (CH), 49.4 (CH), 46.6 (CH), 46.2 (CH), 45.8 (CH), 45.3 (CH), 45.0 (CH), 44.7 (CH), 44.4 (CH), 44.0 (CH), 26.3 (CH_2), 25.0 (CH_3), 7.6 (CH_2), 7.4 (CH_2), 4.9 (CH_2), 4.6 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) 33.8; IR (neat): ν_{max} = 2976, 2932, 2872, 1699, 1414, 1358, 1319, 1142, 1109, 966, 696 cm^{-1}; HRMS (ESI): Calculated for $C_{21}H_{31}BINO_4$ $[M+H]^+$: 500.1391; found: 500.1454.

2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7ba)

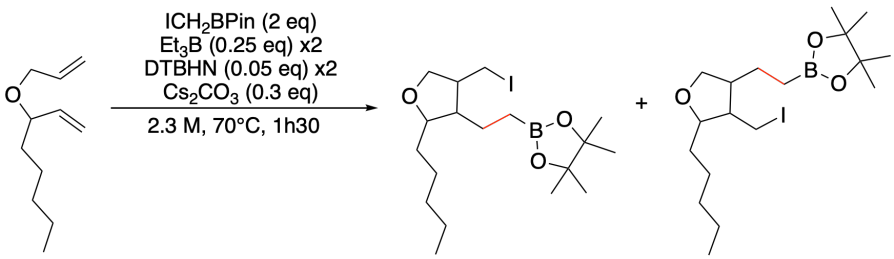


7ba
Chemical Formula: $C_{13}H_{24}BIO_3$
Exact Mass: 366.0863

Followed **GP1** using commercial dially ether (97 mg, 0.988 mmol) as radical trap and ICH_2BPin as radical precursor. Purification by flash column chromatography (10% EtOAc:heptane) provided the desired **7ba** (92 mg, 0.251 mmol, 25%, dr = 6:4 - 30% contaminated by radical precursor).

Light yellow oil; Rf: 0.41 (8:2 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.07–3.90 (m, 2H), 3.73–3.43 (m, 2H), 3.35–3.25 (m, 1H), 3.17–3.03 (m, 1H), 2.68 (dtt, J = 11.4, 6.5, 4.9 Hz, 1H), 2.25–2.14 (m, 2H), 1.83 (dddd, J = 13.0, 8.6, 7.1, 5.9 Hz, 1H), 1.68-1.50 (m, 1H), 1.50–1.33 (m, 1H), 1.30–1.22 (m, 12H), 0.87–0.68 (m, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 83.3 (Cq), 83.3 (Cq), 74.6 (CH_2), 74.3 (CH_2), 74.1 (CH_2), 72.2 (CH_2), 48.7 (CH), 48.1 (CH), 45.7 (CH), 45.7 (CH), 27.4 (CH_2), 25.0 (CH_3), 25.0 (CH_3), 21.2 (CH_2), 9.3 (CH_2), 5.4 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 33.6.

2-[2-[4-(iodomethyl)-2-pentyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7na) and 2-[2-[4-(iodomethyl)-5-pentyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7na')



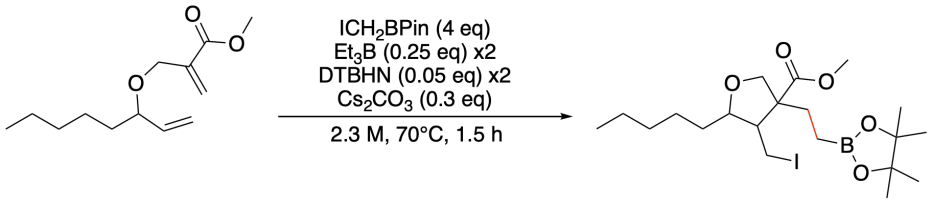
7na + 7na'
Chemical Formula: $C_{13}H_{24}BIO_3$
Exact Mass: 366.0863

Followed **GP1** using **6n** (168 mg, 1 mmol) as radical trap and ICH_2BPin as radical precursor. Purification by flash column chromatography (Macherey-Nagel Silica 60, 0.015–0.04 mm) (10% Et_2O:pentane) provided the desired **7na** (132 mg, 0.303 mmol, 30%, dr = 6:4) and **7na'** (74 mg, 0.136 mmol, 80% contaminated by radical precursor, dr = 85:15). Ratio regioisomers: 65:45.

11d: Yellow oil; Rf: 0.35 (9:1 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.87 (ddd, *J* = 13.1, 8.7, 6.8 Hz, 1H), 3.69 (dt, *J* = 7.5, 4.8 Hz, 1H), 3.52 (ddd, *J* = 13.3, 8.6, 6.6 Hz, 1H), 3.30–3.20 (m, 1H), 3.05 (t, *J* = 9.4 Hz, 1H), 2.33–1.84 (m, 2H), 1.66–1.38 (m, 8H), 1.27–1.14 (m, 12H), 0.90–0.82 (m, 3H), 0.81–0.67 (m, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 85.4 (Cq), 84.3 (CH), 83.2 (CH), 83.2 (CH), 71.8 (CH_2), 71.0 (CH_2), 51.7 (CH), 49.9 (CH), 49.0 (CH), 45.5 (CH), 35.8 (CH_2), 35.0 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 27.7 (CH_2), 26.0 (CH_2), 25.8 (CH_2), 25.0 (CH_3), 22.7 (CH_2), 20.7 (CH_2), 14.2 (CH_3), 10.1 (CH_2), 6.2 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 33.8; IR (neat): ν_{max} = 2976, 2926, 1406, 1370, 1319, 1143, 966, 846, 672, 578 cm^{-1}; HRMS (EI): Calculated for $C_{18}H_{34}BIO_3$ $[M\text{-}CH_3]^+$: 421.1486; found: 421.1406.

11d': Yellow oil; Rf: 0.44 (9:1 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.08–3.84 (m, 1H), 3.81–3.65 (m, 1H), 3.53 (dtd, *J* = 53.6, 7.4, 3.1 Hz, 1H), 3.35–3.21 (m, 1H), 3.19–3.02 (m, 1H), 2.73–2.60 (m, 1H), 1.89–1.66 (m, 1H), 1.63–1.34 (m, 6H), 1.25 (d, *J* = 8.4 Hz, 12H), 0.91–0.83 (m, 3H), 0.78 (ddd, *J* = 9.0, 7.1, 1.6 Hz, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 86.2 (CH), 84.3 (Cq), 83.3 (Cq), 83.3 (CH), 72.9 (CH_2), 53.8 (CH), 50.6 (CH), 48.9 (CH), 45.5 (CH), 35.7 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 30.9 (CH_2), 26.1 (CH_2), 25.0 (CH_3), 22.8 (CH_2), 21.4 (CH_2), 14.2 (CH_3), 11.0 (CH_2), 5.8 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 33.9.

Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]tetrahydrofuran-3-carboxylate (7oa)



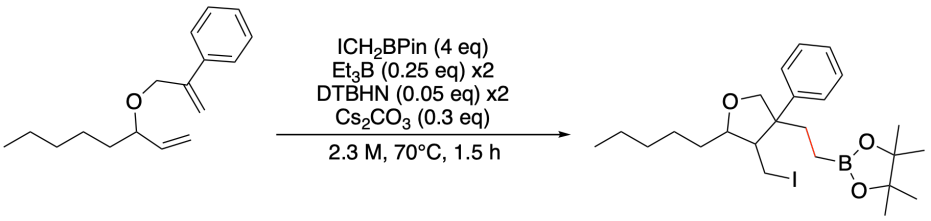
7oa
Chemical Formula: $C_{20}H_{36}BIO_5$
Exact Mass: 494.1700

Followed **GP2** using **6o** (225 mg, 0.994 mmol) as radical trap. Purification by flash column chromatography (Macherey-Nagel Silica 60, 0.015–0.04 mm) (15% Et_2O:pentane) provided the desired **7oa** (128 mg, 0.194 mmol, 20%, single diastereomer, 25% contaminated by ICH_2BPin).

Yellow oil; Rf: 0.43 (8:2 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.01 (dd, *J* = 9.4, 1.0 Hz, 1H), 3.74 (d, *J* = 9.4 Hz, 1H), 3.69 (s, 3H), 3.60 (ddd, *J* = 9.5, 6.7, 3.2 Hz, 1H), 3.30 (dd, *J* = 10.0, 4.3 Hz, 1H), 3.10 (dd, *J* = 10.0, 8.9 Hz, 1H), 2.02–1.86 (m, 2H), 1.80–1.62 (m, 2H), 1.61–1.43 (m, 2H), 1.23 (d, *J* = 14.6 Hz, 20H), 0.94–0.81 (m, 3H), 0.76–0.52 (m, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.2 (Cq), 86.0 (CH), 83.3 (Cq), 71.5 (CH_2), 60.2 (Cq), 54.3 (CH), 52.0 (CH_3), 36.0 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 26.0 (CH_2), 24.9 (CH_3), 22.7 (CH_2), 14.1 (CH_3), 5.3 (CH_2). Due

to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 33.8; IR (neat): ν_{max} = 2977, 2952, 2929, 1772, 1729, 1371, 1324, 1143, 967, 845 cm^{-1}; HRMS (ESI): Calculated for $C_{20}H_{36}BIO_5$ $[M+H]^+$: 495.1700; found: 495.1787.

2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7pa)



7pa
Chemical Formula: $C_{24}H_{38}BIO_3$
Exact Mass: 512.1959

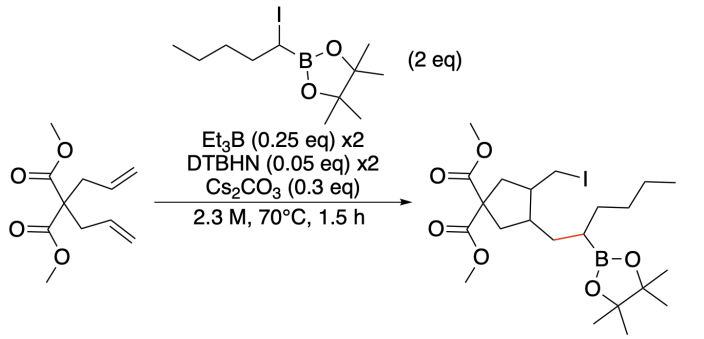
Followed **GP2** using **6p** (246 mg, 1.01 mmol) as radical trap. Purification by flash column chromatography (Gradient 5-10-20% Et_2O:pentane) provided the desired **7pa**. Out of 4 possible diastereoisomers, 2 were collected and analyzed: **DIA1** (115 mg, 0.130 mmol, 13%, 42% contaminated by ICH_2BPin); **DIA2** (176 mg, 0.220 mmol, 22%, 36% contaminated by ICH_2BPin).

DIA1: Yellow oil; Rf: 0.60 (85:15 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.40–7.12 (m, 5H), 4.16 (d, *J* = 9.0 Hz, 1H), 3.99 (d, *J* = 9.0 Hz, 1H), 3.65 (ddd, *J* = 9.5, 6.9, 2.9 Hz, 1H), 3.52–3.39 (m, 0H), 2.97 (dd, *J* = 10.0, 4.6 Hz, 1H), 2.44 (t, *J* = 10.0 Hz, 1H), 2.30 – 2.18 (m, 1H), 1.82 (dddd, *J* = 14.0, 13.0, 10.0, 5.3 Hz, 1H), 1.74–1.53 (m, 1H), 1.50–1.30 (m, 5H), 1.28–1.19 (m, 12H), 1.00–0.82 (m, 5H), 0.58–0.39 (m, 1H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 140.1 (Cq_{Ar}), 128.6 (2 x CH_{Ar}), 128.1 (2 x CH_{Ar}), 126.6 (CH_{Ar}), 86.2 (CH), 83.2 (2 x Cq), 75.0 (CH_2), 56.6 (Cq), 56.1 (CH), 36.6 (CH_2), 33.2 (CH_2), 32.0 (CH_2), 29.8 (CH_2), 26.2 (CH_2), 24.6 (CH_3), 22.8 (CH_2), 14.2 (CH_3), 7.1 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 31.8; IR (neat): ν_{max} = 2976, 2954, 2926, 2855, 1371, 1324, 1143, 967, 845, 701 cm^{-1}; HRMS (ESI): Calculated for $C_{24}H_{38}BIO_3$ $[M+H]^+$: 513.1959; found: 513.2031.

DIA2: Yellow oil; Rf: 0.46 (85:15 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.29 (d, *J* = 9.4 Hz, 1H), 3.87 (d, *J* = 9.4 Hz, 1H), 3.79 (ddd, *J* = 8.6, 5.9, 2.8 Hz, 1H), 3.71–3.58 (m, 1H), 3.54–3.46 (m, 1H), 3.27 (dd, *J* = 11.1, 9.8 Hz, 1H), 2.50 (ddd, *J* = 11.1, 6.1, 4.1 Hz, 1H), 2.07–1.91 (m, 1H), 1.77 (ddd, *J* = 13.7, 11.4, 5.7 Hz, 1H), 1.69–1.56 (m, 1H), 1.26 (d, *J* = 30.3 Hz, 20H), 1.03 – 0.78 (m, 5H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 144.9 (Cq_{Ar}), 128.5 (2 x CH_{Ar}), 126.8 (2 x CH_{Ar}), 126.3 (CH_{Ar}), 86.9 (CH), 84.4 (2 x Cq), 74.1 (CH_2), 57.7 (CH), 55.6 (Cq), 36.3 (CH_2), 31.8 (CH_2), 29.8 (CH_2), 27.4 (CH_2), 26.1 (CH_2), 24.6 (CH_3), 22.7 (CH_2), 14.2

(CH_3), 6.4 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 31.9; IR (neat): ν_{max} = 2977, 2955, 2926, 2855, 1371, 1324, 1143, 967, 845, 733 cm^{-1}; HRMS (ESI): Calculated for $C_{24}H_{38}BIO_3$ $[M+H]^+$: 513.1959; found: 513.2029.

Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate (7ab)

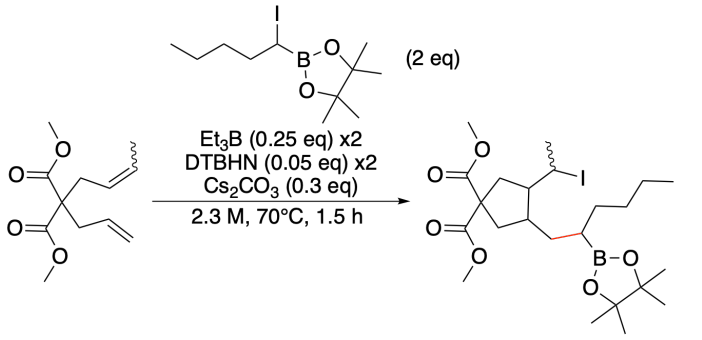


7ab
Chemical Formula: $C_{22}H_{38}BIO_6$
Exact Mass: 536.1806

Followed **GP1** using **6a** (222 mg, 1.05 mmol) as radical trap and **16** as radical precursor. Purification by flash column chromatography (Gradient 5-10% EtOAc:heptane) provided the desired **7ab** (393 mg, 0.733 mmol, 73%, dr = 4:4:1:1).

Light yellow oil; Rf: 0.49 (8:2 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.76–3.65 (m, 6H), 3.42–3.22 (m, 1H), 3.13–2.94 (m, 1H), 2.67–2.43 (m, 2H), 2.43–2.23 (m, 1H), 2.21–1.95 (m, 2H), 1.76–1.57 (m, 1H), 1.55–1.09 (m, 22H), 0.96 (ddt, J = 13.0, 11.3, 5.4 Hz, 1H), 0.87 (td, J = 7.0, 1.9 Hz, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.1 (Cq), 173.1 (Cq), 172.9, (Cq) 83.1 (Cq), 58.6 (Cq), 58.4 (Cq), 57.7 (Cq), 52.9 (CH_3), 52.5 (CH_3), 47.6 (CH), 47.2 (CH), 45.8 (CH), 44.9 (CH), 44.1 (CH), 42.2 (CH), 42.1 (CH), 41.6 (CH_2), 41.0 (CH_2), 40.6 (CH_2), 40.3 (CH_2), 38.7 (CH_2), 38.4 (CH_2), 37.0 (CH_2), 36.0 (CH_2), 34.6 (CH_2), 32.0 (CH_2), 31.5 (CH_2), 31.5 (CH_2), 31.4 (CH_2), 31.3 (CH_2), 30.9 (CH_2), 30.6 (CH_2), 30.3 (CH_2), 25.0 (CH_3), 24.9 (CH_3), 24.9 (CH_3), 23.1 (CH_2), 23.0 (CH_2), 23.0 (CH_2), 14.2 (CH_3), 11.4 (CH_2), 11.1 (CH_2), 8.7 (CH_2), 8.2 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 33.9; IR (neat): ν_{max} = 2976, 2923, 1731, 1434, 1387, 1315, 1252, 1142, 952, 939 cm^{-1}; HRMS (ESI): Calculated for $C_{22}H_{38}BIO_6$ $[M+H]^+$: 537.1391; found: 555.1879.

Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate (7db)

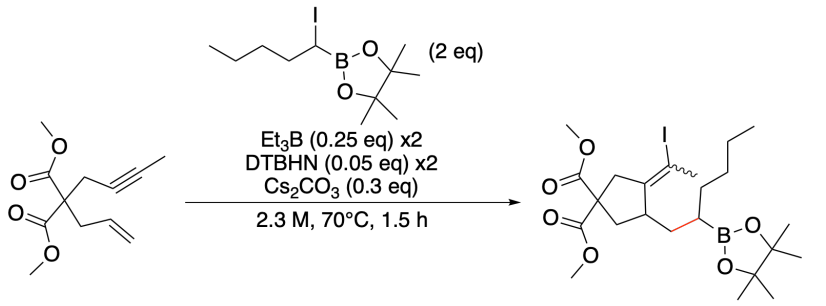


7db
Chemical Formula: $C_{23}H_{40}BIO_6$
Exact Mass: 550.1963

Followed **GP1** using **6d** (223 mg, 0.984 mmol) as radical trap and **16** as radical precursor. Purification by flash column chromatography (15% Et_2O:pentane) provided the desired **7db** (137 mg, 0.249 mmol, 25% (81% brsm)).

Light yellow oil; Rf: 0.51 (8:2 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.52–3.95 (m, 1H), 3.76–3.64 (m, 6H), 2.69–2.55 (m, 1H), 2.53–2.36 (m, 2H), 2.35–2.19 (m, 2H), 2.15 (d, J = 12.8 Hz, 1H), 2.00–1.72 (m, 4H), 1.53–1.11 (m, 21H), 1.06–0.83 (m, 6H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.7, 173.7, 173.6, 173.5, 173.5, 173.5, 173.4, 173.4, 173.3, 173.2, 173.1, 173.1, 173.0, 172.9, 172.8, 172.8, 172.6, 172.5, 83.2, 83.1, 83.1, 83.1, 83.1, 83.0, 83.0, 83.0, 59.7, 59.6, 59.0, 58.9, 58.0, 57.8, 57.7, 57.6, 57.5, 54.6, 54.5, 54.1, 54.0, 54.0, 53.1, 53.0, 53.0, 53.0, 52.9, 52.8, 52.8, 52.8, 52.7, 52.7, 52.7, 45.5, 44.9, 43.8, 43.2, 42.4, 42.1, 42.0, 41.7, 41.2, 40.0, 40.0, 39.9, 39.3, 38.9, 38.8, 38.6, 38.5, 38.4, 37.1, 37.0, 36.8, 36.6, 36.3, 35.7, 35.5, 34.2, 32.5, 32.2, 32.1, 31.7, 31.6, 31.5, 31.5, 31.4, 31.3, 31.2, 30.8, 30.2, 30.1, 30.1, 29.8, 29.7, 29.4, 29.2, 29.0, 28.6, 28.6, 28.5, 28.4, 28.2, 28.1, 27.0, 26.6, 25.6, 25.6, 25.3, 25.2, 25.0, 25.0, 25.0, 24.9, 24.9, 24.9, 24.9, 24.7, 23.7, 23.4, 23.2, 23.1, 23.1, 23.1, 23.0, 23.0, 22.1, 21.3, 21.1, 14.2, 14.2, 14.2, 14.2, 14.1, 12.8, 12.6. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 34.5, 30.5; IR (neat): ν_{max} = 2977, 2953, 2924, 2858, 1733, 1371, 1249, 1142, 856, 732 cm^{-1}; HRMS (EI): Calculated for $C_{23}H_{40}BIO_6$ $[M\text{-}CH_5O_2]^+$: 375.2914; found: 375.2708.

Dimethyl (3E)-3-(1-iodoethylidene)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]-cyclopentane-1,1-dicarboxylate (7sb)

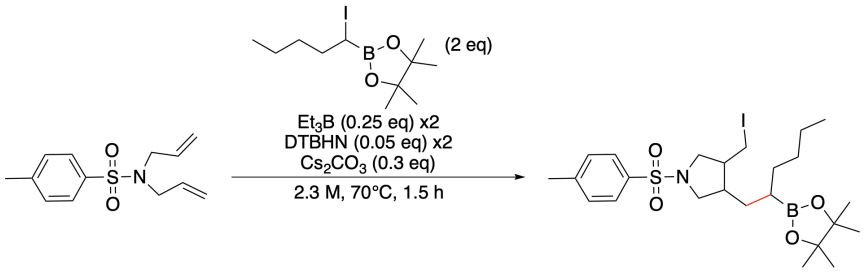


7sb
Chemical Formula: $C_{23}H_{38}BIO_6$
Exact Mass: 548.1806

Followed **GP1** using **6s** (226 mg, 1.01 mmol) as radical trap and **16** as radical precursor. Purification by flash column chromatography (10% Et_2O:pentane) provided the desired **7sb** (125 mg, 0.228 mmol, 23% (48% brsm), dr = 42:37:15:13).

Light yellow oil; Rf: 0.51 (8:2 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.76–3.62 (m, 6H), 3.13–2.84 (m, 2H), 2.82–2.52 (m, 2H), 2.52–2.39 (m, 3H), 2.14 (ddd, *J* = 17.6, 8.3, 4.3 Hz, 1H), 1.72–1.32 (m, 4H), 1.32–1.09 (m, 18H), 1.01–0.80 (m, 4H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 172.7 (Cq), 172.2 (Cq), 172.1 (Cq), 172.1 (Cq), 172.1 (Cq), 172.0 (Cq), 172.0 (Cq), 172.0 (Cq), 148.8 (Cq), 148.6 (Cq), 147.5 (Cq), 91.1 (Cq), 90.5 (Cq), 89.4 (Cq), 89.2 (Cq), 83.1 (Cq), 60.0 (Cq), 60.0 (Cq), 58.5 (Cq), 58.5 (Cq), 58.3 (Cq), 53.0 (2 x CH_3), 48.8 (CH), 48.2 (CH_2), 47.4 (CH), 42.1 (CH), 41.5 (CH_2), 40.4 (CH_2), 40.1 (CH_2), 40.0 (CH_2), 39.7 (CH), 38.0 (CH_2), 38.0 (CH_2), 37.5 (CH_2), 37.4 (CH_2), 36.7 (CH_2), 36.7 (CH_2), 35.4 (CH_2), 33.9 (CH_2), 32.2 (CH_2), 32.1 (CH_2), 31.9 (CH_2), 31.7 (CH_2), 31.6 (CH_2), 31.4 (CH_2), 31.1 (CH_3), 31.0 (CH_3), 30.4 (CH_3), 30.2 (CH_3), 29.7 (CH_2), 29.4 (CH_2), 29.0 (CH_2), 25.3 (CH_3), 25.0 (CH_3), 24.9 (CH_3), 23.1 (CH_2), 23.0 (CH_2), 14.6 (CH_3), 14.2 (CH_3), 14.2 (CH_3), 14.1 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 34.4; IR (neat): ν_{max} = 2976, 2953, 2925, 1735, 1379, 1315, 1248, 1142, 965, 859 cm^{-1}; HRMS (EI): Calculated for $C_{23}H_{38}BIO_6$ $[M+H]^+$: 549.1806; found: 549.1871.

3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]-pyrrolidine (7cb)

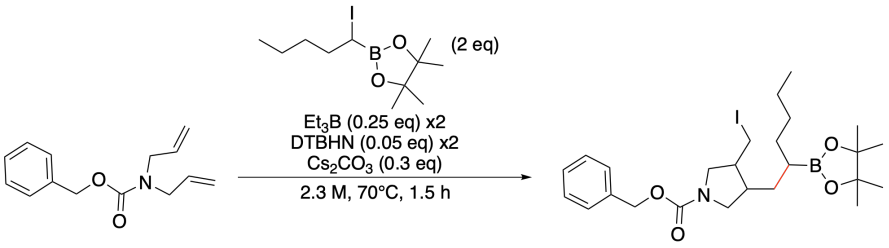


7cb
Chemical Formula: $C_{24}H_{39}BINO_4S$
Exact Mass: 575.1738

Followed **GP1** using **6c** (251 mg, 0.997 mmol) as radical trap and **16** as radical precursor. Purification by flash column chromatography (2% Et_2O:pentane) provided the desired **7cb** (310 mg, 0.552 mmol, 55% (81% brsm), dr = 3:3:2:2).

Colorless sticky oil; Rf: 0.27 (8:2 pentane:Et_2O); ^{1}**H NMR** (400 MHz, CD_2Cl_2) δ 7.73–7.62 (m, 2H), 7.38-7.29 (m, 2H), 3.57–3.29 (m, 2H), 3.28–3.08 (m, 1H), 3.04–2.69 (m, 2H), 2.57–2.44 (m, 1H), 2.42 (d, *J* = 2.4 Hz, 3H), 2.13–2.03 (m, 1H), 1.93–1.68 (m, 1H), 1.41–1.06 (m, 20H), 0.93–0.74 (m, 5H); ^{13}**C NMR** (101 MHz, CD_2Cl_2) δ 144.2 (Cq_{Ar}), 144.1 (Cq_{Ar}), 144.0 (Cq_{Ar}), 134.2 (Cq_{Ar}), 134.2 (Cq_{Ar}), 133.8 (Cq_{Ar}), 133.7 (Cq_{Ar}), 130.2 (CH_{Ar}), 130.1 (CH_{Ar}), 128.0 (CH_{Ar}), 128.0 (CH_{Ar}), 127.8 (CH_{Ar}), 127.8 (CH_{Ar}), 84.3 (2 x Cq), 83.5 (2 x Cq), 54.76 (CH_2), 54.74 (CH_2), 54.3 (CH_2), 54.2 (CH_2), 54.1 (CH_2), 54.0 (CH_2), 53.8 (CH_2), 53.4 (CH_2), 51.7 (CH_2), 51.6 (CH_2), 47.0 (CH), 46.7 (CH), 45.8 (CH), 45.1 (CH), 44.6 (CH), 44.1 (CH), 42.2 (CH), 42.1 (CH), 34.8 (CH_2), 33.7 (CH_2), 32.1 (CH_2), 31.7 (CH_2), 31.6 (CH_2), 31.5 (CH_2), 31.4 (CH_2), 31.3 (CH_2), 30.9 (CH_2), 29.2 (CH_2), 28.8 (CH_2), 25.1 (CH_3), 25.0 (CH_3), 23.4 (CH_2), 23.3 (CH_2), 21.7 (CH_3), 14.2 (CH_3), 8.2 (CH_2), 7.8 (CH_2), 5.1 (CH_2), 4.5 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, CD_2Cl_2) 33.7; IR (neat): ν_{max} = 2975, 2955, 2923, 2855, 1318, 1141, 1109, 662, 586, 546 cm^{-1}; HRMS (EI): Calculated for $C_{24}H_{39}BINO_4S$ $[M+H]^+$: 576.1738; found: 576.1805.

Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine-1-carboxylate (7mb)

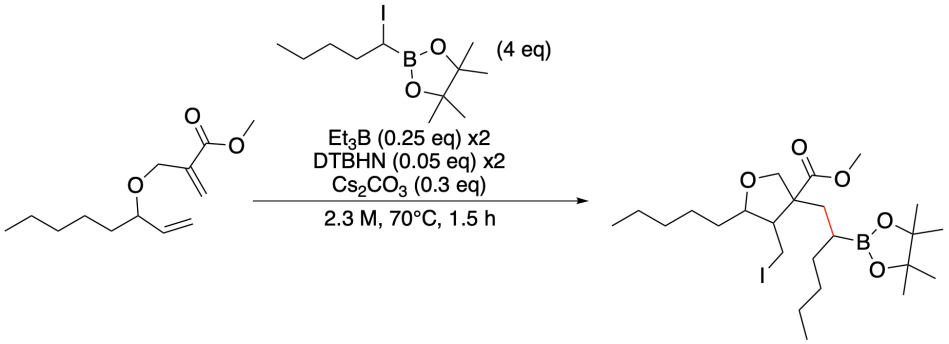


7mb
Chemical Formula: $C_{25}H_{39}BINO_4$
Exact Mass: 555.2017

Followed **GP1** using **6m** (235 mg, 1.02 mmol) as radical trap and **16** as radical precursor. Purification by flash column chromatography (Gradient: 15-40% Et_2O:pentane) provided the desired **7mb** (231 mg, 0.416 mmol, 41% (83% brsm), dr = 3:3:2:2).

Colorless sticky oil; Rf: 0.27 (7:3 pentane:Et_2O); ^{1}**H NMR** (400 MHz, DMSO) δ 7.41 – 7.26 (m, 5H), 5.10 – 4.98 (m, 2H), 3.71 – 3.08 (m, 6H), 2.99 (ddt, *J* = 22.3, 18.9, 8.3 Hz, 1H), 2.61 – 2.51 (m, 1H), 2.20 (tt, *J* = 10.1, 5.5 Hz, 1H), 1.85 (dd, *J* = 8.5, 4.6 Hz, 1H), 1.62 – 1.10 (m, 21H), 0.85 (tq, *J* = 7.2, 3.6 Hz, 4H); ^{13}**C NMR** (101 MHz, DMSO) δ 154.0 (Cq_{Ar}), 154.0 (Cq_{Ar}), 153.9 (Cq_{Ar}), 153.7 (Cq_{Ar}), 137.1 (Cq_{Ar}), 136.9 (Cq_{Ar}), 128.4 (Cq_{Ar}), 128.3 (Cq_{Ar}), 127.8 (CH_{Ar}), 127.7 (CH_{Ar}), 127.6 (CH_{Ar}), 127.5 (CH_{Ar}), 127.4 (CH_{Ar}), 82.8 (4 x Cq), 65.9 (CH_2), 65.8 (CH_2), 65.7 (CH_2), 54.9 (CH_2), 52.5 (CH_2), 52.1 (CH_2), 52.0 (CH_2), 51.5 (CH_2), 51.2 (CH_2), 50.8 (CH_2), 50.5 (CH_2), 49.5 (CH_2), 49.4 (CH_2), 49.0 (CH_2), 48.9 (CH_2), 45.2 (CH), 44.4 (CH), 44.3 (CH), 44.0 (CH), 43.6 (CH), 43.5 (CH), 43.3 (CH), 42.6 (CH), 42.4 (CH), 41.5 (CH), 41.0 (CH), 31.3 (CH_2), 31.2 (CH_2), 30.8 (CH_2), 30.6 (CH_2), 30.5 (CH_2), 28.1 (CH_2), 27.6 (CH_2), 24.7 (CH_3), 24.6 (CH_3), 24.6 (CH_3), 24.5 (CH_3), 22.4 (CH_2), 22.3 (CH_2), 13.9 (CH_3), 10.1 (CH_2), 7.2 (CH_2), 6.9 (CH_2), 6.6 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, DMSO) 36.6; IR (neat): ν_{max} = 2975, 2953, 2924, 1702, 1414, 1358, 1315, 1141, 1112, 695 cm^{-1}; HRMS (EI): Calculated for $C_{25}H_{39}BINO_4$ $[M+H]^+$: 555.2017; found: 555.2088.

Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]tetrahydrofuran-3-carboxylate (7ob)



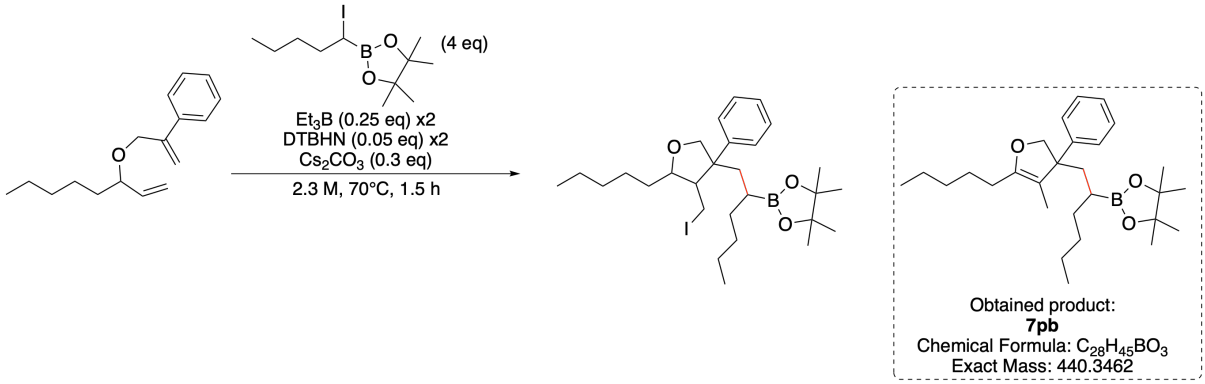
7ob
Chemical Formula: $C_{24}H_{44}BIO_5$
Exact Mass: 550.2326

Followed **GP1** using **6o** (87.6 mg, 0.387 mmol) as radical trap and 4 eq. of **16** as radical precursor. Purification by flash column chromatography (Gradient: 4-6% Et_2O:pentane) provided the desired **7ob** (88 mg, 0.160 mmol, 41%, dr = 42:37:13:3:3:2).

Colorless sticky oil; Rf: 0.31 (94:6 pentane:Et_2O); ^{1}**H NMR** (400 MHz, CD_2Cl_2) δ 3.75 (dd, *J* = 9.3, 7.9 Hz, 1H), 3.68 (t, *J* = 1.8 Hz, 1H), 3.62–3.48 (m, 3H), 3.34 (dt, *J* = 10.1, 4.3 Hz, 1H),

3.17-3.03 (m, 1H), 2.18–1.94 (m, 1H), 1.89–1.62 (m, 1H), 1.62–1.44 (m, 3H), 1.41–1.18 (m, 25H), 0.88 (dt, J = 11.0, 6.7 Hz, 6H), 0.82–0.67 (m, 1H); ^{13}**C NMR** (101 MHz, CD_2Cl_2) δ 181.2 (Cq), 175.3 (Cq), 175.1 (Cq), 173.7 (Cq), 173.7 (Cq), 87.5 (Cq), 86.0 (CH), 85.9 (CH), 85.9 (CH), 84.3 (Cq), 83.8 (Cq), 83.7 (Cq), 83.6 (Cq), 83.5 (Cq), 83.4 (Cq), 76.4 (CH_2), 72.5 (CH_2), 72.5 (CH_2), 72.0 (CH_2), 70.4 (CH_2), 70.1 (CH_2), 60.1 (Cq), 59.9 (Cq), 58.9 (Cq), 58.8 (Cq), 57.8 (Cq), 57.4 (Cq), 55.2 (CH), 54.7 (CH), 54.3 (CH), 54.0 (CH), 53.8 (CH), 53.4 (CH), 52.3 (CH_3), 52.1 (CH_3), 52.0 (CH_3), 50.8 (CH_3), 39.0 (CH_2), 38.9 (CH_2), 36.4 (CH_2), 36.3 (CH_2), 36.1 (CH_2), 36.0 (CH_2), 35.1 (CH_2), 34.4 (CH_2), 33.8 (CH_2), 33.3 (CH_2), 32.9 (CH_2), 32.9 (CH_2), 32.6 (CH_2), 32.2 (CH_2), 32.1 (CH_2), 31.8 (CH_2), 31.6 (CH_2), 31.4 (CH_2), 31.4 (CH_2), 31.3 (CH_2), 31.1 (CH_2), 26.3 (CH_2), 26.3 (CH_2), 26.2 (CH_2), 26.1 (CH_2), 26.0 (CH_2), 25.2 (CH_3), 25.2 (CH_3), 25.1 (CH_3), 25.1 (CH_3), 25.1 (CH_3), 25.0 (CH_3), 23.3 (CH_2), 23.3 (CH_2), 23.2 (CH_2), 23.2 (CH_2), 23.0 (CH_2), 22.4 (CH_2), 20.6 (CH_2), 14.3 (CH_3), 14.2 (CH_3), 14.1 (CH_3), 5.8 (CH_2), 5.7 (CH_2), 5.2 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, CD_2Cl_2) 34.0; IR (neat): ν_{max} = 2954, 2926, 2857, 1772, 1729, 1371, 1316, 1142, 967, 840 cm^{-1}; HRMS (EI): Calculated for $C_{24}H_{44}BIO_5$ $[M+H]^+$: 551.2326; found: 551.2394.

(4,4,5,5-tetramethyl-2-[1-[(4-methyl-5-pentyl-3-phenyl-2H-furan-3-yl)methyl]pentyl]-1,3,2-dioxaborolane (7pb)



Followed **GP1** using **6p** (125 mg, 0.510 mmol) as radical trap and 4 eq. of **16** as radical precursor. Purification by flash column chromatography (2% Et_2O:pentane) provided the **7pb** (77 mg, 0.159 mmol, 31%, dr = 57:43) as final compound.

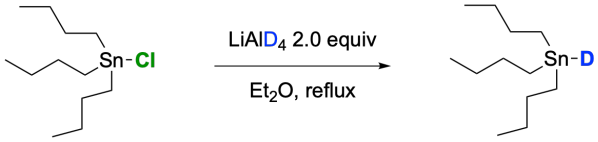
Colorless sticky oil; Rf: 0.35 (98:2 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.06 (m, 5H), 4.33–4.04 (m, 2H), 2.27–1.99 (m, 3H), 1.92–1.62 (m, 1H), 1.51–1.10 (m, 29H), 0.97 (ddtd, J = 20.2, 10.1, 6.4, 3.0 Hz, 1H), 0.82 (dtd, J = 10.6, 7.1, 3.8 Hz, 6H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 152.8 (Cq_{Ar}), 151.9 (Cq_{Ar}), 147.8 (Cq_{Ar}), 147.0 (Cq_{Ar}), 128.2 (2 x CH_{Ar}), 126.8 (2 x CH_{Ar}), 126.0 (CH_{Ar}), 109.6 (Cq), 108.1 (Cq), 84.0 (Cq), 83.1 (Cq), 80.8 (CH_2), 80.2 (CH_2), 57.3 (Cq), 57.1 (Cq), 36.5 (CH_2), 36.0 (CH_2), 34.7 (CH_2), 33.6 (CH_2), 33.6 (CH_2), 33.4 (CH_2), 31.7 (CH_2), 31.7 (CH_2), 31.4 (CH_2), 31.3 (CH_2), 27.0 (CH_2), 26.9 (CH_2), 26.3 (CH_2), 26.3 (CH_2), 25.3

(CH_3), 25.1 (CH_3), 24.9 (CH_3), 24.5 (CH_3), 24.3 (CH_3), 23.2 (CH_2), 23.1 (CH_2), 22.6 (CH_2), 22.1 (CH_2), 14.2 (CH_3), 14.1 (CH_3), 8.5 (CH_3), 8.4 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) 33.7; HRMS (EI): Calculated for $C_{28}H_{45}BO_3$ $[M+H]^+$: 441.3462; found: 441.3532.

3.10.4 Deuteration experiments

Preparation of Tributyltin deuteride ($SnBu_3D$)

All glassware was oven/flame dried and cooled under argon. The reaction was performed under Argon atmosphere.



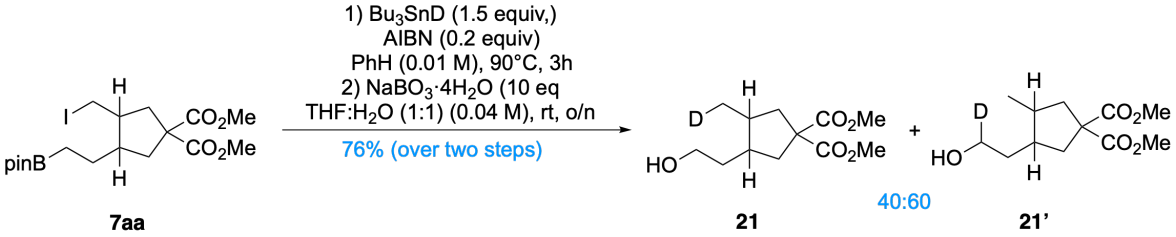
air/moisture sensitive
stored @-20°C

A flame-dried and cooled under Argon 25 mL round bottom flask was filled with dry and degassed Et_2O (20 mL). The solvent was cooled to 0 °C using an ice bath and $LiAlD_4$ (860 mg, 20.0 mmol) was added portion wise over 10 min while stirring. Once the addition finished, the solution was let to stir at room temperature for 20 min for full solubilization. Afterwards, it was let without stirring to decantate the solid for around 10 min. The obtained solution was taken up with a syringe (no filter), portion-wise and transferred to the reaction mixture. Another two-neck round bottom flask equipped with a condenser was charged with dry degassed Et_2O (20 mL). Bu_3SnCl (2.8 mL, 10.0 mmol) was added and the solution was cooled to 0 °C using an ice bath. The previously prepared $LiAlD_4$ (20.0 mL, 20.0 mmol, 1.0M in Et_2O) solution was added via syringe dropwise at 0 °C over 15 min and let to stir for another 15 min at this temperature. Afterwards, the reaction mixture was let to warm up to 40 °C and let to stir until full conversion (2 - 5h, monitoring by ^{13}C NMR in C_6D_6). Upon completion, the reaction mixture cooled down to rt and then to 0 °C using an ice bath. D_2O (2 mL) was slowly added to quench the active species, until no more gas evolution was observed (stir for around 1h). Then dry Na_2SO_4 was added as a solid in the reaction mixture. The mixture was stirred for 1-2 minutes and then was let to sediment. The solution was taken up with a syringe and filtered through dry Na_2SO_4/Celite pad (30 mL volume) under small vacuum using a 50 mL syringe as a drying installation and 100 mL conic flask with a stirring bar. More dry Et_2O (15 mL) was added to wash off all the product in the collecting flask. After concentration under reduced pressure (no more than 15 minutes), the obtained Et_2O solution was concentrated under high vacuum while stirring and heating using an oil bath at 30 °C. The obtained colorless oil (2.15 g, 7.36 mmol, 74%) corresponded to the desired product and was used as such without further purification.

Colorless oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 1.71–1.44 (m, 6H), 1.42–1.27 (m, 6H), 1.07–0.82 (m, 15H); ^{2}**H NMR** (61 MHz, Lock_Off, $CHCl_3$) 5.09; ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 30.3 (CH_2), 27.5 (CH_2), 13.9 (CH_2), 8.3 (CH_3); ^{119}**Sn NMR** (149 MHz, $CDCl_3$) δ -90.43 (t, J = 242.7, 241.7 Hz).

The physical and spectral data are in accordance with literature data: Lu, Y.; Yamago, S. *Angewandte Chemie* **2019**, *131* (12), 3992–3996.

A) Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate (21+21')

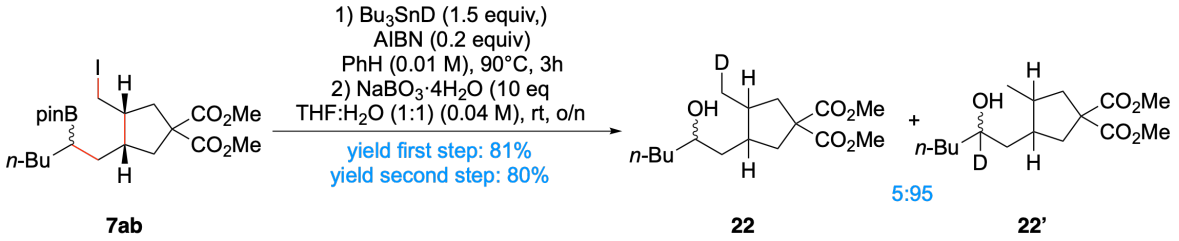


A 100 mL two-neck round-bottom flask under nitrogen was charged with dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate (150 mg, 0.312 mmol) and tributyl tin deuteride (137 mg, 0.467 mmol) and dry benzene (30 mL). AIBN (10 mg, 0.06 mmol) was added and the reaction mixture was stirred at 90 °C for 3h. The reaction mixture was quenched with saturated aq. solution of K_2CO_3 (50 mL). The phases were separated, and the aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic phases were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to deliver the crude a colorless oil. The crude was transferred into a 10 mL one-neck round bottom flask, and dissolved in H_2O/THF (1:1, 8 mL). Sodium perborate (481 mg, 3.12 mmol) was then added in one portion and the reaction mixture was stirred at rt under N_2 atmosphere for 16h. The reaction mixture was partitioned between EtOAc (20 mL) and water (20 mL). The phases were separated and the aqueous layer was extracted EtOAc (3 x 10 mL). The combined organic phases were washed with brine (25 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a colorless oil. Purification by flash column chromatography (60% Et2O:pentane) delivered the deuterated alcohols **21** and **21'** in a 4:6 ratio (58 mg, 0.237 mmol, 76% (over two steps)).

Colorless oil; Rf: 0.4 (1:1 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.69 (d, J = 1.5 Hz, 6H), 3.67–3.58 (m, 2H), 2.58–2.30 (m, 2H), 2.22–2.02 (m, 2H), 2.01–1.94 (m, 1H), 1.90–1.67 (m, 2H), 1.67–1.48 (m, 1H), 1.48–1.20 (m, 1H), 1.00–0.79 (m, 3H); ^{2}**H NMR** (61 MHz, Lock_Off, $CHCl_3$) 3.6, 1.0, 0.8.; ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.6 (Cq), 173.5 (Cq), 173.4 (Cq), 62.0 (CH_2), 61.9 - 61.4 (CH-D), 58.9 (Cq), 58.4 (Cq), 52.8 (CH_3), 43.7 (CH), 42.7 (CH_2), 42.6 (CH_2), 41.6 (CH_2), 41.6 (CH), 40.7 (CH_2), 40.4 (CH), 40.3 (CH), 39.2 (CH), 38.5 (CH_2), 36.5 (CH_2),

36.4 (CH_2), 36.0 (CH), 35.9 (CH), 32.9 (CH_2), 32.7 (CH_2), 17.8 (CH_3), 17.6 - 17.5 (CH_2-D), 15.0 (CH_3), 14.7-13.7 (CH_2-D); IR (neat): ν_{max} = 3373, 2953, 2931, 2875, 1727, 1434, 1249, 1198, 1167, 1056 cm^{-1}; HRMS (EI): Calculated for $C_{12}H_{19}DO_5$ $[M\text{-}CH_4O]^+$: 214.1274; found: 214.1187.

B) Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate (22+22')



7ab **22** **22'**

Step 1: A 100 mL two-neck round-botton flask under Argon was charged with dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate (161 mg, 0.3 mmol), tributyl tin deuteride (131 mg, 0.450 mmol) and dry benzene (30 mL). AIBN (9 mg, 0.06 mmol) was added and the reaction mixture was stirred at 90 °C for 3h. The reaction mixture was quenched with saturated aq. solution of K_2CO_3 (50 mL). The phases were separated, and the aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic phases were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to deliver the crude (100 mg, 0.243 mmol, 81% crude) as a colorless oil.

Step 2: A fraction of the crude product (77 mg, 0.186 mg) was transferred into a 10 mL one-neck round bottom flask and dissolved in H_2O/THF (1:1, 4.4 mL). Sodium perborate (287 mg, 1.86 mmol, 10 eq) was then added in one portion and the reaction mixture was stirred at rt under N_2 atmosphere for 16h. The reaction mixture was partitioned between EtOAc (20 mL) and water (20 mL). The phases were separated and the aqueous layer was extracted EtOAc (3 x 10 mL). The combined organic phases were washed with brine (25 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude product. Purification by flash column chromatography (30% Et2O:pentane) delivered the desired alcohols **22** and **22'** in a 9:95 ratio (45 mg, 0.150 mmol, 80%; 65% over the two steps).

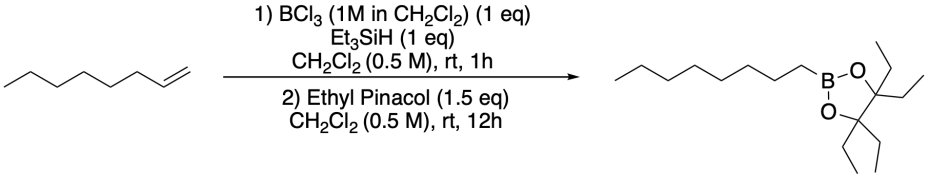
Colorless oil; Rf: 0.4 (1:1 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.69 (d, J = 2.1 Hz, 6H), 2.64–2.30 (m, 2H), 2.24–2.10 (m, 2H), 2.06–1.94 (m, 2H), 1.82–1.19 (m, 10H), 1.00–0.78 (m, 6H); ^{2}**H NMR** (61 MHz, Lock_Off, $CHCl_3$) 3.58; ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.6 (Cq), 173.6 (Cq), 173.5 (Cq), 173.4 (Cq), 173.4 (Cq), 70.9 (Cq-D), 70.7 (Cq-D), 70.5 (Cq-D), 70.5 (Cq-D, 70.3 (Cq-D), 70.1 (Cq-D), 69.9 (Cq-D), 58.9 (Cq), 58.6 (Cq), 58.4 (Cq), 52.9 (CH_3), 52.8 (CH_3), 52.8 (CH_3), 44.5 (CH), 43.1 (CH), 42.8 (CH_2), 42.5 (CH_2), 41.7 (CH_2), 41.6 (CH_2), 41.5 (CH_2), 41.4 (CH_2), 41.2 (CH_2), 40.7 (CH), 40.6 (CH_2), 40.5 (CH), 39.7 (CH), 39.0 (CH), 38.8 (CH_2), 38.4 (CH_2), 38.1 (CH_2), 38.0 (CH_2), 37.8 (CH_2), 37.7 (CH_2), 37.6 (CH_2), 37.5 (CH_2),

37.4 (CH_2), 37.1 (CH_2), 36.5 (CH), 35.7 (CH), 28.0 (CH_2), 27.9 (CH_2), 27.8 (CH_2), 22.9 (CH_2), 22.8 (CH_2), 18.0 (CH_3), 17.6 (CH_3), 15.2 (CH_3), 15.1 (CH_3), 14.2 (CH_3); IR (neat): ν_{max} = 3466, 2954, 2929, 2872, 1730, 1434, 1251, 1251, 1146, 1058 cm^{-1}; HRMS (EI): Calculated for $C_{16}H_{27}DO_5$ $[M\text{-}C_4H_9]^+$: 244.2000; found: 244.1295.

3.10.5 Post-functionalized products

Difference of reactivity between alkyl pinacol boronic esters and alkyl ethylpinacol boronic esters

4,4,5,5-tetraethyl-2-octyl-1,3,2-dioxaborolane (10)



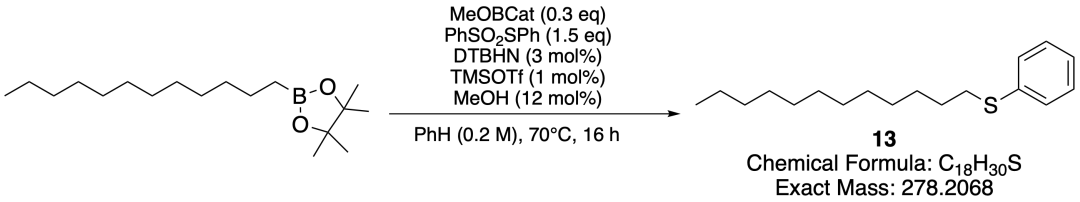
10
Chemical Formula: $C_{18}H_{37}BO_2$
Exact Mass: 296.2887

Boron trichloride (10.2 mL, 10.2 mmol, 1.0 M in DCM) was added to a flask containing a stirring bar under argon atmosphere. A solution of oct-1-ene (1.6 mL, 10.2 mmol) and triethylsilane (1.65 mL, 10.2 mmol) in DCM (20 mL) was then added dropwise to the BCl_3 solution at room temperature. After 1 h, 3,4-diethylhexane-3,4-diol (2.67 g, 15.3 mmol) was added portionwise (vigorous evolution of HCl gas) at room temperature and the reaction mixture was stirred for another 16 h. The solvents were removed under reduced pressure to give the crude boronic ester as an orange oil. Purification by flash column chromatography (5% EtOAc:heptanes) delivered the desired **10** (2.67 g, 9.03 mmol, 89%).

Colorless oil; Rf: 0.35 (96:4 heptanes:EtOAc); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 1.65 (qd, *J* = 7.4, 3.8 Hz, 8H), 1.40 (d, *J* = 14.8 Hz, 2H), 1.25 (s, 10H), 0.90 (t, *J* = 7.4 Hz, 15H), 0.76 (t, *J* = 7.6 Hz, 2H), 0.58–0.46 (m, 1H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 88.0 (Cq), 32.6 (CH_2), 32.1 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 26.5 (4 x CH_2), 24.4 (CH_2), 22.8 (CH_2), 14.3 (CH_3), 9.0 (4 x CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (96 MHz, $CDCl_3$) δ 33.5; IR (neat): ν_{max} = 2923, 2884, 2854, 1458, 1376, 1348, 1285, 1115, 931, 740 cm^{-1}; HRMS (ESI): Calculated for $C_{18}H_{37}BO_2$ $[M+H]^+$: 297.2887; found: 297.2959.

The product was prepared according to a procedure reported in the literature:
Clausen, F.; Kischkewitz, M.; Bergander, K.; Studer, A. *Chemical Science* **2019**, *10* (24), 6210–6214.

Dodecyl(phenyl)sulfane (13)



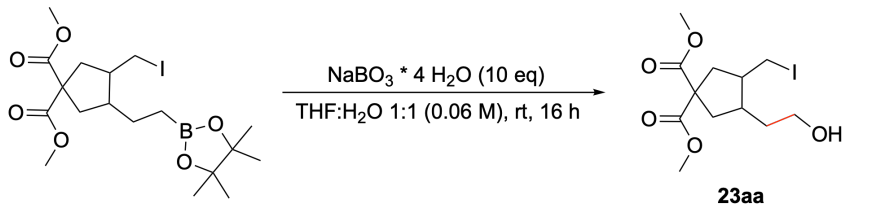
13
Chemical Formula: $C_{18}H_{30}S$
Exact Mass: 278.2068

A flame-dried two neck round-bottom flask, equipped with a reflux condenser, was charged with 2- dodecyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (302 mg, 1.02 mmol) and $PhSO_2SPh$ (376 mg, 1.53 mmol), benzene (5 mL, 0.2 M), and MeOBcat (0.3 mL, 0.3 mmol, 1.0 ML in benzene), TMSOTf (0.2 mL, 0.01 mmol, 0.05 M in DCM,), MeOH (5 μl, 0.122 mmol) and DTBHN (5 mg, 0.029 mmol). The contents were heated up to 70 °C in a pre-heated oil bath and stirred overnight. The mixture was partitioned between Et_2O (30 mL) and water (30 mL). The water phase was extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a dark-brown oil. Purification by flash column chromatography (5% EtOAc:heptanes) delivered the desired **13** (215 mg, 0.772 mmol, 78

Colorless oil; Rf: 0.58 (100% pentane); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.39–7.12 (m, 5H), 2.94 (dd, *J* = 8.0, 6.8 Hz, 2H), 1.67 (tt, *J* = 8.3, 7.0 Hz, 2H), 1.43 (q, *J* = 6.7 Hz, 2H), 1.28 (s, 16H), 0.94–0.85 (m, 3H); ^{1}3**C NMR** (75 MHz, $CDCl_3$) 137.2 (Cq), 129.0 (CH), 128.9 (CH), 125.8 (CH), 117.6 (CH), 33.7 (CH_2), 32.1 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 22.8 (CH_2), 14.3 (CH_3).

Iodohydroxyborylation

Dimethyl 3-(2-hydroxyethyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate (23aa)



23aa
Chemical Formula: $C_{12}H_{19}IO_5$
Exact Mass: 370.0277

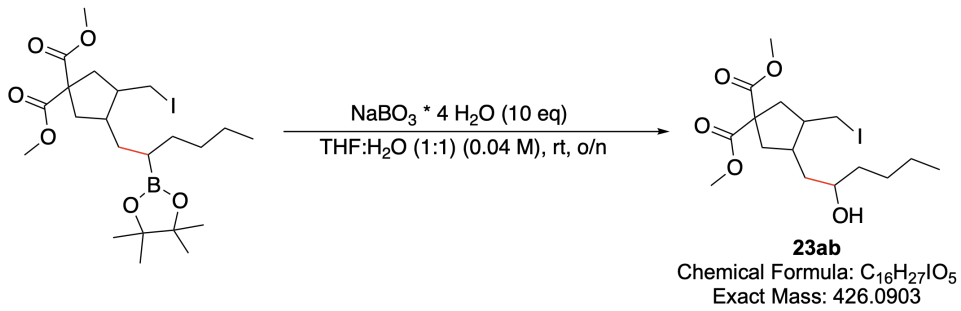
To a solution of dimethyl 3-(iodomethyl)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-cyclopentane-1,1- dicarboxylate (664 mg, 1.35 mmol, 1 eq) in THF/H_2O (1:1, 23 mL) was added sodium perborate (2.08 g, 13.5 mmol) in one portion. The reaction mixture was stirred at rt for 14h. The reaction mixture was then partitioned between Et_2O (20 mL) and water (25 mL). The aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic phases were washed

with brine (25 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford a colorless oil. Purification by flash column chromatography (40% EtOAc:heptanes) delivered the desired **23aa** (456 mg, 1.23 mmol, 91%, dr = 8:2).

Colorless oil; Rf: 0.35 (1:1 heptanes:EtOAc); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 3.79–3.63 (m, 8H), 3.21 (dd, *J* = 9.7, 6.5 Hz, 1H), 3.08 (t, *J* = 9.4 Hz, 1H), 2.64–2.48 (m, 2H), 2.44–2.35 (m, 1H), 2.32–2.10 (m, 3H), 1.87–1.64 (m, 2H), 1.52–1.30 (m, 3H).

The physical and spectral data are in accordance with literature data:
Kitagawa, O.; Inoue, T.; Hirano, K.; Taguchi, T. *Journal of Organic Chemistry* **1993**, *58* (11), 3106–3112.

Dimethyl 3-(2-hydroxyhexyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate (23ab)

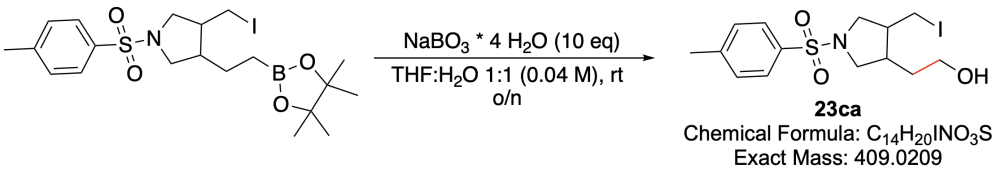


To a solution of dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl- 1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate (233 mg, 0.415 mmol) in THF/H_2O (1:1, 10.4 mL) was added sodium perborate (639 mg, 4.15 mmol) in one portion. The reaction mixture was stirred at rt for 16h. The reaction mixture was then partitioned between EtOAc (20 mL) and water (25 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic phases were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude product as a colorless oil. Purification by flash column chromatography (30% EtOAc:heptanes) delivered the desired **23ab** (146 mg, 0.342 mmol, 83%, dr = 4:4:1:1).

Orange oil; Rf: 0.4 (7:3 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.73–3.66 (m, 6H), 3.59 (dddt, *J* = 14.8, 7.0, 5.1, 2.9 Hz, 1H), 3.39–3.13 (m, 1H), 3.02 (td, *J* = 9.5, 5.6 Hz, 1H), 2.70–2.44 (m, 2H), 2.43–2.31 (m, 1H), 2.23–2.08 (m, 2H), 1.57–1.21 (m, 8H), 0.88 (tt, *J* = 7.3, 2.3 Hz, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.6 (Cq), 173.5 (Cq), 173.4 (Cq), 173.2 (Cq), 173.1 (Cq), 173.0 (Cq), 173.0 (Cq), 172.9 (Cq), 172.8 (Cq), 172.8 (Cq), 172.8 (Cq), 70.9 (Cq), 70.8 (CH), 70.4 (CH), 70.2 (CH), 70.0 (CH), 58.8 (Cq), 58.5 (Cq), 57.9 (Cq), 57.7 (Cq), 53.0 (CH_3), 52.9 (CH_3), 52.9 (CH_3), 52.8 (CH_3), 52.8 (CH_3), 52.8 (CH_3), 47.2 (CH), 46.9 (CH), 45.7 (CH), 45.6 (CH), 42.5 (CH), 41.5 (CH_2), 41.3 (CH_2), 41.3 (CH_2), 41.2 (CH_2), 41.0 (CH_2), 40.7 (CH_2), 40.1 (CH_2), 40.0 (CH), 39.9(CH_2), 39.0 (CH), 38.7 (CH_2), 38.3 (CH_2), 38.2 (CH_2), 38.2 (CH_2), 38.1

(CH_2), 37.4 (CH_2), 37.3 (CH_2), 36.3 (CH_2), 36.0 (CH_2), 27.9 (CH_2), 27.9 (CH_2), 27.8 (CH_2), 27.7 (CH_2), 27.6 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.7 (CH_2), 14.1 (CH_3), 11.2 (CH_2), 10.4 (CH_2), 7.7 (CH_2), 7.6 (CH_2); IR (neat): ν_{max} = 3459, 2952, 2927, 2858, 1727, 1434, 1253, 1197, 1164, 731 cm^{-1}; HRMS (ESI): Calculated for $C_{16}H_{27}IO_5$ $[M+Na]^+$: 449.0903; found: 449.0785.

2-(4-(iodomethyl)-1-tosylpyrrolidin-3-yl)ethan-1-ol (23ca)



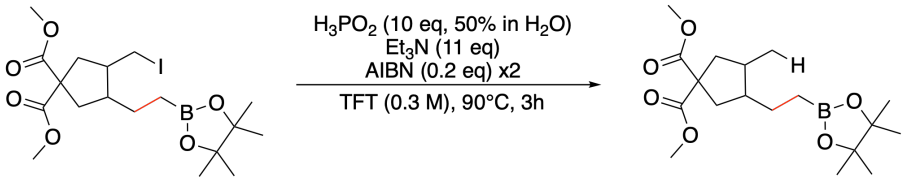
23ca
Chemical Formula: $C_{14}H_{20}INO_3S$
Exact Mass: 409.0209

To a solution of 3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl- 1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine (173 mg, 0.301 mg) in THF/H_2O (1:1, 7.4 mL) was added sodium perborate (463 mg, 3.01 mmol) in one portion. The reaction mixture was stirred at rt for 16h. The reaction mixture was then partitioned between EtOAc (50 mL) and water (50 mL). The aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic phases were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude product as a colorless oil. Purification by flash column chromatography (60% EtOAc:heptanes) delivered the desired **23ca** (108 mg, 0.259 mmol, 86%, dr = 6:4).

Light yellow oil; Rf: 0.2 (1:1 heptanes:EtOAc); ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.1, 5.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 3.59 (qd, *J* = 6.9, 3.4 Hz, 2H), 3.54 – 3.17 (m, 3H), 3.14–2.89 (m, 2H), 2.64 (t, *J* = 10.1 Hz, 1H), 2.49 (dt, *J* = 10.7, 5.4 Hz, 1H), 2.42 (s, 3H), 2.35–2.22 (m, 1H), 1.71 – 1.49 (m, 2H), 1.43–1.20 (m, 1H); ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 143.8 (Cq_{Ar}), 133.7 (Cq_{Ar}), 133.2 (Cq_{Ar}), 129.9 (2 x CH_{Ar}), 127.7 (CH_{Ar}), 127.5 (CH_{Ar}), 60.9 (CH_2), 60.8 (CH_2), 54.1 (CH_2), 53.6 (CH_2), 53.1 (CH_2), 51.2 (CH_2), 46.3 (CH), 45.0 (CH), 41.7 (CH), 39.2 (CH), 34.9 (CH_2), 29.8 (CH_2), 26.3 (CH_2), 8.8 (CH_3), 7.0 (CH_2), 3.9 (CH_2); IR (neat): ν_{max} = 3525, 2935, 2879, 1596, 1336, 1289, 1155, 1015, 812, 584 cm^{-1} ; HRMS (ESI): Calculated for $C_{14}H_{21}O_3NIS$ $[M+H]^+$: 410.0209; found: 410.0283.

Hydroborylalkylation

Dimethyl 3-methyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentane-1,1-dicarboxylate (24aa)

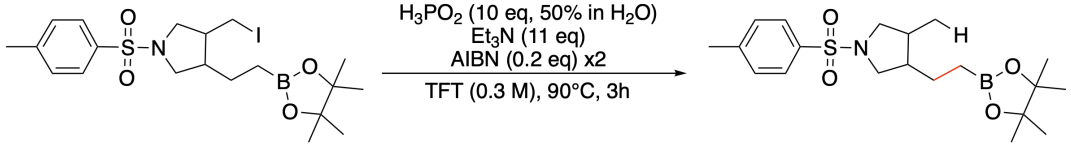


24aa
Chemical Formula: $C_{18}H_{31}BO_6$
Exact Mass: 354.2214

An oven-dried 10 mL two-neck round bottom flask was charged with dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate (250 mg, 0.521 mmol), TFT (1.5 mL), hypophosphorous acid (0.550 mL, 10.1 mmol, 50 % in H_2O,), Et_3N (0.770 mL, 11.0 mmol) and AIBN (16 mg, 0.2 mmol). The reaction mixture was heated at 90 °C for 1.5 h. After partial cooling, another portion of AIBN (16 mg, 0.2 mmol) was added and the reaction mixture heated at 90 °C for an additional 1.5 h. The reaction mixture was then cooled down to rt, partitioned between TBME (25 mL) and 2 M aq. HCl (15 mL). The organic phase was washed with 1 M aq. HCl (15 mL), and the combined aqueous phases were back-extracted with TBME (1 x 10 mL). The combined organic phases were successively washed with 2 M aq. NaOH (15 mL), 1 M aq. NaOH (15 mL), sat. aq. $Na_2S_2O_3$ (25 mL), sat. aq. $NaHCO_3$ (25 mL), and brine (25 mL), then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Filtration over a SiO_2 pad, using Et_2O as eluent (200 mL), delivered the desired **24aa** (159 mg, 0.449 mmol, 86%, dr = 8:2).

Colorless oil; Rf: 0.33 (8:2 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.70 (d, J = 1.5 Hz, 6H), 2.60–2.30 (m, 2H), 2.16 (qd, J = 7.0, 4.7 Hz, 1H), 2.03–1.84 (m, 3H), 1.55 (d, J = 4.6 Hz, 1H), 1.44 (ddt, J = 14.9, 11.8, 5.9 Hz, 1H), 1.32 (ddt, J = 11.9, 8.1, 6.0 Hz, 1H), 1.24 (s, 12H), 0.82 (d, J = 7.2 Hz, 3H), 0.80–0.66 (m, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.8 (Cq), 173.6 (Cq), 83.1 (Cq), 59.0 (Cq), 58.3 (Cq), 52.8 (CH_3), 52.7 (CH_3), 49.2 (CH), 45.2 (CH), 43.1 (CH_2), 41.9 (CH_2), 40.5 (CH_2), 40.0 (CH), 38.4 (CH_2), 35.6 (CH), 29.9 (CH_2), 27.6 (CH_2), 25.0 (CH_3), 24.0 (CH_2), 18.0 (CH_3), 14.9 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 34.0; IR (neat): ν_{max} = 2976, 2953, 2930, 1732, 1371, 1315, 1246, 1143, 966, 846 cm^{-1}; HRMS (ESI): Calculated for $C_{18}H_{31}BO_6$ $[M+H]^+$: 355.2214; found: 355.2287.

3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine (24ca)

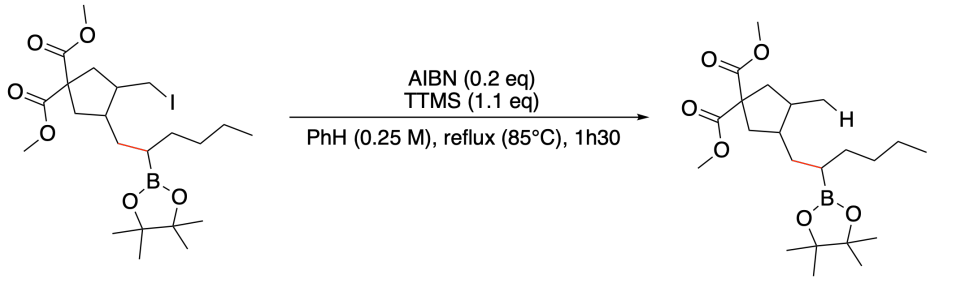


24ca
Chemical Formula: $C_{20}H_{32}BNO_4S$
Exact Mass: 393.2145

An oven-dried 10 mL one-neck round bottom flask was charged withwith 3-(iodomethyl)-1-(p-tolylsulfo- nyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine (342 mg, 0.659 mmol), TFT (2 mL), hypophosphorous acid (0.730 mL, 6.66 mmol, 50 % in H_2O), Et_3N (1 mL, 7.25 mmol) and AIBN (21.6 mg, 0.132 mmol). The reaction mixture was heated at 90 °C for 1.5 h. After partial cooling, another portion of AIBN (21.6 mg, 0.132 mmol) was added and the reaction mixture heated at 90 °C for an additional 1.5 h. The mixture was then cooled to rt, partitioned between TBME (25 mL) and 2 M aq. HCl (15 mL). The organic phase was washed with 1 M aq. HCl (15 mL), and the combined aqueous phases were back-extracted with TBME (1 x 10 mL). The combined organic phases were successively washed with 2 M aq. NaOH (15 mL), 1 M aq. NaOH (15 mL), sat. aq. $Na_2S_2O_3$ (25 mL), sat. aq. $NaHCO_3$ (25 mL), and brine (25 mL), then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (20% EtOAc:heptanes) delivered the desired **24ca** (194 mg, 0.493 mmol, 75%, dr = 6:4).

Sticky colorless oil; Rf: 0.34 (8:2 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.72–7.68 (m, 2H), 7.32–7.28 (m, 2H), 3.54–3.31 (m, 2H), 3.06–2.74 (m, 2H), 2.42 (d, J = 2.8 Hz, 3H), 2.15 (ddq, J = 10.2, 7.0, 3.5 Hz, 1H), 1.97–1.85 (m, 1H), 1.69–1.45 (m, 3H), 1.41–1.30 (m, 1H), 1.21 (d, J = 2.6 Hz, 14H), 0.93–0.62 (m, 5H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 13C NMR 143.3 (Cq_{Ar}), 143.2 (Cq_{Ar}), 134.4 (Cq_{Ar}), 134.1 (Cq_{Ar}), 129.7 (CH_{Ar}), 129.7 (CH_{Ar}), 127.7 (CH_{Ar}), 127.6 (CH_{Ar}), 83.3 (Cq), 83.2 (Cq), 55.3 (CH_2), 55.2 (CH_2), 53.5 (CH_2), 51.0 (CH_2), 48.2 (CH), 44.5 (CH), 38.8 (CH), 35.0 (CH_2), 26.2 (CH_3), 25.3 (CH_3), 25.0 (CH_3), 24.9 (CH_3), 23.6 (CH_3), 22.0 (CH_2), 21.7 (CH_3), 16.6 (CH_3), 13.1 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methylene adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 33.6; IR (neat): ν_{max} = 2974.6, 2933.2, 2871.5, 1301.7, 1250.6, 1157.1, 1090.5, 1027.9, 836.00, 663.39 cm^{-1}; HRMS (EI): Calculated for $C_{20}H_{32}O_4NBS$ $[M+Na]^+$: 416.2145; found: 416.2040.

Dimethyl 3-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane--1,1-dicarboxylate (24ab)

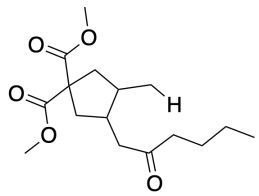


24ab
Chemical Formula: $C_{22}H_{39}BO_6$
Exact Mass: 410.2840

To a solution of dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate (585 mg, 1.09 mmol) in dry benzene (4 mL) were added AIBN (35.8 mg, 0.218 mmol) and TTMS (0.374 mL, 1.21 mmol). The reaction mixture was heated under reflux (90°C) for 90 minutes. After cooling down to rt, the reaction mixture was partitioned between NH_4Cl (30 mL) and Et_2O (30 mL). The aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic phases were then washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a yellow oil. Purification by flash column chromatography (10% Et2O:pentane) delivered the desired **24ab** (378 mg, 0.921 mmol, 85%, dr = 4:4:1:1).

Orange oil; Rf: 0.39 (8:2 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.68 (qt, J = 4.0, 2.2 Hz, 6H), 2.55-2.24 (m, 2H), 2.19–2.04 (m, 1H), 2.04-1.85 (m, 2H), 1.52–1.14 (m, 20H), 0.99–0.74 (m, 6H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.7 (Cq), 173.6 (Cq), 173.6 (Cq), 173.5 (Cq), 173.5 (Cq), 173.5 (Cq), 173.4 (Cq), 173.1 (Cq), 173.1 (Cq), 173.0 (Cq), 172.9 (Cq), 172.8 (Cq), 172.4 (Cq), 83.1 (Cq), 83.1 (Cq), 83.0 (Cq), 83.0 (Cq), 83.0 (Cq), 59.1 (Cq), 58.9 (Cq), 58.8 (Cq), 58.6 (Cq), 58.4 (Cq), 58.4 (Cq), 58.3 (Cq), 52.9 (CH_3), 52.8 (CH_3), 52.7 (CH_3), 52.7 (CH_3), 46.9 (CH), 46.0 (CH), 45.8 (CH), 45.0 (CH), 42.9 (CH_2), 42.7 (CH_2), 42.3 (CH), 42.2 (CH), 42.1 (CH), 42.0 (CH), 41.9 (CH_2), 41.7 (CH_2), 41.0 (CH_2), 40.7 (CH_2), 40.6 (CH), 40.3 (CH_2), 38.8 (CH_2), 38.7 (CH_2), 38.5 (CH_2), 38.4 (CH_2), 36.3 (CH_2), 36.0 (CH_2), 35.2 (CH_2), 34.7 (CH_2), 32.2 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 31.7 (CH_2), 31.6 (CH_2), 31.6 (CH_2), 31.5 (CH_2), 31.4 (CH_2), 30.9 (CH_2), 30.6 (CH_2), 30.6 (CH_2), 30.3 (CH_2), 29.7 (CH_2), 25.0 (CH_3), 24.9 (CH_3), 24.8 (CH_3), 23.1 (CH_2), 23.0 (CH_2), 18.1 (CH_3), 17.9 (CH_3), 15.1 (CH_3), 14.8 (CH_3), 14.2 (CH_3), 14.2 (CH_3). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) 34.5; IR (neat): ν_{max} = 2954, 2922, 1732, 1371, 1314, 1250, 1196, 1142, 965, 732 cm^{-1}; HRMS (EI): Calculated for $C_{22}H_{39}BO_6$ $[M\text{-}CH_3]^+$: 395.2804; found: 395.2606.

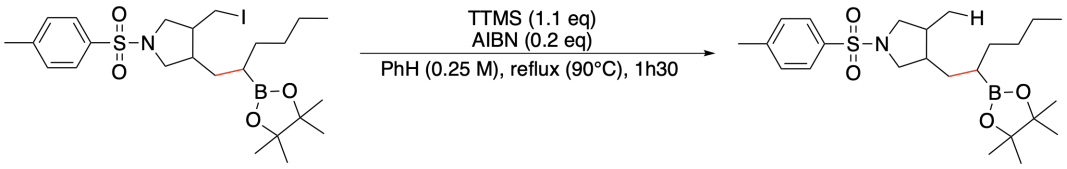
Dimethyl 3-methyl-4-(2-oxohexyl)cyclopentane-1,1-dicarboxylate (24ab')



24ab'
Chemical Formula: $C_{16}H_{26}O_5$
Exact Mass: 298.1780

Orange oil; Rf: 0.38 (8:2 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.70 (d, J = 1.2 Hz, 6H), 2.62–2.42 (m, 2H), 2.42–2.20 (m, 5H), 1.99–1.75 (m, 2H), 1.53 (p, J = 7.5 Hz, 2H), 1.42–1.19 (m, 4H), 0.89 (t, J = 7.4 Hz, 3H), 0.81 (d, J = 7.1 Hz, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 210.5 (Cq), 173.4 (Cq), 173.2 (Cq), 58.9 (Cq), 52.9 (CH_3), 52.8 (CH_3), 43.0 (CH_2), 41.5 (CH_2), 39.0 (CH_2), 37.9 (CH), 35.7 (CH), 26.0 (CH_2), 22.5 (CH_2), 15.3 (CH_3), 14.0 (CH_3); IR (neat): ν_{max} = 2955, 2930, 2870, 1731, 1715, 1435, 1250, 1196, 1144, 1050 cm^{-1}; HRMS (ESI): Calculated for $C_{16}H_{26}O_5$ $[M+H]^+$: 299.1780; found: 299.1856.

3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine (24cb)



24cb
Chemical Formula: $C_{24}H_{40}BNO_4S$
Exact Mass: 449.2771

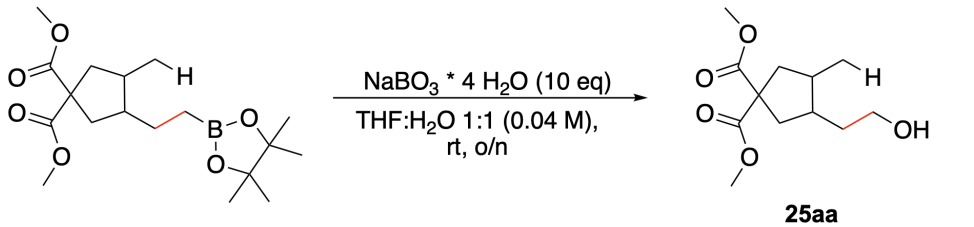
To a solution of 3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetrame- thyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine (255 mg, 0.443 mmol) in dry benzene (2 mL) were added AIBN (15 mg, 0.0913 mmol) and TTMS (0.150 mL, 0.488 mmol). The reaction mixture was heated under reflux (90°C) for 1h30. After cooling down to rt, the reaction mixture was partitioned between NH_4Cl (30 mL) and Et_2O (30 mL). The aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic phases were then washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a yellow oil. Purification by flash column chromatography (Macherey-Nagel Silica 60, 0.015–0.04 mm) (15% Et_2O:pentane) delivered the desired **24cb** (156 mg, 0.346 mmol, 78%, dr = 4:3:2:1).

Colorless oil; Rf: 0.31 (8:2 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.70 (ddd, J = 7.7, 4.4, 3.2 Hz, 2H), 7.32–7.28 (m, 2H), 3.57–3.28 (m, 2H), 3.09–2.70 (m, 2H), 2.42 (d, J = 2.1 Hz, 3H), 2.14 (dddd, J = 13.4, 9.5, 6.3, 2.5 Hz, 1H), 1.97 (m, 1H), 1.69–1.52 (m, 1H), 1.51–1.12 (m, 20H), 1.09–0.94 (m, 1H), 0.93–0.75 (m, 5H), 0.67 (dd, J = 37.9, 7.1 Hz, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 143.3 (Cq_{Ar}), 143.2 (Cq_{Ar}), 143.1 (Cq_{Ar}), 134.5 (CH_{Ar}), 134.4 (CH_{Ar}), 134.3

(CH_{Ar}), 134.2 (CH_{Ar}), 129.7 (CH_{Ar}), 129.7 (CH_{Ar}), 129.6 (CH_{Ar}), 127.7 (CH_{Ar}), 127.6 (CH_{Ar}), 83.4 (Cq), 83.2 (Cq), 83.2 (Cq), 83.1 (Cq), 55.6 (CH_2), 55.0 (CH_2), 54.9 (CH_2), 54.0 (CH_2), 53.9 (CH_2), 51.3 (CH_2), 51.3 (CH_2), 46.0 (CH), 45.3 (CH), 41.8 (CH), 41.6 (CH), 39.5 (CH), 39.2 (CH), 35.8 (CH), 34.8 (CH), 34.3 (CH), 33.2 (CH_2), 31.9 (CH_2), 31.7 (CH_2), 31.5 (CH_2), 31.5 (CH_2), 31.4 (CH_2), 31.3 (CH_2), 30.8 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 25.0 (CH_3), 24.9 (CH_3), 24.8 (CH_3), 23.1 (CH_2), 23.0 (CH_2), 22.9 (CH_2), 22.8 (CH_2), 21.6 (CH_3), 16.7 (CH_3), 16.3 (CH_3), 14.2 (CH_3), 14.1 (CH_3), 13.2 (CH_3), 13.0 (CH_3); **^{11}B NMR** (128 MHz, $CDCl_3$) 33.6. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; IR (neat): ν_{max} = 2957, 2923, 2871, 2856, 1343, 1161, 1142, 662, 588 cm^{-1}; HRMS (EI): Calculated for $C_{24}H_{40}O_4NBS$ $[M+H]^+$: 450.2771; found: 450.2840.

Hydroxymethylation

Dimethyl 3-(2-hydroxyethyl)-4-methyl-cyclopentane-1,1-dicarboxylate (25aa)



25aa
Chemical Formula: $C_{12}H_{20}O_5$
Exact Mass: 244.1311

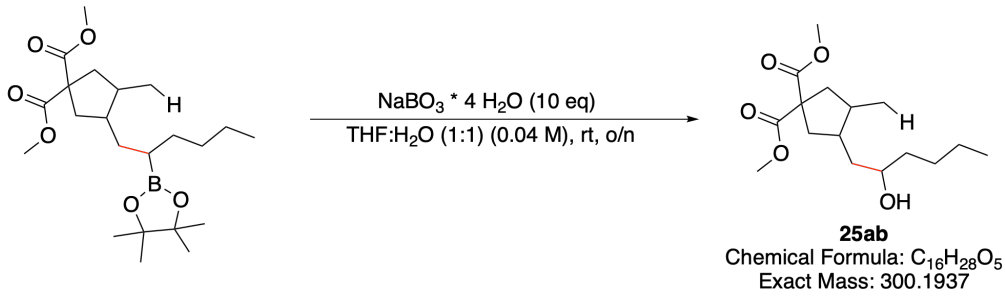
To a solution of dimethyl 3-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate (157 mg, 0.443 mmol) in THF/H_2O (1:1, 11 mL) was added sodium perborate (682 mg, 4.43 mmol) in one portion. The reaction mixture was stirred at rt under N_2 atmosphere for 16h. The reaction mixture was partitioned between Et_2O (30 mL) and water (30 mL). The aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a colorless oil. Purification by flash column chromatography (Macherey-Nagel Silica 60, 0.015–0.04 mm) (40% Et_2O:pentane) delivered the desired **25aa** (76 mg, 0.311 mmol, 70%, dr = 8:2).

Mix of dias: Colorless oil; Rf: 0.18 (6:4 pentane:Et_2O); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.69 (d, J = 1.5 Hz, 6H), 3.63 (dqt, J = 10.5, 6.9, 3.6 Hz, 2H), 2.58–2.30 (m, 2H), 2.17 (qd, J = 6.9, 4.9 Hz, 1H), 2.11–1.94 (m, 3H), 1.88–1.57 (m, 2H), 1.56–1.31 (m, 2H), 1.26–1.16 (m, 1H), 0.91 (dd, J = 56.7, 6.7 Hz, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.6 (Cq), 173.5 (Cq), 65.9 (CH_2), 62.0 (CH_2), 61.9 (CH_2), 58.9 (Cq), 58.4 (Cq), 52.9 (CH_3), 52.8 (CH_3), 43.7 (CH), 42.7 (CH_2), 41.6 (CH_2), 40.7 (CH_2), 40.4 (CH), 39.3 (CH), 38.5 (CH_2), 36.5 (CH_2), 36.0 (CH), 32.9 (CH_2), 17.8 (CH_3), 15.0 (CH_3); IR (neat): ν_{max} = 3398, 2954, 2929, 2891, 1727, 1434, 1252, 1198,

1167, 1141 cm^{-1}; HRMS (ESI): Calculated for $C_{12}H_{20}O_5$ $[M+H]^+$: 245.1311; found: 245.1392.

Major dia: Colorless oil; Rf: 0.18 (6:4 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.70 (d, *J* = 1.5 Hz, 6H), 3.69–3.61 (m, 2H), 2.39 (ddd, *J* = 31.4, 13.1, 6.5 Hz, 2H), 2.18 (qd, *J* = 7.0, 5.1 Hz, 1H), 2.12–1.94 (m, 3H), 1.75 (s, 2H), 1.45 (ddt, *J* = 13.4, 8.5, 6.6 Hz, 1H), 0.85 (d, *J* = 7.1 Hz, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.6 (Cq), 173.5 (Cq), 62.0 (CH_2), 58.9 (Cq), 52.9 (2 x CH_3), 41.6 (CH_2), 39.3 (CH), 38.5 (CH_2), 36.0 (CH), 32.9 (CH_2), 15.0 (CH_3); IR (neat): ν_{max} = 3362, 2953, 2934, 2875, 1727, 1434, 1252, 1197, 1140, 1045 cm^{-1}; HRMS (ESI): Calculated for $C_{12}H_{20}O_5$ $[M+H]^+$: 245.1311; found: 245.1385.

Dimethyl 3-(2-hydroxyhexyl)-4-methyl-cyclopentane-1,1-dicarboxylate (25ab)



25ab
Chemical Formula: $C_{16}H_{28}O_5$
Exact Mass: 300.1937

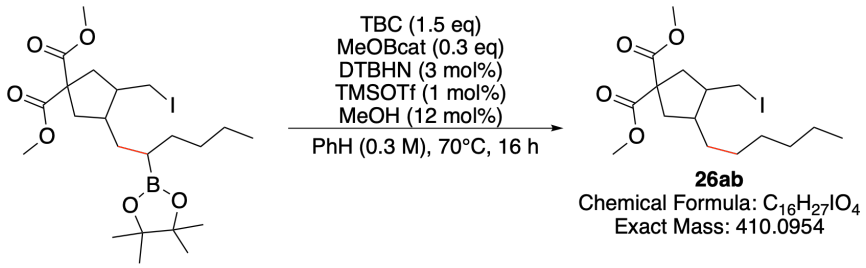
To a solution of dimethyl 3-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate (86.6 mg, 0.211 mmol) in THF/H_2O (1:1, 5 mL) was added sodium perborate (325 mg, 2.11 mmol) in one portion. The reaction mixture was stirred at rt under N_2 atmosphere for 16h. The reaction mixture was partitioned between EtOAc (20 mL) and water (20 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic phases were washed with brine (25 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude product as a colorless oil. Purification by flash column chromatography (40% Et_2O:pentane) delivered the desired **25ab** (48.8 mg, 0.162 mmol, 77%, dr = 37:32:17:14).

Colorless oil; Rf: 0.43 (1:1 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.69 (d, *J* = 2.1 Hz, 6H), 3.59 (q, *J* = 5.5 Hz, 1H), 2.63–2.30 (m, 2H), 2.25–2.08 (m, 2H), 2.06–1.94 (m, 2H), 1.86–1.22 (m, 11H), 1.00–0.78 (m, 7H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.6 (Cq), 173.6 (Cq), 173.5 (Cq), 173.4 (Cq), 173.4 (Cq), 173.4 (Cq), 71.4 (CH), 71.1 (CH), 70.5 (CH), 58.9 (Cq), 52.9 (CH_3), 52.8 (CH_3), 52.8 (CH_3), 52.8 (CH_3), 44.5 (CH), 43.1 (CH), 42.7 (CH_2), 42.5 (CH_2), 41.7 (CH_2), 41.6 (CH_2), 41.4 (CH_2), 41.3 (CH_2), 40.7 (CH), 40.6 (CH_2), 40.5 (CH), 39.7 (CH), 39.0 (CH), 38.8 (CH_2), 38.4 (CH_2), 38.2 (CH_2), 38.1 (CH_2), 37.8 (CH_2), 37.6 (CH_2), 37.5 (CH_2), 37.2 (CH_2), 36.5 (CH), 35.7 (CH), 29.8 (CH_2), 28.0 (CH_2), 27.8 (CH_2), 27.7 (CH_2), 22.8 (CH_2), 18.0 (CH_3), 17.5 (CH_3), 15.1 (CH_3), 15.0 (CH_3), 14.2 (CH_3), 14.2 (CH_3); IR (neat): ν_{max} = 3446, 2954, 2929, 2872, 1730, 1435, 1251, 1197, 1144, 1032 cm^{-1}; HRMS (EI): Calculated for $C_{16}H_{28}O_5$

[M-OH]$^+$: 283.1937; found: 283.1909.

Hydromethylation and hydroalkylation

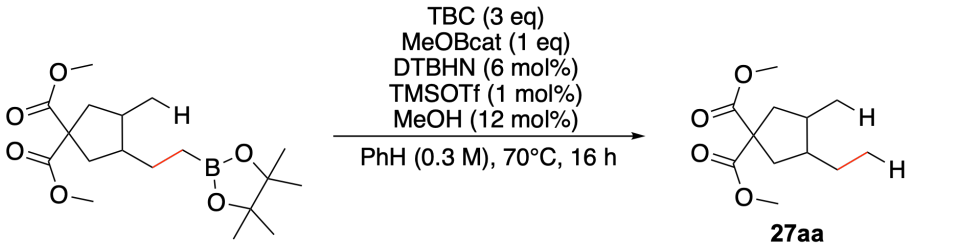
Dimethyl 3-hexyl-4-(iodomethyl)cyclopentane-1,1-dicarboxylate (26ab)



A flame-dried 10 mL round-bottom flask equipped with a reflux condenser was charged with dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate (550 mg, 1.03 mmol), 4-tert-butylcatechol (256 mg, 1.54 mmol), benzene (3 mL), 2-methoxy-1,3,2-benzodioxaborole (0.310 mL, 0.308 mmol, 1 M in benzene), TMSOTf (0.205 mL, 0.05 M in DCM, 0.01 mmol), MeOH (0.005 mL, 0.123 mmol) and DTBHN (5.4 mg, 0.038 mmol). The reaction mixture was heated at 70 °C for 14 h. After cooling down to rt, the reaction mixture was partitioned between TBME (100 mL) and water (100 mL). The aqueous layer was extracted TBME (3 x 40 mL). The combined organic phases were washed with sat. aq. $NaHCO_3$ (2 x 60 mL), brine (100 mL), then dried over Na_2SO_4, filtered over Celite and concentrated under reduced pressure to give the crude as a brown oil. Purification by flash column chromatography (7% Et_2O:pentane) delivered the desired **26ab** (166 mg, 0.405 mmol, 40%, dr 8:2).

Colorless oil; Rf: 0.42 (9:1 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.73–3.65 (m, 6H), 3.36–3.16 (m, 1H), 3.11–2.98 (m, 1H), 2.64–2.41 (m, 2H), 2.39–2.30 (m, 1H), 2.20–2.02 (m, 2H), 2.02–1.79 (m, 1H), 1.38–1.07 (m, 10H), 0.87–0.81 (m, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.1 (Cq), 173.0 (Cq), 172.9 (Cq), 172.8 (Cq), 172.5 (Cq), 172.4 (Cq), 172.3 (Cq), 64.1 (Cq), 62.1 (Cq), 58.6 (Cq), 57.6 (Cq), 52.9 ($CH3_3$), 52.8 ($CH3_3$), 52.6 ($CH3_3$), 52.5 ($CH3_3$), 52.5 ($CH3_3$), 46.9 (CH), 45.5 (CH), 45.1 (CH), 44.9 (CH), 43.4 (CH), 42.6 (CH), 41.9 ($CH3_2$), 41.6 (CH), 41.5 ($CH3_2$), 41.0 ($CH3_2$), 40.8 ($CH3_2$), 40.6 ($CH3_2$), 40.1 ($CH3_2$), 39.3 ($CH3_2$), 38.4 ($CH3_2$), 37.3 ($CH3_2$), 35.3 ($CH3_2$), 34.3 ($CH3_2$), 33.5 ($CH3_2$), 31.8 ($CH3_2$), 31.6 ($CH3_2$), 31.1 ($CH3_2$), 30.9 ($CH3_2$), 29.5 ($CH3_2$), 29.4 ($CH3_2$), 28.6 ($CH3_2$), 28.0 ($CH3_2$), 27.9 ($CH3_2$), 23.0 ($CH3_2$), 22.7 ($CH3_2$), 22.6 ($CH3_2$), 14.2 ($CH3_3$), 14.2 ($CH3_3$), 14.1 ($CH3_3$), 11.0 ($CH3_3$), 7.8 ($CH3_3$); IR (neat): ν_{max} = 2952, 2924, 2854, 1731, 1433, 1249, 1195, 1164, 1141 cm^{-1}; HRMS (ESI): Calculated for $C_{16}H_{27}IO_4$ [M+Na]$^+$: 423.0954; found: 423.1024.

Dimethyl 3-ethyl-4-methyl-cyclopentane-1,1-dicarboxylate (27aa)



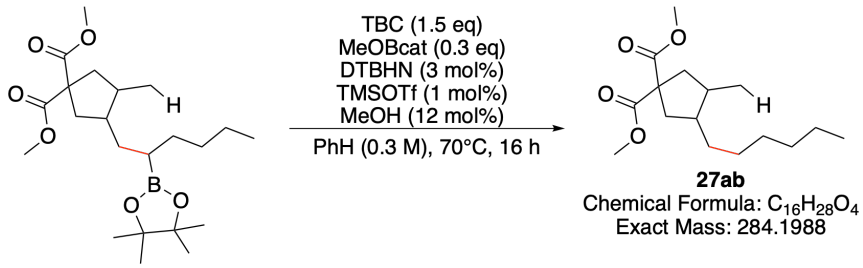
27aa
Chemical Formula: $C_{12}H_{20}O_4$
Exact Mass: 228.1362

A flame-dried round-bottom flask equipped with a reflux condenser was chareged with dimethyl 3- methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate (90.2 mg, 0.255 mmol), 4-tert-butylcatechol (127 mg, 0.764 mmol), benzene (0.8 mL), 2-methoxy-1,3,2-benzodioxaborole (0.255 mL, 0.255 mmol, 1 M in benzene), TMSOTf (0.055 mL, 0.0027 mmol, 0.05 M in DCM), MeOH (1.2 μl, 0.031 mmol) and DTBHN (1.3 mg, 0.00764 mmol). The reaction mixture was heated at 70 °C for 1 h. After partial cooling, another portion of DTBHN (1.3 mg, 0.00764 mmol) was added and the reaction mixture heated for an additionnal 1 h at 70°C. After cooling down to rt, the reaction mixture was partitioned between TBME (50 mL) and water (50 mL). The aqueous layer was extracted TBME (3 x 20 mL). The combined organic phases were washed with sat. aq. $NaHCO_3$ (2 x 30 mL), brine (50 mL), then dried over Na_2SO_4, filtered over Celite and concentrated under reduced pressure to give the crude as a brown oil. Purification by flash column chromatography (Gradient 0-5% EtOAc:heptanes) delivered the desired **27aa** (36.8 mg, 0.161 mmol, 63%, dr = 8:2).

Yellow oil; Rf: 0.64 (8:2 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.70 (s, 6H), 2.58–2.30 (m, 2H), 2.16 (qd, *J* = 7.0, 4.9 Hz, 1H), 2.02–1.91 (m, 2H), 1.91–1.70 (m, 1H), 1.42–1.29 (m, 1H), 1.27–1.14 (m, 2H), 1.02–0.79 (m, 6H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.8 (Cq), 173.6 (Cq), 173.2 (Cq), 59.0 (Cq), 58.3 (Cq), 52.8 (CH), 52.7 (CH), 48.7 (CH), 46.1 (CH), 44.7 (CH_2), 43.3 (CH_2), 43.0 (CH_2), 41.8 (CH_2), 40.4 (CH_2), 40.0 (CH), 38.4 (CH_2), 36.2 (CH), 35.7 (CH), 34.7 (CH), 34.2 (CH), 31.1 (CH_2), 27.6 (CH), 26.1 (CH_2), 24.7 (CH), 22.7 (CH_2), 16.8 (CH_3), 13.2 (CH_3), 12.9 (CH_3), 12.6 (CH_3).

The physical and spectral data are in accordance with literature data:
Kuang, Y.; Anthony, D.; Katigbak, J.; Marrucci, F.; Humagain, S.; Diao, T. *Chem* **2017**, *3* (2), 268–280.

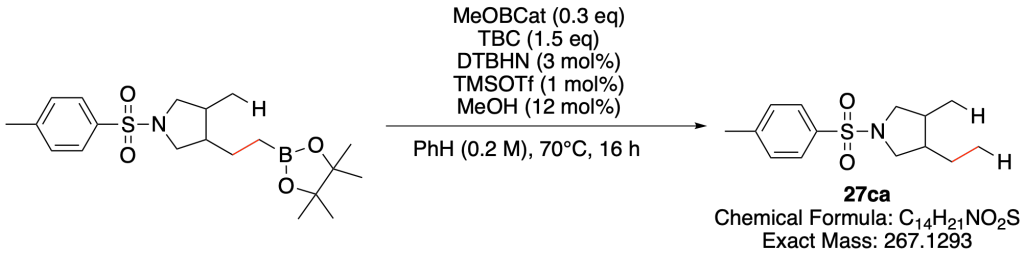
Dimethyl 3-hexyl-4-methyl-cyclopentane-1,1-dicarboxylate (27ab)



A flame-dried 5 mL one neck round-bottom flask, equipped with a cold-finger condenser, was charged with dimethyl 3-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate (198 mg, 0.483 mmol), tert-butyl catechol (120 mg, 0.724 mmol), benzene (1.4 mL), 2-methoxy-1,3,2-benzodioxaborole (MeOBcat) (0.145 mL, 0.145 mmol, 1 M in benzene), TMSOTf (0.1 mL, 0.005 mmol, 0.05 M in DCM), MeOH (2.5 μl, 0.0579 mmol) and DTBHN (2.5 mg, 0.0145 mmol). The reaction mixture was heated at 70 °C for 14 h. After cooling down to rt, the reaction mixture was partitioned between TBME (100 mL) and water (100 mL). The aqueous layer was extracted TBME (3 x 40 mL). The combined organic phases were washed with sat. aq. $NaHCO_3$ (2 x 60 mL), brine (100 mL), then dried over Na_2SO_4, filtered over Celite and concentrated under reduced pressure to give the crude as a brown oil. Purification by flash column chromatography (10% Et_2O:pentane) delivered the desired **27ab** (110 mg, 0.387 mmol, 80% (yield determined by using an internal standard in impure fractions), dr = 8:2).

Light yellow oil; Rf: 0.47 (9:1 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.70 (s, 6H), 2.44–2.29 (m, 2H), 2.14 (qd, J = 7.0, 4.7 Hz, 1H), 2.03–1.89 (m, 3H), 1.33–1.13 (m, 10H), 0.90–0.78 (m, 6H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.8 (Cq), 173.6 (Cq), 59.0 (Cq), 52.8 (CH_3), 42.8 (CH), 41.8 (CH_2), 38.7 (CH_2), 35.8 (CH), 32.0 (CH_2), 29.9 (CH_2), 29.7 (CH_2), 28.5 (CH_2), 22.8 (CH_2), 14.9 (CH_3), 14.2 (CH_3); IR (neat): ν_{max} = 2954, 2924, 2855, 1732, 1434, 1246, 1196, 1168, 1144 cm^{-1}; HRMS (ESI): Calculated for $C_{16}H_{28}O_4$ [M+Na]$^+$: 307.1988; found: 307.1873.

3-Ethyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine (27ca)

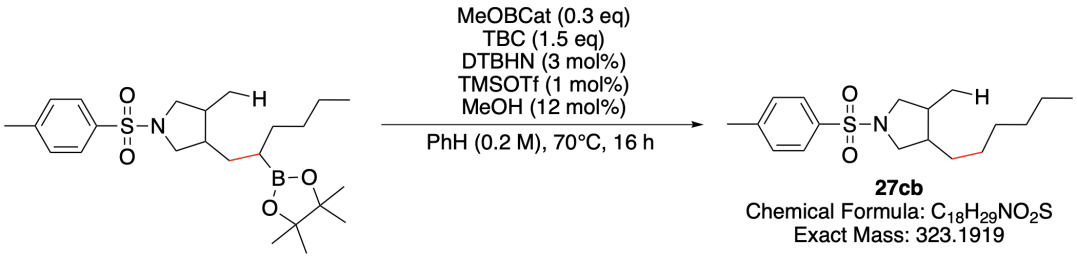


A flame-dried two neck round-bottom flask, equipped with a reflux condenser, was added 3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine (84.3

mg, 0.214 mmol), 4-tert-butylcatechol (TBC) (53.4 mg, 0.321 mmol), benzene (1 mL), 2-methoxy-1,3,2-benzodioxaborole (MeOBcat) (0.06 mL, 0.06 mmol, 1.0 M in benzene), TMSOTf (0.04 mL, 0.002 mmol, 0.05 M in DCM), MeOH (1 μl, 0.0257 mmol) and DTBHN (1 mg, 0.006 mmol). The reaction mixture was heated at 70 °C for 14 h. After cooling down to rt, the reaction mixture was partitioned between TBME (100 mL) and water (100 mL). The aqueous layer was extracted TBME (3 x 40 mL). The combined organic phases were washed with sat. aq. $NaHCO_3$ (2 x 60 mL), brine (100 mL), then dried over Na_2SO_4, filtered over Celite and concentrated under reduced pressure to give the crude as a black oil. Purification by flash column chromatography (10% EtOAc:heptanes) delivered the desired **27ca** (31.9 mg, 0.119 mmol, 56%, dr = 6:4).

Yellow oil; Rf: 0.64 (7:3 heptanes:EtOAc); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.4, 2.3 Hz, 2H), 7.31 (dd, *J* = 8.3, 2.4 Hz, 2H), 3.42 (dddd, *J* = 52.6, 14.7, 9.8, 6.8 Hz, 2H), 3.05–2.73 (m, 2H), 2.42 (d, *J* = 2.1 Hz, 3H), 2.16 (ddq, *J* = 9.9, 6.5, 3.4 Hz, 1H), 1.93–1.82 (m, 1H), 1.73–1.62 (m, 1H), 1.47 (ddq, *J* = 13.5, 7.7, 4.6 Hz, 1H), 1.34 – 1.21 (m, 1H), 1.17–0.98 (m, 1H), 0.90 (d, *J* = 6.5 Hz, 1H), 0.82 (q, *J* = 7.2 Hz, 3H), 0.68 (d, *J* = 7.1 Hz, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 143.3 (Cq_{Ar}), 143.3 (Cq_{Ar}), 134.4 (Cq_{Ar}), 134.1 (Cq_{Ar}), 129.7 (CH_{Ar}), 127.6 (CH_{Ar}), 127.5 (CH_{Ar}), 55.1 (CH_2), 53.3 (CH_2), 51.0 (CH_2), 47.6 (CH), 43.9 (CH), 38.8 (CH), 35.1 (CH), 31.7 (CH), 29.7 (CH), 24.8 (CH_2), 21.6 (CH_3), 20.7 (CH_2), 16.4 (CH_3), 13.0 (CH_3), 12.6 (CH_3), 12.4 (CH_3); IR (neat): ν_{max} = 2960, 2931, 2875, 1598, 1457, 1340, 1152, 1092, 661, 585 cm^{-1}; HRMS (ESI): Calculated for $C_{14}H_{21}NO_2S$ [M+Na]$^+$: 290.1293; found: 290.1181.

3-Hexyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine (27cb)



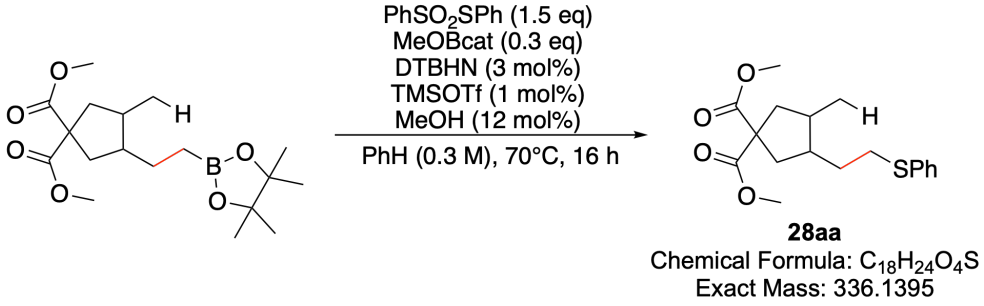
A flame-dried one neck 5 mL round-bottom flask, equipped with a reflux condenser, was charged with 3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine (118.2 mg, 0.263 mmol), TBC (65.6 mg, 0.394 mmo), benzene (1 mL), 2-methoxy-1,3,2-benzodioxaborole (MeOBcat) (0.08 mL, 0.08 mmol, 1.0 M in benzene), TMSOTf (0.05 mL, 0.00263 mmol, 0.05 M in DCM), MeOH (1.3 µl, 0.0316 mmol) and DTBHN (1.4 mg, 0.008 mmol). The reaction mixture was heated at 70 °C for 14 h. After cooling down to rt, the reaction mixture was partitioned between TBME (100 mL) and water (100 mL). The aqueous layer was extracted TBME (3 x 40 mL). The combined organic phases were washed with sat. aq. $NaHCO_3$ (2 x 60 mL), brine (100 mL), then dried over Na_2SO_4, filtered over Celite and concentrated under reduced pressure to give the crude as a black oil. Purification by flash column

chromatography (10% Et_2O:pentane) delivered the desired **27cb** (45.3 mg, 0.140 mmol, 53%, dr 6:4).

Yellow oil; Rf: 0.58 (7:3 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.3, 2.5 Hz, 2H), 7.31 (dd, *J* = 8.3, 2.4 Hz, 2H), 3.42 (dddd, *J* = 48.5, 11.3, 9.7, 6.8 Hz, 2H), 3.04–2.73 (m, 2H), 2.43 (d, *J* = 2.3 Hz, 3H), 2.14 (ddp, *J* = 10.5, 7.0, 3.6 Hz, 1H), 2.00–1.88 (m, 1H), 1.30–0.98 (m, 10H), 0.93–0.83 (m, 4H), 0.69 (d, *J* = 7.1 Hz, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 143.3 (Cq_{Ar}), 143.3 (Cq_{Ar}), 134.4 (CH_{Ar}), 134.2 (CH_{Ar}), 129.7 (CH_{Ar}), 127.6 (CH_{Ar}), 127.5 (CH_{Ar}), 55.1 (CH_2), 55.0 (CH_2), 53.6 (CH_2), 51.3 (CH_2), 46.0 (CH), 42.2 (CH), 39.2 (CH), 35.3 (CH), 32.1 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 29.5 (CH_2), 28.2 (CH_2), 28.1 (CH_2), 27.7 (CH_2), 22.7 (CH_2), 22.7 (CH_2), 21.7 (CH_3), 16.4 (CH_3), 14.2 (CH_3), 13.1 (CH_3); IR (neat): ν_{max} = 2955, 2924, 2855, 1342, 1153, 1092, 1042, 814, 662, 587 cm^{-1}; HRMS (ESI): Calculated for $C_{18}H_{21}NO_2S$ [M+Na]$^+$: 346.1919; found: 346.1811.

Hydrothiolation

Dimethyl 3-methyl-4-(2-phenylsulfanylethyl)cyclopentane-1,1-dicarboxylate (28aa)



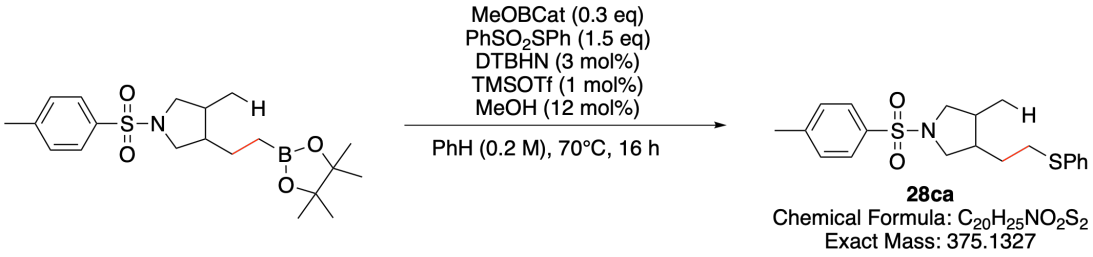
28aa
Chemical Formula: $C_{18}H_{24}O_4S$
Exact Mass: 336.1395

A flame-dried round-bottom flask equipped with a reflux condenser was added dimethyl 3-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate (116 mg, 0.327 mmol), 4-tert-butylcatechol (TBC) (130 mg, 0.779 mmol), benzene (1.5 mL), 2-methoxy-1,3,2-benzodioxaborole (MeOBcat) (0.1 mL, 0.09 mmol, 1.0 M in benzene, 0.3 eq), TMSOTf (0.104 mL, 0.003 mmol, 0.05 M in DCM), MeOH (0.120 mL, 0.035 mmol, 0.5 M in DCM) and DTBHN (1.7 mg, 0.01 mmol). The reaction mixture was heated at 70 °C for 14 h. After cooling down to rt, the reaction mixture was partitioned between TBME (50 mL) and water (50 mL). The aqueous layer was extracted TBME (3 x 20 mL). The combined organic phases were washed with sat. aq. $NaHCO_3$ (2 x 30 mL), brine (50 mL), then dried over Na_2SO_4, filtered over celite and concentrated under reduced pressure to give the crude as a brown oil. Purification by flash column chromatography (15% Et_2O:pentane) delivered the desired **28aa** (93 mg, 0.116 mmol, 35%, dr = 8:2, 58% contaminated by $PhSO_2SPh$).

Light yellow oil; Rf: 0.4 (8:2 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.61–7.15 (m, 19H),

3.73 (d, J = 2.8 Hz, 6H), 3.05–2.82 (m, 2H), 2.49 (dddd, J = 52.6, 29.9, 13.3, 6.6 Hz, 2H), 2.27–2.09 (m, 2H), 2.07–1.97 (m, 2H), 1.58 (dddd, J = 13.8, 9.4, 8.2, 5.8 Hz, 1H), 1.01–0.81 (d, J = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4 (Cq_{Ar}), 173.3 (Cq_{Ar}), 173.2 (Cq_{Ar}), 173.2 (Cq_{Ar}), 143.0 (Cq_{Ar}), 136.7 (CH_{Ar}), 136.6 (CH_{Ar}), 133.7 (CH_{Ar}), 131.5 (CH_{Ar}), 129.5 (CH_{Ar}), 129.1 (CH_{Ar}), 129.1 (CH_{Ar}), 128.9 (CH_{Ar}), 128.9 (CH_{Ar}), 127.9 (CH_{Ar}), 127.6 (CH_{Ar}), 125.9 (CH_{Ar}), 125.9 (CH_{Ar}), 58.8 (Cq), 58.3 (Cq), 52.8 (2 x CH_3), 46.1 (CH), 42.7 (CH_2), 42.0 (CH), 41.5 (CH_2), 40.3 (CH_2), 40.1 (CH), 38.2 (CH_2), 35.8 (CH), 33.0 (CH_2), 32.5 (CH_2), 32.4 (CH_2), 29.5 (CH_2), 17.8 (CH_3), 14.9 (CH_3); IR (neat): ν_{max} = 2951, 1729, 1439, 1325, 1252, 1143, 1076, 748, 685, 537 cm^{-1}; HRMS (ESI): Calculated for $C_{18}H_{24}O_4S$ $[M+H]^+$: 336.1395; found: 336.1393.

3-methyl-4-(2-phenylsulfanylethyl)-1-(p-tolylsulfonyl)pyrrolidine (28ca)



A flame-dried 5 mL one-neck round-bottom flask, equipped with a cold-finger condenser, was charged with 3- methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine (65.5 mg, 0.167 mmol) S-benzyl benzenesulfonothioate (62.2 mg, 0.250 mmol), benzene (0.8 mL), 2-methoxy-1,3,2-benzodioxaborole (MeOBcat) (0.05 mL, 0.05 mmol, 1.0 M in benzene), TMSOTf (0.03 mL, 0.01 mmol, 0.05 M in DCM), MeOH (0.8 μl, 0.02 mmol) and DTBHN (0.8 mg, 0.005 mmol). The reaction mixture was heated at 70 °C for 14 h. After cooling down to rt, the reaction mixture was partitioned between TBME (50 mL) and water (50 mL). The aqueous layer was extracted TBME (3 x 20 mL). The combined organic phases were washed with sat. aq. $NaHCO_3$ (2 x 30 mL), brine (50 mL), then dried over Na_2SO_4, filtered over Celite and concentrated under reduced pressure to give the crude as a black oil. Purification by flash column chromatography (Gradient: 0-10-15% Et_2O:pentane) delivered the desired **28ca** (33.6 mg, 0.0895 mmol, 54% (yield determined by using an internal standard in impure fractions), dr = 6:4) as an inseparable mixture of diastereomers.

Light yellow oil; Rf: 0.35 (7:3 pentane:Et_2O).

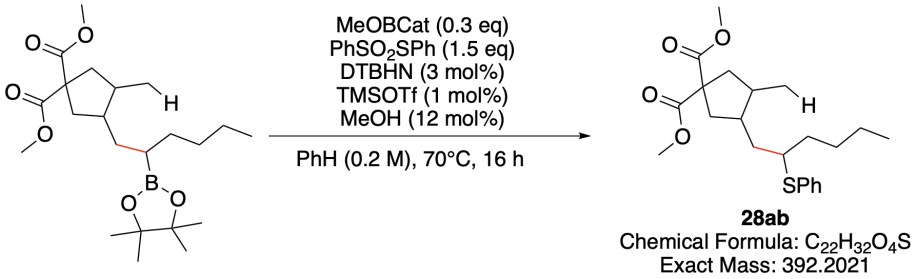
Major diastereomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80–7.75 (m, 2H), 7.42–7.32 (m, 6H), 7.30–7.23 (m, 1H), 3.48 (dd, J = 9.8, 7.1 Hz, 1H), 3.42 (dd, J = 9.8, 5.9 Hz, 1H), 3.11 (dd, J = 9.8, 3.1 Hz, 1H), 3.04 (dd, J = 9.8, 8.0 Hz, 1H), 2.92–2.82 (m, 2H), 2.51 (s, 3H), 2.33–2.17 (m, 2H), 1.72–1.62 (m, 1H), 1.56–1.45 (m, 1H), 0.77 (d, J = 6.7 Hz, 3H); **^{13}C NMR** (101 MHz,

$CDCl_3$) δ 143.45 (Cq), 136.12 (Cq), 134.24 (Cq), 129.76 (2 × CH_{Ar}), 129.52 (2 × CH_{Ar}), 129.09 (2 × CH_{Ar}), 127.50 (2 × CH_{Ar}), 126.34 (CH_{Ar}), 54.88 (CH_2), 50.85 (CH_2), 41.04 (CH), 35.15 (CH), 32.40 (CH_2), 27.36 (CH_2), 21.66 (CH_3), 13.20 (CH_3).

Minor diastereomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80–7.75 (m, 2H), 7.42–7.32 (m, 6H), 7.30–7.23 (m, 1H), 3.63 (dd, *J* = 9.8, 6.8 Hz, 1H), 3.56 (dd, *J* = 9.8, 6.8 Hz, 1H), 3.00–2.79 (m, 4H), 2.52 (s, 3H), 1.89–1.74 (m, 3H), 1.49–1.44 (m, 1H), 0.98 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.50 (Cq), 136.02 (Cq), 133.96 (Cq), 129.78 (2 × CH_{Ar}), 129.59 (2 × CH_{Ar}), 129.09 (2 × CH_{Ar}), 127.61 (2 × CH_{Ar}), 126.37 (CH_{Ar}), 54.80 (CH_2), 53.15 (CH_2), 44.96 (CH), 38.95 (CH), 32.36 (CH_2), 31.51 (CH_2), 21.66 (CH_3), 16.41 (CH_3).

Mixture of isomers: IR (neat): ν_{max} = 2961, 2925, 2875, 1479, 1439, 1339, 1157, 1091, 730, 586 cm^{-1}; HRMS (ESI): Calculated for $C_{20}H_{25}NO_2S_2$ [M+Na]$^+$: 398.1327; found: 398.1212.

Dimethyl 3-methyl-4-(2-phenylsulfanylhexyl)cyclopentane-1,1-dicarboxylate (28ab)

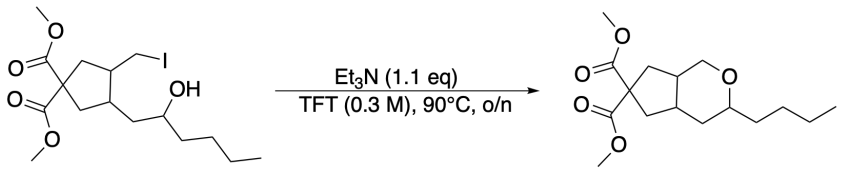


A flame-dried two neck round-bottom flask, equipped with a reflux condenser, was charged with dimethyl 3-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate (156 mg, 0.380 mmol), S-benzyl benzenesulfonothioate (143 mg, 0.570 mmol), benzene (1.3 mL), 2-methoxy-1,3,2-benzodioxaborole (MeOBcat) (0.115 mL, 0.150 mmol, 1.0 M in benzene), TMSOTf (0.08 mL, 0.004 mmol, 0.05 M in DCM), MeOH (1.8 μl, 0.063 mmol) and DTBHN (2 mg, 0.0115 mmol). The reaction mixture was heated at 70 °C for 14 h. After cooling down to rt, the reaction mixture was partitioned between TBME (50 mL) and water (50 mL). The aqueous layer was extracted TBME (3 x 20 mL). The combined organic phases were washed with sat. aq. $NaHCO_3$ (2 x 30 mL), brine (50 mL), then dried over Na_2SO_4, filtered over Celite and concentrated under reduced pressure to give the crude as a black oil. Purification by flash column chromatography (Macherey-Nagel Silica 60, 0.015–0.04 mm) (Gradient: 0-10-15% Et_2O:pentane) delivered the desired **28ab** (38 mg, 0.097 mmol, 26% (yield determined by using an internal standard in impure fractions), dr = 6:4).

Light yellow oil; Rf: 0.25 (9:1 pentane:Et_2O).

Other post-functionalizations

Dimethyl 3-butyl-3,4,4a,5,7,7a-hexahydro-1H-cyclopenta[c]pyran-6,6-dicarboxylate (31)



31
Chemical Formula: $C_{16}H_{26}O_5$
Exact Mass: 298.1780

An 5 mL one-neck round bottom flask was charged with dimethyl 3-(2-hydroxyhexyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate (98.8 mg, 0.232 mmol), TFT (0.9 mL) and Et_3N (0.035 mL, 0.251 mmol, 1.1 eq, distilled over CaH_2 prior to use) and the rection mixture was heated at 90 °C for 16h. The reaction mixture was partitioned between TBME (50 mL) and 2M HCl (50 mL). The organic layer was washed with 1M HCl (50 mL). The combined aqueous phases were back-extracted with TBME (3 x 20 mL). The combined organic phases were then successively washed with saturated aq. $NaHCO_3$ (2 x 50 mL), $Na_2S_2O_3$ (50 mL), and brine (50 mL), dried over Na_2SO_4, filtered, and the solvents removed under reduced pressure to afford the crude product as a light yellow solid. Purification by flash column chromatography (Gradient: 0-5-10% EtOAc:heptanes) delivered the desired **31** (44.2 mg, 0.148 mmol, 64%, dr = 54:46).

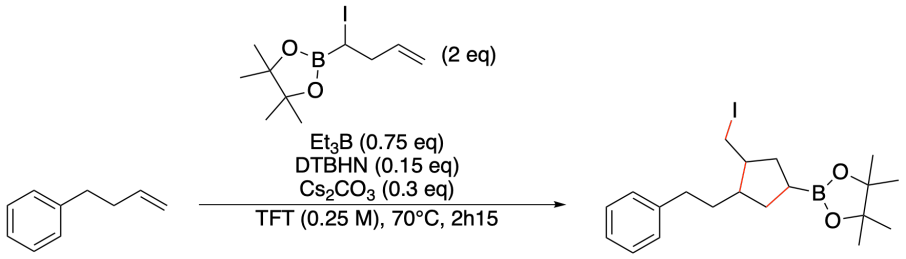
Light yellow oil; Rf: 0.74 (1:1 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.88 (d, J = 11.9 Hz, 1H), 3.73–3.68 (m, 6H), 3.68–3.61 (m, 1H), 3.18–3.07 (m, 1H), 2.41–2.10 (m, 5H), 2.07–1.85 (m, 1H), 1.57–1.39 (m, 3H), 1.39–1.05 (m, 6H), 0.87 (td, J = 7.1, 1.9 Hz, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.8 (Cq), 173.4 (Cq), 173.4 (Cq), 173.3 (Cq), 173.2 (Cq), 173.1 (Cq), 77.3 (CH), 72.3 (CH), 72.0 (CH_2), 67.9 (CH_2), 67.3 (CH_2), 59.2 (Cq), 59.0 (Cq), 58.1 (Cq), 52.9 (CH_3), 52.8 (CH_3), 44.3 (CH_2), 44.2 (CH), 40.4 (CH), 40.2 (CH), 39.3 (CH), 37.2 (CH), 37.0 (CH), 36.9 (CH), 36.5 (CH), 36.1 (CH_2), 36.0 (CH_2), 35.9 (CH_2), 35.6 (CH_2), 35.0 (CH_2), 33.9 (CH_2), 31.4 (CH_2), 28.0 (CH_2), 27.9 (CH_2), 27.8 (CH_2), 22.9 (CH_2), 22.9 (CH_2), 14.1 (CH_3); IR (neat): ν_{max} = 2951, 2931, 2858, 1731, 1434, 1246, 1195, 1145, 1090, 843 cm^{-1}; HRMS (ESI): Calculated for $C_{16}H_{26}O_5$ $[M+Na]^+$: 321.1780; found: 321.1667.

3.10.6 ATRAn products

GP1: *All alkenes used for the substrate scope are either previously purified by distillation or by filtration over SiO_2.* A flame-dried 10 mL two neck round-bottom flask, equipped with a cold-finger reflux condenser, was charged with alkene (0.5 mmol), 2-(1-iodobut-3-enyl)-4,4,5-trimethyl-1,3,2-dioxaborolane (304 mg, 1.00 mmol) and Cs_2CO_3 (50 mg, 0.155 mmol). The contents were dissolved in dry TFT (1.8 mL). Triethylborane (0.110 mL, 0.108 mmol, 1.15 M in TFT) was then added, with the needle immersed in the solution, followed by DTBHN (4 mg, 0.025

mmol). The rection mixture was heated at 70 °C for 45 minutes in a pre-heated oil bath. Two other portions of triethylborane (0.110 mL, 0.108 mmol, 1.15 M in TFT) and DTBHN (4 mg, 0.025 mmol) were added every 45 minutes. The crude product was filtered over a small pad of neutral aluminum oxide (2.0 cm) and eluted with EtOAc. The solvents were removed under reduced pressure, and the crude mixture was purified by flash column chromatography on silica gel. Together with the desired ATRAn products, cyclopropane derivative **39** (4,4,5,5-tetramethyl-2-[1-[[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl]methyl]- but-3-enyl]-1,3,2-dioxaborolane) was also isolated in 15-30% yield.

2-[3-(iodomethyl)-4-(2-phenylethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38a)



38a
Chemical Formula: $C_{20}H_{30}BIO_2$
Exact Mass: 440.1384

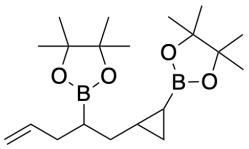
Followed **GP1** with but-3-en-1-ylbenzene (67,4 mg, 0.510 mmol). Purification by column chromatography (5% Et_2O:pentane) provided the desired **38a** (20 mg, 0.0454 mmol, 9%, dr = 50:25:17:8).

Colorless oil; Rf: 0.41 (95:5 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.24–7.05 (m, 5H), 3.44–2.96 (m, 2H), 2.69–2.55 (m, 1H), 2.46 (ddt, J = 13.7, 9.9, 6.9 Hz, 1H), 2.31 (ddt, J = 16.3, 9.7, 6.8 Hz, 1H), 2.12–1.83 (m, 2H), 1.83–1.53 (m, 2H), 1.51–1.26 (m, 3H), 1.26–1.09 (m, 12H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 142.6 (Cq_{Ar}), 128.5 (CH_{Ar}), 128.5 (CH_{Ar}), 128.5 (CH_{Ar}), 128.4 (CH_{Ar}), 128.4 (CH_{Ar}), 125.9 (CH_{Ar}), 125.9 (CH_{Ar}), 125.8 (CH_{Ar}), 83.2 (Cq), 83.2 (Cq), 83.2 (Cq), 83.0 (Cq), 50.2 (CH), 48.2 (CH), 47.8 (CH), 47.1 (CH), 47.0 (CH), 45.8 (CH), 43.6 (CH_2), 43.5 (CH_2), 37.1 (CH_2), 37.1 (CH_2), 36.8 (CH_2), 36.2 (CH_2), 35.3 (CH_2), 34.9 (CH_2), 34.8 (CH_2), 34.8 (CH_2), 34.7 (CH_2), 34.5 (CH_2), 33.7 (CH_2), 32.7 (CH_2), 31.9 (CH_2), 31.4 (CH_2), 30.4 (CH_2), 24.9 (CH_3), 14.5 (CH_2-I), 13.0 (CH_2-I), 10.1 (CH_2-I), 8.8 (CH_2-I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) δ 34.4; IR (neat): ν_{max} = 2976, 2928, 2856, 1378, 1312, 1212, 970, 858, 746, 697 cm^{-1}; HRMS (EI): Calculated for $C_{20}H_{30}BIO_2$ $[M\text{-}CH_3]^+$: 425.1384; found: 425.1143.

Major Diastereomer (*50*:25:17:8) (characteristic signals): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.25 (m, 2H), 7.22–7.15 (m, 3H), 3.27 (dd, J = 9.4, 6.1 Hz, 1H), 3.10 (t, J = 9.7, 9.7 Hz, 1H), 2.79–2.63 (m, 1H), 2.62–2.48 (m, 1H), 2.49–2.31 (m, 1H), 2.14–1.92 (m, 3H), 1.79–1.68 (m, 1H), 1.57–1.36 (m, 6H), 1.26 (s, 12H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 142.6 (Cq), 128.50,

128.49, 128.45, 128.42, 128.40, 125.85, 83.2 (2 × Cq), 47.1 (CH), 43.6 (CH), 34.9 (CH_2), 34.7 (CH_2), 32.7 (CH_2), 31.4 (CH_2), 24.92, 24.91, 10.1 (CH_2–I); Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected.

4,4,5,5-tetramethyl-2-[1-[[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl]methyl]-but-3-enyl]-1,3,2-dioxaborolane (39)



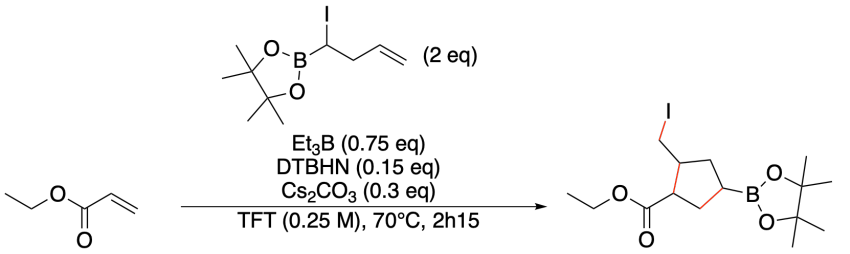
39
Chemical Formula: $C_{20}H_{36}B_2O_4$
Exact Mass: 362.2800

Colorless oil; Rf: 0.32 (98:2 pentane:Et_2O), Four diastereomers (dr = ca: 8:8:1:1).

Two Major diastereomers (dr = ca. 1:1): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 5.85–5.69 (m, 1H, 2 dia), 5.03–4.92 (m, 1H, 2 dia), 4.94–4.85 (m, 1H, 2 dia), 2.22–2.09 (m, 2H, 2 dia), 1.47–1.13 (m, 3H, 2 dia), 1.21 (s, 12H), 1.18 (s, 6H), 1.17 (s, 6H), 0.99–0.85 (m, 1H, 2 dia), 0.70–0.58 (m, 1H, 2 dia), 0.46–0.33 (m, 1H, 2 dia), -0.37– -0.48 (m, 1H, 2 dia); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 138.83 (=CH), 138.75 (=CH), 114.90 (=CH_2), 114.89 (=CH_2), 83.08 (Cq), 83.04 (Cq), 82.80 (Cq), 82.77 (Cq), 36.70 (CH_2), 36.20 (CH_2), 35.78 (CH_2), 35.31 (CH_2), 25.05 (2 × CH_3), 25.03 (2 × CH_3), 24.97 (4 × CH_3), 24.86 (2 × CH_3), 24.82 (2 × CH_3), 24.77 (2 × CH_3), 24.72 (2 × CH_3), 18.16 (CH), 18.01 (CH), 12.11 (CH_2), 12.07 (CH_2). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) δ 33.9; IR (neat): ν_{max} = 2977, 2925, 1419, 1370, 1313, 1216, 1142, 967, 855, 670 cm^{-1}; HRMS (EI): Calculated for $C_{20}H_{36}B_2O_4$ [M-CH_3]$^+$: 347.2800; found: 347.2564.

Minor diastereomer (dr = ca. 1:1, characteristic signals): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 0.78–0.70 (m, 1H, 2 dia), -0.13 (tdd, *J* = 9.3, 9.3, 6.7, 1.1 Hz, 1H, 2 dia). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 114.77 (=CH_2), 114.68 (=CH_2), 83.00 (Cq), 82.98 (Cq), 82.97 (Cq), 82.90 (Cq), 36.23 (CH_2), 35.36 (CH_2), 33.05 (CH_2), 32.25 (CH_2), 18.08 (CH), 17.62 (CH), 11.79 (CH_2), 11.52 (CH_2).

Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (38c)



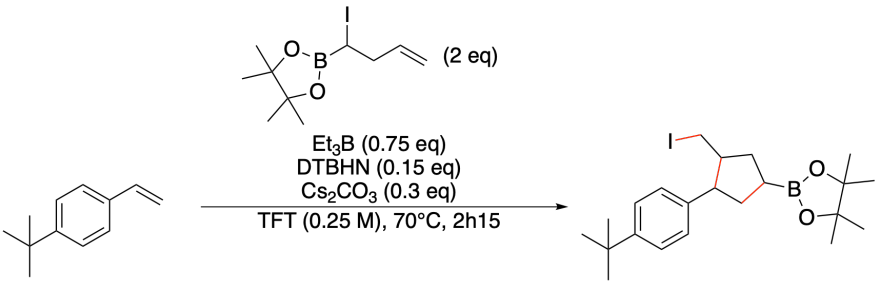
38c
Chemical Formula: $C_{15}H_{26}BIO_4$
Exact Mass: 408.0969

Followed **GP1** with ethyl acrylate (52.2 mg, 0.521 mmol). Purification by column chromatography (5% Et_2O:pentane) provided the desired **38c** (35.9 mg, 0.088 mmol, 17%, dr = 3:3:2:2).

Two major diastereomers (dr = 1:1) Dia 1+2: Colorless oil; Rf: 0.46 (9:1 pentane:Et_2O); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.131 (q, *J* = 7.1 Hz, 2H), 4.128 (q, *J* = 7.1 Hz, 2H), 3.313 (t, *J* = 6.5 Hz, 1H, dia 1), 3.289 (t, *J* = 6.5 Hz, 1H, dia 2), 3.137 (t, *J* = 9.3 Hz, 1H, dia 2), 3.126 (t, *J* = 9.4 Hz, 1H, dia 1), 2.98 (td, *J* = 7.5, 4.9 Hz, 1H), 2.91 (q, *J* = 7.8 Hz, 1H), 2.66–2.51 (m, 2H), 2.18–1.76 (m, 7H, dia 1 + dia 2), 1.76–1.66 (m, 1H), 1.63–1.52 (m, 1H), 1.45–1.33 (m, 1H), 1.274 (t, *J* = 7.1 Hz, 3H, 1 dia), 1.270 (t, *J* = 7.1 Hz, 3H, 1 dia), 1.245 (s, 6H), 1.241 (s, 6H), 1.23 (s, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4 (Cq), 174.1 (Cq), 83.39 (2 × Cq), 83.36 (2 × Cq), 60.4 (2 × CH_2), 48.7 (CH), 48.4 (CH), 47.6 (CH), 47.0 (CH), 35.4 (CH_2), 34.3 (CH_2), 31.7 (CH_2), 31.2 (CH_2), 24.93 (2 × CH_3), 24.90 (2 × CH_3), 24.86 (4 × CH_3), 14.5 (2 × CH_3), 7.7 (CH_2–I), 7.4 (CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.1; IR (neat): ν_{max} = 2976, 2933, 1725, 1371, 1315, 1187, 1165, 1141, 969, 856 cm^{-1}; HRMS (ESI): Calculated for $C_{15}H_{26}BIO_4$ $[M+Na]^+$: 431.0969; found: 431.0856.

Two minor diastereomers (dr = ca. 1:1) Dia 3+4: Colorless oil; Rf: 0.38 (9:1 pentane:Et_2O); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.13 (q, *J* = 7.1 Hz, 2H), 3.40 (dd, *J* = 9.7, 4.9 Hz, 1H), 3.23 (dd, *J* = 9.8, 7.4 Hz, 1H), 2.50 (ddd, *J* = 9.8, 8.4, 5.8 Hz, 1H), 2.44–2.33 (m, 1H), 2.19–2.09 (m, 2H), 2.05–1.99 (m, 1H), 1.53–1.41 (m, 1H), 1.38–1.27 (m, 1H), 1.27–1.21 (s, 15H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.4 (Cq), 83.4 (2 × Cq), 60.7 (CH_2), 50.4 (CH), 47.3 (CH), 37.1 (CH_2), 32.7 (CH_2), 24.9 (4 × CH_3), 14.4 (CH_3), 11.9 (CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.5; IR (neat): ν_{max} = 2977, 2933, 1727, 1370, 1317, 1184, 1163, 1141, 971, 859 cm^{-1}; HRMS (ESI): Calculated for $C_{15}H_{26}BIO_4$ $[M+Na]^+$: 431.0969; found: 431.0854.

2-[3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38e)



38e
Chemical Formula: $C_{22}H_{34}BIO_2$
Exact Mass: 468.1697

Followed **GP1** with 1-(tert-butyl)-4-vinylbenzene (83 mg, 0.518 mmol). Purification by column chromatography (Macherey-Nagel Silica 60, 0.015–0.04 mm) (3% Et_2O:pentane) provided the desired **38e** (67 mg, 0.163 mmol, 17%, dr = 38:29:22:11).

Colorless oil; Rf: 0.47 (95:5 pentane:Et_2O).

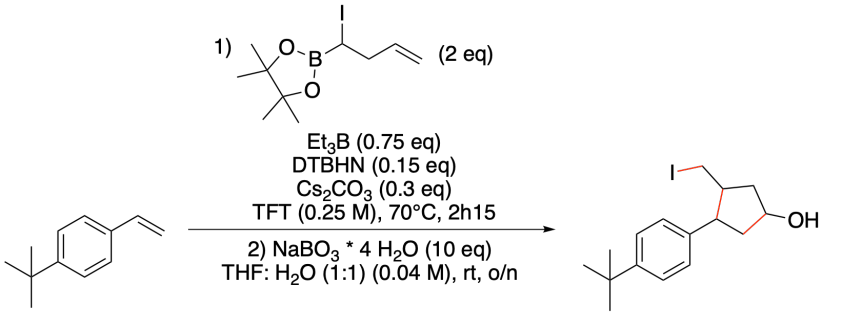
Major diastereomer (*38*:29:22:11): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.30 (m, 2H), 7.18–7.14 (m, 2H), 3.32 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.08 (dd, *J* = 9.5, 8.6 Hz, 1H), 2.73–2.63 (m, 1H), 2.14–2.02 (m, 1H), 2.33–2.21 (m, 2H), 2.11–2.01 (m, 1H), 1.74–1.61 (m, 1H), 1.56–1.45 (m, 1H), 1.35 (s, 9H), 1.30 (bs, 12H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 149.15 (Cq), 141.1 (Cq), 127.1 (2 × CH_{Ar}), 125.49 (2 × CH_{Ar}), 83.2 (Cq), 51.9 (CH), 51.8 (CH), 37.4 (CH_2), 36.9 (CH_2), 34.5 (2 × Cq), 31.5 (3 × CH_3), 24.9 (4 × CH_3), 12.4 (CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected.

Two diastereomers (38:*29*:*22*:11) (characteristic signals): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.30 3.37–3.32 (m, 1H, dia 1), 3.34–3.26 (m, 1H), 3.12 (dd, *J* = 9.7, 7.2 Hz, 1H, dia 1), 2.85 (dd, *J* = 9.4, 4.8 Hz, 1H, dia 2), 2.78 (dd, *J* = 10.7, 9.4 Hz, 1H, dia 2), 2.71–2.61 (m, 2H), 2.32–2.20 (m, 3H, 2 dia), 2.14–1.96 (m, 3H, 2 dia), 1.92–1.83 (m, 1H), 1.81–1.63 (m, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 149.2 (Cq), 149.1 (Cq), 140.2 (Cq), 138.7 (Cq), 128.3 (2 × CH_{Ar}), 127.2 (2 × CH_{Ar}), 125.45 (2 × CH_{Ar}), 125.1 (2 × CH_{Ar}), 83.3 (2 × Cq), 83.2 (2 × Cq), 53.7 (CH), 49.6 (CH), 49.4 (CH), 48.5 (CH), 38.6 (CH_2), 35.5 (CH_2), 35.0 (CH_2), 34.5 (2 × Cq), 33.0 (CH_2), 31.5 (6 × CH_3), 24.91 (8 × CH_3), 14.4 (CH_2–I), 11.9 (CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected.

Minor diastereomer (38:29:22:*11*) (characteristic signals): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 2.88–2.83 (m, 2H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 10.3 (CH_2–I).

Mixture of isomers: ^{11}**B NMR** (128 MHz, $CDCl_3$) δ 34.3; IR (neat): ν_{max} = 2960, 2903, 2868, 1411, 1378, 1371, 1315, 1142, 828, 732 cm^{-1}; HRMS (EI): Calculated for $C_{22}H_{34}BIO_2$ [M-CH_3]$^+$: 453.1697; found: 453.1463.

3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentanol (OX-38e)

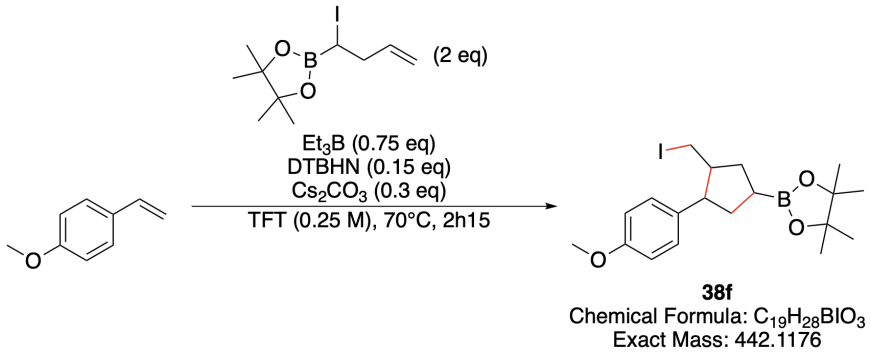


OX-38e
Chemical Formula: $C_{16}H_{23}IO$
Exact Mass: 358.0794

Followed **GP1** with 1-(tert-butyl)-4-vinylbenzene (82.5 mg, 0.515 mmol). After filtration over neutral Alox and concentration under reduced pressure, the crude mixture was dissolved in THF/H_2O (1:1)(10 mL) and sodium perborate (769 mg, 5 mmol) was added in one portion. The reaction mixture was stirred for 14 h at room temperature, then partitioned between EtOAc (20 mL) and water (20 mL). The aqueous phase was extracted EtOAc (3 x 10 mL). The combined organic phases were washed with sat. aq. NaCl (25 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a colorless oil. Purification by column chromatography (30% Et_2O:pentane) provided the desired **OX-38e** (131 mg, 0.366 mmol, 71%, dr = 40:25:24:11).

Colorless oil; Rf: 0.24 (7:3 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.09 (m, 4H, 4 dia), 4.68–4.44 (m, 1H, 4 dia), 3.67–1.53 (m, 8H, 4 dia), 1.35–1.32 (m, 9H, 4 dia); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 149.56 (Cq_{Ar}), 149.50 (Cq_{Ar}), 149.49 (Cq_{Ar}), 149.46 (Cq_{Ar}), 139.8 (Cq_{Ar}), 139.4 (Cq_{Ar}), 137.41 (Cq_{Ar}), 137.39 (Cq_{Ar}), 128.3 (2 × CH_{Ar}), 128.2 (2 × CH_{Ar}), 127.4 (2 × CH_{Ar}), 127.1 (2 × CH_{Ar}), 125.62 (2 × CH_{Ar}), 125.61 (2 × CH_{Ar}), 125.3 (4 × CH_{Ar}), 71.72 (CH), 71.70 (CH), 71.5 (CH), 71.2 (CH), 50 .6 (CH), 49.2 (CH), 48.8 (CH), 47.4 (CH), 46.7 (CH), 46.3 (CH), 45.9 (CH), 45.4 (CH_2), 45.2 (CH), 45.0 (CH_2), 43.5 (CH_2), 43.26 (CH_2), 43.25 (CH_2), 42.6 (CH_2), 41.2 (CH_2), 39.7 (CH_2), 34.5 (4 × Cq), 31.5 (12 × CH_3), 13.4 (CH_2–I), 13.3 (CH_2–I), 11.8 (CH_2–I), 11.2 (CH_2–I); IR (neat): ν_{max} = 3322, 2956, 2901, 2866, 1508, 1460, 1360, 1268, 1017, 826 cm^{-1}; HRMS (ESI): Calculated for $C_{16}H_{23}IO$ [M+Na]$^+$: 381.0794; found: 381.0677.

2-[3-(iodomethyl)-4-(4-methoxyphenyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38f)

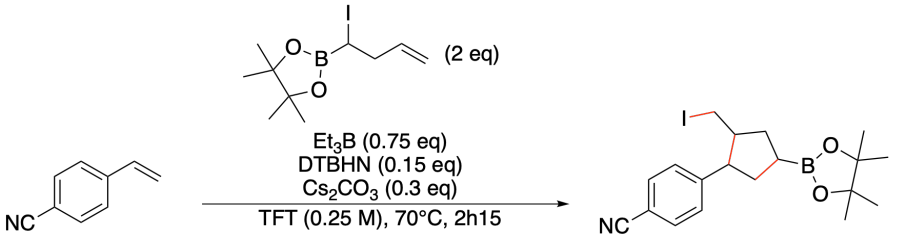


38f
Chemical Formula: $C_{19}H_{28}BIO_3$
Exact Mass: 442.1176

Followed **GP1** with 1-methoxy-4-vinylbenzene (67 mg, 0.499 mmol). Purification by column chromatography (7% Et_2O:pentane) provided the desired **38f** (160 mg, 0.362 mmol, 73%, dr = 36:30:22:12).

Colorless oil; Rf: 0.22 (9:1 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.18–7.09 (m, 2H, 4 dia), 6.88–6.80 (m, 2H, 4 dia), 3.80–3.78 (m, 3H, 4 dia), 3.33–3.20 (m, 1H (2 dia) + 1H (2 dia)), 3.12–3.01 (m, 1H, 2 dia), 2.86–2.70 (m, 2H, 2 dia), 2.69–2.56 (m, 1H, 4 dia), 2.30–1.38 (m, 4H (4 dia) + 1H (2 dia) + 1H (4 dia)), 1.32–1.16 (m, 12H, 4 dia); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 158.2 (Cq_{Ar}), 158.2 (Cq_{Ar}), 158.1 (2 × Cq_{Ar}), 136.2 (Cq_{Ar}), 135.2 (Cq_{Ar}), 133.9 (Cq_{Ar}), 133.6 (Cq_{Ar}), 129.5 (2 × CH_{Ar}), 129.3 (2 × CH_{Ar}), 128.5 (2 × CH_{Ar}), 128.4 (2 × CH_{Ar}) , 113.99 (2 × CH_{Ar}), 113.97 (2 × CH_{Ar}), 113.7 (2 × CH_{Ar}), 113.6 (2 × CH_{Ar}), 83.25 (Cq), 83.23 (Cq), 83.18 (Cq), 83.15 (Cq), 55.31 (CH_3), 55.29 (CH_3), 53.4 (CH), 51.9 (CH), 51.5 (CH), 49.4 (CH), 49.0 (CH), 48.7 (CH), 48.6 (CH), 48.4 (CH), 38.5 (CH_2), 37.4 (CH_2), 36.6 (CH_2), 35.5 (CH_2), 34.8 (CH_2), 34.2 (CH_2), 33.4 (CH_2), 32.2 (CH_2), 24.93 (CH_3), 24.89 (CH_3), 24.87 (CH_3), 24.85 (CH_3), 24.83 (CH_3), 14.2 (CH_2–I), 12.1 (CH_2–I), 11.4 (CH_2–I), 9.9 (CH_2–I). Due to coupling to the quadrupolar 11B and 10B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) δ 34.3; IR (neat): ν_{max} = 2976, 2933, 1512, 1378, 1371, 1314, 1244, 1141, 1036, 827 cm^{-1}; HRMS (ESI): Calculated for $C_{16}H_{23}IO$ $[M+H]^+$: 465.1176; found: 465.1062.

Synthesis of 4-[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl]-benzonitrile (38g)

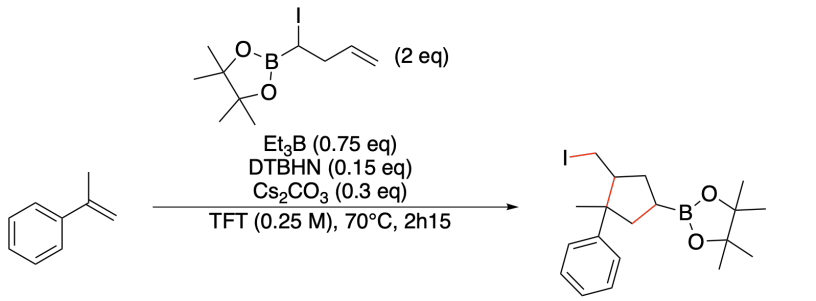


38g
Chemical Formula: $C_{19}H_{25}BINO_2$
Exact Mass: 437.1023

Followed **GP1** with 4-vinylbenzonitrile (63.9 mg, 0.495 mmol). Purification by column chromatography (5% Et_2O:pentane) provided the desired **38g** (118 mg, 0.269 mmol, 54% dr = 35:34:29:12).

Mixture of four diastereomers (contaminated with unknown impurity): Colorless oil; Rf: 0.26 (9:1 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.61–7.54 (m, 2H, 4 dia), 7.40–7.25 (m, 2H, 4 dia), 3.45–3.32 (m, 1H, 2 dia), 3.28–3.21 (m, 1H, 2 dia), 3.10–3.00 (m, 1H, 2 dia), 2.88–2.60 (m, 2H (2 dia) + 1H (4 dia)), 2.35–2.41 (m, 1H (2 dia) + 5H (4 dia)), 1.29–1.22 (m, 12H, 4 dia); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 150.7 (Cq_{Ar}), 150.3 (Cq_{Ar}), 149.4 (Cq_{Ar}), 148.0 (Cq_{Ar}), 132.5 (CH_{Ar}), 132.4 (CH_{Ar}), 132.1 (CH_{Ar}), 132.0 (CH_{Ar}), 129.5 (2 × CH_{Ar}), 129.2 (2 × CH_{Ar}), 128.5 (2 × CH_{Ar}), 128.4 (2 × CH_{Ar}), 119.06 (Cq), 119.04 (Cq), 119.01 (Cq), 118.99 (Cq), 110.30 (Cq), 110.28 (Cq), 110.26 (Cq), 110.24 (Cq), 83.47 (Cq), 83.44 (Cq), 83.39 (Cq), 83.37 (Cq), 54.1 (CH), 52.3 (CH), 51.7 (CH), 49.8 (CH), 49.4 (CH), 49.3 (CH), 48.8 (CH), 48.6 (CH), 38.4 (CH_2), 37.3 (CH_2), 36.7 (CH_2), 35.5 (CH_2), 35.1 (CH_2), 34.2 (CH_2), 33.2 (CH_2), 31.9 (CH_2), 24.92 (CH_3), 24.89 (CH_3), 24.86 (CH_3), 24.83 (CH_3), 13.0 (CH_2–I), 10.9 (CH_2–I), 9.2 (CH_2–I), 8.0 (CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) δ 34.0; IR (neat): ν_{max} = 2976, 2932, 2871, 2226, 1378, 1372, 1316, 1141, 833, 730 cm1; HRMS (ESI): Calculated for $C_{19}H_{25}BINO_2$ $[M+H]^+$: 438.1023; found: 438.1093.

2-[4-(iodomethyl)-3-methyl-3-phenyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38h)



38h
Chemical Formula: $C_{19}H_{28}BIO_2$
Exact Mass: 426.1227

Followed **GP1** with prop-1-en-2-ylbenzene (59.1 mg, 0.500 mmol) of starting alkene. Purification by column chromatography (Macherey-Nagel Silica 60, 0.015–0.04 mm) (2% EtOAc:heptanes) provided the desired **38h** as an unseparable mixture of diastereomers (89.3 mg, 0.210 mmol, 42%, dr = 53:21:19:7).

Colorless oil; Rf: 0.26 (9:1 heptanes:EtOAc).

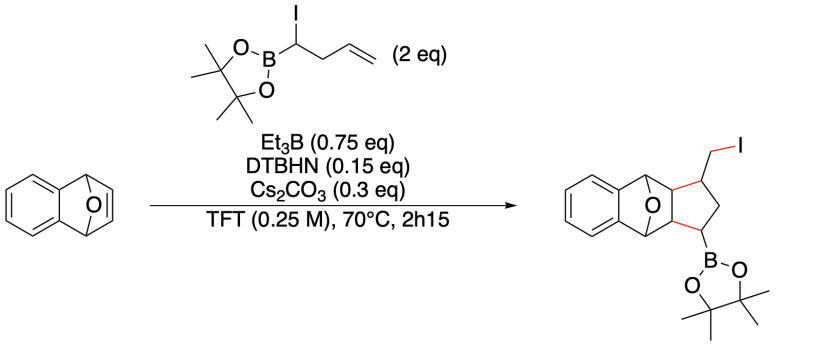
Major diastereomer (*53*:21:19:7): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.43–7.27 (m, 4H), 7.27–7.17 (m, 1H), 3.23 (dd, J = 9.4, 3.3 Hz, 1H), 3.06 (dd, J = 11.5, 9.3 Hz, 1H), 2.70–2.60 (m, 1H), 2.51–2.42 (m, 1H), 2.41–2.31 (m, 1H), 2.00 (dd, J = 13.0, 6.0 Hz, 1H), 1.71–1.56 (m, 2H), 1.30 (s, 12H), 1.23 (s, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 148.64 (Cq), 128.39 (2 × CH_{Ar}), 125.92 (CH_{Ar}), 125.87 (2 × CH_{Ar}), 83.32 (2 × Cq), 54.92 (CH), 49.34 (Cq), 46.21 (CH_2), 34.77 (CH_2), 24.90 (2 × CH_3), 24.85 (2 × CH_3), 20.87 (CH_3), 7.97 (CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) δ 34.5; IR (neat): ν_{max} = 2974, 2928, 2874, 1370, 1312, 1142, 970, 858, 760, 698 cm^{-1}; HRMS (ESI): Calculated for $C_{19}H_{28}BIO_2$ $[M+Na]^+$: 449.1227; found: 449.1120.

Mixture of two diastereomers (characteristic signals, dr = ca. 1:1)(53:*21:19*:7): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.27–3.23 (m, 1H, 1 dia), 3.02–2.97 (m, 1H, 1 dia), 2.77–2.67 (m, 1H, 1 dia), 2.52–2.23(m, 4H, 2 dia); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 147.59 (Cq), 146.84 (Cq), 83.35 (Cq), 83.26 (Cq), 54.14 (CH), 52.52 (CH), 51.85 (Cq), 50.29 (Cq), 46.50 (CH_2), 38.55 (CH_2), 34.08 (CH_2), 33.82 (CH_2), 30.01 (CH_3), 24.88 (4 × CH_3), 18.85 (CH_3), 12.65 (CH_2–I), 8.40 (CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected.

Minor diastereomer (characteristic signals) (53:21:19:*7*): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 146.50 (Cq), 83.37 (Cq), 54.03 (CH), 51.41 (Cq), 38.41 (CH_2), 32.89 (CH_2), 30.70 (CH_3), 11.02

(CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected.

2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38j)



38j
Chemical Formula: $C_{20}H_{26}BIO_3$
Exact Mass: 452.1020

Followed **GP1** with 11-oxatricyclo[6.2.1.02,7]undeca-2,4,6,9-tetraene (69.9 mg, 0.485 mmol). Purification by column chromatography (Gradient 5-10% Et_2O:pentane) provided the desired **38j** (89.3 mg, 0.210 mmol, 71% dr = 34:46:16:4).

Major diastereomer (34:*46*:16:4) (contains traces of solvents): Colorless oil; Rf: 0.48 (85:15 pentane:Et_2O); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.30 (m, 2H), 7.24–7.18 (m, 2H), 5.48 (bs, 1H), 5.42 (bs, 1H), 3.60 (dd, *J* = 9.6, 5.8 Hz, 1H), 3.40 (t, *J* = 9.6 Hz, 1H), 2.54 (dd, *J* = 8.6, 6.5 Hz, 1H), 2.52–2.42 (m, 1H), 2.42 (dd, *J* = 8.1, 6.6 Hz, 1H), 2.04 (dt, *J* = 11.3, 6.6 Hz, 1H), 1.80 (dt, *J* = 13.6, 11.6 Hz, 1H), 1.64 (ddd, *J* = 13.7, 8.6, 6.6 Hz, 1H), 1.423 (s, 6H), 1.416 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.8 (Cq_{Ar}), 146.3 (Cq_{Ar}), 126.5 (2 x CH_{Ar}), 119.1 (CH_{Ar}), 119.0 (CH_{Ar}), 84.2 (CH), 83.5 (2 x Cq), 79.6 (CH), 50.3 (CH), 48.9 (CH), 47.0 (CH), 36.9 (CH_2), 27.2 (bs, CH-B), 25.2 (2 x CH_3), 25.0 (2 x CH_3), 7.5 (CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.9; IR (neat): ν_{max} = 2994, 2975, 2924, 1371, 1318, 1138, 851, 842, 756, 673 cm^{-1}; HRMS (ESI): Calculated for $C_{20}H_{26}BIO_3$ [M+Na]$^+$: 475.1020; found: 475.0900.

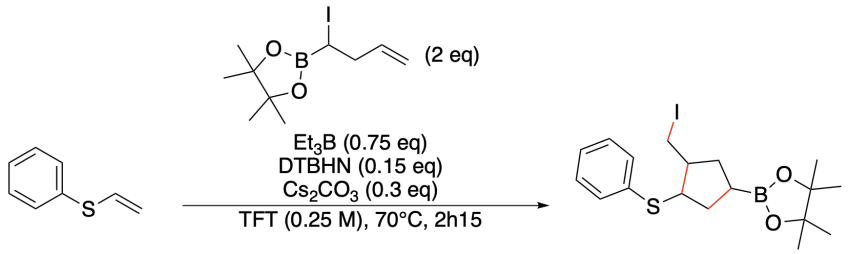
Second Major diastereomer (*34*:46:16:4): Colorless oil; Rf: 0.39 (85:15 pentane:Et_2O); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 2H), 7.18–7.12 (m, 2H), 5.35 (s, 1H), 5.13 (s, 1H), 3.53 (dd, *J* = 9.7, 6.2 Hz, 1H), 3.32 (t, *J* = 9.8 Hz, 1H), 2.51–2.39 (m, 1H), 2.42 (dd, *J* = 6.9, 2.2 Hz, 1H), 2.37–2.32 (m, 1H), 1.97–1.90 (m, 2H), 1.73–1.68 (m, 1H), 1.23 (s, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.5 (Cq_{Ar}), 146.1 (Cq_{Ar}), 126.53 (CH_{Ar}), 126.45 (CH_{Ar}), 119.2 (CH_{Ar}), 119.1 (CH_{Ar}), 87.2 (CH), 83.5 (2 x Cq), 79.7 (CH), 50.3 (CH), 48.8 (CH), 45.4 (CH), 36.4 (CH_2), 27.3 (bs, CH-B), 24.8 (4 x CH_3), 8.0 (CH_2–I); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.2. Due to coupling to

the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.2; IR (neat): ν_{max} = 2977, 2952, 2933, 2869, 1370, 1316, 1214, 1141, 753, 680 cm^{-1}; HRMS (ESI): Calculated for $C_{19}H_{28}BIO_3$ $[M+Na]^+$: 475.1020; found: 475.0901.

Third diastereomer (34:46:*16*:4): Colorless oil; Rf: 0.33 (85:15 pentane:Et_2O); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20–7.13 (m, 2H), 7.08–7.02 (m, 2H), 5.15 (s, 1H), 4.91 (s, 1H), 3.24 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.18 (dd, *J* = 9.7, 7.4 Hz, 1H), 2.28–2.24 (m, 1H), 2.13–2.03 (m, 2H), 1.85–1.78 (m, 1H), 1.30–1.26 (m, 2H), 1.18 (s, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.88 (Cq), 145.69 (Cq), 126.61 (CH_{Ar}), 126.59 (CH_{Ar}), 119.38 (CH_{Ar}), 119.31 (CH_{Ar}), 83.37 (2 × Cq), 83.31 (CH), 83.04 (CH), 55.40 (CH), 51.60 (CH), 47.32 (CH), 39.89 (CH_2), 24.97 (2 × CH_3), 24.85 (2 × CH_3), 11.24 (CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.0; IR (neat): ν_{max} = 2976, 2931, 1415, 1379, 1315, 1140, 848, 751, 731, 654 cm^1; HRMS (ESI): Calculated for $C_{19}H_{28}BIO_3$ $[M+Na]^+$: 475.1020; found: 475.0867.

Minor Diastereomer (34:46:16:*4*): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22–7.11 (m, 2H), 7.09–7.00 (m, 2H), 5.25 (s, 1H), 5.04 (s, 1H), 3.44 (dd, *J* = 9.7, 6.2 Hz, 1H), 3.25–3.22 (m, 1H), 2.42–2.33 (m, 1H), 2.32 (dd, *J* = 6.9, 2.2 Hz, 1H), 2.28–2.24 (m, 1H), 1.85–1.78 (m, 2H), 1.65–1.58 (m, 1H), 1.14 (s, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.52 (Cq), 146.15 (Cq), 126.56 (CH_{Ar}), 126.49 (CH_{Ar}), 119.25 (CH_{Ar}), 119.11 (CH_{Ar}), 87.30 (CH), 83.51 (2 × Cq), 79.71 (CH), 50.38 (CH), 48.82 (CH), 45.46 (CH), 36.43 (CH_2), 24.85 (4 × CH_3), 8.05 (CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected.

2-[3-(iodomethyl)-4-phenylsulfanyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38k)



38k
Chemical Formula: $C_{18}H_{26}BIO_2S$
Exact Mass: 444.0791

Followed **GP1** with phenylvinylsulfide (67.8 mg, 0.498 mmol). Purification by column chromatography (Macherey-Nagel Silica 60, 0.015–0.04 mm) (5% Et_2O:pentane) provided the desired **38k** (92.2 mg, 0.208 mmol, 42% - dr = 38:31:17:14).

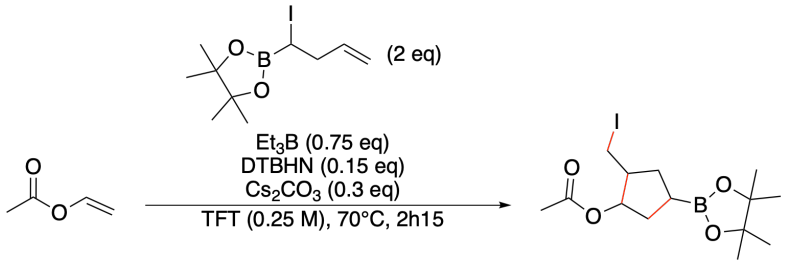
Colorless oil; Rf: 0.55 (9:1 pentane:Et_2O).

Two major diastereomers (dr = ca. 1:1) ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.38 (m, 4H, dia 1 + dia 2), 7.35–7.25 (m, 4H, dia 1 + dia 2), 7.26–7.19 (m, 2H, dia 1 + dia 2), 3.69 (q, J = 6.0 Hz, 1H, 1 dia), 3.51–3.41 (m, 2H, dia 1 + dia 2), 3.34–3.21 (m, 3H, dia 1 + dia 2), 2.66–2.54 (m, 1H, 1 dia), 2.31–2.14 (m, 4H, dia 1 + dia 2), 2.08–1.93 (m, 3H, dia 1 + dia 2), 1.73–1.63 (m, 1H, 1 dia), 1.38 (ddd, J = 12.6, 11.0, 9.3 Hz, 1H, 1 dia), 1.25 (s, 24H, dia 1 + dia 2), 1.16–1.07 (m, 1H, 1 dia), 1.09–1.02 (m, 1H, 1 dia); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 136.15 (Cq), 135.97 (Cq), 131.05 (2 × CH_{Ar}), 130.92 (2 × CH_{Ar}), 129.02 (2 × CH_{Ar}), 128.97 (2 × CH_{Ar}), 126.63 (CH_{Ar}), 126.52 (CH_{Ar}), 83.45 (2 × Cq), 83.34 (2 × Cq), 53.72 (CH), 52.42 (CH), 49.46 (CH), 48.11 (CH), 36.55 (CH_2), 36.03 (CH_2), 35.48 (CH_2), 33.87 (CH_2), 24.87 (4 × CH_3), 24.85 (4 × CH_3), 11.72 (CH_2–I), 9.20 (CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected.

Two minor diastereomers (dr = ca. 1:1; characteristic signals): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.39 (m, 4H, dia 3 + dia 4), 7.35–7.25 (m, 4H, dia 3 + dia 4), 7.26–7.20 (m, 2H, dia 3 + dia 4), 3.83–3.78 (m, 1H, 1 dia), 3.47–3.42 (m, 2H, dia 3 + dia 4), 3.33–3.23 (m, 2H, dia 3 + dia 4), 3.17 (ddd, J = 9.3, 8.0, 6.5 Hz, 1H, 1 dia), 2.39 (dt, J = 12.6, 7.0, 7.0 Hz, 1H, 1 dia), 1.86–1.68 (m, 2H, dia 3 + dia 4), 1.29 (s, 12H), 1.28 (s, 12H), 1.16–1.07 (m, 1H, 1 dia), 1.09–1.02 (m, 1H, 1 dia). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 135.88 (Cq), 135.63 (Cq), 131.78 (2 × CH_{Ar}), 131.12 (2 × CH_{Ar}), 129.02 (2 × CH_{Ar}), 128.97 (2 × CH_{Ar}), 126.91 (CH_{Ar}), 126.55 (CH_{Ar}), 83.36 (2 × Cq), 83.33 (2 × Cq), 54.29 (CH), 53.92 (CH), 48.18, (CH) 47.27 (CH), 37.72 (CH_2), 35.20 (CH_2), 33.99 (CH_2), 32.88 (CH_2), 24.97 (4 × CH_3), 24.83 (4 × CH_3), 13.37 (CH_2–I), 8.01 (CH_2–I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected.

Mixture of 4 diastereomers: ^{11}**B NMR** (128 MHz, $CDCl_3$) δ 34.2; IR (neat): ν_{max} = 2975, 2923, 2868, 1479, 1370, 1314, 1214, 1141, 856, 737, 689 cm^{-1}; HRMS (ESI): Calculated for $C_{18}H_{26}BISO_2$ $[M+Na]^+$: 467.0791; found: 467.0665.

[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl] acetate (38l)



38l
Chemical Formula: $C_{14}H_{24}BIO_4$
Exact Mass: 394.0812

Followed **GP1** with vinyl acetate (52.2 mg, 0.521 mmol). Purification by column chromatography (Macherey-Nagel Silica 60, 0.015–0.04 mm) (5% Et_2O:pentane) provided the desired **38l** (40 mg, 0.102 mmol, 18% dr = 44:28:21:6).

Colorless oil; Rf: 0.21 (9:1 pentane:Et_2O); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 5.26 – 4.74 (m, 1H), 3.38 – 3.10 (m, 2H), 2.48 – 2.19 (m, 1H), 2.19 – 2.06 (m, 1H), 2.02 (d, J = 9.3 Hz, 3H), 1.99 – 1.91 (m, 1H), 1.83 (dddd, J = 19.3, 9.6, 7.2, 3.7 Hz, 1H), 1.59 – 1.37 (m, 1H), 1.23 (d, J = 2.3 Hz, 17H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 170.8 (Cq), 170.5 (Cq), 170.5 (Cq), 83.3 (Cq), 83.3 (Cq), 83.2 (Cq), 82.9 (Cq), 81.0 (CH), 78.2 (CH), 77.6 (CH), 49.8 (CH), 48.6 (CH), 47.3 (CH), 35.1 (CH_2), 35.0 (CH_2), 34.9 (CH_2), 34.8 (CH_2), 34.5 (CH_2), 33.3 (CH_2), 32.7 (CH_2), 32.5 (CH_2), 24.8 (CH_3), 24.8 (CH_3), 24.7 (CH_3), 24.7 (CH_3), 21.3 (CH_3), 21.2 (CH_3), 21.2 (CH_3), 21.2 (CH_3), 10.0 (CH_2-I), 9.5 (CH_2-I), 4.6 (CH_2-I), 4.3 (CH_2-I). Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the methine adjacent to boron was not detected; ^{11}**B NMR** (128 MHz, $CDCl_3$) δ 34.1; IR (neat): ν_{max} = 2975, 2933, 1725, 1371, 1315, 1187, 1165, 1141, 969, 856 cm^{-1}; HRMS (ESI): Calculated for $C_{14}H_{24}BIO_4$ $[M+Na]^+$: 417.0812; found: 417.0695.

A Appendix

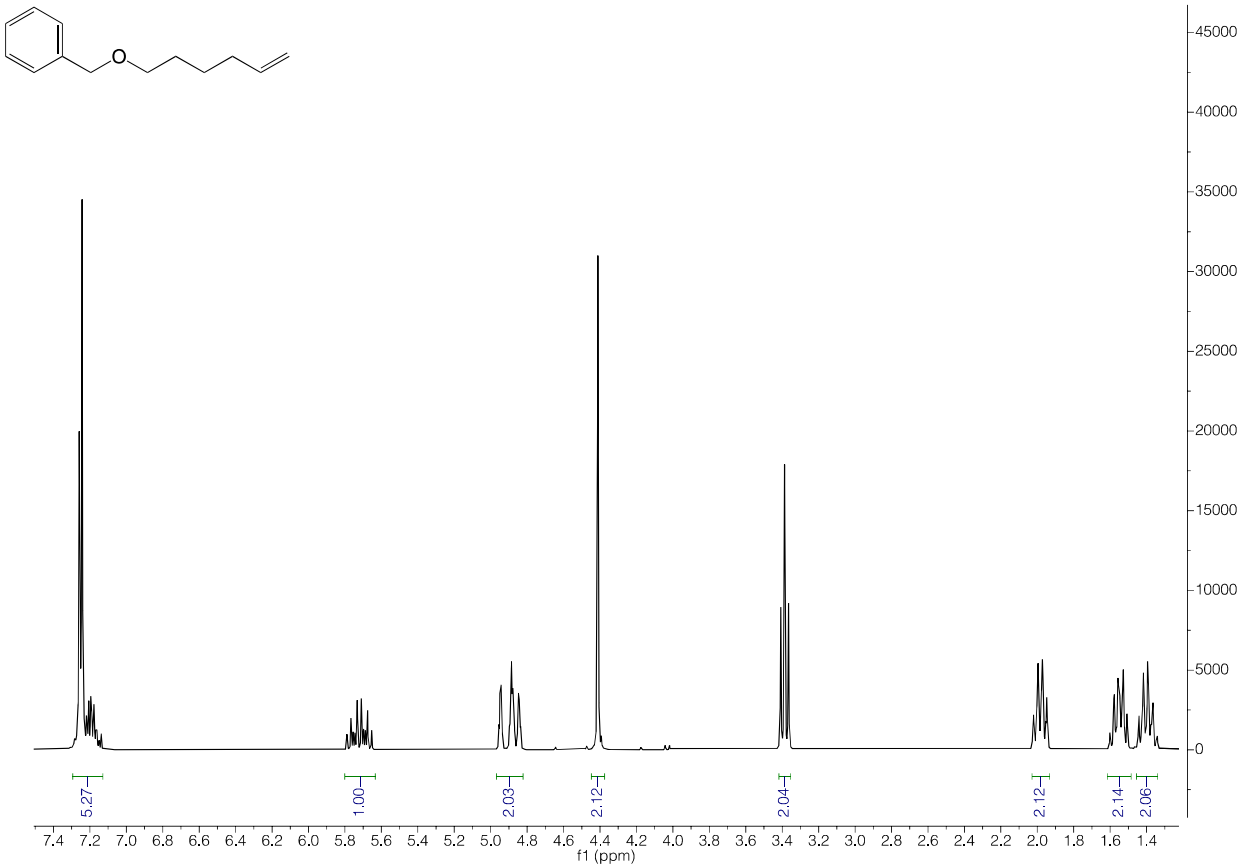
NMR Spectra

A.1 NMR Spectra Chapter 1

Synthesis and Isolation of 1,3-iodopinacol boronic esters via intermolecular Atom Transfer Radical Addition of α-boryl radicals

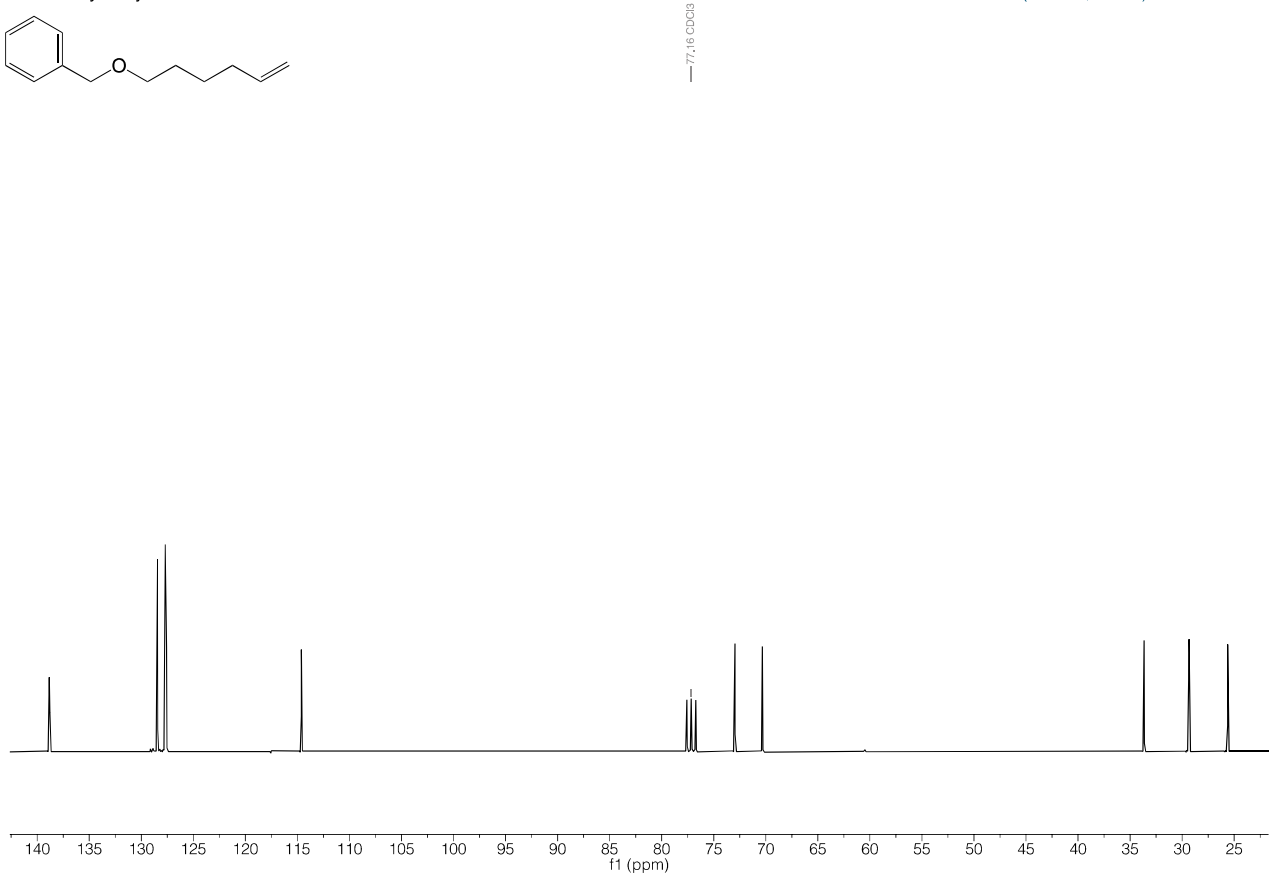
Hex-5-enoxymethylbenzene

^{1}H-NMR (300 MHz, $CDCl_3$)

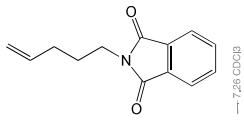


Hex-5-enoxymethylbenzene

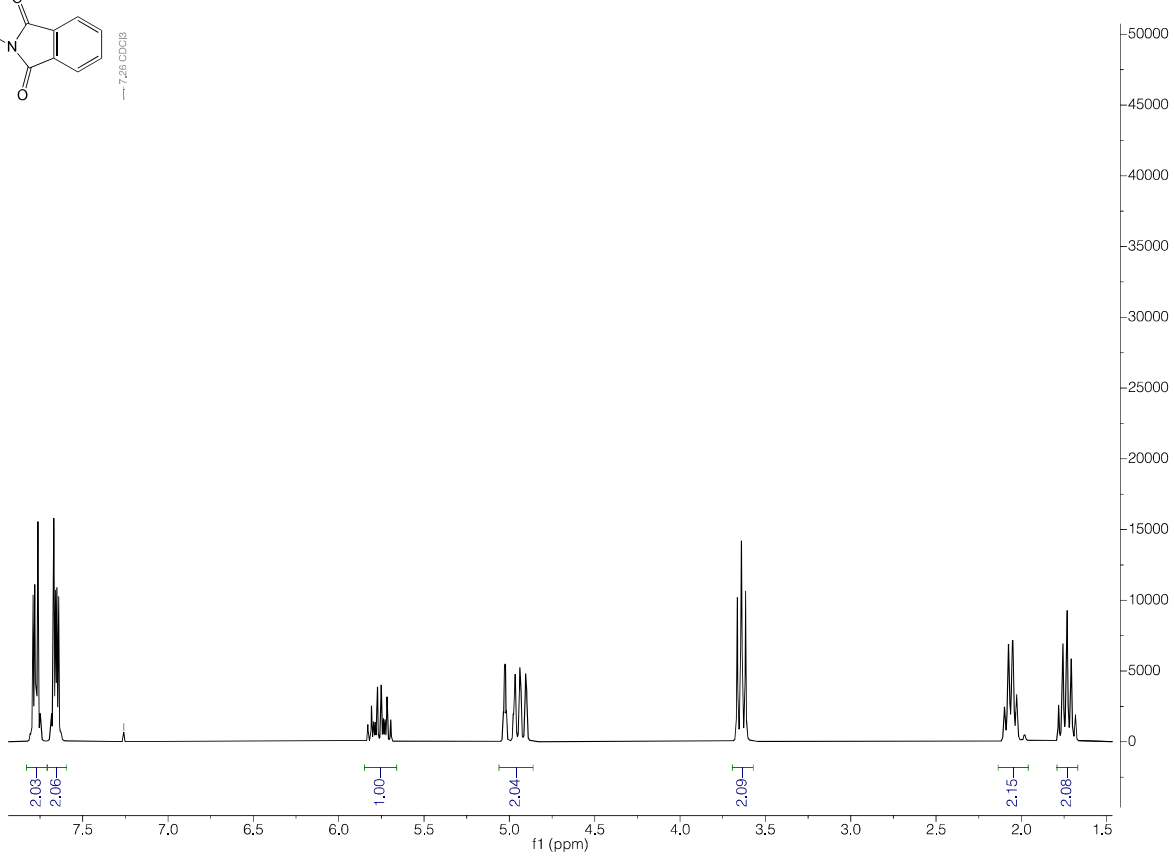
^{13}C-NMR (75 MHz, $CDCl_3$)



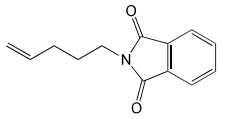
2-(Pent-4-en-1-yl)isoindoline-1,3-dione



^{1}H-NMR (300 MHz, $CDCl_3$)



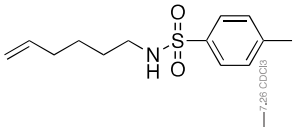
2-(Pent-4-en-1-yl)isoindoline-1,3-dione

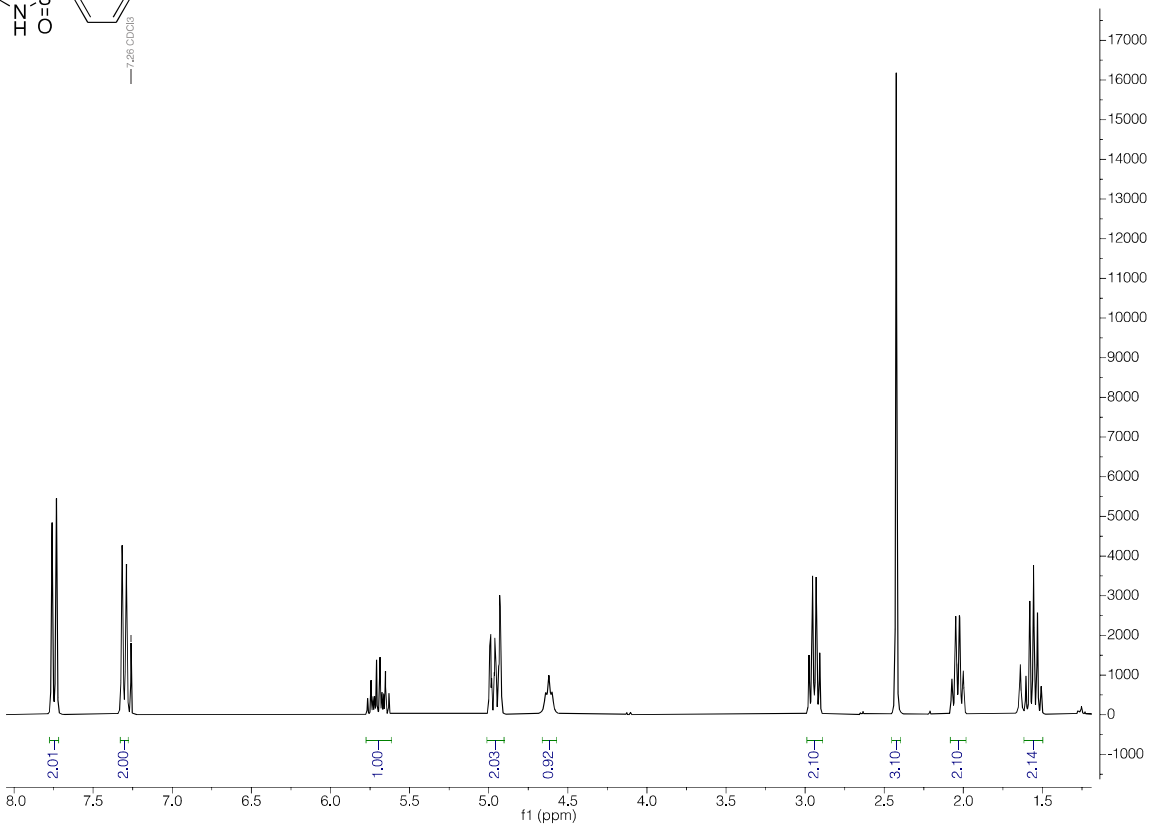


^{13}C-NMR (75 MHz, $CDCl_3$)

4-Methyl-N-pent-4-enyl-benzenesulfonamide

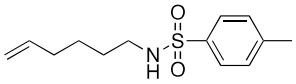
^{1}H-NMR (300 MHz, $CDCl_3$)





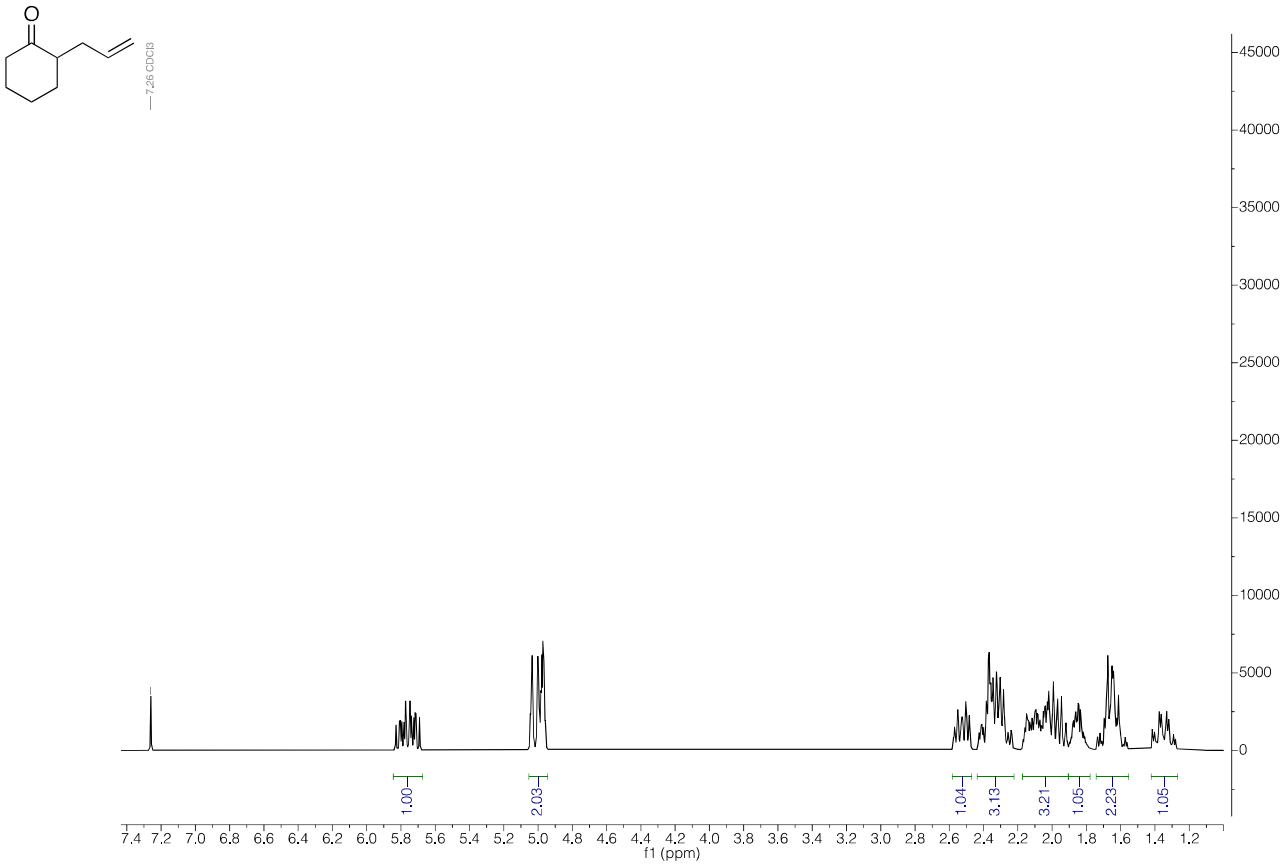
4-Methyl-N-pent-4-enyl-benzenesulfonamide

^{13}C-NMR (75 MHz, $CDCl_3$)



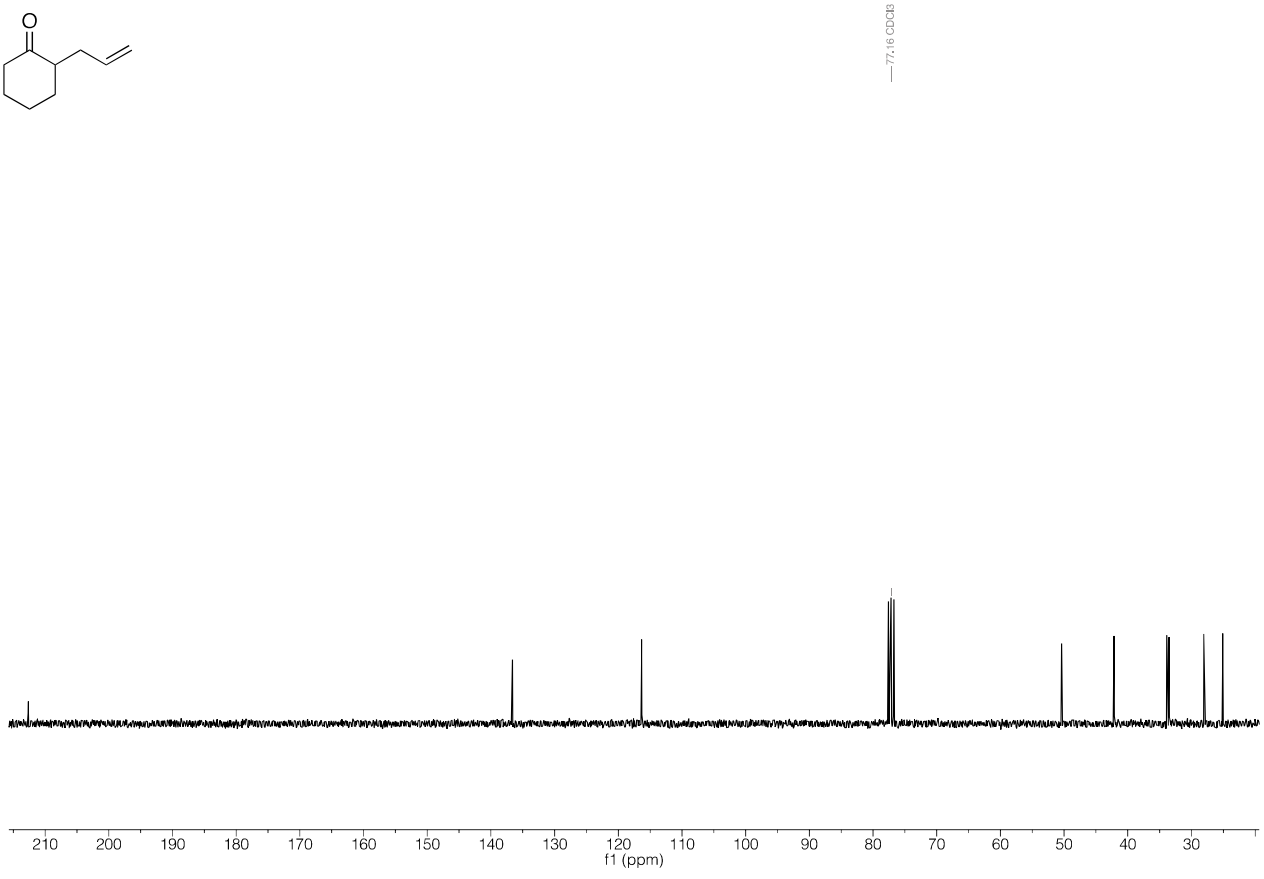
2-Allylcyclohexanone

^{1}H-NMR (300 MHz, $CDCl_3$)



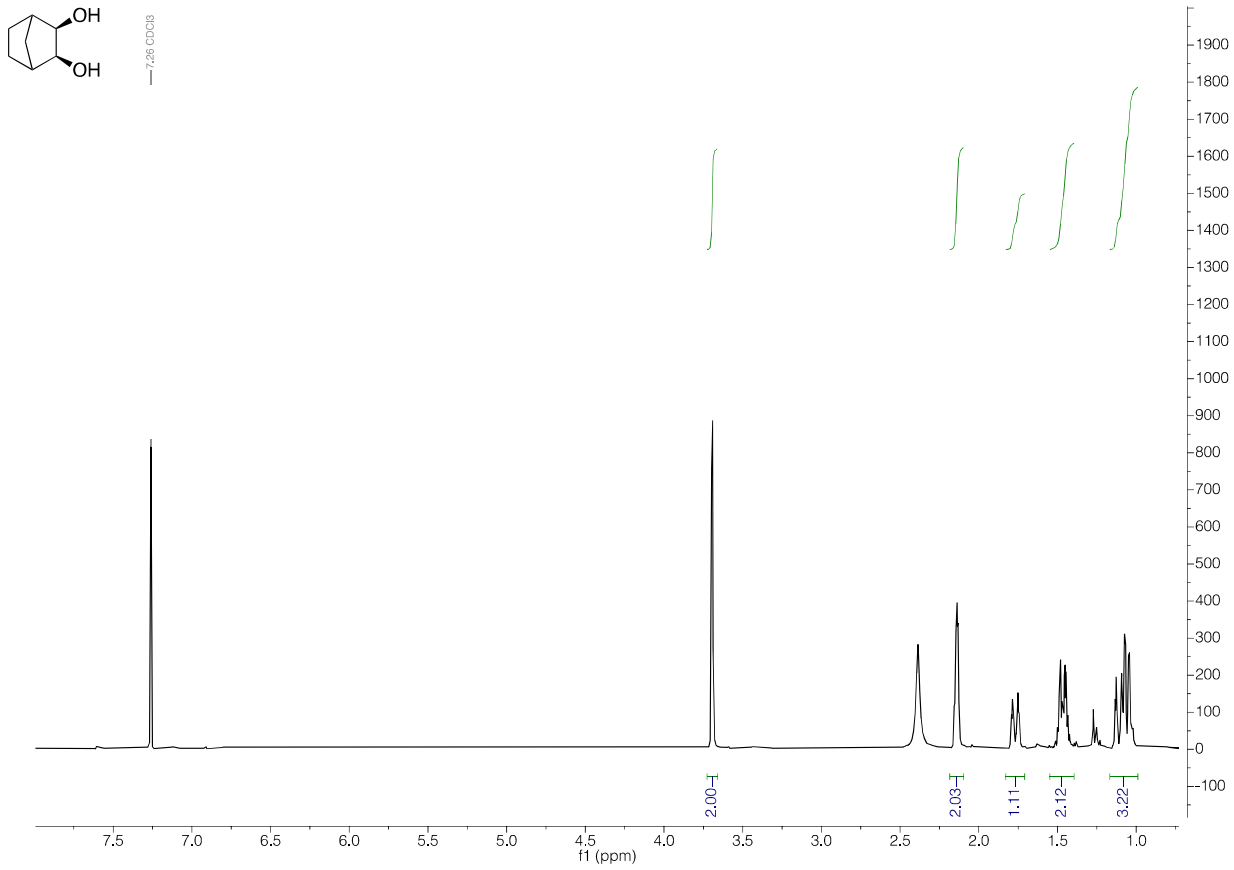
2-Allylcyclohexanone

^{13}C-NMR (75 MHz, $CDCl_3$)



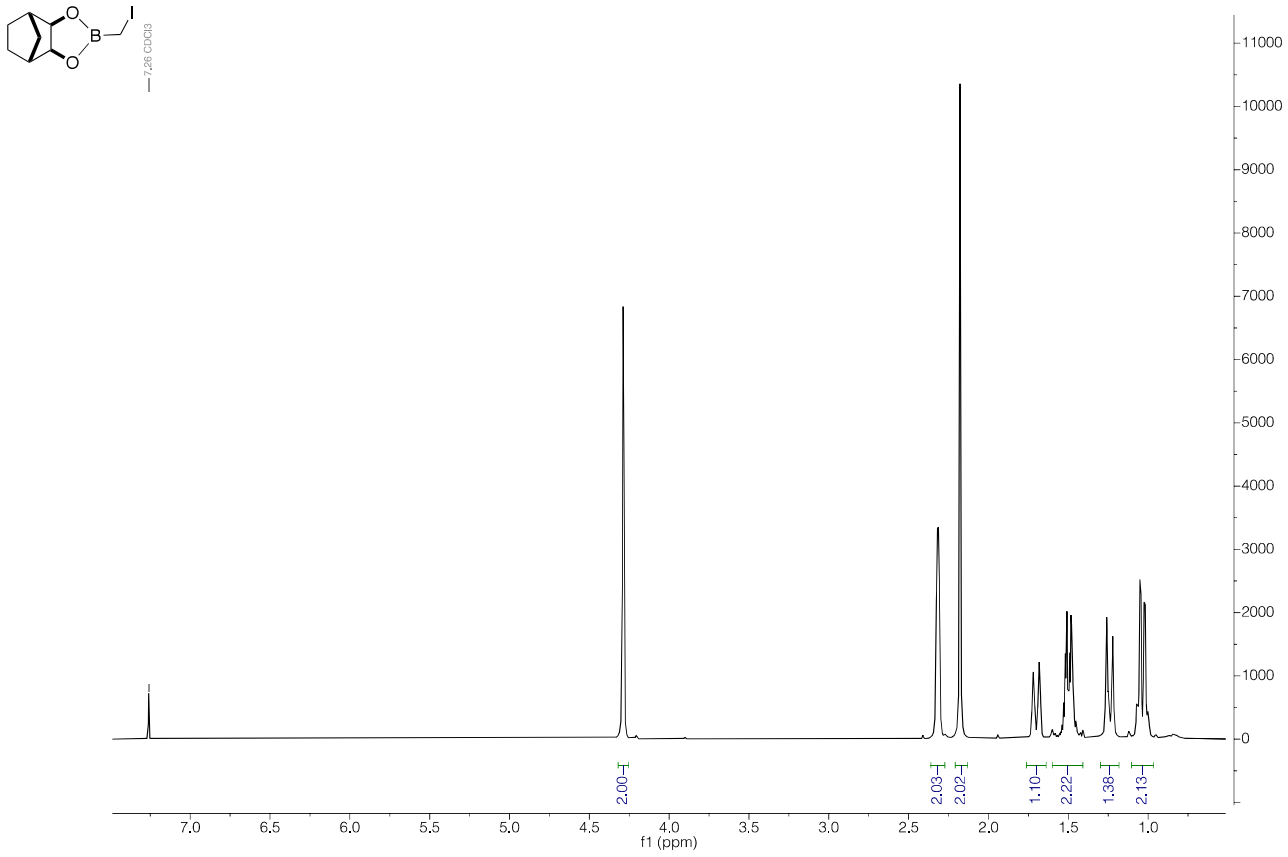
(2R,3S)-norbornane-2,3-diol

^{1}H-NMR (300 MHz, $CDCl_3$)



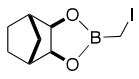
exo,exo-2-(Iodomethyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

^{1}H-NMR (300 MHz, $CDCl_3$)



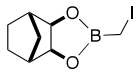
exo,exo-2-(Iodomethyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

^{13}C-NMR (96 MHz, $CDCl_3$)



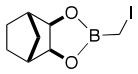
exo,exo-2-(Iodomethyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

^{11}B-NMR (96 MHz, $CDCl_3$)

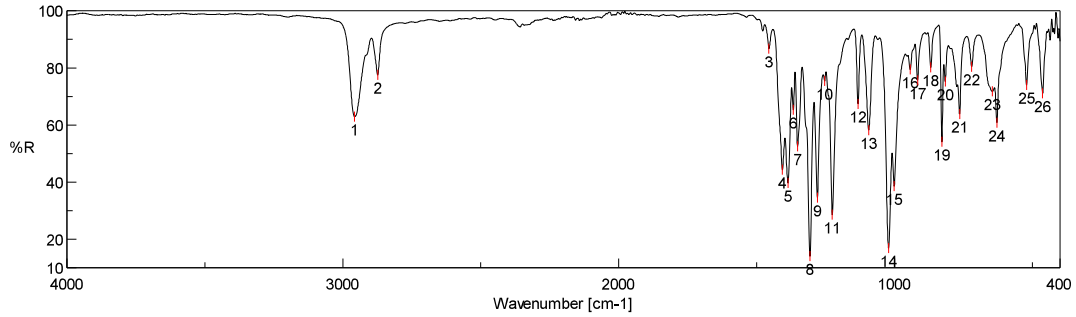


exo,exo-2-(Iodomethyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

FT-IR, ATR-diamond



Peak Find - Memory-2

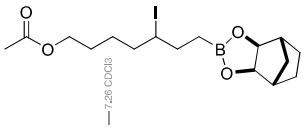


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2957.3	62.9455	2	2873.42	77.4931	3	1455.03	86.6726
4	1406.82	44.3111	5	1386.57	39.651	6	1367.28	65.2648
7	1351.86	52.5138	8	1306.54	14.0621	9	1279.54	34.536
10	1253.5	75.3804	11	1225.54	28.532	12	1132.01	67.393
13	1093.44	58.1405	14	1021.12	16.888	15	1000.87	38.5739
16	943.02	79.3877	17	916.022	75.6386	18	868.774	80.1304
19	828.277	54.131	20	815.742	75.139	21	763.673	63.8561
22	720.282	80.3833	23	645.072	71.7492	24	628.68	60.8142
25	520.686	74.0151	26	462.832	71.0394			

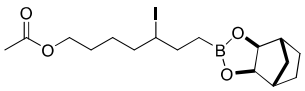
7-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-5-iodoheptyl acetate

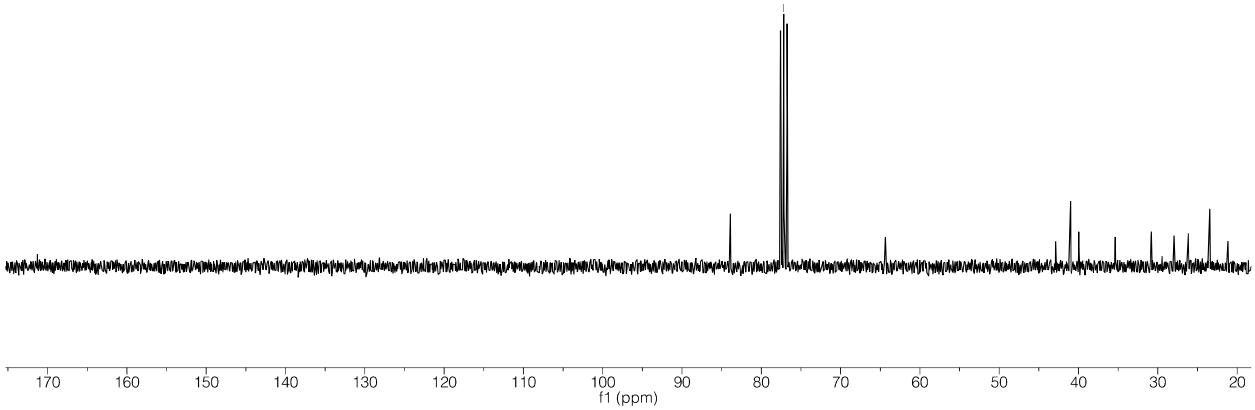
^{1}H-NMR (300 MHz, $CDCl_3$)



7-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-5-iodoheptyl acetate

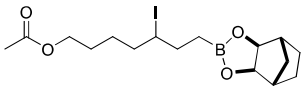
^{13}C-NMR (75 MHz, $CDCl_3$)

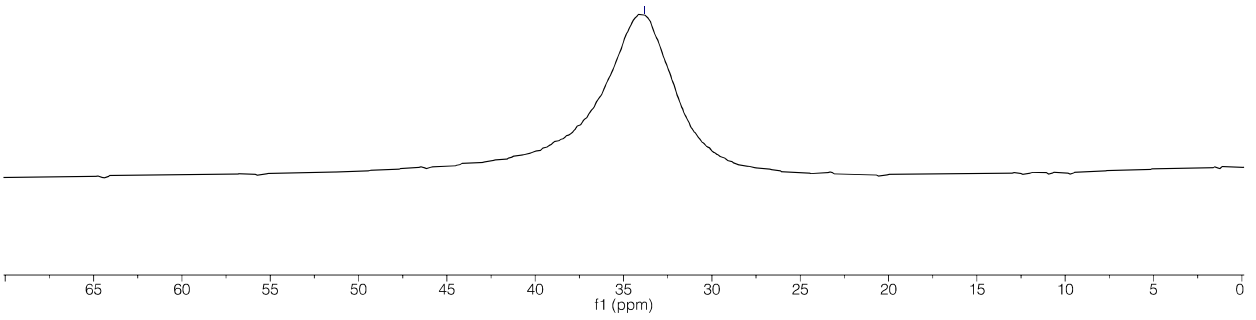




7-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-5-iodoheptyl acetate

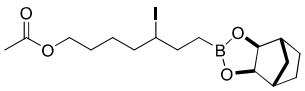
^{11}B-NMR (96 MHz, $CDCl_3$)



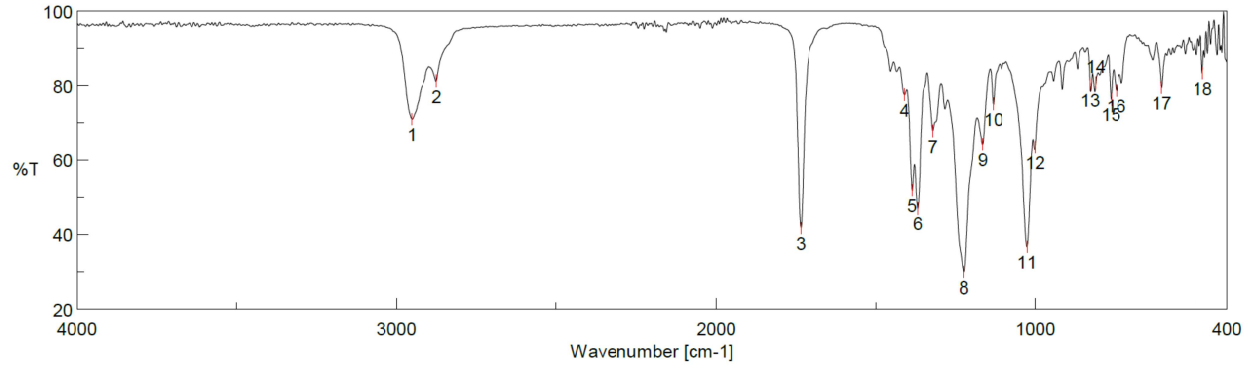


7-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-5-iodoheptyl acetate

FT-IR, ATR-diamond



Peak Find - Memory-2

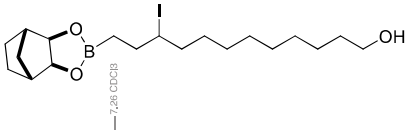


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2951.52	71	2	2873.42	81	3	1735.62	42
4	1409.71	78	5	1386.57	52	6	1368.25	47
7	1321	68	8	1224.58	30	9	1165.76	64
10	1132.01	75	11	1026.91	37	12	1000.87	63
13	830.205	80	14	811.885	81	15	764.637	76
16	748.245	79	17	605.539	79	18	477.296	83

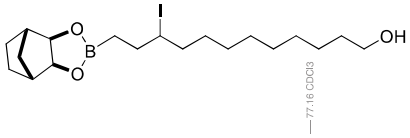
12-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-10-iodododecan-1-ol

^{1}H-NMR (300 MHz, $CDCl_3$)

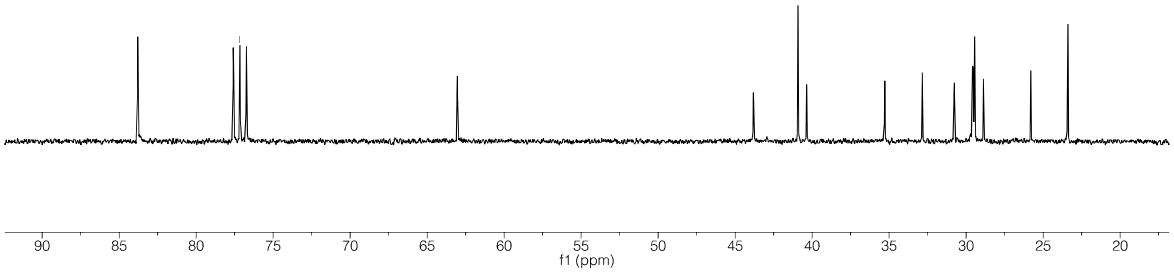


12-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-10-iodododecan-1-ol

^{13}C-NMR (75 MHz, $CDCl_3$)

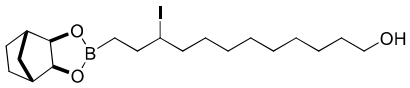


77.16 CDCl3

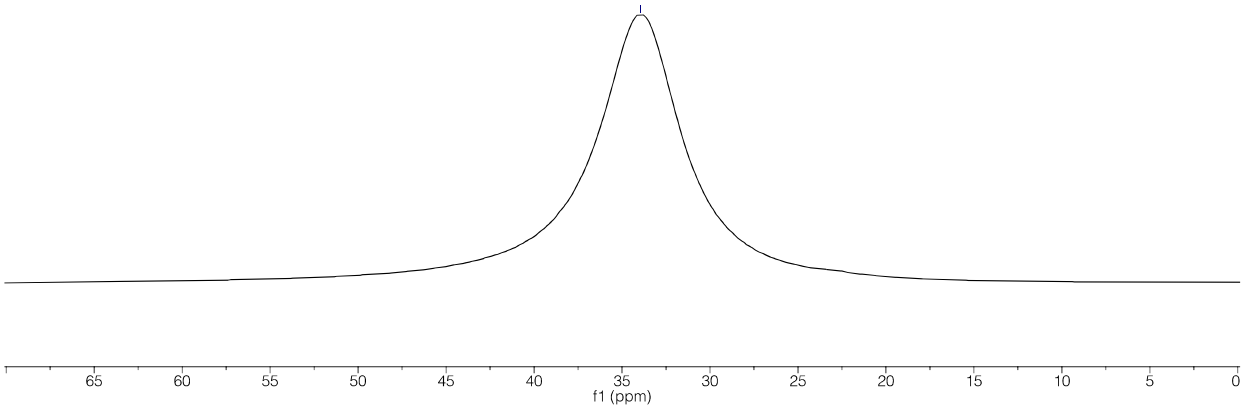


12-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-10-iodododecan-1-ol

^{11}B-NMR (96 MHz, $CDCl_3$)

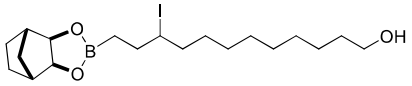


33.97

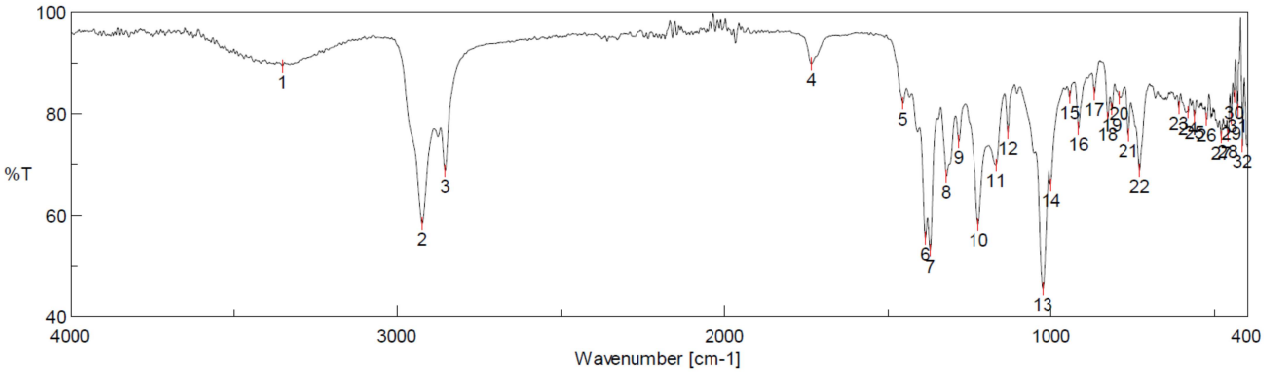


12-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-10-iodododecan-1-ol

FT-IR, ATR-diamond



Peak Find - Memory-33

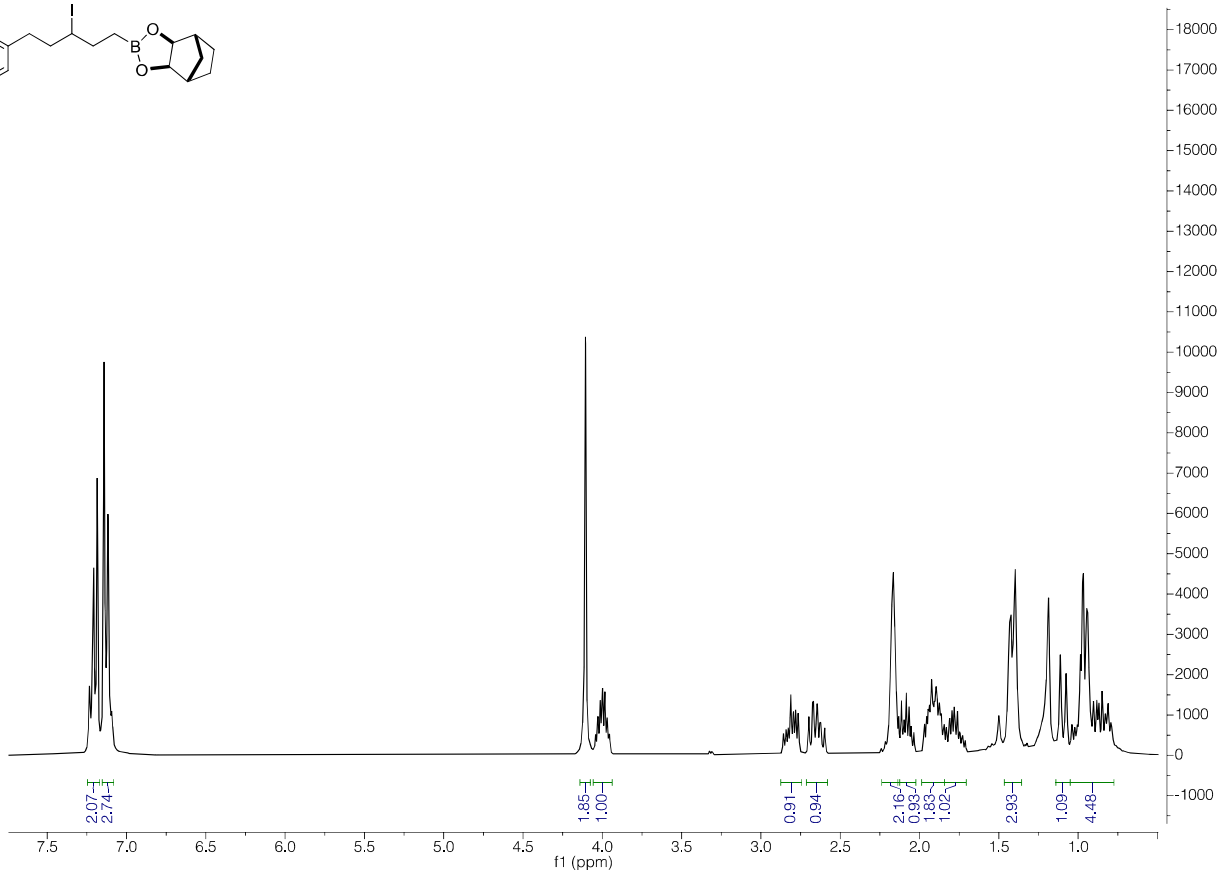


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3352.16	89	2	2924.04	58	3	2852.68	69
4	1734.17	90	5	1455.51	82	6	1385.6	55
7	1370.66	53	8	1321	68	9	1283.39	75
10	1223.61	58	11	1169.13	70	12	1132.49	76
13	1026.91	45	14	1001.84	66	15	943.502	83
16	916.504	77	17	868.774	84	18	828.277	79
19	815.742	81	20	792.6	83	21	764.155	76
22	729.925	69	23	609.396	81	24	580.469	80
25	561.184	79	26	524.543	79	27	480.188	75
28	459.939	76	29	449.333	79	30	440.655	83
31	430.53	81	32	415.585	74			

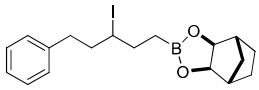
(3aR,4S,7R,7aS)-2-(3-iodo-5-phenylpentyl)Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

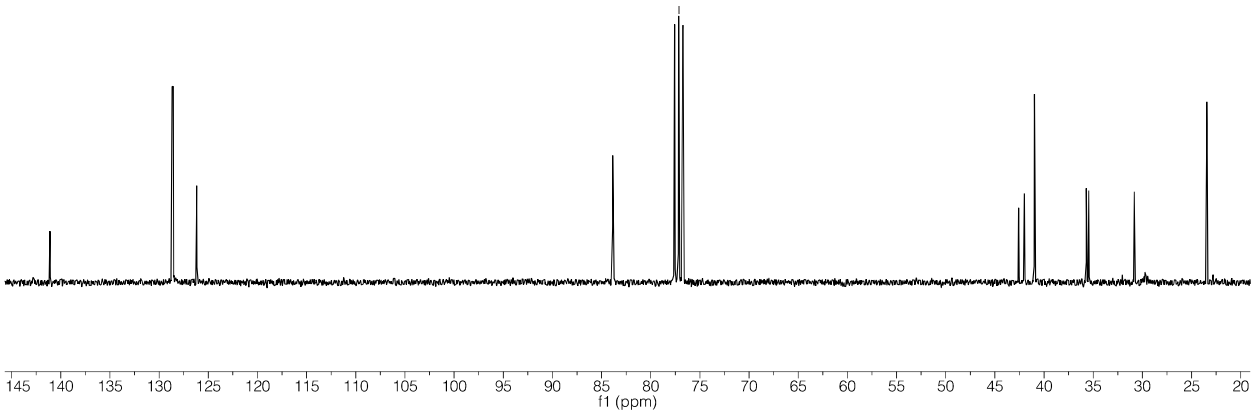
^{1}H-NMR (300 MHz, $CDCl_3$)



(3aR,4S,7R,7aS)-2-(3-iodo-5-phenylpentyl)Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

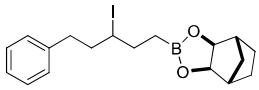
^{13}C-NMR (75 MHz, $CDCl_3$)

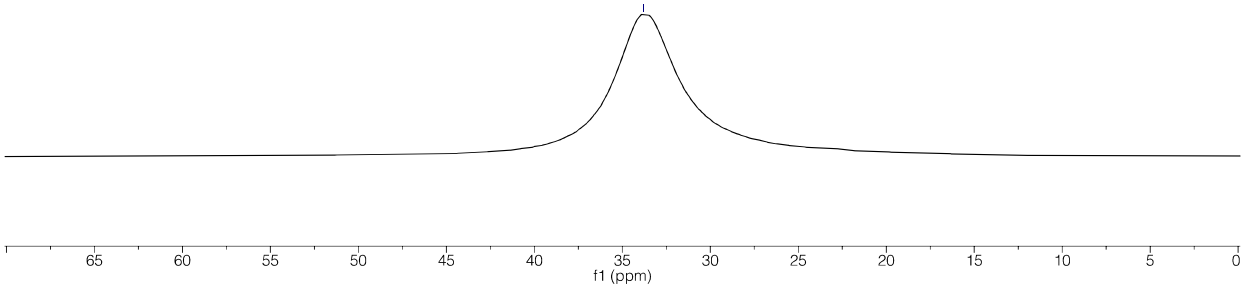




(3aR,4S,7R,7aS)-2-(3-iodo-5-phenylpentyl)Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

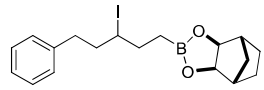
^{11}B-NMR (96 MHz, $CDCl_3$)

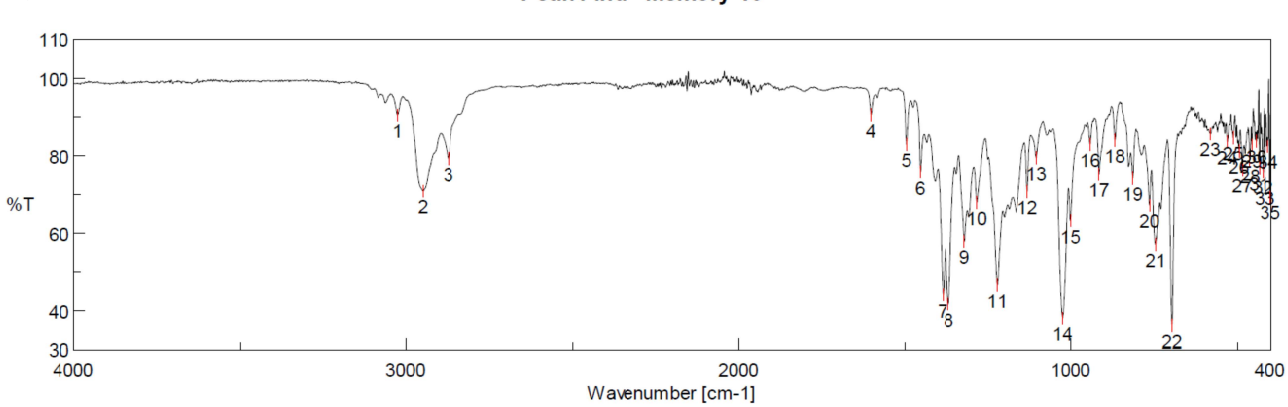




(3aR,4S,7R,7aS)-2-(3-iodo-5-phenylpentyl)Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

FT-IR, ATR-diamond



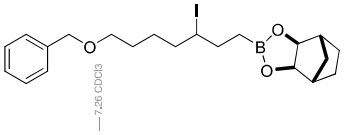


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3025.28	90	2	2949.59	71	3	2873.9	79
4	1602.56	91	5	1495.04	83	6	1453.58	76
7	1385.6	44	8	1369.21	42	9	1321	58
10	1283.88	68	11	1223.13	47	12	1132.49	71
13	1105.01	79	14	1025.94	38	15	1002.32	63
16	943.02	83	17	916.504	75	18	869.256	84
19	815.742	74	20	764.637	67	21	746.317	57
22	697.623	36	23	580.951	86	24	530.328	84
25	513.454	85	26	496.098	81	27	485.974	76
28	463.314	79	29	457.529	83	30	443.547	84
31	434.869	77	32	423.781	76	33	418.477	73
34	407.871	82	35	402.085	69			

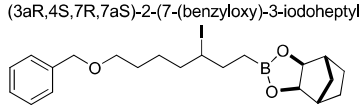
(3aR,4S,7R,7aS)-2-(7-(benzyloxy)-3-iodoheptyl)Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

^{1}H-NMR (400 MHz, $CDCl_3$)



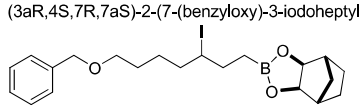
(3aR,4S,7R,7aS)-2-(7-(benzyloxy)-3-iodoheptyl)Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

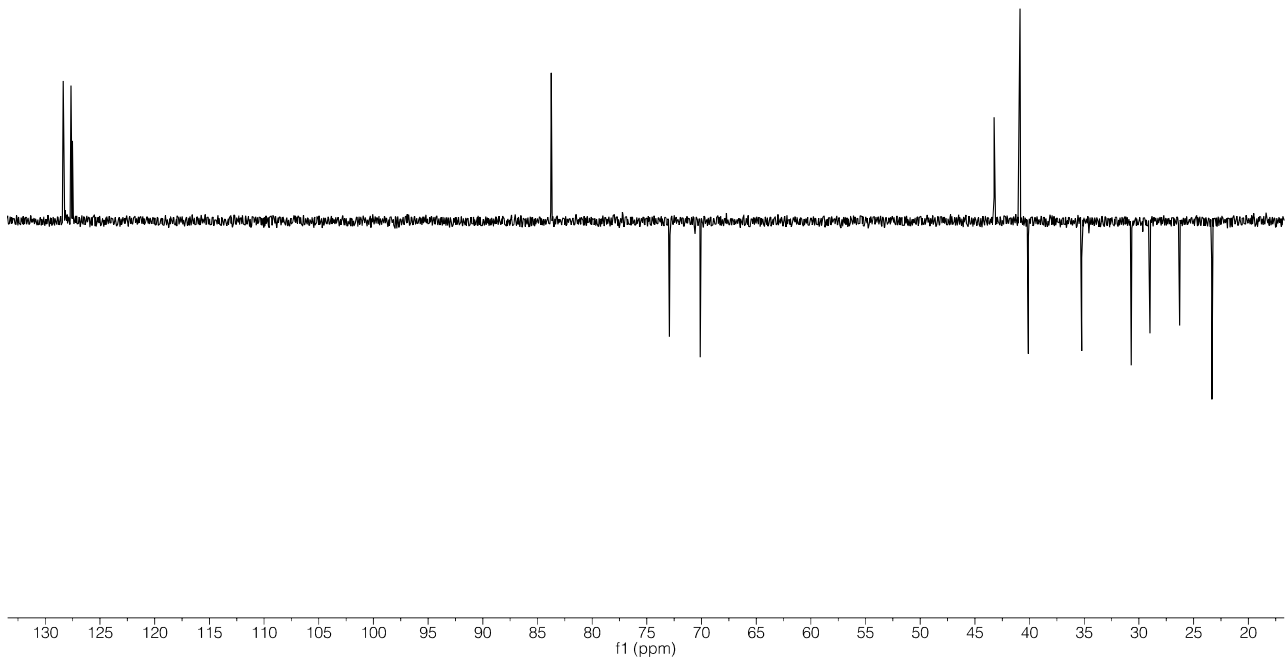
^{13}C-NMR (101 MHz, $CDCl_3$)



(3aR,4S,7R,7aS)-2-(7-(benzyloxy)-3-iodoheptyl)Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

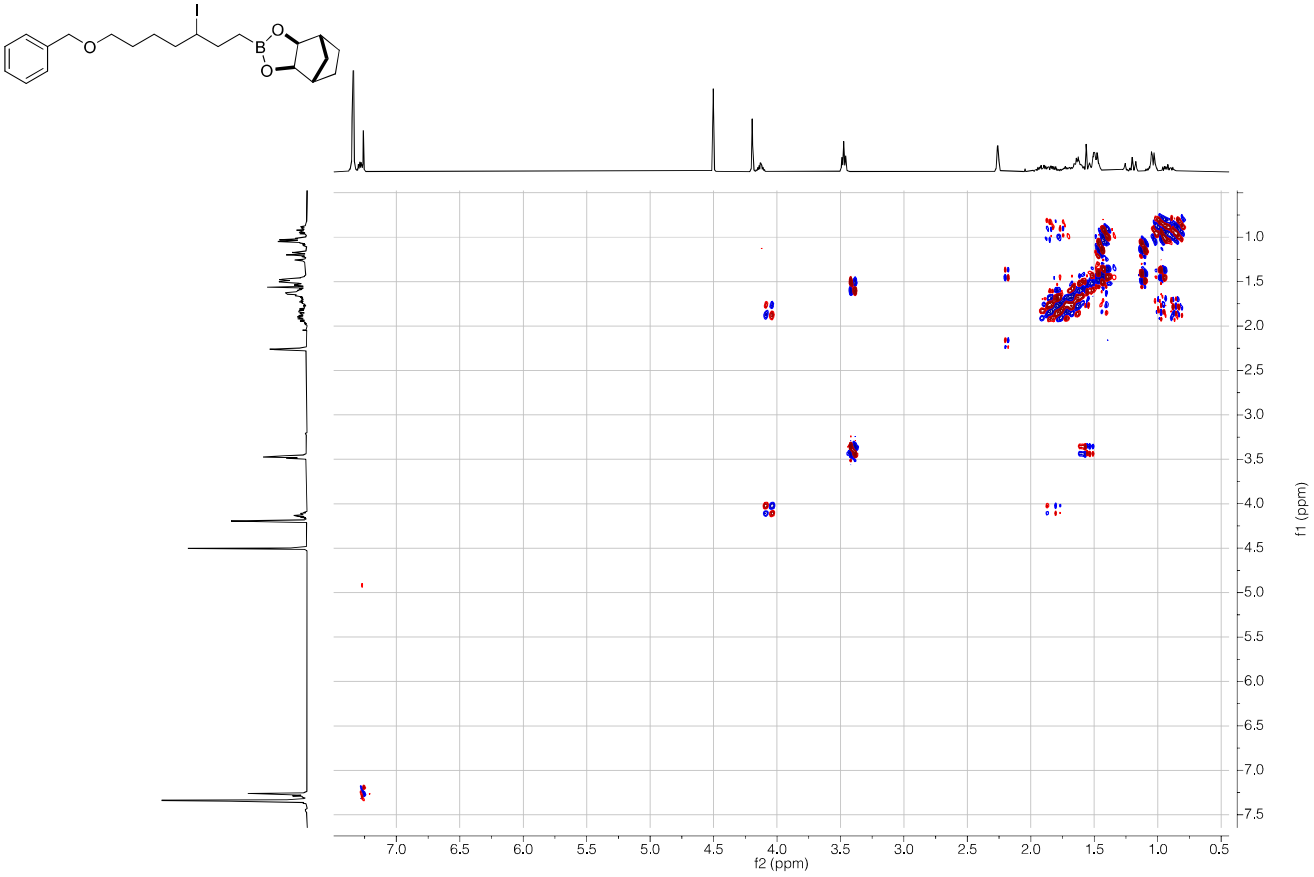
DEPT-135 (101 MHz, $CDCl_3$)





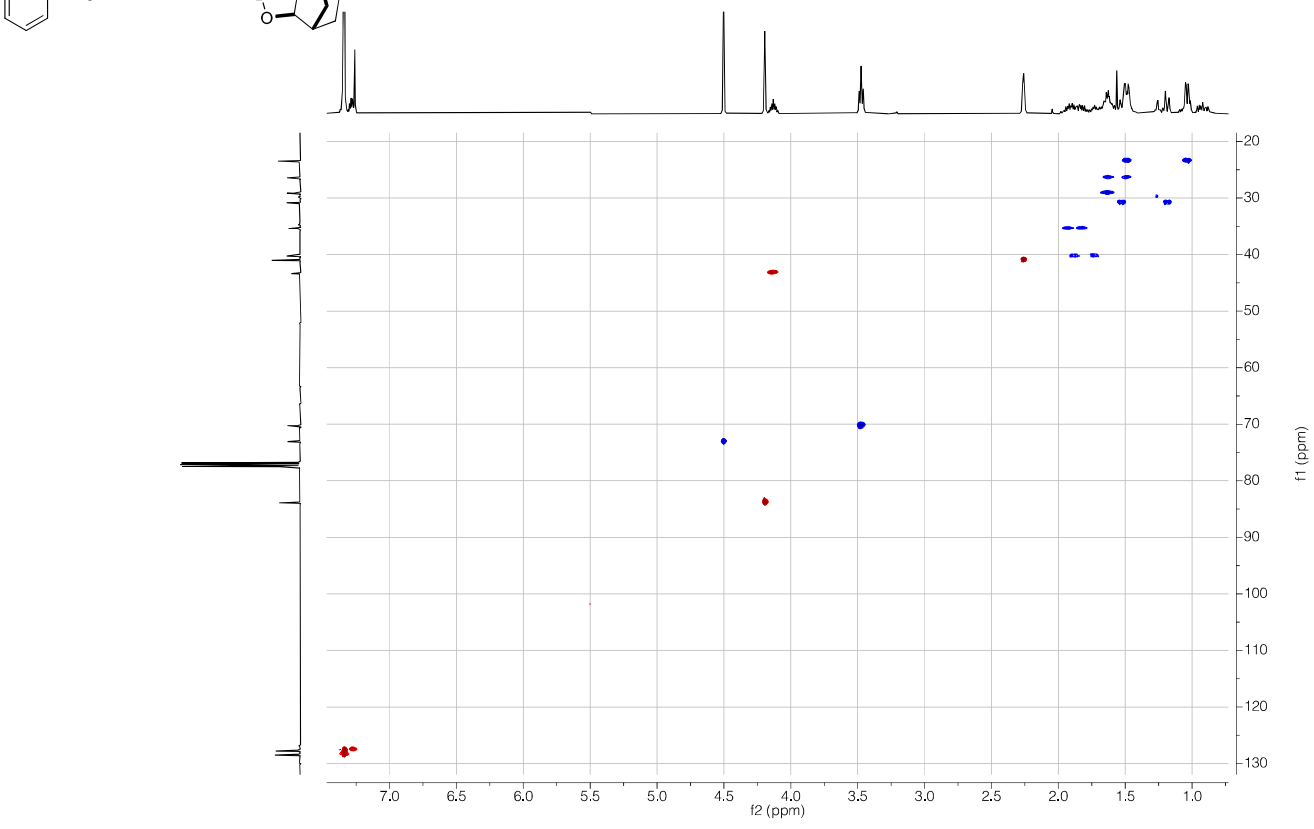
(3aR,4S,7R,7aS)-2-(7-(benzyloxy)-3-iodoheptyl)Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



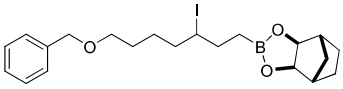
(3aR,4S,7R,7aS)-2-(7-(benzyloxy)-3-iodoheptyl)Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

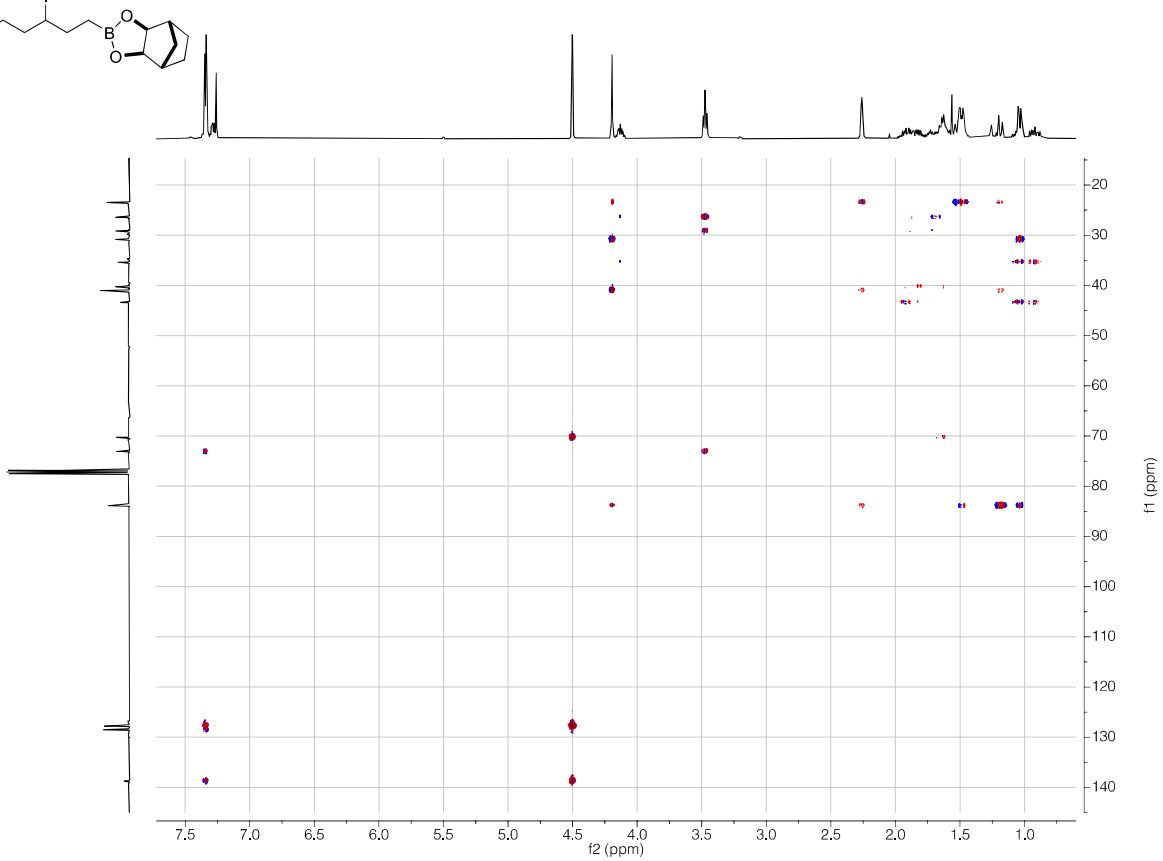
^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



(3aR,4S,7R,7aS)-2-(7-(benzyloxy)-3-iodoheptyl)Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

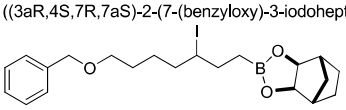
^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



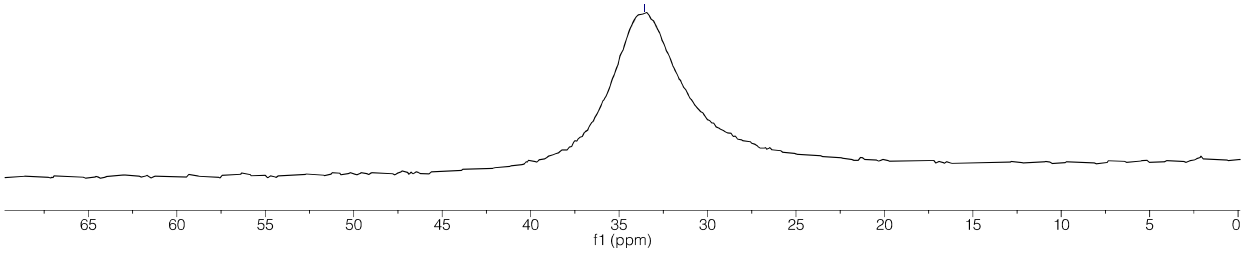


((3aR,4S,7R,7aS)-2-(7-(benzyloxy)-3-iodoheptyl)Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

^{11}B-NMR (96 MHz, $CDCl_3$)

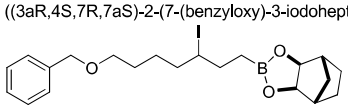


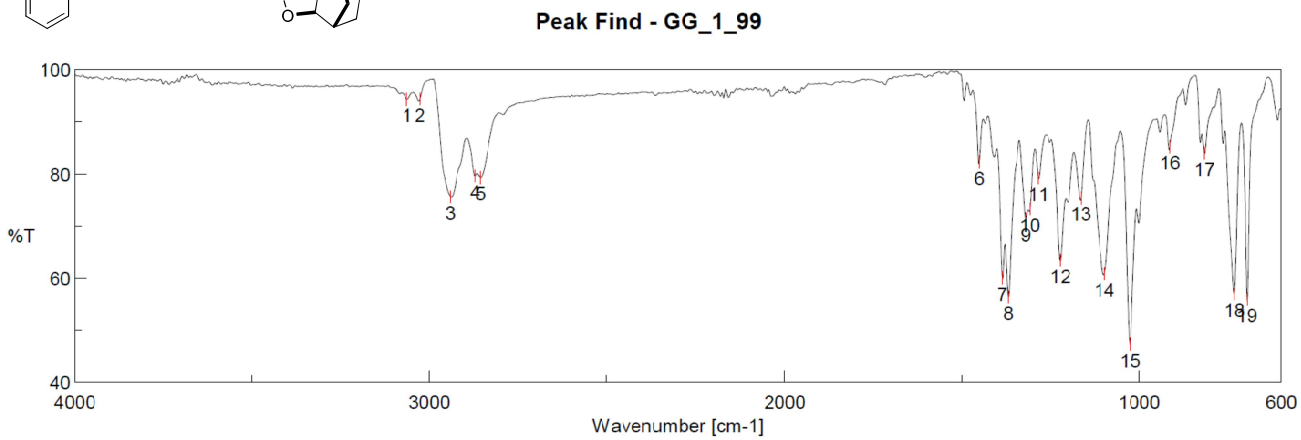
33.56



((3aR,4S,7R,7aS)-2-(7-(benzyloxy)-3-iodoheptyl)Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

FT-IR, ATR-diamond



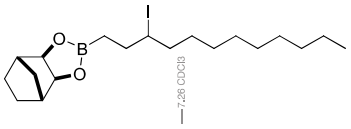


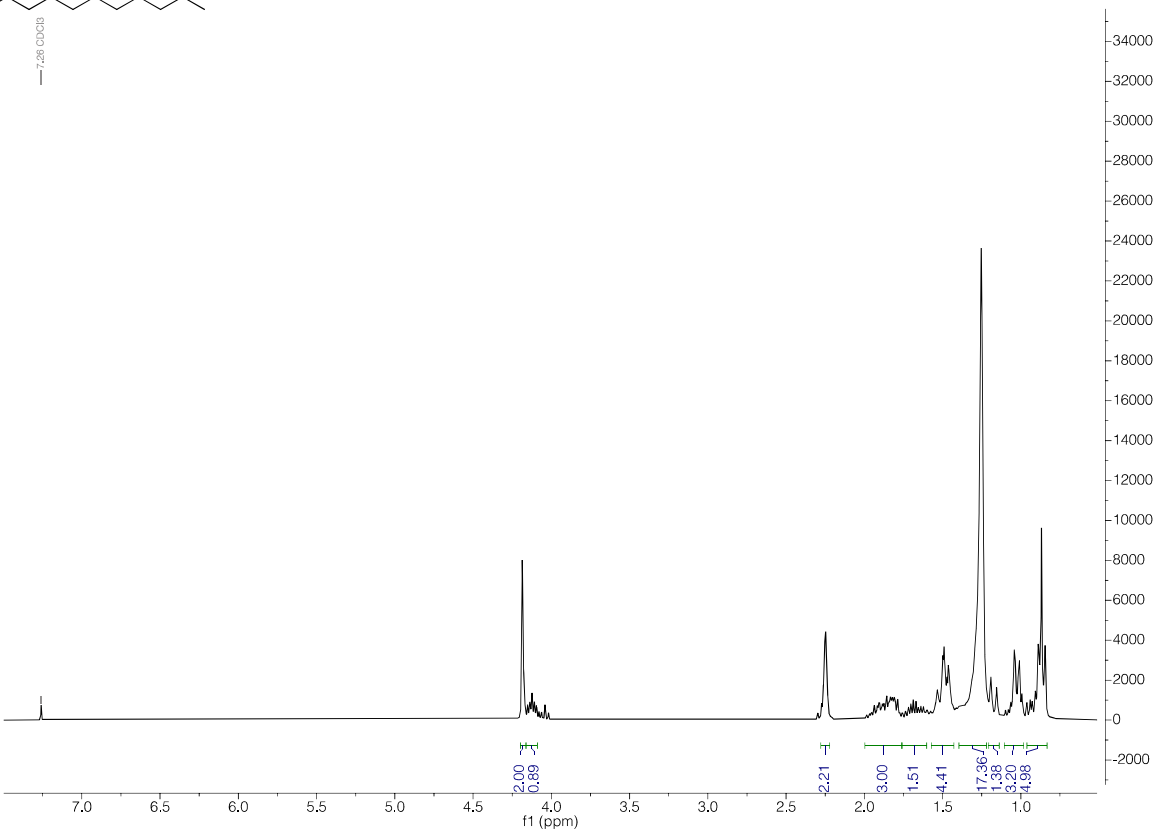
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3063.37	94	2	3026.73	94	3	2940.91	76
4	2870.52	80	5	2856.06	79	6	1452.14	82
7	1386.57	60	8	1369.21	56	9	1320.04	71
10	1308.46	73	11	1284.36	79	12	1222.65	63
13	1164.79	75	14	1099.23	61	15	1025.94	47
16	914.093	85	17	816.706	84	18	731.853	57
19	697.141	56						

(3aR,4S,7R,7aS)-2-(3-Iodododecyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

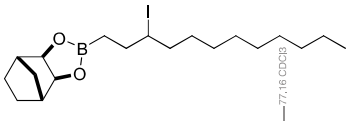
^{1}H-NMR (300 MHz, $CDCl_3$)

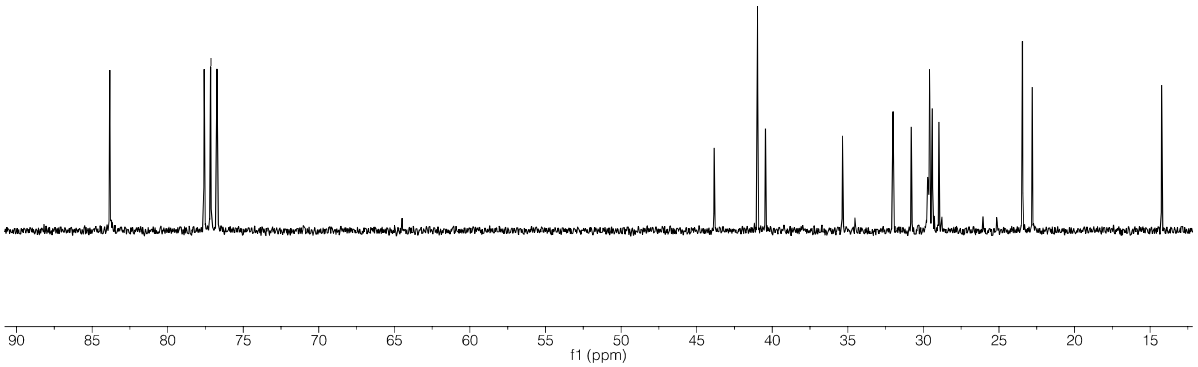




(3aR,4S,7R,7aS)-2-(3-Iodododecyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

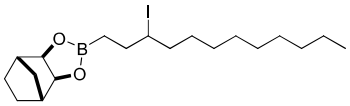
^{13}C-NMR (75 MHz, $CDCl_3$)

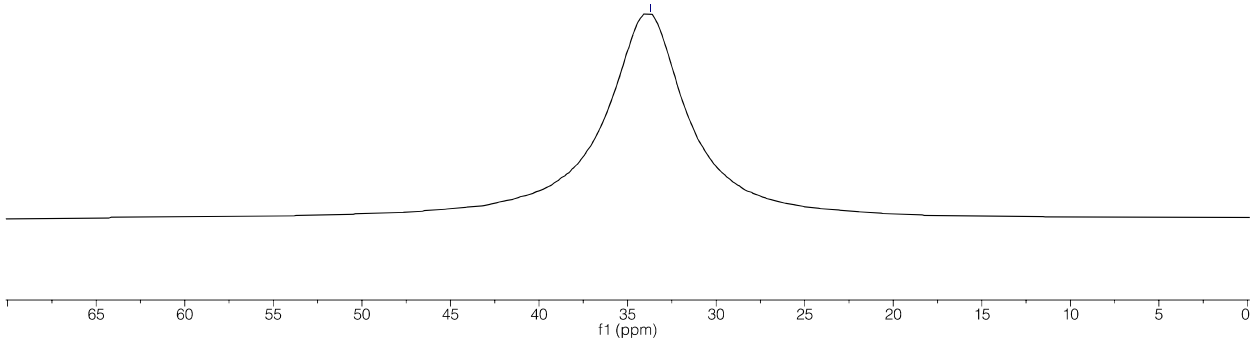




(3aR,4S,7R,7aS)-2-(3-Iodododecyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

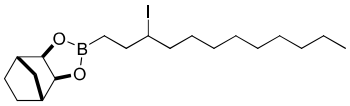
^{11}B-NMR (96 MHz, $CDCl_3$)



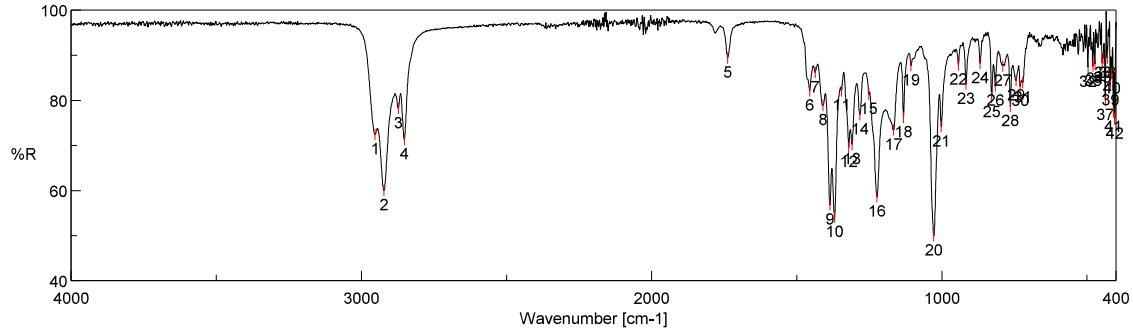


(3aR,4S,7R,7aS)-2-(3-Iodododecyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

FT-IR, ATR-diamond



Peak Find - Memory-2

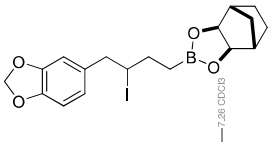


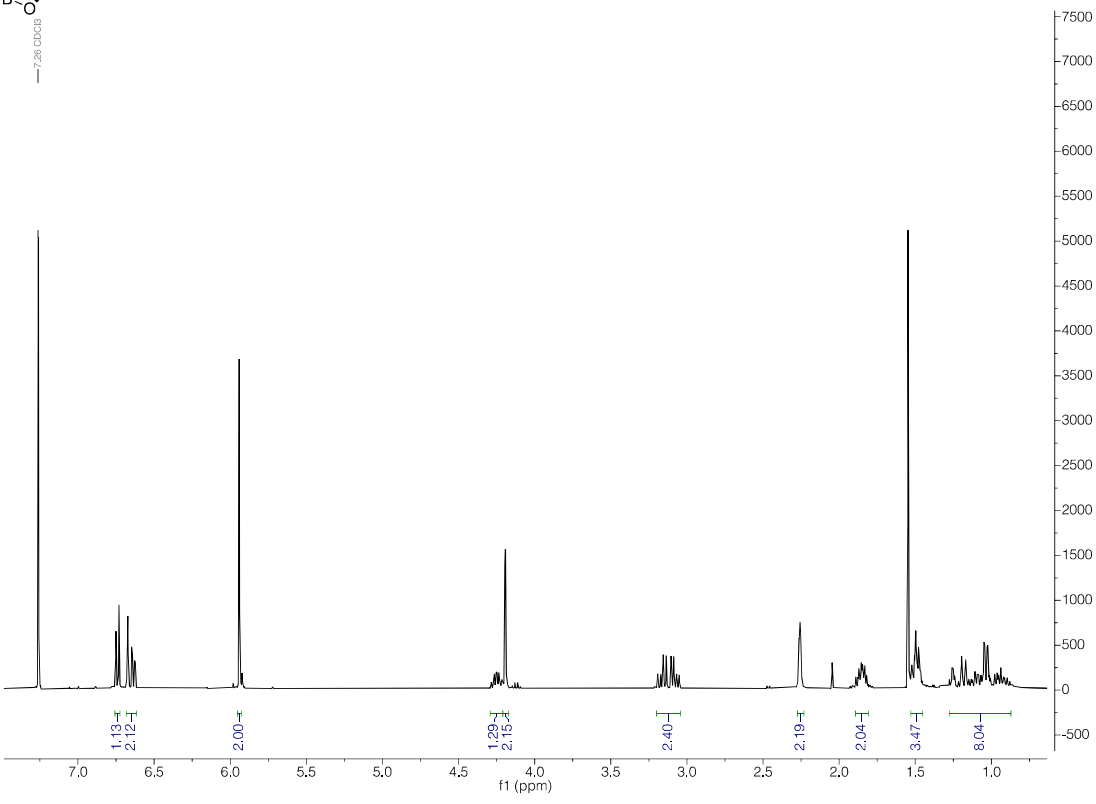
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2952.48	72.4383	2	2922.11	60.0128	3	2872.93	78.1822
4	2852.2	71.2824	5	1738.51	89.3898	6	1455.51	82.1002
7	1436.71	86.1368	8	1409.71	78.8472	9	1386.09	56.8388
10	1370.18	54.0932	11	1346.07	82.0748	12	1321	69.5964
13	1309.91	70.1858	14	1282.91	76.7827	15	1252.06	81.2907
16	1223.61	58.6144	17	1166.24	73.4119	18	1132.49	76.1563
19	1106.46	87.6734	20	1027.87	49.9459	21	1002.32	74.112
22	943.502	87.8559	23	916.986	83.584	24	868.774	88.1382
25	828.277	80.6039	26	815.742	83.1605	27	790.671	87.5901
28	764.637	78.6336	29	744.388	84.3356	30	730.407	83.0792
31	721.247	83.8929	32	497.062	87.34	33	480.188	87.5396
34	473.439	88.0822	35	447.886	88.2352	36	444.512	89.3133
37	437.28	80.0072	38	430.53	89.3349	39	419.924	83.2235
40	414.62	85.82	41	409.317	77.3654	42	404.496	75.8501

(3aR,4S,7R,7aS)-2-(4-(Benzo[d][1,3]dioxol-5-yl)-3-iodobutyl)hexahydro-4,7 methanobenzo[d][1,3,2]dioxaborole

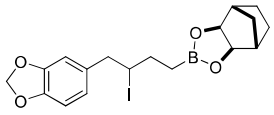
^{1}H-NMR (400 MHz, $CDCl_3$)





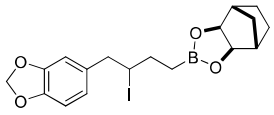
(3aR,4S,7R,7aS)-2-(4-(Benzo[d][1,3]dioxol-5-yl)-3-iodobutyl)hexahydro-4,7 methanobenzo[d][1,3,2]dioxaborole

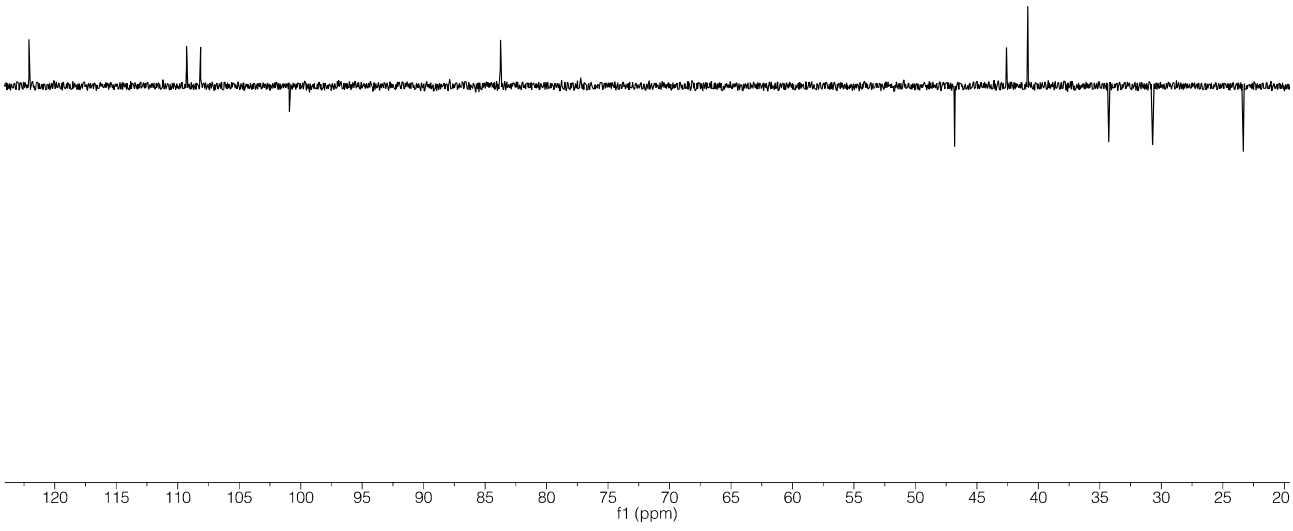
^{13}C-NMR (101 MHz, $CDCl_3$)



(3aR,4S,7R,7aS)-2-(4-(Benzo[d][1,3]dioxol-5-yl)-3-iodobutyl)hexahydro-4,7 methanobenzo[d][1,3,2]dioxaborole

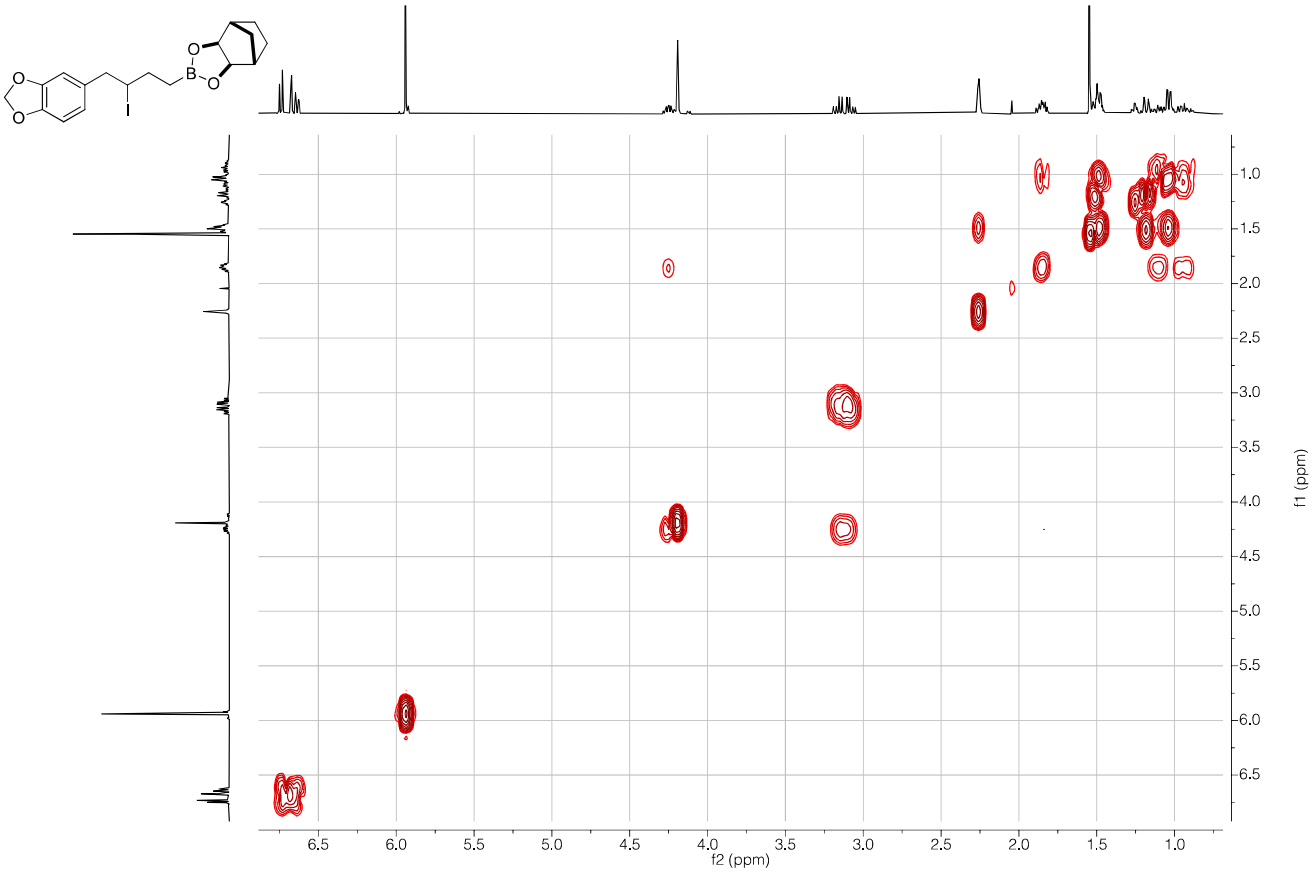
Dept-135 (101 MHz, $CDCl_3$)





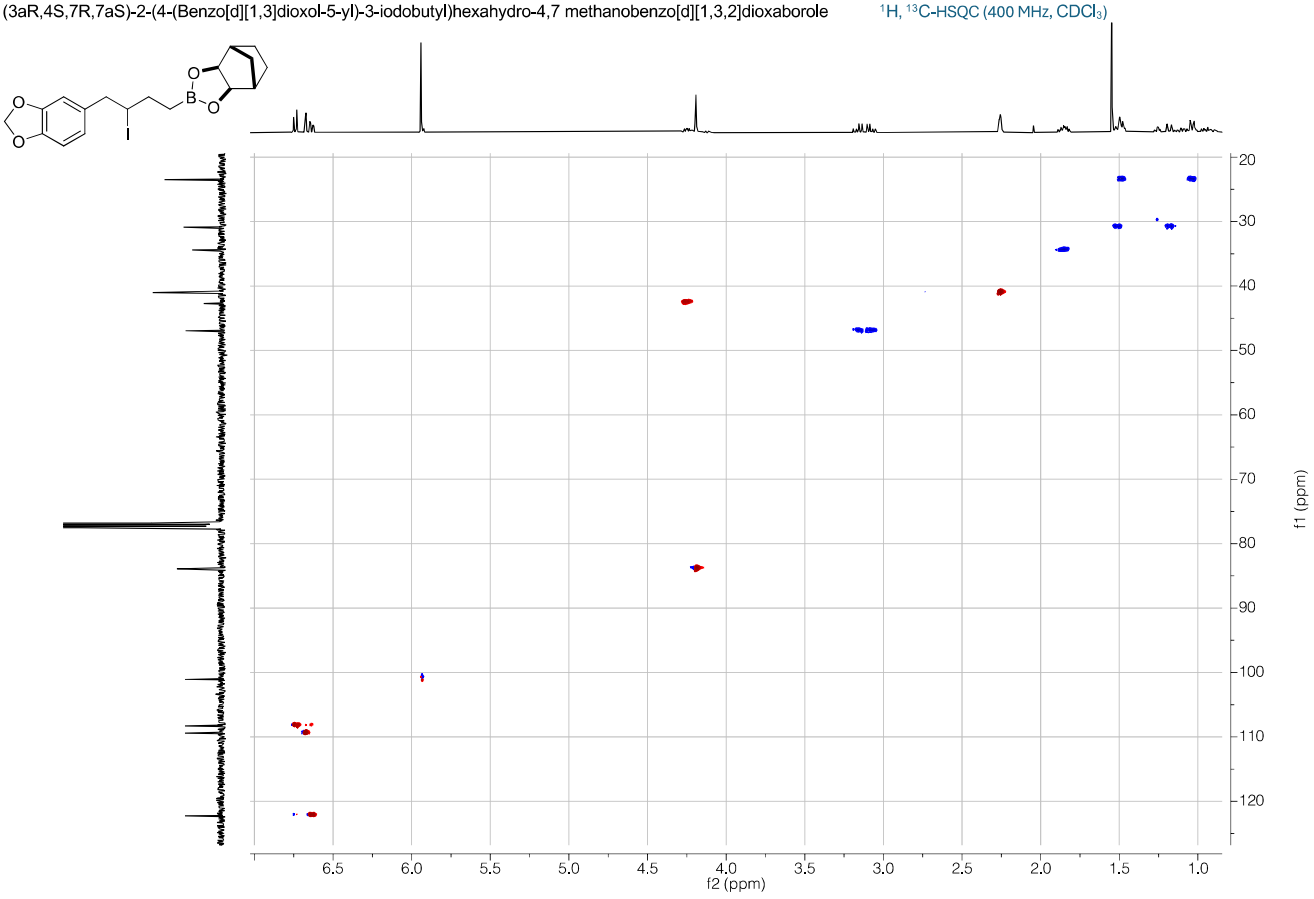
(3aR,4S,7R,7aS)-2-(4-(Benzo[d][1,3]dioxol-5-yl)-3-iodobutyl)hexahydro-4,7 methanobenzo[d][1,3,2]dioxaborole

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



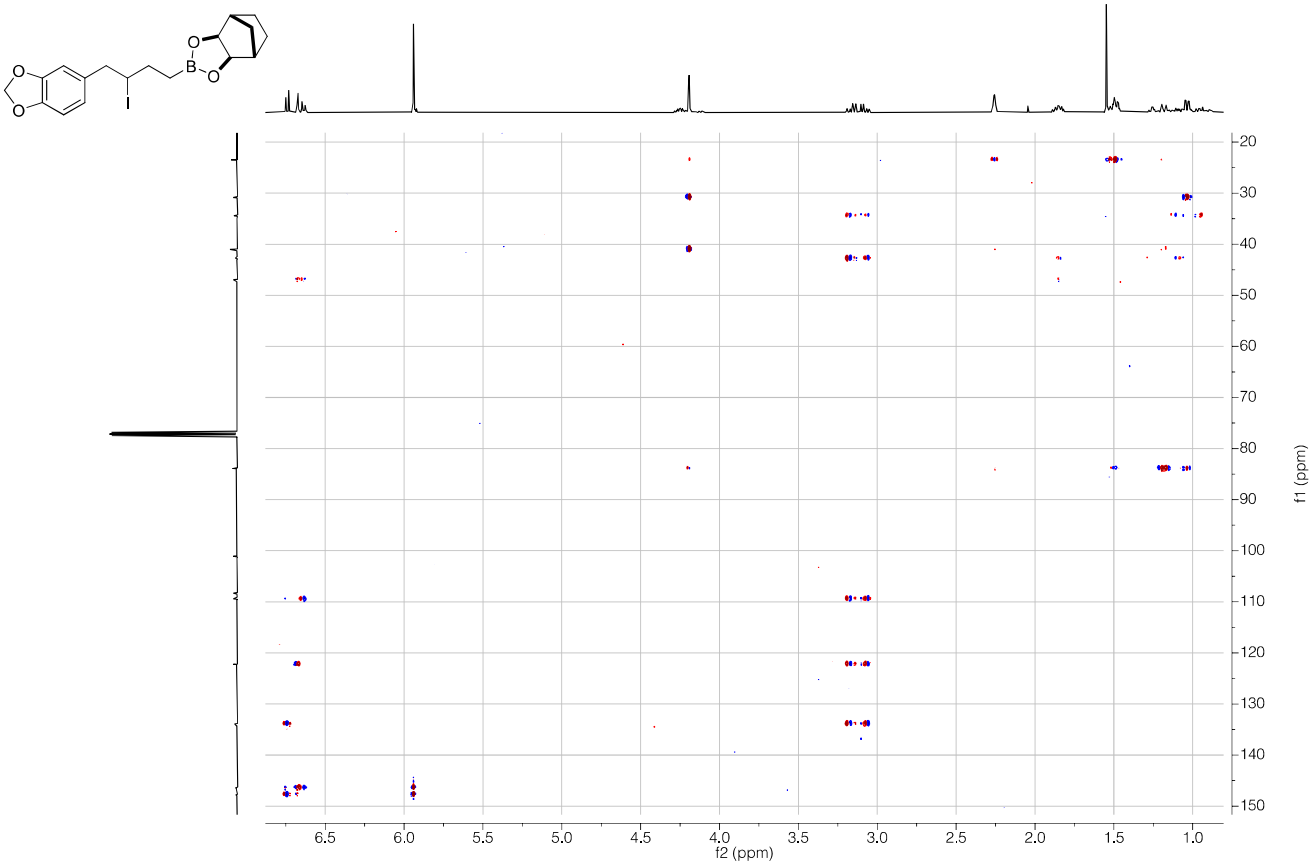
(3aR,4S,7R,7aS)-2-(4-(Benzo[d][1,3]dioxol-5-yl)-3-iodobutyl)hexahydro-4,7 methanobenzo[d][1,3,2]dioxaborole

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



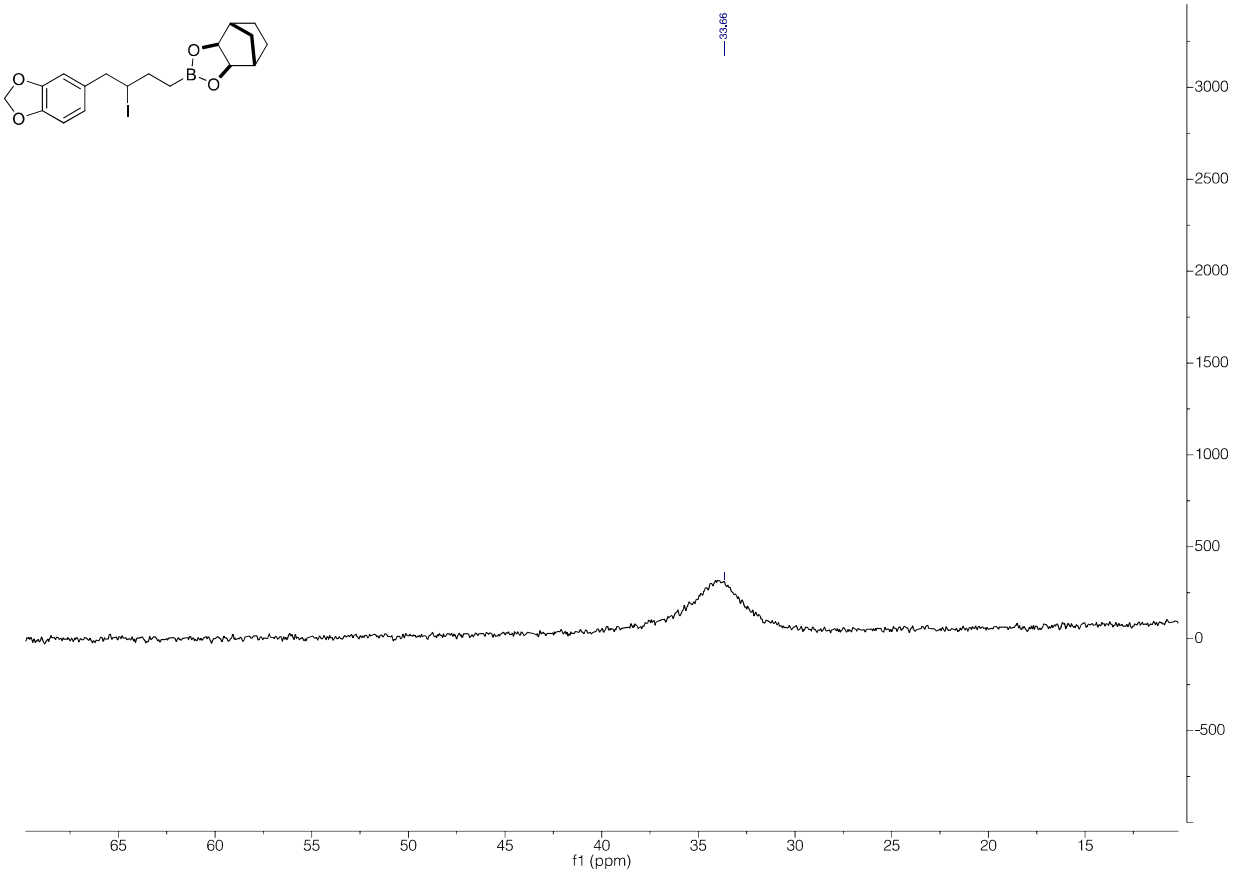
(3aR,4S,7R,7aS)-2-(4-(Benzo[d][1,3]dioxol-5-yl)-3-iodobutyl)hexahydro-4,7 methanobenzo[d][1,3,2]dioxaborole

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



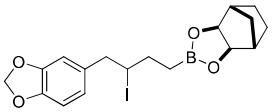
(3aR,4S,7R,7aS)-2-(4-(Benzo[d][1,3]dioxol-5-yl)-3-iodobutyl)hexahydro-4,7 methanobenzo[d][1,3,2]dioxaborole

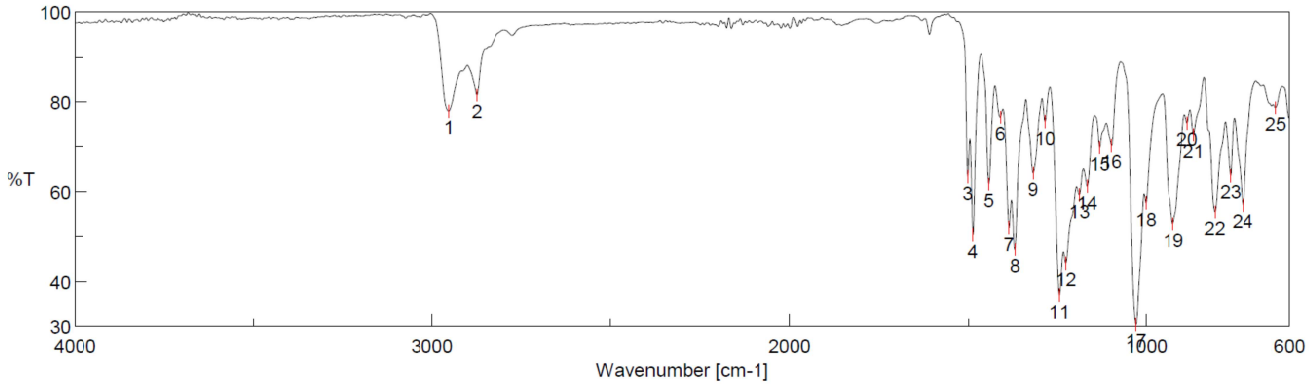
^{11}B-NMR (96 MHz, $CDCl_3$)



(3aR,4S,7R,7aS)-2-(4-(Benzo[d][1,3]dioxol-5-yl)-3-iodobutyl)hexahydro-4,7 methanobenzo[d][1,3,2]dioxaborole

FT-IR, ATR-diamond



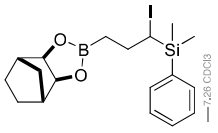


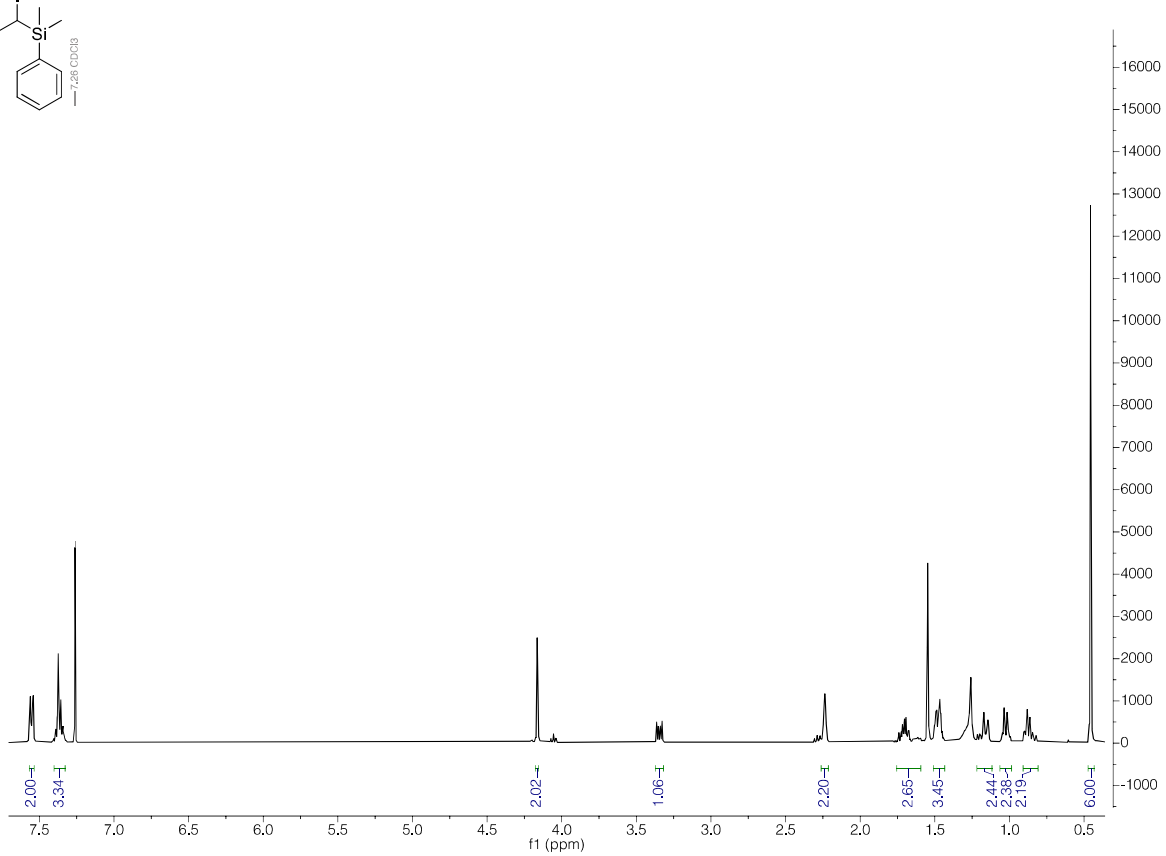
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2952.48	78	2	2874.38	81	3	1502.28	63
4	1487.81	50	5	1441.53	62	6	1409.71	76
7	1385.6	52	8	1369.21	47	9	1318.11	64
10	1283.39	76	11	1243.86	37	12	1226.5	44
13	1188.9	59	14	1166.72	61	15	1132.01	70
16	1098.26	70	17	1029.8	30	18	1001.84	57
19	925.664	53	20	886.131	75	21	867.81	73
22	808.992	55	23	764.637	64	24	729.925	57
25	638.323	79						

(3-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-1-iodopropyl)dimethyl(phenyl)silane

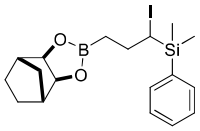
^{1}H-NMR (400 MHz, $CDCl_3$)

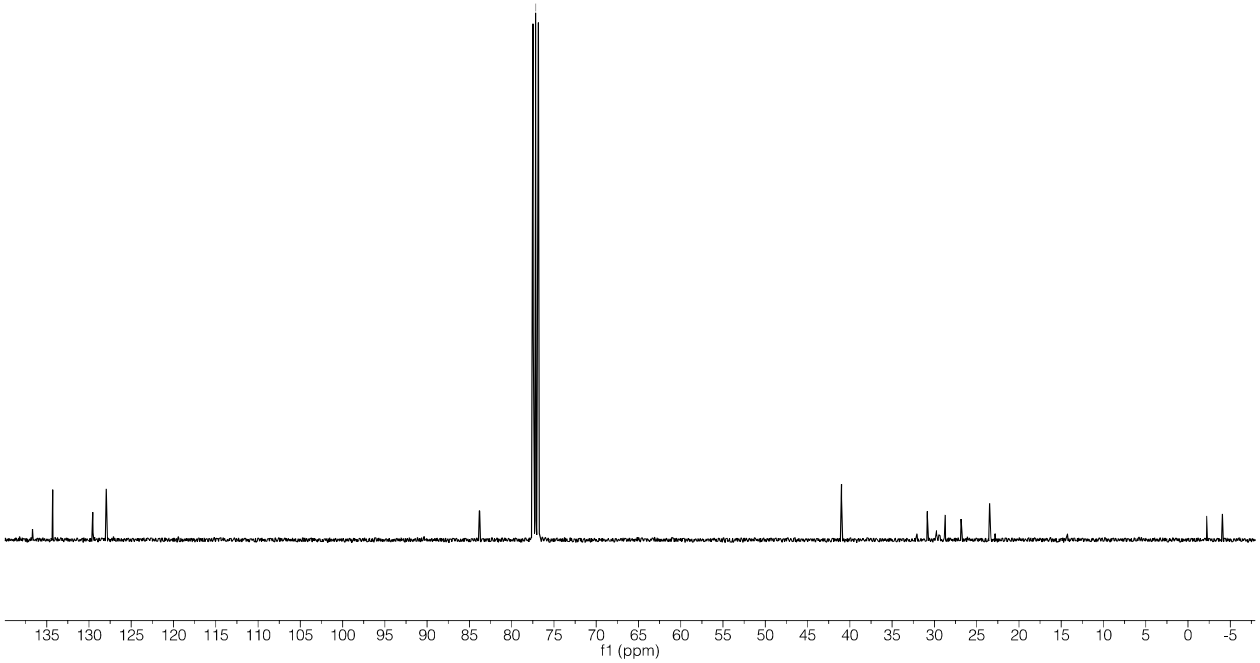




(3-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-1-iodopropyl)dimethyl(phenyl)silane

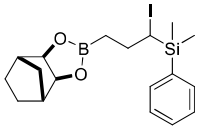
^{13}C-NMR (101 MHz, $CDCl_3$)

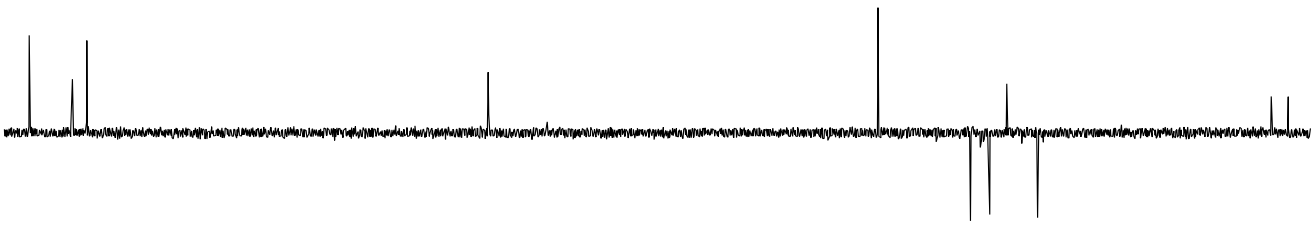


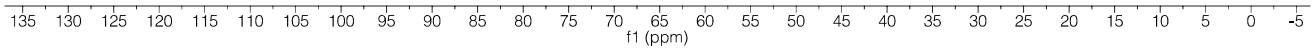


(3-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-1-iodopropyl)dimethyl(phenyl)silane

Dept-135 (101 MHz, $CDCl_3$)

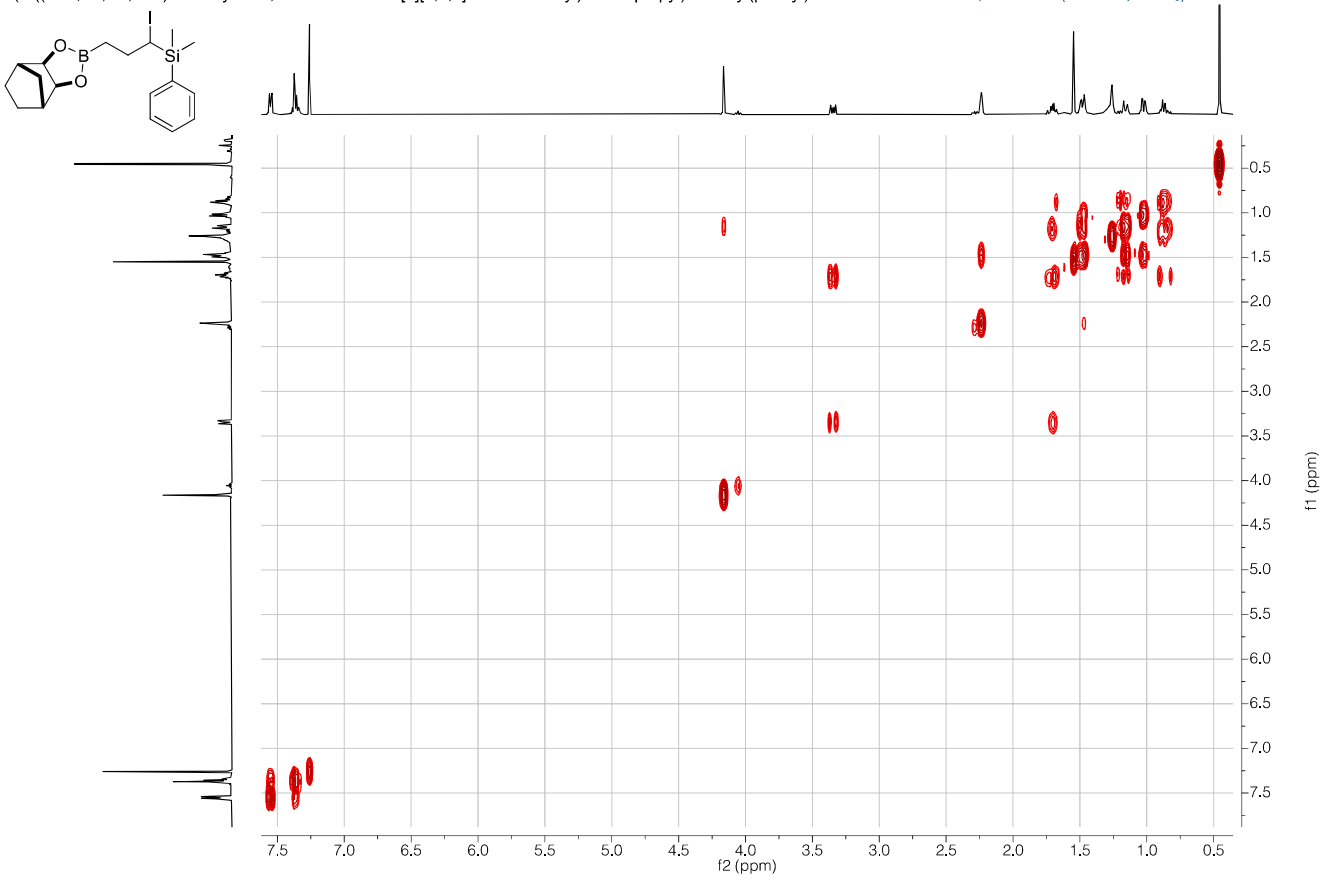






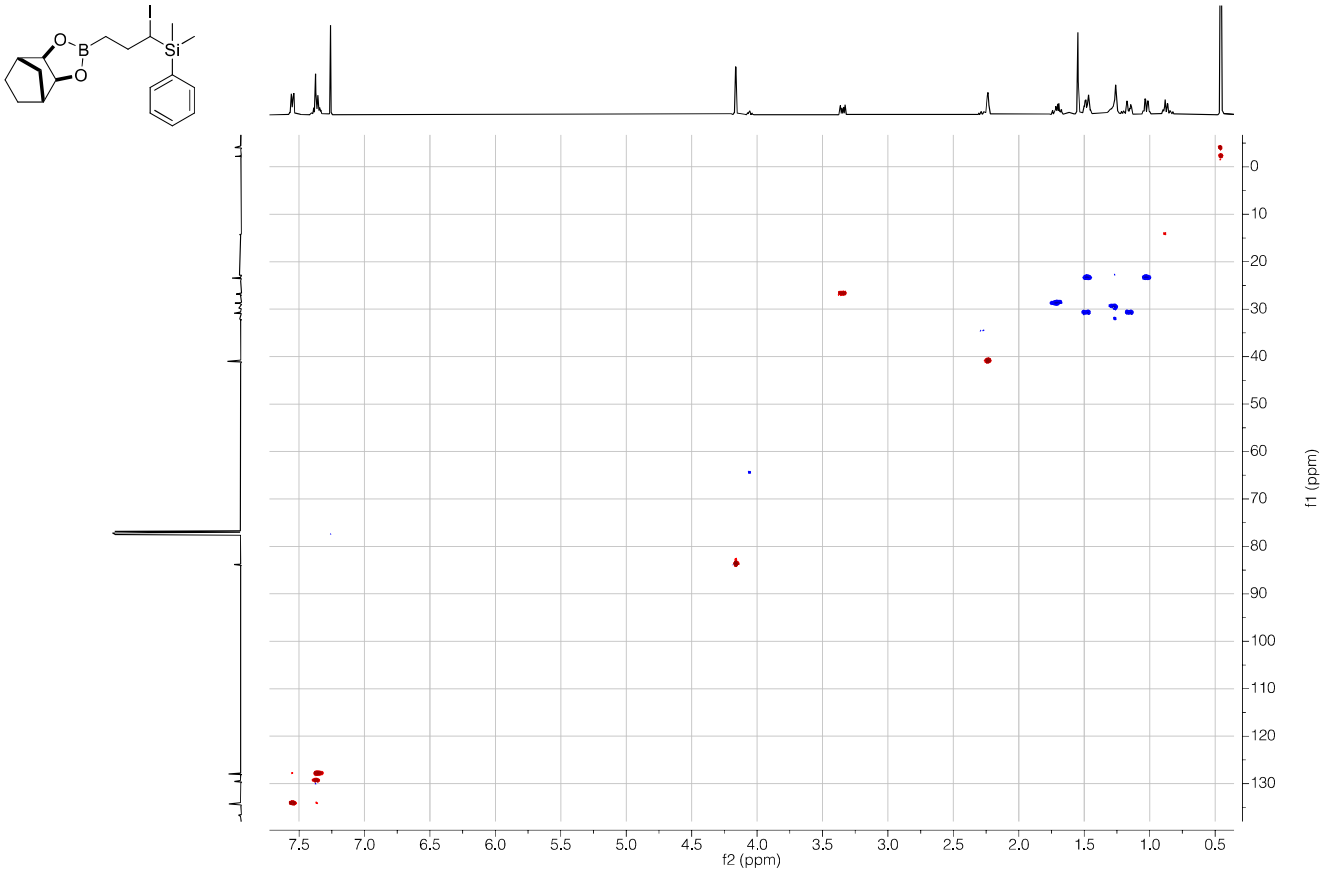
(3-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-1-iodopropyl)dimethyl(phenyl)silane

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)

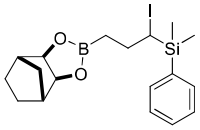


(3-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-1-iodopropyl)dimethyl(phenyl)silane

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)

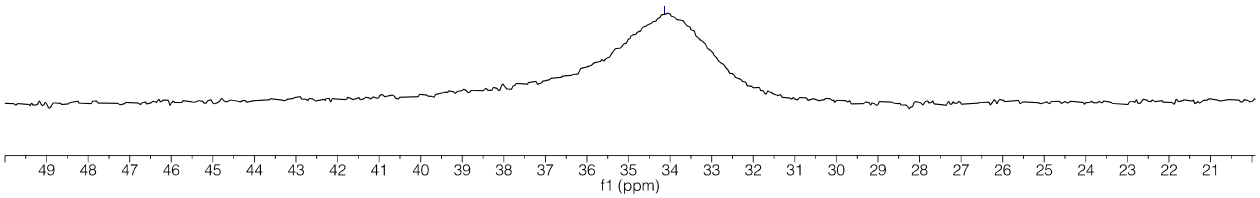


(3-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-1-iodopropyl)dimethyl(phenyl)silane

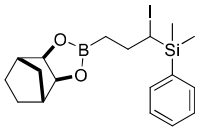


^{11}B-NMR (96 MHz, $CDCl_3$)

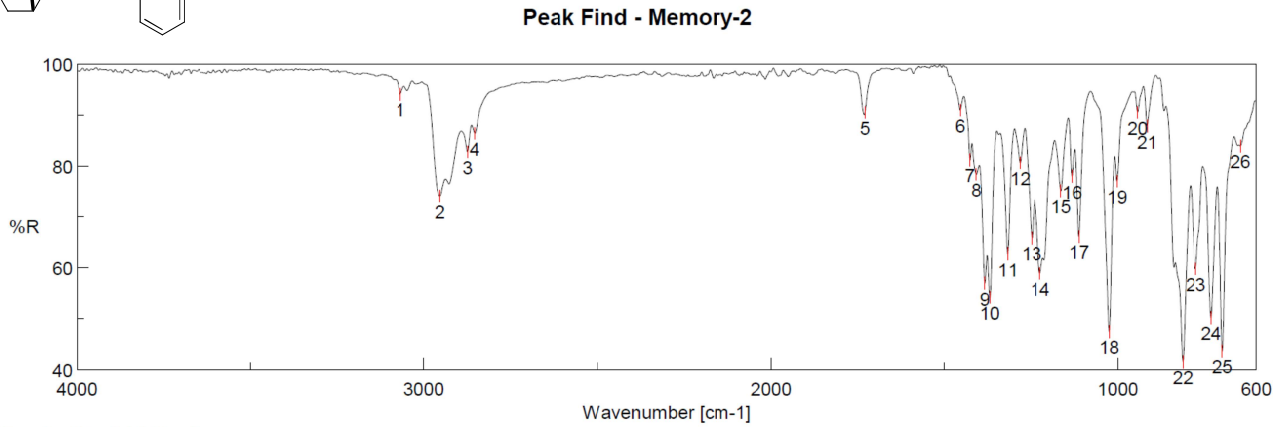
34.12



(3-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-1-iodopropyl)dimethyl(phenyl)silane



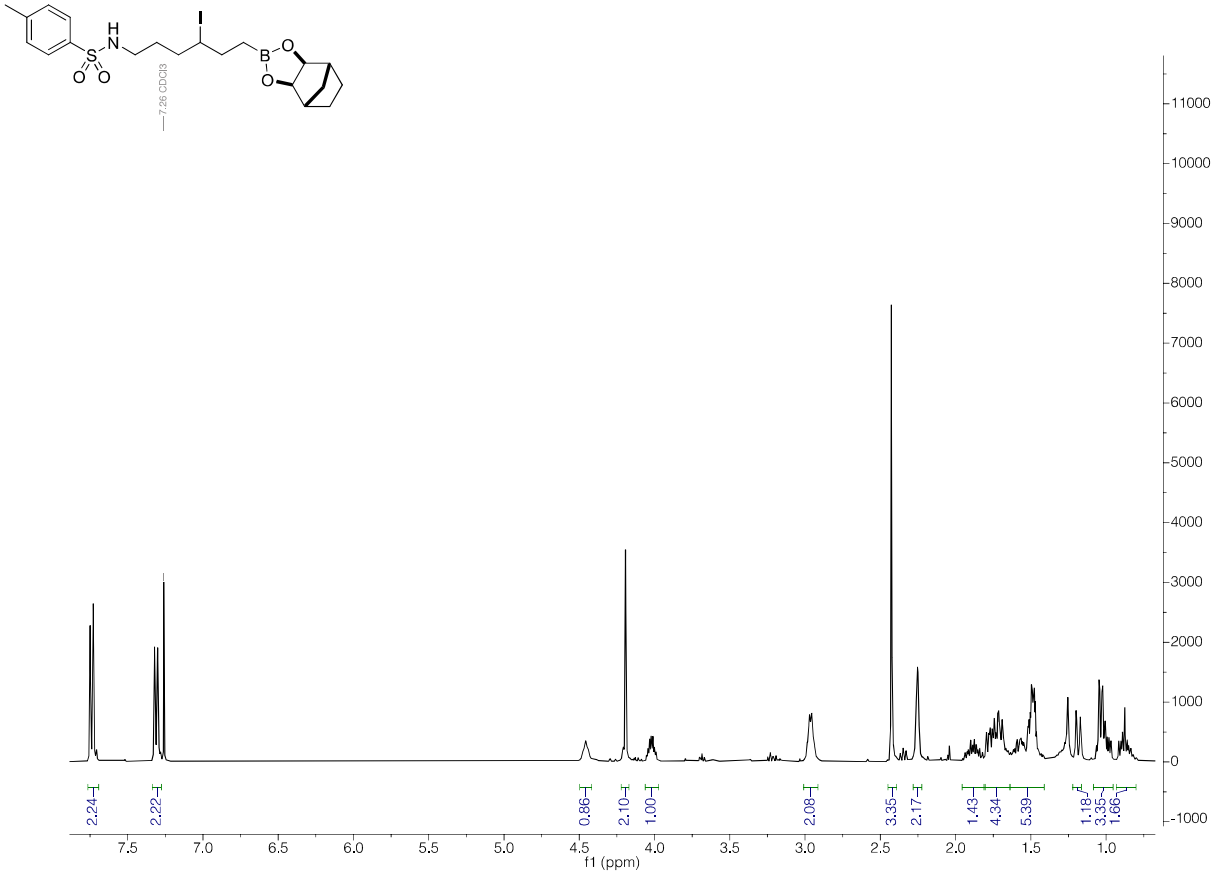
FT-IR, ATR-diamond



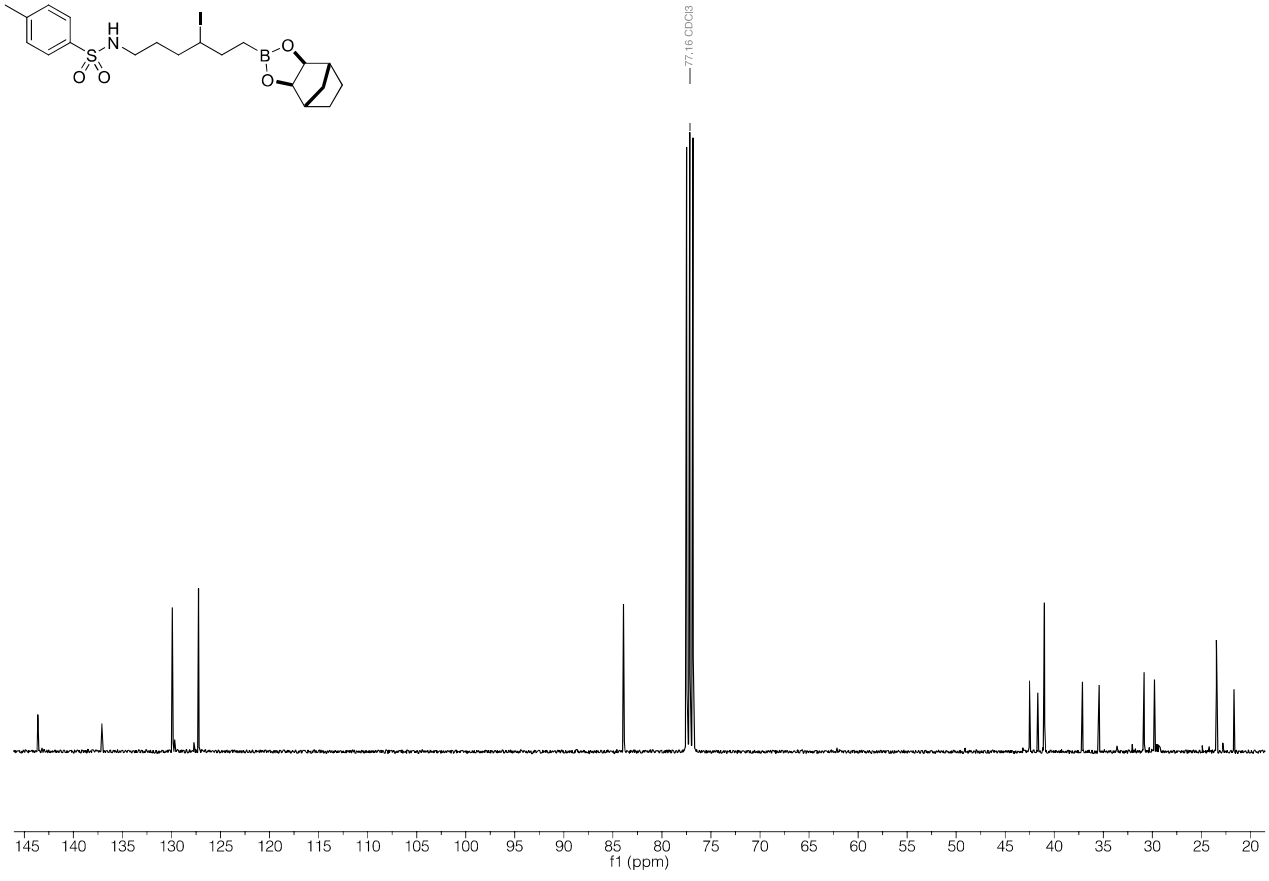
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3068.19	94.0642	2	2953.45	74.0175	3	2874.38	82.7465
4	2853.17	86.3971	5	1730.8	90.4744	6	1455.03	90.8979
7	1427.07	81.1364	8	1408.75	78.3099	9	1384.64	56.939
10	1370.18	54.1849	11	1318.11	62.7553	12	1282.43	80.5598
13	1248.68	65.7972	14	1224.58	58.8585	15	1163.83	75.0547
16	1131.05	77.9197	17	1111.76	66.1137	18	1024.98	47.4703
19	1001.84	76.9684	20	943.02	90.5228	21	916.022	87.8183
22	812.849	41.5337	23	775.244	59.8092	24	729.925	50.158
25	698.105	43.6029	26	646.036	83.878			

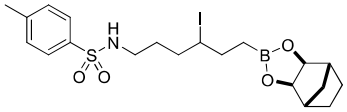
N-(6-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-4-iodohexyl)-4-methylbenzenesulfonamide ^{1}H-NMR (400 MHz, $CDCl_3$)



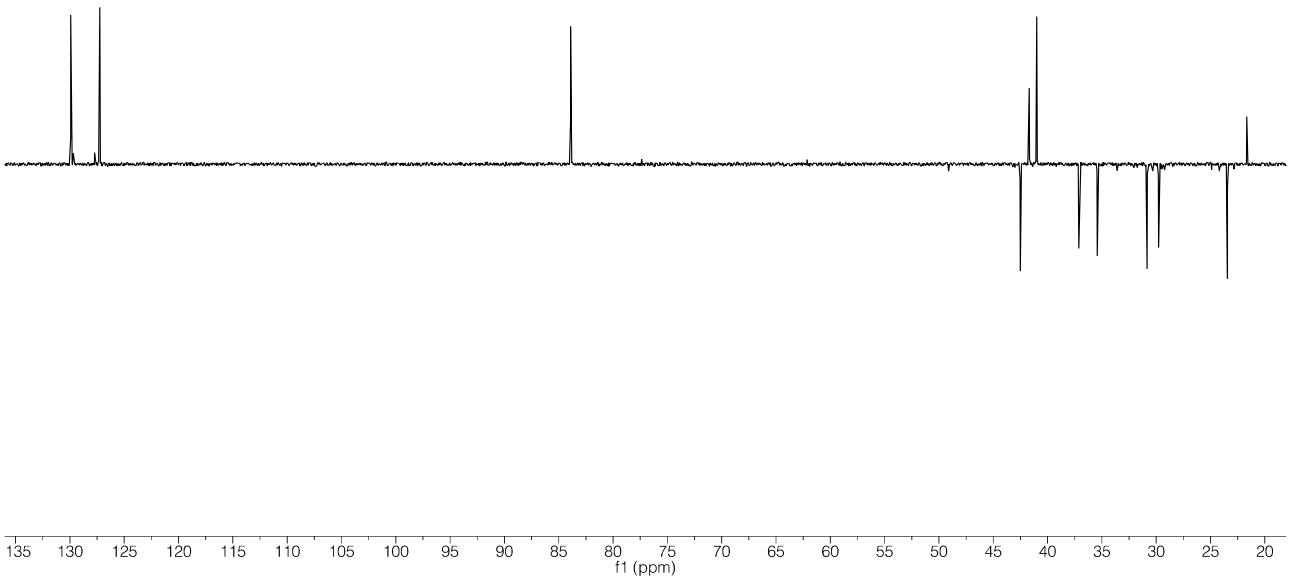
N-(6-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-4-iodohexyl)-4-methylbenzenesulfonamide ^{13}C-NMR (101 MHz, $CDCl_3$)



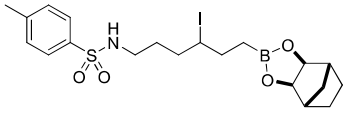
N-(6-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-4-iodohexyl)-4-methylbenzenesulfonamide



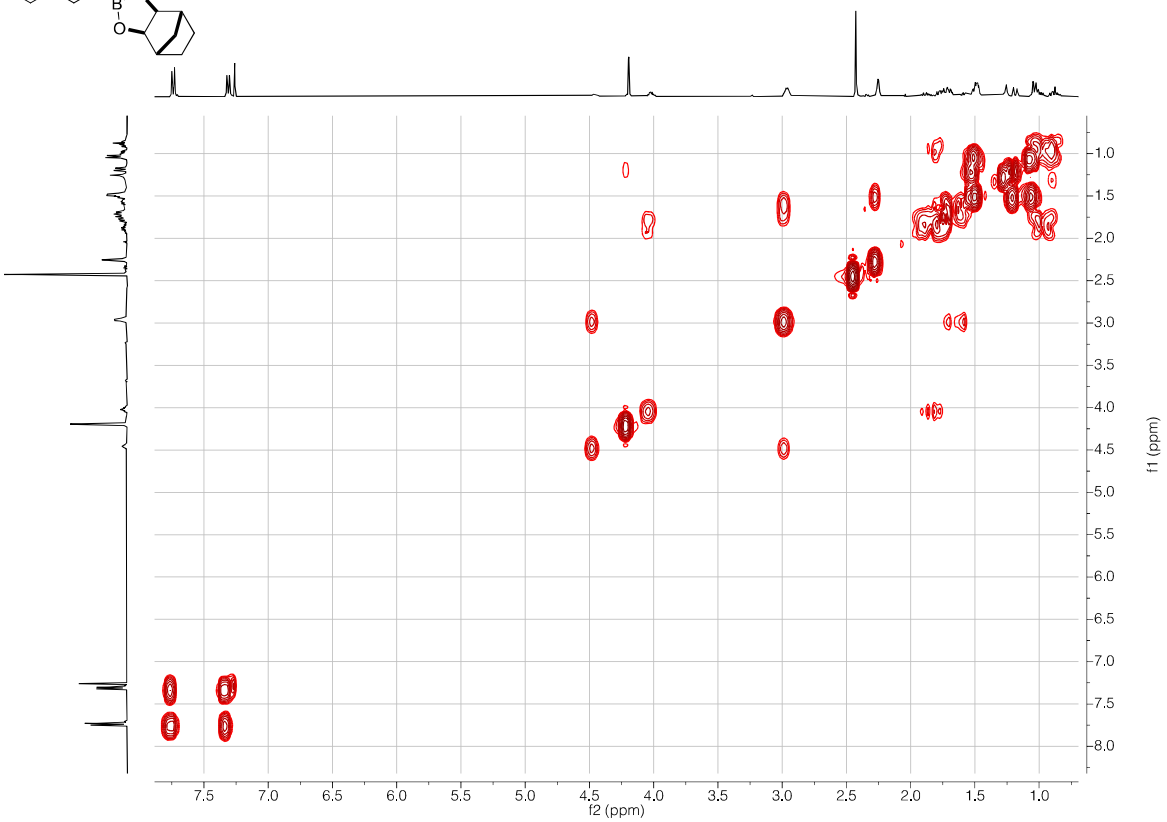
Dept-135 (101 MHz, $CDCl_3$)



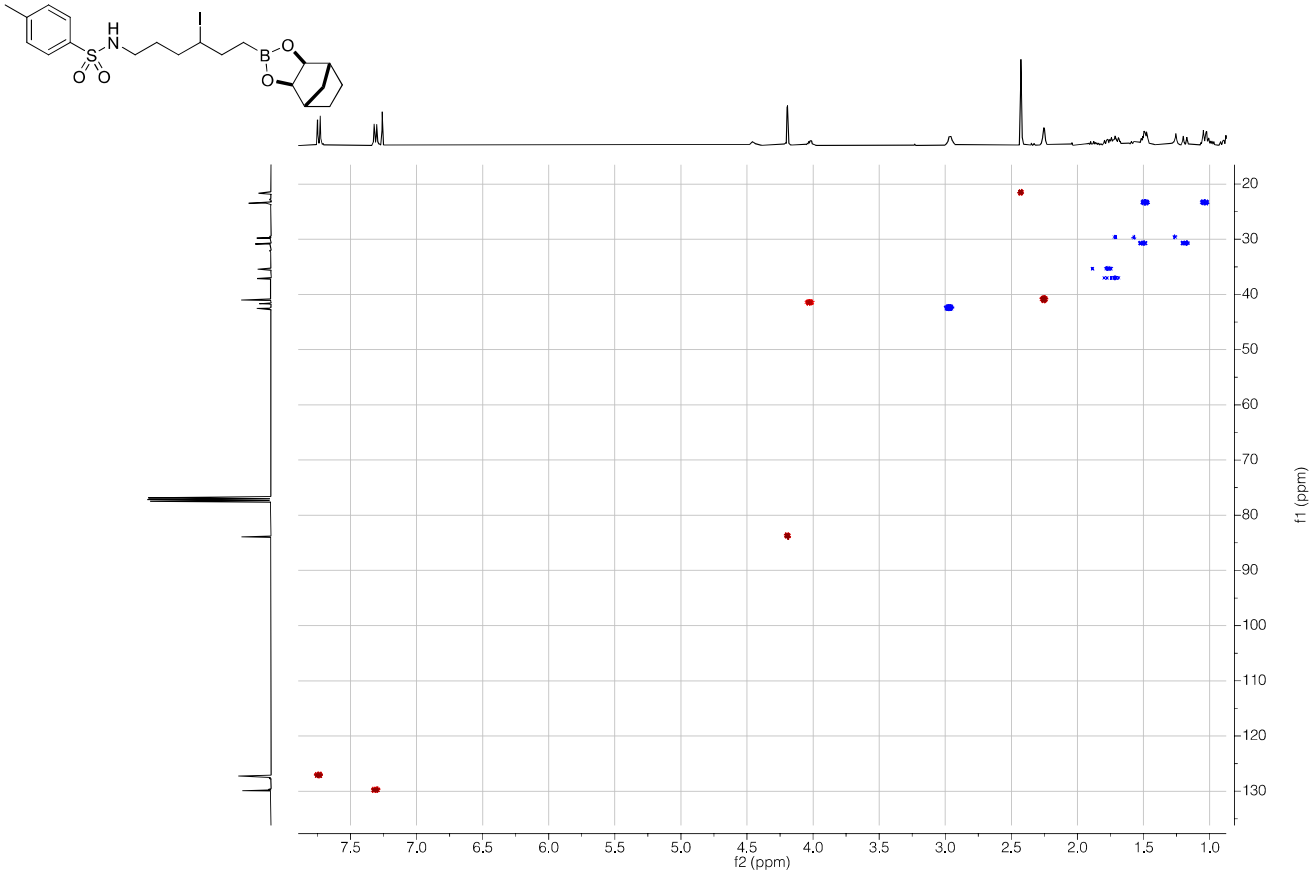
N-(6-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-4-iodohexyl)-4-methylbenzenesulfonamide



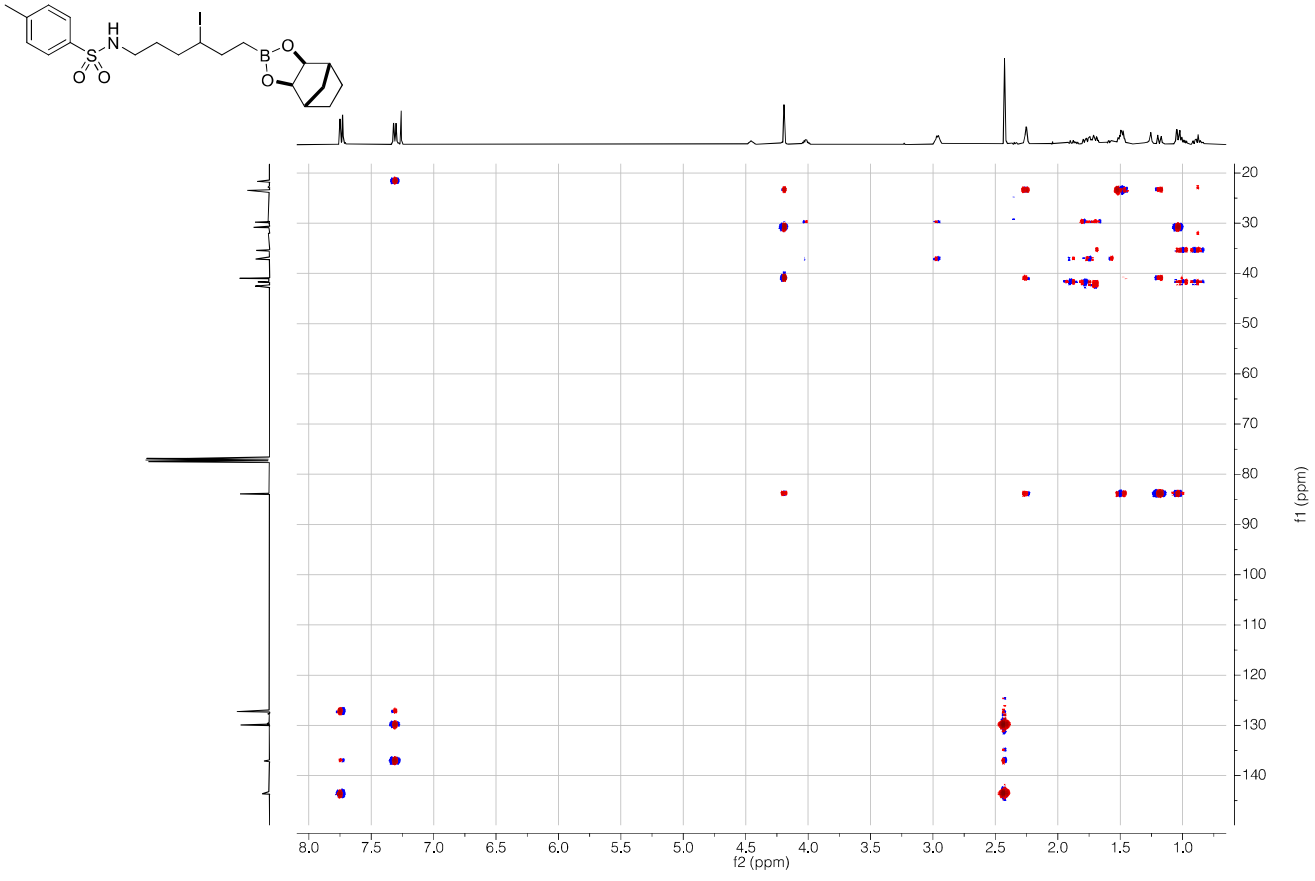
^1H, ^1H-COSY (400 MHz, $CDCl_3$)



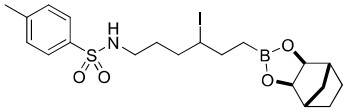
N-(6-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-4-iodohexyl)-4-methylbenzenesulfonamide ^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)

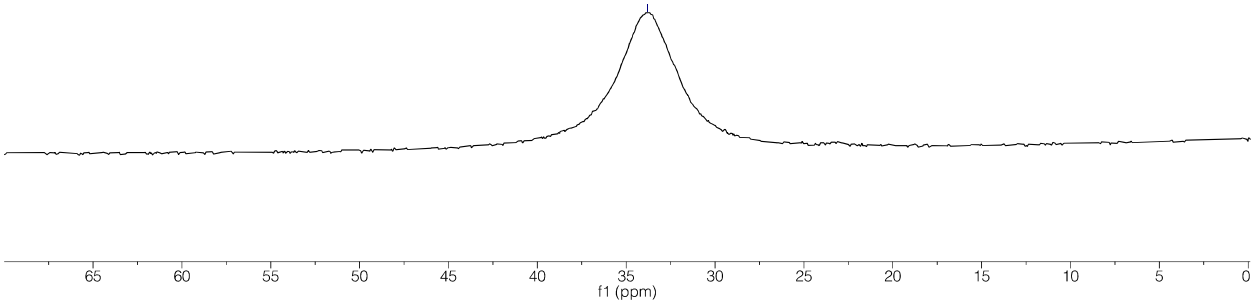


N-(6-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-4-iodohexyl)-4-methylbenzenesulfonamide ^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)

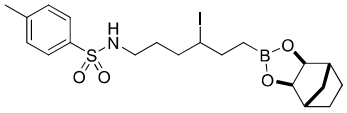


N-(6-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-4-iodohexyl)-4-methylbenzenesulfonamide ^{11}B-NMR (96 MHz, $CDCl_3$)

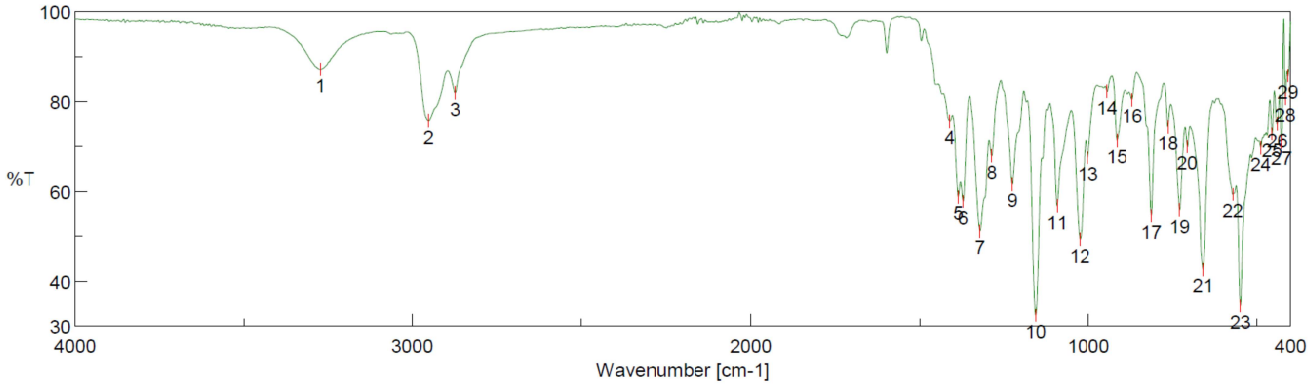




N-(6-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-4-iodohexyl)-4-methylbenzenesulfonamide FT-IR, ATR-diamond



Peak Find - Memory-3

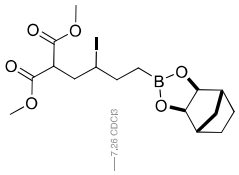


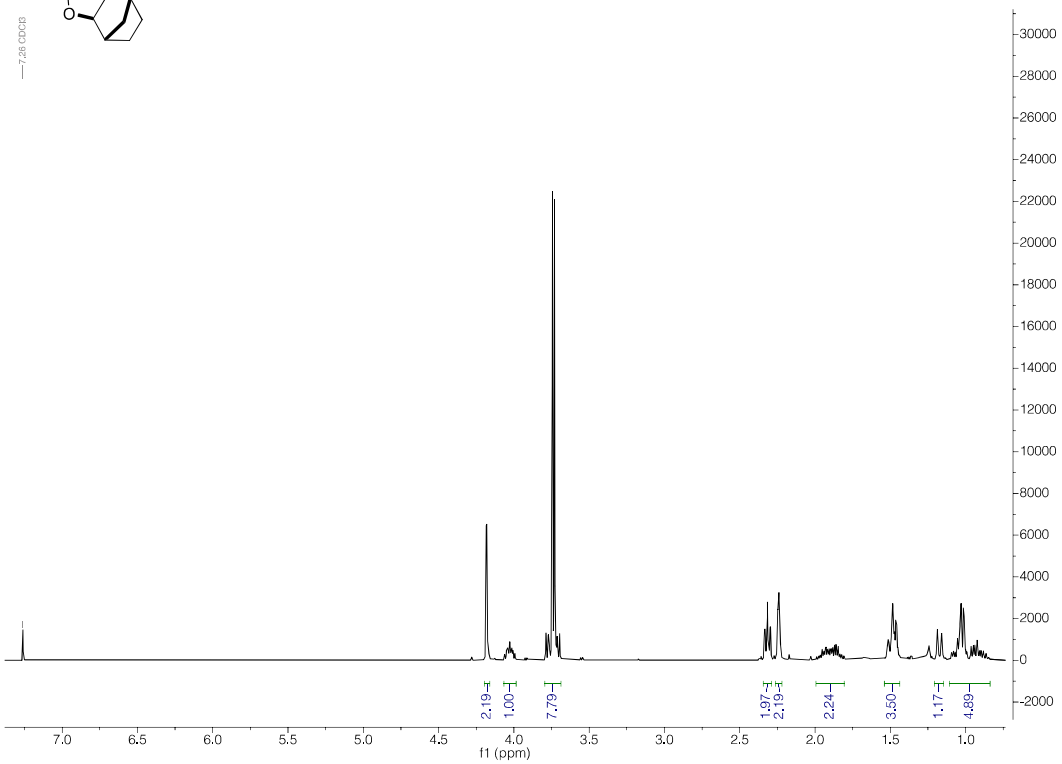
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3273.57	87.0625	2	2951.52	75.6391	3	2874.38	81.8421
4	1410.67	75.5655	5	1385.6	58.6958	6	1371.14	57.7228
7	1321	51.1144	8	1285.32	67.8475	9	1224.58	61.5376
10	1155.15	32.338	11	1092.48	56.6845	12	1024.98	49.2521
13	1001.84	67.4636	14	943.985	32.2006	15	915.058	71.2859
16	869.739	80.3289	17	812.849	54.5245	18	764.637	74.2548
19	729.925	55.8253	20	706.783	69.9032	21	659.536	42.5519
22	570.826	59.2909	23	548.649	34.4638	24	487.902	69.6763
25	454.154	72.7609	26	438.726	74.9181	27	426.191	70.9408
28	415.585	80.5359	29	407.871	85.6806			

Dimethyl 2-(4-((3aR,4S,7R,7aS)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-2-iodobutyl)malonate

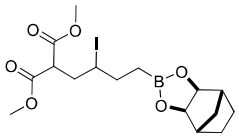
^{1}H-NMR (400 MHz, $CDCl_3$)

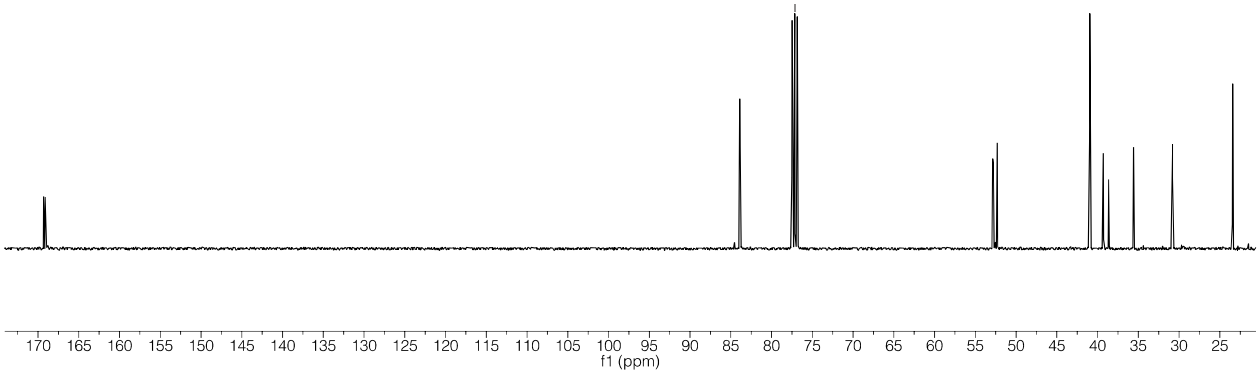




Dimethyl 2-(4-((3aR,4S,7R,7aS)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-2-iodobutyl)malonate

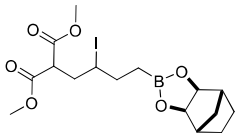
^{13}C-NMR (101 MHz, $CDCl_3$)

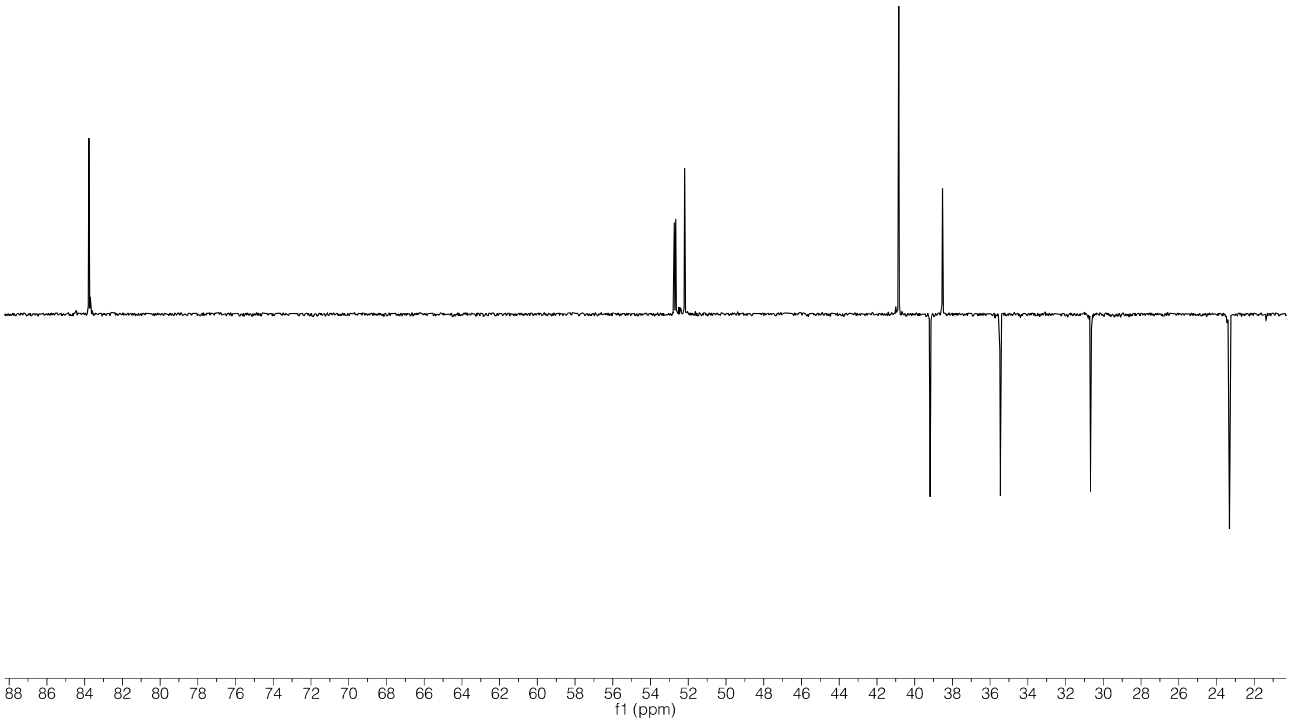




Dimethyl 2-(4-((3aR,4S,7R,7aS)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-2-iodobutyl)malonate

Dept-135 (101 MHz, $CDCl_3$)



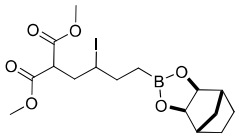


88 86 84 82 80 78 76 74 72 70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22

f1 (ppm)

Dimethyl 2-(4-((3aR,4S,7R,7aS)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-2-iodobutyl)malonate

^1H, ^1H-COSY (400 MHz, $CDCl_3$)



1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5

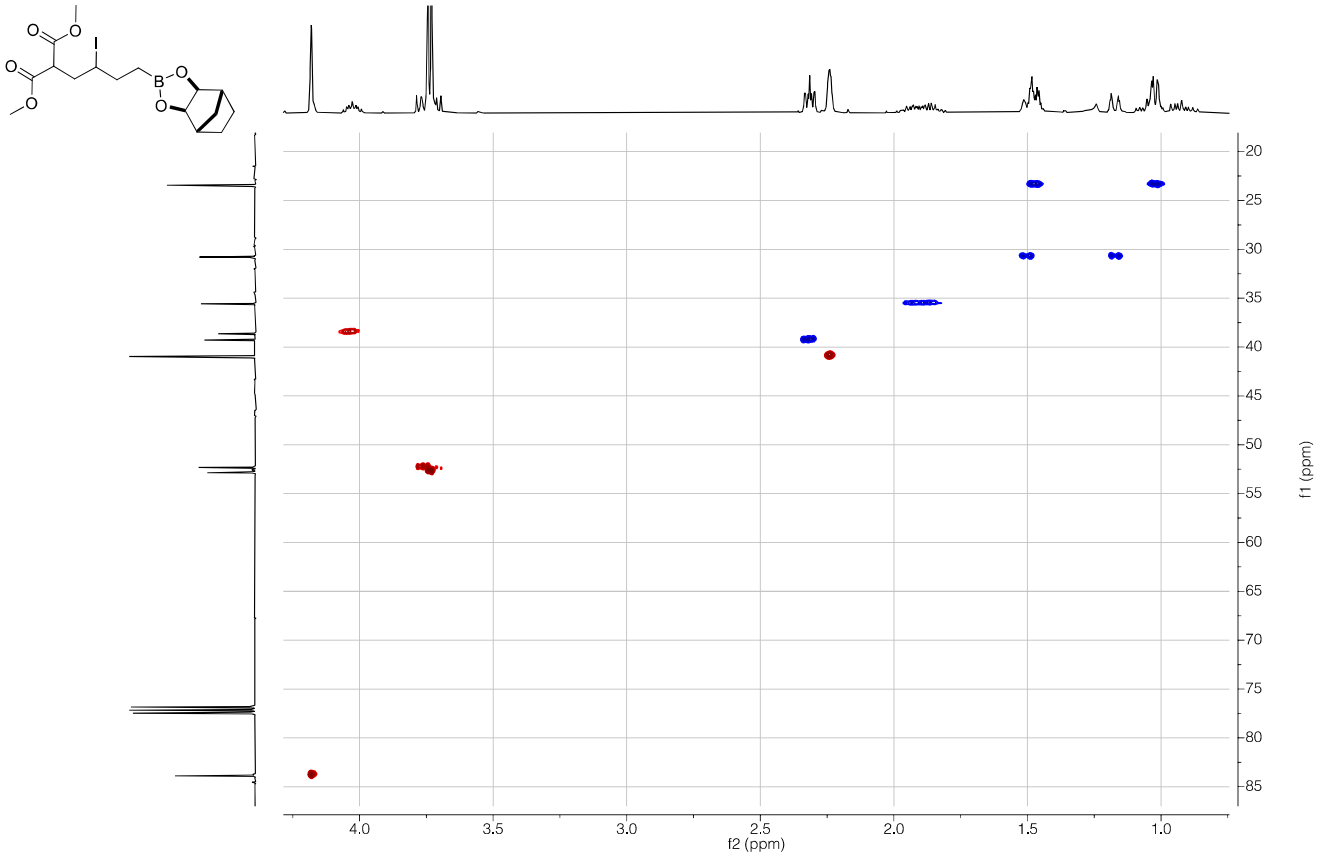
f1 (ppm)

4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8

f2 (ppm)

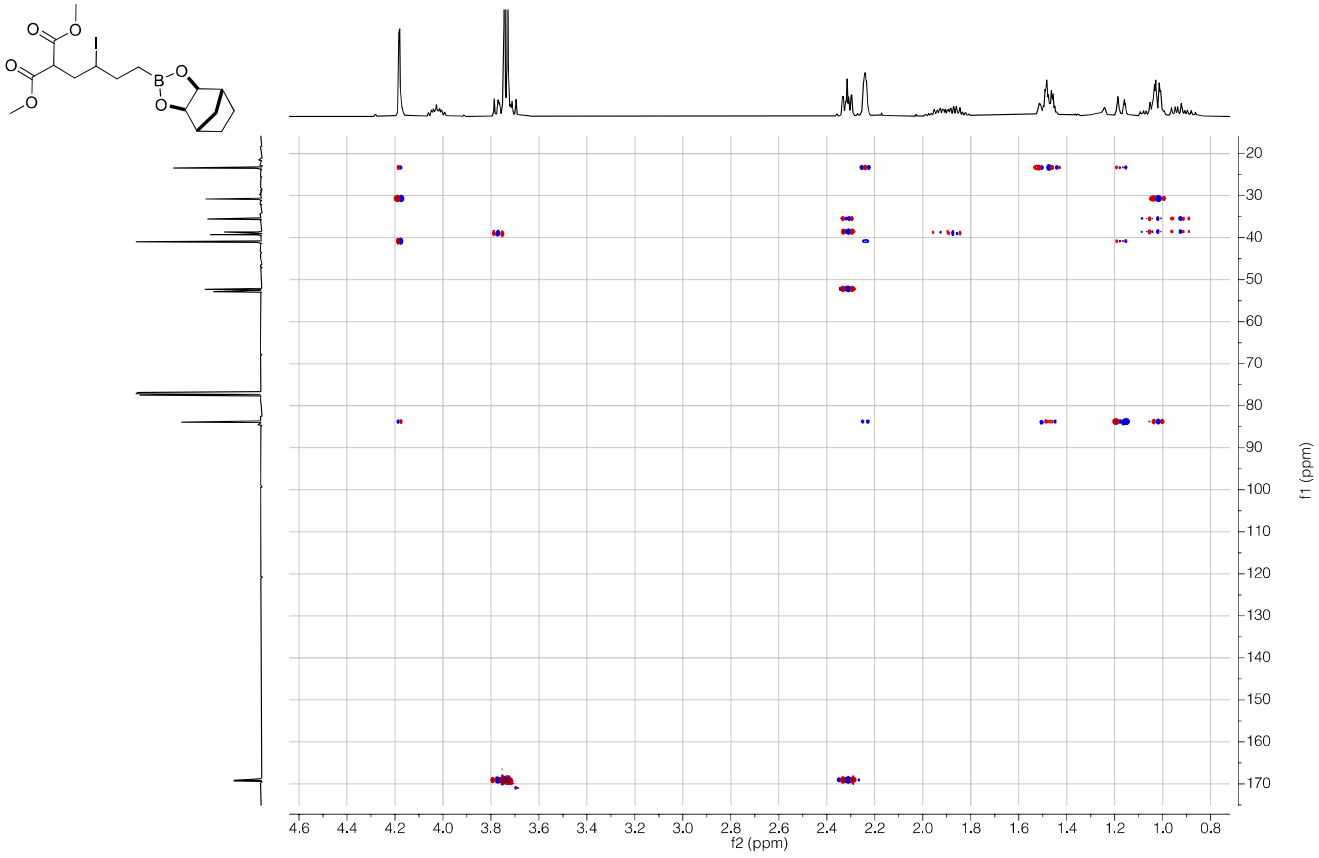
Dimethyl 2-(4-((3aR,4S,7R,7aS)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-2-iodobutyl)malonate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



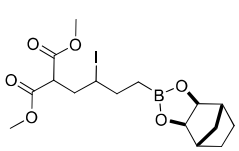
Dimethyl 2-(4-((3aR,4S,7R,7aS)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-2-iodobutyl)malonate

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



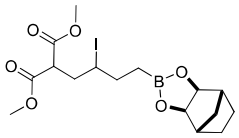
Dimethyl 2-(4-((3aR,4S,7R,7aS)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-2-iodobutyl)malonate

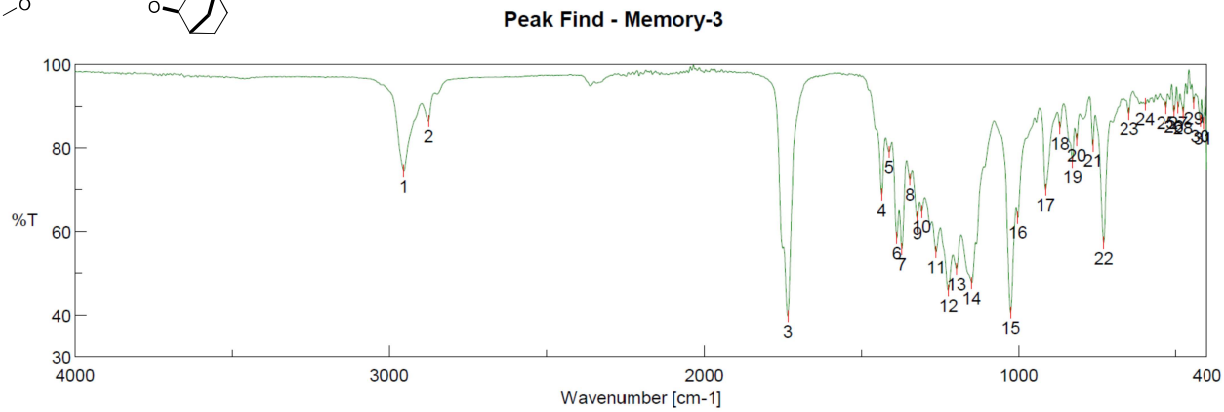
^{11}B-NMR (96 MHz, $CDCl_3$)



Dimethyl 2-(4-((3aR,4S,7R,7aS)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)-2-iodobutyl)malonate

FT-IR, ATR-diamond



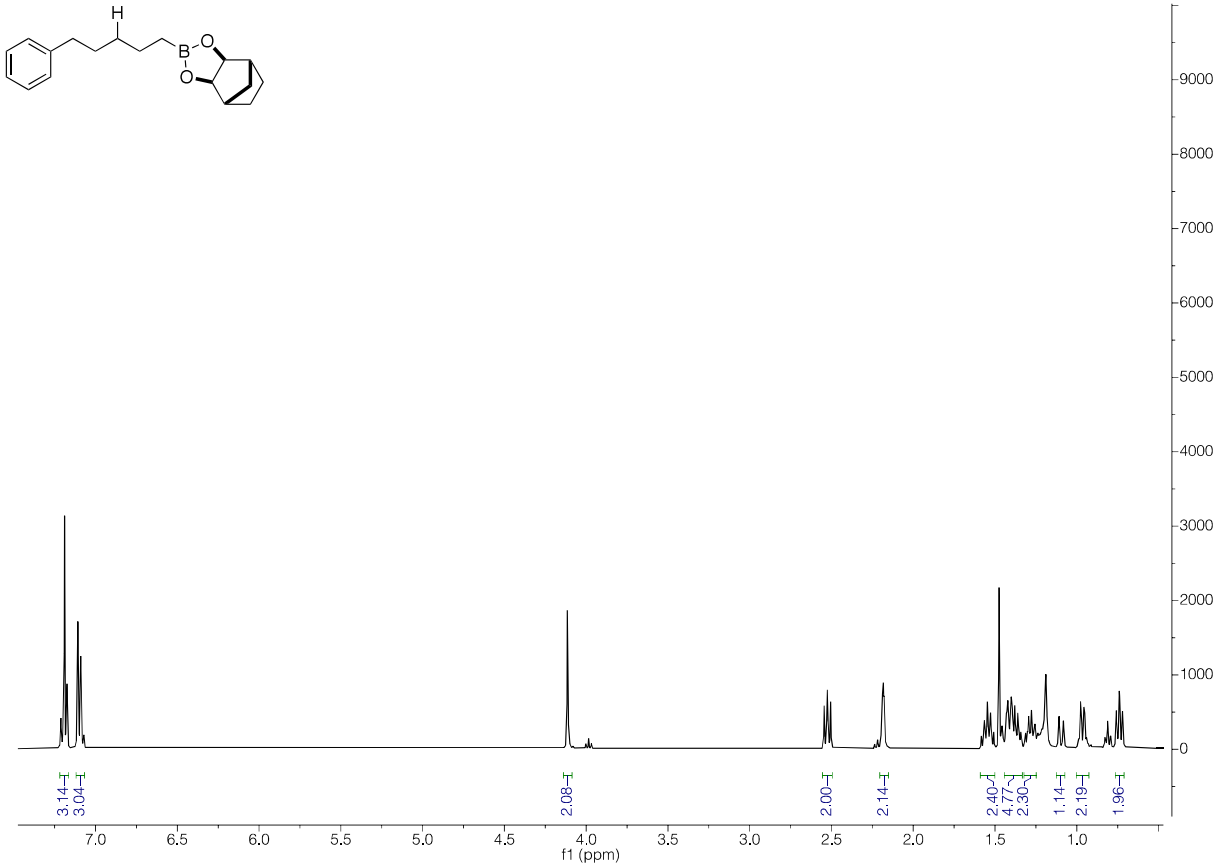


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2953.45	74.4138	2	2875.34	86.3655	3	1732.73	39.6695
4	1434.78	68.7206	5	1411.64	78.9357	6	1386.57	58.3441
7	1371.14	55.7944	8	1345.11	72.408	9	1321.96	63.2337
10	1308.46	64.7391	11	1262.18	54.996	12	1223.61	45.8819
13	1197.58	50.983	14	1149.37	47.6553	15	1025.94	40.4954
16	1002.8	63.2926	17	915.058	69.888	18	868.774	84.7136
19	829.241	76.578	20	815.742	81.8297	21	764.637	80.4783
22	729.925	57.2329	23	647.965	88.0863	24	596.861	90.4131
25	530.328	89.5351	26	505.258	88.6365	27	491.759	89.648
28	476.331	88.296	29	443.547	90.6268	30	423.298	86.4135
31	413.656	85.8765						

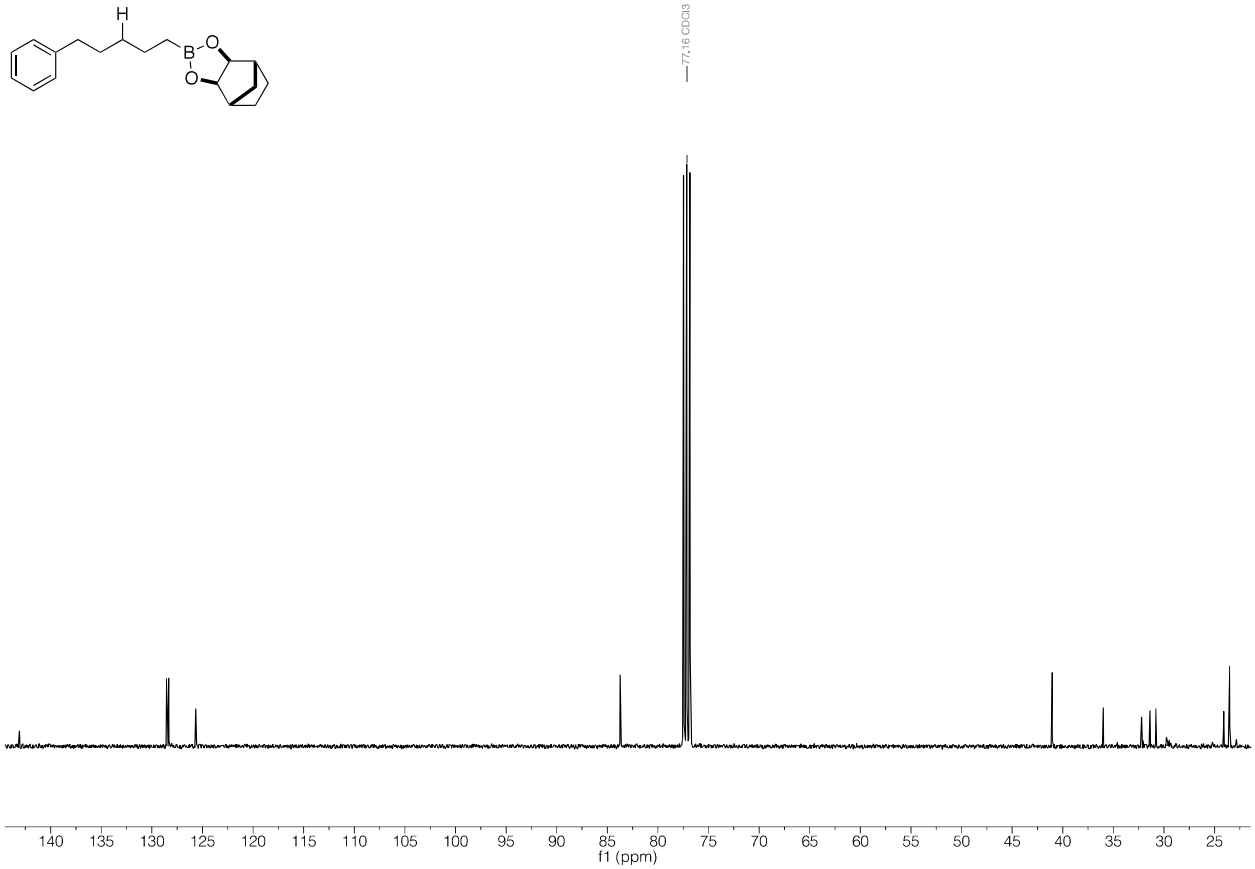
(3aR,4S,7R,7aS)-2-(5-Phenylpentyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

^{1}H-NMR (400 MHz, $CDCl_3$)

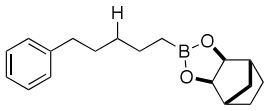


(3aR,4S,7R,7aS)-2-(5-Phenylpentyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

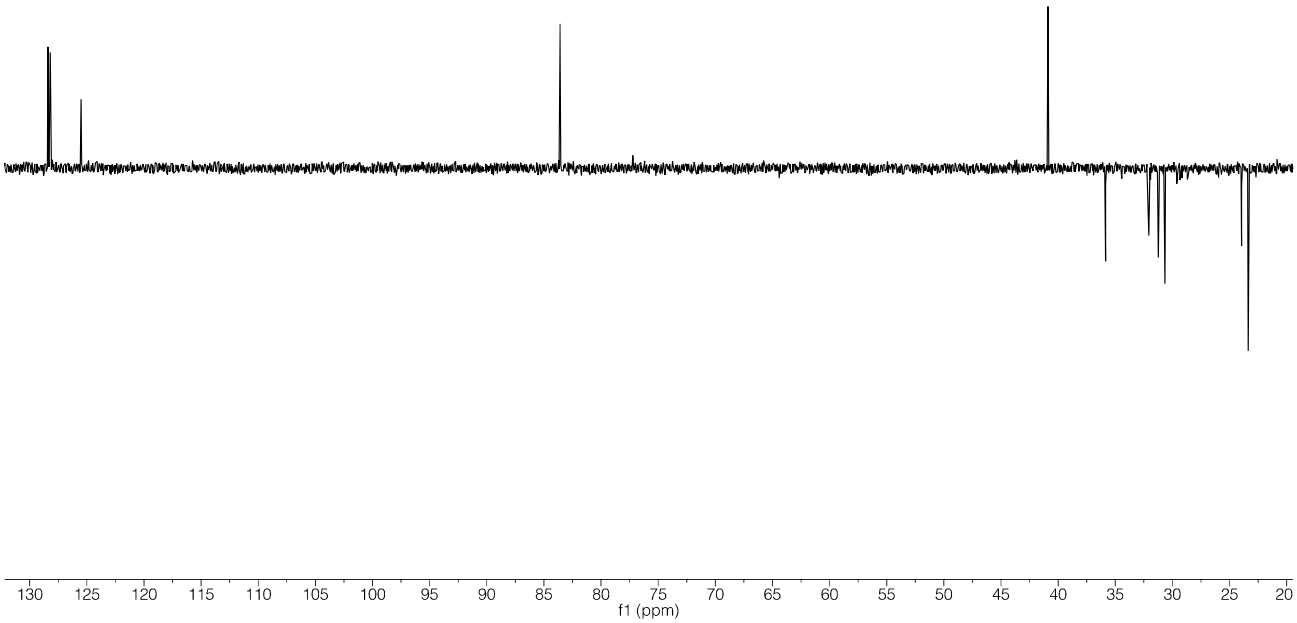
^{13}C-NMR (101 MHz, $CDCl_3$)



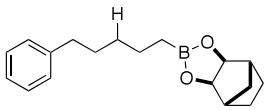
(3aR,4S,7R,7aS)-2-(5-Phenylpentyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole



Dept-135 (101 MHz, $CDCl_3$)



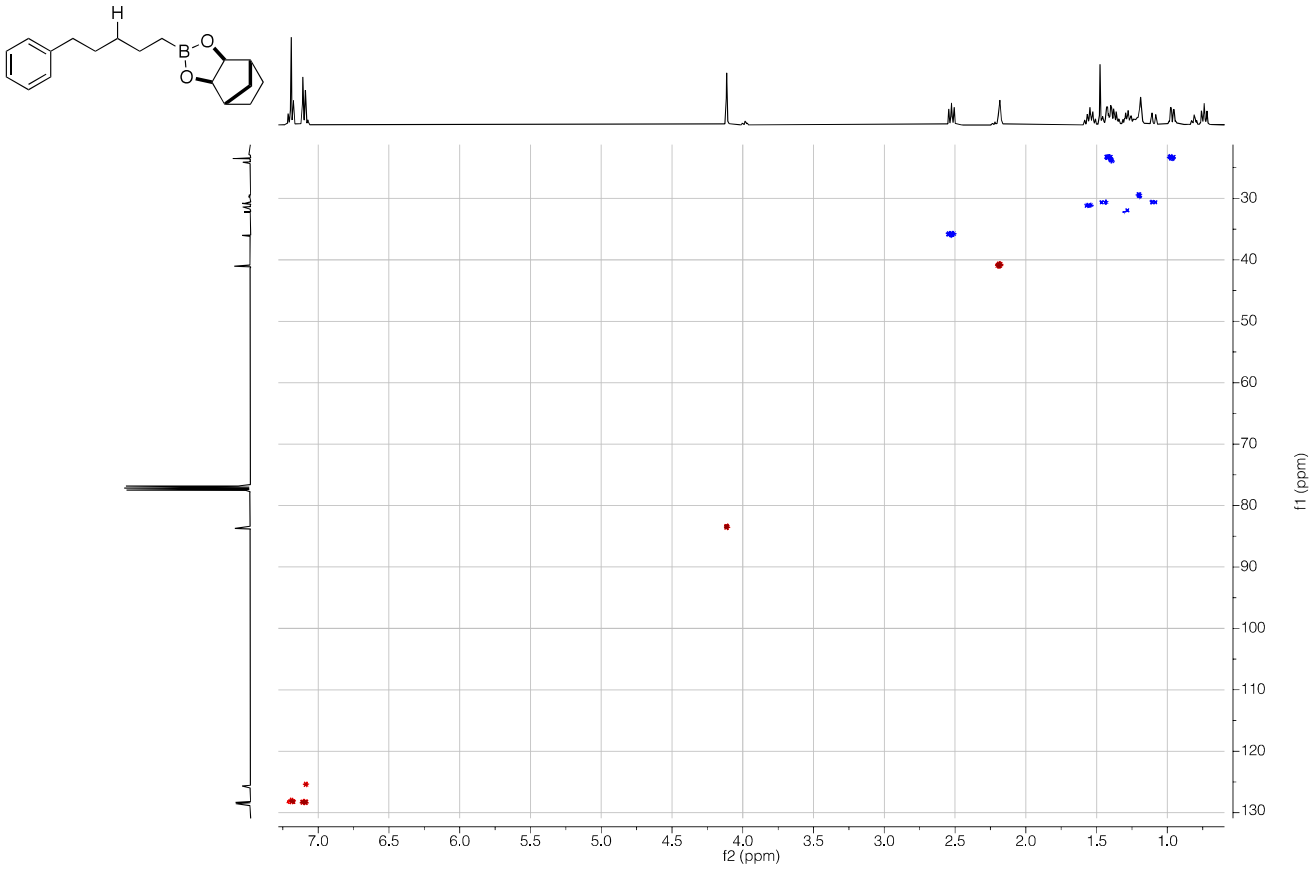
(3aR,4S,7R,7aS)-2-(5-Phenylpentyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole



^1H, ^1H-COSY (400 MHz, $CDCl_3$)

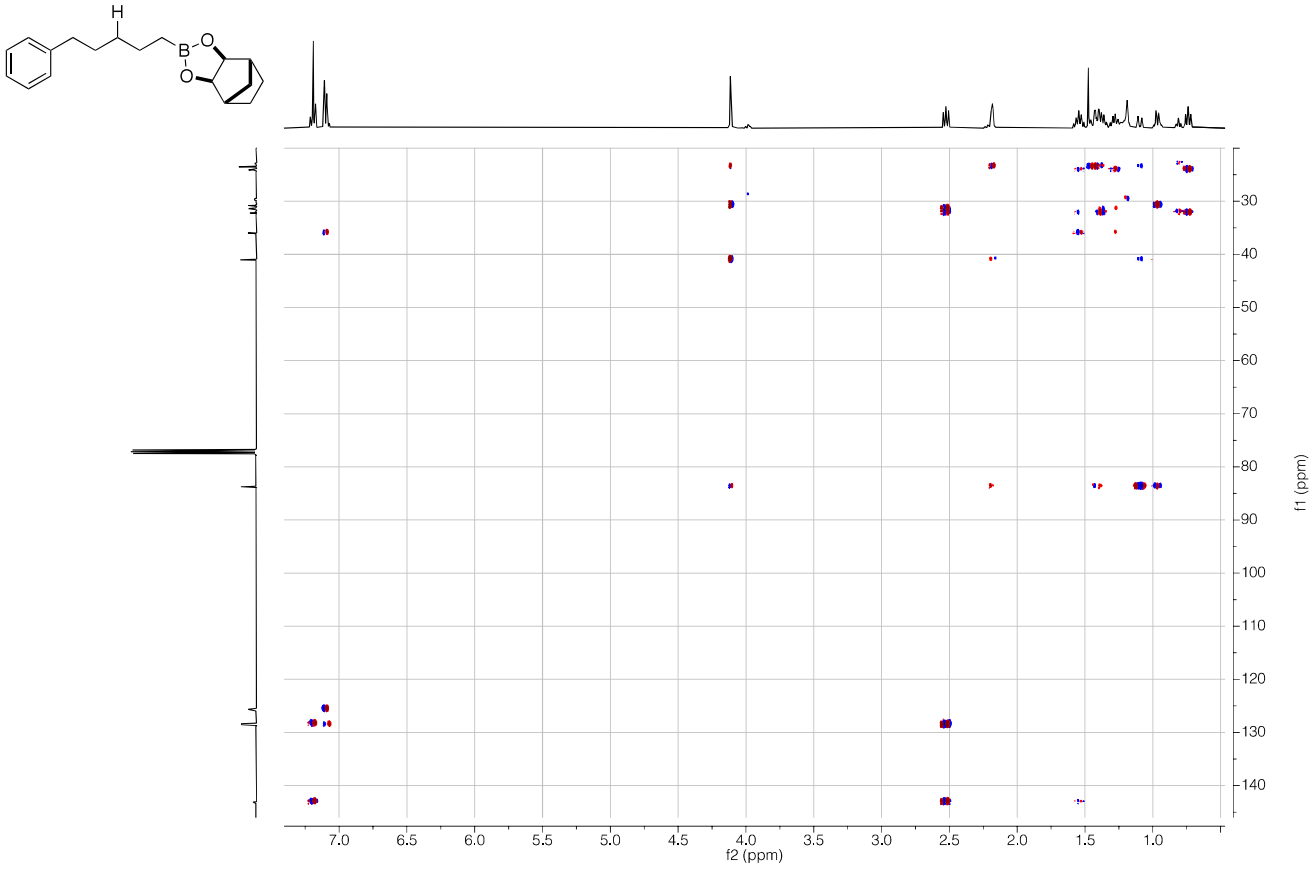
(3aR,4S,7R,7aS)-2-(5-Phenylpentyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



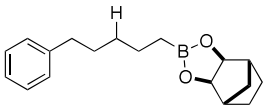
(3aR,4S,7R,7aS)-2-(5-Phenylpentyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)

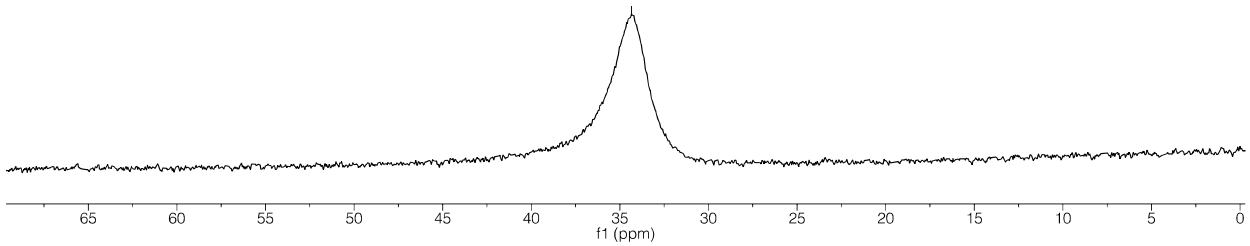


(3aR,4S,7R,7aS)-2-(5-Phenylpentyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

^{11}B-NMR (96 MHz, $CDCl_3$)

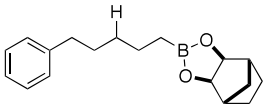


34.32

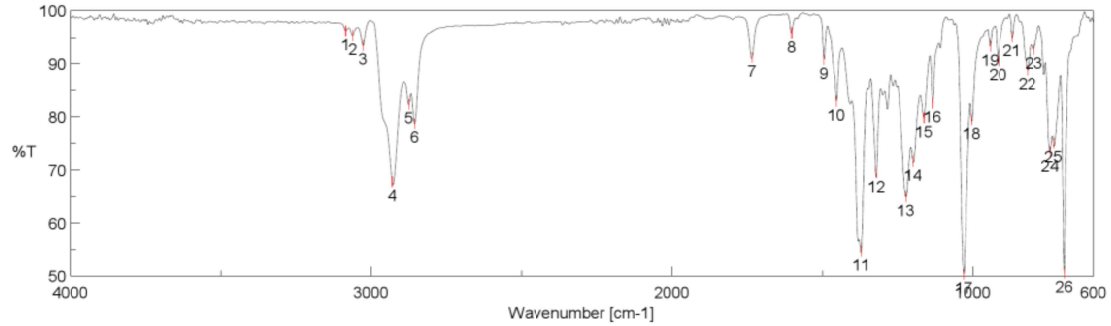


(3aR,4S,7R,7aS)-2-(5-Phenylpentyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

FT-IR, ATR-diamond



Peak Find - Memory-13

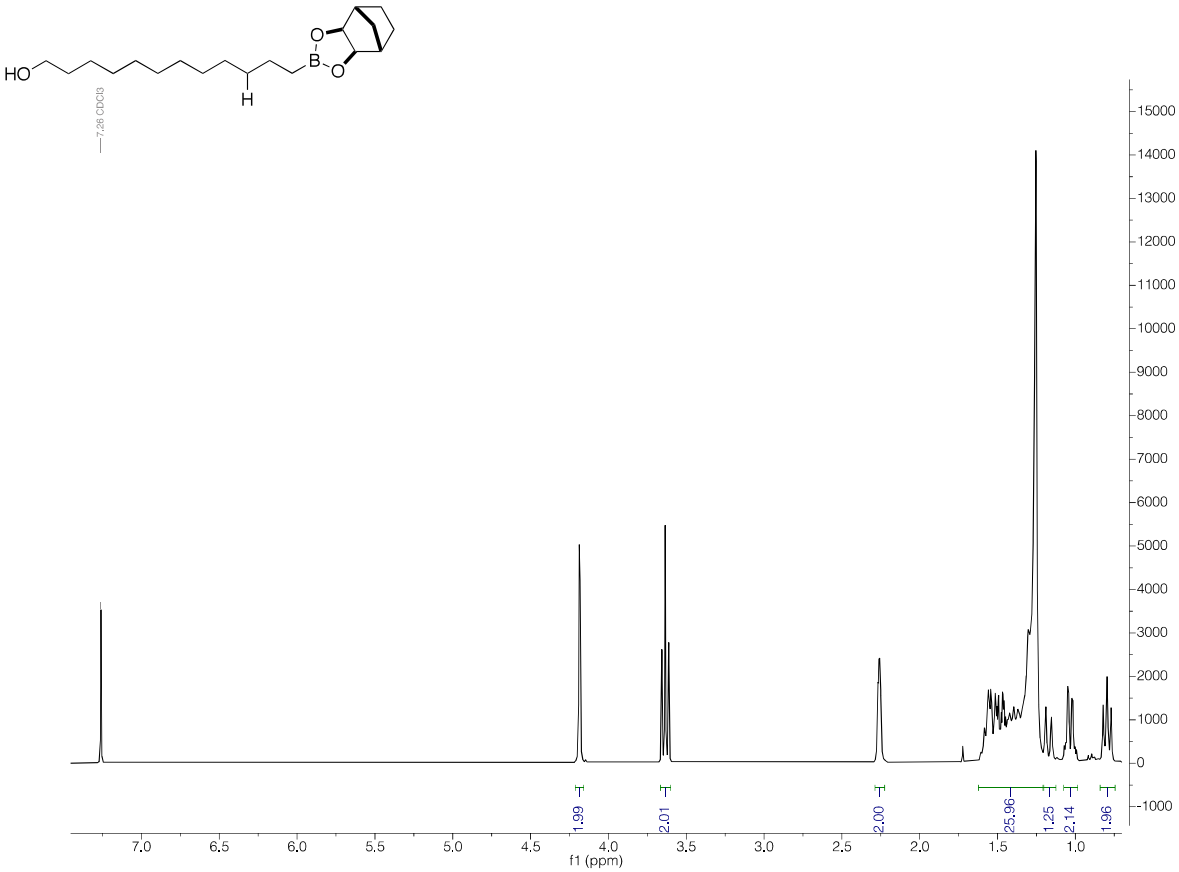


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3084.58	96	2	3060.48	95	3	3026.73	93
4	2929.34	68	5	2873.42	82	6	2854.13	79
7	1733.69	91	8	1602.56	96	9	1495.53	91
10	1454.06	83	11	1371.14	55	12	1320.04	69
13	1222.65	65	14	1198.54	72	15	1161.9	80
16	1132.97	83	17	1028.84	50	18	1003.77	79
19	943.02	93	20	916.022	90	21	869.739	95
22	818.634	89	23	797.421	93	24	743.424	73
25	731.853	75	26	697.141	51			

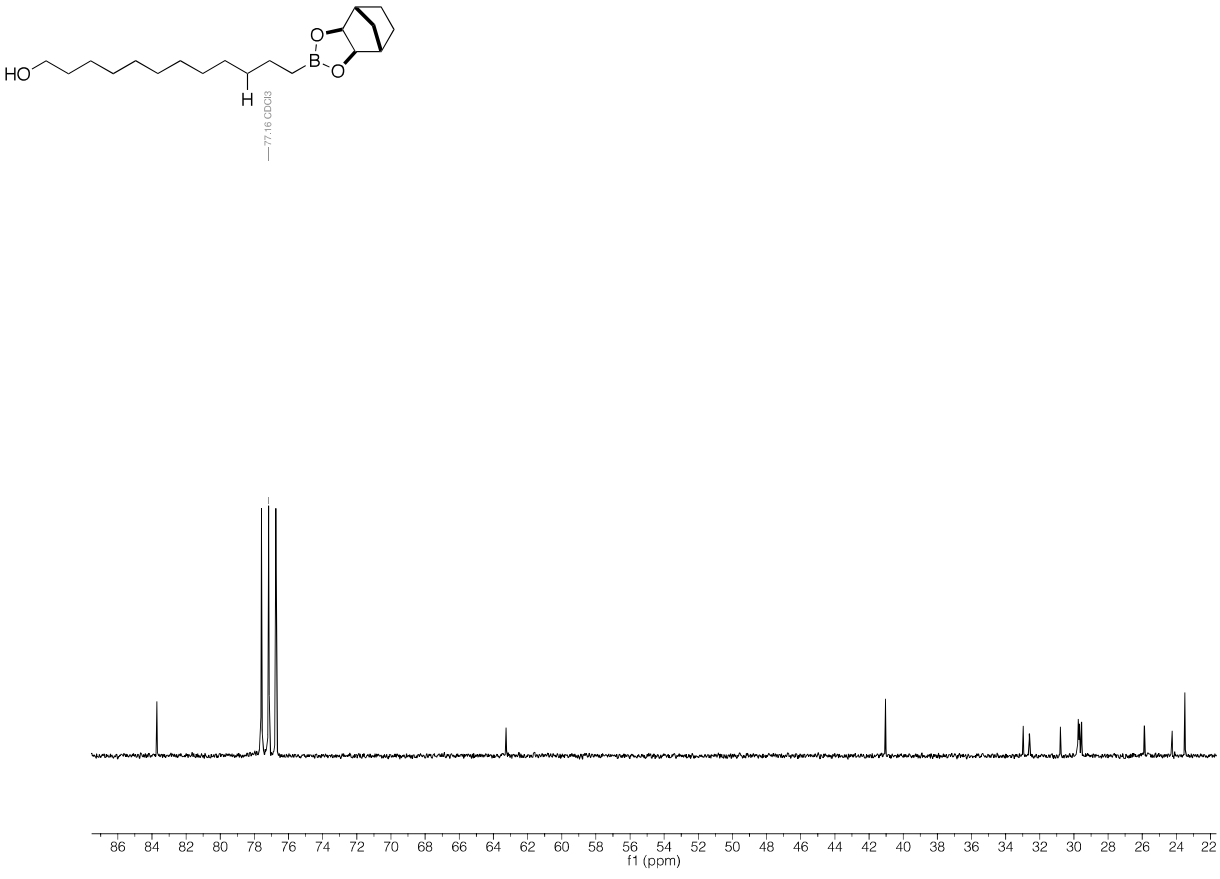
12-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)dodecan-1-ol

^{1}H-NMR (300 MHz, $CDCl_3$)



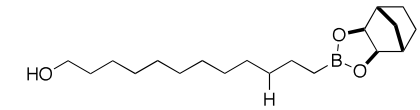
12-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)dodecan-1-ol

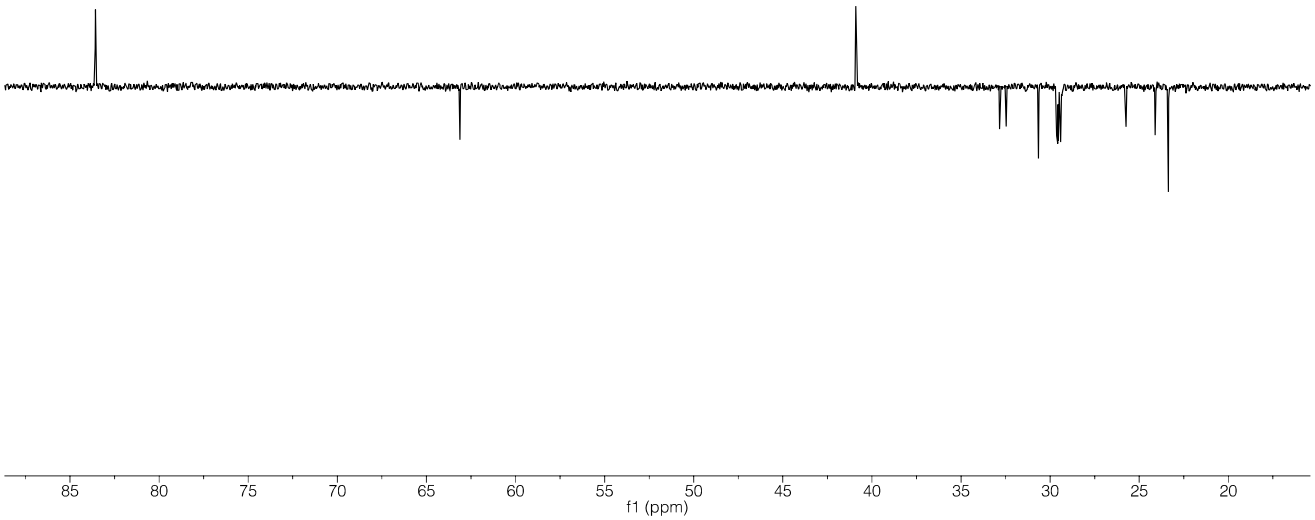
^{13}C-NMR (96 MHz, $CDCl_3$)



12-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)dodecan-1-ol

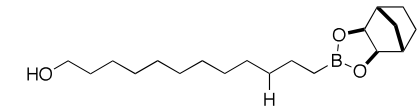
Dept-135 (96 MHz, $CDCl_3$)



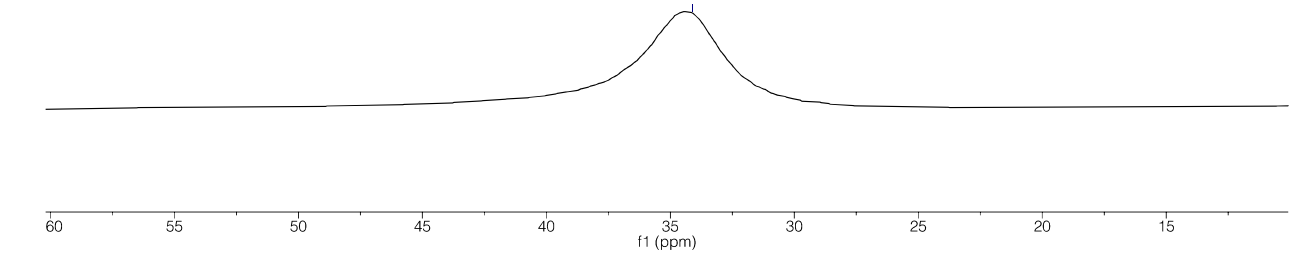


12-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)dodecan-1-ol

^{11}B-NMR (96 MHz, $CDCl_3$)

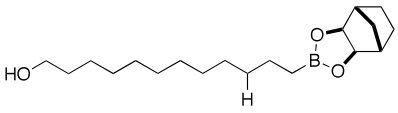


34.09

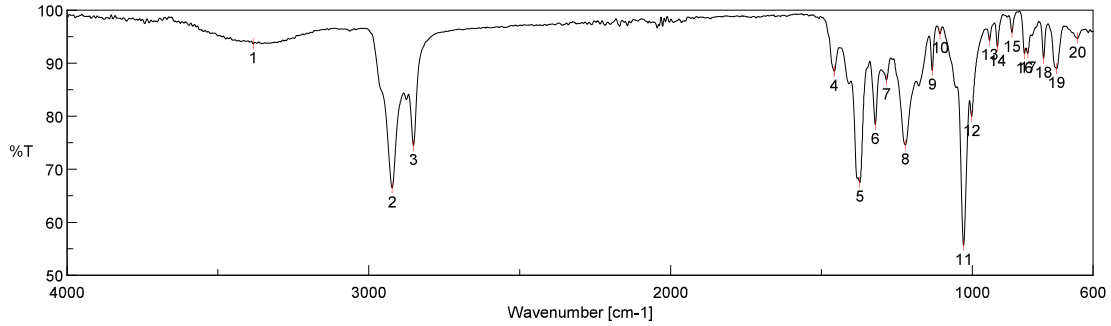


12-((3aR,4S,7R,7aS)-Hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)dodecan-1-ol

FT-IR, ATR-diamond



Peak Find - Memory-3

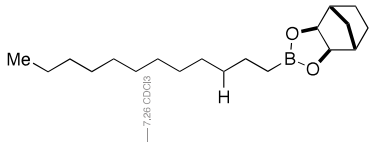


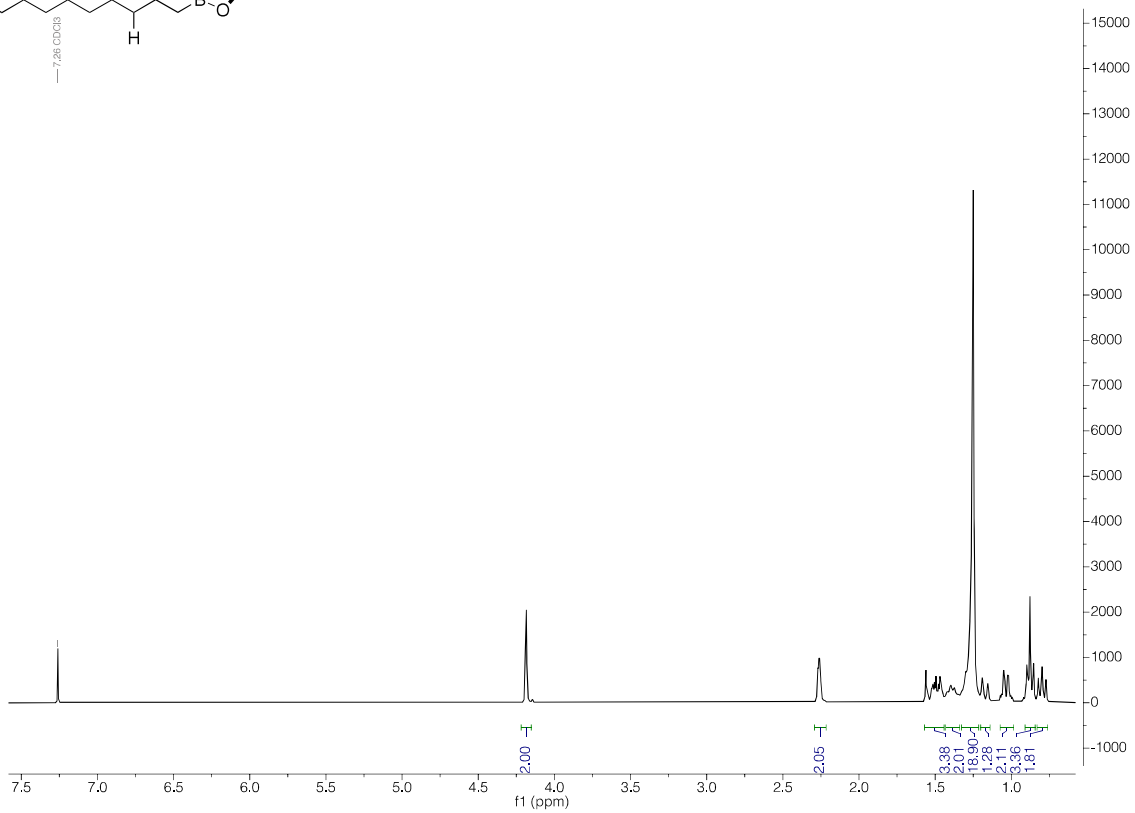
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3383.5	94	2	2922.59	66	3	2852.2	74
4	1457.92	88	5	1373.07	67	6	1321.96	78
7	1284.36	87	8	1222.65	75	9	1132.97	89
10	1106.94	96	11	1028.84	56	12	1002.8	80
13	943.02	94	14	916.986	93	15	868.774	96
16	827.312	92	17	816.706	92	18	764.637	91
19	721.247	89	20	651.822	95			

(3aR,4S,7R,7aS)-2-Dodecylhexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

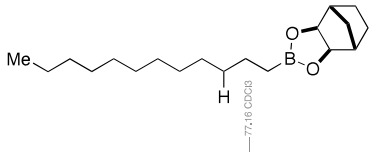
^{1}H-NMR (300 MHz, $CDCl_3$)

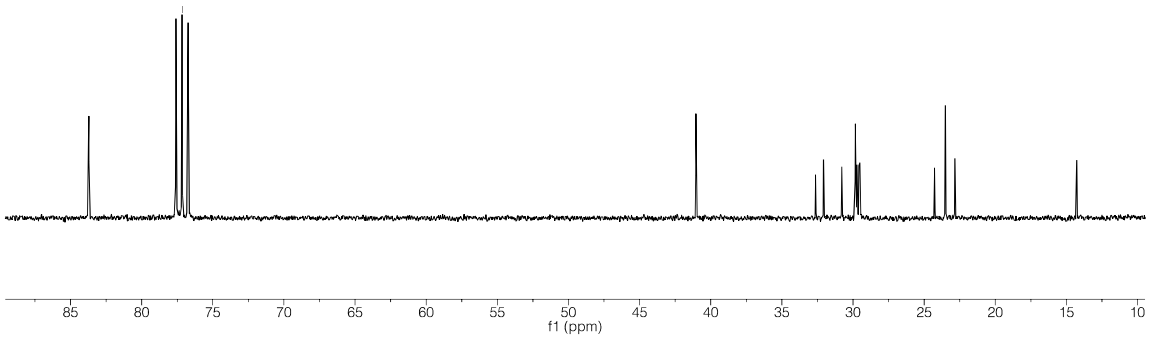




(3aR,4S,7R,7aS)-2-Dodecylhexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

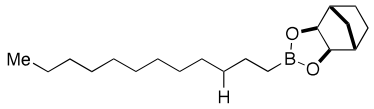
^{13}C-NMR (96 MHz, $CDCl_3$)

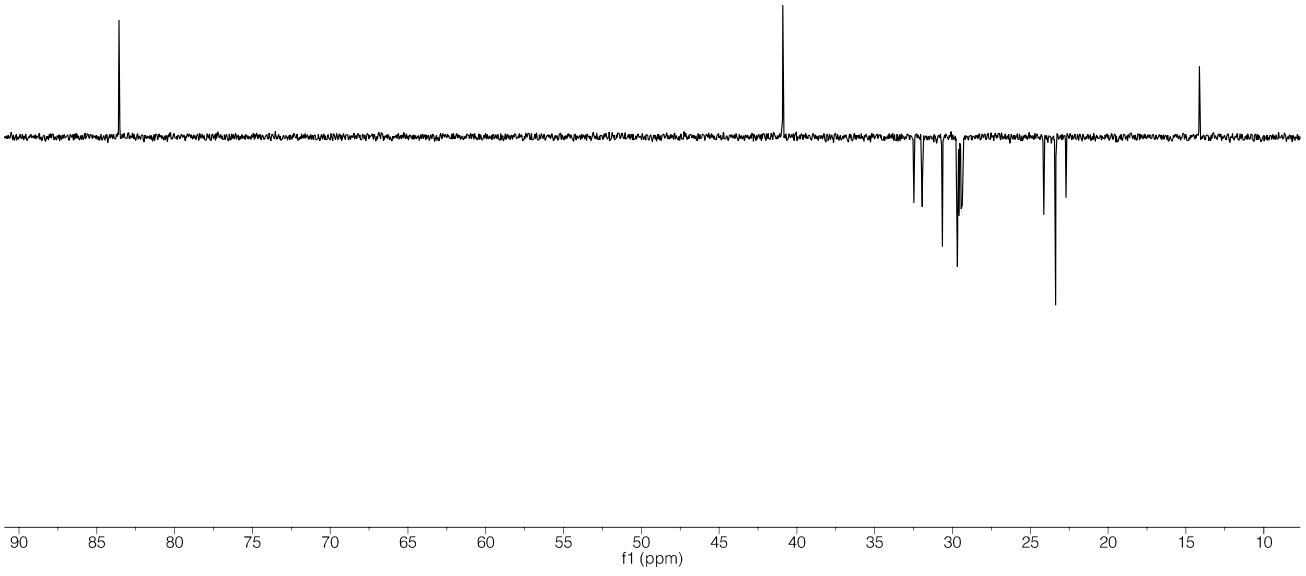




(3aR,4S,7R,7aS)-2-Dodecylhexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

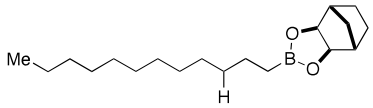
Dept-135 (96 MHz, $CDCl_3$)





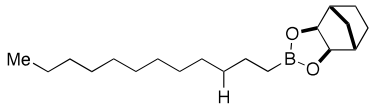
(3aR,4S,7R,7aS)-2-Dodecylhexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

^{11}B-NMR (96 MHz, $CDCl_3$)

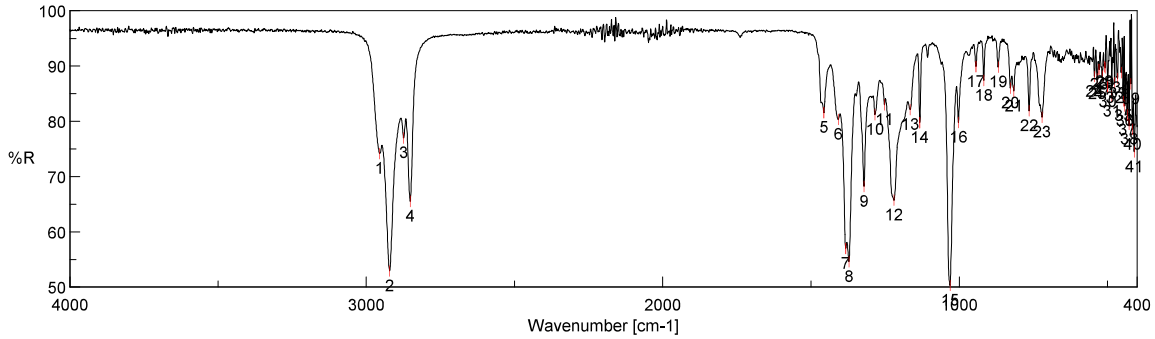


(3aR,4S,7R,7aS)-2-Dodecylhexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

FT-IR, ATR-diamond



Peak Find - Memory-4

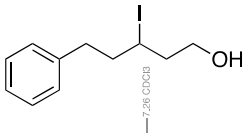


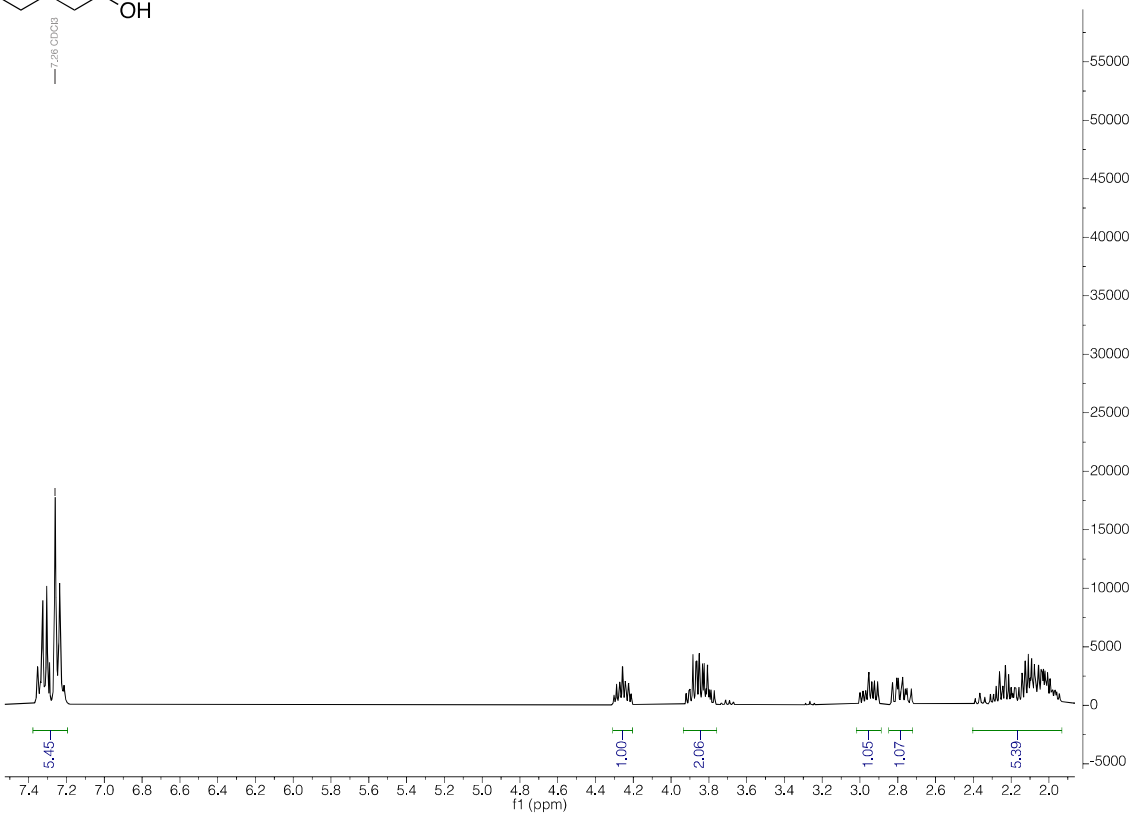
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2955.38	74.1614	2	2921.63	52.9112	3	2874.38	76.9914
4	2852.2	65.5036	5	1456.47	81.5665	6	1408.26	80.3255
7	1382.71	56.9764	8	1372.1	54.564	9	1321.48	68.1848
10	1284.36	81.2032	11	1252.54	82.9679	12	1220.24	65.7321
13	1165.76	82.0881	14	1132.97	79.726	15	1031.25	50.3063
16	1002.8	79.7876	17	943.502	89.8754	18	917.468	87.3709
19	868.774	89.7847	20	827.794	85.9678	21	815.742	85.44
22	764.155	81.8669	23	720.765	80.7334	24	543.828	88.0818
25	534.667	87.6636	26	528.4	89.356	27	517.793	88.1478
28	511.044	89.8826	29	507.669	89.6358	30	499.473	86.1896
31	485.492	84.5082	32	475.849	86.9151	33	465.725	87.7434
34	453.672	88.7772	35	446.922	83.7112	36	441.137	82.7596
37	433.423	81.1354	38	427.155	79.4591	39	420.888	86.7465
40	415.585	78.4916	41	409.799	74.4481			

3-Iodo-5-phenyl-pentan-1-ol

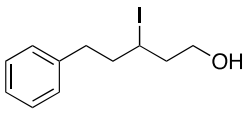
^{1}H-NMR (300 MHz, $CDCl_3$)





3-Iodo-5-phenyl-pentan-1-ol

^{13}C-NMR (96 MHz, $CDCl_3$)

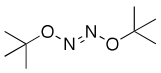


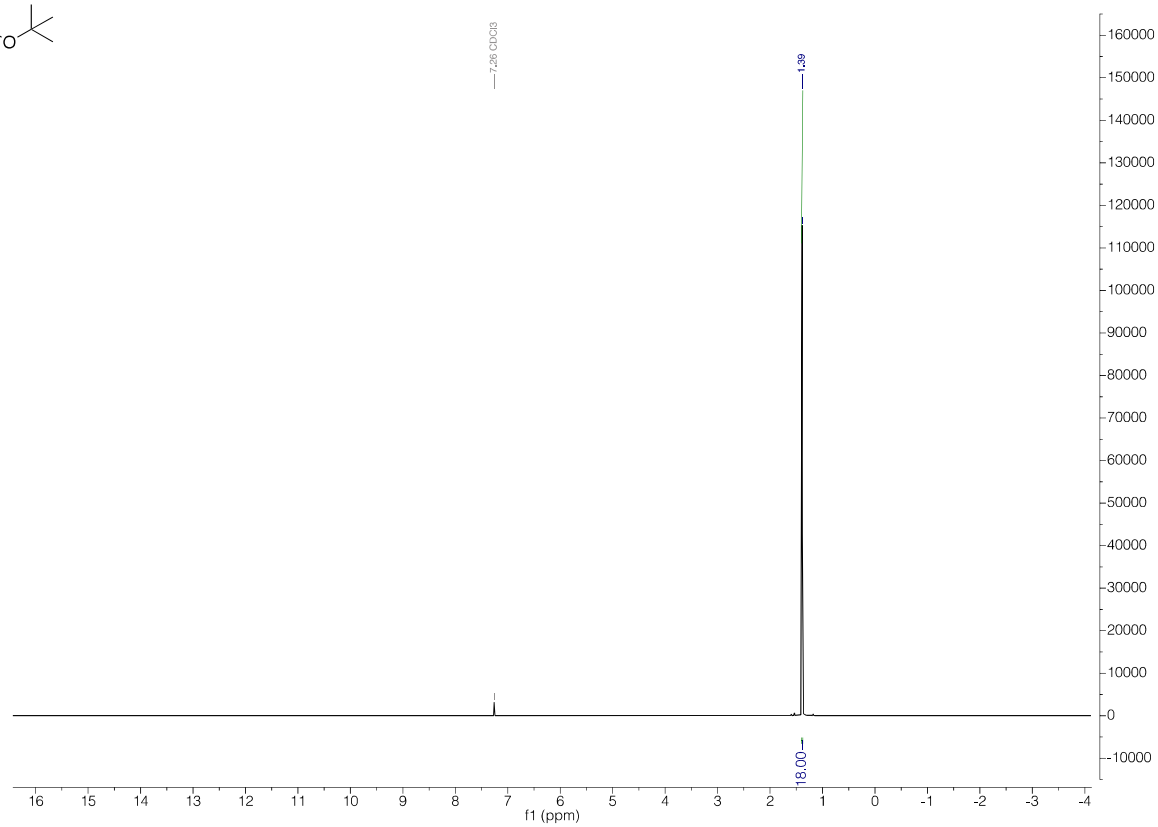
A.2 NMR Spectra Chapter 2

Cyclisation reactions involving α-boryl radicals: Atom Transfer Radical Addition and Cyclisation (ATRAC) and Atom Transfer Radical Addition and Annulation (ATRAn)

DTBHN

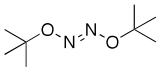
^{1}H-NMR (300 MHz, $CDCl_3$)

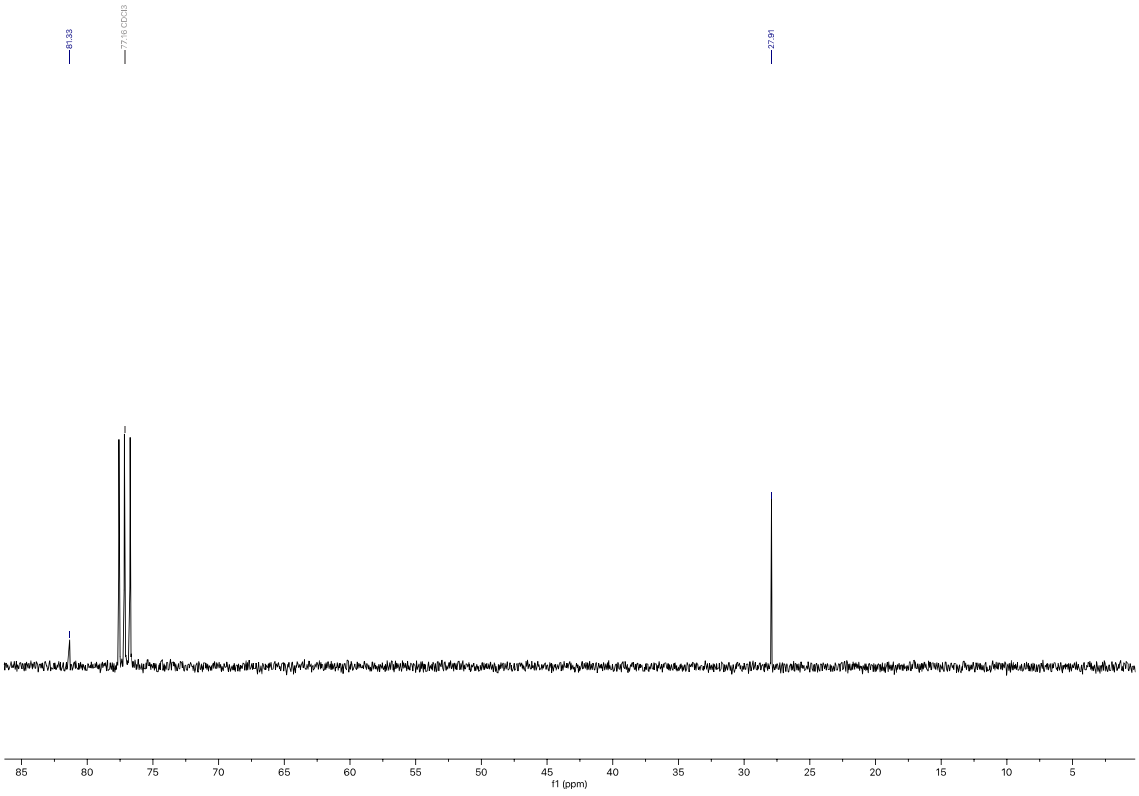




DTBHN

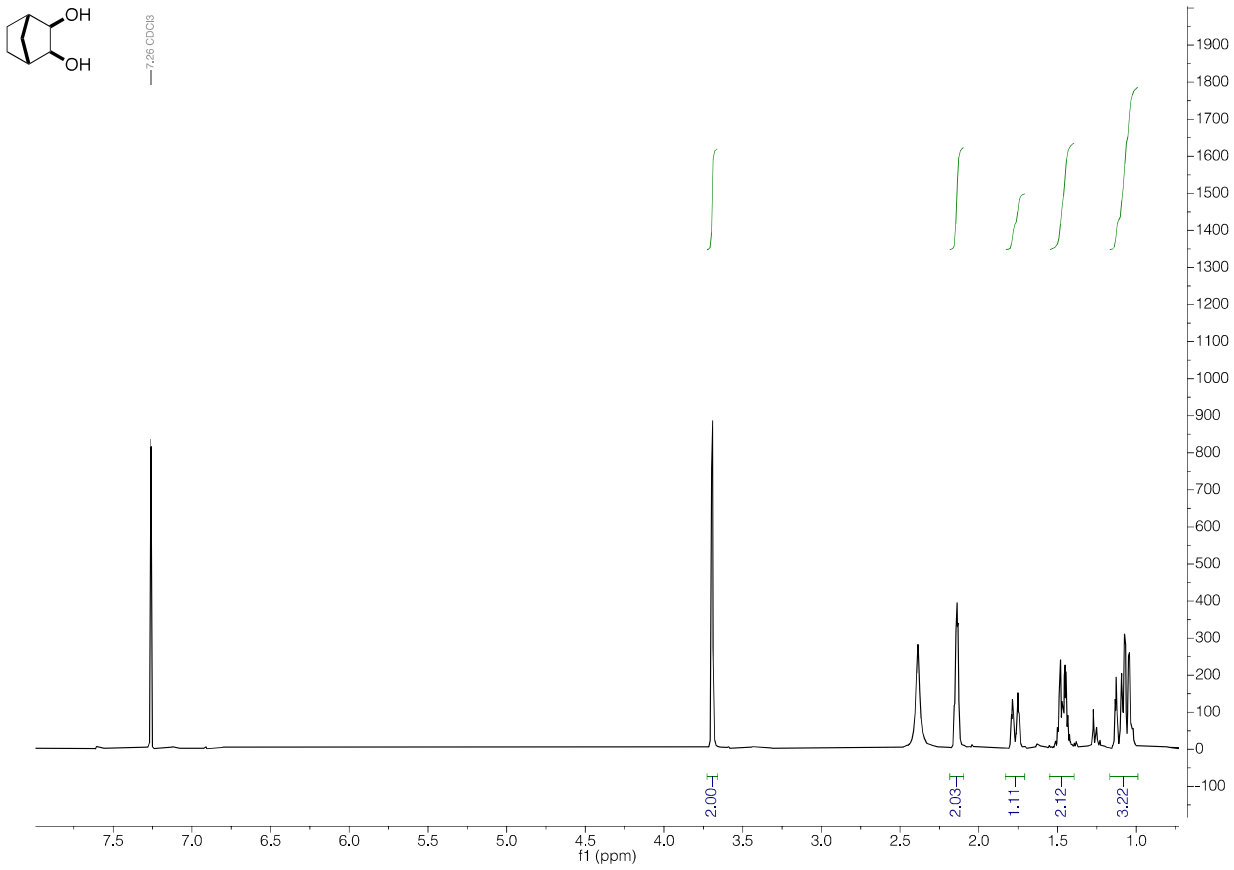
^{1}H-NMR (300 MHz, $CDCl_3$)





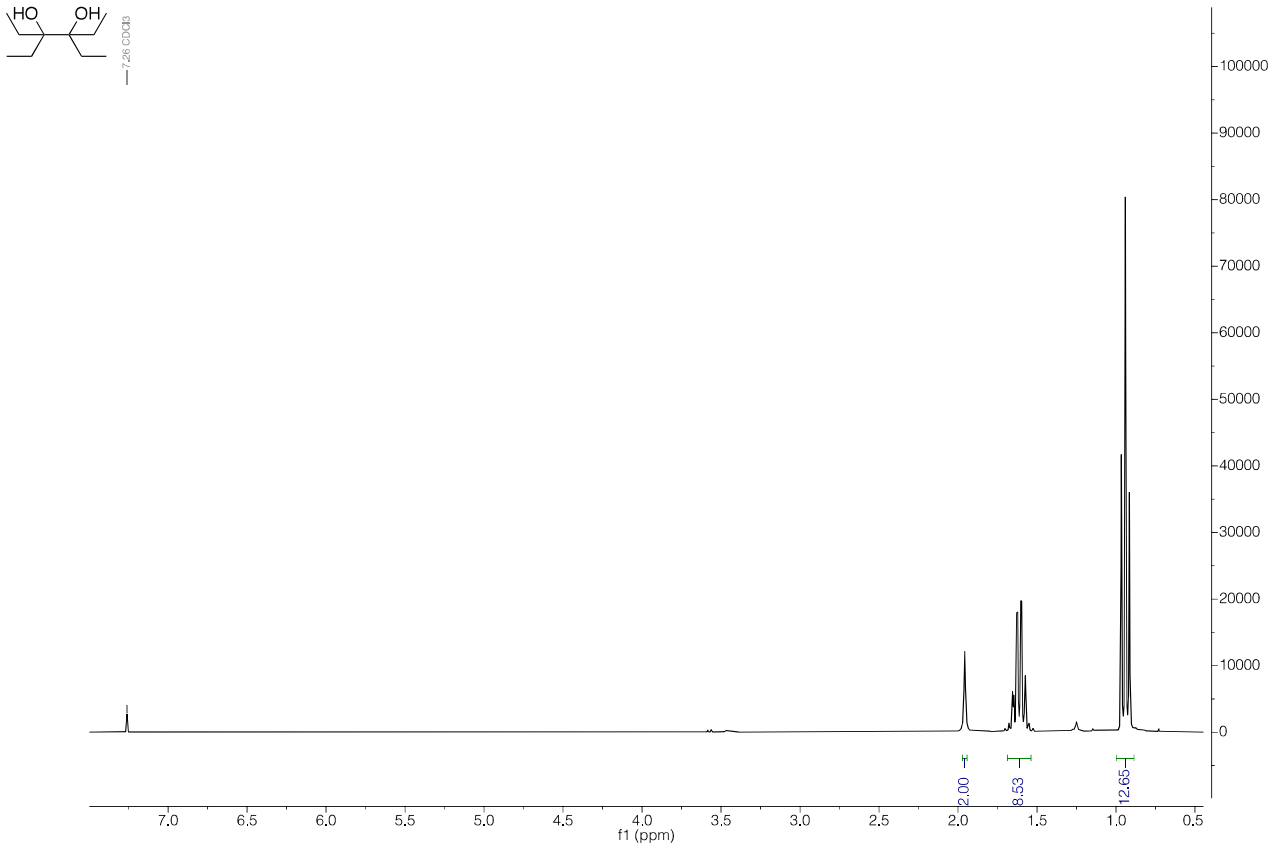
(1*R**,2*S**,3*R**,4*S**)-bicyclo[2.2.1]heptane-2,3-diol

^{1}H-NMR (300 MHz, $CDCl_3$)



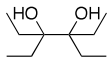
3,4-Diethylhexane-3,4-diol

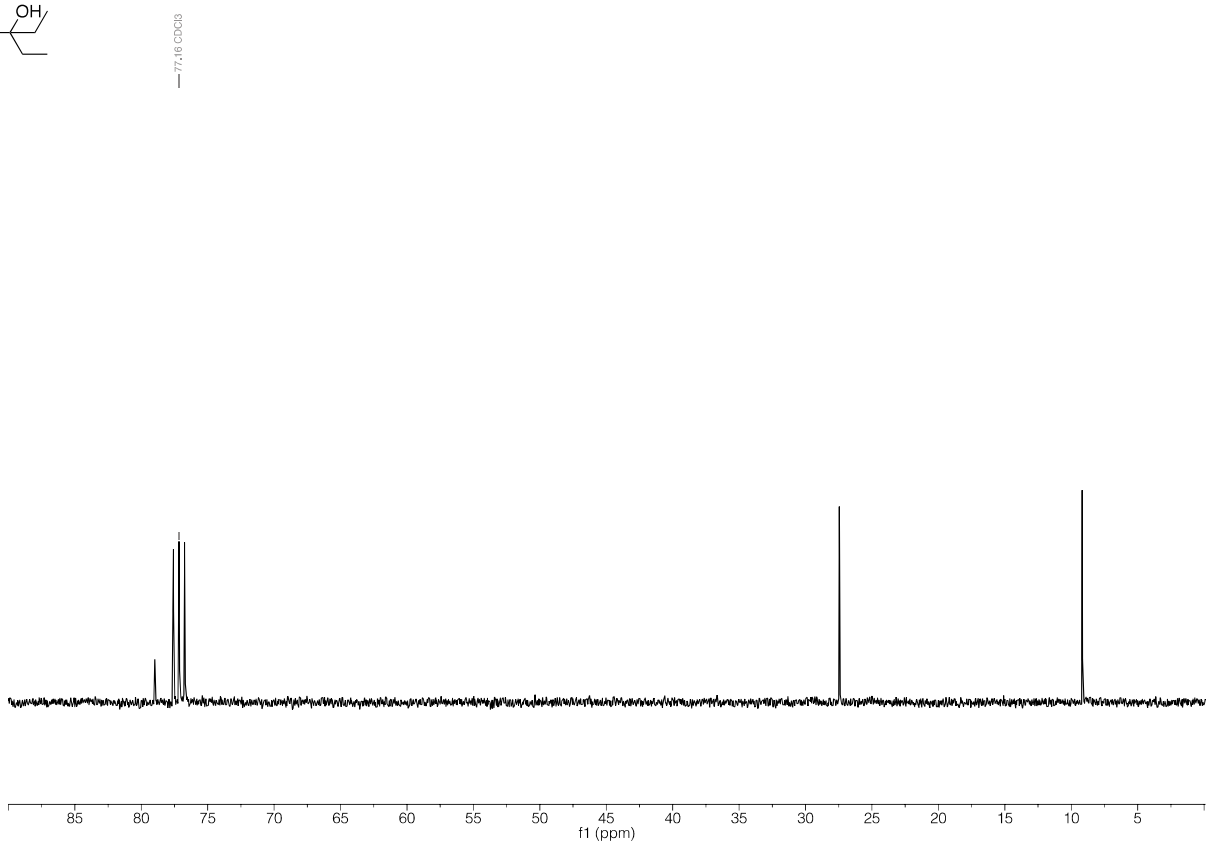
^{1}H-NMR (300 MHz, $CDCl_3$)



3,4-Diethylhexane-3,4-diol

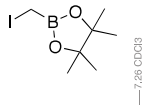
^{13}C-NMR (75 MHz, $CDCl_3$)

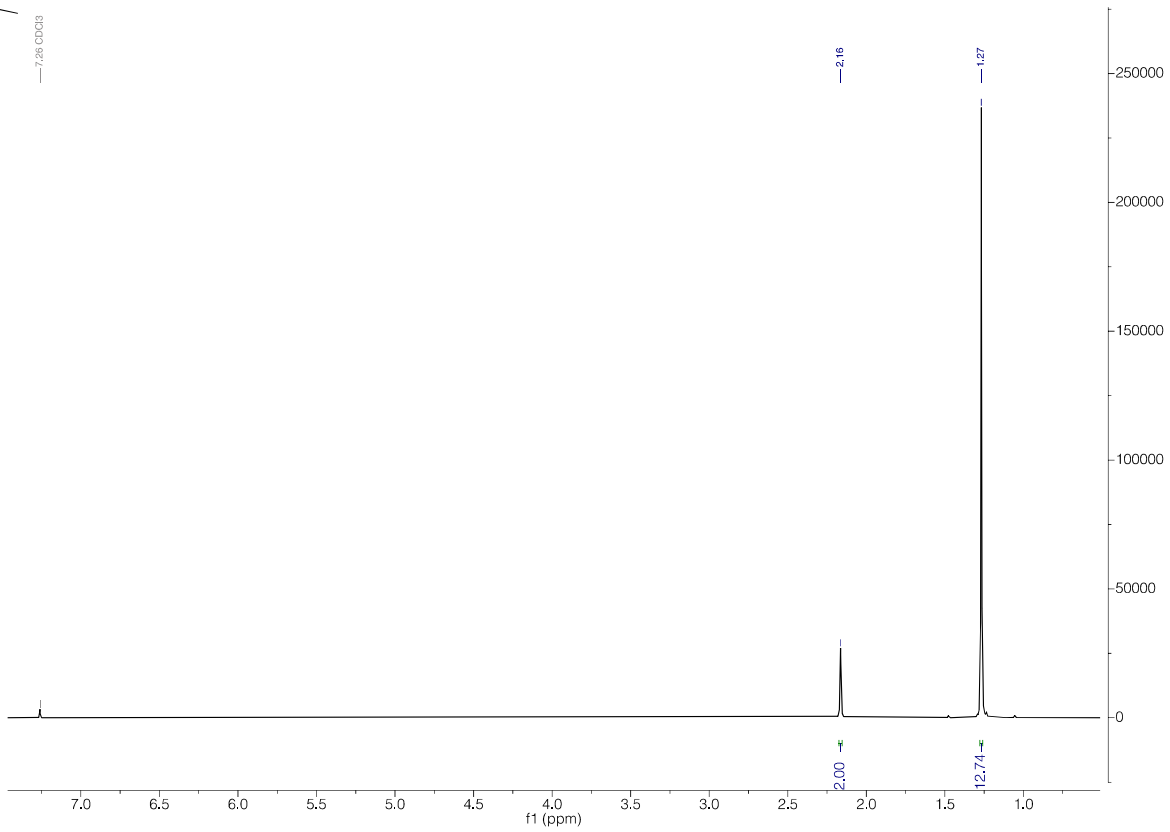




2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

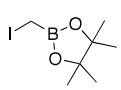
^{1}H-NMR (300 MHz, $CDCl_3$)





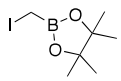
2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{13}C-NMR (75 MHz, $CDCl_3$)



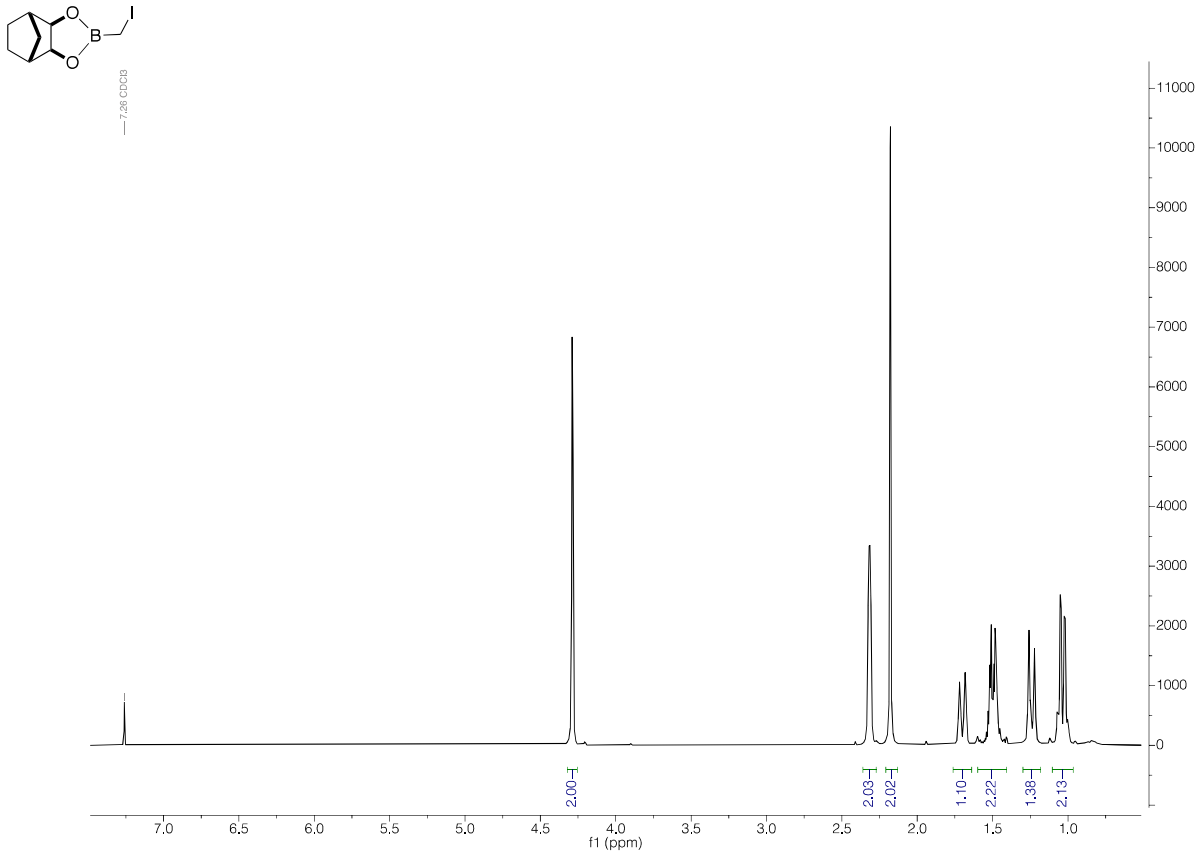
2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{11}B-NMR (96 MHz, $CDCl_3$)



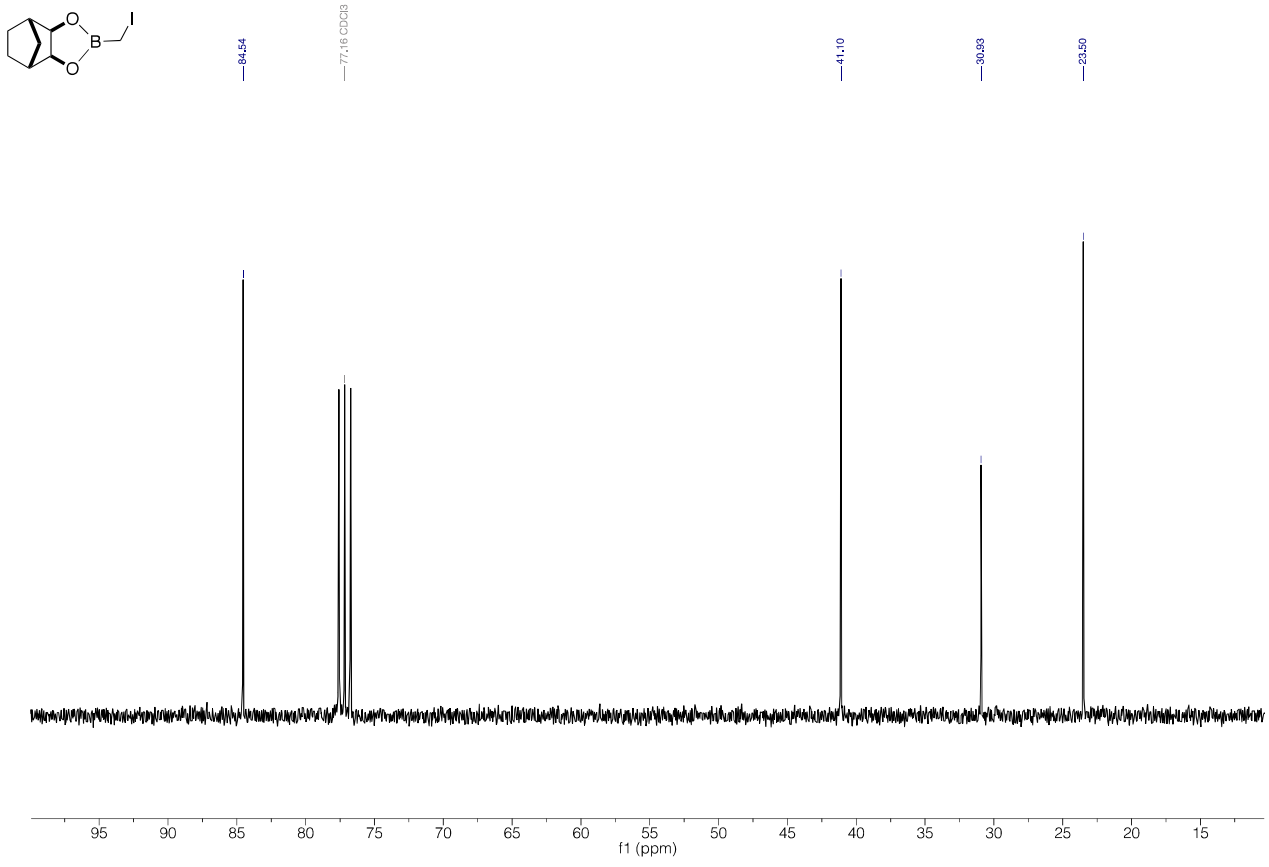
exo,exo-2-(Iodomethyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

^{1}H-NMR (300 MHz, $CDCl_3$)



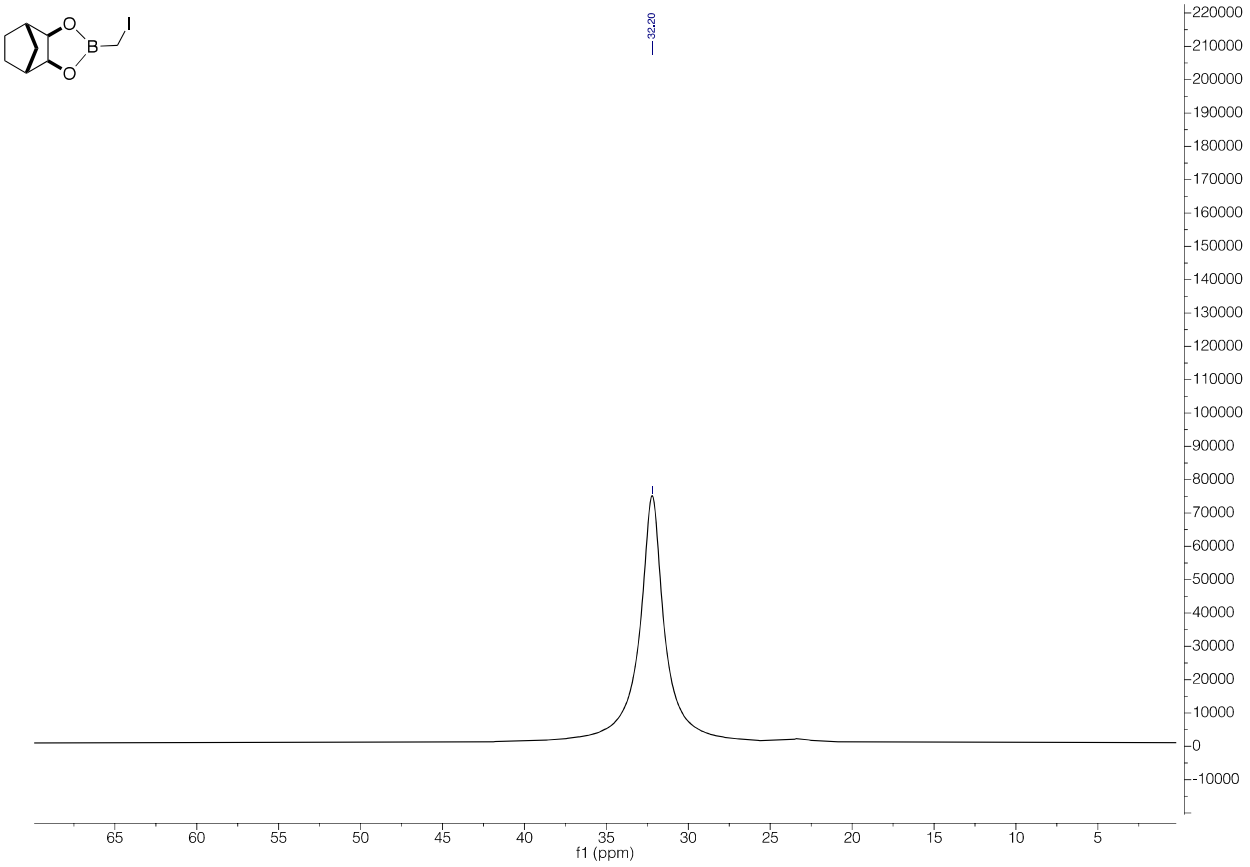
exo,exo-2-(Iodomethyl)hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborole

^{13}C-NMR (96 MHz, $CDCl_3$)



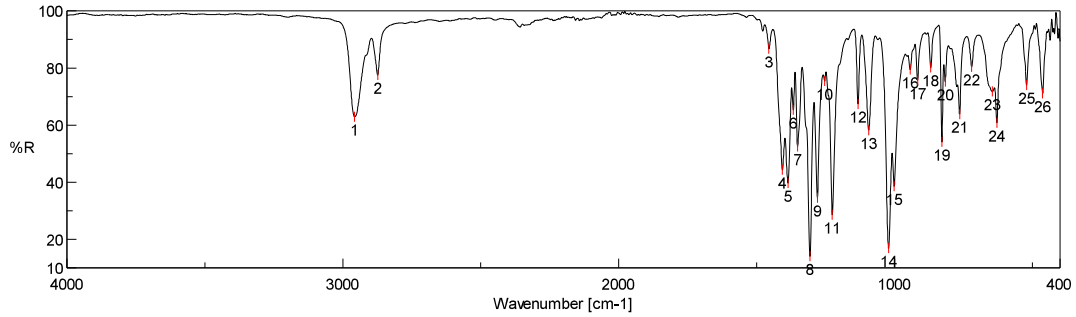
(3a*R**,4*S**,7*R**,7a*S**)-2-(iodomethyl)hexahydro-4,7-methanobenzo[*d*][1,3,2]dioxaborole

^{11}B-NMR (96 MHz, $CDCl_3$)



(3a*R**,4*S**,7*R**,7a*S**)-2-(iodomethyl)hexahydro-4,7-methanobenzo[*d*][1,3,2]dioxaborole

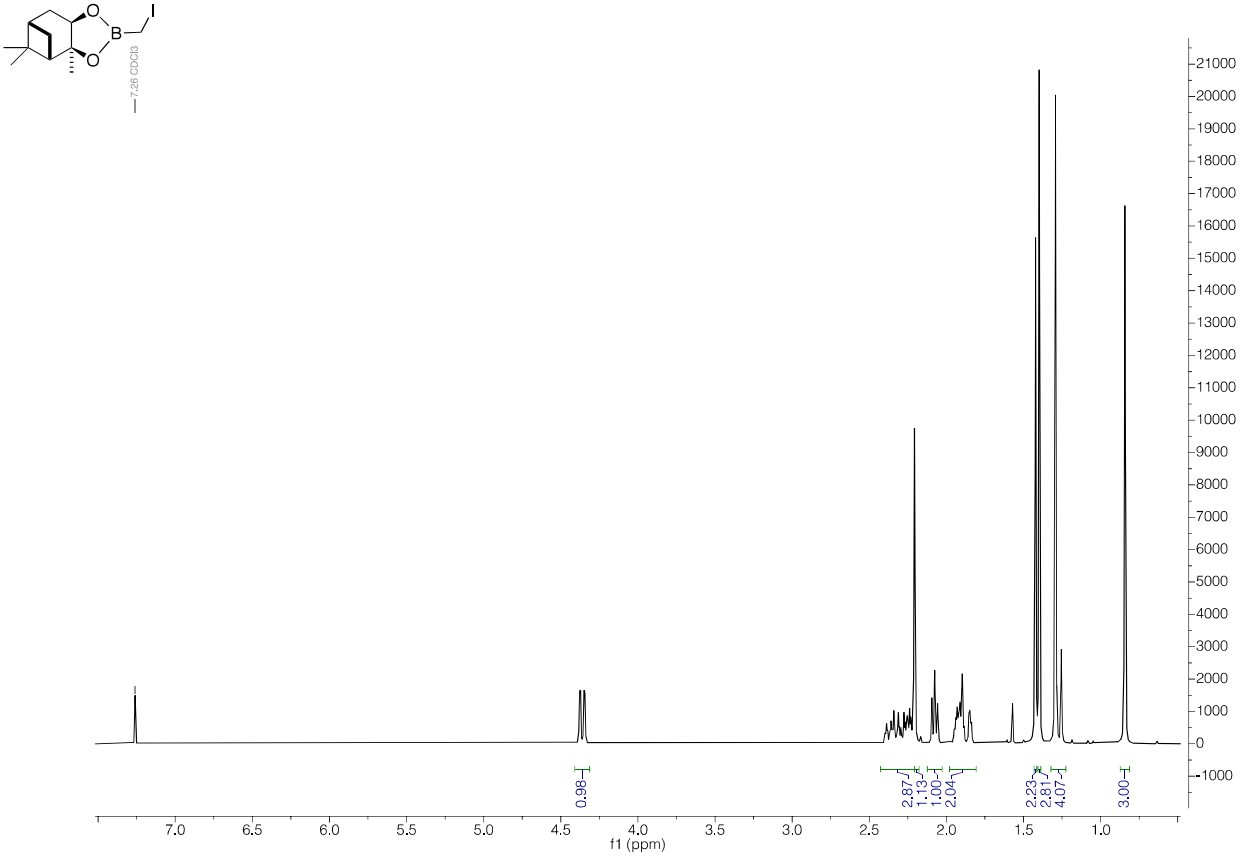
FT-IR, ATR-diamond



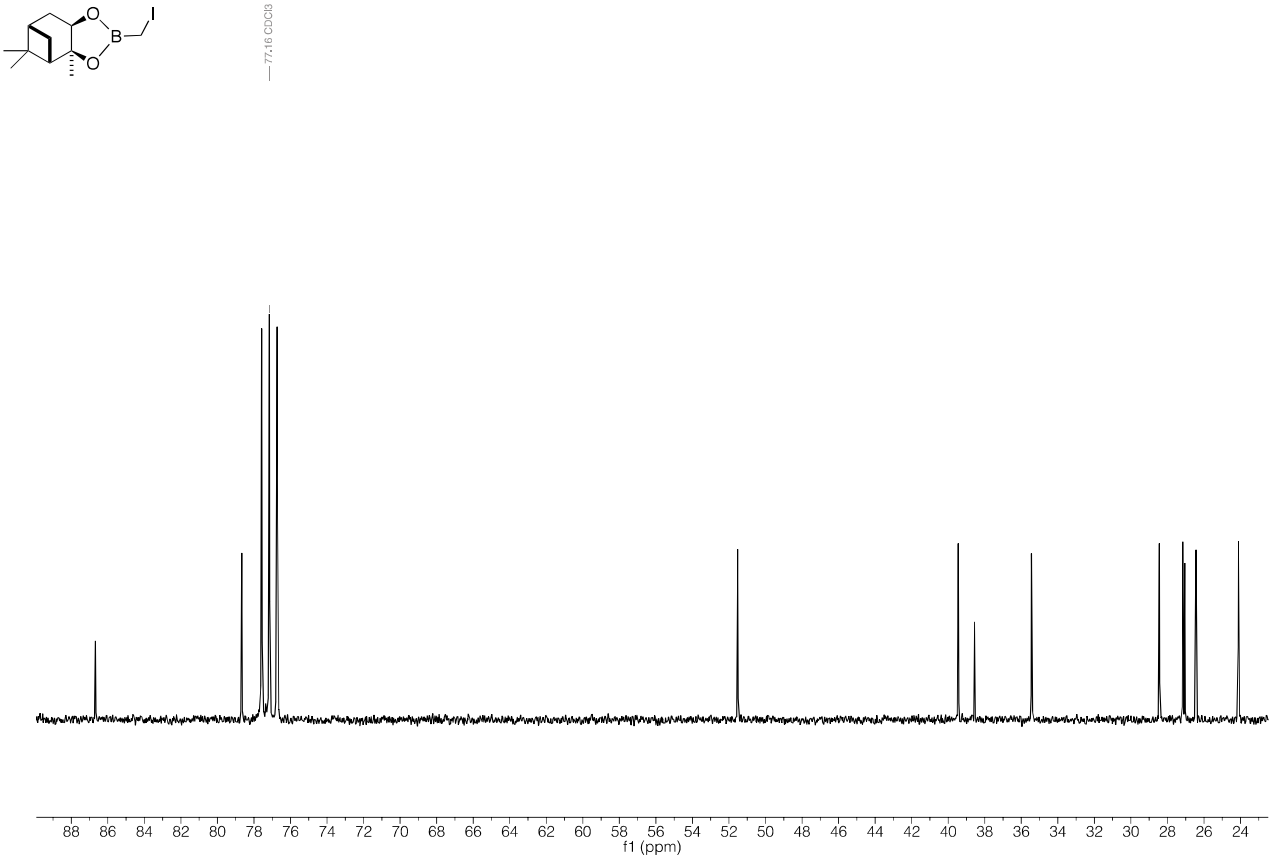
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2957.3	62.9455	2	2873.42	77.4931	3	1455.03	86.6726
4	1406.82	44.3111	5	1386.57	39.651	6	1367.28	65.2648
7	1351.86	52.5138	8	1306.54	14.0621	9	1279.54	34.536
10	1253.5	75.3804	11	1225.54	28.532	12	1132.01	67.393
13	1093.44	58.1405	14	1021.12	16.888	15	1000.87	38.5739
16	943.02	79.3877	17	916.022	75.6386	18	868.774	80.1304
19	828.277	54.131	20	815.742	75.139	21	763.673	63.8561
22	720.282	80.3833	23	645.072	71.7492	24	628.68	60.8142
25	520.686	74.0151	26	462.832	71.0394			

(3a*R*,4*R*,6*R*,7a*S*)-2-(Iodomethyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole ^{1}H-NMR (96 MHz, $CDCl_3$)

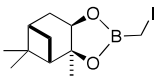


(3a*R*,4*R*,6*R*,7a*S*)-2-(Iodomethyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole ^{13}C-NMR (96 MHz, $CDCl_3$)



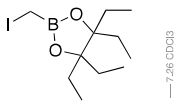
(3a*R*,4*R*,6*R*,7a*S*)-2-(Iodomethyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole

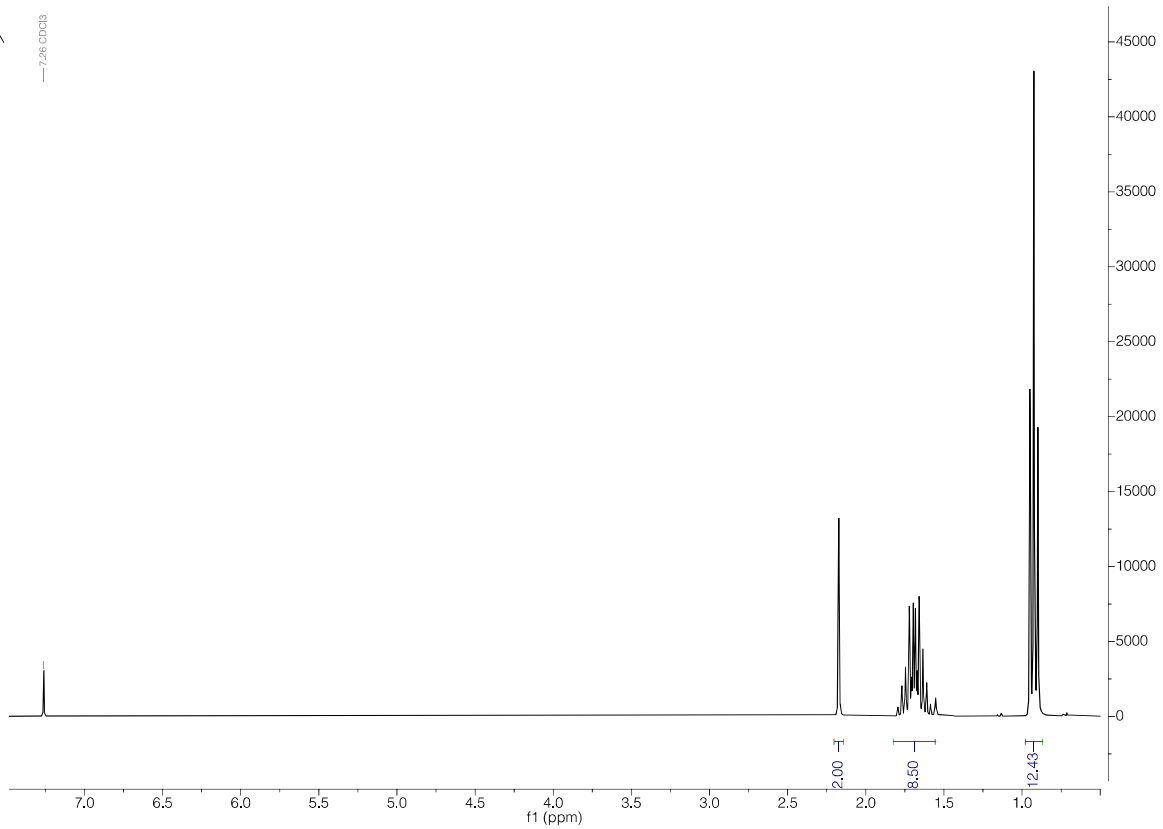
^{11}B-NMR (96 MHz, $CDCl_3$)



4,4,5,5-tetraethyl-2-(iodomethyl)-1,3,2-dioxaborolane

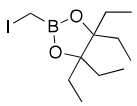
^{1}H-NMR (300 MHz, $CDCl_3$)

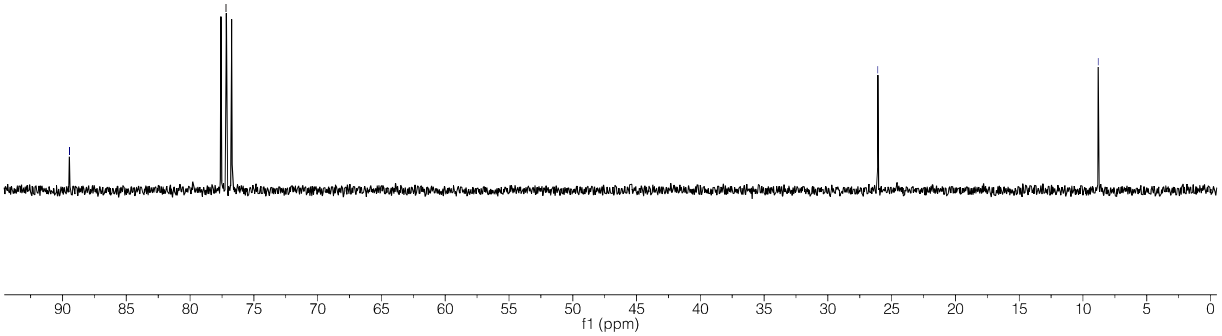




4,4,5,5-tetraethyl-2-(iodomethyl)-1,3,2-dioxaborolane

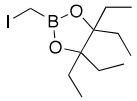
^{13}C-NMR (75 MHz, $CDCl_3$)





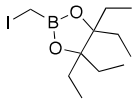
4,4,5,5-tetraethyl-2-(iodomethyl)-1,3,2-dioxaborolane

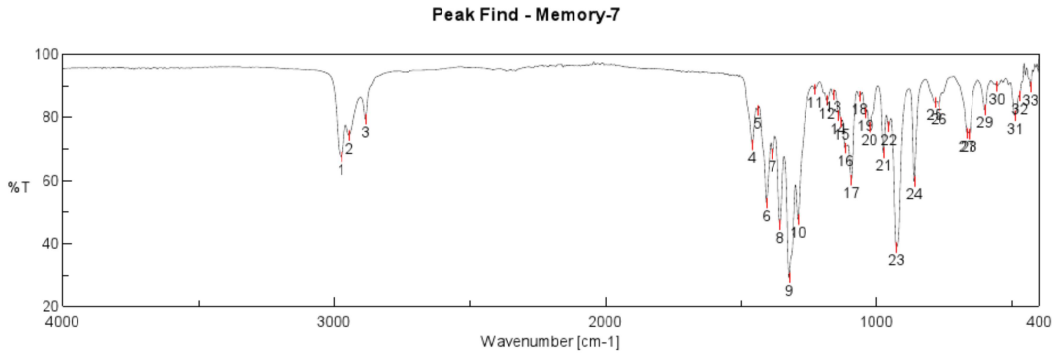
^{11}B-NMR (96 MHz, $CDCl_3$)



4,4,5,5-tetraethyl-2-(iodomethyl)-1,3,2-dioxaborolane

FT-IR, ATR-diamond



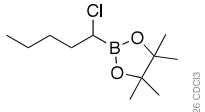


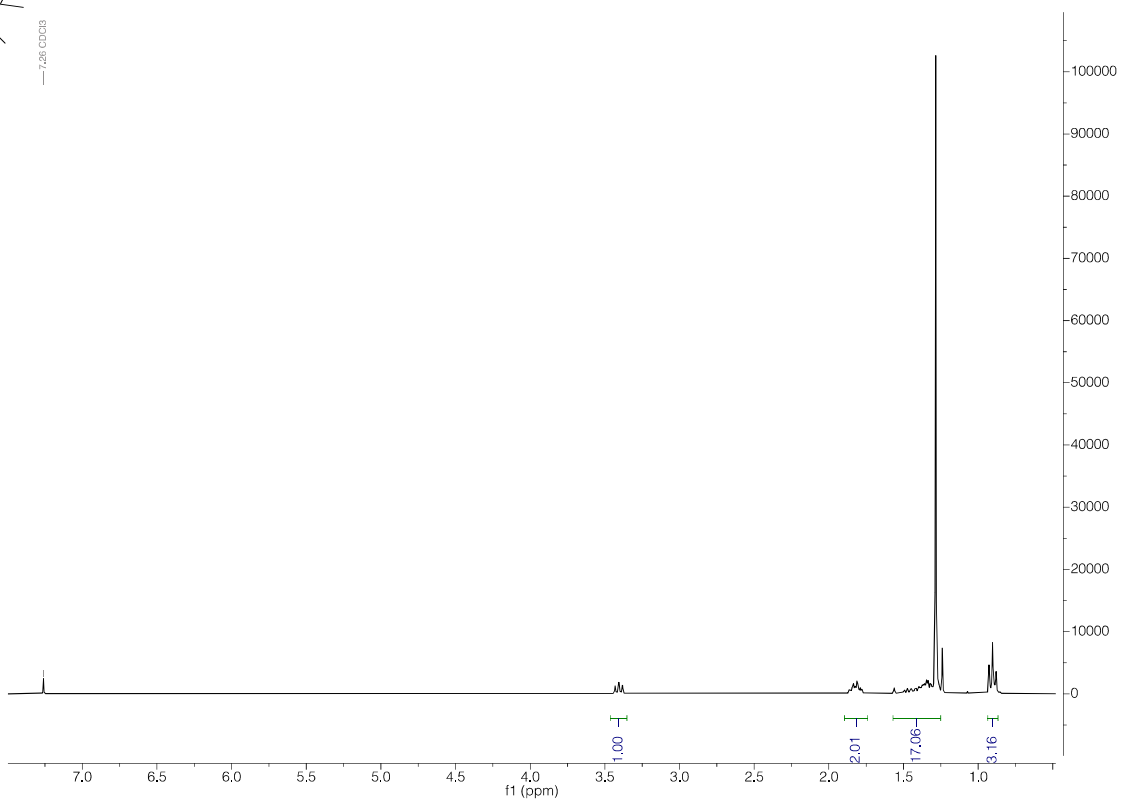
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2971.77	67.285	2	2942.84	74.0964	3	2883.06	79.1859
4	1456.96	71.065	5	1438.64	81.9844	6	1405.85	52.6262
7	1383.68	68.1985	8	1355.71	45.8814	9	1321.96	29.0479
10	1289.18	47.4105	11	1226.5	88.6495	12	1183.11	85.1582
13	1159.97	86.9588	14	1140.69	80.3453	15	1128.15	78.2928
16	1113.69	70.0725	17	1091.51	59.9237	18	1061.62	86.4902
19	1040.41	81.1574	20	1024.98	76.7044	21	971.947	68.5614
22	953.627	76.8742	23	925.664	38.5649	24	859.132	59.5219
25	786.815	84.5338	26	770.423	83.3242	27	667.25	74.7696
28	658.571	74.4875	29	599.753	82.1802	30	556.363	89.6221
31	488.866	80.2917	32	472.474	86.5541	33	432.941	89.4093

2-(1-chloropentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

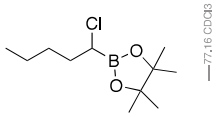
^{1}H-NMR (300 MHz, $CDCl_3$)

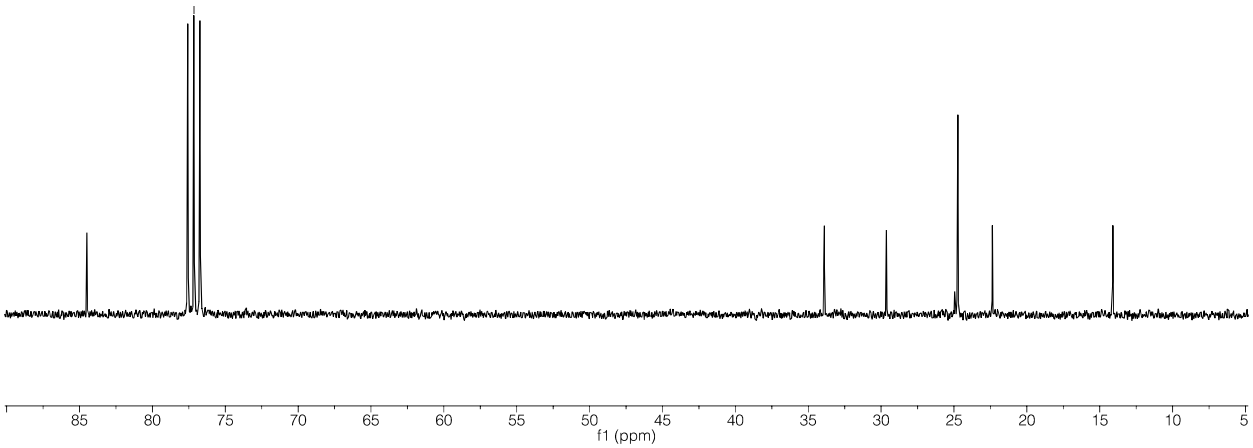




2-(1-chloropentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

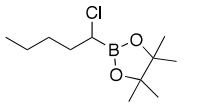
^{13}C-NMR (75 MHz, $CDCl_3$)

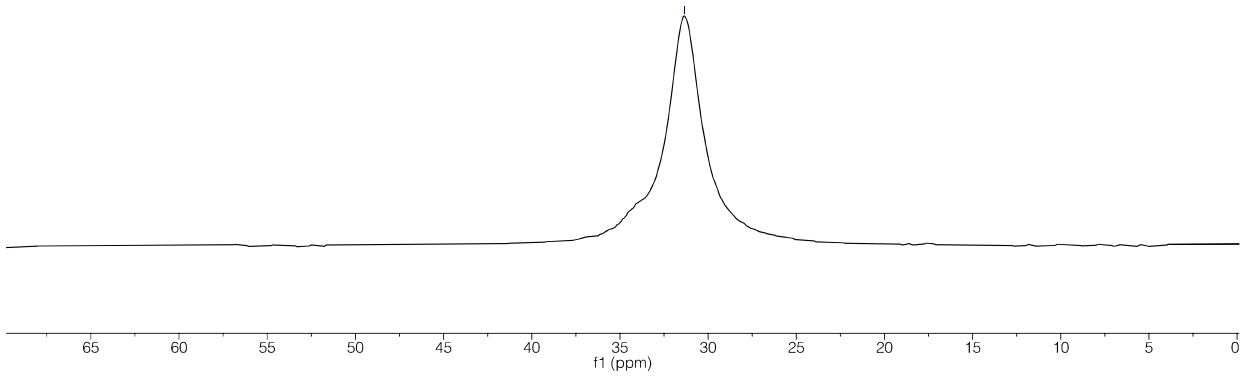




2-(1-chloropentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

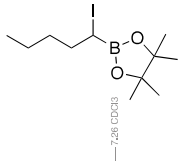
^{11}B-NMR (96 MHz, $CDCl_3$)

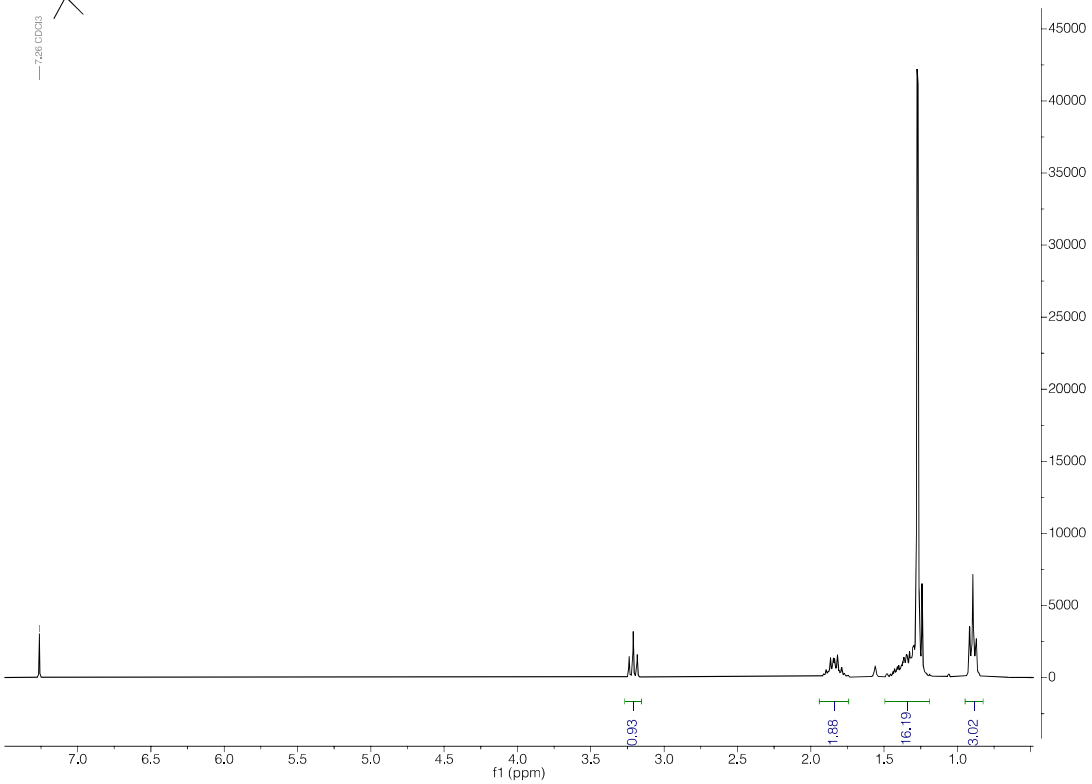




2-(1-iodopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

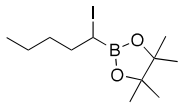
^{1}H-NMR (300 MHz, $CDCl_3$)

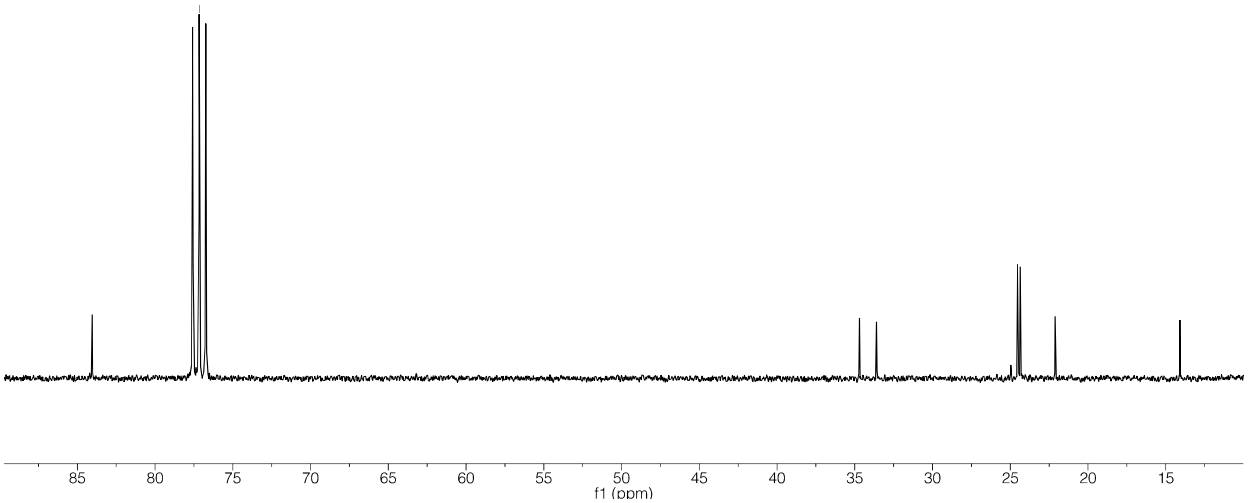




2-(1-iodopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

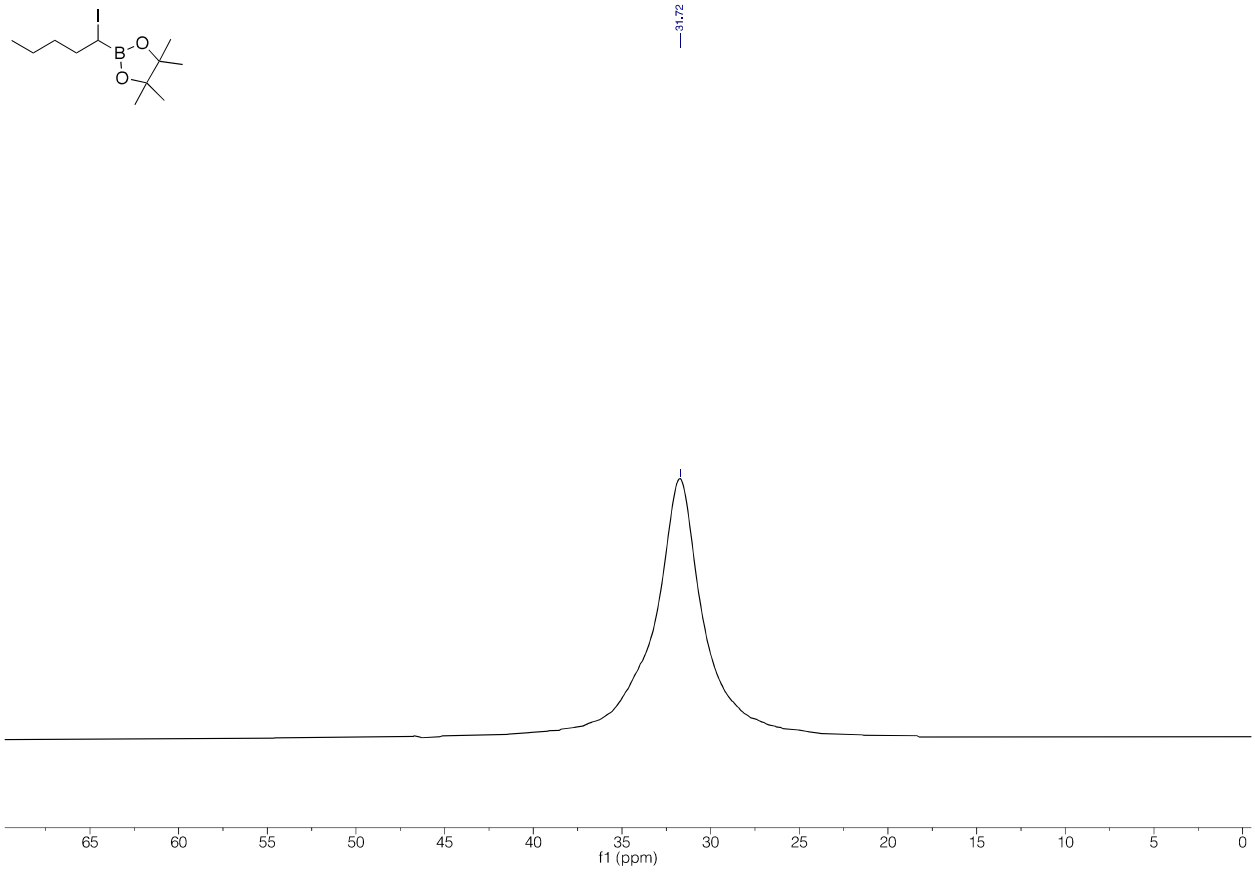
^{13}C-NMR (75 MHz, $CDCl_3$)





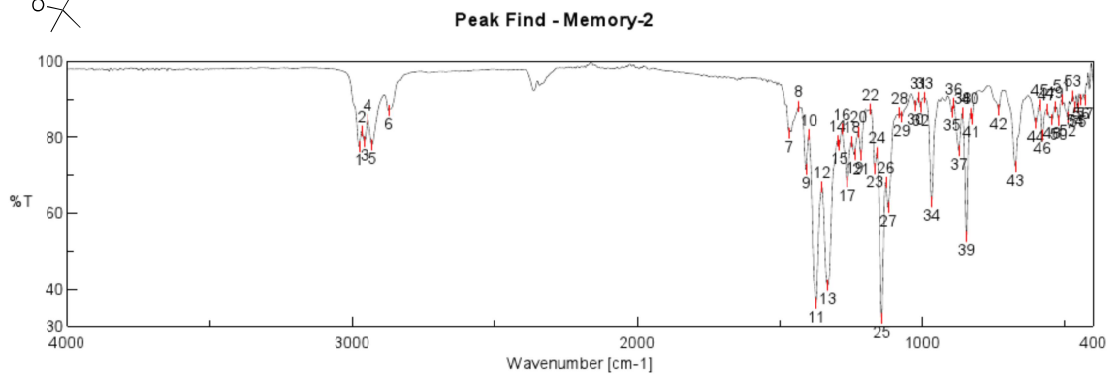
2-(1-iodopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{11}B-NMR (96 MHz, $CDCl_3$)



2-(1-iodopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

FT-IR, ATR-diamond

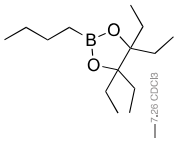


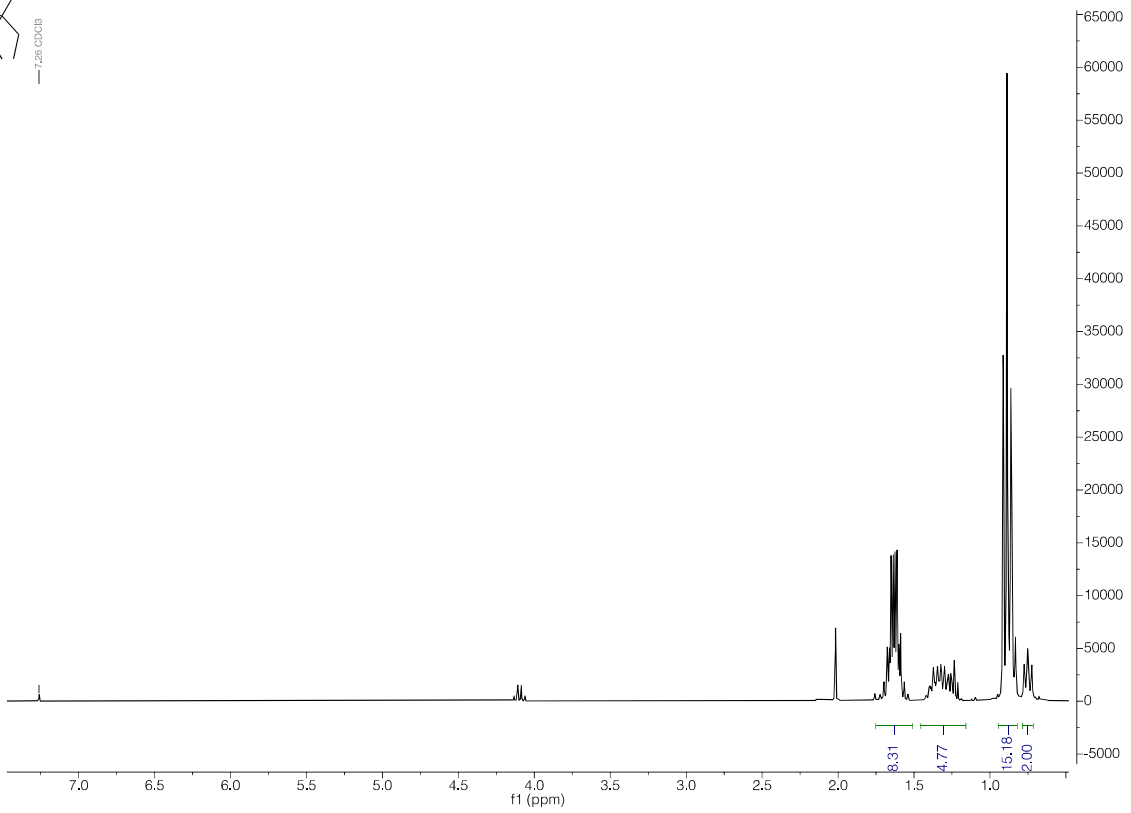
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2976.59	77.3774	2	2966.95	81.4736	3	2957.3	78.6927
4	2944.77	84.5314	5	2928.38	77.8564	6	2870.52	86.8674
7	1465.53	80.9442	8	1432.85	87.9487	9	1406.82	71.3945
10	1397.17	80.5965	11	1371.14	36.09	12	1350.89	66.7487
13	1330.54	40.8661	14	1296.89	78.8972	15	1290.14	77.8102
16	1281.47	82.0704	17	1262.18	68.1068	18	1246.75	78.6952
19	1237.11	75.3088	20	1222.65	81.1974	21	1213.97	75.2145
22	1181.19	87.2891	23	1165.76	71.6042	24	1158.04	75.816
25	1141.55	32.1458	26	1127.19	67.9882	27	1119.48	61.3422
28	1078.98	86.3331	29	1071.26	85.2647	30	1023.05	88.1301
31	1012.45	90.3188	32	1004.73	87.8063	33	991.232	90.3473
34	966.152	62.8229	35	895.773	86.5143	36	889.023	88.8373
37	870.703	76.3302	38	858.168	86.2028	39	844.669	53.6825
40	831.159	86.1171	41	826.348	84.6884	42	730.889	87.0667
43	672.071	72.1611	44	600.717	83.5604	45	588.182	88.3759
46	577.576	80.4152	47	563.112	87.1928	48	543.828	84.5099
49	535.15	87.9032	50	520.686	84.2991	51	511.044	89.7454

2-butyl-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

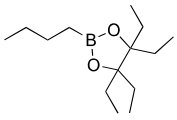
^{1}H-NMR (300 MHz, $CDCl_3$)



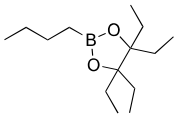


2-butyl-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

^{13}C-NMR (75 MHz, $CDCl_3$)

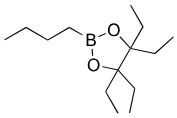


2-butyl-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

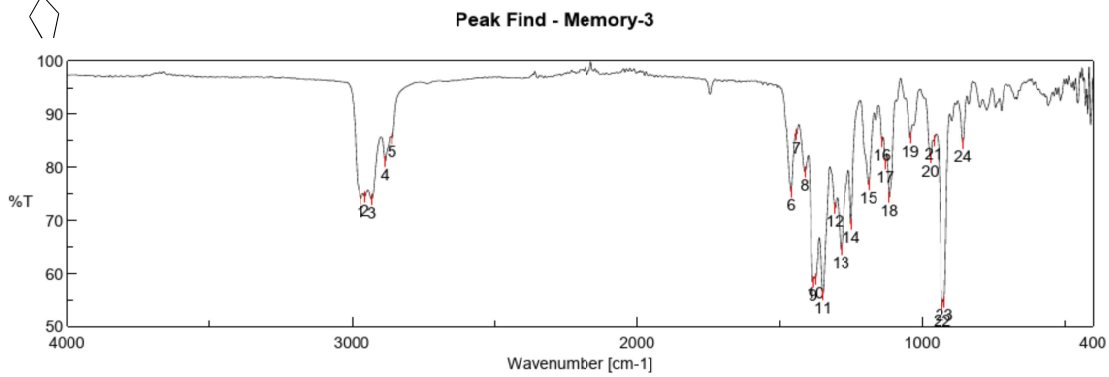


^{11}B-NMR (96 MHz, $CDCl_3$)

2-butyl-4,4,5,5-tetraethyl-1,3,2-dioxaborolane



FT-IR, ATR-diamond

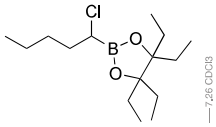


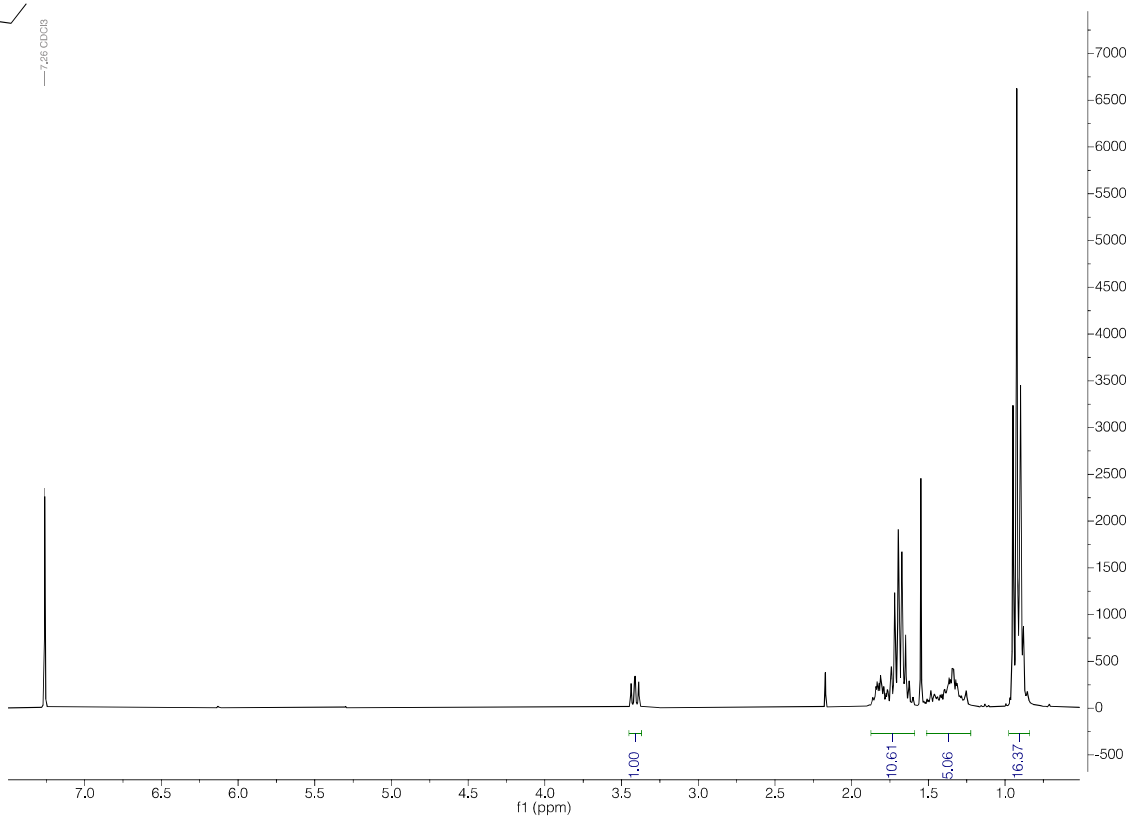
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2968.87	74.006	2	2953.45	74.4131	3	2930.31	73.9438
4	2883.06	81.0983	5	2859.92	85.3518	6	1457.92	75.3611
7	1439.6	86.1406	8	1409.71	79.0824	9	1381.75	58.3736
10	1373.07	58.9345	11	1347.03	56.041	12	1305.57	72.3126
13	1284.36	64.472	14	1247.72	69.2832	15	1186.97	76.7219
16	1139.72	84.7903	17	1128.15	80.6349	18	1114.65	74.3564
19	1041.37	85.5131	20	971.947	81.8402	21	960.377	84.9767
22	929.521	53.6192	23	922.771	54.636	24	857.204	84.486

2-(1-chloropentyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

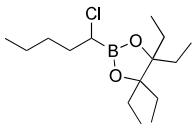
^{1}H-NMR (300 MHz, $CDCl_3$)





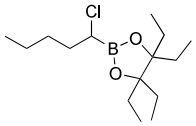
2-(1-chloropentyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

^{13}C-NMR (75 MHz, $CDCl_3$)



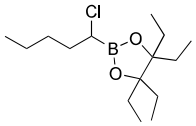
2-(1-chloropentyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

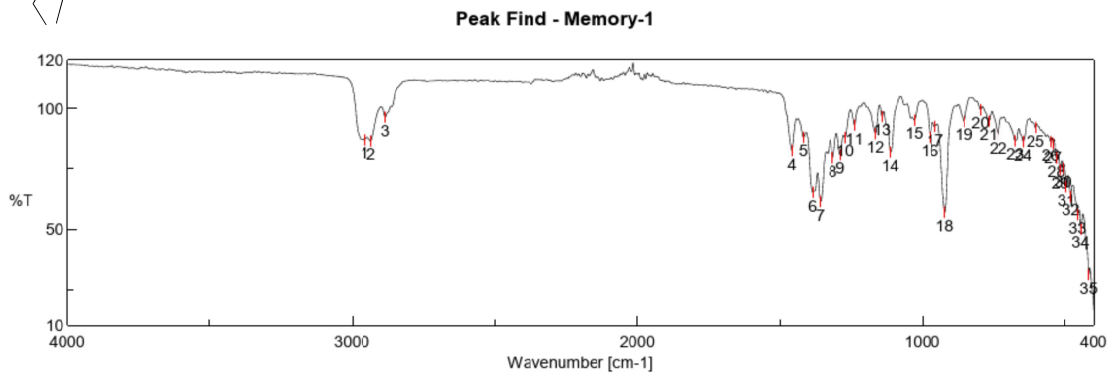
^{11}B-NMR (96 MHz, $CDCl_3$)



2-(1-chloropentyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

FT-IR, ATR-diamond



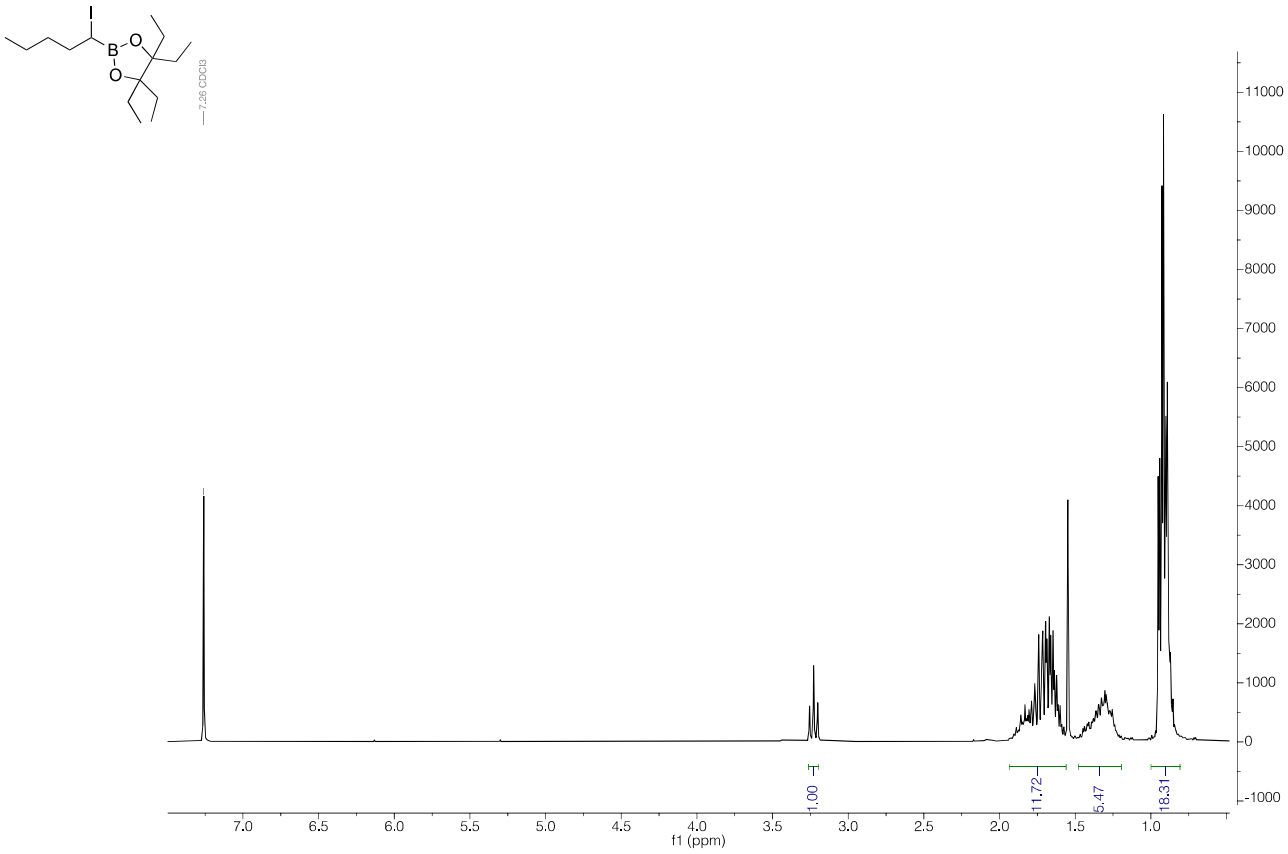


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2955.38	86.8432	2	2934.16	86.387	3	2884.02	96.2357
4	1457.92	82.3581	5	1416.46	87.8604	6	1385.6	65.2384
7	1358.6	61.3911	8	1314.25	79.4181	9	1288.22	80.8015
10	1270.86	87.7773	11	1239.04	93.036	12	1164.79	89.4242
13	1140.69	96.5672	14	1111.76	81.7984	15	1028.84	94.9835
16	972.912	87.8477	17	955.555	92.4102	18	920.843	56.8849
19	854.311	94.5496	20	796.457	99.3417	21	768.494	94.6425
22	733.782	89.1151	23	673.999	86.4864	24	647.001	86.1343
25	603.61	91.9213	26	549.613	86.1067	27	540.935	85.3681
28	529.364	79.4097	29	515.865	74.5791	30	505.258	75.0741
31	493.688	67.4608	32	479.224	63.5044	33	455.118	55.9696
34	444.512	49.828	35	417.513	31.0956			

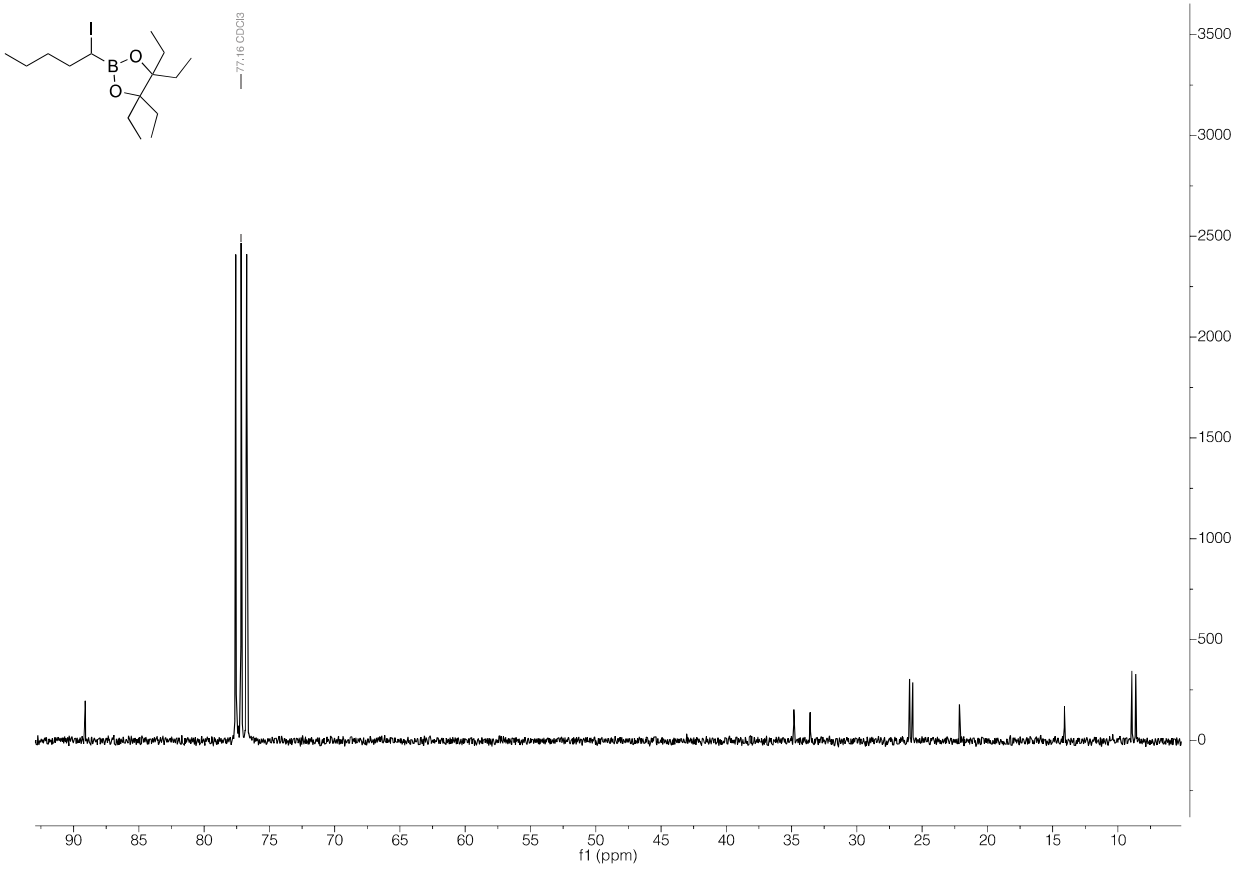
2-(1-iodopentyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

^{1}H-NMR (300 MHz, $CDCl_3$)



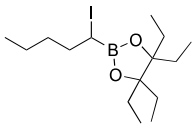
2-(1-iodopentyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

^{13}C-NMR (75 MHz, $CDCl_3$)



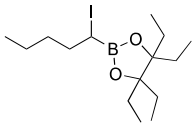
2-(1-iodopentyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

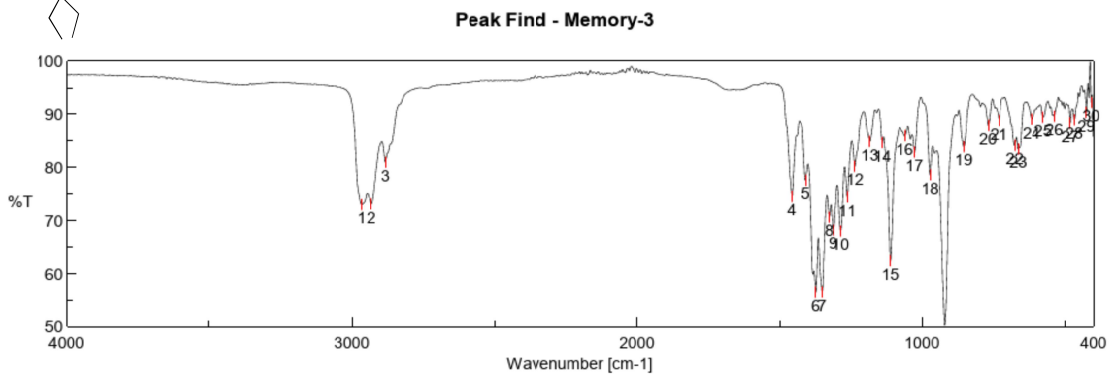
^{11}B-NMR (96 MHz, $CDCl_3$)



2-(1-iodopentyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

FT-IR, ATR-diamond



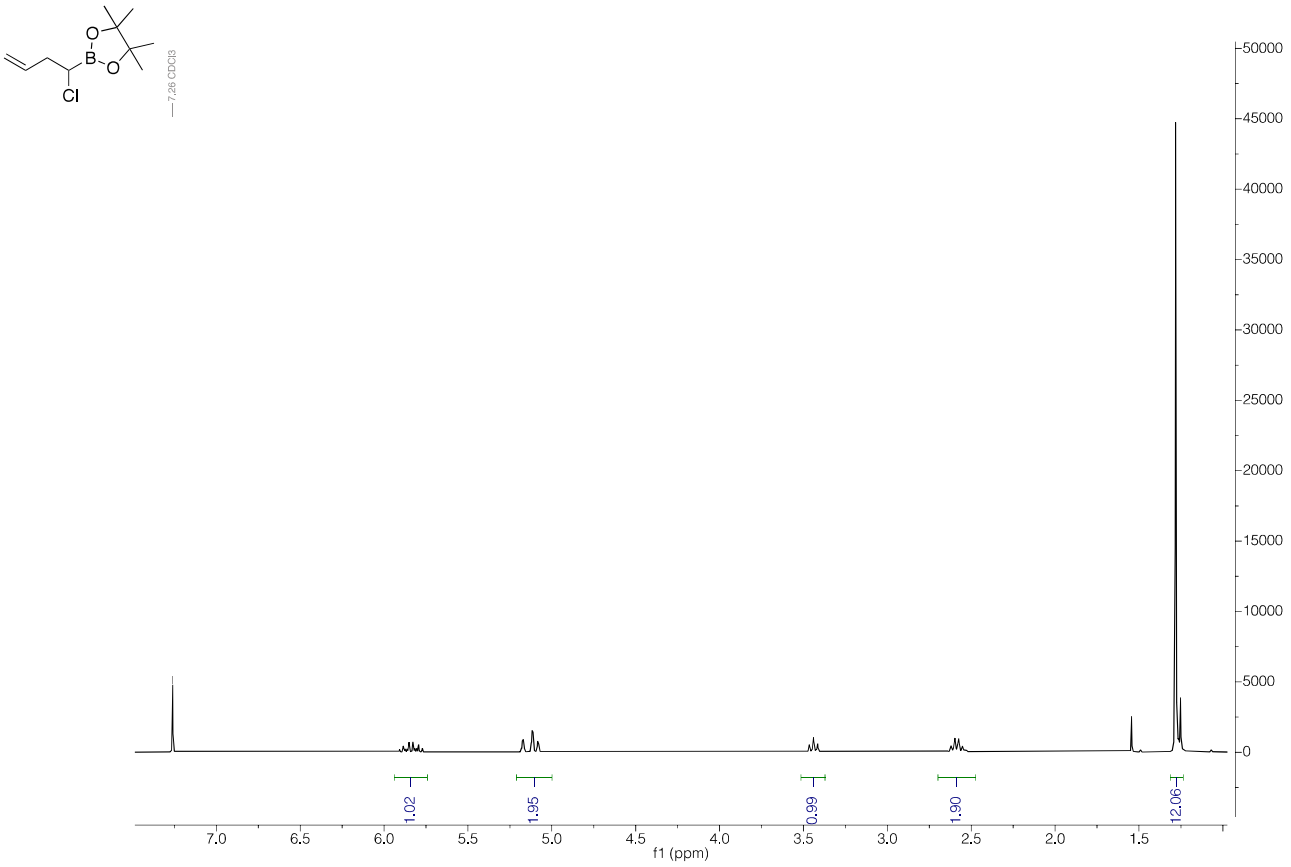


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2965.02	73.0254	2	2931.27	73.1257	3	2882.09	80.9409
4	1456.96	74.5023	5	1410.67	77.5323	6	1374.03	56.5073
7	1351.86	56.5335	8	1326.79	70.6293	9	1312.32	68.1501
10	1287.25	67.9944	11	1263.15	74.4268	12	1236.15	80.1825
13	1184.08	84.8584	14	1139.72	84.6475	15	1111.76	62.412
16	1061.62	85.9308	17	1026.91	82.858	18	971.947	78.5854
19	853.347	83.8698	20	769.458	87.8633	21	730.889	88.7888
22	675.928	84.1173	23	663.393	83.4244	24	616.145	89.0258
25	575.647	89.3875	26	537.078	89.5914	27	482.117	88.3108
28	467.653	88.9074	29	425.227	90.3089	30	407.871	92.2078

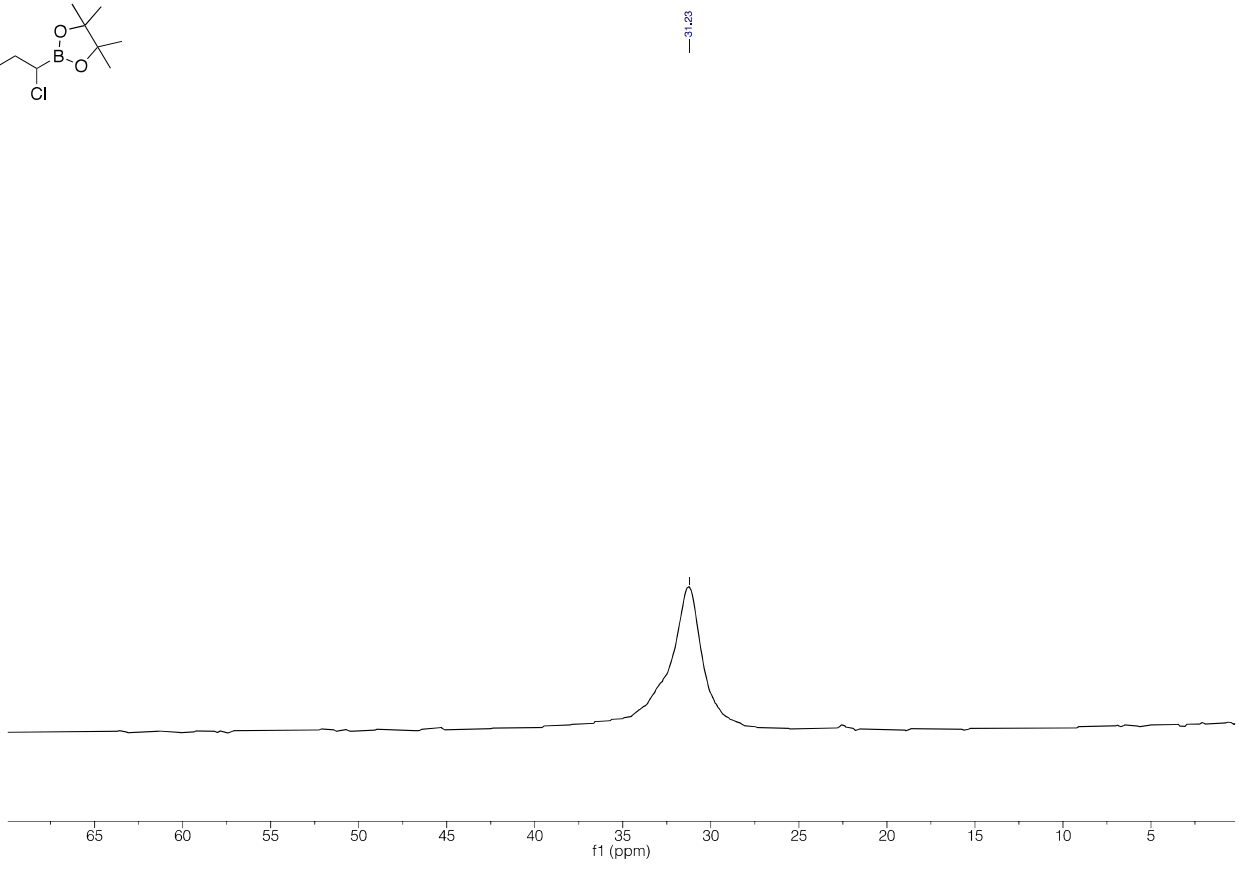
2-(1-chlorobut-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H-NMR (300 MHz, $CDCl_3$)



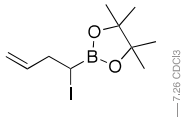
2-(1-chlorobut-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

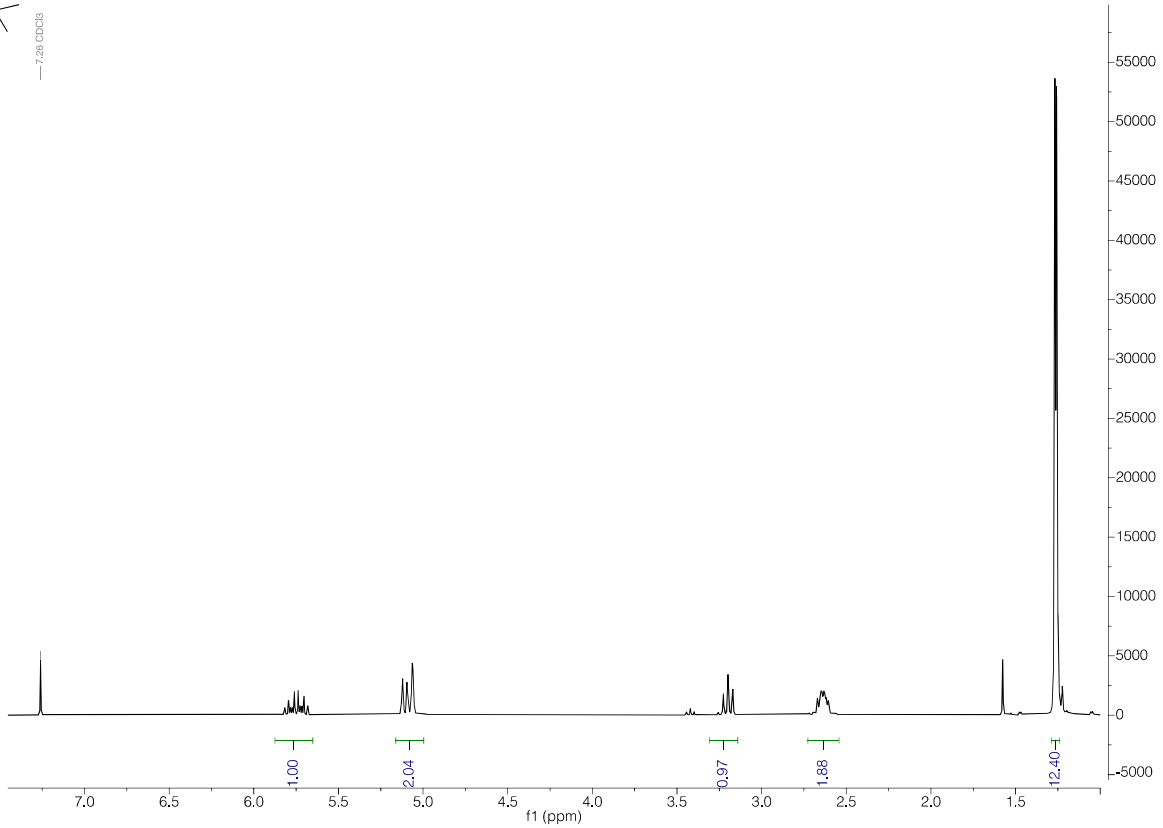
^{11}B-NMR (96 MHz, $CDCl_3$)



2-(1-iodobut-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

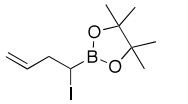
^{1}H-NMR (300 MHz, $CDCl_3$)

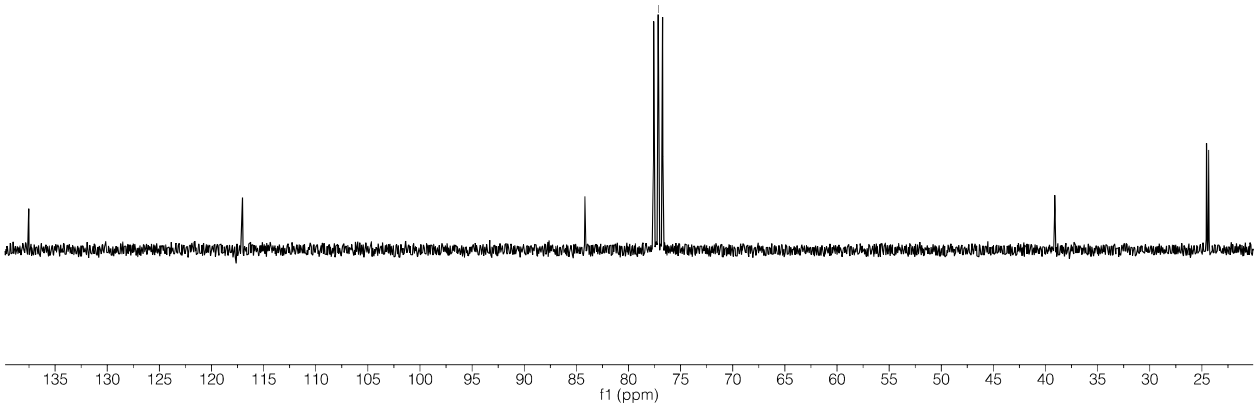




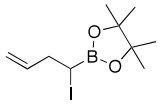
2-(1-iodobut-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{13}C-NMR (75 MHz, $CDCl_3$)



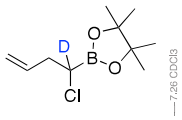


2-(1-iodobut-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

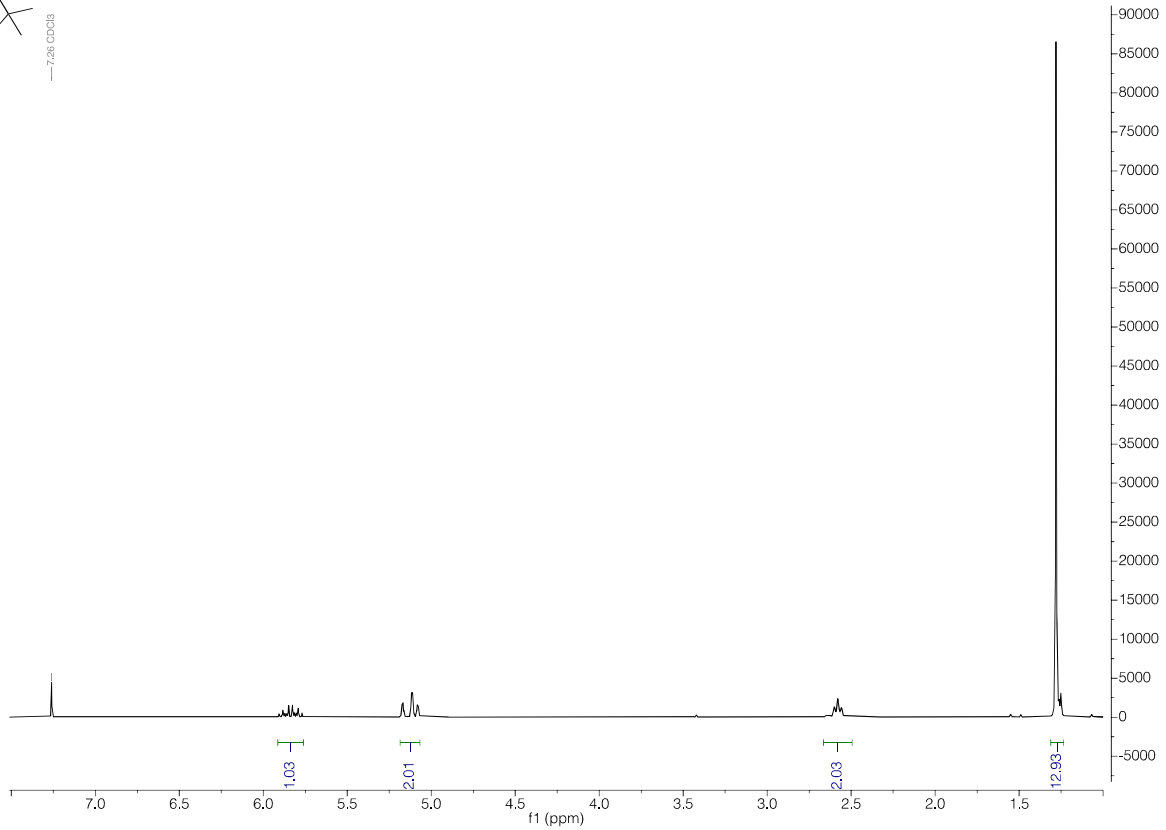


^{11}B-NMR (96 MHz, $CDCl_3$)

2-(1-chloro-1-deuterio-but-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

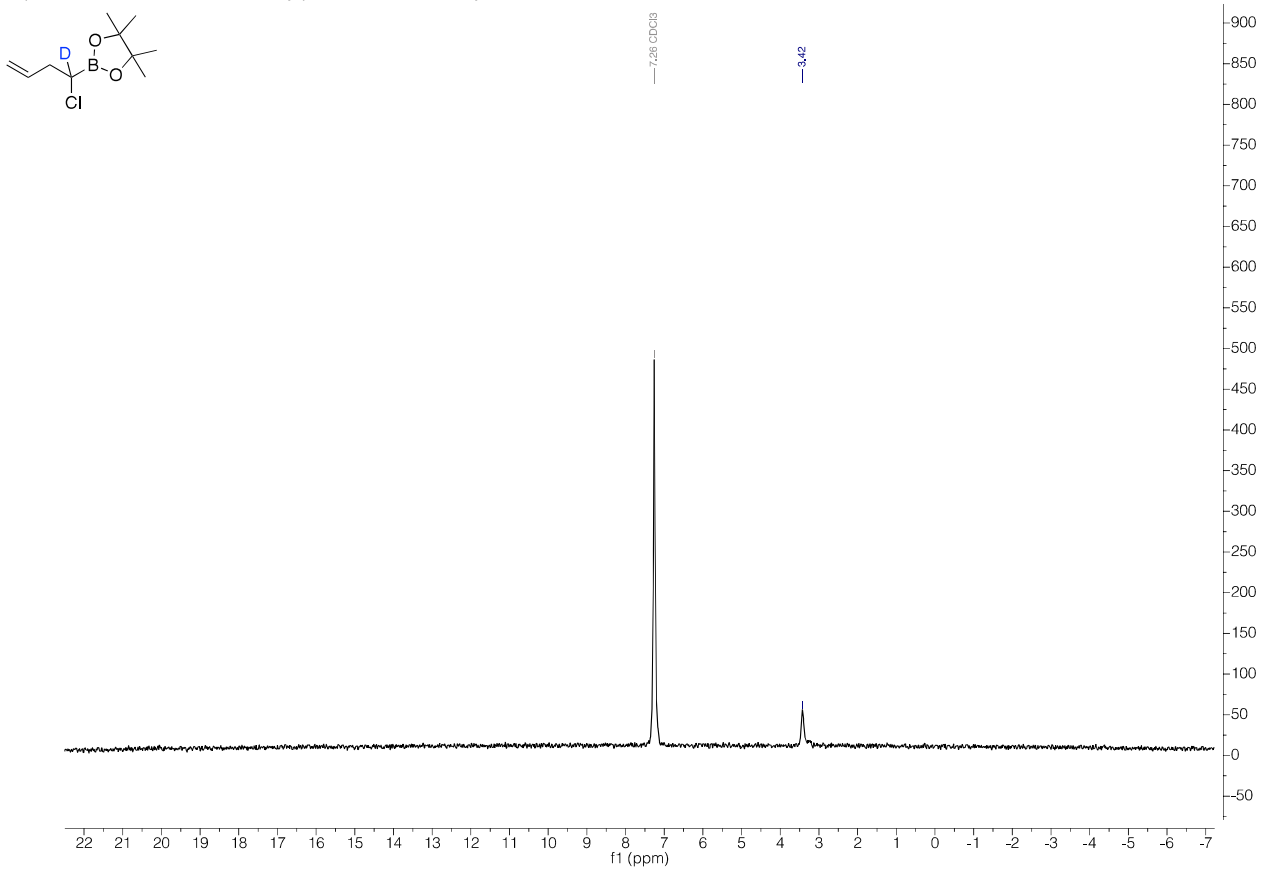


^{1}H-NMR (300 MHz, $CDCl_3$)



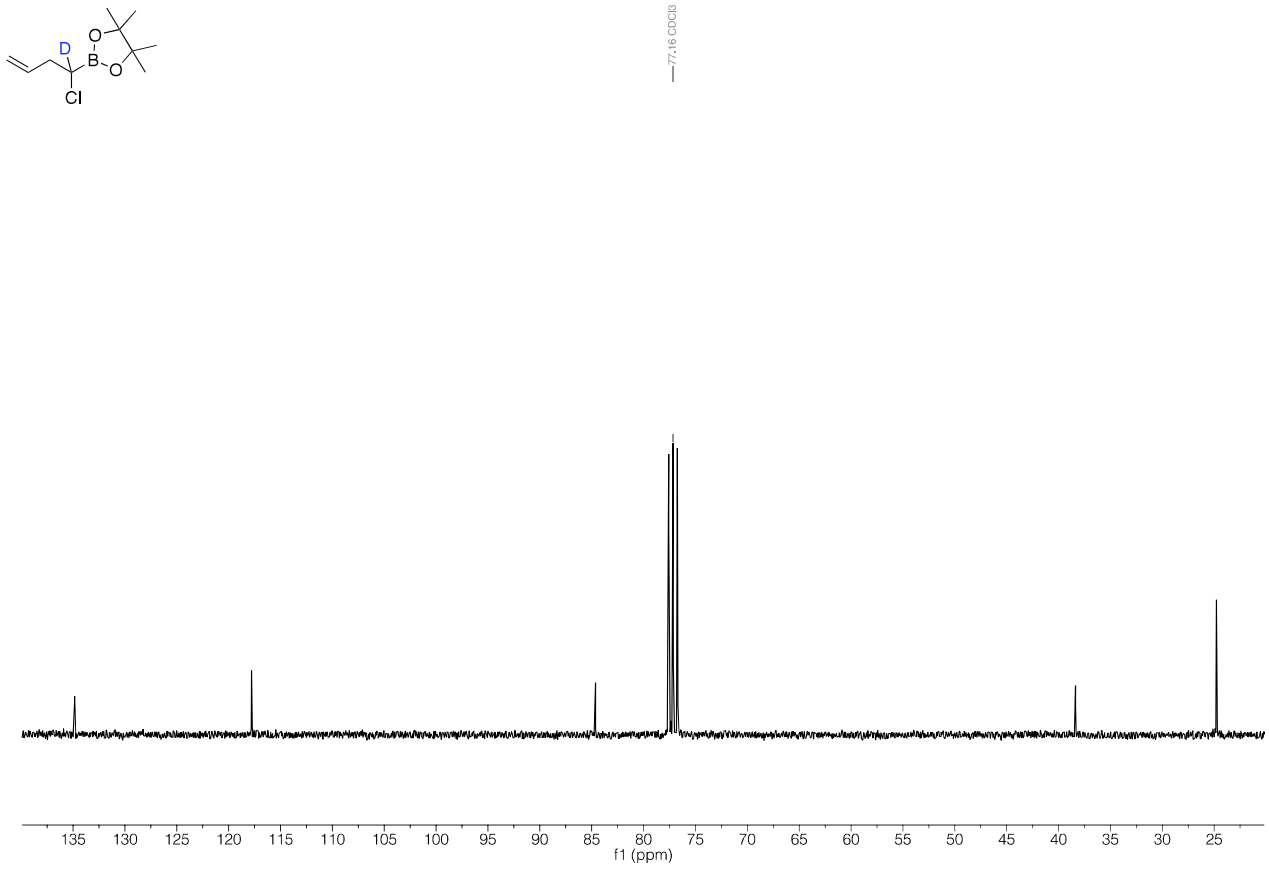
2-(1-chloro-1-deuterio-but-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{2}H-NMR (61 MHz, $CHCl_3$)

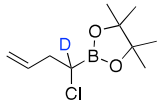


2-(1-chloro-1-deuterio-but-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

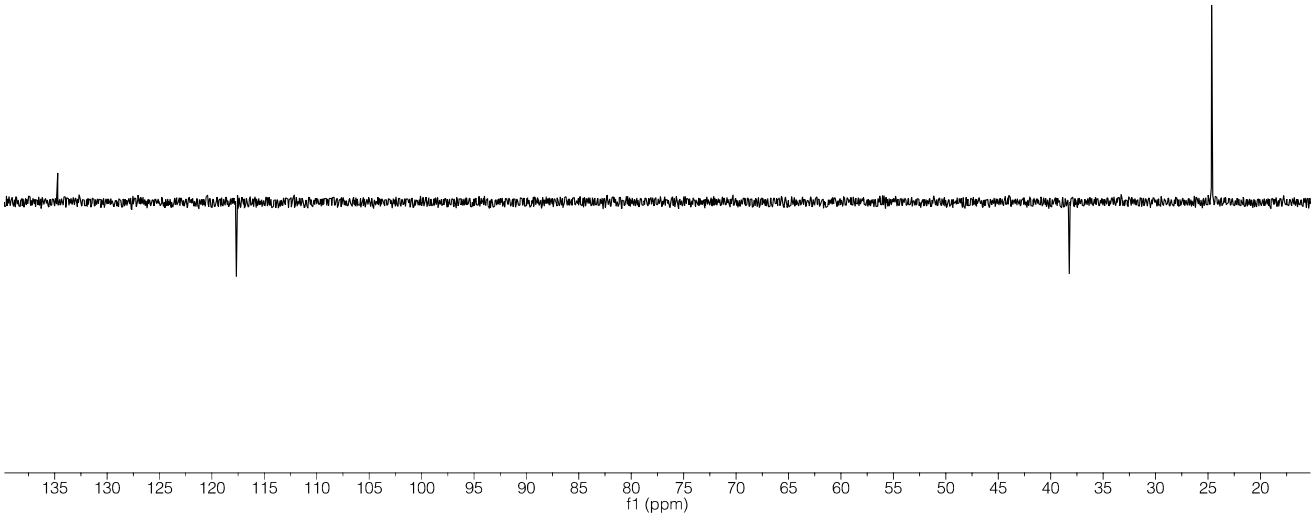
^{13}C-NMR (75 MHz, $CDCl_3$)



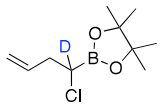
2-(1-chloro-1-deuterio-but-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



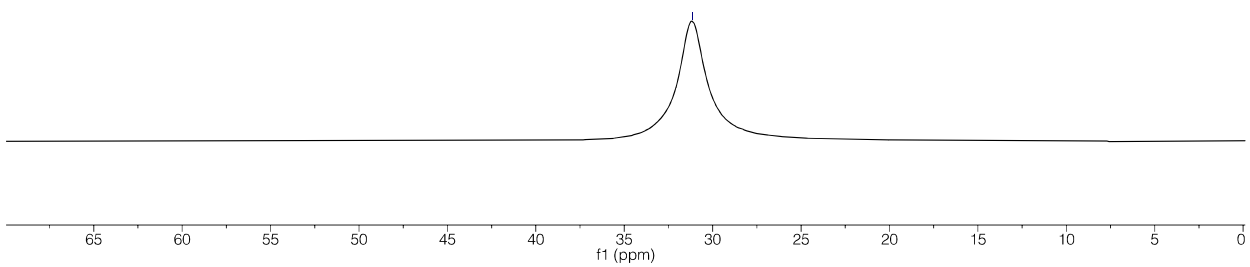
DEPT-135 NMR (300 MHz, $CDCl_3$)



2-(1-chloro-1-deuterio-but-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

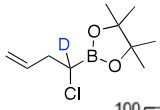


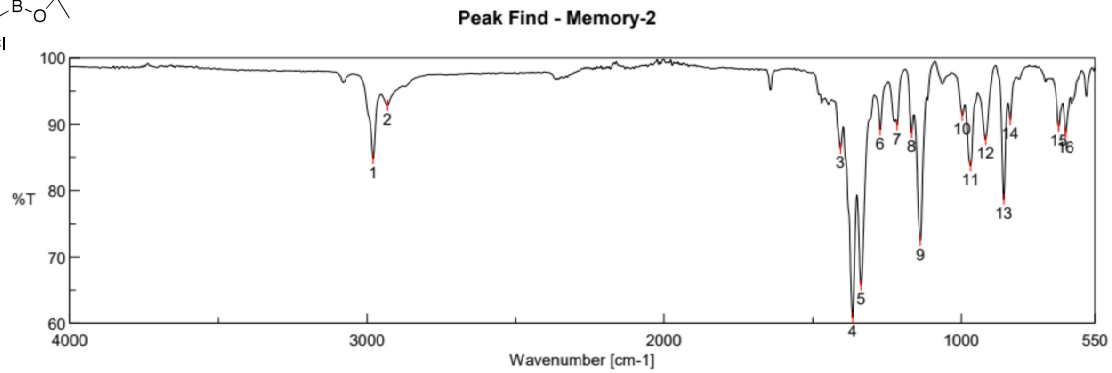
^{11}B-NMR (96 MHz, $CDCl_3$)



2-(1-chloro-1-deuterio-but-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

FT-IR, ATR-diamond



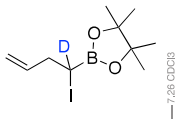


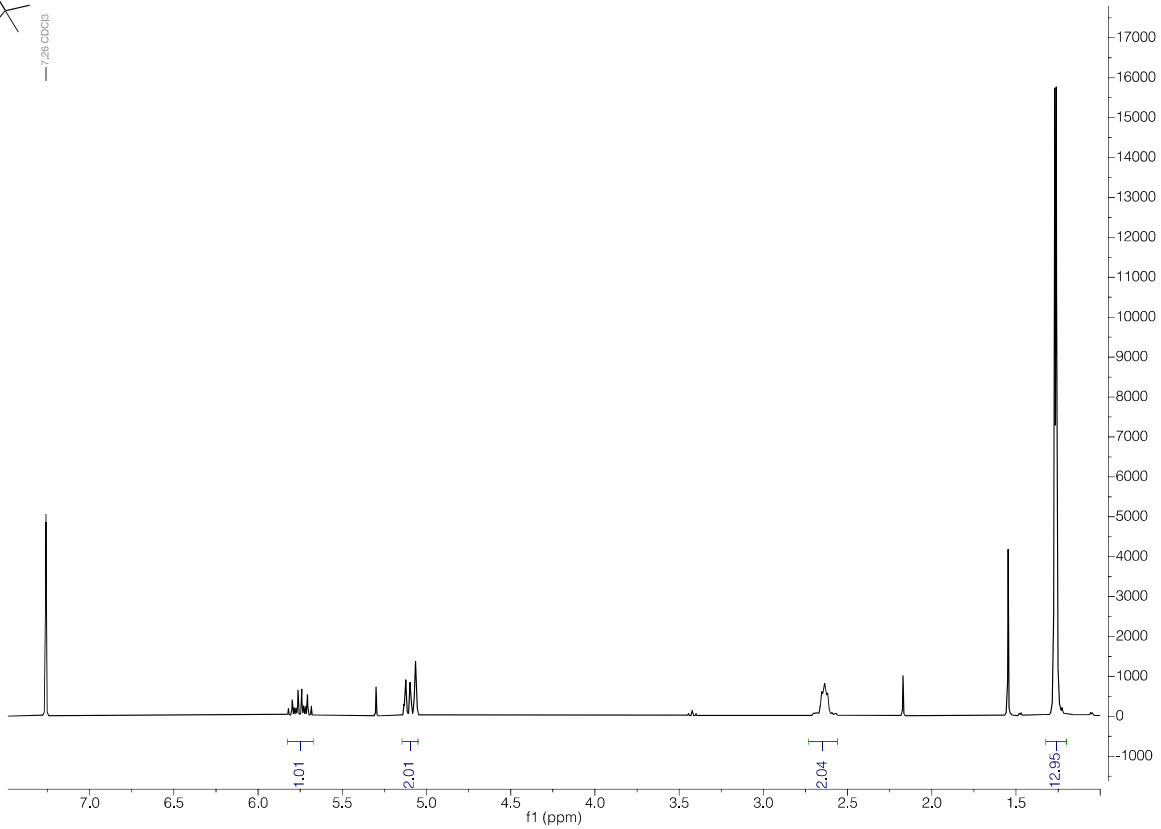
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2979.48	84.8	2	2931.27	92.8431	3	1406.82	86.3056
4	1365.35	60.8438	5	1337.39	65.7165	6	1272.79	89.1695
7	1214.93	89.8732	8	1166.72	88.7256	9	1137.8	72.5048
10	997.017	91.3291	11	969.055	83.7422	12	917.95	87.6736
13	856.239	78.6588	14	834.062	90.6816	15	672.071	89.6731
16	647.965	88.6193						

2-(1-deuterio-1-iodo-but-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

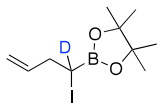
^{1}H-NMR (300 MHz, $CDCl_3$)





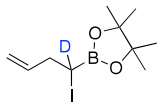
2-(1-deuterio-1-iodo-but-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{2}H-NMR (61 MHz, $CHCl_3$)

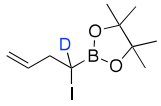


2-(1-deuterio-1-iodo-but-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

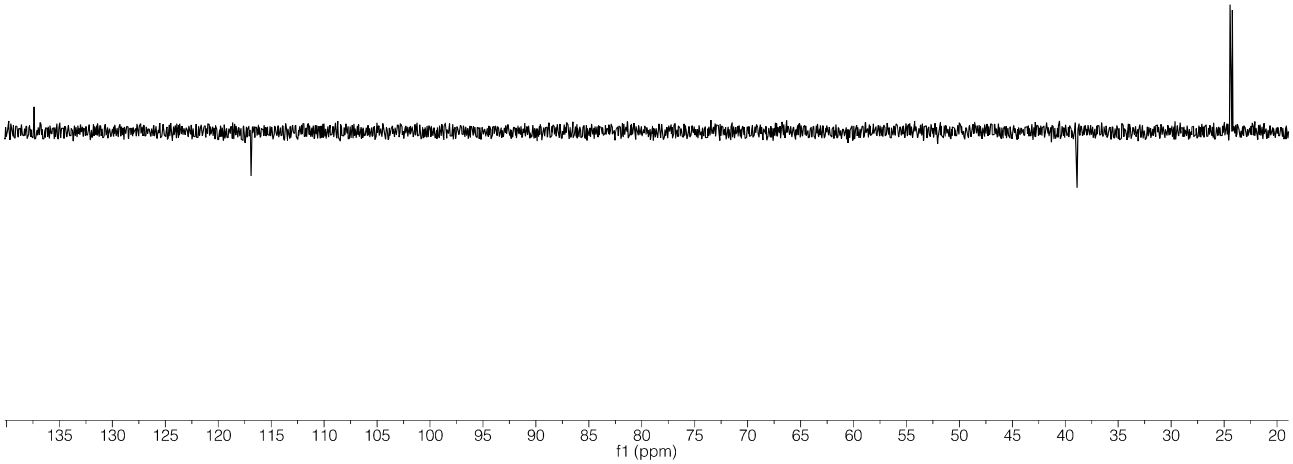
^{13}C-NMR (75 MHz, $CDCl_3$)



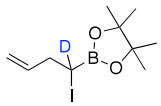
2-(1-deuterio-1-iodo-but-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



DEPT-135 NMR (300 MHz, $CDCl_3$)



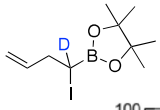
2-(1-deuterio-1-iodo-but-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

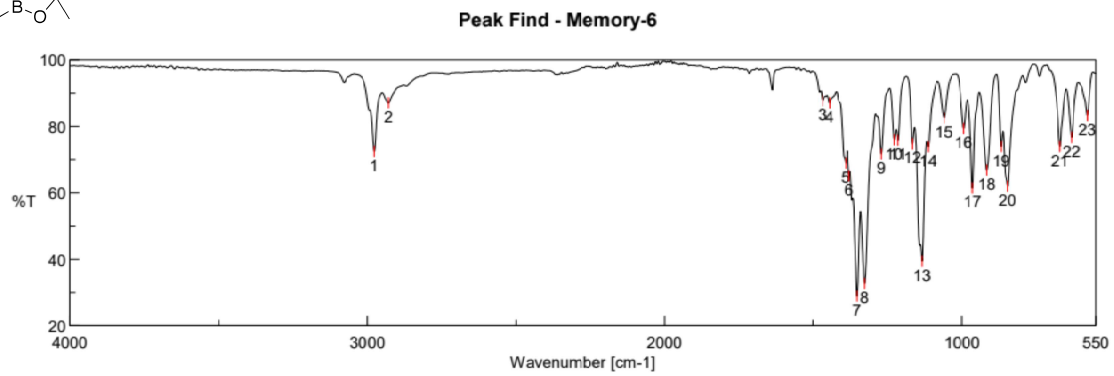


^{11}B-NMR (96 MHz, $CDCl_3$)

2-(1-deuterio-1-iodo-but-3-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

FT-IR, ATR-diamond



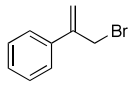


[Result of Peak Picking]

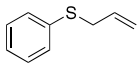
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2977.55	72.4094	2	2929.34	87.0498	3	1468.53	87.7105
4	1445.39	87.0081	5	1390.42	68.8662	6	1379.82	65.015
7	1353.78	28.8762	8	1327.75	32.6607	9	1271.82	71.6676
10	1227.47	75.861	11	1214.93	75.7526	12	1165.76	74.6936
13	1132.97	39.4281	14	1112.73	73.8397	15	1060.66	82.5069
16	994.125	79.2924	17	965.198	61.4318	18	916.986	66.7438
19	867.81	73.9031	20	846.597	61.9219	21	671.106	73.906
22	631.573	76.6713	23	578.54	83.1951			

(3-bromoprop-1-en-2-yl)benzene

^{1}H-NMR (300 MHz, $CDCl_3$)

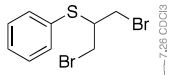


Allyl phenyl thioether



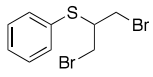
^{1}H-NMR (300 MHz, $CDCl_3$)

[2-bromo-1-(bromomethyl)ethyl]sulfanylbenzene



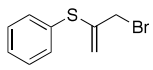
^{1}H-NMR (300 MHz, $CDCl_3$)

[2-bromo-1-(bromomethyl)ethyl]sulfanylbenzene



^{13}C-NMR (75 MHz, $CDCl_3$)

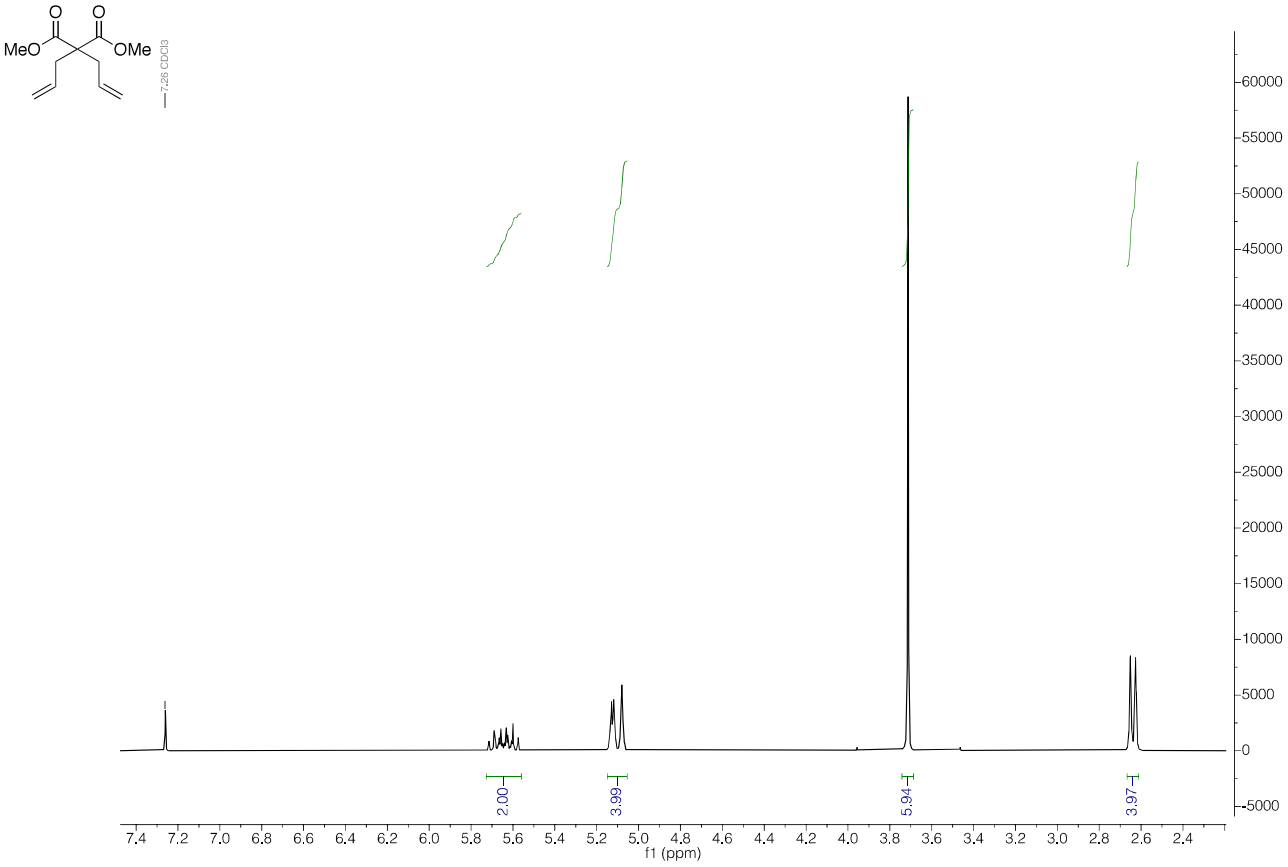
1-(bromomethyl)vinylsulfanylbenzene



^{1}H-NMR (300 MHz, $CDCl_3$)

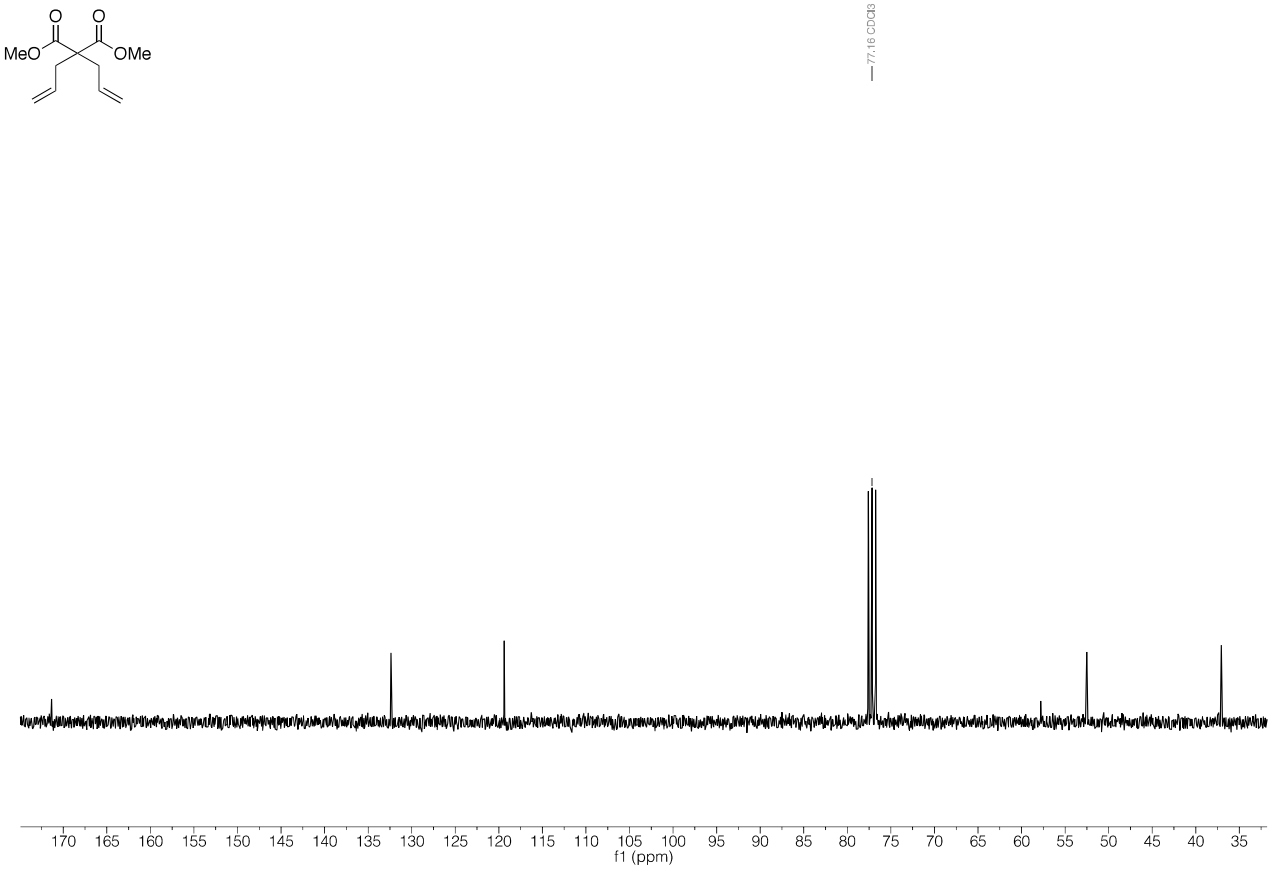
Dimethyl 2,2-diallylpropanedioate

^{1}H-NMR (300 MHz, $CDCl_3$)



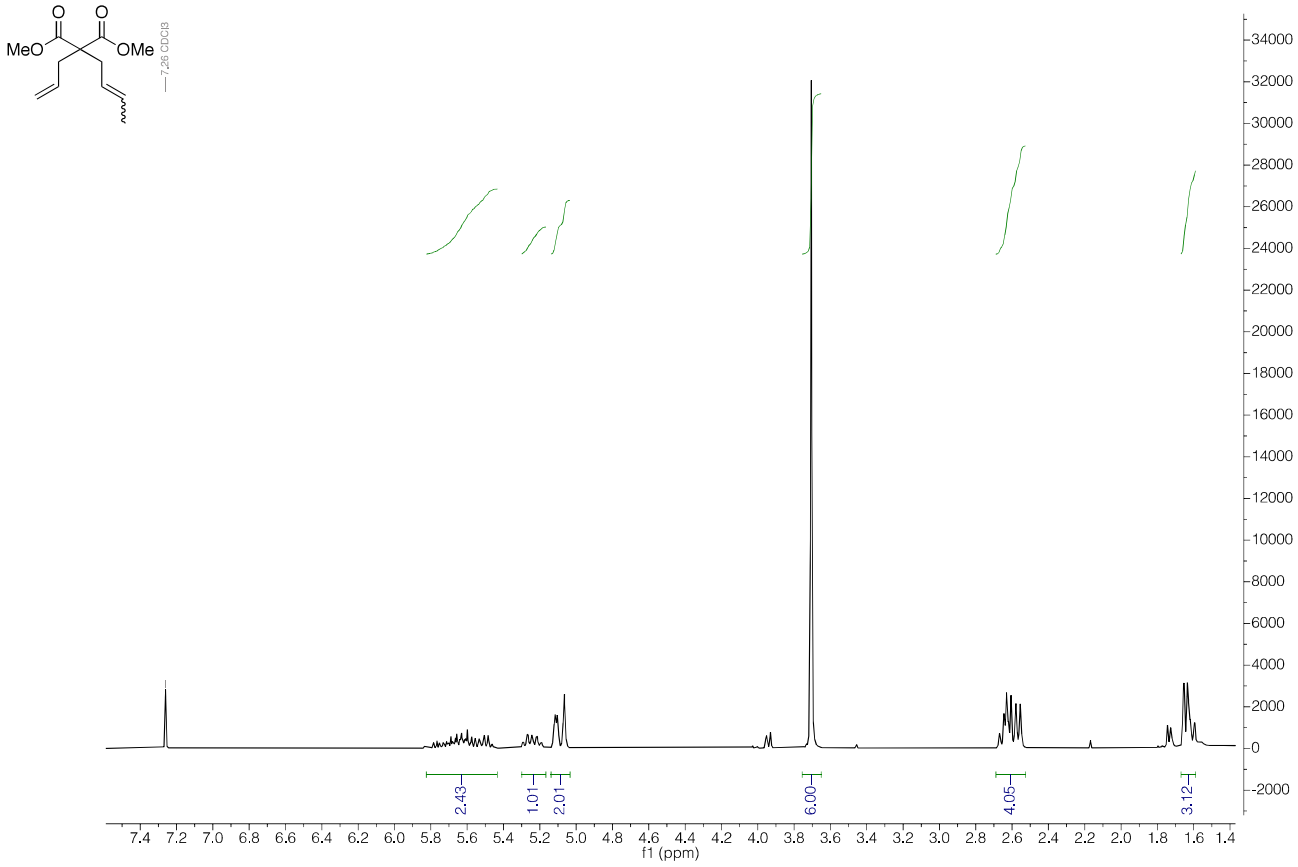
Dimethyl 2,2-diallylpropanedioate

^{13}C-NMR (75 MHz, $CDCl_3$)



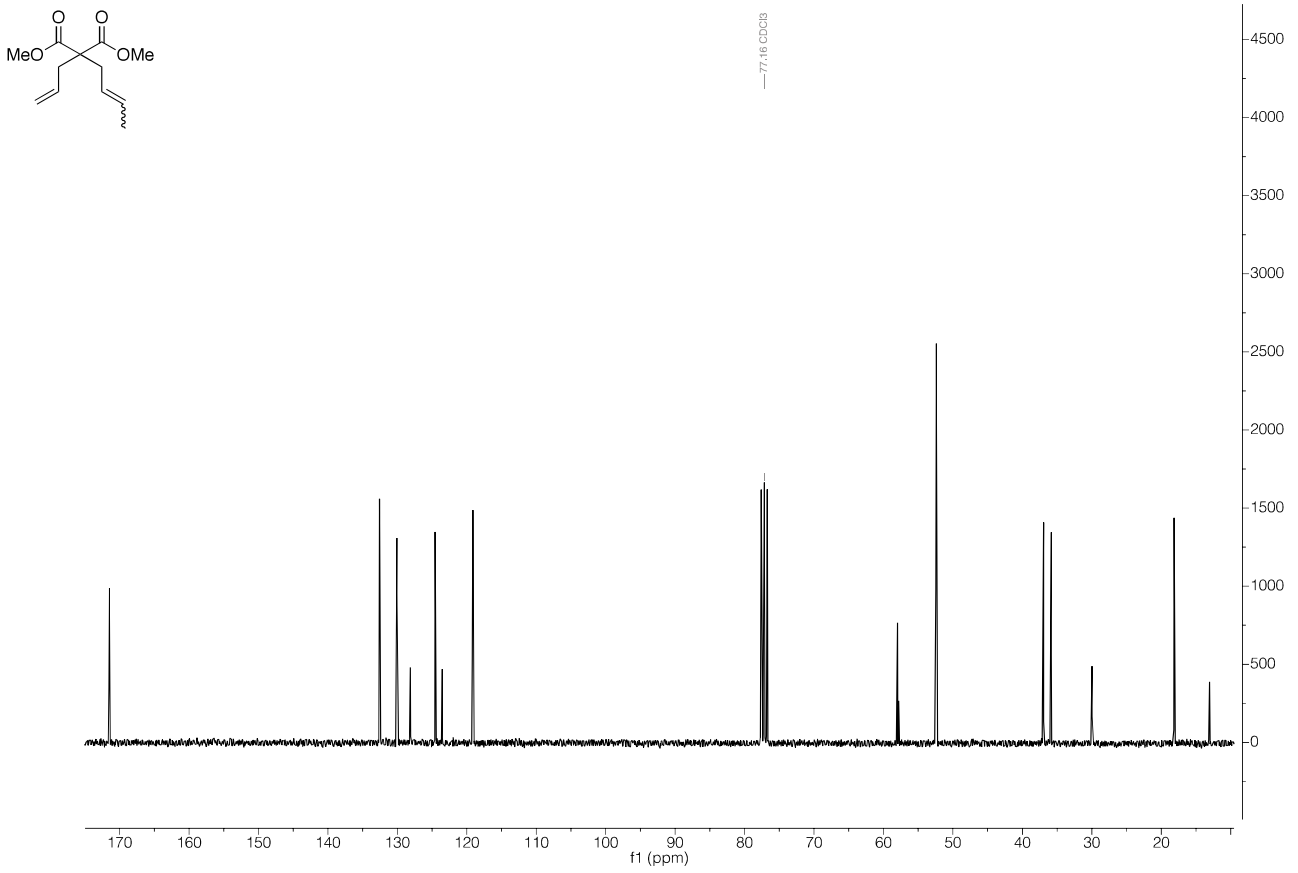
Dimethyl 2-allyl-2-(but-2-en-1-yl)malonate

^{1}H-NMR (300 MHz, $CDCl_3$)



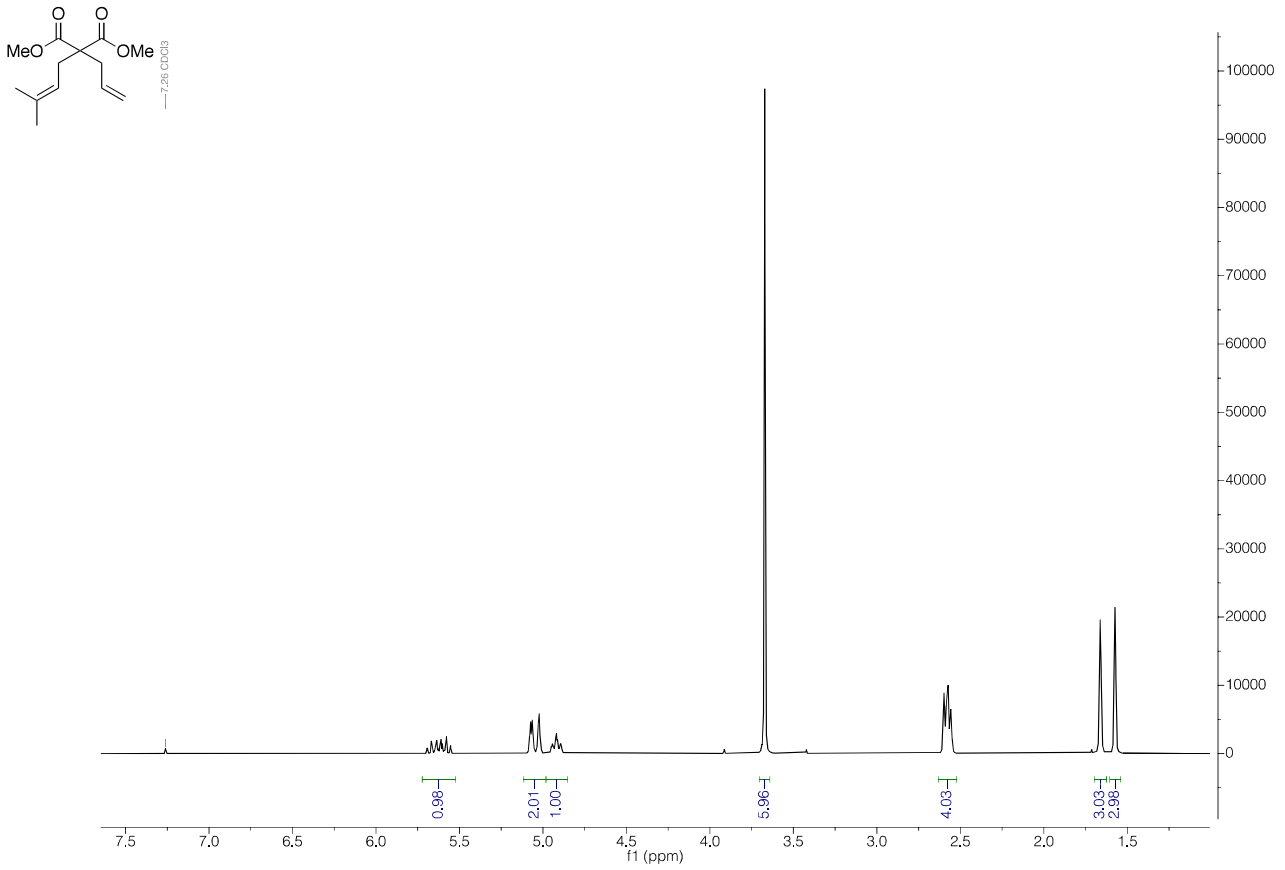
Dimethyl 2-allyl-2-(but-2-en-1-yl)malonate

^{13}C-NMR (75 MHz, $CDCl_3$)



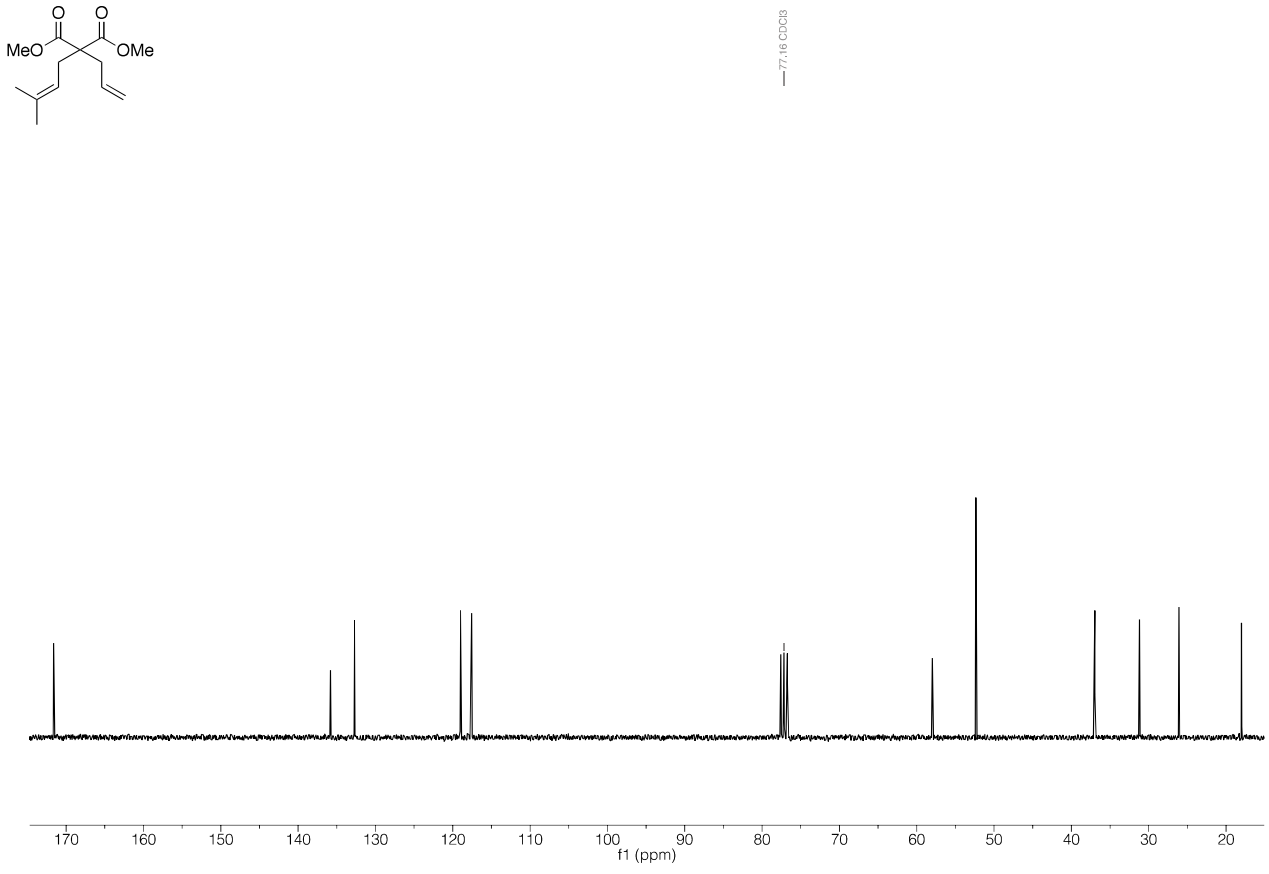
Dimethyl 2-allyl-2-(3-methylbut-2-en-1-yl)malonate

^{1}H-NMR (300 MHz, $CDCl_3$)



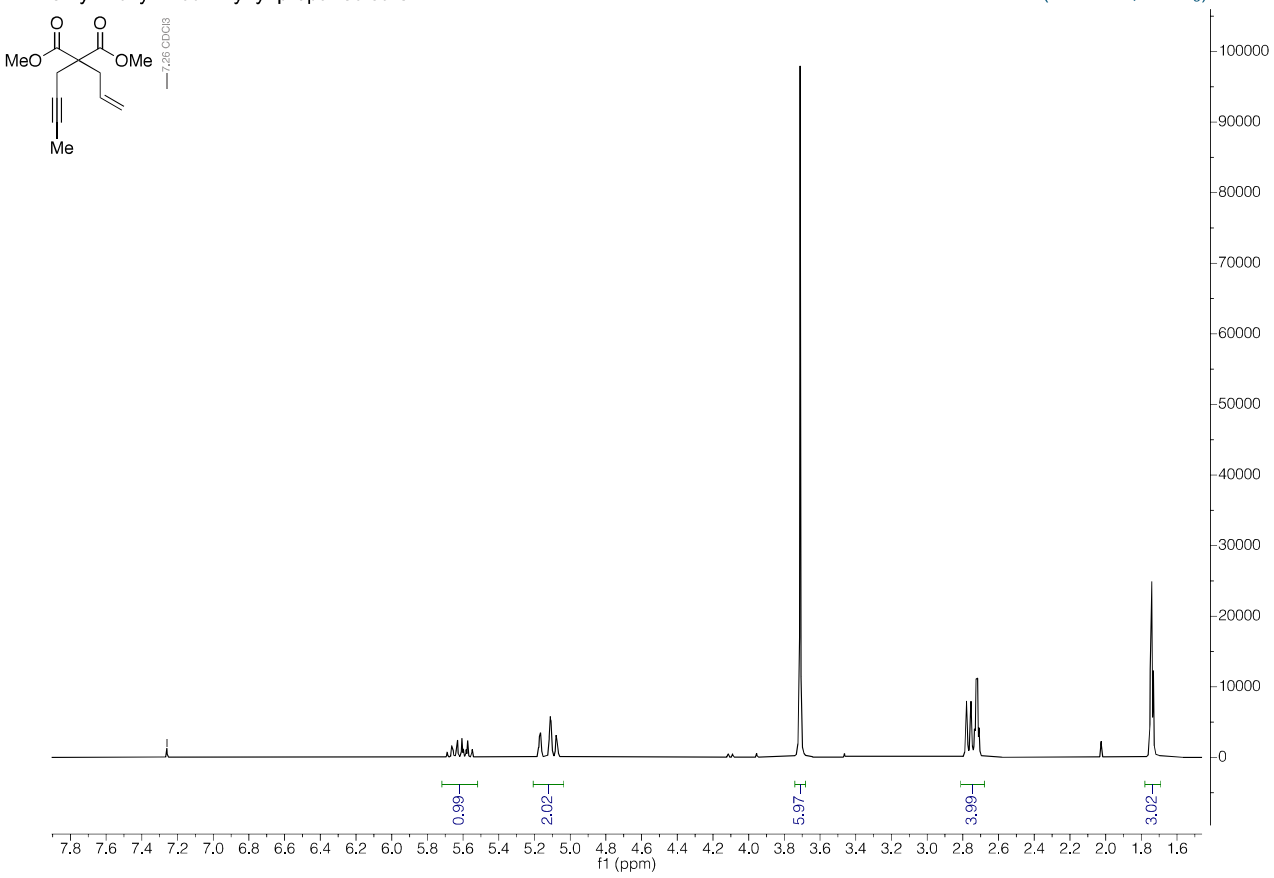
Dimethyl 2-allyl-2-(3-methylbut-2-en-1-yl)malonate

^{13}C-NMR (75 MHz, $CDCl_3$)



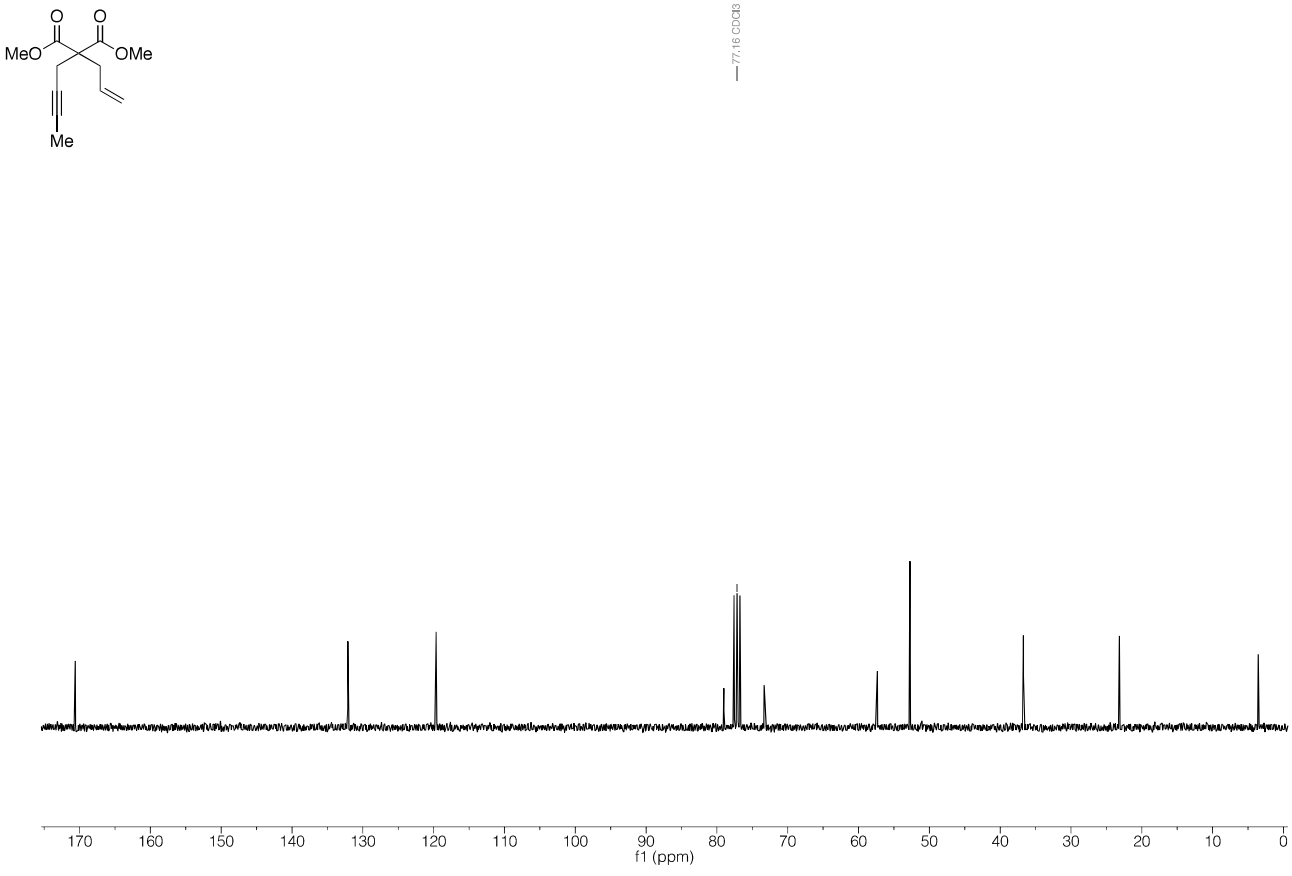
Dimethyl 2-allyl-2-but-2-ynyl-propanedioate

^{1}H-NMR (300 MHz, $CDCl_3$)



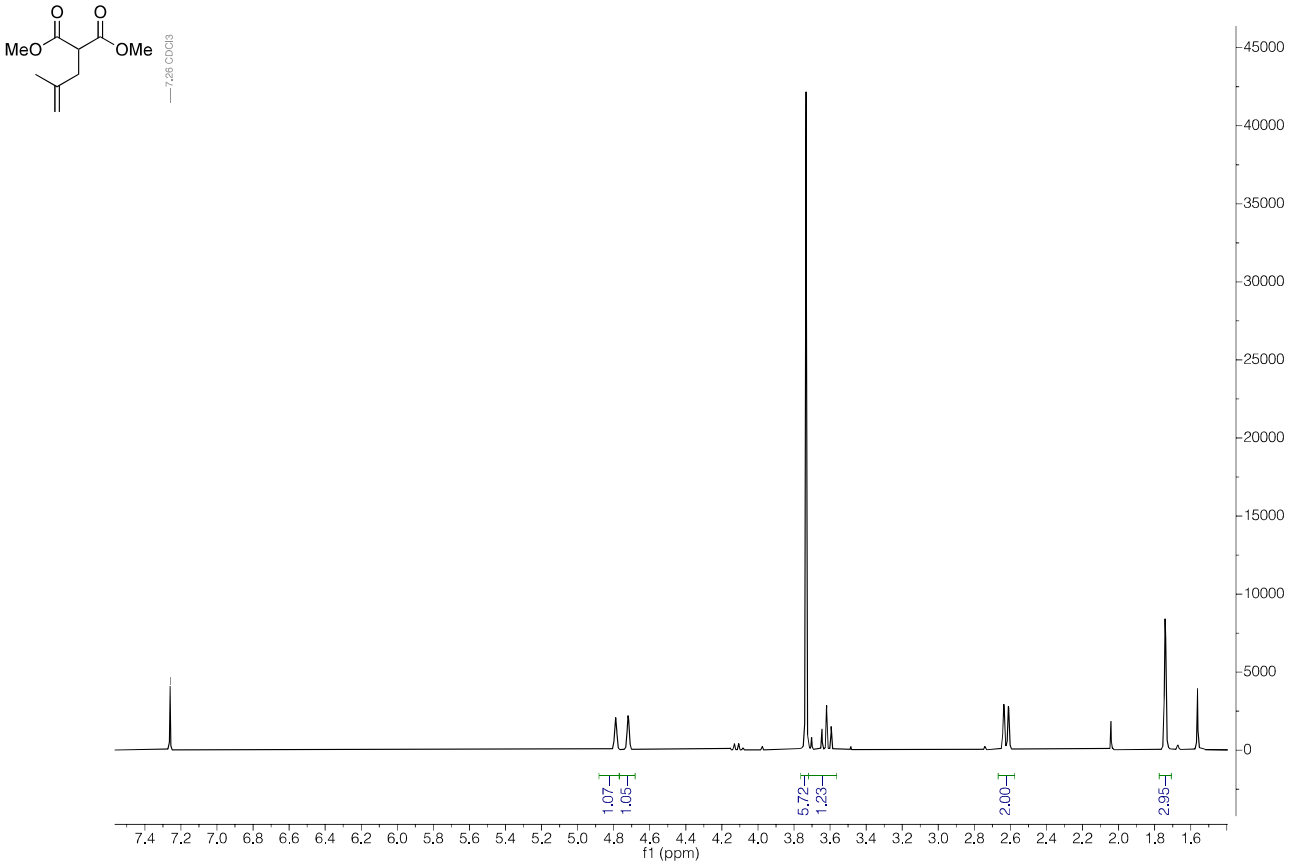
Dimethyl 2-allyl-2-but-2-ynyl-propanedioate

^{13}C-NMR (75 MHz, $CDCl_3$)



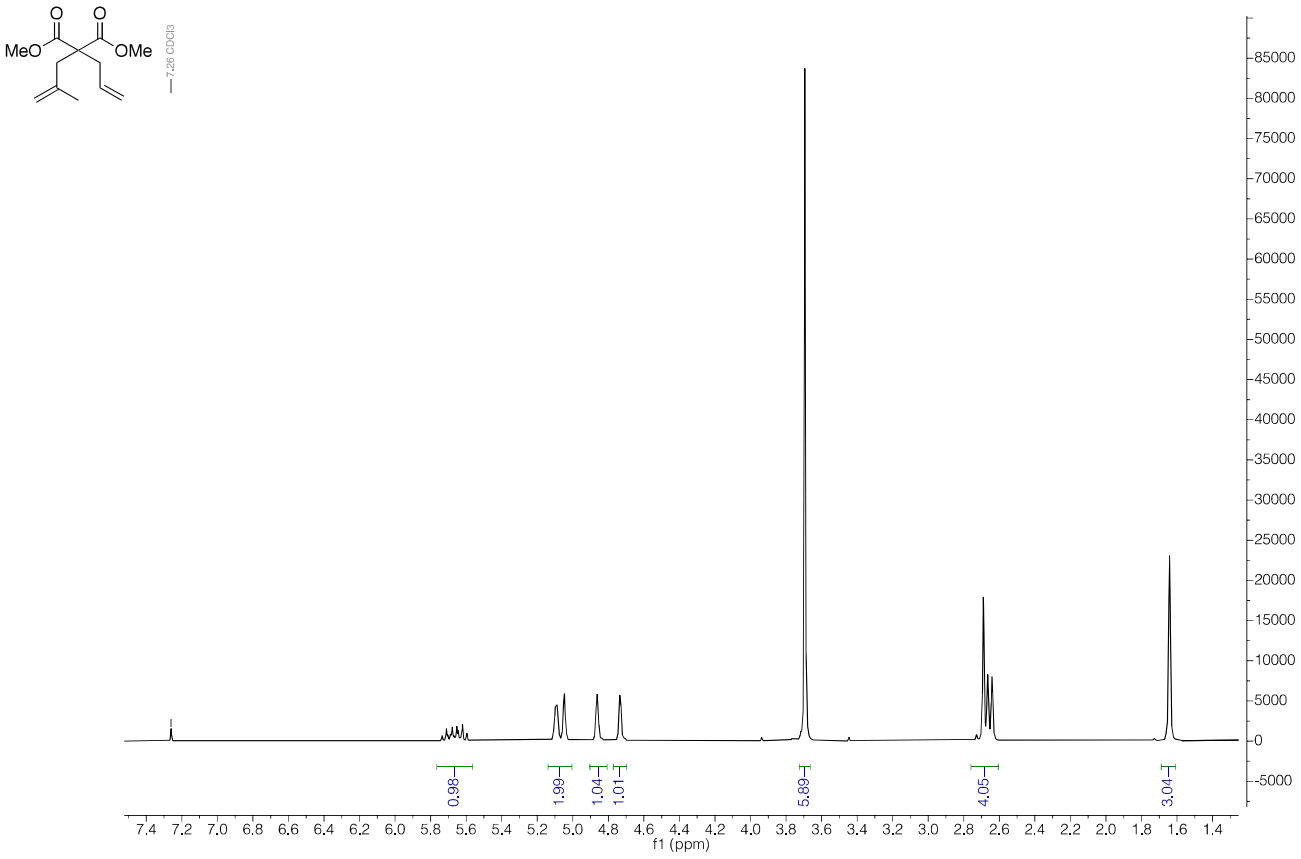
dimethyl 2-(2-methylallyl)malonate

^{1}H-NMR (300 MHz, $CDCl_3$)

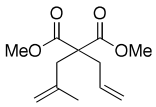


dimethyl 2-allyl-2-(2-methylallyl)malonate

^{1}H-NMR (300 MHz, $CDCl_3$)

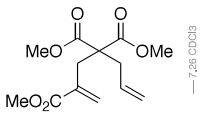


dimethyl 2-allyl-2-(2-methylallyl)malonate

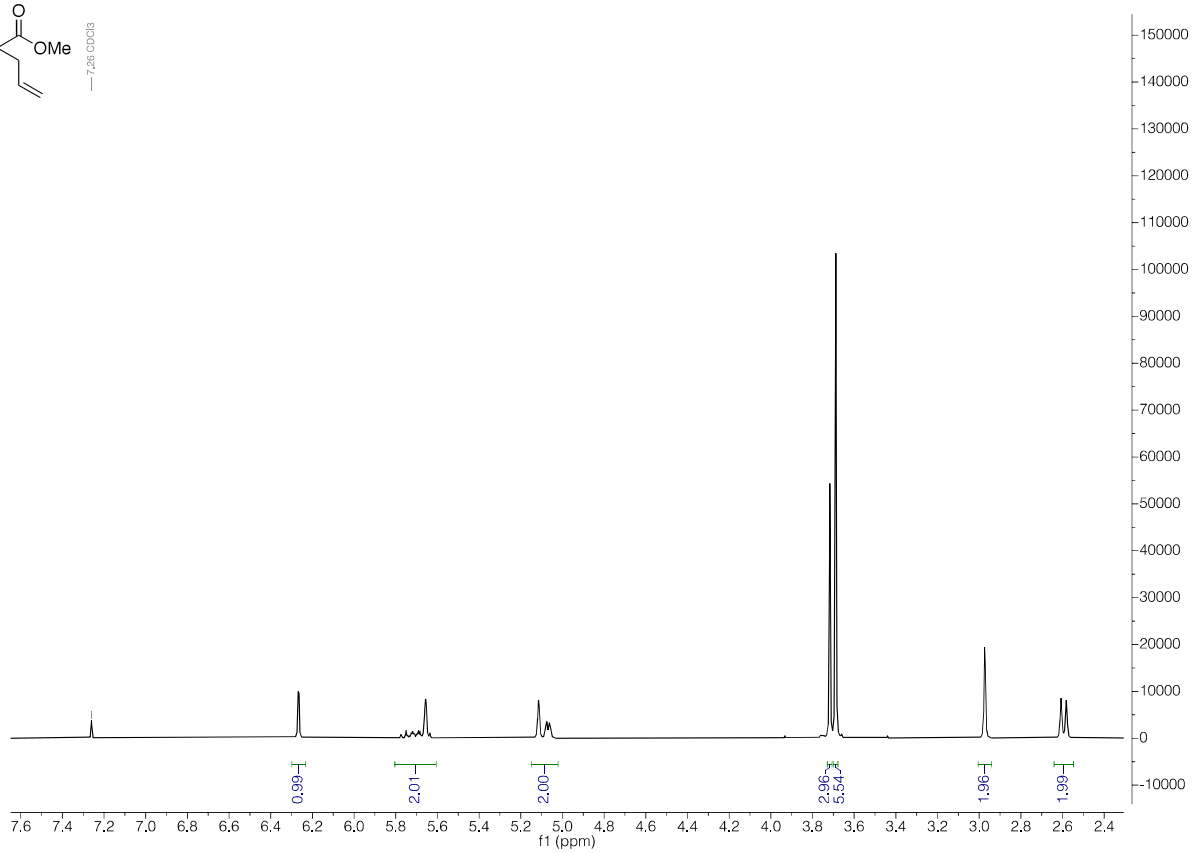


^{13}C-NMR (75 MHz, $CDCl_3$)

Trimethyl hepta-1,6-diene-2,4,4-tricarboxylate

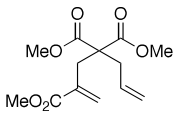


^{1}H-NMR (300 MHz, $CDCl_3$)



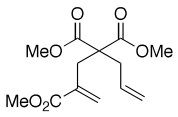
Trimethyl hepta-1,6-diene-2,4,4-tricarboxylate

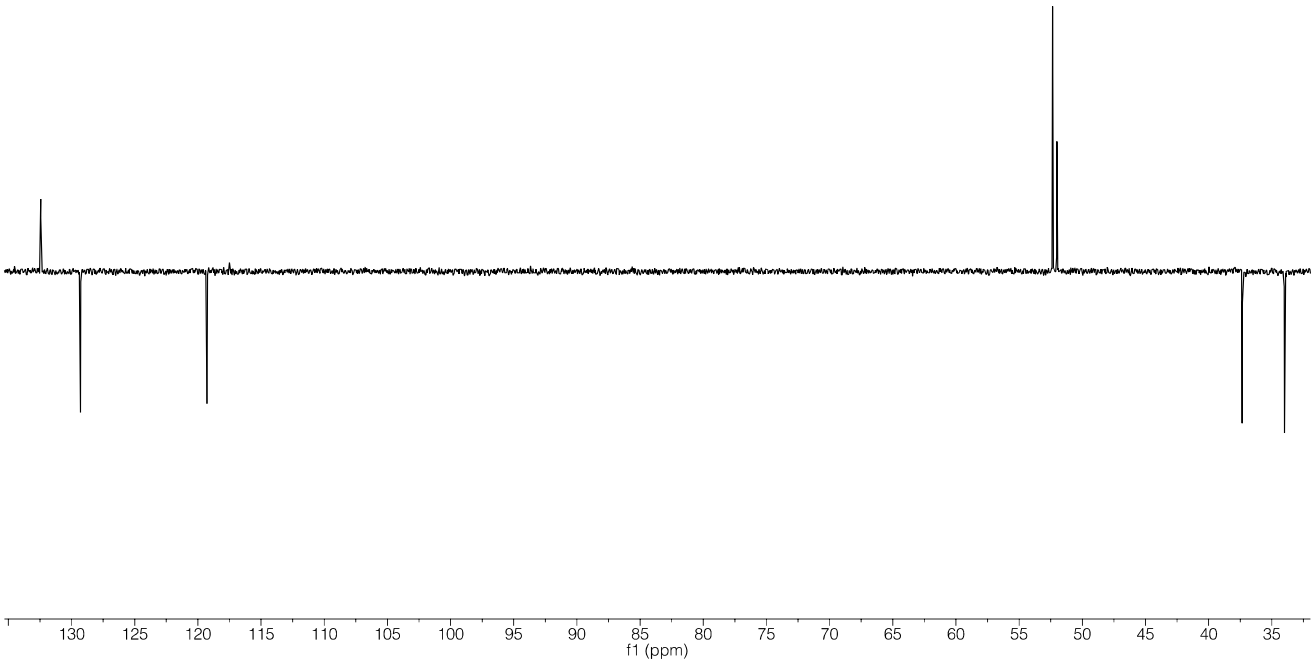
^{13}C-NMR (75 MHz, $CDCl_3$)



Trimethyl hepta-1,6-diene-2,4,4-tricarboxylate

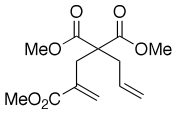
DEPT-135 NMR (75 MHz, $CDCl_3$)

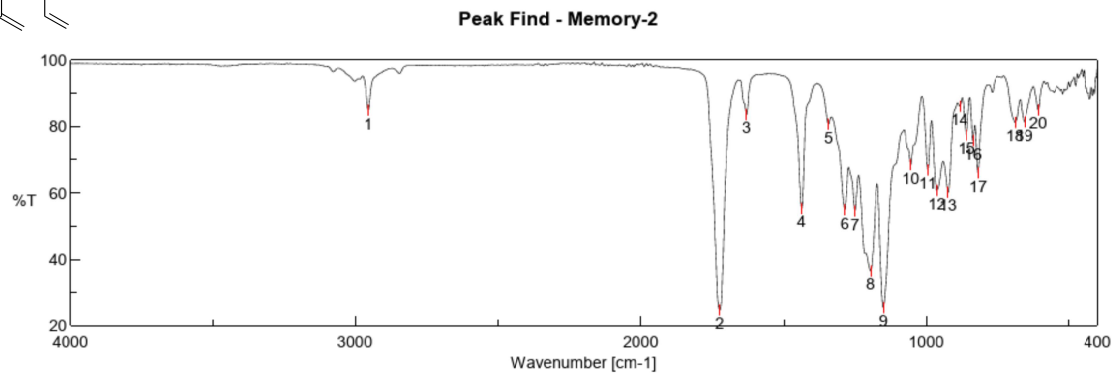




Trimethyl hepta-1,6-diene-2,4,4-tricarboxylate

FT-IR, ATR-diamond



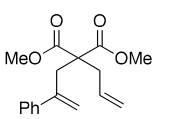


[Result of Peak Picking]

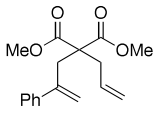
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2953.45	84.8745	2	1724.05	24.7371	3	1629.55	83.5843
4	1436.71	55.2864	5	1342.21	80.6666	6	1285.32	54.9083
7	1249.65	54.5375	8	1195.65	36.4332	9	1150.33	25.4889
10	1054.87	68.5296	11	995.089	66.8771	12	963.269	60.717
13	923.736	60.1874	14	883.238	86.0657	15	858.168	77.3728
16	834.062	75.7404	17	816.706	65.9922	18	688.463	81.1632
19	655.679	81.3647	20	506.503	84.9589			

Dimethyl 2-allyl-2-(2-phenylallyl)malonate

^{1}H-NMR (300 MHz, $CDCl_3$)

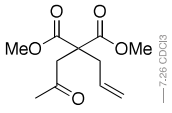


Dimethyl 2-allyl-2-(2-phenylallyl)malonate

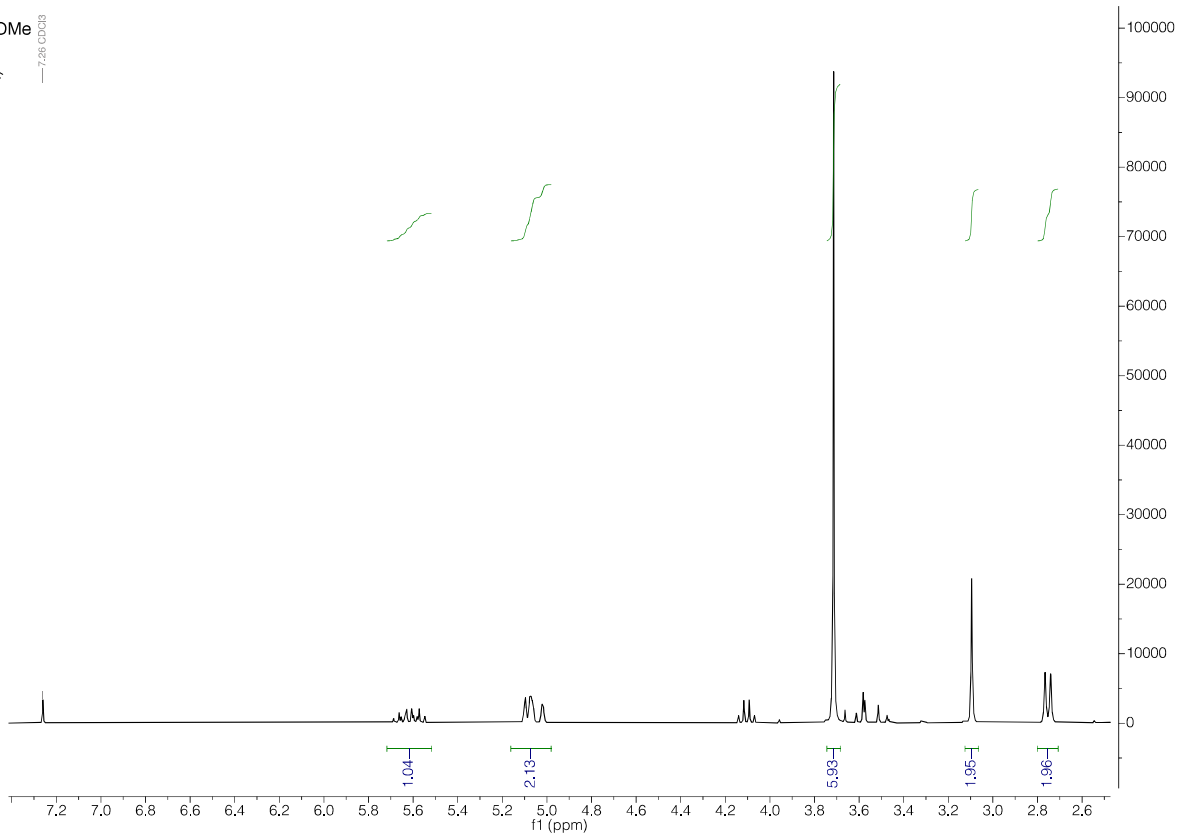


^{13}C-NMR (75 MHz, $CDCl_3$)

Dimethyl 2-allyl-2-(2-oxopropyl)malonate

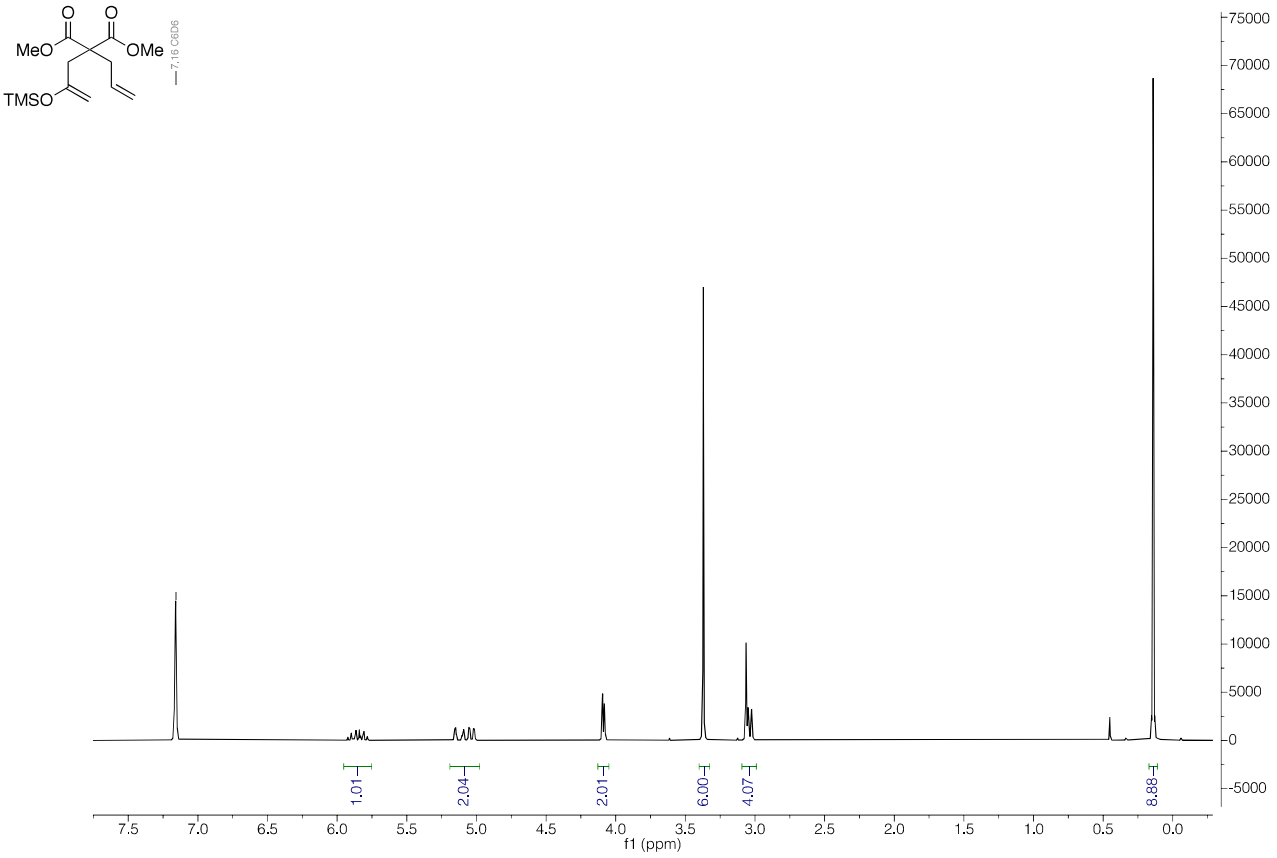


^{1}H-NMR (300 MHz, $CDCl_3$)



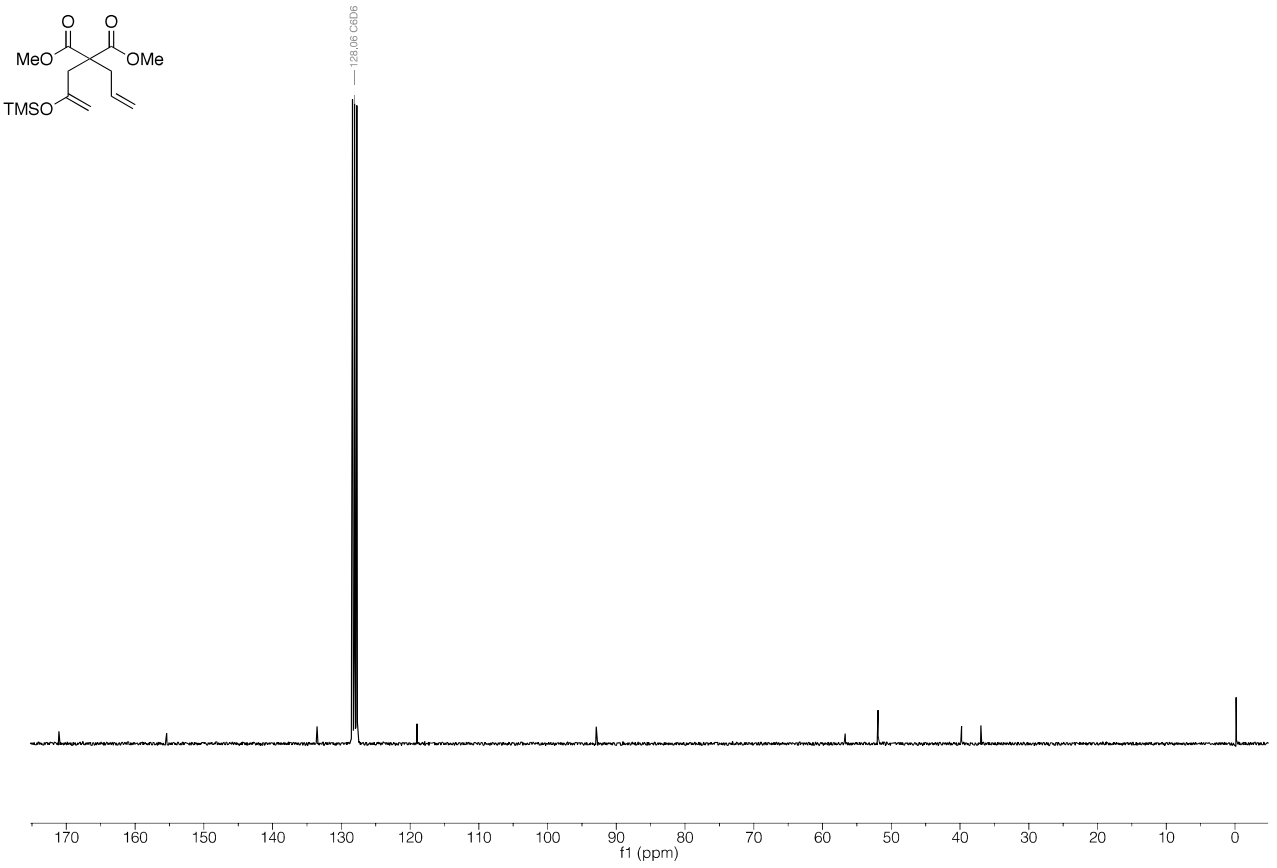
Dimethyl 2-allyl-2-(2-((trimethylsilyl)oxy)allyl)malonate

^{1}H-NMR (300 MHz, C_6D_6)



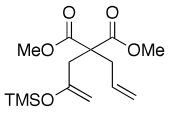
Dimethyl 2-allyl-2-(2-((trimethylsilyl)oxy)allyl)malonate

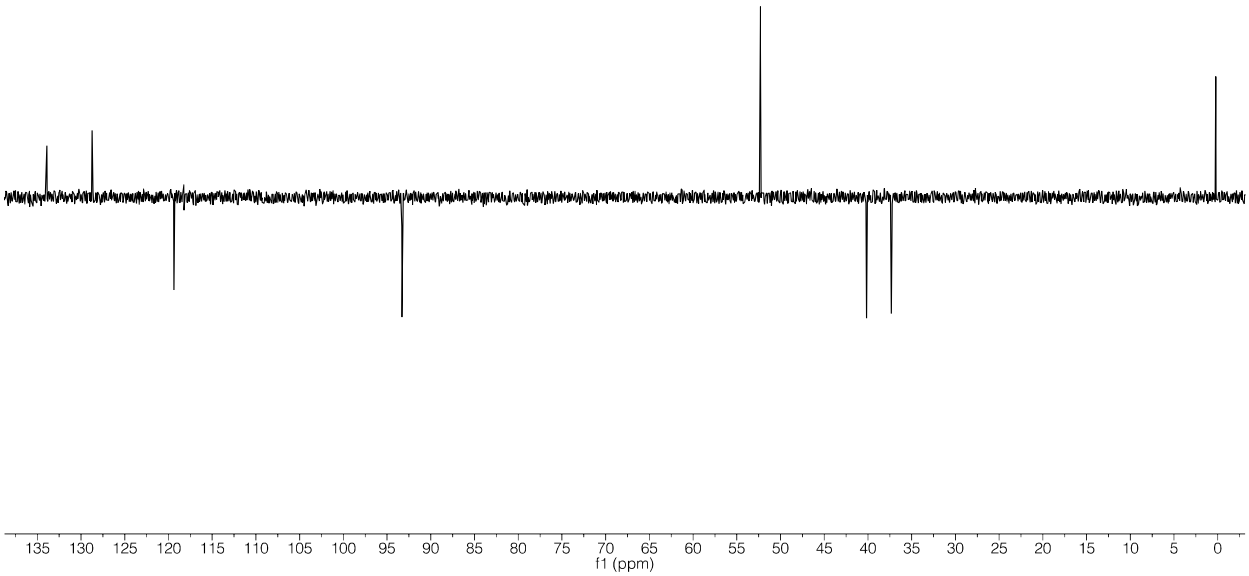
^{13}C-NMR (75 MHz, C_6D_6)



Dimethyl 2-allyl-2-(2-((trimethylsilyl)oxy)allyl)malonate

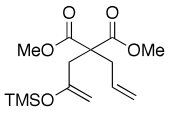
DEPT-135 NMR (75 MHz, C_6D_6)

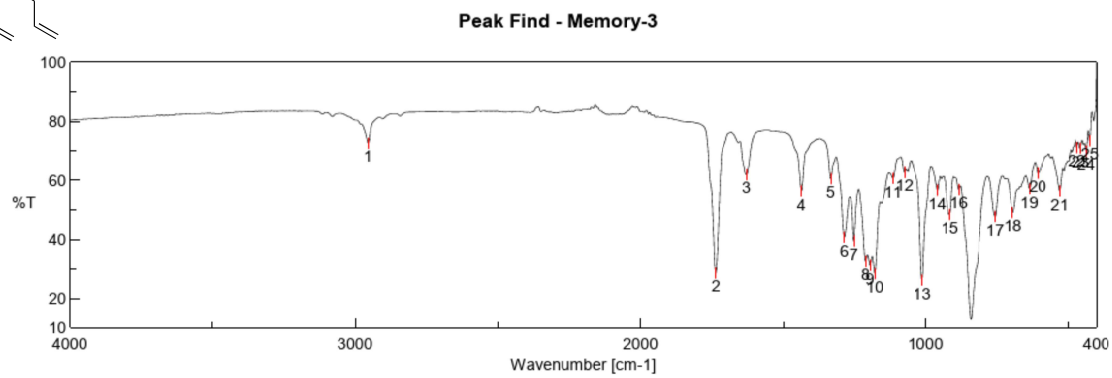




Dimethyl 2-allyl-2-(2-((trimethylsilyl)oxy)allyl)malonate

FT-IR, ATR-diamond



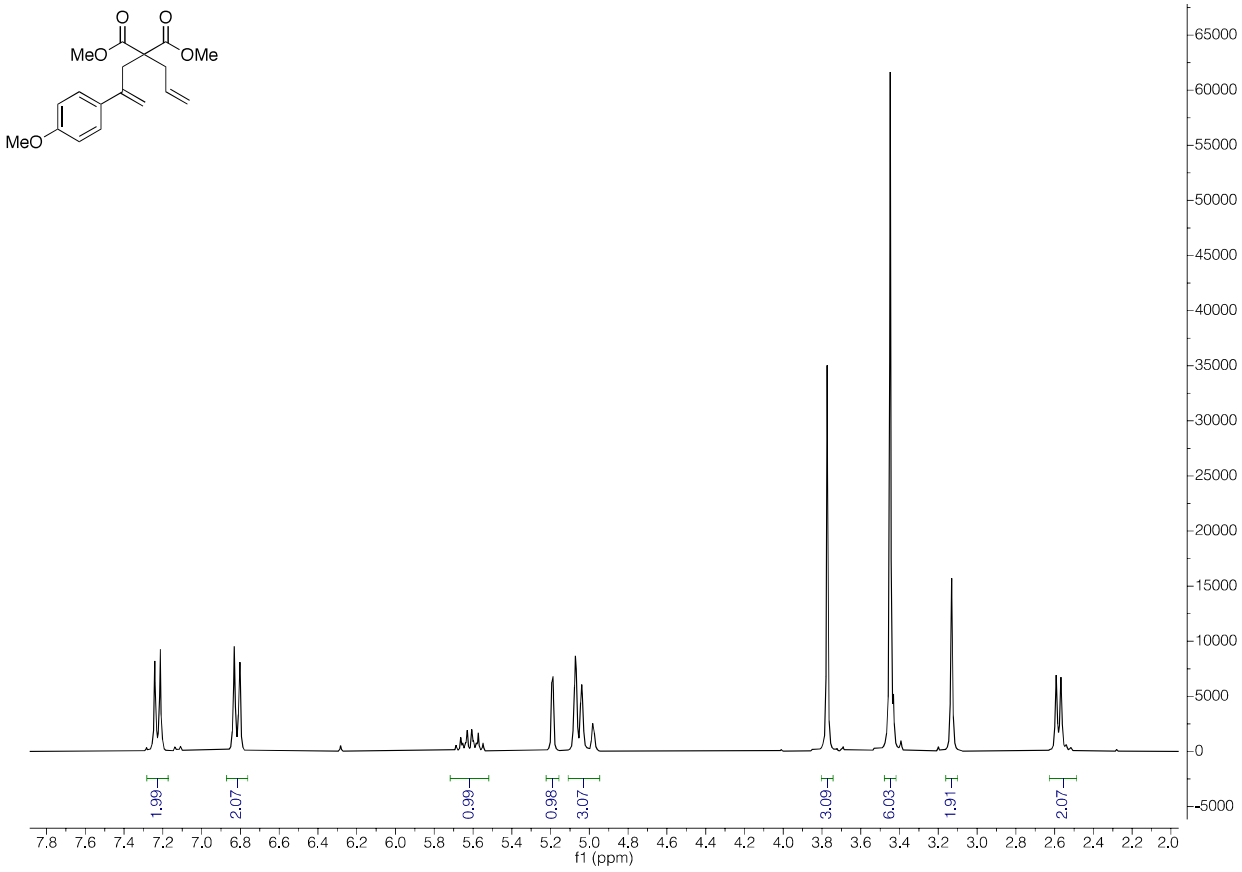


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2954.41	72.5156	2	1735.62	28.531	3	1628.59	61.9099
4	1435.74	56.3324	5	1333.53	60.5473	6	1285.32	40.6697
7	1252.54	39.3369	8	1211.08	32.4981	9	1195.65	31.1711
10	1178.29	28.372	11	1112.73	60.6596	12	1073.19	62.6911
13	1011.48	26.1229	14	957.484	56.5961	15	915.058	48.3498
16	882.274	56.7868	17	754.995	47.6177	18	693.284	49.0508
19	635.43	57.1494	20	605.539	62.434	21	529.364	56.3467
22	468.617	70.9929	23	457.047	70.7667	24	435.834	69.892
25	423.298	73.3571						

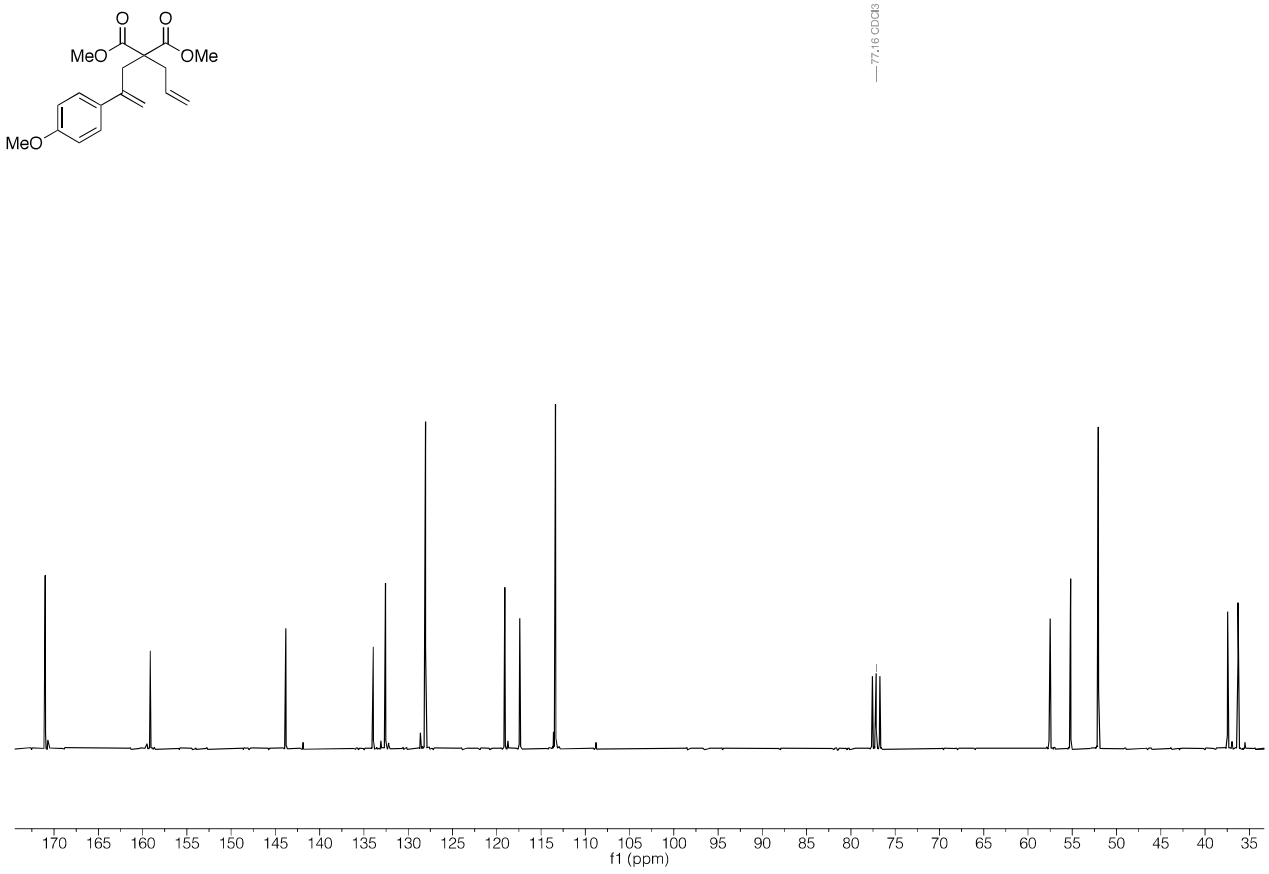
Dimethyl 2-allyl-2-[2-(4-methoxyphenyl)allyl]propanedioate

^{1}H-NMR (300 MHz, $CDCl_3$)



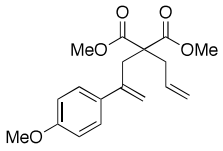
Dimethyl 2-allyl-2-[2-(4-methoxyphenyl)allyl]propanedioate

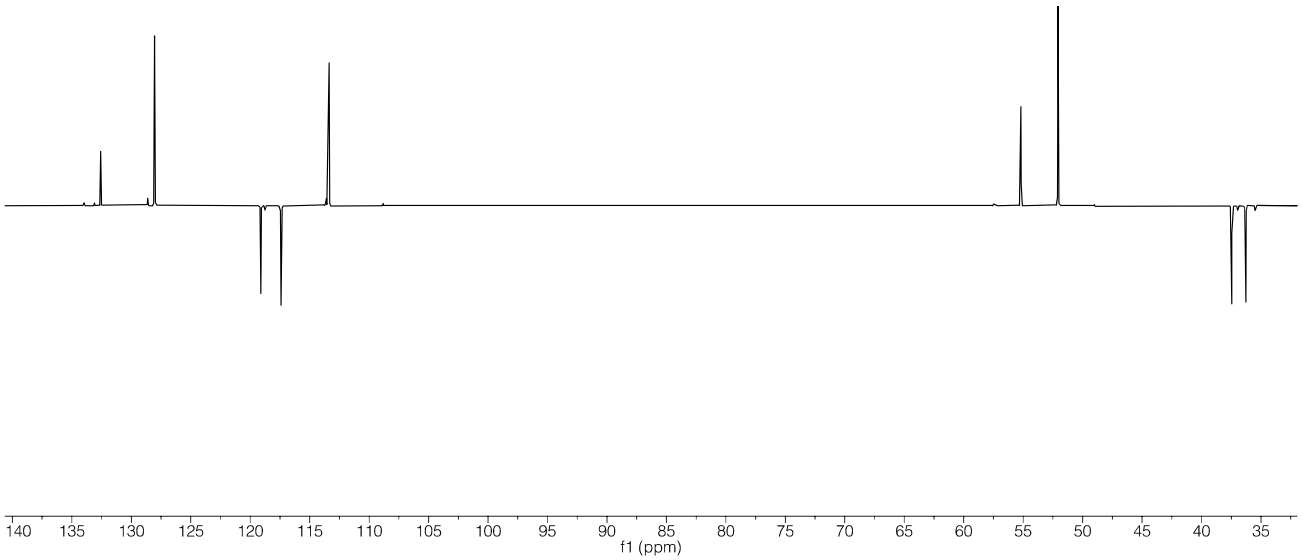
^{13}C-NMR (75 MHz, $CDCl_3$)



Dimethyl 2-allyl-2-[2-(4-methoxyphenyl)allyl]propanedioate

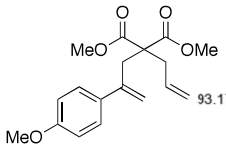
DEPT-135 NMR (75 MHz, $CDCl_3$)

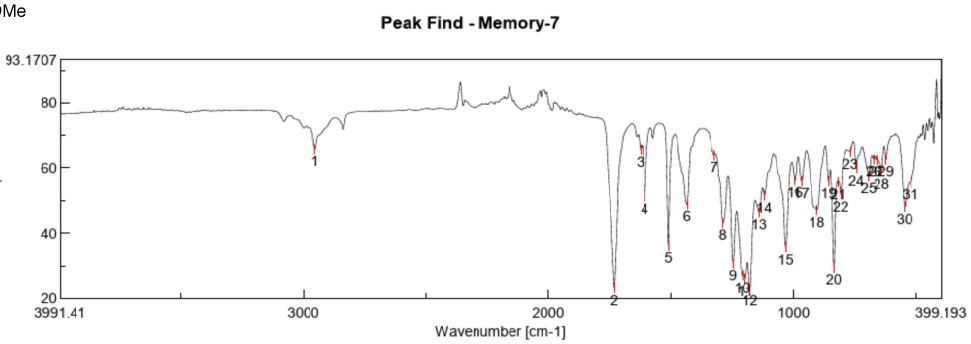




Dimethyl 2-allyl-2-[2-(4-methoxyphenyl)allyl]propanedioate

FT-IR, ATR-diamond



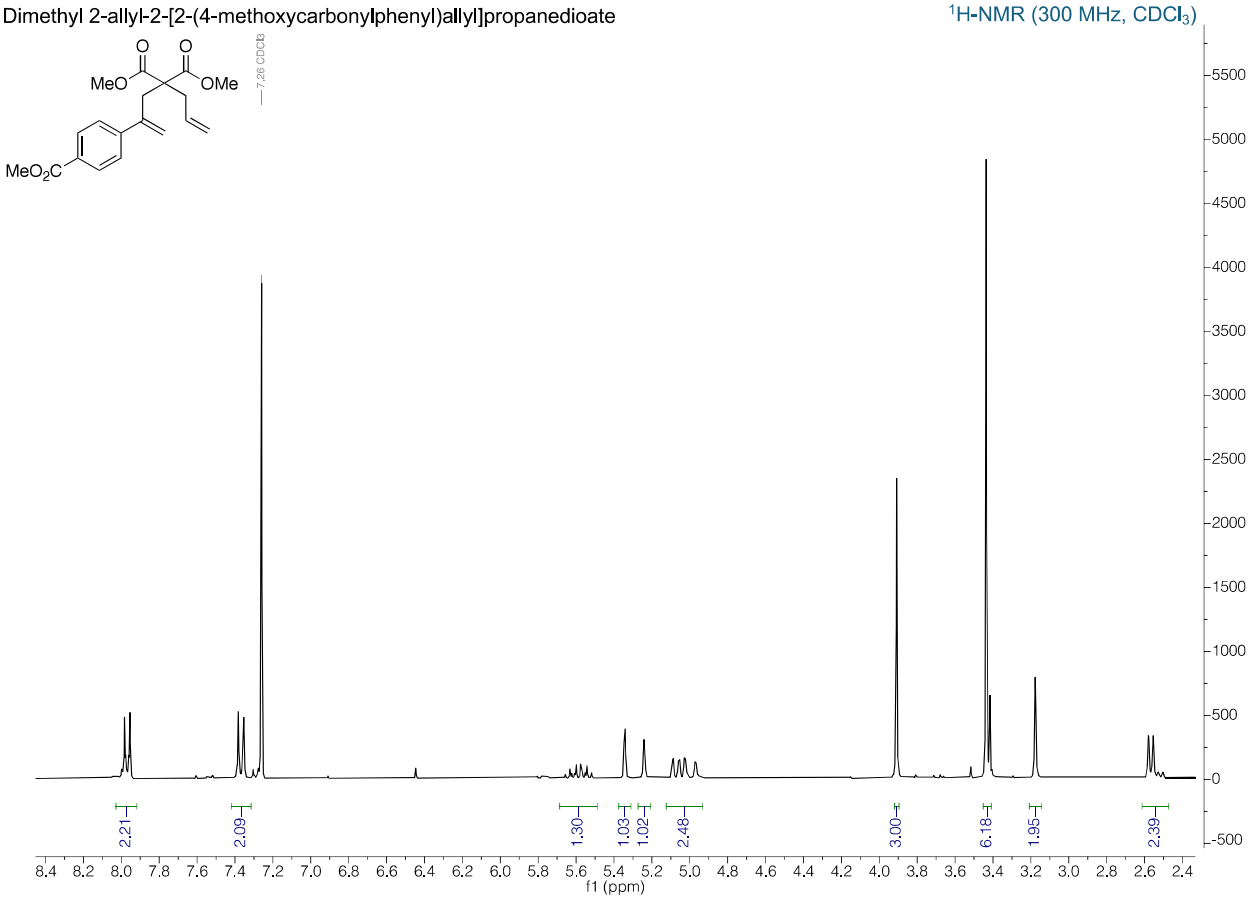


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2951.52	65.7208	2	1730.8	23.247	3	1623.77	65.5309
4	1606.41	51.2974	5	1509.99	36.0438	6	1434.78	48.8232
7	1322.93	63.8374	8	1287.25	43.0943	9	1246.75	30.6408
10	1209.15	27.0194	11	1197.58	26	12	1178.29	22.9517
13	1140.69	46.4145	14	1118.51	51.5771	15	1031.73	35.6594
16	994.125	56.2463	17	968.09	55.9171	18	906.379	47.0337
19	857.204	55.9153	20	835.99	29.28	21	818.634	55.6561
22	807.063	51.8739	23	769.458	64.9028	24	744.388	59.9119
25	694.248	57.4019	26	673.999	62.5598	27	662.428	62.4686
28	641.215	58.9649	29	621.931	62.5299	30	545.756	48.0756
31	523.579	55.5253						

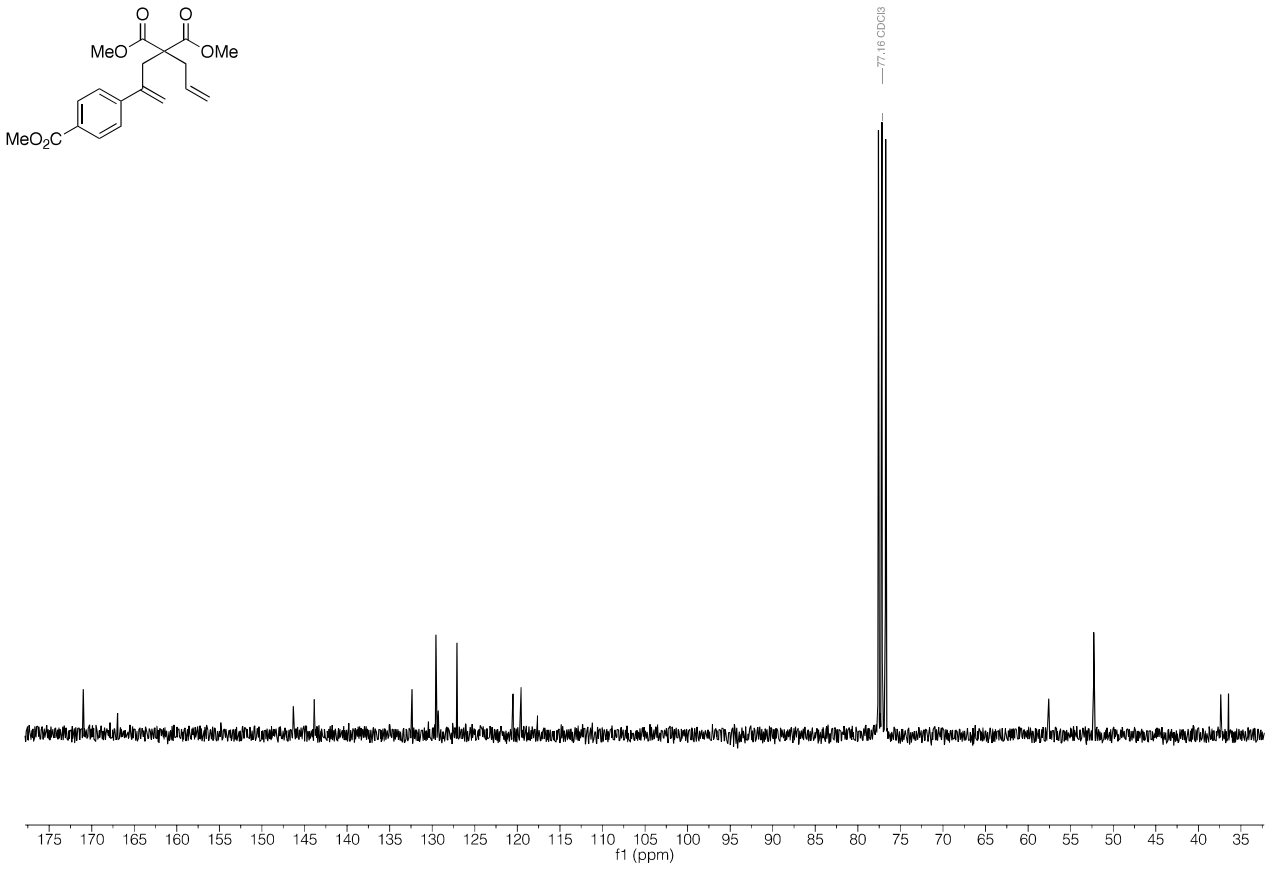
Dimethyl 2-allyl-2-[2-(4-methoxycarbonylphenyl)allyl]propanedioate

^{1}H-NMR (300 MHz, $CDCl_3$)



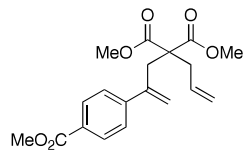
Dimethyl 2-allyl-2-[2-(4-methoxycarbonylphenyl)allyl]propanedioate

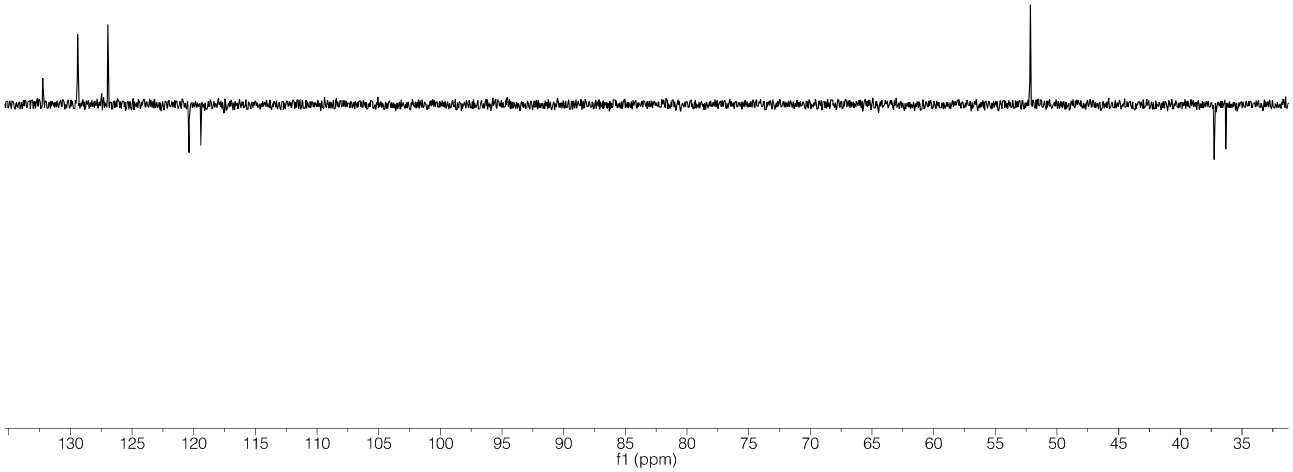
^{13}C-NMR (75 MHz, $CDCl_3$)



Dimethyl 2-allyl-2-[2-(4-methoxycarbonylphenyl)allyl]propanedioate

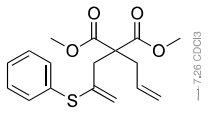
DEPT-135 NMR (75 MHz, $CDCl_3$)

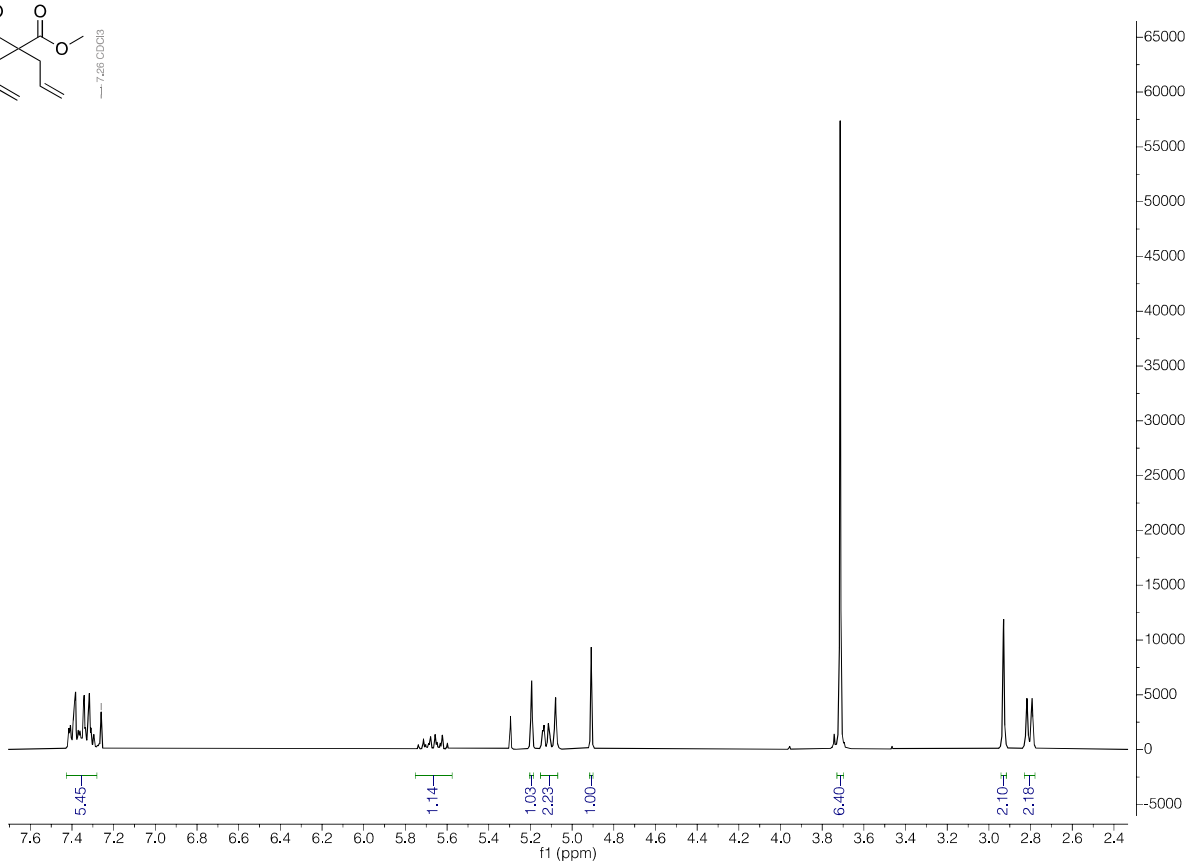




Dimethyl 2-allyl-2-(2-phenylsulfanylallyl)propanedioate

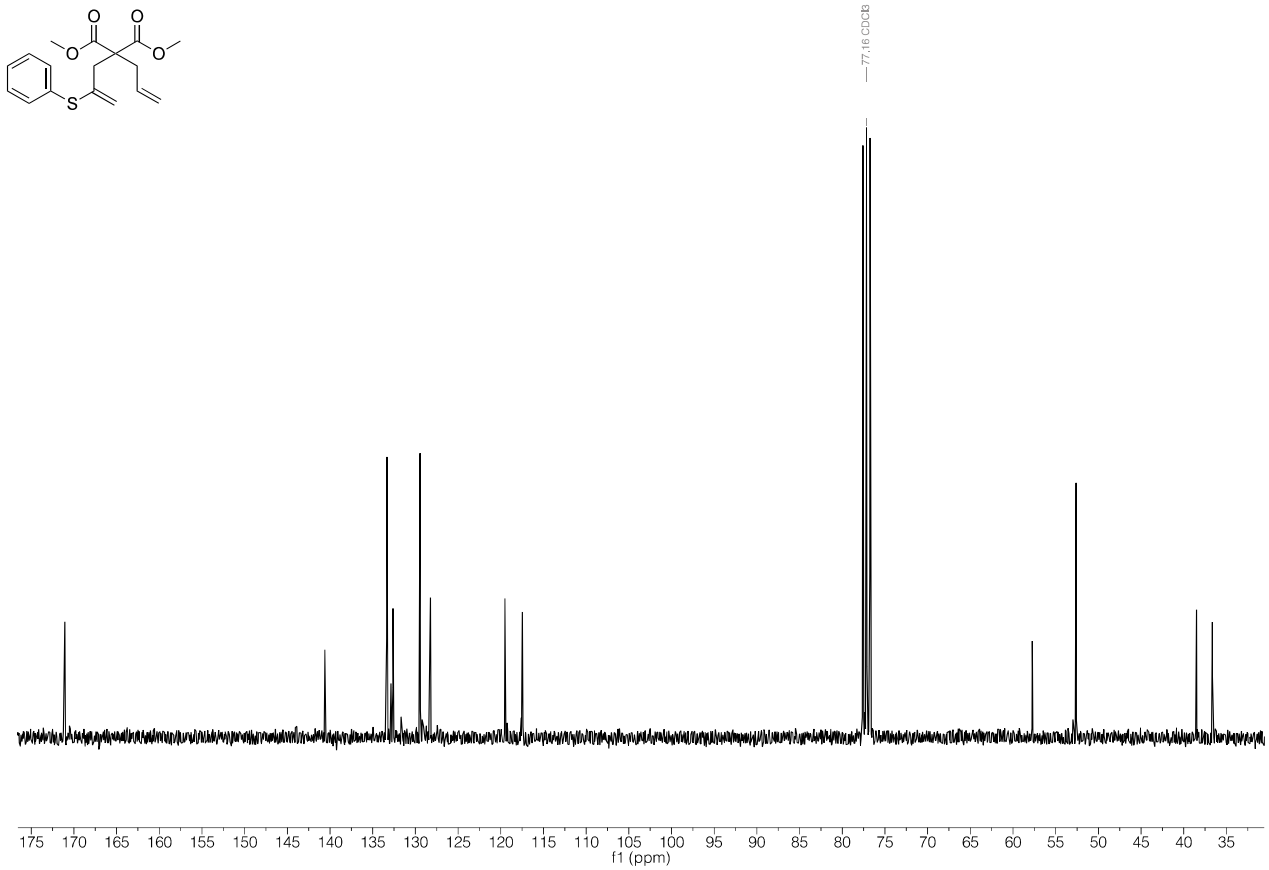
^{1}H-NMR (300 MHz, $CDCl_3$)





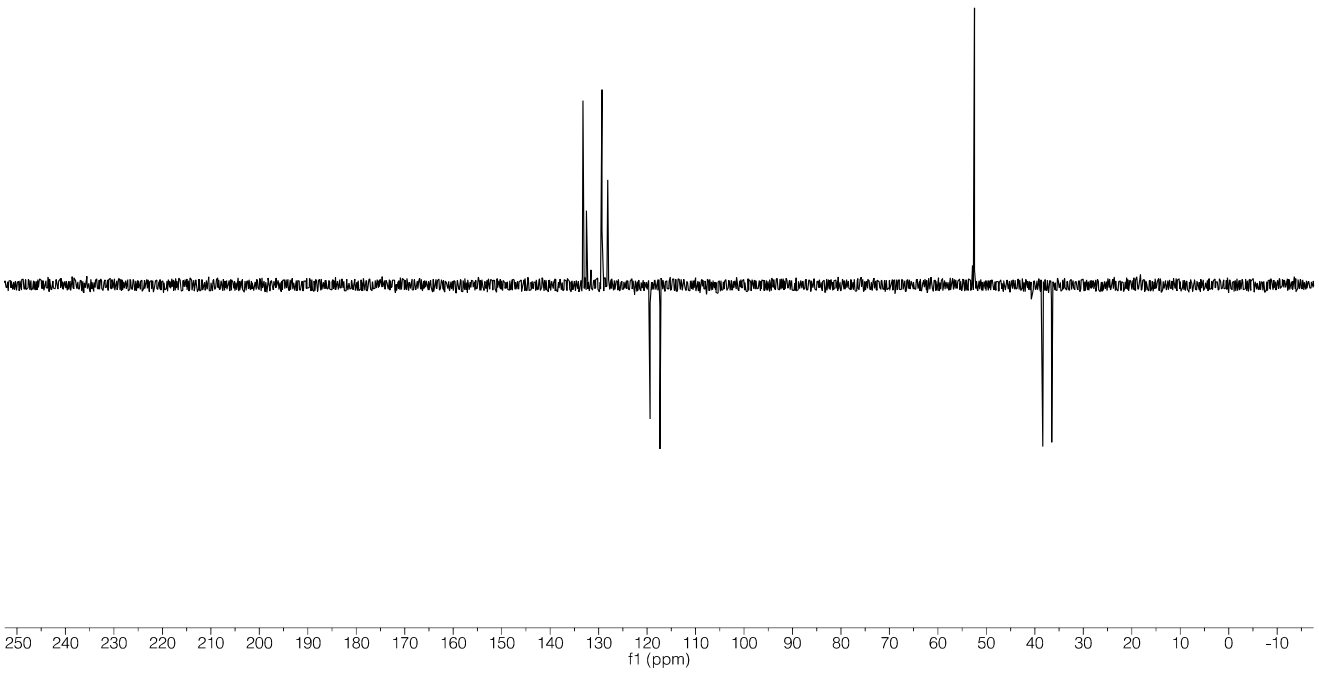
Dimethyl 2-allyl-2-(2-phenylsulfanylallyl)propanedioate

^{13}C-NMR (75 MHz, $CDCl_3$)



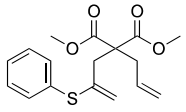
Dimethyl 2-allyl-2-(2-phenylsulfanylallyl)propanedioate

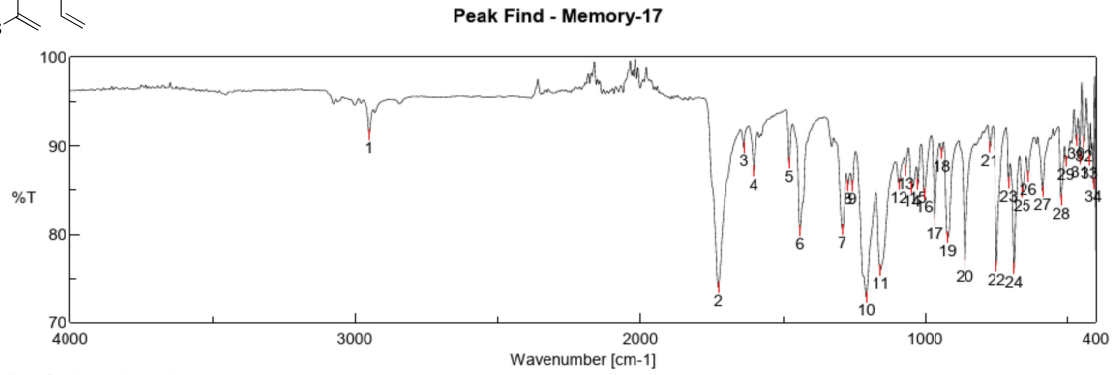
DEPT-135 NMR (75 MHz, $CDCl_3$)



Dimethyl 2-allyl-2-(2-phenylsulfanylallyl)propanedioate

FT-IR, ATR-diamond



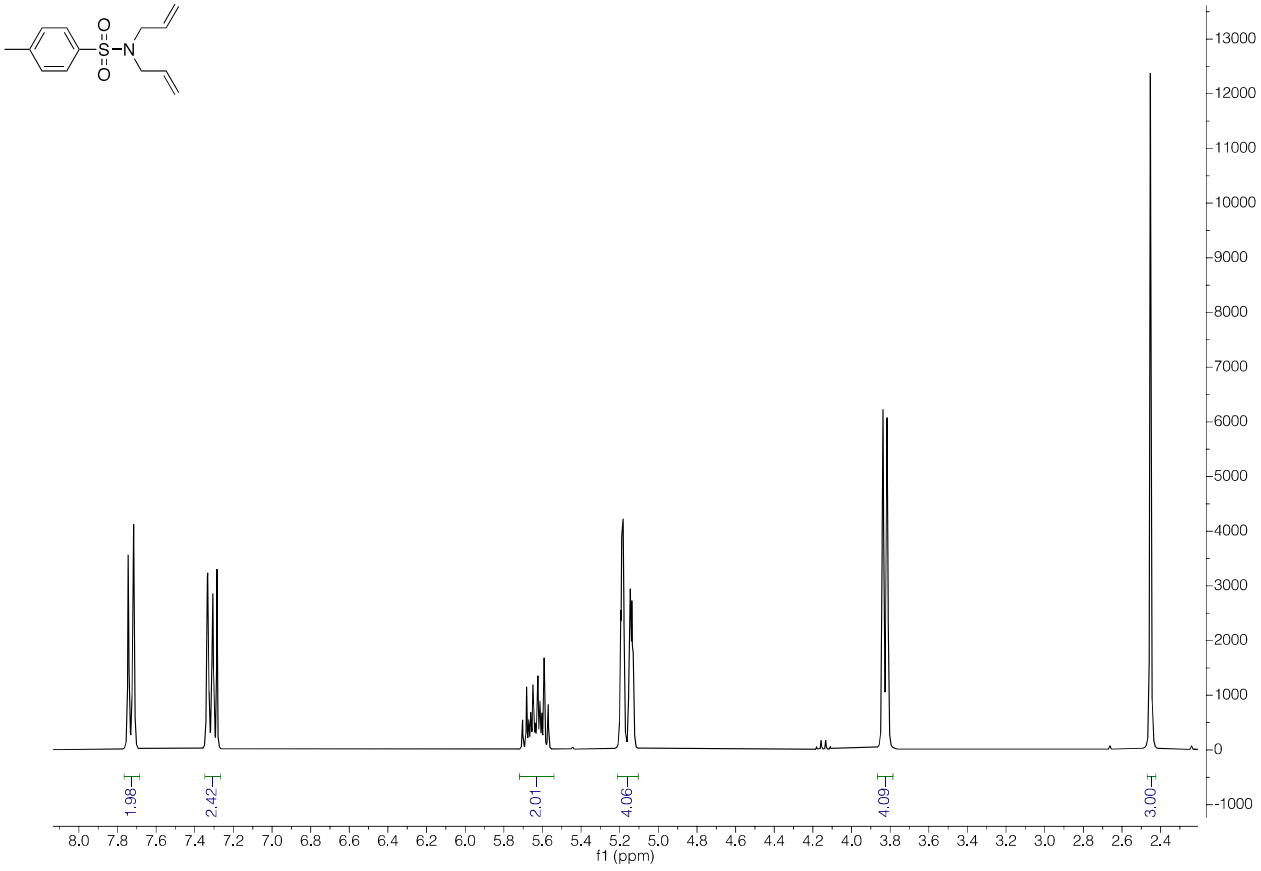


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2949.59	91.2438	2	1726.94	73.997	3	1637.27	89.7701
4	1601.59	87.1353	5	1478.17	88.0485	6	1440.56	80.3825
7	1291.11	80.5336	8	1269.9	85.4875	9	1254.47	85.4628
10	1207.22	72.901	11	1156.12	75.9268	12	1092.48	85.6568
13	1068.37	87.207	14	1046.19	85.2578	15	1024.98	85.6481
16	1003.77	84.5445	17	967.126	81.542	18	942.056	89.1756
19	920.843	79.647	20	861.06	76.7307	21	774.279	89.8304
22	750.174	76.4371	23	707.747	85.7937	24	689.427	76.1489
25	660.5	84.7741	26	638.323	86.5229	27	587.218	84.8351
28	521.65	83.858	29	505.258	88.2591	30	468.617	90.5793
31	457.047	88.5231	32	441.619	90.3988	33	423.298	88.369
34	408.835	85.7237						

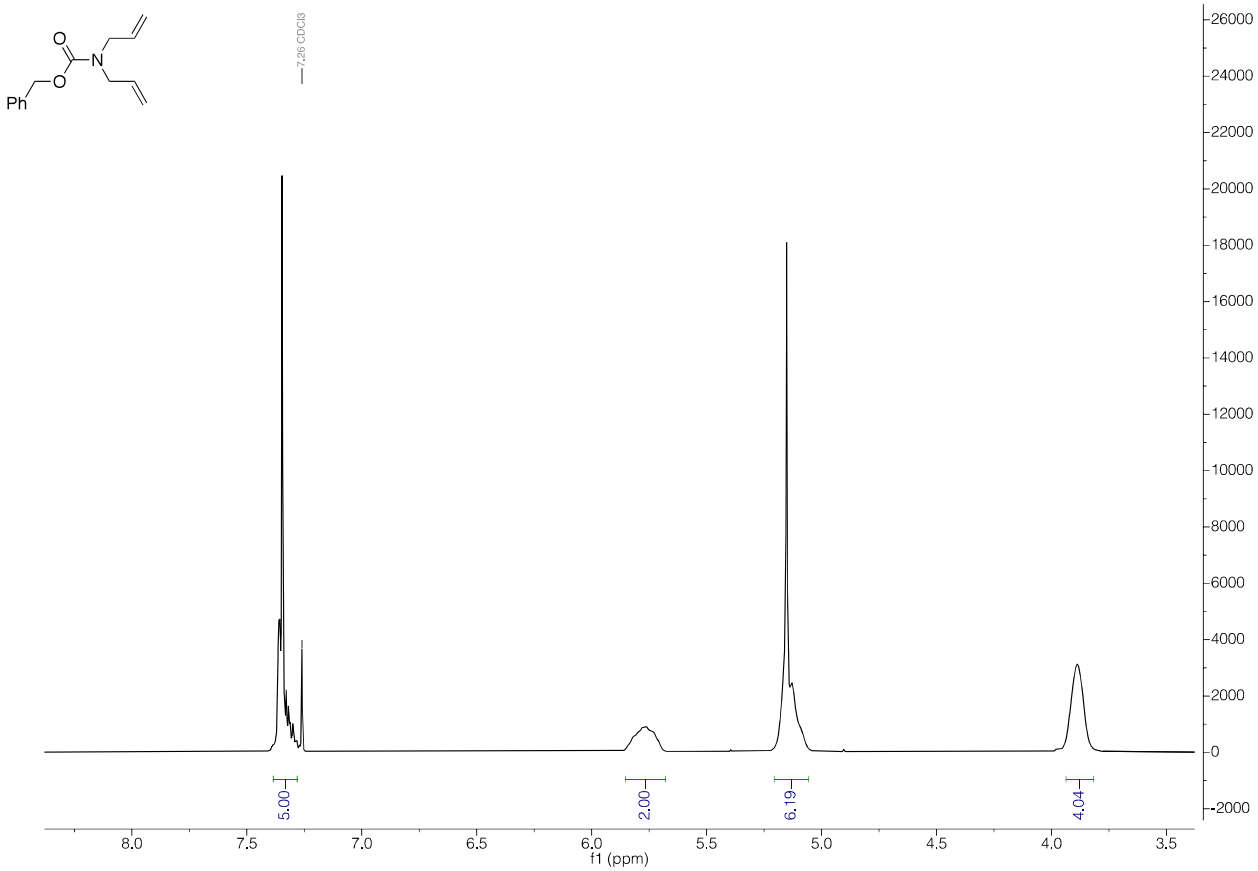
N,*N*-Diallyl-p-toluenesulfonamide

^{1}H-NMR (300 MHz, $CDCl_3$)



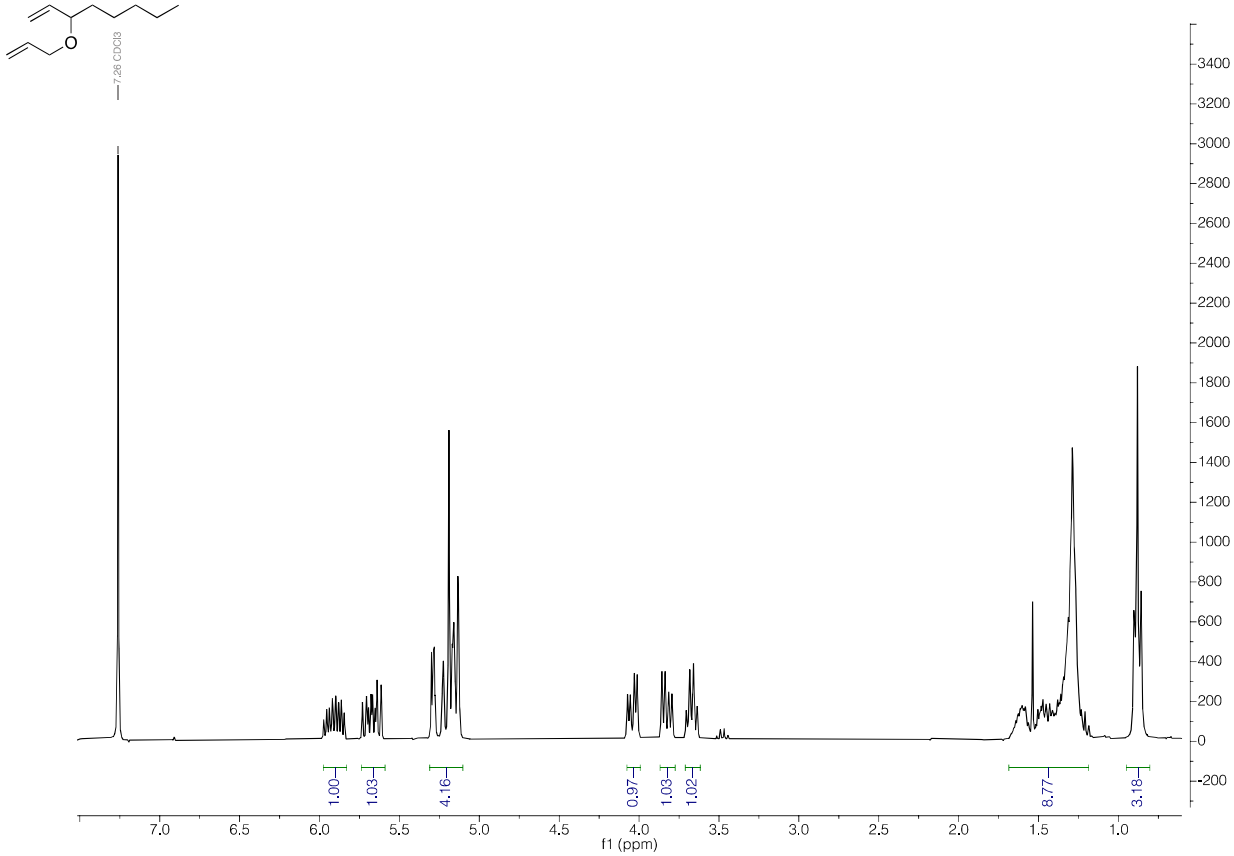
Benzyl *N*,*N*-diallylcarbamate

^{1}H-NMR (300 MHz, $CDCl_3$)

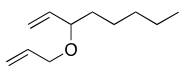


3-allyloxyoct-1-ene

^{1}H-NMR (300 MHz, $CDCl_3$)

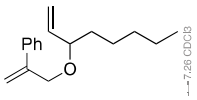


3-allyloxyoct-1-ene



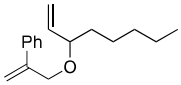
^{13}C-NMR (75 MHz, $CDCl_3$)

1-(1-vinylhexoxymethyl)vinylbenzene



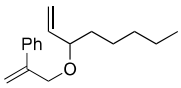
^{1}H-NMR (300 MHz, $CDCl_3$)

1-(1-vinylhexoxymethyl)vinylbenzene

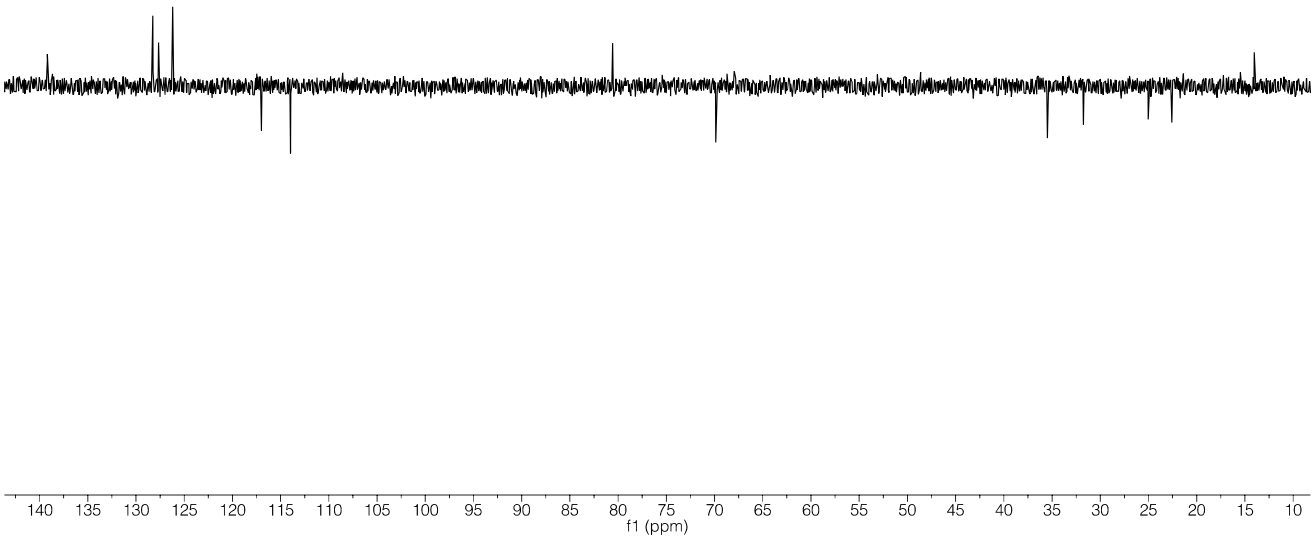


^{13}C-NMR (75 MHz, $CDCl_3$)

1-(1-vinylhexoxymethyl)vinylbenzene

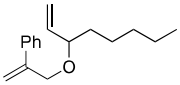


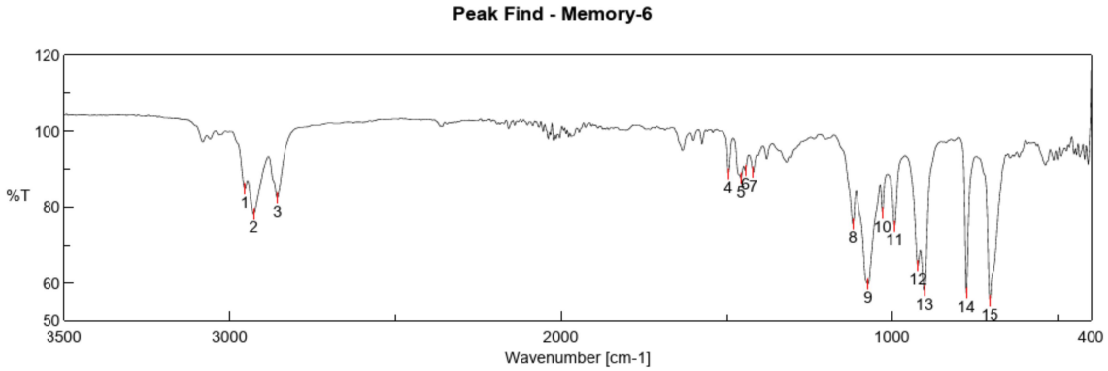
DEPT-135 NMR (75 MHz, $CDCl_3$)



1-(1-vinylhexoxymethyl)vinylbenzene

FT-IR, ATR-diamond



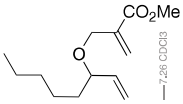


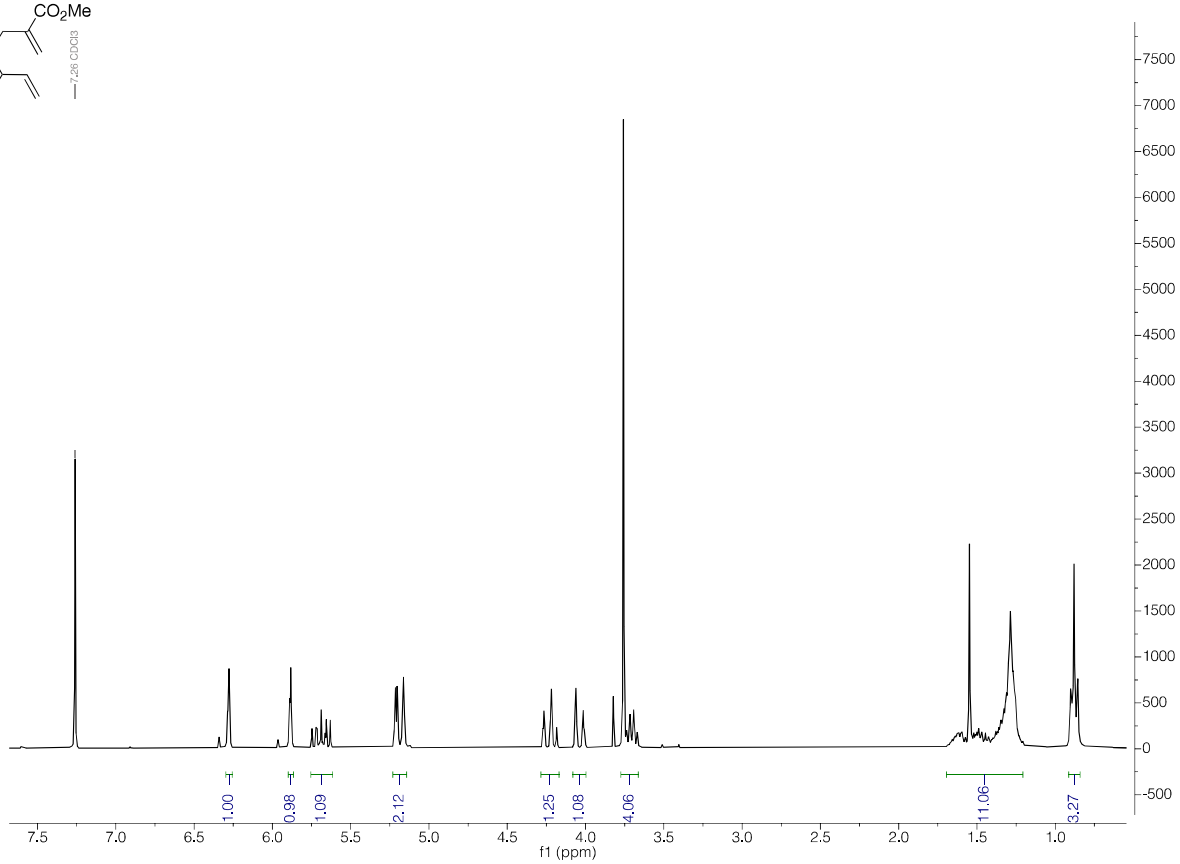
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2954.41	84.777	2	2928.38	78.0948	3	2857.02	82.3345
4	1495.53	88.6098	5	1456.96	87.5262	6	1444.42	89.5567
7	1420.32	89.0919	8	1119.48	75.4569	9	1071.26	59.72
10	1027.87	78.3743	11	992.196	74.8579	12	921.807	64.511
13	902.523	57.9487	14	777.172	57.3019	15	705.819	55.2592

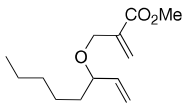
methyl 2-((oct-1-en-3-yloxy)methyl)acrylate

^{1}H-NMR (300 MHz, $CDCl_3$)



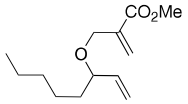


methyl 2-((oct-1-en-3-yloxy)methyl)acrylate

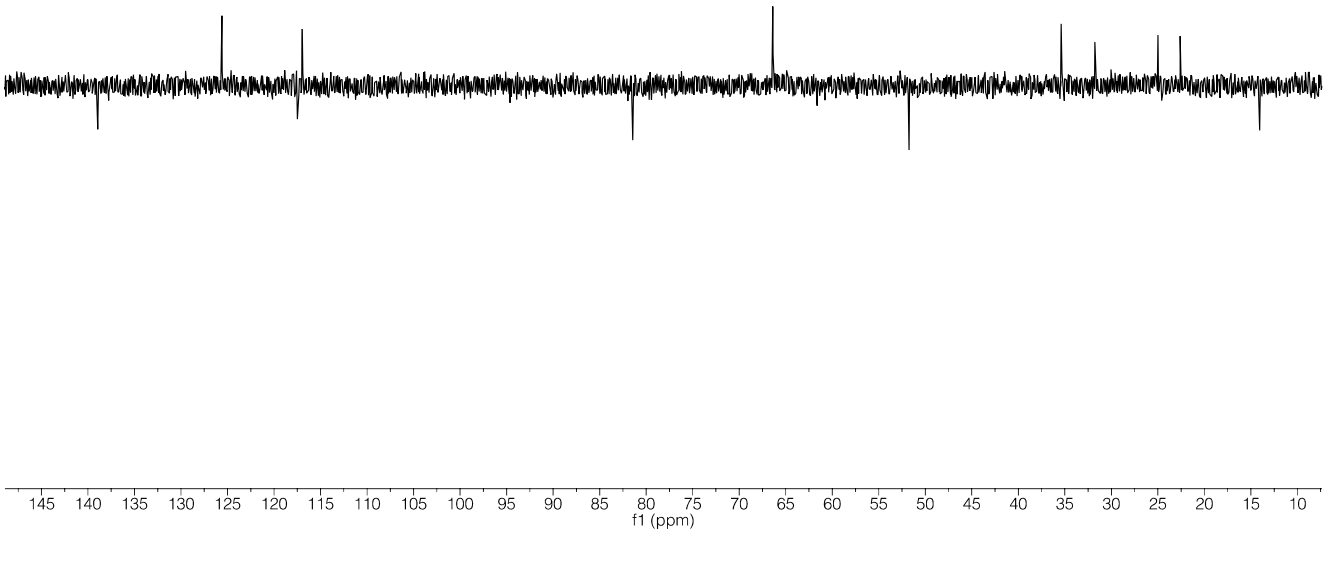


^{13}C-NMR (75 MHz, $CDCl_3$)

methyl 2-((oct-1-en-3-yloxy)methyl)acrylate

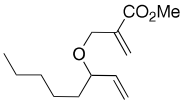


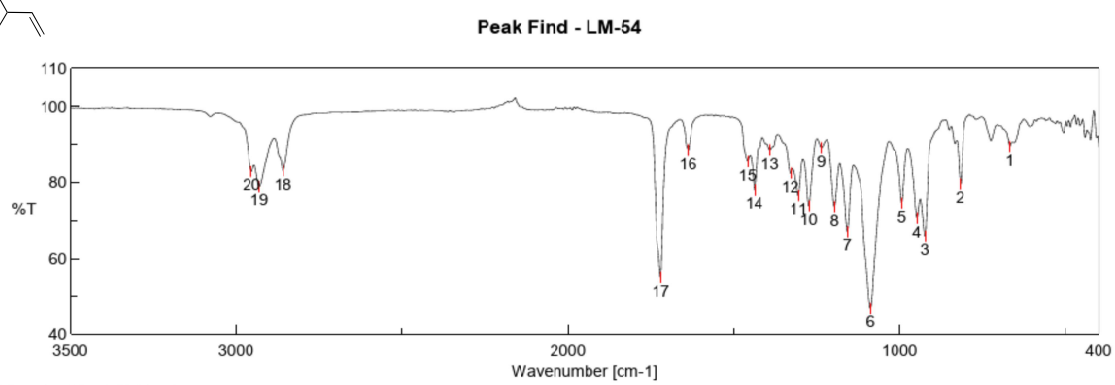
DEPT-135 NMR (75 MHz, $CDCl_3$)



methyl 2-((oct-1-en-3-yloxy)methyl)acrylate

FT-IR, ATR-diamond



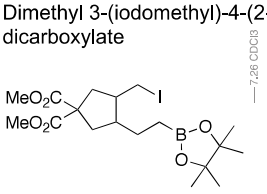


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	667.25	89.3467	2	816.706	79.5431	3	924.7	65.7517
4	947.842	70.5769	5	993.16	74.4575	6	1087.66	46.7427
7	1158.04	66.9564	8	1195.65	73.525	9	1236.15	89.0726
10	1273.75	73.7603	11	1304.61	76.517	12	1329.68	82.3813
13	1391.39	88.4859	14	1437.67	77.9349	15	1457.92	85.4833
16	1637.27	88.4532	17	1720.19	54.9911	18	2858.95	83.048
19	2930.31	78.8257	20	2953.45	82.8374			

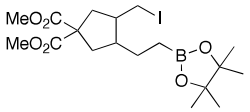
Dimethyl 3-(iodomethyl)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

^{1}H-NMR (300 MHz, $CDCl_3$)



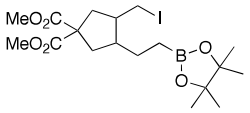
Dimethyl 3-(iodomethyl)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

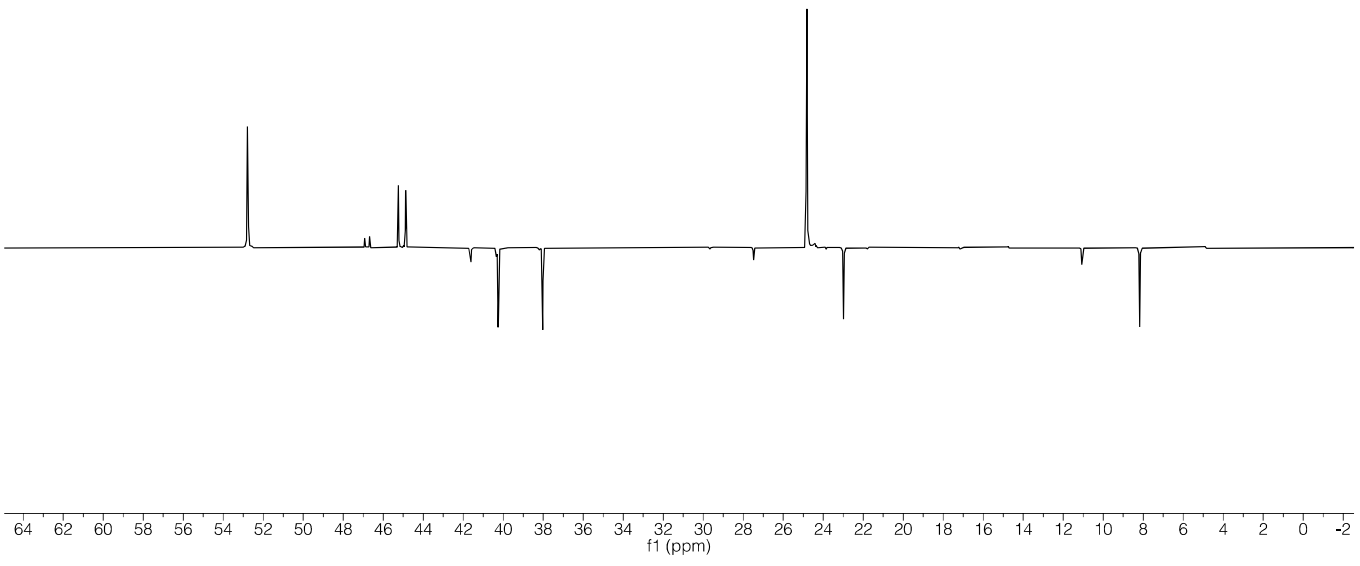
^{13}C-NMR (75 MHz, $CDCl_3$)



Dimethyl 3-(iodomethyl)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

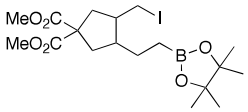
DEPT-135 NMR (75 MHz, $CDCl_3$)





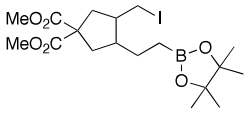
Dimethyl 3-(iodomethyl)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

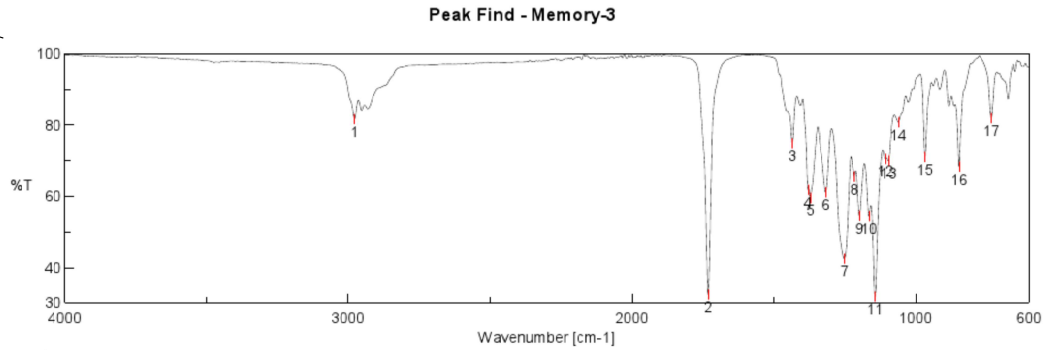
^{11}B-NMR (96 MHz, $CDCl_3$)



Dimethyl 3-(iodomethyl)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



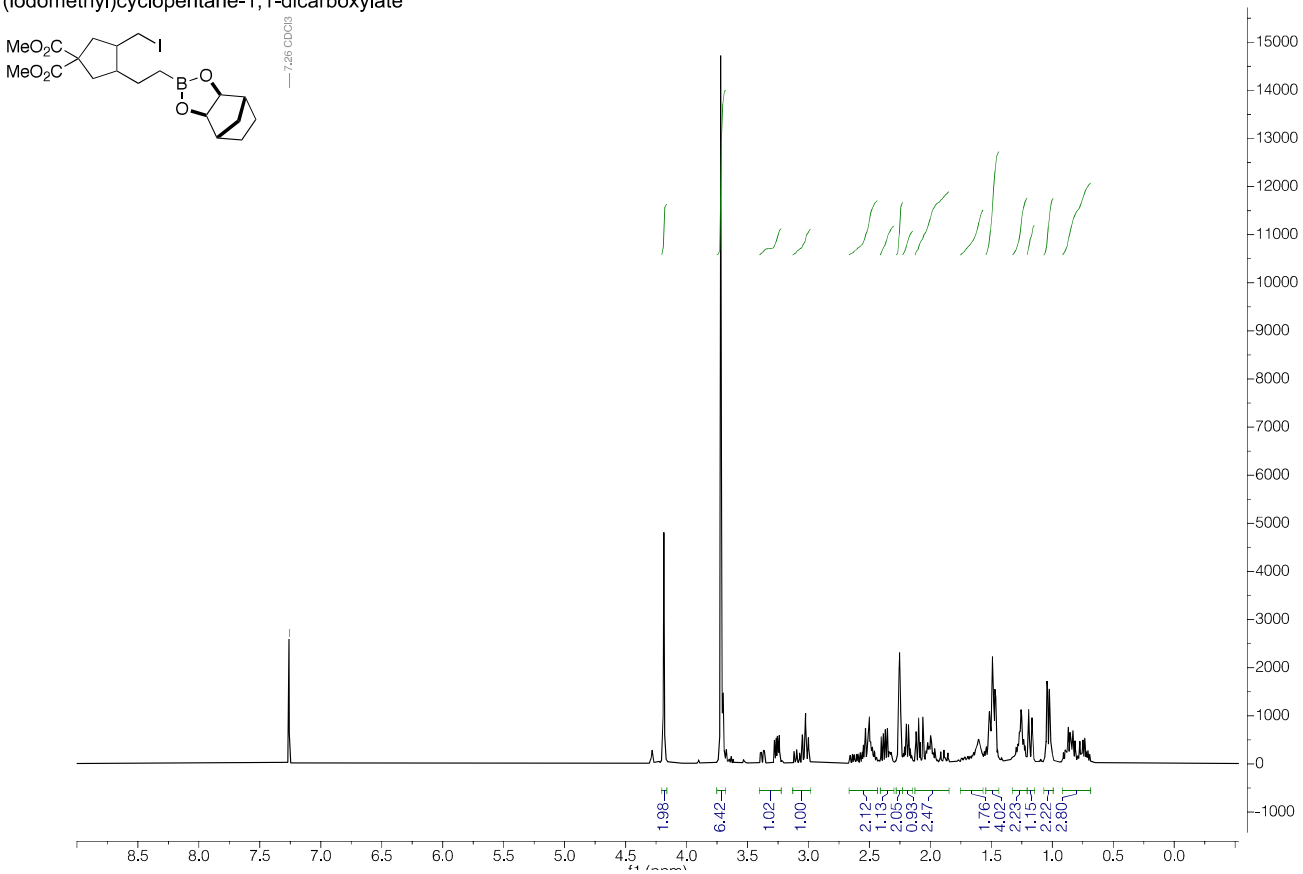


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2976.59	81.5502	2	1730.8	32.2739	3	1433.82	74.6755
4	1377.89	61.6516	5	1370.18	59.3965	6	1316.18	60.9502
7	1250.61	42.3615	8	1215.9	65.3705	9	1197.58	54.4172
10	1163.83	54.3169	11	1142.62	31.7492	12	1105.98	70.3746
13	1095.37	69.8581	14	1060.66	80.7053	15	966.162	70.9035
16	846.597	68.1892	17	732.817	81.813			

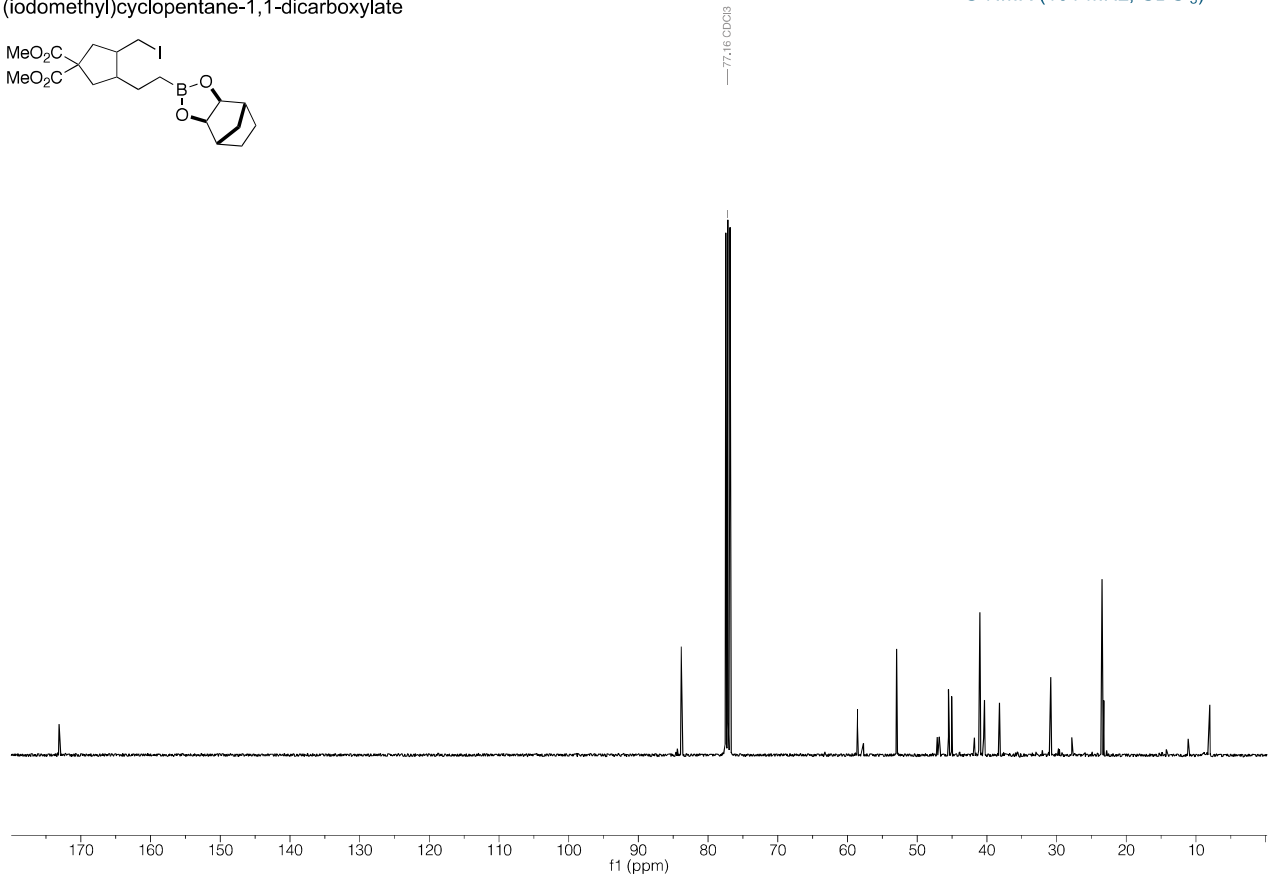
Dimethyl 3-(2-((3a*R**,4*S**,7*R**,7a*S**)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)



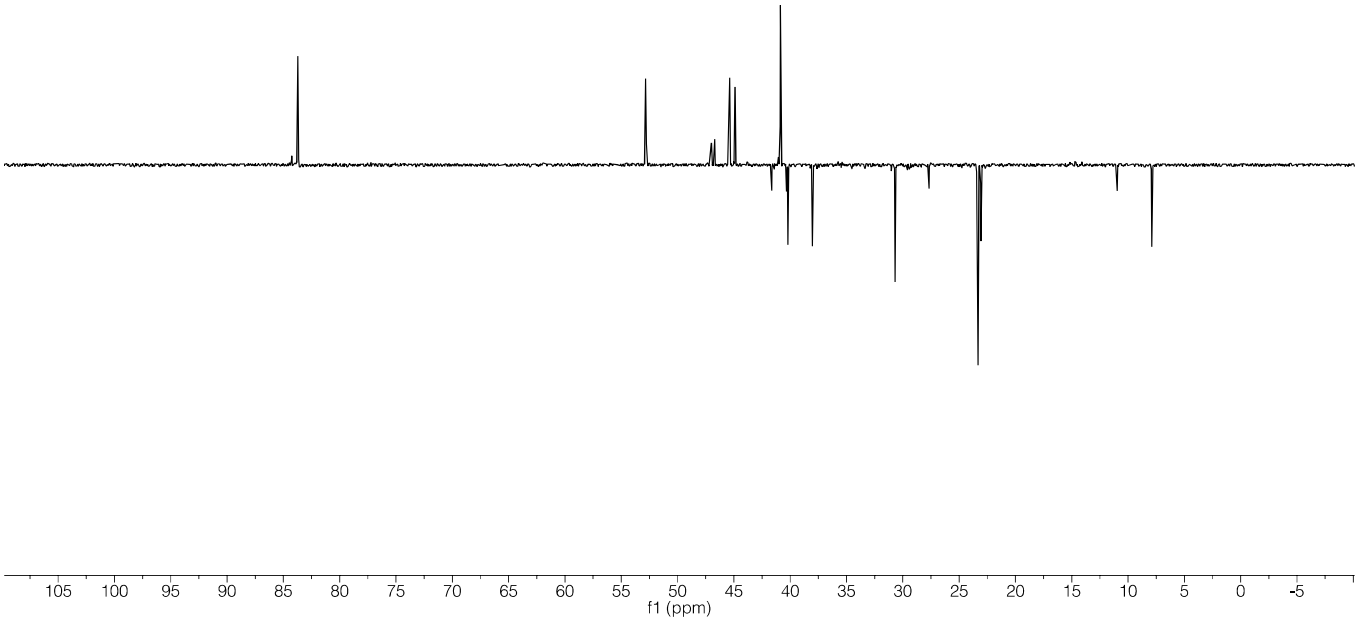
Dimethyl 3-(2-((3a*R**,4*S**,7*R**,7a*S**)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

^{13}C-NMR (101 MHz, $CDCl_3$)



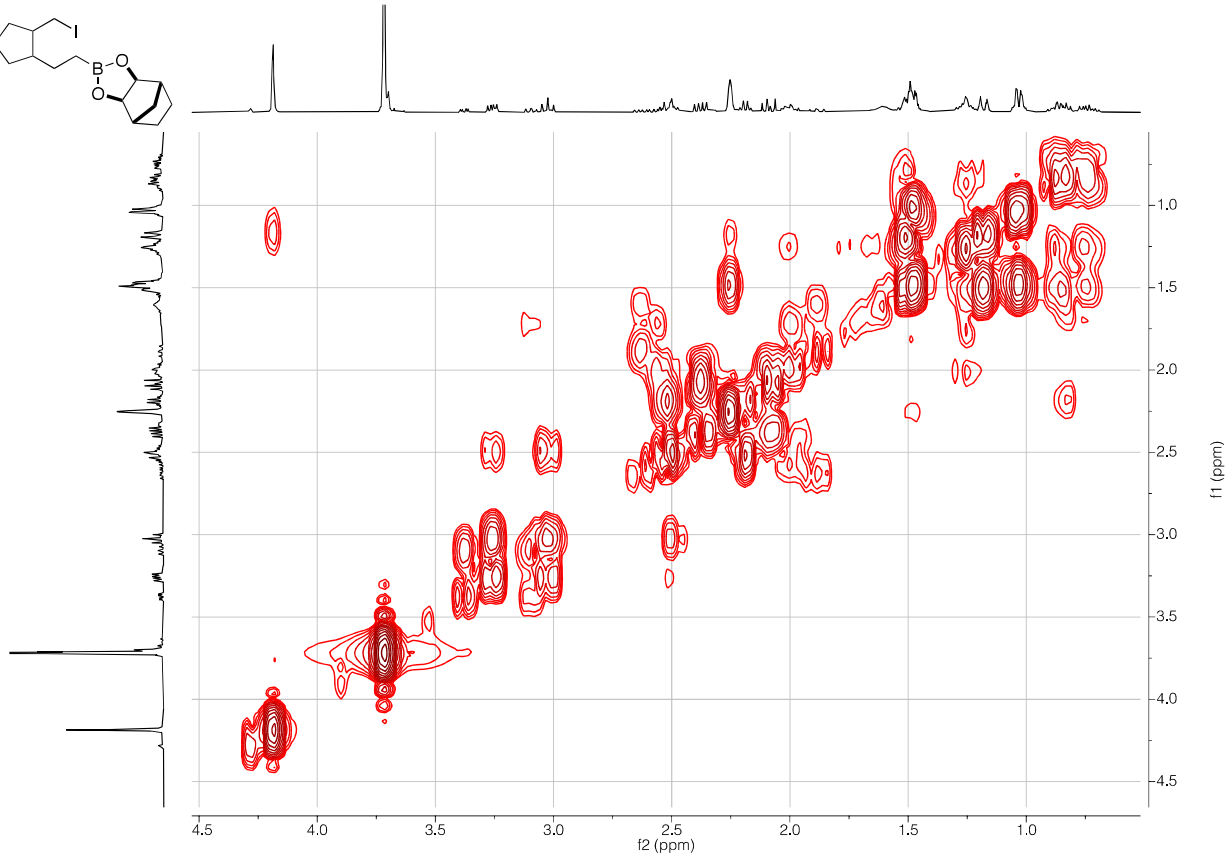
Dimethyl 3-(2-((3a*R**,4*S**,7*R**,7a*S**)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

DEPT-135 NMR (101 MHz, $CDCl_3$)



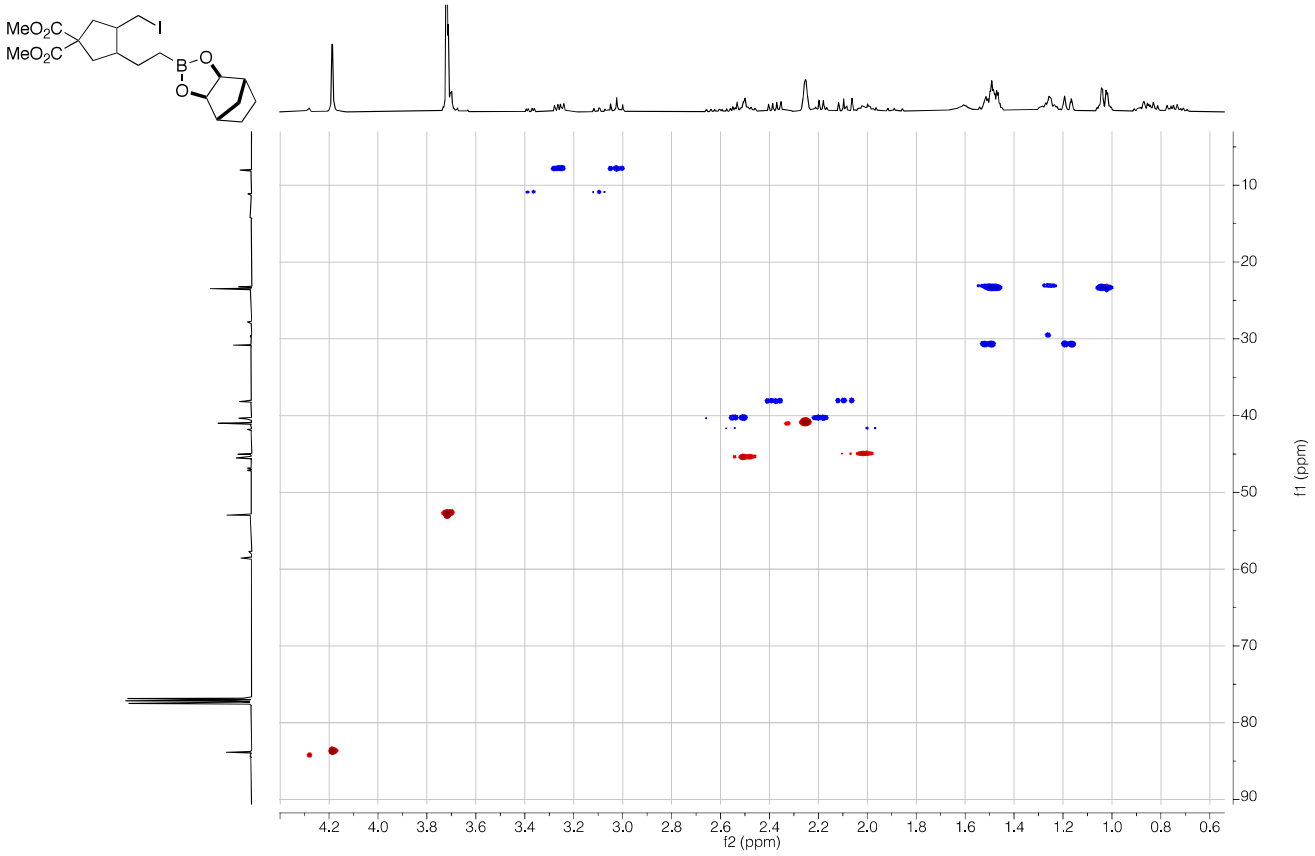
Dimethyl 3-(2-((3a*R**,4*S**,7*R**,7a*S**)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

^1H, ^1H-COSY (400 MHz, $CDCl_3$)



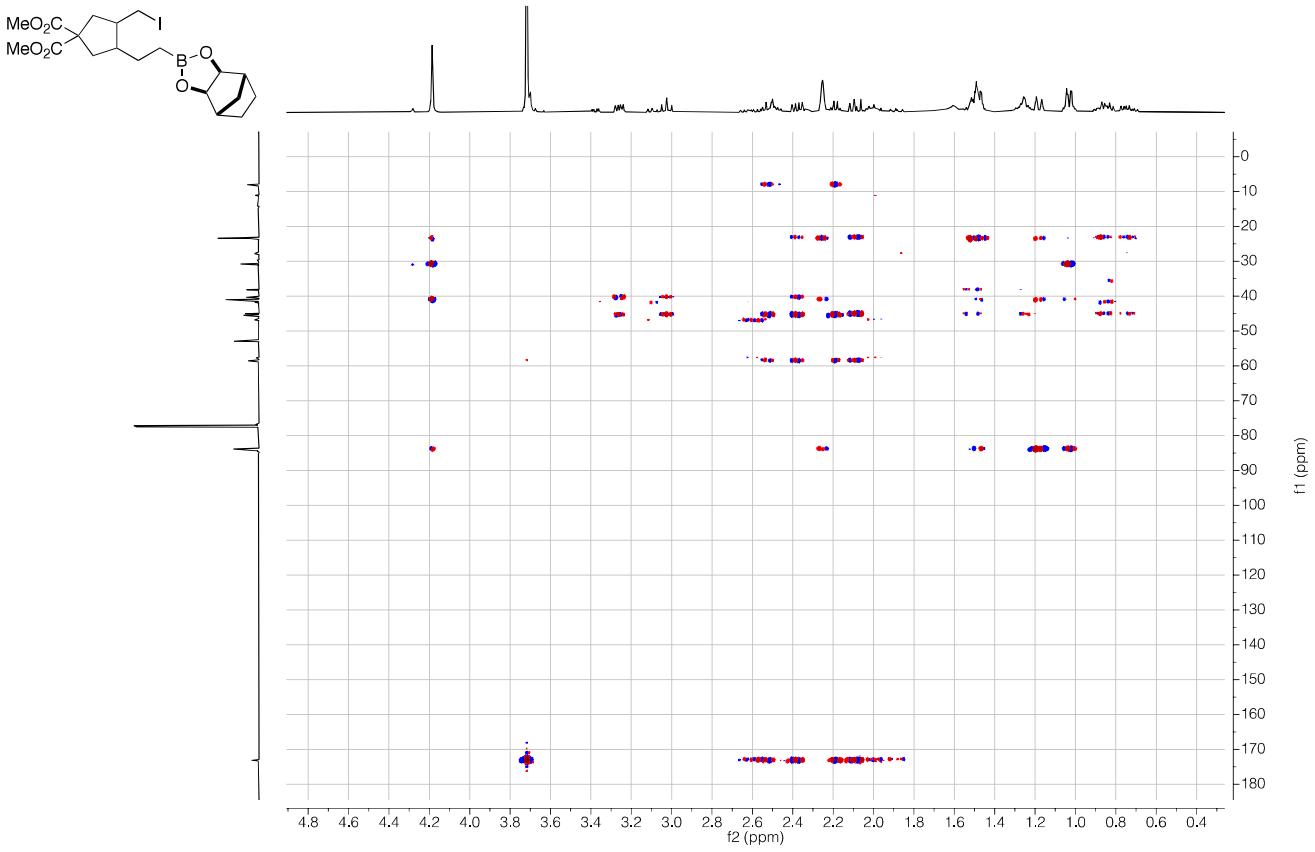
Dimethyl 3-(2-((3a*R**,4*S**,7*R**,7a*S**)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



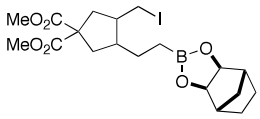
Dimethyl 3-(2-((3a*R**,4*S**,7*R**,7a*S**)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



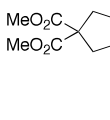
Dimethyl 3-(2-((3a*R**,4*S**,7*R**,7a*S**)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

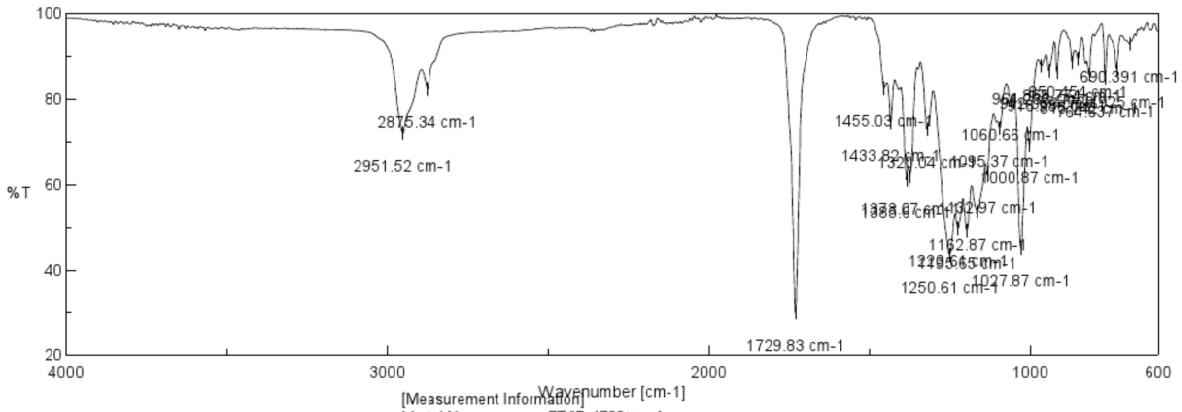
^{11}B-NMR (128 MHz, $CDCl_3$)



Dimethyl 3-(2-((3a*R**,4*S**,7*R**,7a*S**)-hexahydro-4,7-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond





[Measurement Information]
Model Name FT/IR-4700typeA
Serial Number C009661788

GG_1_170

Accessory ATR PRO ONE
Accessory S/N A0026161809
Incident angle 45 deg

Measurement Date 04.10.2021 15:31

Light Source Standard
Detector TGS
Accumulation 128
Resolution 4 cm-1
Zero Filling On
Apodization Cosine
Gain Auto (16)

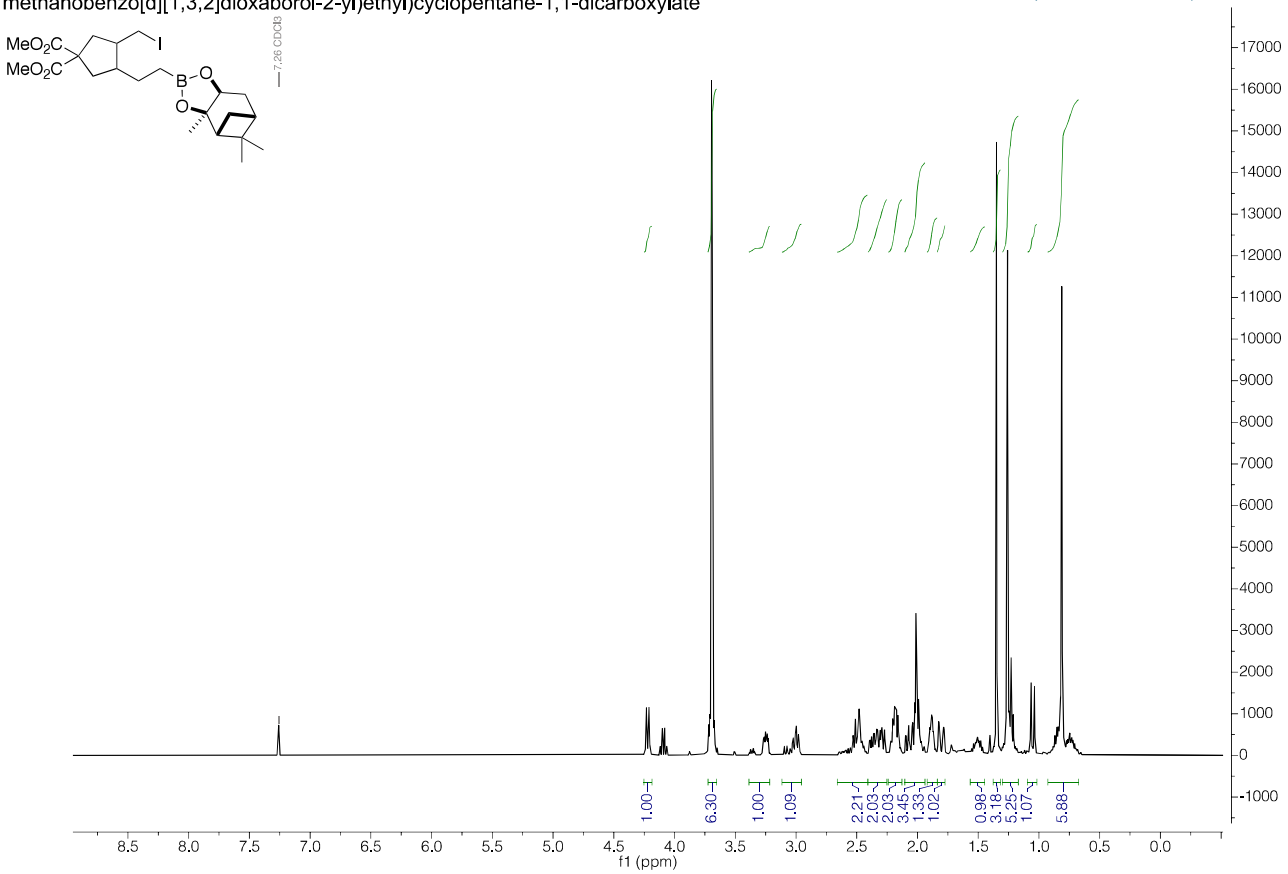
[Comments]
Sample name
Comment
User
Division
Company

[Detailed Information]
Creation date 04.10.2021 15:34

Data array type Linear data array
Horizontal axis Wavenumber [cm-1]
Vertical axis %T
Start 599.753 cm-1
End 4000.6 cm-1

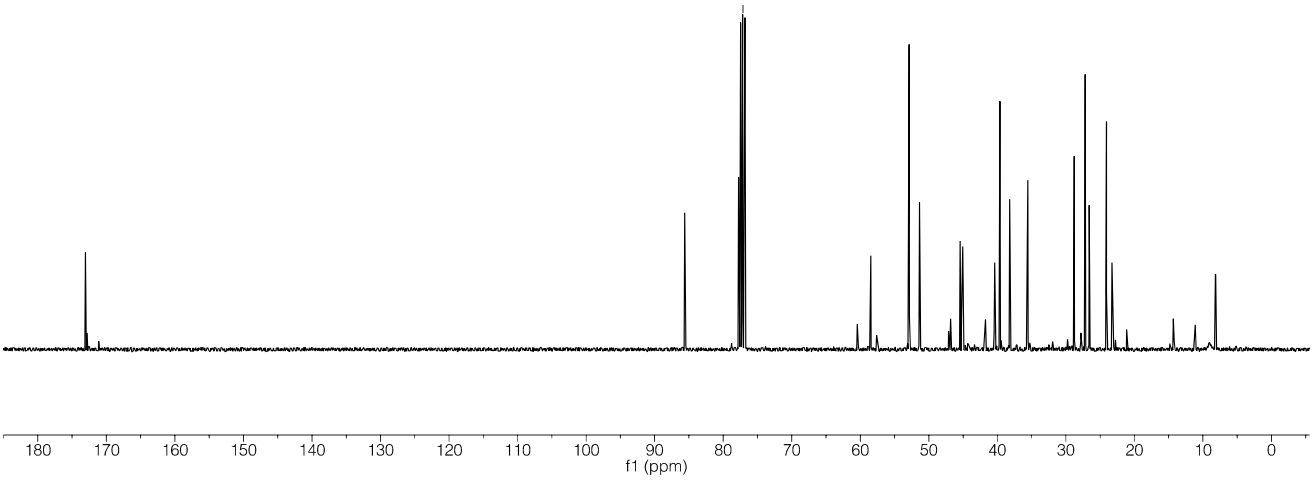
Dimethyl 3-(iodomethyl)-4-(2-((3aR,4R,6R,7aS)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)



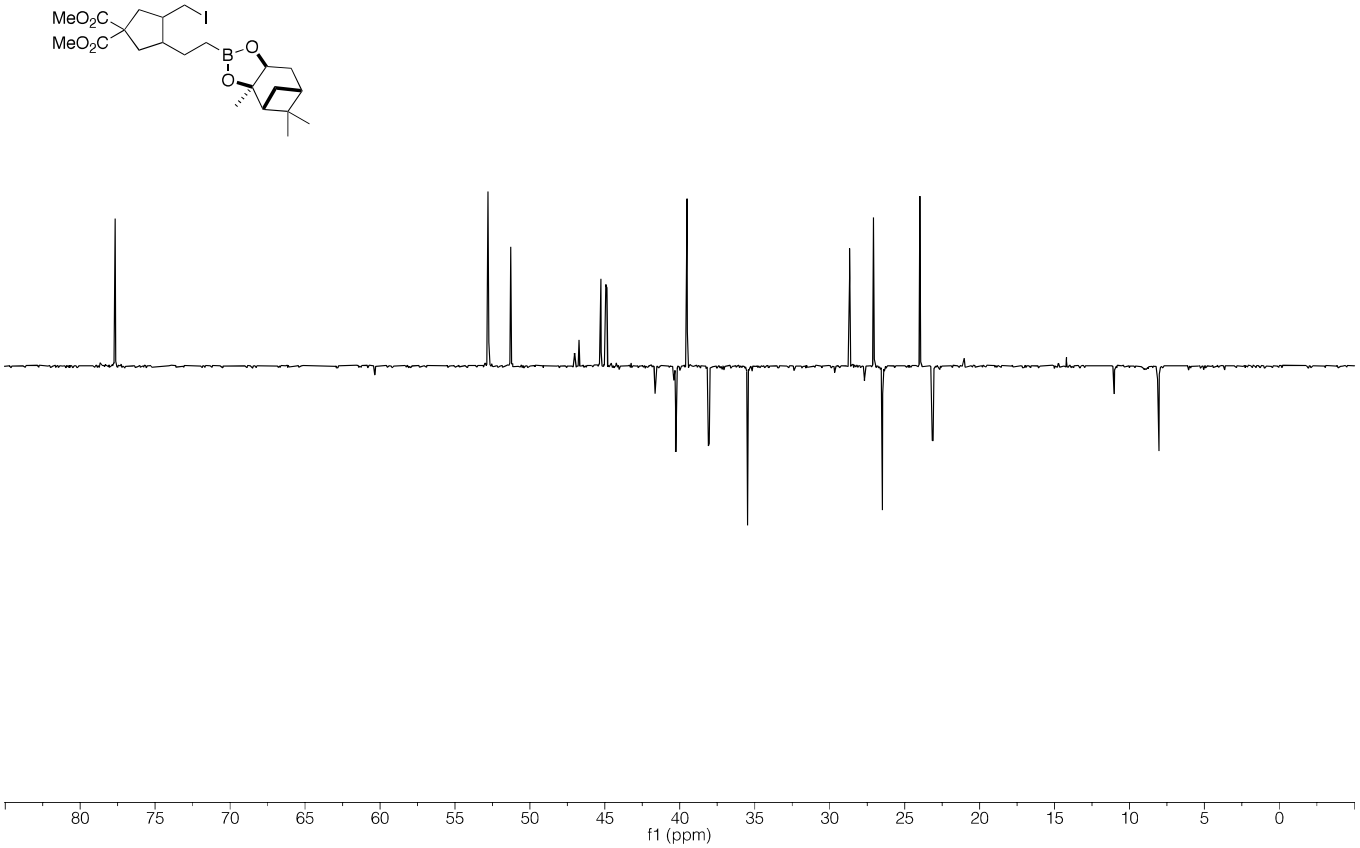
Dimethyl 3-(iodomethyl)-4-(2-((3aR,4R,6R,7aS)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

^{13}C-NMR (101 MHz, $CDCl_3$)



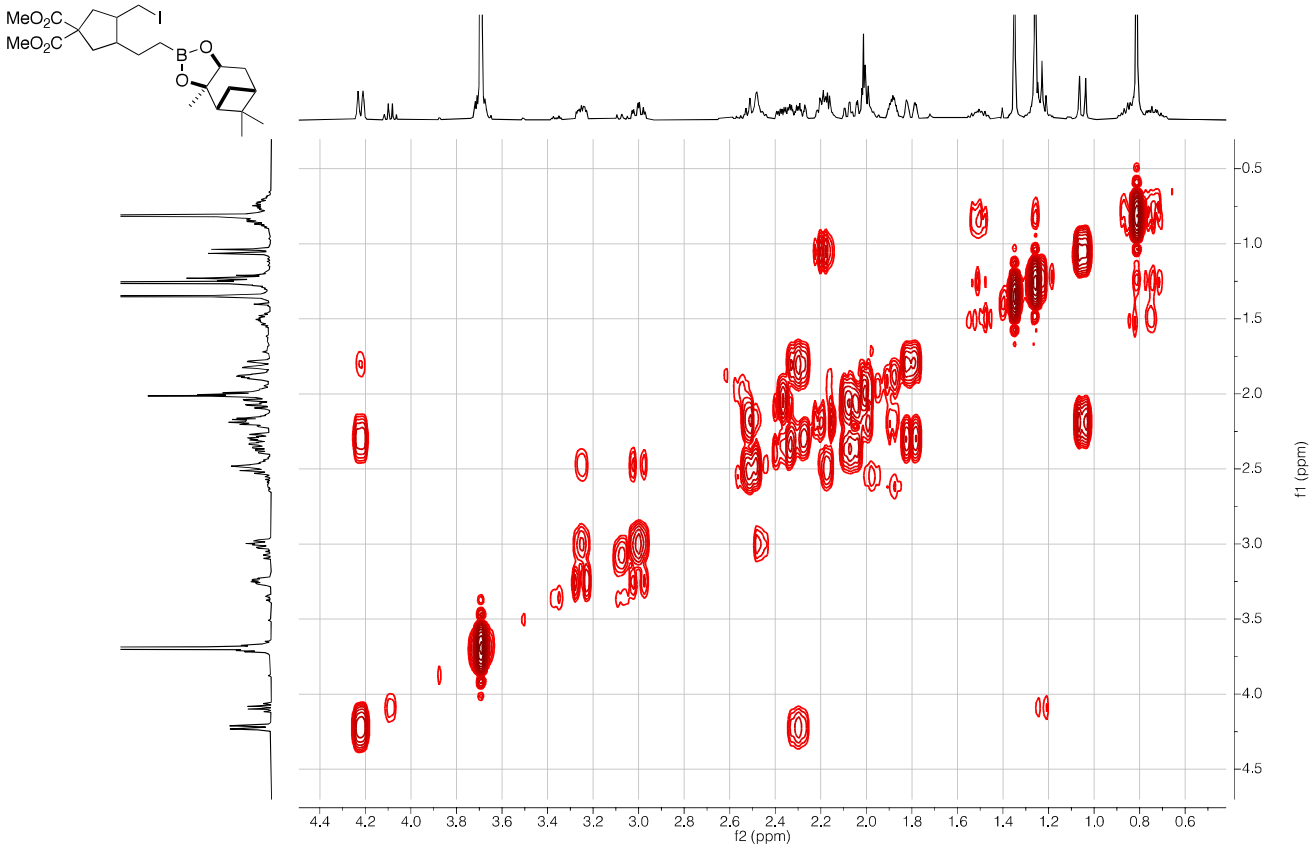
Dimethyl 3-(iodomethyl)-4-(2-((3aR,4R,6R,7aS)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

DEPT-135 NMR (101 MHz, $CDCl_3$)



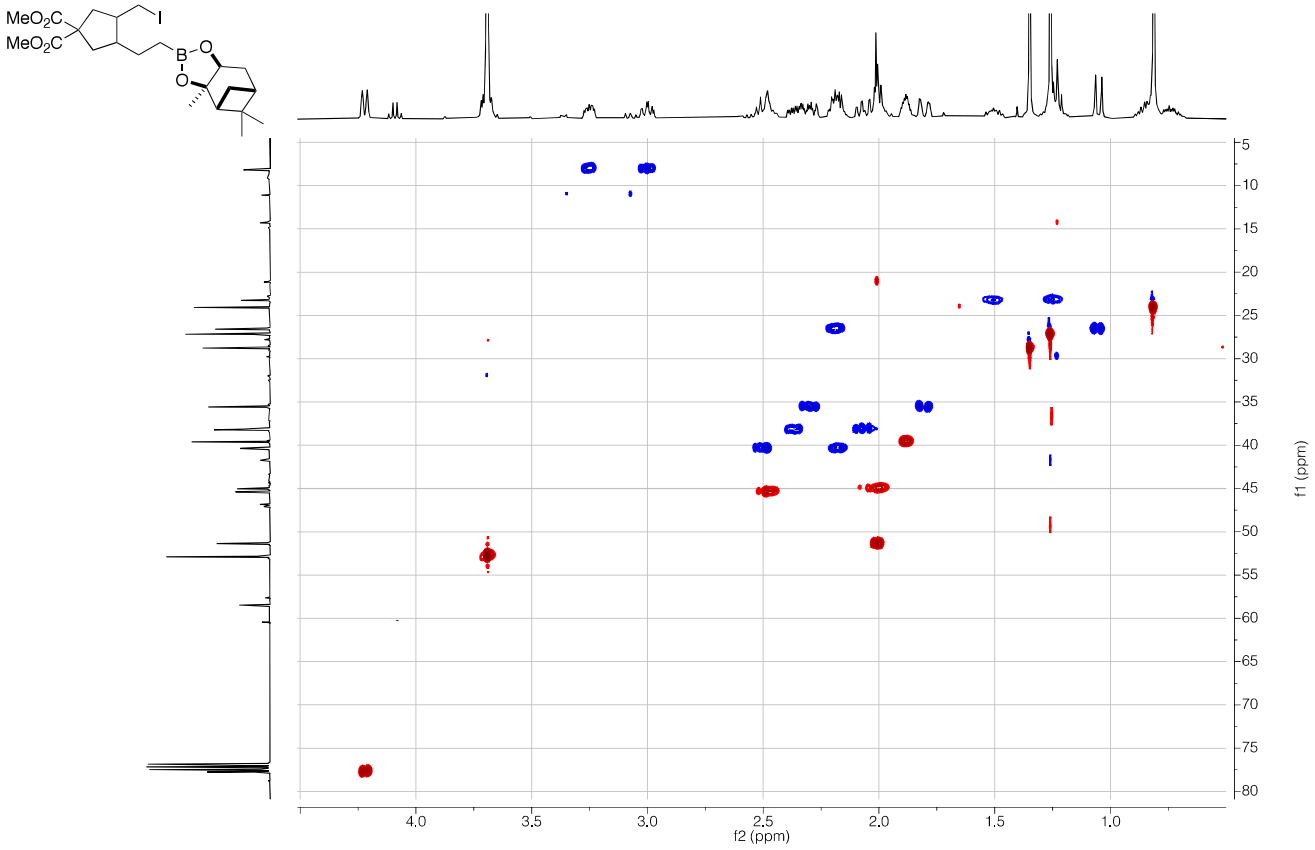
Dimethyl 3-(iodomethyl)-4-(2-((3aR,4R,6R,7aS)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

^1H, ^1H-COSY (400 MHz, $CDCl_3$)



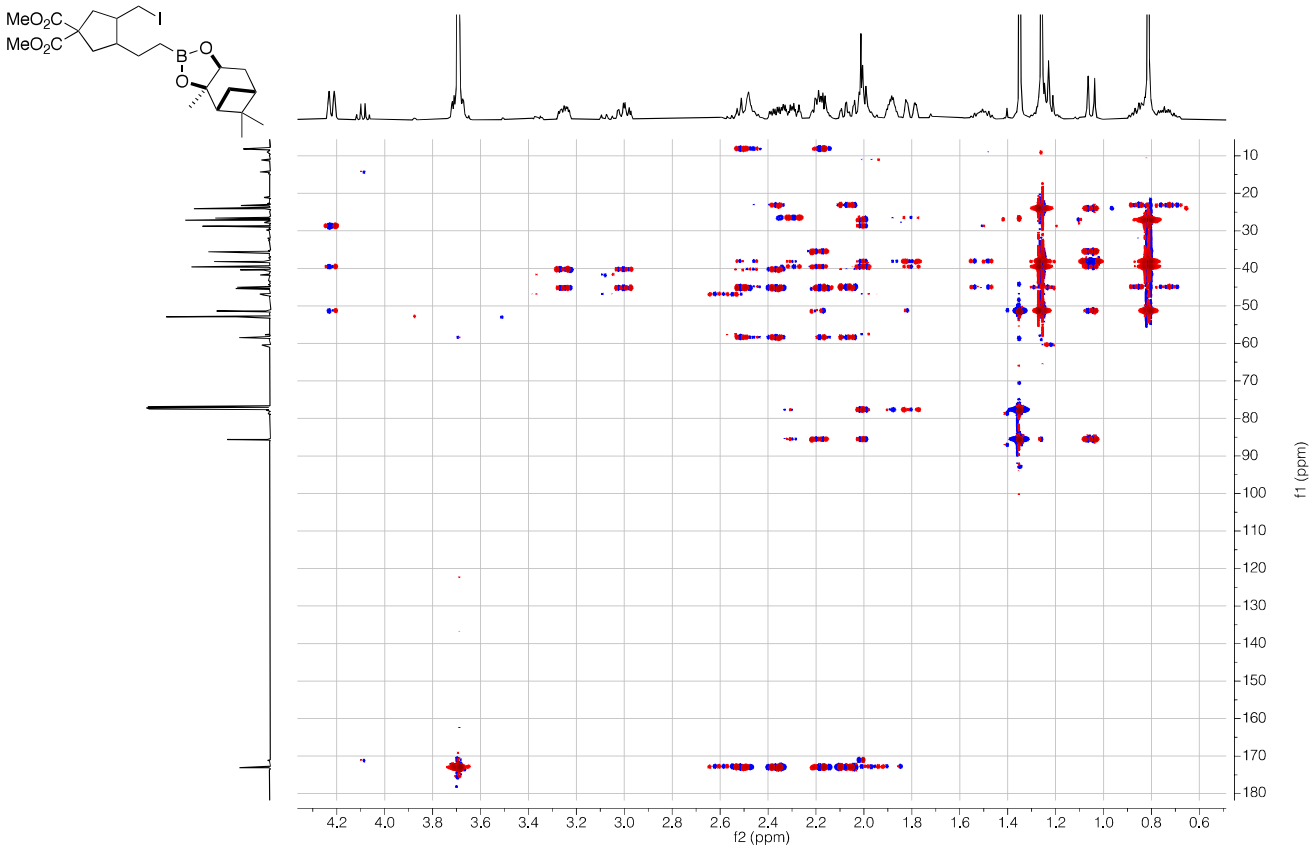
Dimethyl 3-(iodomethyl)-4-(2-((3aR,4R,6R,7aS)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



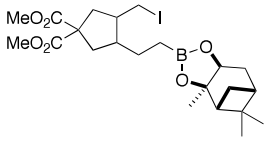
Dimethyl 3-(iodomethyl)-4-(2-((3aR,4R,6R,7aS)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



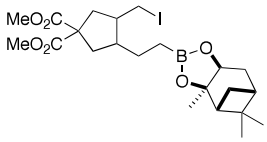
Dimethyl 3-(iodomethyl)-4-(2-((3aR,4R,6R,7aS)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

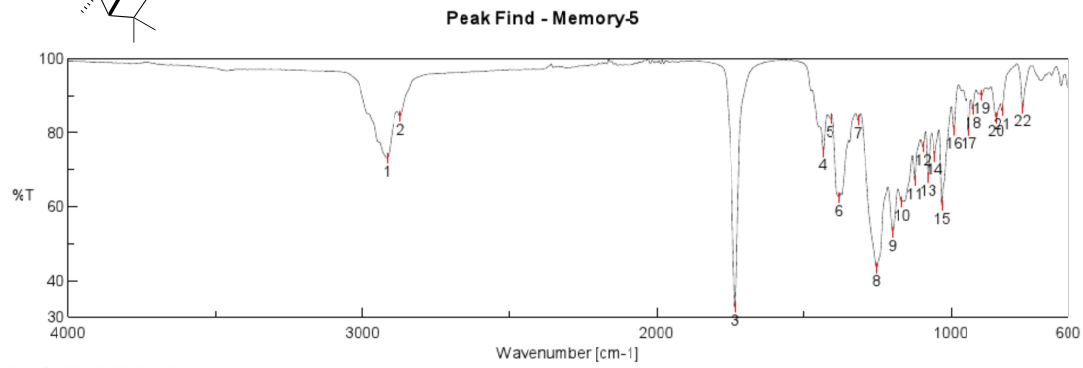
^{11}B-NMR (128 MHz, $CDCl_3$)



Dimethyl 3-(iodomethyl)-4-(2-((3aR,4R,6R,7aS)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



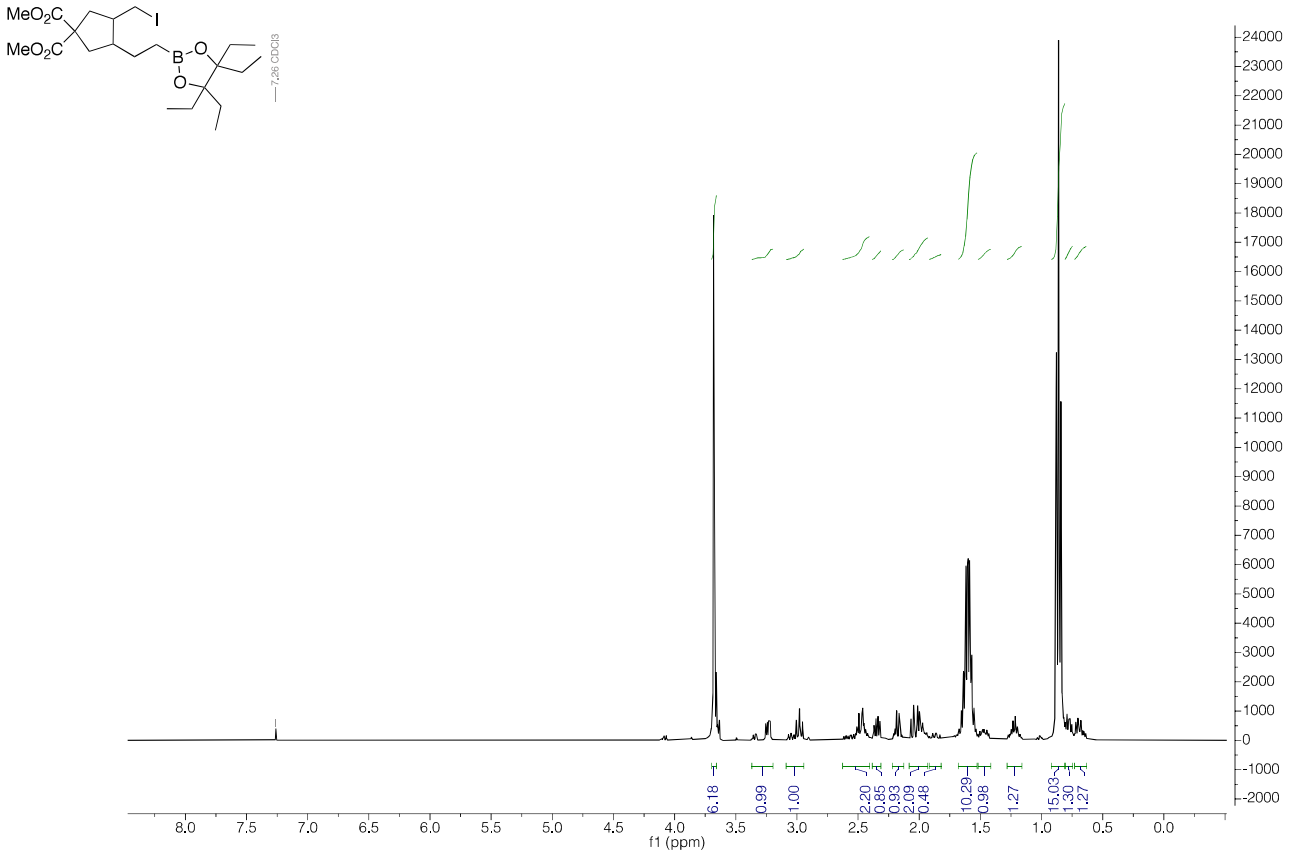


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2916.81	72.952	2	2869.56	84.2728	3	1730.8	32.6687
4	1433.82	74.6285	5	1409.71	83.6557	6	1375.96	62.2645
7	1313.29	83.2442	8	1249.65	43.2004	9	1196.61	52.9459
10	1164.79	61.0977	11	1121.4	66.8871	12	1094.4	76.0247
13	1077.05	67.6771	14	1054.87	73.4086	15	1029.8	60.2073
16	990.268	80.4562	17	938.199	80.4289	18	922.771	86.1968
19	892.88	89.9241	20	843.704	83.7593	21	823.455	85.8069
22	754.995	86.4708						

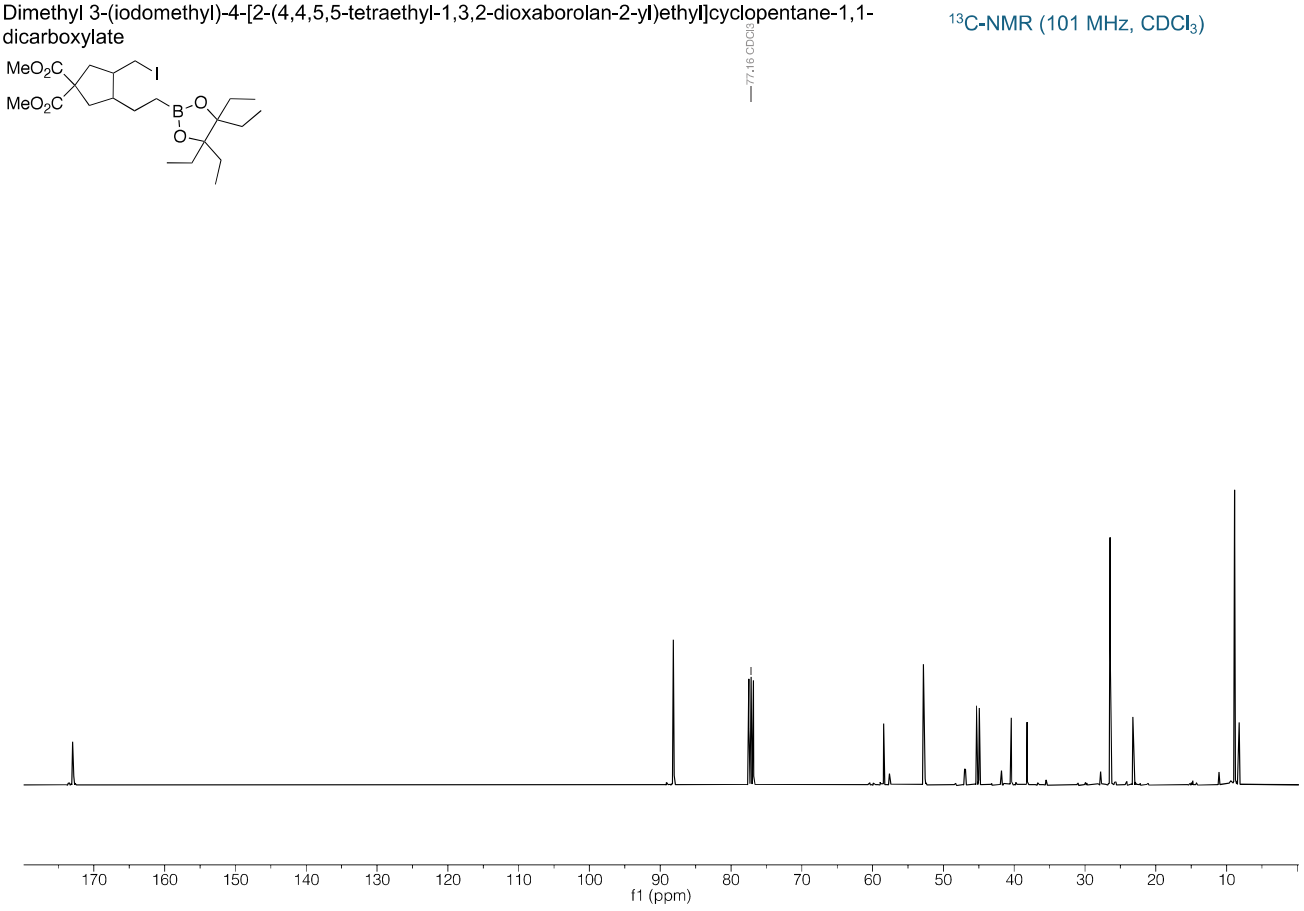
Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)

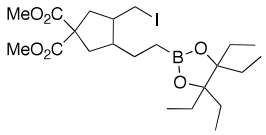


Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

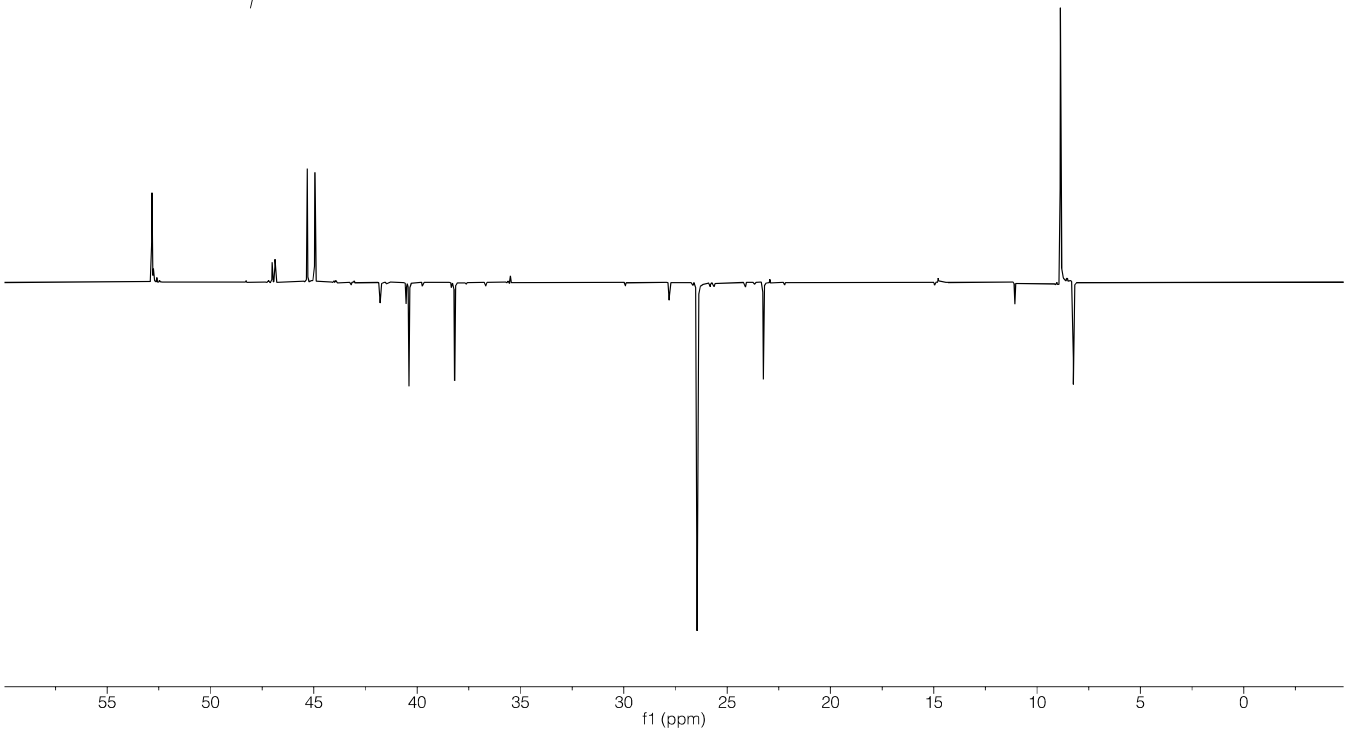
^{13}C-NMR (101 MHz, $CDCl_3$)



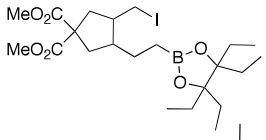
Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate



DEPT-135 NMR (101 MHz, $CDCl_3$)



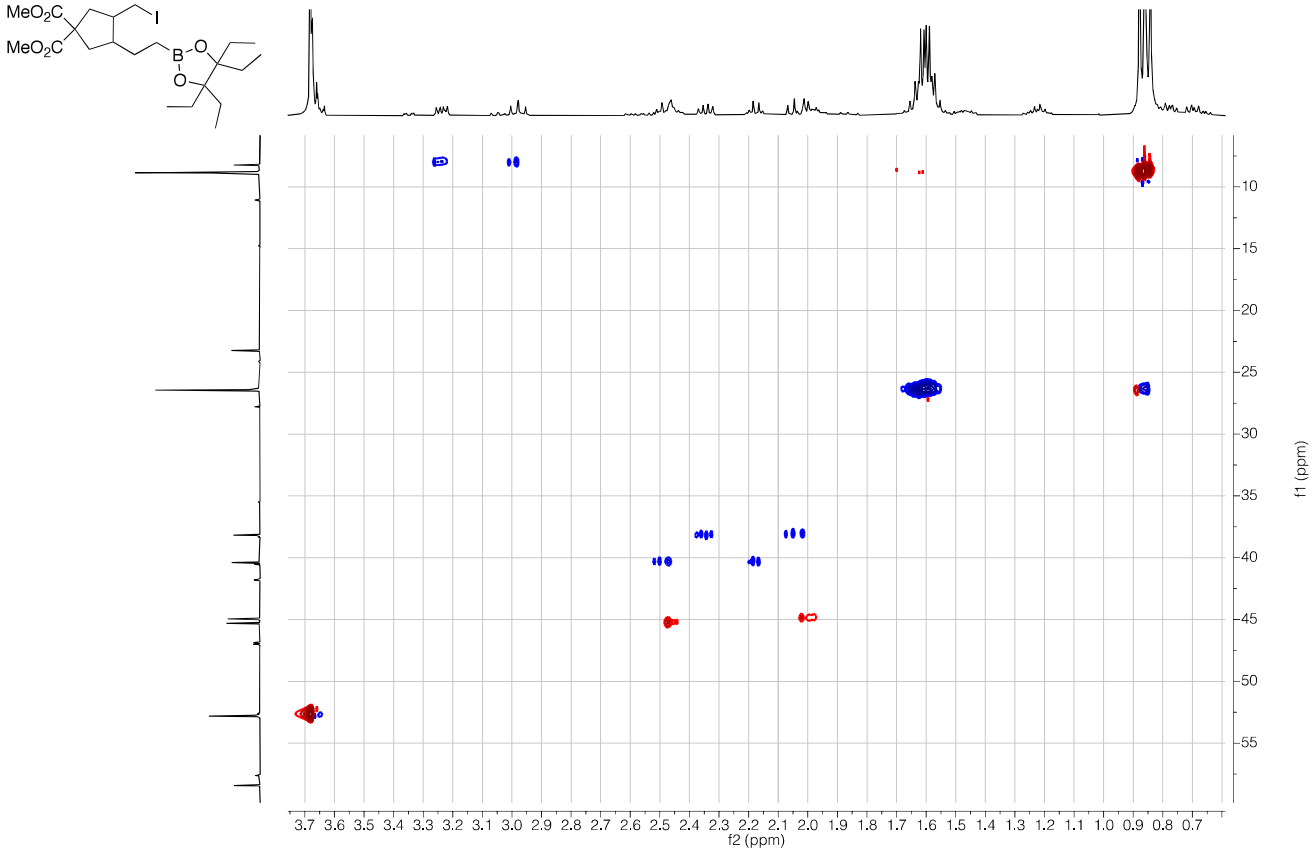
Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate



^1H, ^1H-COSY (400 MHz, $CDCl_3$)

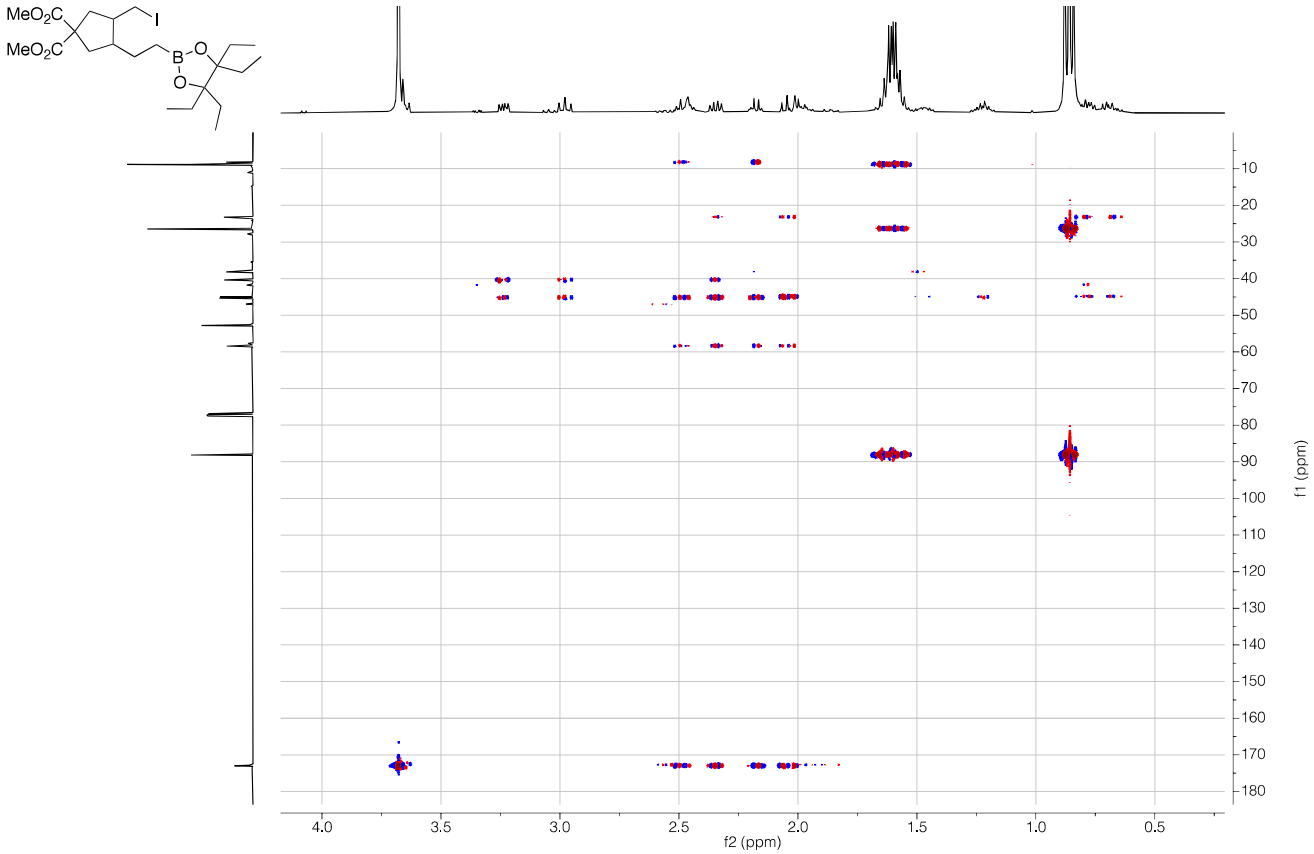
Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)

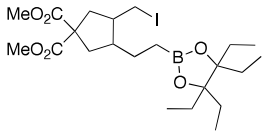


Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

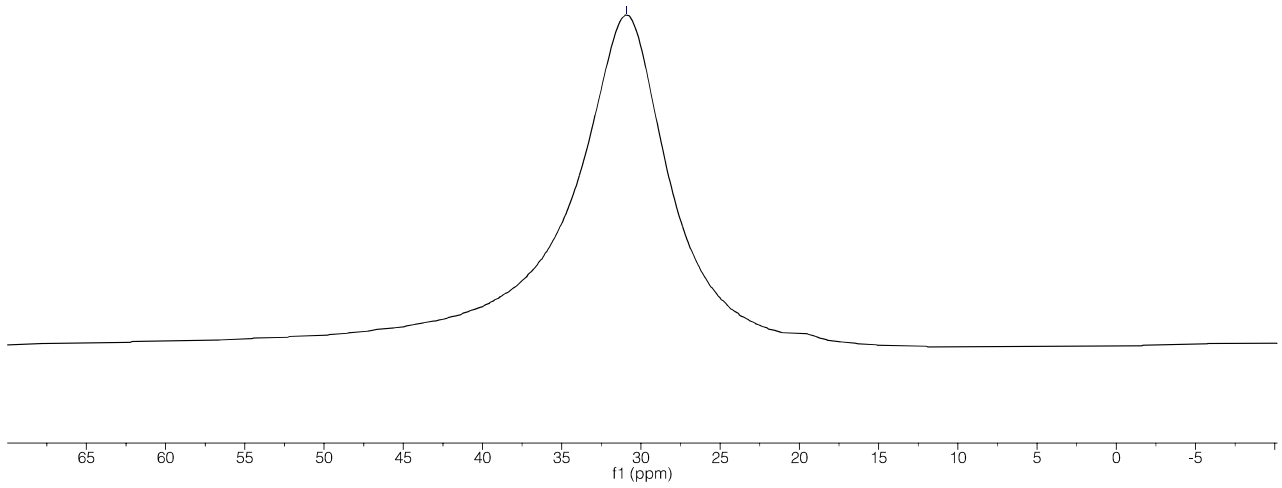
^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



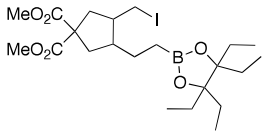
Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate



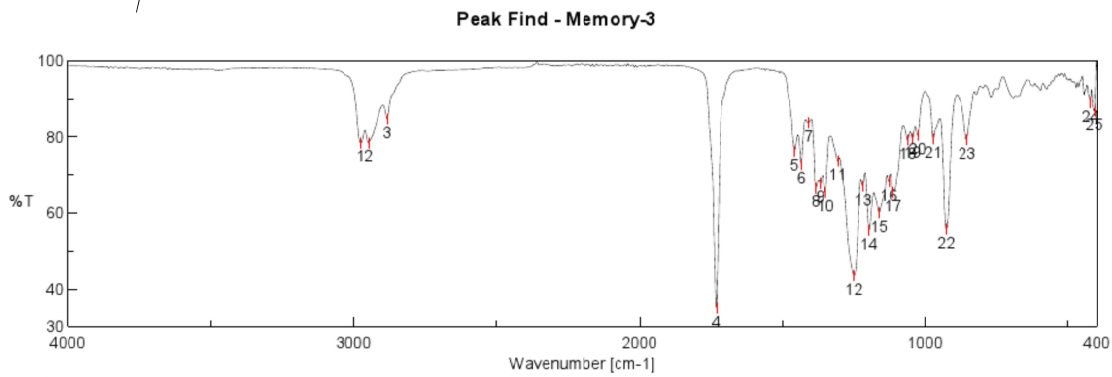
^{11}B-NMR (128 MHz, $CDCl_3$)



Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate



FT-IR, ATR-diamond

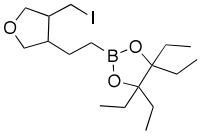


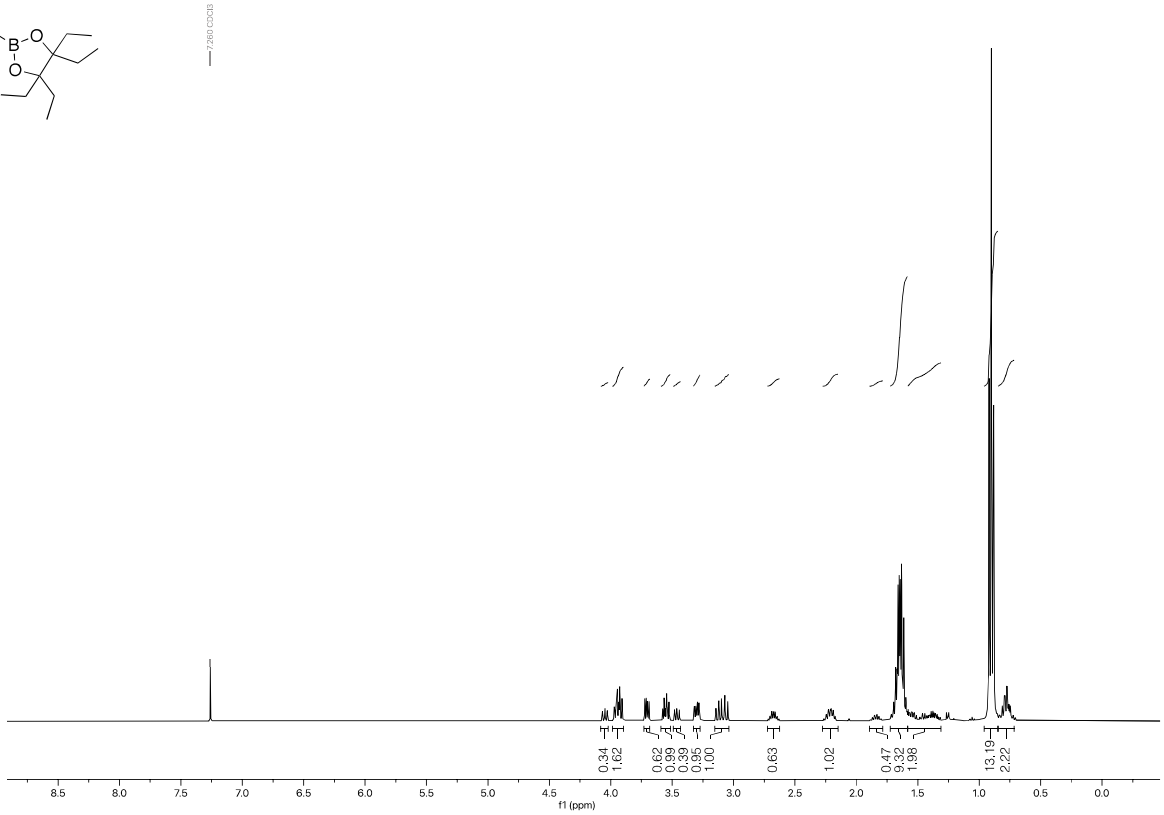
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2973.7	78.2179	2	2947.66	78.2659	3	2883.06	84.5227
4	1731.76	34.9309	5	1456.96	76.0002	6	1433.82	72.5582
7	1408.75	83.5515	8	1383.68	66.4028	9	1367.28	67.6246
10	1348.96	65.2246	11	1305.57	73.5021	12	1249.65	43.4323
13	1218.79	66.8998	14	1196.51	55.331	15	1160.94	59.9628
16	1127.19	68.1727	17	1112.73	65.2173	18	1060.66	79.0226
19	1043.3	79.3791	20	1025.94	80.2736	21	970.983	79.3248
22	926.628	55.6796	23	854.311	79.1699	24	422.334	88.8442
25	409.799	86.6245						

4,4,5,5-tetraethyl-2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-1,3,2-dioxaborolane

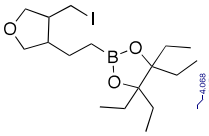
^{1}H-NMR (400 MHz, $CDCl_3$)

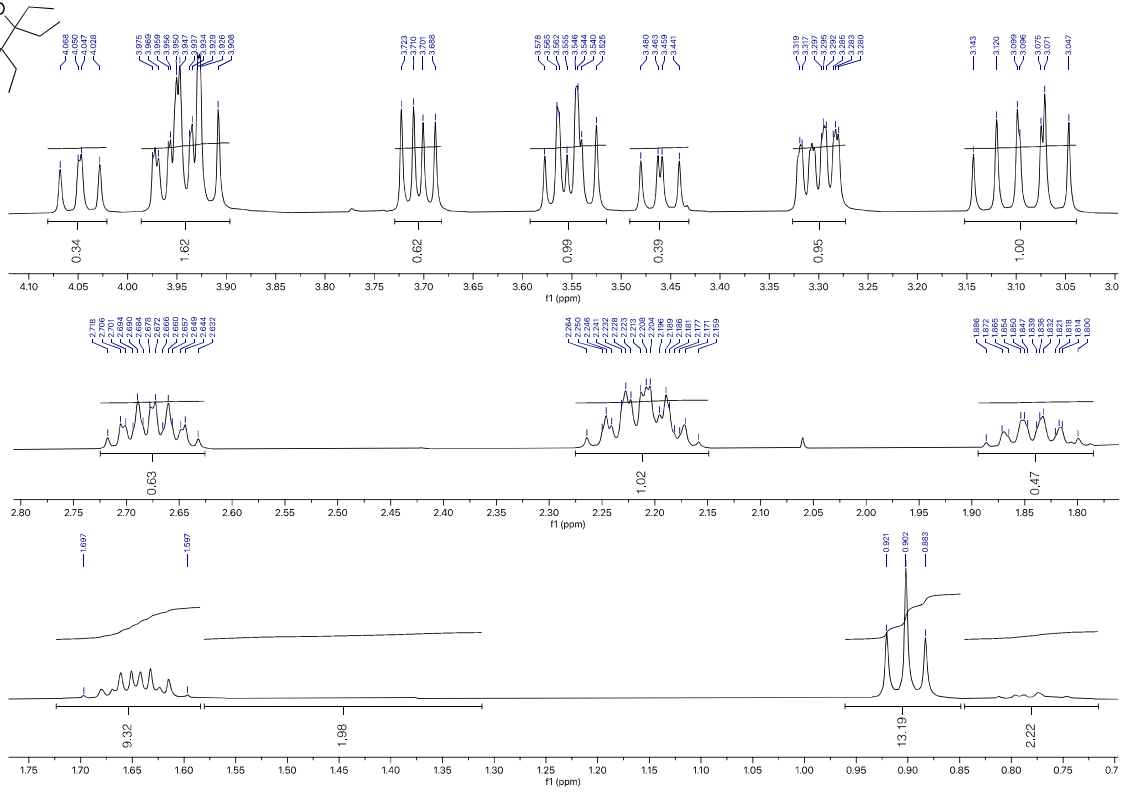




4,4,5,5-tetraethyl-2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-1,3,2-dioxaborolane

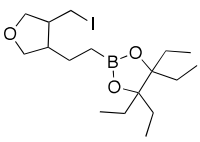
^{1}H-NMR (400 MHz, $CDCl_3$)





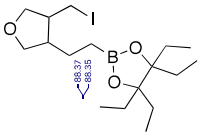
4,4,5,5-tetraethyl-2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-1,3,2-dioxaborolane

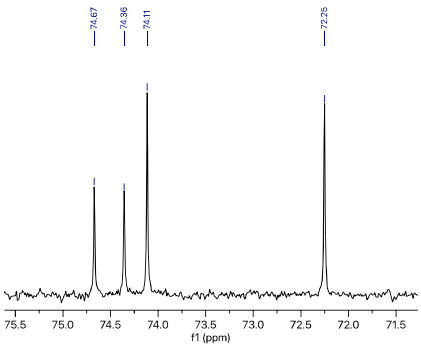
^{13}C-NMR (101 MHz, $CDCl_3$)

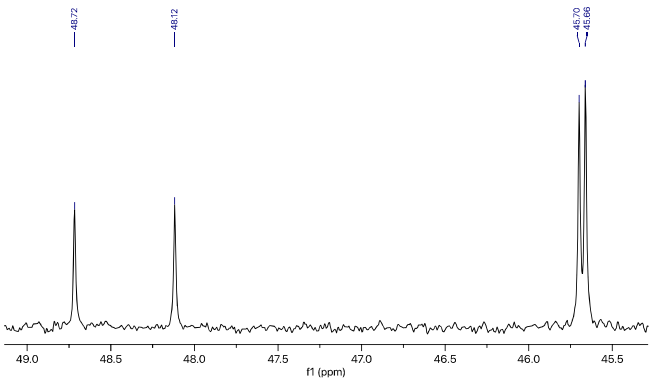


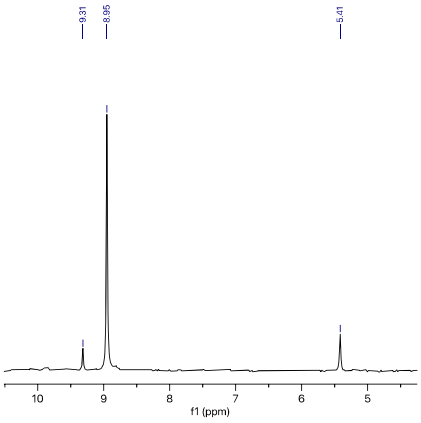
4,4,5,5-tetraethyl-2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-1,3,2-dioxaborolane

^{13}C-NMR (101 MHz, $CDCl_3$)



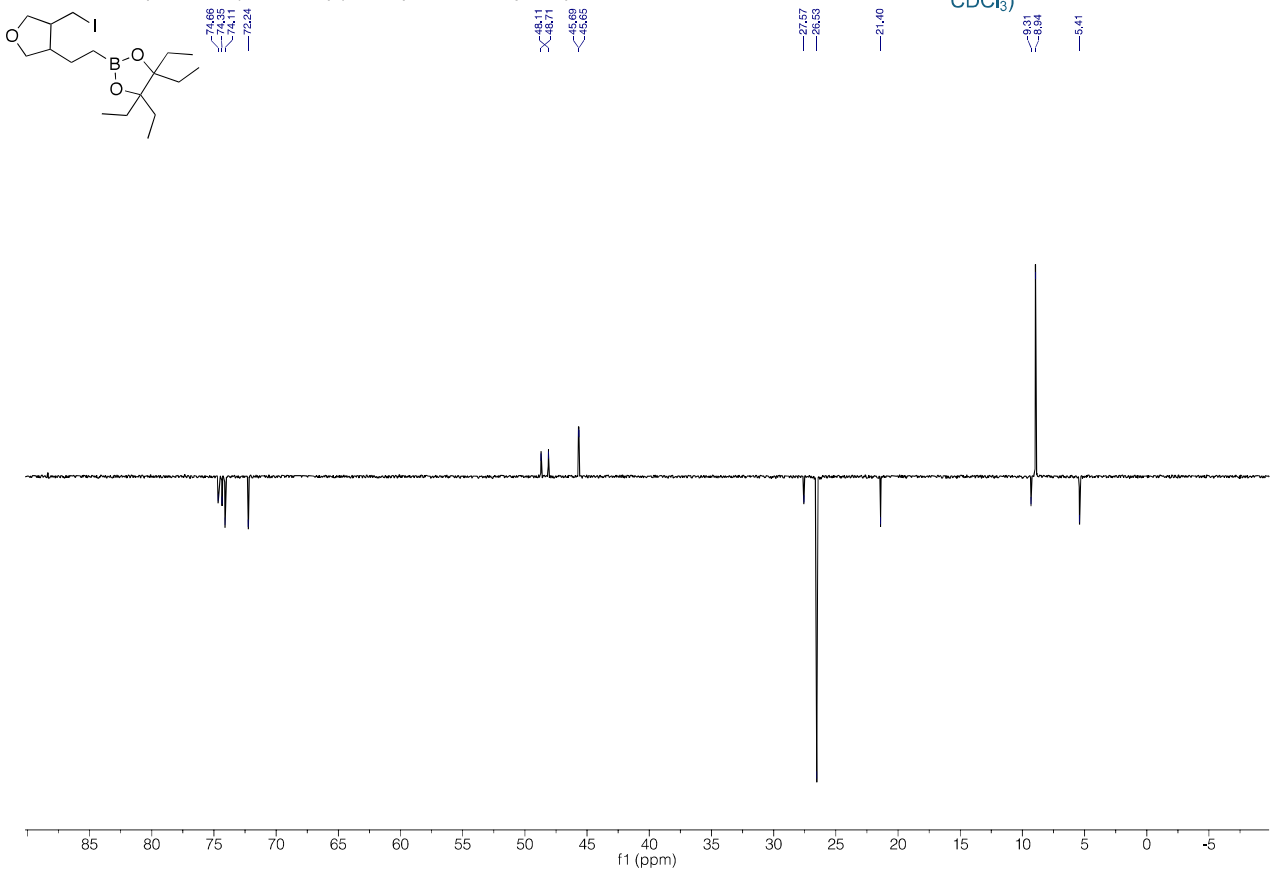






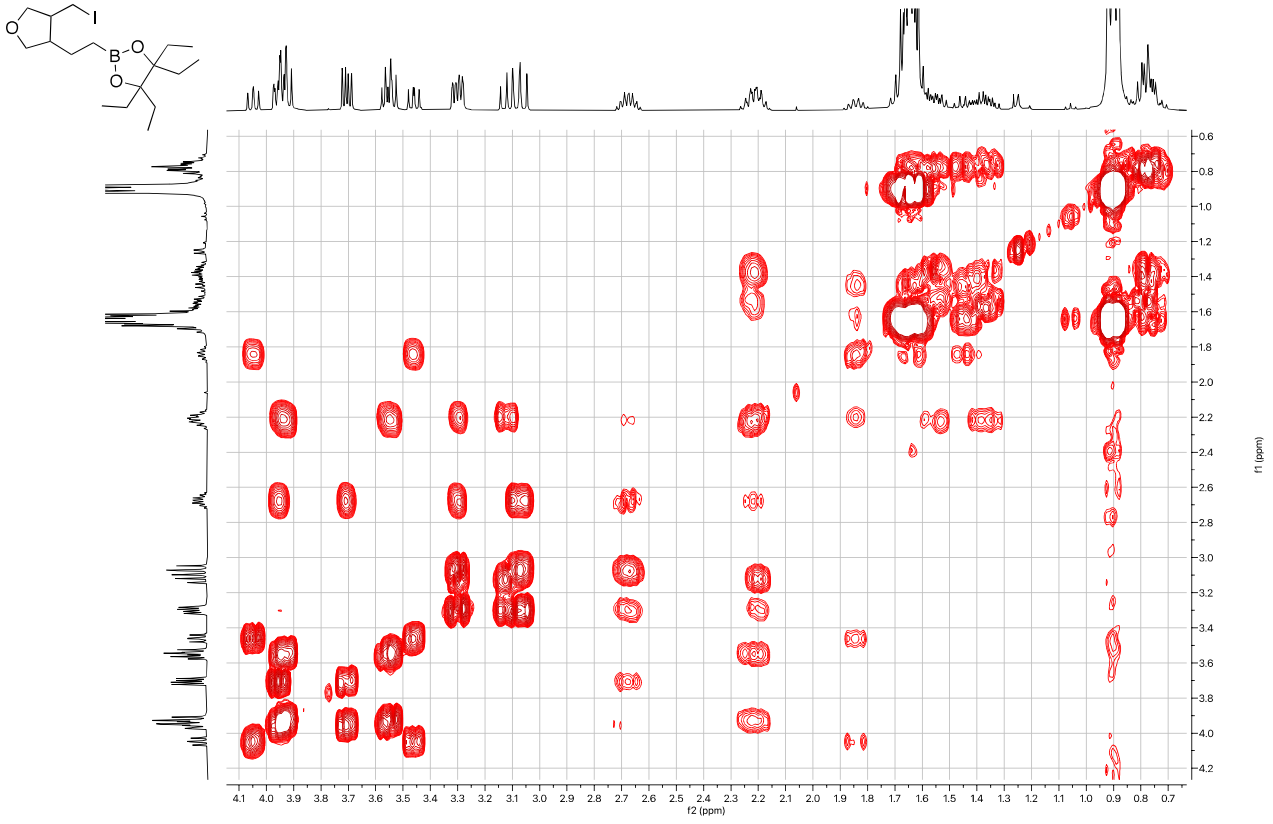
4,4,5,5-tetraethyl-2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-1,3,2-dioxaborolane

DEPT-135 NMR (101 MHz, $CDCl_3$)



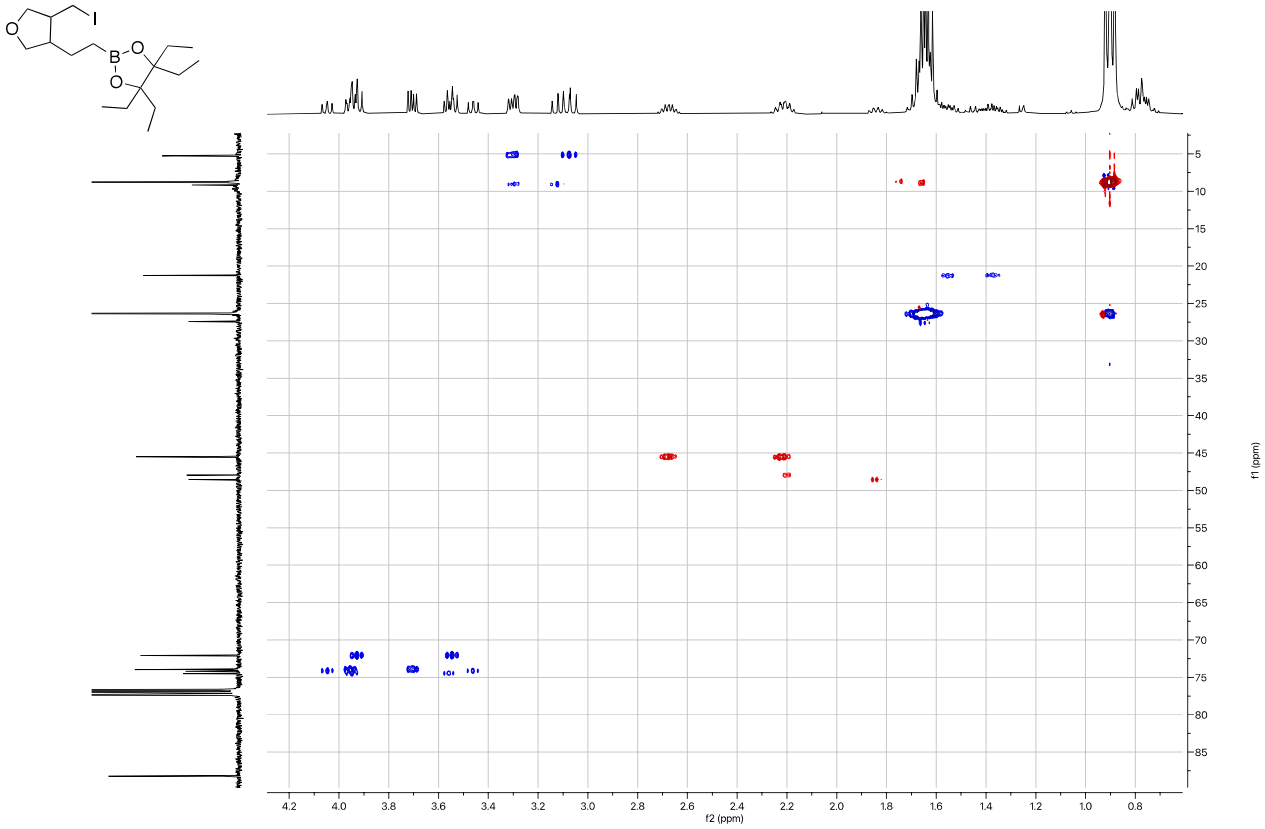
4,4,5,5-tetraethyl-2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-1,3,2-dioxaborolane

^1H, ^1H-COSY (400 MHz, $CDCl_3$)



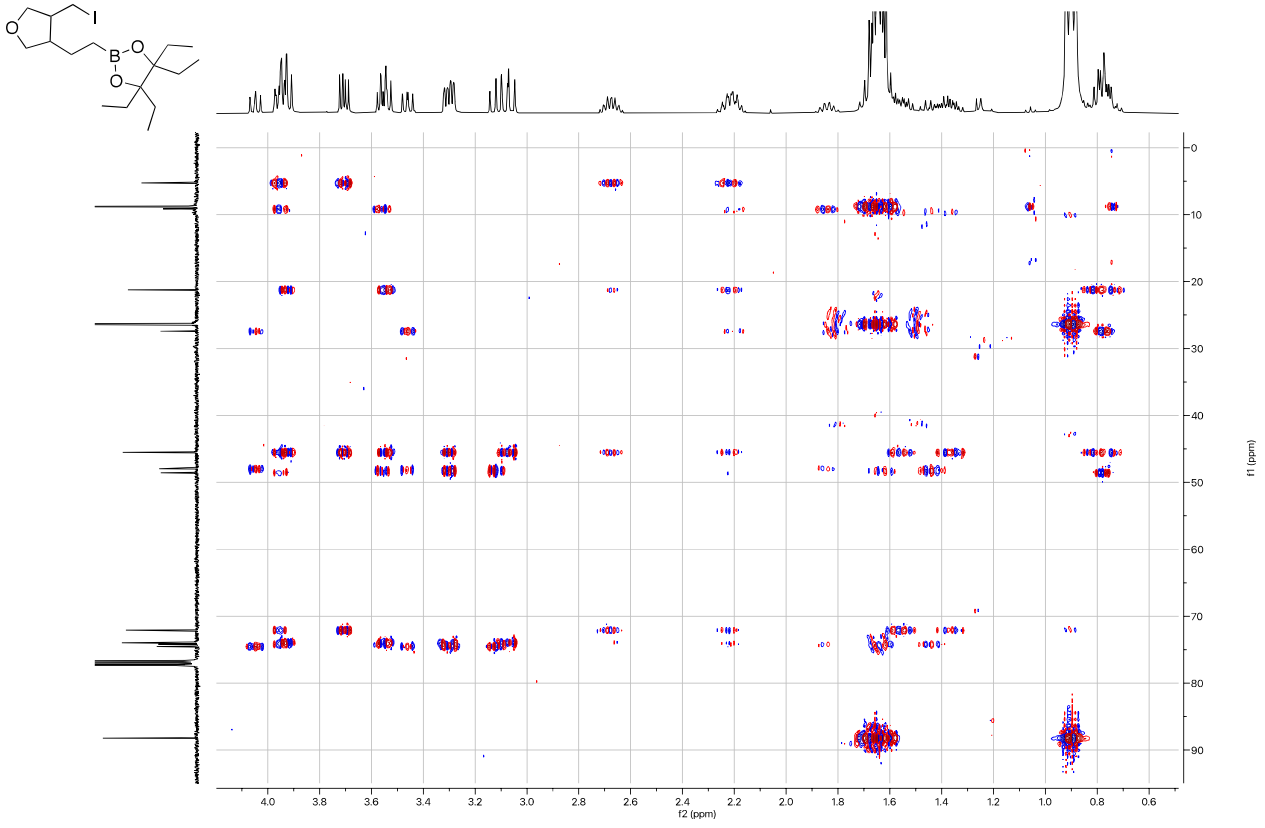
4,4,5,5-tetraethyl-2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-1,3,2-dioxaborolane

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



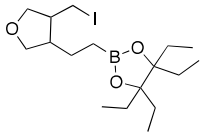
4,4,5,5-tetraethyl-2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-1,3,2-dioxaborolane

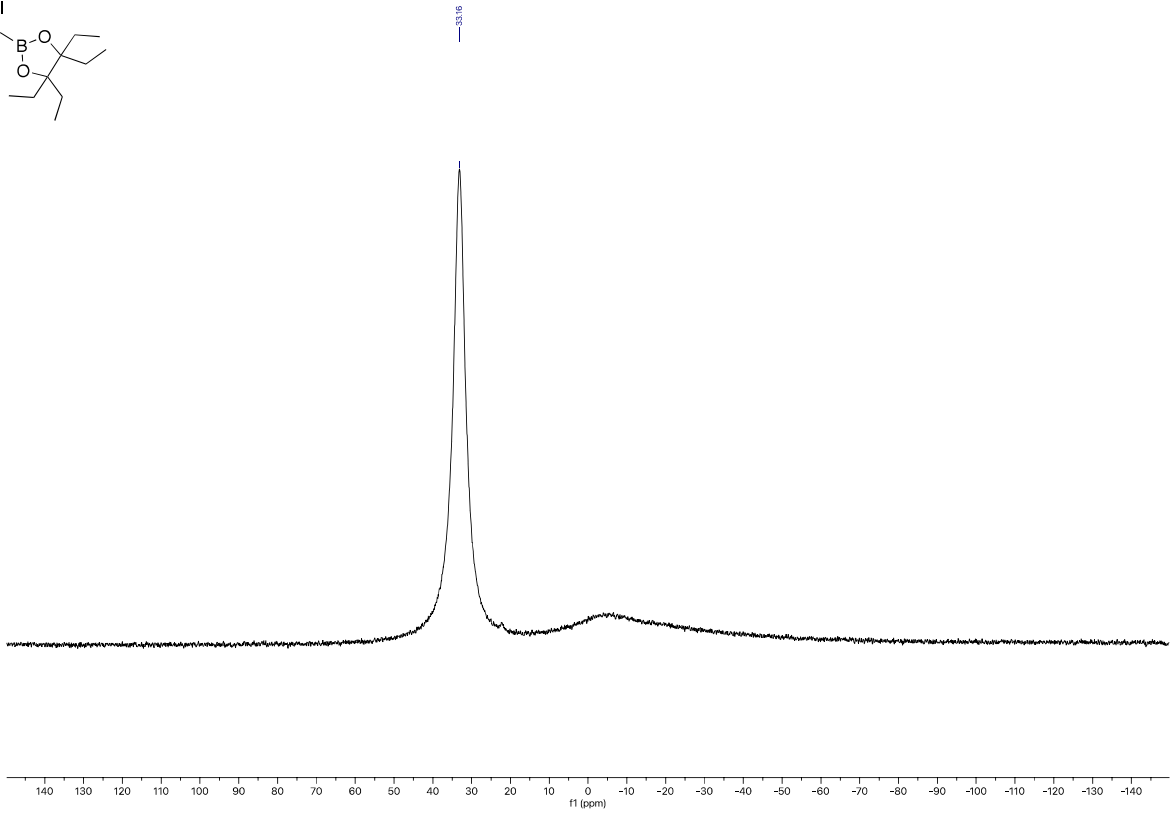
^{1}H, ^{13}C-HMBC(400 MHz, $CDCl_3$)



4,4,5,5-tetraethyl-2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-1,3,2-dioxaborolane

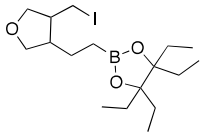
^{11}B-NMR (128 MHz, $CDCl_3$)

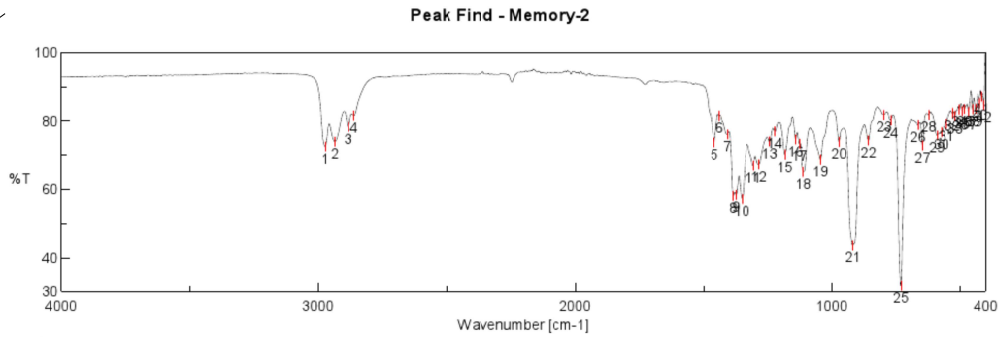




4,4,5,5-tetraethyl-2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-1,3,2-dioxaborolane

FT-IR, ATR-diamond



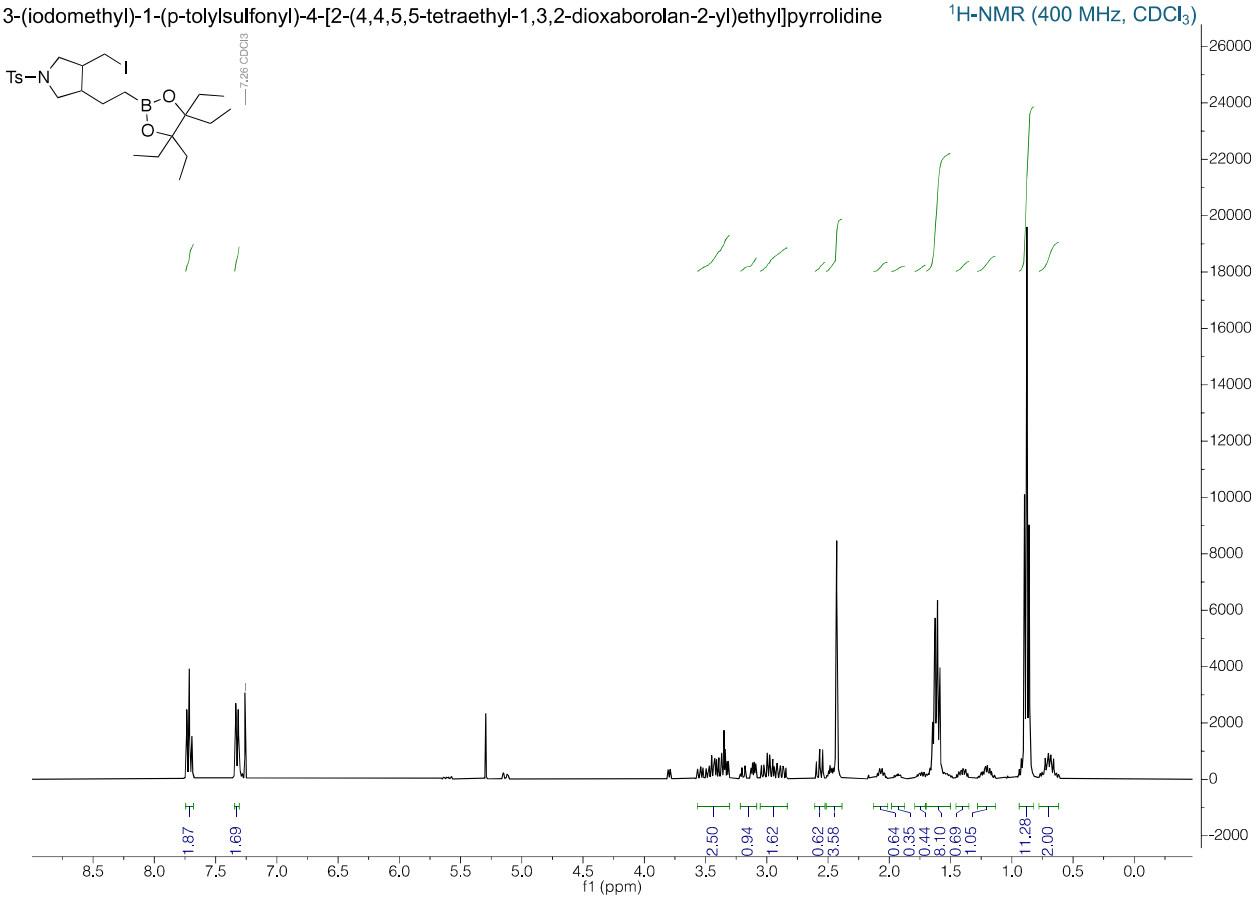


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2971.77	72.3341	2	2933.2	73.7789	3	2882.09	78.1649
4	2859.92	81.4025	5	1456.96	73.5559	6	1437.67	81.3465
7	1406.82	75.93	8	1383.68	57.9027	9	1372.1	58.1929
10	1348.96	57.0668	11	1305.57	66.8039	12	1283.39	67.151
13	1241.93	73.8481	14	1221.68	76.8002	15	1183.11	70.0193
16	1140.69	74.4411	17	1126.22	73.1665	18	1111.76	64.9948
19	1044.26	68.5442	20	970.983	73.7048	21	917.95	43.4875
22	856.239	74.103	23	795.493	81.6195	24	769.458	80.0768
25	729.925	31.6828	26	664.357	78.7044	27	647.001	72.6384
28	623.859	81.593	29	591.075	75.6722	30	572.755	76.6315
31	554.434	79.007	32	531.293	82.1975	33	519.722	81.2683
34	503.33	83.166	35	491.759	82.7064	36	483.081	83.308
37	467.653	82.5022	38	453.19	83.2415	39	441.619	83.3545
40	423.298	85.0257	41	415.585	86.9663	42	406.907	84.5606

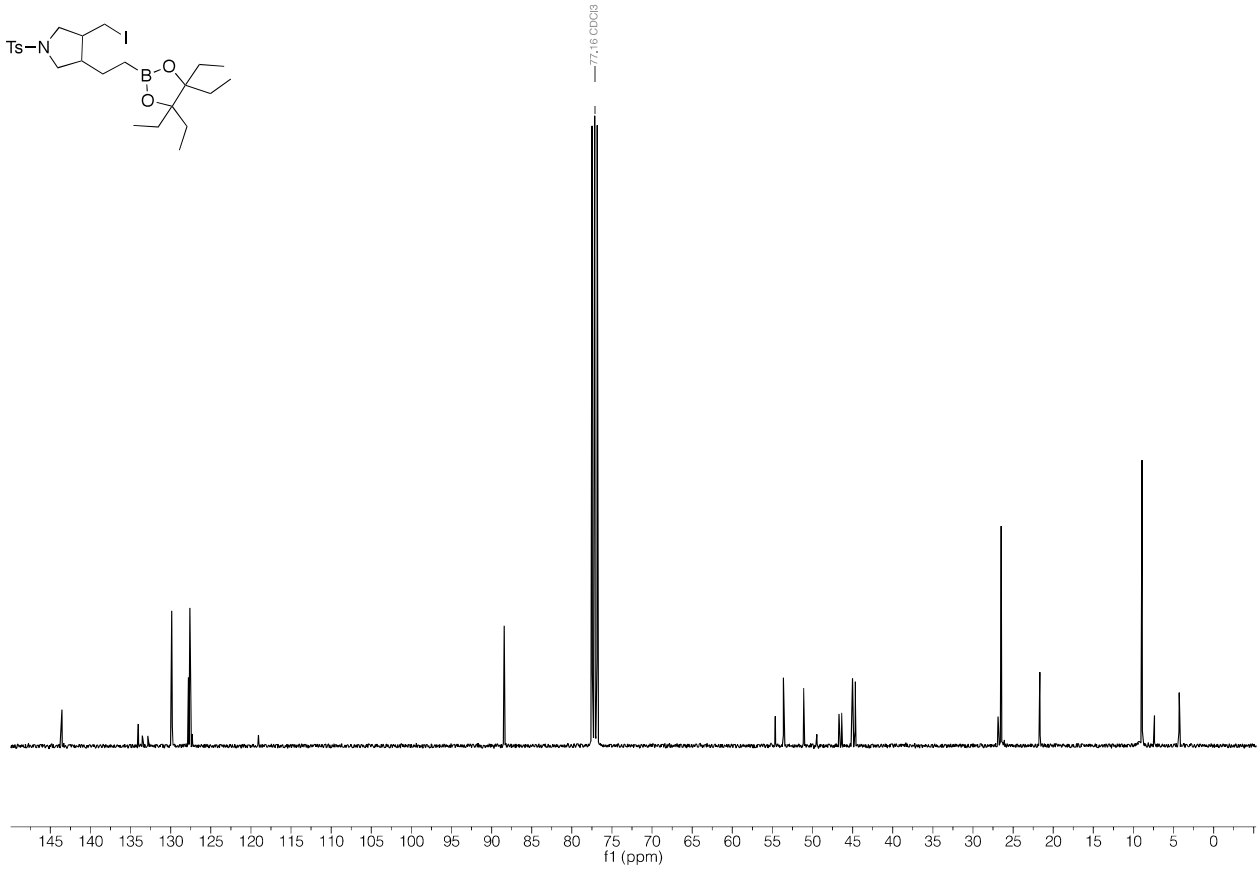
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

^{1}H-NMR (400 MHz, $CDCl_3$)



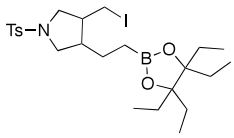
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

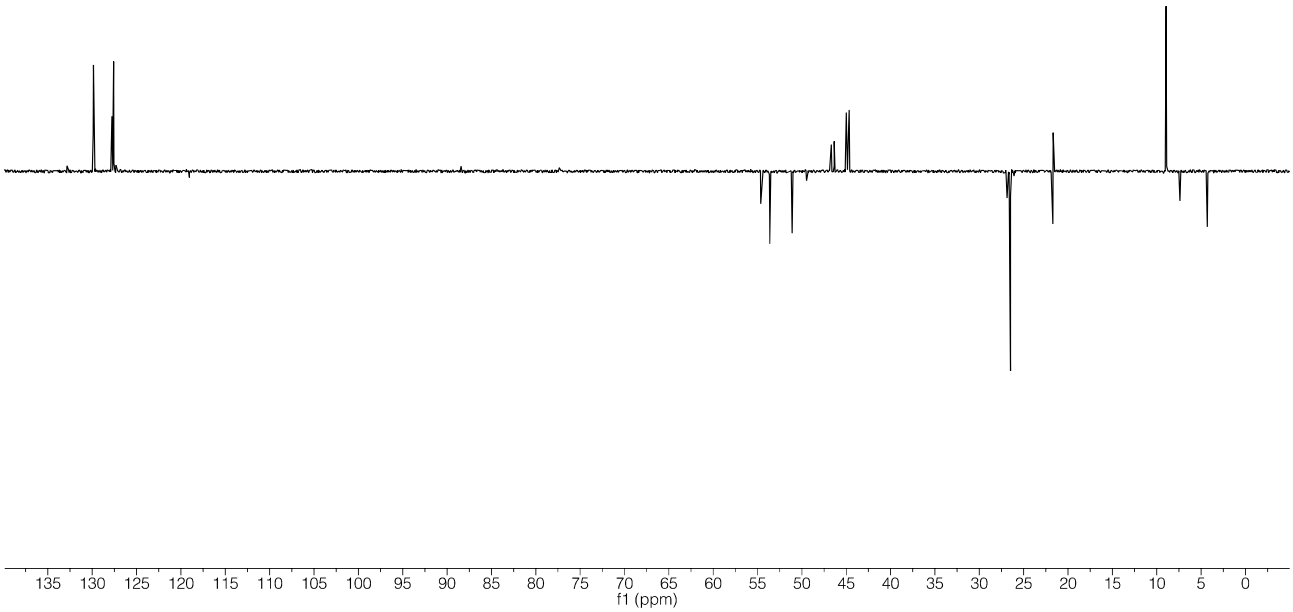
^{13}C-NMR (101 MHz, $CDCl_3$)



3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

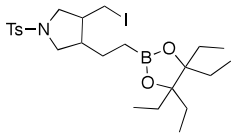
DEPT-135 NMR (101 MHz, $CDCl_3$)





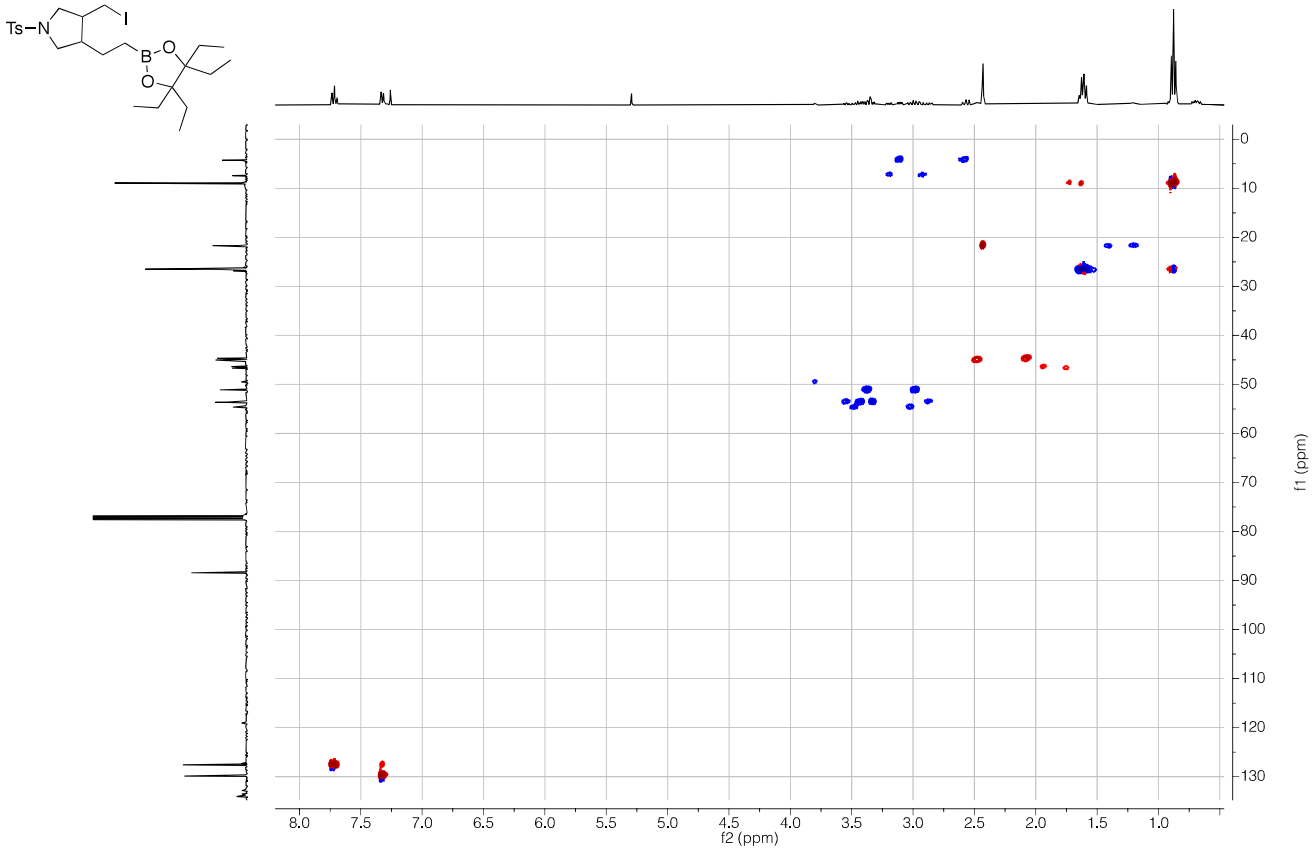
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

^1H, ^1H-COSY (400 MHz, $CDCl_3$)



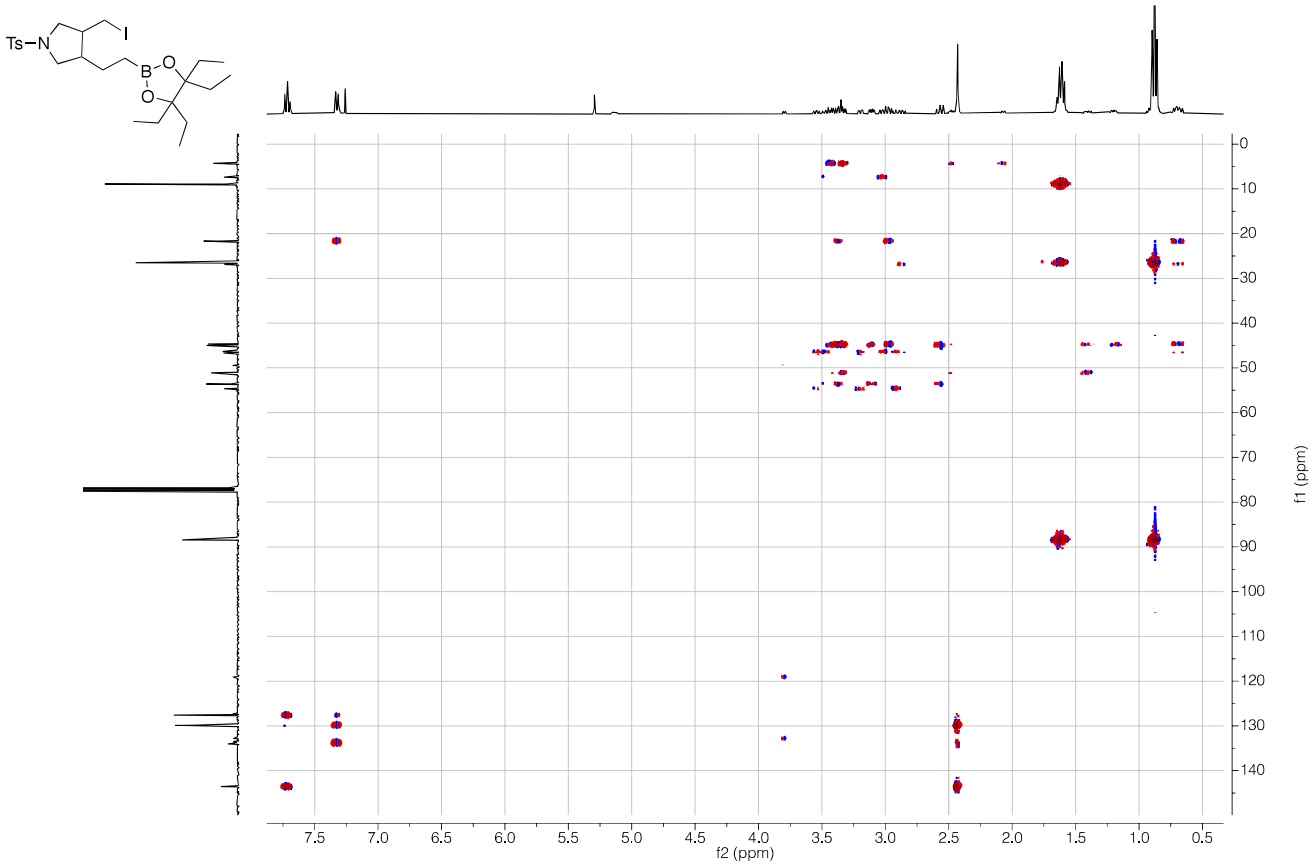
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)

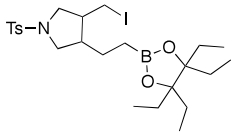


3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

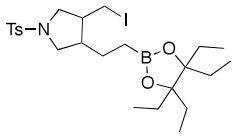
^{1}H, ^{13}C-HMBC(400 MHz, $CDCl_3$)

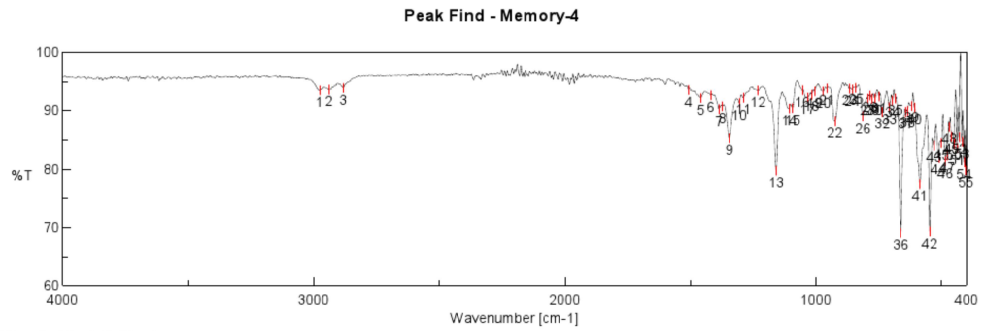


3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine ^{11}B-NMR (128 MHz, $CDCl_3$)



3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine FT-IR, ATR-diamond



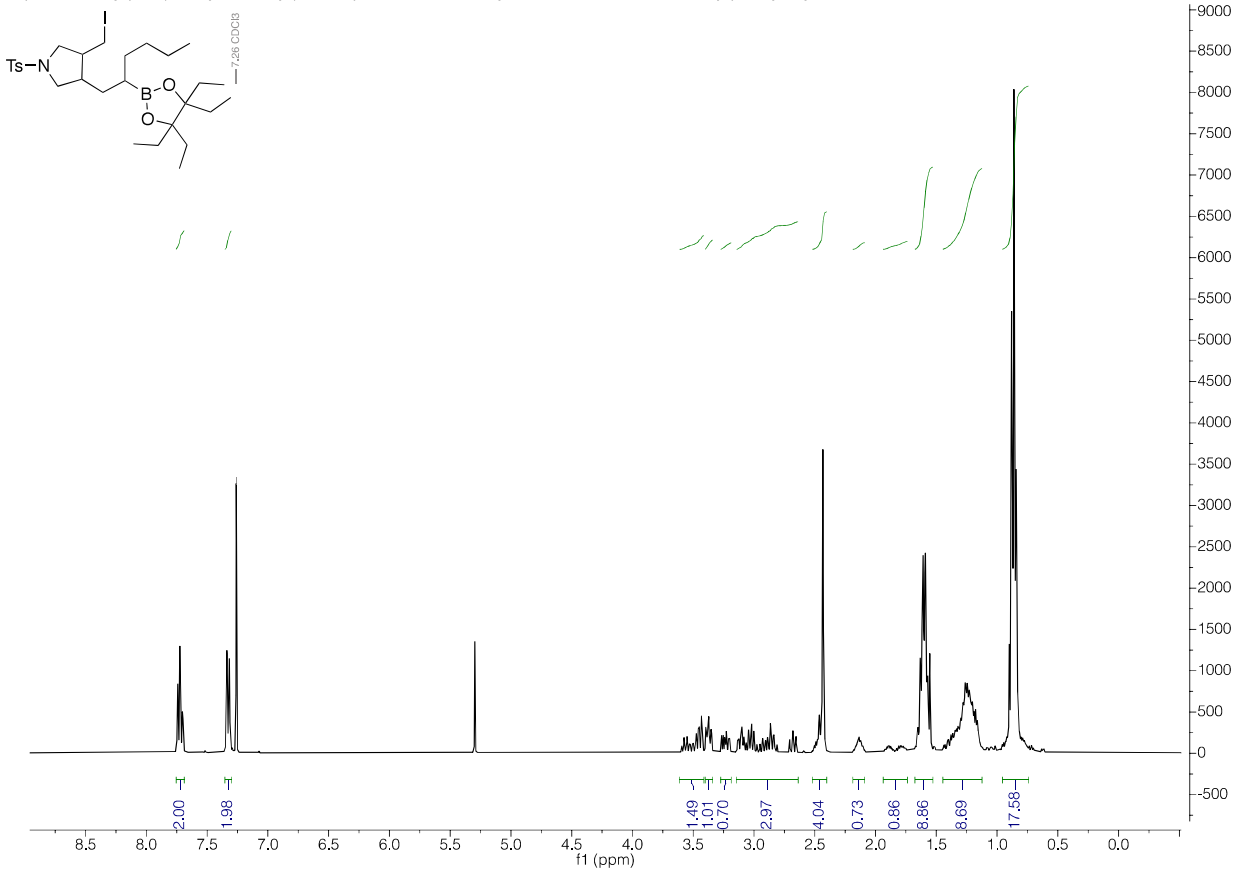


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2976.59	93.4167	2	2938.98	93.5201	3	2881.13	93.8117
4	1506.13	93.4519	5	1457.92	92.0646	6	1418.39	92.5765
7	1385.6	90.1836	8	1371.14	90.6494	9	1344.14	85.189
10	1304.61	91.2268	11	1288.22	92.1225	12	1229.4	93.3769
13	1157.08	79.6263	14	1105.98	90.2335	15	1091.51	90.3174
16	1053.91	93.4365	17	1033.66	92.1598	18	1016.3	92.646
19	1004.73	93.2416	20	970.019	93.2259	21	956.52	93.7535
22	924.7	88.1095	23	865.882	93.6991	24	855.275	93.5548
25	839.847	93.8399	26	811.885	88.9705	27	793.564	91.9916
28	784.886	92.4985	29	776.208	91.9581	30	764.637	92.0327
31	747.281	92.3396	32	734.746	89.6742	33	706.783	90.5245
34	694.248	91.593	35	682.677	91.9924	36	661.464	69.0126
37	641.215	89.6852	38	634.466	89.8661	39	619.038	90.7091
40	607.467	90.4293	41	585.29	77.3554	42	545.756	69.2588
43	528.4	83.9486	44	511.044	81.8391	45	499.473	84.3597
46	483.081	81.2497	47	475.367	82.2568	48	467.653	87.1267
49	458.975	85.476	50	450.297	84.2921	51	436.798	83.5051

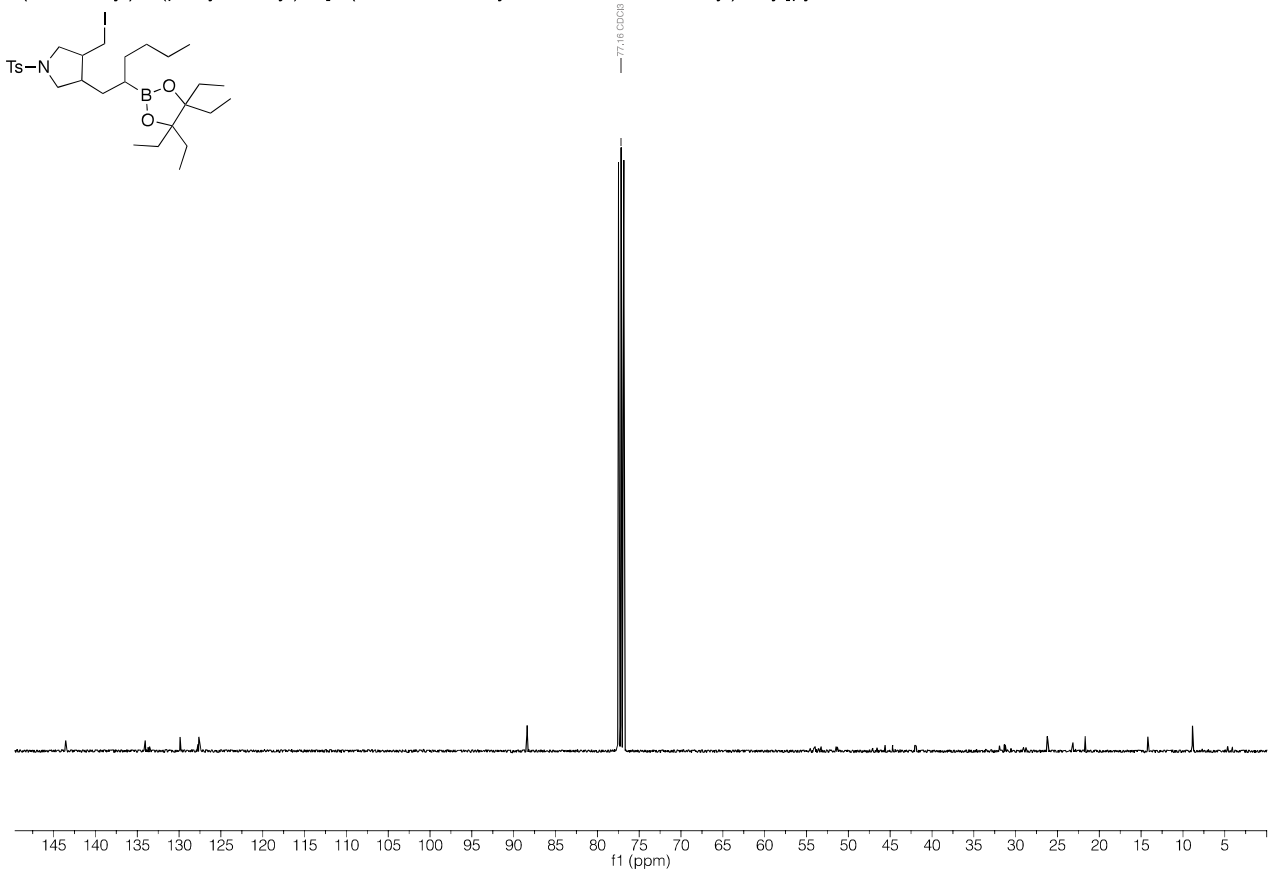
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

^{1}H-NMR (400 MHz, $CDCl_3$)



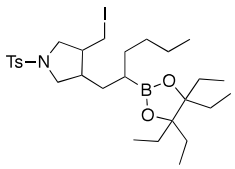
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

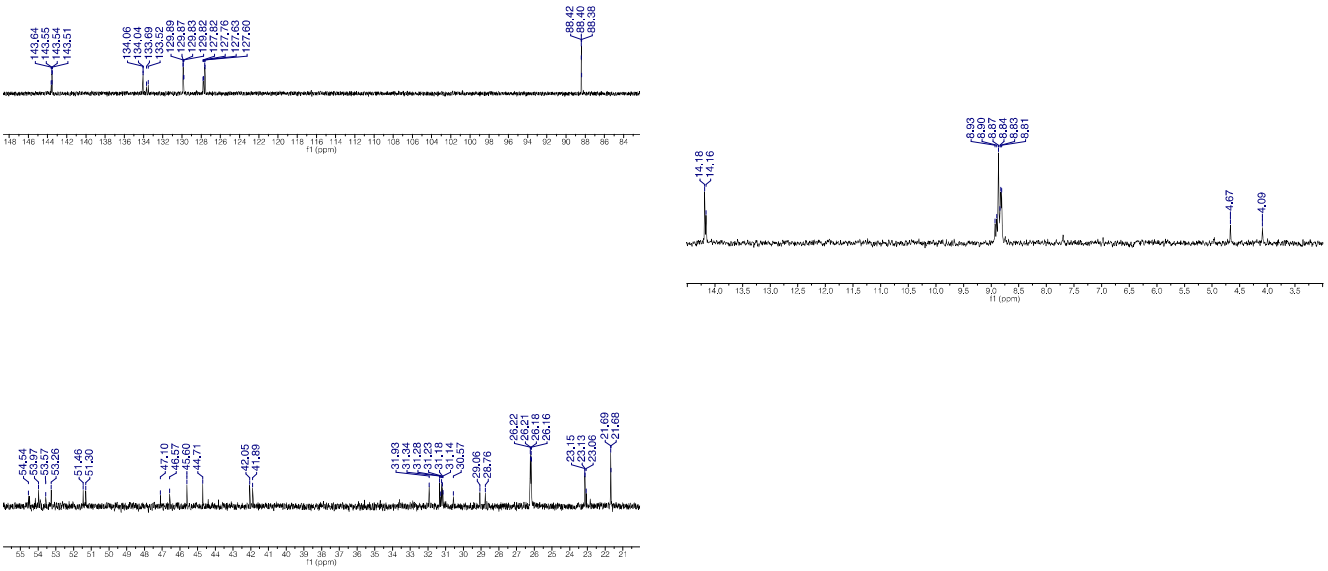
^{13}C-NMR (101 MHz, $CDCl_3$)



3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

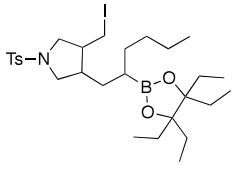
^{13}C-NMR (101 MHz, $CDCl_3$)

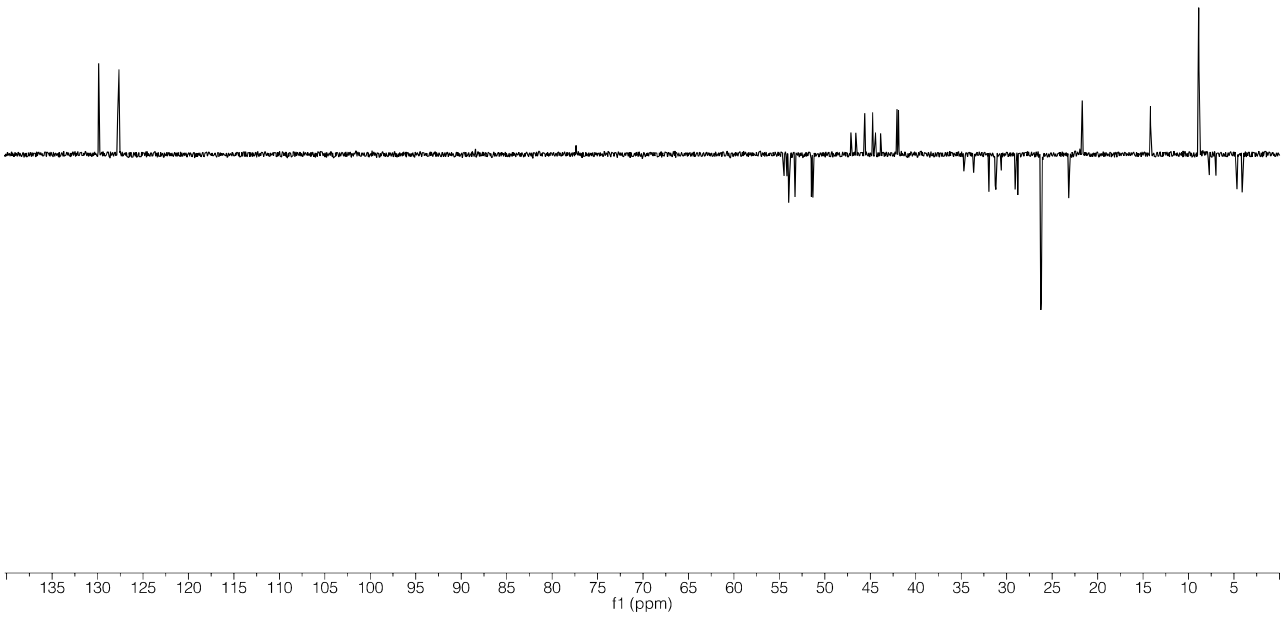




3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

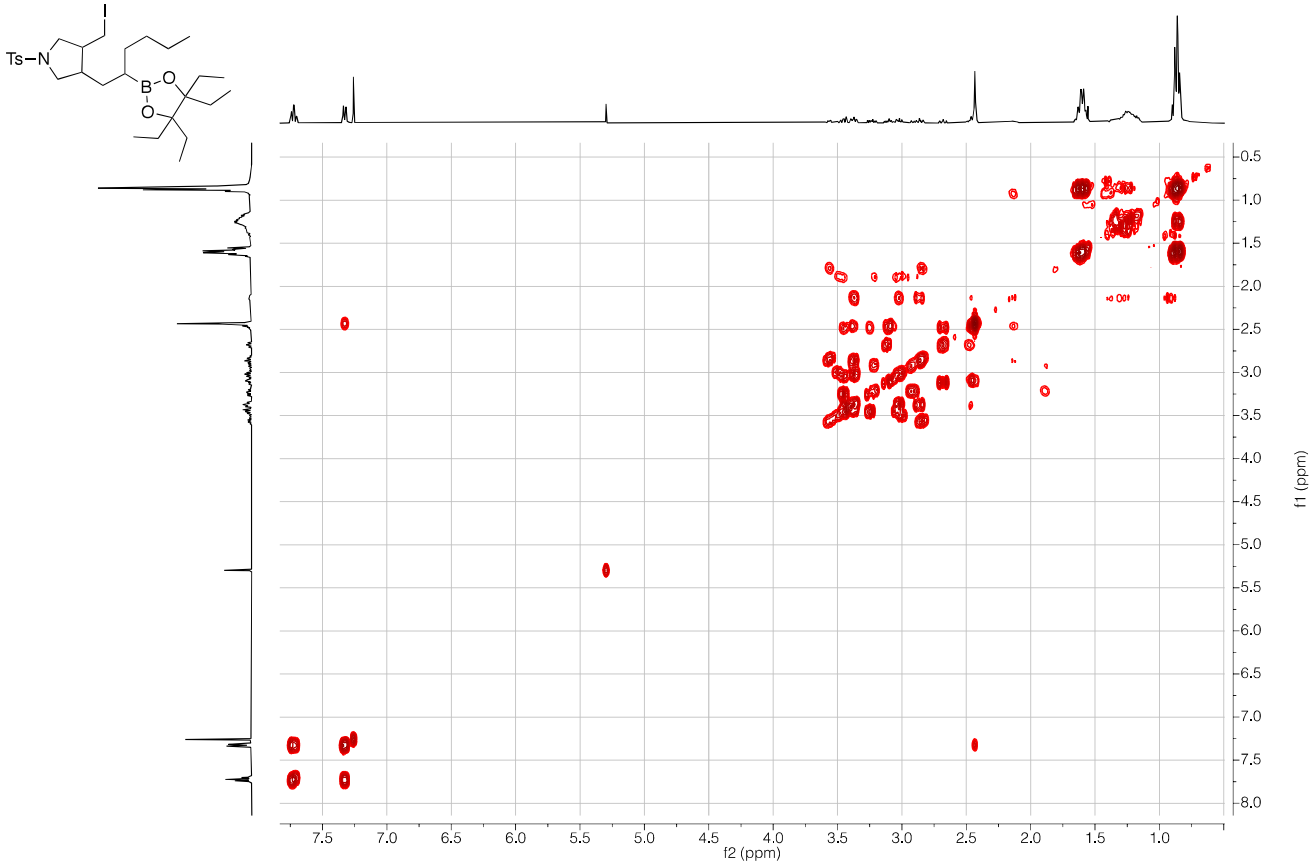
DEPT-135 NMR (101 MHz, $CDCl_3$)





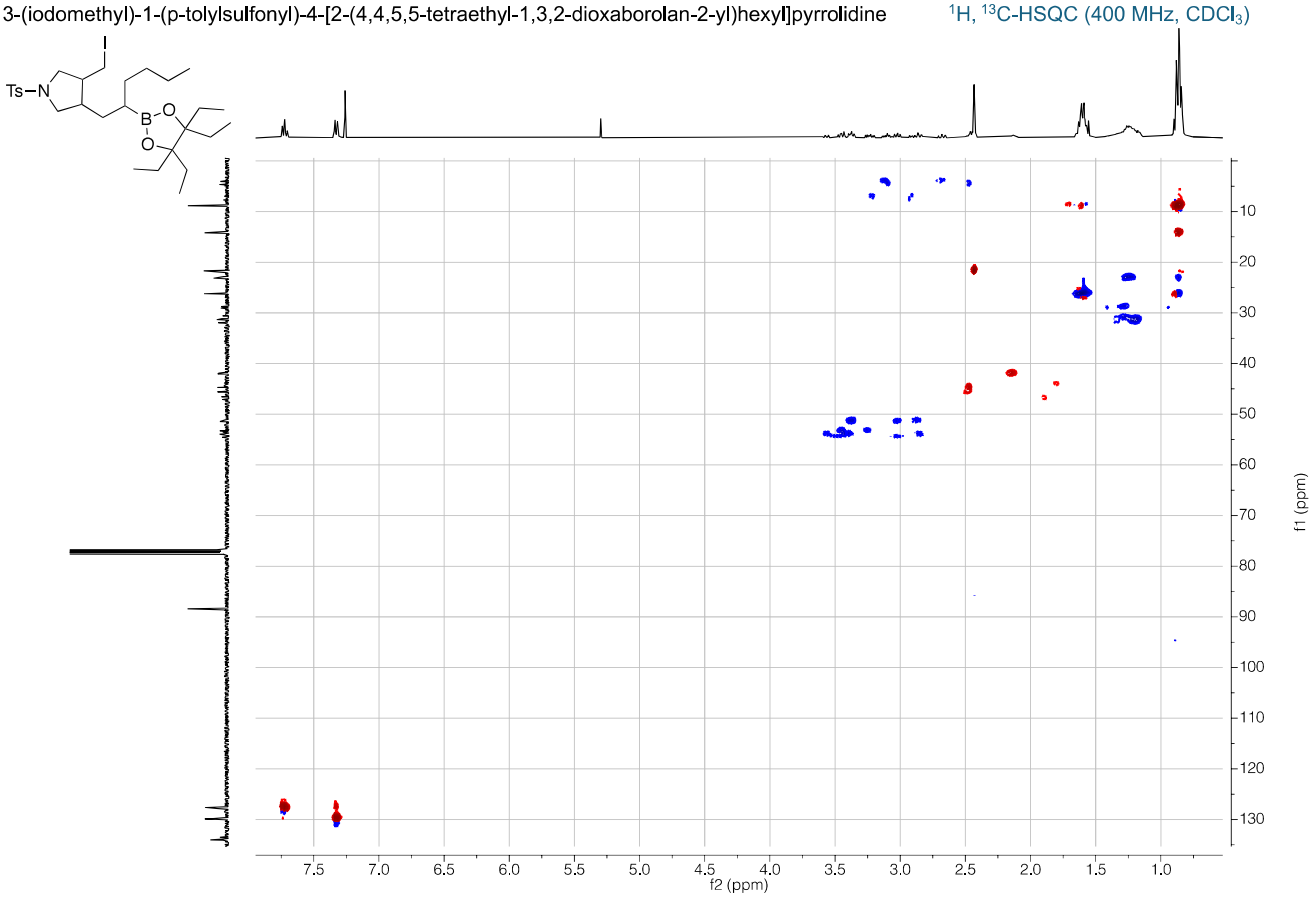
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



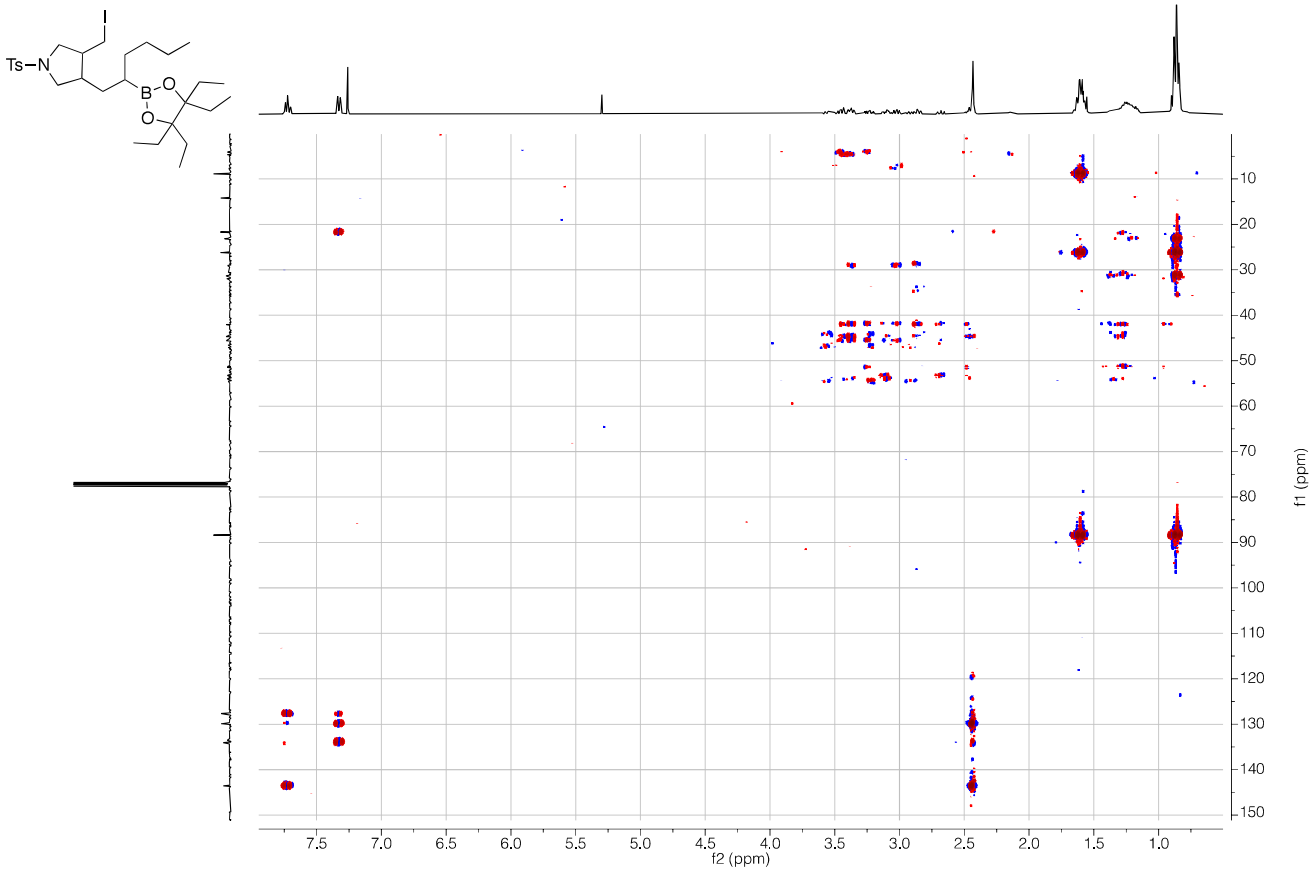
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



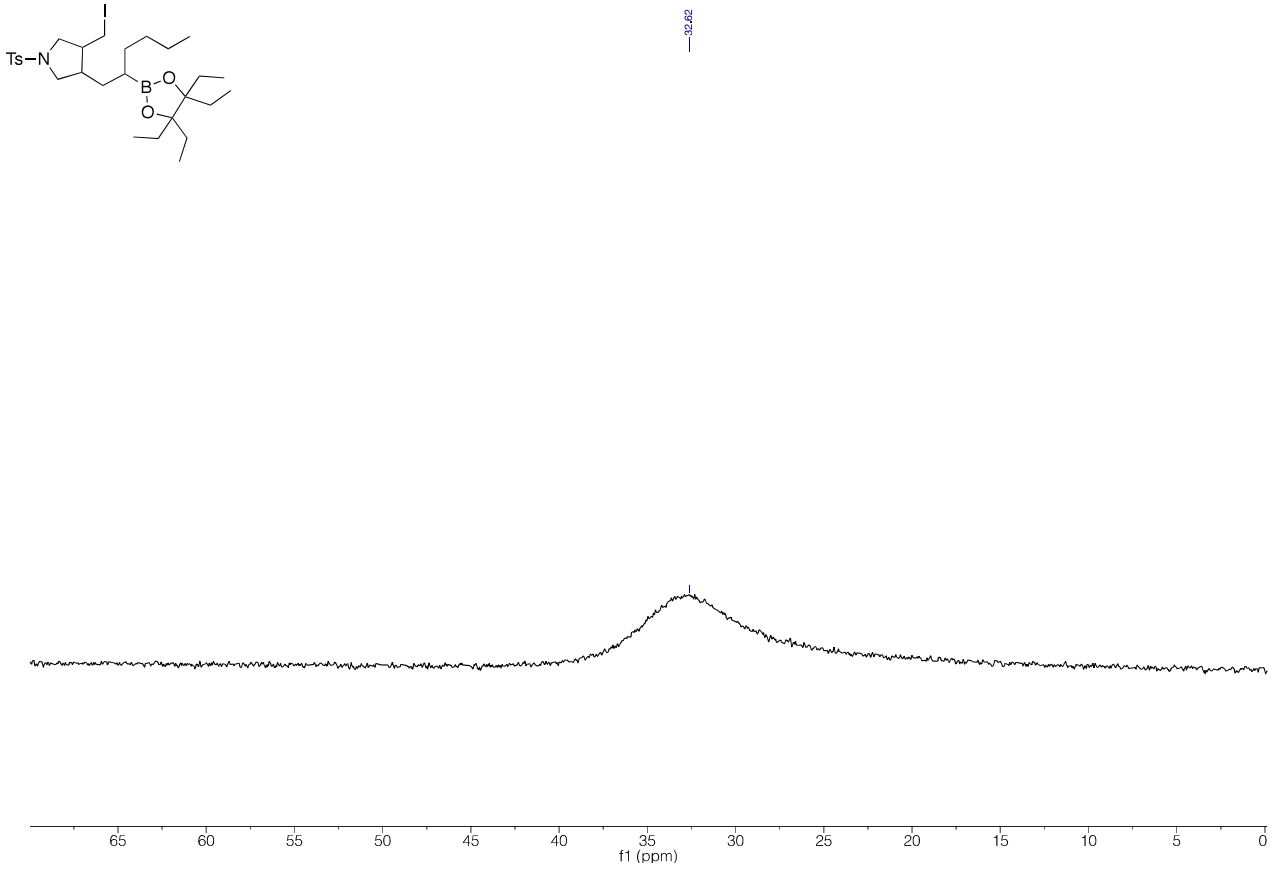
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

^{1}H, ^{13}C-HMBC(400 MHz, $CDCl_3$)

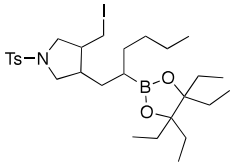


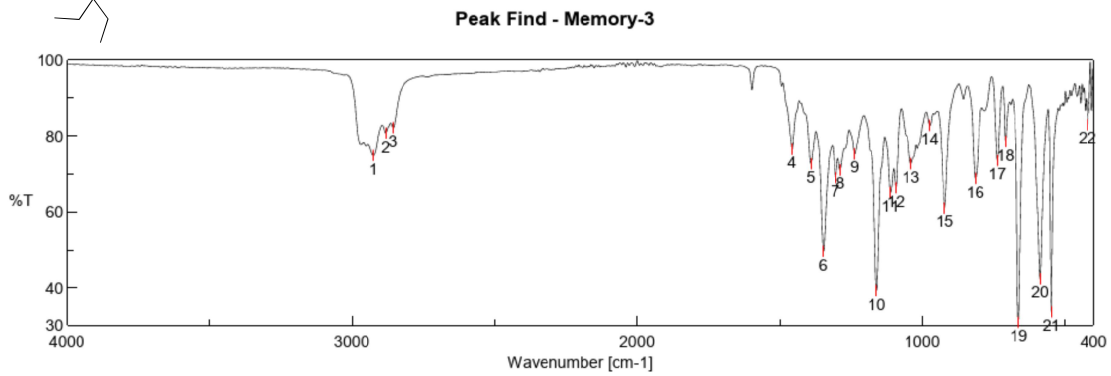
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

^{11}B-NMR (128 MHz, $CDCl_3$)



3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine FT-IR, ATR-diamond

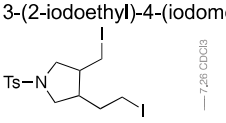




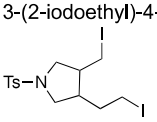
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2924.52	74.8173	2	2882.09	80.6768	3	2856.06	82.0901
4	1456.96	76.4525	5	1389.46	72.6624	6	1346.07	49.5937
7	1303.64	68.9871	8	1287.25	70.971	9	1236.15	75.2507
10	1159.97	39.2262	11	1110.8	65.0871	12	1091.51	66.3189
13	1039.44	72.6444	14	972.912	82.7141	15	920.843	60.8869
16	812.849	68.7298	17	735.71	73.5135	18	707.747	78.4764
19	661.464	30.8854	20	586.254	42.2844	21	546.72	33.5887
22	421.37	82.8862						

3-(2-iodoethyl)-4-(iodomethyl)-1-(p-tolylsulfonyl)pyrrolidine ^{1}H-NMR (400 MHz, $CDCl_3$)

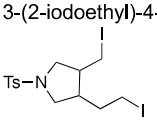


3-(2-iodoethyl)-4-(iodomethyl)-1-(p-tolylsulfonyl)pyrrolidine

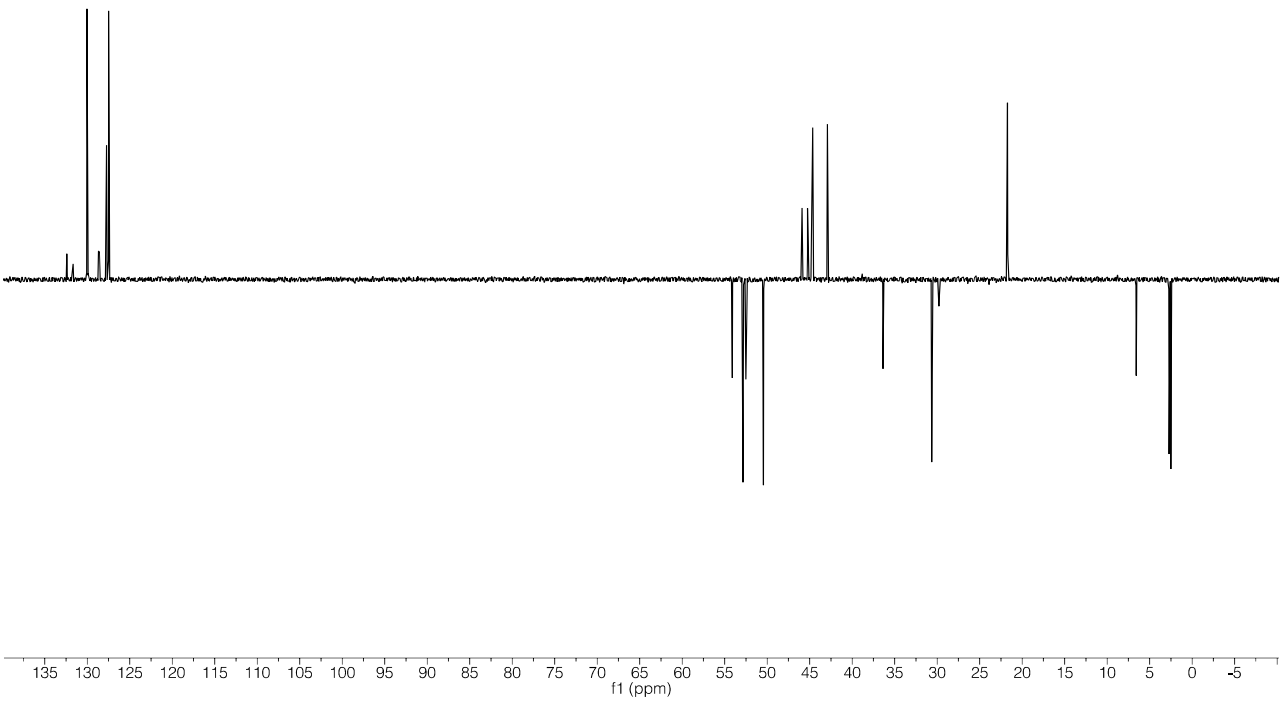


^{13}C-NMR (101 MHz, $CDCl_3$)

3-(2-iodoethyl)-4-(iodomethyl)-1-(p-tolylsulfonyl)pyrrolidine

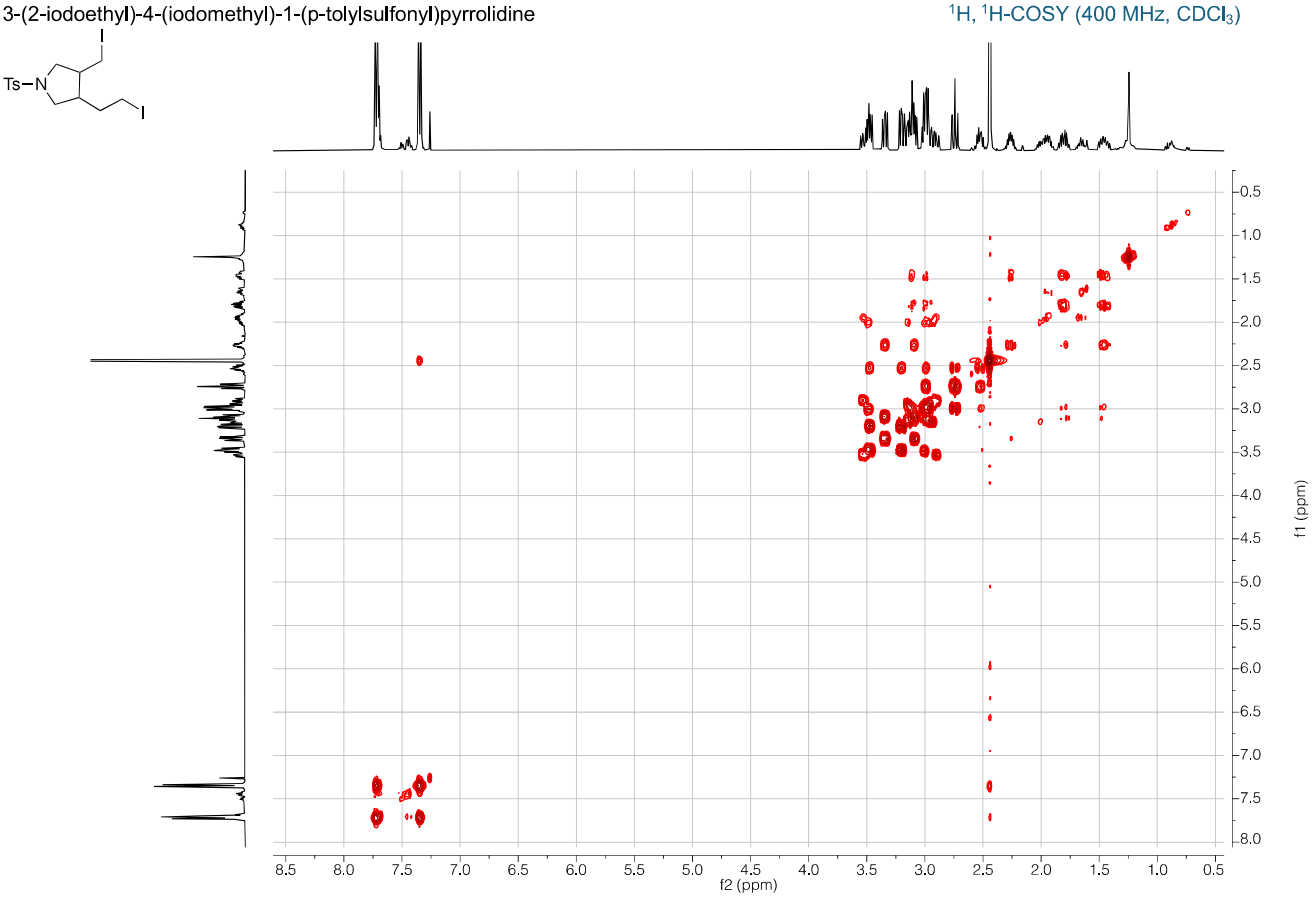


DEPT-135 NMR (101 MHz, $CDCl_3$)



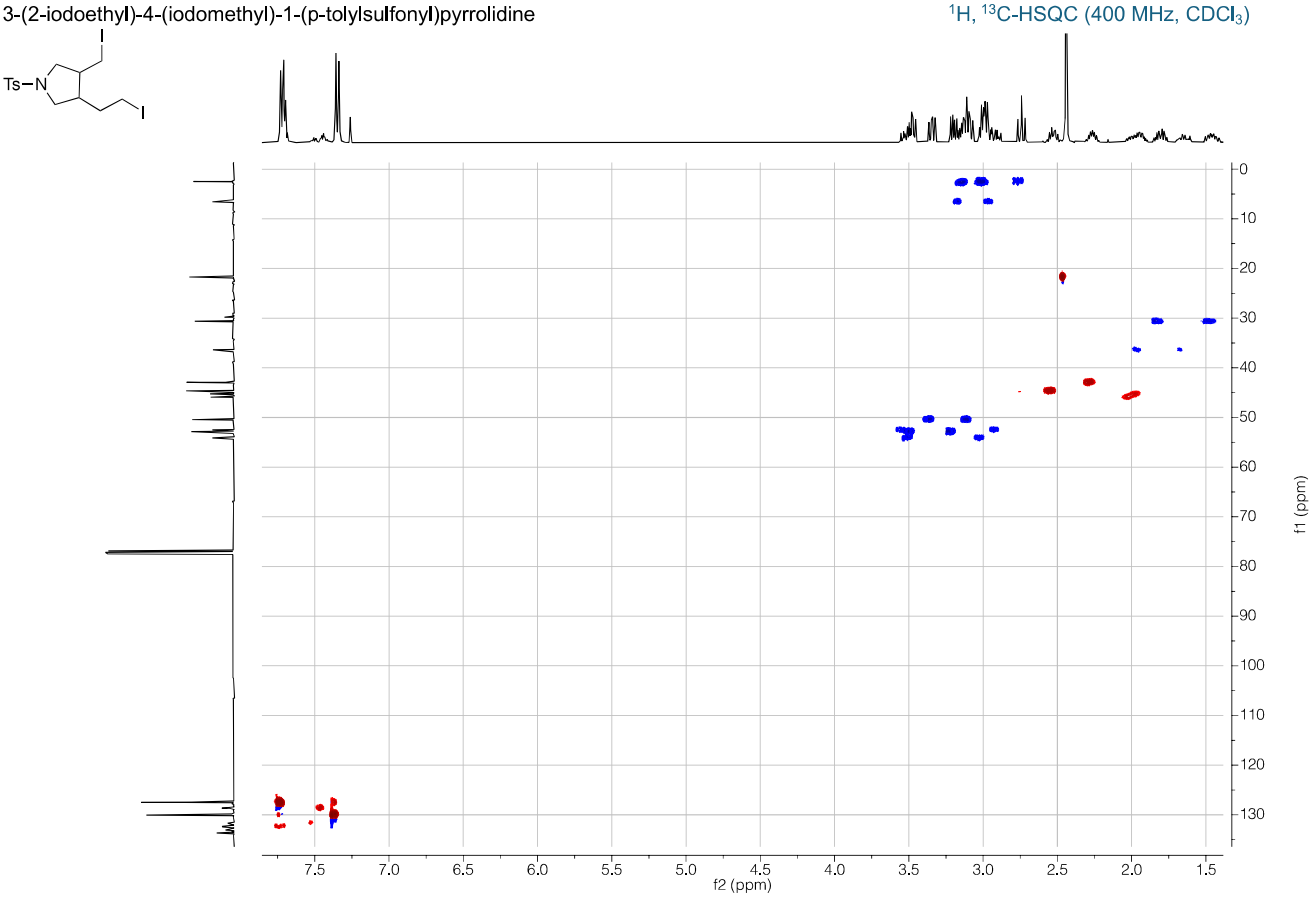
3-(2-iodoethyl)-4-(iodomethyl)-1-(p-tolylsulfonyl)pyrrolidine

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)

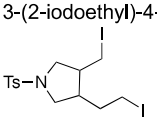


3-(2-iodoethyl)-4-(iodomethyl)-1-(p-tolylsulfonyl)pyrrolidine

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)

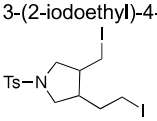


3-(2-iodoethyl)-4-(iodomethyl)-1-(p-tolylsulfonyl)pyrrolidine

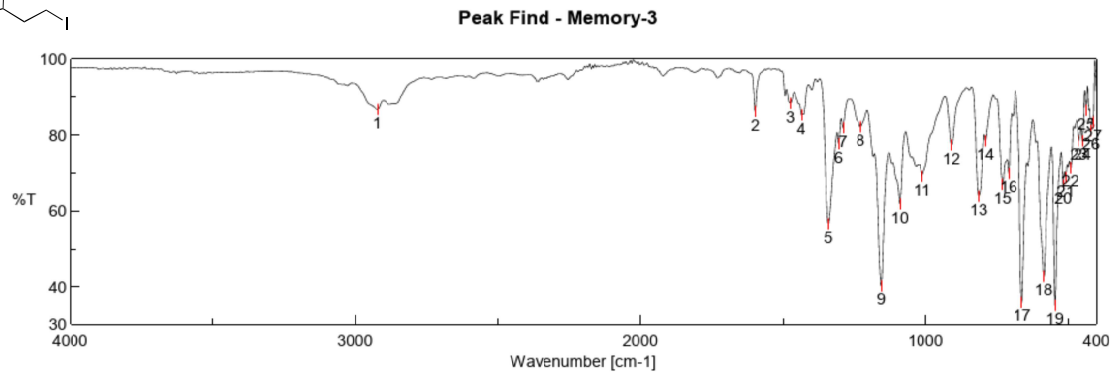


^{1}H, ^{13}C-HMBC(400 MHz, $CDCl_3$)

3-(2-iodoethyl)-4-(iodomethyl)-1-(p-tolylsulfonyl)pyrrolidine



FT-IR, ATR-diamond

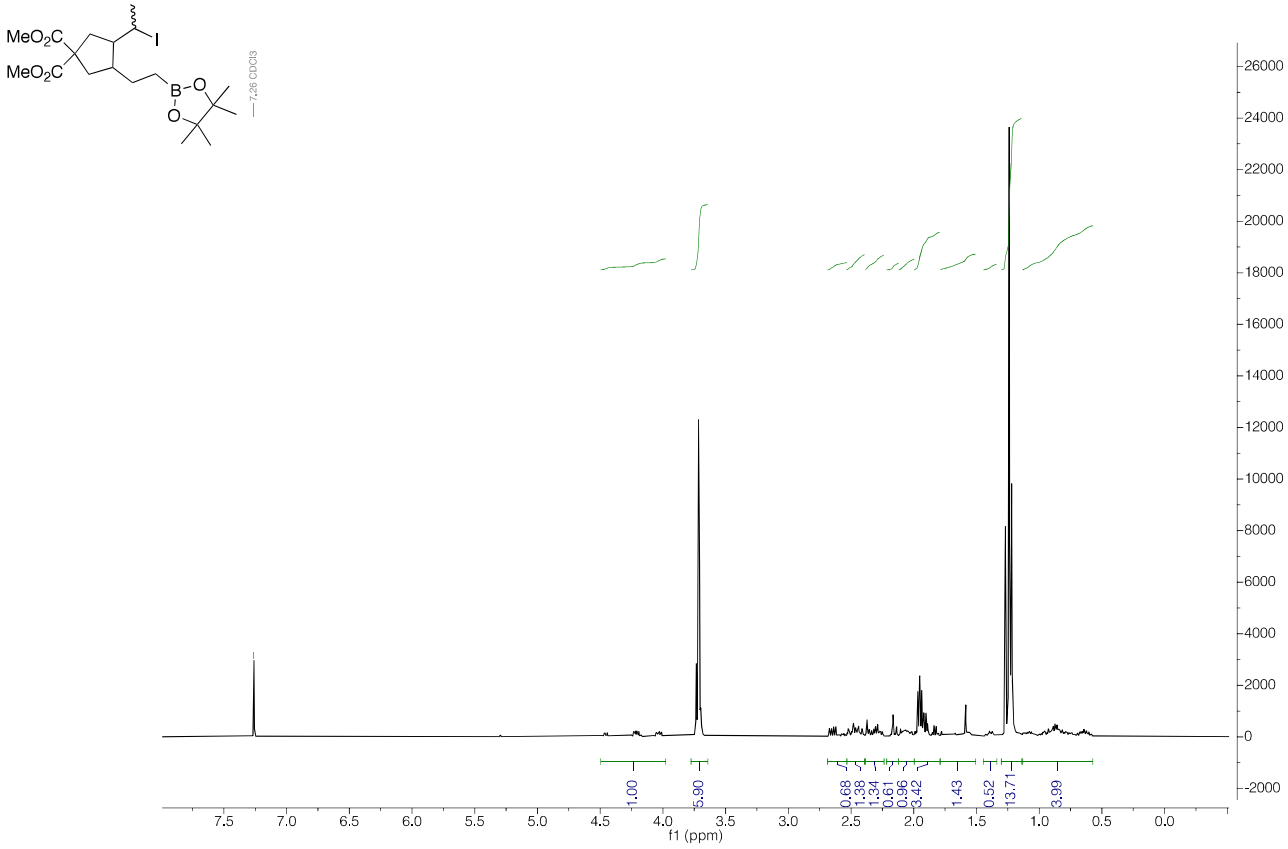


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2923.56	86.6641	2	1595.81	86.1639	3	1473.35	88.3221
4	1434.78	85.2184	5	1339.32	56.5013	6	1303.64	77.615
7	1289.18	81.8288	8	1226.5	82.1177	9	1154.19	40.1586
10	1089.58	61.7846	11	1012.45	69.0622	12	909.272	77.3084
13	811.885	63.8292	14	788.743	78.3961	15	728.961	66.9156
16	707.747	69.8158	17	660.5	35.8526	18	584.325	42.702
19	545.756	35.1082	20	517.793	66.8192	21	509.115	68.7079
22	491.759	71.2744	23	461.868	78.4042	24	448.369	78.4124
25	435.834	86.4288	26	418.477	81.1406	27	411.728	83.331

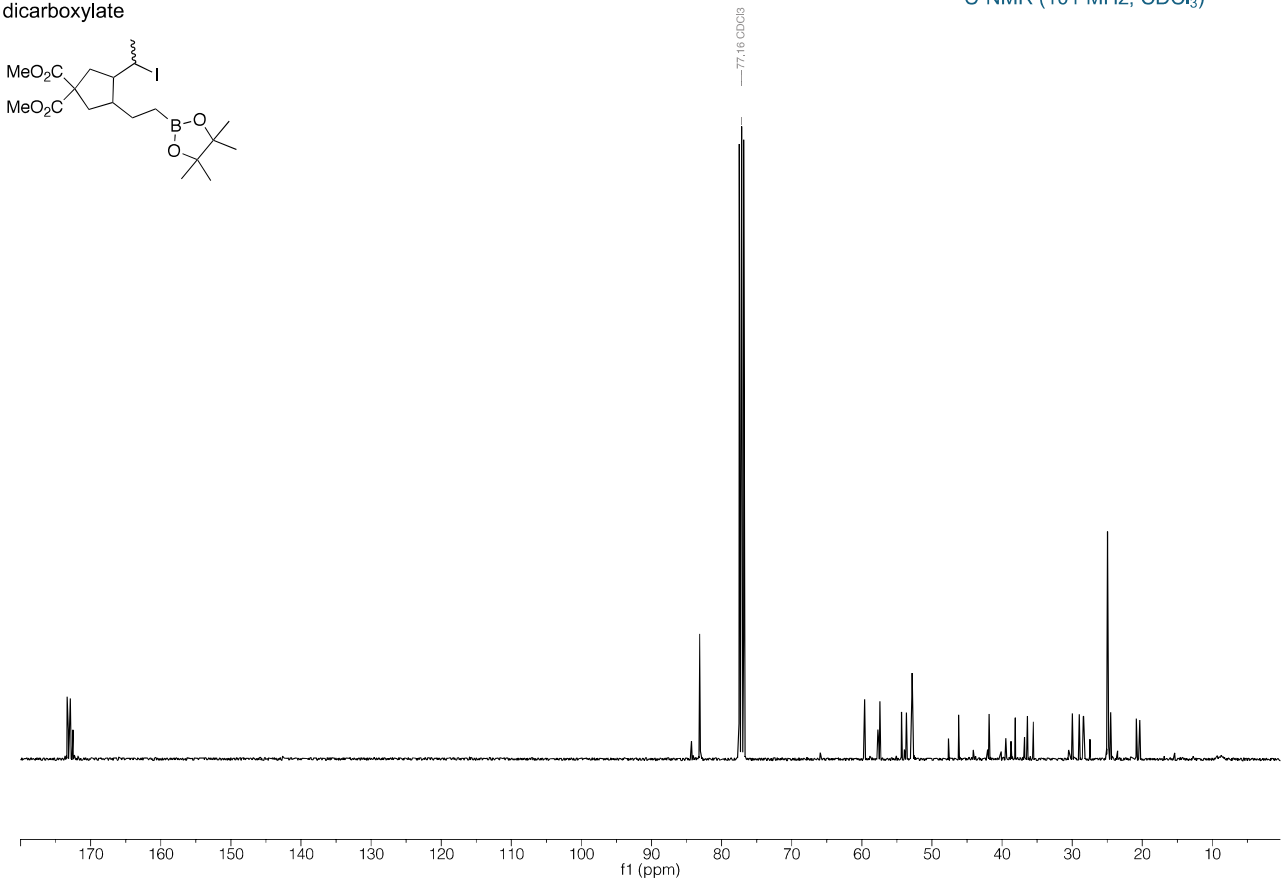
Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)



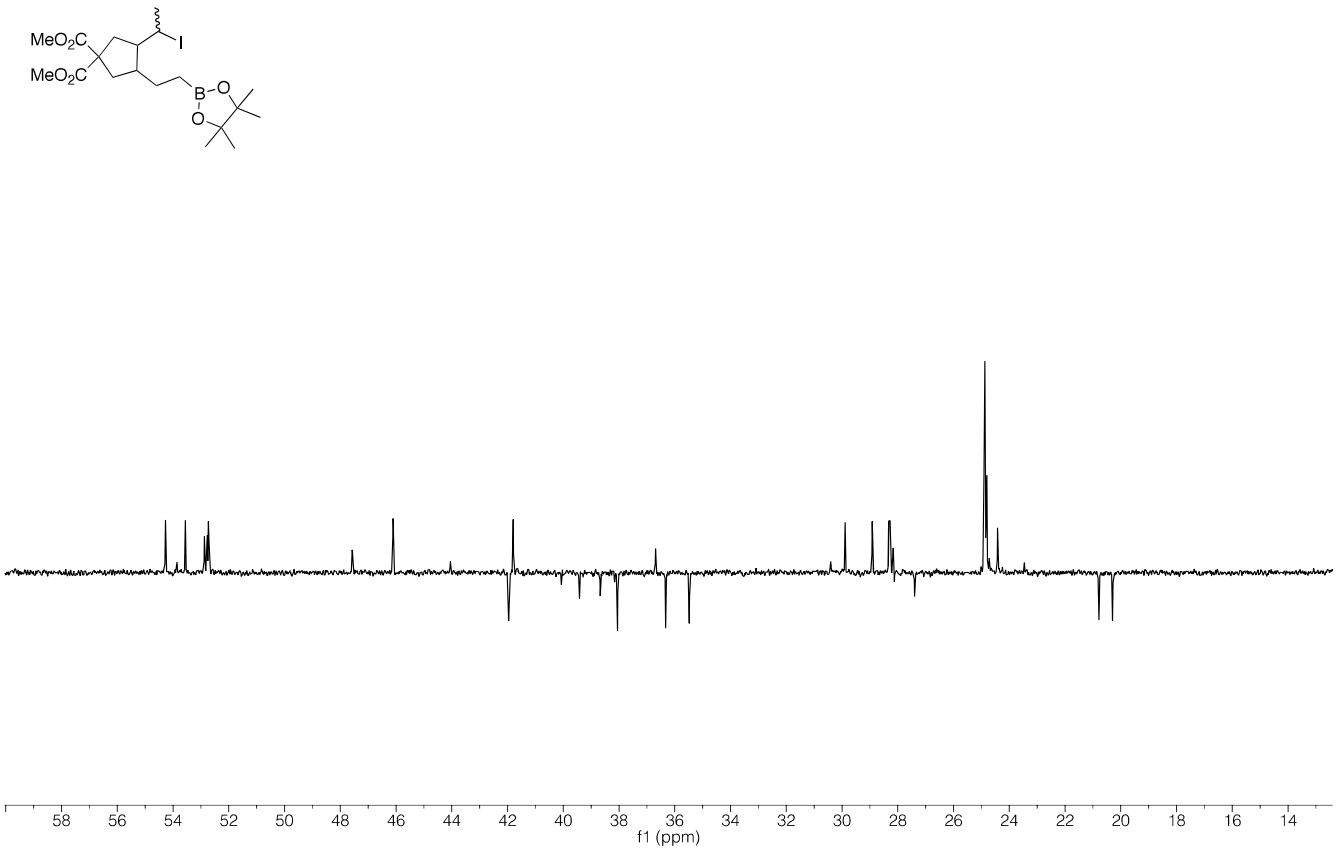
Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{13}C-NMR (101 MHz, $CDCl_3$)



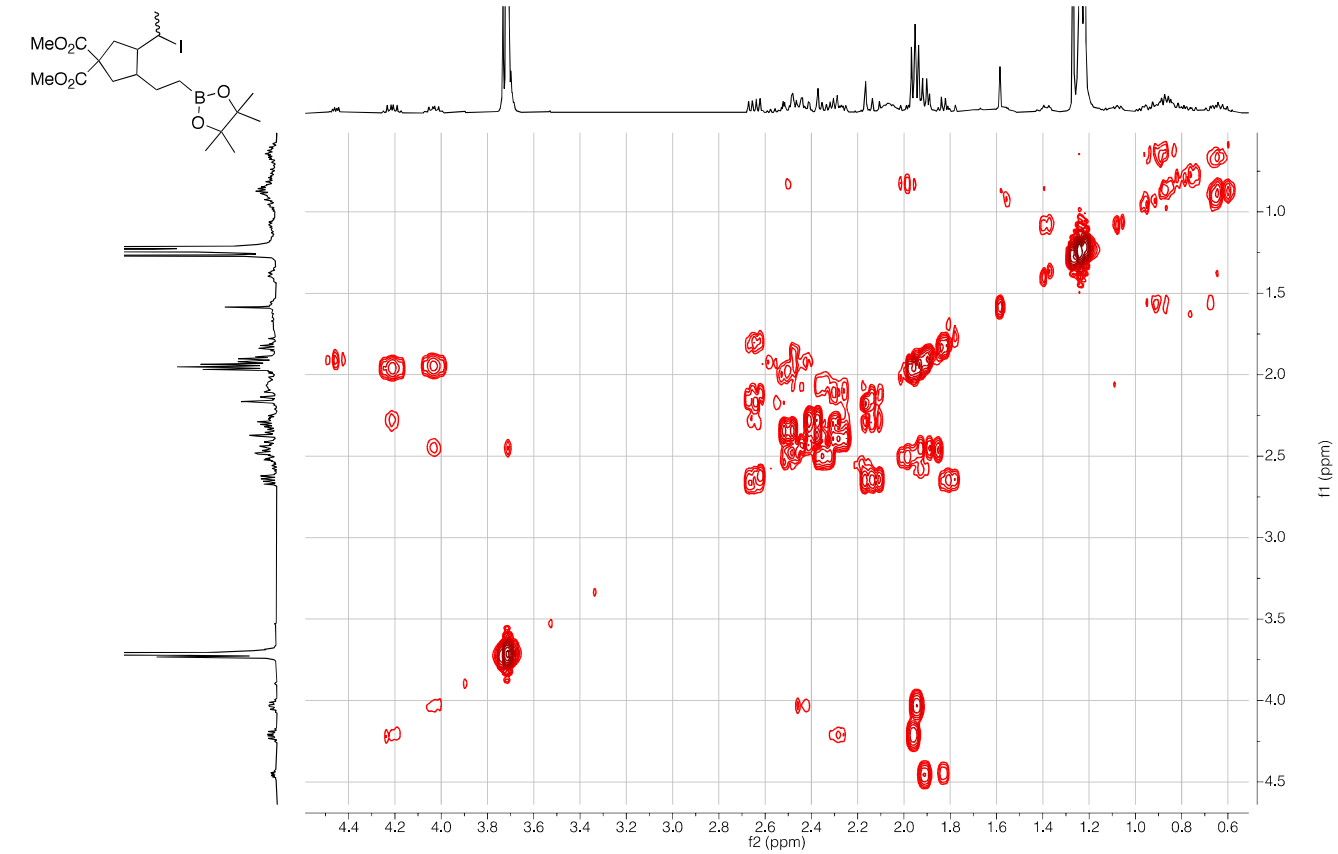
Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

DEPT-135 NMR (101 MHz, $CDCl_3$)



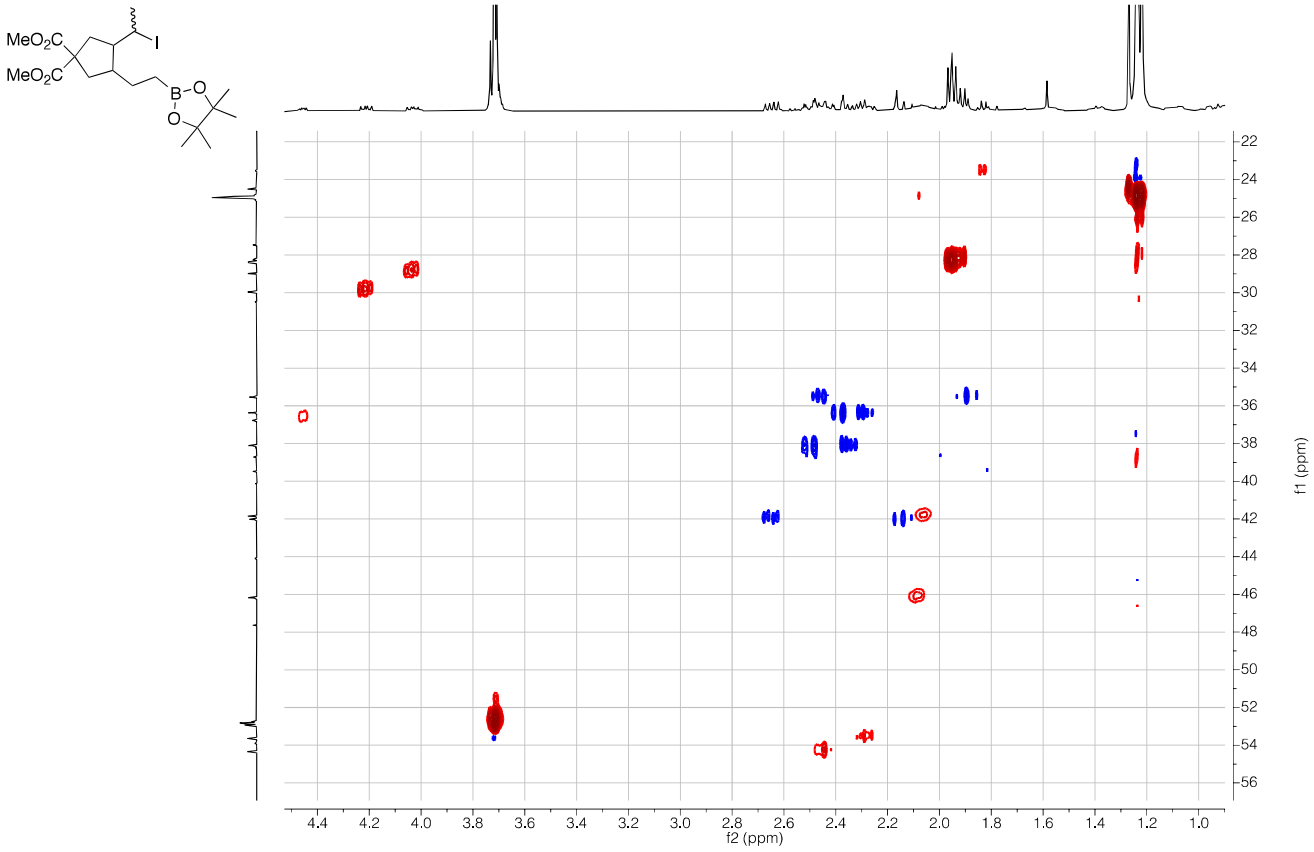
Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^1H, ^1H-COSY (400 MHz, $CDCl_3$)



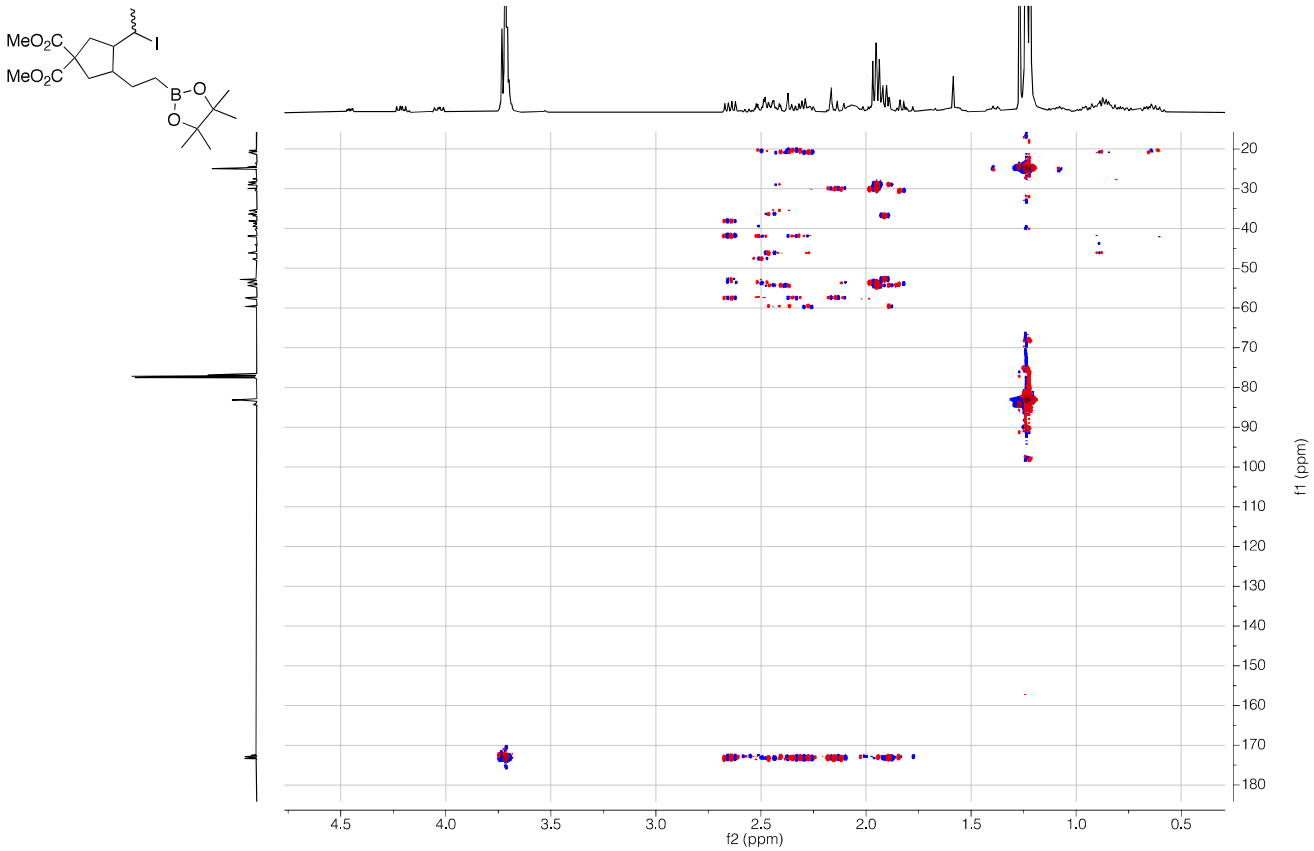
Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



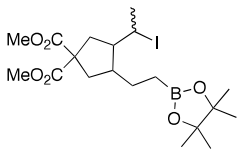
Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC(400 MHz, $CDCl_3$)



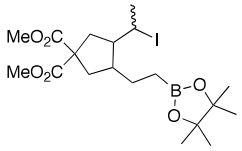
Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

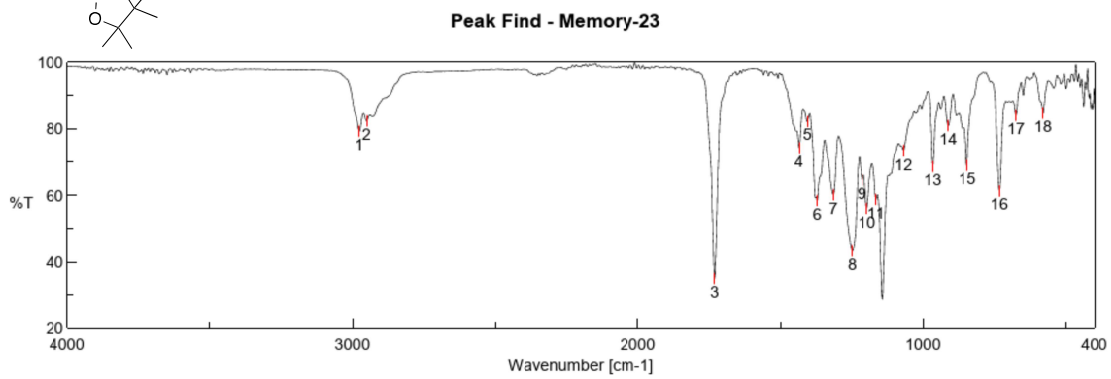
^{11}B-NMR (128 MHz, $CDCl_3$)



Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



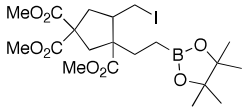


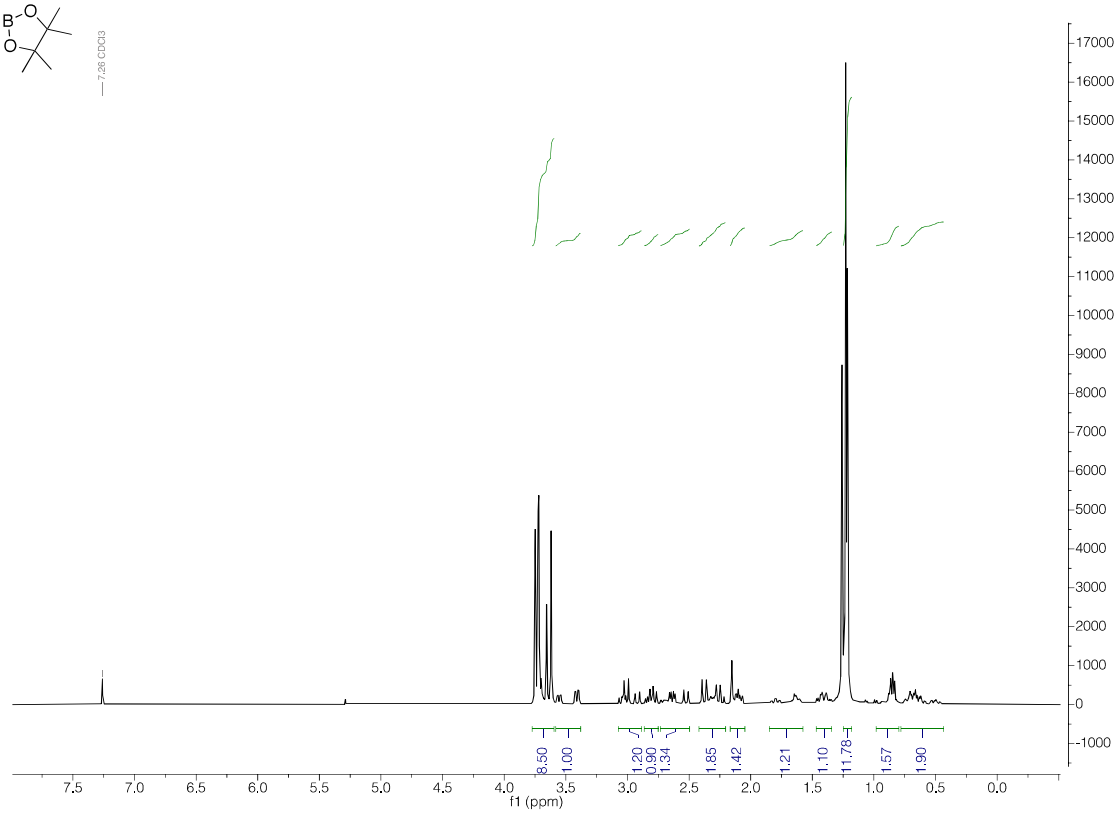
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2976.59	79.2285	2	2951.52	82.3237	3	1731.76	34.9521
4	1434.78	74.1523	5	1405.85	82.17	6	1371.14	58.3216
7	1315.21	60.093	8	1248.68	43.2844	9	1213.97	64.5977
10	1196.61	55.9831	11	1164.79	58.682	12	1068.37	73.3945
13	966.162	68.7063	14	912.165	80.937	15	845.633	69.0166
16	731.853	61.2305	17	673.999	83.9944	18	579.504	84.6995

Trimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1,3-tricarboxylate

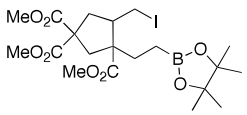
^{1}H-NMR (400 MHz, $CDCl_3$)



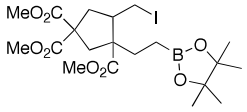


Trimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1,3-tricarboxylate

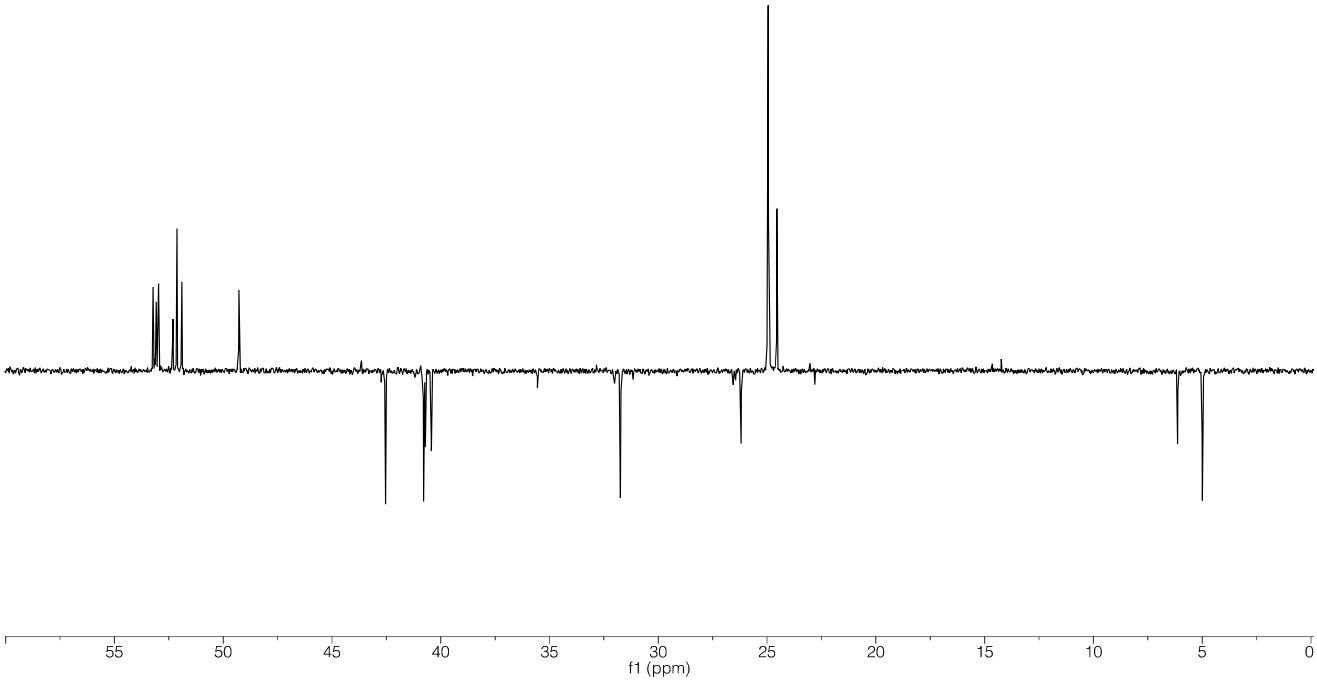
^{13}C-NMR (101 MHz, $CDCl_3$)



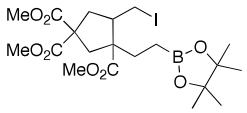
Trimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1,3-tricarboxylate



DEPT-135 NMR (101 MHz, $CDCl_3$)



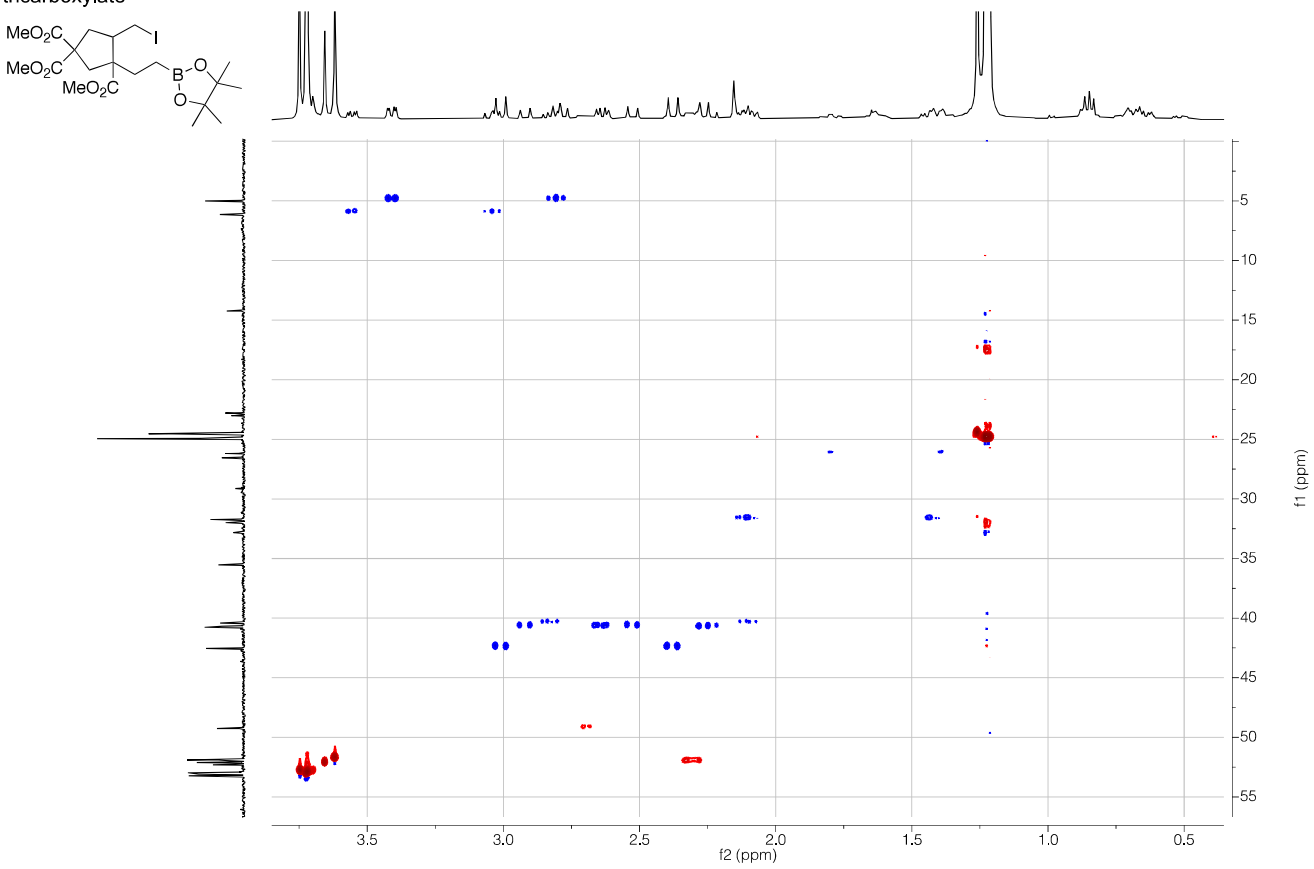
Trimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1,3-tricarboxylate



^1H, ^1H-COSY (400 MHz, $CDCl_3$)

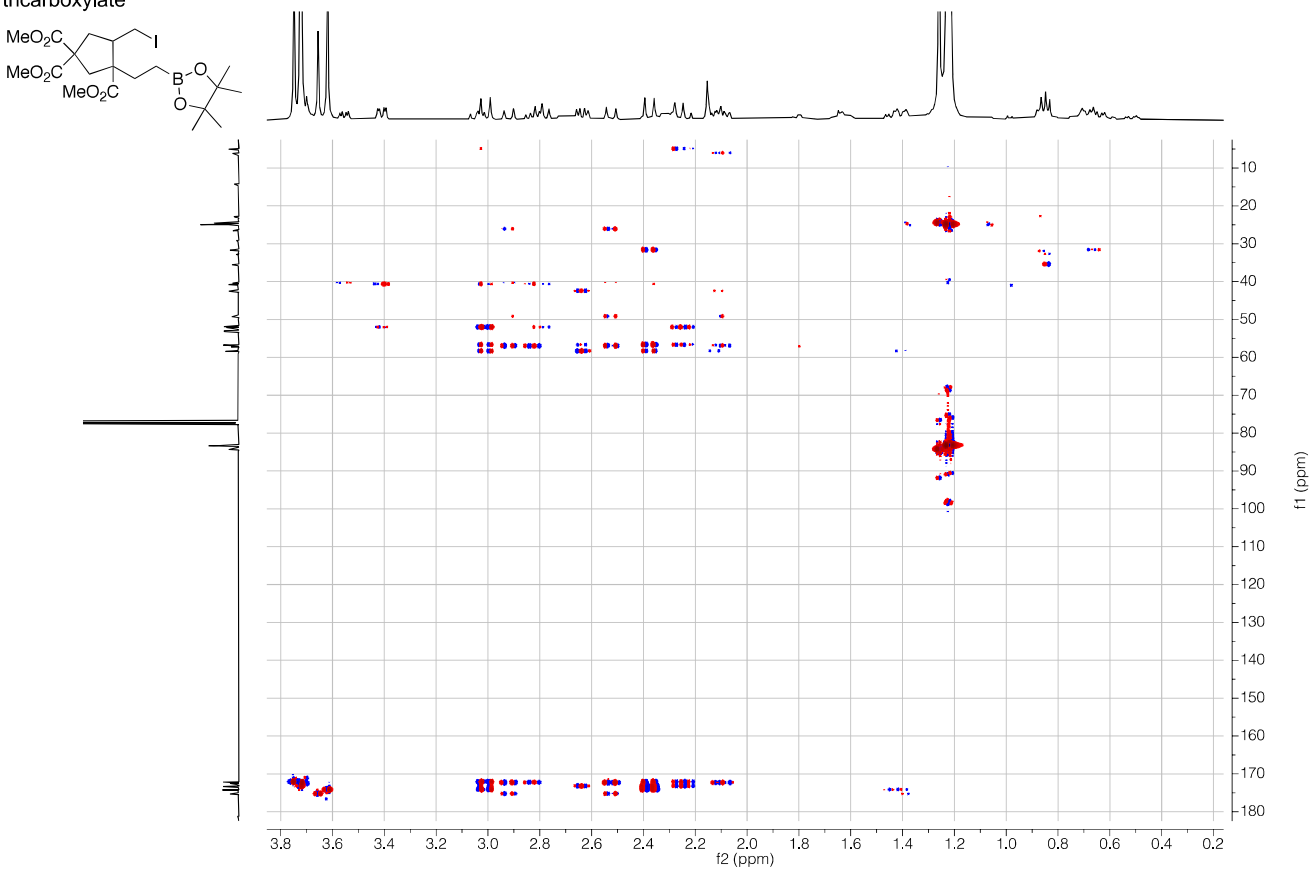
Trimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1,3-tricarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



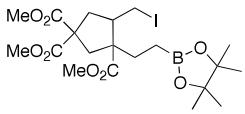
Trimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1,3-tricarboxylate

^{1}H, ^{13}C-HMBC(400 MHz, $CDCl_3$)



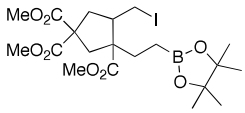
Trimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1,3-tricarboxylate

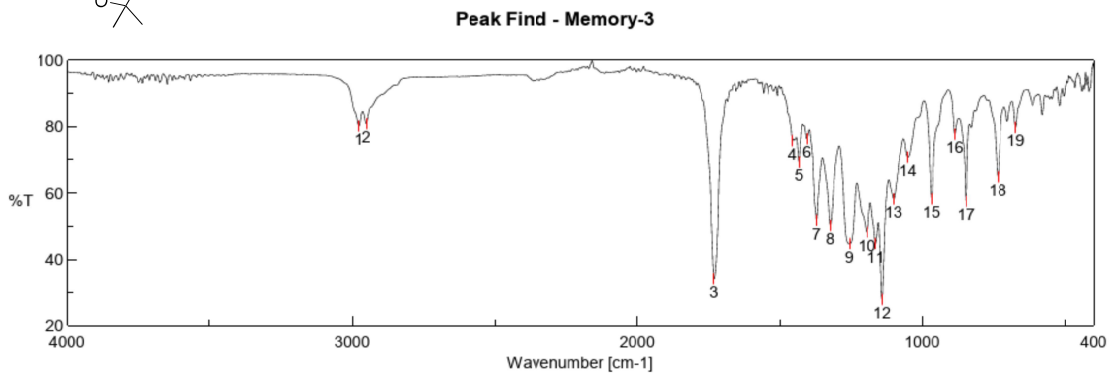
^{11}B-NMR (128 MHz, $CDCl_3$)



Trimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1,3-tricarboxylate

FT-IR, ATR-diamond



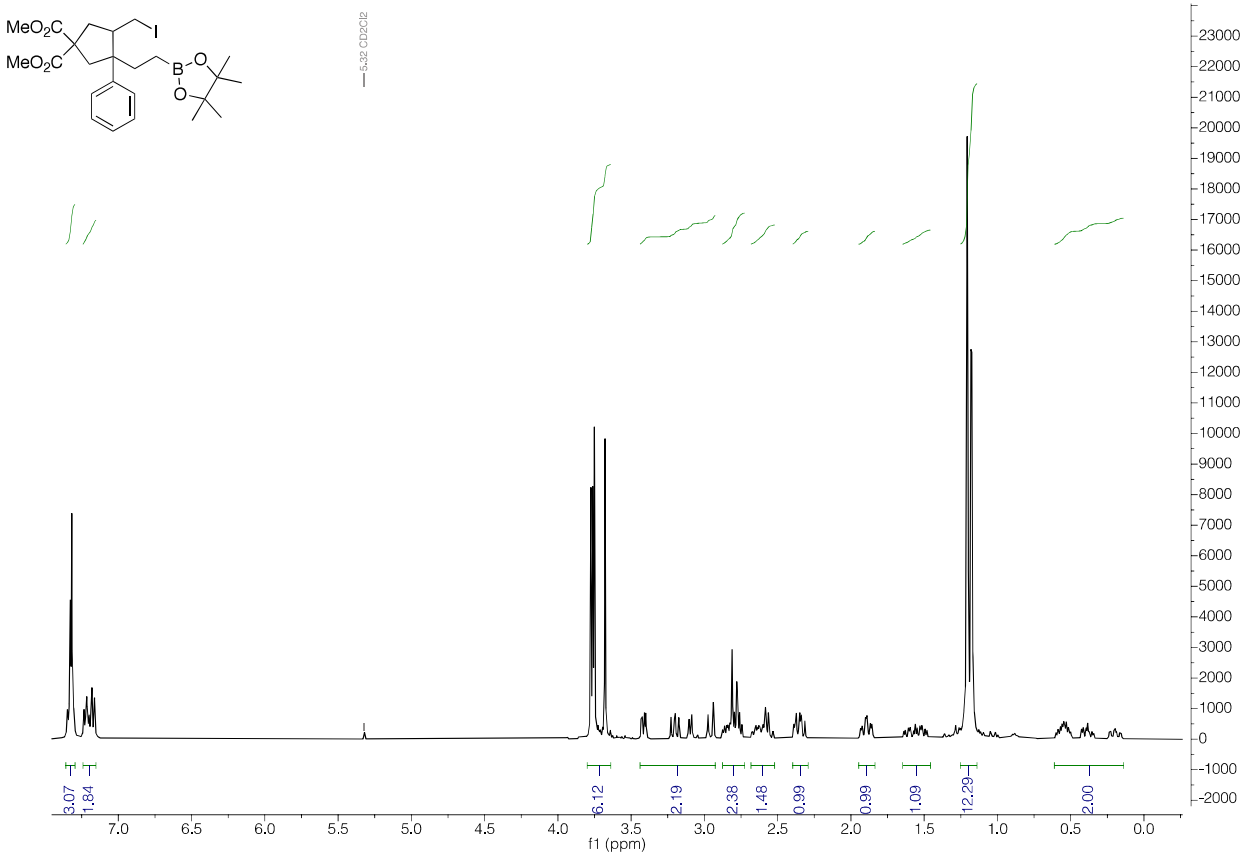


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2976.59	80.1516	2	2951.52	80.8693	3	1730.8	34.161
4	1455.99	75.7151	5	1433.82	69.2936	6	1405.85	76.2735
7	1372.1	51.7713	8	1323.89	50.2058	9	1256.4	44.7599
10	1194.69	48.2118	11	1163.83	44.7219	12	1141.65	27.9792
13	1100.19	58.1599	14	1050.05	70.7901	15	967.126	58.2538
16	885.166	77.6764	17	845.633	57.4846	18	735.71	64.8371
19	673.999	79.7366						

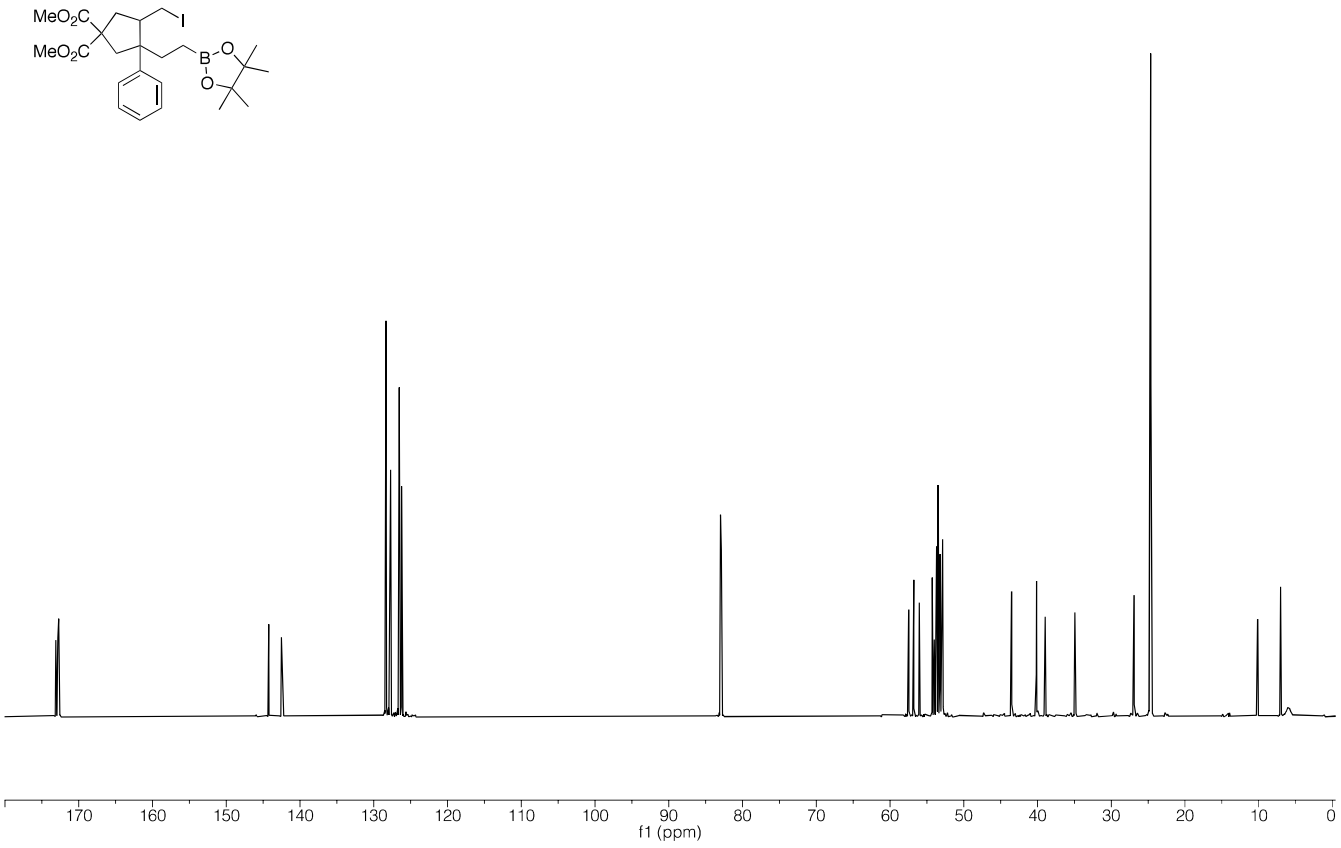
Dimethyl 4-(iodomethyl)-3-phenyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, CD_2Cl_2)

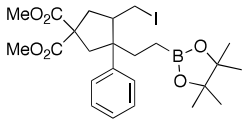


Dimethyl 4-(iodomethyl)-3-phenyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

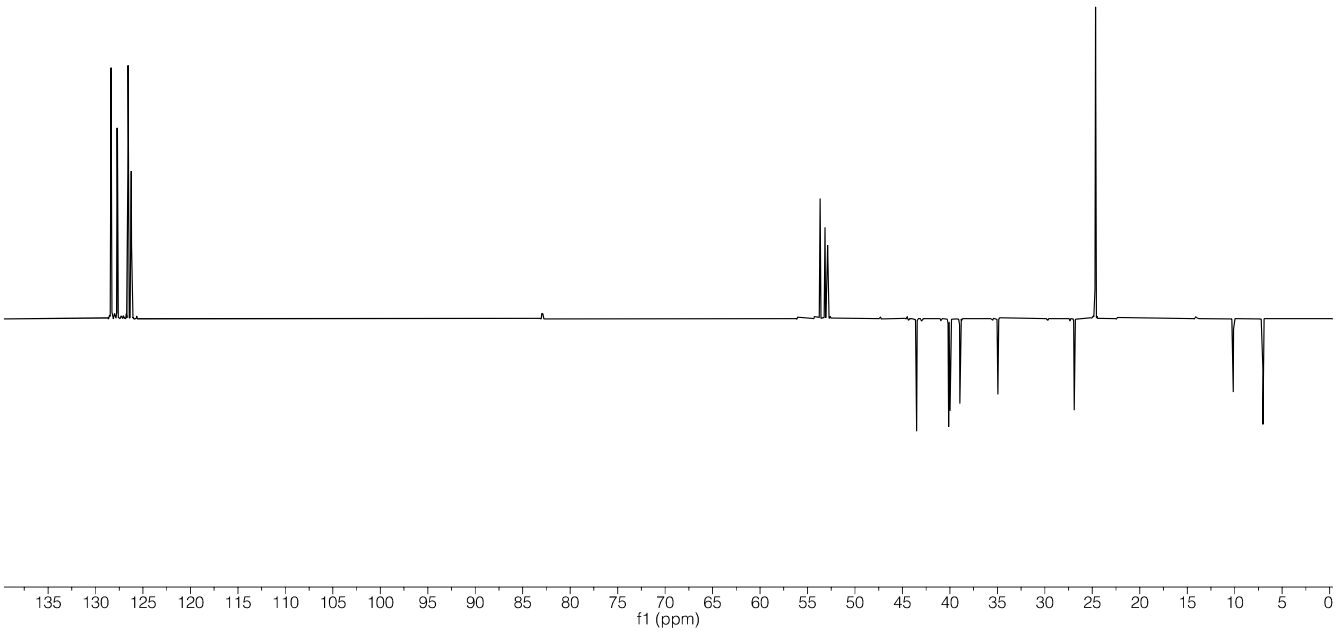
^{13}C-NMR (101 MHz, CD_2Cl_2)



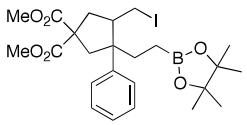
Dimethyl 4-(iodomethyl)-3-phenyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate



DEPT-135 NMR (101 MHz, CD_2Cl_2)



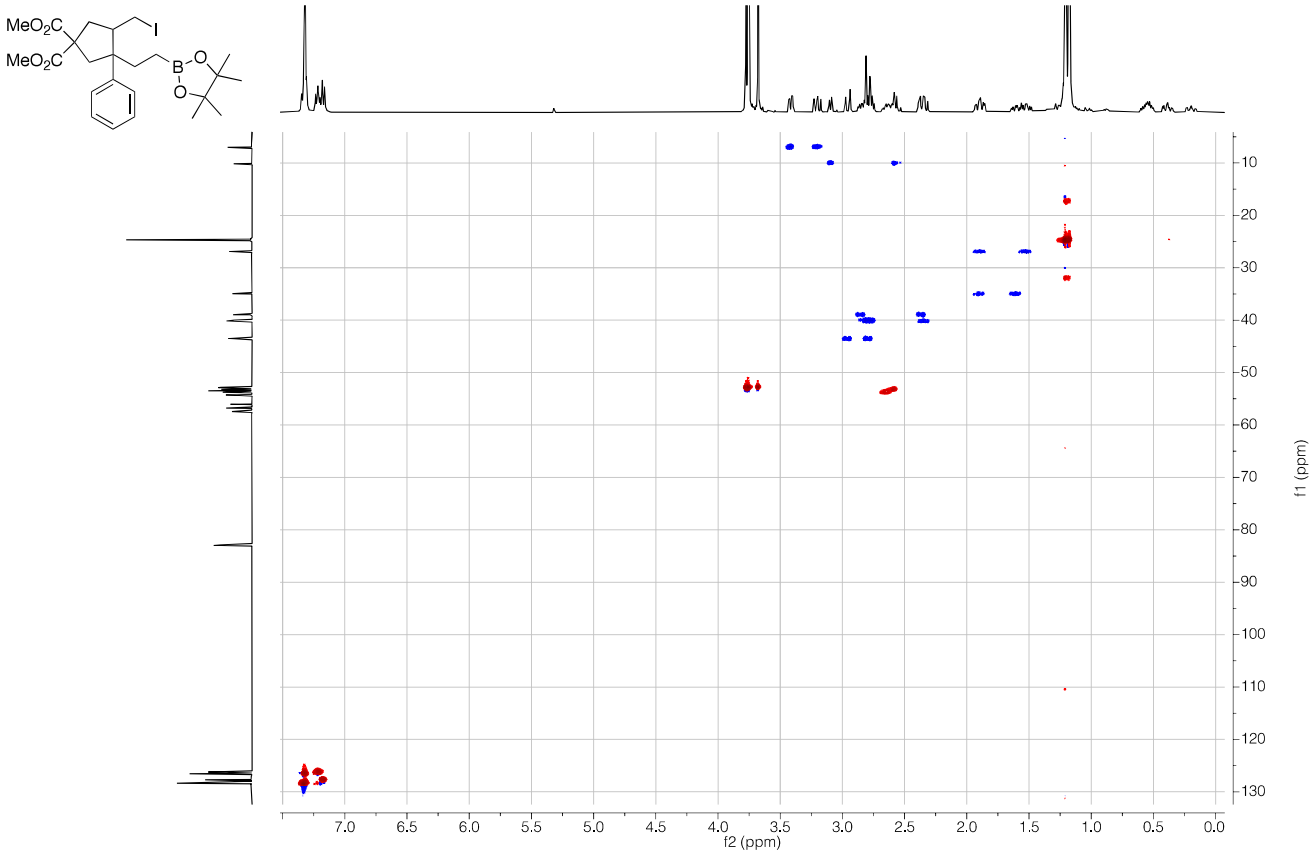
Dimethyl 4-(iodomethyl)-3-phenyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate



^1H, ^1H-COSY (400 MHz, CD_2Cl_2)

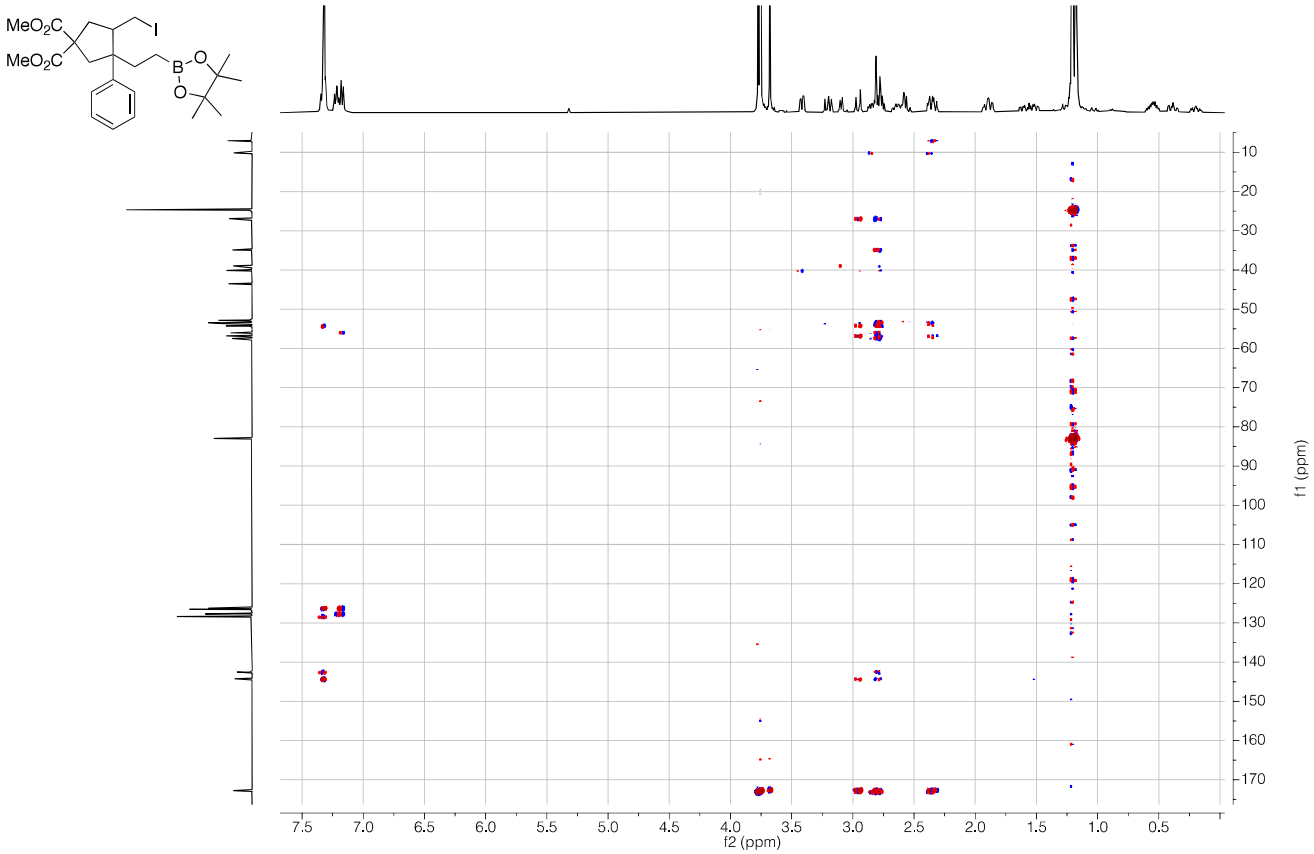
Dimethyl 4-(iodomethyl)-3-phenyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, CD_2Cl_2)



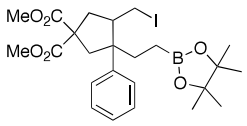
Dimethyl 4-(iodomethyl)-3-phenyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC(400 MHz, CD_2Cl_2)



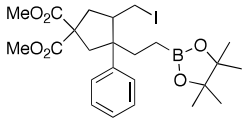
Dimethyl 4-(iodomethyl)-3-phenyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

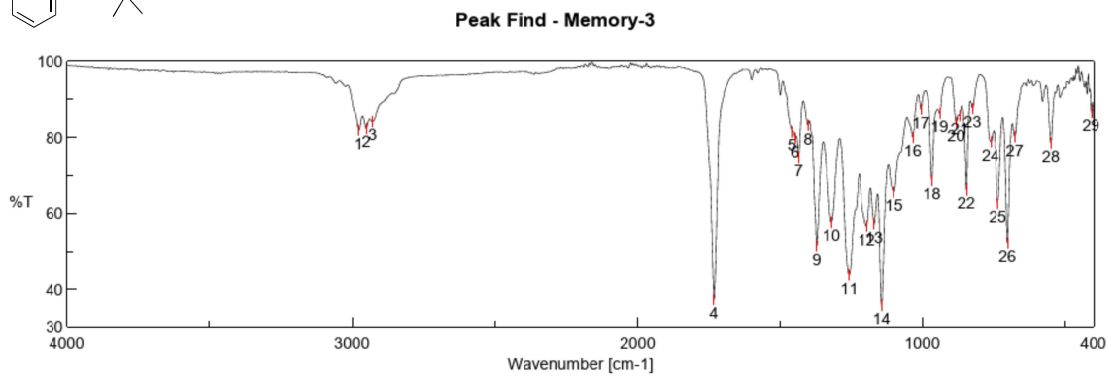
^{11}B-NMR (128 MHz, CD_2Cl_2)



Dimethyl 4-(iodomethyl)-3-phenyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



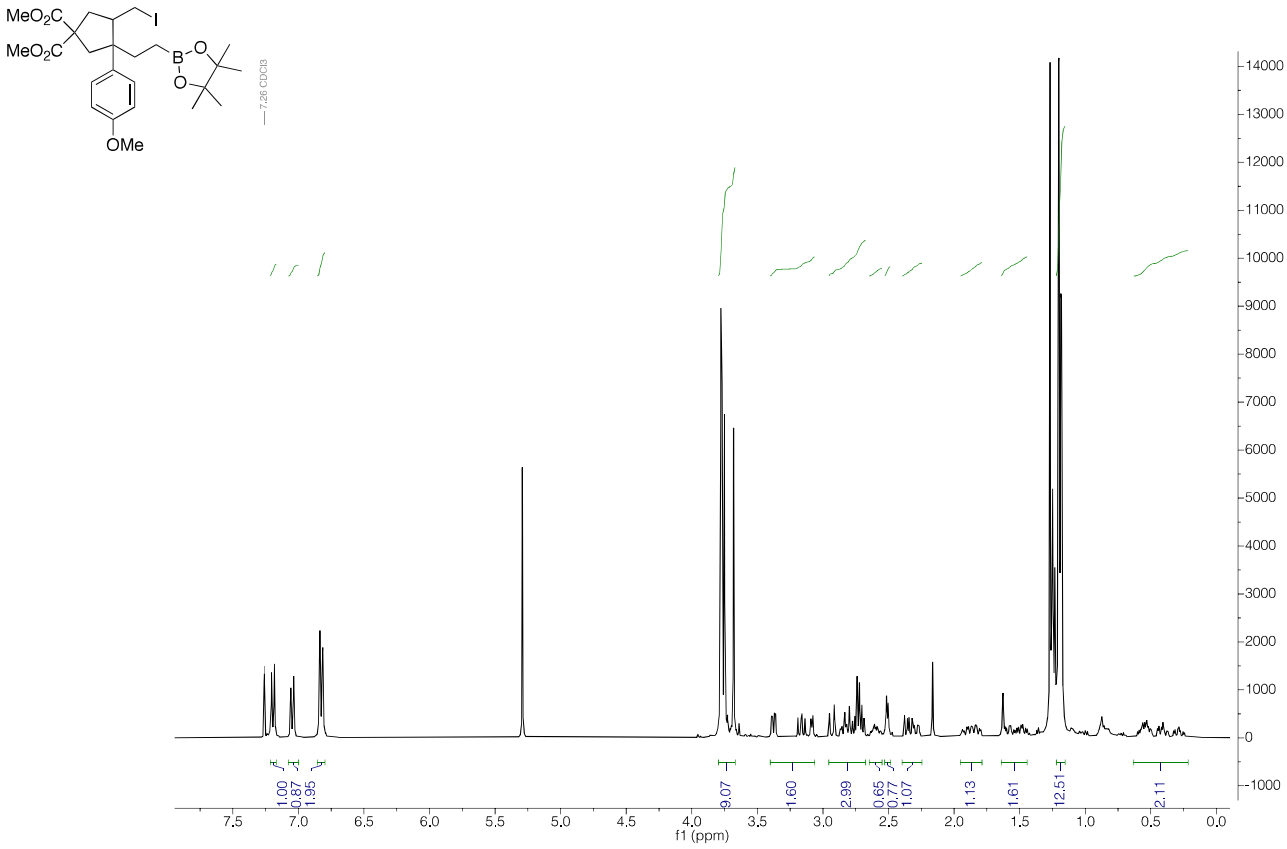


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2976.59	81.8748	2	2950.55	82.2586	3	2928.38	84.0944
4	1730.8	37.2763	5	1455.99	81.3981	6	1445.39	79.7125
7	1433.82	74.6392	8	1401.03	83.1081	9	1370.18	51.3664
10	1320.04	57.5309	11	1257.36	43.7406	12	1195.65	56.6029
13	1167.69	57.2002	14	1141.65	35.6844	15	1099.23	65.5688
16	1032.69	79.9403	17	1004.73	87.4016	18	967.126	68.5718
19	940.128	86.2603	20	882.274	83.8062	21	870.703	85.6712
22	846.597	66.0958	23	825.384	87.5499	24	760.78	78.7322
25	735.71	62.5334	26	700.998	52.0931	27	674.963	80.0891
28	549.613	78.3873	29	408.835	86.5179			

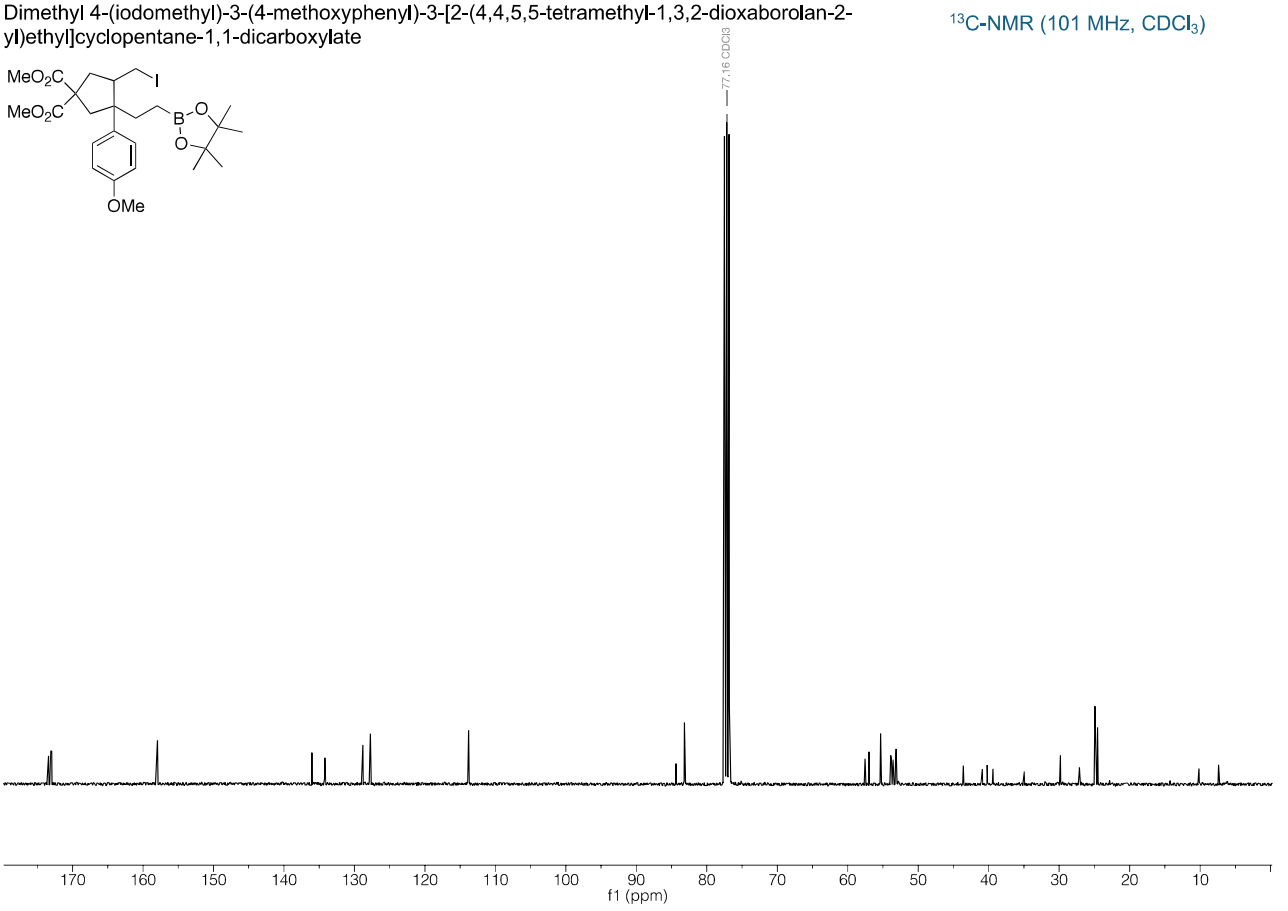
Dimethyl 4-(iodomethyl)-3-(4-methoxyphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)



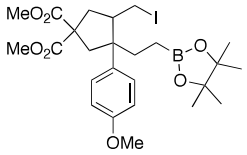
Dimethyl 4-(iodomethyl)-3-(4-methoxyphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

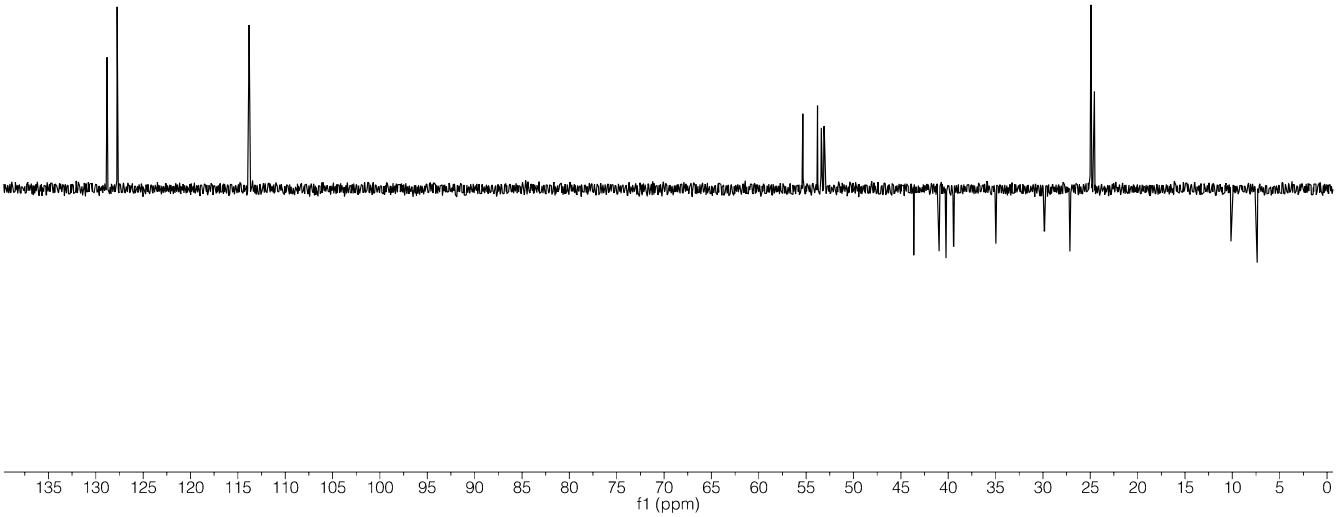
^{13}C-NMR (101 MHz, $CDCl_3$)



Dimethyl 4-(iodomethyl)-3-(4-methoxyphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

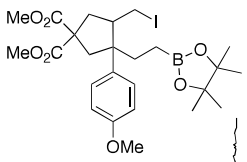
DEPT-135 NMR (101 MHz, $CDCl_3$)





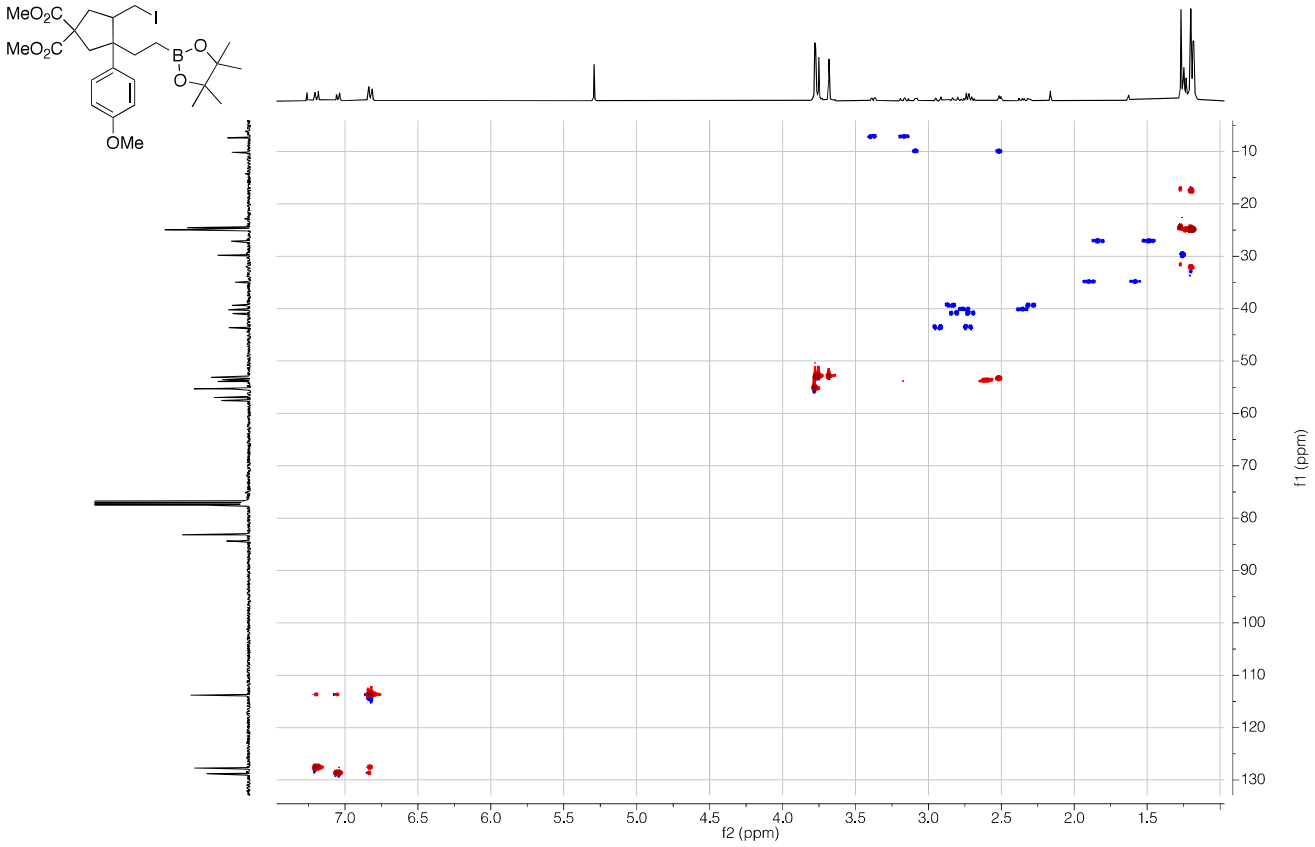
Dimethyl 4-(iodomethyl)-3-(4-methoxyphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^1H, ^1H-COSY (400 MHz, $CDCl_3$)



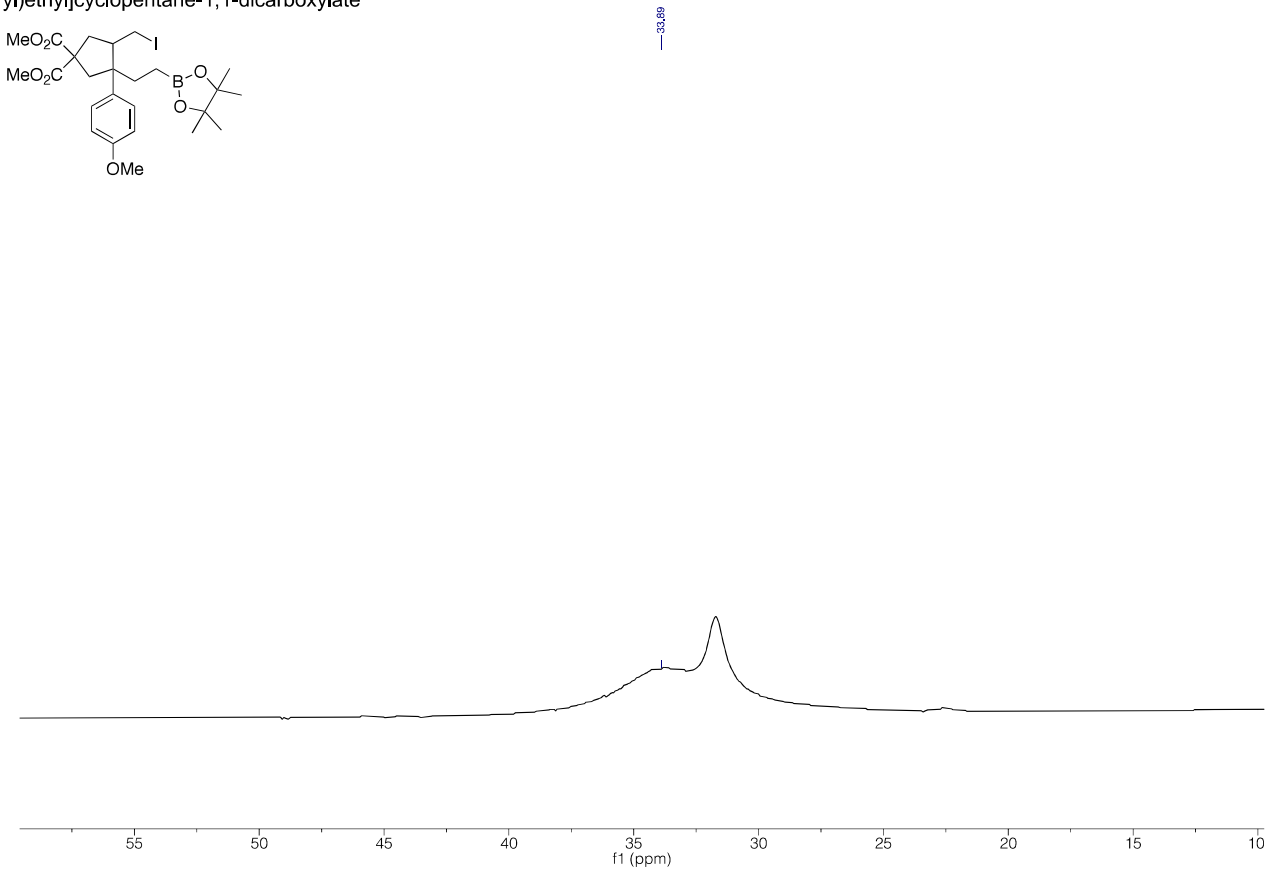
Dimethyl 4-(iodomethyl)-3-(4-methoxyphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



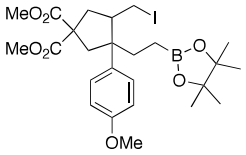
Dimethyl 4-(iodomethyl)-3-(4-methoxyphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

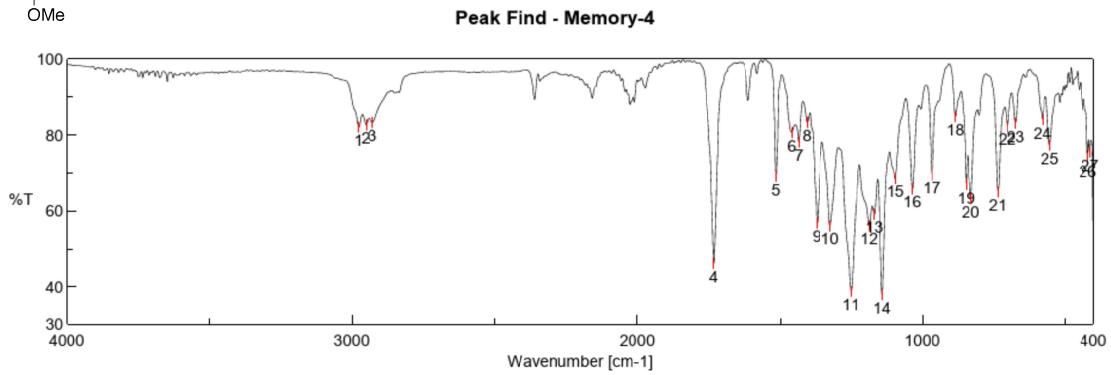
^{11}B-NMR (128 MHz, $CDCl_3$)



Dimethyl 4-(iodomethyl)-3-(4-methoxyphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



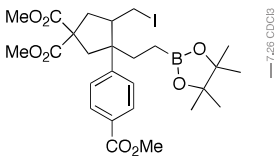


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2976.59	81.9966	2	2951.52	82.604	3	2930.31	83.275
4	1730.8	46.1356	5	1513.85	69.1011	6	1457.92	80.5653
7	1433.82	78.1256	8	1404.89	83.2909	9	1371.14	56.6934
10	1323.89	56.0008	11	1250.61	38.7505	12	1186.01	56.0235
13	1167.69	59.055	14	1141.65	37.8815	15	1094.4	68.4621
16	1034.62	65.7119	17	967.126	69.4262	18	884.202	84.8189
19	845.633	66.8899	20	830.205	63.2103	21	735.71	64.9921
22	702.926	82.2399	23	673.999	83.0972	24	578.54	84.0559
25	553.47	77.2809	26	419.442	73.7249	27	411.728	75.4979

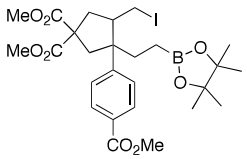
Dimethyl 4-(iodomethyl)-3-(4-methoxycarbonylphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)



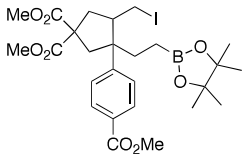
Dimethyl 4-(iodomethyl)-3-(4-methoxycarbonylphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

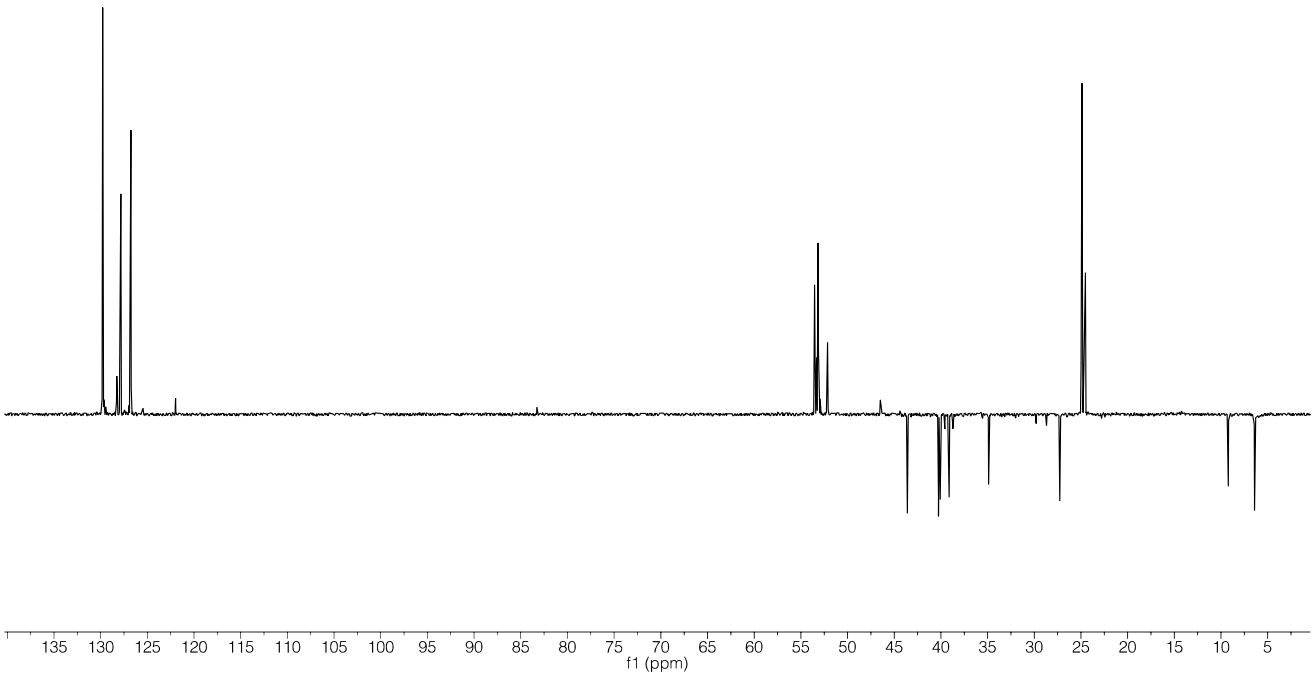
^{13}C-NMR (101 MHz, $CDCl_3$)



Dimethyl 4-(iodomethyl)-3-(4-methoxycarbonylphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

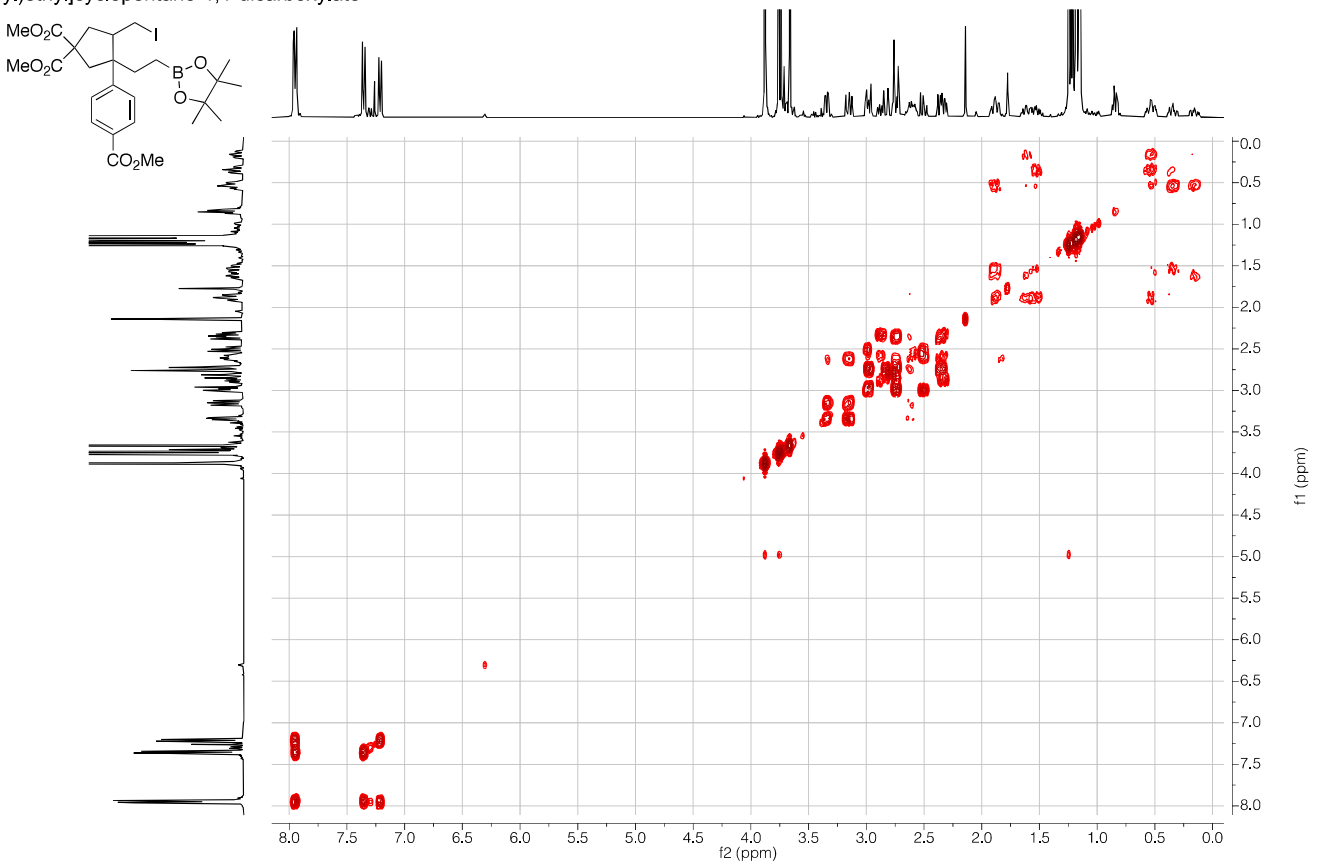
DEPT-135 NMR (101 MHz, $CDCl_3$)





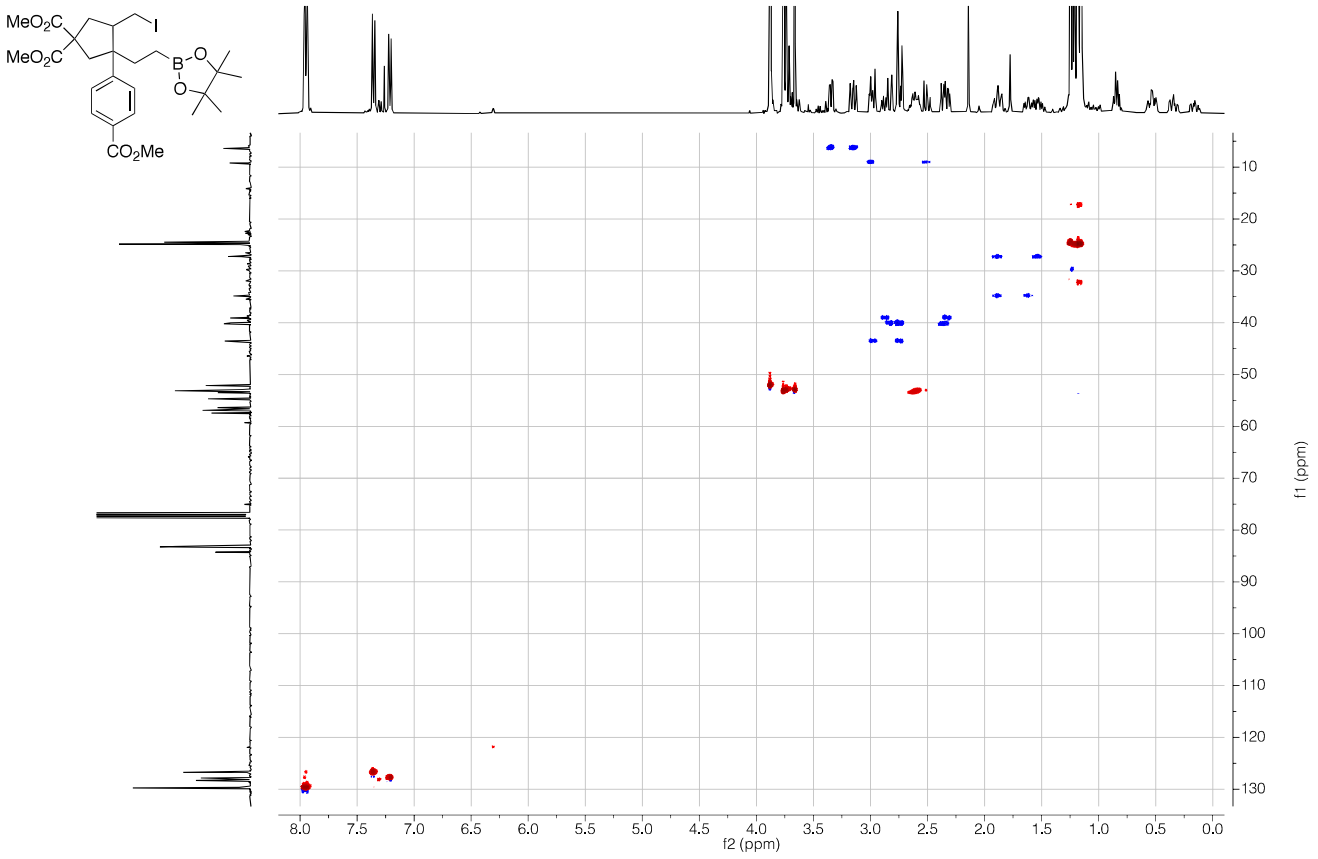
Dimethyl 4-(iodomethyl)-3-(4-methoxycarbonylphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



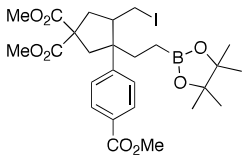
Dimethyl 4-(iodomethyl)-3-(4-methoxycarbonylphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



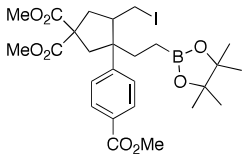
Dimethyl 4-(iodomethyl)-3-(4-methoxycarbonylphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

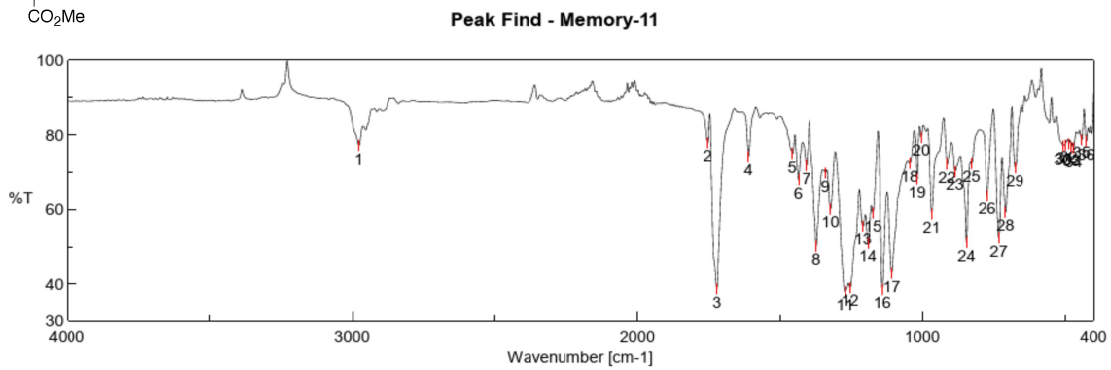
^{11}B-NMR (128 MHz, $CDCl_3$)



Dimethyl 4-(iodomethyl)-3-(4-methoxycarbonylphenyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



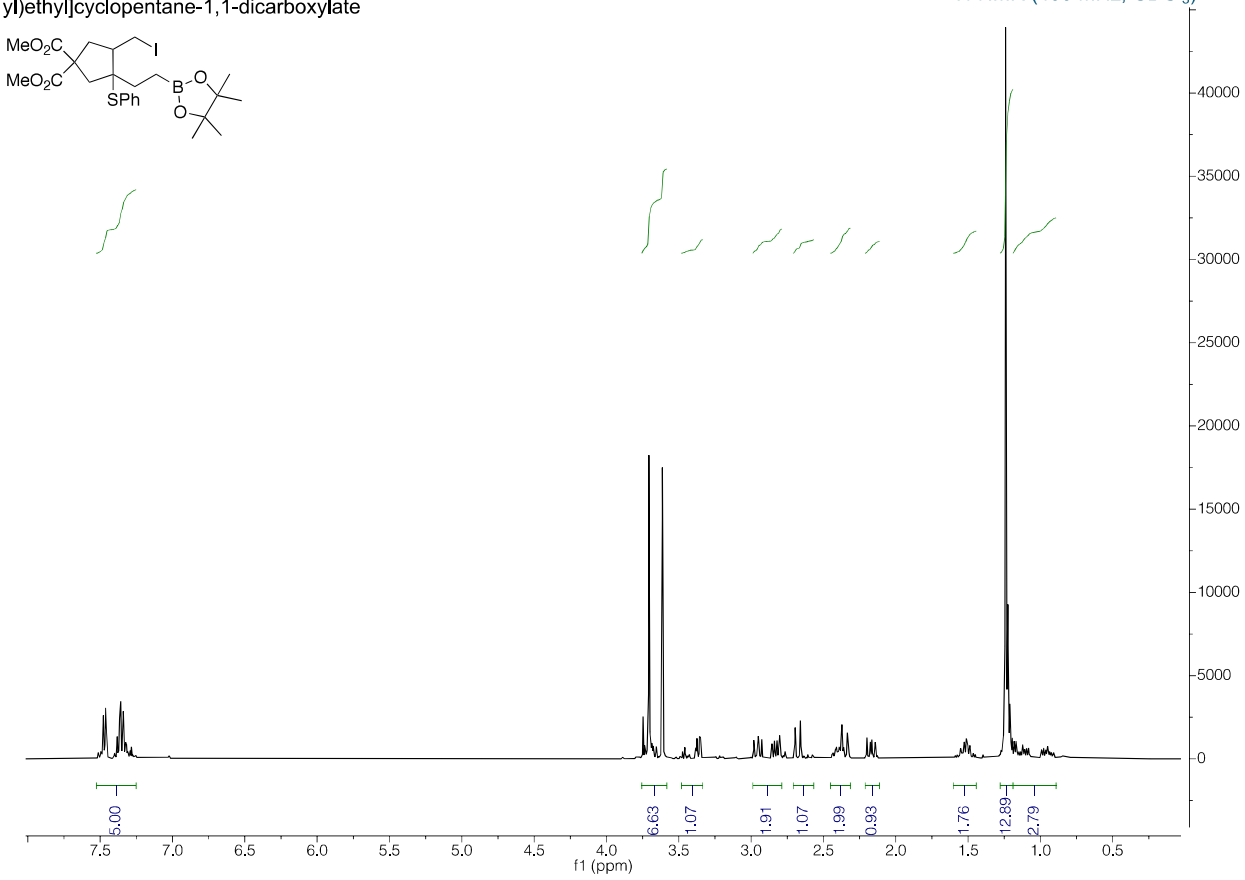


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2977.55	76.9997	2	1752.01	77.7123	3	1720.19	38.5739
4	1609.31	74.0937	5	1455.99	74.8384	6	1434.78	67.8821
7	1406.82	71.7447	8	1371.14	49.9543	9	1339.32	69.7095
10	1321.96	59.9797	11	1271.82	37.8045	12	1254.47	38.9123
13	1209.15	55.3874	14	1190.83	50.8237	15	1173.47	58.9187
16	1140.69	38.4329	17	1107.9	42.7905	18	1044.26	72.2988
19	1018.23	68.0009	20	1003.77	79.188	21	967.126	58.6533
22	912.165	72.1132	23	885.166	70.0458	24	845.633	51.0538
25	828.277	72.254	26	773.315	63.6099	27	731.853	52.2425
28	708.712	59.1305	29	674.963	71.131	30	508.151	76.9366
31	501.401	77.0522	32	486.938	77.5034	33	478.26	76.6489
34	470.546	76.3491	35	441.619	78.5843	36	425.227	78.1983

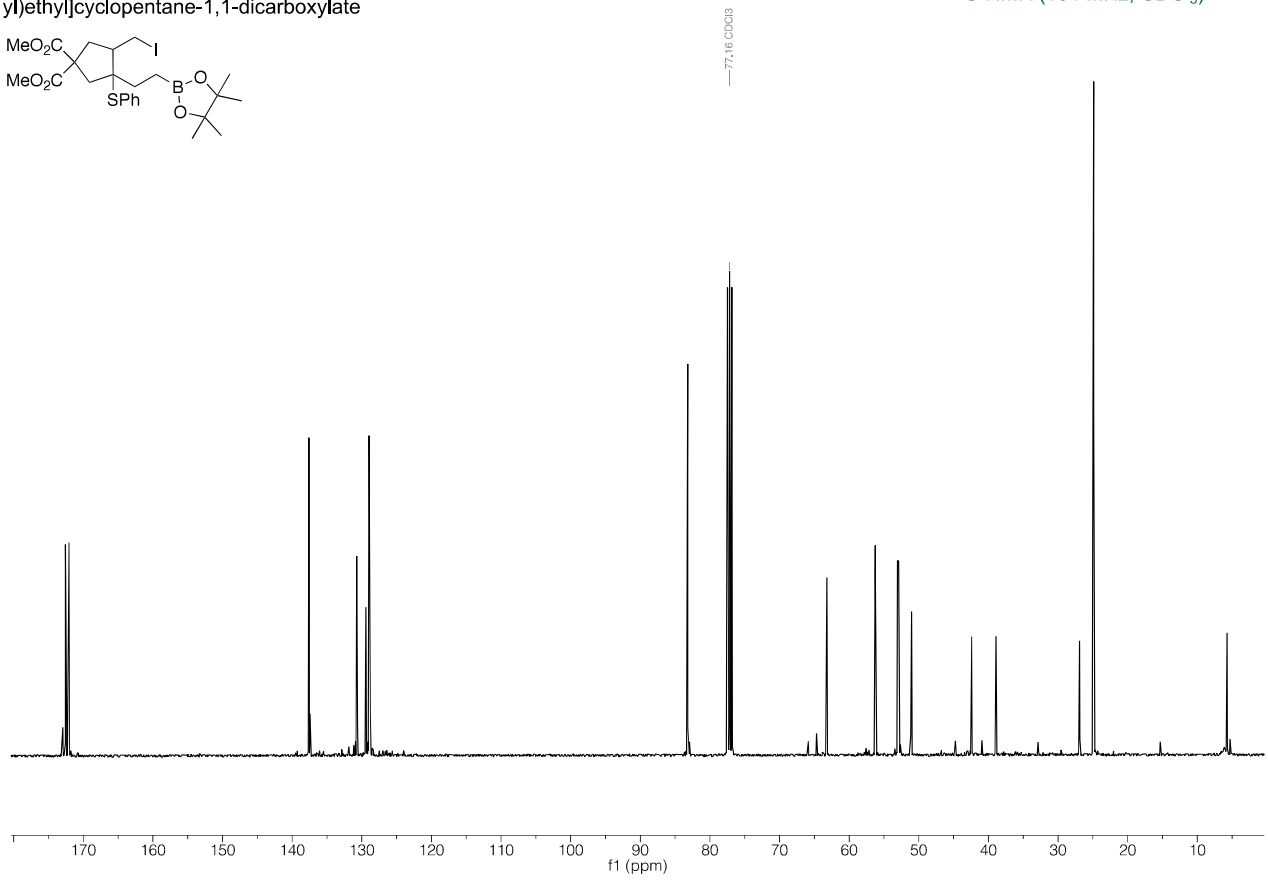
Dimethyl 4-(iodomethyl)-3-phenylsulfanyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)

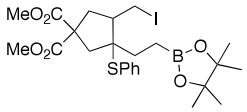


Dimethyl 4-(iodomethyl)-3-phenylsulfanyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{13}C-NMR (101 MHz, $CDCl_3$)

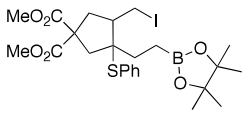


Dimethyl 4-(iodomethyl)-3-phenylsulfanyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate



DEPT-135 NMR (101 MHz, $CDCl_3$)

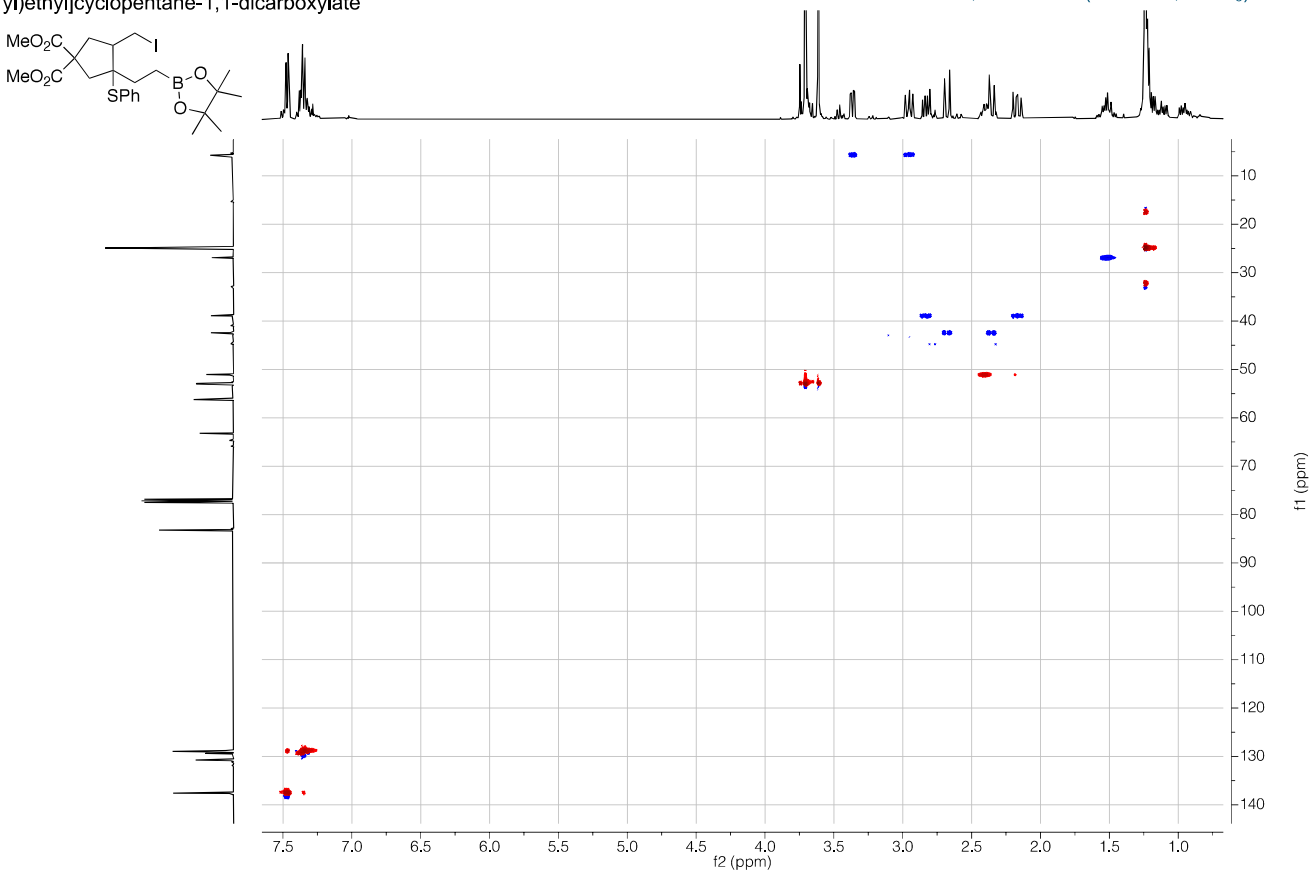
Dimethyl 4-(iodomethyl)-3-phenylsulfanyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate



^1H, ^1H-COSY (400 MHz, $CDCl_3$)

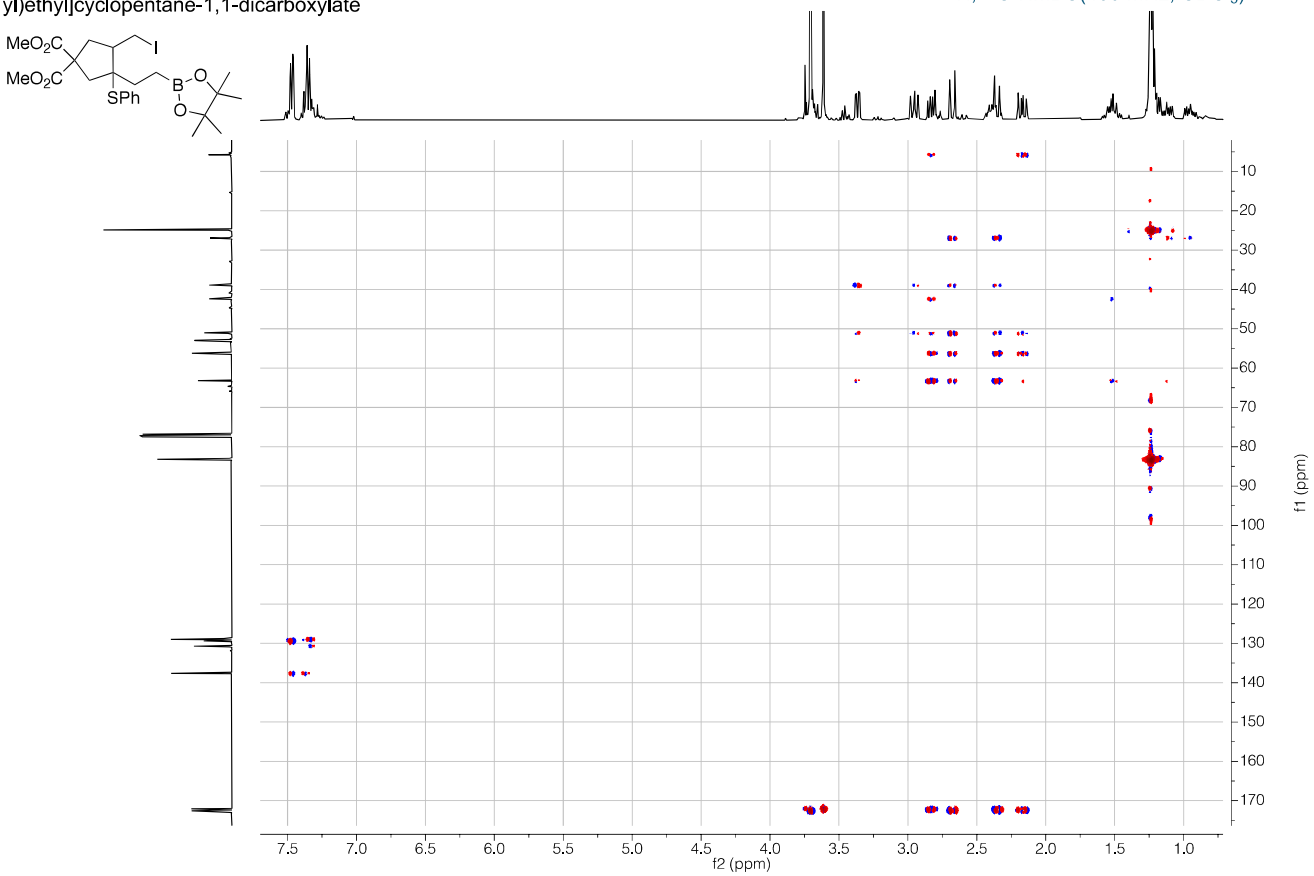
Dimethyl 4-(iodomethyl)-3-phenylsulfanyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



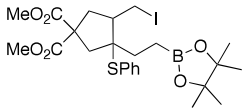
Dimethyl 4-(iodomethyl)-3-phenylsulfanyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC(400 MHz, $CDCl_3$)



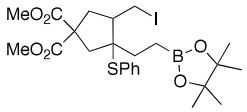
Dimethyl 4-(iodomethyl)-3-phenylsulfanyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

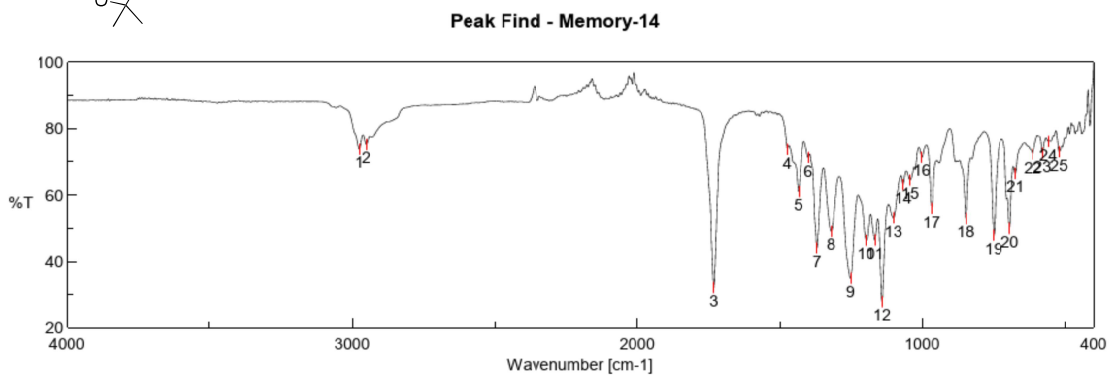
^{11}B-NMR (128 MHz, $CDCl_3$)



Dimethyl 4-(iodomethyl)-3-phenylsulfanyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



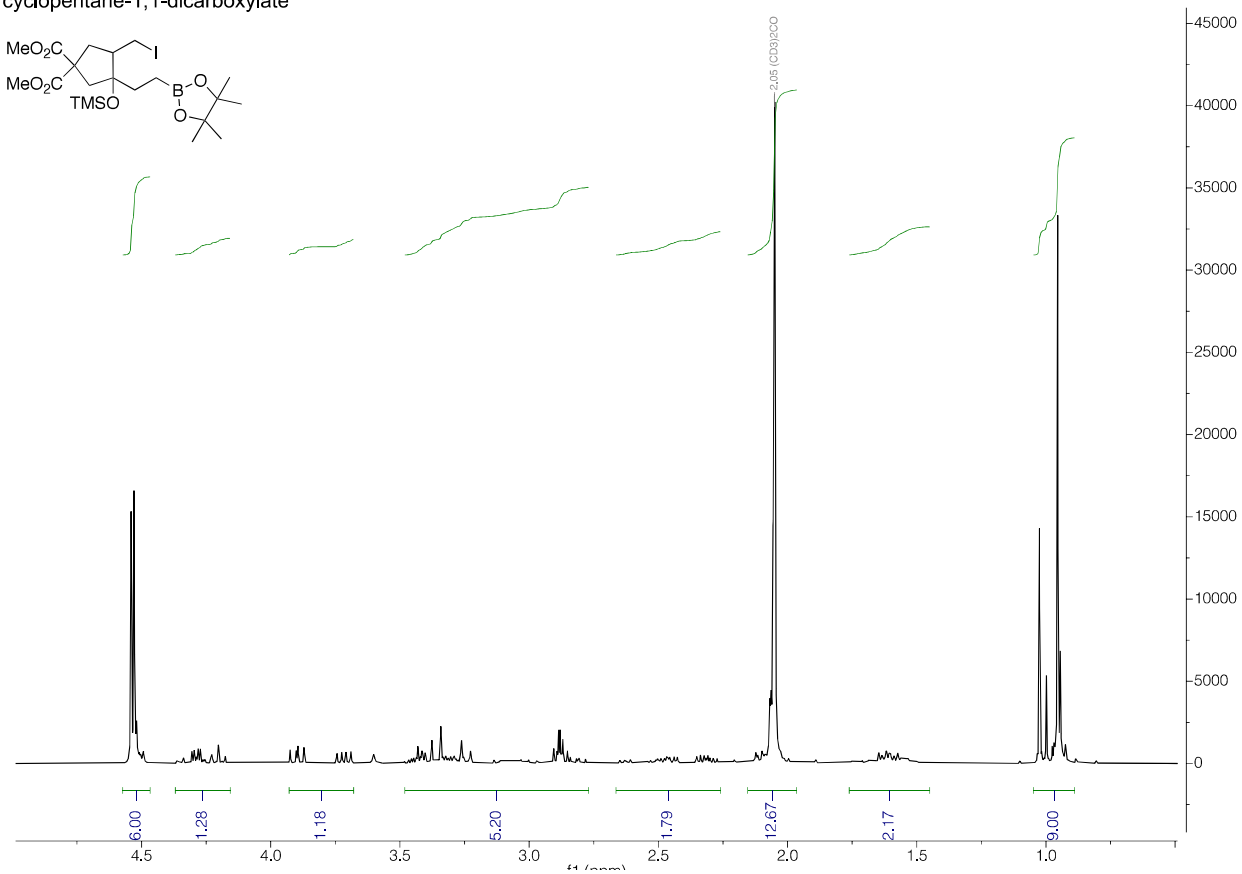


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	73.7717	2	2950.55	75.1768	3	1731.76	32.1369
4	1473.35	73.7361	5	1434.78	61.0001	6	1402	71.2875
7	1370.18	44.0546	8	1320.04	49.0575	9	1252.54	34.9581
10	1196.61	46.3675	11	1166.72	46.4387	12	1141.65	27.8496
13	1101.15	53.0891	14	1067.41	63.1103	15	1042.34	64.5246
16	1000.87	71.3507	17	966.162	55.9518	18	846.597	52.8971
19	750.174	47.8981	20	694.248	49.9363	21	673.999	66.4625
22	613.252	72.3693	23	577.576	72.5688	24	557.327	76.1325
25	520.686	73.0603						

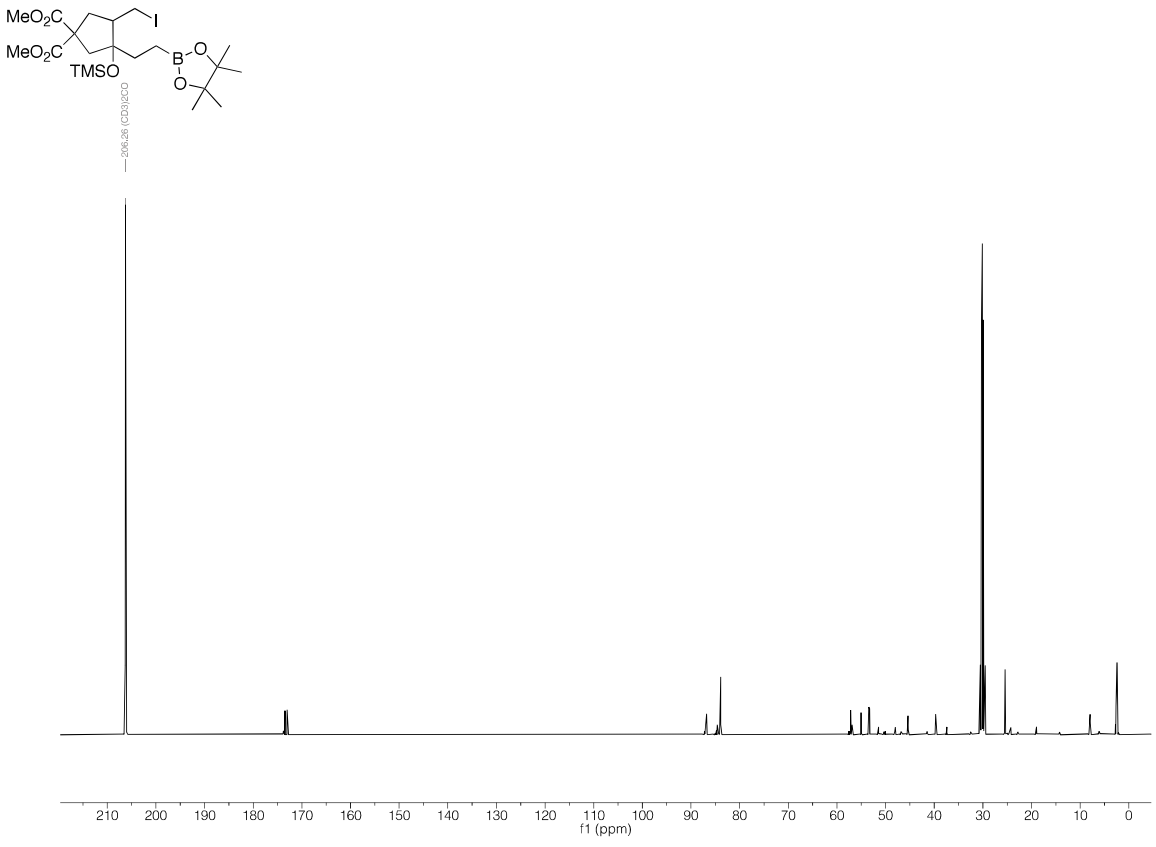
Dimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-3-trimethylsilyloxy-cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $(CD_3)_2CO$)



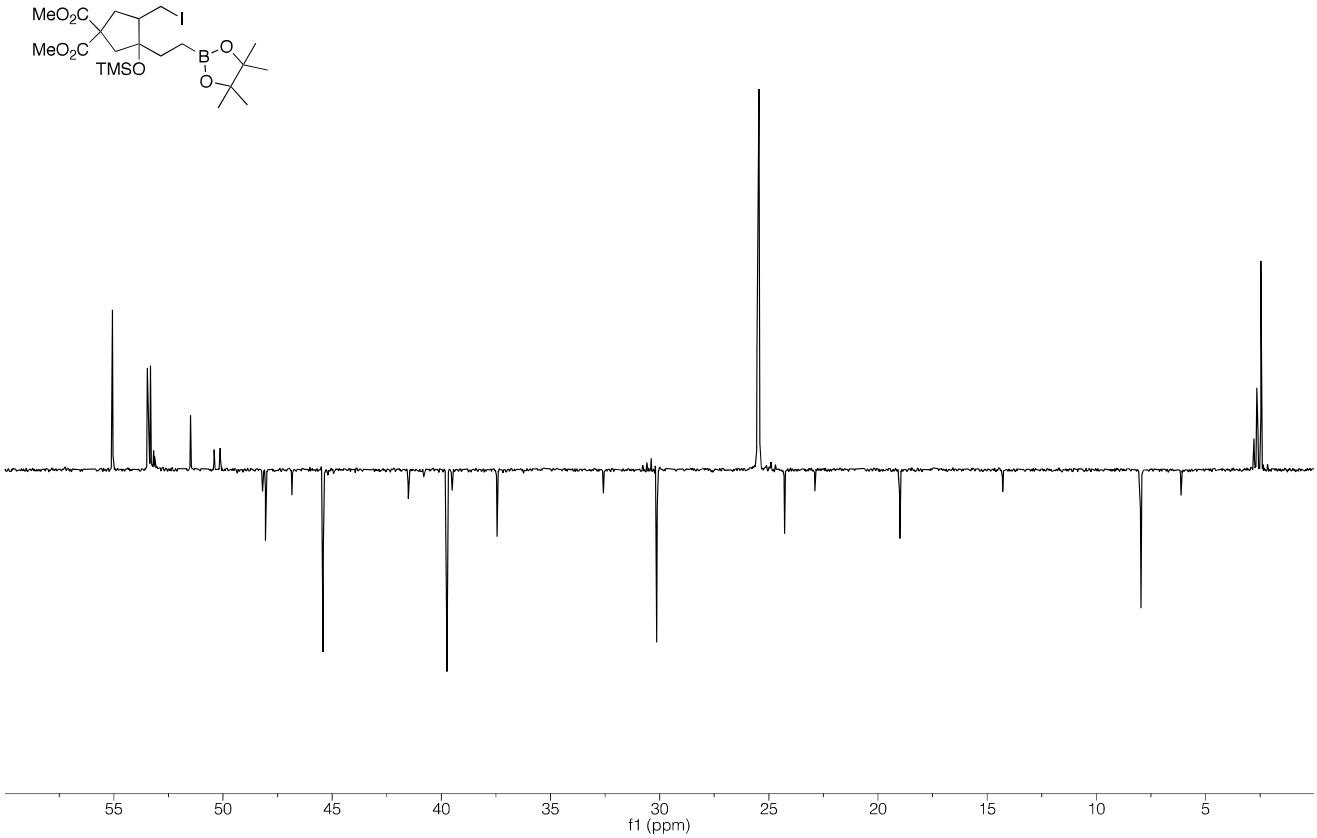
Dimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-3-trimethylsilyloxy-cyclopentane-1,1-dicarboxylate

^{13}C-NMR (101 MHz, $(CD_3)_2CO$)



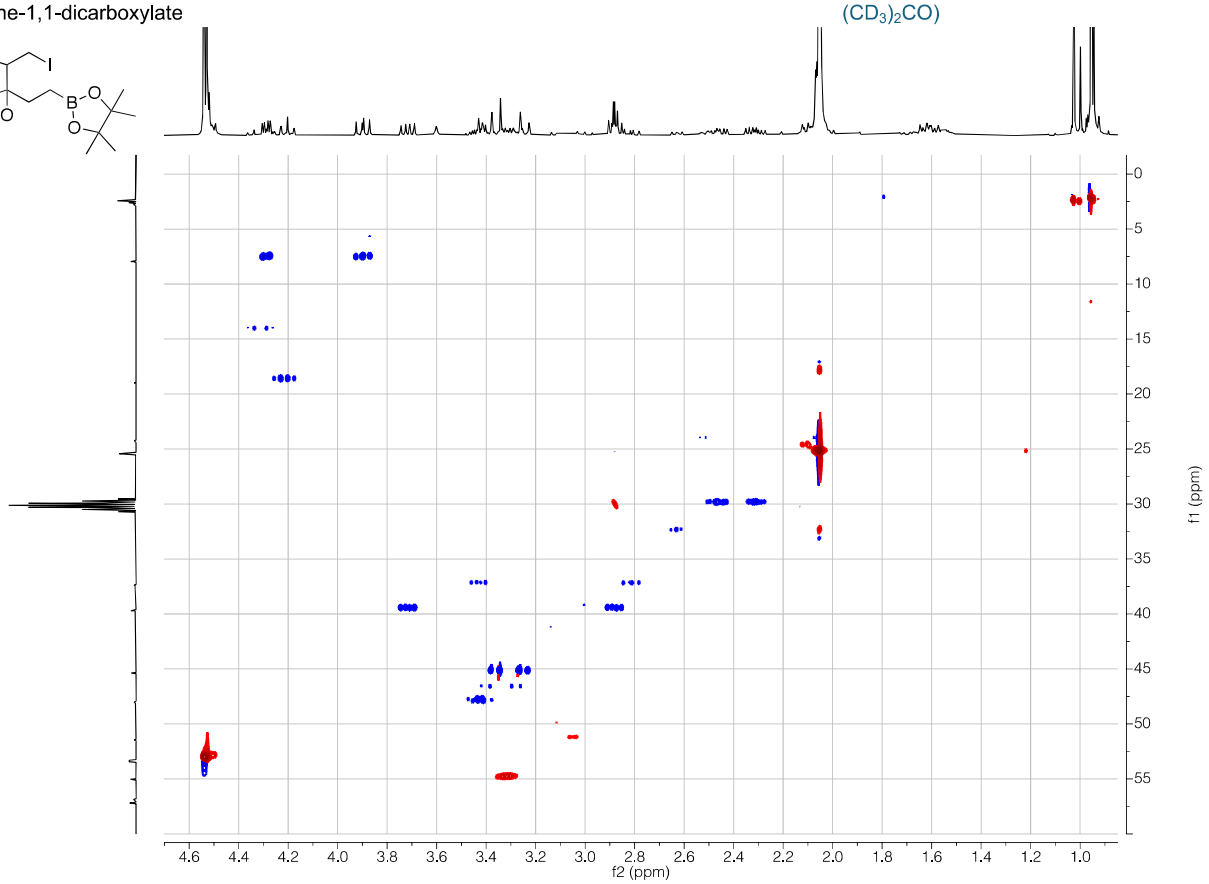
Dimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-3-trimethylsilyloxy-cyclopentane-1,1-dicarboxylate

DEPT-135 NMR (101 MHz, $(CD_3)_2CO$)



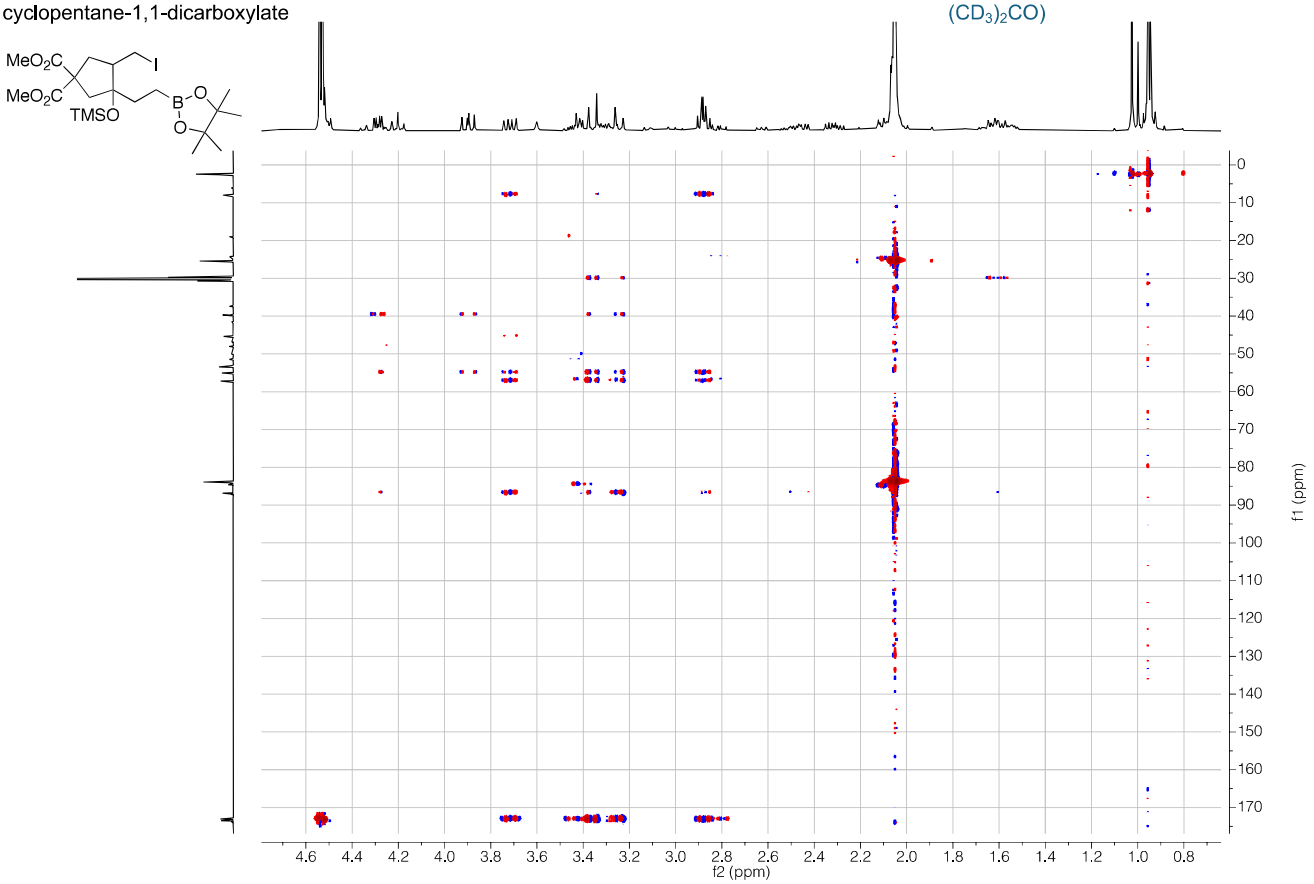
Dimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-3-trimethylsilyloxy-cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $(CD_3)_2CO$)



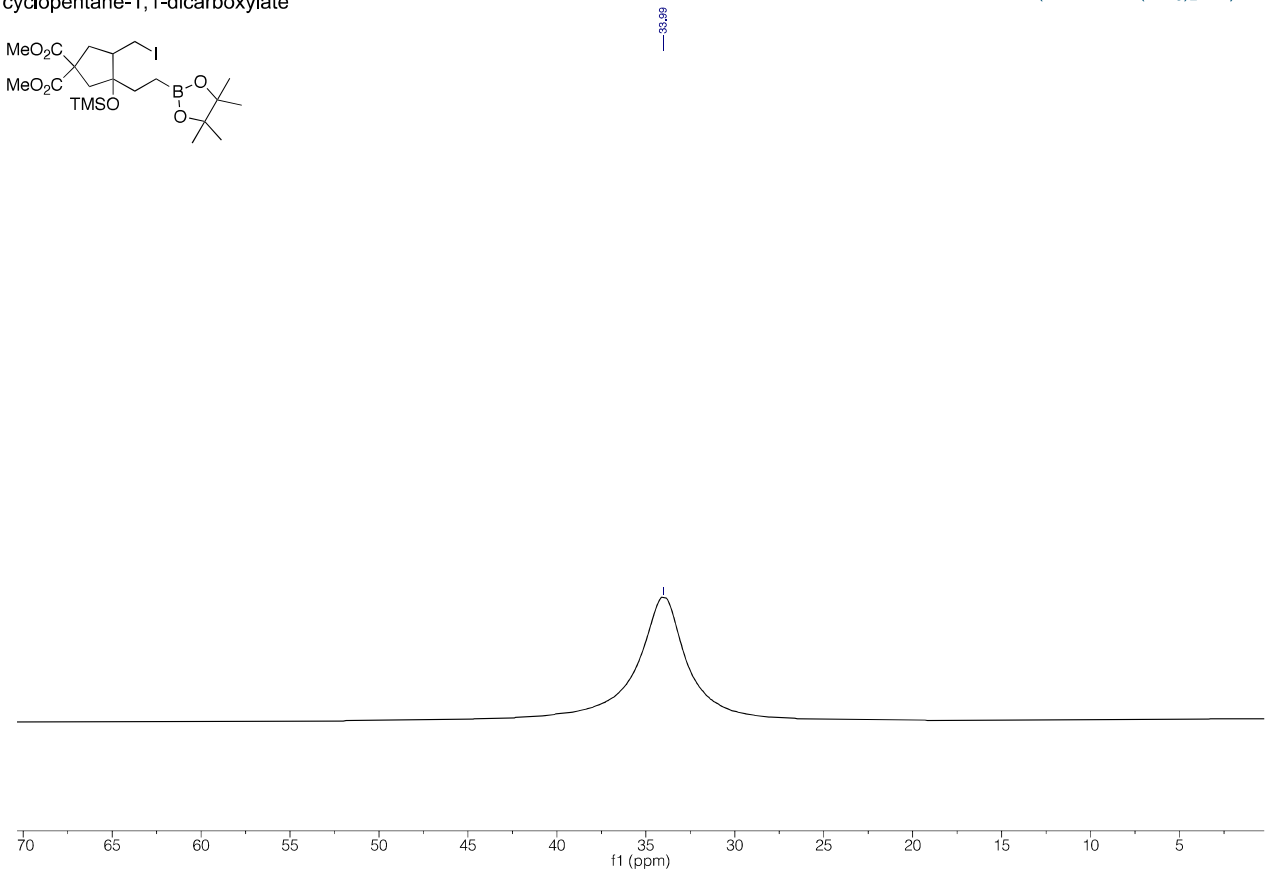
Dimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-3-trimethylsilyloxy-cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC(400 MHz, $(CD_3)_2CO$)



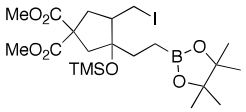
Dimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-3-trimethylsilyloxy-cyclopentane-1,1-dicarboxylate

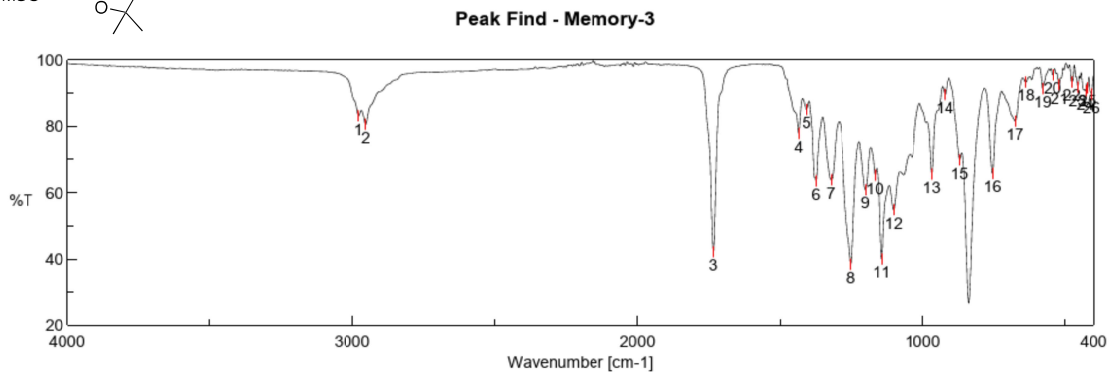
^{11}B-NMR (128 MHz, $(CD_3)_2CO$)



Dimethyl 4-(iodomethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-3-trimethylsilyloxy-cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



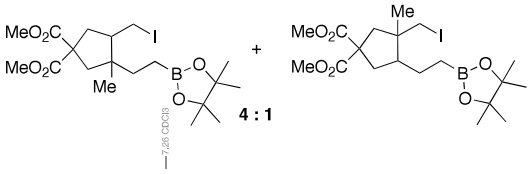


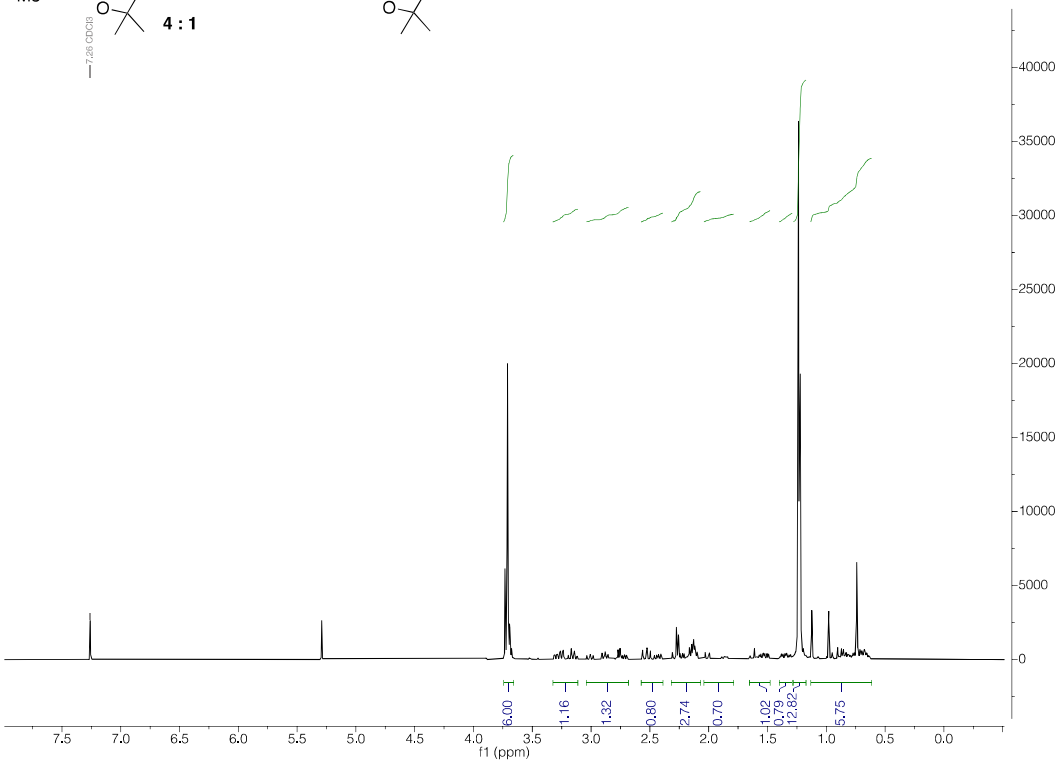
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2976.59	83.1497	2	2952.48	80.5751	3	1732.73	42.169
4	1433.82	77.8286	5	1405.85	85.0138	6	1372.1	63.4988
7	1321	63.8762	8	1249.65	38.3979	9	1199.51	60.8526
10	1165.76	65.2425	11	1142.62	39.9843	12	1101.15	54.8568
13	967.126	65.5856	14	920.843	89.5929	15	868.774	69.8636
16	753.066	65.771	17	675.928	81.502	18	636.394	93.2998
19	577.576	91.3383	20	542.863	95.4795	21	518.758	92.5421
22	476.331	93.3211	23	456.082	91.7404	24	429.084	90.6315
25	421.37	91.5859	26	407.871	89.7266			

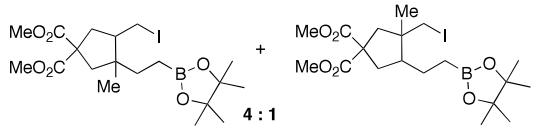
Dimethyl 4-(iodomethyl)-3-methyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)



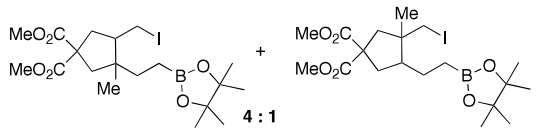


Dimethyl 4-(iodomethyl)-3-methyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

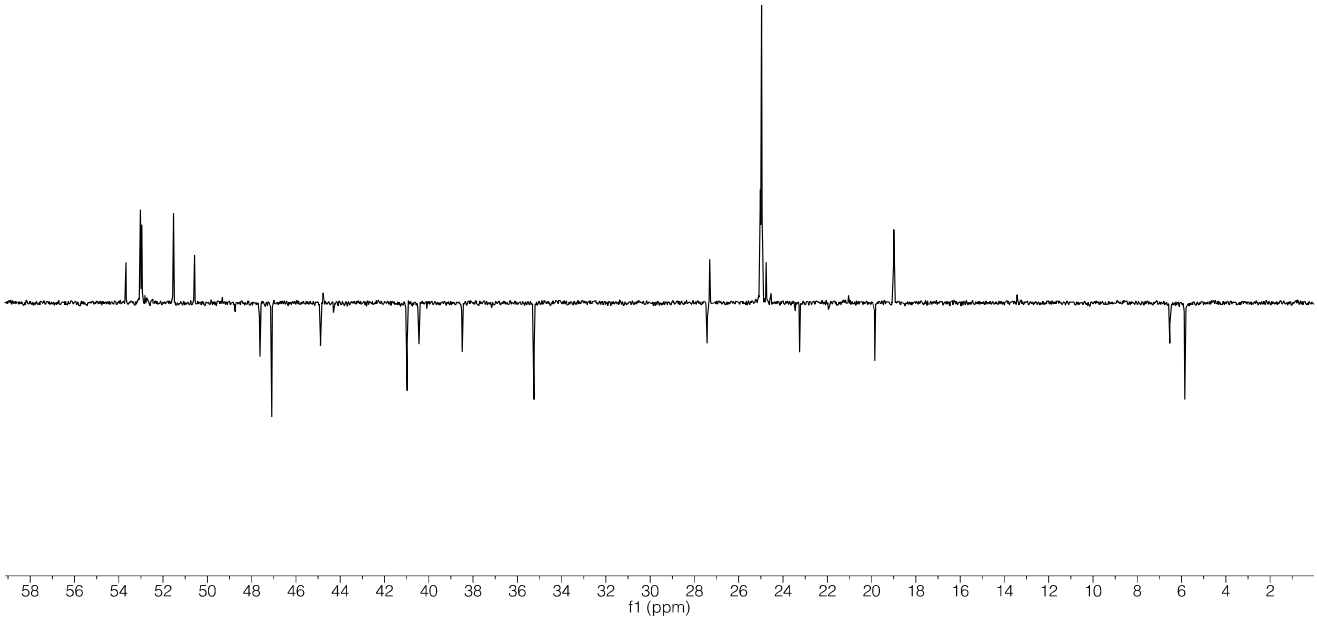


^{13}C-NMR (101 MHz, $CDCl_3$)

Dimethyl 4-(iodomethyl)-3-methyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

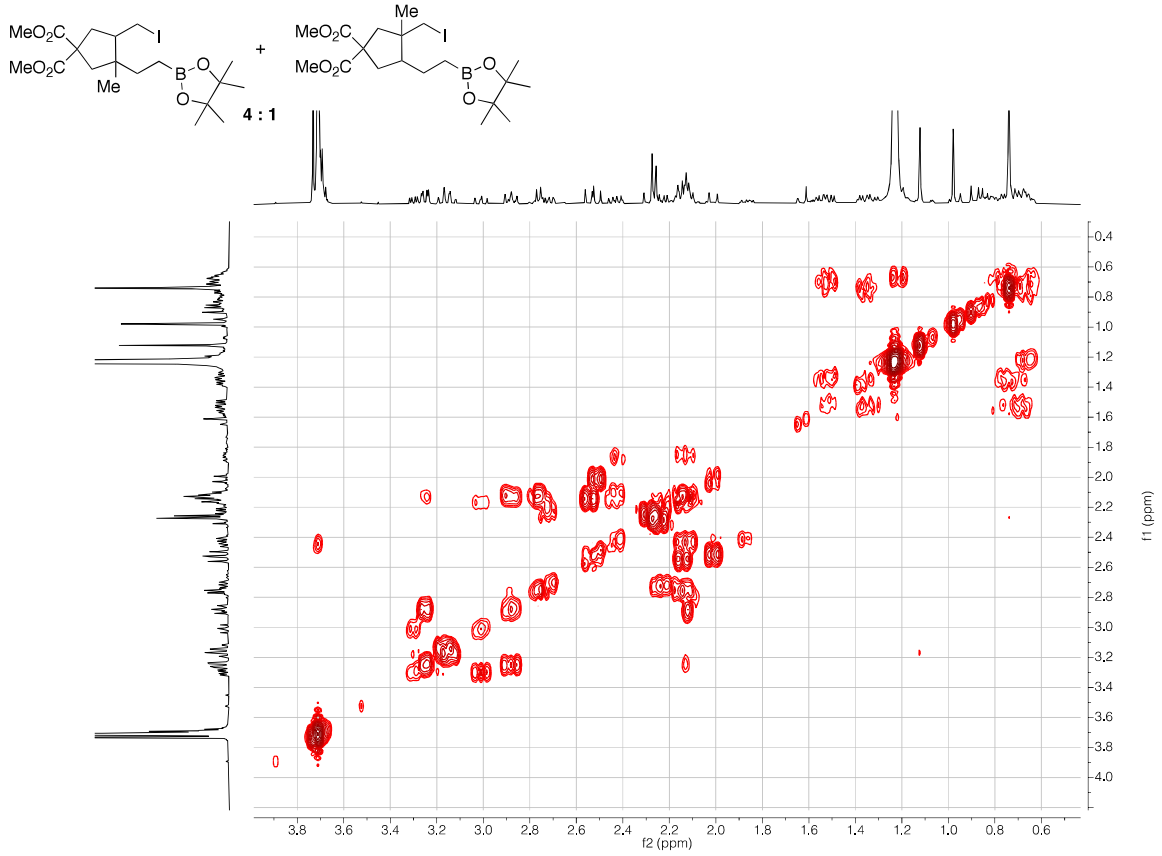


DEPT-135 NMR (101 MHz, $CDCl_3$)



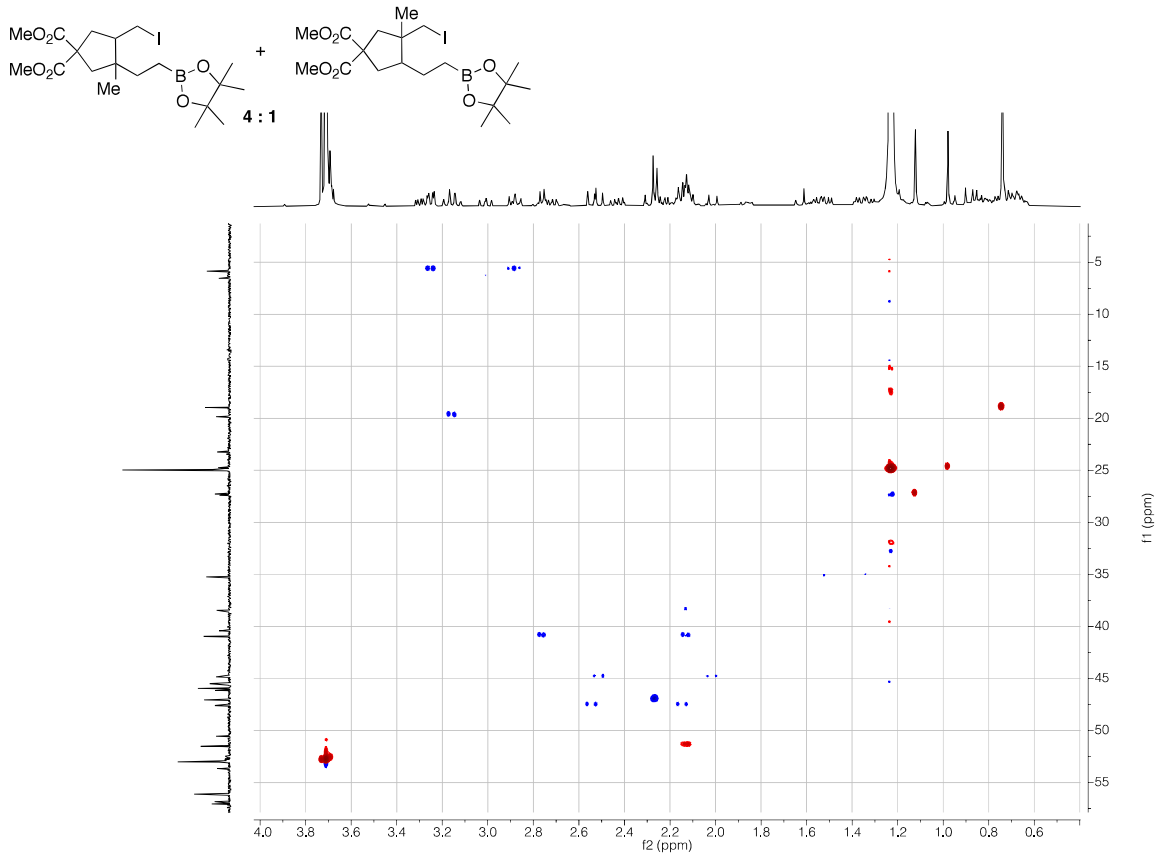
Dimethyl 4-(iodomethyl)-3-methyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



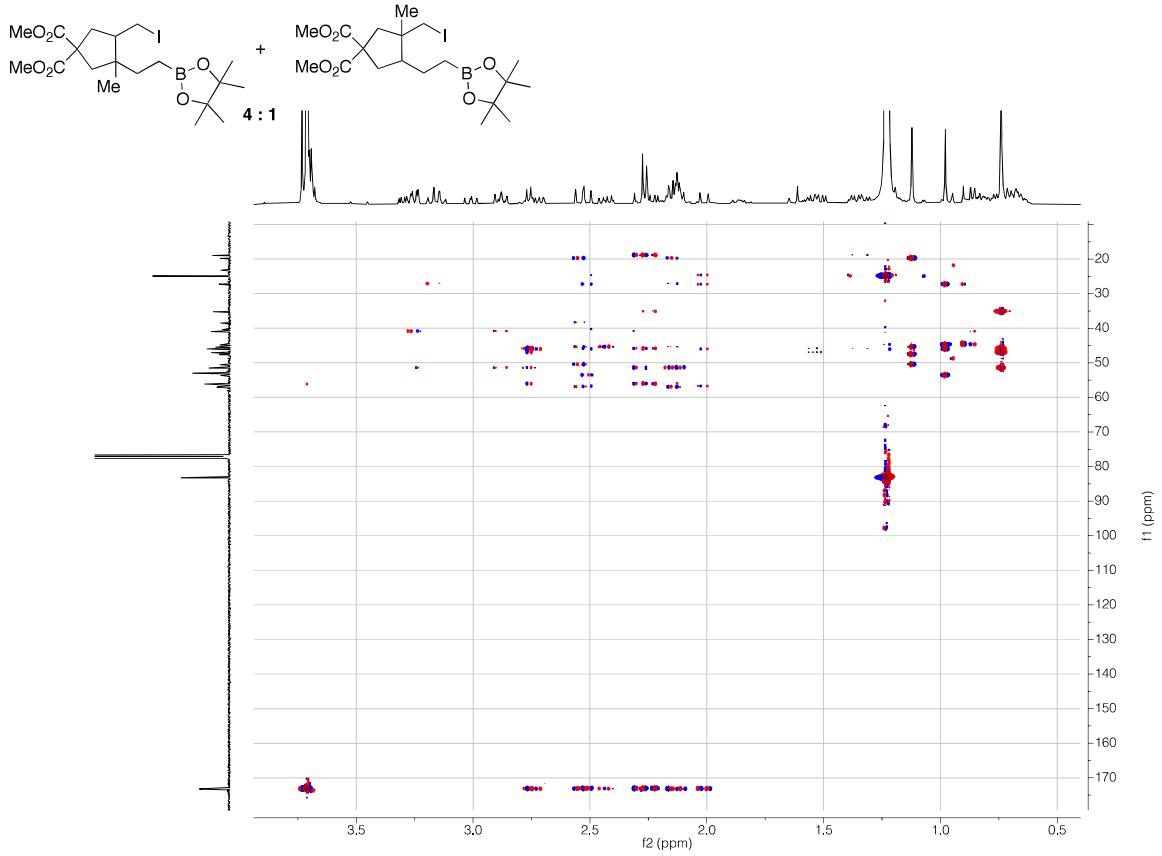
Dimethyl 4-(iodomethyl)-3-methyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



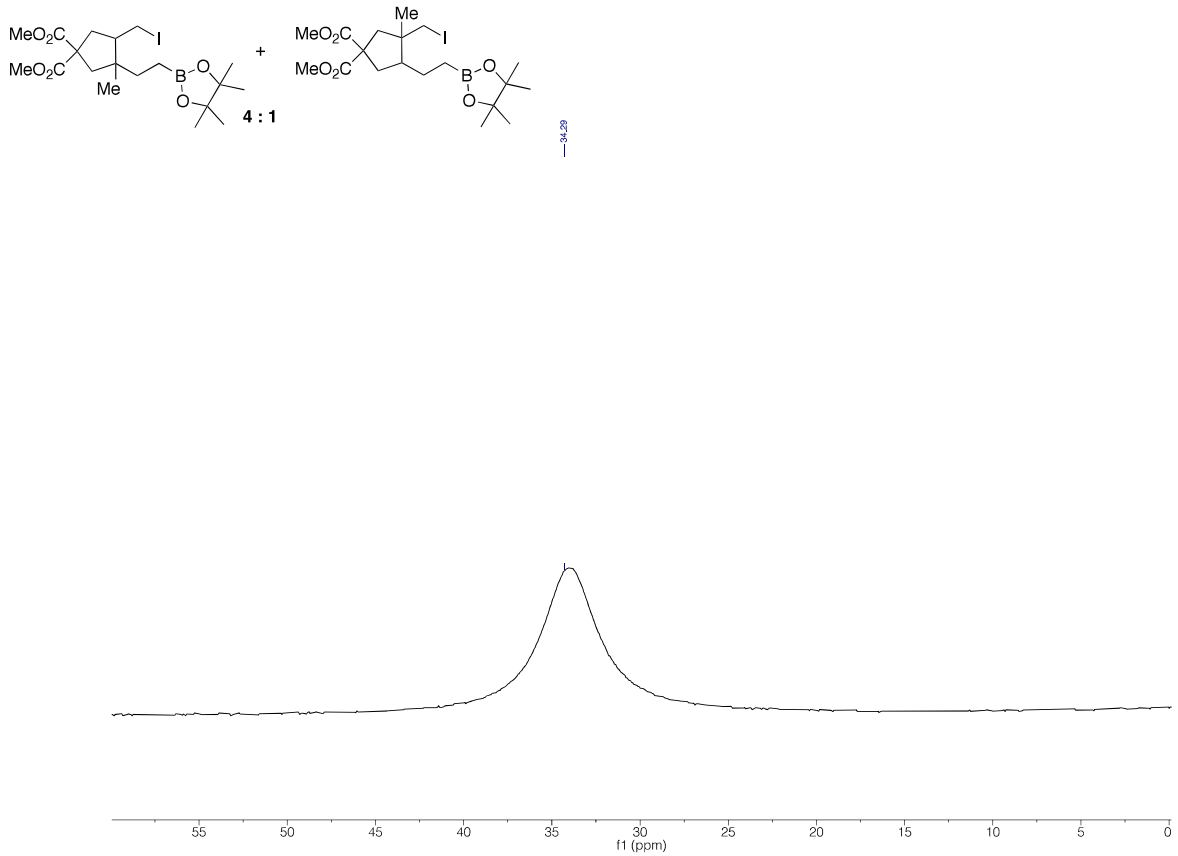
Dimethyl 4-(iodomethyl)-3-methyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC(400 MHz, $CDCl_3$)



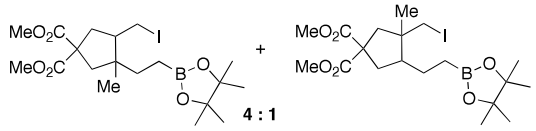
Dimethyl 4-(iodomethyl)-3-methyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

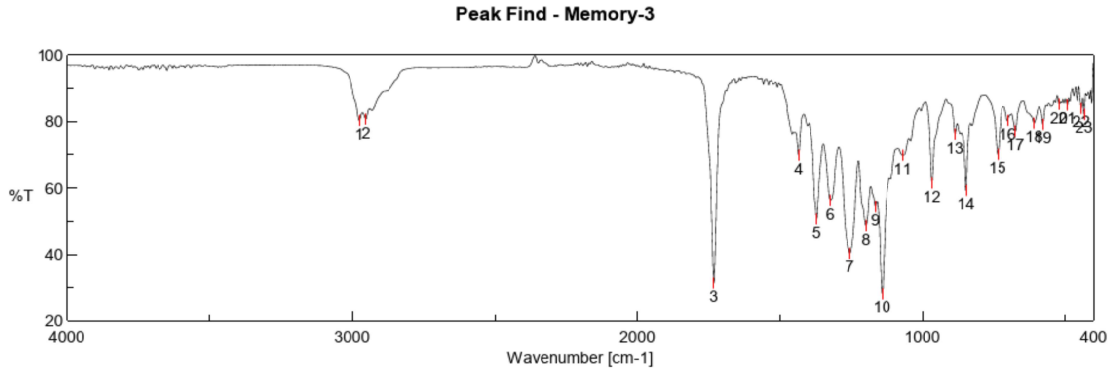
^{11}B-NMR (128 MHz, $CDCl_3$)



Dimethyl 4-(iodomethyl)-3-methyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



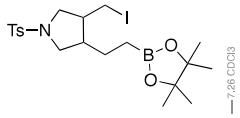


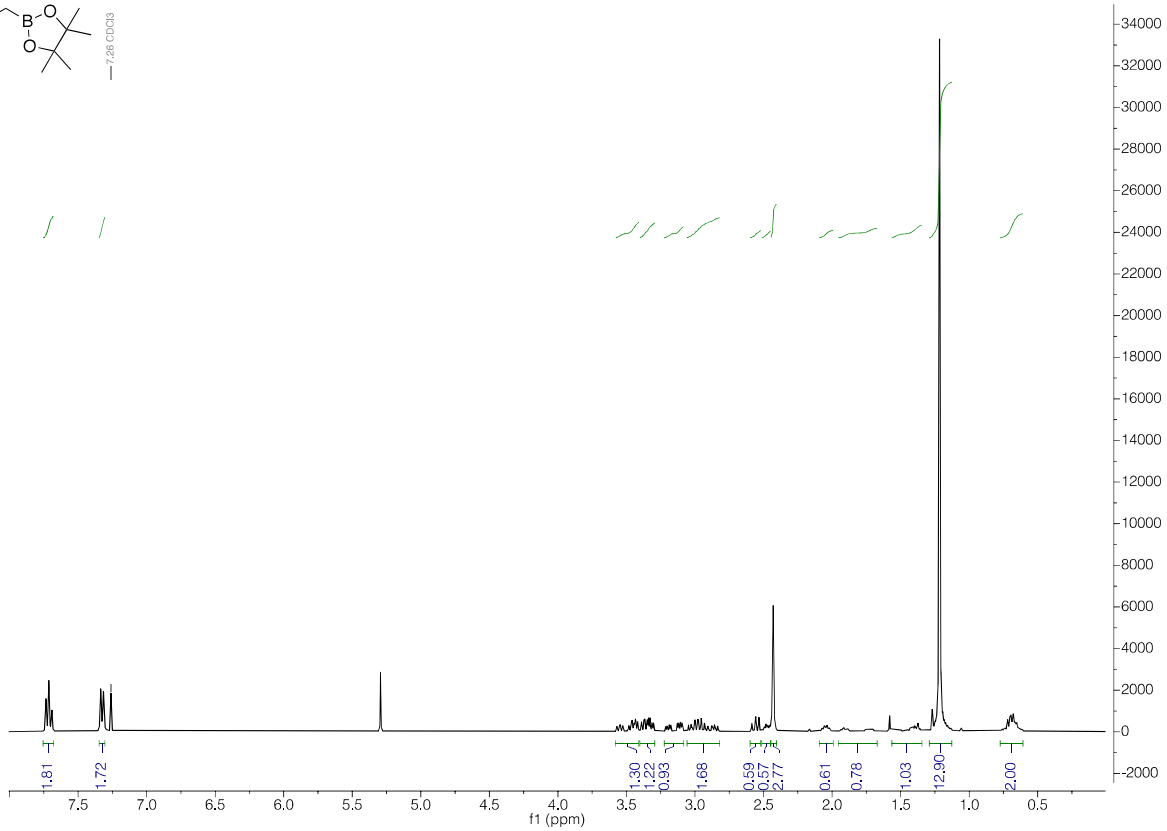
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	80.2992	2	2952.48	80.7287	3	1730.8	31.401
4	1433.82	69.8522	5	1371.14	50.6673	6	1321.96	56.2612
7	1254.47	40.2929	8	1198.54	48.6384	9	1165.76	54.3724
10	1141.65	28.1438	11	1068.37	69.8657	12	967.126	61.5051
13	885.166	76.2033	14	846.597	59.283	15	736.674	70.1161
16	700.998	80.3033	17	673.035	77.0932	18	608.431	79.4926
19	577.576	79.1232	20	520.686	85.2296	21	491.759	85.0067
22	442.583	83.9767	23	432.941	82.1478			

3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

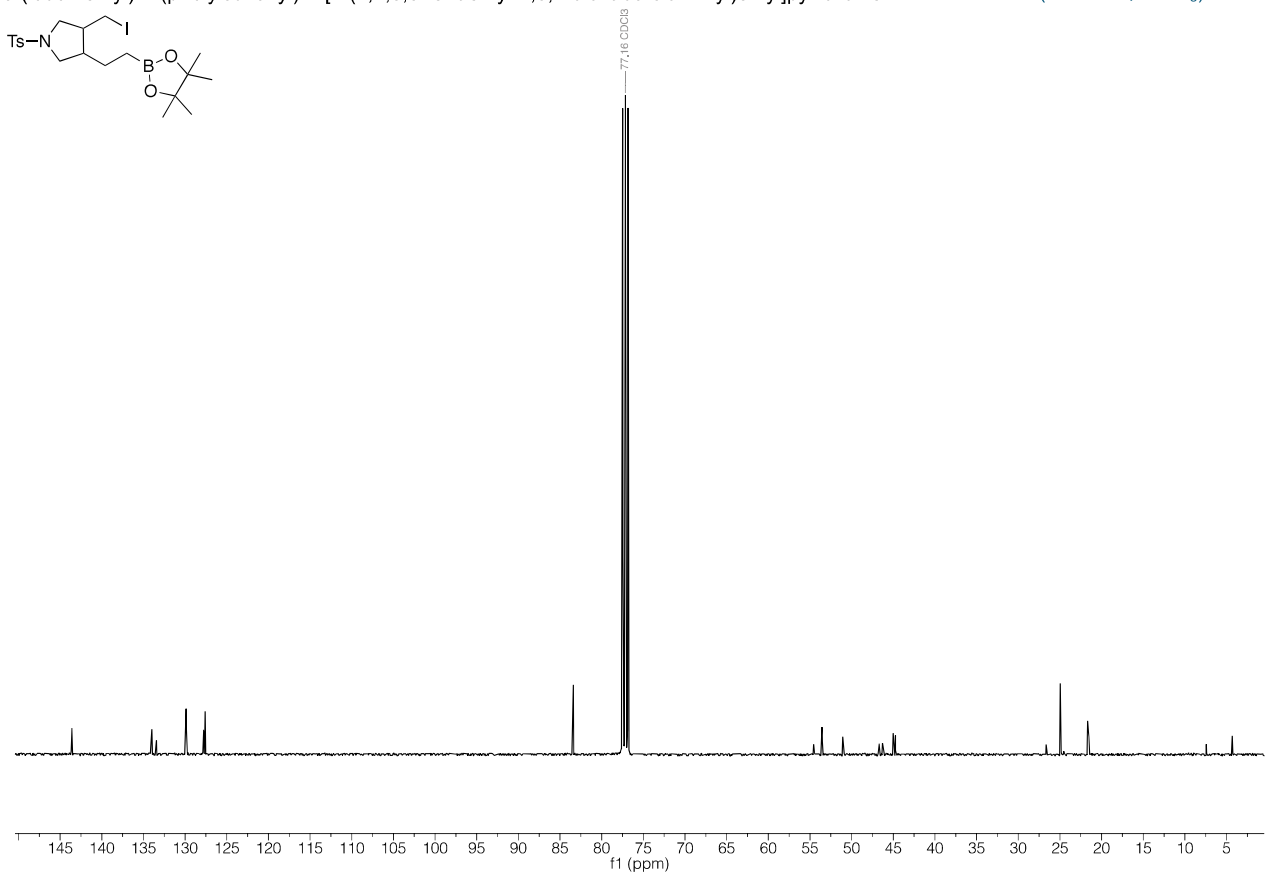
^{1}H-NMR (400 MHz, $CDCl_3$)





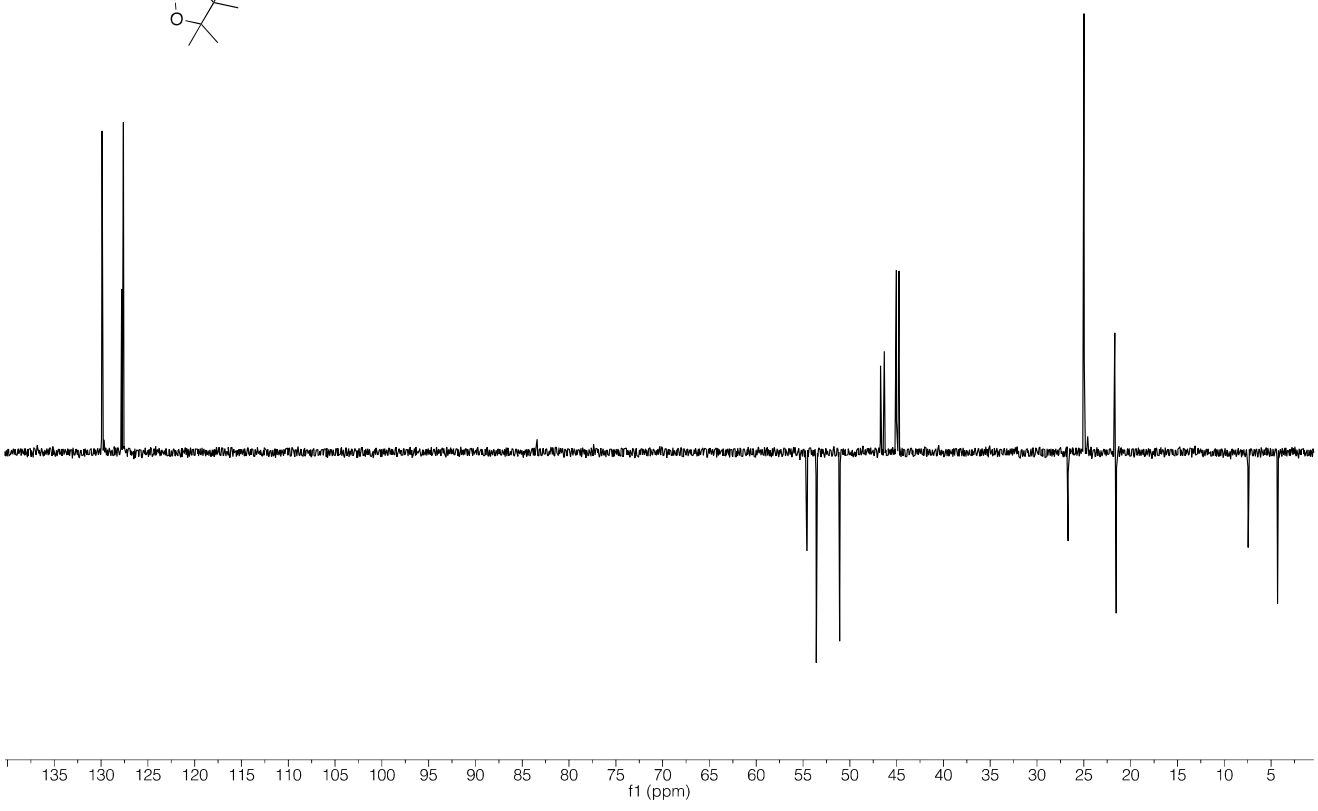
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

^{13}C-NMR (101 MHz, $CDCl_3$)



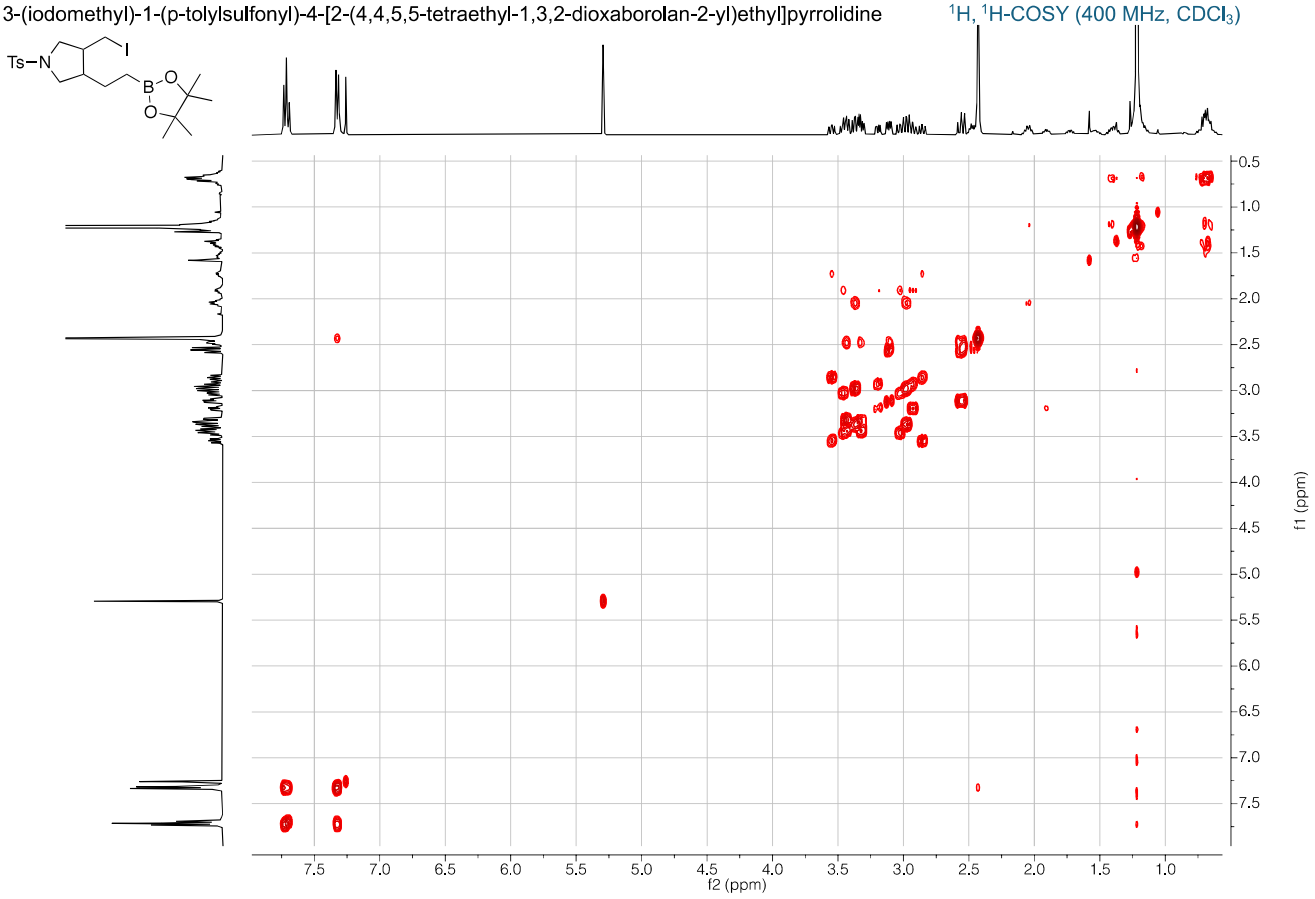
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

DEPT-135 NMR (101 MHz, $CDCl_3$)



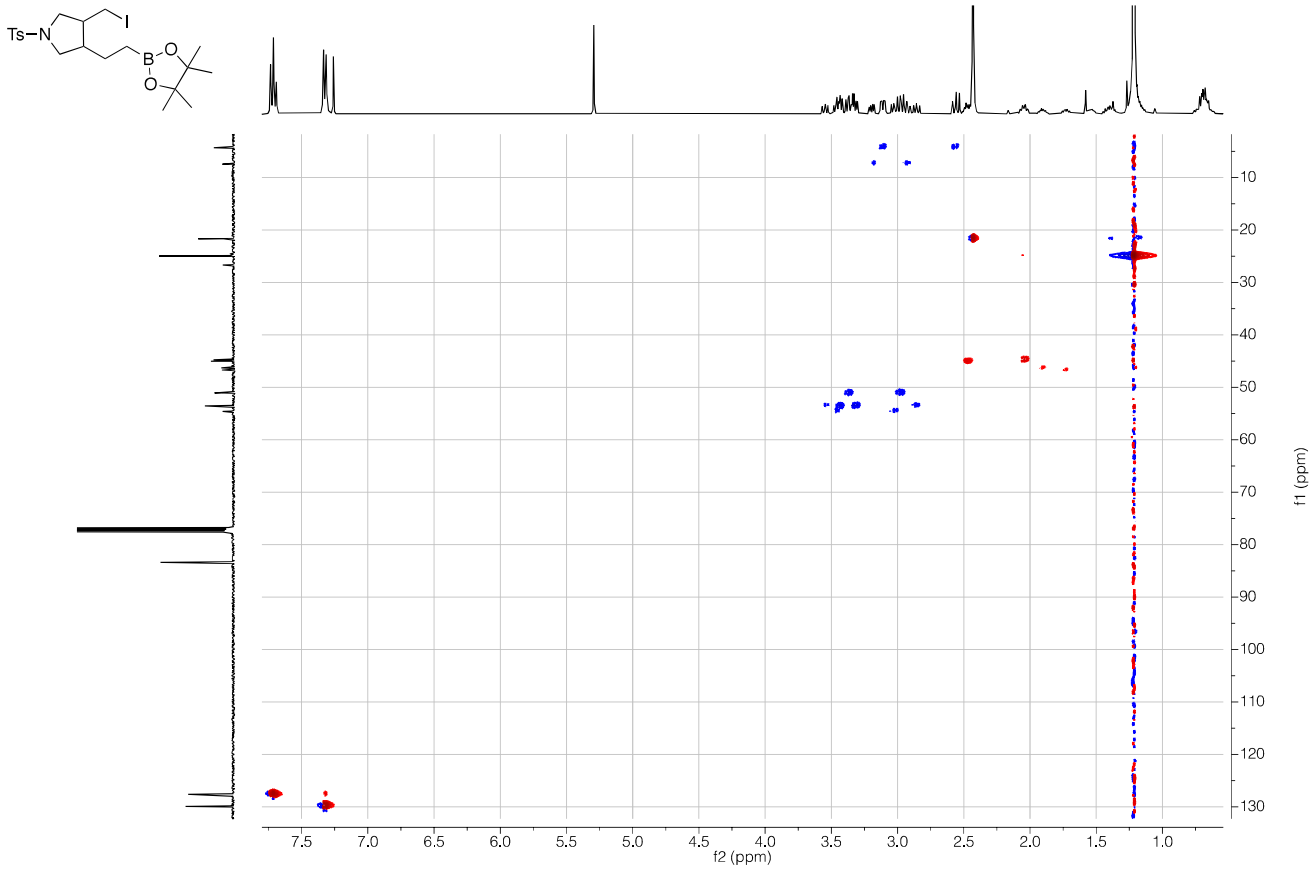
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



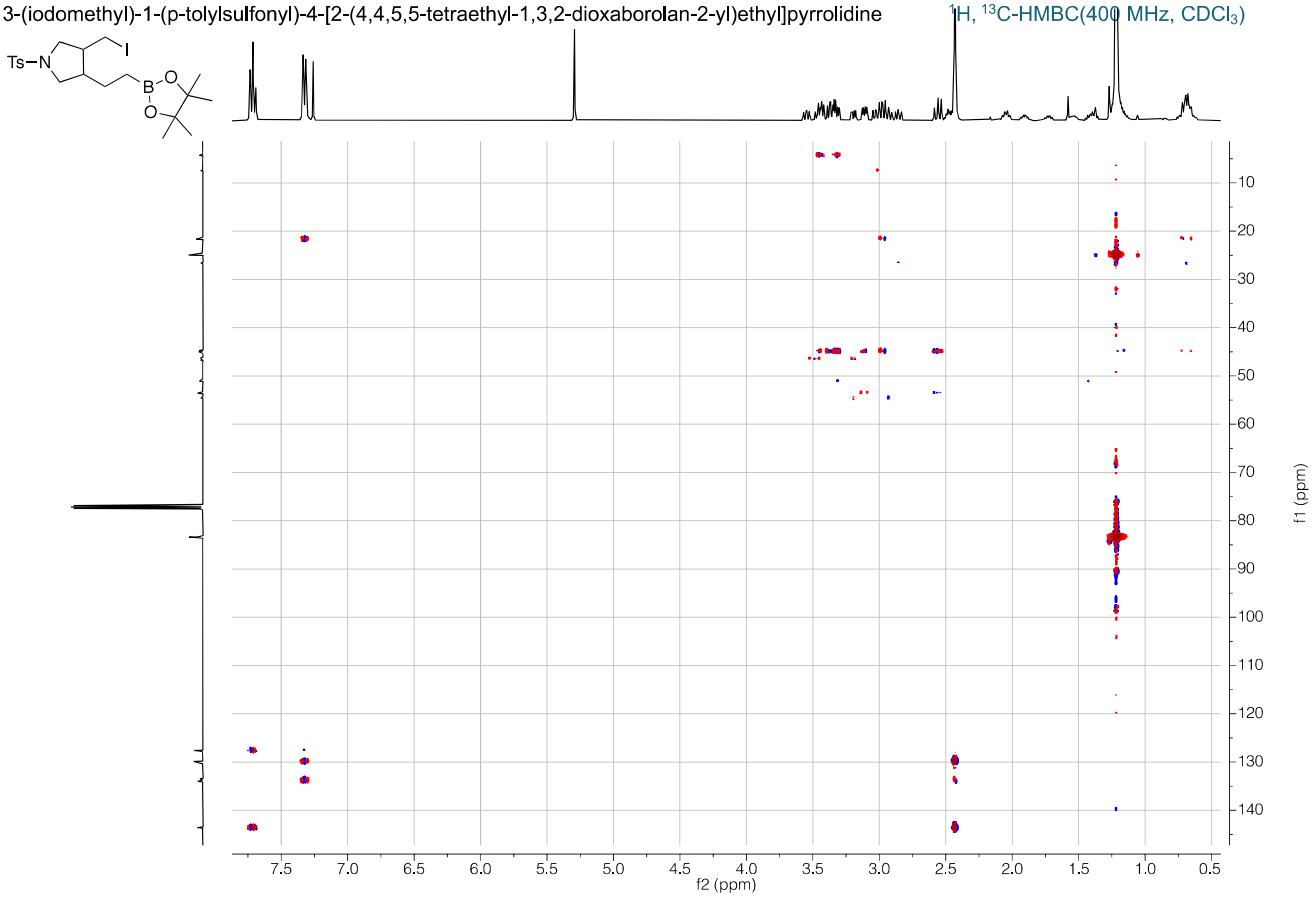
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



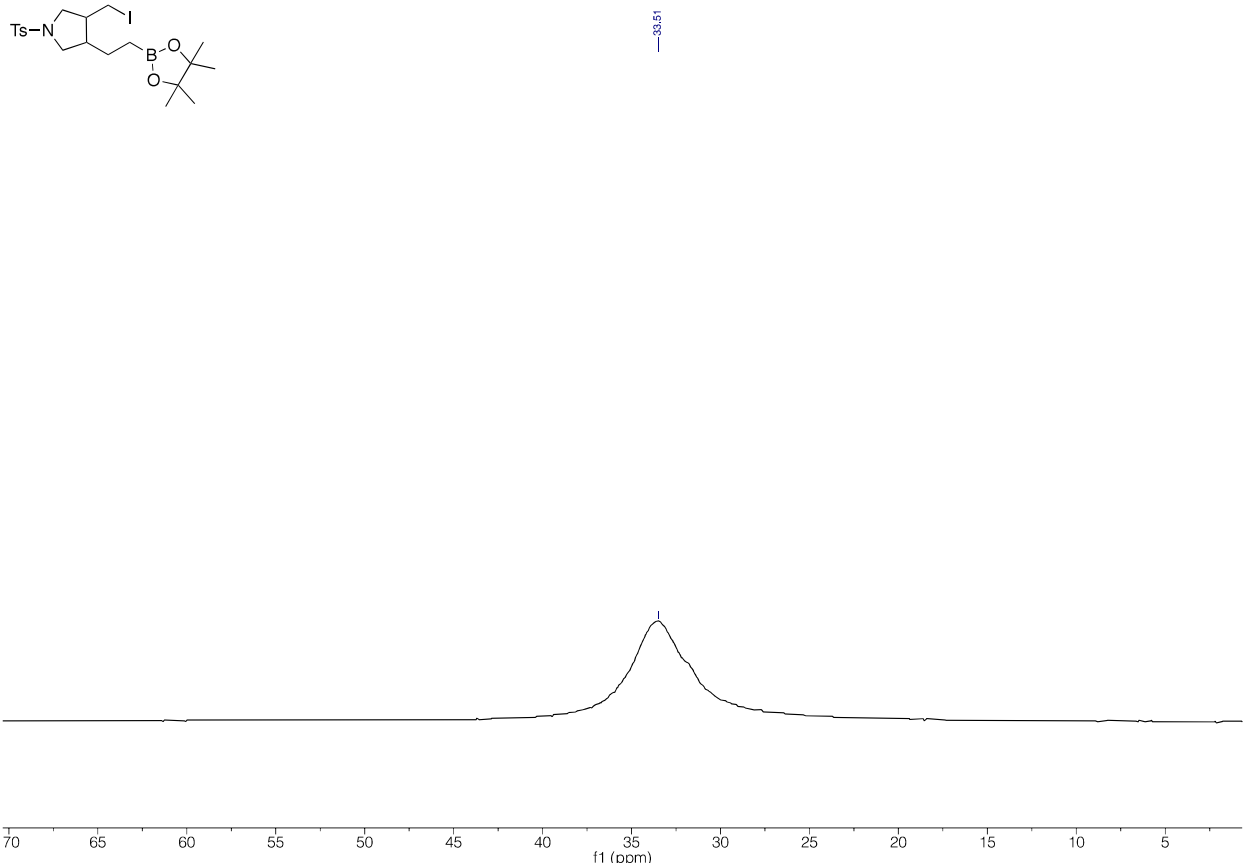
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

^{1}H, ^{13}C-HMBC(400 MHz, $CDCl_3$)

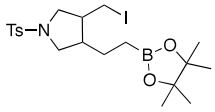


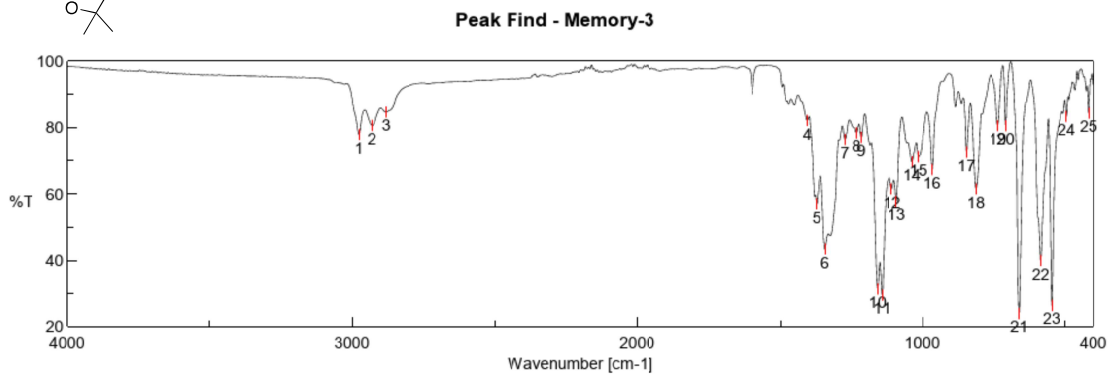
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

^{11}B-NMR (128 MHz, $CDCl_3$)



3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine FT-IR, ATR-diamond

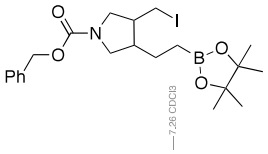


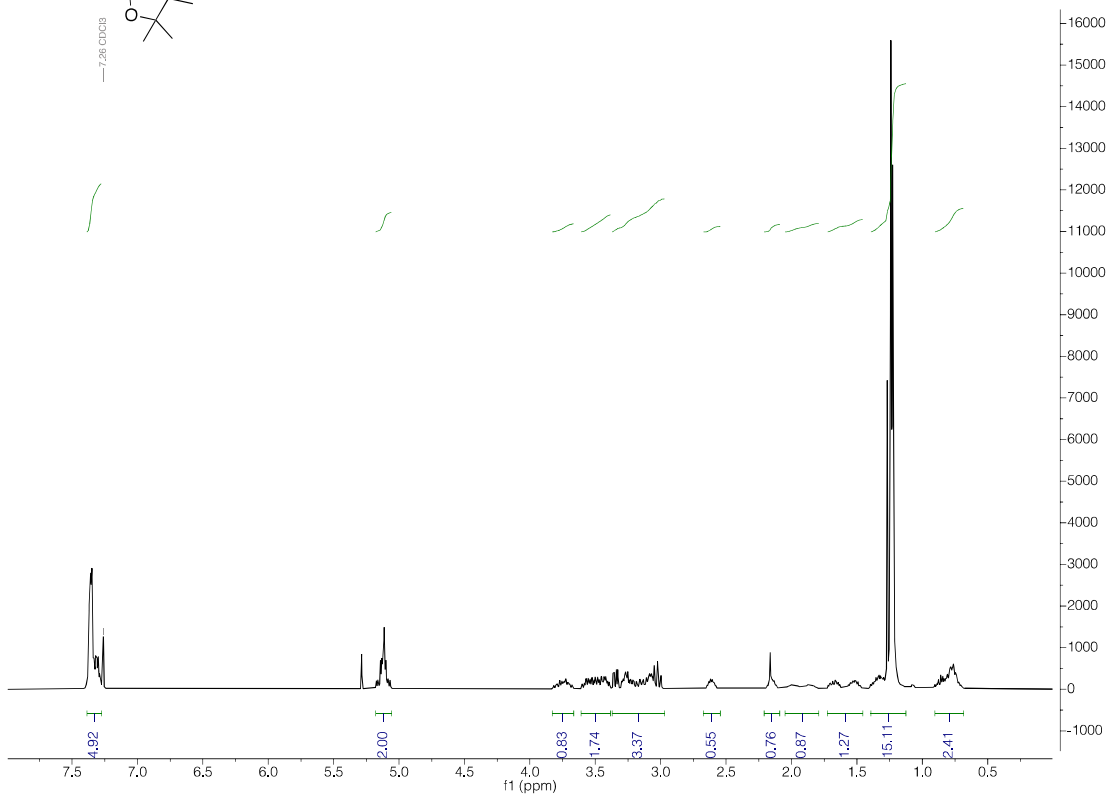


[Result of Peak Picking]

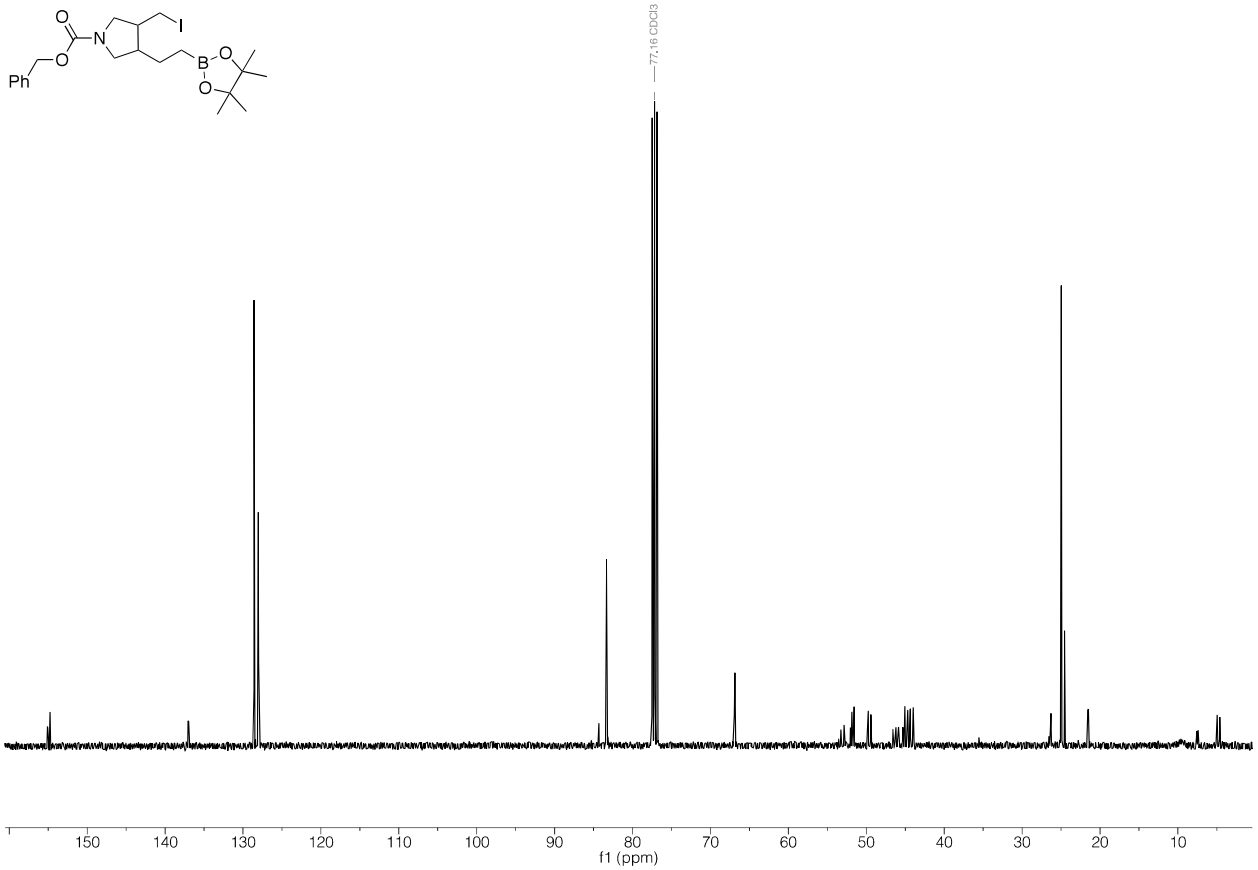
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	77.8371	2	2929.34	80.5703	3	2880.17	84.6389
4	1403.92	82.1282	5	1370.18	56.9973	6	1341.25	43.4161
7	1270.86	76.342	8	1230.36	78.3548	9	1213.97	76.9714
10	1158.04	31.3776	11	1141.65	29.5407	12	1106.94	61.4543
13	1090.55	57.678	14	1036.55	69.6666	15	1013.41	71.203
16	966.162	67.3263	17	845.633	72.5705	18	812.849	61.501
19	735.71	80.5459	20	707.747	80.5549	21	661.464	23.9563
22	585.29	39.9143	23	545.756	26.3981	24	494.652	83.3249
25	416.549	84.3216						

Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine-1-carboxylate ^{1}H-NMR (400 MHz, $CDCl_3$)

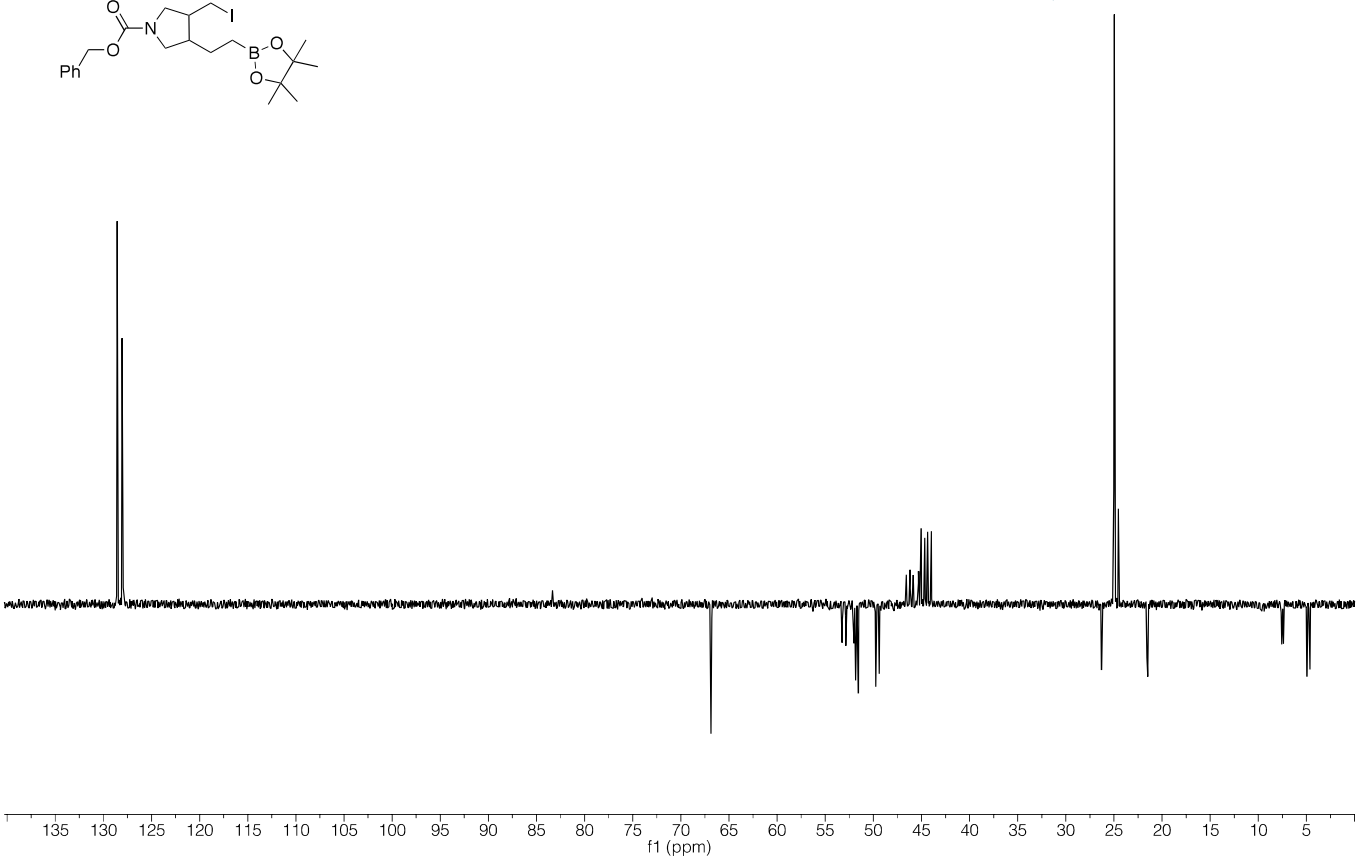




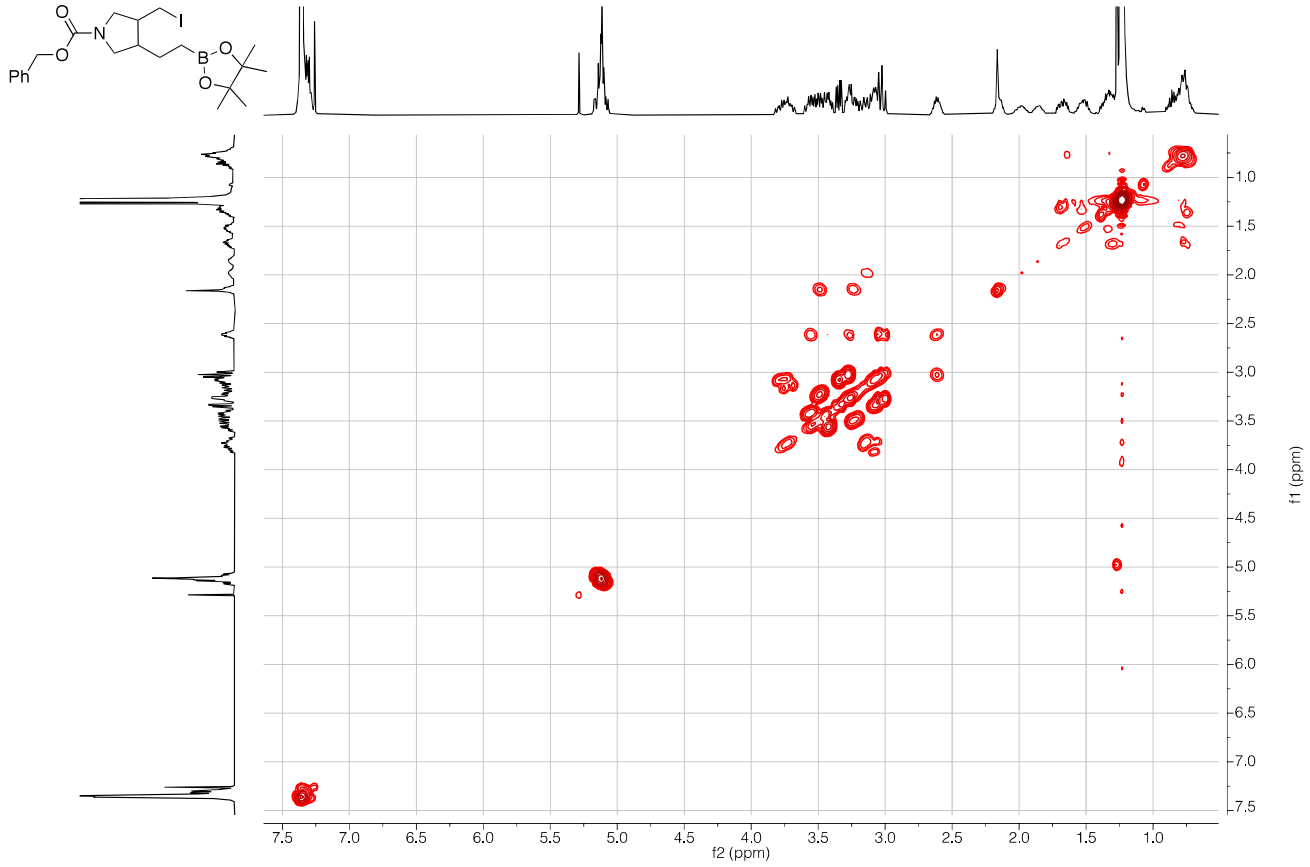
Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine-1-carboxylate ^{13}C-NMR (101 MHz, $CDCl_3$)



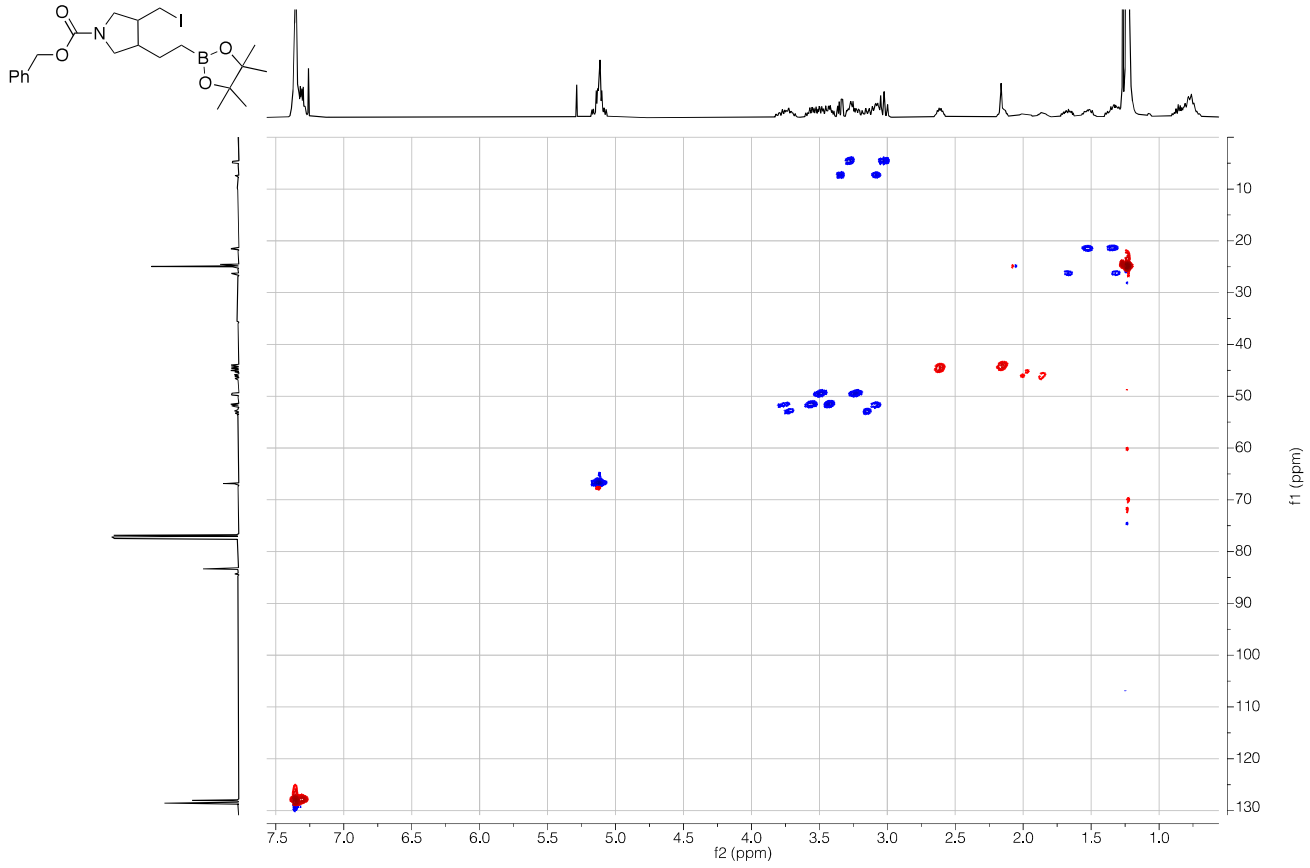
Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine-1-carboxylate DEPT-135 NMR (101 MHz, $CDCl_3$)



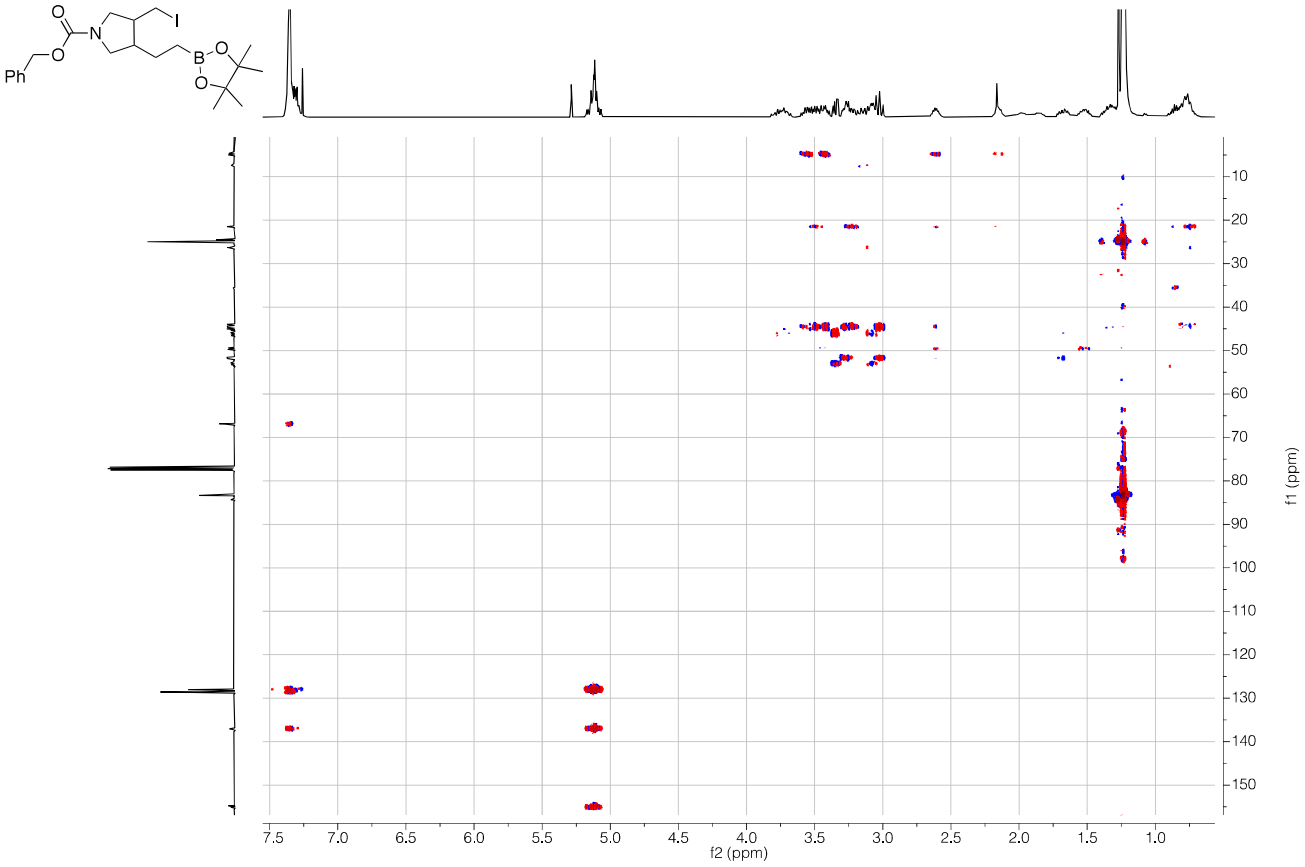
Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine-1-carboxylate ^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



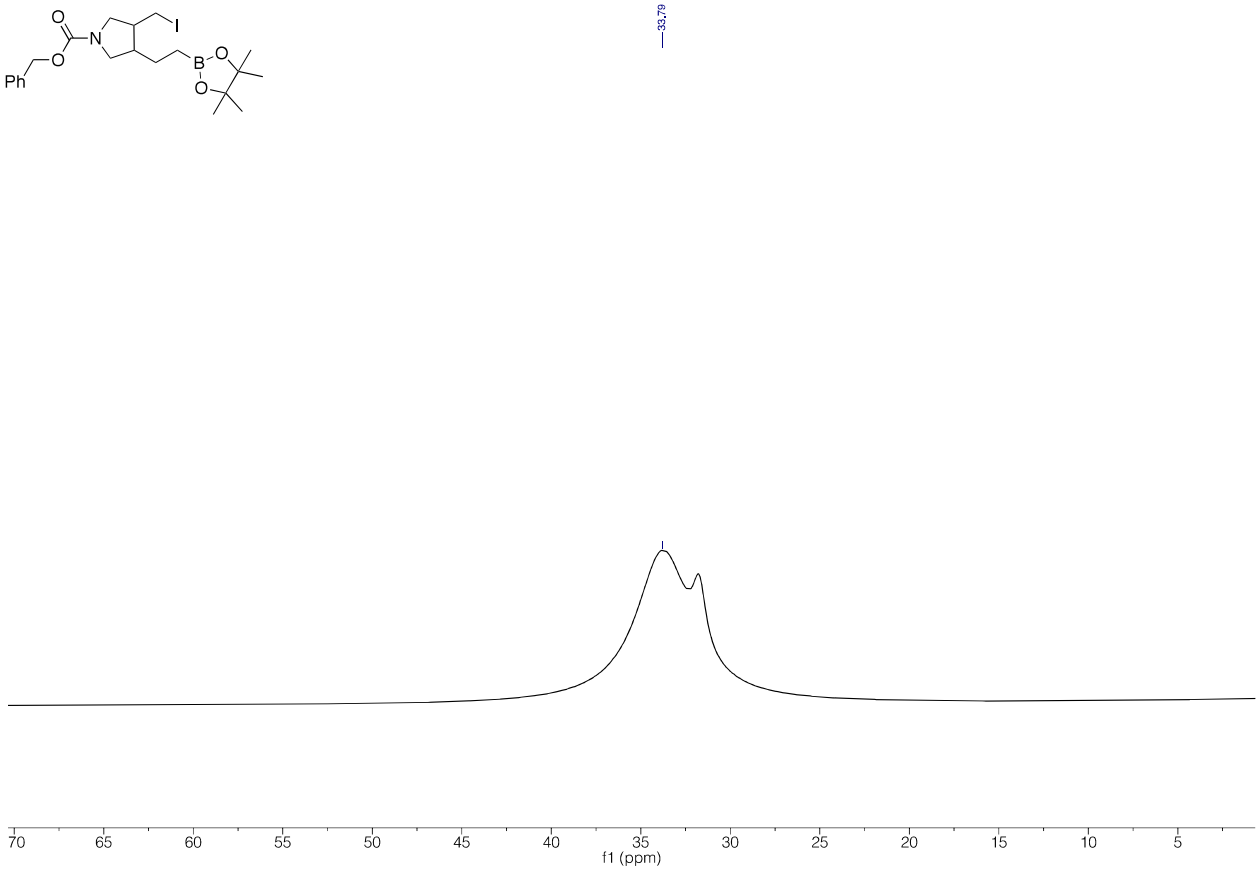
Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine-1-carboxylate ^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



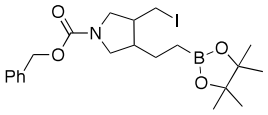
Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine-1-carboxylate ^{1}H, ^{13}C-HMBC(400 MHz, $CDCl_3$)

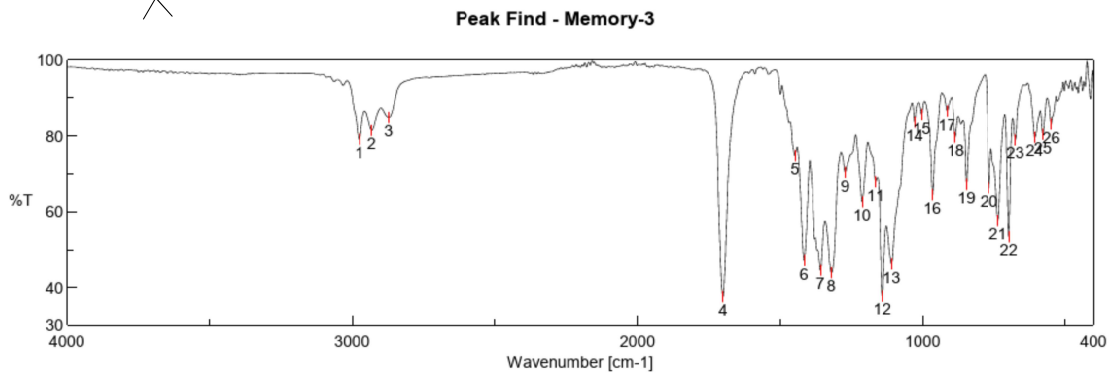


Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine-1-carboxylate ^{11}B-NMR (128 MHz, $CDCl_3$)



Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine-1-carboxylate FT-IR, ATR-diamond

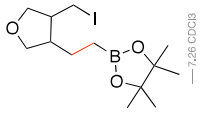




[Result of Peak Picking]

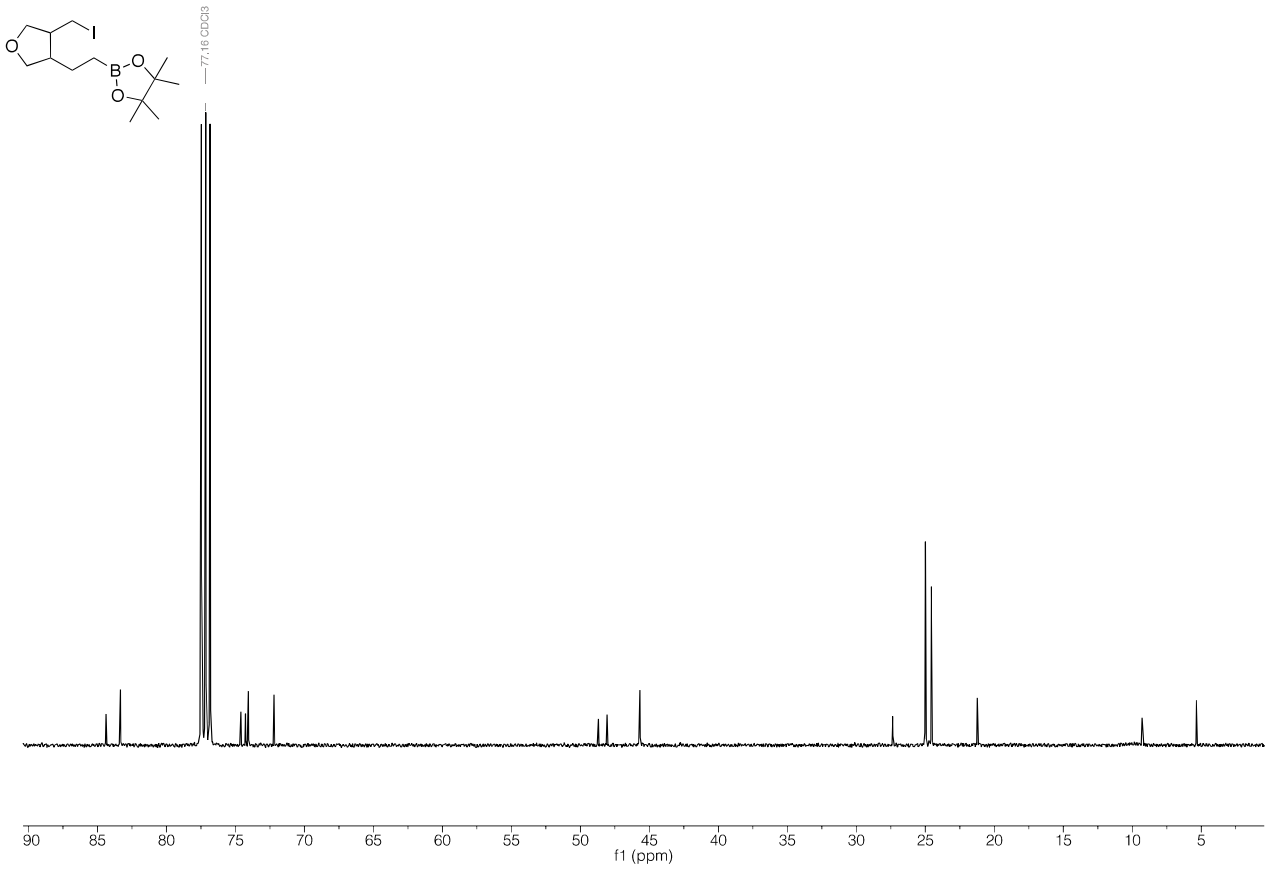
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	79.0435	2	2932.23	81.4138	3	2872.45	84.8047
4	1698.98	37.5735	5	1446.35	74.7494	6	1414.53	47.1096
7	1357.64	44.548	8	1319.07	43.8961	9	1270.86	70.3099
10	1212.04	62.5384	11	1164.79	67.8186	12	1141.65	37.6676
13	1108.87	46.2262	14	1028.84	83.6012	15	1003.77	85.5609
16	966.162	64.4183	17	914.093	86.4125	18	884.202	79.6042
19	844.669	67.1455	20	766.566	66.2676	21	734.746	57.618
22	696.177	53.3248	23	673.035	78.841	24	605.539	79.5514
25	576.612	80.3599	26	547.685	83.0835			

2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ^{1}H-NMR (400 MHz, $CDCl_3$)



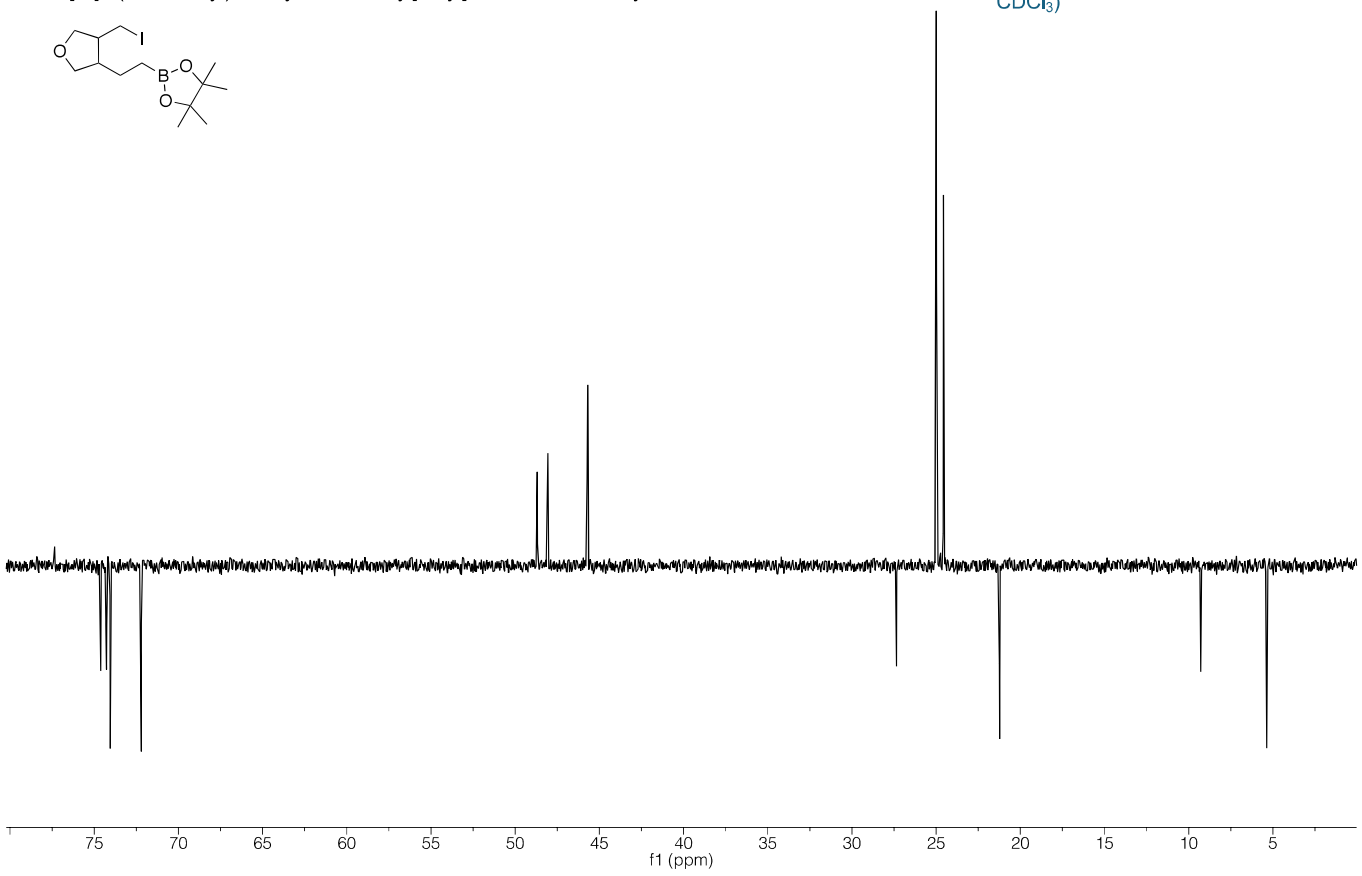
2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{13}C-NMR (101 MHz, $CDCl_3$)



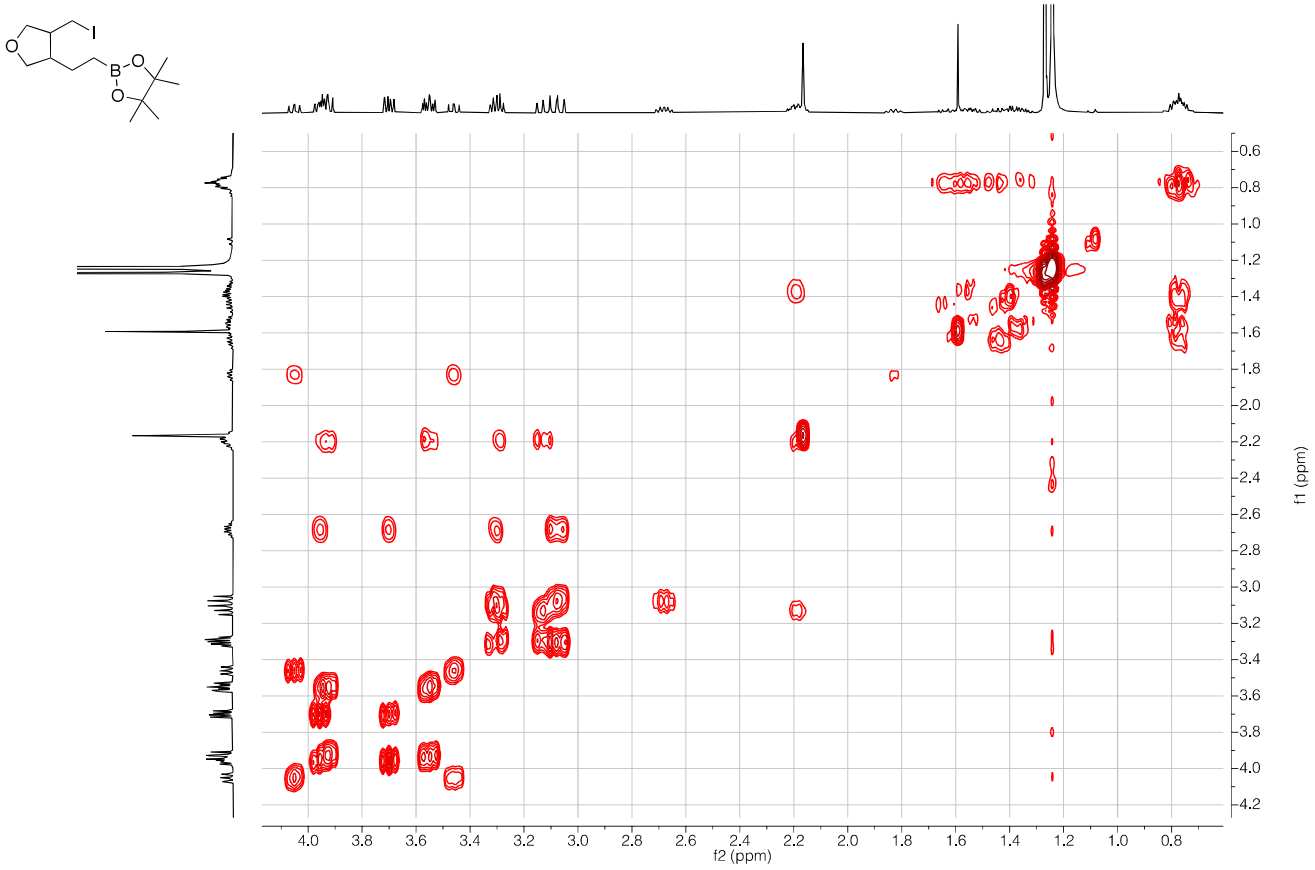
2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

DEPT-135 NMR (101 MHz, $CDCl_3$)



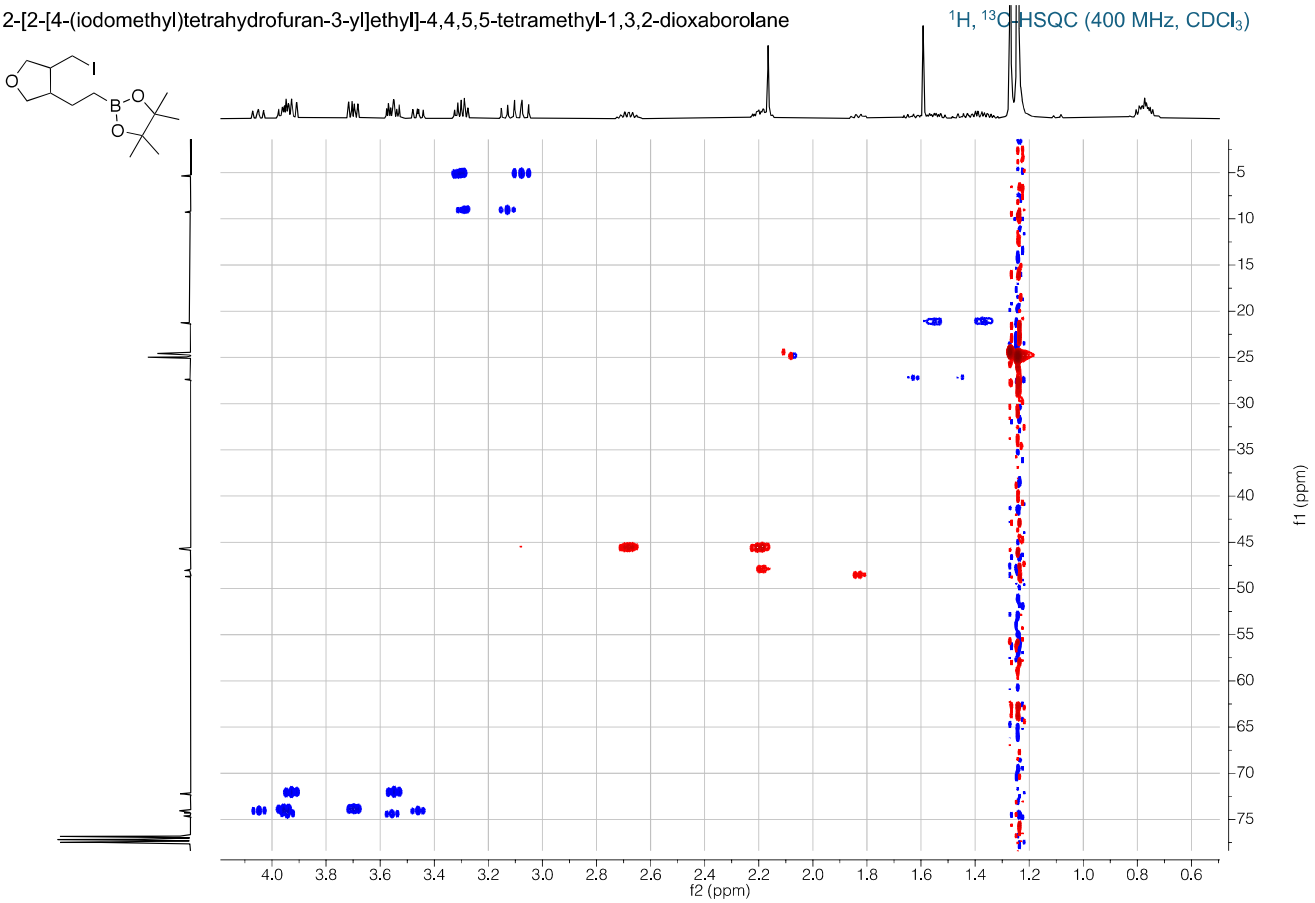
2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



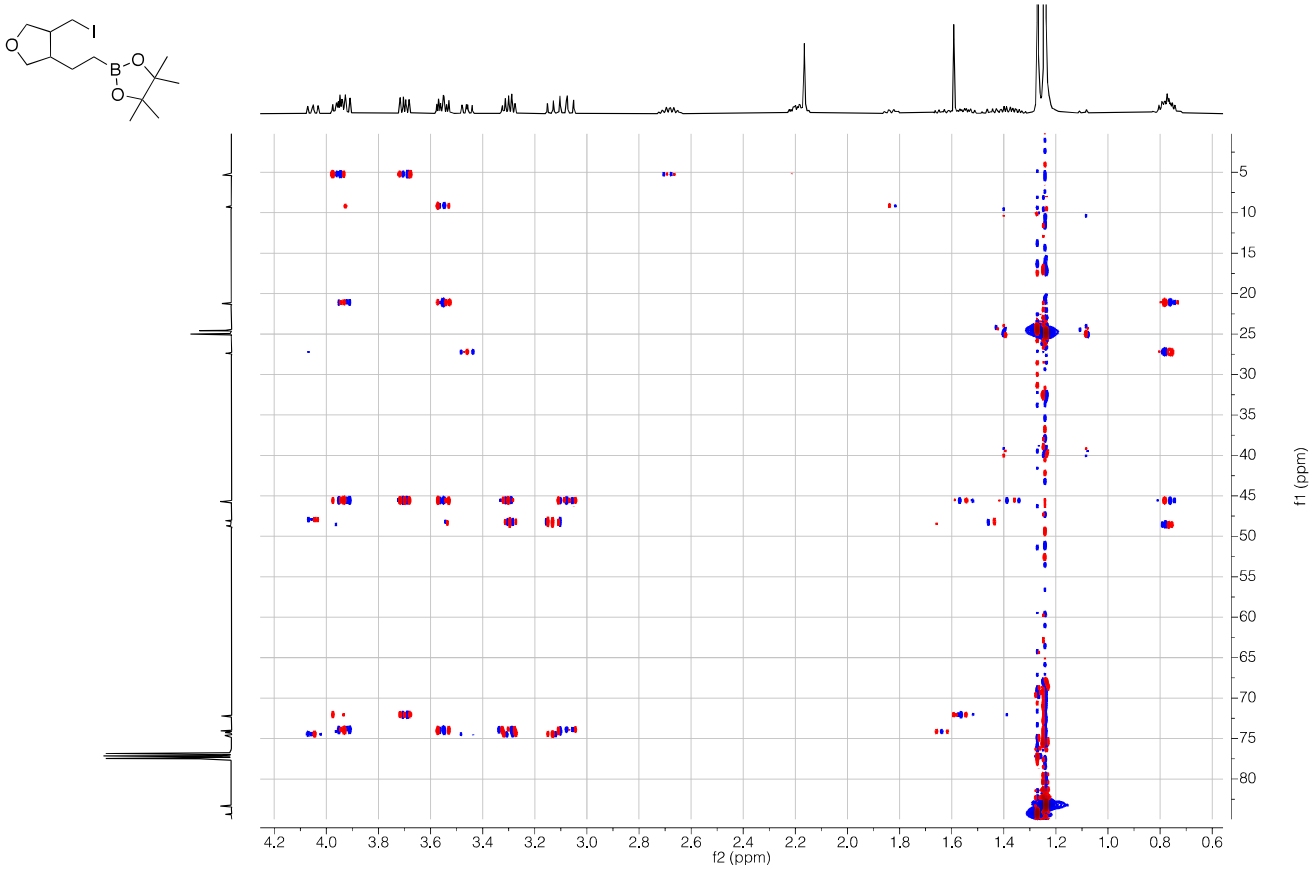
2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



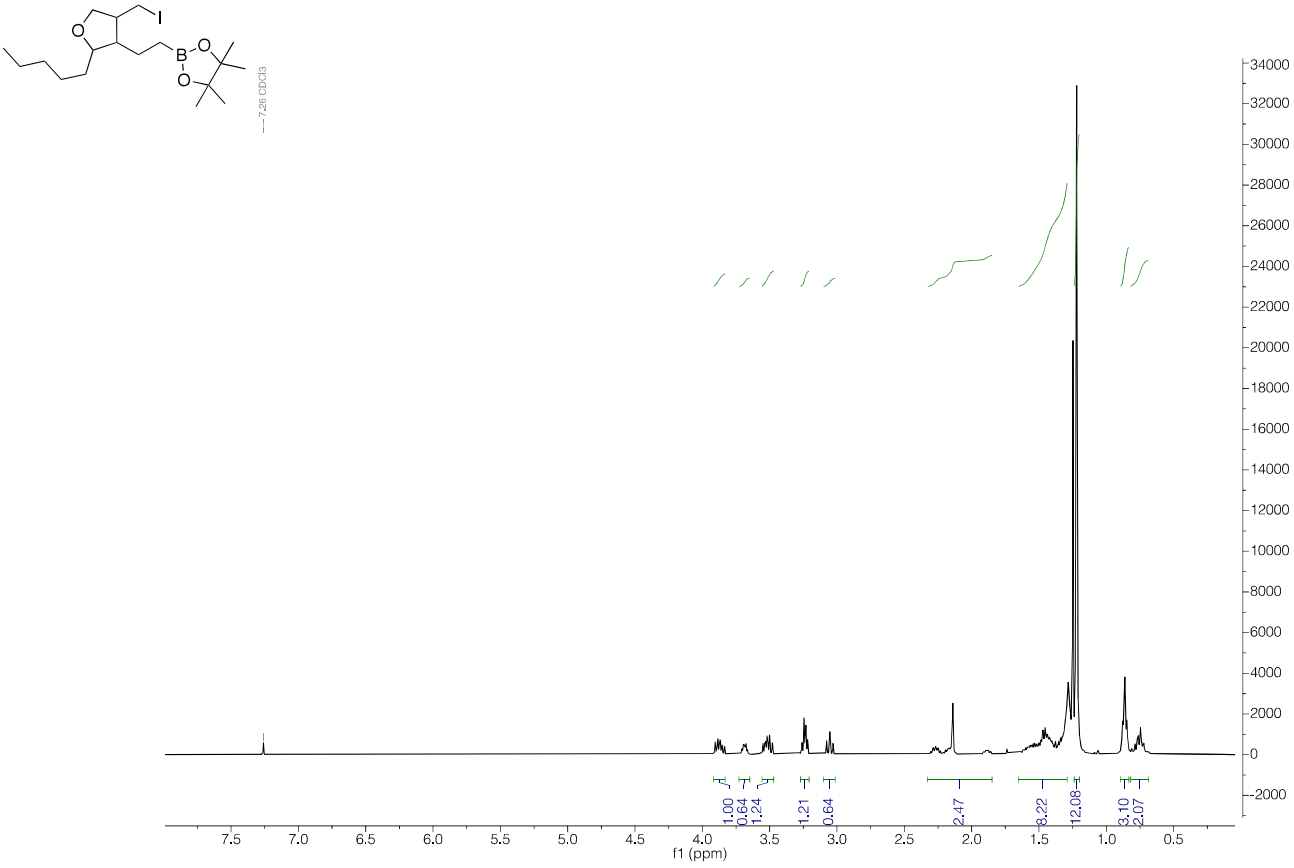
2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{13}C-HMBC(400 MHz, $CDCl_3$)



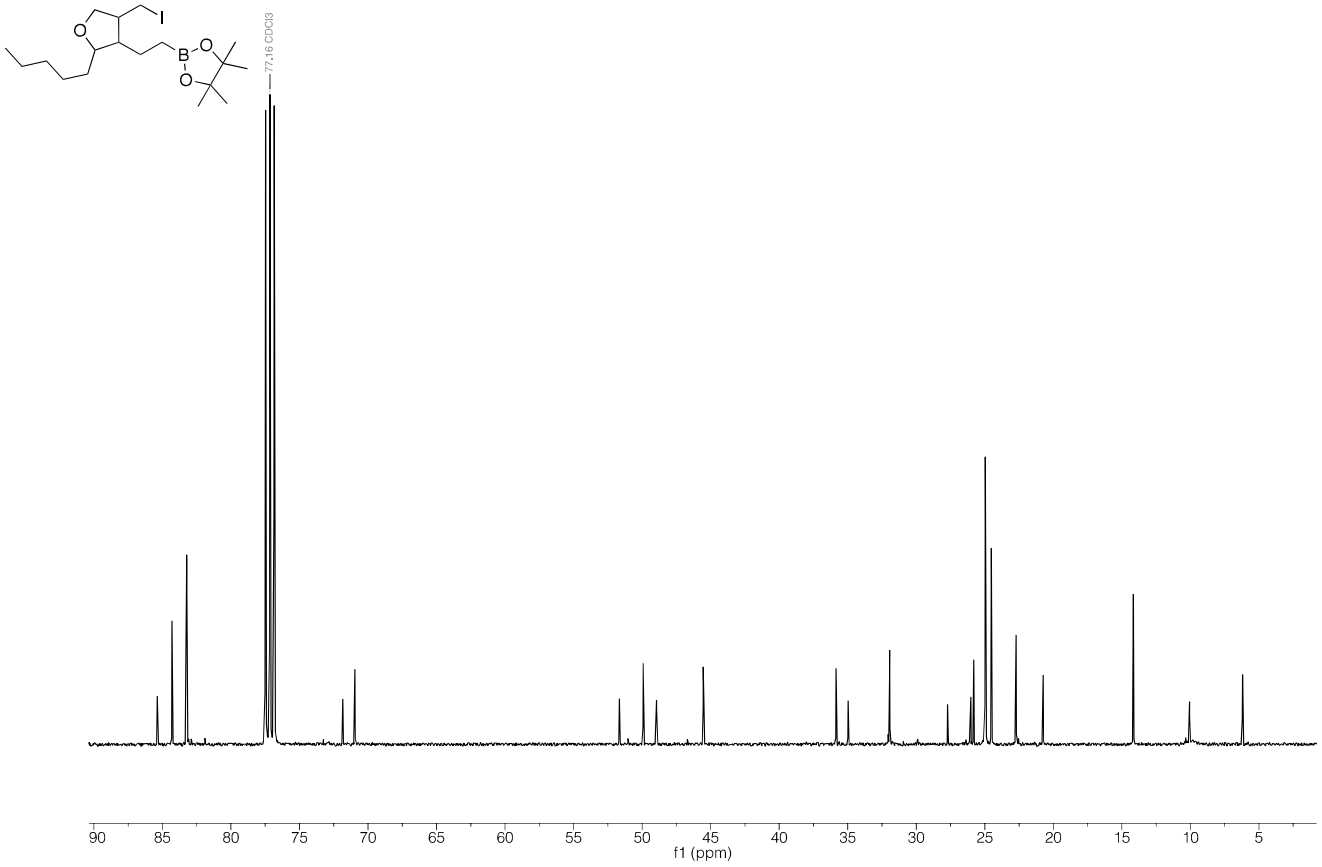
2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H-NMR (400 MHz, $CDCl_3$)



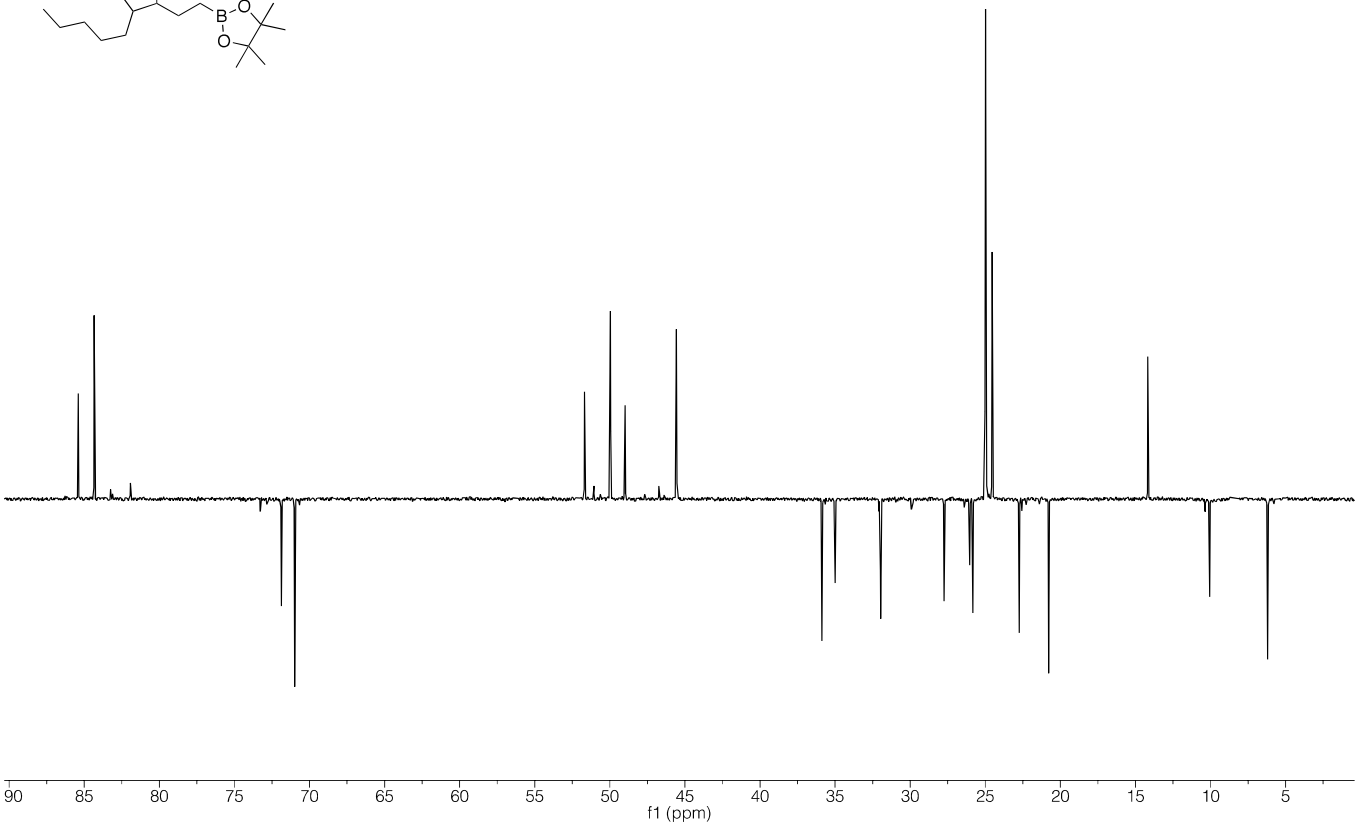
2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{13}C-NMR (101 MHz, $CDCl_3$)



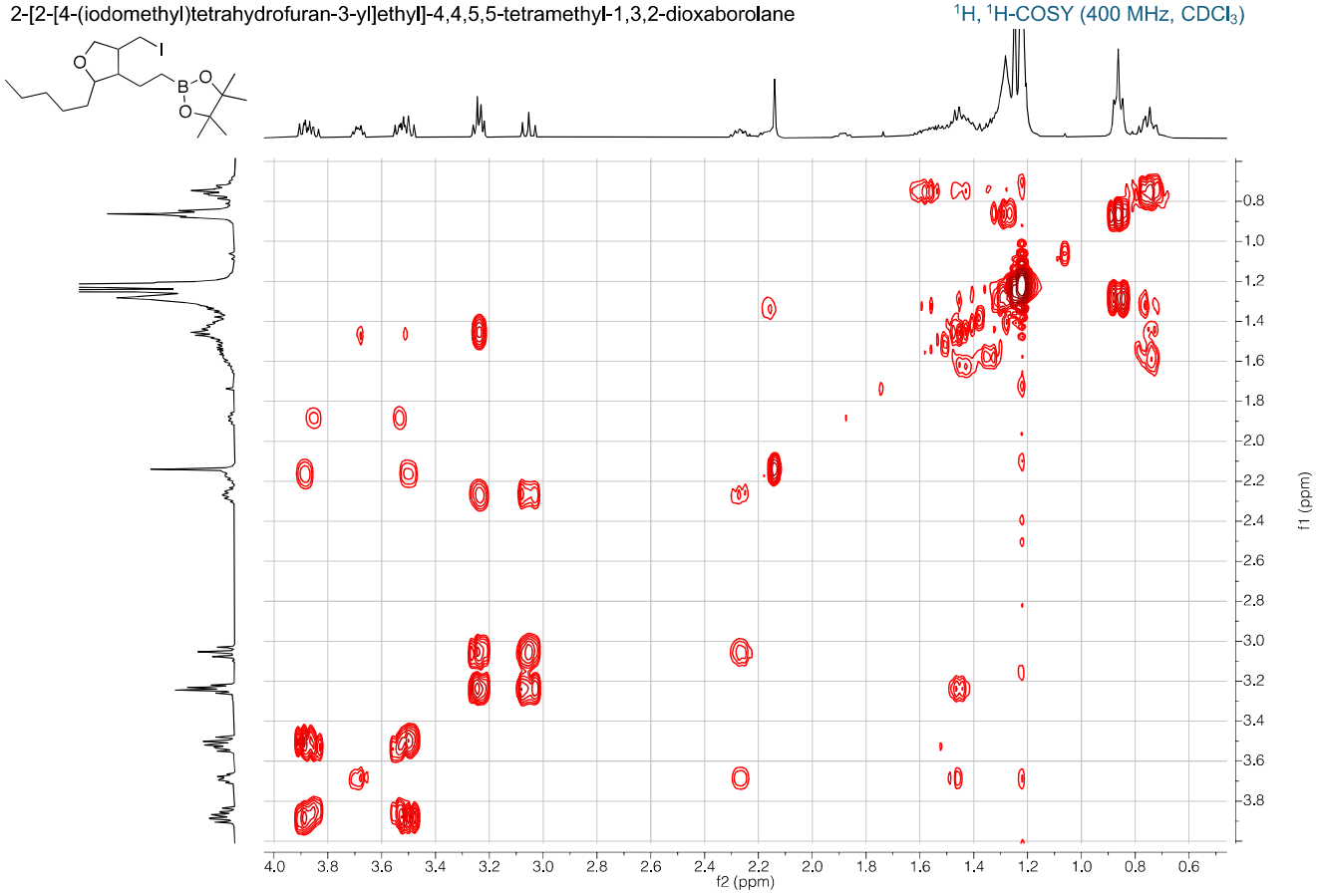
2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

DEPT-135 NMR (101 MHz, $CDCl_3$)



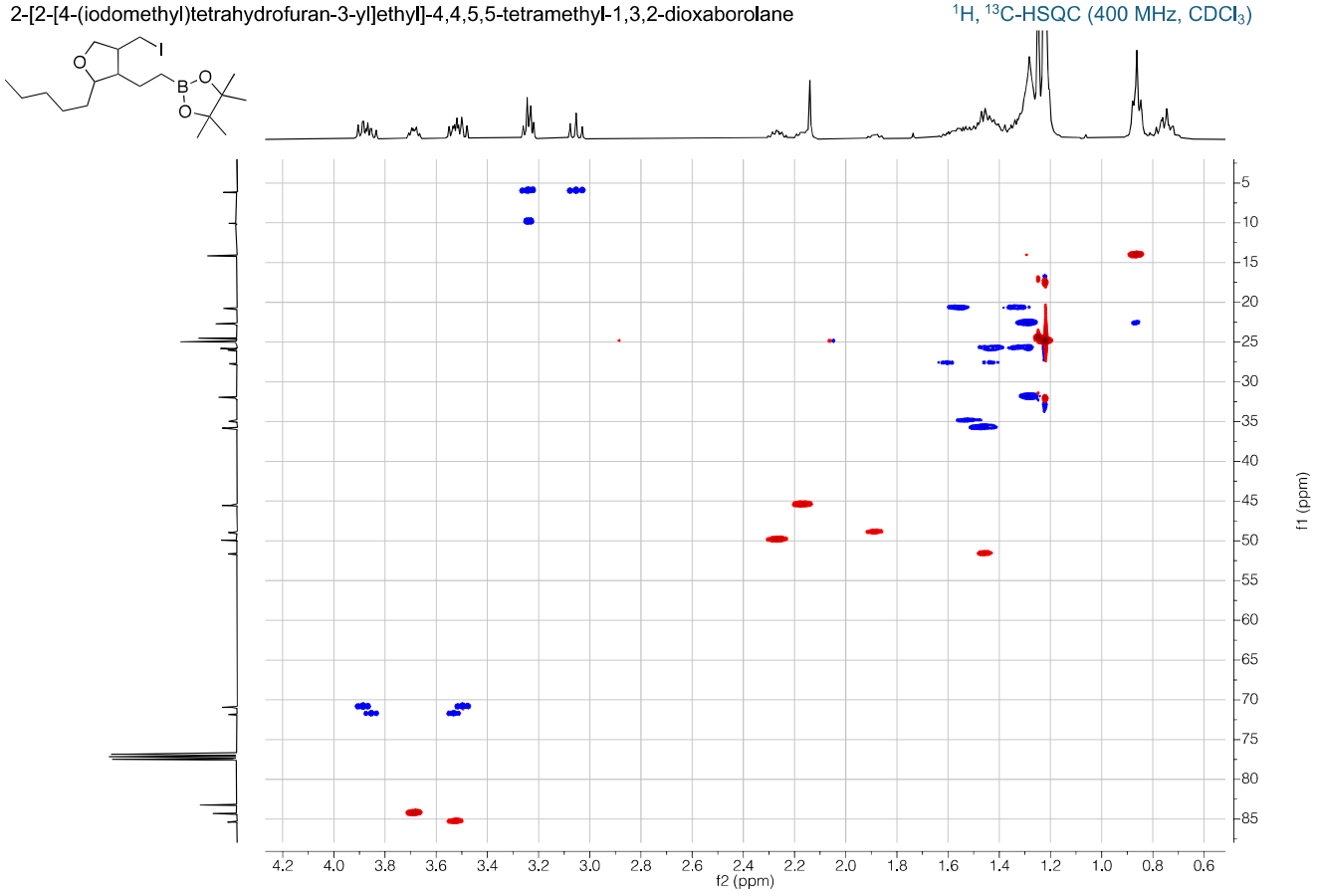
2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)

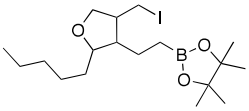


2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)

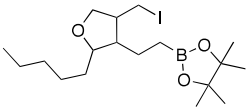


2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

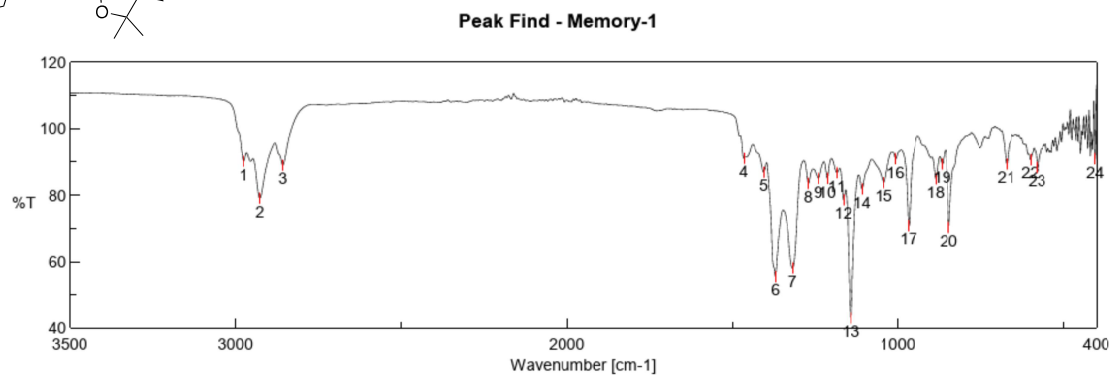


^{11}B-NMR (128 MHz, $CDCl_3$)

2-[2-[4-(iodomethyl)tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



FT-IR, ATR-diamond

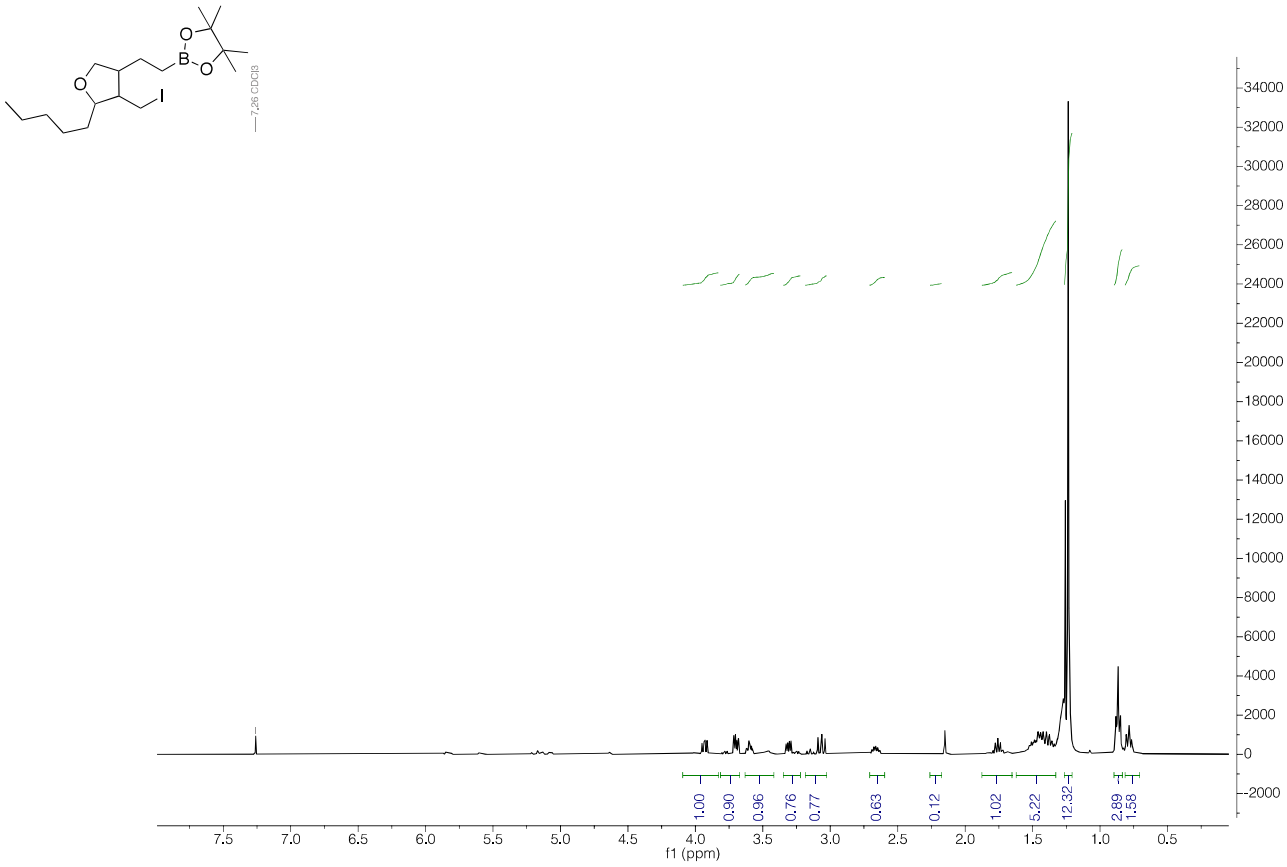


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	90.1771	2	2926.45	79.0616	3	2857.02	88.9631
4	1465.63	91.0404	5	1405.85	86.888	6	1370.18	55.4321
7	1319.07	58.0736	8	1270.86	83.5033	9	1240.97	85.0379
10	1213.97	85.0489	11	1185.04	86.7105	12	1164.79	78.5543
13	1142.62	43.0498	14	1108.87	81.827	15	1042.34	83.7226
16	1005.7	90.9697	17	966.162	70.8205	18	885.166	84.8871
19	865.882	89.3853	20	845.633	70.2955	21	672.071	89.354
22	599.753	90.6662	23	578.54	88.3471	24	404.014	90.9302

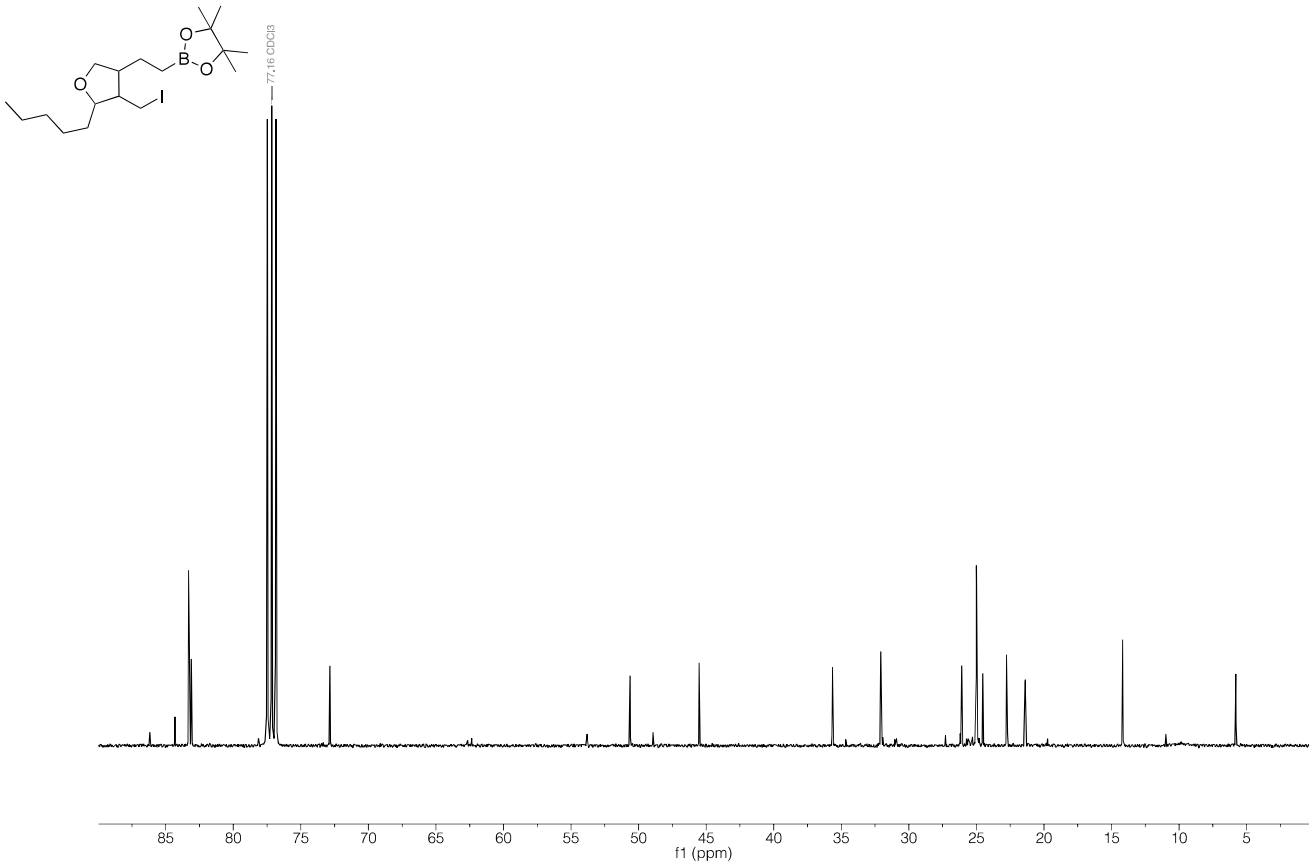
2-[2-[4-(iodomethyl)-5-pentyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H-NMR (400 MHz, $CDCl_3$)



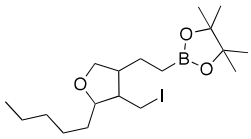
2-[2-[4-(iodomethyl)-5-pentyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{13}C-NMR (101 MHz, $CDCl_3$)



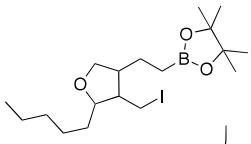
2-[2-[4-(iodomethyl)-5-pentyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

DEPT-135 NMR (101 MHz, $CDCl_3$)



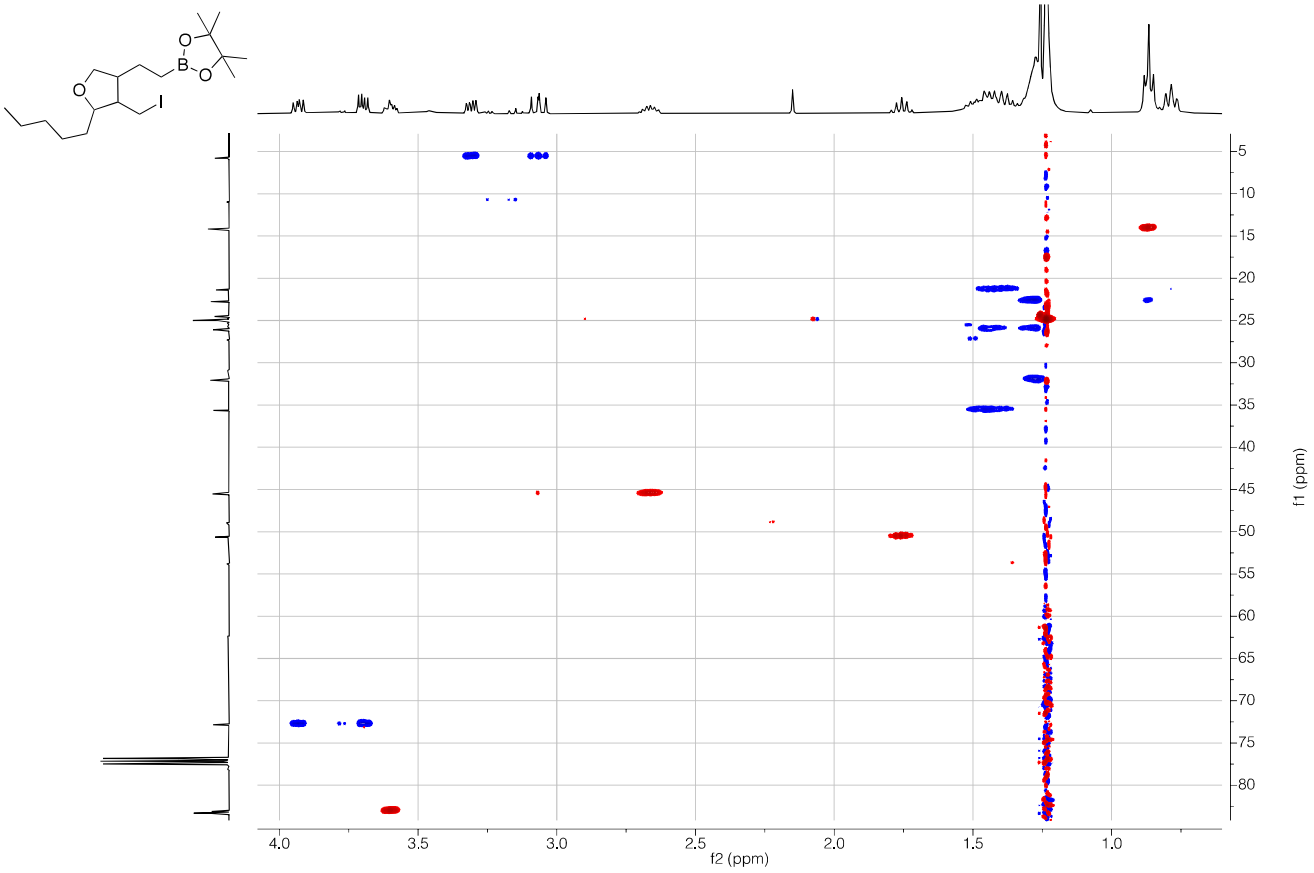
2-[2-[4-(iodomethyl)-5-pentyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^1H, ^1H-COSY (400 MHz, $CDCl_3$)



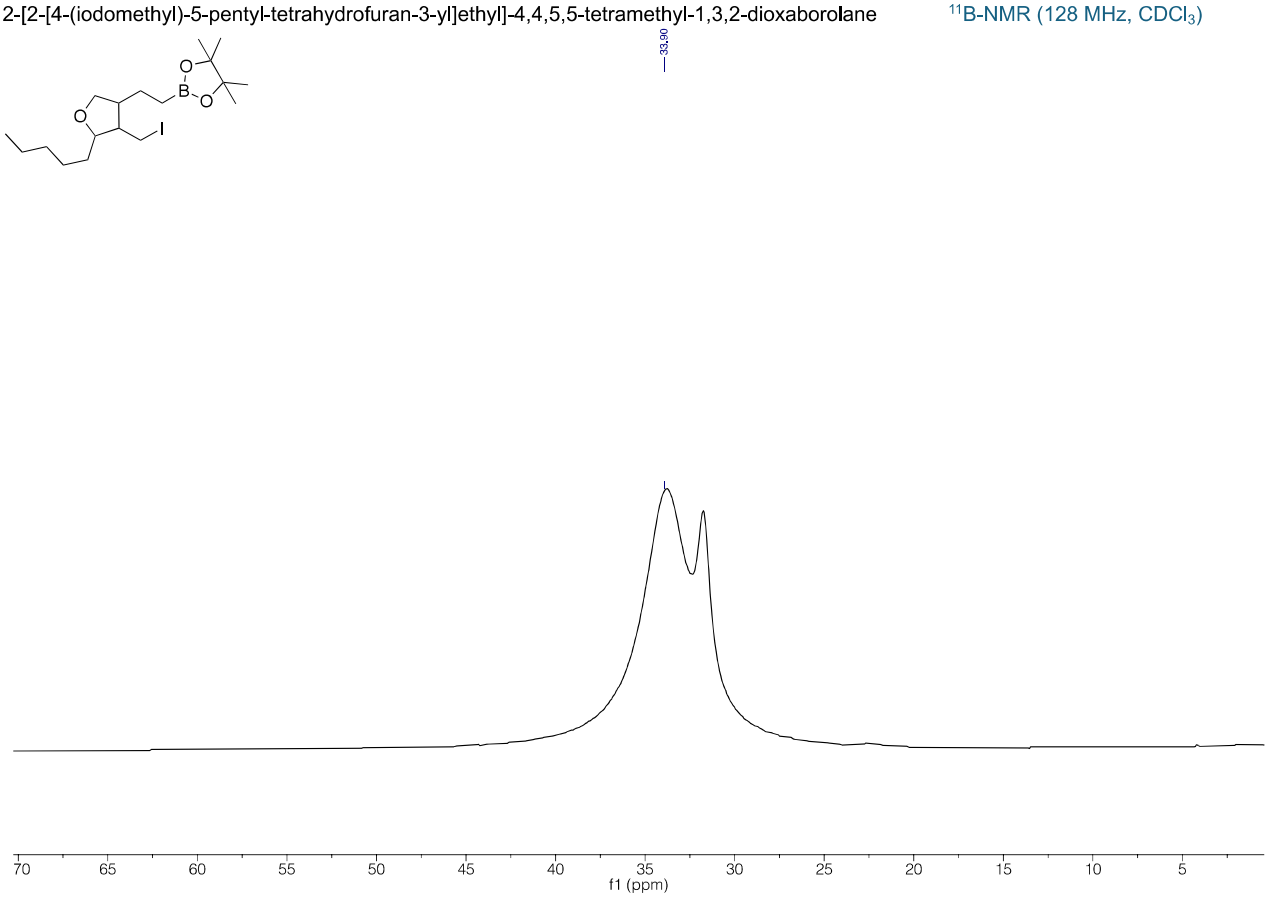
2-[2-[4-(iodomethyl)-5-pentyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)

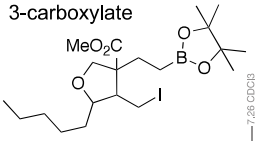


2-[2-[4-(iodomethyl)-5-pentyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

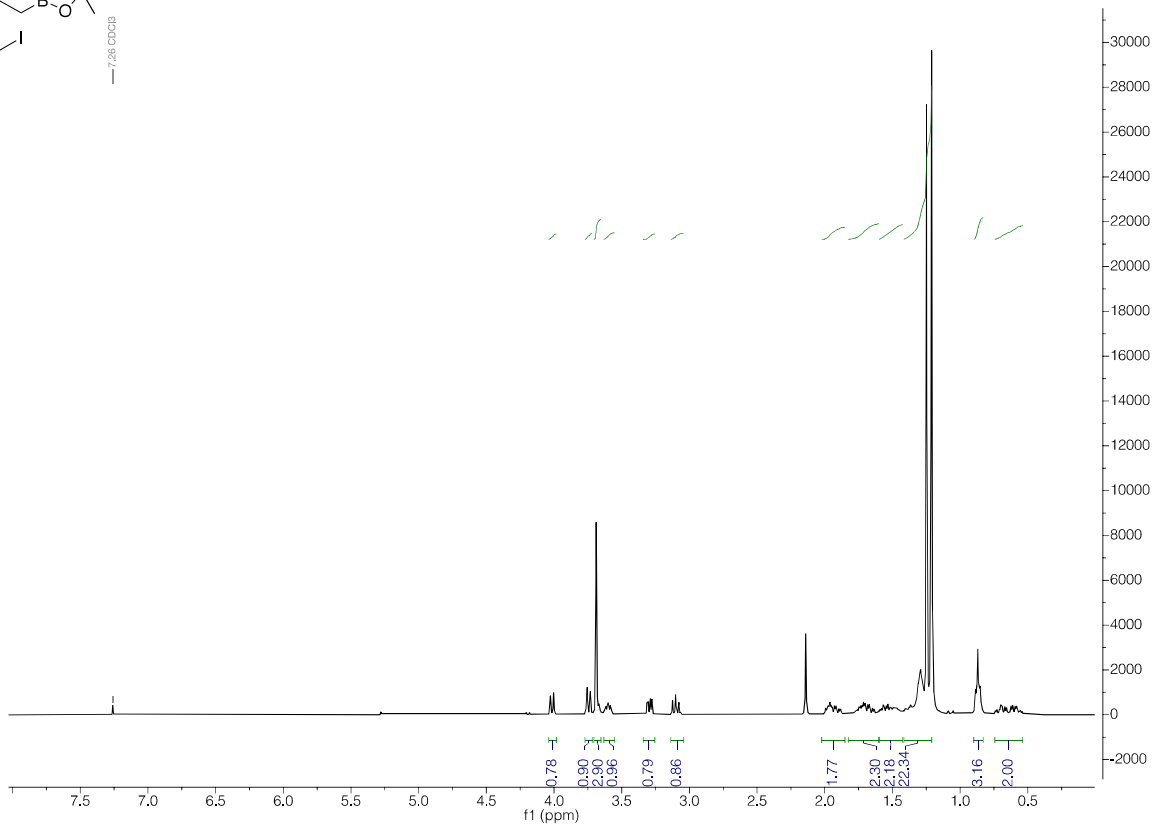
^{11}B-NMR (128 MHz, $CDCl_3$)



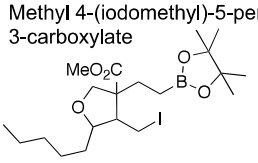
Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]tetrahydrofuran-3-carboxylate



^{1}H-NMR (400 MHz, $CDCl_3$)

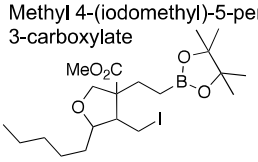


Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]tetrahydrofuran-3-carboxylate



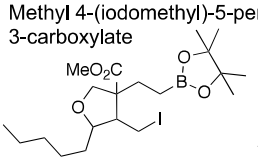
^{13}C-NMR (101 MHz, $CDCl_3$)

Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]tetrahydrofuran-3-carboxylate



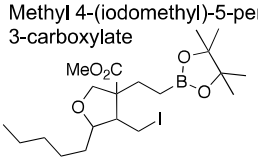
DEPT-135 NMR (101 MHz, $CDCl_3$)

Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]tetrahydrofuran-3-carboxylate



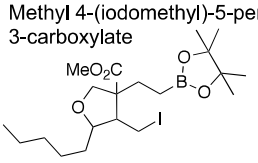
^1H, ^1H-COSY (400 MHz, $CDCl_3$)

Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]tetrahydrofuran-3-carboxylate



^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)

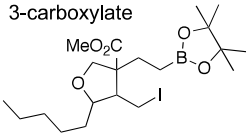
Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]tetrahydrofuran-3-carboxylate

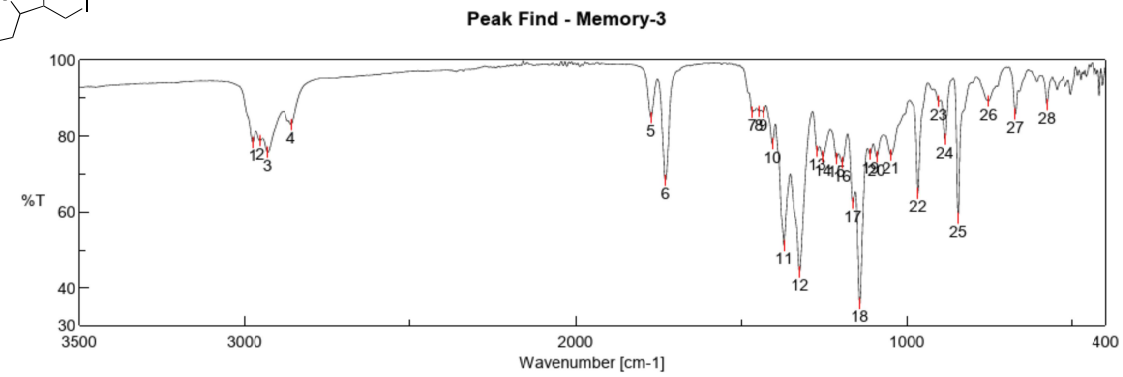


^{11}B-NMR (128 MHz, $CDCl_3$)

Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]tetrahydrofuran-3-carboxylate

FT-IR, ATR-diamond



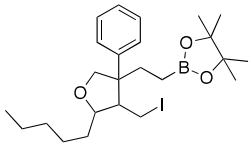


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2976.59	78.2622	2	2952.48	78.7459	3	2929.34	75.6994
4	2858.95	82.9683	5	1772.26	84.8226	6	1728.87	68.2652
7	1466.6	86.232	8	1446.35	86.4189	9	1433.82	86.1984
10	1405.85	77.9256	11	1371.14	51.0959	12	1323.89	44.1262
13	1270.86	75.9673	14	1253.5	74.522	15	1213.01	74.037
16	1195.65	72.969	17	1162.87	62.2728	18	1142.62	35.8502
19	1110.8	75.1857	20	1091.51	74.4344	21	1048.12	74.9239
22	967.126	64.8656	23	904.451	89.1035	24	885.166	79.0897
25	845.633	58.3355	26	754.031	89.1692	27	673.035	85.7915
28	577.576	88.2148						

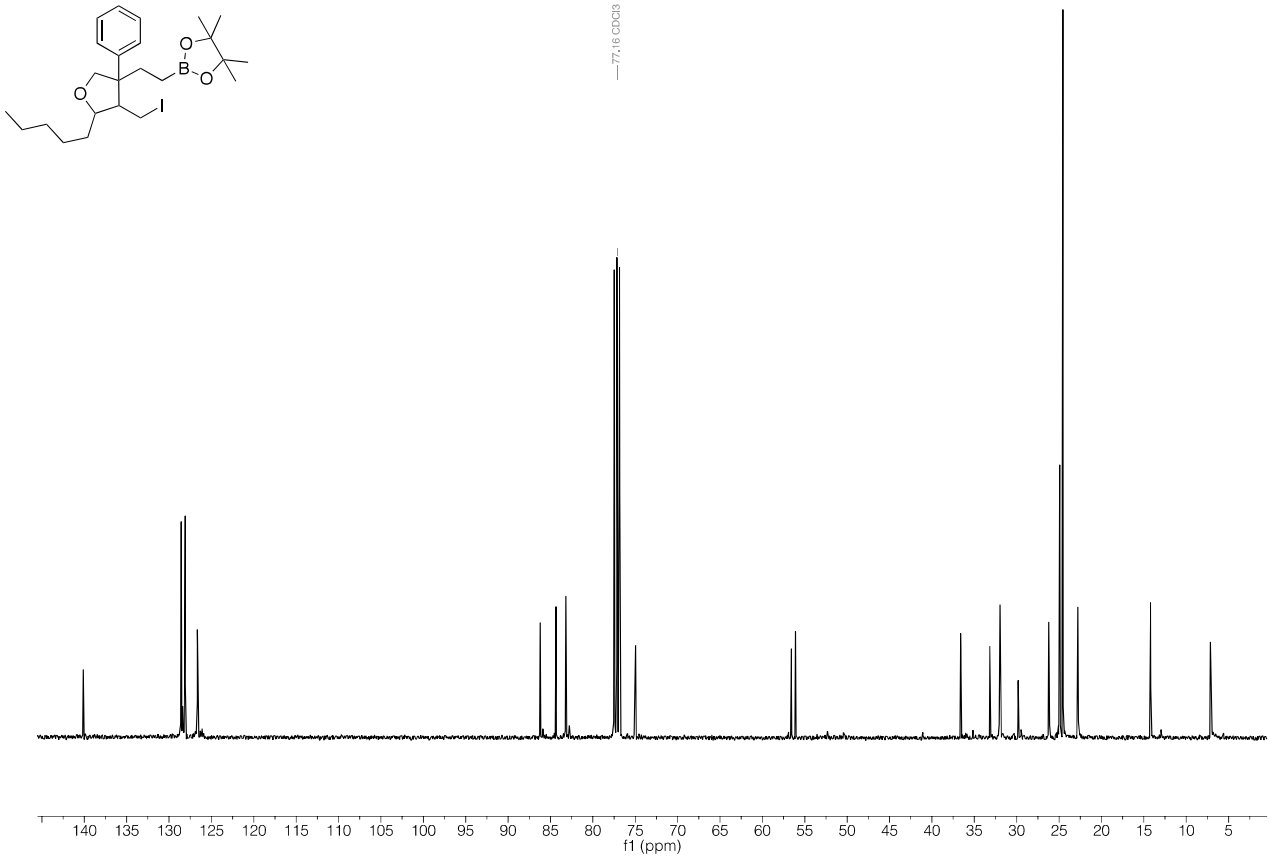
2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DIA 1)

^{1}H-NMR (400 MHz, $CDCl_3$)



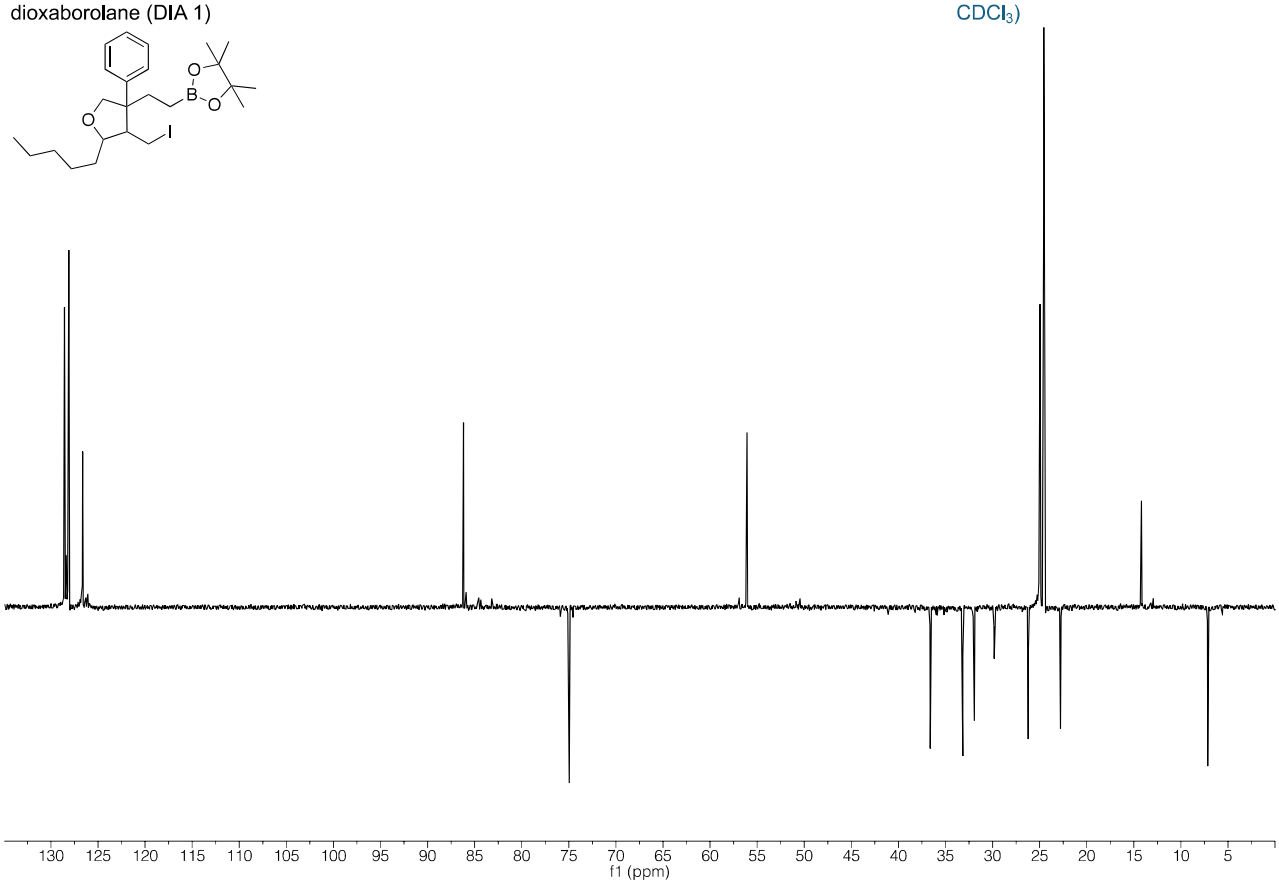
2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DIA 1)

^{13}C-NMR (101 MHz, $CDCl_3$)



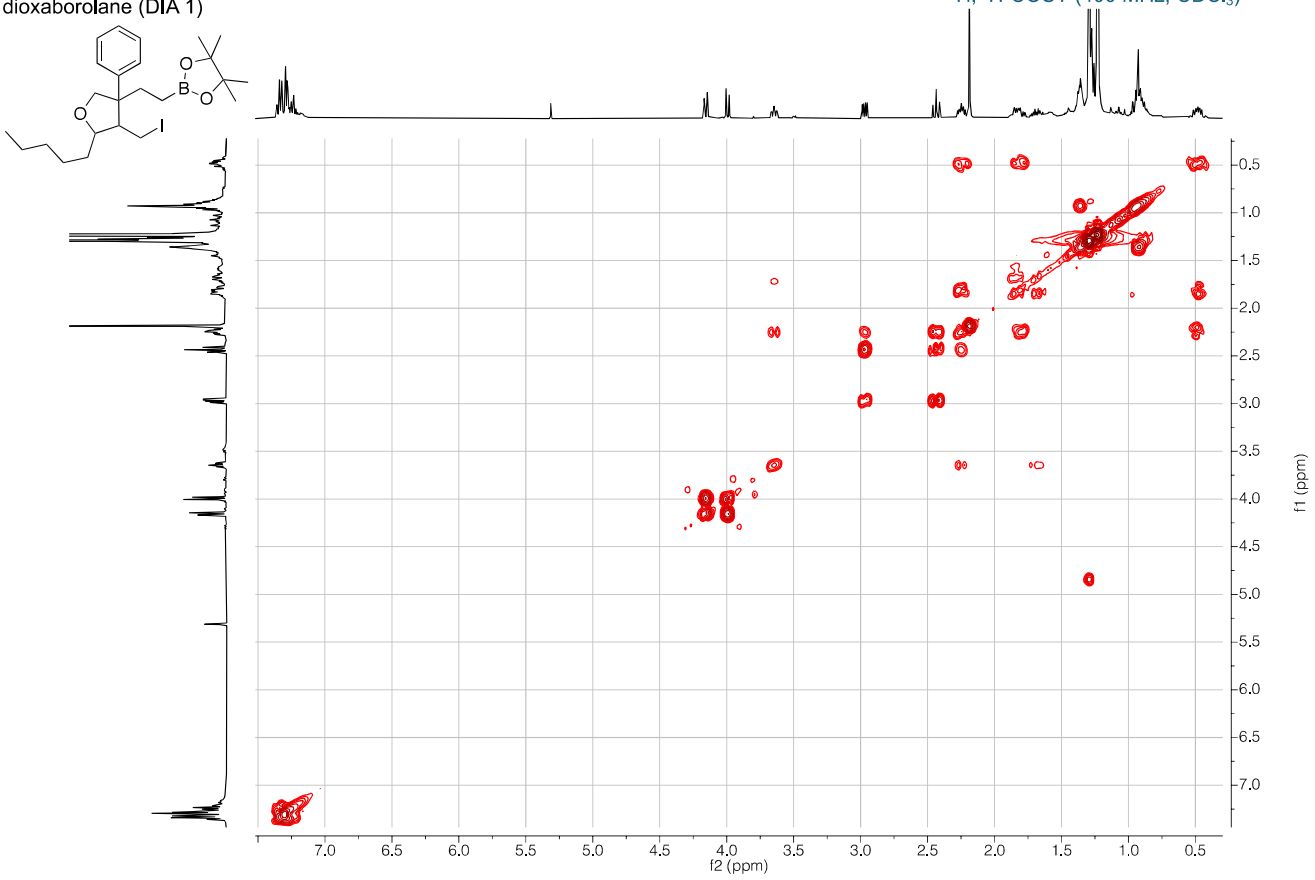
2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DIA 1)

DEPT-135 NMR (101 MHz, $CDCl_3$)



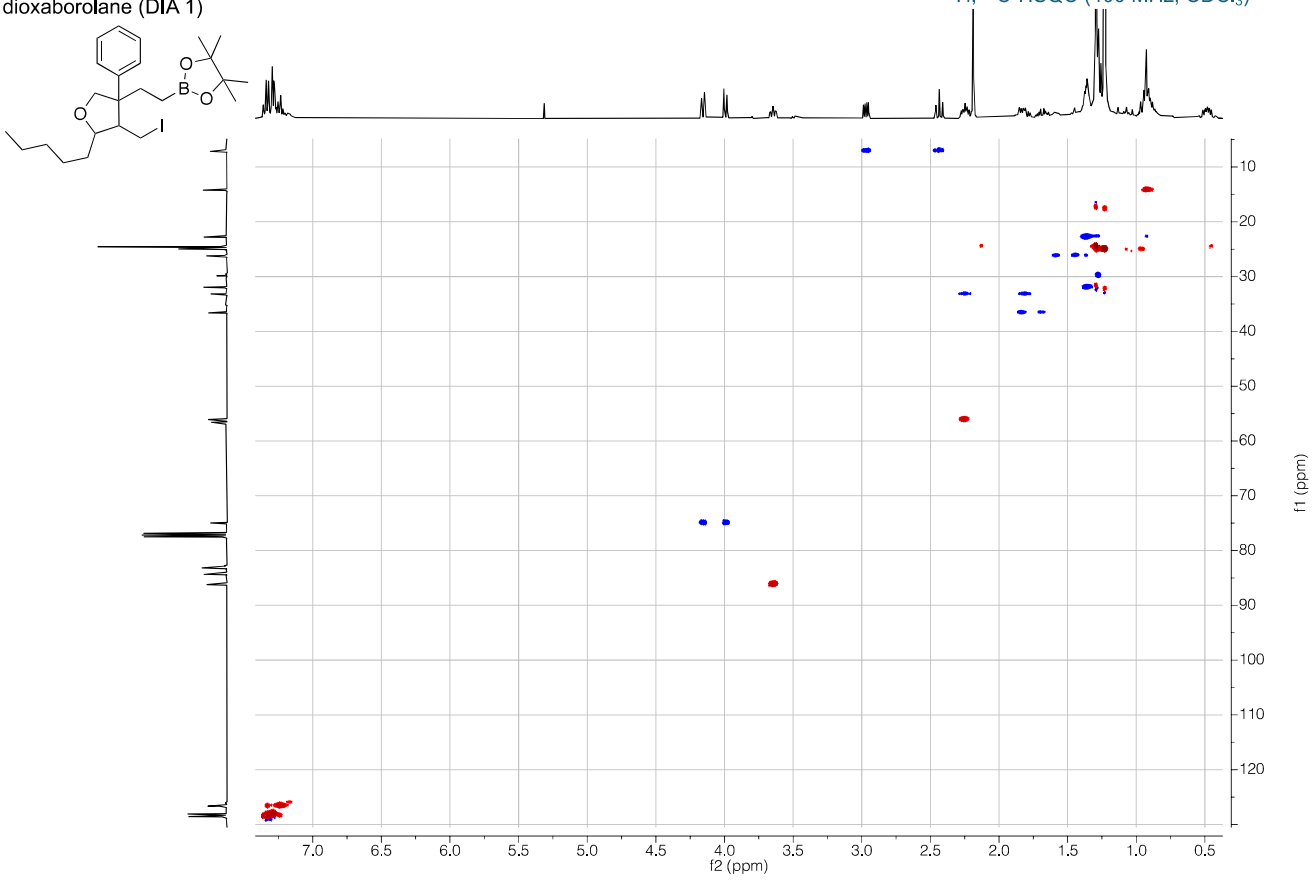
2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DIA 1)

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



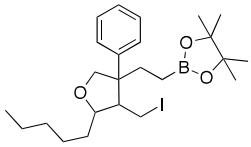
2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DIA 1)

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



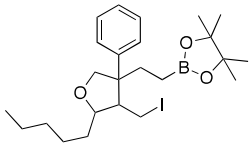
2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DIA 1)

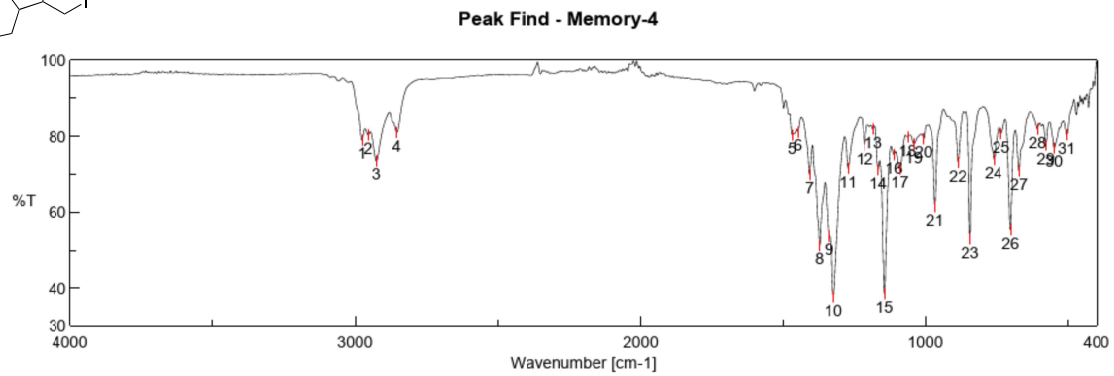
^{11}B-NMR (128 MHz, $CDCl_3$)



2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DIA 1)

FT-IR, ATR-diamond



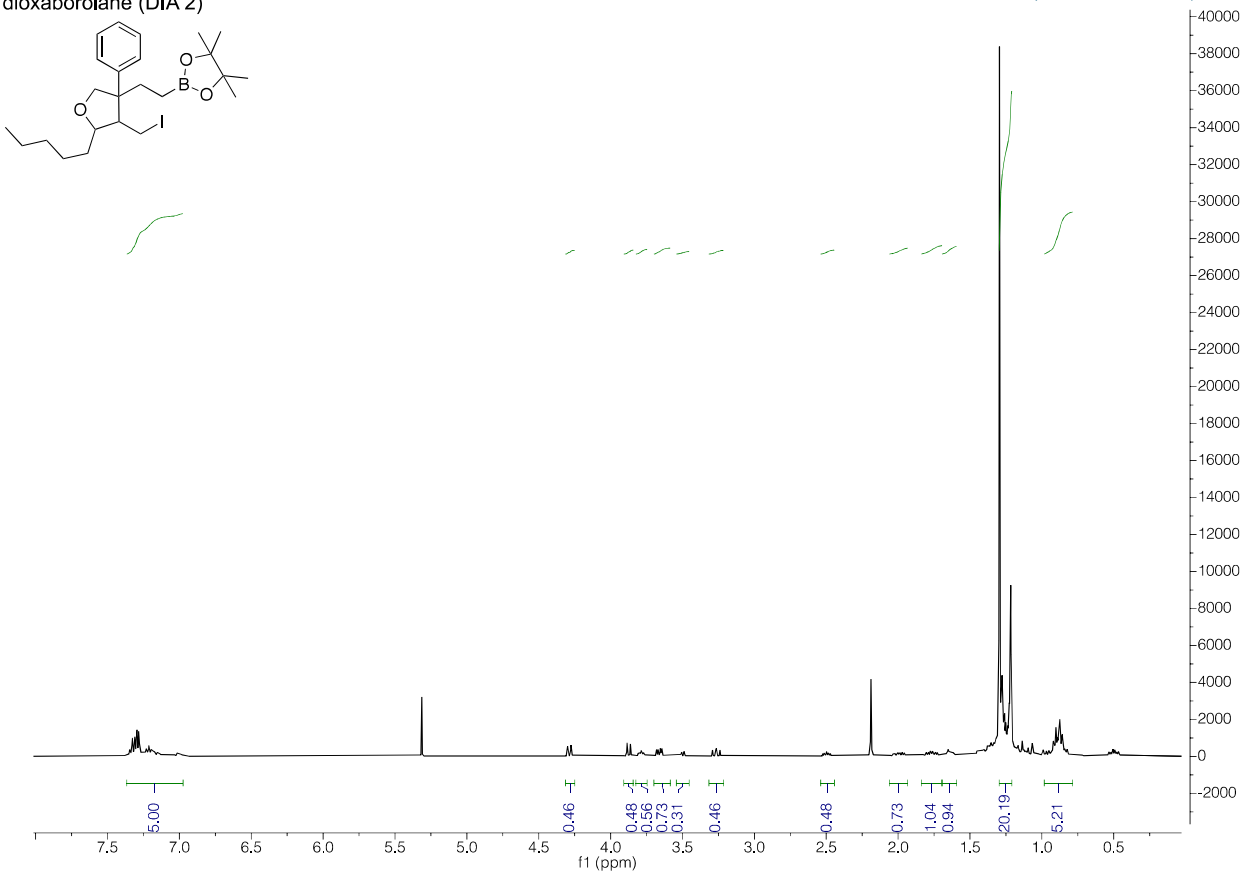


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	78.8975	2	2954.41	80.2562	3	2926.45	73.3882
4	2855.1	80.935	5	1465.63	80.2029	6	1446.35	81.0539
7	1405.85	69.8613	8	1371.14	51.1403	9	1337.39	53.5737
10	1323.89	37.6205	11	1271.82	71.4775	12	1213.01	77.5647
13	1182.15	81.8587	14	1164.79	71.148	15	1142.62	38.4797
16	1108.87	75.0694	17	1088.62	71.3232	18	1061.62	79.7672
19	1040.41	77.9327	20	1005.7	79.2542	21	967.126	61.3766
22	886.131	73.0604	23	844.669	52.9269	24	760.78	73.7894
25	734.746	80.6452	26	700.998	55.3017	27	671.106	70.7801
28	606.503	81.781	29	577.576	77.6478	30	548.649	76.7948
31	505.258	80.3085						

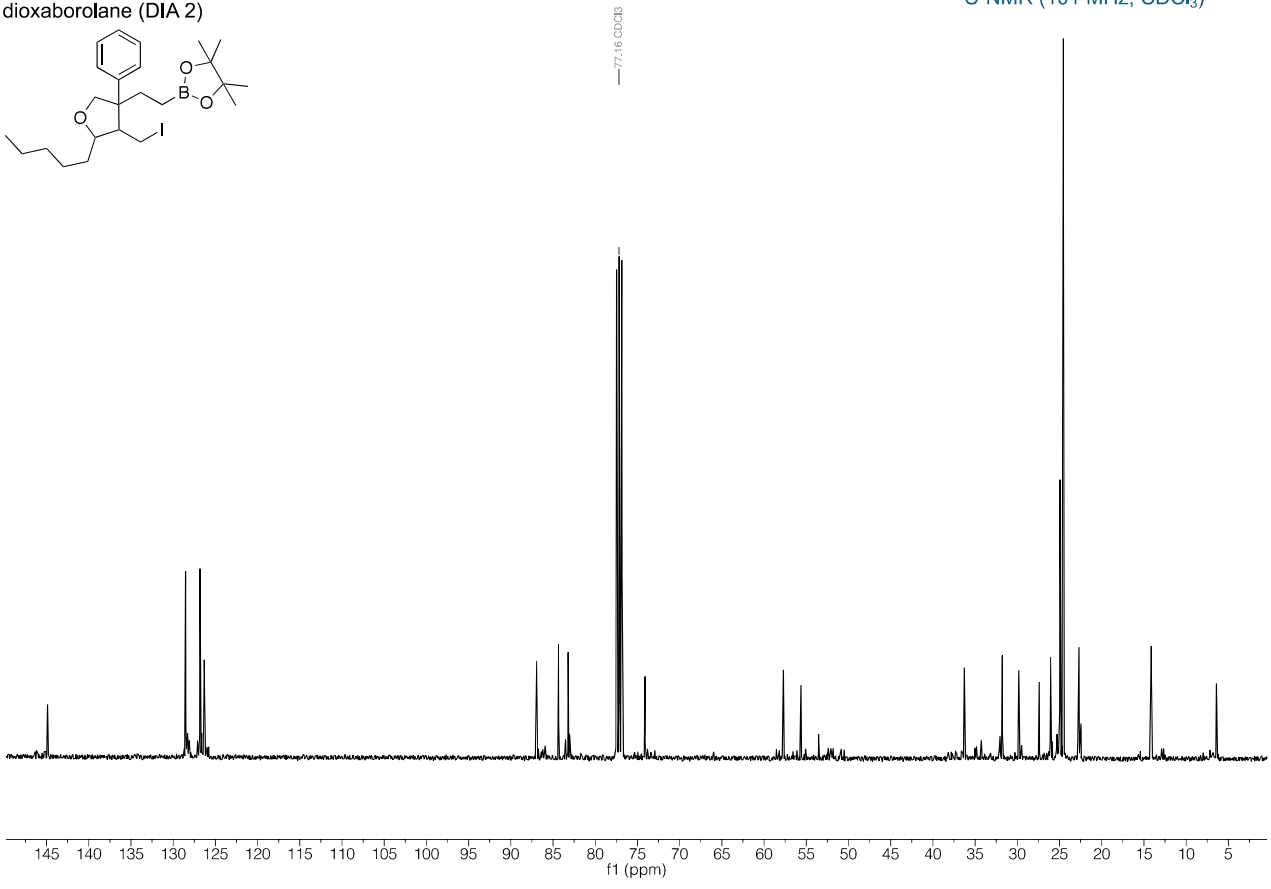
2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DIA 2)

^{1}H-NMR (400 MHz, $CDCl_3$)

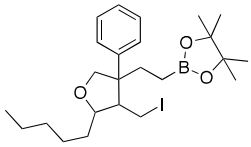


2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DIA 2)

^{13}C-NMR (101 MHz, $CDCl_3$)

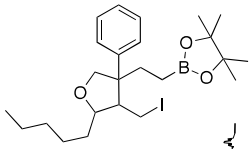


2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DIA 2)



DEPT-135 NMR (101 MHz, $CDCl_3$)

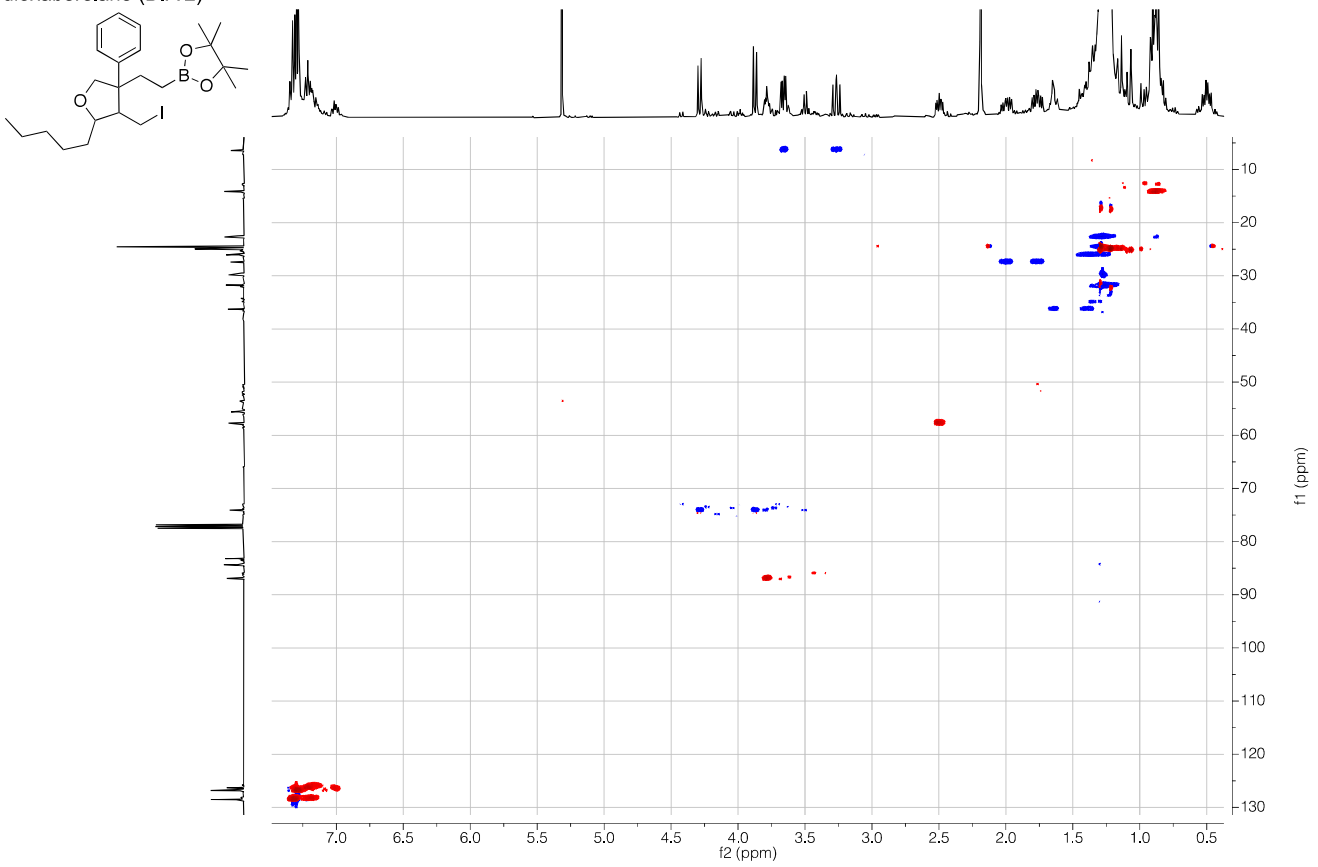
2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DIA 2)



^1H, ^1H-COSY (400 MHz, $CDCl_3$)

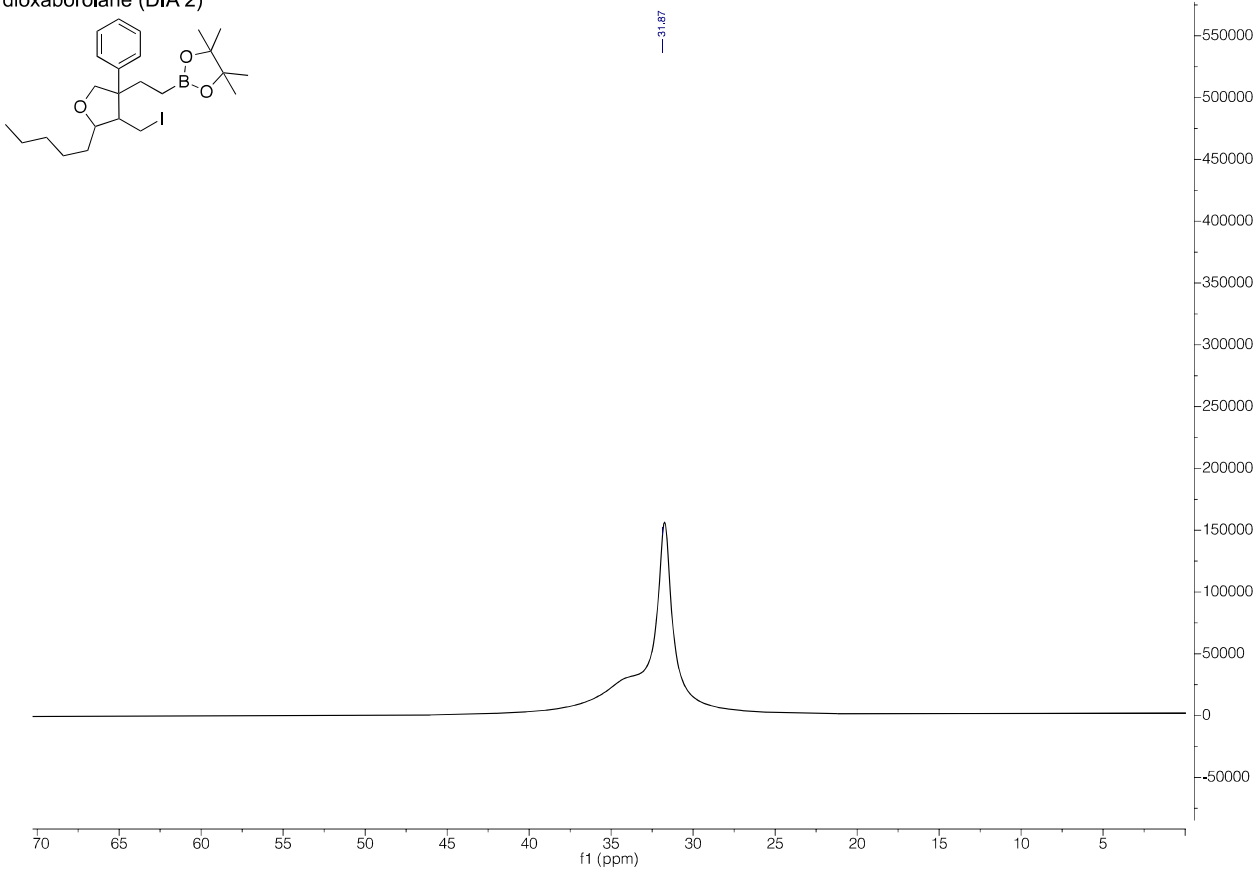
2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DIA 2)

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



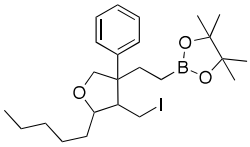
2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DIA 2)

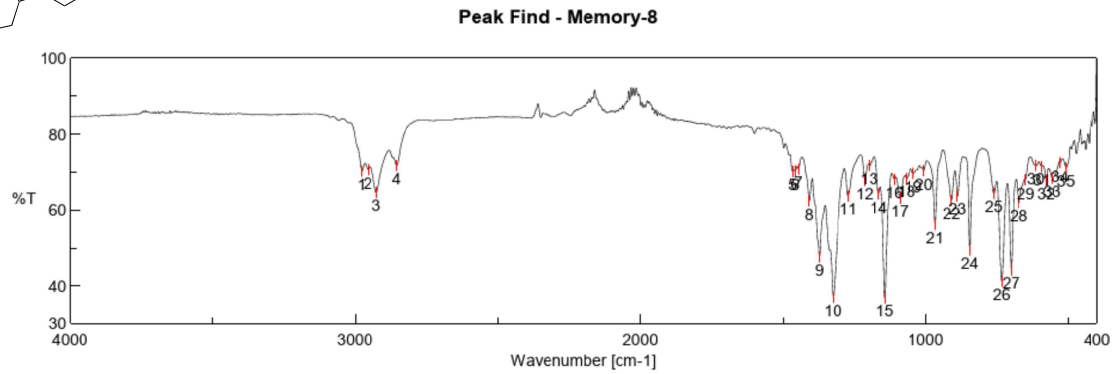
^{11}B-NMR (128 MHz, $CDCl_3$)



2-[2-[4-(iodomethyl)-5-pentyl-3-phenyl-tetrahydrofuran-3-yl]ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DIA 2)

FT-IR, ATR-diamond



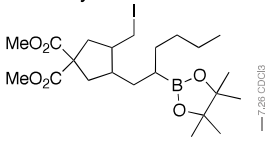


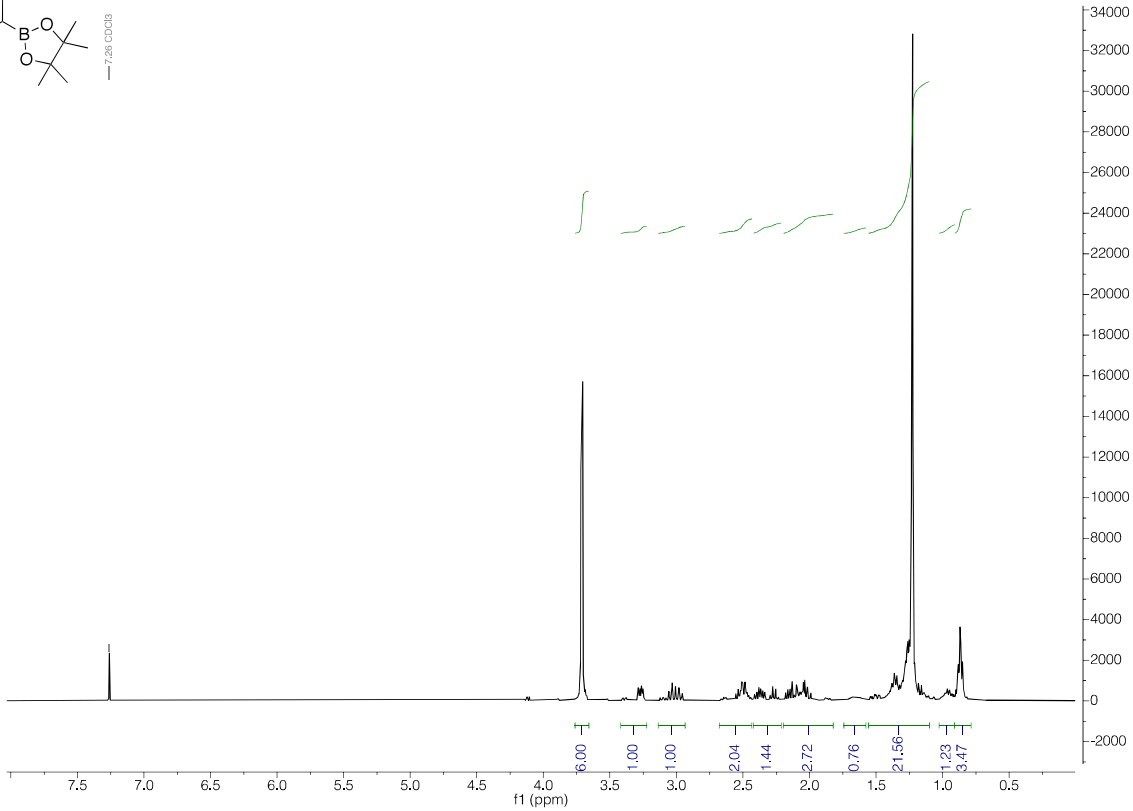
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2976.59	70.2232	2	2955.38	70.5581	3	2926.45	64.571
4	2855.1	71.6349	5	1465.63	70.0525	6	1457.92	70.2952
7	1446.35	70.7433	8	1406.82	62.3326	9	1371.14	47.5669
10	1323.89	36.8983	11	1270.86	63.5981	12	1213.01	67.7345
13	1196.61	71.6827	14	1164.79	64.1697	15	1142.62	36.7587
16	1108.87	67.9976	17	1089.58	62.9986	18	1066.44	68.2095
19	1043.3	69.6182	20	1005.7	70.3344	21	967.126	56.1581
22	908.308	62.4276	23	887.095	63.6204	24	844.669	49.38
25	759.816	64.3091	26	732.817	41.2005	27	699.069	44.1534
28	672.071	61.8066	29	648.929	67.8904	30	613.252	71.6628
31	592.039	71.3881	32	576.612	67.7013	33	556.363	68.3049
34	527.436	72.4086	35	507.187	70.9963			

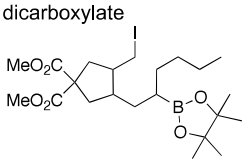
Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)

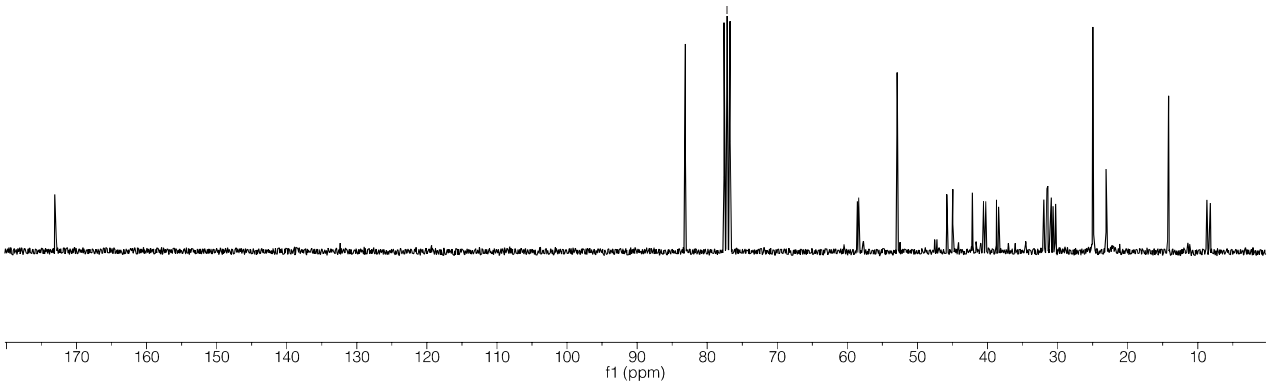




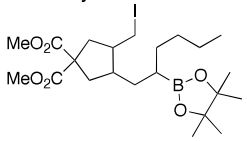
Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate



^{13}C-NMR (101 MHz, $CDCl_3$)



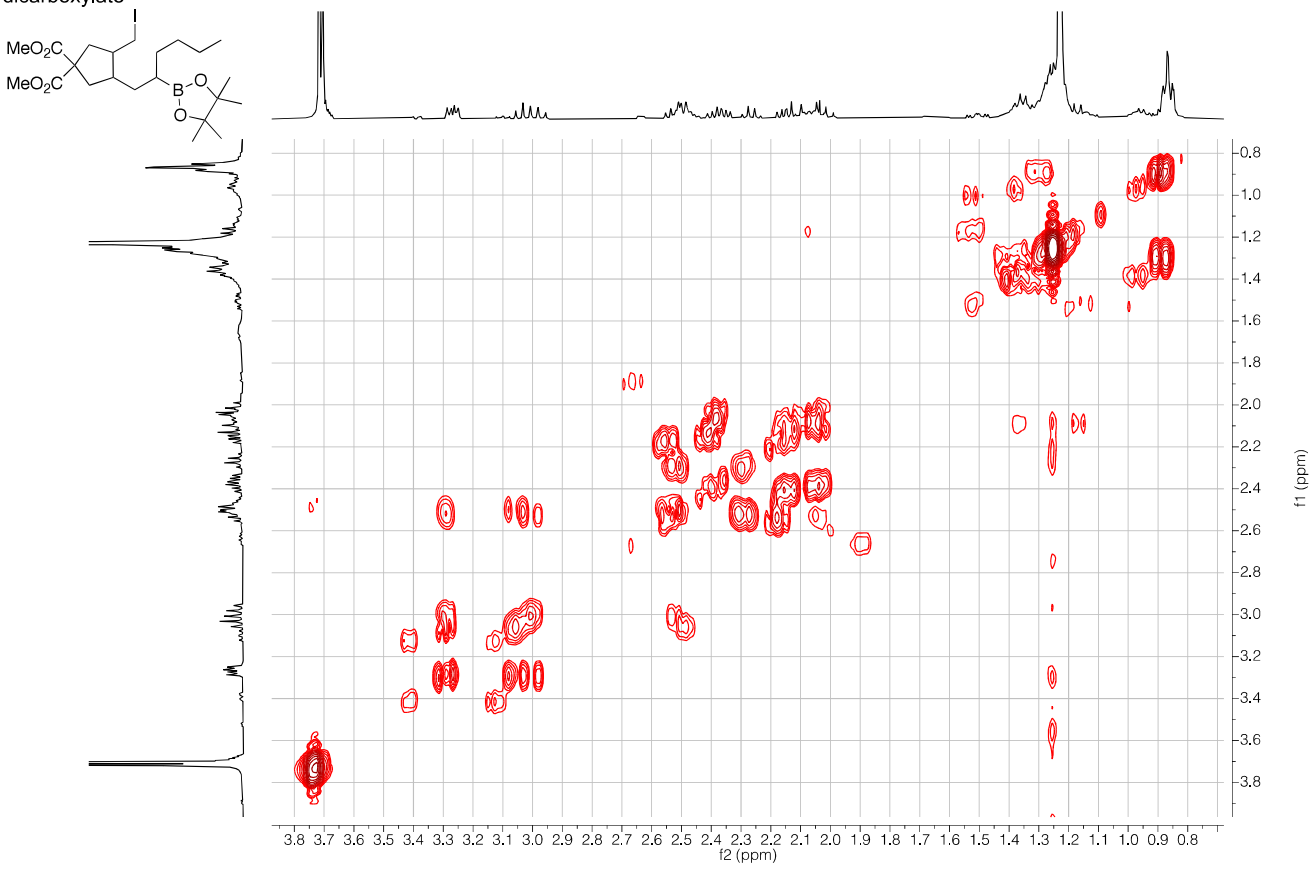
Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate



DEPT-135 NMR (101 MHz, $CDCl_3$)

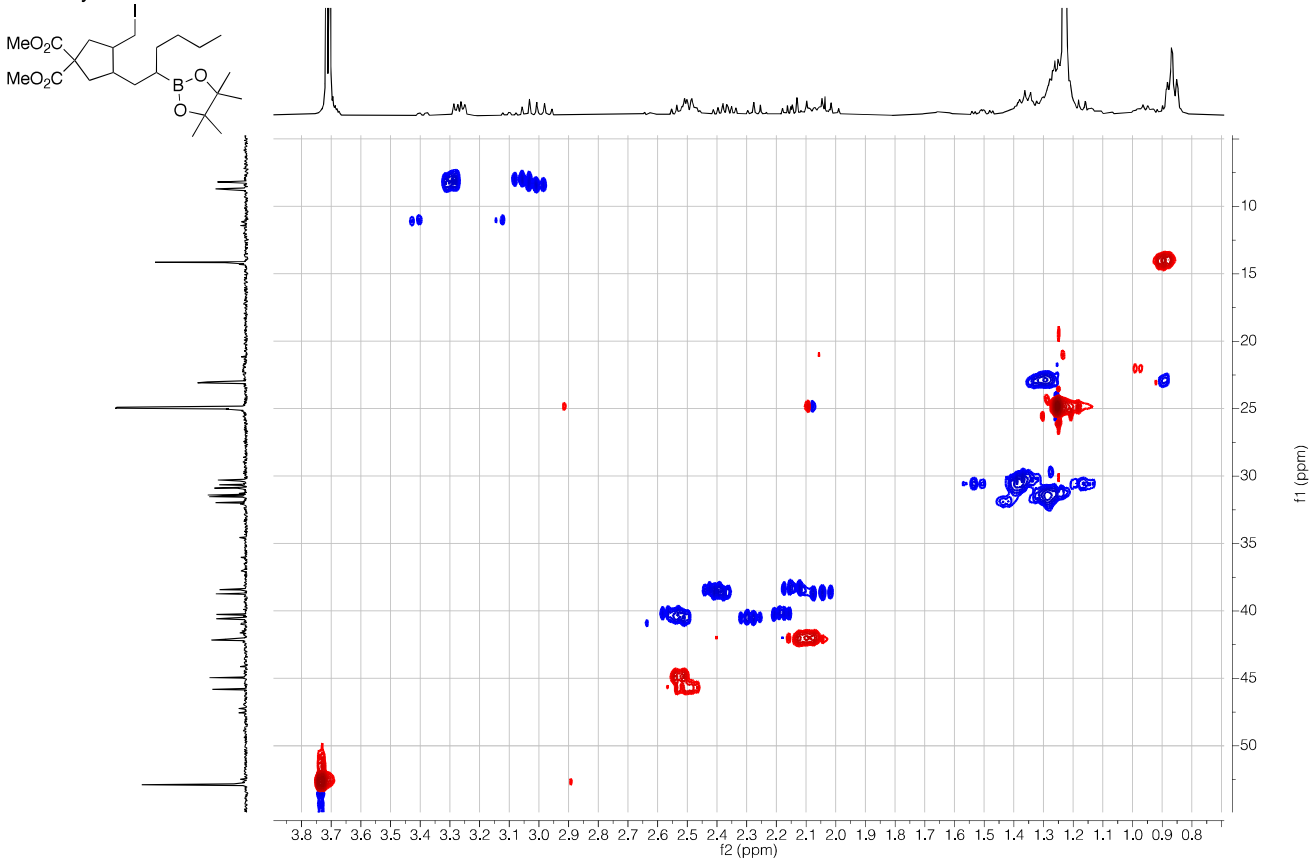
Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



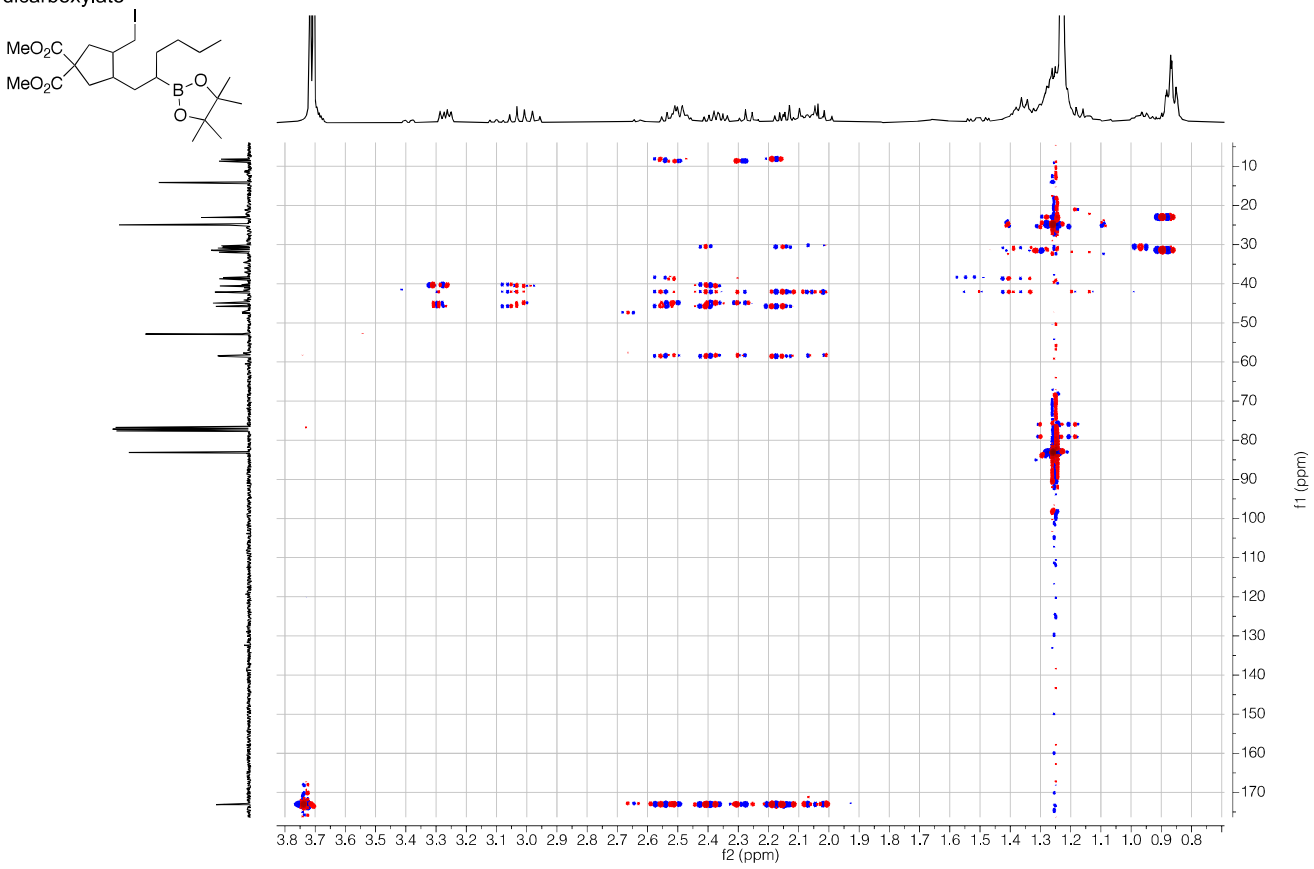
Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



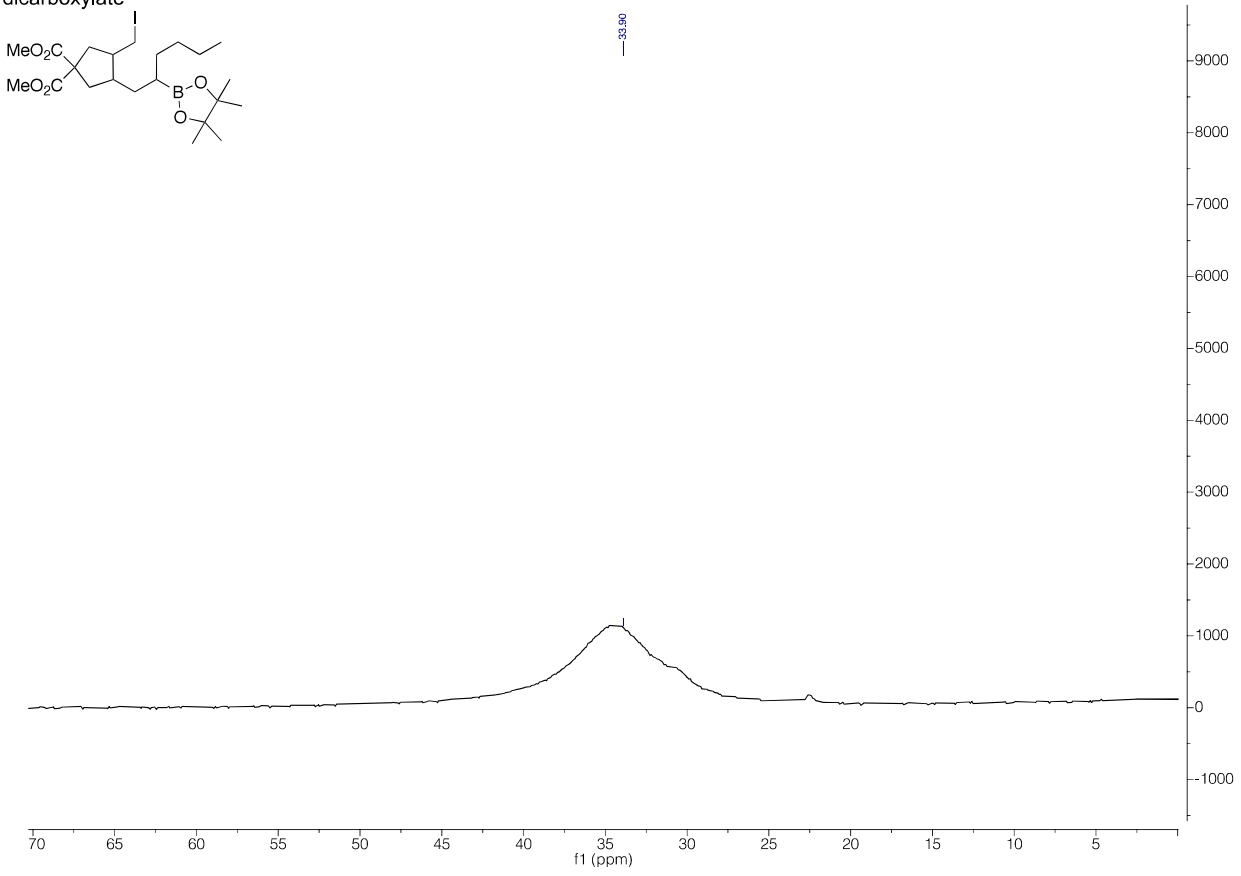
Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



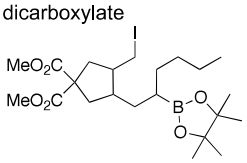
Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

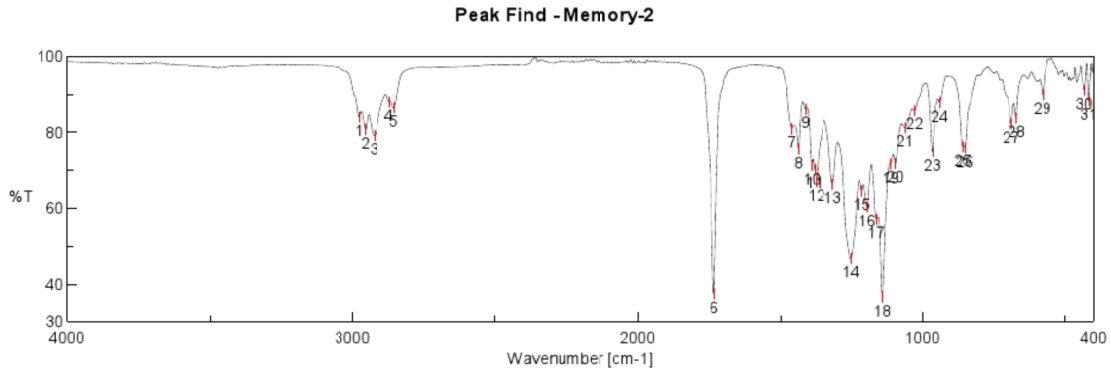
^{11}B-NMR (128 MHz, $CDCl_3$)



Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



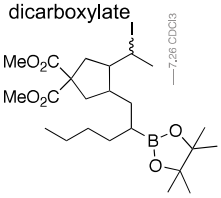


[Result of Peak Picking]

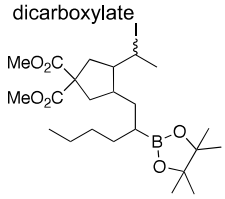
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	83.8787	2	2953.45	80.5172	3	2922.59	78.9409
4	2870.52	87.8494	5	2855.1	86.3473	6	1731.76	37.3691
7	1456.96	80.7228	8	1433.82	75.4918	9	1409.71	85.9171
10	1387.53	71.1388	11	1378.85	70.0455	12	1371.14	66.9654
13	1315.21	66.2063	14	1251.58	46.6343	15	1213.97	64.3832
16	1195.65	60.2173	17	1162.87	56.9174	18	1141.65	36.4796
19	1112.73	71.5375	20	1095.37	71.5245	21	1061.62	81.0834
22	1027.87	85.5987	23	965.198	74.806	24	939.163	87.6758
25	858.168	76.0389	26	850.454	75.797	27	689.427	82.1283
28	671.106	83.6407	29	579.504	89.8054	30	433.905	91.0583
31	417.513	88.1043						

Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)

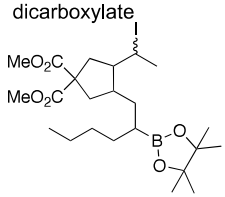


Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate



^{13}C-NMR (101 MHz, $CDCl_3$)

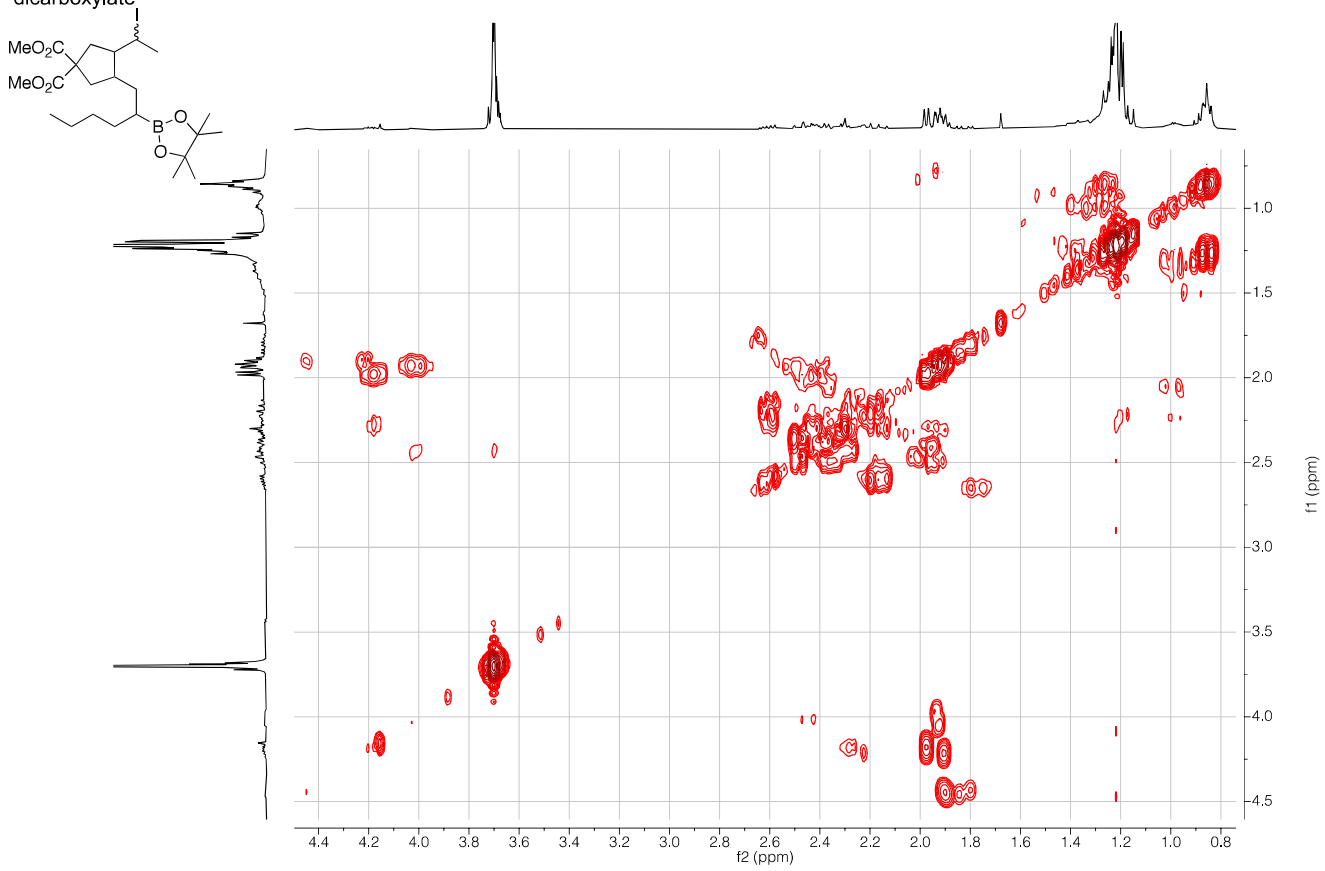
Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate



DEPT-135 NMR (101 MHz, $CDCl_3$)

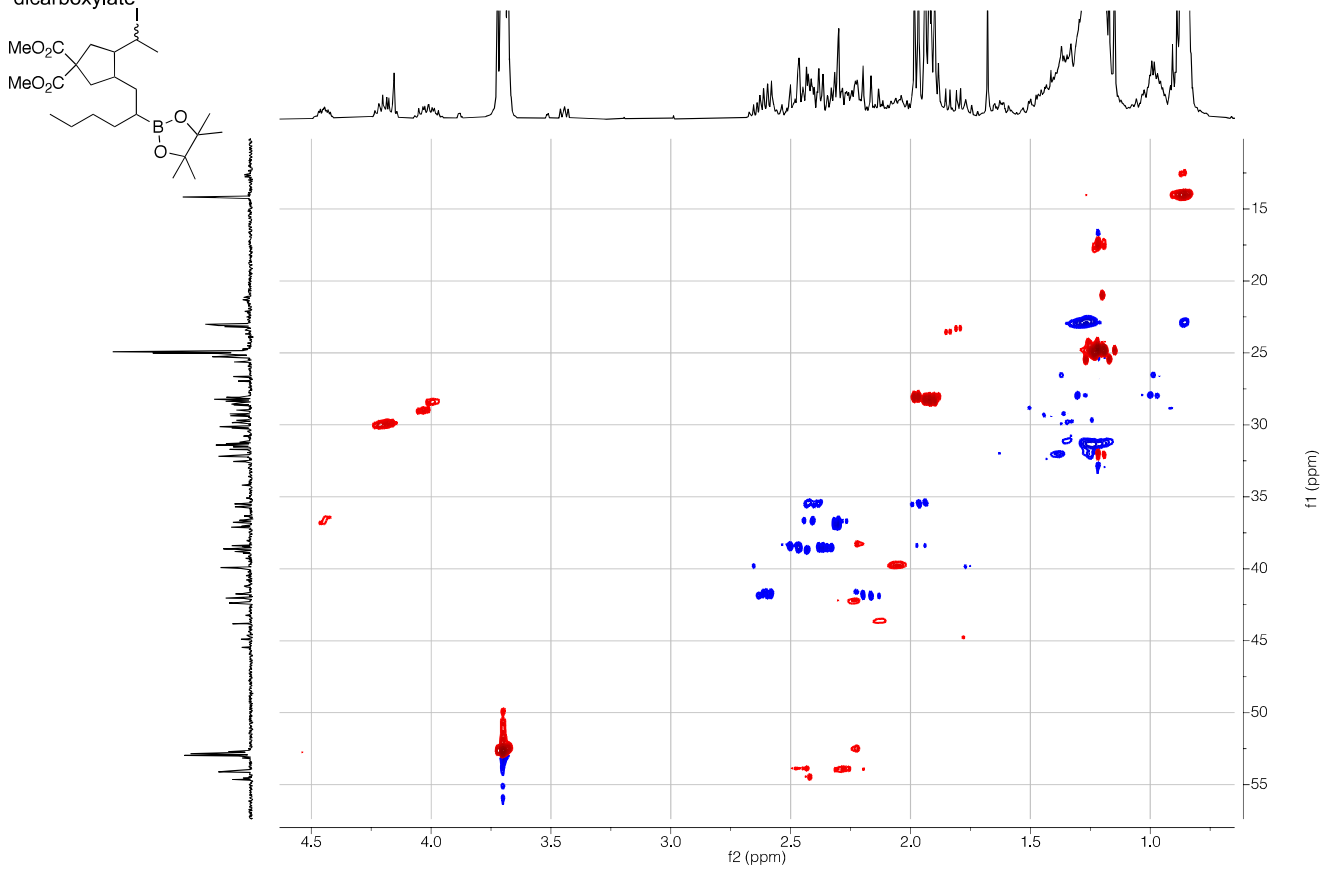
Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)

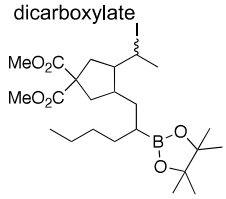


Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)

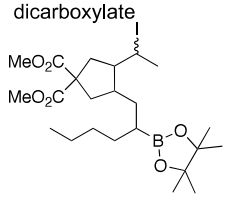


Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate



^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)

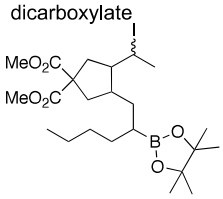
Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

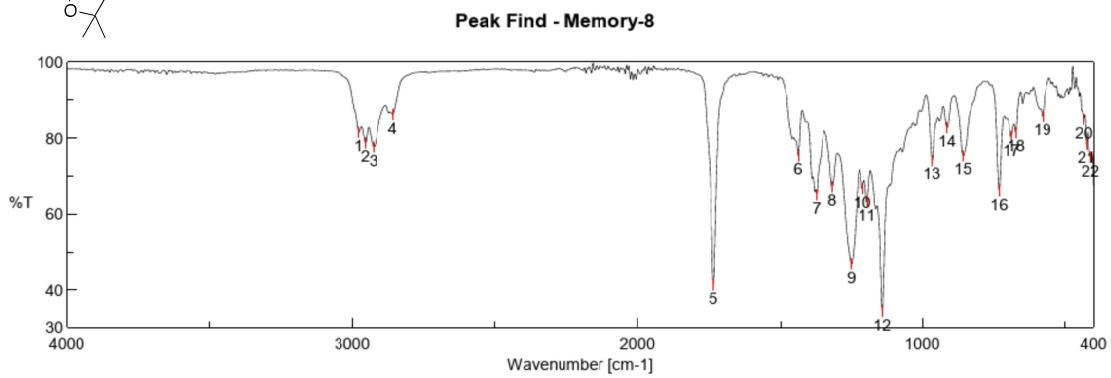


^{11}B-NMR (128 MHz, $CDCl_3$)

Dimethyl 3-(1-iodoethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



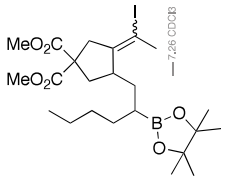


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2976.59	81.5136	2	2953.45	78.6258	3	2924.52	77.5769
4	2857.99	86.1805	5	1732.73	41.2415	6	1434.78	75.2581
7	1371.14	64.9984	8	1315.21	67.0547	9	1248.68	46.7764
10	1212.04	66.6521	11	1195.65	63.1078	12	1141.65	34.271
13	966.162	73.9773	14	912.165	82.7298	15	856.239	75.2401
16	731.853	66.0514	17	688.463	80.3789	18	671.106	81.3392
19	578.54	85.6039	20	433.905	84.9737	21	424.263	78.3029
22	411.728	74.871						

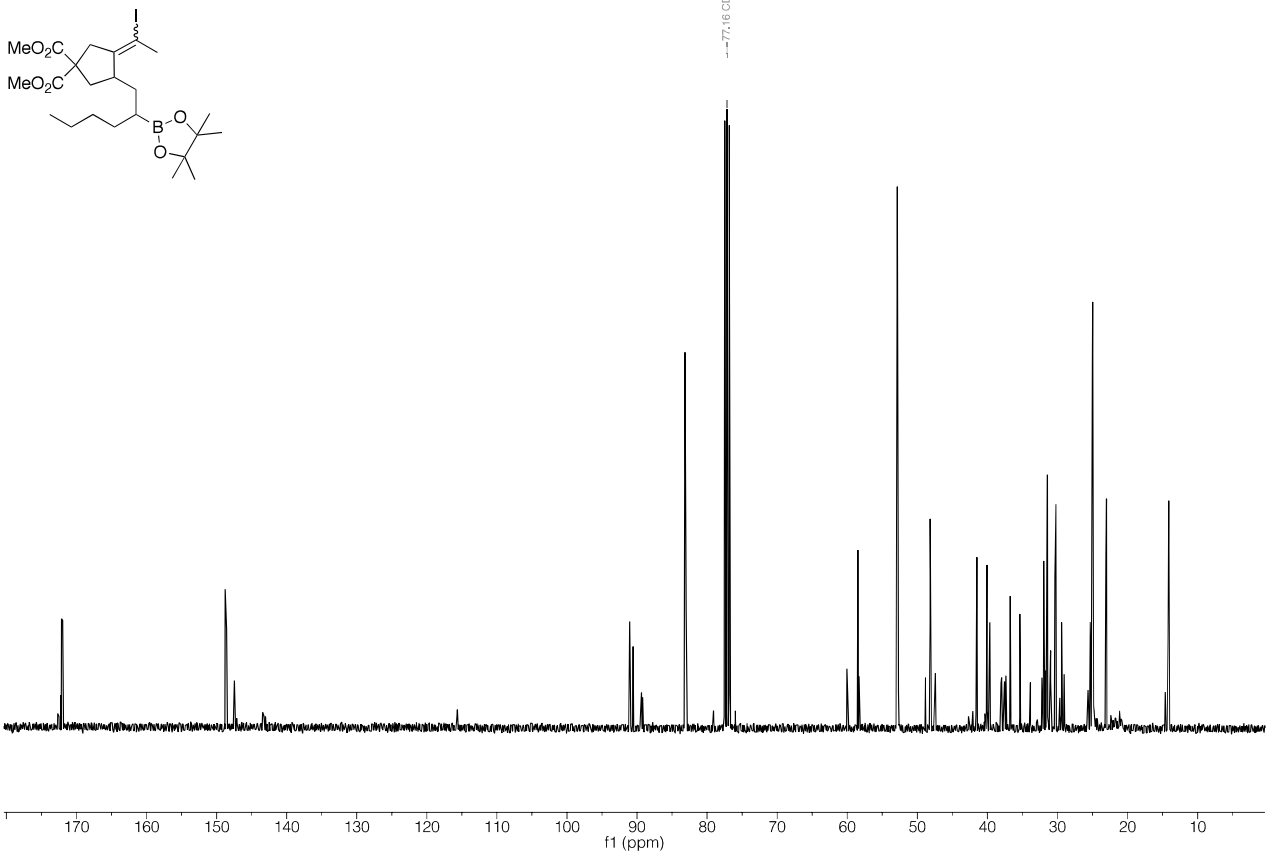
Dimethyl (3E)-3-(1-iodoethylidene)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)



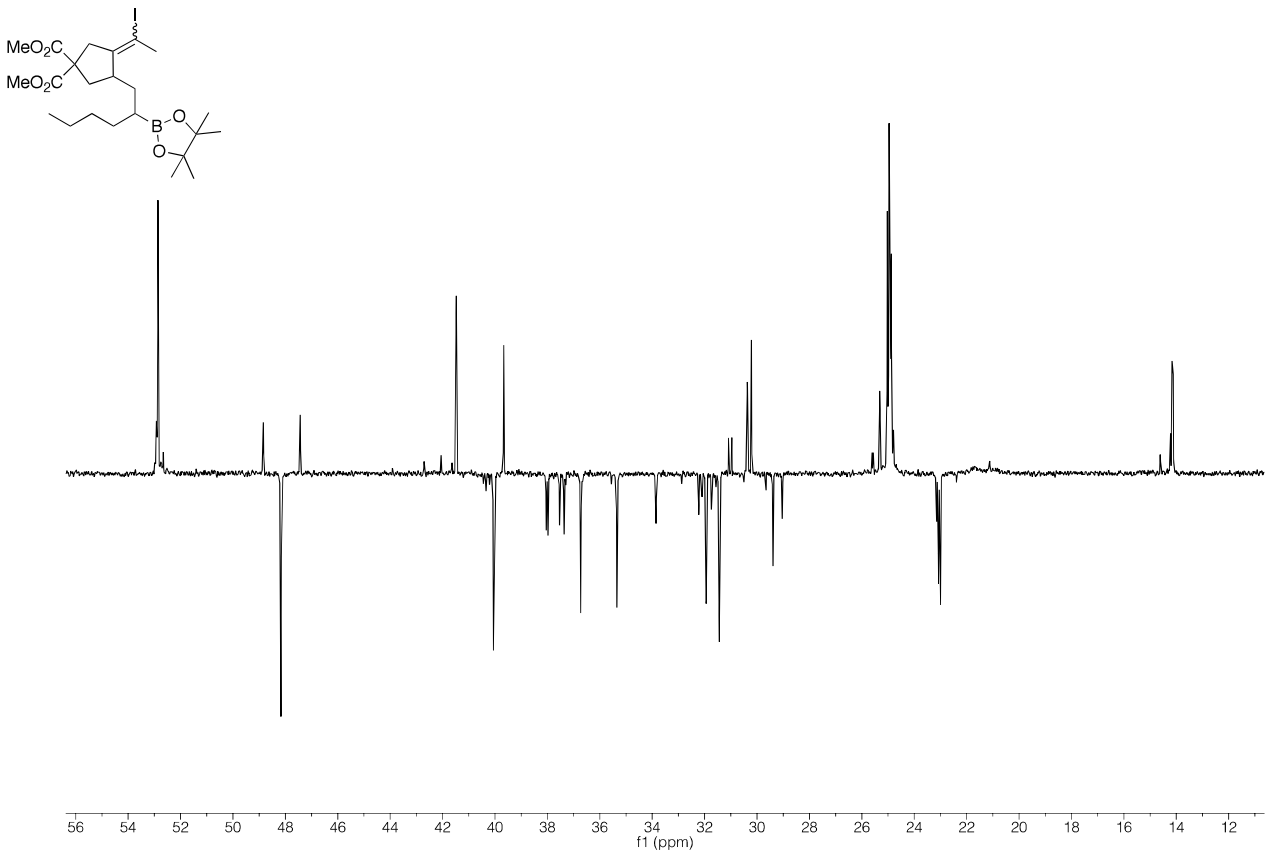
Dimethyl (3E)-3-(1-iodoethylidene)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{13}C-NMR (101 MHz, $CDCl_3$)



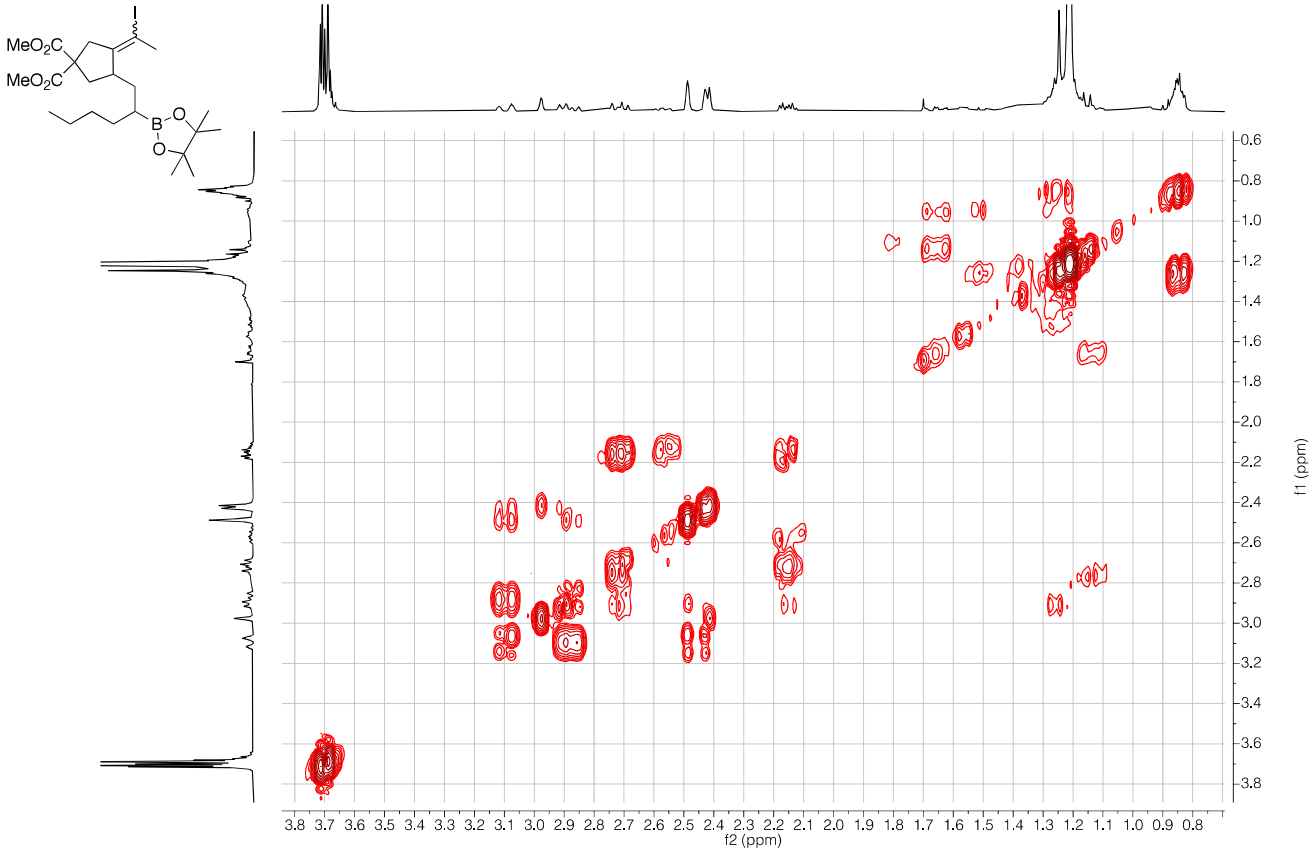
Dimethyl (3E)-3-(1-iodoethylidene)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

DEPT-135 NMR (101 MHz, $CDCl_3$)



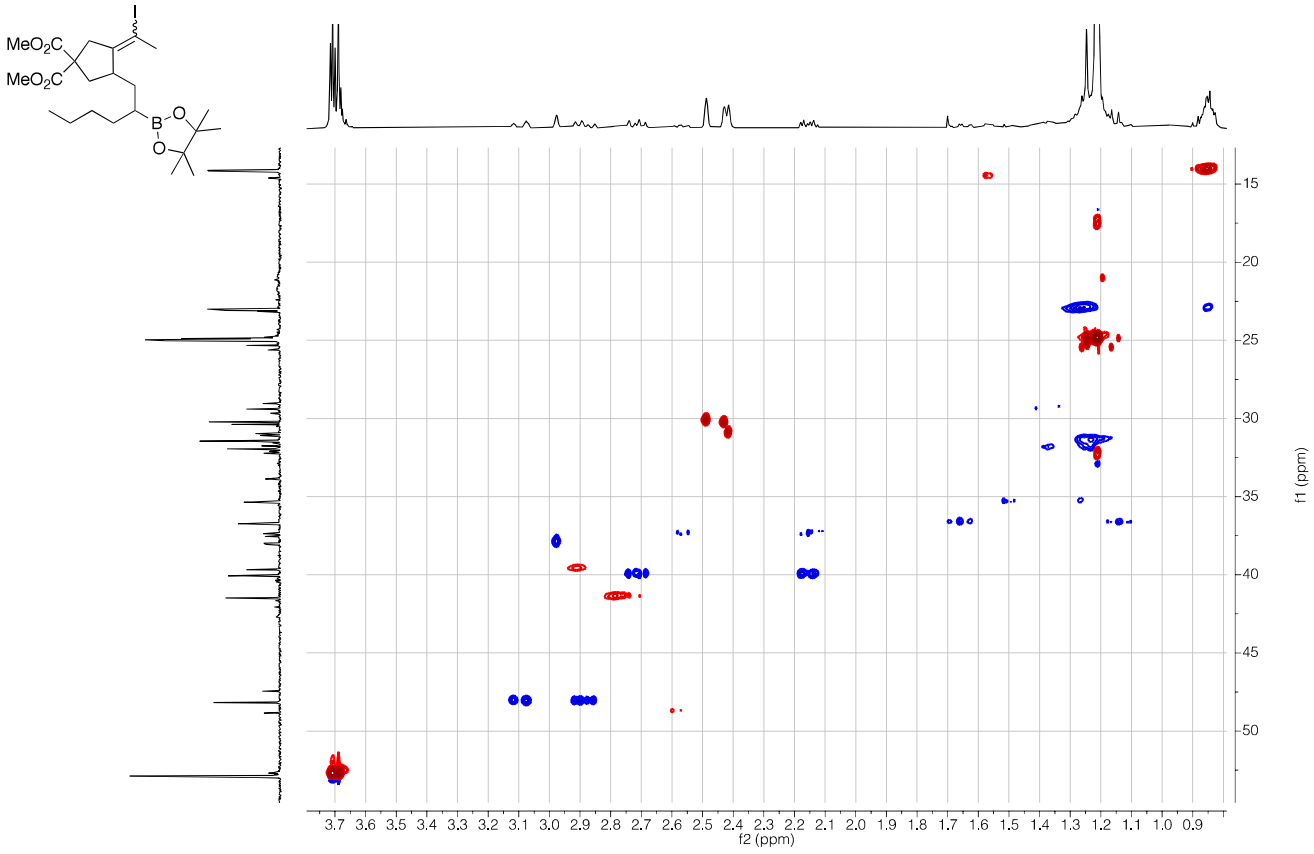
Dimethyl (3E)-3-(1-iodoethylidene)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



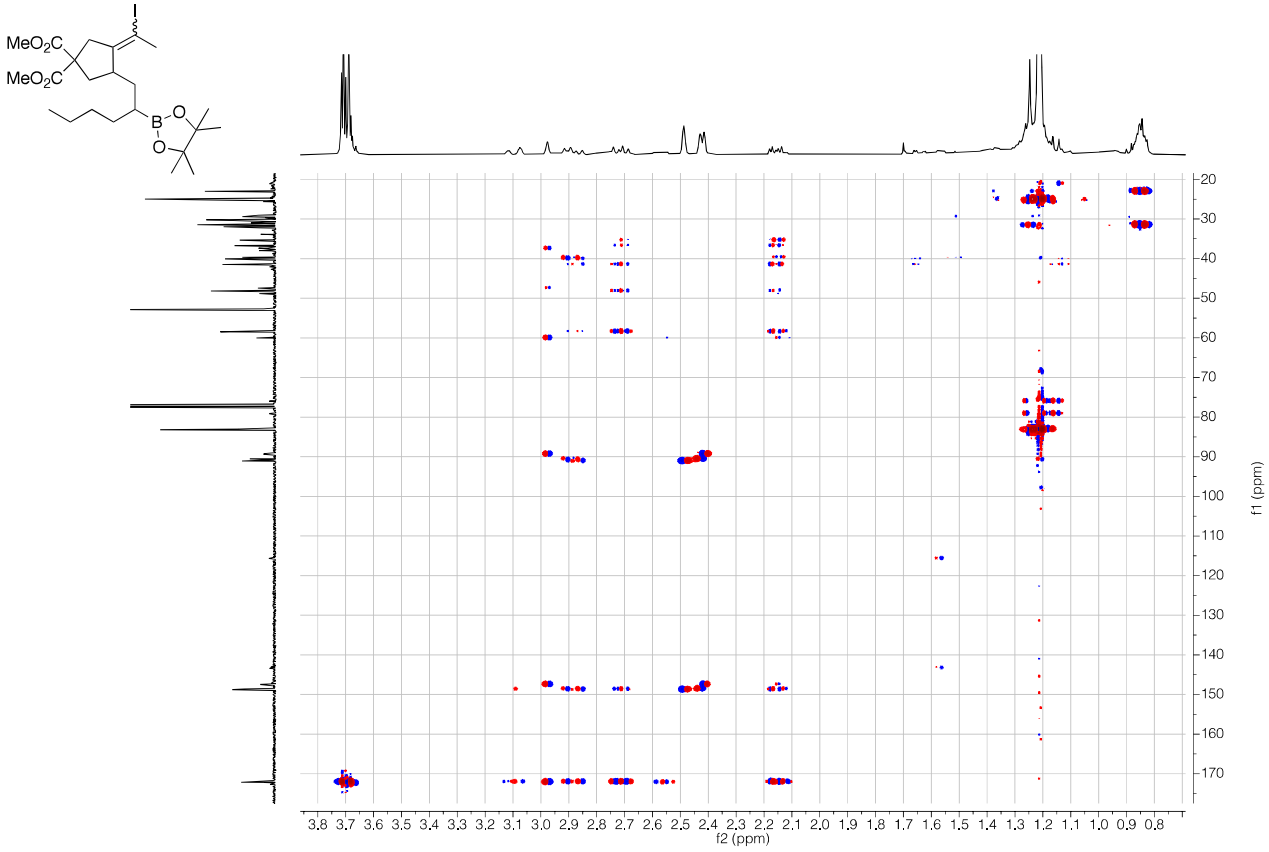
Dimethyl (3E)-3-(1-iodoethylidene)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



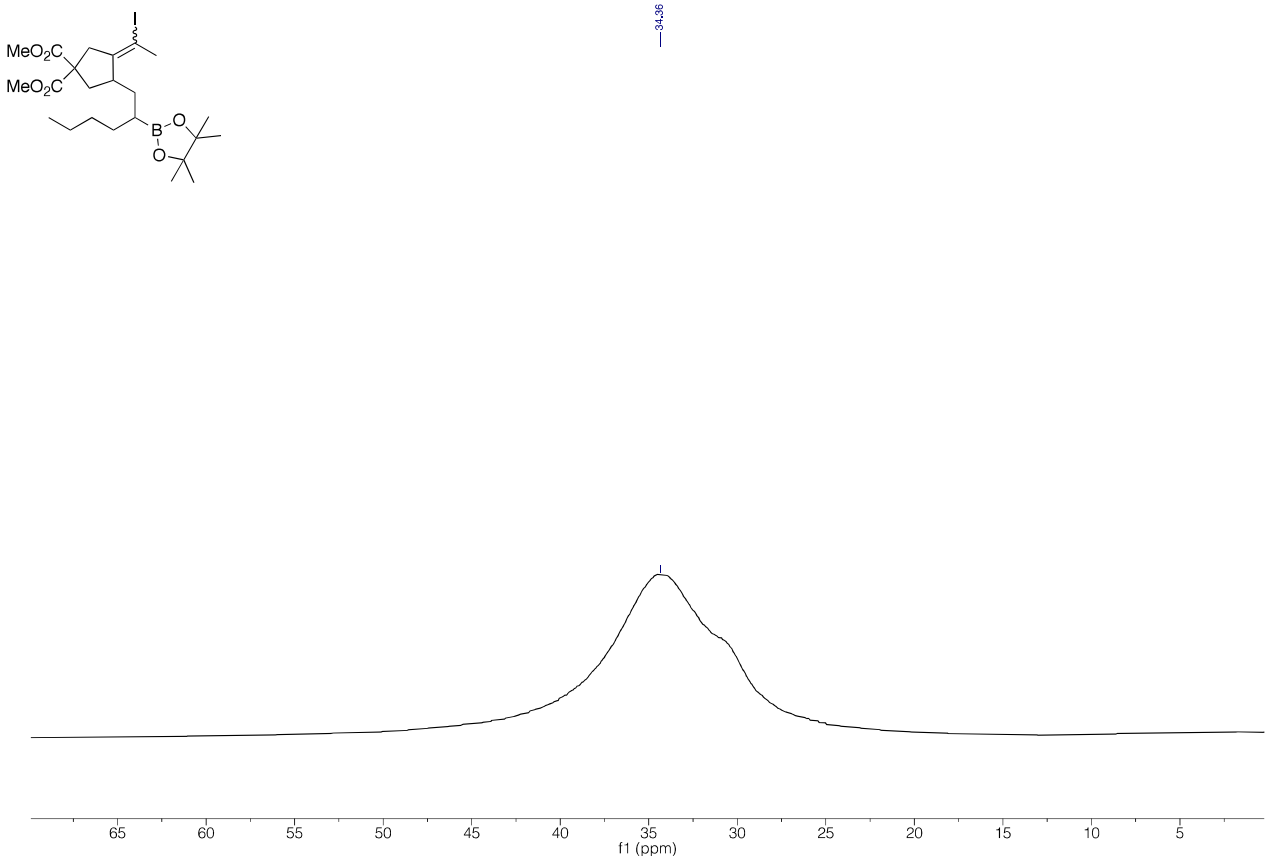
Dimethyl (3E)-3-(1-iodoethylidene)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



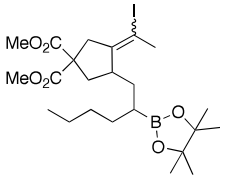
Dimethyl (3E)-3-(1-iodoethylidene)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

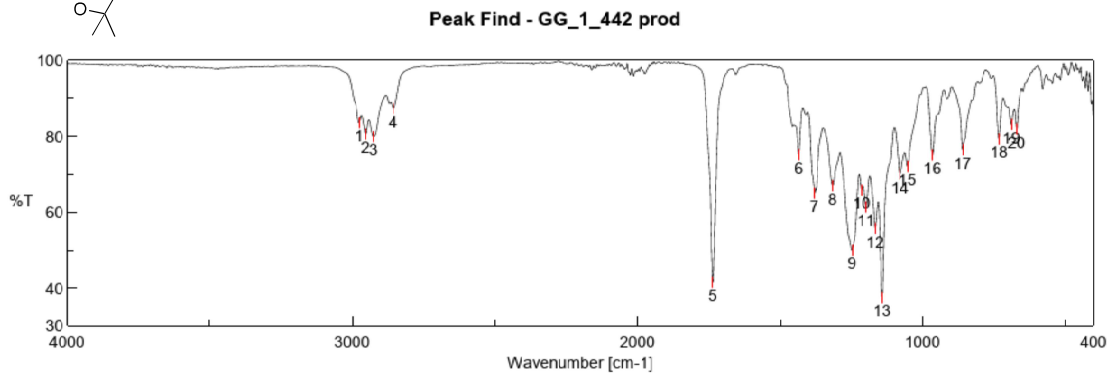
^{11}B-NMR (128 MHz, $CDCl_3$)



Dimethyl (3E)-3-(1-iodoethylidene)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



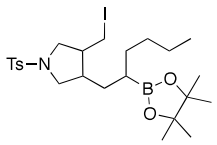


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	83.5239	2	2953.45	80.5483	3	2925.48	79.886
4	2856.06	87.2829	5	1734.66	41.4956	6	1433.82	75.1153
7	1378.85	64.9546	8	1315.21	66.9067	9	1247.72	49.9106
10	1213.01	65.7402	11	1197.58	61.3361	12	1165.76	55.6926
13	1141.65	37.414	14	1078.98	69.9828	15	1052.94	71.9753
16	965.198	75.0491	17	859.132	76.3988	18	731.853	79.1867
19	688.463	83.082	20	670.142	81.8359			

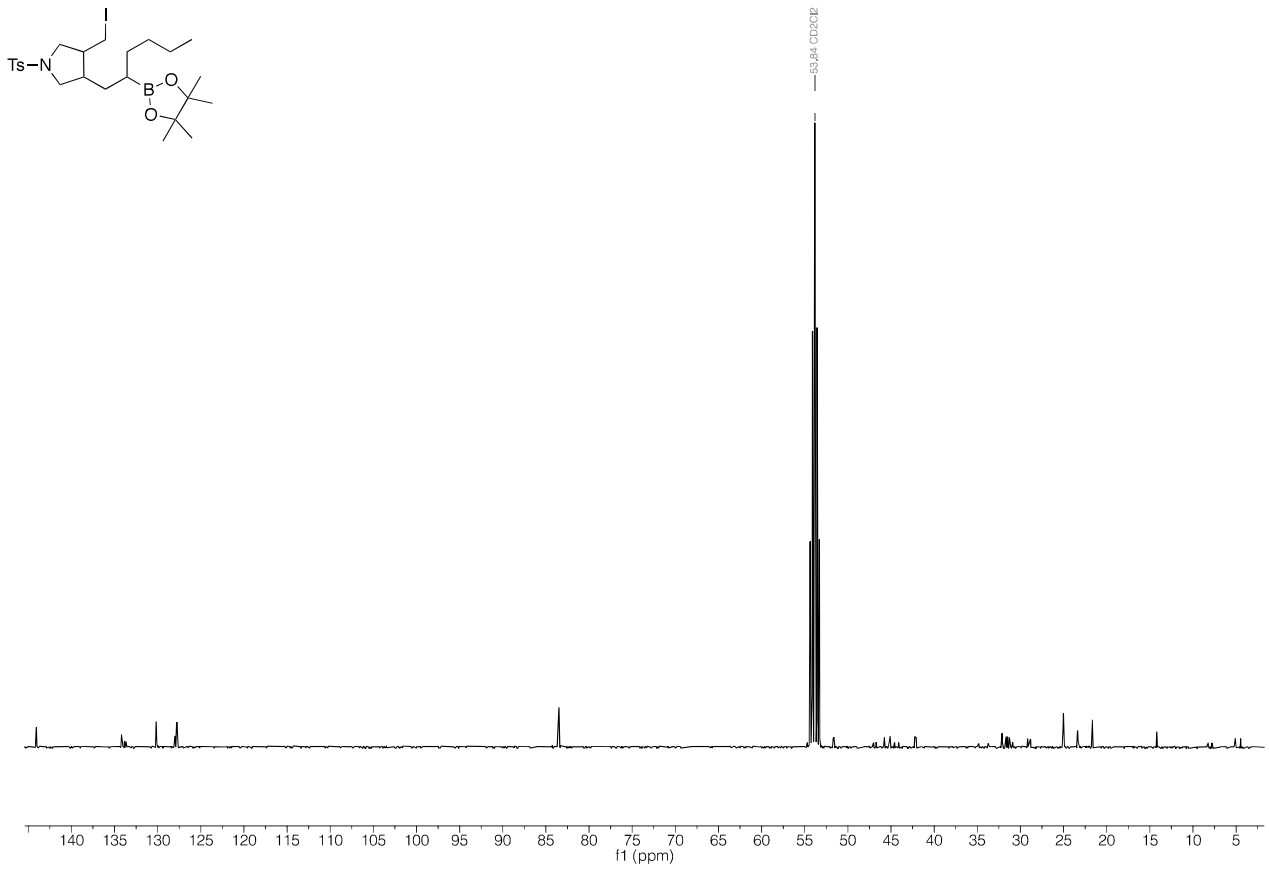
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]pyrrolidine

^{1}H-NMR (400 MHz, CD_2Cl_2)



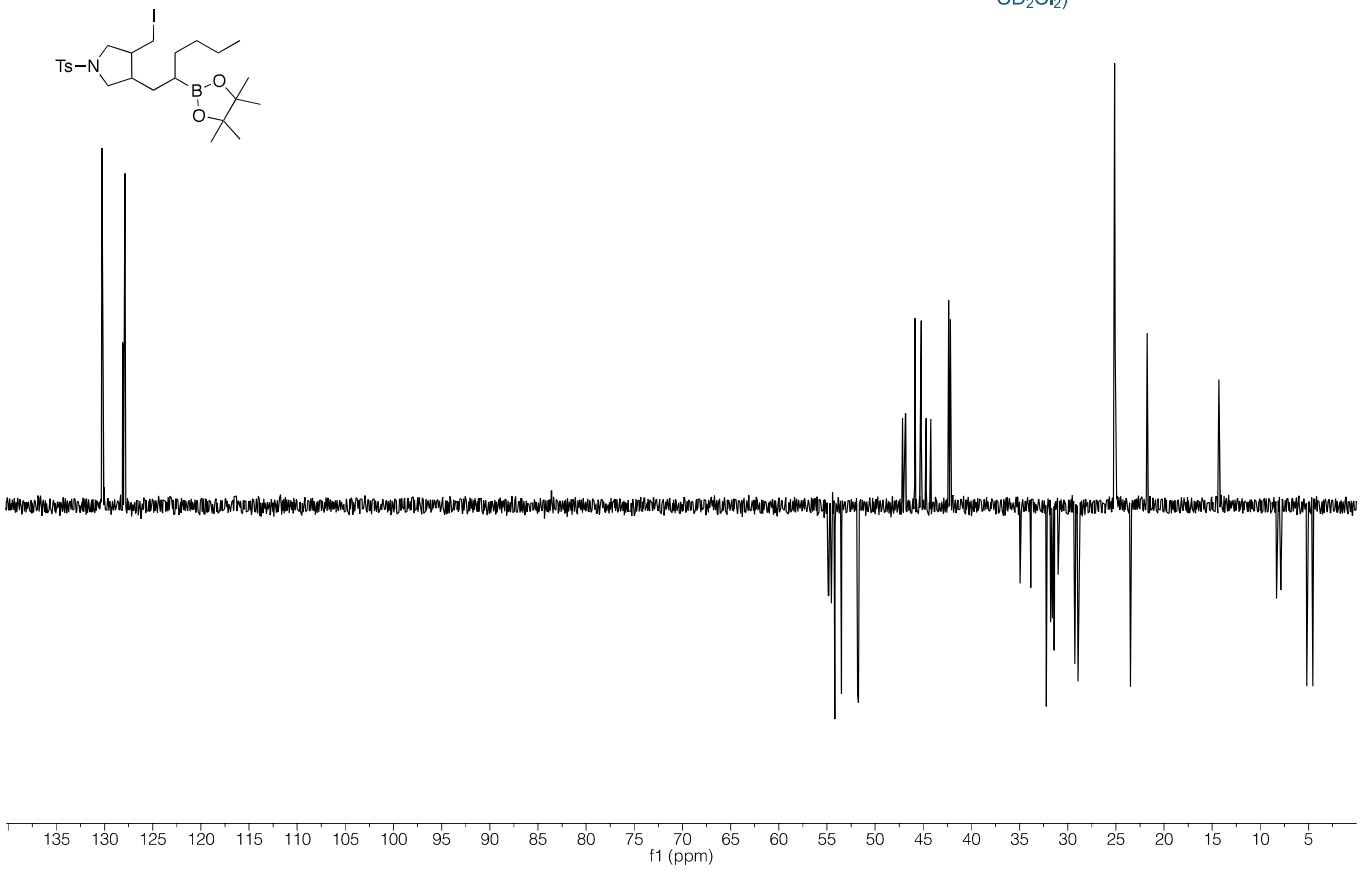
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]pyrrolidine

^{13}C-NMR (101 MHz, CD_2Cl_2)

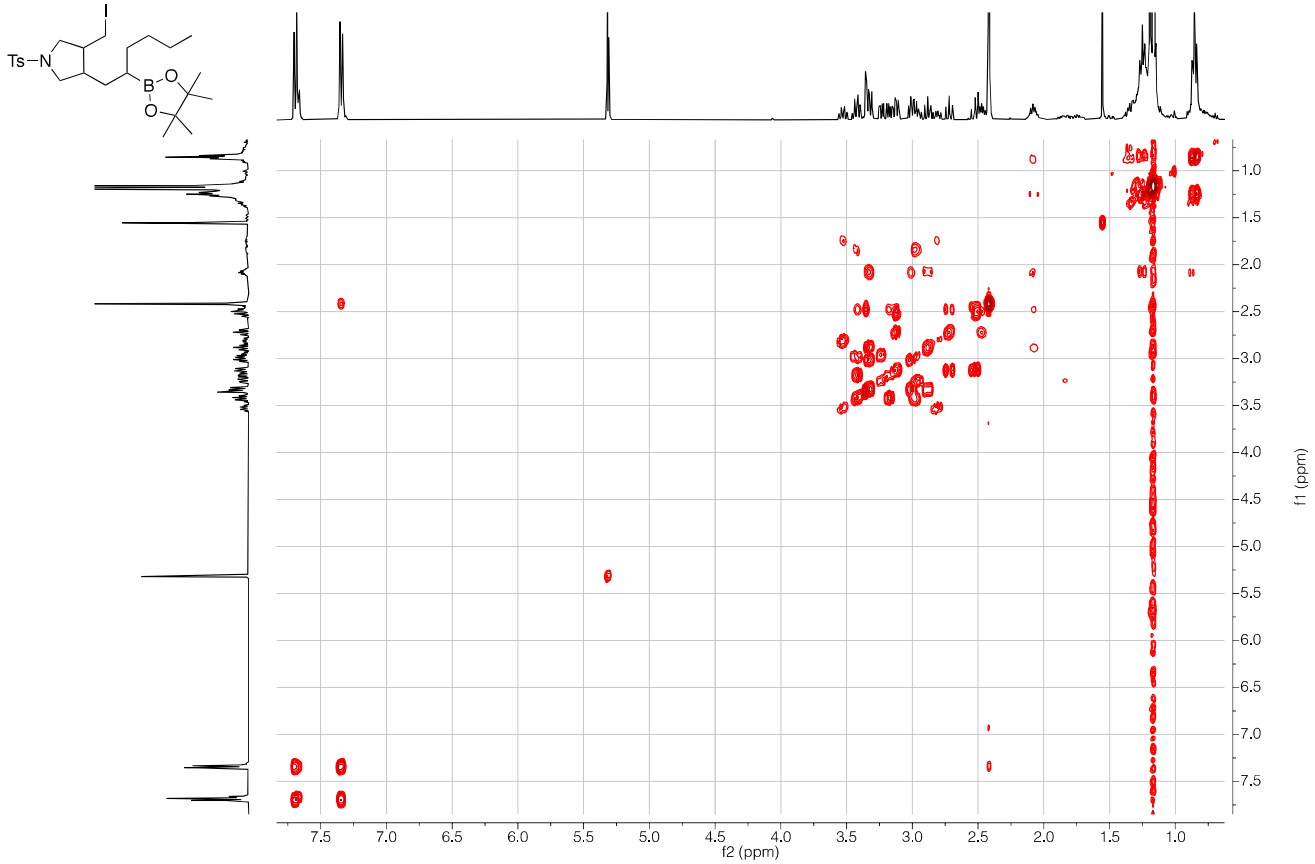


3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]pyrrolidine

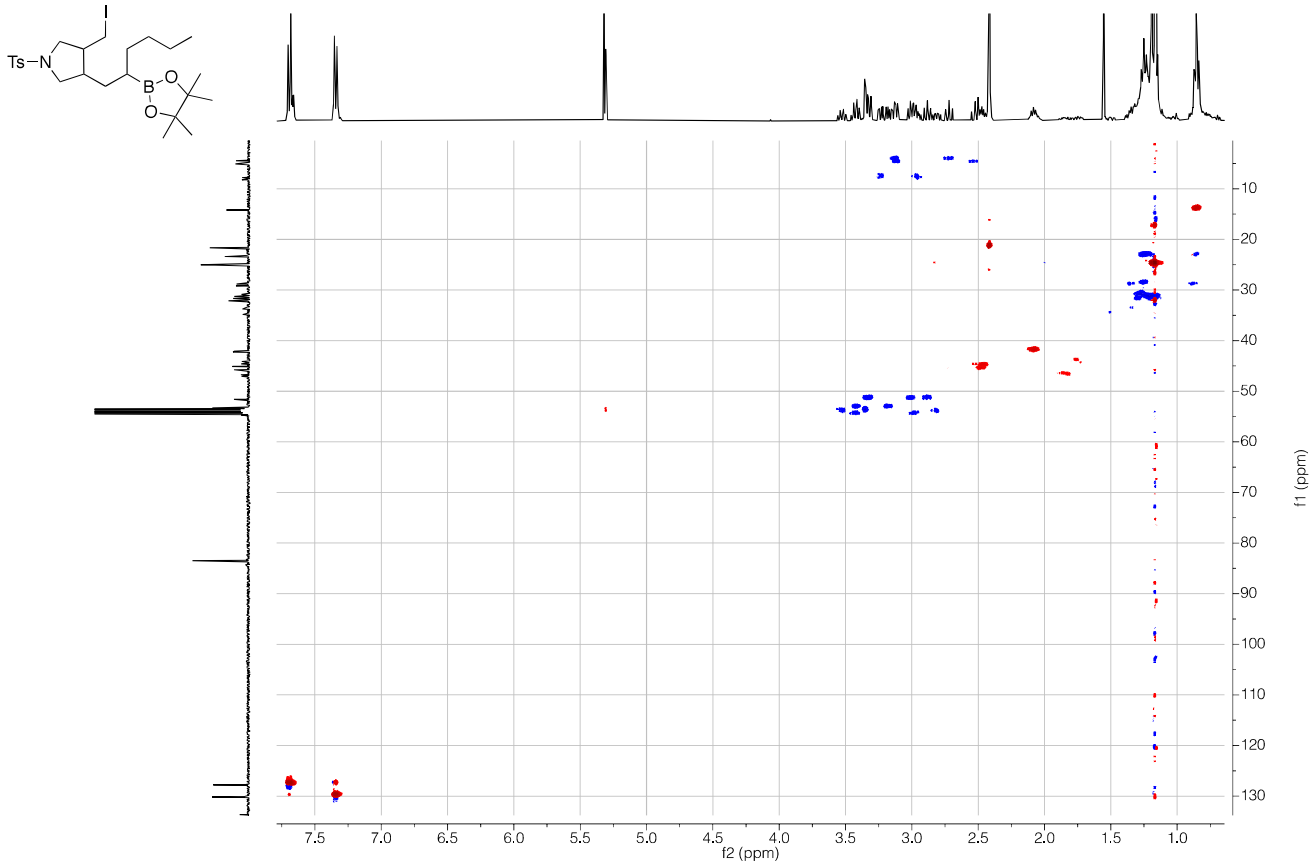
DEPT-135 NMR (101 MHz, CD_2Cl_2)



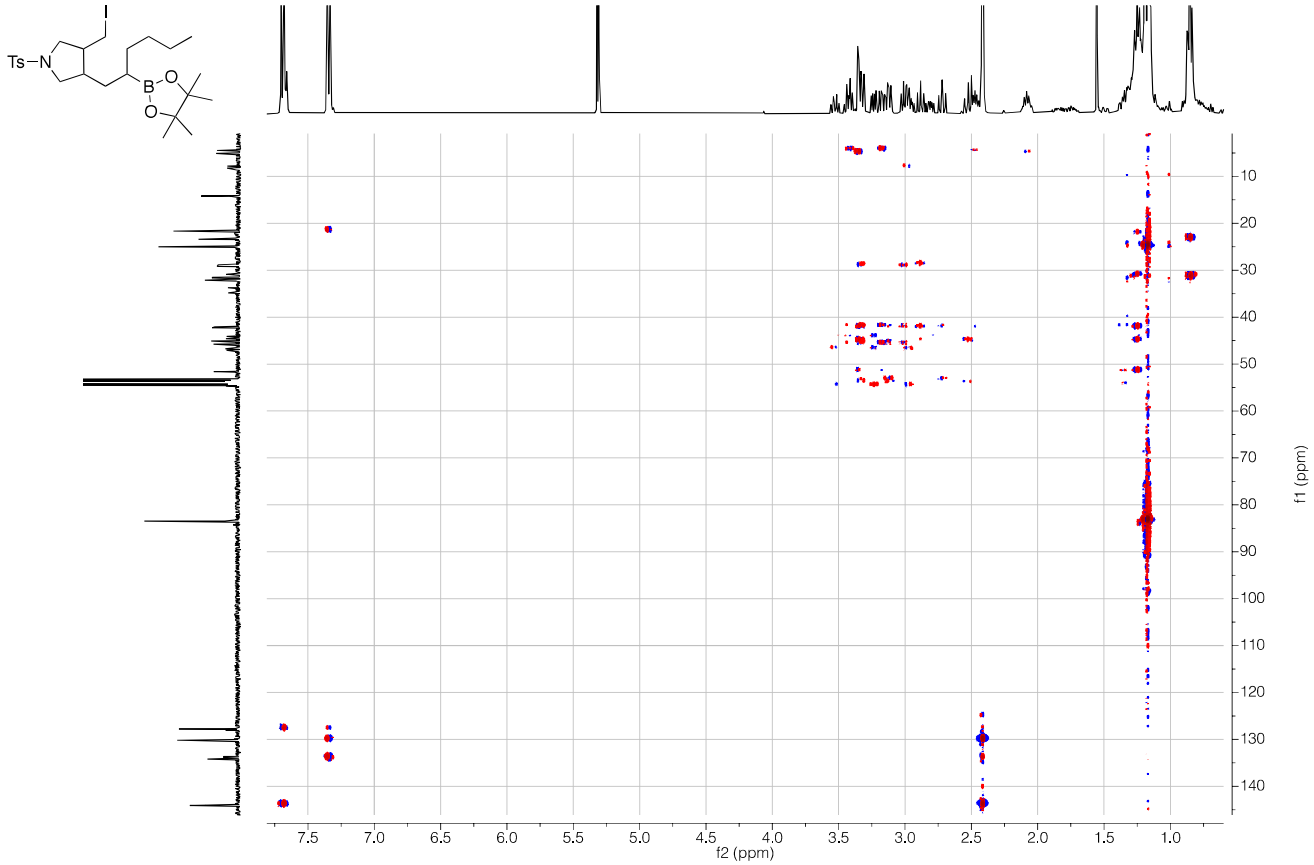
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]pyrrolidine ^{1}H, ^{1}H-COSY (400 MHz, CD_2Cl_2)



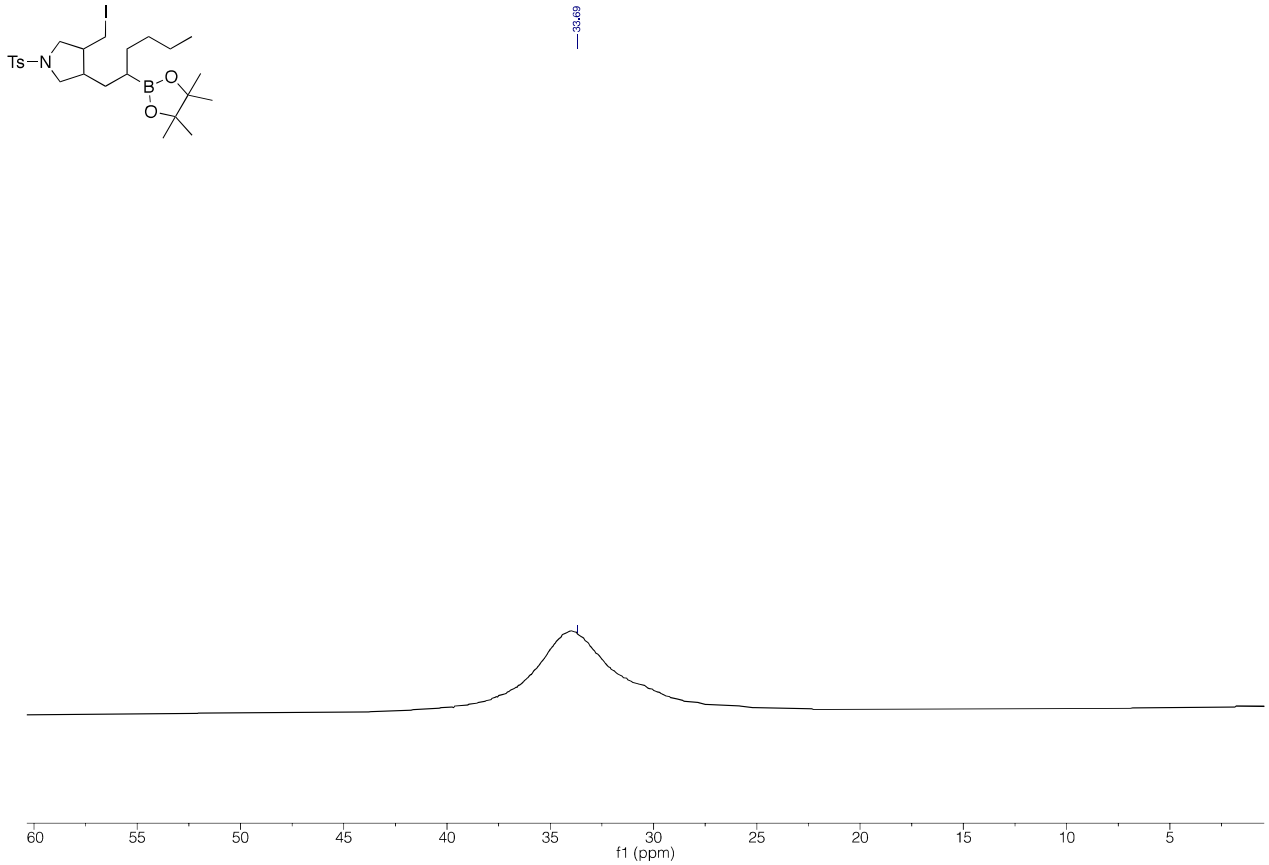
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]pyrrolidine ^{1}H, ^{13}C-HSQC (400 MHz, CD_2Cl_2)



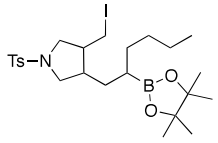
3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]pyrrolidine ^{1}H, ^{13}C-HMBC (400 MHz, CD_2Cl_2)

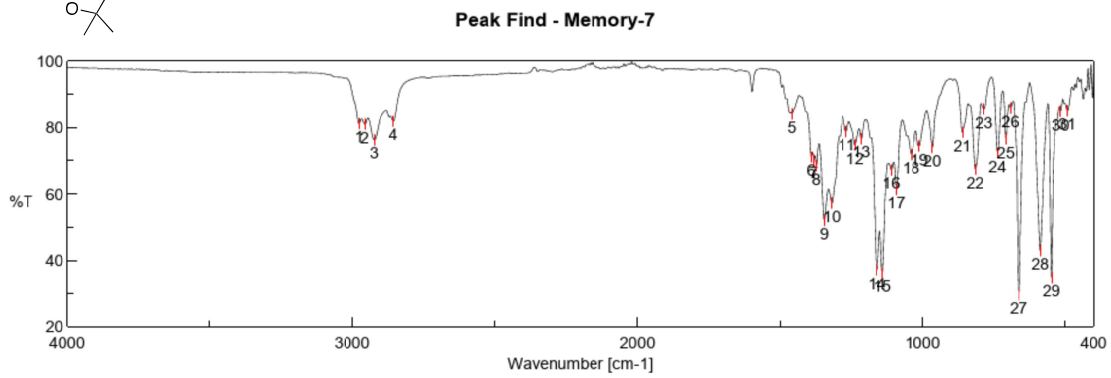


3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]pyrrolidine ^{11}B-NMR (128 MHz, CD_2Cl_2)



3-(iodomethyl)-1-(p-tolylsulfonyl)-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]pyrrolidine FT-IR, ATR-diamond

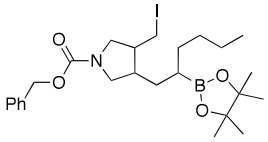




[Result of Peak Picking]

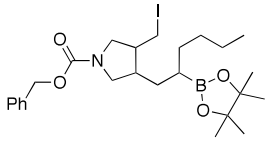
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2974.66	81.1598	2	2955.38	80.9811	3	2922.59	75.2469
4	2855.1	81.8664	5	1457.92	84.0855	6	1388.5	71.0508
7	1379.82	70.2629	8	1371.14	68.4795	9	1344.14	52.0166
10	1318.11	57.2648	11	1266.04	78.7173	12	1235.18	74.7224
13	1213.01	76.6058	14	1159.01	37.1088	15	1140.69	36.1639
16	1108.87	67.1861	17	1091.51	61.2869	18	1039.44	71.8331
19	1010.52	74.4015	20	965.198	73.9967	21	859.132	78.5525
22	813.813	67.4058	23	782.958	85.5401	24	735.71	72.3643
25	707.747	76.5571	26	691.355	85.8312	27	662.428	29.7196
28	586.254	42.8781	29	546.72	34.7811	30	514.901	84.8662
31	491.759	85.0323						

Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine-1-carboxylate



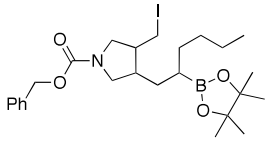
^{1}H-NMR (400 MHz, $(CD_3)_2CO$)

Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine-1-carboxylate



^{13}C-NMR (101 MHz, $(CD_3)_2CO$)

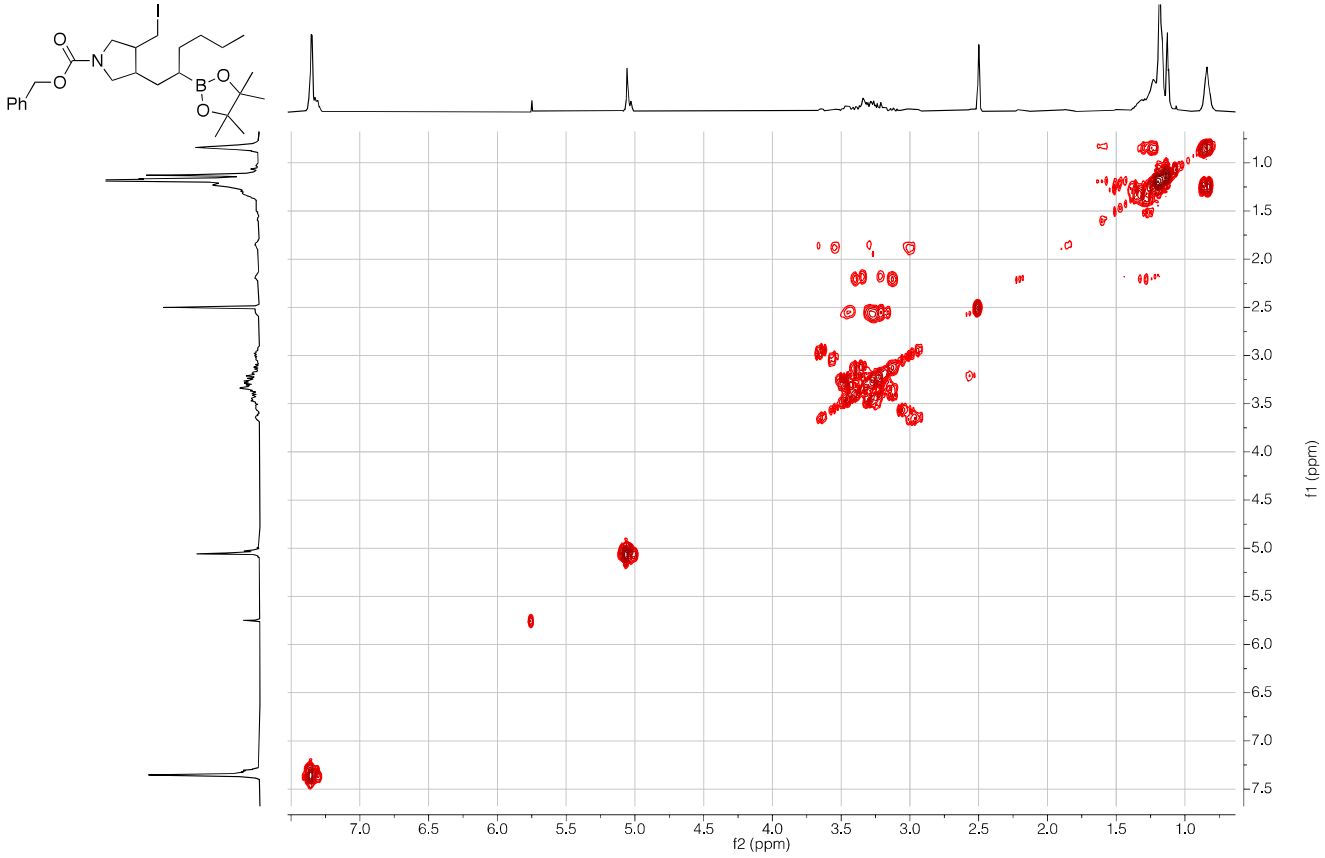
Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine-1-carboxylate



DEPT-135 NMR (101 MHz, $(CD_3)_2CO$)

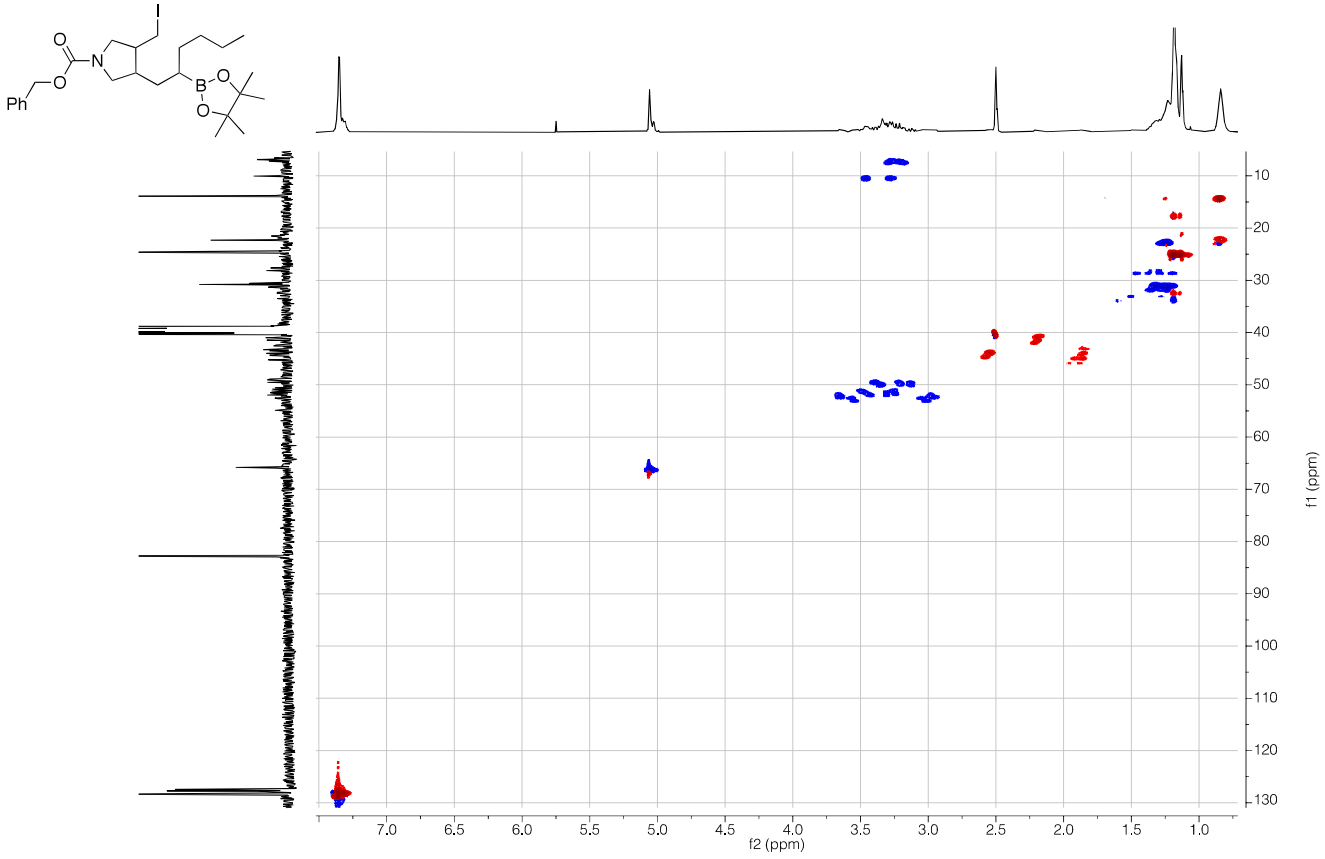
Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine-1-carboxylate

^{1}H, ^{1}H-COSY (400 MHz, $(CD_3)_2CO$)



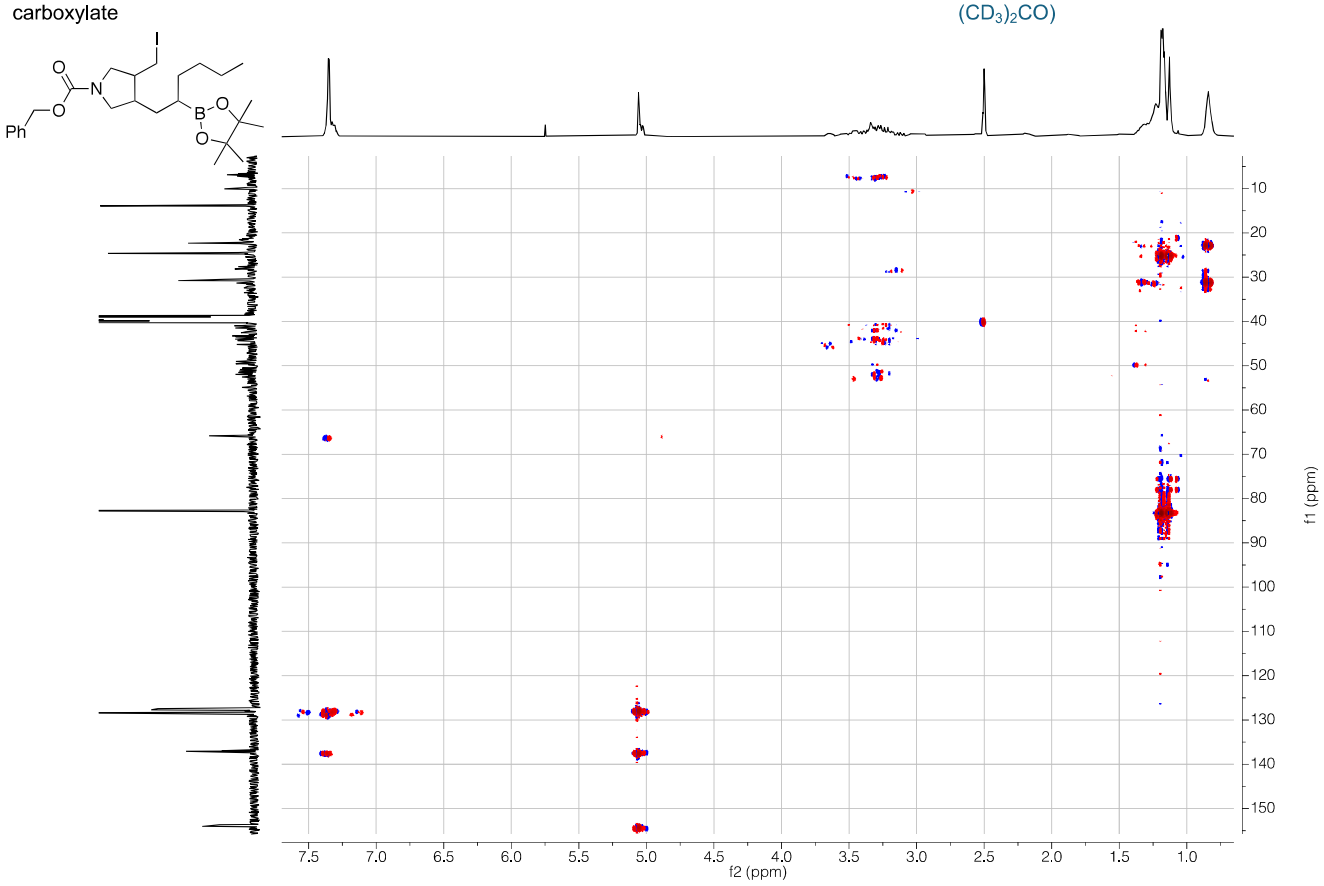
Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine-1-carboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $(CD_3)_2CO$)



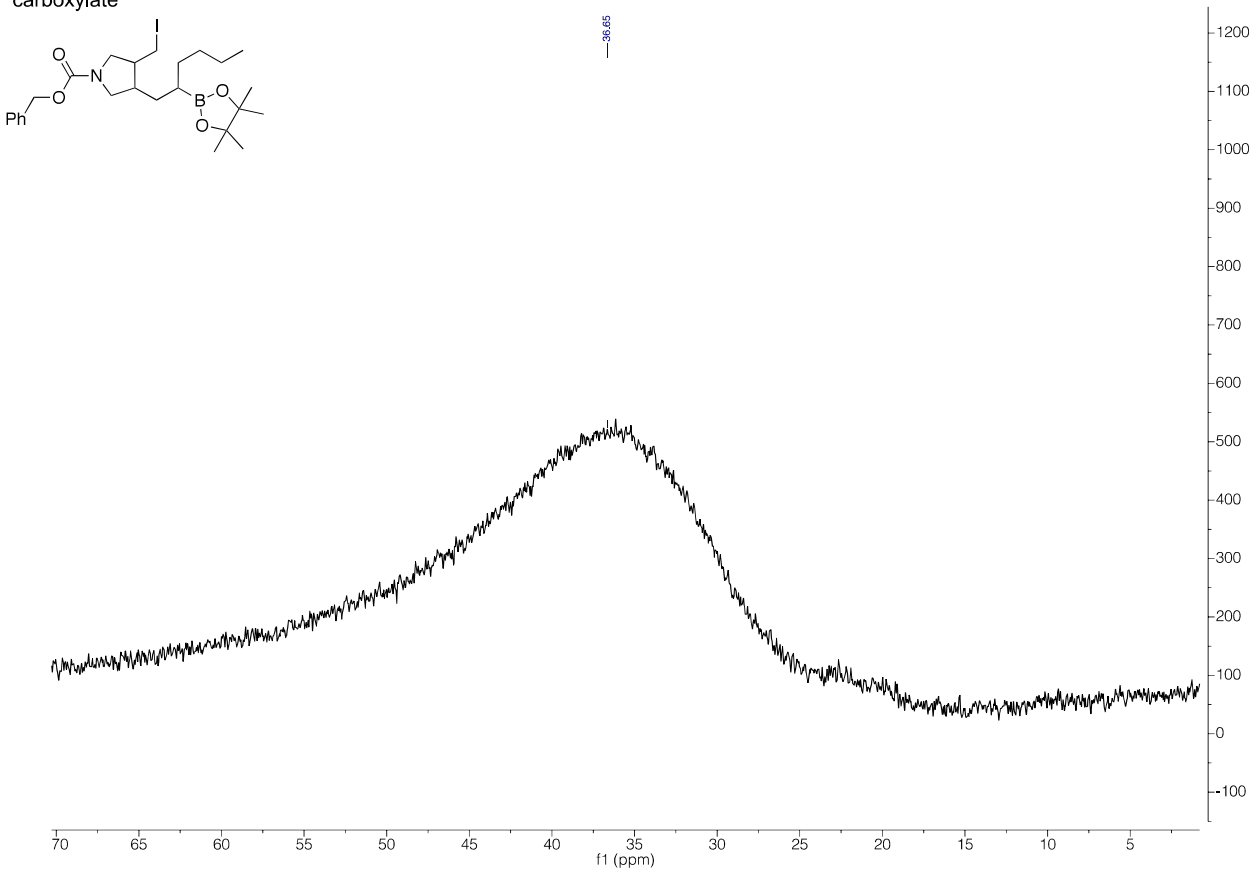
Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine-1-carboxylate

^{1}H, ^{13}C-HMBC (400 MHz, $(CD_3)_2CO$)



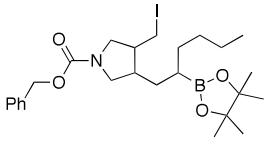
Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine-1-carboxylate

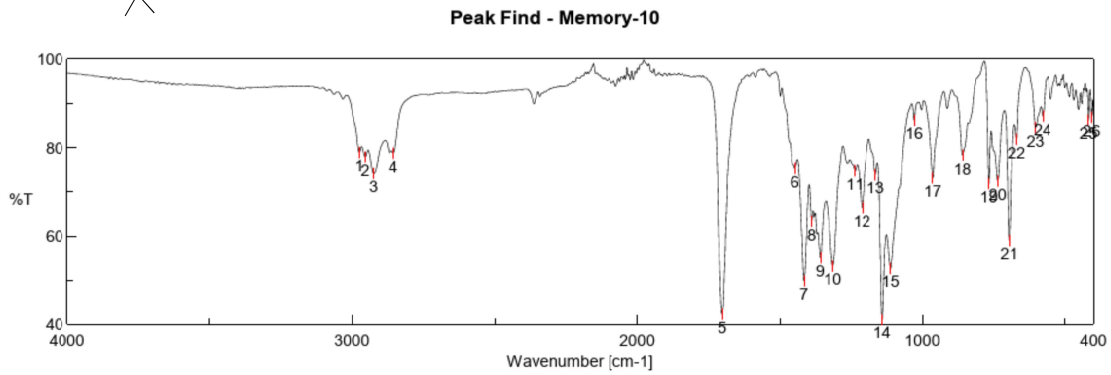
^{11}B-NMR (128 MHz, $(CD_3)_2CO$)



Benzyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine-1-carboxylate

FT-IR, ATR-diamond



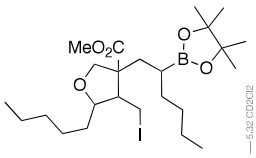


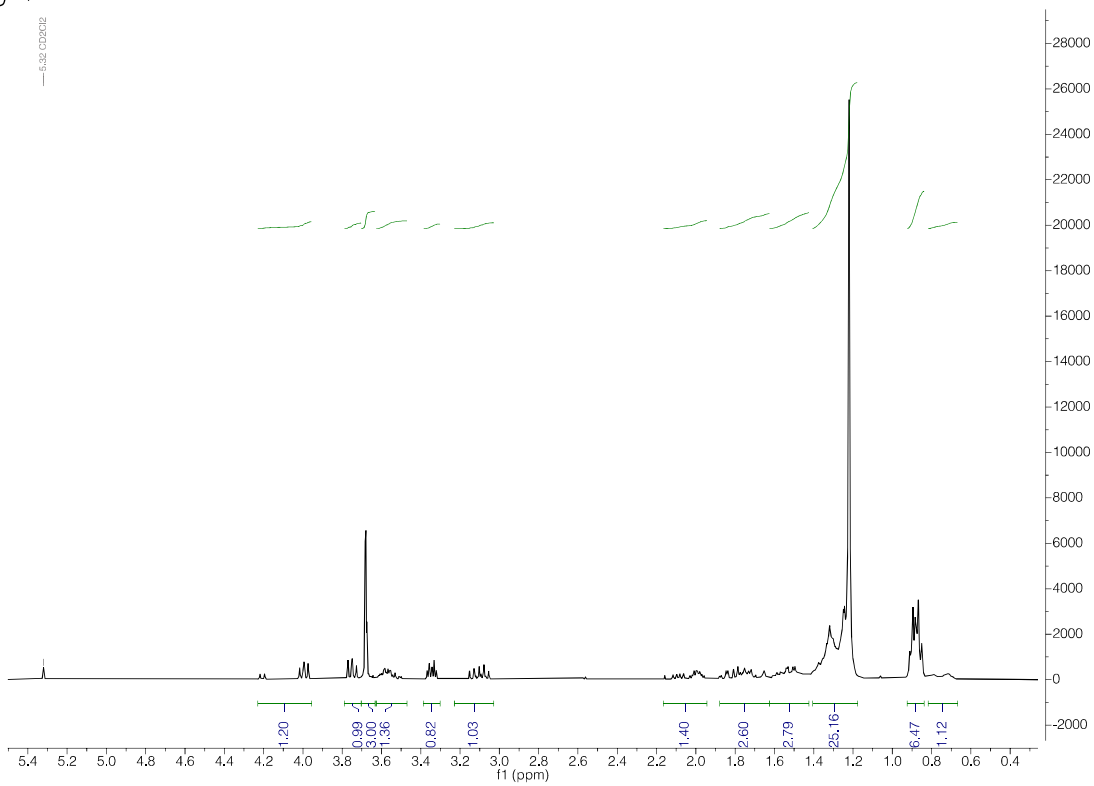
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2974.66	78.7942	2	2953.45	77.8156	3	2924.52	74.0999
4	2857.02	78.6655	5	1701.87	42.2907	6	1446.35	75.2674
7	1414.53	49.806	8	1387.53	63.2728	9	1357.64	55.0643
10	1315.21	53.1585	11	1237.11	74.7061	12	1212.04	66.3494
13	1164.79	73.8338	14	1140.69	41.1108	15	1110.8	52.6563
16	1028.84	86.037	17	964.233	73.1241	18	859.132	78.2046
19	766.566	71.8424	20	735.71	72.3656	21	695.212	58.915
22	670.142	81.7838	23	604.574	84.5051	24	578.54	87.017
25	417.513	86.0809	26	405.942	86.7505			

Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]tetrahydrofuran-3-carboxylate

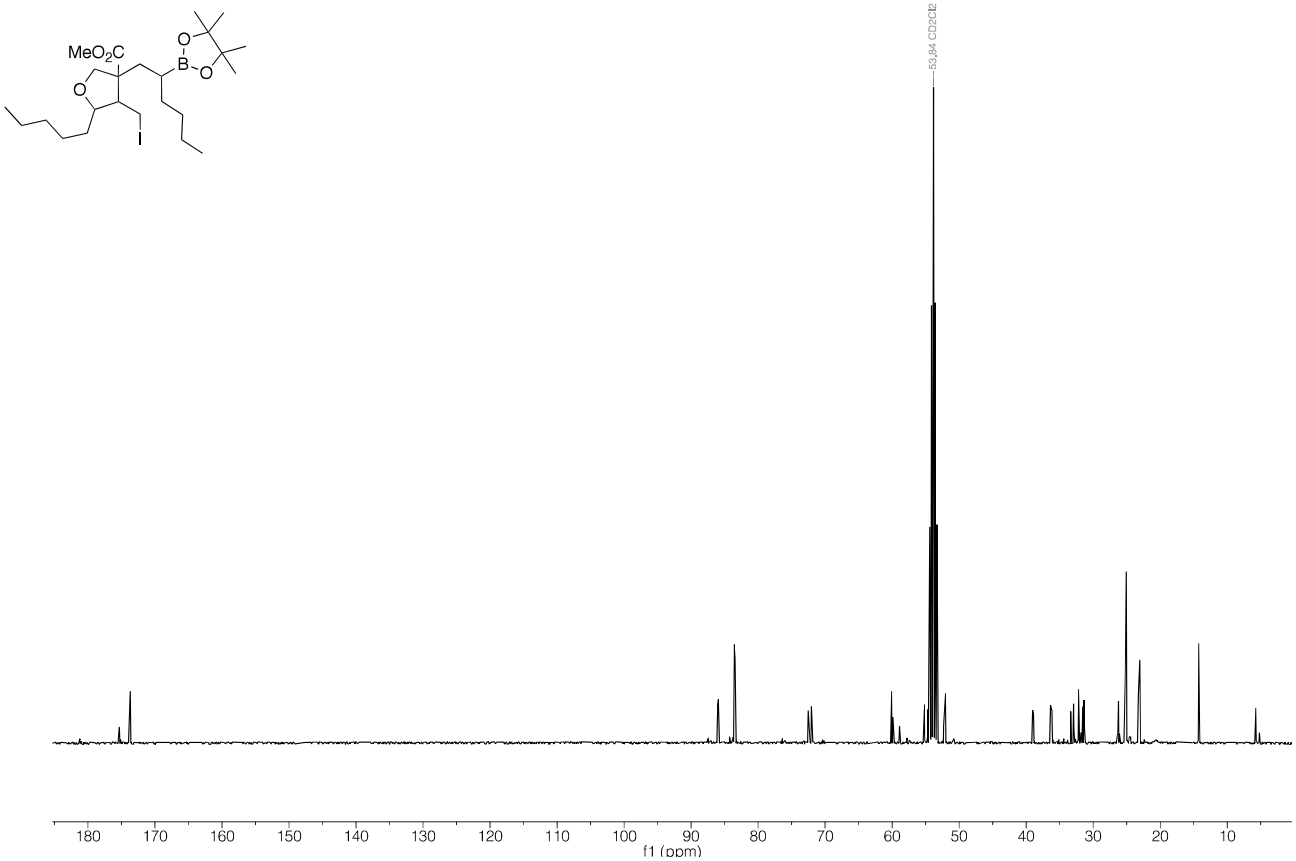
^{1}H-NMR (400 MHz, CD_2Cl_2)





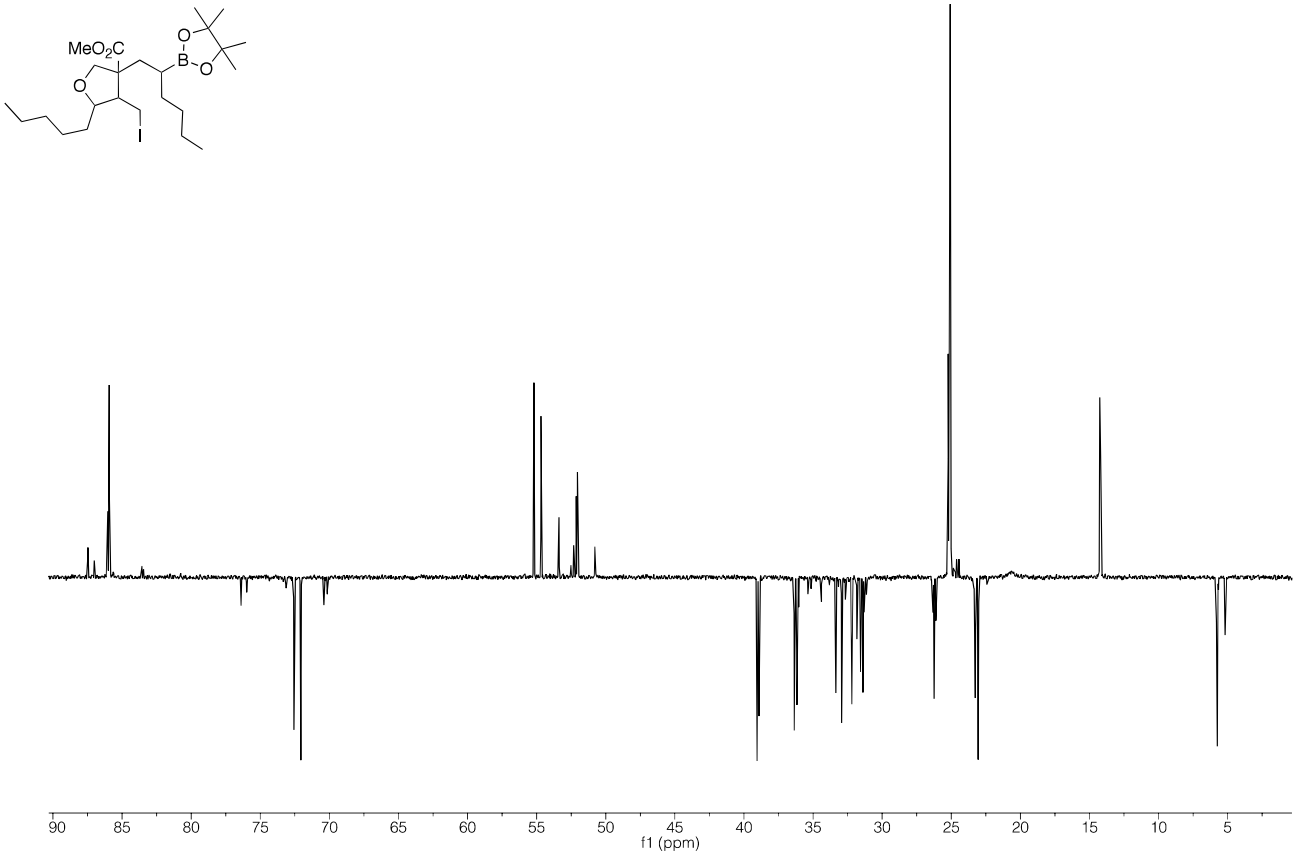
Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]tetrahydrofuran-3-carboxylate

^{13}C-NMR (101 MHz, CD_2Cl_2)



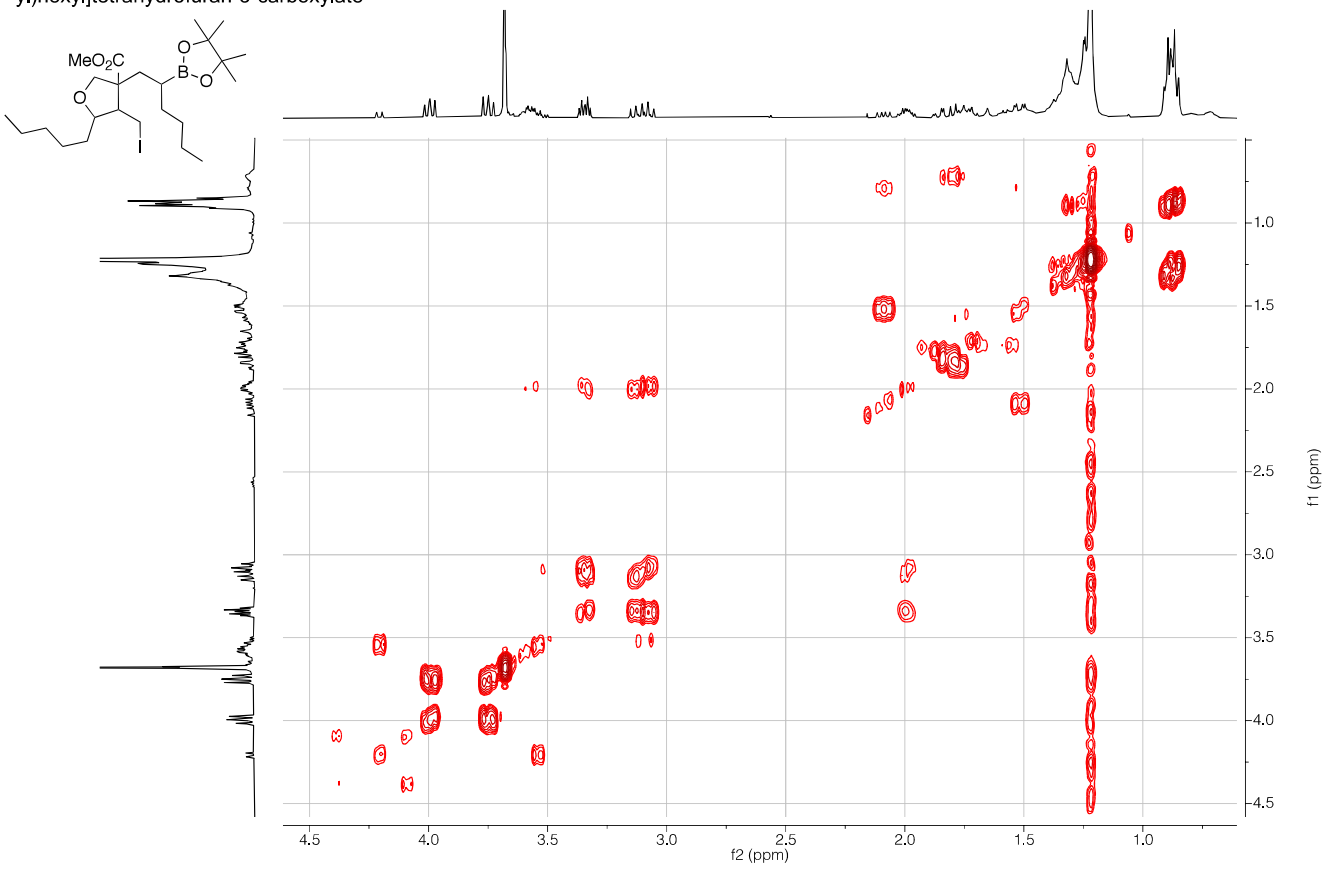
Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]tetrahydrofuran-3-carboxylate

DEPT-135 NMR (101 MHz, CD_2Cl_2)



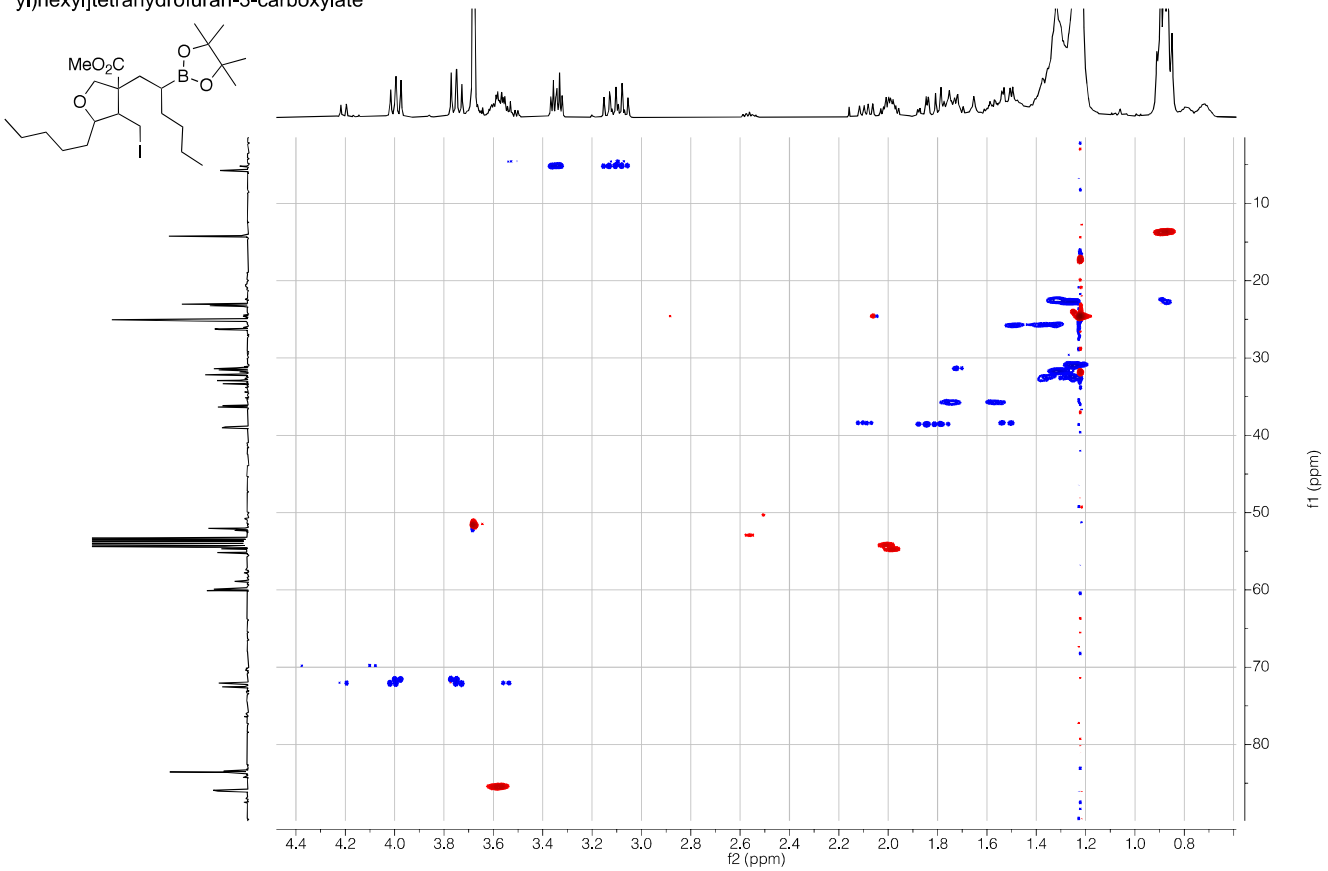
Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]tetrahydrofuran-3-carboxylate

^{1}H, ^{1}H-COSY (400 MHz, CD_2Cl_2)



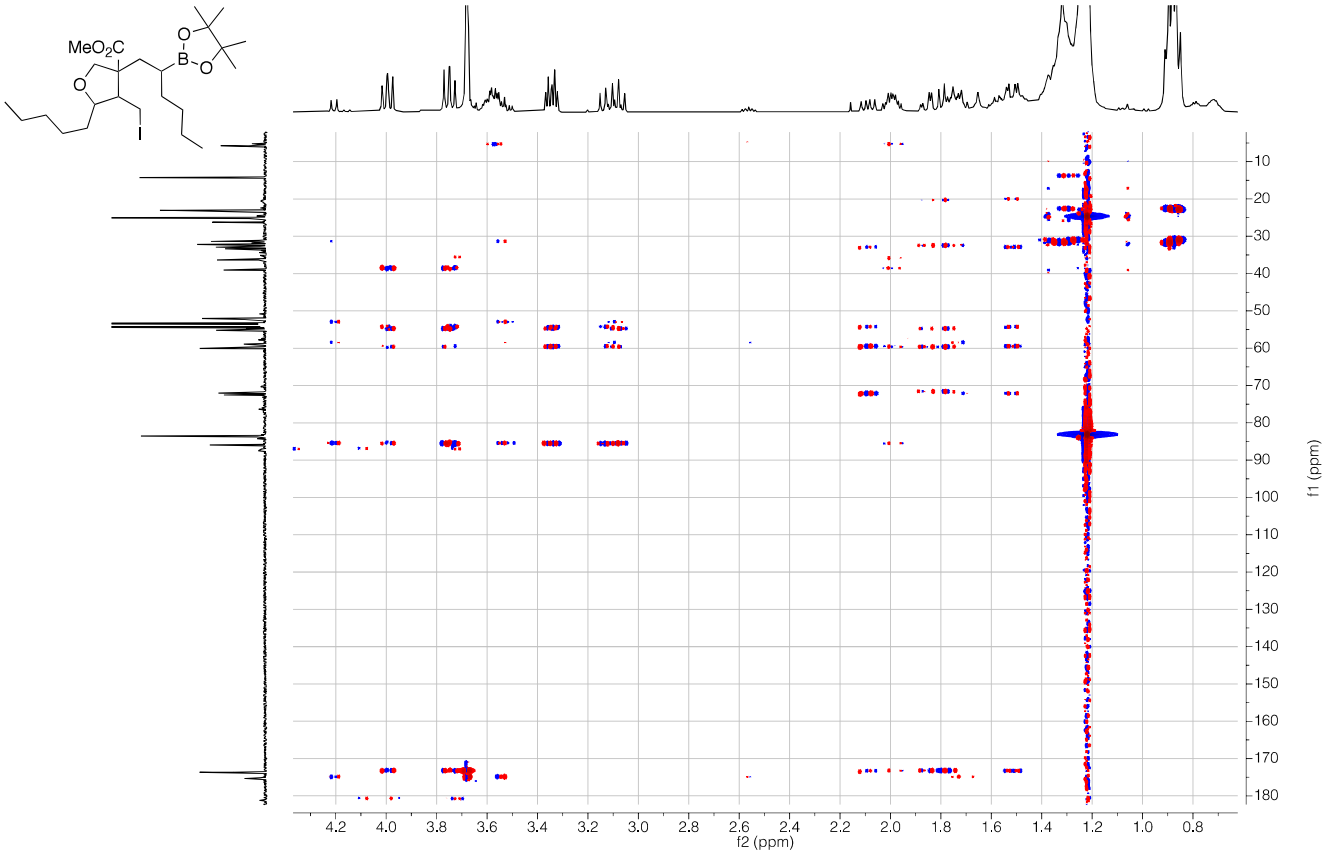
Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]tetrahydrofuran-3-carboxylate

^{1}H, ^{13}C-HSQC (400 MHz, CD_2Cl_2)



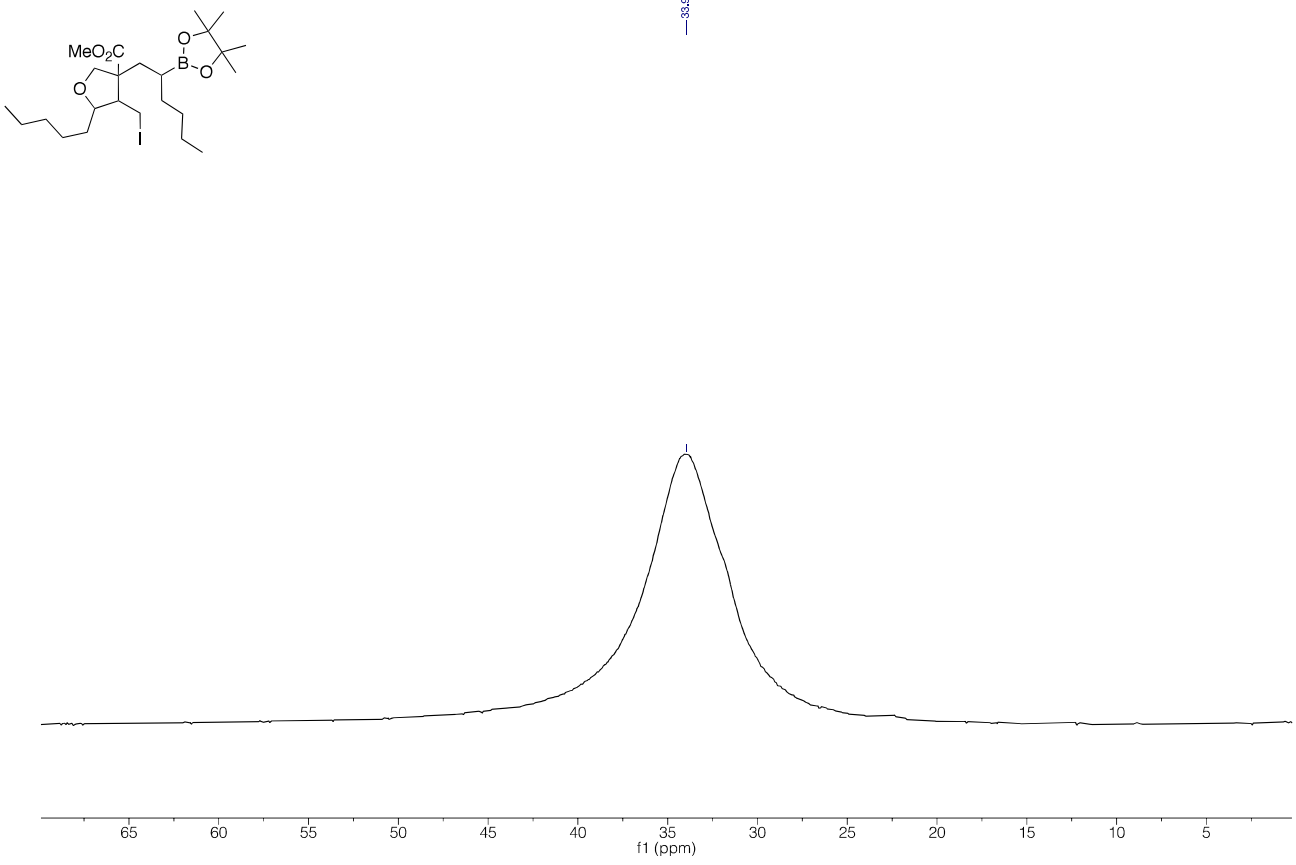
Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]tetrahydrofuran-3-carboxylate

^{1}H, ^{13}C-HMBC (400 MHz, CD_2Cl_2)



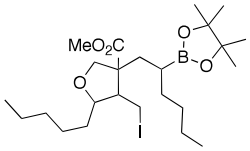
Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]tetrahydrofuran-3-carboxylate

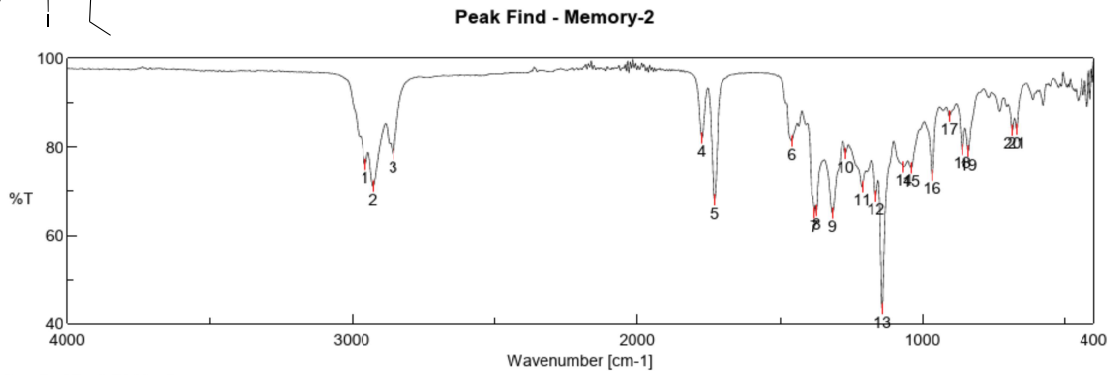
^{11}B-NMR (128 MHz, CD_2Cl_2)



Methyl 4-(iodomethyl)-5-pentyl-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]tetrahydrofuran-3-carboxylate

FT-IR, ATR-diamond

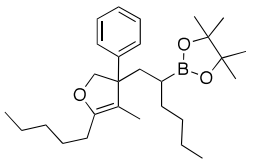




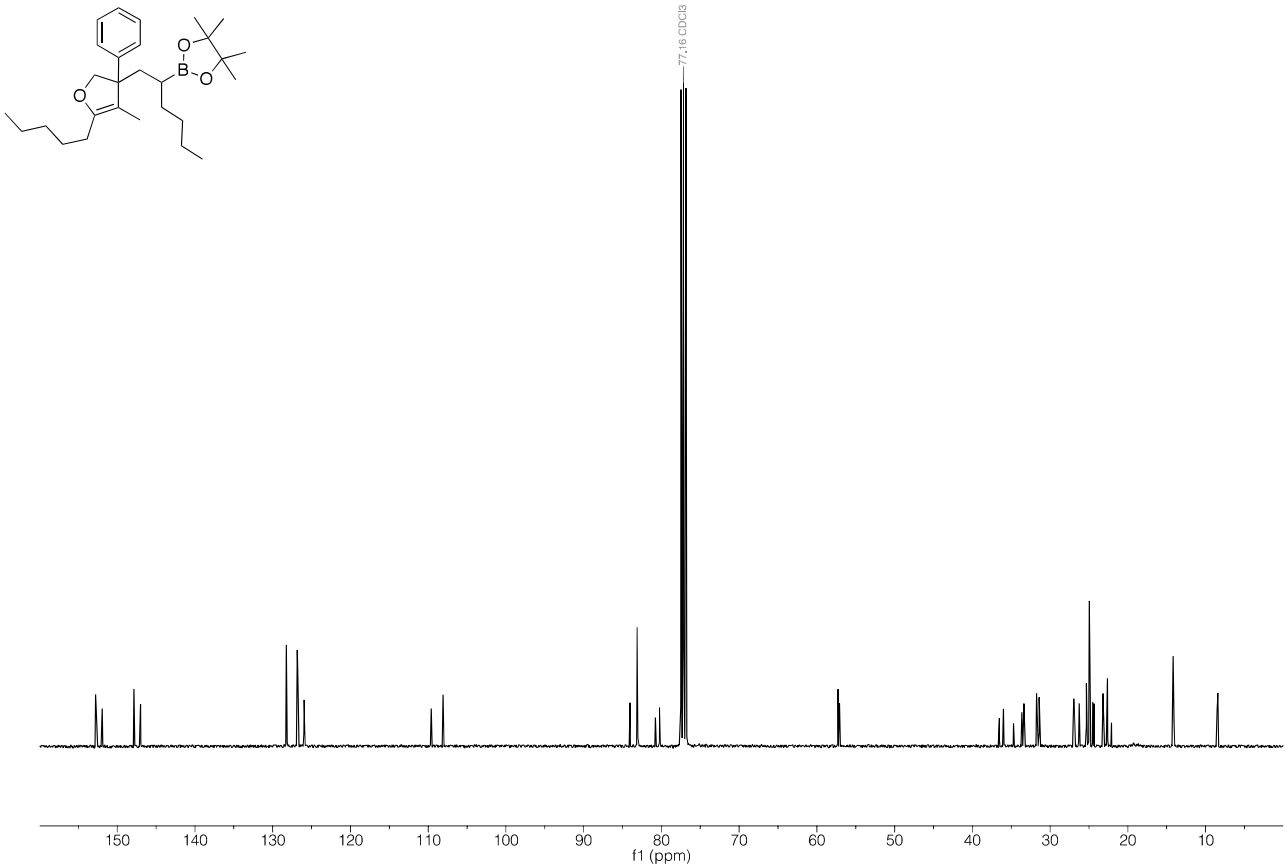
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2954.41	75.9757	2	2926.45	71.053	3	2857.02	78.3092
4	1772.26	81.9425	5	1728.87	67.9967	6	1457.92	81.2692
7	1378.85	65.0392	8	1371.14	65.5977	9	1316.18	64.994
10	1270.86	78.474	11	1212.04	70.9495	12	1164.79	68.8066
13	1141.65	43.4057	14	1065.48	75.4437	15	1039.44	75.1889
16	967.126	73.5523	17	906.379	86.8816	18	861.06	79.3333
19	839.847	79.0163	20	685.57	83.7037	21	671.106	83.9373

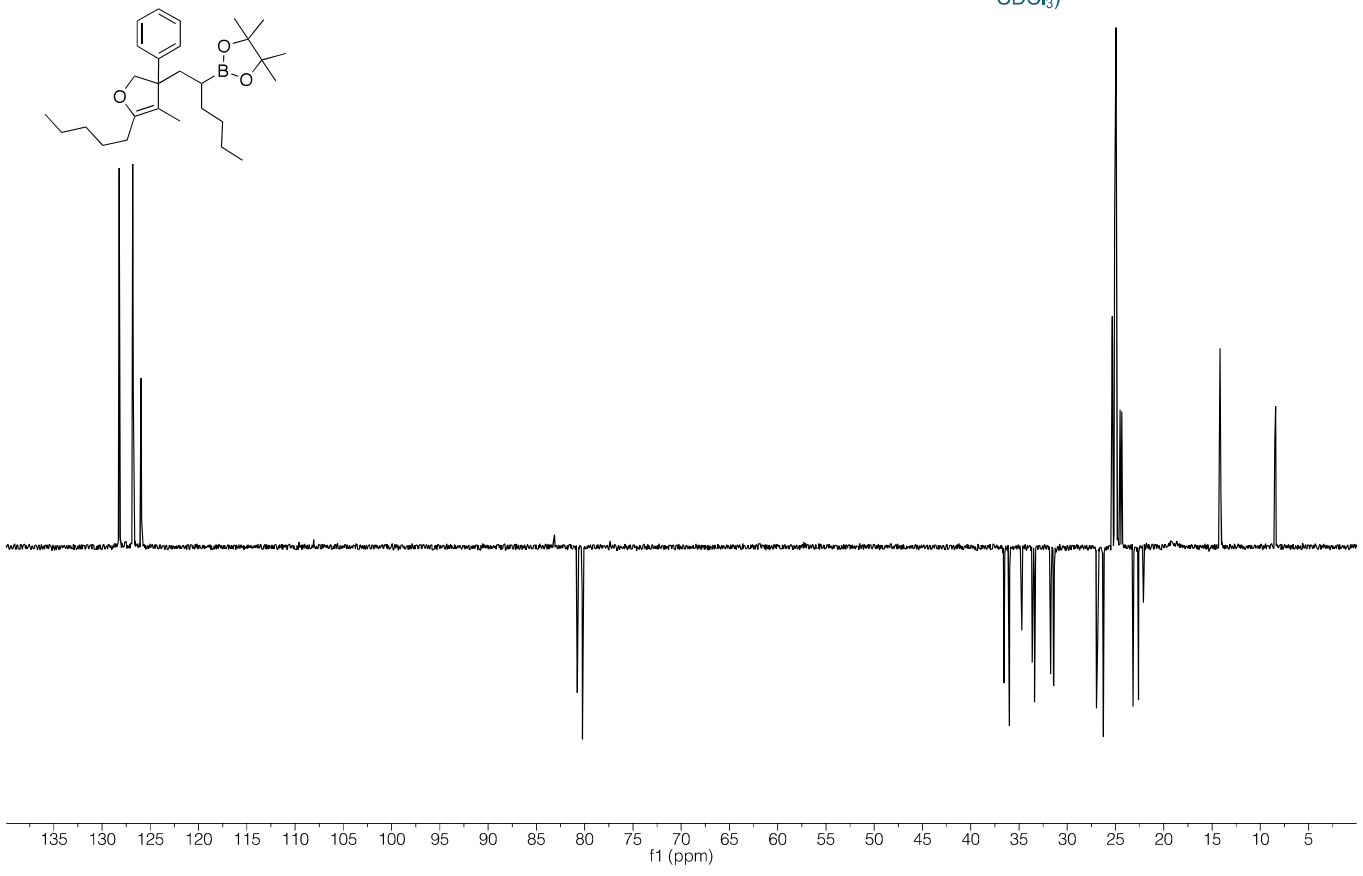
4,4,5,5-tetramethyl-2-[1-[(4-methyl-5-pentyl-3-phenyl-2H-furan-3-yl)methyl]pentyl]-1,3,2-dioxaborolane ^{1}H-NMR (400 MHz, $CDCl_3$)



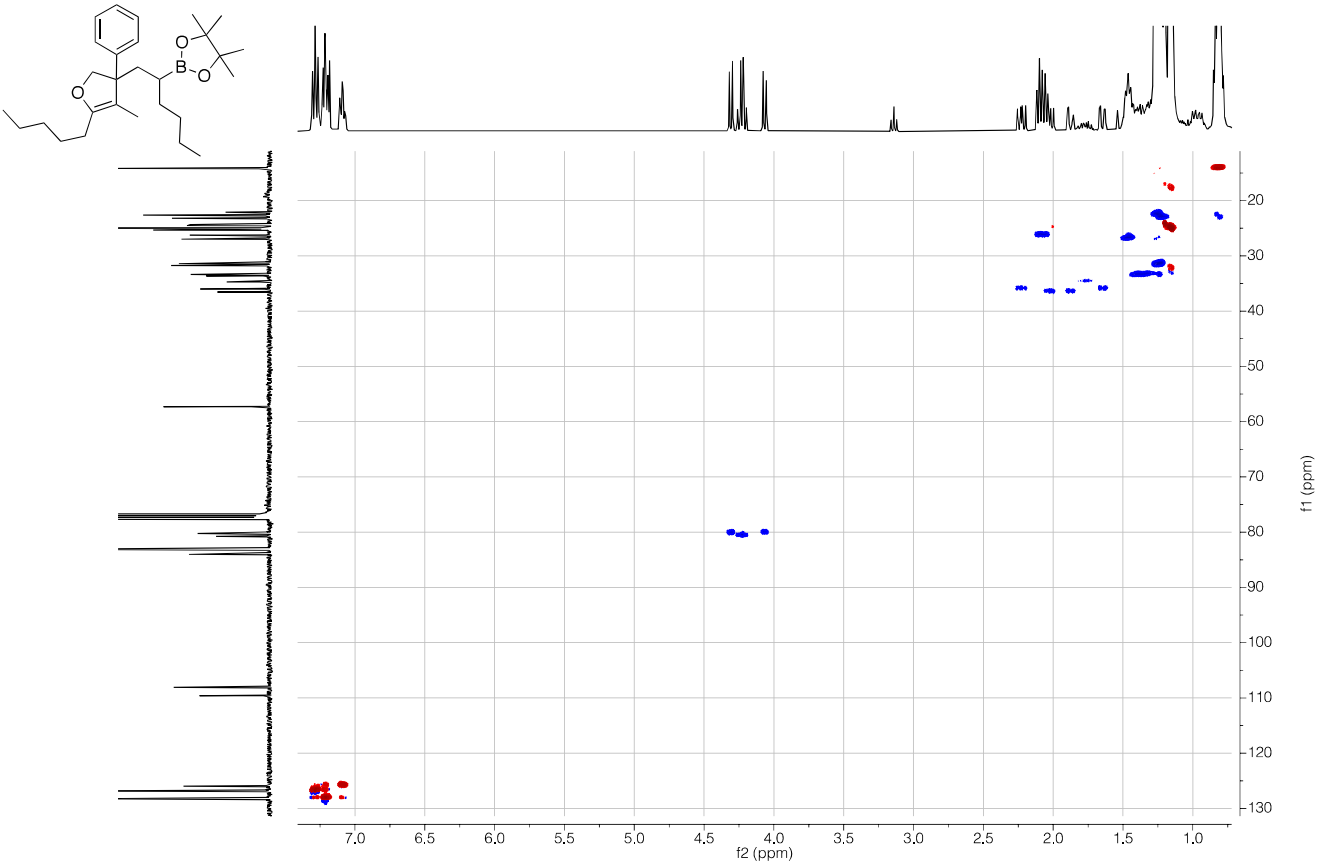
4,4,5,5-tetramethyl-2-[1-[(4-methyl-5-pentyl-3-phenyl-2H-furan-3-yl)methyl]pentyl]-1,3,2-dioxaborolane ^{13}C-NMR (101 MHz, $CDCl_3$)



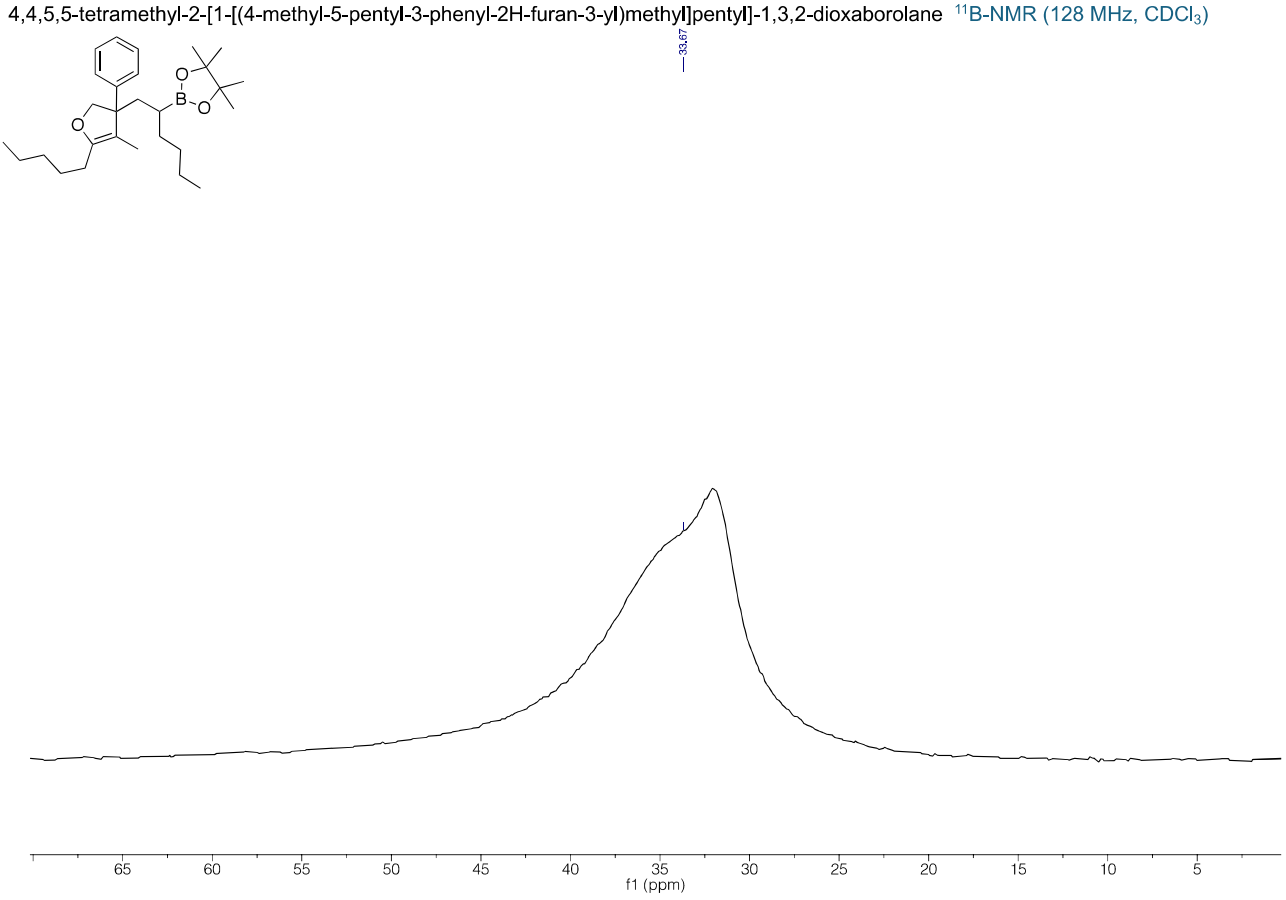
4,4,5,5-tetramethyl-2-[1-[(4-methyl-5-pentyl-3-phenyl-2H-furan-3-yl)methyl]pentyl]-1,3,2-dioxaborolane DEPT-135 NMR (101 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-[1-[(4-methyl-5-pentyl-3-phenyl-2H-furan-3-yl)methyl]pentyl]-1,3,2-dioxaborolane ^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)

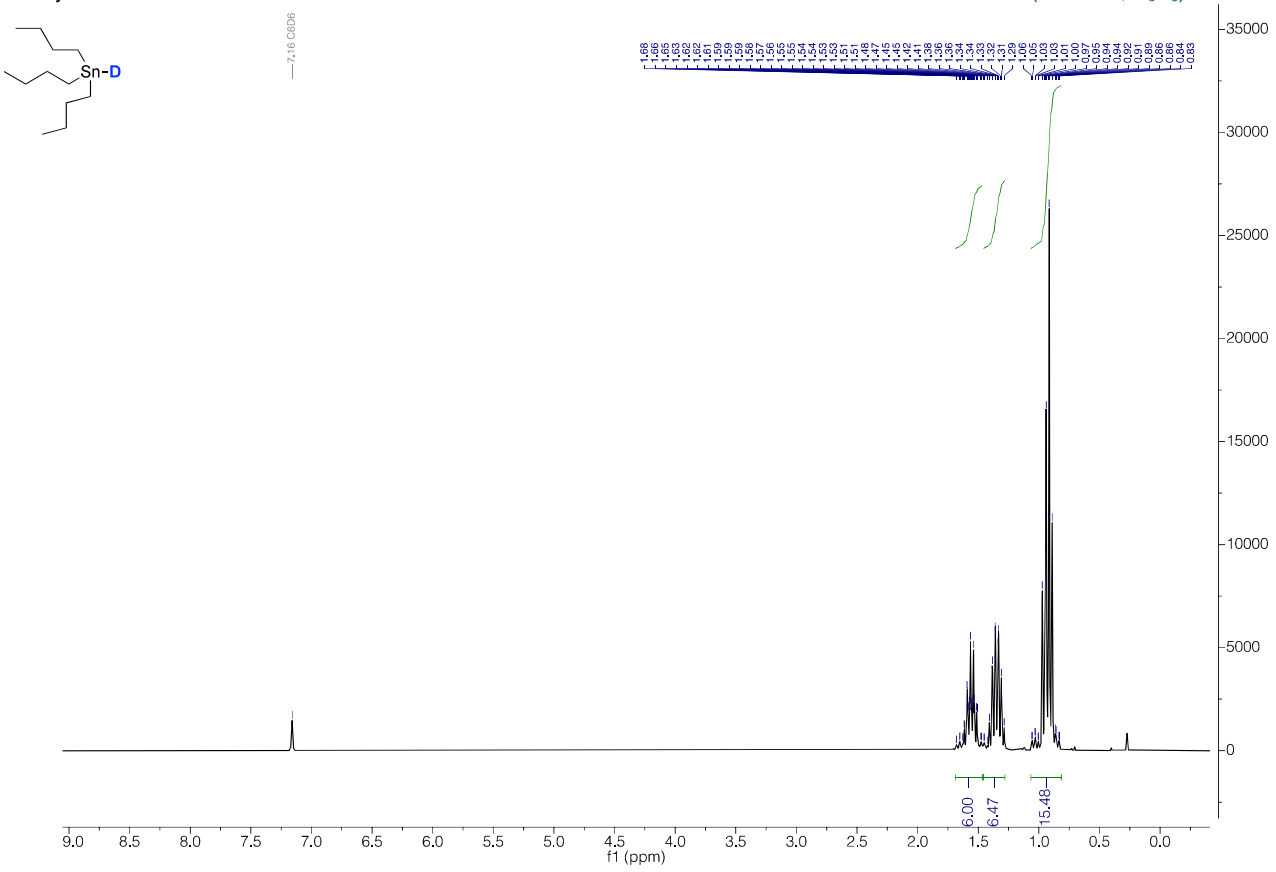


4,4,5,5-tetramethyl-2-[1-[(4-methyl-5-pentyl-3-phenyl-2H-furan-3-yl)methyl]pentyl]-1,3,2-dioxaborolane ^{11}B-NMR (128 MHz, $CDCl_3$)



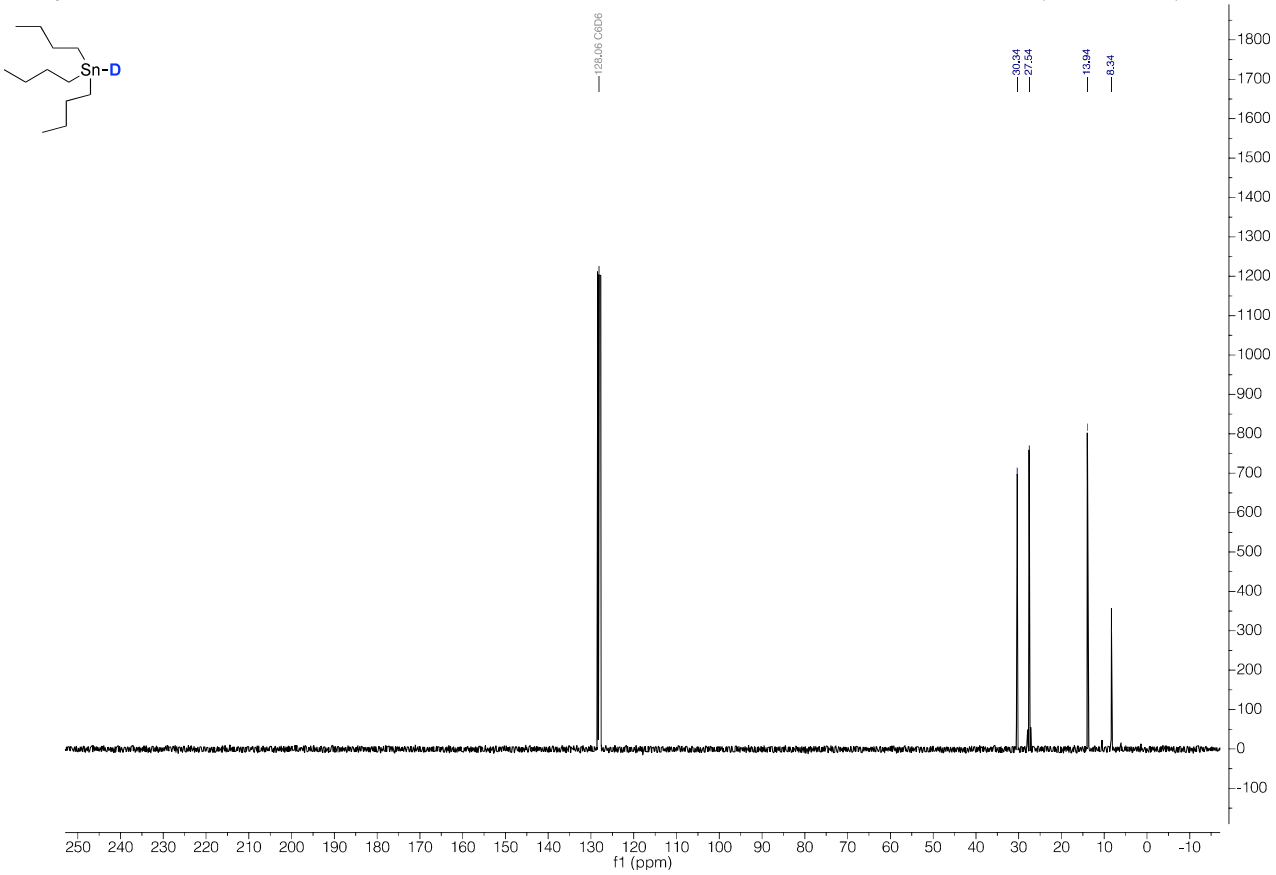
Tributyltin deuteride

^{1}H-NMR (300 MHz, C_6D_6)



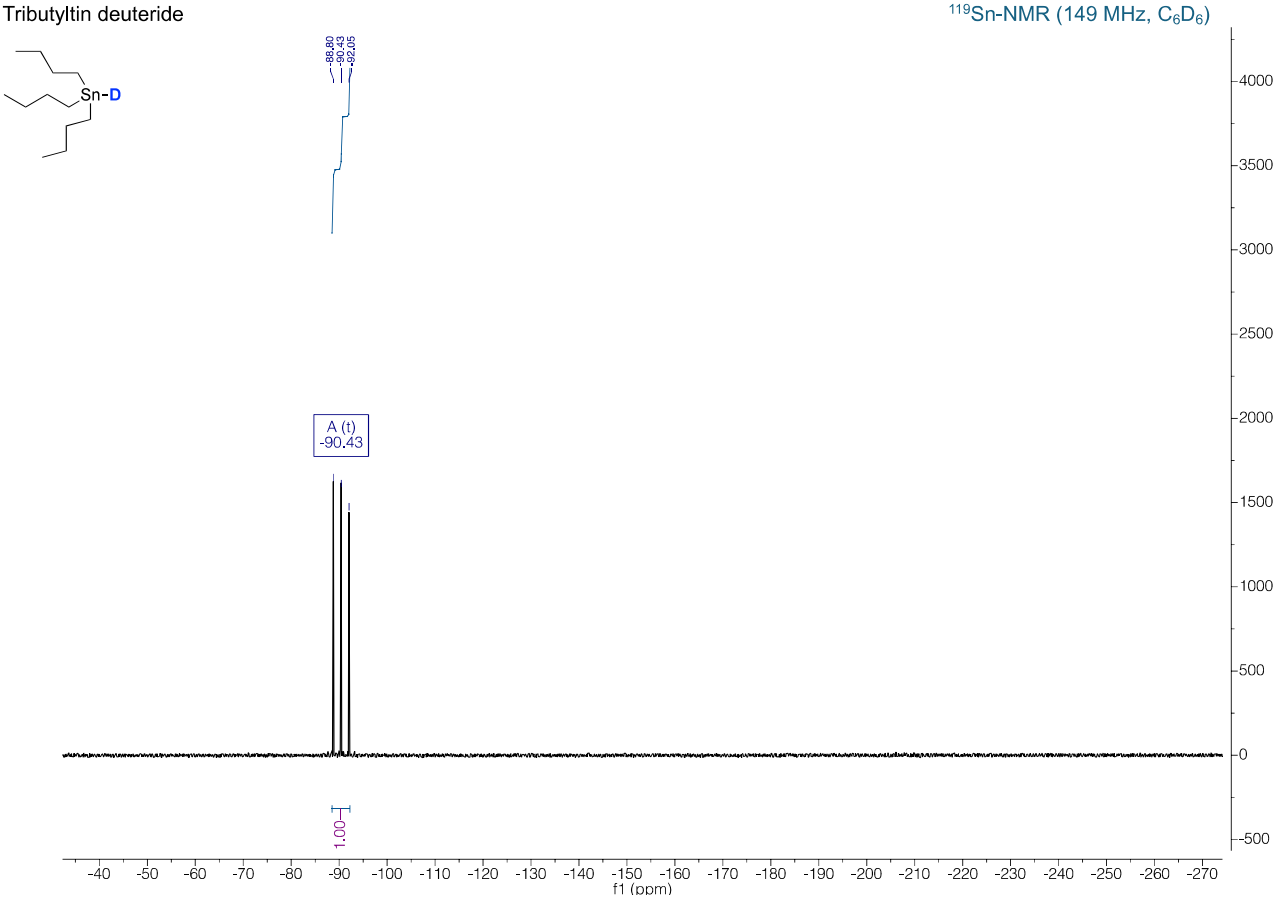
Tributyltin deuteride

^{13}C-NMR (75 MHz, C_6D_6)



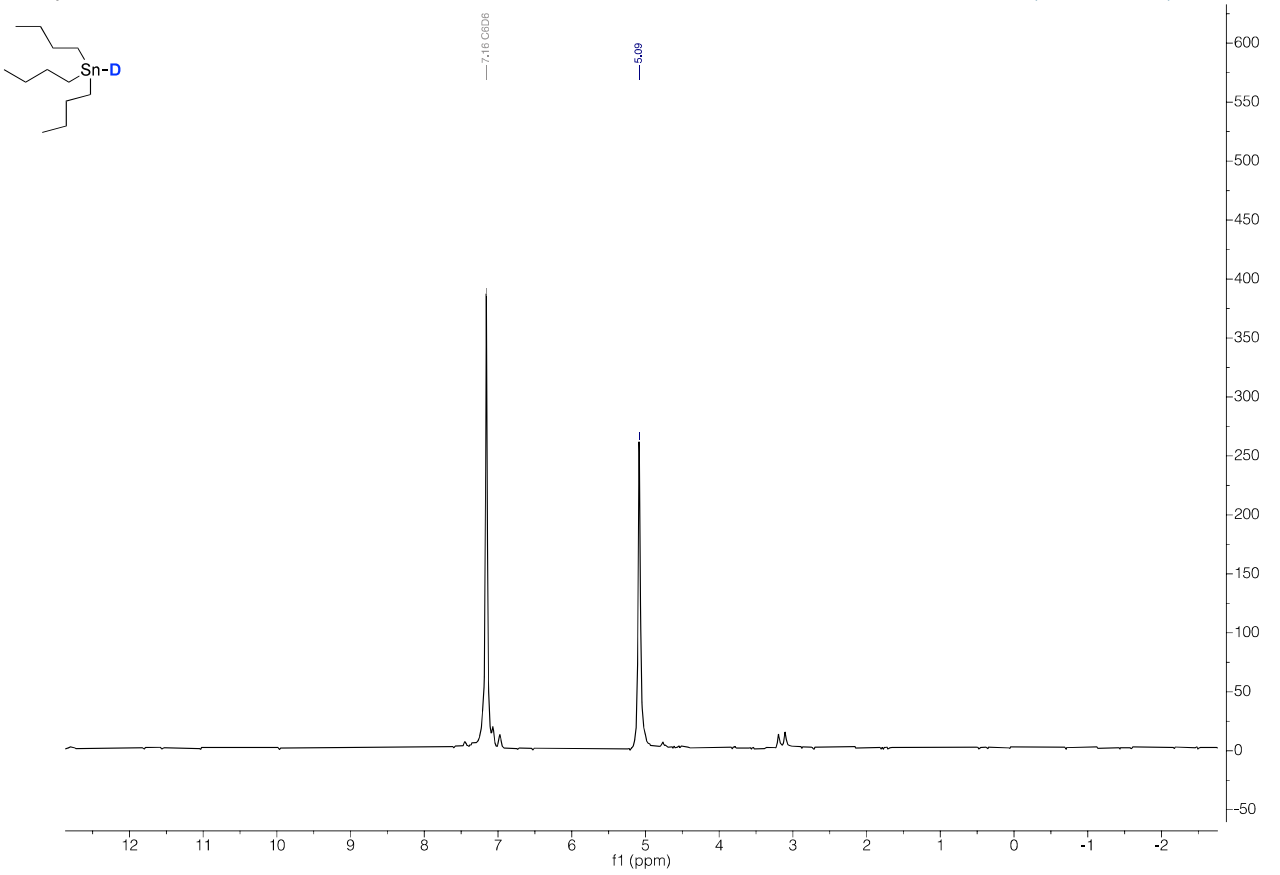
Tributyltin deuteride

^{119}Sn-NMR (149 MHz, C_6D_6)



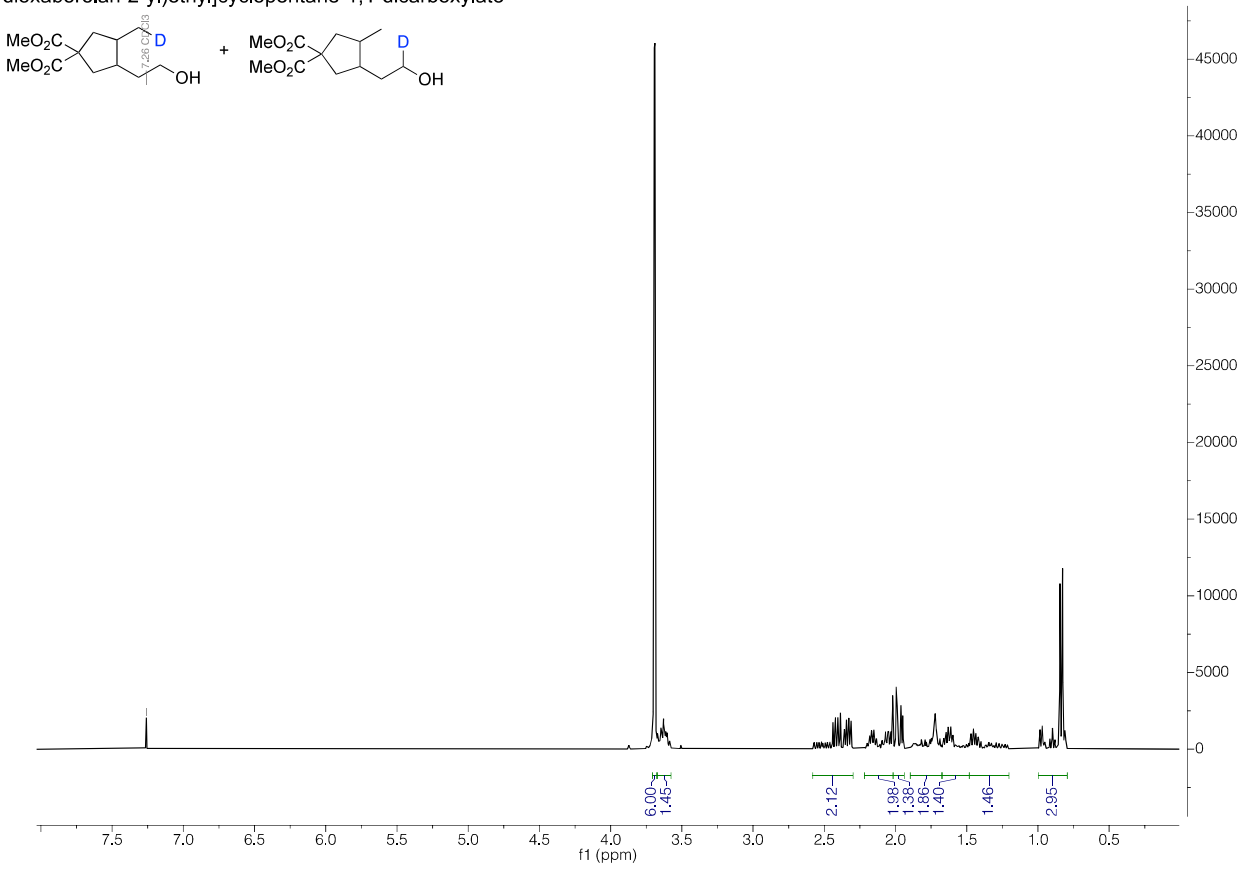
Tributyltin deuteride

^{2}H-NMR (61 MHz, C_6D_6)



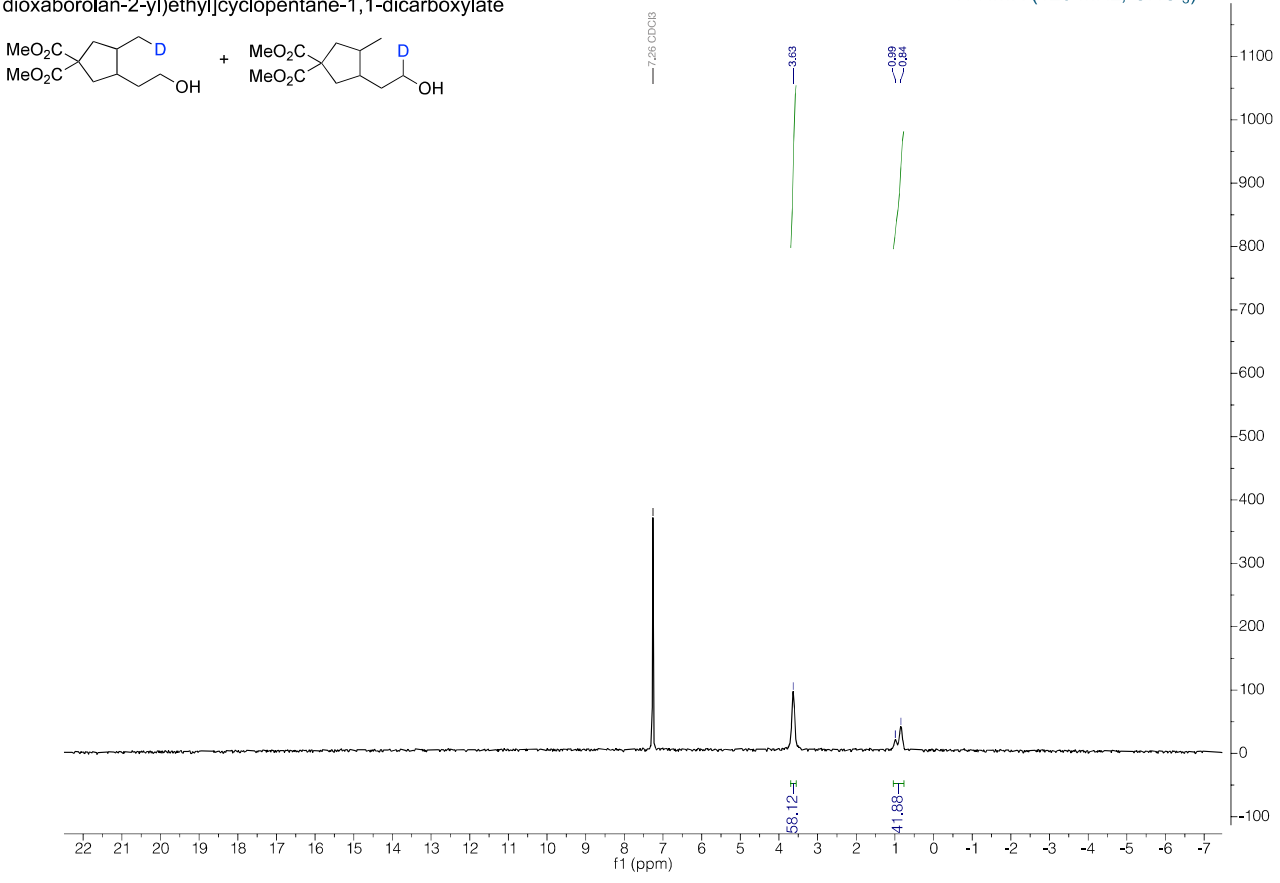
Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)



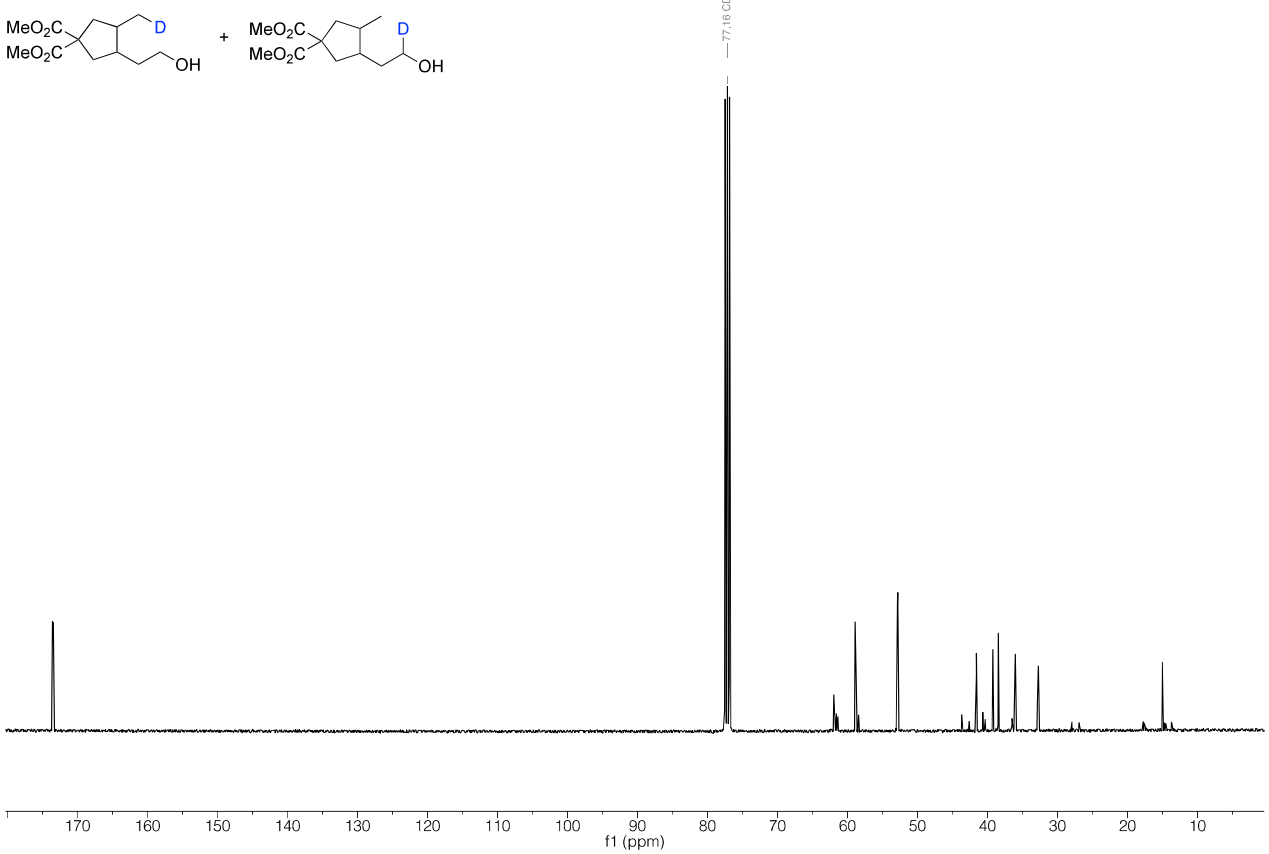
Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{2}H-NMR (128 MHz, $CHCl_3$)



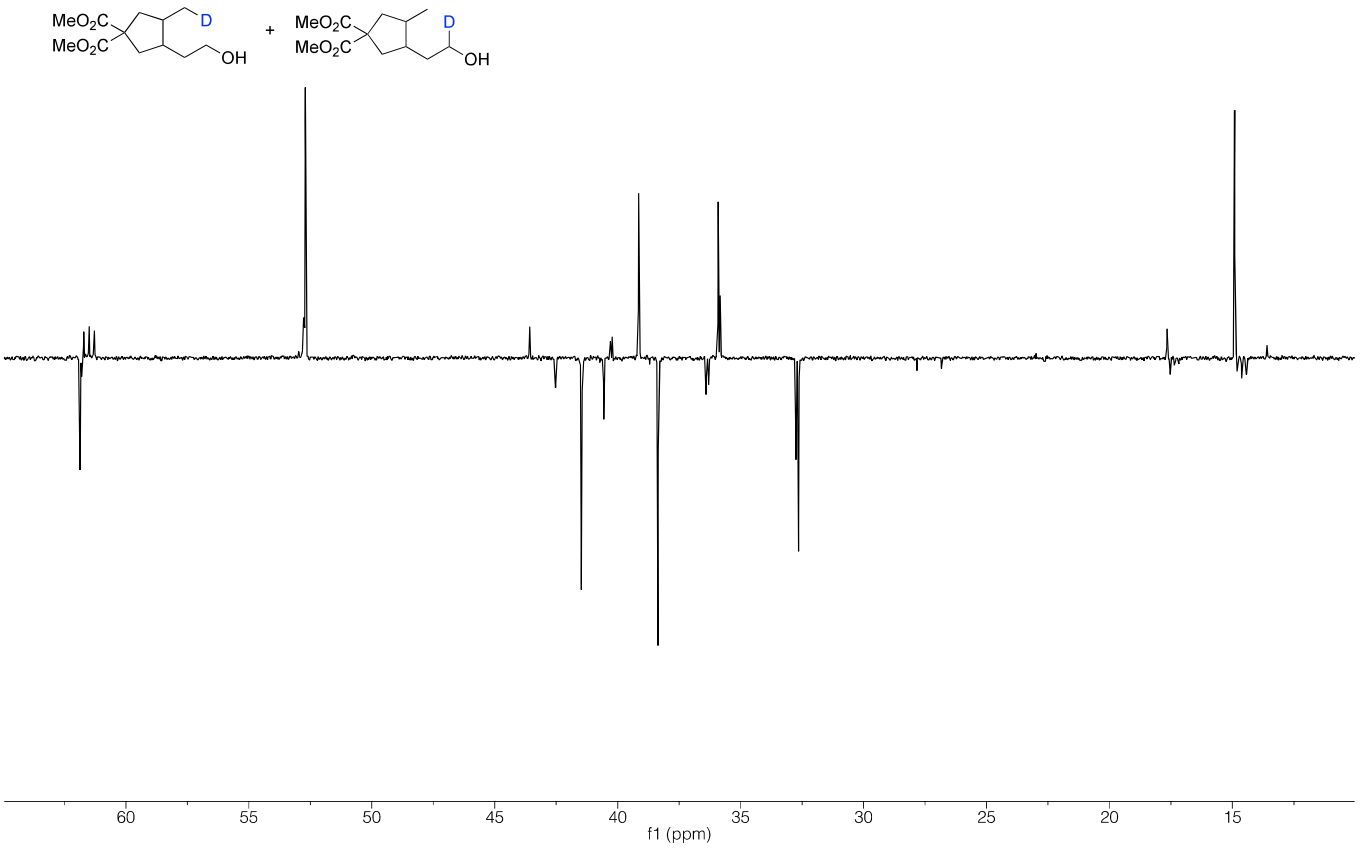
Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{13}C-NMR (101 MHz, $CDCl_3$)



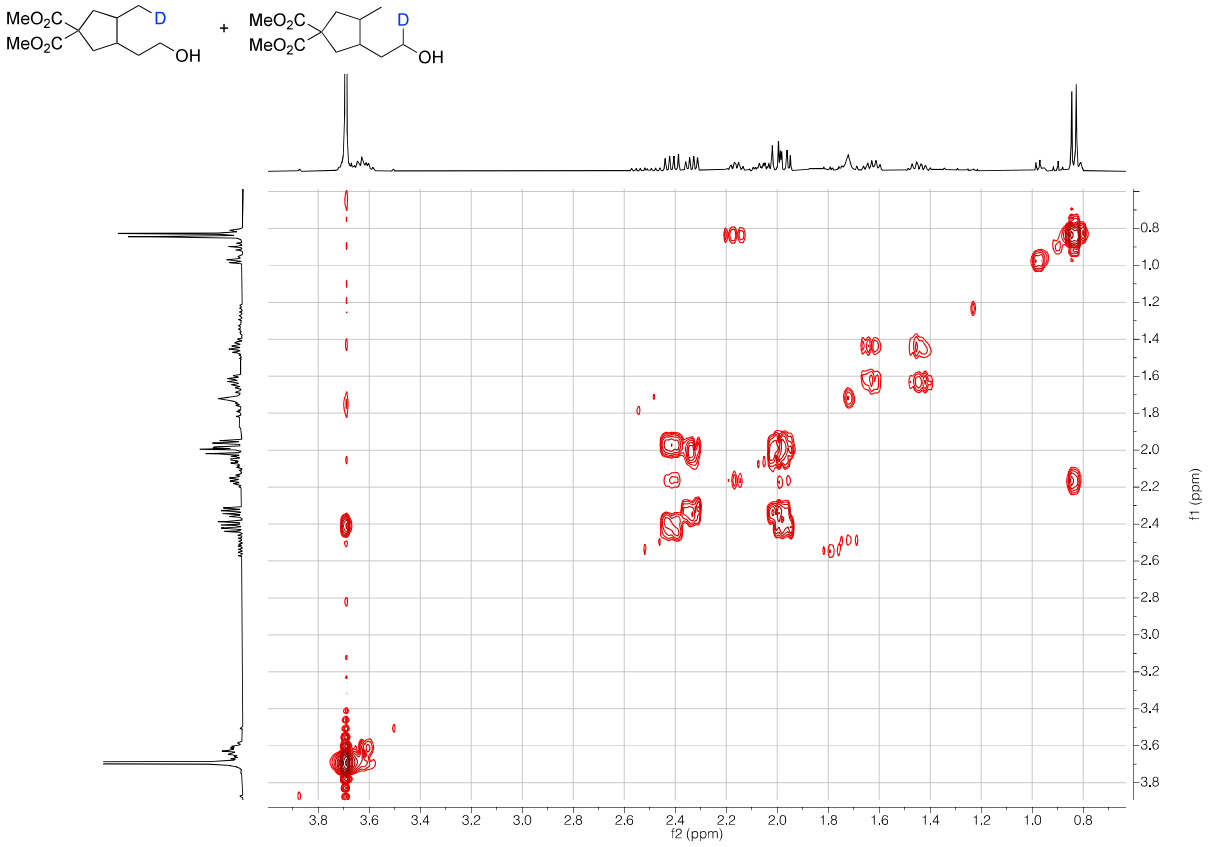
Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

DEPT-135 NMR (101 MHz, $CDCl_3$)



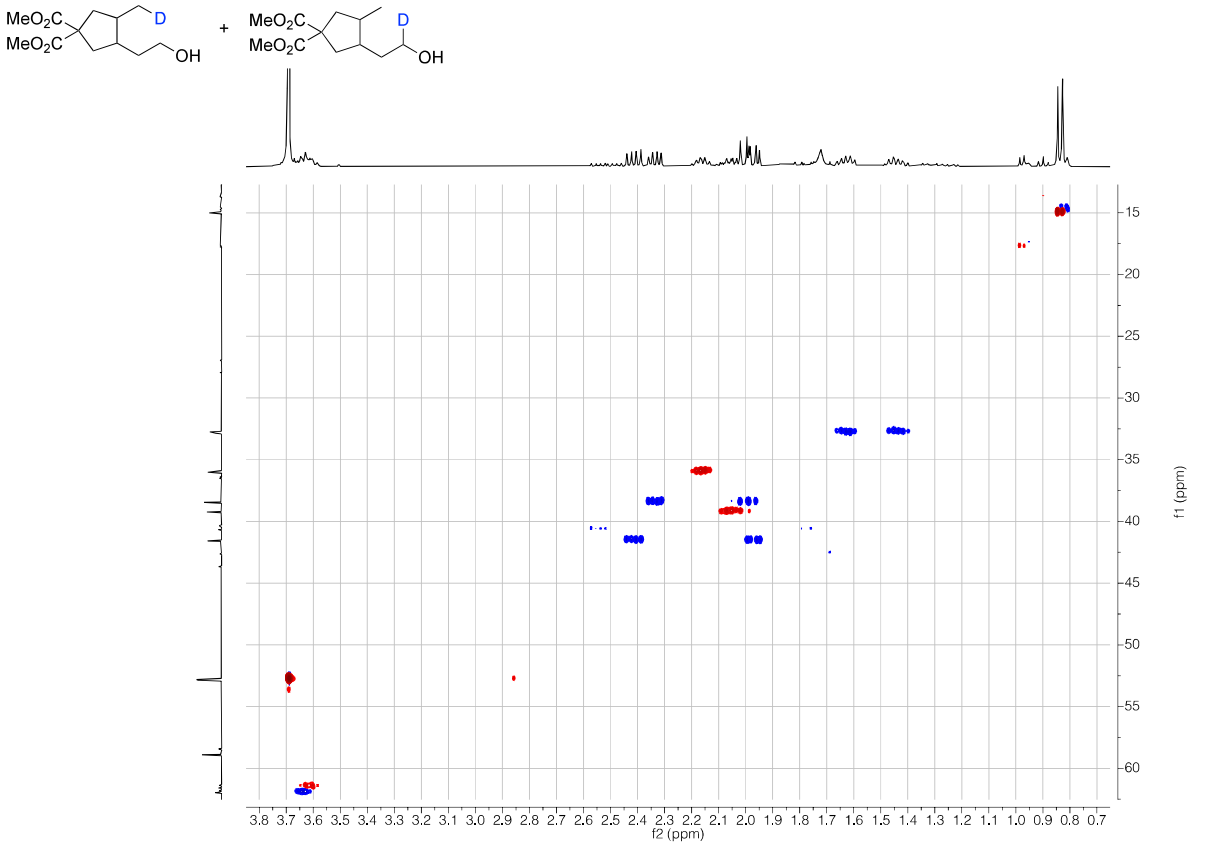
Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



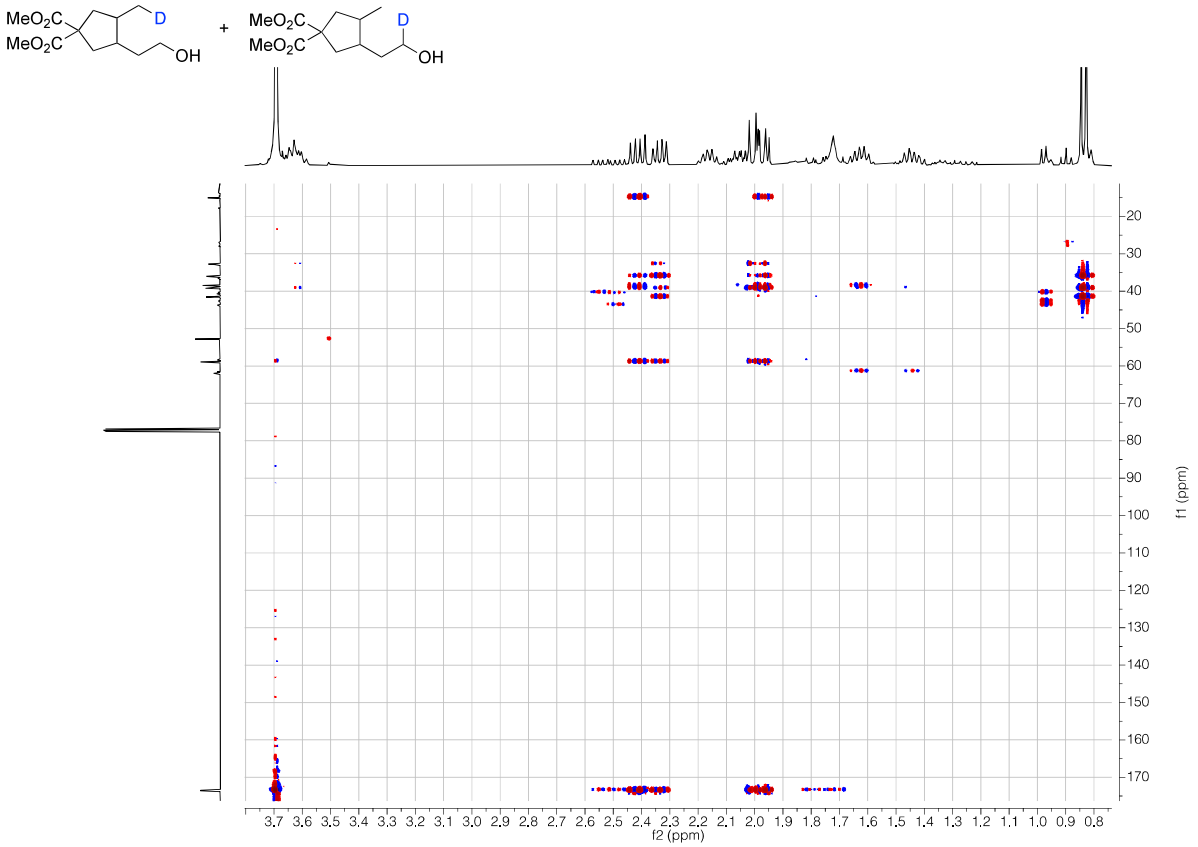
Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



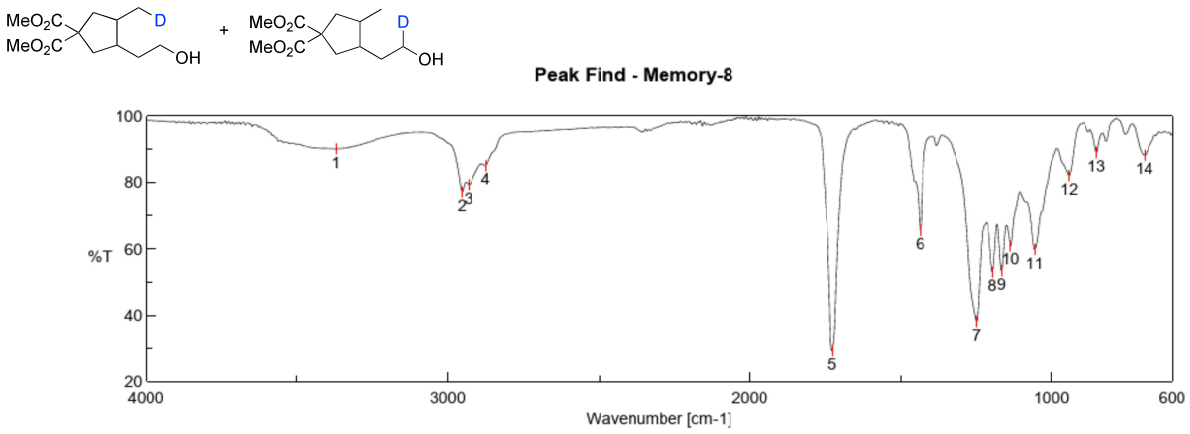
Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond

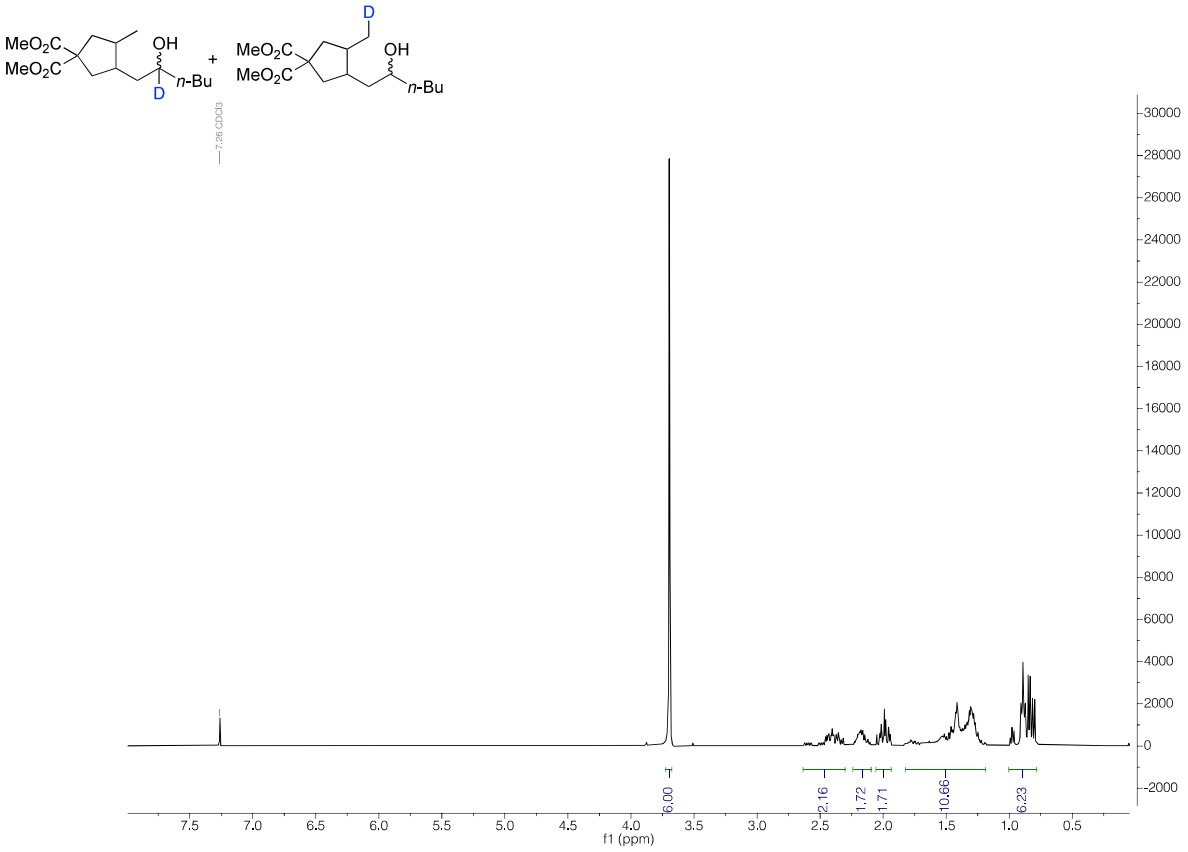


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3372.89	90.0582	2	2953.45	77.0707	3	2931.27	79.2826
4	2875.34	84.9438	5	1726.94	29.3747	6	1433.82	65.5112
7	1248.68	38.0449	8	1197.58	52.9602	9	1166.72	53.3424
10	1136.83	60.8718	11	1055.84	59.817	12	943.02	81.9959
13	851.418	88.972	14	692.32	88.1595			

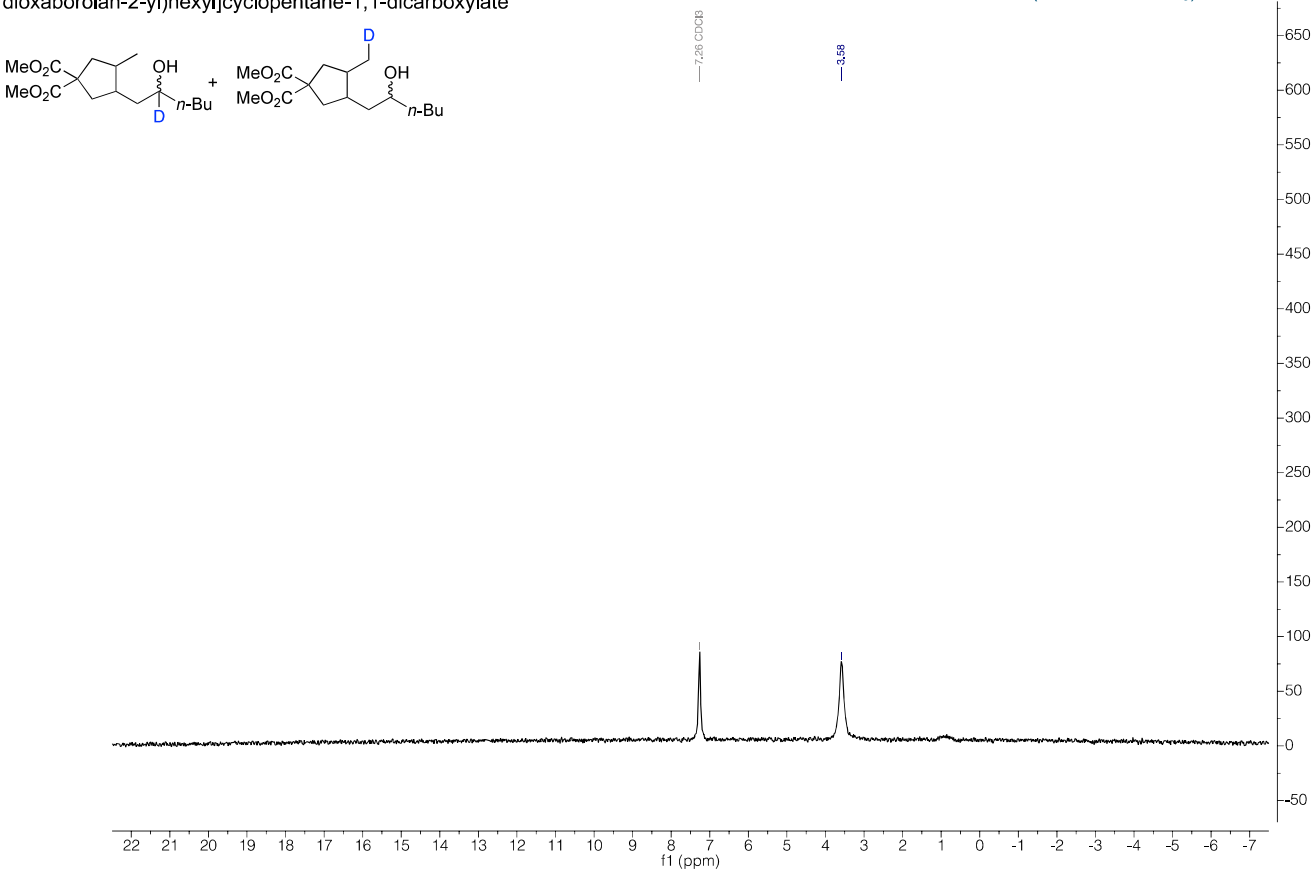
Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)



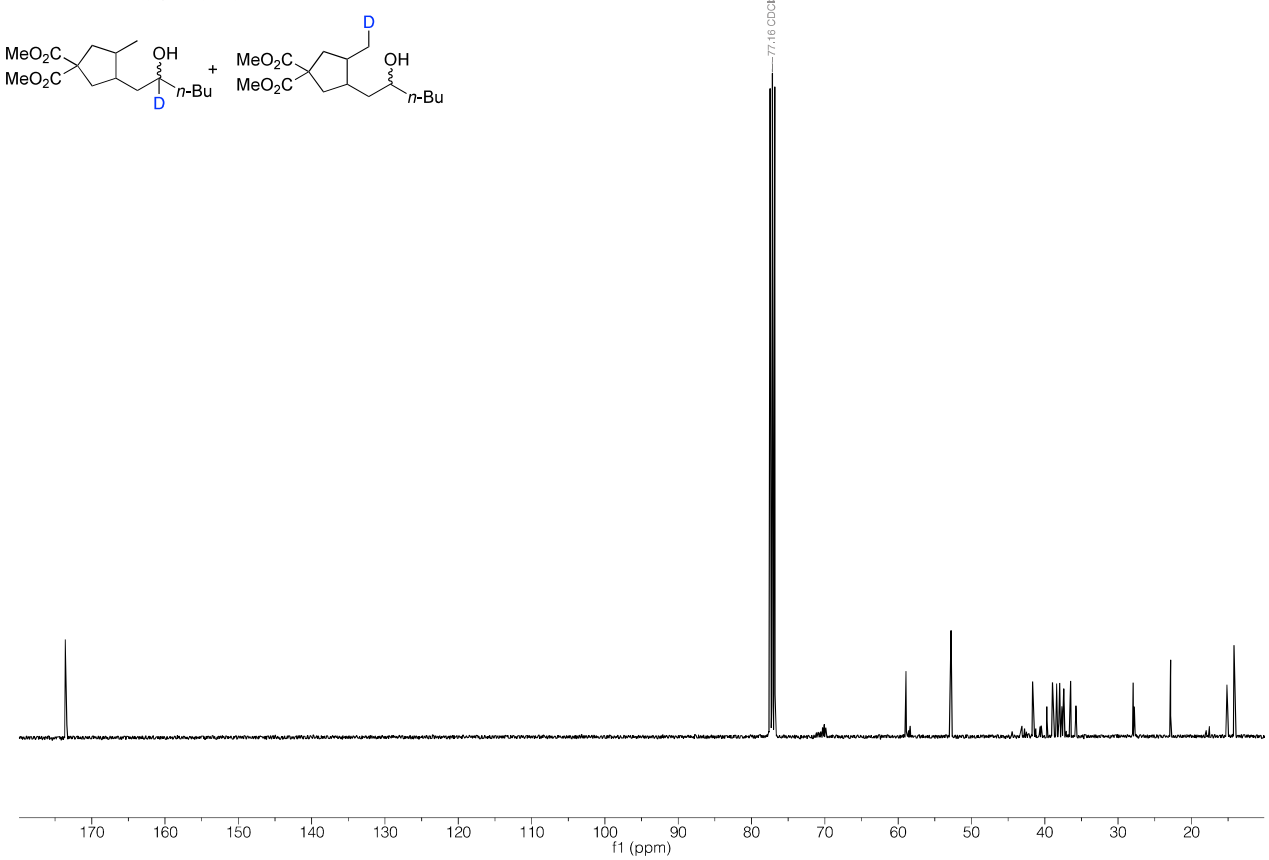
Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{2}H-NMR (128 MHz, $CDCl_3$)



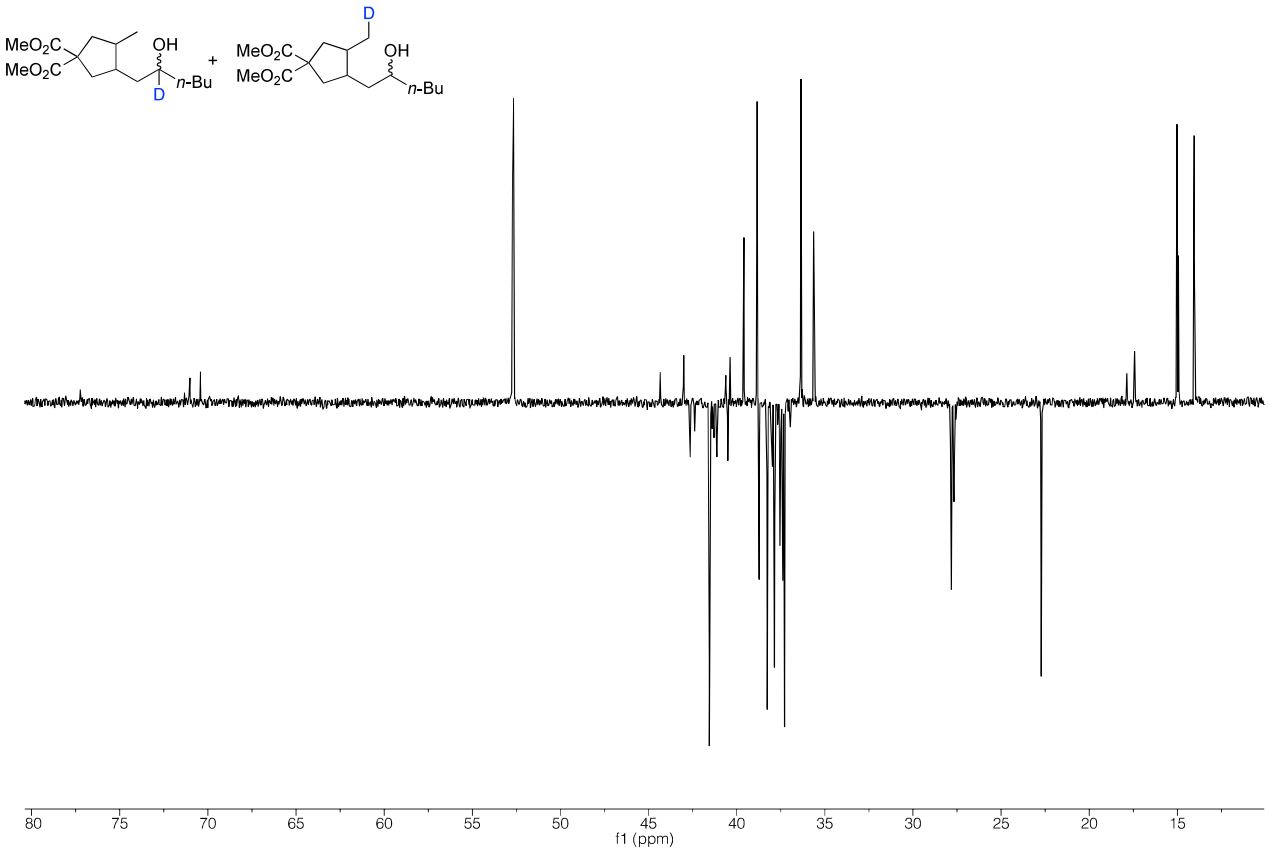
Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{13}C-NMR (101 MHz, $CDCl_3$)



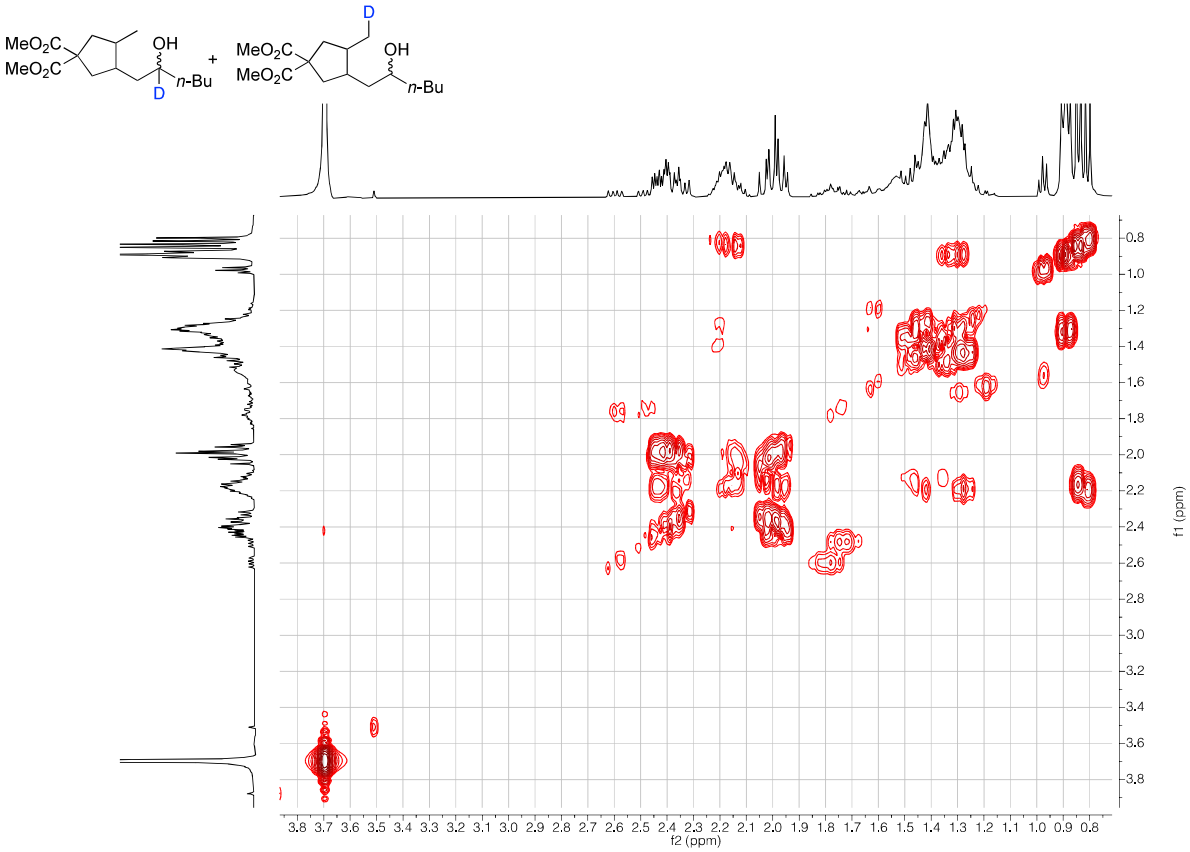
Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

DEPT-135 NMR (101 MHz, $CDCl_3$)



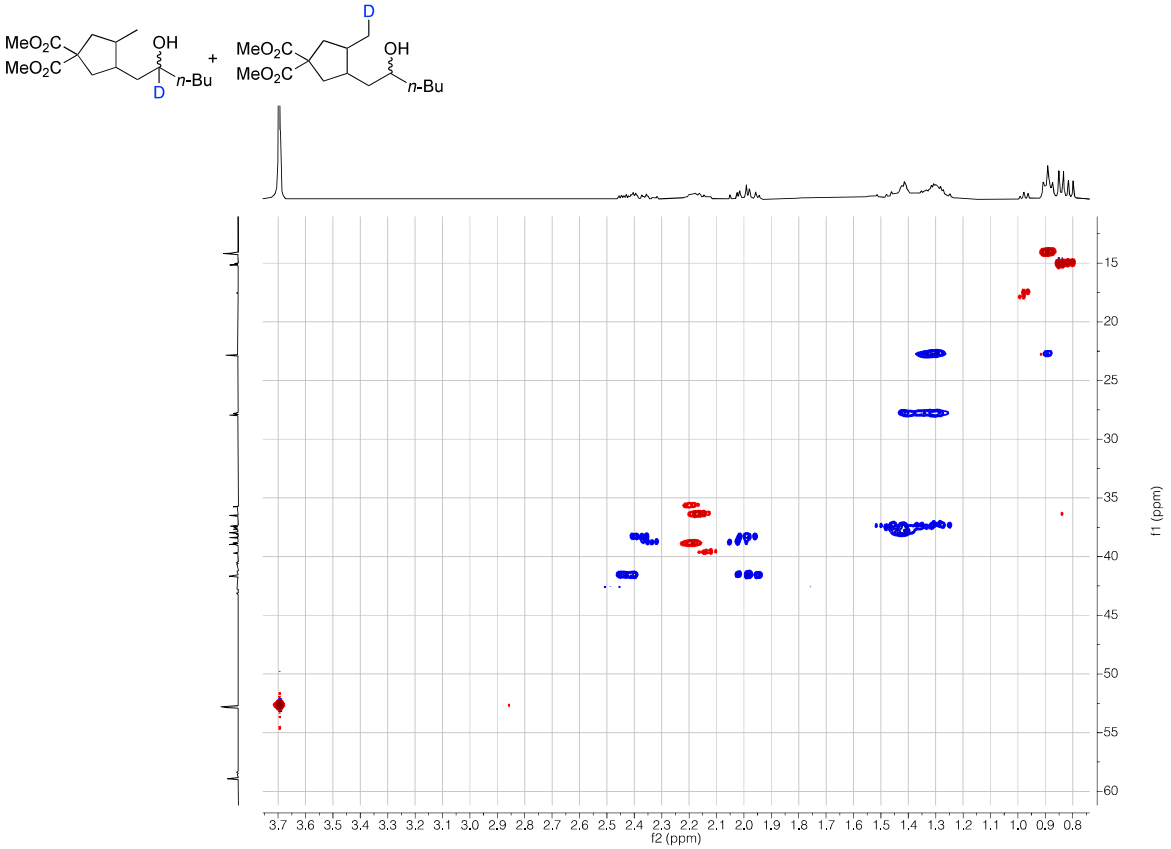
Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



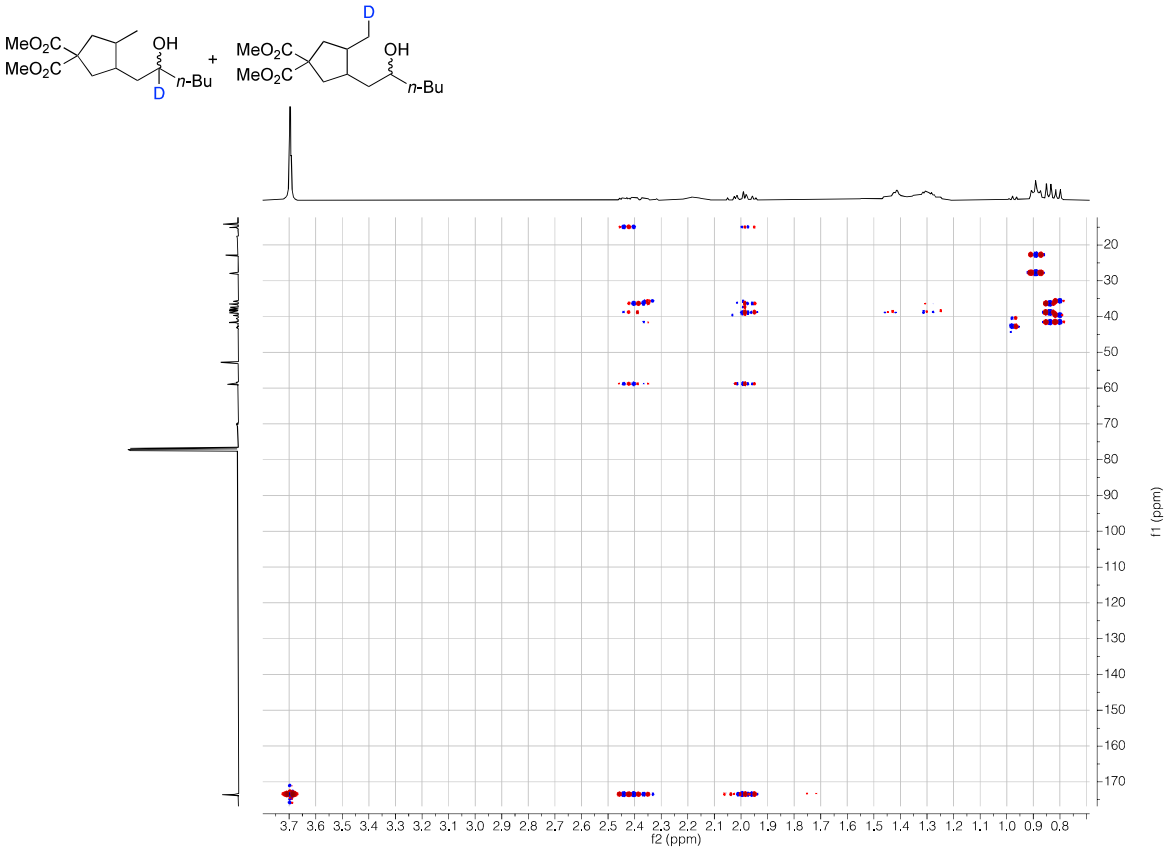
Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



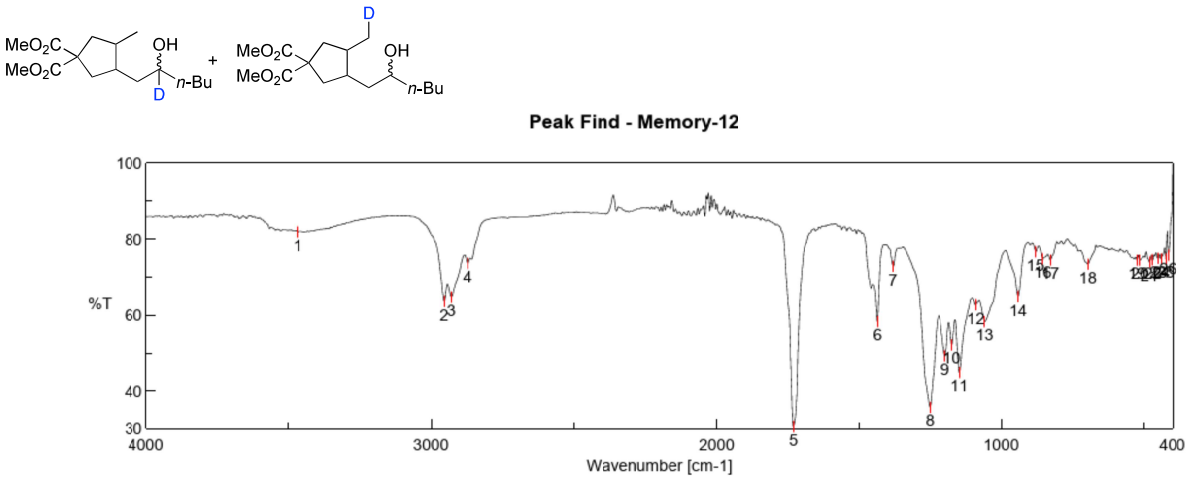
Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



Deuteration experiment + Oxidation of Dimethyl 3-(iodomethyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



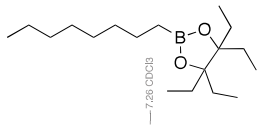
Peak Find - Memory-12

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3466.42	81.8233	2	2954.41	63.5411	3	2929.34	64.6784
4	2872.45	73.5742	5	1729.83	30.5431	6	1433.82	58.2186
7	1379.82	72.7747	8	1250.61	35.6012	9	1196.61	49.1628
10	1172.51	52.0794	11	1146.47	44.7804	12	1088.62	62.6667
13	1057.76	58.2105	14	941.092	64.815	15	880.345	76.6389
16	855.275	74.8028	17	829.241	74.4361	18	695.212	73.3298
19	524.543	74.3809	20	514.901	74.3592	21	481.153	73.8962
22	469.582	74.477	23	450.297	74.9121	24	440.655	74.7484
25	424.263	74.6684	26	415.585	75.6316			

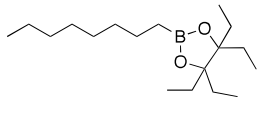
4,4,5,5-tetraethyl-2-octyl-1,3,2-dioxaborolane

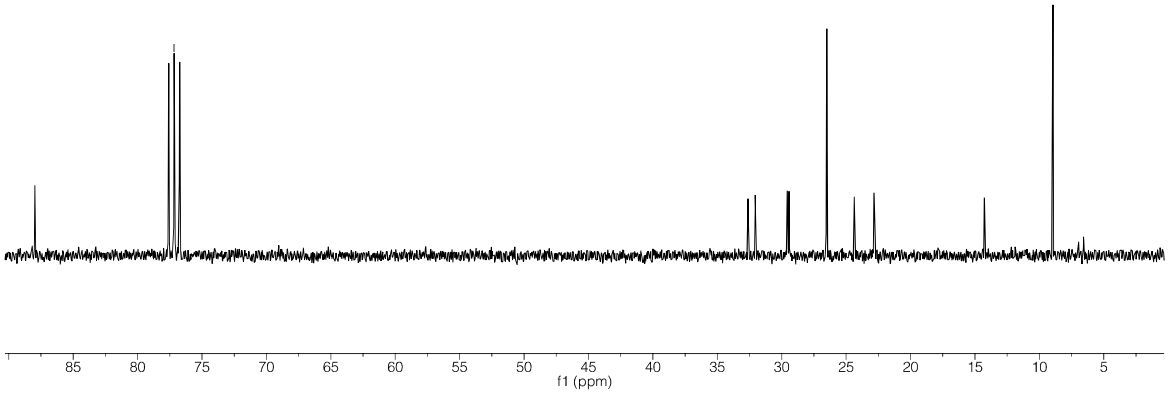
^{1}H-NMR (300 MHz, $CDCl_3$)



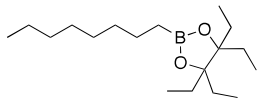
4,4,5,5-tetraethyl-2-octyl-1,3,2-dioxaborolane

^{13}C-NMR (75 MHz, $CDCl_3$)

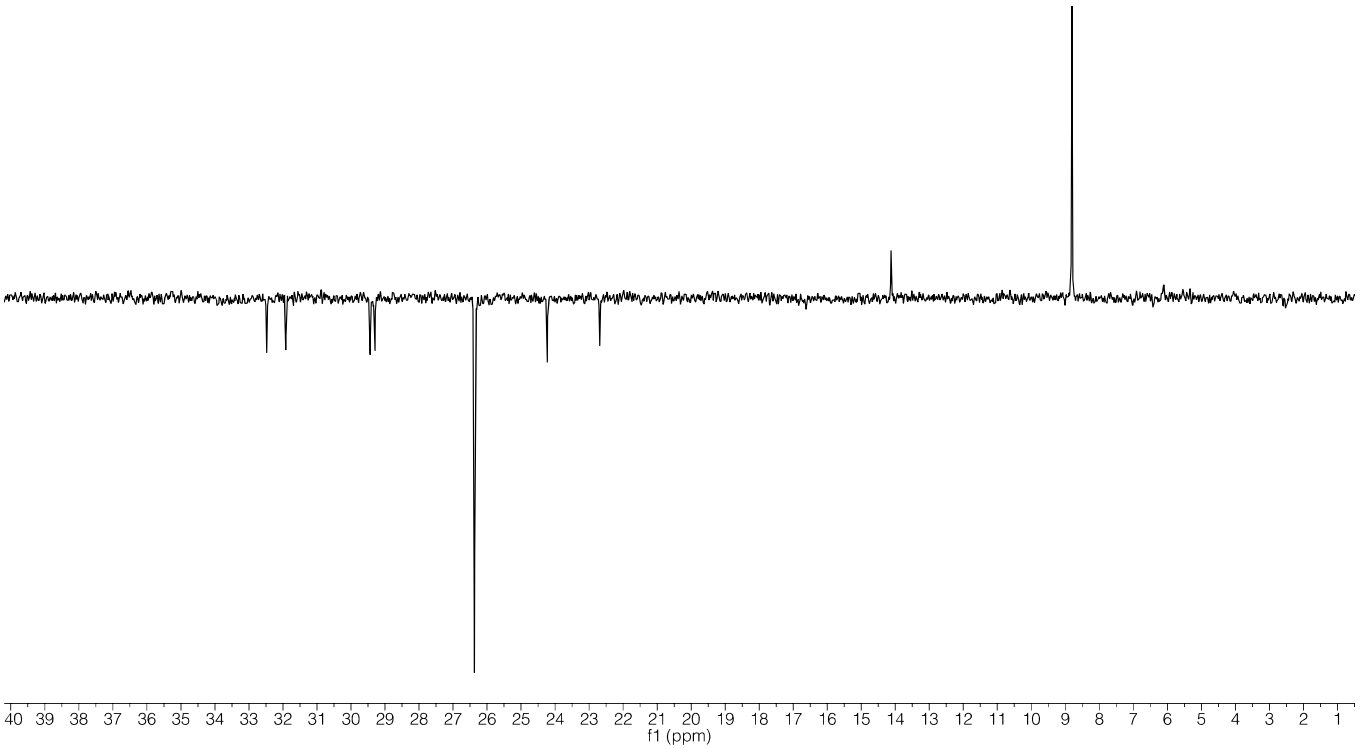




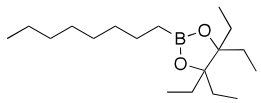
4,4,5,5-tetraethyl-2-octyl-1,3,2-dioxaborolane



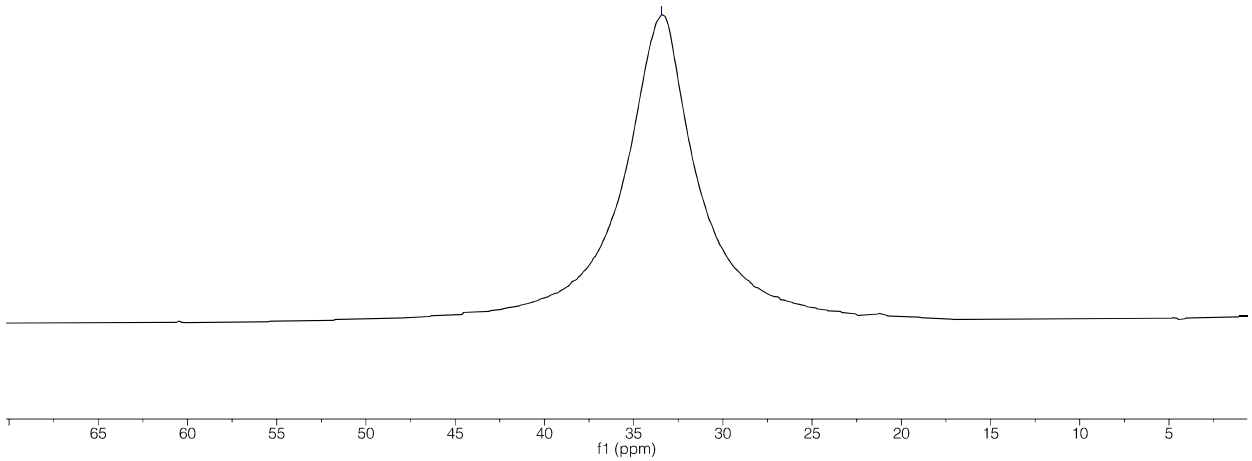
DEPT-135 NMR (75 MHz, $CDCl_3$)



4,4,5,5-tetraethyl-2-octyl-1,3,2-dioxaborolane

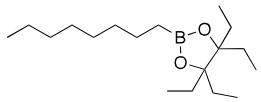


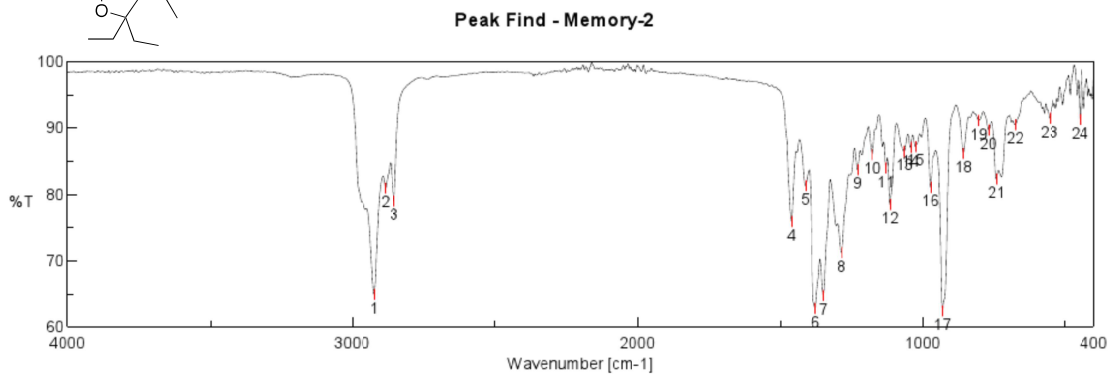
^{11}B-NMR (96 MHz, $CDCl_3$)



4,4,5,5-tetraethyl-2-octyl-1,3,2-dioxaborolane

FT-IR, ATR-diamond



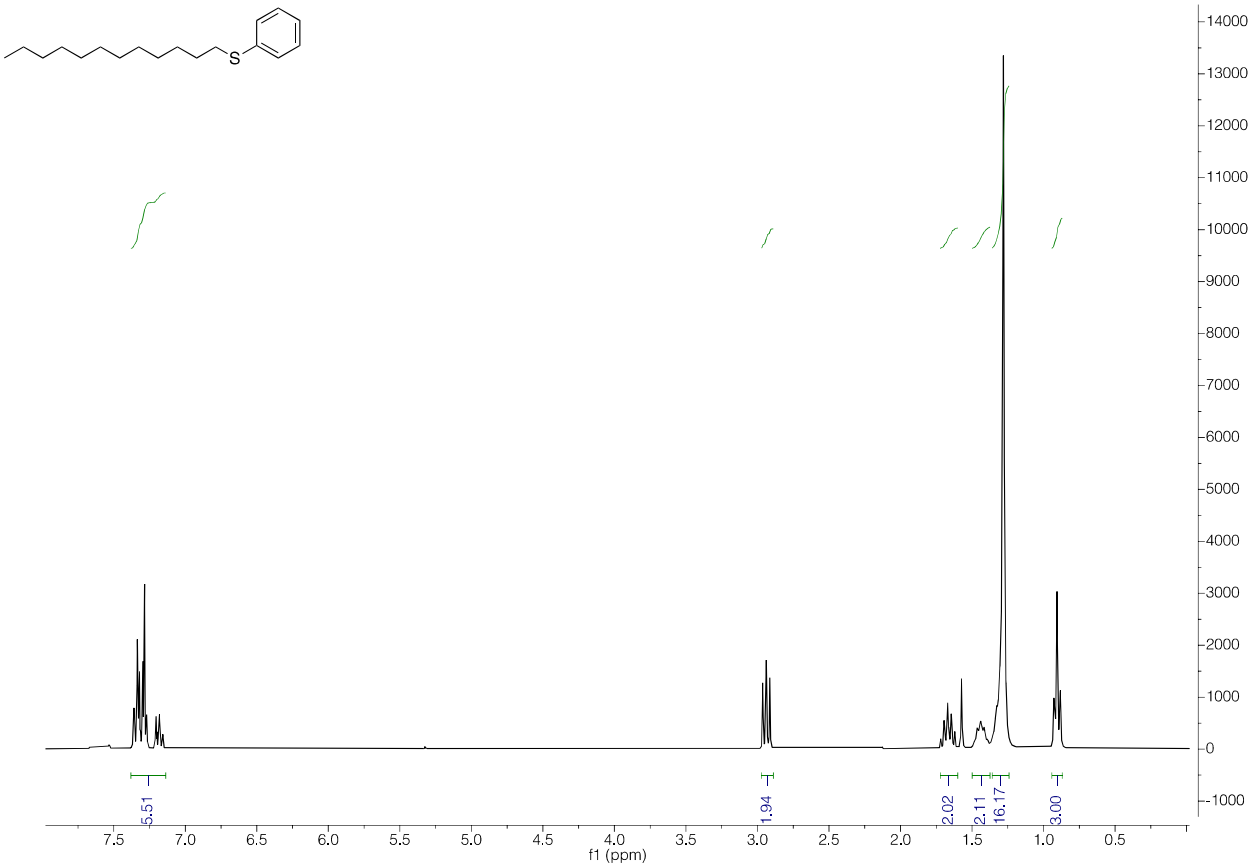


[Result of Peak Picking]

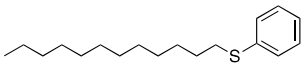
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2922.59	64.8698	2	2884.02	80.8593	3	2854.13	78.9147
4	1457.92	75.8188	5	1410.67	81.2223	6	1375.96	62.7649
7	1348	64.6916	8	1285.32	71.1725	9	1228.43	83.6044
10	1176.36	85.9007	11	1128.15	83.9136	12	1114.65	78.3744
13	1063.55	86.3676	14	1042.34	86.9351	15	1024.98	87.1055
16	972.912	80.9809	17	930.485	62.3862	18	857.204	86.0767
19	803.206	91.0477	20	769.458	89.5935	21	740.531	82.212
22	675.928	90.4082	23	555.398	91.3512	24	447.404	91.2026

Dodecyl(phenyl)sulfane

^{1}H-NMR (300 MHz, $CDCl_3$)

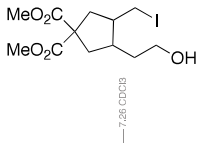


Dodecyl(phenyl)sulfane

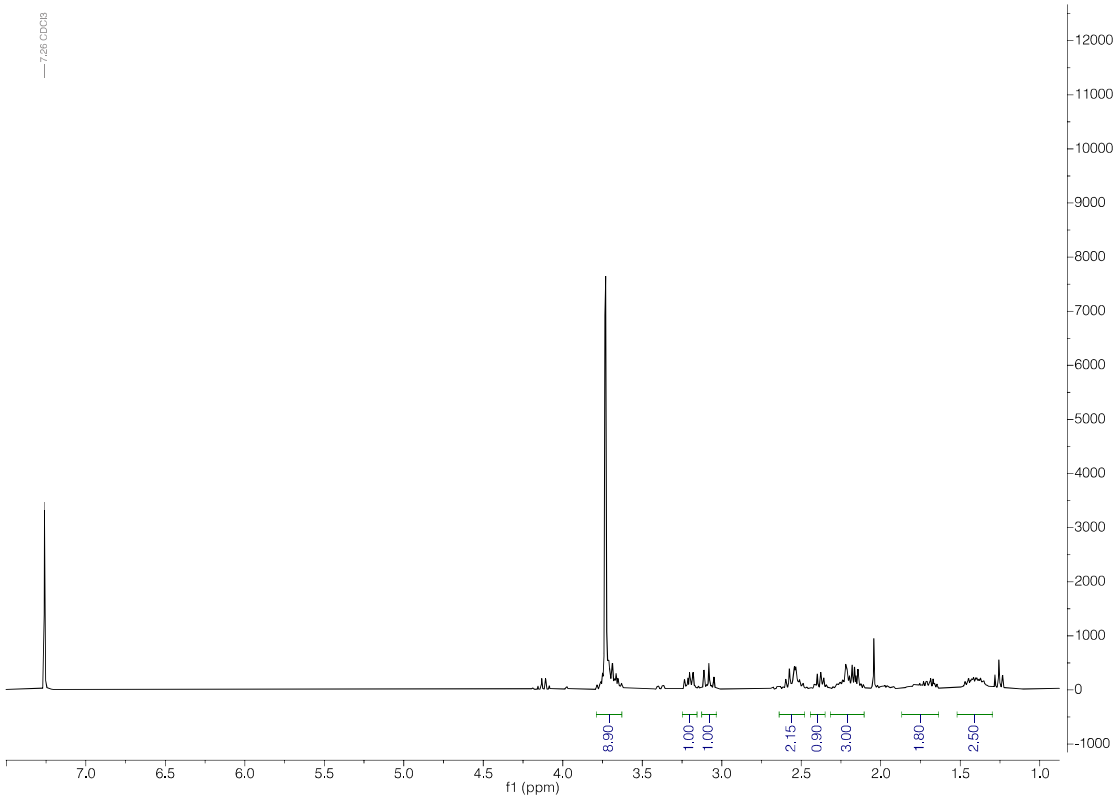


^{13}C-NMR (75 MHz, $CDCl_3$)

Dimethyl 3-(2-hydroxyethyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

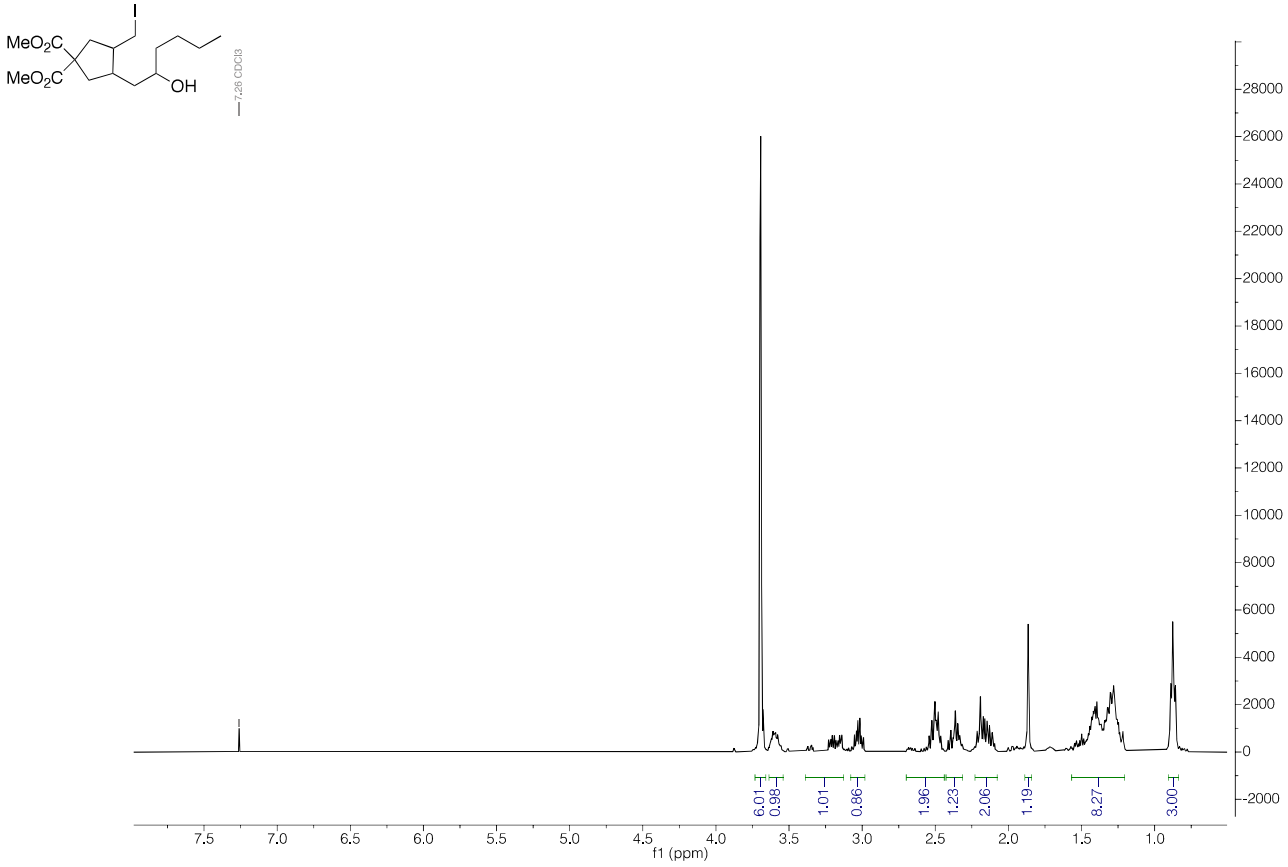


^{1}H-NMR (300 MHz, $CDCl_3$)



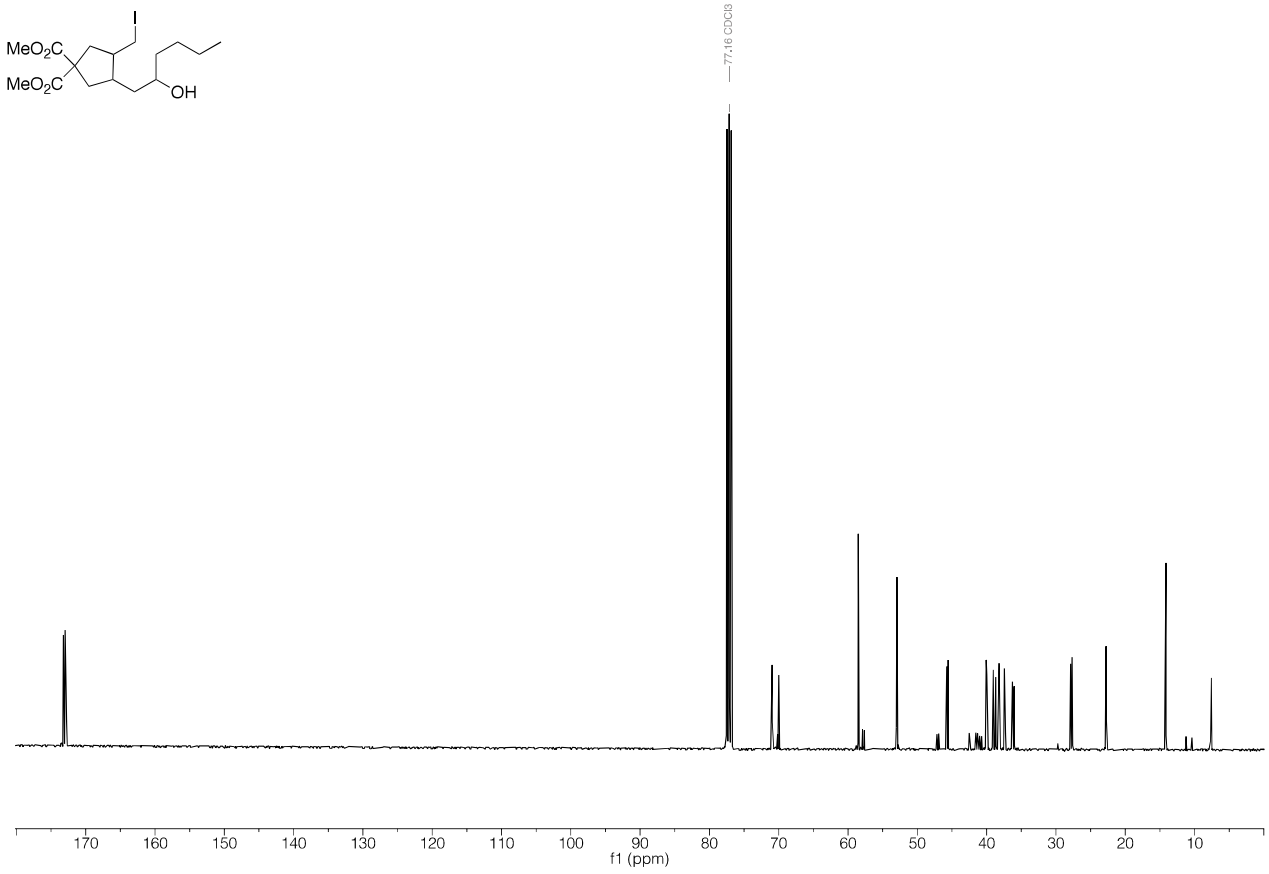
Dimethyl 3-(2-hydroxyhexyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)

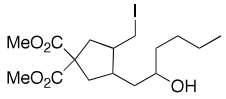


Dimethyl 3-(2-hydroxyhexyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

^{13}C-NMR (101 MHz, $CDCl_3$)

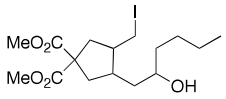


Dimethyl 3-(2-hydroxyhexyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate



DEPT-135 NMR (101 MHz, $CDCl_3$)

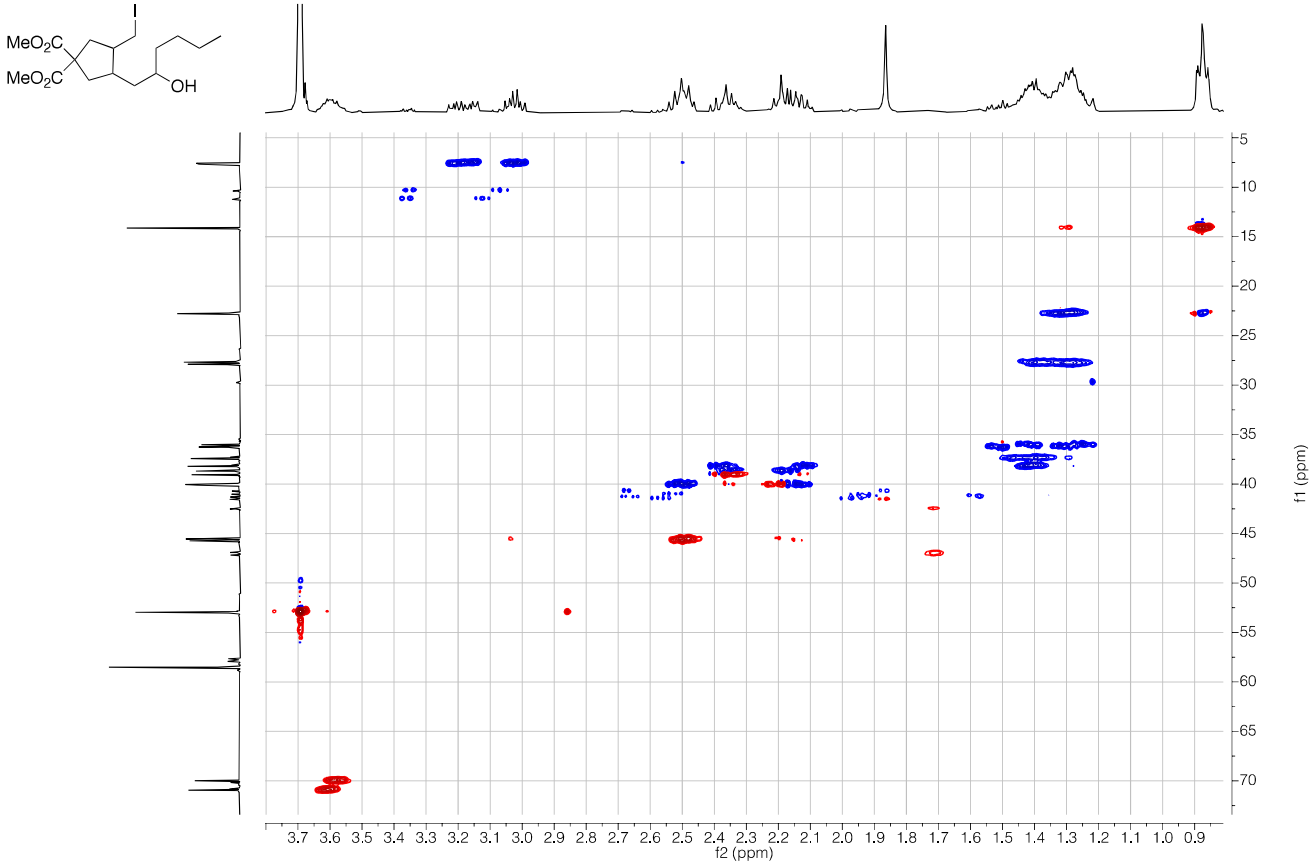
Dimethyl 3-(2-hydroxyhexyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate



^1H, ^1H-COSY (400 MHz, $CDCl_3$)

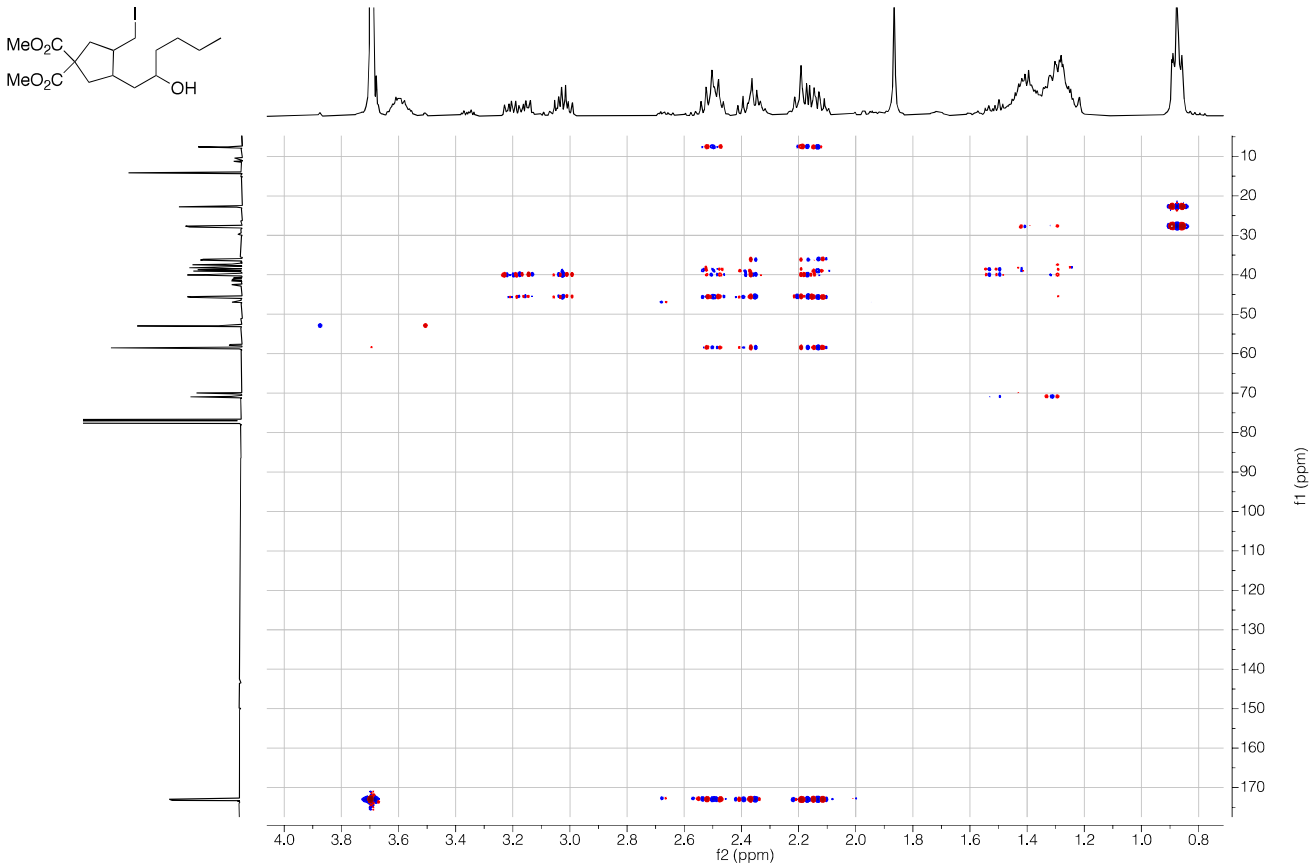
Dimethyl 3-(2-hydroxyhexyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



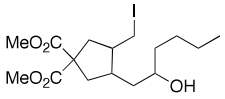
Dimethyl 3-(2-hydroxyhexyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

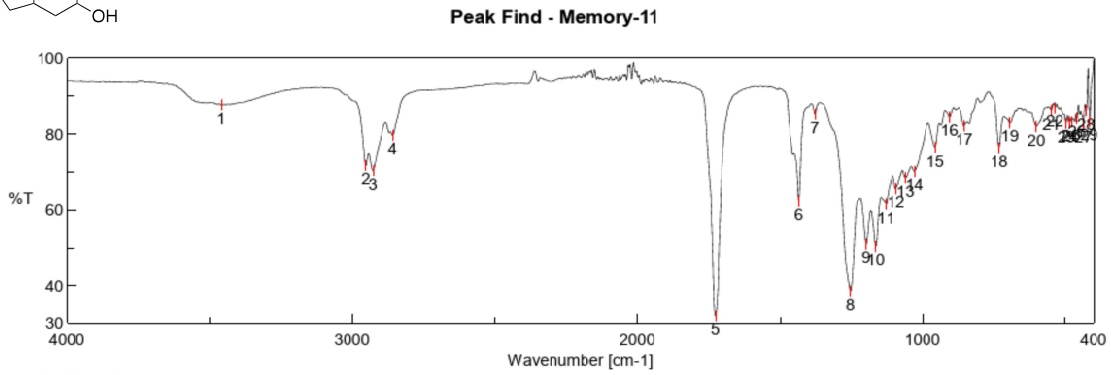
^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



Dimethyl 3-(2-hydroxyhexyl)-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



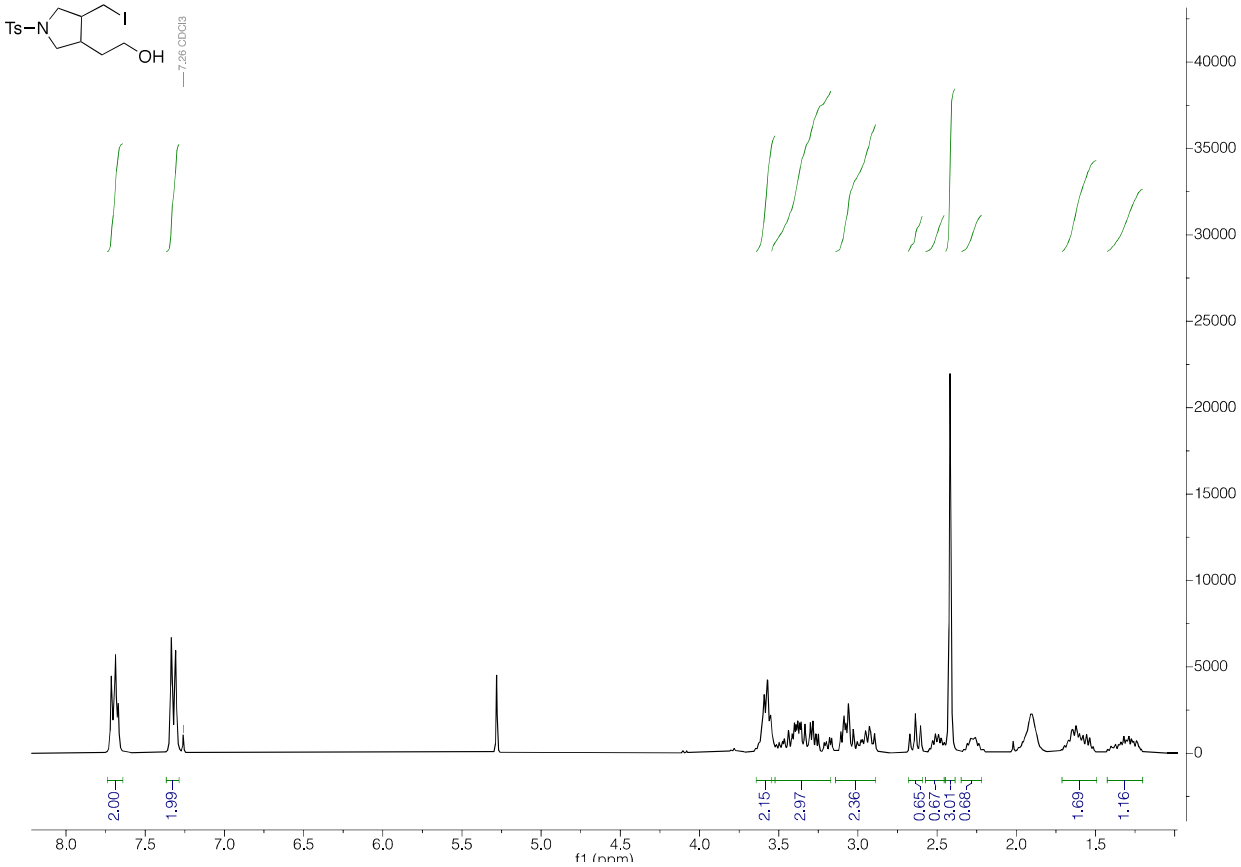


[Result of Peak Picking]

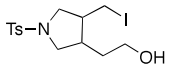
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3458.71	87.6301	2	2952.48	71.691	3	2927.41	70.3178
4	2857.99	79.5582	5	1726.94	31.9838	6	1433.82	62.2158
7	1377.89	85.1995	8	1253.5	38.5104	9	1196.61	50.9132
10	1163.83	50.2825	11	1128.15	61.4608	12	1093.44	65.5406
13	1058.73	68.4065	14	1028.84	70.0388	15	955.555	76.409
16	905.415	84.4147	17	854.311	82.1009	18	730.889	76.2732
19	693.284	82.9338	20	599.753	81.9226	21	548.649	86.0995
22	536.114	86.8552	23	495.616	82.789	24	485.009	83.121
25	477.296	83.134	26	458.011	84.0742	27	435.834	82.6379
28	426.191	86.1825	29	414.62	83.3144			

2-(4-(iodomethyl)-1-tosylpyrrolidin-3-yl)ethan-1-ol

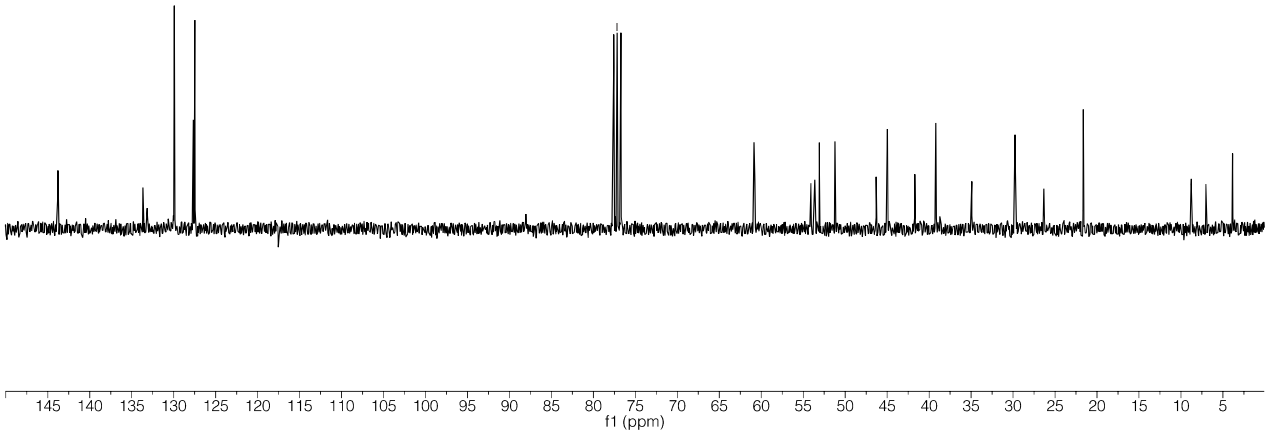
^{1}H-NMR (300 MHz, $CDCl_3$)



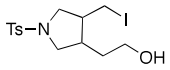
2-(4-(iodomethyl)-1-tosylpyrrolidin-3-yl)ethan-1-ol



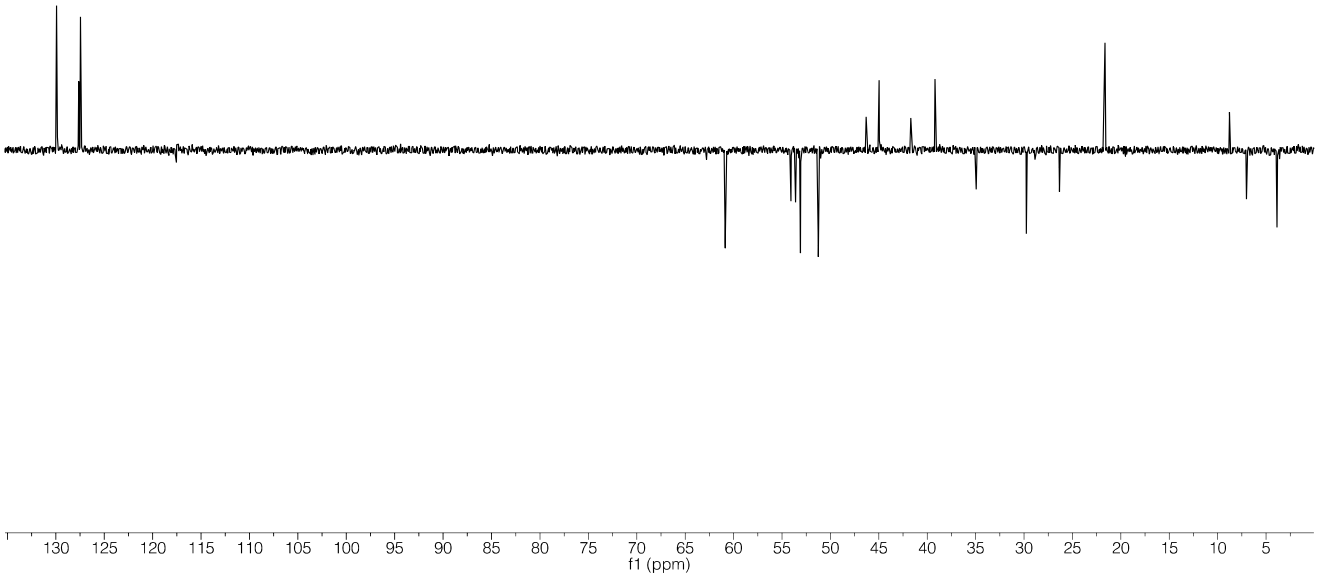
^{13}C-NMR (75 MHz, $CDCl_3$)



2-(4-(iodomethyl)-1-tosylpyrrolidin-3-yl)ethan-1-ol

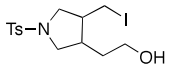


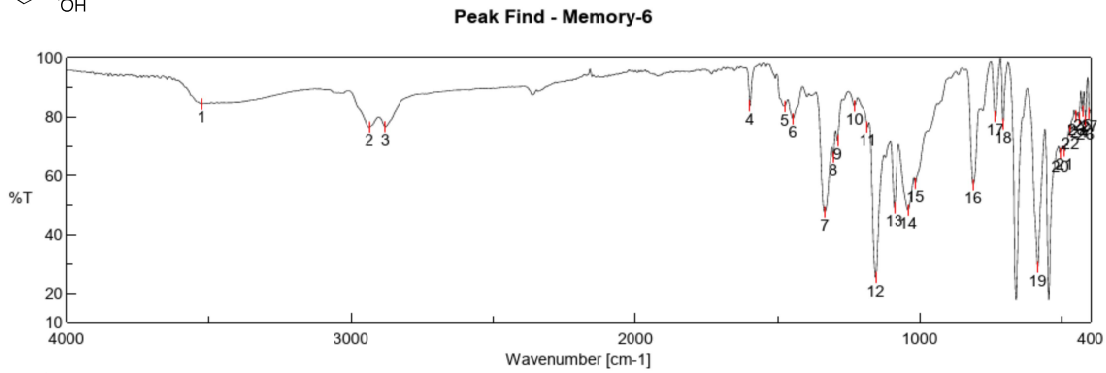
DEPT-135 NMR (75 MHz, $CDCl_3$)



2-(4-(iodomethyl)-1-tosylpyrrolidin-3-yl)ethan-1-ol

FT-IR, ATR-diamond



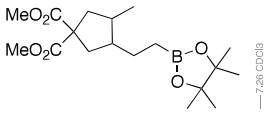


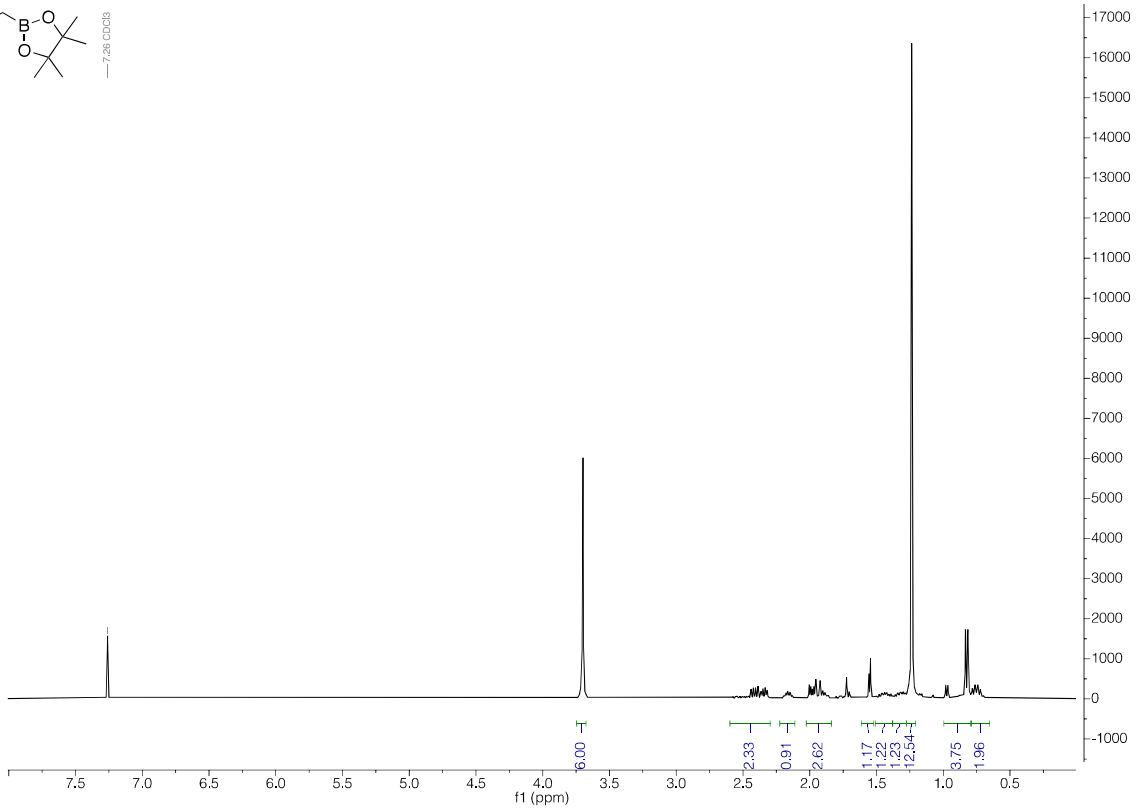
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3525.24	84.2623	2	2935.13	76.3444	3	2879.2	76.4382
4	1596.77	83.6471	5	1474.31	83.4211	6	1445.39	79.1822
7	1336.43	47.4879	8	1304.61	66.2266	9	1289.18	71.8241
10	1230.36	83.6004	11	1183.11	76.3398	12	1155.15	25.2826
13	1089.58	48.9486	14	1040.41	48.1778	15	1015.34	57.2409
16	812.849	56.7572	17	733.782	79.9739	18	706.783	77.409
19	584.325	28.8806	20	505.258	67.5075	21	490.795	68.3031
22	470.546	75.3679	23	449.333	80.1904	24	440.655	79.4955
25	429.084	81.7826	26	418.477	78.4653	27	404.978	81.0914

Dimethyl 3-methyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

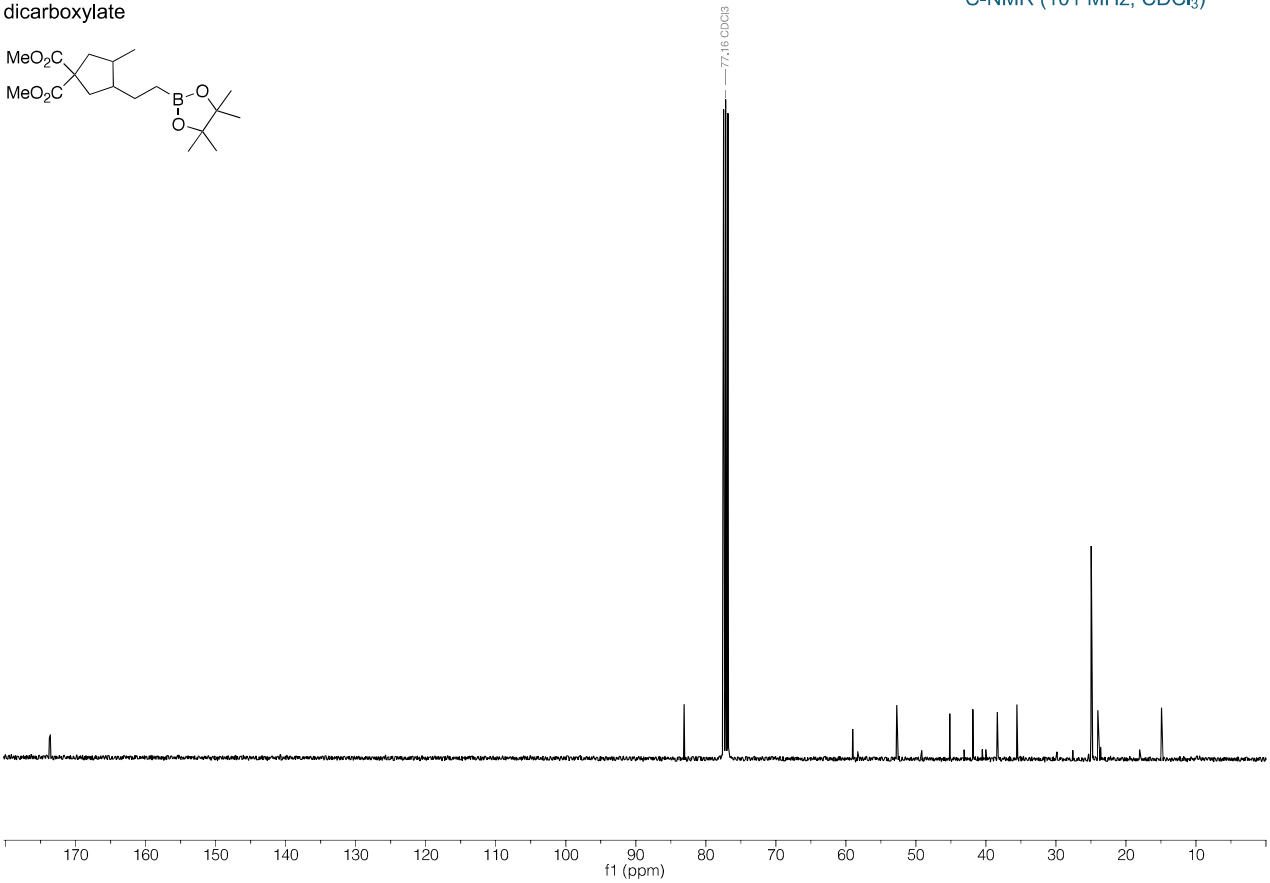
^{1}H-NMR (400 MHz, $CDCl_3$)





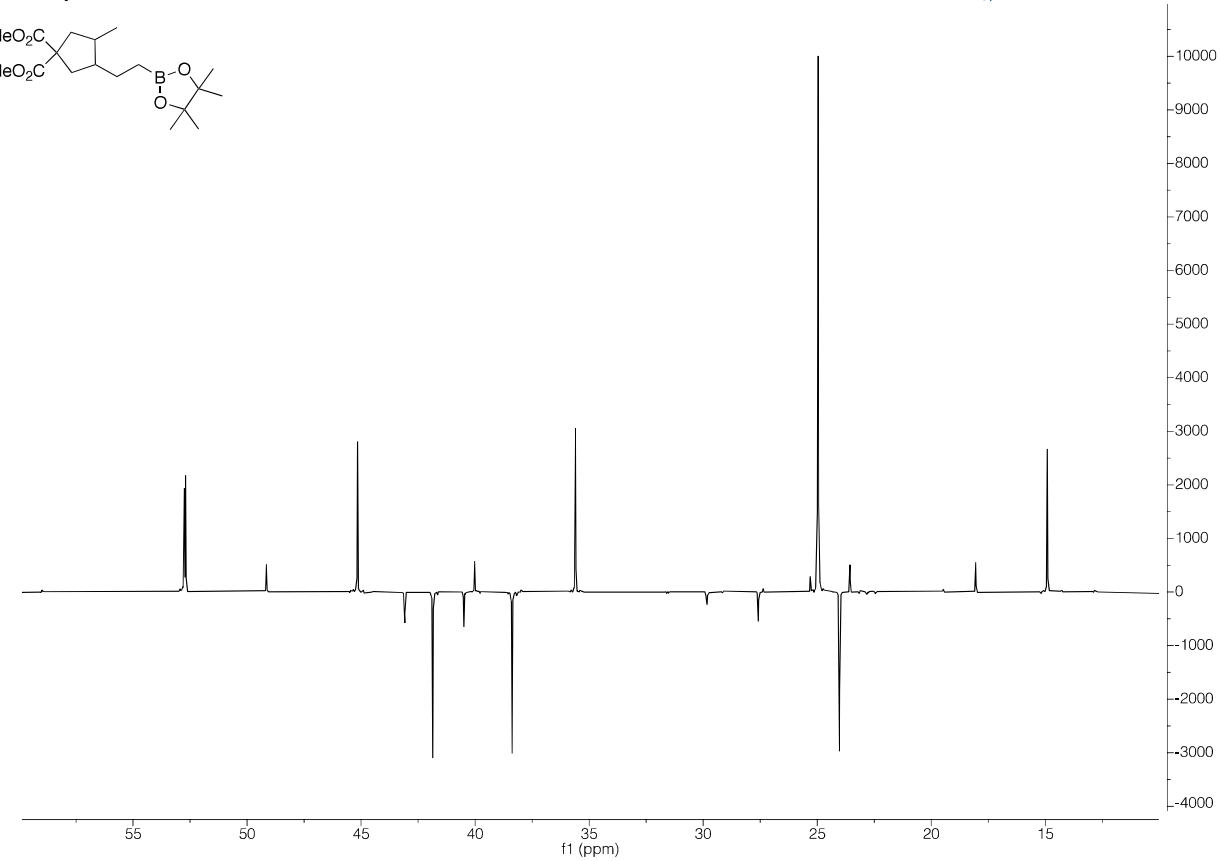
Dimethyl 3-methyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

^{13}C-NMR (101 MHz, $CDCl_3$)



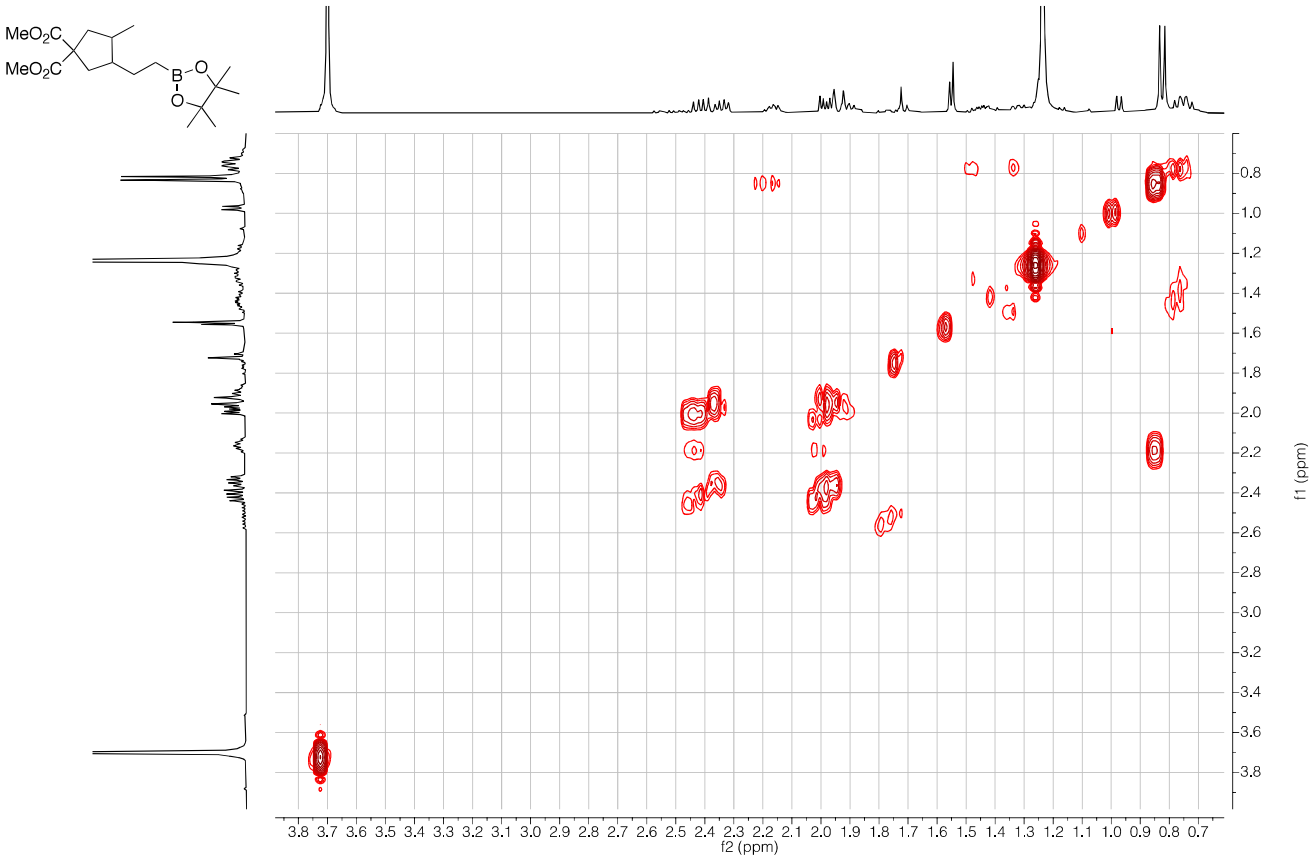
Dimethyl 3-methyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

DEPT-135 NMR (101 MHz, $CDCl_3$)



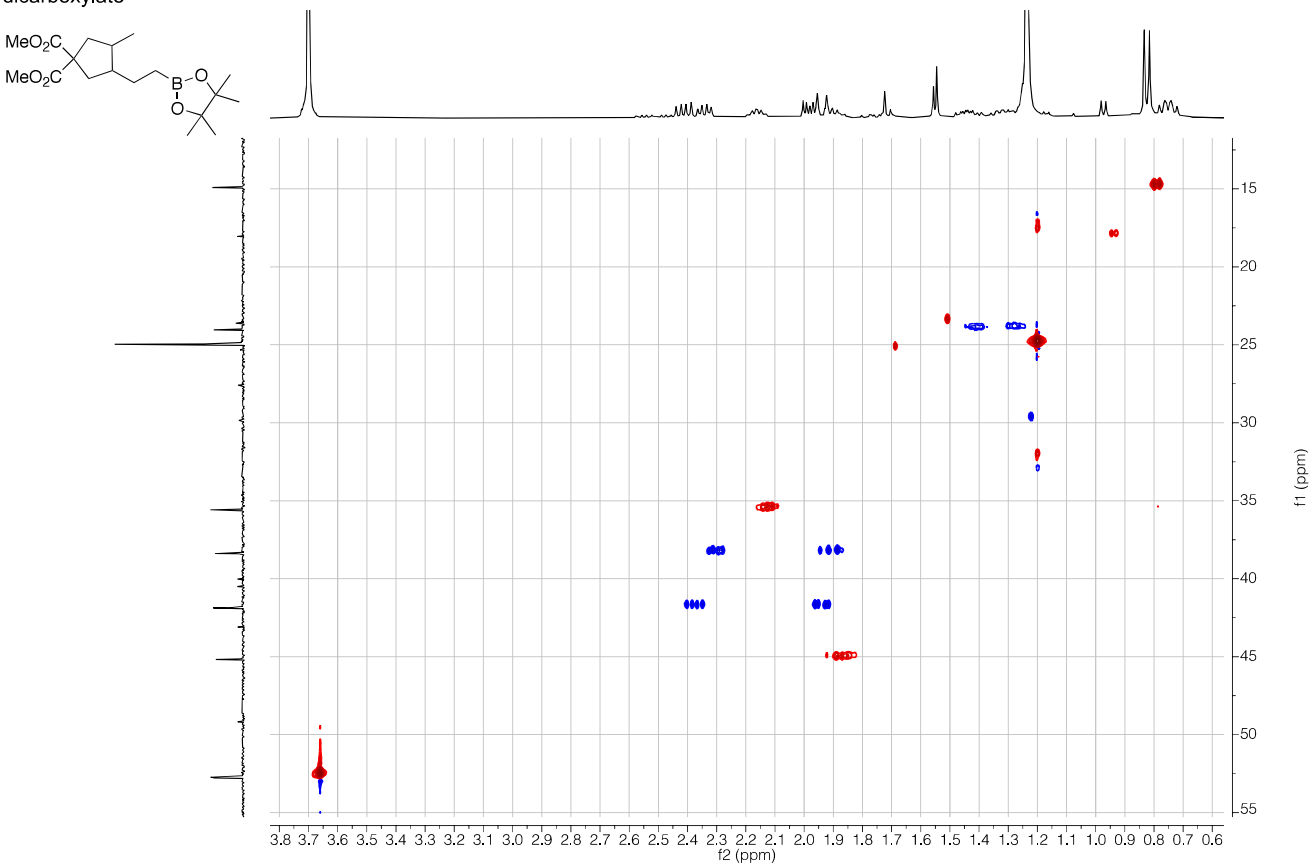
Dimethyl 3-methyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



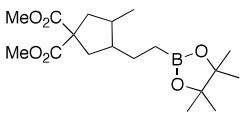
Dimethyl 3-methyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



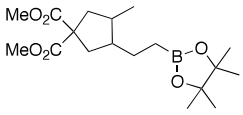
Dimethyl 3-methyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

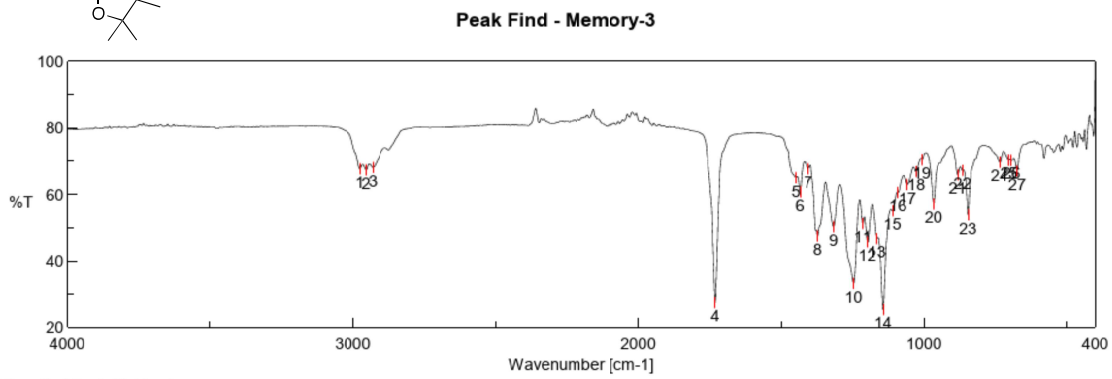
^{11}B-NMR (128 MHz, $CDCl_3$)



Dimethyl 3-methyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



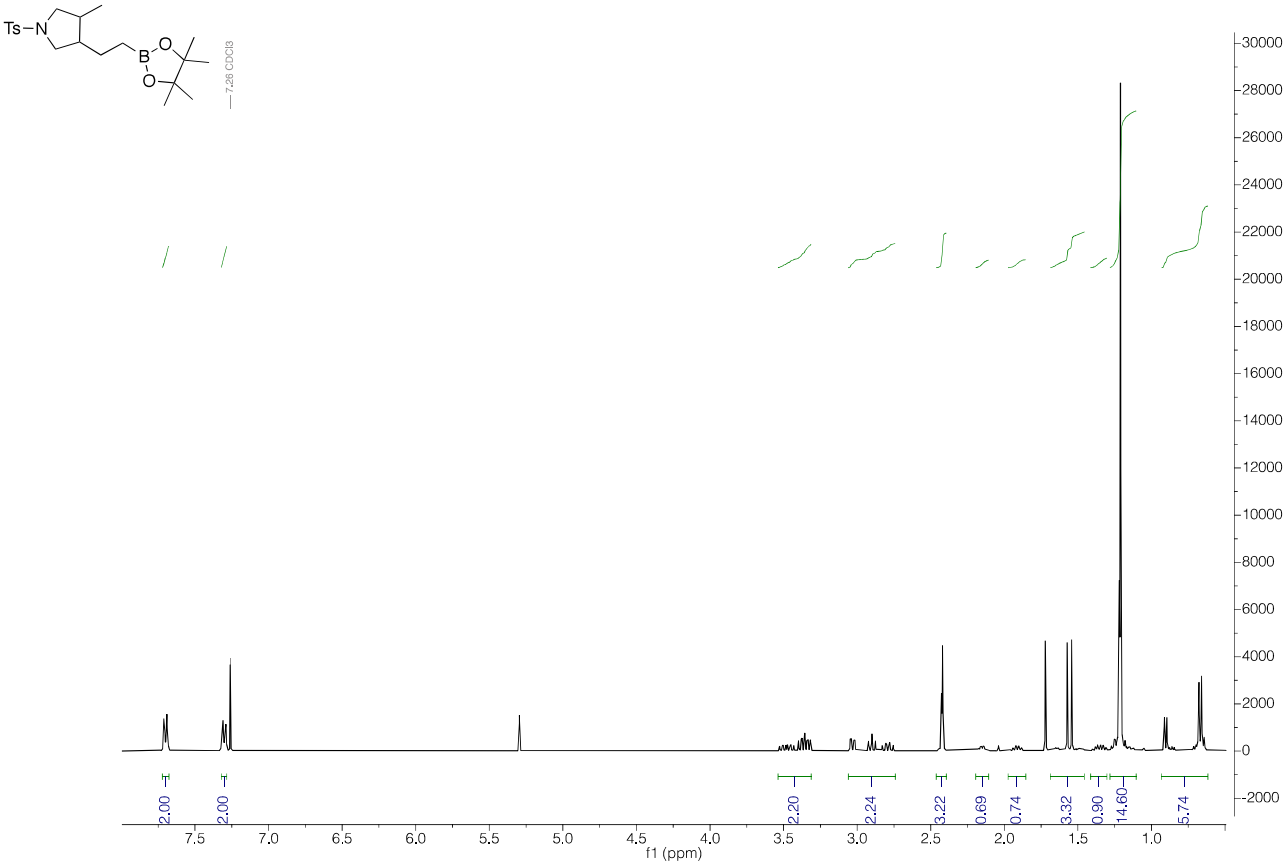


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	67.5833	2	2953.45	67.3643	3	2930.31	68.1221
4	1731.76	27.4919	5	1448.28	65.0471	6	1434.78	60.7195
7	1405.85	67.7233	8	1371.14	47.461	9	1315.21	50.2462
10	1245.79	33.2506	11	1213.97	51.2555	12	1196.61	45.7574
13	1163.83	46.7412	14	1142.62	25.3883	15	1109.83	55.0881
16	1090.55	60.5729	17	1057.76	62.9333	18	1026.91	66.8556
19	1006.66	70.4107	20	966.162	57.1035	21	883.238	65.9114
22	865.882	67.2609	23	846.597	53.8488	24	735.71	69.6926
25	702.926	70.3119	26	693.284	70.2388	27	673.999	67.0758

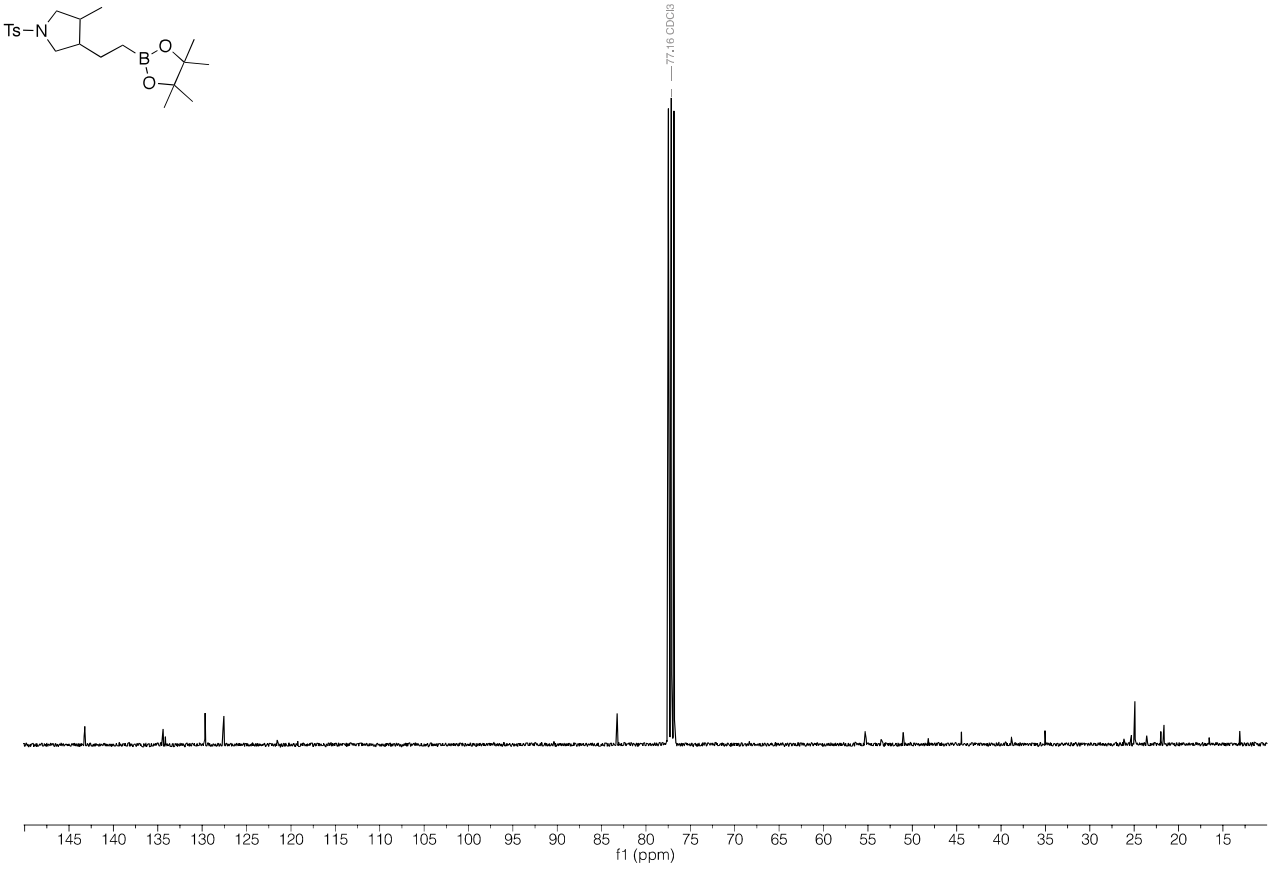
3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

^{1}H-NMR (400 MHz, $CDCl_3$)

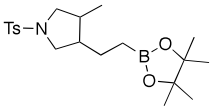


3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

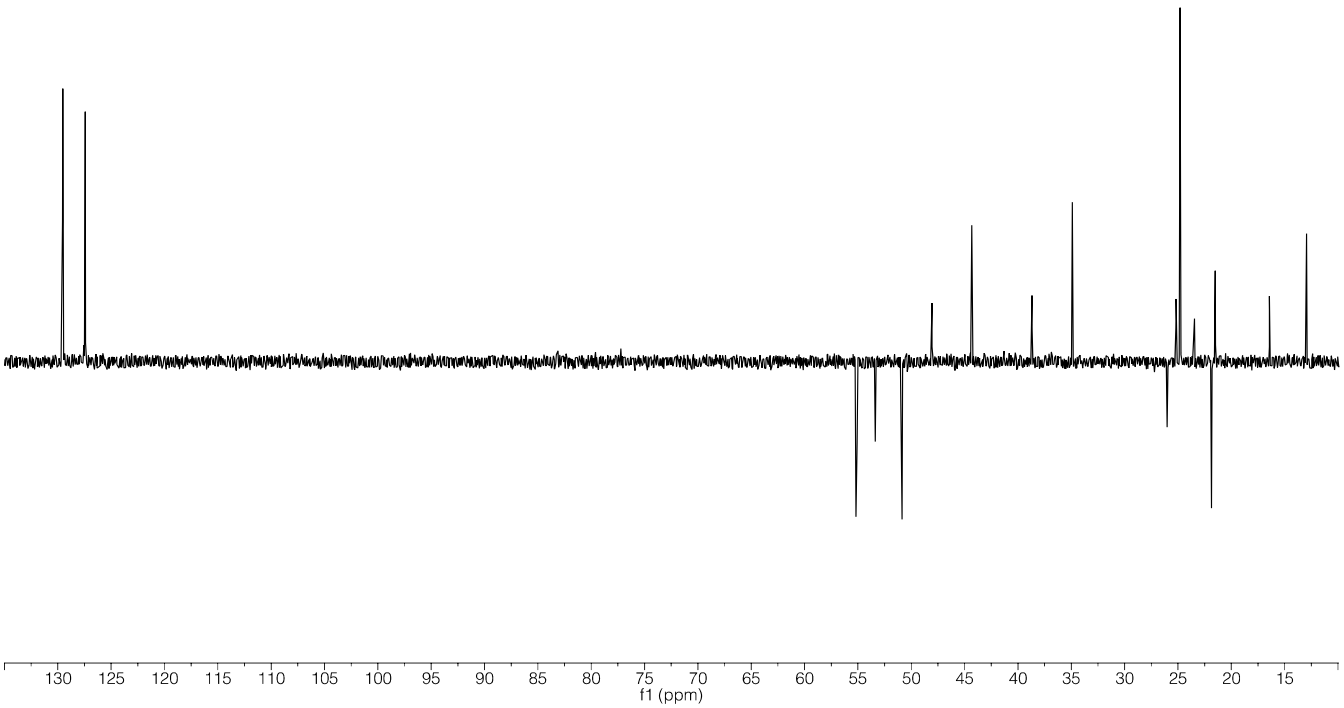
^{13}C-NMR (101 MHz, $CDCl_3$)



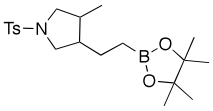
3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine



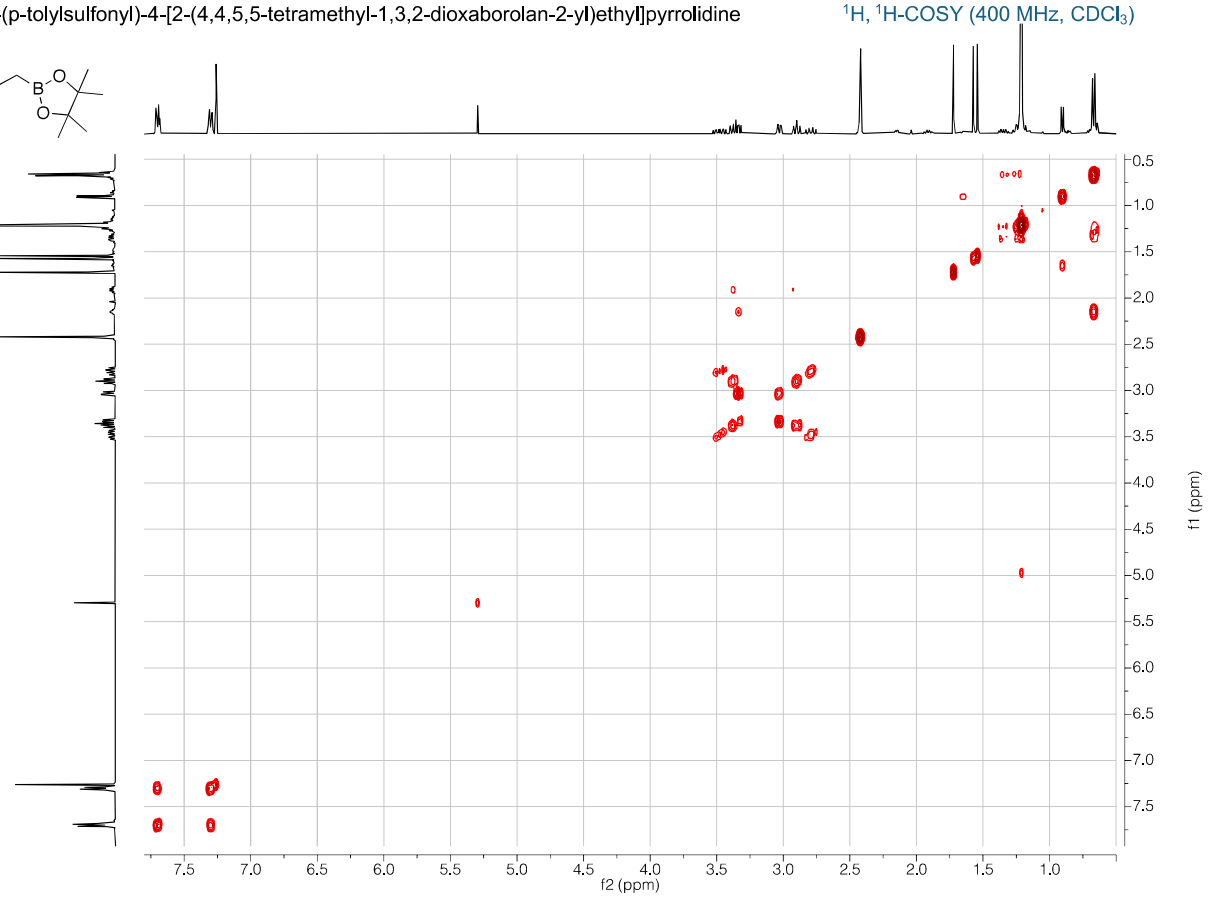
DEPT-135 NMR (101 MHz, $CDCl_3$)



3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

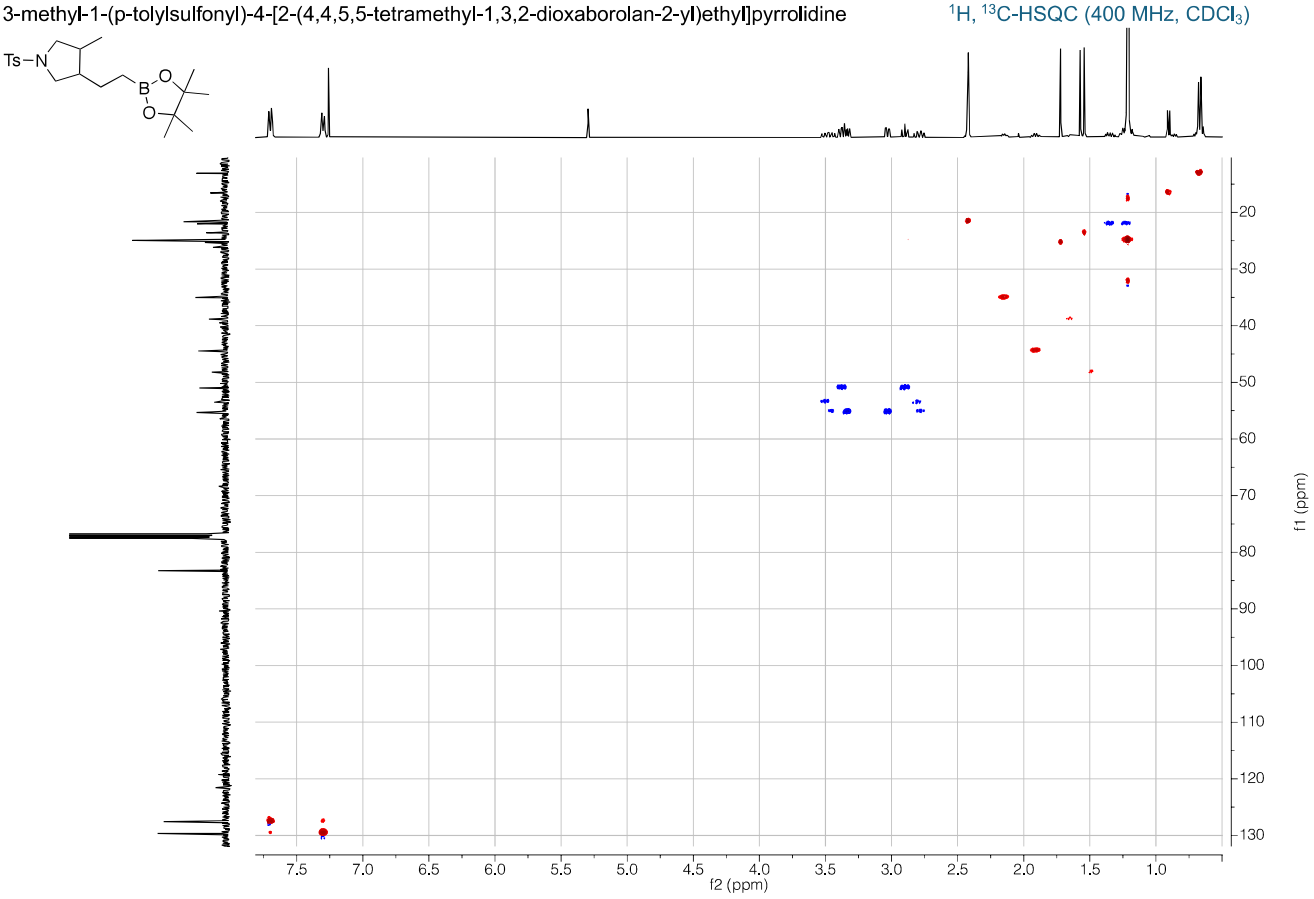


^1H, ^1H-COSY (400 MHz, $CDCl_3$)



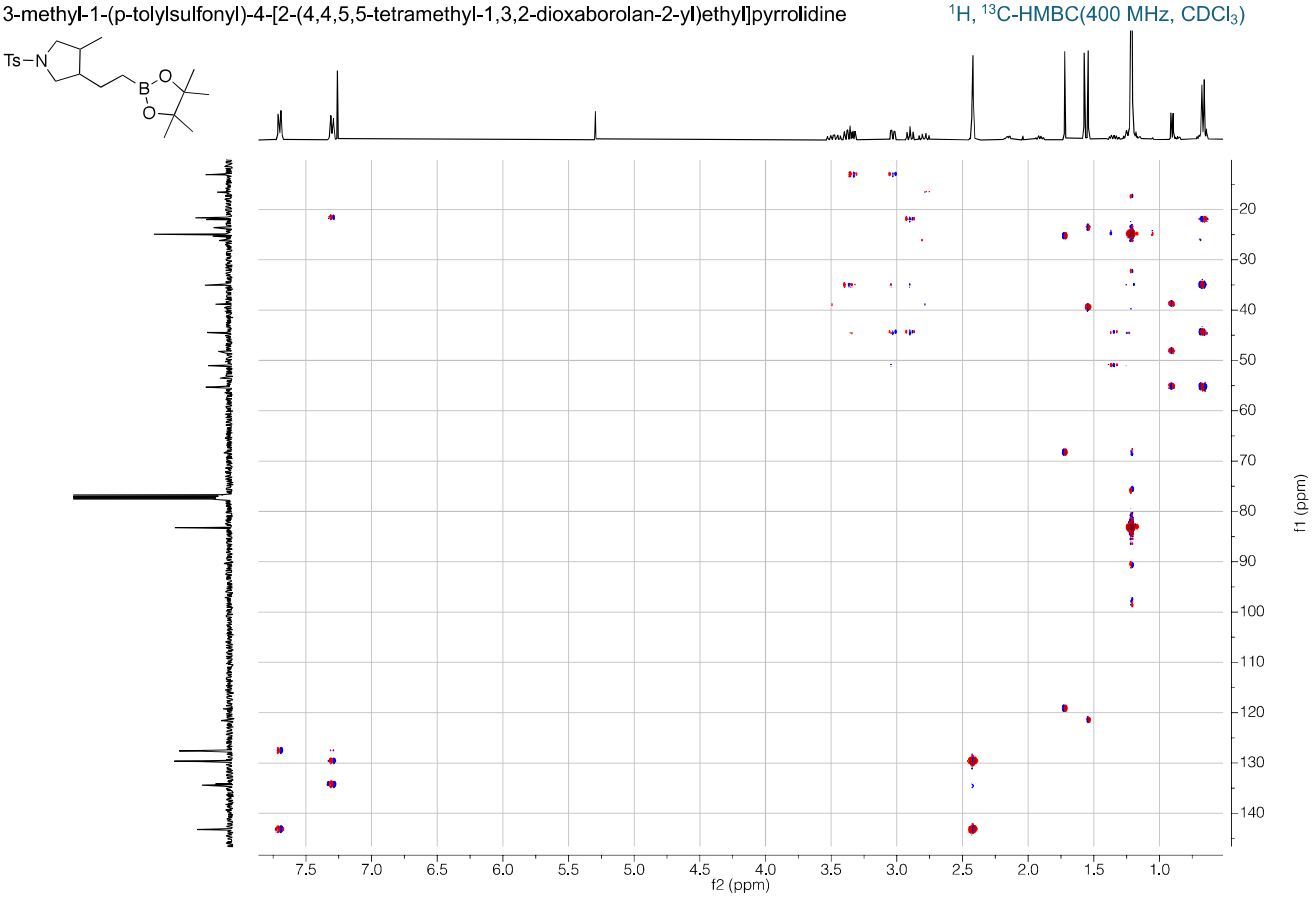
3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



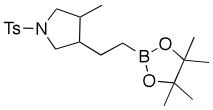
3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

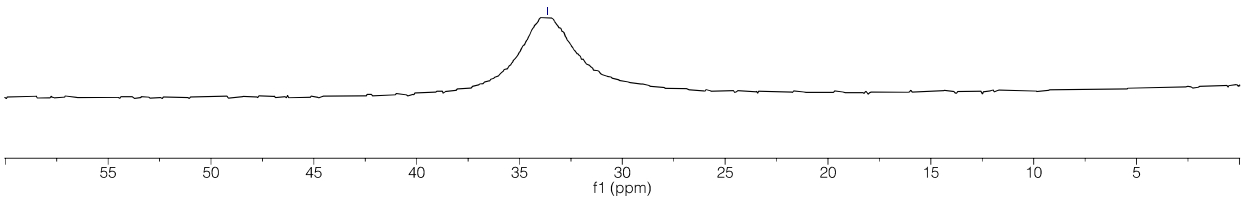
^{1}H, ^{13}C-HMBC(400 MHz, $CDCl_3$)



3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

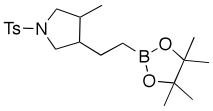
^{11}B-NMR (128 MHz, $CDCl_3$)

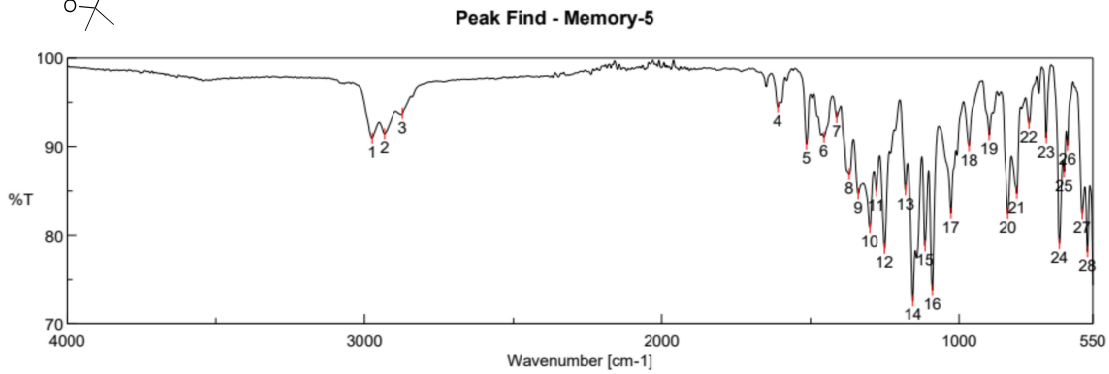




3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyrrolidine

FT-IR, ATR-diamond



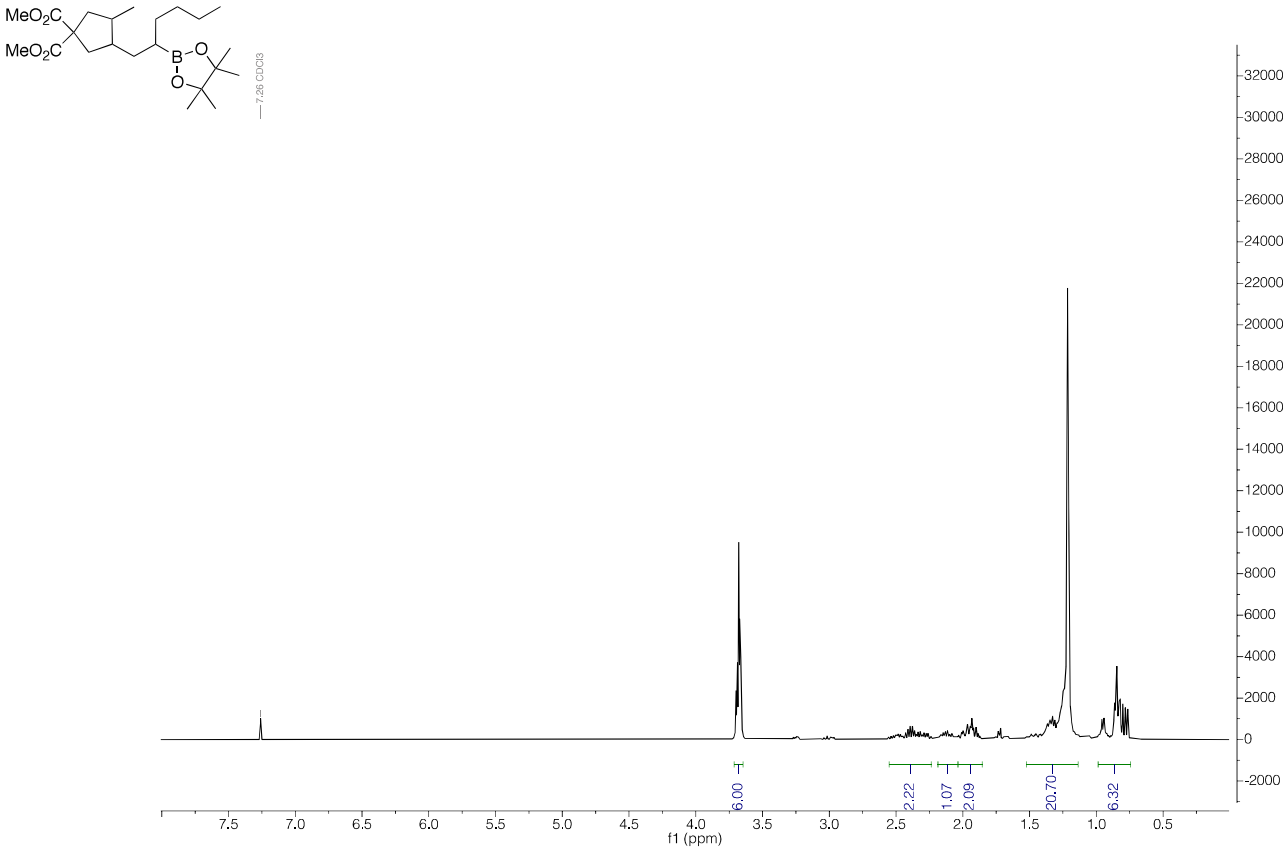


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2974.66	90.915	2	2933.2	91.4115	3	2871.49	93.7576
4	1610.27	94.4457	5	1513.85	90.2695	6	1455.03	91.0497
7	1411.64	93.2905	8	1370.18	86.8747	9	1340.28	84.669
10	1301.72	80.8522	11	1279.54	84.968	12	1250.61	78.5141
13	1181.19	85.1179	14	1157.08	72.5826	15	1115.62	78.8092
16	1090.55	73.7876	17	1027.87	82.4821	18	966.162	90.0711
19	899.63	91.2966	20	835.99	82.4477	21	806.099	84.7202
22	765.601	92.6171	23	707.747	90.9774	24	663.393	79.0543
25	647.001	87.1359	26	635.43	90.1239	27	586.254	82.3882
28	567.934	78.1279						

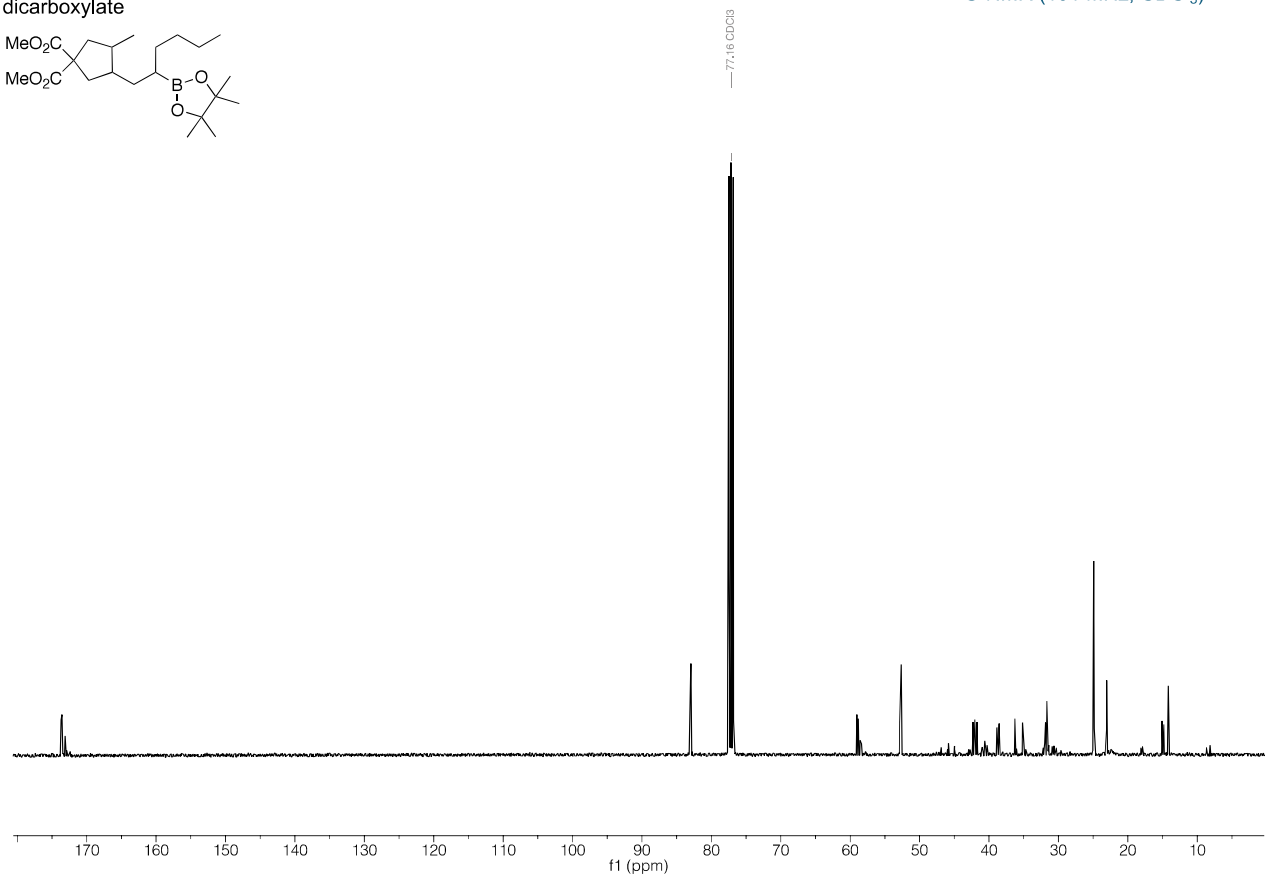
Dimethyl 3-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)

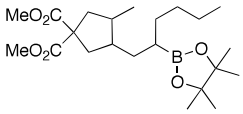


Dimethyl 3-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

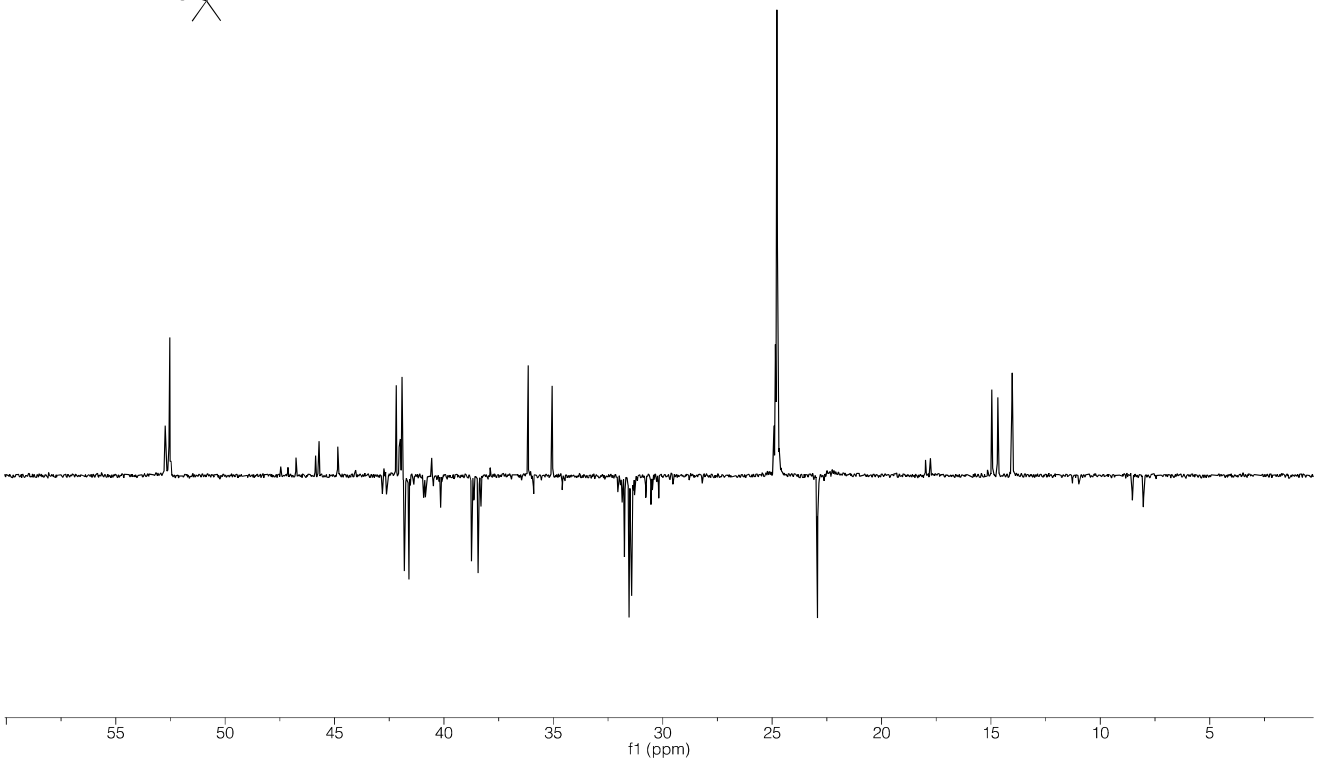
^{13}C-NMR (101 MHz, $CDCl_3$)



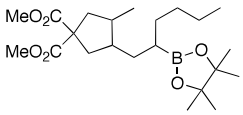
Dimethyl 3-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate



DEPT-135 NMR (101 MHz, $CDCl_3$)



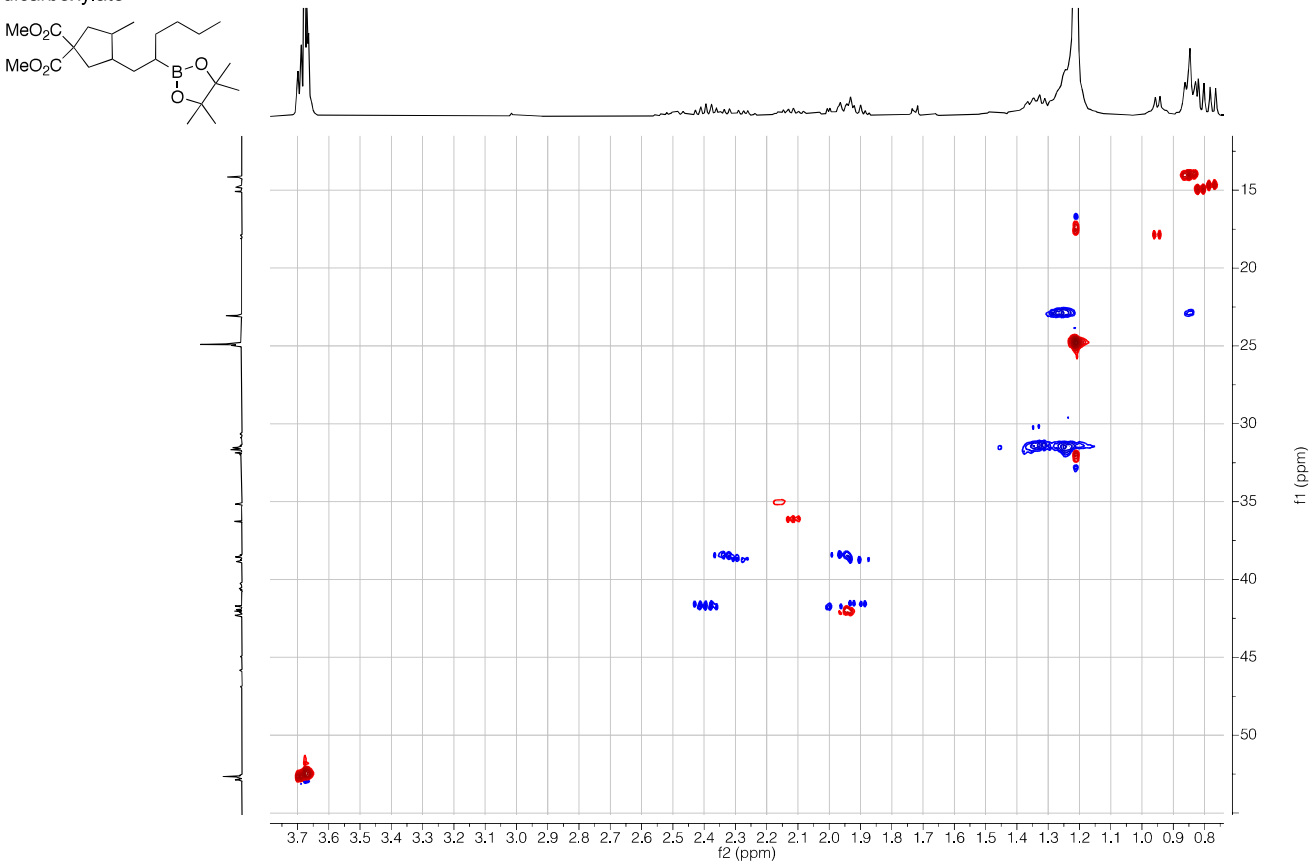
Dimethyl 3-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate



^1H, ^1H-COSY (400 MHz, $CDCl_3$)

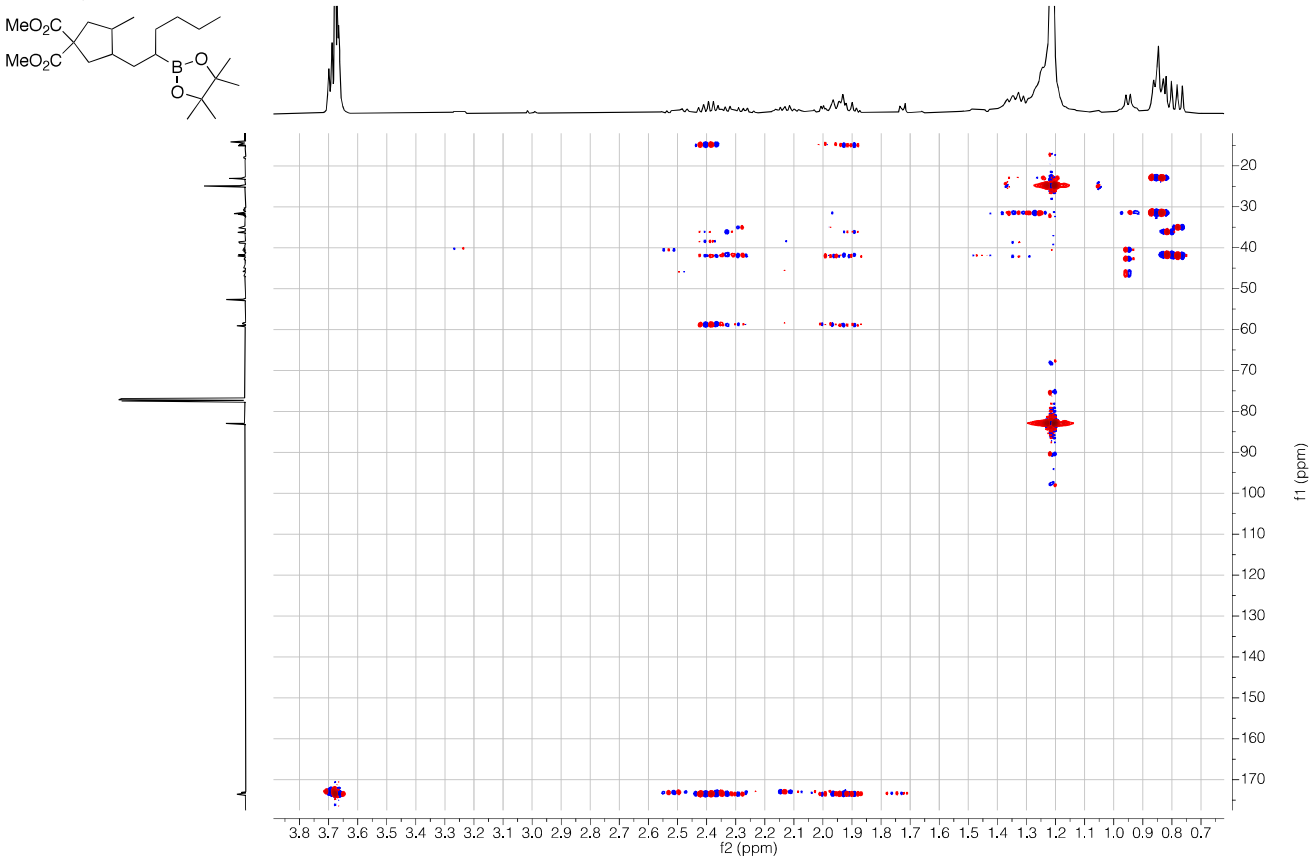
Dimethyl 3-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



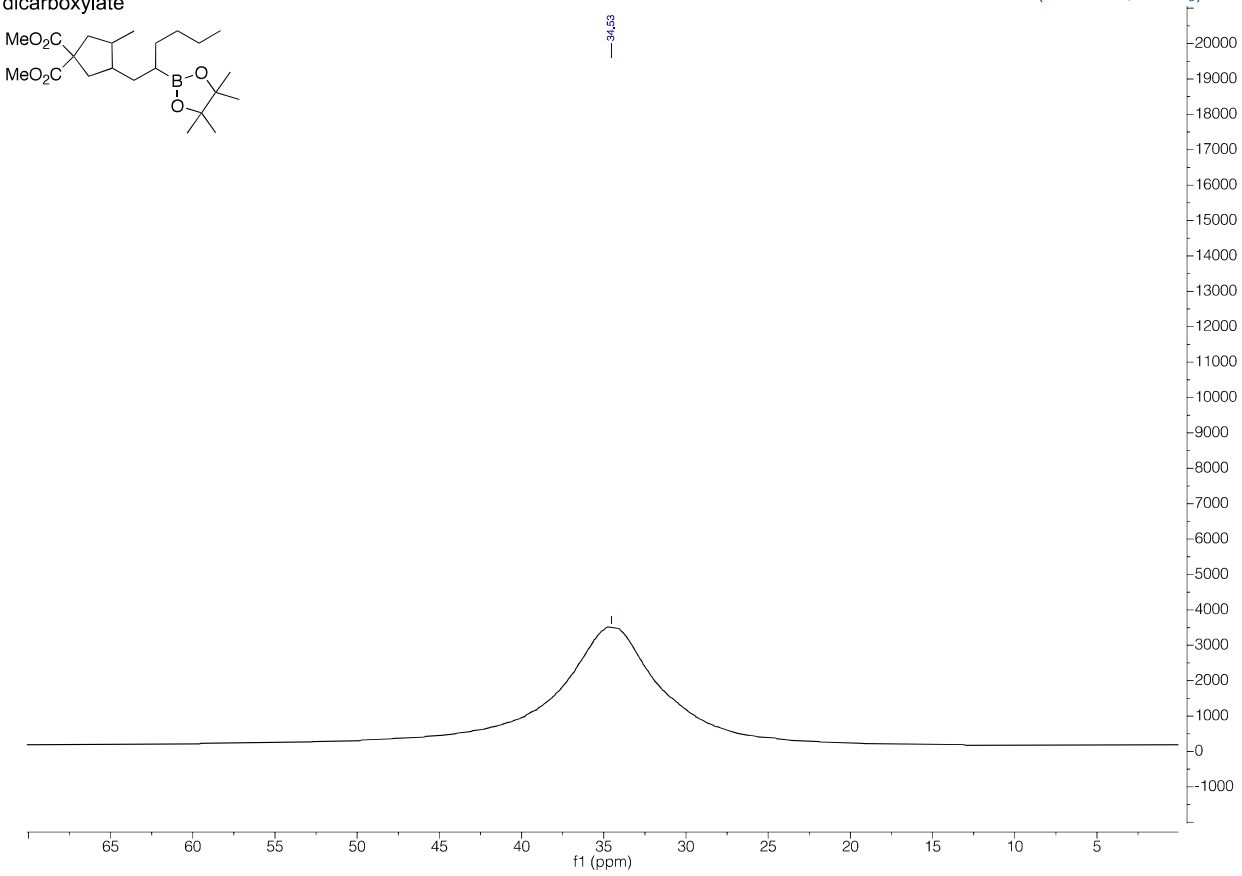
Dimethyl 3-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



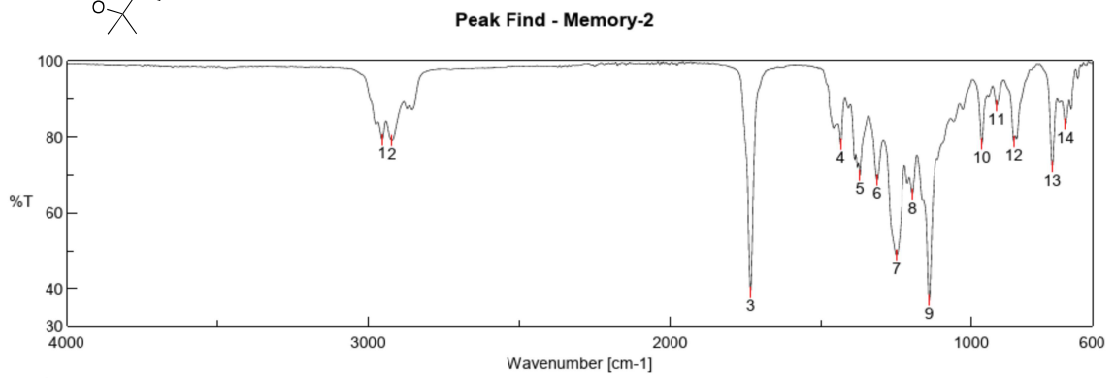
Dimethyl 3-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

^{11}B-NMR (128 MHz, $CDCl_3$)



Dimethyl 3-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond

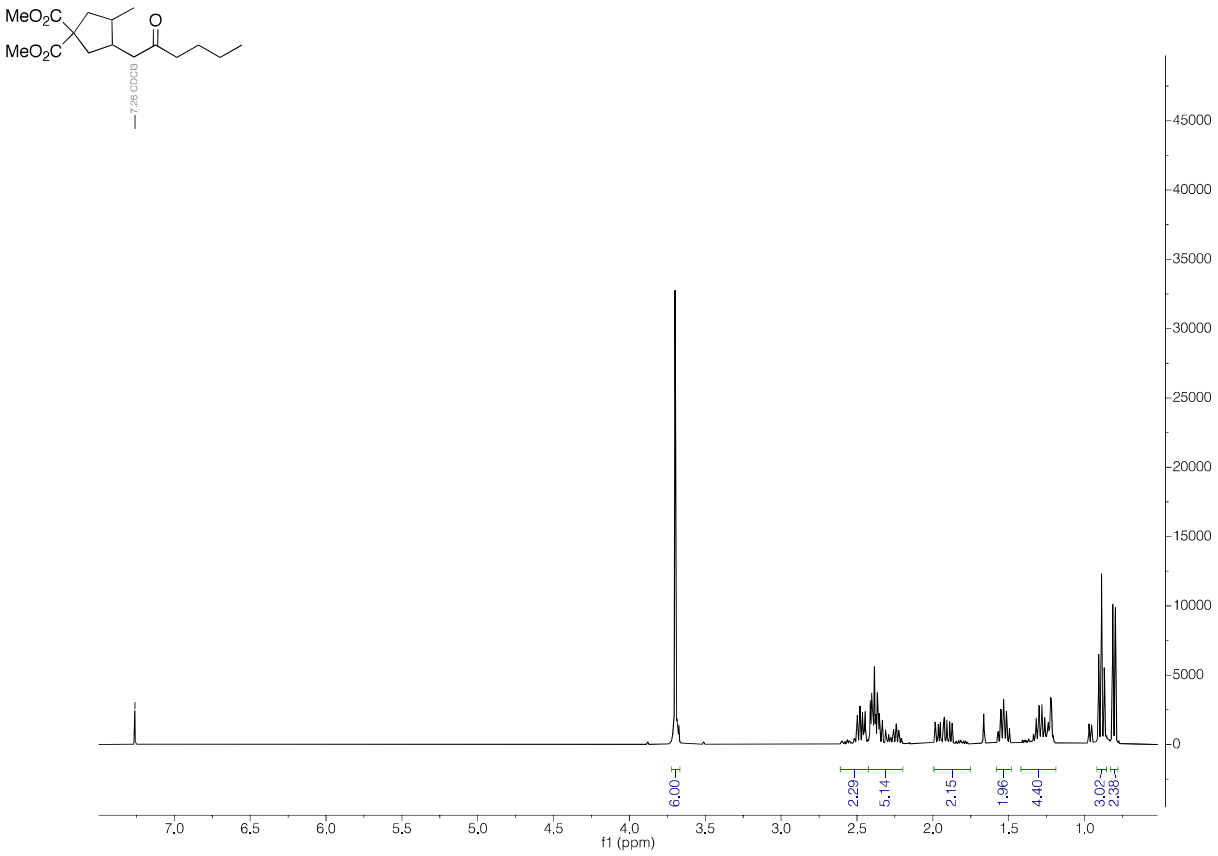


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2954.41	79.2319	2	2921.63	79.0574	3	1731.76	38.9759
4	1434.78	78.0219	5	1371.14	69.8316	6	1314.25	68.5824
7	1249.65	48.7377	8	1195.65	64.8321	9	1141.65	36.9662
10	965.198	78.1632	11	916.022	88.2283	12	860.096	78.7446
13	732.817	72.1523	14	689.427	83.386			

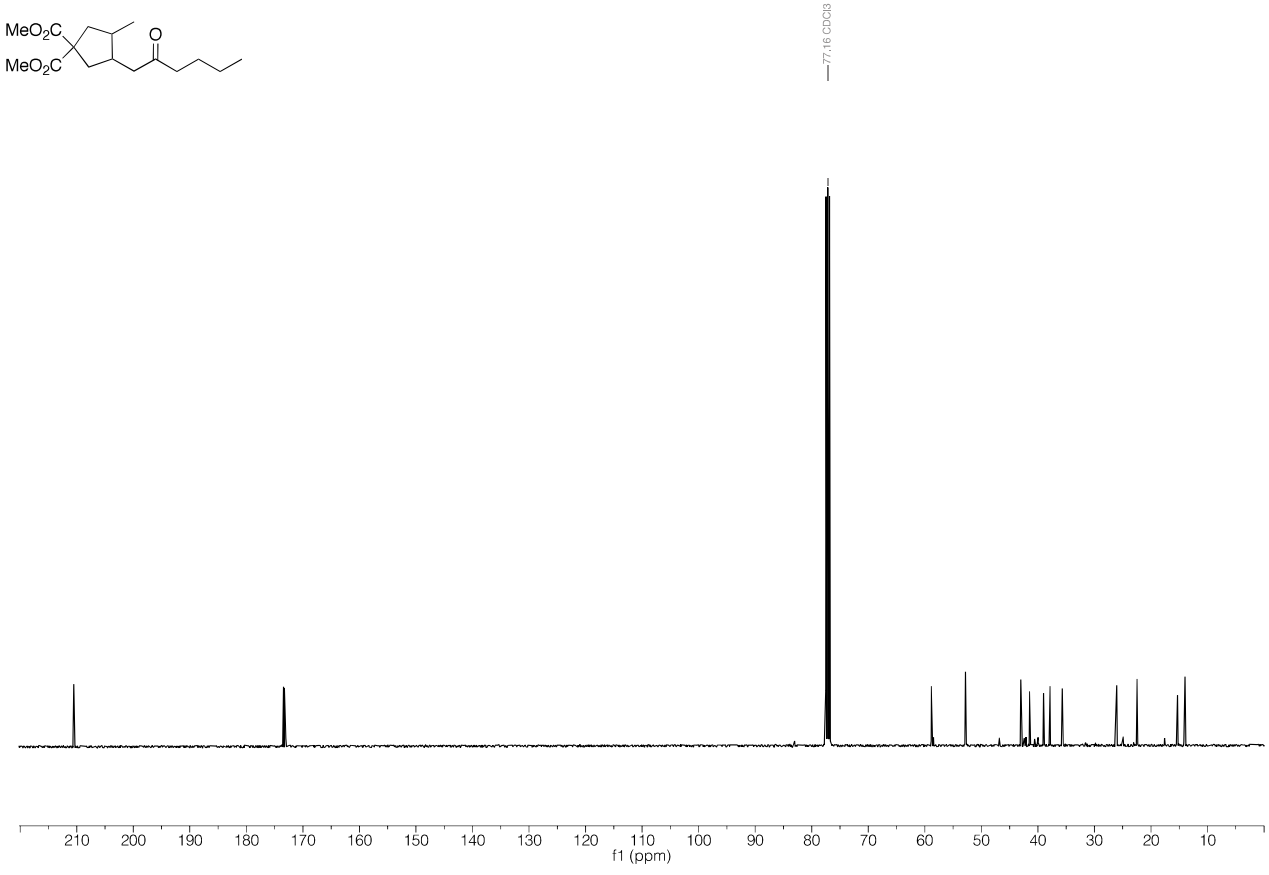
Dimethyl 3-methyl-4-(2-oxohexyl)cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)

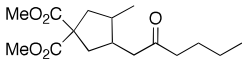


Dimethyl 3-methyl-4-(2-oxohexyl)cyclopentane-1,1-dicarboxylate

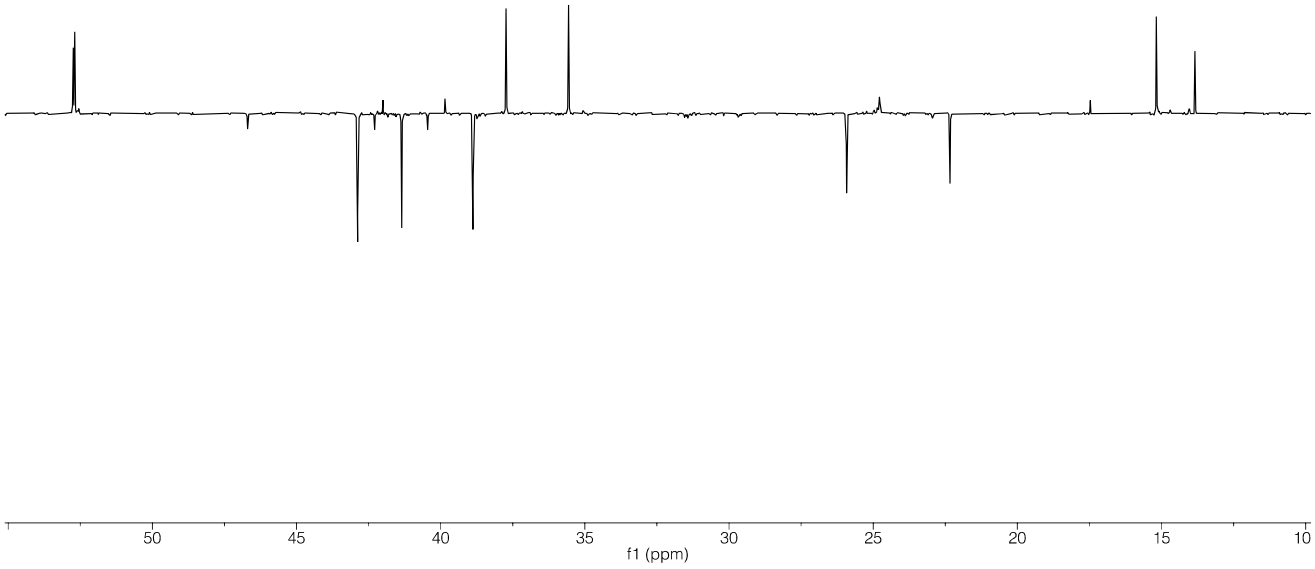
^{13}C-NMR (101 MHz, $CDCl_3$)



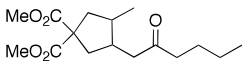
Dimethyl 3-methyl-4-(2-oxohexyl)cyclopentane-1,1-dicarboxylate



DEPT-135 NMR (101 MHz, $CDCl_3$)



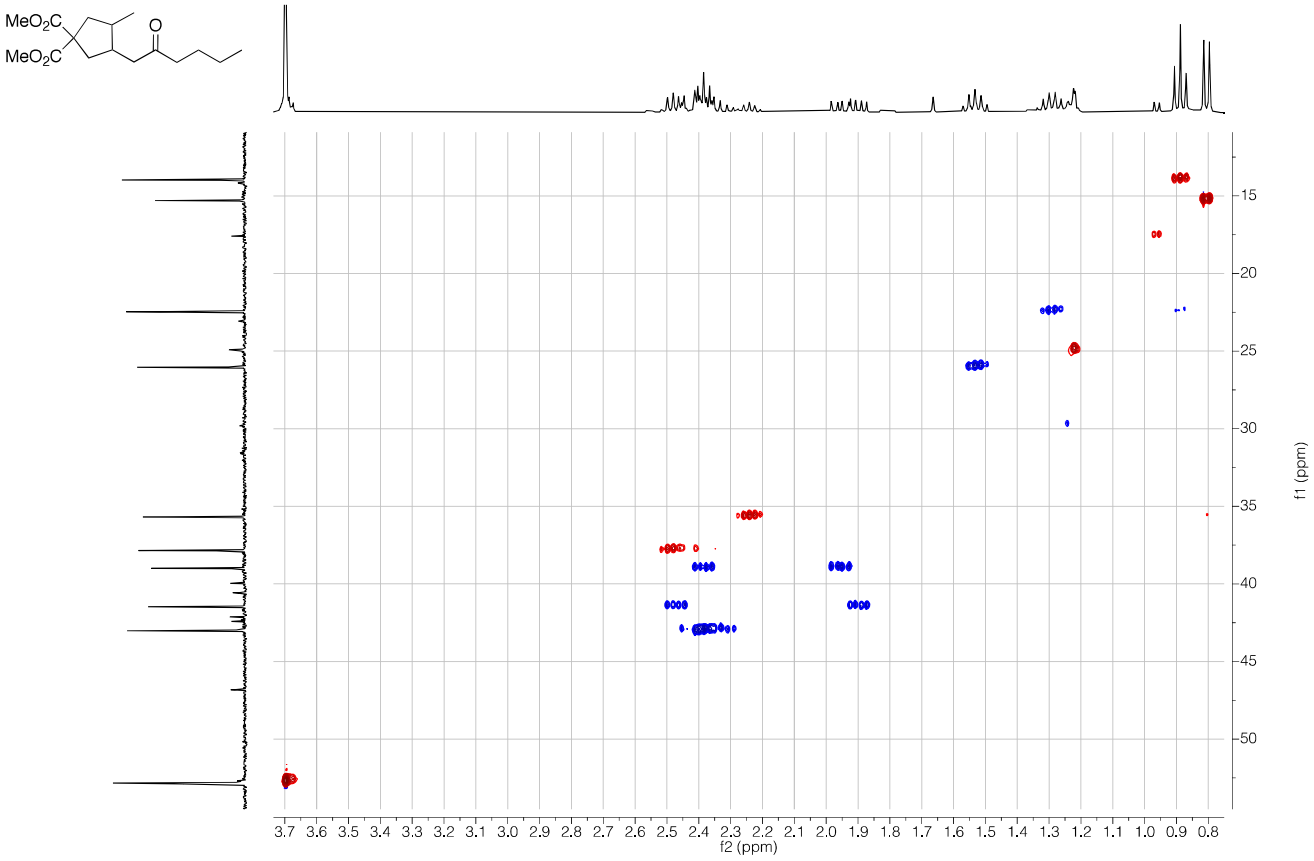
Dimethyl 3-methyl-4-(2-oxohexyl)cyclopentane-1,1-dicarboxylate



^1H, ^1H-COSY (400 MHz, $CDCl_3$)

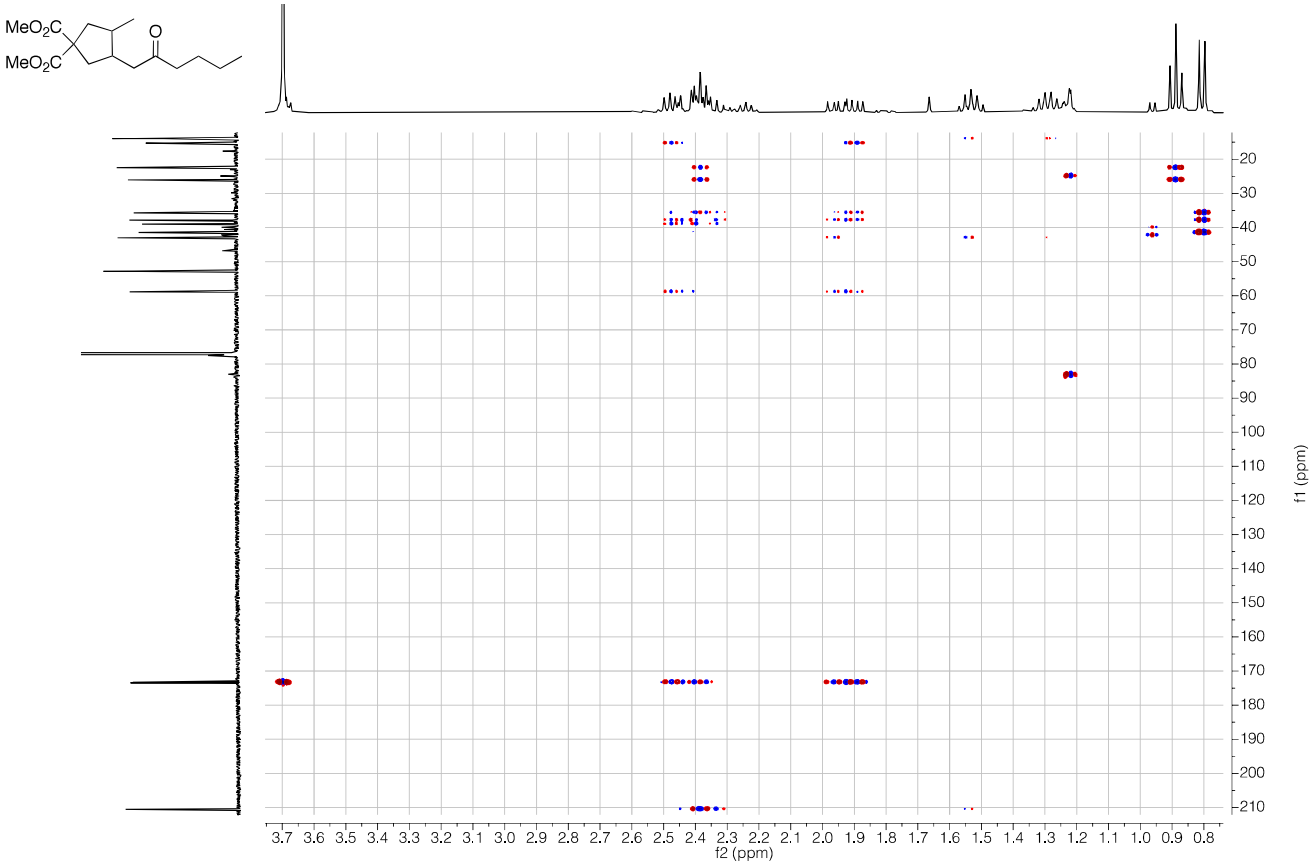
Dimethyl 3-methyl-4-(2-oxohexyl)cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



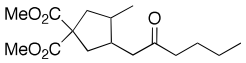
Dimethyl 3-methyl-4-(2-oxohexyl)cyclopentane-1,1-dicarboxylate

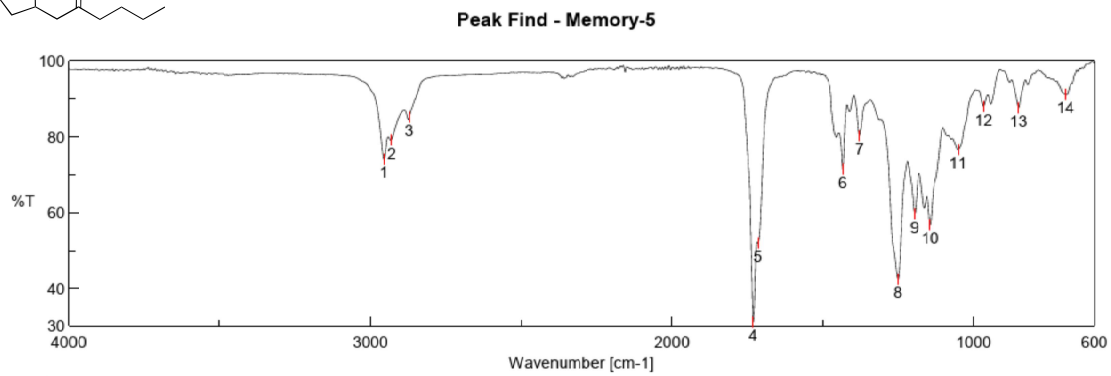
^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



Dimethyl 3-(2-hydroxyethyl)-4-methyl-cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



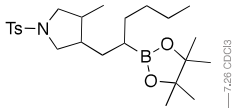


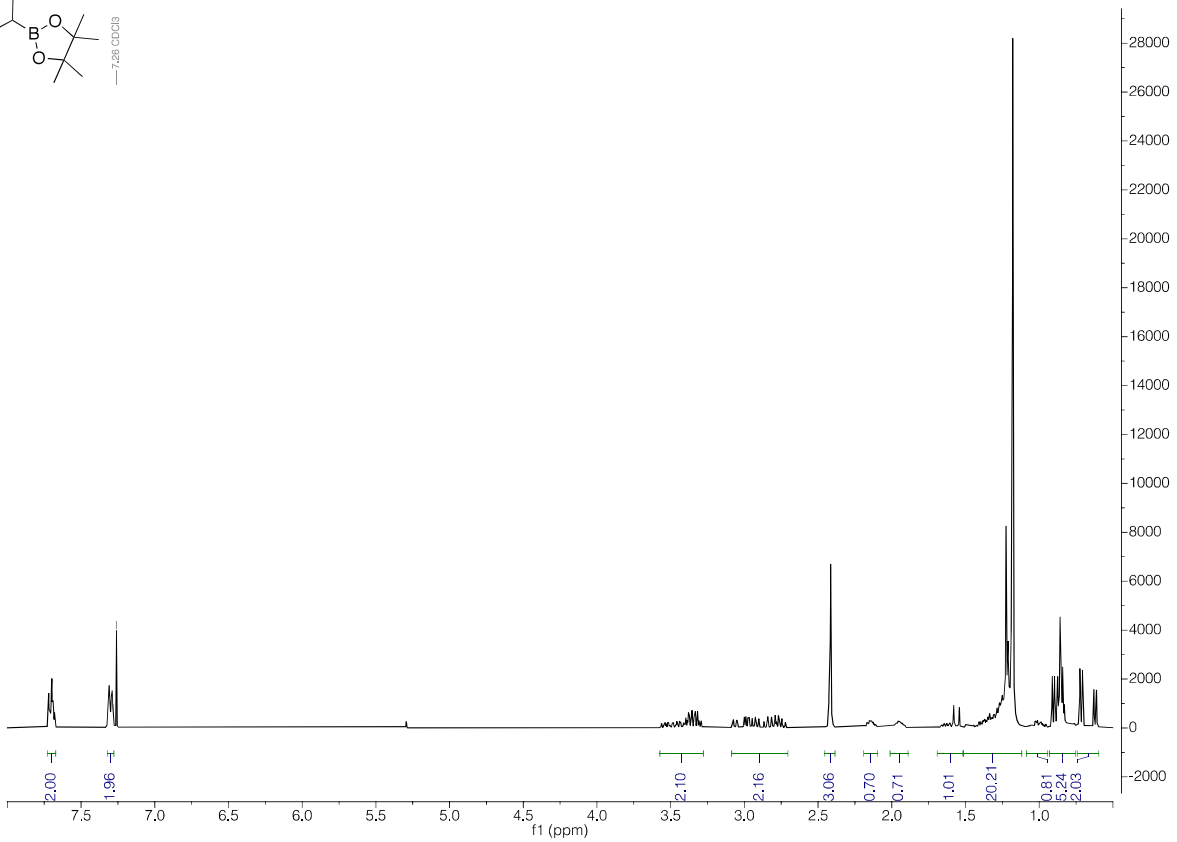
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2955.38	74.0213	2	2930.31	79.1617	3	2870.52	85.1752
4	1730.8	31.0684	5	1715.37	51.8982	6	1434.78	71.4468
7	1378.85	80.2405	8	1249.65	42.3552	9	1195.65	59.6558
10	1144.55	56.752	11	1051.98	76.576	12	967.126	87.9585
13	850.454	87.5954	14	695.212	91.1474			

3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

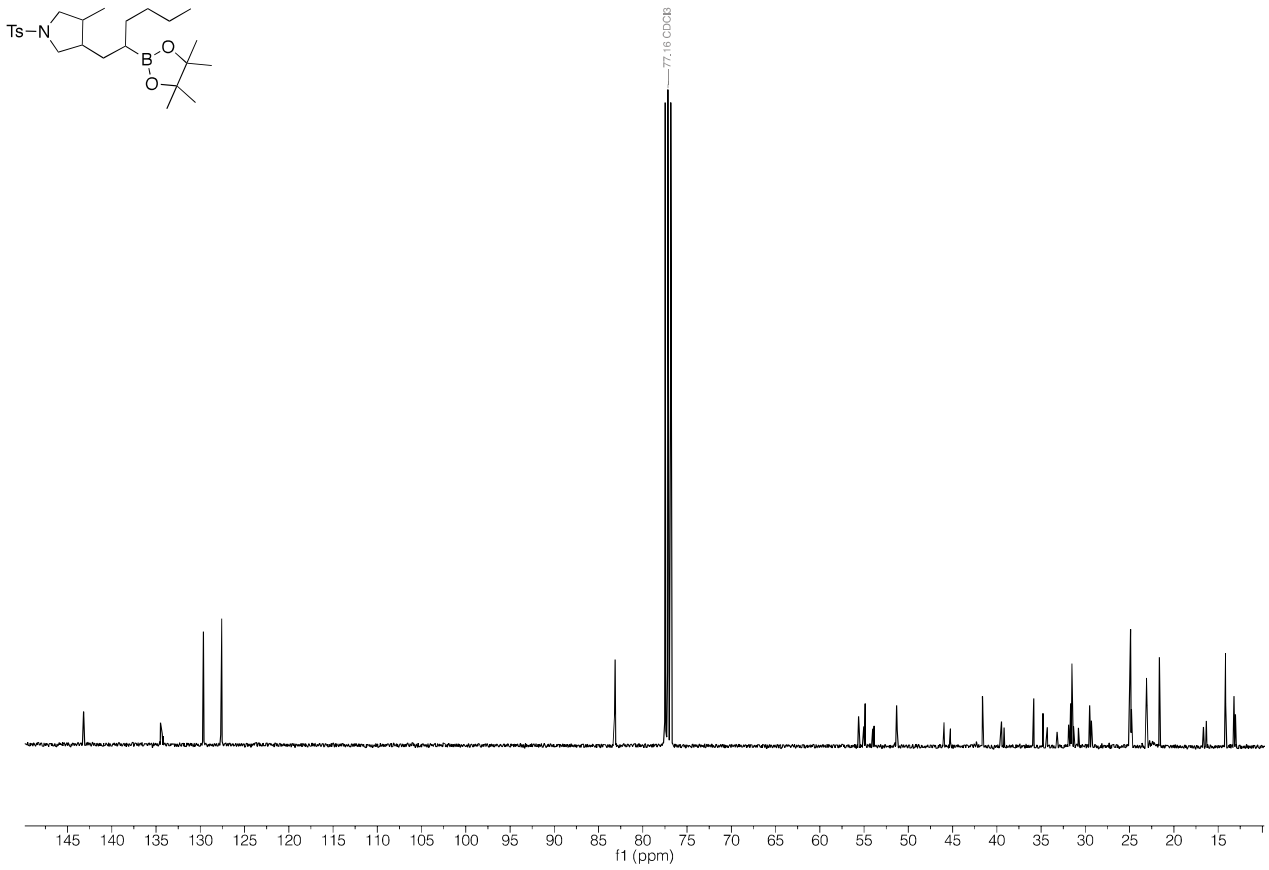
^{1}H-NMR (400 MHz, $CDCl_3$)





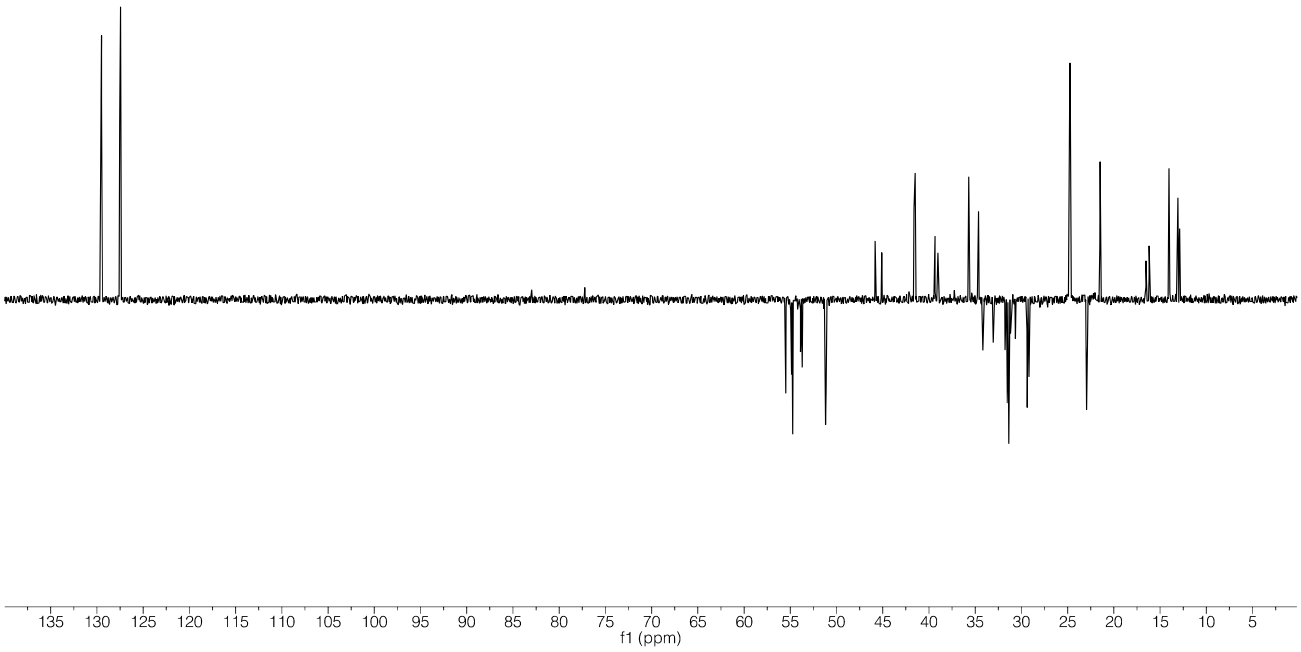
3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

^{13}C-NMR (101 MHz, $CDCl_3$)



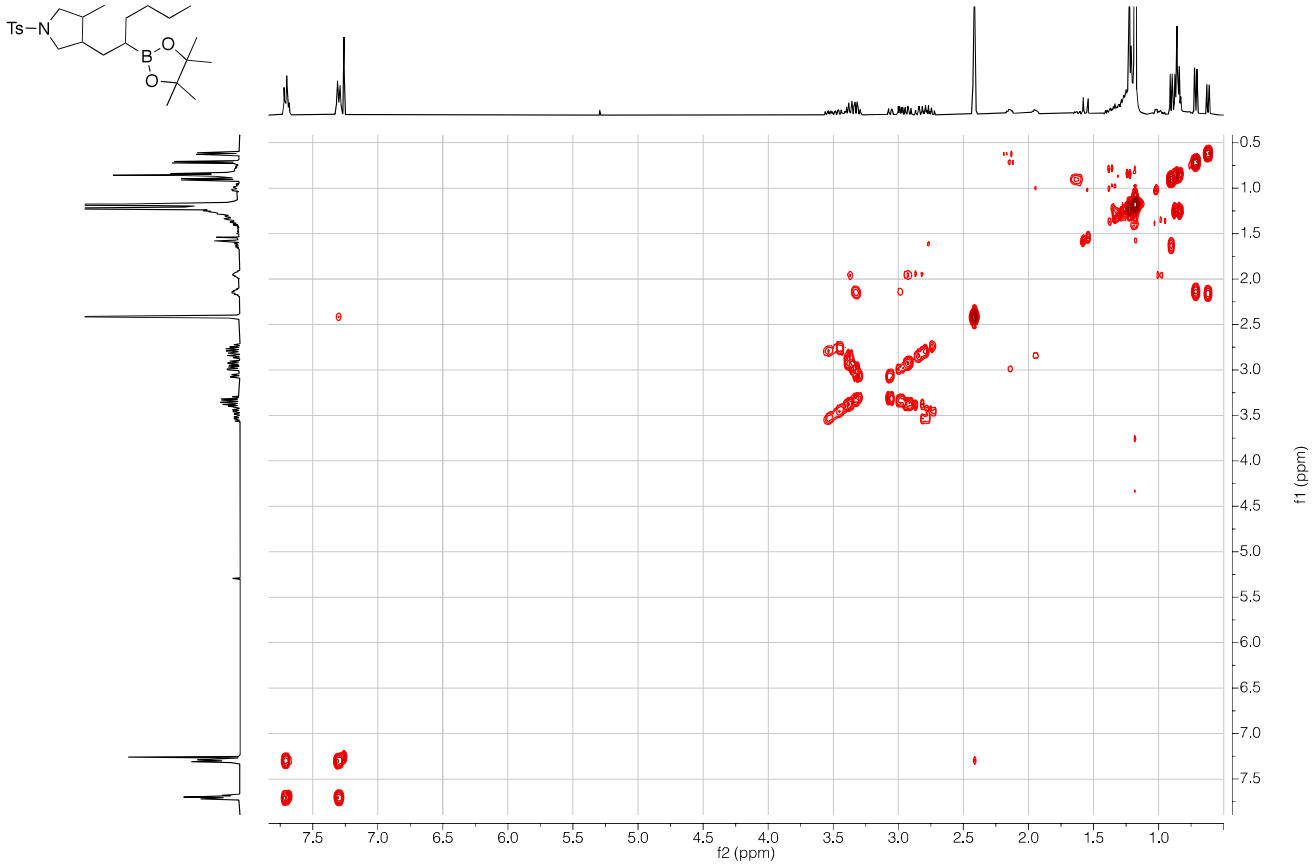
3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

DEPT-135 NMR (101 MHz, $CDCl_3$)



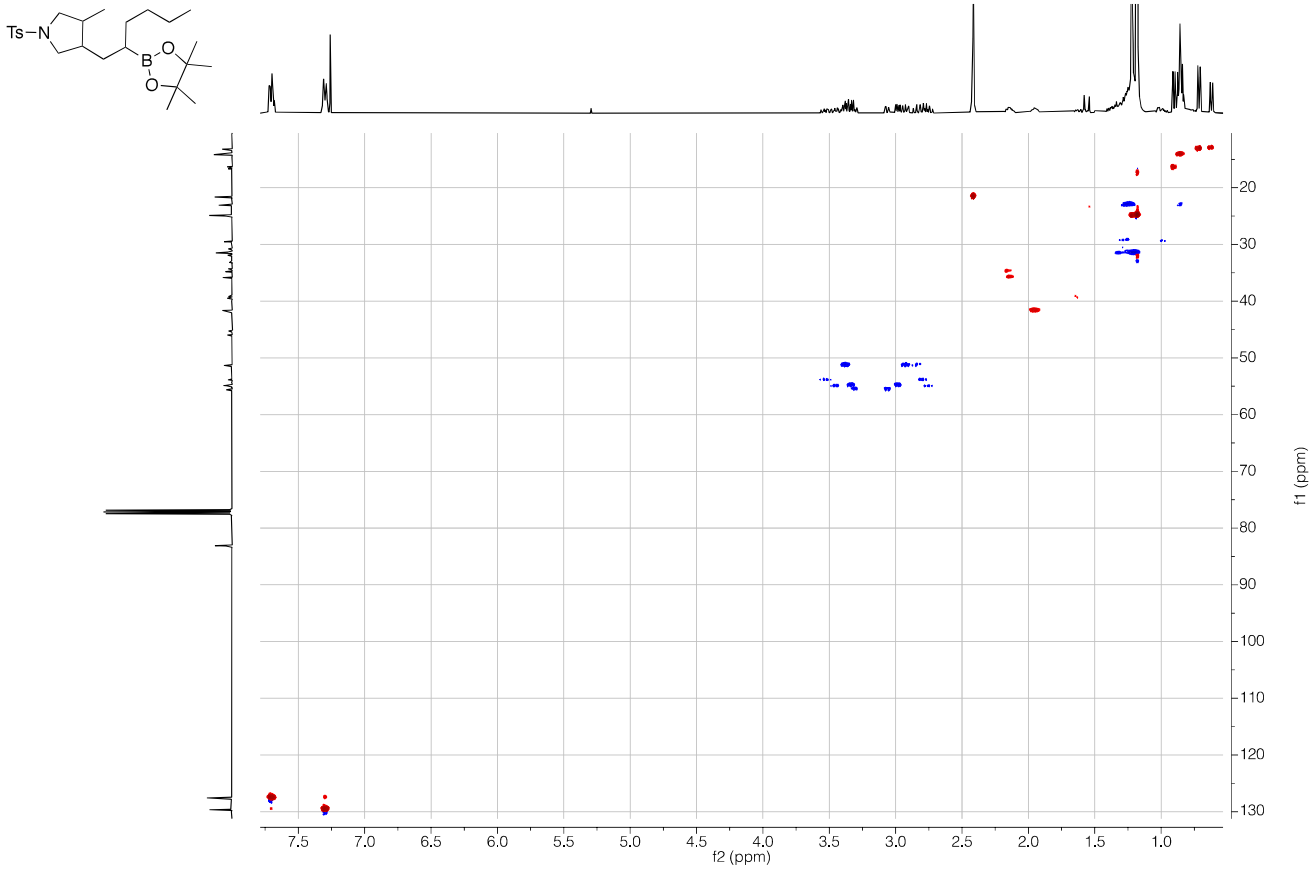
3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



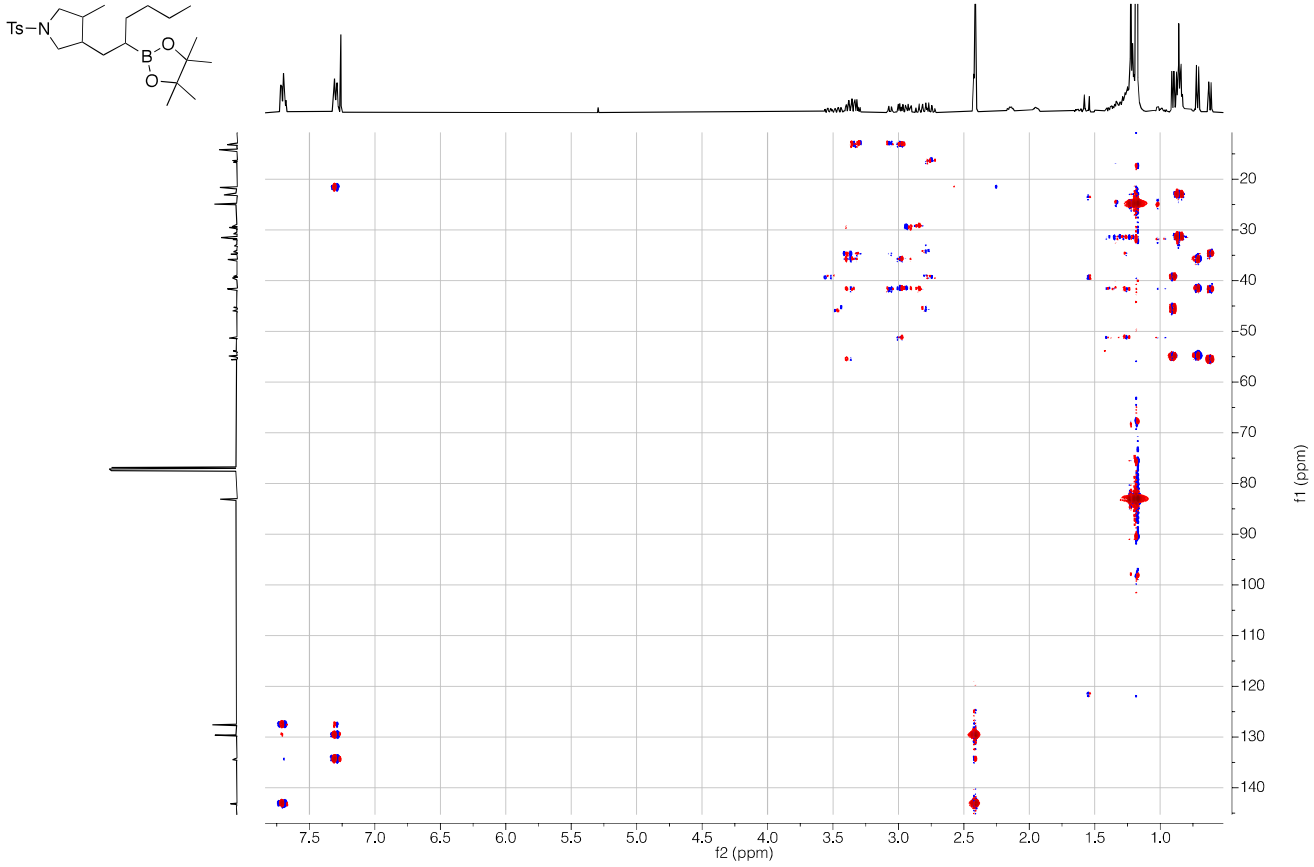
3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



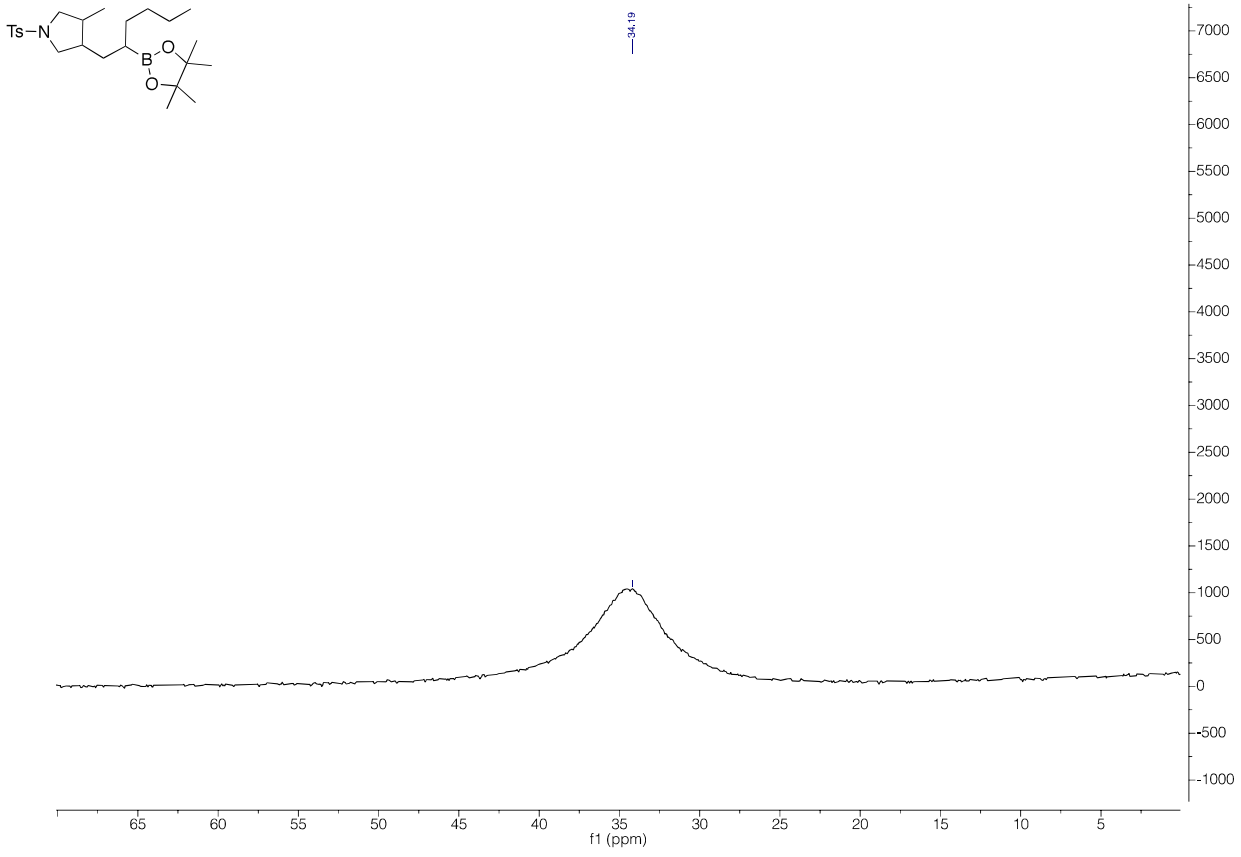
3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

^{1}H, ^{13}C-HMBC(400 MHz, $CDCl_3$)



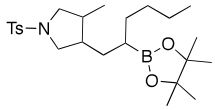
3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

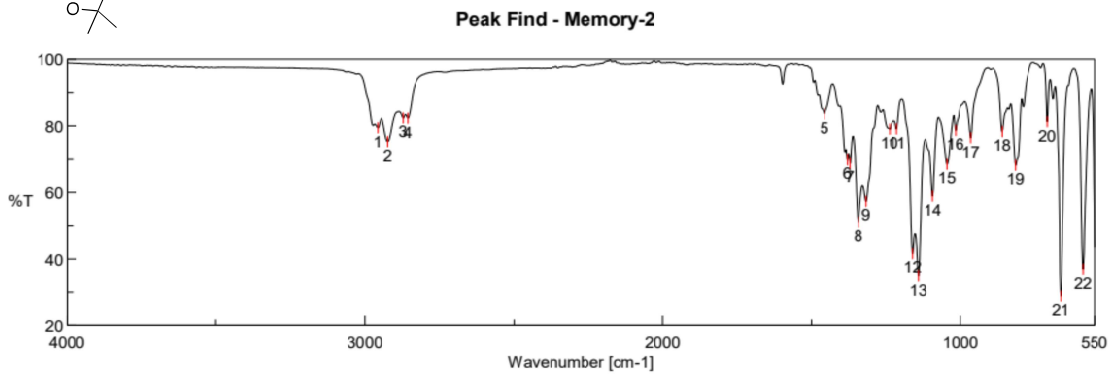
^{11}B-NMR (128 MHz, $CDCl_3$)



3-methyl-1-(p-tolylsulfonyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl]pyrrolidine

FT-IR, ATR-diamond



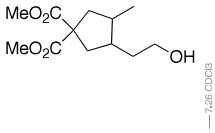


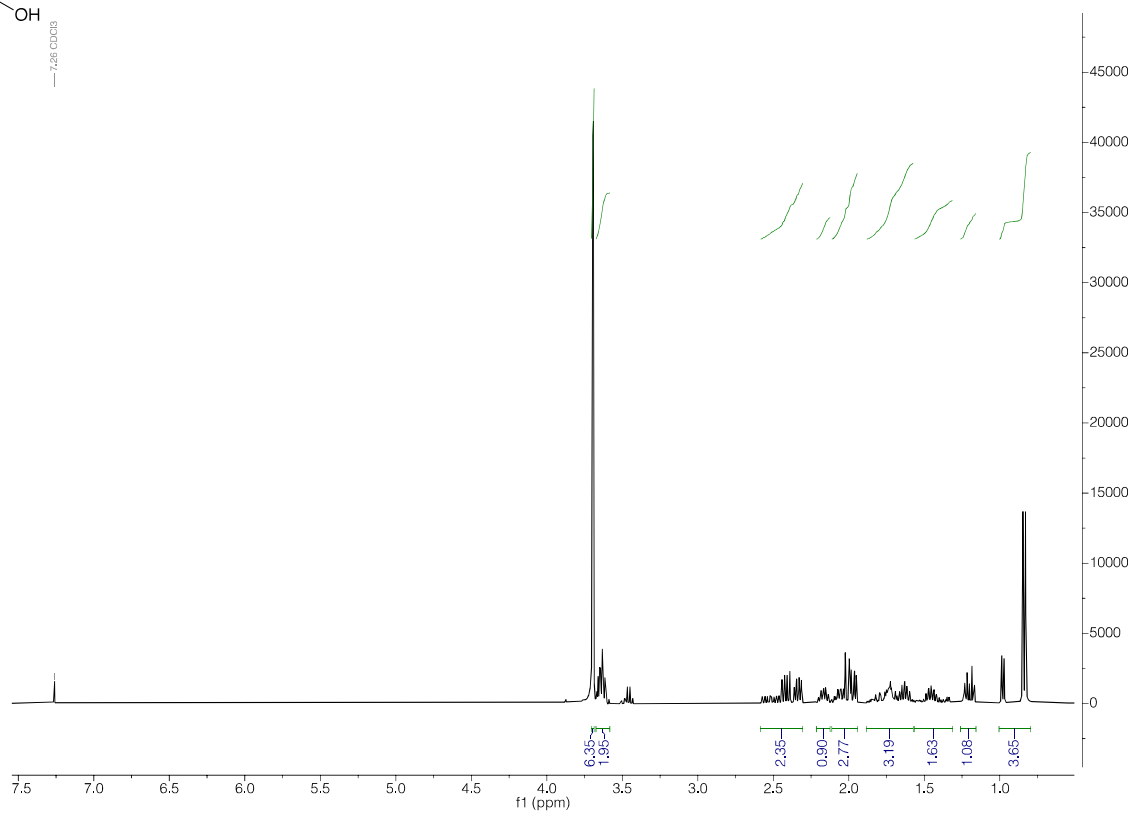
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2957.3	79.3656	2	2922.59	75.1991	3	2871.49	82.3592
4	2856.06	82.2933	5	1456.96	83.5704	6	1379.82	69.8121
7	1371.14	68.7621	8	1343.18	51.0252	9	1316.18	57.2372
10	1238.08	78.9518	11	1213.97	79.048	12	1160.94	41.5386
13	1141.65	34.8843	14	1093.44	58.8438	15	1045.23	68.4607
16	1016.3	78.5601	17	965.198	76.331	18	859.132	78.2289
19	814.777	68.1515	20	708.712	81.2293	21	662.428	28.7506
22	588.182	36.8193						

Dimethyl 3-(2-hydroxyethyl)-4-methyl-cyclopentane-1,1-dicarboxylate (mix of dias)

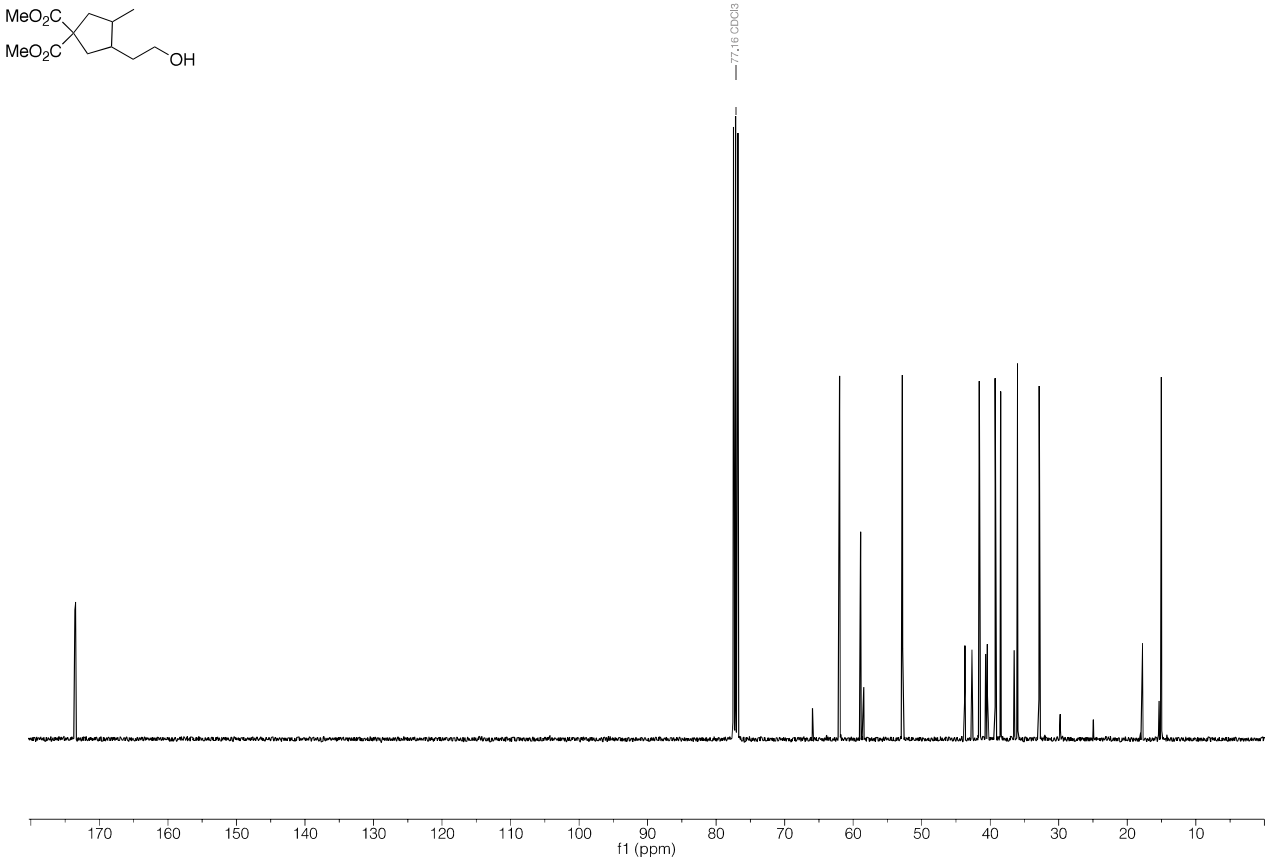
^{1}H-NMR (400 MHz, $CDCl_3$)





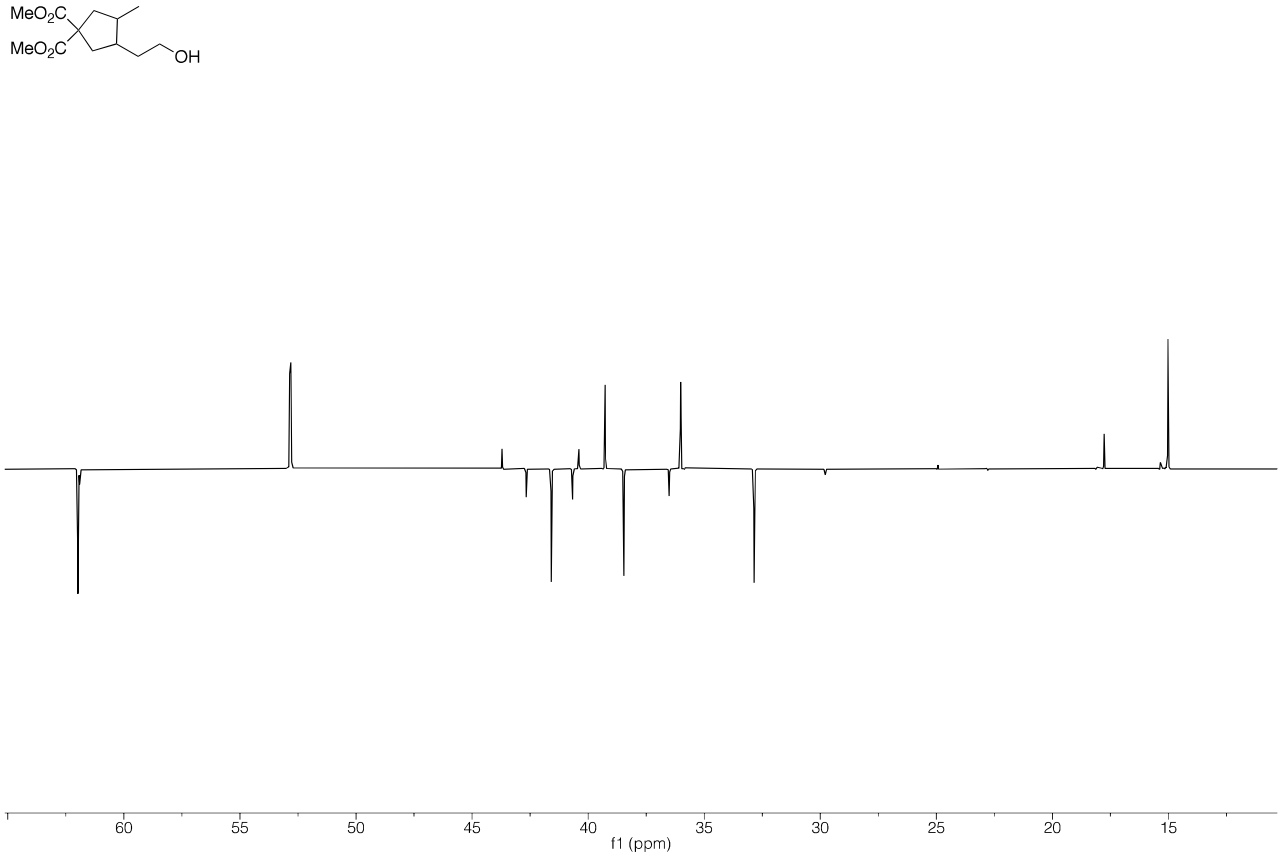
Dimethyl 3-(2-hydroxyethyl)-4-methyl-cyclopentane-1,1-dicarboxylate (mix of dias)

^{13}C-NMR (101 MHz, $CDCl_3$)



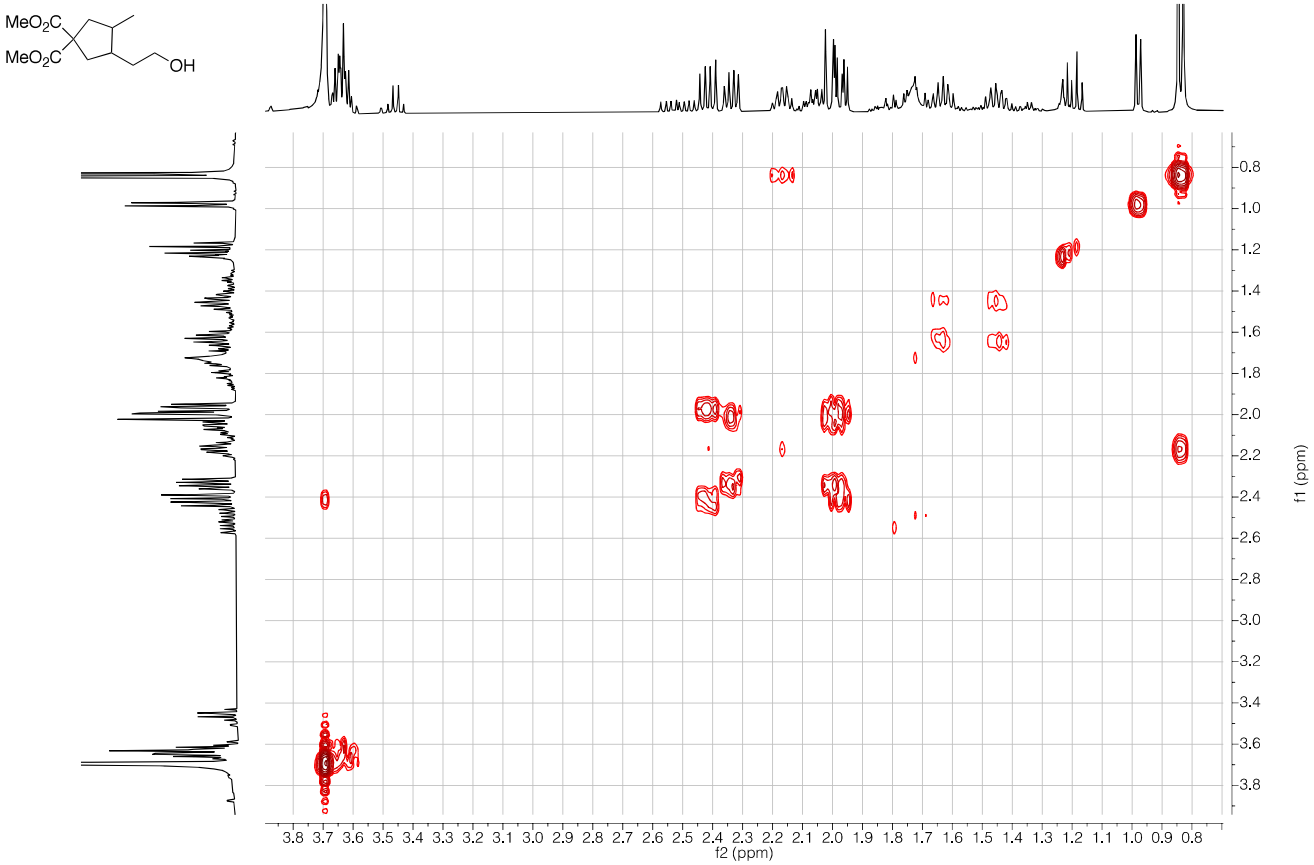
Dimethyl 3-(2-hydroxyethyl)-4-methyl-cyclopentane-1,1-dicarboxylate (mix of dias)

DEPT-135 NMR (101 MHz, $CDCl_3$)



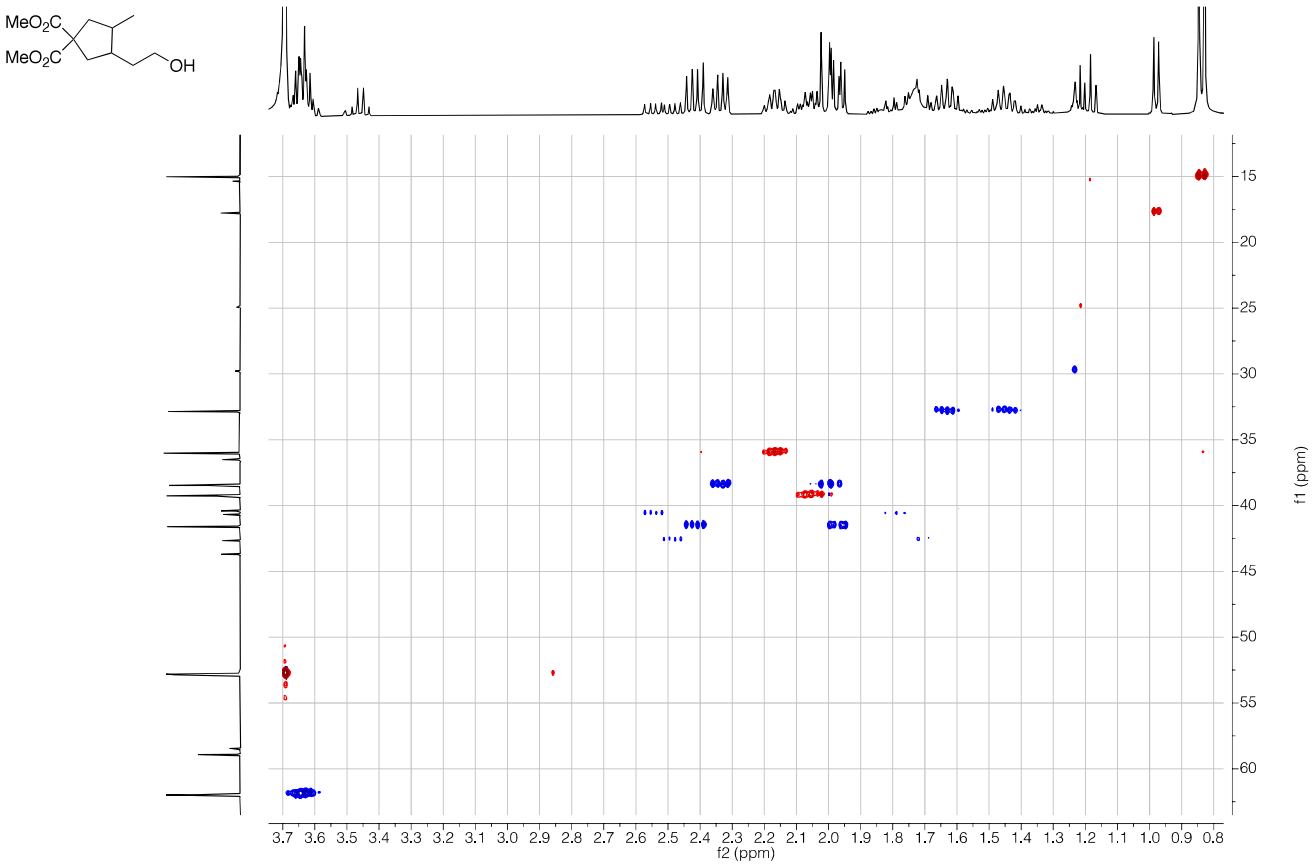
Dimethyl 3-(2-hydroxyethyl)-4-methyl-cyclopentane-1,1-dicarboxylate (mix of dias)

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



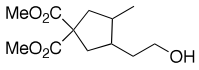
Dimethyl 3-(2-hydroxyethyl)-4-methyl-cyclopentane-1,1-dicarboxylate (mix of dias)

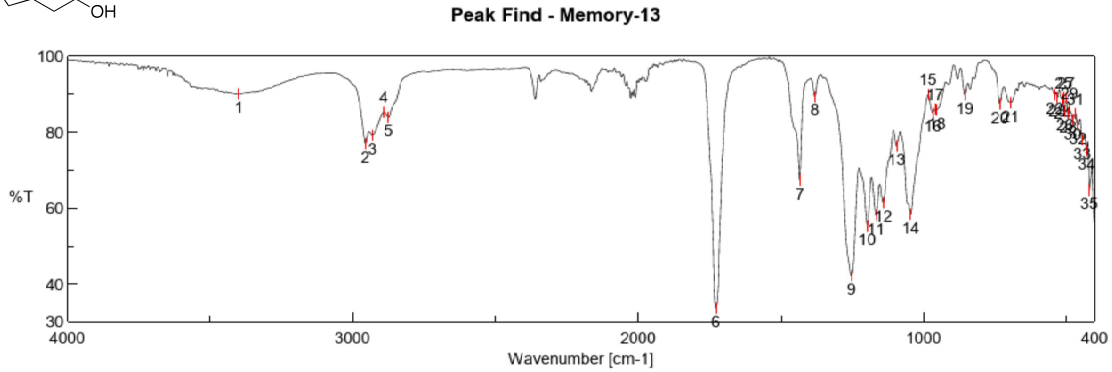
^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



Dimethyl 3-(2-hydroxyethyl)-4-methyl-cyclopentane-1,1-dicarboxylate (mix of dias)

FT-IR, ATR-diamond



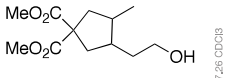


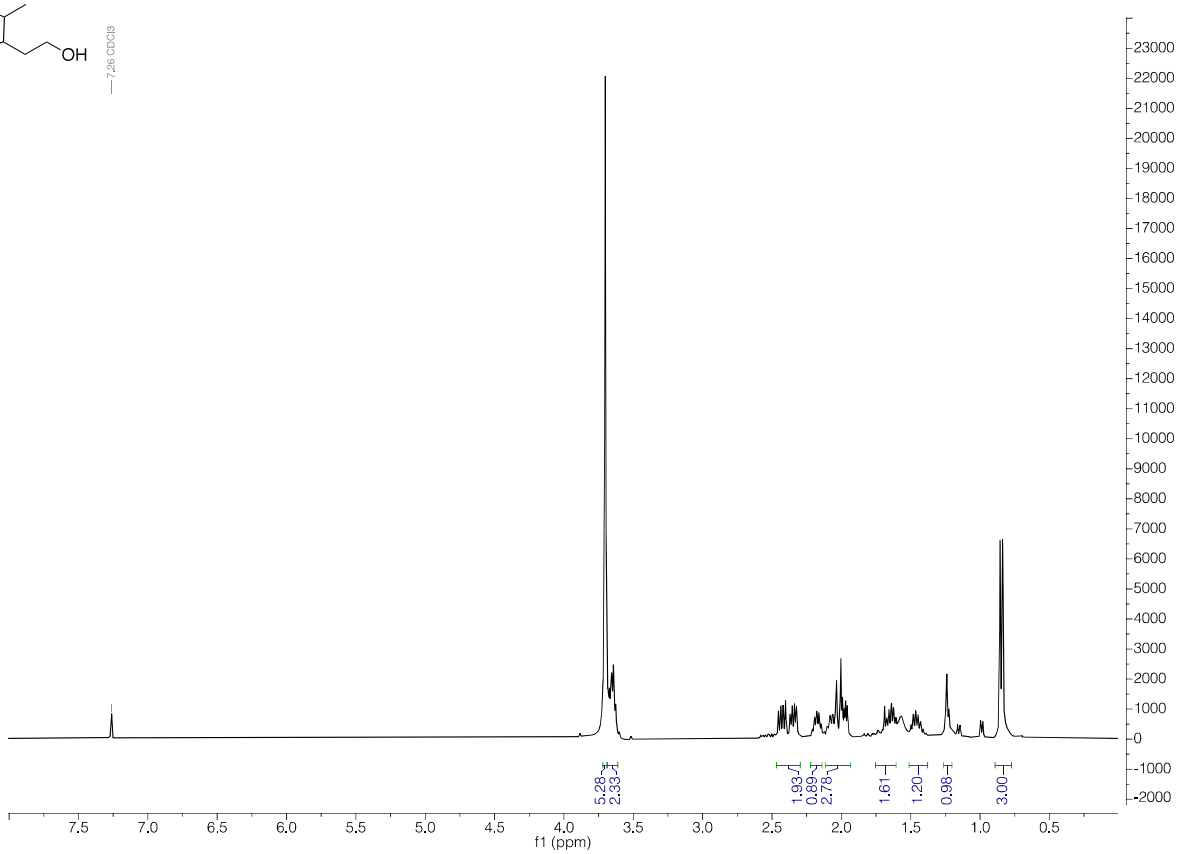
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3397.96	90.0425	2	2954.41	76.8709	3	2929.34	79.1252
4	2890.77	85.1856	5	2875.34	83.8378	6	1726.94	33.6099
7	1433.82	67.2871	8	1380.78	89.2281	9	1251.58	42.142
10	1197.58	55.1911	11	1166.72	58.0714	12	1140.69	61.3573
13	1094.4	76.3107	14	1045.23	58.3196	15	984.482	89.8206
16	968.09	85.0063	17	959.412	85.95	18	952.663	85.8365
19	854.311	89.7725	20	731.853	87.3637	21	695.212	87.7136
22	539.971	89.8163	23	531.293	89.061	24	512.972	88.5746
25	509.115	89.0993	26	504.294	85.4651	27	499.473	88.9093
28	492.723	84.7829	29	487.902	86.0996	30	476.331	83.1123
31	466.689	84.8319	32	458.011	81.7976	33	442.583	77.932
34	427.155	75.0827	35	418.477	64.55			

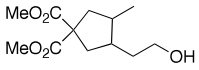
Dimethyl 3-(2-hydroxyethyl)-4-methyl-cyclopentane-1,1-dicarboxylate (major dia)

^{1}H-NMR (400 MHz, $CDCl_3$)



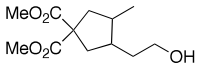


Dimethyl 3-(2-hydroxyethyl)-4-methyl-cyclopentane-1,1-dicarboxylate (major dia)

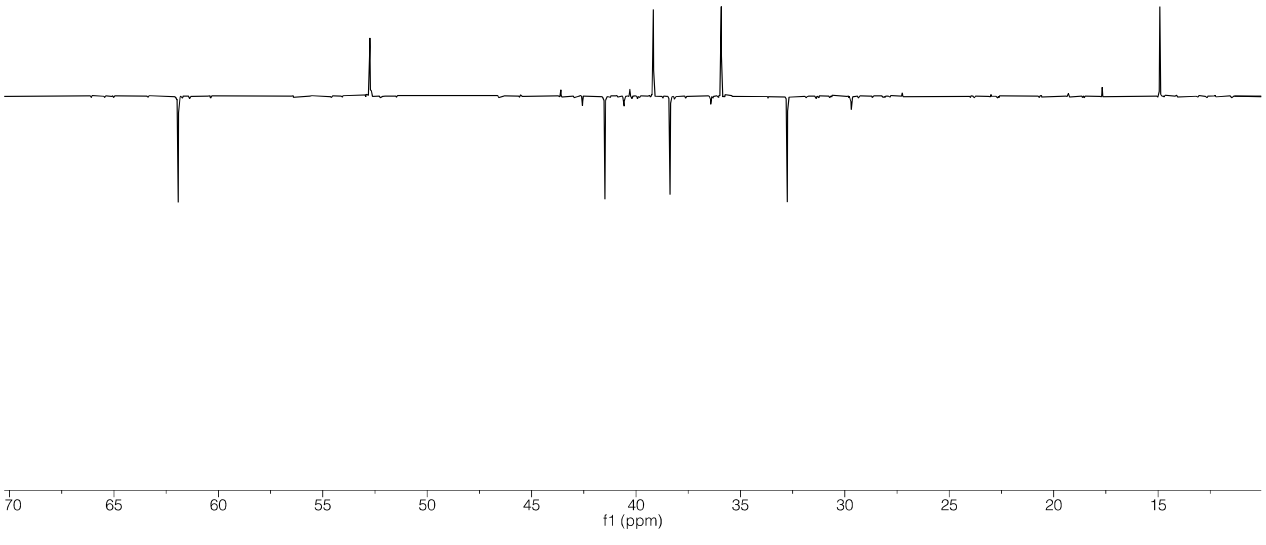


^{13}C-NMR (101 MHz, $CDCl_3$)

Dimethyl 3-(2-hydroxyethyl)-4-methyl-cyclopentane-1,1-dicarboxylate (major dia)

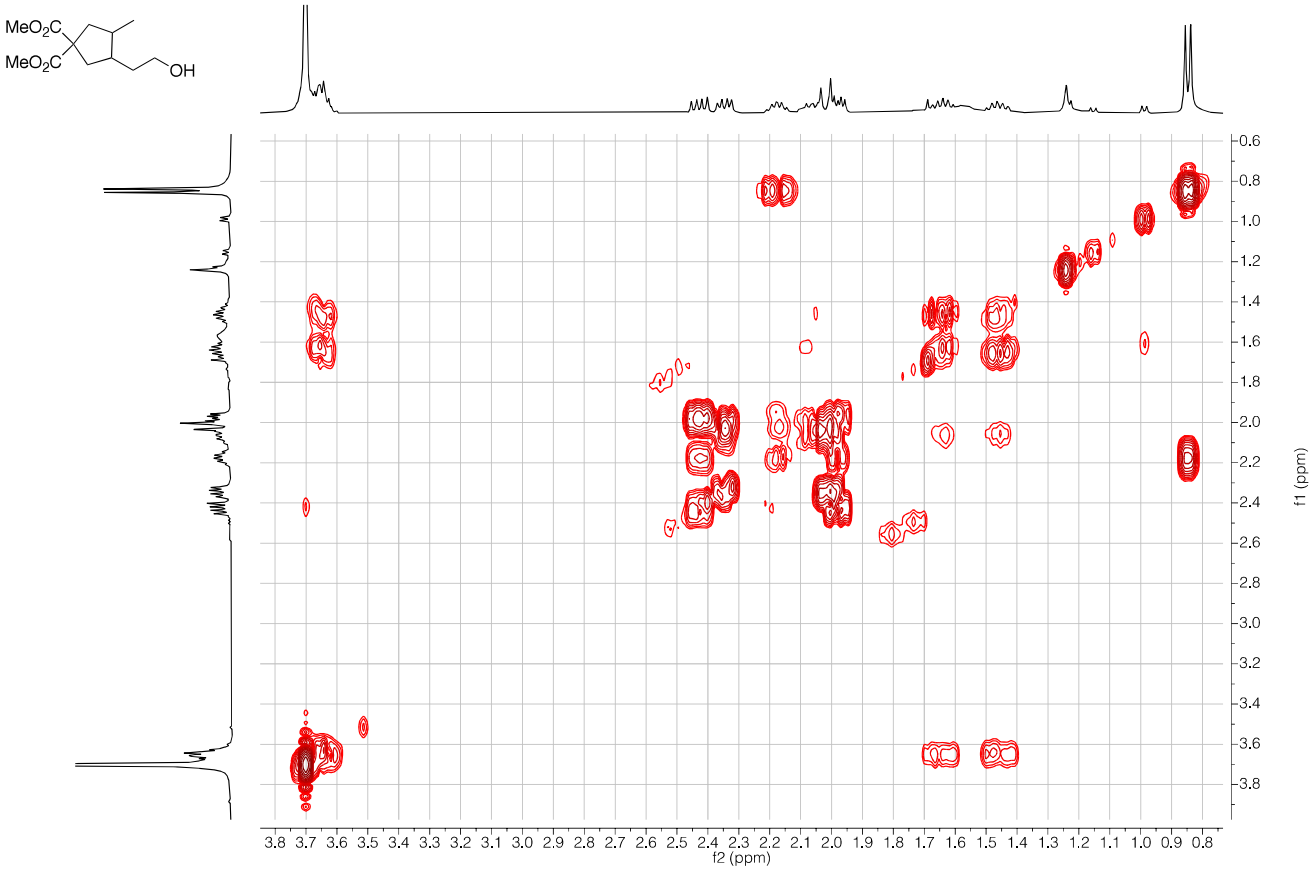


DEPT-135 NMR (101 MHz, $CDCl_3$)



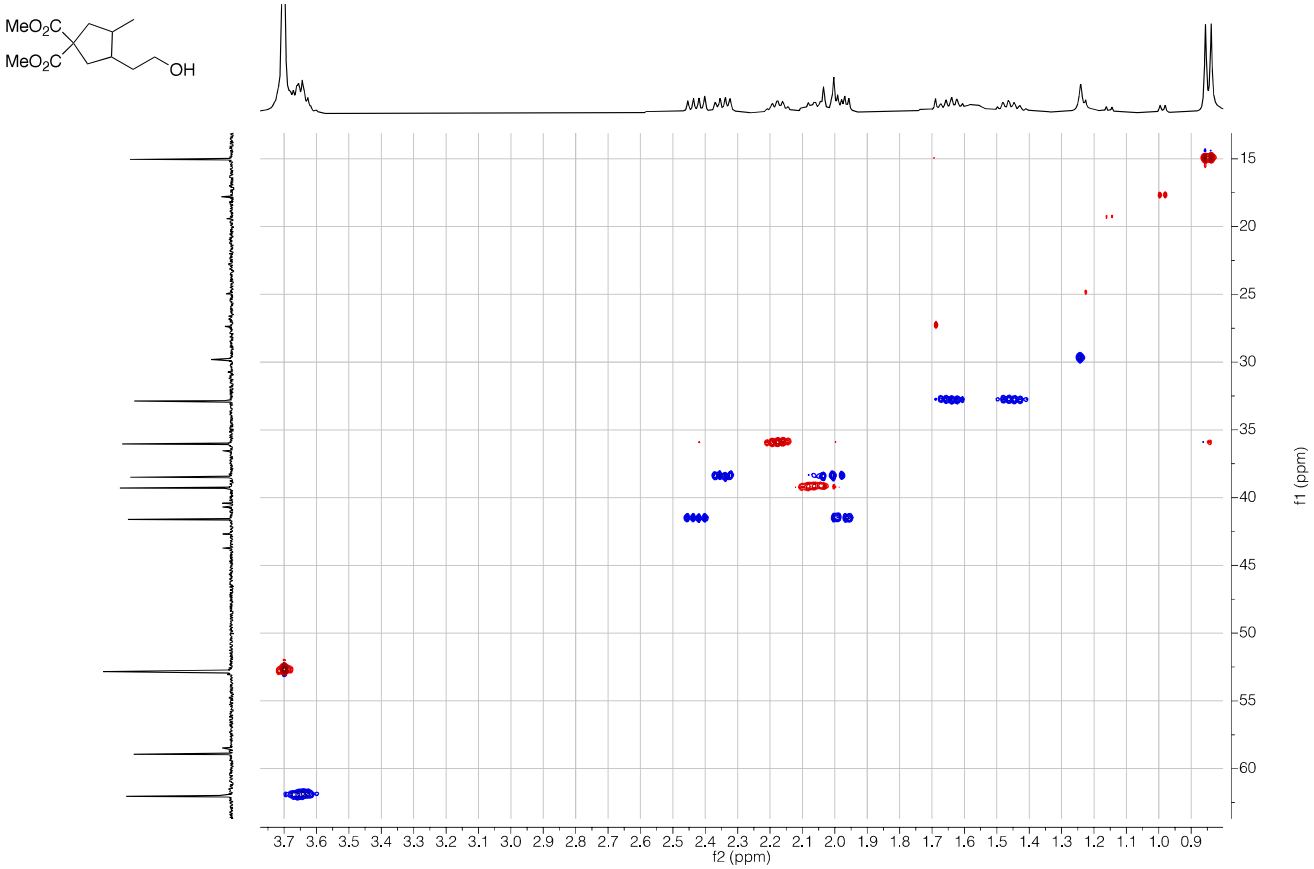
Dimethyl 3-(2-hydroxyethyl)-4-methyl-cyclopentane-1,1-dicarboxylate (major dia)

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



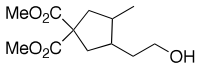
Dimethyl 3-(2-hydroxyethyl)-4-methyl-cyclopentane-1,1-dicarboxylate (major dia)

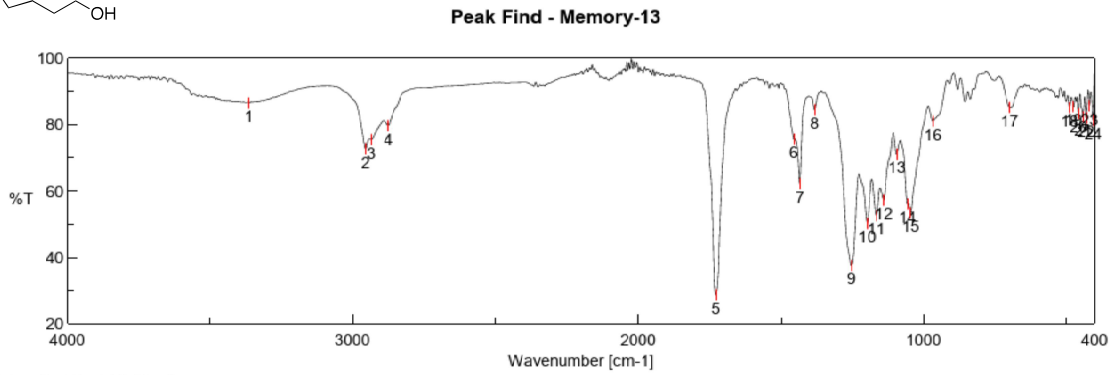
^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



Dimethyl 3-(2-hydroxyethyl)-4-methyl-cyclopentane-1,1-dicarboxylate (major dia)

FT-IR, ATR-diamond



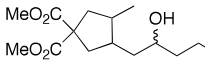


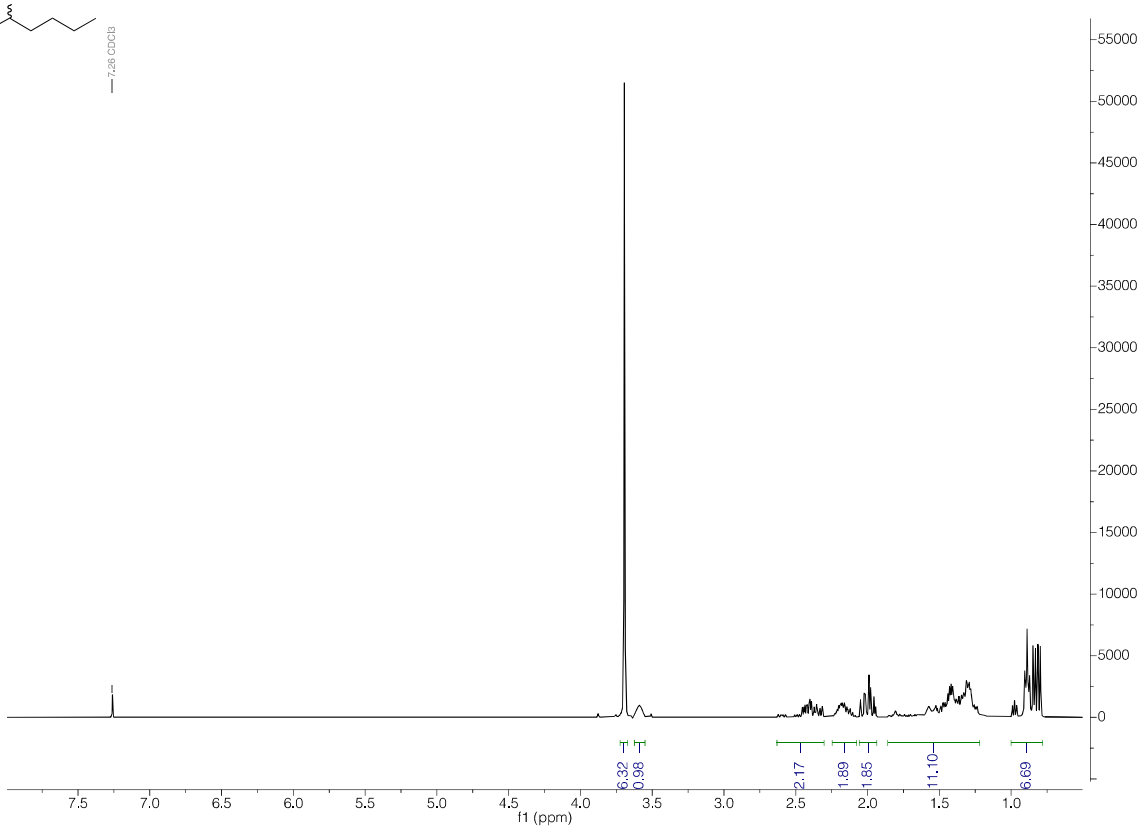
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3362.28	86.4513	2	2953.45	72.6597	3	2934.16	75.5074
4	2875.34	79.5731	5	1726.94	28.7298	6	1455.03	75.5951
7	1433.82	62.1681	8	1381.75	84.4211	9	1251.58	37.5206
10	1196.61	50.2146	11	1165.76	52.5928	12	1139.72	57.2443
13	1093.44	70.998	14	1056.8	56.0587	15	1045.23	53.4286
16	967.126	81.0062	17	698.105	85.1251	18	487.902	85.0549
19	473.439	85.3531	20	456.082	83.2954	21	439.69	82.2203
22	429.084	81.9464	23	417.513	85.5674	24	404.014	81.2429

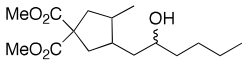
Dimethyl 3-(2-hydroxyhexyl)-4-methyl-cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)



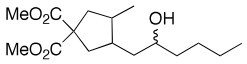


Dimethyl 3-(2-hydroxyhexyl)-4-methyl-cyclopentane-1,1-dicarboxylate

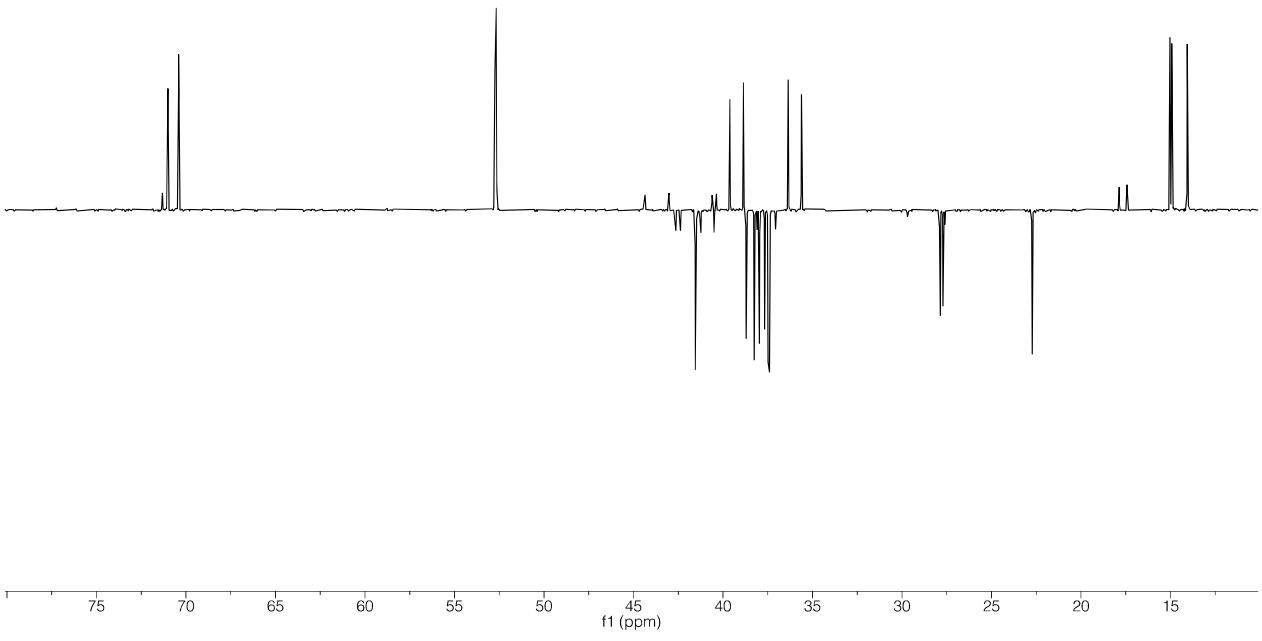


^{13}C-NMR (101 MHz, $CDCl_3$)

Dimethyl 3-(2-hydroxyhexyl)-4-methyl-cyclopentane-1,1-dicarboxylate

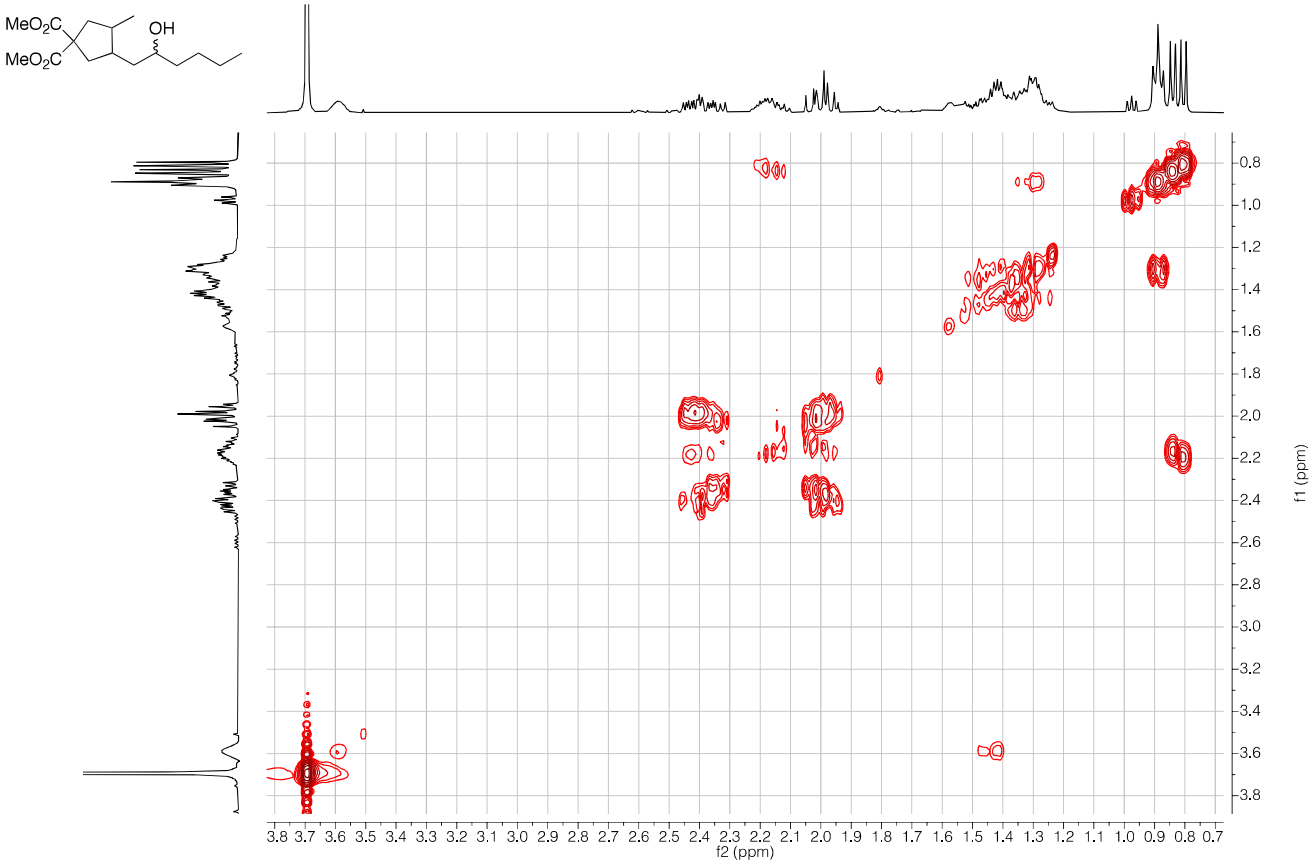


DEPT-135 NMR (101 MHz, $CDCl_3$)



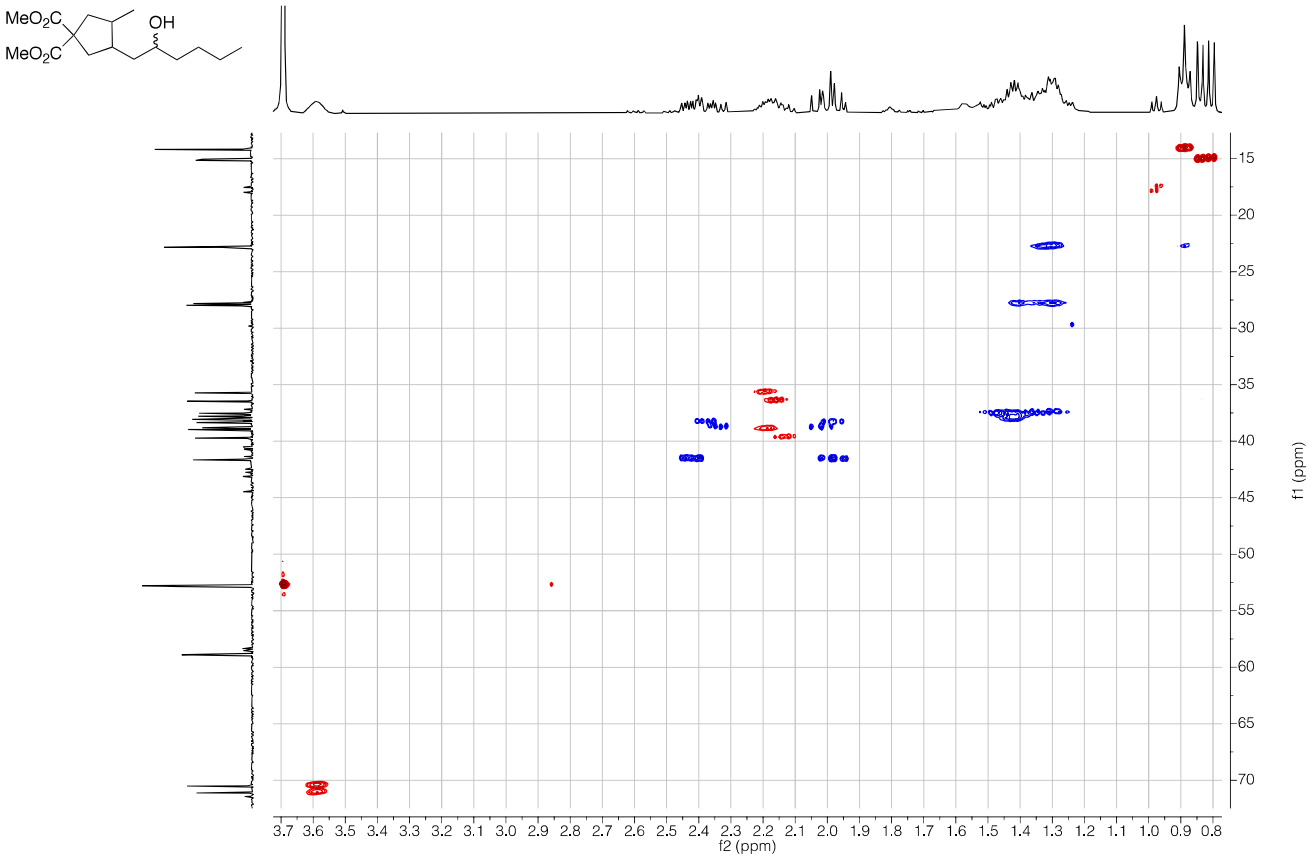
Dimethyl 3-(2-hydroxyhexyl)-4-methyl-cyclopentane-1,1-dicarboxylate

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



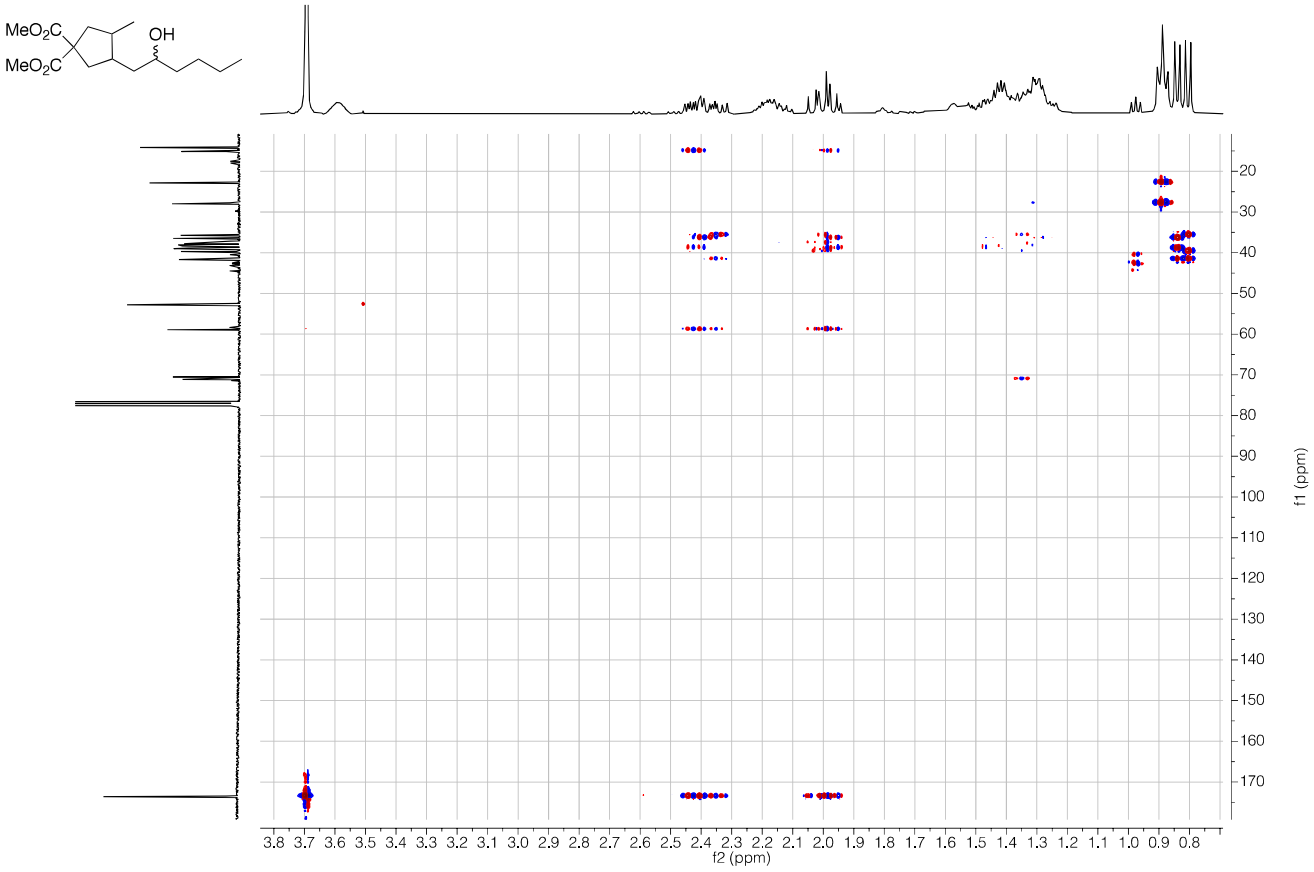
Dimethyl 3-(2-hydroxyhexyl)-4-methyl-cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



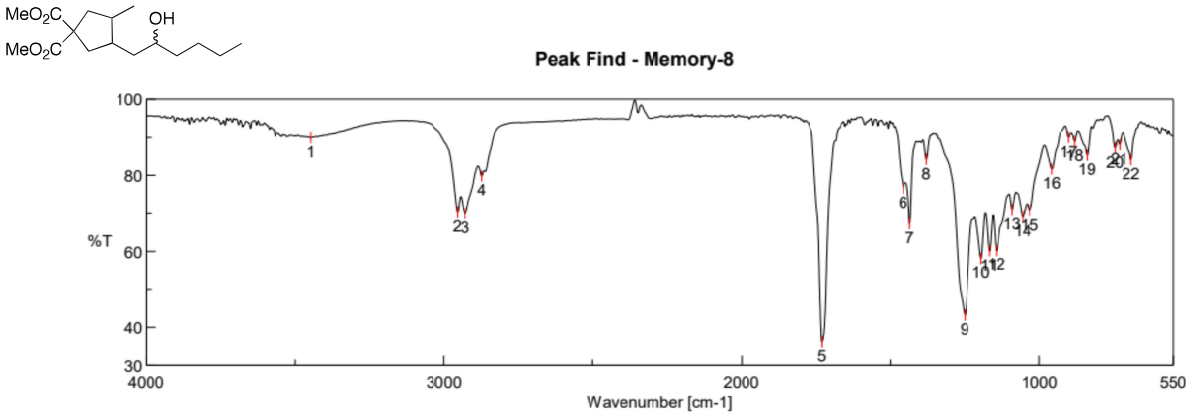
Dimethyl 3-(2-hydroxyhexyl)-4-methyl-cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



Dimethyl 3-(2-hydroxyhexyl)-4-methyl-cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond

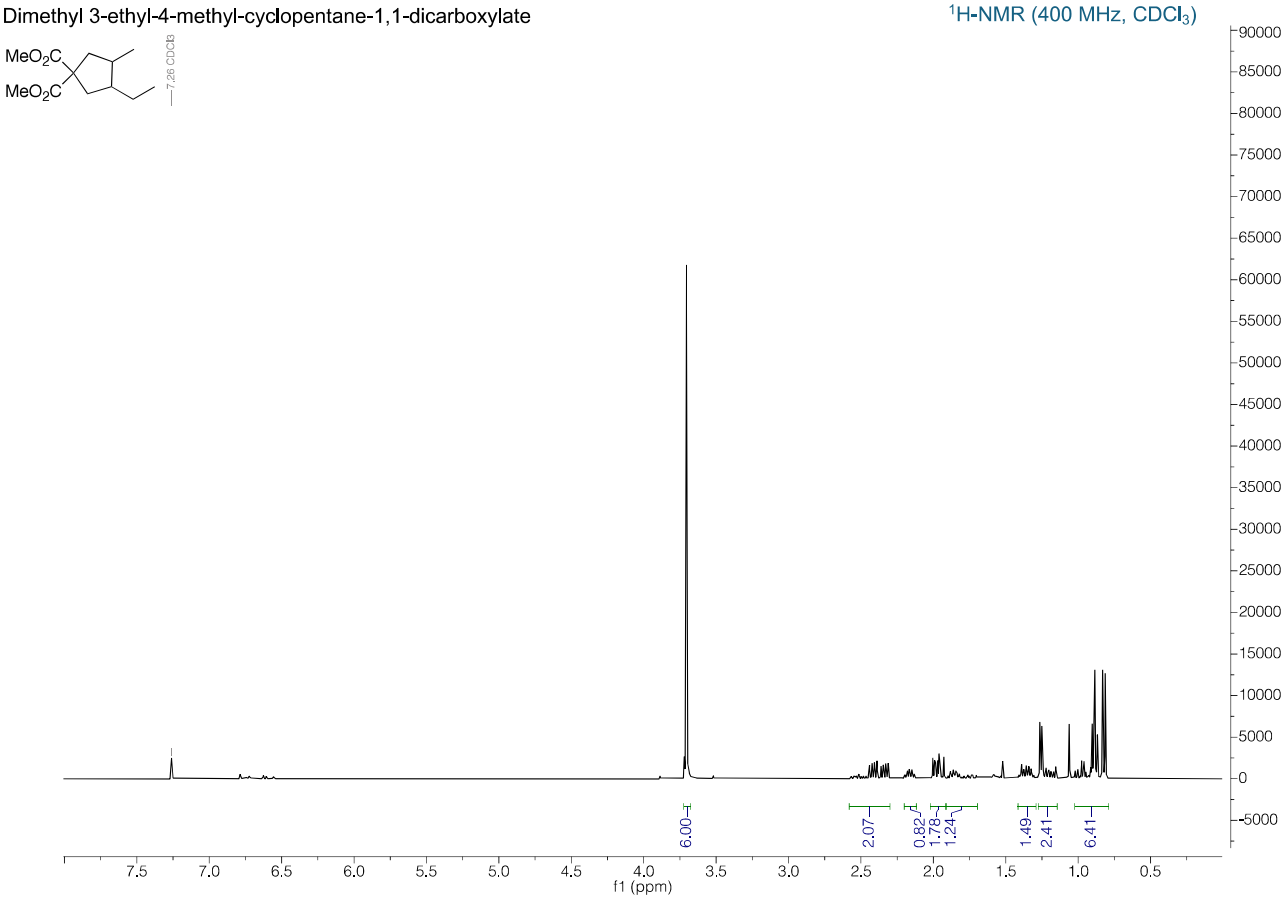


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3446.17	89.8727	2	2954.41	70.2159	3	2929.34	69.9649
4	2872.45	79.7446	5	1729.83	36.1079	6	1456.96	76.5154
7	1434.78	67.3132	8	1379.82	84.211	9	1250.61	43.2114
10	1196.61	58.0122	11	1167.69	60.1157	12	1144.55	60.1623
13	1091.51	70.8734	14	1054.87	69.0989	15	1031.73	70.7554
16	958.448	81.6612	17	900.594	89.9882	18	880.345	88.9677
19	838.883	85.3304	20	746.317	87.23	21	730.889	88.0703
22	692.32	84.0997						

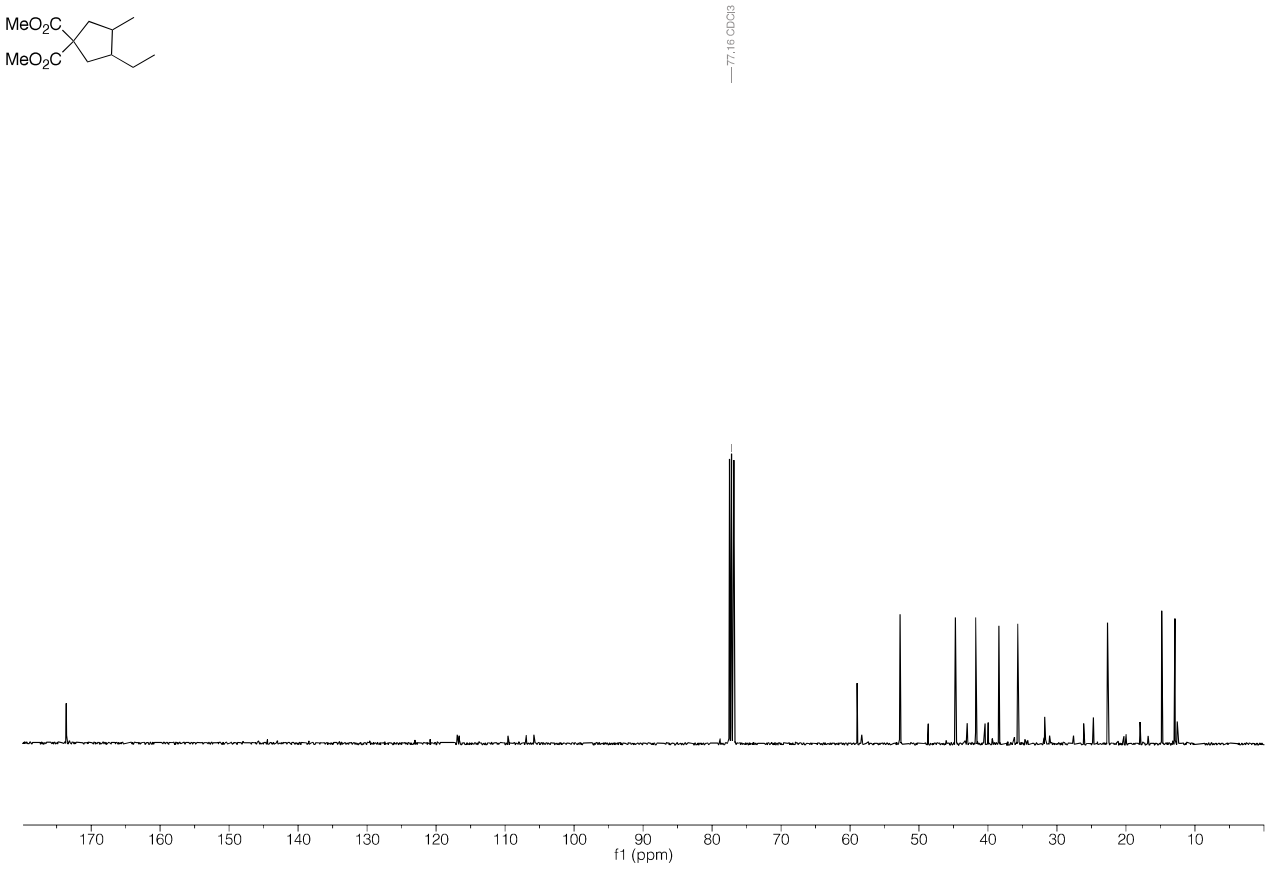
Dimethyl 3-ethyl-4-methyl-cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)

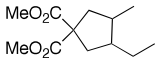


Dimethyl 3-ethyl-4-methyl-cyclopentane-1,1-dicarboxylate

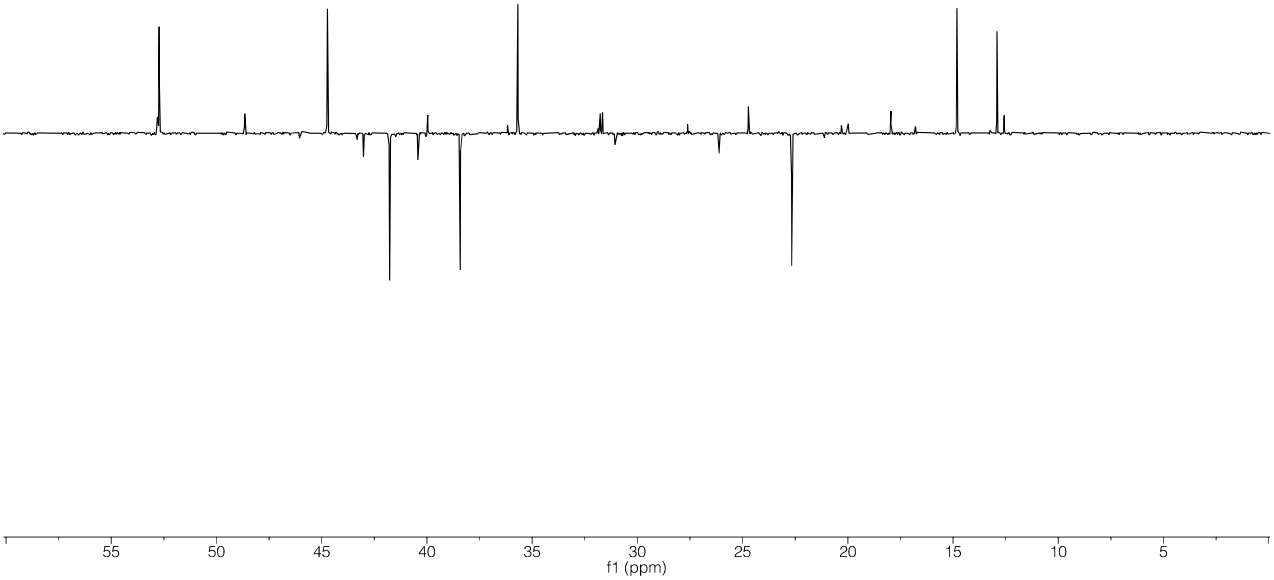
^{13}C-NMR (101 MHz, $CDCl_3$)



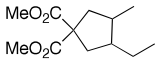
Dimethyl 3-ethyl-4-methyl-cyclopentane-1,1-dicarboxylate



DEPT-135 NMR (101 MHz, $CDCl_3$)



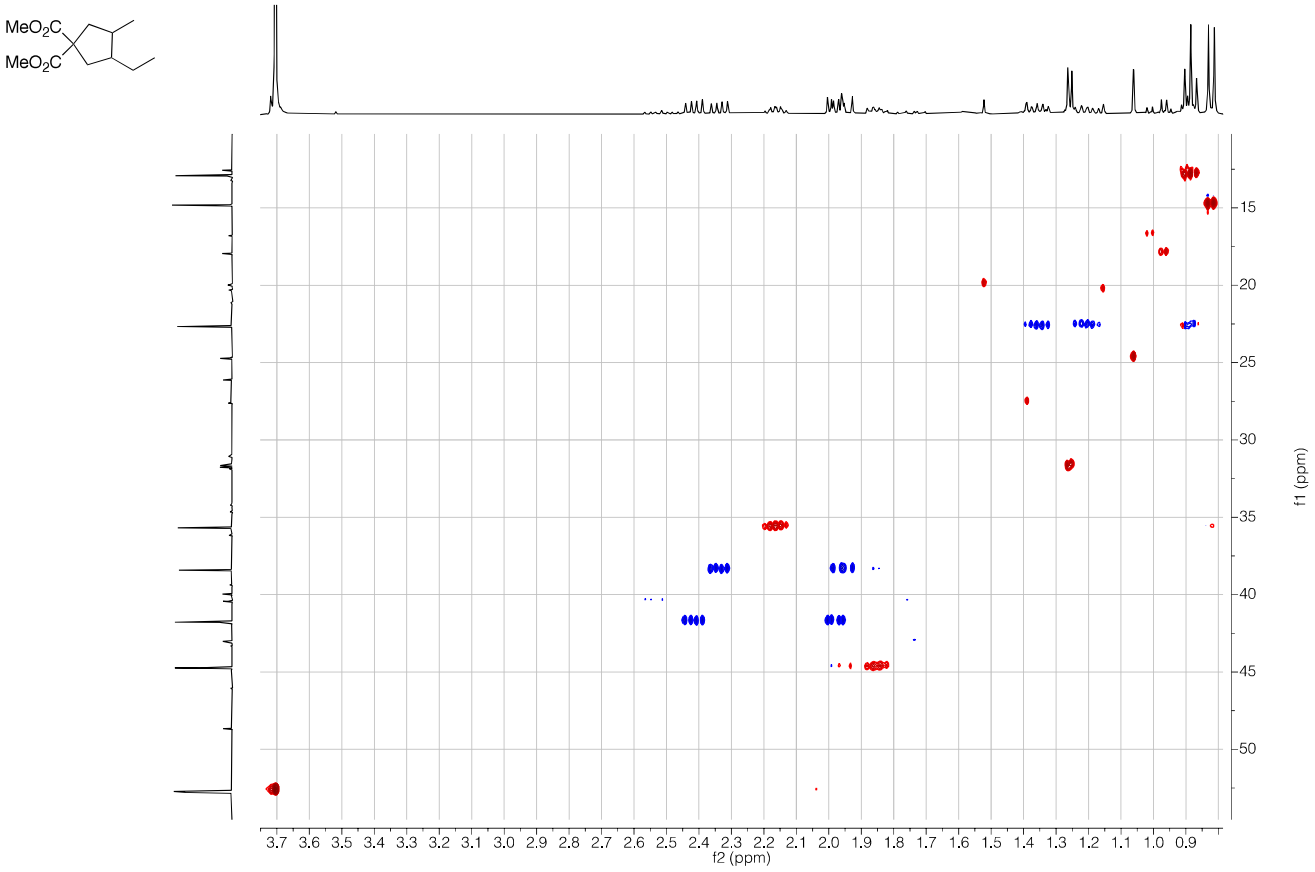
Dimethyl 3-ethyl-4-methyl-cyclopentane-1,1-dicarboxylate



^1H, ^1H-COSY (400 MHz, $CDCl_3$)

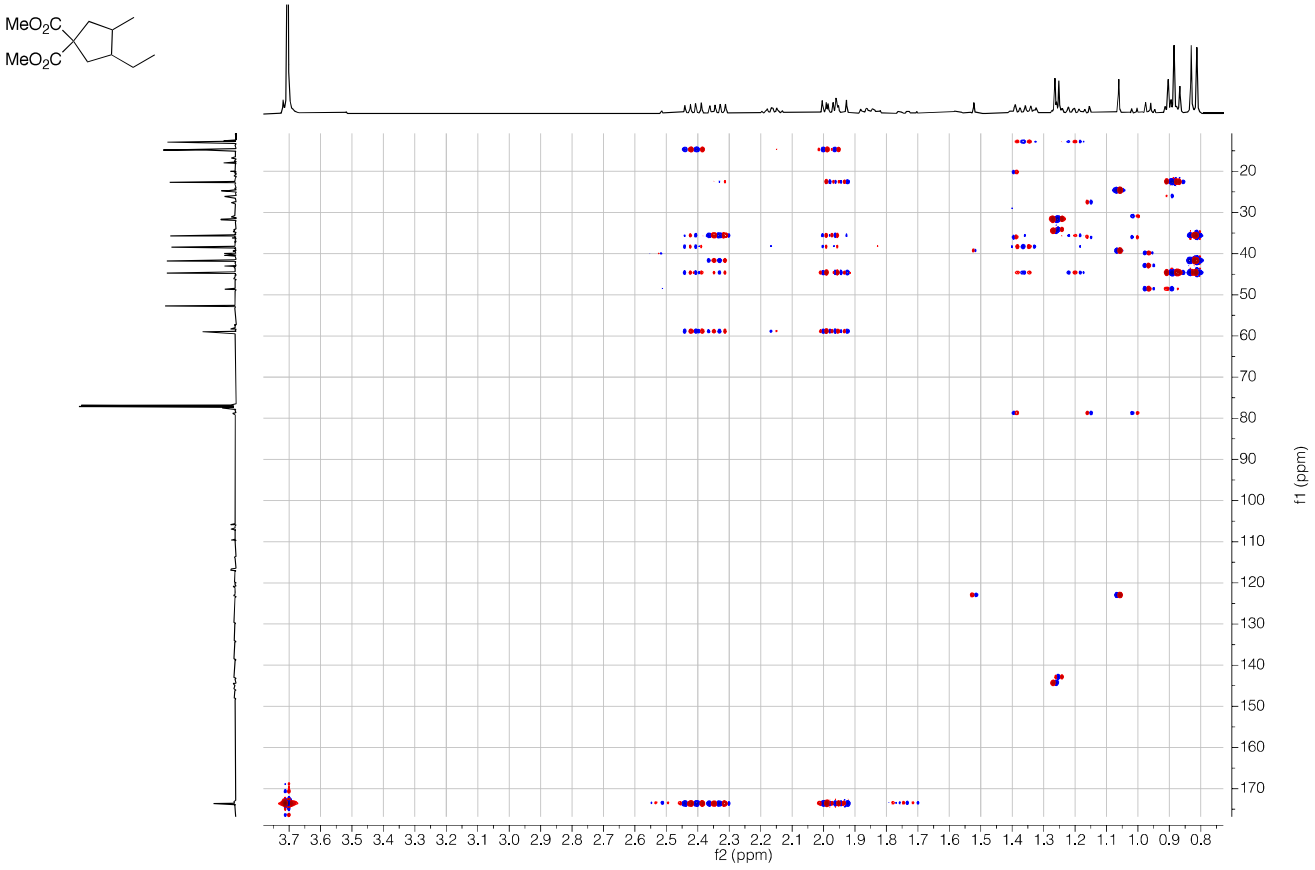
Dimethyl 3-ethyl-4-methyl-cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



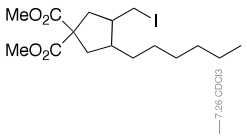
Dimethyl 3-ethyl-4-methyl-cyclopentane-1,1-dicarboxylate

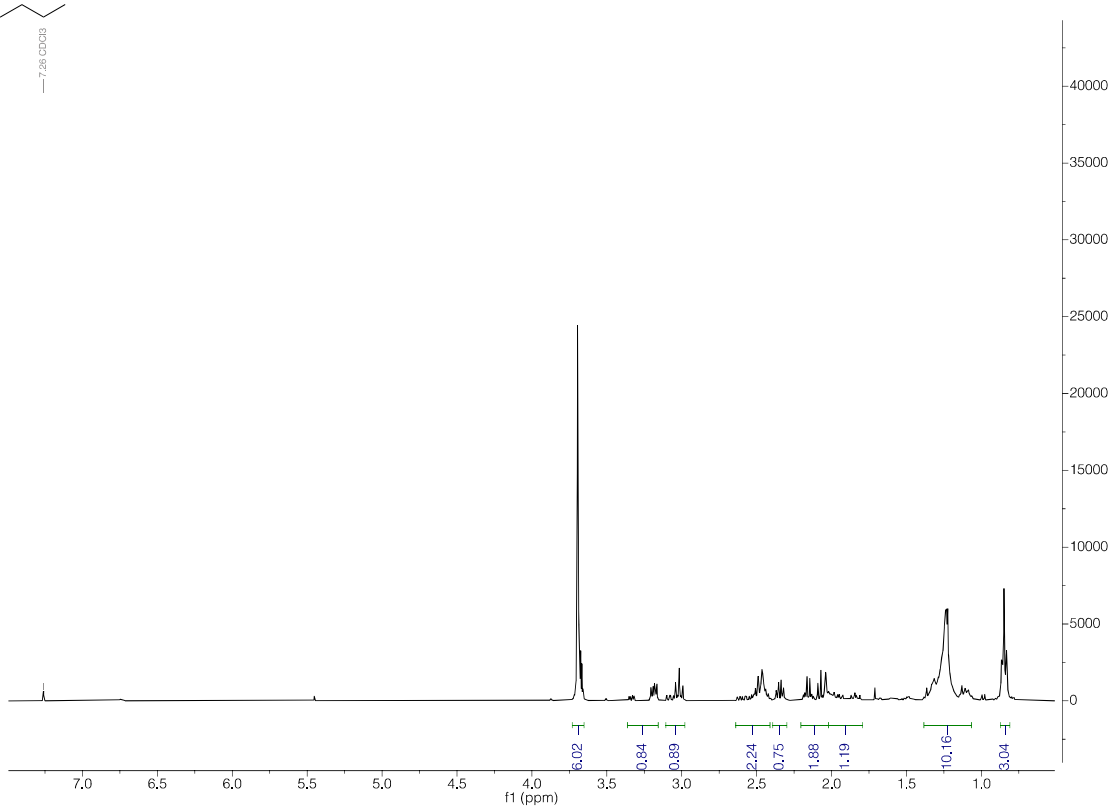
^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



Dimethyl 3-hexyl-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

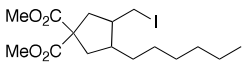
^{1}H-NMR (400 MHz, $CDCl_3$)





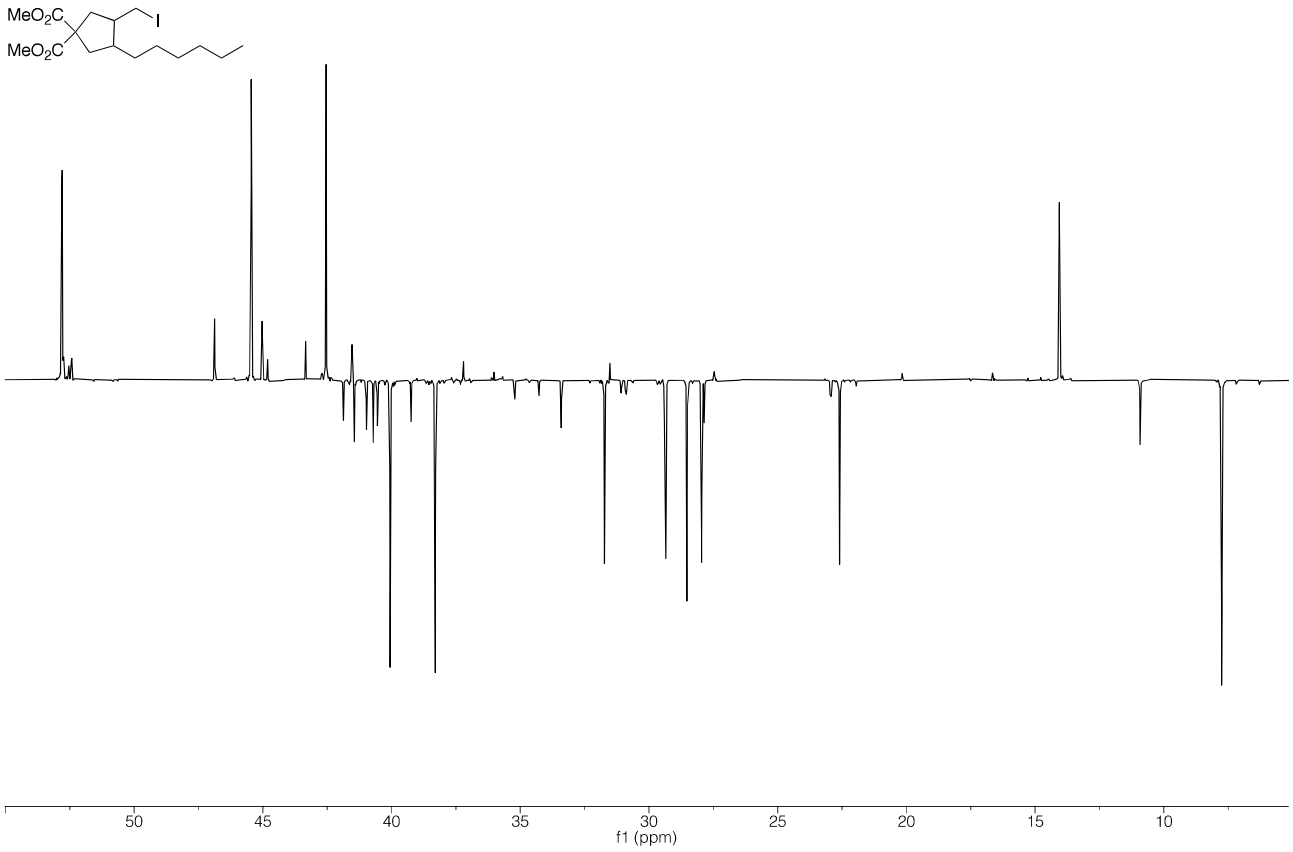
Dimethyl 3-hexyl-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

^{13}C-NMR (101 MHz, $CDCl_3$)



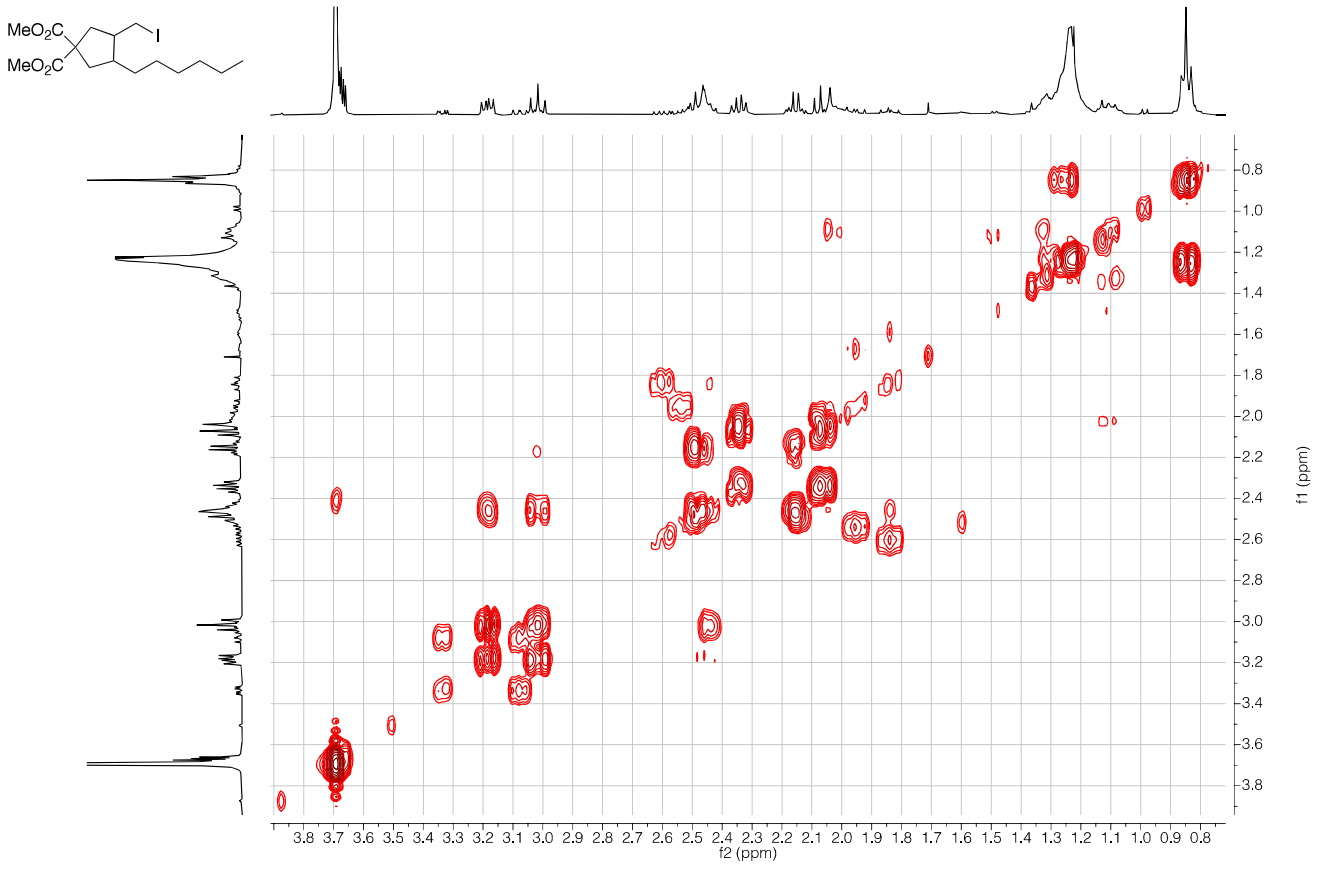
Dimethyl 3-hexyl-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

DEPT-135 NMR (101 MHz, $CDCl_3$)



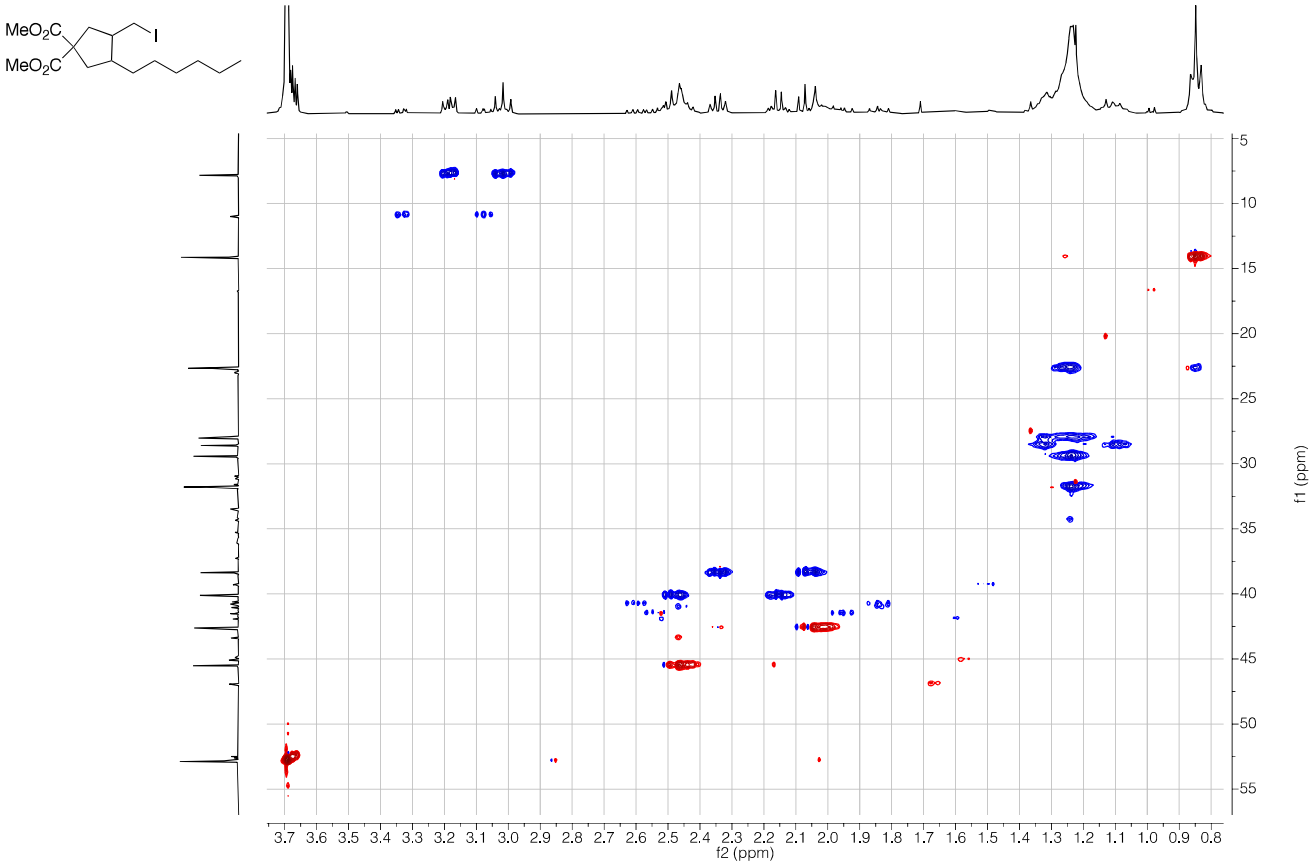
Dimethyl 3-hexyl-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

^1H, ^1H-COSY (400 MHz, $CDCl_3$)



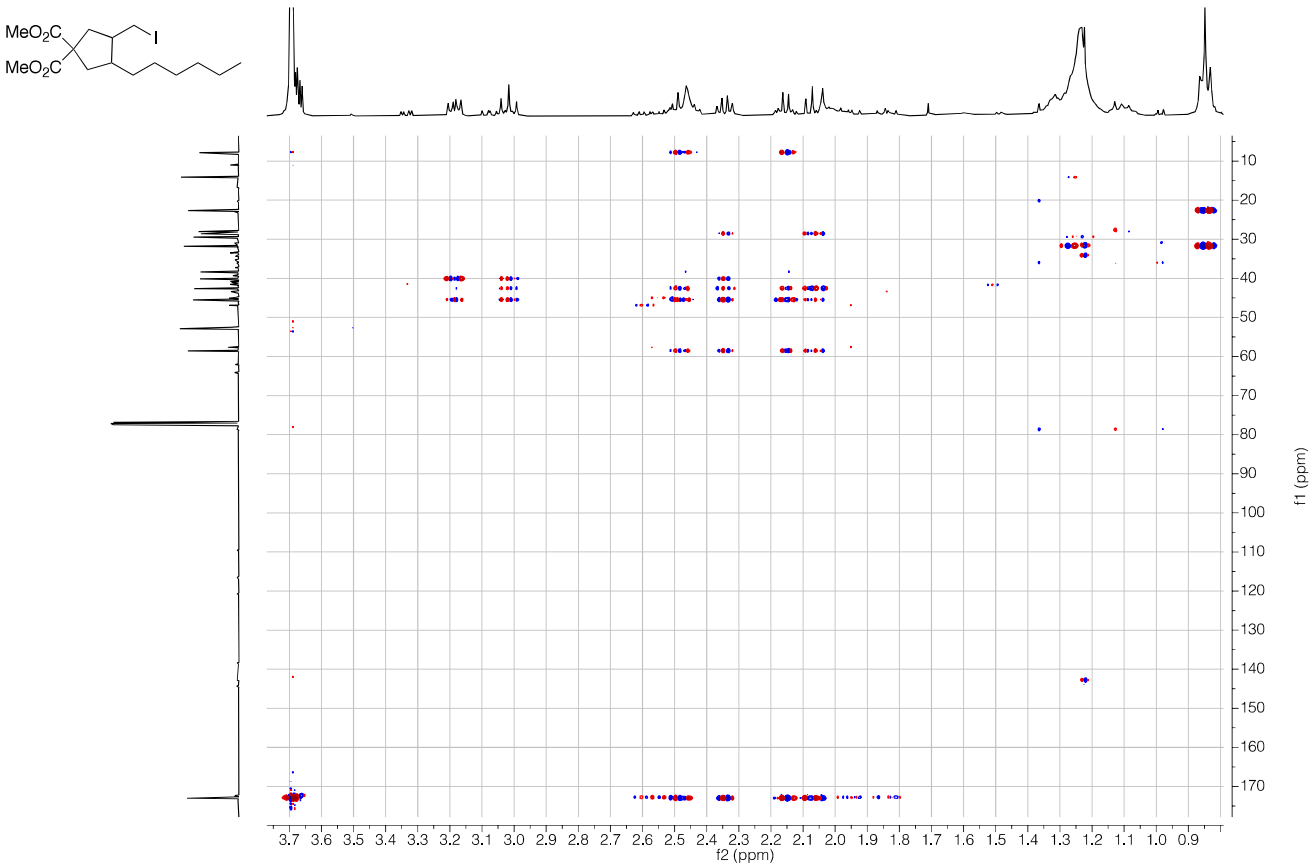
Dimethyl 3-hexyl-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



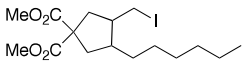
Dimethyl 3-hexyl-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

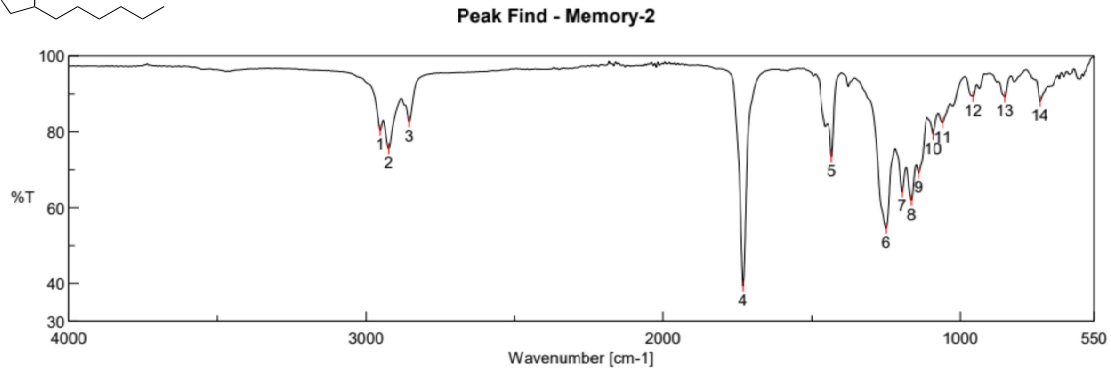
^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



Dimethyl 3-hexyl-4-(iodomethyl)cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond



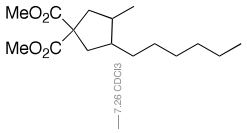


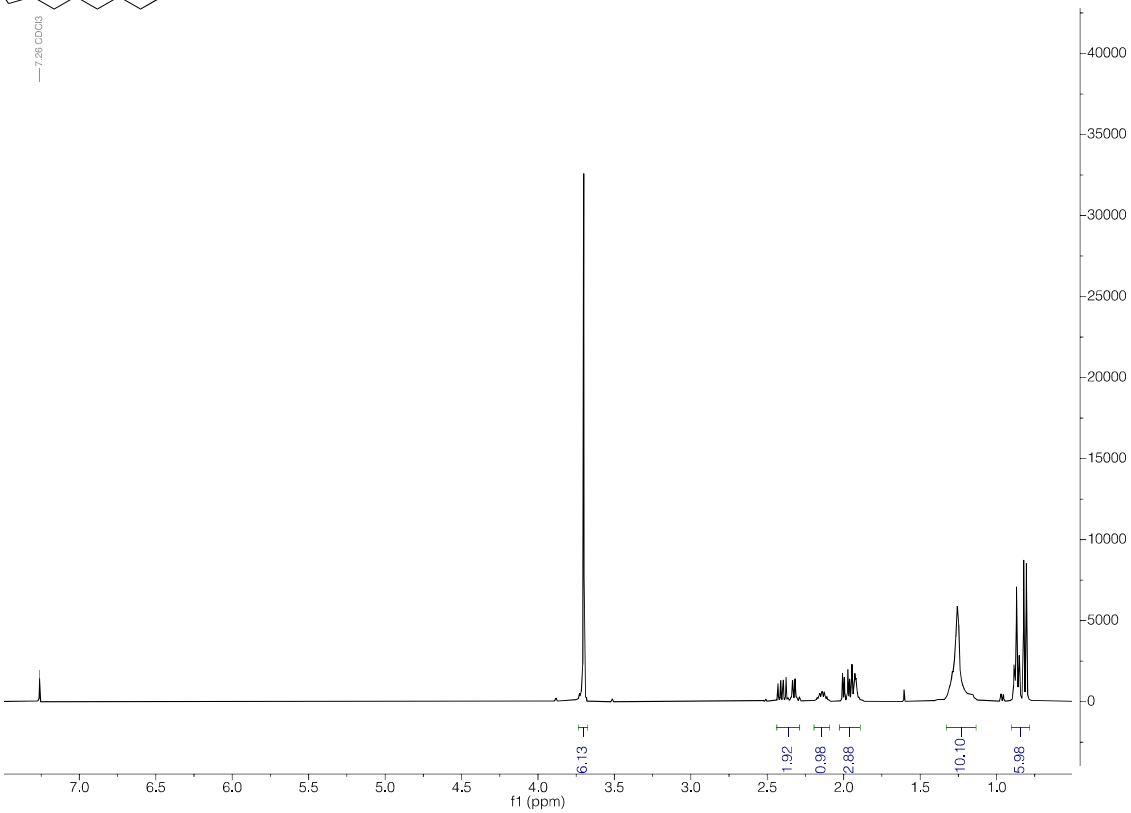
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2952.48	80.3693	2	2923.56	75.5117	3	2854.13	82.5992
4	1730.8	39.3234	5	1432.85	73.3598	6	1248.68	54.4896
7	1194.69	64.1247	8	1163.83	61.9133	9	1140.69	69.1135
10	1091.51	79.183	11	1059.59	82.3764	12	956.52	89.2668
13	849.49	89.1675	14	731.853	88.0073			

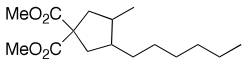
Dimethyl 3-hexyl-4-methyl-cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)



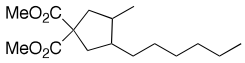


Dimethyl 3-hexyl-4-methyl-cyclopentane-1,1-dicarboxylate

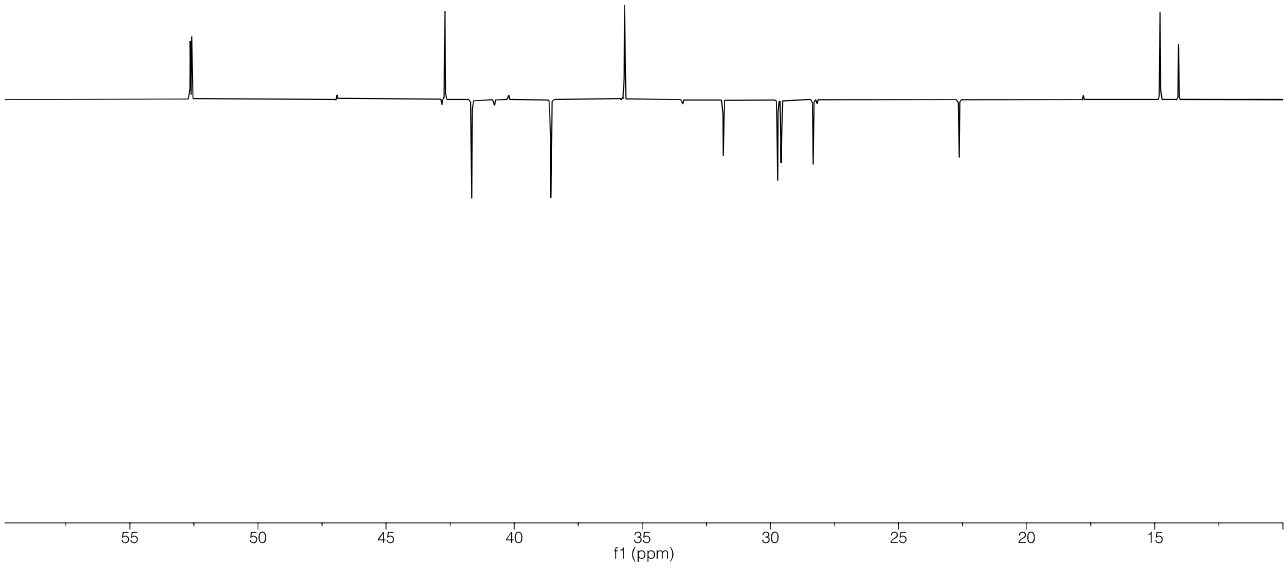


^{13}C-NMR (101 MHz, $CDCl_3$)

Dimethyl 3-hexyl-4-methyl-cyclopentane-1,1-dicarboxylate

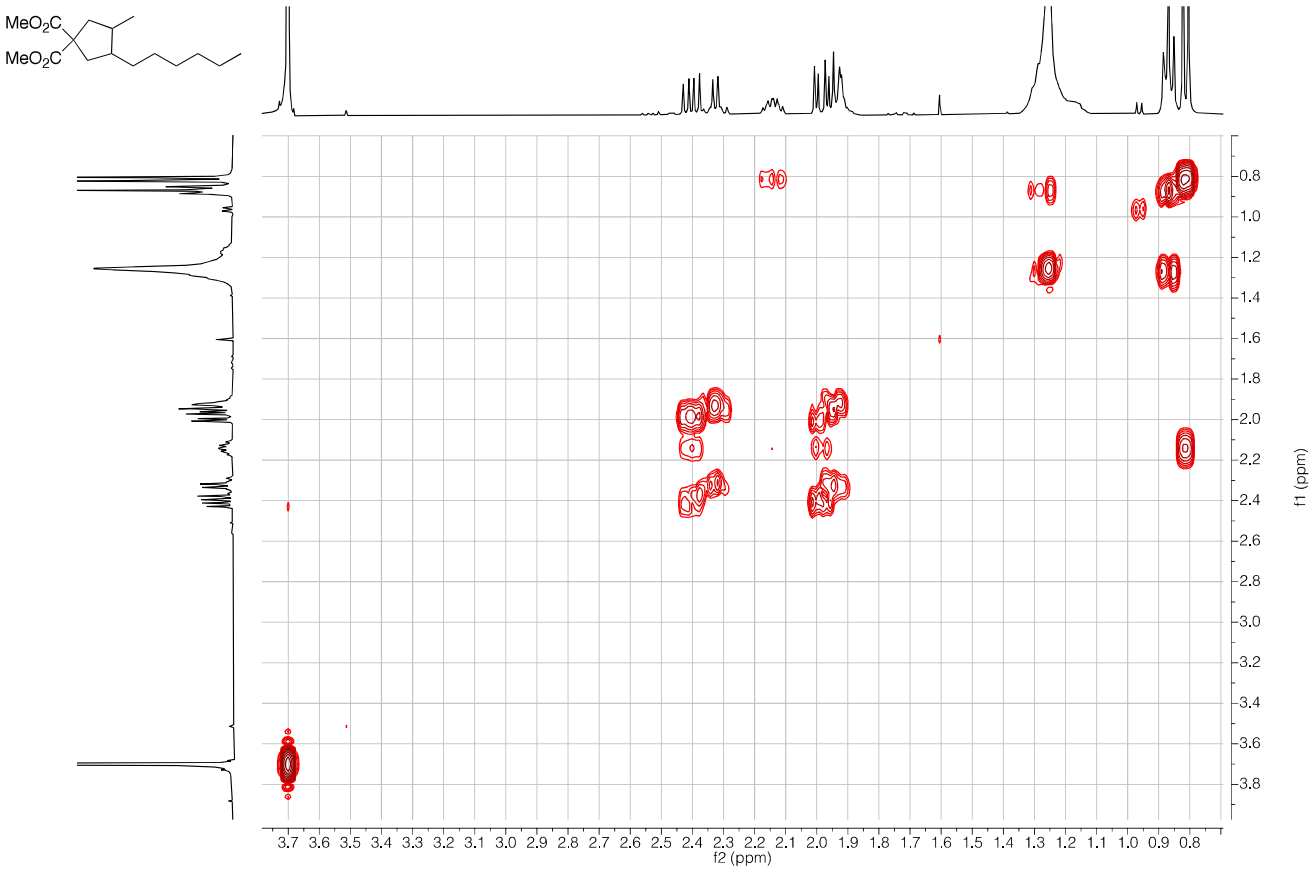


DEPT-135 NMR (101 MHz, $CDCl_3$)



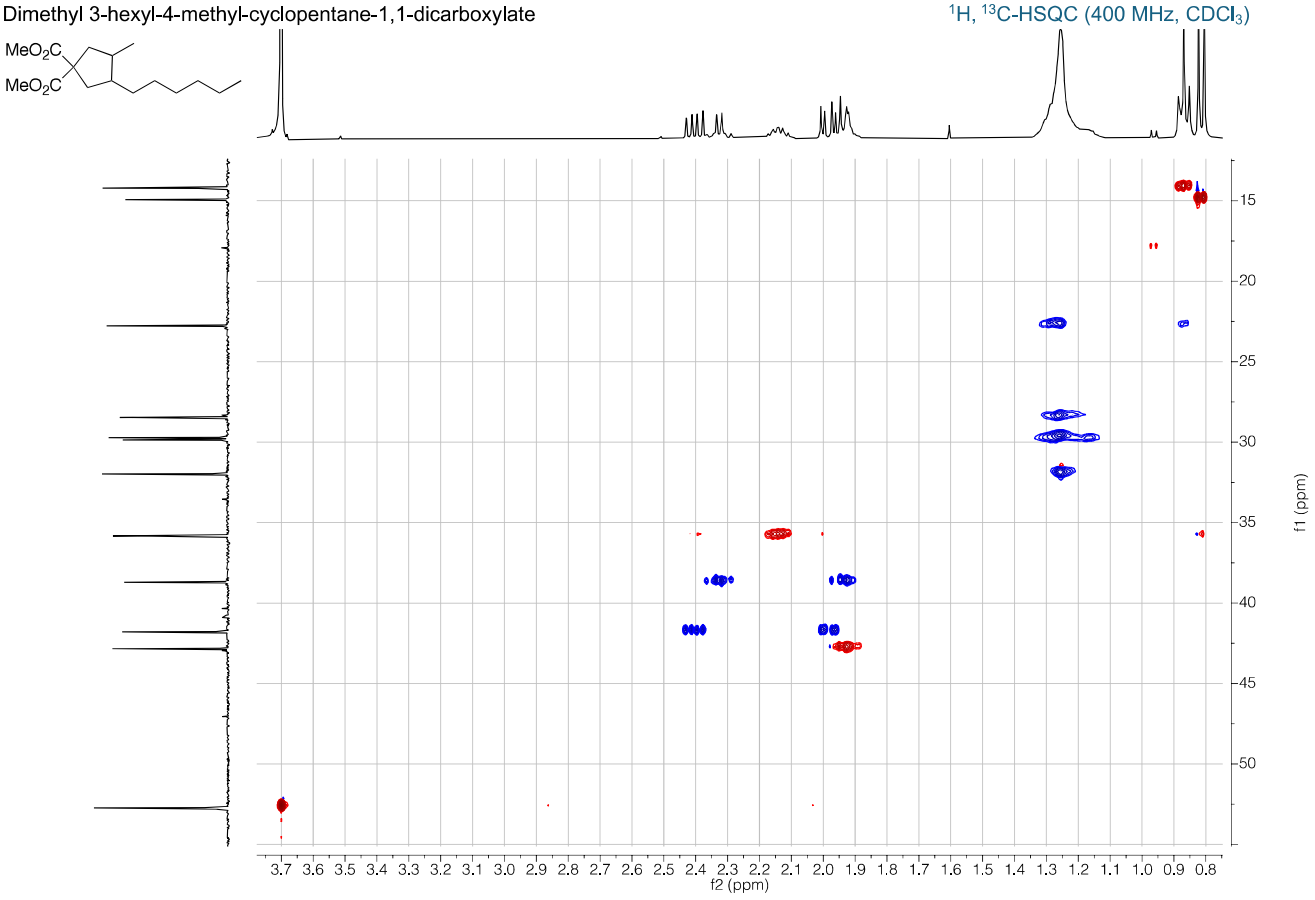
Dimethyl 3-hexyl-4-methyl-cyclopentane-1,1-dicarboxylate

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



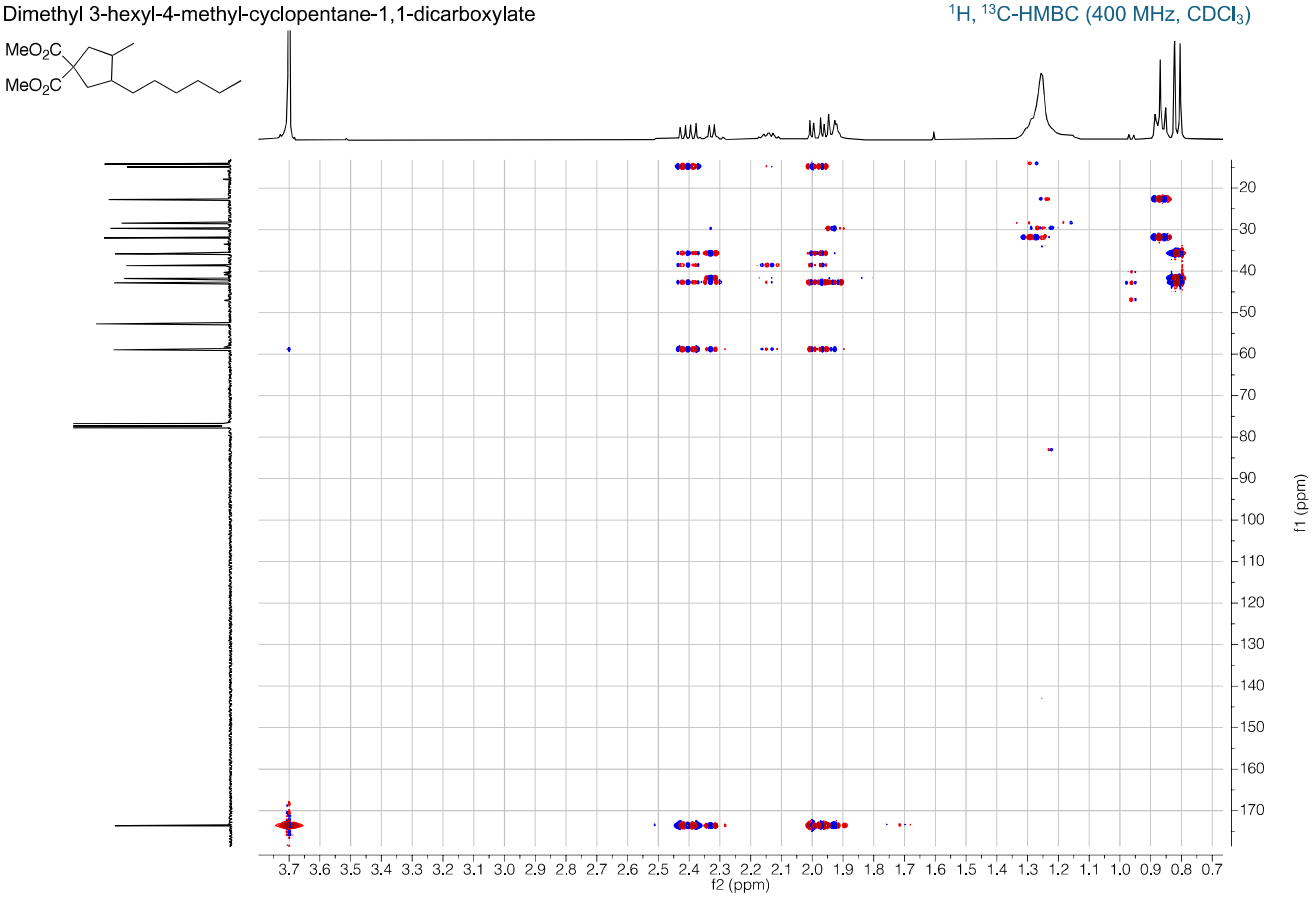
Dimethyl 3-hexyl-4-methyl-cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



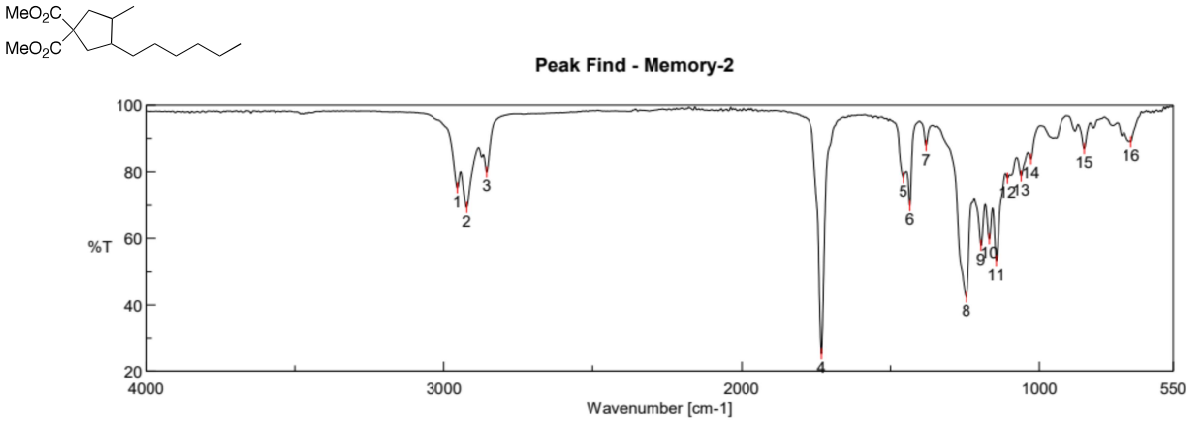
Dimethyl 3-hexyl-4-methyl-cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



Dimethyl 3-hexyl-4-methyl-cyclopentane-1,1-dicarboxylate

FT-IR, ATR-diamond

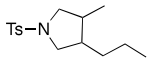


Peak Find - Memory-2

[Result of Peak Picking]

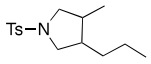
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2954.41	75.0487	2	2923.56	69.3198	3	2855.1	79.8932
4	1731.76	25.2969	5	1456.96	78.1822	6	1433.82	69.846
7	1379.82	87.8487	8	1245.79	42.3537	9	1195.65	57.7952
10	1167.69	59.7993	11	1144.55	53.1653	12	1107.9	78.0456
13	1060.66	78.6741	14	1027.87	83.8098	15	848.525	86.9044
16	592.32	88.9878						

3-Ethyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine



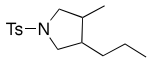
^{1}H-NMR (400 MHz, $CDCl_3$)

3-Ethyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine

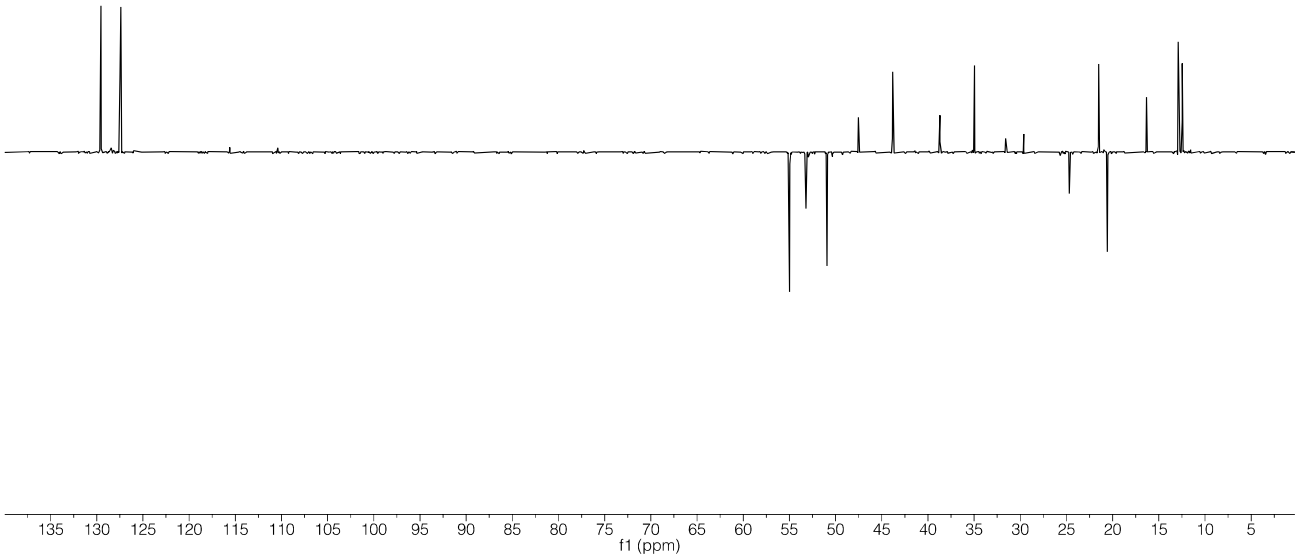


^{13}C-NMR (101 MHz, $CDCl_3$)

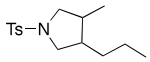
3-Ethyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine



DEPT-135 NMR (101 MHz, $CDCl_3$)

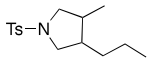


3-Ethyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine

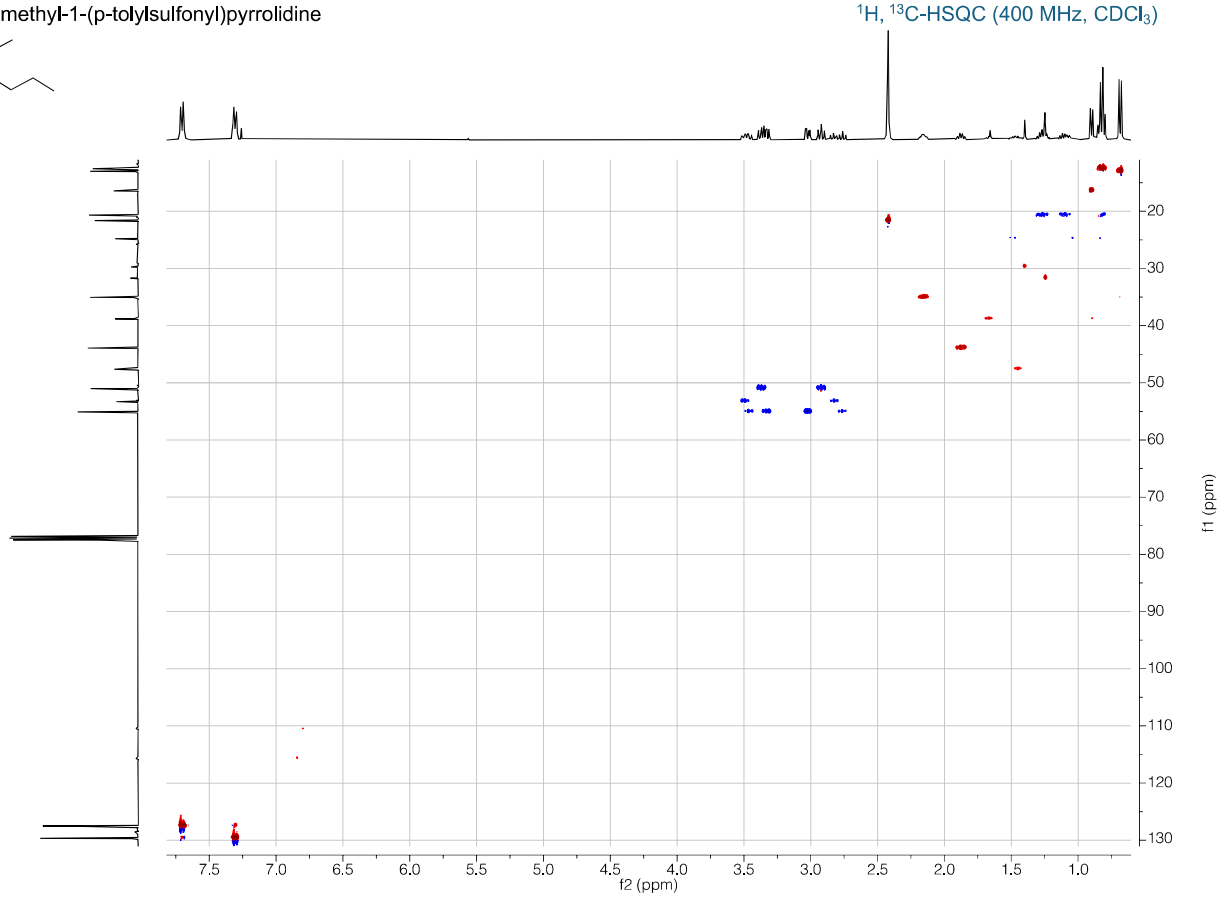


^1H, ^1H-COSY (400 MHz, $CDCl_3$)

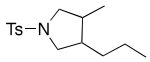
3-Ethyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine



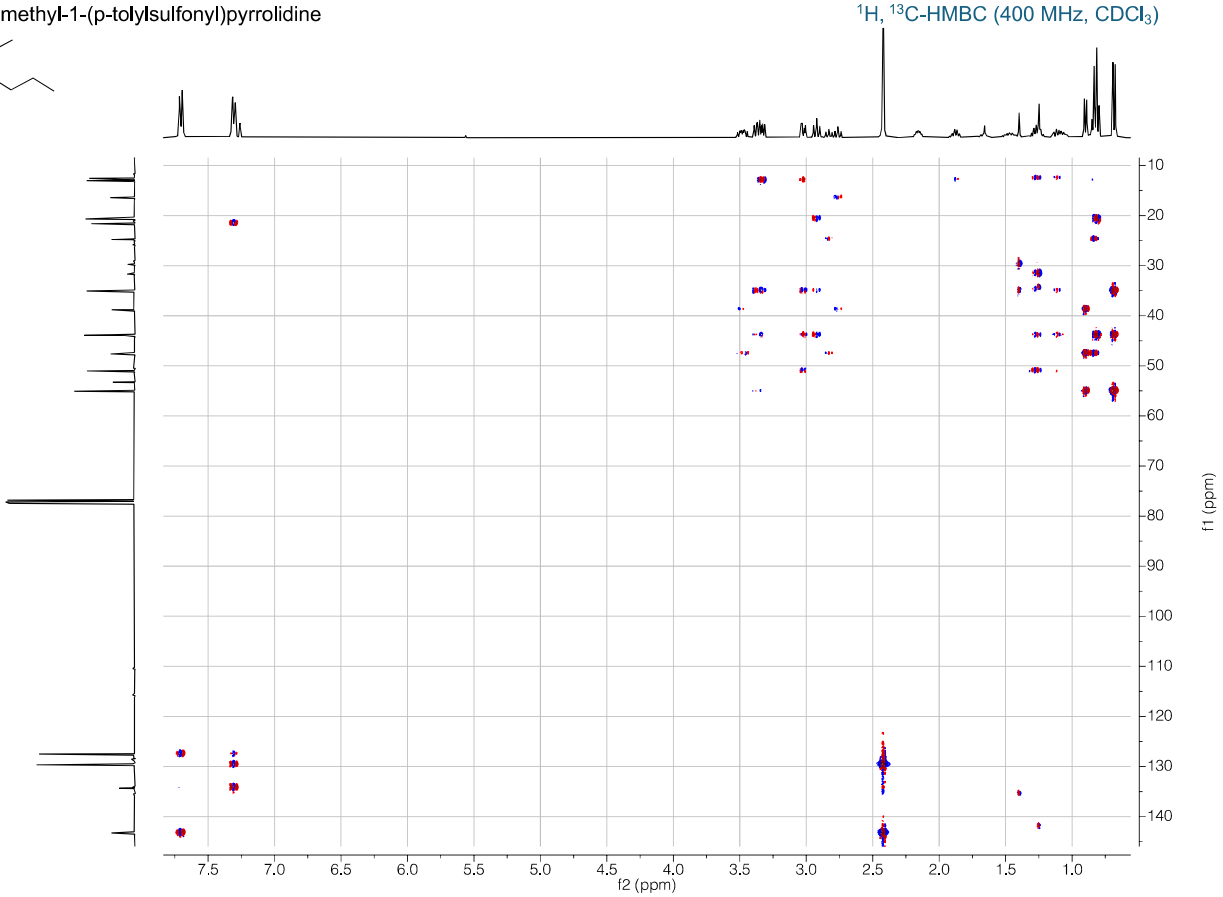
^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



3-Ethyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine

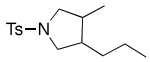


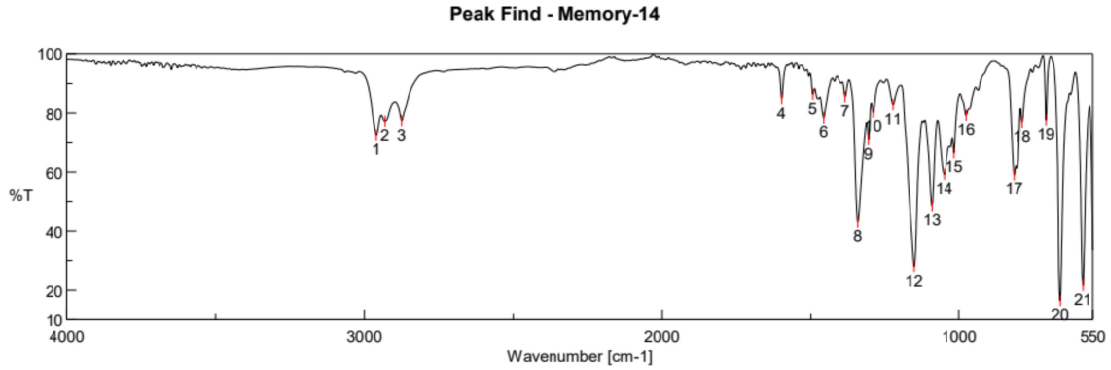
^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



3-Ethyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine

FT-IR, ATR-diamond



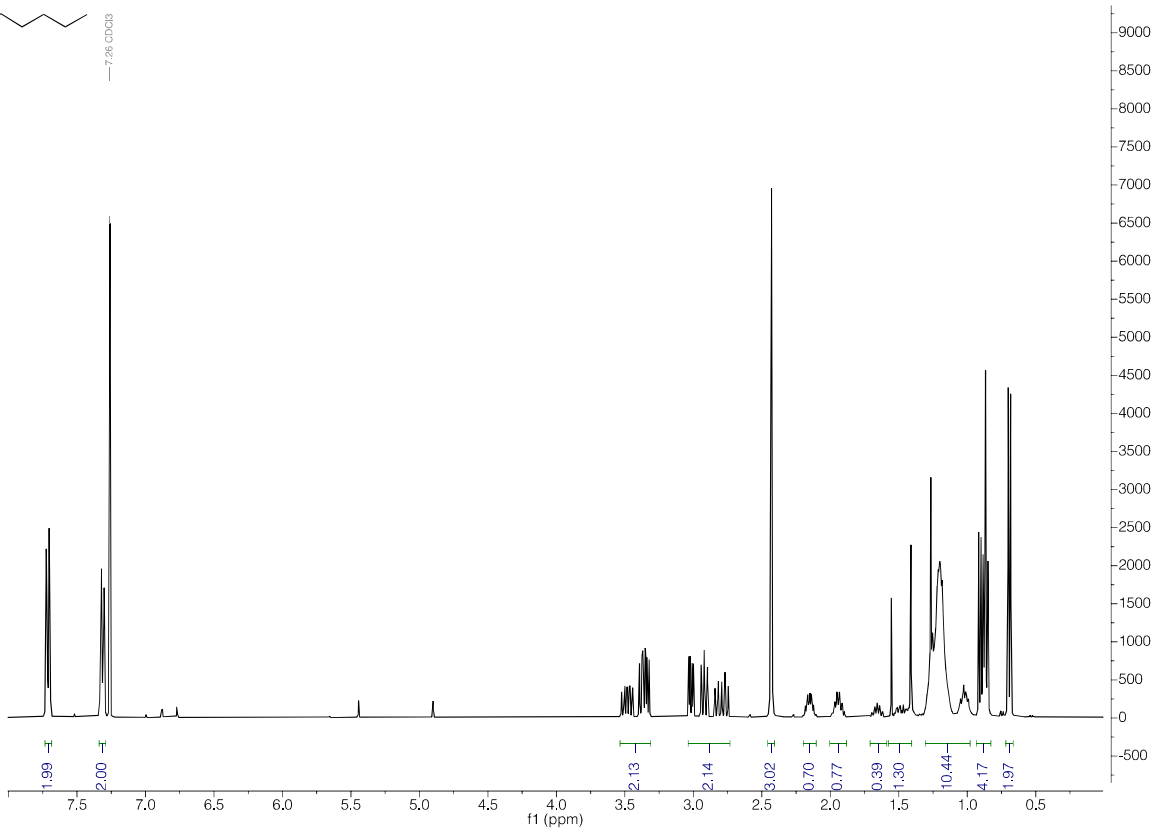


[Result of Peak Picking]

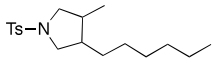
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2960.2	72.447	2	2931.27	77.0969	3	2875.34	77.3348
4	1597.73	84.7538	5	1493.6	86.2804	6	1456.96	78.1676
7	1382.71	85.4476	8	1340.28	43.0157	9	1304.61	70.9997
10	1288.22	80.2051	11	1222.65	82.7779	12	1152.26	27.9148
13	1092.48	48.443	14	1051.01	59.1328	15	1016.3	66.4546
16	975.804	79.1397	17	814.777	58.9581	18	788.743	76.7474
19	708.712	77.5051	20	661.464	16.3632	21	585.29	21.5867

3-Hexyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine

^{1}H-NMR (400 MHz, $CDCl_3$)

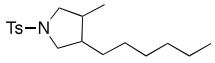


3-Hexyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine

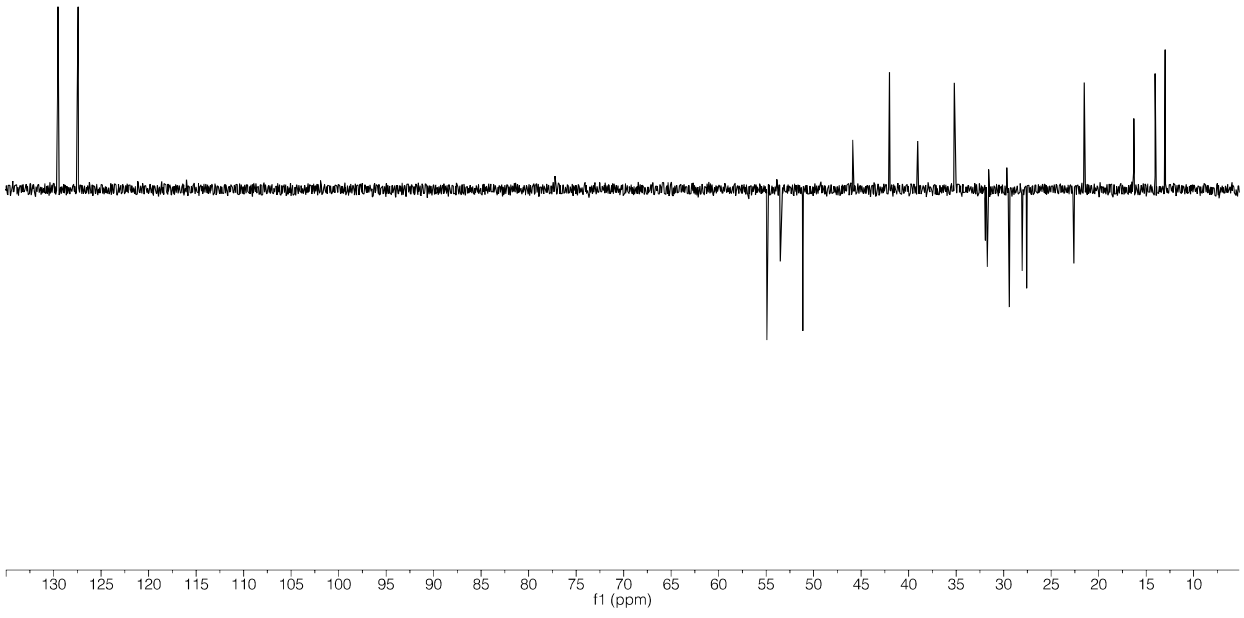


^{13}C-NMR (101 MHz, $CDCl_3$)

3-Hexyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine

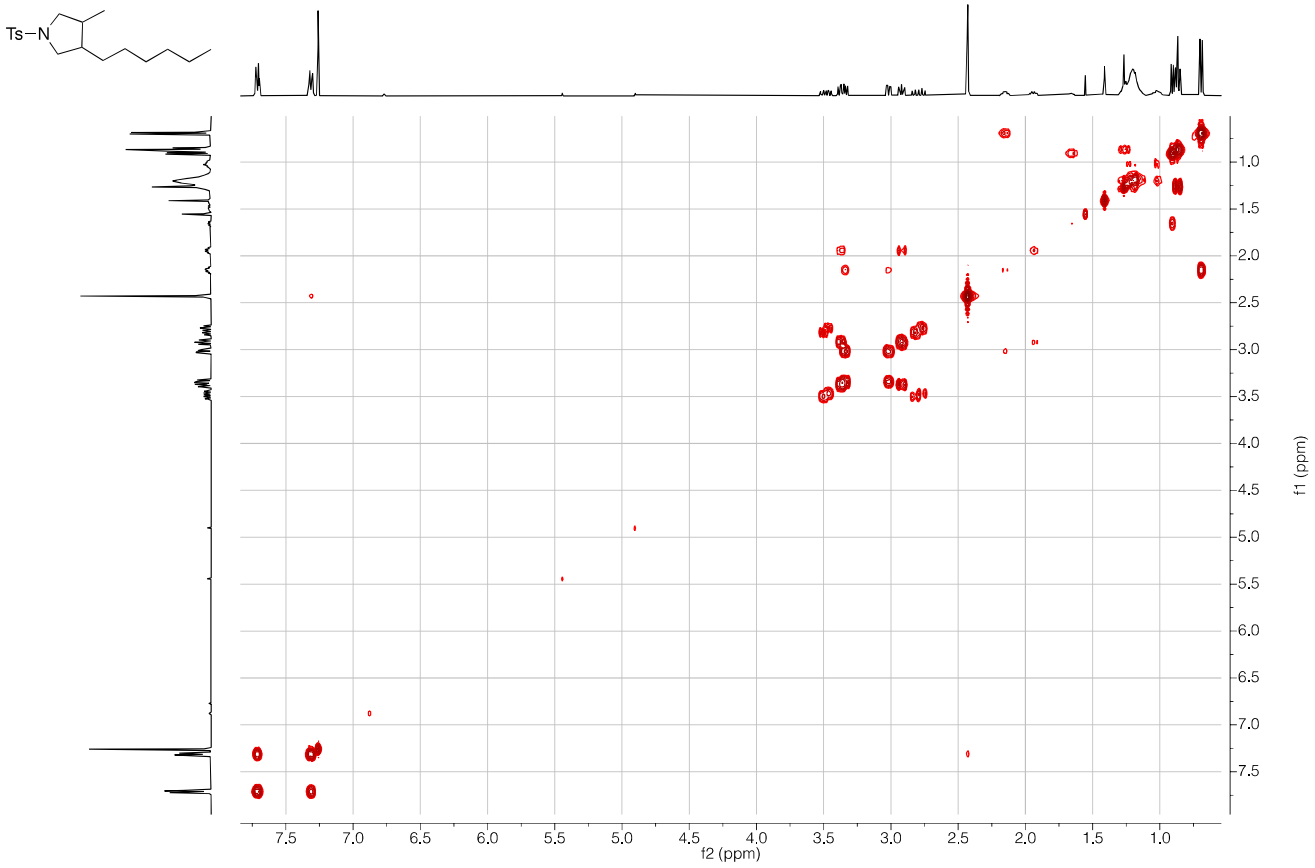


DEPT-135 NMR (101 MHz, $CDCl_3$)



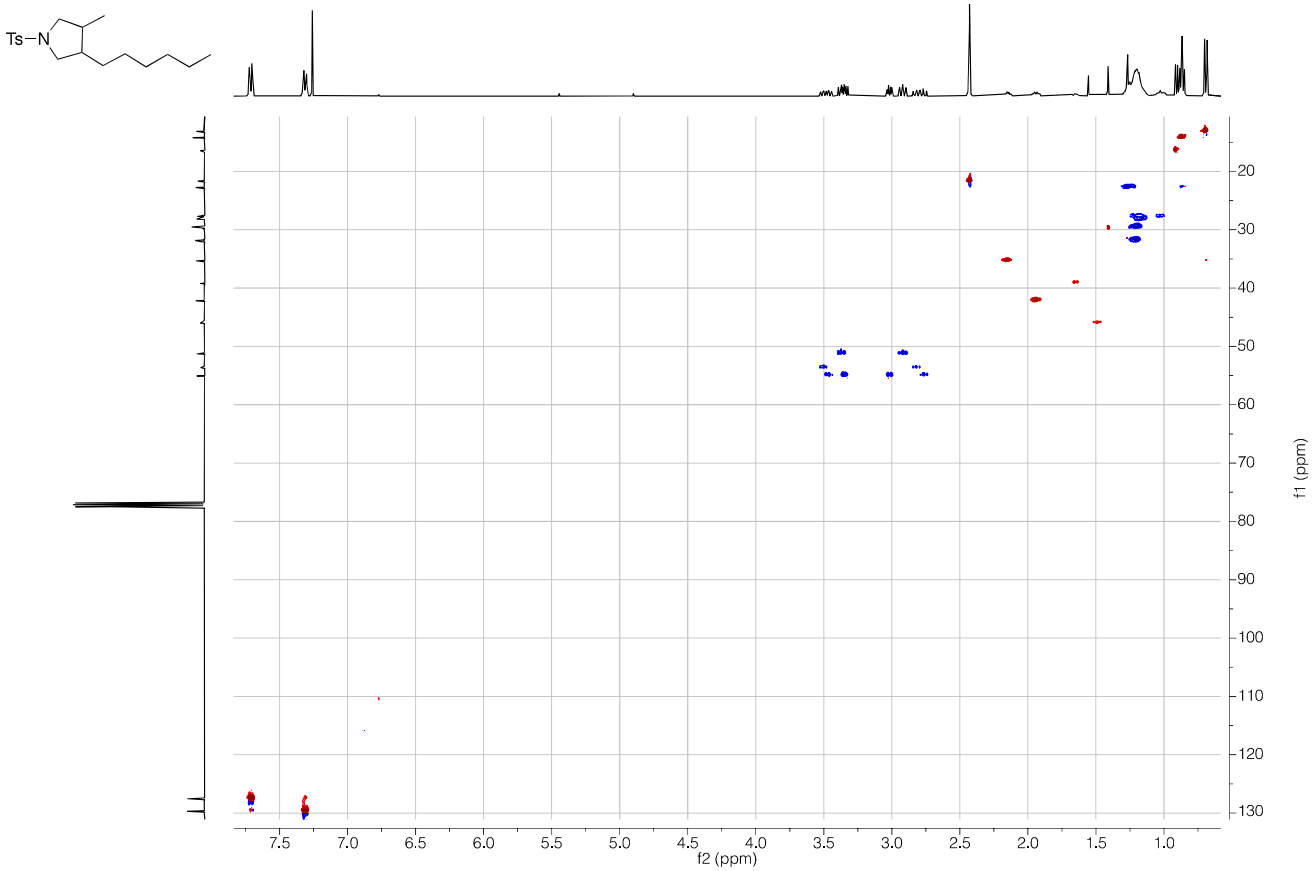
3-Hexyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



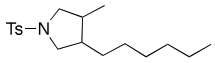
3-Hexyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine

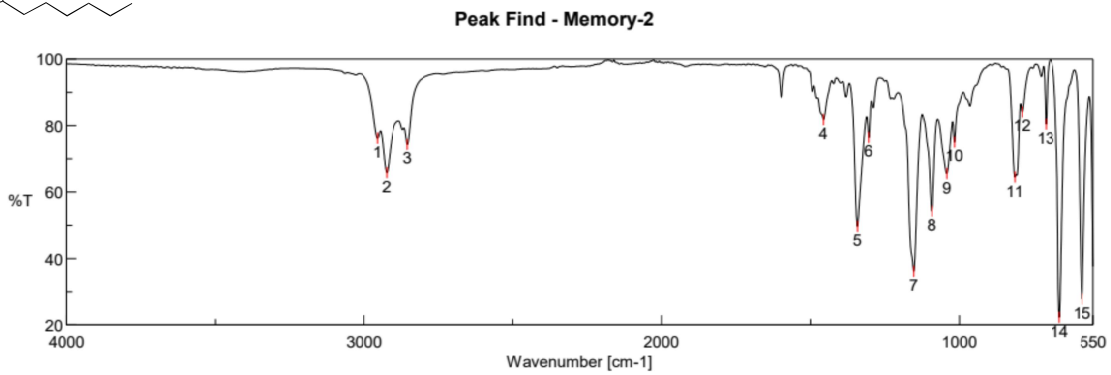
^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



3-Hexyl-4-methyl-1-(p-tolylsulfonyl)pyrrolidine

FT-IR, ATR-diamond



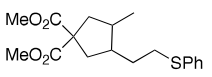


[Result of Peak Picking]

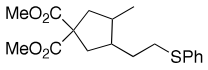
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2955.38	76.1613	2	2924.52	65.8198	3	2855.1	74.3426
4	1455.99	81.7748	5	1342.21	49.611	6	1304.61	76.4304
7	1153.22	36.1189	8	1092.48	54.2081	9	1042.34	65.5284
10	1016.3	75.0215	11	813.813	64.4768	12	788.743	84.0865
13	708.712	80.4089	14	562.428	22.2775	15	587.218	27.8013

Dimethyl 3-methyl-4-(2-phenylsulfanylethyl)cyclopentane-1,1-dicarboxylate

^{1}H-NMR (400 MHz, $CDCl_3$)

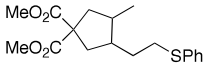


Dimethyl 3-methyl-4-(2-phenylsulfanylethyl)cyclopentane-1,1-dicarboxylate

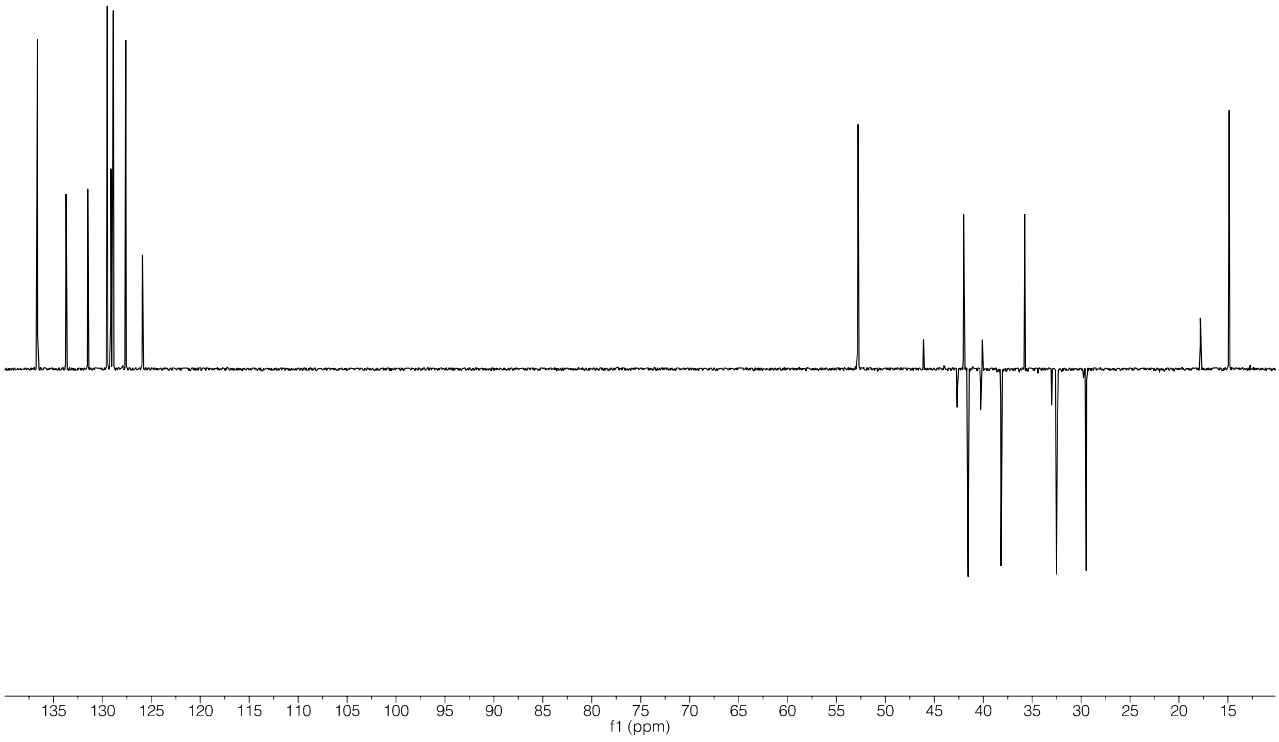


^{13}C-NMR (101 MHz, $CDCl_3$)

Dimethyl 3-methyl-4-(2-phenylsulfanylethyl)cyclopentane-1,1-dicarboxylate

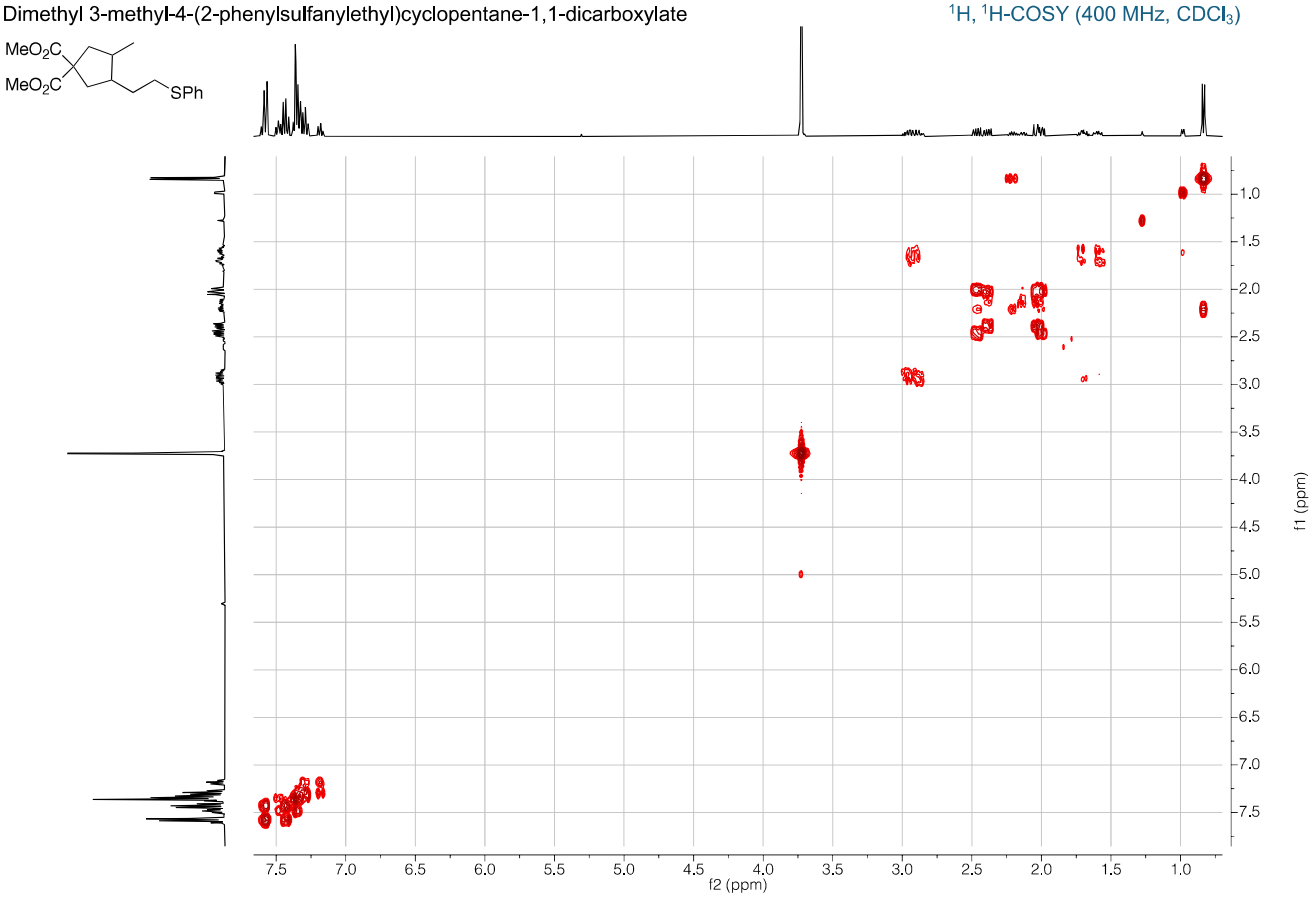


DEPT-135 NMR (101 MHz, $CDCl_3$)



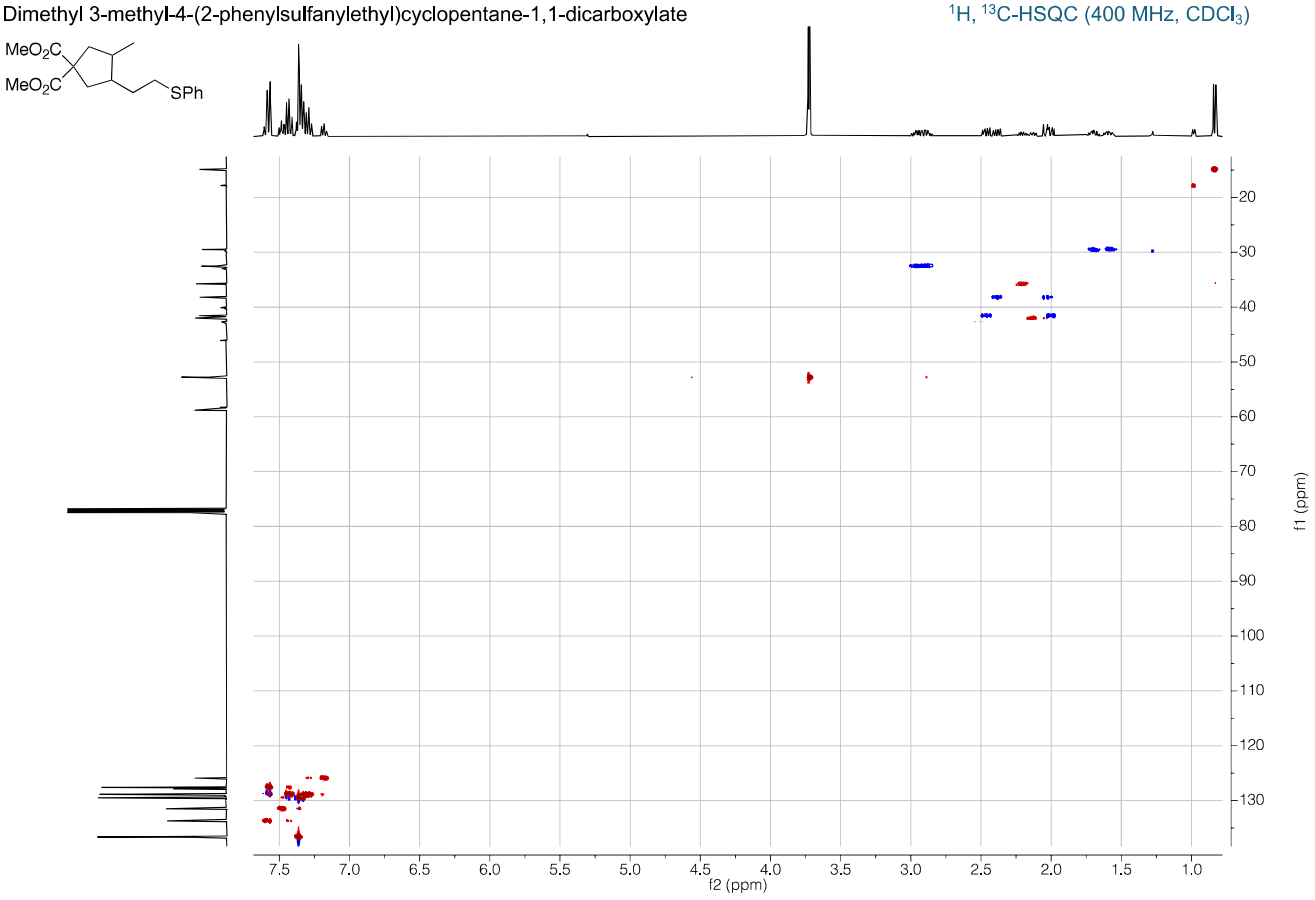
Dimethyl 3-methyl-4-(2-phenylsulfanylethyl)cyclopentane-1,1-dicarboxylate

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



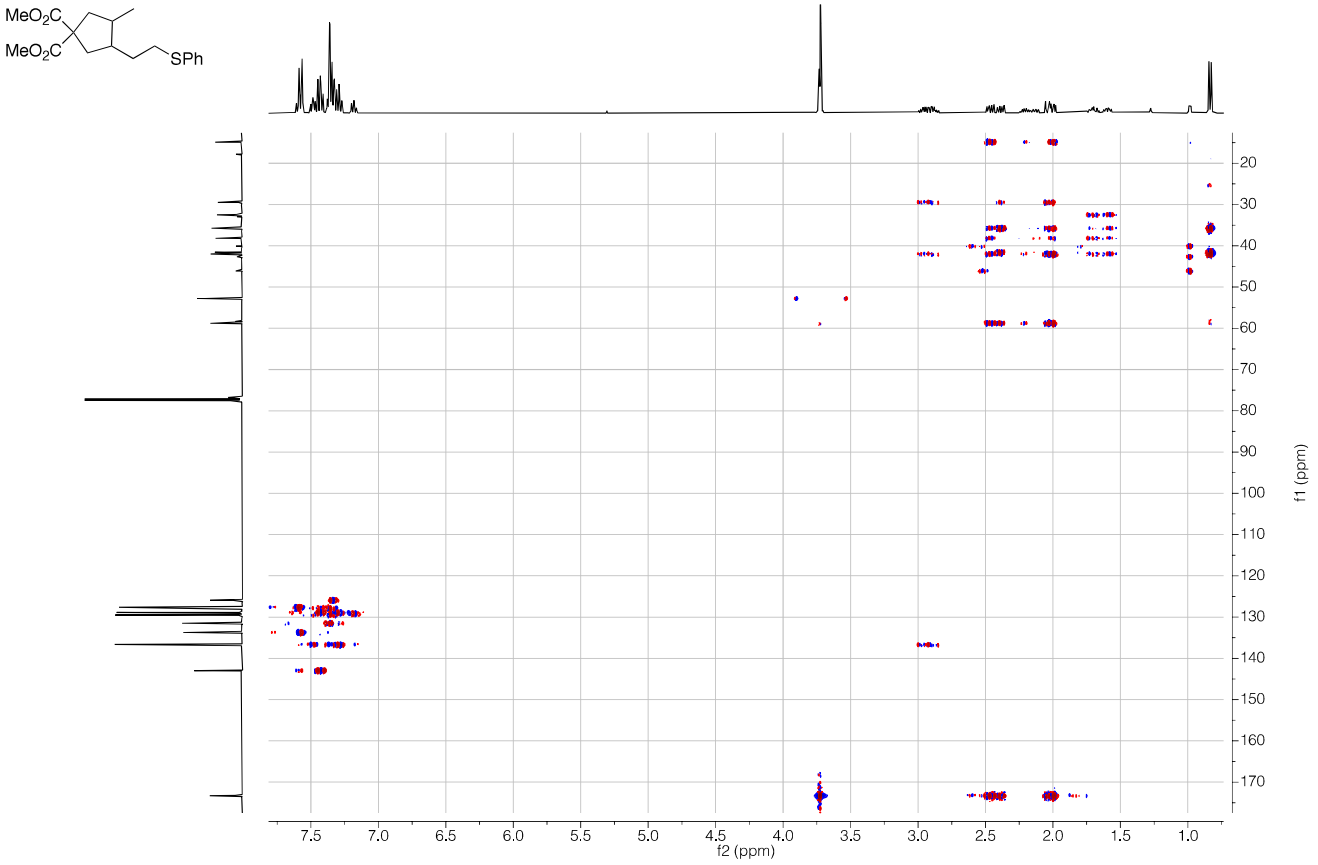
Dimethyl 3-methyl-4-(2-phenylsulfanylethyl)cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



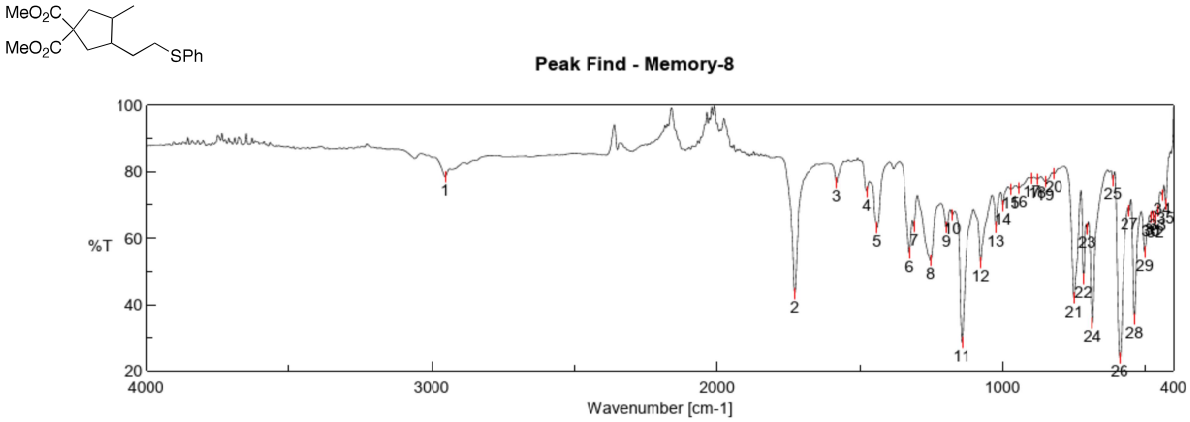
Dimethyl 3-methyl-4-(2-phenylsulfanylethyl)cyclopentane-1,1-dicarboxylate

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



Dimethyl 3-methyl-4-(2-phenylsulfanylethyl)cyclopentane-1,1-dicarboxylate

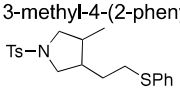
FT-IR, ATR-diamond



[Result of Peak Picking]

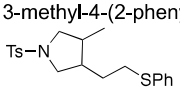
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2951.52	78.4381	2	1728.87	43.283	3	1581.34	76.6527
4	1474.31	73.9076	5	1438.64	63.1383	6	1324.86	55.5666
7	1308.46	63.4901	8	1251.58	53.2671	9	1196.61	63.2526
10	1176.36	66.93	11	1142.62	28.6694	12	1076.08	52.6666
13	1023.05	63.3012	14	998.946	69.7422	15	970.983	74.6913
16	943.02	75.0464	17	896.737	77.9932	18	877.452	77.726
19	850.454	77.0058	20	819.598	79.4135	21	748.245	42.0412
22	715.461	47.7685	23	702.926	62.7419	24	684.606	34.466
25	614.217	77.3124	26	590.111	23.9469	27	555.398	68.2418
28	537.078	35.6919	29	501.401	55.8249	30	481.153	66.2811
31	471.51	66.4588	32	464.761	65.9147	33	457.047	68.1888
34	439.69	72.9143	35	428.12	70.2246			

3-methyl-4-(2-phenylsulfanylethyl)-1-(p-tolylsulfonyl)pyrrolidine



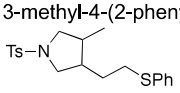
^{1}H-NMR (400 MHz, $CDCl_3$)

3-methyl-4-(2-phenylsulfanylethyl)-1-(p-tolylsulfonyl)pyrrolidine

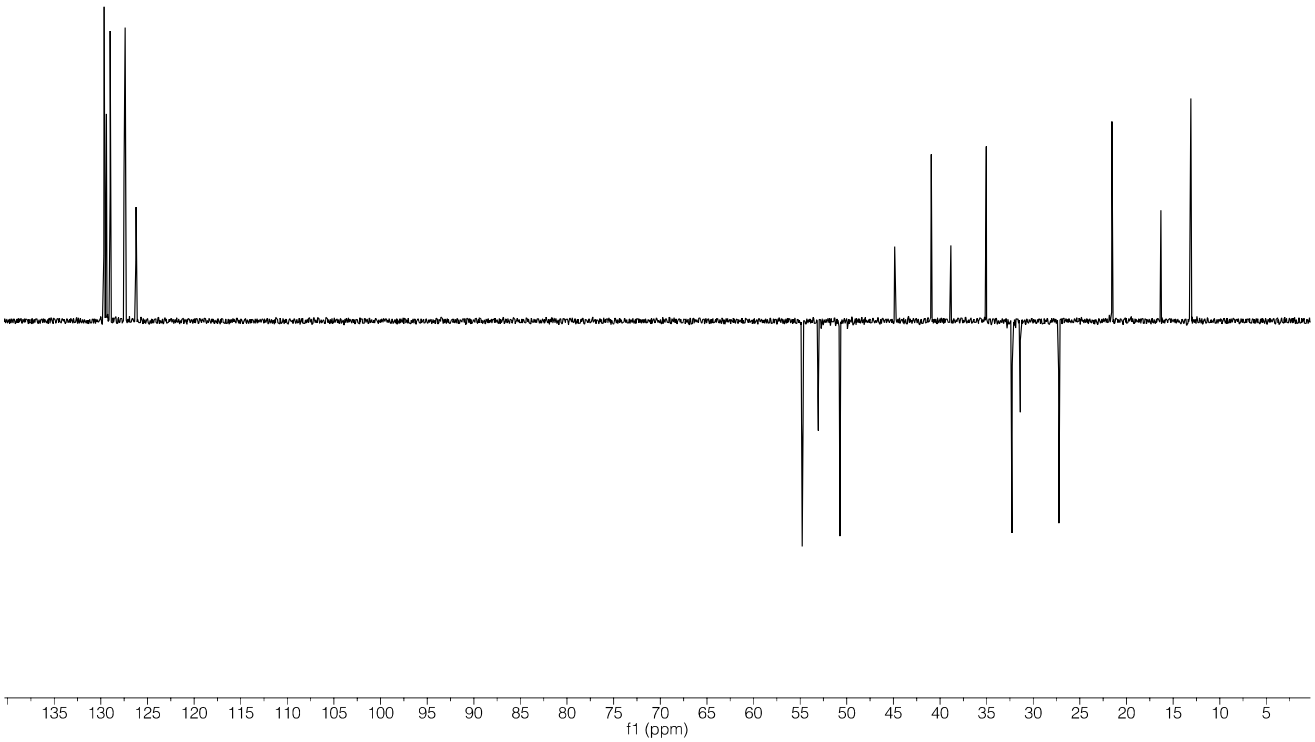


^{13}C-NMR (101 MHz, $CDCl_3$)

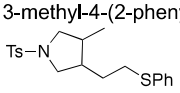
3-methyl-4-(2-phenylsulfanylethyl)-1-(p-tolylsulfonyl)pyrrolidine



DEPT-135 NMR (101 MHz, $CDCl_3$)

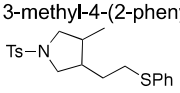


3-methyl-4-(2-phenylsulfanylethyl)-1-(p-tolylsulfonyl)pyrrolidine



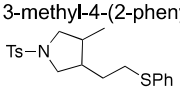
^1H, ^1H-COSY (400 MHz, $CDCl_3$)

3-methyl-4-(2-phenylsulfanylethyl)-1-(p-tolylsulfonyl)pyrrolidine



^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)

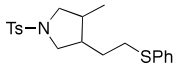
3-methyl-4-(2-phenylsulfanylethyl)-1-(p-tolylsulfonyl)pyrrolidine

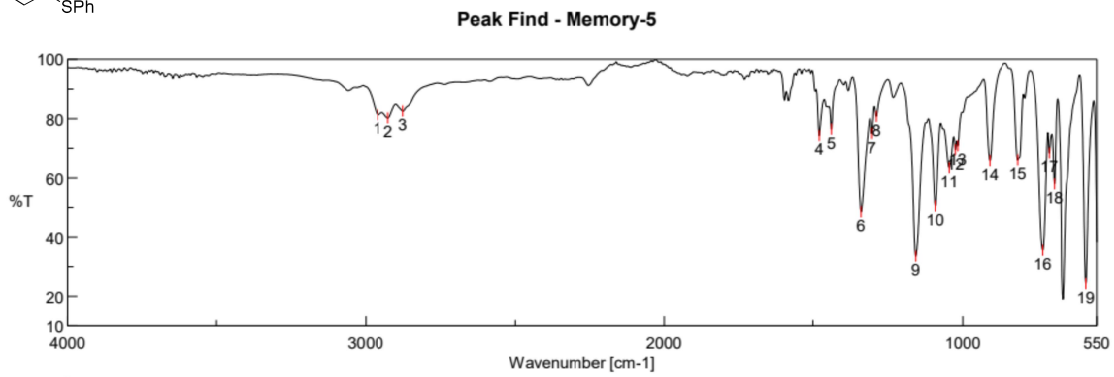


^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)

3-methyl-4-(2-phenylsulfanylethyl)-1-(p-tolylsulfonyl)pyrrolidine

FT-IR, ATR-diamond



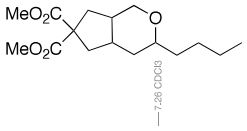


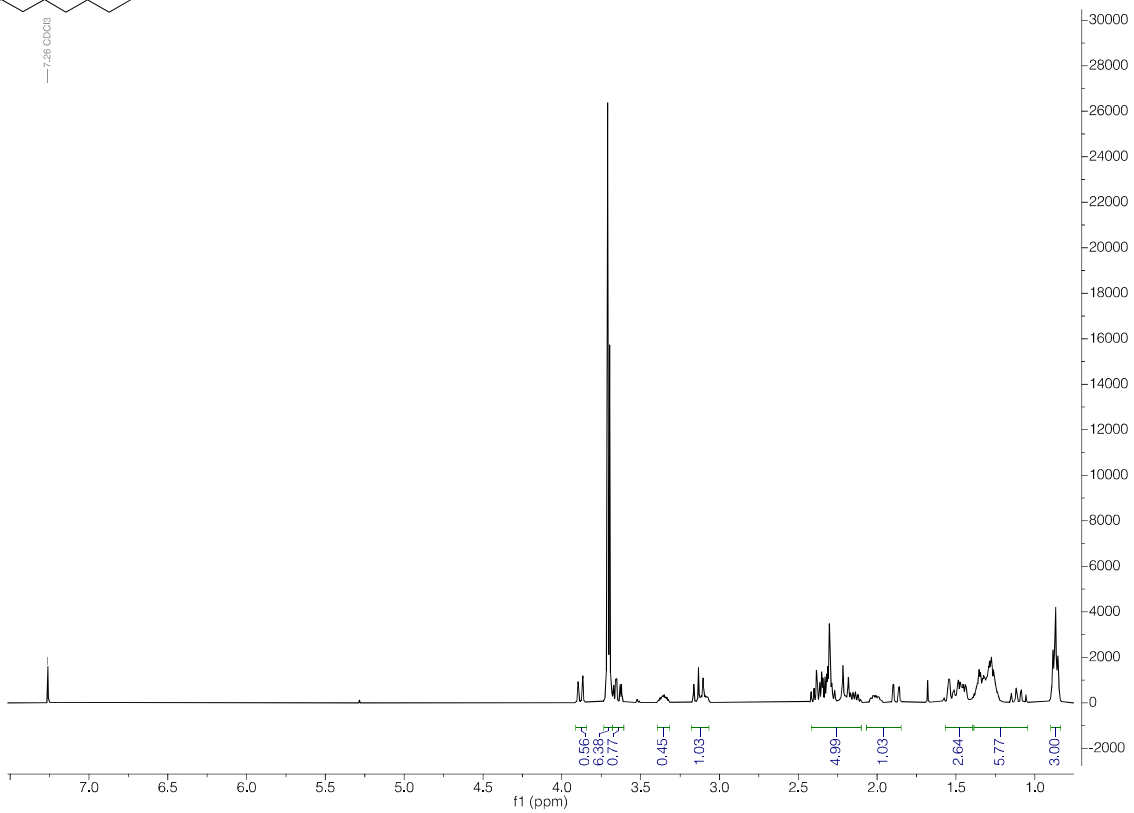
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2961.16	81.3241	2	2925.48	80.1788	3	2875.34	82.5334
4	1479.13	74.2369	5	1438.54	76.4151	6	1339.32	48.5261
7	1303.64	74.9933	8	1288.22	80.7139	9	1157.08	33.5383
10	1091.51	50.4618	11	1045.23	63.3788	12	1024.98	69.5014
13	1016.3	70.8142	14	909.272	65.7659	15	813.813	65.9848
16	729.925	35.5827	17	707.747	68.3705	18	690.391	57.9426
19	586.254	24.2458						

Dimethyl 3-butyl-3,4,4a,5,7,7a-hexahydro-1H-cyclopenta[c]pyran-6,6-dicarboxylate

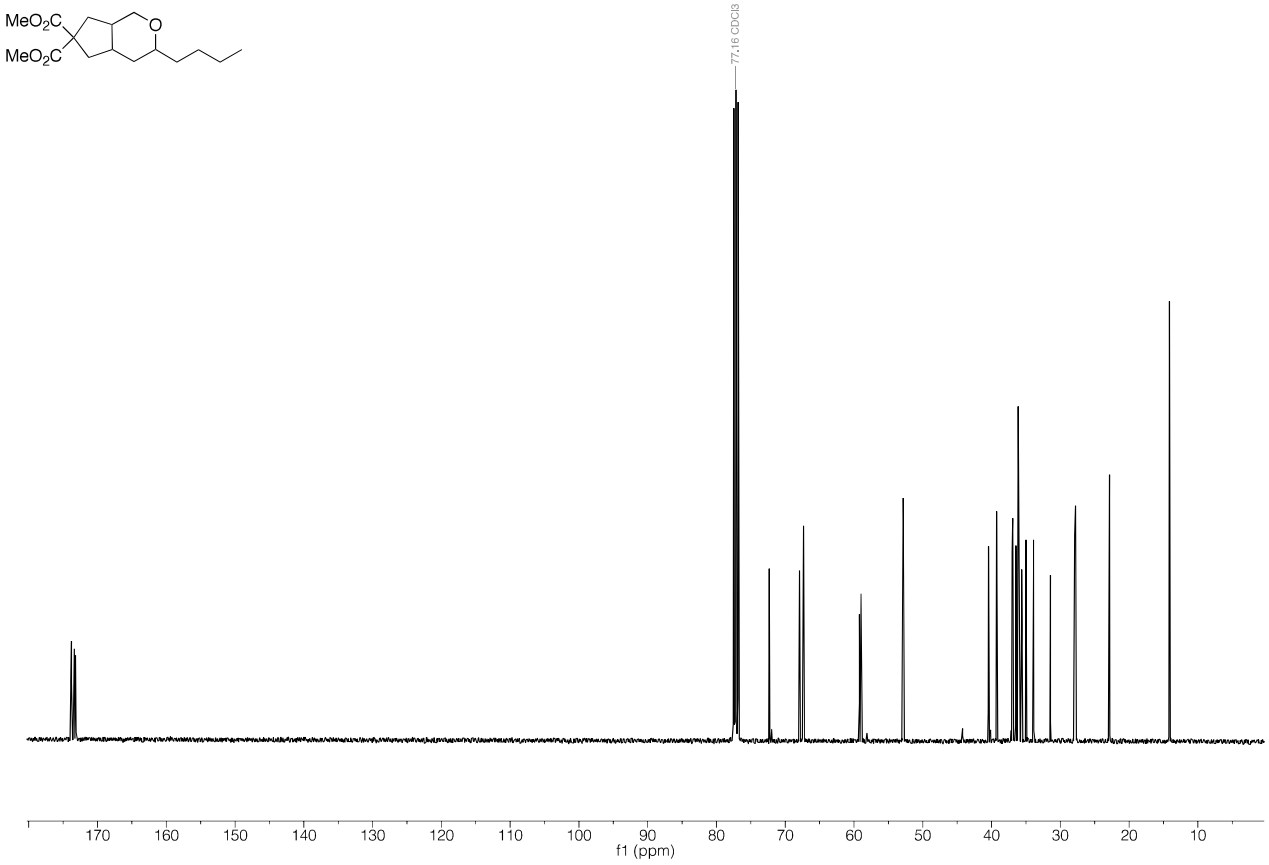
^{1}H-NMR (400 MHz, $CDCl_3$)





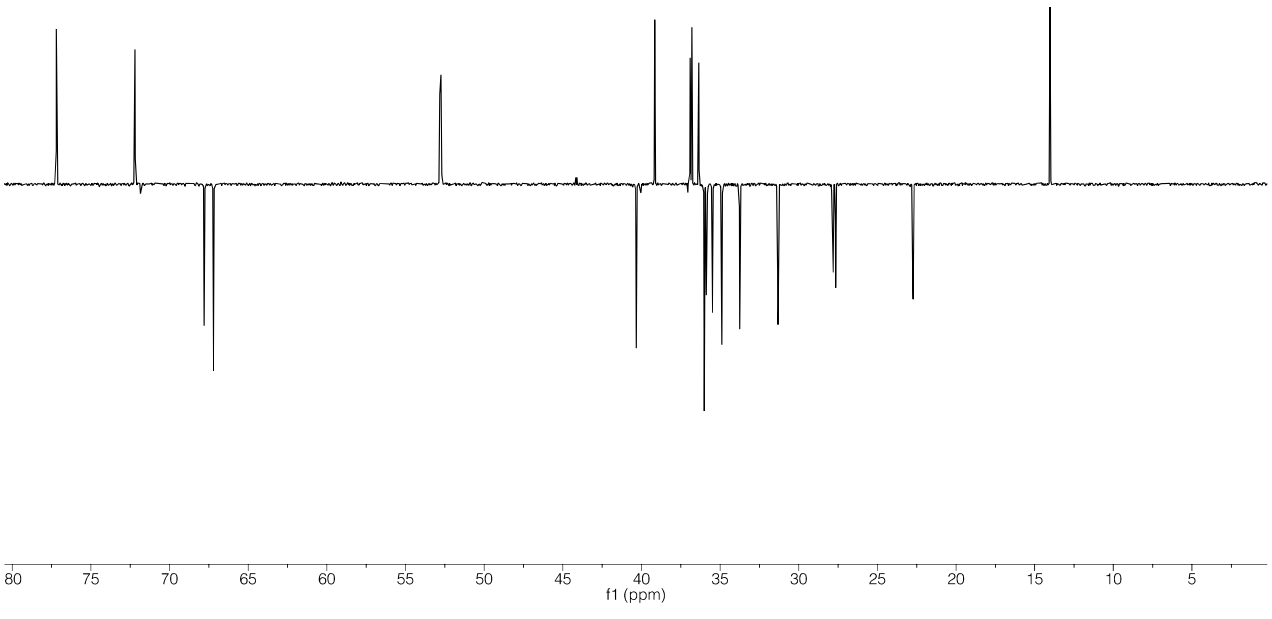
Dimethyl 3-butyl-3,4,4a,5,7,7a-hexahydro-1H-cyclopenta[c]pyran-6,6-dicarboxylate

^{13}C-NMR (101 MHz, $CDCl_3$)



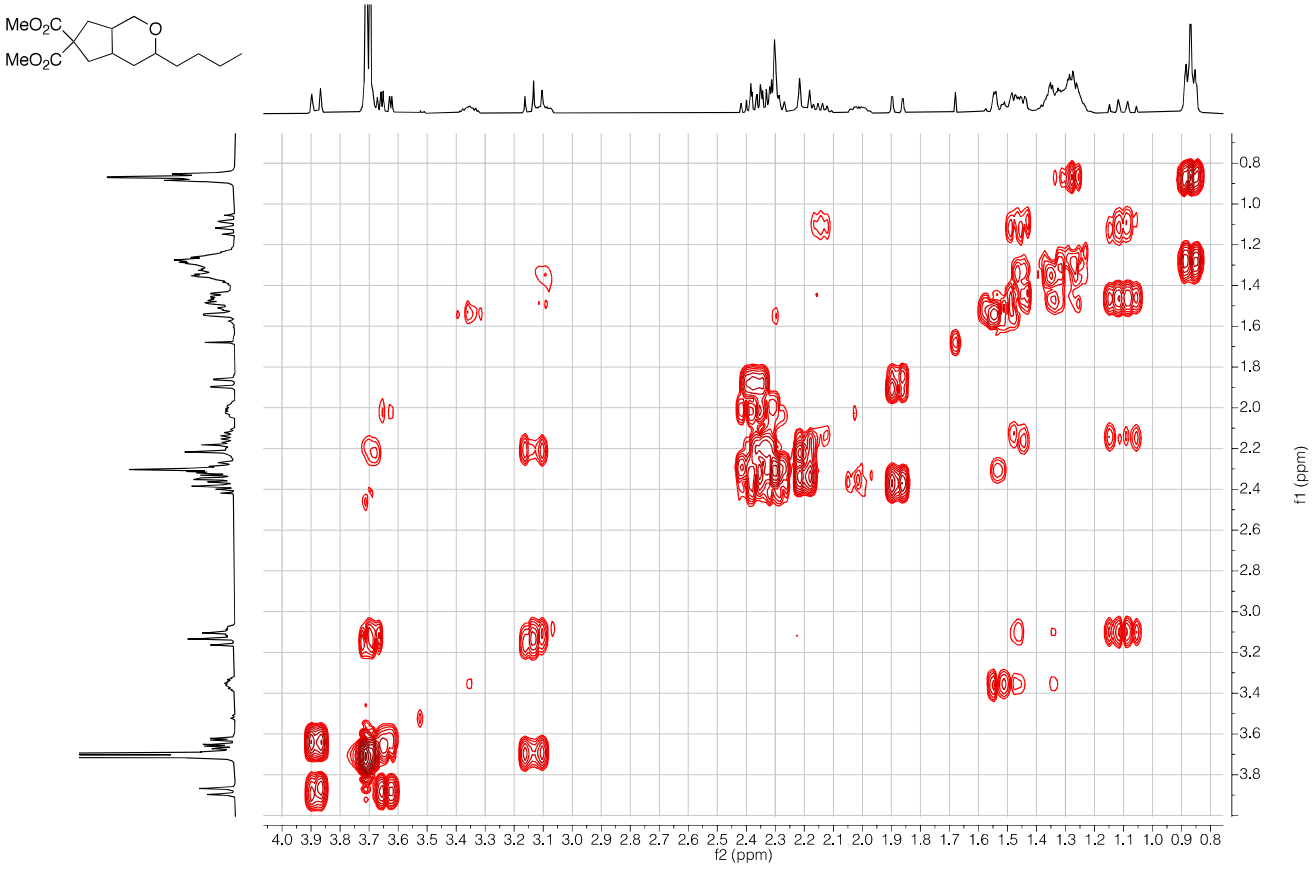
Dimethyl 3-butyl-3,4,4a,5,7,7a-hexahydro-1H-cyclopenta[c]pyran-6,6-dicarboxylate

DEPT-135 NMR (101 MHz, $CDCl_3$)



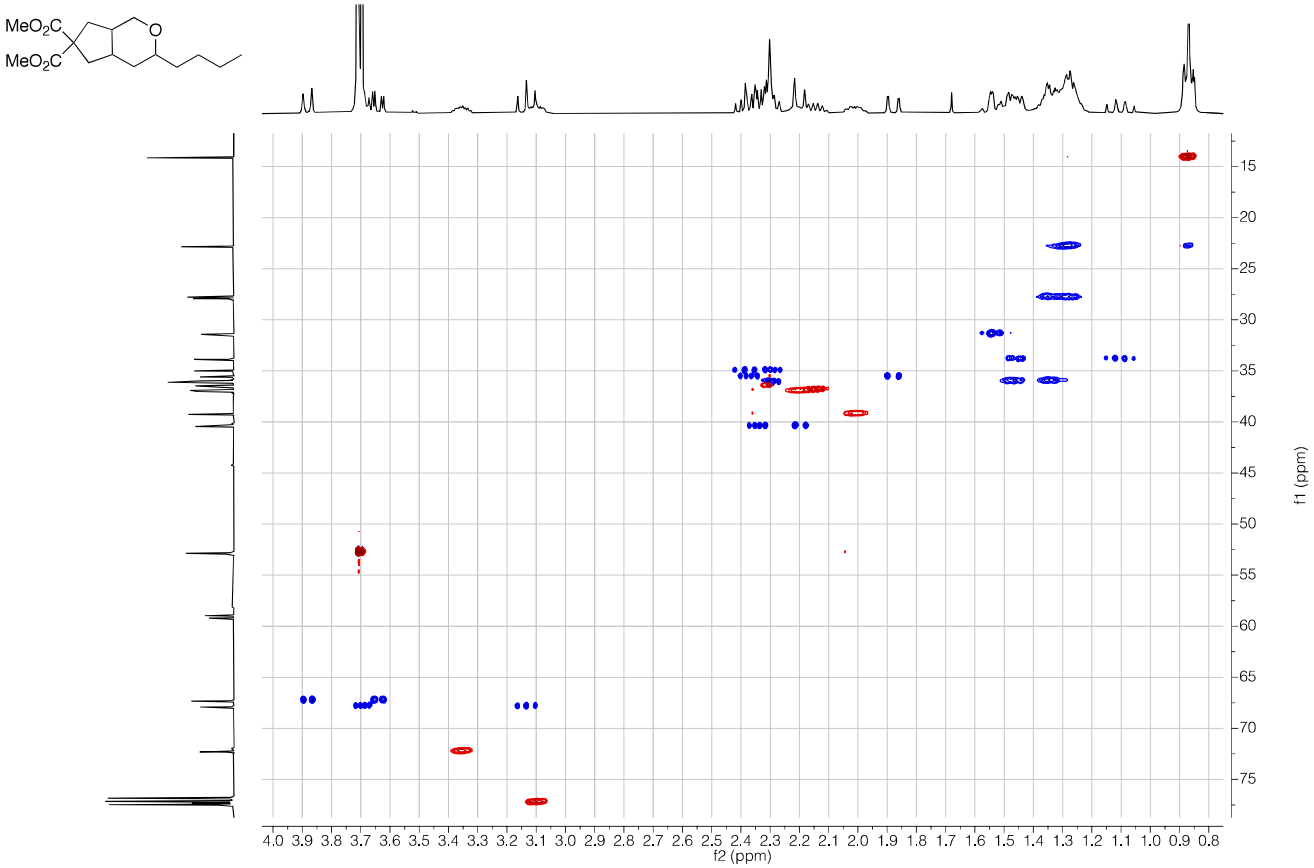
Dimethyl 3-butyl-3,4,4a,5,7,7a-hexahydro-1H-cyclopenta[c]pyran-6,6-dicarboxylate

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



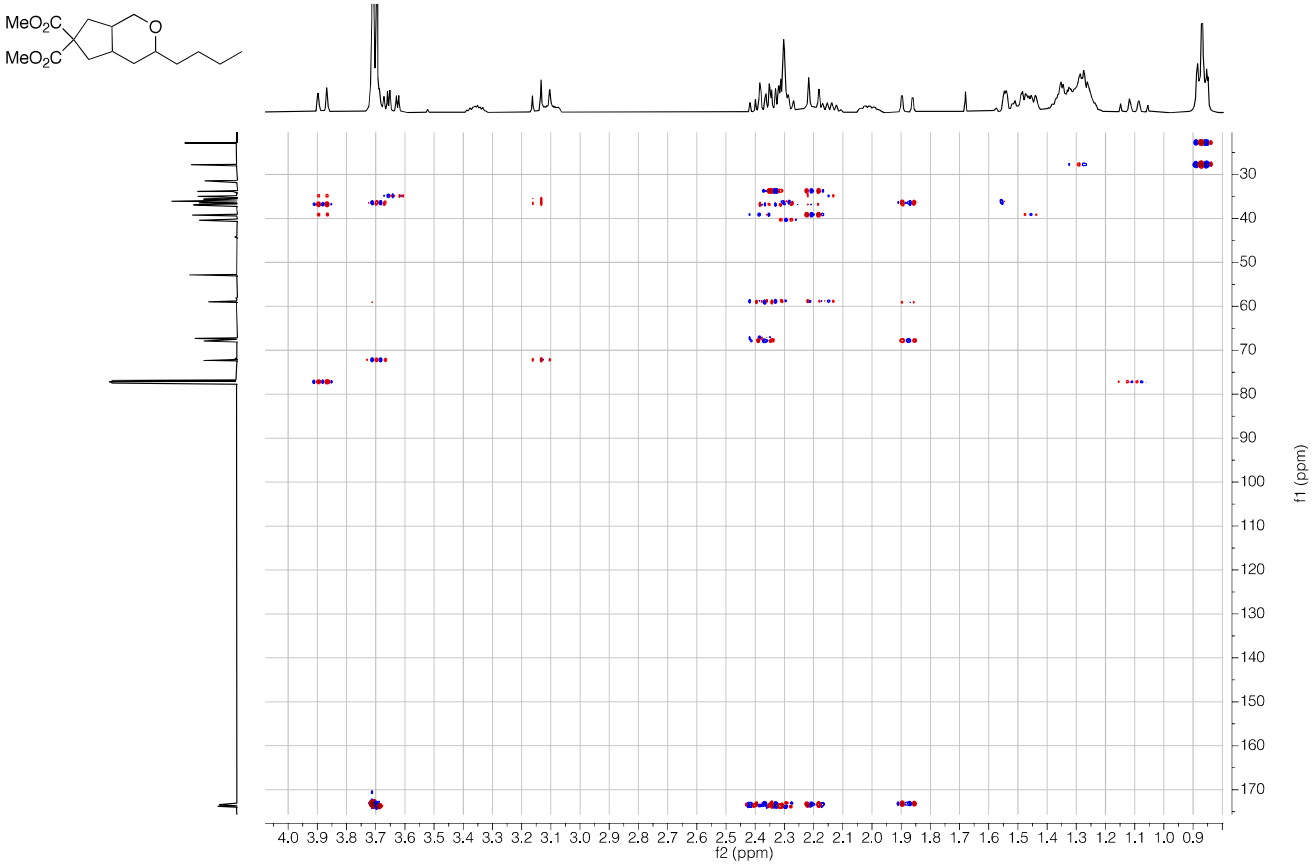
Dimethyl 3-butyl-3,4,4a,5,7,7a-hexahydro-1H-cyclopenta[c]pyran-6,6-dicarboxylate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



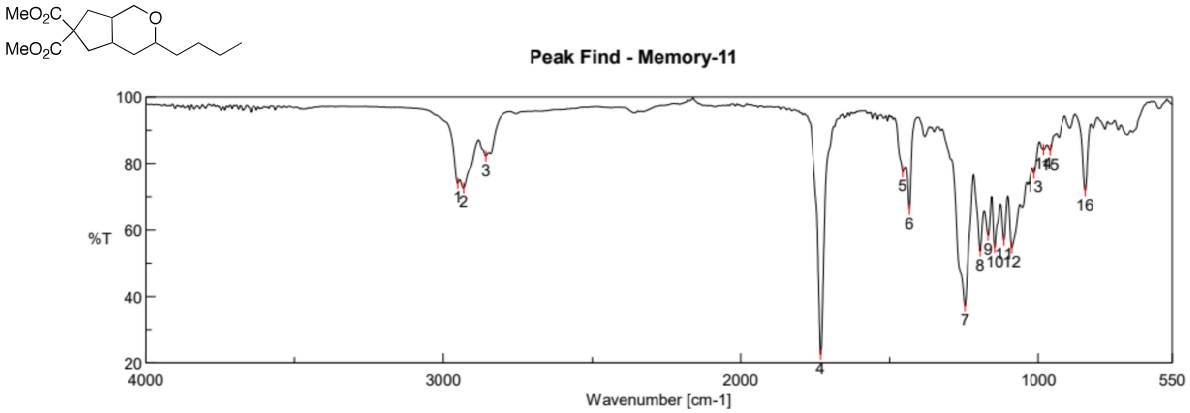
Dimethyl 3-butyl-3,4,4a,5,7,7a-hexahydro-1H-cyclopenta[c]pyran-6,6-dicarboxylate

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



Dimethyl 3-butyl-3,4,4a,5,7,7a-hexahydro-1H-cyclopenta[c]pyran-6,6-dicarboxylate

FT-IR, ATR-diamond

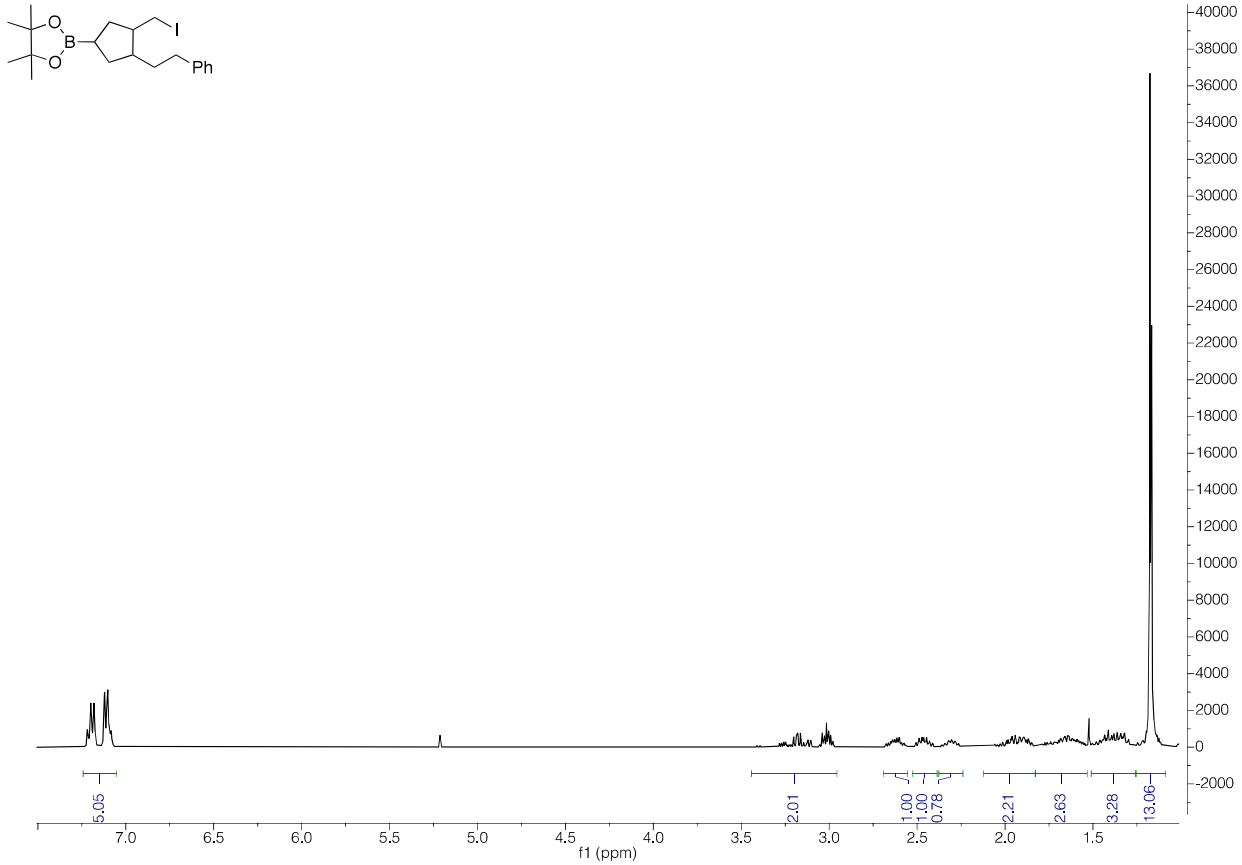


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2951.52	74.0298	2	2931.27	72.5727	3	2857.99	82.1723
4	1730.8	22.5334	5	1455.99	77.4981	6	1433.82	66.2508
7	1245.79	37.0805	8	1194.69	53.6476	9	1167.69	58.4488
10	1145.51	54.7195	11	1115.62	56.899	12	1089.58	54.5927
13	1014.37	77.1857	14	982.554	84.1227	15	960.377	83.9773
16	842.74	71.7651						

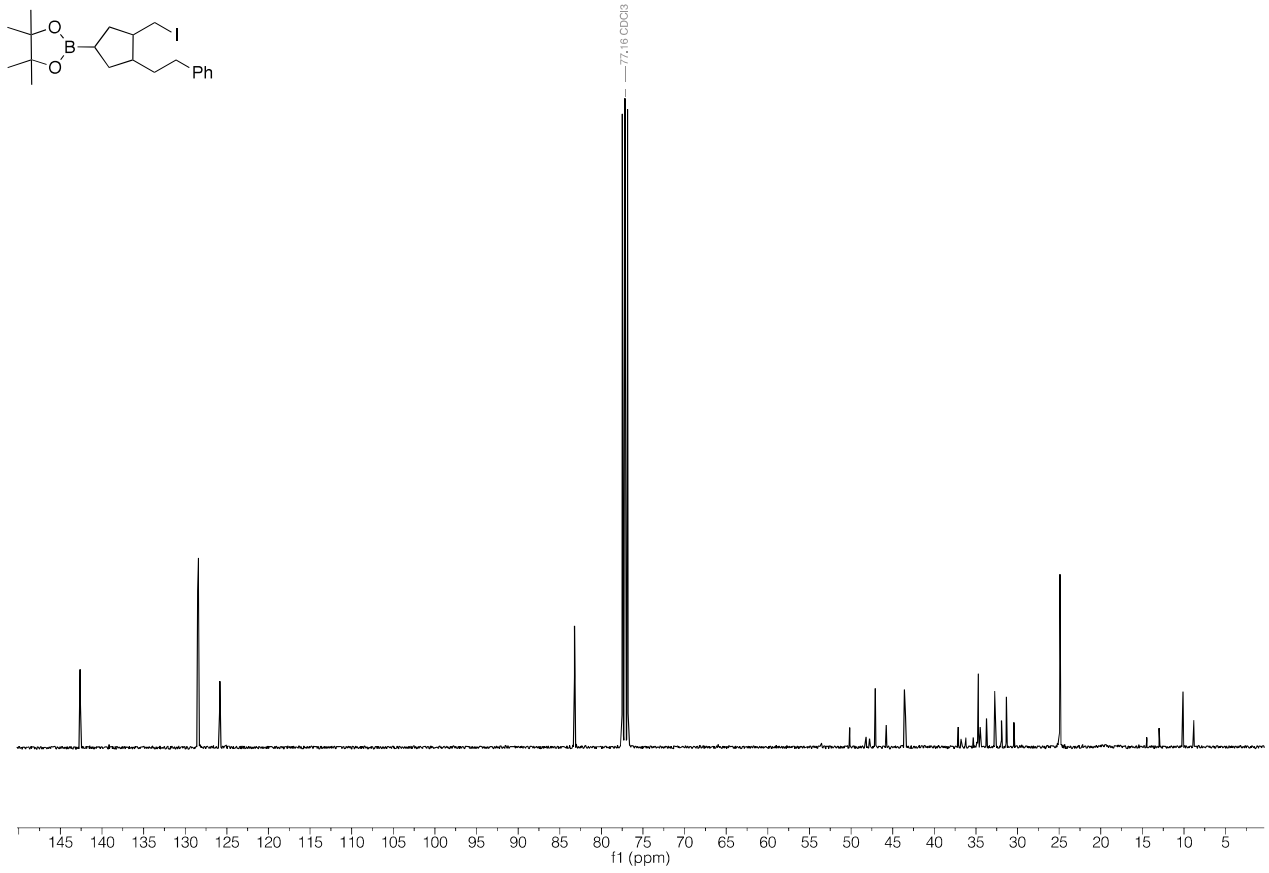
2-[3-(iodomethyl)-4-(2-phenylethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H-NMR (400 MHz, $CDCl_3$)

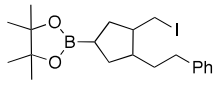


2-[3-(iodomethyl)-4-(2-phenylethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{13}C-NMR (101 MHz, $CDCl_3$)

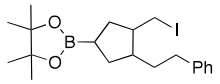


2-[3-(iodomethyl)-4-(2-phenylethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



DEPT-135 NMR (101 MHz, $CDCl_3$)

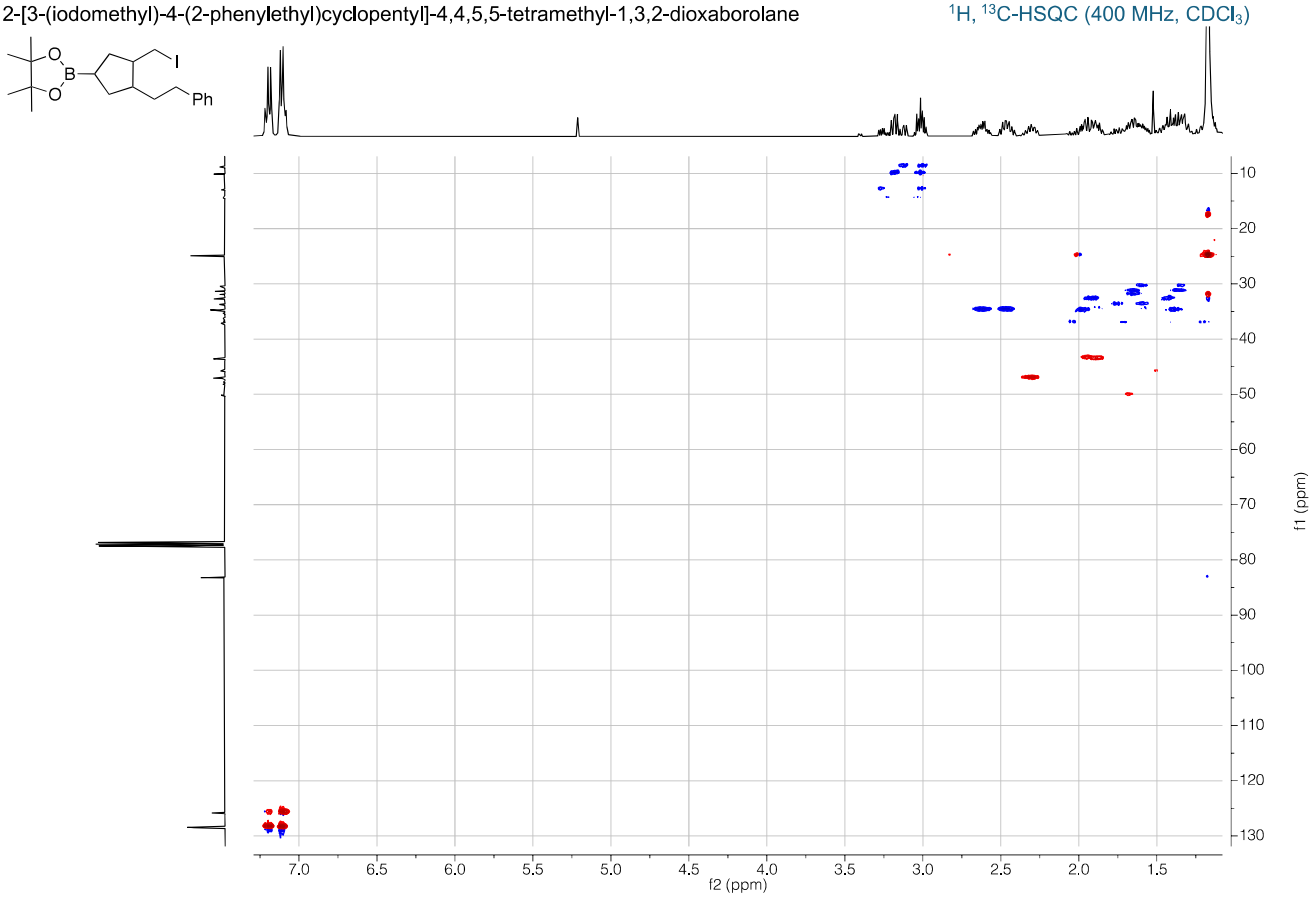
2-[3-(iodomethyl)-4-(2-phenylethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



^1H, ^1H-COSY (400 MHz, $CDCl_3$)

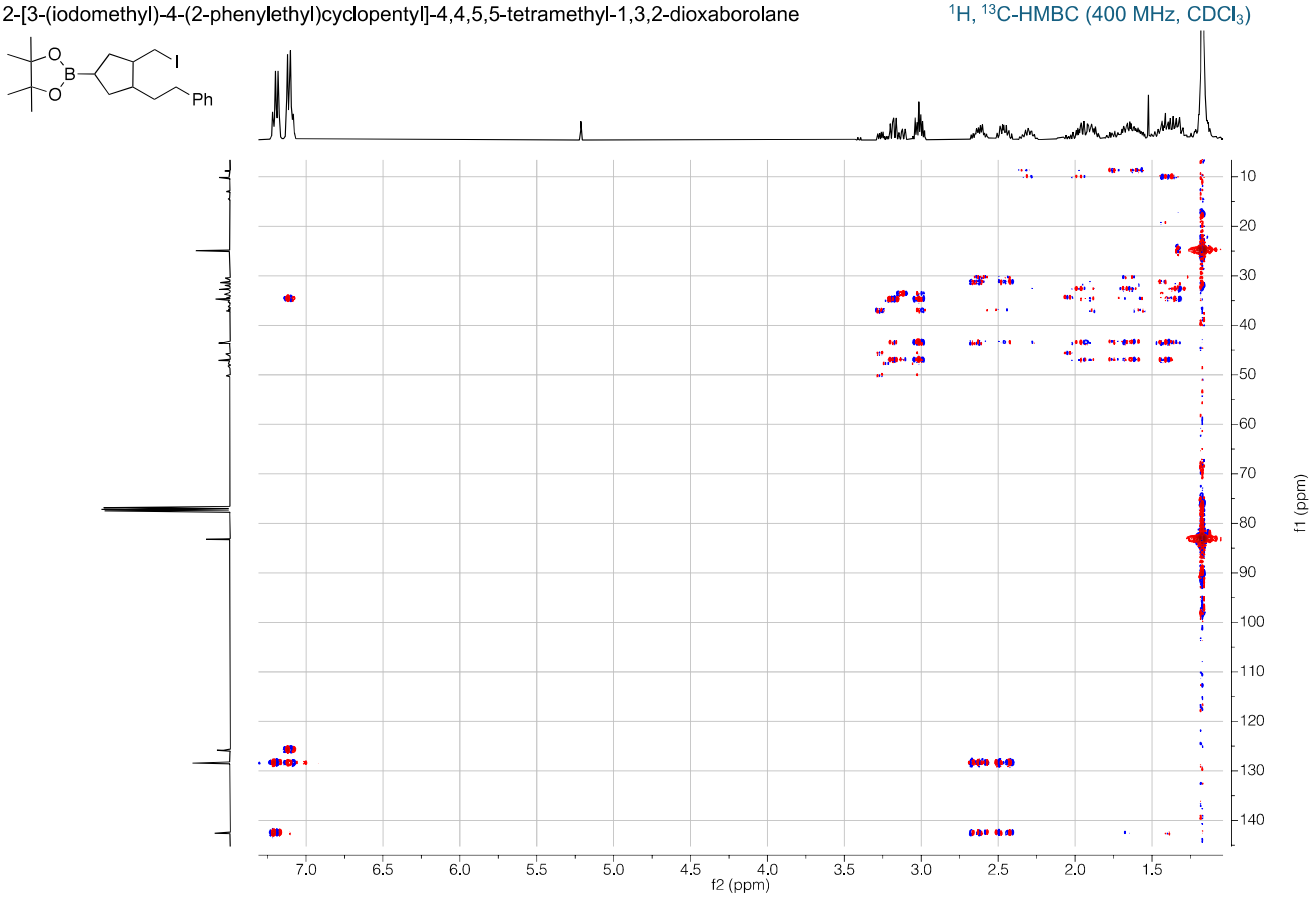
2-[3-(iodomethyl)-4-(2-phenylethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



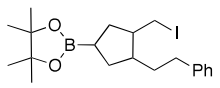
2-[3-(iodomethyl)-4-(2-phenylethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



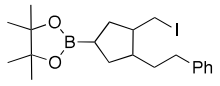
2-[3-(iodomethyl)-4-(2-phenylethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

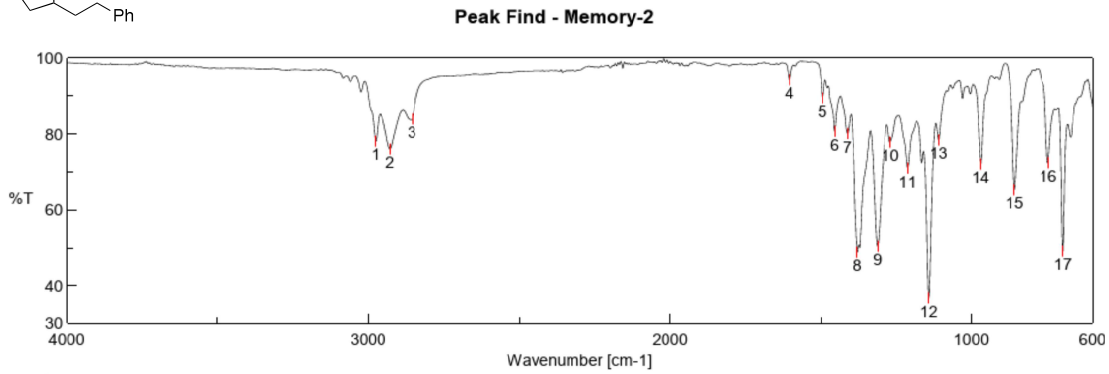
^{11}B-NMR (128 MHz, $CDCl_3$)



2-[3-(iodomethyl)-4-(2-phenylethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

FT-IR, ATR-diamond



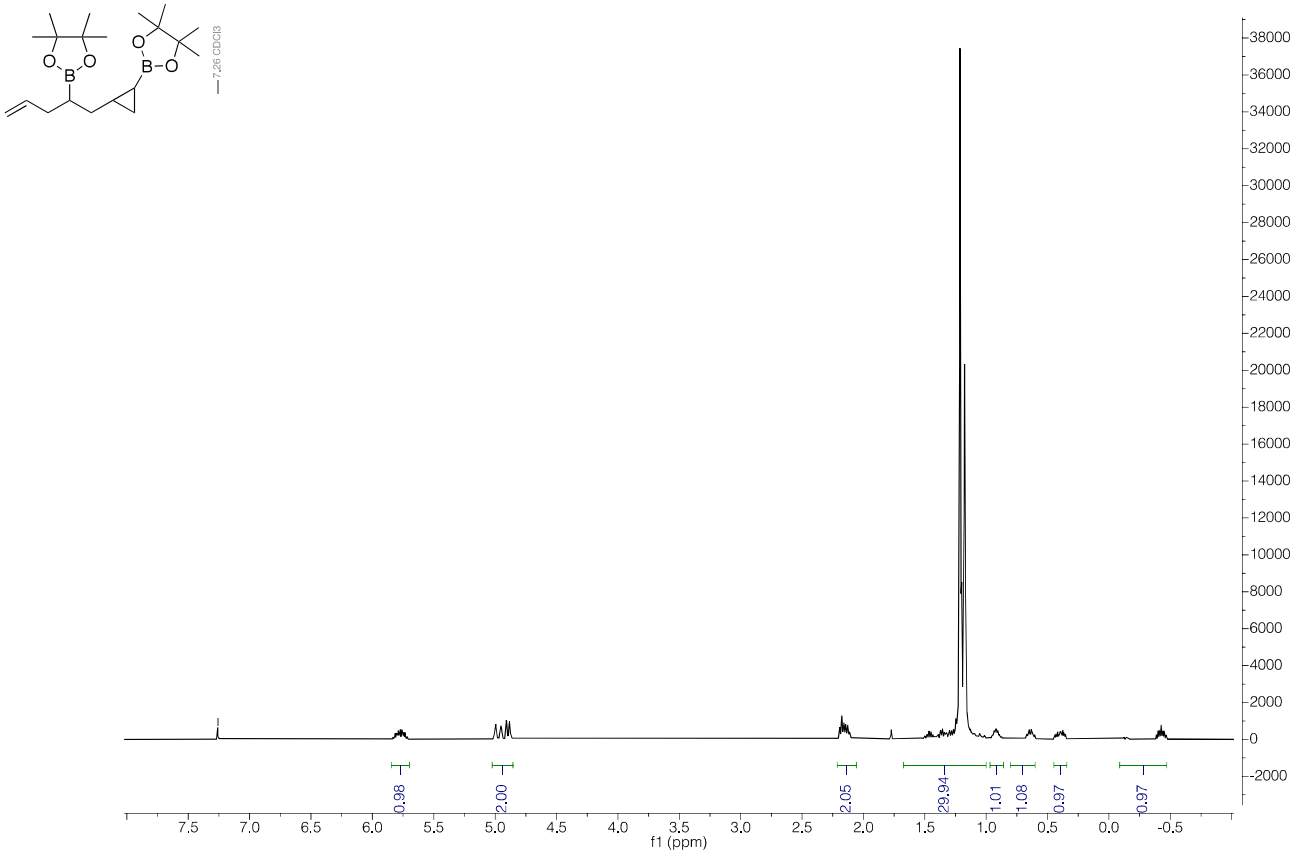


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	78.0443	2	2928.38	75.9781	3	2856.06	83.9193
4	1602.56	94.2601	5	1495.53	89.4189	6	1454.06	80.6358
7	1411.64	80.0825	8	1377.89	48.7691	9	1312.32	50.3201
10	1269.9	77.7795	11	1212.04	70.9235	12	1141.65	36.6987
13	1108.87	78.3234	14	970.019	71.9746	15	858.168	65.2485
16	746.317	72.3595	17	697.141	49.0599			

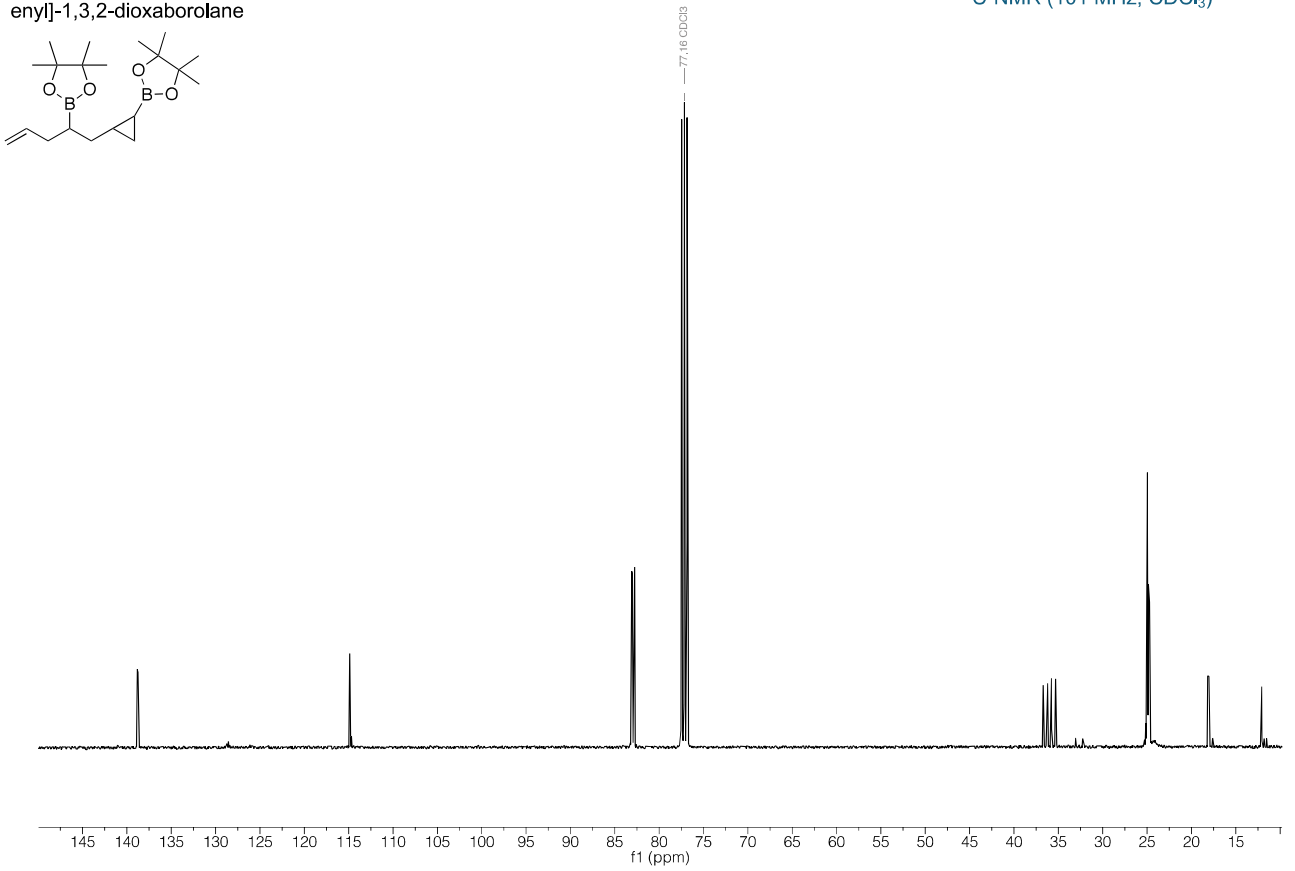
4,4,5,5-tetramethyl-2-[1-[[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl]methyl]but-3-enyl]-1,3,2-dioxaborolane

^{1}H-NMR (400 MHz, $CDCl_3$)

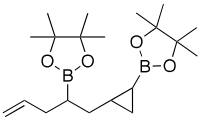


4,4,5,5-tetramethyl-2-[1-[[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl]methyl]but-3-enyl]-1,3,2-dioxaborolane

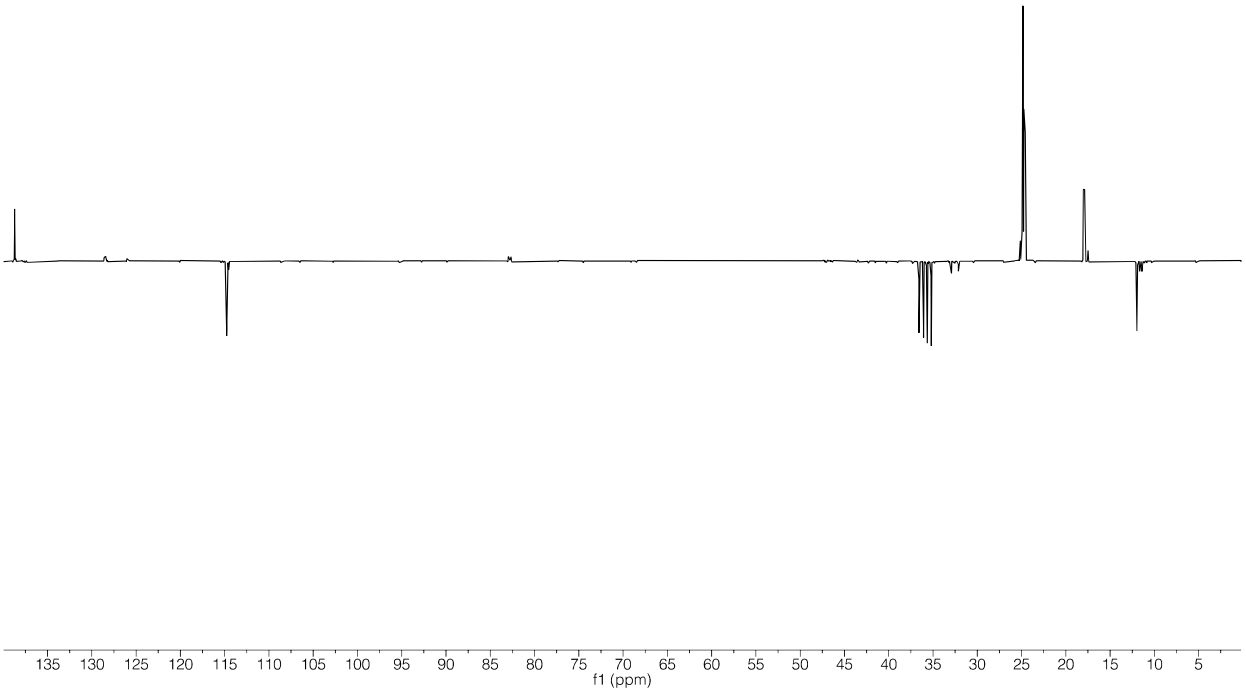
^{13}C-NMR (101 MHz, $CDCl_3$)



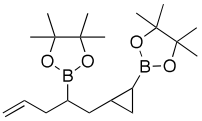
4,4,5,5-tetramethyl-2-[1-[[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl]methyl]but-3-enyl]-1,3,2-dioxaborolane



DEPT-135 NMR (101 MHz, $CDCl_3$)

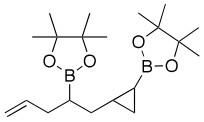


4,4,5,5-tetramethyl-2-[1-[[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl]methyl]but-3-enyl]-1,3,2-dioxaborolane



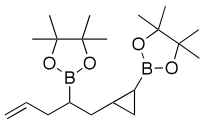
^1H, ^1H-COSY (400 MHz, $CDCl_3$)

4,4,5,5-tetramethyl-2-[1-[[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl]methyl]but-3-enyl]-1,3,2-dioxaborolane



^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)

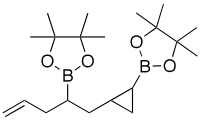
4,4,5,5-tetramethyl-2-[1-[[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl]methyl]but-3-enyl]-1,3,2-dioxaborolane



^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)

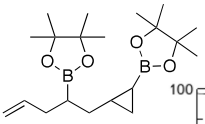
4,4,5,5-tetramethyl-2-[1-[[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl]methyl]but-3-enyl]-1,3,2-dioxaborolane

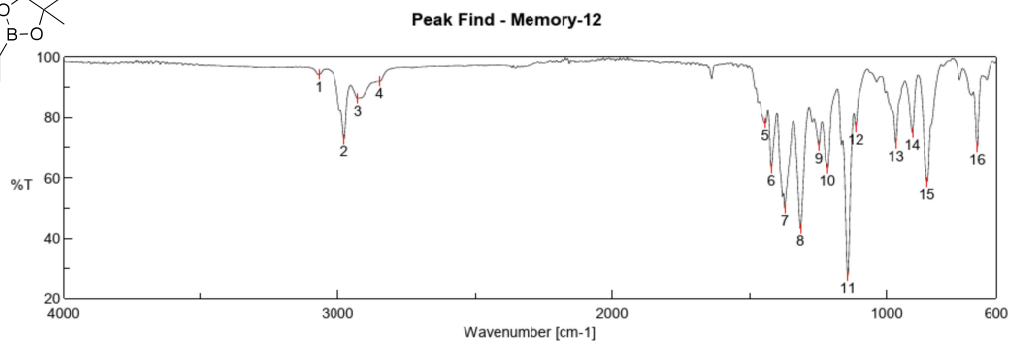
^{11}B-NMR (128 MHz, $CDCl_3$)



4,4,5,5-tetramethyl-2-[1-[[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl]methyl]but-3-enyl]-1,3,2-dioxaborolane

FT-IR, ATR-diamond

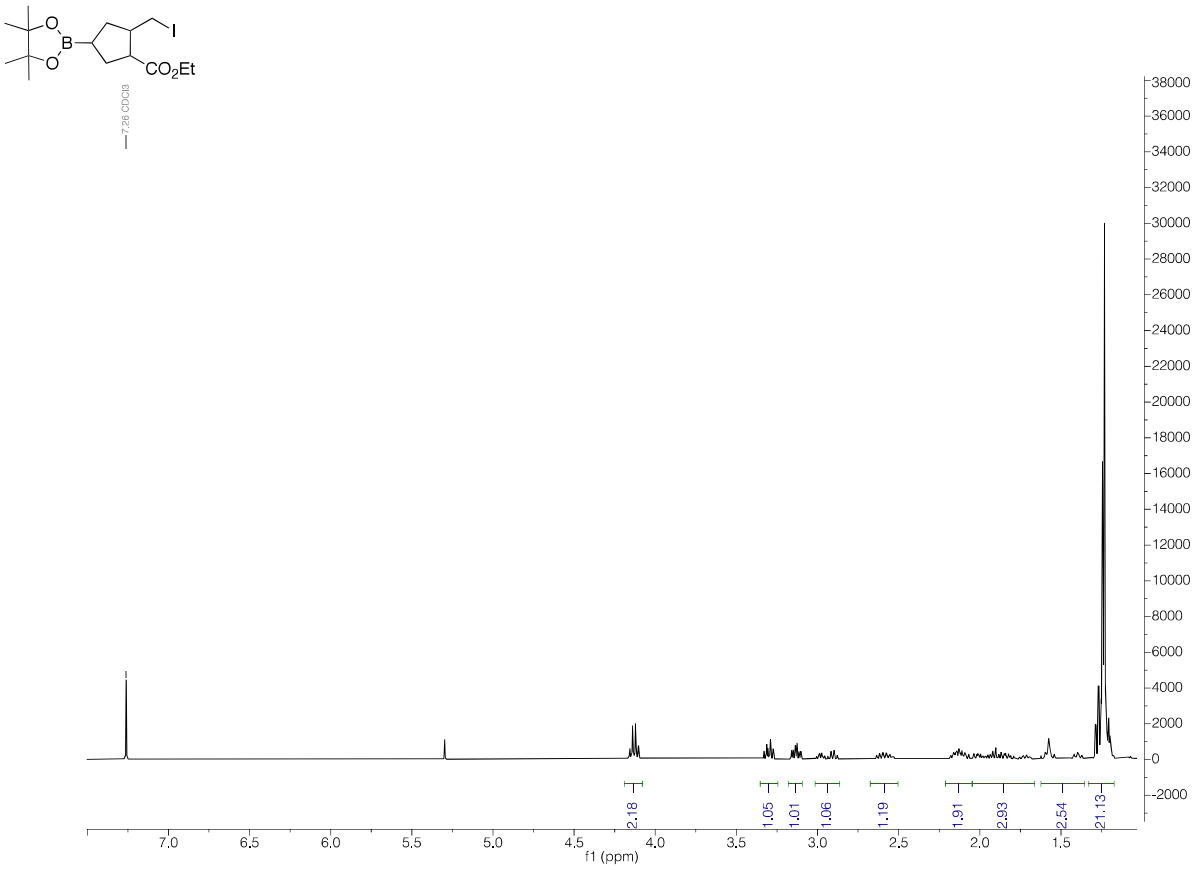




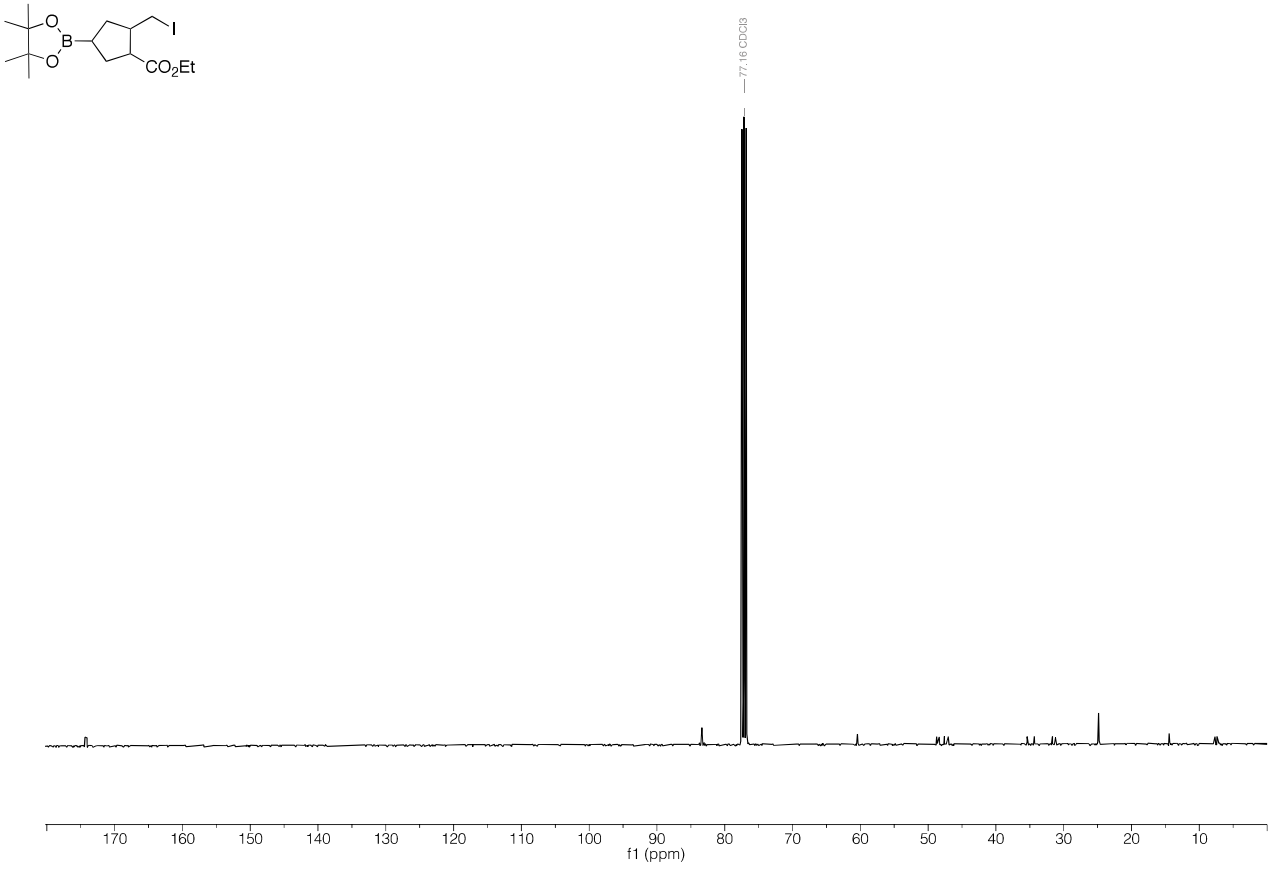
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3070.12	94.2417	2	2976.59	72.7296	3	2925.48	86.3046
4	2847.38	91.9552	5	1441.53	78.1345	6	1419.35	63.1697
7	1370.18	49.8369	8	1313.29	43.2063	9	1245.79	70.6255
10	1215.9	63.0531	11	1141.65	27.5717	12	1111.76	76.8461
13	967.126	71.3231	14	907.344	75.0455	15	855.275	58.5436
16	670.142	70.1161						

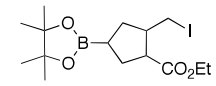
Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 1+2) ^{1}H-NMR (400 MHz, $CDCl_3$)

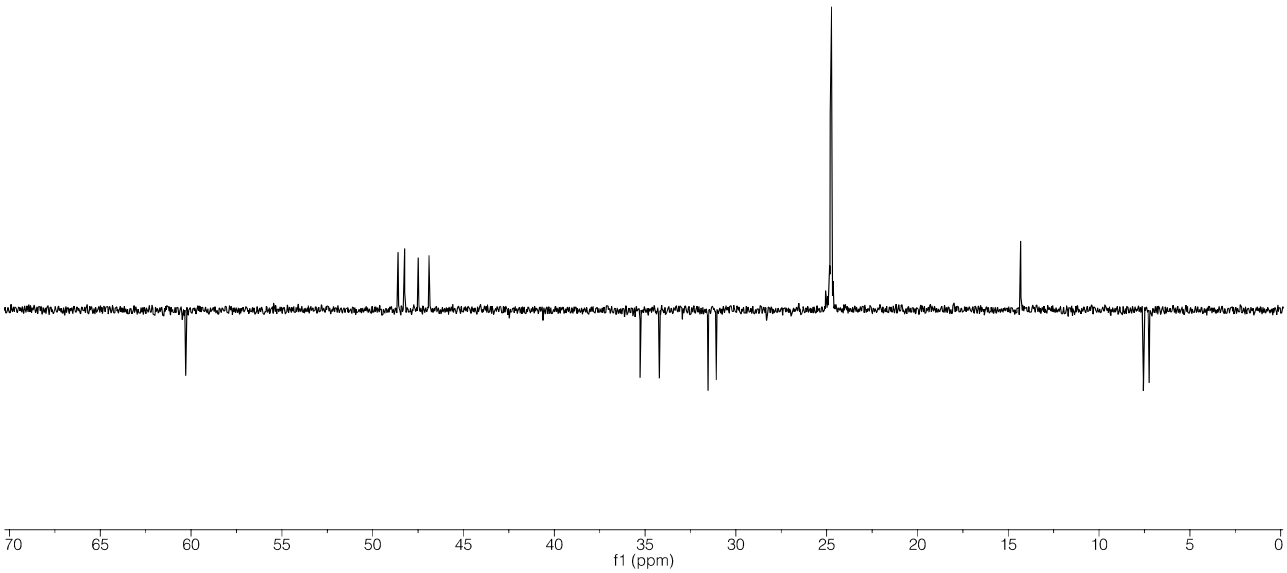


Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 1+2) ^{13}C-NMR (101 MHz, $CDCl_3$)

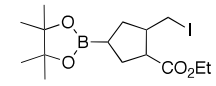


Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 1+2) DEPT-135 NMR (101 MHz, $CDCl_3$)

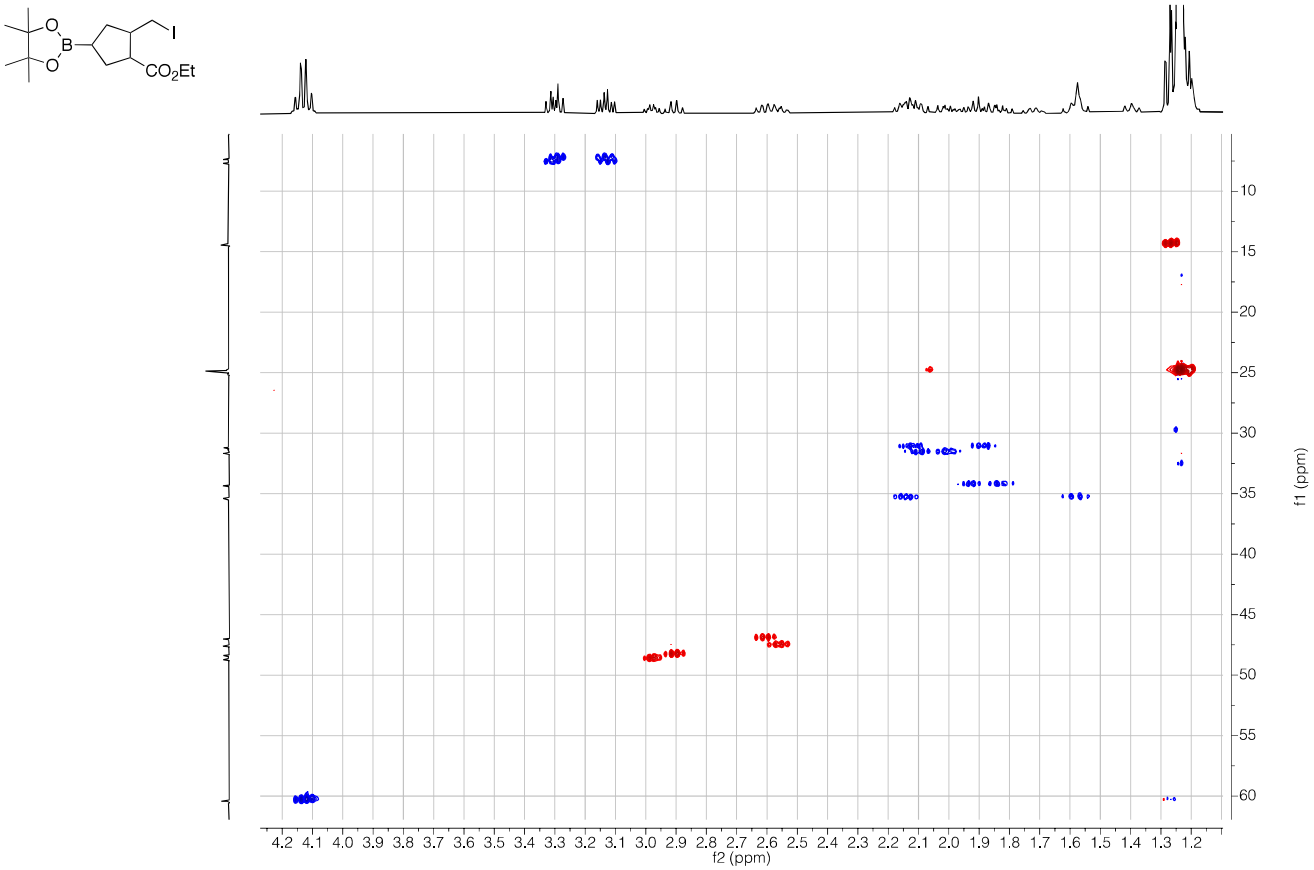




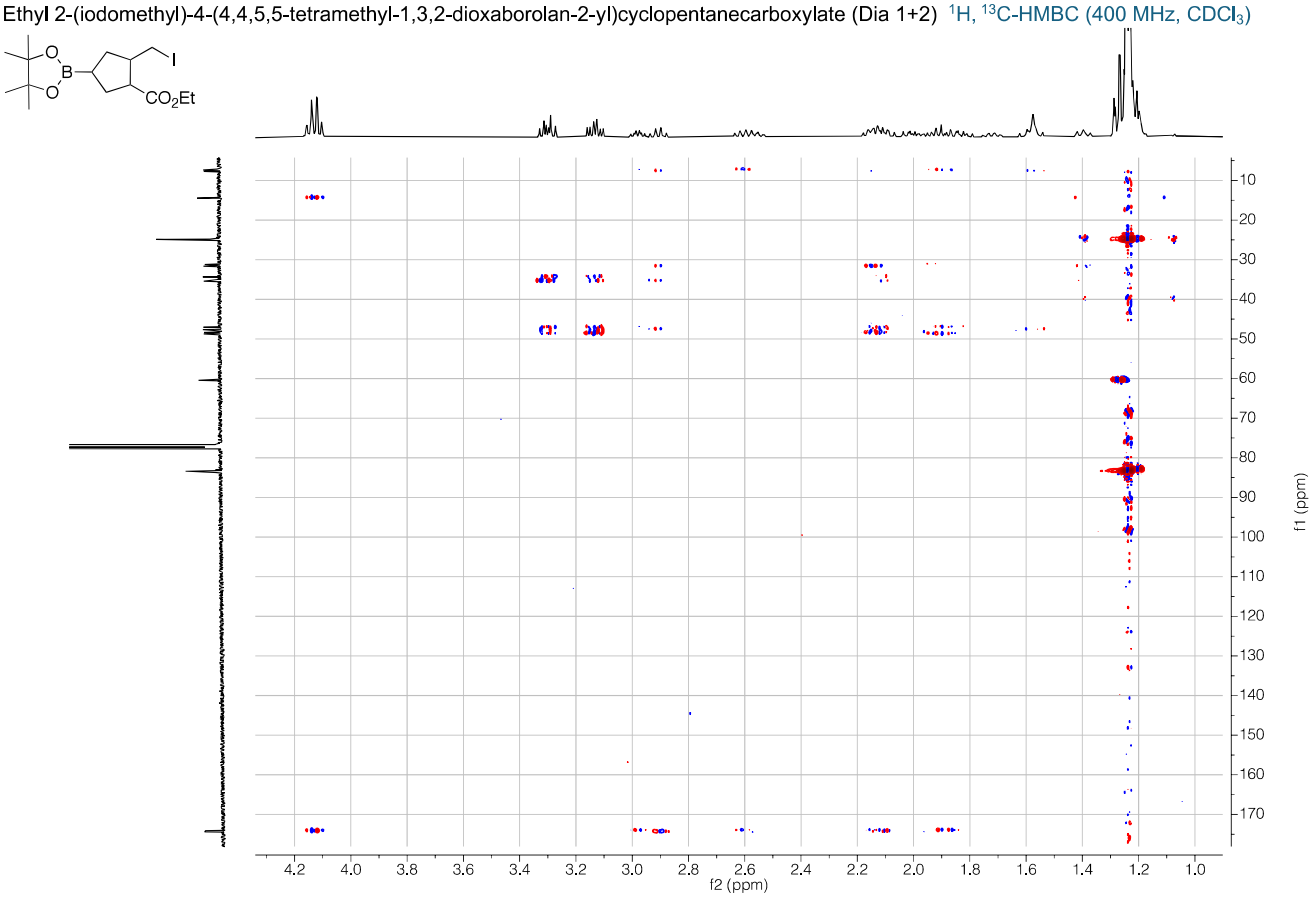
Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 1+2) ^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



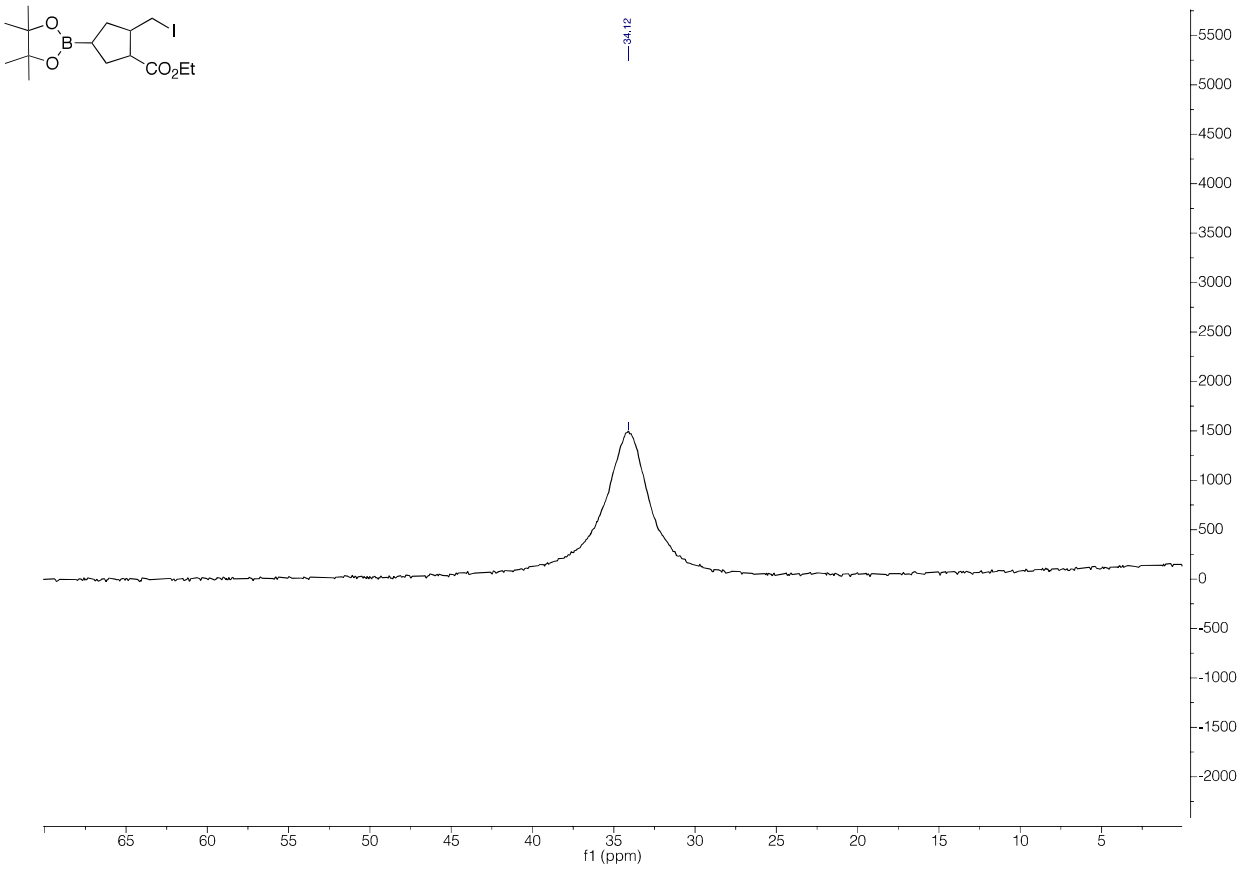
Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 1+2) ^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



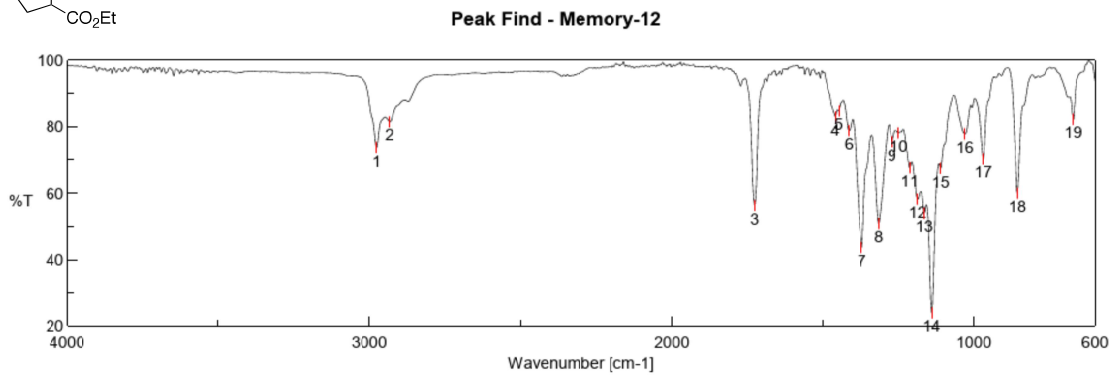
Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 1+2) ^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 1+2) ^{11}B-NMR (128 MHz, $CDCl_3$)



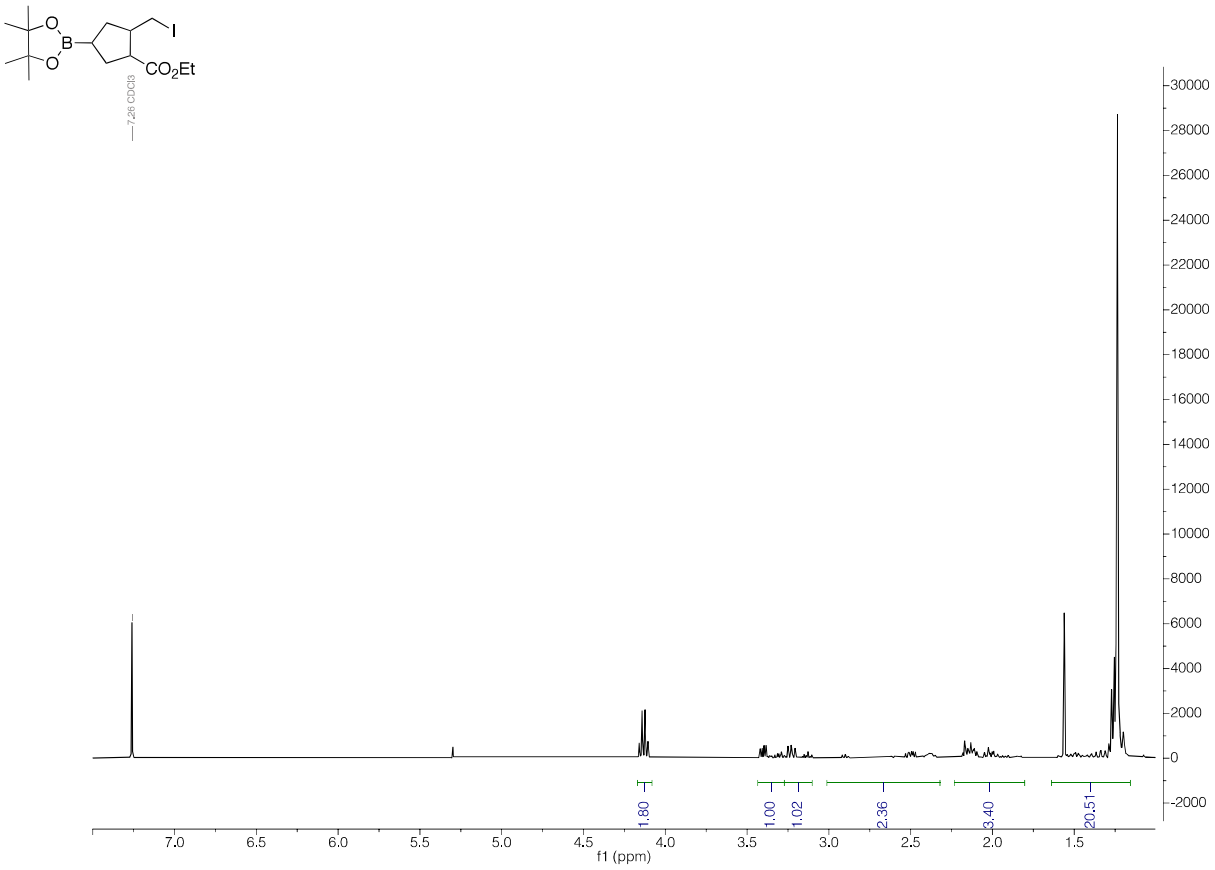
Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 1+2) FT-IR, ATR-diamond



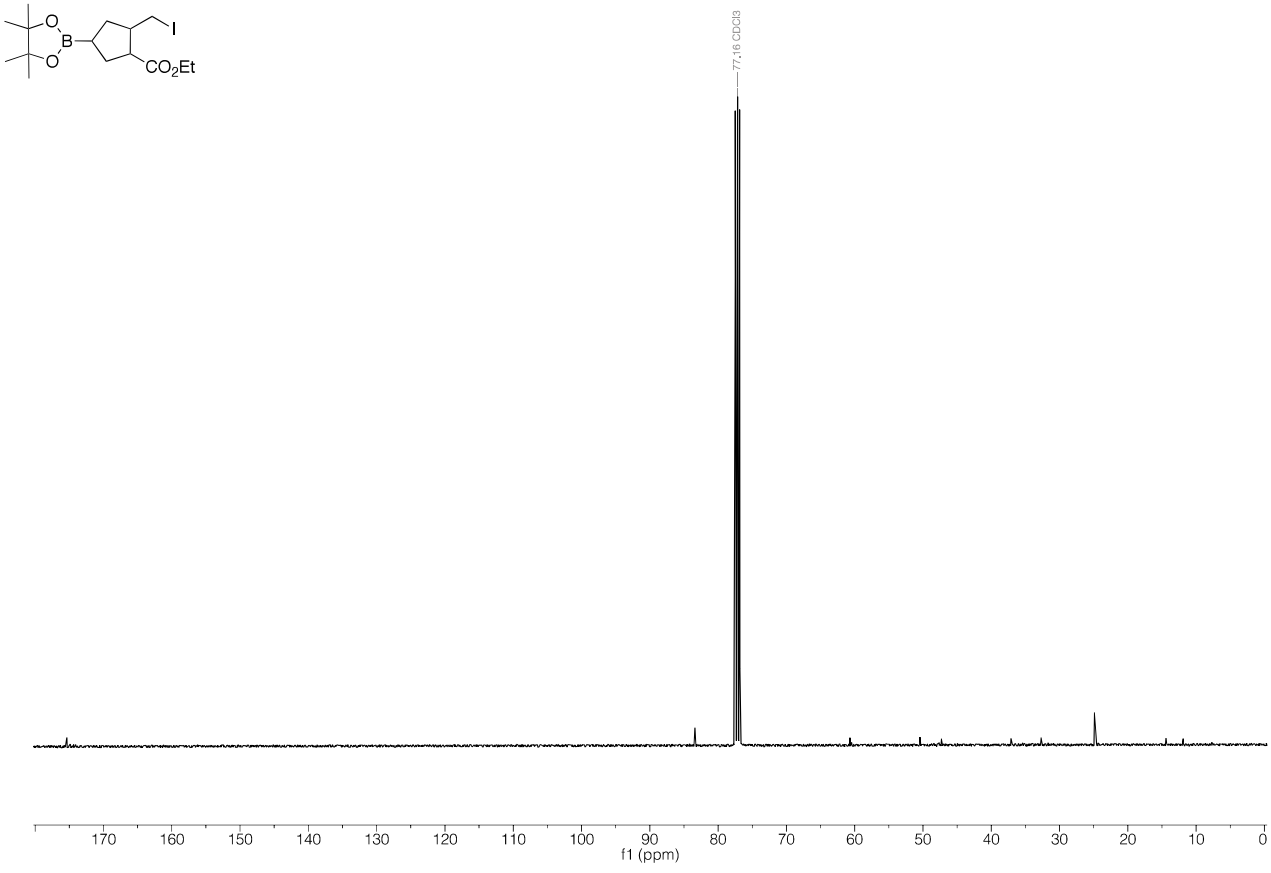
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	73.7065	2	2933.2	81.4183	3	1725.01	56.2551
4	1457.92	82.8914	5	1447.31	84.7445	6	1412.6	78.8096
7	1371.14	43.6523	8	1315.21	50.8599	9	1270.86	75.4083
10	1248.68	78.0762	11	1212.04	67.6269	12	1186.97	58.1615
13	1164.79	53.9302	14	1140.69	23.9756	15	1110.8	67.4553
16	1029.8	77.8127	17	969.055	70.2375	18	856.239	59.9576
19	670.142	82.188						

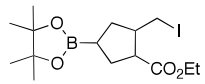
Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 3+4) ^{1}H-NMR (400 MHz, $CDCl_3$)

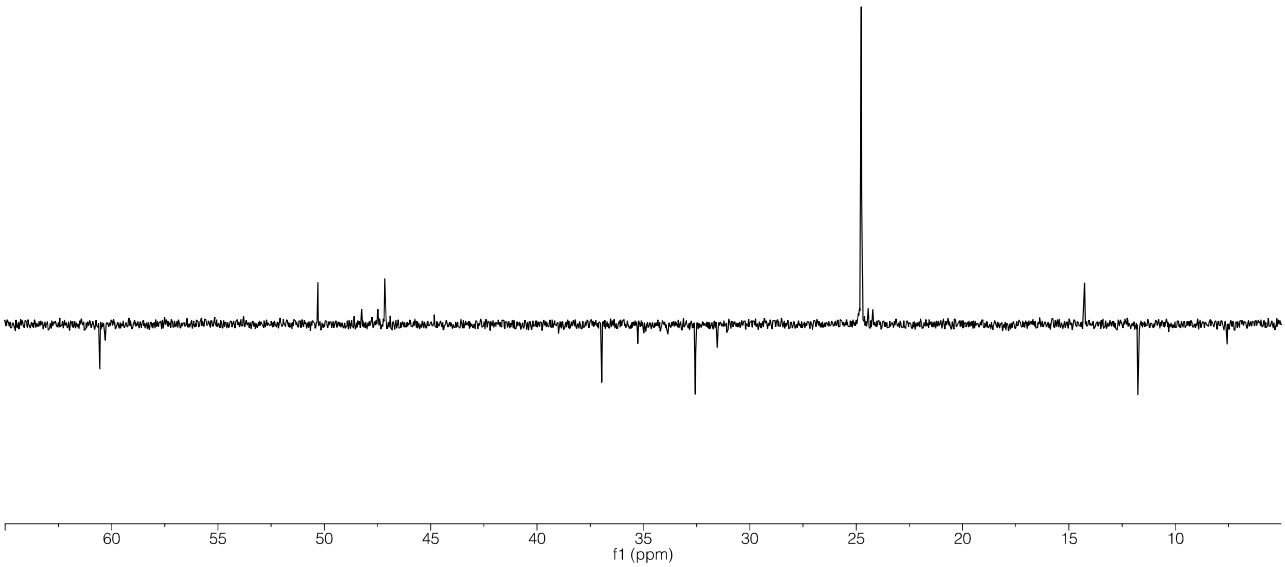


Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 3+4) ^{13}C-NMR (101 MHz, $CDCl_3$)

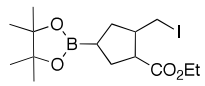


Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 3+4) DEPT-135 NMR (101 MHz, $CDCl_3$)

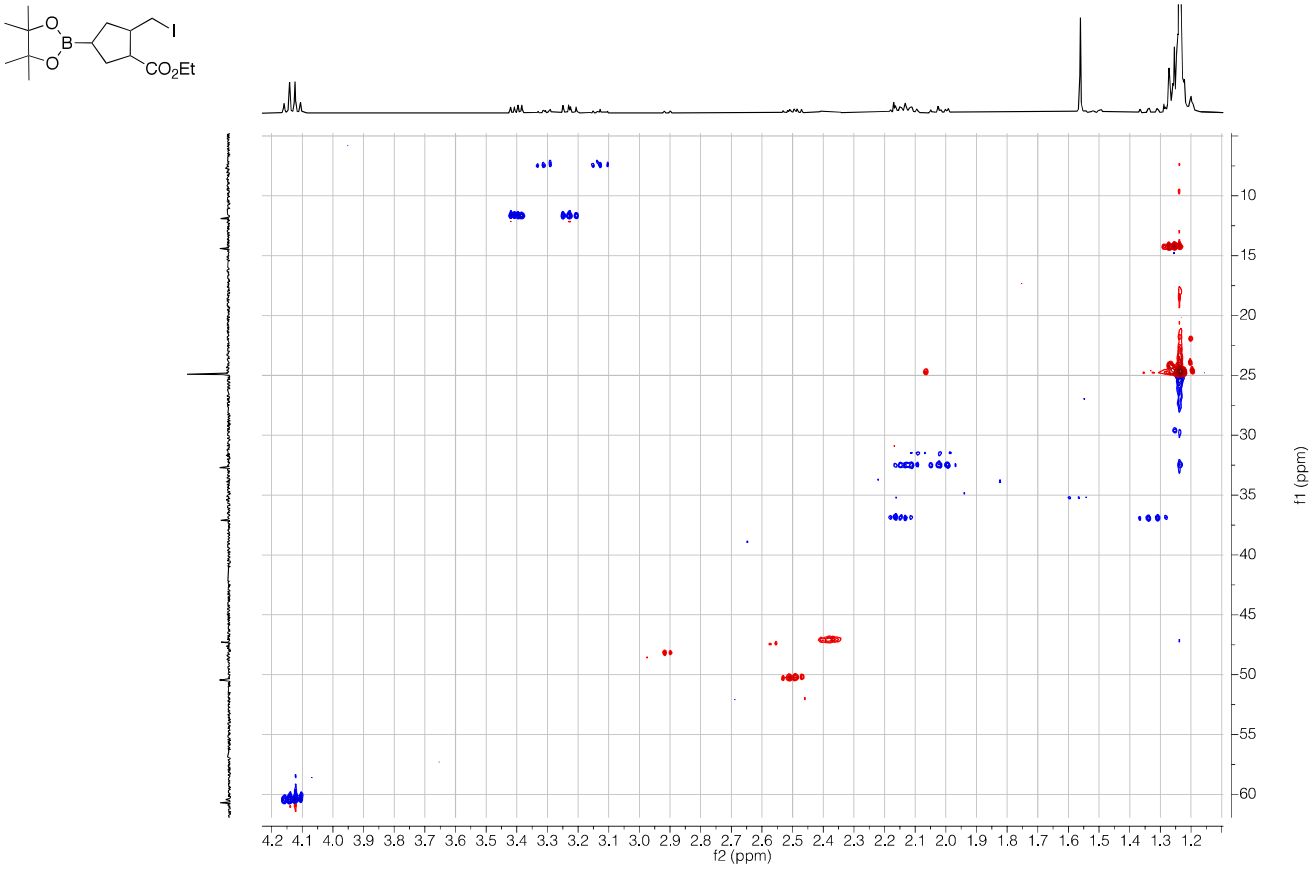




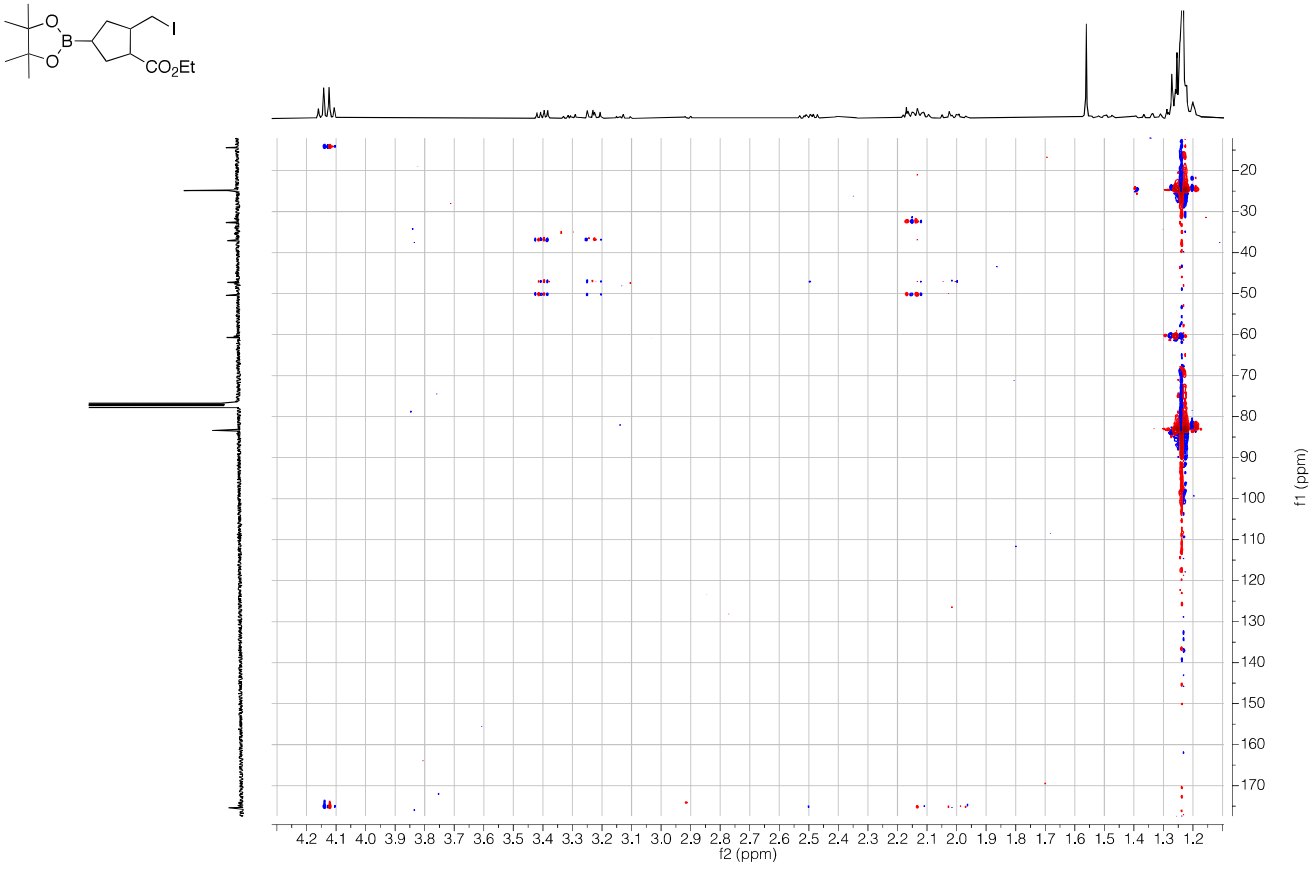
Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 3+4) ^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



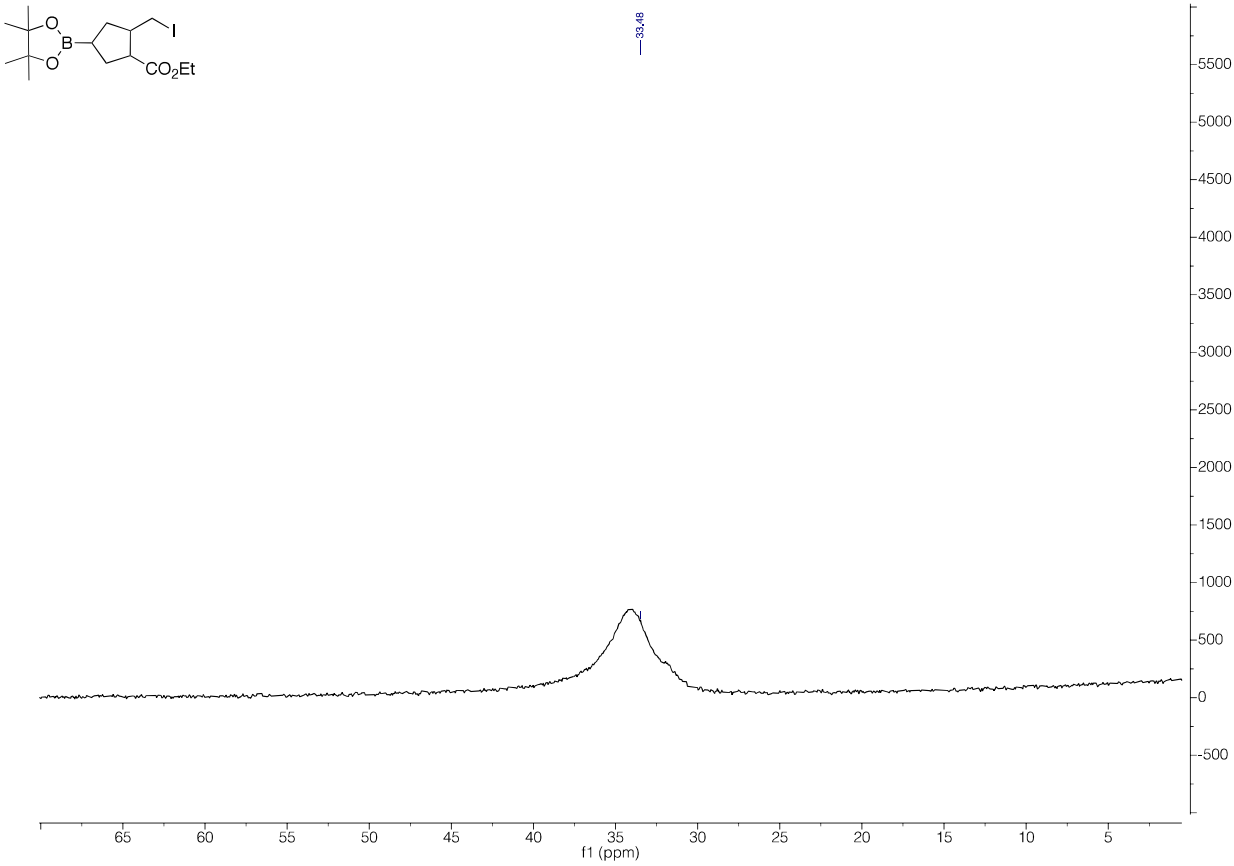
Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 3+4) ^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



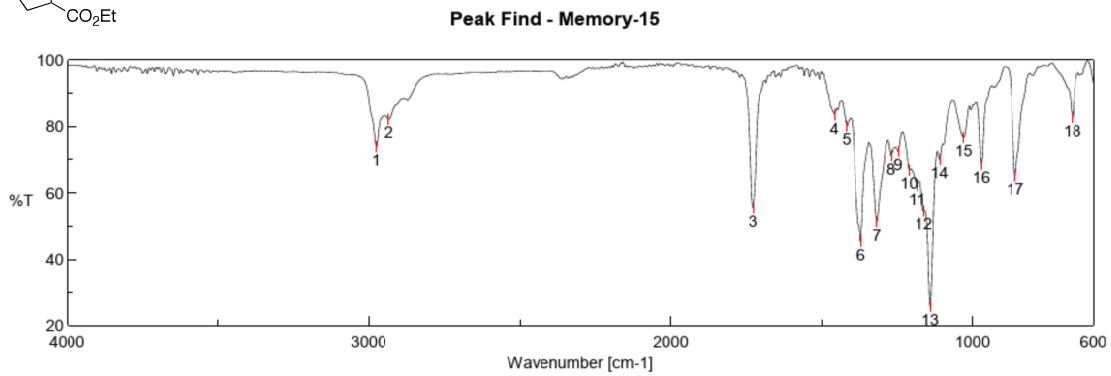
Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 3+4) ^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 3+4) ^{11}B-NMR (128 MHz, $CDCl_3$)



Ethyl 2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (Dia 3+4) FT-IR, ATR-diamond

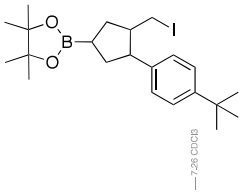


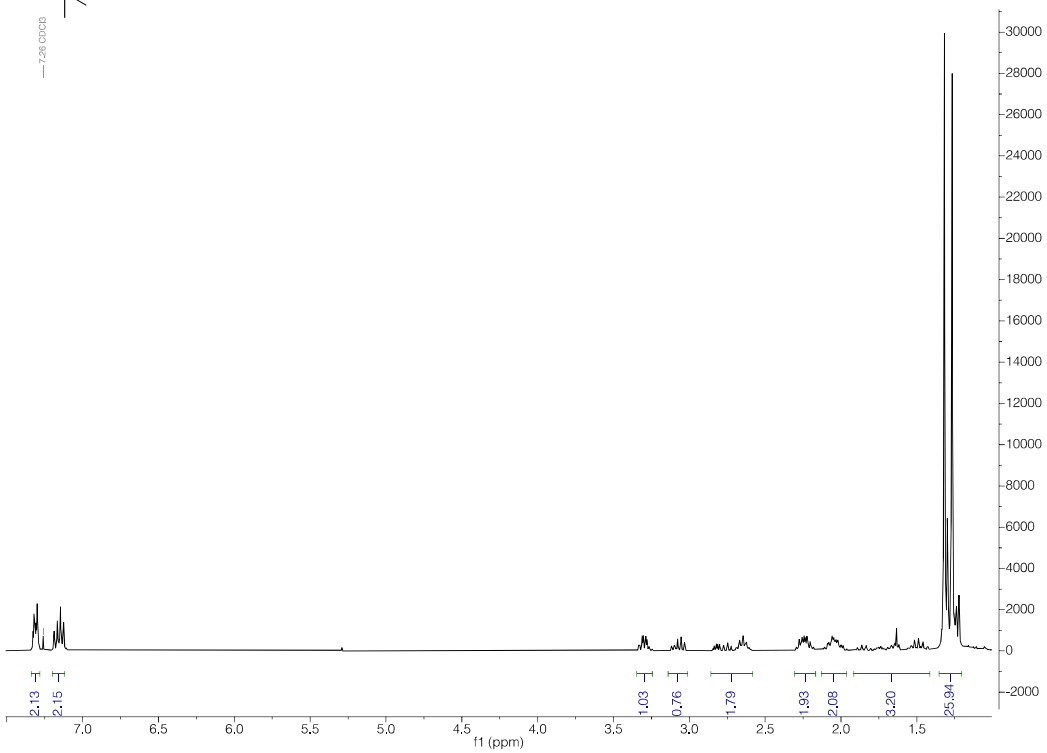
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2976.59	73.898	2	2933.2	82.1766	3	1726.94	55.4789
4	1457.92	83.4506	5	1417.42	80.0696	6	1370.18	45.4345
7	1317.14	51.3807	8	1270.86	71.158	9	1247.72	72.5482
10	1211.08	66.7979	11	1184.08	62.2581	12	1162.87	54.5978
13	1140.69	25.8438	14	1109.83	70.0829	15	1029.8	76.7046
16	970.983	68.6204	17	859.132	65.0586	18	670.142	82.7841

2-[3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

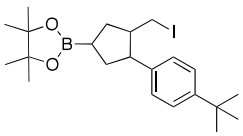
^{1}H-NMR (400 MHz, $CDCl_3$)



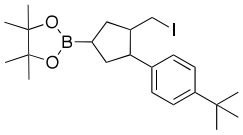


2-[3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

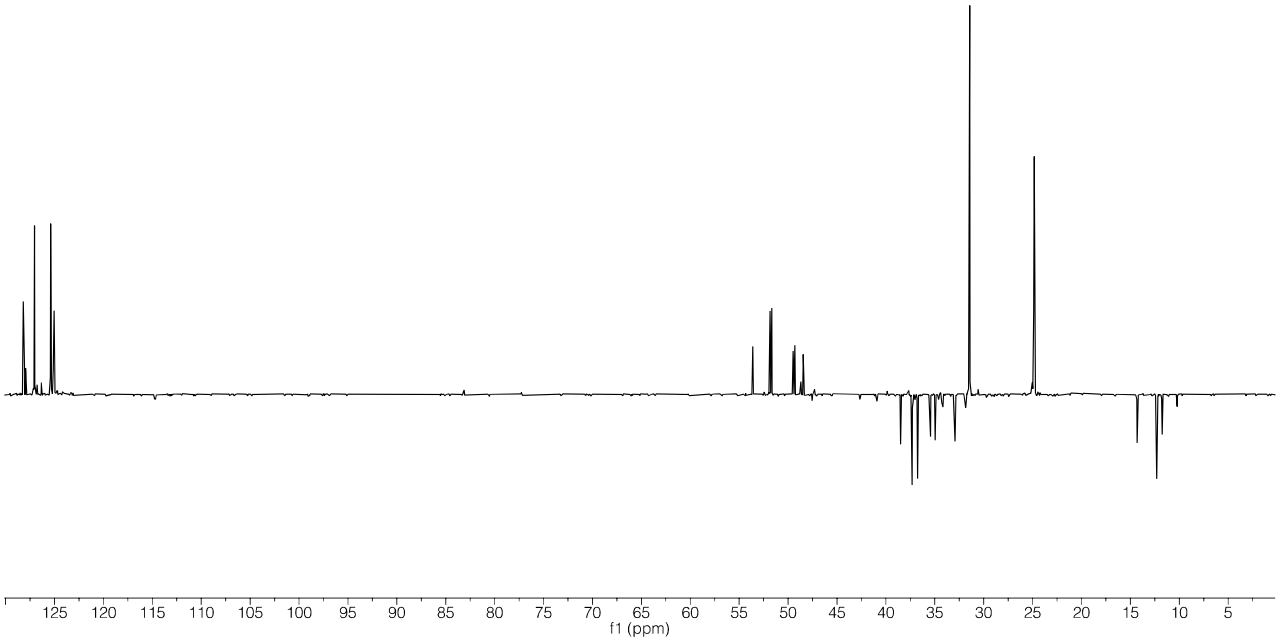
^{13}C-NMR (101 MHz, $CDCl_3$)



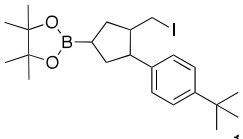
2-[3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



DEPT-135 NMR (101 MHz, $CDCl_3$)



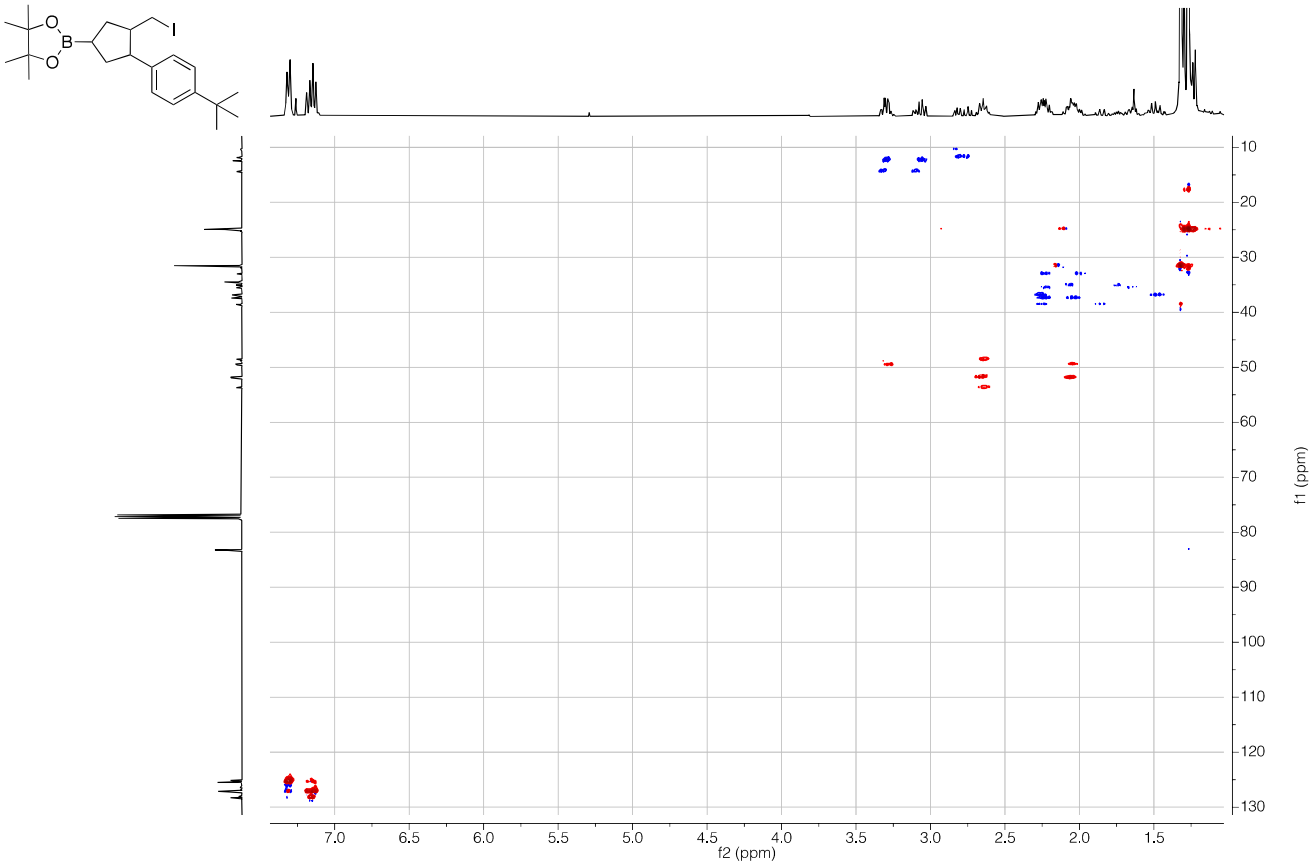
2-[3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



^1H, ^1H-COSY (400 MHz, $CDCl_3$)

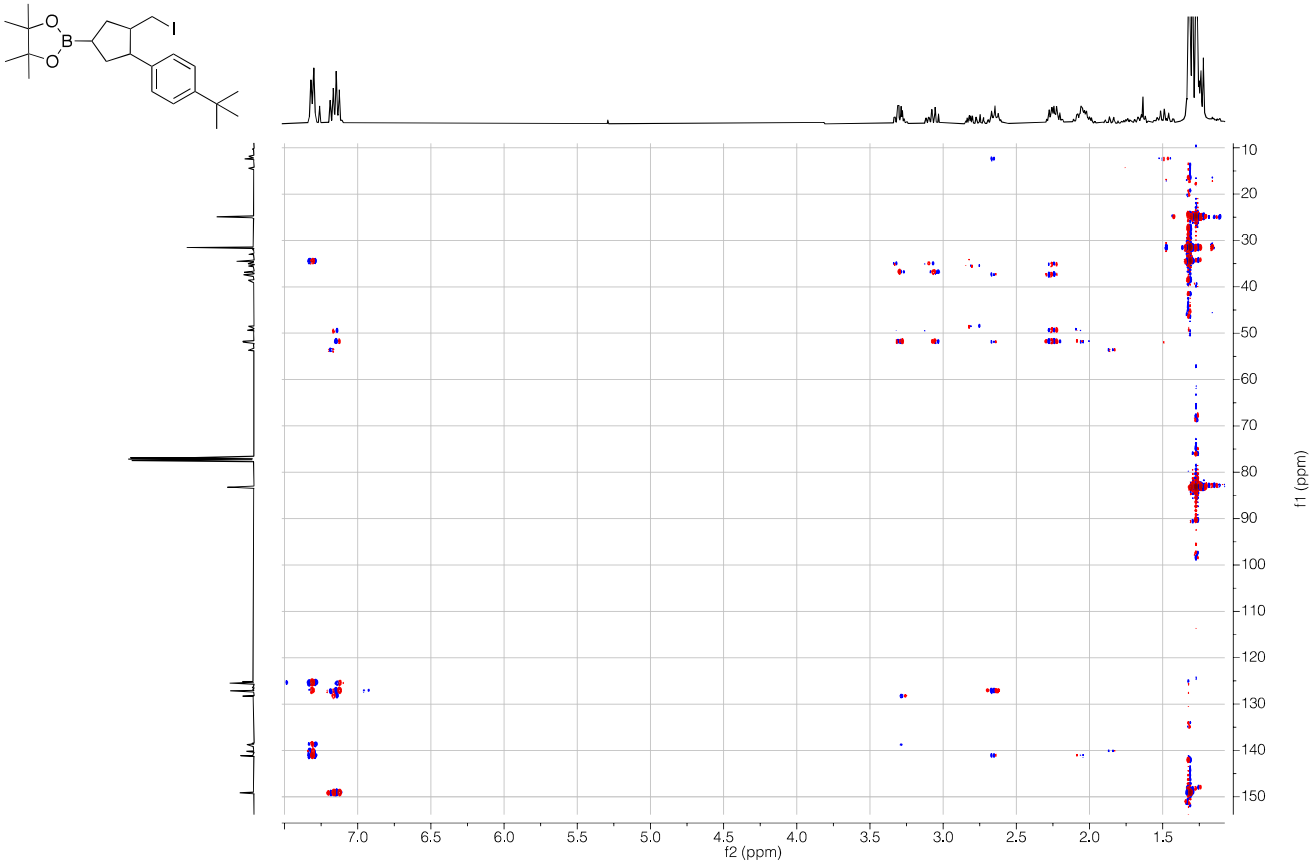
2-[3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



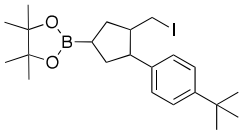
2-[3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

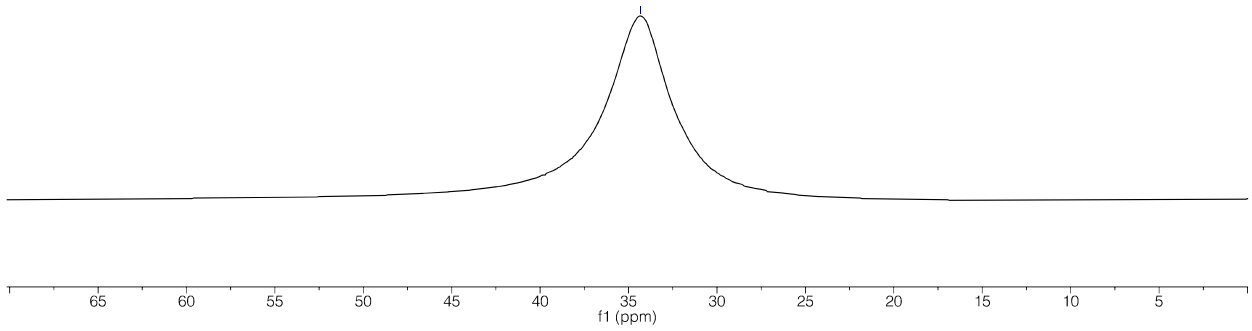
^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



2-[3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

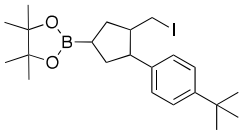
^{11}B-NMR (128 MHz, $CDCl_3$)

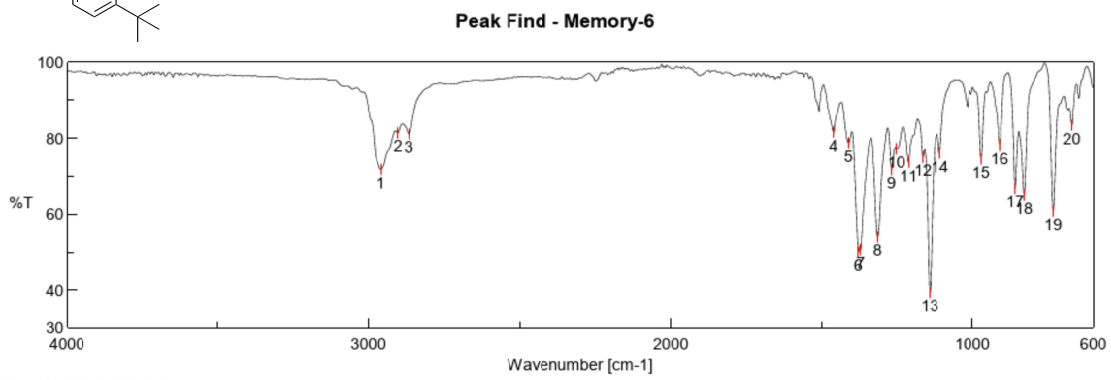




2-[3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

FT-IR, ATR-diamond

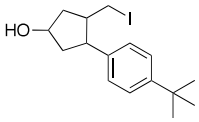




[Result of Peak Picking]

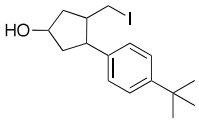
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2960.2	71.7534	2	2903.31	81.3353	3	2867.63	81.0777
4	1459.85	81.5312	5	1410.67	78.7017	6	1377.89	50.0598
7	1371.14	50.6536	8	1315.21	53.9388	9	1268.93	71.6668
10	1251.58	77.1644	11	1213.01	73.6719	12	1164.79	74.9159
13	1141.65	39.2819	14	1108.87	76.0777	15	970.983	74.5
16	909.272	78.1303	17	858.168	66.6869	18	828.277	64.9206
19	731.853	60.6975	20	671.106	83.4293			

3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentanol



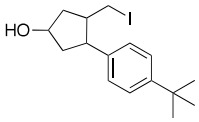
^{1}H-NMR (400 MHz, $CDCl_3$)

3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentanol

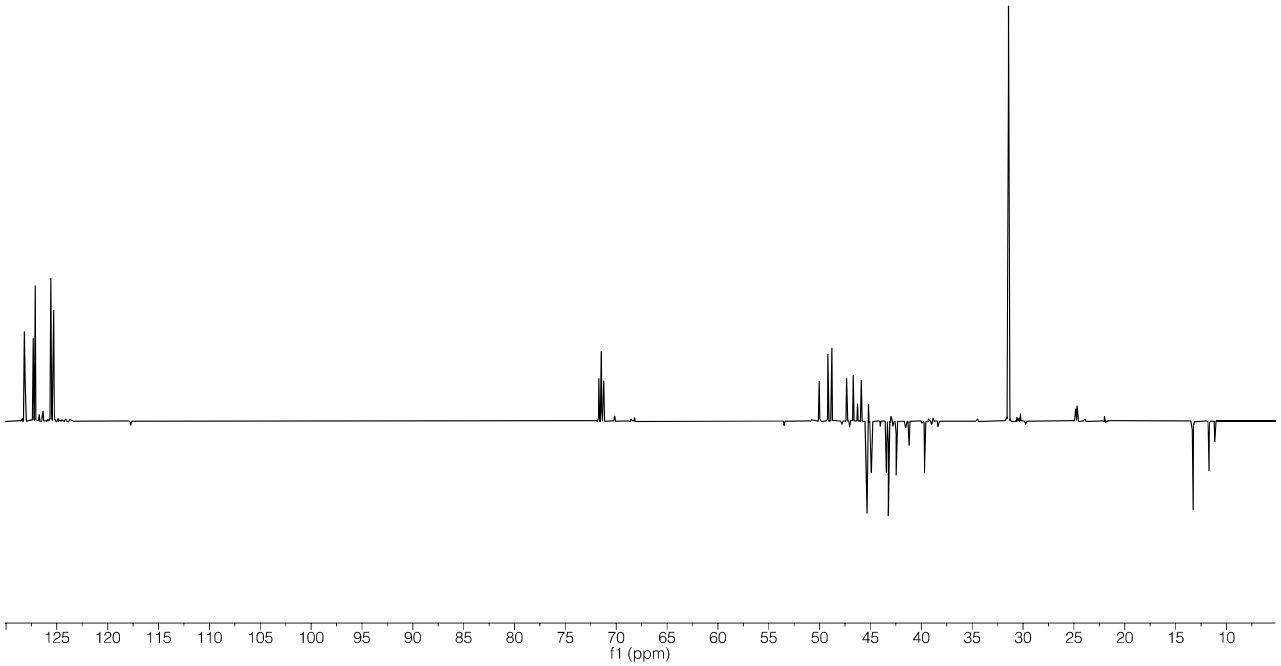


^{13}C-NMR (101 MHz, $CDCl_3$)

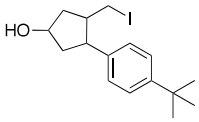
3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentanol



DEPT-135 NMR (101 MHz, $CDCl_3$)



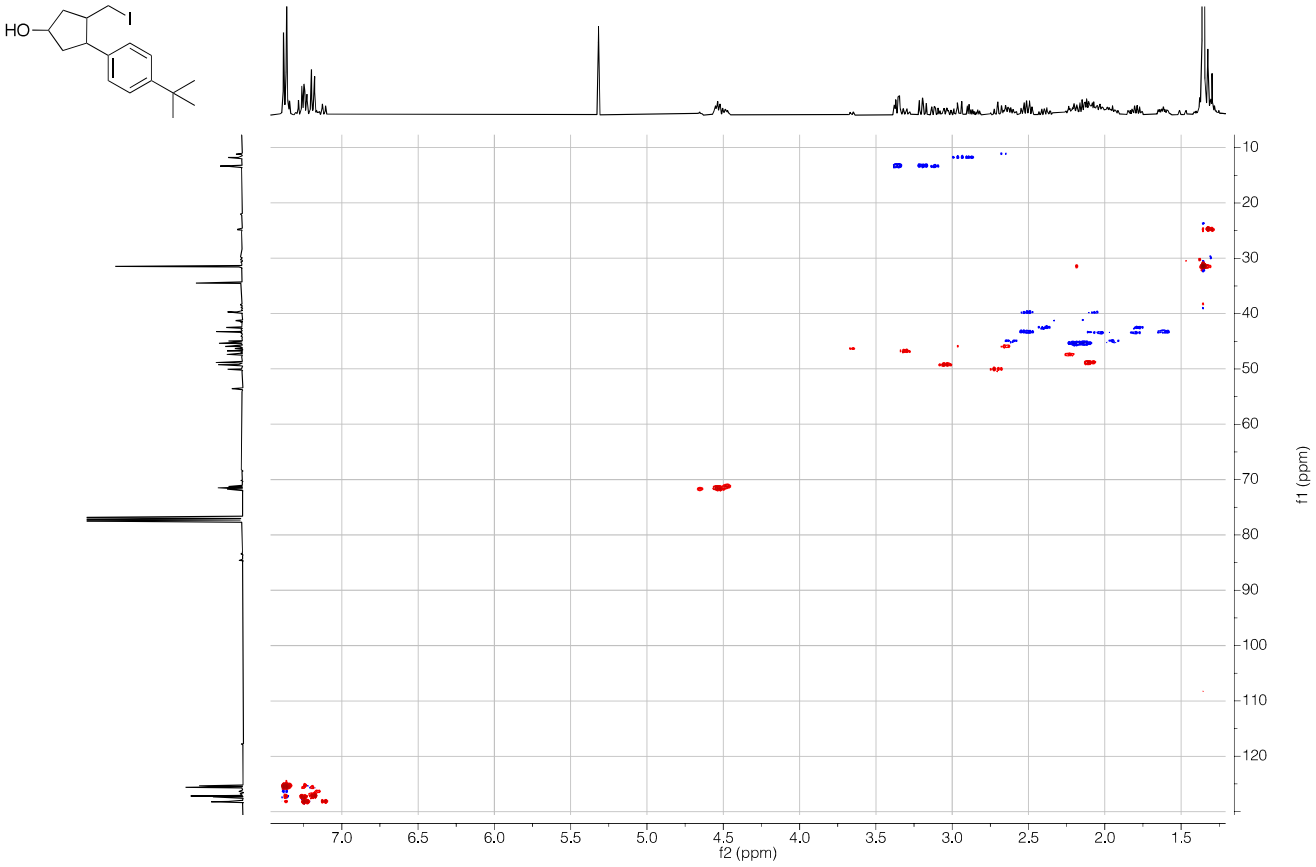
3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentanol



^1H, ^1H-COSY (400 MHz, $CDCl_3$)

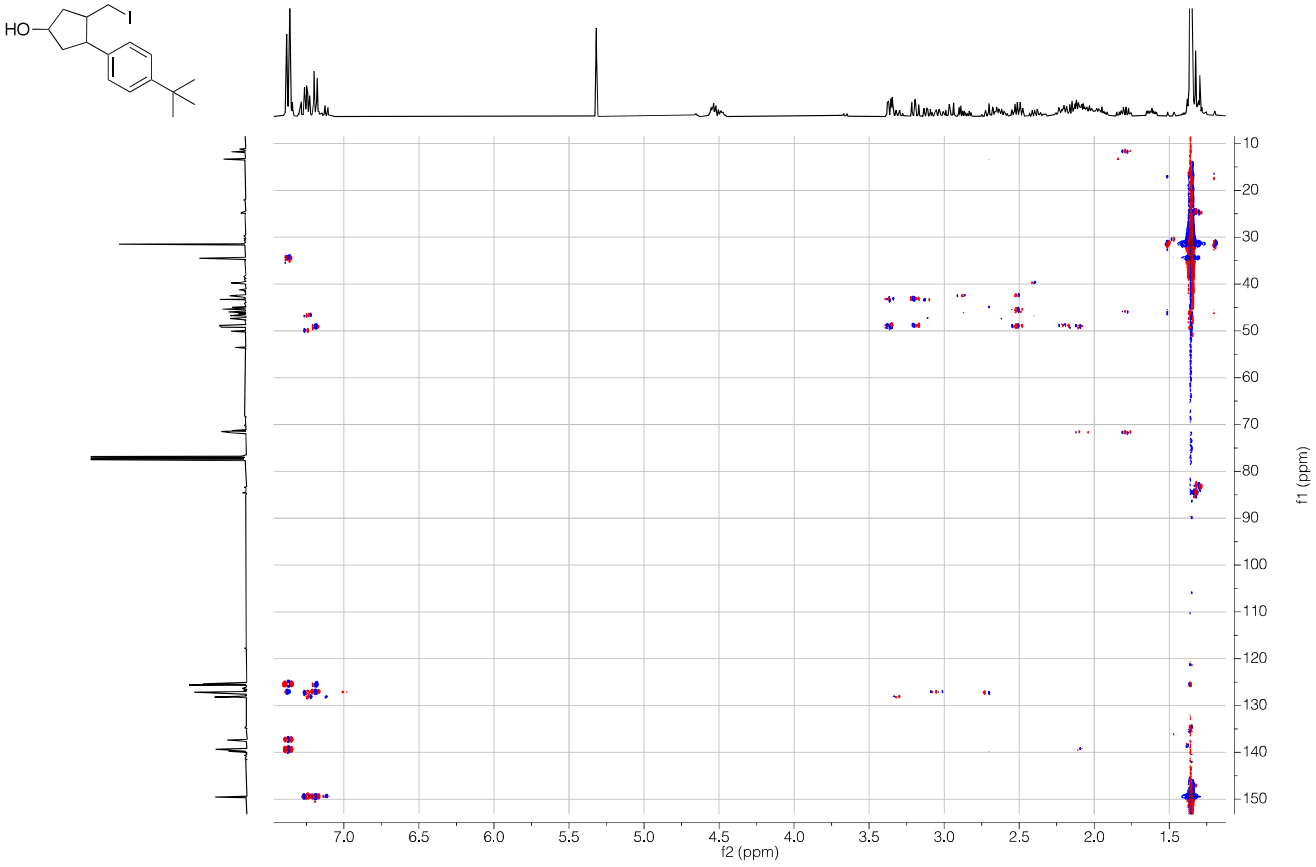
3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentanol

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



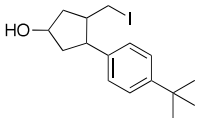
3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentanol

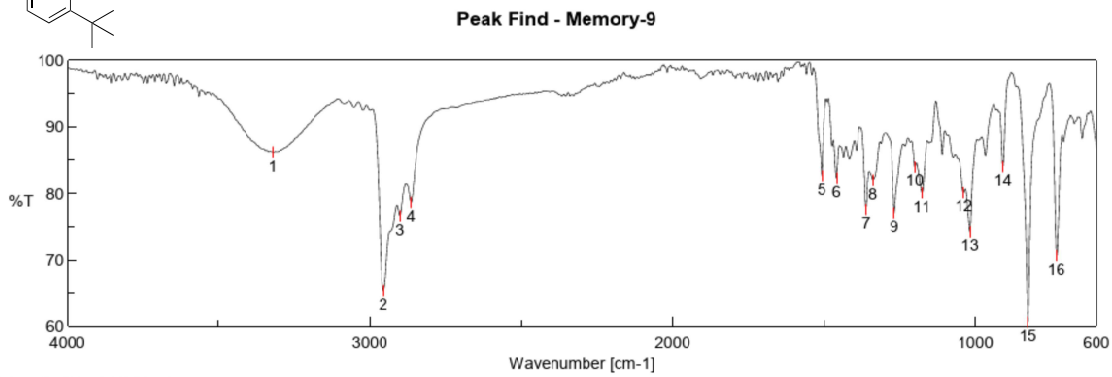
^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



3-(4-tert-butylphenyl)-4-(iodomethyl)cyclopentanol

FT-IR, ATR-diamond



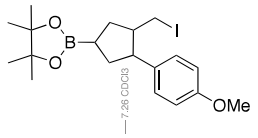


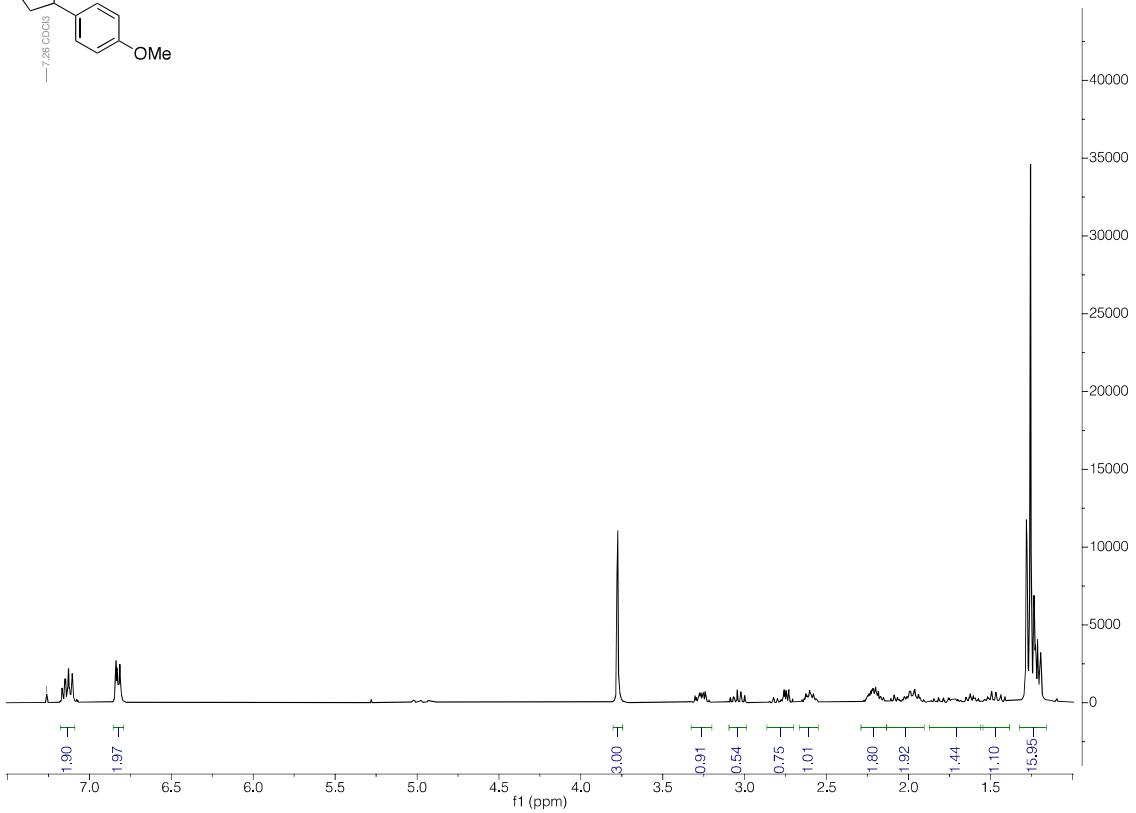
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3321.78	86.1585	2	2956.34	65.3725	3	2901.38	76.589
4	2865.7	78.6314	5	1508.06	82.6061	6	1458.89	82.2463
7	1360.53	77.5475	8	1338.36	81.9541	9	1267.97	77.0331
10	1200.47	83.9243	11	1177.33	80.0829	12	1038.48	80.0938
13	1017.27	74.1614	14	908.308	83.9867	15	826.348	60.6765
16	731.853	70.6294						

2-[3-(iodomethyl)-4-(4-methoxyphenyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

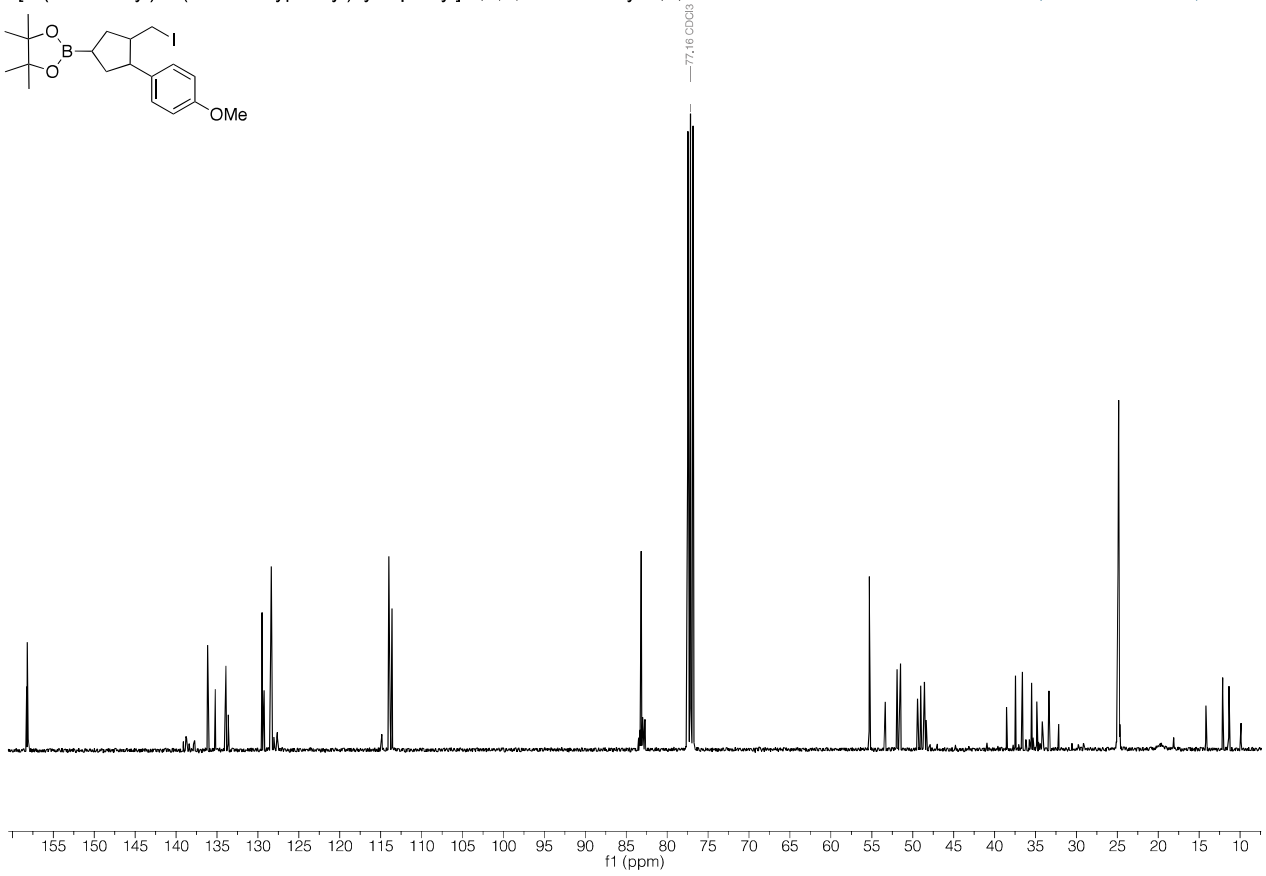
^{1}H-NMR (400 MHz, $CDCl_3$)





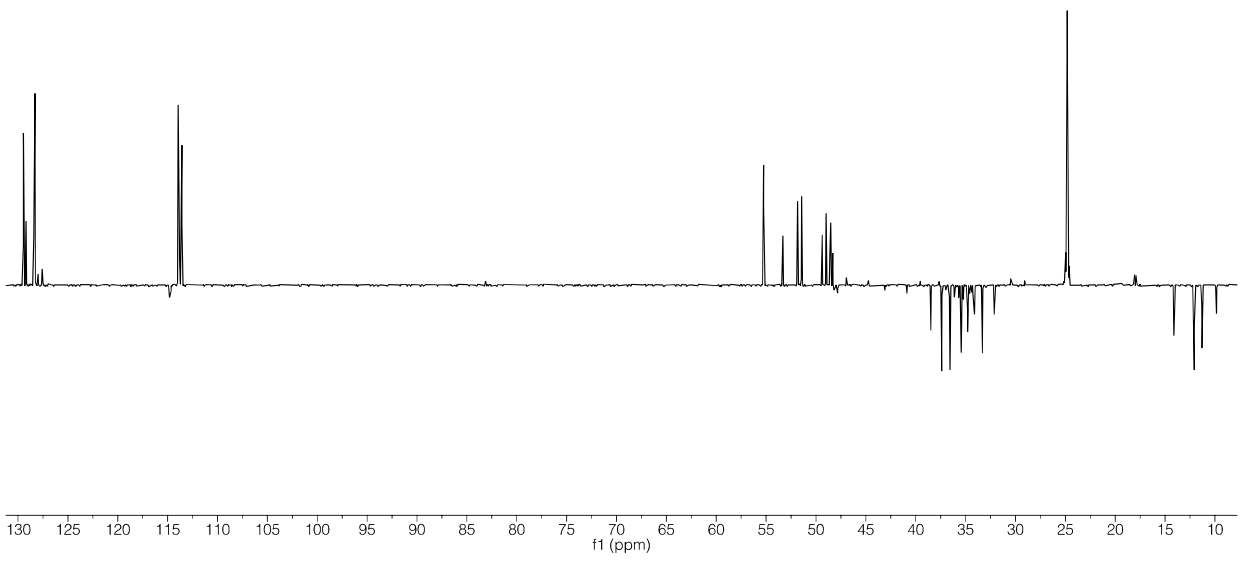
2-[3-(iodomethyl)-4-(4-methoxyphenyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{13}C-NMR (101 MHz, $CDCl_3$)



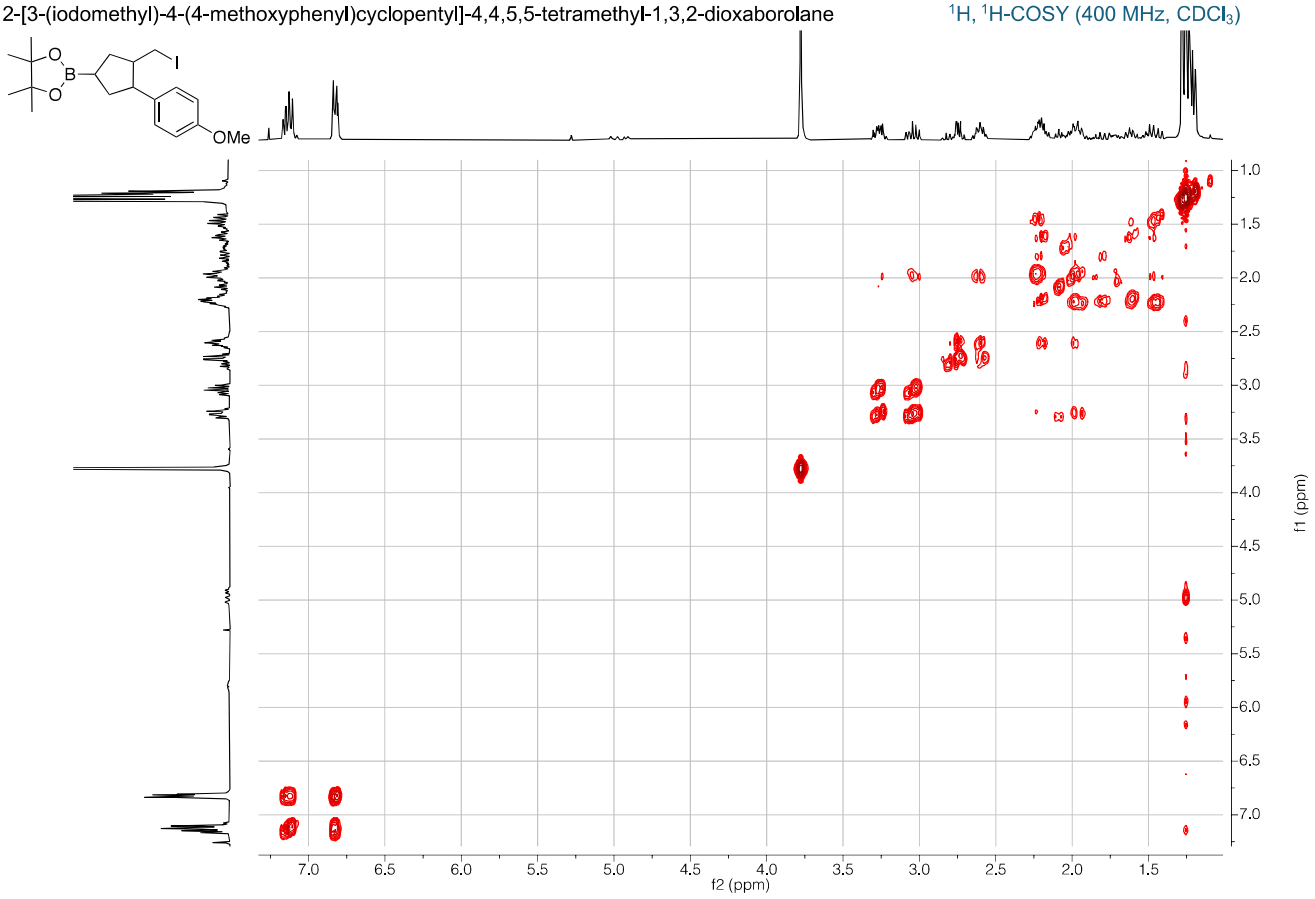
2-[3-(iodomethyl)-4-(4-methoxyphenyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

DEPT-135 NMR (101 MHz, $CDCl_3$)



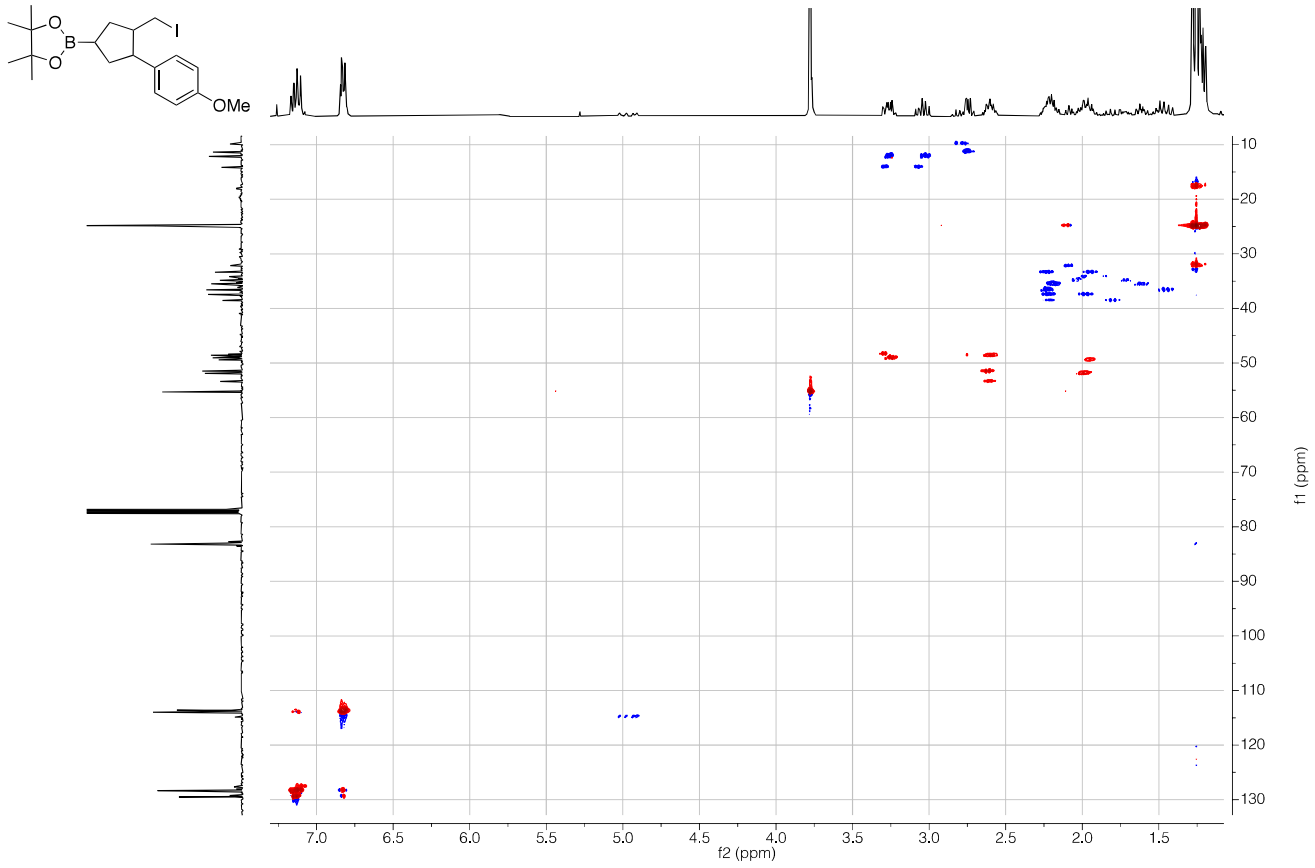
2-[3-(iodomethyl)-4-(4-methoxyphenyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



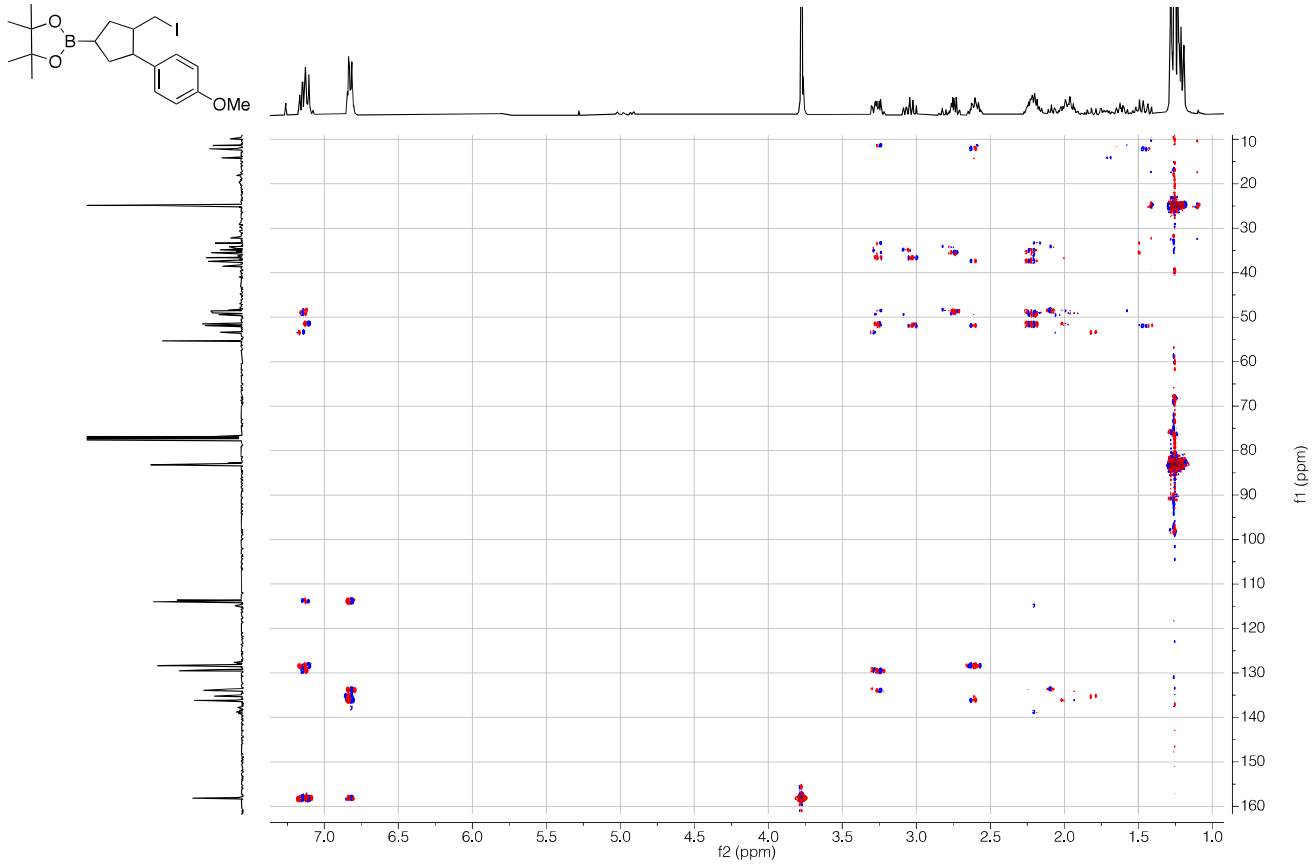
2-[3-(iodomethyl)-4-(4-methoxyphenyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



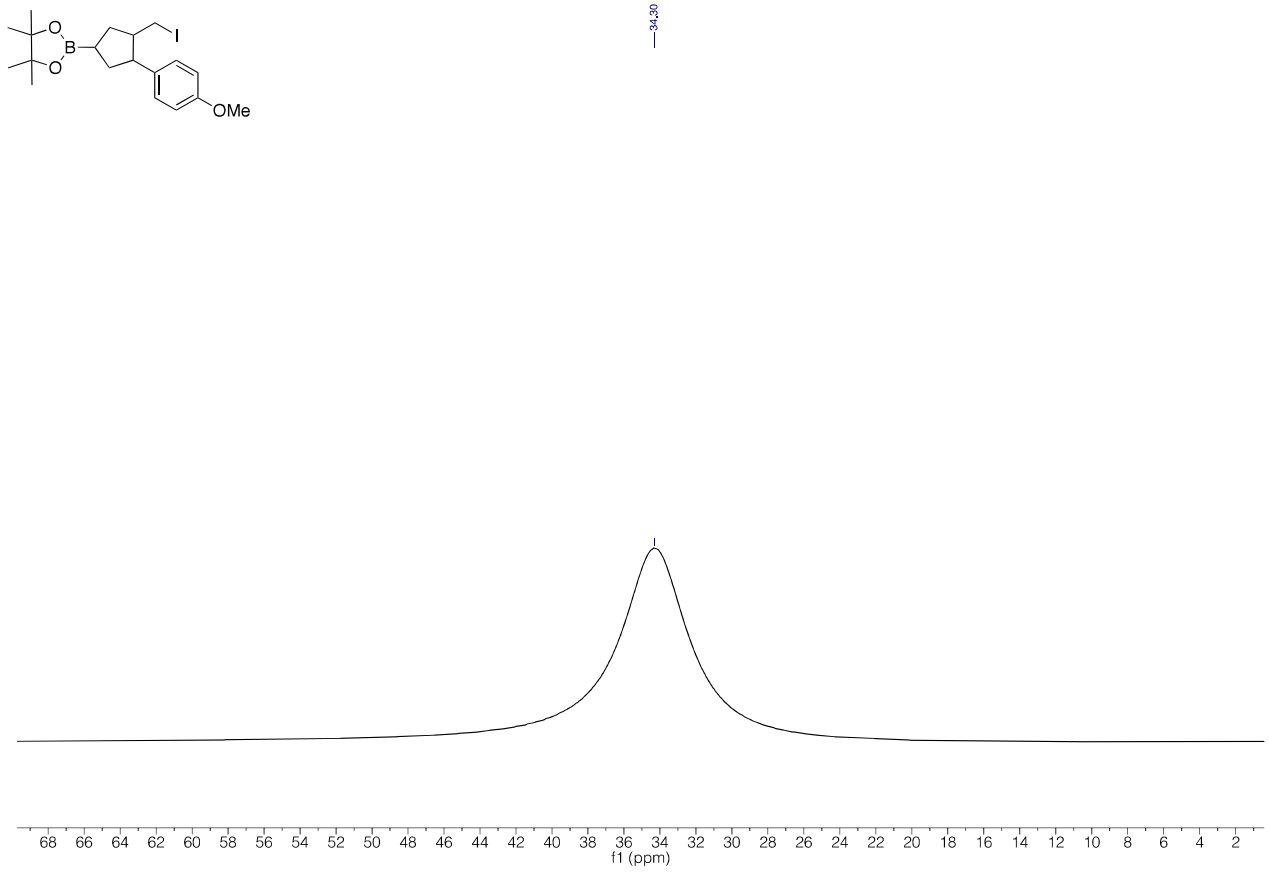
2-[3-(iodomethyl)-4-(4-methoxyphenyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



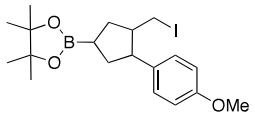
2-[3-(iodomethyl)-4-(4-methoxyphenyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

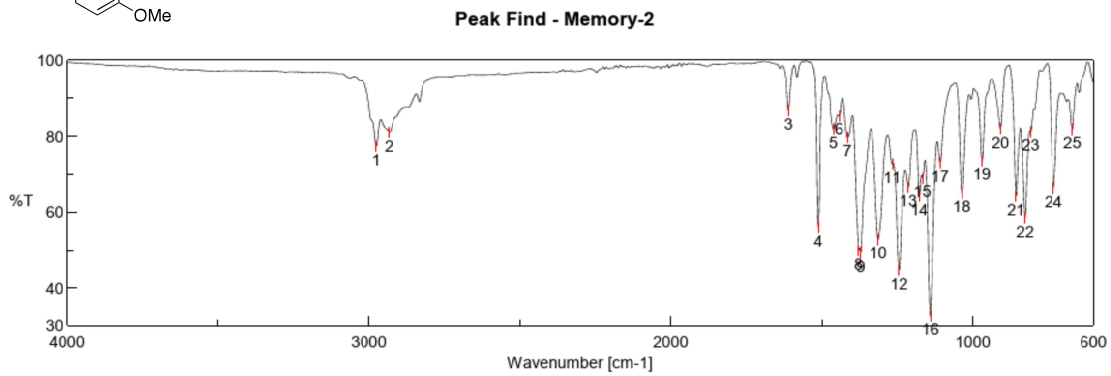
^{11}B-NMR (128 MHz, $CDCl_3$)



2-[3-(iodomethyl)-4-(4-methoxyphenyl)cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

FT-IR, ATR-diamond



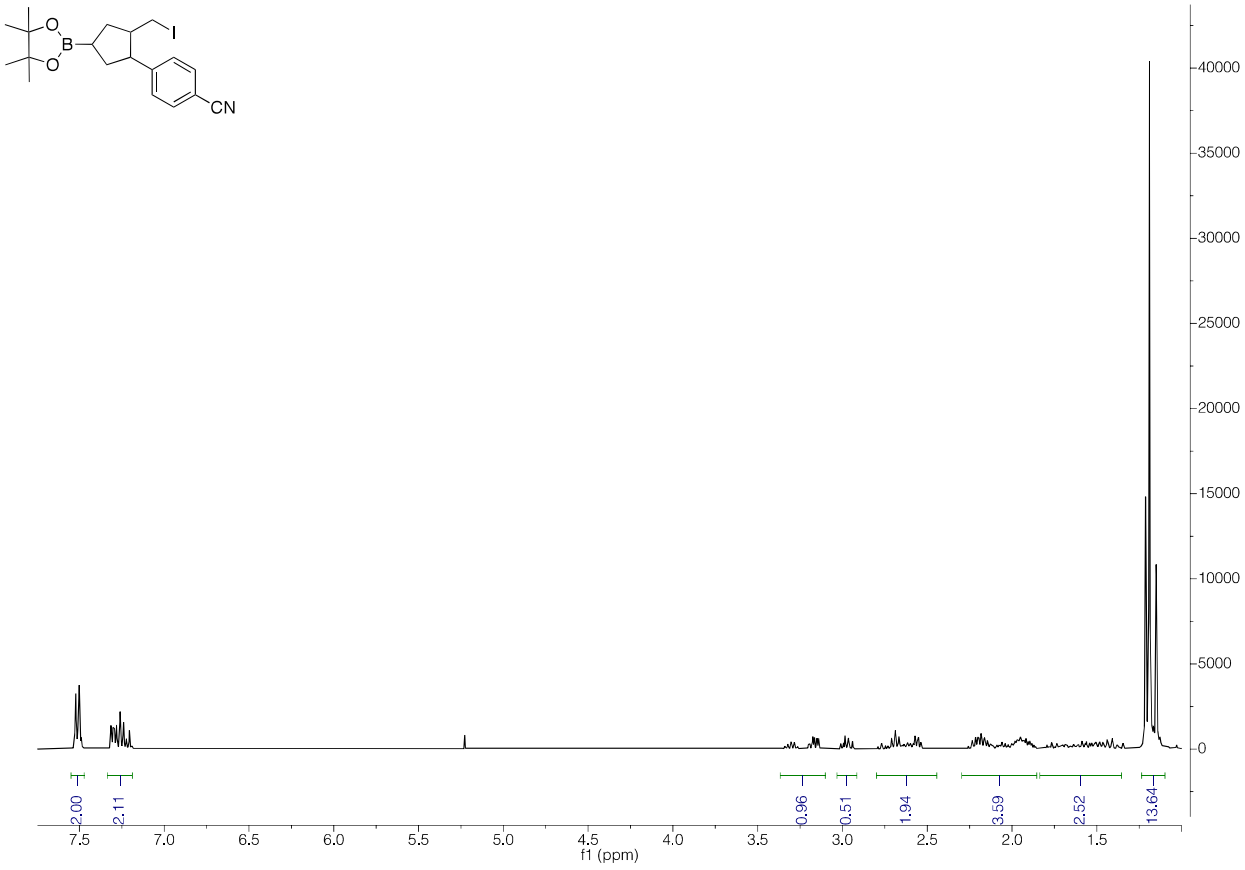


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	77.3365	2	2933.2	80.9501	3	1610.27	86.6752
4	1511.92	55.9317	5	1461.78	81.7785	6	1442.49	85.3011
7	1415.49	79.617	8	1377.89	49.8459	9	1371.14	49.2871
10	1314.25	52.6947	11	1267	72.5918	12	1243.86	44.6196
13	1213.97	66.4984	14	1177.33	64.2003	15	1166.72	68.8255
16	1140.69	32.5513	17	1108.87	72.912	18	1036.55	64.9294
19	970.019	73.4084	20	909.272	81.883	21	857.204	64.1591
22	827.312	58.3989	23	808.992	81.0401	24	731.853	66.2278
25	670.142	81.6663						

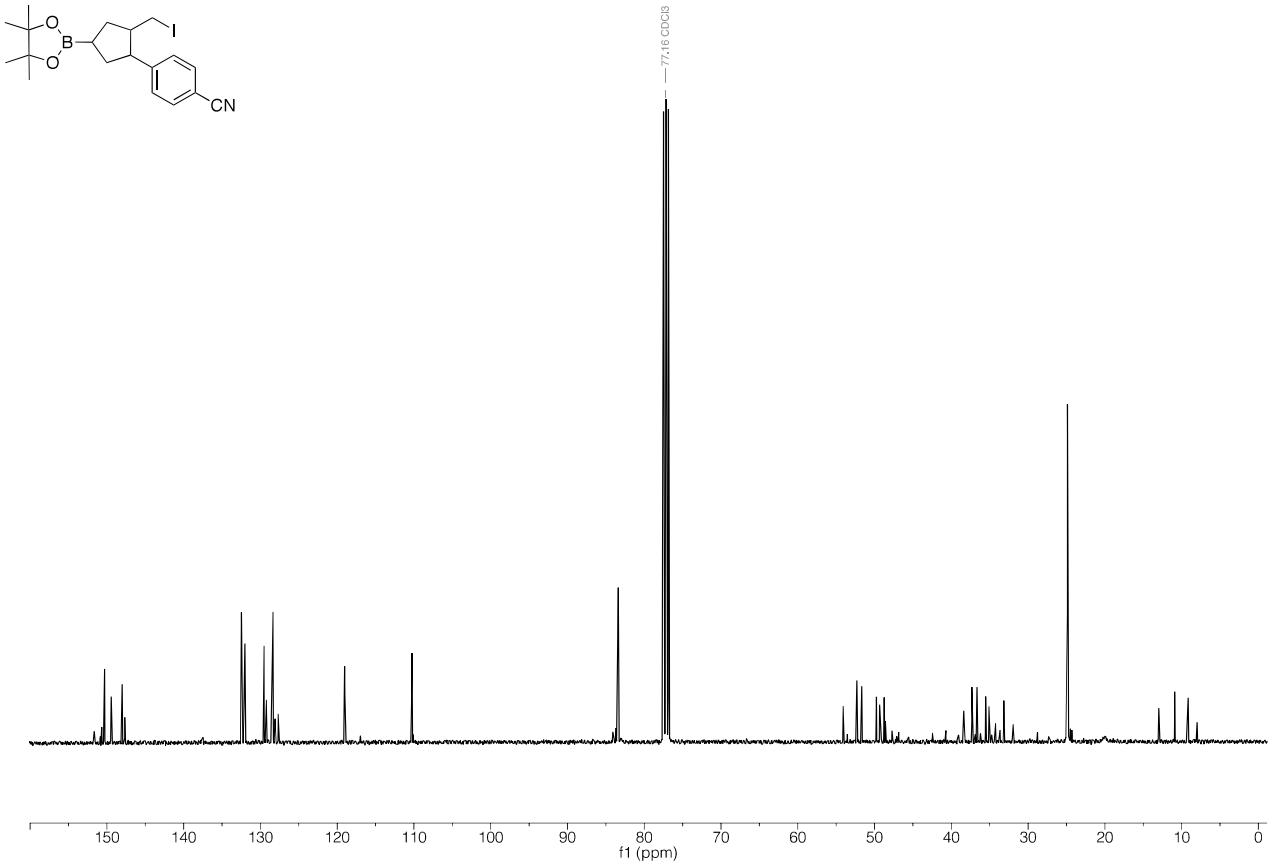
4-[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl]benzonitrile

^{1}H-NMR (400 MHz, $CDCl_3$)



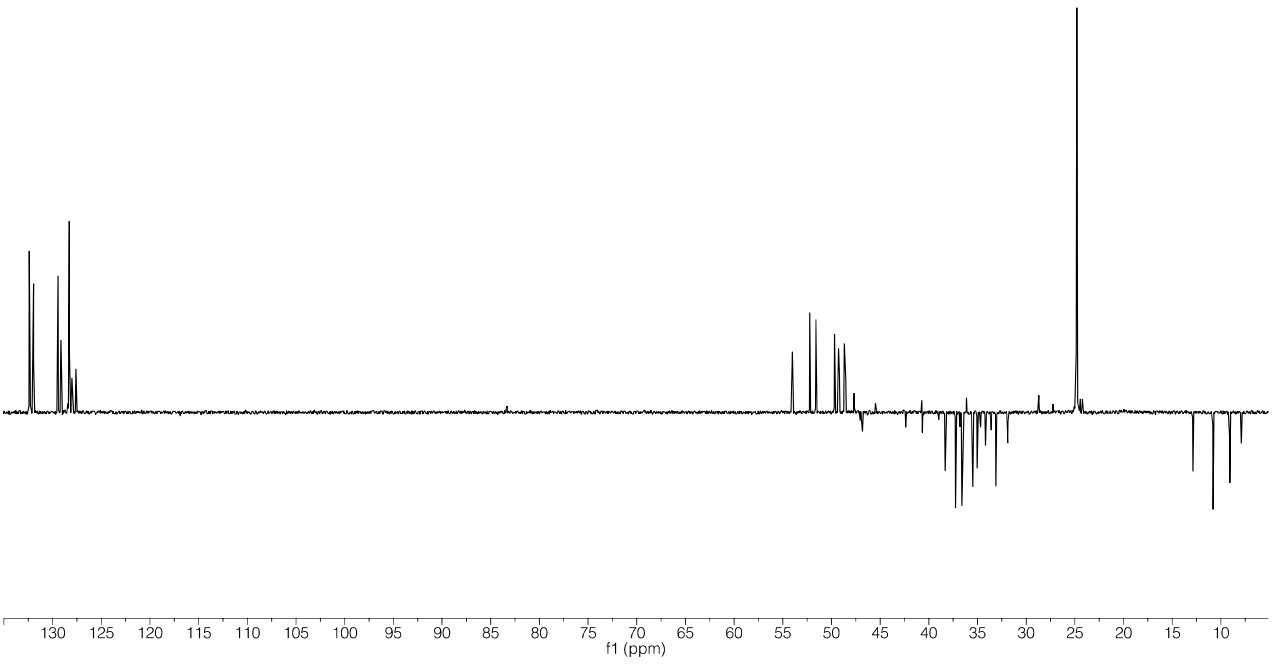
4-[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl]benzonitrile

^{13}C-NMR (101 MHz, $CDCl_3$)



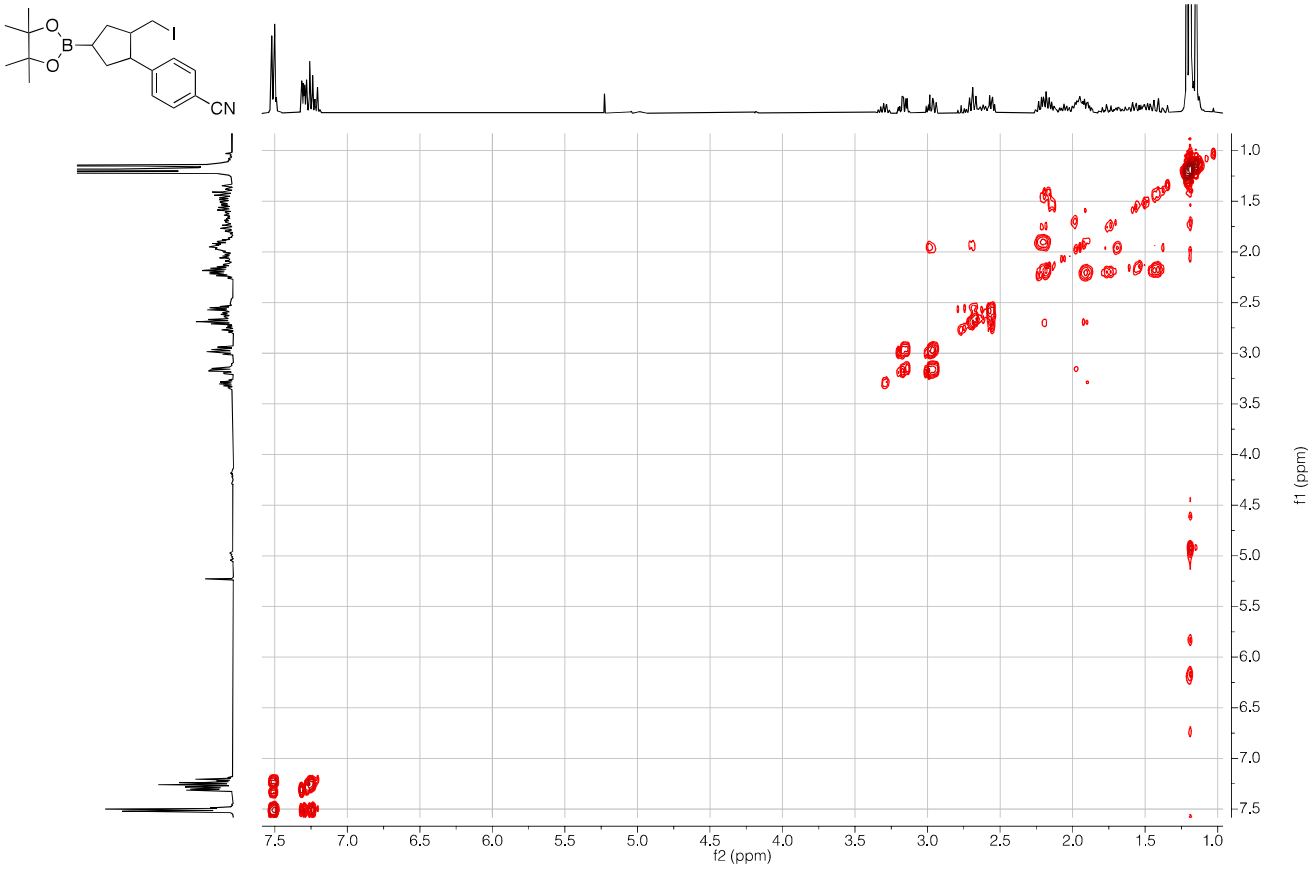
4-[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl]benzonitrile

DEPT-135 NMR (101 MHz, $CDCl_3$)



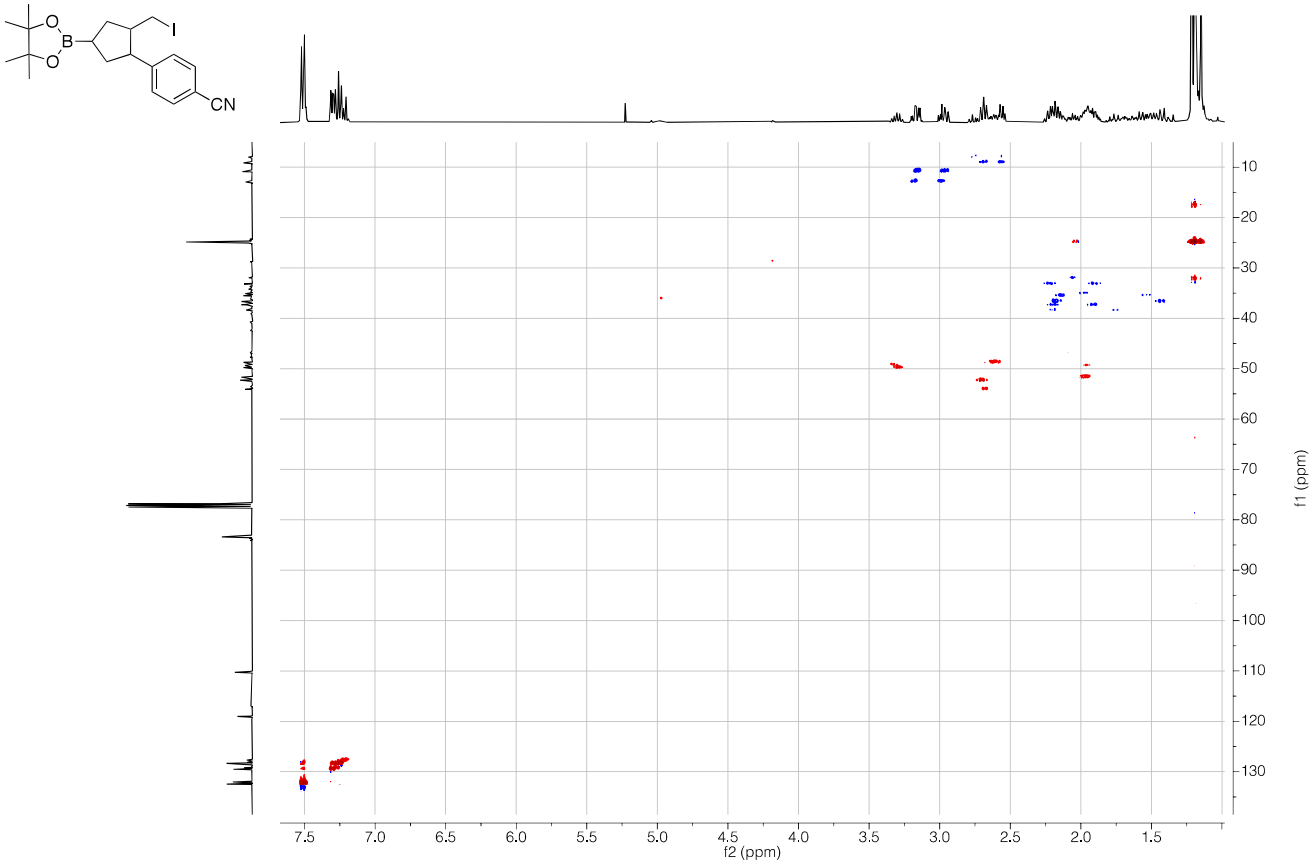
4-[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl]benzonitrile

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



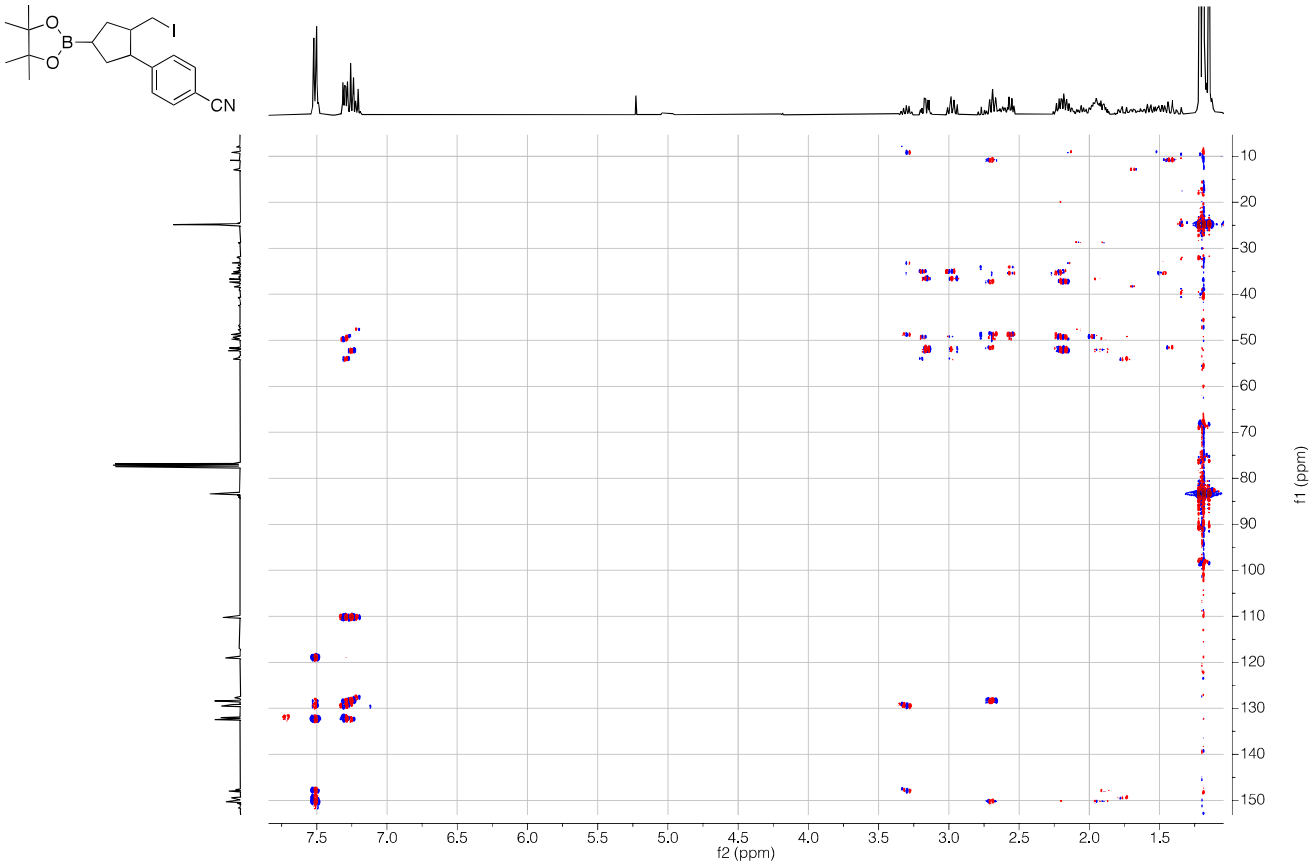
4-[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl]benzonitrile

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



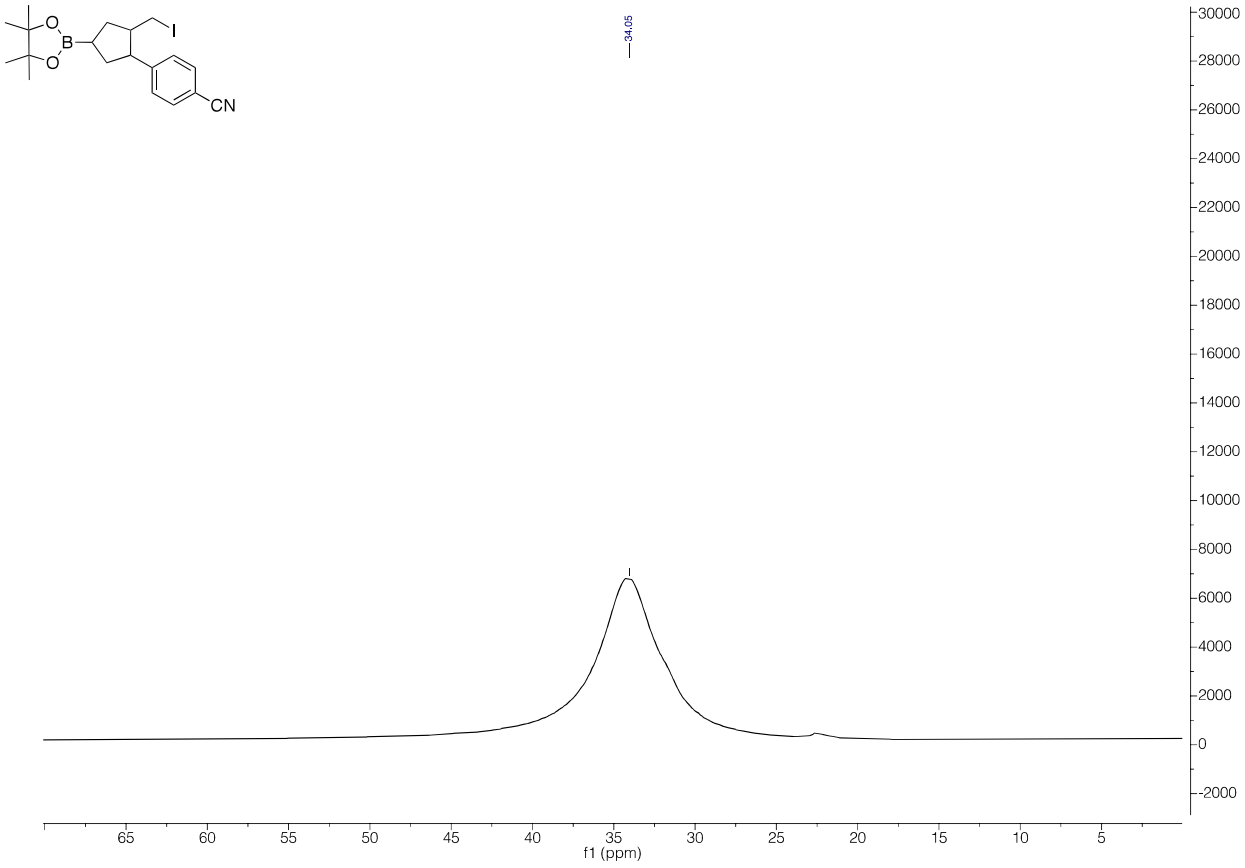
4-[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl]benzonitrile

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



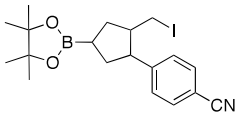
4-[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl]benzonitrile

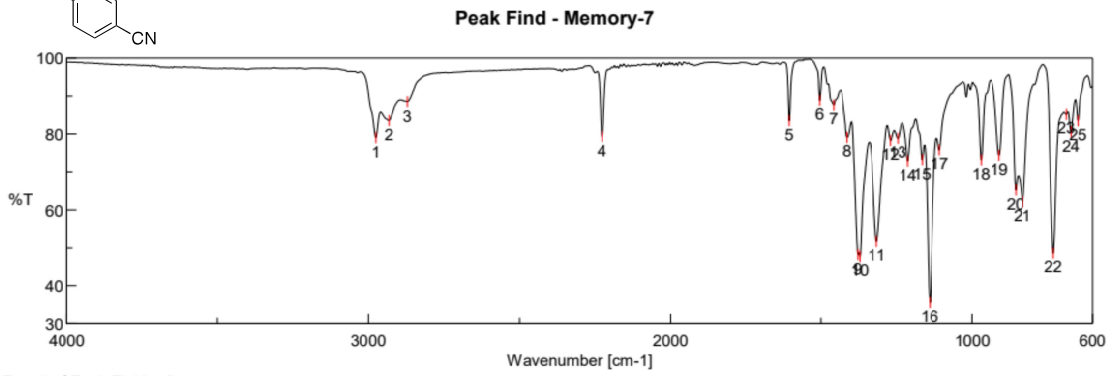
^{11}B-NMR (128 MHz, $CDCl_3$)



4-[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl]benzonitrile

FT-IR, ATR-diamond



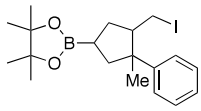


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	78.9864	2	2932.23	83.5266	3	2871.49	88.4837
4	2226.42	79.3164	5	1607.38	83.5017	6	1504.2	88.7927
7	1458.89	87.5794	8	1413.57	79.0541	9	1377.89	48.191
10	1372.1	47.6256	11	1316.18	51.6475	12	1270.86	78.2307
13	1246.75	78.8086	14	1213.01	72.7871	15	1165.76	73.1362
16	1140.69	35.5455	17	1108.87	75.7379	18	970.019	73.1107
19	911.201	74.3113	20	856.239	65.2342	21	833.098	62.1069
22	729.925	48.5667	23	686.534	85.1426	24	671.106	80.5138
25	647.965	83.4723						

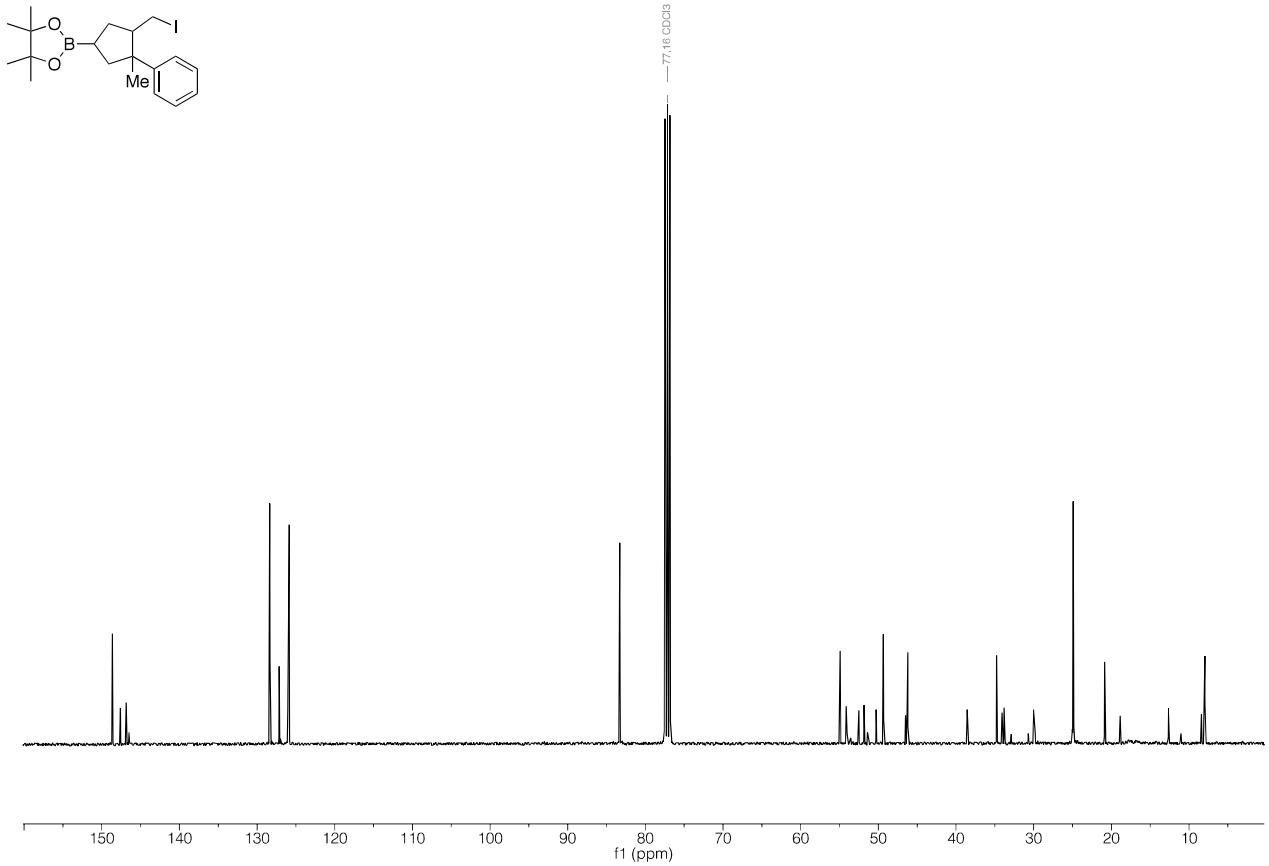
2-[4-(iodomethyl)-3-methyl-3-phenyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H-NMR (400 MHz, $CDCl_3$)



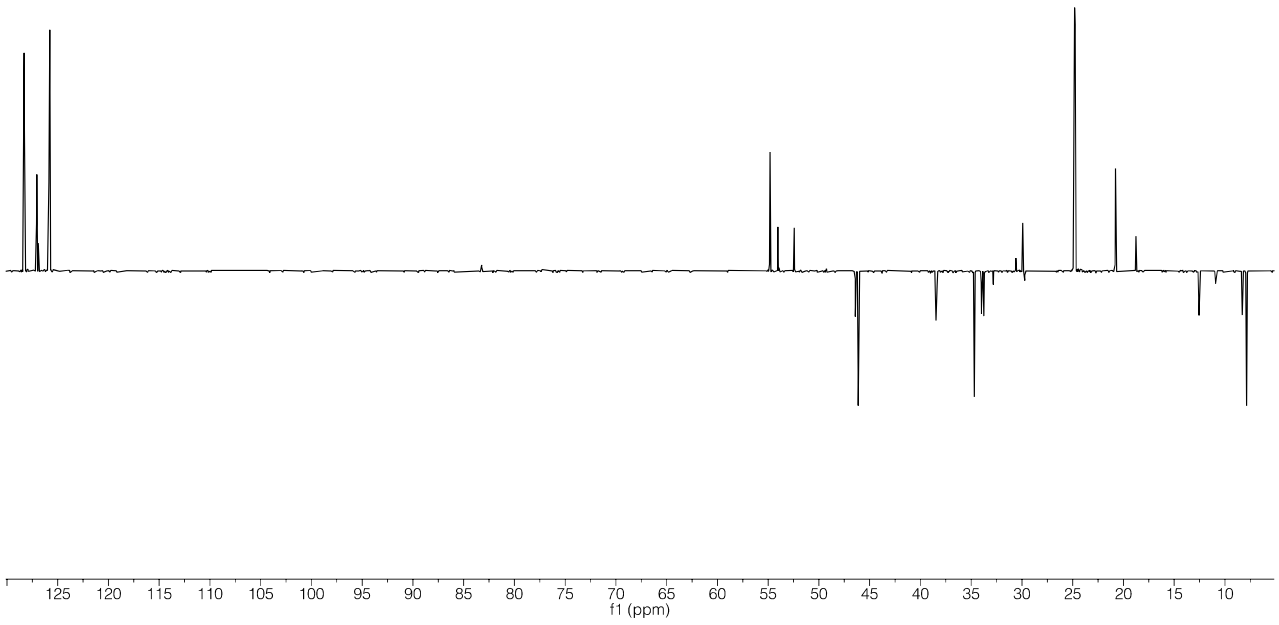
2-[4-(iodomethyl)-3-methyl-3-phenyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{13}C-NMR (101 MHz, $CDCl_3$)



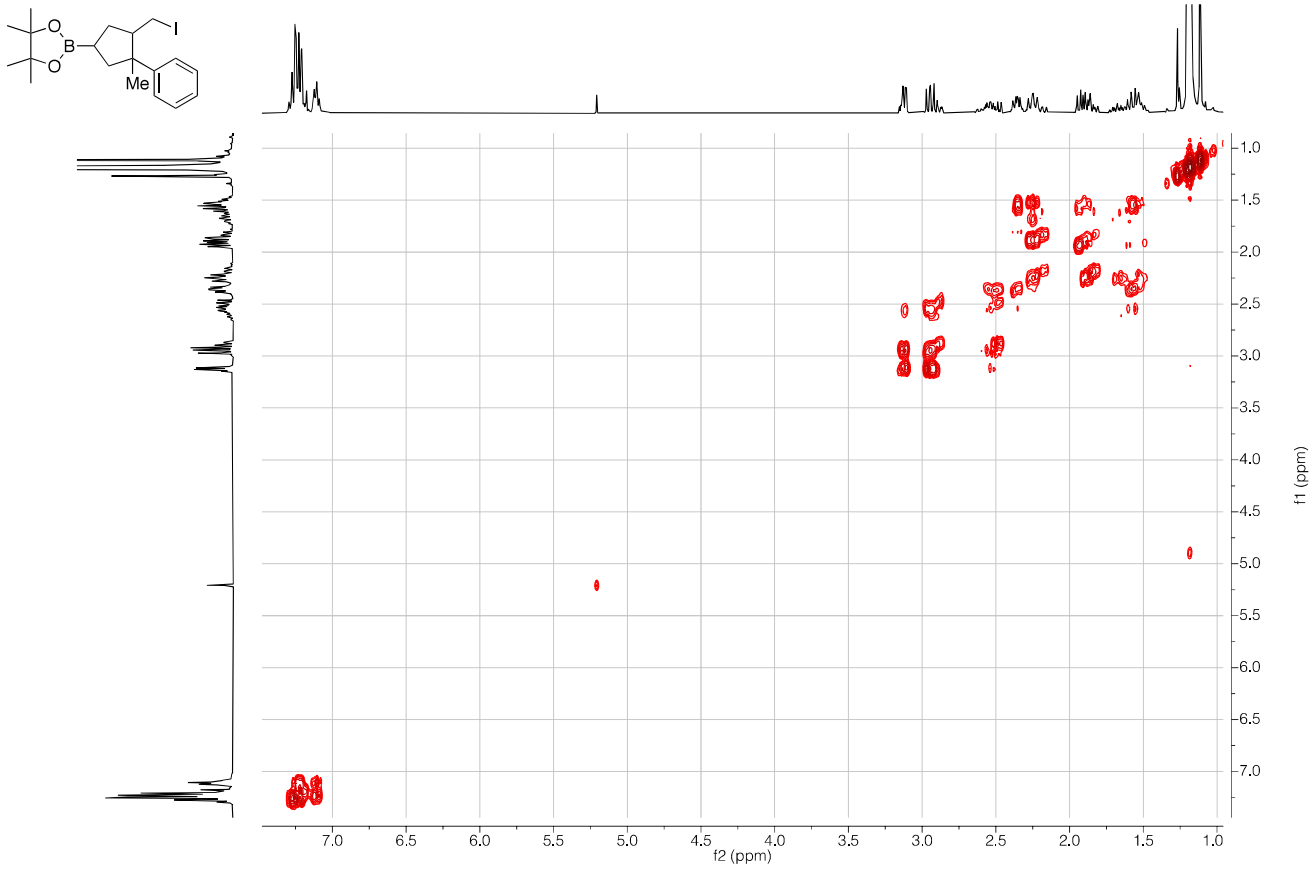
2-[4-(iodomethyl)-3-methyl-3-phenyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

DEPT-135 NMR (101 MHz, $CDCl_3$)



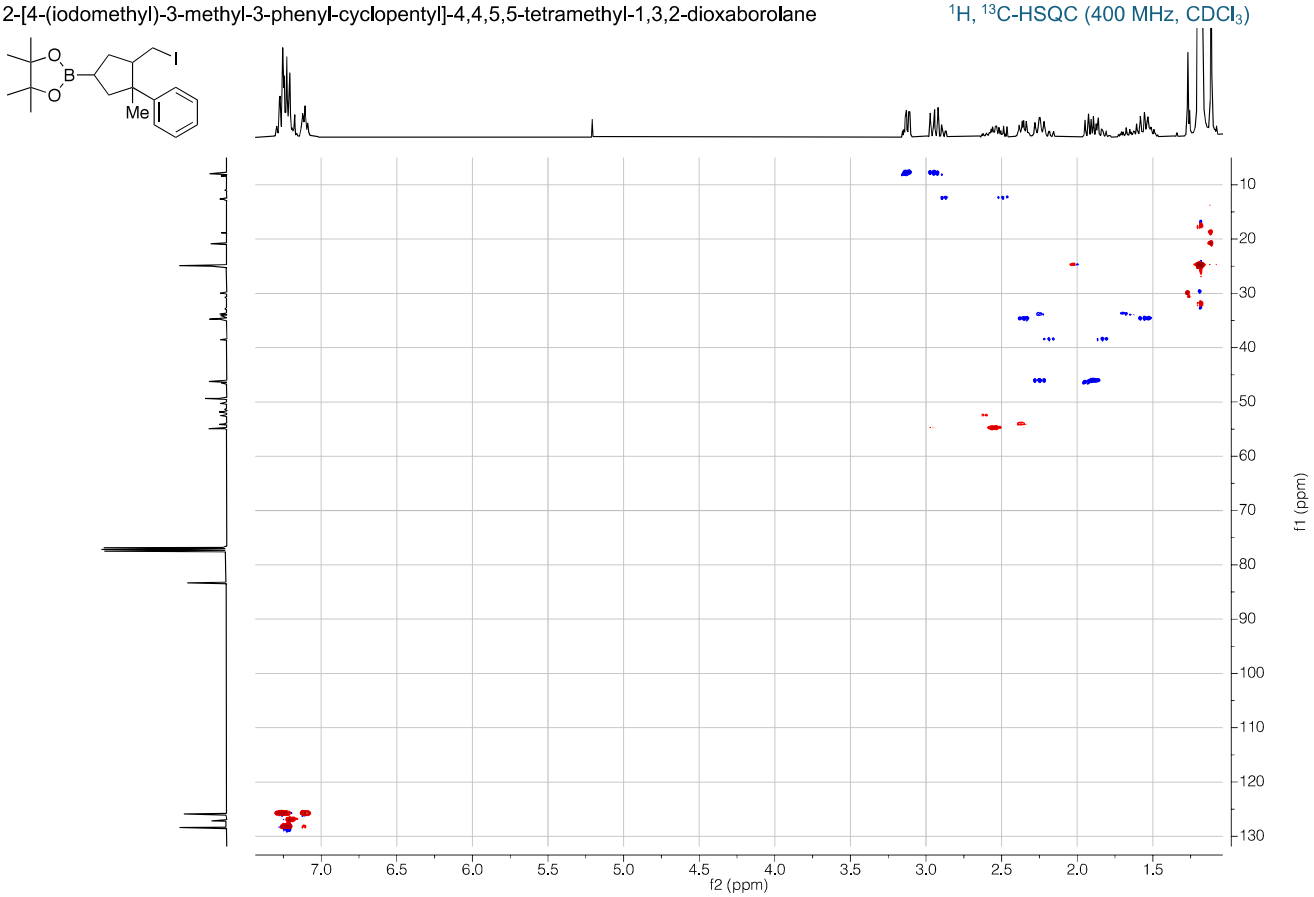
2-[4-(iodomethyl)-3-methyl-3-phenyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



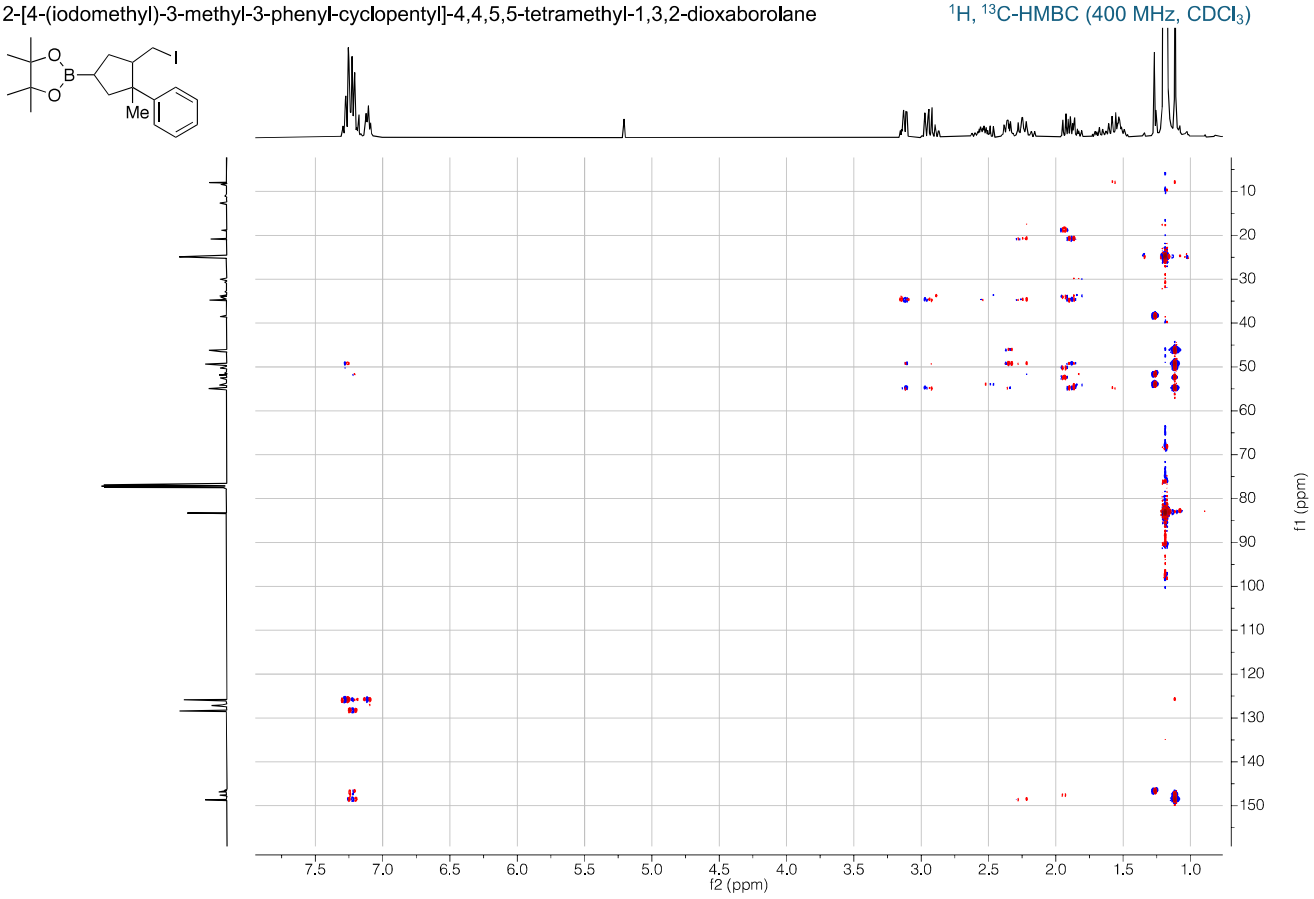
2-[4-(iodomethyl)-3-methyl-3-phenyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



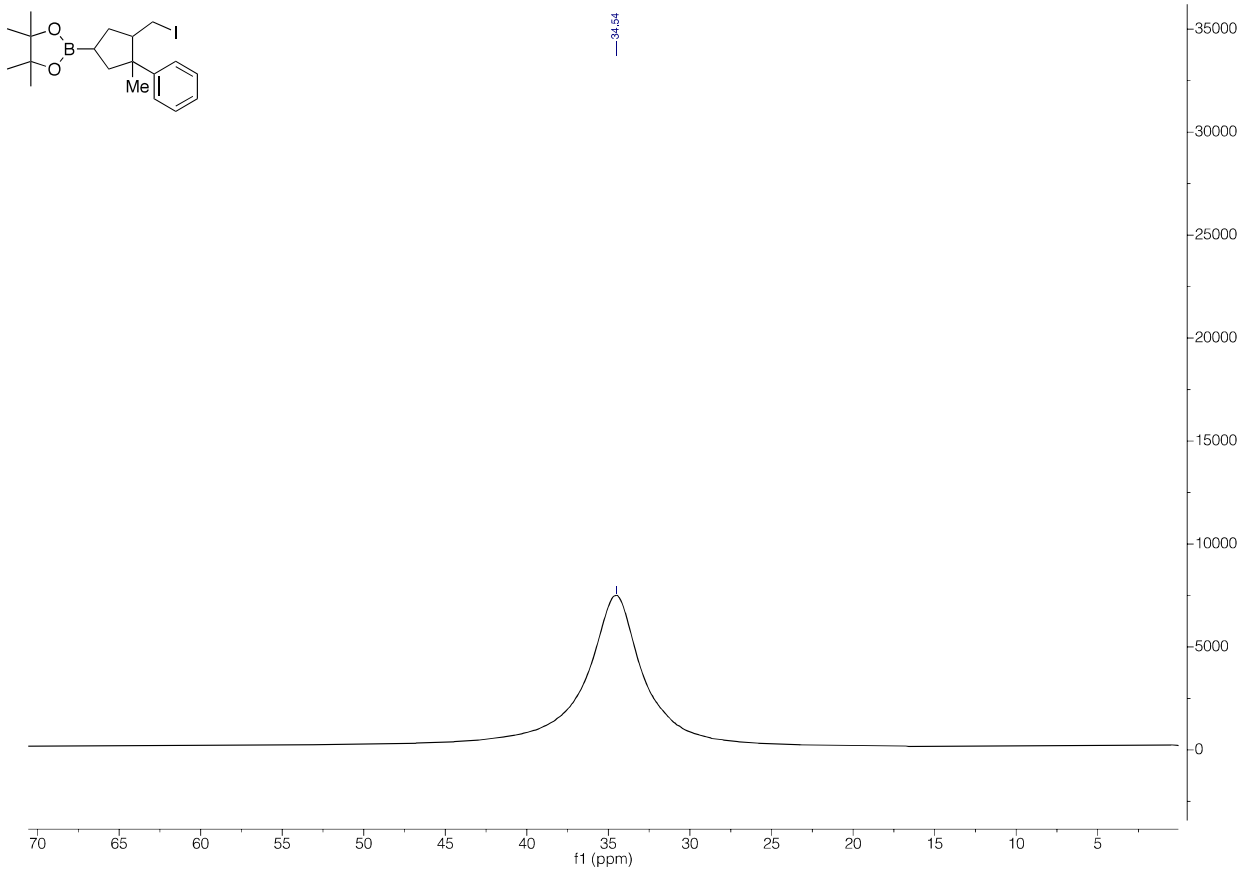
2-[4-(iodomethyl)-3-methyl-3-phenyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)

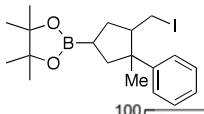


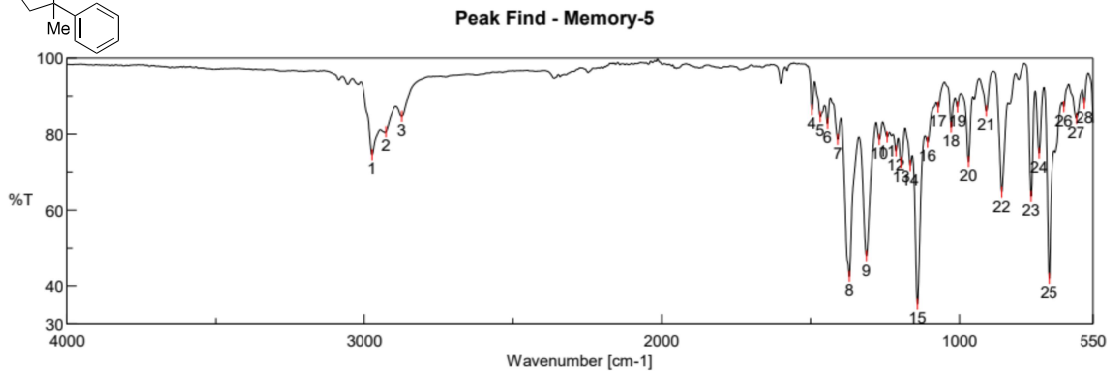
2-[4-(iodomethyl)-3-methyl-3-phenyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{11}B-NMR (128 MHz, $CDCl_3$)



2-[4-(iodomethyl)-3-methyl-3-phenyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane FT-IR, ATR-diamond

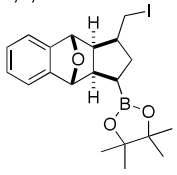




[Result of Peak Picking]

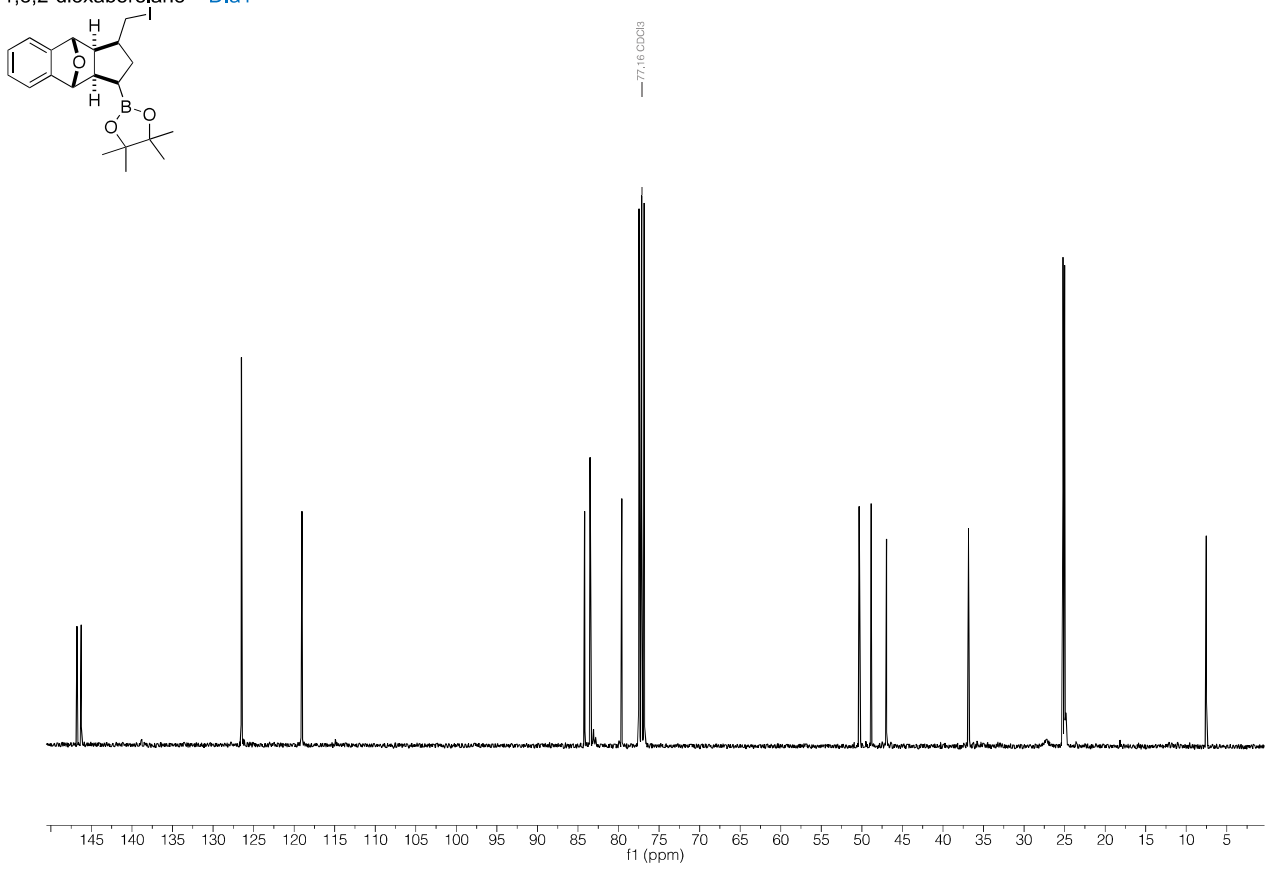
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2973.7	74.4944	2	2928.38	80.5691	3	2874.38	84.6662
4	1495.53	86.4009	5	1467.56	84.5691	6	1443.46	82.7508
7	1408.75	78.617	8	1370.18	42.5153	9	1312.32	47.9116
10	1269.9	78.5409	11	1242.9	79.2185	12	1213.01	75.4732
13	1195.65	72.4725	14	1165.76	71.622	15	1141.65	35.2336
16	1106.94	77.8531	17	1072.23	87.0189	18	1027.87	81.8173
19	1006.66	87.1007	20	970.019	72.6935	21	910.236	86.0496
22	858.168	64.6468	23	759.816	63.6017	24	732.817	74.9207
25	698.105	41.9638	26	647.965	87.1881	27	606.503	84.0878
28	578.54	88.0687						

2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa1 ^{1}H-NMR (400 MHz, $CDCl_3$)



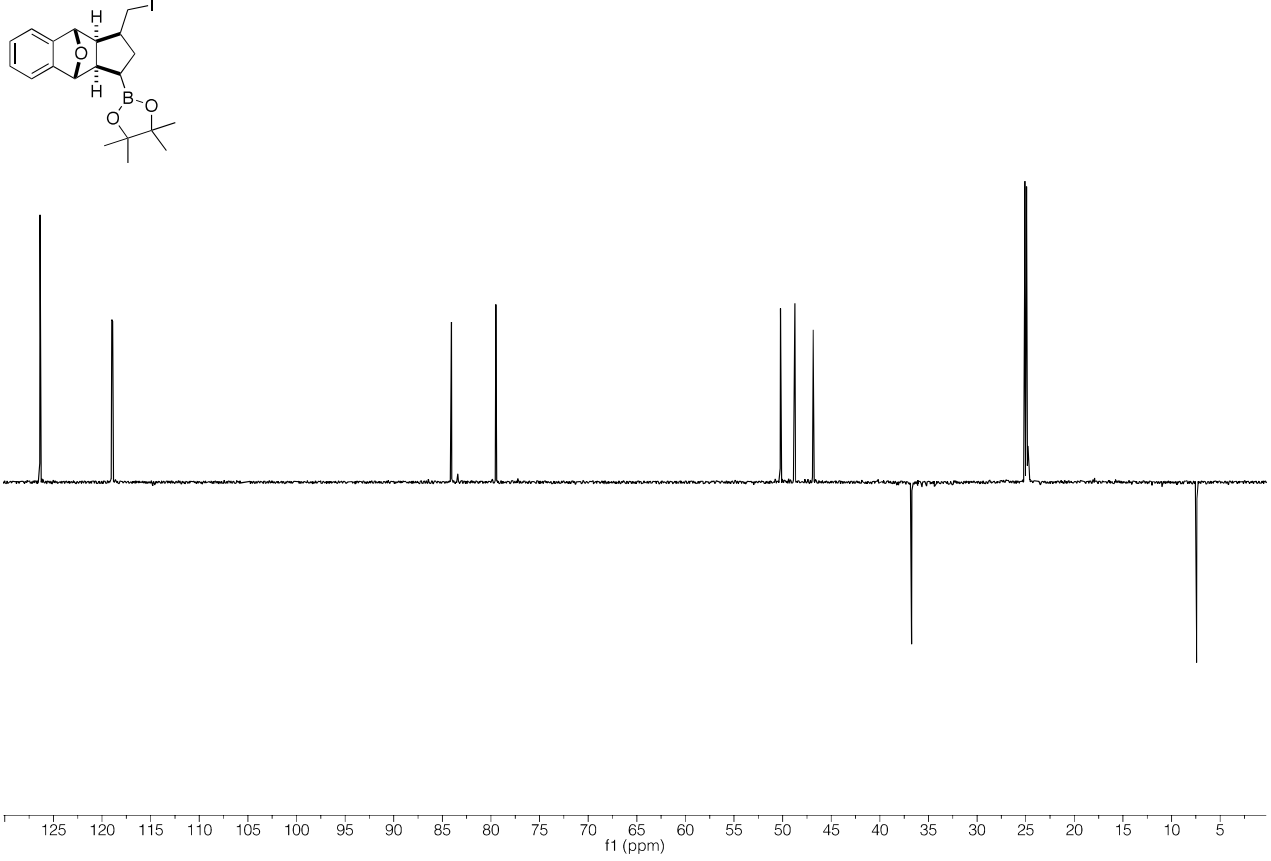
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa1

^{13}C-NMR (101 MHz, $CDCl_3$)



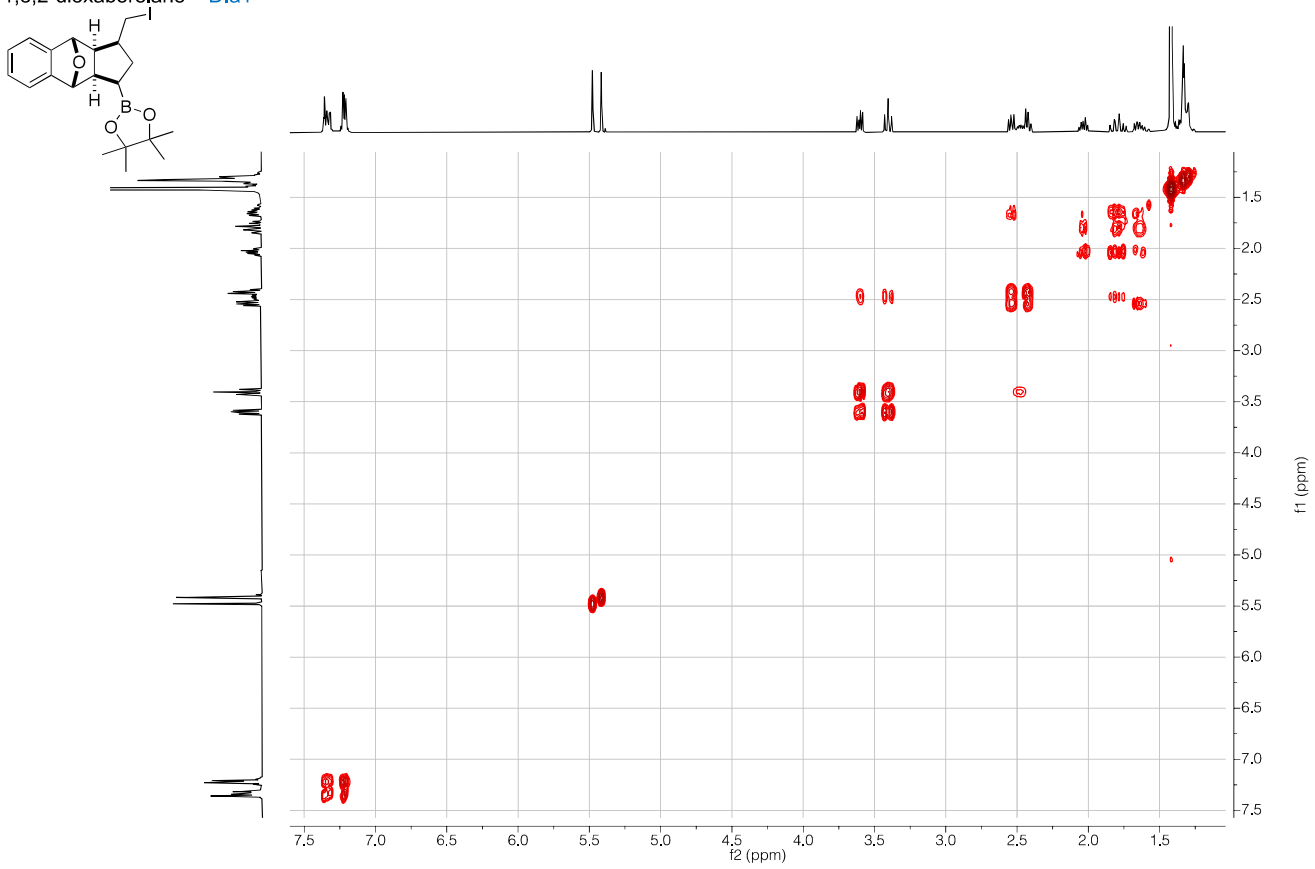
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa1

DEPT-135 NMR (101 MHz, $CDCl_3$)



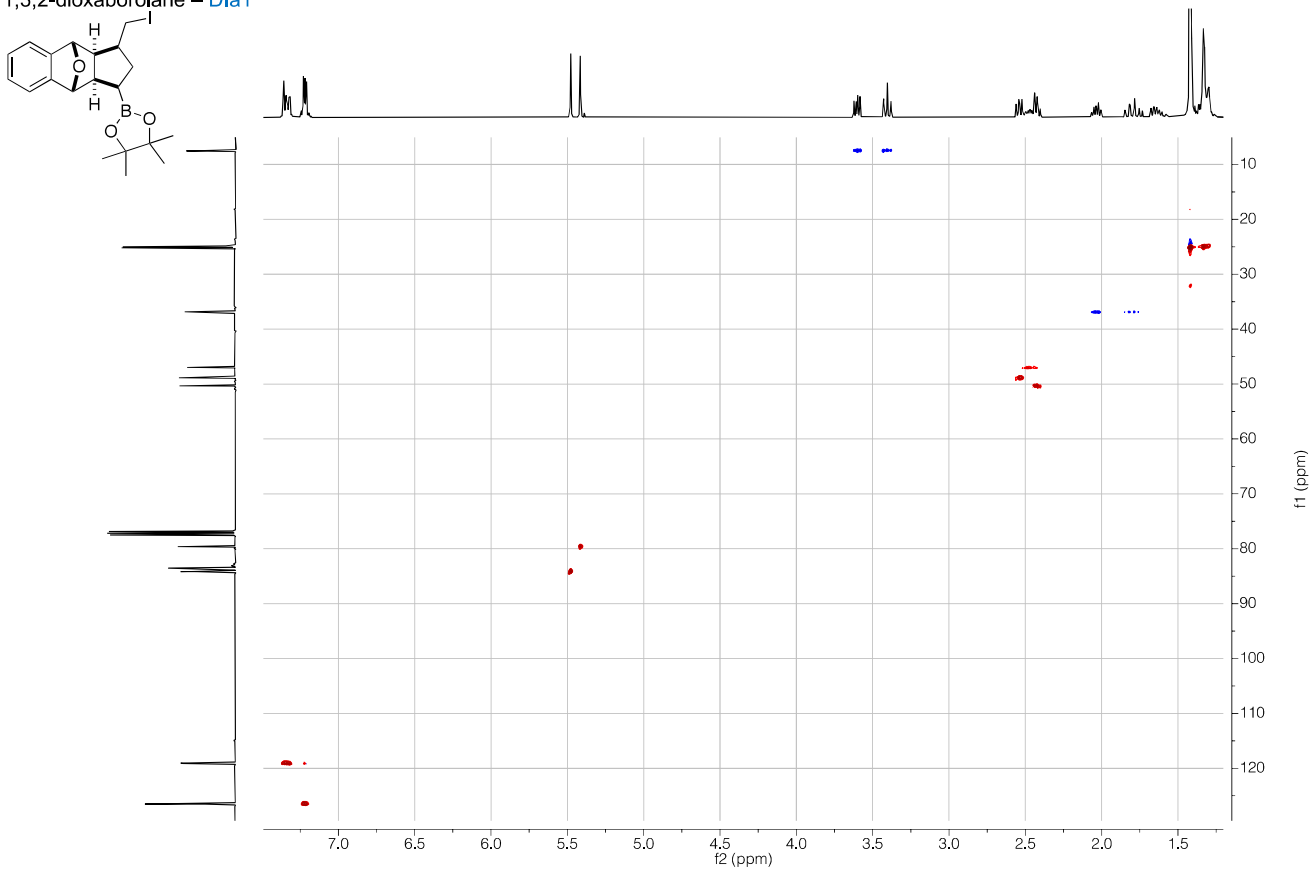
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa1

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



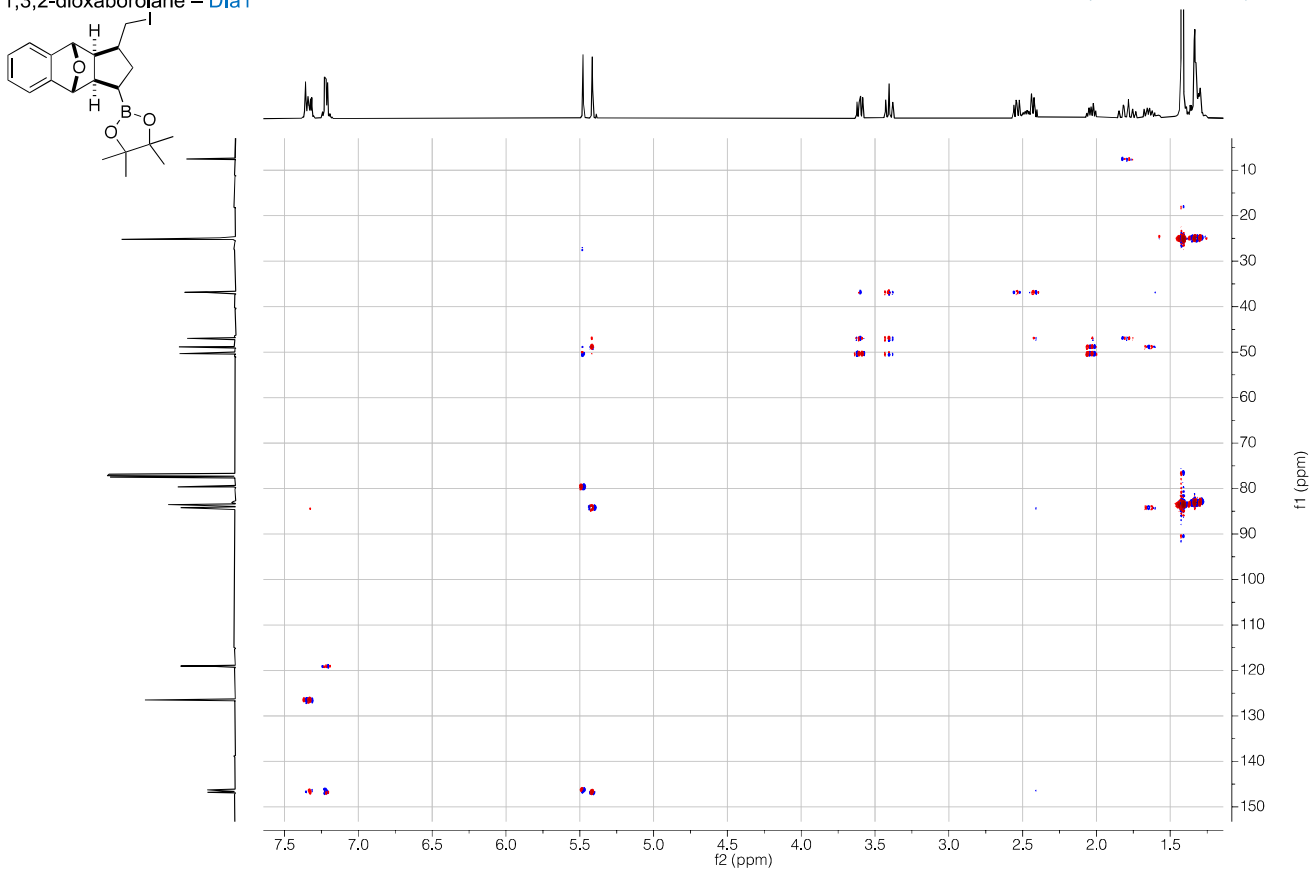
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa1

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



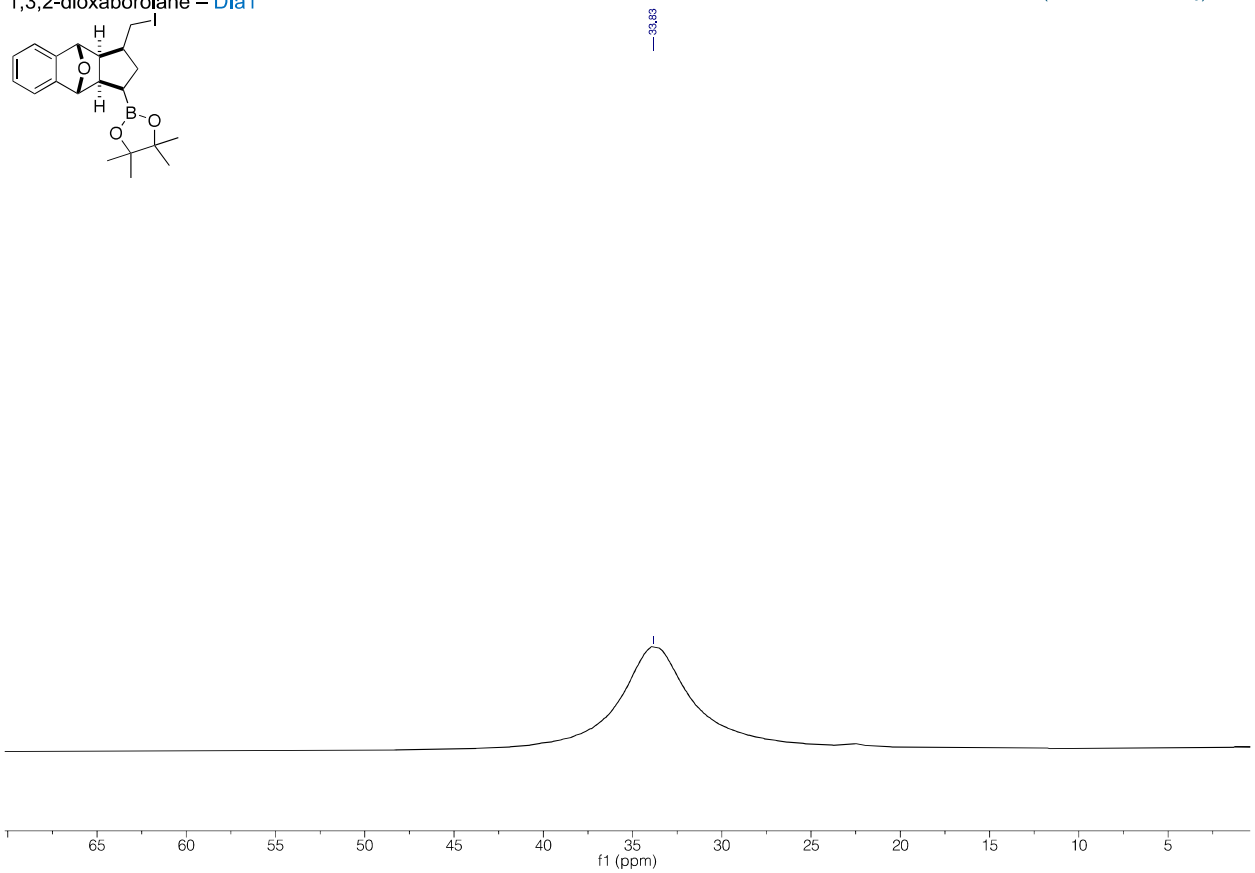
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa1

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



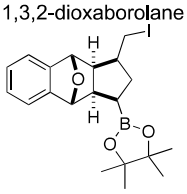
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa1

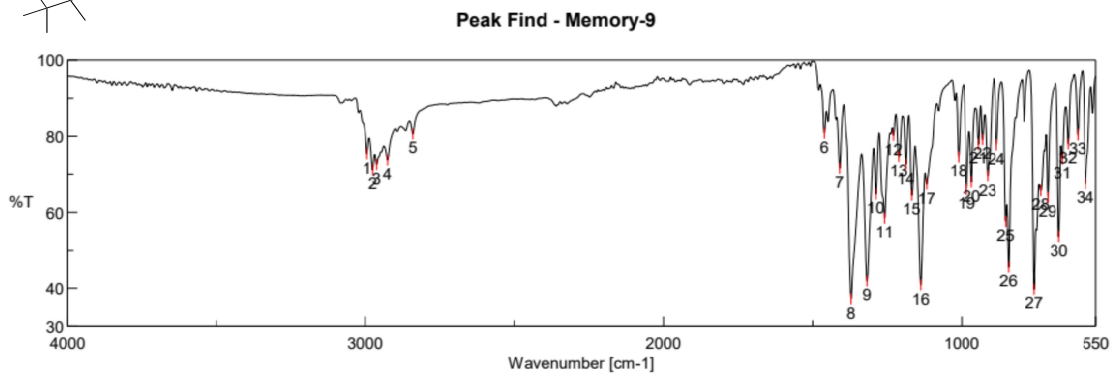
^{11}B-NMR (128 MHz, $CDCl_3$)



2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa1

FT-IR, ATR-diamond



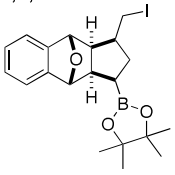


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2993.94	75.3458	2	2974.66	71.103	3	2961.16	72.5247
4	2924.52	73.7386	5	2839.67	80.5672	6	1460.81	80.7992
7	1409.71	71.5394	8	1371.14	37.1719	9	1318.11	41.9156
10	1288.22	64.758	11	1259.29	58.4256	12	1229.4	80.2182
13	1211.08	74.643	14	1187.94	72.5557	15	1167.69	64.4656
16	1137.8	40.8908	17	1117.55	67.432	18	1010.52	74.4667
19	982.554	66.0559	20	966.162	67.9922	21	943.02	77.8196
22	929.521	79.1118	23	912.165	69.5449	24	882.274	77.6905
25	851.418	57.5678	26	841.776	45.5742	27	755.959	39.7025
28	733.782	65.6629	29	710.64	63.8349	30	673.035	53.5376
31	661.464	73.9647	32	642.179	77.9743	33	610.36	80.3289
34	584.325	67.5042						

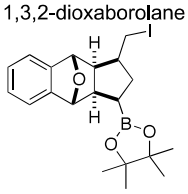
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa2

^{1}H-NMR (400 MHz, $CDCl_3$)



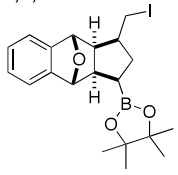
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa2

^{13}C-NMR (101 MHz, $CDCl_3$)



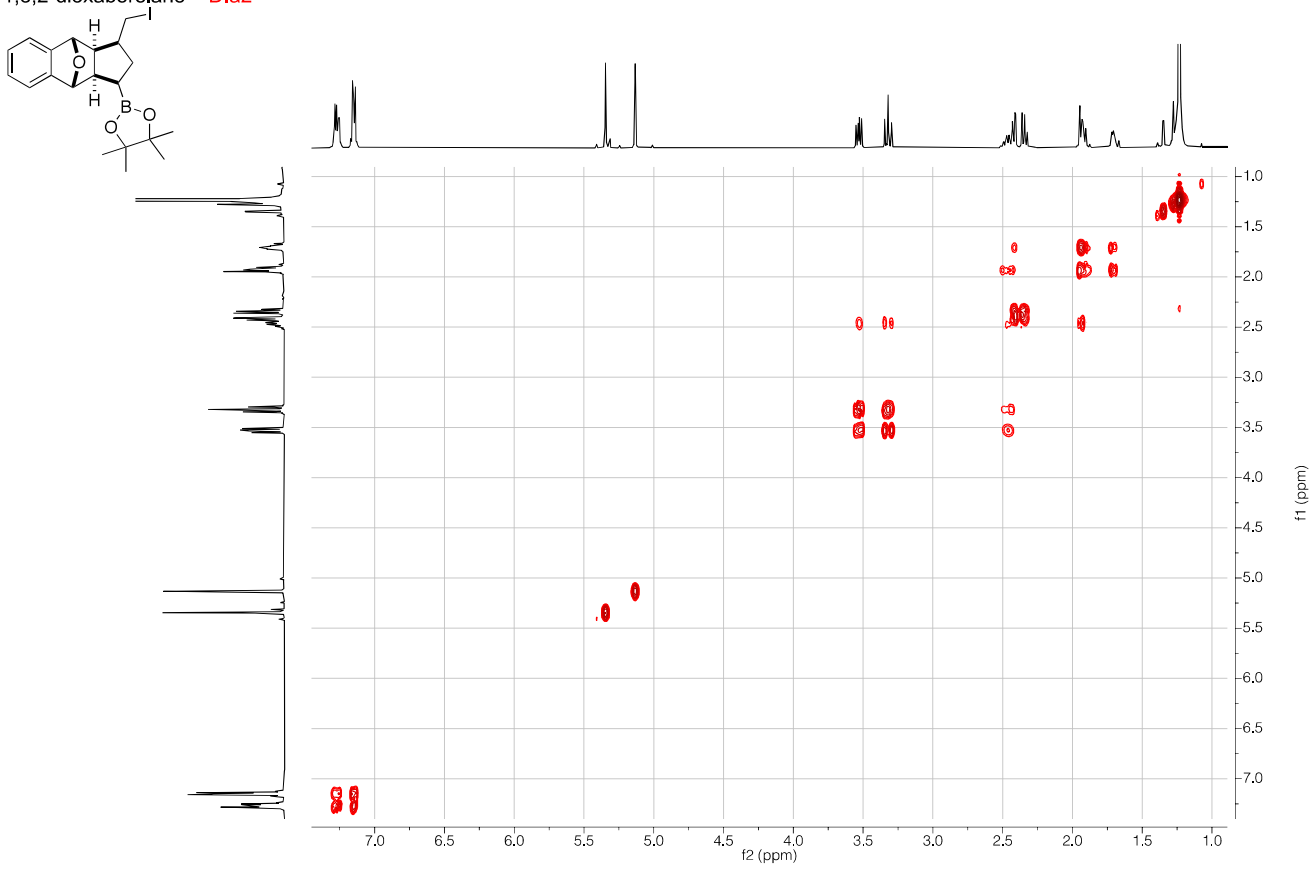
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa2

DEPT-135 NMR (101 MHz, $CDCl_3$)



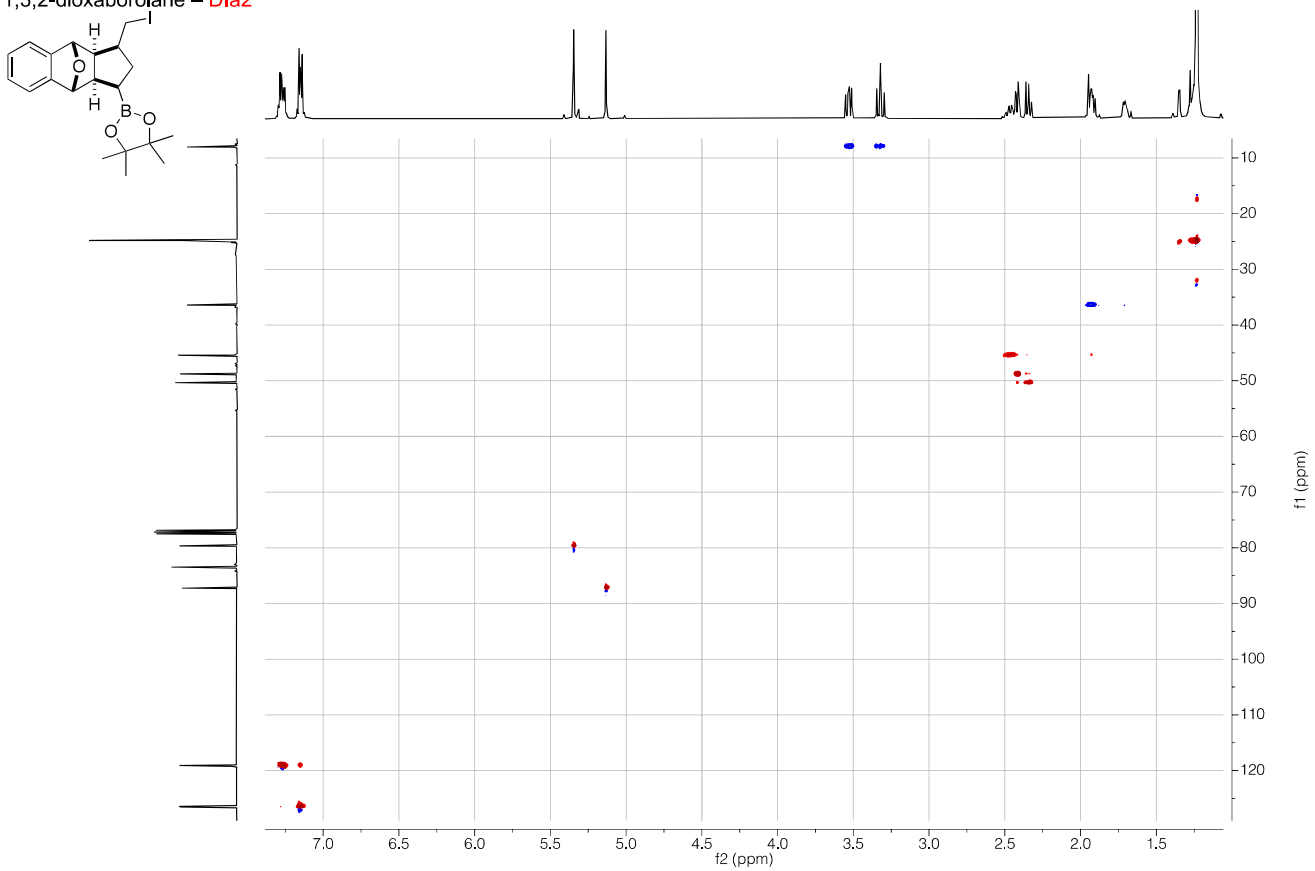
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa2

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



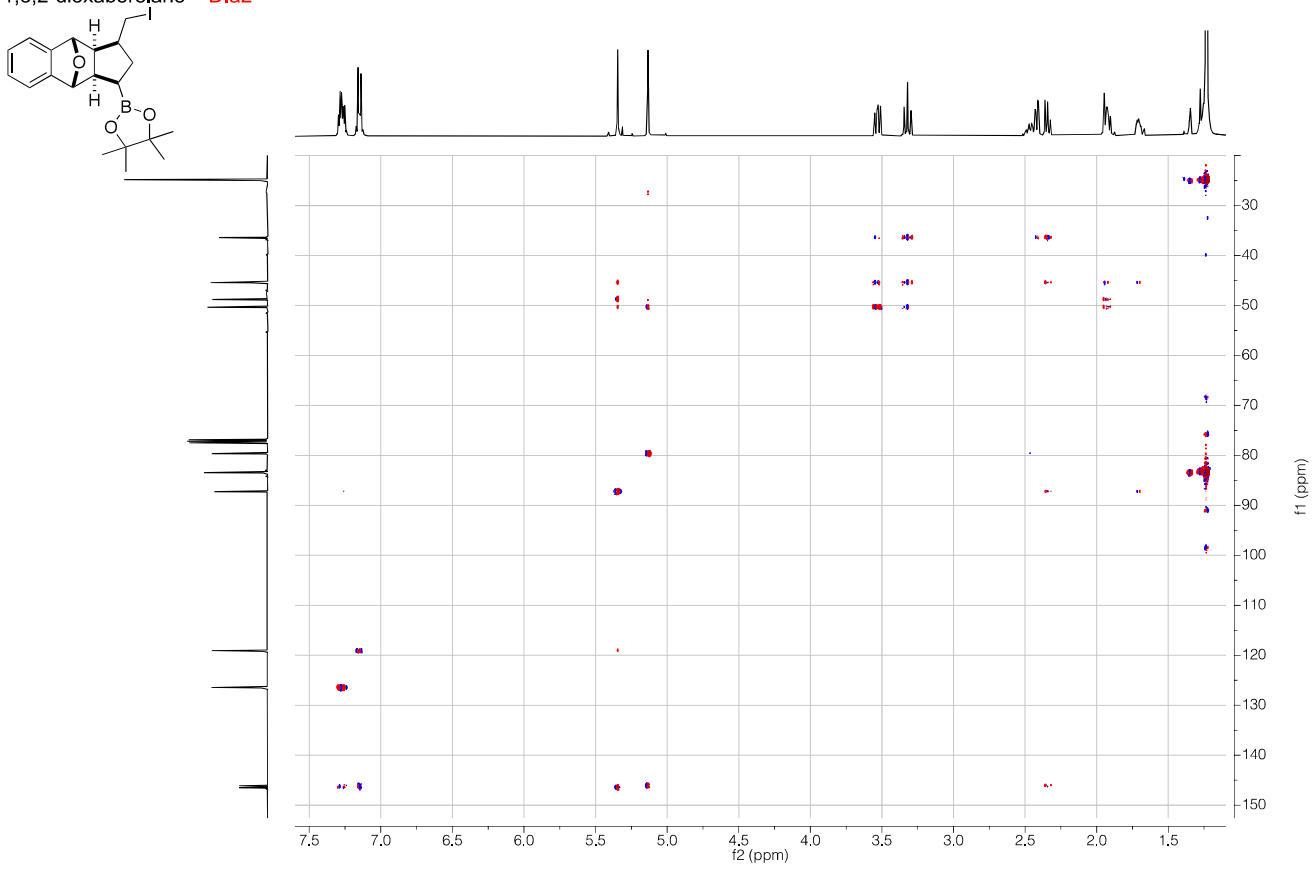
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa2

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



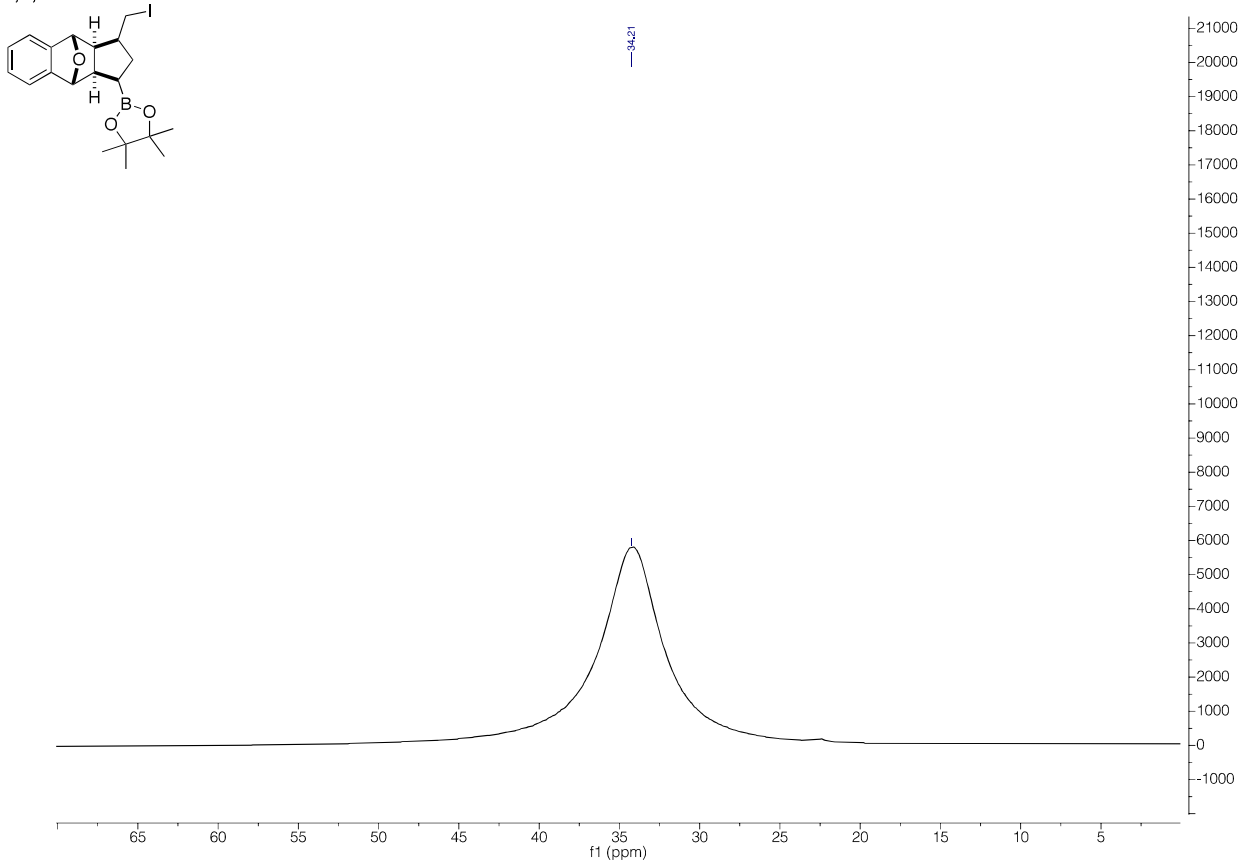
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa2

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



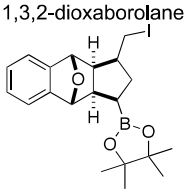
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa2

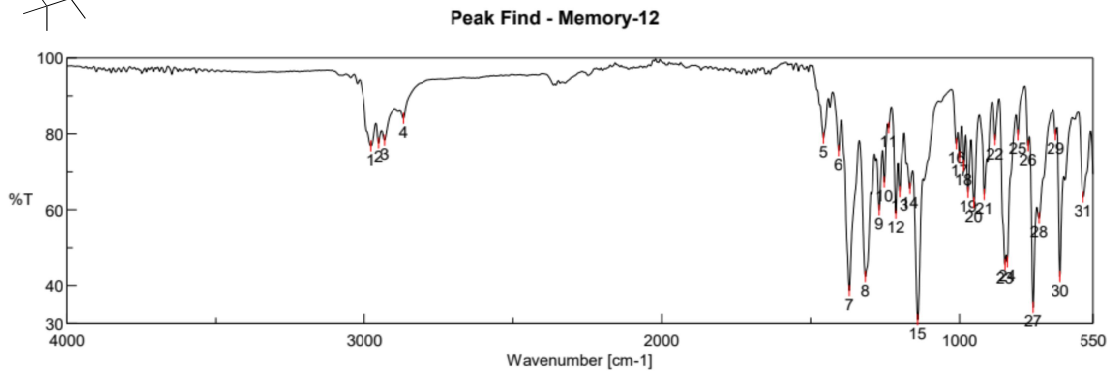
^{11}B-NMR (128 MHz, $CDCl_3$)



2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – DIa2

FT-IR, ATR-diamond



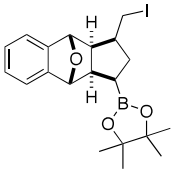


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2977.55	76.7534	2	2952.48	77.549	3	2933.2	78.3014
4	2868.59	84.0823	5	1456.96	78.8085	6	1405.85	75.4949
7	1370.18	38.6373	8	1316.18	42.3388	9	1269.9	59.9009
10	1252.54	67.2573	11	1238.08	81.5581	12	1213.97	59.0353
13	1200.47	64.729	14	1166.72	65.595	15	1140.69	30.9863
16	1010.52	77.3254	17	999.91	73.8973	18	986.411	71.6112
19	971.947	64.5517	20	951.698	61.8335	21	916.986	64.014
22	881.309	78.4203	23	847.561	45.484	24	839.847	46.2112
25	804.171	79.6573	26	769.458	76.8046	27	753.066	34.1969
28	732.817	57.7622	29	675.928	79.7032	30	660.5	42.3369
31	583.361	63.2793						

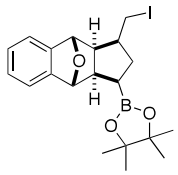
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – Mix Dia3 & Dia4

^{1}H-NMR (400 MHz, $CDCl_3$)



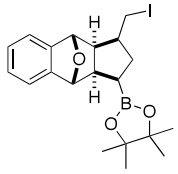
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – Mix Dia3 & Dia4

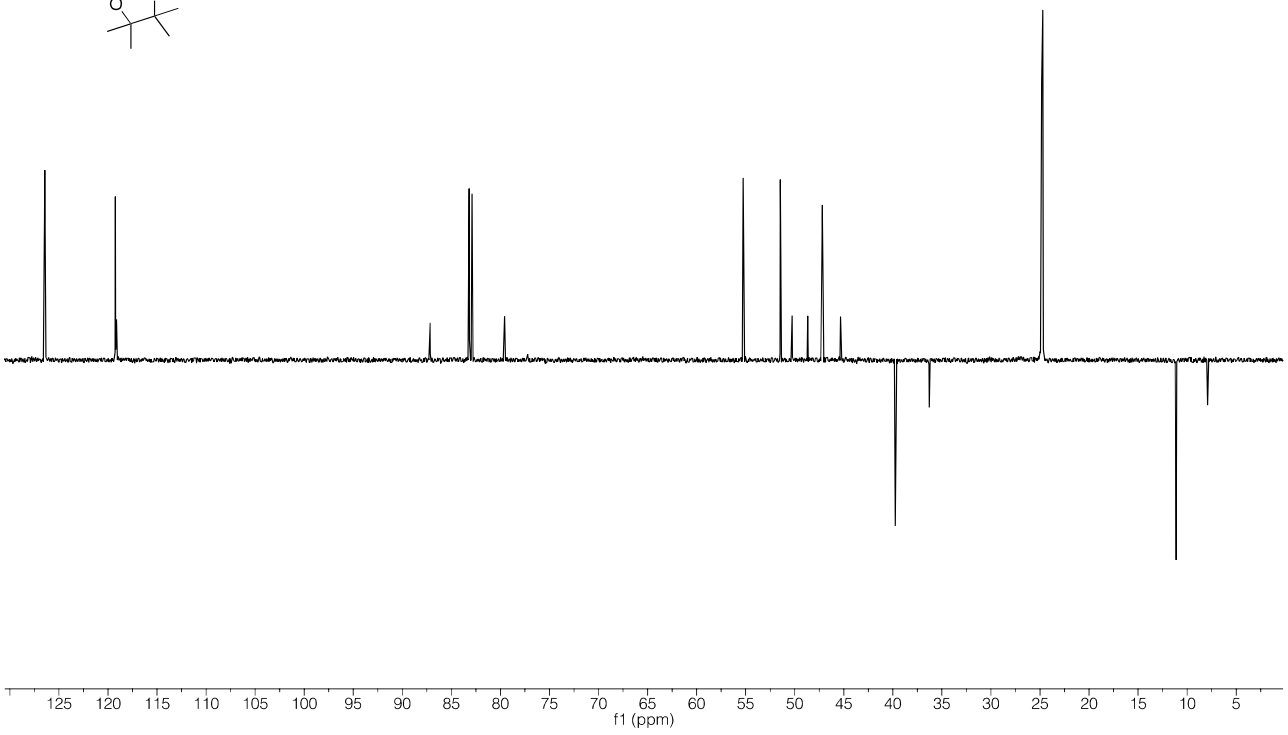
^{13}C-NMR (101 MHz, $CDCl_3$)



2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – Mix Dia3 & Dia4

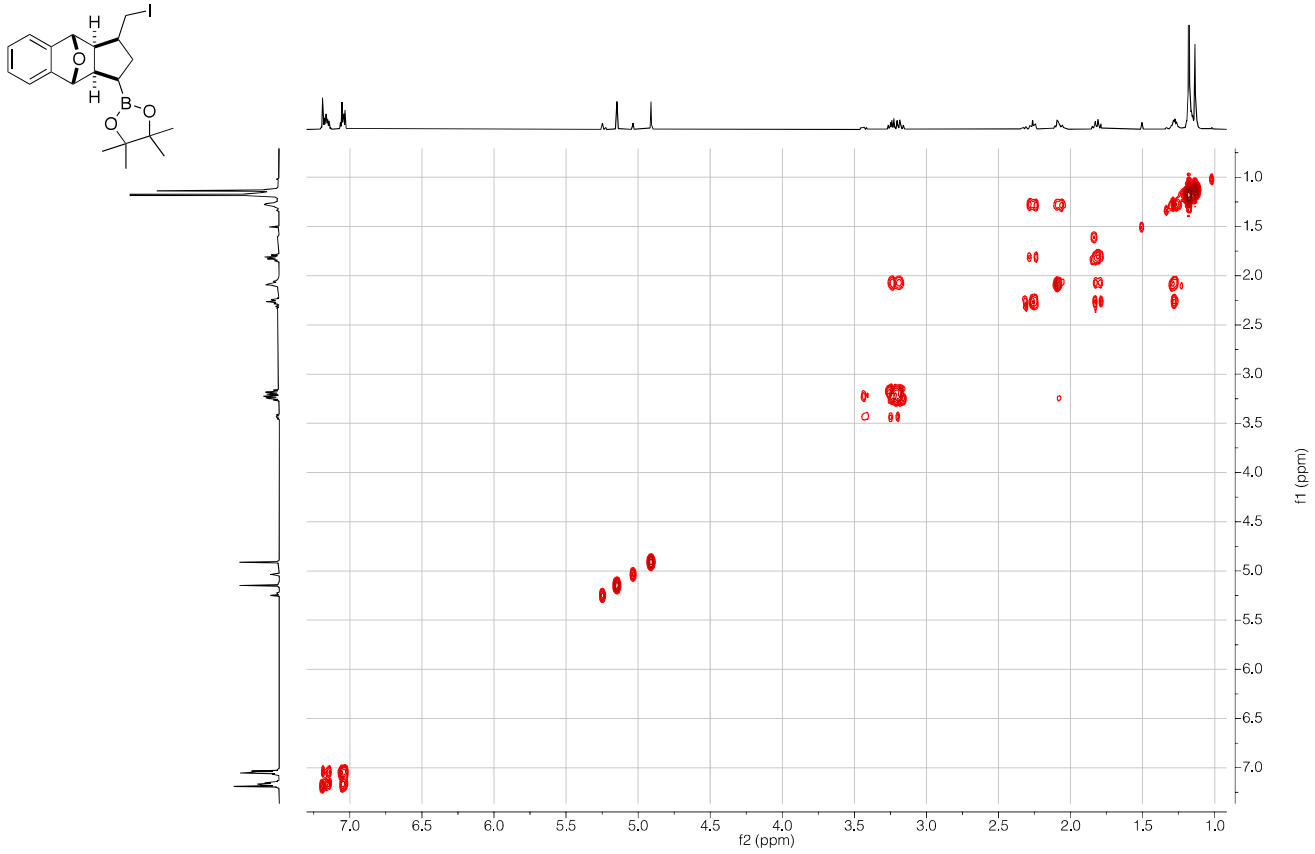
DEPT-135 NMR (101 MHz, $CDCl_3$)





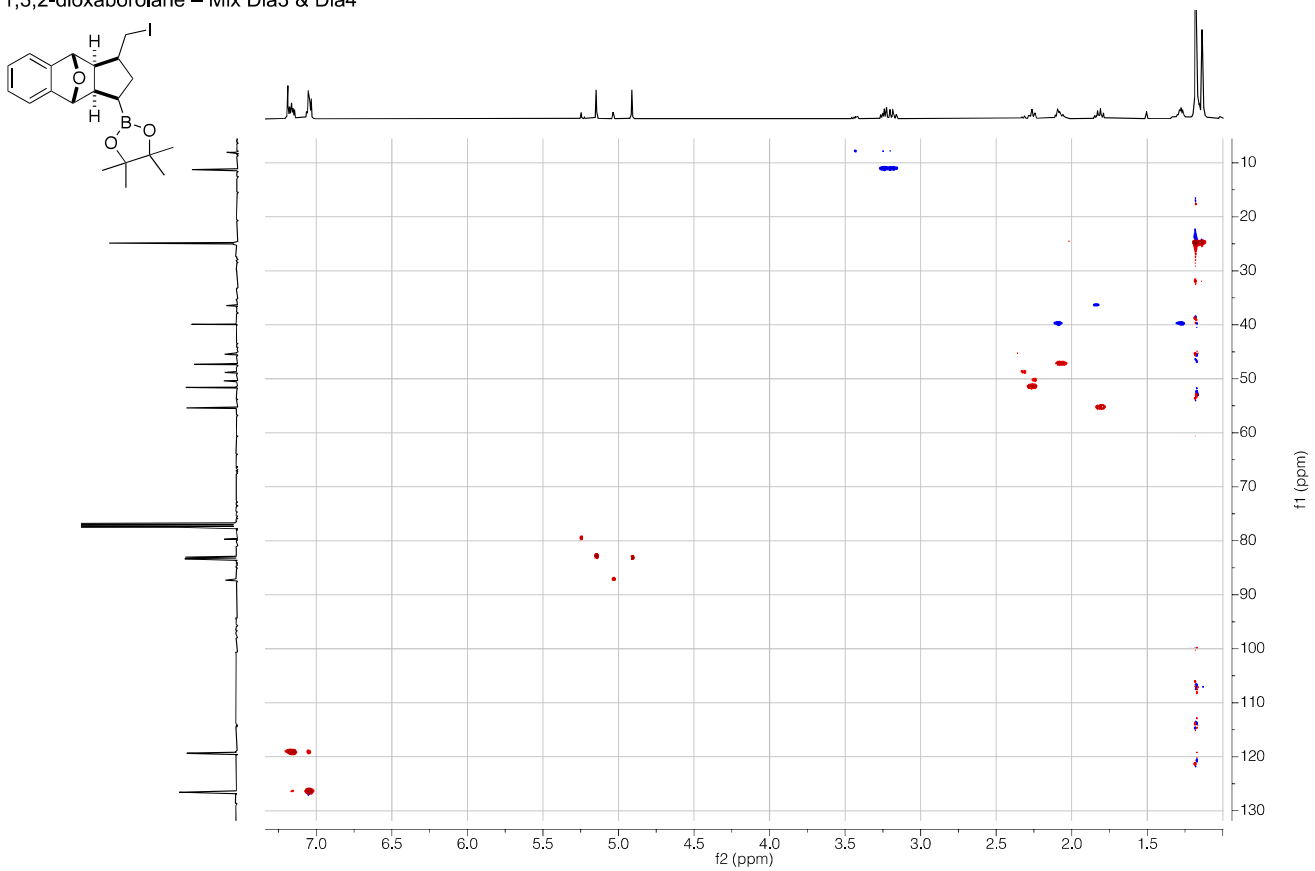
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – Mix Dia3 & Dia4

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



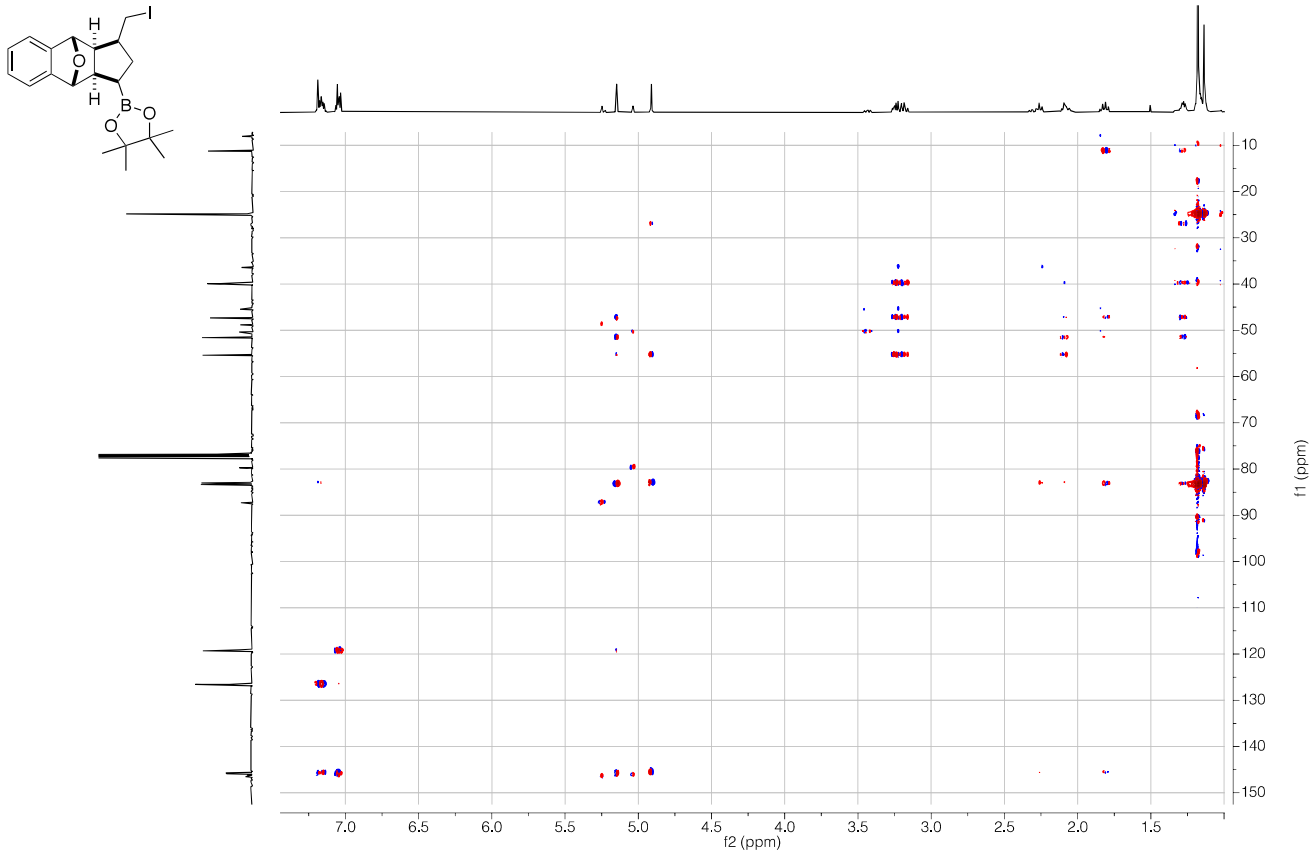
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – Mix Dia3 & Dia4

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



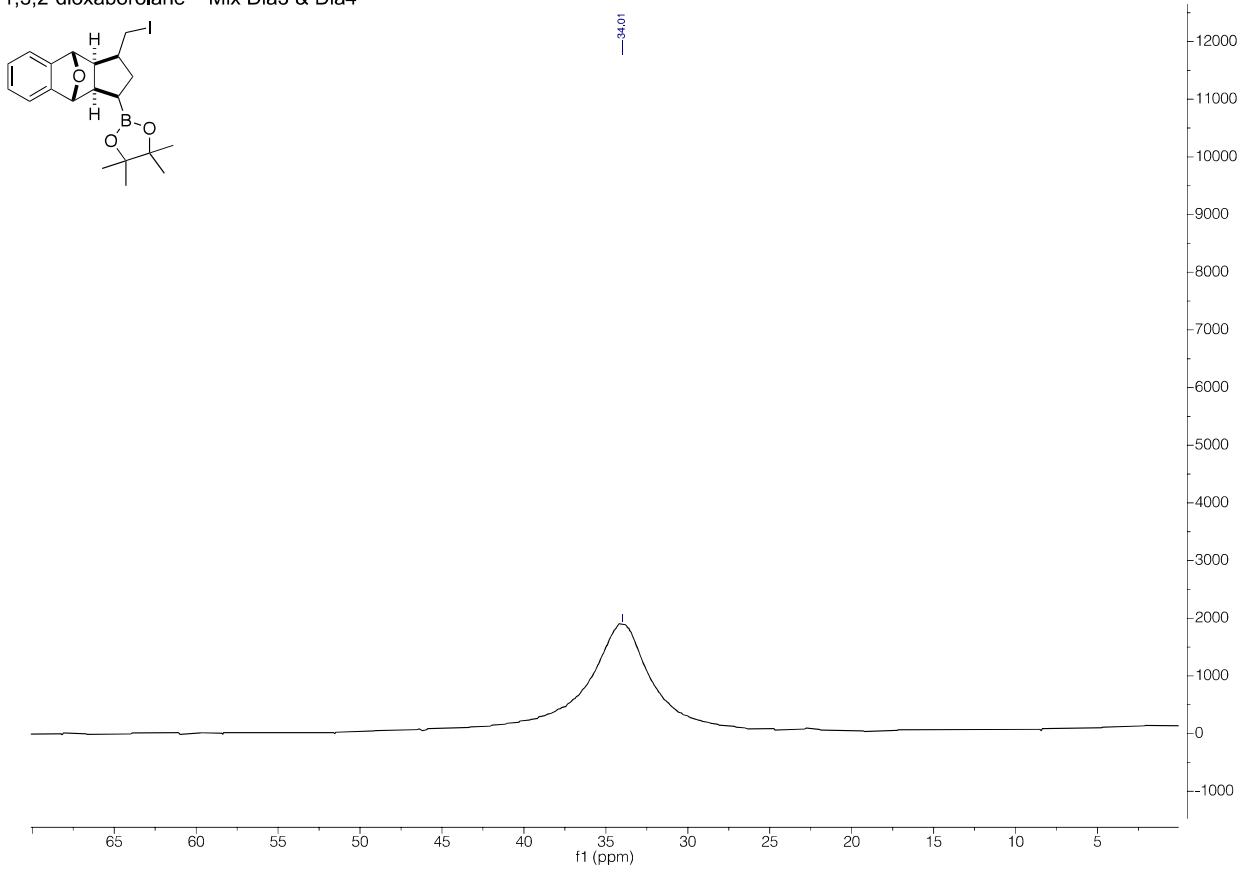
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – Mix Dia3 & Dia4

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



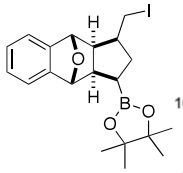
2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – Mix Dia3 & Dia4

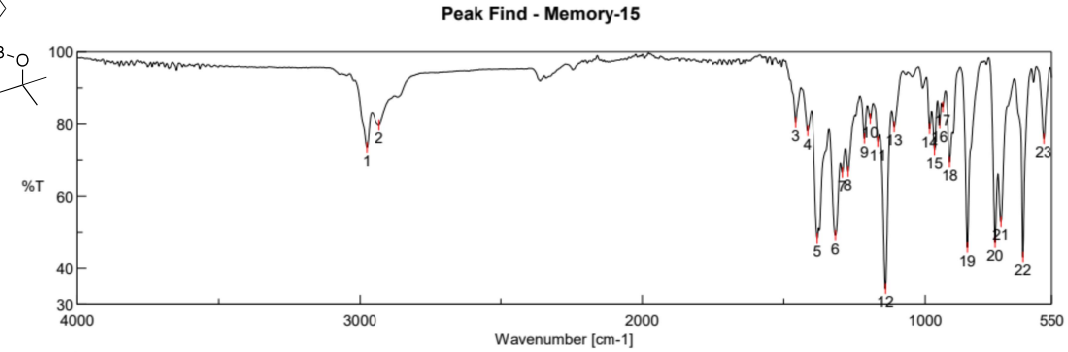
^{11}B-NMR (128 MHz, $CDCl_3$)



2-[12-(iodomethyl)-14-oxatetracyclo[6.5.1.02,7.09,13]tetradeca-2,4,6-trien-10-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane – Mix Dia3 & Dia4

FT-IR, ATR-diamond



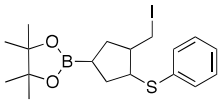


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	73.4374	2	2931.27	79.6537	3	1457.92	80.3834
4	1415.49	78.0957	5	1378.85	48.2454	6	1315.21	49.0972
7	1290.14	66.52	8	1270.86	66.7494	9	1213.01	75.9437
10	1192.76	81.4036	11	1165.76	75.0417	12	1139.72	34.2746
13	1108.87	79.1435	14	984.482	78.6423	15	967.126	72.6777
16	948.806	80.1838	17	938.199	84.6597	18	911.201	69.4163
19	848.525	45.7435	20	751.138	47.1558	21	730.889	52.8498
22	653.75	43.0542	23	579.504	75.8732			

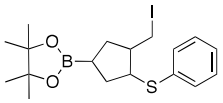
2-[3-(iodomethyl)-4-phenylsulfanyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

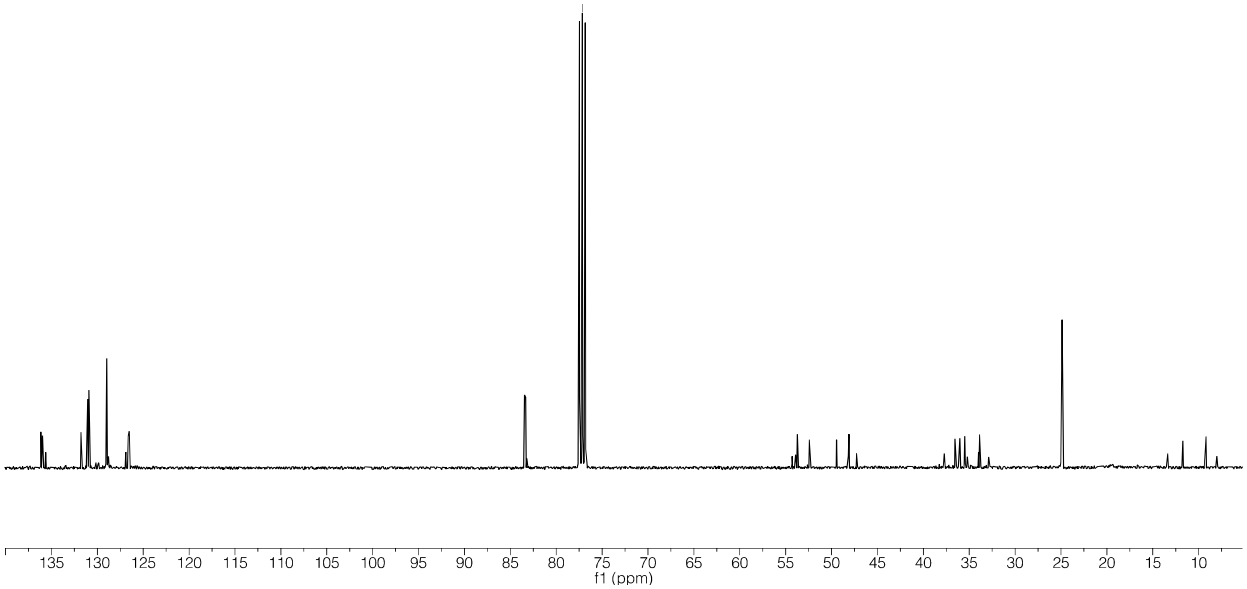
^{1}H-NMR (400 MHz, $CDCl_3$)



2-[3-(iodomethyl)-4-phenylsulfanyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

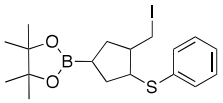
^{13}C-NMR (101 MHz, $CDCl_3$)

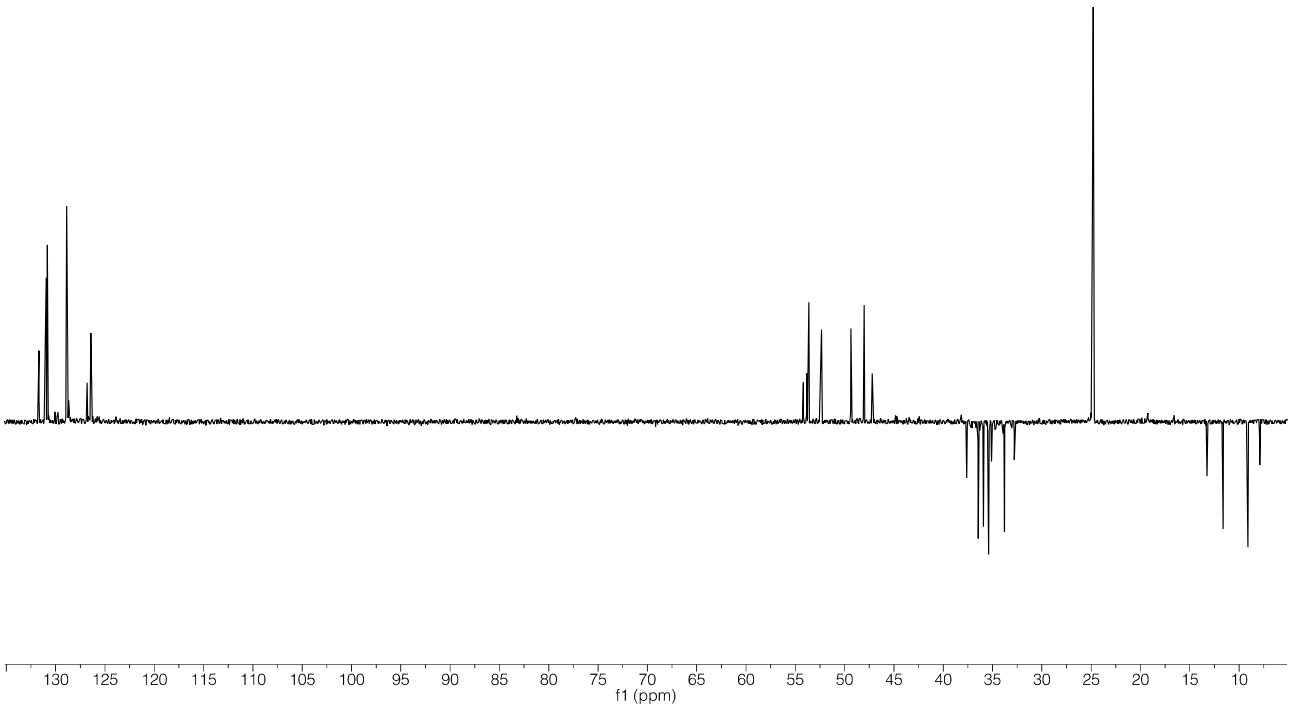




2-[3-(iodomethyl)-4-phenylsulfanyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

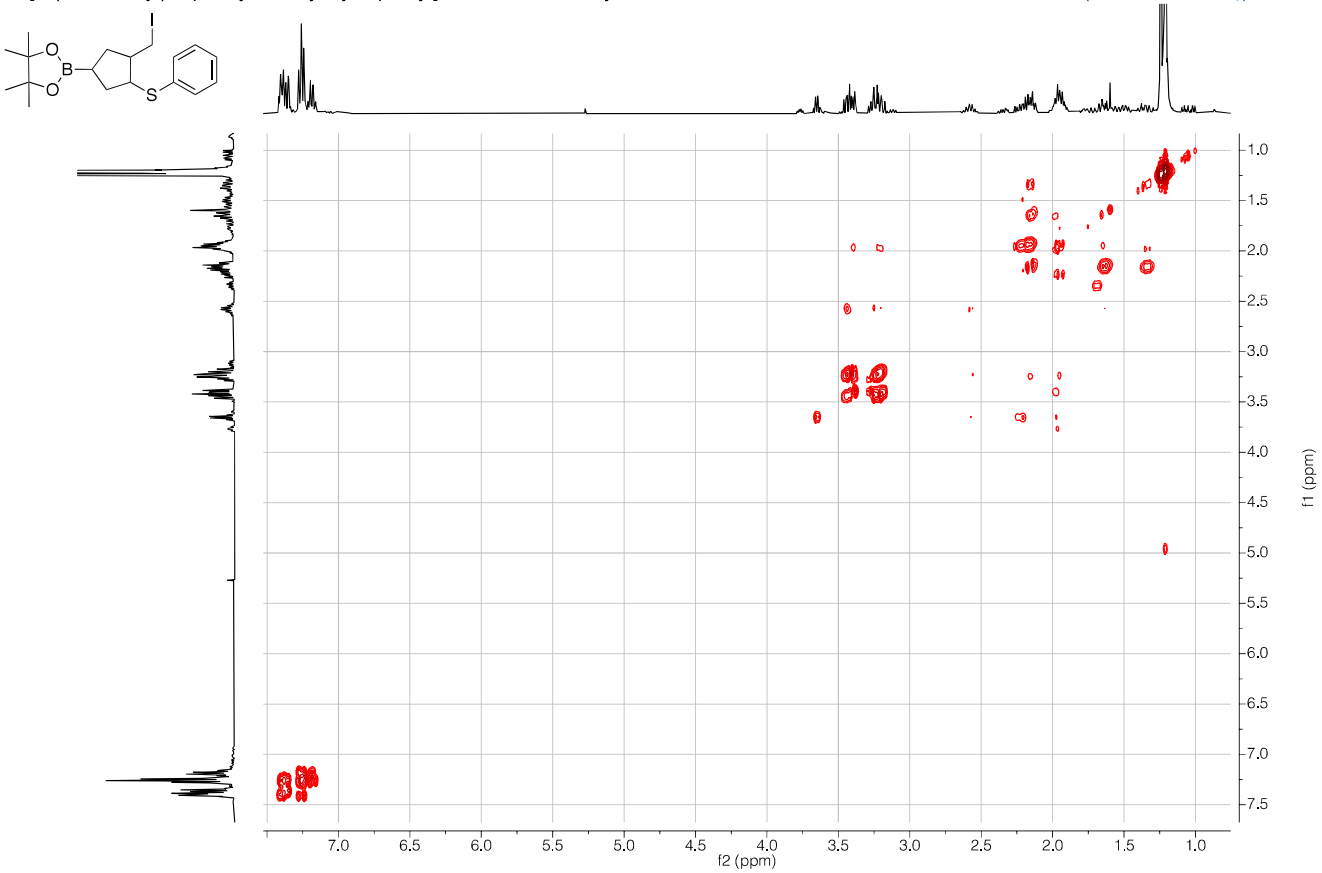
DEPT-135 NMR (101 MHz, $CDCl_3$)





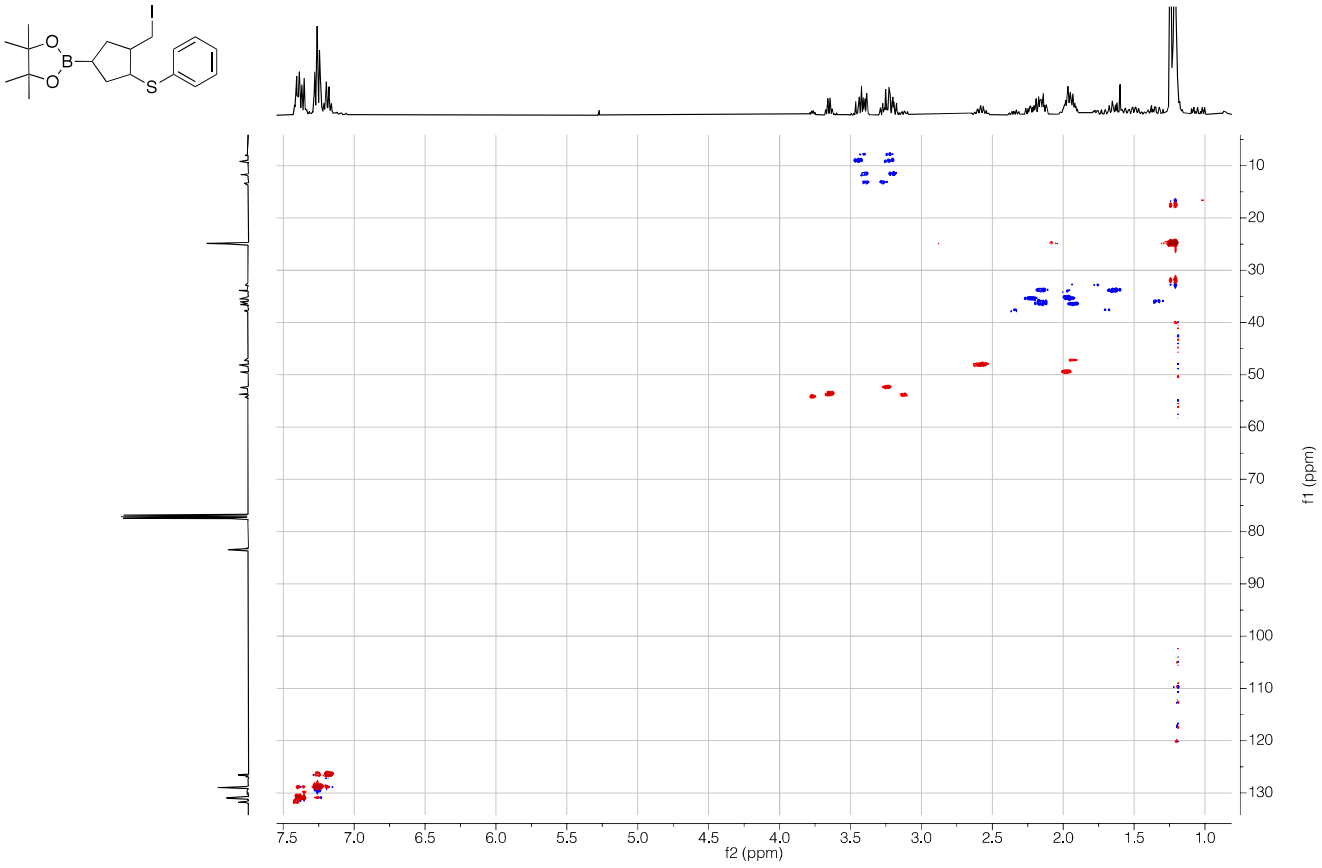
2-[3-(iodomethyl)-4-phenylsulfanyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



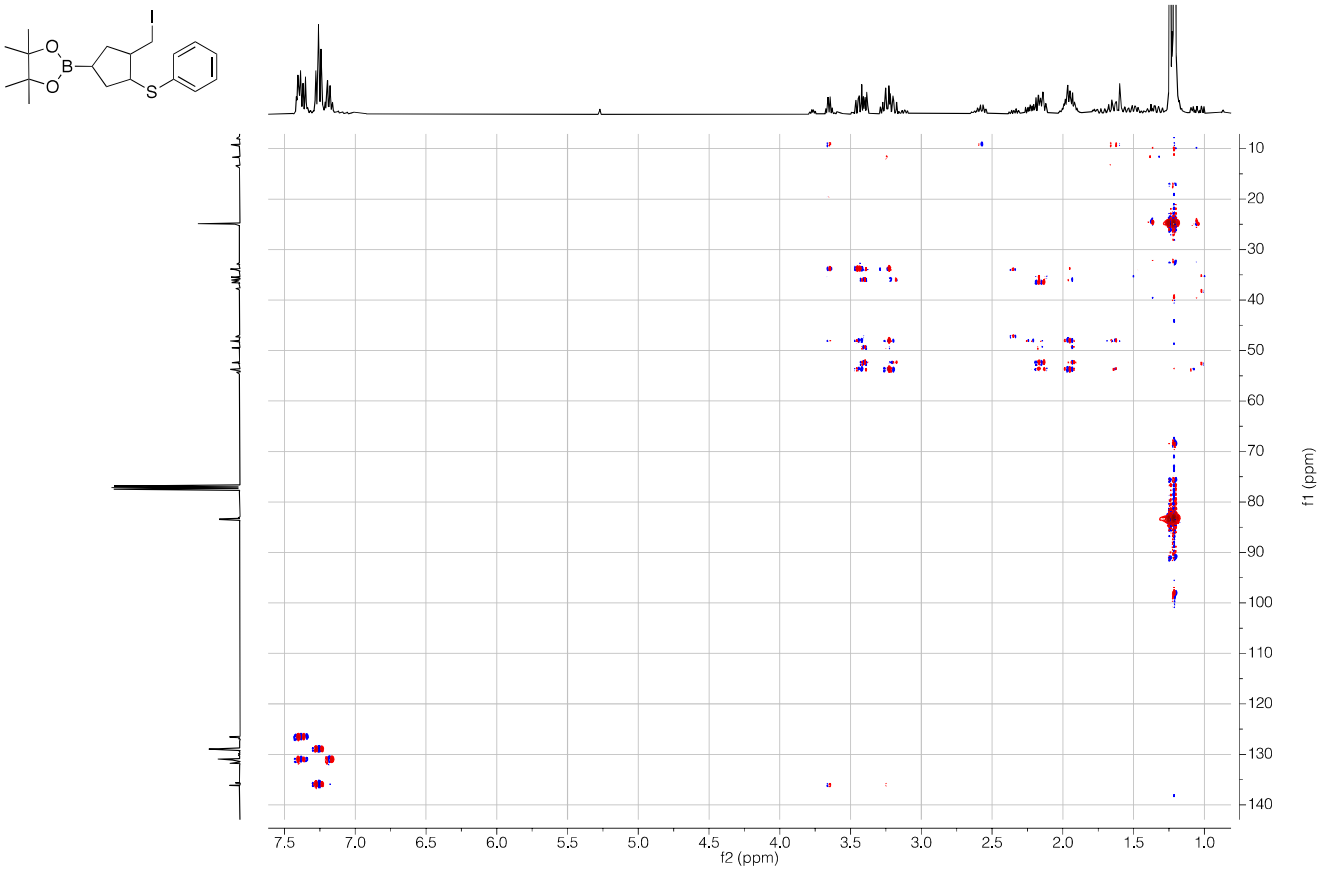
2-[3-(iodomethyl)-4-phenylsulfanyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



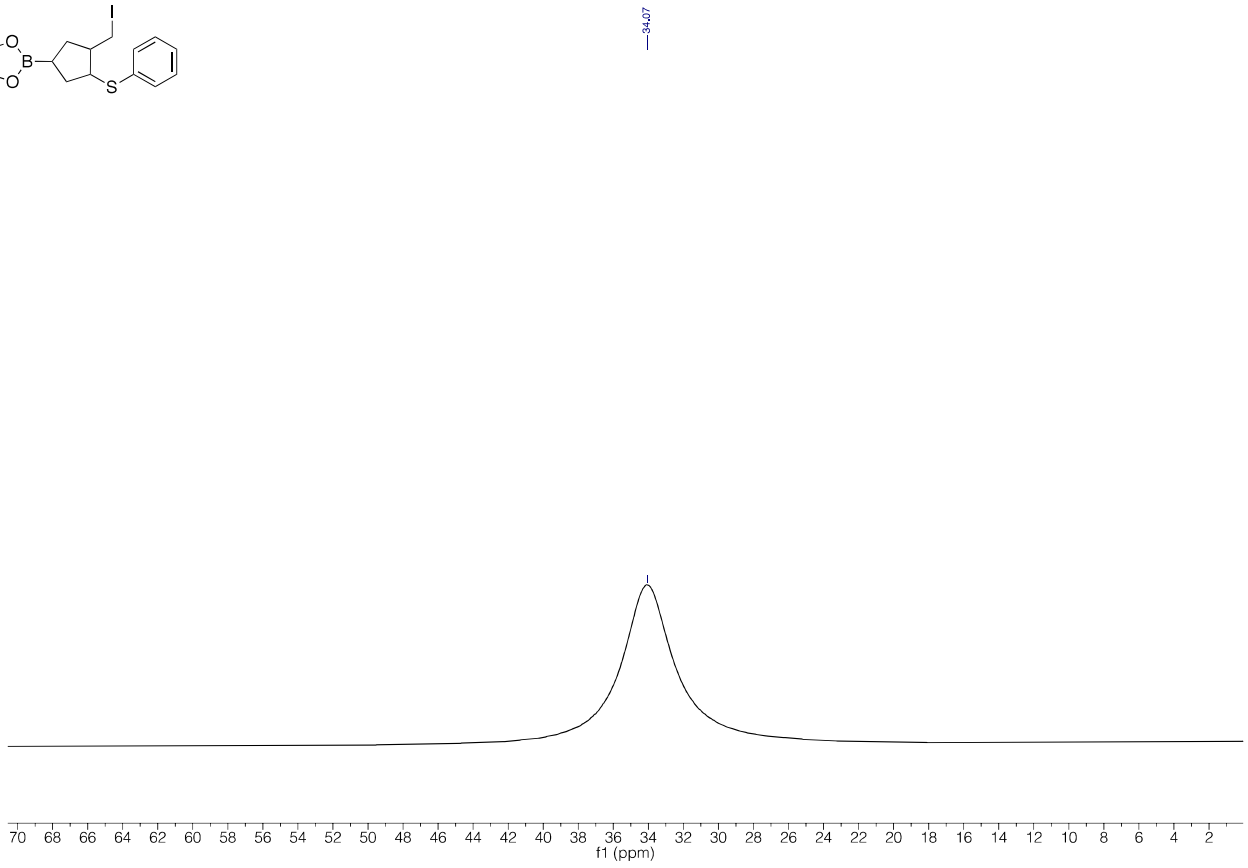
2-[3-(iodomethyl)-4-phenylsulfanyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)



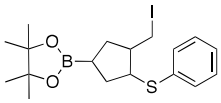
2-[3-(iodomethyl)-4-phenylsulfanyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

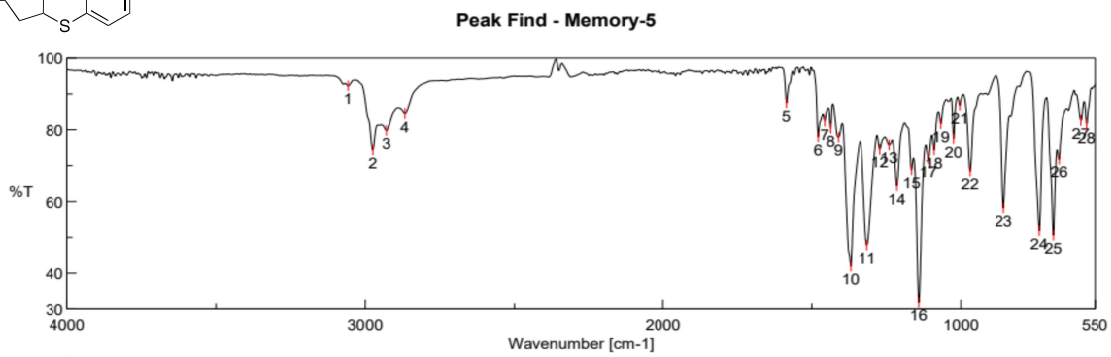
^{11}B-NMR (128 MHz, $CDCl_3$)



2-[3-(iodomethyl)-4-phenylsulfanyl-cyclopentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

FT-IR, ATR-diamond



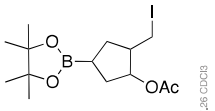


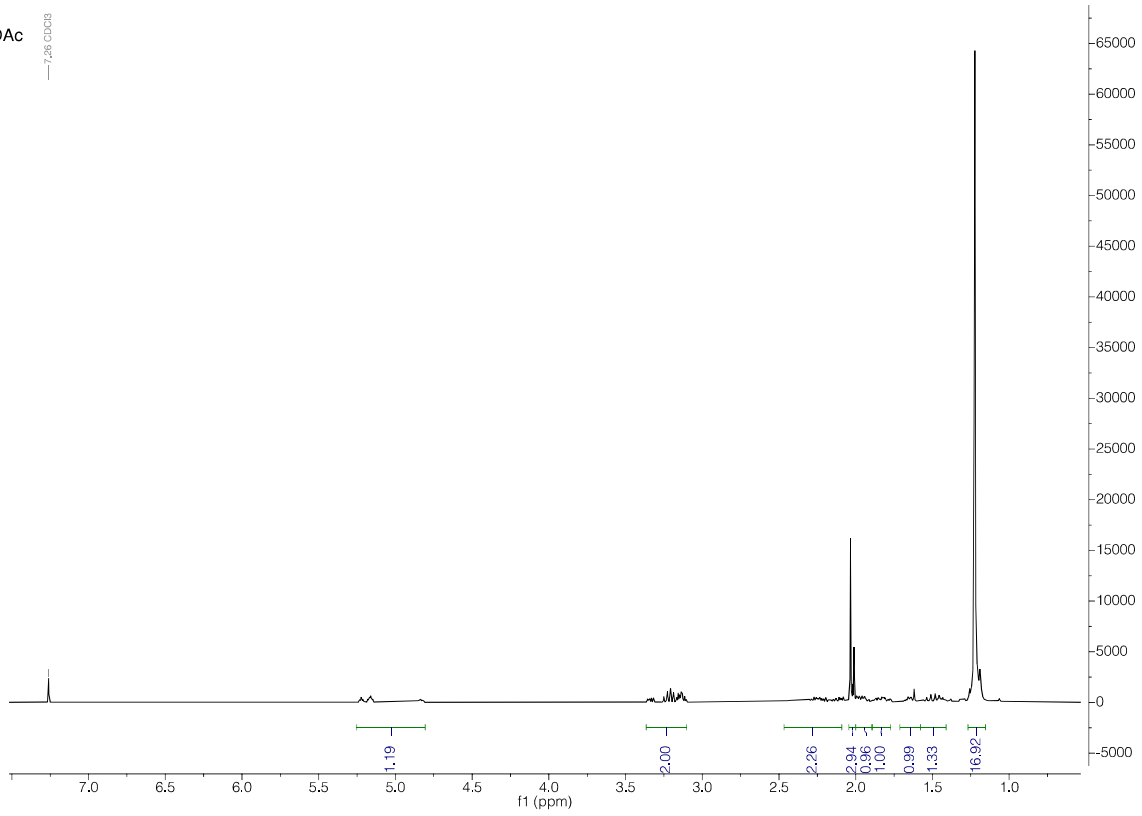
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3056.62	92.1979	2	2974.66	74.3102	3	2929.34	79.7708
4	2867.63	84.4862	5	1584.24	87.4334	6	1479.13	77.9733
7	1456.96	82.3854	8	1437.67	80.3897	9	1411.64	77.864
10	1370.18	41.9337	11	1314.25	47.7359	12	1270.86	74.4589
13	1240	75.7425	14	1213.97	64.3867	15	1164.79	68.7206
16	1140.69	31.7581	17	1108.87	71.9607	18	1090.55	74.3245
19	1067.41	81.6319	20	1024.98	77.4584	21	1003.77	86.7292
22	970.019	68.3669	23	856.239	58.1694	24	736.674	51.8321
25	689.427	50.5232	26	670.142	71.7584	27	597.825	82.5887
28	578.54	81.4352						

[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl] acetate

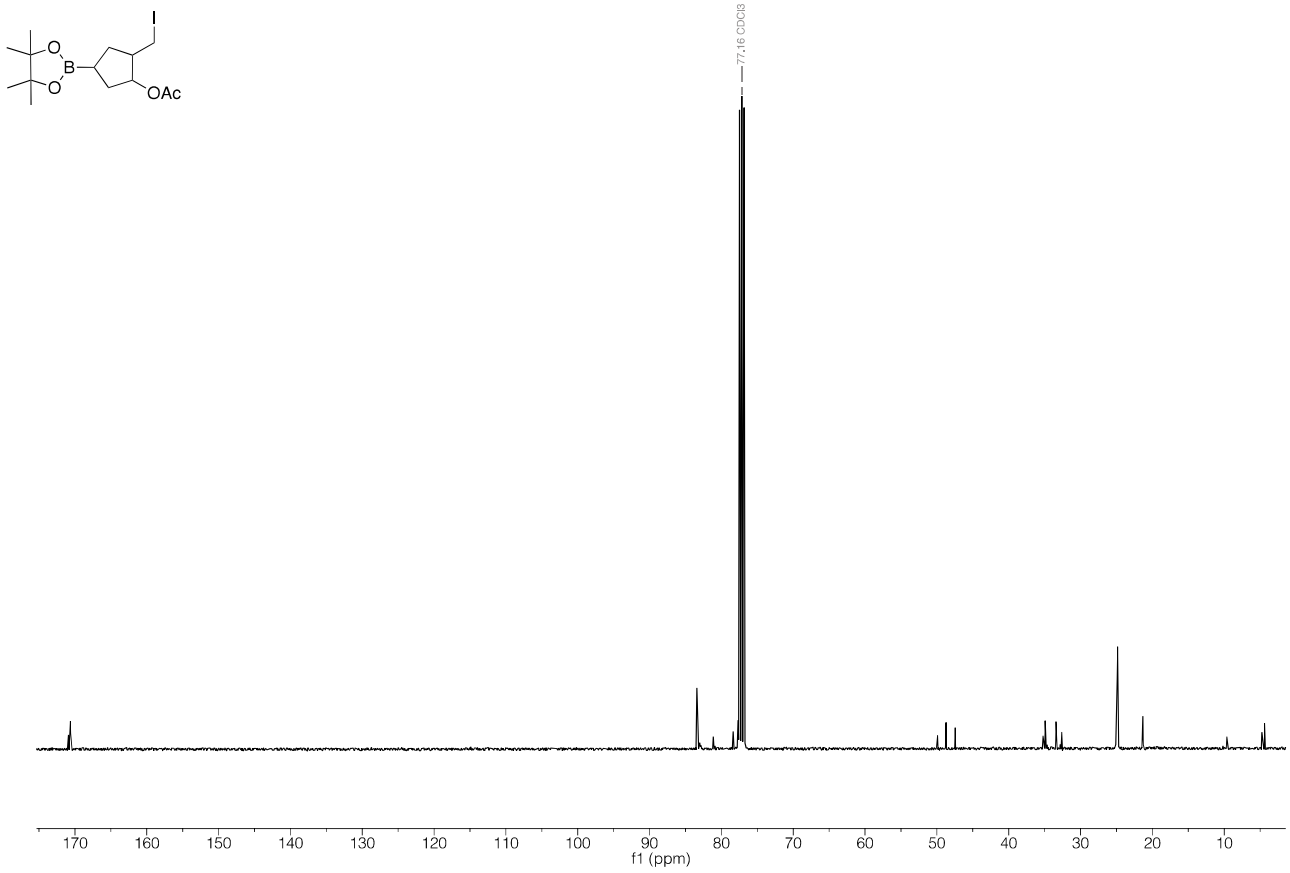
^{1}H-NMR (400 MHz, $CDCl_3$)





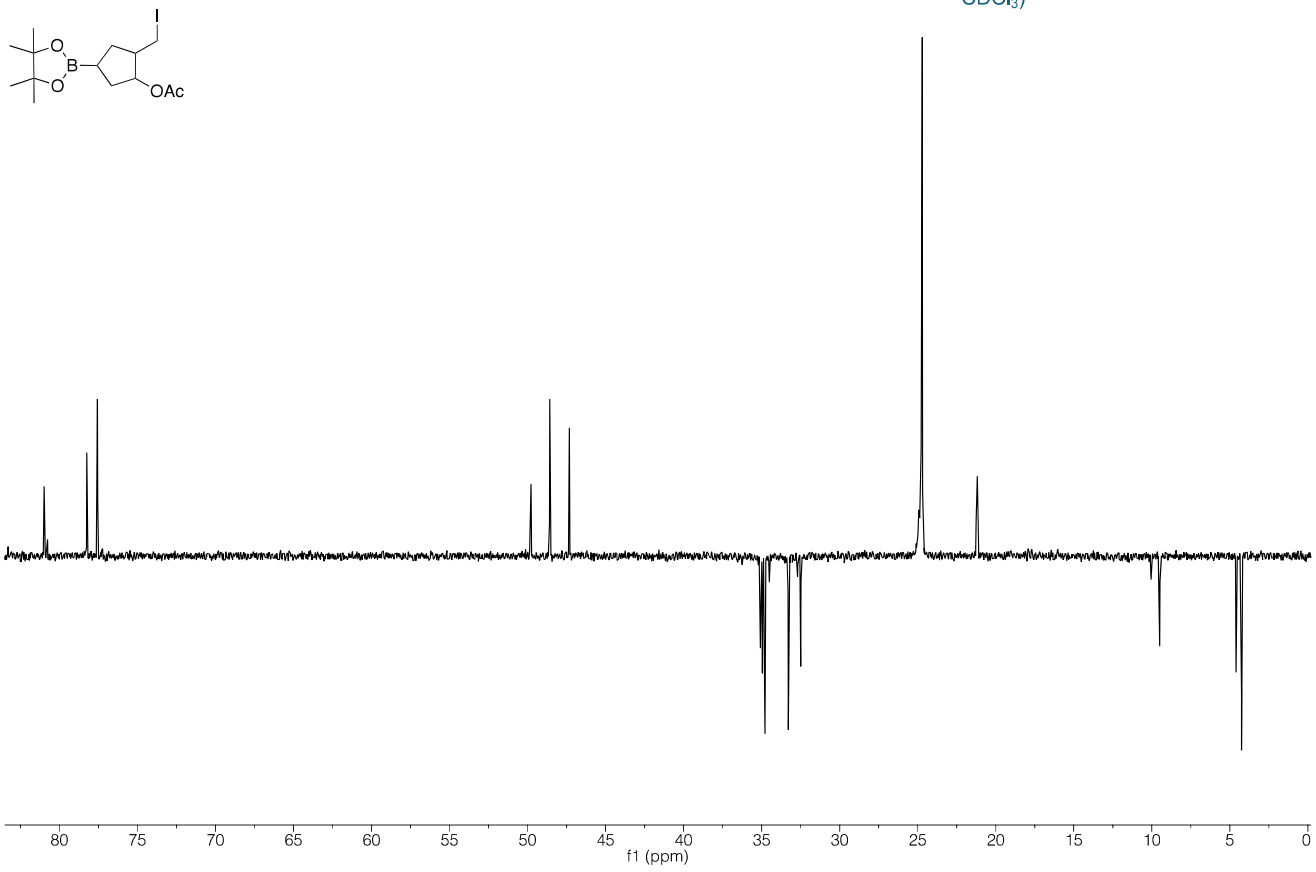
[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl] acetate

^{13}C-NMR (101 MHz, $CDCl_3$)



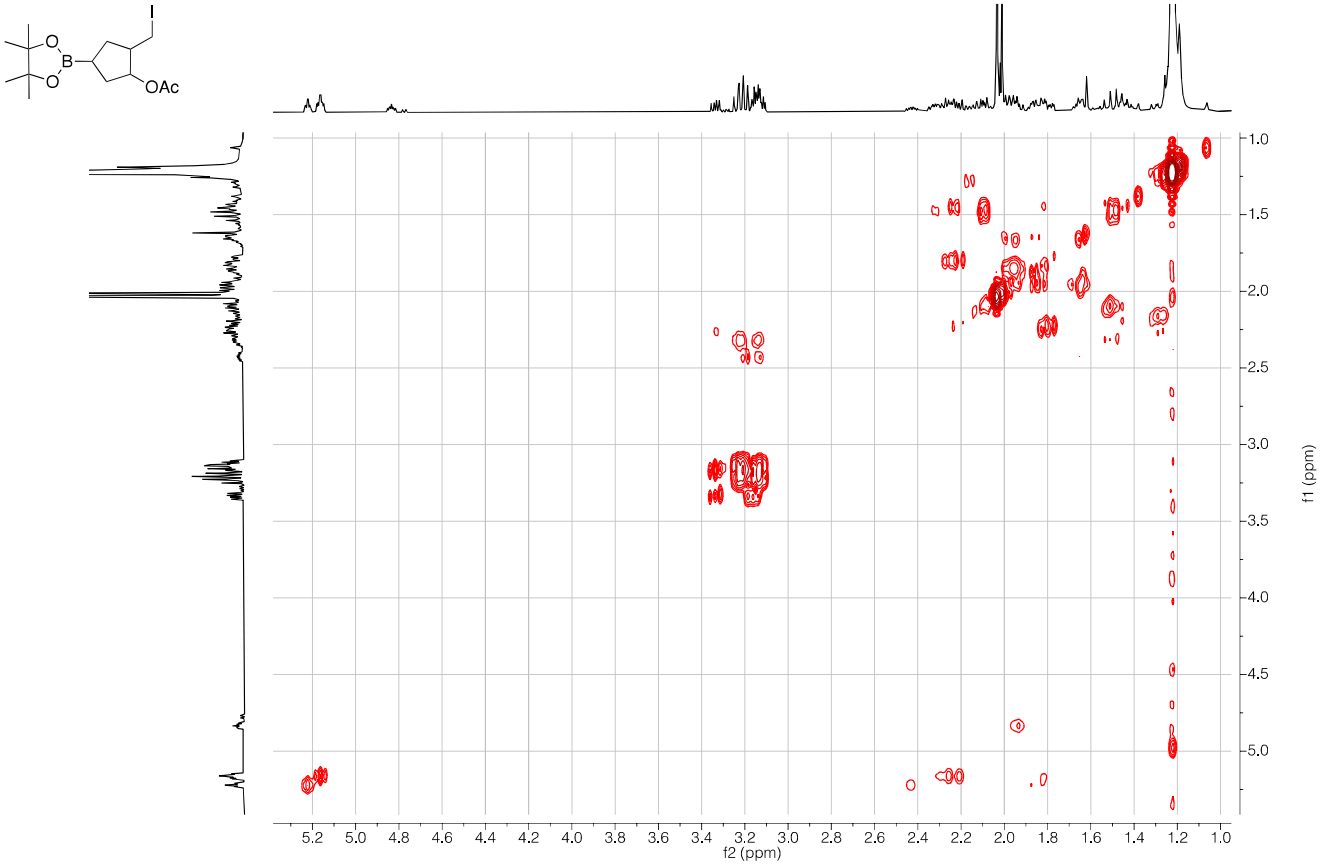
[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl] acetate

DEPT-135 NMR (101 MHz, $CDCl_3$)



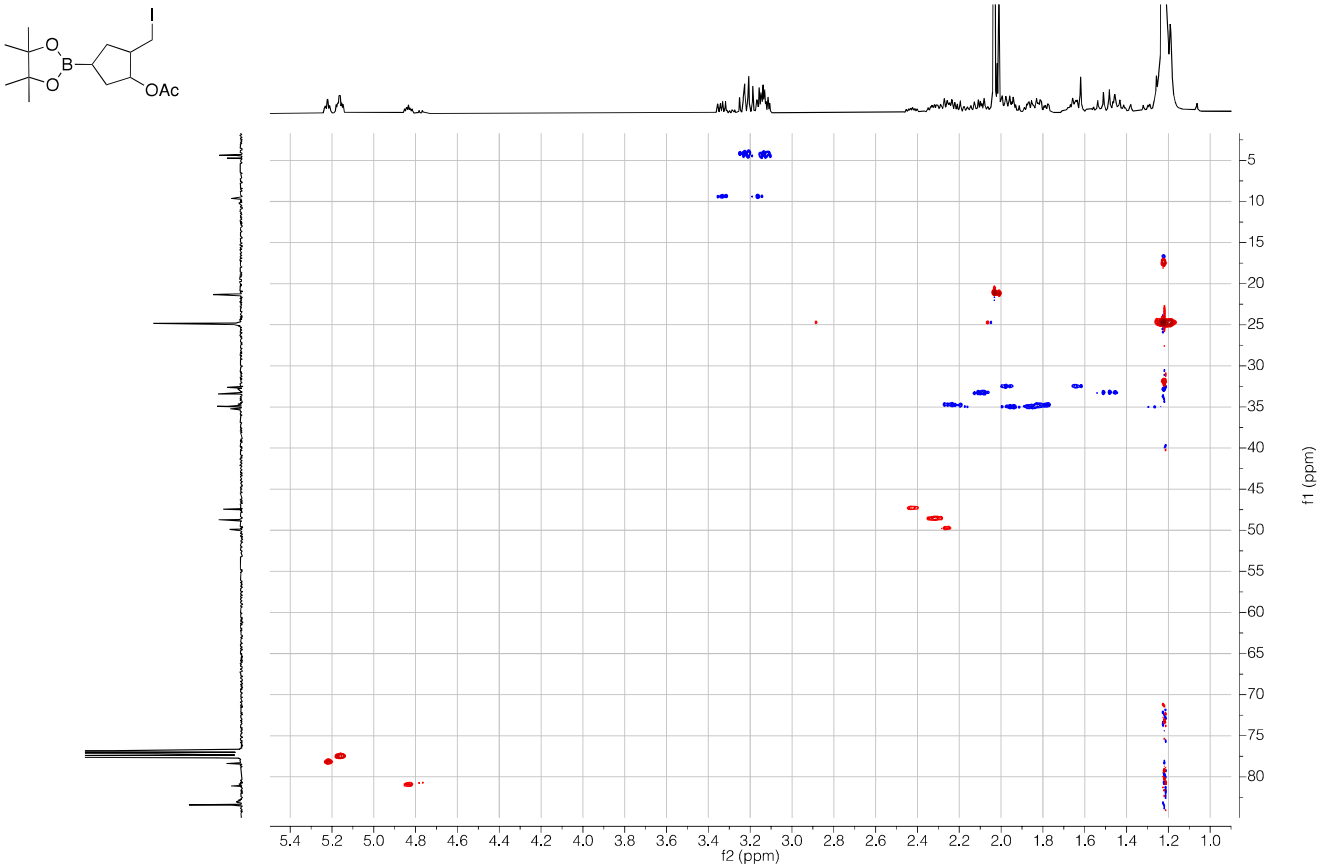
[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl] acetate

^{1}H, ^{1}H-COSY (400 MHz, $CDCl_3$)



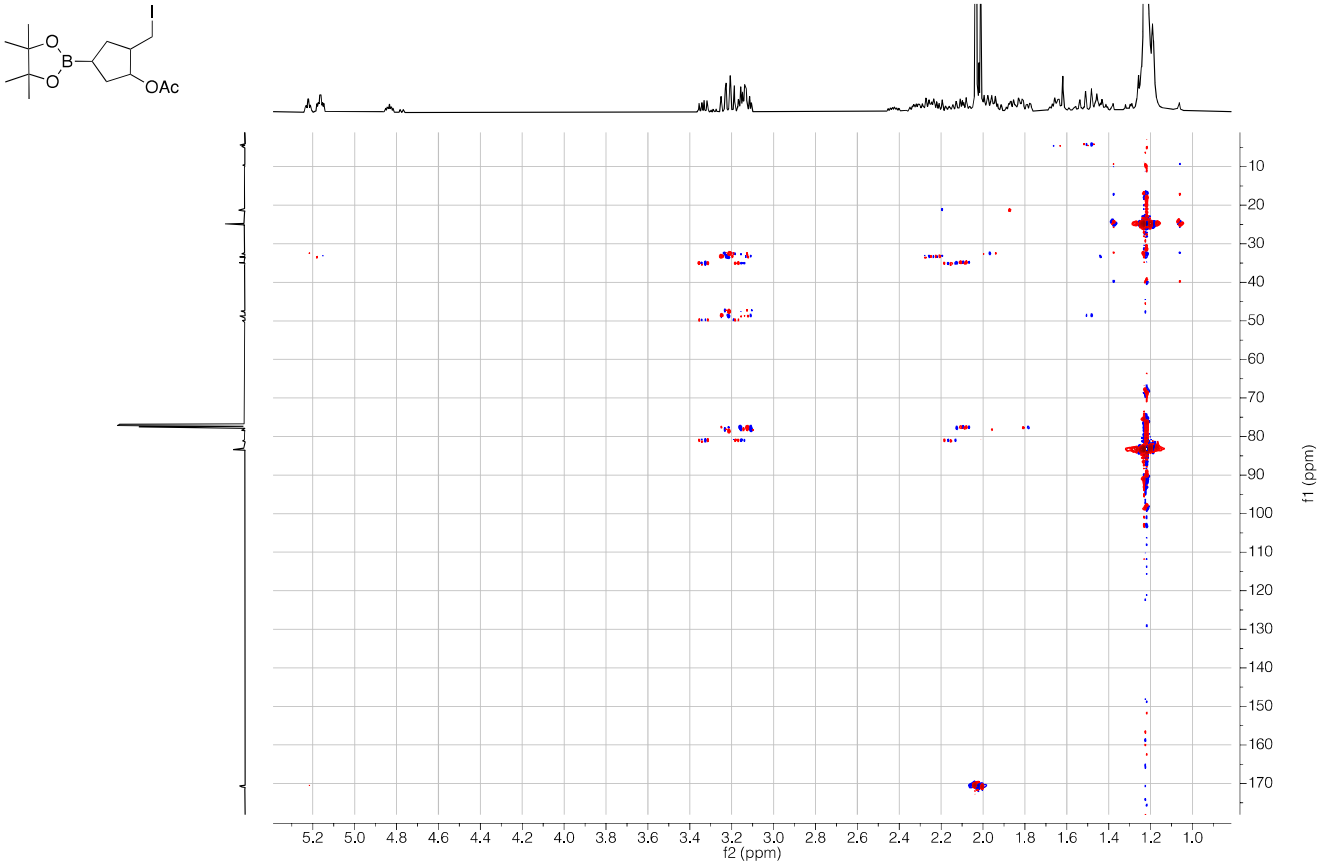
[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl] acetate

^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)



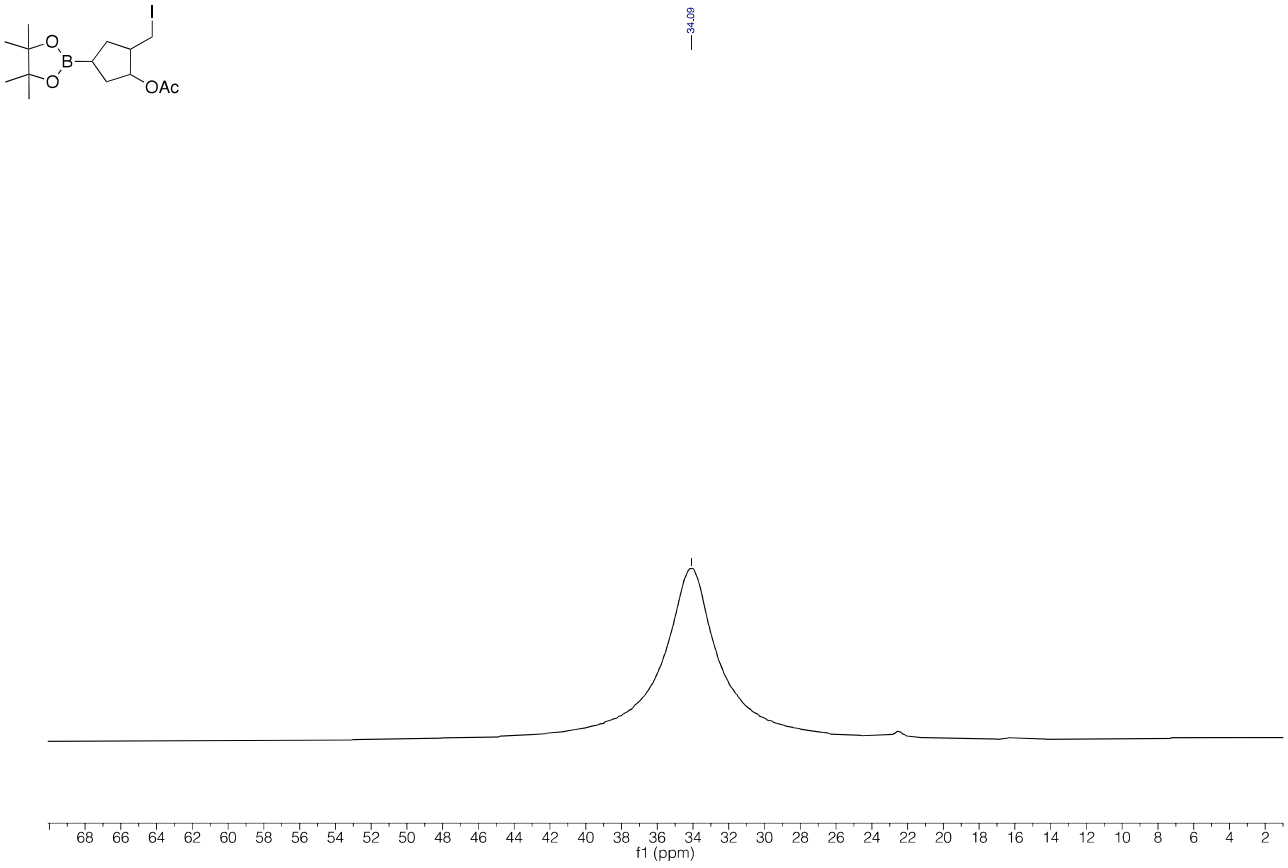
[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl] acetate

^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)

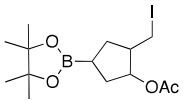


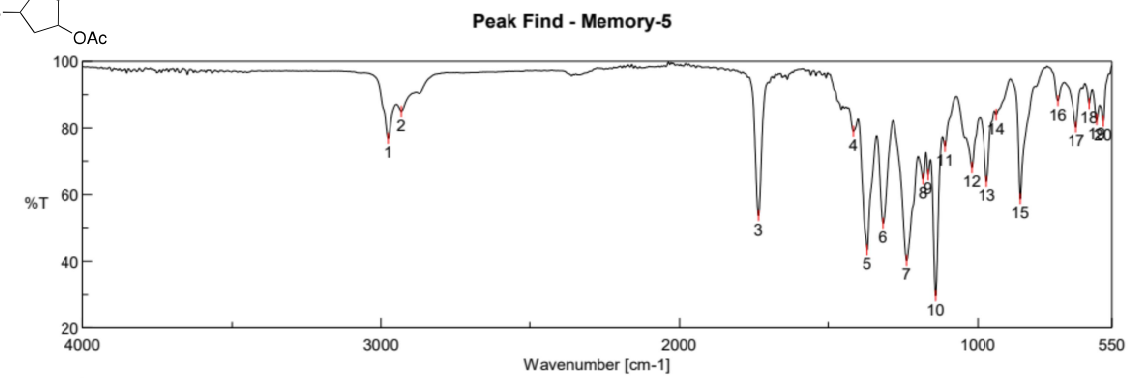
[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl] acetate

^{11}B-NMR (128 MHz, $CDCl_3$)



[2-(iodomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl] acetate FT-IR, ATR-diamond





[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.62	76.8199	2	2932.23	84.9023	3	1734.66	53.675
4	1416.46	78.9559	5	1371.14	43.3677	6	1316.18	51.3112
7	1237.11	40.1741	8	1182.15	64.705	9	1165.76	65.9397
10	1140.69	29.6474	11	1109.83	74.5131	12	1020.16	68.0764
13	970.019	63.9048	14	937.235	83.9381	15	857.204	58.6692
16	731.853	88.1541	17	670.142	80.2309	18	624.823	87.245
19	599.753	82.4953	20	578.54	81.987			