A Boron Alkylidene-Alkene Cycloaddition Reaction: Application to the Synthesis of Aphanamal

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A Boron Alkylidene-Alkene Cycloaddition Reaction: Application to the Synthesis of Aphanamal

A Thesis

By

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Abstract

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A Boron Alkylidene-Alkene Cycloaddition Reaction: Application to the Synthesis of Aphanamal

(Under the direction of James P. Morken)

Described herein is the exploration of a novel methodology whereby boronate-ester bearing cyclopentanes are produced by reaction between an unactivated olefin and what is described as a boron alkylidene. The mechanism is evaluated and concluded to proceed through a boracyclic intermediate that is achieved by a closed-shell, carbanion addition to the olefin. This mechanistic conclusion is arrived upon by considering two likely alternative routes (an open-shell, radical cyclization and a [2+2] concerted process) and providing evidence to refute them. A reaction scope is established as well as the utility of the methodology through the racemic synthesis of a natural sesquiterpene: aphanamal. Finally, the future of the reaction development will be considered by providing a single example of a 6-endo cyclization.

ACKNOWLEDGEMENTS

Above all, I would like to thank Jesus for the strength to persevere through adversity.

I would like to thank my research advisor, Professor James P. Morken for his unwavering support throughout my graduate study. I would additionally like to thank my thesis committee members, Professors Jeffery A. Byers and Shih-Yuan Liu for reading and critiquing this work. Thanks to Xun Liu for her help in my research and thesis, especially in the form of profound scientific discourse; my apologies for continuously bouncing half-baked theories off you. Thanks to Dr. Jason Shields for his wealth of knowledge in the chemical literature and for being a great role model. Thanks to Maximilian Palkowitz for being a continuous reminder of the joy of scientific exploration. Of course, my family deserves special mention for providing the opportunity and encouragement to accomplish my goals.

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List of Abbreviations

Å: angstrom

$AlMe_3$: trimethylaluminum

Ar: aryl

aq: aqueous

Bn: benzyl

BnBr: benzyl bromide

CAM: ceric ammonium nitrate

CCl_4: carbon tetrachloride

$(COCl)_2$: oxalyl chloride

COSY: correlation spectroscopy

Cy: cyclohexyl

DART: direct analysis in real time

DCM: dichloromethane

DFT: density functional theory

DMAP: 4-dimethylaminopyridine

DMF: dimethylformamide

DMP: Dess-Martin periodinane

DMSO: dimethyl sulfoxide

dr: diastereomeric ratio

ee: enantiomeric excess

er: enantiomeric ratio

ESI: electrospray ionization

$EtCO_2H$: propionic acid

Et_2O: diethyl ether

EtOAc: ethyl acetate

$(EtO)_3CMe$: trimethyl orthoacetate

h: hour(s)

HCl: hydrogen chloride

HGII: Hoveyda-Grubbs catalyst™ 2nd generation

H_2O_2: hydrogen peroxide

HPLC: high performance liquid chromatography

HRMS: high resolution mass spectrometry

I_2: iodine

IPr: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene

$KMnO_4$: potassium permanganate

KO*t*Bu: potassium *tert*-butoxide

LAH: lithium aluminum hydride

LTMP: lithium 2,2,6,6-tetramethylpiperidide

M: molar or metal

mCPBA: *meta*-chloroperoxybenzoic acid

MeI: methyl iodide

MeOH: methanol

min: minute(s)

MO: molecular orbital

$NaBH_4$: sodium borohydride

NaOMe: sodium methoxide

NaO*t*Bu: sodium *tert*-butoxide

NBS: *N*-bromosuccinimide

*n*BuLi: *n*-butyllithium

NCS: *N*-chlorosuccinimide

NEt_3: trimethylamine

NMP: *N*-methyl-2-pyrrolidone

NOESY: nuclear overhauser effect spectroscopy

Nu: nucleophile

OTf: trifluoromethanesulfonate

Ph: phenyl

PhMe: toluene

pin: pinacol

PMA: phosphomolybdic acid

PMHS: polymethylhydrosiloxane

PPh_3: triphenylphosphine

*p*TsOH: *para*-toluenesulfonic acid

rt: room temperature

SeO_2: Selenium dioxide

SFC: supercritical fluid chromatography

SiO_2: silica gel

TBAF: tetrabutylammonium fluoride

TBAI: tetrabutylammonium iodide

TBDPS: *tert*-butyldiphenylsilyl

TBME: *tert*-butyl methyl ether

TBS: *tert*-butyldimethylsilyl

*t*BuLi: *tert*-butyllithium

TEMPO: 2,2,6,6-Tetramethyl-1-piperidi-nyloxy

THF: tetrahydrofuran

TMANO: trimethylamine *N*-oxide

TMSCl: trimethylsilyl chloride

TS: transition state

TsCl: 4-toluenesulfonyl chloride

I. Introduction and Background

The discovery and expansion of a boron-alkylidene/alkene 2+2 is described in detail herein; a unique reaction whereby a nucleophilic boron-alkylidene reacts intramolecularly, in a net 2+2 fashion with an unactivated alkene to furnish a boracyclobutane. The resultant boracyclobutane has the capacity to react productively with a number of electrophiles to result in a highly functionalized cyclopentane (Figure 1).

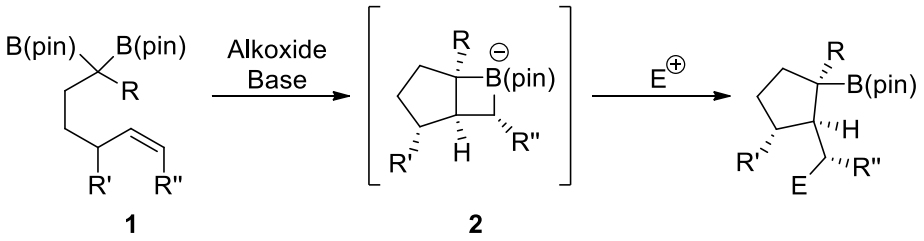

Figure 1 - A general depiction of the title reaction - A deborylative cyclization

In the text that follows, the intermediacy of a boracyclobutane will be supported and the utility of the final products will be validated. Moreover, a substantial amount of effort will be focused on arriving at a mechanistic conclusion for how the starting compound **1** arrives at intermediate **2**.

A. Background

Geminal bis(boronates), correctly identified in 1960 by H. C. Brown and G. Zweifel, have recently garnered renewed interest as practical synthetic intermediates.[1,2,3,4] Recently disclosed by our

1. Brown, H. C.; Zweifel, G., Hydroboration. XI. The Hydroboration of Acetylenes—A Convenient Conversion of Internal Acetylenes into cis-Olefins and of Terminal Acetylenes into Aldehydes. *J. Am. Chem. Soc.* **1961,** *83* (18), 3834-3840.
2. Coombs, J. R.; Zhang, L.; Morken, J. P., Synthesis of Vinyl Boronates from Aldehydes by a Practical Boron–Wittig Reaction. *Org. Lett.* **2015,** *17* (7), 1708-1711.
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4. Sun, C.; Potter, B.; Morken, J. P., A Catalytic Enantiotopic-Group-Selective Suzuki Reaction for the Construction of Chiral Organoboronates. *J. Am. Chem. Soc.* **2014,** *136* (18), 6534-6537.

group is the deborylation of geminal bis(boronates) to generate boron-alkylidenes, which could subsequently be trapped by alkyl halides (Figure 2).[5]

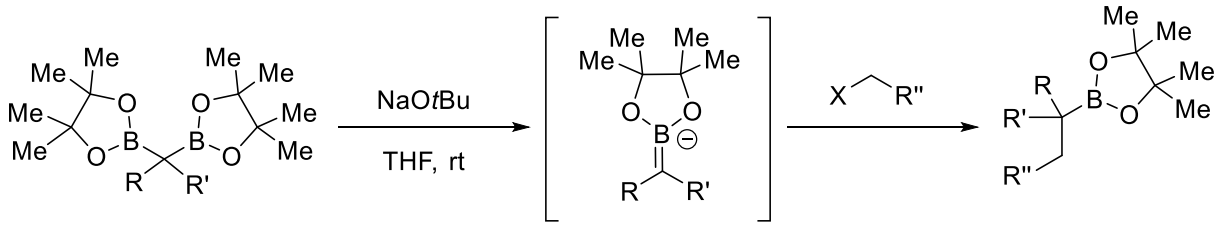


Figure 2 - Previous reported deborylative alkylation

Presented in this communication was strong support for the intermediacy of a boron-alkylidene, which had been speculated upon in prior works. H. C. Brown and G. Zweifel had suggested that geminal bis(*boranes*) were extremely susceptible to hydrolytic cleavage under alkaline conditions to generate a stabilized anion (Figure 3).[1] In their work, Brown and Zweifel also provided evidence that the analogous, less Lewis-acidic geminal bis(*boronates*) had an increased hydrolytic stability.

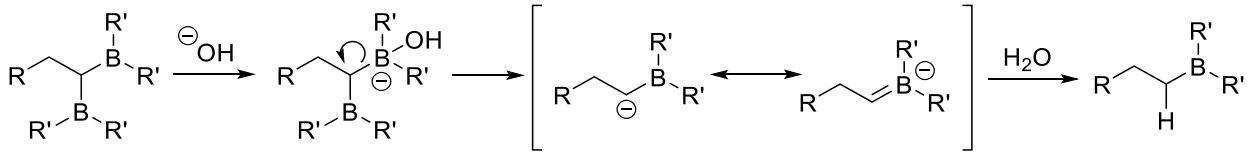


Figure 3 - Brown and Zweifel's proposed deborylation pathway

In a separate publication, G. Zweifel suggested a similar intermediate was obtainable by subjecting geminal bis(boranes) to organolithium bases. In this work, it was suggested that the addition of a second equivalent of base prevented the reverse reaction by coordinating to the fragmented, lewis-acidic borane (Figure 4).[6]

5. Hong, K.; Liu, X.; Morken, J. P., Simple Access to Elusive α-Boryl Carbanions and Their Alkylation: An Umpolung Construction for Organic Synthesis. *J. Am. Chem. Soc.* **2014,** *136* (30), 10581-10584.
1. Brown, H. C.; Zweifel, G., Hydroboration. XI. The Hydroboration of Acetylenes—A Convenient Conversion of Internal Acetylenes into cis-Olefins and of Terminal Acetylenes into Aldehydes. *J. Am. Chem. Soc.* **1961,** *83* (18), 3834-3840.
6. Zweifel, G.; Fisher, R. P.; Horng, A., A Convenient Procedure for the Synthesis of Secondary Alcohols From 1-Alkynes via the Alkylation of Boron-Stabilized Carbanions. *Synthesis* **1973,** *1973* (01), 37-38.

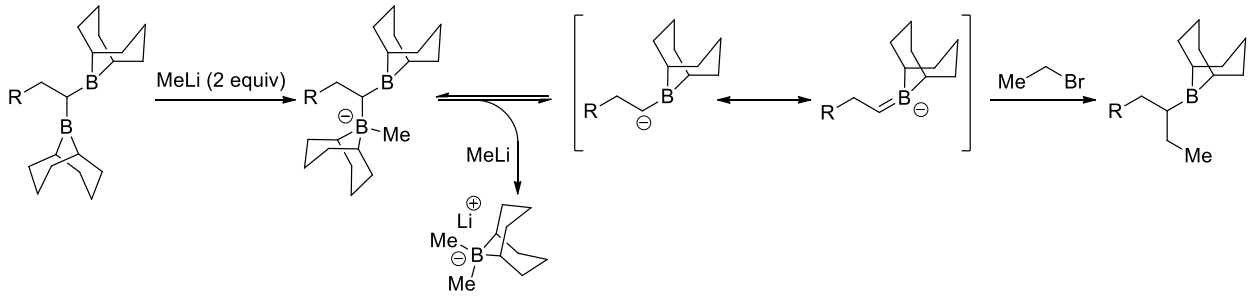


Figure 4 - Zweifel's deborylative alkylation; note the use of 2 equivalents of base to prevent the recapture of the departing borane

G. Zweifel and H. C. Brown's original proposition of a boron-alkylidene intermediate was later validated by other groups. The existence of a boron-alkylidene was substantiated by our group with two experiments. First, a ^{13}C enriched geminal bis(boronate) was prepared and its alkoxide-induced deborylation was monitored by ^{13}C NMR spectroscopy. The deborylated species was assigned to a broad singlet with a chemical shift of 49.1 ppm (Figure 5). The downfield chemical-shift of this species implies the structure has alkylidene character.[7,8,9]

7. Fox, T.; Hausmann, H.; Günther, H., NMR spectroscopy of organolithium compounds. XXVI—The aggregation behaviour of methyllithium in the presence of LiBr and LiI in diethyl ether and tetrahydrofuran. *Magn. Reson. Chem.* **2004,** *42* (9), 788-794.
8. O'Brien, D. H.; Hart, A. J.; Russell, C. R., Carbon-13 magnetic resonance of allyl, pentadienyl, and arylmethyl carbanions. Empirical calculation of .pi.-electron densities. *J. Am. Chem. Soc.* **1975,** *97* (15), 4410-4412.
9. Oakes, F. T.; Yang, F. A.; Sebastian, J. F., Allylic vs. vinylic deprotonation reactions of cyclic vinyl ethers. 7-Lithio-2,3,4,5-tetrahydrooxepin: synthesis and carbon-13 NMR spectrum. *J. Org. Chem.* **1982,** *47* (16), 3094-3097.

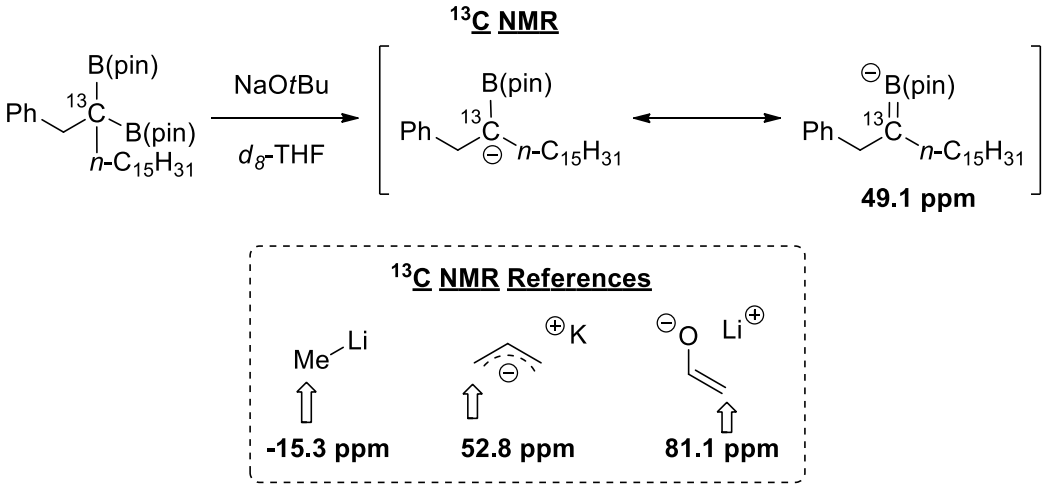


Figure 5 - ^{13}C NMR analysis of deborylative alkylation intermediates. Inset is ^{13}C NMR references depicting the general trend of more π-character, further downfield

Secondly, an enantioenriched, ^{10}B-labeled substrate was prepared and subjected to the deborylative-alkylation conditions. The enantiomeric products were then separated on chiral-phase SFC and analyzed by mass spectrometry. The results of this experiment show a statistical distribution of ^{10}B-labeled compound for each enantiomer of product, implying a stereo-randomizing step is involved in the mechanism (Figure 6). Had the process been stereospecific, the ^{10}B-labeling would have only been present in one product isomer, and the mass distribution for both isomers would have been closer to a singular value.

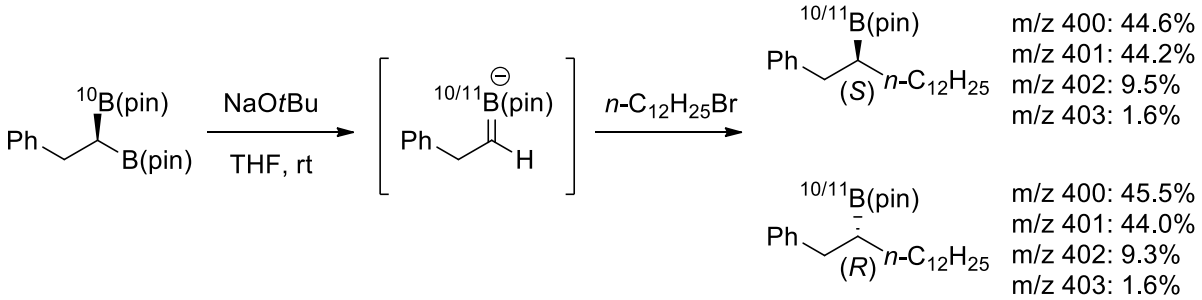


Figure 6 - Mass spectrometric evaluation of deborylative alkylation reaction products after separation of enantiomers: stereo-randomization observed

Though this stereo-randomization could be explained by direct pyramidal inversion of the carbanion, it is most readily explained by the formation of the boron-alkylidene.[10] Additionally, Boron-Carbon double bonds have been observed in the solid state via X-ray crystallography (Figure 7).[11]

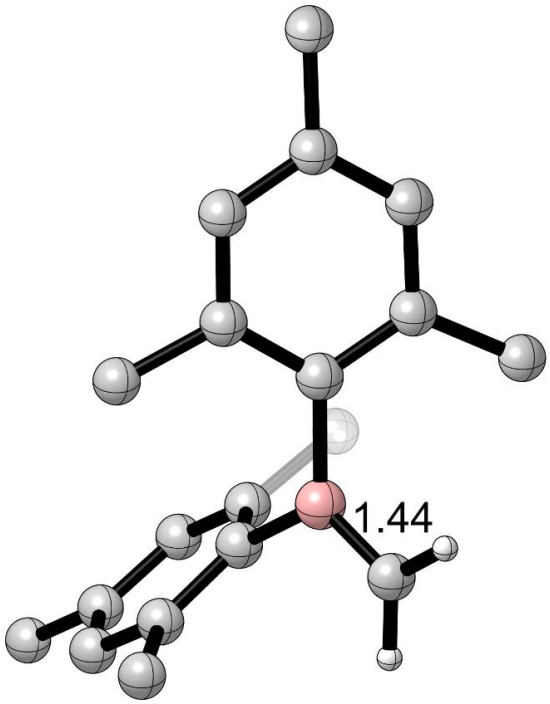


Figure 7 - Crystal structure of a boron-alkylidene with the B-C double-bond distance labeled in Å (hydrogen atoms calculated)

B. Discovery

In the presence of metal alkoxides, geminal bis(boronates) are known to generate carbon-centered, α-borylanions. Based on previously reported ^{13}C NMR analysis of these deborylated complexes, it was determined that their structure is more accurately described by that of an anionic, boron-alkylidene, and hence forth will be referred to as such (Figure 2).[5]

10. Rauk, A.; Allen, L. C.; Mislow, K., Pyramidal Inversion. *Angew. Chem. Int. Ed.* **1970,** *9* (6), 400-414.
11. Olmstead, M. M.; Power, P. P.; Weese, K. J.; Doedens, R. J., Isolation and x-ray crystal structure of the boron methylidenide ion [Mes2BCH2]- (Mes = 2,4,6-Me3C6H2): a boron-carbon double bonded alkene analog. *J. Am. Chem. Soc.* **1987,** *109* (8), 2541-2542.
5. Hong, K.; Liu, X.; Morken, J. P., Simple Access to Elusive α-Boryl Carbanions and Their Alkylation: An Umpolung Construction for Organic Synthesis. *J. Am. Chem. Soc.* **2014,** *136* (30), 10581-10584.

In the course of investigating the mechanism of this reaction, coined deborylative-alkylation, it was discovered that if R=pent-4-enyl, a substrate shown to be competent in the reaction, an alternate reactivity path was followed if the electrophile were initially omitted (Figure 8).

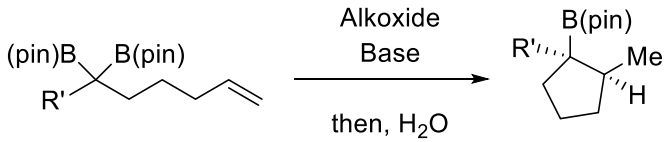


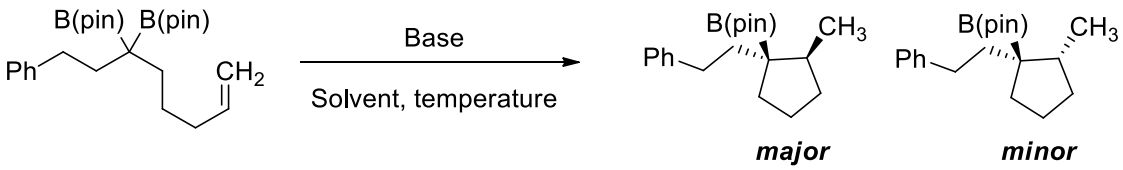
Figure 8 – Serendipitous discovery of deborylative cyclization; omitted electrophile in deborylative alkylation

Discovery of this novel reactivity prompted us to undertake a full practical development and mechanistic investigation of this "deborylative cyclization". This reactivity mode was considered to be unique in nature and appealed to our interest in the reactivity of bis(boronic) esters. We anticipated that these boronic ester-containing cyclopentanes would be powerful synthons in the context of natural product synthesis, and we sought to give credence to this concept.

II. Development of a Boron-Alkylidene/Alkene 2+2 Cycloaddition Reaction

A. Optimization

The discovery that the boron-alkylidenes react intramolecularly with tethered olefins led to the exploration of this reaction pathway as a novel methodology. The reaction is found to be optimal with potassium *tert*-butoxide as the metal oxide and competent in both toluene and THF as solvents. THF is selected as the reaction solvent due to higher observed diastereoselectivites and comparable yields to toluene (Figure 9).



entry	base	solvent	yield (%)	dr
1	NaO*t*Bu	THF	12	13:1
2	NaO*t*Bu	toluene	<5	N/A
3	KOMe	toluene	<5	N/A
4	KO*t*Bu	DCE	<5	N/A
5	KO*t*Bu	hexanes	39	2.2:1
6	KO*t*Bu	THF	51	5:1[b]
7	KO*t*Bu	THF	52	4:1
8	KO*t*Bu	toluene	52	2:1[b]
9	KO*t*Bu	toluene	61	1.2:1

Figure 9 - Deborylative cyclization optimization results. [a] Reaction conditions: 1,1-diboronate ester (0.10 mmol, 0.2 M), and base (0.20 mmol) at rt. Yield refers to the isolated yield of purified material. [b] Reaction conducted at 50 °C

B. Substrate Exploration

With the optimum conditions established, attention was turned to identifying competent reaction substrates. The scope of the reaction is shown in Figure 10.

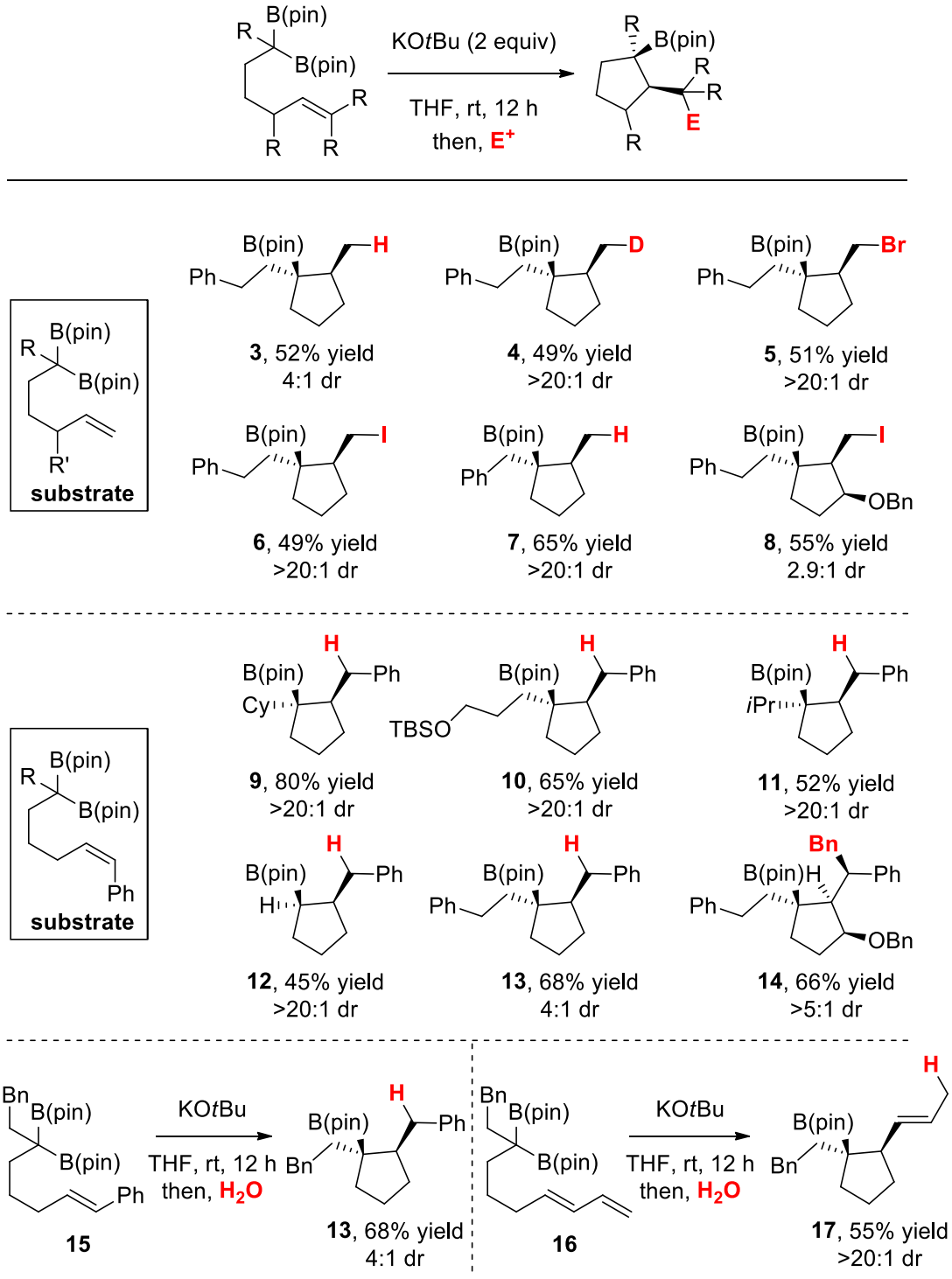


Figure 10 - Substrate scope of deborylative cyclization

Early in the course of exploring the substrate compatibility of the reaction, it was observed that olefin substitution is largely untolerated. Of the tested substrates, only π-conjugating olefin-

substituents afforded the desired reactivity. Specifically, phenyl (**9-15**) and vinyl (**16**) olefin-substituents were tolerated while alkyl, such as methyl, were not. This observation perhaps provides some insight into the reaction mechanism. During the reaction studies, it was also discovered that a range of electrophiles could be incorporated into the product with high fidelity if anhydrous conditions were maintained. As illustrated in Figure 10, deuterium could be installed if the reaction was quenched with D_2O (**4**). Similarly, bromine or iodine could be incorporated if the reaction were quenched with *N*-bromosuccinimide (**5**) or molecular iodine (**6** & **8**), respectively. Notably, an enhanced diastereoselectivity is observed for products **4-6** when compared to the protonated analogue **3** (>20:1 dr vs. 4:1 dr). This upgraded diastereomeric ratio is attributed to protonation of the minor, *trans*- diastereomer prior to the addition of an electrophile. This selective protonolysis of the minor isomer, in effect, siphons off the minor diastereomer, while the major persists until the electrophile is introduced into the mixture. Below, calculations are provided that support the notion of a higher-reactivity, *trans*- diastereomer. The source of the proton has yet to be determined; the use of d_8-THF and d_9-KO*t*Bu did not result in deuterated products. Substrates bearing allylic substituents were also discovered to be tolerated, and even induced stereocontrol (**8**). Substitution about the bis(boronate)-carbon was found to be largely tolerated, and some examples include cyclohexyl (**9**), isopropyl (**11**), and even no substituent (**12**).

C. Mechanistic Investigation

i) Boracyclobutane Intermediate and Background

With a useful substrate scope established, a working understanding of the mechanism at play was then sought. Spectroscopic investigations were among the first mechanistic experiments for the boron-alkylidene/alkene [2+2] cycloaddition reaction. Two ^{13}C-enriched substrates were prepared then subjected to the reaction conditions while monitoring via ^{13}C NMR (Figure 11).

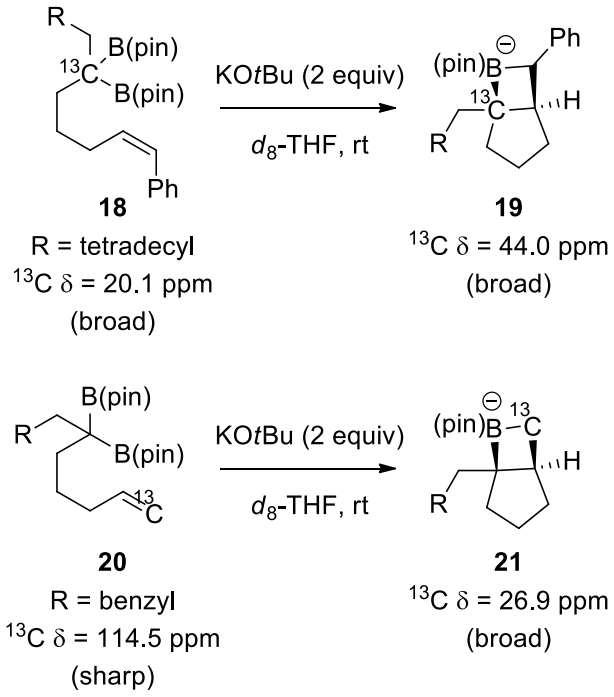


Figure 11 - ^{13}C NMR analysis of deborylative cyclization intermediates and proposed structure

The compound having its boron-pendent carbon labeled (**18**) was found to have a significant downfield shift when exposed to the reaction conditions. A broad singlet (broad due to the boron quadrupole) at 20.1 ppm in the starting material is replaced by a broad signal at 44.0 ppm. The signal at 44.0 ppm is assigned to the boracyclobutane containing structure shown above (**19**). To confirm the assignment of the boracyclobutane as an intermediate structure, an olefin-labeled compound (**20**) was exposed to the reaction conditions under spectroscopic scrutinization. This time, a sharp signal at 114.5 ppm in the starting material is replaced by a broad signal at 26.9 ppm. A broad signal strongly supports a boracyclobutane intermediate as it is hard to conceive an alternative intermediate where the labeled carbon atom is bonded to the quadrupolar boron atom. In both cases, the signal assigned to the intermediate boracyclobutane disappears upon addition of water to the mixture.

Regarding the reaction mechanism, perhaps a reasonable assumption would be a single electron pathway since radical, 5-exo cyclizations are plentiful in the literature; whereas, concerted 2+2

reactions and anion-additions to unactivated olefins are exceedingly rare.[12] According to Woodward and Hoffmann, concerted 2+2 reactions are disfavored due to HOMO/LUMO orbital-symmetry mismatch between the two reacting species (Figure 12).[13]

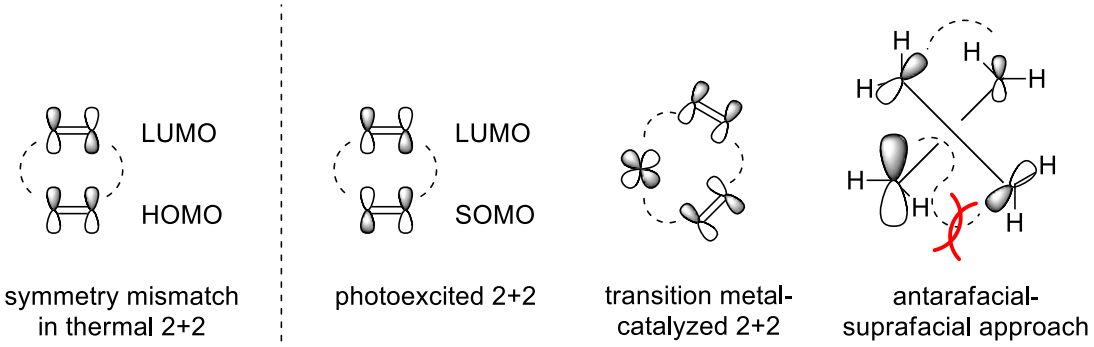


Figure 12 - Left: intrinsic obstacle of concerted 2+2 cyclization. Right: 3 possible pathways of concerted 2+2 reaction

This symmetry mismatch, however, does not "forbid" the 2+2 cycloaddition from occurring. It is still possible that the two can react via one of the following ways: 1) photoexcitation of one of the species whereby the resulting singly occupied orbital (SOMO) symmetry now matches the LUMO 2) transition metal-catalyzed 2+2 or 3) antarafacial-suprafacial orbital alignment.[14,15,16] Early in the study of the reaction, the process was shown to perform comparably with or without the exclusion of light – leading to the conclusion that photoexcitation was not necessary. In order to address the possibility of a transition metal-catalyzed pathway, trace-metal impurities were considered.[17] The KO*t*Bu was sourced from several vendors of varying quality (eg. sublimed grade)

12. Julia, M., Free-radical cyclizations. *Acc. Chem. Res.* **1971,** *4* (11), 386-392.
13. Hoffmann, R.; Woodward, R. B., Conservation of orbital symmetry. *Acc. Chem. Res.* **1968,** *1* (1), 17-22.
14. Hoffmann, N., Photochemical Reactions as Key Steps in Organic Synthesis. *Chem. Rev.* **2008,** *108* (3), 1052-1103.
15. Schmidt, V. A.; Hoyt, J. M.; Margulieux, G. W.; Chirik, P. J., Cobalt-Catalyzed [2π + 2π] Cycloadditions of Alkenes: Scope, Mechanism, and Elucidation of Electronic Structure of Catalytic Intermediates. *J. Am. Chem. Soc.* **2015,** *137* (24), 7903-7914.
16. Alcaide, B.; Almendros, P.; Aragoncillo, C., Exploiting [2+2] cycloaddition chemistry: achievements with allenes. *Chemical Society Reviews* **2010,** *39* (2), 783-816.
17. Takai, K.; Tagashira, M.; Kuroda, T.; Oshima, K.; Utimoto, K.; Nozaki, H., Reactions of alkenylchromium reagents prepared from alkenyl trifluoromethanesulfonates (triflates) with chromium(II) chloride under nickel catalysis. *J. Am. Chem. Soc.* **1986,** *108* (19), 6048-6050.

and found to have no effect on the reaction outcome. Antarafacial-suprafacial reactivity is possible even though the steric clash between the two reacting species makes this unlikely; it still is an avenue that need be explored.

Although rare addition of carbon nucleophiles to unactivated olefins have been presented in the literature. Bailey et al. demonstrated that carbo-lithium species can intramolecularly add to olefins (Figure 13).[18]

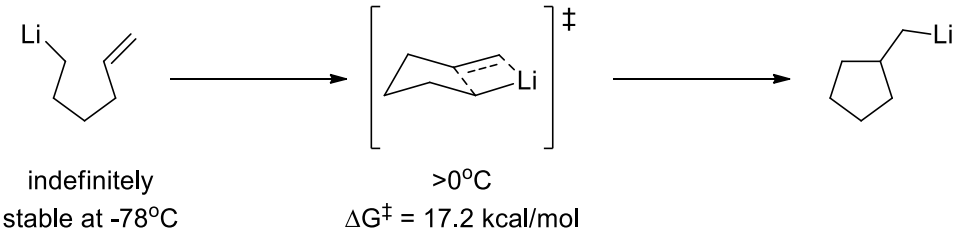


Figure 13 - Bailey's carbo-lithiation of unactivated olefins (activation energy based on ab initio MO calculations, 3-21G basis set)

In their report, Bailey et al. rule out the intermediacy of a carboradical by demonstrating spectroscopically that 5-hexenyllithium is produced in near-quantitative yield via low-temperature, lithium-iodide exchange. 5-hexeneyllithium is then indefinitely stable until warmed above 0°C, whereupon it isomerizes to (cyclopentylmethyl)lithium. The authors also perform ab initio molecular orbital calculations of the anionic cyclization, at the 3-21G level, which suggest a reasonable energy barrier of 17.2 kcal/mol.[19]

Other examples of carbo-alkali metallation of unactivated alkenes have been reported as early as 1956: Magnus and Levine demonstrated that carbanions derived from various nitriles treated with

18. Bailey, W. F.; Gavaskar, K. V., Anionic cyclization of olefinic alkyllithiums: ring closure of terminally substituted 5-hexenyllithiums. *Tetrahedron* **1994,** *50* (20), 5957-5970.
19. Bailey, W. F.; Khanolkar, A. D.; Gavaskar, K.; Ovaska, T. V.; Rossi, K.; Thiel, Y.; Wiberg, K. B., Stereoselectivity of cyclization of substituted 5-hexen-1-yllithiums: regiospecific and highly stereoselective insertion of an unactivated alkene into a carbon-lithium bond. *J. Am. Chem. Soc.* **1991,** *113* (15), 5720-5727.

sodium metal could add to 2- and 4-vinylpyridines.[20] Following this seminal work, other bases have been shown to react comparably (Figure 14).[21]

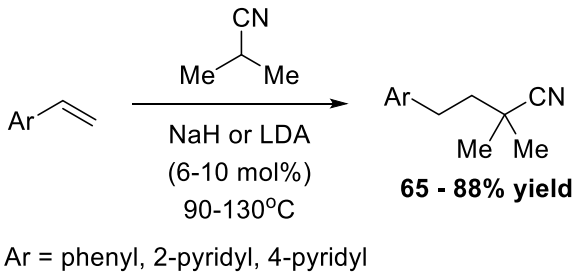


Figure 14 – Example of carbanion addition to an unactivated olefin

Additional examples include the KO*t*Bu promoted addition of DMSO to styrenes resulting in a sulfoxide which could then be pyrolyzed to the homologue of the starting olefin (Figure 15)[22] and Knochel's KO*t*Bu catalyzed addition of carbonyl derivatives to styrenes (Figure 16).[23]

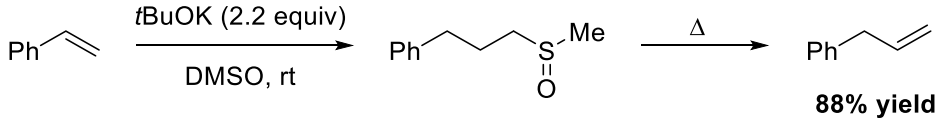


Figure 15 - Example of a stabilized carbanion addition to an unactivated olefin

20. Magnus, G.; Levine, R., The Pyridylethylation of Active Hydrogen Compounds. V. The Reaction of Ammonia, Certain Amines, Amides and Nitriles with 2- and 4-Vinylpyridine and 2-Methyl-5-vinylpyridine1. *J. Am. Chem. Soc.* **1956,** *78* (16), 4127-4130.
21. Narula, A. P. S., The Search for New Fragrance Ingredients for Functional Perfumery. *Chem. Biodiversity* **2004,** *1* (12), 1992-2000.
22. Walling, C.; Bollyky, L., The Addition of Dimethyl Sulfoxide Anion to Olefins and the Pyrolysis of Sulfoxides1. *J. Org. Chem.* **1964,** *29* (9), 2699-2701.
23. Rodriguez, A. L.; Bunlaksananusorn, T.; Knochel, P., Potassium tert-Butoxide Catalyzed Addition of Carbonyl Derivatives to Styrenes. *Org. Lett.* **2000,** *2* (21), 3285-3287.

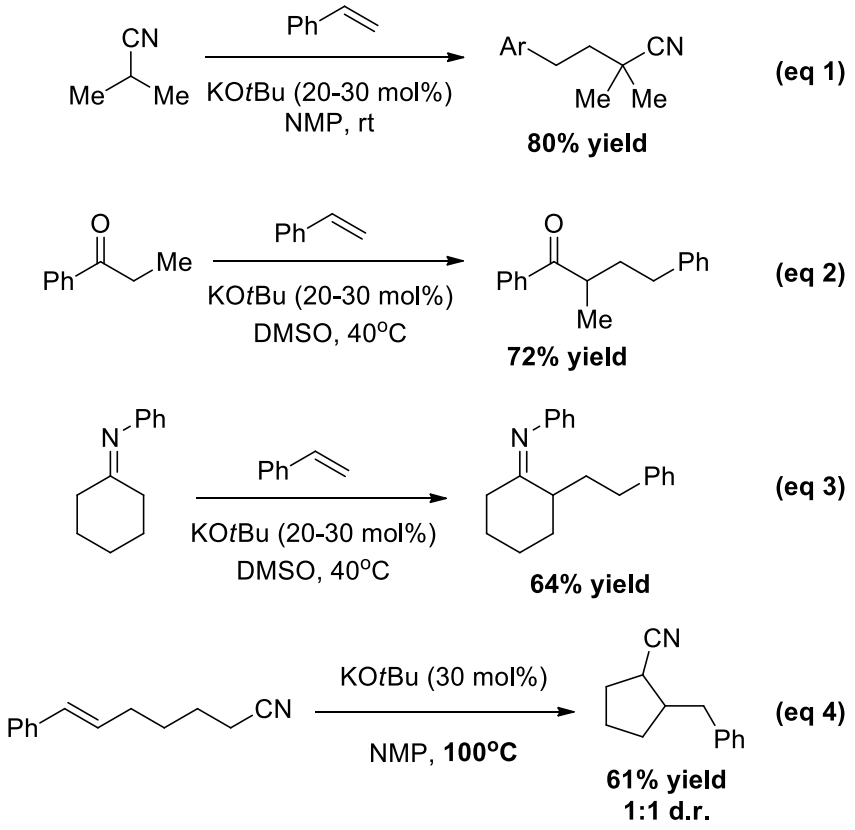


Figure 16 - Knochel's alkoxide-catalyzed addition of stabilized carbanion additions to unactivated olefins

Notably, in the former report, the reaction fails with simple aliphatic olefins. In the report by Knochel et al., potassium salts of nitriles, ketones and imines (eqs 1-3) were shown to all be competent reaction partners with styrenes. Interestingly, the authors demonstrate that 2-substituted olefins react much more sluggishly (eq 4), supporting the proposed, anionic pathway. These listed examples also bear the similarity with the title reaction of being mesomerically stabilized anions. Though stabilized alkali-carbanion additions to alkenes are rare, this pathway need be explored as well.

With strong spectroscopic evidence for two intermediate structures in the reaction pathway (the boron-alkylidene and the boracyclobutane), three separate mechanistic possibilities are devised (Figure 17). All three mechanistic possibilities (an anionic pathway, a radical pathway, and a concerted pathway) share common intermediates supported by spectroscopic evidence. In order to

establish mechanistic understanding of the reaction, experimentation was conceived and carried out, described below.

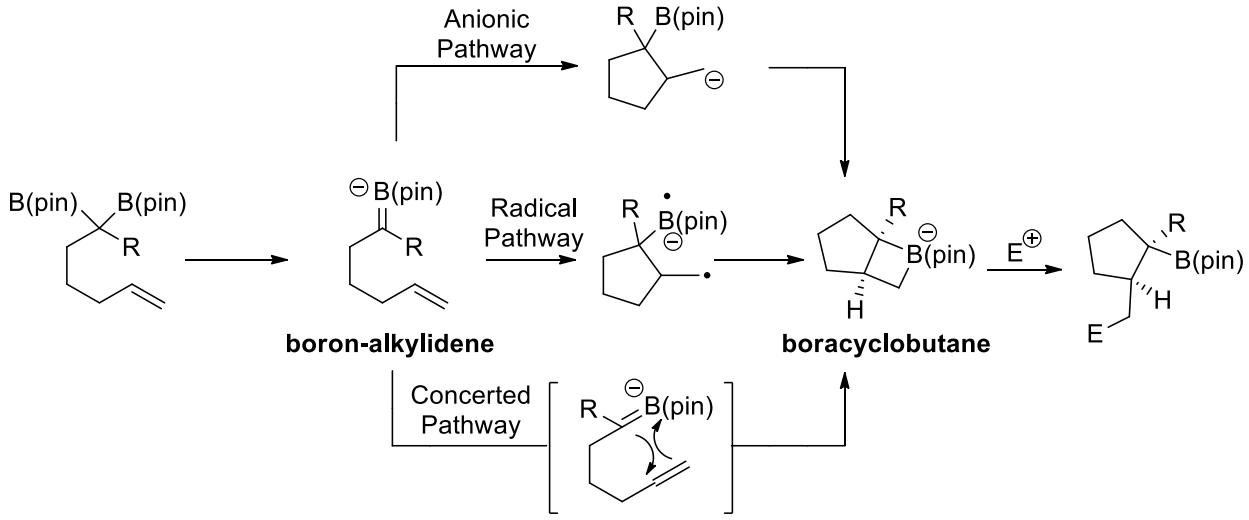


Figure 17 - Proposed, possible mechanisms of deborylative cyclization; all include 2 common intermediates

ii) Empirical Observations Addressing the Concerted [2+2] Cycloaddition

Experimentation to examine the concerted mechanistic possibility was planned. If two substrates were constructed that varied only about the geometry of the olefin, these two compounds could be treated with the reaction conditions and trapped with the same electrophile and the outcome evaluated. A concerted mechanism would presumably result in epimeric products for the two isomeric substrates.

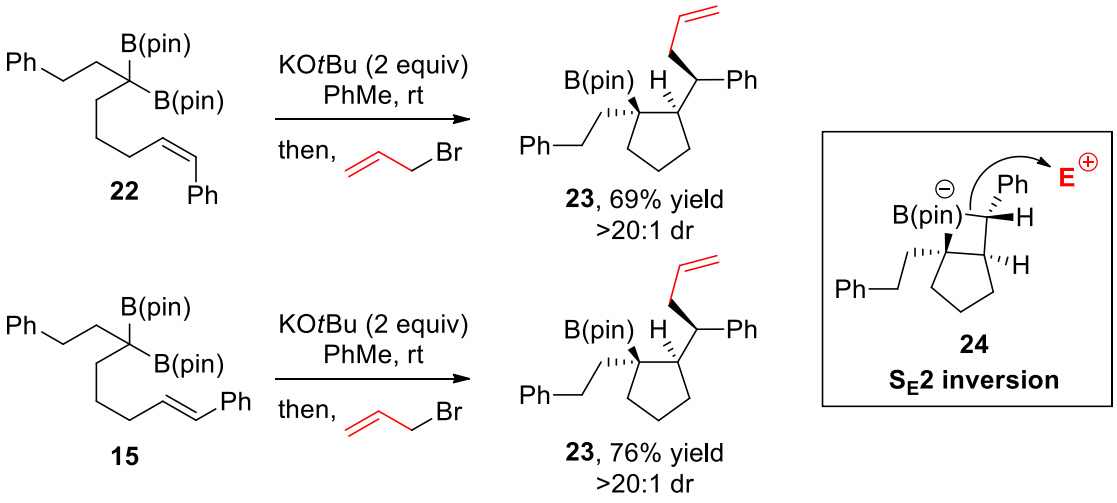


Figure 18 - Mechanistic experiment showing convergent nature of reaction. Inset is a depiction of typical S_E2 reactivity of quaternary boronates, providing insight into the configuration of the intermediate

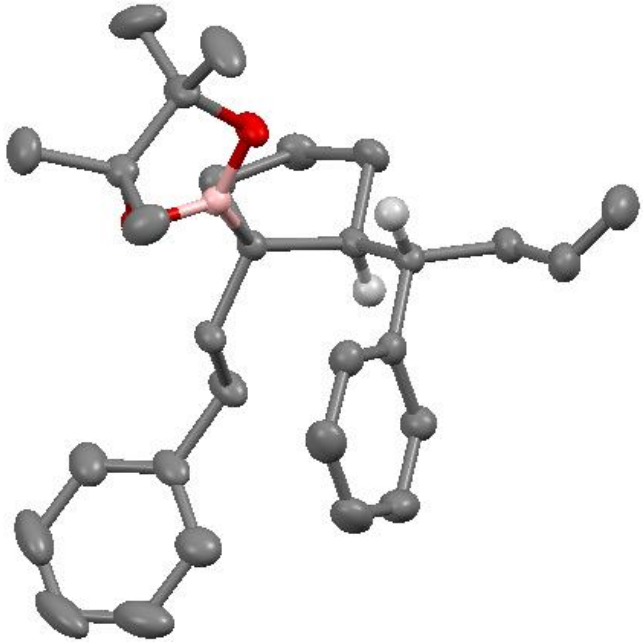


Figure 19 - Crystal structure of reaction product from Figure 18

The aforementioned substrates (**22** & **15**, Figure 18) are prepared and subjected to the reaction conditions whereby the reaction outcomes are then inspected. A stereoconvergent process is discovered to be operative, indicating a step-wise mechanism whereby a bond rotation can occur prior to cyclization to the boracycle (Figure 18). The relative configuration is assigned by

crystallography and is presumably achieved via an invertive, S_E2 electrophilic trapping by the boracycle (**24**, Figure 18).[24]

By similar logic, a *cis*-deuterated compound **25** is prepared and subjected to the reaction conditions (Figure 20). Product **26** is then isolated and revealed to be a 1:1 mixture of epimers about the iodinated carbon. This result again is inconsistent with a concerted pathway and supports an anionic or radical intermediate that is capable of inversion prior to closure to the boracycle.

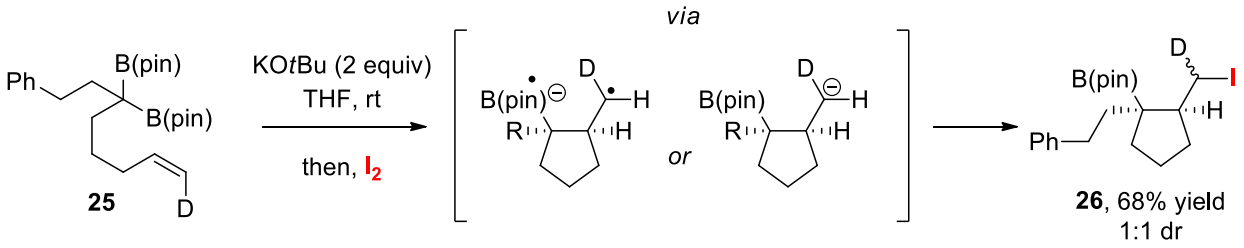


Figure 20 - Mechanistic experiment showing the stereo-randomization of the cyclization, eliminating a concerted process from consideration

iii) Empirical Observations Addressing the Anionic vs. Radical Pathways

With the concerted possibility dismissed from consideration, attention was then turned to discerning between the anionic or the radical mechanism. Initial experiments were designed to probe the nature of the boron-alkylidene. The introduction of a stereo-defined, secondary alkylbromide (**28**) as an electrophile in the deborylative-alkylation process results in a strictly invertive process (Figure 21). This result demonstrates the proclivity of the boron-alkylidene to react by a two-electron process as opposed to a single electron transfer to the alkyl halide, followed by fragmentation and radical combination.

24. Larouche-Gauthier, R.; Elford, T. G.; Aggarwal, V. K., Ate Complexes of Secondary Boronic Esters as Chiral Organometallic-Type Nucleophiles for Asymmetric Synthesis. *J. Am. Chem. Soc.* **2011,** *133* (42), 16794-16797.

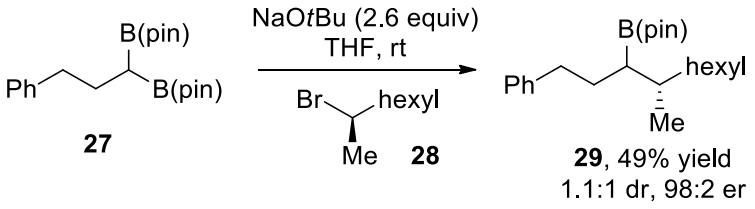


Figure 21 - Mechanistic experiment showing the proclivity of the deborylated species to react via a closed-shell process

A radical-clock experiment was also carried out by constructing a cyclopropane-pendant substrate (**30**) and subjecting it to the reaction conditions (Figure 22). No ring opening product was observed and reasonable yields of the typical cyclization product (**31**) were recorded.

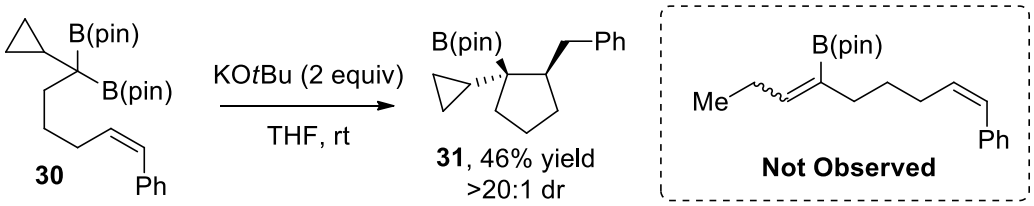


Figure 22 - Radical-clock experiment

Although the radical fragmentation of a cyclopropyl group is 1,000 times faster than a radical, 5-exo cyclization, this result does not preclude the existence of a radical mechanism.[25] The observed results could still be explained by a reversible cyclopropyl fragmentation and an irreversible radical, 5-exo cyclization.

iv) DFT Calculations

In order to provide insight into the operating mechanism, the reaction was studied with Density Functional Theory (DFT) by Dr. Fredrik Haeffner (Figure 23).

25. Anslyn, E. V.; Dougherty, D. A., *Modern Physical Organic Chemistry*. University Science Books: 2006.

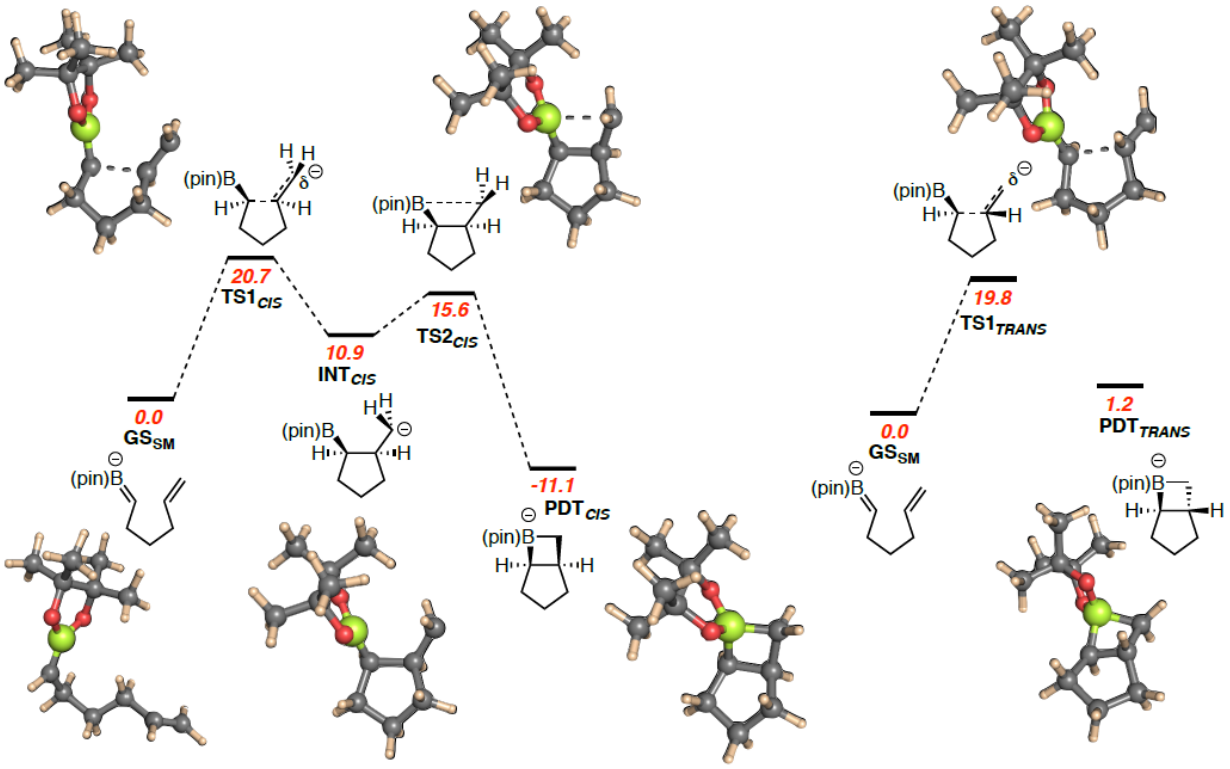


Figure 23 - DFT analysis of a closed-shell mechanism with omission of cation. M06-2x/6-31+G* with PCM solvent model (THF)

These calculations revealed that starting from the boron-alkylidene (**GSSM**), intermediate (**INT*CIS***) is achievable through an energy barrier of 20.7 kcal/mol (**TS1*CIS***). Because nucleophilic additions to C-C multiple bonds requires the activation via complexation with a metal salt, the omission of the potassium ion likely inflates the activation barrier values.[26] The intermediate (**INT*CIS***) could undergo a bond rotation and inversion prior to combining with the adjacent boronate ester to form the boracycle (**PDT*CIS***). This could explain the stereoconvergence found with the *cis* and *trans*-styrene derivatives as well as the stereochemical scrambling observed with deuterium-labeled terminal alkene substrate. Also depicted is the activation energy (**TS1*TRANS***) to achieve the *trans*-boracycle (**PDTTRANS**). The relatively, much larger ground-state energy of the **PDTTRANS** offers

26. Dénès, F.; Pérez-Luna, A.; Chemla, F., Addition of Metal Enolate Derivatives to Unactivated Carbon−Carbon Multiple Bonds. *Chem. Rev.* **2010,** *110* (4), 2366-2447.

an explanation as to why the *trans*- isomer of the product is not persistent under the reaction conditions.

D. Application to the Racemic Synthesis of Aphanamal

Cyclopentanoid containing natural products' ubiquitous nature (>49,000 natural isolates according to the Reaxys database) inspired an attempt to demonstrate the utility of the reaction products in the context of total synthesis. It was deemed worthwhile to determine how the substitution pattern and the stereogenicity of the reaction products would impact further transformations. In order to address this question, the natural product 10-oxo-isodauc-3-en-15-al (aphanamal) was chosen as a synthetic target (Figure 24).[27]

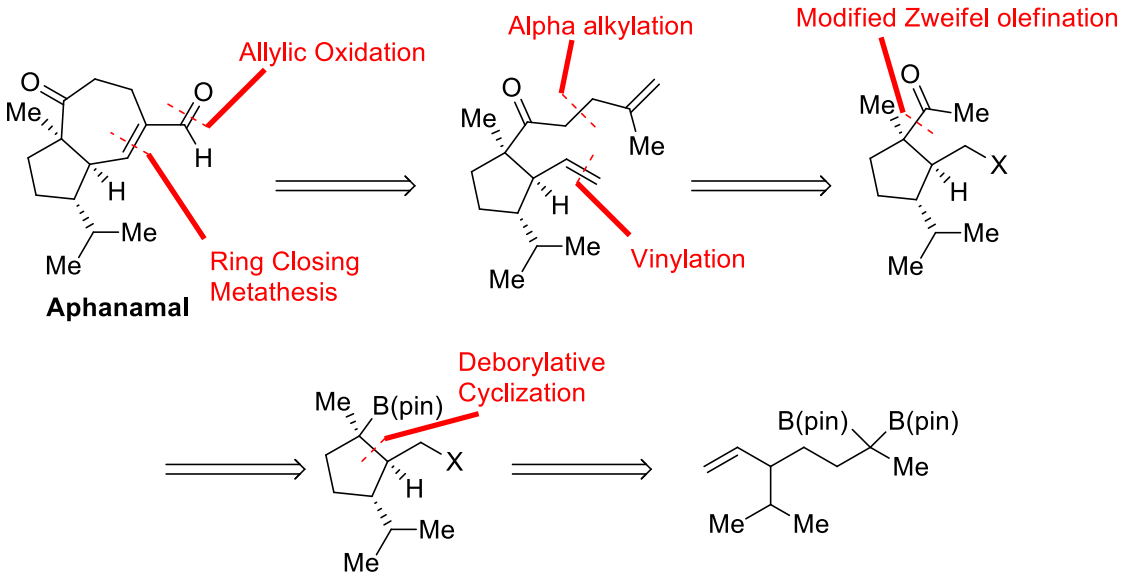


Figure 24 - Retrosynthetic analysis of natural product aphanamal

As depicted in Figure 24, aphanamal was retrosynthetically deconstructed. An allylic oxidation is proposed to install the aldehyde functionality in the final step of the synthesis. A ring closing metathesis is proposed to immediately precede the allylic oxidation. The two olefins are proposed

27. Hansson, T.; Wickberg, B., A short enantiospecific route to isodaucane sesquiterpenes from limonene. On the absolute configuration of (+)-aphanamol I and II. *J. Org. Chem.* **1992,** *57* (20), 5370-5376.

to be installed via α-allylation and a vinylation. This vinylation step will prove to be a problematic step and will be discussed in detail below. The methyl ketone can be installed via modified-Zweifel reaction and the cyclopentane is proposed to be constructed with the title reaction, trapping with an electrophile that can later be transformed into the vinyl moiety.

The vinyl fragment was originally proposed to be installed via a Wittig route. This was proposed to be carried out by first performing the deborylative cyclization and trapping with iodine. The resultant alkyl iodide **33** could then be converted into a phosphonium salt which could be utilized in the Wittig reaction (Figure 25). The phosphonium salt **34** was constructed without difficulty; however, when attempting the subsequent Wittig reaction, none of the desired product **35** was formed under several reaction conditions. Instead, an unexpected phosphine oxide was the major isolated product (**36**).

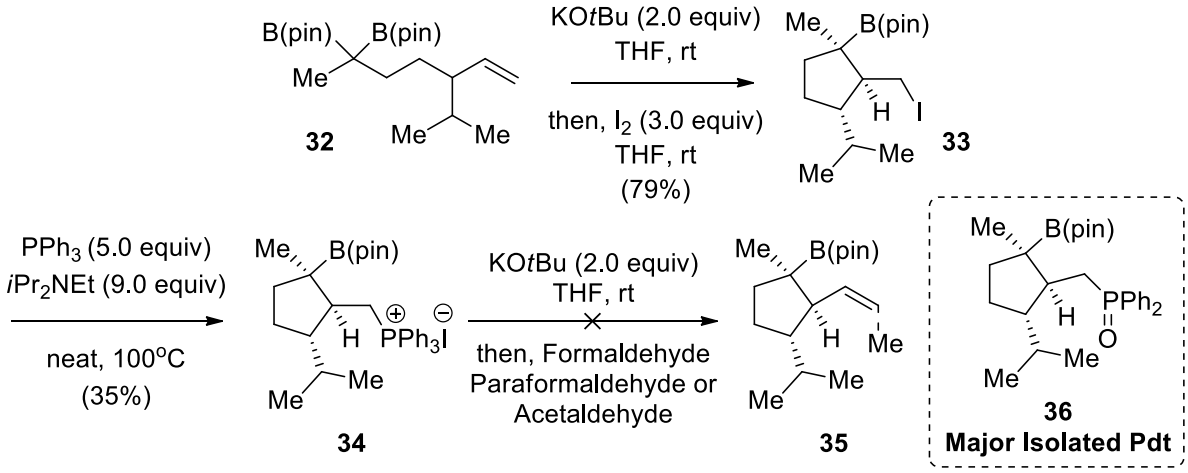


Figure 25 - Explored route to install vinyl fragment

This phosphine oxide product can be rationalized by considering the ylide to be pseudo-stable and unreactive with aldehydes. The ylide pseudo-stability could arise from its coordination to the adjacent boronate ester to form a boracyclobutane – similar to the intermediate in the title reaction. Upon water work-up, the unreacted ylide could be protonated and the resultant phosphonium salt

reacted with water, under the alkaline conditions, to extrude benzene and form the isolated phosphine oxide.[28]

A second route, continuing from the iodinated compound **33** was then devised that exploits the Ramberg-Bäcklund reaction in order to install the vinyl fragment (Figure 26).[29]

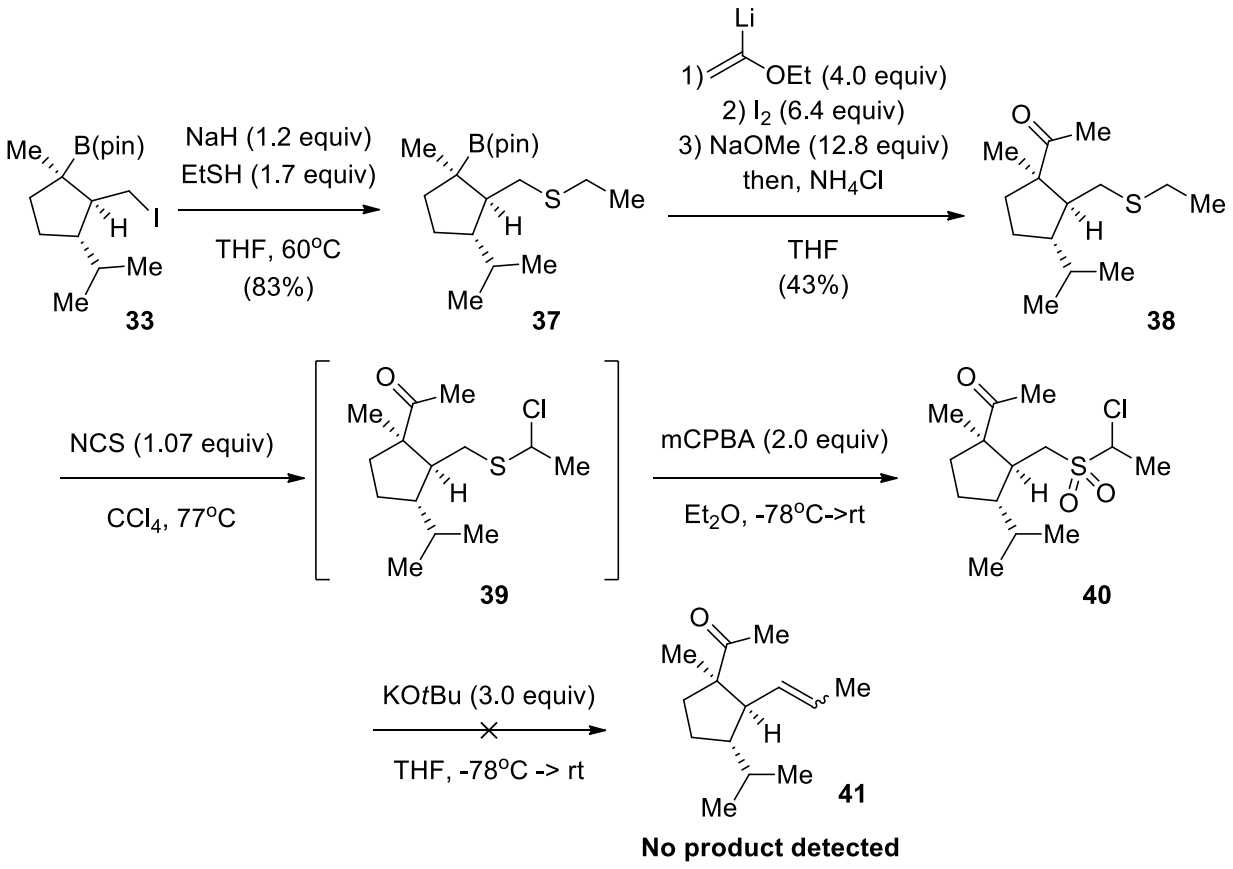


Figure 26 – Additional, explored route to install vinyl fragment

When attempting this proposed route, no product was detected after exposing the α-chloro sulfone (**40**) to typical Ramberg-Bäcklund conditions. A likely cause of the reaction failure is neighboring-group interference from the flanking ketone. Indeed, ketones are generally protected in Ramberg-

28. Worrall, D. E., STUDIES IN THE DIPHENYL SERIES. III. SOME PHOSPHORUS DERIVATIVES OF DIPHENYL. *J. Am. Chem. Soc.* **1930,** *52* (7), 2933-2937.
29. Paquette, L. A., The base-induced rearrangement of .alpha.-halo sulfones. *Acc. Chem. Res.* **1968,** *1* (7), 209-216.

Bäcklund reactions as the corresponding ketal.[30] While attempts to protect the sterically hindered ketone as a ketal failed, it was shown that a ketone reduction/silyl-protection prior to the Ramberg-Bäcklund was productive, but deemed impractical (Figure 27).

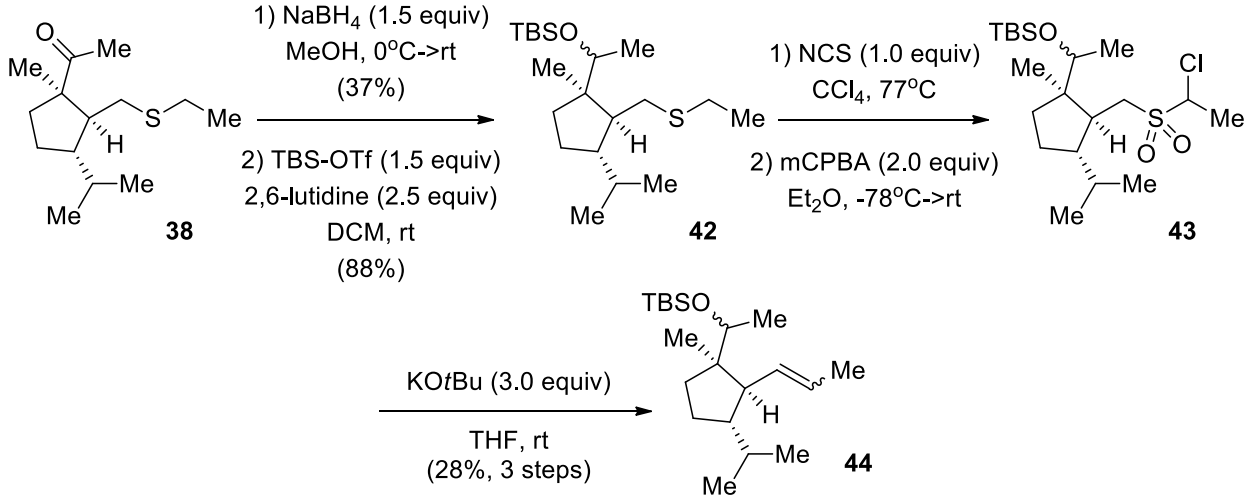


Figure 27 - A successful vinyl installation utilizing the Ramberg-Bäcklund reaction: ultimately deemed impractical

After failing to find a productive route to aphanamal from alkyl iodide **33**, a new electrophilic partner was sought in the deborylative cyclization. A single carbon electrophile that could later be eliminated was proposed to be an ideal electrophile. While carbon dioxide could fill this role, it was found to be an unreactive partner in the reaction. Eschenmoser's salt was then selected as an ideal candidate as the resultant tertiary amine could then be eliminated via Cope or Hofmann eliminations. This route was explored and indeed discovered to be effective (Figure 28).

30. Taylor, R. J. K.; Casy, G., The Ramberg-Bäcklund Reaction. In *Organic Reactions*, John Wiley & Sons, Inc.: 2004.

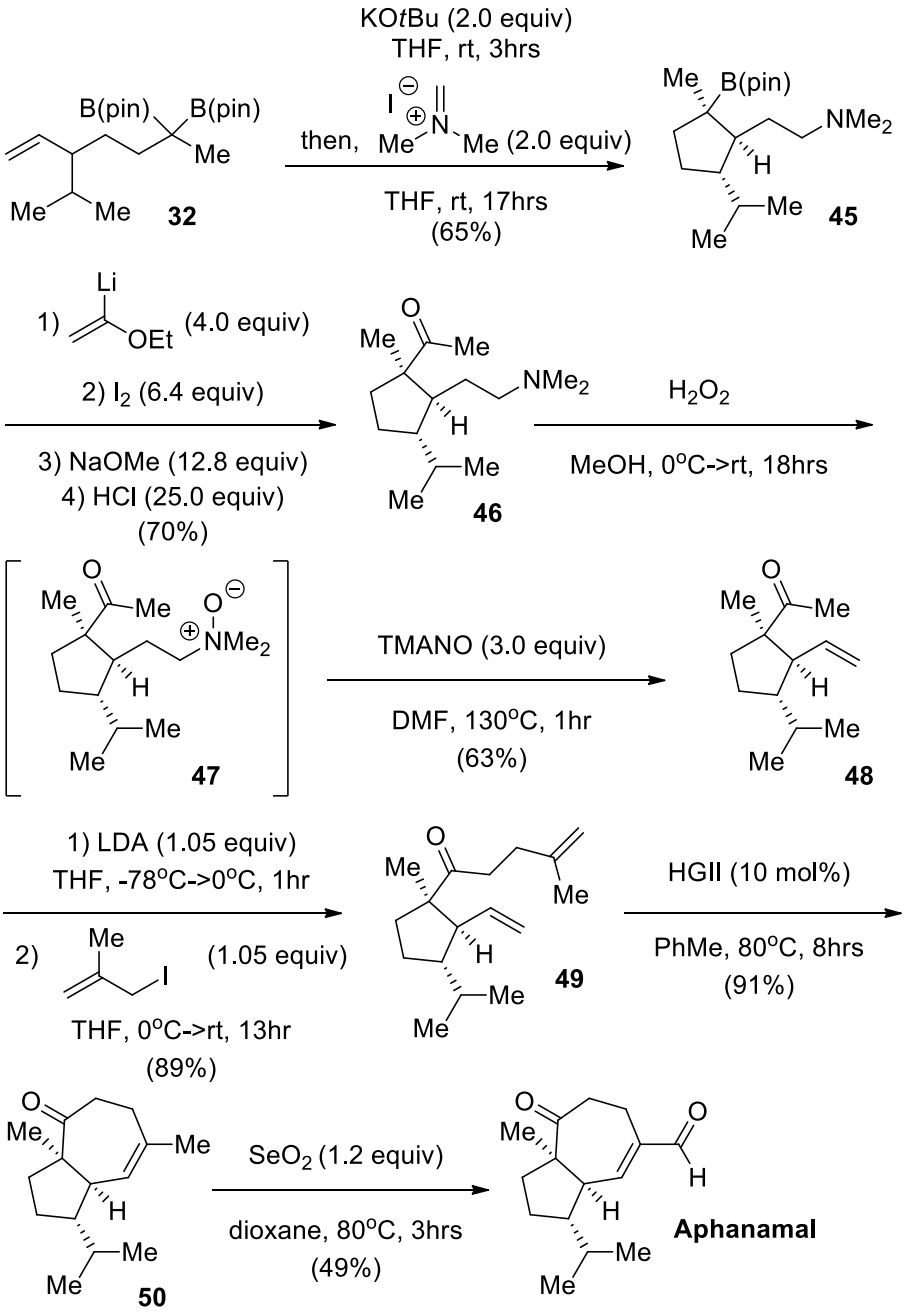


Figure 28 - Total synthesis of natural product aphanamal (isolated yields in parenthesis)

Starting from compound **32**, the title reaction was performed with standard conditions, trapping with freshly prepared Eschenmoser's salt yielded compound **45**.[31] Compound **45** is then subjected

31. Schreiber, J.; Maag, H.; Hashimoto, N.; Eschenmoser, A., Dimethyl(methylene)ammonium Iodide. *Angew. Chem. Int. Ed.* **1971,** *10* (5), 330-331.

to modified-Zweifel conditions, resulting in ketone **46**. A Cope elimination is then achieved by oxidizing **46** to *N*-oxide **47** with hydrogen peroxide and subsequently heating in the presence of trimethylamine *N*-oxide (TMANO) in DMF. The addition of TMANO was shown to increase yields in small-scale trials (41% yield with no TMANO versus a 90% yield with 3 equivalents TMANO; ^{1}H NMR of product compared to 1,1,2,2-tetrachloroethane). The addition of TMANO is thought to act as a sacrificial oxidant; thereby, preserving some of the starting *N*-oxide substrate. The route of reduction of the *N*-oxide is illustrated in Figure 29.[32]

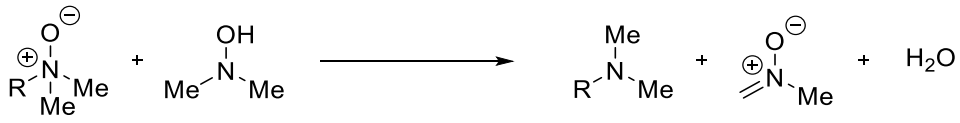


Figure 29 – *N*-oxide disproportionation pathway

The conventional method to avoid this degradation pathway is to remove the forming *N,N*-dimethylhydroxylamine by conducting the high-temperature reaction in vacuo. This method was avoided due to the possible volatility of the desired alkene. With Cope-elimination product **48** in hand, an α-allylation is then performed using freshly-prepared LDA and methallyl iodide to give compound **49**. Methallyl iodide is chosen over methallyl bromide due to the significant level of bis-allylation product observed when using the methallyl bromide (3.6 : 3.6 : 1, Product : SM : bis-allylation). Next, the seven-member ring **50** is fashioned via olefin metathesis using Hoveyda-Grubbs 2nd Generation Catalyst in toluene.[33] Finally, a selenium oxide mediated allylic oxidation is performed to furnish the final product, aphanamal.[34] The regioselectivity of the allylic oxidation

32. Laughlin, R. G., Reversible Cycloelimination and Disproportionation Reactions in Aliphatic Amine Oxide-N,N-Dimethylhydroxylamine-Olefin Systems. *J. Am. Chem. Soc.* **1973,** *95* (10), 3295-3299.
33. Hoveyda, A. H.; Zhugralin, A. R., The remarkable metal-catalysed olefin metathesis reaction. *Nature* **2007,** *450* (7167), 243-251.
34. Bennett, N. B.; Stoltz, B. M., A Unified Approach to the Daucane and Sphenolobane Bicyclo[5.3.0]decane Core: Enantioselective Total Syntheses of Daucene, Daucenal, Epoxydaucenal B, and 14-para-Anisoyloxydauc-4,8-diene. *Chemistry – A European Journal* **2013,** *19* (52), 17745-17750.

is surprising due to the typical endocyclic oxidation of cyclic-olefins.[35] An alternative approach, had the allylic oxidation not been productive, would have been to allylate with an oxygenated allyl fragment prior to ring-closing metathesis; in fact, this option was briefly explored and shown to be viable (Figure 30). This route was abandoned after the above synthesis was completed.

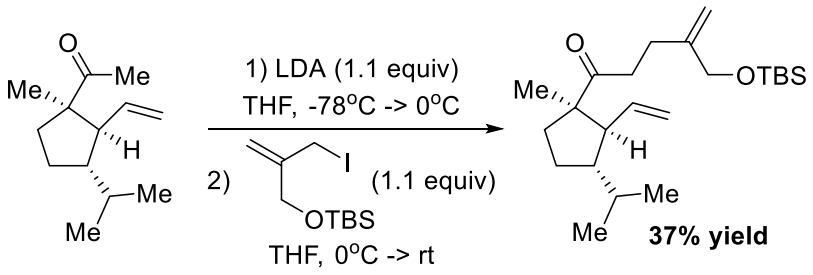


Figure 30 - Alternative route to allylic oxidized species

III. Conclusion

Based on empirical evidence, the title reaction was determined not to proceed through a concerted [2+2] mechanism. Likewise, experimentation suggests radical intermediates are not involved in the reaction. Supported by DFT computations, a carbanion addition to an unactivated olefin is deemed to be operational. As previously illustrated, the addition of stabilized anions to unactivated olefins is a known phenomenon, however, a rare observance in the literature. The reaction products also proved to be functionally modifiable; this was demonstrated through the synthesis of aphanamal. As Evans, Seebach and Hudlicky have noted: "the inherent synthetic dissonance present in any ring of an odd number of atoms makes the particular design of connective reagents difficult".[36] As such, this reaction is sure to find use as a powerful synthetic tool to access cyclopentanoids. Further development of this reaction could give rise to its application towards a

35. McNally, J. J.; Jackson, Y. A.; Downer-Riley, N. K., Selenium(IV) Oxide–tert-butyl Hydroperoxide. In *Encyclopedia of Reagents for Organic Synthesis*, John Wiley & Sons, Ltd: 2001.
36. Hudlicky, T.; Price, J. D., Anionic approaches to the construction of cyclopentanoids. *Chem. Rev.* **1989,** *89* (7), 1467-1486.

variety of ring sizes (eg. 4, 6, 7). Preliminary results show that 6-endo cyclizations are feasible, given an electron-stabilizing group is located in the correct position (Figure 31).

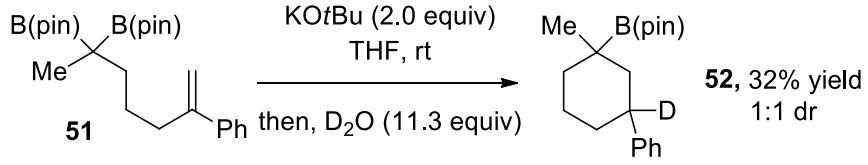


Figure 31 - Preliminary result showing the reactivity can be used to access different ring sizes

This result gives great optimism towards future development of the reaction.

IV. Experimental

A. General Information

^{1}H NMR spectra were recorded on a Varian Gemini-500 (500 MHz), or a Varian Inova-500 (500 MHz), or a Varian Inova-600 (600 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, THF-d_8: 3.58 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qi = quintet, sx = sextet, sp = septet, m = multiplet, br = broad), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Gemini-500 (125 MHz), or a Varian Inova-500 (125 MHz), or a Varian Inova-600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm, THF-d_8: 67.57 ppm). Infrared (IR) spectra were recorded on a Bruker alpha-P Spectrometer. Frequencies are reported in wavenumbers (cm^{-1}) as follows: strong (s), broad (br), medium (m), and weak (w). High-resolution mass spectrometry (DART+) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA.

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230 x 400 Mesh) purchased from Silicycle. Thin layer chromatography (TLC) was performed on 25 μm silica gel glass backed plates from Silicycle. Visualization was performed

using ultraviolet light (254 nm), phosphomolybdic acid (PMA) in ethanol and ceric ammonium molybdate (CAM) in ethanol and potassium permanganate ($KMnO_4$) in water.

Analytical chiral supercritical fluid chromatography (SFC) was performed on a TharSFC Method Station II equipped with Waters 2998 Photodiode Array Detector.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), diethyl ether (EtO_2), dichloromethane (DCM) and toluene (PhMe) were purified using Pure Solv MD-4 solvent purification system, from Innovative Technology, Inc., by passing the solvent through two activated alumina columns after being purged with argon.

Bis(pinacolato)diboron was purchased from Frontier Scientific and used without further purification. Triethylamine (NEt_3) was purchased from Alfa Aesar and distilled over calcium hydride (CaH_2) prior to use. The following reagents were purchased and used without purification: copper (I) iodide (CuI) (Strem), lithium 2,2,6,6-tetramethylpiperidide (LTMP) (Aldrich), potassium *tert*-butoxide (KO*t*Bu) (Aldrich, reagent or sublimed grade), palmitic acid-1-^{13}C (Cambridge Isotope Laboratories), and *N*,*N*-dimethylformamide (DMF) (Acros). All other reagents were purchased from either Aldrich, Alfa Aesar or Acros and used without further purification.

B. Reaction Substrates

i) Representative Procedures for Preparation of geminal-Diboronate Esters

Method A:

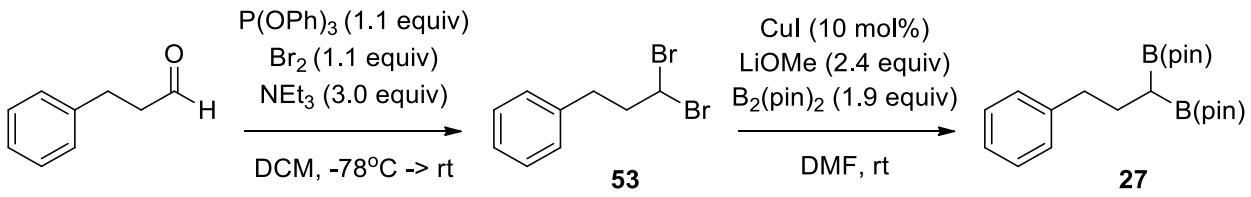


Figure 32 - Method A for geminal-Diboronate Ester synthesis

The 1,1-dibromide **53** was prepared according to the literature procedure with modification.[37] To a stirred solution of triphenyl phosphite (8.53 g, 27.5 mmol) in anhydrous DCM (250 mL) at -78 ^{o}C under N_2 was added bromine (1.41 mL, 27.5 mmol) dropwise. Freshly distilled triethylamine (10.45 mL, 75.0 mmol) and hydrocinnamaldehyde (3.29 mL, 25.0 mmol) were added at -78 ^{o}C. The reaction mixture was allowed to warm to room temperature and stirred for 2 hours. Upon completion, the solvent was evaporated in vacuo and the crude reaction mixture was purified on silica gel (100% hexanes) to afford the **53**.

In the glove box, an oven-dried 100 mL round-bottom flask with magnetic stir bar was charged with CuI (190 mg, 1.00 mmol), LiOMe (949 mg, 25.0 mmol) and $B_2(pin)_2$ (5.08 g, 20.0 mmol). The flask was sealed with a rubber septum, removed from the glove box, followed by the addition of DMF (20 mL) under N_2. After stirring at room temperature for 10 min, a solution of **51** (2.92 g, 10.5 mmol) in DMF (5 mL) was added via syringe at room temperature. The reaction mixture was allowed to stir at room temperature for 12 hours. Upon completion, 40 mL diethyl ether was added. The slurry was filtered through a silica gel plug, rinsed with diethyl ether, and concentrated in vacuo. The crude reaction mixture (DMF solution) was directly purified on silica gel (hexanes: diethyl ether = 10:1) to afford **27** as a white solid (3.09 g, 83%).

37. Spaggiari, A.; Vaccari, D.; Davoli, P.; Torre, G.; Prati, F., A Mild Synthesis of Vinyl Halides and gem-Dihalides Using Triphenyl Phosphite−Halogen-Based Reagents. *J. Org. Chem.* **2007,** *72* (6), 2216-2219.

Method B:

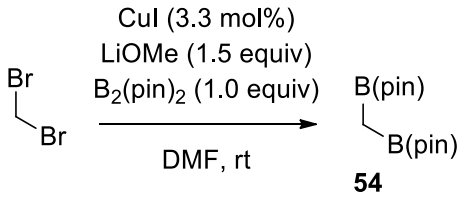


Figure 33 - Method B for geminal-Diboronate Ester synthesis

In the glove box, an oven-dried 500 mL round-bottom flask with magnetic stir bar was charged with CuI (1.428 g, 7.500 mmol), LiOMe (8.543 g, 225 mmol) and $B_2(pin)_2$ (38.09 g, 150.0 mmol). The flask was sealed with a rubber septum, removed from the glove box, followed by the addition of DMF (150 mL) under N_2. After stirring at room temperature for 10 min, dibromomethane (10.53 mL, 150.0 mmol) was added via syringe at room temperature. The reaction mixture was allowed to stir at room temperature for 12 hours. Upon completion, 200 mL diethyl ether was added. The slurry was filtered through a silica gel plug, rinsed with diethyl ether, and concentrated in vacuo. The crude reaction mixture in DMF was diluted with hexanes (300 mL), washed with H_2O (75 mL × 4), dried over Na_2SO_4, then concentrated in vacuo to afford **54** as a white solid (15.72 g, 78%) and used without further purification.

Method C:

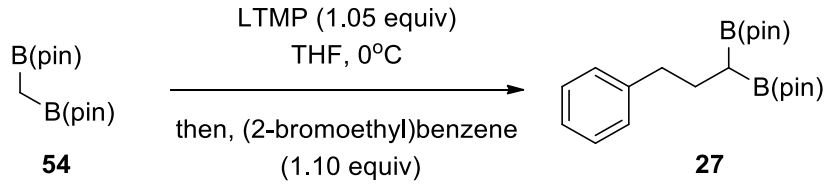


Figure 34 - Method C for geminal-Diboronate Ester synthesis

In the glove box, an oven-dried 25 mL round-bottom flask with magnetic stir bar was charged with LTMP (773 mg, 5.25 mmol). The flask was sealed with a rubber septum, removed from the glove box, followed by the addition of THF (20 mL) under N_2. The reaction mixture was cooled to 0 °C,

and a solution of **54** (1.34 g, 5.00 mmol) in THF (5 mL) was added via syringe and the mixture was allowed to stir at 0 °C for 10 minutes. (2-Bromoethyl)benzene (751 µL, 5.50 mmol) was added dropwise and the reaction was allowed to stir at 0 ºC for 15 min. Upon completion, the reaction mixture was warmed to room temperature, filtered through a silica gel plug, rinsed with diethyl ether, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 9:1) to afford **27** as a white solid (1.54 g, 83%).

Method D:

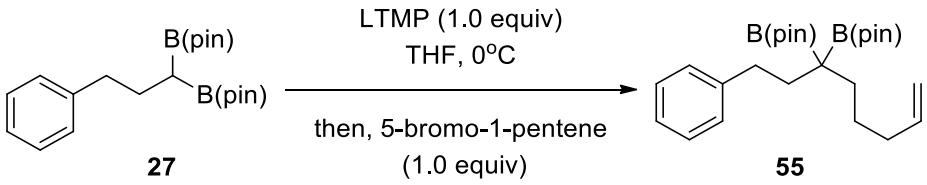


Figure 35 - Method D for geminal-Diboronate Ester synthesis

In the glove box, an oven-dried 2 dram vial with magnetic stir bar was charged with LTMP (147 mg, 1.0 mmol). The flask was sealed with a rubber septum, removed from the glove box, followed by the addition of THF (2 mL) under N_2. The reaction mixture was cooled to 0 ºC, and was transferred into a solution of **27** (372 mg, 1.0 mmol) in THF (2 mL) via syringe at 0 °C and the mixture was allowed to stir at 0 °C for 10 minutes. Then, 5-bromopent-1-ene (120 µL, 1.0 mmol) was added into the above mixture via syringe at 0 °C. The reaction mixture was allowed to stir at 0 ºC for 15 min, then warmed to room temperature, filtered through a silica gel plug, rinsed with diethyl ether, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 20:1) to afford **55** as a white solid (360 mg, 84%).

Method E:

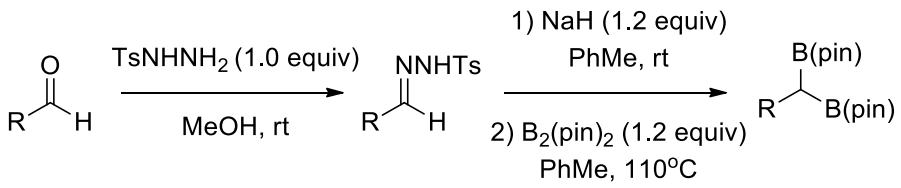


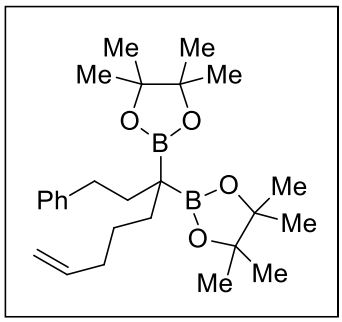
Figure 36 - Method E for geminal-Diboronate Ester synthesis

The geminal bis(pinacolato)dibronate esters were prepared according to the literature procedure.[38] A 6-dram vial with magnetic stir bar is charged with aldehyde (1.0 equiv), tosylhydrazine (1.0 equiv), and methanol (5 mL). The mixture was stirred at room temperature. *N*-tosylhydrazone precipitates after ca. 15 minutes and the reaction is monitored by TLC analysis (disappearance of aldehyde). The precipitate is then collected, washed with pentane (3x 5 mL), and dried under vacuum.

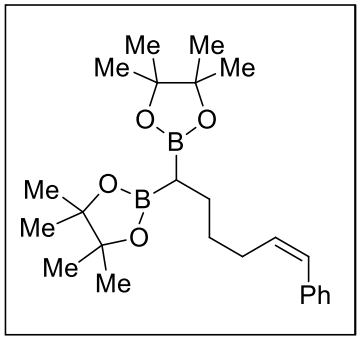
In the glove box, an oven-dried 6-dram vial with a magnetic stir bar is charged with *N*-tosylhydrazone (1.00 mmol, 1.00 equiv), NaH (1.20 mmol, 1.20 equiv), and toluene (8 mL). The mixture is then stirred at room temperature for 1 hour. Next, $B_2(pin)_2$ (1.20 mmol, 1.20 equiv) in toluene is added, then the vial sealed and removed from the glove box and heated at 110 °C for 12 hours. Upon completion, the reaction mixture is allowed to cool to room temperature, and Et_2O (10 mL) and H_2O (10 mL) added. The mixture is stirred vigorously for 10 minutes. After separation of the organic layer, the aqueous layer was extracted with Et_2O (2x5 mL). The combined organic layers are washed with brine (10 mL) and dried over anhydrous Na_2SO_4. After the solvent is evaporated, the crude product is purified by silica gel chromatography.

ii) Full Characterization of geminal-Diboronate Esters

38. Li, H.; Shangguan, X.; Zhang, Z.; Huang, S.; Zhang, Y.; Wang, J., Formal Carbon Insertion of N-Tosylhydrazone into B–B and B–Si Bonds: gem-Diborylation and gem-Silylborylation of sp3 Carbon. *Org. Lett.* **2014,** *16* (2), 448-451.



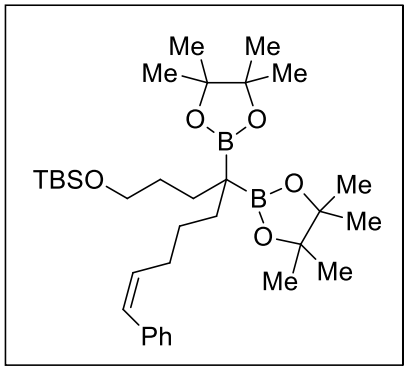
2,2'-(1-phenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (55). The reaction was performed according to *Representative Procedure (Method D)* with diboronate ester (372 mg, 1.0 mmol), LTMP (147 mg, 1.0 mmol), 5-bromo-1-pentene (120 µL, 1.0 mmol) and THF (4 mL). The crude reaction mixture was purified by column chromatography on silica gel (20:1 hexanes/diethyl ether, stain in CAM) to afford **53** as a white solid (360 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26-7.23 (m, 2H), 7.20-7.19 (m, 2H), 7.15-7.12 (m, 1H), 5.86 (ddt, *J* = 17.1, 10.3, 6.9 Hz, 1H), 5.01 (ddt, *J* = 17.1, 2.0, 1.5 Hz, 1H), 4.93 (ddt, *J* = 10.3, 2.4, 1.0 Hz , 1H), 2.52-2.49 (m, 2H), 2.10-2.06 (m, 2H), 1.91-1.88 (m, 2H), 1.74-1.71 (m, 2H), 1.41-1.35 (m, 2H), 1.23 (s, 24H); The ^{1}H NMR spectrum was in accord with previously reported data.[5]



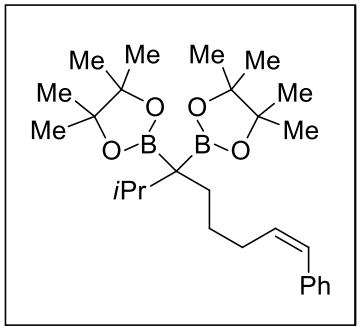
(*Z*)-2,2'-(6-phenylhex-5-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)) (56). The reaction was performed according to *Representative Procedure (Method D)* with methyl diboronate ester **54** (429 mg, 1.60 mmol), LTMP (236 mg, 1.60 mmol), (*Z*)-(5-bromopent-1-en-1-yl)benzene (361 mg, 1.60 mmol) and THF (8 mL). The crude reaction mixture was purified by column chromatography on silica gel (50:1 – 20:1 hexanes/ethyl acetate, stain in CAM) to afford a white solid (500 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.22 (m, 4H), 7.22 – 7.17 (m, 1H), 6.37 (d, *J* = 11.7 Hz, 1H), 5.67 (dt, *J* = 11.6, 7.3 Hz, 1H), 2.31 (qd, *J* = 7.5, 1.9 Hz, 2H), 1.60 (q, *J* = 7.8 Hz, 2H), 1.50 – 1.40 (m, 2H), 1.22 (s, 12H), 1.21 (s, 12H), 0.74 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.79, 133.27, 128.68, 128.43, 128.01, 126.27, 82.89, 82.83, 76.67, 32.88, 28.85, 25.56, 24.83, 24.47; IR

5. Hong, K.; Liu, X.; Morken, J. P., Simple Access to Elusive α-Boryl Carbanions and Their Alkylation: An Umpolung Construction for Organic Synthesis. *J. Am. Chem. Soc.* **2014,** *136* (30), 10581-10584.

(neat): 2976.8 (m), 2927.3 (w), 1368.7 (m), 1311.6 (s), 1267.5 (m), 1214.5 (w), 1139.3 (s), 969.4 (m), 849.7 (m), 699.8 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{24}{}^{1}H_{39}{}^{11}B_2{}^{16}O_4$ $[M+H]^+$: calculated: 413.3034, found: 413.3052.

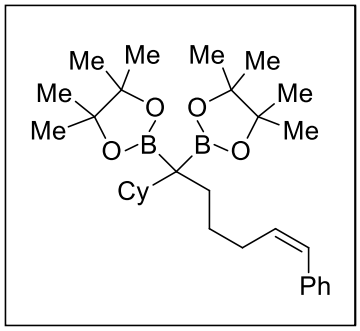


(*Z*)-*tert*-butyldimethyl((9-phenyl-4,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)non-8-en-1-yl)oxy)silane) (57). Prepared according to *Representative Procedure (Method D)* with LTMP (177 mg, 1.0 mmol), diboronate ester **56** (412 mg, 1.0 mmol), (3-bromopropoxy)-*tert*-butyldimethylsilane (253 mg, 1.0 mmol), and THF (5 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 50:1) to afford the desired product as a white solid (455 mg, 77%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 – 7.22 (m, 4H), 7.21 – 7.16 (m,1H), δ 6.36 (d, *J* = 11.7 Hz, 1H), 5.68 (dt, *J* = 11.6, 7.3 Hz, 1H), 3.58 (t, *J* = 7.2 Hz, 2H), 2.31 (dt, *J* = 8.4, 6.5 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.60 – 1.55 (m, 2H), 1.51 – 1.44 (m, 2H), 1.39 – 1.34 (m, 2H), 1.21 (s, 24H), 0.88 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.85, 133.44, 128.73, 128.38, 128.02, 126.27, 82.92, 64.32, 30.64, 29.55, 28.95, 27.59, 26.02, 24.74, 24.70, 18.40, -5.19; IR (neat): 2977.1 (m), 2929.4 (m), 2857.6 (w), 1461.6 (w), 1378.1.5 (m), 1371.8 (m), 1355.5 (m), 1307.2 (m), 1139.6 (s), 973.4 (w), 853.3 (m), 853.8 (m), 774.4 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{33}{}^{1}H_{59}{}^{11}B_2{}^{16}O_5{}^{28}Si_1$ $[M+H]^+$: calculated: 585.4318, found: 585.4309.



(*Z*)-2,2'-(2-methyl-8-phenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (58). The reaction was performed according to *Representative Procedure (Method D)* with 2,2'-(2-methylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (509 mg, 1.6 mmol, made according to previous

procedure[38]), LTMP (236 mg, 1.60 mmol), (*Z*)-(5-bromopent-1-en-1-yl)benzene (361 mg, 1.60 mmol) and THF (8 mL). The crude reaction mixture was purified by column chromatography on silica gel (100:1 – 50:1 hexanes/ethyl acetate, stain in CAM) to afford **58** as a white solid (530 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.25 (m, 4H), 7.19 (m, 1H), 6.36 (d, *J* = 11.7, 1H), 5.71 (dt, *J* = 11.6, 7.2 Hz, 1H), 2.31 (qd, *J* = 7.4, 1.8 Hz, 2H), 2.04 (p, *J* = 6.8 Hz, 1H), 1.68 – 1.59 (m, 2H), 1.59 – 1.45 (m, 2H), 1.21 (s, 24H), 0.98 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.94, 133.71, 128.76, 128.75, 128.24, 128.01, 126.24, 82.55, 30.04, 29.75, 29.21, 28.43, 24.81, 24.77, 21.29; IR (neat): 2976.8 (m), 2929.6 (m), 1728.5 (w), 1459.8 (w), 1378.0 (m), 1370.6 (m), 1296.1 (s), 1264.8 (m), 1215.1 (w), 1140.7 (s), 972.8 (w), 854.0 (w), 757.8 (s), 699.5 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{27}{}^{1}H_{45}{}^{11}B_2{}^{16}O_4$ $[M+H]^+$: calculated: 455.3504, found: 455.3504.

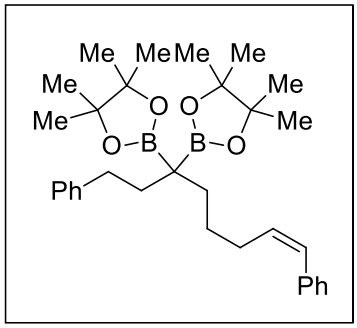


(*Z*)-2,2'-(1-cyclohexyl-6-phenylhex-5-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**59**). The reaction was performed according to *Representative Procedure (Method D)* with 2,2'-(cyclohexylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (350 mg, 1.0 mmol; made according to previously reported procedure[5]), LTMP (147 mg, 1.0 mmol), (*Z*)-(5-bromopent-1-en-1-yl)benzene (225 mg, 1.60 mmol) and THF (5 mL). The crude reaction mixture was purified by column chromatography on silica gel (100:1 – 50:1 hexanes/ethyl acetate, stain in CAM) to afford **59** as a colorless oil (378 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.28 (m, 4H), 7.31 – 7.15 (m, 1H), 6.37 (d, *J* = 11.6, 1H), 5.72 (dt, *J* = 11.6, 7.2 Hz, 1H), 2.30 (qd, *J* = 7.4, 1.8 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.73

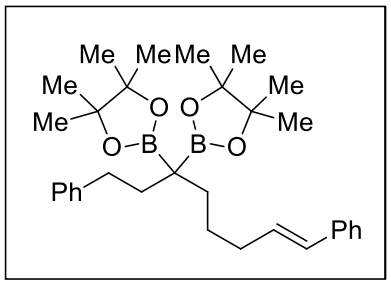
38. Li, H.; Shangguan, X.; Zhang, Z.; Huang, S.; Zhang, Y.; Wang, J., Formal Carbon Insertion of N-Tosylhydrazone into B–B and B–Si Bonds: gem-Diborylation and gem-Silylborylation of sp3 Carbon. *Org. Lett.* **2014,** *16* (2), 448-451.

5. Hong, K.; Liu, X.; Morken, J. P., Simple Access to Elusive α-Boryl Carbanions and Their Alkylation: An Umpolung Construction for Organic Synthesis. *J. Am. Chem. Soc.* **2014,** *136* (30), 10581-10584.

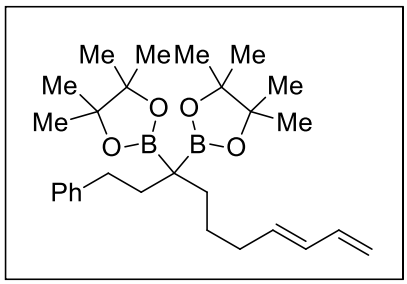
– 1.58 (m, 6H), 1.57 – 1.46 (m, 2H), 1.21 (s, 24H), 1.31 – 1.02 (m, 4H), 0.91 – 0.82 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.97, 133.80, 128.78, 128.20, 128.01, 126.24, 82.56, 40.24, 31.53, 30.12, 29.41, 28.66, 27.42, 26.96, 24.83, 24.80; IR (neat): 2977.4 (m), 2925.9 (m), 2851.9 (w), 1447.1 (w), 1377.5 (m), 1370.6 (m), 1344.1 (m), 1293.8 (m), 1137.7 (s), 974.0 (w), 850.9 (w), 699.5 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{30}{}^{1}H_{49}{}^{11}B_2{}^{16}O_4$ $[M+H]^+$: calculated: 495.3817, found: 495.3819.



(*Z*)-2,2'-(1,8-diphenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)) (22). The reaction was performed according to *Representative Procedure (Method D)* with diboronate ester **27** (441 mg, 1.18 mmol), LTMP (174.5 mg, 1.18 mmol), (*Z*)-(5-bromopent-1-en-1-yl)benzene (267 mg, 1.186 mmol) and THF (6 mL). The crude reaction mixture was purified by column chromatography on silica gel (20:1 hexanes/ethyl acetate, stain in CAM) to afford **22** as a white solid (543 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.10 (m, 10H), 6.40 (d, J = 11.7 Hz, 1H), 5.73 (dt, J = 11.6, 7.3 Hz, 1H), 2.56 – 2.48 (m, 2H), 2.37 (qd, J = 7.4, 1.8 Hz, 2H), 1.96 – 1.88 (m, 2H), 1.82 – 1.73 (m, 2H), 1.52 – 1.41 (m, 2H), 1.24 (two sets of singlet, 24H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.71, 137.83, 133.37, 128.73, 128.52, 128.45, 128.08, 128.04, 126.32, 125.35, 82.98, 33.82, 31.92, 29.56, 28.96, 27.68, 24.78, 24.70; IR (neat): 2977.2 (m), 2928.4 (w), 1454.5 (w), 1370.5 (m), 1352.4 (m), 1308.8 (s), 1254.6 (m), 1214.1 (w), 1138.1 (s), 968.9 (w), 854.6 (w), 699.2 (m) cm^{-1}. HRMS-(DART+) for $^{12}C_{32}{}^{1}H_{47}{}^{11}B_2{}^{16}O_4$ $[M+H]^+$: calculated: 517.3660, found: 517.3639.

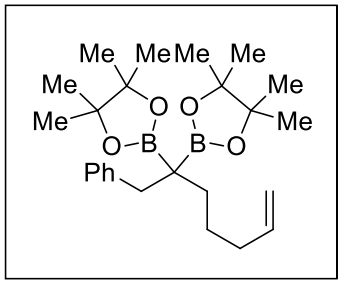


(*E*)-2,2'-(1,8-diphenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (15). The reaction was performed according to *Representative Procedure (Method D)* with diboronate ester **27** (1.0 g, 2.69 mmol), LTMP (417 mg, 2.83 mmol), (*E*)-(5-bromopent-1-en-1-yl)benzene (636 mg, 2.83 mmol) and THF (10.8 mL). The crude reaction mixture was purified by column chromatography on silica gel (20:1 hexanes/ethyl acetate, stain in CAM) to afford **15** as a white solid (543 mg, 39%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.32 – 7.22 (m, 4H), 7.23 – 7.17 (m, 3H), 7.20 – 7.11 (m, 1H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.28 (dt, *J* = 15.9, 6.7 Hz, 1H), 2.56 – 2.49 (m, 2H), 2.25 (q, *J* = 6.9 Hz, 2H), 1.95 – 1.89 (m, 2H), 1.81 – 1.75 (m, 2H), 1.52 – 1.43 (m, 2H), 1.24 (s, 24H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.72, 138.06, 131.42, 129.47, 128.48, 128.40, 128.09, 126.62, 125.91, 125.35, 83.00, 33.86, 33.83, 31.90, 28.76, 27.09, 24.81, 24.71; IR (neat): 2977.5 (w), 2929.4 (w), 1453.7 (w), 1378.5 (m), 1307.6 (m), 1253.4 (m), 1138.4 (s), 967.5 (w), 851.2 (w), 751.4 (m), 698.1 (w) cm^{-1} HRMS-(DART+) for $^{12}C_{32}{}^{1}H_{47}{}^{11}B_2{}^{16}O_4$ $[M+H]^+$: calculated: 517.3660, found: 517.3664.



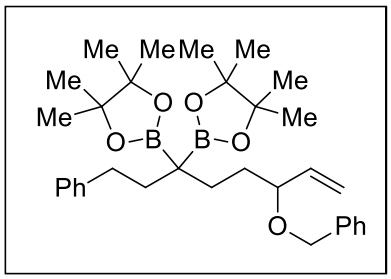
(*E*)-2,2'-(1-phenyldeca-7,9-diene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (16). The reaction was performed according to *Representative Procedure (Method D)* with diboronate ester **27** (633 mg, 1.7 mmol), LTMP (250 mg, 1.7 mmol), (*E*)-7-bromohepta-1,3-diene (296 mg, 1.7 mmol) and THF (7 mL). The crude reaction mixture was purified by column chromatography on silica gel (50:1 hexanes/ethyl acetate, stain in CAM) to afford **16** as a white solid (713 mg, 90%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 – 7.10 (m, 5H), 6.32 (dt, *J* = 17.0, 10.3 Hz, 1H), 6.06 (dd, *J* = 15.3, 10.3 Hz, 1H), 5.75 (dt, *J* = 14.5, 6.8 Hz, 1H), 5.08 (dd, *J* = 17.0, 1.7 Hz, 1H), 4.94 (dd, *J* = 10.1, 1.7 Hz, 1H), 2.53 – 2.47 (m, 2H), 2.11

(q, *J* = 7.2 Hz, 2H), 1.92 – 1.86 (m, 2H), 1.75 – 1.69 (m, 2H), 1.42 – 1.34 (m, 2H), 1.23 (s, 24H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.74, 137.51, 135.85, 130.64, 128.47, 128.09, 125.35, 114.37, 82.99, 33.84, 33.33, 31.87, 28.75, 26.89, 24.80, 24.70; IR (neat): 2976.8 (w), 2929.1 (w), 1455.0 (w), 1378.0 (m), 1305.6 (m), 1252.2 (m), 1137.0 (s), 1003.9 (m), 852.2 (m), 699.2 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{28}{}^{1}H_{45}{}^{11}B_2{}^{16}O_4$ $[M+H]^+$: calculated: 467.3504, found: 467.3519.



2,2'-(1-phenylhept-6-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)) (60). The reaction was performed according to *Representative Procedure (Method D)* with 2,2'-(2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (429.7 mg, 1.2 mmol, made according to previous procedure[5]), LTMP (194.3 mg, 1.32 mmol), 5-bromo-1-pentene (197 mg, 1.32 mmol) and THF (6 mL). The crude reaction mixture was purified by column chromatography on silica gel (50:1 hexanes/ethyl acetate, stain in CAM) to afford **60** as a colorless oil (450 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 – 7.17 (m, 4H), 7.15 – 7.07 (m, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 4.97 (dq, *J* = 17.2, 1.8 Hz, 1H), 4.90 (ddt, *J* = 10.2, 2.4, 1.3 Hz, 1H), 2.97 (s, 2H), 2.00 (q, *J* = 7.1 Hz, 2H), 1.56 – 1.51 (m, 2H), 1.49 – 1.41 (m, 2H), 1.24 (s, 12H), 1.20 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.82, 139.32, 129.70, 127.65, 125.41, 113.82, 83.16, 34.58, 34.44, 28.44, 26.77, 25.00, 24.69; IR (neat): 2978.4 (m), 2931.7 (w), 2862.9 (m), 1378.4 (m), 1353.4 (m), 1261.8 (m), 1138.8 (s), 854.3 (w), 699.9 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{25}{}^{1}H_{41}{}^{11}B_2{}^{16}O_4$ $[M+H]^+$: calculated: 427.3191, found: 427.3189.

5. Hong, K.; Liu, X.; Morken, J. P., Simple Access to Elusive α-Boryl Carbanions and Their Alkylation: An Umpolung Construction for Organic Synthesis. *J. Am. Chem. Soc.* **2014,** *136* (30), 10581-10584.



2,2'-(6-(benzyloxy)-1-phenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)) (**61**). The reaction was performed according to *Representative Procedure (Method D)* with diboronate ester **27** (186 mg, 0.5 mmol), LTMP (73.6 mg, 0.5 mmol), 3-(benzyloxy)pent-4-en-1-yl 4-methylbenzenesulfonate (193 mg, 0.56 mmol) and THF (5 mL). The crude reaction mixture was purified by column chromatography on silica gel (100:2 – 100:4 hexanes/ethyl acetate, stain in CAM) to afford **61** as a colorless oil (220 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.30 (m, 4H), 7.26 – 7.21 (m, 3H), 7.20 – 7.16 (m, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 5.84 – 5.69 (m, 1H), 5.25 – 5.22 (m, 2H), 4.60 (d, *J* = 12.1 Hz, 1H), 4.40 (d, *J* = 12.1 Hz, 1H), 3.73 (q, *J* = 6.8 Hz, 1H), 2.50 (td, *J* = 7.3, 3.7 Hz, 2H), 1.88 (dd, *J* = 10.7, 6.9 Hz, 2H), 1.80 – 1.63 (m, 4H), 1.22 (s, 24H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.76, 139.03, 128.51, 128.21, 128.07, 127.58, 127.21, 125.32, 117.22, 82.99, 81.33, 69.77, 33.79, 32.81, 31.95, 24.91, 24.78, 24.65; IR (neat): 2977.4 (m), 2932.1 (w), 1378.5 (w), 1370.5 (w), 1309.9 (s), 1138.56 (s), 851.8 (w), 698.5 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{33}{}^{1}H_{52}{}^{11}B_2{}^{16}O_5{}^{14}N_1$ $[M+NH_4]^+$: calculated: 564.4032, found: 564.4058.

The 3-(benzyloxy)pent-4-en-1-yl 4-methylbenzenesulfonate **was prepared as shown in the scheme below:**

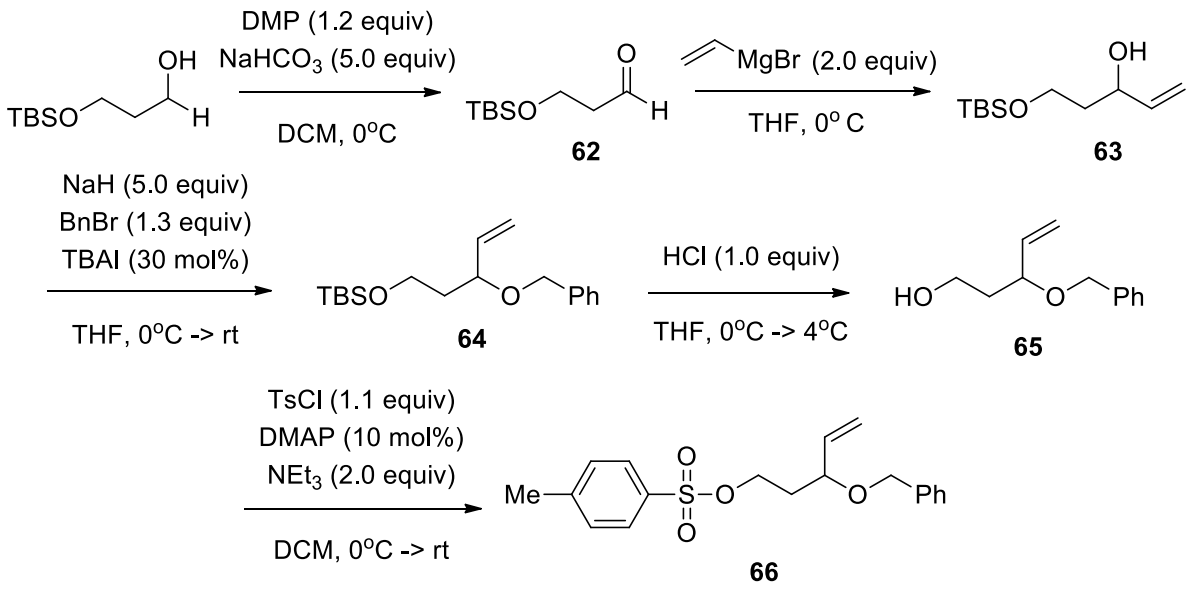
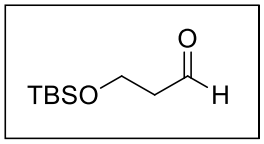
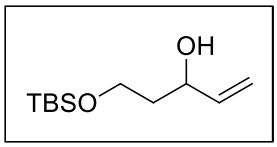


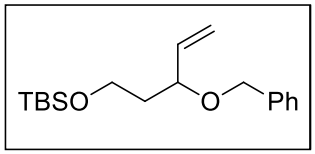
Figure 37 – Forward synthesis of 3-(benzyloxy)pent-4-en-1-yl 4-methylbenzenesulfonate



3-((*tert*-butyldimethylsilyl)oxy)propanal (62). To an oven dried 20 mL vial, 3-((*tert*-butyldimethylsilyl)oxy)propan-1-ol (522 mg, 2.9 mmol) is added followed by anhydrous DCM (6 mL). The solution is brought to 0°C then Dess-Martin periodinane (1.48 g, 3.48 mmol) and $NaHCO_3$ (1.22 g, 14.5 mmol) added. The reaction is then allowed to stir for 4h, gradually reaching room temperature. At this point, the mixture is concentrated in vacuo then extracted with 1:1 hexane/Et_2O and the combined extracts filtered through a pad of silica gel, rinsing with 1:1 hexane/Et_2O. The filtrate is concentrated in vacuo and the resulting crude oil is purified by column chromatography on silica gel (80:20 pentane/diethyl ether, stain in PMA) to afford **62** as a clear, colorless oil (380 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.80 (s, 1H), 3.98 (t, J = 6.0 Hz, 2H), 2.59 (td, J = 6.1, 2.0 Hz, 2H), 0.88 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.93, 57.38, 46.54, 25.78, 18.18, -5.48; IR (neat): 2868.7 (m), 1725.6 (w), 1256.2 (w), 1141.3 (s), 908.6 (s), 835.7 (s), 778.1 (m), 732.3 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_9{}^{1}H_{21}{}^{28}Si^{16}O_2$ $[M+H]^+$: calculated: 189.1311, found: 189.1319.

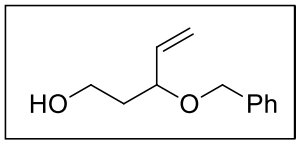


5-((*tert*-butyldimethylsilyl)oxy)pent-1-en-3-ol (63). An oven-dried 125 mL round bottom flask fitted with magnetic stir bar is sealed and evacuated/refilled with N_2 3x then charged with 3-((*tert*-butyldimethylsilyl)oxy)propanal (**62**) (3.18 g, 16.9 mmol) followed by anhydrous THF (32 mL). The vessel and contents are then cooled to 0°C and vinylmagnesium bromide solution (33.8 mL, 1 M in THF, 33.8 mmol) added across ca. 15 min. The resulting clear, yellow solution is allowed to stir overnight at room temperature, then quenched with a saturated aqueous solution of ammonium chloride. The reaction mixture is then poured into a separatory funnel where it is diluted with deionized water and the organics are extracted with diethyl ether 5x. The combined organics are dried over Na_2SO_4 then concentrated in vacuo. The crude residue is then purified by column chromatography on silica gel (100:3 to 80:20 pentane/diethyl ether, stain in $KMnO_4$) to afford **63** as a clear, orange oil. (1566 mg, 43%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.01 – 5.77 (m, 1H), 5.29 (dd, *J* = 17.2, 2.1 Hz, 1H), 5.11 (dd, *J* = 10.5, 2.1 Hz, 1H), 4.39 – 4.33 (m, 1H), 3.95 – 3.87 (m, 1H), 3.81 (ddt, *J* = 10.1, 7.3, 4.1 Hz, 1H), 3.31 (d, *J* = 3.6 Hz, 1H), 1.85 – 1.67 (m, 2H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.51, 113.98, 72.32, 61.78, 38.15, 25.73, 18.00, -5.65; IR (neat): 3462.4(broad), 2954.5 (w), 2857.9 (w), 1255.4 (w), 1082.1 (w), 906.4 (s), 834.6 (s), 777.4 (m), 729.4 (s), 648.5 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{11}{}^{1}H_{25}{}^{28}Si_{1}{}^{16}O_2$ $[M+H]^+$: calculated: 217.1624, found: 217.1632.



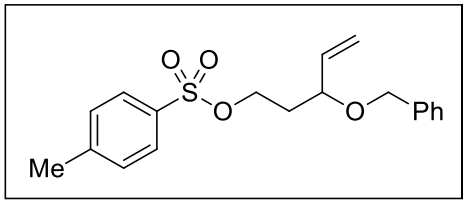
((3-(benzyloxy)pent-4-en-1-yl)oxy)(*tert*-butyl)dimethylsilane) (64). An oven-dried 20 mL vial is charged with sodium hydride (220 mg, 60 wt%, 5.5 mmol), and anhydrous THF (5 mL) then cooled to 0°C. A solution of 5-((*tert*-butyldimethylsilyl)oxy) pent-1-en-3-ol (**63**) (237 mg, 1.1 mmol) in anhydrous THF (2 mL) is then gradually added to the reaction vessel and the resulting mixture allowed to stir

for 30 minutes at 0°C. Benzyl bromide (0.17 mL, 1.43 mmol) is then added followed by tetrabutylammonium iodide (122 mg, 0.33 mmol). The resulting light yellow slurry is allowed to stir overnight, gradually warming to room temperature. Upon return, the mixture is brought back to 0°C where it is quenched by a saturated aqueous solution of ammonium chloride. Organics are then extracted with diethyl ether 3x and combined organics dried over Na_2SO_4, and concentrated in vacuo. The crude reaction mixture was purified by column chromatography on silica gel (100:2 to 100:5 pentane/diethyl ether, stain in $KMnO_4$) to afford **64** as a clear, colorless oil (313 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.23 (m, 3H), 7.22 – 7.16 (m, 2H), 5.73 – 5.64 (m, 1H), 5.21 – 5.12 (m, 2H), 4.52 (d, *J* = 11.7 Hz, 1H), 4.28 (d, *J* = 11.6 Hz, 1H), 3.93 – 3.83 (m, 1H), 3.67 (ddd, *J* = 10.1, 7.2, 5.8 Hz, 1H), 3.63 – 3.58 (m, 1H), 1.80 (ddt, *J* = 13.7, 7.7, 5.9 Hz, 1H), 1.69 – 1.58 (m, 1H), 0.81 (s, 9H), -0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.89, 128.27, 127.75, 127.67, 127.35, 116.98, 70.23, 59.31, 38.72, 25.91, 18.24, -5.34; IR (neat): 2953.7 (w), 2928.0 (w), 2856.4 (w), 1253.8 (m), 1090.6 (s), 925.3 (m), 834.8 (s), 775.2 (m), 733.2 (m), 696.7 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{18}{}^{1}H_{31}{}^{28}Si_{1}{}^{16}O_2$ $[M+H]^+$: calculated: 307.2093, found: 307.2089.



3-(benzyloxy)pent-4-en-1-ol (65). A 125 mL round bottom flask is charged with ((3-(benzyloxy)pent-4-en-1-yl)oxy)(*tert*-butyl) dimethylsilane) (**64**) (180 mg, 0.54 mmol), and THF (54 mL) then cooled to 0°C and HCl (0.54 mL, 1N, 0.54 mmol) slowly added. The resulting clear, colorless solution is then allowed to stir at 4°C overnight. Upon completion, the reaction is cooled to 0°C and slowly treated with saturated, aqueous $NaHCO_3$ solution (0.54 mL). The mixture is then concentrated in vacuo and the crude residue purified by column chromatography on silica gel (100:3 to 80:20 pentane/diethyl ether, stain in $KMnO_4$) to afford **65** as a clear, colorless oil (101 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.15 (m, 5H), 5.73 (ddd, *J* = 17.6, 10.5, 7.8 Hz,

1H), 5.20 (d, J = 17.1 Hz, 1H), 5.19 (d, J = 10.5 Hz, 1H), 4.56 (d, J = 11.8 Hz, 1H), 4.29 (d, J = 11.7 Hz, 1H), 3.95 (td, J = 8.0, 4.4 Hz, 1H), 3.79 – 3.61 (m, 2H), 2.31 (dd, J = 6.5, 4.4 Hz, 1H), 1.81 (dtd, J = 15.3, 7.7, 4.2 Hz, 1H), 1.73 (ddt, J = 10.5, 6.7, 4.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.17, 138.10, 128.45, 127.79, 127.67, 117.51, 79.88, 70.29, 60.58, 37.78; IR (neat): 3383.2 (w, broad), 2865.8 (w), 1454.3(w), 1055.7 (s), 927.9 (m), 736.3 (m), 698.0 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{12}{}^{1}H_{17}{}^{16}O_2$ $[M+H]^+$: calculated: 193.1229, found: 193.1229.



3-(benzyloxy)pent-4-en-1-yl 4-methylbenzenesulfonate (66). An oven dried 20 mL vial equipped with magnetic stir bar is charged with 4-toluenesulfonyl chloride (203.4 mg, 1.07 mmol), DMAP (11.8 mg, 0.097 mmol), DCM (2 mL), and reagent grade triethylamine (0.27 mL, 1.94 mmol) in succession. The vessel and contents are then cooled to 0°C and a solution of 3-(benzyloxy)pent-4-en-1-ol (**65**) (187 mg, 0.97 mmol) in DCM (2 mL) is slowly added under nitrogen protection. The resulting clear-yellow solution is then allowed to stir overnight and upon return is quenched by deionized H_2O. The organics are then extracted with DCM, and dried over Na_2SO_4 and the combined organics concentrated in vacuo. The crude residue is then purified by column chromatography on silica gel (50:1 to 100:5 hexanes/ethyl acetate, stain in $KMnO_4$) to afford **66** as a clear, colorless oil (268 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 – 7.75 (m, 2H), 7.35 – 7.29 (m, 4H), 7.29 – 7.27 (m, 1H), 7.24 – 7.21 (m, 2H), 5.67 (ddd, J = 17.1, 10.4, 7.7 Hz, 1H), 5.25 – 5.19 (m, 2H), 4.51 (d, J = 11.5 Hz, 1H), 4.27 – 4.17 (m, 2H), 4.10 (dt, J = 9.7, 5.6 Hz, 1H), 3.87 (td, J = 8.0, 4.9 Hz, 1H), 2.42 (s, 3H), 2.02 – 1.80 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.67, 138.18, 137.61, 133.09, 129.79, 128.32, 127.90, 127.66, 127.55, 118.14, 76.47, 70.36, 67.15, 34.87, 21.60; IR (neat): 2927.4 (w), 2865.8 (w), 1598.2 (w), 1496.2 (w), 1454.5

(w),1359.8 (m), 1176.5 (s), 916.0 (m), 836.7 (w), 739.9 (w), 664.0 (m), 554.5 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{19}{}^{1}H_{26}{}^{14}N_{1}{}^{32}S_{1}{}^{16}O_{4}$ $[M+NH_4]^+$: calculated: 364.1583, found: 364.158.

C. Reaction Products

i) Representative Procedure for Deborylative Cyclization

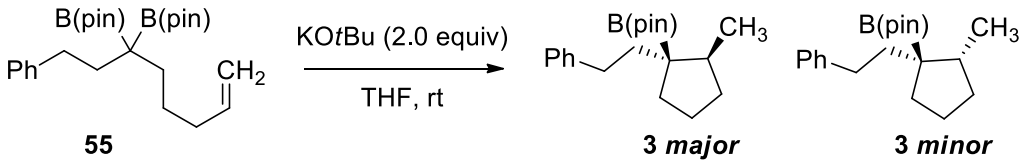
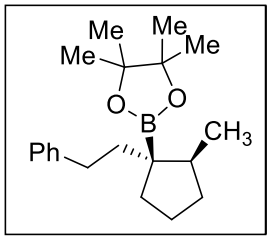


Figure 38 - Representative deborylative cyclization

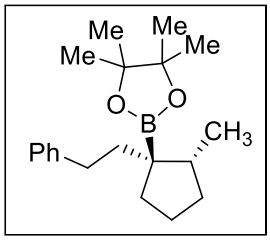
In the glove box, an oven-dried 2-dram vial equipped with magnetic stir bar is charged with 1,1-diboronate ester **55** (48.4 mg, 0.10 mmol), base (0.20 mmol) and THF (0.50 mL). The vial is sealed with a polypropylene cap, removed from the glove box, and allowed to stir at room temperature for overnight. Upon completion, the reaction mixture is diluted with wet diethyl ether (2 mL), filtered through a silica gel plug, rinsed with diethyl ether, and concentrated in vacuo. Diastereomeric ratio is determined by ^{1}H NMR of the crude residue, then purification is done on silica gel (hexanes: ethyl acetate = 100 : 0.8) to afford the desired products **3** ***major*** and **3** ***minor***.

ii) Full Characterization of Reaction Products and Proof of Stereochemistry

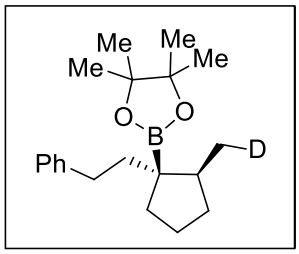


4,4,5,5-tetramethyl-2-(2-methyl-1-phenethylcyclopentyl)-1,3,2-dioxaborolane (3, *major diastereomer*).The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **55** (88 mg, 0.2 mmol), KO*t*Bu (44.8 mg, 0.4 mmol) and THF (1 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8) to afford the desired product as a colorless oil (32.7 mg, 52%, 4:1 dr). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.25(m, 2H), 7.20 (d, *J* = 7.3 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 2.59-2.53 (m, 2H), 2.05-1.95 (m, 2H), 1.84-1.78 (m, 1H), 1.77-1.70 (m, 1H), 1.64-1.56 (m, 2H), 1.40-1.22

(m,3H), 1.27 (12H, s, overlap), 1.00 (d, J = 6.9 Hz, 3H); The ^{1}H NMR spectrum was in accord with previously reported data.[1]



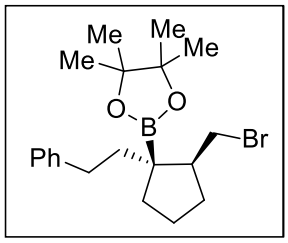
4,4,5,5-tetramethyl-2-(1-phenyltetradecan-2-yl)-1,3,2-dioxaborolane (3, *minor diastereomer*). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (t, J = 7.3 Hz, 2H), 7.21 (d, J = 7.3 Hz, 2H), 7.18-7.15 (m, 1H), 2.58-2.49 (m, 2H), 2.04 (sx, J = 7.3 Hz, 1H), 1.89-1.83 (m, 1H), 1.79-1.54 (m, 5H), 1.44-1.36 (m, 1H), 1.31-1.24 (m, 1H), 1.27 (s, overlap, 12H), 0.91 (dd, J = 7.3, 1.4 Hz, 3H); The ^{1}H NMR spectrum was in accord with previously reported data.[5]



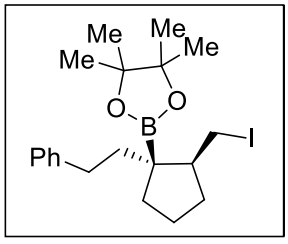
4,4,5,5-tetramethyl-2-((1*R*,2*S*)-2-(methyl-*d*)-1-phenethylcyclopentyl)-1,3,2-dioxaborolane (4). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **55** (88 mg, 0.2 mmol), KO*t*Bu (44.8 mg, 0.4 mmol) and THF (1 mL). Upon completion, the reaction mixture was quenched with D_2O (100 μL, 5.0 mmol), then diluted with diethyl ether (2 mL) and filtered through a silica gel plug, rinsing with diethyl ether, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a colorless oil (31 mg, 49%, 4:1 dr). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (t, J = 7.6 Hz, 2H), 7.23 – 7.14 (m, 3H), 2.63 – 2.50 (m, 2H), 2.07 – 1.92 (m, 2H), 1.86 – 1.68 (m, 2H), 1.63 – 1.55 (m, 2H), 1.39 – 1.20 (m, 3H), 1.27 (s, 12H), 0.99 (d, J = 7.0, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.88, 128.30, 128.19, 125.40, 125.40, 82.89, 44.93, 41.24, 34.26, 34.19, 34.14, 25.28, 24.82, 22.70, 17.63, 17.50, 17.37; IR (neat): 2977.4 (m), 2931.9 (m), 2857.6 (w), 1730.2 (w), 1454.4 (w),

5. Hong, K.; Liu, X.; Morken, J. P., Simple Access to Elusive α-Boryl Carbanions and Their Alkylation: An Umpolung Construction for Organic Synthesis. *J. Am. Chem. Soc.* **2014,** *136* (30), 10581-10584.

1387.8 (m), 1301.7 (m), 1195.1 (w), 1143.6 (s), 966.8 (w), 855.5 (w), 748.8 (w), 698.9 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{20}{}^{1}H_{31}{}^{11}B_{1}{}^{16}O_{2}$ $[M+H]^{+}$: calculated: 316.2558, found: 316.2560.



2-((1*R*,2*S*)-2-(bromomethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5). The reaction was performed according to *Representative Procedure for Deborylative Cyclization n* with 1,1-diboronate ester **55** (88 mg, 0.2 mmol), KO*t*Bu (44.8 mg, 0.4 mmol) and THF (1 mL). Upon completion, the reaction mixture was quenched with NBS (71.2 mg, 0.4 mmol) in anhydrous THF (1 mL), then diluted with diethyl ether (2 mL) and filtered through a silica gel plug, rinsing with diethyl ether. Filtrate was then concentrated in vacuo and crude purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (40.3 mg, 51.2%, >20:1 dr). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.23 (m, 2H), 7.18 (dd, *J* = 7.7, 1.1 Hz, 2H), 3.72 (dd, *J* = 9.6, 3.7 Hz, 1H), 3.37 (dd, *J* = 11.4, 9.6 Hz, 1H), 2.62 – 2.50 (m, 2H), 2.18 – 2.04 (m, 2H), 2.06 – 1.91 (m, 2H), 1.79 – 1.56 (m, 2H), 1.51 – 1.37 (m, 3H), 1.26 (d, *J* = 1.6 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.13, 128.30, 128.23, 125.64, 83.31, 53.24, 41.18, 37.96, 35.71, 33.87, 32.22, 25.10, 24.82, 22.35; IR (neat): 2976.4 (m), 2956.2 (m), 2932.3 (m), 2868.7 (w), 1454.3 (w), 1381.0 (m), 1312.3 (m), 1210.3 (m), 1142.9 (s), 967.1 (w), 855.0 (w), 748.5 (w), 698.8 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{20}{}^{1}H_{31}{}^{11}B_{1}{}^{79}Br_{1}{}^{16}O_{2}$ $[M+H]^{+}$: calculated: 393.1601, found: 393.1608.



2-((1*R*,2*S*)-2-(iodomethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **55** (88 mg, 0.2 mmol), KO*t*Bu (44.8 mg, 0.4 mmol) and THF (1 mL). Upon completion, the reaction mixture was quenched with I_2 (101.5 mg, 0.4

mmol) in anhydrous THF (1 mL), then diluted with diethyl ether (2 mL) and filtered through a silica gel plug, rinsing with diethyl ether. Filtrate was then concentrated in vacuo and the crude residue purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (43mg, 49%, >20:1 dr). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 3.53 (dd, *J* = 9.4, 3.3 Hz, 1H), 3.14 (dd, *J* = 12.1, 9.4 Hz, 1H), 2.61 – 2.50 (m, 2H), 2.20 – 2.10 (m, 2H), 2.04 – 1.94 (m, 2H), 1.81 – 1.70 (m, 1H), 1.69 – 1.57 (m, 1H), 1.48 – 1.40 (m, 2H), 1.43 – 1.32 (m, 1H), 1.26 (s, 6H) , 1.26 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.13, 128.30, 128.22, 125.64, 83.30, 53.97, 41.19, 36.08, 33.90, 25.11, 24.82, 21.83, 11.61; IR (neat): 2976.5 (m), 2956.3 (m), 2932.3 (m), 2867.2 (w), 1454.1 (w), 1380.7 (m), 1345.3 (m), 1210.3 (w), 1142.4 (s), 966.8 (w), 854.2 (w), 755.1 (m), 698.4 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{20}{}^{1}H_{31}{}^{11}B_{1}{}^{127}I_{1}{}^{16}O_{2}$ $[M+H]^{+}$: calculated: 441.1462, found: 441.1478. The relative stereochemistry was assigned by X-ray crystallography.

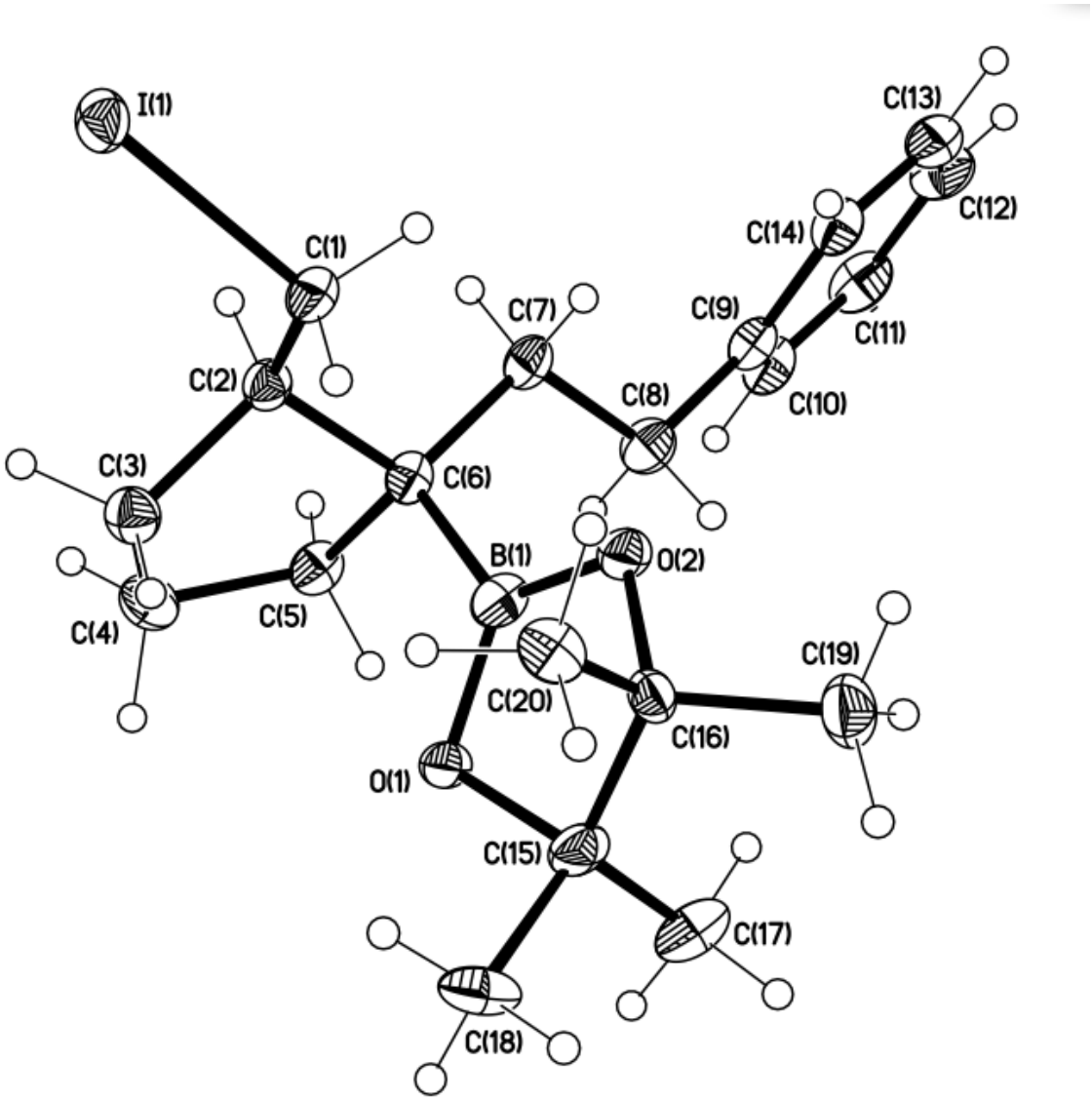
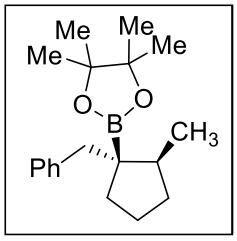
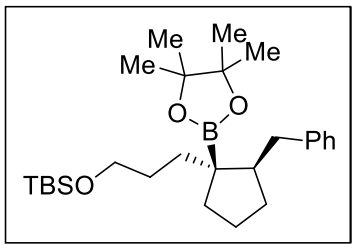


Figure 39 - Crystal of 2-((1*R*,2*S*)-2-(iodomethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

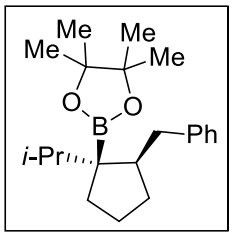


2-((1*R*,2*S*)-1-benzyl-2-methylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **60** (85.2 mg, 0.2 mmol), KO*t*Bu (44.8 mg, 0.4 mmol) and THF (1 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a colorless oil (39.2 mg, 65%, > 20:1 dr). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 – 7.18 (m, 4H), 7.17 – 7.10 (m, 1H), 2.97 (d, *J* = 13.2 Hz, 1H), 2.43 (d, *J* = 13.3 Hz, 1H),

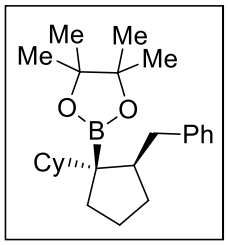
1.87 – 1.79 (m, 2H), 1.75 – 1.50 (m, 3H), 1.47 – 1.36 (m, 1H), 1.30 – 1.20 (m, 1H), 1.19 (s, 6H), 1.14 (s, 6H), 1.05 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.15, 130.14, 127.56, 125.49, 82.91, 44.35, 42.89, 33.97, 33.77, 25.14, 24.93, 22.24, 17.55; IR (neat): 2976.8 (m), 2953.6 (m), 2930.1 (m), 2869.0 (w), 1453.4 (w), 1387.9 (m), 1298.8 (m), 1211.8 (w), 1143.0 (s), 965.7 (w), 858.5 (w), 758.5 (w), 701.1 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{19}{}^{1}H_{29}{}^{11}B_{1}{}^{16}O_{2}$ $[M+H]^+$: calculated: 301.2339, found: 301.2336.



(3-((1*R*,2*R*)-2-benzyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)propoxy)(*tert*-butyl)dimethylsilane (10). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **57** (58.5 mg, 0.1 mmol), KO*t*Bu (22.4 mg, 0.2 mmol) and THF (0.5 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (30 mg, 65%, > 20:1 dr). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 7.18 – 7.13 (m, 3H), 3.67 – 3.54 (m, 2H), 2.98 (dd, J = 13.2, 3.3 Hz, 1H), 2.33 (dd, J = 13.2, 11.6 Hz, 1H), 1.98 (ddd, J = 12.5, 8.7, 4.8 Hz, 1H), 1.82 – 1.43 (m, 7H), 1.35 – 1.21 (m, 2H), 1.27 (s, 12H), 1.21 – 1.06 (m, 1H), 0.91 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.00, 128.80, 128.07, 125.41, 82.93, 64.26, 53.02, 39.37, 34.41, 34.35, 31.36, 30.94, 26.02, 25.12, 24.89, 22.41, 18.40, -5.17; IR (neat): 2975.9 (w), 2951.9 (m), 2929.1 (m), 2856.3 (m), 1453.9 (w), 1386.9 (m), 1299.6 (m), 1253.8 (m), 1215.5 (w), 1142.3 (s), 1098.6 (m), 990.1 (w), 835.3 (s), 775.1 (m), 698.6 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{27}{}^{1}H_{48}{}^{11}B_{1}{}^{16}O_{3}{}^{28}Si_{1}$ $[M+H]^+$: calculated: 459.3466, found: 459.3454.



2-((1*R*, 2*R*)-2-benzyl-1-isopropylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **58** (90.9 mg, 0.2 mmol), KO*t*Bu (44.8 mg, 0.4 mmol) and THF (1 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (34.5 mg, 52.5%, > 20:1 dr). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 – 7.22 (m, 2H), 7.19 – 7.12 (m, *J* = 6.9, 5.7, 1.4 Hz, 3H), 2.97 (dd, *J* = 13.2, 3.1 Hz, 1H), 2.34 (dd, *J* = 13.3, 11.7 Hz, 1H), 2.02 – 1.75 (m, 3H), 1.74 – 1.61 (m, 1H), 1.64 – 1.52 (m, 1H), 1.45 – 1.32 (m, 2H), 1.28 (s, 12H), 1.28 – 1.18 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.29, 128.77, 128.07, 125.39, 82.83, 48.45, 39.32, 31.82, 31.14, 29.17, 25.19, 24.93, 22.49, 21.15, 17.15; IR (neat): 2955.3 (m), 2870.1 (w), 1495.1 (w), 1380.1 (m), 1297.7 (m), 1212.7 (w), 1140.6 (s), 982.1 (w), 864.9 (w), 745.6 (w), 699.2 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{21}{}^{1}H_{34}{}^{11}B_{1}{}^{16}O_2$ $[M+H]^+$: calculated: 329.2652, found: 329.2655.



2-((1*R*,2*R*)-2-benzyl-1-cyclohexylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **59** (98.9 mg, 0.2 mmol), KO*t*Bu (44.8 mg, 0.4 mmol) and THF (1 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (59 mg, 80%, > 20:1 dr). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 – 7.21 (m, 2H), 7.21 – 7.12 (m, 3H), 2.97 (dd, *J* = 13.3, 3.2 Hz, 1H), 2.34 (dd, *J* = 13.3, 11.9 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.84 – 1.76 (m, 1H), 1.79 – 1.67 (m, 3H), 1.66 – 1.58 (m, 3H), 1.61 – 1.50 (m, 2H), 1.45 – 1.31 (m, 2H), 1.33 – 1.19 (m, 14H), 1.22 – 1.17 (m, 2H), 1.17 – 1.08 (m, 1H), 1.09 – 0.95 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.30, 128.78, 128.05, 125.36, 82.80, 47.14,

41.83, 39.18, 31.65, 31.56, 30.06, 27.34, 27.12, 27.08, 27.04, 25.22, 24.90, 22.39; IR (neat): 2976.2 (m), 2925.3 (s), 2851.6 (m), 1449.0 (w), 1378.7 (m), 1297.3 (m), 1212.8 (w), 1141.8 (s), 864.2 (w), 746.5 (w), 698.8 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{24}{}^{1}H_{38}{}^{11}B_{1}{}^{16}O_{2}$ $[M+H]^{+}$: calculated: 369.2965, found: 369.2967. The relative stereochemistry was assigned by X-ray crystallography.

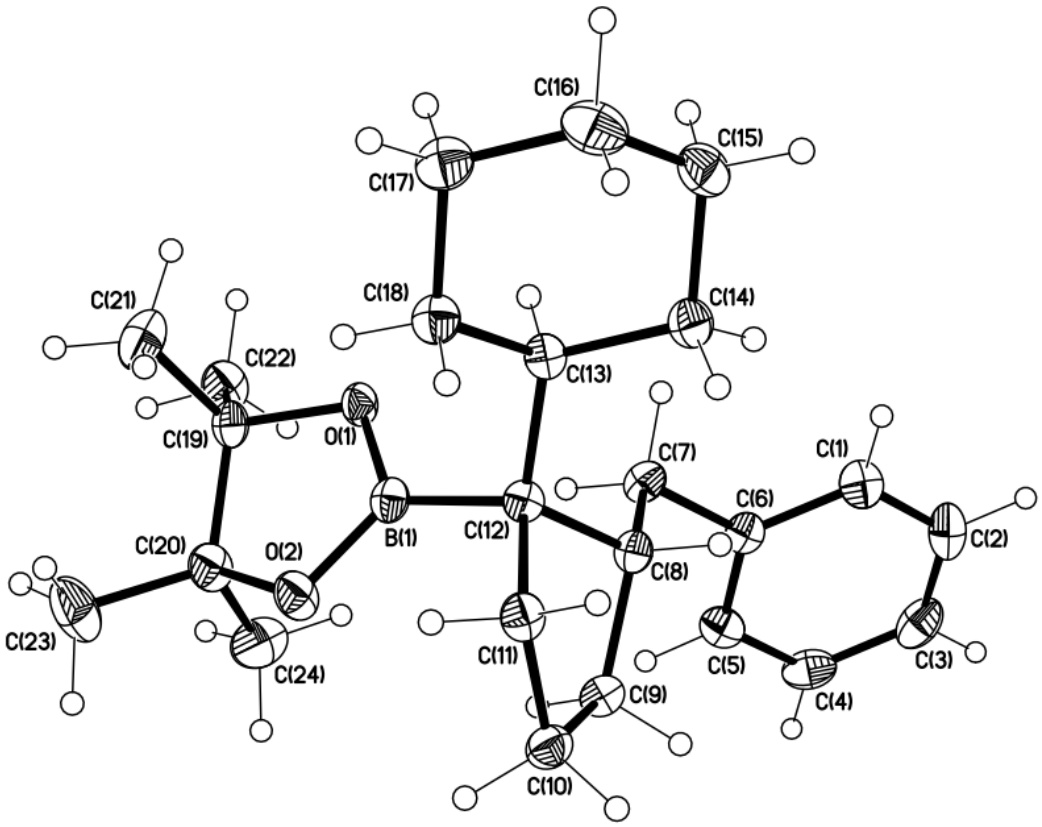
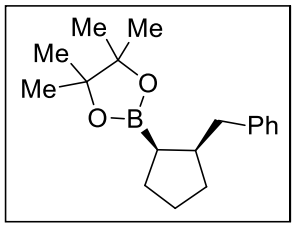


Figure 40 – Crystal of 2-((1*R*,2*R*)-2-benzyl-1-cyclohexylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



2-((1*R*,2*R*)-2-benzylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **56** (82.4 mg, 0.2 mmol), KO*t*Bu (44.8 mg, 0.4 mmol) and THF (1 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a colorless oil (25.7 mg, 45%, > 20:1 dr).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 – 7.21 (m, 2H), 7.20 – 7.12 (m, 3H), 2.78 (dd, *J* = 13.4, 5.9 Hz, 1H), 2.51 (dd, *J* = 13.4, 8.6 Hz, 1H), 2.21 – 2.11 (m, 1H), 1.87 – 1.77 (m, 1H), 1.77 – 1.65 (m, 1H), 1.66 – 1.44 (m, 3H), 1.27 (d, *J* = 4.5 Hz, 1H), 1.18 (s, 6H), 1.17 (s, 6H), 0.99 – 0.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.22, 128.98, 128.05, 125.48, 82.72, 45.07, 42.49, 33.51, 28.47, 25.84, 24.72, 24.70; IR (neat): 2956.1 (s), 2932.8 (m), 2919.8 (m), 2876.6 (w), 2861.0 (w), 2361.0 (m), 2163.9 (s), 2013.9 (w), 1728.4 (s), 1379.0 (m), 1290.6 (s), 1316.8 (m), 1145.8 (m), 763.7 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{18}{}^{1}H_{27}{}^{11}B_{1}{}^{16}O_2$ $[M+H]^+$: calculated: 287.2182, found: 287.2194. Relative configuration was determined after oxidation and comparison with reported data.[39] To a 20 mL vial containing **12** (10 mg, 0.035mmol), NaOH solution (3M, 1 mL) is added followed by THF (1 mL). The vial is then cooled to 0°C and H_2O_2 (30 wt%, 1 mL) is carefully added. The reaction mixture is then allowed to stir at room temperature for three hours, at which point, the mixture is cooled back to 0°C and saturated, aqueous $Na_2S_2O_3$ (1 mL) is added to degrade excess H_2O_2. The mixture is then extracted with ethyl acetate three times and the combined organics dried over Na_2SO_4, and concentrated in vacuo. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 3.96 – 3.87 (m, 1H), 2.76 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.55 (dd, *J* = 13.6, 8.2 Hz, 1H), 2.08 – 2.00 (m, 1H), 1.99 – 1.92 (m, 1H), 1.89 – 1.80 (m, 1H), 1.77 – 1.66 (m, 1H), 1.66 – 1.54 (m, 2H), 1.34 – 1.25 (m, 1H), 1.23 (d, *J* = 4.1 Hz, 1H).

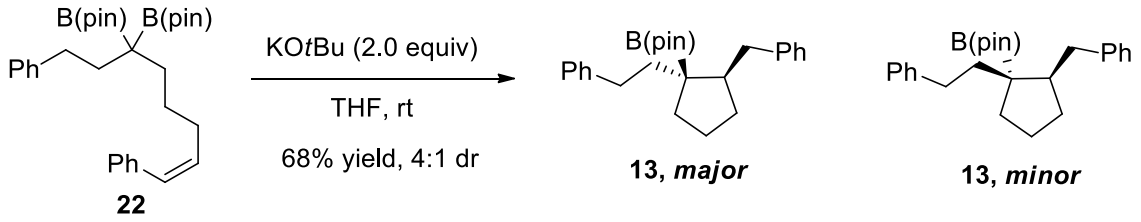
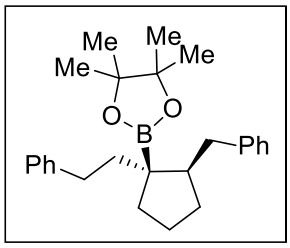


Figure 41 – Deborylative cyclization of (*Z*)-2,2'-(1,8-diphenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

39. Simpson, A. F.; Bodkin, C. D.; Butts, C. P.; Armitage, M. A.; Gallagher, T., Asymmetric reduction of prochiral cycloalkenones. The influence of exocyclic alkene geometry. *Perkin Trans. 1* **2000,** (18), 3047-3054.



2-((1*R*,2*R*)-2-benzyl-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13, *major diastereomer*). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **22** (103.3 mg, 0.2 mmol), KO*t*Bu (44.8 mg, 0.4 mmol) and THF (1 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (52.7 mg, 68%, 4:1 dr). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.12 (m, 10H), 3.01 (dd, *J* = 13.2, 3.3 Hz, 1H), 2.62 (ddd, *J* = 10.4, 5.8, 3.5 Hz, 2H), 2.36 (dd, *J* = 13.2, 11.6 Hz, 1H), 2.20 – 2.04 (m, 2H), 1.81 – 1.47 (m, 5H), 1.46 – 1.31 (m, 2H), 1.31 (s, 6H), 1.31 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.76, 142.91, 128.80, 128.34, 128.25, 128.09, 125.50, 125.44, 83.07, 53.06, 41.31, 39.41, 34.42, 34.17, 31.42, 25.28, 24.89, 22.49; ; IR (neat): 2976.2 (m), 2930.8 (m), 2857.6 (w), 1495.3 (w), 1453.6 (m), 1386.7 (m), 1344.8 (w), 1300.7 (m), 1213.8 (m), 1141.2 (s), 1029.5 (w), 967.3 (w), 855.4 (w), 746.9 (m), 697.9 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{26}{}^{1}H_{39}{}^{11}B_{1}{}^{14}N_{1}{}^{16}O_{2}$ $[M+NH_4]^+$: calculated: 408.3074, found: 408.3091. The relative stereochemistry was assigned by X-ray crystallography.

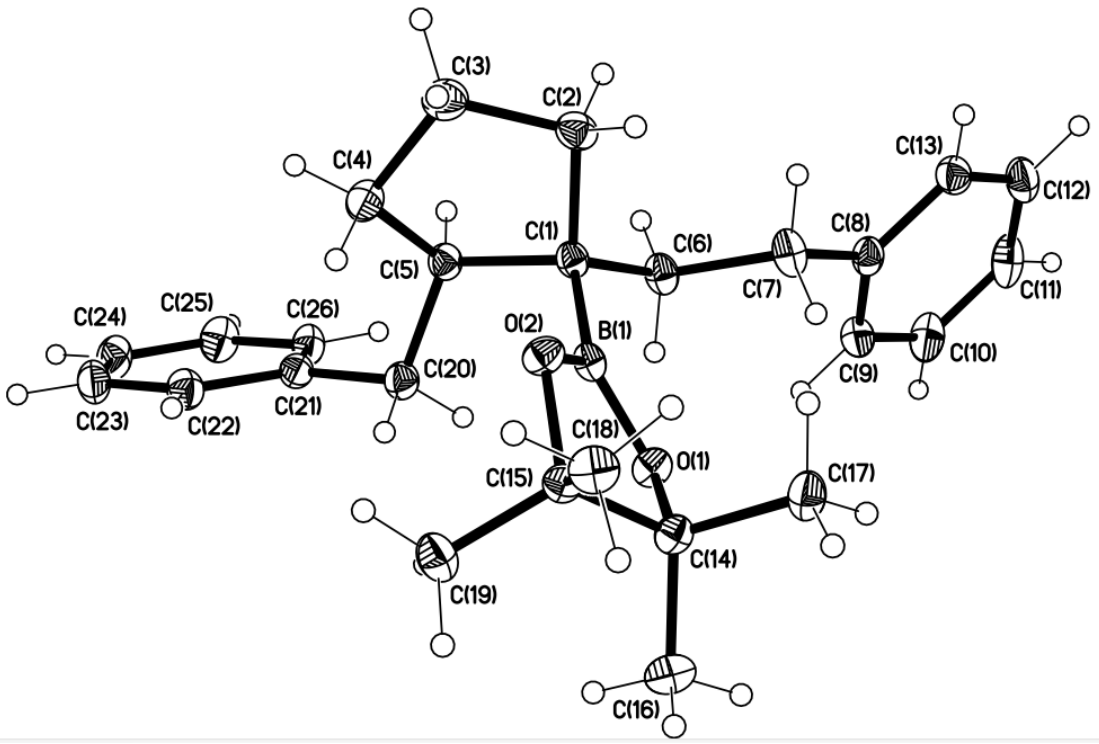
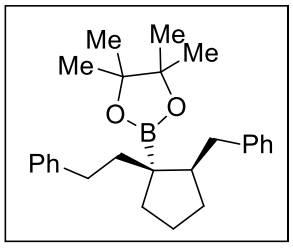


Figure 42 - Crystal of 2-((1*R*,2*R*)-2-benzyl-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



2-((1*S*,2*R*)-2-benzyl-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13, *minor diastereomer*). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.16 (m, 4H), 7.19 – 7.07 (m, 4H), 2.96 (dd, *J* = 13.1, 3.3 Hz, 1H), 2.63 – 2.55 (m, 2H), 2.29 (dd, *J* = 13.1, 11.8 Hz, 1H), 2.18 – 2.10 (m, 1H), 1.87 (ddd, *J* = 13.3, 10.4, 6.4 Hz, 2H), 1.74 – 1.64 (m, 2H), 1.61 – 1.44 (m, 3H), 1.38 – 1.27 (m, 1H), 1.31 (s, 6H), 1.31 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.80, 142.83, 128.81, 128.38, 128.28, 128.11, 125.55, 125.42, 83.05, 48.64, 36.78, 34.07, 33.33, 32.55, 29.80, 24.99, 24.71, 22.71; IR (neat): 2957.0 (s), 2930.9 (s), 2863.3 (m), 1728.6 (m), 1455.6 (w), 1376.6 (m), 1272.7 (m), 1142.1 (s), 1072.5 (w), 747.1 (w), 699.6 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{26}{}^{1}H_{39}{}^{11}B_{1}{}^{14}N_{1}{}^{16}O_{2}$ $[M+NH_4]^+$: calculated: 408.3074, found: 408.3079.

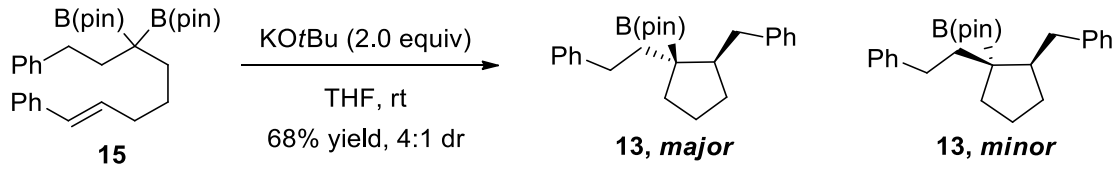
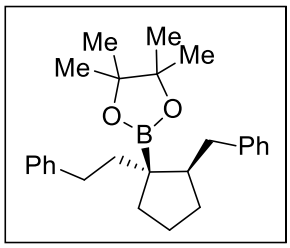
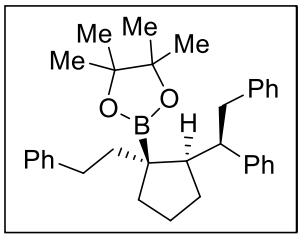


Figure 43 - Deborylative cyclization of (*E*)-2,2'-(1,8-diphenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)



2-((1*R*,2*R*)-2-benzyl-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13, *major diastereomer*). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **15** (103.3 mg, 0.2 mmol), KO*t*Bu (44.8 mg, 0.4 mmol) and THF (1 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (53.5 mg, 68%, 4:1 dr). The spectra is the same as **13** above.



2-((1*R*,2*R*)-2-((*R*)-1,2-diphenylethyl)-1-phenethylcyclopentyl)-4,5,5,5-tetramethyl-1,3,2-dioxaborolane (67). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **22** (103.2 mg, 0.2 mmol), KO*t*Bu (44.8 mg, 0.4 mmol) and THF (1 mL). Upon completion, the reaction mixture is quenched with benzyl bromide (171 mg, 1.0 mmol) and allowed to stir for an additional two hours. Mixture is then diluted with diethyl ether (2 mL) and filtered through a silica gel plug, rinsing with diethyl ether, and concentrated in vacuo. The crude residue is then purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (64 mg, 66 %, >20:1 dr). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (t, *J* = 7.5 Hz, 2H), 7.12 – 6.98 (m, 9H), 6.86 (d, *J* = 7.6 Hz, 4H), 3.19 (dd, *J* = 13.1, 3.7 Hz, 1H), 3.13 (ddd, *J* = 12.1, 8.6, 3.8 Hz, 1H), 2.69 (dd, *J* = 13.2, 11.6 Hz, 1H), 2.40 (td, *J* = 13.2, 4.5 Hz, 1H), 2.37 – 2.29 (m, 1H), 2.17 – 2.07 (m, 1H), 2.00 (ddd,

J = 12.5, 8.4, 3.9 Hz, 2H), 1.84 – 1.67 (m, 2H), 1.68 – 1.57 (m, 1H), 1.45 – 1.33 (m, 1H), 1.32 – 1.24 (m, 1H), 1.27 (s, 6H), 1.27 (s, 6H), 0.84 (td, *J* = 12.9, 5.1 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.65, 141.22, 129.03, 128.71, 128.36, 128.10, 127.87, 127.59, 127.53, 125.51, 125.12, 125.10, 82.77, 54.96, 50.49, 41.69, 39.54, 35.67, 32.65, 30.95, 25.33, 24.83, 21.93; IR (neat): 3026.1 (w), 2929.9 (m), 2859.7 (w), 1728.7 (w), 1495.2 (w), 1453.2 (w), 1380.2 (m), 1141.5 (s), 967.6 (w), 862.8 (w), 746.1 (w), 697.9 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{33}{}^{1}H_{42}{}^{11}B_{1}{}^{16}O_{2}$ $[M+H]^+$: calculated: 481.3278, found: 481.3291. The relative stereochemistry was assigned by X-ray crystallography.

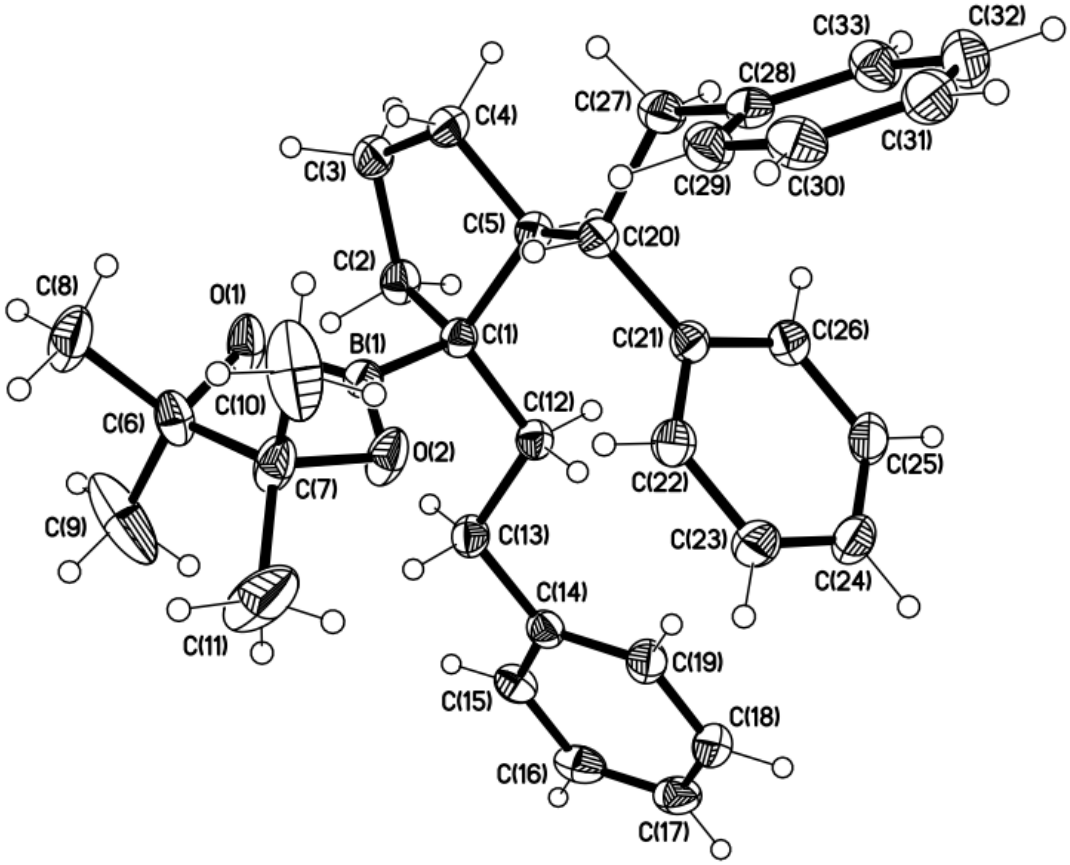
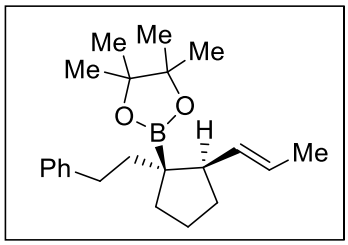
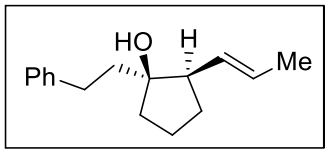


Figure 44 - Crystal of 2-((1*R*,2*R*)-2-((*R*)-1,2-diphenylethyl)-1-phenethylcyclopentyl)-4,5,5,5-tetramethyl-1,3,2-dioxaborolane



4,4,5,5-tetramethyl-2-((1*R*,2*R*)-1-phenethyl-2-((*E*)-prop-1-en-1-yl)cyclopentyl)-1,3,2-dioxaborolane (**17**). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **16** (46.6 mg, 0.1 mmol), KO*t*Bu (22.4 mg, 0.2 mmol) and THF (0.5 mL). Upon completion, the reaction mixture is diluted with diethyl ether (2 mL) and filtered through a silica gel plug, rinsing with diethyl ether, and concentrated in vacuo. The crude residue is then purified on silica gel (hexanes: diethyl ether = 100 : 1, stain in CAM) to afford the desired product as a colorless oil (18.8 mg, 55%, >20:1 dr). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.22 (m, 2H), 7.21 – 7.13 (m, 3H), 5.52 – 5.35 (m, 2H), 2.57 (td, *J* = 12.8, 4.9 Hz, 2H), 2.47 (td, *J* = 12.9, 5.0 Hz, 1H), 1.99 – 1.82 (m, 1H), 1.80 – 1.66 (m, 3H), 1.65 (dd, *J* = 4.8, 0.7 Hz, 3H), 1.63 – 1.55 (m, 2H), 1.53 – 1.47 (m, 1H), 1.42 (td, *J* = 12.9, 5.0 Hz, 1H), 1.26 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.93, 132.52, 128.35, 128.16, 125.39, 124.38, 82.98, 49.25, 34.75, 34.01, 33.06, 31.10, 24.86, 24.71, 23.10, 18.07; IR (neat): 2976.5 (m), 2955.3 (m), 2870.6 (m), 1726.8 (w), 1454.8 (w), 1379.3 (s), 1304.3 (m), 1272.9 (m), 1143.3 (s), 968.1 (w), 857.0 (w), 757.3 (s), 699.3 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{22}{}^{1}H_{34}{}^{11}B_{1}{}^{16}O_2$ $[M+H]^+$: calculated: 341.2652, found: 341.2660.



(1*S*,2*R*)-1-phenethyl-2-((*E*)-prop-1-en-1-yl)cyclopentan-1-ol (**68**). This reaction was performed to comfirm the structure of compound **17**. A 20 mL vial containing compound **17** (25 mg, 0.0745 mmol) is charged with THF (1 mL) followed by aqueous NaOH (0.6 mL, 3 M, 1.8 mmol) then cooled to 0 °C. Hydrogen peroxide (0.3 mL, 30% in H_2O) is then added dropwise and the resulting mixture is allowed to stir overnight, slowly reacting room temperature. Upon return, the reaction is cooled to 0 °C and carefully quenched with saturated, aqueous $Na_2S_2O_3$ (1 mL) and stirred for 30 minutes.

The mixutre is then extrated with diethyl ether, dried over Na_2SO_4, and the combined extracts evaporated in vacuo. The crude residue is then purified by column chromatography (hexanes: ethyl acetate = 100 : 5 to 100 : 10, stain in CAM) on silica gel to afford desired product (11.8 mg, 70 % yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 5.49 (dqd, *J* = 15.1, 6.4, 0.9 Hz, 1H), 5.29 (ddq, *J* = 15.1, 9.2, 1.6 Hz, 1H), 2.80 (ddd, *J* = 13.4, 9.4, 7.5 Hz, 1H), 2.69 (ddd, *J* = 13.5, 9.6, 7.7 Hz, 1H), 2.51 – 2.40 (m, 1H), 2.10 – 2.02 (m, 1H), 1.84 – 1.71 (m, 5H), 1.70 – 1.65 (m, overlap, 1H), 1.67 (dd, *J* = 6.4, 1.7 Hz, 3H), 1.53 – 1.45 (m, 1H), 1.32 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.99, 131.63, 128.88, 128.37, 125.96, 125.68, 83.62, 54.55, 39.24, 37.23, 30.28, 30.19, 21.02, 18.07. The structure was further confirmed by COSY spectra, shown below.

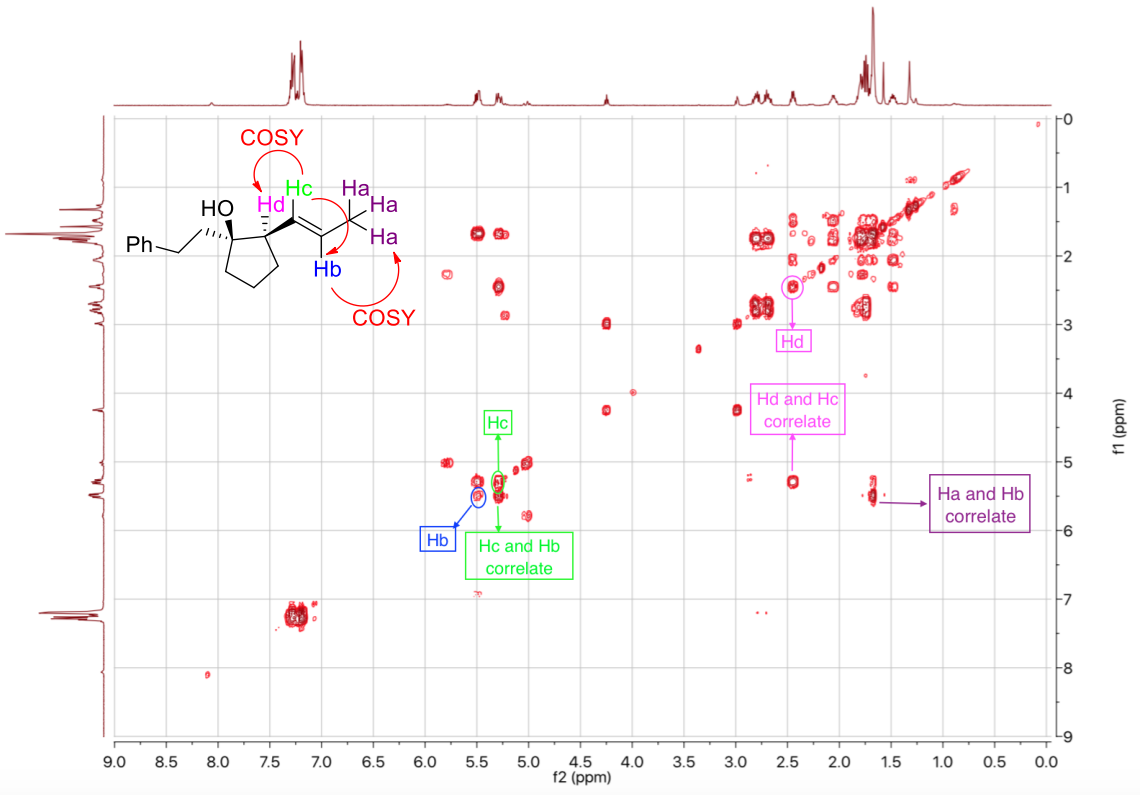
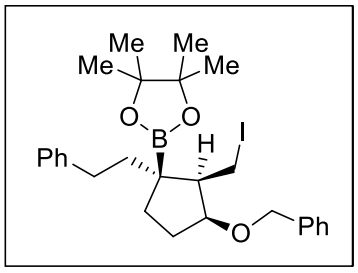


Figure 45 - COSY of (1*S*,2*R*)-1-phenethyl-2-((*E*)-prop-1-en-1-yl)cyclopentan-1-ol



(1*S*,2*R*,3*S*)-2-(iodomethyl)-3-phenethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl benzoate (8, *major product*). The reaction was performed according to *Representative Procedure for Deborylative cyclization* with diboronate ester **61** (55 mg, 0.1 mmol), KO*t*Bu (22.4 mg, 0.20 mmol) and THF (0.5 mL) for overnight. Upon completion, the reaction mixture is quenched with a solution of I_2 (50.8 mg, 0.20 mmol) in anhydrous THF (0.3 mL) and allowed to stir at room temperature for three hours. Reaction mixture is then diluted with diethyl ether (2 mL) and filtered through a silica gel plug, rinsing with diethyl ether. Filtrate is then concentrated in vacuo and the crude residue purified by column chromatography on silica gel (100 : 0.8 Hexanes/EtOAc, gradient to 100 : 3 Hexanes/EtOAc, stain in CAM) to afford a colorless oil (29.3 mg, 55%, product **8** : product **69** = 2.9 : 1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 – 7.38 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.24 (m, 3H), 7.20 – 7.14 (m, 3H), 4.55 (d, *J* = 1.9 Hz, 2H), 3.81 (qd, *J* = 4.6, 3.2 Hz, 1H), 3.52 (dd, *J* = 9.8, 4.8 Hz, 1H), 3.21 (t, *J* = 10.1 Hz, 1H), 2.67 – 2.50 (m, 2H), 2.28 (dt, *J* = 10.0, 4.8 Hz, 1H), 2.10 – 1.94 (m, 3H), 1.85 – 1.75 (m, 1H), 1.75 – 1.61 (m, 2H), 1.26 (two sets of singlet, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.05, 138.81, 128.30, 128.26, 128.24, 127.85, 127.36, 125.59, 87.16, 83.41, 71.26, 57.60, 41.33, 33.47, 33.27, 30.50, 25.07, 24.90, 8.22; IR (neat): 2975.4 (w), 2926.7 (w), 2855.7 (w), 1495.8 (w), 1378.8 (m), 1310.9 (m), 1198.9 (m), 1166.4 (s), 1140.4 (s), 1099.2 (m), 1066.9 (m), 856.9 (m), 735.0 (s), 697.3 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{27}{}^{1}H_{36}{}^{11}B_{1}{}^{16}O_{3}{}^{127}I_{1}{}^{23}Na_{1}$ $[M+Na]^+$: calculated: 569.1700, found: 569.1707. The relative stereochemistry was assigned by COSY and NOESY spectra, shown below.

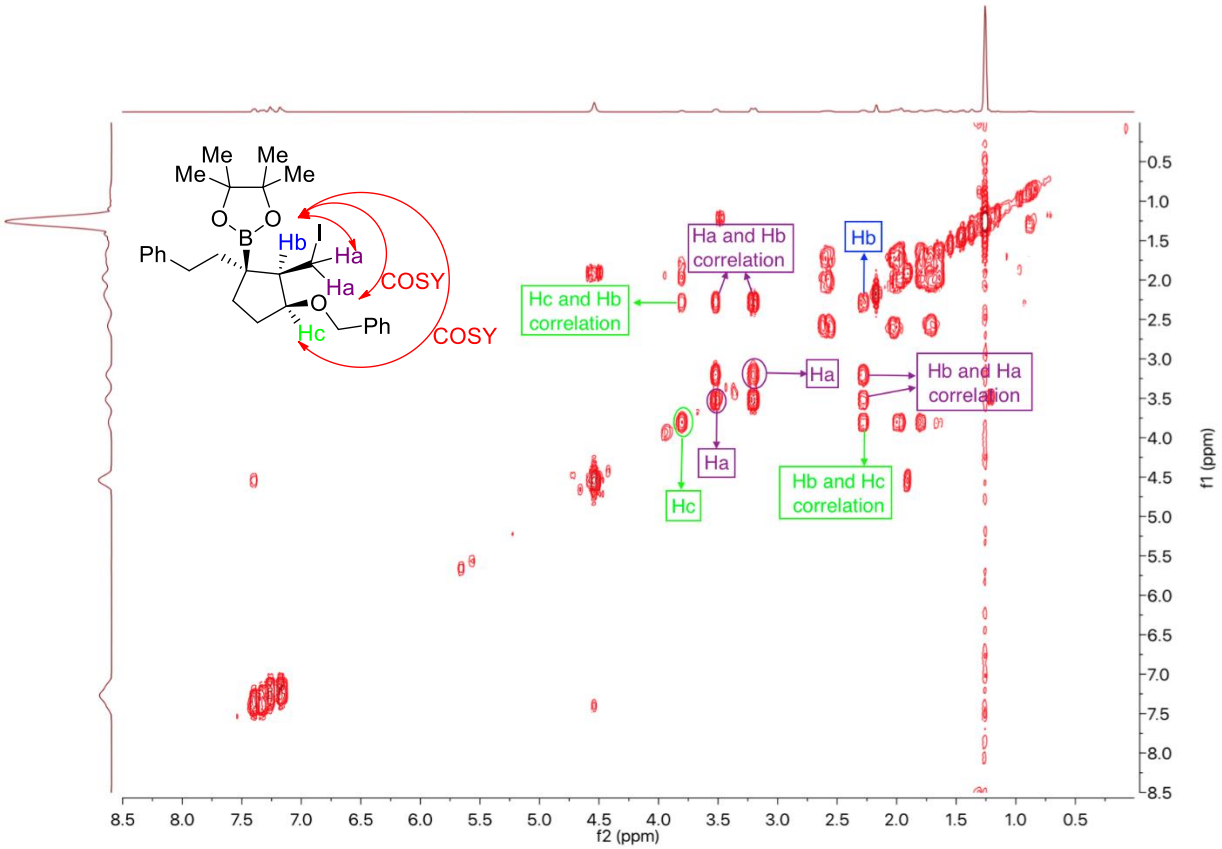


Figure 46 - COSY of (1*S*,2*R*,3*S*)-2-(iodomethyl)-3-phenethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl benzoate

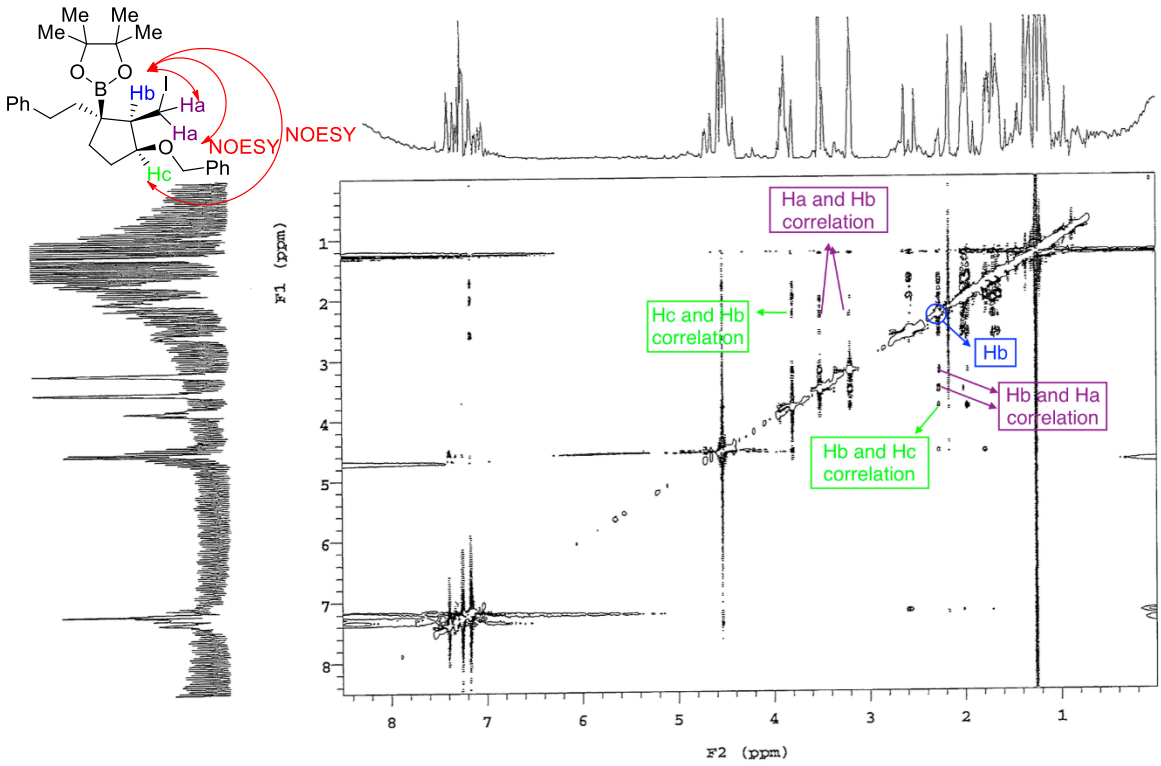
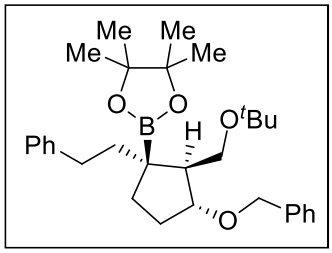


Figure 47 - NOESY of (1*S*,2*R*,3*S*)-2-(iodomethyl)-3-phenethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl benzoate



2-((1*S*,2*S*,3*R*)-3-(benzyloxy)-2-(*tert*-butoxymethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (69, *minor product*). This product was isolated along side the above product (**8**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.28 – 7.22 (m, 3H), 7.21 – 7.17 (m, 2H), 7.17 – 7.13 (m, 1H), 4.57 (d, *J* = 12.3 Hz, 1H), 4.50 (d, *J* = 12.3 Hz, 1H), 3.82 (dt, *J* = 6.9, 3.5 Hz, 1H), 3.52 (dd, *J* = 8.8, 5.0 Hz, 1H), 3.18 (dd, *J* = 9.8, 8.8 Hz, 1H), 2.68 – 2.47 (m, 2H), 2.07 – 1.92 (m, 3H), 1.87 (ddd, *J* = 11.5, 7.1, 4.1 Hz, 1H), 1.83 – 1.67 (m, 2H), 1.63 (ddd, *J* = 11.9, 9.5, 7.4 Hz, 1H), 1.26 (s, 12H), 1.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.68, 139.66, 128.39, 128.17, 128.12, 127.59, 127.00, 125.38, 84.60, 82.99, 72.49, 70.49, 62.86, 56.23, 41.83, 33.73, 32.97, 31.65, 27.66, 25.11, 24.93; IR (neat): 3026.0 (w), 2972.8 (s), 2927.6 (m), 2857.0 (m), 1496.0 (m), 1378.4 (s), 1307.1 (m), 1198.5 (m),

1143.6 (s), 1073.9 (m), 857.5 (w), 698.5 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{31}{}^{1}H_{45}{}^{11}B_{1}{}^{16}O_{4}{}^{23}Na_{1}$ $[M+Na]^{+}$: calculated: 515.3309, found: 515.3320. The relative stereochemistry was assigned by X-ray crystallography, shown below:

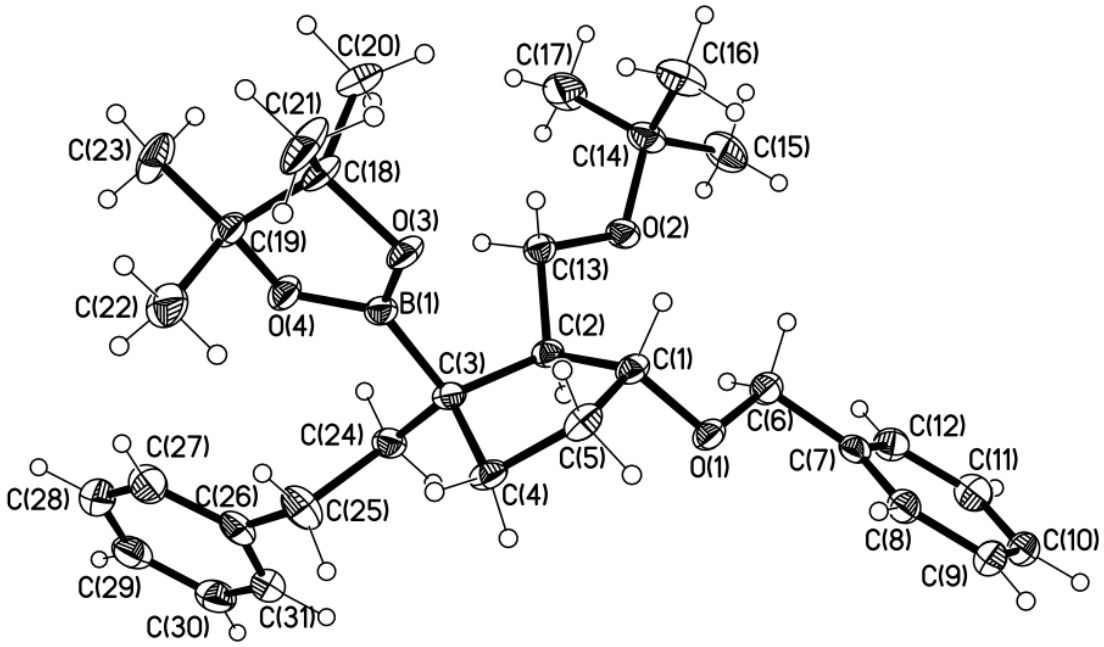
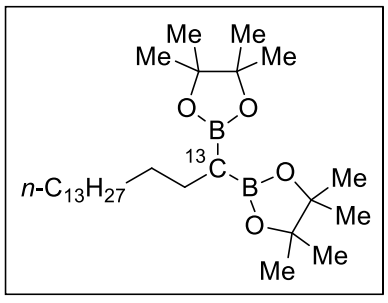


Figure 48 – Crystal of 2-((1*S*,2*S*,3*R*)-3-(benzyloxy)-2-(*tert*-butoxymethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

D. Mechanistic Studies

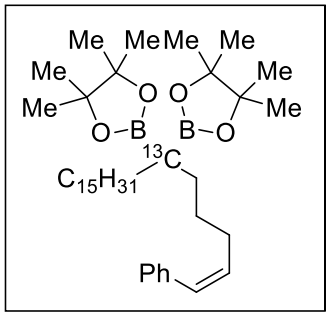
i) Analysis of Reaction Intermediates by ^{13}C NMR Experiments



2,2'-(hexadecane-1,1-diyl-1-13C)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane (70). Prepared from palmitic acid-1-^{13}C according to the literature procedure.[5] ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.55-1.53 (m, 2H), 1.31-1.22 (m, 50H), 0.88 (t, J = 6.9 Hz, 3H), 0.71 (2dt, J = 111.5, 7.8 Hz, 1H). ^{13}C NMR (125 MHz,

5. Hong, K.; Liu, X.; Morken, J. P., Simple Access to Elusive α-Boryl Carbanions and Their Alkylation: An Umpolung Construction for Organic Synthesis. *J. Am. Chem. Soc.* **2014,** *136* (30), 10581-10584.

CDCl3): δ 82.8, 32.6, 31.9, 29.71, 29.70, 29.67, 29.65, 29.62, 29.59, 29.55, 29.4, 25.8, 25.6, 24.8, 24.5, 22.7, 14.1, 10.7 (br, ^{13}***C***-B).



(*Z*)-2,2'-(1-phenylhenicos-1-ene-6,6-diyl-6-^{13}*C*)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (18). Prepared according to *Representative Procedure for Preparation of geminal-Diboronate Esters (Method D)* with **70** (250 mg, 0.52 mmol), LTMP (92 mg, 0.624 mmol), (*Z*)-(5-bromopent-1-en-1-yl)benzene (141 mg, 0.624mmol) and THF (2.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (100:1 hexanes/ethyl acetate, stain in CAM) to afford a colorless oil (191 mg, 59%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.24 (m, 4H), 7.19 (t, *J* = 7.0 Hz, 1H), 6.36 (d, *J* = 11.7 Hz, 1H), 5.70 (dt, *J* = 11.8, 7.2 Hz, 1H), 2.60 – 2.22 (m, 2H), 1.71 – 1.63 (m, 2H), 1.59 (dt, *J* = 7.8, 4.1 Hz, 2H), 1.37 (t, *J* = 7.9 Hz, 2H), 1.31 – 1.22 (m, 26H), 1.21 (s, 24H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{1}H NMR (500 MHz, THF-d_8): δ 7.38 – 7.20 (m, 4H), 7.20 – 7.11 (m, 1H), 6.48 – 6.25 (d, *J* = 11.8 Hz, 1H), 5.71 – 5.58 (m, 1H), 2.36 – 2.22 (m, 2H), 1.67 – 1.52 (m, 4H), 1.48 – 1.37 (m, 2H), 1.29 (d, *J* = 2.6 Hz, 26H), 1.22 – 1.11 (m, 24H), 0.93 – 0.84 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.87, 133.55, 128.73, 128.34, 128.01, 126.27, 82.84, 31.91, 30.40, 30.37, 29.71, 29.69, 29.66, 29.64, 29.61, 29.34, 29.01, 28.94, 28.78, 28.70, 27.67, 27.11, 24.71, 22.67, 19.28 (br, ^{13}***C***-B), 14.09; ^{13}C NMR (125 MHz, THF-d_8): δ 139.00, 134.07, 129.71, 129.61, 128.95, 127.25, 83.55, 33.05, 31.73, 30.84, 30.78, 30.76, 30.49, 30.36, 28.81, 28.17, 23.74, 20.13(br, ^{13}***C***-B), 14.60; IR (neat): 2958.2 (m), 2924.6 (s), 2854.5 (m), 1729.3 (m), 1463.0 (w), 1377.4 (w), 1344.6 (w), 1288.6 (s), 1269.5 (s), 1138.7 (s), 1072.3 (w), 854.8 (w), 700.0 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{38}{}^{13}C_1{}^1H_{68}{}^{11}B_2{}^{16}O_4$ $[M+H]^+$: 624.5416, found: 624.5418.

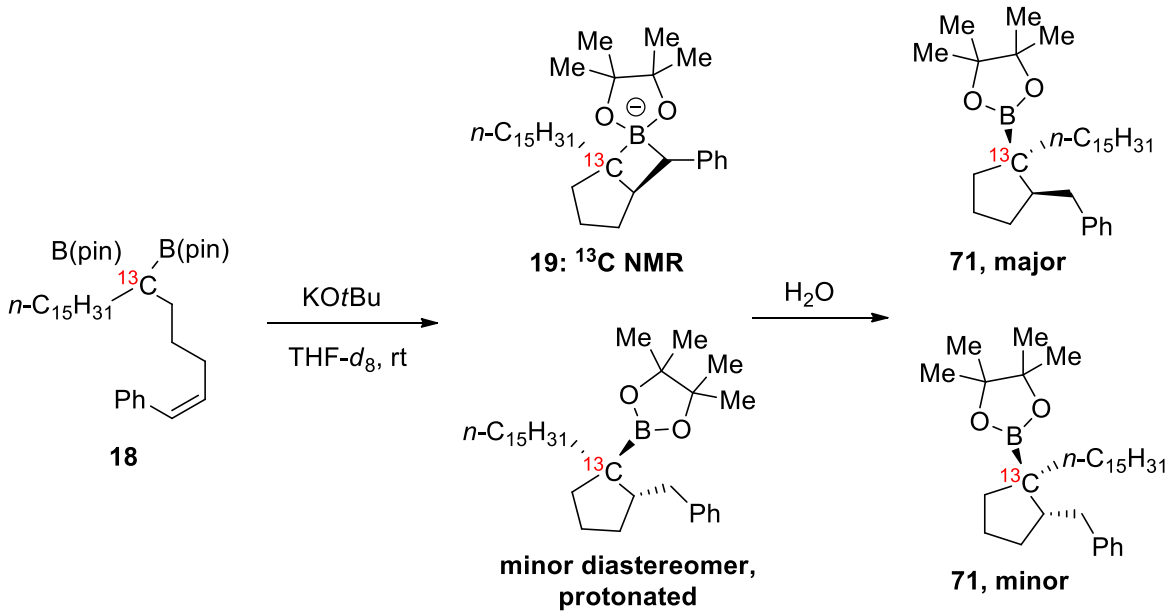


Figure 49 - ^{13}C NMR experiment of (*Z*)-2,2'-(1-phenylhenicos-1-ene-6,6-diyl-6-^{13}*C*)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

In the glove box, an oven-dried NMR tube is charged with diboronate ester **18** (31.2 mg, 0.05 mmol), KO*t*Bu (11.2 mg, 0.1 mmol) and THF-d_8 (0.60 mL). The NMR tube is then sealed with a rubber septum, removed from the glove box, and monitored by ^{13}C NMR at 25 °C. After 7 hours, water (2.7 µL, 0.15 mmol) is added via syringe, and the mixture again observed by ^{13}C NMR. At this point, the reaction mixture is diluted with diethyl ether, filtered through a silica gel plug, rinsed with diethyl ether, and concentrated in vacuo. The crude reaction mixture is purified on silica gel (hexanes: ethyl acetate = 100:0.6) to afford the desired product **71** (19.6 mg, 79% yield, dr > 10:1) together with protodeborylation byproduct (2.1 mg).

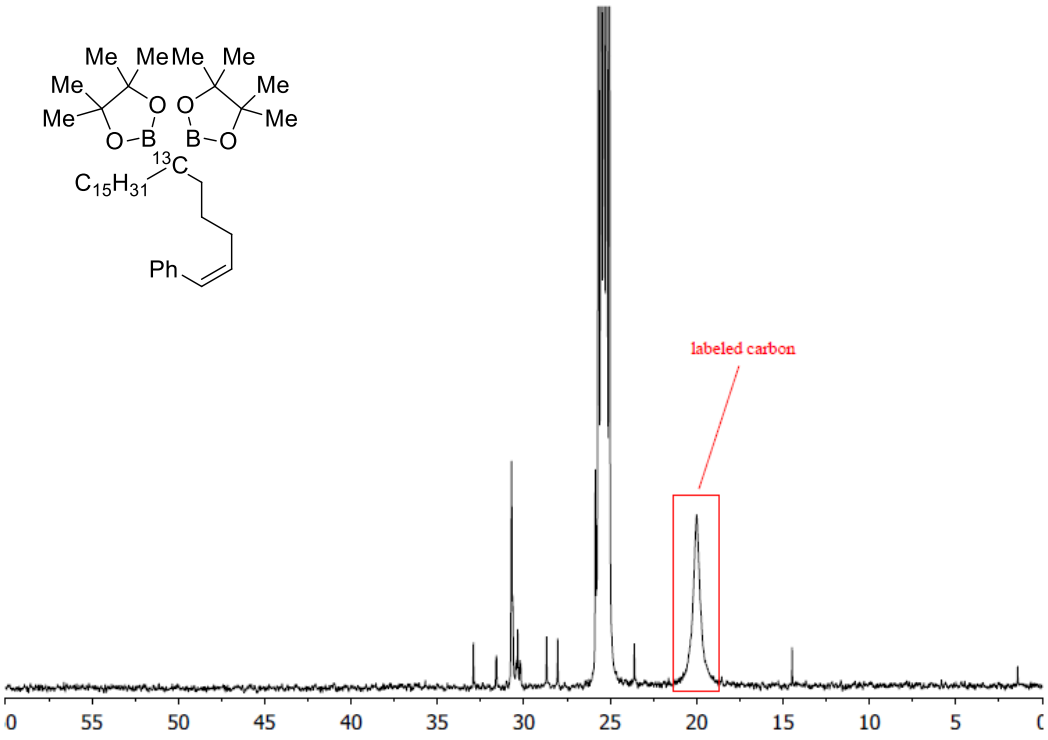


Figure 50 - ^{13}C NMR of ^{13}C labeled starting material **18** in d_8-THF

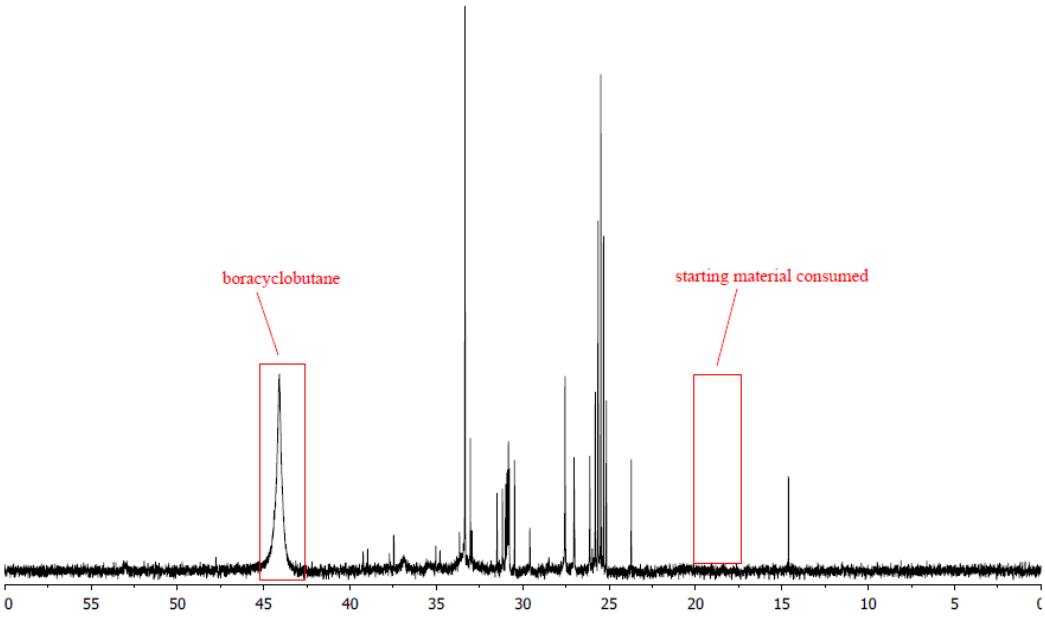


Figure 51 – *in situ* ^{13}C NMR analysis of the reaction of ^{13}C-labeled substrate **18** with KO*t*Bu after 30 minutes in d_8-THF

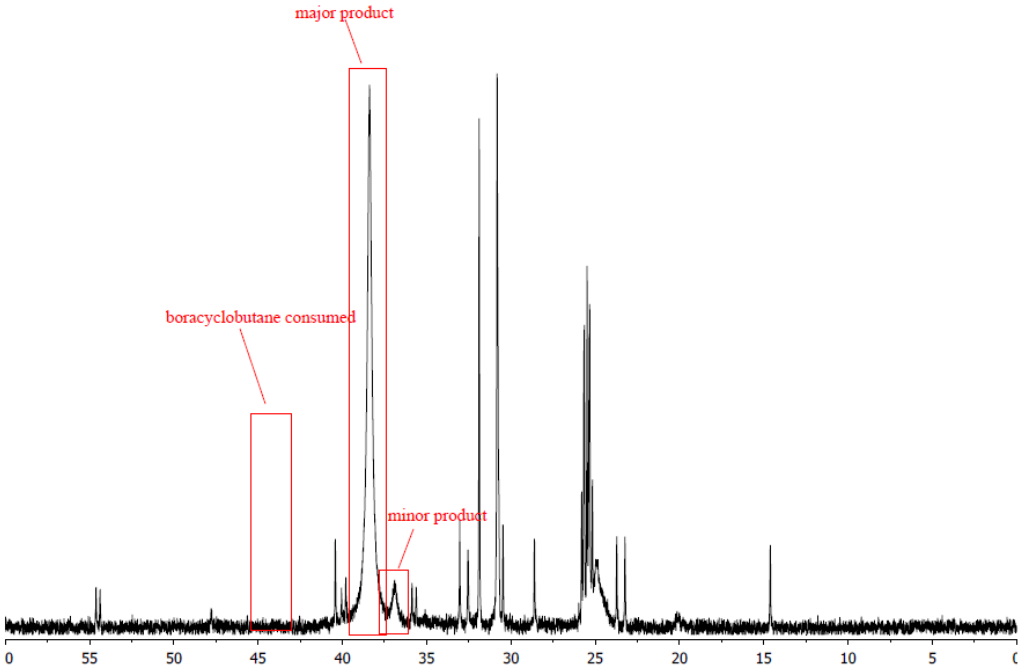


Figure 52 - *in situ* ^{13}C NMR analysis of reaction of ^{13}C-labeled substrate **18** with KO*t*Bu, 1 minute after quenching with H_2O

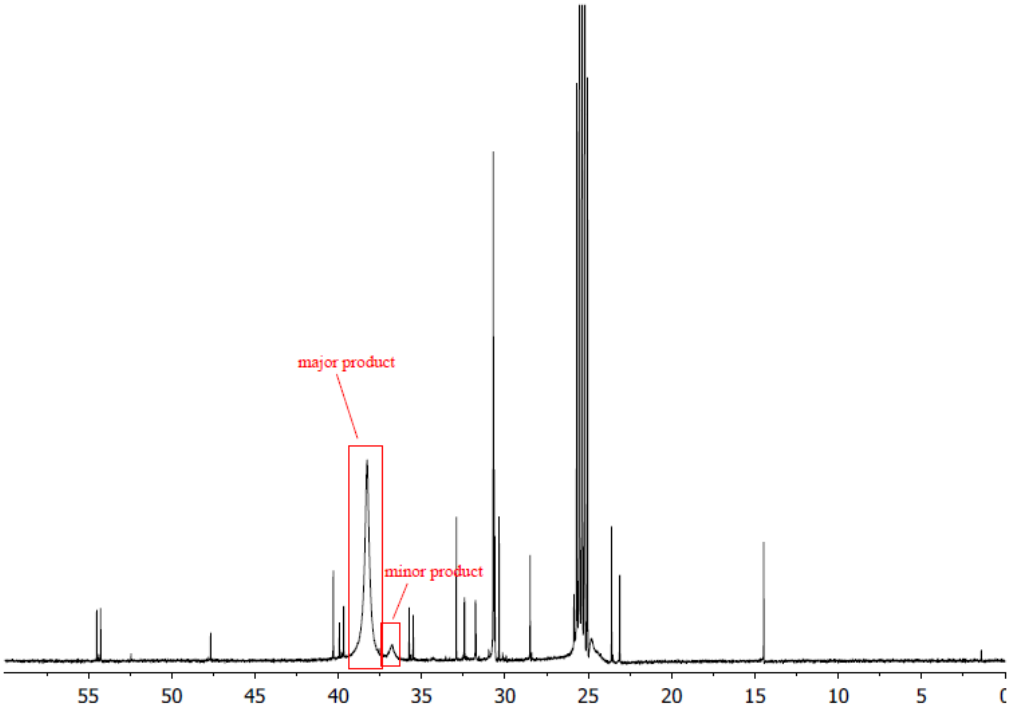
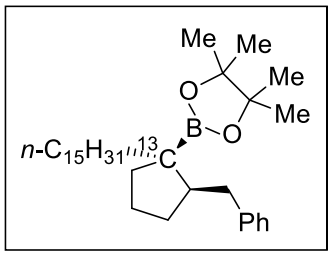


Figure 53 - ^{13}C NMR of 2-(2-benzyl-1-pentadecylcyclopentyl-1-^{13}C)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in d_8-THF



2-(2-benzyl-1-pentadecylcyclopentyl-1-^{13}C)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (**71, *major diastereomer*)** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.22 (m, 2H), 7.17 – 7.13 (m, 3H), 2.99 (dt, J = 13.4, 2.4 Hz, 1H), 2.32 (ddd, J = 13.1, 11.5, 1.4 Hz, 1H), 1.97 (dddd, J = 12.5, 8.7, 4.7, 1.5 Hz, 1H), 1.82 – 1.74 (m, 1H), 1.73 – 1.56 (m, 3H), 1.52 – 1.41 (m, 1H), 1.35 – 1.18 (m, 40H), 1.12 – 1.03 (m, 1H), 0.88 (t, J = 6.9 Hz, 3H); ^{1}H NMR (500 MHz, THF-d_8): δ 7.21 – 7.16 (m, 2H), 7.13 – 7.06 (m, 3H), 2.98 (dt, J = 13.5, 2.6 Hz, 1H), 2.41 – 2.28 (m, 1H), 2.08 – 1.96 (m, 1H), 1.90 – 1.78 (m, 1H), 1.67 – 1.52 (m, 2H), 1.51 – 1.41 (m, 2H), 1.37 – 1.23 (m, 38H), 1.22 – 1.14 (m, 2H), 1.11 – 1.02 (m, 1H), 0.89 (td, J = 6.9, 2.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.12, 128.80, 128.03, 125.35, 82.85, 53.05, 52.82, 39.37, 38.77, 38.52(br, ^{13}***C***-B), 37.33, 34.40, 34.16, 31.91, 31.32, 31.29, 30.70, 30.66, 29.69, 29.67, 29.64, 29.62, 29.34, 27.45, 25.14, 24.83, 24.79, 22.67, 22.38, 14.09; ^{13}C NMR (125 MHz, THF-d_8): δ 144.03, 144.00, 129.64, 128.94, 126.31, 83.89, 54.63, 54.40, 47.79, 40.43, 40.07, 39.81, 38.41(br, ^{13}***C***-B), 35.88, 35.64, 33.05, 32.57, 32.55, 31.91, 31.88, 30.86, 30.83, 30.79, 30.74, 30.49, 28.62, 23.74, 23.25, 14.61; IR (neat): 2956.4 (m), 2923.6 (s), 2853.7 (m), 1728.8 (m), 1462.6 (w), 1378.0 (w), 1287.5 (m), 1141.5 (m), 1072.2 (w), 743.0 (w), 699.7 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{32}{}^{13}C_1{}^{1}H_{58}{}^{11}B_1{}^{16}O_2$ $[M+H]^+$: calculated: 498.4563, found: 498.4574.

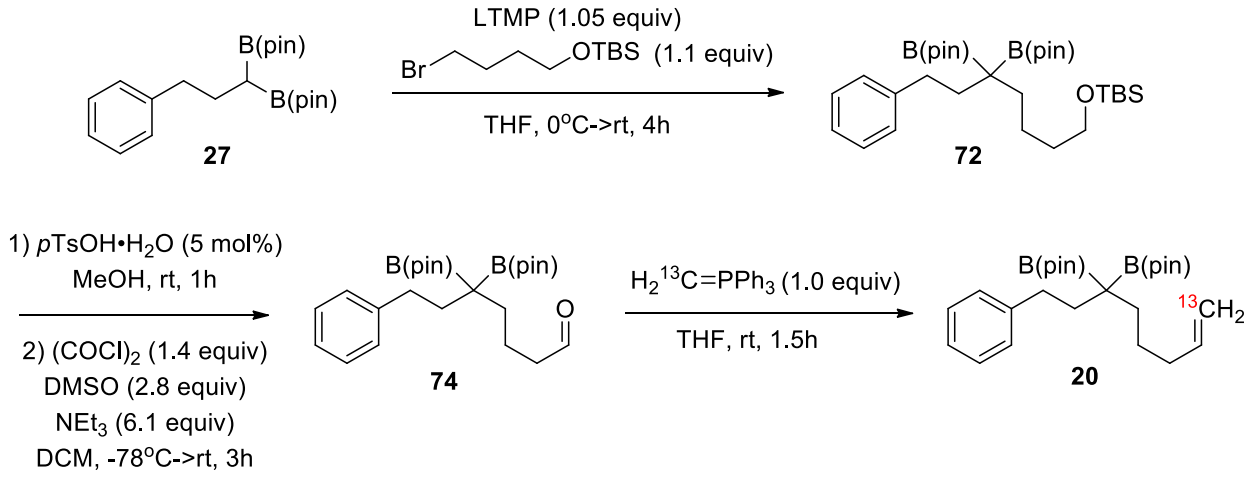
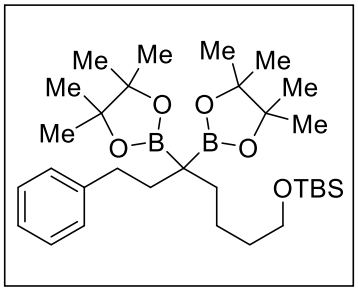
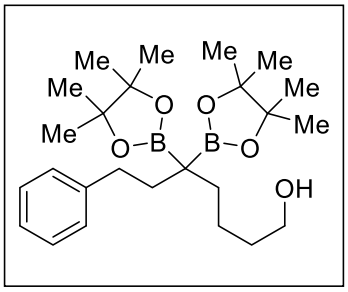


Figure 54 - Forward synthesis of 2,2'-(1-phenyloct-7-ene-3,3-diyl-8-13C)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

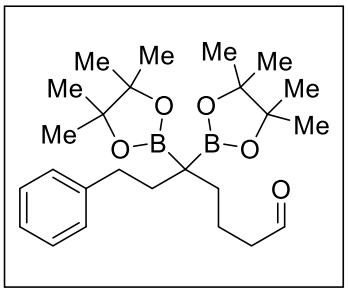


***tert*-butyldimethyl((7-phenyl-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)oxy)silane (72).** The reaction was performed according to *Representative Procedure (Method D)* with diboronate ester **27** (372.3 mg, 1.0 mmol), LTMP (155 mg, 1.05 mmol), (4-bromobutoxy)(*tert*-butyl)dimethylsilane (294.0 mg, 1.10 mmol) and THF (4 mL). The crude reaction mixture was purified by column chromatography on silica gel (1% EtOAc/Hexanes, gradient to 3% EtOAc/Hexanes, visualized with CAM stain) to afford a clear, colorless oil (522.9 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.21 (m, 2H), 7.21 – 7.17 (m, 2H), 7.16 – 7.10 (m, 1H), 3.62 (t, J = 6.5 Hz, 2H), 2.55 – 2.45 (m, 2H), 1.94 – 1.84 (m, 2H), 1.76 – 1.66 (m, 2H), 1.58 – 1.49 (m, 2H), 1.38 – 1.27 (m, 2H), 1.23 (s, 24H), 0.89 (s, 9H), 0.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.83 (s), 128.50 (s), 128.07 (s), 125.32 (s), 82.95 (s), 63.52 (s), 33.89 (s), 33.84 (s), 31.92 (s), 29.02 (s), 26.00 (s), 24.82 (s), 24.70 (s), 23.64 (s), 18.34 (s), -5.22 (s); IR (neat): 2977.0 (w), 2928.8 (m), 2857.4 (w), 1349.2 (m), 1306.0 (m), 1253.9

(m), 1138.3 (s), 1101.4 (m), 850.4 (m), 835.8 (m), 775.0 (m), 699.0 (m) cm^{-1}. HRMS-(DART+) for $^{12}C_{31}{}^{1}H_{57}{}^{11}B_2{}^{16}O_5{}^{28}Si_1$ [M+H]: calculated: 559.4161, found: 559.4183.

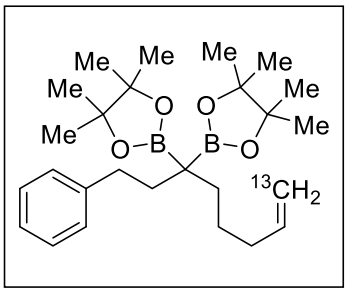


7-phenyl-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-1-ol (73). A 20 mL vial containing **72** (482 mg, 0.86 mmol, 1.0 equiv) and magnetic stirbar is loaded with reagent grade MeOH (6.9 mL, 0.125 M). The heterogeneous mixture is set to stir at room temperature, then *p*-TsOH monohydrate added (8.2 mg, 0.04 mmol, 0.05 equiv). The mixture almost immediately becomes homogeneous. Allowed to stir 1h at rt then volatile components removed in vacuo. Resulting crude oil is then purified by SiO_2 chromatography (5% EtOAc/Hexanes, gradient to 25% EtOAc/Hexanes, visualized with $KMnO_4$ stain). Product isolated as white solid (356.3 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.22 (m, 2H), 7.22 – 7.17 (m, 2H), 7.16 – 7.11 (m, 1H), 3.73 – 3.65 (m, 2H), 2.56 – 2.48 (m, 2H), 1.93 – 1.85 (m, 2H), 1.75 – 1.64 (m, 3H), 1.64 – 1.56 (m, 2H), 1.44 – 1.31 (m, 2H), 1.23 (s, 24H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.67 (s), 128.46 (s), 128.11 (s), 125.39 (s), 83.06 (s), 62.33 (s), 33.84 (s), 32.72 (s), 32.13 (s), 27.98 (s), 24.79 (s), 24.66 (s), 23.03 (s); IR (neat): 3457.7 (w, br), 2977.0 (w), 2929.0 (w), 2861.0 (w), 1348.8 (m), 1307.5 (s), 1250.7 (m), 1137.6 (s), 853.2 (m), 699.8 (w) cm^{-1}. HRMS-(DART+) for $^{12}C_{25}{}^{1}H_{43}{}^{11}B_2{}^{16}O_5$ [M+H]: calculated: 445.3297, found: 445.3286.



7-phenyl-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanal (74). A flame dried 20 mL vial equipped with magnetic stirbar is sealed with rubber septum then evacuated/backfilled with N_2 3x. The vial is then charged with $(COCl)_2$ (71.1 μL, 0.84 mmol, 1.4 equiv) followed by anhydrous DCM (0.3 mL). The solution is

then set to stir at -78ºC and anhydrous DMSO (119 µL, 1.67 mmol, 2.8 equiv) was added dropwise, significant gas evolution noted. The mixture was allowed to stir at -78ºC for ca. 10min. A solution of **73** in anhydrous DCM (0.3 mL) is then added dropwise, followed immediately by the slow addition of freshly distilled NEt_3 (507 µL, 3.64 mmol, 6.1 equiv; salt formation observed). The vessel and contents were then allowed to warm to room temperature and stir an additional 3h. Volatiles were then removed by high vacuum and the organics redissolved in EtOAc. Organics were washed with a saturated, aqueous Na_2CO_3 solution then concentrated to yield crude oil. Oil purified by SiO_2 chromatography (5% EtOAc/Hexanes, gradient to 10% EtOAc/Hexanes, visualized with CAM stain). Product isolated as white solid (232 mg, 0.52 mmol, 88%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.27 – 7.22 (m, 2H), 7.22 – 7.18 (m, 2H), 7.18 – 7.11 (m, 1H), 2.55 – 2.49 (m, 2H), 2.46 – 2.40 (m, 2H), 1.95 – 1.89 (m, 2H), 1.75 – 1.69 (m, 2H), 1.66 – 1.59 (m, 2H), 1.23 (s, 24H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 203.07 (s), 143.53 (s), 128.48 (s), 128.14 (s), 125.45 (s), 83.12 (s), 44.61 (s), 33.83 (s), 31.89 (s), 28.98 (s), 24.81 (s), 24.72 (s), 19.86 (s); IR (neat): 2977.3 (w), 2931.7 (w), 1708.3 (m), 1454.9 (w), 1310.4 (m), 1252.4 (m), 1137.5 (s), 853.9 (w) cm^{-1}. HRMS-(DART+) for $^{12}C_{25}{}^{1}H_{41}{}^{11}B_2{}^{16}O_5$ [M+H]: calculated: 443.3140, found: 443.3138.



2,2'-(1-phenyloct-7-ene-3,3-diyl-8-^{13}*C*)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (20). A flame dried, 20 mL vial equipped with magnetic stirbar is charged with Methyl-^{13}*C*-triphenylphosphonium iodide[40] (212 mg, 0.52 mmol, 1 equiv) and KO*t*Bu (59 mg, 0.52 mmol, 1 equiv) inside an argon-filled glovebox. Anhydrous THF is

40. Christopher Braddock, D.; Clarke, J.; Rzepa, H. S., Epoxidation of bromoallenes connects red algae metabolites by an intersecting bromoallene oxide - Favorskii manifold. *Chem. Commun.* **2013,** *49* (95), 11176-11178.

then charged into the vessel (1.5 mL) to give a vivid yellow solution. Vessel is sealed with a rubber septum and moved to the fume hood where it is allowed to stir for 1h at room temperature. A solution of **74** (231 mg, 0.52 mmol, 1 equiv) in anhydrous THF (1.5 mL) is then added to the reaction vessel. The yellow color fades and a white suspension remains. The suspension is allowed to stir for 1.5h at room temperature at which point it is passed through a pad of SiO_2, rinsing with Et_2O. The resulting clear, colorless solution is concentrated to give a white solid. Product is isolated by SiO_2 chromatography (1% EtOAc/Hexanes, gradient to 5% EtOAc/Hexanes, visualized by CAM stain) to give white solid (208 mg, 0.47 mmol, 91%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26 – 7.22 (m, 2H), 7.22 – 7.18 (m, 2H), 7.16 – 7.09 (m, 1H), 5.86 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H), 5.01 (ddd, *J* = 153.4, 17.2, 1.8 Hz, 1H), 4.93 (ddd, *J* = 156.8, 10.2, 2.0 Hz, 1H), 2.54 – 2.47 (m, 2H), 2.11 – 2.04 (m, 2H), 1.93 – 1.85 (m, 2H), 1.75 – 1.69 (m, 2H), 1.43 – 1.34 (m, 2H), 1.23 (s, 24H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.78 (s), 139.32 (d, *J* = 69.2 Hz), 128.49 (s), 128.09 (s), 125.35 (s), 113.98 (s, ^{13}***C***), 82.98 (s), 34.55 (s), 33.84 (s), 31.88 (s), 28.67 (s), 26.65 (d, *J* = 3.6 Hz), 24.80 (s), 24.71 (s); ^{13}C NMR (150 MHz, THF-d_8): δ 144.93 (s), 140.06 (d, *J* = 69.4 Hz), 129.10 (s), 128.85 (s), 126.08 (s), 114.36 (s, ^{13}***C***), 94.79 (s), 83.58 (s), 35.70 (s), 34.87 (s), 33.59 (s), 29.96 (s), 27.61 (d, *J* = 3.6 Hz); IR (neat): 2977.9 (w), 2927.4 (w), 2858.9 (w), 1352.9 (w), 1307.7 (2), 1255.5 (w), 1139.2 (m), 855.6 (w) cm^{-1}. HRMS-(DART+) for $^{12}C_{25}{}^{13}C_1{}^{1}H_{43}{}^{11}B_2{}^{16}O_4$ [M+H]: calculated: 442.3381, found: 442.3388.

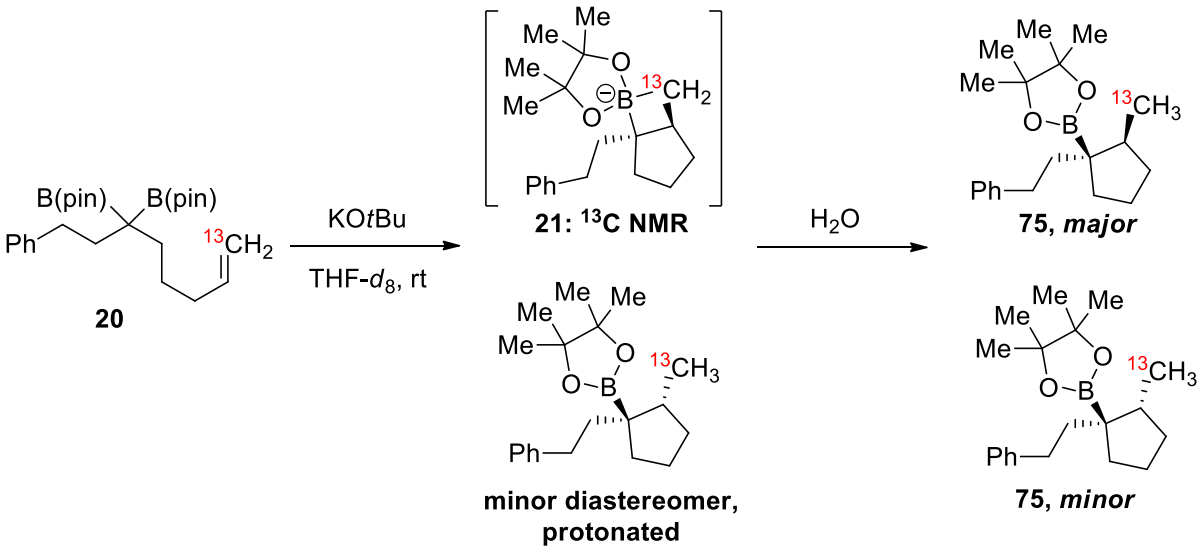


Figure 55 - ^{13}C NMR experiment of 2,2'-(1-phenyloct-7-ene-3,3-diyl-8-^{13}*C*)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

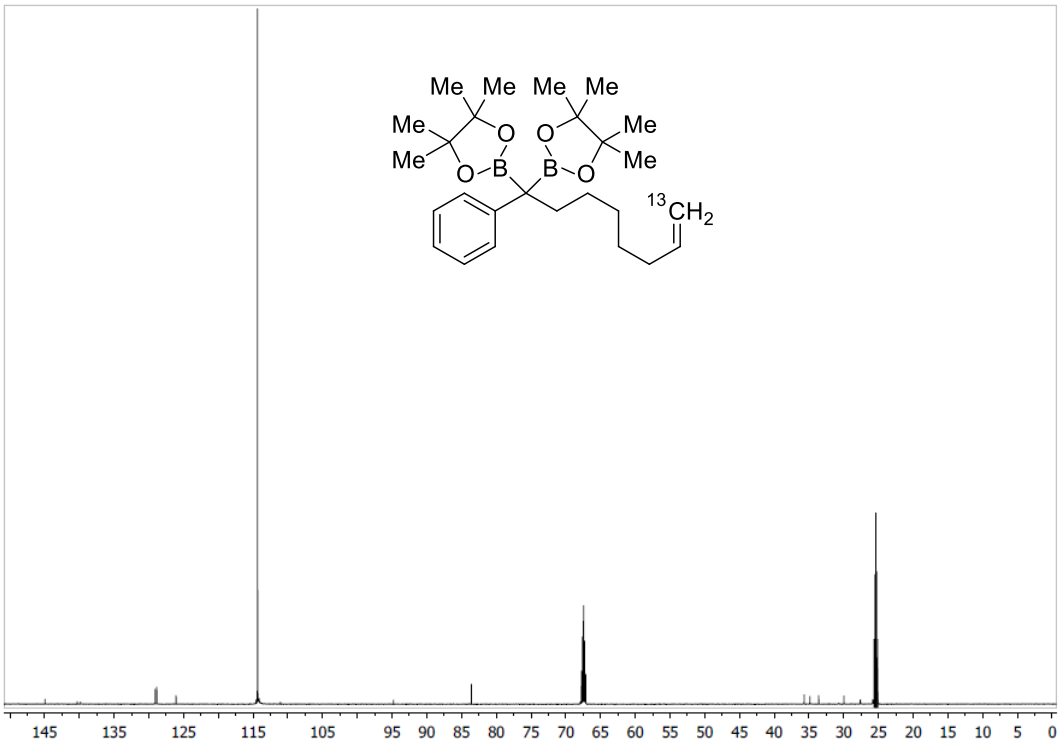


Figure 56 - ^{13}C NMR of ^{13}C-labeled starting material **20** in d_8-THF

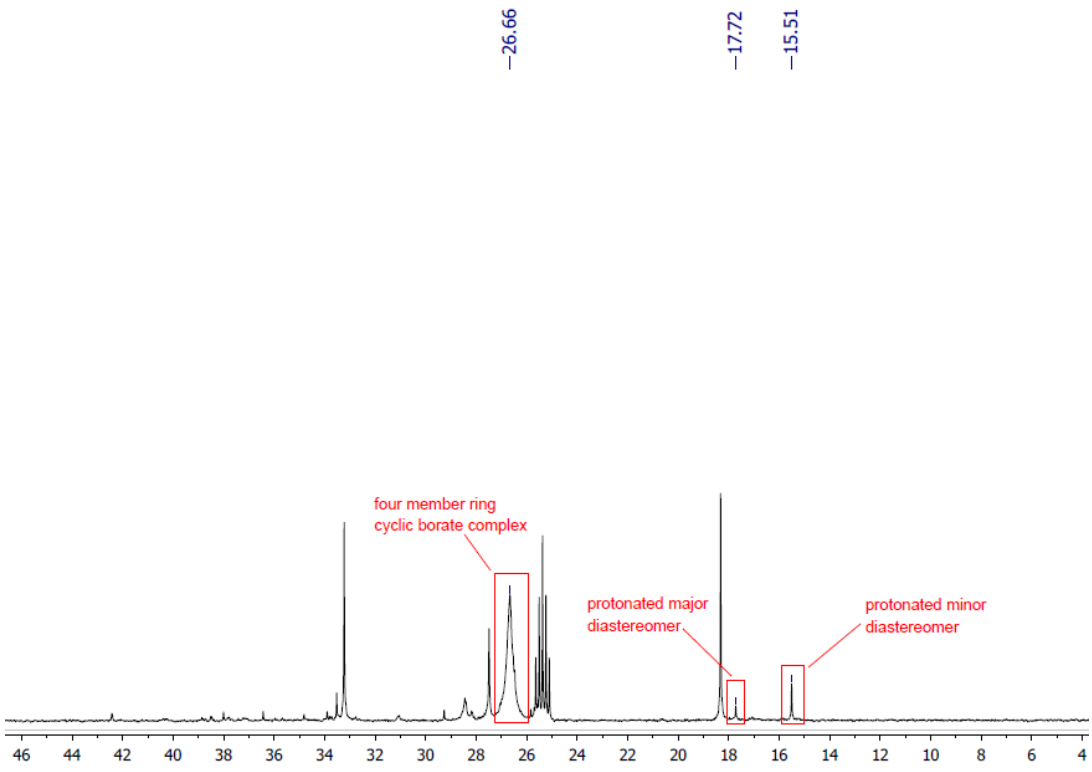


Figure 57 - in situ ^{13}C NMR analysis of the reaction of ^{13}C-labeled substrate **20** with KO*t*Bu after 20 minutes in d_8-THF

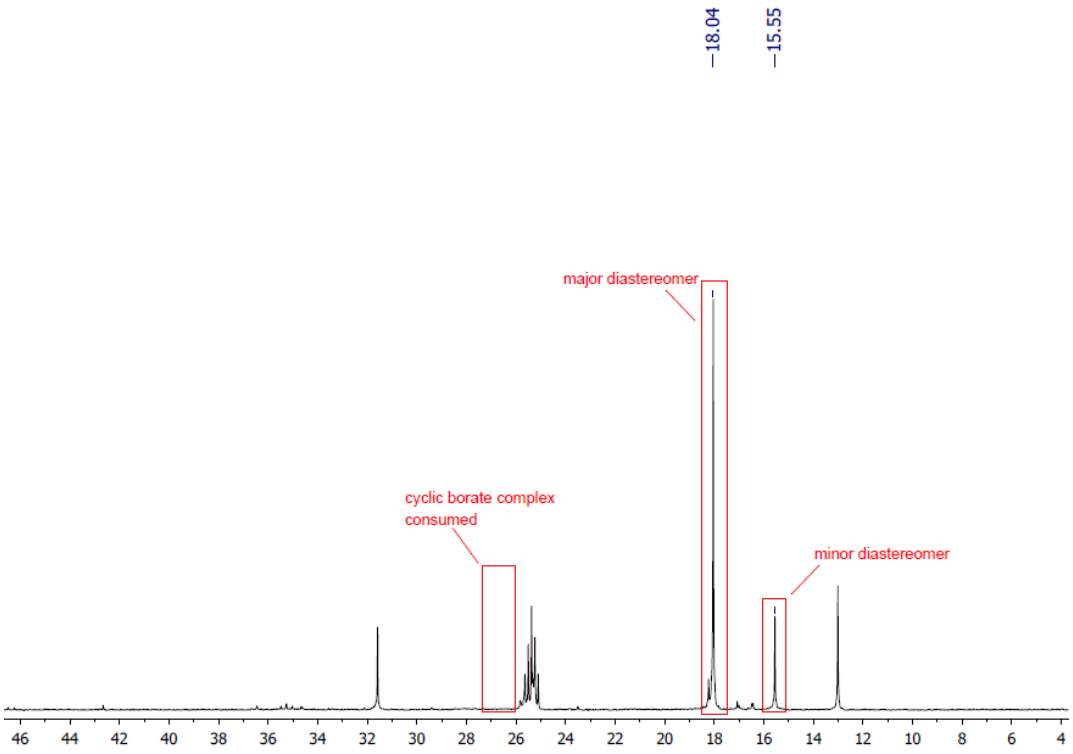


Figure 58 - in situ ^{13}C NMR analysis of reaction of 13C-labeled substrate **20** with KO*t*Bu, 1 minute after quenching with H_2O

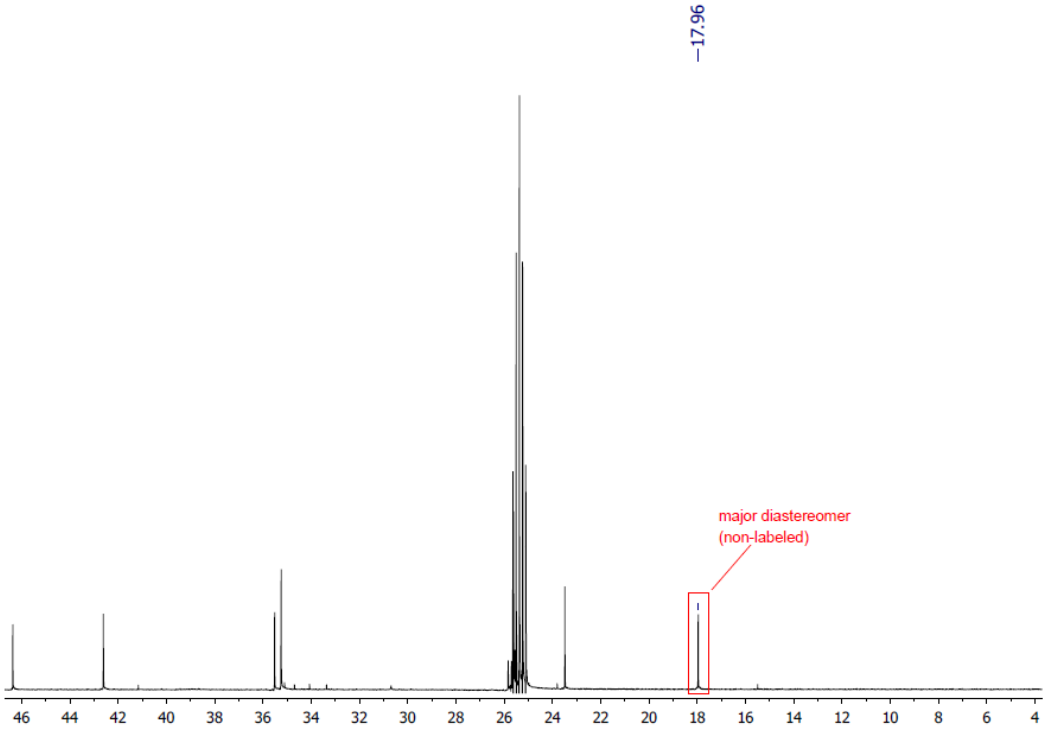


Figure 59 – ^{13}C NMR of 4,4,5,5-tetramethyl-2-(2-methyl-1-phenethylcyclopentyl)-1,3,2-dioxaborolane (non-^{13}C labeled) in d_8-THF

ii) Concerted 2+2 Cycloaddition Pathway

Convergent Alkene-Diastereomer Experiment

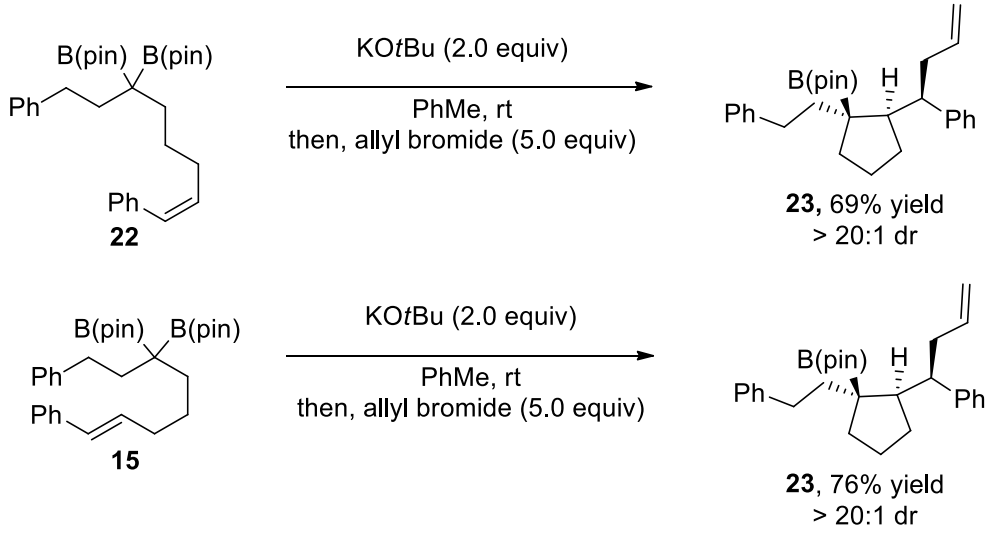
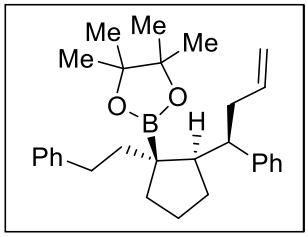


Figure 60 – (*E*) and (*Z*) Phenyl-substituted alkene substrates converging to the same epimer product



4,4,5,5-tetramethyl-2-((1*R*,2*R*)-1-phenethyl-2-((*R*)-1-phenylbut-3-en-1-yl)cyclopentyl)-1,3,2-dioxaborolane (23). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with (*Z*)-2,2'-(1,8-diphenyloct-7- ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**22**) (56.13 mg, 0.1 mmol), KO*t*Bu (22.4 mg, 0.2 mmol) and toluene (0.5 mL). Upon completion, the reaction mixture is quenched with allyl bromide (60.5 mg, 0.5 mmol) and allowed stir an additional two hours. Mixture then diluted with diethyl ether (2 mL) and filtered through a silica gel plug, rinsing with diethyl ether. Filtrate is then concentrated in vacuo and the crude residue purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (30.7 mg, 69%, >20:1 dr). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.18 (m, 4H), 7.19 – 7.11 (m, 3H), 7.14 – 7.04 (m, 1H), 6.91 – 6.85 (m, 2H), 5.50 (dddd, *J* = 18.0, 10.0, 7.4, 6.0 Hz, 1H), 4.85 (dd, *J* = 17.1, 1.7 Hz, 1H), 4.81 – 4.76 (d, *J* = 10.0, 1H), 2.92 (td, *J* = 10.2, 8.8, 3.7 Hz, 1H), 2.59 – 2.47 (m, 1H), 2.40 (td, *J* = 13.2, 4.5 Hz, 1H), 2.36

– 2.25 (m, 2H), 1.97 (td, *J* = 8.9, 8.4, 4.8 Hz, 2H), 1.87 (q, *J* = 8.7 Hz, 1H), 1.73 (p, *J* = 9.9, 8.7 Hz, 1H), 1.66 – 1.49 (m, 2H), 1.43 – 1.31 (m, 2H), 1.29 (s, 6H), 1.28 (s, 6H), 0.83 (td, *J* = 13.0, 5.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.71, 143.69, 137.68, 128.66, 128.13, 127.90, 127.78, 125.68, 125.13, 115.16, 82.78, 55.13, 48.35, 39.72, 39.16, 35.60, 32.68, 30.42, 25.29, 24.91, 22.08; IR (neat): 2956.9 (s), 2930.5 (s), 2872.6 (m), 1729.4 (s), 1457.5 (m), 1379.2 (m), 1288.9 (s), 1239.1 (w), 1141.6 (s), 1073.0 (m), 755.5 (m), 700.3 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{29}{}^{1}H_{40}{}^{11}B_{1}{}^{6}O_{2}$ $[M+H]^+$: calculated: 431.3121, found: 431.3115. The relative stereochemistry was assigned by X-ray crystallography.

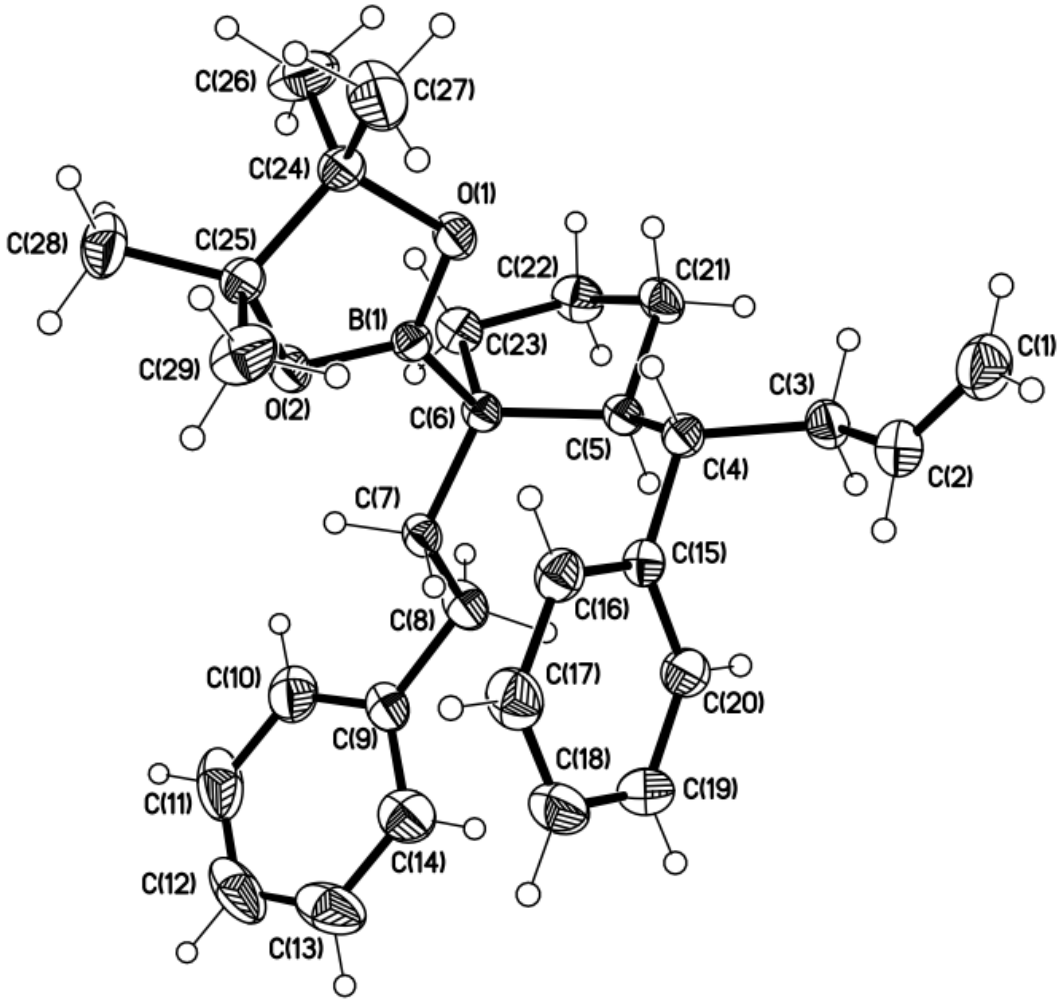
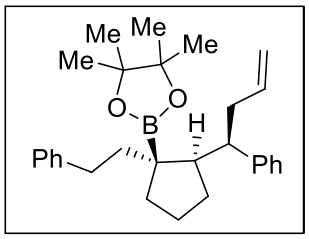


Figure 61 – Crystal of 4,4,5,5-tetramethyl-2-((1*R*,2*R*)-1-phenethyl-2-((*R*)-1-phenylbut-3-en-1-yl)cyclopentyl)-1,3,2-dioxaborolane



4,4,5,5-tetramethyl-2-((1*R*,2*R*)-1-phenethyl-2-((*R*)-1-phenylbut-3-en-1-yl)cyclopentyl)-1,3,2-dioxaborolane (23). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with (*E*)-2,2'-(1,8-diphenyloct-7- ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**15**) (56.13 mg, 0.1 mmol), KO*t*Bu (22.4 mg, 0.2 mmol) and toluene (0.5 mL). Upon completion, the reaction mixture was quenched with allyl bromide (60.5 mg, 0.5 mmol), stir for another two hours, then diluted with diethyl ether (2 mL), filtered through a silica gel plug, rinsed with diethyl ether, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (32.7 mg, 76%, >20:1 dr). ^{1}H and ^{13}C NMR spectral data and X-ray crystallographic data identical to that **above**.

^{2}D-Labeled Experiment

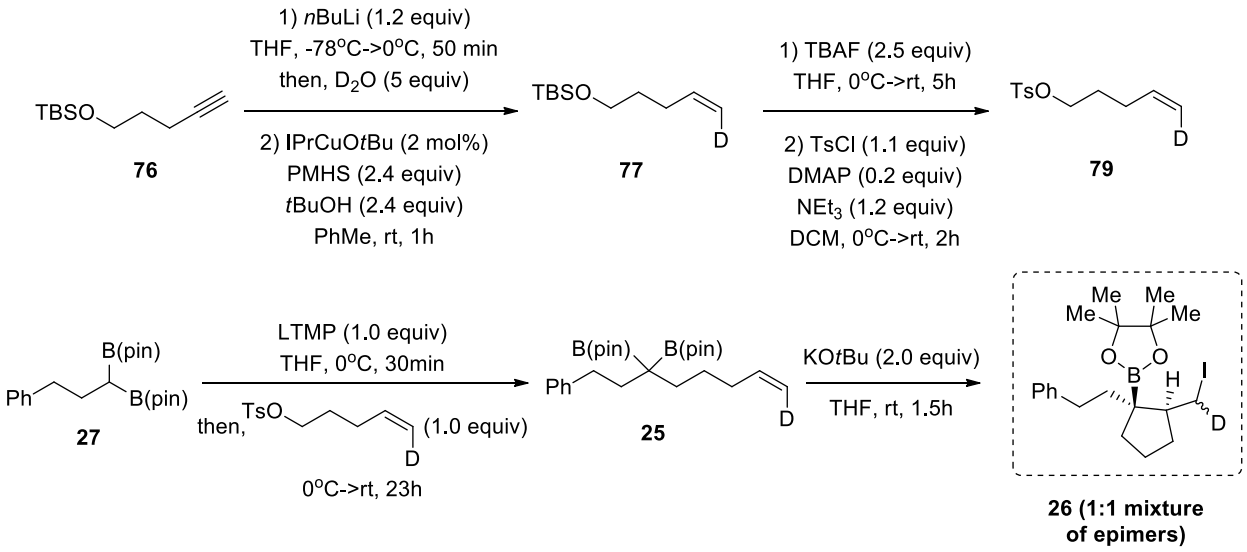
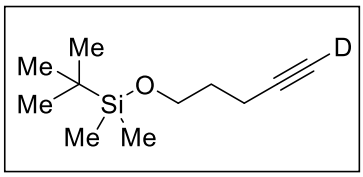
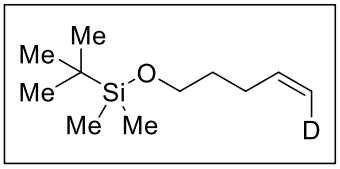


Figure 62 - Forward synthesis and reaction of (*Z*)-2,2'-(1-phenyloct-7-ene-3,3-diyl-8-*d*)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)



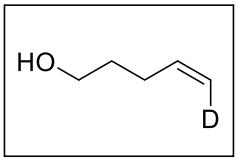
***tert*-butyldimethyl((pent-4-yn-1-yl-5-*d*)oxy)silane (76).** A flame dried 20 mL vial equipped with stir bar is charged with *tert*-butyldimethyl(pent-4-yn-1-yloxy)silane (1.87 g, 9.43 mmol, 1.0 equiv), then sealed and evacuated/backfilled with N_2 3x. Anhydrous THF (9.4 mL) is then charged in the vessel and the clear, colorless solution set to stir at -78ºC. A solution of *n*BuLi in Hexanes (4.20 mL, 2.70 M, 11.3 mmol, 1.2 equiv) is then added dropwise, resulting in a clear, yellow solution. After stirring for 30min at -78ºC, the mixture is brought to 0ºC and allowed to stir an additional 20min. At this point, the reaction is quenched by slow addition of D_2O (853 µL, 47.2 mmol, 5.0 equiv), resulting in a white slurry. The resulting mixture is allowed to stir for 4h, then directly dried over Na_2SO_4 and passed through a pad of SiO_2, rinsing with Et_2O. Filtrate is then concentration to yield clear, colorless oil (1.88 g, 9.43 mmol, quantitative). No further purification necessary. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.70 (t, *J* = 6.0 Hz, 2H), 2.27 (t, *J* = 7.1 Hz, 2H), 1.78 – 1.68 (m, 2H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 61.41, 31.51, 25.90, 18.29, 14.78, -5.38; IR (neat): 2988.3 (s), 2946.7 (w), 2870.2 (s), 1393.6 (w), 1142.5 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{11}{}^{1}H_{22}{}^{2}D_{1}{}^{29}Si_{1}{}^{16}O_{1}$ $[M+H]^+$: calculated: 200.1581, found: 200.1572.



(*Z*)-*tert*-butyldimethyl((pent-4-en-1-yl-5-*d*)oxy)silane (77). Adapted from published procedure.[41] A flame dried 250 mL round bottom equipped with magnetic stir bar is charged with **76** (1.43 g, 7.2 mmol, 1.0 equiv) inside an argon-filled glovebox. *t*BuOH (990 mg, 13.4 mmol, 2.4 equiv) is then added to the vessel, followed by toluene (60 mL) then Polymethylhydrosiloxane (979 µL, 17.3 mmol (monomer), 2.4 equiv). The mixture is set to stir, then IPrCuO*t*Bu[42] (75.6 mg, 0.14

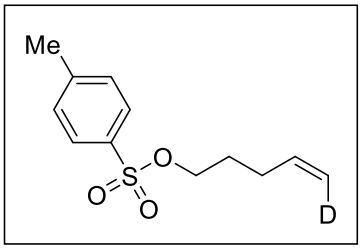
41. Whittaker, A. M.; Lalic, G., Monophasic Catalytic System for the Selective Semireduction of Alkynes. *Org. Lett.* **2013,** *15* (5), 1112-1115.
42. Mankad, N. P.; Laitar, D. S.; Sadighi, J. P., Synthesis, Structure, and Alkyne Reactivity of a Dimeric (Carbene)copper(I) Hydride. *Organometallics* **2004,** *23* (14), 3369-3371.

mmol, 2 mol %) is added, at which point bubbling is observed. The vessel is sealed with a rubber septum, then moved to the fume hood where it is allowed to stir for 1h at room temperature. At this point, the reaction mixture turns dark brown and it is passed through a pad of silica gel, rinsing with Et_2O. The filtrate is concentrated then SiO_2 chromatography performed (0% Et_2O/Pentanes, gradient to 2.5% Et_2O/Pentanes, visualizing with $KMnO_4$). Product coelutes with PMHS and yield is carried across two steps. ^{1}H NMR (600 MHz, cdcl$_3$) δ 5.85 – 5.77 (m, 1H), 4.94 (d, *J* = 10.2 Hz, 1H), 3.62 (t, *J* = 6.5 Hz, 2H), 2.10 (td, *J* = 7.6, 0.9 Hz, 2H), 1.64 – 1.58 (m, 2H), 1.33 – 1.26 (m, 12H), 0.90 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): 138.45 (s), 114.19 (t, *J*=23.5 Hz), 62.53 (s), 31.99 (s), 29.97 (s), 25.95 (s), 18.34 (s), -5.30 (s); IR (neat): 2987.3 (m), 2871.0 (m), 1142.4 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{11}{}^{1}H_{24}{}^{2}D_{1}{}^{29}Si_{1}{}^{16}O_{1}$ $[M+H]^+$: calculated: 202.1737, found: 202.1741.

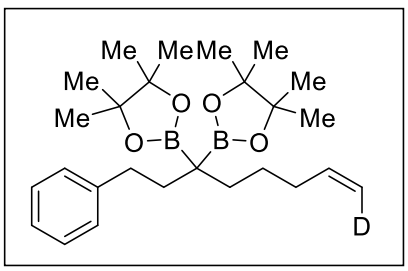


(*Z*)-pent-4-en-5-*d*-1-ol (78). A 50 mL round bottom equipped with magnetic stir bar is charged with a solution of **77** (1.36 g, 6.75 mmol, 1.0 equiv; mixed with PMHS, see above) in anhydrous THF (6.75 mL). The vessel and contents are then brought to 0°C, at which point TBAF solution in THF (16.8 mL, 1 M, 16.8 mmol, 2.5 equiv) is added dropwise (exothermic process). After addition, the mixture is allowed to stir at room temperature for 5h. The reaction mixture is then poured into a seperatory funnel containing ca. 10 mL brine and the organics are extracted 3x with ca. 10 mL Et_2O. Combined organics are then dried over Na_2SO_4 and concentrated to yield crude oil. Oil is purified by SiO_2 chromatography (2.5% Et_2O/Pentanes, gradient to 10% Et_2O/Pentanes, visualized with $KMnO_4$ to yield clear, colorless oil (343.9 mg, 3.95 mmol, 55% *across 2 steps*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87 – 5.79 (m, 1H), 4.97 (d, *J* = 10.2 Hz, 1H), 3.67 (t, *J* = 6.5 Hz, 2H), 2.15 (td, *J* = 7.6, 0.8 Hz, 2H), 1.71 – 1.64 (m, 2H), 1.57 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.30 (s), 114.81 (t, *J*=23.5

Hz), 62.65 (s), 31.95 (s), 30.20 (s); IR (neat): 2988.5 (w), 2869.8 (w), 1141.9 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_5{}^{1}H_{10}{}^{2}D_1{}^{16}O_1$ $[M+H]^+$: calculated: 88.0873, found: 88.0870.

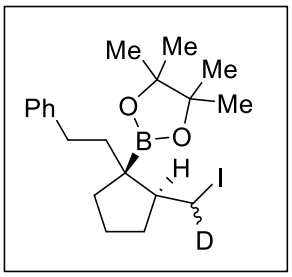


(*Z*)-pent-4-en-1-yl-5-*d* 4-methylbenzenesulfonate (79). A flame dried 20 mL vial equipped with magnetic stir bar is charged with TsCl (904 mg, 4.74 mmol, 1.10 equiv) followed by DMAP (105 mg, 0.86 mmol, 0.20 equiv). The vial is sealed and evacuated/refilled with N_2 3x, then a solution of **78** (375 mg, 4.31 mmol, 1.0 equiv) in anhydrous DCM (21.6 mL) is charged in. The mixture is brought to 0°C then reagent grade NEt_3 (720 µL, 5.17 mmol, 1.2 equiv) is added dropwise. The reaction is then allowed to stir at room temperature for 2h. At this point, the reaction mixture is treated with ca. 5 mL H_2O and the organics are extracted 3x with ca. 5 mL DCM. Combined organics are dried over Na_2SO_4 then concentrated to yield crude oil. Crude material is purified by SiO_2 chromatography (2.5% Et_2O/Pentanes, gradient to 10% Et_2O/Pentanes, visualized with CAM stain) to render clear, colorless oil (666 mg, 2.76 mmol, 64%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 5.72 – 5.64 (m, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 4.04 (t, *J* = 6.4 Hz, 2H), 2.45 (s, 3H), 2.08 (q, *J* = 7.1 Hz, 2H), 1.74 (p, *J* = 6.9 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.66 (s), 136.51 (s), 133.19 (s), 129.80 (s), 127.89 (s), 115.56 (t, *J*=23.6 Hz), 69.78 (s), 29.32 (s), 27.99 (s), 21.63 (s); IR (neat): 2957.1 (w), 1598.4 (w), 1359.0 (s), 1188.7 (s), 1097.8 (w), 928.0 (m), 810.6 (m), 664.2 (m), 554.6 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{12}{}^{1}H_{15}{}^{2}D_1{}^{32}S_1{}^{16}O_3{}^{23}Na_1$ $[M+Na]^+$: calculated: 264.0781, found: 264.0780.



(*Z*)-2,2'-(1-phenyloct-7-ene-3,3-diyl-8-*d*)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (25). A flame dried 20 mL vial equipped with magnetic stir bar is charged with LTMP (405 mg, 2.75 mmol, 1.0 equiv) inside an argon-filled glovebox. The

vial is sealed then moved to the hood where it is charged with anhydrous THF (9 mL). The orange solution is set to stir at 0°C then charged with a solution of **27** (1.02 g, 2.75 mmol, 1.0 equiv) in anhydrous THF (2 mL) where it is allowed to stir for 30 min. At this point, a solution of **79** (663 mg, 2.75 mmol, 1.0 equiv) in anhydrous THF (2 mL) is added gradually. The mixture is brought to room temperature and allowed to stir overnight (23h). Upon return, the reaction mixture is diluted with Et_2O and passed through a pad of silica gel, rinsing with Et_2O. Filtrate is concentrated to render crude solid. Solid is purified by SiO_2 chromatography (0% EtOAc/Hexanes, gradient to 3% EtOAc/Hexanes, visualized with CAM stain). Product isolated as a white solid (938 mg, 2.13 mmol, 77%). ^{1}H NMR (500 MHz, $CDCl_3$): δ ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.25 – 7.21 (m, 2H), 7.22 – 7.16 (m, 2H), 7.16 – 7.10 (m, 1H), 5.89 – 5.80 (m, 1H), 4.92 (d, *J* = 10.3 Hz, 1H), 2.54 – 2.46 (m, 2H), 2.08 (q, *J* = 7.0 Hz, 2H), 1.93 – 1.86 (m, 2H), 1.75 – 1.69 (m, 2H), 1.42 – 1.34 (m, 2H), 1.23 (s, 24H; ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.93 (s), 139.40 (s), 128.63 (s), 128.24 (s), 125.50 (s), 113.85 (t, *J*=23.5 Hz), 83.13 (s), 34.65 (s), 33.99 (s), 32.04 (s), 28.82 (s), 26.80 (s), 24.95 (s), 24.86 (s); IR (neat): 2978.5 (m), 2931.5 (w), 2858.9 (w), 1456.2 (w), 1378.6 (m), 1309.7 (s), 1255.2 (w), 1138.6 (s), 968.9 (w), 909.9 (m), 853.4 (m), 733.1 (s), 699.4 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{26}{}^{1}H_{42}{}^{2}D_1{}^{11}B_2{}^{16}O_4$ $[M+H]^+$: calculated: 442.3410, found: 442.3422.



2-((1*R*,2*S*)-2-(iodomethyl-*d*)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with **25** (88.2 mg, 0.2 mmol, 1.00 equiv), KO*t*Bu (44.9 mg, 0.4 mmol, 2.0 equiv) in THF (1 mL) for 1h 30min. Yellow reaction mixture was then quenched with an I_2 solution in anhydrous THF (0.8 mL, 0.5 M, 0.4 mmol, 2.0 equiv), where the reaction turns white, then purple. The crude reaction mixture was purified by SiO_2 chromatography (0% EtOAc/Hexanes,

gradient to 1% EtOAc/Hexanes, visualized with CAM stain) to afford a white solid (60.0 mg, 0.136 mmol, 68%; 1:1 mixture of epimers). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 3.52 (d, *J* = 3.1 Hz, 0.5H), 3.13 (d, *J* = 12.1 Hz, 0.5H), 2.60 – 2.51 (m, 2H), 2.20 – 2.11 (m, 2H), 2.03 – 1.94 (m, 2H), 1.79 – 1.70 (m, 1H), 1.68 – 1.59 (m, 1H), 1.47 – 1.40 (m, 2H), 1.40 – 1.33 (m, 1H), 1.26 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.12 (s), 128.30 (s), 128.22 (s), 125.64 (s), 83.30 (s), 53.87 (s), 53.85 (s), 41.20 (s), 41.18 (s), 36.11 (s), 36.08 (s), 33.91 (s), 33.88 (s), 25.12 (s), 24.83 (s), 21.86 (s), 21.84 (s), 11.49 (t, *J*=22.9 Hz), 11.47 (t, *J*=22.9 Hz); IR (neat): 2976.1 (m), 2930.8 (m), 2867.2 (w), 1454.0 (w), 1380.7 (s), 1311.3 (s), 1199.0 (w), 1141.5 (s), 966.9 (w), 853.6 (w), 748.3 (w), 698.5 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{20}{}^{1}H_{29}{}^{2}D_{1}{}^{11}B_{1}{}^{16}O_{2}{}^{127}I_{1}{}^{23}Na_{1}$ $[M+Na]^+$: calculated: 464.1344, found: 464.1339.

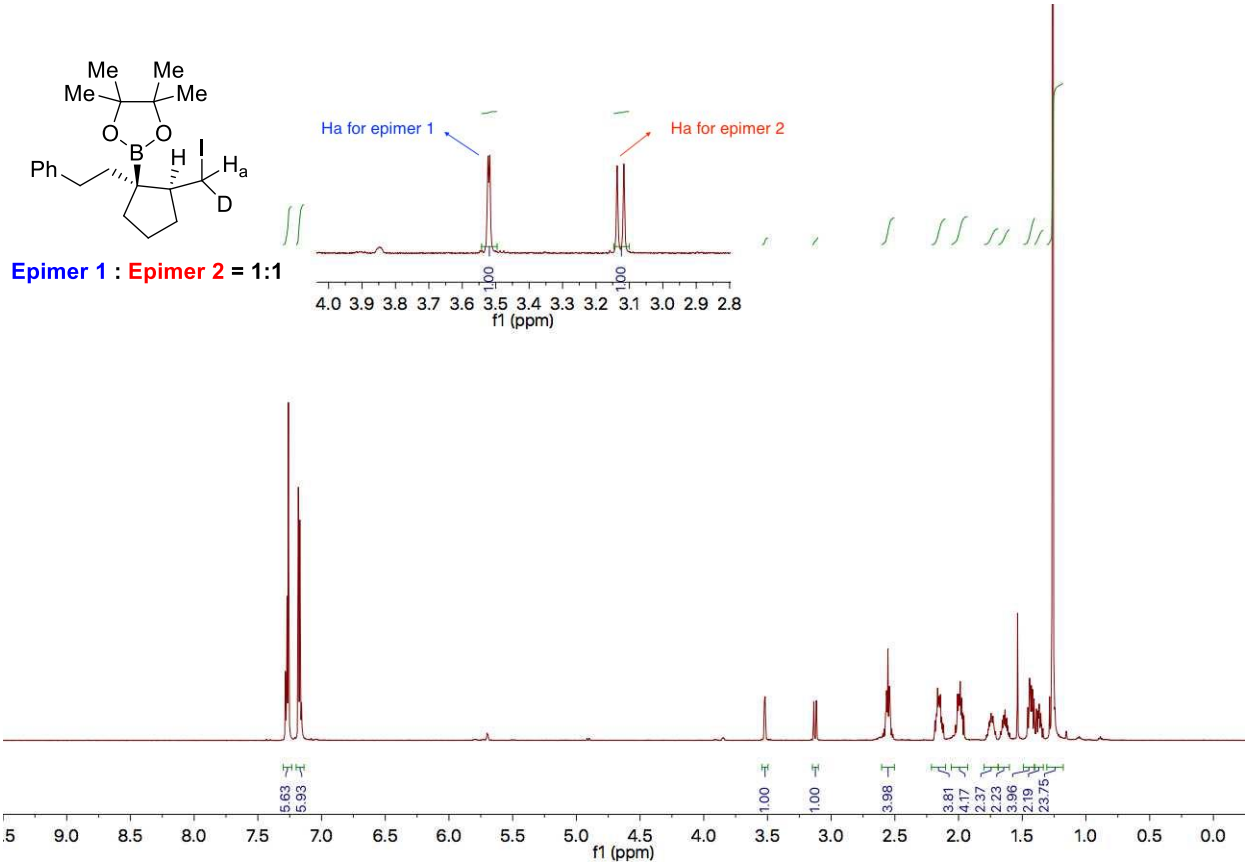


Figure 63 – ^{1}H NMR of 2-((1*R*,2*S*)-2-(iodomethyl-*d*)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

iii) Radical vs. Anionic Pathway

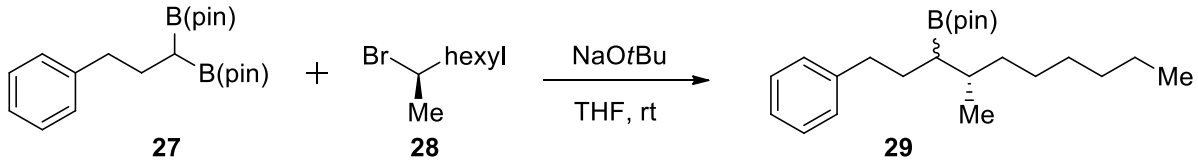
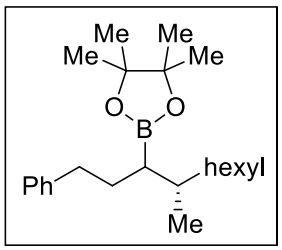
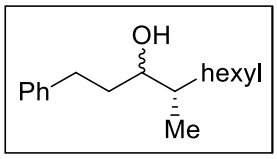


Figure 64 – Stereo-invertive deborylative alkylation with enriched, secondary alkylhalide



4,4,5,5-tetramethyl-2-((4*S*)-4-methyl-1-phenyldecan-3-yl)-1,3,2-dioxaborolane (29). In the glove box, an oven-dried 2-dram vial equipped with magnetic stir bar is charged with 1,1-diboronate ester **27** (96.8 mg, 0.26 mmol), NaO*t*Bu (50 mg, 0.52 mmol), and THF (1 mL). The reaction mixture is allowed to stir at room temperature for 15 min, then (*R*)-2-bromooctane (**28**) (35.1 μL, 0.20 mmol) is charged in the reaction vessel. The vial is then sealed with a polypropylene cap, removed from the glove box, and allowed to stir at room temperature overnight. Upon completion, the reaction mixture is diluted with diethyl ether (2 mL), filtered through a silica gel plug, rinsed with diethyl ether, and concentrated in vacuo. The crude residue is then purified on silica gel (hexanes: ethyl acetate = 100:1 to 50:1) to isolate the desired product (35 mg, 49%, 1.1:1 dr 98:2 er). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 – 7.26 (m, 3H), 7.21 – 7.13 (m, 2H), 2.72 – 2.57 (m, 1H), 2.57 – 2.43 (m, 1H), 1.87 – 1.68 (m, 1H), 1.68 – 1.56 (m, 2H), 1.43 – 1.33 (m, 1H), 1.32 – 1.19 (m, 8 H, overlap), 1.27 (s, 12H), 1.18 – 1.07 (m, 1H), 1.04 - 0.98 (m, 1H), 0.93 – 0.84 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.26, 128.37, 128.17, 125.48, 82.83, 36.42, 36.14, 36.09, 35.91, 34.62, 34.37, 31.89, 31.51, 30.20, 29.58, 29.56, 27.52, 27.25, 25.08, 25.06, 24.79, 22.64, 18.75, 18.43, 14.09; IR (neat): 2956.5 (m), 2926.9 (s), 2856.3 (m), 1729.6 (w), 1456.9 (w), 1379.1 (m), 1313.8 (m), 1270.7 (w), 1143.9 (s), 699.1 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{23}{}^{1}H_{40}{}^{11}B_{1}{}^{16}O_2$ $[M+H]^+$: calculated: 359.3121, found: 359.3139.



(4*S*)-4-methyl-1-phenyldecan-3-ol (80). To a 20 mL vial containing compound **29** (35 mg, 0.1 mmol) in THF (1 mL), aqueous NaOH (0.6 mL, 3 M, 1.8 mmol) is added then the vial is cooled 0 °C. Aqueous Hydrogen Peroxide (0.3 mL, 30% in H_2O) is then slowly added to the reaction vessel and reaciton allowed to stir overnight. Upon return, the vessel is cooled back to 0 °C and quenched slowly with saturated, aqueous $Na_2S_2O_3$ (1 mL), stirred for 30 minutes, then extrated with diethyl ether. Combined extracts are then dried over Na_2SO_4 and concentrated in vacuo. The crude residue is then purified by column chromatography on silica gel. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 4H), 7.24 – 7.16 (m, 2H), 3.58 – 3.51 (m, 1H), 3.48 (dtd, *J* = 9.8, 5.1, 2.9 Hz, 1H), 2.95 – 2.78 (m, 2H), 2.73 – 2.59 (m, 2H), 1.84 – 1.73 (m, 4H), 1.57 – 1.47 (m, 2H), 1.46 – 1.38 (m, 2H), 1.38 – 1.22 (m, 17H), 1.21 –1.14 (m, 2H), 1.14 – 1.05 (m, 1H), 0.95 – 0.84 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 142.36, 142.30, 128.42, 128.39, 128.36, 125.76, 75.44, 74.72, 39.01, 38.45, 36.26, 35.19, 33.23, 32.70, 32.56, 31.92, 31.85, 29.69, 29.60, 29.57, 27.31, 27.24, 22.65, 15.20, 14.09, 13.69; IR (neat): 3357.0 (w), 2956.7 (m), 2927.8 (s), 2855.0 (m), 1724.7 (m), 1455.3 (w), 1275.3 (w), 1131.9 (w), 751.2 (m), 698.4 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{17}{}^{1}H_{27}$ $[M+H-H_2O]^+$: calculated: 231.2113, found: 231.2118.

Proof of Stereochemistry:

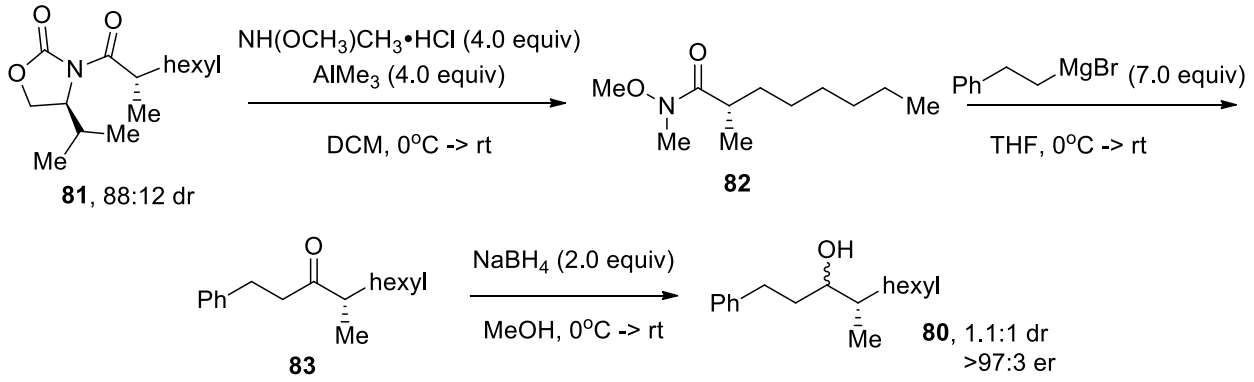
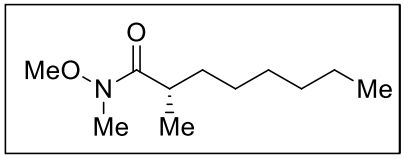


Figure 65 - Authentic synthesis of (4*S*)-4-methyl-1-phenyldecan-3-ol via Evans Auxiliary

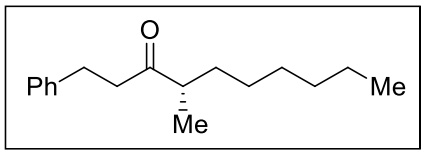
(*S*)-*N*-methoxy-*N*,2-dimethyloctanamide (82).



Adapted from literature procedure.[43] To a stirred solution of *N*,*O*-dimethylhydroxylamine hydrochloride (312.1 mg, 3.2 mmol) in DCM (5 ml) at 0 °C, neat $AlMe_3$ (307 µL, 3.2 mmol) is carefully added. The reaction mixture is stirred at 0 °C for 10 min and then one hour at room temperature. The mixture is then cooled back to 0 °C and a solution of **81**[44,45] (227 mg, 0.8 mmol) in DCM (5 ml) is added to the reaction vessel. The resulting mixture is then allowed to stir overnight, gradually reaching room temperature. Upon return, the reaction solution is diluted with DCM (10 mL) and poured into a separatory funnel containing ice-cold aqueous 0.5 N HCl (25 ml) and organics are extracted 3x with DCM. The combined extracts are then washed with saturated, aqueous $NaHCO_3$ and saturated, aqueous NaCl, in succession, then dried over Na_2SO_4. Volatiles are then removed in vacuo and the crude, colorless oil is then purified by silica gel chromatography (8:2 pentane:Et_2O, gradient to

43. Micalizio, G. C.; Pinchuk, A. N.; Roush, W. R., Synthesis of the C(29)−C(45) Bis-pyran Subunit (E−F) of Spongistatin 1 (Altohyrtin A). *J. Org. Chem.* **2000,** *65* (25), 8730-8736.
44. Evans, D. A.; Ennis, M. D.; Le, T.; Mandel, N.; Mandel, G., Asymmetric acylation reactions of chiral imide enolates. The first direct approach to the construction of chiral .beta.-dicarbonyl synthons. *J. Am. Chem. Soc.* **1984,** *106* (4), 1154-1156.
45. Minko, Y.; Pasco, M.; Lercher, L.; Botoshansky, M.; Marek, I., Forming all-carbon quaternary stereogenic centres in acyclic systems from alkynes. *Nature* **2012,** *490* (7421), 522-526.

7:3 pentane:Et_2O) to afford (*S*)-*N*-methoxy-*N*,2-dimethyloctanamide **82** as a colorless oil (38.2 mg, 22 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.68 (s, 3H), 3.19 (s, 3H), 2.86 (s, 1H), 1.67 (ddd, *J* = 13.2, 8.3, 5.3 Hz, 1H), 1.32 – 1.18 (m, 9H), 1.11 (d, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 61.40, 35.09, 33.83, 31.73, 29.68, 29.31, 27.50, 22.61, 17.45, 14.04; IR (neat): 2964.0 (m), 2930.4 (m), 2871.7 (m), 1779.3 (s), 1699.3 (m), 1385.5 (m), 1300.8 (w), 1204.9 (m), 1141.6 (m), 911.6 (w), 733.4 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{11}{}^{1}H_{24}{}^{14}N_{1}{}^{16}O_2$ $[M+H]^+$: calculated: 202.1807, found: 202.1797.



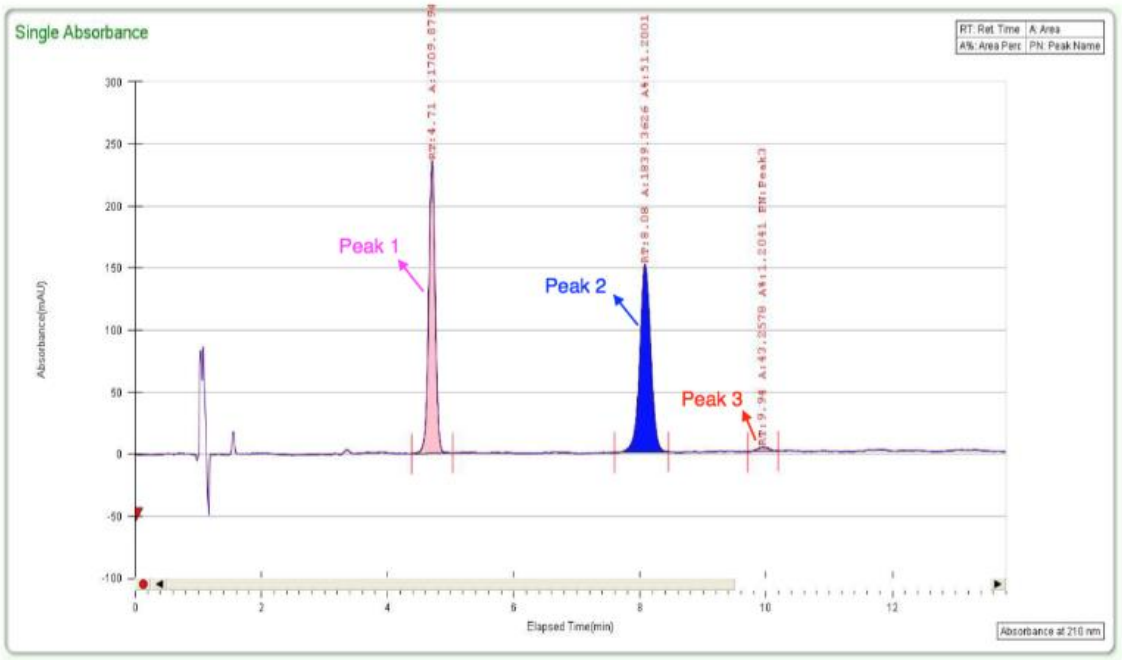
(*S*)-4-methyl-1-phenyldecan-3-one (**83**)**.** To a dried flask fitted with magnetic stir bar and charged with Mg^0 (36.5 mg, 1.5 mmol) and anhydrous THF (5 mL), (2-bromoethyl)benzene (0.17 mL, 1.25 mmol) is added slowly under N_2. Mixture is then stirred at 60 °C for two hours and the resulting Grignard solution is cooled back to room temperature where it is added to a solution of amide **82** (38.2 mg, 0.177 mmol) in anhydrous THF (1 mL) drop wise at 0 °C. The reaction mixture is allowed to stir for 3h, gradually warming to room temperature. Upon completion, reaction is cooled to 0 °C and quenched with saturated, aqueous NH_4Cl (1 mL). Organics are then extracted with diethyl ether (3 × 3 mL) and the combined extracts washed with brine and dried over anhydrous Na_2SO_4. Volatiles are then removed in vacuo and the crude residue was purified on silica gel (hexane: ethyl acetate= 100:1, gradient to 20:1) to afford compound **83** as an colorless oil (34 mg, 78%).^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.26 (m, 2H), 7.21 – 7.16 (m, 3H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.78 – 2.70 (m, 2H), 2.48 (h, *J* = 6.9 Hz, 1H), 1.65 – 1.56 (m, 1H), 1.35 – 1.12 (m, 9H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 213.81, 141.35, 128.41, 128.33, 126.00, 46.54, 42.65, 32.94, 31.63, 29.74, 29.30, 27.18, 22.56, 16.16, 14.03; IR (neat): 2958.0 (s), 2928.3 (s), 2858.2 (m), 1728.0 (s), 1462.1 (m), 1272.6

(s), 1122.5 (m), 1072.6 (m), 744.7 (w), 699.4 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{17}{}^{1}H_{27}{}^{16}O_{1}$ $[M+H]^{+}$: calculated: 247.2062, found: 247.2053.

To a vial containing a solution of (*S*)-4-methyl-1-phenyldecan-3-one **83** (34 mg, 0.14 mmol) in MeOH (1 mL), $NaBH_4$ (10.6 mg, 0.28 mmol) is added at 0 °C. The reaction mixture is then allowed to stir for 20 min at room temperature, then quenched with saturated aqueous NH_4Cl (1 mL). Organics are then extracted with diethyl ether (3x 3 mL) and the combined organic layers washed with brine and dried over anhydrous Na_2SO_4. Volatiles are then removed in vacuo and the crude residue purified on silica gel (hexane: ethyl acetate = 10:1) to yield (4*S*)-4-methyl-1-phenyldecan-3-ol **80** as a colorless oil (32 mg, 92%, 1.1:1 dr, 97:3 er). (diastereoselectivity was determined based on NMR integration). The spectra data is the same as shown above.

Analysis of Stereochemistry

The enantioselectivity was determined by SFC analysis of the reaction products (shown below).



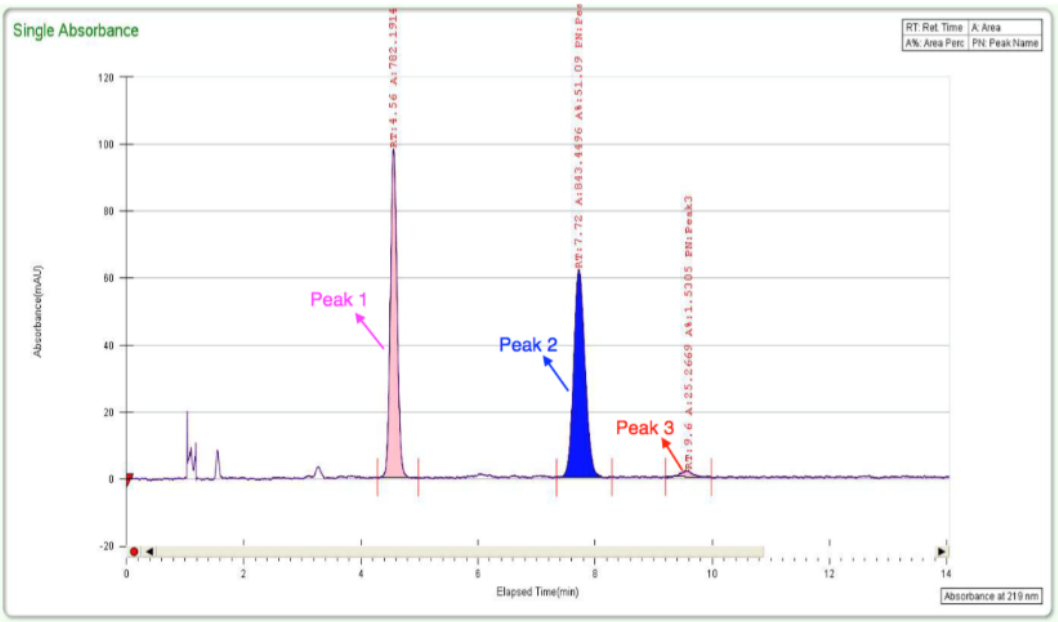
General Info	
Log Author	
Log Date	9/13/2015 6:29:58 PM
Report By	current_User
Report Date	4/10/2017
Method Name	potterbo.met
Notes	OD-H, 100 bar, 10% IPA, 3 mL/min, 35 deg C

Injection Info			
Inj Vol	10	**Temp**	34.8
Solvent	IPA	**Flow**	3
Column	OD-H	**% Modifier**	10
Sample	xl-4-098-fineagain	**Pressure**	100
Well location	P1: 1A		

Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	47.5958	1709.8794	4.71	236.3671	0.0042
2	51.2001	1839.3626	8.08	151.5557	0.0073
3	1.2041	43.2578	9.94	3.6284	0.009
Total:	100	3592.4998			

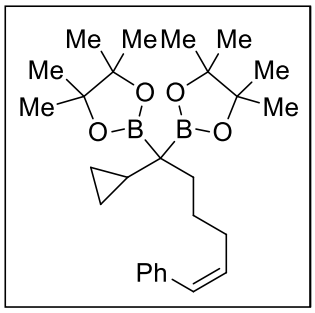
Figure 66 - SFC trace of base promoted deborylative alkylation product (after oxidation) (OD-H, Chiraldex, 3 mL/min, 10% *i*-PrOH, 100 bar, 35 °C)



General Info					
Log Author					
Log Date	10/19/2015 5:12:06 PM				
Report By	current_User				
Report Date	4/10/2017				
Method Name	potterbo.met				
Notes	ODH, 100 bar, 10% iPA, 3 mL/min, 35 deg C				
Injection Info					
Inj Vol	10				
Solvent	IPA				
Column	OD-H				
Sample	xl-4-271-finediluteagain				
Well location	P1: 3A				
Temp	35				
Flow	3				
% Modifier	10				
Pressure	101				
Peak Info					
Peak No	**% Area**	**Area**	**RT (min)**	**Height (mV)**	**K'**
1	47.3795	782.1914	4.56	97.939	0.0044
2	51.09	843.4496	7.72	62.1709	0.0075
3	1.5305	25.2669	9.6	1.8841	0.0093
Total:	100	1650.9079			

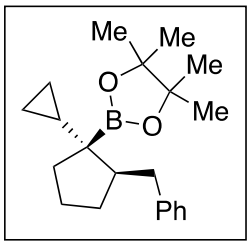
Figure 67 - SFC trace of authentic product prepared from Evans auxiliary. (OD-H, Chiraldex, 3 mL/min, 10% *i*-PrOH, 100 bar, 35 °C)

Radical Clock Experiment



(*Z*)-2,2'-(1-cyclopropyl-6-phenylhex-5-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**30**). The reaction was performed according to *Representative Procedure (Method D)* with 2,2'-(cyclopropylmethylene)bis(4,4,5,5-tetramethyl-1,3,2- dioxaborolane)

(154 mg, 0.5 mmol, made according to previous procedure[5]), LTMP (77.3 mg, 0.53 mmol), (*Z*)-(5-bromopent-1-en-1-yl)benzene (118.2 mg, 0.53mmol) and THF (2 mL). The crude reaction mixture was purified by column chromatography on silica gel (100:1 – 50:1 hexanes/ethyl acetate, stain in CAM) to afford a white solid (226 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.24 (m, 4H), 7.25 – 7.17 (m, 1H), 6.38 (d, *J* = 11.7 Hz, 1H), 5.73 (dt, *J* = 11.5, 7.7 Hz, 1H), 2.35 (q, *J* = 7.0 Hz, 2H), 1.82 – 1.53 (m, 4H), 1.22 (s, 24H), 0.86 (tt, *J* = 8.1, 5.6 Hz, 1H), 0.49 – 0.28 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.92, 133.70, 128.76, 128.27, 128.02, 126.26, 82.76, 33.04, 29.80, 28.64, 24.72, 24.71, 12.93, 3.62; IR (neat): 2977.3 (m), 2931.1 (w), 1378.7 (m), 1342.2 (m), 1305.2 (s), 1268.1 (m), 1214.4 (w), 1137.5 (s), 853.5 (w), 699.2 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{30}{}^{1}H_{49}{}^{11}B_2{}^{16}O_4$ $[M+H]^+$: calculated: 495.3817, found: 495.3819.



2-((1*R*,2*R*)-2-benzyl-1-cyclopropylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (31). The reaction was performed according to *Representative Procedure for Deborylative cyclization* with diboronate ester **30** (45.2 mg, 0.1 mmol), KO*t*Bu (22.4 mg, 0.2 mmol), and THF (0.5 mL) for 6 hours. The crude reaction mixture was purified by column chromatography on silica gel (100:0.8 hexanes/ethyl acetate, stain in CAM) to afford a colorless oil (15 mg, 46 %, dr > 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 – 7.22 (m, 2H), 7.24 – 7.12 (m, 3H), 3.07 (dd, *J* = 13.2, 3.5 Hz, 1H), 2.43 (dd, *J* = 13.2, 11.7 Hz, 1H), 1.87 (tdd, *J* = 9.0, 6.6, 3.5 Hz, 1H), 1.76 – 1.62 (m, 1H), 1.66 – 1.57 (m, 2H), 1.52 – 1.40 (m, 1H), 1.35 – 1.19 (m, 1H), 1.26 (s, 12H), 1.15 – 1.02 (m, 1H), 0.86 (ddt, *J* = 11.3, 8.6, 3.7 Hz, 1H), 0.44 – 0.26 (m, 1H), 0.29 – 0.16 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.17, 128.88, 128.04, 125.35, 82.84, 52.53, 39.17, 30.96, 30.57, 24.91, 24.83, 22.42, 16.75, 2.07, 0.29; IR (neat): 2976.4 (w), 2954.8 (w), 2866.4 (w), 1495.0 (w), 1387.8 (m),

5. Hong, K.; Liu, X.; Morken, J. P., Simple Access to Elusive α-Boryl Carbanions and Their Alkylation: An Umpolung Construction for Organic Synthesis. *J. Am. Chem. Soc.* **2014,** *136* (30), 10581-10584.

1299.9 (m), 1214.2 (w), 1141.6 (s), 1013.6 (w), 967.5 (w), 862.4 (w), 744.8 (w), 699.3 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{21}{}^{1}H_{32}{}^{11}B_{1}{}^{16}O_{2}$ $[M+H]^{+}$: calculated: 327.2495, found: 327.2492.

E. Total Synthesis of Aphanamal

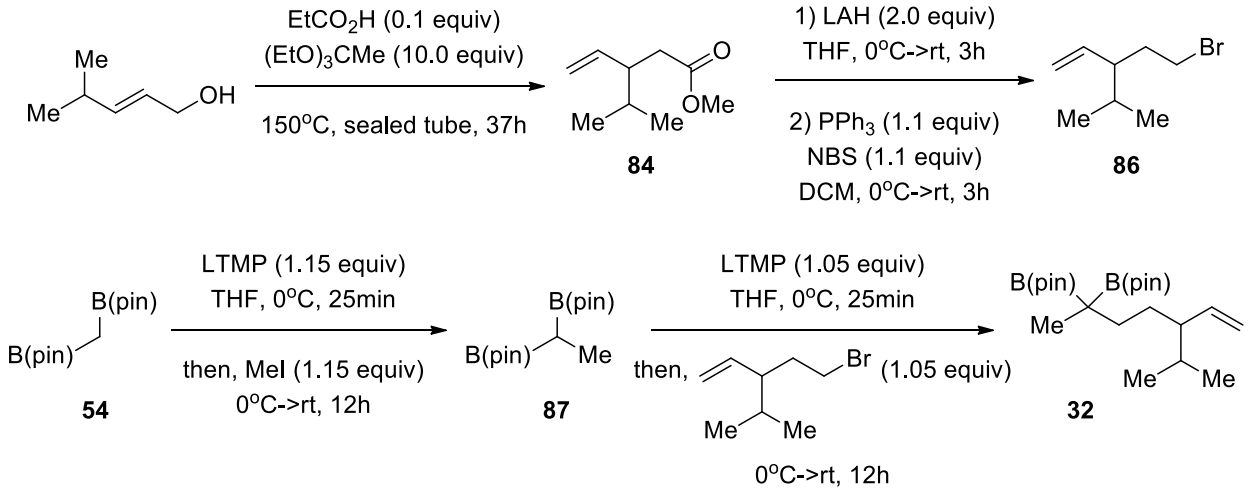
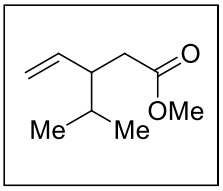


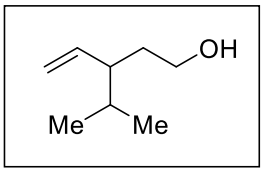
Figure 68 - Forward synthesis of aphanamal precursor, 2,2'-(5-isopropylhept-6-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)



Ethyl 3-isopropylpent-4-enoate (84). A flame dried 150 mL pressure vessel equipped with magnetic stir bar is charged with (*E*)-4-methylpent-2-en-1-ol[46] (3.17 g, 31.6 mmol, 1.0 equiv), triethyl orthoacetate (57.9 mL, 316 mmol, 10 equiv) and propionic acid (239 µL, 3.20 mmol, 0.1 equiv) in succession. The vessel is sealed with a threaded, teflon cap and allowed to stir heated at 150°C for 1.5 days. At this point, the vessel and contents are cooled to 0°C and the excess triethyl orthoacetate consumed by combining the reaction mixture with 50 mL H_2O, 50 mL THF and ca. 20 mg *p*-TsOH•H_2O (this process is exothermic). Organics are then extracted 3x with Et_2O and dried of Na2SO4. Concentration of solution yields clear, yellow oil with fruity fragrence (4.66 g, 27.4 mmol, 87%). No further purification necessary. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.65 (ddd, *J* = 17.1, 10.4, 8.6 Hz, 1H), 5.05 – 4.98 (m, 2H), 4.10

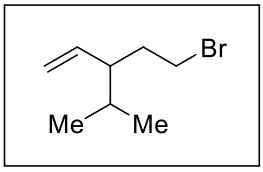
46. Crimmins, M. T.; Al-awar, R. S.; Vallin, I. M.; Hollis, W. G.; O'Mahony, R.; Lever, J. G.; Bankaitis-Davis, D. M., Asymmetric Total Synthesis of (+)-Milbemycin D. *J. Am. Chem. Soc.* **1996,** *118* (32), 7513-7528.

(q, J = 7.1 Hz, 2H), 2.44 – 2.35 (m, 2H), 2.32 – 2.24 (m, 1H), 1.68 – 1.61 (m, 1H), 1.23 (t, J = 7.1 Hz, 3H), 0.90 (d, J = 6.8 Hz, 3H), 0.86 (d, J = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 172.94 (s), 138.76 (s), 115.97 (s), 60.14 (s), 46.70 (s), 37.49 (s), 31.29 (s), 20.25 (s), 18.79 (s), 14.25 (s); IR (neat): 2962.8 (m), 2876.7 (m), 1732.2 (s), 1465.7 (w), 1387.4 (w), 1265.6 (m), 1182.5 (m), 1142.6 (m), 1034.6 (w), 914.7 (s), 733.4 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{10}{}^{1}H_{19}{}^{16}O_2$ $[M+H]^+$: calculated: 171.1385, found: 171.1379.

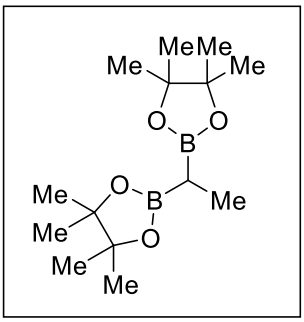


3-isopropylpent-4-en-1-ol (85). A flame dried 500 mL round bottom equipped with magnetic stir bar is charged with LAH (1.60 g, 29.2 mmol, 2.0 equiv) inside an argon-filled glovebox. The vessel is sealed with a rubber septum and moved to the fume hood where it is brought to 0ºC and charged with anhydrous THF (200 mL). A solution of **84** (4.66 g, 27.4 mmol, 1.0 equiv) in anhydrous THF (15 mL) is then added to the reaction vessel dropwise. The reaction mixture is then allowed to stir for 3h, slowly reaction room temperature. At this point, the vessel and contents are brought back to 0ºC and the excess LAH carefully quenched with 1.6 mL H_2O, 1.6 mL 3M NaOH and 4.8 mL H_2O in succession. The grey slurry is then brought to rt and ca. 5 g Na_2SO_4 added. This mixture is allowed to stir for 10 min then passed through a pad of celite, rinsing with Et_2O. Concentration of the filtrate yields a clear, colorless oil (3.31 g, 25.8 mmol, 94%). No further purification necessary. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.60 (ddd, J = 17.1, 10.2, 9.5 Hz, 1H), 5.04 (dd, J = 10.2, 2.1 Hz, 1H), 5.00 (ddd, J = 17.1, 2.1, 0.7 Hz, 1H), 3.67 (ddd, J = 10.7, 7.0, 5.5 Hz, 1H), 3.59 (dt, J = 10.6, 7.1 Hz, 1H), 1.97 – 1.90 (m, 1H), 1.75 – 1.68 (m, 1H), 1.63 – 1.54 (m, 1H), 1.54 – 1.46 (m, 1H), 1.41 (br s, 1H), 0.89 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.56 (s), 115.84 (s), 61.67 (s), 47.53 (s), 34.85 (s), 31.83 (s), 20.45 (s), 18.92 (s); IR (neat): 3325.1 (w, br), 2988.0 (m), 2870.1 (s), 1450.4 (w), 1391.6 (m), 1360.6 (w), 1295.9 (w), 1141.8

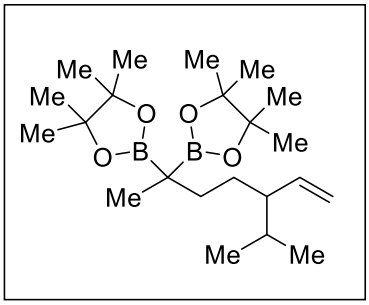
(s), 1073.6 (w), 911.4 (w), 734.3 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_8{}^{1}H_{17}{}^{16}O_1$ $[M+H]^+$: calculated: 129.1279, found: 129.1281.



5-bromo-3-isopropylpent-1-ene (86). A flame dried 100 mL round bottom equipped with magnetic stir bar is charged with PPh_3 (3.41 g, 12.7 mmol, 1.1 equiv) then sealed with a rubber septum. A solution of **85** (1.47 g, 11.5 mmol, 1.0 equiv) in anhydrous DCM (11.5 mL) is then charged into the reaction vessel. The homogeneous mixture is allowed to stir at 0°C and the vessel temporarily opened to allow for the slow addition of solid NBS (2.25 g, 12.7 mmol, 1.1 equiv; this process is highly exothermic). Vessel is re-sealed and allowed to stir at rt for 3h, at which point it is concentrated in vacuo to render crude solid/oil mixutre. Solid is suspended in Pentanes and loaded onto a SiO_2 column. The column is then eluted with 1% Et_2O/Pentane, visualizing the product with $KMnO_4$. Product isolated as clear, colorless oil (1.80 g, 9.42 mmol, 82%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.50 (ddd, *J* = 17.0, 10.3, 9.3 Hz, 1H), 5.09 (dd, *J* = 10.3, 2.1 Hz, 1H), 5.04 (dd, *J* = 17.1, 2.0 Hz, 1H), 3.45 (ddd, *J* = 9.6, 7.7, 4.6 Hz, 1H), 3.29 (m, 1H), 2.03 – 1.93 (m, 2H), 1.82 – 1.74 (m, 1H), 1.60 (m, 1H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.85 (s), 116.88 (s), 49.18 (s), 34.98 (s), 32.55 (s), 31.53 (s), 20.43 (s), 19.04 (s); IR (neat): 3076.2 (w), 2959.5 (s), 2929.7 (m), 2873.3 (m), 1638.1 (w), 1465.5 (w), 1368.8 (w), 1256.9 (m), 1212.1 (w), 999.3 (m), 917.4 (s), 639.5 (w), 568.5 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_8{}^{1}H_{16}{}^{79}Br_1$ $[M+H]^+$: calculated: 191.0435, found: 191.0438.



2,2'-(ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (87). The reaction was performed according to *Representative Procedure (Method C)* with 1,1-diborylmethane **54** (2.68 g, 10.0 mmol, 1.00 equiv), LTMP (1.69 g, 11.5 mmol, 1.15 equiv), Iododmethane (716 µL, 11.5 mmol, 1.15 equiv) and THF (40 mL). The crude reaction mixture was purified by column chromatography on silica gel (0% EtOAc/Hexanes, gradient to 6% EtOAc/Hexanes, visualized with CAM stain) to afford a clear, colorless oil (1.80 g, 6.38 mmol, 64%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.21 (s, 12H), 1.21 (s, 12H), 1.02 (d, *J* = 7.2 Hz, 3H), 0.70 (q, *J*= 7.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 82.85 (s), 24.80 (s), 24.50 (s), 9.02 (s); IR (neat): 2976.8 (w), 2934.5 (w), 2879.4 (w), 1460.5 (w), 1304.2 (s), 1268.8 (m), 1216.1 (w), 1142.1 (s), 1105.9 (m), 846.1 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{14}{}^{1}H_{29}{}^{11}B_2{}^{16}O_4$ $[M+H]^+$: calculated: 283.2252, found: 283.2265.



2,2'-(5-isopropylhept-6-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (32). The reaction was performed according to *Representative Procedure (Method D)* with diboronate ester **87** (1.76 g, 6.24 mmol, 1.00 equiv), LTMP (964 mg, 6.55 mmol, 1.05 equiv), alkyl bromide **86** (1.25 g, 6.55 mmol, 1.05 equiv) and THF (25 mL). The crude reaction mixture was purified by column chromatography on silica gel (1% EtOAc/Hexanes, gradient to 3% EtOAc/Hexanes, visualized with CAM stain) to afford a clear, colorless oil (2.32 g, 5.92 mmol, 94%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.56 (ddd, *J* = 17.0, 10.3, 9.0 Hz, 1H), 4.97 (dd, *J* = 10.3, 2.3 Hz, 1H), 4.92 (dd, *J* = 17.1, 2.3 Hz, 1H), 1.78 – 1.69 (m, 1H), 1.60 (ddd, *J* = 13.6, 12.1, 6.8 Hz, 1H), 1.55 – 1.41 (m, 2H), 1.42 – 1.33 (m, 1H), 1.28 – 1.22 (m, 1H), 1.22 – 1.18 (m, 24H), 1.03 (s, 3H), 0.84 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H). ^{13}C

NMR (150 MHz, $CDCl_3$): δ 141.17 (s), 114.87 (s), 82.82 (s), 82.80 (s), 51.01 (s), 31.82 (s), 31.24 (s), 29.67 (s), 24.73 (s), 24.70 (s), 24.61 (s), 20.58 (s), 18.79 (s), 15.99 (s). IR (neat): 2976.3 (w), 2930.3 (w), 2869.8 (w), 1458.9 (w), 1298.5 (s), 1138.0 (s), 1080.9 (w), 968.3 (w), 848.9 (m), 668.7 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{22}{}^{1}H_{43}{}^{11}B_{2}{}^{16}O_4$ $[M+H]^+$: calculated: 393.3347, found: 393.3358.

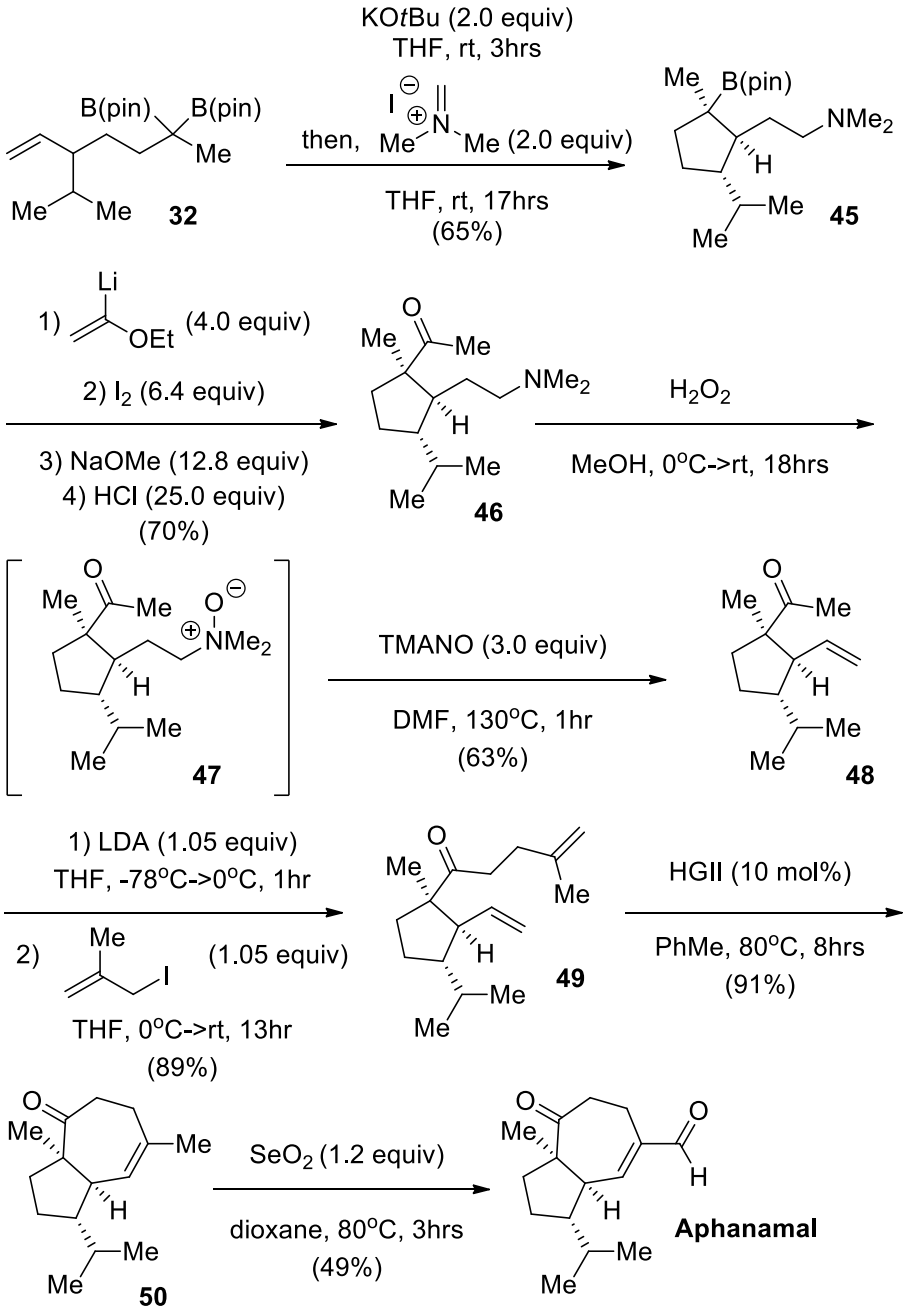
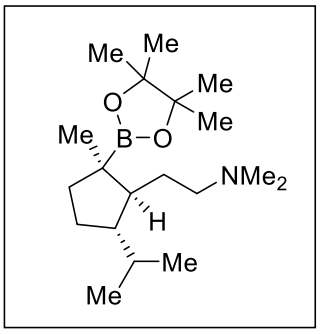
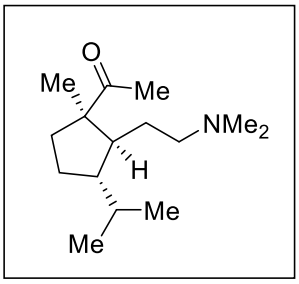


Figure 69 - Total synthesis of aphanamal



2-((1*S*,2*S*,5*S*)-5-isopropyl-2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)-*N*,*N*-dimethylethan-1-amine (45). A flame-dried, 250mL round bottom equipped with magnetic stirbar is charged with **32** (2.97 g, 7.57 mmol) inside an Argon filled glovebox. A solution is then prepared with anhydrous THF (37.9 mL, 0.2 M). KO*t*Bu (1.70 g, 15.1 mmol, 2 equiv.) is then added to the solution neat, in one portion. The reaction mixture is allowed to stir for 3hrs inside the glovebox at room temperature and gradually becomes clear, pale yellow. At this point, freshly prepared Eschenmoser's Salt[31] (2.80 g, 15.1 mmol, 2 equiv.) is added neat, in one portion; white slurry results. The sealed reaction vessel is then brought to the fume hood where it is allowed to stir for 17h at room temperature. Mixture is then diluted with reagent grade Et_2O and passed through a pad of silica, rinsing with 50% EtOAc/1.5% NEt_3/Hexanes. After concentration, ^{1}H NMR suggests ca. 7:1 epimeric ratio (presumably about the isopropyl group). SiO_2 chromatography performed (5% NEt_3/Hexanes, then 5% NEt_3/5% EtOAc/Hexanes), rendering product of acceptable purity as clear, colorless oil (1.59 g, 4.92 mmol, 65%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.30 – 2.24 (m, 2H), 2.20 (s, 6H), 1.79 – 1.71 (m, 1H), 1.70 – 1.60 (m, 4H), 1.58 – 1.48 (m, 1H), 1.40 – 1.32 (m, 1H), 1.21 (s, 12H), 1.19 – 1.08 (m, 2H), 1.01 (s, 3H), 0.89 (d, J = 6.7 Hz, 3H), 0.78 (d, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 82.60 (s), 59.82 (s), 52.54 (s), 51.78 (s), 45.55 (s), 37.69 (s), 31.97 (s), 30.01 (s), 24.87 (s), 24.83 (s), 24.78 (s), 24.75 (s), 22.71 (s), 16.93 (s). IR (neat): 2949.7 (br m), 2867.3 (w), 1460.8 (m), 1379.8 (s), 1369.2 (s), 1300.1 (s), 1142.2 (s), 856.5 (m), 693.4 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{19}{}^{1}H_{39}{}^{11}B_{1}{}^{14}N_{1}{}^{16}O_{2}$ $[M+H]^+$: calculated: 324.3074, found: 324.3063.

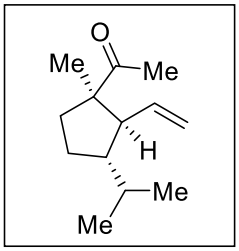
31. Schreiber, J.; Maag, H.; Hashimoto, N.; Eschenmoser, A., Dimethyl(methylene)ammonium Iodide. *Angew. Chem. Int. Ed.* **1971,** *10* (5), 330-331.



1-((1*R*,2*S*,3*S*)-2-(2-(dimethylamino)ethyl)-3-isopropyl-1-methylcyclopentyl)ethan-1-one (46). Adapted from published procedure.[47] A flame-dried, 500mL round bottom equipped with magnetic stirbar is sealed then evacuated/refilled with Nitrogen gas 3x. The vessel is then charged with Ethyl vinyl ether (3.00 mL, 31.3 mmol, 6.4 equiv.) followed by 60 mL anhydrous THF. The solution is allowed to then stir at -78ºC, and *t*-BuLi in Pentanes (11.5 mL, 1.7 M, 19.6 mmol, 4.0 equiv.) added across ca. 10min. The resulting mixture is a bright yellow solution. This solution is allowed to stir for 30min at -78ºC, then the mixture brought to 0ºC, where it is allowed to stir for an additional 30min (mixture becomes clear, colorless during the heating process and a black discoloration of the Teflon stirbar is noted). Mixture is cooled back to -78ºC and a solution of **45** (1.58 g, 4.89 mmol, 1.0 equiv) in 60 mL anhydrous THF added across ca. 10min. The mixture is allowed to stir for 30min at -78ºC, then brought to room temperature where it is allowed to stir for 5min (warming with a water bath). Mixture is again lowered to -78ºC and a solution of I_2 in anhydrous THF (62.6 mL, 0.5 M, 31.3 mmol, 6.4 equiv.) added gradually across ca. 10min. The resulting deep purple mixture is allowed to stir for 30min at -78ºC, then brought to room temperature where it is allowed to stir an additional 10min (warming with a water bath). Mixture is cooled back to -78ºC and a solution of NaOMe in methanol (62.6 mL, 1.0 M, 62.6 mmol, 12.8 equiv.) is added gradually. The mixture is then allowed to stir overnight at room temperature. Upon return, the mixture is pale yellow. An aqueous solution of HCl is added gradually (122 mL, 1.0 M, 122 mmol, 25 equiv.). Mixture becomes orange. A saturated, aqueous solution of $Na_2S_2O_3$ then added (ca. 30 mL) and the mixture made basic with

47. Sonawane, R. P.; Jheengut, V.; Rabalakos, C.; Larouche-Gauthier, R.; Scott, H. K.; Aggarwal, V. K., Enantioselective Construction of Quaternary Stereogenic Centers from Tertiary Boronic Esters: Methodology and Applications. *Angew. Chem. Int. Ed.* **2011,** *50* (16), 3760-3763.

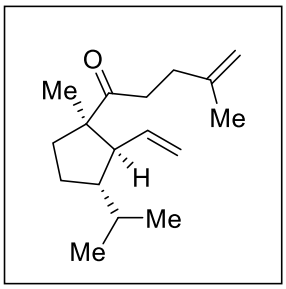
saturated, aqueous $NaHCO_3$. Organics are then extracted 3x with Et_2O and combined organics washed 2x with H_2O and once with Brine. Organics dried over Na_2SO_4 then concentrated to give crude oil. Crude oil purified by SiO_2 chromatography (10% EtOAc/pentane, then 25% EtOAc/pentane, then 10% EtOAc/5% NEt_3/Pentane, then 25% EtOAc/5% NEt_3/Pentane), visualizing with Cerium Ammonium Molybdate stain. Product isolated as pale yellow oil (823 mg, 3.44 mmol, 70%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.19 (t, *J* = 7.8 Hz, 2H), 2.16 (s, 6H), 2.13 (s, 3H), 2.03 – 1.95 (m, 1H), 1.77 – 1.58 (m, 3H), 1.55 – 1.48 (m, 1H), 1.48 – 1.31 (m, 4H), 1.21 (s, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 213.22 (s), 58.80 (s), 58.71 (s), 52.19 (s), 50.52 (s), 45.46 (s), 35.69 (s), 31.09 (s), 30.27 (s), 28.25 (s), 25.27 (s), 24.97 (s), 22.65 (s), 17.64 (s).IR (neat): 2953.9 (br s), 2871.7 (m), 2763.9 (w), 1698.0 (s), 1461.2 (s), 1352.6 (m), 1041.4 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{15}{}^{1}H_{30}{}^{14}N_{1}{}^{16}O_{1}$ $[M+H]^+$: calculated: 240.2327, found: 240.2337.



1-((1*R*,2*S*,3*S*)-3-isopropyl-1-methyl-2-vinylcyclopentyl)ethan-1-one (48). Adapted from published procedure.[48] A 50 mL round bottom equipped with magnetic stirbar is charged with **46** (823 mg, 3.44 mmol) and solution made with reagent grade MeOH (18.8 mL, 0.18 M). The reaction vessel and contents are brought to 0°C and aqueous H_2O_2 (2.96 mL, ca. 30% w/w) added gradually. The mixture is allowed to stir overnight (19.5h), slowly reaching room temperature. Upon return, excess H_2O_2 is degraded by adding two spatula tips (ca. 50 mg) MnO_2 to mixture and stirring for 1h at room temperature (or until bubbling ceases). The mixture is then filtered through a pad of celite, rinsing with MeOH. Filtrate concentrated, then redissolved in DCM and dried over Na_2SO_4. Solution decanted then concentrated to yield crude, *N*-oxide intermediate **47** as a yellow oil. A 40

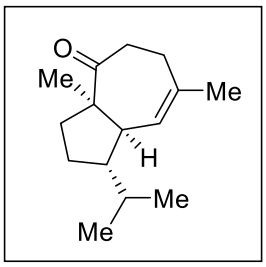
48. White, J. D.; Ihle, D. C., Tandem Photocycloaddition−Retro-Mannich Fragmentation of Enaminones. A Route to Spiropyrrolines and the Tetracyclic Core of Koumine. *Org. Lett.* **2006,** *8* (6), 1081-1084.

mL vial containing *N*-oxide intermediate and magnetic stirbar is charged with TMANO dihydrate (1.15 g, 10.3 mmol, 3.0 equiv.). The vessel is then charged with 14.5 mL DMF (purchased as anhydrous from Acros, stored over sieves in sealed container with septum). Reaction vessel is sealed and set to stir at 130°C in preheated oil bath for 1h, where the mixture gradually becomes more yellow in color. Reaction removed from oil bath and allowed to cool to room temperature then poured into a separatory funnel and diluted with Et_2O (ca. 50 mL). Organics washed 4x with ca. 10 mL H_2O the once with Brine. Organics dried over Na_2SO_4 then decanted and concentrated to yield yellow oil. Crude yellow oil is purified by SiO_2 chromatography (2% Et_2O/pentane, visualized with $KMnO_4$ stain) to render product as pale yellow oil with pleasant, turpentine-like smell. (425 mg, 2.19 mmol, 63%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.57 (dt, *J* = 17.0, 10.0 Hz, 1H), 5.03 – 4.96 (m, 2H), 2.16 (m, 1H), 2.06 (s, 3H), 2.01 (m, 1H), 1.82 – 1.73 (m, 2H), 1.63 – 1.54 (m, 1H), 1.45 – 1.35 (m, 1H), 1.35 – 1.29 (m, 1H), 1.26 (s, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 213.07 (s), 139.94 (s), 115.90 (s), 59.57 (s), 59.51 (s), 51.03 (s), 35.21 (s), 30.35 (s), 28.61 (s), 25.92 (s), 24.41 (s), 21.95 (s), 18.19 (s). IR (neat): 2956.8 (s), 2872.6 (m), 1700.7 (s), 1464.5 (m), 1352.7 (m), 1002.7 (w), 912.2 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{13}{}^{1}H_{23}{}^{16}O_1$ $[M+H]^+$: calculated: 195.1749, found: 195.1750.



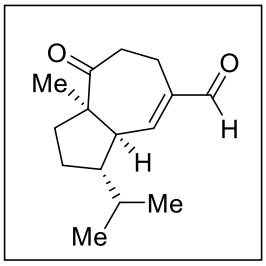
1-((1*R*,2*S*,3*S*)-3-isopropyl-1-methyl-2-vinylcyclopentyl)-4-methylpent-4-en-1-one (49). A flamed dried 20 mL vial equipped with magnetic stirbar is sealed with rubber septum, then evacuated/refilled with N_2 3x. LDA is prepared freshly in the vial at -78°C by slow addition of *n*BuLi in Hexanes (812 μL, 2.5 M, 1.05 equiv.) to a solution of diisopropyl amine (285 μL, 2.03 mmol, 1.05 equiv.) in 0.5 mL anhydrous THF. Mixture is allowed to stir for ca. 15min at -78°C then a solution of **48** (376 mg, 1.93 mmol, 1.0 equiv.) in 1.5 mL

anhydrous THF added dropwise. Resulting mixture allowed to stir for 40min at -78ºC then 20min at 0ºC. At this point, freshly prepared, neat methallyl iodide (218 μL, 2.03 mmol, 1.05 equiv.) charged in at once. Resulting mixture allowed to stir overnight (14h), slowly reaching room temperature. Upon return, mixture is quenched with ca. 1 mL H_2O then extracted 3x with ca. 5 mL Et_2O. Combined organics dried over Na_2SO_4 then decanted and concentrated to render crude oil. Crude oil purified by SiO_2 chromatography (pentane, then 1% Et_2O/pentane, visualized with $KMnO_4$). Product isolated as clear, colorless oil (428 mg, 1.73 mmol, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.54 (ddd, *J* = 17.3, 9.9 Hz, 9.9 Hz, 1H), 5.05 – 4.92 (m, 2H), 4.70 (s, 1H), 4.65 (s, 1H), 2.51 (t, *J* = 7.7 Hz, 2H), 2.31 – 2.07 (m, 3H), 2.02 (t, *J* = 9.1 Hz, 1H), 1.84 – 1.74 (m, 2H), 1.71 (s, 3H), 1.63 – 1.52 (m, 1H), 1.47 – 1.29 (m, 2H), 1.28 (s, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 214.04 (s), 145.18 (s), 140.02 (s), 115.82 (s), 109.88 (s), 59.83 (s), 59.38 (s), 51.10 (s), 38.76 (s), 35.43 (s), 31.44 (s), 30.44 (s), 26.01 (s), 24.15 (s), 22.65 (s), 21.96 (s), 18.27 (s). IR (neat): 2956.4 (s), 2872.7 (m), 1700.0 (s), 1649.7 (w), 1459.4 (m), 1375.9 (w), 1003.2 (m), 911.3 (m), 887,0 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{17}{}^{1}H_{29}{}^{16}O_1$ $[M+H]^+$: calculated: 249.2198, found: 249.2220.



(1*S*,3a*R*,8a*R*)-1-isopropyl-3a,7-dimethyl-2,3,3a,5,6,8a-hexahydroazulen-4(2*H*)-one (50). A 25 mL, 2-neck round bottom is fixed with a stopcock side-arm and a reflux condenser. The vessel is equipped with a magnetic stirbar then the whole apparatus flame dried. Upon cooling to near room temperature, the vessel is charged with Hoveyda-Grubbs 2nd Generation (94 mg, 0.15 mmol, 10 mol%) then sealed and evacuated/refilled with N_2 3x. A solution of **49** (368 mg, 1.48 mmol, 1.0 equiv.) in 8.9 mL anhydrous toluene is then transferred to the reaction vessel. The green mixture is then set to stir at 80ºC with a steady stream of N_2 blowing across the solution, from the

side-arm out the reflux condenser (in order to remove forming ethylene from solution). Reaction is allowed to stir for 8.5h then cooled to room temperature. The reaction solution is then concentrated in vacuo and crude oil purified by SiO_2 chromatography (1% Et_2O/Pentane, then 2.5% Et_2O/Pentane, visualized with $KMnO_4$). Clear, colorless oil results (298 mg, 1.35 mmol, 91%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.22 (d, *J* = 4.2 Hz, 1H), 2.74 (ddd, *J* = 14.6, 5.6, 4.0 Hz, 1H), 2.61 – 2.49 (m, 1H), 2.42 (ddd, *J* = 14.6, 12.0, 5.7 Hz, 1H), 2.27 – 2.18 (m, 1H), 2.09 – 1.98 (m, 2H), 1.79 – 1.73 (m, 1H), 1.71 (s, 3H), 1.61 (ddd, *J* = 14.7, 10.5, 7.4 Hz, 1H), 1.55 (dq, *J* = 13.6, 6.7 Hz, 1H),1.38 – 1.26 (m, 2H), 1.22 (s, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 212.06 (s), 192.63 (s), 158.54 (s), 143.71 (s), 59.58 (s), 55.32 (s), 53.10 (s), 38.86 (s), 35.09 (s), 32.30 (s), 26.74 (s), 24.94 (s), 21.91 (s), 19.62 (s), 19.41 (s). IR (neat): 2953.7 (m), 2869.7 (m), 1698.7 (s), 1459.0 (w), 1446.4 (w), 1384.9 (w), 1072.2 (w), 1006.4 (w), 816.1 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{15}{}^{1}H_{25}{}^{16}O_1$ $[M+H]^+$: calculated: 221.1905, found: 221.1904.

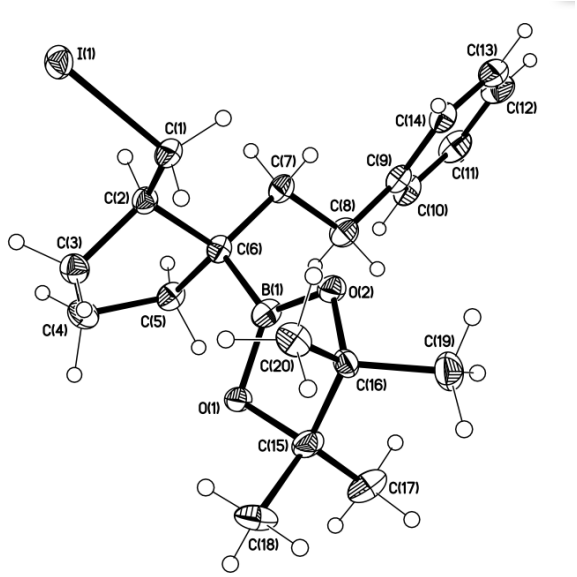


(3*S*,3a*R*,8a*R*)-3-isopropyl-8a-methyl-8-oxo-1,2,3,3a,6,7,8,8a-octahydroazulene-5-carbaldehyde (Aphanamal). A 20 mL vial containing **50** (294 mg, 1.33 mmol, 1.0 equiv.) was equipped with magnetic stirring bar and charged with SeO_2 (177 mg, 1.6 mmol, 1.2 equiv.). The vial was then sealed with a rubber septum and evacuated/refilled with N_2 3x. Anhydrous 1,4-dioxane (6.6 mL, 0.2 M) was then charged in and the resulting, heterogeneous mixture set to stir (ca. 800 rpm) at 80ºC in a preheated oil bath. The mixture becomes clear, orange in appearance and homogeneous within 30min of heating. After stirring at 80ºC for 3h, the mixture is cooled to room temperature then passed through a pad of SiO_2, rinsing with Et_2O. The filtrate is concentrated to render crude, orange oil. SiO_2 chromatography performed (5% Et_2O/Pentane, gradient to 20%

Et_2O/Pentane). Product isolated as yellow oil (153 mg, 0.65 mmol, 49%). ^{13}C and ^{1}H NMR spectra are in accord with published values.[49] ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.33 (s, 1H), 6.62 (d, *J* = 5.3 Hz, 1H), 2.80 – 2.75 (m, 1H), 2.73 – 2.67 (m, 1H), 2.52 (dd, *J* = 8.7, 5.4 Hz, 1H), 2.51 – 2.46 (m, 1H), 2.45 – 2.39 (m, 1H), 2.24 – 2.15 (m, 1H), 1.88 – 1.76 (m, 2H), 1.64 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.47 – 1.36 (m, 2H), 1.31 (s, 3H), 0.92 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 212.06 (s), 192.63 (s), 158.54 (s), 143.71 (s), 59.58 (s), 55.32 (s), 53.10 (s), 38.86 (s), 35.09 (s), 32.30 (s), 26.74 (s), 24.94 (s), 21.91 (s), 19.62 (s), 19.41 (s). IR (neat): 2957.2 (m), 2871.5 (w), 1683.9 (s), 1635.7 (w), 1459.1 (w), 1313.1 (w), 1173.5 (w), 793.5 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{15}{}^{1}H_{23}{}^{16}O_2$ $[M+H]^+$: calculated: 235.1698, found: 235.1701.

49. Moriyasu, M.; Takeuchi, S.; Ichimaru, M.; Nakatani, N.; Nishiyama, Y.; Kato, A.; Mathenge, S. G.; Juma, F. D.; ChaloMutiso, P. B., Pyrenes and pyrendiones from Uvaria lucida. *J. Nat. Med.* **2012,** *66* (3), 453-458.

F. X-ray crystallographic data



Crystal data and structure refinement for **2-((1*R*,2*S*)-2-(iodomethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**. **(Compound 6).**

Identification code	C20H30BIO2	
Empirical formula	C20 H30 B I O2	
Formula weight	440.15	
Temperature	100(2) K	
Wavelength	0.71073 ≈	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.5129(8) ≈	α= 99.987(2)∞.
	b = 13.4237(16) ≈	β= 95.992(2)∞.
	c = 23.452(3) ≈	γ = 96.163(2)∞.
Volume	1991.7(4) $\approx^3$	
Z	4	

Density (calculated)	1.468 Mg/m^3
Absorption coefficient	1.617 mm^{-1}
F(000)	896
Crystal size	0.400 x 0.210 x 0.150 mm^3
Theta range for data collection	1.639 to 28.450∞.
Index ranges	-8<=h<=8, -17<=k<=17, -31<=l<=31
Reflections collected	38081
Independent reflections	10019 [R(int) = 0.0443]
Completeness to theta = 25.242∞	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6368
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10019 / 1 / 500
Goodness-of-fit on F^2	1.014
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0648
R indices (all data)	R1 = 0.0501, wR2 = 0.0718
Extinction coefficient	na
Largest diff. peak and hole	1.372 and -0.705 e.$\approx^{-3}$

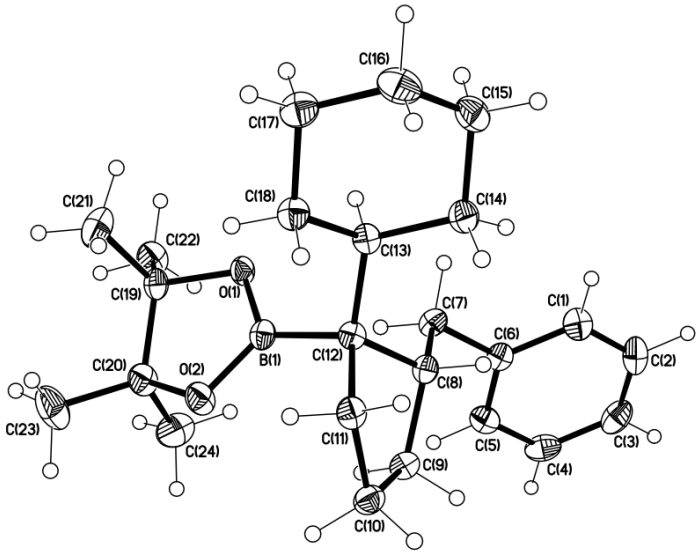
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($\approx^2$x 10^3)

for C20H30BIO2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)

I(1)	-2688(1)	8964(1)	2686(1)	22(1)
O(2)	53(3)	6298(1)	3911(1)	20(1)
B(1)	1532(5)	7128(2)	4056(1)	21(1)
C(1)	-1455(4)	8104(2)	3314(1)	20(1)
C(2)	292(4)	8747(2)	3743(1)	18(1)
C(3)	2305(4)	8995(2)	3486(1)	22(1)
C(4)	3922(4)	9401(2)	4024(1)	24(1)
C(5)	3035(4)	8990(2)	4538(1)	20(1)
C(6)	1022(4)	8255(2)	4272(1)	17(1)
C(7)	-613(4)	8255(2)	4702(1)	20(1)
C(8)	141(4)	7877(2)	5255(1)	24(1)
C(9)	-1343(4)	7918(2)	5712(1)	20(1)
C(10)	-665(4)	8360(2)	6286(1)	26(1)
C(11)	-1990(5)	8377(2)	6714(1)	30(1)
C(12)	-4042(5)	7939(2)	6566(1)	31(1)
C(13)	-4752(4)	7494(2)	5993(1)	28(1)
C(14)	-3424(4)	7487(2)	5567(1)	22(1)
O(1)	3490(10)	6911(6)	3899(3)	18(1)
C(15)	3369(4)	5794(2)	3800(1)	24(1)
C(16)	971(8)	5454(4)	3569(3)	17(1)
C(17)	4185(11)	5443(5)	4300(3)	28(2)
C(18)	4715(9)	5507(5)	3275(3)	26(1)
C(19)	138(11)	4472(5)	3748(3)	29(2)
C(20)	314(7)	5426(4)	2926(2)	22(1)
O(1X)	3508(11)	6877(7)	4129(3)	18(1)
C(15X)	3369(4)	5794(2)	3800(1)	24(1)
C(16X)	1111(8)	5382(4)	3915(3)	21(1)
C(17X)	5083(10)	5330(6)	4167(4)	27(2)
C(18X)	3761(13)	5791(6)	3223(3)	33(2)
C(19X)	925(10)	5039(5)	4499(3)	31(2)
C(20X)	69(12)	4557(6)	3430(4)	37(2)
I(2)	1188(1)	-112(1)	1601(1)	24(1)
O(3)	7717(3)	2663(1)	800(1)	22(1)
O(4)	4297(3)	2481(1)	432(1)	21(1)
B(2)	5722(4)	2670(2)	924(1)	15(1)
C(21)	2576(4)	1186(2)	1285(1)	20(1)
C(22)	4214(4)	1849(2)	1738(1)	17(1)
C(23)	6177(4)	1364(2)	1884(1)	24(1)
C(24)	7890(4)	2260(2)	2137(1)	27(1)
C(25)	6965(4)	3230(2)	2028(1)	22(1)

C(26)	5057(4)	2869(2)	1558(1)	16(1)
C(27)	3411(4)	3617(2)	1599(1)	18(1)
C(28)	4219(4)	4659(2)	1471(1)	21(1)
C(29)	2722(4)	5441(2)	1529(1)	18(1)
C(30)	3393(4)	6433(2)	1827(1)	21(1)
C(31)	2049(4)	7166(2)	1876(1)	25(1)
C(32)	-7(4)	6927(2)	1629(1)	26(1)
C(33)	-689(4)	5951(2)	1328(1)	26(1)
C(34)	644(4)	5209(2)	1282(1)	23(1)
C(35)	7617(4)	2262(2)	171(1)	24(1)
C(36)	5453(4)	2521(2)	-69(1)	19(1)
C(37)	7693(5)	1120(2)	109(1)	40(1)
C(38)	9428(4)	2782(3)	-62(1)	43(1)
C(39)	5514(5)	3600(2)	-188(1)	33(1)
C(40)	4339(4)	1753(2)	-595(1)	30(1)



Crystal data and structure refinement for **2-((1*R*,2*R*)-2-benzyl-1-cyclohexylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 9).**

Identification code	C24H37BO2
Empirical formula	C24 H37 B O2
Formula weight	368.34

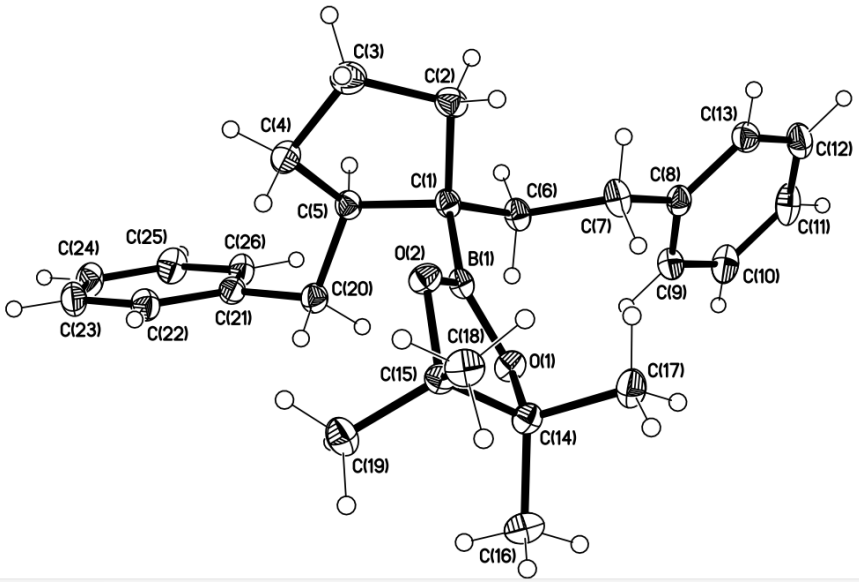
Temperature	100(2) K	
Wavelength	0.71073 ≈	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.6816(10) ≈	α= 90∞.
	b = 18.2436(19) ≈	β= 106.083(2)∞.
	c = 12.6856(13) ≈	γ = 90∞.
Volume	2152.9(4) $≈^3$	
Z	4	
Density (calculated)	1.136 Mg/m^3	
Absorption coefficient	0.069 mm^{-1}	
F(000)	808	
Crystal size	0.400 x 0.250 x 0.180 mm^3	
Theta range for data collection	1.671 to 28.339∞.	
Index ranges	-12<=h<=12, -24<=k<=24, -16<=l<=16	
Reflections collected	38756	
Independent reflections	10716 [R(int) = 0.0408]	
Completeness to theta = 25.242∞	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6888	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10716 / 1 / 496	
Goodness-of-fit on F^2	1.057	

Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.0949
R indices (all data)	R1 = 0.0609, wR2 = 0.1035
Extinction coefficient	na
Largest diff. peak and hole	0.249 and -0.204 e.≈$^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3) for c24h37bo2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6063(2)	4076(1)	7419(1)	19(1)
O(2)	6763(2)	5252(1)	7239(1)	24(1)
B(1)	6938(3)	4526(2)	7027(2)	18(1)
C(1)	11365(3)	2530(1)	8609(2)	25(1)
C(2)	12672(3)	2314(2)	9307(2)	29(1)
C(3)	13283(3)	2698(2)	10260(2)	29(1)
C(4)	12581(3)	3300(2)	10513(2)	28(1)
C(5)	11273(3)	3523(1)	9810(2)	23(1)
C(6)	10647(2)	3139(1)	8850(2)	19(1)
C(7)	9233(2)	3383(1)	8077(2)	21(1)
C(8)	9426(2)	3951(1)	7244(2)	18(1)
C(9)	10151(2)	4665(1)	7754(2)	20(1)
C(10)	9808(2)	5230(1)	6811(2)	23(1)
C(11)	8642(2)	4870(1)	5868(2)	20(1)
C(12)	8029(2)	4227(1)	6396(2)	17(1)
C(13)	7216(2)	3644(1)	5562(2)	18(1)
C(14)	8149(3)	3167(1)	5037(2)	23(1)
C(15)	7238(3)	2616(1)	4224(2)	27(1)
C(16)	6051(3)	2994(2)	3343(2)	31(1)
C(17)	5109(3)	3456(1)	3861(2)	26(1)
C(18)	6018(2)	4008(1)	4658(2)	21(1)
C(19)	5048(2)	4539(1)	7778(2)	21(1)
C(20)	5866(3)	5281(1)	7999(2)	24(1)
C(21)	3694(3)	4582(2)	6819(2)	33(1)

C(22)	4731(3)	4186(1)	8765(2)	28(1)
C(23)	4945(3)	5960(2)	7749(2)	38(1)
C(24)	6899(3)	5330(2)	9148(2)	35(1)
O(3)	1073(2)	6054(1)	2477(1)	20(1)
O(4)	1855(2)	4917(1)	2164(1)	23(1)
B(2)	1950(3)	5655(1)	2006(2)	18(1)
C(25)	6537(3)	7496(1)	3698(2)	26(1)
C(26)	7861(3)	7636(2)	4440(2)	33(1)
C(27)	8243(3)	7291(2)	5448(2)	32(1)
C(28)	7300(3)	6804(1)	5718(2)	29(1)
C(29)	5981(3)	6663(1)	4973(2)	24(1)
C(30)	5581(2)	7007(1)	3951(2)	20(1)
C(31)	4174(2)	6830(1)	3121(2)	20(1)
C(32)	4379(2)	6281(1)	2263(2)	18(1)
C(33)	5108(2)	5562(1)	2723(2)	22(1)
C(34)	4916(3)	5073(1)	1708(2)	24(1)
C(35)	3644(2)	5405(1)	814(2)	20(1)
C(36)	2997(2)	6011(1)	1393(2)	16(1)
C(37)	2178(2)	6619(1)	607(2)	17(1)
C(38)	3124(3)	7113(1)	117(2)	22(1)
C(39)	2237(3)	7686(1)	-658(2)	28(1)
C(40)	1044(3)	7337(2)	-1563(2)	32(1)
C(41)	82(3)	6861(2)	-1076(2)	28(1)
C(42)	968(3)	6282(1)	-312(2)	22(1)
C(43)	556(2)	5554(1)	3189(2)	22(1)
C(44)	711(3)	4793(1)	2691(2)	23(1)
C(45)	-962(3)	5768(2)	3167(2)	31(1)
C(46)	1562(3)	5657(2)	4346(2)	33(1)
C(47)	-614(3)	4567(2)	1789(2)	36(1)
C(48)	1180(3)	4174(2)	3511(2)	35(1)



Crystal data and structure refinement for **2-((1*R*,2*R*)-2-benzyl-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 13, major diastereomer).**

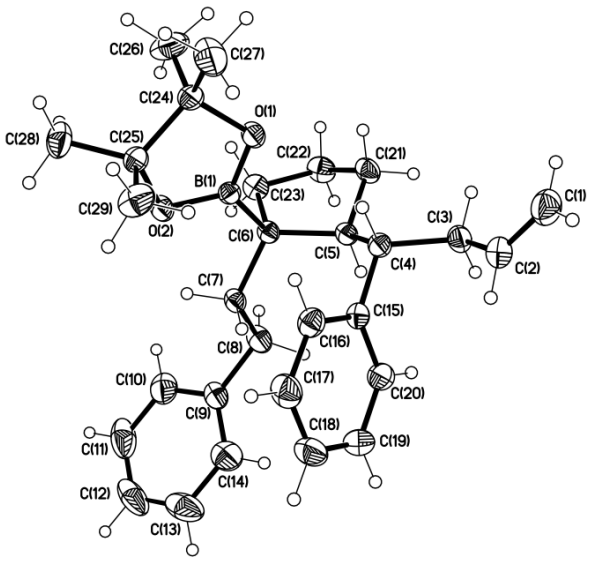
Identification code	C26H35BO2	
Empirical formula	C26 H35 B O2	
Formula weight	390.35	
Temperature	100(2) K	
Wavelength	0.71073 ≈	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.0652(19) ≈	α= 90∞.
	b = 17.228(3) ≈	β= 98.660(3)∞.
	c = 11.842(2) ≈	γ = 90∞.
Volume	2231.7(7) $\approx^3$	
Z	4	
Density (calculated)	1.162 Mg/m^3	

Absorption coefficient	0.070 mm^{-1}
F(000)	848
Crystal size	0.530 x 0.400 x 0.220 mm^3
Theta range for data collection	2.103 to 28.324∞.
Index ranges	-14<=h<=14, -22<=k<=20, -15<=l<=15
Reflections collected	43822
Independent reflections	5557 [R(int) = 0.0352]
Completeness to theta = 25.242∞	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.7070
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5557 / 0 / 266
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.0983
R indices (all data)	R1 = 0.0474, wR2 = 0.1046
Extinction coefficient	na
Largest diff. peak and hole	0.390 and -0.188 e.$\approx^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($\approx^2$x 10^3) for C26H35BO2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	3744(1)	6957(1)	6459(1)	16(1)

C(1)	4240(1)	6174(1)	6004(1)	16(1)
C(2)	3572(1)	5462(1)	6436(1)	20(1)
C(3)	4263(1)	5252(1)	7628(1)	25(1)
C(4)	5459(1)	5724(1)	7780(1)	21(1)
C(5)	5581(1)	6018(1)	6580(1)	17(1)
C(6)	4146(1)	6187(1)	4692(1)	19(1)
C(7)	2834(1)	6200(1)	4049(1)	22(1)
C(8)	2736(1)	6139(1)	2762(1)	19(1)
C(9)	3493(1)	6557(1)	2143(1)	24(1)
C(10)	3359(1)	6505(1)	960(1)	28(1)
C(11)	2472(1)	6028(1)	371(1)	28(1)
C(12)	1717(1)	5606(1)	971(1)	26(1)
C(13)	1848(1)	5658(1)	2154(1)	21(1)
C(14)	2901(1)	8165(1)	6432(1)	17(1)
C(15)	3167(1)	7859(1)	7684(1)	17(1)
C(16)	3325(1)	8988(1)	6262(1)	25(1)
C(17)	1568(1)	8068(1)	5898(1)	23(1)
C(18)	2107(1)	7938(1)	8356(1)	22(1)
C(19)	4338(1)	8192(1)	8354(1)	24(1)
C(20)	6468(1)	6702(1)	6570(1)	19(1)
C(21)	7791(1)	6466(1)	6917(1)	18(1)
C(22)	8387(1)	6573(1)	8030(1)	22(1)
C(23)	9608(1)	6368(1)	8336(1)	25(1)
C(24)	10256(1)	6054(1)	7529(1)	26(1)
C(25)	9672(1)	5936(1)	6420(1)	26(1)
C(26)	8448(1)	6137(1)	6121(1)	22(1)
O(1)	3615(1)	7630(1)	5831(1)	18(1)
O(2)	3387(1)	7033(1)	7515(1)	18(1)



Crystal data and structure refinement for **4,4,5,5-tetramethyl-2-((1*R*,2*R*)-1-phenethyl-2-((*R*)-1-phenylbut-3-en-1-yl)cyclopentyl)-1,3,2-dioxaborolane (Compound 23).**

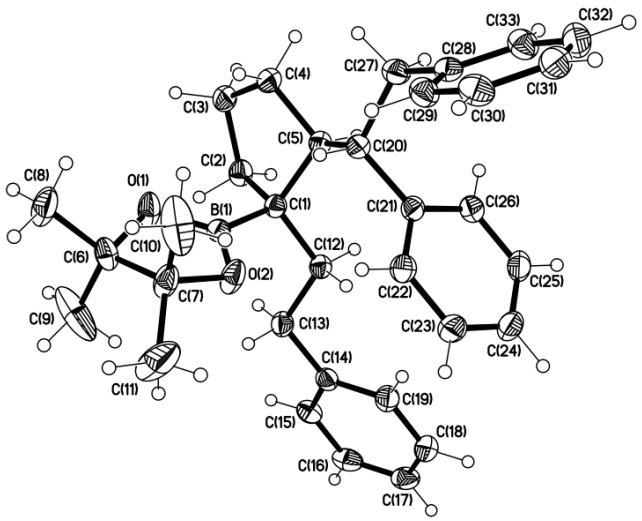
Identification code	C29H39BO2	
Empirical formula	C29 H39BO2	
Formula weight	430.41	
Temperature	173(2) K	
Wavelength	1.54178 ≈	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9886(5) ≈	α= 69.073(2)∞.
	b = 10.2525(5) ≈	β= 84.917(2)∞.
	c = 13.6756(7) ≈	γ = 76.535(2)∞.
Volume	1272.13(11) $\approx^3$	
Z	2	
Density (calculated)	1.124 Mg/m^3	

Absorption coefficient	0.516 mm^{-1}
F(000)	468
Crystal size	0.520 x 0.400 x 0.080 mm^3
Theta range for data collection	3.460 to 66.686∞.
Index ranges	-11<=h<=11, -12<=k<=12, -16<=l<=16
Reflections collected	24493
Independent reflections	4448 [R(int) = 0.0249]
Completeness to theta = 66.750∞	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.6785
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4448 / 0 / 293
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.0981
R indices (all data)	R1 = 0.0407, wR2 = 0.0993
Extinction coefficient	na
Largest diff. peak and hole	0.313 and -0.208 e.≈$^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($\approx^2$x 10^3) for C29H39BO2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1652(1)	3532(1)	4221(1)	33(1)
O(2)	3289(1)	1550(1)	4287(1)	28(1)
B(1)	2635(1)	2887(1)	3680(1)	22(1)
C(1)	2312(2)	9366(2)	2921(1)	47(1)
C(2)	3111(1)	8405(1)	2586(1)	38(1)
C(3)	2640(1)	7591(1)	2017(1)	31(1)
C(4)	3085(1)	5954(1)	2560(1)	25(1)
C(5)	2623(1)	5150(1)	1936(1)	24(1)
C(6)	2891(1)	3481(1)	2455(1)	23(1)
C(7)	4324(1)	2676(1)	2218(1)	25(1)
C(8)	4718(1)	2968(1)	1061(1)	36(1)
C(9)	6021(1)	1925(1)	966(1)	34(1)
C(10)	5970(2)	619(2)	909(1)	47(1)
C(11)	7174(2)	-372(2)	882(1)	66(1)
C(12)	8432(2)	-70(2)	912(1)	70(1)
C(13)	8499(2)	1219(2)	968(1)	62(1)
C(14)	7301(2)	2214(2)	996(1)	45(1)
C(15)	4629(1)	5496(1)	2730(1)	26(1)
C(16)	5180(1)	4679(1)	3714(1)	32(1)
C(17)	6591(1)	4191(2)	3858(1)	42(1)
C(18)	7480(1)	4540(2)	3019(1)	44(1)
C(19)	6948(1)	5389(2)	2037(1)	41(1)
C(20)	5542(1)	5858(1)	1894(1)	33(1)
C(21)	1088(1)	5601(1)	1657(1)	31(1)
C(22)	902(1)	4471(1)	1239(1)	35(1)
C(23)	1712(1)	3076(1)	1998(1)	30(1)
C(24)	1417(1)	2419(1)	5208(1)	32(1)
C(25)	2800(1)	1298(1)	5365(1)	27(1)
C(26)	222(1)	1858(2)	5013(1)	58(1)
C(27)	1065(2)	3067(2)	6056(1)	59(1)
C(28)	2684(2)	-255(1)	5849(1)	43(1)

C(29)	3884(1)	1544(2)	5945(1)	43(1)



Crystal data and structure refinement for **2-((1*R*,2*R*)-2-((*R*)-1,2-diphenylethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 67).**

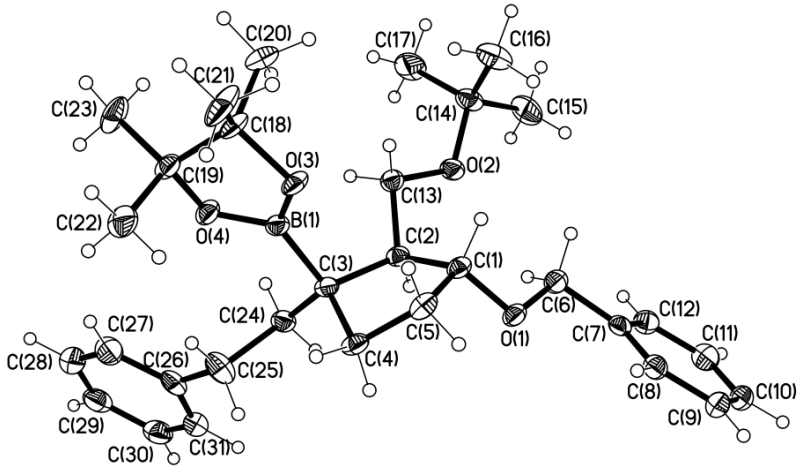
Identification code	C33H41BO2	
Empirical formula	C33 H41BO2	
Formula weight	480.47	
Temperature	100(2) K	
Wavelength	0.71073 ≈	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 13.8342(16) ≈	α= 90∞.
	b = 17.292(2) ≈	β= 90∞.
	c = 23.666(3) ≈	γ = 90∞.
Volume	5661.4(11) $\approx^3$	
Z	8	
Density (calculated)	1.127 Mg/m^3	

Absorption coefficient	0.067 mm^{-1}
F(000)	2080
Crystal size	0.550 x 0.380 x 0.180 mm^3
Theta range for data collection	1.721 to 28.335∞.
Index ranges	-18<=h<=18, -23<=k<=22, -31<=l<=31
Reflections collected	94700
Independent reflections	7044 [R(int) = 0.0525]
Completeness to theta = 25.242∞	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.7017
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7044 / 821 / 406
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0439, wR2 = 0.1041
R indices (all data)	R1 = 0.0649, wR2 = 0.1172
Extinction coefficient	na
Largest diff. peak and hole	0.320 and -0.237 e.≈$^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($\approx^2$x 10^3) for C33H41BO2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5645(1)	1765(1)	4124(1)	33(1)
O(2)	5909(1)	2977(1)	4455(1)	33(1)
C(6)	5676(1)	1686(1)	4741(1)	27(1)
C(7)	5546(1)	2534(1)	4940(1)	31(1)
C(8)	4873(2)	1142(1)	4932(1)	42(1)
C(9)	6661(2)	1356(2)	4881(1)	72(1)
C(10)	4480(2)	2753(1)	5008(1)	57(1)
C(11)	6116(3)	2768(2)	5452(1)	75(1)
O(1X)	5206(10)	1976(8)	4159(4)	36(3)
O(2X)	6309(10)	2822(9)	4479(5)	32(3)
C(6X)	5140(10)	1968(9)	4782(5)	43(3)
C(7X)	6040(10)	2389(9)	4986(5)	37(3)
C(8X)	4178(15)	2328(17)	4931(12)	84(7)
C(9X)	5248(19)	1109(11)	4917(13)	53(6)
C(10X)	5920(30)	2950(18)	5468(12)	49(5)
C(11X)	6951(15)	1978(16)	5134(11)	82(6)
B(1)	5869(1)	2514(1)	3994(1)	21(1)
C(1)	6077(1)	2810(1)	3372(1)	20(1)
C(2)	6219(1)	2117(1)	2963(1)	25(1)
C(3)	5199(1)	1834(1)	2804(1)	29(1)
C(4)	4509(1)	2497(1)	2966(1)	26(1)
C(5)	5157(1)	3196(1)	3107(1)	21(1)
C(12)	6954(1)	3358(1)	3365(1)	21(1)
C(13)	7903(1)	2997(1)	3563(1)	24(1)
C(14)	8758(1)	3546(1)	3539(1)	22(1)
C(15)	9683(1)	3258(1)	3433(1)	26(1)
C(16)	10479(1)	3747(1)	3407(1)	31(1)
C(17)	10366(1)	4538(1)	3484(1)	32(1)
C(18)	9455(1)	4833(1)	3593(1)	31(1)
C(19)	8658(1)	4343(1)	3621(1)	28(1)
C(20)	4625(1)	3832(1)	3443(1)	22(1)

C(21)	5249(1)	4538(1)	3565(1)	22(1)
C(22)	5498(1)	4731(1)	4119(1)	25(1)
C(23)	6105(1)	5355(1)	4232(1)	30(1)
C(24)	6456(1)	5803(1)	3793(1)	32(1)
C(25)	6198(1)	5629(1)	3242(1)	30(1)
C(26)	5598(1)	5003(1)	3128(1)	26(1)
C(27)	3697(1)	4073(1)	3121(1)	27(1)
C(28)	3181(1)	4766(1)	3368(1)	25(1)
C(29)	2927(1)	4793(1)	3938(1)	28(1)
C(30)	2451(1)	5429(1)	4162(1)	32(1)
C(31)	2214(1)	6049(1)	3818(1)	33(1)
C(32)	2465(1)	6032(1)	3253(1)	34(1)
C(33)	2947(1)	5397(1)	3030(1)	31(1)



Crystal data and structure refinement for **2-((1*S*,2*S*,3*R*)-3-(benzyloxy)-2-(*tert*-butoxymethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 69).**

Identification code	C31H45BO4
Empirical formula	C31 H45 B O4
Formula weight	492.48
Temperature	100(2) K
Wavelength	1.54178 ≈

Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	a = 26.2433(11) ≈ α= 90∞.
	b = 17.5408(7) ≈ β= 90∞.
	c = 6.2731(3) ≈ γ = 90∞.
Volume	2887.7(2) $≈^3$
Z	4
Density (calculated)	1.133 Mg/m^3
Absorption coefficient	0.564 mm^{-1}
F(000)	1072
Crystal size	0.360 x 0.240 x 0.180 mm^3
Theta range for data collection	3.030 to 69.934∞.
Index ranges	-31<=h<=31, -21<=k<=18, -6<=l<=7
Reflections collected	22546
Independent reflections	4866 [R(int) = 0.0631]
Completeness to theta = 67.679∞	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.5608
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4866 / 393 / 401
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0899
R indices (all data)	R1 = 0.0368, wR2 = 0.0912

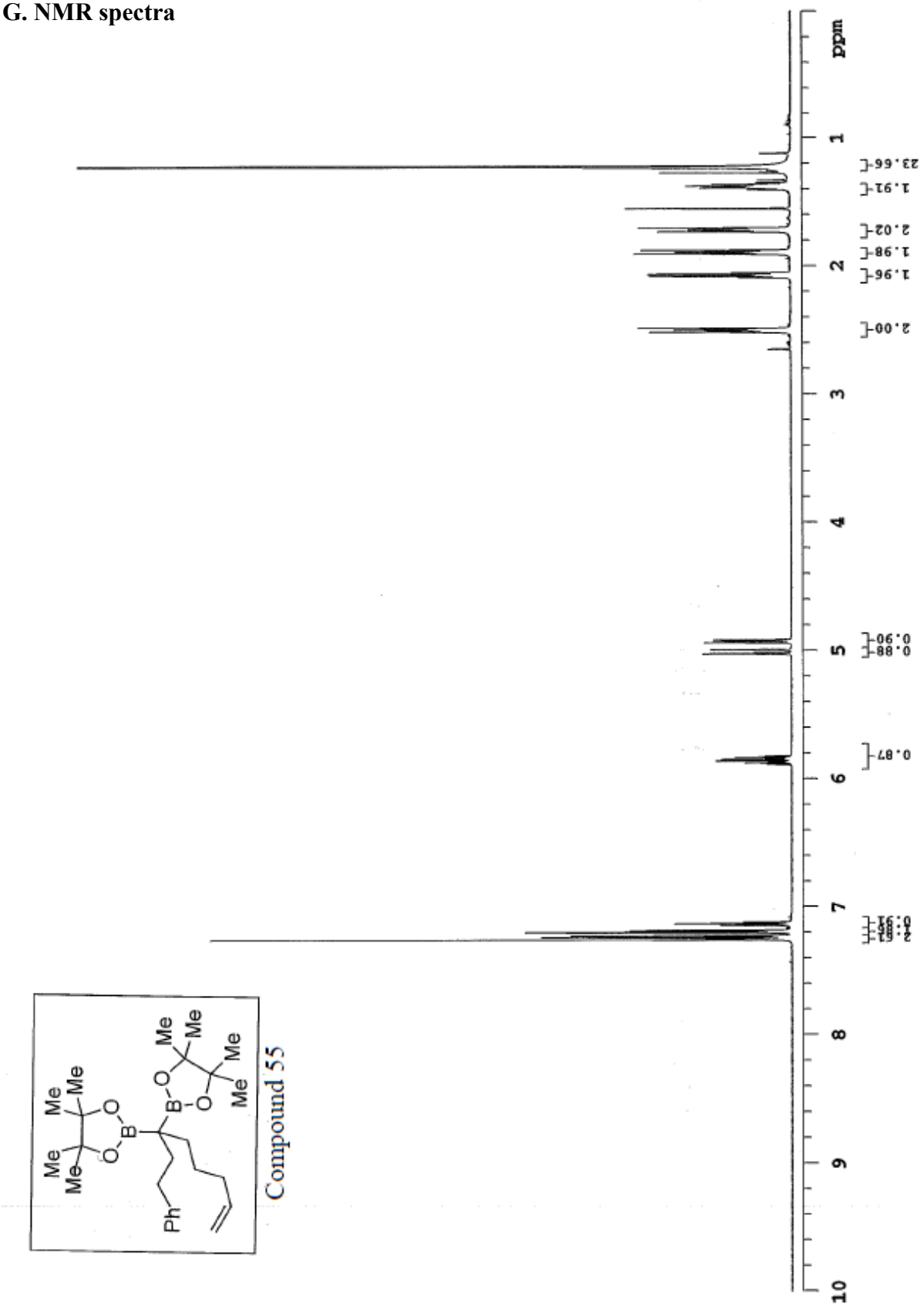
Absolute structure parameter	0.06(12)
Extinction coefficient	n/a
Largest diff. peak and hole	0.189 and -0.169 e.≈$^{-3}$

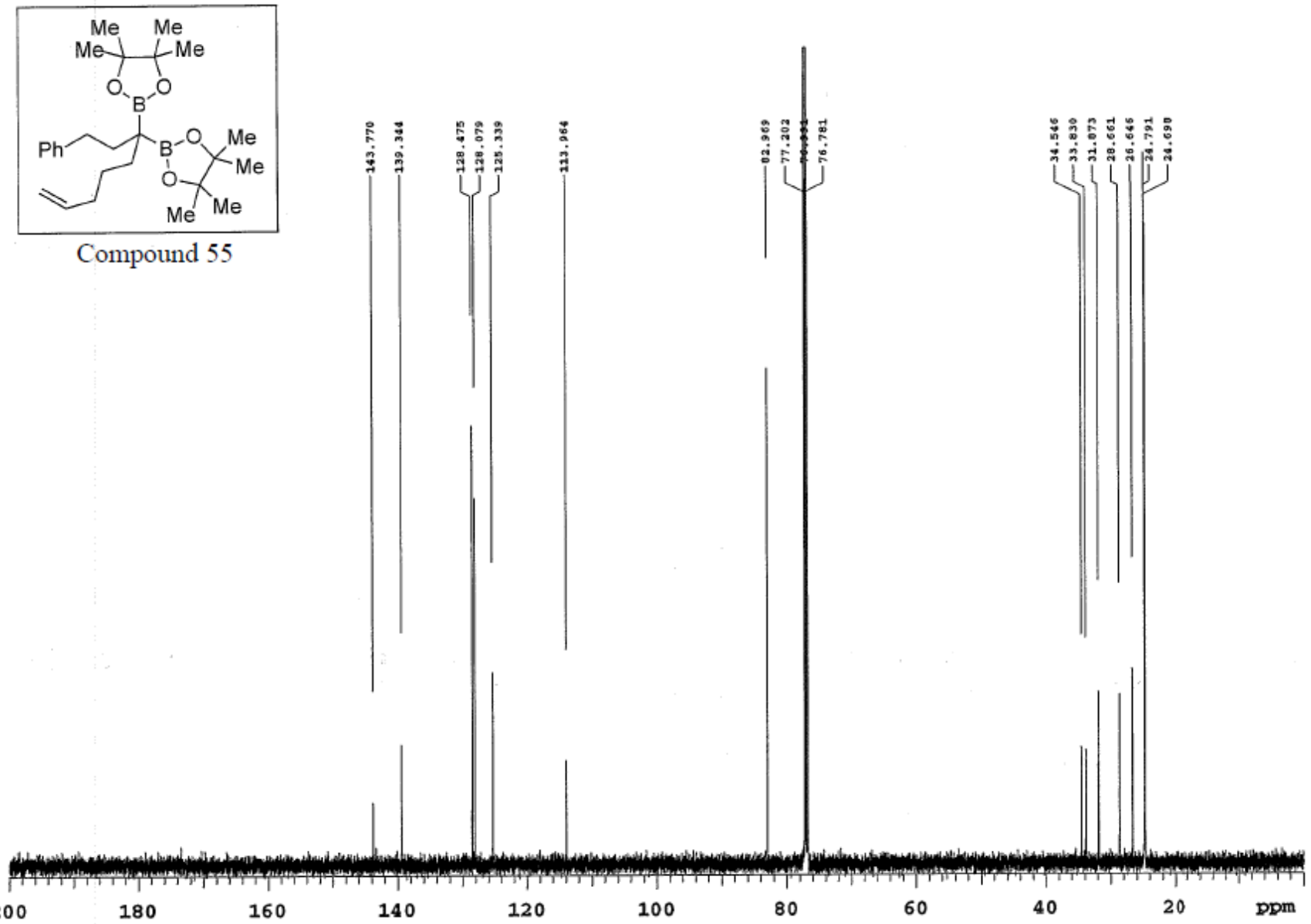
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3) for C31H45BO4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3636(1)	6170(1)	3554(2)	21(1)
O(2)	3680(1)	4596(1)	7018(2)	22(1)
B(1)	2301(1)	4380(1)	3302(4)	20(1)
C(1)	3375(1)	5467(1)	3104(3)	19(1)
C(2)	3037(1)	5197(1)	4987(3)	18(1)
C(3)	2474(1)	5196(1)	4159(3)	18(1)
C(4)	2499(1)	5778(1)	2310(3)	21(1)
C(5)	3011(1)	5617(1)	1255(3)	22(1)
C(6)	4045(1)	6079(1)	5011(4)	22(1)
C(7)	4374(1)	6783(1)	5004(3)	20(1)
C(8)	4436(1)	7217(1)	3181(4)	22(1)
C(9)	4763(1)	7844(1)	3176(4)	26(1)
C(10)	5036(1)	8028(1)	5001(4)	27(1)
C(11)	4976(1)	7596(1)	6831(4)	28(1)
C(12)	4643(1)	6977(1)	6840(4)	24(1)
C(13)	3210(1)	4446(1)	5971(3)	20(1)
C(14)	3998(1)	3956(1)	7578(4)	26(1)
C(15)	4426(1)	4324(1)	8857(4)	38(1)
C(16)	4212(1)	3580(1)	5589(4)	38(1)
C(17)	3708(1)	3388(1)	8954(5)	39(1)
O(3)	2500(2)	4007(2)	1709(8)	22(1)
C(18)	2256(2)	3251(2)	1658(8)	25(1)
C(19)	1744(2)	3408(2)	2781(6)	22(1)
O(4)	1884(2)	4016(2)	4264(6)	22(1)
C(20)	2606(3)	2722(5)	2866(16)	36(2)
C(21)	2217(8)	3017(12)	-680(20)	43(4)

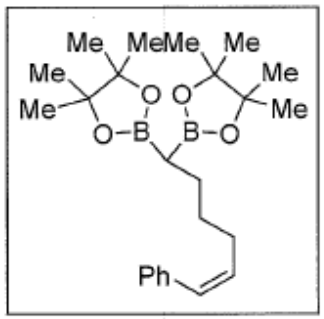
C(22)	1342(2)	3742(3)	1316(12)	35(1)
C(23)	1527(7)	2728(7)	3990(30)	36(3)
O(3X)	2323(2)	4150(2)	1138(7)	24(1)
C(18X)	2014(2)	3453(2)	974(8)	26(1)
C(19X)	2053(2)	3127(2)	3272(7)	22(1)
O(4X)	2122(2)	3817(2)	4544(5)	18(1)
C(20X)	2218(9)	2932(12)	-710(20)	32(3)
C(21X)	1480(3)	3709(4)	370(12)	36(2)
C(22X)	1582(6)	2724(7)	4070(20)	28(3)
C(23X)	2525(3)	2630(5)	3601(14)	26(2)
C(24)	2109(1)	5444(1)	5954(3)	21(1)
C(25)	1567(1)	5633(1)	5174(4)	33(1)
C(26)	1199(1)	5684(1)	7013(4)	27(1)
C(27)	842(1)	5110(1)	7365(4)	32(1)
C(28)	530(1)	5128(1)	9155(5)	36(1)
C(29)	566(1)	5715(1)	10595(4)	32(1)
C(30)	912(1)	6299(1)	10249(4)	32(1)
C(31)	1223(1)	6281(1)	8467(4)	29(1)

G. NMR spectra



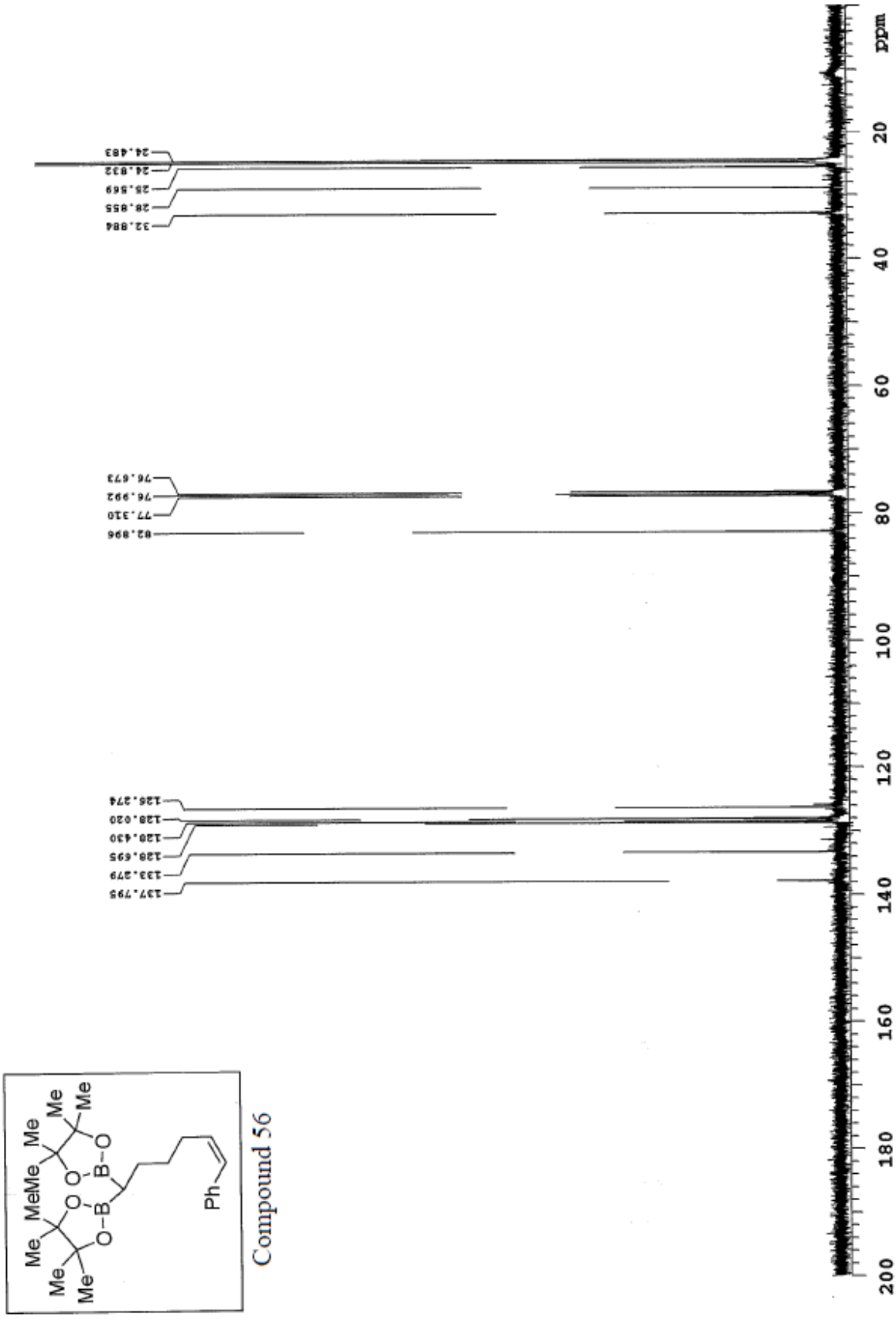

Me
Me
Me
Me
O
B
O
Ph
B
O
Me
Me
O
Me
Me
143.770
139.344
128.475
128.079
125.339
113.964
82.969
77.202
76.781
34.546
33.830
31.073
28.661
26.646
24.791
24.690
200
180
160
140
120
100
80
60
40
20
ppm

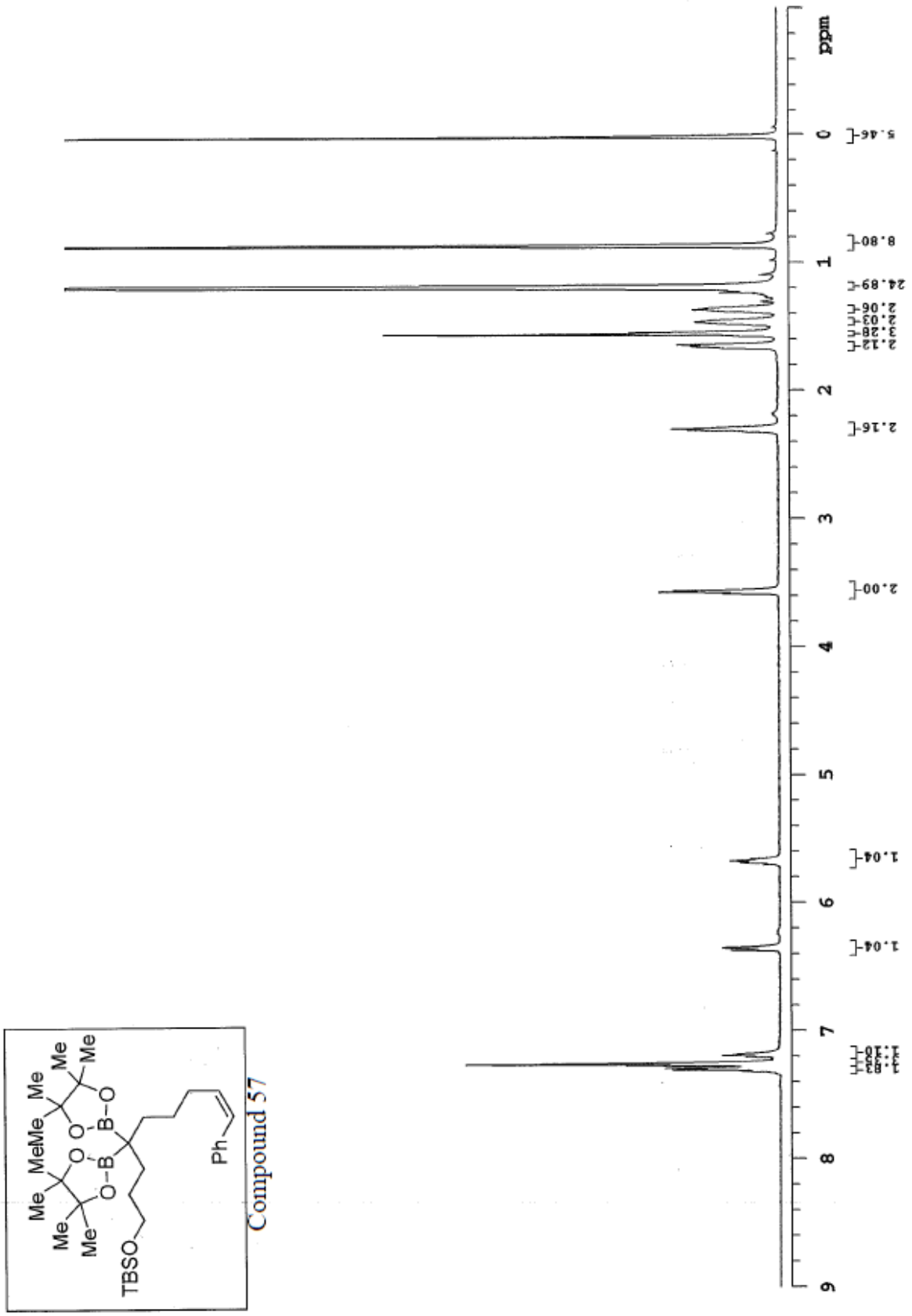
Compound 55

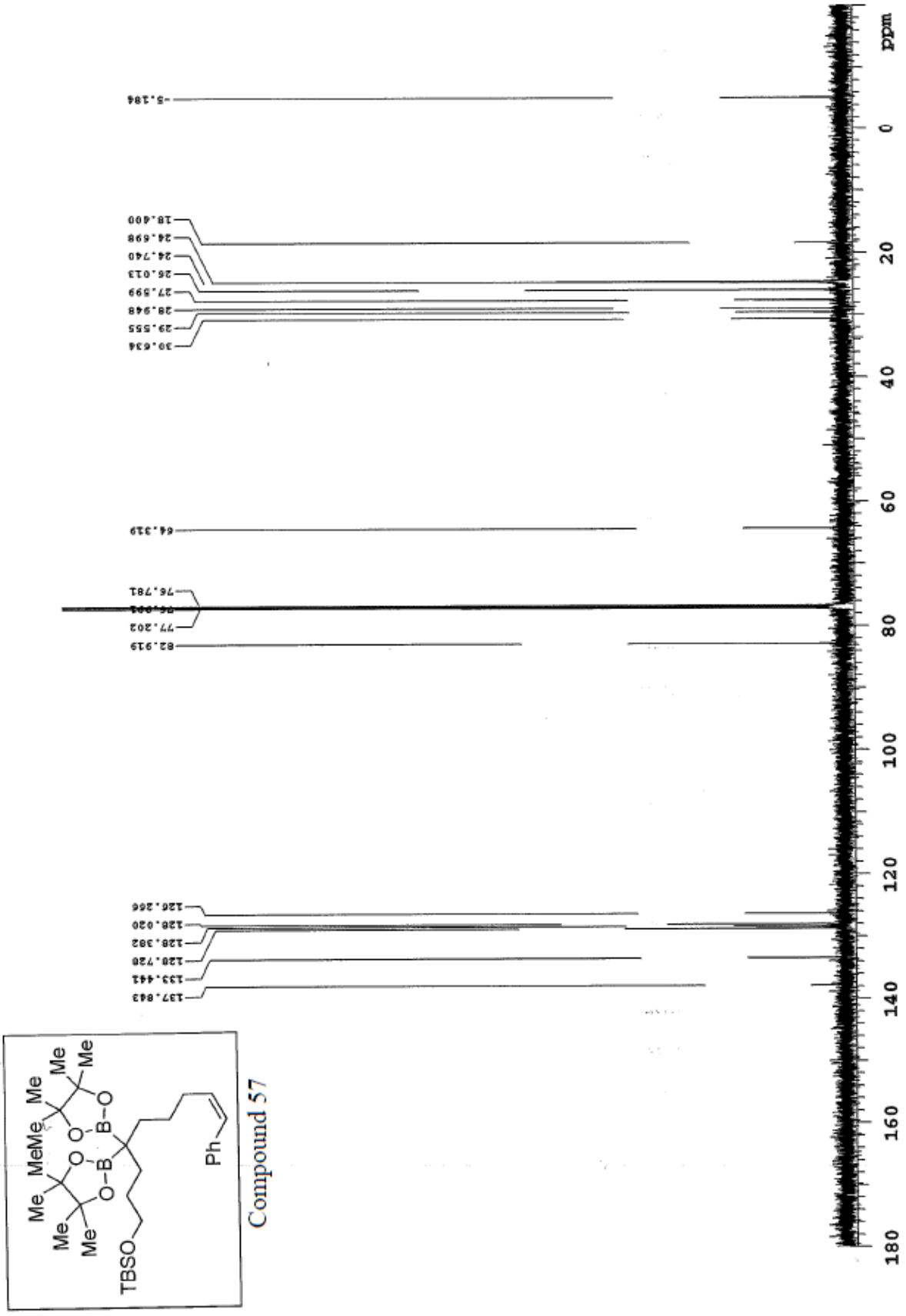

Me
Me
Me
Me
Me
Me
O
O
O–B
B–O
Ph

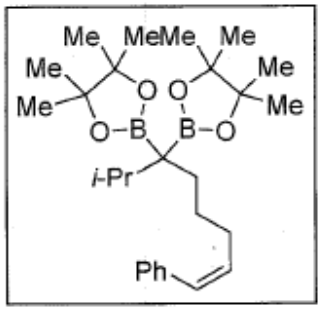
Compound 56

10
9
8
7
6
5
4
3
2
1
ppm
1.04
0.99
2.00
2.22
2.15
26.08
1.08


Me
Me
Me
Me
Me
O
B
O
O
B
O
Ph
Compound 56
137.795
133.279
128.695
128.430
128.020
126.374
82.896
77.310
76.992
76.673
32.884
28.855
25.569
24.832
24.483
ppm
20
40
60
80
100
120
140
160
180
200

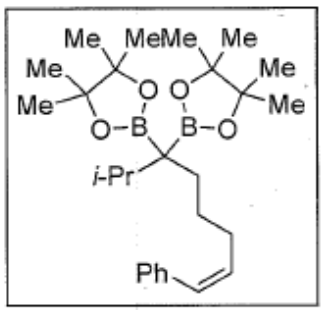

Me
Me
Me
Me
Me
Me
O
O
B
O
B
O
TBSO
Ph
Compound 57
ppm
0
1
2
3
4
5
6
7
8
9
5.46
8.80
24.89
2.06
2.03
3.28
2.12
2.16
2.00
1.04
1.04


Me
Me
Me
Me
Me
Me
O
B
O
O
B
O
TBSO
Ph
Compound 57
-5.184
18.400
24.698
24.740
26.013
27.599
28.948
29.555
30.634
64.319
76.781
77.203
82.919
126.266
128.020
128.382
128.728
133.441
137.843
ppm
0
20
40
60
80
100
120
140
160
180


Me
Me
Me
Me
Me
Me
O
O
O-B
B-O
i-Pr
Ph

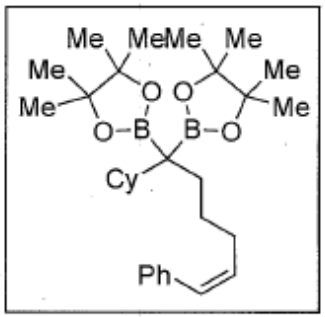
Compound 58

10
9
8
7
6
5
4
3
2
1
ppm
3.51
0.86
0.92
0.91
1.92
1.03
2.06
2.00
23.95
5.88


Me
MeMe
Me
Me
Me
Me
O
O
O–B
B–O
i-Pr
Ph

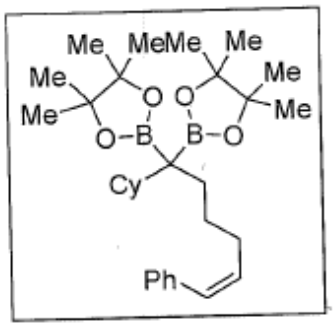
Compound 58

137.943
133.704
128.756
128.241
128.005
126.235
82.555
77.244
76.931
76.738
30.040
29.745
29.214
28.422
24.814
24.772
21.291
200
180
160
140
120
100
80
60
40
20
ppm


Me
Me
Me
Me
Me
Me
O
O
O–B
B–O
Cy
Ph

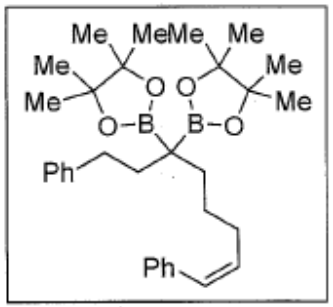
Compound 59

10
9
8
7
6
5
4
3
2
1
ppm
3.69
0.88
0.96
0.96
2.00
2.27
6.46
2.09
24.86
3.84
0.99


Me
MeMe
Me
Me
Me
Me
O
O
O-B
B-O
Cy
Ph

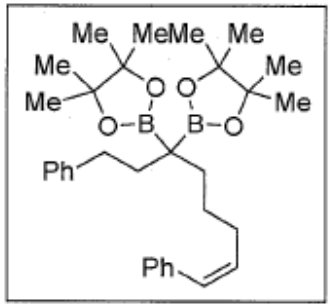
Compound 59

137.970
133.798
128.774
128.201
128.015
126.237
82.565
77.254
77.001
76.748
40.241
31.534
30.126
29.410
28.659
27.420
26.957
24.834
24.799
200
180
160
140
120
100
80
60
40
20
ppm


Me
MeMe
Me
Me
Me
Me
Me
O
O
O–B
B–O
Ph
Ph

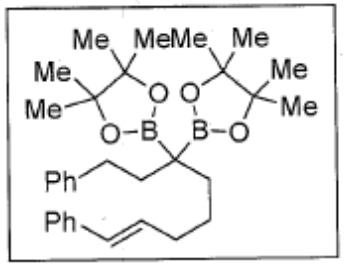
Compound 22

10
9
8
7
6
5
4
3
2
1
ppm
0.92
0.91
2.00
1.92
2.00
2.02
1.99
24.62


Me
Me
Me
Me
Me
Me
O
O
O
B
B
O
Ph
Ph

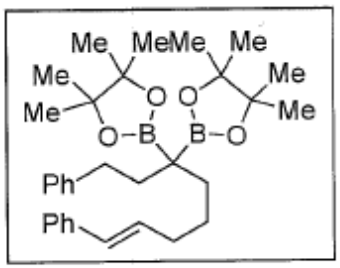
Compound 22

143.717
137.834
133.375
128.730
128.528
128.460
128.081
128.039
126.319
125.342
82.976
77.244
76.983
76.730
33.825
31.920
29.560
28.953
27.680
24.780
24.705
200
180
160
140
120
100
80
60
40
20
ppm


Me
MeMe
Me
Me
Me
Me
Me
O
O
O–B
B–O
Ph
Ph

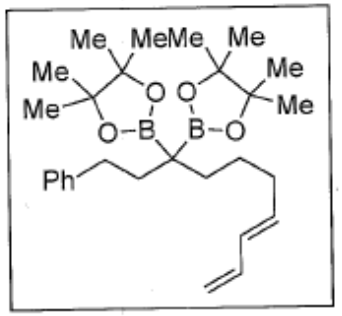
Compound 15

10
9
8
7
6
5
4
3
2
1
ppm
1.91
7.30
1.12
1.03
1.03
2.00
1.93
2.03
2.00
2.04
24.18


Me
Me
Me
Me
Me
Me
O
O
O-B
B-O
Ph
Ph

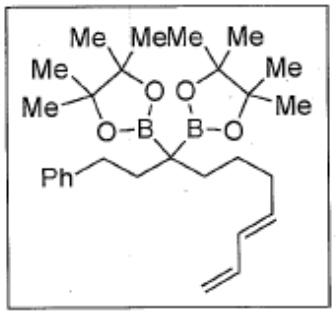
Compound 15

143.729
138.069
131.424
129.482
128.480
128.397
128.093
126.622
125.908
125.347
83.000
77.242
76.734
33.833
31.906
28.773
27.096
24.805
24.714
200
180
160
140
120
100
80
60
40
20
ppm


Me
MeMe
Me
Me
Me
Me
Me
O
O
O–B
B–O
Ph

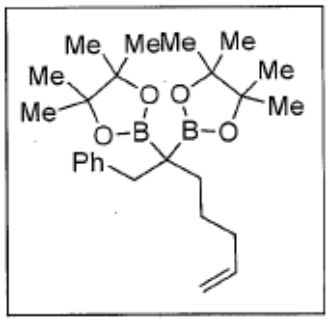
Compound 16

10
9
8
7
6
5
4
3
2
1
ppm
0.96
0.95
0.96
1.02
0.99
2.00
1.90
1.97
2.06
2.23
24.01


Me
MeMe
Me
Me
Me
Me
Me
O
O
O-B
B-O
Ph

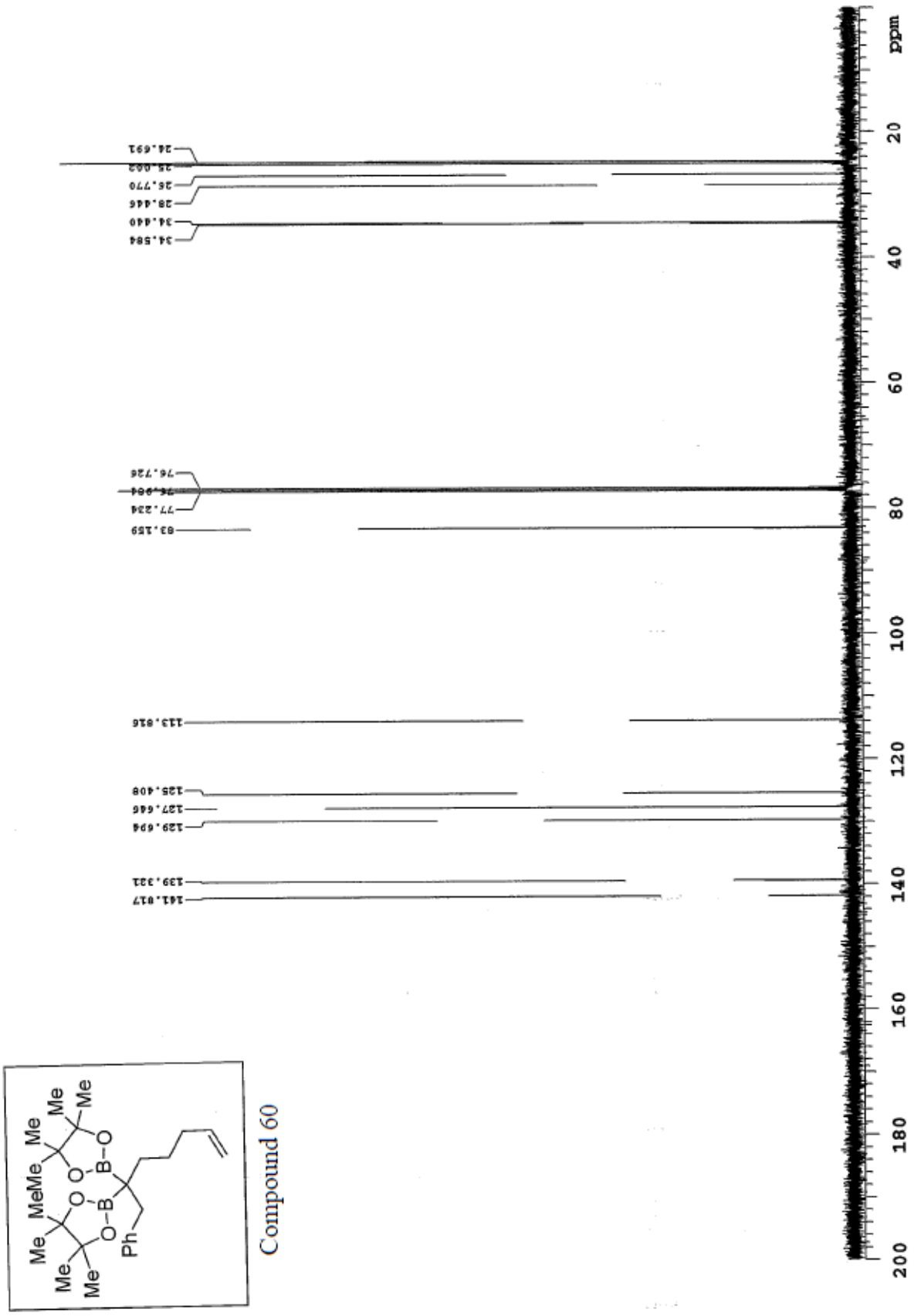
Compound 16

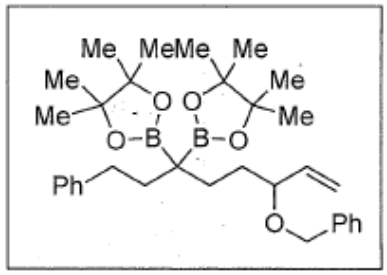
143.740
137.516
135.852
130.640
128.479
128.088
125.351
114.367
82.986
77.198
76.777
33.037
33.338
31.867
28.755
26.852
24.799
24.707
200
180
160
140
120
100
80
60
40
20
ppm


Me
Me
Me
Me
Me
Me
Me
O
O
O–B
B–O
Ph

Compound 60

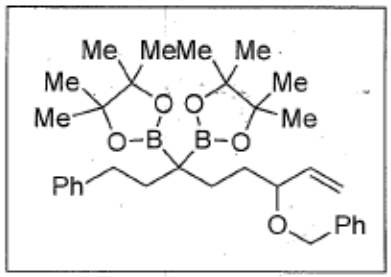
10
9
8
7
6
5
4
3
2
1
ppm
3.74
0.92
0.84
0.89
0.89
2.00
2.00
1.99
1.15
12.21


Me
Me
Me
Me
Me
Me
O
B
O
O
B
O
Ph
Compound 60
ppm
20
40
60
80
100
120
140
160
180
200


Me
MeMe
Me
Me
Me
Me
Me
O
O
O–B
B–O
Ph
O
Ph

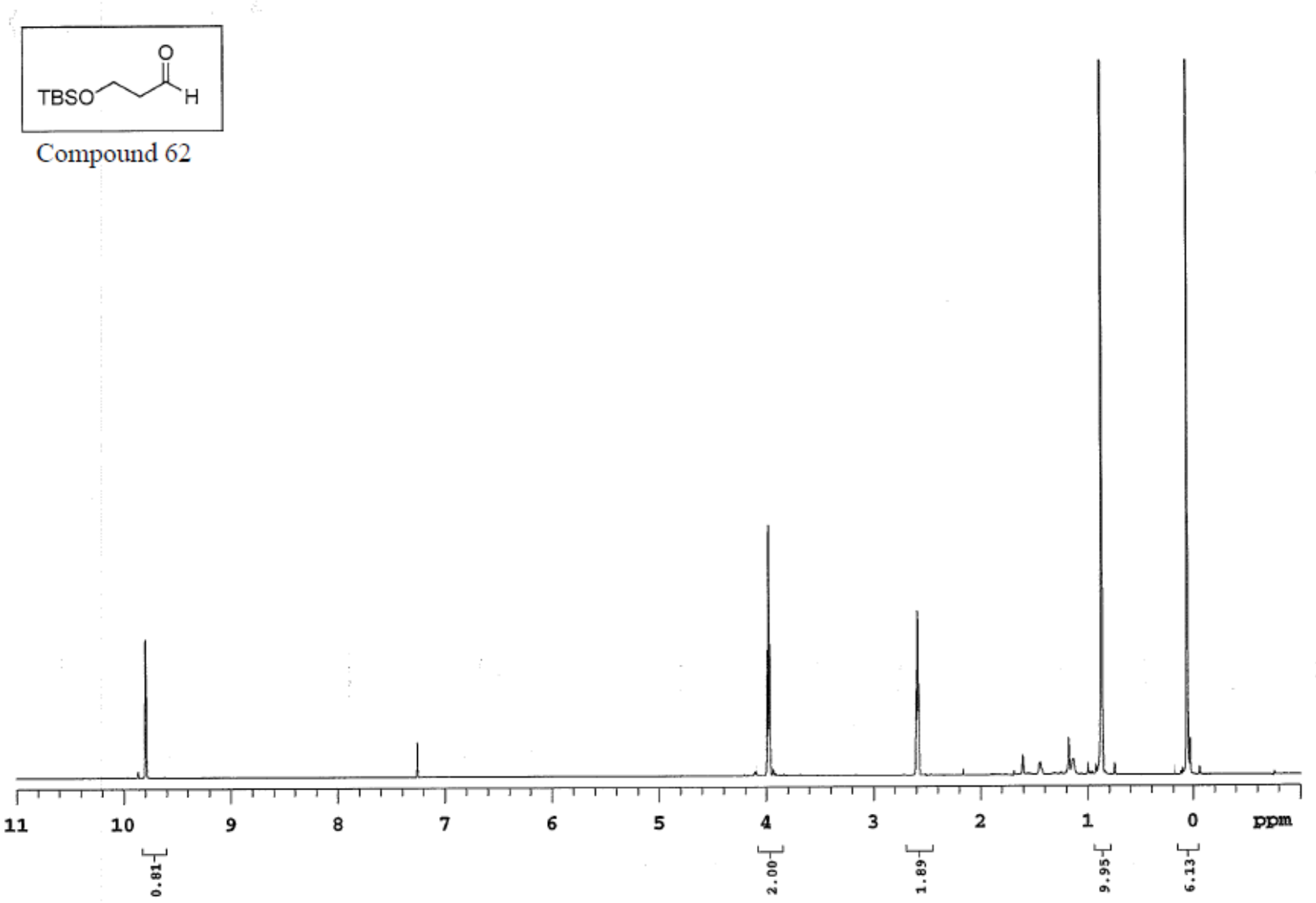
Compound 61

10
9
8
7
6
5
4
3
2
1
ppm
3.75
0.97
2.06
1.04
1.04
1.02
2.00
2.25
3.22
0.95
26.82

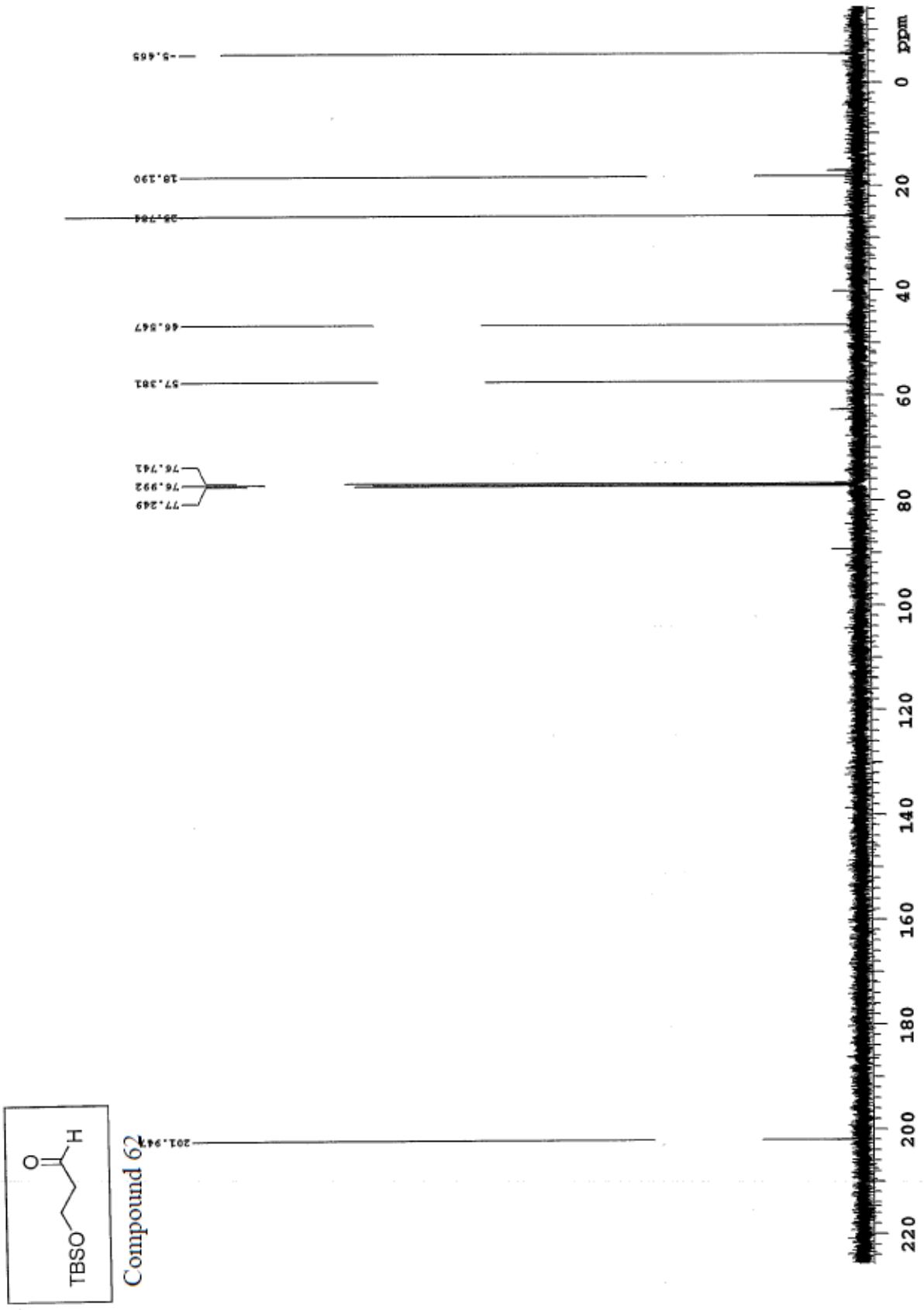

Me
Me
Me
Me
Me
Me
O
O
O
B
B
O
Ph
O
Ph

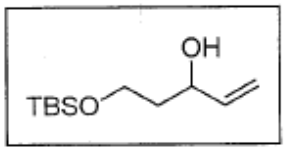
Compound 61

143.762
139.032
128.509
128.214
128.071
127.582
127.202
125.322
117.219
82.986
81.325
77.202
76.781
69.766
33.788
32.809
31.958
24.782
24.749
24.732
24.648
24.513
200
180
160
140
120
100
80
60
40
20
ppm



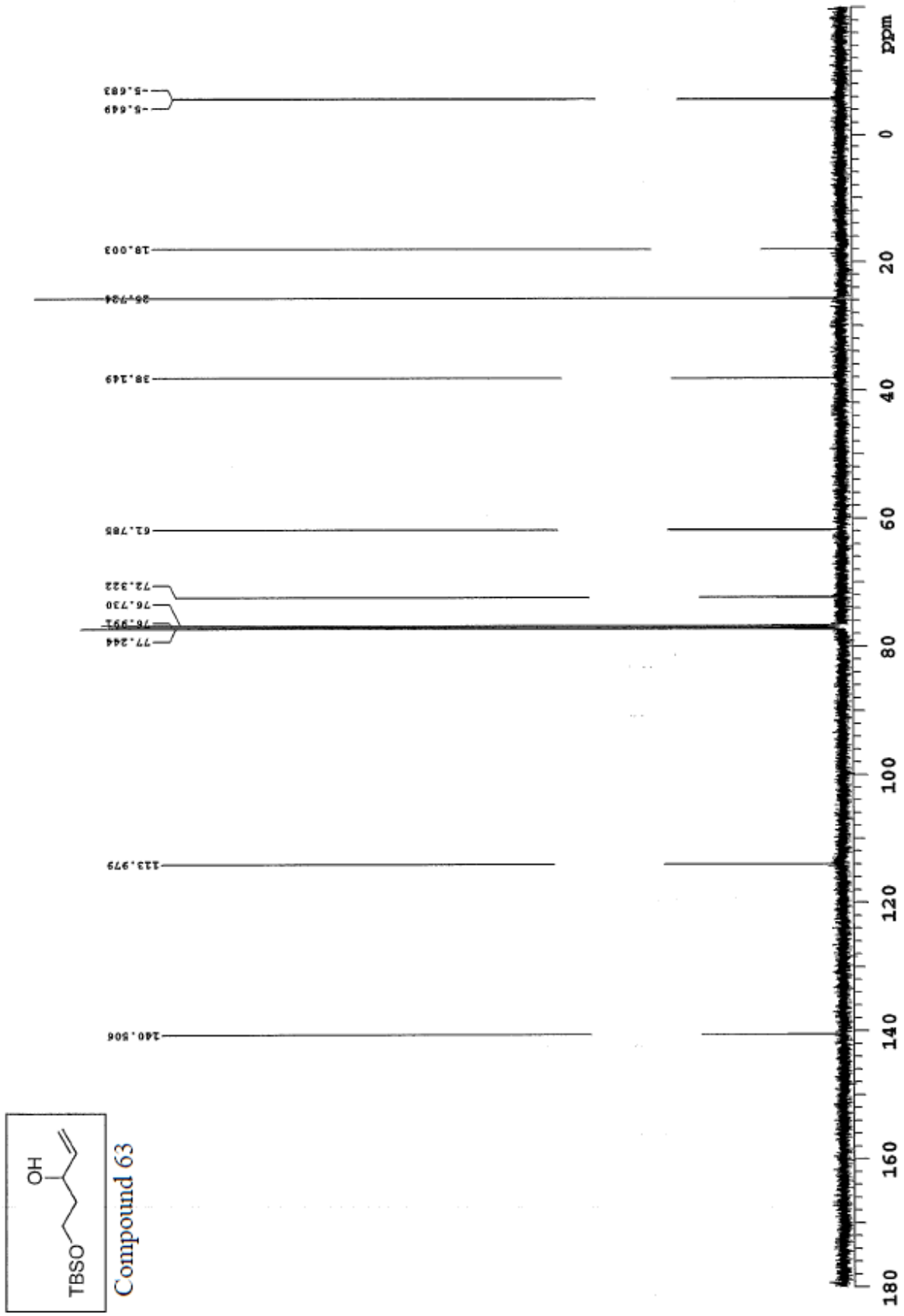
Compound 62

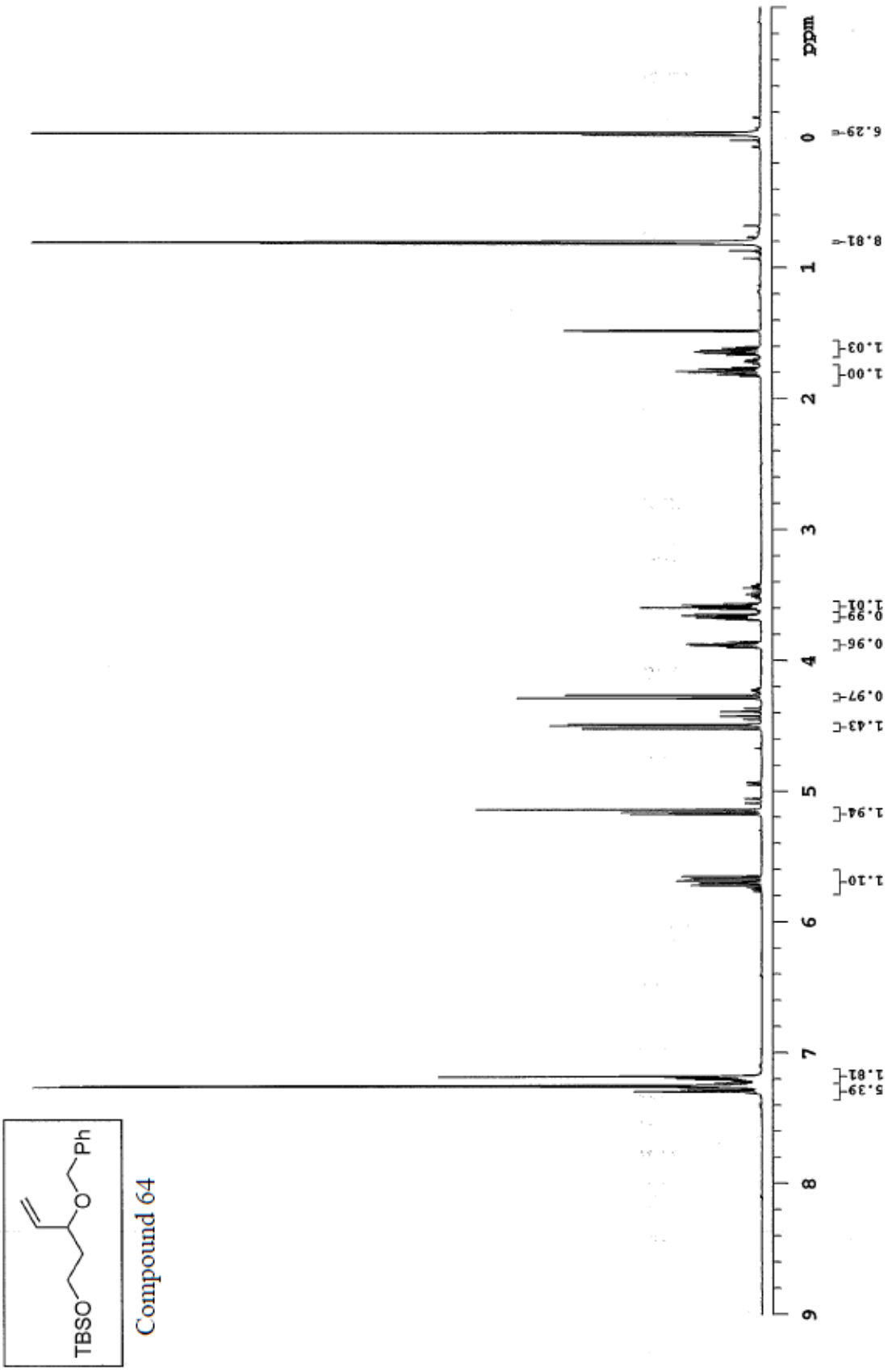

TBSO
O
H
Compound 62
201.947
77.249
76.992
76.743
57.381
46.847
25.784
18.390
-5.465
ppm
0
20
40
60
80
100
120
140
160
180
200
220

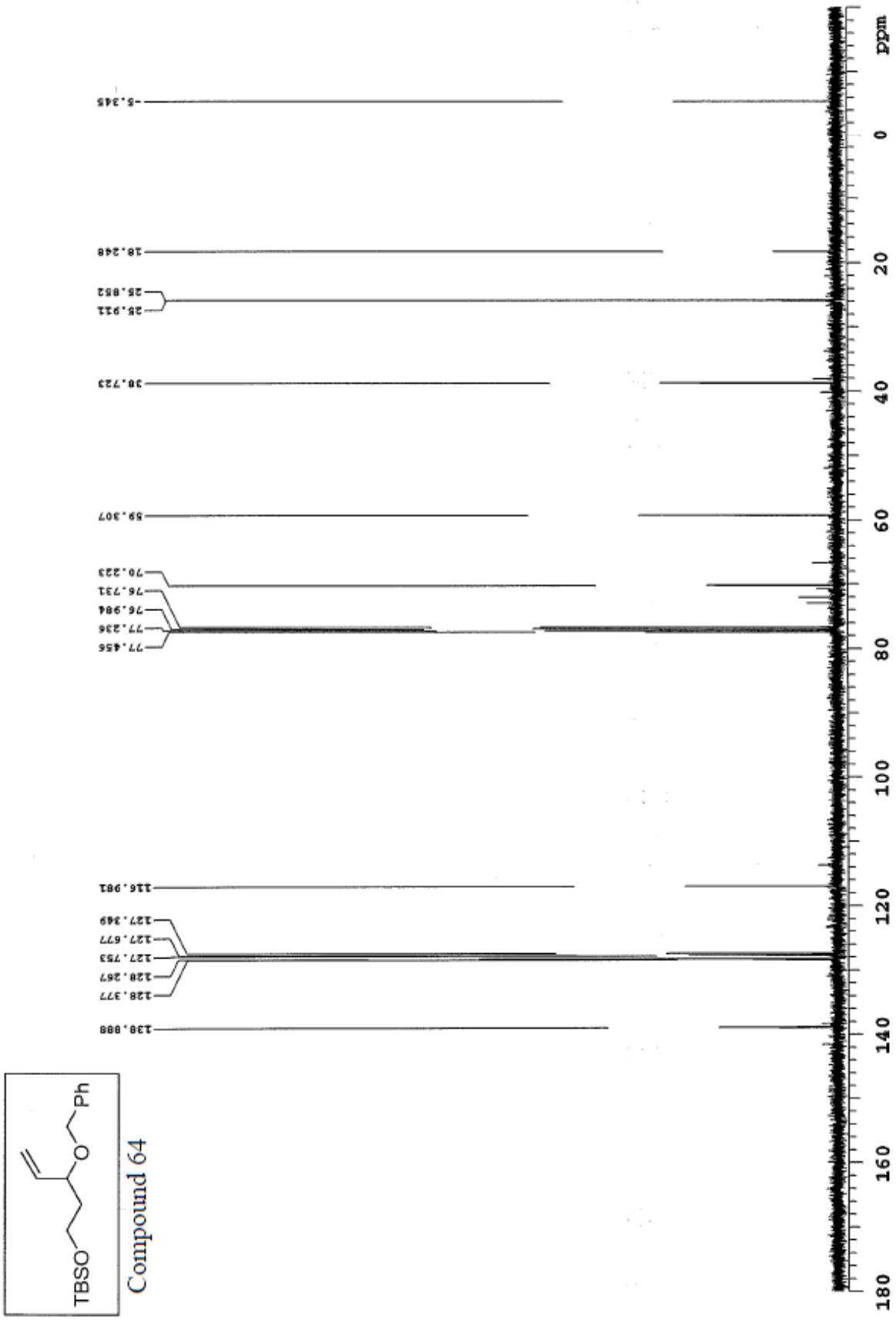

OH
TBSO

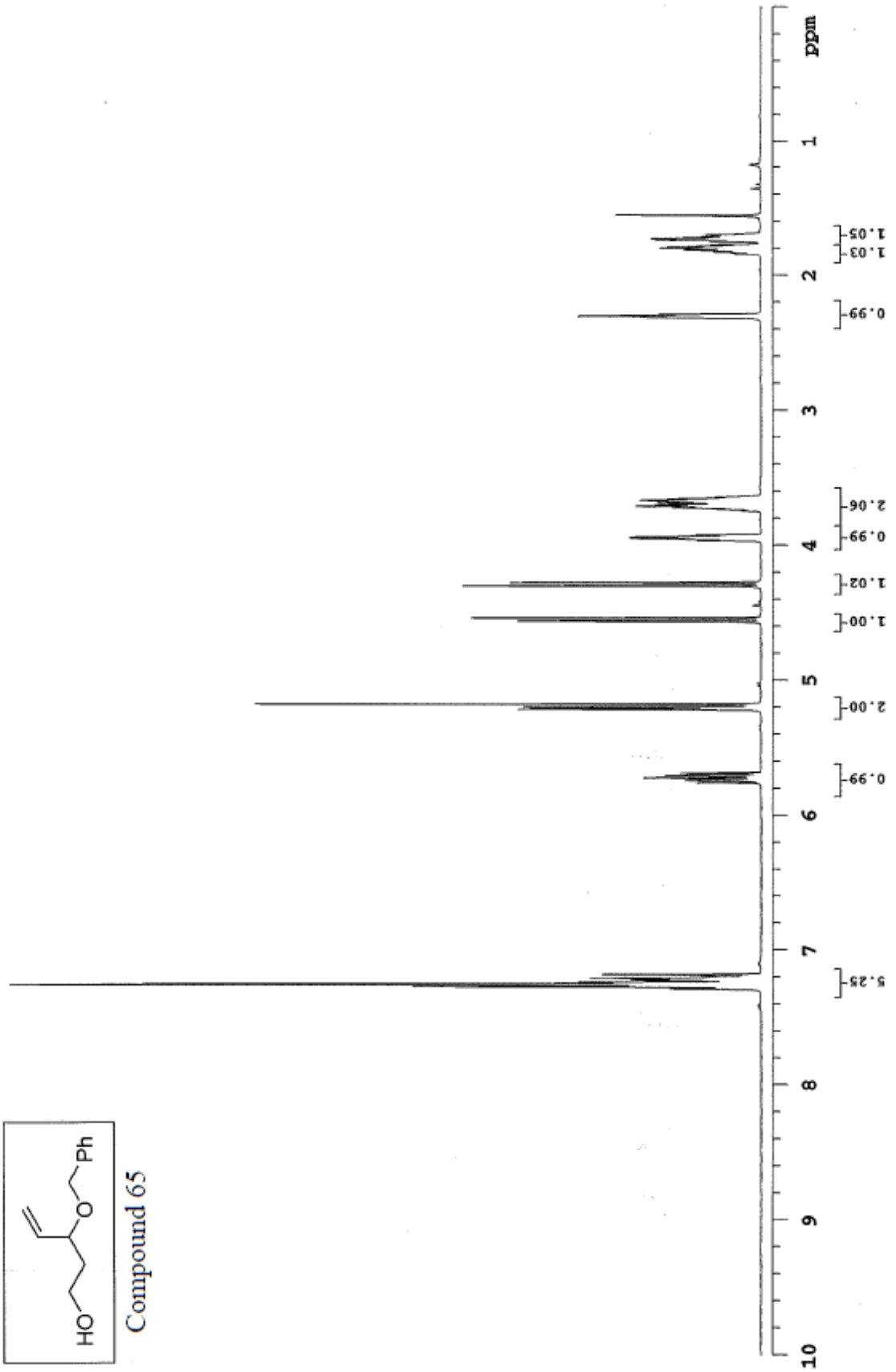
Compound 63

9
8
7
6
5
4
3
2
1
0
ppm
0.93
0.97
1.01
0.95
1.03
1.27
1.00
2.16
10.23
6.40

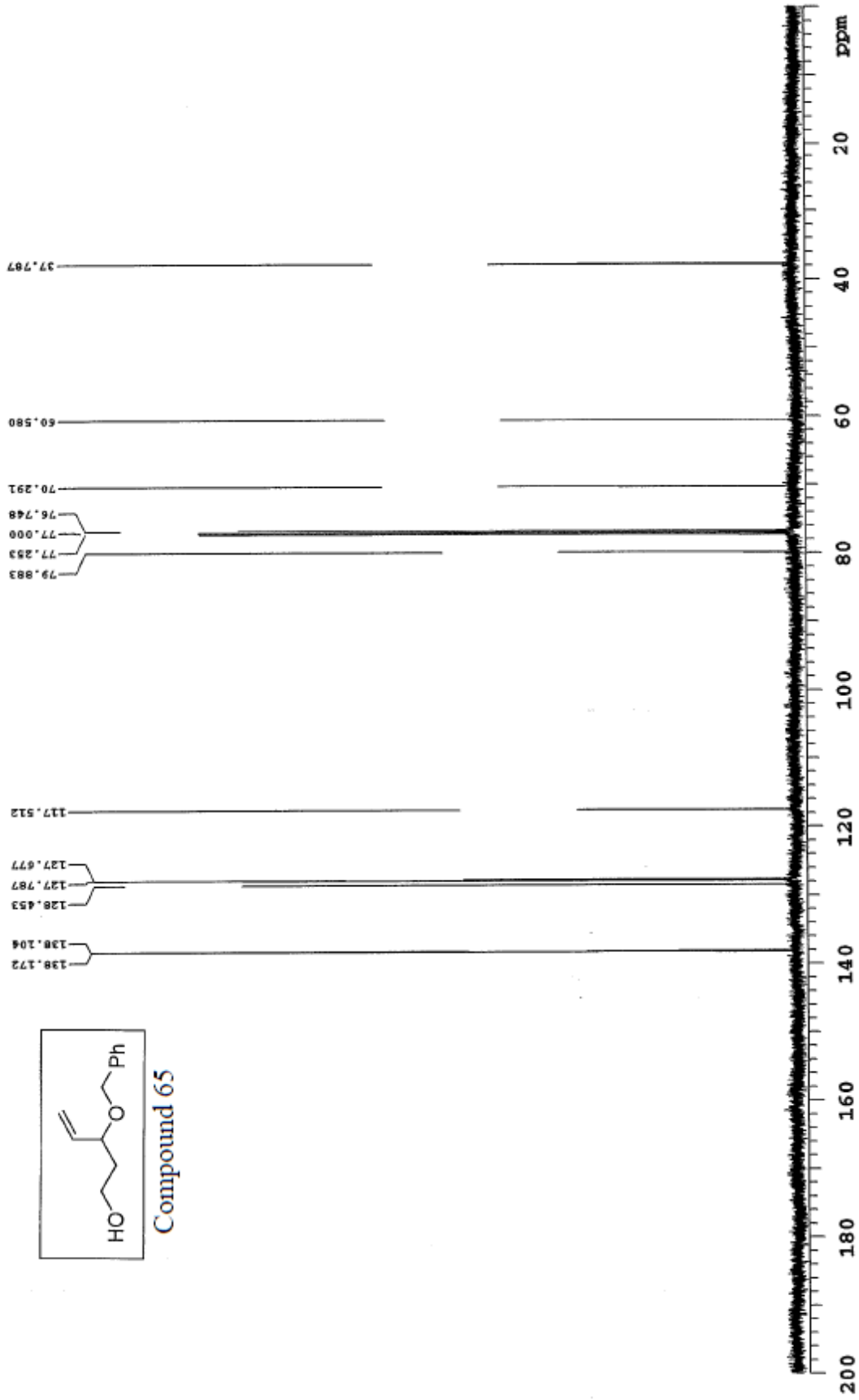

OH
TBSO
Compound 63
-5.683
-5.649
18.003
25.924
38.149
61.785
72.323
76.730
76.991
77.244
113.979
140.506
ppm
0
20
40
60
80
100
120
140
160
180

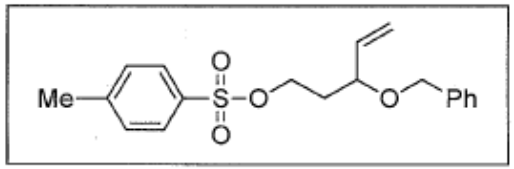

TBSO
Ph
O
Compound 64
ppm
6.29
8.81
1.03
1.00
1.01
0.99
0.96
0.97
1.43
1.94
1.10
5.39
1.81


TBSO
O
Ph
Compound 64
-5.345
18.248
25.852
25.911
30.723
59.307
70.223
76.731
76.984
77.236
77.456
116.981
127.349
127.677
127.753
128.267
128.377
138.888
ppm
0
20
40
60
80
100
120
140
160
180



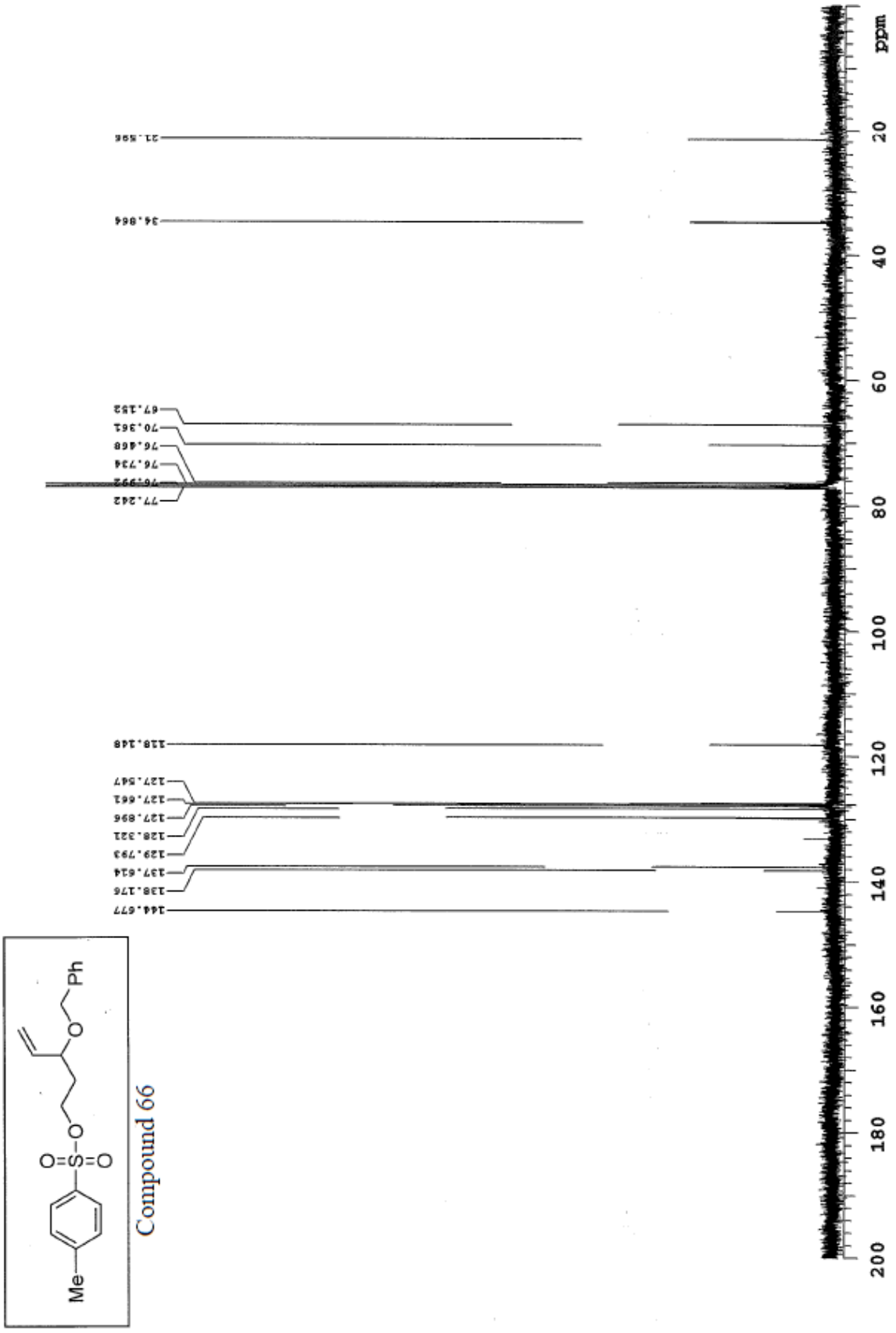
Compound 65

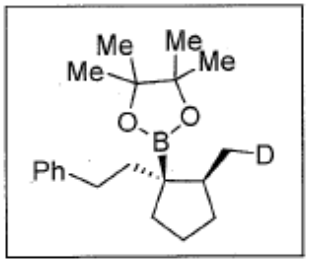

37.787
60.580
70.291
76.748
77.000
77.253
79.883
117.512
127.677
127.787
128.453
138.104
138.172
HO
O
Ph
Compound 65
ppm
20
40
60
80
100
120
140
160
180
200


Me
O
S
O
O
O
Ph

Compound 66

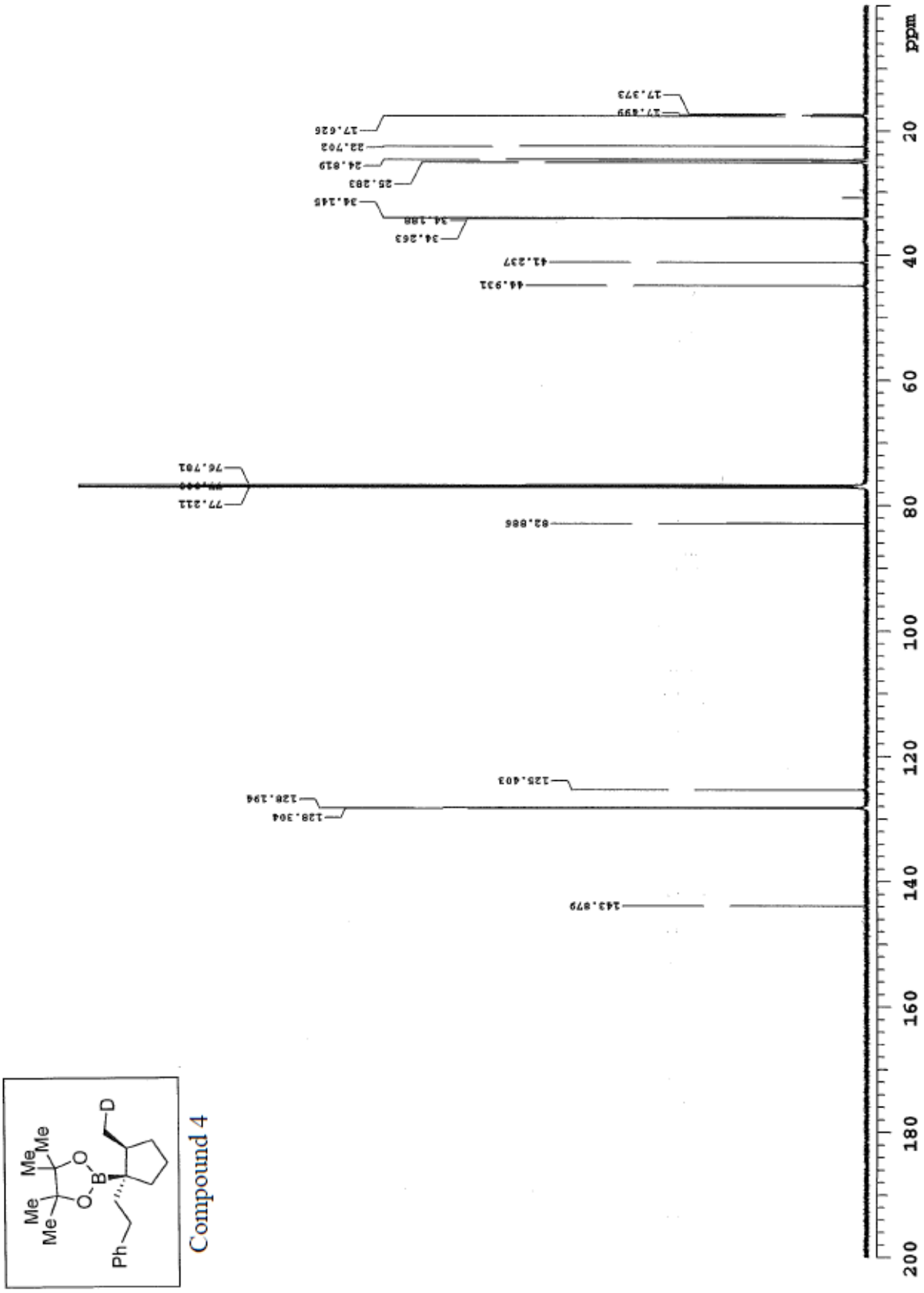
10
9
8
7
6
5
4
3
2
1
ppm
2.03
1.00
2.02
1.01
2.04
1.04
1.01
3.11
2.09

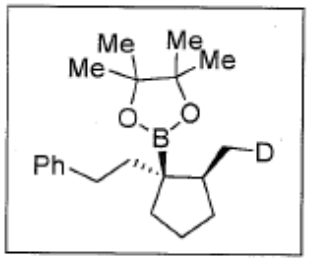

Ph
O
O
O=S=O
Me
Compound 66
144.677
138.176
137.614
129.793
128.321
127.896
127.661
127.547
118.148
77.242
76.992
76.734
76.468
70.361
67.152
34.864
21.596
ppm
20
40
60
80
100
120
140
160
180
200


Me
Me
Me
Me
O
O
B
Ph
D

Compound 4

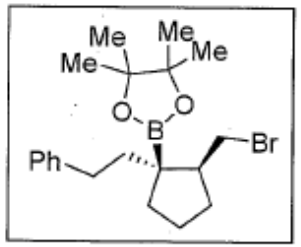
10
9
8
7
6
5
4
3
2
1
ppm
2.26
2.74
2.00
2.01
1.08
0.97
1.94
14.98
1.92


Me
Me
Me
Me
O
O
B
D
Ph
Compound 4
143.879
128.304
128.194
125.403
83.886
77.211
76.783
44.931
43.237
34.263
34.188
34.145
25.383
24.819
23.703
17.626
17.399
17.373
ppm
200
180
160
140
120
100
80
60
40
20


Me
Me
Me
Me
O
O
B
Ph
D

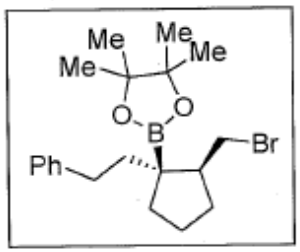
Compound 4

25.883
24.918
23.708
17.626
17.499
17.373
28
26
24
22
20
18
16
14
12
ppm


Me
Me
Me
Me
O
O
B
Ph
Br

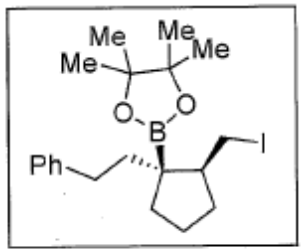
Compound 5

10
9
8
7
6
5
4
3
2
1
ppm
0.83
0.84
2.00
1.75
1.85
1.14
1.02
2.94
12.11


Me
Me
Me
Me
O
O
B
Ph
Br

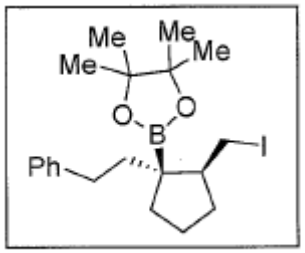
Compound 5

143.122
128.295
128.228
126.635
83.310
77.252
76.749
53.245
41.187
37.965
35.716
33.870
32.226
25.110
24.825
22.358
200
180
160
140
120
100
80
60
40
20
ppm


Me
Me
Me
Me
O
O
B
Ph
I

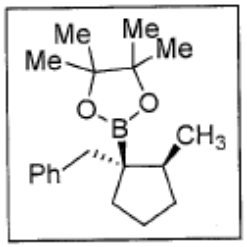
Compound 6

10
9
8
7
6
5
4
3
2
1
ppm
4.97
2.57
0.93
0.90
2.00
1.80
1.88
1.11
1.03
12.19


Me
Me
Me
Me
O
O
B
Ph
I

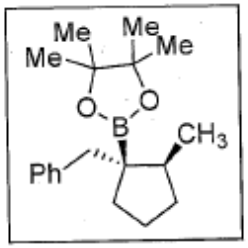
Compound 6

143.121
138.298
128.222
125.634
83.398
77.202
76.781
53.973
41.190
36.089
33.905
25.120
24.825
21.840
11.621
200
180
160
140
120
100
80
60
40
20
ppm

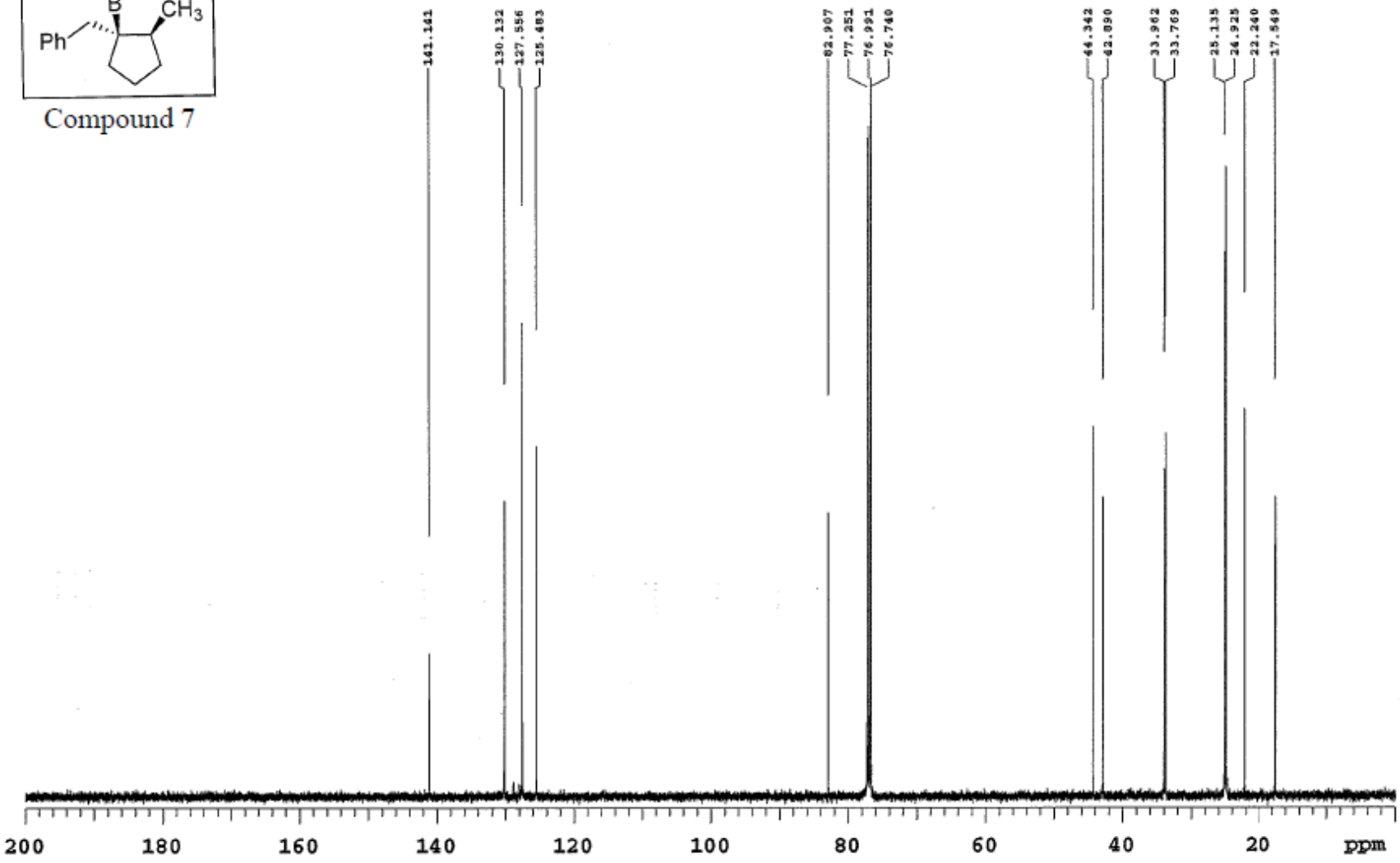

Me
Me
Me
Me
O
O
B
CH3
Ph

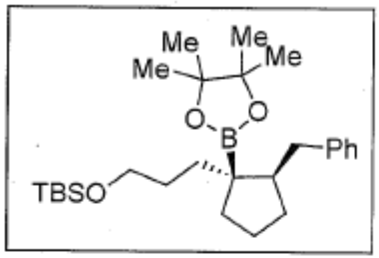
Compound 7

10
9
8
7
6
5
4
3
2
1
ppm
3.59
0.88
1.00
1.00
1.96
1.98
1.62
1.14


Me
Me
Me
Me
O
O
B
CH3
Ph

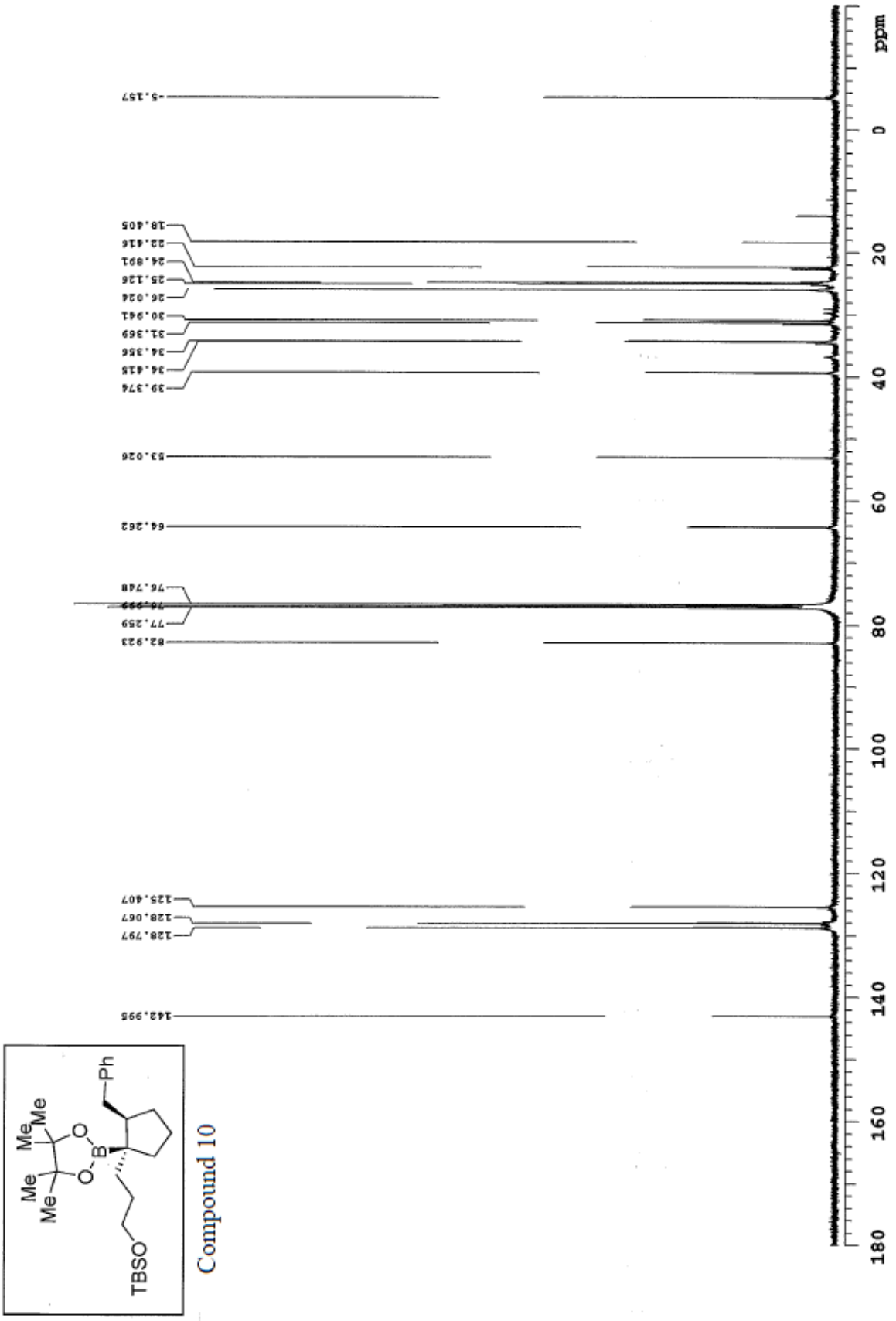
Compound 7

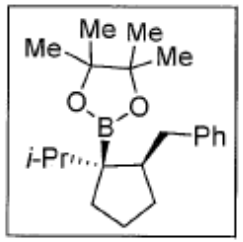

141.141
130.132
127.556
125.483
82.907
77.251
76.991
76.740
44.342
42.890
33.962
33.769
25.135
24.925
22.240
17.549
200
180
160
140
120
100
80
60
40
20
ppm


Me
Me
Me
Me
O
B
O
Ph
TBSO

Compound 10

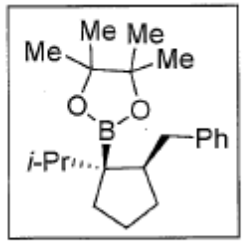
9
8
7
6
5
4
3
2
1
0
ppm
2.31
2.72
1.87
0.96
1.00
0.94
1.05
13.97
1.01
9.11
5.21


Me
Me
Me
Me
O
O
B
Ph
TBSO
Compound 10
-5.157
18.405
22.416
24.891
25.126
26.024
30.941
31.369
34.356
34.815
39.374
53.026
64.262
76.748
76.999
77.259
82.923
125.407
128.067
128.797
143.995
ppm
0
20
40
60
80
100
120
140
160
180


Me
Me
Me
Me
O
O
B
Ph
i-Pr

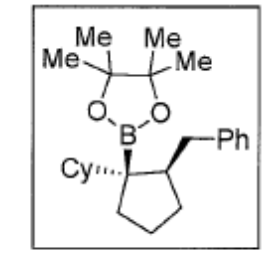
Compound 11

10
9
8
7
6
5
4
3
2
1
ppm
3.52
2.62
0.99
1.00
0.97
0.99
1.02
0.98
1.05
2.06
12.82
2.98
2.96

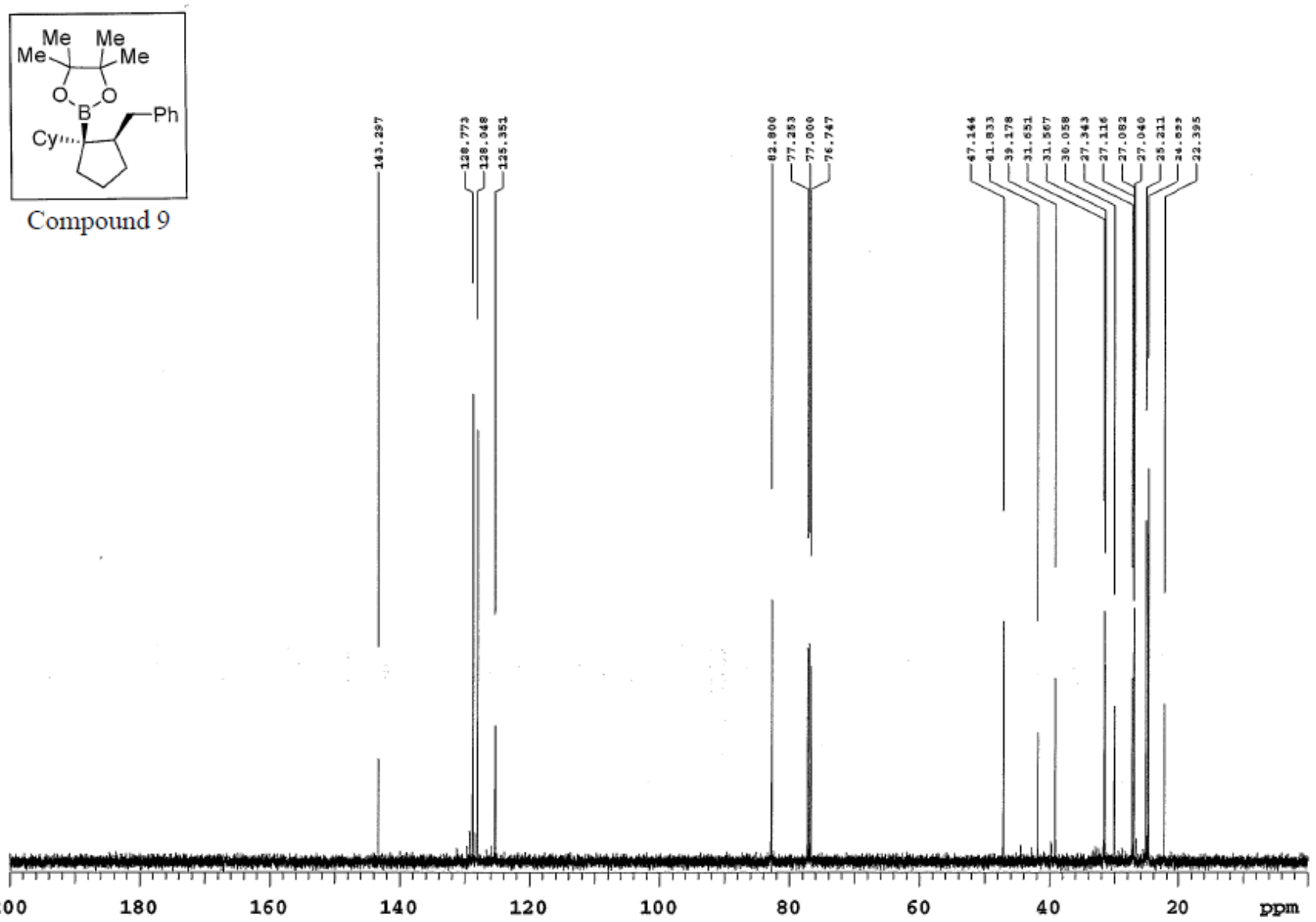

Me
Me
Me
Me
O
O
B
Ph
i-Pr

Compound 11

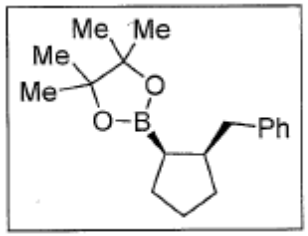
143.289
128.772
128.067
125.382
82.823
77.251
76.739
48.445
39.315
31.022
31.134
29.162
25.193
24.933
21.449
17.146
200
180
160
140
120
100
80
60
40
20
ppm



Compound 9

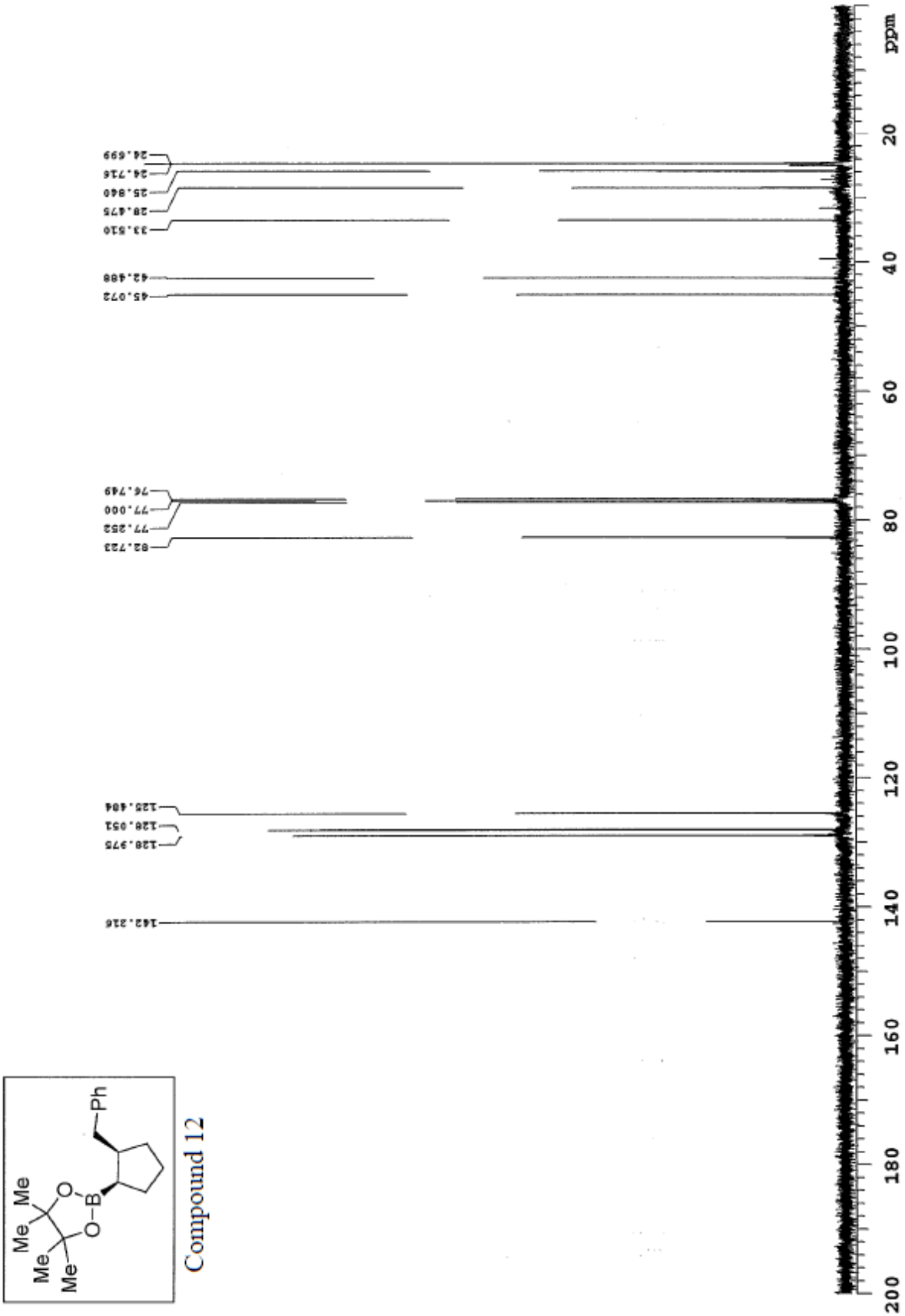

Me
Me
Me
Me
O
O
B
Ph
Cy
143.297
128.773
128.048
125.351
82.800
77.253
77.000
76.747
47.144
41.833
39.178
31.651
31.567
30.058
27.343
27.116
27.082
27.040
25.211
24.639
22.395
200
180
160
140
120
100
80
60
40
20
ppm

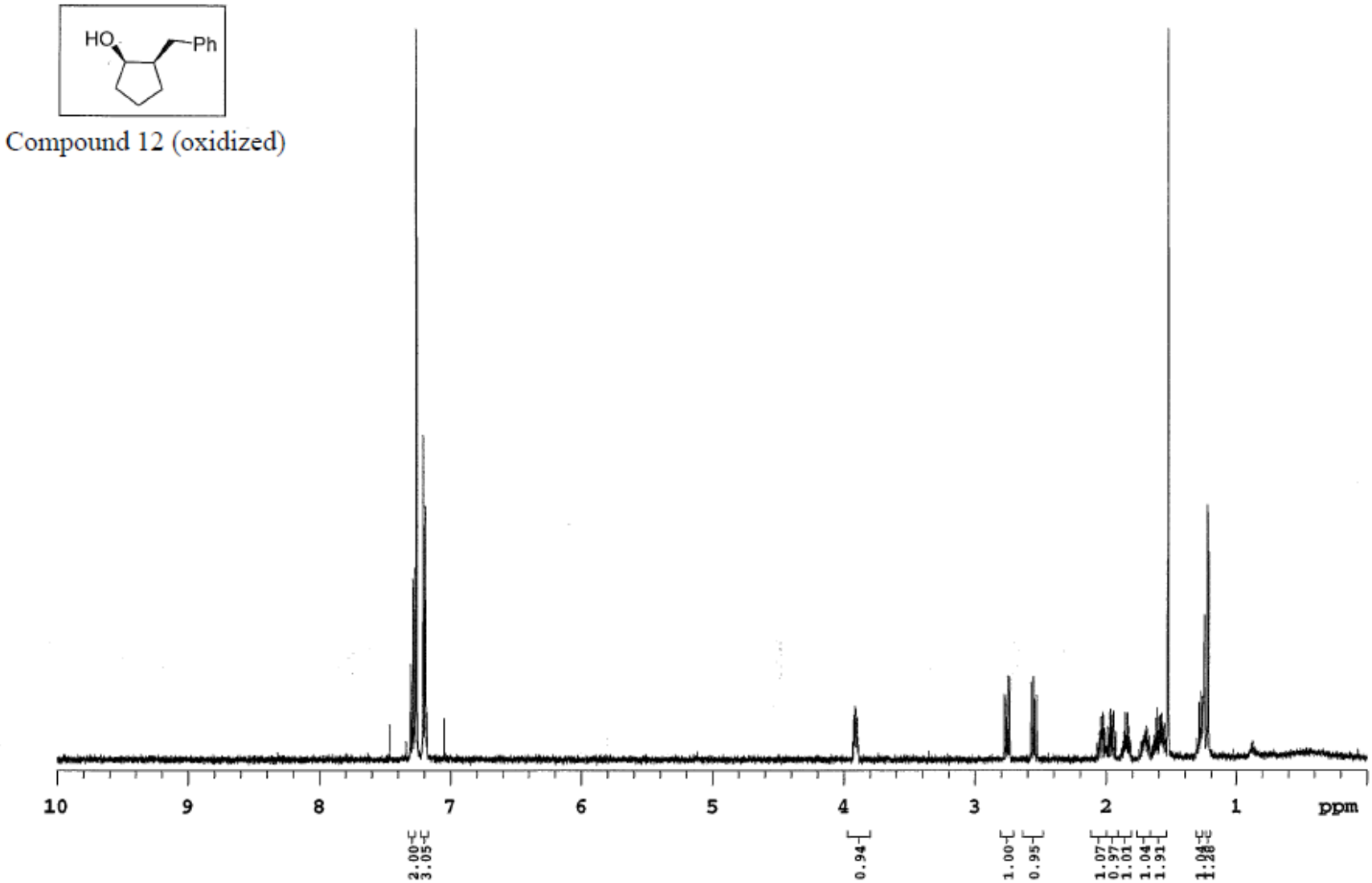
Compound 9


Me
Me
Me
Me
O
O–B
Ph

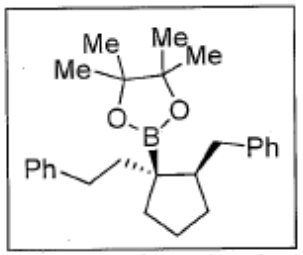
Compound 12

10
9
8
7
6
5
4
3
2
1
ppm
3.01
2.83
1.00
1.00
0.98
1.12
1.30
4.09
1.42
12.04
0.92

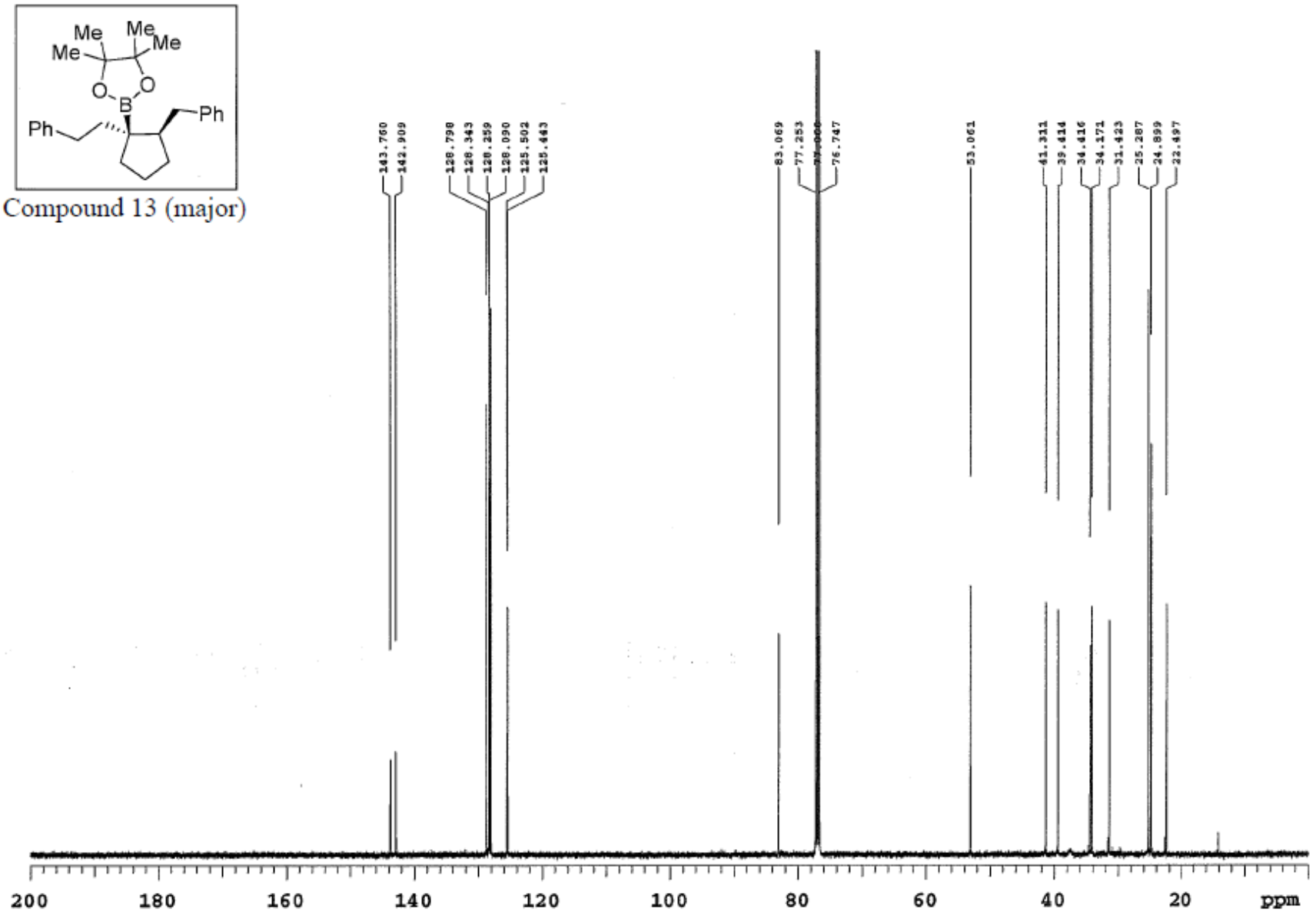

Me
Me
Me
O
O
B
Ph
Compound 12
142.216
128.975
128.051
125.484
82.723
77.253
77.000
76.749
45.072
42.488
33.510
28.475
25.840
24.716
24.699
ppm
200
180
160
140
120
100
80
60
40
20



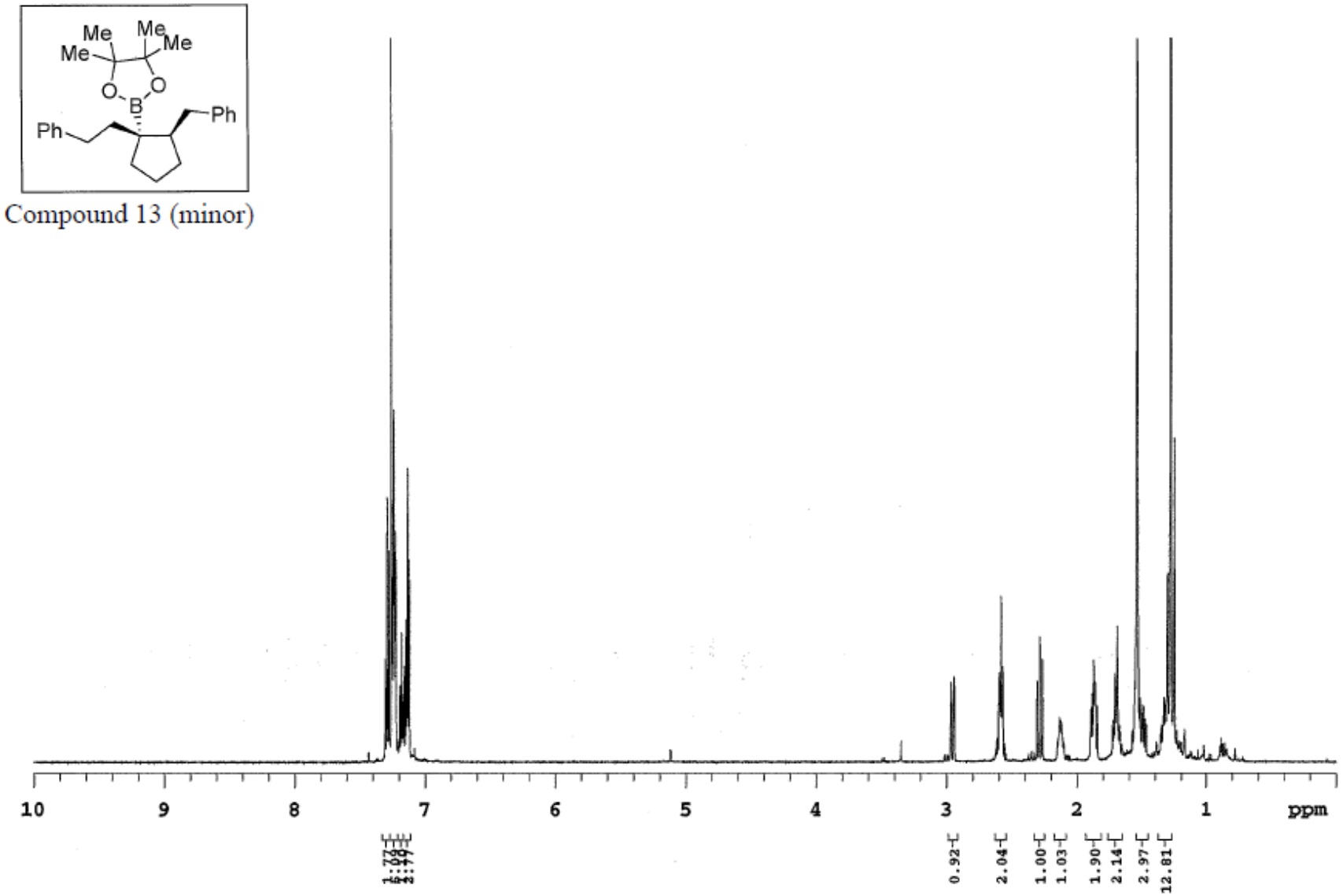
Compound 12 (oxidized)



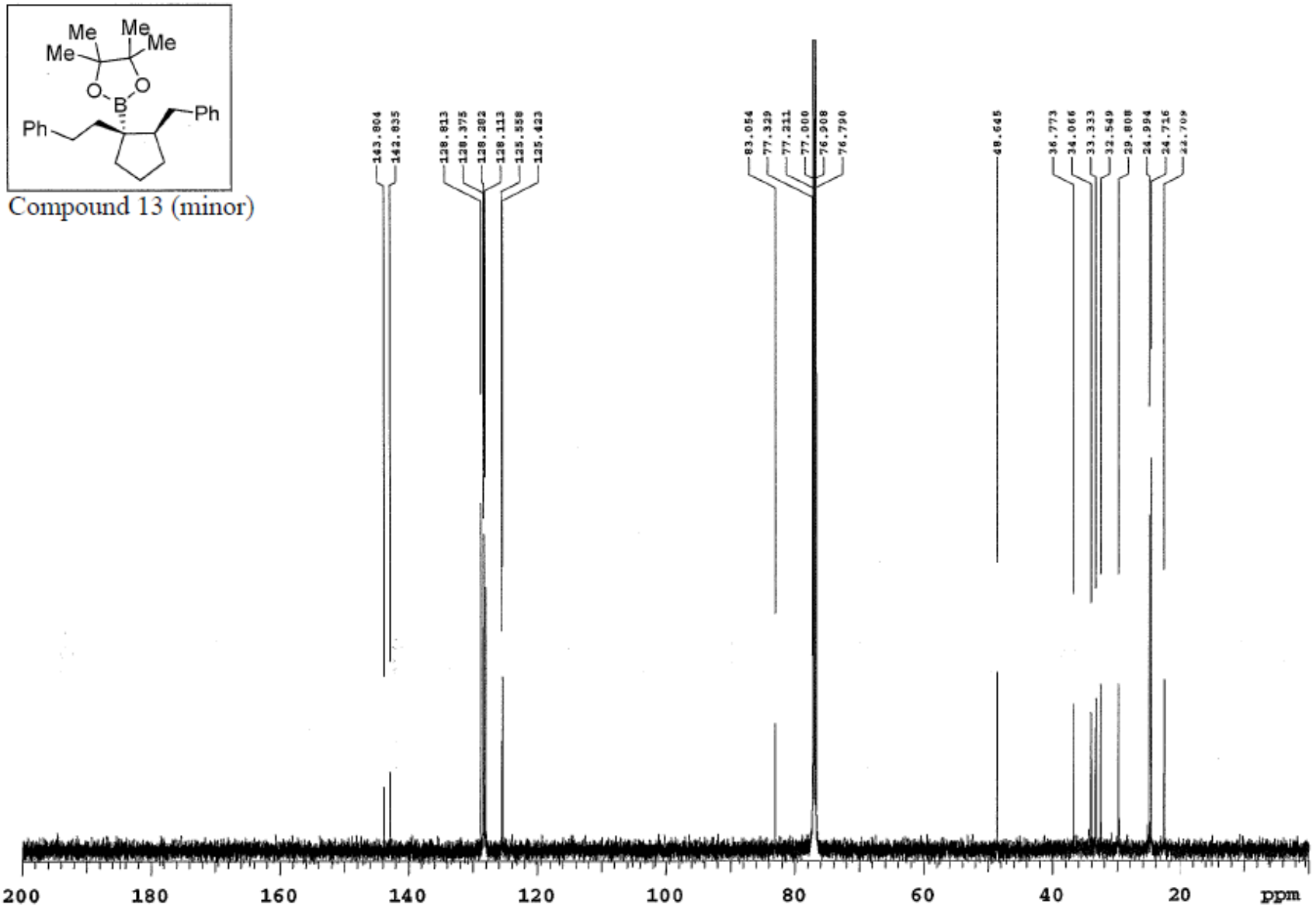
Compound 13 (major)



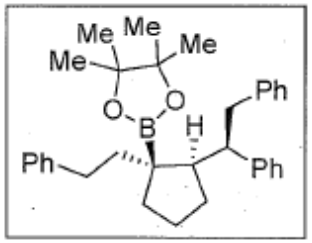
Compound 13 (major)



Compound 13 (minor)

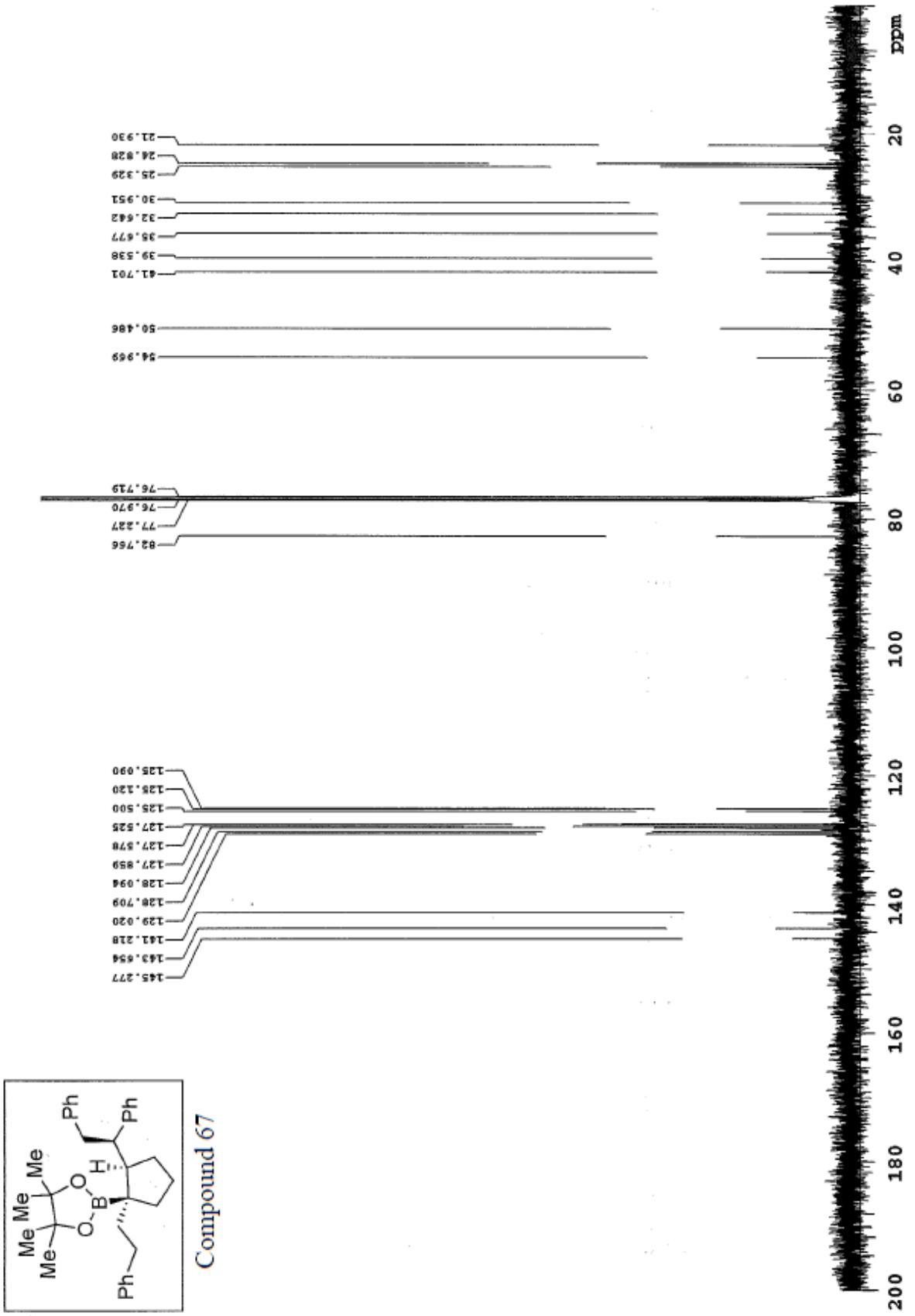


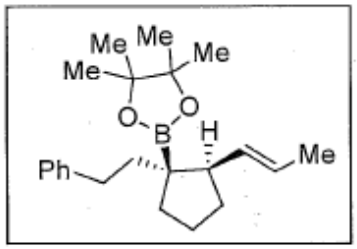
Compound 13 (minor)


Me
Me
Me
Me
O
O
B
H
Ph
Ph
Ph

Compound 67

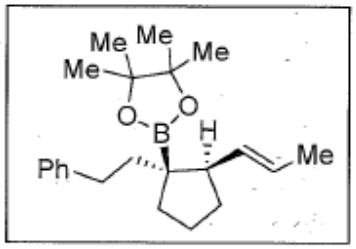
10
9
8
7
6
5
4
3
2
1
ppm
2.52
1.96
3.85
0.15
1.00
0.96
0.31
1.30
0.39
2.33
1.41
2.11
2.27
1.46
1.35


Compound 67
Me
Me
Me
Me
O
O
B
H
Ph
Ph
Ph
21.930
24.828
25.329
30.951
32.642
35.677
39.538
41.701
50.486
54.969
76.719
76.970
77.227
82.766
125.090
125.120
125.500
127.525
127.578
127.859
128.094
128.709
129.020
141.218
143.654
145.277
ppm
20
40
60
80
100
120
140
160
180
200


Me
Me
Me
Me
O
O
B
H
Ph
Me

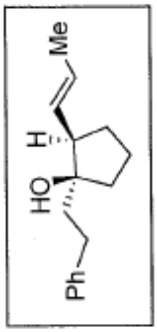
Compound 17

10
9
8
7
6
5
4
3
2
1
ppm
5.11
2.93
1.84
2.00
1.06
0.94
3.12
1.00
0.96
0.99
12.93

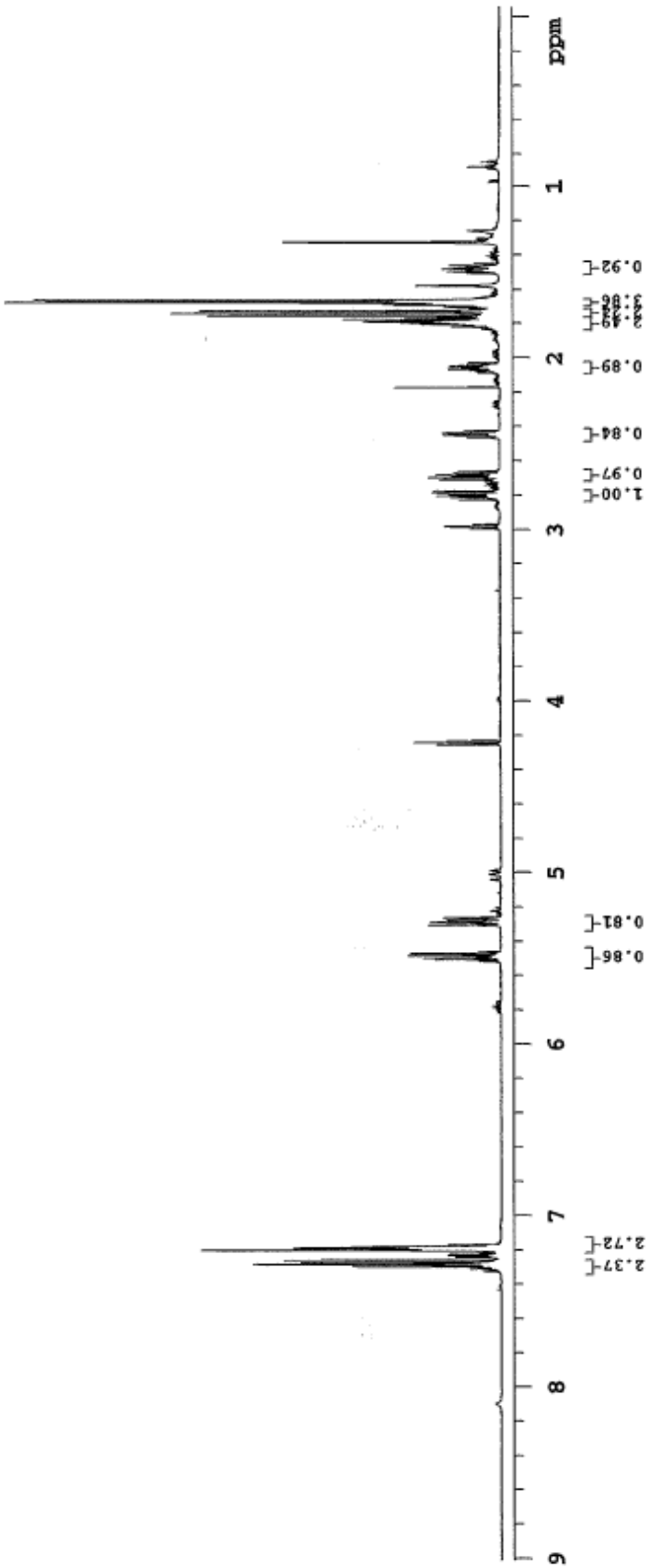

Me
Me
Me
Me
O
O
B
H
Ph
Me

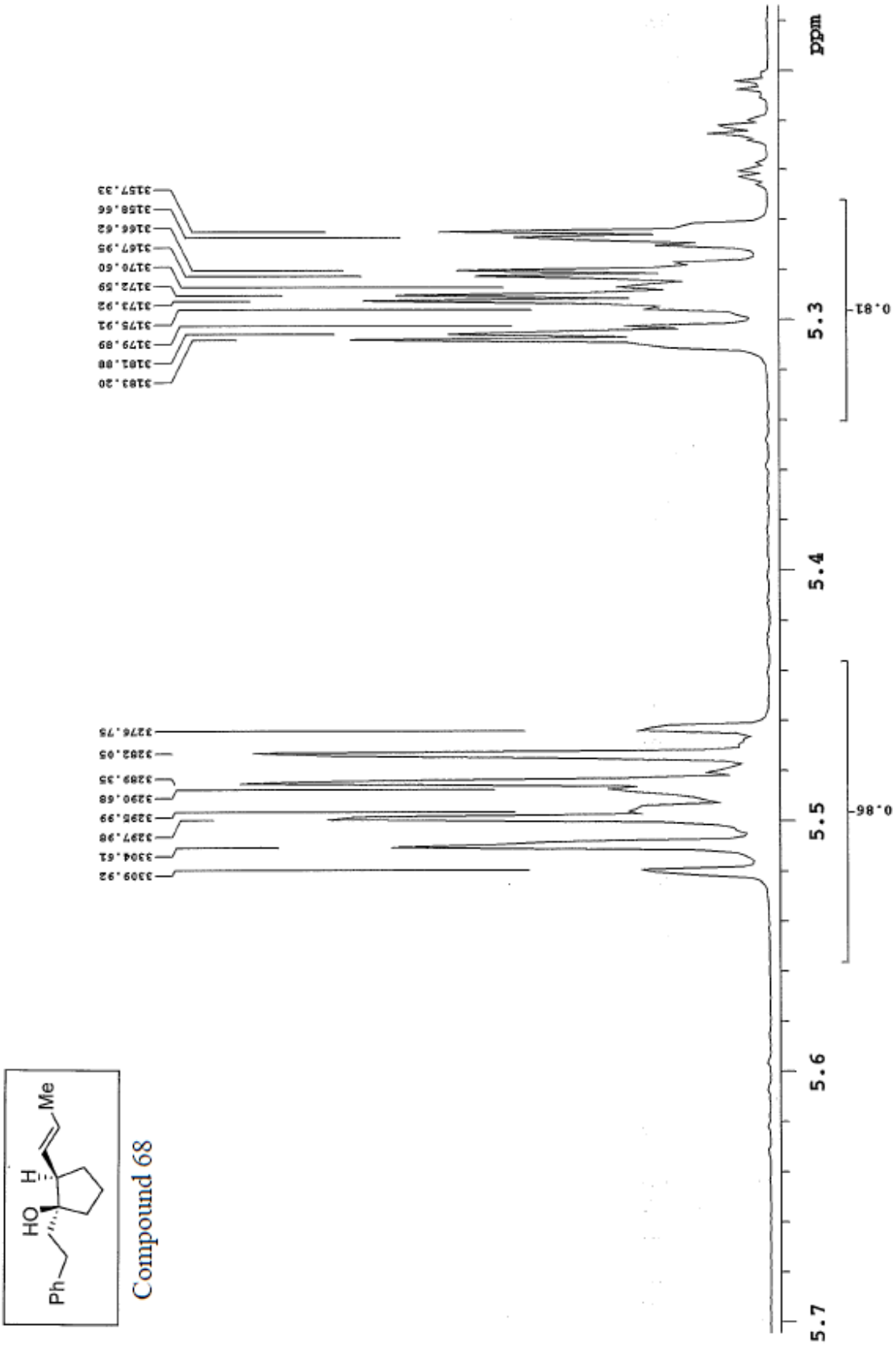
Compound 17

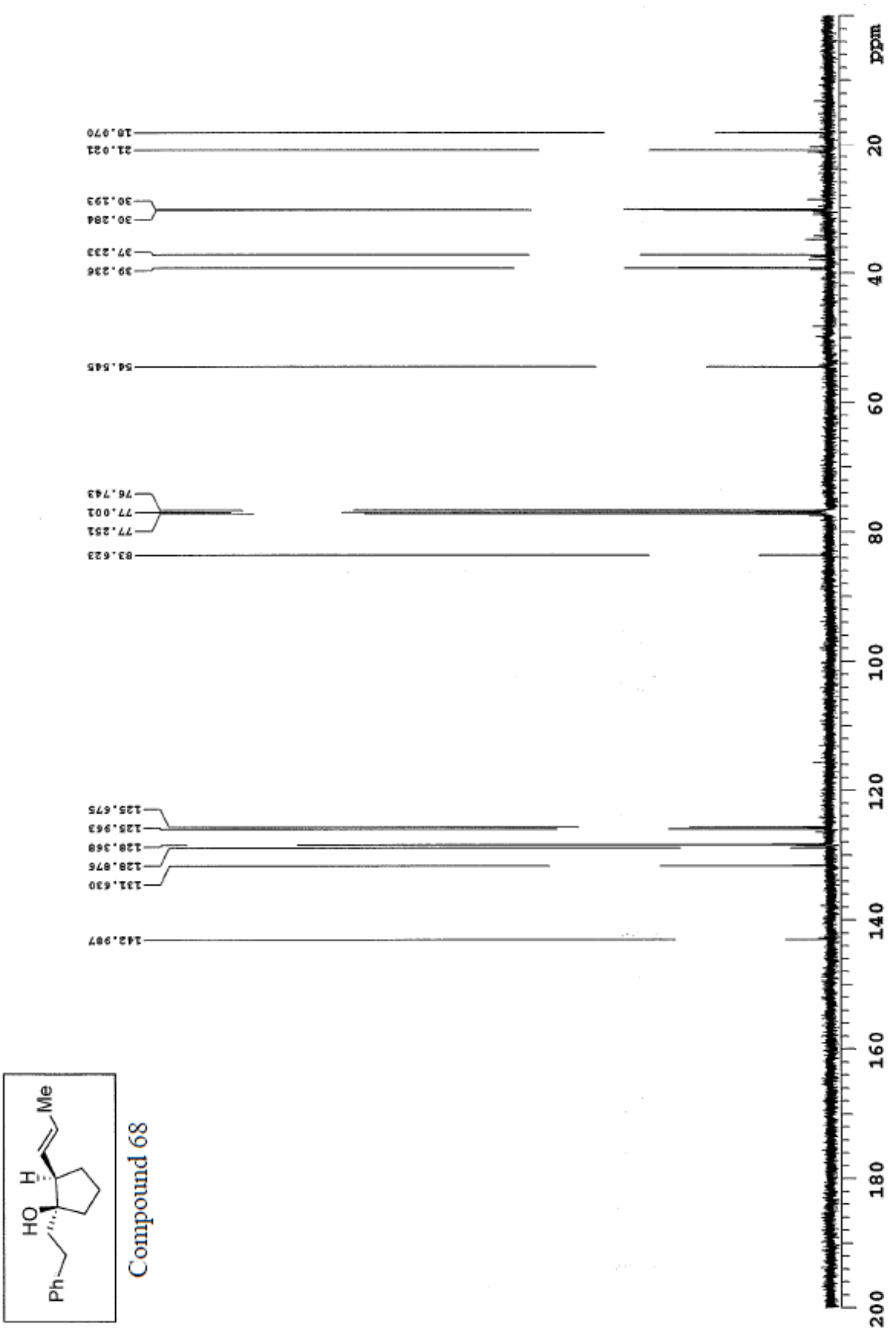
143.934
132.516
128.351
128.152
125.305
124.384
82.985
77.242
76.984
76.734
49.248
34.751
34.007
33.059
31.094
24.858
24.714
23.098
10.076
200
180
160
140
120
100
80
60
40
20
ppm

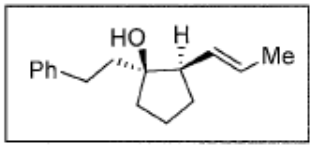


Compound 68

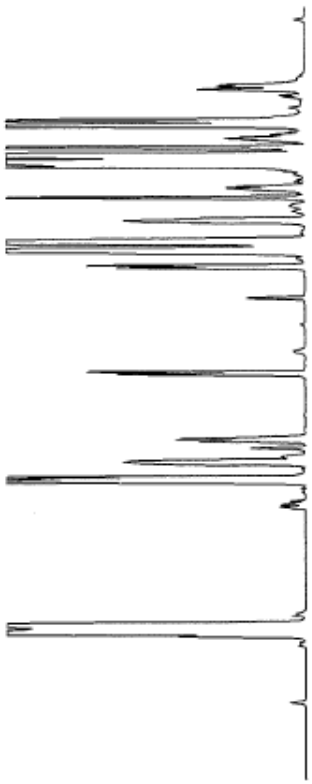


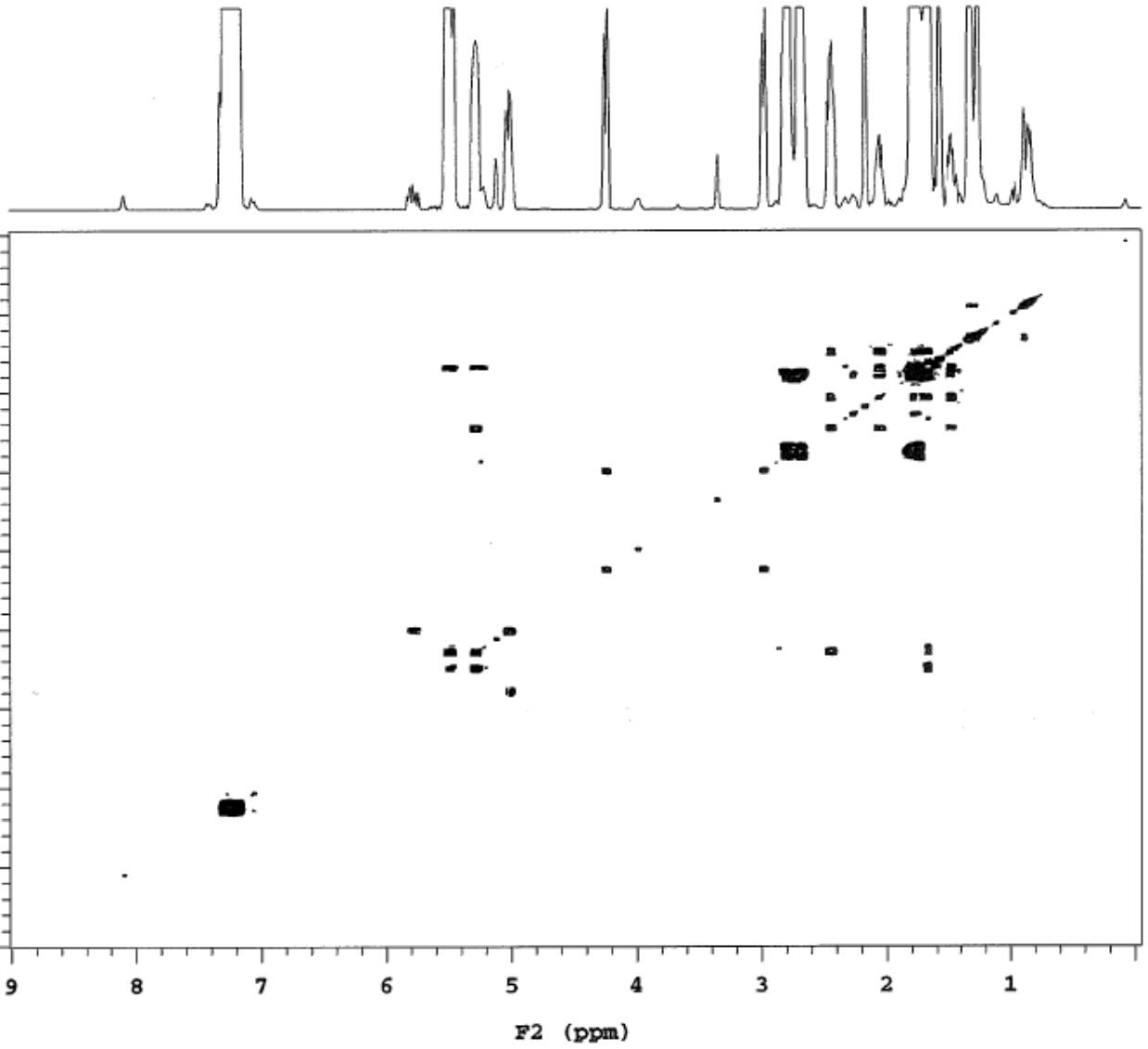

HO
H
Me
Ph
Compound 68
3309.92
3304.61
3297.98
3290.99
3289.35
3282.05
3276.75
3183.20
3181.88
3179.89
3175.92
3173.92
3172.59
3170.60
3167.95
3166.62
3158.66
3157.33
5.7
5.6
5.5
5.4
5.3
ppm
0.86
0.81

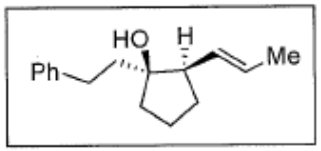

Me
H
HO
Ph
Compound 68
142.987
131.630
128.876
128.368
125.963
125.675
83.623
77.251
77.001
76.743
54.545
39.236
37.233
30.284
30.193
22.021
18.070
ppm
200
180
160
140
120
100
80
60
40
20



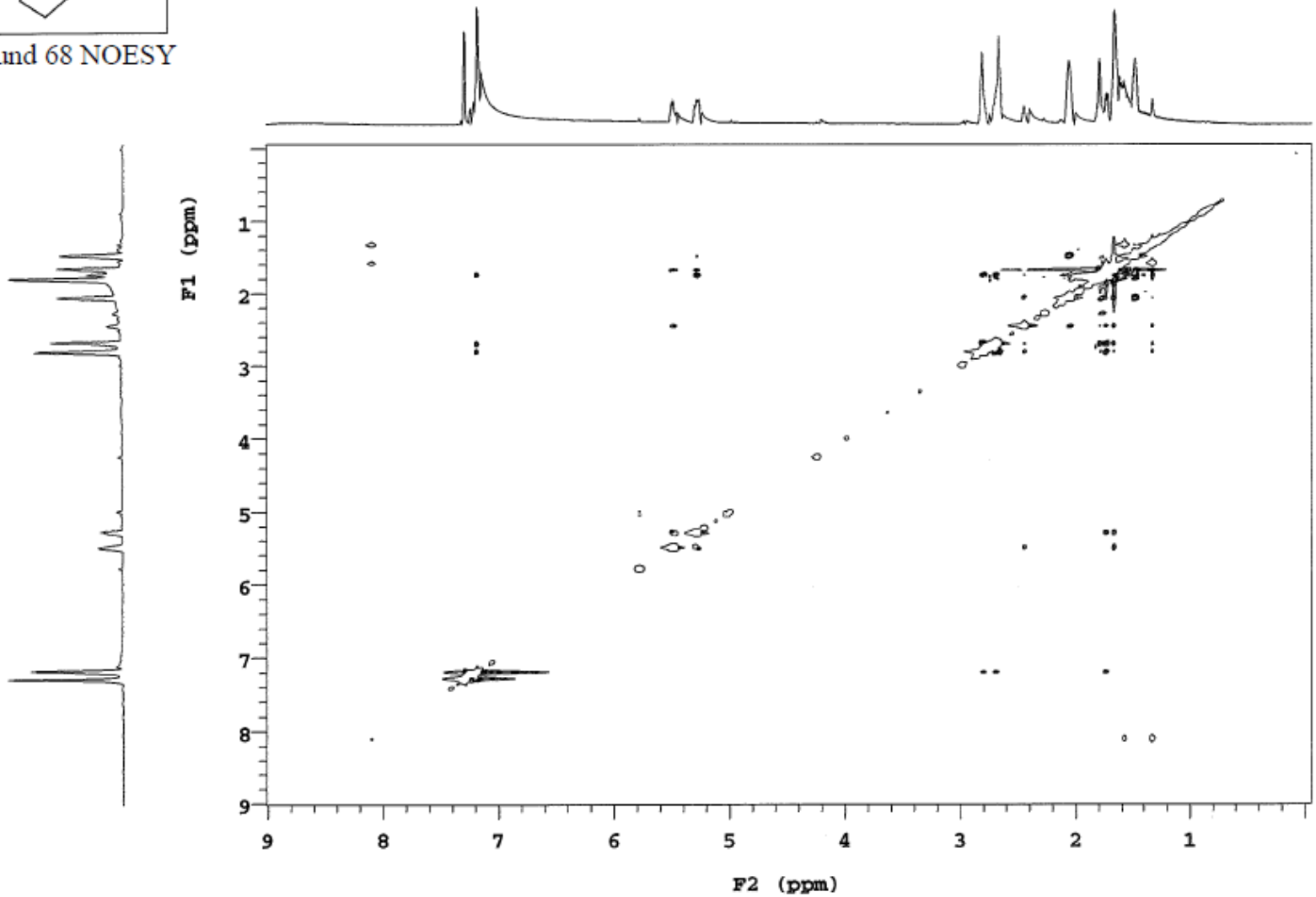
Compound 68 COSY

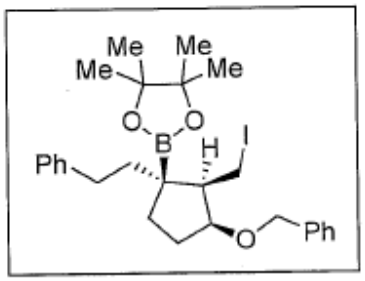






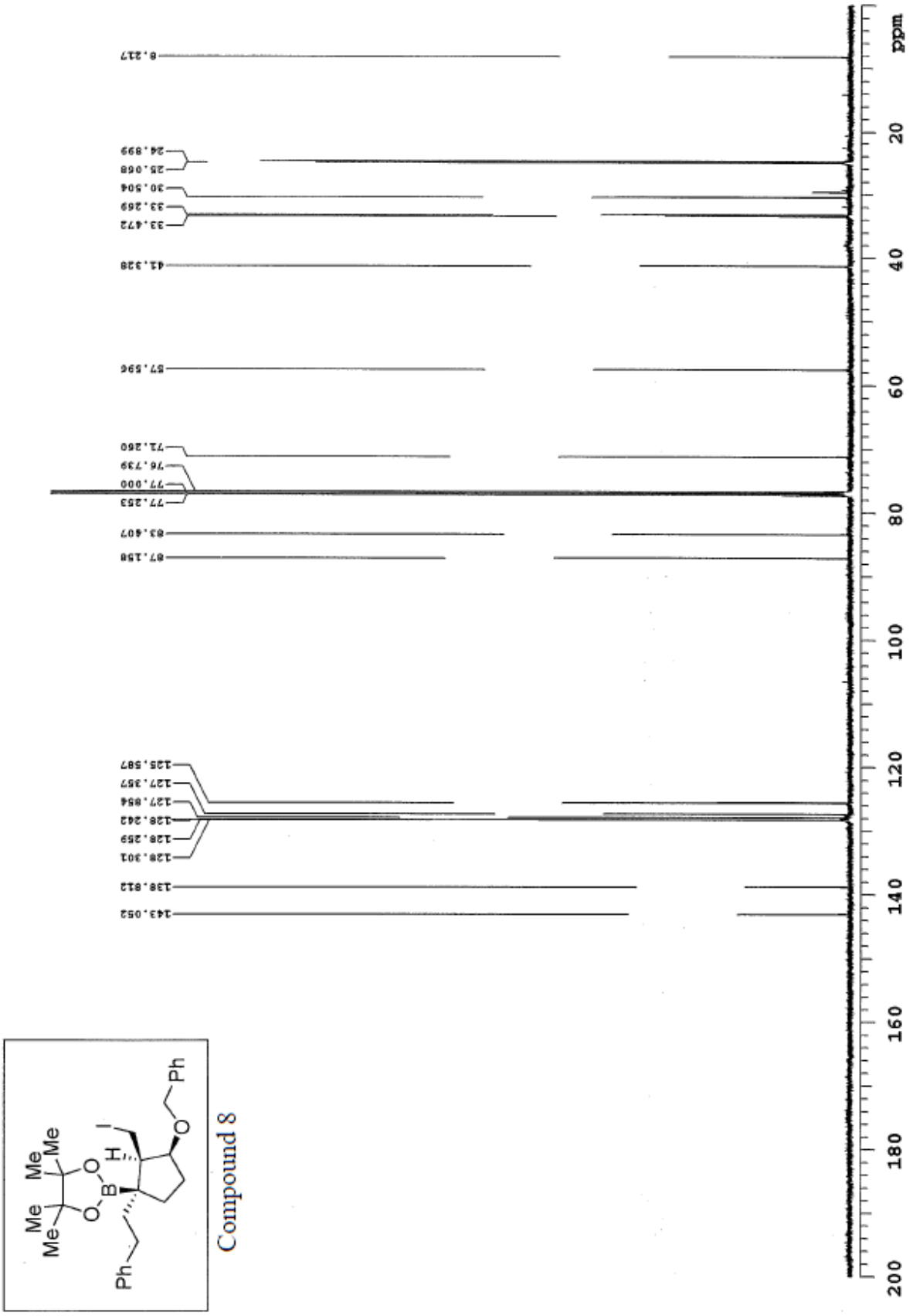
Compound 68 NOESY

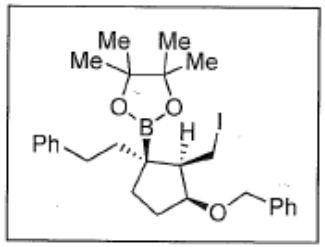



Me
Me
Me
Me
O
O
B
H
I
Ph
O
Ph

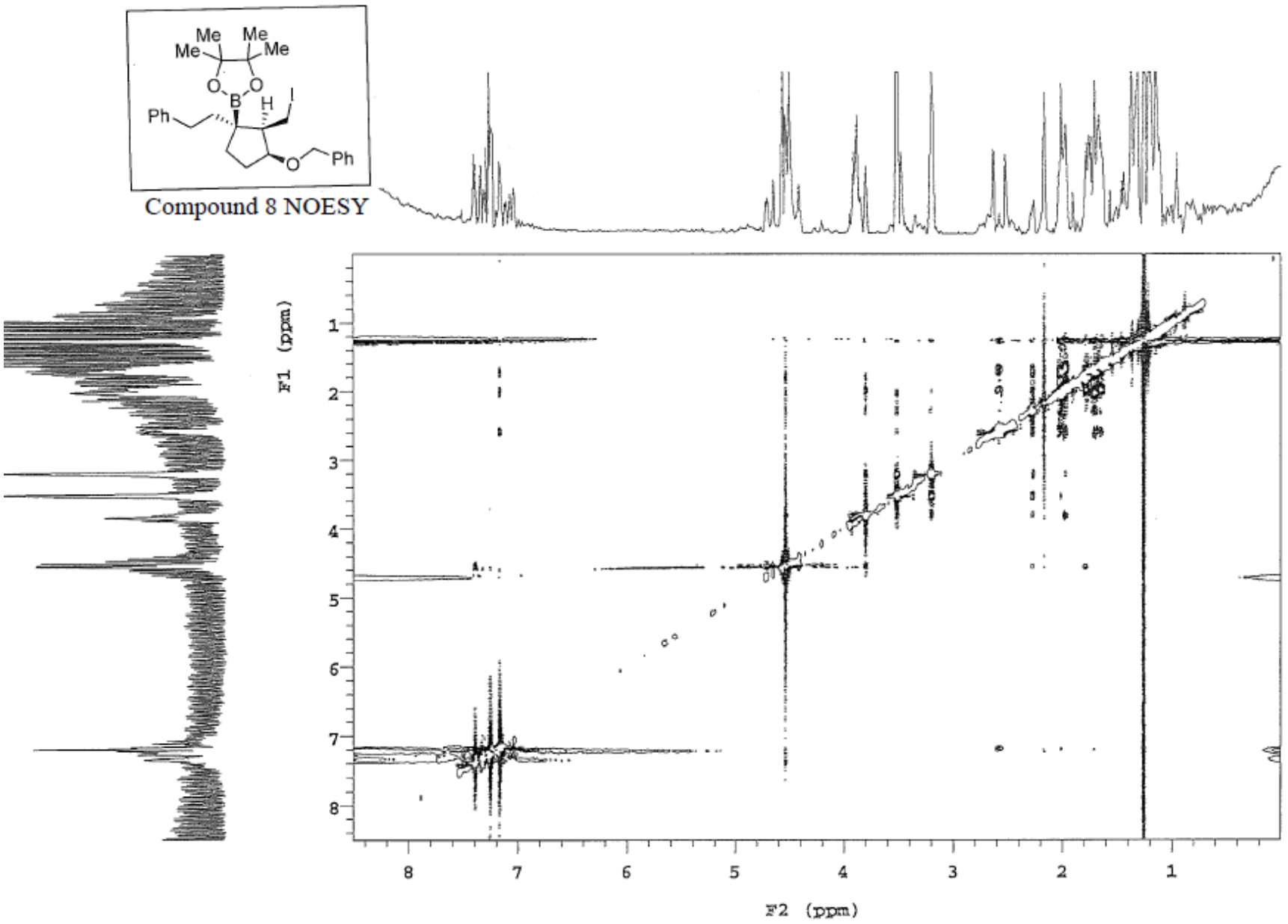
Compound 8

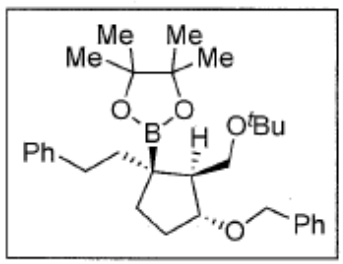
10
9
8
7
6
5
4
3
2
1
ppm
2.02
0.98
1.00
1.00
2.07
1.01
3.12
12.70


Me
Me
Me
Me
O
O
B
H
O
Ph
Ph
Compound 8
8.217
24.899
25.068
30.504
33.269
33.472
41.338
57.596
71.260
76.739
77.000
77.253
83.407
87.158
125.587
127.357
127.854
128.242
128.259
128.301
138.812
143.052
ppm
20
40
60
80
100
120
140
160
180
200



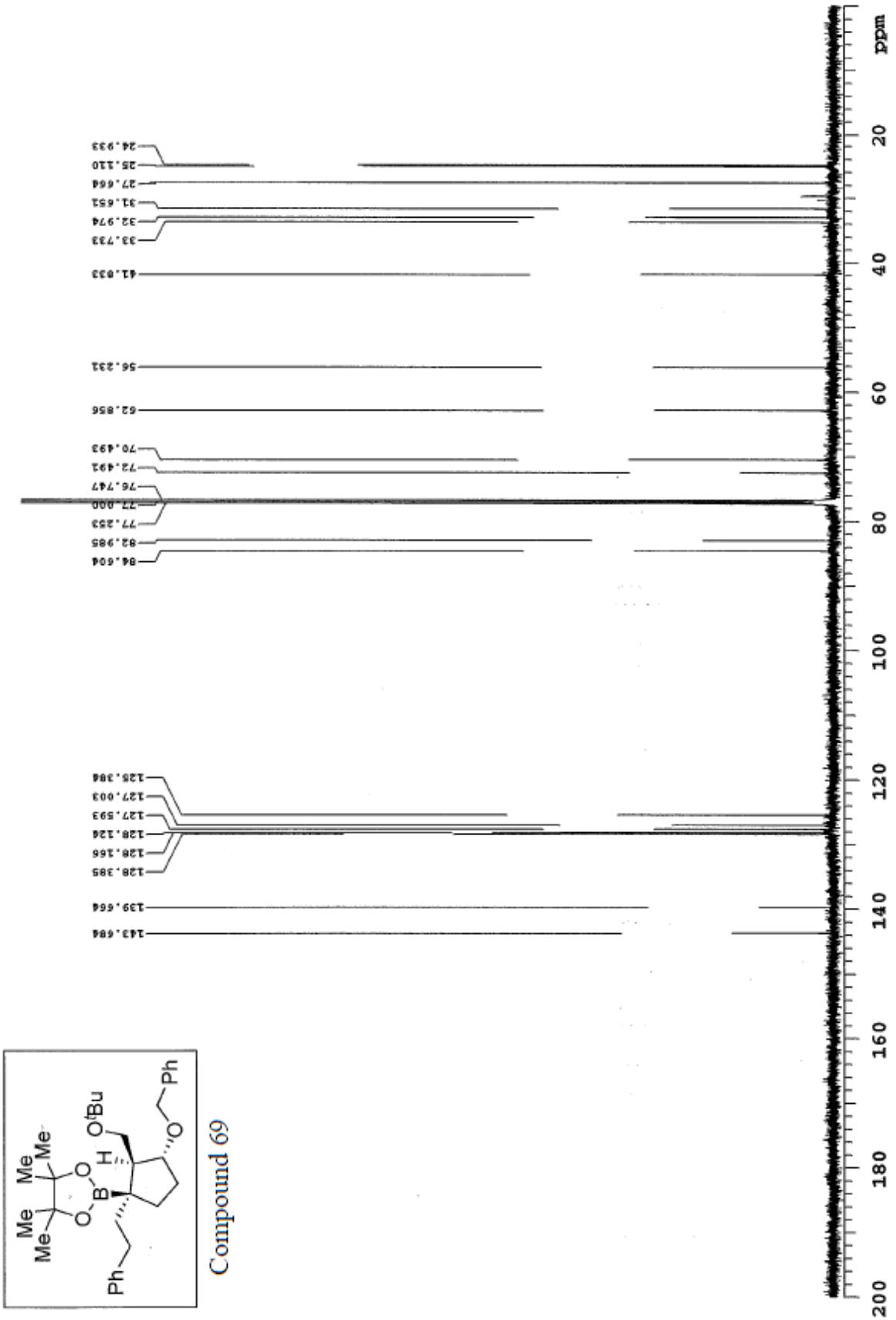
Compound 8 COSY

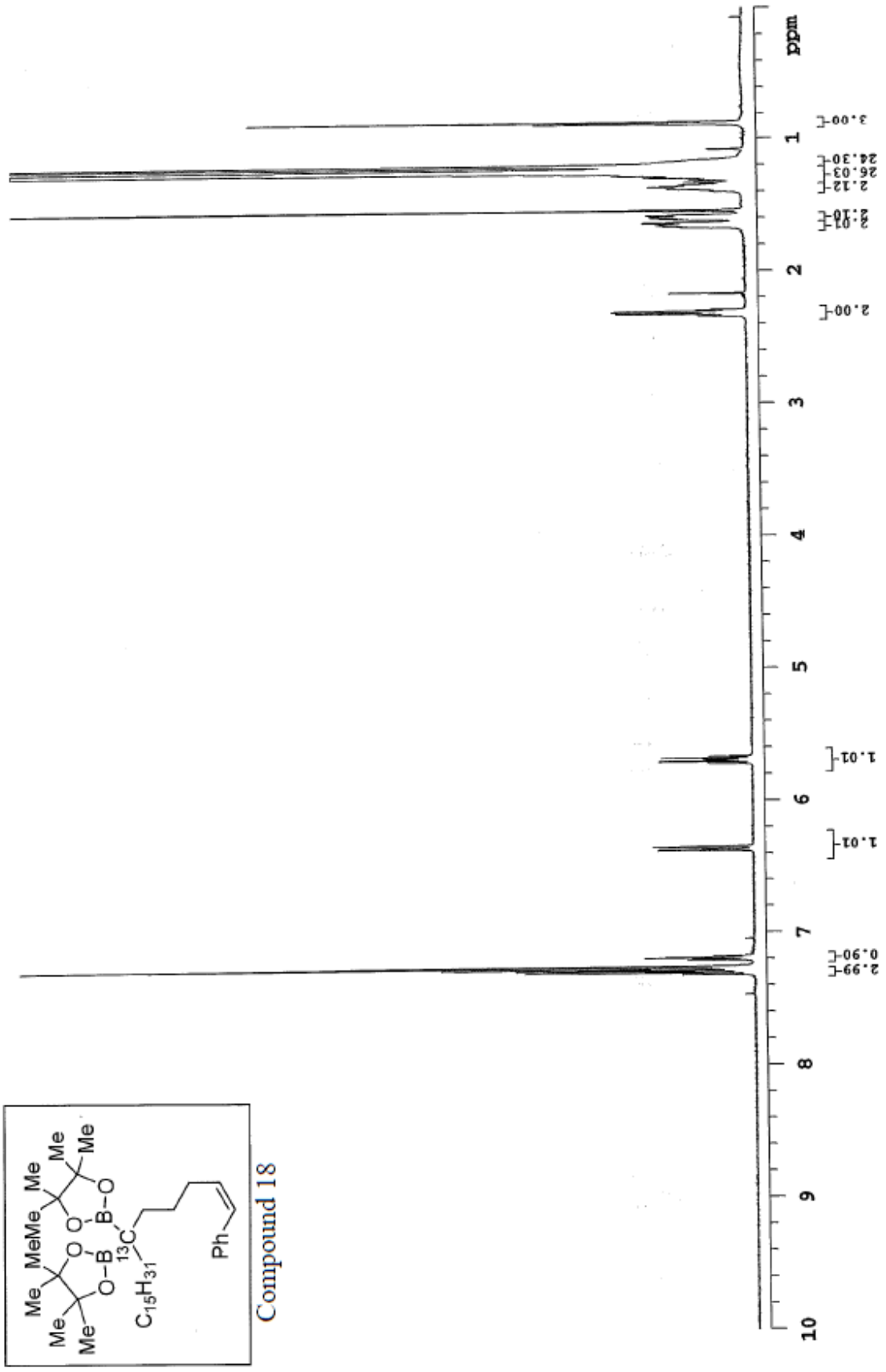

Me
Me
Me
Me
O
O
B
H
Ph
Ph
Compound 8 NOESY
F1 (ppm)
F2 (ppm)
1
2
3
4
5
6
7
8

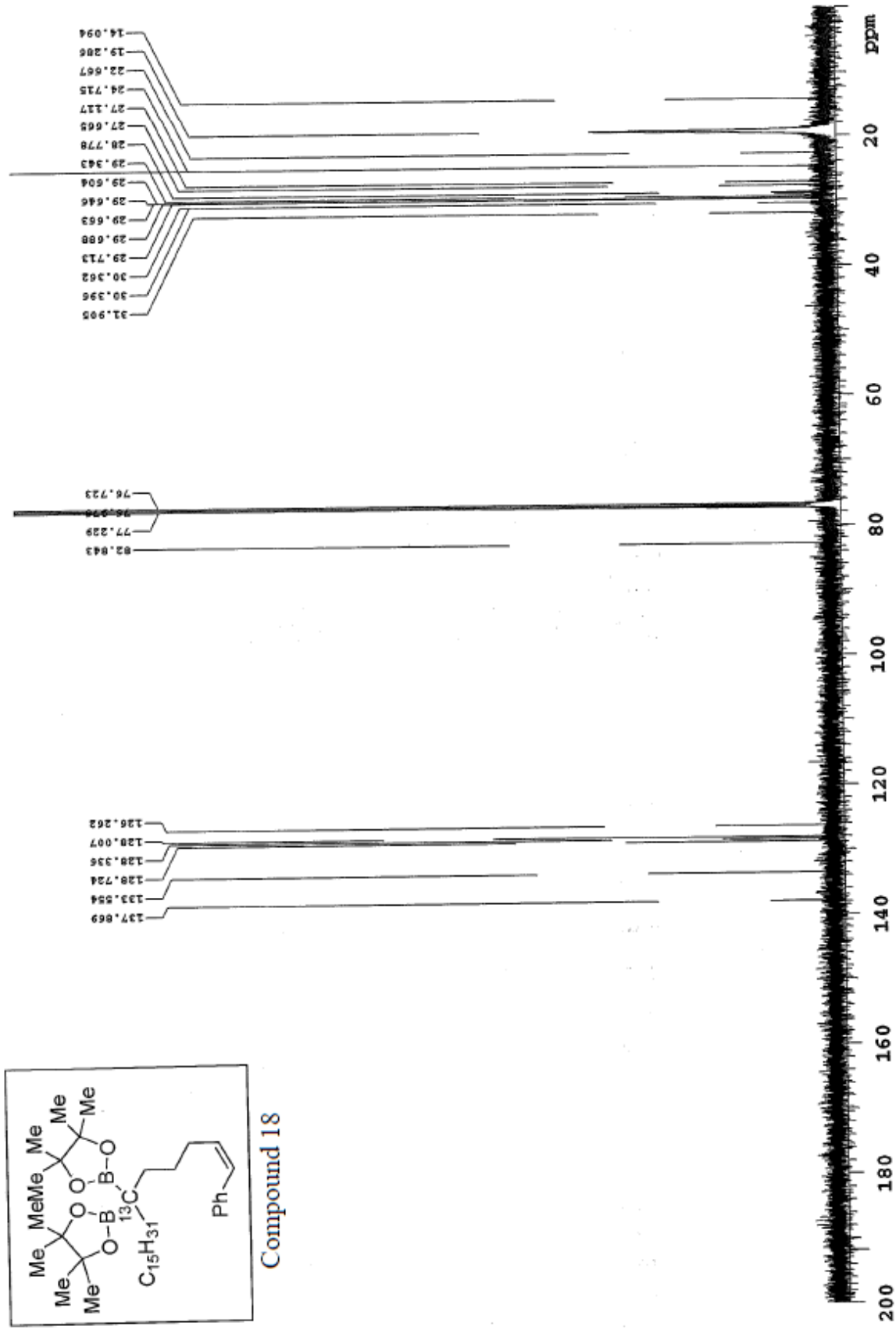

Me
Me
Me
Me
O
O
B
H
O
tBu
Ph
O
Ph

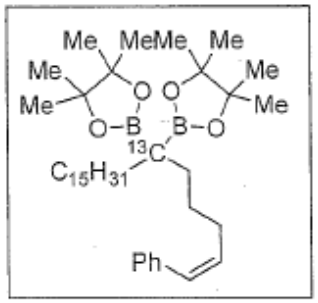
Compound 69

10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.99
0.99
1.01
1.00
2.06
3.10
1.06
2.14
1.14
12.67
8.82

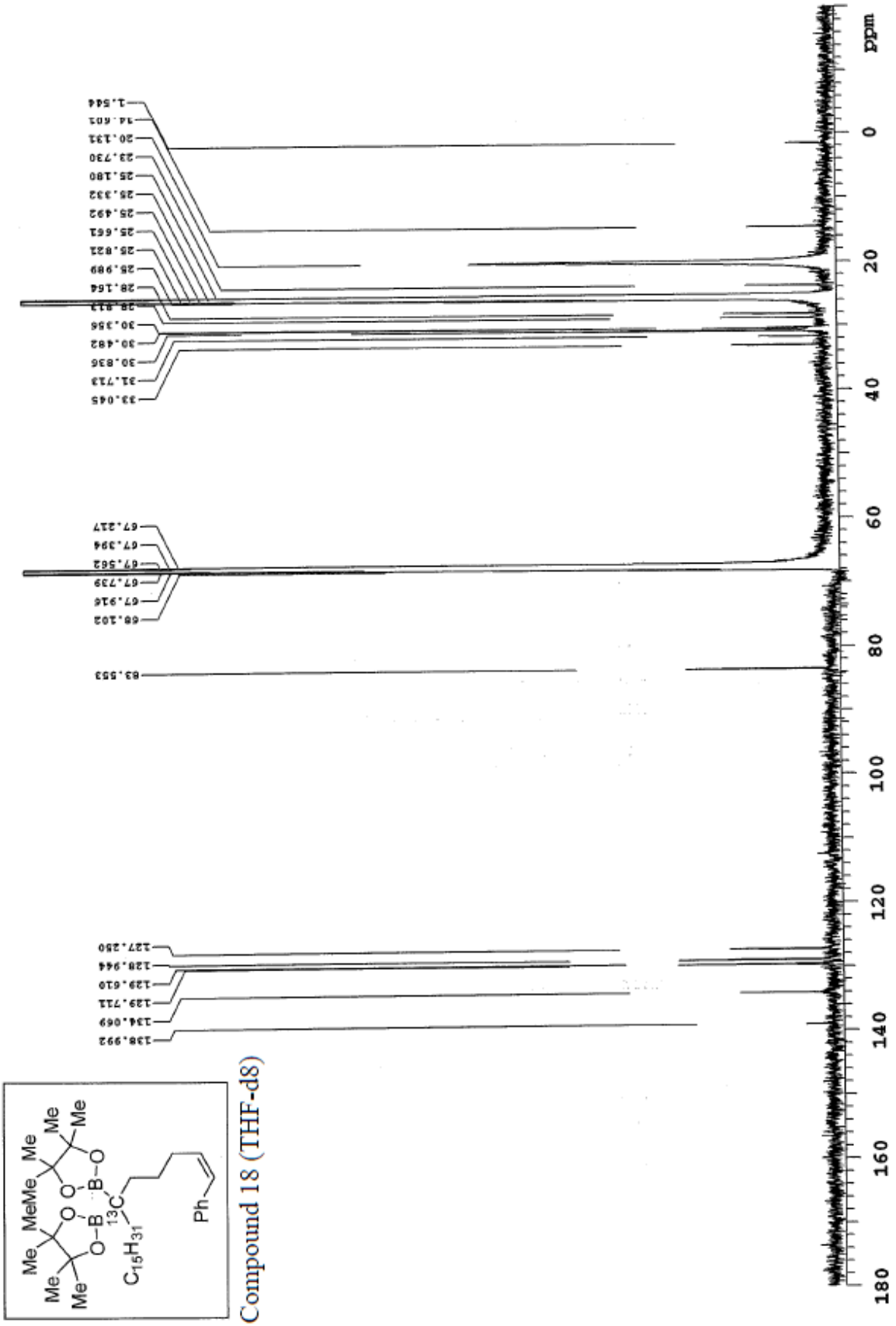

Me
Me
Me
Me
O
O
B
H
OtBu
O
Ph
Ph
Compound 69
34.933
35.110
27.664
31.652
32.974
33.733
41.033
56.232
62.856
70.493
73.493
76.747
77.000
77.253
82.985
84.604
125.384
127.003
127.593
128.124
128.166
128.385
139.664
143.684
ppm
20
40
60
80
100
120
140
160
180
200

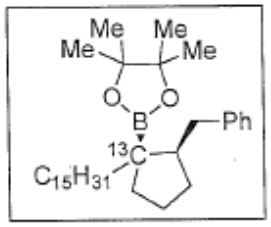

Me
Me
Me
Me
Me
Me
O
O
B
O
O
B
13C
C15H31
Ph
Compound 18
ppm
1
2
3
4
5
6
7
8
9
10
3.00
24.30
26.03
2.12
2.20
2.01
2.00
1.01
1.01
0.90
2.99


14.094
19.386
22.667
24.715
27.117
27.665
28.778
29.343
29.604
29.646
29.663
29.688
29.713
30.362
30.396
31.905
76.723
77.229
82.843
128.007
128.336
128.724
133.554
137.869
Me
Me
Me
Me
Me
Me
O
O
B
O
O
B
13C
C15H31
Ph
Compound 18
ppm
20
40
60
80
100
120
140
160
180
200



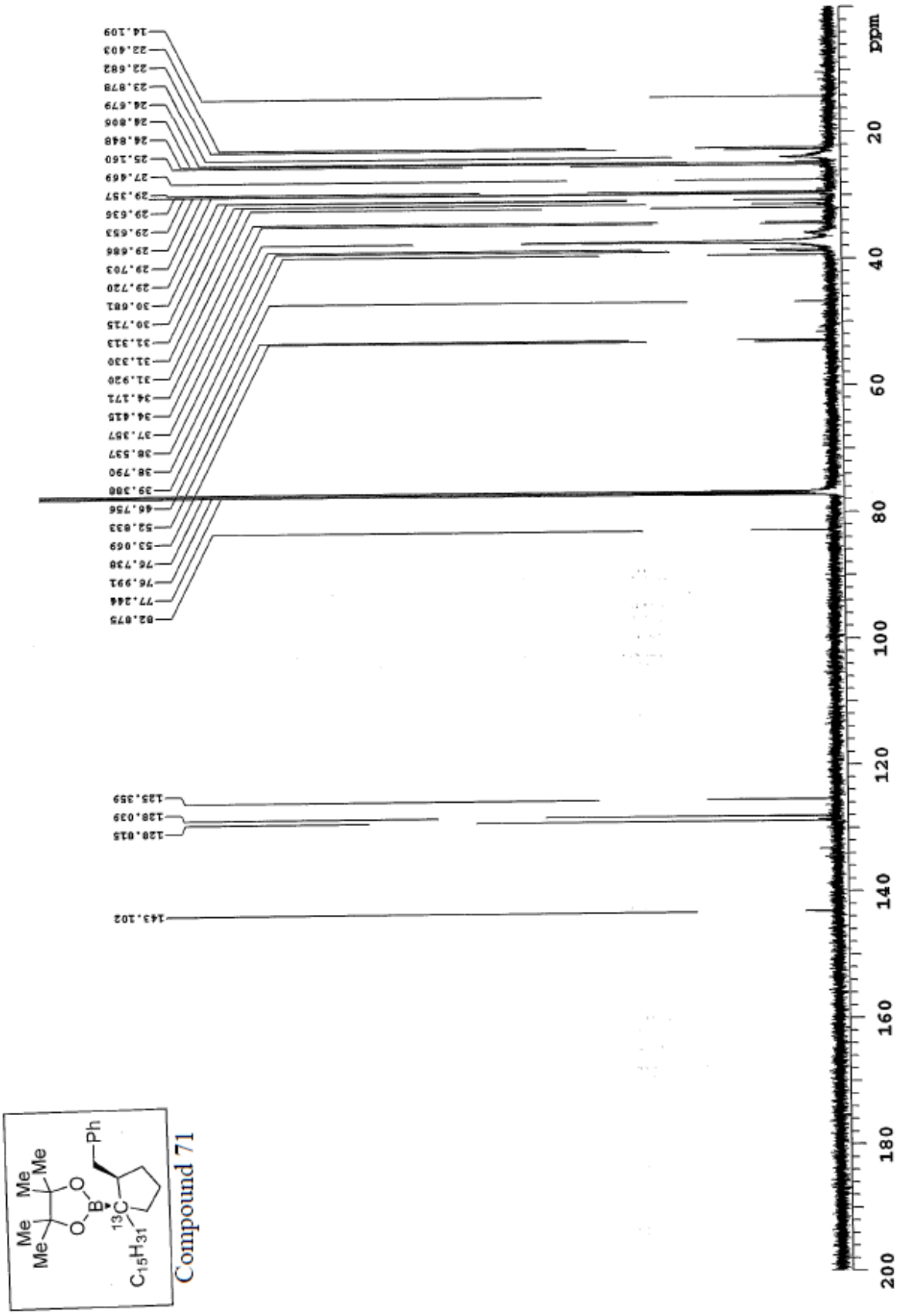
Compound 18 (THF-d8)


Me
Me
Me
Me
Me
Me
O
O
B
B
O
O
13C
C15H31
Ph
Compound 18 (THF-d8)
138.992
134.069
133.711
129.610
128.944
127.280
83.553
68.103
67.916
67.739
67.562
67.394
67.217
33.045
31.713
30.836
30.482
30.356
28.913
28.164
25.989
25.821
25.661
25.492
25.332
25.180
23.730
20.131
14.601
1.544
ppm
0
20
40
60
80
100
120
140
160
180

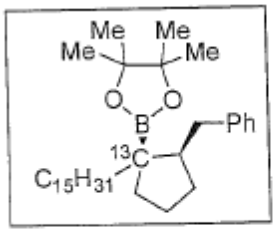

Me
Me
Me
Me
O
O
B
Ph
13C
C15H31

Compound 71

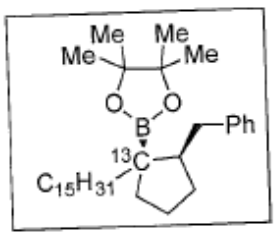
10
9
8
7
6
5
4
3
2
1
ppm
4.32
2.45
0.82
1.00
0.84
0.95
2.86
1.24
39.69
1.02
3.25


14.109
22.403
22.682
23.878
24.679
24.806
24.848
25.160
27.469
29.357
29.636
29.653
29.686
29.703
29.720
30.681
30.735
31.313
31.330
31.920
34.171
34.415
37.357
38.537
38.790
39.388
46.756
52.833
53.069
76.738
76.991
77.244
82.075
125.359
128.039
128.815
143.102
ppm
20
40
60
80
100
120
140
160
180
200

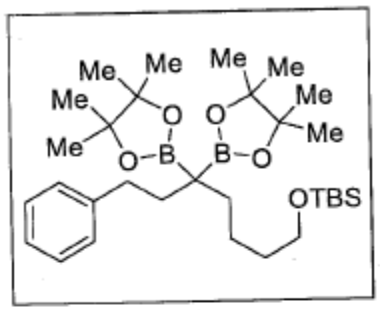
Compound 71



Compound 71 (THF-d8)

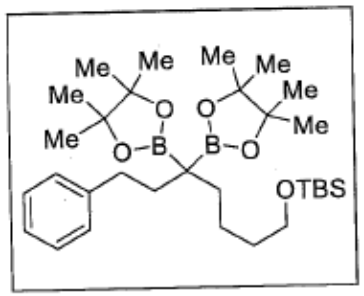


Compound 71 (THF-d8)

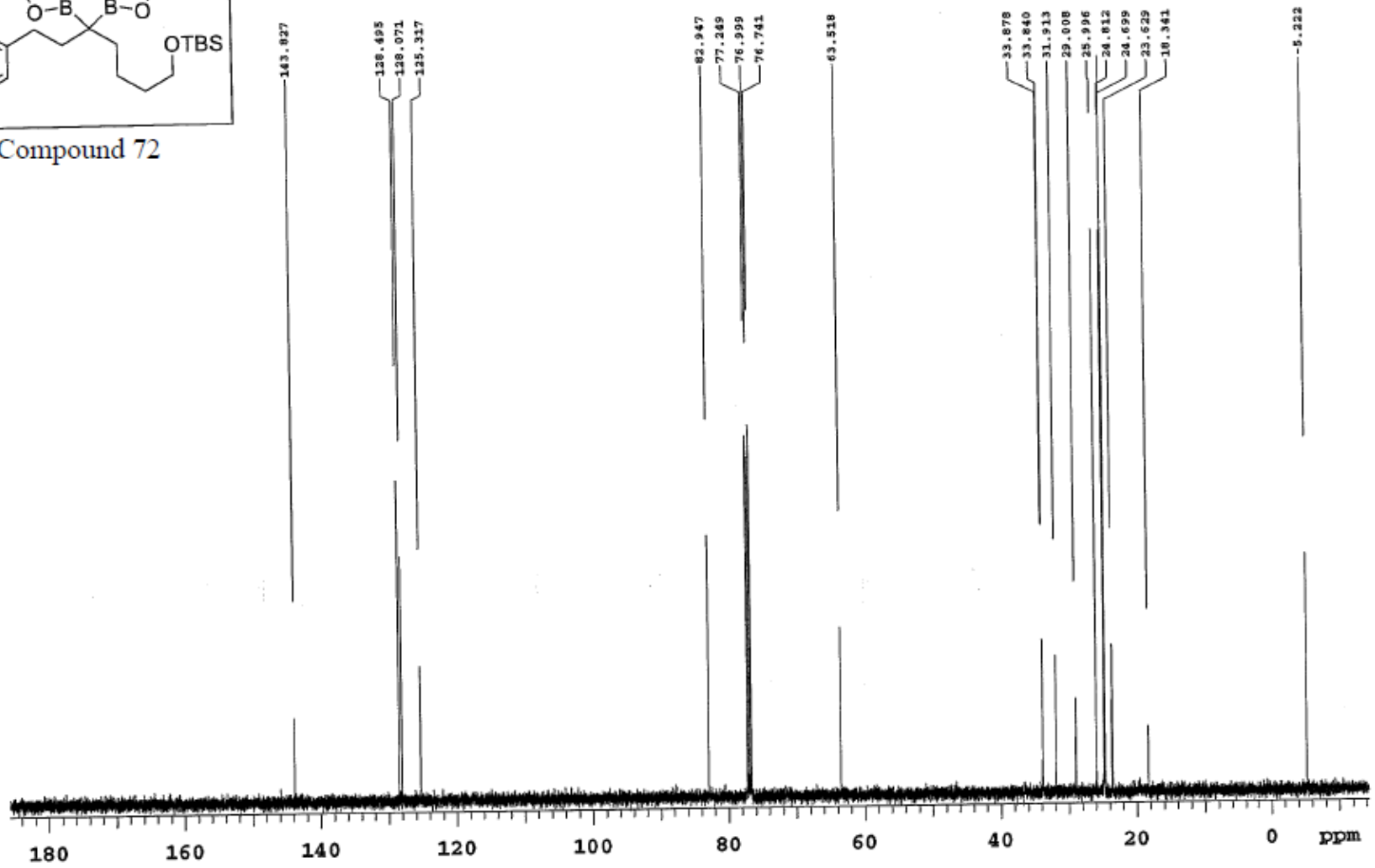

Me
Me
Me
Me
Me
Me
O
O
O
B
B
O
OTBS

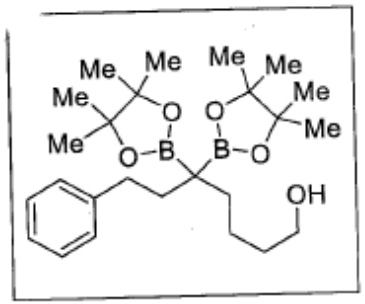
Compound 72

10
9
8
7
6
5
4
3
2
1
0
ppm
2.06
1.98
2.00
2.07
2.14
2.42
24.08
9.44
6.18


Me
Me
Me
Me
Me
Me
O
O
O
B
B
O
OTBS

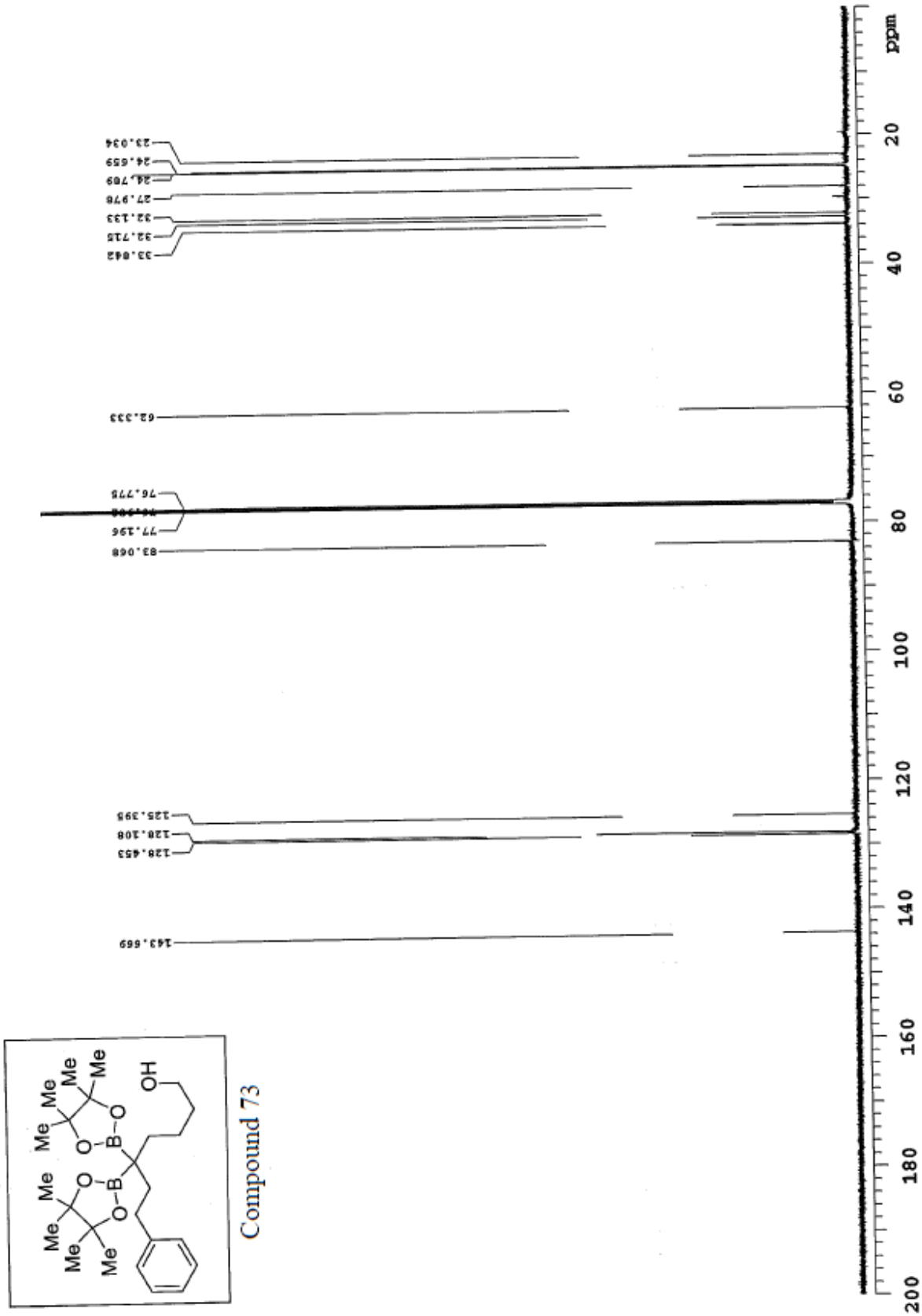
Compound 72


143.927
128.495
128.071
125.317
82.947
77.289
76.999
76.741
63.518
33.878
33.840
31.913
29.008
25.996
24.812
24.699
23.629
18.341
-5.222
180
160
140
120
100
80
60
40
20
0
ppm

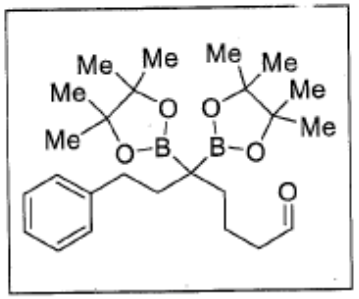

Me
Me
Me
Me
Me
Me
O
O
B
B
O
O
OH

Compound 73

10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.98
2.00
2.97
2.12
2.16
23.86

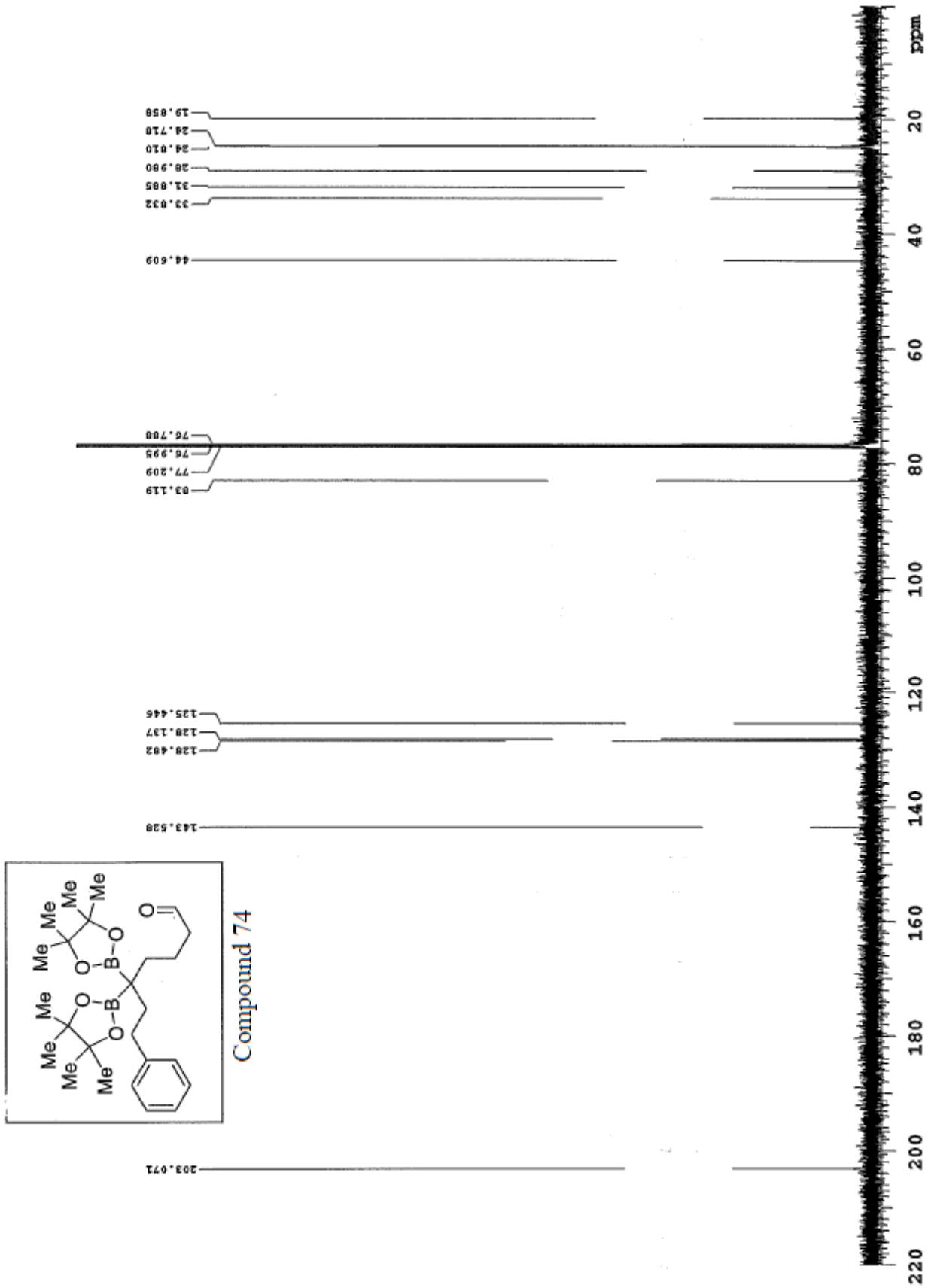

143.669
138.453
138.308
135.395
83.068
77.396
76.775
63.333
33.843
33.715
33.133
27.978
24.789
24.659
23.034
ppm
20
40
60
80
100
120
140
160
180
200
OH
Me
Me
Me
Me
Me
Me
Me
Me
O
O
O
O
B
B

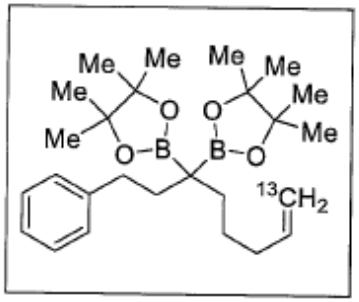
Compound 73


Me
Me
Me
Me
Me
Me
O
O
O
B
B
O
O

Compound 74

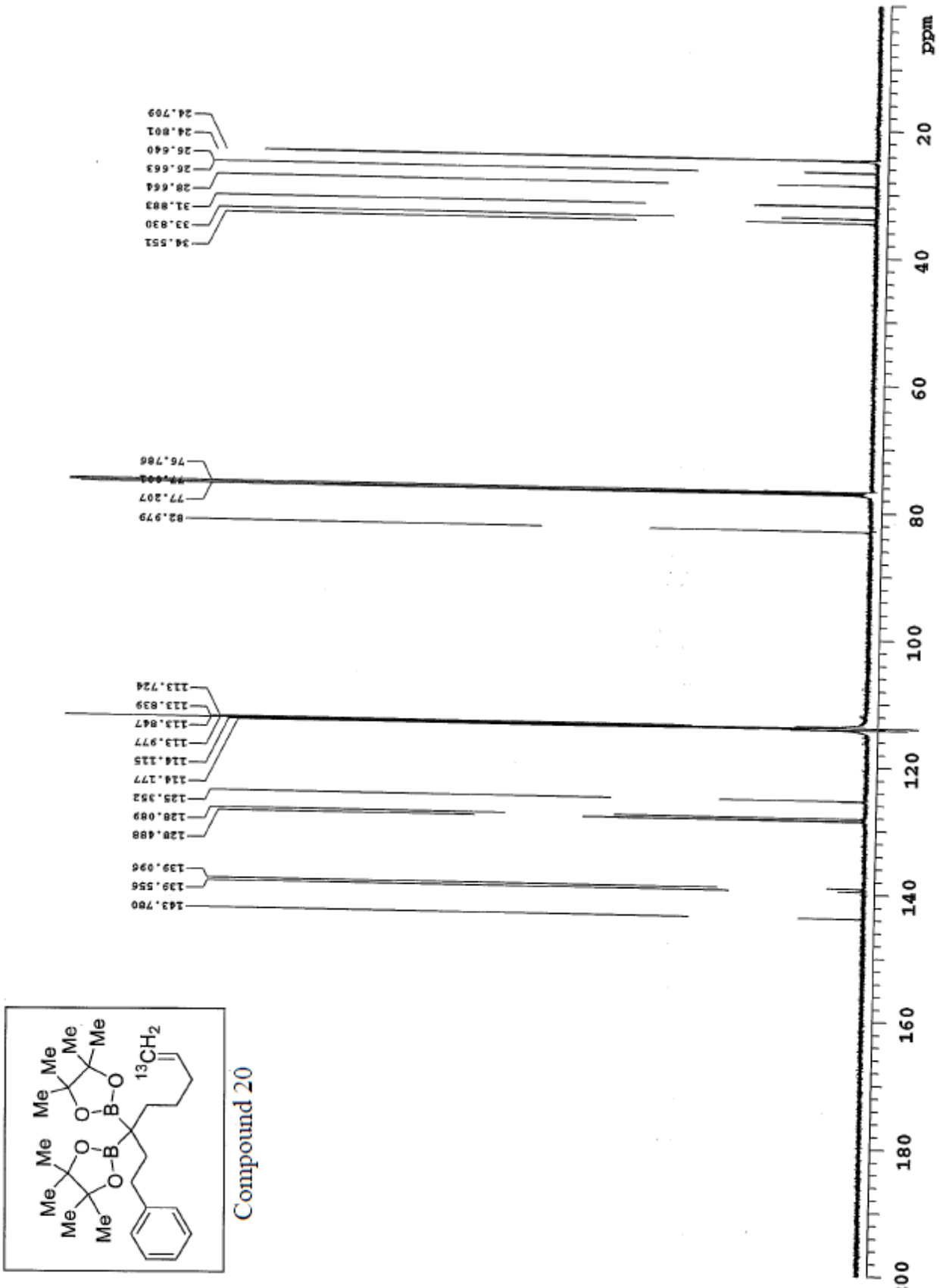
11
10
9
8
7
6
5
4
3
2
1
ppm
0.95
1.00
1.00
1.99
2.01
2.01
2.00
23.81

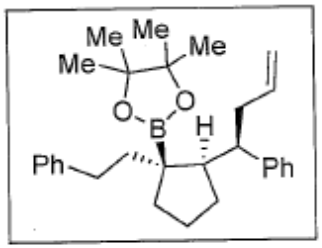

Compound 74
Me
Me
Me
Me
Me
Me
O
O
B
O
O
B
O
O
19.858
24.718
24.810
28.980
31.885
33.032
44.609
76.788
76.995
77.209
83.119
125.446
128.137
128.482
143.528
203.071
ppm
20
40
60
80
100
120
140
160
180
200
220


Me
Me
Me
Me
Me
Me
O
O
O
B
B
O
$^{13}CH_2$

Compound 20

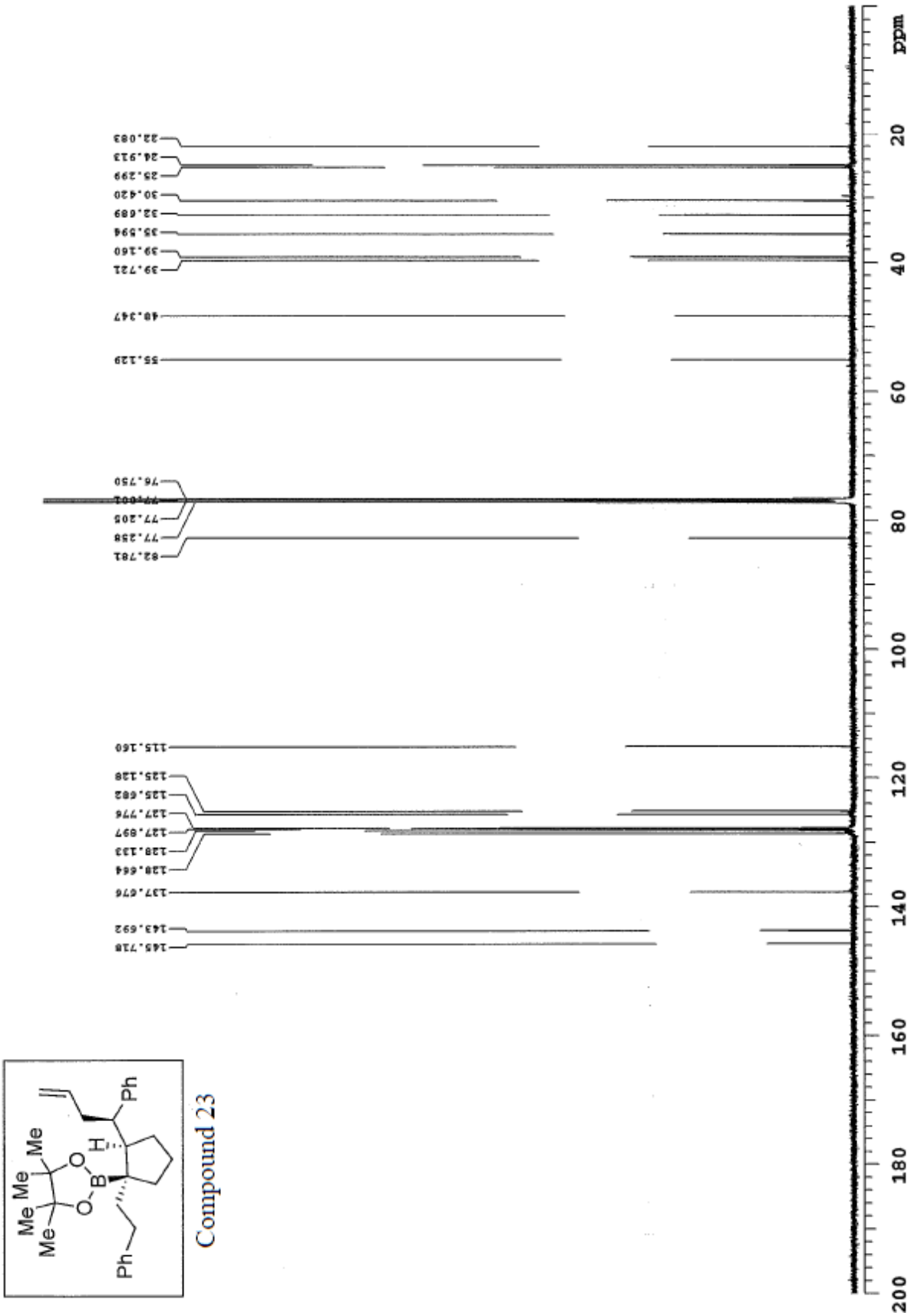
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.51
0.51
0.52
0.51
1.99
2.00
1.99
1.98
2.21
23.89

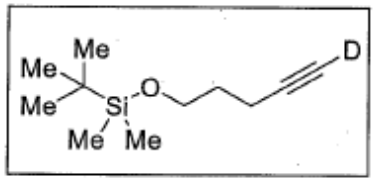

Me
Me
Me
Me
Me
Me
Me
O
B
O
O
B
O
$^{13}CH_2$
Compound 20
143.780
139.556
139.096
128.488
128.089
125.352
114.177
114.115
113.977
113.847
113.839
113.734
82.979
77.307
76.786
34.551
33.830
31.883
28.664
26.663
26.640
24.801
24.709
200
180
160
140
120
100
80
60
40
20
ppm


Me
Me
Me
Me
O
O
B
H
Ph
Ph

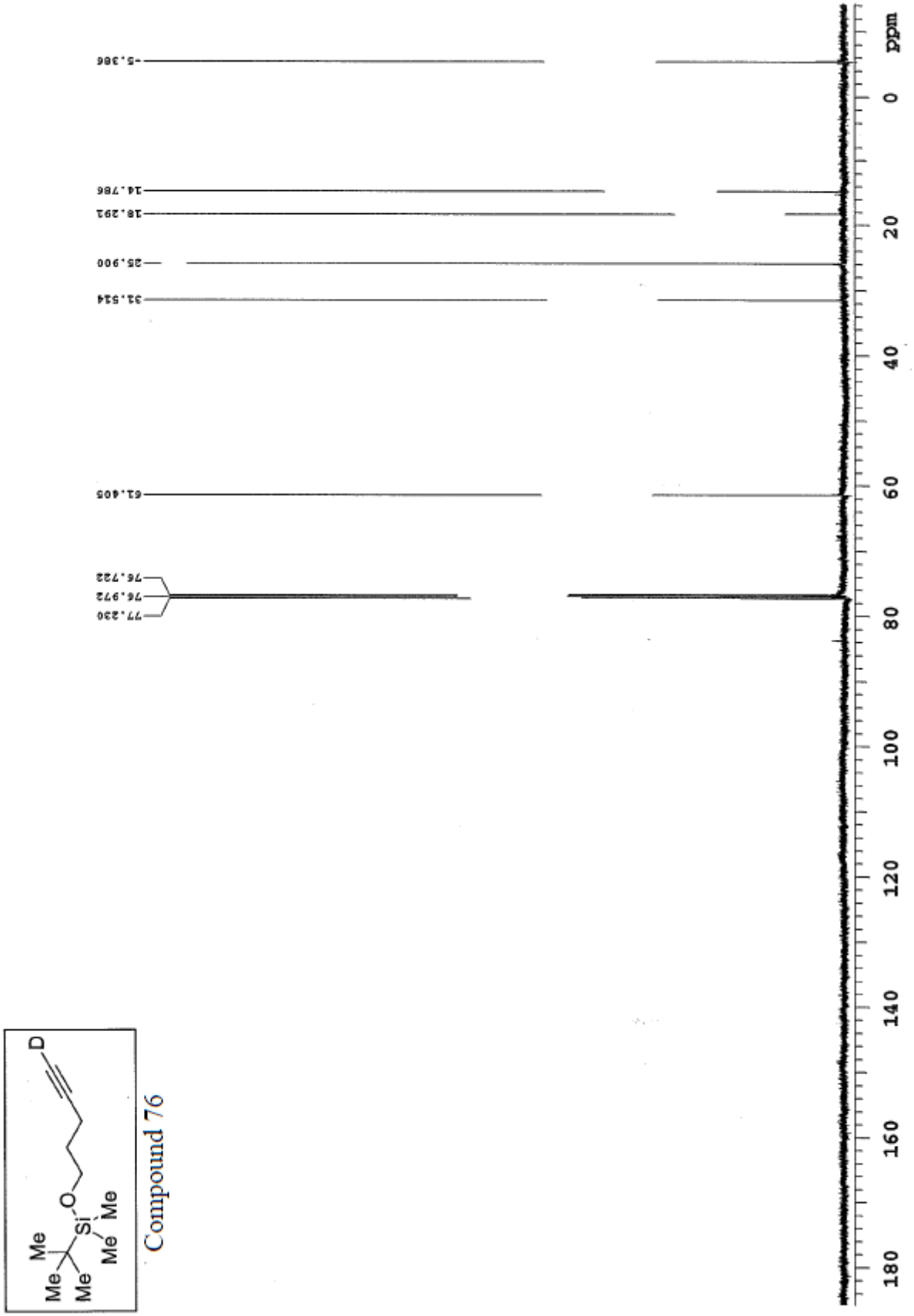
Compound 23

10
9
8
7
6
5
4
3
2
1
ppm
1.86
0.93
1.00
0.98
1.00
1.98
1.94
1.09
1.20
1.91
2.08
11.88
1.08

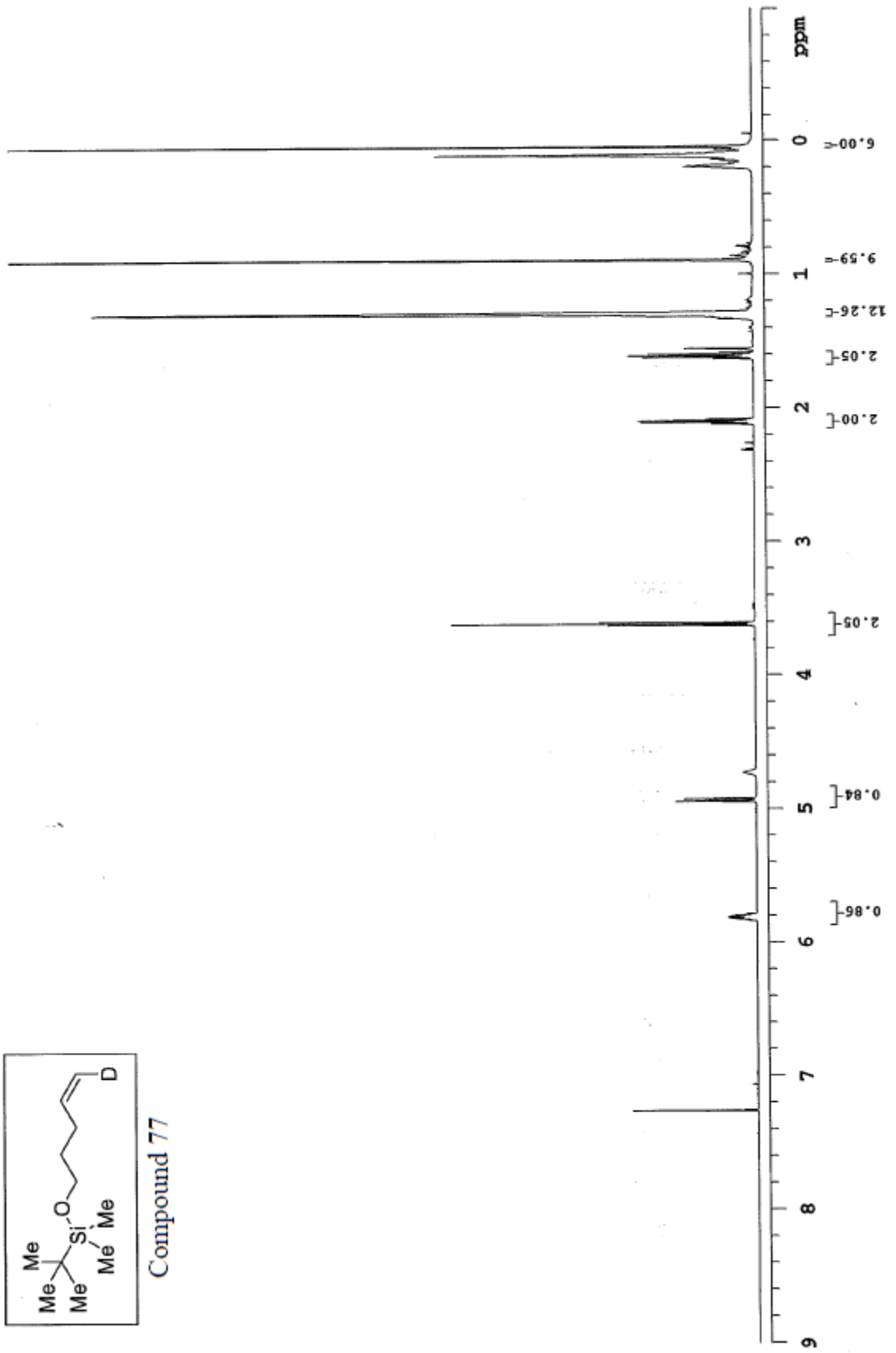

Me
Me
Me
O
B
O
H
Ph
Ph
Compound 23
ppm
20
40
60
80
100
120
140
160
180
200
22.083
24.913
25.299
30.420
32.689
35.594
39.160
39.721
48.347
55.129
76.750
77.001
77.205
77.258
82.781
115.160
125.138
125.682
127.776
127.897
128.133
128.664
137.676
143.692
145.718



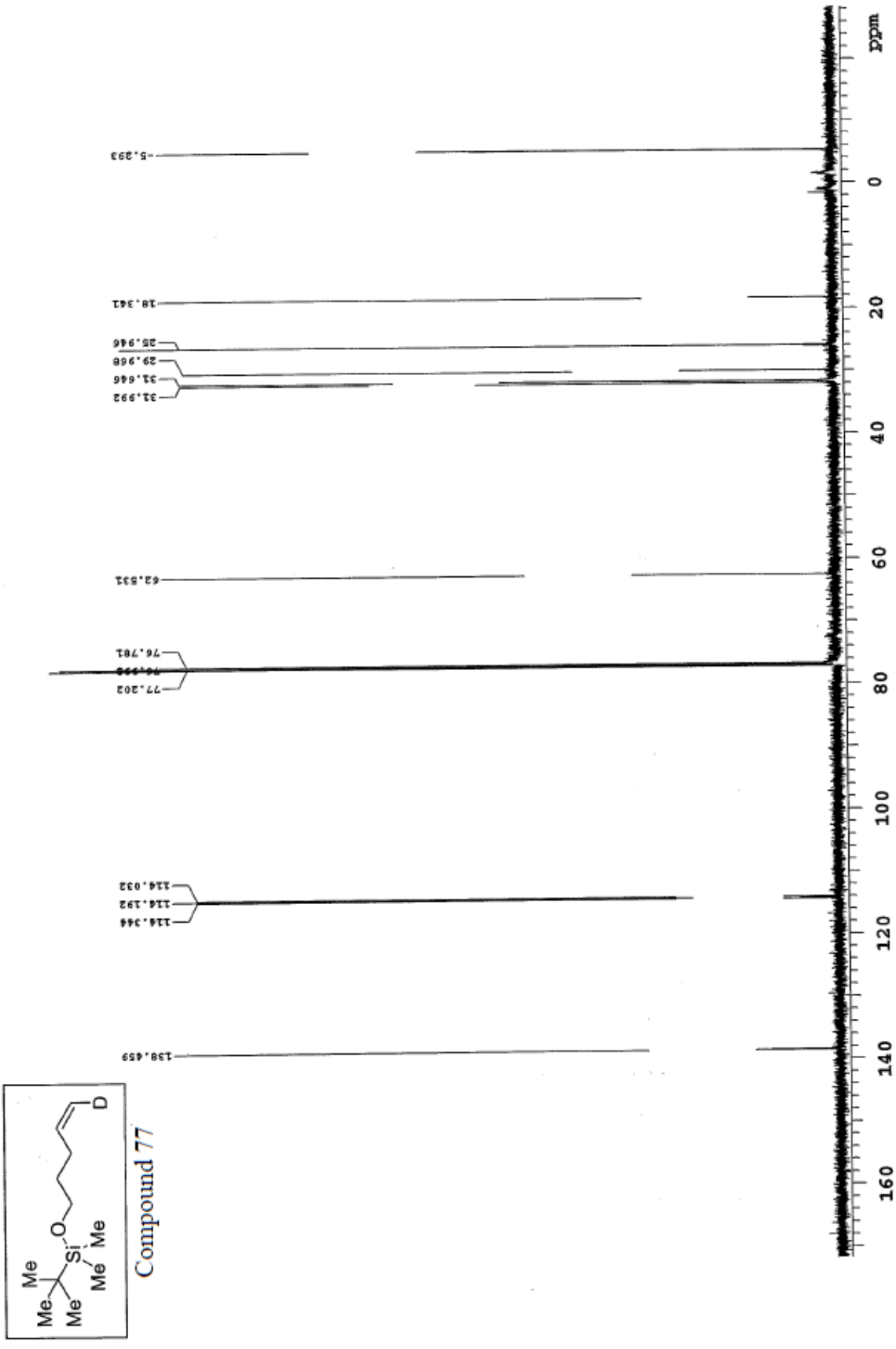
Compound 76

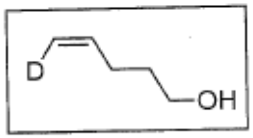

-5.386
14.786
18.291
25.900
31.514
61.405
76.722
76.972
77.230
ppm
0
20
40
60
80
100
120
140
160
180
Me
Me
Me
Si
O
Me
Me
D

Compound 76

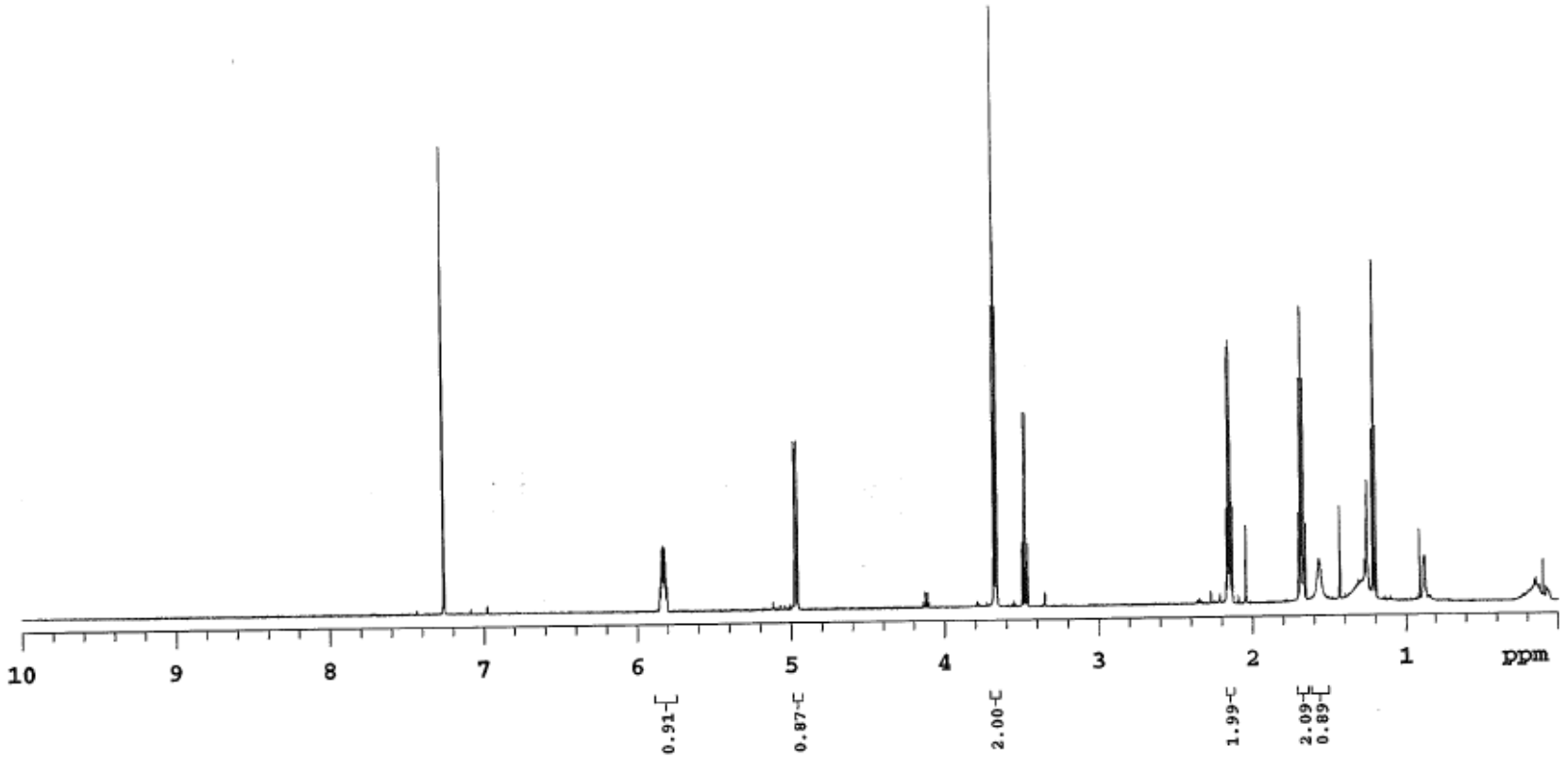

Me
Me
Me
Si
O
Me
Me
D
ppm
0
1
2
3
4
5
6
7
8
9
6.00
9.59
12.26
2.05
2.00
2.05
0.84
0.86

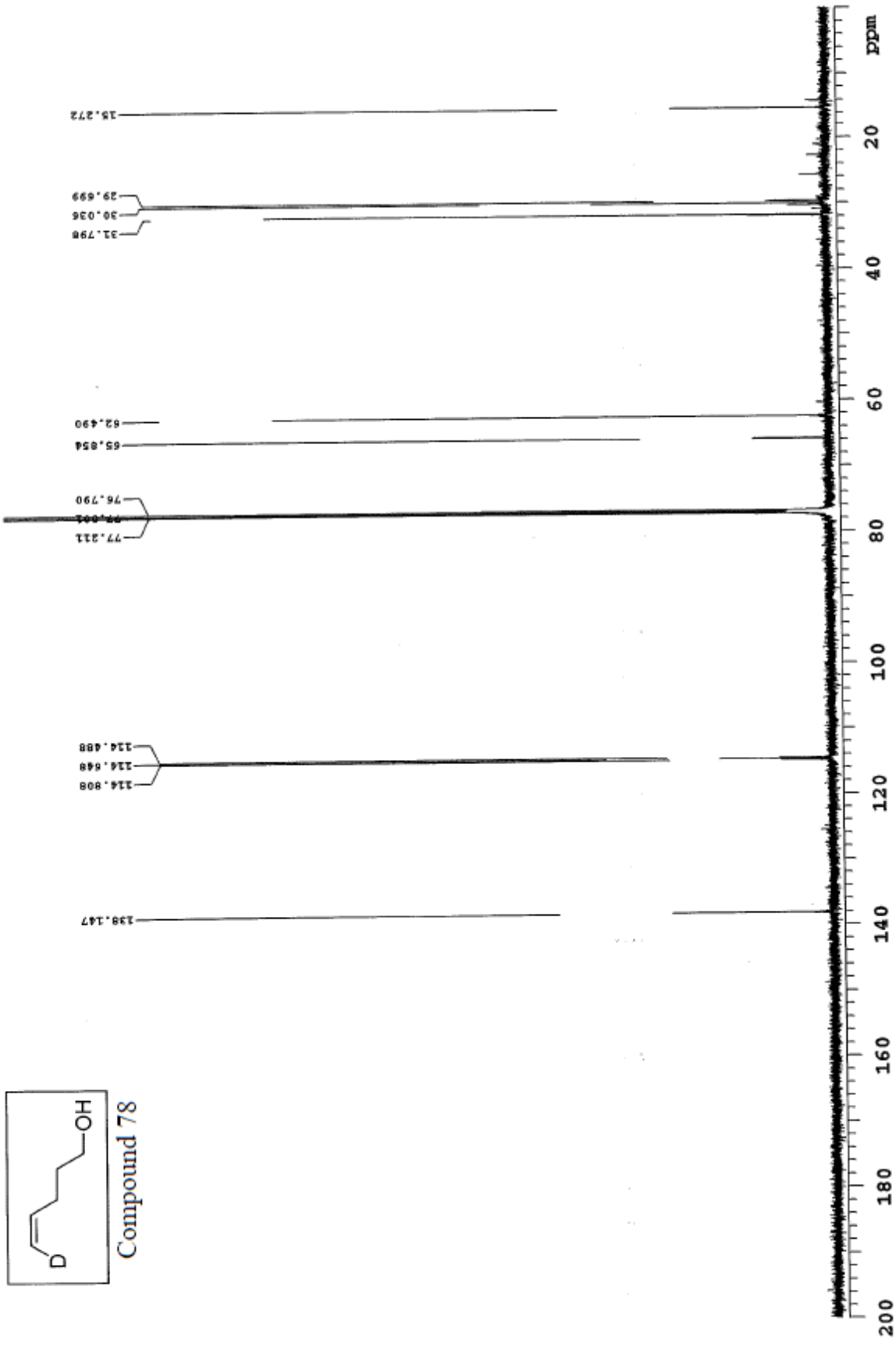
Compound 77

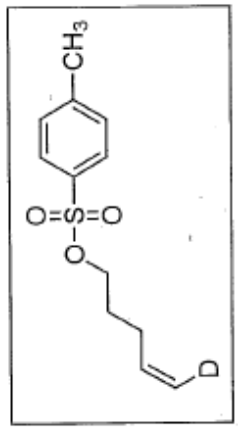

Me
Me
Me
Si
O
Me
Me
D
Compound 77
138.659
114.032
114.193
114.344
77.203
76.998
76.781
63.532
32.992
31.646
29.968
25.946
18.341
-5.393
ppm
160
140
120
100
80
60
40
20
0



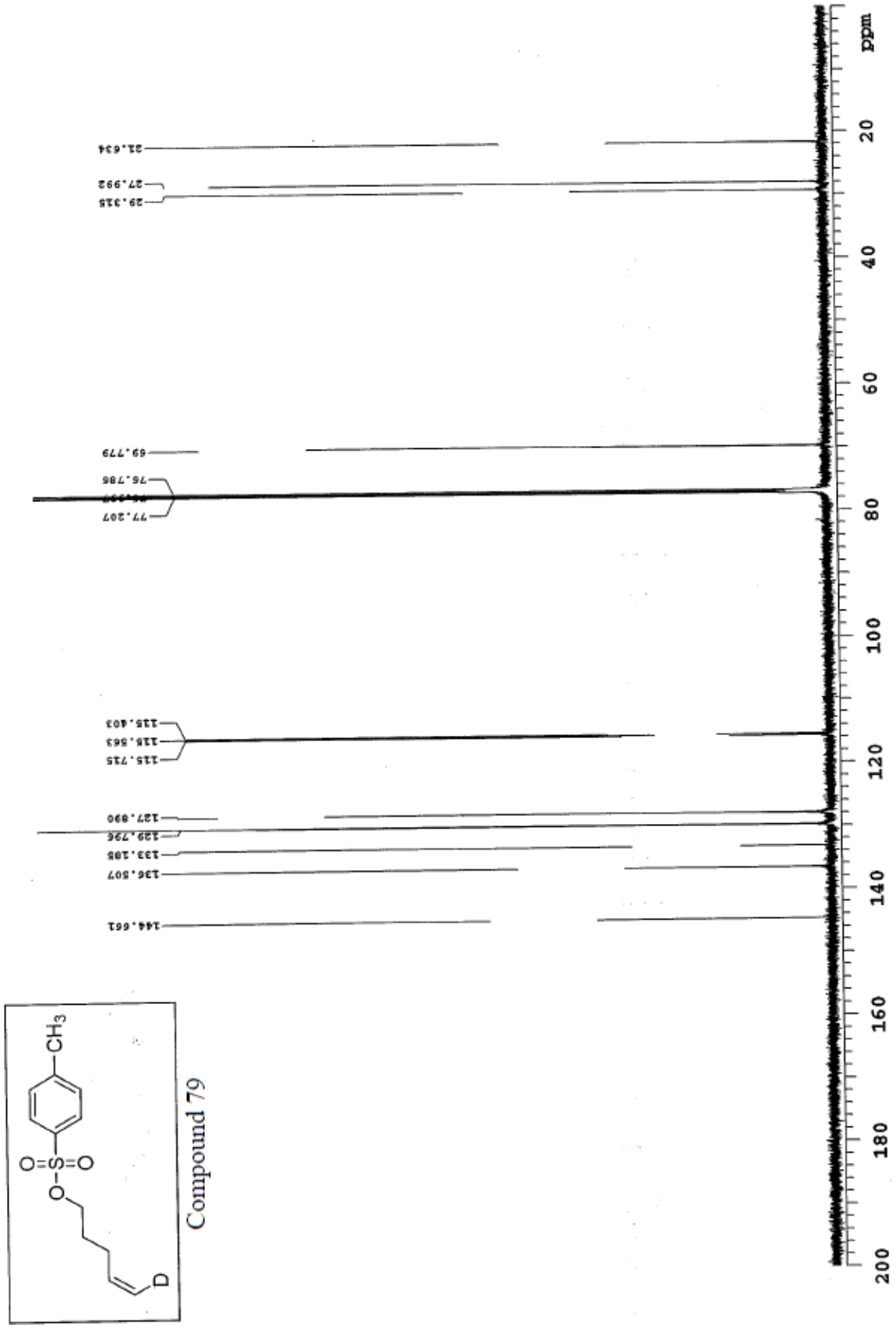
Compound 78



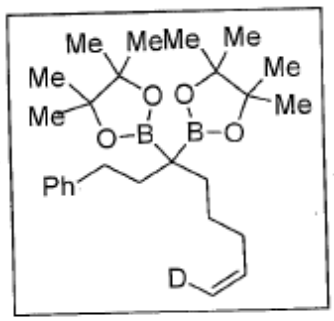

OH
D
Compound 78
138.147
114.808
114.648
114.488
77.311
76.790
65.854
62.490
31.798
30.036
29.699
15.272
ppm
200
180
160
140
120
100
80
60
40
20



Compound 79

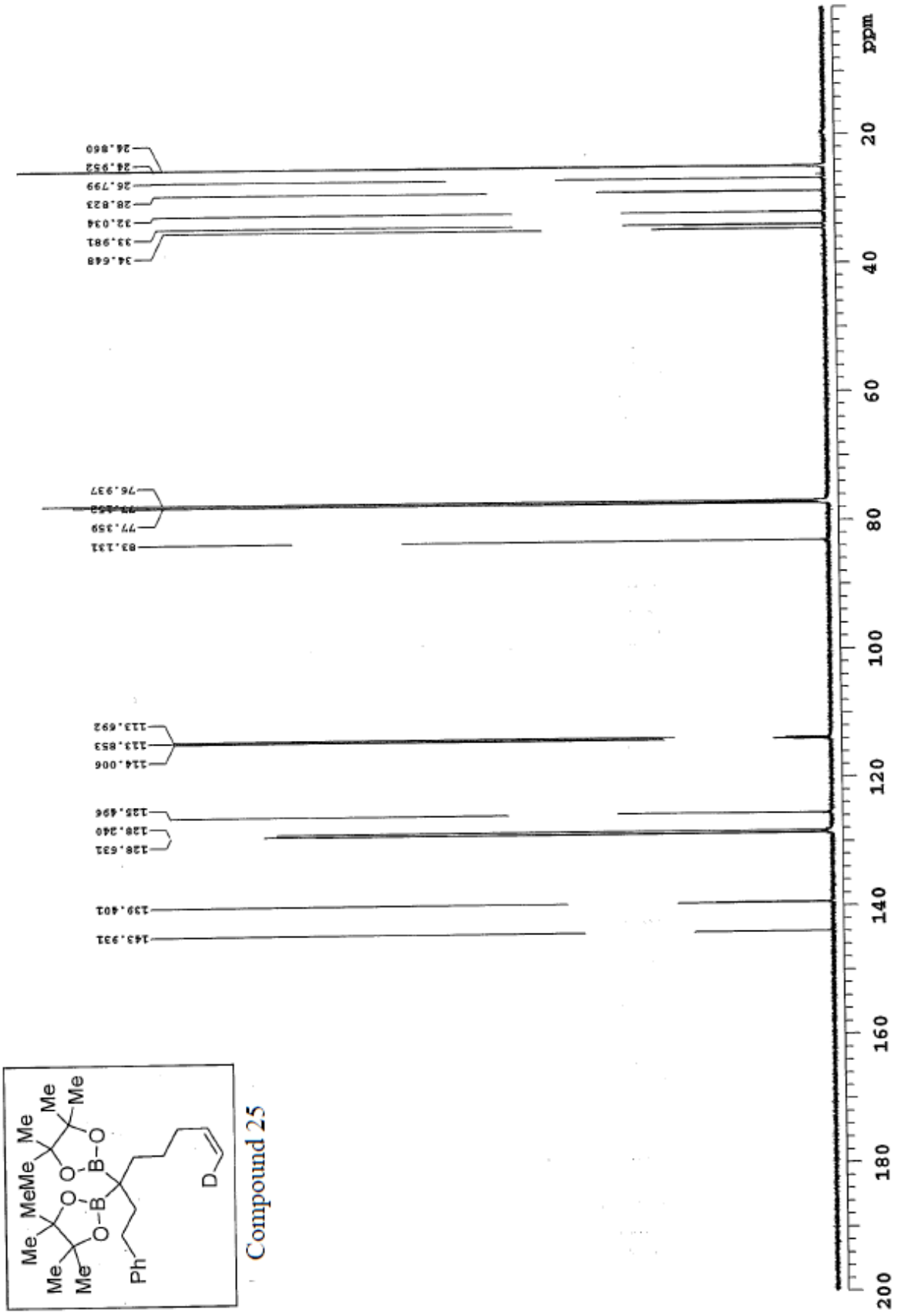

ppm
20
40
60
80
100
120
140
160
180
200
31.634
27.992
29.335
69.779
76.786
77.307
115.403
115.563
115.715
127.890
129.796
133.185
136.507
144.661
O=S=O
O
CH3
D

Compound 79

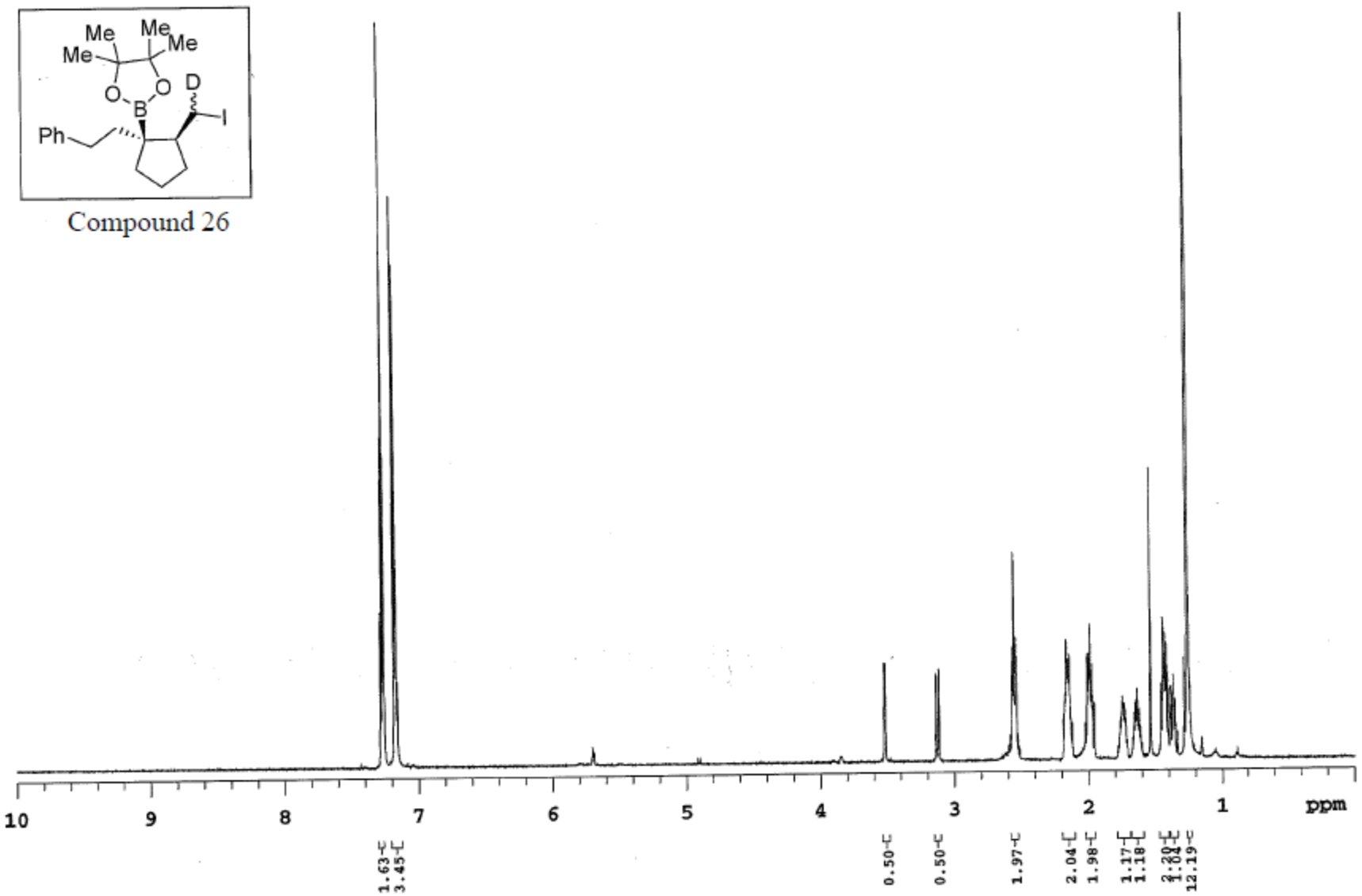

Me
MeMe
Me
Me
Me
Me
Me
O
O
O-B
B-O
Ph
D

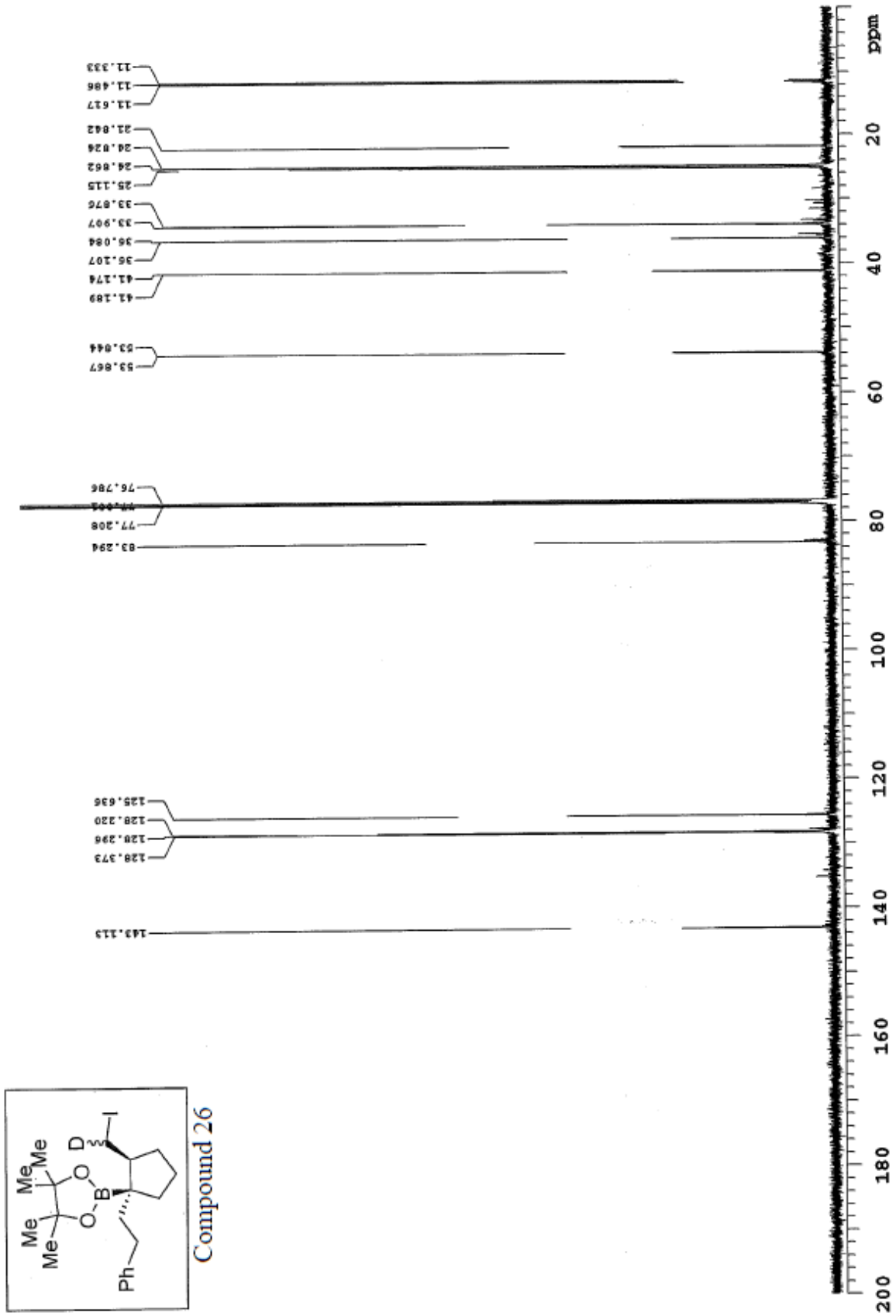
Compound 25

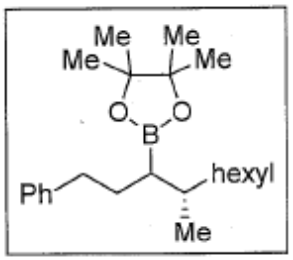
10
9
8
7
6
5
4
3
2
1
ppm
0.97
0.93
2.00
1.96
2.00
2.06
2.12
23.72


24.860
24.952
26.799
28.823
32.034
33.981
34.648
76.937
77.359
83.131
113.692
113.853
114.006
128.631
128.240
135.496
139.401
143.931
ppm
20
40
60
80
100
120
140
160
180
200
Me
Me
Me
Me
Me
Me
O
B
O
O
B
O
Ph
D

Compound 25

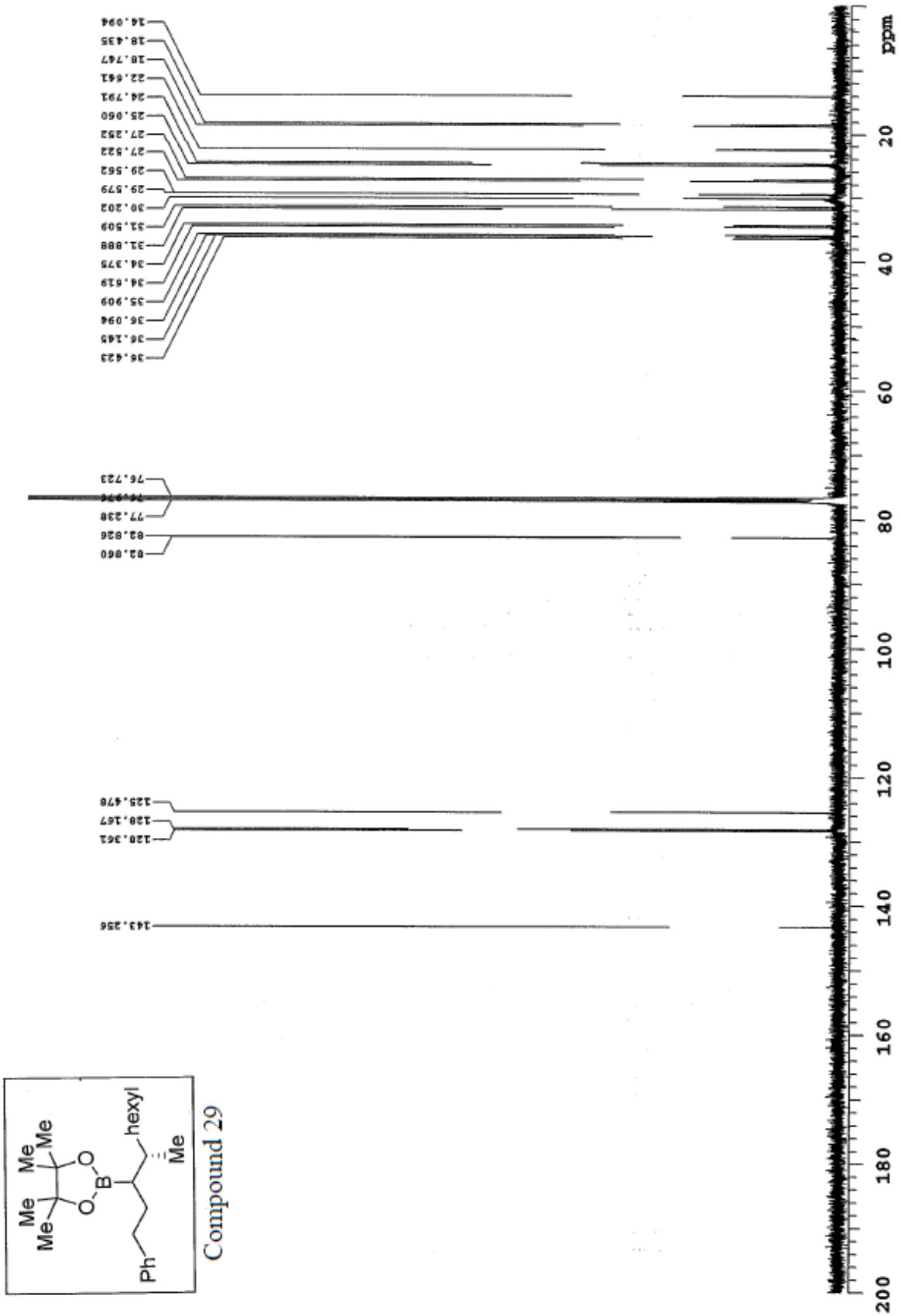

Me
Me
Me
Me
O
O
B
D
I
Ph
Compound 26
10
9
8
7
6
5
4
3
2
1
ppm
1.63
3.45
0.50
0.50
1.97
2.04
1.98
1.17
1.18
12.19

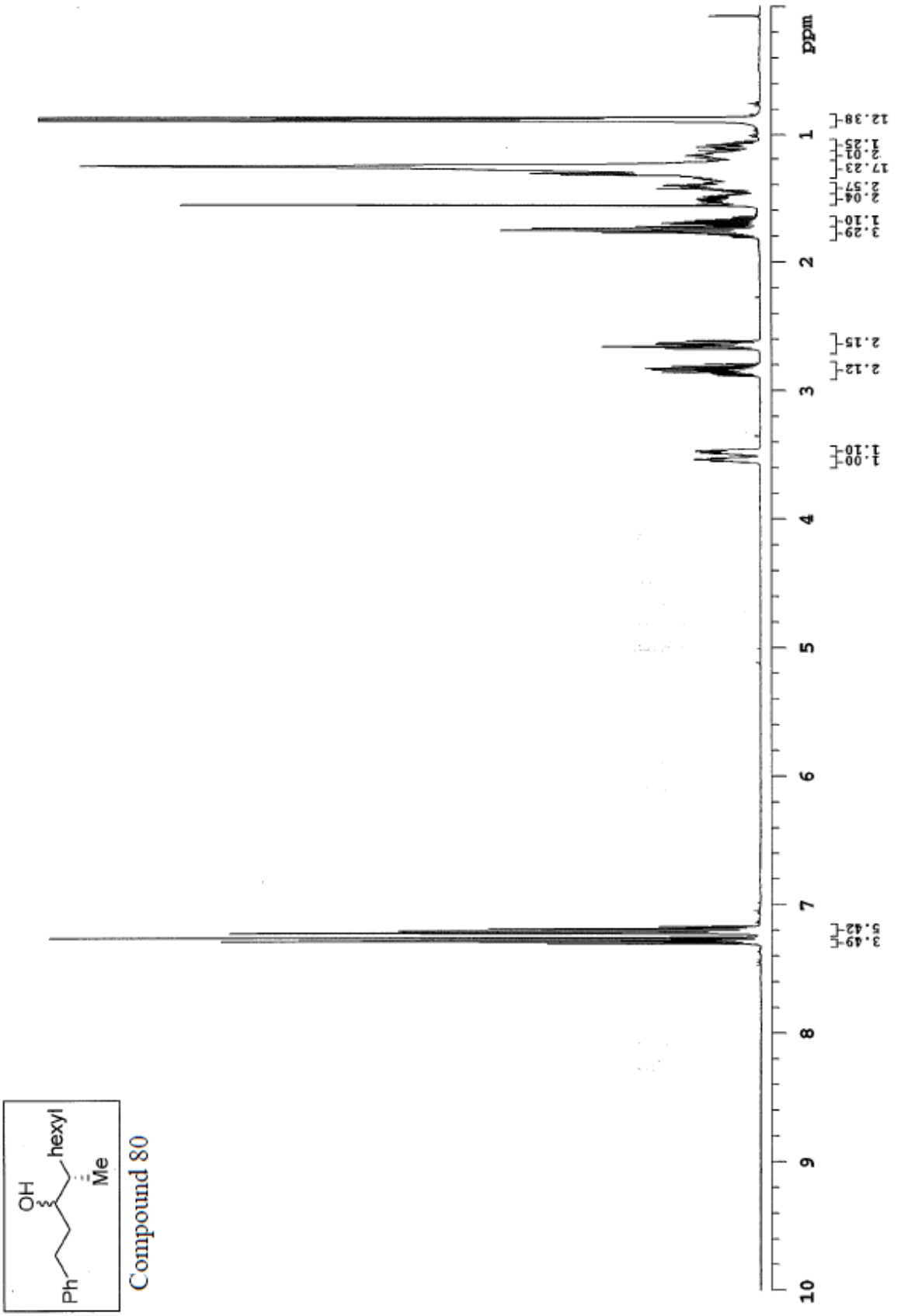

Me
Me
Me
Me
O
O
B
D
I
Ph
Compound 26
11.333
11.486
11.617
21.842
24.826
24.862
25.115
33.876
33.907
36.084
36.107
41.174
41.189
53.044
53.067
76.786
77.308
83.294
125.636
128.220
128.396
128.373
143.113
ppm
200
180
160
140
120
100
80
60
40
20


Me
Me
Me
Me
O
O
B
Ph
hexyl
Me

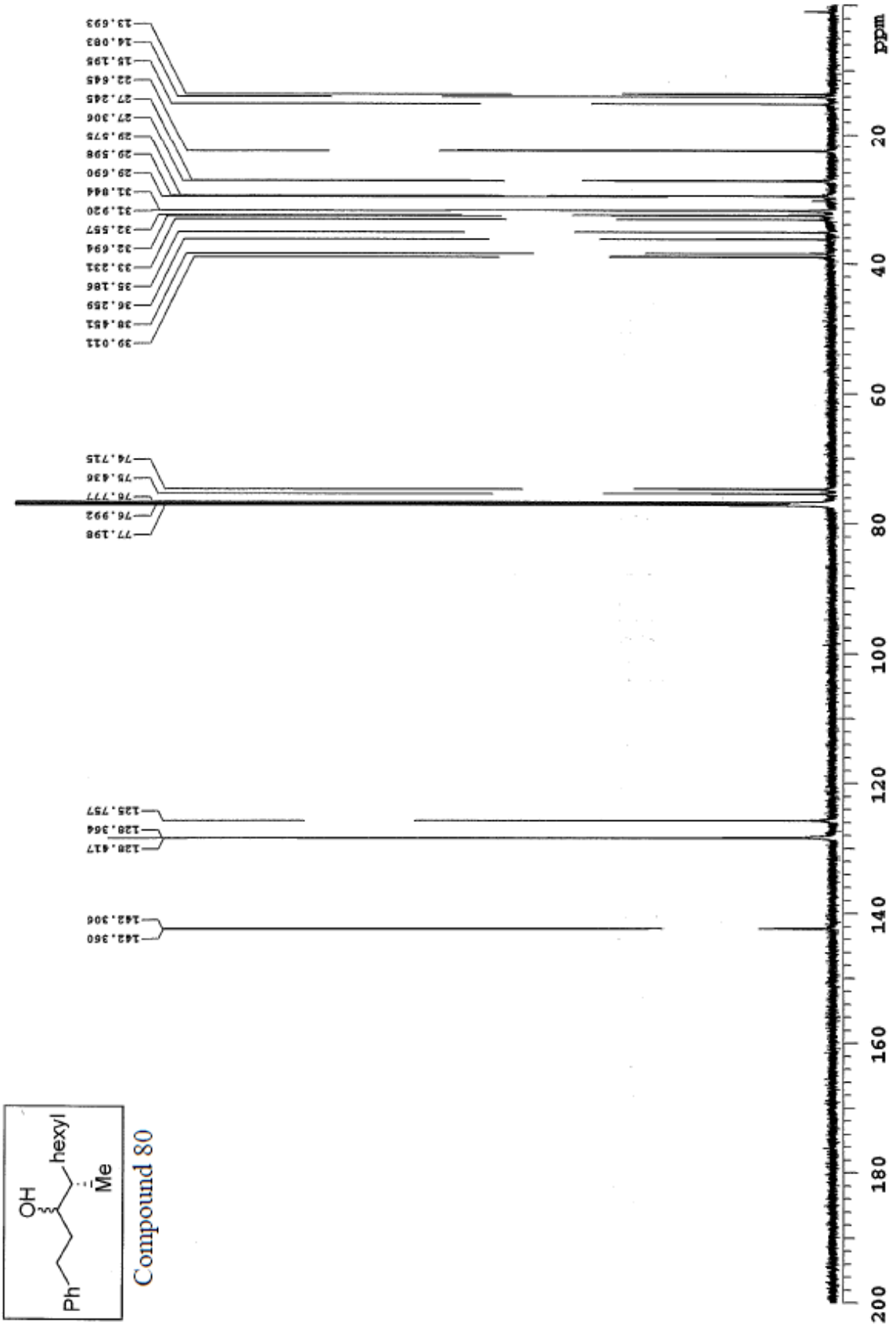
Compound 29

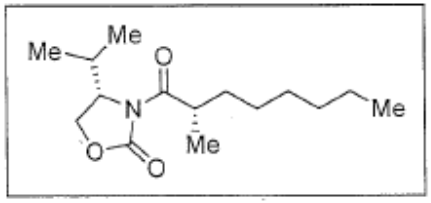
10
9
8
7
6
5
4
3
2
1
ppm
3.72
2.51
1.02
1.00
1.14
2.14
1.01
19.85
1.04
1.13
5.72


Me
Me
Me
Me
O
O
B
hexyl
Me
Ph
Compound 29
14.094
18.435
18.747
22.661
24.791
25.060
27.252
27.522
29.562
29.579
30.202
31.509
31.888
34.375
34.619
35.909
36.094
36.145
36.423
76.723
77.238
82.826
82.860
120.361
128.167
135.478
143.256
ppm
200
180
160
140
120
100
80
60
40
20


OH
hexyl
Me
Ph
ppm
12.38
1.25
2.01
17.23
2.57
2.04
3.29
1.10
2.15
2.12
1.00
1.10
3.49
5.42

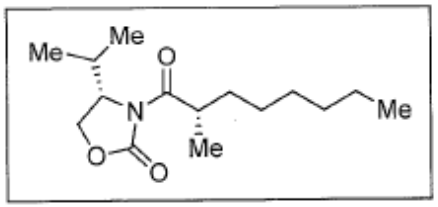
Compound 80


OH
hexyl
Me
Ph
Compound 80
13.693
14.083
15.195
22.645
27.245
27.306
29.575
29.598
29.690
31.844
31.920
32.557
32.694
33.331
35.186
36.259
38.451
39.011
74.715
75.436
76.777
76.992
77.198
125.757
128.364
128.417
142.306
142.360
ppm
20
40
60
80
100
120
140
160
180
200


Me
Me
O
N
Me
Me
O
O

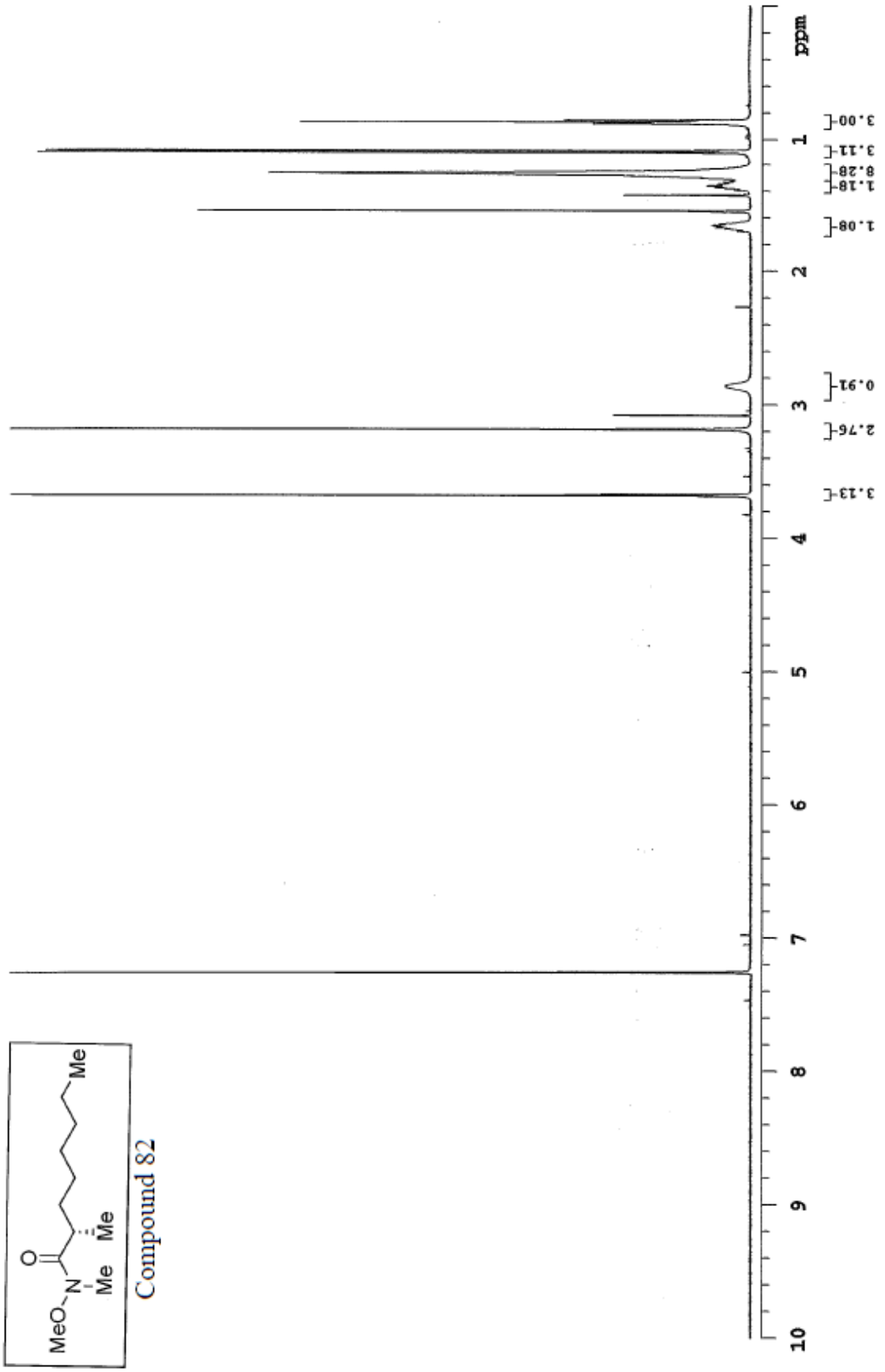
Compound 81

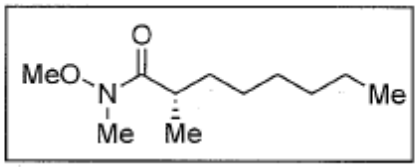
10
9
8
7
6
5
4
3
2
1
ppm
0.98
1.04
1.02
0.93
1.00
1.09
3.00
1.19
8.17
2.89
3.15


Me
Me
O
N
Me
Me
O
O

Compound 81

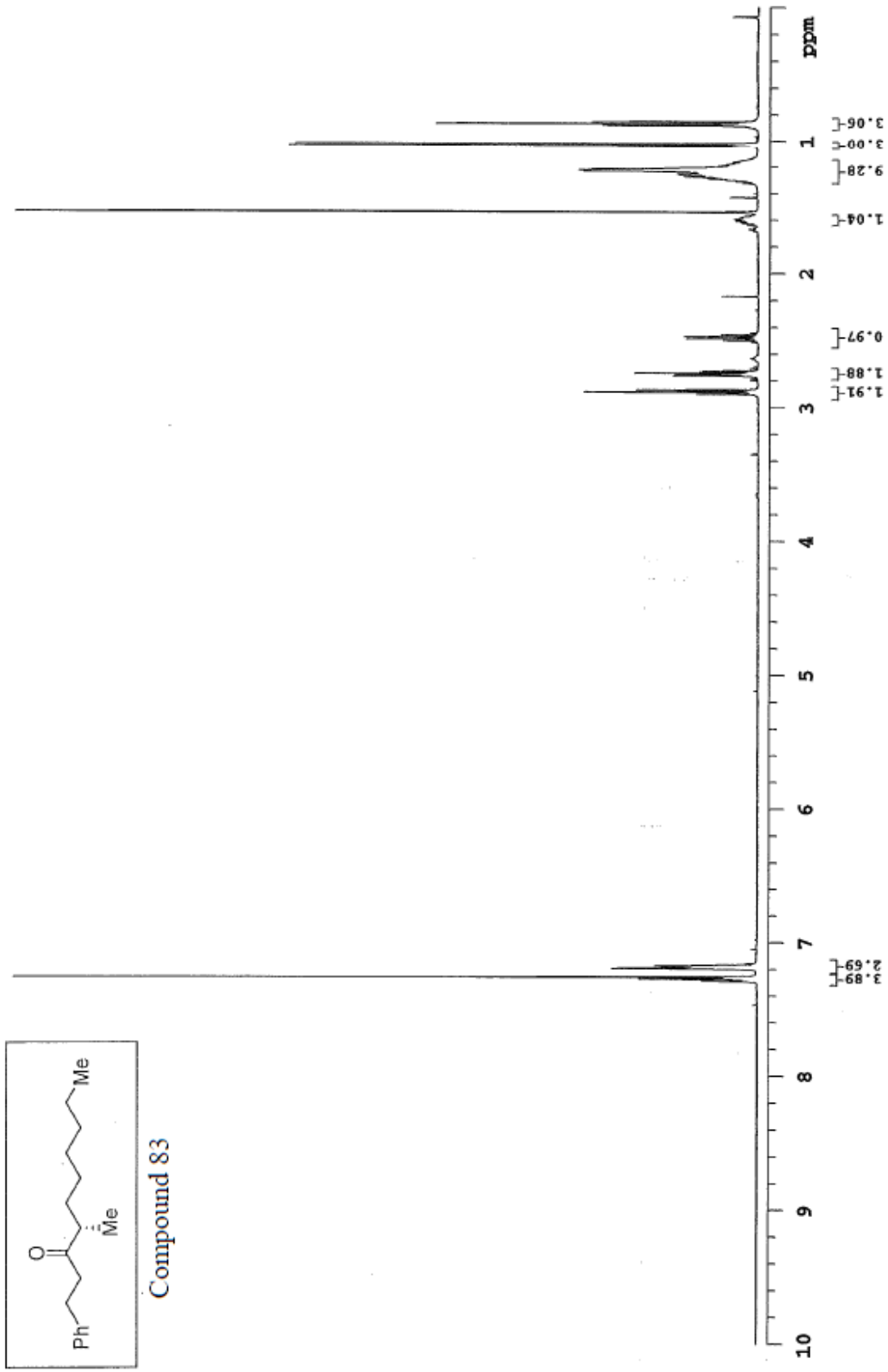
77.192
76.771
63.162
58.423
37.707
33.112
31.687
29.300
28.424
27.235
22.572
17.935
17.842
14.680
14.040
200
180
160
140
120
100
80
60
40
20
ppm


MeO
N
Me
Me
O
Me
Me
Compound 82
ppm
10
9
8
7
6
5
4
3
2
1
3.13
2.76
0.91
1.08
1.18
8.28
3.11
3.00

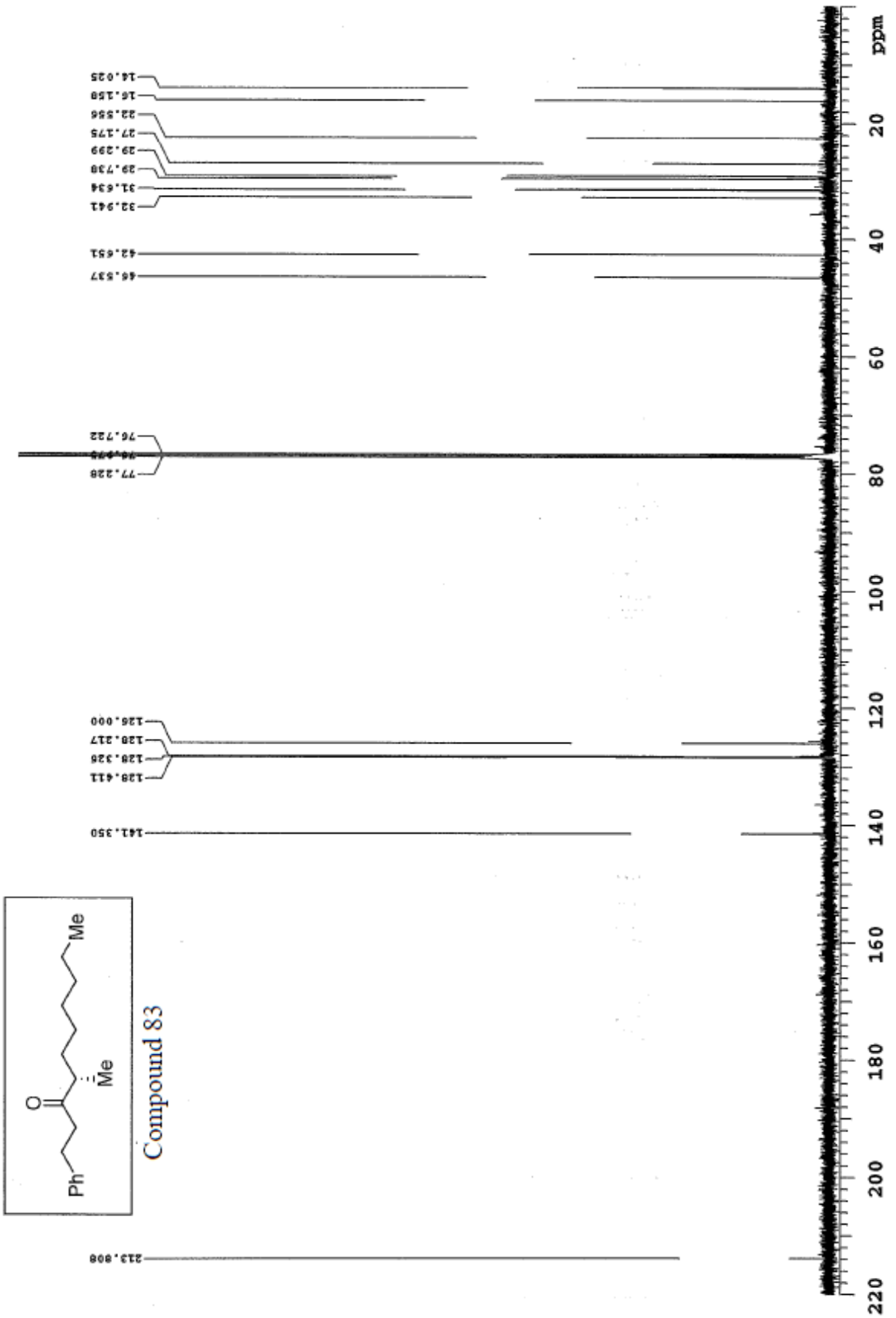

MeO
N
O
Me
Me
Me

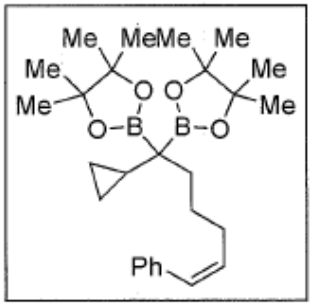
Compound 82

77.228
77.177
76.975
76.722
61.398
35.090
33.826
31.727
29.679
29.308
27.504
22.606
17.448
14.042
200
180
160
140
120
100
80
60
40
20
ppm



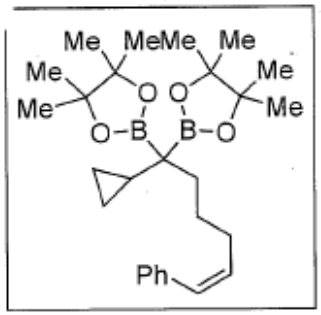
Compound 83


Me
Me
O
Ph
Compound 83
213.808
141.350
138.611
138.328
138.317
136.000
77.228
76.722
46.537
42.651
33.941
31.634
29.738
29.399
27.175
22.556
16.158
14.025
ppm
220
200
180
160
140
120
100
80
60
40
20


Me
Me
Me
Me
Me
Me
O
O
O-B
B-O
Ph

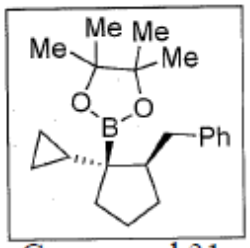
Compound 30

9
8
7
6
5
4
3
2
1
0
ppm
3.72
0.94
0.97
0.96
2.00
24.94
1.03
4.23


Me
MeMe
Me
Me
Me
Me
O
O
O-B
B-O
Me
Ph

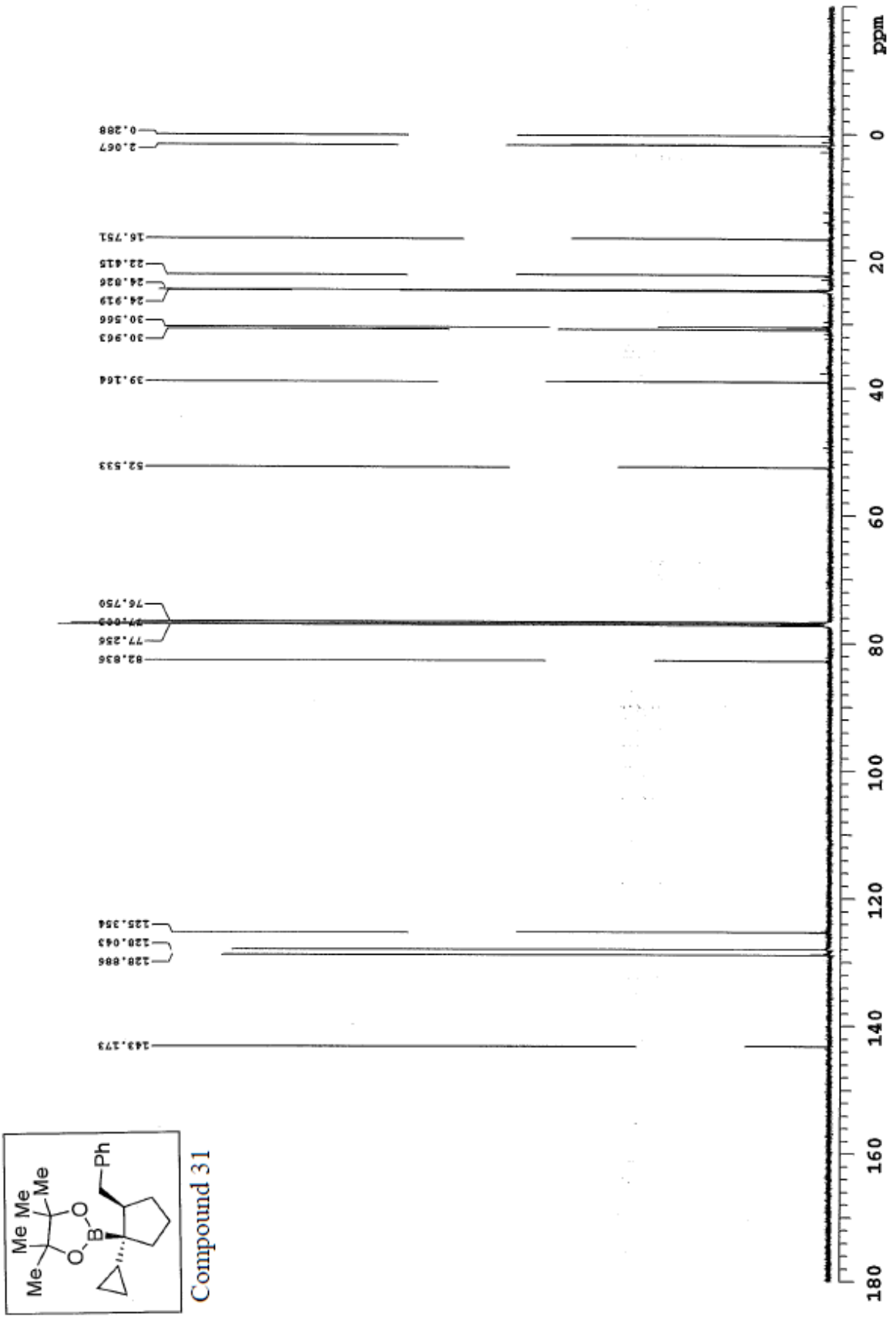
Compound 30

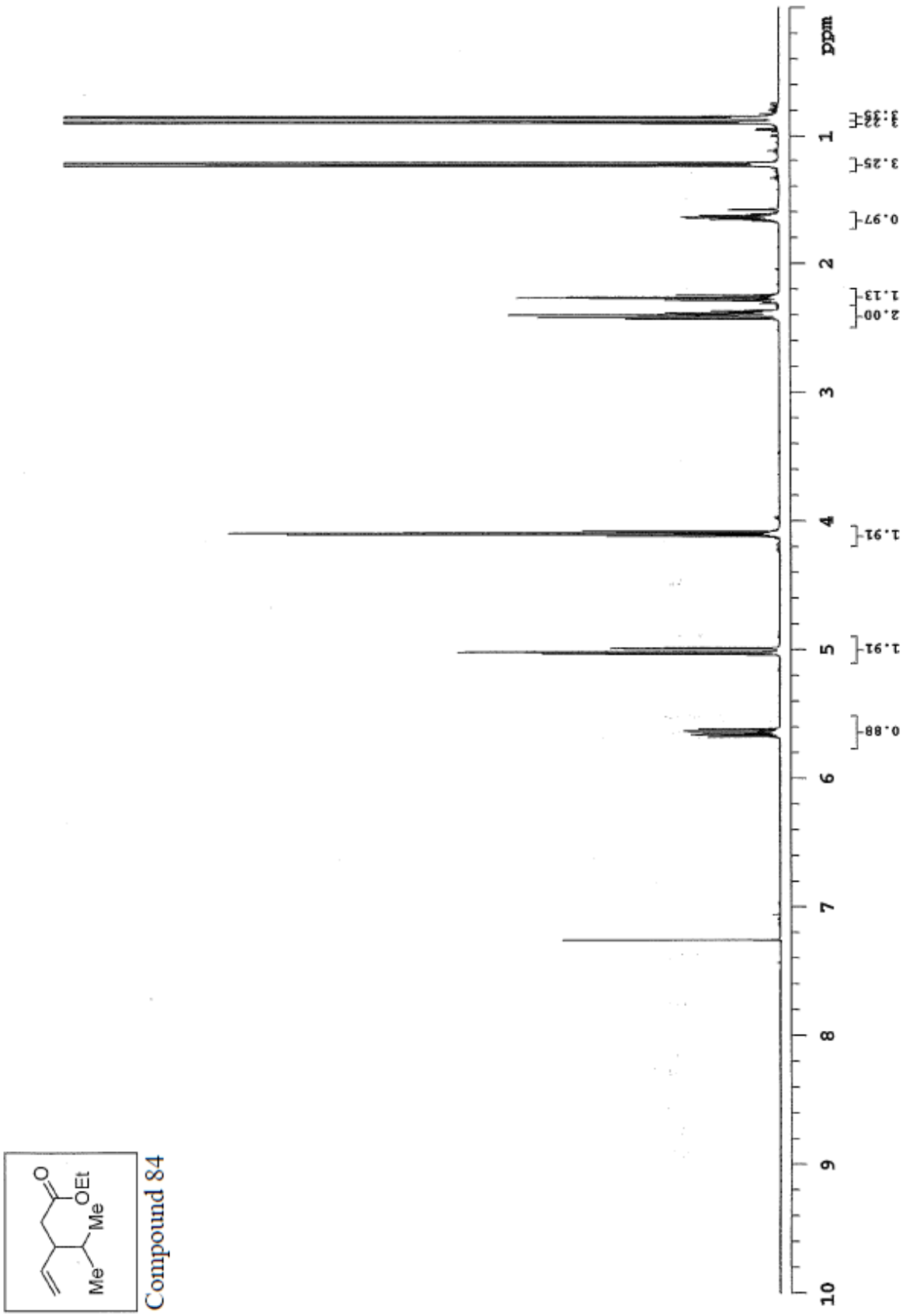
137.918
133.700
128.761
128.275
128.017
126.257
82.757
77.249
76.992
76.741
33.036
29.797
28.636
24.721
24.706
12.932
3.616
180
160
140
120
100
80
60
40
20
0
ppm

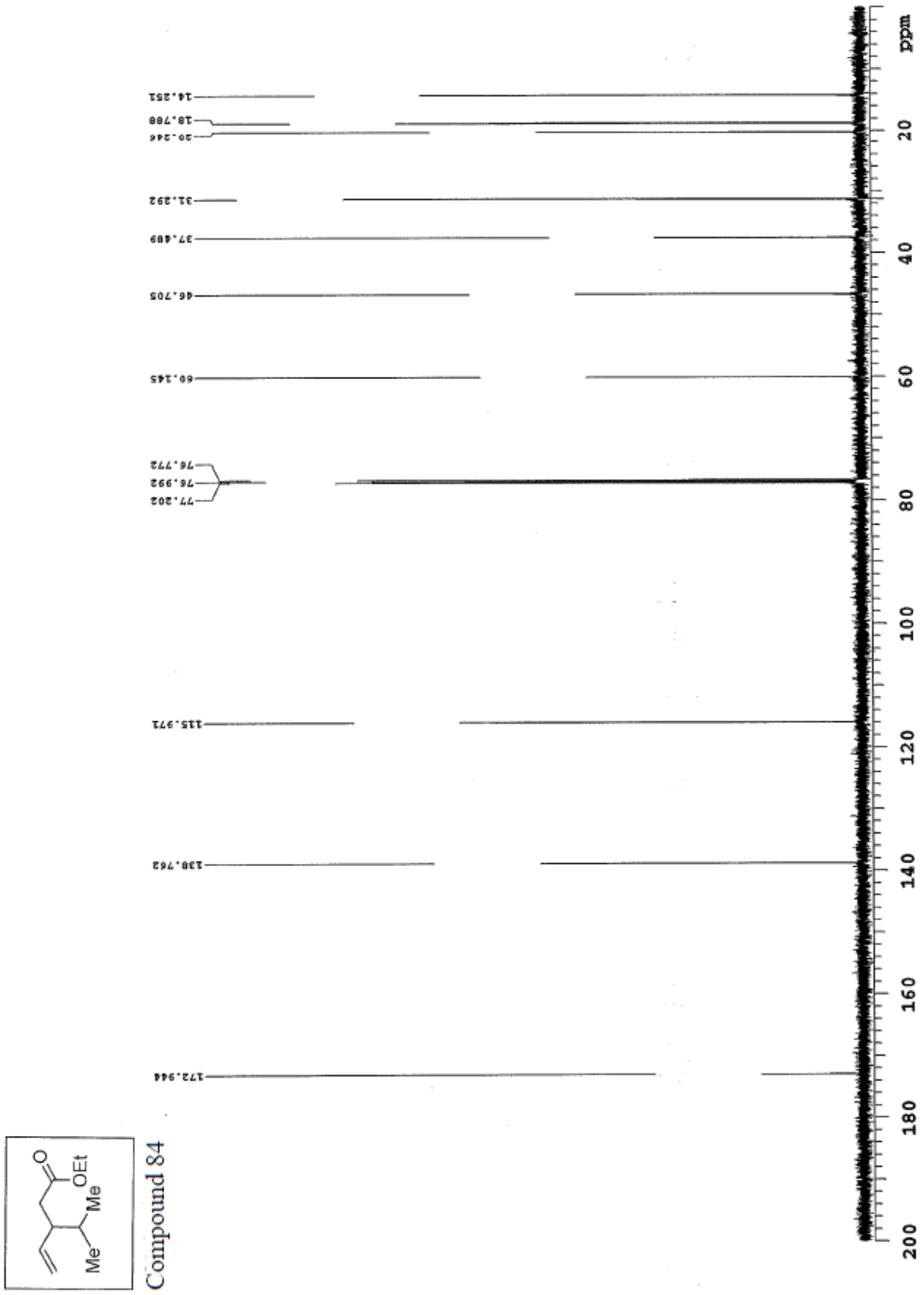

Me
Me
Me
Me
O
O
B
Ph

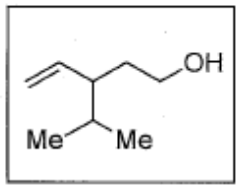
Compound 31

9
8
7
6
5
4
3
2
1
0
ppm
3.46
2.78
0.04
0.99
0.04
1.00
1.03
1.14
2.09
1.18
12.23
1.05
1.41
1.18
0.97


Me Me
Me
O
O
B
Ph
Compound 31
143.173
128.886
128.043
125.354
83.836
77.256
77.003
76.750
52.533
39.164
30.963
30.566
24.939
24.836
23.615
16.751
2.067
0.288
ppm
180
160
140
120
100
80
60
40
20
0

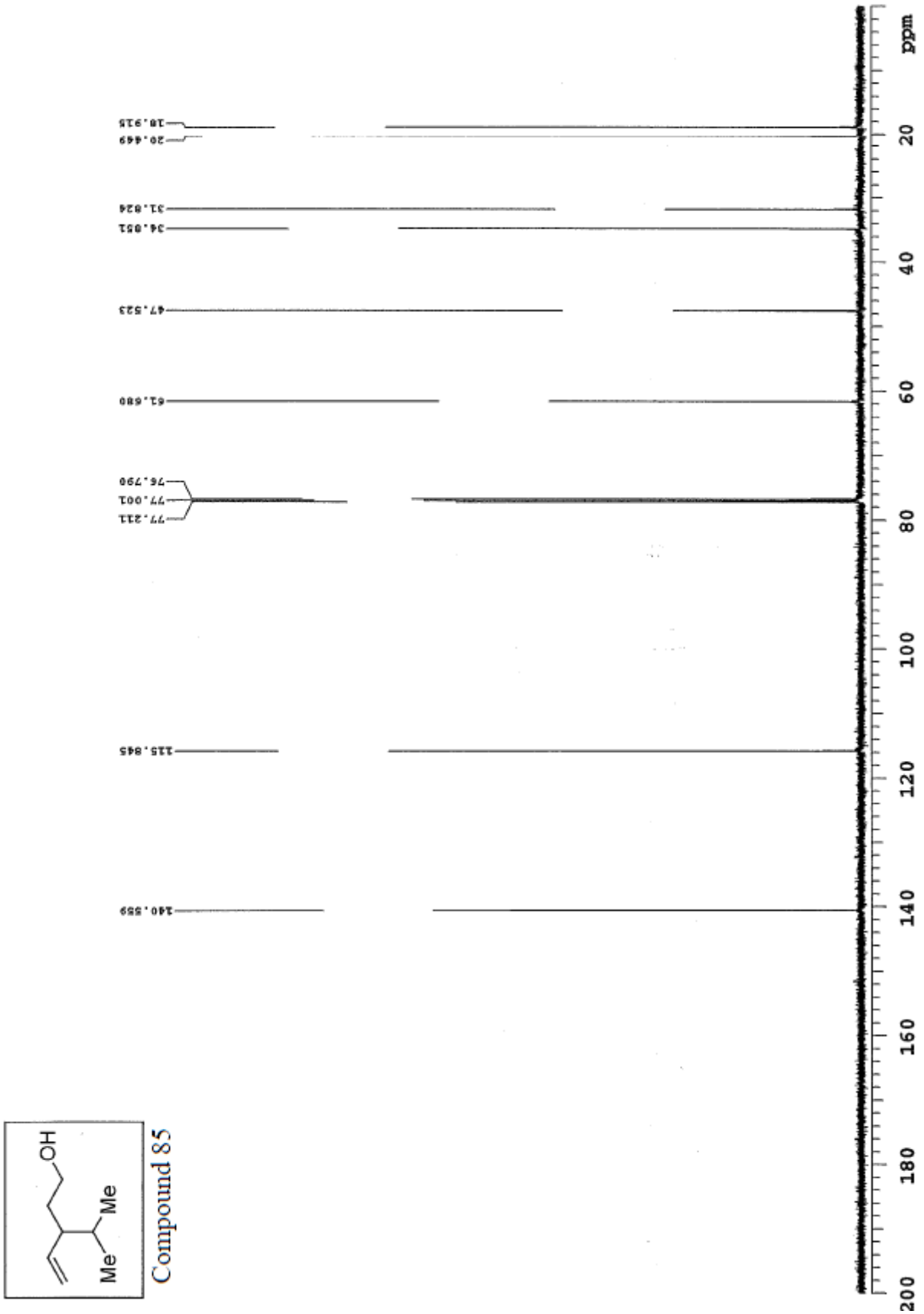

O
OEt
Me
Me
Compound 84
ppm
10
9
8
7
6
5
4
3
2
1
0.88
1.91
1.91
1.91
2.00
1.13
0.97
3.25
3.22
3.35

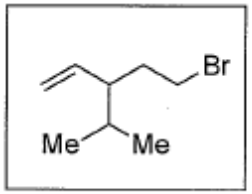

O
OEt
Me
Me
Compound 84
172.944
138.763
115.971
77.202
76.992
76.772
60.145
46.705
37.489
31.292
30.246
18.788
14.251
ppm
200
180
160
140
120
100
80
60
40
20


OH
Me
Me

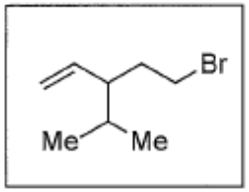
Compound 85

10
9
8
7
6
5
4
3
2
1
ppm
0.88
0.92
0.96
1.00
0.99
0.92
1.02
1.00
1.04
0.91
3.15

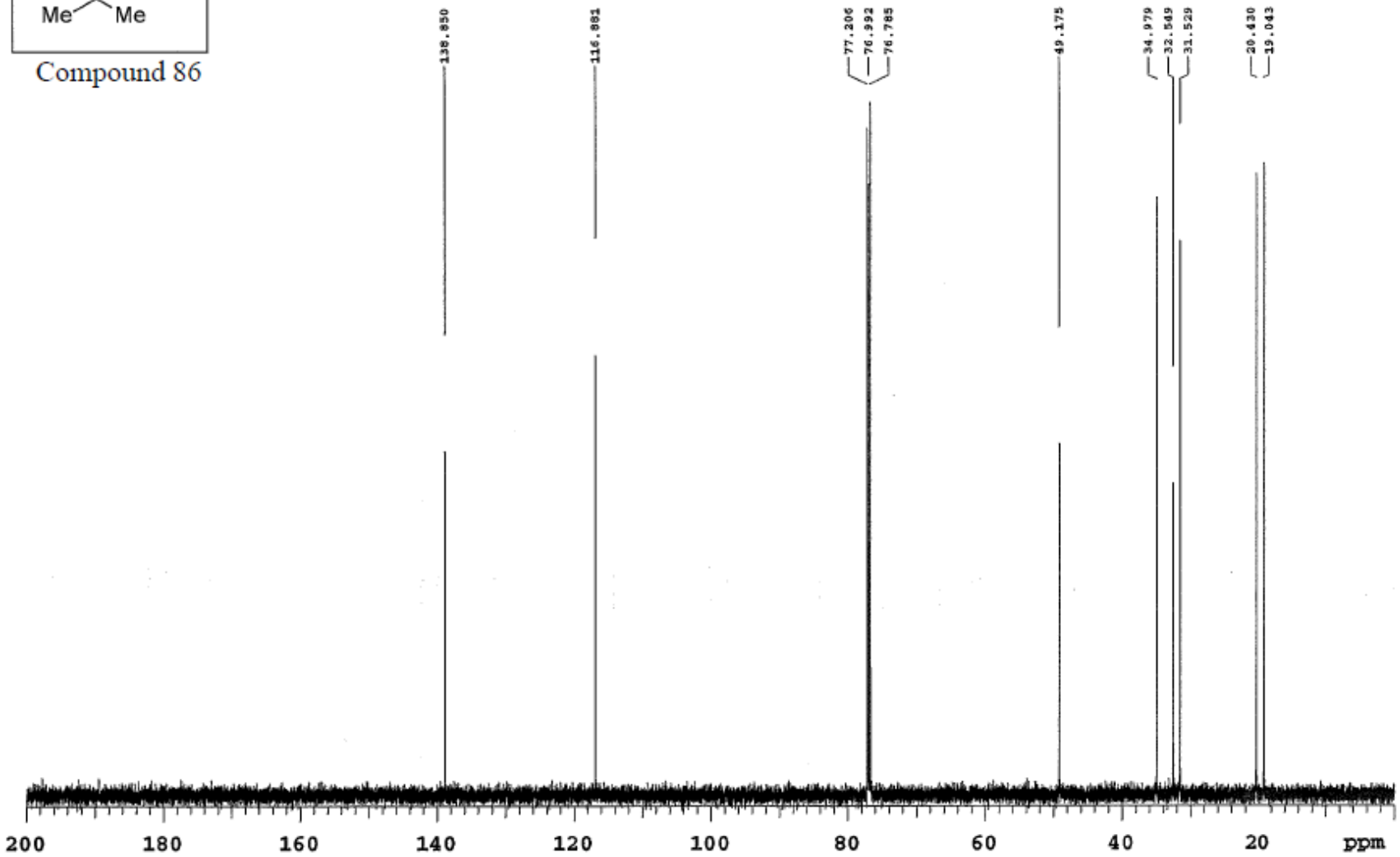

OH
Me
Me
Compound 85
18.915
20.469
31.824
34.051
47.523
61.680
76.790
77.001
77.211
115.845
140.559
ppm
20
40
60
80
100
120
140
160
180
200

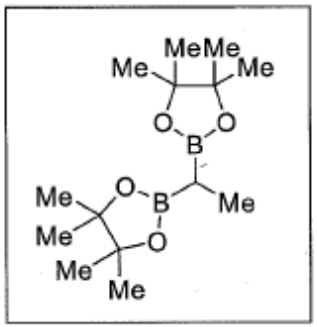


Compound 86


Br
Me
Me

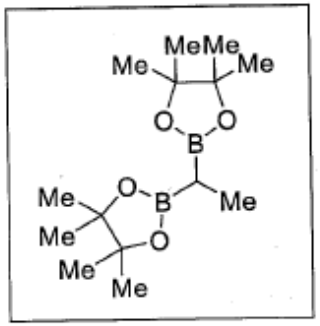
Compound 86


138.850
116.881
77.206
76.992
76.785
49.175
34.979
32.549
31.529
20.430
19.043
200
180
160
140
120
100
80
60
40
20
ppm


Me
MeMe
Me
O
O
B
Me
O
B
Me
Me
O
Me
Me
Me

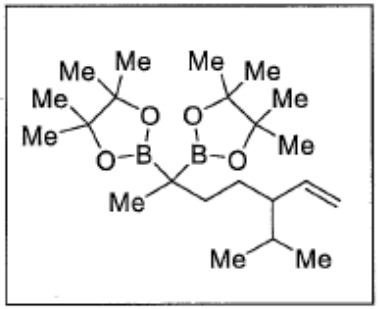
Compound 87

10
9
8
7
6
5
4
3
2
1
0
ppm
23.92
3.01
0.98


Me
Me
Me
O
B
O
Me
O
B
Me
Me
O
Me
Me

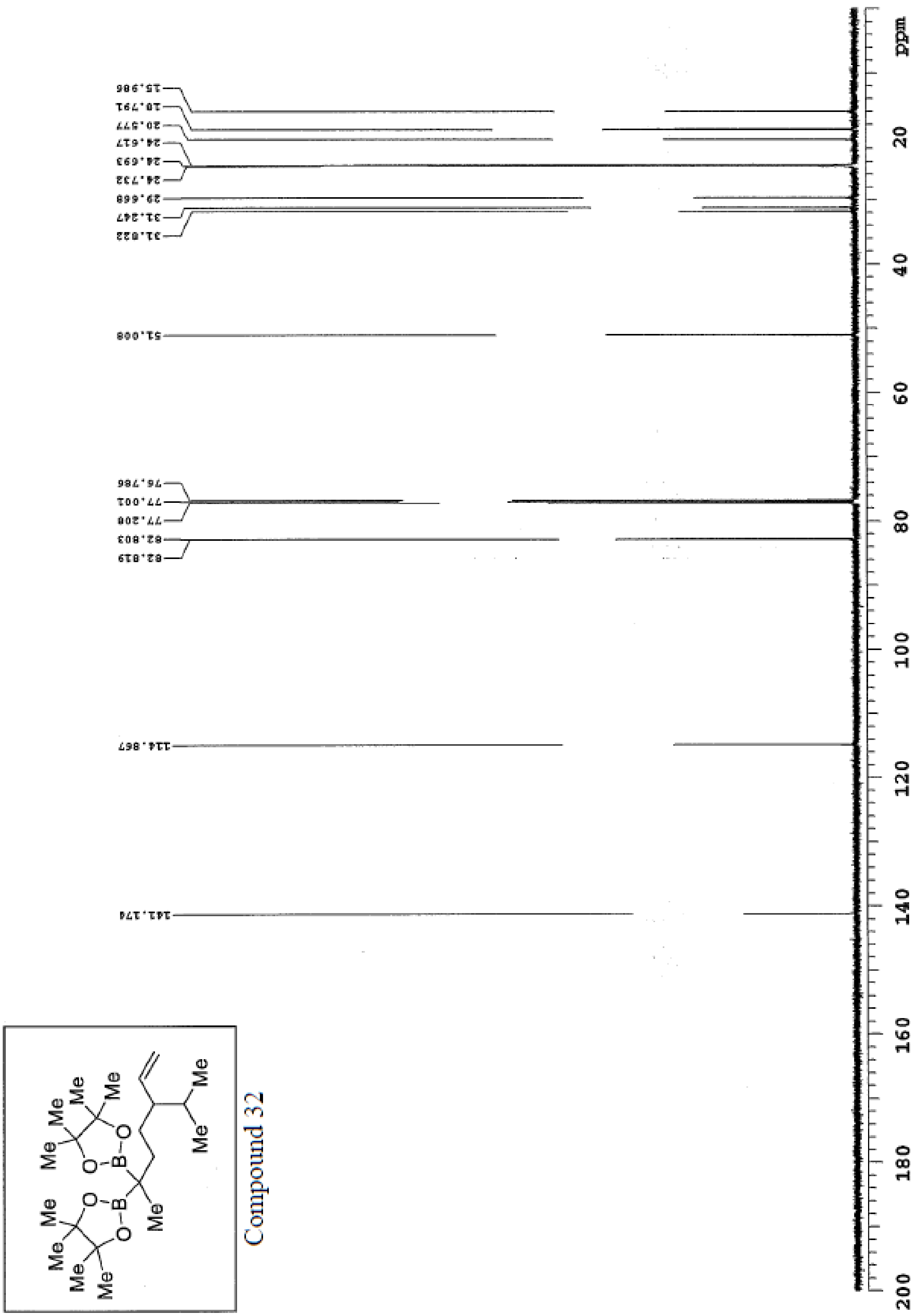
Compound 87

82.856
77.257
77.000
76.749
24.798
24.502
9.018
200
180
160
140
120
100
80
60
40
20
ppm

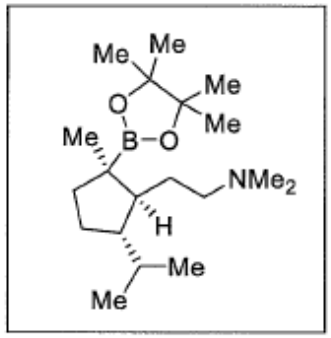

Me
Me
Me
Me
Me
Me
O
O
B
B
O
O
Me
Me
Me
Me
Me

Compound 32

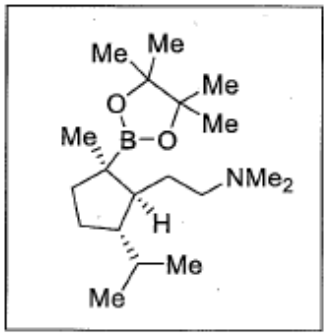
9
8
7
6
5
4
3
2
1
0
ppm
0.99
1.00
1.02
1.03
2.08
1.06
25.33
3.02
2.99
3.00


15.986
18.791
20.577
24.617
24.693
24.733
29.668
31.347
31.822
51.008
76.786
77.001
77.208
82.803
82.819
114.867
141.174
ppm
20
40
60
80
100
120
140
160
180
200

Compound 32

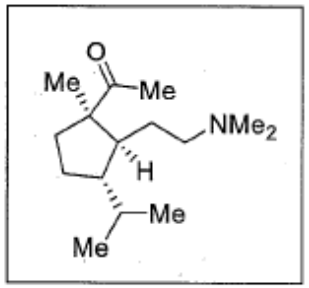


Compound 45


Me
Me
Me
Me
O
B
O
Me
NMe2
H
Me
Me

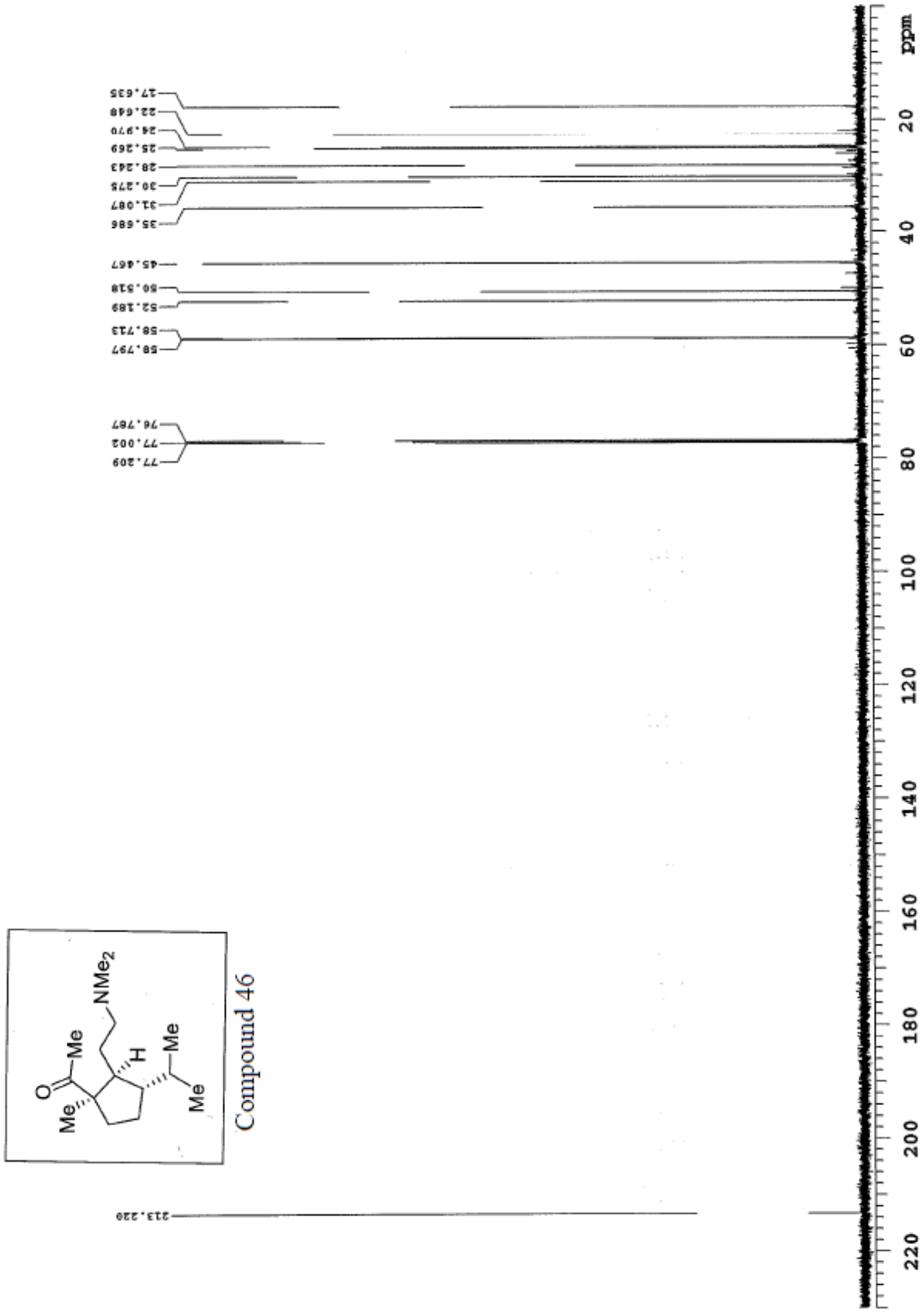
Compound 45

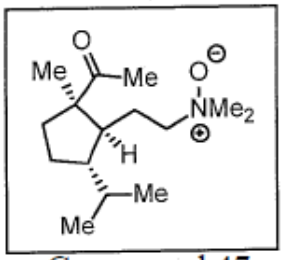
82.604
77.208
77.001
76.786
59.815
52.541
51.775
45.550
37.694
31.968
30.005
24.870
24.824
24.785
24.755
22.708
16.929
200
180
160
140
120
100
80
60
40
20
ppm


O
Me
Me
NMe2
H
Me
Me

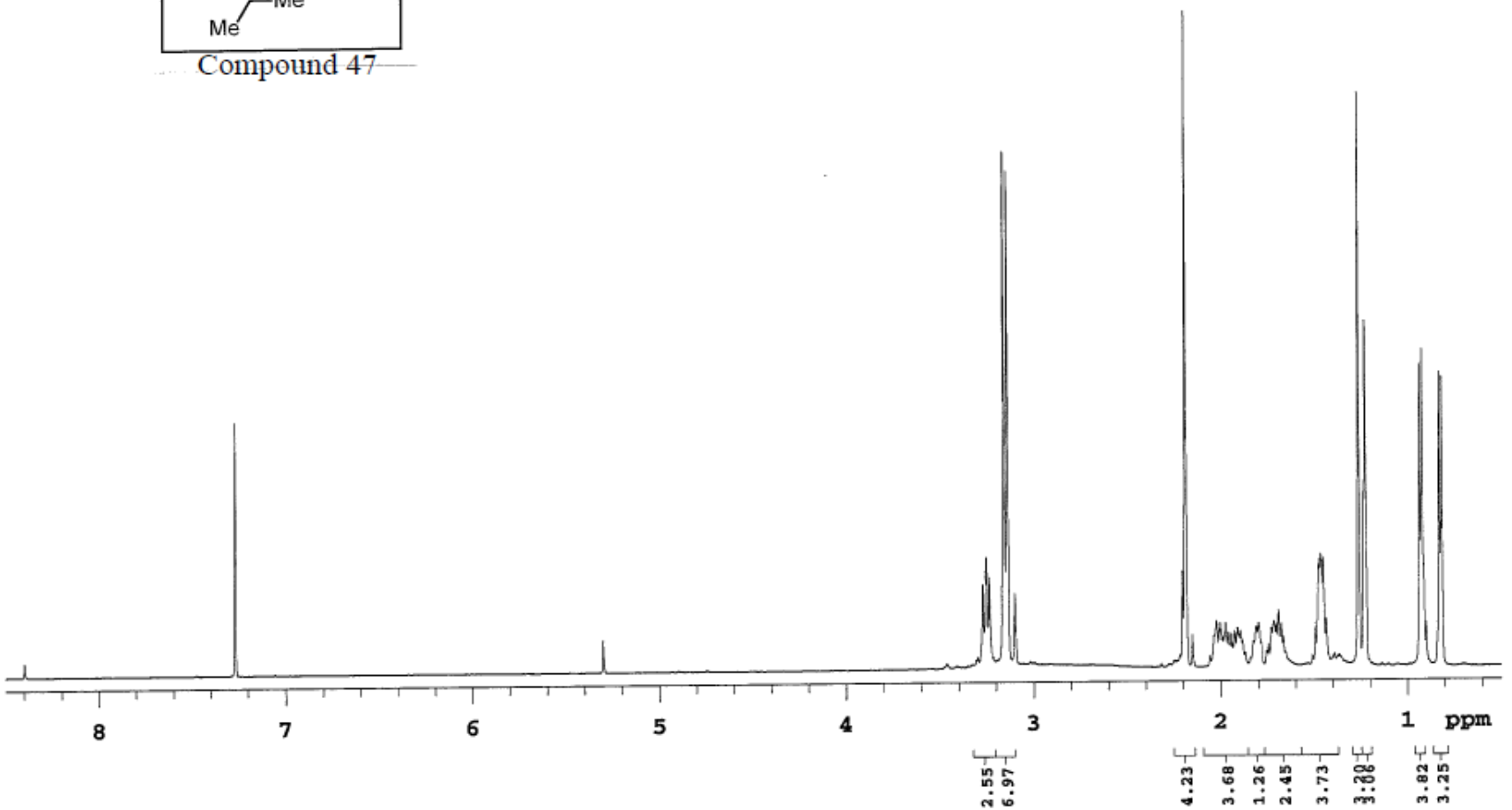
Compound 46

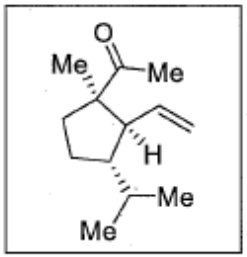
9
8
7
6
5
4
3
2
1
0
ppm
1.05
1.93
1.11
1.06
4.12
3.37
3.06
3.00


Me
O
Me
NMe2
H
Me
Me
Compound 46
213.220
77.209
77.002
76.787
58.797
58.713
52.189
50.538
45.467
35.686
31.087
30.275
28.243
25.269
24.970
22.648
17.635
ppm
220
200
180
160
140
120
100
80
60
40
20

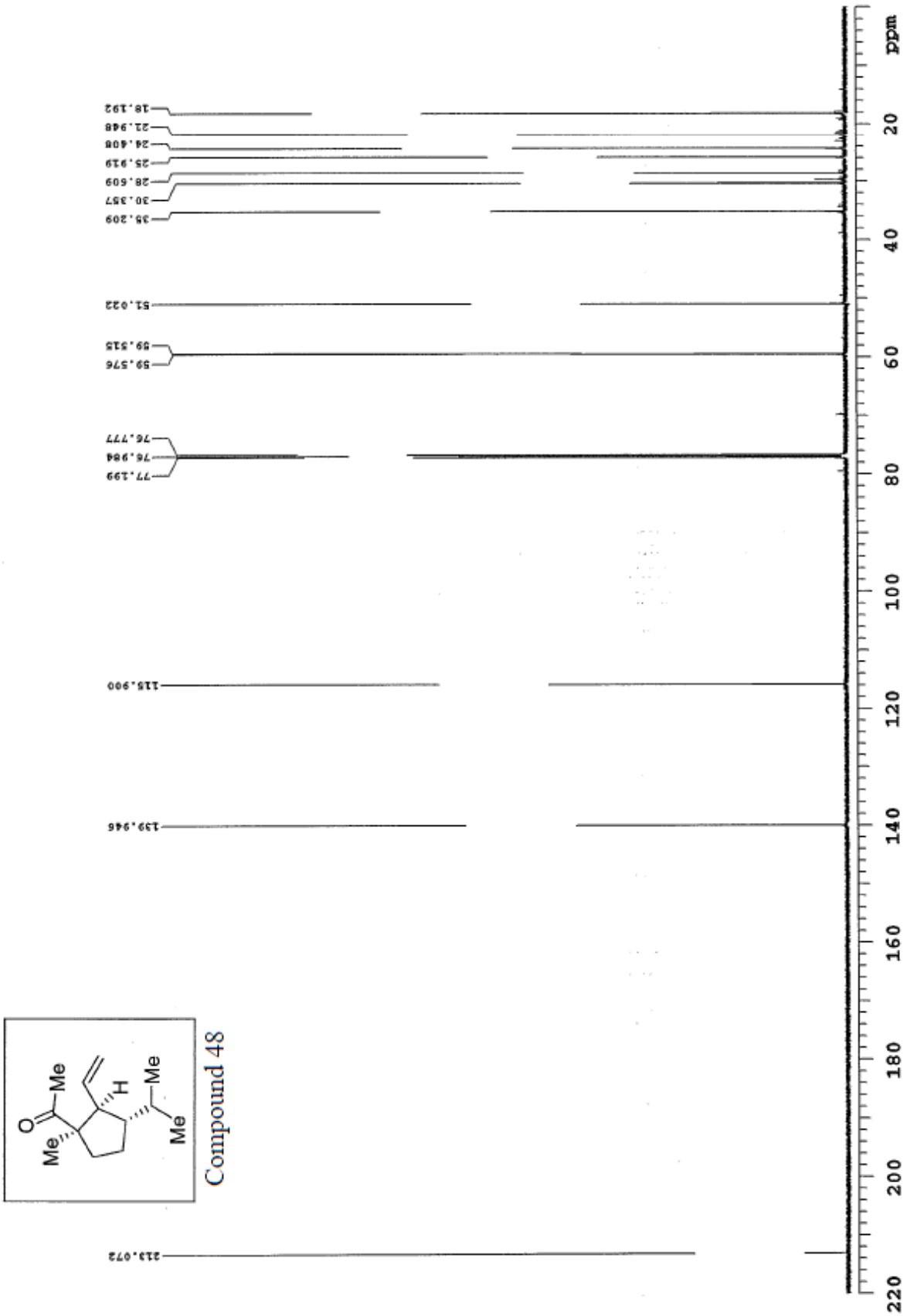

O
Me
Me
O
NMe2
H
Me
Me

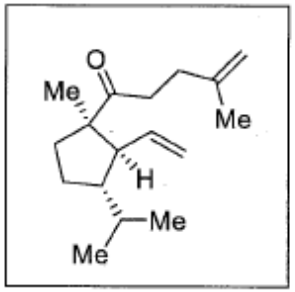
Compound 47


8
7
6
5
4
3
2
1
ppm
2.55
6.97
4.23
3.68
1.26
2.45
3.73
3.82
3.25



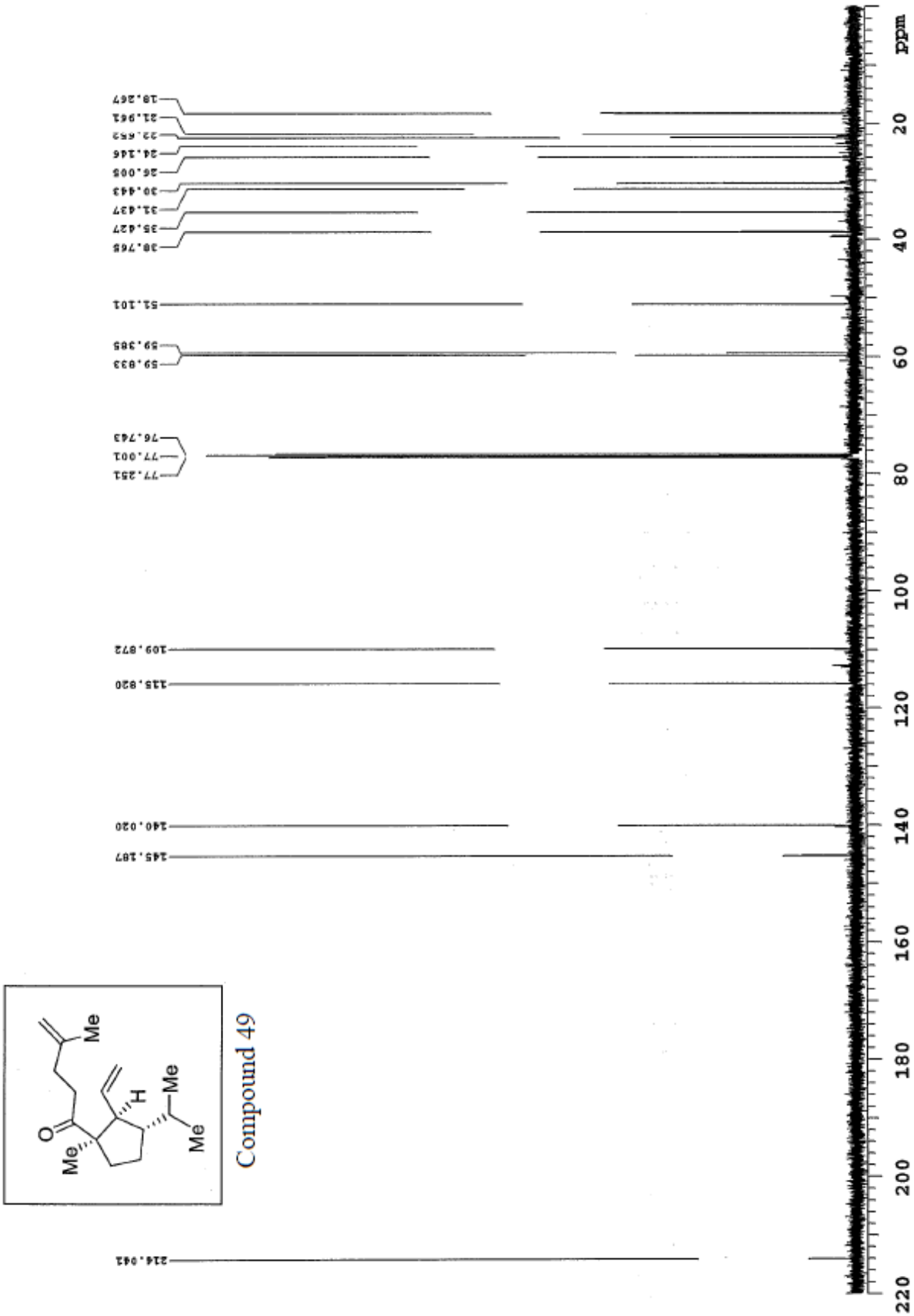
Compound 48

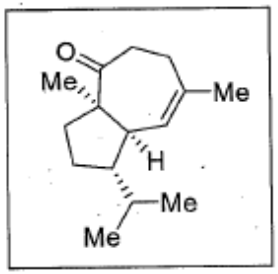

Me
O
Me
H
Me
Me
Compound 48
213.073
139.946
115.900
77.199
76.984
76.777
59.576
59.515
51.022
35.209
30.357
28.609
25.919
24.608
21.948
18.192
ppm
220
200
180
160
140
120
100
80
60
40
20


O
Me
Me
H
Me
Me

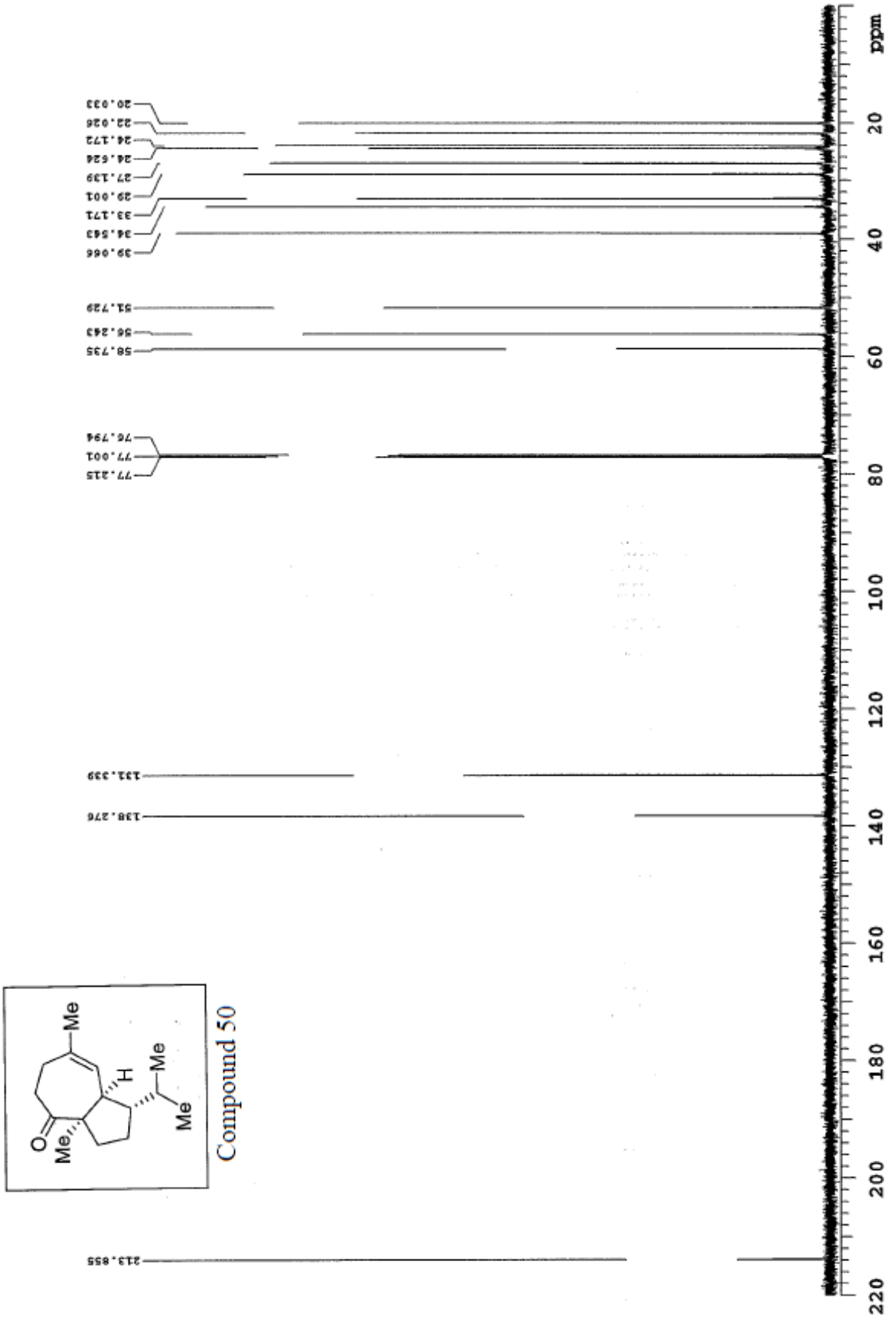
Compound 49

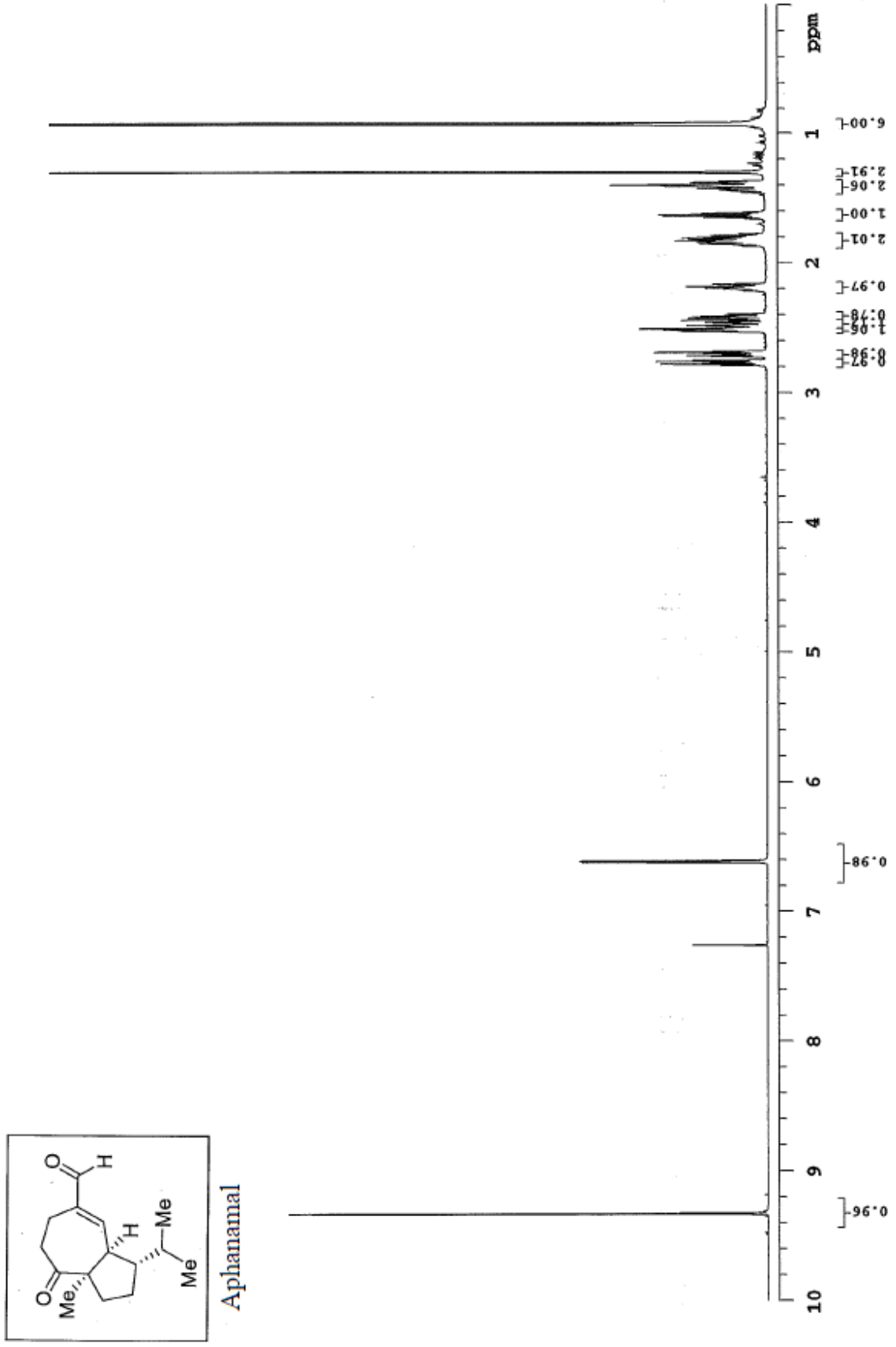
9
8
7
6
5
4
3
2
1
0
ppm
0.91
1.97
2.07
1.83
2.94
1.09
1.95
3.14
1.50
0.94
1.28
2.90
3.04
3.00

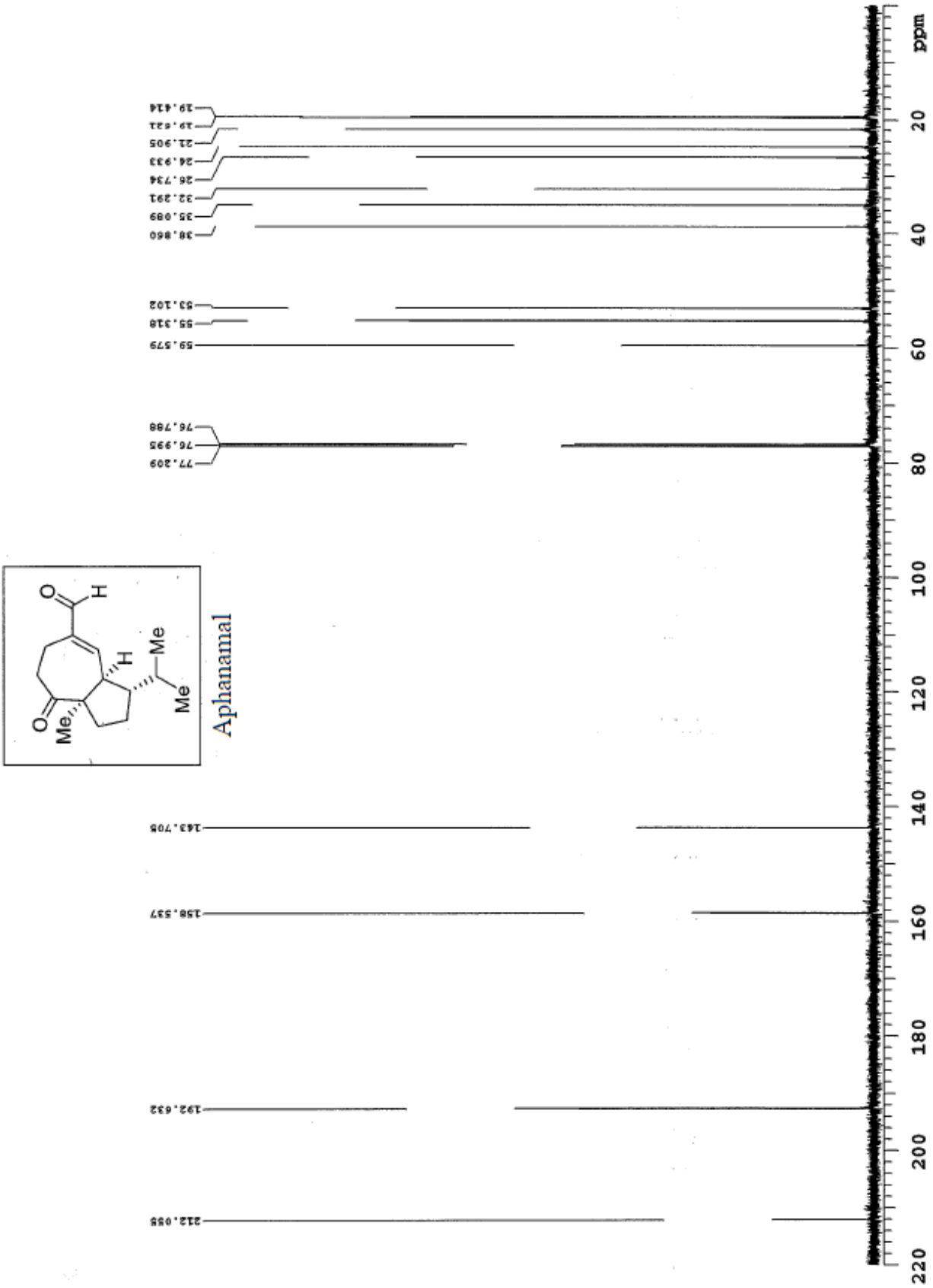

Me
Me
H
Me
Me
O
Compound 49
18.367
21.961
22.453
24.146
26.005
30.443
31.437
35.427
38.765
51.101
59.385
59.833
76.743
77.001
77.251
109.872
135.820
140.020
145.187
216.041
ppm
20
40
60
80
100
120
140
160
180
200
220

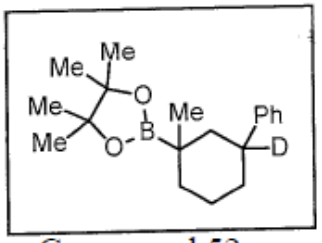


Compound 50


Me
H
Me
Me
O
Me
Compound 50
213.855
138.276
133.339
77.225
77.001
76.794
58.735
56.243
51.729
39.066
34.543
33.171
29.001
27.139
24.634
24.172
23.026
20.033
ppm
220
200
180
160
140
120
100
80
60
40
20


O
H
H
Me
Me
O
Me
Aphanamal
ppm
1
2
3
4
5
6
7
8
9
10
6.00
2.91
2.06
1.00
2.01
0.97
0.78
1.06
1.24
0.98
0.97
0.98
0.96


Aphanamal
O
H
Me
H
Me
O
Me
212.055
192.632
158.537
143.705
77.209
76.993
76.788
59.579
55.318
53.102
39.860
35.089
32.291
26.734
24.933
21.905
19.621
19.414
ppm
220
200
180
160
140
120
100
80
60
40
20


Me
Me
Me
Me
O
B
O
Me
Ph
D

Compound 52

7
6
5
4
3
2
1
ppm
3.01
3.08
1.96
0.92
0.93
2.32
0.53
0.98
2.91
1.10
2.30
12.47
12.29
3.10
1.06
3.00