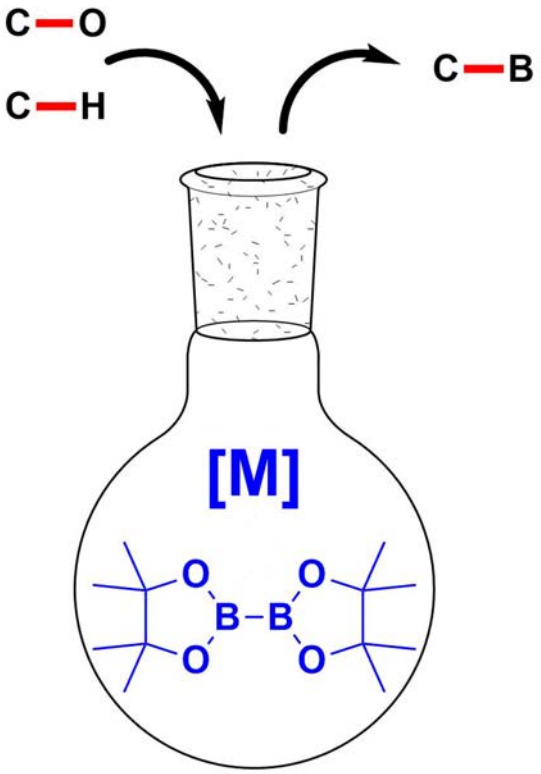
Transition Metal-Catalyzed Construction of Benzyl/Allyl sp^3 and Vinyl/Allenyl sp^2 C-B Bonds



Dissertation zur Erlangung des naturwissenschaftlichen Doktorgrades

der Julius-Maximilians-Universität Würzburg

Lujia Mao

aus Changchun, V.R. China

Würzburg, 2017

Eingereicht bei der Fakultät für Chemie und Pharmazie am:

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Gutachter der schriftlichen Arbeit
1. Gutachter: Prof. Dr. Todd B. Marder
2. Gutachter: Prof. Kálmán J. Szabó

Prüfer des öffentlichen Promotionskolloquiums
1. Prüfer: Prof. Dr. Todd B. Marder
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积累多了是经验，经验多了可以应变，应变多了就是智慧。

—— 郎平

Accumulation grows to experience, which leads to variation, and wisdom is simply lots of variation.

—— Lang, Ping

谨此献给我的父母

Für meine Eltern

Die Experimente zur vorliegenden Arbeit wurden in der Zeit von Oktober 2013 bis September 2017 am Institut für Anorganische Chemie der Julius-Maximilians-Universität Würzburg unter der Aufsicht von Prof. Dr. Todd B. Marder durchgeführt.

Affidavit

I hereby confirm that my thesis entitled “Transition Metal-Catalyzed Construction of Benzyl/Allyl sp^3 and Vinyl/Allenyl sp^2 C-B Bonds” is the result of my own work. I did not receive any help or support from commercial consultants. All sources and / or materials applied are listed and specified in the thesis. Furthermore, I confirm that this thesis has not yet been submitted as part of another examination process either in identical or in similar form.

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List of Publications

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Publication	Position
L. Mao, K. J. Szabó, T. B. Marder, *Org. Lett.* **2017**, *19*, 1204-1207.	Chapter 2 Reprinted with permission from {L. Mao, K. J. Szabó, T. B. Marder, *Org. Lett.* **2017**, *19*, 1204-1207.}. Copyright © 2017 American Chemical Society.
L. Mao, R. Bertermann, K. Emmert, K. J. Szabó, T. B. Marder, *Submitted*.	Chapter 3
L. Mao, R. Bertermann, S. Rachor, K. J. Szabó, T. B. Marder, *Submitted*.	Chapter 4

List of Abbreviations

acac	Acetylacetonate
9-BBN	9-Borabicyclo(3.3.1)nonane
B_2cat_2	2,2'-Bi-1,3,2-benzodioxaborole
bpy	2,2'-Bipyridine
B_2pin_2	4,4,4',4',5,5,5',5'-Octamethyl-2,2'-bi-1,3,2-dioxaborolane
BQ	1,4-Benzoquinone
BDP, dppbe, dppbz	1,2-Bis(diphenylphosphino)benzene
CB	Carbon black
cod	1,5-Cyclooctadiene
Cp*	1,2,3,4,5-Pentamethylcyclopentadienyl
CPA	Chiral phosphoric acids
CPME	Cyclopentyl methyl ether
Cy	Cyclohexyl
dan	Naphthalene-1,8-diaminato
dba	Dibenzylideneacetone
DBU	1,8-Diazabicyclo[5.4.0]undecane
DCE	1,2-Dichloroethene
DCPF	1,1'-Bis(dicyclohexylphosphino)ferrocene
DIBAH	Diisobutylaluminium hydride
DMA	*N*,*N*-Dimethylacetamide
DMAP	4-Dimethylaminopyridine
DMBQ	2,6-Dimethylbenzoquinone
DME	1,2-Dimethoxyethane
DMF	*N*,*N*-Dimethylmethanamide
DMSO	Dimethyl sulfoxide
dppe	1,2-Bis(diphenylphosphino)ethane
dppp	1,3-Bis(diphenylphosphino)propane
dtbpy	4,4'-Di-*tert*-butyl-2,2'-bipyridine
GC-MS	Gas chromatography-mass spectrometry
etpo	4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane
HBcat	Catecholborane
HBpin	4,4,5,5-Tetramethyl-1,3,2-dioxaborolane
HRMS	High-resolution mass spectrometry
Me_4phen	3,4,7,8-Tetramethyl-1,10-phenanthroline
MHz	Mega Hertz
MTBE	2-Methoxy-2-methylpropane (Methyl *t*-butyl ether)
NBE	Norbornene
NFSI	*N*-Fluorobenzenesulfonimide
NHC	*N*-Heterocyclic carbene
NMR	Nuclear magnetic resonance

NOE	Nuclear Overhauser effect
NPs	Nanoparticles
NQ	1,4-Naphthoquinone
PEG	Polyethylene glycol
r.t.	Room temperature
RuPhos	2-Dicyclohexylphosphino-2',6'-diisopropoxybiphenyl
TFA	Trifluoroacetate, Trifluoroacetic acid
THF	Tetrahydrofuran
TMEDA	Tetramethylethylenediamine
UV-Vis	Ultra violet-visible
Xantphos	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene

Abstract

Organoboron compounds, such as benzyl-, allyl-, allenyl-, vinyl-, and 2-boryl allyl-boronates, have been synthesized via metal-catalyzed borylations of sp^3 C-O and C-H bonds. Thus, Cu-catalyzed borylations of alcohols and their derivatives provide benzyl-, allyl-, allenyl-, vinyl-, and 2-boryl allyl-boronates via nucleophilic substitution. The employment of $Ti(O^iPr)_4$ turns the OH moiety into a good leaving group ('OTi'). The products of Pd-catalyzed oxidative borylations of allylic C-H bonds of alkenes were isolated and purified, and their application in the one-pot synthesis of stereodefined homoallyl alcohols was also investigated.

Chapter 2 presents a copper-catalyzed synthesis of benzyl-, allyl-, and allenyl-boronates from benzylic, allylic, and propargylic alcohols, respectively, employing a commercially available catalyst precursor, $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$, and Xantphos as the ligand. The borylation of benzylic alcohols was carried out at 100 °C with 5-10 mol % $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$, which afforded benzylic boronates in 32%-95% yields. With 10 mol % $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$, allylic boronates were provided in 53%-89% yields from the borylation of allylic alcohols at 60 or 100 °C. Secondary allylboronates were prepared in 72%-84% yields from the borylation of primary allylic alcohols, which also suggests that a nucleophilic substitution pathway is involved in this reaction. Allenylboronates were also synthesized in 72%-89% yields from the borylation of propargylic alcohols at 40 or 60 °C. This methodology can be extended to borylation of benzylic and allylic acetates. This protocol exhibits broad reaction scope (40 examples) and high efficiency (up to 95% yield) under mild conditions, including the preparation of secondary allylic boronates. Preliminary mechanistic studies suggest that nucleophilic substitution is involved in this reaction.

Chapter 3 reports an efficient methodology for the synthesis of vinyl-, allyl-, and (*E*)-2-boryl allyl-boronates from propargylic alcohols via copper-catalyzed borylation reactions under mild conditions. In the presence of a commercially available catalyst precursor ($Cu(OAc)_2$ or $Cu(acac)_2$) and ligand (Xantphos), the reaction affords the desired products in up to 92% yield with a broad substrate scope (43 examples). Vinylboronates were synthesized in 50%-83% yields via Cu-

catalyzed hydroboration of mono-substituted propargylic alcohols. With 1,1-disubstituted propargylic alcohols as the starting materials and $Cu(OAc)_2$ as the catalyst precursor, a variety of allylboronates were synthesized in 44%-83% yields. The (*E*)-2-boryl allylboronates were synthesized in 54%-92% yields via the Cu-catalyzed diboration of propargylic alcohols. The stereoselectivity is different from the $Pd(dba)_2$-catalyzed diboration of allenes that provided (*Z*)-2-boryl allylboronates predominantly. The isolation of an allenyl boronate as the reaction intermediate suggests that an S_N2'-type reaction, followed by borylcupration, is involved in the mechanism of the diboration of propargylic alcohols.

In chapter 4, a Pd-catalyzed allylic C-H borylation of alkenes is reported. The transformation exhibits high regioselectivity with a variety of linear alkenes, employing a Pd-pincer complex as the catalyst precursor, and the allylic boronate products were isolated and purified. This protocol can also be extended to one-pot carbonyl allylation reactions to provide homoallyl alcohols efficiently. An interesting mechanistic feature is that the reaction proceeds via a Pd(II)/Pd(IV) catalytic cycle. Formation of the Pd(IV) intermediate occurs by a unique combination of an NCN-pincer complex and application of F-TEDA-BF_4 as the oxidant. An important novelty of the present C-H borylation reaction is that all allyl-Bpin products can be isolated with usually high yields. This is probably a consequence of the application of the NCN-pincer complex as catalyst, which selectively catalyzes C-B bond formation avoiding subsequent C-B bond cleavage based side-reactions.

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Chapter One

Introduction

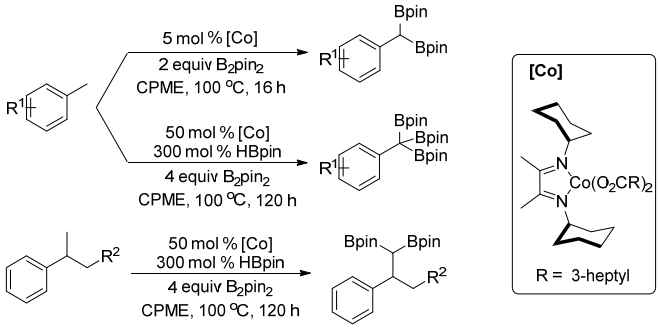
1. Introduction

1.1 Metal-Catalyzed Bond Activation and Construction of Benzylic and Allylic sp^3 C-B Bonds

1.1.1 Metal-Catalyzed Borylation of Benzylic C-H Bonds

1.1.1.1 Co-Catalyzed Borylation of Benzylic C-H Bonds

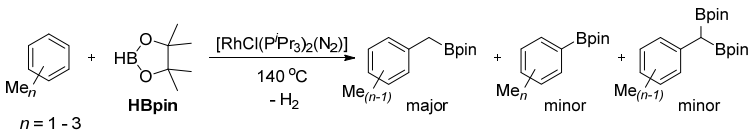
Co(II) dialkyl and bis(carboxylate) complexes bearing α-diimine ligands were synthesized by Chirik and co-workers, and were demonstrated to be active for the benzylic[1] C-H borylation[2] as well as remote, unactivated sp^3 C-H bonds. This method utilizes readily available, air-stable Co(II)-precursors and provides a direct synthetic route to valuable geminal diboronate and polyboronate compounds as well as a new strategy to borylate remote, unactivated sp^3 C-H bonds (Scheme 1-1).



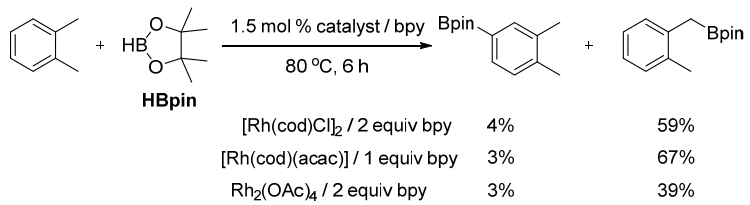
Scheme 1-1

1.1.1.2 Rh-Catalyzed Borylation of Benzylic C-H Bonds

Marder and co-workers reported the first catalyzed benzylic C-H borylation.[3a] $[RhCl(P^iPr_3)_2(N_2)]$ proved to be an efficient catalyst precursor for the borylation of benzylic C-H bonds with HBpin (Scheme 1-2A). The high degree of benzylic selectivity with toluene, *p*-xylene and mesitylene is attributed to the formation of η^3-benzyl intermediates,[3b] in which the minor products of 1,1-diboration of benzylic C-H bonds were also observed. Later on, Beller's group also found that benzylic activation of *o*-xylene was the main reaction pathway for certain Rh catalysts, and the best yields of borylated products were obtained using [Rh(cod)(acac)] in the presence of 1 equiv of bpy giving 67% of 4,4,5,5-tetramethyl-2-(*o*-tolymethyl)-1,3,2-dioxaborolane (Scheme 1-2B).[3c]



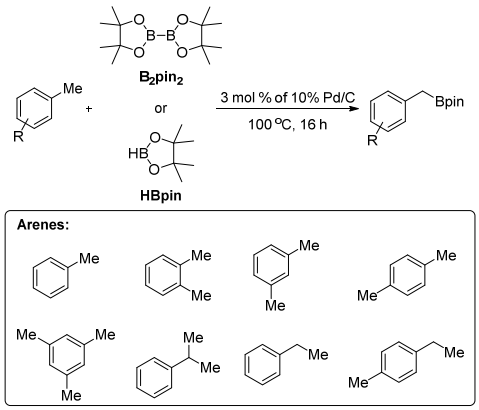
Scheme 1-2A



Scheme 1-2B

1.1.1.3 Pd-Catalyzed Borylation of Benzylic C-H Bonds

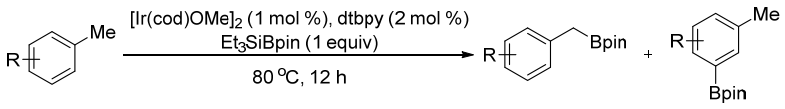
A palladium-catalyzed borylation of alkylbenzenes with either B_2pin_2 or HBpin was established by Ishiyama, Miyaura and co-workers.[4] A number of alkylbenzenes underwent benzylic borylation with either B_2pin_2 or HBpin in the presence of 3 mol % of 10% Pd/C at 100 °C (Scheme 1-3).



Scheme 1-3

1.1.1.4 Ir-Catalyzed Borylation of Benzylic C-H Bonds

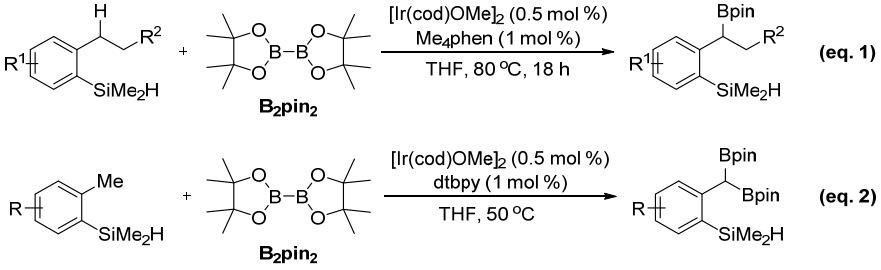
Hartwig and co-workers reported that silylboranes can react with methylarenes at both the aryl and methyl C-H bonds with $[Ir(cod)OMe]_2$ as catalyst precursor at 80 °C in the presence of dtbpy (Scheme 1-4).[5] The reaction of $Et_3SiBpin$ with toluene under the standard reaction conditions formed benzylic boronates as the major products. With electron-rich *m*-xylene, the ratio of benzylic to aryl C-H bond borylation is 9:1, but the ratio dropped to 4:6 with more electron-deficient 3-chlorotoluene as starting material. Mesitylene and 2,3,4,5,6-pentafluorotoluene underwent exclusive benzylic C-H borylation. However, the borylation of ethylbenzene formed no benzylic boronate. The ratio of aryl to benzyl C-H bond borylation also varied with the size of the silyl group. Reactions with more hindered silyboranes formed more of the product from benzylic borylation.



Scheme 1-4

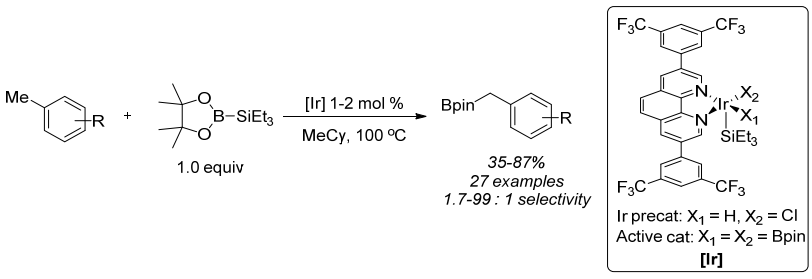
An iridium-catalyzed borylation of secondary benzylic C-H bonds directed by a hydrosilyl group

was developed by Hartwig and co-workers.[6a] With $[Ir(cod)OMe]_2$ as catalyst precursor combined with 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen) as the ligand, a variety of substrates can be borylated with B_2pin_2 at 80 °C (eq. 1, Scheme 1-5). When they replaced Me_4phen with 4,4'-di-*tert*-butyl-2,2'-bypridine (dtbpy), diborylation of primary benzylic C-H bonds occurred to provide 1,1-benzyldiboronate esters with B_2pin_2 at 50 °C in good yields (eq. 2, Scheme 1-5).[6b] The hydrosilyl directing group is readily removed or transformed to other functional groups after the borylation reaction.



Scheme 1-5

The borylation of primary benzylic C-H bonds without a directing group, catalyzed by a new iridium catalyst containing an electron-deficient phenanthroline as ligand was reported by the same research group (Scheme 1-6).[7] An Ir diboryl monosilyl complex ligated by phenanthroline was isolated and determined to be the resting state of the catalyst, which is kinetically competent to be an intermediate in the catalytic process. Kinetic studies of benzylic and aryl C-H borylation catalyzed by Ir complexes show that the rate of benzylic C-H borylation is less sensitive to the degree of electron density at the metal center of the Ir catalyst than the aryl C-H borylation. Combined with computational studies, the turnover-limiting step of the borylation of benzylic C-H bonds appears to be an isomerization of the Ir intermediate prior to C-B reductive elimination.

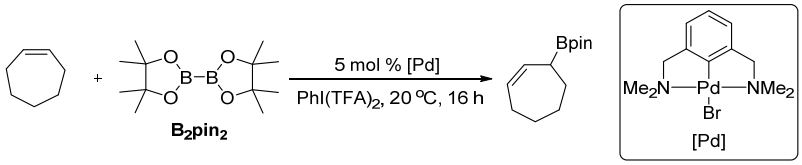


Scheme 1-6

1.1.2 Metal-Catalyzed Borylation of Allylic C-H Bonds

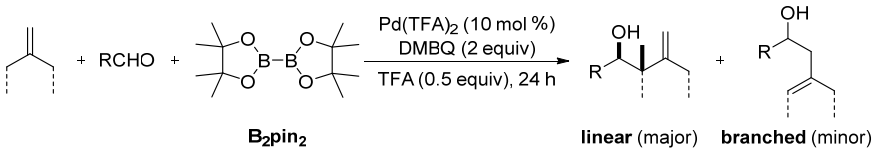
1.1.2.1 Pd-Catalyzed Borylation of Allylic C-H Bonds

A selective C-H borylation of alkenes by a palladium-pincer complex catalyzed oxidative functionalization was also established by Szabó and co-workers, in which a Pd(IV) complex was proposed to be a key intermediate.[8] This borylation reaction provided mainly vinyl boronates; however, an allyl boronate was formed with cycloheptene as the starting material (Scheme 1-7), for which the selectivity is controlled by conformational factors.



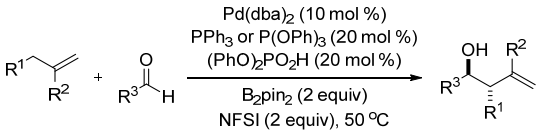
Scheme 1-7

Szabó and co-workers developed an allylic sp^3 C-H borylation of exocyclic alkenes employing $Pd(TFA)_2$ as catalyst (Scheme 1-8).[9] An (η^3-allyl)palladium(II) complex was proposed to be the key intermediate in this reaction, which assisted to avoid the termination of the reaction by β-hydride elimination, so that the addition of 2,6-dimethylbenzoquinone (DMBQ) is required to close the catalytic cycle.

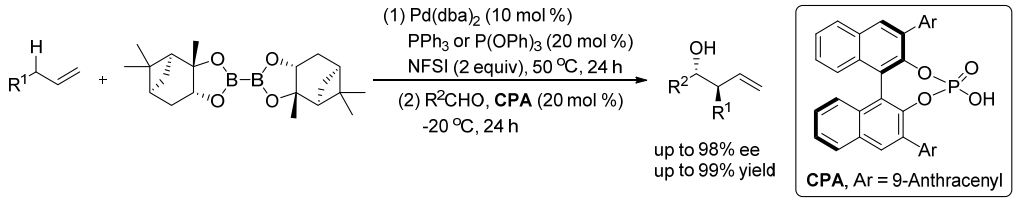


Scheme 1-8

Alternatively, Gong and co-workers reported a cascade oxidative allylic C-H borylation of allylbenzene and its derivatives and an allylation of aldehydes. They employed $Pd(dba)_2$ as catalyst precursor, *N*-fluorobenzenesulfonimide (NFSI) as the oxidant, and the addition of $(PhO)_2PO_2H$ to catalyze the allylation reaction (Scheme 1-9A).[10a] It was proposed that palladium(0) was first oxidized by NFSI, which was revealed to play a key role in the allylic C-H activation-based allylation, to generate a palladium(II)-F species, which might be the active catalyst for the reaction. By replacing $(PhO)_2PO_2H$ with chiral phosphoric acids (CPA), this protocol can be applied to a one-pot enantioselective carbonyl allylation of aldehydes with allylbenzenes (Scheme 1-9B).[10b]



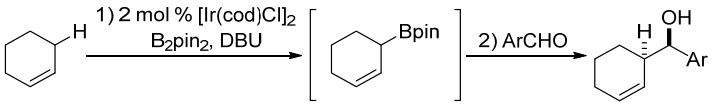
Scheme 1-9A



Scheme 1-9B

1.1.2.2 Ir-Catalyzed Borylation of Allylic C-H Bonds

The first iridium-catalyzed borylation of unactivated cycloalkenes to provide transient allylic boronates followed by C-C bond-forming reactions in a one-pot sequence was demonstrated by Szabó and co-workers (Scheme 1-10).[11a] The regioselectivity can be controlled by addition of 1,8-diazabicyclo[5.4.0]undecane (DBU) or methylimidazole,[11b] which can retard the rearrangement of allyl boronates leading to formation of vinyl boronates. Isotope labeling experiments revealed that the reaction proceeds via a dehydrogenative borylation mechanism.[11b]



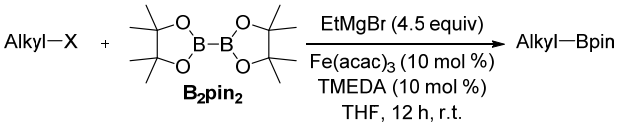
Scheme 1-10

1.1.3 Metal-Catalyzed Borylation of Benzylic and Allylic C-Halogen Bonds

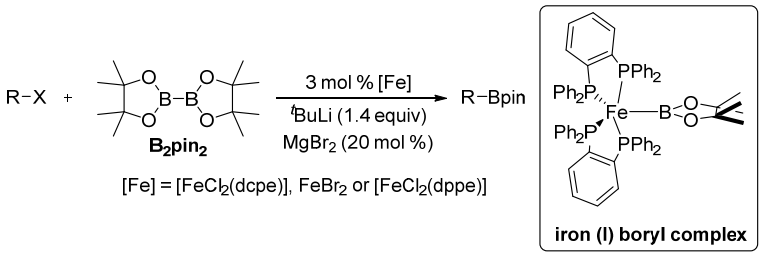
1.1.3.1 Fe-Catalyzed Borylation of Benzylic and Allylic C-Halogen Bonds

A direct cross-coupling of alkyl halides[12a] with B_2pin_2[12b,c] catalyzed by low-cost iron(III) acetoacetate ($Fe(acac)_3$) coordinated with tetramethylethylenediamine (TMEDA) was reported by Cook and co-workers.[13a] With this approach, a variety of primary, secondary and tertiary boronates is provided derived from benzylic or allylic chlorides, tosylates and mesylates (Scheme 1-11A). The mechanism for the reaction is unclear. The only byproducts of the reaction are EtBpin, probably due to the addition of 4.5 equiv EtMgBr, which is a drawback, as Grignard reagents can be employed stochiometrically to prepare organoboron compounds in the absence of catalysts. Meanwhile, an alternative iron-catalyzed borylation of alkyl, allyl, and aryl halides was established by Bedford and co-workers, and an iron(I) boryl complex was also isolated under catalytically relevant conditions (Scheme 1-11B),[13b] but was shown not to be an intermediate in the catalytic cycle. Additionally,

^{t}BuLi was added as an activating reagent, which is a drawback of the catalytic borylations, as classic methodologies also employ a stochiometric amount of organolithium or Grignard reagents.



Scheme 1-11A

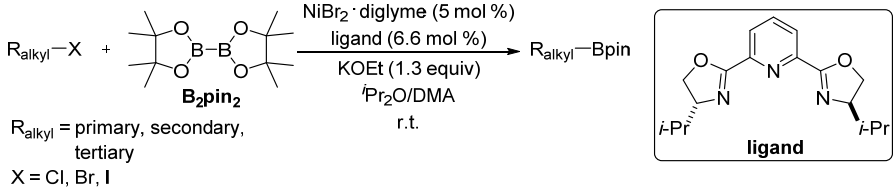


Scheme 1-11B

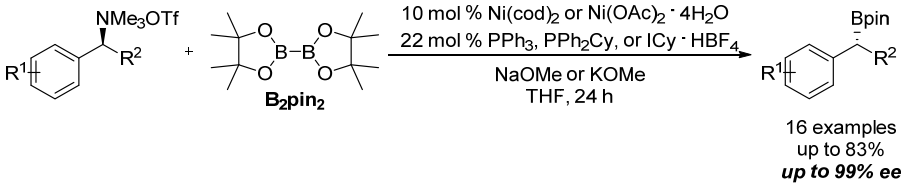
1.1.3.2 Ni-Catalyzed Borylation of Benzylic and Allylic C-Halogen Bonds

A nickel-containing catalyst formed *in situ* from $NiBr_2$•diglyme and a pybox ligand has been developed by Fu and co-workers, which accomplishes Miyaura-type borylations of unactivated tertiary, secondary, and primary alkyl halides with B_2pin_2 to furnish alkyl boronates including benzyl as well as allyl boronates (Scheme 1-12A).[14a] The method exhibits good functional-group compatibility and is regiospecific, both of which can be issues with traditional approaches to the synthesis of alkylboronates. Tertiary halides are more active than secondary or primary halides in this nickel-catalyzed C-B bond-forming reaction, which suggests that this transformation follows a one-electron pathway for oxidative addition, involving Ni(I)/Ni(II)/Ni(III) species. The enhanced reactivity with greater substitution can be rationalized by a radical pathway, in which the stability of the carbon radicals plays a key role in determining the course of the reaction. Borylation of either *exo*- or *endo*-2-boromonorbornane provides the *exo* products with 20:1 diastereoselectivity, which also suggests a radical pathway. The reactivity as a function of the leaving group is I > Br > Cl > OTs, which is consistent with an electron-transfer pathway for oxidative addition, as alkyl chlorides and tosylates are unreactive under the borylation conditions. A detailed theoretical study of the mechanism has been reported by Lin, Marder and co-workers. The proposed Ni(I)/Ni(III) catalytic cycle was studied computationally by means of DFT calculations at the B3LYP level, which indicate that the rate-determining step for this reaction is the atom-transfer step.[14b] Very recently, a

stereospecific, nickel-catalyzed borylation of secondary benzylic ammonium salts to deliver highly enantioenriched benzylic boronates was developed by Watson and co-workers (Scheme 1-12B).[14c] This reaction has broad scope, enabling the synthesis of a variety of secondary benzylic boronates in good yields and excellent ee's. It is likely that the reaction proceedes via an oxidative addition to generate a benzylic nickel species, which undergoes transmetalation and reductive elimination to deliver enantioenriched benzylic boronates.



Scheme 1-12A

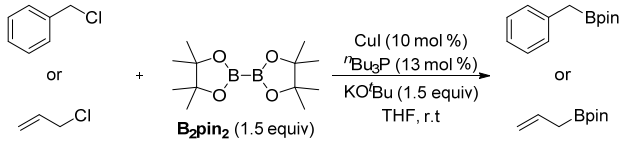


Scheme 1-12B

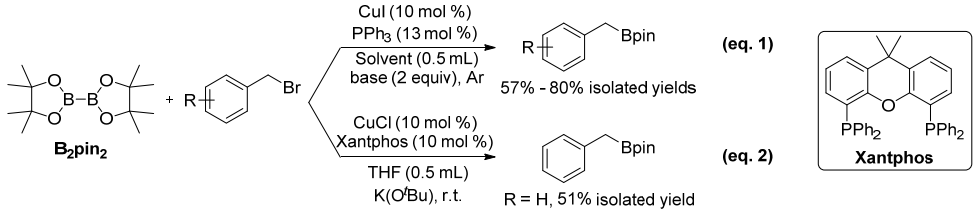
1.1.3.3 Cu-Catalyzed Borylation of Benzylic and Allylic C-Halogen Bonds

Marder, Lin and co-workers reported the first copper-catalyzed borylation of aryl halides with alkoxy diboron reagents, which is also applicable to the borylation of benzyl and allyl halides (Scheme 1-13A).[15a] Benzylic boronate was isolated in yield of 61% from the borylation of benzyl chloride, and allyl-Bpin was isolated in 9% yield as a result of decomposition during the workup. Later on, Marder, Liu, Steel and co-workers established a copper-catalyzed borylation of primary and secondary alkyl halides and pseudohalides,[15b] which can be extended to the synthesis of benzyl boronates. This was the first report of allyl halide borylation with any metal. They employed an inexpensive copper source (CuI) as catalyst precursor and PPh_3 as ligand, and four benzylic boronates were successfully synthesized and isolated in good yields of 57%-80% (eq. 1, Scheme 1-13B). Alternatively, a boryl substitution of unactivated alkyl halides reported by Ito and co-workers, provided alkyl boronates, including benzyl boronates, in the presence of a copper(I)/Xantphos catalyst (eq. 2, Scheme 1-13B).[15c] The reaction works with normal and secondary alkyl chlorides, bromides, and iodides, but alkyl sulfonates did not react. Ring-opening products were observed with cyclopropylmethyl bromide as the starting material, which suggests that a radical pathway is

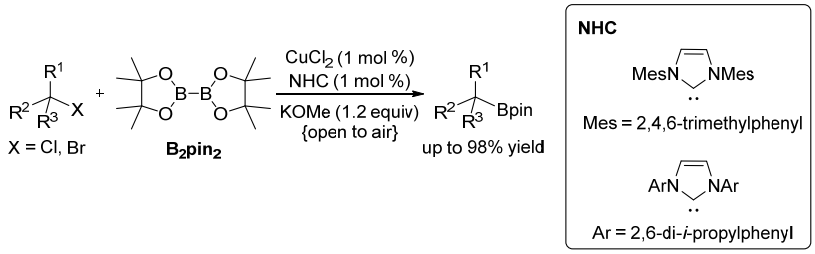
involved in this reaction. Very recently, a Cu(II)-catalyzed borylation of alkyl halides has been developed by Marder and co-workers, which afforded both allyl and benzyl boronates.[15d] This reaction can be carried out in air, and a variety of functional groups are tolerated. Preliminary mechanistic investigations reveal that one-electron processes are involved in this reaction (Scheme 1-13C).



Scheme 1-13A

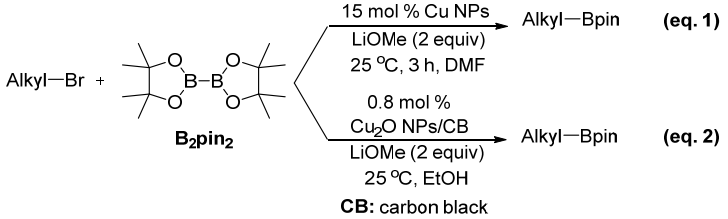


Scheme 1-13B



Scheme 1-13C

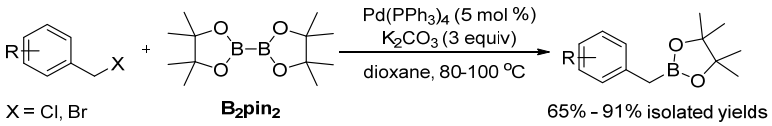
Chung and co-workers employed commercially available copper nanoparticles, which catalyzed the borylation of alkyl bromides at room temperature with broad substrate scope and good functional group tolerance (eq. 1, Scheme 1-14).[16a] A benzyl boronate was afforded in a yield of 58% with benzylbromide as starting material. A similar protocol was also developed by Xu and co-workers with a lower loading of Cu_2O nanoparticles (0.8 mol%) (eq. 2, Scheme 1-14).[16b]



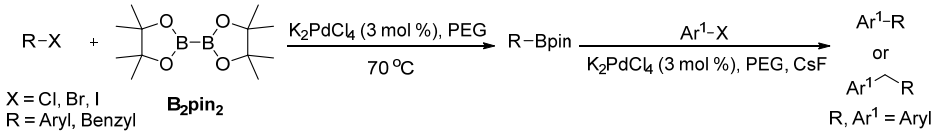
Scheme 1-14

1.1.3.4 Pd-Catalyzed Borylation of Benzylic and Allylic C-Halogen Bonds

A synthesis of diverse benzyl boronates under Miyaura palladium-catalyzed conditions using B_2pin_2 was reported by Giroux in 2003.[17a] Both benzyl-chlorides and -bromides can be borylated by employing $Pd(PPh_3)_4$ as the catalyst precursor, and the corresponding products were isolated in yields of 65%-91%. Sensitive functionalities, such as esters and nitriles, are tolerated and the desired products were isolated in good to high yields (Scheme 1-15A). The first example of a palladium nanoparticle-catalyzed borylation of aryl/benzyl halides to afford aryl/benzyl boronates was reported by Sarkar and co-workers, which was carried out under ligand free conditions and applied to one-pot coupling reactions to provide unsymmetrical biaryls and diarylmethanes (Scheme 1-15B).[17b]

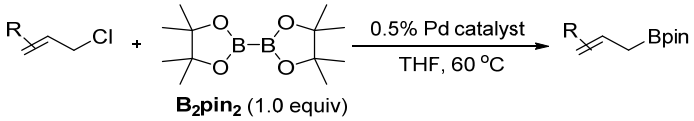


Scheme 1-15A



Scheme 1-15B

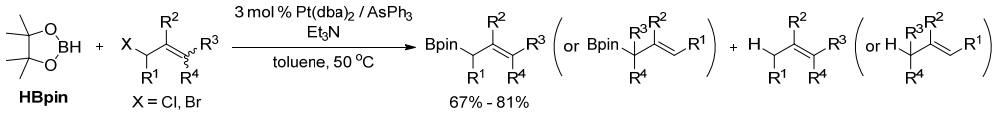
Morken and co-workers demonstrated that allylboron reagents can be effectively synthesized via the borylation of allylic halides (chlorides and bromides) in the presence of a number of commercially available Pd catalysts (e.g., $Pd_2(dba)_3$, $PdCl_2$, Pd/C) without the assistance of a drybox (Scheme 1-16).[18]



Scheme 1-16

1.1.3.5 Pt-Catalyzed Borylation of Allylic C-Halogen Bonds

Masuda and co-workers reported the first platinum(0)-catalyzed borylation of allyl halides with pinacolborane to provide the corresponding allylboronates in good yields (Scheme 1-17).[19] Triphenylarsine, which weakly coordinates with transition metals, stabilized the complex to prevent the precipitation of platinum black during the reaction. However, allyl acetates were less reactive toward the borylation.



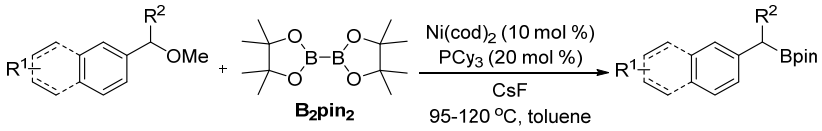
Scheme 1-17

1.1.4 Metal-Catalyzed Borylation of Benzylic and Allylic C-O Bonds

1.1.4.1 Metal-Catalyzed Borylation of Benzylic C-O Bonds

1.1.4.1.1 Ni-Catalyzed Borylation of Benzylic C-O Bonds

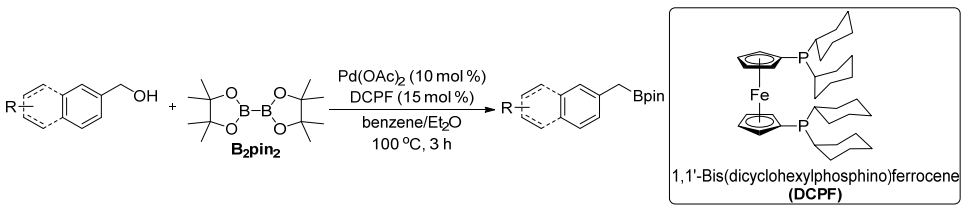
A nickel-catalyzed borylation of aryl ethers via sp^3 C-OMe cleavage was described by Martin and co-workers (Scheme 1-18).[20] The borylation reaction was carried out with $Ni(cod)_2$ as catalyst precursor and PCy_3 as ligand at 95-120 °C. The desired products were provided in yields of 50%-81%.



Scheme 1-18

1.1.4.1.2 Pd-Catalyzed Borylation of Benzylic C-O Bonds

Shi and co-workers developed a $Pd(OAc)_2$-catalyzed sp^3 C-O activation and borylation of arylmethanols to synthesize benzyl boronates under mild conditions in the absence of bases, in which 15 mol % DCPF was required as ligand (Scheme 1-19).[21] With naphthylmethanols, the desired products were isolated in yields of 34%-64%. When they employed benzylmethanols as starting material, addition of 0.75 equiv of $Ti(O^iPr)_4$ was required, and corresponding benzylboronates were isolated in yields of 44%-74%. They proposed that an oxidative addition of benzylic C-O bonds to Pd(0), followed by transmetallation, provides a Pd(II)-B species undergoing reductive elimination to afford benzylic boronates.

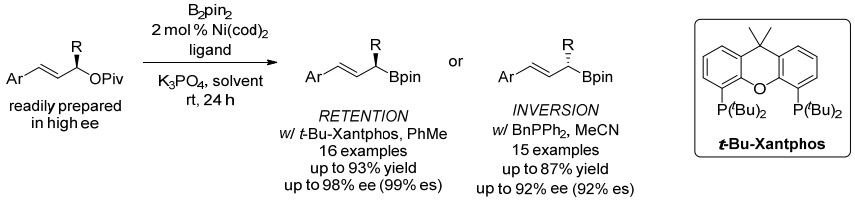


Scheme 1-19

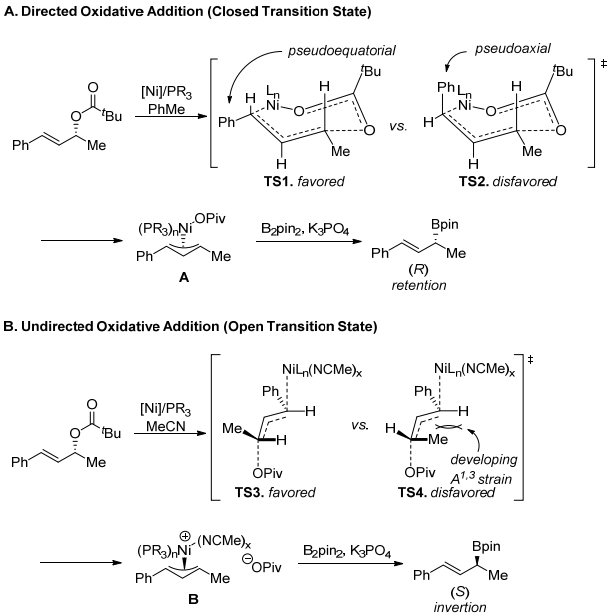
1.1.4.2 Metal-Catalyzed Borylation of Allylic C-O Bonds

1.1.4.2.1 Ni-Catalyzed Borylation of Allylic C-O Bonds

A stereospecific nickel-catalyzed Miyaura borylation of allylic pivalates was reported by Watson and co-workers (Scheme 1-20A),[22] which delivers highly enantioenriched α-stereogenic γ-aryl allylboronates with good yields and regioselectivities. They proposed that the reaction proceeds via a π-allyl nickel intermediate. The stereochemical switch from stereoretention to stereoinversion depends upon solvent, probably due to the competitive pathways for the oxidative addition. The stereoretentive pathway stems from a directed oxidative addition by pivalate leaving group, when the reaction is carried out in nonpolar solvents. The stereoinvertive pathway is dominant when MeCN blocks coordination of the pivalate group by binding the nickel catalyst (Scheme 1-20B).



Scheme 1-20A

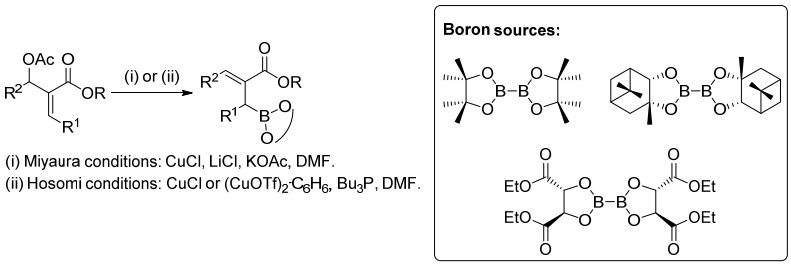


Scheme 1-20B

1.1.4.2.2 Cu-Catalyzed Borylation of Allylic C-O Bonds

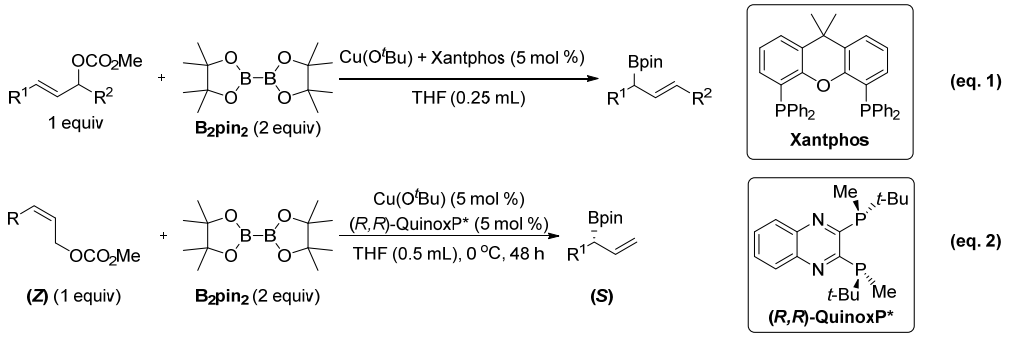
Copper catalysts have been found to be active for the borylation of sp^3 C-O bonds. Ramachandran and co-workers reported a copper-catalyzed synthesis of various highly functionalized chiral and achiral allylboronates via an S_N2' reaction on acetates of alcohols derived from vinylalumination

(VA) or Baylis-Hillman (BH) reaction of aldehydes (Scheme 1-21).[23]



Scheme 1-21

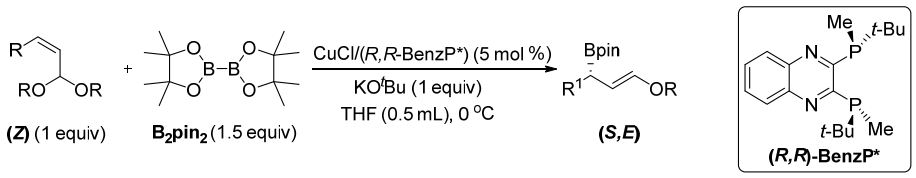
Ito, Sawamura and co-workers reported a copper-catalyzed γ-selective and stereospecific substitution reaction of allylic carbonates with B_2pin_2 (eq. 1, Scheme 1-22).[24a] A chelating phosphine (Xantphos) featuring a large natural bite-angle has been found to produce a remarkable rate-acceleration for copper-catalyzed borylation of allylic carbonates. Xantphos-ligated Cu-OR would react with a diboron reagent to form a Cu-B species useful as a 'formal boryl nucleophile'.[24b] Formal S_N2' attack of the Cu-B species on an allylic carbonate would allow γ-selective formation of an allylboron compound. Alternatively, optically active α-chiral allyl boronates were also prepared via a similar methodology, in which they employed Cu(O-*t*-Bu) as the catalyst precursor, and (*R,R*)-QuinoxP* as a chiral ligand (eq. 2, Scheme 1-22).[24c] Later on, they further developed this protocol by employing readily available CuCl as the catalyst precursor in combination with stoichiometric K(O-*t*-Bu) instead of Cu(O-*t*-Bu). Therefore, sublimation of Cu(O-*t*-Bu) is not necessary before carrying out the reactions.[24d]



Scheme 1-22

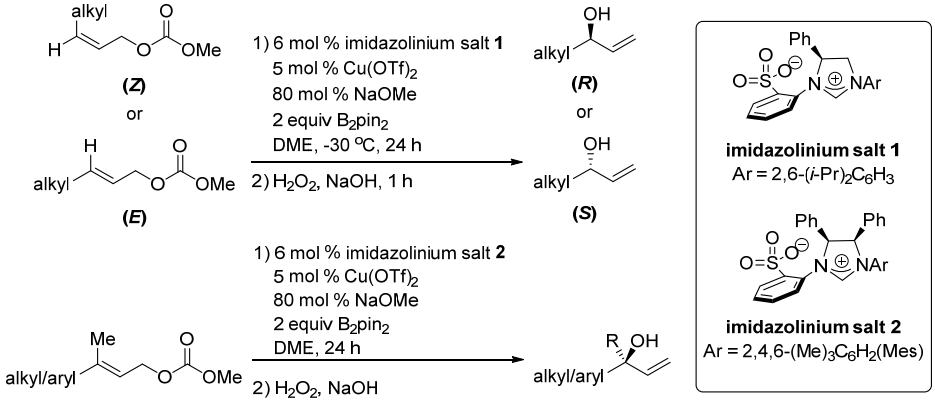
Ito and co-workers applied this catalytic system to the catalytic asymmetric synthesis of α-chiral linear or carbocyclic (γ-alkoxyallyl)-boronates via a Cu(I)-catalyzed γ-boryl substitution of allyl acetals (Scheme 1-23).[25] This reaction afforded the desired products in high yields with excellent *E*:*Z* selectivities and enantioselectivities (only (*E*)-product, 91-98% ee) and also exhibited high

functional group compatibility.

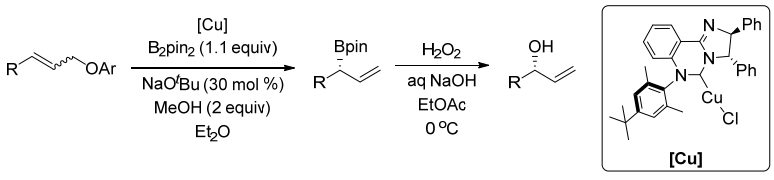


Scheme 1-23

Hoveyda and co-workers established a NHC-Cu-catalyzed boryl substitution of *E*-allylic carbonates, which provided α-substituted allylboronates bearing B-substituted tertiary or quaternary carbon stereogenic centers (Scheme 1-24A).[26a] A chiral bidentate Cu-NHC complex proved to be the most efficient catalyst, with which desired products were afforded in high yields (up to >98%) and site selectivities (>98% S_N2'), and in up to > 99:1 enantiomer ratios. Alternatively, a 6-membered NHC-ligated Cu(I) complex-catalyzed borylation of allylic aryl ethers was developed by McQuade and co-workers, which provides α-substituted allyl boronates by employing pure *E* or *Z* or *E*/*Z* alkene mixtures as starting materials (Scheme 1-24B).[26b] This stereoconvergent reaction exhibits high yields (av 86%), high S_N2' selectivity (>99:1), and high ee (av 94%).



Scheme 1-24A

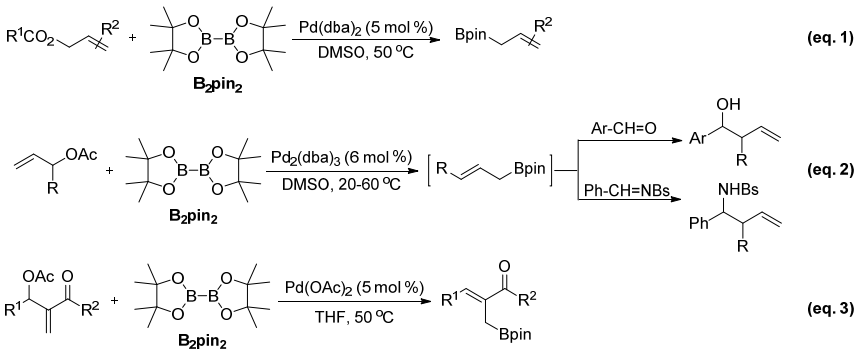


Scheme 1-24B

1.1.4.2.3 Pd-Catalyzed Borylation of Allylic C-O Bonds

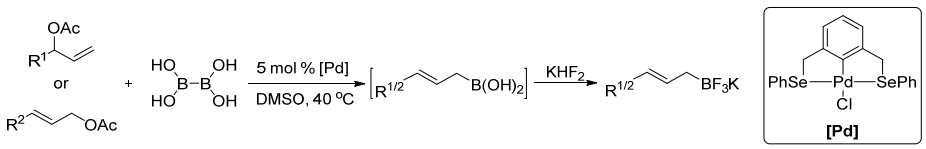
Miyaura and co-workers developed the first synthesis of allylboronates via $Pd(dba)_2$-catalyzed cross-coupling of allyl acetates and B_2pin_2 (eq. 1, Scheme 1-25).[27a] This protocol exhibits regio-

and *E*-stereoselectivity and provides the corresponding allylboronates in high yields. Later on, Szabó and co-workers reported a one-pot coupling of allyl acetates with aldehydes and imines via transient allyl boronates synthesized through the $Pd_2(dba)_3$-catalyzed borylation of allyl acetates (eq. 2, Scheme 1-25),[27b] which can be applied to prepare enatioenriched homoallyl alcohols.[27c] In 2004, a variety of functionalized allyl boronates was synthesized by Kabalka and co-workers via the $Pd(OAc)_2$-catalyzed borylation of Baylis-Hillman acetate adducts at 50 °C (eq. 3, Scheme 1-25).[27d]

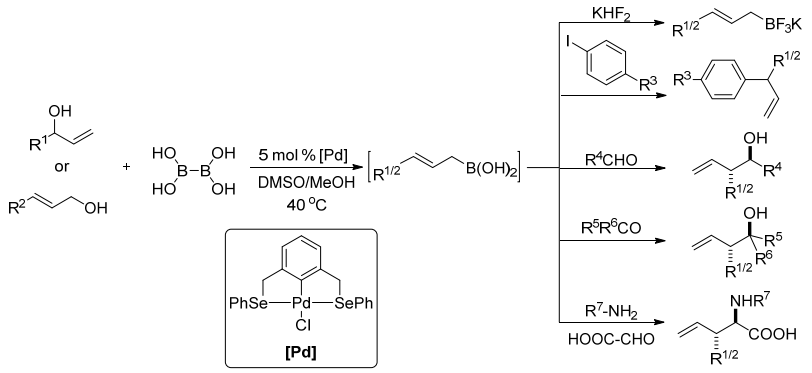


Scheme 1-25

Palladium-pincer complexes have been widely used in the borylation of allylic sp^3 C-O bonds, with pioneering work reported by Szabó and co-workers. In 2005, they first reported the synthesis of allylboronic acids from allyl acetates catalyzed by a palladium-pincer complex, with the products readily transformed into potassium trifluoro(allyl)borates (Scheme 1-26A).[28a] This protocol was successfully extended to the borylation of allylic alcohols to provide allylboronic acids,[28b,c] which can be employed directly either in Suzuki-Miyaura couplings,[28d] or C-C coupling with aldehydes,[28e] ketones[28f] and amines (Scheme 1-26B).[28f]

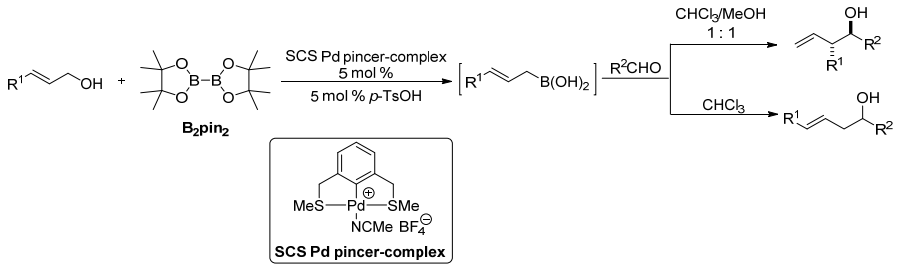


Scheme 1-26A



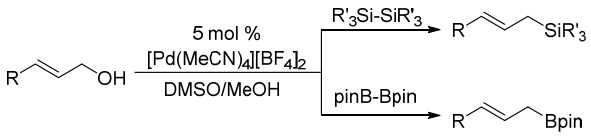
Scheme 1-26B

An SCS palladium pincer-complex was also employed as the catalyst for the borylation of allylic alcohols with B_2pin_2, followed by allylation with aldehydes, for which the regioselectivity of the borylation depends on the applied solvent. In $CHCl_3$, only linear allylic products were obtained, while branched allylic products were formed when MeOH was added to the reaction mixture (Scheme 1-27).[29]



Scheme 1-27

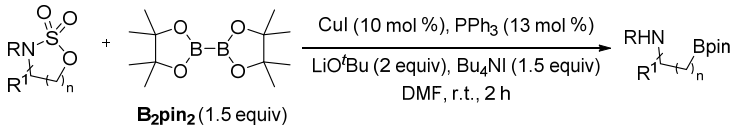
Szabó and co-workers also employed $[Pd(MeCN)_4][BF_4]_2$ as the catalyst precursor for both silylation and borylation of allylic alcohols (Shceme 1-28).[30a,b] Following a detailed mechanistic study, the tetrafluoroborate counterion of the palladium catalyst was proposed to play an important role in both catalyst activation as well as the transmetalation step. BF_3 is found to be generated in both processes and was proposed to be responsible for the activation of the substrate hydroxyl group. An (η^3-allyl)palladium complex was identified as the catalyst resting state.[30b]



Scheme 1-28

Gallagher and co-workers reported a copper-catalyzed borylation of cyclic sulfamidates to provide a range of stereochemically defined and enantomerically pure (aminoalkyl)boronic esters (Scheme

1-29).[31] Mechanistic studies suggest that *N*-sulfonated intermediates are key participants in the borylation reaction instead of simple alkyl iodides, though external iodide is essential.



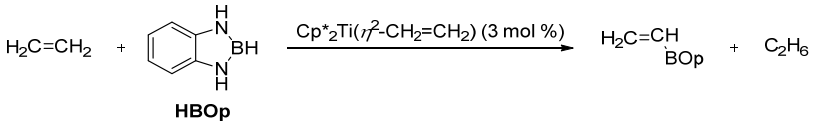
Scheme 1-29

1.2 Metal-Catalyzed Boryl Addition and Construction of Vinyl sp^2 C-B Bonds

1.2.1 Metal-Catalyzed Dehydrogenative Borylation of Alkenes

1.2.1.1 Ti-Catalyzed Dehydrogenative Borylation of Alkenes

Smith and co-workers reported a stochiometric dehydrogenative borylation of ethylene mediated by $Cp^*_2Ti(\eta^2\text{-}CH_2{=}CH_2)$,[32a] in which 2 equiv of an unactivated olefin and 1 equiv of a hydroborane are converted to 1 equiv of an alkane and 1 equiv of a vinylborane ester. Later on, they extended this method to a catalytic dehydrogenative borylation of alkenes to provide vinylboronates, in which $Cp^*_2Ti(\eta^2\text{-}CH_2{=}CH_2)$ was employed as the catalyst and benzo-1,3,2-diazaborolane was used as the boron source (Scheme 1-30).[32b]



Scheme 1-30

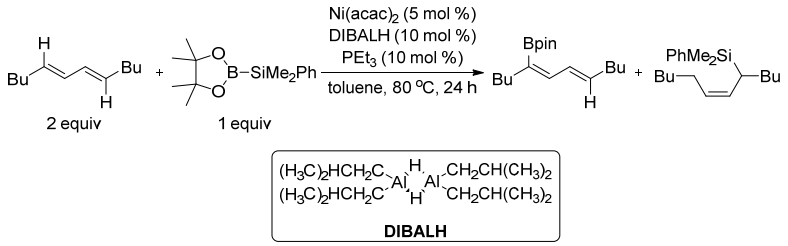
1.2.1.2 Fe-Catalyzed Dehydrogenative Borylation of Alkenes

Hartwig and co-workers reported a synthesis of vinylboronate esters via dehydrogenative borylation of alkenes with $CpFe(CO)_2Bcat$ and $(CO)_5ReBcat$ under UV-irradiation.[33] The terminal hexenylboronate ester was formed in 90% yield and 10% hexylboronate ester after $CpFe(CO)_2Bcat$ was dissolved in 1-hexene under irradiation. When $(CO)_5ReBcat$ was employed in the borylation of 1-hexene, the terminal hexenylboronate ester was obtained in 55% yield and 25% hexylboronate ester was formed as well. The reaction with internal alkenes was not as selective as for the terminal ones, as isomeric products were obtained. However, the mechanism for this reaction remains unclear.

1.2.1.3 Ni-Catalyzed Dehydrogenative Borylation of Alkenes

Dienyl boronates were obtained by Moberg and co-workers from a Ni-catalyzed Si-B addition to 1,3-dienes including a disproportionation process (Scheme 1-31),[34] in which the allylsilanes and dienyboranes were formed in a 1:1 ratio. Deuterium-labeling experiments suggest that the diene acts

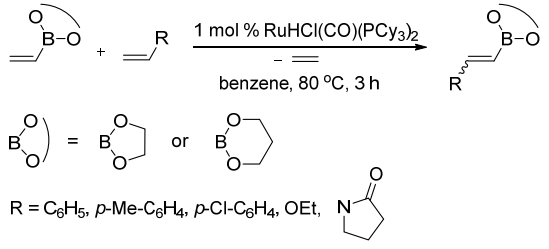
as the hydrogen source in the reaction.



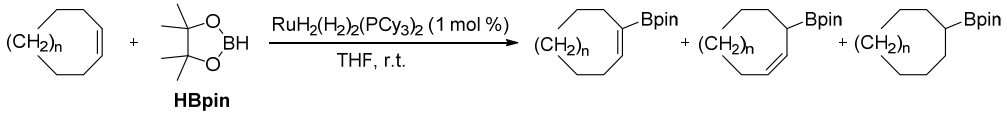
Scheme 1-31

1.2.1.4 Ru-Catalyzed Dehydrogenative Borylation of Alkenes

Marder, Baker and co-workers observed the formation of 9-vinyl-BBN in the addition of 9-H-BBN to Ru(η-C_2H_4)(PMe_3)$_4$, which also gave *cis*-$RuH_2(PMe_3)_4$.[35a] A Ru-catalyzed transfer of a boronate moiety for one alkene (vinyldioxaborolane) to another (styrene) was reported by Marciniec and co-workers (Scheme 1-32A),[35b] in which $RuHCl(CO)(PCy_3)_2$ was employed as the catalyst. The detailed DFT studies of the mechanism was investigated by Marder, Lin and co-workers,[35c] which supported the proposed mechanism involving (1) insertion of a coordinated vinylboronate into the Ru-H bond of the catalyst (hydride migration), followed by a β-boryl elimination; (2) ligand substitution of the coordinatd alkene by a substituted alkene; (3) insertion of the coordinated substituted alkene into the Ru-B bond (boryl migration), followed by a β-hydride elimination to afford a new vinyl boronate. Another Ru-catalyzed dehydrogenative borylation of linear and cyclic alkenes with HBpin has been presented by Sabo-Etienne and co-workers (Scheme 1-32B),[35d] in which conformational properties have a dramatic influence on both the rate and the selectivity of the reactions. Hydroboration of a C6 ring was selectively achieved, whereas allylboronate (for C7), a mixture of allylboronate and vinylboronate (for C8), and only vinylboronate (for C10) were isolated, respectively.



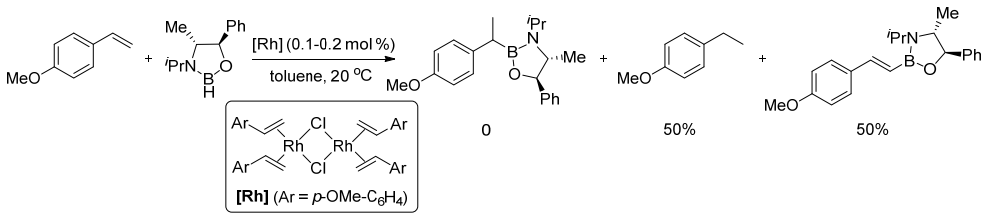
Scheme 1-32A



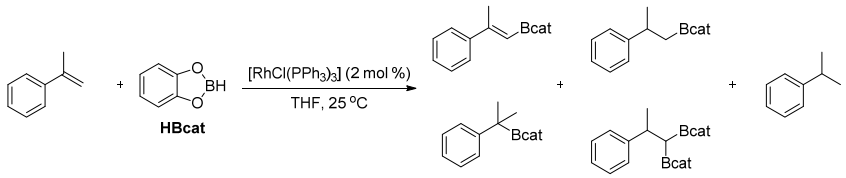
Scheme 1-32B

1.2.1.5 Rh-Catalyzed Dehydrogenative Borylation of Alkenes

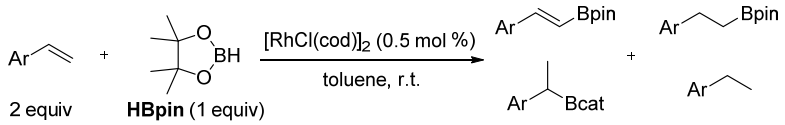
Brown and co-workers developed a dehydrogenative borylation of vinylarenes catalyzed by (*bis*-alkene) rhodium chloride complexes (Scheme 1-33A),[36a] in which 50% of the alkene is sacrificed to hydrogenation. Mechanistic studies revealed that the reaction is initiated by the formation of a Rh-H species with subsequent reversible and regiospecific H-transfer to the terminal carbon of the coordinated alkene, giving an intermediate which adds the borane and then eliminates the hydrocarbon product. Further migration of the secondary borane fragment from Rh to the β-carbon of the coordinated alkene occurs, followed by Rh-H β-elimination which produces the vinylborane product and regenerates the initial catalytic species.[36b] Marder and co-workers demonstrated a variety of Rh-catalyzed dehydrogenative borylations of alkenes to provide vinylboronates.[36c-e] In 1993, they employed Wilkinson's catalyst,[36f] [$RhCl(PPh_3)_3$], for the addition of HBcat to vinylarenes, in which vinylboronates were provided with α-substituted vinylarenes as starting materials (Scheme 1-33B).[36c] When they replaced Wilkinson's catalyst with *trans*-[$Rh(Cl)(CO)(PPh_3)_2$], the vinylboronates were afforded in high yields without consumption of half of the alkene substrate by hydrogenation.[36d] A mechanistic study revealed that, with the CO-containing catalyst system employed, the reaction probably involves insertion of the alkene into a Rh-B bond, followed by β-hydride elimination instead of direct C-H bond oxidative addition.[36e] A variety of indenyl rhodium(I) complexes were also synthesized by Westcott, Marder and co-workers. The vinyl boronate ester was obtained as the major borylation product with 5 mol % (η^5-C_9H_7)$Rh(coe)_2$ as the catalyst.[36g] Masuda and co-workers presented a $[RhCl(cod)]_2$-catalyzed dehydrogenative borylation of vinylarenes with HBpin to provide (*E*)-2-arylethenylboronates (Scheme 1-33C).[36h]



Scheme 1-33A



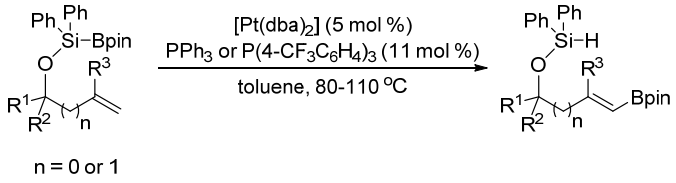
Scheme 1-33B



Scheme 1-33C

1.2.1.6 Pd- and Pt-Catalyzed Dehydrogenative Borylation of Alkenes

Sneddon and co-workers found that $PdBr_2$ is a better catalyst than chloroplatinic acid (H_2PtCl_6•$6H_2O$) or $PtBr_2$ for the dehydrogenative borylation of alkenes.[37a] Chloroplatinic acid- or $PtBr_2$-catalyzed borylation of ethylene with *arachno*-6,8-$C_2B_7H_{13}$ only yielded a hydroboration product. When they employed 1-pentene or styrene as the starting material, both hydroboration and dehydrogenative borylation products were obtained. However, $PdBr_2$-catalyzed borylation of ethylene, 1-pentene, or styrene predominantly provided dehydrogenative borylation products. The reaction mechanism probably involves competitive hydride-migration/reductive elimination and boryl-migration/*β*-hydride elimination steps. Another Pt-catlayzed dehydrogenative borylation of homoallylic and allylic silyl ethers containing geminally disubstituted C=C bonds to afford *cis*-*β*-methyl- and phenyl-substituted alkenylboronates was reported by Suginome and co-workers (Scheme 1-31).[37b]

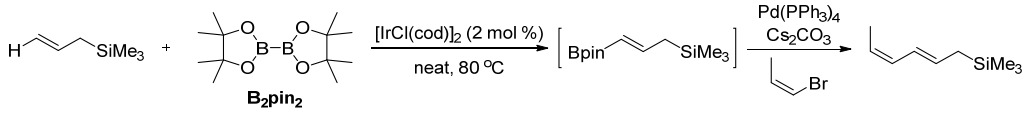


Scheme 1-31

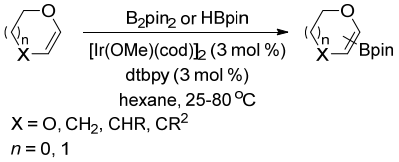
1.2.1.7 Ir-Catalyzed Dehydrogenative Borylation of Alkenes

Szabó and co-workers developed an Ir-catalyzed vinyl C-H borylation of allylsilanes and various vinyl substrates followed by a one-pot Pd-catalyzed Suzuki-Miyaura coupling reaction to afford allylsilanes and dienylsilanes (Scheme 1-32A).[38a] Ishiyama, Miyaura and co-workers disclosed an alternative Ir(I)-dtbpy-catalyzed vinylic C-H borylation of cyclic vinyl ethers with B_2pin_2, in which they proposed that the oxidative addition of sp^2 C-H bonds to an Ir(III)-trisboryl intermediate is

involved in the rate-determining step (Scheme 1-32B).[38b,c]



Scheme 1-32A

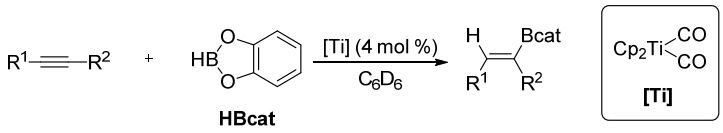


Scheme 1-32B

1.2.2 Metal-Catalyzed Borylation of Alkynes

1.2.2.1 Ti-Catalyzed Borylation of Alkynes

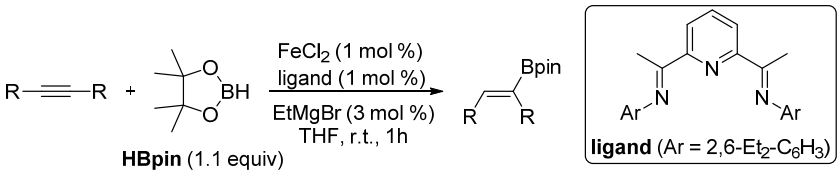
Hartwig and co-workers reported dicarbonyltitanocene-catalyzed selective additions of HBcat to alkynes to provide vinylboronate esters with *anti*-Markovnikov regioselectivity that ranges from good to exclusive (Scheme 1-33).[39] Detailed mechanistic studies suggested a σ bond metathesis between HBcat and titanocene alkyne complexes that possesses metallacyclopropene character as the B-C bond-forming step, which was observed directly in model reactions.



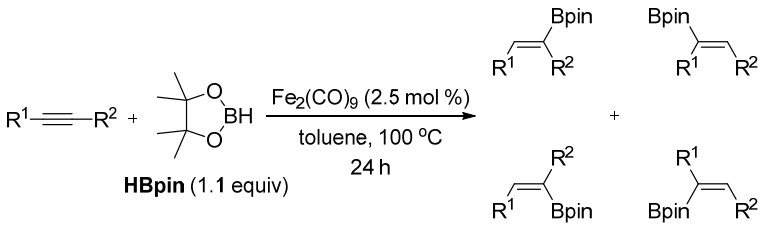
Scheme 1-33

1.2.2.2 Fe-Catalyzed Borylation of Alkynes

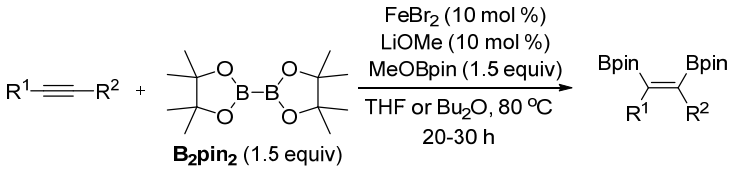
A highly chemo-, regio-, and stereoselective synthesis of vinyl boronate esters via the Fe-catalyzed borylation of alkynes[40] with HBpin has been reported by Thomas and co-workers (Scheme 1-34A).[41a] Alternatively, Enthaler and co-workers demonstrated that an $Fe_2(CO)_9$-catalyzed hydroboration of alkynes affords vinylboronates in good to excellent yields and selectivities (Scheme 1-34B).[41b] An Fe-catalyzed diboration and carboboration of alkynes was reported by Nakamura and co-workers (Scheme 1-34C).[41c] With diboration reactions, diverse symmetrical or unsymmetrical *cis*-1,2-diborylalkenes were afforded in high yields, which was extended to the carboboration of alkynes with primary and secondary alkyl halides providing various tetrasubstituted monoboryl alkenes with high stereoselectivities.



Scheme 1-34A



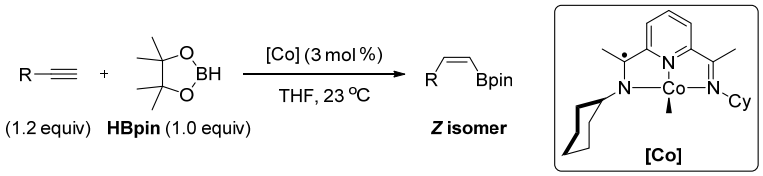
Scheme 1-34B



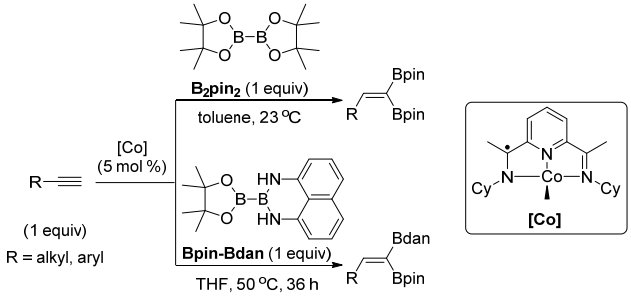
Scheme 1-34C

1.2.2.3 Co-Catalyzed Borylation of Alkynes

Marder, Norman and co-workers reported the synthesis and characterization of a 17-electron Co(II) complex, $[Co(PMe_3)_3(Bcat)_2]$, via oxidative addition of B_2cat_2 to $[Co(PMe_3)_4]$.[42a] Later on, Lin, Marder, Norman and co-workers synthesized the paramagnetic Co(II) bisboryl complexes $[Co(PMe_3)_3\{B(4\text{-}Mecat)\}_2]$ and $[Co(PMe_2Ph)_3\{B(cat)\}_2]$, respectively.[42b] Preliminary reactivity studies demonstrated that the $[Co(PMe_3)_4]$-catalyzed diboration of alkynes yielded both *cis*- and some *trans*-products most likely associated with the paramagnetic nature of the catalyst. Chirik and co-workers reported a bis(imino)pyridine cobalt-catalyzed hydroboration of terminal alkynes with HBpin, which provides vinylboronate esters with high yields and (*Z*) selectivity (Scheme 1-35A).[42c] A selective insertion of an alkynyl-boronate ester into a Co-H bond was proposed to be involved in the reaction mechanism, which accounts for the (*Z*) selectivity. Alternatively, they described another Co-catalyzed 1,1-diboration of terminal alkynes with B_2pin_2 (Scheme 1-35B),[42d] which proceeds efficiently at 23 °C with excellent 1,1-selectivity and broad functional group tolerance. This reaction can also be extended to the unsymmetrical diboron reagent (Bpin-Bdan).



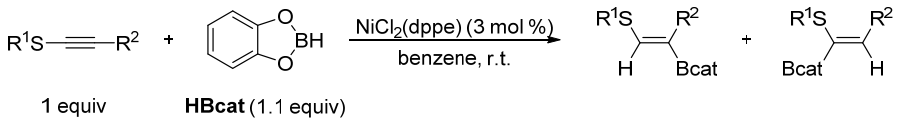
Scheme 1-35A



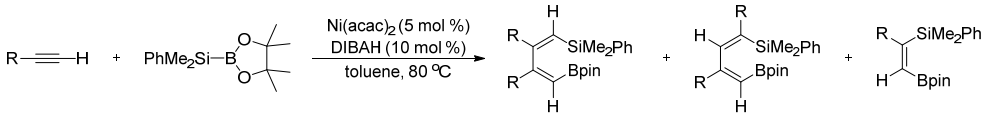
Scheme 1-35B

1.2.2.4 Ni-Catalyzed Borylation of Alkynes

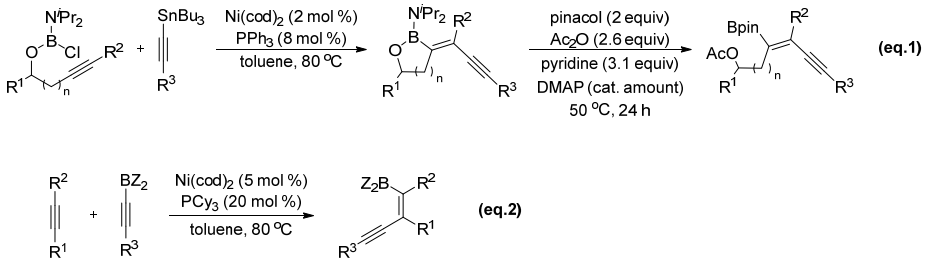
A regio- and stereoselective synthesis of *β*-(alkylthio)alkenyl-1,3,2-benzodioxaboroles via a Ni-catalyzed hydroboration of thioacetylenes with HBcat was reported by Miyaura, Suzuki and co-workers (Scheme 1-36A),[43a] in which $NiCl_2$(dppe) or $NiCl_2$(dppp) was employed as the catalyst precursor. Later on, Ito and co-workers described a Ni-catalyzed silaborative dimerization of alkynes to provide *cis*,*cis*-1-silyl-4-boryl-1,3-butadiene derivatives, in which a double insertion of alkynes into the Si-B bond of (dimethylphenylsilyl)pinacolborane is involved (Scheme 1-36B).[43b] Suginome and co-workers developed a $Ni(cod)_2$-catalyzed *trans*-alkynylboration of alkynes via activation of a B-Cl bond (eq. 1, Scheme 1-36C),[43c,d] and an addition of alkynylboranes to alkynes to afford 1-borylbut-1-en-3-yne derivatives (eq. 2, Scheme 1-36C).[43e] Cheng and co-workers disclosed a Ni-catalyzed highly regio- and stereoselective three-component coupling of alkynes, alkenes, and B_2pin_2 to provide multi-substituted alkenyl boronates in good to excellent yields (Scheme 1-36D).[43f]



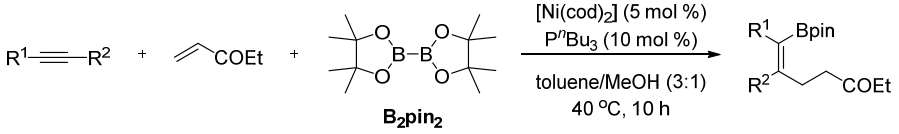
Scheme 1-36A



Scheme 1-36B



Scheme 1-36C

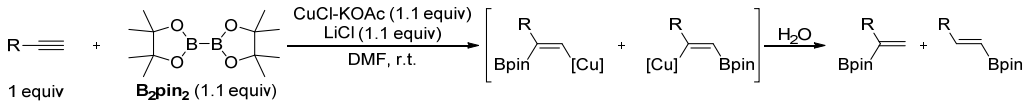


Scheme 1-36D

1.2.2.5 Cu-Catalyzed Borylation of Alkynes

Copper-catalyzed borylation of C≡C bonds has been found to be an efficient methodology for the construction of vinyl sp^2 C-B bonds,[40a,40e,44] as vinyl boronates are widely employed in cross-coupling reactions to generate new C-C bonds.

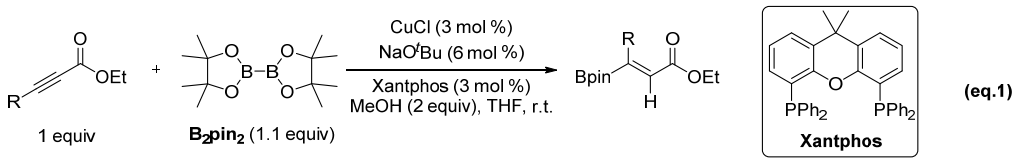
Miyaura and co-workers reported a stochiometric addition of B_2pin_2 to terminal alkynes mediated by a borylcopper species, which was proposed to be generated *in situ* from a mixture of CuCl, KOAc, LiCl and B_2pin_2, to afford either 2-boryl-1-alkenes or 1-boryl-1-alkenes at room temperature (Scheme 1-37).[45]

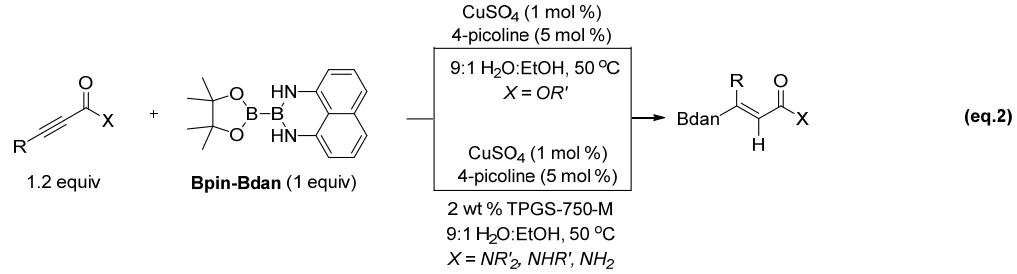


Scheme 1-37

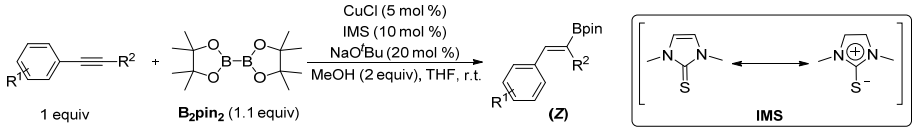
Yun and co-workers have developed a variety of efficient methodologies for the borylation of alkynes and their derivatives. In 2008, they reported the first example of catalytic and stereoselective preparation of β-borylated-α,β-ethylenic esters in high yields in the presence of CuCl and Xantphos at room temperature (eq. 1, Scheme 1-38A).[46a] This protocol was further extended to the borylation of internal alkynes bearing various electron withdrawing groups with either B_2pin_2 or Bpin-Bdan to afford vinylboronates with high regio- and stereoselectivities by both Yun and Santos (eq. 2, Scheme 1-38A), respectively.[46b,c] Santos and co-workers made additional progress in that all of their borylation reactions were carried out in aqueous media and open to air.[46c] Later on, a bis(imidazoline-2-thione)-copper(I) catalyst was employed by Yun and co-workers for the

regioselective hydroboration of internal alkynes to provide (*Z*)-alkenyl boronates as the sole products (Schemes 1-38B).[46d] The yields of alkenyl boronates were sensitive to steric effects of the alkyl groups and electronic effects of the aryl groups. When imidazoline-2-thione was replaced by P(*p*-tolyl)$_3$, the efficiency of the catalyst was further improved, as steric effects of alkyl groups had little influence on the yields (Scheme 1-38C).[46e] With a slight modification, this protocol was also applied to the synthesis of boron-substituted enynes via borylation of conjugated diynes (Scheme 1-38D).[46f] The synthesis of (*Z*)-*β*-(borylvinyl)silanes via copper-catalyzed monoborylation of silylalkynes was developed by Yun, Lee and co-workers, in which the NHC ligand (SIMes•HCl) worked efficiently for the borylation of alkyl-substituted 1-trimethylsilyl-1-alkynes, and the phosphine ligand (Xantphos) was effective for the borylation of aryl-substituted silylalkynes (Scheme 1-38E).[46g] A Cu-catalyzed highly *Z*-stereoselective hydroboration of alkynes with HBdan has been disclosed by Yun, Lee and co-workers (Scheme 1-38F).[46h] With DPEphos-ligated Cu catalysts, alkenyboron compounds were produced with excellent *Z*-stereoselectivity, and *E*-hydroboration products were provided exclusively with an SIPr-CuCl complex as the pre-catalyst. In 2011, Hoveyda and co-workers also established an alternative NHC-Cu-catalyzed hydroboration of terminal alkynes to afford internal or *α*-vinylboronates (Scheme 1-38G).[46i] The *α*-selective hydroboration of terminal alkynes (bearing an allylic O- or N-based substituent, or an aromatic substituent) exhibits high site selectivity (up to >98:2) and up to 95% yield of the pure isomer. When they replaced the *N*-aryl-substituted NHC-Cu complex with an *N*-alkyl-substituted NHC-Cu complex, *β*-selective hydroboration afforded the major products. Higher *β*-selectivity was also found for the hydroboration of alkyl-substituted terminal alkynes, regardless of the nature of the NHC-Cu complex.

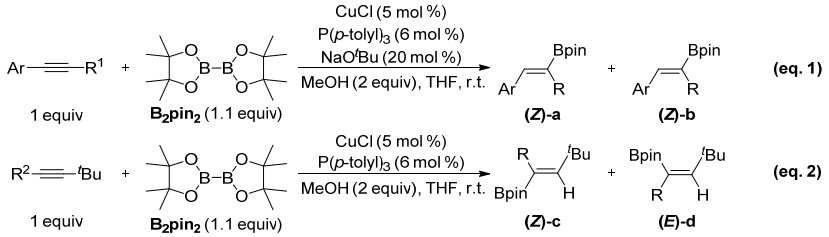




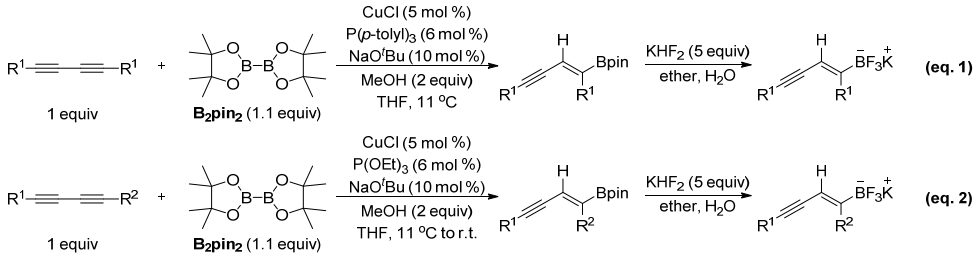
Scheme 1-38A



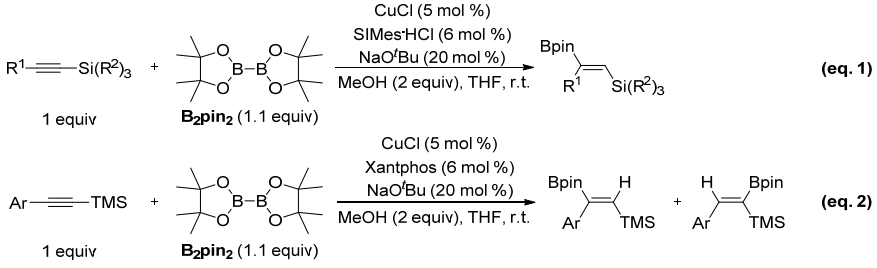
Scheme 1-38B



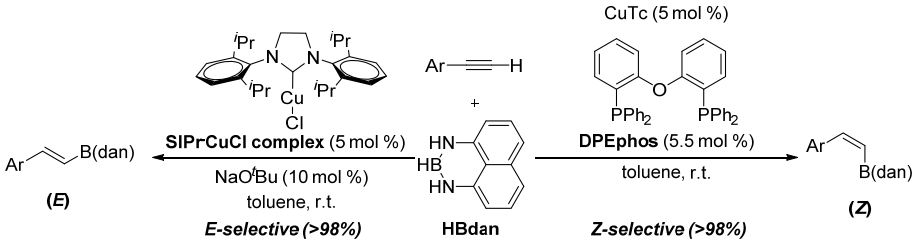
Scheme 1-38C



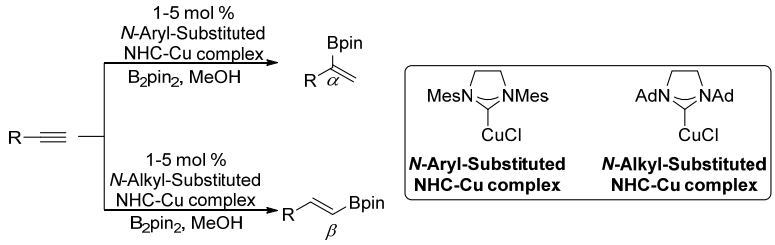
Scheme 1-38D



Scheme 1-38E

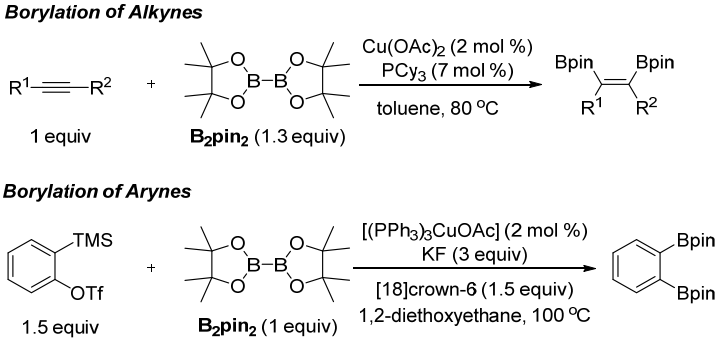


Scheme 1-38F

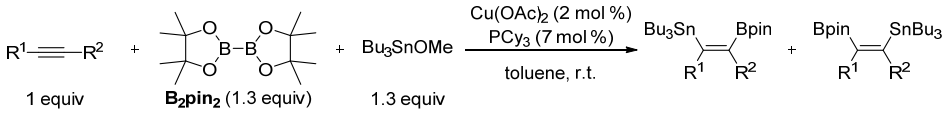


Scheme 1-38G

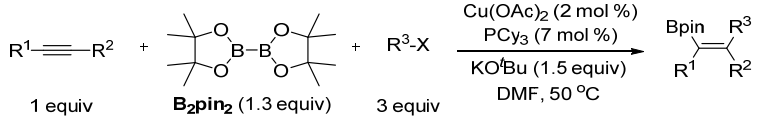
In 2012, Yoshida and co-workers demonstrated the first Cu-catalyzed diboration of alkynes and arynes to provide *cis*-*vic*-diborylalkenes (from alkynes) and *vic*-diborylarenes (from arynes) (Scheme 1-39A).[47a] This protocol was also applied to the regio- and stereoselective installation of boryl and stannyl moieties onto a C≡C bond via a three-component borylstannylation of alkynes (Scheme 1-39B).[47b] With a slight modification, a three-component carboboration of alkynes readily proceeds via copper-catalyzed addition of boryl nucleophiles and carbon electrophiles to afford diverse multisubstituted borylalkenes in a straightforward manner (Scheme 1-39C).[47c] A regio- and stereoselective hydroboration of internal alkynes with a diboron reagent masked with 1,8-diaminonaphthalene (dan) in the presence of readily available [$(PPh_3)_3CuCl$] was disclosed by Yoshida and co-workers to provide a variety of B-protected alkenylboronates in high yield (Scheme 1-39D).[47d] When they replaced [$(PPh_3)_3CuCl$] with a Cu-NHC catalyst, terminal alkynes underwent α-selective hydroboration with a masked diboron reagent to afford branched alkenylboron compounds exclusively (Scheme 1-39E).[47e]



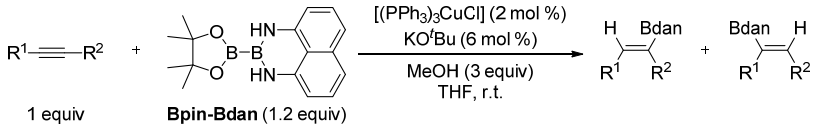
Scheme 1-39A



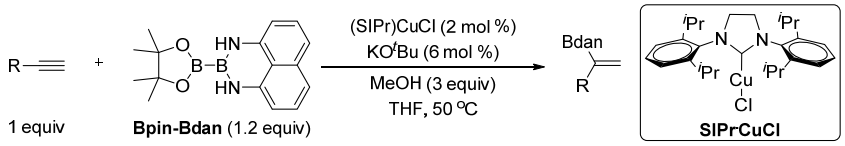
Scheme 1-39B



Scheme 1-39C

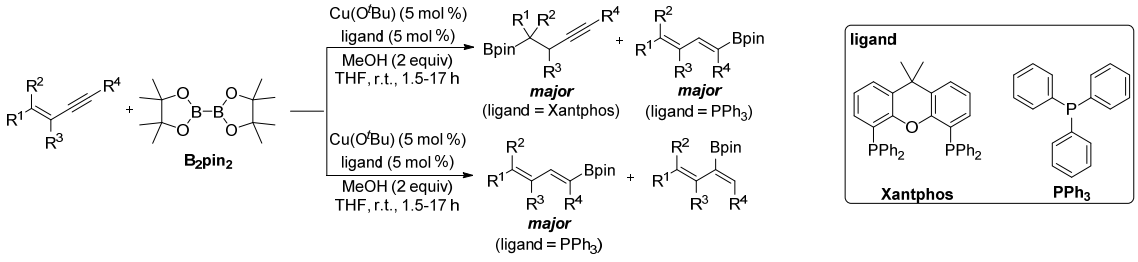


Scheme 1-39D

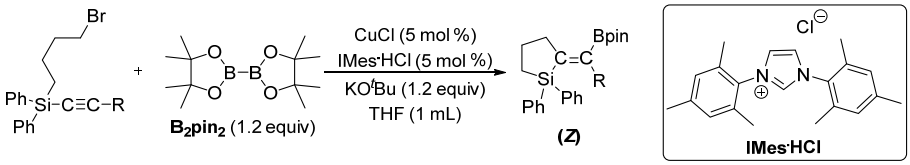


Scheme 1-39E

Ito and co-workers presented a Cu(I)-catalyzed regioselective monoborylation of 1,3-enynes bearing internal C≡C bonds to provide 1,3-dienylboronates or 3-alkynylboronates with high regioselectivity (Scheme 1-40A).[48a] Later on, a synthesis of cyclic alkenyl boronates via a stereoselective copper-catalyzed silicon-tethered alkylboration of alkynes, which exhibits high efficiency (up to 99% yield), and excellent regio- and *syn*- selectivities (*E*/*Z* < 1:99) was established by the same research group (Scheme 1-40B).[48b]



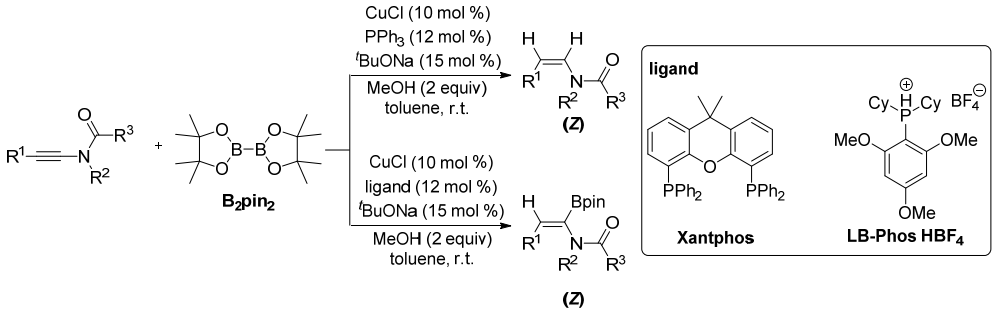
Scheme 1-40A



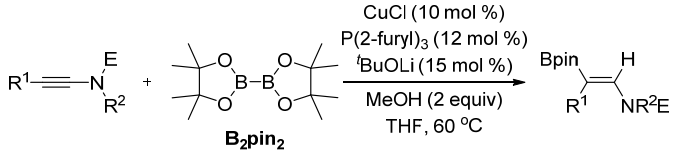
Scheme 1-40B

Zhu and co-workers developed a copper(I)-catalyzed regio- and stereoselective hydroboration of

alkynamides to afford alkenylamides and α-alkenylamide boronates (Scheme 1-41A).[49a,b] The reaction proceeds by the addition of a copper-boryl complex to *N*-alkynylamides with high regio- and stereoselectivity to provide the desired products in high yields (up to quantitative yield). Bai, Zhu and co-workers demonstrated a copper-catalyzed β-selective hydroboration of ynamides to afford (*E*)-β-alkenylamide boronates, by replacing Xantphos or LB-Phos HBF_4 with P(2-furyl)$_3$ (Scheme 1-41B).[49c]

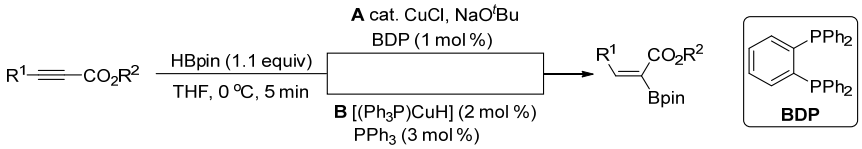


Scheme 1-41A

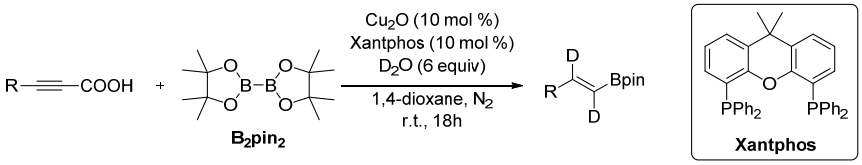


Scheme 1-41B

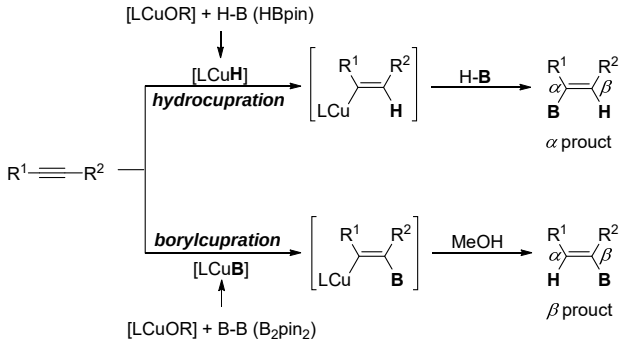
A CuH-catalyzed borylation of acetylenic esters via a 1,2-addition/transmetalation pathway to provide alkenylboronates was developed by Aue, Lipshutz and co-workers (Scheme 1-42A),[50a] which highlights a remarkable copper-to-boron transmetalation on an sp^2-like hybridized carbon, directly forming α-vinylboronates bearing a carboalkoxy group. Later on, Song and co-workers disclosed a copper-catalyzed decarboxylation borylation of alkynyl carboxylic acids to provide vinylboronates (Scheme 1-42B).[50b] The α- and β-selective hydroborations of unsymmetrical internal alkynes (Scheme 1-42C) have been investigated by Tsuji,[50c] Ma,[50d] Zhu,[50e] Qian,[50e] and Cazin,[50f] respectively. The selectivity is dominated by the choice of copper catalyst. With Cu-H species generated from HBpin, α-hydroboration of the terminal alkynes occurs as the main reaction. With Cu-B species generated from B_2pin_2, β-hydroboration of the terminal alkynes occurs as the main reaction. However, a (CAAC)CuX-catalyzed hydroboration of terminal alkynes with HBpin, which afforded (*E*)-β-hydroboration products exclusively, has been reported by Bertrand and co-workers (Scheme 1-42D).[50g]



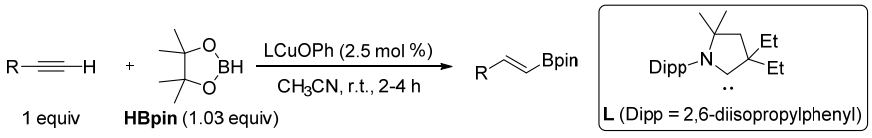
Scheme 1-42A



Scheme 1-42B

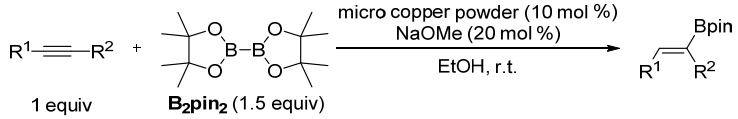


Scheme 1-42C



Scheme 1-42D

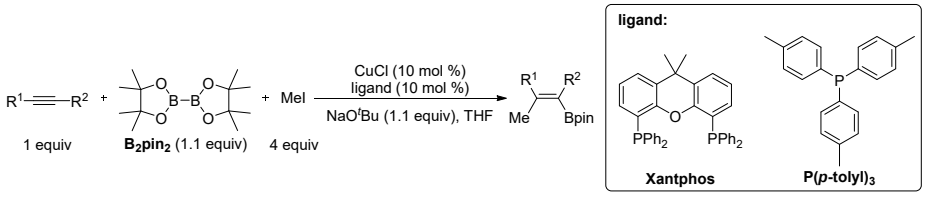
A heterogeneous copper-powder-catalyzed hydroboration of alkynes was reported by Fu, Li and co-workers in the absence of ligands (Scheme 1-43).[51] With 10 mol % copper powder (0.3-1 μm), terminal and internal alkynes were hydroborylated with high efficiency (up to 96% yield) and regioselectivity at room temperature.



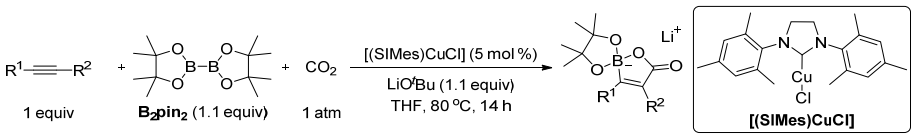
Scheme 1-43

In the past five years, copper-catalyzed carboboration[52a] of alkynes has been received more and more attention. Tortosa and co-workers established the first copper-catalyzed formal carboboration of alkynes with a C-B bond and a C-C bond created in a single catalytic cycle (Scheme 1-44A).[52b] The reaction exhibits high regioselectivity and *syn*-stereoselectivity and provides tri- and tetrasubstituted vinylboronic esters with B_2pin_2. A NHC-Cu-catalyzed boracarboxylation of alkynes

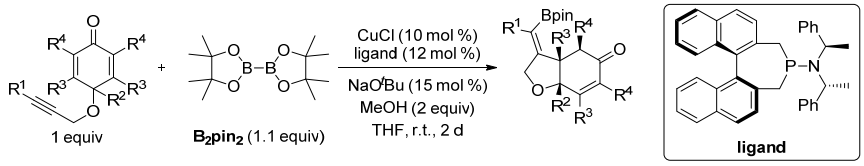
with B_2pin_2 and CO_2 has been demonstrated by Hou and co-workers (Scheme 1-44B),[52c] which affords α,β-unsaturated β-boralactone derivatives regio- and stereoselectively. Later on, the first Cu-catlayzed asymmetric borylative cyclization of 1,6-enynes bearing a cyclohexadienone group, via a tandem process involving selective β-borylation of propargylic ether and subsequent conjugate addition to cyclohexadienone, was disclosed by Tian, Lin and co-workers (Scheme 1-44C).[52d] In 2015, Zhong and co-workers presented the synthesis of boron-substituted 1,4-dienes via the Cu-catalyzed boryl-allylation of alkynes with allyl phosphate and B_2pin_2 (Scheme 1-44D),[52e] of which the regioselectivity is determined by the structure of alkynes and allyl phosphates. For example, the borylcupration of alkynes bearing one aryl substituent affords a β-boryl-α-aryl-α-alkenylcopper species, which reacts with secondary allyl phophates to provide γ-(4*E*)-selective boron-substituted 1,4-dienes. A ligand-controlled, regiodivergent, copper-catalyzed alkylboration of unactivated terminal alkynes was developed by Xiao, Fu and co-workers (Scheme 1-44E),[52f] in which *anti*-Markovnikov alkylboration products were provided when dppbz was used as the ligand, and Markovnikov alkylboration products were obtained with DMAP as the ligand. Kanai and co-workers reported the first Cu-catalyzed regio- and stereoselective borylalkylation of unactivated internal alkynes with B_2pin_2 and alkyl halides (Scheme 1-44F).[52g]



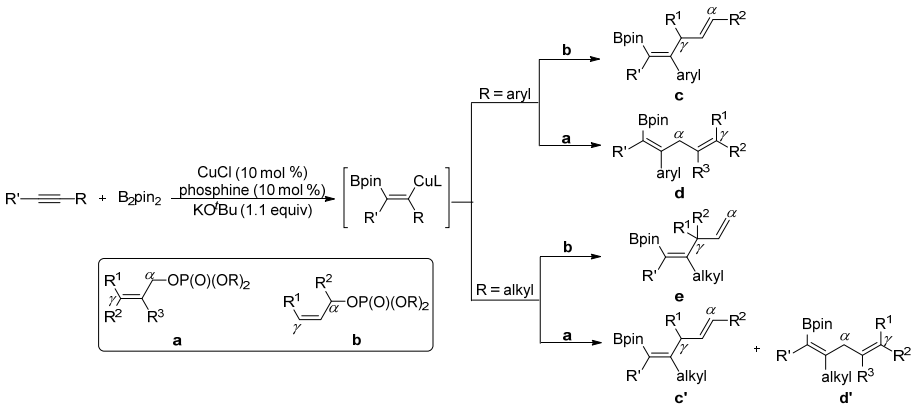
Scheme 1-44A



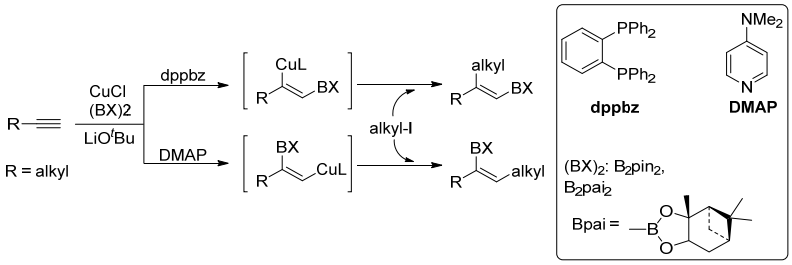
Scheme 1-44B



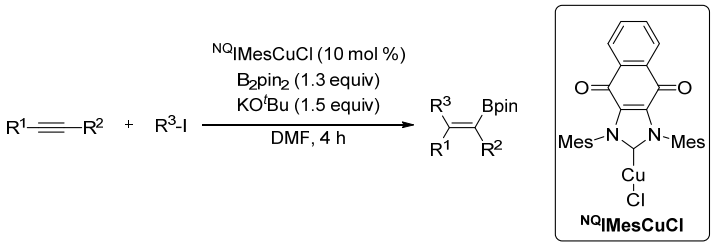
Scheme 1-44C



Scheme 1-44D



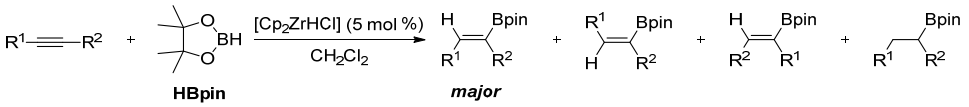
Scheme 1-44E



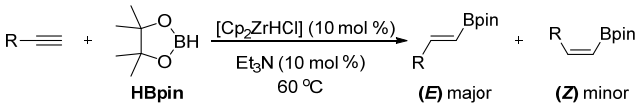
Scheme 1-44F

1.2.2.6 Zr-Catalyzed Borylation of Alkynes

The Schwarz reagent [Cp_2ZrHCl] has also been applied to the hydroboration of alkynes with HBcat (Scheme 1-45A)[53a] or HBpin (Scheme 1-45B)[53b] to afford vinyl boronates, by Srebnik[53a] and Wang,[53b] respectively.



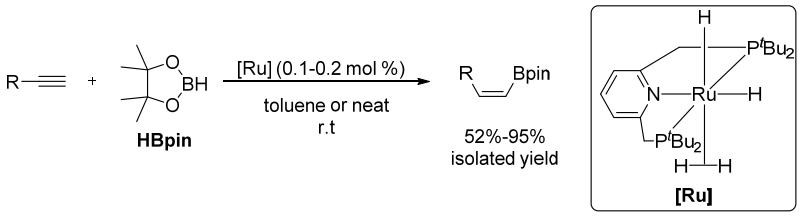
Scheme 1-45A



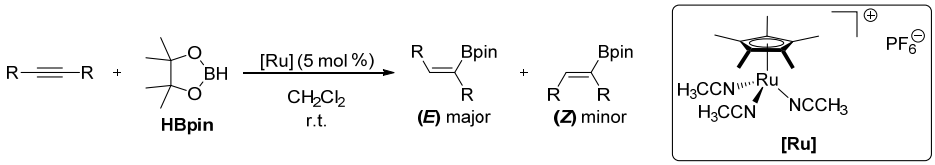
Scheme 1-45B

1.2.2.7 Ru-Catalyzed Borylation of Alkynes

Leitner and co-workers developed a Ru-catalyzed *anti*-Markovnikov addition of HBpin to terminal alkynes providing *Z*-vinylboronates under mild conditions (Scheme 1-46A),[54a] in which [Ru(PNP)(H)$_2$(HBpin)] was characterized as the active intermediate for the reaction. Fürstner and co-workers reported a cationic Ru-complex-catalyzed *trans*-selective hydroboration of internal alkynes to afford *E*-configured alkenylboronates (Scheme 1-46B).[54b]



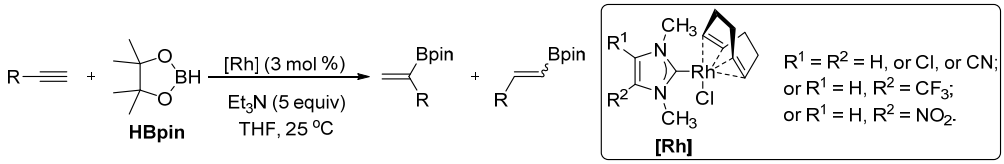
Scheme 1-46A



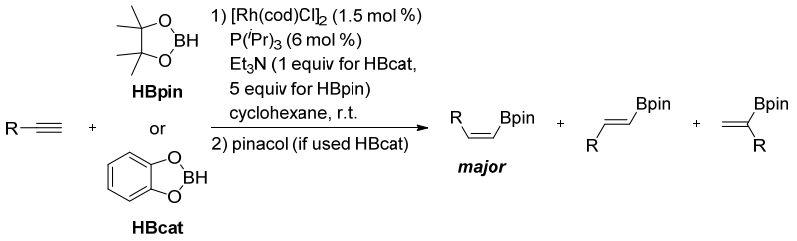
Scheme 1-46B

1.2.2.8 Rh-Catalyzed Borylation of Alkynes

An NHC-Rh-catalyzed hydroboration of phenylacetylenes was established by Bielawski and co-workers (Scheme 1-47A),[55a] in which NHCs bearing π-withdrawing groups were found to afford lower yields of products compared to σ-withdrawing analogues. However, no differences were observed in the hydroboration of 1-octyne under identical conditions. Alternatively, a Rh-catalyzed non-conventional *trans*-hydroboration of alkynes was reported initially by Miyaura (Scheme 1-47B)[55b] and subsequently reinvestigated by Fernández and co-workers,[55c] in which [Rh(cod)Cl]$_2$ and PCy$_3$ were employed as catalyst precursor and ligand, respectively. The presence of Et$_3$N favored the non-conventional *trans*-hydroboration over the classic *cis*-hydroboration. A mechanism involving Rh-vinylidene intermediates was proposed.



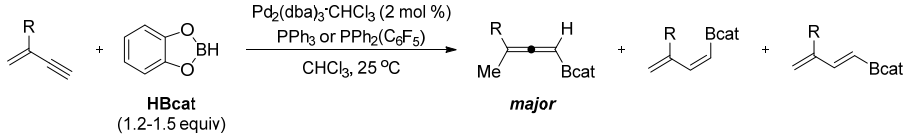
Scheme 1-47A



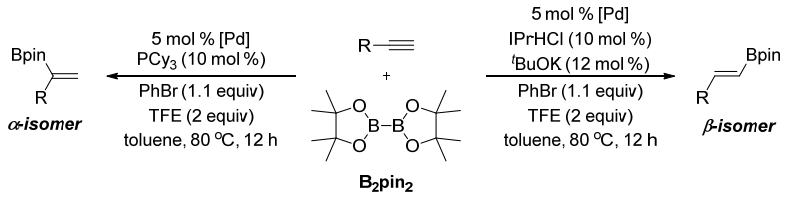
Scheme 1-47B

1.2.2.9 Pd-Catalyzed Borylation of Alkynes

Hayashi and co-workers developed a Pd(0)-catalyzed hydroboration of 1-buten-3-ynes with HBcat to provide allenylboranes selectively (Scheme 1-48A).[56a] Very recently, Prabhu and co-workers presented a synthesis of α- or β-vinylboronates via the Pd-catalyzed ligand-controlled selective hydroboration of alkynes (Scheme 1-48B),[56b] in which the high α-selectivity can be switched to furnish β-vinylboronates by changing the ligand from PCy_3 to IPr•HCl. They proposed that the reaction starts with Pd(0) and undergoes oxidative addition of PhBr to generate a Pd(II) species, which is found to furnish Ph-Bpin as the byproduct in almost quantitative yields.

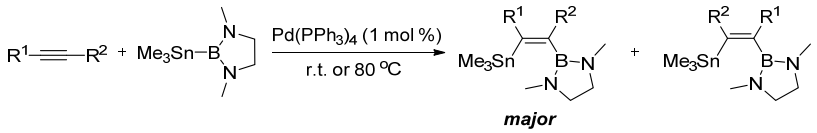


Scheme 1-48A

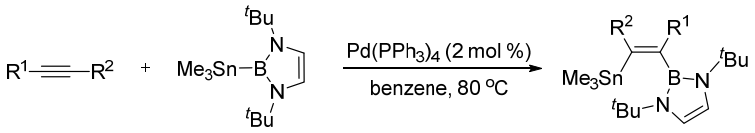


Scheme 1-48B

The synthesis of (β-stannylalkenyl)boranes was accomplished by Tanaka and co-workers via the Pd-catalyzed *cis* addition of borylstannanes to alkynes at room temperature or 80 °C (Scheme 1-49A).[57a] Weber and co-workers disclosed a $Pd(PPh_3)_4$-catalyzed insertion of alkynes into the Sn-B bond of 1,3-di-*tert*-butyl-2[(*Z*)-2-phenyl-2-trimethylstannylethenyl]-2,3-dihydro-1*H*-1,3,2-diazaborole to afford (*Z*)-alkenylboranes selectively (Scheme 1-49B).[57b]

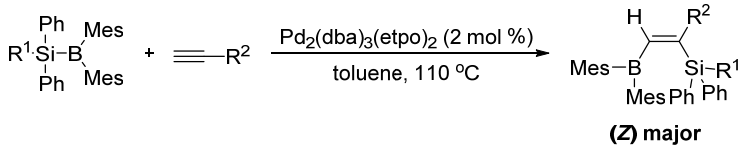


Scheme 1-49A



Scheme 1-49B

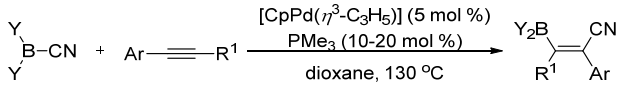
A Pd-catalyzed borylsilylation of alkynes and borylsilylative carbocyclization of diynes and an enyne compound to provide various of vinylboranes was demonstrated by Tanaka et al.[58a] Later, Birot, Pillot and co-workers developed the synthesis of organosilylboranes via a $Pd_2(dba)_2(etpo)_2$-catalyzed silylboration of terminal alkynes (Scheme 1-50).[58b]



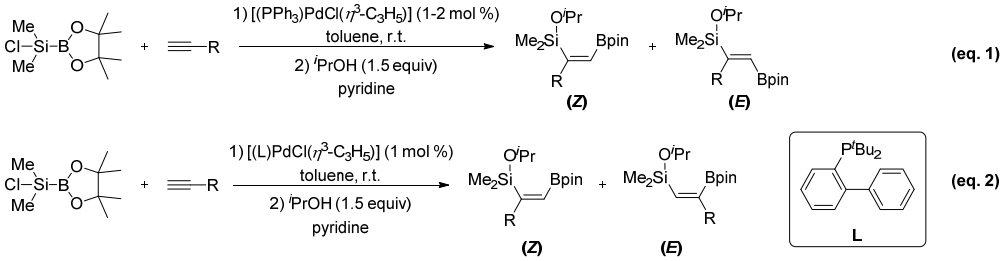
Scheme 1-50

Suginome, Murakami and co-workers reported a regio- and stereoselective synthesis of α,β-unsaturated β-boryl nitriles via Pd-catalyzed cyanoboration of alkynes (Scheme 1-51A),[59a] in which a (2-borylalkenyl)palladium(II) cyanide complex was proposed to be the key intermediate, generated via the reaction of a palladium-PMe_3 complex with a cyanoborane bearing a tethered C≡C bond.[59b] A (η^3-C_3H_5)PdCl(PPh_3)-catalyzed *cis*- and *trans*-silaboration of terminal alkynes via the addition of (chorodimethylsilyl)pinacolborane (Scheme 1-51B), of which the selectivity can be dominated by the ratio of alkynes and (chorodimethylsilyl)pinacolborane[59c] or replacement of PPh_3 with P(*t*-Bu)$_2$(biphenyl-2-yl).[59d] The (*Z*)-1-boryl-2-silylalk-1-enes were obtained in the presence of excess alkyne, and the (*E*)-1-boryl-2-silylalk-1-enes were obtained in the presence of excess silylborane,[59c] in which the *E* selectivity was also not applicable to the sterically demanding alkynes (eq. 1, Scheme 1-51B). However, the reason for this selectivity was not mentioned in the report. On the other hand, with PPh_3 as the ligand and in the presence of excess of alkyne, the (*Z*)-1-boryl-2-silylalk-1-enes were obtained as major products. With P(*t*-Bu)$_2$(biphenyl-2-yl) as the ligand, the (*E*)-2-boryl-1-silylalk-1-enes were obtained as major products (eq. 2, Scheme 1-51B). They proposed that the selectivity is derived by regioisomeric insertion of an alkyne into the B-Pd bond (Scheme 1-51C), in which path **a** is favored by employing PPh_3, and path **b** is favored by employing P(*t*-Bu)$_2$(biphenyl-2-yl). A three-component coupling of bis(dialkylamino)chloroborane, alkynes and organozirconium reagents catalyzed by Cp(η^3-C_3H_5)Pd to afford stereo-defined

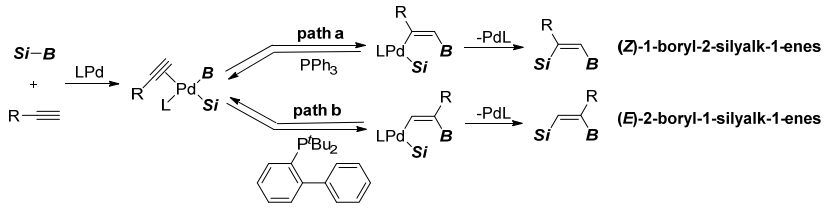
alkenylborane derivatives was developed by Suginome and co-workers (Scheme 1-51D).[59e] Later on, they disclosed a Pd-catalyzed cyclizative carboboration employing alkynes tethered to chloroborane moieties and organozirconium reagents to provide a variety of alkenylboranes, for which the selectivity is ligand-dependent (Scheme 1-51E).[59f] Monobenzo-fused 1,4-azaborines have been synthesized by Liu and co-workers, who have also demonstrated that a palladium(0) complex supported by a 1,4-azaborine-based phosphine ligand can catalyze the hydroboration of 1-buten-3-yne with unique selectivity (Scheme 1-51F).[59g]



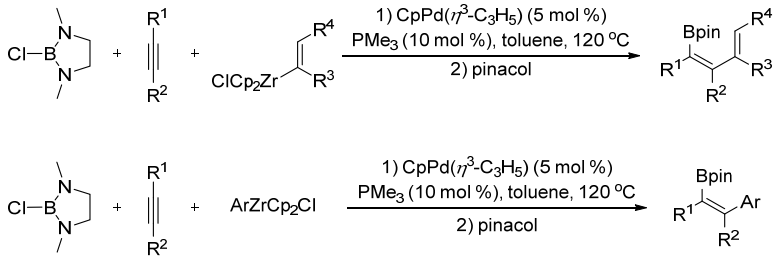
Scheme 1-51A



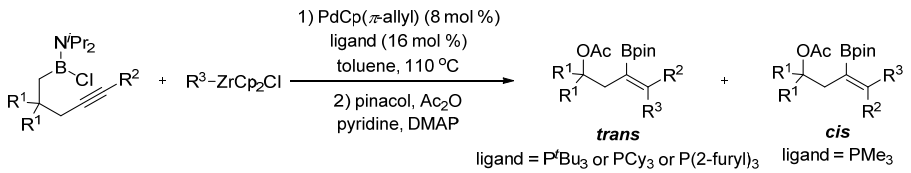
Scheme 1-51B



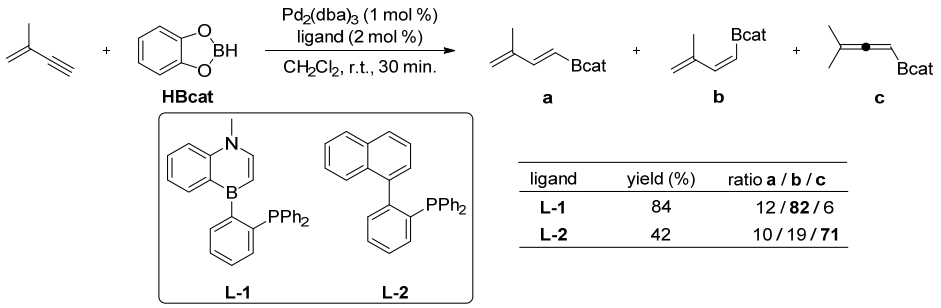
Scheme 1-51C



Scheme 1-51D



Scheme 1-51E

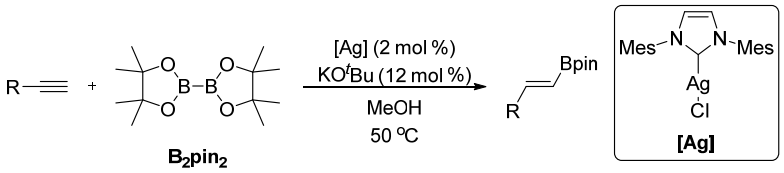


ligand	yield (%)	ratio **a** / **b** / **c**
L-1	84	12 / **82** / 6
L-2	42	10 / 19 / **71**

Scheme 1-51F

1.2.2.10 Ag-Catalyzed Borylation of Alkynes

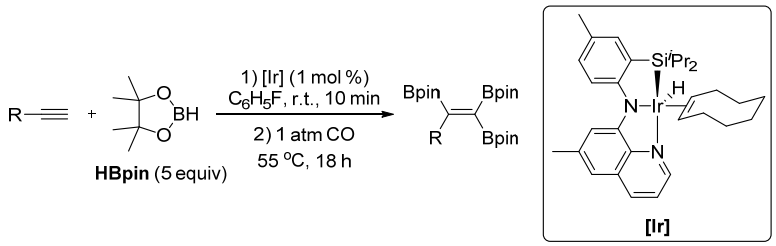
Yoshida and co-workers described a Ag(I)-NHC-catalyzed *β*-selective hydroboration of alkynes with B_2pin_2 to provide a variety of alkenylboronates (Scheme 1-52),[60] which can be extended to the hydroboration of allenes and enones.



Scheme 1-52

1.2.2.11 Ir-Catalyzed Borylation of Alkynes

A [(1,2-phenylenedioxy)boryl]iridium hydride complex was synthesized and characterized by Merola and co-workers, which was established as a model system for studying the catalytic hydroboration of alkynes.[61a] A two-step synthesis of triborylalkenes from terminal alkynes via an Ir-catalyzed tandem C-H borylation and diboration with HBpin has recently been demonstrated by Ozerov and co-workers (Scheme 1-53),[61b] in which treatment of the reaction mixture with CO in the second step generated a new catalyst *in situ* to mediate the dehydrogenative diboration of an alkynylboronate with HBpin.

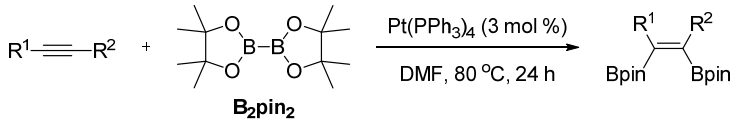


Scheme 1-53

1.2.2.12 Pt-Catalyzed Borylation of Alkynes

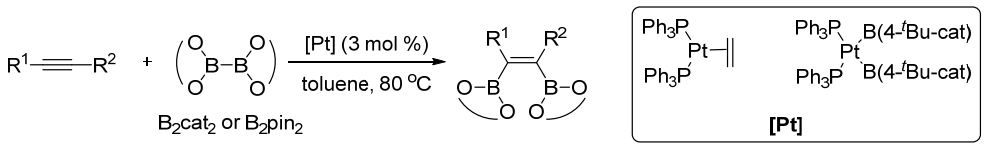
Miyaura, Suzuki and co-workers demonstrated a Pt(0)-catalyzed addition of B_2pin_2 to alkynes to

provide *cis*-1,2-bis(boryl)alkenes selectively (Scheme 1-54).[62a] This was the first catalyzed alkyne diboration. Later on, Miyaura and co-workers reported a similar Pt(0)-catalyzed addition of tetrakis(methoxy)- and bis(pinacolato)diboron to both terminal and internal alkynes, which afforded stereodefined *cis*-bis(boryl)alkenes.[62b] A *cis*-Pt($BO_2C_2Me_4$)(PPh_3)$_2$ complex was generated from the oxidative addition of B_2pin_2 to $Pt(PPh_3)_4$, which exhibited high reactivity for insertion of alkynes providing the desired product in high yields.

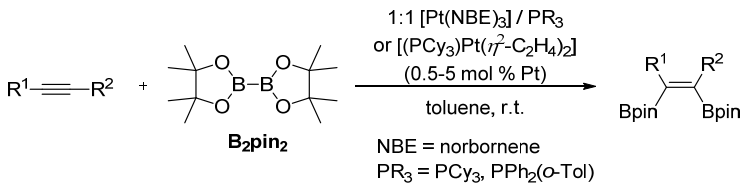


Scheme 1-54

Marder and co-workers reported that the Pt(0)-bis(phosphine) complex [(PPh_3)$_2$Pt(η-C_2H_4)] reacts with B_2cat_2 or B_2(4-^{t}Bu-Cat)$_2$ to afford *cis*-bis(boryl) Pt(II) complexes *cis*-[(PPh_3)$_2$Pt(Bcat)$_2$] or *cis*-[(PPh_3)$_2$Pt(B-4-^{t}Bu-Cat)$_2$], respectively (Scheme 1-55A).[63a] All three Pt-complexes were active catalyst precursors for the diboration of alkynes[63b] and 1,3-diynes. *In situ*-generated monophosphine Pt complexes and the isolable and stable compound [Pt(PCy_3)(η^2-C_2H_4)$_2$] were identified by the same research group as excellent catalysts for alkyne diboration at room temperature (Scheme 1-55B),[63c] in which [Pt(NBE)$_3$] was employed for the *in situ* preparation of diboration catalysts.



Scheme 1-55A



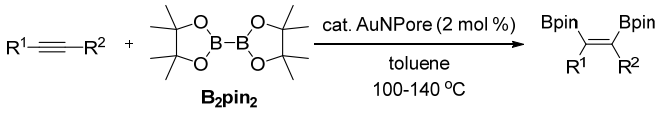
Scheme 1-55B

A related synthesis of the bis(boryl) organoplatinum complex (Ph_3P)$_2$Pt(Bcat)$_2$ was reported by Smith and co-workers via reaction of B_2cat_2 with (Ph_3P)$_2$Pt(η^2-4-octyne),[64a] which mediated the diboration of alkynes under stoichiometric and catalytic conditions.[64b] Later on, a Pt(0)-catalyzed diboration reaction of various 1-alkynylphosphonates and 1-alkynylboronates with B_2pin_2 to provide *cis*-1,2-diboronated vinylphosphonate and trisboronated alkene products was disclosed by

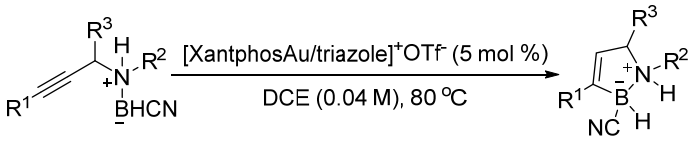
Srebnik and co-workers.[64c]

1.2.2.13 Au-Catalyzed Borylation of Alkynes

Jin and co-workers presented a diboration of alkynes with B_2pin_2 catalyzed by nanoporous gold (Scheme 1-56A),[65a] which revealed that gold is able to cleave the B-B bond of B_2pin_2 in the absence of additives. The first triazole-Au(I)-catalyzed alkyne hydroboration of propargyl amine boranenitriles to prepare 1,2-B,N-cyclopentenes in good to excellent yields was reported by Shi and co-workers (Scheme 1-56B).[65b]



Scheme 1-56A

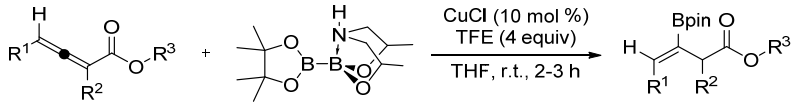


Scheme 1-56B

1.2.3 Metal-Catalyzed Borylation of Allenes

1.2.3.1 Cu-Catalyzed Borylation of Allenes

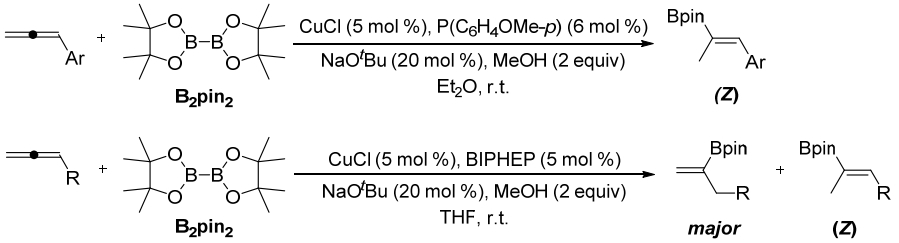
In 2011, Santos and co-workers presented a copper-catalyzed borylation of electron deficient allenoates using an sp^2-sp^3 hybridized diboron reagent to provide β-borylated β,γ-unsaturated esters with exclusive (*Z*)-double bond geometry (Scheme 1-57).[66]



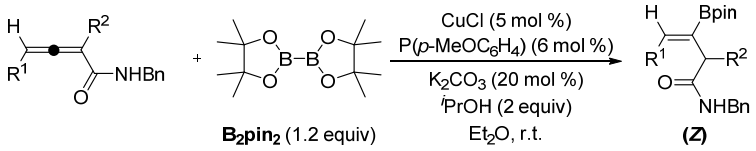
Scheme 1-57

In 2012, Ma and co-workers reported copper-catalyzed highly selective borylcuprations of allenes with B_2pin_2, which provide two different types of alkenylboronates via a ligand effect (Scheme 1-58A).[67a] With tris-(*para*-methoxyphenyl)phosphine as the ligand, the hydroboration of aryl-1,2-dienes affords 2-alken-2-yl boronates as single products with exclusive *Z*-geometry. With the bidentate phosphine ligand (2,2'-bis(diphenylphosphino)biphenyl) as the ligand, 1-alken-2-yl boronates were provided as the major products. Later on, they developed an alternative copper-catalyzed amide-controlled highly regio- and stereoselective borylcupration of substituted 2,3-allenamides with B_2pin_2 providing *Z*-β-borylated β,γ-unsaturated enamides (Scheme 1-58B).[67b]

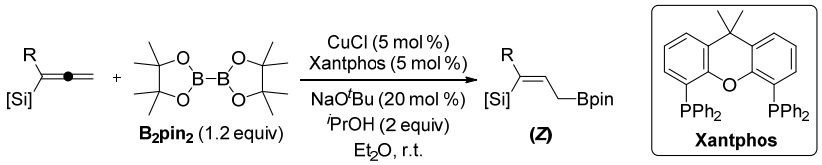
With a catalytic amount of CuCl, P(*p*-MeOC$_6$H$_4$)$_3$ as the ligand, and K$_2$CO$_3$ as well as ^{i}PrOH as the proton source, the desired products were produced with exclusive *Z* C=C bond geometry. This unique selectivity was explained by a DFT study suggesting that a borylcupration of a C=C double bond next to the amide group followed by a Cu migration forms a more stable six-membered cyclic intermediate via chelation involving the C=O moiety. Very recently, a highly regio- and stereoselective copper-catalyzed borylcupration of 1,2-allenylsilanes was reported by the same research group, which affords exclusively allylic boronates with a thermodynamically disfavored *Z* geometry (Scheme 1-58C).[67c] Control experiments show that both steric effects of the ligand and substrates determine the regio- and stereoselectivities.



Scheme 1-58A



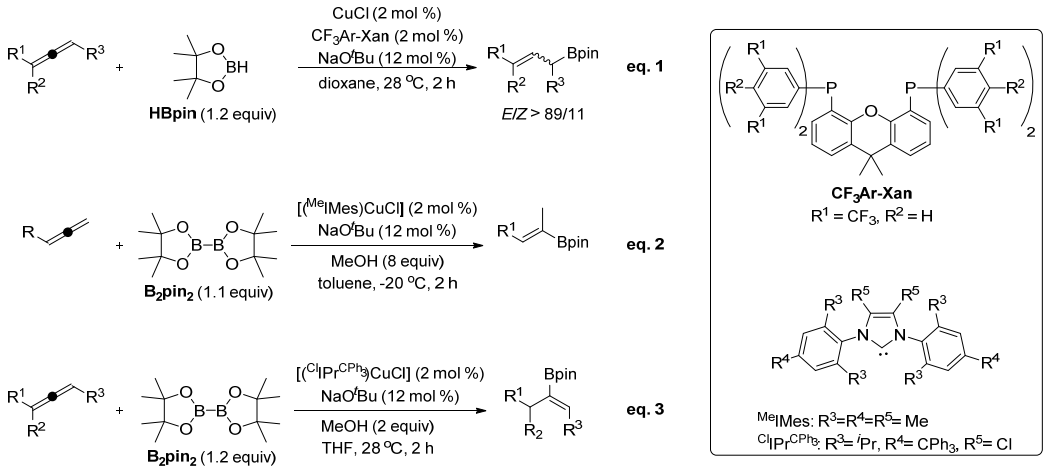
Scheme 1-58B



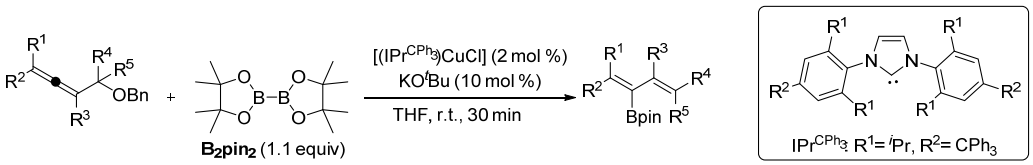
Scheme 1-58C

In the past five years, Tsuji and co-workers also developed hydroboration,[68a] boryl substitution,[68b] and carboboration[68c,d] of allenes and their derivatives. Allyl- and alkenyl-boronates are provided via a copper-catalyzed hydroboration of allenes (Scheme 1-59A).[68a] With copper hydride as the catalytic species, (*E*)-allylboronates are afforded selectively in high yields. Alkenylboronates are obtained selectively with a boryl copper complex as the catalytic species, of which the selectivity is controlled by the choice of an appropriate ligand. Alternatively, 2-boryl 1,3-butadienes can be synthesized via the copper-catalyzed borylation of α-alkoxy allenes with B$_2$pin$_2$ (Scheme 1-59B).[68b] The products are useful intermediates for the synthesis of cyclic vinyl boranes, α,β-

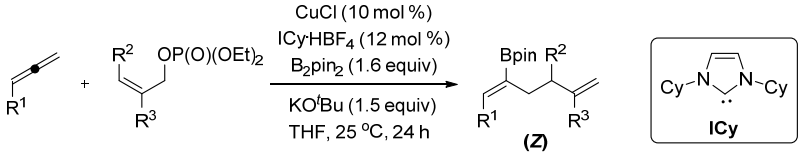
unsaturated ketones, and functionalized multisubstituted dienes. The borylation of allenes can be extended to C-C coupling reactions. Borylative allyl-allyl coupling was accomplished by using allenes, B_2pin_2, and allyl phosphates (Scheme 1-59C),[68c] which afforded boryl-substituted 1,5-diene derivatives in good to high yields with high regioselectivity and *Z* selectivity. Boraformylation of allenes with B_2pin_2 and a formate ester was carried out in the presence of a copper catalyst (Scheme 1-59D),[68d] which provided selectively *β*-boryl *β,γ*-unsaturated aldehydes in good to high yields.



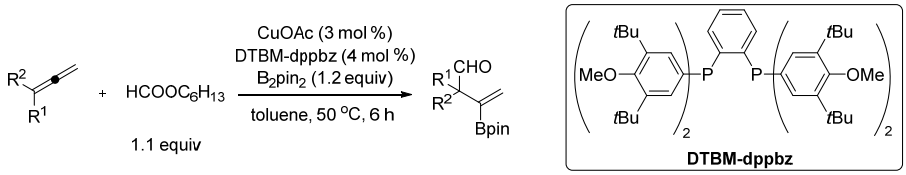
Scheme 1-59A



Scheme 1-59B



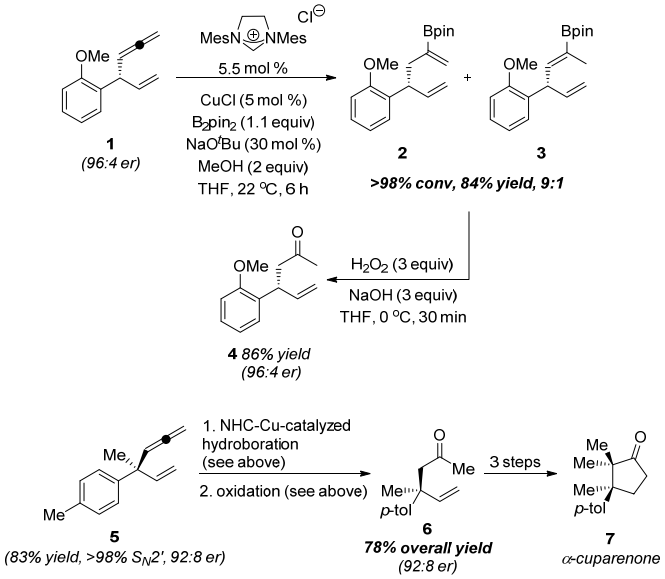
Scheme 1-59C



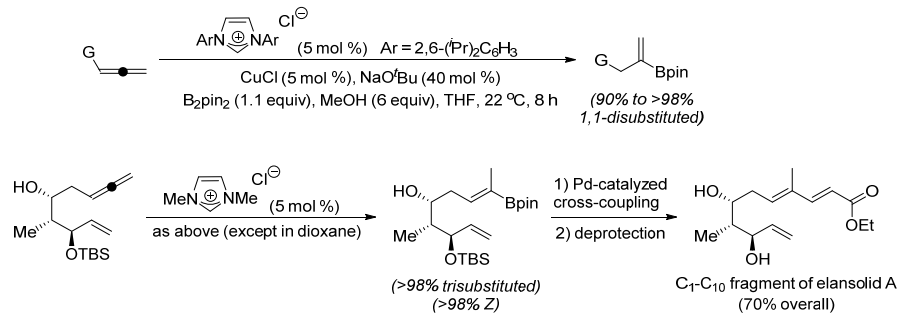
Scheme 1-59D

Hoveyda and co-workers developed the NHC-Cu-catalyzed borylation of allenes aiming at the preparation of multifunctional organoboron compounds for scalable natural product synthesis. For

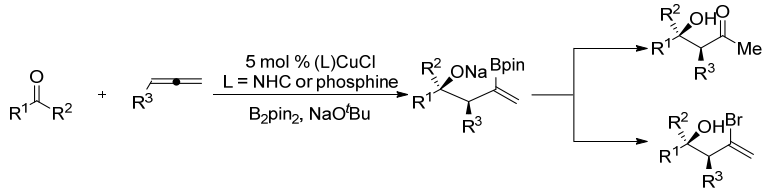
example, NHC-Cu-catalyzed hydroboration of allenyl allene **1** resulted in the formation of **2** and **3**, followed by oxidation to furnish enantiomerically enriched methyl ketone **4**, which was applied to the synthesis of α-cuparenone **7** (Scheme 1-60A).[69a] Stereoselective synthesis of the C_1-C_{10} fragment of macrolide antibiotic elansolid A was also realized via a similar methodology (Scheme 1-60B).[69b] 2-(Pinacolato)boron-substituted homoallylic alkoxides have been synthesized via a sustainable, three-component, single-vessel catalytic protocol for the chemo-, diastereo- and enantioselective conversion of B_2pin_2, monosubstituted allenes and aldehydes or ketones (Scheme 1-60C).[69c] Proto-boryl additions to 1,1-disubstituted allenes in the presence of chiral NHC-Cu complexes, B_2pin_2, and *t*-BuOH affords alkenyl-Bpin products in up to 98% yield, > 98:2 site selectivity, and 98:2 er (Scheme 1-60D).[69d] Multifunctional organoboron compounds, containing a stereogenic carbon center, a monosubstituted alkene and an easily functionalizable *Z*-trisubstituted alkenylboron group, have been prepared via a chemoselective, site-selective and diastereoselective copper-boron addition to a monosubstituted allene, followed by a similarly selective allylic substitution (Scheme 1-60E).[69e] The NHC-Cu-catalyzed carboboration of allenes has also been developed by Brown and co-workers to provide access to highly substituted and stereodefined vinyl boronic esters (Scheme 1-60F).[69f]



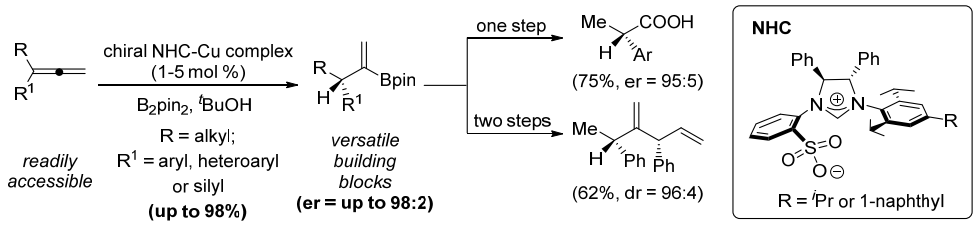
Scheme 1-60A



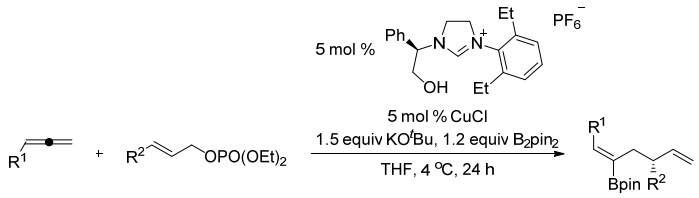
Scheme 1-60B



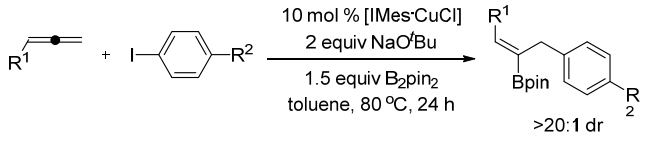
Scheme 1-60C



Scheme 1-60D



Scheme 1-60E

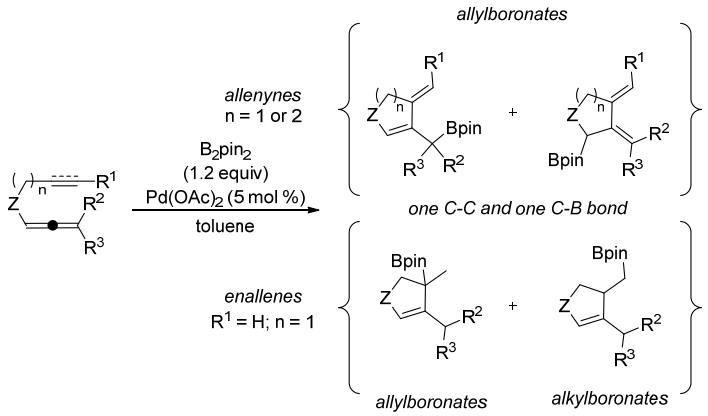


Scheme 1-60F

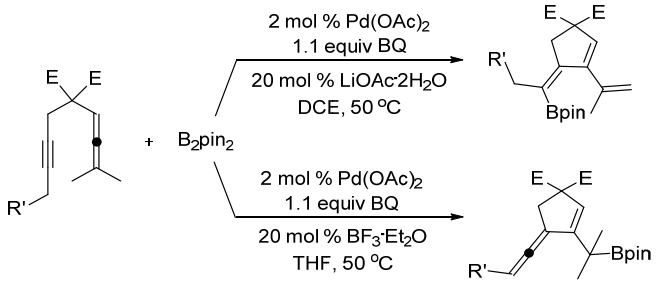
1.2.3.2 Pd-Catalyzed Borylation of Allenes

Pd-catalyzed borylative cyclizations of allenynes under either neutral or oxidative conditions have been developed by Cárdenas and Bäckvall, respectively. With Cárdenas' protocol, the borylative cyclization of 1,5- and 1,6-allenynes and 1,5-enallenes with B_2pin_2 affords synthetically useful allylboronates in a formal hydroborylative carbocyclization reaction (Scheme 1-61A).[70a] Bäckvall

and co-workers demonstrated an unprecedented selective Pd^{II}-catalyzed carbocyclization/borylation of allenynes under oxidative conditions. Trienes or vinylallenes were provided selectively by controlling the reaction conditions (Scheme 1-61B).[70b]



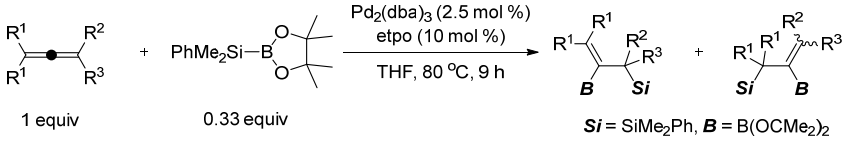
Scheme 1-61A



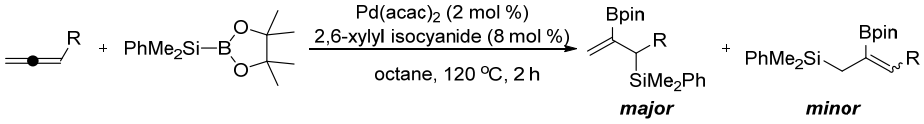
Scheme 1-61B

The Pd-catalyzed regioselective addition of a borylsilane to allenes[71a] has been developed as an efficient methodology for the construction of vinyl C(sp^2)-B bonds by Tanaka,[71b] Ito,[71c,d] Suginome,[71d-g] Murakami[71e] and their co-workers. In 1999, Tanaka and co-workers reported a $Pd_2(dba)_3$-catalyzed addition of borylsilane to 1,2-dienes, which affords high yields of alkenylboronates bearing allylsilane moieties (Scheme 1-62A).[71b] Alternatively, a regioselective silaboration of allenes catalyzed by a $Pd(acac)_2$/2,6-xylyl isocyanide complex was reported by Ito and co-workers (Scheme 1-62B).[71c] A detailed investigation of the silaboration of allenes was reported by Suginome, Ito and co-workers.[71d] With terminal allenes bearing electron-donating substituents, the Si-B bond added to the internal C=C bond with the regioselective B-C and Si-C bond formation at the central and substituted carbon atoms of allenes. With allenes bearing electron-withdrawing groups, the silaborane preferably added to the terminal C=C bond with exclusive Si-C bond formation at the terminal carbon atom. An enantioface-selective Cp(allyl)Pd-catalyzed silaboration of terminal allenes via double asymmetric induction was reported by Suginome,

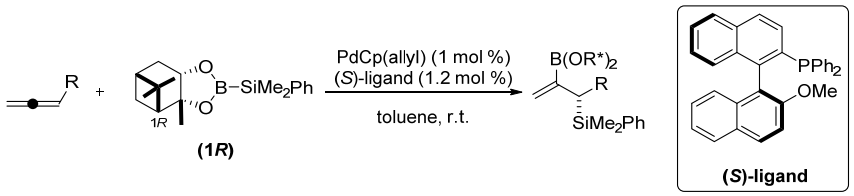
Murakami and co-workers (Scheme 1-62C).[71e] A palladium-catalyzed asymmetric silaboration of terminal allenes was also reported by Suginome and co-workers, which affords synthetically useful β-borylallylsilanes with high ee (Scheme 1-62D).[71f] They also disclosed a palladium-catalyzed highly enantioface-selective silaboration of allenes bearing an α-stereogenic center via a double asymmetric induction system employing a chiral silylborane and a chiral ligand, which provides enantiopure diastereomers of β-borylallylsilanes (Scheme 1-62E).[71g]



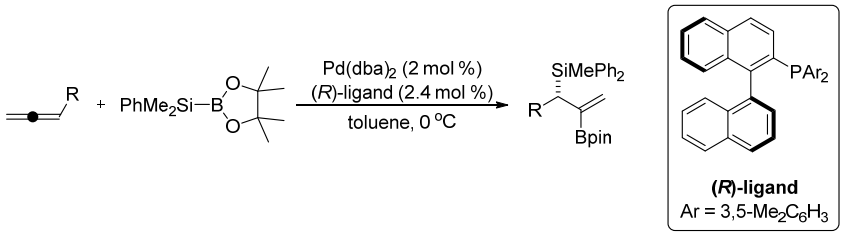
Scheme 1-62A



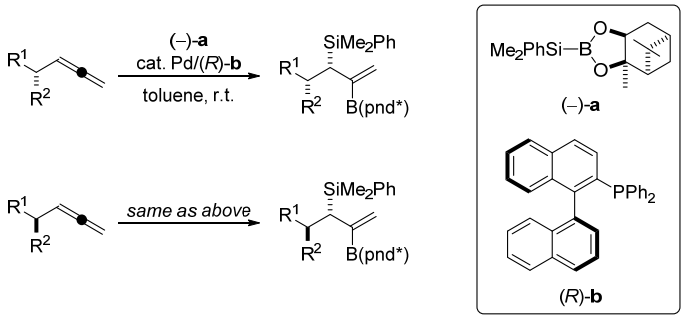
Scheme 1-62B



Scheme 1-62C



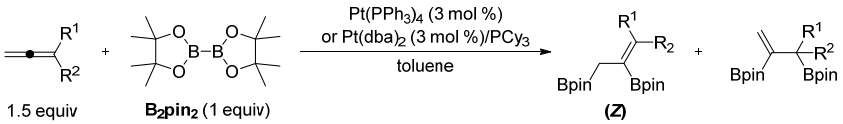
Scheme 1-62D



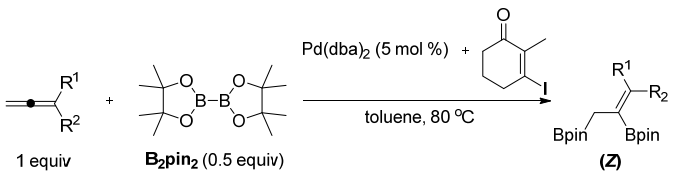
Scheme 1-62E

1.2.4 Metal-Catalyzed Diboration of Allenes

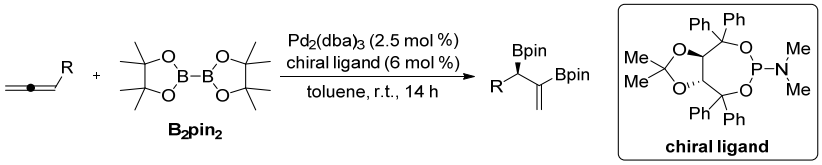
The diboration of allenes has been reported by the groups of Miyaura,[72a] Cheng,[72b] and Morken.[72c-f] Miyaura and co-workers demonstrated the first Pt-catalyzed diboration of allenes (Scheme 1-63A),[72a] which afforded 2-boryl allylboronates in excellent yields. With monosubstituted allenes, the addition of B_2pin_2 occurred at internal C=C bonds, and terminal diboration products were obtained regioselectively when the sterically bulky phosphine ligand PCy_3 and 1,1-disubstituted allenes were employed. A Pd-catalyzed diboration of allenes in the presence of organic iodides was disclosed by Cheng and co-workers (Scheme 1-63B),[72b] which provided predominantly (*Z*)-2-boryl allylboronates. The diboration reaction was proposed to proceed via the oxidative addition of an I-B bond to the palladium center instead of the oxidative addition of a B-B bond to the metal center. The asymmetric diboration of allenes was established by Morken and co-workers.[72c-f] Access to chiral allene diboration products in an enantioselective fashion provides new opportunities for asymmetric synthesis through a tandem reaction sequence (Scheme 1-63C),[72c-e] in which they employed prochiral allenes as substrates and $Pd_2(dba)_3$ as the catalyst precursor. The chiral allylboron intermediate is a versatile reagent for the allylation of carbonyls (Scheme 1-63D),[72d] and it can be reacted, *in situ*, with a hydroborating reagent to form a novel triboron intermediate, followed by cross-coupling/oxidation to provide chiral diols in a concise single-pot fashion (Scheme 1-63E).[72e] Isotopic-labeling experiments, stereodifferentiating reactions, kinetic analysis, and computational studies suggest that the catalytic cycle proceeds by a mechanism involving rate-determining oxidative addition of the diboron reagent to Pd followed by coordination and insertion of the more accessible terminal alkene of the allene substrate, by a mechanism that directly provides the η^3 π-allyl complex in a stereospecific, concerted fashion.[72f]



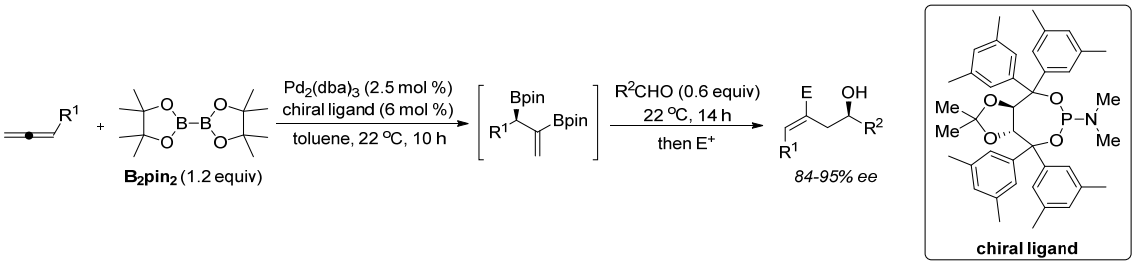
Scheme 1-63A



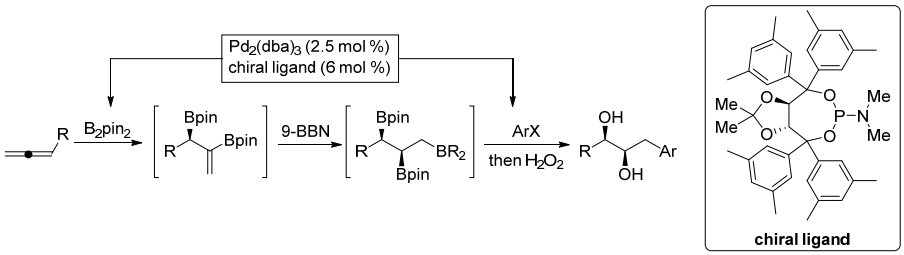
Scheme 1-63B



Scheme 1-63C



Scheme 1-63D

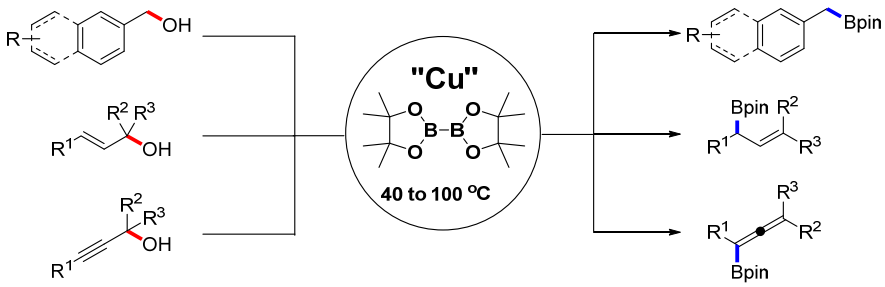


Scheme 1-63E

As organoboron compounds have found significant applications in organic synthesis,[73] our group has long been focused on the development of metal-catalyzed direct borylation reactions of C-H and C-halogen bonds,[74] in which we employed not only traditional iridium- or rhodium-complexes as catalysts, but also novel copper- and zinc-complexes. In this thesis, I employed more readily available starting materials, such as alcohols and alkenes, to synthesize benzyl-, allyl-, vinyl-, and allenyl-boronates and their derivatives.

Chapter Two

Synthesis of Benzyl-, Allyl-, and Allenyl-boronates via Copper-catalyzed Borylation of Alcohols



mild conditions, 40 examples, up to 95% yield

2. Synthesis of Benzyl-, Allyl-, and Allenyl-boronates via Copper-catalyzed Borylation of Alcohols

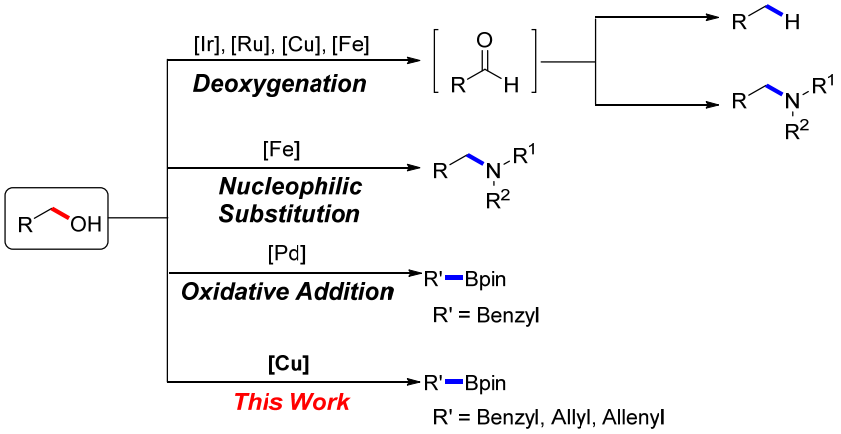
2.1 Introduction

Concerns about environmental and economic issues have directed synthetic chemistry toward the development of efficient methods for forming desired products from readily available and environmentally benign feedstocks. From this point of view, alcohols constitute a highly attractive class of starting material as they are inexpensive and often easily derived from natural sources. The main challenge lies in the activation of sp^3 C–O bonds of alcohols by metal-catalysts, as the OH group is not readily replaced by other nucleophiles.[75a] In recent years, metal-catalyzed deoxygenation and functionalization (alkylation[75a-d] and amination[75e]) of alcohols have been successfully developed. Saito and co-workers reported an iron-catalyzed amination of alcohols via nucleophilic substitution.[76]

2.2 Motivation

Organoboron compounds have found widespread application in organic synthesis.[73] For example, benzylic trifluoroborates can release benzyl radicals through a single-electron transfer pathway,[77] and both allyl-[73] and allenyl-[73,78] boronates are useful synthetic intermediates in organic synthesis. However, the preparation of benzyl-, allyl-, allenyl-boronates still remains a challenge,[73] due to poor substrate scope of the classical methodology using Grignard or lithium reagents.[79] In the past 15 years, metal-catalyzed borylation[2a,b] of benzylic[1,3a,4,13] and allylic[9,10a,11a,b,18] C–X (X = H, halogen) bonds has been developed. Marder and others have recently focused on the development of copper-[12a,15] or zinc-[74c-e,80] catalyzed borylations of organic halides to synthesize various organoboron compounds including benzyl- and allyl-boronates.[15a,b] Alternatively, the borylation of sp^3 C–O bonds, which is more desirable, has emerged as an efficient way to construct sp^3 C–B bonds. Palladium catalysts have been found to be capable of borylation of both benzylic[21,81] and allylic[27a,28b,d,f,30] sp^3 C–O bonds. Recently, a few examples have established that nickel catalysts have the same potential for the borylation of sp^3 C–O bonds.[20,22] Ito and Sawamura developed the copper-catalyzed synthesis of allyl- and allenyl-boronates from organic carbonates.[24a,c,25,82] Szabó and co-workers reported bimetallic (Pd and Cu) catalysis to prepare allenylboronates, in which CuI was employed as the co-catalyst.[83] Nevertheless, the borylations of benzyl- and allyl-alcohols require different Pd catalysts and different conditions. [21,28b,d,f,30,81] Pd-catalyzed borylation of

acyclic allylic alcohols gives, preferentially, linear products. [27a,28b,d,f,30] The development of a general and straightforward methodology for direct borylation of alcohols to obtain branched acyclic products is highly desirable. This chapter presents the first copper-catalyzed direct borylation of alcohols to synthesize allyl-, benzyl-, and allenyl-boronates under mild conditions (Scheme 2-1).



Scheme 2-1. Transition Metal-catalyzed Functionalization of sp^3 C–O Bonds of Alcohols.

2.3 Results and Discussion

2.3.1 Optimization of Reaction Conditions

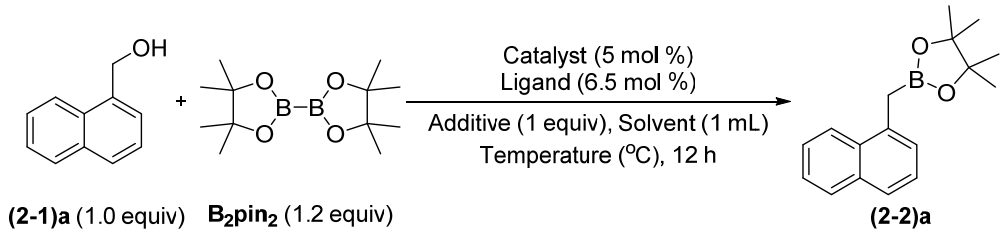
Initially, 5 mol % $CuCl_2$ was employed as the catalyst precursor and Xantphos as the ligand for the borylation of **(2-1)a**. The addition of 1 equiv $Ti(O^iPr)_4$ can transform an OH group into a better leaving group.[21] However, the desired product (**2-2)a** could not be detected by GC-MS after 24 h at 100 °C (Table 2-1, entry 1). When $CuCl_2$ was replaced with $Cu(OTf)_2$, (**2-2)a** was generated in a moderate yield of 48% (Table 2-1, entry 2). Surprisingly, when $[Cu(MeCN)_4]^{2+}[BF_4^-]_2$ was employed as the copper source, which is more Lewis acidic and readily reacts with Xantphos, (**2-2)a** was obtained in a 94% yield (Table 2-1, entry 3). Other coper salts, such as $Cu(OAc)_2$, $[Cu(MeCN)_4]^{+}[BF_4]^{-}$, also gave (**2-2)a** in yields of 76% and 81%, respectively (Table 2-1, entries 4 and 5). Control experiments suggest that the benzylic sp^3 C-O activation and borylation is catalyzed by $[Cu(MeCN)_4]^{2+}[BF_4^-]_2$ (Table 2-1, entry 6), in combination with the supporting ligand (Xantphos), and that $Ti(O^iPr)_4$ is also crucial for the reaction as it can turn the OH group into a good leaving group[21] (Table 2-1, entries 7 and 8). Next, other *P*- or *N*-containing ligands were tested for this reaction. When 6.5 mol % of PCy_3 was added to this reaction, the desired product (**2-2)a** was obtained in a yield of 52% (Table 2-1, entry 9). P(*p*-tol)$_3$ and dppe were not as efficient as Xantphos,

as (**2-2)a** could be obtained in yields of only 25% and 31%, respectively (Table 2-1, entries 10 and 11). Nevertheless, other ligands, such as dppp, dppbe, Ru-phos and dtbpy, did not promote the reaction at all (Table 2-1, entries 12-15). When the reaction was run at 75 ºC, the yield of (**2-2)a** was significantly reduced to 20% (Table 2-1, entry 16). When THF, toluene or benzene was used as the solvent for this reaction, the desired product (**2-2)a** was obtained in 81%, 67% and 80% yields, respectively (Table 2-1, entries 17-19). Other Lewis- or Brønsted acids were also tested, such as $AlCl_3$, Et_3B and TFA, but none of them provided the desired product (**2-2)a** (Table 2-1, entries 20-22).

Next, 10 mol % of $CuCl_2$ was employed as the catalyst precursor and Xantphos as the ligand for the borylation of **(2-3)f**, but less than 5% of **(2-4)f** was detected by GC-MS after 24 h at 60 ºC (Table 2-2, entry 1). When $CuCl_2$ was replaced with $Cu(OTf)_2$, only a trace amount of **(2-4)f** was observed by GC-MS (Table 2-2, entry 2). Surprisingly, when $[Cu(MeCN)_4]^{2+}[BF_4^-]_2$ was employed as the copper source, **(2-4)f** was obtained in a 96% yield (Table 2-2, entry 3). However, the yield of **(2-4)f** decreased to 73%, when the loading of catalyst and ligand were decreased (Table 2-2, entry 4). Other copper salts, such as $Cu(OAc)_2$ and $[Cu(MeCN)_4]^+[BF_4]^-$, also gave **(2-4)f** in yields of 76% and 72%, respectively (Table 2-2, entries 5 and 6). Control experiments suggest that the allylic $C(sp^3)$-O activation and borylation is catalyzed by $[Cu(MeCN)_4]^{2+}[BF_4^-]_2$ (Table 2-2, entry 7), in combination with the supporting ligand (Xantphos), and that $Ti(O^iPr)_4$ is also crucial for the reaction (Table 2-2, entries 8 and 9). When $[Cu(MeCN)_4]^{2+}[BF_4^-]_2$ was replaced with $[Cu(MeCN)_4]^+[BF_4]^-$ in the absence of Xantphos, the yield of **(2-4)f** dropped to 5% (Table 2-2, entry 10). Next, other *P*- or *N*-containing ligands were tested for this reaction in combination with $[Cu(MeCN)_4]^{2+}[BF_4^-]_2$. When 13 mol % of PCy_3 was added, the desired product **(2-4)f** was obtained in a yield of 52% (Table 2-2, entry 11). P(*p*-tol)$_3$, dppe, dppbe and dppp were not as efficient as Xantphos, as **(2-4)f** was obtained in yields of only 30%, 22%, 23%, and 10%, respectively (Table 2-2, entries 12-15). Less than 5% of **(2-4)f** was detected by GC-MS with dtbpy as ligand (Table 2-2, entry 16). When the reaction temperature was lowered to 40 ºC, the yield of **(2-4)f** was significantly reduced to 34% (Table 2-2, entry 17). No **(2-4)f** was detected by GC-MS, when the reaction was run at room temperature for 24 h (Table 2-2, entry 18). THF, toluene and benzene were also tested as solvents for this reaction, and **(2-4)f** was obtained in 81%, 67% and 80% yields, respectively (Table 2-2, entries 19-21). Other Lewis- or Brønsted acids, such as $AlCl_3$, Et_3B and TFA, failed to promote the

formation of **(2-4)f** (Table 2-2, entries 22-24).

Table 2-1. Condition Screening for Benzylic Alcohols[a]

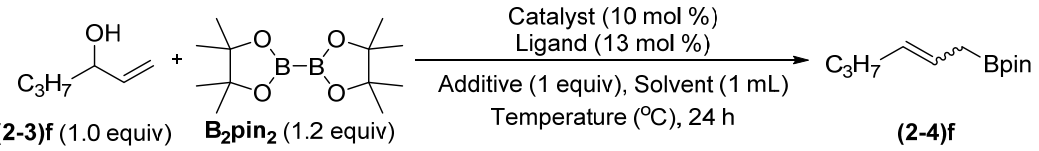


(2-1)a (1.0 equiv) **B_2pin_2** (1.2 equiv) **(2-2)a**

Entry	Catalyst	Ligand	Additive	Temperature (°C)	Solvent	Yield (%)[b]
1	$CuCl_2$	Xantphos	$Ti(O^iPr)_4$	100	MTBE	N.D.[c]
2	$Cu(OTf)_2$	Xantphos	$Ti(O^iPr)_4$	100	MTBE	48
3	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	Xantphos	$Ti(O^iPr)_4$	100	MTBE	94(87[d])
4	$Cu(OAc)_2$	Xantphos	$Ti(O^iPr)_4$	100	MTBE	76
5	$[Cu(CH_3CN)_4]^{+}[BF_4]^-$	Xantphos	$Ti(O^iPr)_4$	100	MTBE	81
6	-	Xantphos	$Ti(O^iPr)_4$	100	MTBE	N.D.[c]
7	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	-	$Ti(O^iPr)_4$	100	MTBE	N.D.[c]
8	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	Xantphos	-	100	MTBE	N.D.[c]
9	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	PCy_3	$Ti(O^iPr)_4$	100	MTBE	52
10	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	P(*p*-tol)$_3$	$Ti(O^iPr)_4$	100	MTBE	25
11	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	dppe	$Ti(O^iPr)_4$	100	MTBE	31
12	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	dppp	$Ti(O^iPr)_4$	100	MTBE	N.D.[c]
13	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	dppbe	$Ti(O^iPr)_4$	100	MTBE	N.D.[c]
14	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	Ru-phos	$Ti(O^iPr)_4$	100	MTBE	N.D.[c]
15	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	dtbpy	$Ti(O^iPr)_4$	100	MTBE	N.D.[c]
16	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	Xantphos	$Ti(O^iPr)_4$	75	MTBE	20
17	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	Xantphos	$Ti(O^iPr)_4$	100	THF	81
18	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	Xantphos	$Ti(O^iPr)_4$	100	Toluene	67
19	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	Xantphos	$Ti(O^iPr)_4$	100	Benzene	80
20	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	Xantphos	$AlCl_3$	100	MTBE	N.D.[c]
21	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	Xantphos	Et_3B	100	MTBE	N.D.[c]
22	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	Xantphos	TFA	100	MTBE	N.D.[c]

[a] Standard condition: All reactions were carried out on a 0.2 mmol scale. **(2-1)a** (1 equiv), B_2pin_2 (0.24 mmol, 1.2 equiv), catalyst (5 mol %), ligand (6.5 mol %), additive (0.2 mmol, 1 equiv), solvent (1 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] N.D. = not detected. [d] Isolated yield.

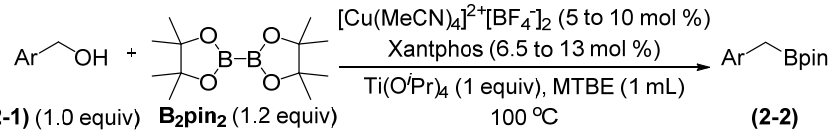
Table 2-2. Condition Screening for Allylic Alcohols[a]

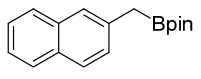


Entry	Catalyst	Ligand	Additive	Temperature (°C)	Solvent	Yield (%)[b]
1	$CuCl_2$	Xantphos	$Ti(O^iPr)_4$	60	MTBE	< 5
2	$Cu(OTf)_2$	Xantphos	$Ti(O^iPr)_4$	60	MTBE	Trace
3	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	Xantphos	$Ti(O^iPr)_4$	60	MTBE	96(89[c])
4	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	Xantphos	$Ti(O^iPr)_4$	60	MTBE	73[d]
5	$Cu(OAc)_2$	Xantphos	$Ti(O^iPr)_4$	60	MTBE	76
6	$[Cu(CH_3CN)_4]^+[BF_4]^-$	Xantphos	$Ti(O^iPr)_4$	60	MTBE	72
7	-	Xantphos	$Ti(O^iPr)_4$	60	MTBE	N.D.[e]
8	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	-	$Ti(O^iPr)_4$	60	MTBE	6
9	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	Xantphos	-	60	MTBE	N.D.[e]
10	$[Cu(MeCN)_4]^+[BF_4]^-$	-	$Ti(O^iPr)_4$	60	MTBE	5
11	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	PCy_3	$Ti(O^iPr)_4$	60	MTBE	52
12	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	P(*p*-tol)$_3$	$Ti(O^iPr)_4$	60	MTBE	30
13	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	dppe	$Ti(O^iPr)_4$	60	MTBE	22
14	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	dppbe	$Ti(O^iPr)_4$	60	MTBE	23
15	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	dppp	$Ti(O^iPr)_4$	60	MTBE	10
16	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	dtbpy	$Ti(O^iPr)_4$	60	MTBE	< 5
17	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	Xantphos	$Ti(O^iPr)_4$	40	MTBE	34
18	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	Xantphos	$Ti(O^iPr)_4$	r.t.	MTBE	N.D.[e]
19	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	Xantphos	$Ti(O^iPr)_4$	60	THF	81
20	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	Xantphos	$Ti(O^iPr)_4$	60	Toluene	67
21	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	Xantphos	$Ti(O^iPr)_4$	60	Benzene	80
22	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	Xantphos	$AlCl_3$	60	MTBE	N.D.[e]
23	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	Xantphos	Et_3B	60	MTBE	N.D.[e]
24	$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$	Xantphos	TFA	60	MTBE	N.D.[e]

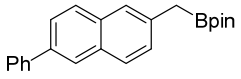
[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **(2-3)f** (1 equiv), B_2pin_2 (0.24 mmol, 1.2 equiv), catalyst (10 mol %), ligand (13 mol %), additive (0.2 mmol, 1 equiv), solvent (1 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] Isolated yield. [d] $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ (5 mol %), Xantphos (6.5 mol %). [e] N.D. = Not detected.

2.3.2 Investigation of Reaction Scope

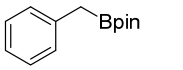




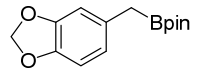
(2-2)b (73%, 12 h)[a]



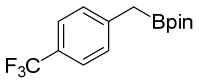
(2-2)c (79%, 8 h)[a]



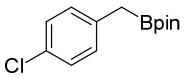
(2-2)d (73%, 30 h)[b]
(2-2)d (54%, 24 h)[b,d]



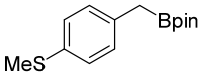
(2-2)e (95%, 24 h)[a]



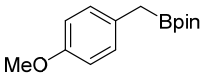
(2-2)f (92%, 20 h)[a]



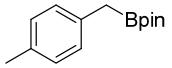
(2-2)g (69%, 22 h)[a]



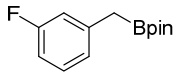
(2-2)h (76%, 24 h)[b]



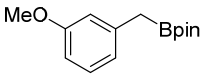
(2-2)i (63%, 16 h)[a]



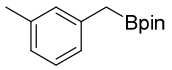
(2-2)j (59%, 16 h)[a]



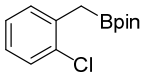
(2-2)k (61%, 24 h)[b]



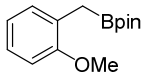
(2-2)l (55%, 30 h)[b]



(2-2)m (32%, 16 h)[b]



(2-2)n (52%, 24 h)[a]



(2-2)o (51%, 24 h)[b]

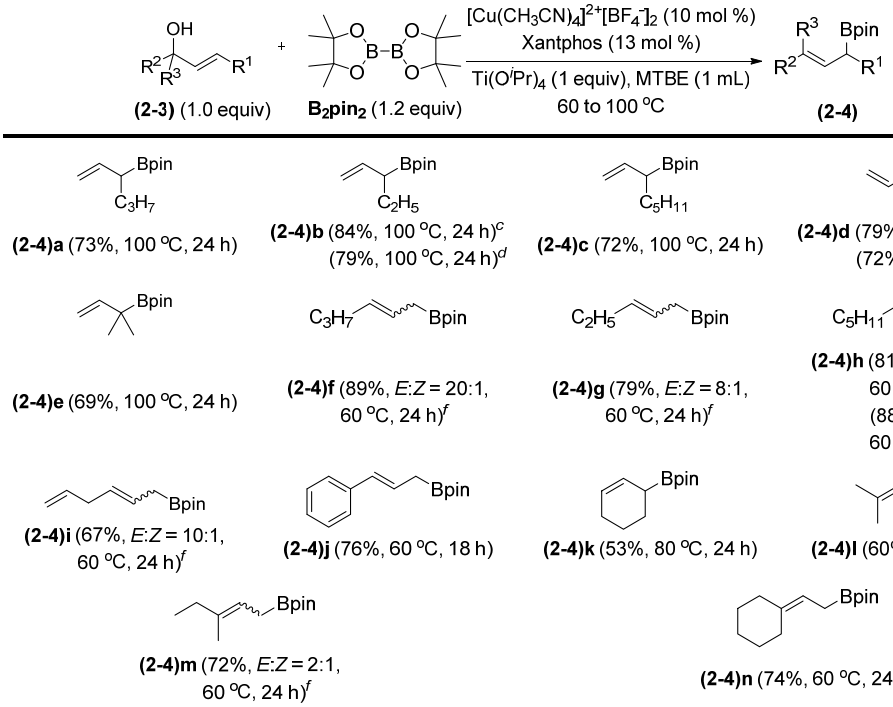
[a] Condition **A**: **(2-1)** (0.2 mmol), B_2pin_2 (0.24 mmol), $[Cu(MeCN)_4]^{2+}[BF_4^-]_2$ (5 mol %), Xantphos (6.5 mol %), $Ti(O^iPr)_4$ (0.2 mmol), MTBE (1 mL). [b] Condition **B**: **(2-1)** (0.2 mmol), B_2pin_2 (0.24 mmol), $[Cu(MeCN)_4]^{2+}[BF_4^-]_2$ (10 mol %), Xantphos (13 mol %), $Ti(O^iPr)_4$ (0.2 mmol), MTBE (1 mL). [c] Isolated yields. [d] Benzyl acetate was used as the substrate.

Scheme 2-2. Synthesis of Benzyl Boronates[a,b,c]

With the optimized conditions in hand, the substrate scope for the borylation reaction of benzylic alcohols was investigated (Scheme 2-2). Thus, naphthalen-2-ylmethanol **(2-1)b** and its derivative **(2-1)c** gave the corresponding products **(2-2)b** and **(2-2)c** in yields of 73% and 79%, respectively. Benzyl alcohol **(2-1)d** gave **(2-2)d** in a 73% yield with 10 mol % catalyst after 30 h. When benzyl acetate **(2-1)d'** was employed as the starting material, **(2-2)d** was also obtained in a 56% yield. The compound 3,4-(methylenedioxy)benzyl alcohol **(2-1)e** worked efficiently, giving **(2-2)e** in an excellent yield of 95%. Compound **(2-2)f** was isolated in a 92% yield, when 4-(trifluoromethyl)benzyl alcohol **(2-1)f** was employed as starting material. With (4-chlorophenyl)methanol **(2-1)g** as substrate, the desired product **(2-2)g** was isolated in a yield of 69%.

When 4-methylthiobenzyl alcohol **(2-1)h**, 4-methoxy benzyl alcohol **(2-1)i** and 4-methyl benzyl alcohol **(2-1)j** were employed in this borylation reaction, the isolated yields of **(2-2)h**, **(2-2)i** and **(2-2)j** were 76%, 63% and 59%, respectively. The *meta* substituted benzyl boronates **(2-2)k-m** were also isolated in modest yields of 32%-61%. With *ortho* substituted benzylic alcohols **(2-1)n** and **(2-1)o**, **(2-2)n** and **(2-2)o** were isolated in yields of 52% and 51%, respectively. Due to the fact that benzyl boronates are unstable on silica gel, and they are volatile compounds as well, flash chromatography and rotary evaporation of solvents contribute to yield losses to varying extents.[21]

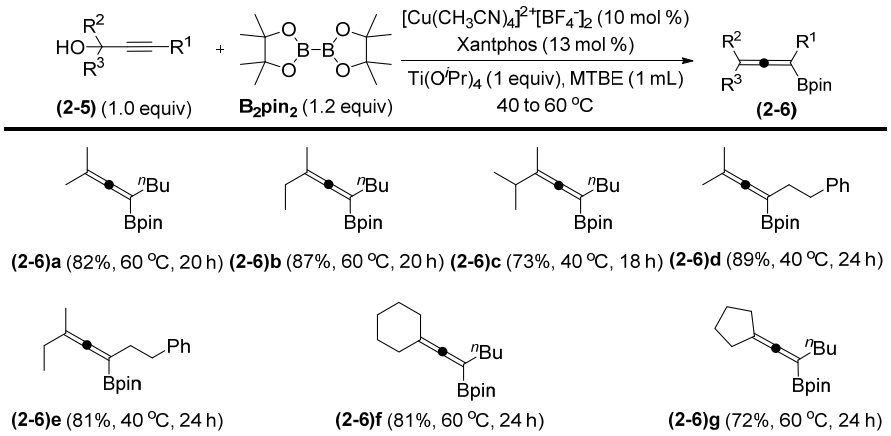
With primary allylic alcohols, such as **(2-3)a-c**, (Scheme 2-3) secondary allyl boronates **(2-4)a-c** were obtained as the sole products in yields of 72% to 84%. This is a unique feature of the current Cu-catalyzed method, as Pd-catalyzed borylation of allylic alcohols **(2-3)a-c** gives the corresponding linear allylboronate isomer.[28b,d,f,30a] The reason is that the Pd-catalyzed reaction proceeds via an η^3-allyl palladium complex,[30b] while the present Cu-catalyzed reaction apparently follows another mechanism (see below). The double bond geometry of the starting material did not affect this reaction. Compound **(2-4)b** was obtained in 79% yield, when (*E*)-pent-2-en-1-ol **(2-3)b** was replaced with its isomer (*Z*)-pent-2-en-1-ol **(2-3)b'** as the substrate. Both allylic alcohol **(2-3)d** and acetate **(2-3)d'** were suitable substrates for this reaction, giving allyl boronate **(2-4)d** in yields of 79% and 72%, respectively. With 3-methylbut-2-en-1-ol **(2-3)e**, the tertiary allylic boronate **(2-4)e** was obtained in 69% yield. Formation of **(2-4)a-c** and **(2-4)e** from **(2-3)a-c** and **(2-3)e** indicates an S_N2' mechanism for the borylation reaction. Similar regioselectivity was reported by Ito and Sawamura for the Cu-catalyzed borylation of allylic carbonates.[24a,c,d] This suggests that our process could potentially be extended to the catalytic asymmetric borylation of allylic alcohols. Secondary allylic alcohols, such as **(2-3)g-j**, can be borylated at 60 ºC, giving the corresponding primary boronates **(2-4)g-j** in yields of 67% to 89%. Oct-1-en-3-yl acetate **(2-3)h'** was also a suitable substrate for the borylation reaction giving **(2-4)h** in 88% yield. With cyclohex-2-en-1-ol **(2-3)k** as the substrate, **(2-4)k** was obtained in a yield of 53%. Next, tertiary allylic alcohols **(2-3)l**, **(2-3)m** and **(2-3)n** were tested for this reaction at 60 ºC, and the linear boronates **(2-4)l**, **(2-4)m** and **(2-4)n** were obtained in moderate yields of 60%, 72% and 74%, respectively. The above results also suggested that a nucleophilic substitution pathway is probably involved in this reaction.



[a] Standard conditions: **(2-3)** (0.2 mmol), B_2pin_2 (0.24 mmol), $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ (10 mol %), Xantphos (13 mol %), $Ti(O^iPr)_4$ (0.2 mmol), MTBE (1 mL), 60 to 100 °C. [b] Isolated yield. [c] (*E*)-Pent-2-en-1-ol was used as the substrate. [d] (*Z*)-Pent-2-en-1-ol was used as the substrate. [e] Allyl acetate was used as the substrate. [f] *E*/*Z* isomer ratios were determined by ^1H NMR spectroscopy of the crude product. [g] Oct-1-en-3-yl acetate was used as the substrate.

Scheme 2-3. Synthesis of Allyl Boronates[a,b]

Few examples have been reported for the synthesis of allenyl boronates,[82-84] which are useful reagents for the preparation of stereo- and regio-defined allenes via C-C bond formation.[73,78] The Cu-catalyzed borylation reaction can be also applied to the synthesis of allenylboronates from propargylic alcohols (Scheme 2-4). This is again a unique feature of the present study. Palladium-catalysis cannot be used for the synthesis of allenylboronates from propargylic alcohols.[83] Thus, at 60 °C, **(2-5)a** and **(2-5)b** gave the allenyl boronates **(2-6)a** and **(2-6)b** in yields of 82% and 87%, respectively, and at 40 °C, the desired products **(2-6)c-e** were also obtained in yields of 73%-89%. The cyclohexyl (**(2-5)f**) and cyclopentyl (**(2-5)g**) derivatives gave the corresponding products **(2-6)f** and **(2-6)g** in yields of 81% and 72%, respectively. The observed regioselectivity with propargyl alcohols also suggests that the reaction proceeds via an S_N2'-type pathway (Scheme 2-5).[85]



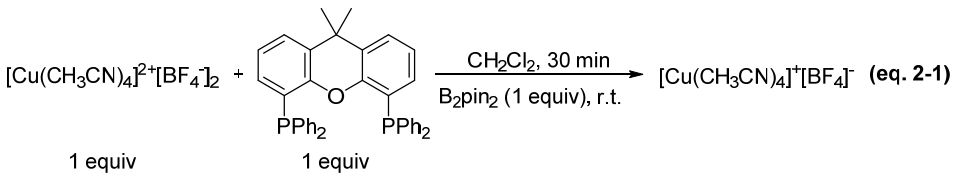
[a] Standard conditions: **(2-5)** (0.2 mmol), B_2pin_2 (0.24 mmol), $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ (10 mol %), Xantphos (13 mol %), $Ti(O^iPr)_4$ (0.2 mmol), MTBE (1 mL), 40 to 60 °C. [b] Isolated yield.

Scheme 2-4. Synthesis of Allenyl Boronates[a,b]

2.3.3 Mechanistic Study

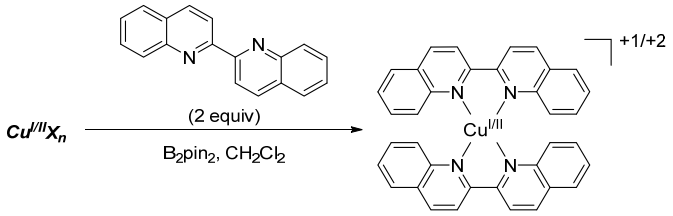
2.3.3.1 Identification of a Cu^I Species

According to the experimental results as well as literature reports,[86] the precatalyst $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ is at least partly reduced *in situ* to Cu^I by a boryl anion nucleophile.[87] Thus, reaction of 1 equiv of $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ (10 mg) and 1 equiv Xantphos (14.5 mg) in CH_2Cl_2 (1 mL) was stirred for 5 min. at room temperature under argon, followed by the addition of 1 equiv of B_2pin_2 (6.3 mg). The mixture was stirred for another 25 min., and was then filtered. The organic layer was stored at -30 °C under argon. Crystals of $[Cu(CH_3CN)_4]^+[BF_4]^-$ formed (eq. 2-1), confirmed by single-crystal X-ray diffraction, as the unit cell is the same as that previously reported.[88] Additionally, with $[Cu(CH_3CN)_4]^+[BF_4]^-$ as the precatalyst, the desired product **(2-2)a** was obtained in 81% yield (Table 1-1, entry 5). However, no product **(2-2)a** was detected by GC-MS using $[Cu(CH_3CN)_4]^+[BF_4]^-$ in the absence of Xantphos.



2.3.3.2 $Cu^{I/II}$ Trapping Experiment

Table 2-3. $Cu^{I/II}$ Trapping Experiment

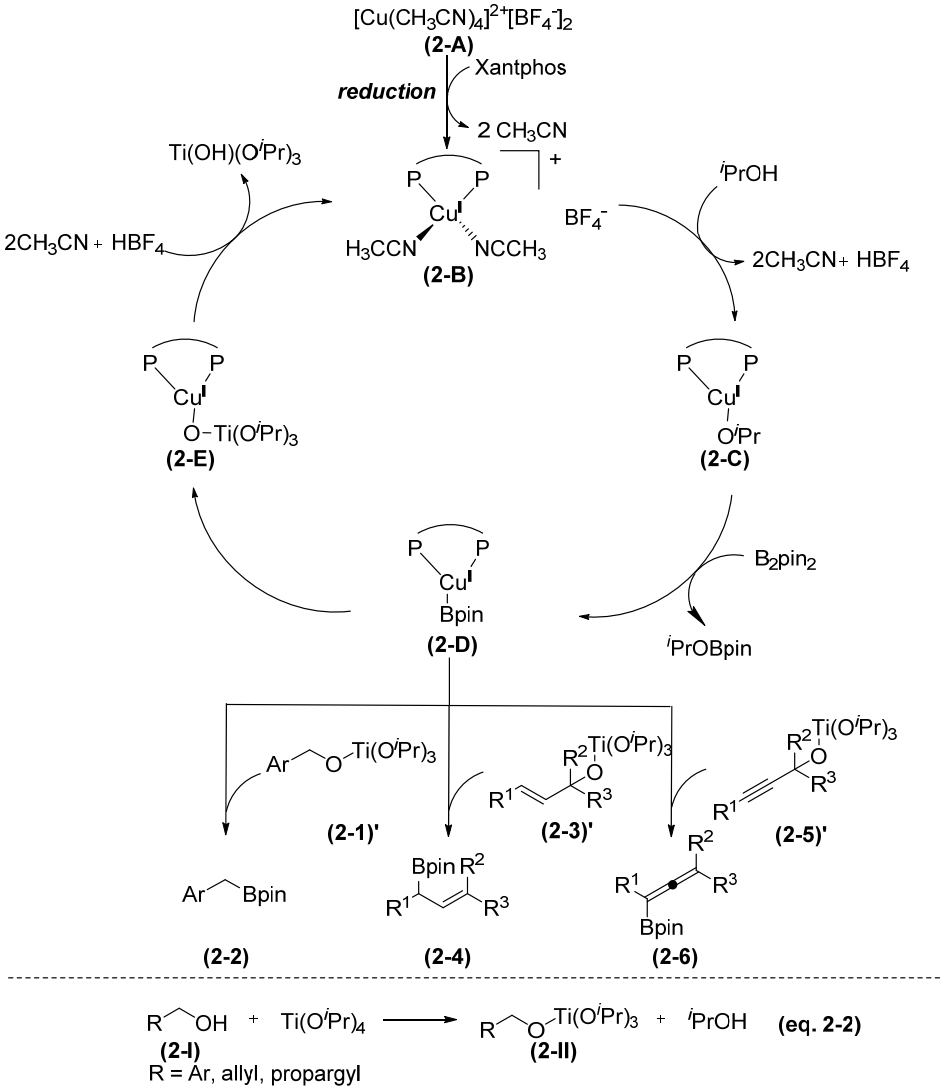


[Cu]	solvent	λ_{max} (nm)	color
$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ + Xantphos	CH_2Cl_2	540	dark purple solution
$[Cu(CH_3CN)_4]^{+}[BF_4]^-$ + Xantphos	CH_2Cl_2	540	dark purple solution
$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ (without B_2pin_2)	CH_2Cl_2	na	green precipitate
$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ + Xantphos	THF	550	dark purple solution

According to a literature procedure,[86f] the copper complex (0.05 mmol, 1 equiv) and Xantphos (0.05 mmol, 28.9 mg, 1 equiv) were dissolved in CH_2Cl_2 (1.5 mL) or THF (1.5 mL) in a vial in the glove-box under argon, and B_2pin_2 (0.06 mmol, 15.2 mg) was added. The reaction mixture was stirred for 20 min. To the mixture, 2,2'-biquinoline (0.1 mmol, 25.6 mg, 2 equiv) was added. The reaction was then diluted with 3 mL of the corresponding solvent and analyzed via UV-Vis spectrometry. The appearance of the purple color and corresponding absorption at ca. 540 nm indicates the presence of Cu^I.

2.3.4 Plausible Mechanism

It is proposed that the active catalyst is a Cu^I species.[89] The active Cu^I species **(2-B)** could be generated via reduction by a boryl anion nucleophile (Table 2-3).[87] Alcohols (**2-I**) can be activated by $Ti(O^iPr)_4$ to generate **(2-II)** (**(2-1)'**, **(2-3)'**, **(2-5)'**) and ^{i}PrOH (eq. 2-2). Next, Cu species **(2-B)** could react with ^{i}PrOH to give **(2-C)** followed by transmetalation with B_2pin_2 to generate the Cu^I-Bpin species **(2-D)**.[90] Nucleophilic substitution involving **(2-II)** (**(2-1)'** or **(2-3)**', or **(2-5)**') and Cu^I-Bpin **(2-D)** would form the borylation products **(2-2**, **2-4**, or **2-6)** and intermediate **(2-E)**. Finally, **(2-E)** could react with HBF_4 and CH_3CN to regenerate **(2-B)**.



Scheme 2-5. Plausible Mechanism for the Catalytic Borylation.

2.4 Summary

Chapter 2 reports the first example of a Cu-catalyzed direct borylation of alcohols, which offers an efficient methodology to synthesize a broad range of benzyl-, allyl-, and allenyl-boronates under mild conditions.

2.5 Experimental Procedure and Characterization Data

2.5.1 General Information

All reagents were purchased from Alfa-Aesar, Aldrich, ABCR or VWR, and were checked for purity by GC-MS and/or ^{1}H NMR spectroscopy and used as received. B_2pin_2 was kindly provided by AllylChem Co. Ltd. (Dalian, China). HPLC grade solvents were argon saturated, dried using an Innovative Technology Inc. Pure-Solv Solvent Purification System, and further deoxygenated using

the freeze-pump-thaw method. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, and dried over 4Å molecular sieves, deoxygenated using the freeze-pump-thaw method and vacuum transferred into a sealed vessel.

Automated flash chromatography was performed using a Biotage® Isolera Four system, on silica gel (Biotage SNAP cartridge KP-Sil 10 g and KP-Sil 25 g). Commercially available, precoated TLC plates (Polygram® Sil G/UV254) were purchased from Machery-Nagel. The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 30 °C.

GC-MS analyses were performed using an Agilent 7890A gas chromatograph (column: HP-5MS 5% phenyl methyl siloxane, 10 m, ∅ 0.25 mm, film 0.25 μm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C (20 °C min^{-1}); carrier gas: He (1.2 mL min^{-1})) equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A series auto sampler/injector. HRMS analyses were performed using a Thermo Fischer Scientific Exactive Plus Orbitrap MS system (ASAP, ESI or HESI probe). Elemental analyses were performed on a Leco CHNS-932 Elemental Analyzer in the Institute.

All NMR spectra were recorded at ambient temperature using Bruker Avance III HD 300 NMR (^1H, 300 MHz; $^{13}C\{^1H\}$, 75 MHz; ^{11}B, 96 MHz), Bruker Avance 400 NMR (^1H, 400 MHz; $^{13}C\{^1H\}$, 100 MHz; ^{11}B, 128 MHz) or Bruker Avance 500 NMR (^1H, 500 MHz; $^{13}C\{^1H\}$, 125 MHz; ^{11}B, 160 MHz; ^{19}F, 470 MHz) spectrometers. ^1H NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm) whereas $^{13}C\{^1H\}$ NMR spectra are reported relative to TMS *via* the carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm). ^{11}B NMR chemical shifts are quoted relative to $BF_3{\cdot}Et_2O$ as external standard. ^{19}F NMR chemical shifts are quoted relative to $CFCl_3$ as external standard. All ^{13}C NMR spectra were broad-band ^1H decoupled.

2.5.2 Preparation of Catalyst Precursor and Starting Materials

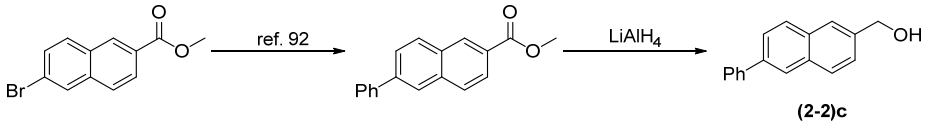
2.5.2.1 Preparation of $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$

$$Cu + NOBF_4 \xrightarrow[(2)\ CH_3CN]{(1)\ EtOAc,\ r.t.,\ 12\ h} [Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$$

The preparation of $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ followed a literature procedure.[91] The product was characterized by elemental analysis; calcd for ($C_8H_{12}B_2CuF_8N_4$): C, 23.94; H, 3.01; N, 13.96. found: C, 23.96; H, 3.02; N, 13.94.

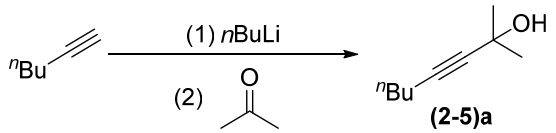
2.5.2.2 Preparation of (2-2)c, (2-5)a-f

Compound **(2-2)c** was synthesized via the following method. The characterization data (^{1}H NMR and ^{13}C NMR) are in accordance with those in the literature.[92]



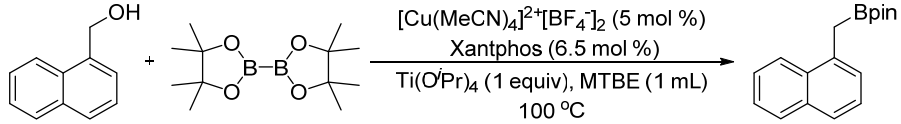
(2-2)c

Compounds **(2-5)a-f** were synthesized according to a literature procedure.[83] The characterization data (^{1}H NMR and ^{13}C NMR) are in accordance with those in the literature.



(2-5)a

2.5.3 Experimental Procedure ((2-1)a as an example)

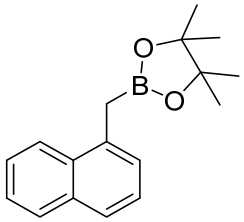


(2-1)a (1.0 equiv) **B_2pin_2** (1.2 equiv) **(2-2)a**

$[Cu(MeCN)_4]^{2+}[BF_4^-]_2$ (5 mol %, 4 mg) and Xantphos (6.5 mol %, 7.5 mg) were dissolved in 0.5 mL of MTBE in a dried vial in the glove-box under argon and the reaction was stirred for 5 min. Then, B_2pin_2 (1.2 equiv, 60.9 mg, 0.24 mmol), **(2-1)a** (1 equiv, 31.6 mg, 0.2 mmol), and $Ti(O^iPr)_4$ (1 equiv, 59.2 μL, 0.2 mmol) were added in this order. Finally, another 0.5 mL of MTBE was added to the mixture. The reaction was heated at 100 °C under argon until the starting material was completely consumed (determined by GC-MS). The crude mixture was filtered through a pad of Celite. Then, the solvent was removed on a rotary evaporator (30 °C, 350 mbar). All products were purified by flash chromatography, during which some decomposition occurs.

2.5.4 Characterization Data

4,4,5,5-Tetramethyl-2-(naphthalen-1-ylmethyl)-1,3,2-dioxaborolane (2-2)a



Isolated yield: 89% (47.9 mg, white solid, flash chromatography: pentane/EtOAc = 97/3).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03–7.99 (m, 1H), 7.85–7.81 (m, 1H), 7.68–7.65 (m, 1H),

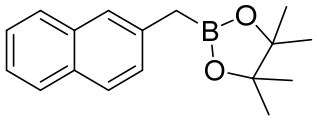
7.51–7.42 (m, 2H), 7.40–7.33 (m, 2H), 2.69 (s, 2H), 1.20 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 135.8, 133.9, 132.6, 128.6, 126.6, 125.9 (2C), 125.5, 125.4, 124.7, 83.7, 24.8, 18.5 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.5.

HRMS (ASAP): *m/z* calcd for $C_{17}H_{22}BO_2$ [$M+H^+$]: 269.1707, found: 269.1706.

4,4,5,5-Tetramethyl-2-(naphthalen-2-ylmethyl)-1,3,2-dioxaborolane (2-2)b



Isolated yield: 73% (39.3 mg, white solid, flash chromatography: pentane/EtOAc = 97/3).

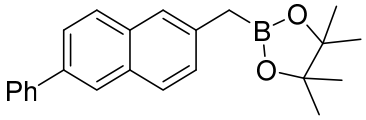
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79–7.71 (m, 3H), 7.62 (s, 1H), 7.45–7.32 (m, 3H), 2.46 (s, 2H), 1.24 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 136.5, 133.9, 131.7, 128.4, 127.8, 127.7, 127.4, 126.8, 125.8, 124.8, 83.7, 24.9, 20.9 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* calcd for $C_{17}H_{22}BO_2$ [$M+H^+$]: 269.1707, found: 269.1705.

4,4,5,5-Tetramethyl-2-((6-phenylnaphthalen-2-yl)methyl)-1,3,2-dioxaborolane (2-2)c



Isolated yield: 79% (54.5 mg, white solid, flash chromatography: pentane/EtOAc = 97/3).

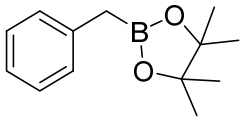
^{1}H NMR (300 MHz, $CDCl_3$) 7.98 (d, *J* = 2 Hz, 1H), 7.80 (t, *J* = 9 Hz, 2H), 7.73–7.68 (m, 3H), 7.64 (s, 1H), 7.50–7.44 (m, 2H), 7.39–7.33 (m, 2H), 2.47 (s, 2H), 1.24 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 141.5, 137.6, 136.7, 133.2, 131.9, 128.9, 128.8, 128.1, 127.9, 127.5, 127.3, 126.5, 125.7, 125.6, 83.7, 24.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{23}H_{26}BO_2$ [$M+H^+$]: 345.2020, found: 345.2018

2-Benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-2)d



Isolated yield: 73% (with benzyl methanol as starting material, 32.0 mg, colorless liquid, flash chromatography: petane/EtOAc = 97/2), 56% (with benzyl acetate as starting material, 24.5 mg, colorless liquid, flash chromatography: petane/EtOAc = 97/2).

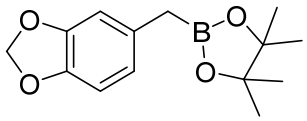
^{1}H NMR (300 MHz, $CDCl_3$) 7.27−7.21 (m, 2H), 7.20−7.17 (m, 2H), 7.15−7.09 (m, 1H), 2.30 (s, 2H), 1.23 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 138.8, 129.1, 128.4, 124.9, 83.6, 24.9, 20.2 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{13}H_{20}BO_2$ [M+H$^+$]: 219.1551, found: 219.1548.

2-(Benzo[*d*][1,3]dioxo-5-ylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-2)e



Isolated yield: 95% (50.0 mg, colorless liquid, flash chromatography: pentane/EtOAc = 97/3).

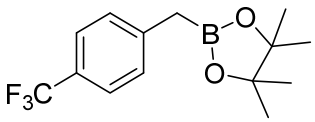
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70−6.68 (m, 2H), 6.62−6.60 (m, 1H), 5.90 (s, 2H), 2.21 (s, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 147.6, 145.1, 132.4, 121.6, 109.8, 108.3, 100.8, 83.6, 24.9, 19.6 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{20}BO_4$ [M+H$^+$]: 263.1449, found: 263.1445.

4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)benzyl)-1,3,2-dioxaborolane (2-2)f



Isolated yield: 92% (52.8 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50−7.46 (m, 2H), 7.29−7.26 (m, 2H), 2.35 (s, 2H), 1.23 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.3, 129.3, 127.4 (q, $J_{C\text{-}F}$ = 33 Hz), 125.3 (q, $J_{C\text{-}F}$ = 4 Hz),

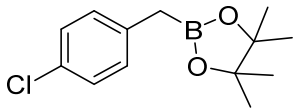
124.7 (q, $J_{C\text{-}F}$ = 272 Hz), 83.8, 24.9, 20.3 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 32.8.

^{19}F NMR (470 MHz, $CDCl_3$) δ -62.6.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{19}BF_3O_2$ [M+H$^+$]: 287.1425, found: 287.1422.

2-(4-Chlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-2)g



Isolated yield: 69% (34.9 mg, white solid, flash chromatography: pentane/EtOAc = 97/3).

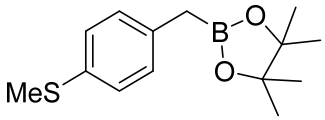
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22–7.17 (m, 2H), 7.13–7.08 (m, 2H), 2.25 (s, 2H), 1.23 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 137.3, 130.7, 130.4, 128.4, 83.7, 24.9, 20.1 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 32.9.

HRMS (ASAP): *m/z* calcd for $C_{13}H_{19}BClO_2$ [M+H$^+$]: 253.1161, found: 253.1160.

4,4,5,5-Tetramethyl-2-(4-(methylthio)benzyl)-1,3,2-dioxaborolane (2-2)h



Isolated yield: 76% (40.3 mg, colorless liquid, flash chromatography: pentane/EtOAc = 97/3).

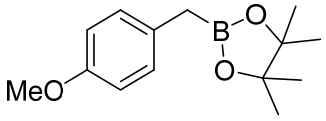
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19–7.15 (m, 2H), 7.13–7.09 (m, 2H), 2.45 (s, 3H), 2.25 (s, 2H), 1.23 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 136.1, 134.1, 129.7, 127.6, 83.6, 24.9, 20.1 (broad, low intensity), 16.7.

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{22}BO_2S$ [M+H$^+$]: 265.1428, found: 265.1425.

2-(4-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-2)i



Isolated yield: 63% (31.4 mg, colorless liquid, flash chromatography: pentane/EtOAc = 97/3).

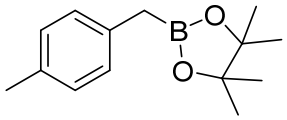
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12–7.07 (m, 2H), 6.81–6.77 (m, 2H), 3.77 (s, 3H), 2.23 (s, 2H), 1.23 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 157.3, 130.6, 129.9, 113.9, 83.5, 55.4, 24.9, 19.3 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{22}BO_3$ [M+H$^+$]: 249.1657, found: 249.1654.

4,4,5,5-Tetramethyl-2-(4-methylbenzyl)-1,3,2-dioxaborolane (2-2)j



Isolated yield: 59% (27.5 mg, colorless liquid, flash chromatography: pentane/EtOAc = 97/3).

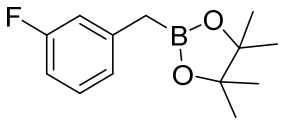
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09–7.02 (m, 4H), 2.29 (s, 3H), 2.25 (s, 2H), 1.23 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 135.5, 134.3, 129.1, 128.9, 83.5, 24.9, 21.1, 19.2 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.2.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{22}BO_2$ [M+H$^+$]: 233.1707, found: 233.1703.

2-(3-Fluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-2)k



Isolated yield: 61% (28.9 mg, colorless liquid, flash chromatography: pentane/EtOAc = 97/3).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22–7.14 (m, 1H), 6.96–6.87 (m, 2H), 6.85–6.77 (m, 1H), 2.29 (s, 2H), 1.23 (s, 12H).

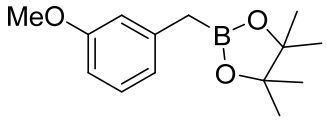
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 240 Hz), 141.4 (d, $J_{C\text{-}F}$ = 8 Hz), 129.6 (d, $J_{C\text{-}F}$ = 9 Hz), 124.8 (d, $J_{C\text{-}F}$ = 3 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21 Hz), 111.9 (d, $J_{C\text{-}F}$ = 21 Hz), 83.7, 24.9, 20.9 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 32.9.

^{19}F NMR (470 MHz, $CDCl_3$) δ -113.1.

HRMS (ASAP): *m/z* calcd for $C_{13}H_{19}BFO_2$ [M+H$^+$]: 237.1457, found: 237.1455.

2-(3-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-2)l



Isolated yield: 55% (27.4 mg, colorless liquid, flash chromatography: pentane/EtOAc = 97/3).

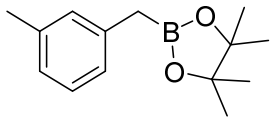
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18–7.12 (m, 1H), 6.79–6.66 (m, 3H), 3.78 (s, 3H), 2.27 (s, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 159.7, 140.4, 129.3, 121.7, 114.8, 110.6, 83.6, 55.2, 24.9, 20.2 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 32.8.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{22}BO_3$ [M+H$^+$]: 249.1657, found: 249.1656.

4,4,5,5-Tetramethyl-2-(3-methylbenzyl)-1,3,2-dioxaborolane (2-2)m



Isolated yield: 32% (14.9 mg, colorless liquid, flash chromatography: pentane/EtOAc = 97/3).

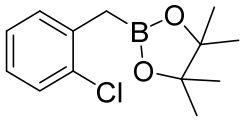
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15–7.10 (m, 1H), 7.01–6.91 (m, 3H), 2.30 (s, 3H), 2.26 (s, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 138.6, 137.9, 130.0, 128.3, 126.1, 125.8, 83.5, 24.9, 21.6, 19.7 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{22}BO_2$ [M+H$^+$]: 233.1707, found: 233.1706.

2-(2-Chlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-2)n



Isolated yield: 52% (26.3 mg, colorless liquid, flash chromatography: pentane/EtOAc = 97/3).

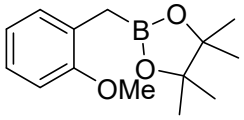
^{1}H NMR (500 MHz, $CDCl_3$) 7.30 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 1H), 7.22 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 1H), 7.14 (dt, J_1 = 7 Hz, J_2 = 1 Hz, 1H), 7.08 (dt, J_1 = 7 Hz, J_2 = 1 Hz, 1H), 2.38 (s, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 137.7, 134.0, 130.9, 129.2, 126.8, 126.6, 83.7, 24.9, 18.9 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 32.0.

HRMS (ASAP): *m/z* calcd for $C_{13}H_{19}BClO_2$ [M+H$^+$]: 253.1161, found: 253.1164.

2-(2-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-2)o



Isolated yield: 51% (25.4 mg, colorless liquid, flash chromatography: pentane/EtOAc = 97/3).

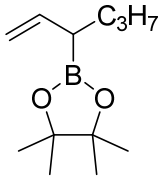
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15–7.09 (m, 2H), 6.87–6.78 (m, 2H), 3.80 (s, 3H), 2.18 (s, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 157.3, 130.7, 128.2, 126.4, 120.6, 109.9, 83.3, 55.2, 24.9, 18.5 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.5.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{22}BO_3$ [M+H$^+$]: 249.1657, found: 249.1656.

2-(Hex-1-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-4)a



Isolated yield: 73% (30.8 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

^{1}H NMR (300 MHz, $CDCl_3$) 5.78 (ddd, J_1 = 17 Hz, J_2 = 10 Hz, J_3 = 8.5 Hz, 1H), 4.97 (m, 2H), 1.84

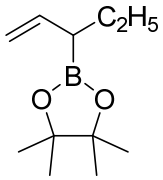
(q, *J* = 7.4 Hz, 1H), 1.59–1.25 (m, 4H), 1.23 (s, 12H), 0.88 (t, *J* = 7 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 139.9, 113.5, 83.3, 32.6, 29.8 (broad, low intensity), 24.9, 24.8, 22.2, 14.2.

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{12}H_{23}BO_2$ $[M+H^+]$: 211.1864 found: 211.1861.

4,4,5,5-Tetramethyl-2-(pent-1-en-3-yl)-1,3,2-dioxaborolane (2-4)b



Isolated yield: 84% (with **(2-3)b** as starting material, 32.9 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3), 79% (with **(2-3)b'** as starting material, 30.9 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

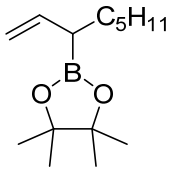
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79 (ddd, J_1 = 17 Hz, J_2 = 10 Hz, J_3 = 8.6 Hz, 1H), 5.01–4.91 (m, 2H), 1.74 (q, *J* = 7.9 Hz, 1H), 1.67–1.41 (m, 2H), 1.24 (s, 12H), 0.91 (t, *J* = 7 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 139.7, 113.7, 83.3, 32.1 (broad, low intensity), 24.9, 24.8, 23.6, 13.7.

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (APCI): *m/z* calcd for $C_{11}H_{21}BO_2$ $[M+H^+]$: 196.1707, found: 196.1706.

4,4,5,5-Tetramethyl-2-(oct-1-en-3-yl)-1,3,2-dioxaborolane (2-4)c



Isolated yield: 72% (34.4 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

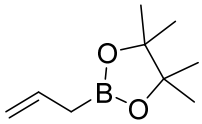
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (ddd, J_1 = 17 Hz, J_2 = 10 Hz, J_3 = 8.5 Hz, 1H), 5.00–4.90 (m, 2H), 1.82 (q, *J* = 7.4 Hz, 1H), 1.39–1.24 (m, 8H), 1.23 (s, 12H), 0.87 (t, *J* = 7 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 139.9, 113.5, 83.3, 32.0, 30.4, 29.0 (broad, low intensity), 28.8, 24.9, 24.8, 22.7, 14.2.

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.2.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{28}BO_2$ [M+H$^+$]: 239.2177, found: 239.2174.

2-Allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-4)d



Yield: 79% (with **(2-3)d** as starting material, yield was determined by ^{1}H NMR, colorless liquid, flash chromatography: pentane/Et_2O = 97/3), 72% (with **(2-3)d'** as starting material, yield was determined by ^{1}H NMR, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

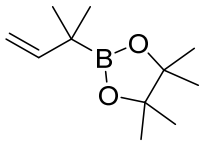
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91–5.82 (m, 1H), 5.02–4.91 (m, 2H), 1.73 (d, *J* = 8 Hz, 2H), 1.25 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 134.2, 115.0, 83.4, 24.9, 18.1 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 32.0.

HRMS (ASAP): *m/z* calcd for $C_9H_{18}BO_2$ [M+H$^+$]: 169.1394, found: 169.1392.

4,4,5,5-Tetramethyl-2-(3-methylbut-2-en-1-yl)-1,3,2-dioxaborolane (2-4)e



Isolated yield: 69% (27.2 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

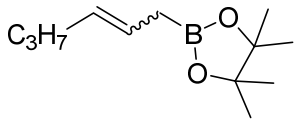
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.99–5.89 (m, 1H), 4.90 (dd, J_1 = 2 Hz, J_2 = 18 Hz, 1H), 4.89 (dd, J_1 = 2 Hz, J_2 = 10 Hz, 1H), 1.21 (s, 12H), 1.05 (s, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 146.7, 110.1, 83.3, 24.7, 23.6. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.7.

HRMS (ASAP): *m/z* calcd for $C_{11}H_{22}BO_2$ [M+H$^+$]: 197.1707, found: 197.1706.

2-(Hex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-4)f



Isolated yield: 89% (*E*:*Z* = 20:1, 37.6 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

(2-4)f-*major isomer*

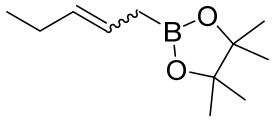
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47–5.33 (m, 2H), 1.99–1.90 (m, 2H), 1.65–1.61 (m, 2H), 1.34 (tq, J_1 = 7 Hz, J_2 = 7 Hz, 2H), 1.24 (s, 12H), 0.86 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 130.9, 125.0, 83.3, 35.0, 24.9, 22.9, 16.1 (broad, low intensity), 13.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* calcd for $C_{12}H_{24}BO_2$ [M+H$^+$]: 211.1864, found: 211.1867.

4,4,5,5-Tetramethyl-2-(pent-2-en-1-yl)-1,3,2-dioxaborolane (2-4)g



Isolated yield: 79% (*E*:*Z* = 8:1, 31.1 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3)**.**

(2-4)g-*major product*

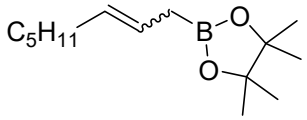
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50–5.33 (ov. m, 2H), 2.04–1.93 (m, 2H), 1.66–1.58 (ov. m, 2H), 1.24 (s, 12H), 0.94 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 132.8, 123.8, 83.3, 25.9, 24.9, 16.3 (broad, low intensity), 14.2.

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* calcd for $C_{11}H_{22}BO_2$ [M+H$^+$]: 197.1707, found: 197.1706.

4,4,5,5-Tetramethyl-2-(oct-2-en-1-yl)-1,3,2-dioxaborolane (2-4)h



Isolated yield: 81% (*E*:*Z* = 35:1, with **(2-3)h** as starting material, 38.7 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3); 88% (*E* : *Z* = 57 : 1, with **(2-3)h'** as starting material, 42.1 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

(2-4)h-*major product*

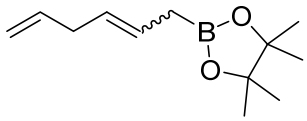
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48–5.33 (m, 2H), 1.99-1.92 (m, 2H), 1.63 (d, *J* = 6 Hz, 2H), 1.37–1.19 (m, 6H), 1.24 (s, 12H), 0.87 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 131.2, 124.8, 83.3, 32.8, 31.5, 29.5, 24.9, 22.7, 16.4 (broad, low intensity), 14.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{28}BO_2$ [M+H$^+$]: 239.2177, found: 239.2174.

2-(Hexa-2,5-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-4)i



Isolated yield: 67% (*E*:*Z* = 10:1, 28.0 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

(2-4)i-*major product*

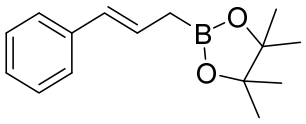
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88–5.75 (m, 1H), 5.54–5.35 (m, 2H), 5.04–4.98 (m, 1H), 4.97–4.91 (m, 1H), 2.78–2.70 (m, 2H), 1.66 (d, *J* = 7 Hz, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 137.8, 128.3, 126.4, 114.7, 83.3, 37.0, 27.7 (broad, low intensity), 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* calcd for $C_{12}H_{22}BO_2$ [M+H$^+$]: 209.1707, found: 209.1704.

2-Cinnamyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-4)j



Isolated yield: 76% (37.2 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

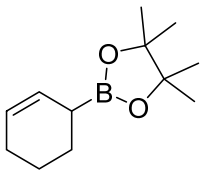
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.31 (m, 2H), 7.30–7.23 (m, 2H), 7.19–7.13 (m, 1H), 6.41–6.24 (m, 2H), 1.87 (d, *J* = 7 Hz, 2H), 1.26 (s, 12H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.3, 130.4, 128.5, 126.6, 126.4, 126.0, 83.5, 24.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{15}H_{22}BO_2$ [M+H$^+$]: 245.1707, found: 245.1704.

2-(Cyclohex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-4)k



Isolated yield: 53% (22.2 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

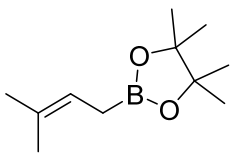
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75–5.64 (m, 2H), 2.02–1.95 (m, 2H), 1.83–1.72 (m, 2H), 1.70–1.56 (m, 3H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 127.7, 126.2, 83.3, 25.1, 24.9, 24.8, 24.3, 22.7, 21.4 (broad, low intensity).

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.5.

HRMS (ASAP): *m/z* calcd for $C_{12}H_{22}BO_2$ [M+H$^+$]: 209.1707, found: 209.1703.

4,4,5,5-Tetramethyl-2-(3-methylbut-2-en-1-yl)-1,3,2-dioxaborolane (2-4)l



Isolated yield: 60% (23.6 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.22 (tqq, J_1 = 8 Hz, J_2 = 2 Hz, J_3 = 1 Hz, 1H), 1.69–1.68 (m, 3H),

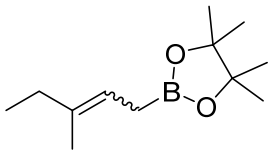
1.62−1.57 (m, 5H), 1.24 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 131.7, 118.7, 83.2, 25.9, 24.9, 17.8, 12.0 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.2.

HRMS (ASAP): *m/z* calcd for $C_{11}H_{22}BO_2$ [M+H$^+$]: 197.1707, found: 197.1705.

4,4,5,5-Tetramethyl-2-(3-methylpent-2-en-1-yl)-1,3,2-dioxaborolane (2-4)m



Isolated yield: 72% (*E*:*Z* = 2:1, 30.4 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

(2-4)m-*a mixture of isomers*

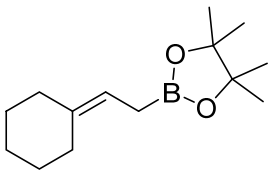
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26–5.16 (m, 1H), 2.04–1.95 (m, 2H), 1.68–1.66 and 1.62−1.56 (m, 5H), 1.23 (s, 12H), 0.99–0.92 (m, 3H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 137.24, 137.21, 118.1, 117.2, 83.20, 83.21, 32.6, 24.89, 24.88, 24.76, 23.0, 15.9, 13.1, 12.6, 11.2 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{12}H_{24}BO_2$ [M+H$^+$]: 211.1864, found: 211.1862.

2-(2-Cyclohexylideneethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-4)n



Isolated yield: 74% (35.1 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

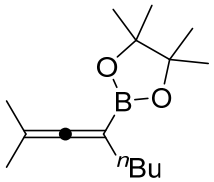
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 (tquint, J_1 = 8 Hz, J_2 = 1 Hz, 1H), 2.12–2.04 (m, 4H), 1.60 (d, *J* = 8 Hz, 2H), 1.54–1.45 (m, 6H), 1.24 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 139.9, 115.1, 83.2, 37.2, 28.8, 28.7, 27.8, 27.1, 24.9, 11.2 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{26}BO_2$ [M+H$^+$]: 237.2020, found: 237.2019.

4,4,5,5-Tetramethyl-2-(2-methylocta-2,3-dien-4-yl)-1,3,2-dioxaborolane (2-6)a



Isolated yield: 82% (41.2 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

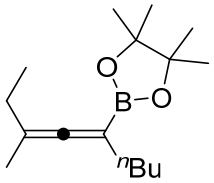
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.99 (t, *J* = 7 Hz, 2H), 1.69 (s, 6H), 1.39–1.29 (m, 4H), 1.25 (s, 12H), 0.88 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 210.8, 91.0, 90.0 (broad, low intensity), 83.2, 31.7, 30.2, 24.9, 22.3, 20.1, 14.2.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.6.

HRMS (ASAP): *m/z* calcd for $C_{15}H_{28}BO_2$ [M+H$^+$]: 251.2177, found: 251.2173.

4,4,5,5-Tetramethyl-2-(3-methylnona-3,4-dien-5-yl)-1,3,2-dioxaborolane (2-6)b



Isolated yield: 87% (46.1 mg, colorless liquid, flash chromatography: pentane/EtOAc = 99/1).

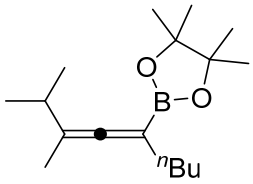
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02–1.91 (m, 4H), 1.69 (s, 3H), 1.39–1.30 (m, 4H), 1.24 (s, 6H), 1.23 (s, 6H), 0.97 (t, *J* = 7 Hz, 3H), 0.88 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 210.1, 97.3, 91.6 (broad, low intensity), 83.2, 31.8, 30.2, 26.7, 24.9, 24.7, 22.5, 18.5, 14.3, 12.6.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.8.

HRMS (ASAP): *m/z* calcd for $C_{16}H_{30}BO_2$ [M+H$^+$]: 265.2333, found: 265.2330.

2-(2,3-Dimethylnona-3,4-dien-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-6)c



Isolated yield: 73% (40.7 mg, colorless liquid, flash chromatography: pentane/EtOAc = 99/1).

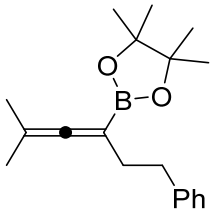
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02–1.97 (m, 2H), 1.71 (sept., *J* = 7 Hz, 1H), 1.65 (s, 3H), 1.45–1.27 (m, 4H), 1.24 (s, 6H), 1.22 (s, 6H), 0.91 (d, *J* = 7 Hz, 3H), 0.90 (d, *J* = 7 Hz, 3 H), 0.88 (t, *J* = 7Hz, 3 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 211.0, 94.0, 90.2 (broad, low intensity), 83.2, 31.9, 30.2, 26.5, 25.1, 24.6, 22.8, 22.7, 22.4, 18.5, 14.2.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.7.

HRMS (ASAP): *m/z* calcd for $C_{17}H_{32}BO_2$ [M+H$^+$]: 279.2490, found: 279.2487.

4,4,5,5-Tetramethyl-2-(5-methyl-1-phenylhexa-3,4-dien-3-yl)-1,3,2-dioxaborolane (2-6)d



Isolated yield: 89% (53.2 mg, colorless liquid, flash chromatography: pentane/EtOAc = 99/1).

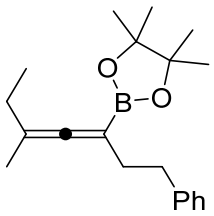
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.10 (m, 5H), 2.75–2.66 (m, 2H), 2.37–2.29 (m, 2H), 1.62 (s, 6H), 1.25 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 211.0, 142.8, 128.8, 128.2, 125.6, 91.7, 87.9 (broad, low intensity), 83.3, 35.8, 32.3, 24.9, 20.0.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.6.

HRMS (ASAP): *m/z* calcd for $C_{19}H_{28}BO_2$ [M+H$^+$]: 299.2177, found: 299.2175.

4,4,5,5-Tetramethyl-2-(5-methyl-1-phenylhepta-3,4-dien-3-yl)-1,3,2-dioxaborolane (2-6)e



Isolated yield: 81% (50.7 mg, colorless liquid, flash chromatography: pentane/EtOAc = 99/1).

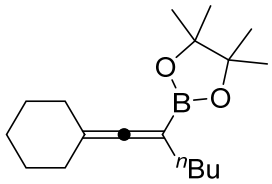
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.12 (m, 5H), 2.76–2.68 (m, 2H), 2.39–2.31 (m, 2H), 1.93 (m, 2H), 1.64 (s, 3H), 1.26 (s, 6H), 1.25 (s, 6H), 0.95 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 210.3, 142.9, 128.7, 128.2, 125.6, 97.9, 91.6 (broad, low intensity), 83.3, 35.9, 32.4, 26.6, 25.0, 24.7, 18.4, 12.5.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.7

HRMS (ASAP): *m/z* calcd for $C_{20}H_{30}BO_2$ [M+H$^+$]: 313.2333, found: 313.2330.

2-(1-Cyclohexylidenehex-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-6)f



Isolated yield: 81% (47.1 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

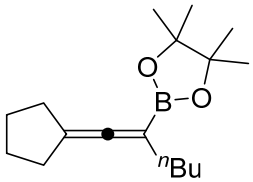
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.16–2.06 (m, 4H), 2.00 (t, *J* = 7 Hz, 2H), 1.70–1.66 (m, 2H), 1.60–1.45 (m, 4H), 1.44–1.28 (m, 4H), 1.24 (s, 12H), 0.89 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 207.5, 98.7, 89.3 (broad, low intensity), 83.2, 31.6, 31.2, 30.0, 27.8, 26.5, 24.9, 22.3, 14.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.7.

HRMS (ASAP): *m/z* calcd for $C_{18}H_{32}BO_2$ [M+H$^+$]: 291.2490, found: 291.2487.

2-(1-Cyclopentylidenehex-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-6)g



Isolated yield: 72% (39.9 mg, colorless liquid, flash chromatography: pentane/Et_2O = 97/3).

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.47–2.32 (m, 4H), 2.02 (t, *J* = 7 Hz, 2H), 1.72–1.60 (m, 4H), 1.39–1.27 (m, 4H), 1.25 (s, 12H), 0.88 (t, *J* = 7 Hz, 3H).

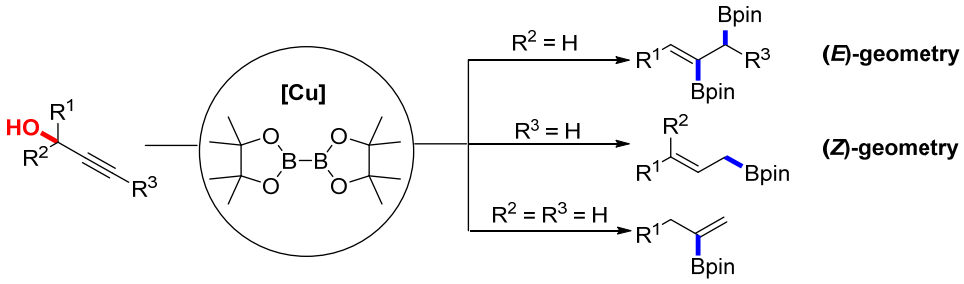
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 206.4, 99.6, 91.9 (broad, low intensity), 83.2, 31.6, 30.9, 30.3, 27.4, 24.9, 22.4, 14.2.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.8.

HRMS (ASAP): *m/z* calcd for $C_{17}H_{30}BO_2$ [M+H$^+$]: 277.2333, found: 277.2330.

Chapter Three

Synthesis of Vinyl-, Allyl-, and 2-Boryl Allyl-boronates via a Highly Selective Copper-catalyzed Borylation of Propargylic Alcohols



3. Synthesis of Vinyl-, Allyl-, and 2-Boryl Allyl-boronates via a Highly Selective Copper-catalyzed Borylation of Propargylic Alcohols

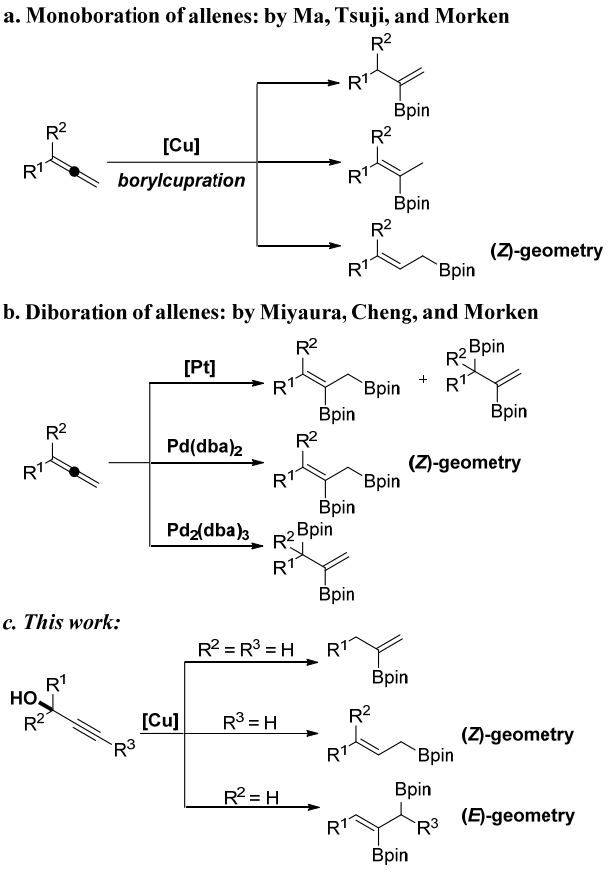
3.1 Introduction

Alcohols constitute a highly attractive class of starting materials as they are inexpensive and often easily derived from natural sources. In particular, propargylic alcohols are useful building blocks in organic synthesis,[93] as they possess inherent alkynyl and hydroxyl functional groups and can be easily accessed from terminal alkynes and aldehydes or ketones. For example, the Meyer-Schuster rearrangement of propargylic alcohols to α,β-unsaturated aldehydes or ketones promoted by Brønsted or Lewis acids has been extensively applied to convert readily available materials into versatile enone products.[93a] Recently, significant progress has been made to synthesize allene derivatives via trapping of allenyl intermediates, generated from propargylic alcohols and their derivatives, with various reagents, such as B_2pin_2.[82,83,94] Ito and co-workers reported a Cu(I)-catalyzed synthesis of allenyl boronates via borylation of propargylic carbonates.[82] A Pd/Cu bimetallic system was also developed by Szabó and co-workers for the catalyzed synthesis of allenyl boronates from propargylic carbonates.[83] The first copper-catalyzed borylation of benzyl-, allyl-, and propargyl alcohols providing the corresponding organic boronates using a commercially available copper catalyst under mild condition was recently reported by Marder, Szabó and co-workers.[94]

3.2 Motivation

Vinyl boronates are widely used in Suzuki-Miyaura coupling reactions,[95a] and allyl boronates are valuable building blocks for the synthesis of homoallyl alcohols.[78,95b,96] Among other approaches,[97] borylcupration of allenes,[66,68b,d,69f] which can be synthesized from propargylic alcohols,[98] has been established by Ma,[67] Tsuji,[68a,b] Hoveyda[69a-e] and co-workers as an efficient means to synthesize vinyl- and allyl-boronates. It is noteworthy that bis(boronate) esters are useful synthetic intermediates in a number of one-pot C-C bond forming sequences.[72d,e,99] Alkenes and alkynes are well-known feedstocks for metal-catalyzed diborations,[62a,63b,c,95,100] and the diboration of allenes has emerged as a powerful tool for the preparation of bis(boronate) esters.[72a-c,f] Miyaura and co-workers developed the first Pt-catalyzed diboration of allenes with B_2pin_2 providing 2-boryl allylboronates,[72a] and Cheng reported the diboration of allenes catalyzed by $Pd(dba)_2$ and organic iodides, which afforded (*Z*)-2-boryl allylboronates with C=C bonds at an internal position as major

products.[72b] Subsequently, Morken and co-workers developed enantioselective diborations of allenes by employing $Pd_2(dba)_3$ as a catalyst precursor to provide 2-boryl allylboronates with C=C bonds at the terminal position.[72c-f] Recently, Szabó and co-workers reported the borylative opening of strained rings (e.g. cyclopropanes and epoxides) with an allenyl moiety affording boryl-allylboronates.[101] So far, a general protocol for the selective synthesis of vinyl-, allyl- and (*E*)-2-boryl allyl-boronates from more readily available propargylic alcohols via copper-catalysis has not been established. Marder and others have developed copper-[12a,15] or zinc-[74c-e,80] catalyzed borylations of organic halides, as Cu and Zn have relatively low toxicity and are inexpensive. Chapter 3 reports the catalytic borylation of propargylic alcohols to synthesize vinyl-, allyl- and (*E*)-2-boryl allyl-boronates (Scheme 3-1).



Scheme 3-1. Transition Metal-catalyzed Borylation of Allene and its Derivatives

3.3 Results and Discussion

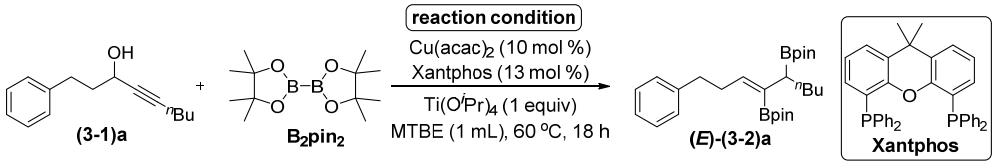
3.3.1 Optimization of Reaction Conditions

3.3.1.1 Condition Screening for the Synthesis of (*E*)-2-Boryl Allyl-boroantes

In the previous study, allenylboronates were prepared from multi-substituted propargylic alcohols catalyzed by 10 mol % $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ and 1.2 equiv of B_2pin_2 at 40-60 °C.[94] However,

when the reaction was carried out with **(3-1)a** as the starting material, 30% of the diboration product **(3-2)a** was obtained instead of the expected allenylboronate (Table 3-2, entry 2). Therefore, an exploration of the borylation of propargylic alcohols using other Cu salts as catalyst precursors was began, and Xantphos as the ligand was began (Table 3-1). The desired (*E*)-2-boryl allylboronate **(3-2)a** was obtained in 66% yield, when 10 mol % $Cu(acac)_2$ was employed as catalyst precursor, 13 mol % Xantphos as ligand, and 1 equiv of $Ti(O^iPr)_4$ as a Lewis acid (Table 3-1, entry 1). However, the yield of **(3-2)a** dropped to 57% when $[Cu(CH_3CN)_4]^+[BF_4]^-$ was used instead of $Cu(acac)_2$ (Table 3-1, entry 2). Control experiments revealed that the diboration reaction is catalyzed by Cu, in combination with Xantphos as the ligand (Table 3-1, entries 3-4). The yield of **(3-2)a** dropped to 20% in the absence of $Ti(O^iPr)_4$, which turns the OH moiety into a good leaving group (Table 3-1, entry 5).[13] When MTBE was replaced with CH_2Cl_2 as the solvent, **(3-1)a** was fully converted and the desired product **(3-2)a** was obtained in 87% yield (Table 3-1, entry 6). Other screening details are listed in Tables 3-2 to 3-9.

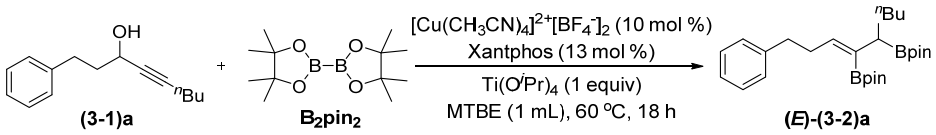
Table 3-1. Condition Screening[a,b,c]



Entry	Varation from the reaction condition	% Product (3-2)a	% S.M.[d]
1	no change	66	25
2	$[Cu(CH_3CN)_4]^+[BF_4]^-$ instead of $Cu(acac)_2$	57	34
3	without catalyst	N.D.[e]	94
4	without Xantphos	N.D.[e]	93
5	without $Ti(O^iPr)_4$	20	67
6	CH_2Cl_2 was used instead of MTBE	87 (81)[f]	-

All reactions were carried out on a 0.2 mmol scale. [a] Reaction condition: $Cu(acac)_2$ (10 mol %), Xantphos (13 mol %), **(3-1)a** (1 equiv), B_2pin_2 (2.2 equiv), $Ti(O^iPr)_4$ (1 equiv), MTBE (1 mL), 60 °C, 18 h. [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] The geometry of C=C bonds was determined by ^1H, ^1H NOESY NMR. [d] Unreacted starting material. [e] N.D. = not detected. [f] Isolated yield.

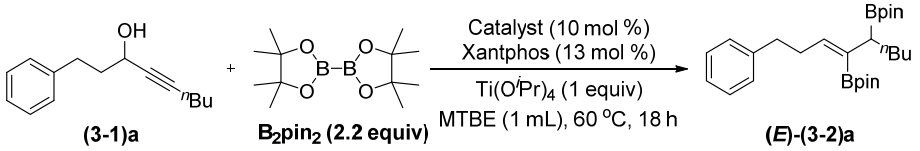
Table 3-2. Loading of B_2pin_2[a]



Entry	B_2pin_2	% Product (3-2)a[b]	% S.M.[c]
1	0.6 equiv	6	82
2	1.2 equiv	30	54
3	1.5 equiv	34	56
4	2.2 equiv	63	29

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **(3-1)a** (1 equiv), B_2pin_2 (x equiv), $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ (10 mol %), Xantphos (13 mol %), $Ti(O^iPr)_4$ (1 equiv), MTBE (1 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] Unreacted starting material.

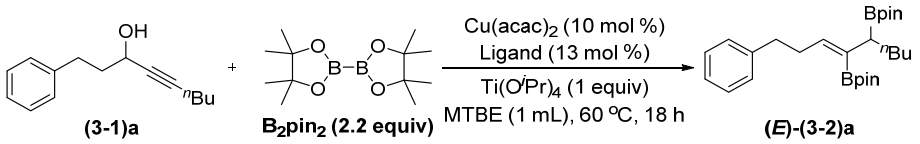
Table 3-3. Catalysts[a]



Entry	Catalyst (10%)	% Product (3-2)a[b]	% S.M.[c]
1	$CuCl_2$	N.D.[d]	91
2	$CuBr_2$	N.D.[d]	87
3	$Cu(OAc)_2•H_2O$	41	52
4	$Cu(NO_3)_2•3H_2O$	N.D.[d]	95
5	$Cu(acac)_2$	66	25
6	$CuSO_4$	N.D.[d]	84
7	$Cu(OTf)_2$	N.D.[d]	93
8	CuCl	N.D.[d]	87
9	CuI	N.D.[d]	92
10	$[Cu(CH_3CN)_4]^+[BF_4]^-$	57	34
11	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	63	29
12	$Cu(OAc)_2$	50	42
13	None	N.D.[d]	90

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **(3-1)a** (1 equiv), B_2pin_2 (2.2 equiv), catalyst (10 mol %), Xantphos (13 mol %), $Ti(O^iPr)_4$ (1 equiv), MTBE (1 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] Unreacted starting material. [d] N.D. = Not detected.

Table 3-4. Ligands[a]



Entry	Ligand (13%)	% Product (3-2)a[b]	% S.M.[c]
1	Xantphos	66	25
2	P(*n*-Bu)$_3$	24	68
3	PMe$_3$	4	87
4	PCy$_3$	16	81
5	P(*p*-tol)$_3$	28	64
6	dppp	45	42
7	dppe	23	67
8	dppbe	24	61
9	4,4'-di-*tert*-butyl-2,2'-bipyridine	< 5	87
10	None	< 5	91

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **(3-1)a** (1 equiv), B_2pin_2 (2.2 equiv), $Cu(acac)_2$ (10 mol %), Ligand (13 mol %), $Ti(O^iPr)_4$ (1 equiv), MTBE (1 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] Unreacted starting material.

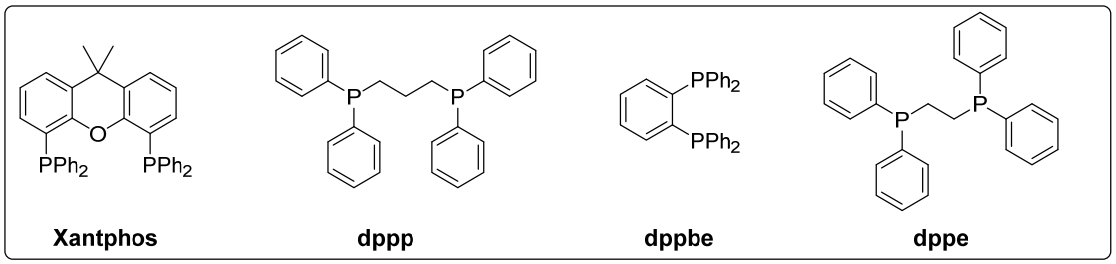
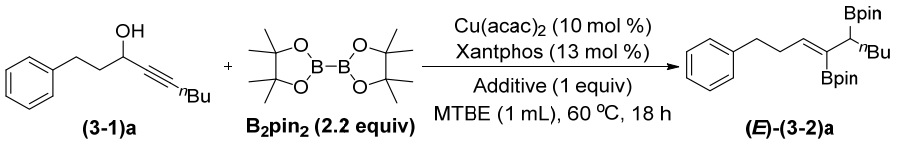


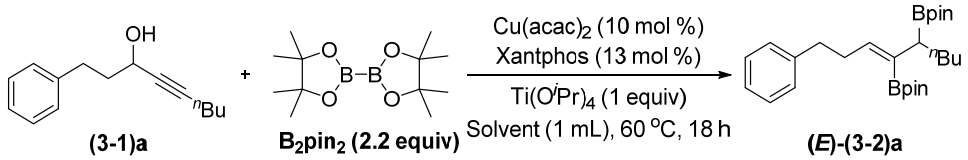
Table 3-5. Additives[a]



Entry	Additive	% Product (3-2)a[b]	% S.M.[c]
1	$Ti(O^iPr)_4$ (1.0 equiv)	66	25
2	$Ti(O^iPr)_4$ (1.5 equiv)	68	21
3	$Ti(O^iPr)_4$ (2.0 equiv)	63	20
4	$BF_3•Et_2O$	N.D.[d]	94
5	$AlCl_3$	N.D.[d]	90
6	TFA	N.D.[d]	82
7	$TsOH•H_2O$	N.D.[d]	87
8	$HBF_4•Et_2O$	N.D.[d]	94
9	None	20	67

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **(3-1)a** (1 equiv), B_2pin_2 (2.2 equiv), $Cu(acac)_2$ (10 mol %), Xantphos (13 mol %), Additive (1 equiv), MTBE (1 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] Unreacted starting material. [d] N.D. = Not detected.

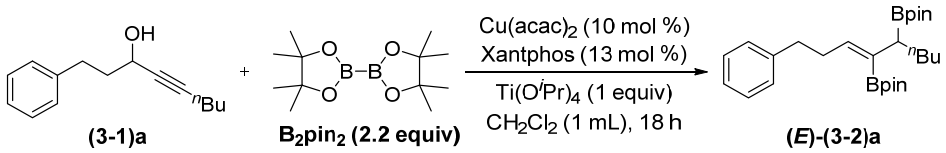
Table 3-6. Solvents[a]



Entry	Solvent	% Product (3-2)a[b]	% S.M.[c]
1	MTBE	66	25
2	THF	69	18
3	toluene	70	15
4	benzene	68	17
5	CH_2Cl_2	87	-
6	CH_3CN	67	21

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **(3-1)a** (1 equiv), B_2pin_2 (2.2 equiv), $Cu(acac)_2$ (10 mol %), Xantphos (13 mol %), $Ti(O^iPr)_4$ (1 equiv), Solvent (1 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] Unreacted starting material.

Table 3-7. Temperature[a]

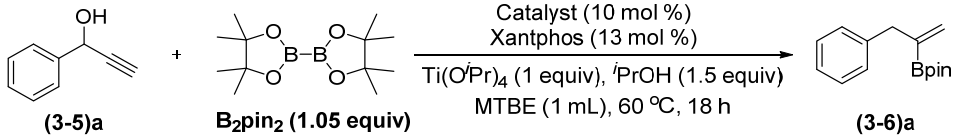


Entry	Temperature	% Product (3-2)a[b]	% S.M.[c]
1	60	87	-
2	40	65	27
3	room temperature	61	30

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **(3-1)a** (1 equiv), B_2pin_2 (2.2 equiv), $Cu(acac)_2$ (10 mol %), Xantphos (13 mol %), $Ti(O^iPr)_4$ (1 equiv), CH_2Cl_2 (1 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] Unreacted starting material.

3.3.1.2 Condition Screening for the Synthesis of Vinylboroantes

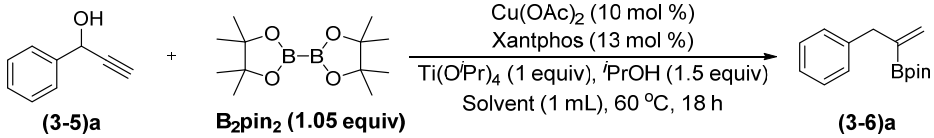
Table 3-8. Catalysts[a]



Entry	Catalyst (10%)	% Product (3-6)a[b]	% S.M.[c]
1	$CuCl_2$	N.D.[d]	84
2	$CuBr_2$	N.D.[d]	92
3	$Cu(OAc)_2•H_2O$	46	45
4	$Cu(NO_3)_2•3H_2O$	N.D.[d]	91
5	$Cu(acac)_2$	52	42
6	$CuSO_4$	N.D.[d]	84
7	$Cu(OTf)_2$	N.D.[d]	88
8	CuCl	N.D.[d]	89
9	CuI	N.D.[d]	93
10	$[Cu(CH_3CN)_4]^+[BF_4]^-$	48	42
11	$[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	26	69
12	$Cu(OAc)_2$ (anhydrous)	74	15
13	None	N.D.[d]	92

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **(3-5)a** (1 equiv), B_2pin_2 (1.05 equiv), catalyst (10 mol %), Xantphos (13 mol %), $Ti(O^iPr)_4$ (1 equiv), ^{i}PrOH (1.5 equiv), MTBE (1 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] Unreacted starting material. [d] N.D. = Not detected.

Table 3-9. Solvents[a]



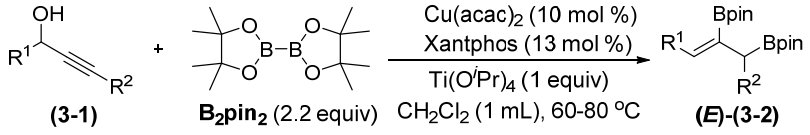
Entry	Solvent	% Product (3-6)a[b]	% S.M.[c]
1	THF	44	48
2	toluene	89	-
3[d]	toluene	72	17
4[e]	toluene	82	-
5	benzene	59	36
6	CH_2Cl_2	23	68
7	CH_3CN	12	74

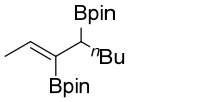
[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **(3-5)a** (1 equiv), B_2pin_2 (1.05 equiv), $Cu(OAc)_2$ (10 mol %), Xantphos (13 mol %), $Ti(O^iPr)_4$ (1 equiv), ^{i}PrOH (1.5 equiv), Solvent (1 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] Unreacted starting material. [d] With 1 equiv ^{i}PrOH as additive. [e] With 2 equiv ^{i}PrOH as additive.

3.3.2 Investigation of Reaction Scope

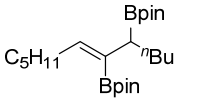
With optimized conditions in hand, the scope of the diboration reaction was investigated (Scheme 3-2). The desired products **(3-2)b-e** were obtained in yields of 86% to 91% from the diboration of **(3-1)b-e**. The yields of **(3-2)f** and **(3-2)g** dropped to 74% and 63%, respectively, when bulkier functional groups, such as isopropyl, or cyclohexyl were present. Diboration products **(3-2)h-j** were obtained in good to excellent yields of 81% to 92%, upon replacement of ^{n}Bu by ethyl or phenethyl groups. Propargylic alcohols bearing aromatic substituents were also good substrates for diboration, giving **(3-2)k-n** in good yields of 69% to 78%. With a phenyl ring bearing an OMe group at the *meta* position, **(3-2)o** was formed 71% yield. The yields of **(3-2)p-r** dropped to 60%, 54%, and 57% respectively, when OMe, Me and F were introduced at the *ortho* position. Naphthyl-containing substrate **(3-1)s** gave **(3-2)s** in 72% yield. Again, the ^{n}Bu group can be replaced by a phenethyl group, and the corresponding products **(3-2)t** and **(3-2)u** were formed in yields of 76% and 72%, respectively. The regio- and stereo-selectivity of our Cu-catalyzed diborations are different from those of Pd-catalyzed allene diborations,[72a-c,f] which afforded (*E*)-2-boryl allyl boronates. Pd-catalyzed diboration of allenes gives either (*Z*)-2-boryl allyl boronates[72b] or 2-boryl allyl boronates with C=C bonds at the terminal position.[72c,f] The regioselectivity of our diborations also suggests that a cascade involving the copper-catalyzed S_N2' borylation of propargyl alcohols[94] and a

borylcupration of the resulting allenyl boronates might be taking place.[67,68a,b,69,94]

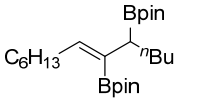




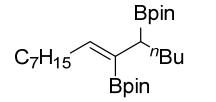
(3-2)b (89%, 60 °C, 18 h)



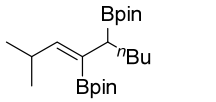
(3-2)c (91%, 60 °C, 18 h)



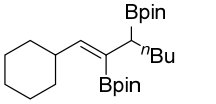
(3-2)d (90%, 60 °C, 18 h)



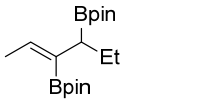
(3-2)e (86%, 60 °C, 18 h)



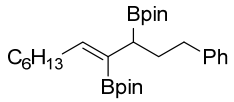
(3-2)f (74%, 60 °C, 24 h)



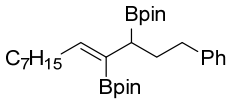
(3-2)g (63%, 60 °C, 24 h)



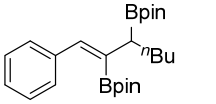
(3-2)h (81%, 60 °C, 18 h)



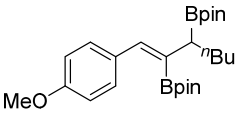
(3-2)i (92%, 60 °C, 18 h)



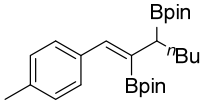
(3-2)j (89%, 60 °C, 18 h)



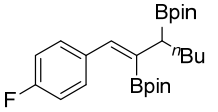
(3-2)k (74%, 80 °C, 24 h)



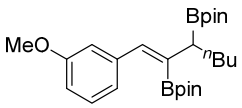
(3-2)l (78%, 80 °C, 24 h)



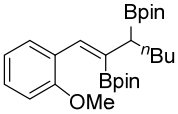
(3-2)m (77%, 80 °C, 24 h)



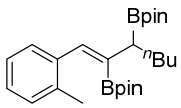
(3-2)n (69%, 80 °C, 24 h)



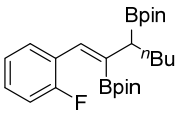
(3-2)o (71%, 80 °C, 24 h)



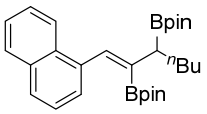
(3-2)p (60%, 80 °C, 24 h)



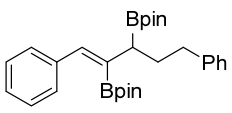
(3-2)q (54%, 80 °C, 24 h)



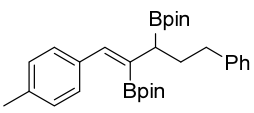
(3-2)r (57%, 80 °C, 24 h)



(3-2)s (72%, 80 °C, 24 h)



(3-2)t (76%, 80 °C, 24 h)



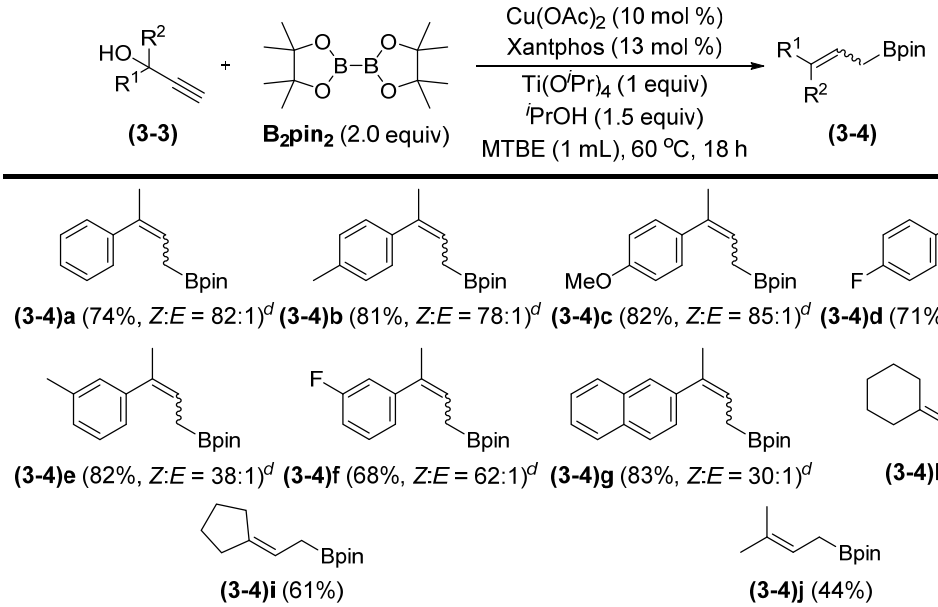
(3-2)u (72%, 80 °C, 24 h)

[a] Standard conditions: **(3-1)** (0.20 mmol), $Cu(acac)_2$ (10 mol %), Xantphos (13 mol %), B_2pin_2 (0.44 mmol), $Ti(O^iPr)_4$ (0.2 mmol), CH_2Cl_2 (1 mL), 60-80 °C, 18-24 h. [b] Isolated yield. [c] The geometry of the C=C bonds was determined by ^1H, ^1H NOESY NMR.

Scheme 3-2. Synthesis of 2-Boryl Allyl Boronates[a,b,c]

With 1,1-disubstituted propargyl alcohols as substrates and 1.5 equiv of ^{i}PrOH were added, allyl boronates were obtained from the borylation reaction (Scheme 3-3). With 2-phenylbut-3-yn-2-ol **(3-3)a** as the starting material, the desired allyl boronate **(3-4)a** was formed in 74% yield. Allyl boronates **(3-4)b-f** were obtained in moderate to good yields of 68%-82% with the phenyl ring bearing different substituents **(3-3)b-f**. Substrate **(3-3)g,** with a fused ring system, provided **(3-4)g** in 83% yield. The geometry of the C=C bonds was determined by ^1H, ^1H NOESY, and the NMR data are identical to those in the literature.[102] When the phenyl ring system was replaced by aliphatic substituents, such as **(3-3)h-j**, allyl boronates **(3-4)h-j** were also afforded in yields of 44%-61%. Due to the fact that the alkyl-substituted allyl boronates are unstable on silica gel, and they

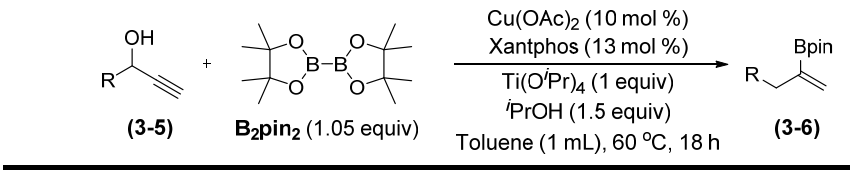
are volatile compounds as well, flash chromatography and rotary evaporation of solvents contribute to yield losses to varying extents. The regio- and stereo-selectivity of the borylation reaction suggest mechanistic similarities to the borylcupration of allenylsilanes reported by Ma and co-workers.[67c]

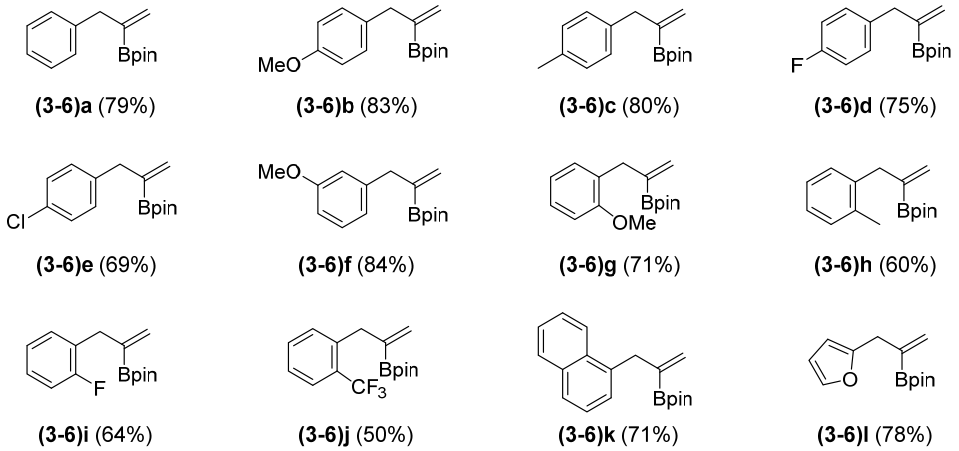


[a] Standard conditions: **(3-3)** (0.2 mmol), $Cu(OAc)_2$ (10 mol %), Xantphos (13 mol %), B_2pin_2 (0.4 mmol), $Ti(O^iPr)_4$ (0.2 mmol), ^{i}PrOH (0.3 mmol), MTBE (1 mL), 60 °C, 18 h. [b] Isolated yield. [c] The geometry of the C=C bonds was determined by ^{1}H, ^{1}H NOESY NMR. [d] *Z*/*E* isomer ratios were determined by ^{1}H NMR spectroscopy of the crude product, and the isolated yields of **(*Z*)-(3-4)a-g** are given in the table.

Scheme 3-3. Synthesis of Allyl Boronates[a,b,c]

With mono-substituted propargyl alcohols in the presence of 1.5 equiv of added ^{i}PrOH, vinyl boronates were afforded from the borylation reactions (Scheme 3-4). When 1-phenylprop-2-yn-1-ol **(3-5)a** was employed as the starting material, vinyl boronate **(3-5)b** was obtained in 79% yield. Vinyl boronates **(3-6)b** and **(3-6)c** were formed in yields of 83% and 80% with the phenyl ring bearing electron-donating groups. Products **(3-6)d** and **(3-6)e** were formed in 75% and 69% yields, respectively, when the *para* substituents were F or Cl, and **(3-6)f** was formed in 84% yield with an OMe group at the *meta* position. With an OMe group at the *ortho* position, **(3-6)g** was formed in 71% yield. With other groups at the *ortho* position, borylation products **(3-6)h-j** were obtained in yields of 50-64%. Compound **(3-5)k**, bearing a fused ring system, and heterocyclic compound **(3-5)l** gave corresponding products **(3-6)k** and **(3-6)l** in yields of 71% and 78%, respectively. The regioselectivity of the borylation reaction is in agreement with a mechanism reported for the borylcupration of alkynes.[45,46i]



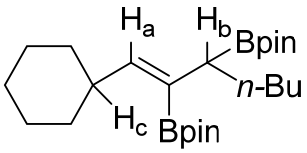


[a] Standard conditions: **(3-5)** (0.2 mmol), $Cu(OAc)_2$ (10 mol %), Xantphos (13 mol %), B_2pin_2 (0.21 mmol), $Ti(O^iPr)_4$ (0.2 mmol), ^{i}PrOH (0.3 mmol), toluene (1 mL), 60 °C, 18 h. [b] Isolated yield.

Scheme 3-4. Synthesis of Vinyl Boronates[a,b]

3.3.3 NOE Study

3.3.3.1 Determination of the Geometry of the C=C Bond in Compound (3-2)g



H_a: 5.74 ppm, doublet, $^3J_{Ha\text{-}Hc}$ = 9.1 Hz

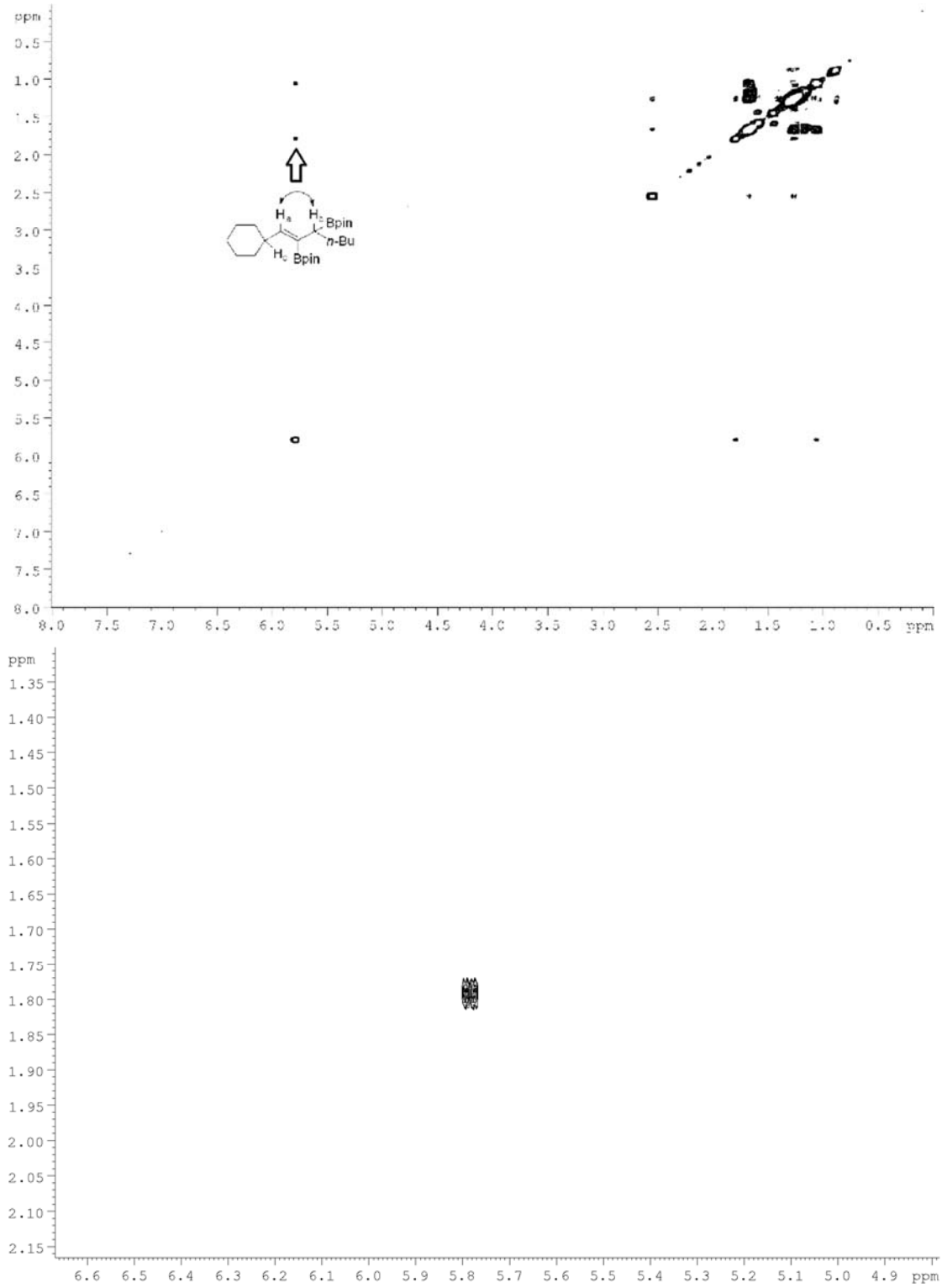
H_b: 1.74 ppm, triplet, $^3J_{Hb\text{-}CH2}$ = 7.7 Hz

H_c: 2.44-2.55, multiplet

NOE-enhancements in [%]

irrad.	H_a	H_b	H_c
H_a		8.4	2.2
H_b	11.5		-4.7
H_c	2.9	-5.8	

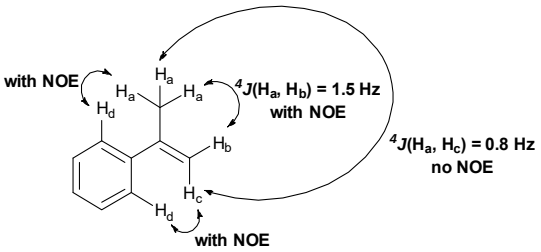
The $^4J(H_a,H_b)$ coupling constant is too small to be observed in the ^{1}H NMR, but the NOE between them is large in ^{1}H,^{1}H NOESY and NOE Difference experiments, indicating that these protons are close to one another. The $^3J(H_a,H_c)$ coupling constant is 9 Hz in the 1D ^{1}H NMR, but there is only a very small NOE observed in ^{1}H,^{1}H NOESY and NOE Difference experiments, indicating, that these protons are strongly coupled through bonds, but not close in space. The NOE studies and the *J* coupling of 9 Hz between H_a and H_c suggest that the C=C bonds have an *E* configuration. From the Karplus relation we calculate a torsion angle between H_a and H_c of ca. 170°.



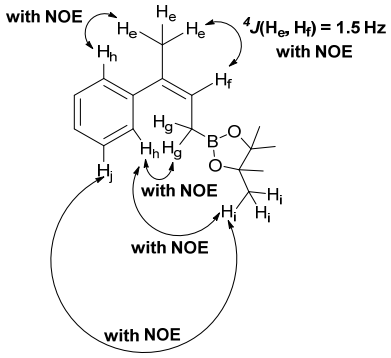
3.3.3.2 Determination of the Geometry of the C=C Bond in Compound (3-4)a

To assign the geometry of the C=C bond of **(3-4)a**, we used α-methyl styrene as a model compound to investigate the relationship between ^4J coupling constants and the geometry of the C=C bond, as well as the NOE study (*vide infra*). In α-methyl styrene, $^4J(H_a, H_b)$ = 1.5 Hz, and $^4J(H_a, H_c)$ = 0.8 Hz. The $^4J(H_a, H_b)$ coupling constant is identical to the $^4J(H_e, H_f)$ coupling constant in compound

(3-4)a. A ^{1}H,^{1}H NOESY study of α-methyl styrene also suggests that there is NOE between H_a and H_b, H_a and H_d, as well as H_c and H_d.



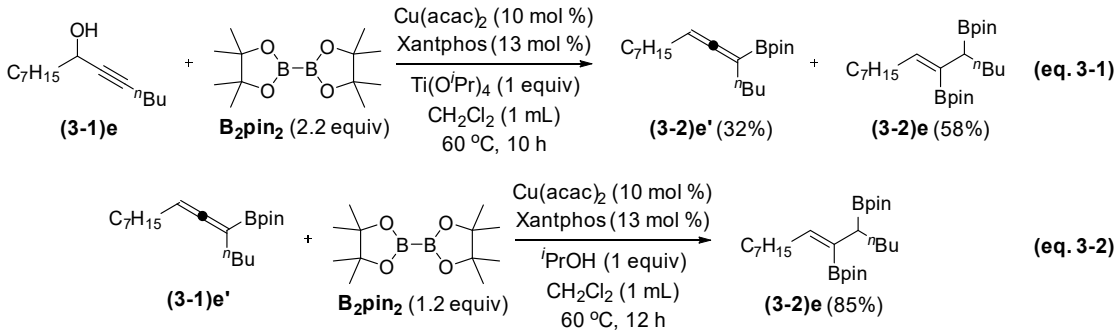
A ^{1}H,^{1}H NOESY study has also been carried out on compound **(3-4)a**. There is also NOE between H_e and H_f, H_e and H_h, H_h and H_i as well as H_i and H_j. The NOE between H_g and H_h, H_h and H_i, as well as H_i and H_j, in combination with $^4J(H_e, H_f)$ = 1.5 Hz suggests that the C=C has the *Z* configuration. Additionally, the ^{1}H and ^{13}C NMR data of compound **(3-4)a** are identical to those in a literature report.[102a]



3.3.4 Mechanistic Study

3.3.4.1 Identification of an Allenyl Boronate Intermediate

Allenyl boronate **(3-2)e'** was isolated as a reaction intermediate after the reaction of **(3-1)e** was carried out for 10 h (eq. 3-1); **(3-2)e'** can also be prepared according to a literature procedure.[83] The borylation of isolated **(3-2)e'** under the modified conditions gave the diboration product **(3-2)e** in a yield of 85% (eq. 3-2). These results suggest that a copper-catalyzed S_N2' borylation of propargyl alcohols,[94] followed by a borylcupration of the resulting allenyl boronates[67,68a,b,69] and finally a protonolysis of the Cu-C bond are involved in the mechanism.



Characterization data of allenyl boronate **(3-2)e'** are listed below:

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.04 (dt, J_1 = 7 Hz, J_2 = 3 Hz, 1H), 2.04–1.97 (m, 4H), 1.43–1.35 (m, 5H), 1.34–1.27 (m, 9H), 1.26 (s, 6H), 1.25 (s, 6H), 0.90–0.86 (ov. m, 6H).

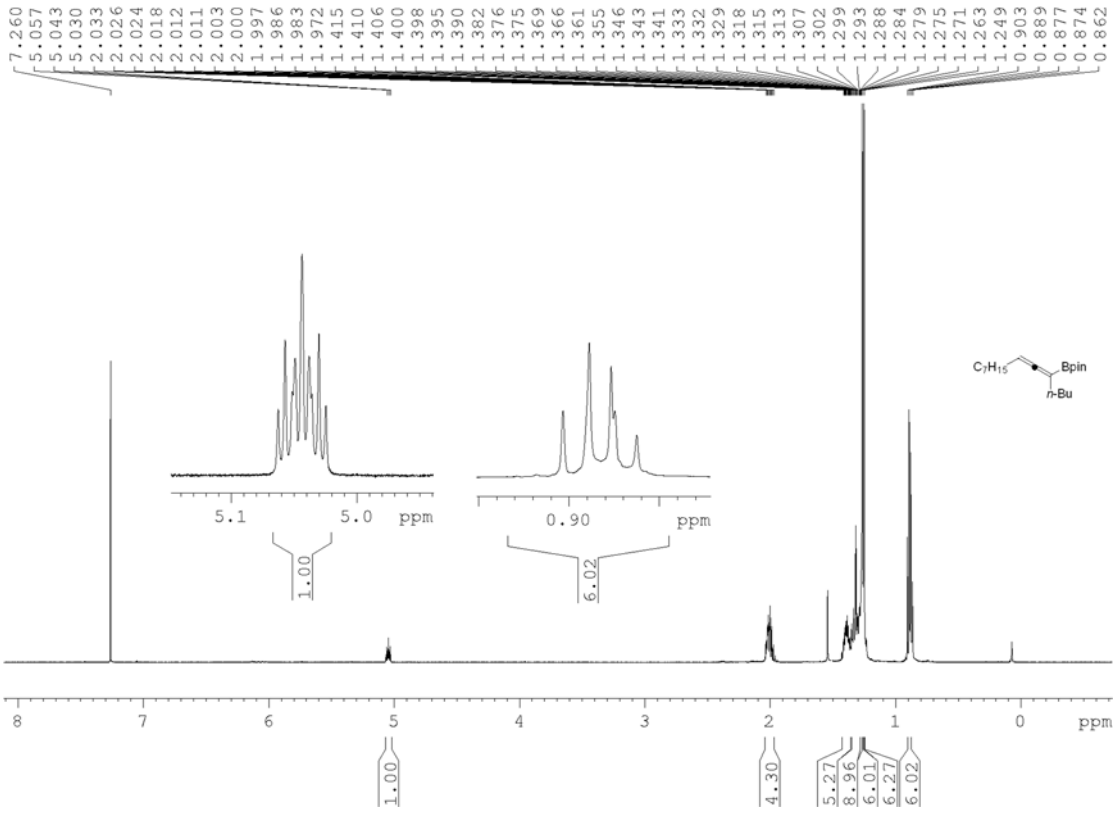
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 212.0, 92.3 (broad, low intensity), 87.4, 83.5, 32.0, 31.7, 29.7, 29.5, 29.4, 29.1, 28.2, 25.0, 24.7, 22.9, 22.5, 14.3, 14.2.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.7.

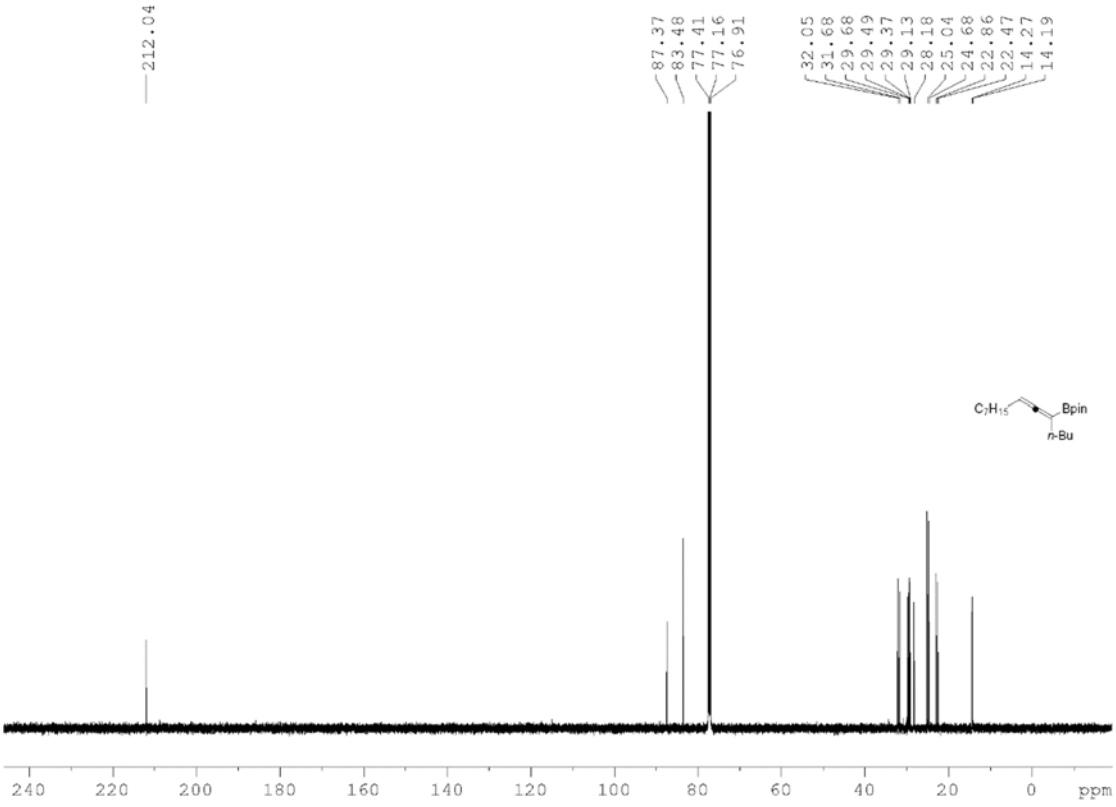
HRMS (ASAP) *m/z* calcd for $C_{20}H_{38}BO_2$ [M+H$^+$]: 321.2959, found: 321.2953.

Spectra of (3-2)e'

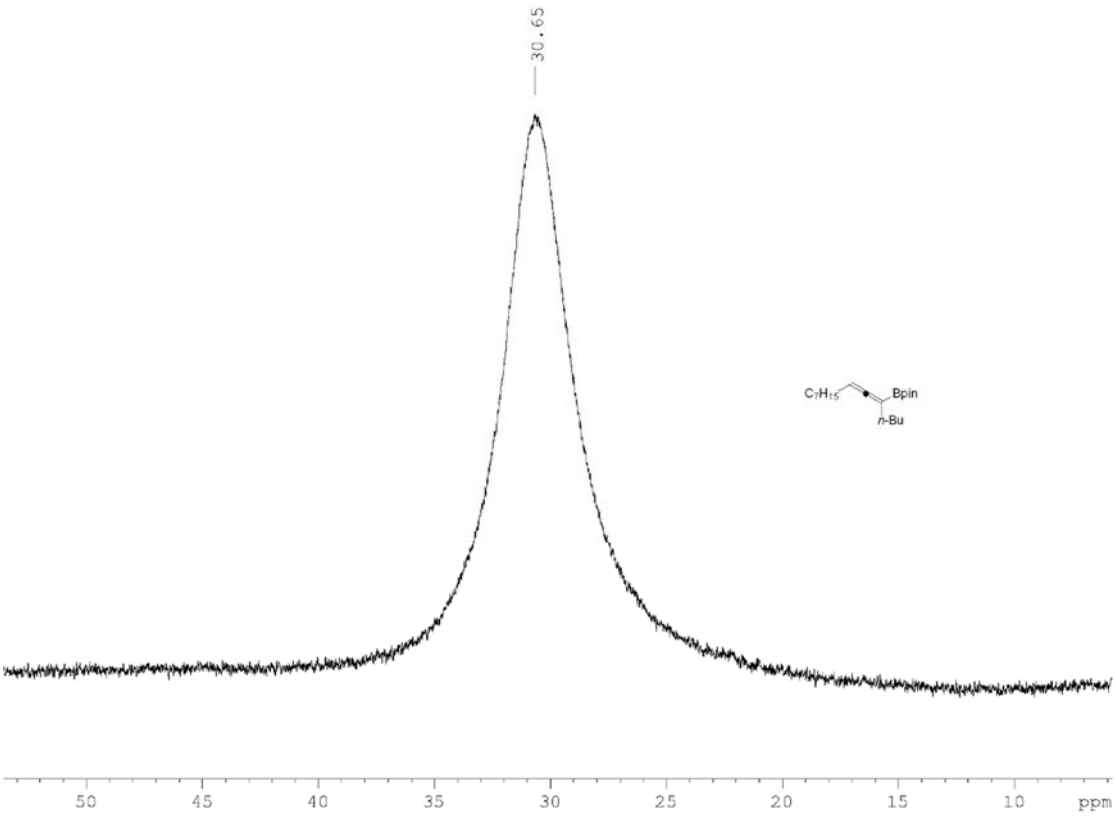
^{1}H NMR (500 MHz, $CDCl_3$)



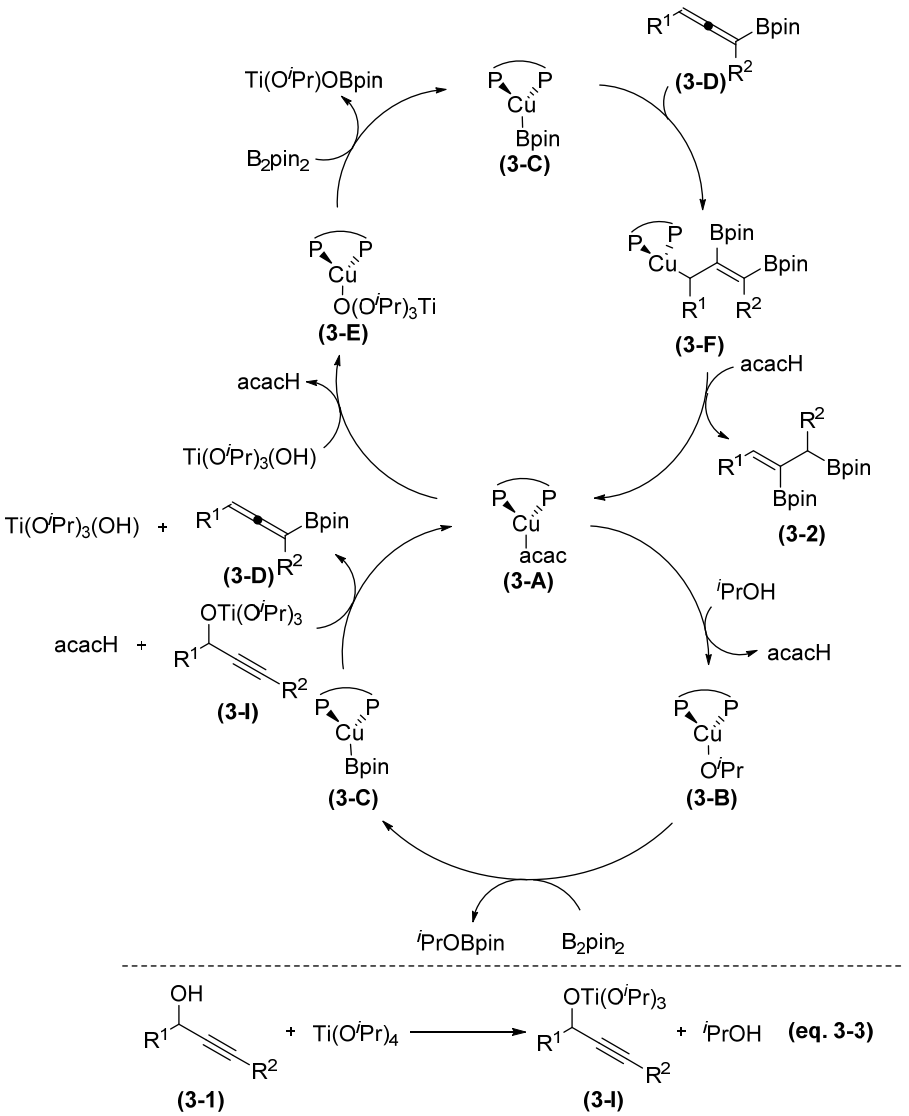
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)

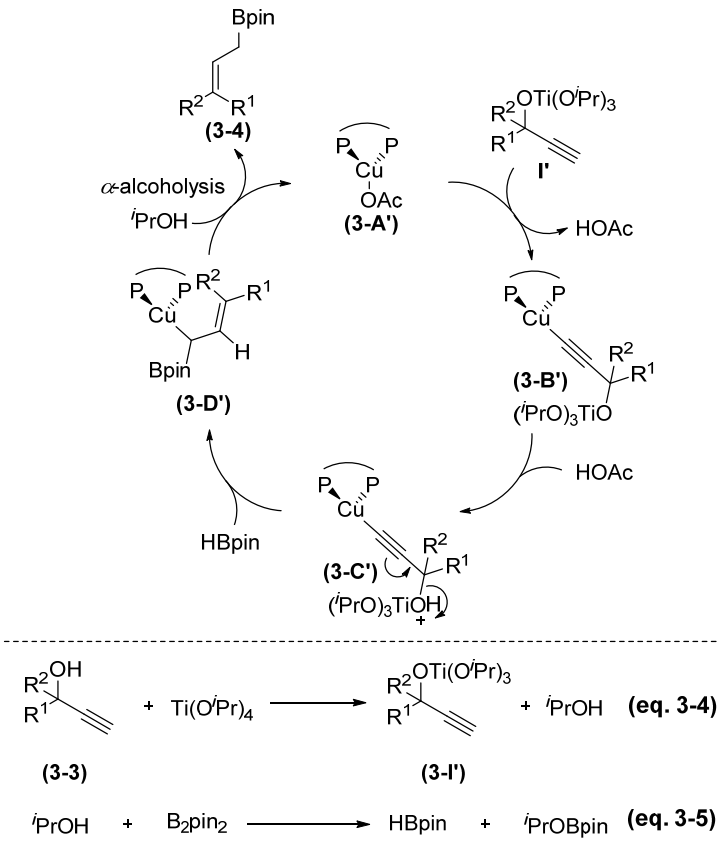


3.3.4.2 Plausible Mechanism



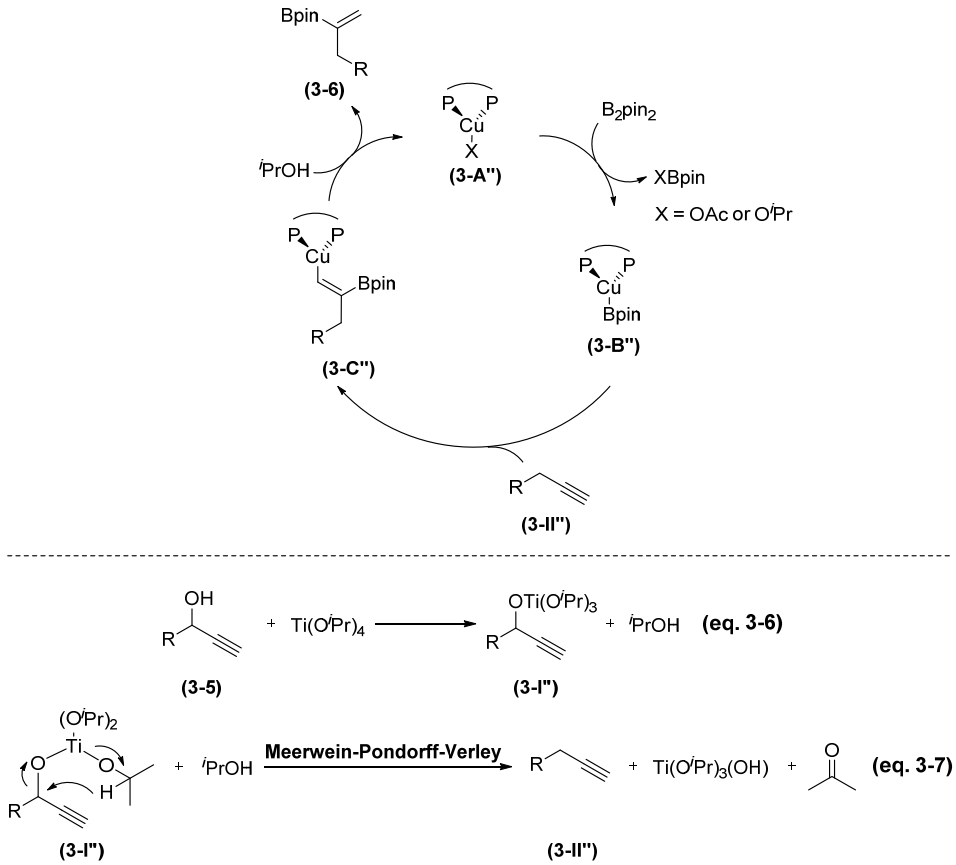
Scheme 3-5. Plausible Mechanism for the Diboration of Propargylic Alcohols **(3-1)**

Propargylic alcohols **(3-1)** can be activated by $Ti(O^iPr)_4$ to generate **(3-I)** and ^{i}PrOH (eq. 3-3).[21] It is proposed that the active catalyst is a Cu^I species. The active Cu^I species **(3-A)** could be generated via reduction by a boryl anion nucleophile.[87] Copper species **(3-A)** could react with ^{i}PrOH to provide **(3-B)**. Transmetalation between **(3-B)** and B_2pin_2 affords Cu-Bpin species **(3-C)**.[24a,94] An S_N2' reaction occurrs between **(3-C)** and **(3-I)** to provide allenylboronates **(3-D)**,[24a,94] and catalytic species **(3-A)** is regenerated. $Ti(OH)(O^iPr)_3$ reacts with **(3-A)** to afford **(3-E)**, and transmetalation between **(3-E)** and B_2pin_2 regenerates Cu-Bpin species **(3-C)**. The borylcupration of allenylboronates **(3-D)** affords **(3-F)**.[67a,b,68a] Because the (*E*)-geometry is more thermodynamically stable than the (*Z*)-geometry, the desired (*E*)-2-boryl allylboronates **(3-2)** were afforded via protonation of **(3-F)**.[67a,b,68a]



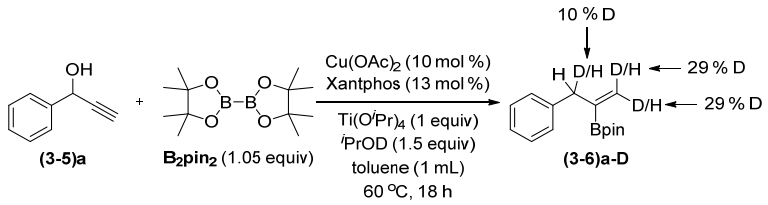
Scheme 3-6. Plausible Mechanism for the Monoboration of Propargylic Alcohols **(3-3)**

Propargylic alcohols **(3-3)** can be activated by $Ti(O^iPr)_4$ to generate **(3-I')** and ^{i}PrOH (eq. 3-4).[21] HBpin could be generated from the reaction of ^{i}PrOH with B_2pin_2 (eq. 3-5).[87,103a] Copper species **(3-A')** reacted with **(3-I')** to provide **(3-B')**. Species **(3-B')** might be activated by HOAc, generated in the earlier step, to afford intermediate **(3-C')**, to which rearrangement of propargylic compounds[93a] followd by the addition of HBpin to give species **(3-D')**. Allylboronates **(3-4)** were obtained from α-protonation of **(3-D')**.[67c] The regio- and stereoselectivity of the monoboration is in agreement with the copper-catalyzed hydroboration of allenylsilanes.[67c]



Scheme 3-7. Plausible Mechanism for the Monoboration of Propargylic Alcohols **(3-5)**

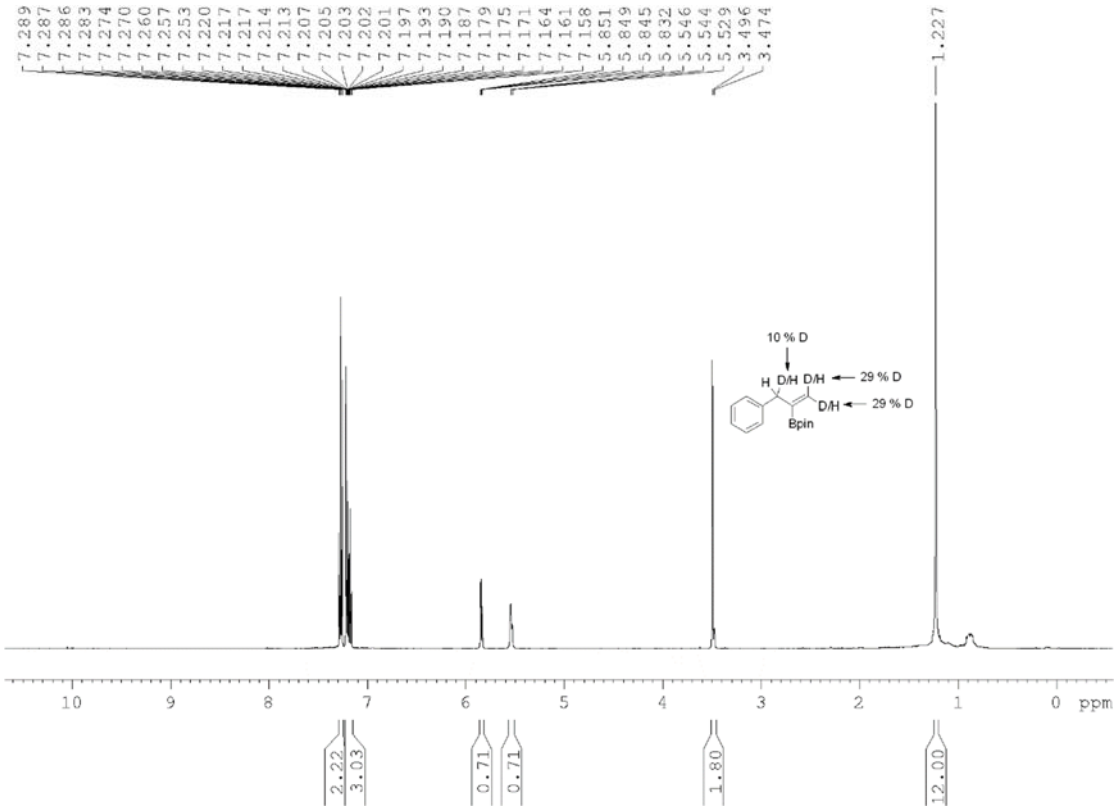
Propargylic alcohols **(3-5)** can be activated by $Ti(O^iPr)_4$ to generate **(3-I")** and ^{i}PrOH (eq. 3-6),[21] followed by a Meerwein-Pondorff-Verley type of reaction to generate **(3-II")** (eq. 3-7).[103b,c] Transmetalation between copper species **(3-A")** and B_2pin_2 provided Cu-B species **(3-B")**.[24a,94] Borycupration occurred to **(3-II")** to afford **(3-C")**,[45,46i] followed by the alcoholysis of **(3-C")** to generate vinylboronates **(3-6)**.[40a,e,44,45,46a,c,i,48a]



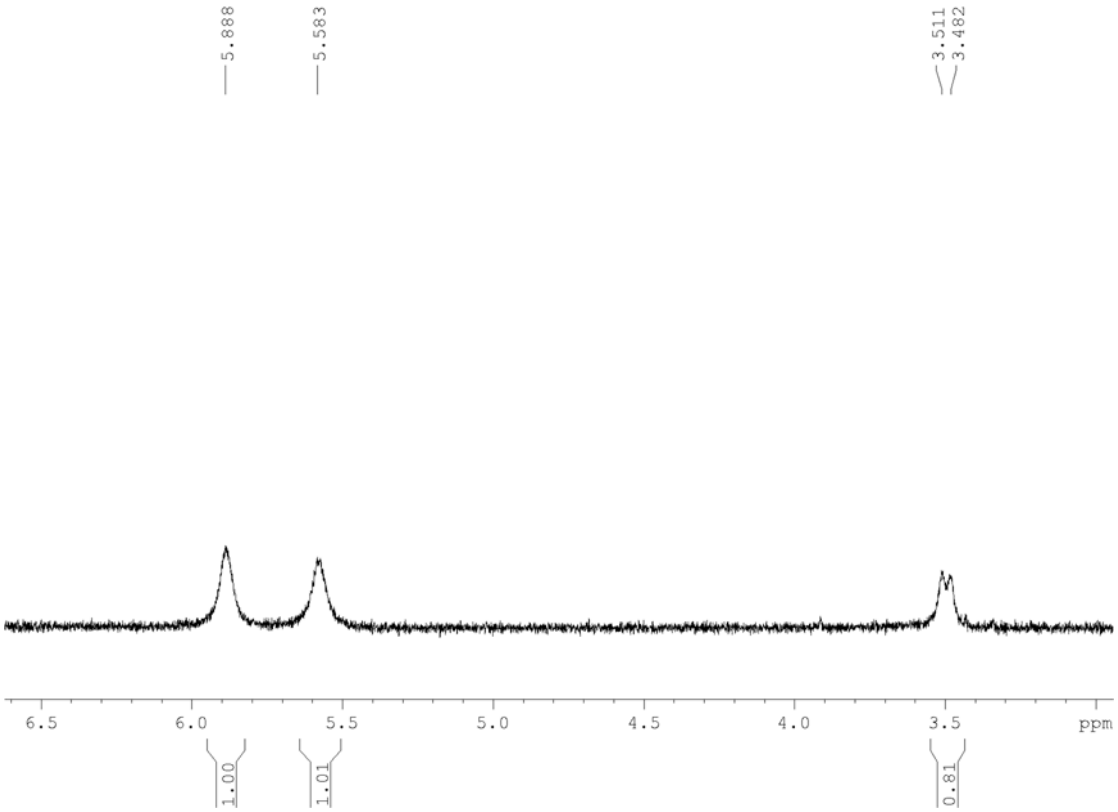
When ^{i}PrOH was replaced by ^{i}PrOD, vinylic boronate **(3-6)a-D** was obtained from the borylation reaction. Both vinylic protons were replaced by deuterium in 29%, respectively, which suggests that hydroboration of intermediate **II"** might be involved in the mechanism.

Compound (3-6)a-D

^{1}H NMR (500 MHz, $CDCl_3$, quan.)



^{2}D NMR (77 MHz, $CDCl_3$)



3.4 Summary

Chapter 3 reports the methodology for the synthesis of vinyl-, allyl- and 2-boryl allyl-boronates from propargyl alcohols under mild conditions, broadening the utility of alcohols in synthetic methodology. An S_N2' type of reaction followed by a borylcupration of the allenyl boronate intermediate are apparently involved in the overall mechanism.

3.5 Experimental Procedure and Characterization Data

3.5.1 General Information

All reagents were purchased from Alfa-Aesar, Aldrich, ABCR or VWR, and were checked for purity by GC-MS and/or ^{1}H NMR spectroscopy and used as received. B_2pin_2 was kindly provided by AllylChem Co. Ltd. (Dalian, China). HPLC grade solvents were argon saturated, dried using an Innovative Technology Inc. Pure-Solv Solvent Purification System, and further deoxygenated using the freeze-pump-thaw method. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, and dried over 4Å molecular sieves, deoxygenated using the freeze-pump-thaw method and vacuum transferred into a sealed vessel.

Automated flash chromatography was performed using a Biotage® Isolera Four system, on silica gel (Biotage SNAP cartridge KP-Sil 10 g and KP-Sil 25 g). Commercially available, precoated TLC plates (Polygram® Sil G/UV254) were purchased from Machery-Nagel. The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 30 °C.

GC-MS analyses were performed using an Agilent 7890A gas chromatograph (column: HP-5MS 5% phenyl methyl siloxane, 10 m, ∅ 0.25 mm, film 0.25 μm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C (20 °C min^{-1}); carrier gas: He (1.2 mL min^{-1})) equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A series auto sampler/injector. HRMS analyses were performed using a Thermo Fischer Scientific Exactive Plus Orbitrap MS system (ASAP, ESI or HESI probe). Elemental analyses were performed on a Leco CHNS-932 Elemental Analyzer in our Institute.

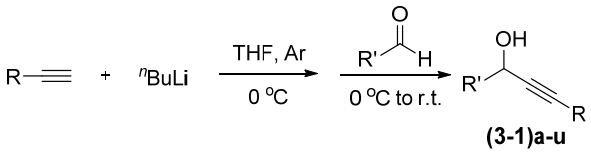
All NMR spectra were recorded at ambient temperature using Bruker Avance III HD 300 NMR (^{1}H, 300 MHz; ^{13}C{^{1}H}, 75 MHz; ^{11}B, 96 MHz), or Bruker Avance 500 NMR (^{1}H, 500 MHz; ^{13}C{^{1}H}, 125 MHz; ^{11}B, 160 MHz; ^{19}F, 470 MHz) spectrometers. ^{1}H NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm) whereas ^{13}C{^{1}H} NMR spectra are reported relative to TMS *via* the

carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm). ^{11}B NMR chemical shifts are quoted relative to $BF_3 \cdot Et_2O$ as external standard. ^{19}F NMR chemical shifts are quoted relative to $CFCl_3$ as external standard. All ^{13}C NMR spectra were broad-band ^{1}H decoupled.

3.5.2 Preparation of Starting Materials

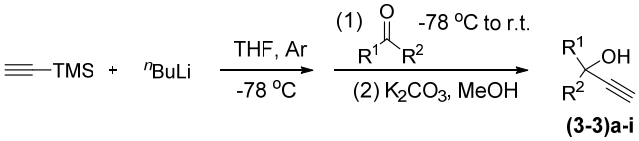
3.5.2.1 Preparation of Propargylic Alcohols (3-1)a-u

Compounds **(3-1)a-u** were synthesized via the following method. The characterization data (^{1}H NMR and ^{13}C NMR) are in accordance with those in the literature.[83]



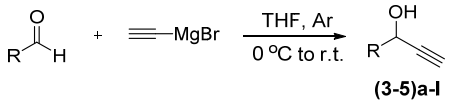
3.5.2.2 Preparation of Propargylic Alcohols (3-3)a-i

Compounds **(3-3)a-i** were synthesized via the following method. The characterization data (^{1}H NMR and ^{13}C NMR) are in accordance with those in the literature.[104]



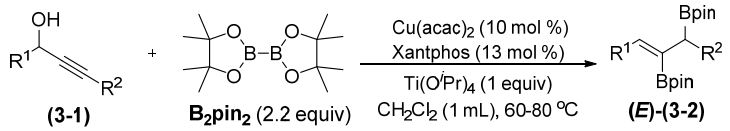
3.5.2.3 Preparation of Propargylic Alcohols (3-5)a-l

Compounds **(3-5)a-l** were synthesized via the following method. The characterization data (^{1}H NMR and ^{13}C NMR) are in accordance with those in the literature.[105]



3.5.3 Experimetal Procedure

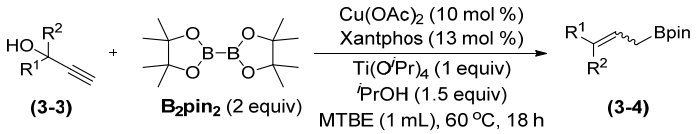
3.5.3.1 Synthesis of (*E*)-2-Boryl Allyl-boronates (Method 3A)



$Cu(acac)_2$ (10 mol %, 5.2 mg) and Xantphos (13 mol %, 15 mg) were dissolved in 0.5 mL of CH_2Cl_2 in a dried vial in the glove-box under argon and the reaction was stirred for 5 min. Then, B_2pin_2 (2.2 equiv, 111.7 mg, 0.44 mmol), **(3-1)** (1 equiv, 0.2 mmol), and $Ti(O^iPr)_4$ (1 equiv, 59.2 μL, 0.2 mmol) were added in this order. Finally, another 0.5 mL of CH_2Cl_2 was added to the mixture. The reaction was heated at 60 or 80 °C under argon until the starting material was completely consumed

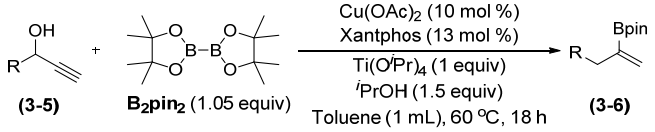
(determined by GC-MS). The crude mixture was filtered through a pad of Celite. Then, the solvent was removed on a rotary evaporator. All products were purified by flash chromatography.

3.5.3.2 Synthesis of Allyl Boronates (Method 3B)



$Cu(OAc)_2$ (10 mol %, 3.6 mg) and Xantphos (13 mol %, 15 mg) were dissolved in 0.5 mL of MTBE in a dried vial in the glove-box under argon and the reaction was stirred for 5 min. Then, B_2pin_2 (2 equiv, 101.6 mg, 0.4 mmol), **(3-3)** (1 equiv, 0.2 mmol), $Ti(O^iPr)_4$ (1 equiv, 59.2 μL, 0.2 mmol) and ^{i}PrOH (1.5 equiv, 22.9μL, 0.3 mmol) were added in this order. Finally, another 0.5 mL of toluene was added to the mixture. The reaction was heated at 60 °C under argon until the starting material was completely consumed (determined by GC-MS). The crude mixture was filtered through a pad of Celite. Then, the solvent was removed on a rotary evaporator. All products were purified by flash chromatography.

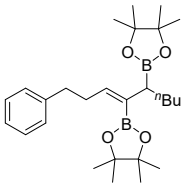
3.5.3.3 Synthesis of Vinyl Boronates (Method 3C)



$Cu(OAc)_2$ (10 mol %, 3.6 mg) and Xantphos (13 mol %, 15 mg) were dissolved in 0.5 mL of toluene in a dried vial in the glove-box under argon and the reaction was stirred for 5 min. Then, B_2pin_2 (1.05 equiv, 53.3 mg, 0.21 mmol), **(3-5)** (1 equiv, 0.2 mmol), $Ti(O^iPr)_4$ (1 equiv, 59.2 μL, 0.2 mmol) and ^{i}PrOH (1.5 equiv, 22.9μL, 0.3 mmol) were added in this order. Finally, another 0.5 mL of toluene was added to the mixture. The reaction was heated at 60 °C under argon until the starting material was completely consumed (determined by GC-MS). The crude mixture was filtered through a pad of Celite. Then, the solvent was removed on a rotary evaporator. All products were purified by flash chromatography.

3.5.4 Characterization Data

(*E*)-2,2'-(1-Phenylnon-3-ene-4,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)a



Following method 3A, a colorless oil in 81% yield (74 mg) from **(3-1)a** (43 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 18 h at 60 ºC.

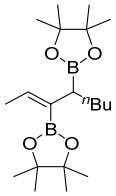
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.20 (m, 4H), 7.18–7.13 (m, 1H), 6.03 (t, *J* = 7 Hz, 1H), 2.74–2.52 (m, 4H), 1.80 (t, *J* = 8 Hz, 1H), 1.63–1.53 (m, 1H), 1.50–1.40 (m, 1H), 1.39–1.14 (m, 4H), 1.25 (s, 6H), 1.24 (s, 6H), 1.23 (s, 6H), 1.22 (s, 6H), 0.87 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.9, 142.8, 133.4 (broad, low intensity), 128.7, 128.2, 125.6, 82.9, 37.0, 33.4, 32.6 (broad, low intensity), 31.6, 30.5, 25.1, 25.0, 24.84, 24.83, 22.9, 14.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.5, 30.5.

HRMS (ASAP): *m/z* calcd for $C_{27}H_{45}B_2O_4$ [M+H$^+$]: 455.3498, found: 455.3492.

(*E*)-2,2'-(Oct-2-ene-3,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)b



Following method 3A, a colorless oil in 89% yield (65 mg) from **(3-1)b** (25 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 18 h at 60 ºC.

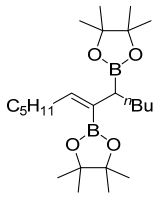
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (q, *J* = 7 Hz, 1H), 1.88 (dd, J_1 = 7 Hz, J_2 = 0.5 Hz, 3H), 1.76 (br. t, *J* = 8 Hz, 1H), 1.63–1.38 (m, 2H), 1.36–1.12 (m, 4H), 1.25 (s, 12H), 1.23 (s, 6H) 1.22 (s, 6H), 0.85 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.2, 132.2 (broad, low intensity), 83.0, 82.9, 32.9 (broad, low intensity), 31.6, 30.5, 25.2, 25.0, 24.9, 24.8, 22.9, 17.6, 14.3.

^{11}B NMR (96 MHz, $CDCl_3$) δ 32.8, 30.6.

HRMS (ASAP): *m/z* calcd for $C_{20}H_{39}B_2O_4$ [M+H$^+$]: 365.3029, found: 365.3024.

(*E*)-2,2'-(Dodec-6-ene-5,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)c



Following method 3A, a colorless oil in 91% yield (77 mg) from **(3-1)c** (37 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 18 h at 60 ºC.

Isolated yield: 91%.

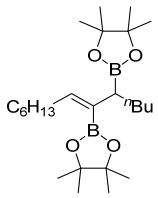
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 (t, *J* = 7 Hz, 1H), 2.33 (dq, J_1 = 14 Hz, J_2 = 7 Hz, 1H), 2.24 (dq, J_1 = 14 Hz, J_2 = 7 Hz, 1H), 1.78 (t, *J* = 8 Hz, 1H), 1.63–1.52 (m, 1H), 1.49-1.40 (m, 1H), 1.38–1.14 (m, 10H), 1.24 (s, 12H), 1.22 (s, 6H), 1.21 (s, 6H), 0.87 (t, *J* = 7 Hz, 3H), 0.85 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 145.0, 132.4 (broad, low intensity), 82.9, 82.8, 32.5 (broad, low intensity), 31.7, 31.4, 31.3, 30.6, 30.0, 25.1, 25.0, 24.9, 24.8, 22.9, 22.7, 14.31, 14.27.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.5, 30.7.

HRMS (ASAP): *m/z* calcd for $C_{24}H_{47}B_2O_4$ [M+H$^+$]: 421.3655, found: 421.3650.

(*E*)-2,2'-(Tridec-6-ene-5,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)d



Following method 3A, a colorless oil in 90% yield (78 mg) from **(3-1)d** (39 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 18 h at 60 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93 (t, *J* = 8 Hz, 1H), 2.40–2.16 (m, 2H), 1.78 (t, *J* = 8 Hz, 1H), 1.63–1.41 (m, 2H), 1.39–1.12 (m, 12H), 1.24 (s, 12H), 1.22 (s, 6H), 1.21 (s, 6H), 0.87 (t, *J* = 7 Hz, 3H), 0.85 (t, *J* = 7 Hz, 3H).

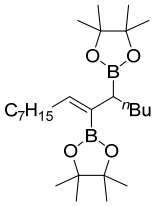
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.0, 132.4 (broad, low intensity), 82.9, 82.8, 32.5 (broad, low

intensity), 31.9, 31.6, 31.4, 30.6, 30.2, 28.9, 25.1, 25.0, 24.9, 24.8, 22.9, 22.8, 14.30, 14.28.

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1, 30.6.

HRMS (ASAP): *m/z* calcd for $C_{25}H_{49}B_2O_4$ [M+H$^+$]: 435.3811, found: 435.3806.

(*E*)-2,2'-(Tetradec-6-ene-5,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)e



Following method 3A, a colorless oil in 86% yield (77 mg) from **(3-1)e** (42 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 18 h at 60 ºC.

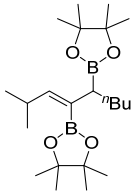
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93 (t, *J* = 8 Hz, 1H), 2.40–2.16 (m, 2H), 1.78 (t, *J* = 8 Hz, 1H), 1.66–1.40 (m, 2H), 1.40–1.12 (m, 14H), 1.24 (s, 12H), 1.22 (s, 6H), 1.21 (s, 6H), 0.87 (t, *J* = 7 Hz, 3H), 0.85 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.0, 132.5 (broad, low intensity), 82.9, 82.8, 32.5 (broad, low intensity), 32.1, 31.6, 31.4, 30.6, 30.3, 29.4, 29.2, 25.1, 25.0, 24.9, 24.8, 22.91, 22.86, 14.30, 14.27.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.4, 30.6.

HRMS (ASAP): *m/z* calcd for $C_{26}H_{51}B_2O_4$ [M+H$^+$]: 449.3968, found: 449.3964.

(*E*)-2,2'-(2-Methylnon-3-ene-4,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)f



Following method 3A, a colorless oil in 74% yield (58 mg) from **(3-1)f** (31 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 18 h at 60 ºC.

complete within 18 h at 60 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (d, *J* = 9 Hz, 1H), 2.89 (dsept., J_1 = 9 Hz, J_2 = 7 Hz, 1H), 1.76 (t, *J* = 8 Hz, 1H), 1.63–1.35 (m, 2H), 1.33–1.23 (m, 4H), 1.24 (s, 12H), 1.21 (s, 6H), 1.20 (s, 6H),

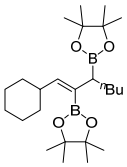
0.93 (d, *J* = 7 Hz, 3H), 0.92 (d, *J* = 7 Hz, 3H), 0.85 (t, *J* = 7 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 152.0, 130.4 (broad, low intensity), 82.84, 82.80, 31.8 (broad, low intensity), 31.7, 30.8, 30.2, 25.02, 24.96, 24.9, 24.8, 23.9, 23.8, 22.9, 14.3.

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1, 30.6.

HRMS (ASAP): *m/z* calcd for $C_{22}H_{43}B_2O_4$ $[M+H^+]$: 393.3342, found: 393.3338.

(*E*)-2,2'-(1-Cyclohexylhept-1-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)g



Following method 3A, a colorless oil in 63% yield (55 mg) from **(3-1)g** (39 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 18 h at 60 ºC.

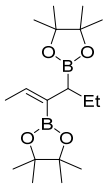
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.75 (d, *J* = 9 Hz, 1H), 2.59–2.43 (m, 1H), 1.75 (t, *J* = 8 Hz, 1H), 1.71–1.35 (m, 8H), 1.35–0.92 (m, 8H), 1.24 (s, 12H), 1.21 (s, 6H), 1.19 (s, 6H), 0.84 (t, *J* = 7 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 150.0, 131.1 (broad, low intensity), 82.83, 82.79, 40.0, 34.2, 31.9 (broad, low intensity), 31.6, 30.7, 26.3, 26.2, 25.0, 24.95, 24.83, 24.75, 22.9, 14.3.

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1, 30.7.

HRMS (ASAP): *m/z* calcd for $C_{25}H_{47}B_2O_4$ $[M+H^+]$: 433.3655, found: 433.3652.

(*E*)-2,2'-(Hex-2-ene-3,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)h



Following method 3A, a colorless oil in 81% yield (54 mg) from **(3-1)h** (20 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 18 h at 60 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (q, *J* = 7 Hz, 1H), 1.87 (d, *J* = 7 Hz, 3H), 1.68 (t, *J* = 7 Hz, 1H), 1.67–1.54 (m, 1H), 1.50–1.33 (m, 1H), 1.25 (s, 12H), 1.22 (s, 6H), 1.21 (s, 6H), 0.84 (t, *J* = 7 Hz,

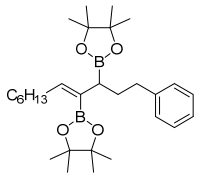
3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 139.3, 133.2 (broad, low intensity), 82.9, 82.88, 34.6 (broad, low intensity), 25.1, 25.0, 24.9, 24.8, 24.0, 17.6, 13.9.

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.2, 30.6.

HRMS (ASAP): *m/z* calcd for $C_{18}H_{35}B_2O_4$ $[M+H^+]$: 337.2716, found: 337.2711.

(*E*)-2,2'-(1-Phenylundec-4-ene-3,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)i



Following method 3A, a colorless oil in 92% yield (89 mg) from **(3-1)i** (49 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 18 h at 60 ºC.

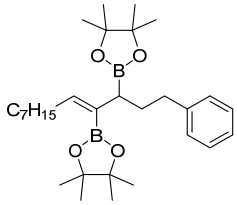
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.22 (m, 2H), 7.21–7.17 (m, 2H), 7.16–7.12 (m, 1H), 5.99 (t, *J* = 8 Hz, 1H), 2.69–2.59 (m, 1H), 2.55–2.46 (m, 1H), 2.39 (dq, J_1 = 14 Hz, J_2 = 7 Hz, 1H), 2.29 (dq, J_1 = 14 Hz, J_2 = 7 Hz, 1H), 1.95–1.75 (ov. m, 3H), 1.42–1.18 (m, 8H), 1.27 (s, 12H), 1.25 (s, 6H), 1.23 (s, 6H), 0.89 (t, *J* = 7 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 145.7, 143.7, 132.2 (broad, low intensity), 128.7, 128.2, 125.4, 83.0, 82.9, 35.7, 33.0, 32.6 (broad, low intensity), 31.9, 31.4, 30.2, 28.9, 25.1, 25.0, 24.8, 22.8, 14.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.3, 30.7.

HRMS (ASAP): *m/z* calcd for $C_{29}H_{49}B_2O_4$ $[M+H^+]$: 483.3811, found: 483.3807.

(*E*)-2,2'-(1-Phenyldodec-4-ene-3,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)j



Following method 3A, a colorless oil in 89% yield (88 mg) from **(3-1)j** (52 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 18 h at 60 ºC.

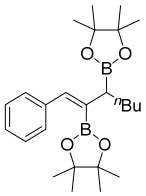
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.24 (m, 2H), 7.22–7.18 (m, 2H), 7.18–7.14 (m, 1H), 6.00 (t, *J* = 7 Hz, 1H), 2.71–2.62 (m, 1H), 2.56–2.48 (m, 1H), 2.41 (dq, J_1 = 14 Hz, J_2 = 7 Hz, 1H), 2.31 (dq, J_1 = 14 Hz, J_2 = 7 Hz, 1H), 1.97–1.78 (ov. m, 3H), 1.46–1.11 (m, 10H), 1.29 (s, 12H), 1.25 (s, 6H), 1.24 (s, 6H), 0.90 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 145.7, 143.7, 132.2 (broad, low intensity), 128.7, 128.2, 125.4, 83.0, 82.8, 35.6, 33.0, 32.6 (broad, low intensity), 32.1, 31.4, 30.3, 29.3, 29.2, 25.1, 25.0, 24.8, 22.8, 14.2.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.2, 30.7.

HRMS (ASAP): *m/z* calcd for $C_{30}H_{51}B_2O_4$ [M+H$^+$]: 497.3968, found: 497.3962.

(*E*)-2,2'-(1-Phenylhept-1-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)k



Following method 3A, a colorless oil in 74% yield (63 mg) from **(3-1)k** (38 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 24 h at 80 ºC.

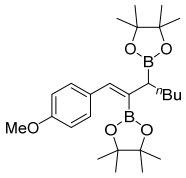
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.29 (m, 2H), 7.27–7.12 (m, 3H), 6.89 (s, 1H), 2.02 (t, *J* = 8 Hz, 1H), 1.78–1.51 (m, 2H), 1.43–1.29 (m, 4H), 1.26 (s, 6H), 1.25 (s, 18H), 0.89 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.7, 138.7, 137.4 (broad, low intensity), 128.3, 127.8, 126.6, 83.5, 83.2, 34.4 (broad, low intensity), 31.8, 30.5, 25.04, 25.00, 24.8, 22.9, 14.2.

^{11}B NMR (96 MHz, $CDCl_3$) δ 31.4 (2B).

HRMS (ASAP): *m/z* calcd for $C_{25}H_{41}B_2O_4$ [M+H$^+$]: 427.3185, found: 427.3180.

(*E*)-2,2'-(1-(4-Methoxyphenyl)hept-1-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)l



Following method 3A, a colorless oil in 78% yield (71 mg) from **(3-1)l** (44 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 24 h at 80 ºC.

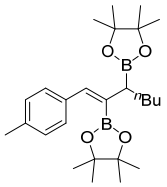
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.23 (m, 2H), 6.82 (s, 1H), 6.80–6.74 (m, 2H), 3.78 (s, 3H), 1.98 (t, *J* = 8 Hz, 1H), 1.76–1.48 (m, 2H), 1.42–1.17 (m, 4H), 1.26 (s, 6H), 1.25 (s, 12H), 1.24 (s, 6H), 0.88 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 158.6, 138.5, 135.0 (broad, low intensity), 132.5, 129.5, 113.3, 83.4, 83.2, 55.4, 34.2 (broad, low intensity), 31.8, 30.6, 25.0, 24.8, 24.7, 22.9, 14.2.

^{11}B NMR (96 MHz, $CDCl_3$) δ 31.2 (2B).

HRMS (ASAP): *m/z* calcd for $C_{26}H_{43}B_2O_5$ [M+H$^+$]: 457.3291, found: 457.3286.

(*E*)-2,2'-(1-(*p*-Tolyl)hept-1-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)m



Following method 3A, a colorless oil in 77% yield (68 mg) from **(3-1)m** (41 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 24 h at 80 ºC.

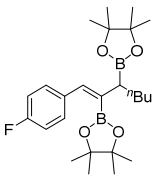
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.19 (m, 2H), 7.07–7.00 (m, 2H), 6.84 (s, 1H), 2.30 (s, 3H), 2.00 (t, *J* = 8 Hz, 1H), 1.77–1.50 (m, 2H), 1.42–1.14 (m, 4H), 1.26 (s, 12H), 1.25 (s, 6H), 1.24 (s, 6H), 0.88 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 138.7, 136.8, 136.2, 135.9 (broad, low intensity), 128.5, 128.2, 83.5, 83.2, 34.4 (broad, low intensity), 31.8, 30.6, 25.0, 24.8, 22.9, 21.3, 14.3.

^{11}B NMR (96 MHz, $CDCl_3$) δ 31.3 (2B).

HRMS (ASAP): *m/z* calcd for $C_{26}H_{43}B_2O_4$ [M+H$^+$]: 441.3342, found: 441.3338.

(*E*)-2,2'-(1-(4-Fluorophenyl)hept-1-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)n



Following method 3A, a colorless oil in 69% yield (61 mg) from **(3-1)n** (41 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 24 h at 80 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.25 (m, 2H), 6.95–6.89 (m, 2H), 6.84 (s, 1H), 2.00 (t, *J* = 8 Hz, 1H), 1.75–1.64 (m, 1H), 1.61–1.51 (m, 1H), 1.41–1.27 (m, 4H), 1.26 (s, 6H), 1.25 (s, 6H), 1.24 (s, 12H), 0.89 (t, *J* = 7 Hz, 3H).

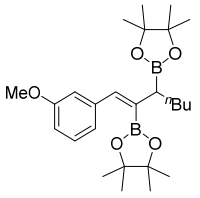
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 161.9 (d, $J_{C\text{-}F}$ = 246 Hz), 137.7, 137.4 (broad, low intensity), 135.8 (d, $J_{C\text{-}F}$ = 3 Hz), 129.9 (d, $J_{C\text{-}F}$ = 8 Hz), 114.6 (d, $J_{C\text{-}F}$ = 21 Hz), 83.6, 83.3, 34.5 (broad, low intensity), 31.8, 30.4, 25.03, 25.00, 24.97, 24.8, 22.9, 14.2.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.0, 31.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ -116.4 (m, 1F).

HRMS (ASAP): *m/z* calcd for $C_{25}H_{40}B_2FO_4$ [M+H$^+$]: 445.3091, found: 445.3086.

(*E*)-2,2'-(1-(3-Methoxyphenyl)hept-1-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)o



Following method 3A, a colorless oil in 71% yield (65 mg) from **(3-1)o** (44 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 24 h at 80 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (t, *J* = 8 Hz, 1H), 6.94–6.87 (m, 2H), 6.85 (s, 1H), 6.72 (ddd,

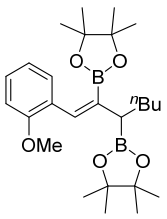
J_1 = 1 Hz, J_2 = 3 Hz, J_3 = 8 Hz, 1H), 3.78 (s, 3H), 2.00 (t, J = 8 Hz, 1H), 1.74–1.64 (m, 1H), 1.62–1.53 (m, 1H), 1.41–1.28 (m, 4H), 1.25 (s, 6H), 1.24 (s, 6H), 1.23 (s, 12H), 0.88 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.4, 141.2, 138.4, 137.8 (broad, low intensity), 128.8, 120.9, 114.0, 112.2, 83.6, 83.3, 55.3, 34.6 (broad, low intensity), 31.8, 30.5, 25.1, 25.03, 25.00, 24.8, 22.9, 14.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.1, 31.3.

HRMS (ASAP): *m/z* calcd for $C_{26}H_{43}B_2O_5$ [M+H$^+$]: 457.3291, found: 457.3289.

(*E*)-2,2'-(1-(2-Methoxyphenyl)hept-1-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)p



Following method 3A, a colorless oil in 60% yield (55 mg) from **(3-1)p** (44 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 24 h at 80 °C.

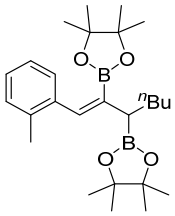
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, J_1 = 2 Hz, J_2 = 7 Hz, 1H), 7.14 (ddd, J_1 = 2 Hz, J_2 = 8 Hz, J_3 = 8 Hz, 1H), 7.02 (s, 1H), 6.80 (ddd, J_1 = 1 Hz, J_2 = 7 Hz, J_3 = 7 Hz, 1H), 6.77 (dd, J_1 = 1 Hz, J_2 = 8 Hz, 1H), 3.77 (s, 3H), 2.04 (t, J = 8 Hz, 1H), 1.74–1.65 (m, 1H), 1.63–1.55 (m, 1H), 1.40–1.28 (m, 4H), 1.26 (s, 6H), 1.25 (s, 6H), 1.212 (s, 6H), 1.208 (s, 6H), 0.88 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.1, 136.7 (broad, low intensity), 134.7, 129.9, 129.2, 128.1, 119.8, 110.6, 83.3, 83.1, 55.6, 34.2 (broad, low intensity), 31.8, 30.6, 25.02, 24.97, 24.8, 22.9, 14.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.1, 31.3.

HRMS (ASAP): *m/z* calcd for $C_{26}H_{43}B_2O_5$ [M+H$^+$]: 457.3291, found: 457.3285.

(*E*)-2,2'-(1-(*o*-Tolyl)hept-1-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)q



Following method 3A, a colorless oil in 54% yield (48 mg) from **(3-1)q** (41 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 24 h at 80 ºC.

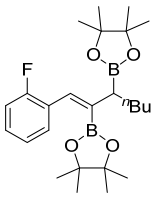
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (br. d, *J* = 8 Hz, 1H), 7.11–7.02 (ov. m, 3H), 6.94 (s, 1H), 2.29 (s, 3H), 2.05 (t, *J* = 8 Hz, 1H), 1.77–1.67 (m, 1H), 1.65–1.56 (m, 1H), 1.43–1.29 (m, 4H), 1.27 (s, 6H), 1.26 (s, 6H), 1.163 (s, 6H), 1.155 (s, 6H), 0.90 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 139.3, 137.7, 137.5 (broad, low intensity), 135.9, 129.4, 128.9, 126.8, 125.1, 83.3, 83.2, 33.9 (broad, low intensity), 31.7, 30.3, 25.0, 24.84, 24.79, 22.8, 20.2, 14.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.2, 31.2.

HRMS (ASAP): *m/z* calcd for $C_{26}H_{43}B_2O_4$ [M+H$^+$]: 441.3342, found: 441.3335.

(*E*)-2,2'-(1-(2-Fluorophenyl)hept-1-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)r



Following method 3A, a colorless oil in 57% yield (51 mg) from **(3-1)r** (41 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 24 h at 80 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.32 (m, 1H), 7.20–7.07 (m, 1H), 7.01–6.92 (m, 2H), 6.90 (s, 1H), 2.06 (t, *J* = 8 Hz, 1H), 1.75–1.65 (m, 1H), 1.63–1.54 (m, 1H), 1.40–1.28 (m, 4H), 1.26 (s, 6H), 1.25 (s, 6H), 1.220 (s, 6H), 1.219 (s, 6H), 0.89 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 160.2 (d, $J_{C\text{-}F}$ = 247 Hz), 139.6 (broad, low intensity), 131.3 (d, $J_{C\text{-}F}$ = 3 Hz), 130.4 (d, $J_{C\text{-}F}$ = 4 Hz), 128.3 (d, $J_{C\text{-}F}$ = 8 Hz), 127.6 (d, $J_{C\text{-}F}$ = 14 Hz), 123.2 (d, $J_{C\text{-}$

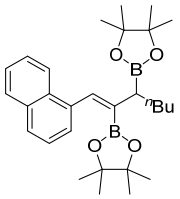
$_F$ = 4 Hz), 115.1 (d, $J_{C\text{-}F}$ = 22 Hz), 83.5, 83.3, 34.5 (broad, low intensity), 31.7, 30.3, 25.00, 24.99, 24.96, 24.8, 22.9, 14.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.0, 30.8.

^{19}F NMR (470 MHz, $CDCl_3$) δ -115.9 (dddd, J_1 = 10 Hz, J_2 = 8 Hz, J_3 = 5 Hz, J_4 = 1 Hz, 1F).

HRMS (ASAP): *m/z* calcd for $C_{25}H_{40}B_2FO_4$ [M+H$^+$]: 445.3091, found: 445.3089.

(*E*)-2,2'-(1-(Naphthalen-1-yl)hept-1-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)s



Following method 3A, a colorless oil in 72% yield (95 mg) from **(3-1)s** (48 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 24 h at 80 ºC.

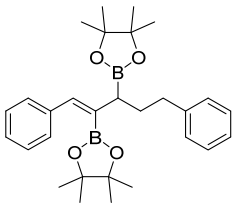
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17–8.10 (m, 1H), 7.84–7.77 (m, 1H), 7.73–7.68 (m, 1H), 7.49–7.32 (m, 5H), 2.19 (t, *J* = 8 Hz, 1H), 1.89–1.60 (m, 2H), 1.53–1.25 (m, 4H), 1.31 (s, 6H), 1.30 (s, 6H), 1.06 (s, 6H), 1.03 (s, 6H), 0.94 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 140.2 (broad, low intensity), 137.8, 136.5, 133.5, 132.3, 128.1, 127.1, 126.1, 125.8, 125.52, 125.51, 125.2, 83.3, 83.2, 34.2 (broad, low intensity), 31.9, 30.3, 25.1, 24.9, 24.8, 24.7, 22.9, 14.3.

^{11}B NMR (96 MHz, $CDCl_3$) δ 31.3 (2B).

HRMS (ASAP): *m/z* calcd for $C_{29}H_{43}B_2O_4$ [M+H$^+$]: 477.3342, found: 477.3336.

(*E*)-2,2'-(1,5-Diphenylpent-1-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)t



Following method 3A, a colorless oil in 76% yield (72 mg) from **(3-1)t** (47 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The

reaction was complete within 24 h at 80 ºC.

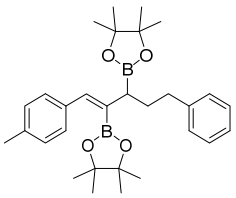
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.33 (m, 2H), 7.29–7.25 (m, 3H), 7.24–7.21 (m, 3H), 7.20–7.15 (m, 2H), 6.91 (s, 1H), 2.78–2.69 (m, 1H), 2.63–2.55 (m, 1H), 2.11 (t, *J* = 8 Hz, 1H), 2.05–1.89 (m, 2H), 1.272 (s, 6H), 1.270 (s, 12H), 1.265 (s, 6H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.3, 139.6, 139.4, 136.4 (broad, low intensity), 128.8, 128.31, 128.27, 127.9, 126.8, 125.6, 83.6, 83.4, 35.7, 34.2 (broad, low intensity), 32.9, 25.09, 25.06, 25.03, 24.8.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.0, 31.3.

HRMS (ASAP): *m/z* calcd for $C_{29}H_{41}B_2O_4$ [M+H$^+$]: 475.3185, found: 475.3180.

(*E*)-2,2'-(5-Phenyl-1-(p-tolyl)pent-1-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2)u



Following method 3A, a colorless oil in 72% yield (70 mg) from **(3-1)u** (50 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5). The reaction was complete within 24 h at 80 ºC.

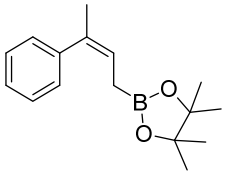
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.12 (m, 7H), 7.09–7.03 (m, 2H), 6.87 (br. s, 1H), 2.80–2.67 (m, 1H), 2.65–2.52 (m, 1H), 2.32 (s, 3H), 2.10 (t, *J* = 7 Hz, 1H), 2.06–1.85 (m, 2H), 1.28 (s, 12H), 1.27 (s, 6H), 1.26 (s, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.3, 139.4, 136.7, 136.4, 136.2 (broad, low intensity), 128.8, 128.6, 128.24, 128.18, 125.5, 83.5, 83.3, 35.7, 34.3 (broad, low intensity), 32.9, 25.1, 25.0, 24.8, 21.3.

^{11}B NMR (96 MHz, $CDCl_3$) δ 31.3 (2B).

HRMS (ASAP): *m/z* calcd for $C_{30}H_{43}B_2O_4$ [M+H$^+$]: 489.3342, found: 489.3339.

(*Z*)-4,4,5,5-Tetramethyl-2-(3-phenylbut-2-en-1-yl)-1,3,2-dioxaborolane (3-4)a



Following method 3B, a colorless oil in 74% yield (38 mg) from (**3-3)a** (29 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

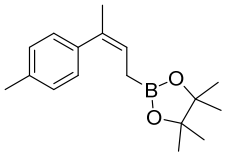
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.29 (m, 2H), 7.23–7.18 (m, 3H), 5.60 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.03 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.62 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.23 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 142.2, 136.1, 128.3, 128.2, 126.4, 122.0, 83.3, 25.7, 24.9, 13.6 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* calcd for $C_{16}H_{24}BO_2$ [M+H$^+$]: 259.1864, found: 259.1861.

(*Z*)-4,4,5,5-Tetramethyl-2-(3-(p-tolyl)but-2-en-1-yl)-1,3,2-dioxaborolane (3-4)b



Following method 3B, a colorless oil in 81% yield (44 mg) from **(3-3)b** (32 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

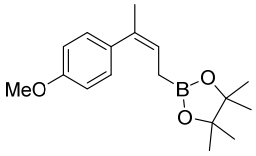
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17–7.07 (m, 4H), 5.58 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.34 (s, 3H), 2.03 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.64 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.2, 135.9 (2C), 128.8, 128.2, 121.7, 83.3, 25.7, 24.9, 21.3, 13.8 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{17}H_{26}BO_2$ [M+H$^+$]: 273.2020, found: 273.2016.

(*Z*)-2-(3-(4-Methoxyphenyl)but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-4)c



Following method 3B, a colorless oil in 82% yield (47 mg) from **(3-3)c** (35 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

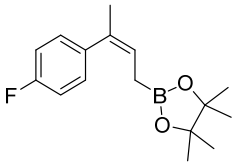
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20–7.13 (m, 2H), 6.90–6.83 (m, 2H), 5.56 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 3.80 (s, 3H), 2.02 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.65 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 158.1, 135.4, 134.5, 129.3, 121.5, 113.5, 83.2, 55.3, 25.7, 24.9, 13.7 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.2.

HRMS (ASAP): *m/z* calcd for $C_{17}H_{26}BO_3$ [M+H$^+$]: 289.1970, found: 289.1965.

(*Z*)-2-(3-(4-Fluorophenyl)but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-4)d



Following method 3B, a colorless oil in 71% yield (39 mg) from **(3-3)d** (33 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22–7.13 (m, 2H), 7.04–6.95 (m, 2H), 5.59 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.01 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.60 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.23 (s, 12H).

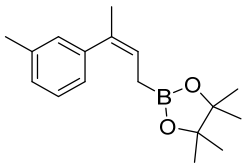
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 161.6 (d, $J_{C\text{-}F}$ = 244 Hz), 138.1 (d, $J_{C\text{-}F}$ = 3 Hz), 135.1, 129.8 (d, $J_{C\text{-}F}$ = 8 Hz), 122.4, 114.9 (d, $J_{C\text{-}F}$ = 21 Hz), 83.3, 25.7, 24.9, 13.6 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ -116.7 (tt, J_1 = 6 Hz, J_2 = 9 Hz, 1F).

HRMS (ASAP): *m/z* calcd for $C_{16}H_{23}BFO_2$ [M+H$^+$]: 277.1770, found: 277.1764.

(*Z*)-4,4,5,5-Tetramethyl-2-(3-(m-tolyl)but-2-en-1-yl)-1,3,2-dioxaborolane (3-4)e



Following method 3B, a colorless oil in 82% yield (45 mg) from **(3-3)e** (32 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

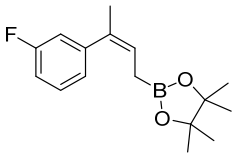
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.17 (m, 1H), 7.08–7.00 (m, 3H), 5.59 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.35 (s, 3H), 2.03 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.64 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.25 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.2, 137.5, 136.1, 129.0, 128.0, 127.2, 125.3, 121.8, 83.3, 25.7, 24.9, 21.6, 13.7 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{17}H_{26}BO_2$ [M+H$^+$]: 273.2020, found: 273.2018.

(*Z*)-2-(3-(3-Fluorophenyl)but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-4)f



Following method 3B, a colorless oil in 68% yield (38 mg) from **(3-3)f** (33 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.22 (m, 1H), 7.02–6.85 (m, 3H), 5.61 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.01 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.62 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.24 (s, 12H).

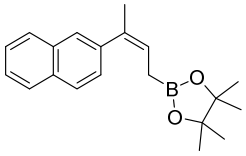
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 245 Hz), 144.6 (d, $J_{C\text{-}F}$ = 7 Hz), 134.9 (d, $J_{C\text{-}F}$ = 2 Hz), 129.6 (d, $J_{C\text{-}F}$ = 8 Hz), 123.9 (d, $J_{C\text{-}F}$ = 3 Hz), 122.9, 115.2 (d, $J_{C\text{-}F}$ = 21 Hz), 113.2 (d, $J_{C\text{-}F}$ = 21 Hz), 83.4, 25.5, 24.9, 13.8 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ -114.0 (ddd, J_1 = 1.5 Hz, J_2 = 6 Hz, J_3 = 9 Hz, 1F).

HRMS (ASAP): *m/z* calcd for $C_{16}H_{23}BFO_2$ [M+H$^+$]: 277.1770, found: 277.1766.

(*Z*)-4,4,5,5-Tetramethyl-2-(3-(naphthalen-2-yl)but-2-en-1-yl)-1,3,2-dioxaborolane (3-4)g



Following method 3B, a colorless oil in 83% yield (51 mg) from (**3-3)g** (39 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

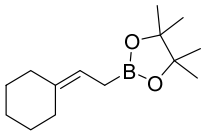
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85–7.77 (m, 3H), 7.70 (s, 1H), 7.48–7.37 (m, 3H), 5.71 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.14 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.71 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.25 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.7, 136.0, 133.5, 132.3, 127.9, 127.7, 127.6, 126.9, 126.8, 125.9, 125.5, 122.6, 83.3, 25.7, 24.9, 14.0 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{20}H_{26}BO_2$ [M+H$^+$]: 309.2020, found: 309.2016.

2-(2-Cyclohexylideneethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-4)h



Following method 3B, a colorless oil in 60% yield (28 mg) from **(3-3)h** (25 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:Et_2O = 95:3). The reaction was complete within 18 h at 60 ºC.

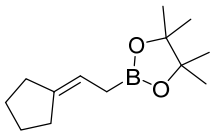
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 (tquint., J_1 = 8 Hz, J_2 = 1 Hz, 1H), 2.12–2.04 (m, 4H), 1.60 (d, J = 8 Hz, 2H), 1.54–1.45 (m, 6H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 139.9, 115.1, 83.2, 37.2, 28.8, 28.7, 27.8, 27.1, 24.9, 11.2 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{26}BO_2$ [M+H$^+$]: 237.2020, found: 237.2016.

2-(2-Cyclopentylideneethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-4)i



Following method 3B, a colorless oil in 61% yield (27 mg) from (**3-3)i** (22 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:Et_2O = 95:3). The reaction was complete within 18 h at 60 ºC.

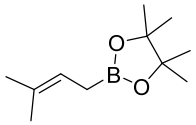
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.33 (tquint., J_1 = 8 Hz, J_2 = 2 Hz, 1H), 2.25–2.12 (m, 4H), 1.71−1.53 (ov. m, 6H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.7, 114.1, 83.2, 33.7, 28.9, 26.8, 26.4, 24.9, 11.0 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{13}H_{24}BO_2$ [M+H$^+$]: 223.1864, found: 223.1857.

4,4,5,5-Tetramethyl-2-(3-methylbut-2-en-1-yl)-1,3,2-dioxaborolane (3-4)j



Following method 3B, a colorless oil in 41% yield (40 mg) from (**3-3)j** (42 mg, 0.5 mmol) was obtained via purification by flash chromatography on silica gel (pentane:Et_2O = 95:3). The reaction was complete within 18 h at 60 ºC.

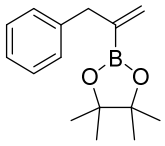
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.22 (qqt, J_1 = 2 Hz, J_2 = 1 Hz, J_3 = 8 Hz, 1H), 1.69−1.68 (m, 3H), 1.62−1.57 (m, 5H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 131.7, 118.7, 83.2, 25.9, 24.9, 17.8, 12.0 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.2.

HRMS (ASAP): *m/z* calcd for $C_{11}H_{22}BO_2$ [M+H$^+$]: 197.1707, found: 197.1702.

4,4,5,5-Tetramethyl-2-(3-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (3-6)a



Following method 3C, a light yellow oil in 79% yield (39 mg) from **(3-5)a** (26 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

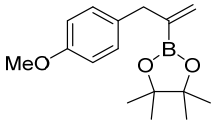
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.24 (m, 2H), 7.23–7.14 (m, 3H), 5.85 (dt, J_1 = 3 Hz, J_2 = 1 Hz, 1H), 5.55 (dt, J_1 = 3Hz, J_2 = 2 Hz, 1H), 3.50 (br. s, 2H), 1.23 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 140.9, 130.0, 129.3, 128.2, 125.8, 83.6, 41.5, 24.8. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.1.

HRMS (ASAP): *m/z* calcd for $C_{15}H_{22}BO_2$ [M+H$^+$]: 245.1707, found: 245.1702.

2-(3-(4-Methoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-6)b



Following method 3C, a light yellow oil in 83% yield (46 mg) from **(3-5)b** (32 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

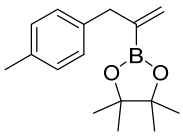
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13–7.07 (m, 2H), 6.84–6.78 (m, 2H), 5.80 (dt, J_1 = 3 Hz, J_2 = 1 Hz, 1H), 5.50 (dt, J_1 = 3 Hz, J_2 = 2 Hz, 1H), 3.78 (s, 3H), 3.41 (br. s, 2H), 1.21 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 157.9, 132.9, 130.2, 129.6, 113.7, 83.6, 55.4, 40.6, 24.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.1.

HRMS (ASAP): *m/z* calcd for $C_{16}H_{24}BO_3$ [M+H$^+$]: 275.1813, found: 275.1809.

4,4,5,5-Tetramethyl-2-(3-(p-tolyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (3-6)c



Following method 3C, a light yellow oil in 80% yield (42 mg) from **(3-5)c** (29 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

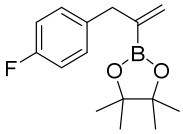
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10–7.05 (m, 4H), 5.81 (dt, J_1 = 3 Hz, J_2 = 1 Hz, 1H), 5.50 (dt, J_1 = 3 Hz, J_2 = 2 Hz, 1H), 3.43 (br. s, 2H), 2.30 (s, 3H), 1.22 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 141.6 (broad, low intensity), 137.7, 135.2, 129.8, 129.2, 128.9, 83.6, 40.9, 24.9, 21.2.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.2.

HRMS (ASAP): *m/z* calcd for $C_{16}H_{24}BO_2$ [M+H$^+$]: 259.1864, found: 259.1859.

2-(3-(4-Fluorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-6)d



Following method 3C, a light yellow oil in 75% yield (39 mg) from **(3-5)d** (30 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17–7.12 (m, 2H), 6.96–6.90 (m, 2H), 5.82 (dt, J_1 = 3 Hz, J_2 = 1 Hz, 1H), 5.53 (dt, J_1 = 3 Hz, J_2 = 2 Hz, 1H), 3.44 (br. s, 2H), 1.20 (s, 12H).

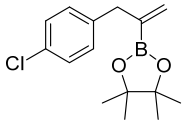
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 161.4 (d, $J_{C\text{-}F}$ = 242 Hz), 141.3 (broad, low intensity), 136.5 (d, $J_{C\text{-}F}$ = 3 Hz), 130.6 (d, $J_{C\text{-}F}$ = 8 Hz), 130.0, 114.9 (d, $J_{C\text{-}F}$ = 21 Hz), 83.7, 40.8, 24.8.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ -118.2 (ttt, J_1 = 1 Hz, J_2 = 6 Hz, J_3 = 9 Hz, 1F).

HRMS (ASAP): *m/z* calcd for $C_{15}H_{21}BFO_2$ [M+H$^+$]: 263.1389, found: 263.1383.

2-(3-(4-Chlorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-6)e



Following method 3C, a light yellow oil in 69% yield (38 mg) from **(3-5)e** (33 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

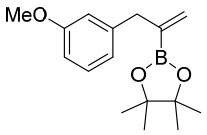
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.20 (m, 2H), 7.14–7.11 (m, 2H), 5.84 (dt, J_1 = 3 Hz, J_2 = 1 Hz, 1H), 5.53 (dt, J_1 = 3 Hz, J_2 = 2 Hz, 1H), 3.43 (br. s, 2H), 1.21 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 141.0 (broad, low intensity), 139.4, 131.6, 130.6, 130.3, 128.3, 83.7, 40.9, 24.8.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.0.

HRMS (ASAP): *m/z* calcd for $C_{15}H_{21}BClO_2$ [M+H$^+$]: 279.1318, found: 279.1315.

2-(3-(3-Methoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-6)f



Following method 3C, a light yellow oil in 84% yield (46 mg) from **(3-5)f** (32 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

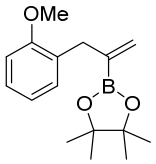
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21–7.14 (m, 1H), 6.83–6.68 (m, 3H), 5.84 (dt, J_1 = 3 Hz, J_2 = 1 Hz, 1H), 5.54 (dt, J_1 = 3 Hz, J_2 = 2 Hz, 1H), 3.78 (s, 3H), 3.46 (br. s, 2H), 1.22 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 159.7, 142.5, 130.1, 129.2, 121.7, 114.7, 111.5, 83.6, 55.3, 41.5, 24.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.1.

HRMS (ASAP): *m/z* calcd for $C_{16}H_{24}BO_3$ [M+H$^+$]: 275.1813, found: 275.1807.

2-(3-(2-Methoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-6)g



Following method 3C, a light yellow oil in 71% yield (39 mg) from **(3-5)g** (34 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

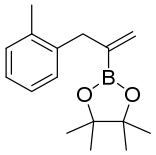
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19–7.10 (m, 2H), 6.89–6.82 (m, 2H), 5.83 (dt, J_1 = 3 Hz, J_2 = 1 Hz, 1H), 5.45 (dt, J_1 = 3 Hz, J_2 = 2 Hz, 1H), 3.80 (s, 3H), 3.48 (br. s, 2H), 1.25 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.7, 140.4 (broad, low intensity), 130.6, 129.8, 129.3, 127.1, 120.3, 110.5, 83.5, 55.5, 34.8, 24.9.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.2.

HRMS (ASAP): *m/z* calcd for $C_{16}H_{24}BO_3$ [M+H$^+$]: 275.1813, found: 275.1810.

4,4,5,5-Tetramethyl-2-(3-(o-tolyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (3-6)h



Following method 3C, a light yellow oil in 60% yield (31.0 mg) from **(3-5)h** (29.2 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

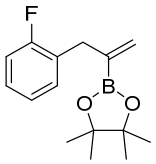
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14–7.09 (m, 4H), 5.81 (dt, J_1 = 3 Hz, J_2 = 1 Hz, 1H), 5.32 (dt, J_1 = 3 Hz, J_2 = 2 Hz, 1H), 3.47–3.46 (m, 2H), 2.26 (s, 3H), 1.26 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 141.3 (broad, low intensity), 138.7, 136.9, 130.2, 130.1, 129.8, 126.1, 125.8, 83.7, 38.3, 24.9, 19.6.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.1.

HRMS (ASAP): *m/z* calcd for $C_{16}H_{24}BO_2$ [M+H$^+$]: 259.1864, found: 259.1860.

2-(3-(2-Fluorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-6)i



Following method 3C, a light yellow oil in 64% yield (34 mg) from **(3-5)i** (30 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22–7.17 (m, 1H), 7.17–7.13 (m, 1H), 7.06–7.01 (m, 1H), 7.01–6.97 (m, 1H), 5.87 (dt, J_1 = 3 Hz, J_2 = 1 Hz, 1H), 5.50–5.49 (br. m, 1H), 3.52–3.48 (m, 2H), 1.23 (s, 12H).

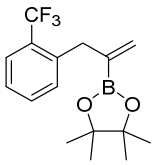
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 161.3 (d, $J_{C\text{-}F}$ = 245 Hz), 139.6 (broad, low intensity), 131.5 (d, $J_{C\text{-}F}$ = 5 Hz), 130.4, 127.7 (d, $J_{C\text{-}F}$ = 8 Hz), 127.7 (d, $J_{C\text{-}F}$ = 8 Hz), 123.8 (d, $J_{C\text{-}F}$ = 4 Hz), 115.2 (d, $J_{C\text{-}F}$ = 22 Hz), 83.7, 33.9 (d, $J_{C\text{-}F}$ = 3 Hz), 24.8.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ -117.9 (m, 1F).

HRMS (ASAP): *m/z* calcd for $C_{15}H_{21}BFO_2$ [M+H$^+$]: 263.1389, found: 263.1385.

4,4,5,5-Tetramethyl-2-(3-(2-(trifluoromethyl)phenyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (3-6)j



Following method 3C, a light yellow oil in 50% yield (31 mg) from **(3-5)j** (40 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8 Hz, 1H), 7.43 (t, J = 7 Hz, 1H), 7.31–7.26 (m, 2H), 5.91 (dt, J_1 = 3 Hz, J_2 = 1 Hz, 1H), 5.33–5.32 (br. m, 1H), 3.67 (br. s, 2H), 1.24 (s, 12H).

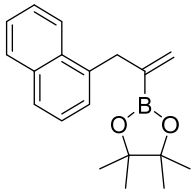
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 140.2 (broad, low intensity), 139.4 (q, $J_{C\text{-}F}$ = 2 Hz), 131.9, 131.5 (q, $J_{C\text{-}F}$ = 1 Hz), 131.0, 129.1 (q, $J_{C\text{-}F}$ = 30 Hz), 126.0, 125.9 (q, $J_{C\text{-}F}$ = 6 Hz), 124.7 (q, $J_{C\text{-}F}$ = 274 Hz), 83.7, 37.1 (q, $J_{C\text{-}F}$ = 2 Hz), 24.8.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ -59.9.

HRMS (ASAP): *m/z* calcd for $C_{16}H_{21}BF_3O_2$ [M+H$^+$]: 313.1581, found: 313.1578.

4,4,5,5-Tetramethyl-2-(3-(naphthalen-1-yl)prop-1-en-2-yl)-1,3,2-dioxaborolane (3-6)k



Following method 3C, a light yellow oil in 71% yield (42 mg) from **(3-5)k** (36 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

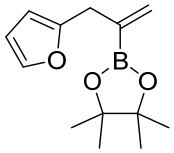
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03–7.97 (m, 1H), 7.86–7.82 (m, 1H), 7.73 (d, J = 8 Hz, 1H), 7.51–7.44 (m, 2H), 7.41 (dd, J_1 = 7 Hz, J_2 = 8 Hz, 1H), 7.34 (br. d, J = 8 Hz, 1H), 5.90 (dt, J_1 = 3 Hz, J_2 = 1 Hz, 1H), 5.37 (dt, J_1 = 3 Hz, J_2 = 2 Hz, 1H), 3.95 (br. s, 2H), 1.28 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 140.2 (broad, low intensity), 136.9, 133.9, 132.4, 130.8, 128.6, 127.2, 126.8, 125.7, 125.6, 125.5, 124.9, 83.7, 37.7, 24.9.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.3.

HRMS (ASAP): *m/z* calcd for $C_{19}H_{24}BO_2$ [M+H$^+$]: 295.1864, found: 295.1859.

2-(3-(Furan-2-yl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-6)l



Following method 3C, a light yellow oil in 78% yield (37 mg) from **(3-5)l** (24 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:3). The reaction was complete within 18 h at 60 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, J_1 = 1 Hz, J_2 = 2 Hz, 1H), 6.27 (ddt, J_1 = 2 Hz, J_2 = 3 Hz, J_3 = 0.5 Hz, 1H), 5.99 (ddt, J_1 = 3 Hz, J_2 = 1 Hz, J_3 = 1 Hz, 1H), 5.87 (dt, J_1 = 3 Hz, J_2 = 1 Hz, 1H), 5.61 (dt, J_1 = 3 Hz, J_2 = 2 Hz, 1H), 3.48 (ddd, J_1 = 1 Hz, J_2 = 1 Hz, J_3 = 1 Hz, 2H), 1.24 (s, 12H).

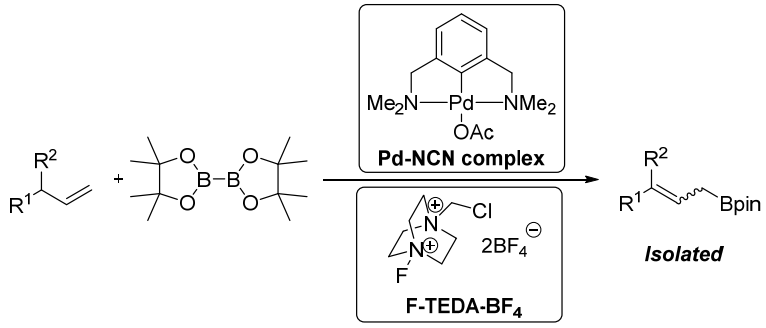
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.7, 141.1, 137.9 (broad, low intensity), 130.8, 110.3, 106.0,

83.7, 33.7, 24.8.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.0.

HRMS (ASAP): *m/z* calcd for $C_{13}H_{20}BO_3$ [$M+H^+$]: 235.1500, found: 235.1496.

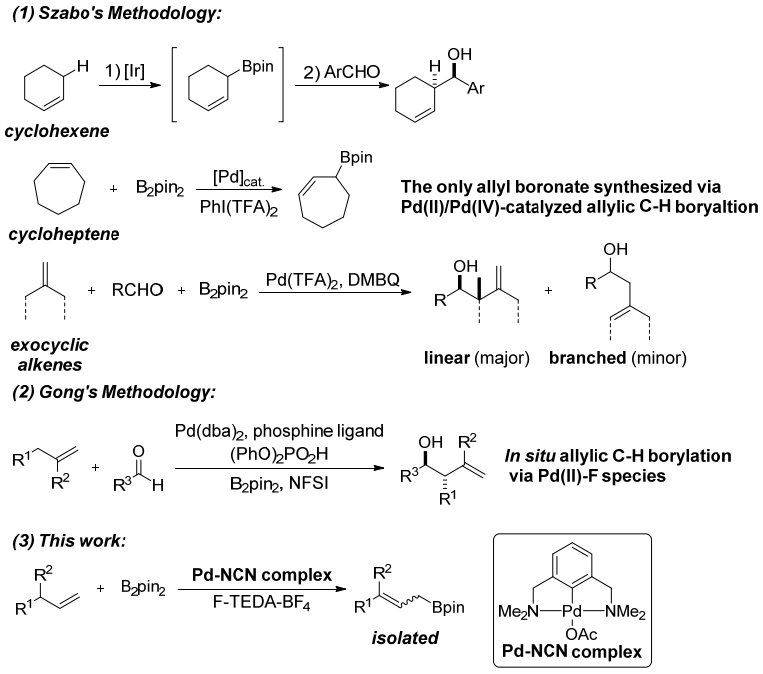
Chapter Four
Palladium-catalyzed Oxidative Borylation of Allylic C-H Bonds in Alkenes



4. Palladium-catalyzed Oxidative Borylation of Allylic C-H Bonds in Alkenes

4.1 Introduction

Allyl boronates are important synthetic intermediates that react with aldehydes to afford stereo-defined homoallylic alcohols.[95b,96,106] Therefore, there is a great demand for efficient methodologies to synthesize allyl boronates from readily available substrates. Although the borylations of allylic halides,[14,18,19] carbonates,[18,22,24a,27b,d] ethers,[26b] and alcohols[28b-d,f,30] have been successfully developed, they all require extra steps to prepare the pre-functionalized starting-materials. Szabó and co-workers developed an iridium-catalyzed allylic borylation of cycloalkenes, in which the selectivity was controlled by the addition of 1,8-diazabicyclo[5.4.0]undecane (DBU) or methylimidazole,[11] and a $Pd(TFA)_2$-catalyzed allylic borylation of exocyclic alkenes via allyl-Pd(II) intermediates.[9] Recently, Gong and co-workers reported a Pd-catalyzed allylation of simple alkenes via oxidative C-H borylation, which mainly focused on allyl benzene and its derivatives.[10] A general problem with these allylic C-H borylation methods is that the catalysts react with the allyl-Bpin products, and therefore they must be trapped within the reaction system. Accordingly, several methods for one-pot C-H borylation–allylboration reactions have been reported. However, a more general allylic C-H borylation process, which allows the isolation of the allyl-Bpin reagents, is still highly desirable (Scheme 4-1).



Scheme 4-1. Transition Metal-catalyzed Borylation of Allylic C-H Bonds.

4.2 Motivation

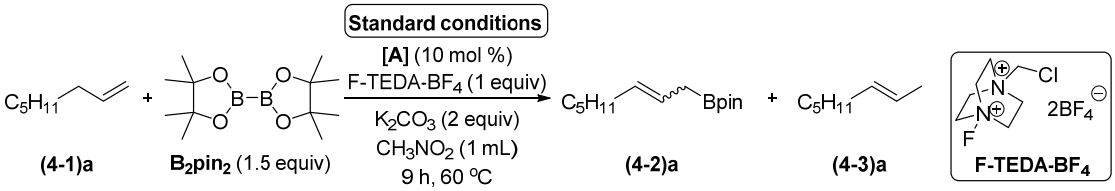
Palladium-catalyzed C-H bond functionalization reactions have emerged as powerful strategies in organic synthesis,[107] and oxidative C-H borylation reactions have been reported by several research groups,[9,10,108] in which Pd(II) species were proposed to be generated *in situ* and act as the active catalyst. Alternatively, C-H functionalization mediated by high-valent palladium species with unique reactivity and selectivity[8,109] was also shown to be an efficient methodology to transform allylic C-H bonds into C-O[110] and C-Si[111] bonds. To the best of our knowledge, only the allylic C-H borylation of cycloheptene has been demonstrated by Szabó and coworkers, involving Pd(IV) species as the key intermediate, in which the selectivity is controlled by conformational factors.[8] Marder and co-workers have reported catalytic borylations of both C-H and C-X bonds,[2a,b,15a,b,d,74c-e,94] including the synthesis of allyl boronates.[15d,94] Chapter 4 presents a Pd-catalyzed highly regio- and stereo-selective allylic C-H borylation of alkenes, the isolation of the allyl-Bpin products, and also a one-pot route to homoallyl alcohols directly from alkenes.

4.3 Results and Discussion

4.3.1 Optimization of Reaction Conditions

As palladium pincer complexes have proved to be highly selective catalysts for many C-H functionalization reactions,[109e] these catalysts were applied in the C-H borylation reactions. It was found that, in the presence of F-TEDA-BF_4 as an oxidant, NCN pincer complex **A** is an effective catalyst precursor for allylic C-H borylation, giving the desired product **(4-2)a** in 89% isolated yield with excellent regio- and stereochemistry (Table 4-1, entry 1). A much lower yield of **(4-2)a** (42%) was obtained at ca. 49% conversion,[112] when **A** was replaced with its bromide analogue **B** (Table 4-1, entry 2). The yields of **(4-2)a** dropped to 24% and 15%, and isomerization product **(4-3)a** was formed in yields of 67% and 79% using Se-pincers **C** or **D** (Table 4-1, entries 3 and 4), respectively, possibly because they are less stable.[113] F-TEDA-PF_6 was similar to its BF_4^- salt as an oxidant and the desired product **(4-2)a** was obtained in 82% yield (Table 4-1, entry 5).[114] No desired product **(4-2)a** was afforded in the absence of Pd-catalyst or F-TEDA-BF_4 (Table 4-1, entries 6 and 7). Product **(4-2)a** formed in only 14% yield without K_2CO_3 (Table 4-1, entry 8), but the use of Na_2CO_3 as an alternative was successful (Table 4-1, entry 9), whereas KF was significantly less effective (Table 4-1, entry 10). THF and CH_2Cl_2 proved less effective as solvents than CH_3NO_2 (Table 1, entries 11 and 12).[114] Other screening details are listed in Tables 4-2 to 4-5.

Table 4-1. Optimization of Conditions[a]



Entry	Varation from standard conditions	% (4-2)a[b]	*E*:*Z*[c]	% (4-3)a[d]	% Conversion
1	no change	89% (83%)[e]	50:1	-	100%
2	Pd-pincer complex **B** instead of **A**	42%	42:1	-	49%
3	Pd-pincer complex **C** instead of **A**	24%	-	67%	100%
4	Pd-pincer complex **D** instead of **A**	15%	-	79%	100%
5	F-TEDA-PF_6 instead of F-TEDA-BF_4	82%	43:1	-	100%
6	without Pd-pincer complex **A**	N.D.[f]	-	-	6%
7	without F-TEDA-BF_4	N.D.[f]	-	73%	77%
8	without K_2CO_3	14%	-	-	17%
9	Na_2CO_3 instead of K_2CO_3	79%	48:1	-	84%
10	KF instead of K_2CO_3	54%	35:1	-	59%
11	THF instead of CH_3NO_2	59%	41:1	-	65%
12	CH_2Cl_2 instead of CH_3NO_2	39%	39:1	-	46%

All reactions were carried out on a 0.2 mmol scale. [a] Standard conditions: Pd-NCN complex **A** (10 mol %), **(4-1)a** (1 equiv), K_2CO_3 (2 equiv), B_2pin_2 (1.5 equiv), F-TEDA-BF_4 (1 equiv), CH_3NO_2 (1 mL), 60 °C. [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] *E*/*Z* isomer ratios were determined by ^{1}H NMR spectroscopy of the crude product. [d] Yields were determined by ^{1}H NMR spectroscopy of the crude product. [e] Isolated yield. [f] N.D. = not detected.

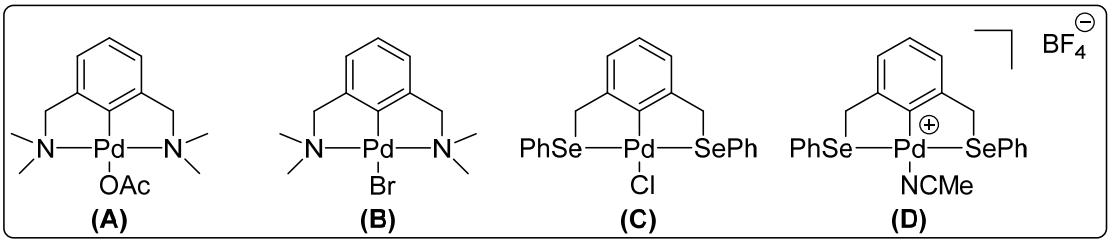
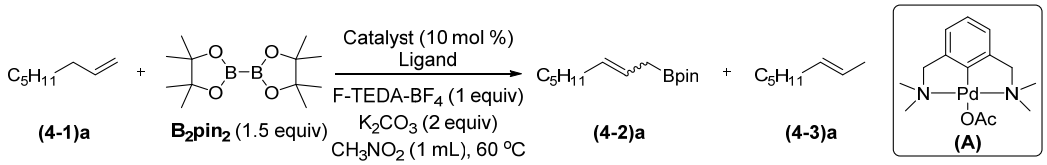


Table 4-2. Catalysts and ligands[a]



Entry	Catalyst	Ligand	% (4-2)a[b]	*E*:*Z*[c]	% (4-3)a[d]	% Conversion
1	**A**	-	89%	50:1	-	100%
2	$Pd(OAc)_2$	-	N.D.[e]	-	21%	24%
3	$PdCl_2$	-	N.D.[e]	-	43%	48%
4	$Pd(TFA)_2$	-	N.D.[e]	-	34%	39%
5	$Pd(PPh_3)_4$	-	N.D.[e]	-	68%	73%
6	$Pd(dba)_2$	-	N.D.[e]	-	72%	79%
7	$Pd(OAc)_2$	dtbpy	N.D.[e]	-	29%	33%
8	$Pd(OAc)_2$	1,10-Phen	N.D.[e]	-	24%	29%
9	$Pd(OAc)_2$	4,4'-Me_2-Phen	N.D.[e]	-	29%	33%
10	$Pd(OAc)_2$	bpy	N.D.[e]	-	24%	27%
11	$Pd(OAc)_2$	Py	N.D.[e]	-	21%	25%

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **(4-1)a** (1 equiv), B_2pin_2 (1.5 equiv), Catalyst (10 mol %), Ligand, K_2CO_3 (2 equiv), F-TEDA-BF_4 (1 equiv), CH_3NO_2 (1 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] *E*/*Z* isomer ratios were determined by ^1H NMR spectroscopy of the crude product. [d] Yields were determined by ^1H NMR analysis *vs.* an internal standard and are averages of two experiments. [e] N.D. = not detected.

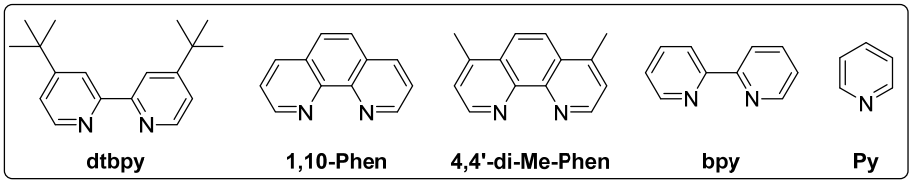
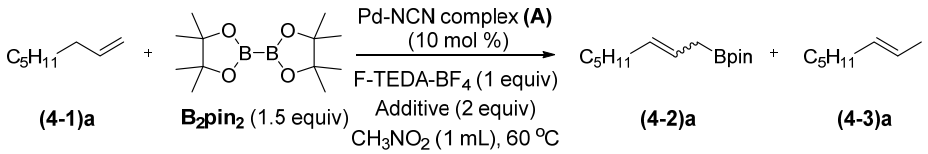


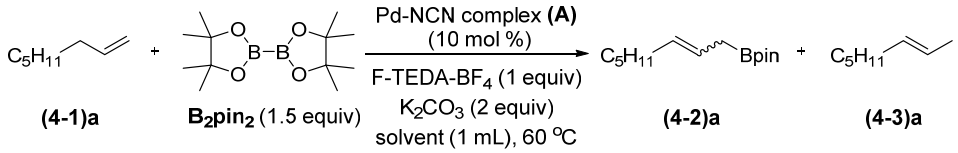
Table 4-3. Additives[a]



Entry	Base	% (4-2)a[b]	*E*:*Z*[c]	% (4-3)a[d]	% Conversion
1	K_2CO_3	89%	50:1	-	100%
2	Li_2CO_3	61%	44:1	-	68%
3	Cs_2CO_3	74%	47:1	-	79%
4	LiF	58%	41:1	-	64%
5	NaF	52%	48:1	-	55%
6	CsF	55%	43:1	-	59%
7	$NaHCO_3$	43%	45:1	-	49%
8	$KHCO_3$	49%	50:1	-	56%
9	KO^{t}Bu	N.D.[e]	-	47%	53%

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **(4-1)a** (1 equiv), B_2pin_2 (1.5 equiv), Pd-NCN complex **(A)** (10 mol %), Additive (2 equiv), F-TEDA-BF_4 (1 equiv), CH_3NO_2 (1 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] *E*/*Z* isomer ratios were determined by ^{1}H NMR spectroscopy of the crude product. [d] Yields were determined by ^{1}H NMR analysis *vs.* an internal standard and are averages of two experiments. [e] N.D. = not detected.

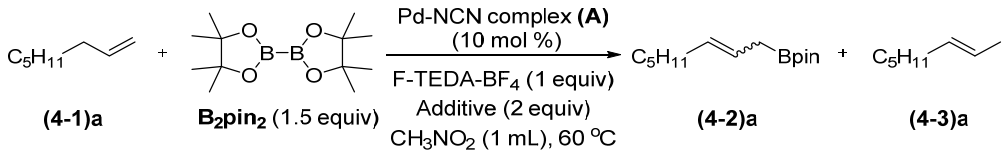
Table 4-4. Solvents[a]



Entry	Solvent	% (4-2)a [b]	*E*:*Z*[c]	% (4-3)a[d]	% Conversion
1	CH_3NO_2	89%	50:1	-	100%
2	toluene	49%	43:1	27%	81%
3	benzene	54%	47:1	29%	85%
4	MTBE	N.D.[e]	-	34%	39%
5	CH_3CN	N.D.[e]	-	42%	48%

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **(4-1)a** (1 equiv), B_2pin_2 (1.5 equiv), Pd-NCN complex **(A)** (10 mol %), K_2CO_3 (2 equiv), F-TEDA-BF_4 (1 equiv), solvent (1 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] *E*/*Z* isomer ratios were determined by ^{1}H NMR spectroscopy of the crude product. [d] Yields were determined by ^{1}H NMR analysis *vs.* an internal standard and are averages of two experiments. [e] N.D. = not detected.

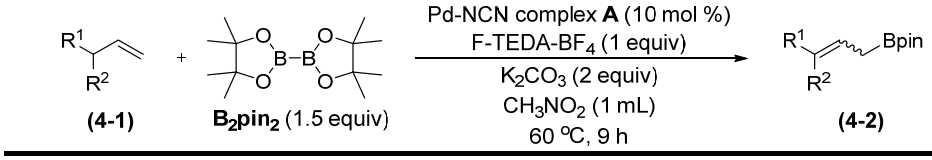
Table 4-5. Temperature[a]

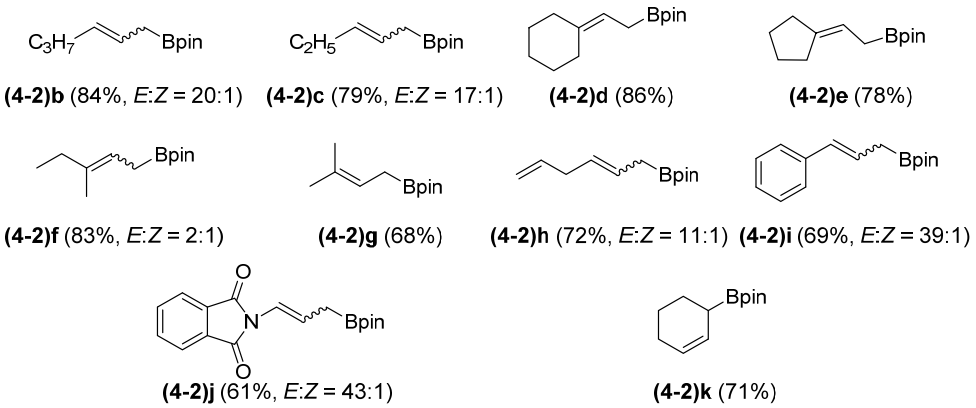


Entry	Temperature (°C)	% (4-2)a [b]	*E*:*Z*	% (4-3)a[c]	% Conversion
1	80	74%	48:1	21%	100%
2	60	89%	50:1	-	100%
3	40	63%	50:1	32%	100%
4	room temperature	39%	43:1	35%	79%

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **(4-1)a** (1 equiv), B_2pin_2 (1.5 equiv), Pd-NCN complex **(A)** (10 mol %), K_2CO_3 (2 equiv), F-TEDA-BF_4 (1 equiv), CH_3NO_2 (1 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c]Yields were determined by ^{1}H NMR analysis *vs.* an internal standard and are averages of two experiments.

4.3.2 Investigation of Reaction Scope



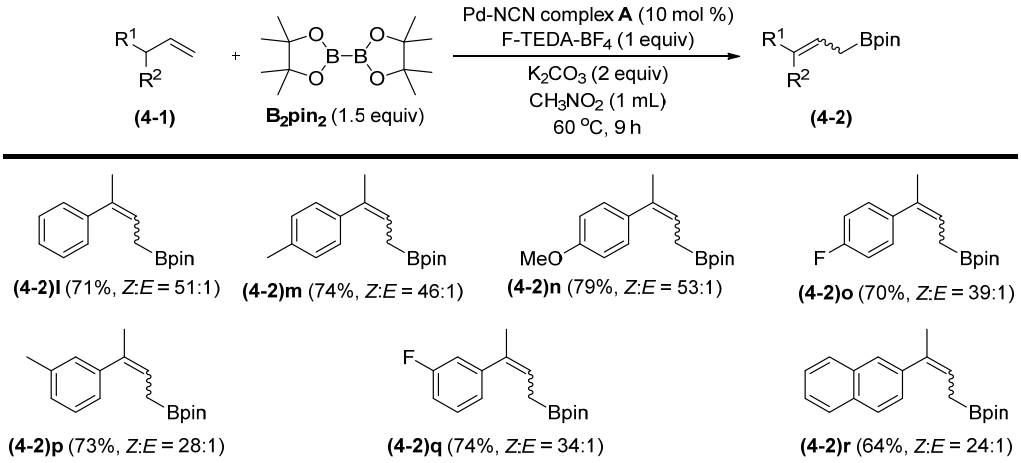


[a] Standard conditions: **(4-1)** (0.2 mmol, 1 equiv), Pd-NCN complex **A** (10 mol %), F-TEDA-BF_4 (0.2 mmol, 1 equiv), K_2CO_3 (0.4 mmol, 2 equiv), B_2pin_2 (0.3 mmol, 1.5 equiv), CH_3NO_2 (1 mL), 60 °C. [b] Isolated yield. [c] *E*/*Z* isomer ratios were determined by ^{1}H NMR spectroscopy of the crude product.

Scheme 4-2. Substrate Scope I[a,b,c]

With the optimized conditions in hand, the scope of the reaction was investigated (Scheme 4-2). Simple alkenes, such as 1-hexene **(4-1)b** and 1-pentene **(4-1)c**, are suitable for the allylic C-H borylation, and corresponding products **(4-2)b** and **(4-2)c** were afforded in good yields of 84% and 79%, respectively. A particular merit of this reaction is that the allyl boronate products **(4-2)b**-**c** (as

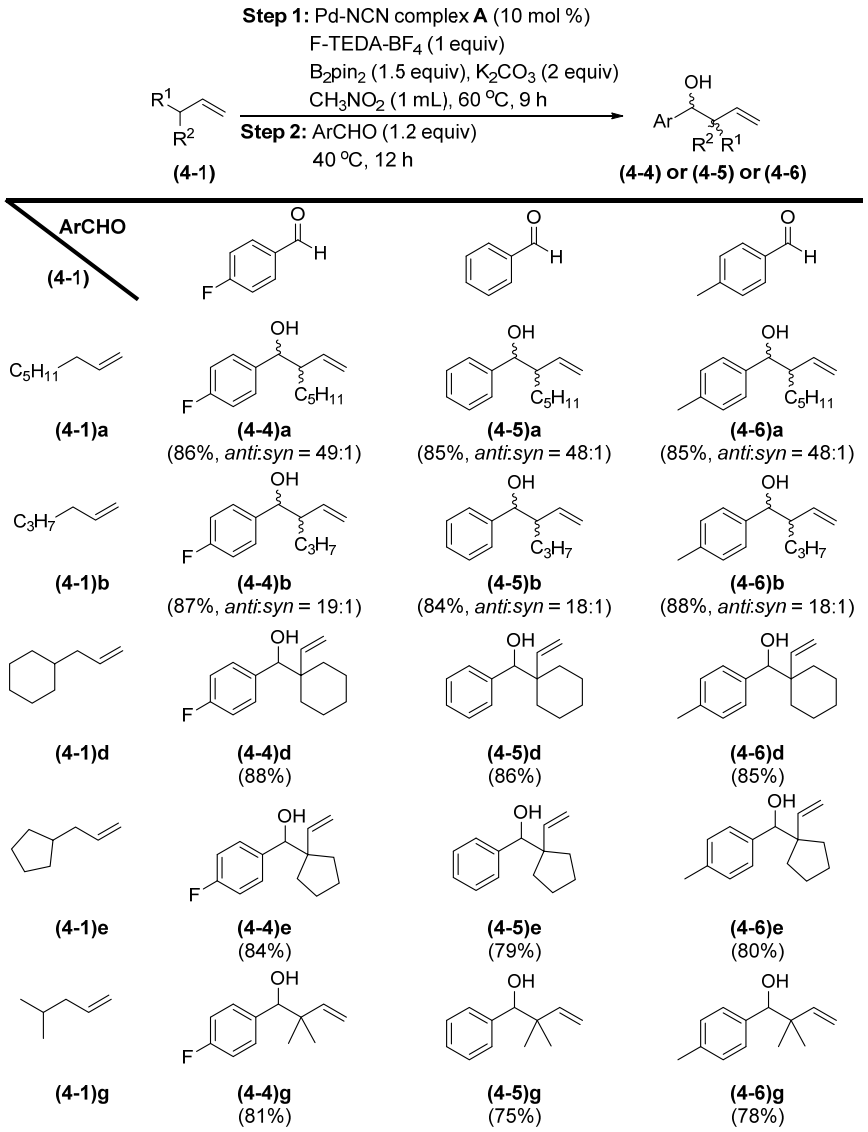
well as the rest of the allyl-Bpin products) could be isolated (The isolated yield is limited by some decomposition of the allylic boronate on silica gel.). As mentioned above, the previously reported palladium- (and iridium-) catalyzed C-H borylation methods usually did not allow isolation of the allylboronate products.[9,10,11] Exocyclic-allylboronates **(4-2)d** and **(4-2)e** were provided from the allylic C-H borylation in yields of 86% and 78%, respectively. With disubstituted alkenes **(4-1)f** and **(4-1)g**, the desired allylboronates **(4-2)f** and **(4-2)g** were obtained in yields of 83% and 68%, respectively. The noncojugated diene **(4-1)h** was borylated smoothly and **(4-2)h** was produced in a 72% yield. With allylbenzene **(4-1)i** as the starting material, product **(4-2)i** was formed in a moderate yield of 69%. Allyl boronate **(4-2)j** was obtained in a 61% yield, when allyl phthalimide **(4-1)j** was employed as starting material. Cyclohexene **(4-1)k** was also borylated smoothly and provided the allylic product **(4-2)k** in a 71% yield.



[a] Standard conditions: **(4-1)** (0.2 mmol, 1 equiv), Pd-NCN complex **A** (10 mol %), F-TEDA-BF_4 (0.2 mmol, 1 equiv), K_2CO_3 (0.4 mmol, 2 equiv), B_2pin_2 (0.3 mmol, 1.5 equiv), CH_3NO_2 (1 mL), 60 °C. [b] Isolated yield. [c] *E*/*Z* isomer ratios were determined by ^1H NMR spectroscopy of the crude product, and geometry of C=C bonds is confirmed by ^1H, ^1H NOESY.

Scheme 4-3. Substrate Scope II[a,b,c]

α-Methyl allylbenzene **(4-1)l** gave the allylboronate **(4-2)l** in 71% yield with the *Z*-geometry at the C=C bond (Scheme 4-3). With the phenyl ring bearing the Me, OMe, or F substituents **(4-1)m-q**, corresponding allylboronates **(4-2)m-q** were provided in good yields of 70%-79% with good stereoselectivity. When the phenyl group was replaced by a naphthalenyl group, the desired product **(4-2)r** was obtained in a 64% yield.



[a] Step **1**: **(4-1)** (0.2 mmol, 1 equiv), Pd-NCN complex **A** (10 mol %), F-TEDA-BF_4 (0.2 mmol, 1 equiv), K_2CO_3 (0.4 mmol, 2 equiv), B_2pin_2 (0.3 mmol, 1.5 equiv), CH_3NO_2 (1 mL), 60 °C. Step **2**: ArCHO (0.24 mmol, 1.2 equiv), 40 °C. [b] Isolated yield. [c] The *anti*/*syn* ratios were determined by ^{1}H NMR spectroscopy of the crude product.

Scheme 4-4. Application in One-pot Carbonyl Allylation Reactions[a,b,c]

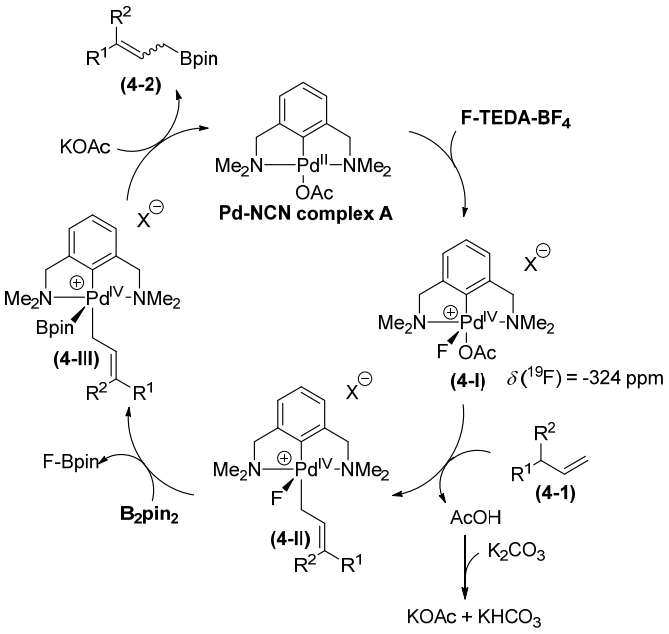
As allylboronates have significant applications in synthesis of homoallyl alcohols,[95b,96,106] the application of our allylic C-H borylation of alkenes in a one-pot carbonyl allylation reaction was investigated (Scheme 4-4). The allylic C-H borylation of **(4-1)a** accomplished under the standard conditions, followed by addition of 1.2 equiv of an aldehyde, such as 4-fluorobenzaldehyde, benzaldehyde, and *p*-tolualdehyde, gave homoallyl alcohols **(4-4)a**, **(4-5)a** and **(4-6)a** in high overall yields of 86%, 85% and 85%, respectively. When **(4-1)b** was employed as the substrate, the one-pot, two-step carbonyl allylation reactions also proceeded with high efficiency, affording **(4-4)b**, **(4-**

5)b and **(4-6)b** in overall yields of 87%, 84% and 88%, respectively. When acyclic alkyl groups were replaced with cyclohexal **(4-1)d** or cyclopentyl **(4-1)e** groups, the allylation reactions proceeded smoothly giving the desired homoallyl alcohols **(4-4)d**, **(4-5)d**, **(4-6)d**, **(4-4)e**, **(4-5)e**, and **(4-6)e** in high overall yields. With disubstituted alkene **(4-1)g** as starting material, products **(4-4)g, (4-5)g** and **(4-6)g** were obtained in overall yields of 75%-81%. It suggests that homoallyl alcohols can thus be prepared directly from alkenes in high efficiency and high yields.

4.3.3 Assignment of Geometry of the C=C Bond in Compound (4-2)l

See chapter 3, section 3.3.3.2, page 91.

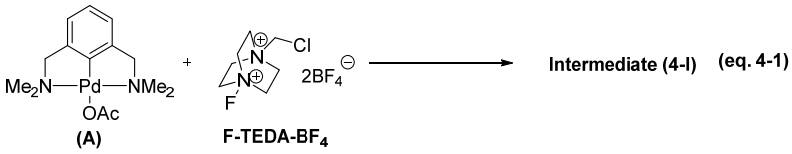
4.3.4 Mechanistic Study



Scheme 4-4. Plausible Mechanism of the Allylic C-H Borylation.

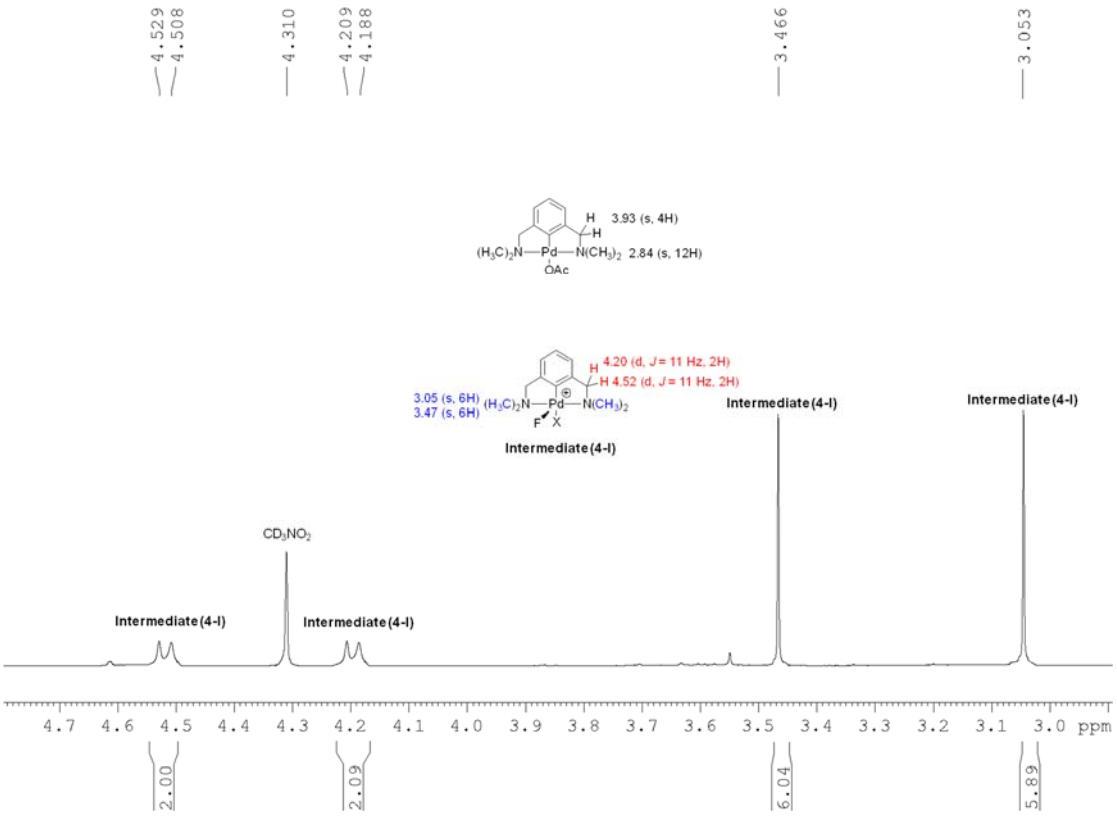
The mechanistic features of the above Pd-catalyzed allylic C-H borylation reactions have been briefly studied. F-TEDA-BF_4 is reported to be capable of oxidizing Pd(II) to form a Pd(IV)-F species.[115] Observation of a ^{19}F signal at -324.9 ppm is consistent with the presence of a fluoride ligand coordinated to Pd(IV). For example, Sanford and co-workers reported a ^{19}F shift at -324 ppm for a Pd(IV)-F species.[109c] In addition, NCN pincer complexes are known to form Pd(IV) complexes. For example, the groups of Canty[115c] and Szabó[8] reported oxidation of Pd(II) NCN complexes to their Pd(IV) analogues by using strong oxidants, such as hypervalent iodine reagents. Indeed, when I monitored the change of the ^1H NMR spectrum of NCN pincer complex **A** on addition of F-TEDA-BF_4, the systematic changes of the ^1H NMR signals were observed

characteristic of the increase in coordination number from square-planar Pd(II) to a Pd(IV) species with a square-pyramidal or octahedral geometry (see below). Therefore, it is proposed that in the initial step, NCN pincer complex **A** is oxidized by F-TEDA-BF_4 to generate a Pd(IV)-F species **(4-I)** containing a vacant coordination site (Scheme 4-4). Then, alkene **(4-1)** undergoes C-H activation to form η^1-allyl complex **(4-II)**. The C-H activation step probably proceeds by a CMD-type mechanism,[116] in which the coordinated acetate assists in the deprotonation of **(4-1)**. Subsequently, B_2pin_2 undergoes transmetallation with Pd(IV)-F to give **(4-III)**, facilitated by the formation of F-Bpin. Finally, C-B reductive elimination gives product **(4-2)** and regenerates the catalyst. A possible explanation of the surprising *Z*-selectivity of the product formation is that η^1-allyl palladium complexes (**(4-II)** and **(4-III)**) are involved in the reaction, which are unable to undergo isomerization to give thermodynamically more stable *E*-product.

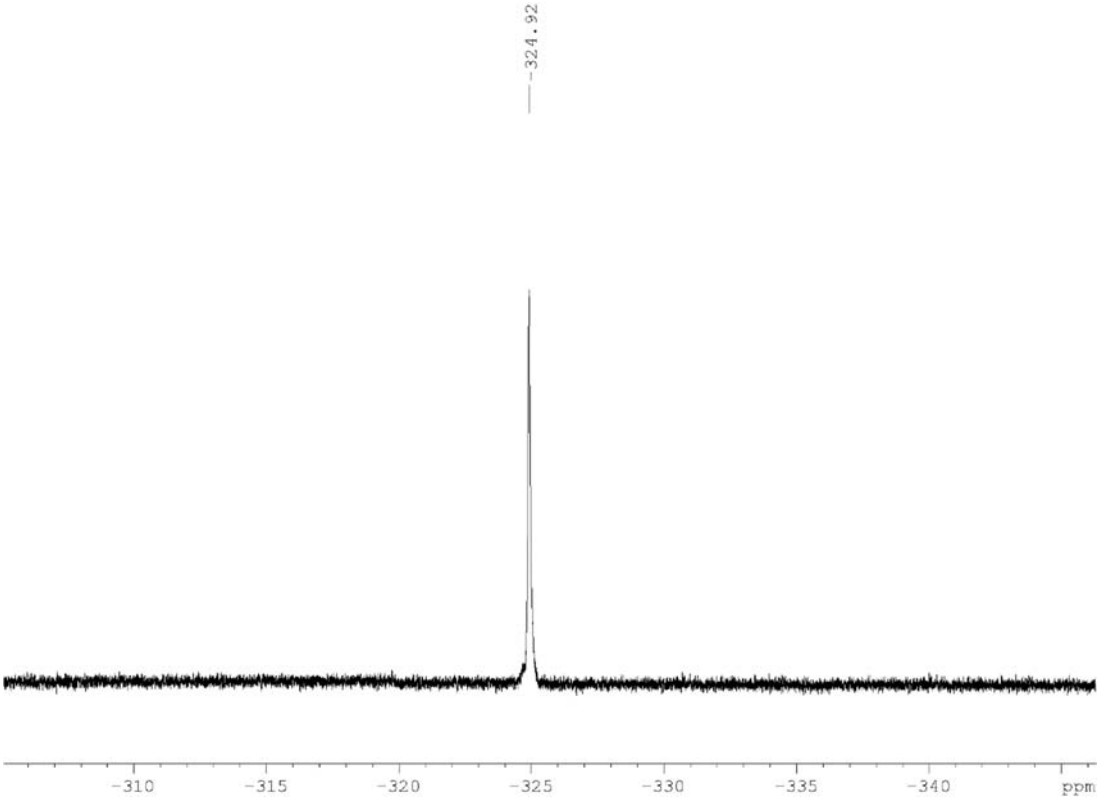


Palladium complex **A** (38 mg, 0.1 mmol, 1 equiv) was dissolved in CD_3NO_2 (0.5 mL), and F-TEDA-BF_4 (53 mg, 0.15 mmol, 1.5 equiv) was added. The sample was vigorously stirred for 5 min. to give a homogeneous solution. *In situ* ^1H and ^{19}F NMR were recorded at room temperature. Spectroscopic data for the relevant benzyl and methyl protons of proposed intermediate **(4-I)**: ^1H NMR (500 MHz, CD_3NO_2): δ 4.52 (d, J = 11 Hz, 2H, Ar-CH_2), 4.20 (d, J = 11 Hz, 2H, Ar-CH_2), 3.47 (s, 6H, NCH_3), 3.05 (s, 6H, NCH_3). The inequivalence of the benzylic protons and also the NMe_2 groups indicates that the Pd no longer has a square planar geometry and is likely square pyramidal with a vacant coordination site or octahedral with the two axial ligands being different. A single peak at -324.9 ppm was found by an *in situ* ^{19}F NMR study of the reaction mixture of **A** and F-TEDA-BF_4 in CD_3NO_2 at room temperature. These results suggest that a Pd(IV) intermediate was generated *in situ* from the reaction of palladium pincer-complex **A** with F-TEDA-BF_4.[8,109]

^{1}H NMR (500 MHz, CD_3NO_2)



^{19}F NMR (470 MHz, CD_3NO_2)



4.4 Summary

Chapter 4 reports an efficient methodology to synthesize and isolate allyl boronates, that exhibits high regio- and stereoselectivity with a variety of alkenes, and which is extended to a one-pot carbonyl allylation reaction with high overall yields. An interesting mechanistic feature is that the reaction proceeds via Pd(II)/Pd(IV) catalytic cycle. Formation of the Pd(IV) intermediate occurs by a unique combination of NCN-pincer complex **A** and application of F-TEDA-BF_4 as the oxidant. An important novelty of the present C-H borylation reaction is that all allyl-Bpin products can be isolated with usually high yields. This is probably a consequence of the application of pincer complex **A** as catalyst, which selectively catalyzes C-B bond formation avoiding subsequent C-B bond cleavage based side-reactions. Another interesting and fortunate feature of the catalyst system is that F-TEDA-BF_4 is able to oxidize Pd(II) to Pd(IV) in the pincer complex, but it does not oxidize boron in either the diboron reagent or the allylboronate product.

4.5 Experimental Procedure and Characterization Data

4.5.1 General Information

All reagents were purchased from Alfa-Aesar, Aldrich, ABCR or VWR, and were checked for purity by GC-MS and/or ^{1}H NMR spectroscopy and used as received. B_2pin_2 was kindly provided by AllylChem Co. Ltd. (Dalian, China). HPLC grade solvents were argon saturated, dried using an Innovative Technology Inc. Pure-Solv Solvent Purification System, and further deoxygenated using the freeze-pump-thaw method. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, and dried over 4Å molecular sieves, deoxygenated using the freeze-pump-thaw method and vacuum transferred into a sealed vessel.

Automated flash chromatography was performed using a Biotage® Isolera Four system, on silica gel (Biotage SNAP cartridge KP-Sil 10 g and KP-Sil 25 g). Commercially available, precoated TLC plates (Polygram® Sil G/UV254) were purchased from Machery-Nagel. The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 30 °C.

GC-MS analyses were performed using an Agilent 7890A gas chromatograph (column: HP-5MS 5% phenyl methyl siloxane, 10 m, ∅ 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C (20 °C min^{-1}); carrier gas: He (1.2 mL min^{-1})) equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A series auto sampler/injector. HRMS analyses were performed using a Thermo Fischer Scientific Exactive Plus

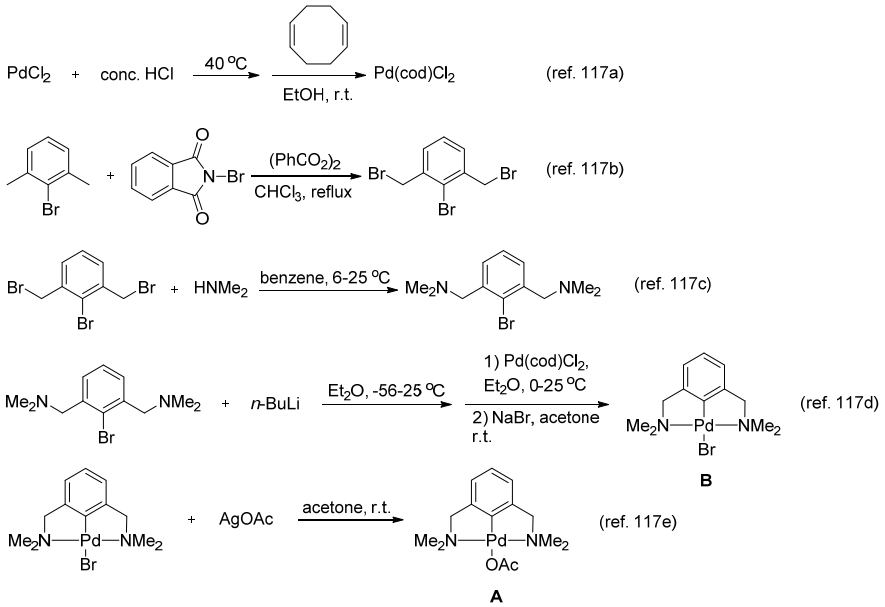
Orbitrap MS system (ASAP, ESI or HESI probe). Elemental analyses were performed on a Leco CHNS-932 Elemental Analyzer in our Institute.

All NMR spectra were recorded at ambient temperature using Bruker Avance III HD 300 NMR (^{1}H, 300 MHz; ^{13}C{^{1}H}, 75 MHz; ^{11}B, 96 MHz), or Bruker Avance 400 NMR (^{1}H, 400 MHz; ^{13}C{^{1}H}, 100 MHz; ^{11}B, 128 MHz), or Bruker Avance 500 NMR (^{1}H, 500 MHz; ^{13}C{^{1}H}, 125 MHz; ^{11}B, 160 MHz; ^{19}F, 470 MHz) spectrometers. ^{1}H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm) whereas ^{13}C{^{1}H} NMR spectra are reported relative to TMS *via* the carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm). ^{11}B NMR chemical shifts are quoted relative to $BF_3{\cdot}Et_2O$ as external standard. ^{19}F NMR chemical shifts are quoted relative to $CFCl_3$ as external standard. All ^{13}C NMR spectra were broad-band ^{1}H decoupled.

4.5.2 Preparation of Catalysts and Starting Materials

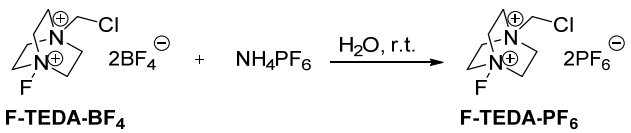
4.5.2.1 Preparation of Pd-pincer Complexes A and B

The Pd-pincer complexes **A** and **B** were prepared via the following method. The characterization data (^{1}H, ^{13}C NMR and elemental analysis) are in accordance with those in the literature.[117]



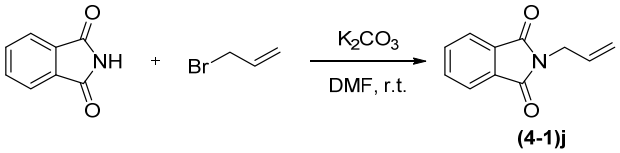
4.5.2.2 Preparation of F-TEDA-PF_6

F-TEDA-PF_6 was prepared via anion exchange from the commercial BF_4^- salt. The characterization data (^{1}H, ^{13}C and ^{19}F NMR) are in accordance with those in the literature.[118]



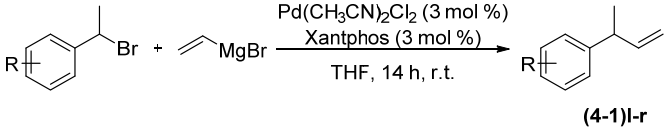
4.5.2.3 Preparation of Compound (4-1)j

Compound **(4-1)j** was prepared via the following method. Their characterization data (^{1}H and ^{13}C NMR) are in accordance with those in the literature.[119a]

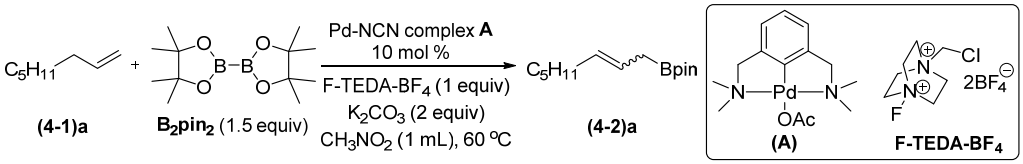


4.5.2.4 Preparation of Compounds (4-1)l-r

Compounds **(4-1)l-r** were prepared via the following method. The characterization data (^{1}H and ^{13}C NMR) are in accordance with those in the literature.[119b]

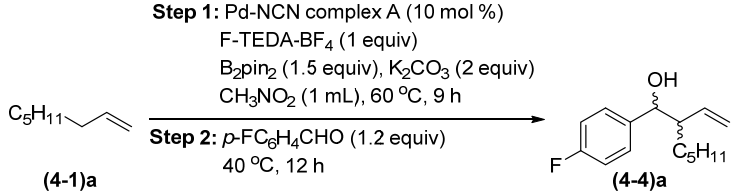


4.5.3 Allylic C-H Borylation of Alkenes (Method 4A)



Pd-NCN complex **A** (10 mol %, 7.1 mg) and F-TEDA-BF_4 (1 equiv, 70.9 mg, 0.2 mmol) were dissolved in 0.5 mL of CH_3NO_2 in a dried vial in a glove-box under argon and the reaction was stirred for 5 min. Then, B_2pin_2 (1.5 equiv, 76.2 mg, 0.3 mmol), **(4-1)a** (1 equiv, 31.4 μL, 0.2 mmol), and K_2CO_3 (2 equiv, 55.3 mg, 0.4 mmol) were added in this order. Finally, another 0.5 mL of CH_3NO_2 was added to the mixture. The reaction was heated at 60 °C under argon until the starting material was completely consumed (determined by GC-MS). The crude mixture was filtered through a pad of Celite. Then, the solvent was slowly removed on a rotary evaporator (30 °C, 300 mbar). A colorless oil in 83% yield (39.5 mg, *E*:*Z* = 50:1) was obtained via purification by flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs.

4.5.4 Application in One-pot Carbonyl Allylation Reactions (Method 4B)



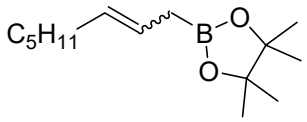
Step 1: Pd-NCN complex **A** (10 mol %, 7 mg) and F-TEDA-BF_4 (1 equiv, 71 mg, 0.2 mmol) were

dissolved in 0.5 mL of CH_3NO_2 in a dried vial in a glove-box under argon and the reaction was stirred for 5 min. Then, B_2pin_2 (1.5 equiv, 76 mg, 0.3 mmol), **(4-1)a** (1 equiv, 31 μL, 0.2 mmol), and K_2CO_3 (2 equiv, 55 mg, 0.4 mmol) were added in this order. Finally, another 0.5 mL of CH_3NO_2 was added to the mixture. The reaction was heated at 60 °C under argon until the starting material was completely consumed (determined by GC-MS).

Step 2: 4-Fluorobenzaldehyde (1.2 equiv, 26 μL, 0.24 mmol) was added to the reaction mixture after it cooled to room temperature, and the reaction was heated at 40 °C for 12 h. The crude mixture was filtered through a pad of Celite. Then, the solvent was removed on a rotary evaporator. A colorless oil in 86% yield (41 mg, *anti*:*syn* = 49:1) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7).

4.5.5 Characterization Data

4,4,5,5-Tetramethyl-2-(oct-2-en-1-yl)-1,3,2-dioxaborolane (4-2)a



(4-2)a-*major (E)-isomer*

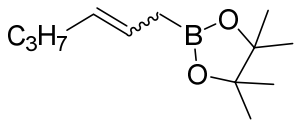
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48–5.33 (m, 2H), 1.99-1.92 (m, 2H), 1.63 (d, *J* = 6 Hz, 2H), 1.37–1.19 (m, 6H), 1.24 (s, 12H), 0.87 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 131.2, 124.8, 83.3, 32.8, 31.5, 29.5, 24.9, 22.7, 16.4 (broad, low intensity), 14.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{28}BO_2$ [M+H$^+$]: 239.2177, found: 239.2172.

2-(Hex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4-2)b



Following method 4A, a colorless oil in 84% yield (35.3 mg, *E*:*Z* = 20:1) from **(4-1)b** (25.0 μL, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

(4-2)b-*major (E)-isomer*

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47–5.33 (m, 2H), 1.99–1.90 (m, 2H), 1.65–1.61 (m, 2H), 1.34 (tq,

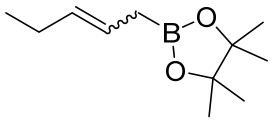
J_1 = 7 Hz, J_2 = 7 Hz, 2H), 1.24 (s, 12H), 0.86 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 130.9, 125.0, 83.3, 35.0, 24.9, 22.9, 16.1 (broad, low intensity), 13.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* calcd for $C_{12}H_{24}BO_2$ [M+H$^+$]: 211.1864, found: 211.1860.

4,4,5,5-Tetramethyl-2-(pent-2-en-1-yl)-1,3,2-dioxaborolane (4-2)c



Following method 4A, a colorless oil in 79% yield (31.0 mg, *E*:*Z* = 17:1) from **(4-1)c** (21.9 μL, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

(4-2)c-*major (E)-isomer*

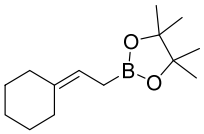
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50–5.33 (ov. m, 2H), 2.04–1.93 (m, 2H), 1.66–1.58 (ov. m, 2H), 1.24 (s, 12H), 0.94 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 132.8, 123.8, 83.3, 25.9, 24.9, 16.3 (broad, low intensity), 14.2.

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* calcd for $C_{11}H_{22}BO_2$ [M+H$^+$]: 197.1707, found: 197.1704.

2-(2-Cyclohexylideneethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4-2)d



Following method 4A, a colorless oil in 86% yield (40.6 mg) from **(4-1)d** (30.9 μL, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 (tquint, J_1 = 8 Hz, J_2 = 1 Hz, 1H), 2.12–2.04 (m, 4H), 1.60 (d, J = 8 Hz, 2H), 1.54–1.45 (m, 6H), 1.24 (s, 12H).

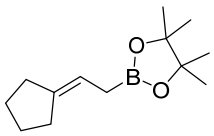
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 139.9, 115.1, 83.2, 37.2, 28.8, 28.7, 27.8, 27.1, 24.9, 11.2

(broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.2.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{26}BO_2$ [M+H$^+$]: 237.2020, found: 237.2018.

2-(2-Cyclopentylideneethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4-2)e



Following method 4A, a colorless oil in 78% yield (34.7 mg) from **(4-1)e** (27.8 μL, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

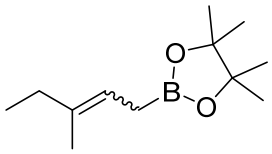
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.33 (tquint., J_1 = 8 Hz, J_2 = 1 Hz, 1H), 2.25–2.12 (m, 4H), 1.71–1.53 (ov. m, 6H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.7, 114.1, 83.2, 33.7, 28.9, 26.8, 26.4, 24.9, 11.0 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{13}H_{24}BO_2$ [M+H$^+$]: 223.1864, found: 223.1861.

4,4,5,5-Tetramethyl-2-(3-methylpent-2-en-1-yl)-1,3,2-dioxaborolane (4-2)f



Following method 4A, a colorless oil in 83% yield (34.9 mg, *E*:*Z* = 2:1) from **(4-1)f** (25.1 μL, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

(4-2)f-*a mixture of isomers*

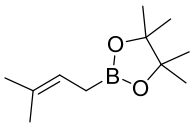
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26–5.16 (m, 1H), 2.04–1.95 (m, 2H), 1.68–1.66 and 1.62–1.56 (m, 5H), 1.23 (s, 12H), 0.99–0.92 (m, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 137.24, 137.21, 118.1, 117.2, 83.20, 83.17, 32.6, 24.89, 24.88, 23.0, 15.9, 13.1, 12.6, 11.9 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{12}H_{24}BO_2$ [M+H$^+$]: 211.1864, found: 211.1860.

4,4,5,5-Tetramethyl-2-(3-methylbut-2-en-1-yl)-1,3,2-dioxaborolane (4-2)g



Following method 4A, a colorless oil in 68% yield (26.7 mg) from **(4-1)g** (22.4 μL, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

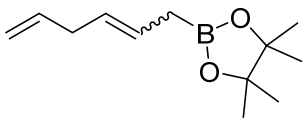
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.22 (tqq, J_1 = 8 Hz, J_2 = 2 Hz, J_3 = 1 Hz, 1H), 1.69–1.68 (m, 3H), 1.62–1.57 (m, 5H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 131.7, 118.7, 83.2, 25.9, 24.9, 17.8, 12.0 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.2.

HRMS (ASAP): *m/z* calcd for $C_{11}H_{22}BO_2$ [M+H$^+$]: 197.1707, found: 197.1703.

2-(Hexa-2,5-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4-2)h



Following method 4A, a colorless oil in 72% yield (30.0 mg, *E*:*Z* = 11:1) from **(4-1)h** (23.7 μL, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

(4-2)h-*major (E)-isomer*

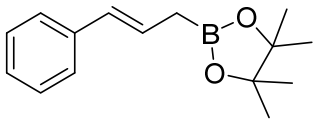
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88–5.75 (m, 1H), 5.54–5.35 (m, 2H), 5.04–4.98 (m, 1H), 4.97–4.91 (m, 1H), 2.78–2.70 (m, 2H), 1.66 (d, *J* = 7 Hz, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 137.8, 128.3, 126.4, 114.7, 83.3, 37.0, 27.7 (broad, low intensity), 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* calcd for $C_{12}H_{22}BO_2$ [M+H$^+$]: 209.1707, found: 209.1700.

(*E*)-2-Cinnamyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4-2)i



Following method 4A, a colorless oil in 69% yield (33.7 mg) from **(4-1)i** (26.5 μL, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

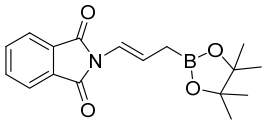
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.31 (m, 2H), 7.30–7.23 (m, 2H), 7.19–7.13 (m, 1H), 6.41–6.24 (m, 2H), 1.87 (d, *J* = 7 Hz, 2H), 1.26 (s, 12H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.3, 130.4, 128.5, 126.6, 126.4, 126.0, 83.5, 24.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{15}H_{22}BO_2$ [M+H$^+$]: 245.1707, found: 245.1702.

(*E*)-2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)isoindoline-1,3-dione (4-2)j



Following method 4A, a colorless oil in 69% yield (43.2 mg) from **(4-1)j** (37.4 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

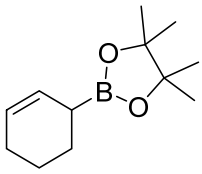
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86–7.81 (m, 2H), 7.73–7.68 (m, 2H), 6.67–6.57 (m, 2H), 1.81 (d, *J* = 6 Hz, 2H), 1.26 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 166.8, 134.3, 131.9, 123.5, 119.0, 117.9, 83.7, 24.9, 14.4 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 32.9.

HRMS (ASAP): *m/z* calcd for $C_{17}H_{20}BNO_4$ [M+H$^+$]: 313.1485, found: 313.1481.

2-(Cyclohex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4-2)k



Following method 4A, a colorless oil in 71% yield (29.6 mg) from **(4-1)k** (20.3 μL, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

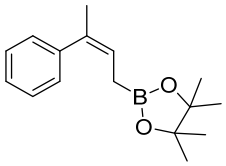
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75–5.64 (m, 2H), 2.02–1.95 (m, 2H), 1.83–1.72 (m, 2H), 1.70–1.56 (m, 3H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 127.7, 126.2, 83.3, 25.1, 24.9, 24.8, 24.3, 22.7, 21.4 (broad, low intensity).

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.5.

HRMS (ASAP): *m/z* calcd for $C_{12}H_{22}BO_2$ [M+H$^+$]: 209.1707, found: 209.1701.

(*Z*)-4,4,5,5-Tetramethyl-2-(3-phenylbut-2-en-1-yl)-1,3,2-dioxaborolane (4-2)l



Following method 4A, a colorless oil in 71% yield (36.7 mg) from **(4-1)l** (26.4 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

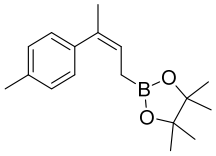
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.29 (m, 2H), 7.23–7.18 (m, 3H), 5.60 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.03 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.62 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.23 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 142.2, 136.1, 128.3, 128.2, 126.4, 122.0, 83.3, 25.7, 24.9, 13.6 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* calcd for $C_{16}H_{24}BO_2$ [M+H$^+$]: 259.1864, found: 259.1861.

(*Z*)-4,4,5,5-Tetramethyl-2-(3-(p-tolyl)but-2-en-1-yl)-1,3,2-dioxaborolane (4-2)m



Following method 4A, a colorless oil in 74% yield (40.3 mg) from **(4-1)m** (29.2 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

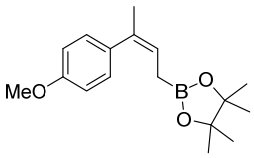
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17–7.07 (m, 4H), 5.58 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.34 (s, 3H), 2.03 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.64 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.2, 135.9 (2C), 128.8, 128.2, 121.7, 83.3, 25.7, 24.9, 21.3, 13.8 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{17}H_{26}BO_2$ [M+H$^+$]: 273.2020, found: 273.2016.

(*Z*)-2-(3-(4-Methoxyphenyl)but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4-2)n



Following method 4A, a colorless oil in 79% yield (45.5 mg) from **(4-1)n** (32.4 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

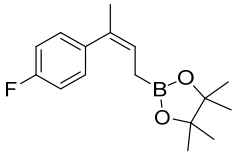
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20–7.13 (m, 2H), 6.90–6.83 (m, 2H), 5.56 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 3.80 (s, 3H), 2.02 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.65 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 158.1, 135.4, 134.5, 129.3, 121.5, 113.5, 83.2, 55.3, 25.7, 24.9, 13.7 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.2.

HRMS (ASAP): *m/z* calcd for $C_{17}H_{26}BO_3$ [M+H$^+$]: 289.1970, found: 289.1965.

(*Z*)-2-(3-(4-Fluorophenyl)but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4-2)o



Following method 4A, a colorless oil in 70% yield (38.7 mg) from **(4-1)o** (30.0 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22–7.13 (m, 2H), 7.04–6.95 (m, 2H), 5.59 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.01 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.60 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.23 (s, 12H).

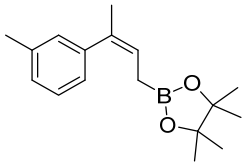
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 161.6 (d, $J_{C\text{-}F}$ = 244 Hz), 138.1 (d, $J_{C\text{-}F}$ = 3 Hz), 135.1, 129.8 (d, $J_{C\text{-}F}$ = 8 Hz), 122.4, 114.9 (d, $J_{C\text{-}F}$ = 21 Hz), 83.3, 25.7, 24.9, 13.6 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ -116.7 (tt, J_1 = 6 Hz, J_2 = 9 Hz, 1F).

HRMS (ASAP): *m/z* calcd for $C_{16}H_{23}BFO_2$ [M+H$^+$]: 277.1770, found: 277.1764.

(*Z*)-4,4,5,5-Tetramethyl-2-(3-(m-tolyl)but-2-en-1-yl)-1,3,2-dioxaborolane (4-2)p



Following method 4A, a colorless oil in 73% yield (39.7 mg) from **(4-1)p** (29.2 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

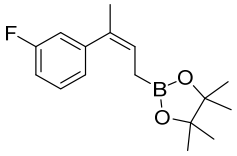
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.17 (m, 1H), 7.08–7.00 (m, 3H), 5.59 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.35 (s, 3H), 2.03 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.64 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.25 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.2, 137.5, 136.1, 129.0, 128.0, 127.2, 125.3, 121.8, 83.3, 25.7, 24.9, 21.6, 13.7 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{17}H_{26}BO_2$ [M+H$^+$]: 273.2020, found: 273.2018.

(*Z*)-2-(3-(3-Fluorophenyl)but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4-2)q



Following method 4A, a colorless oil in 74% yield (40.9 mg) from **(4-1)q** (30.0 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.22 (m, 1H), 7.02–6.85 (m, 3H), 5.61 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.01 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.62 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.24 (s, 12H).

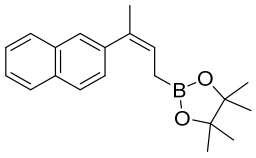
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 245 Hz), 144.6 (d, $J_{C\text{-}F}$ = 7 Hz), 134.9 (d, $J_{C\text{-}F}$ = 2 Hz), 129.6 (d, $J_{C\text{-}F}$ = 8 Hz), 123.9 (d, $J_{C\text{-}F}$ = 3 Hz), 122.9, 115.2 (d, $J_{C\text{-}F}$ = 21 Hz), 113.2 (d, $J_{C\text{-}F}$ = 21 Hz), 83.4, 25.5, 24.9, 13.8 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ -114.0 (ddd, J_1 = 1.5 Hz, J_2 = 6 Hz, J_3 = 9 Hz, 1F).

HRMS (ASAP): *m/z* calcd for $C_{16}H_{23}BFO_2$ [M+H$^+$]: 277.1770, found: 277.1766.

(*Z*)-4,4,5,5-Tetramethyl-2-(3-(naphthalen-2-yl)but-2-en-1-yl)-1,3,2-dioxaborolane (4-2)r



Following method 4A, a colorless oil in 64% yield (39.5 mg) from **(4-1)r** (36.5 mg, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

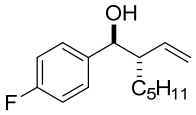
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85–7.77 (m, 3H), 7.70 (s, 1H), 7.48–7.37 (m, 3H), 5.71 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.14 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.71 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.25 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.7, 136.0, 133.5, 132.3, 127.9, 127.7, 127.6, 126.9, 126.8, 125.9, 125.5, 122.6, 83.3, 25.7, 24.9, 14.0 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* calcd for $C_{20}H_{26}BO_2$ [M+H$^+$]: 309.2020, found: 309.2016.

1-(4-Fluorophenyl)-2-vinylheptan-1-ol (4-4)a



Following method 4B, a colorless oil in 86% yield (41 mg, *anti*:*syn* = 49:1) from **(4-1)a** (31 μL, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7).

(4-4)a-major-anti-isomer

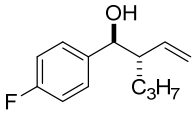
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.25 (m, 2H), 7.05–6.99 (m, 2H), 5.63 (ddd, J_1 = 9 Hz, J_2 = 10 Hz, J_3 = 17 Hz, 1H), 5.25 (dd, J_1 = 2 Hz, J_2 = 10 Hz, 1H), 5.17 (ddd, J_1 = 1 Hz, J_2 = 2 Hz, J_3 = 17 Hz, 1H), 4.35 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 1H), 2.33–2.30 (m, 1H), 2.26–2.19 (m, 1H), 1.37–1.04 (ov. m, 8H, slightly overlapped with the *syn* isomer), 0.83 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 245 Hz), 139.3, 138.4 (d, $J_{C\text{-}F}$ = 3 Hz), 128.6 (d, $J_{C\text{-}F}$ = 8 Hz), 119.0, 115.1 (d, $J_{C\text{-}F}$ = 21 Hz), 76.1, 53.1, 31.8, 30.4, 26.9, 22.6, 14.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ -115.1 (tt, J_1 = 5 Hz, J_2 = 8 Hz, 1F).

HRMS (ASAP): *m/z* calcd for $C_{15}H_{22}FO$ [M+H$^+$]: 237.1649, found: 237.1646.

1-(4-Fluorophenyl)-2-vinylpentan-1-ol (4-4)b



Following method 4B, a colorless oil in 87% yield (39 mg, *anti*:*syn* = 19:1) from **(4-1)b** (25 μL, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7).

(4-4)b-major-anti-isomer

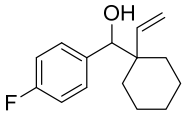
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.25 (m, 2H), 7.05–7.00 (m, 2H), 5.63 (ddd, J_1 = 9 Hz, J_2 = 10 Hz, J_3 = 17 Hz, 1H), 5.25 (dd, J_1 = 2 Hz, J_2 = 10 Hz, 1H), 5.17 (ddd, J_1 = 1 Hz, J_2 = 2 Hz, J_3 = 17 Hz, 1H), 4.36 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 1H), 2.32–2.28 (m, 1H), 2.28–2.21 (m, 1H), 1.41–1.06 (ov. m, 4H, slightly overlapped with the *syn* isomer), 0.79 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 245 Hz), 139.3, 138.4 (d, $J_{C\text{-}F}$ = 3 Hz), 128.6 (d, $J_{C\text{-}F}$ = 8 Hz), 119.1, 115.1 (d, $J_{C\text{-}F}$ = 21 Hz), 76.1, 52.8 (d, J = 1 Hz), 32.6, 20.4, 14.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ -115.1 (tt, J_1 = 5 Hz, J_2 = 8 Hz, 1F).

HRMS (ASAP): *m/z* calcd for $C_{15}H_{22}FO$ [M+H$^+$]: 209.1336, found: 209.1333.

(4-Fluorophenyl)(1-vinylcyclohexyl)methanol (4-4)d



Following method 4B, a colorless oil in 88% yield (41 mg) from **(4-1)d** (31 μL, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7).

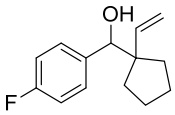
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24–7.18 (m, 2H), 7.01–6.95 (m, 2H), 5.53 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.41 (dd, J_1 = 2 Hz, J_2 = 11 Hz, 1H), 5.10 (dd, J_1 = 2 Hz, J_2 = 18 Hz, 1H), 4.33 (d, J = 5 Hz, 1H), 2.13 (d, J = 5 Hz, 1H), 1.93–1.83 (m, 1H), 1.61-1.27 (m, 8 H), 1.16–1.05 (m, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 247 Hz), 141.8, 136.5 (d, $J_{C\text{-}F}$ = 3 Hz), 129.6 (d, $J_{C\text{-}F}$ = 8 Hz), 117.9, 114.3 (d, $J_{C\text{-}F}$ = 21 Hz), 80.5, 45.8 (d, J = 1 Hz), 33.0, 31.2, 26.5, 22.2, 22.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ -115.5 (tt, J_1 = 5 Hz, J_2 = 8 Hz, 1F).

HRMS (ASAP): *m/z* calcd for $C_{15}H_{20}FO$ [M+H$^+$]: 235.1493, found: 235.1490.

(4-Fluorophenyl)(1-vinylcyclopentyl)methanol (4-4)e



Following method 4B, a colorless oil in 84% yield (37 mg) from **(4-1)e** (28 μL, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7).

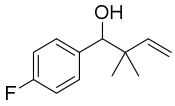
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27–7.22 (m, 2H), 7.01–6.94 (m, 2H), 5.74 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.18 (dd, J_1 = 1 Hz, J_2 = 11 Hz, 1H), 5.02 (dd, J_1 = 1 Hz, J_2 = 18 Hz, 1H), 4.51 (d, J = 4 Hz, 1H), 2.17–2.12 (m, 1H), 1.84–1.76 (m, 1H), 1.71–1.49 (m, 6H), 1.43–1.35 (m, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.2 (d, $J_{C\text{-}F}$ = 246 Hz), 141.5, 137.8 (d, $J_{C\text{-}F}$ = 3 Hz), 129.1 (d, $J_{C\text{-}F}$ = 8 Hz), 115.3, 114.5 (d, $J_{C\text{-}F}$ = 21 Hz), 79.8, 55.3 (d, J = 1 Hz), 34.3, 33.2, 23.50, 23.48.

^{19}F NMR (470 MHz, $CDCl_3$) δ -115.5 (tt, J_1 = 5 Hz, J_2 = 8 Hz, 1F).

HRMS (ASAP): *m/z* calcd for $C_{14}H_{18}FO$ [M+H$^+$]: 221.1336, found: 221.1331.

1-(4-Fluorophenyl)-2,2-dimethylbut-3-en-1-ol (4-4)g



Following method 4B, a colorless oil in 81% yield (31 mg) from **(4-1)g** (31 μL, 0.2 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7).

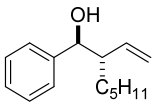
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.23 (m, 2H), 7.03–6.96 (m, 2H), 5.89 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.15 (dd, J_1 = 1 Hz, J_2 = 11 Hz, 1H), 5.07 (dd, J_1 = 1 Hz, J_2 = 18 Hz, 1H), 4.41 (d, J = 3 Hz, 1H), 2.07–2.02 (m, 1H), 0.99 (s, 3H), 0.94 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 245 Hz), 145.0, 136.5 (d, $J_{C\text{-}F}$ = 3 Hz), 129.4 (d, $J_{C\text{-}F}$ = 8 Hz), 114.5 (d, $J_{C\text{-}F}$ = 21 Hz), 114.3, 80.1, 42.4 (d, J = 1 Hz), 24.6, 21.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ -115.4 (tt, J_1 = 5 Hz, J_2 = 8 Hz, 1F).

HRMS (ASAP): *m/z* calcd for $C_{12}H_{16}FO$ [M+H$^+$]: 195.1180, found: 195.1177.

1-Phenyl-2-vinylheptan-1-ol (4-5)a



Following method 4B, a colorless oil in 85% yield (37 mg, *anti*:*syn* = 48:1) from **(4-1)a** (31 μL, 0.2 mmol) and benzaldehyde (1.2 equiv, 24 μL, 0.24 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7). The characterization data (^{1}H and ^{13}C NMR) are in accordance with those in the literature.[28f]

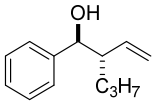
(4-5)a-major-anti-isomer

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.25 (m, 5H, slightly overlapped with *syn* isomer), 5.67 (ddd, J_1 = 9 Hz, J_2 = 10 Hz, J_3 = 17 Hz, 1H), 5.25 (dd, J_1 = 2 Hz, J_2 = 10 Hz, 1H), 5.18 (ddd, J_1 = 1 Hz, J_2 = 2 Hz, J_3 = 17 Hz, 1H), 4.39 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 1H), 2.37–2.20 (ov. m, 2H), 1.38–1.05 (m, 8H, slightly overlapped with *syn* isomer), 0.85 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.7, 139.5, 128.3, 127.6, 127.0, 118.7, 76.8, 52.8, 31.8, 30.5, 26.9, 22.6, 14.1.

HRMS (ASAP): *m/z* calcd for $C_{15}H_{23}O$ [M+H$^+$]: 219.1743, found: 219.1740.

1-Phenyl-2-vinylpentan-1-ol (4-5)b



Following method 4B, a colorless oil in 84% yield (32 mg, *anti*:*syn* = 18:1) from **(4-1)b** (25 μL, 0.2 mmol) and benzaldehyde (1.2 equiv, 24 μL, 0.24 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7).

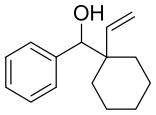
(4-5)b-major-anti-isomer

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.25 (m, 5H, slightly overlapped with *syn* isomer), 5.69 (ddd, J_1 = 9 Hz, J_2 = 10 Hz, J_3 = 17 Hz, 1H), 5.28 (dd, J_1 = 2 Hz, J_2 = 10 Hz, 1H), 5.20 (ddd, J_1 = 1 Hz, J_2 = 2 Hz, J_3 = 17 Hz, 1H), 4.41 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 1H), 2.50–2.31 (m, 1H), 2.30 (d, J = 2 Hz, 1H), 1.63–1.08 (m, 4H, slightly overlapped with *syn* isomer), 0.83 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.7, 139.5, 128.3, 127.7, 127.1, 118.7, 76.8, 52.6, 32.7, 20.4, 14.0.

HRMS (ASAP): *m/z* calcd for $C_{13}H_{19}O$ [M+H$^+$]: 191.1430, found: 191.1427.

Phenyl(1-vinylcyclohexyl)methanol (4-5)d



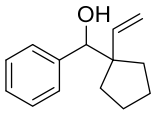
Following method 4B, a colorless oil in 86% yield (37 mg) from **(4-1)d** (31 μL, 0.2 mmol) and benzaldehyde (1.2 equiv, 24 μL, 0.24 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7). The characterization data (^{1}H and ^{13}C NMR) are in accordance with those in the literature.[28f]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.22 (m, 5H), 5.56 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.41 (dd, J_1 = 2 Hz, J_2 = 11 Hz, 1H), 5.11 (dd, J_1 = 2 Hz, J_2 = 18 Hz, 1H), 4.35 (d, J = 5 Hz, 1H), 2.12 (d, J = 5 Hz, 1H), 1.96–1.86 (m, 1H), 1.58–1.27 (m, 9H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.0, 140.9, 128.2, 127.5, 127.4, 117.7, 81.2, 45.9, 33.0, 31.5, 26.5, 22.24, 22.15.

HRMS (ASAP): *m/z* calcd for $C_{15}H_{21}O$ [M+H$^+$]: 217.1587, found: 217.1583.

Phenyl(1-vinylcyclopentyl)methanol (4-5)e



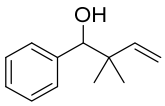
Following method 4B, a colorless oil in 79% yield (32 mg) from **(4-1)e** (28 μL, 0.2 mmol) and benzaldehyde (1.2 equiv, 24 μL, 0.24 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.22 (m, 5H), 5.78 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.19 (dd, J_1 = 1 Hz, J_2 = 11 Hz, 1H), 5.05 (dd, J_1 = 1 Hz, J_2 = 18 Hz, 1H), 4.54 (d, J = 4 Hz, 1H), 2.09 (d, J = 4 Hz, 1H), 1.67–1.87 (m, 2H), 1.51–1.65 (m, 5H), 1.90–1.36 (m, 8H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.1, 141.8, 127.7, 127.6, 127.5, 115.1, 80.4, 55.4, 34.3, 33.3, 23.53, 23.51.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{19}O$ [M+H$^+$]: 203.1430, found: 203.1427.

2,2-Dimethyl-1-phenylbut-3-en-1-ol (4-5)g



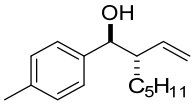
Following method 4B, a colorless oil in 75% yield (26 mg) from **(4-1)g** (31 μL, 0.2 mmol) and benzaldehyde (1.2 equiv, 24 μL, 0.24 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.23 (m, 5H), 5.92 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.15 (dd, J_1 = 1 Hz, J_2 = 11 Hz, 1H), 5.08 (dd, J_1 = 1 Hz, J_2 = 18 Hz, 1H), 4.43 (d, J = 3 Hz, 1H), 2.03 (br. d, J = 3 Hz, 1H), 1.02 (s, 3H), 0.97 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.2, 140.9, 127.9, 127.63, 127.55, 114.0, 80.8, 42.4, 24.6, 21.2.

HRMS (ASAP): *m/z* calcd for $C_{12}H_{17}O$ [M+H$^+$]: 177.1274, found: 177.1271.

1-(*p*-Tolyl)-2-vinylheptan-1-ol (4-6)a



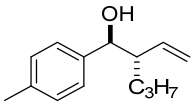
Following method 4B, a colorless oil in 85% yield (39 mg, *anti*:*syn* = 48:1) from **(4-1)a** (31 μL, 0.2 mmol) and *p*-tolualdehyde (1.2 equiv, 28 μL, 0.24 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.20 (m, 2H), 7.19–7.13 (m, 2H), 5.67 (ddd, J_1 = 9 Hz, J_2 = 10 Hz, J_3 = 17 Hz, 1H), 5.26 (dd, J_1 = 2 Hz, J_2 = 10 Hz, 1H), 5.18 (ddd, J_1 = 1 Hz, J_2 = 2 Hz, J_3 = 17 Hz, 1H), 4.36 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 1H), 2.37 (s, 3H), 2.34–2.23 (ov. m, 2H), 1.39–1.05 (m, 8H, slightly overlapped with the *syn* isomer), 0.85 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.7, 137.2, 129.0, 126.9, 118.5, 76.6, 52.7, 31.8, 30.5, 26.9, 22.6, 21.2, 14.1.

HRMS (ASAP): *m/z* calcd for $C_{16}H_{25}O$ [M+H$^+$]: 233.1900, found: 233.1897.

1-(*p*-Tolyl)-2-vinylpentan-1-ol (4-6)b



Following method 4B, a colorless oil in 88% yield (36 mg, *anti*:*syn* = 18:1) from **(4-1)b** (25 μL, 0.2 mmol) and *p*-tolualdehyde (1.2 equiv, 28 μL, 0.24 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7).

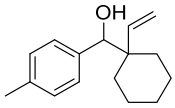
(4-6)b-major-anti-isomer

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.20 (m, 2H), 7.17–7.13 (m, 2H), 5.67 (ddd, J_1 = 9 Hz, J_2 = 10 Hz, J_3 = 17 Hz, 1H), 5.25 (ddd, J_1 = 1 Hz, J_2 = 2 Hz, J_3 = 10 Hz, 1H), 5.19 (ddd, J_1 = 1 Hz, J_2 = 2 Hz, J_3 = 17 Hz, 1H), 4.35 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 1H), 2.36 (s, 3H), 2.35-2.25 (m, 1H), 2.22 (dd, J_1 = 1 Hz, J_2 = 2 Hz, 1H), 1.44–1.10 (m, 4H, slightly overlapped with *syn* isomer), 0.81 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.7 (2C), 137.3, 129.0, 127.0, 118.6, 76.6, 52.6, 32.7, 21.2, 20.4, 14.0.

HRMS (ASAP): *m/z* calcd for $C_{14}H_{21}O$ [M+H$^+$]: 205.1587, found: 205.1583.

***p*-Tolyl(1-vinylcyclohexyl)methanol (4-6)d**



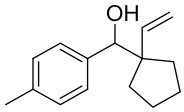
Following method 4B, a colorless oil in 81% yield (37 mg) from **(4-1)d** (31 μL, 0.2 mmol) and *p*-tolualdehyde (1.2 equiv, 28 μL, 0.24 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17–7.07 (m, 4H), 5.56 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.39 (dd, J_1 = 2 Hz, J_2 = 11 Hz, 1H), 5.11 (dd, J_1 = 2 Hz, J_2 = 18 Hz, 1H), 4.31 (d, J = 5 Hz, 1H), 2.34 (s, 3H), 2.08 (d, J = 5 Hz, 1H), 1.95–1.84 (m, 1H), 1.62–1.25 (m, 9H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.1, 138.0, 137.0, 128.2, 128.0, 117.5, 81.0, 45.9, 33.0, 31.5, 26.5, 22.24, 22.15, 21.2.

HRMS (ASAP): *m/z* calcd for $C_{16}H_{23}O$ [M+H$^+$]: 231.1743, found: 231.1740.

***p*-Tolyl(1-vinylcyclopentyl)methanol (4-6)e**



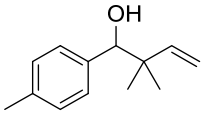
Following method 4B, a colorless oil in 80% yield (35 mg) from **(4-1)e** (28 μL, 0.2 mmol) and *p*-tolualdehyde (1.2 equiv, 28 μL, 0.24 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21–7.15 (m, 2H), 7.15–7.08 (m, 2H), 5.79 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.18 (dd, J_1 = 1 Hz, J_2 = 11 Hz, 1H), 5.04 (dd, J_1 = 1 Hz, J_2 = 18 Hz, 1H), 4.51 (d, J = 4 Hz, 1H), 2.35 (s, 3H), 2.08 (d, J = 4 Hz, 1H), 1.87–1.37 (m, 8H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.0, 139.1, 137.0, 128.4, 127.5, 114.9, 80.3, 55.3, 34.3, 33.3, 23.5 (2C), 21.2.

HRMS (ASAP): *m/z* calcd for $C_{15}H_{21}O$ [M+H$^+$]: 217.1587, found: 217.1583.

2,2-Dimethyl-1-(p-tolyl)but-3-en-1-ol (4-6)g



Following method 4B, a colorless oil in 78% yield (30 mg) from **(4-1)g** (31 μL, 0.2 mmol) and *p*-tolualdehyde (1.2 equiv, 28 μL, 0.24 mmol) was obtained via purification by flash chromatography on silica gel (pentane:EtOAc = 93:7).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21−7.16 (m, 2H), 7.15−7.09 (m, 2H), 5.92 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.13 (dd, J_1= 1 Hz, J_2 = 11 Hz, 1H), 5.07 (dd, J_1 = 1 Hz, J_2 = 18 Hz, 1H), 4.41 (d, J = 3 Hz, 1H), 2.34 (s, 3H), 1.94 (d, J = 3 Hz, 1H), 1.01 (s, 3H), 0.96 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.4, 138.0, 137.2, 128.4, 127.8, 113.9, 80.7, 42.4, 24.7, 21.3, 21.2.

HRMS (ASAP): *m/z* calcd for $C_{13}H_{19}O$ [M+H$^+$]: 191.1430, found: 191.1426.

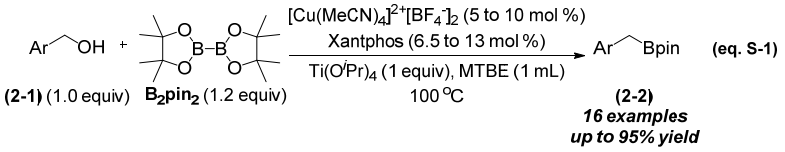
Summary

Efficient methodologies have been developed for the construction of benzyl/allyl sp^3 and vinyl/allenyl sp^2 C-B bonds via copper- or palladium-catalyzed borylations of corresponding alcohols or alkenes, which are readily available substrates.

Chapter 2

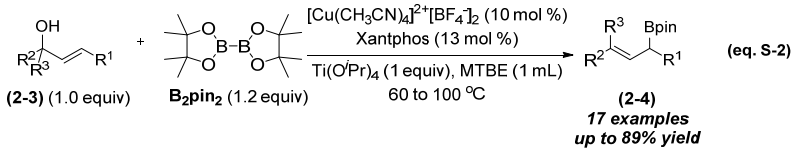
Chapter 2 presents the first example of the Cu-catalyzed direct borylation of alcohols (40 examples), an efficient methodology to synthesize a broad range of benzyl-, allyl-, and allenyl-boronates under mild conditions. The employment of $Ti(O^iPr)_4$ turns the OH moiety into a good leaving group ('OTi'), which plays an important role in the borylation of alcohols. Although we employed a Cu(II) complex as the catalyst precursor, a Cu(I) species was proposed to be the active catalyst for the borylation reactions.

Benzylic boronates were synthesized via Cu-catalyzed borylation of benzylic alcohols (eq. S-1); both the copper catalyst precursor, $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$, and Xantphos ligand are commercially available. In the borylation of benzylic alcohols, the loading of the copper catalyst is 5 mol %, which suggests a high efficiency of this methodology. All benzylboronates were isolated in moderate to high yields (up to 95%). This protocol can also be extended to the borylation of a benzylic acetate providing a benzylboronate in 54% yield, which also suggests it is a general methodology.

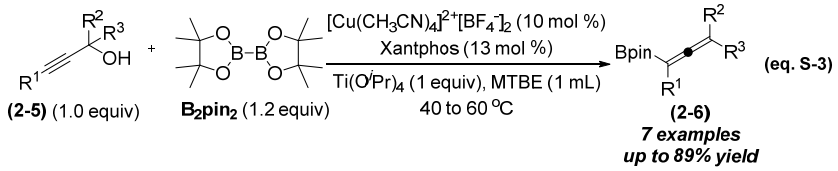


Allylic boronates were also synthesized via a similar protocol to that of the benzylic boronates (eq. S-2), in which the reaction temperature can be lowered to 60 °C. In the borylation of allylic alcohols, secondary allylboronates were obtained from the borylation of primary allyl alcohols, which is different from the earlier Pd-catalyzed borylation of allylic alcohols, which afforded only linear allylic boronates due to the formation of a (η^3-allyl)Pd intermediate. These results suggest that a nucleophilic substitution pathway is probably involved in the mechanism and indicate the potential to synthesize chiral allylboronates from various primary allyl alcohols, which have significant applications in asymmetric synthesis. To the best of our knowledge, this is also the first example of

the catalytic synthesis of secondary allylboronates directly from alcohols. Secondary and tertiary allylic alcohols could be used in the borylation reaction as well, and also afforded corresponding allylboronates in good yields.



This Cu-catalyzed borylation reaction can be further extended to the borylation of propargylic alcohols (eq. S-3), which provides allenylboronates in good yields. The reaction temperature can be further lowered to 40 °C. The regioselectivity of the borylation of propargylic alcohols also suggests that the reaction proceeds via a nucleophilic substitution pathway.



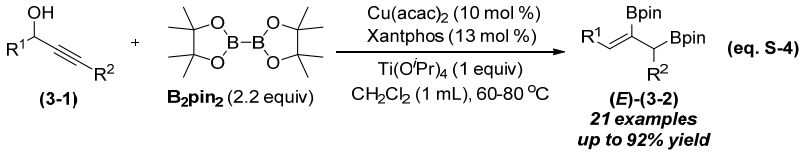
The results shown in Chapter 2 suggest that the Cu-catalyzed borylation of alcohols offers a general methodology to synthesize benzyl-, allyl-, and allenyl-boronates.

Chapter 3

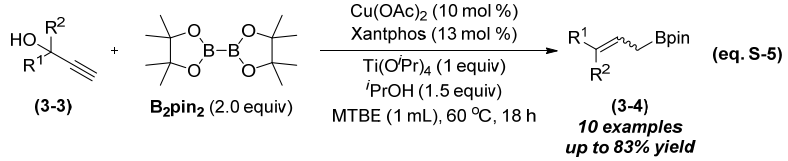
Chapter 3 reports a methodology for the synthesis of vinyl-, allyl- and (*E*)-2-boryl allyl-boronates via Cu-catalyzed borylation of propargylic alcohols (43 examples), in which commercially available copper catalyst precursors, such as $Cu(acac)_2$ and $Cu(OAc)_2$, were employed. In this protocol, $Ti(O^iPr)_4$ is also required to react with alcohols to enhance the "OH" (OTi) leaving group ability.

The (*E*)-2-boryl allylboronates were provided via Cu-catalyzed diboration of propargylic alcohols (eq. S-4). The reaction can be carried out at 60 or 80 °C. The regioselectivity of this Cu-catalyzed diboration reaction is different from that of the $Pd_2(dba)_3$-catalyzed diboration of allenes, which afforded 2-boryl allyl-boronates with C=C double bonds at the terminal position. The stereoselectivity is also different from that of the $Pd(dba)_2$-catalyzed diboration of allenes, which provided predominantly (*Z*)-2-boryl allyl-boronates with C=C double bonds at the internal position. This reveals a unique feature of our Cu-catalyzed diboration of propargylic alcohols, which broadens the utility of alcohols in the development of synthetic methodology. The isolation of an allenyl boronate as the reaction intermediate suggests that an S_N2'-type reaction, followed by

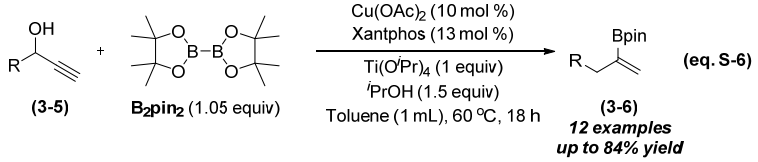
borylcupration is involved in the mechanism of the diboration of propargylic alcohols.



The borylation of 1,1-disubstituted propargylic alcohols affords (*Z*)-allylic boronates as the major products (eq. S-5) employing $Cu(OAc)_2$ as the catalyst precursor. The regio- and stereo-selectivity is in agreement with the Cu-catalyzed borylcupration of allenylsilanes, which is different from the Pd-catalyzed borylation of allylic alcohols, which gives (*E*)-allylic boronates predominantly. It suggests that the Cu-catalyzed borylation of 1,1-disubstituted propargylic alcohols offers an alternative way to prepare (*Z*)-allylic boronates, as the starting materials are either commercially available or easy to synthesize.



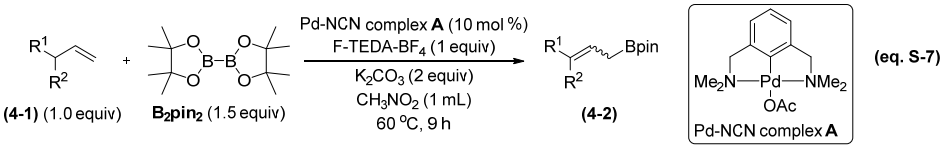
Vinyl boronates were also synthesized via the Cu-catalyzed borylation of mono-substituted propargylic alcohols (eq. S-6), in which the regioselectivity is in agreement with that of the Cu-catalyzed borylcupration of alkynes. Compared to the borylcupration of allenes, the borylation of mono-substituted propargylic alcohols offers a more direct way to prepare vinyl boronates, as allenes are usually prepared from propargylic alcohols.

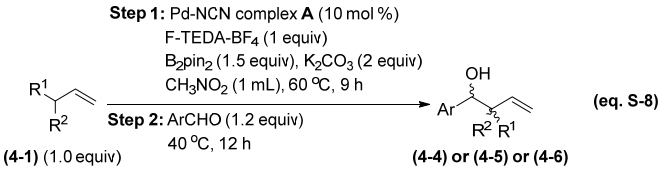


All of the results in Chapter 3 suggest that the Cu-catalyzed borylation of propargylic alcohols is a unique methodology to synthesize vinyl-, allyl-, and (*E*)-2-boryl allyl-boronates, representing a general protocol to synthesize organoboron compounds with easily accessible starting materials. The regio- and stereo-selectivity are also different from those of previously reported methodologies. Although Cu(II) catalyst precursors are employed, a Cu(I) species is probably the active catalytic species, as the borylation reactions are carried out under reducing conditions.

Chapter 4

Chapter 4 reports a Pd-catalyzed oxidative borylation of allylic C-H bonds of alkenes (eq. S-7), which afforded a variety of linear allylic boronates in good yields (eq. S-7). Additionally, the allylic boronates were all isolated and purified, which represents a unique feature of this methodology. An interesting mechanistic feature is that the reaction proceeds via a Pd(II)/Pd(IV) catalytic cycle. Formation of the Pd(IV) intermediate occurs by a unique combination of NCN-pincer complex **A** and application of F-TEDA-BF_4 as the oxidant. An important novelty of the present C-H borylation reaction is that all allyl-Bpin products can be isolated with usually high yields. This is probably a consequence of the application of pincer complex **A** as the catalyst, which selectively catalyzes C-B bond formation avoiding subsequent C-B bond cleavage based side-reactions. Additionally, our protocol can also be extended to one-pot carbonyl allylation reactions with aldehydes to provide homoallyl alcohols (eq. S-8).





In summary, a variety of borylation reactions were developed to synthesize benzyl-, allyl-, allenyl-, vinyl- and 2-boryl allyl-boronates via Cu- or Pd-catalyzed borylation of alcohols or alkenes, which are easily accessible starting materials. The isolation and purification of the reactive organoboron compounds suggest that our methodologies provide potential tools to investigate their reactivities. The synthesis of secondary allylboronates and 2-boryl allylboronates also possesses the potential to be applied in asymmetric synthesis to provide valuable homochiral organoboron compounds.

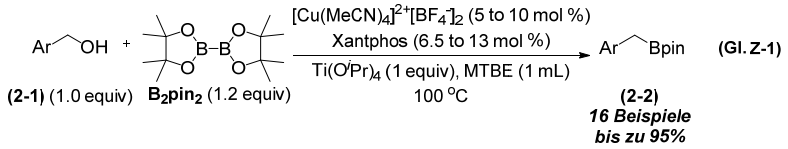
Zusammenfassung

Bisher ist es uns gelungen, effiziente Methoden zur Erzeugung von Benzyl/Allyl-sp^3- und Vinyl/Allenyl-sp^2-C-B-Bindungen mit Hilfe von Kupfer- oder Palladium-katalysierter Borylierung der entsprechenden Alkohole oder Alkene zu entwickeln, bei welchen es sich um leicht zugängliche Substrate handelt.

Kapitel 2

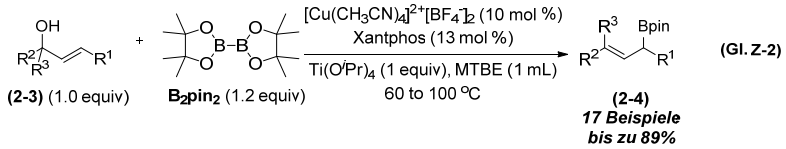
In Kapitel 2 wird das erste Beispiel einer Cu-katalysierten, direkten Borylierung von Alkoholen (40 Beispiele) vorgestellt. Dies stellt eine effiziente Methode dar, um ein breites Spektrum an Benzyl-, Allyl- und Allenyl-Boronaten unter milden Bedingungen herzustellen. Die Verwendung von $Ti(O^iPr)_4$ wandelt den OH-Rest in eine hervorragende Abgangsgruppe (‚OTi') um, was eine wichtige Rolle bei der Borylierung von Alkoholen spielt. Obwohl ein Cu(II)-Komplex als Vorstufe für den Katalysator eingesetzt wurde, wird davon ausgegangen, dass der aktive Katalysator für die Borylierungsreaktion eine Cu(I)-Spezies ist.

Benzylboronate wurden mit Hilfe einer Cu-katalysierten Borylierung von Benzylalkoholen (Gl. Z-1) dargestellt, wobei sowohl der Kupferkomplex $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ als auch der Xantphos-Ligand kommerziell erhältlich sind. Für die Borylierung von Benzylalkoholen wurde eine Katalysatorladung von 5 mol% des Kupferkatalysators verwendet, was auf eine hohe Effizienz dieser Methode schließen lässt. Alle Benzylboronate wurden in moderaten bis hohen Ausbeuten (bis zu 95%) isoliert. Diese Vorgehensweise lässt sich ebenso auf die Borylierung von Benzylacetaten anwenden, wobei ein Benzylboronat mit 54% Ausbeute erhalten werden kann. Dies lässt darauf schließen, dass es sich um eine allgemein anwendbare Methode handelt.

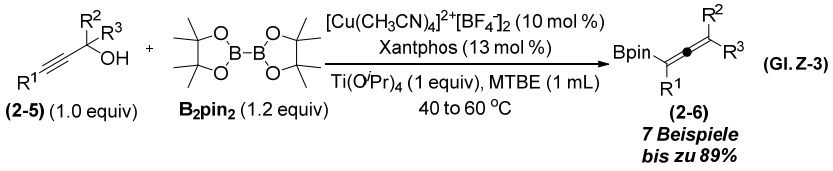


Ferner wurden Allylboronate mit Hilfe einer vergleichbaren Route wie die Benzylboronate dargestellt (Gl. Z-2), wobei die Temperatur auf 60 °C abgesenkt werden kann. Bei der Borylierung von Allylalkoholen wurden ausgehend von primären Allylalkoholen sekundäre Allylboronate erhalten. Diese Reaktion unterscheidet sich daher von früheren Pd-katalysierten Borylierungen von

Allylalkoholen, welche ausschließlich zu linearen Allylboronaten aufgrund der Bildung von (η^3-Allyl)Pd-Intermediaten führten. Anhand dieses Ergebnisses wird angenommen, dass eine nukleophile Substitution Teil des entsprechenden Mechanismus ist. Weiterhin weist diese Reaktion die Möglichkeit auf, chirale Allylboronate ausgehend von verschiedenen primären Allylalkoholen zu erhalten. Diese finden signifikante Anwendung bei der asymmetrischen Synthese. Unseres Wissens nach stellt diese Methode außerdem das erste Beispiel einer katalytischen Synthese von sekundären Allylboronaten dar, die direkt von Alkoholen ausgeht. Die Borylierung konnte ebenfalls mit sekundären und tertiären Allylalkoholen durchgeführt werden, wobei die entsprechenden Allylboronate in guten Ausbeuten erhalten wurden.



Diese Cu-katalysierte Borylierungsreaktion kann außerdem Anwendung in der Borylierung von Propargylalkoholen finden (Gl. Z-3), wobei die Darstellung von Allenylboronaten in guten Ausbeuten erreicht wird. Hierbei kann die Reaktionstemperatur weiter auf 40 °C abgesenkt werden. Des Weiteren weist die Regioselektivität der Borylierung von Propargylakoholen darauf hin, dass die Reaktion über eine nukleophile Substitution verläuft.

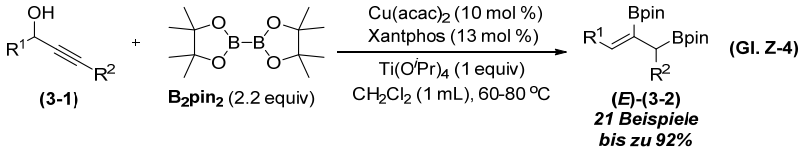


Die in Kapitel 2 vorgestellten Ergebnisse lassen darauf schließen, dass die Cu-katalysierte Borylierung von Akoholen eine allgemein anwendbare Methode zur Synthese von Benzyl-, Allyl- und Allenylboronaten darstellt.

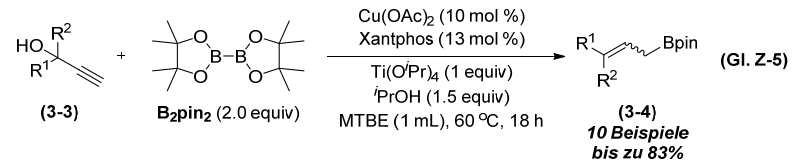
Kapitel 3

In Kapitel 3 wird eine Methode zur Synthese von Vinyl-, Allyl- und (*E*)-2-Boryl-Allyl-Boronaten mit Hilfe von Cu-katalysierter Borylierung von Propargylalkoholen (43 Beispiele) vorgestellt. Hierzu wurden kommerziell erhältliche Kupferkatalysatoren wie $Cu(acac)_2$ und $Cu(OAc)_2$ eingesetzt. In dieser Vorschrift wird erneut $Ti(O^iPr)_4$ verwendet, um durch die Reaktion mit Alkoholen (OH) in eine bessere Abgangsgruppe (OTi) zu erhalten.

Zugang zu den (*E*)-2-Boryl-Allylboronaten wurde mit Hilfe von Cu-katalysierter Diborylierung von Propargylalkoholen (Gl. Z-4) ermöglicht. Die Reaktion kann bei 60 oder 80 °C durchgeführt werden. Die Regioselektivität dieser Cu-katalysierten Diborylierungsreaktion unterscheidet sich von der $Pd_2(dba)_3$-katalysierten Diborylierung von Allenen, bei der 2-Boryl-Allyl-Boronate mit C=C Doppelbindungen an der terminalen Position erhalten werden. Die Stereoselektivität weist ebenfalls einen Unterschied zur $Pd(dba)_2$-katalysierten Diborylierung von Allenen auf. Bei dieser werden vorranging (*Z*)-2-Boryl-Allyl-Boronate mit C=C-Doppelbindungen an der internen Position erzeugt. Dies offenbart eine einzigartige Eigenschaft unserer Cu-katalysierten Diborylierung von Propargylalkoholen, welche die Nützlichkeit von Alkoholen in der Entwicklung der synthetischen Methode erweitert. Die Isolierung eines Allenylboronates als Zwischenprodukt während der Reaktion lässt vermuten, dass der Mechanismus der Diborylierung von Propargylalkoholen gemäß einer S_N2'-Reaktion verläuft, auf die eine Borylcuprierung folgt.

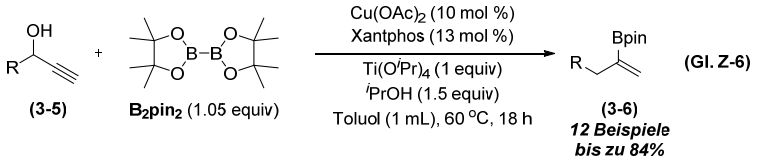


Die Borylierung von 1,1-disubstituierten Propargylalkoholen, bei der $Cu(OAc)_2$ als Vorstufe des Katalysators eingesetzt wird, führt zur Bildung von (*Z*)-Allylboronaten als Hauptprodukt (Gl. Z-5). Die Regio- und Stereoselektivität dieser Reaktion und der Cu-katalysierten Borylcuprierung von Allenylsilanen stimmen überein, wobei ein Unterschied zur Pd-katalysierten Borylierung von Allylalkoholen besteht, bei der vorrangig (*E*)-Allylboronate entstehen. Es liegt nahe, dass die Cu-katalysierte Borylierung von 1,1-disubstituierten Propargylalkoholen eine alternative Route zur Herstellung von (*Z*)-Allylboronaten darstellt, da die Startmaterialien entweder kommerziell erhältlich oder einfach herzustellen sind.



Vinylboronate werden ebenfalls mit Hilfe der Cu-katalysierten Borylierung von mono-substituierten Propargylalkoholen (Gl. Z-6) dargestellt. Die Regioselektivität hierbei stimmt mit der der Cu-katalysierten Borylcuprierung von Alkinen überein. Verglichen mit der Borylcuprierung von Allenen bietet die Borylierung von mono-substituierten Propargylalkoholen einen direkteren

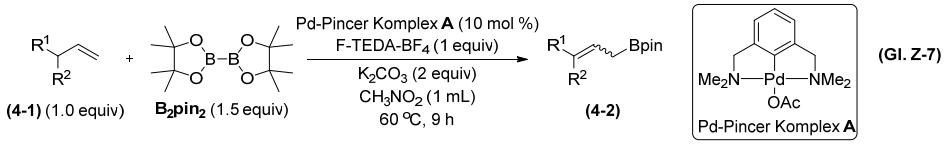
Zugang zur Darstellung von Vinylboronaten, da Allene in der Regel ausgehend von Propargylalkoholen dargestellt werden.



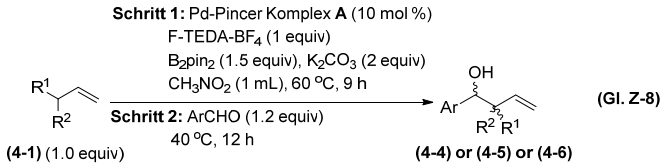
Alle in Kapitel 3 diskutierten Ergebnisse weisen darauf hin, dass die Cu-katalysierte Borylierung von Propargylalkoholen eine einzigartige Methode zur Synthese von Vinyl-, Allyl- und (*E*)-2-Boryl-Allylboronaten bietetund eine allgemein anwendbare Vorschrift zur Herstellung von Organobor-Verbindungen mit einfach zugänglichen Startmaterialien darstellt. Die Regio- und Stereoselektivität unterscheidet sich außerdem von den bereits bekannten Methoden. Obwohl Cu(II)-Vorstufen der Katalysatoren eingesetzt werden, handelt es sich bei der katalytisch aktiven Spezies vermutlich um eine Cu(I)-Verbindung, da die Borylierungsreaktionen unter reduktiven Bedingungen durchgeführt werden.

Kapitel 4

In Kapitel 4 wurde eine Pd-katalysierte oxidative Borylierung der C-H Bindungen von Alkenen (Gl. Z-7) vorgestellt, bei der eine Vielzahl an linearen Allylboronaten in guten Ausbeuten erzeugt wurde (Gl. Z-7). Außerdem konnten alle Allylboronate isoliert und gereinigt werden, was eine einzigartige Eigenschaft dieser Methode darstellt. Ein interessanter mechanistischer Aspekt dieser Reaktion ist das Durchlaufen eines Pd(II)/Pd(IV)-Katalysezyklus. Die Bildung des Pd(IV)-Intermediates erfolgt durch eine einzigartige Kombination des NCN-Pincerkomplexes **A** als Katalysaror und F-TEDA-BF_4 als Oxidationsreagenz. Eine wichtige Neuerung der vorgestellten C-H-Borylierungsreaktion ist, dass sämtliche Allyl-BPin-Produkte für gewöhnlich in hohen Ausbeuten isoliert werden können. Dies ist vermutlich eine Folge der Verwendung des Pincer-Komplexes **A** als Katalysator, welcher selektiv die C-B-Bindungsbildung katalysiert und anschließend, als Pd(IV)-Spezies, C-B-Bindungsspaltungen als Nebenreaktionen vermeidet. Außerdem kann unsere Vorschrift auf Eintopf-Reaktionen von Aldehyden mit Allylen angewendet werden, um Homoallylalkohole zu erhalten (Gl. Z-8).



(Gl. Z-7)



(Gl. Z-8)

Zusammengefasst haben wir eine Vielzahl an Borylierungsreaktionen entwickelt, um Benzyl-, Allyl-, Allenyl-, Vinyl- und 2-Boryl-Allylboronate mit Hilfe von Cu- oder Pd-katalysierter Borylierung von Alkoholen und Alkenen, bei denen es sich um leicht zugängliche Startmaterialien handelt, darzustellen. Die Reinigung dieser reaktiven Organobor-Verbindungen weist darauf hin, dass unsere Methoden die Werkzeuge zur Untersuchung der Reaktivität dieser Verbindungen liefern könnten. Die Synthese von sekundären Allylboronaten und 2-Boryl-Allylboronaten beinhaltet außerdem die potenzielle Anwendung in der asymmetrischen Synthese zur Erzeugung wertvoller asymmetrischer Organobor-Verbindungen.

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[112] Conversions were determined via ^{1}H NMR of the crude reaction mixtures.

[113] A black precipitate formed right after F-TEDA-BF_4 was added to the solution of Pd-pincer complex. The yield of isomerization product **(4-3)a** was determined by ^{1}H NMR spectra of crude reaction mixture.

[114] F-TEDA-BF_4 is more soluble in CH_3NO_2 than in THF or CH_2Cl_2. The solubility of F-TEDA-PF_6 in THF or CH_2Cl_2 is better than F-TEDA-BF_4, but it is not commercially available. Therefore, we chose F-TEDA-BF_4 as the oxidant. Additionally, F-TEDA-BF_4 is not only used for electrophilic fluorination, but can act as an oxidant in the metal catalyzed functionalization of C-H bonds. For reviews, see: a) K. M. Engle, T.–S. Mei, X. Wang, J.–Q. Yu, *Angew. Chem. Int. Ed.* **2011**, *50*, 1478-1491; b) T. Liang, C. N. Neumann, T. Ritter, *Angew. Chem. Int. Ed.* **2013**, *52*, 8214-8264.

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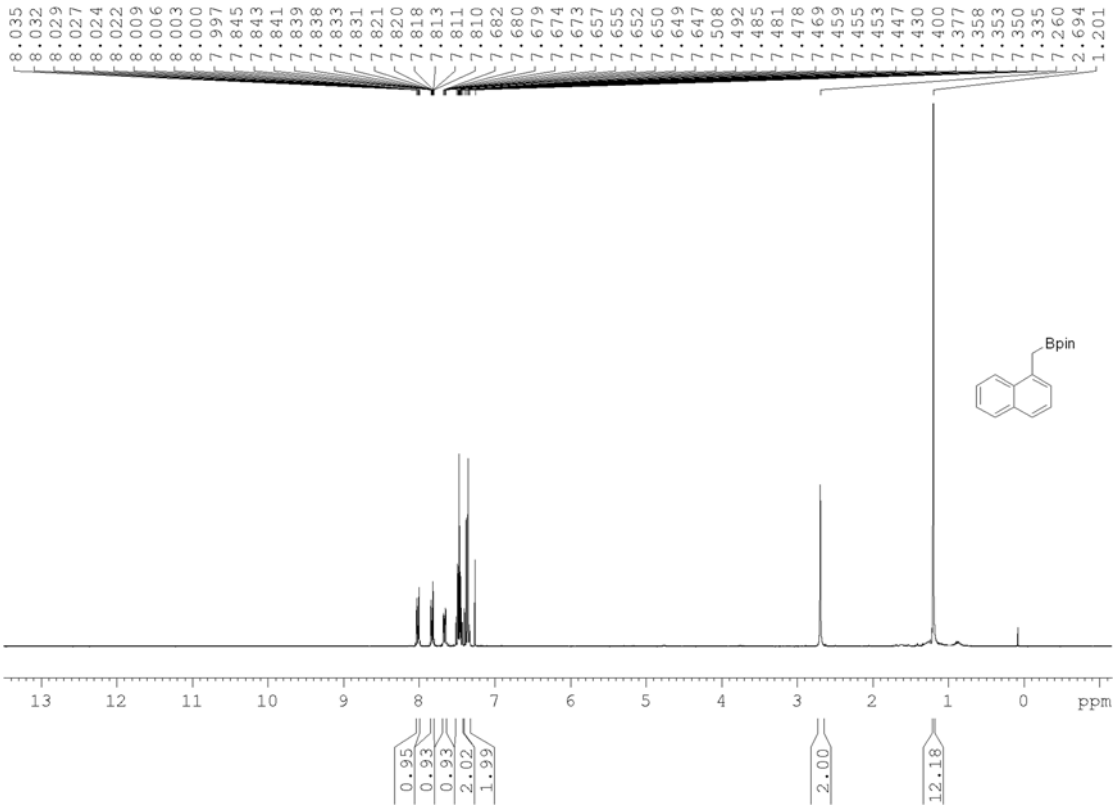
Appendix

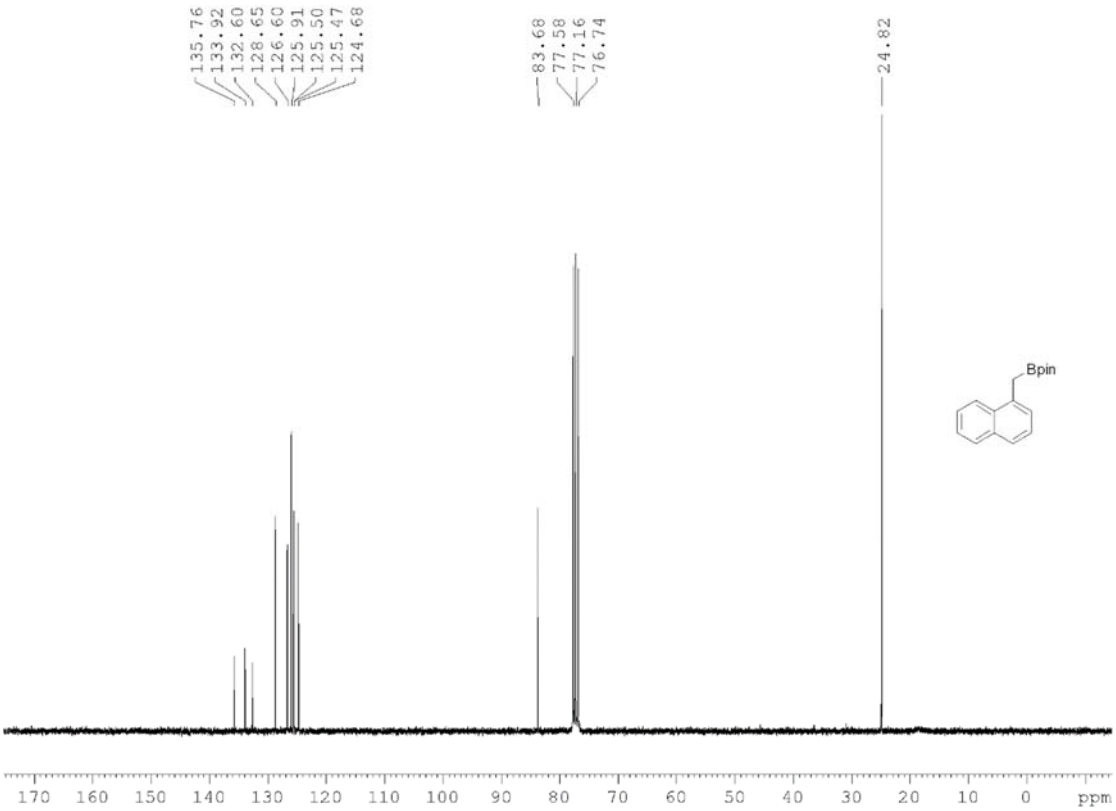
1. ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR Spectra

Compound (2-2)a

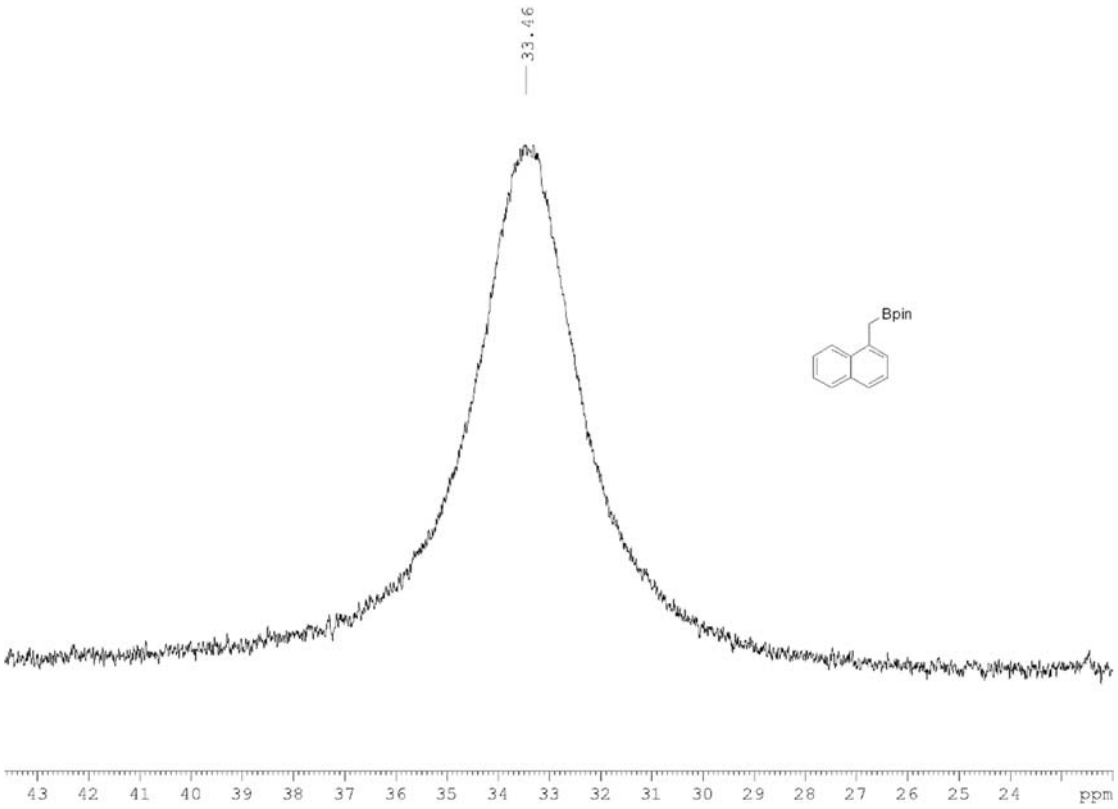
^{1}H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

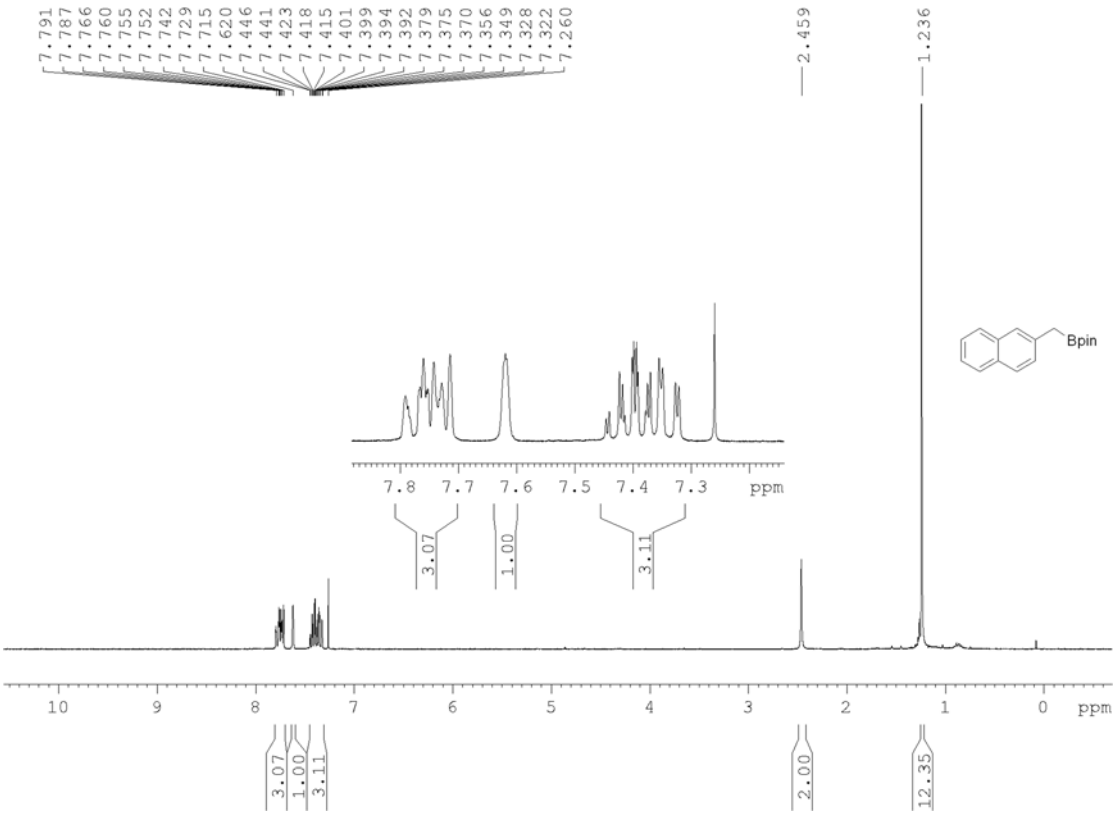


^{11}B NMR (96 MHz, $CDCl_3$)

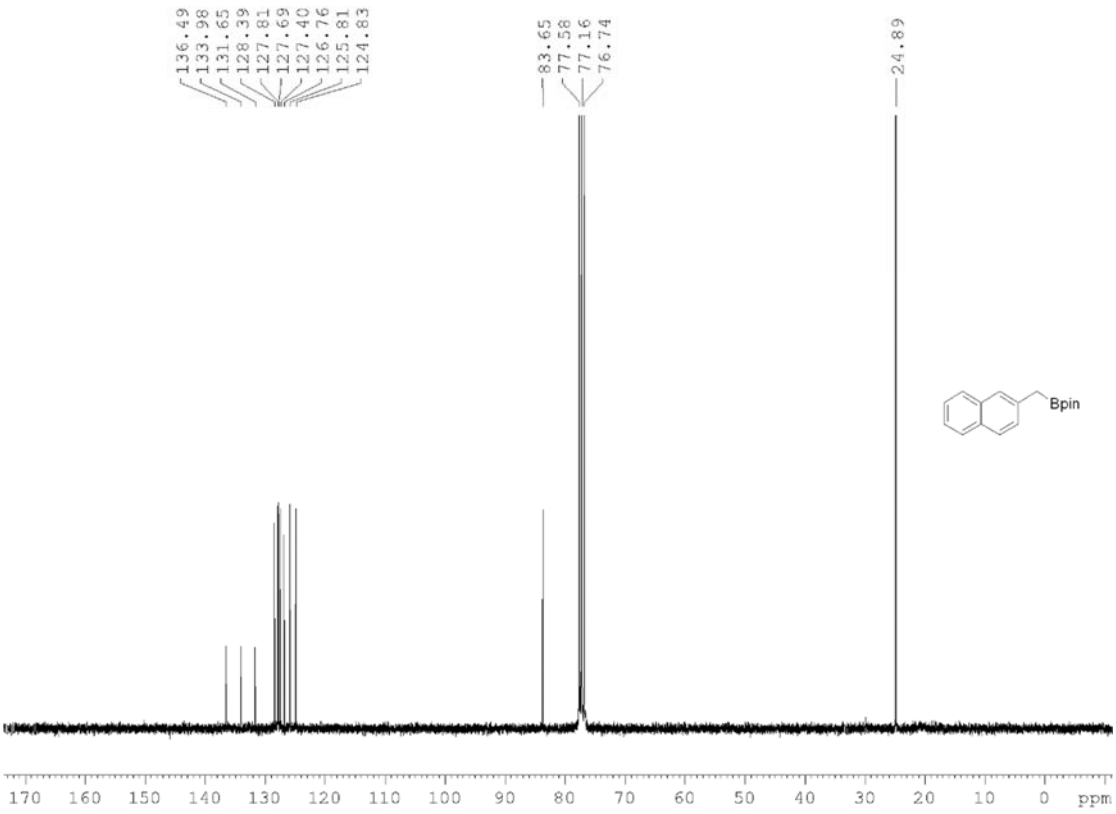


Compound (2-2)b

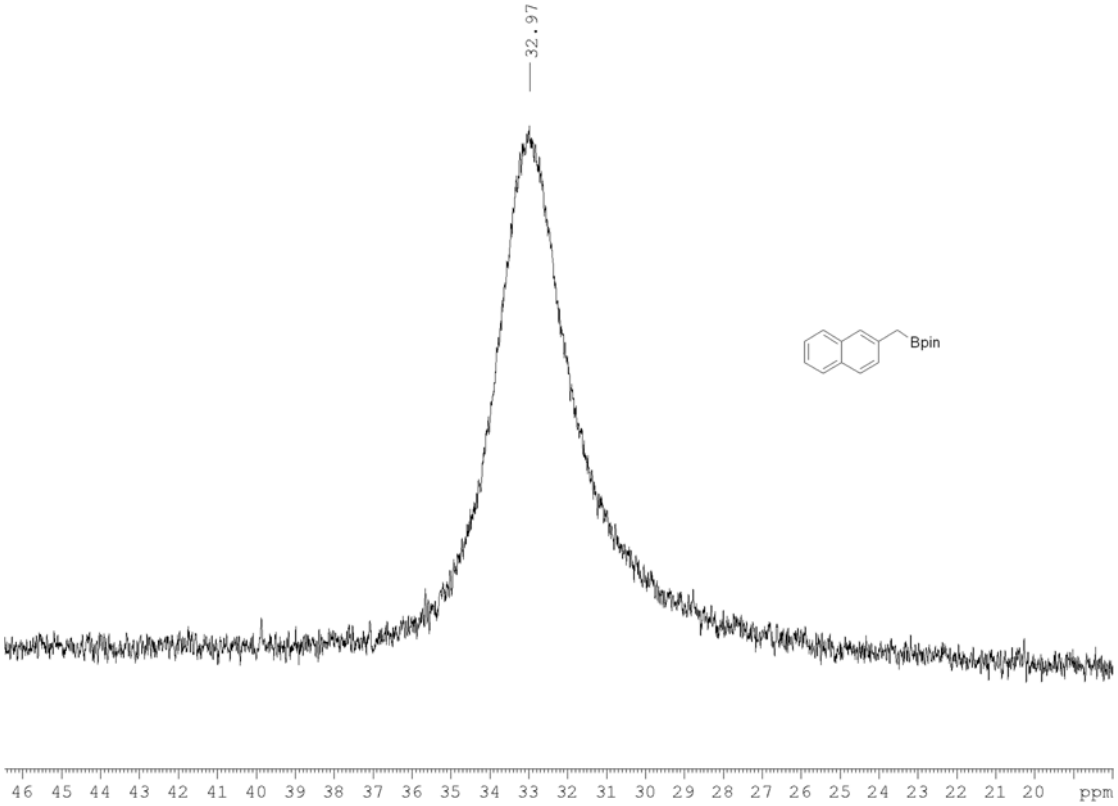
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

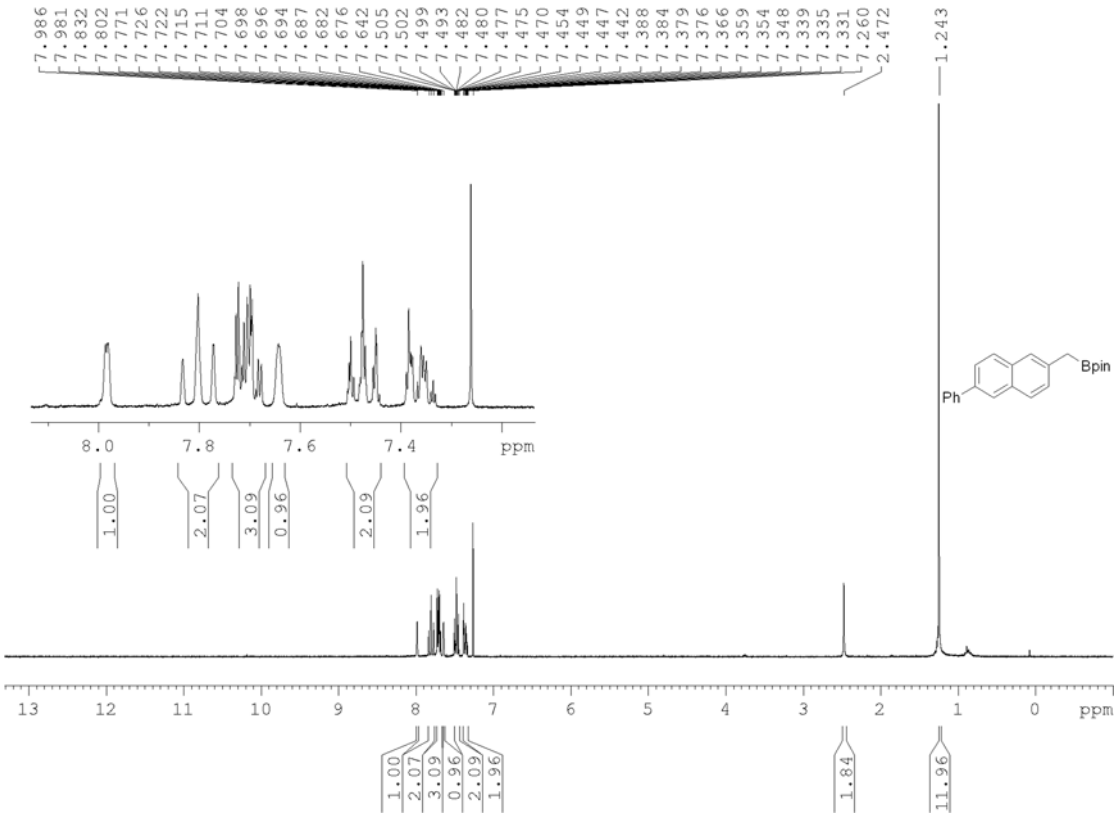


^{11}B NMR (96 MHz, $CDCl_3$)

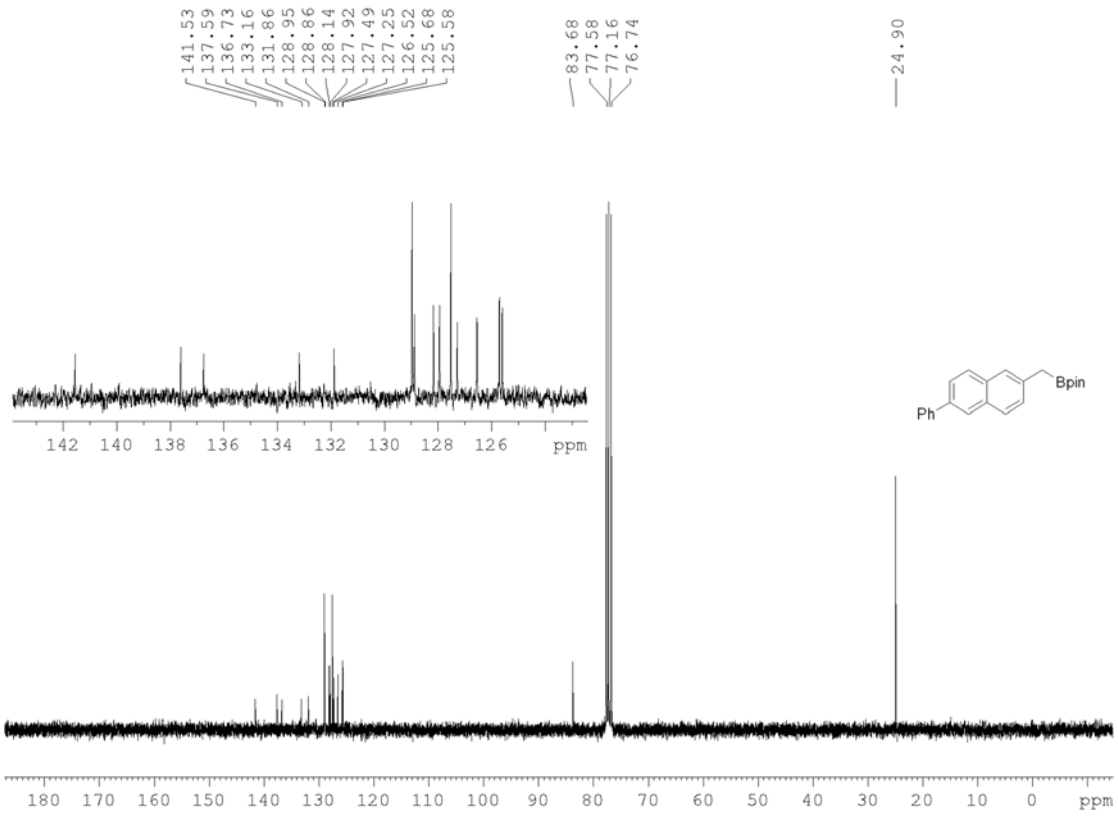


Compound (2-2)c

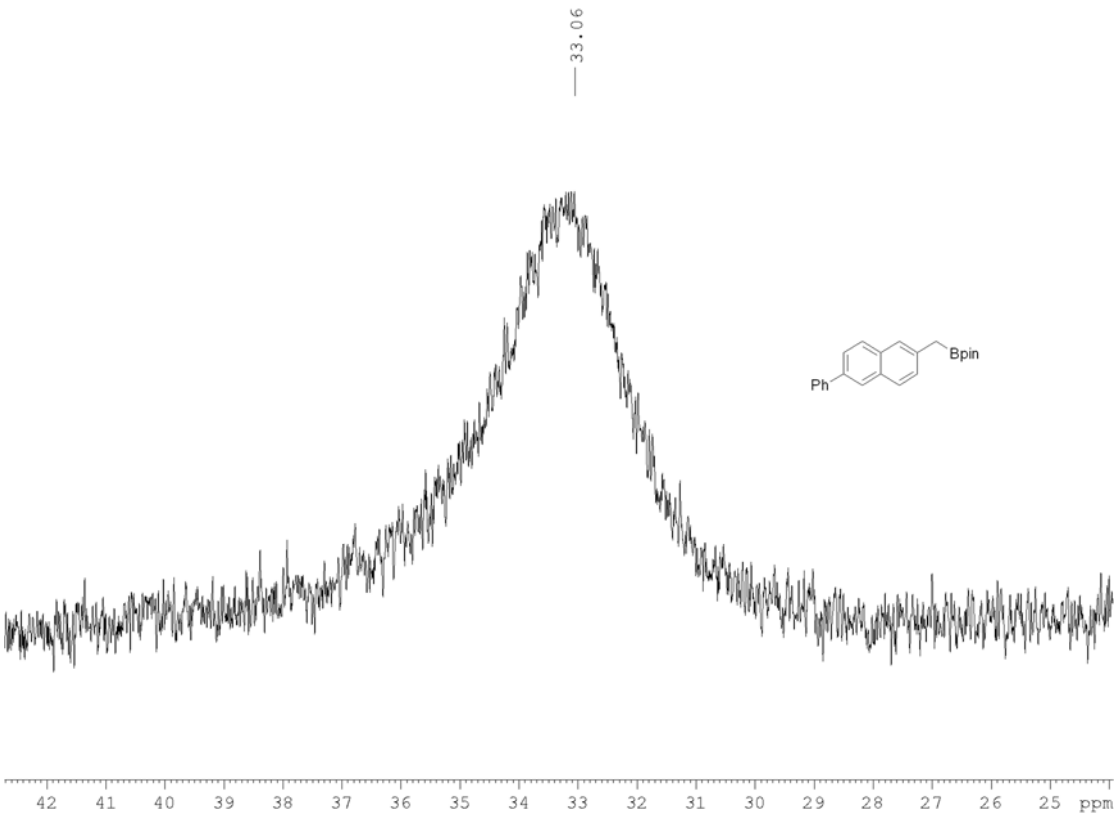
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

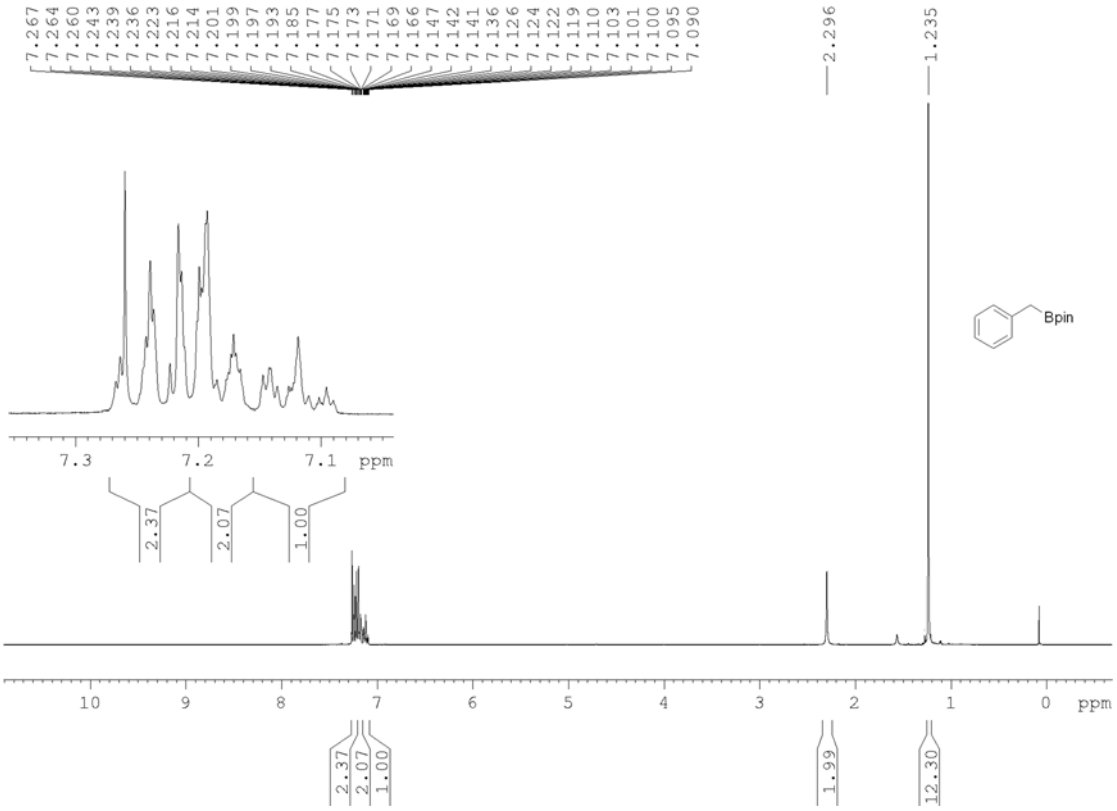


^{11}B NMR (96 MHz, $CDCl_3$)

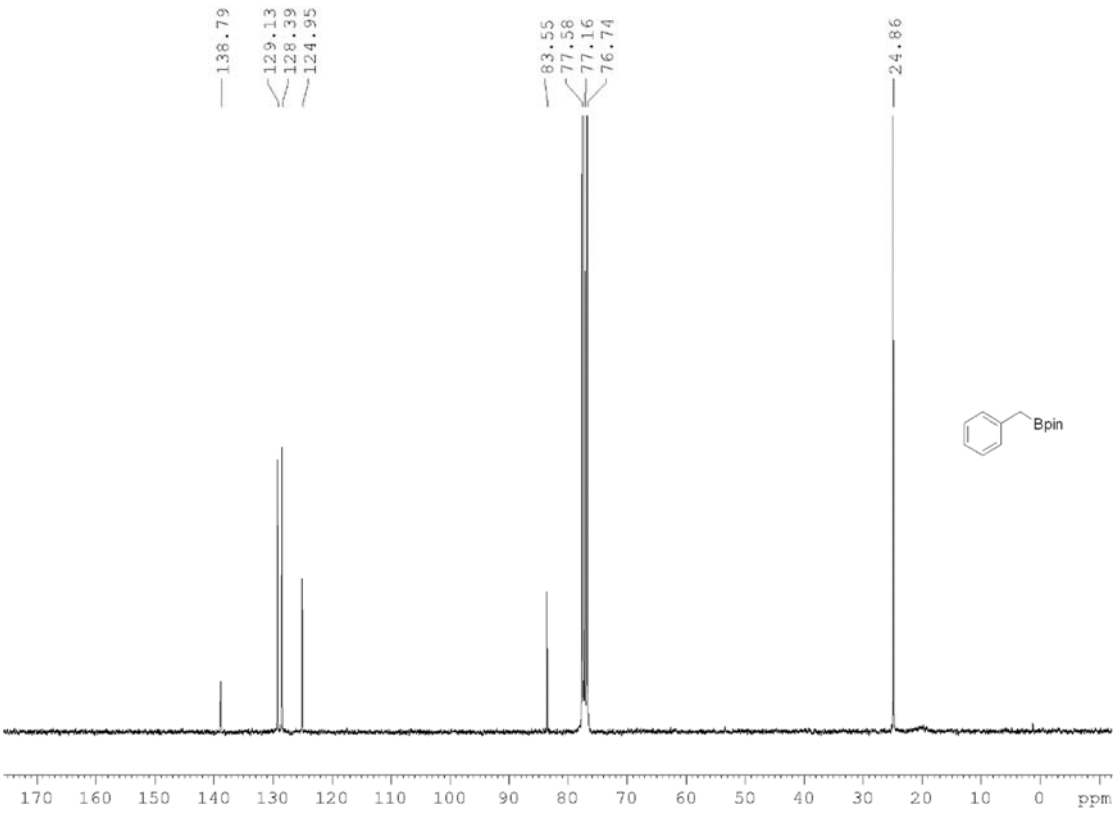


Compound (2-2)d

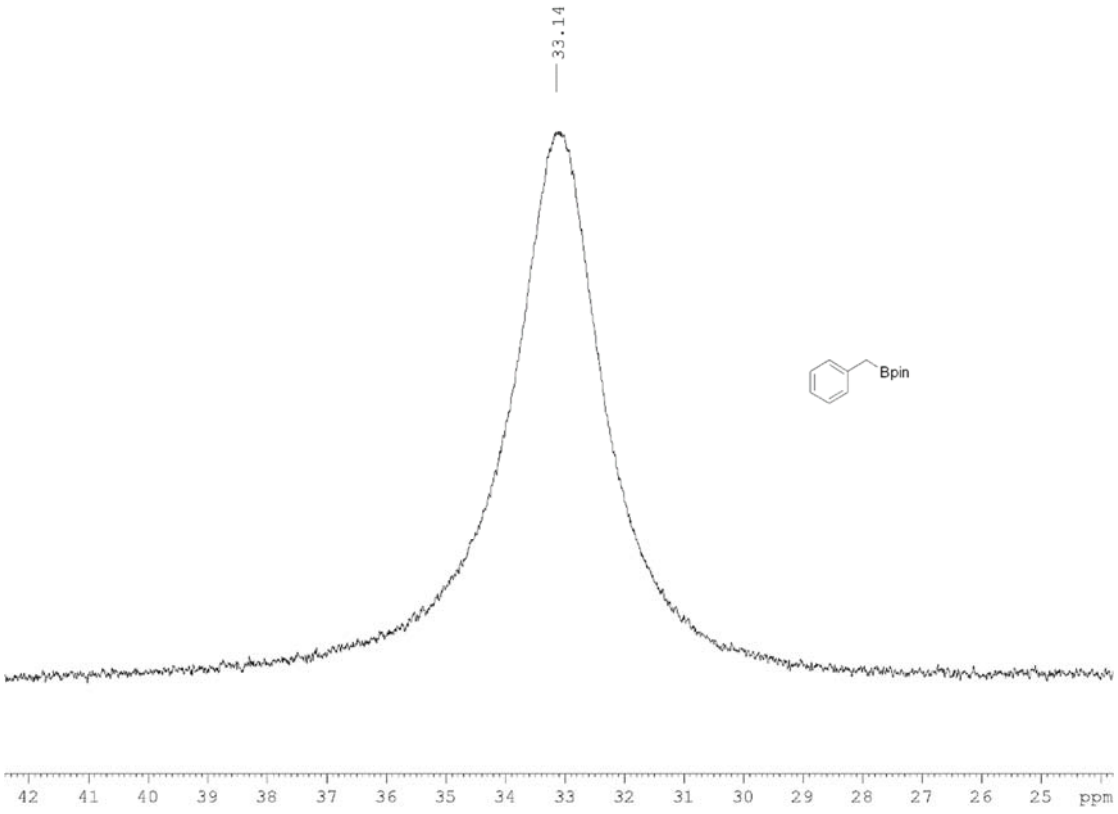
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

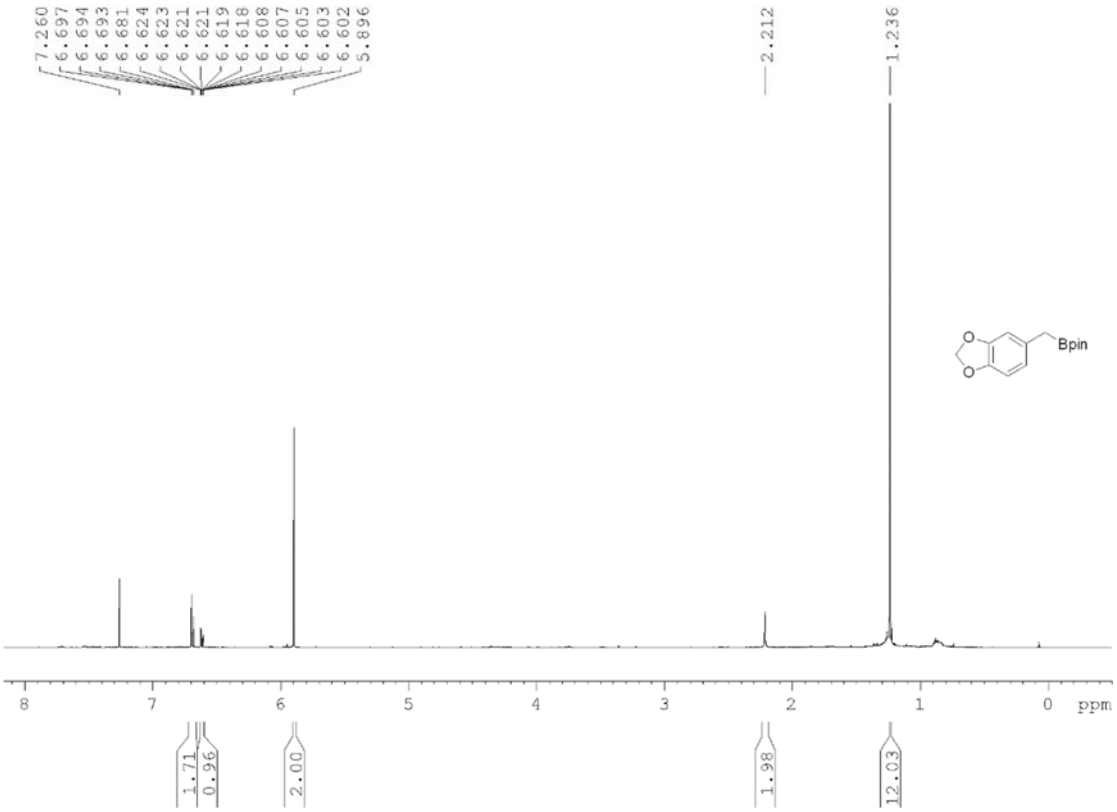


^{11}B NMR (96 MHz, $CDCl_3$)

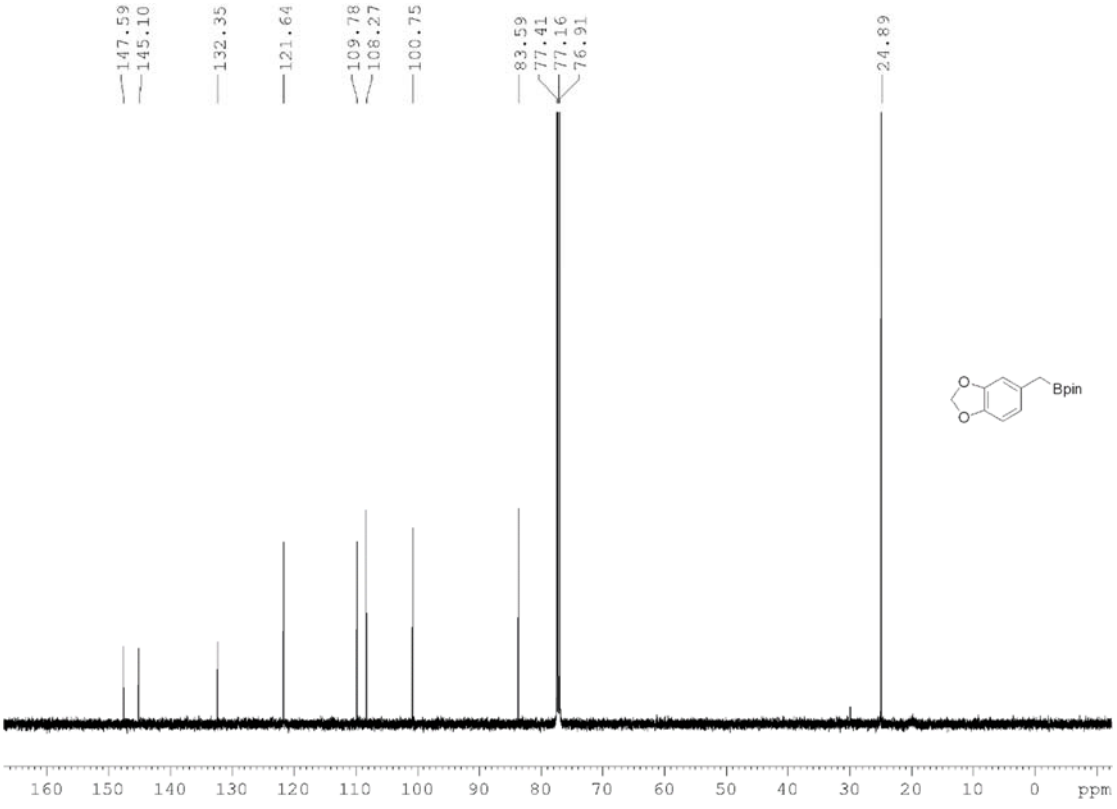


Compound (2-2)e

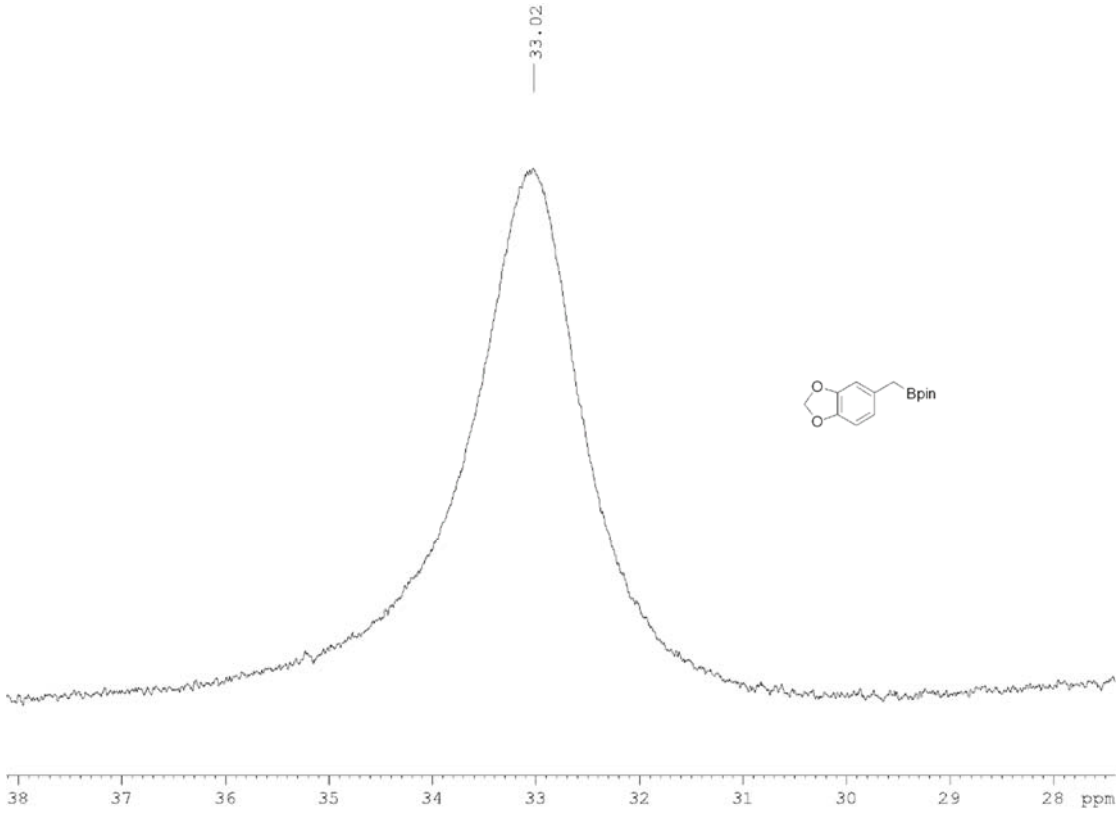
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

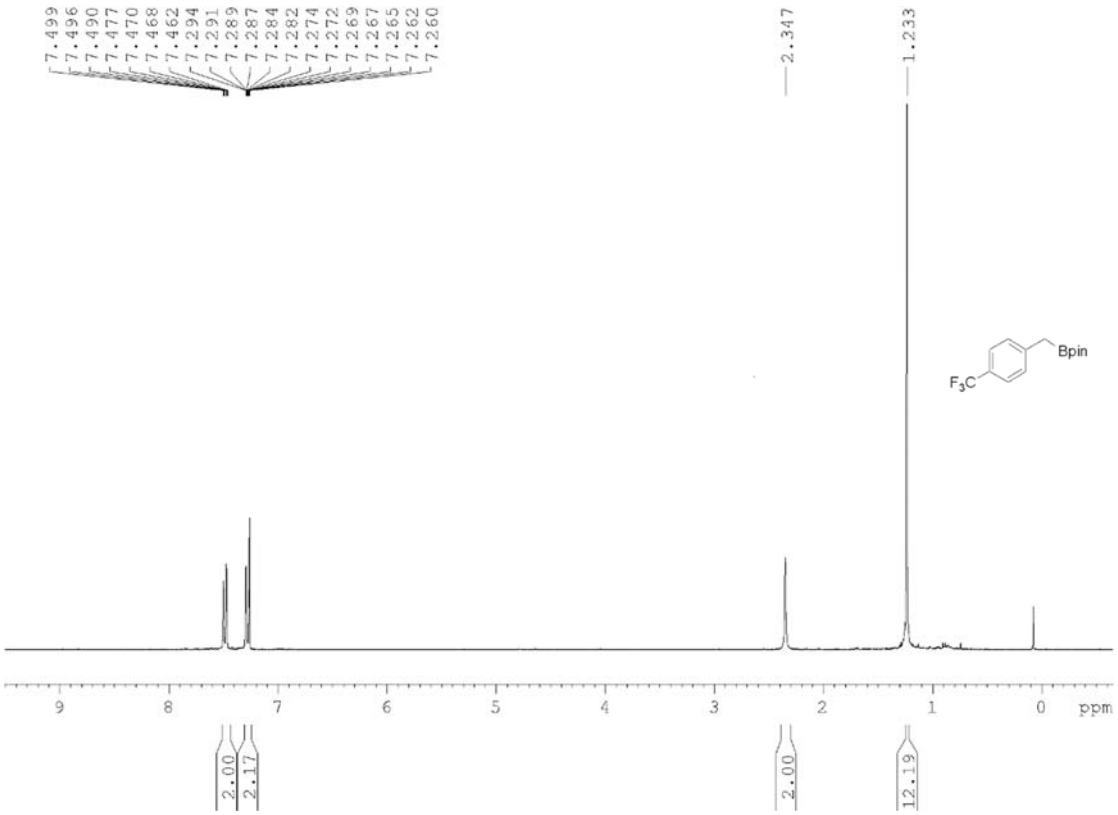


^{11}B NMR (160 MHz, $CDCl_3$)

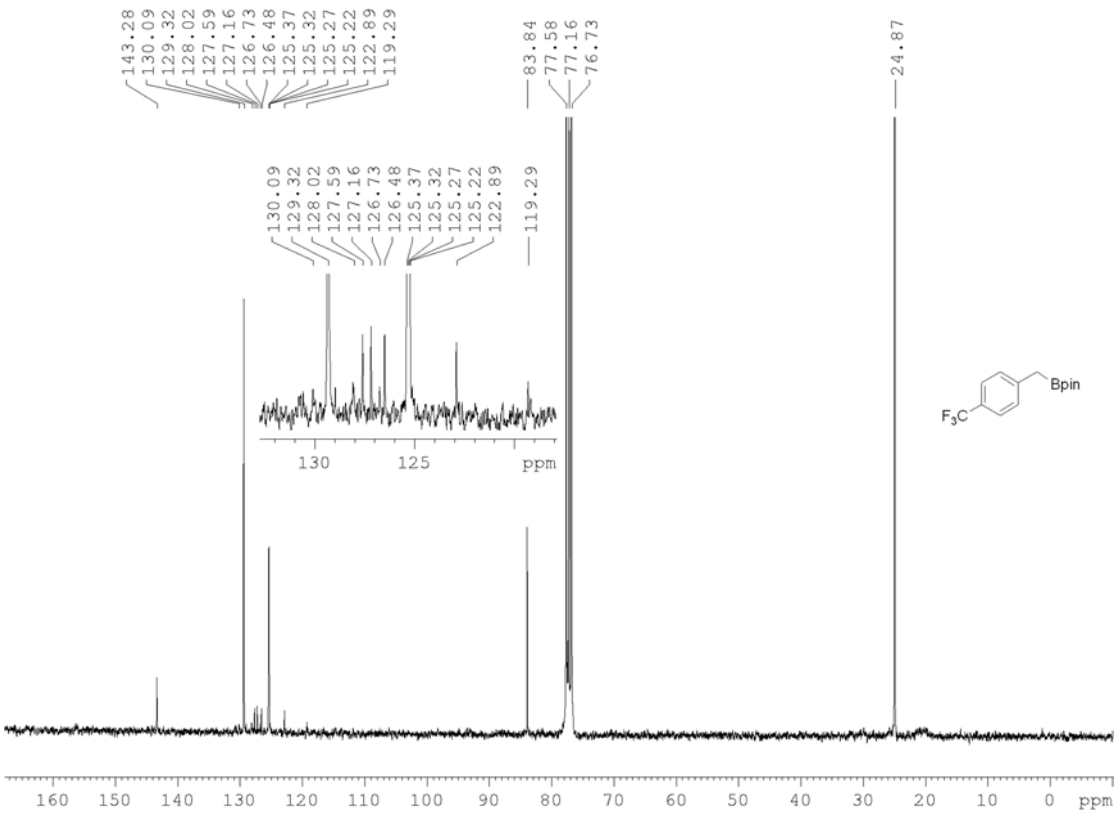


Compound (2-2)f

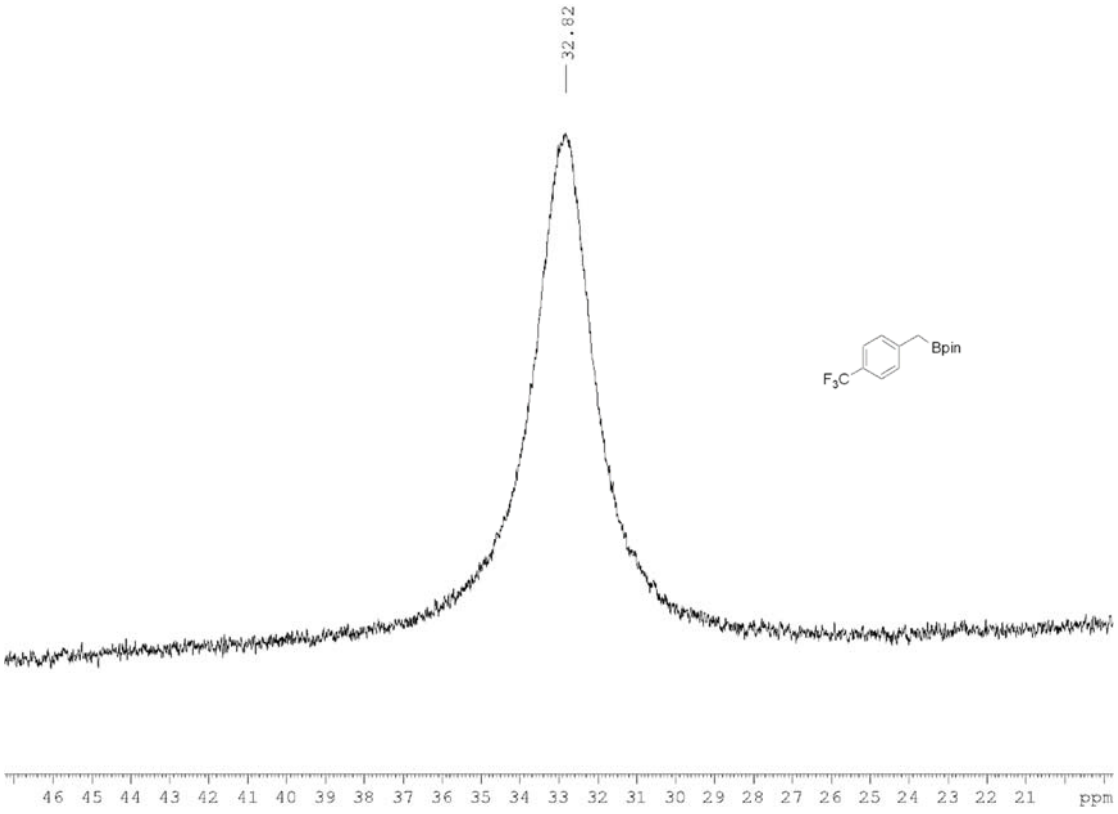
^{1}H NMR (300 MHz, $CDCl_3$)



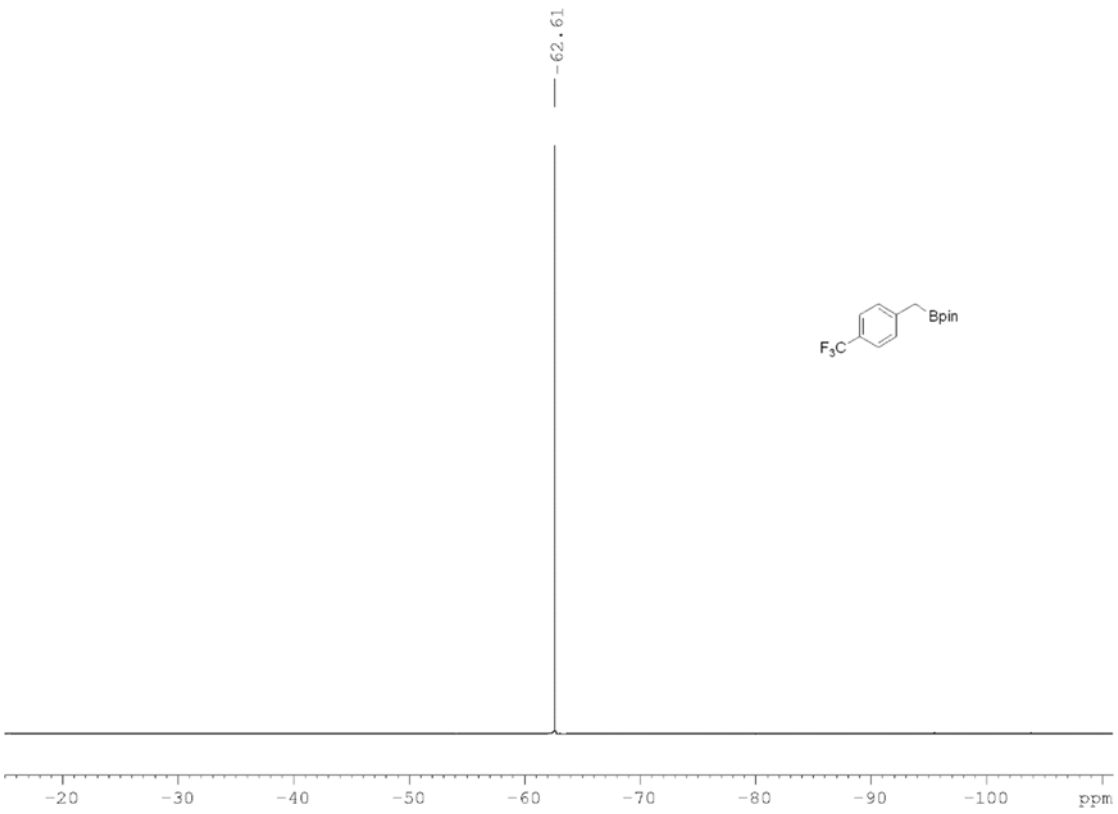
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



^{11}B NMR (96 MHz, $CDCl_3$)

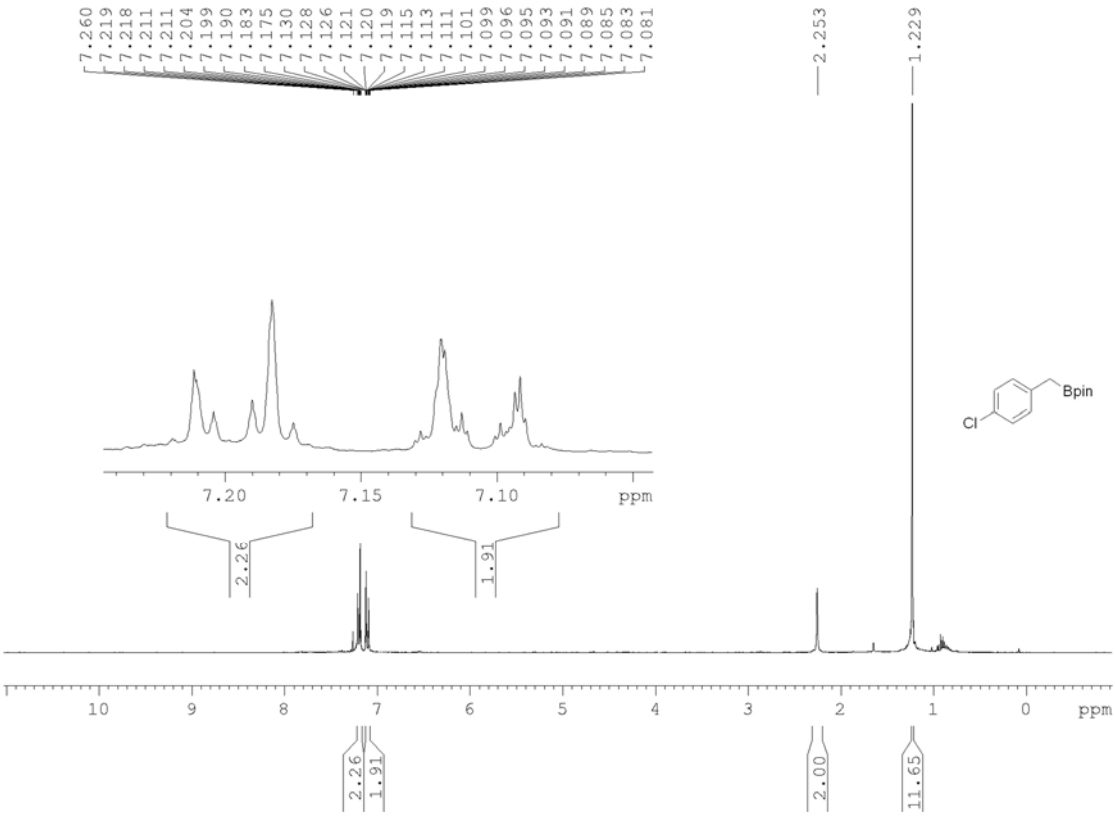


^{19}F NMR (470 MHz, $CDCl_3$)

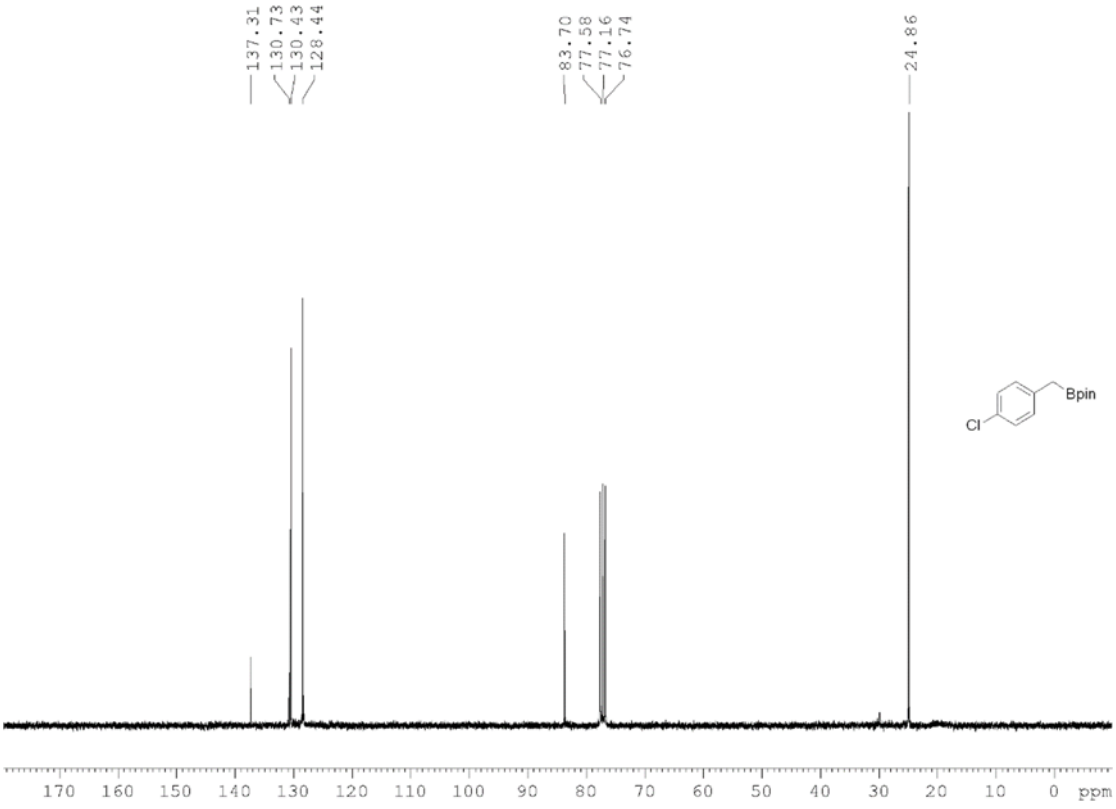


Compound (2-2)g

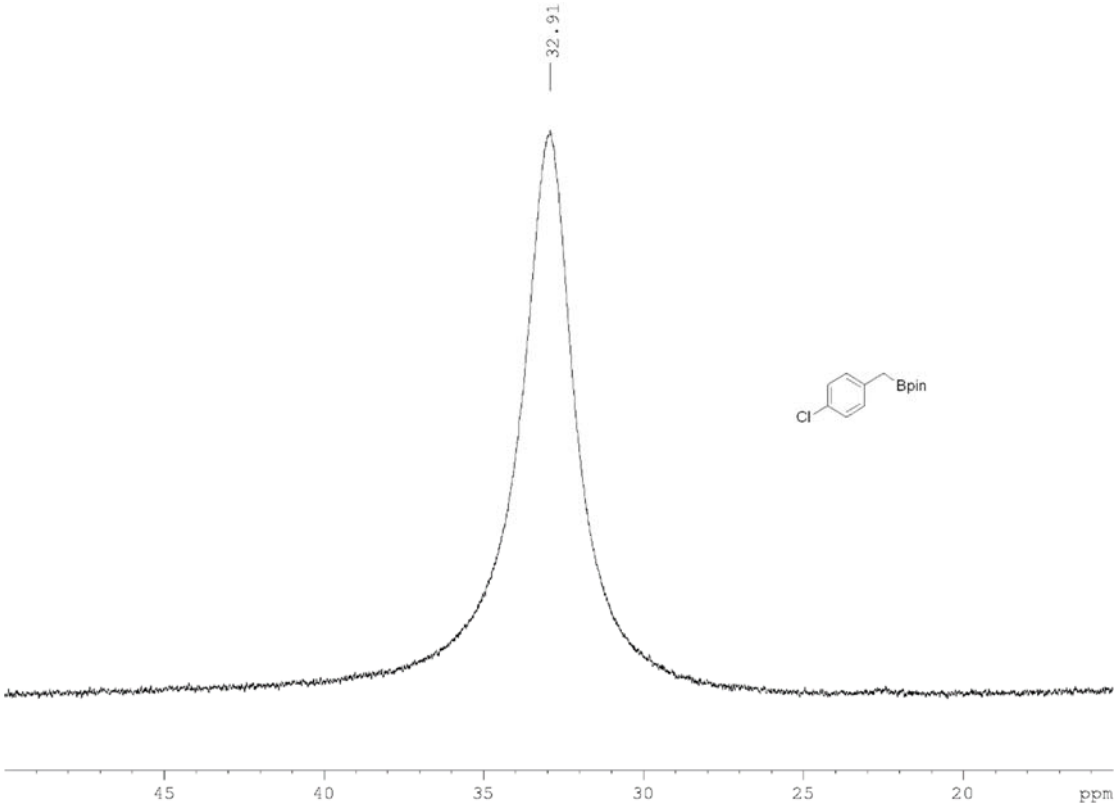
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

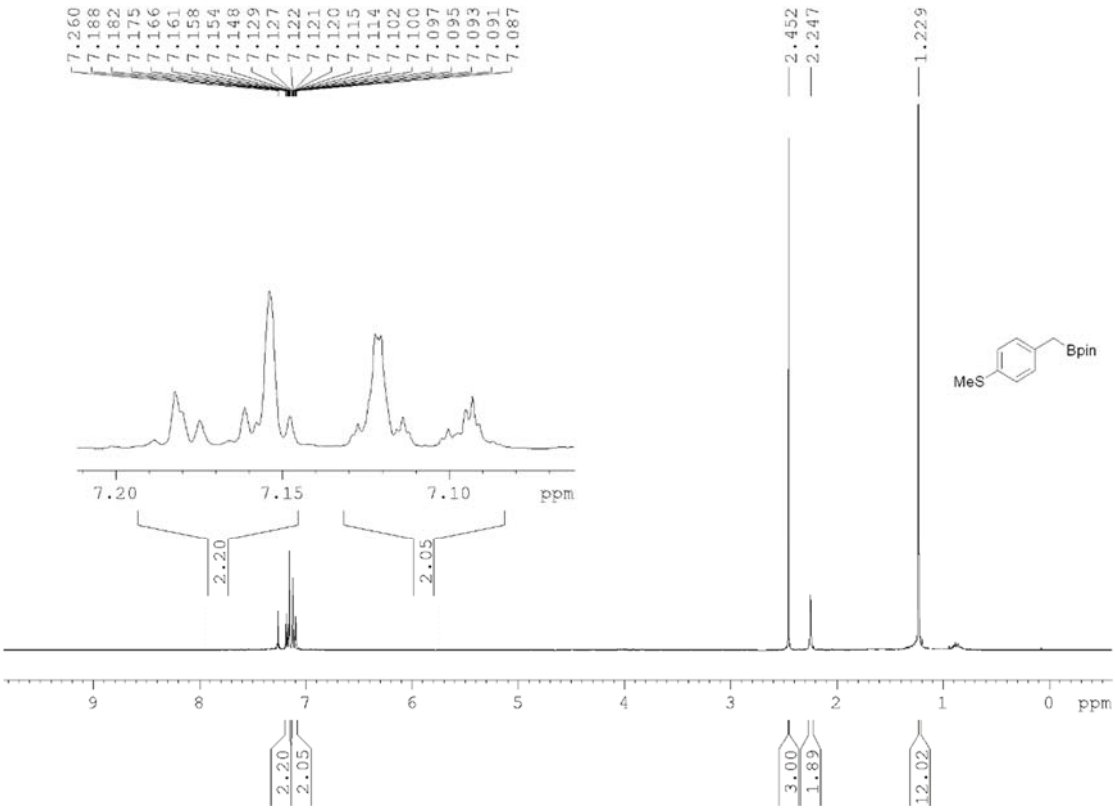


^{11}B NMR (96 MHz, $CDCl_3$)

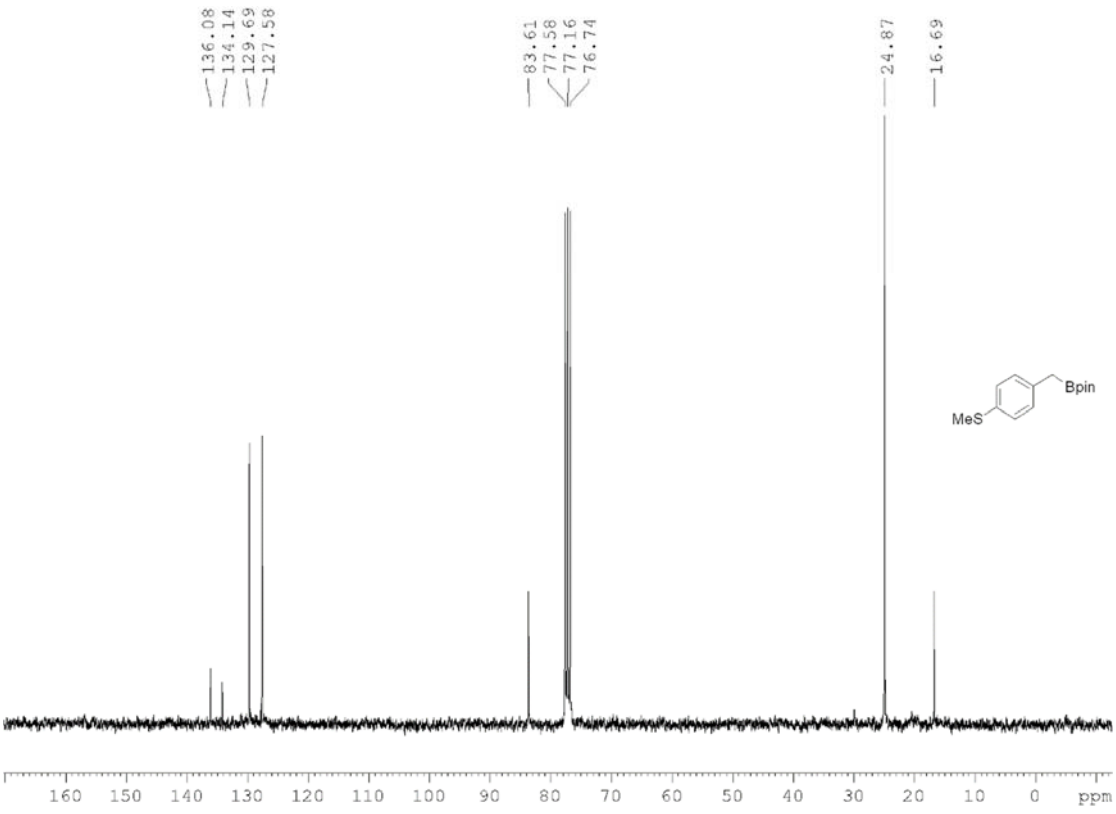


Compound (2-2)h

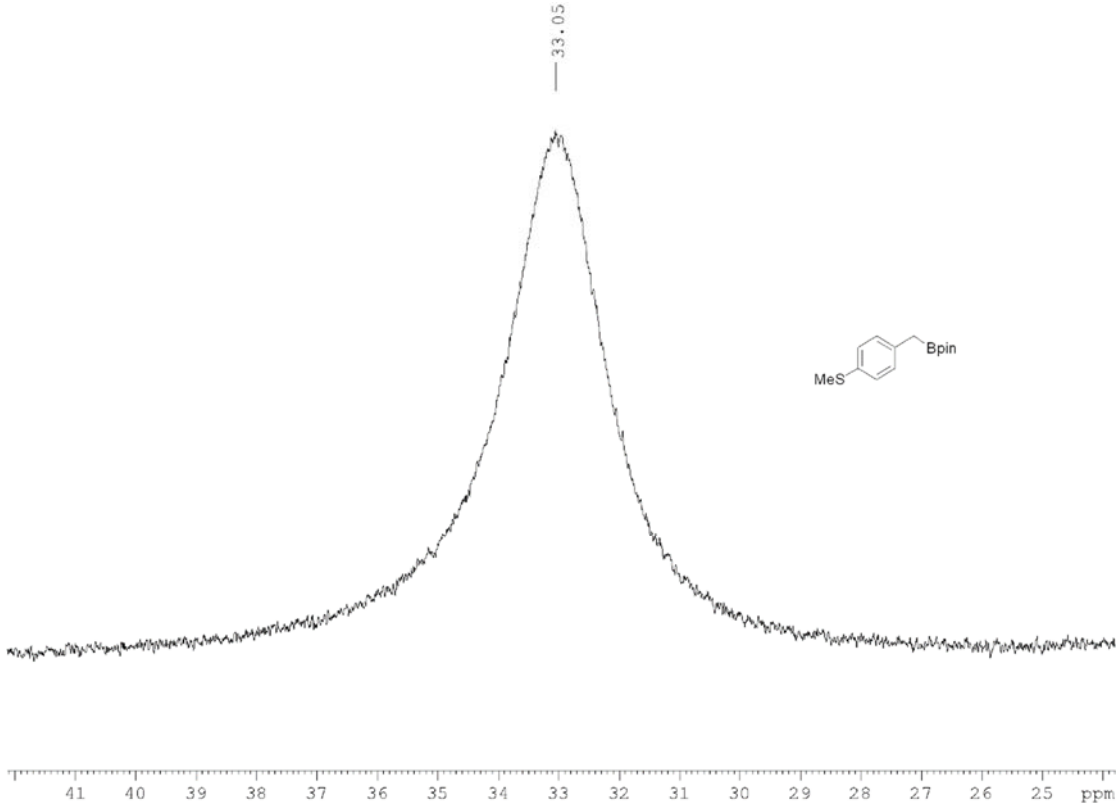
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

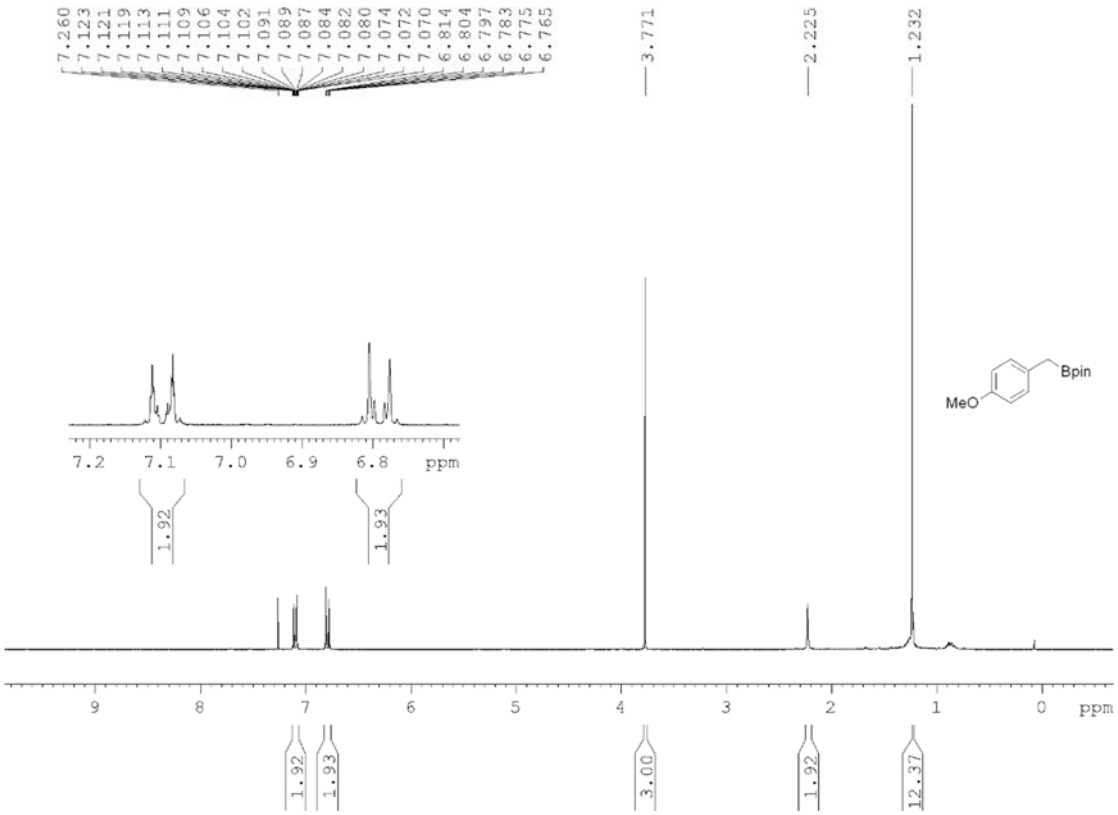


^{11}B NMR (96 MHz, $CDCl_3$)

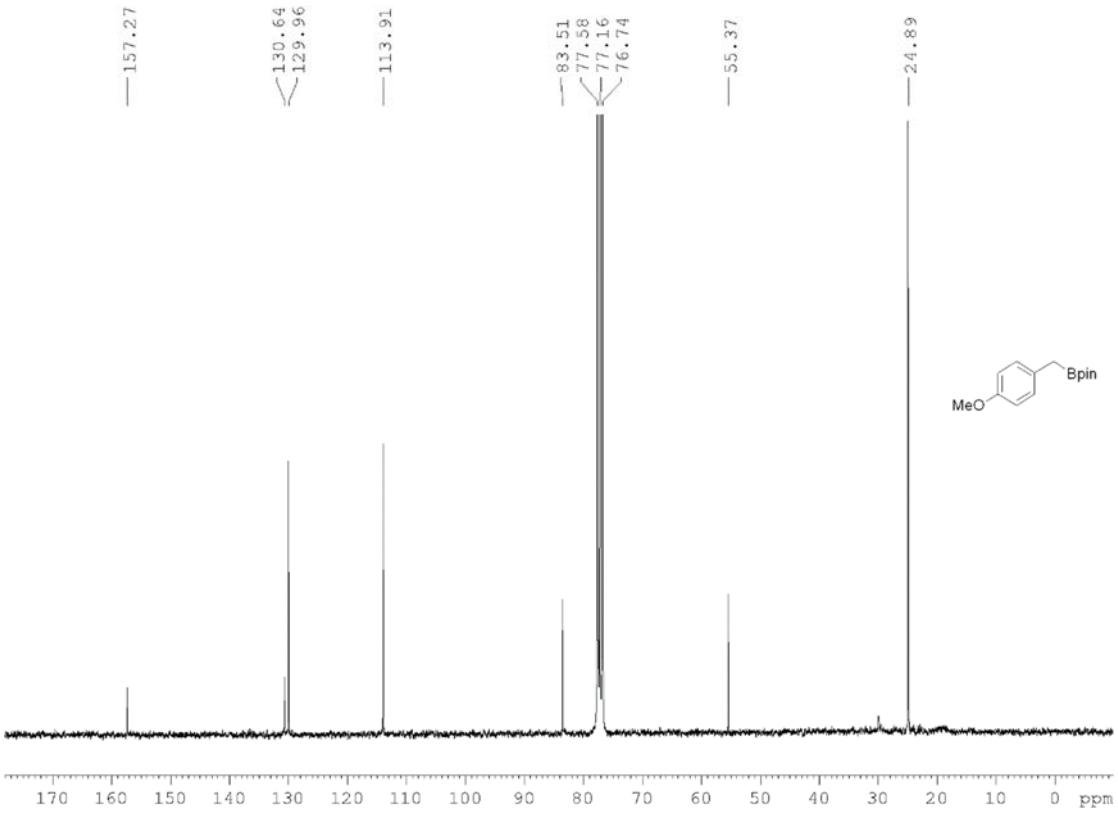


Compound (2-2)i

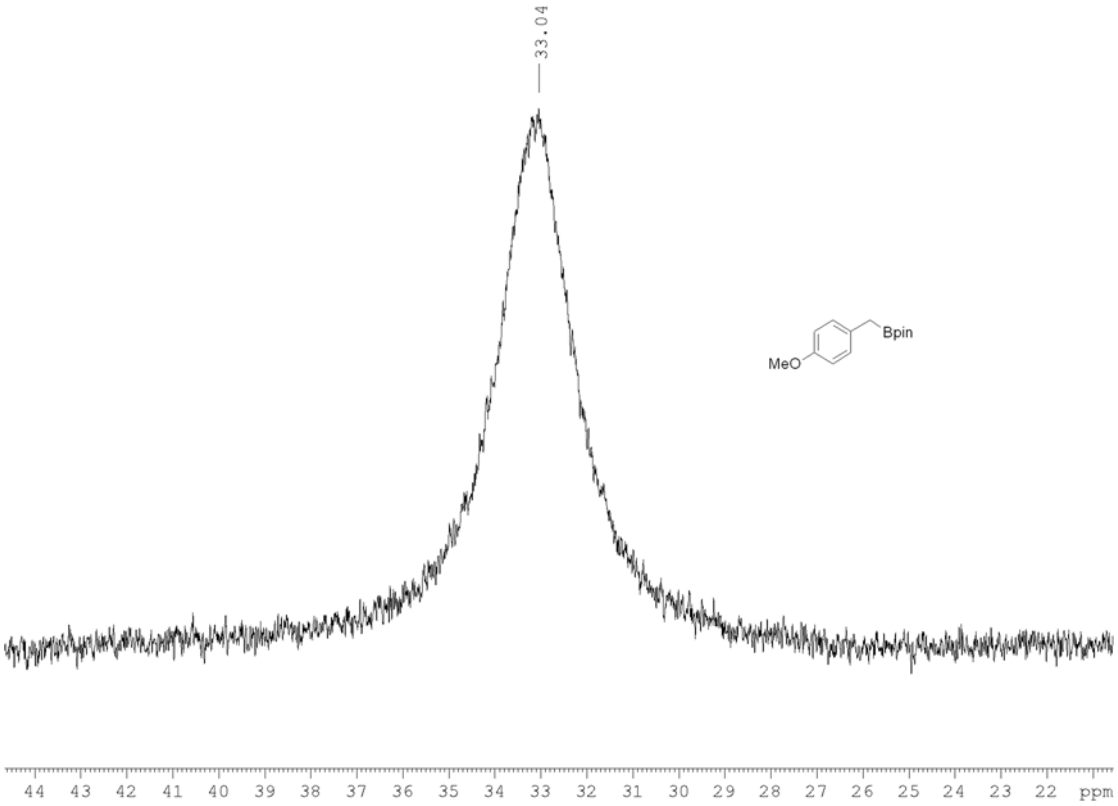
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

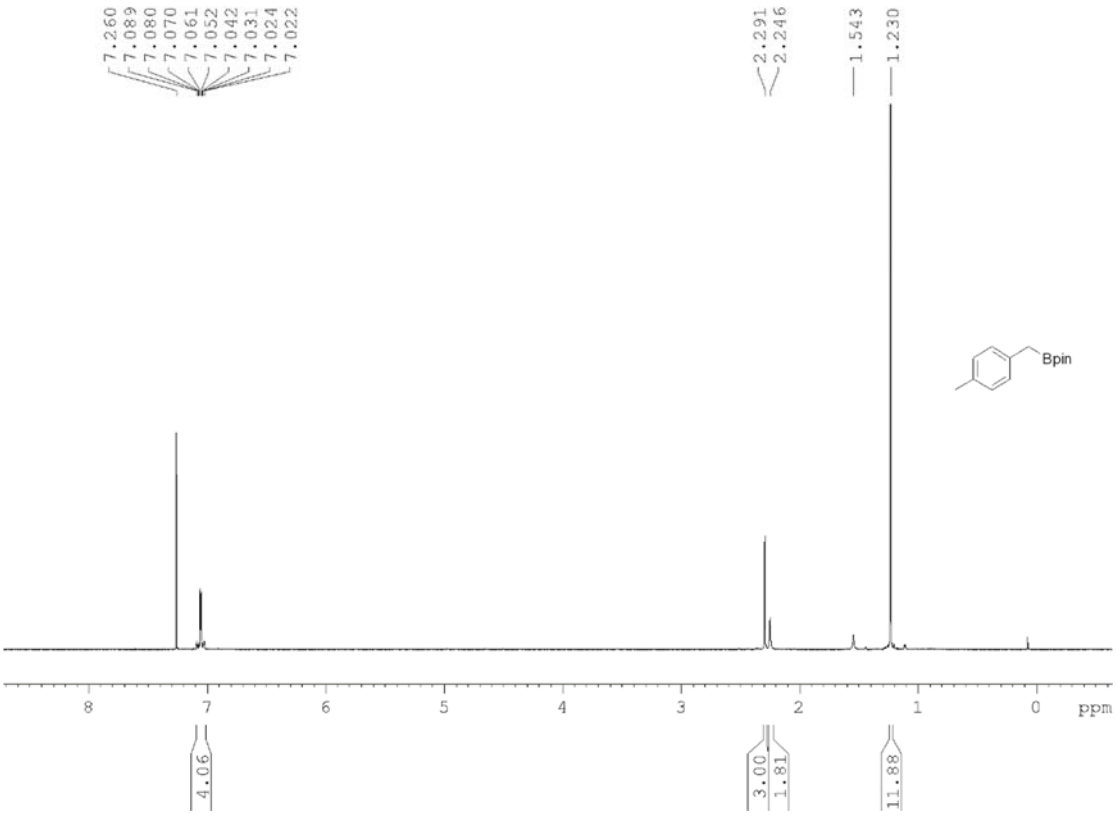


^{11}B NMR (96 MHz, $CDCl_3$)

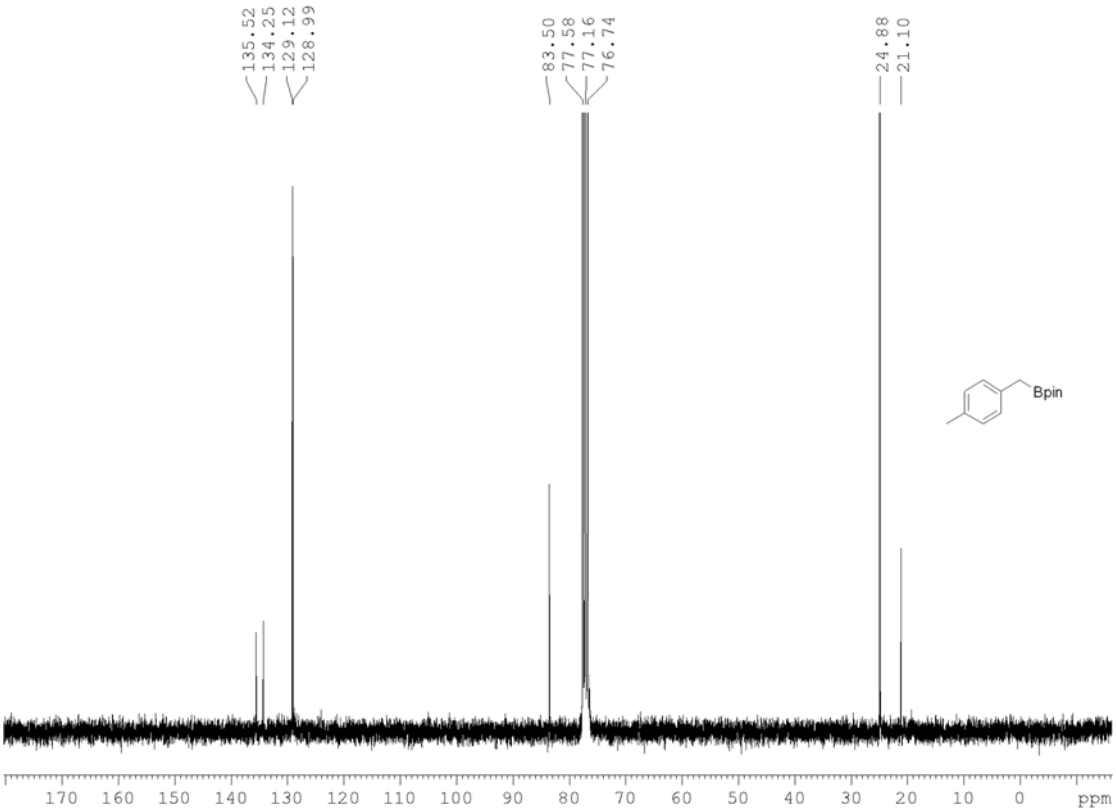


Compound (2-2)j

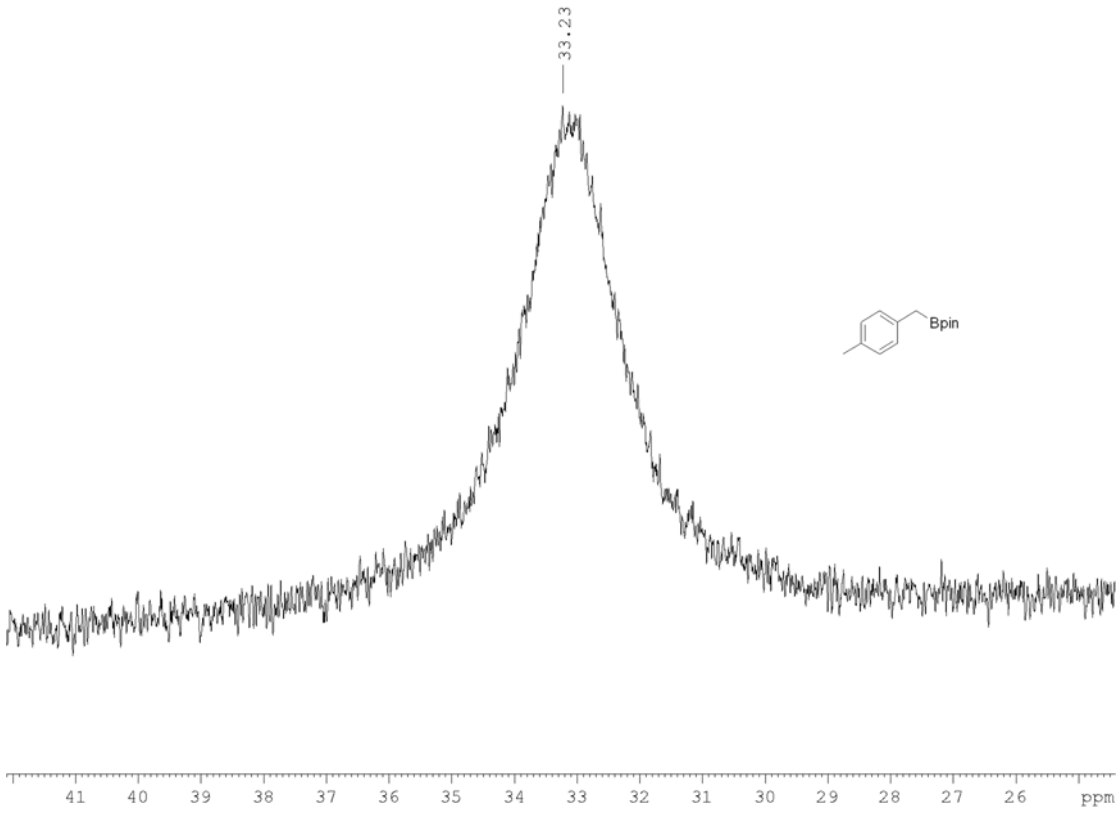
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

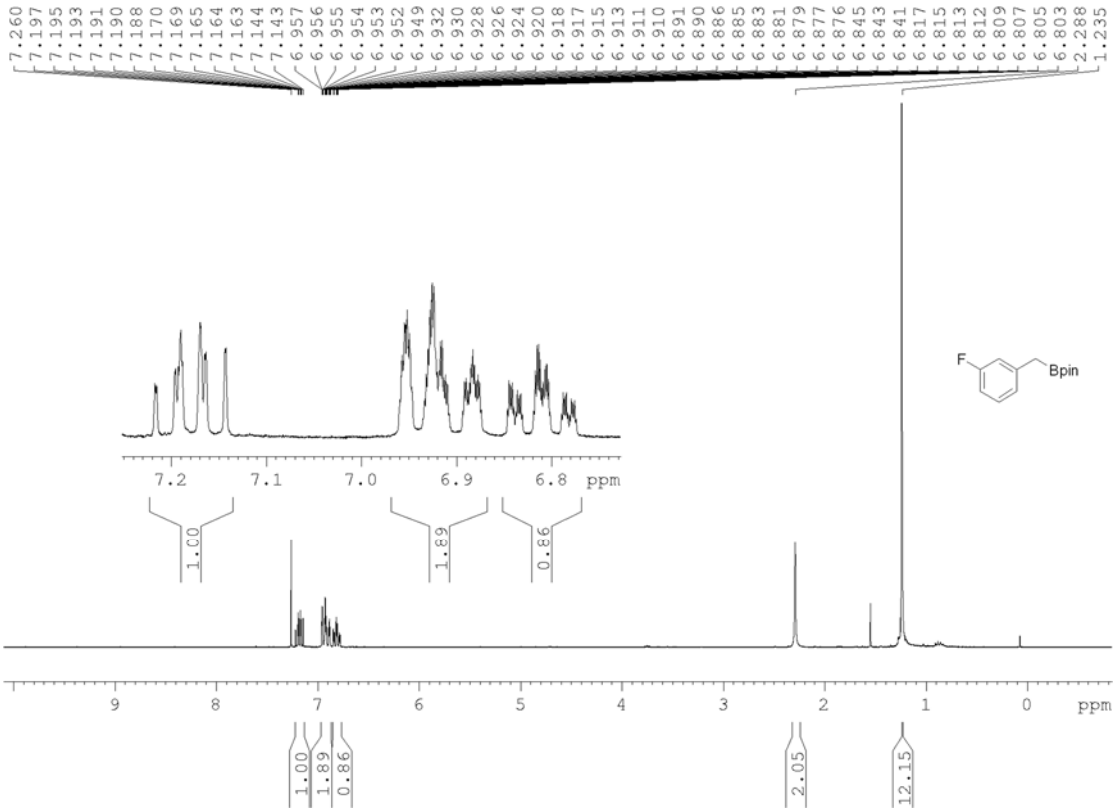


^{11}B NMR (96 MHz, $CDCl_3$)

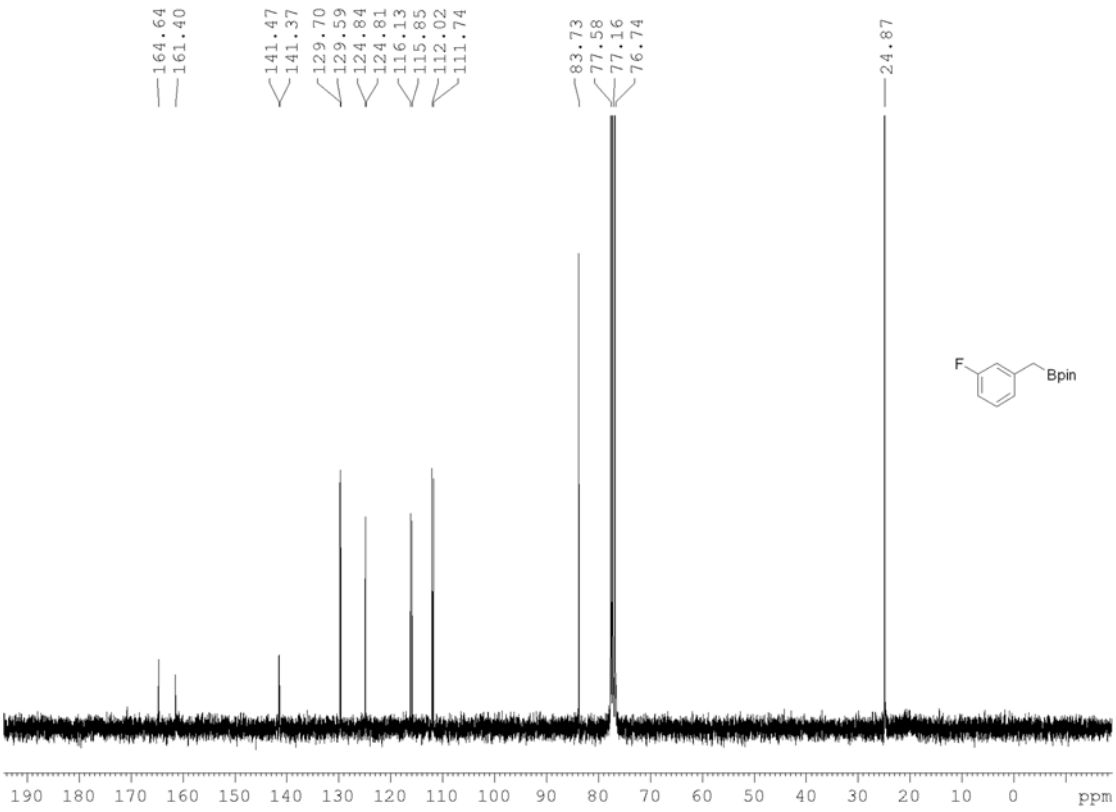


Compound (2-2)k

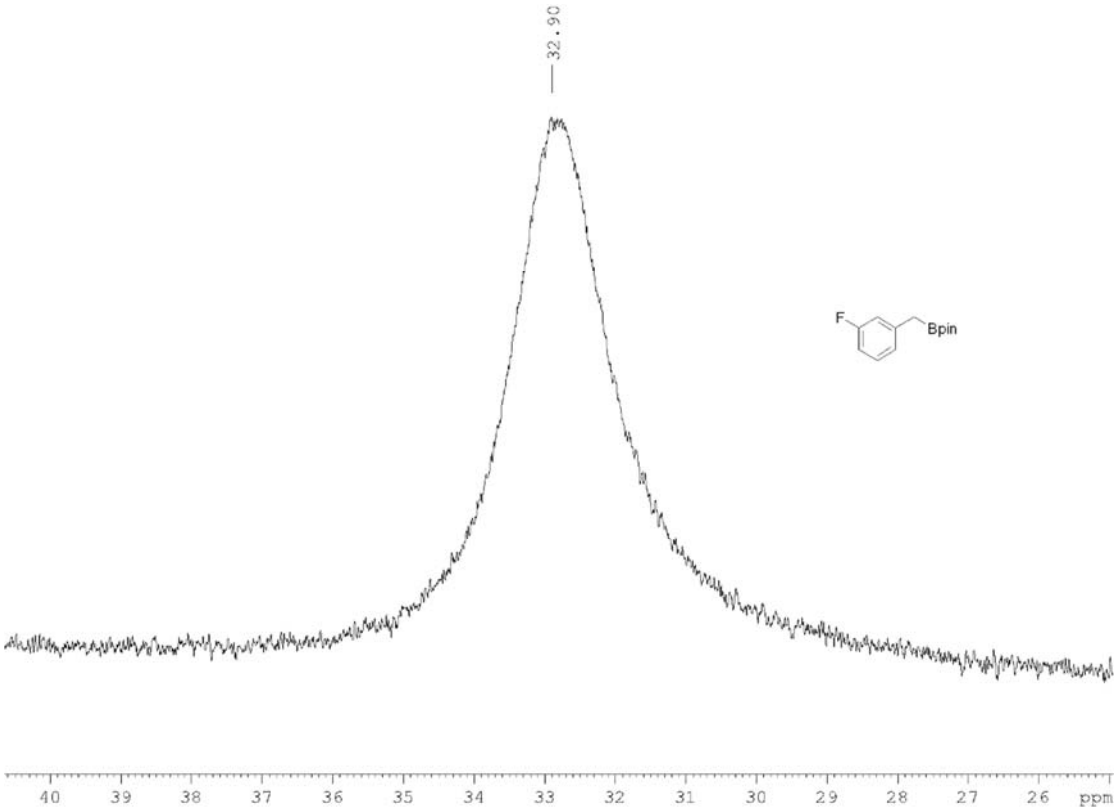
^{1}H NMR (300 MHz, $CDCl_3$)



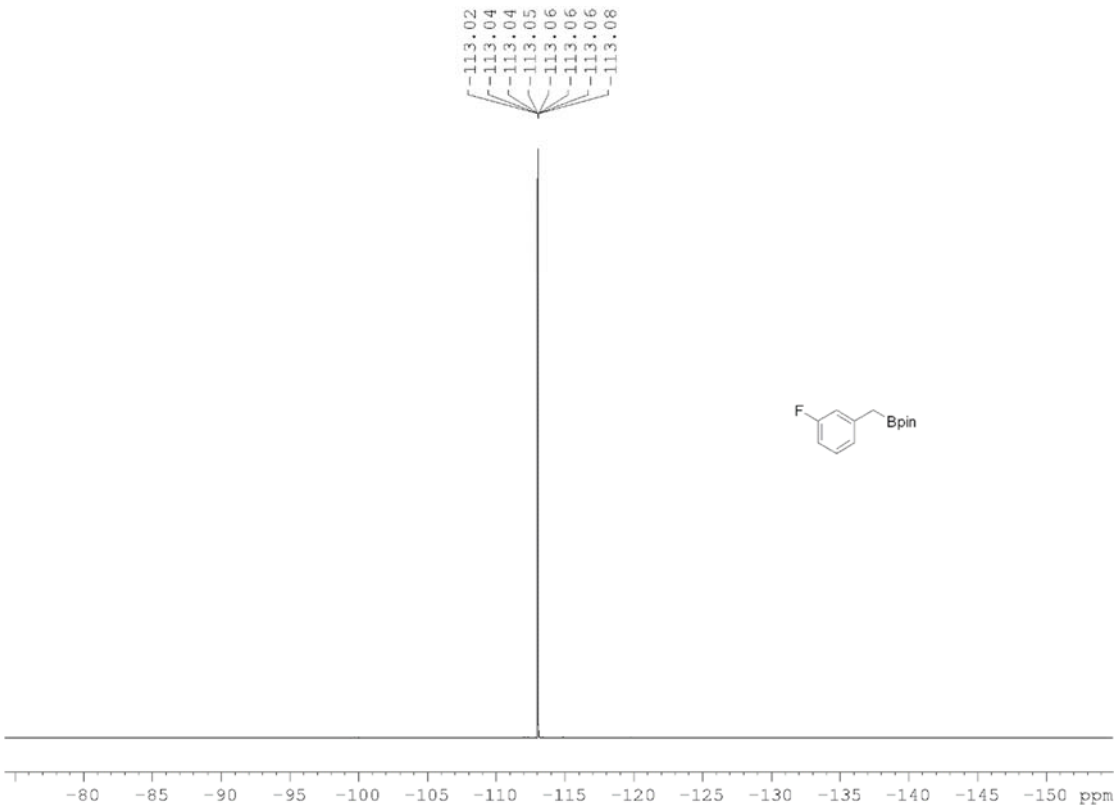
^{13} C{^{1}H} NMR (75 MHz, $CDCl_3$)



^{11}B NMR (96 MHz, $CDCl_3$)

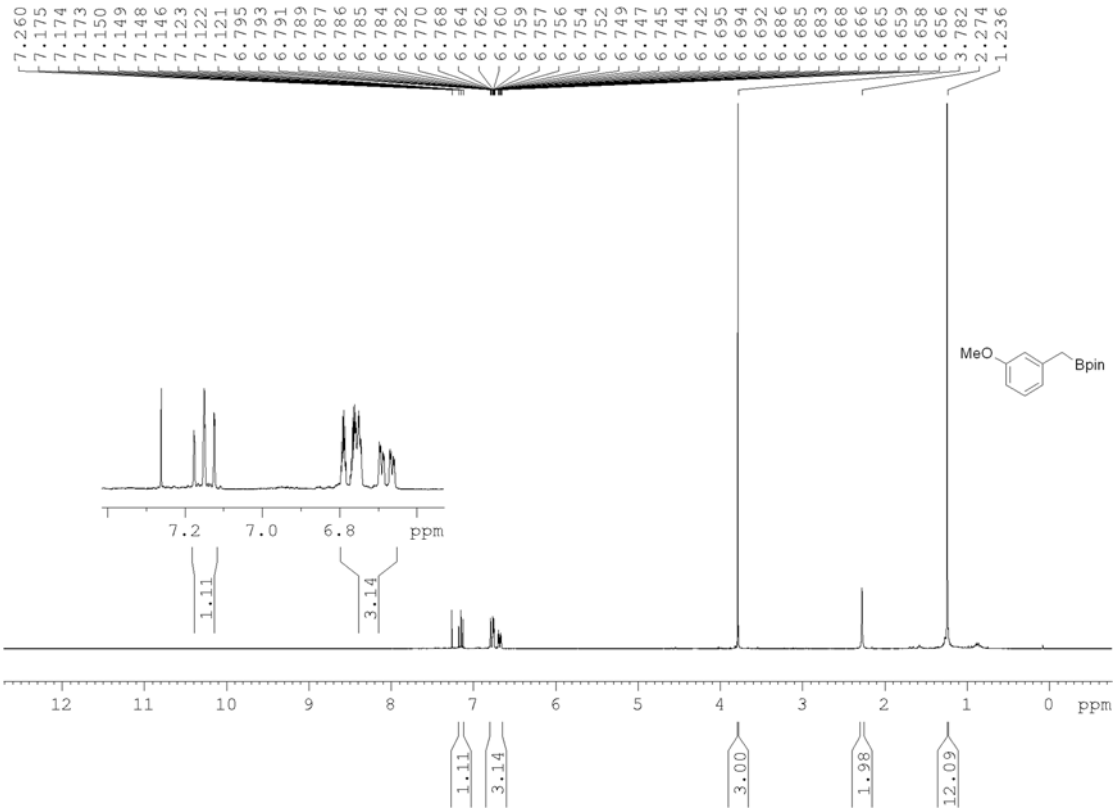


^{19}F NMR (470 MHz, $CDCl_3$)

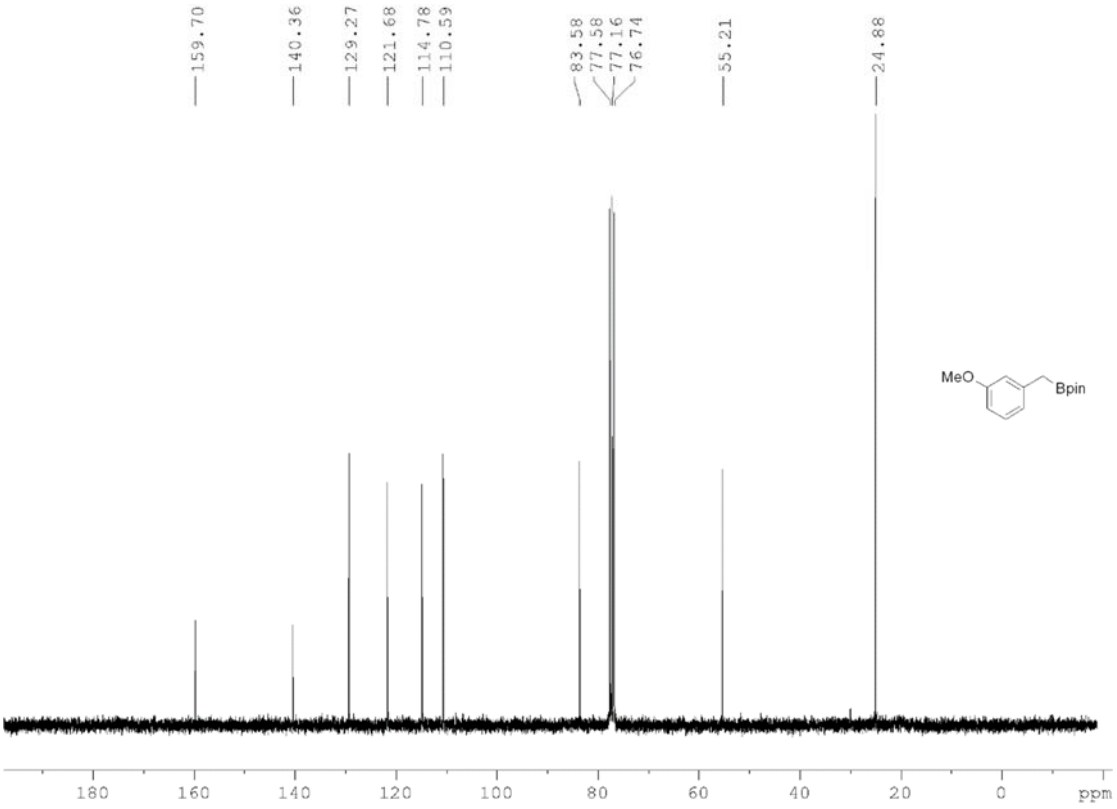


Compound (2-2)l

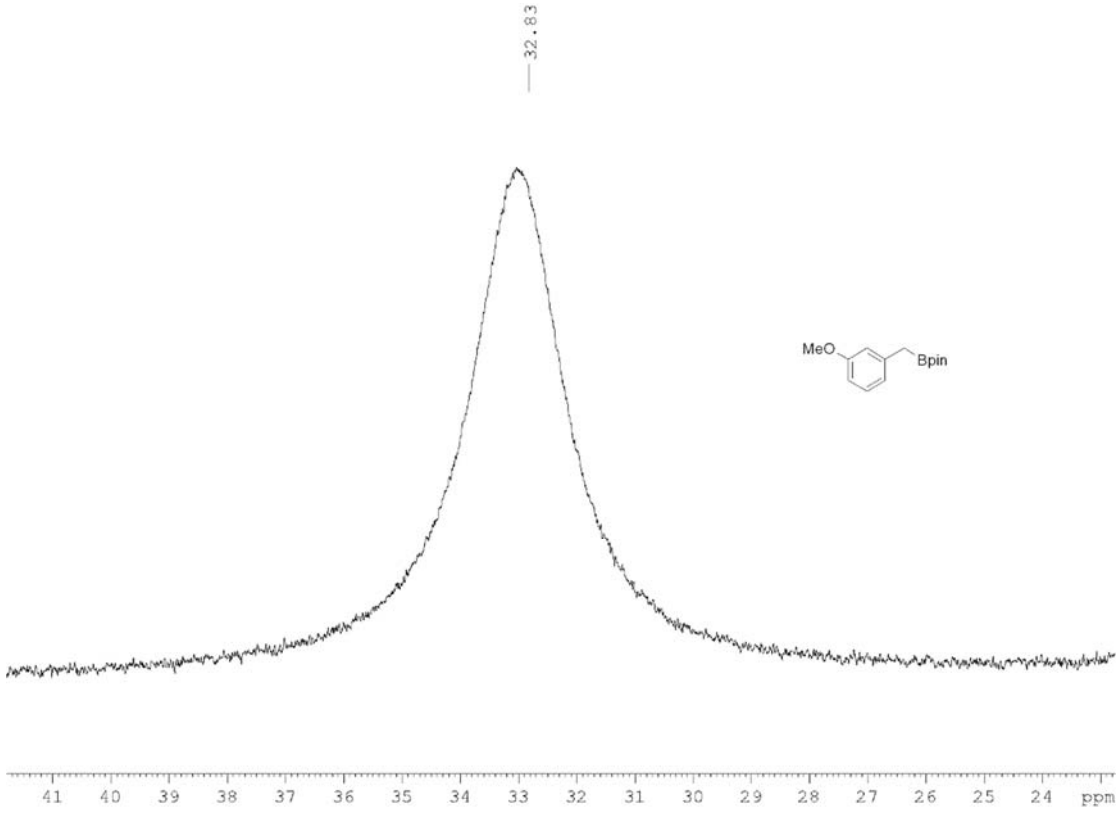
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

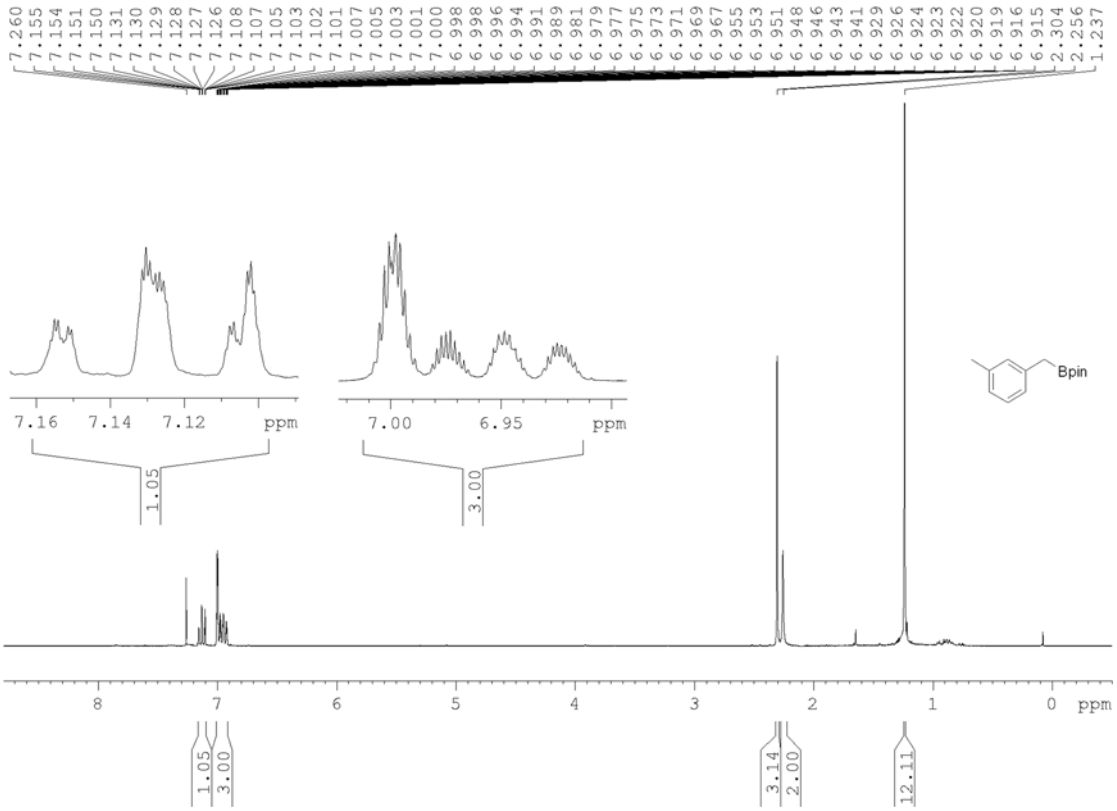


^{11}B NMR (96 MHz, $CDCl_3$)

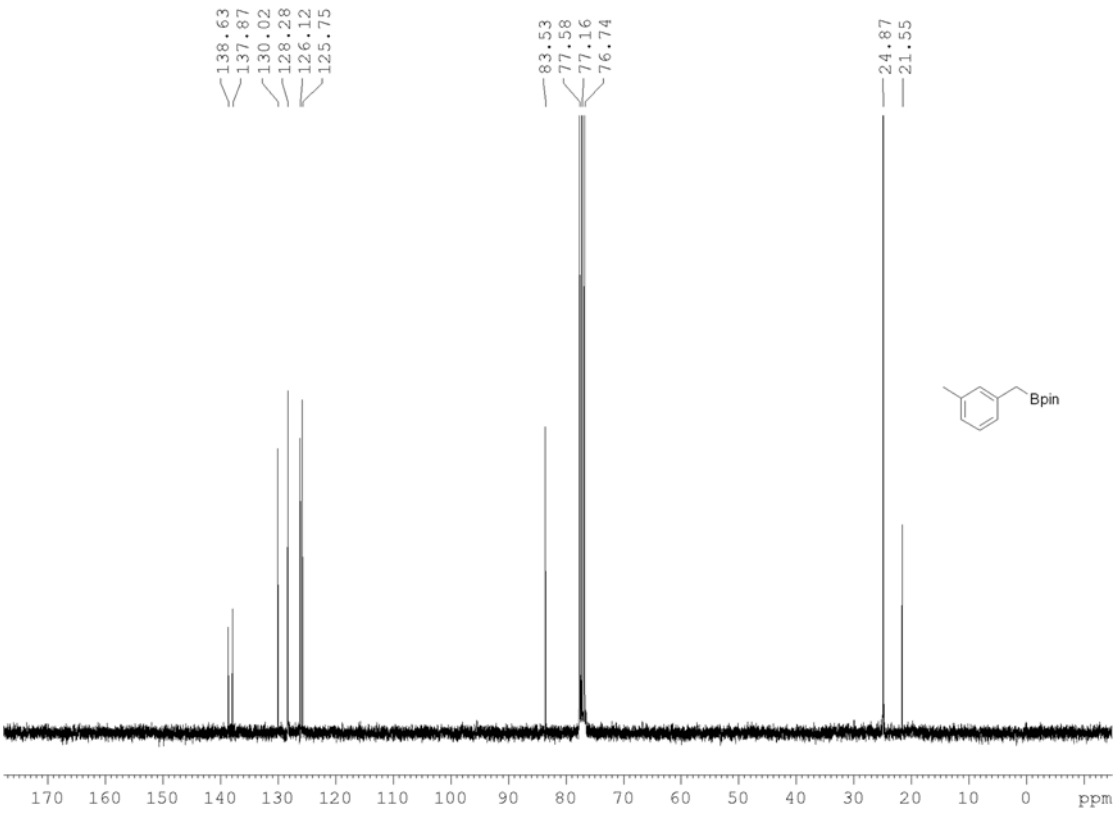


Compound (2-2)m

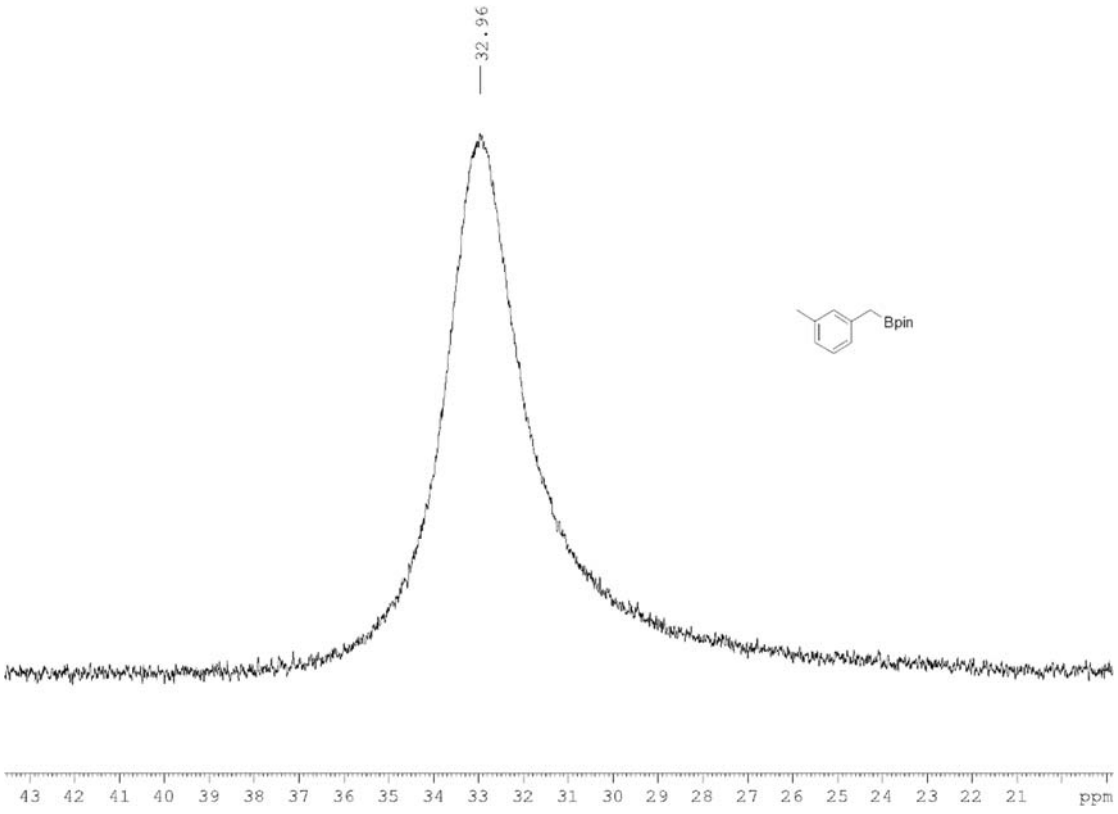
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

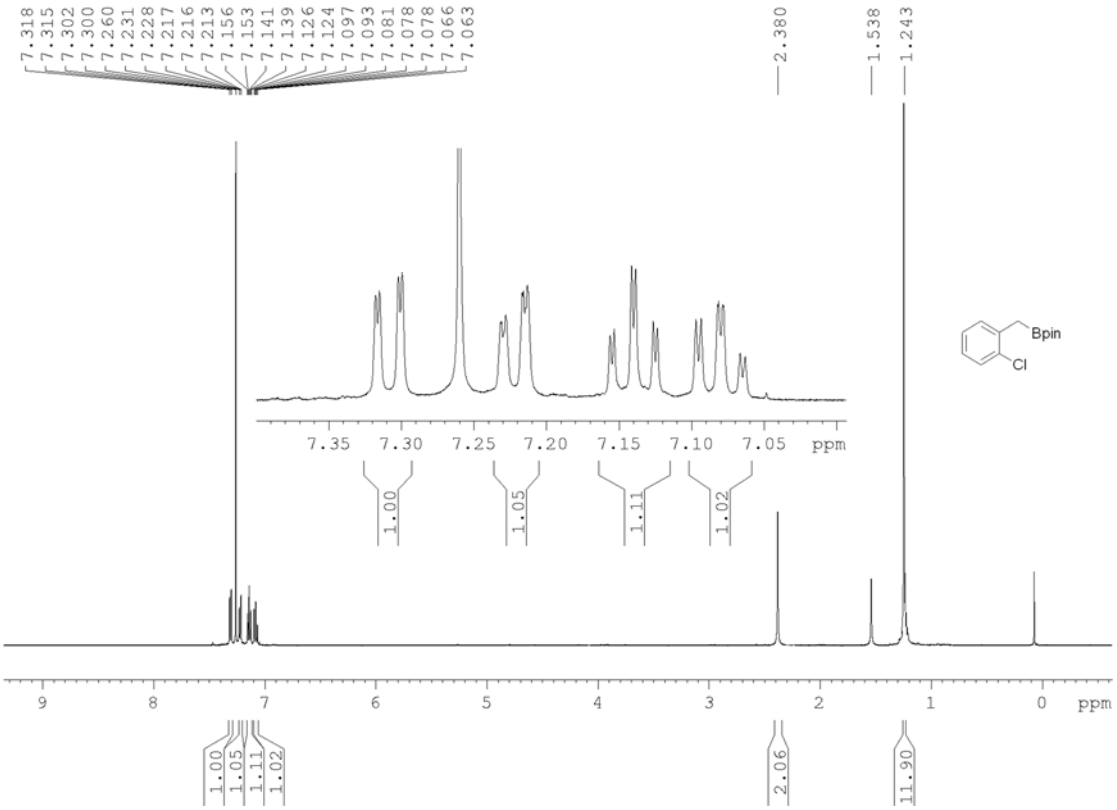


^{11}B NMR (96 MHz, $CDCl_3$)

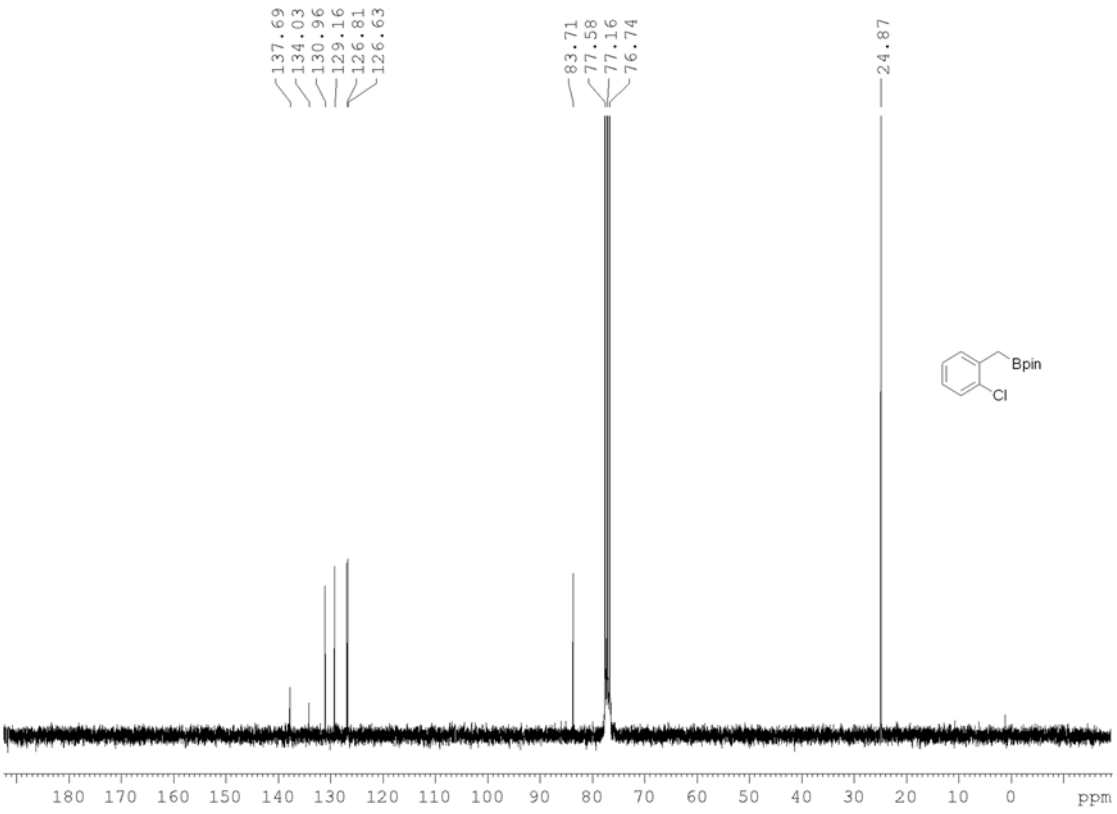


Compound (2-2)n

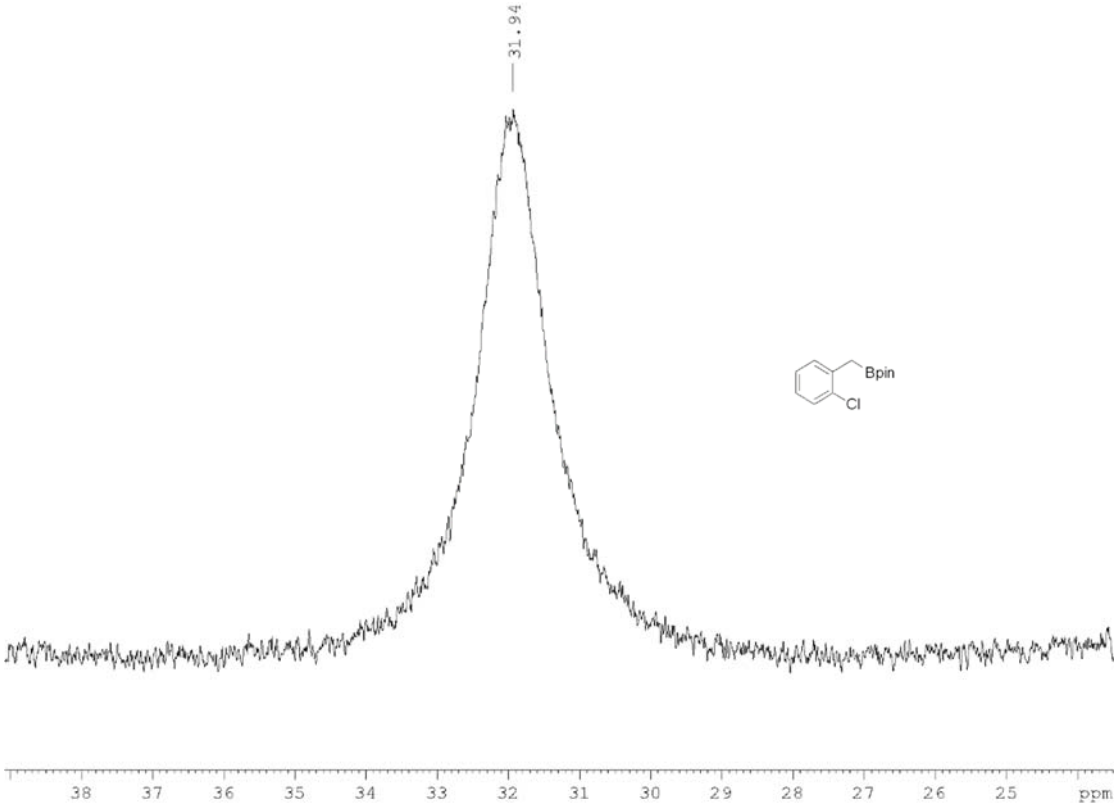
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

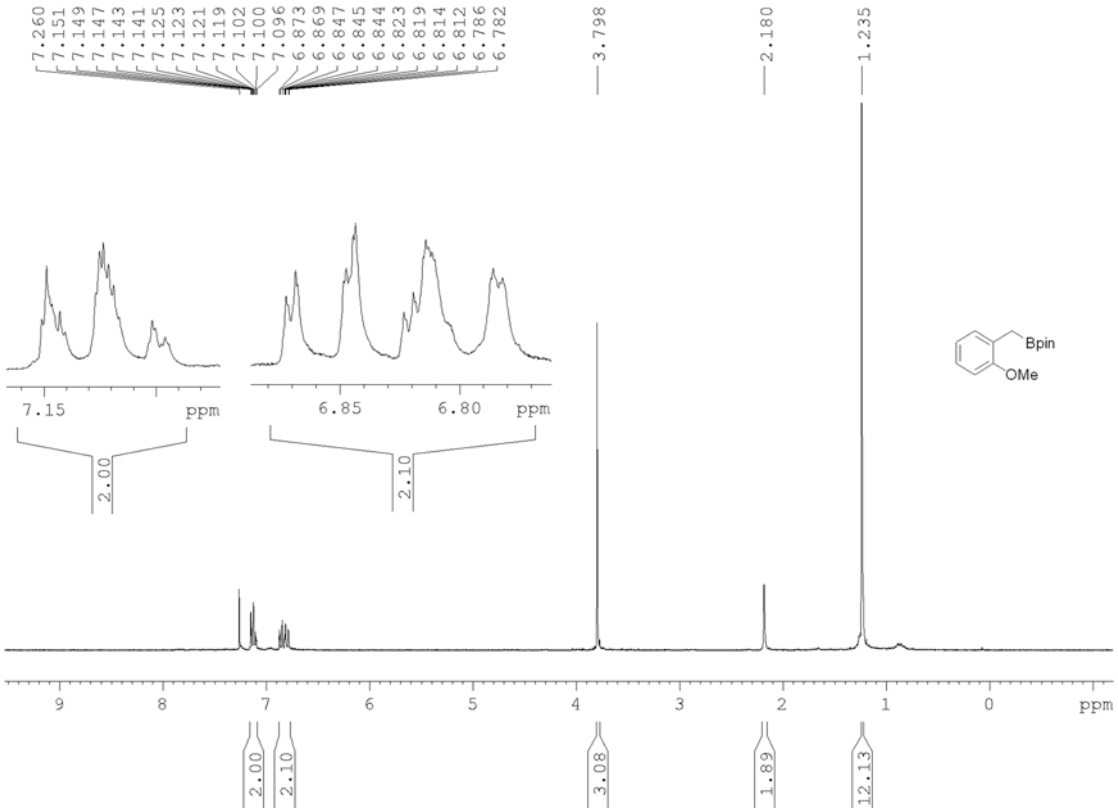


^{11}B NMR (160 MHz, $CDCl_3$)

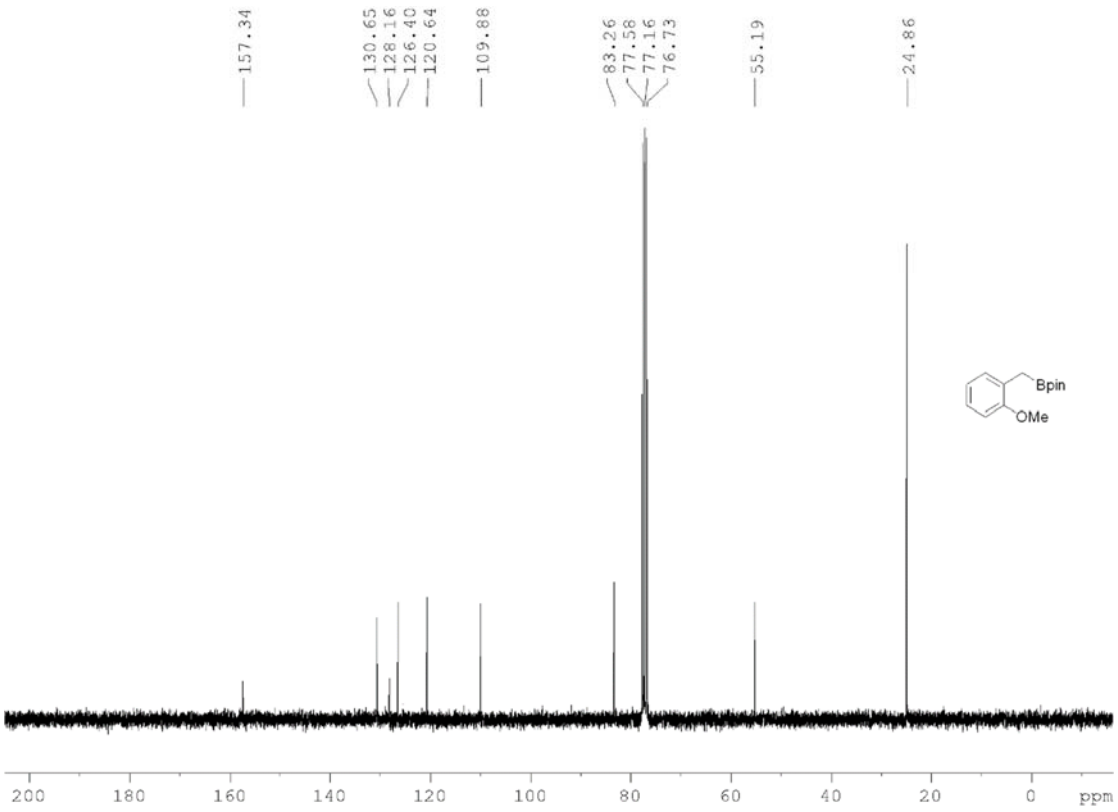


Compound (2-2)o

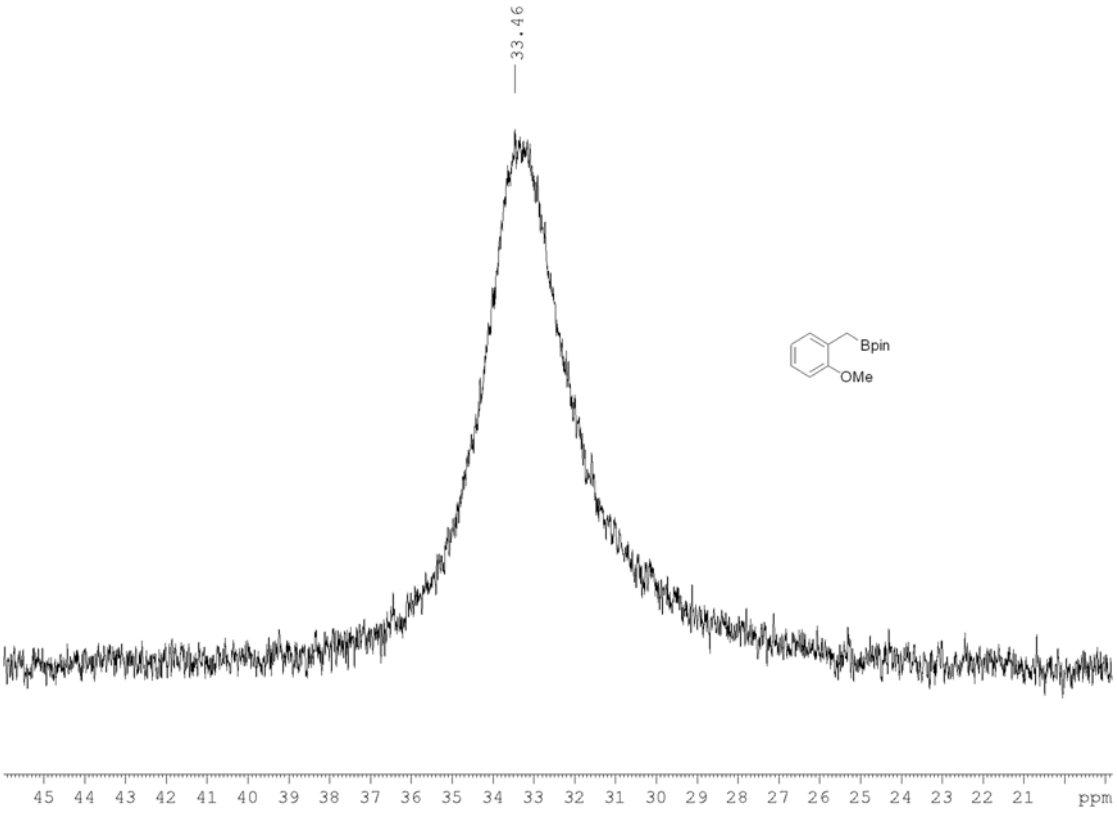
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

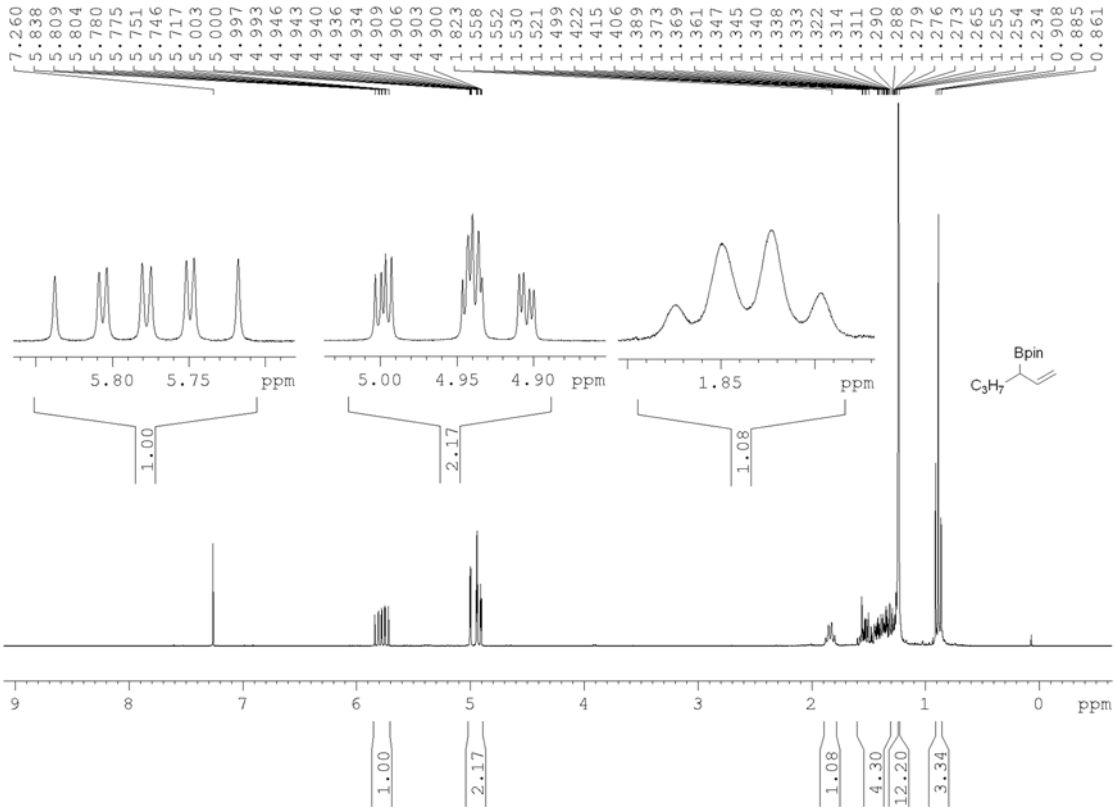


^{11}B NMR (96 MHz, $CDCl_3$)

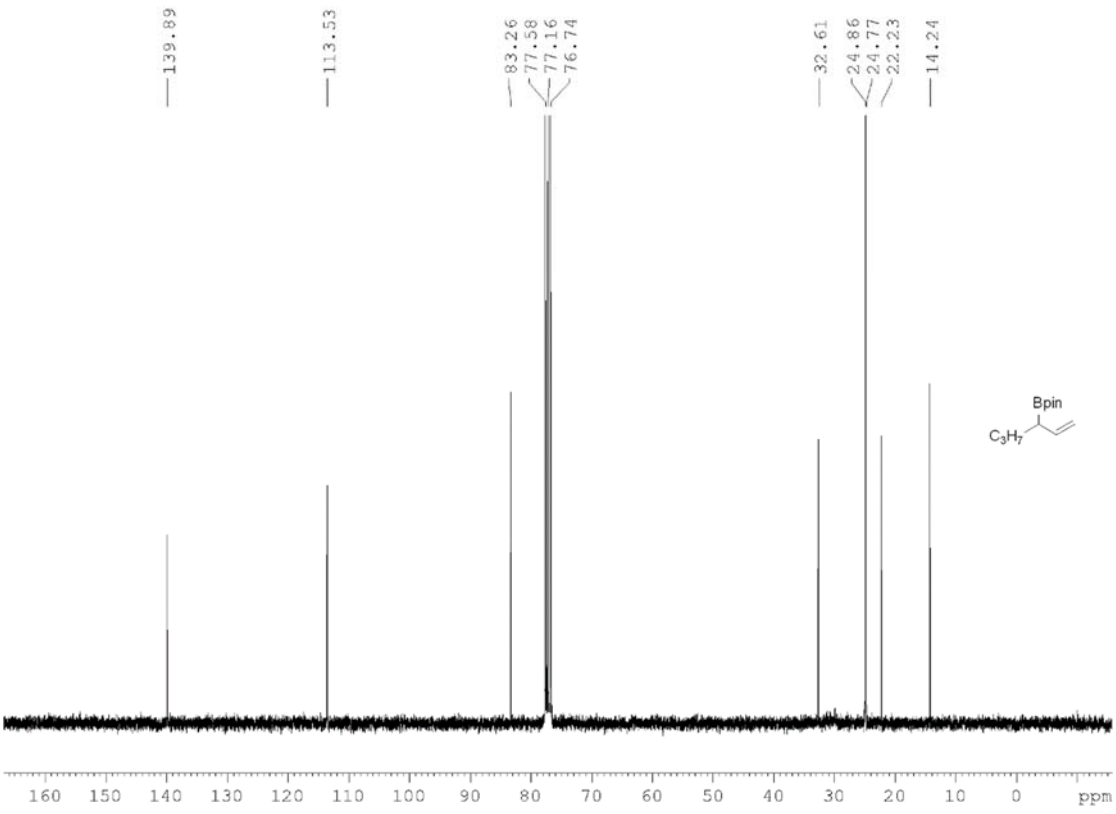


Compound (2-4)a

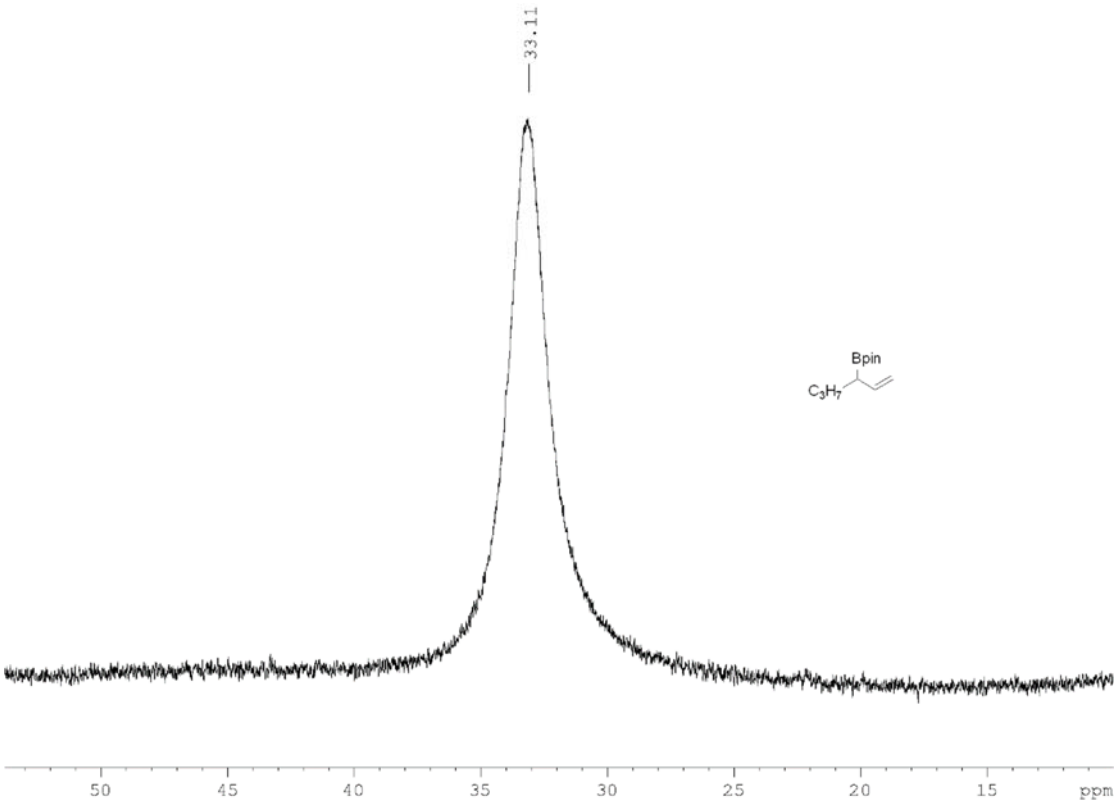
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

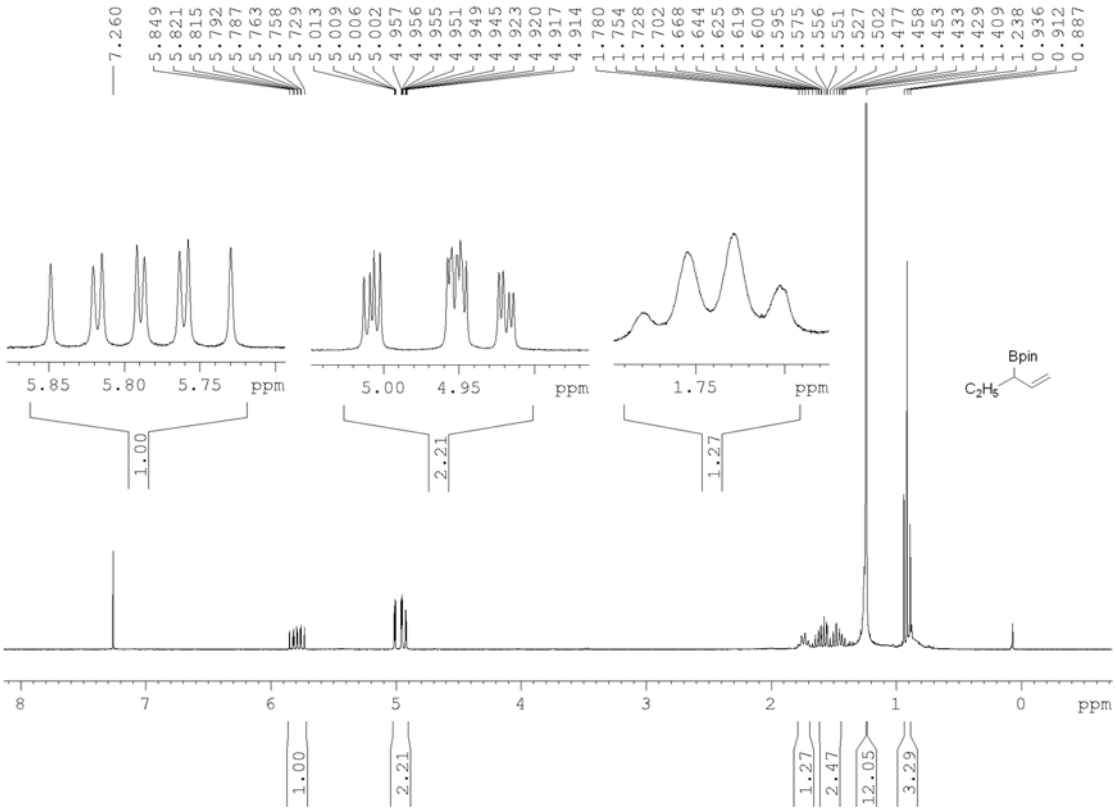


^{11}B NMR (96 MHz, $CDCl_3$)

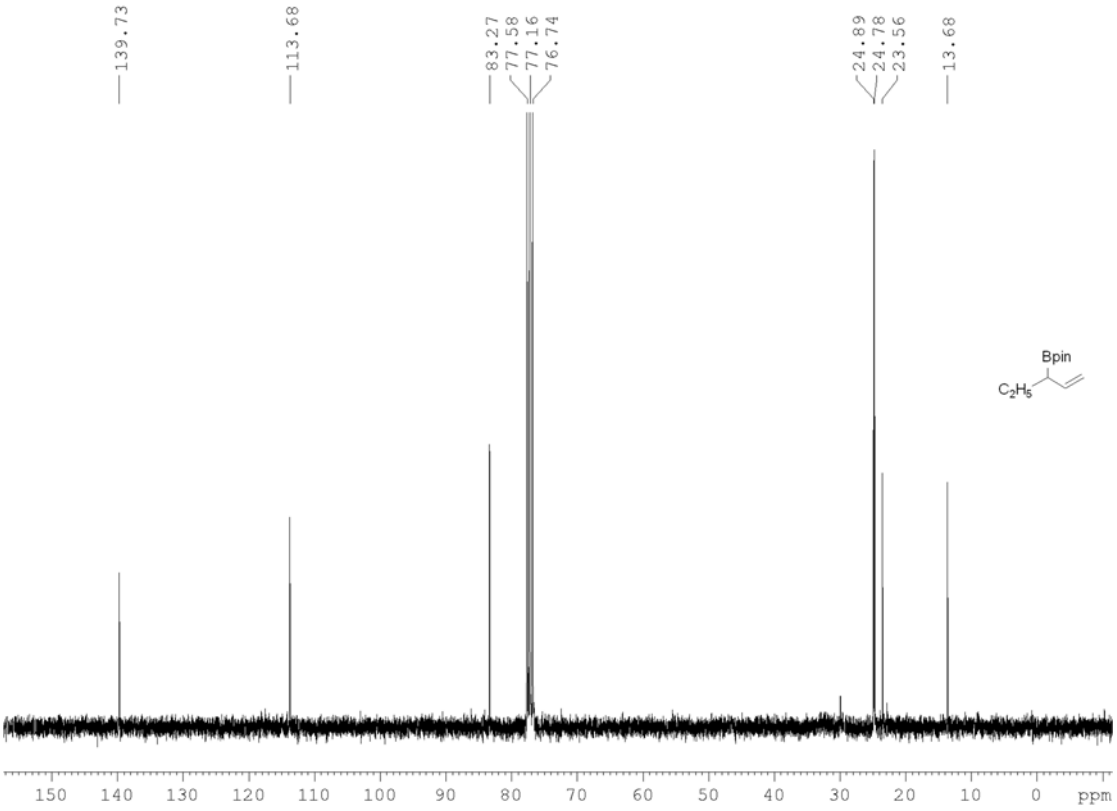


Compound (2-4)b

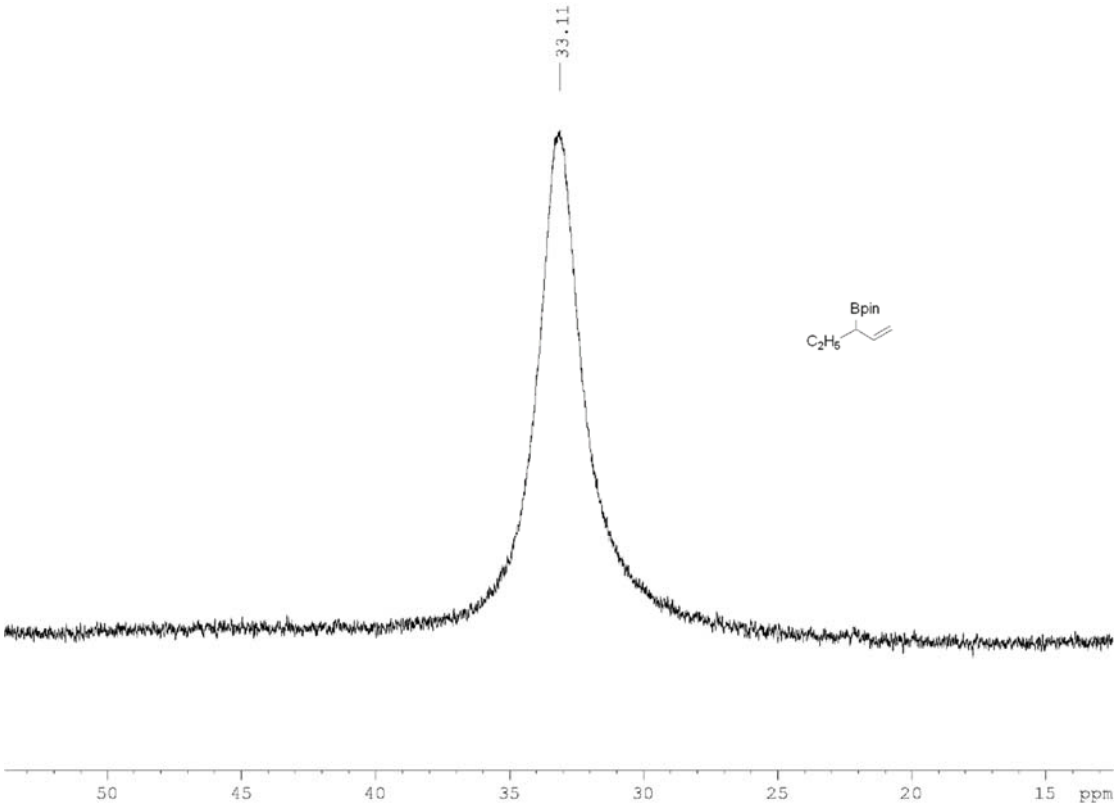
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

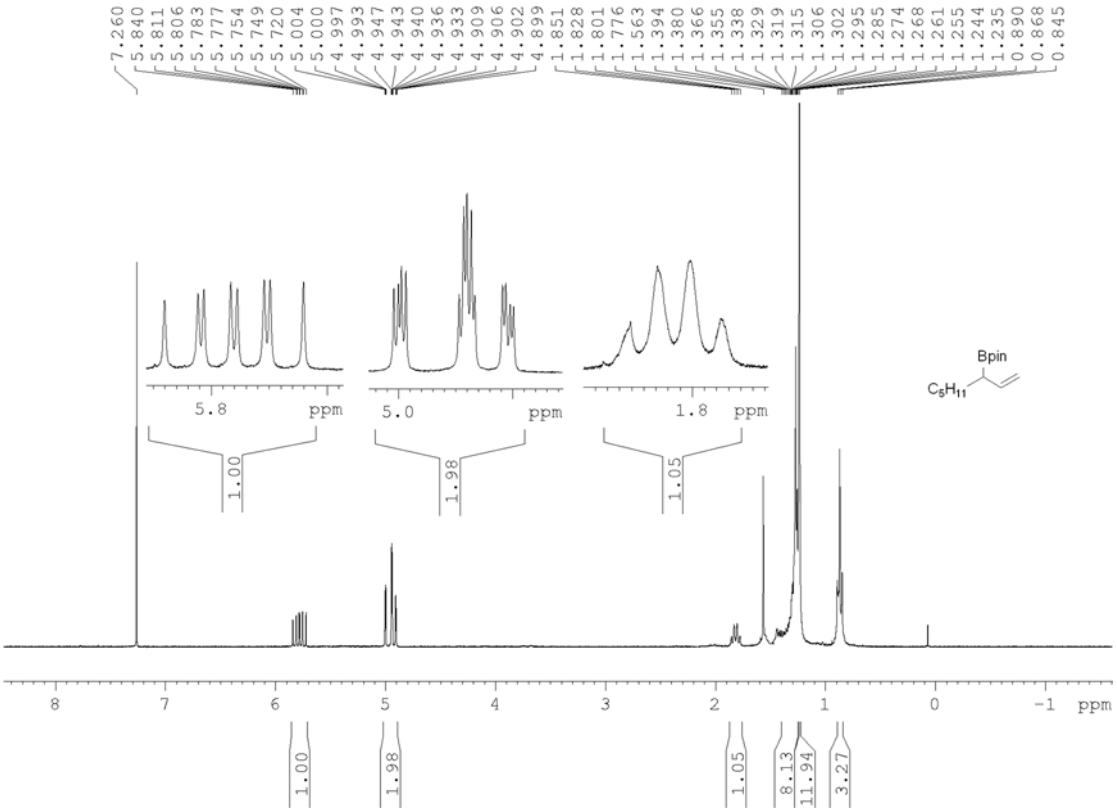


^{11}B NMR (96 MHz, $CDCl_3$)

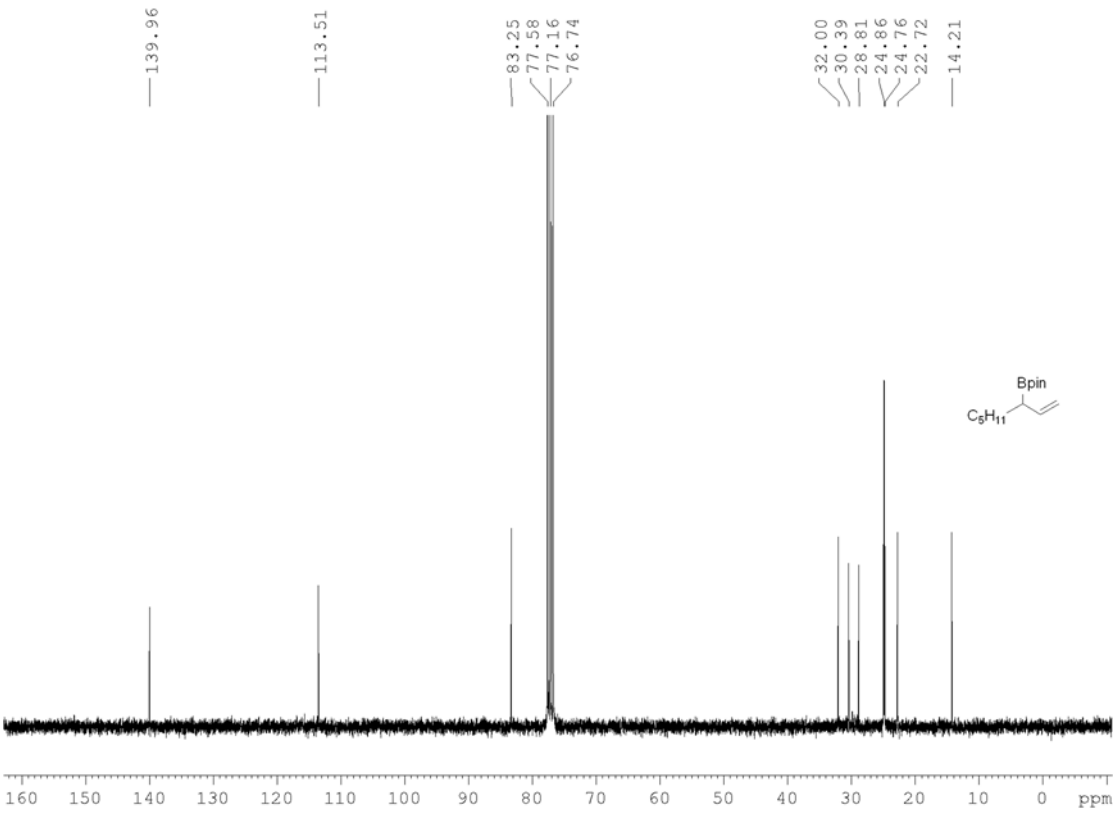


Compound (2-4)c

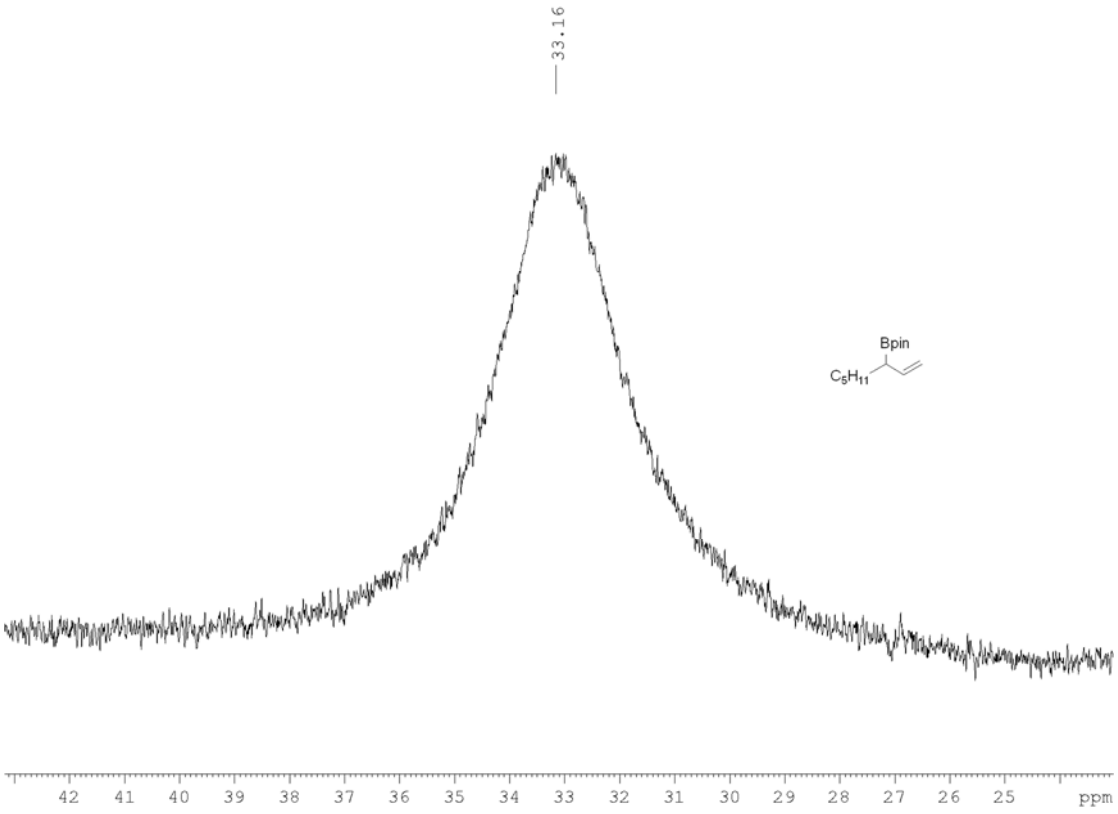
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

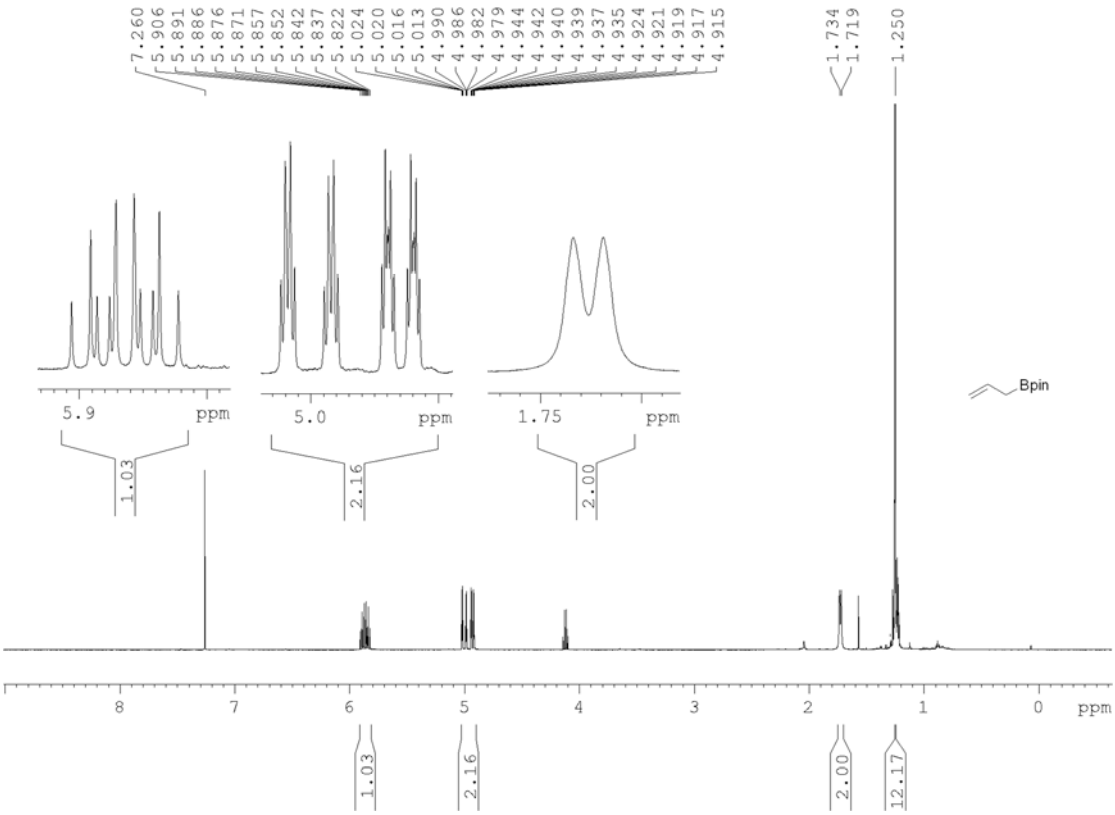


^{11}B NMR (96 MHz, $CDCl_3$)

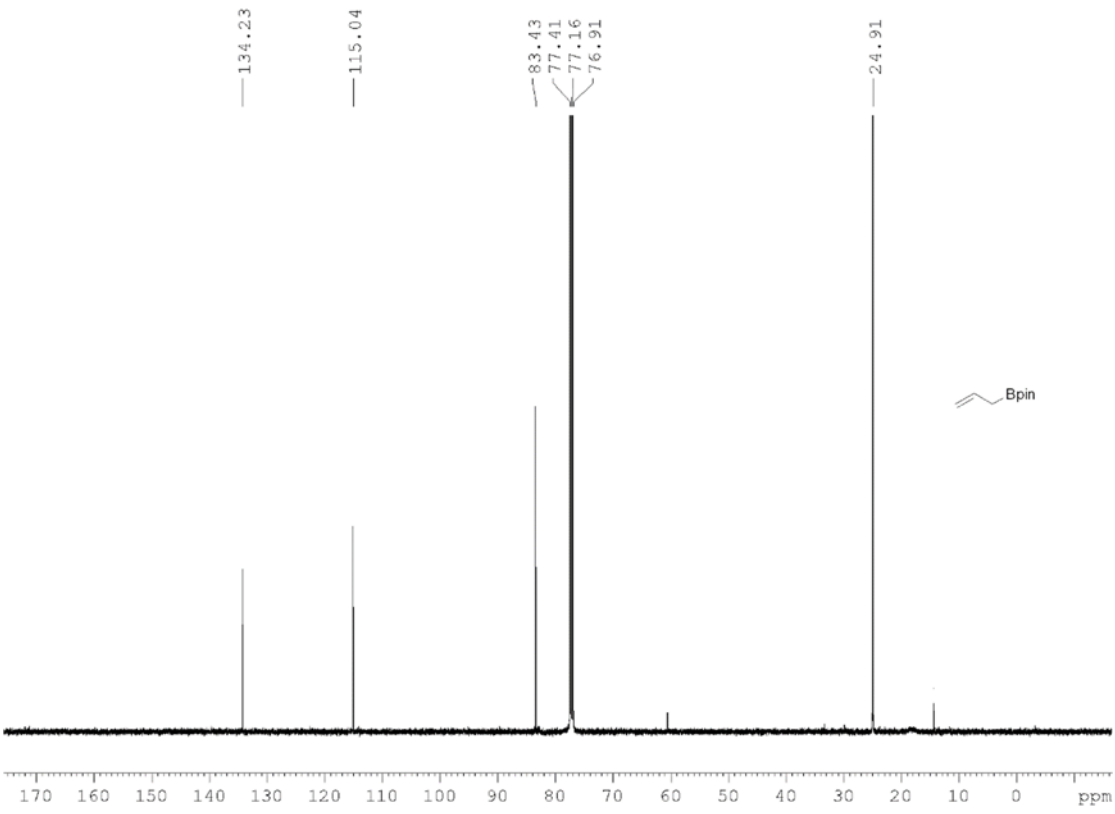


Compound (2-4)d

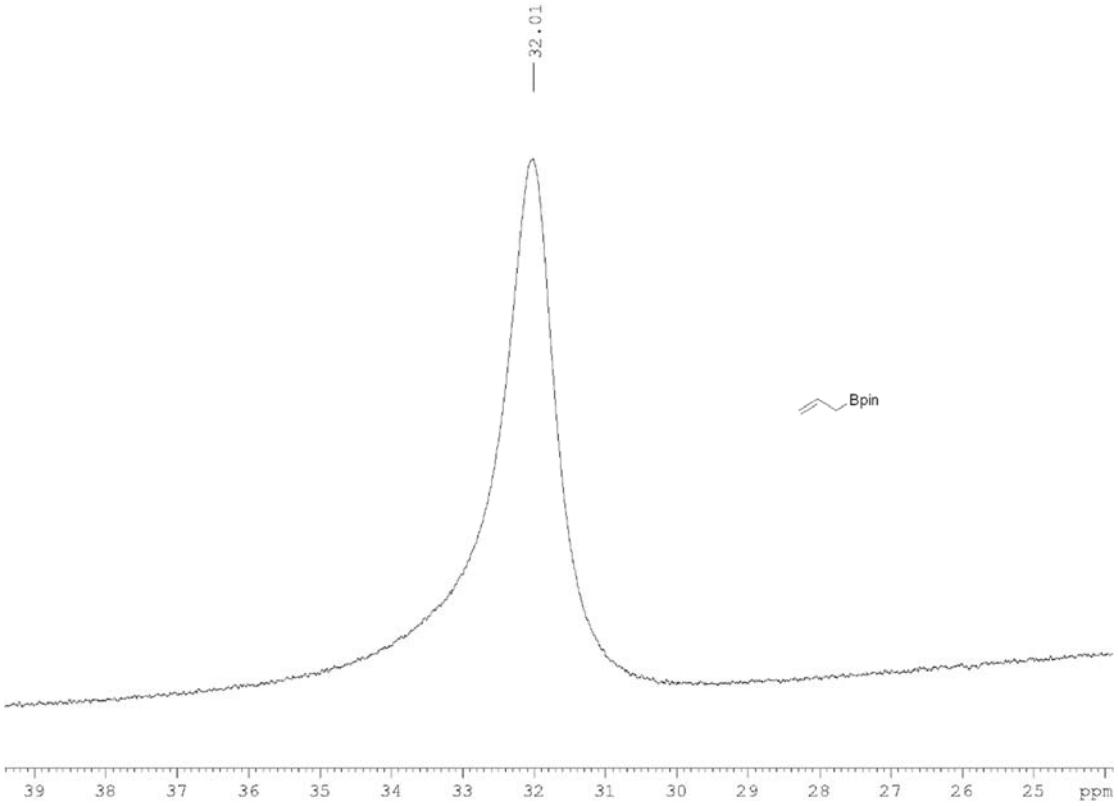
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

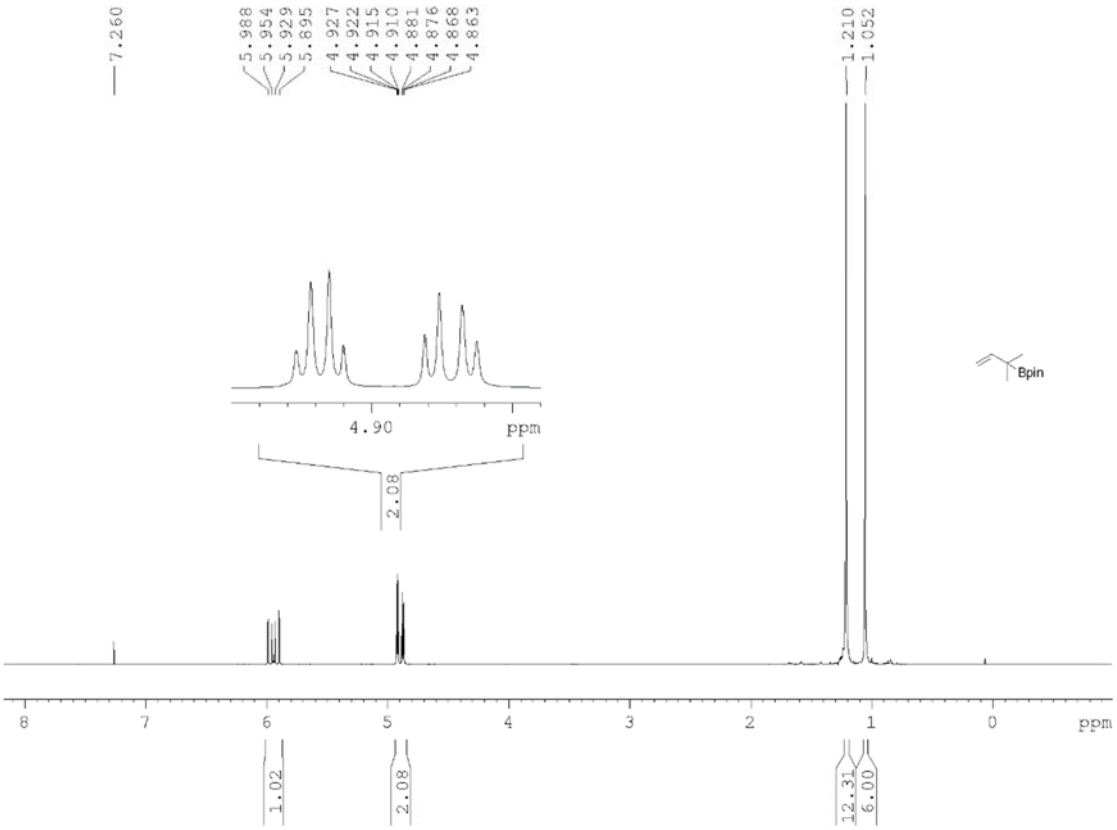


^{11}B NMR (160 MHz, $CDCl_3$)

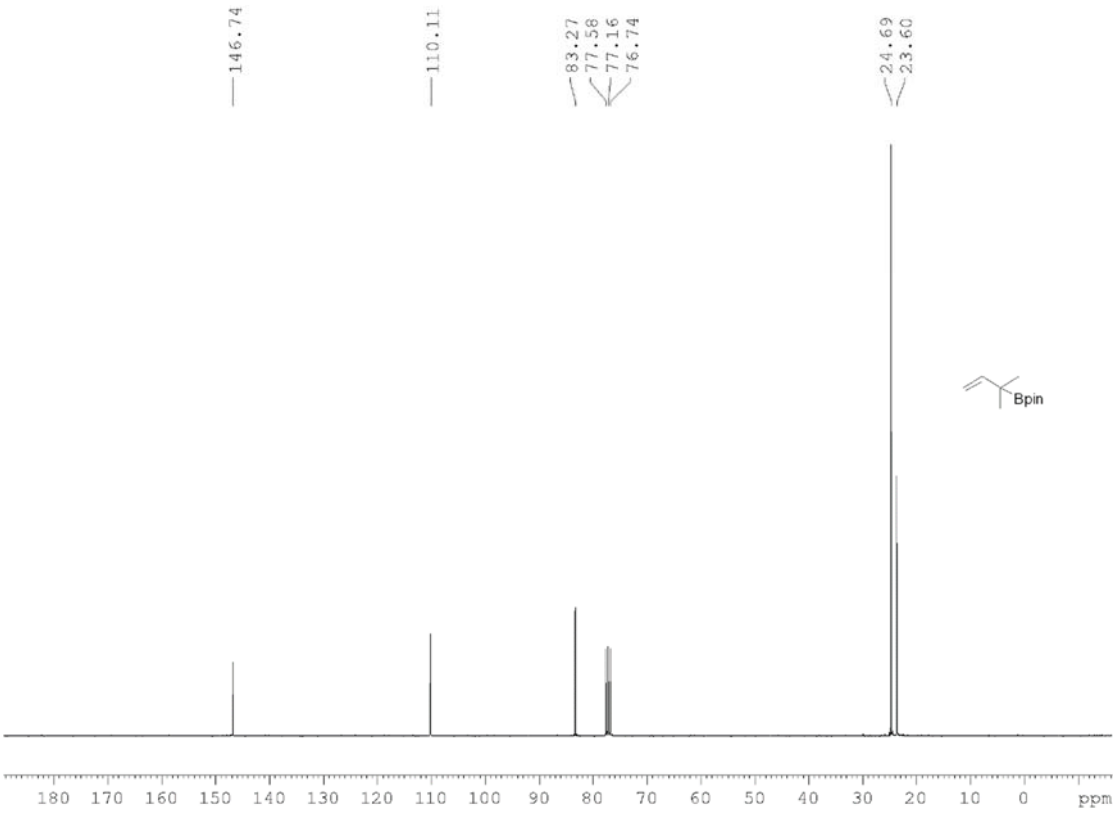


Compound (2-4)e

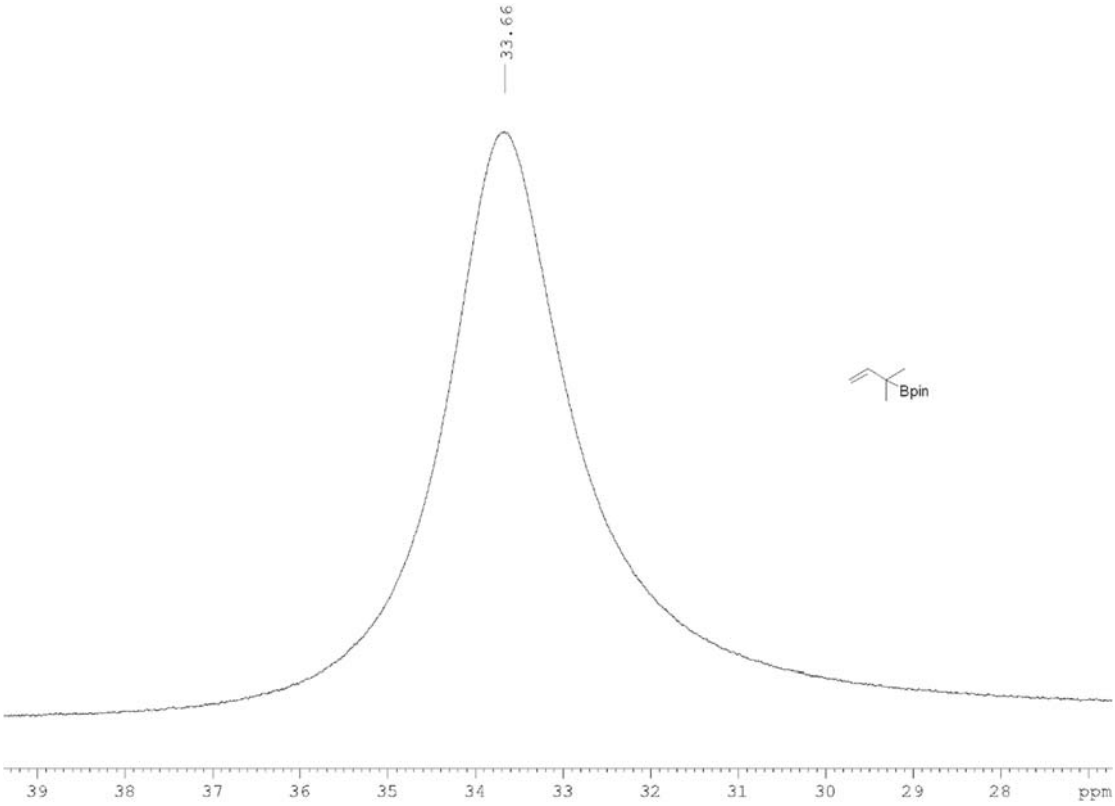
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

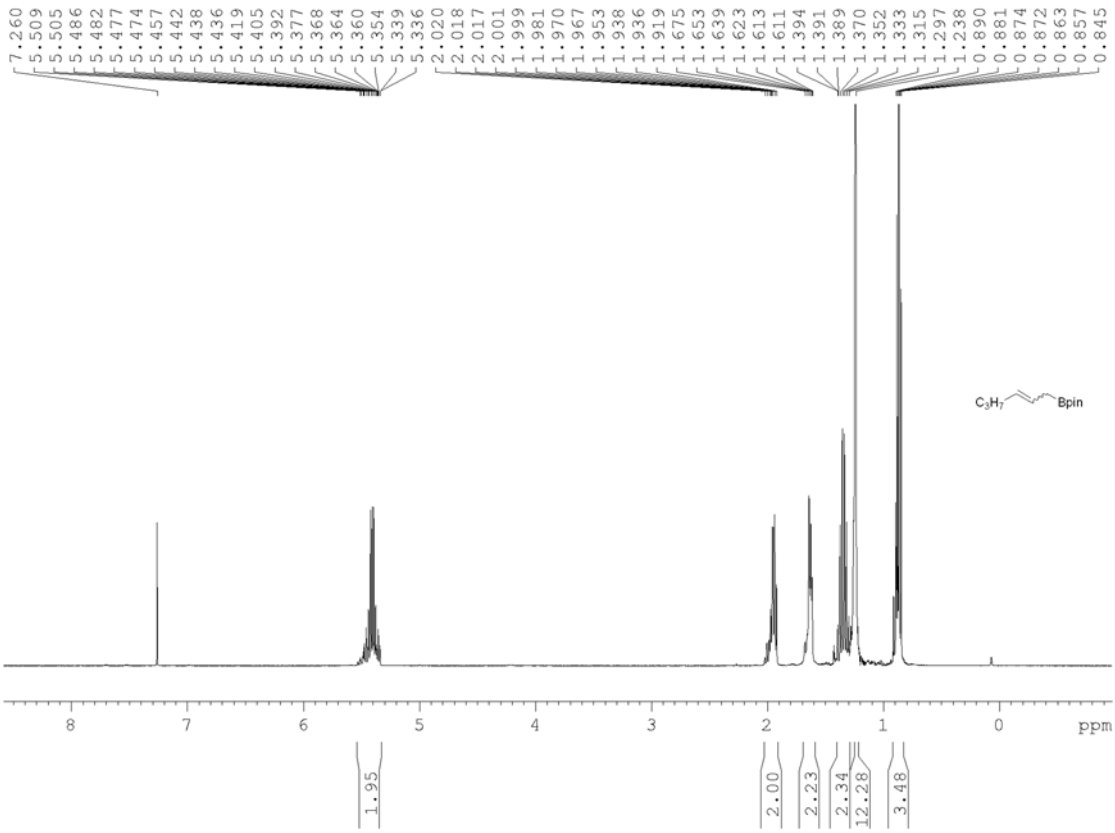


^{11}B NMR (96 MHz, $CDCl_3$)

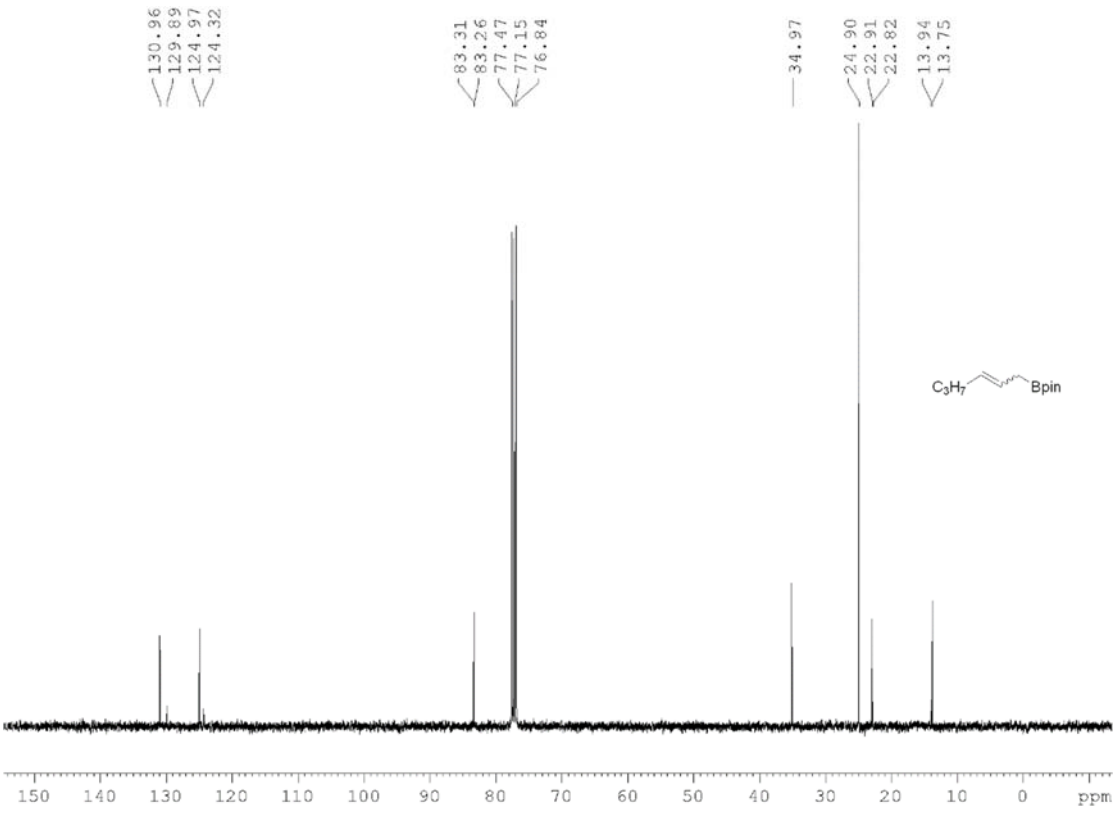


Compound (2-4)f or (4-2)b

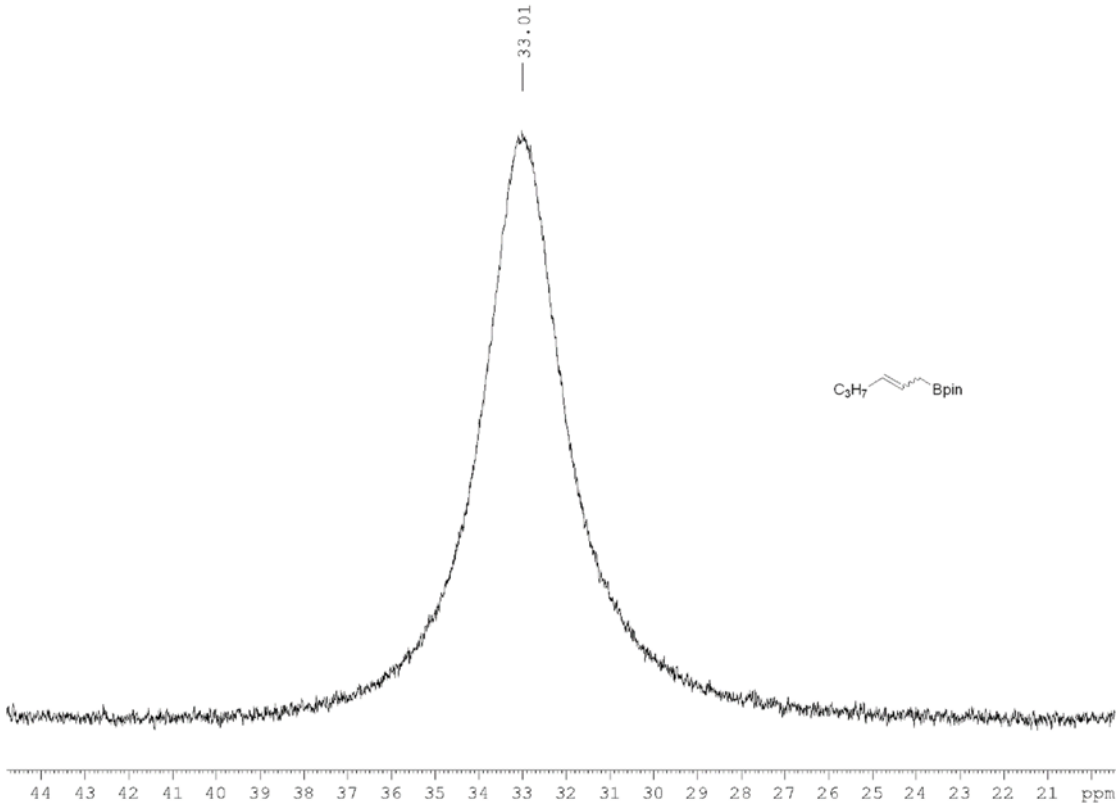
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

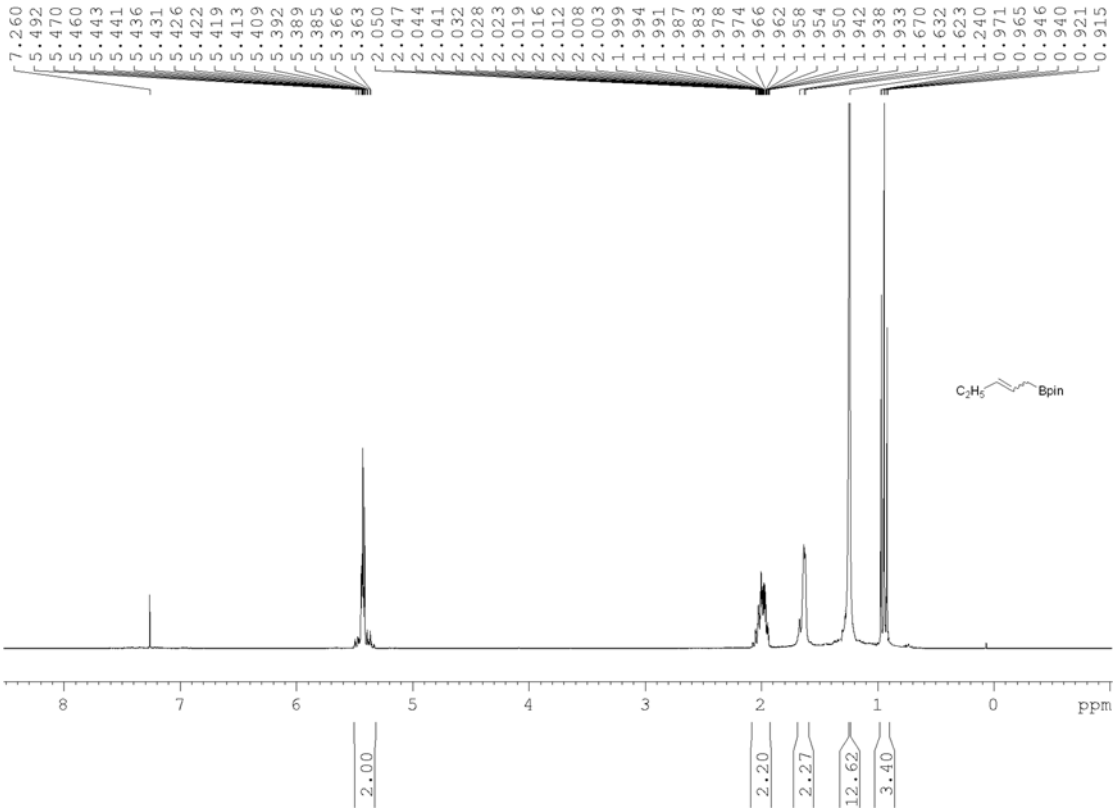


^{11}B NMR (128 MHz, $CDCl_3$)

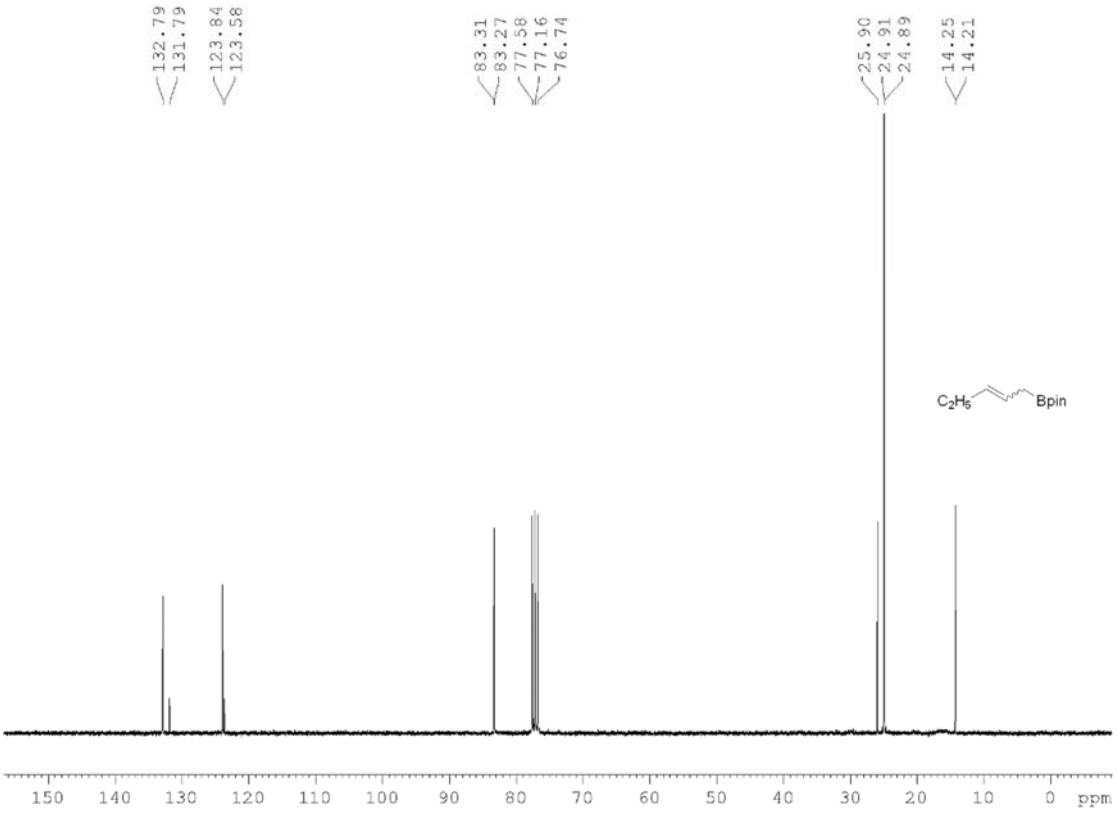


Compound (2-4)g or (4-2)c

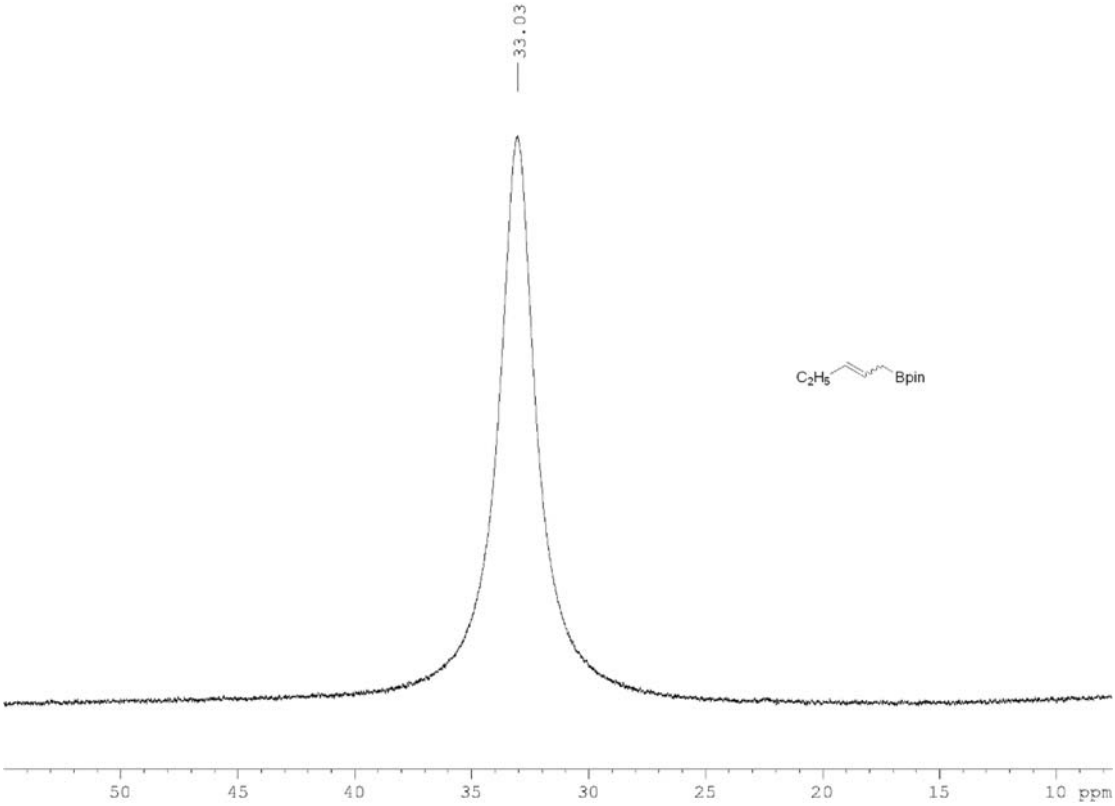
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

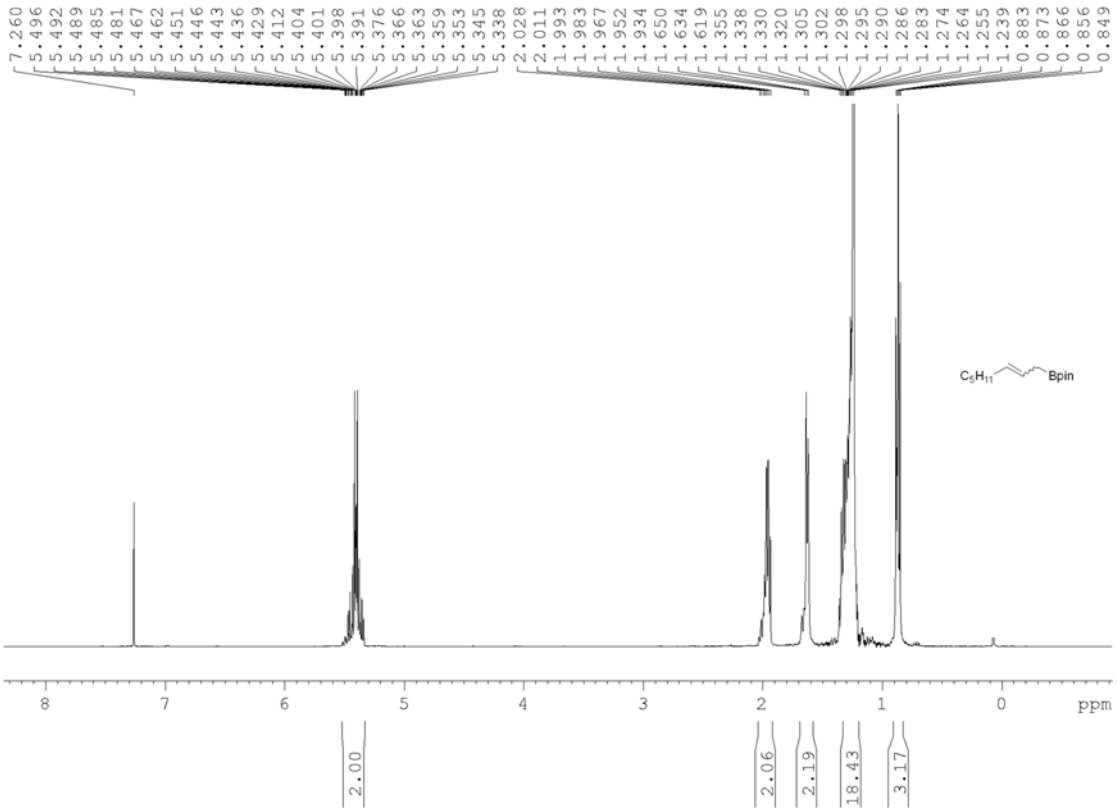


^{11}B NMR (96 MHz, $CDCl_3$)

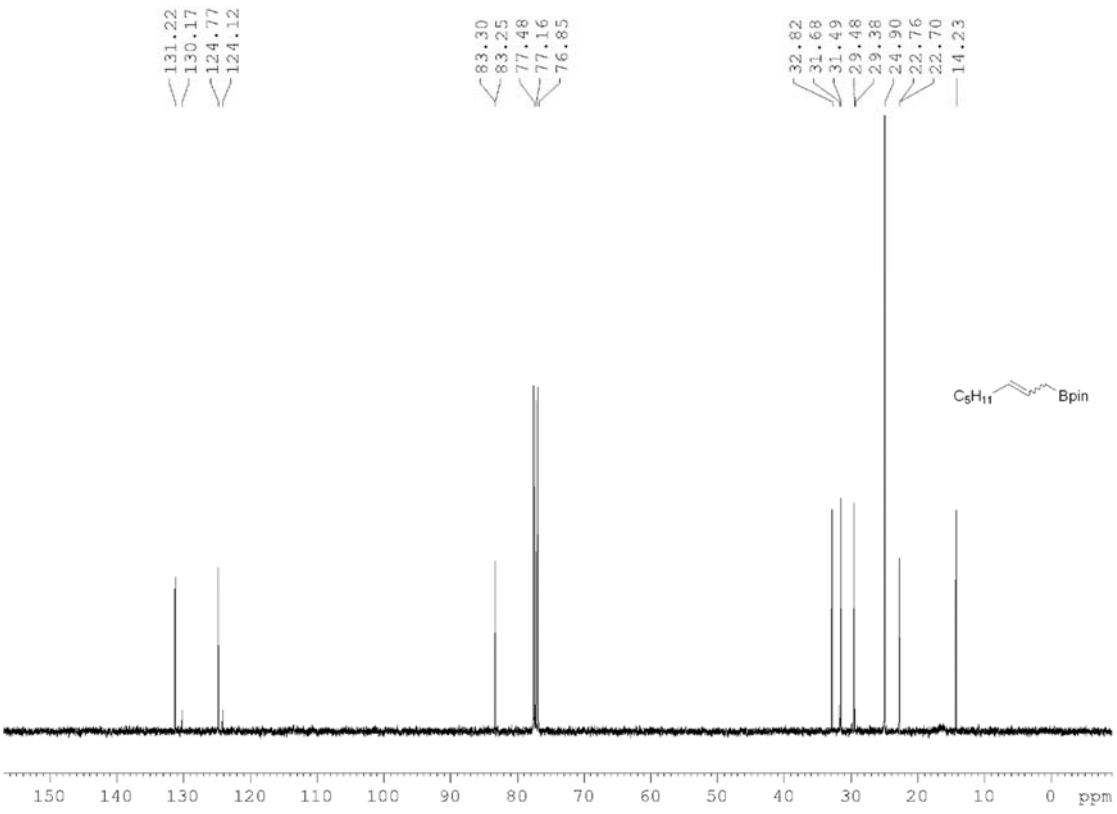


Compound (2-4)h or (4-2)a

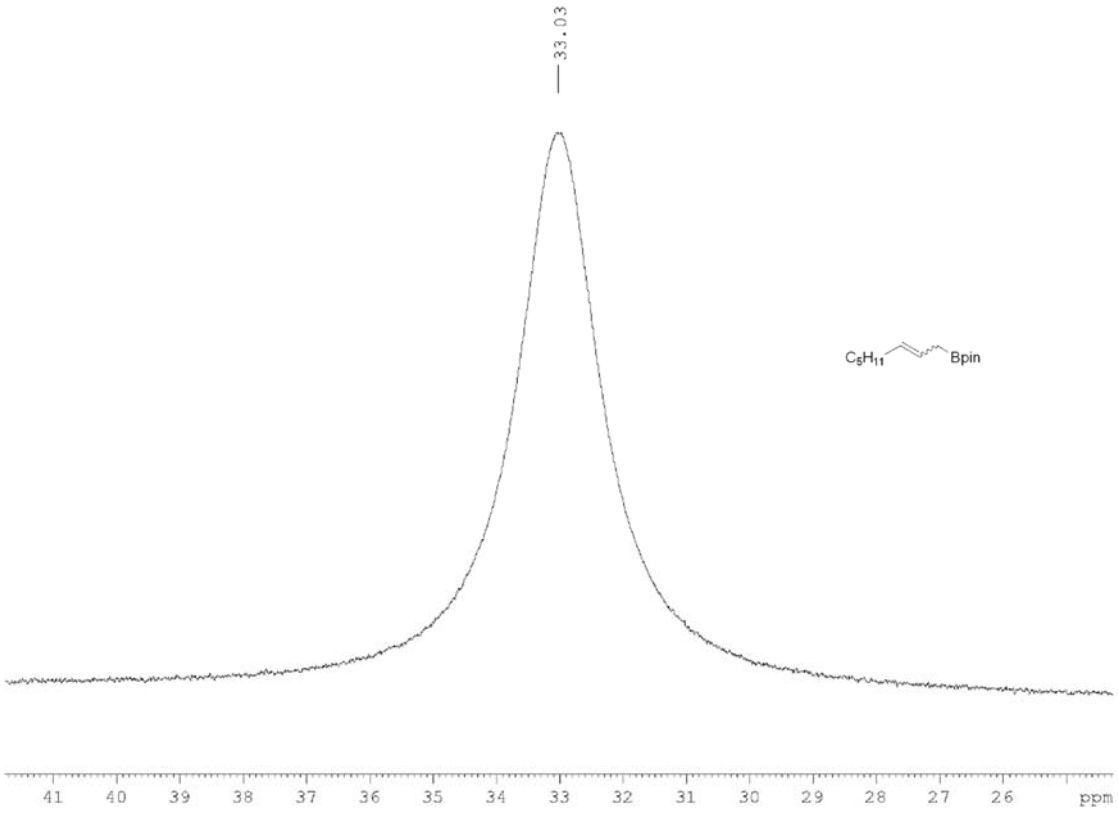
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

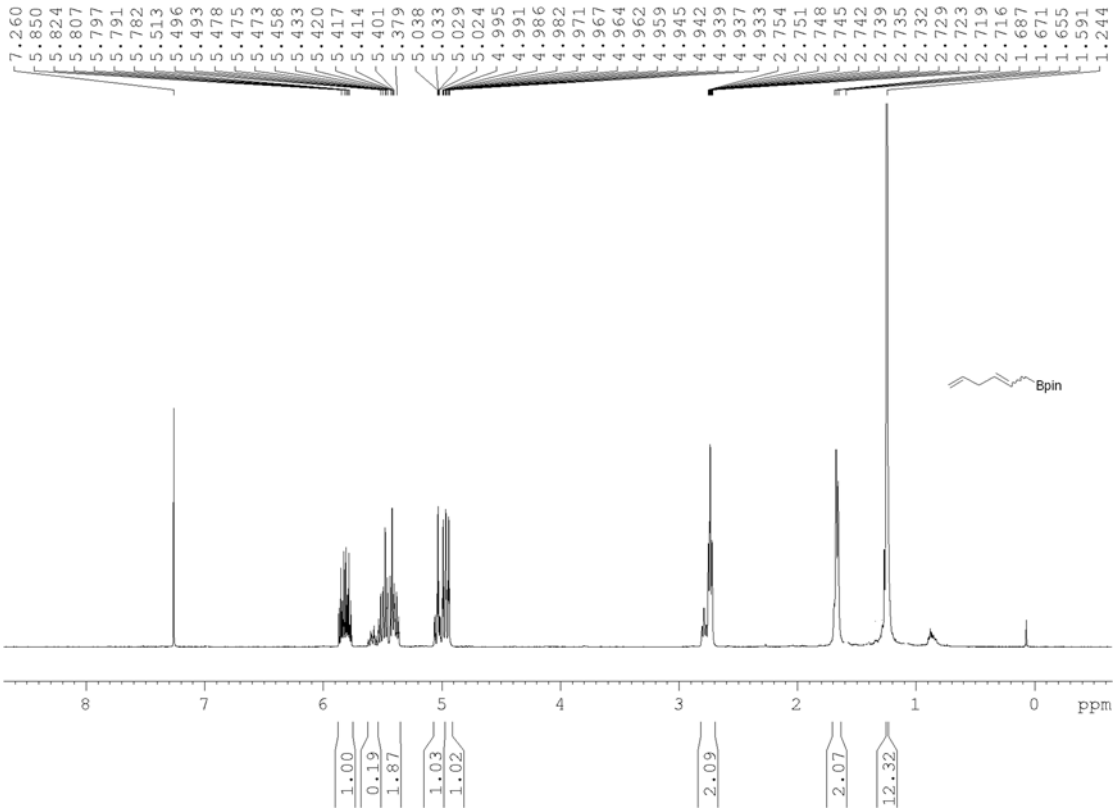


^{11}B NMR (128 MHz, $CDCl_3$)

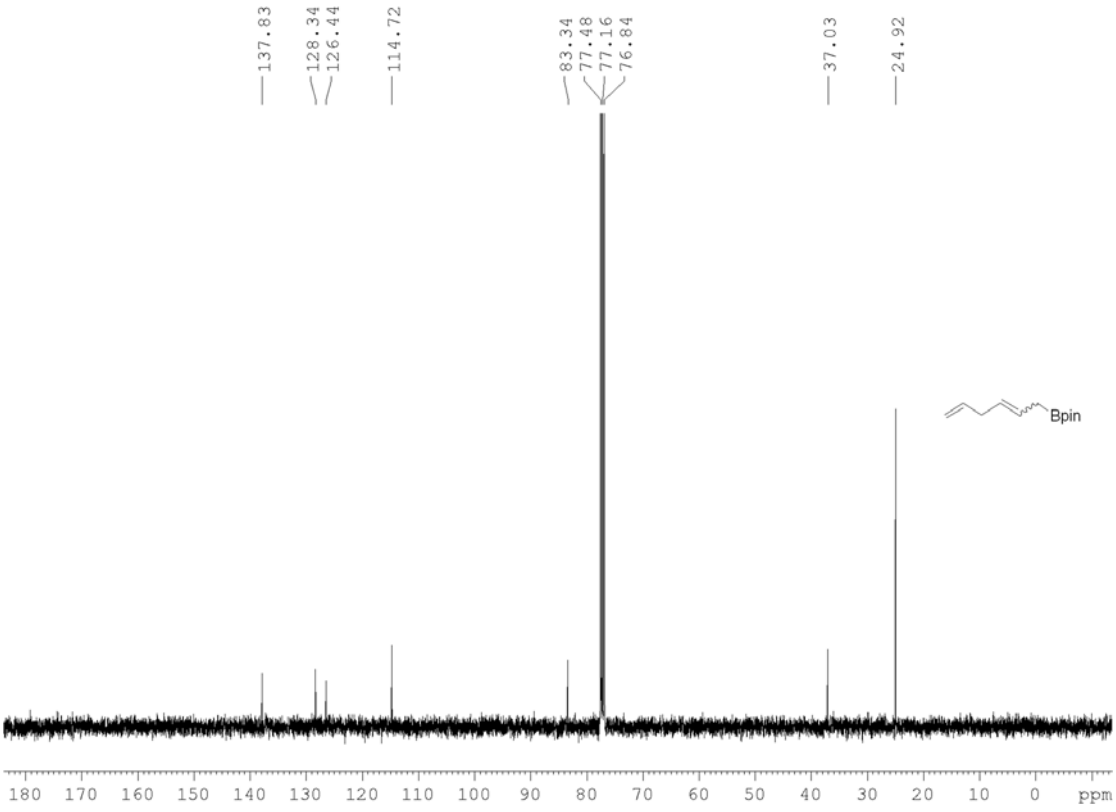


Compound (2-4)i or (4-2)h

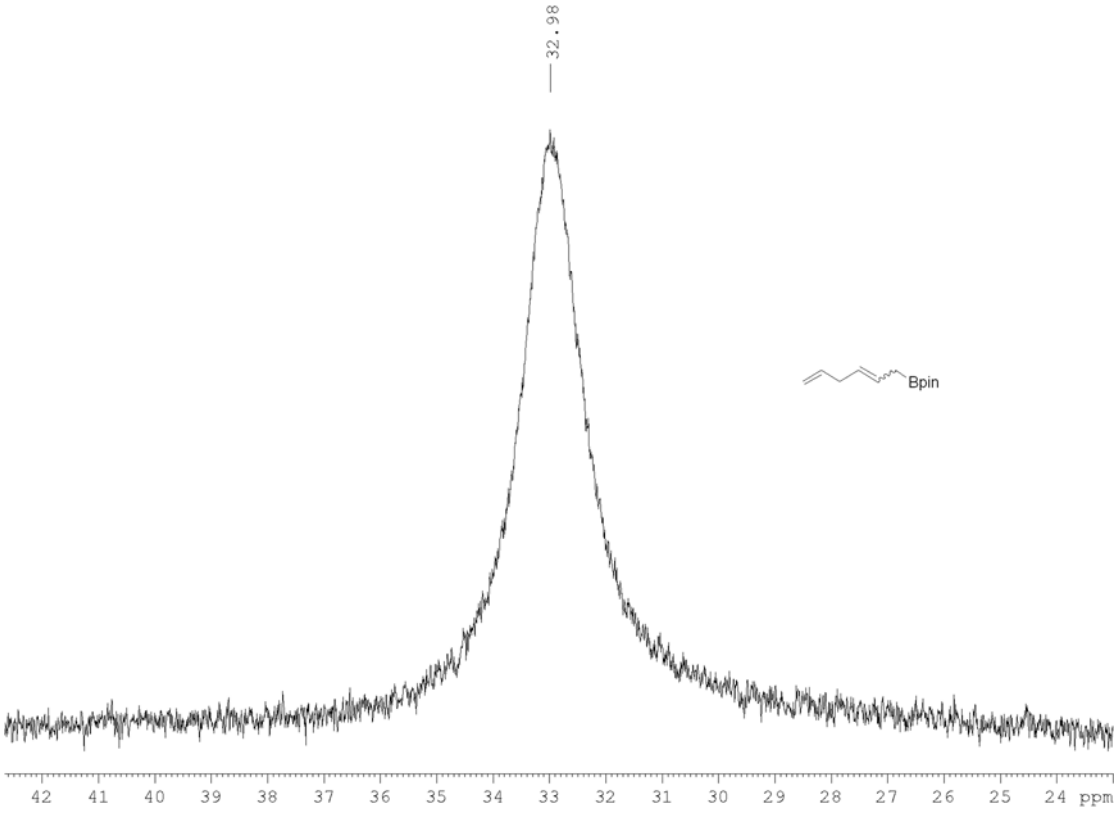
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

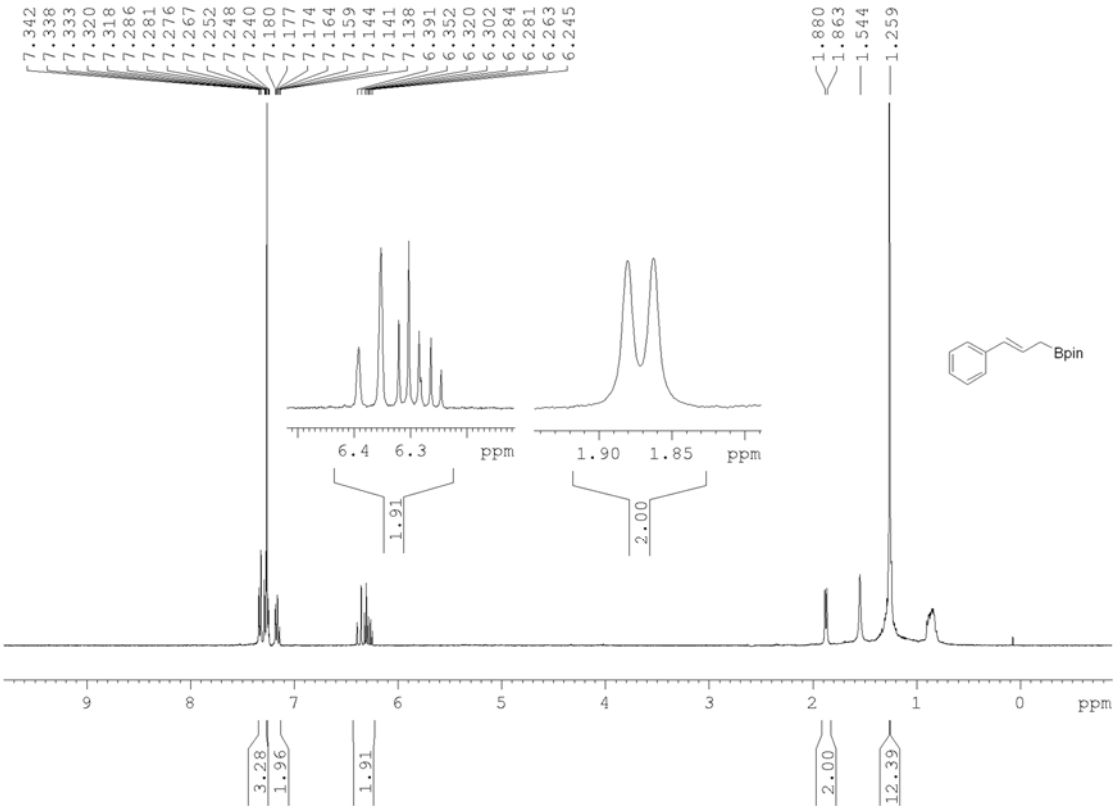


^{11}B NMR (128 MHz, $CDCl_3$)

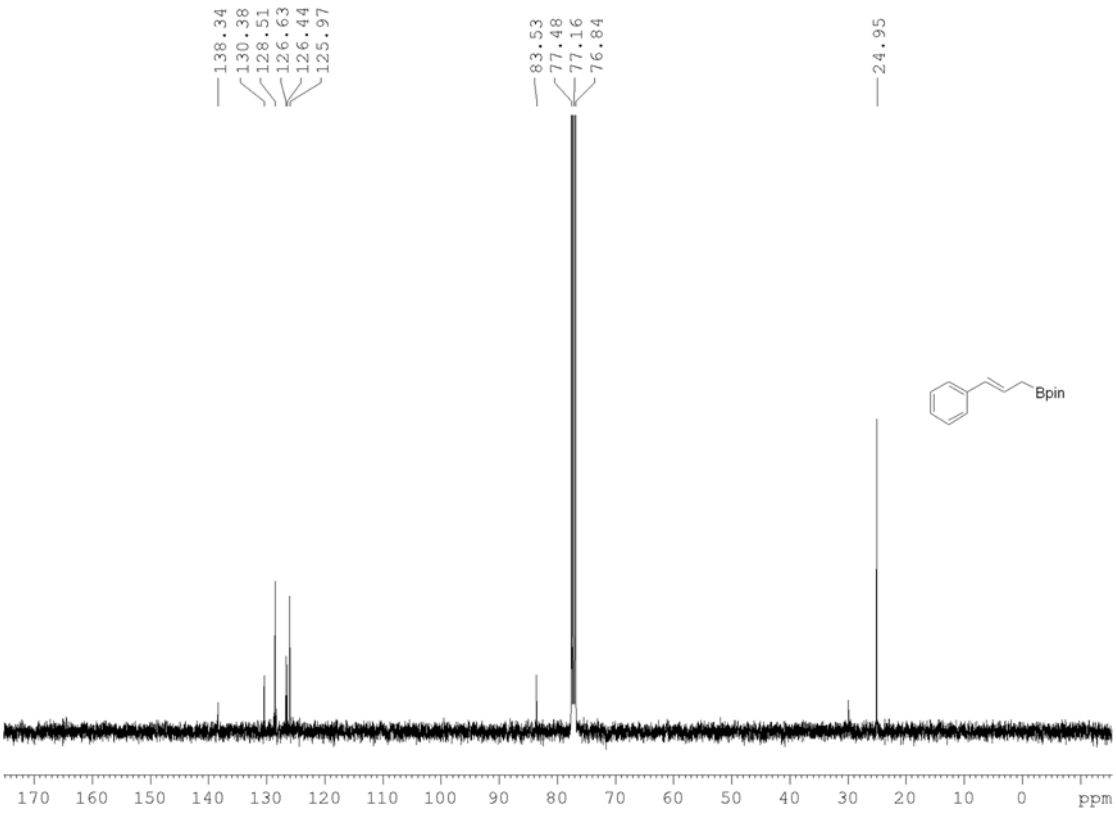


Compound (2-4)j or (4-2)i

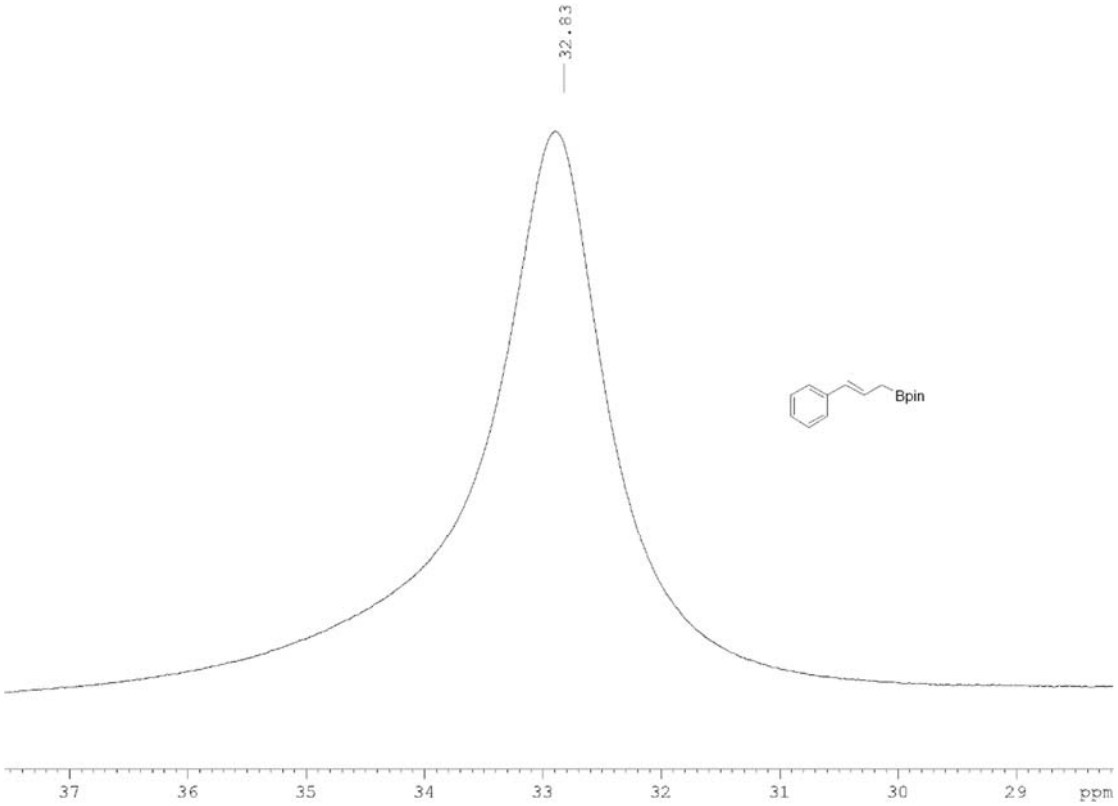
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

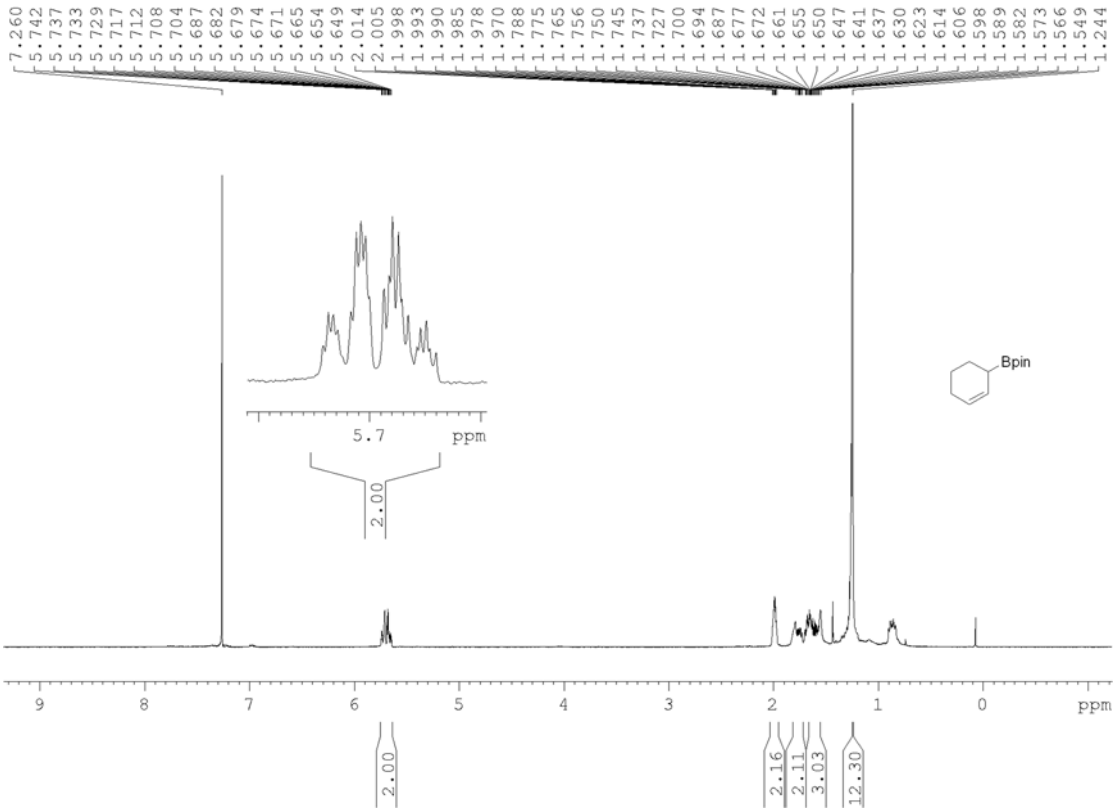


^{11}B NMR (128 MHz, $CDCl_3$)

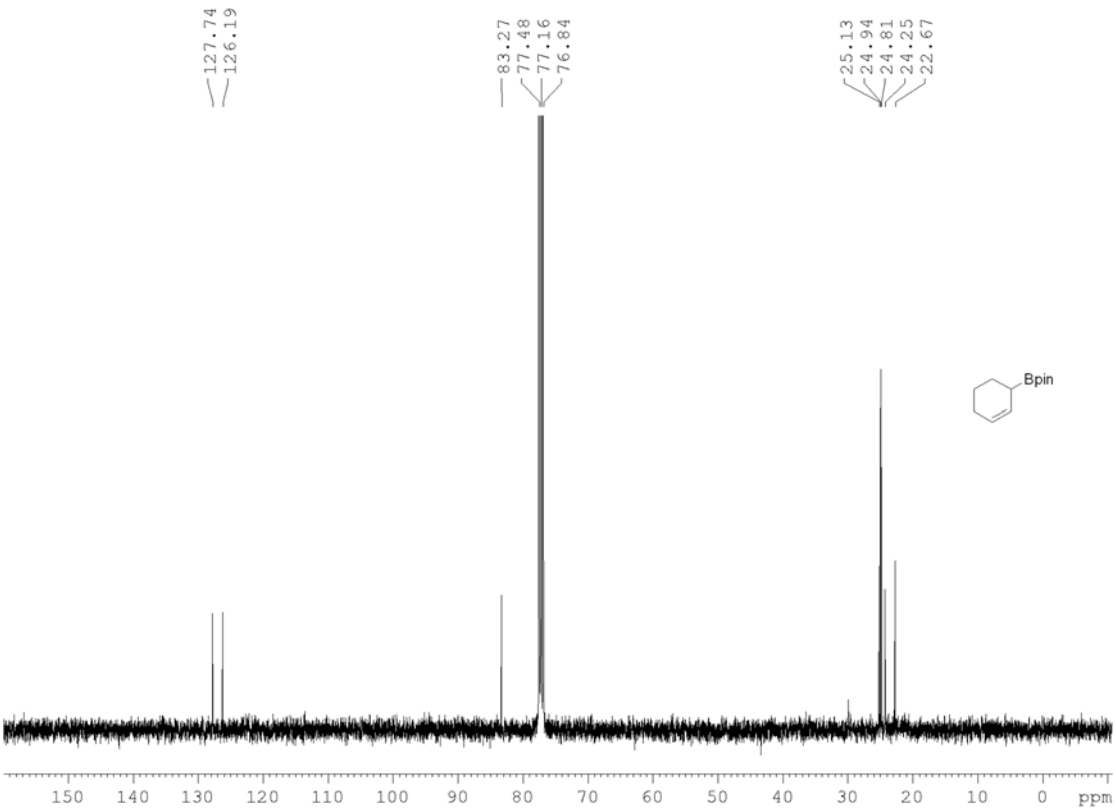


Compound (2-4)k or (4-2)k

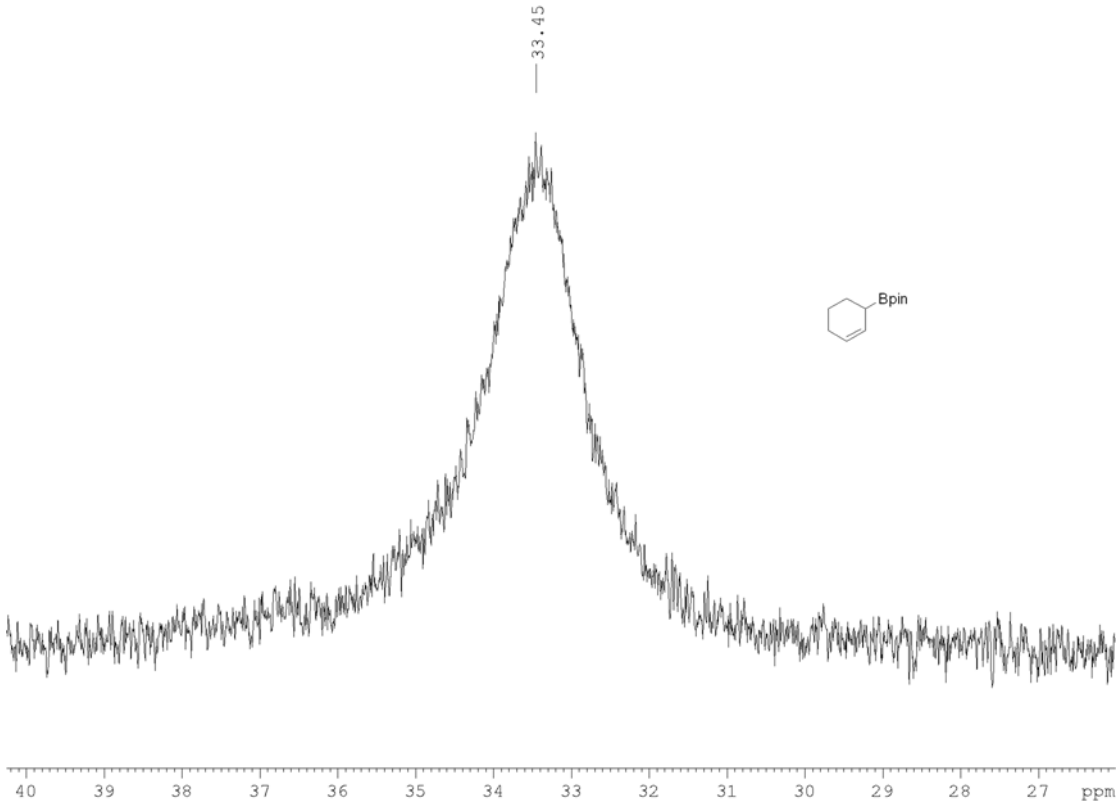
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

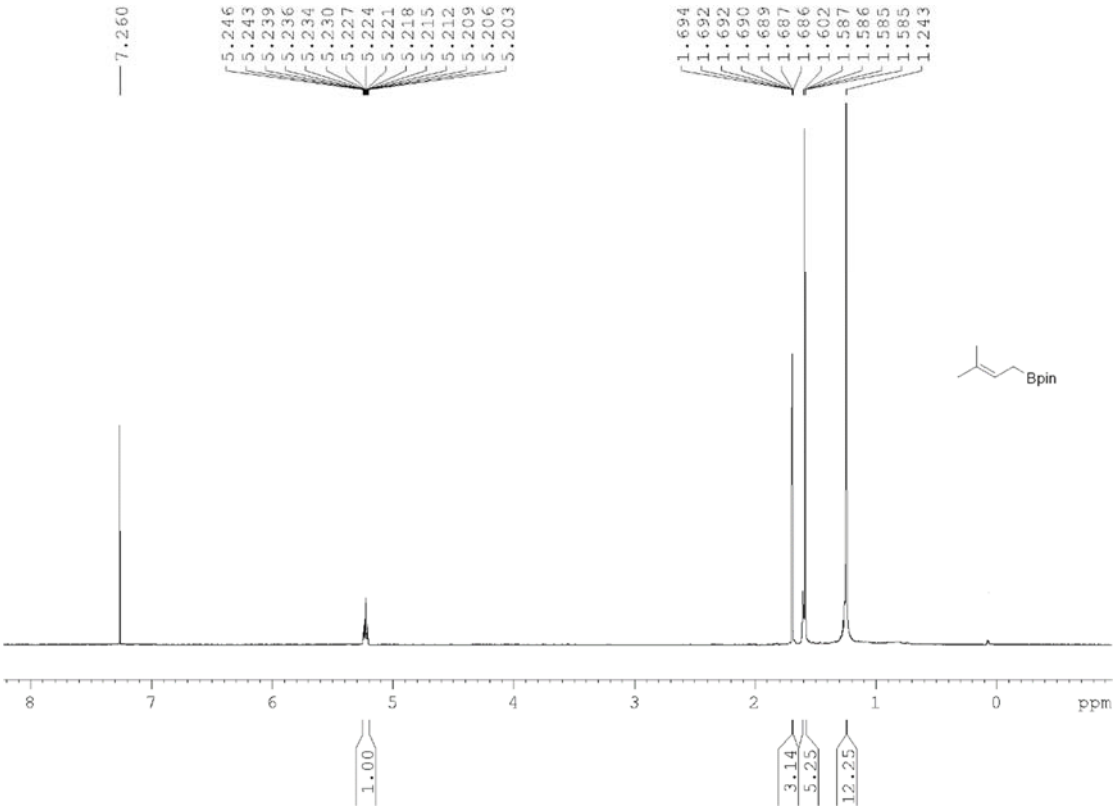


^{11}B NMR (128 MHz, $CDCl_3$)

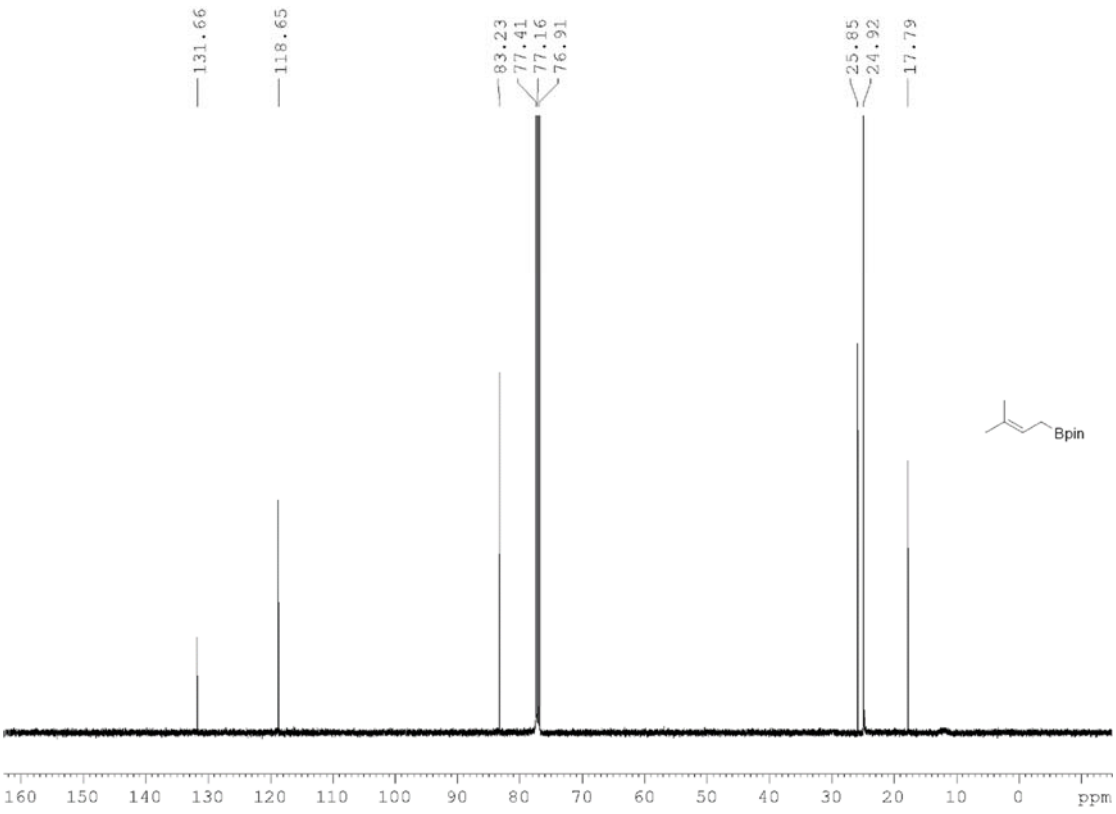


Compound (2-4)l or (3-4)j or (4-2)g

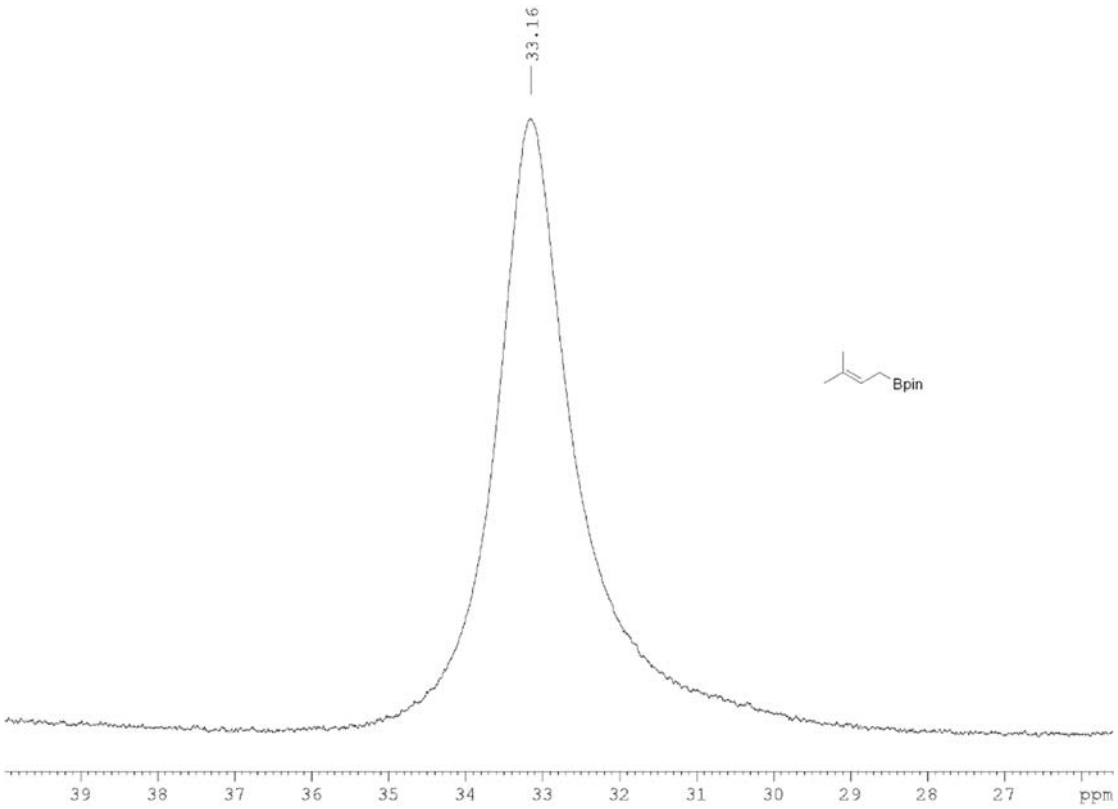
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

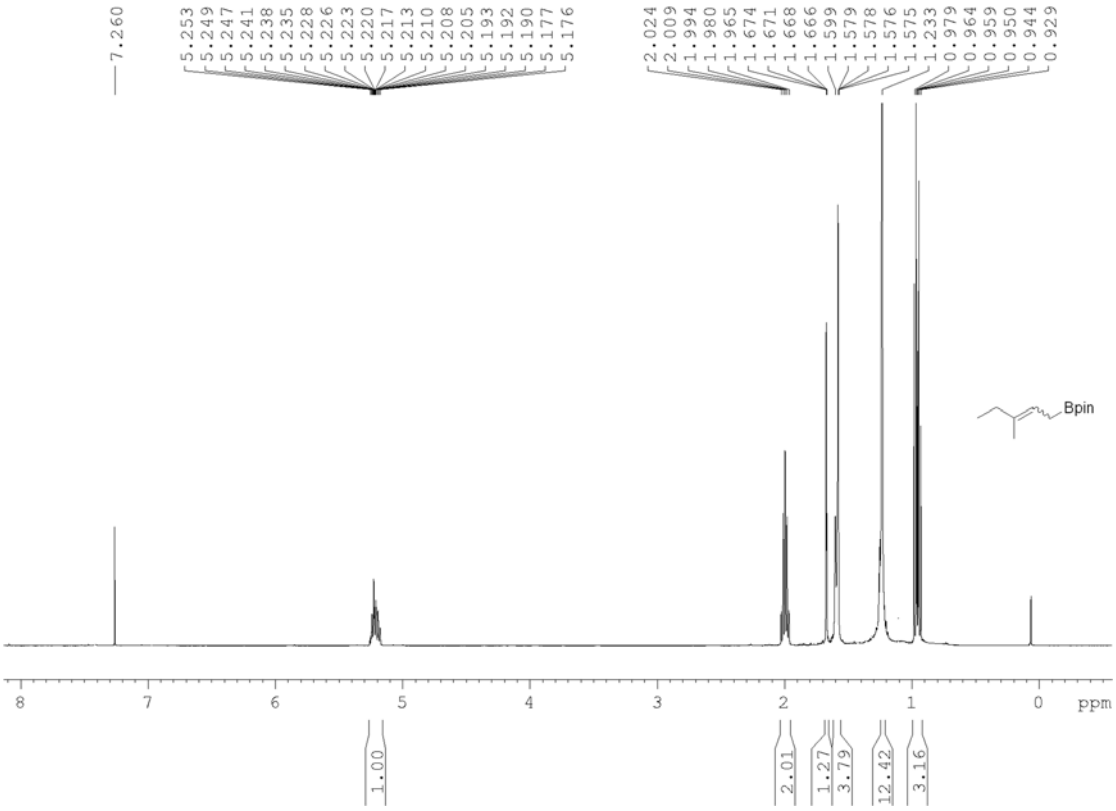


^{11}B NMR (160 MHz, $CDCl_3$)

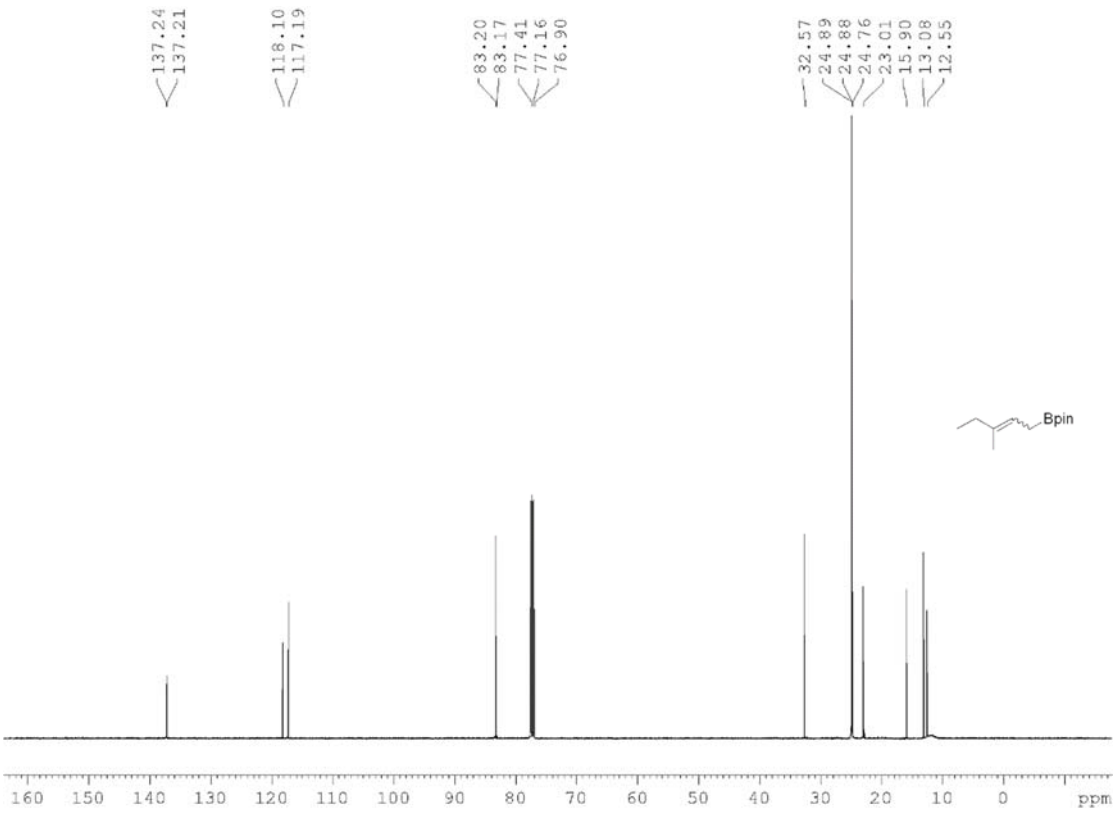


Compound (2-4)m or (4-2)f

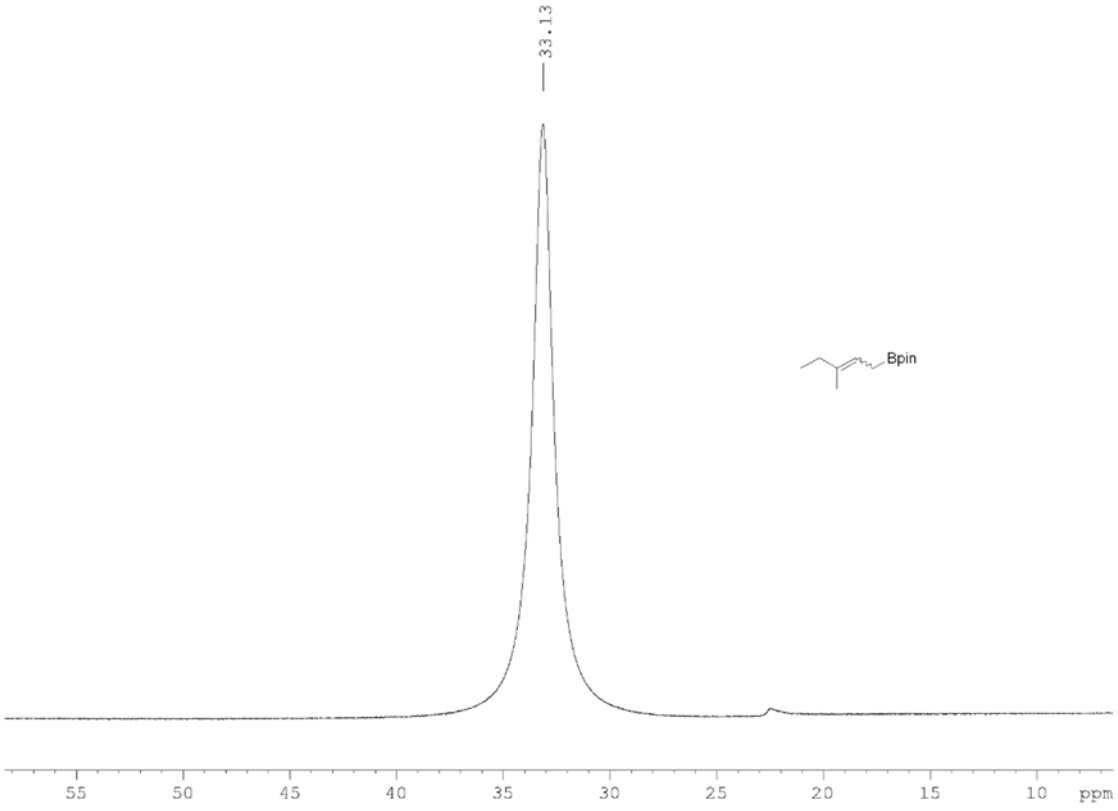
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

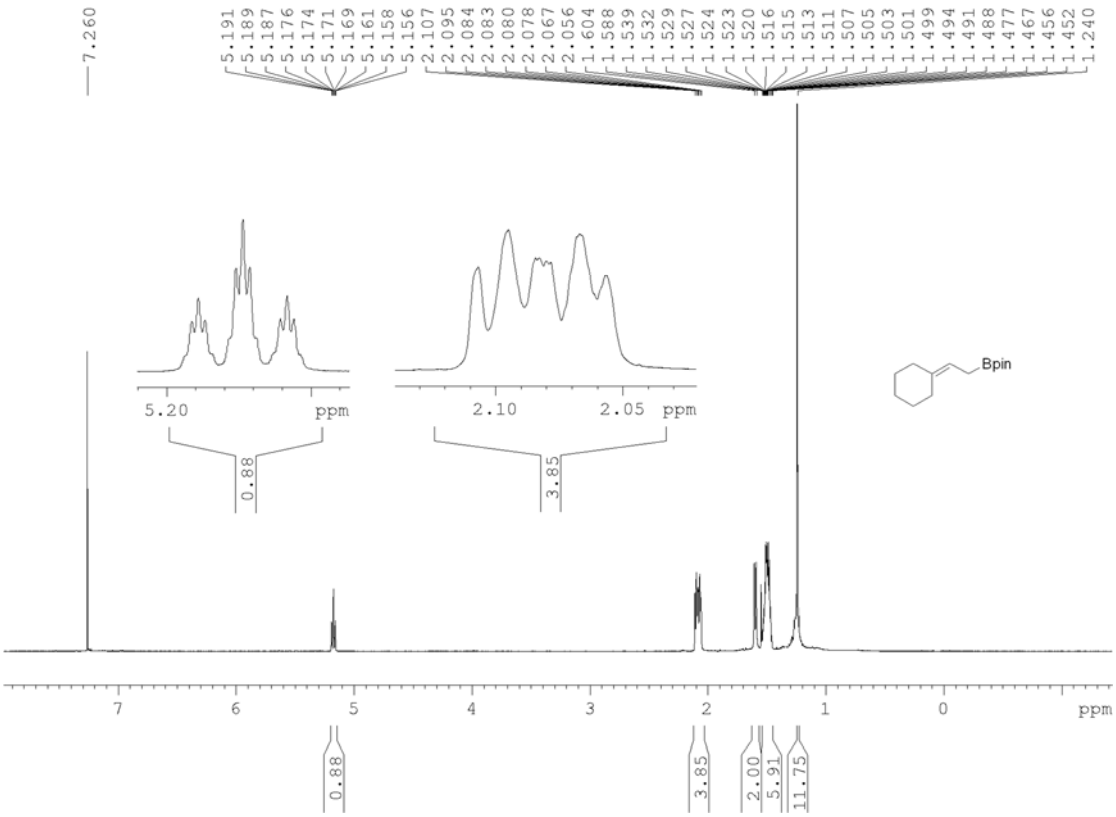


^{11}B NMR (160 MHz, $CDCl_3$)

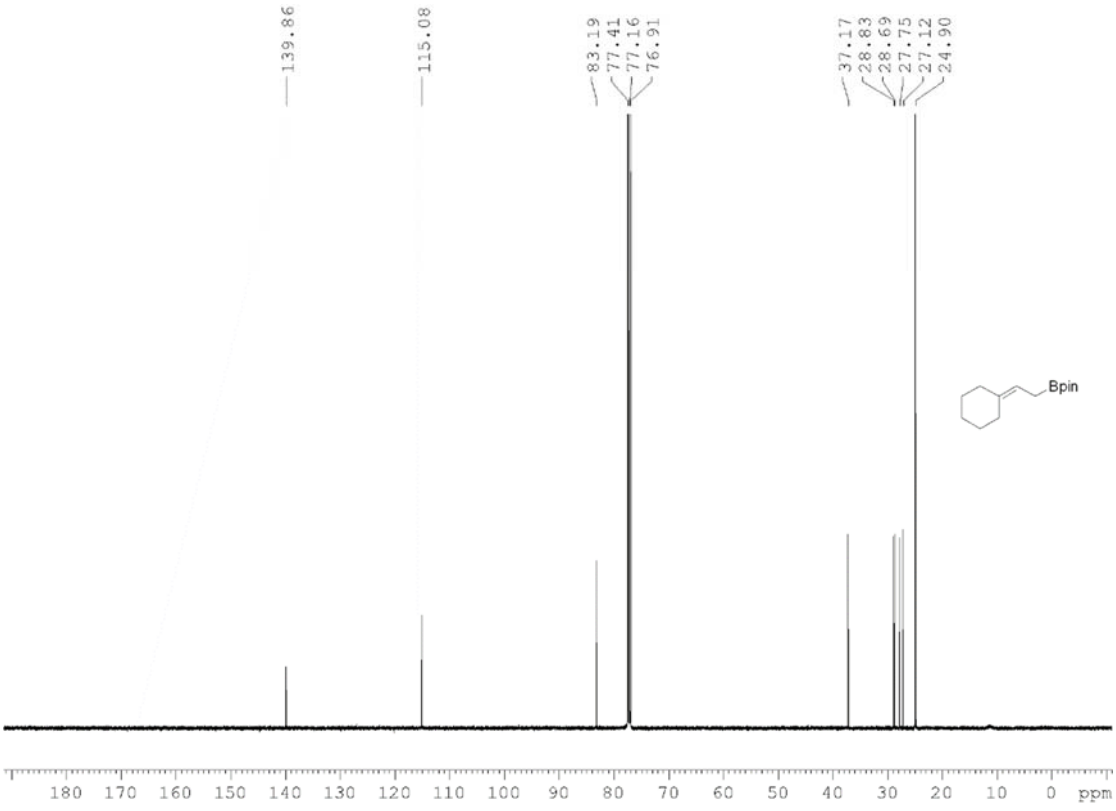


Compound (2-4)n or (3-4)h or (4-2)d

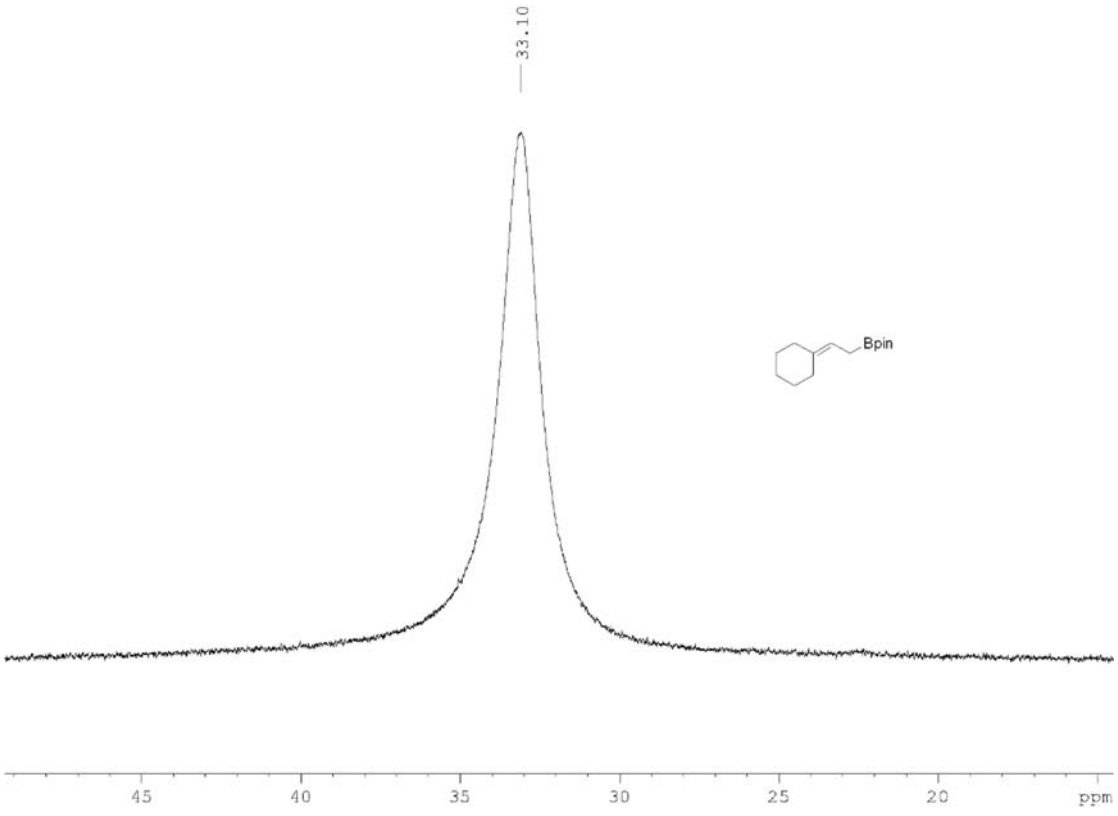
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

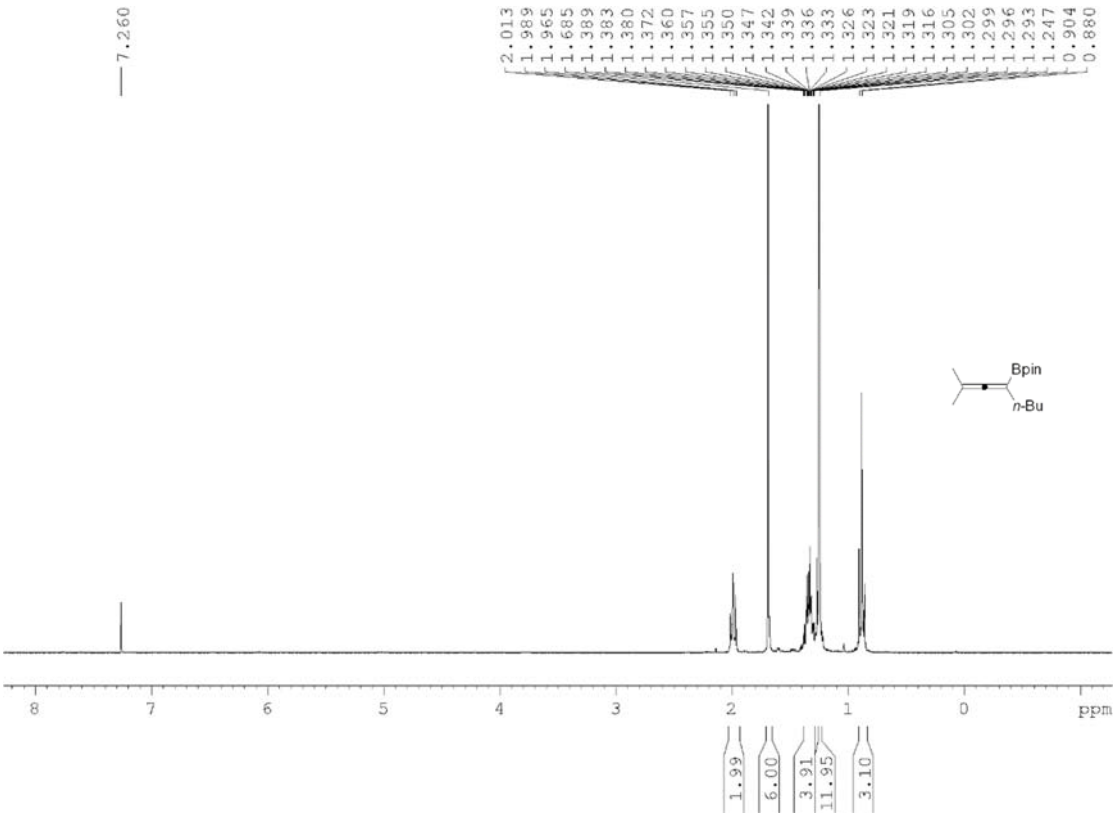


^{11}B NMR (160 MHz, $CDCl_3$)

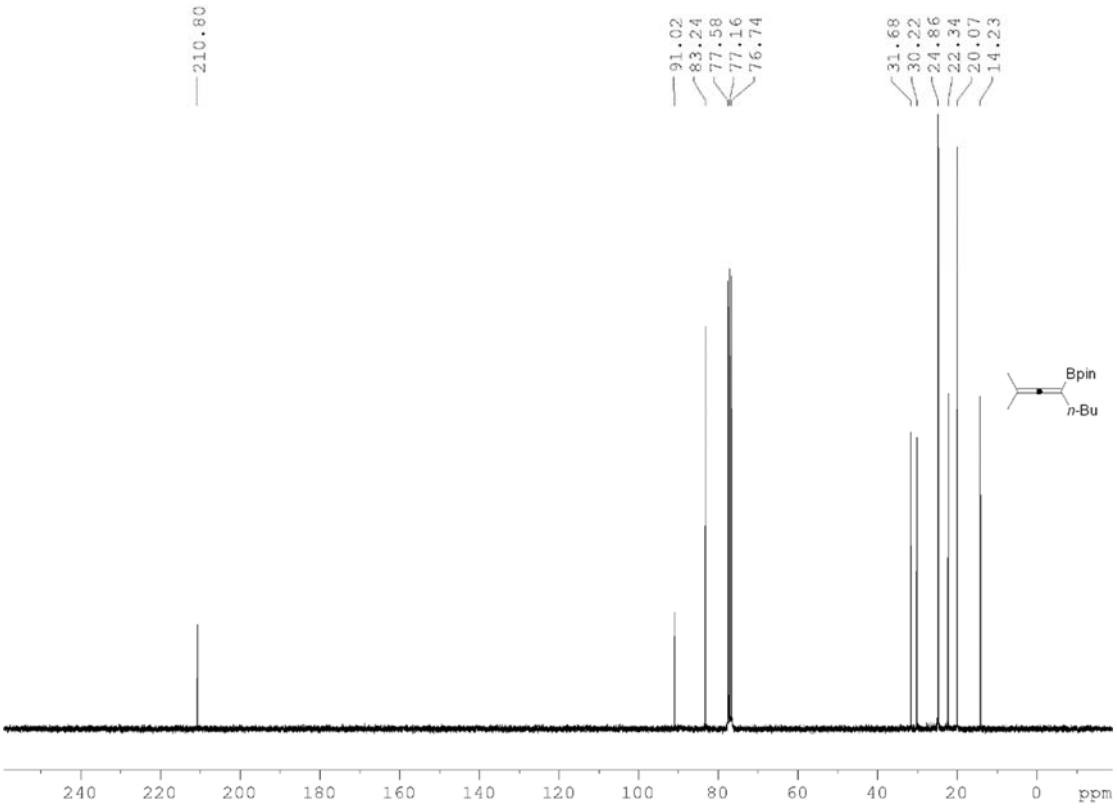


Compound (2-6)a

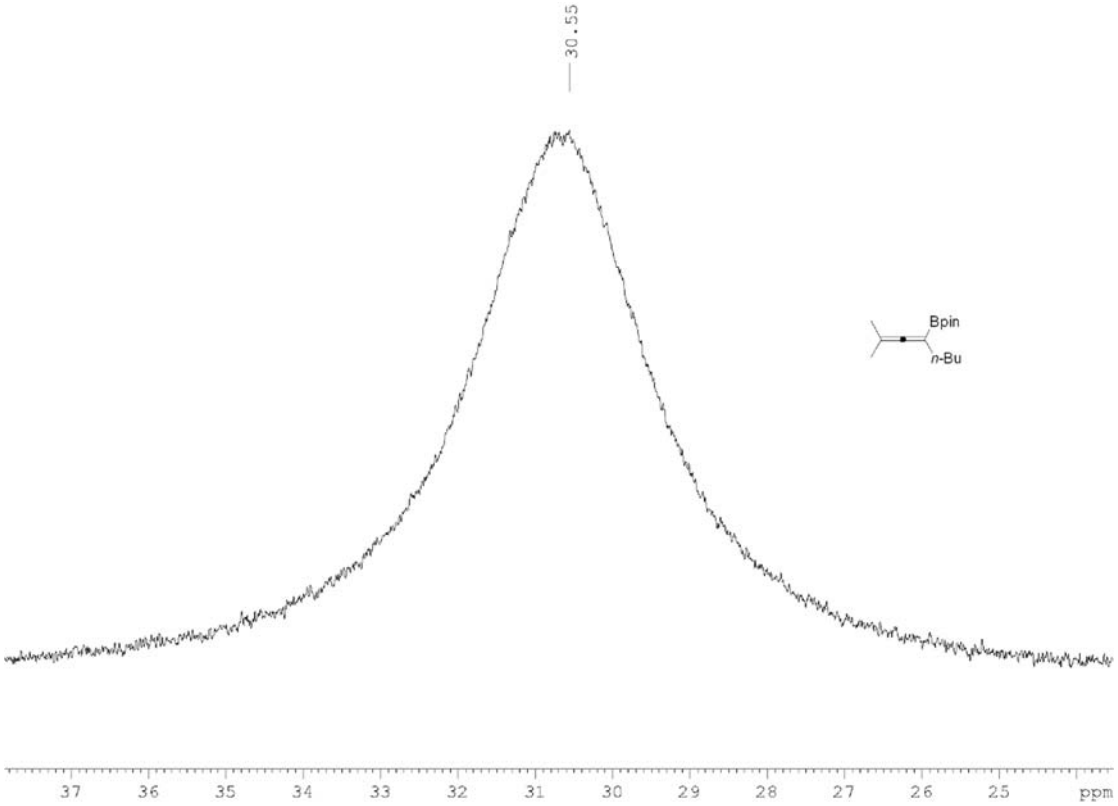
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

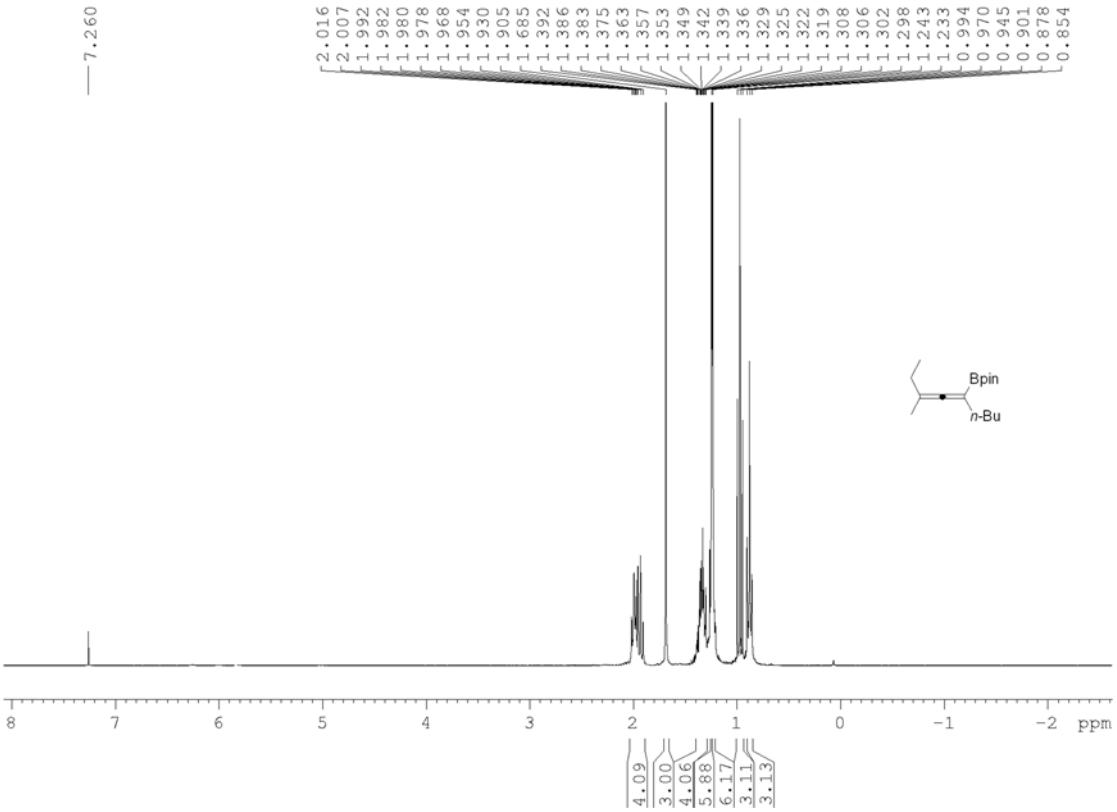


^{11}B NMR (96 MHz, $CDCl_3$)

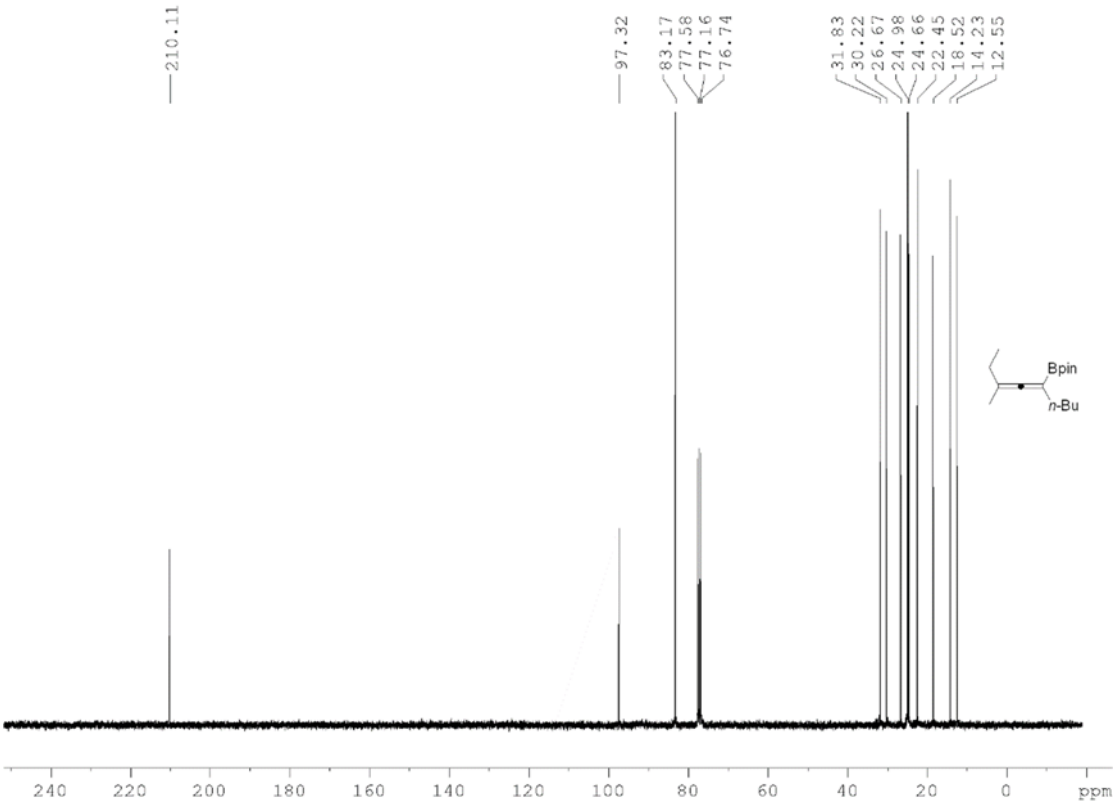


Compound (2-6)b

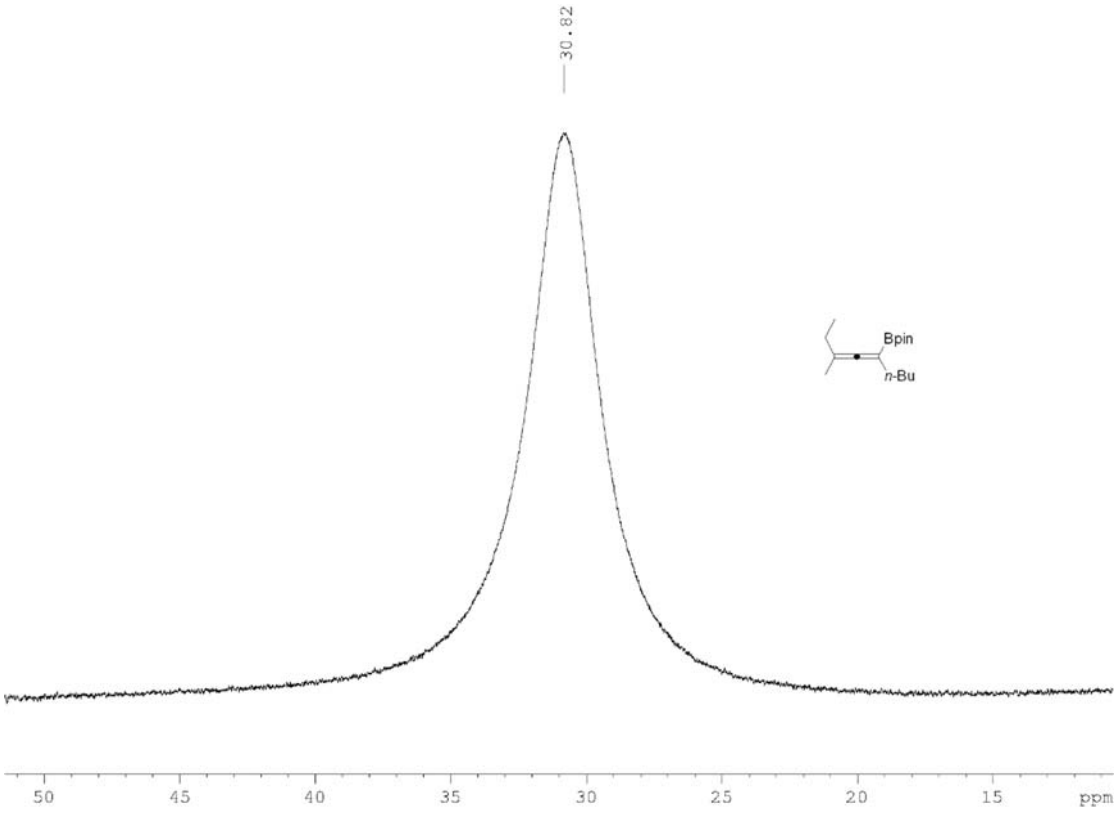
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

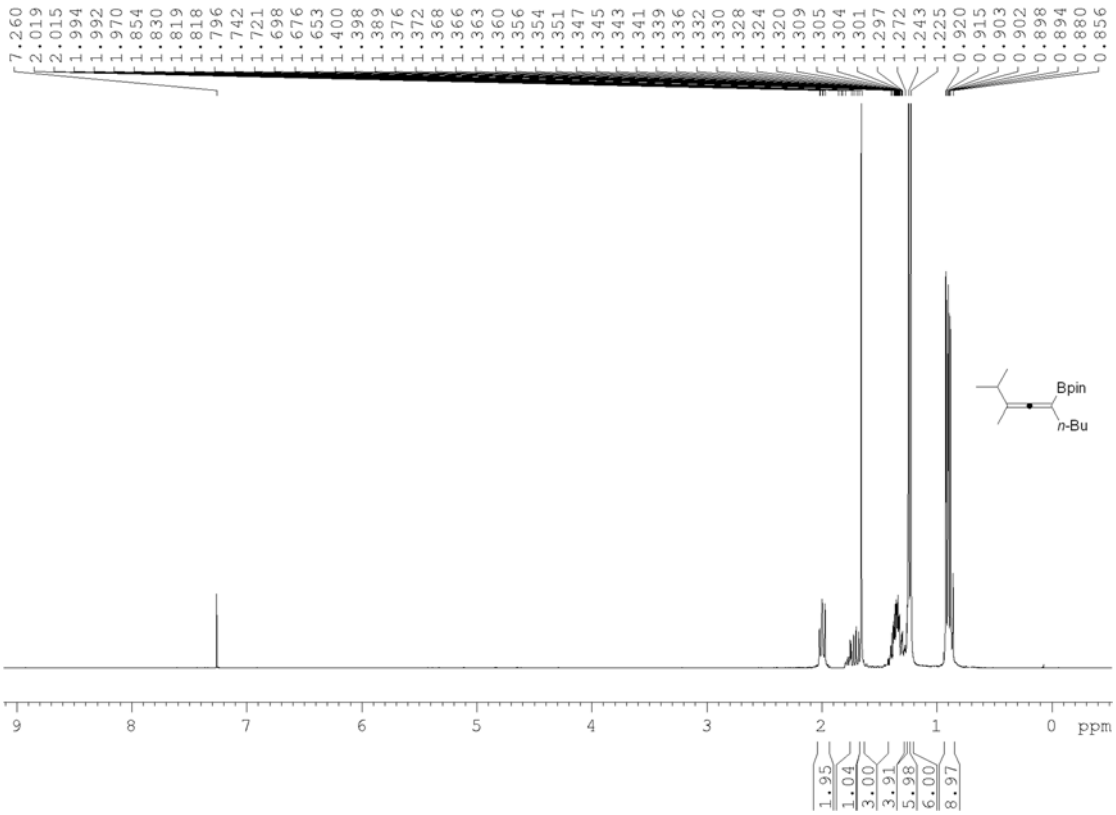


^{11}B NMR (96 MHz, $CDCl_3$)

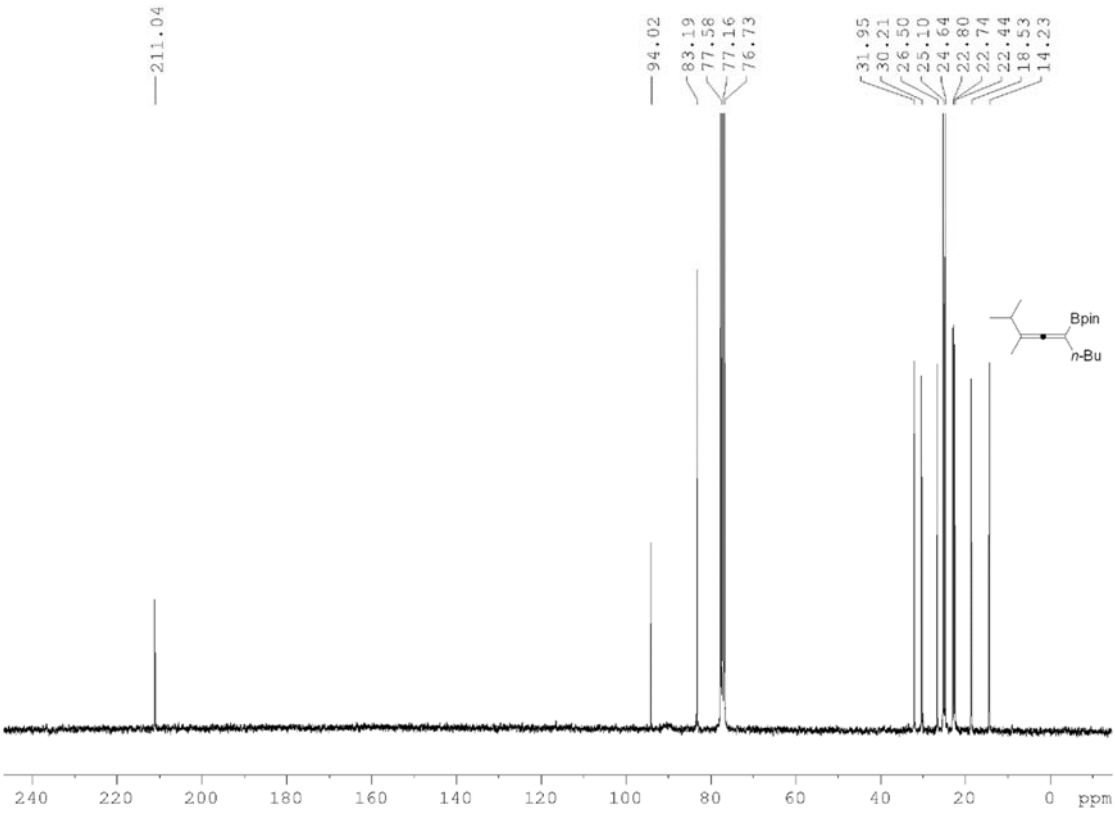


Compound (2-6)c

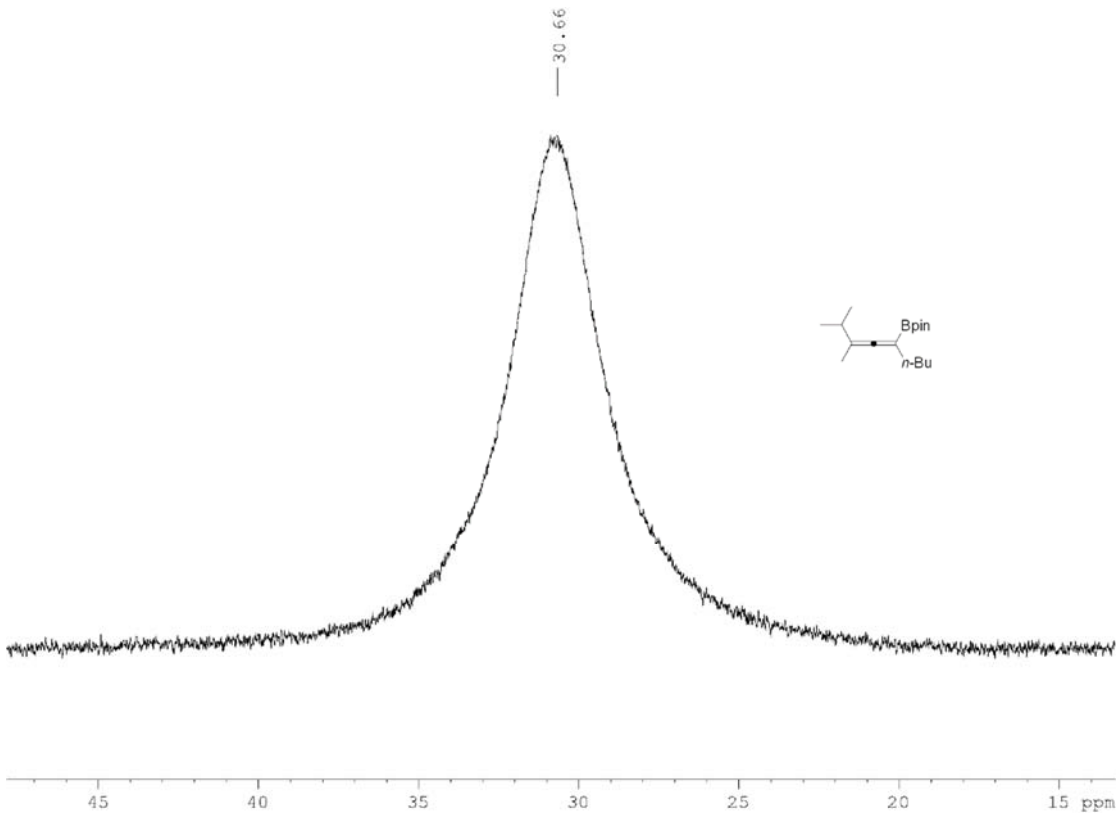
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

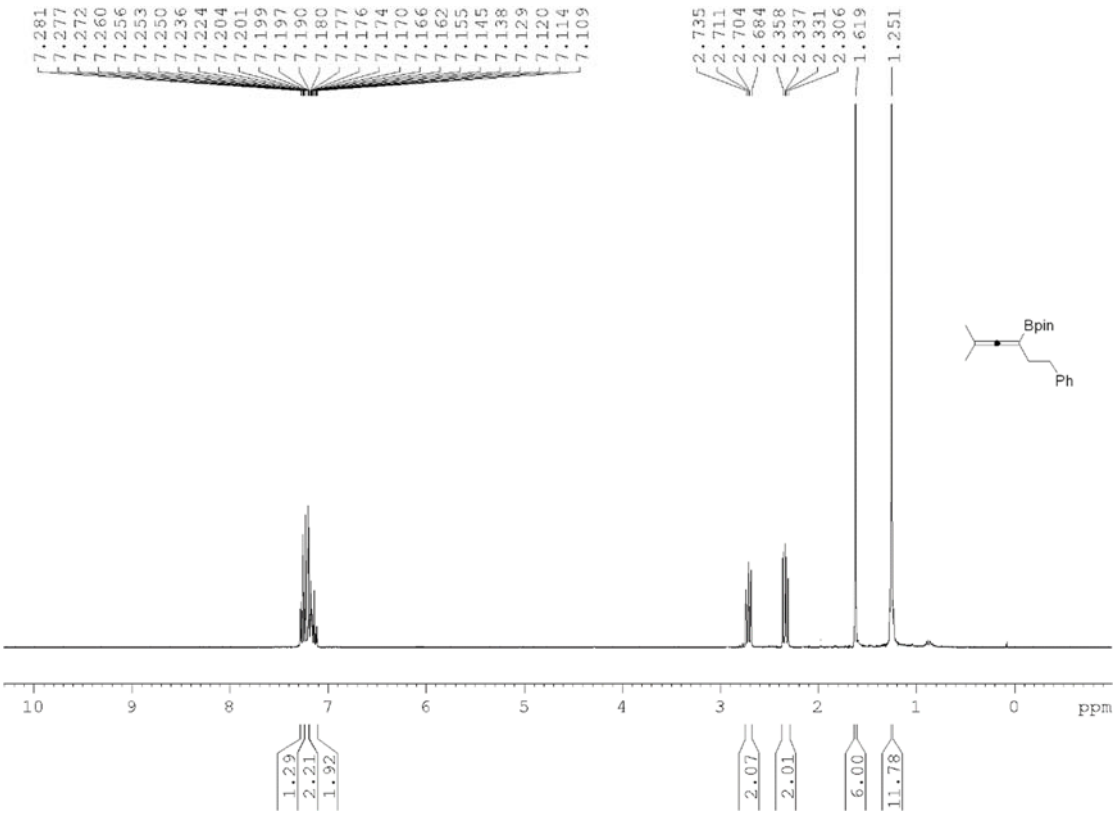


^{11}B NMR (96 MHz, $CDCl_3$)

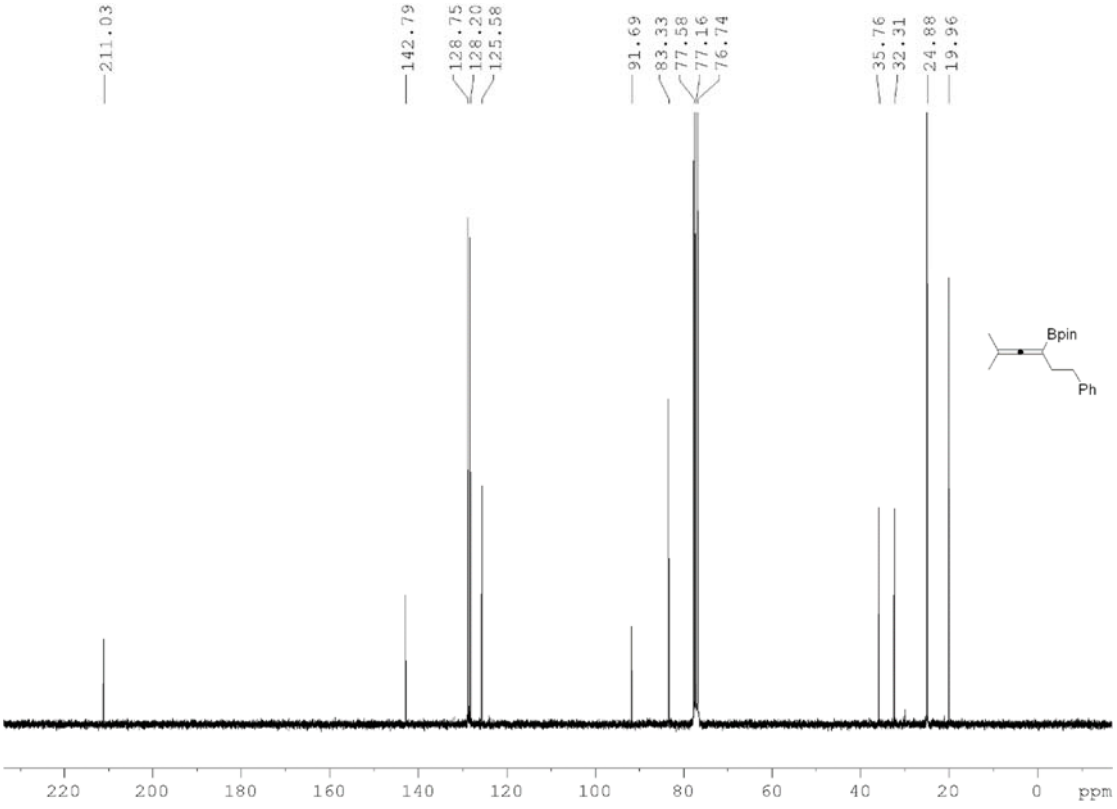


Compound (2-6)d

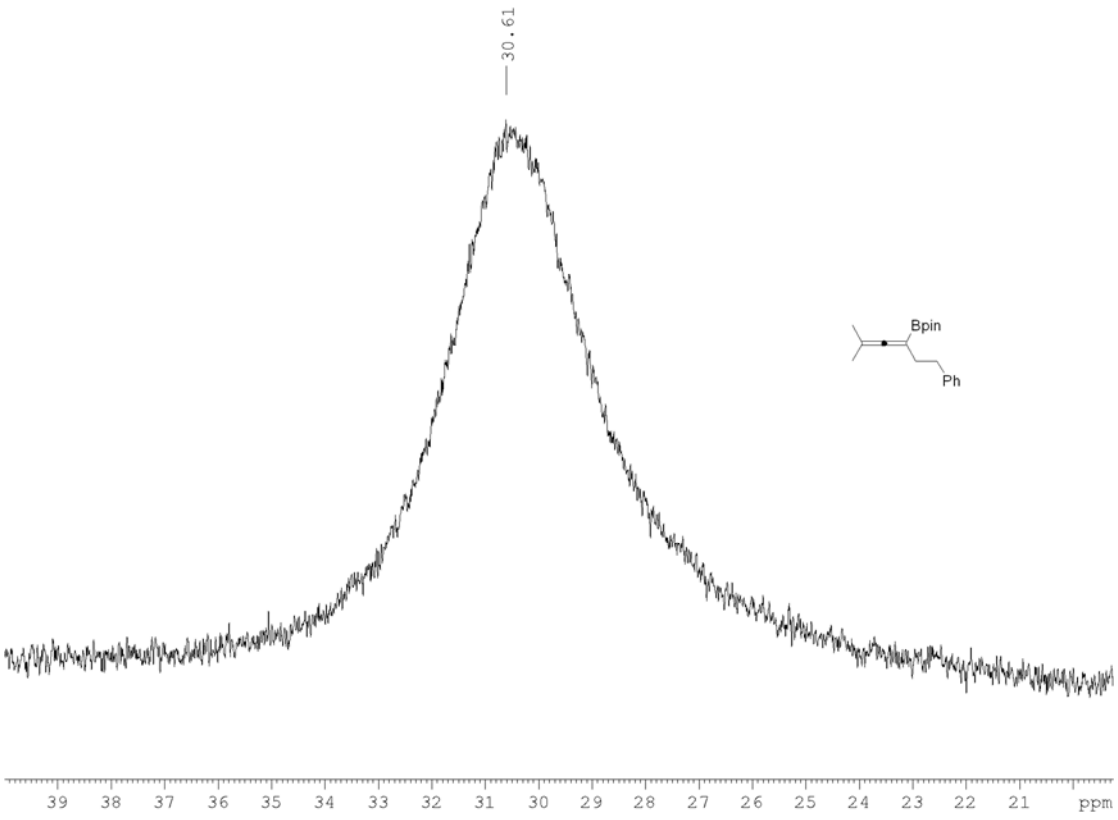
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

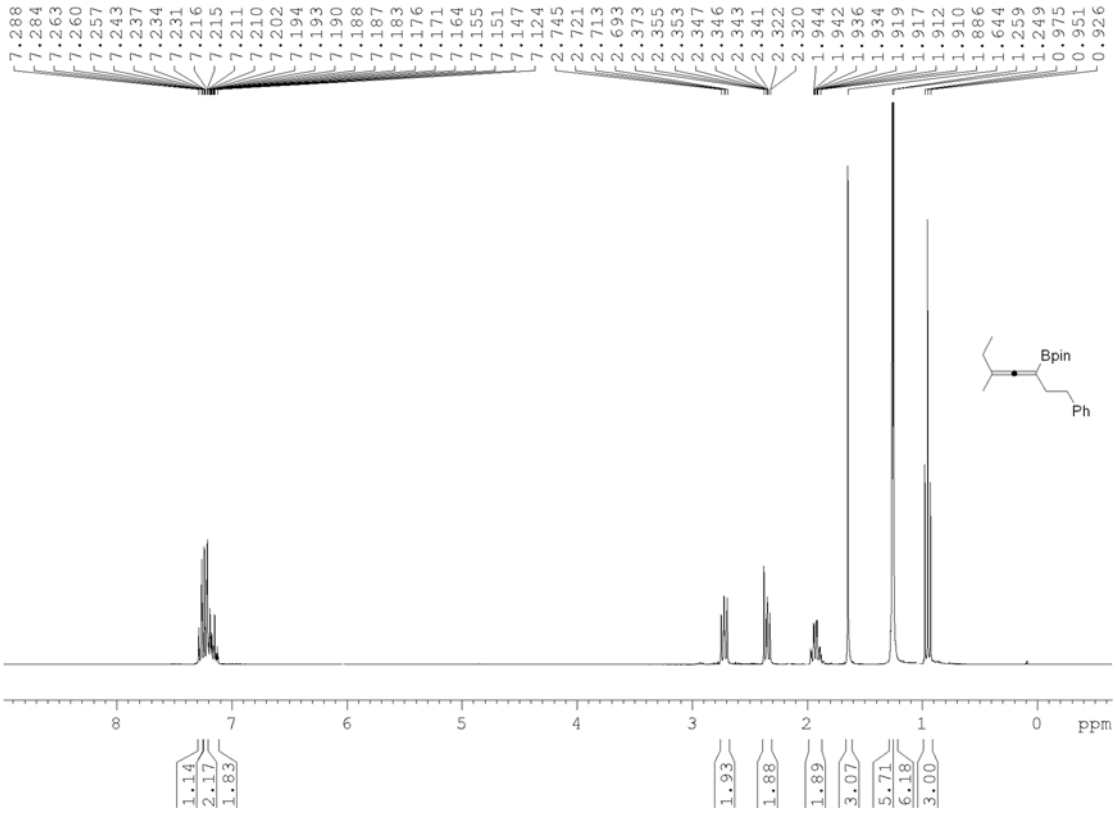


^{11}B NMR (96 MHz, $CDCl_3$)

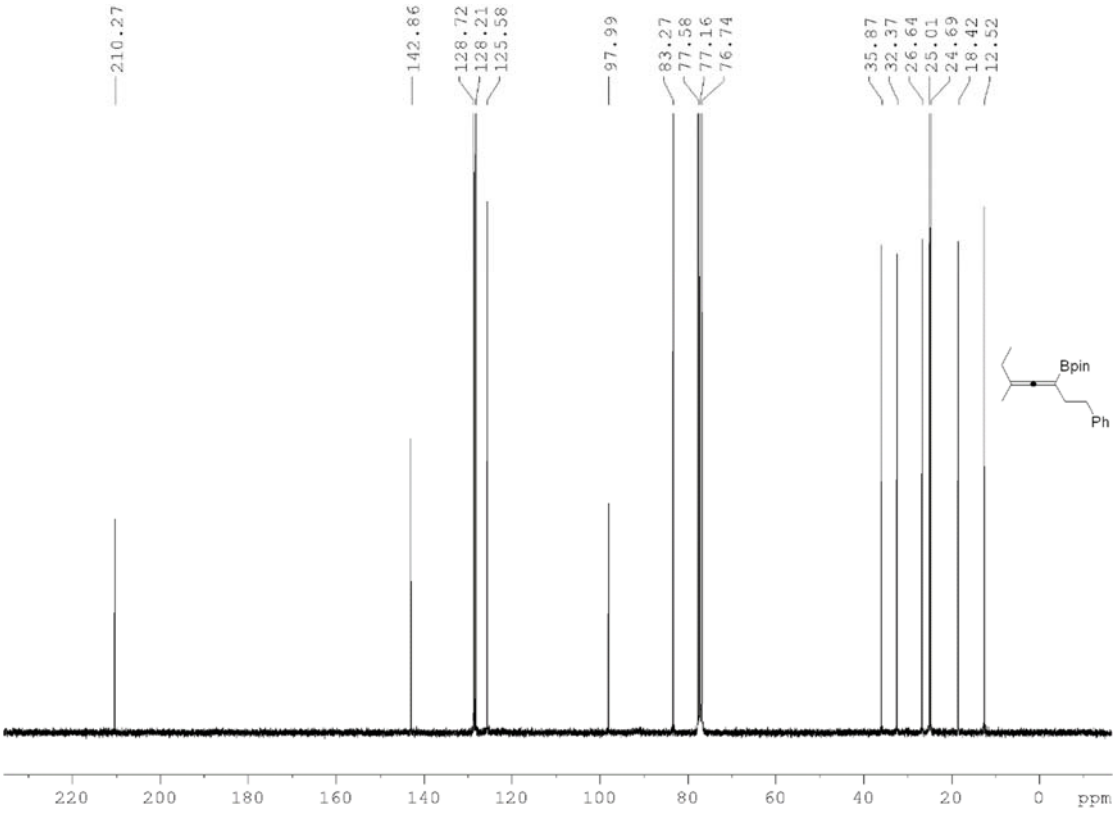


Compound (2-6)e

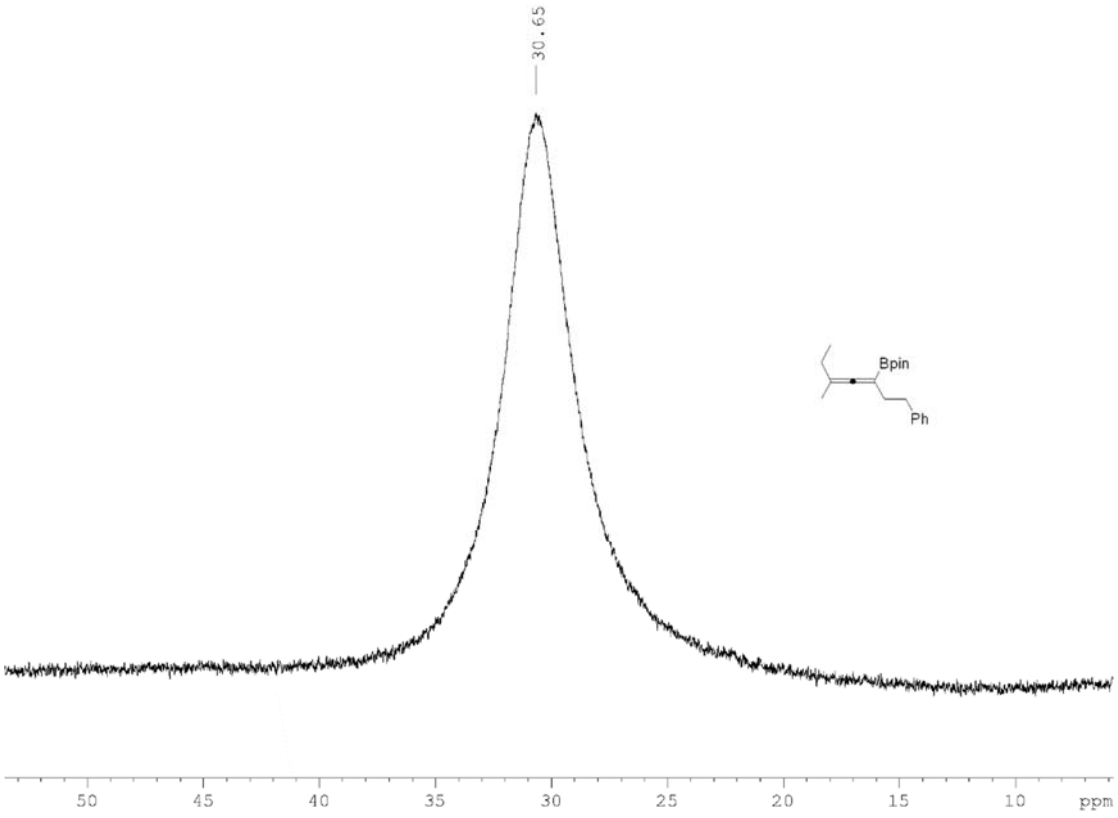
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

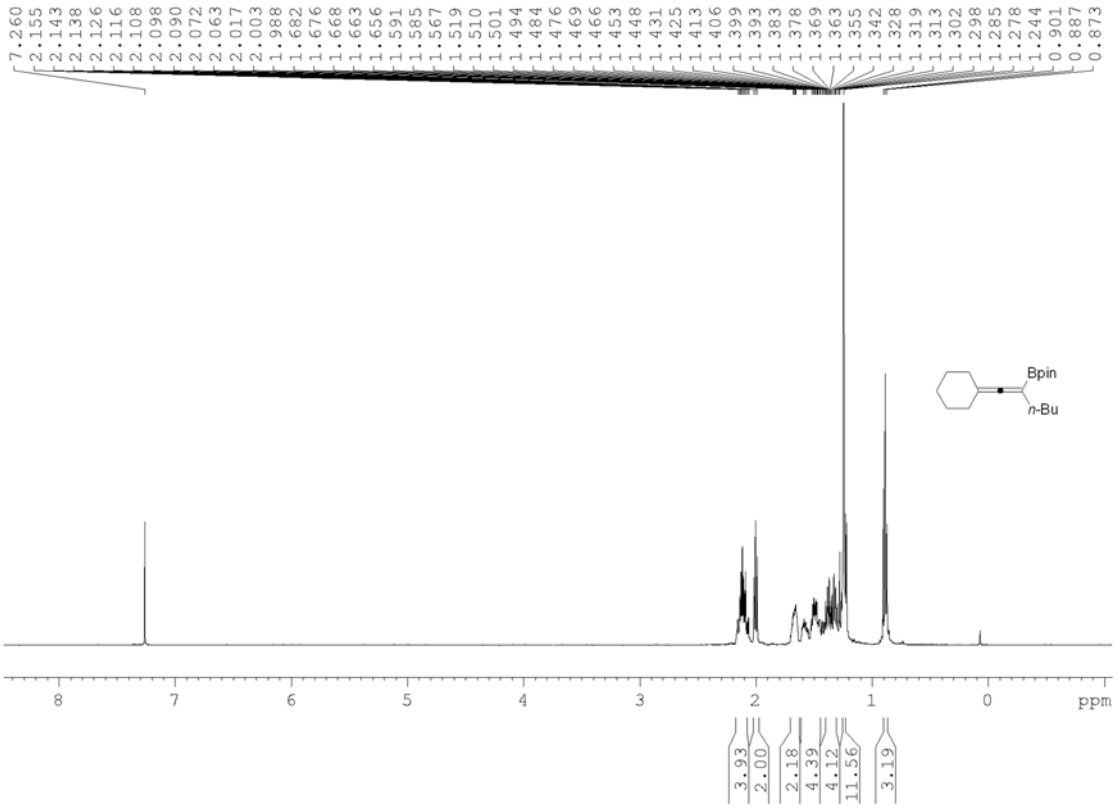


^{11}B NMR (96 MHz, $CDCl_3$)

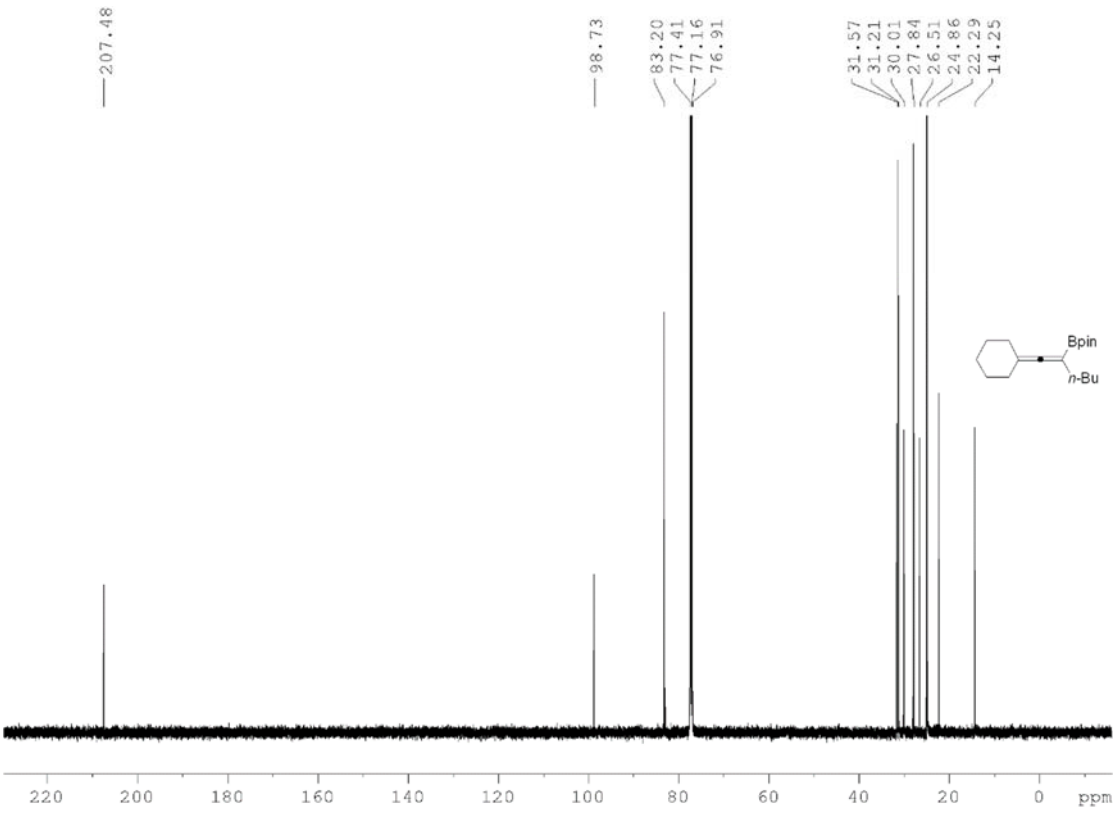


Compound (2-6)f

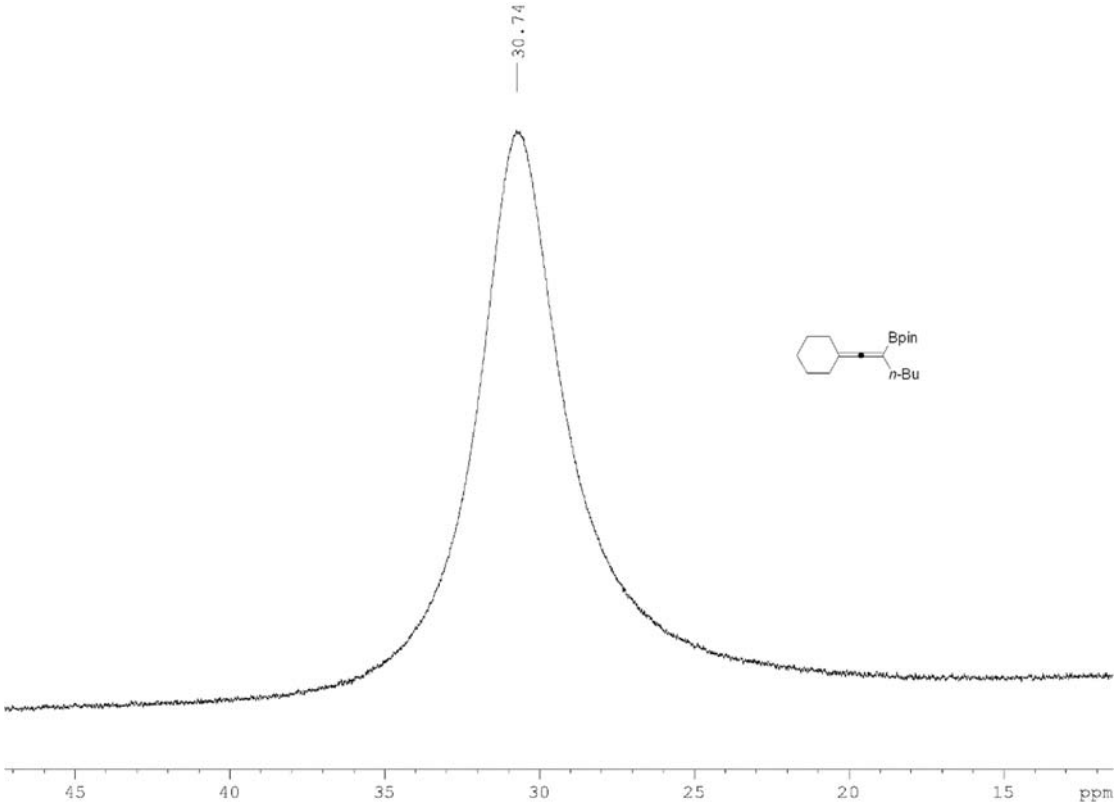
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

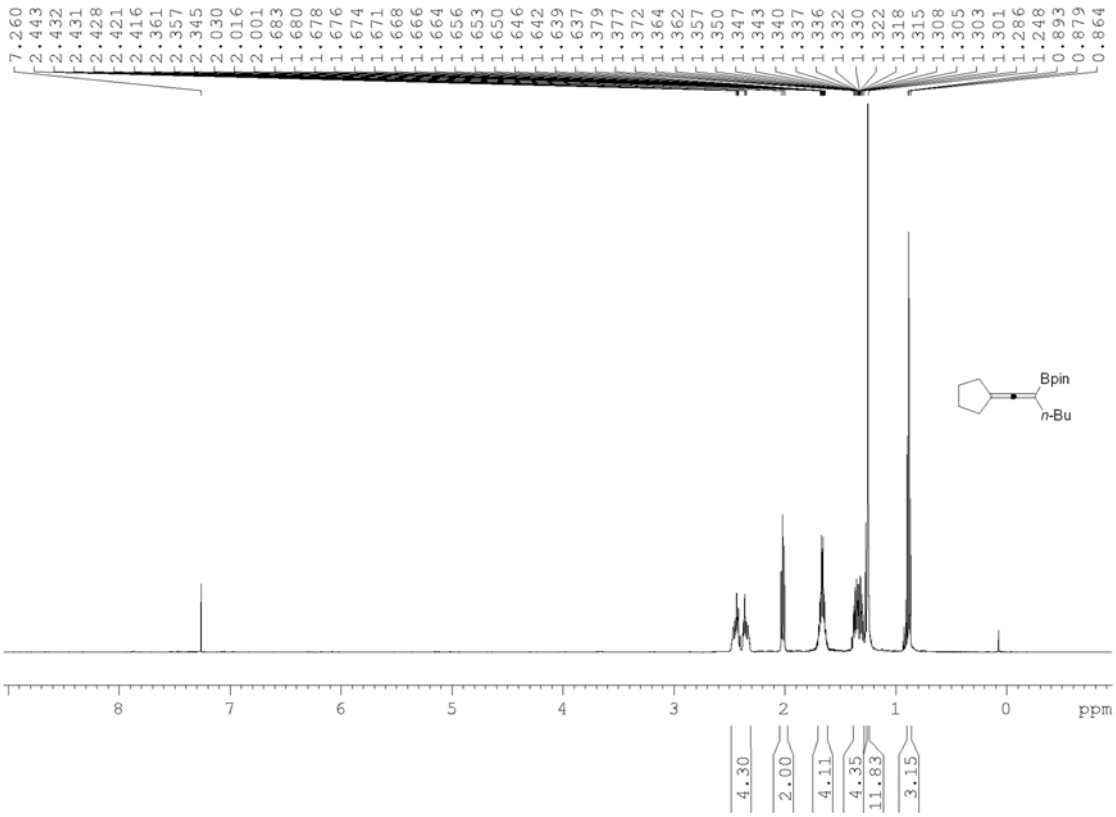


^{11}B NMR (160 MHz, $CDCl_3$)

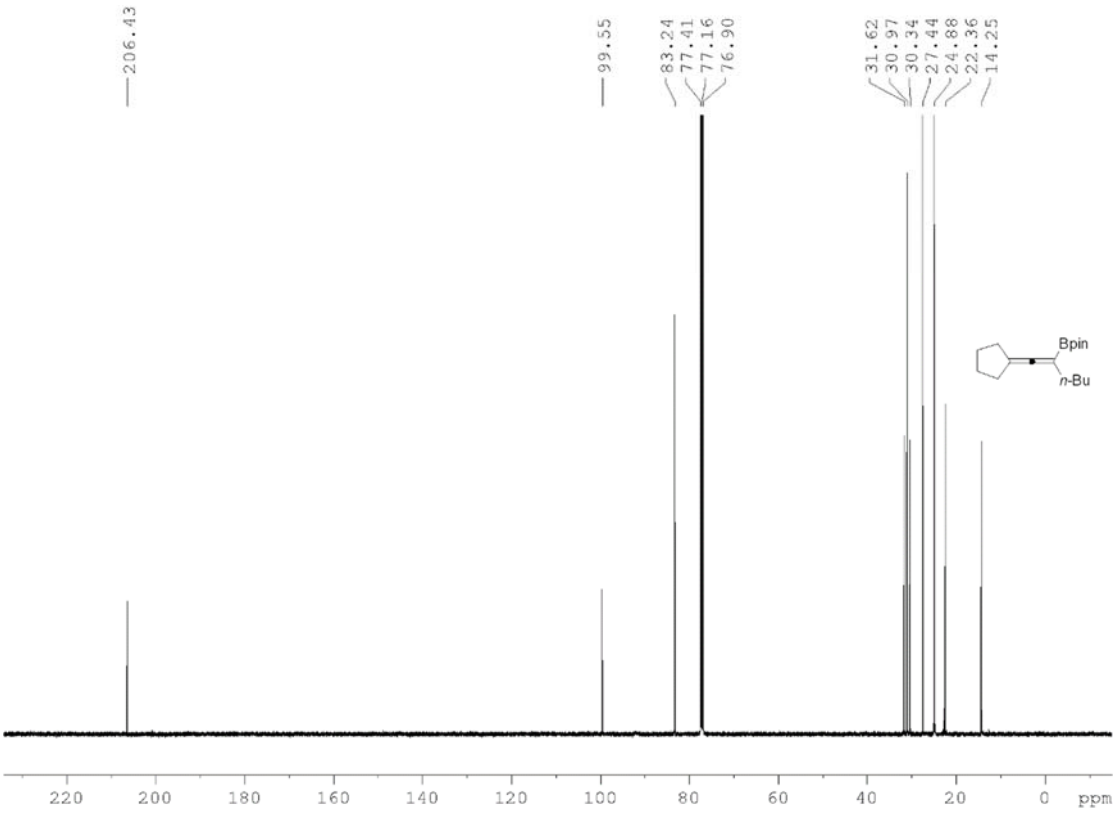


Compound (2-6)g

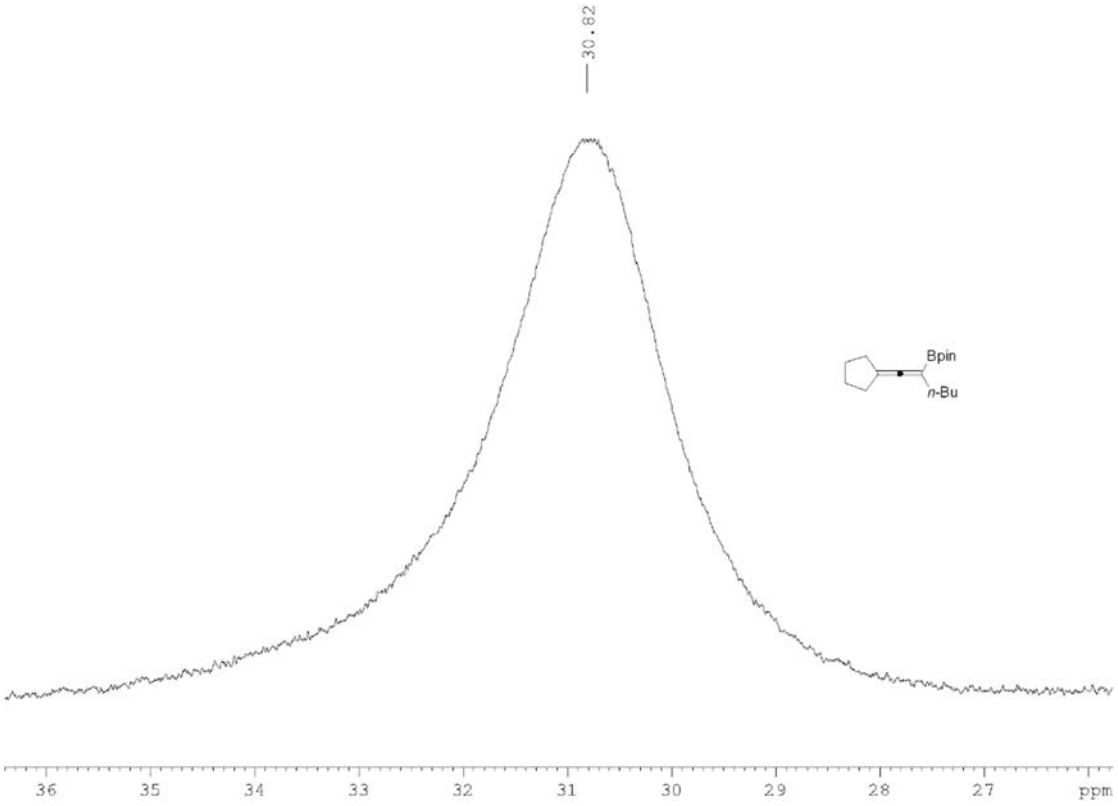
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

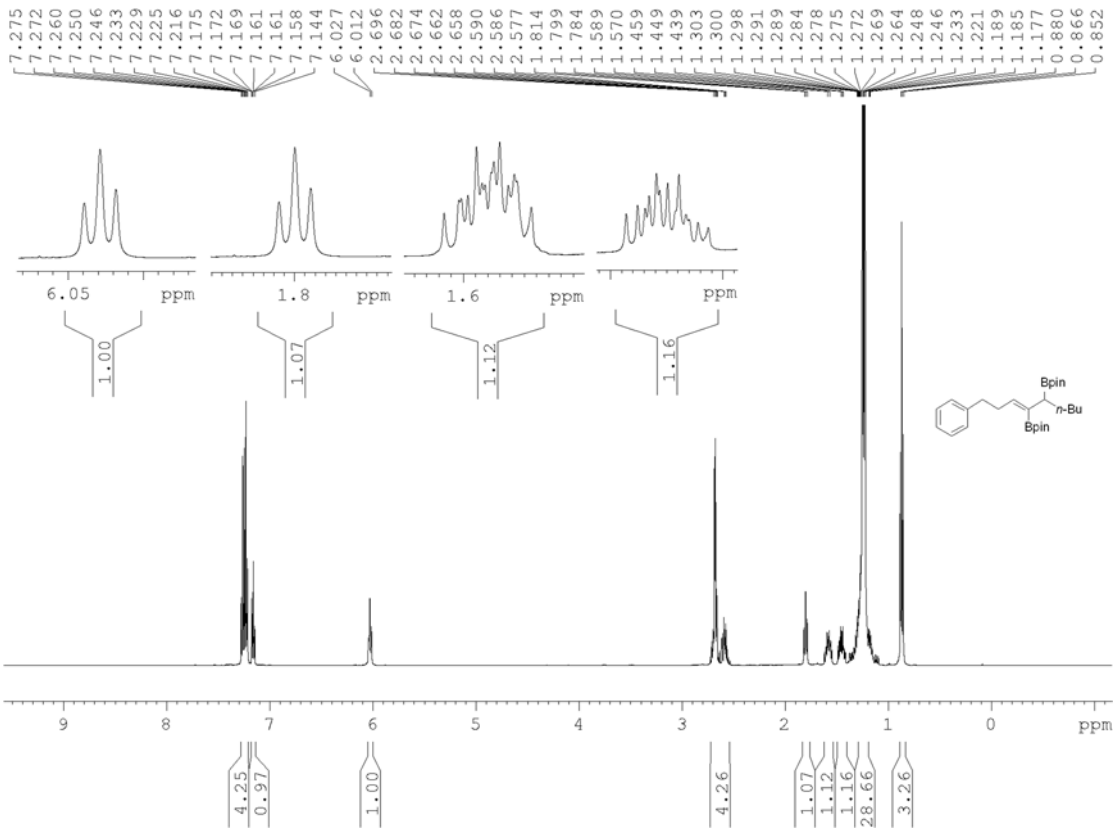


^{11}B NMR (160 MHz, $CDCl_3$)

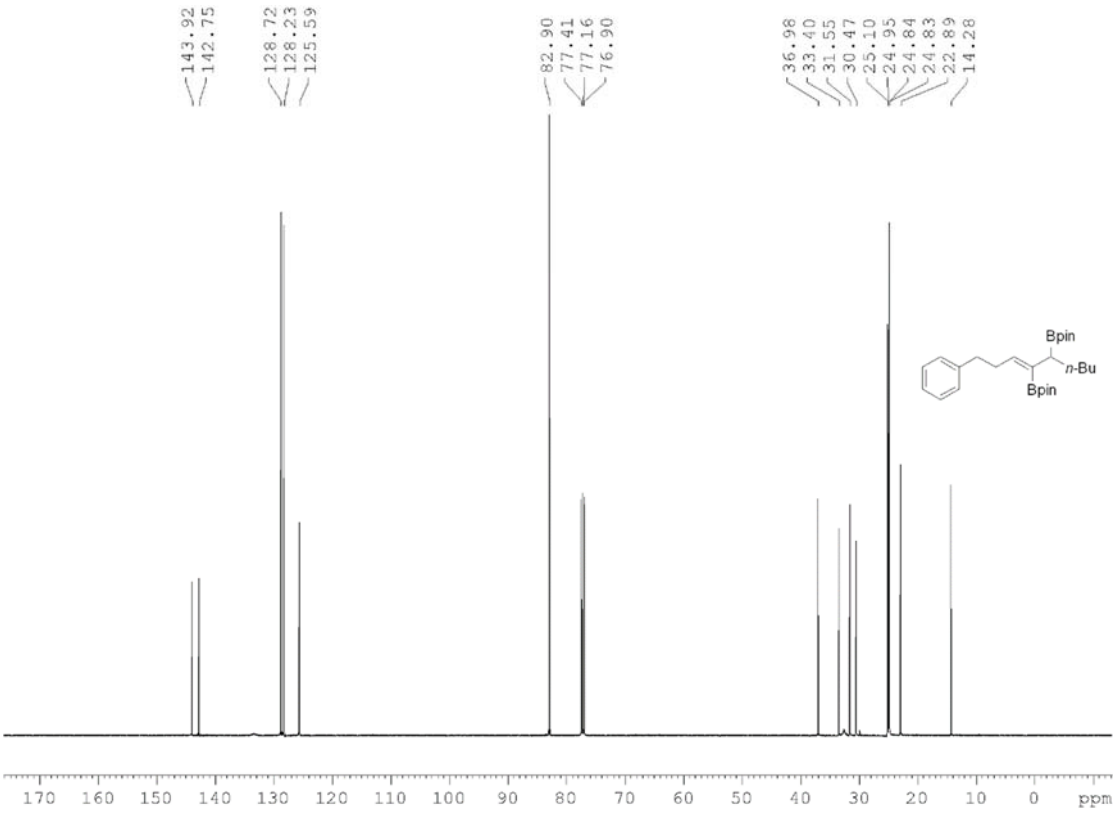


Compound (3-2)a

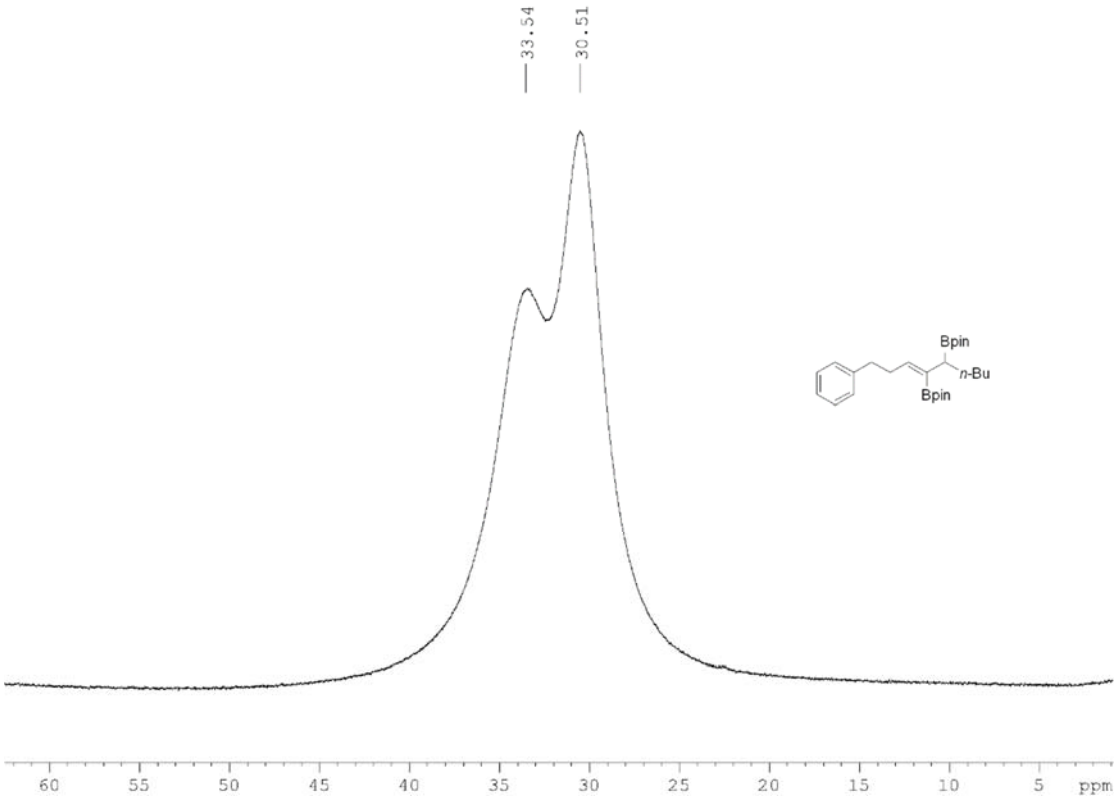
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

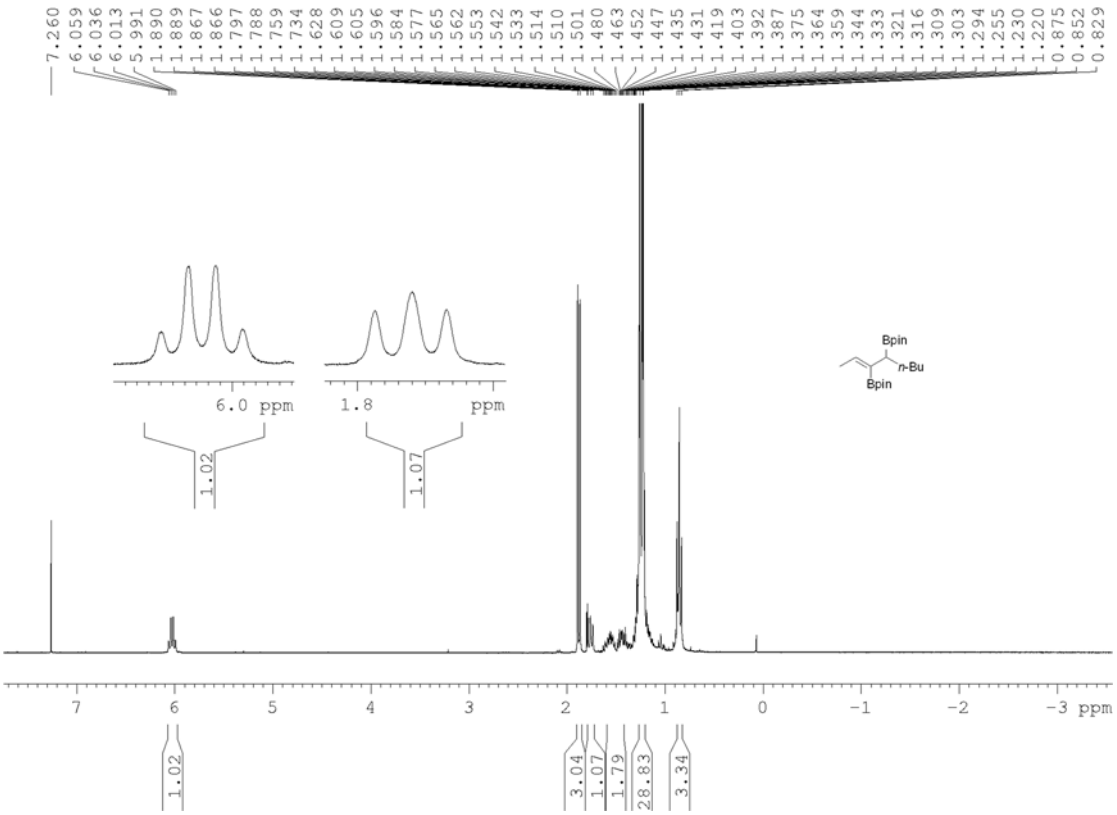


^{11}B NMR (160 MHz, $CDCl_3$)

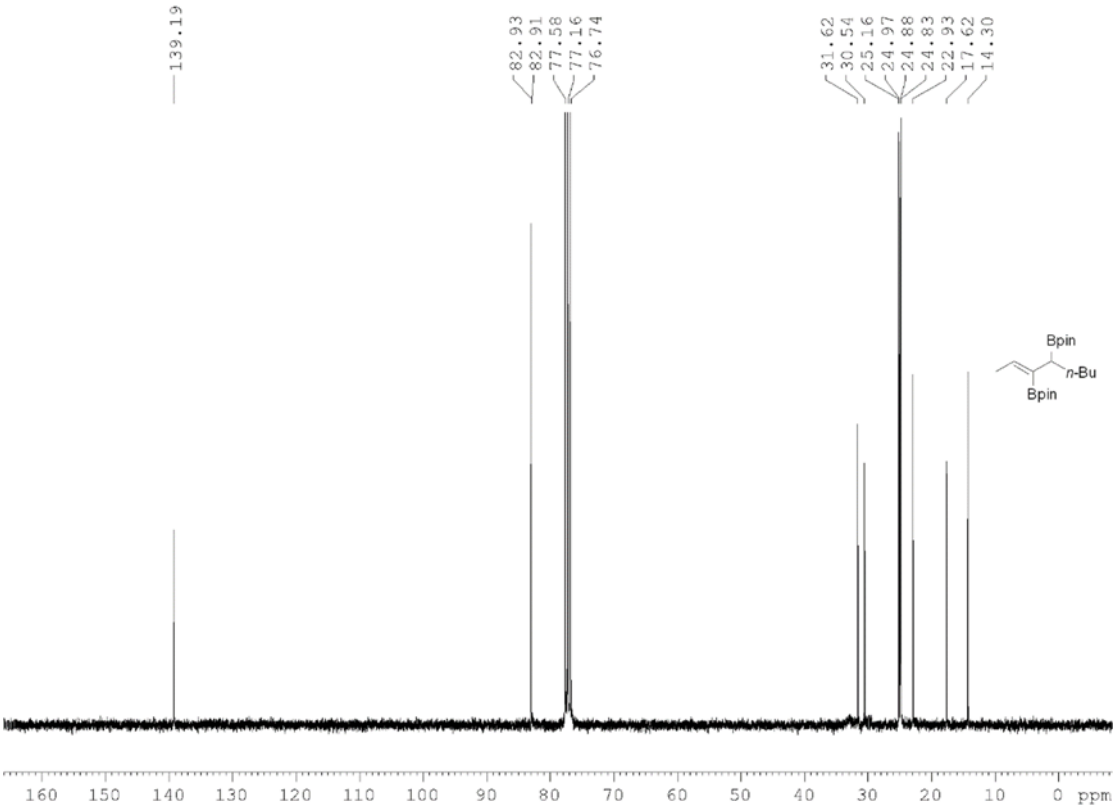


Compound (3-2)b

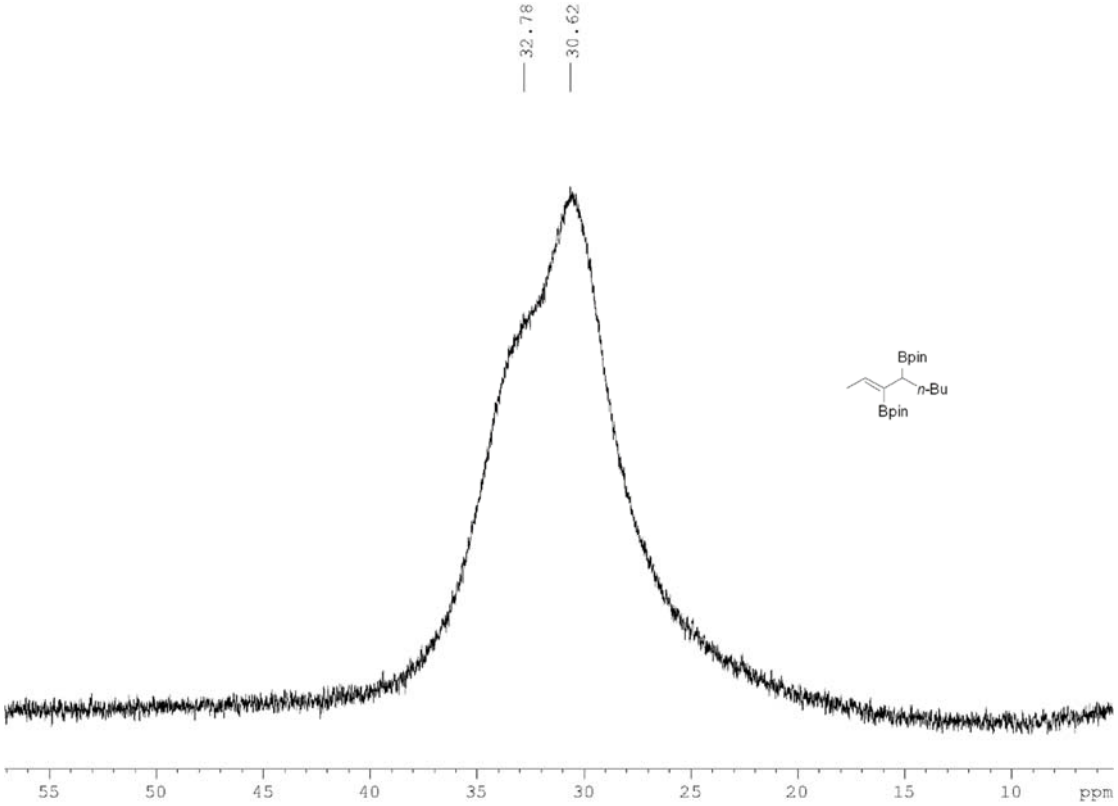
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

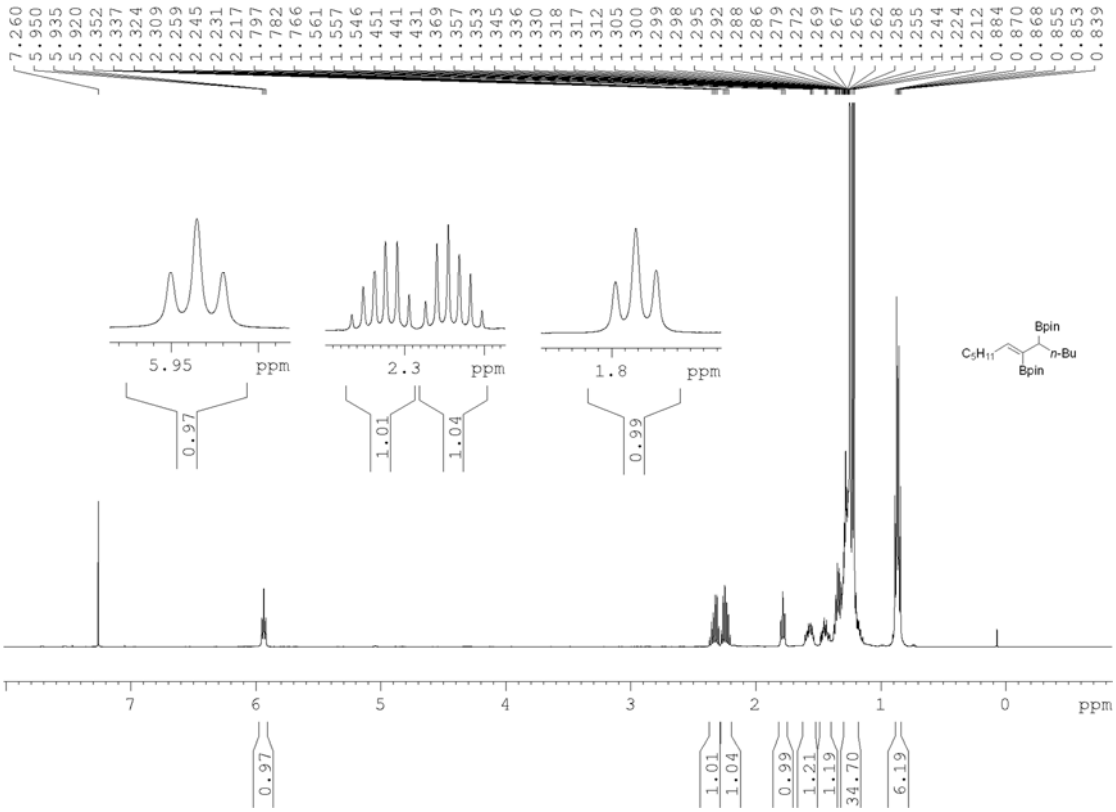


^{11}B NMR (96 MHz, $CDCl_3$)

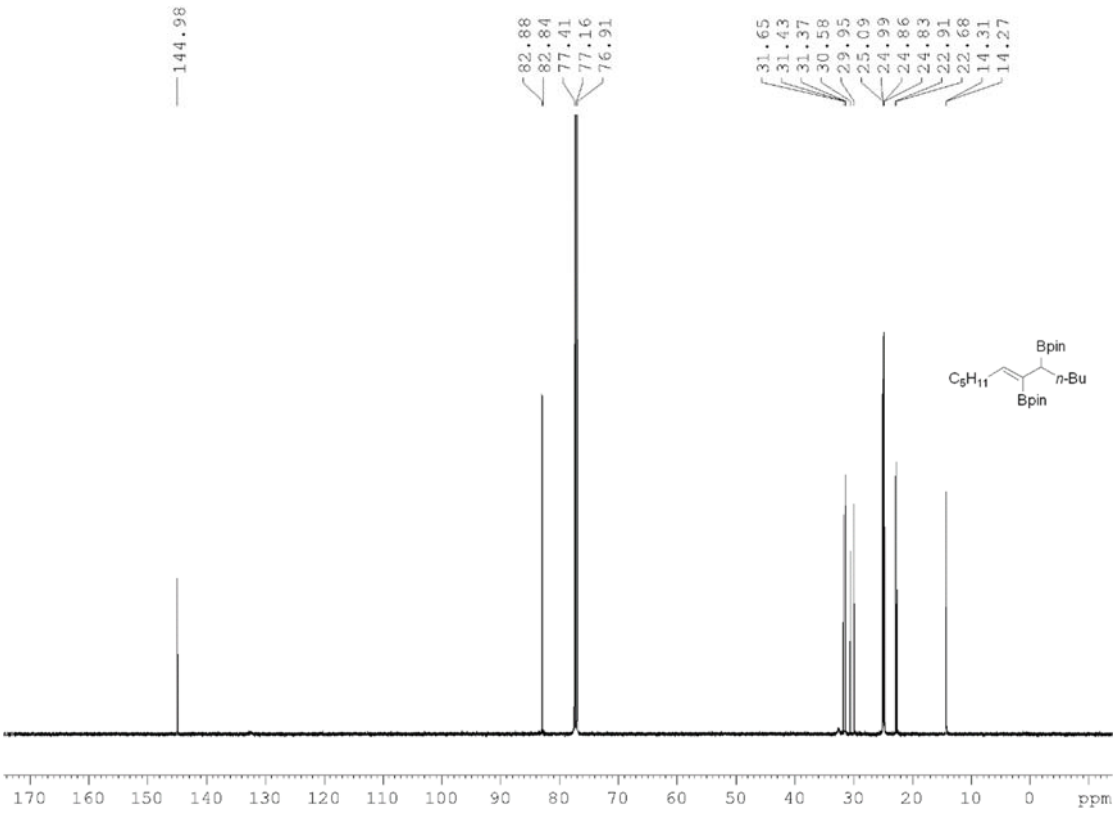


Compound (3-2)c

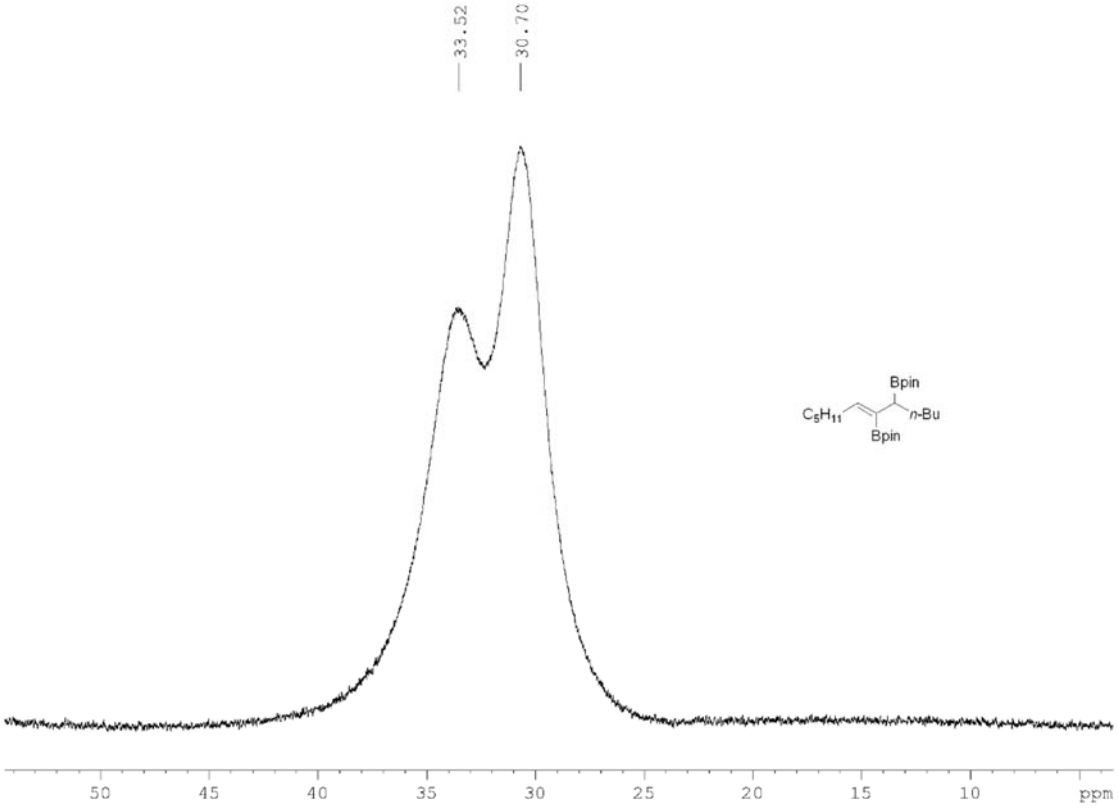
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

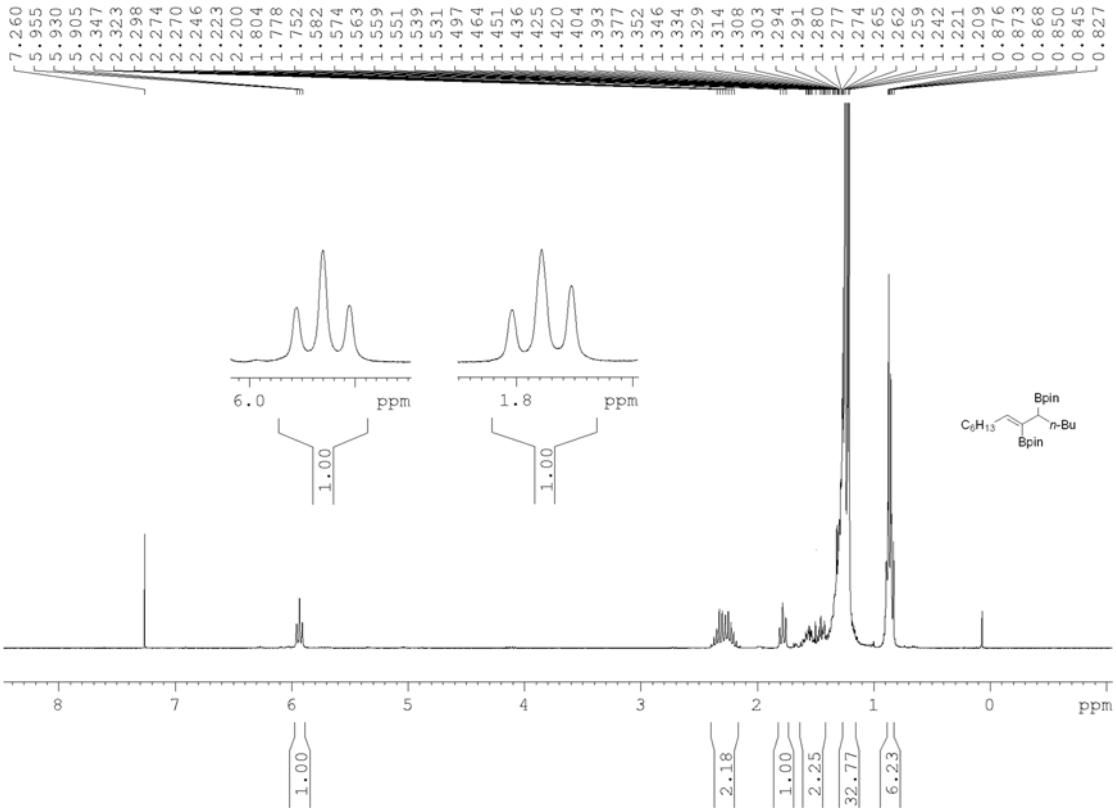


^{11}B NMR (160 MHz, $CDCl_3$)

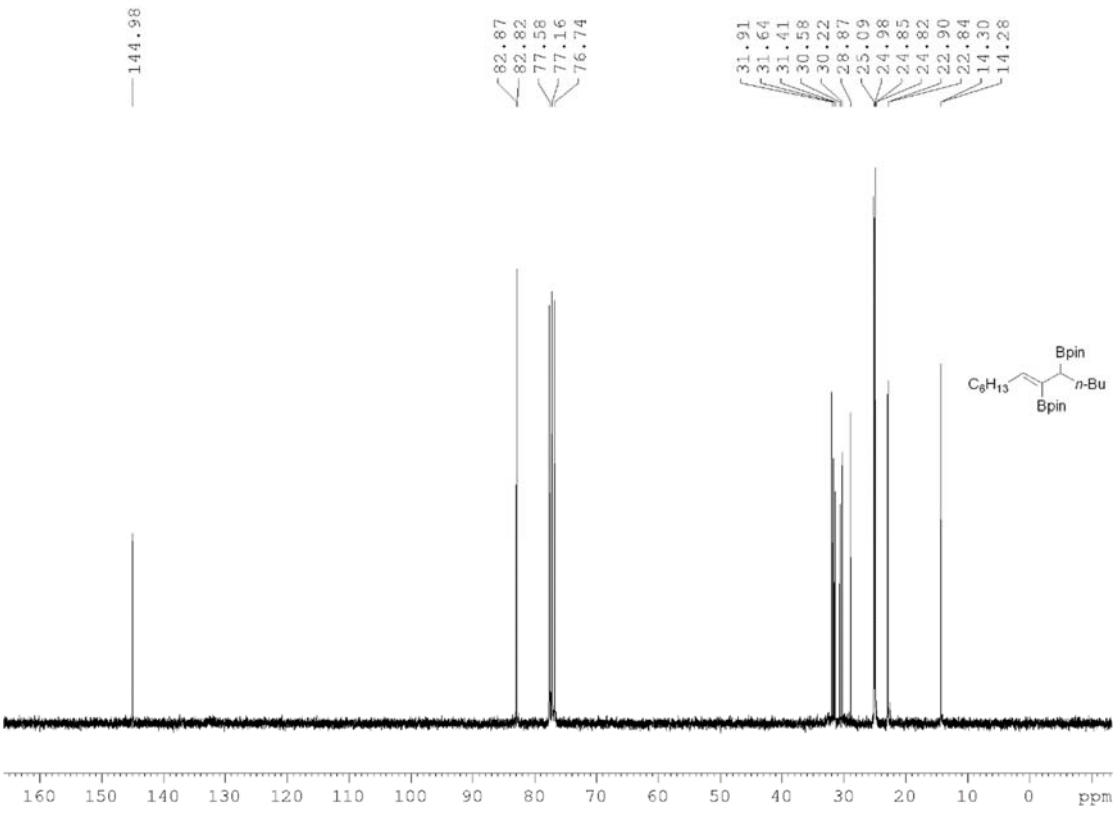


Compound (3-2)d

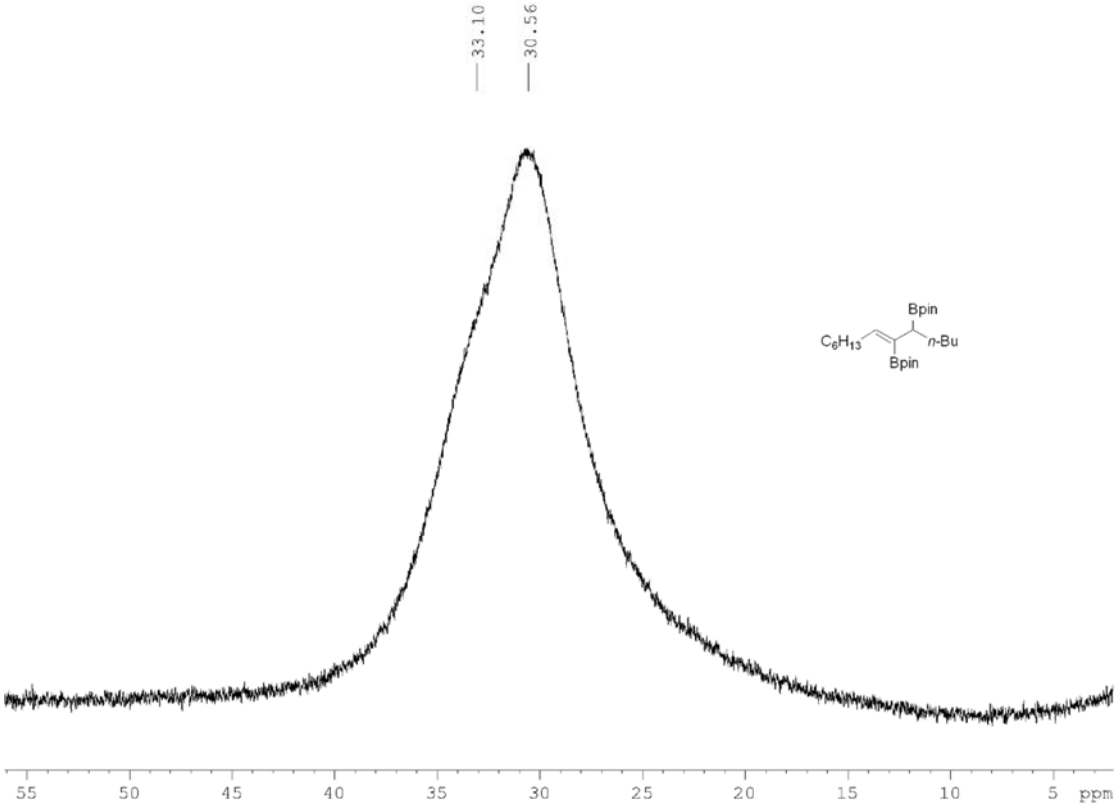
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

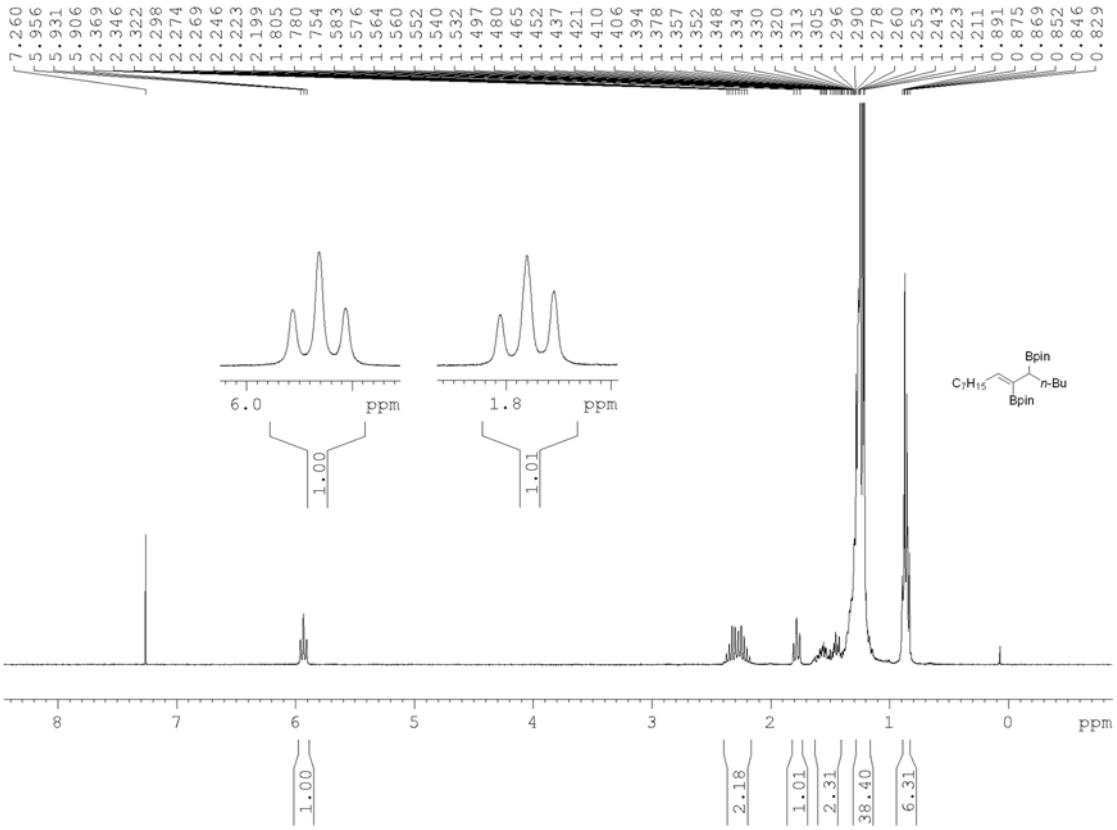


^{11}B NMR (96 MHz, $CDCl_3$)

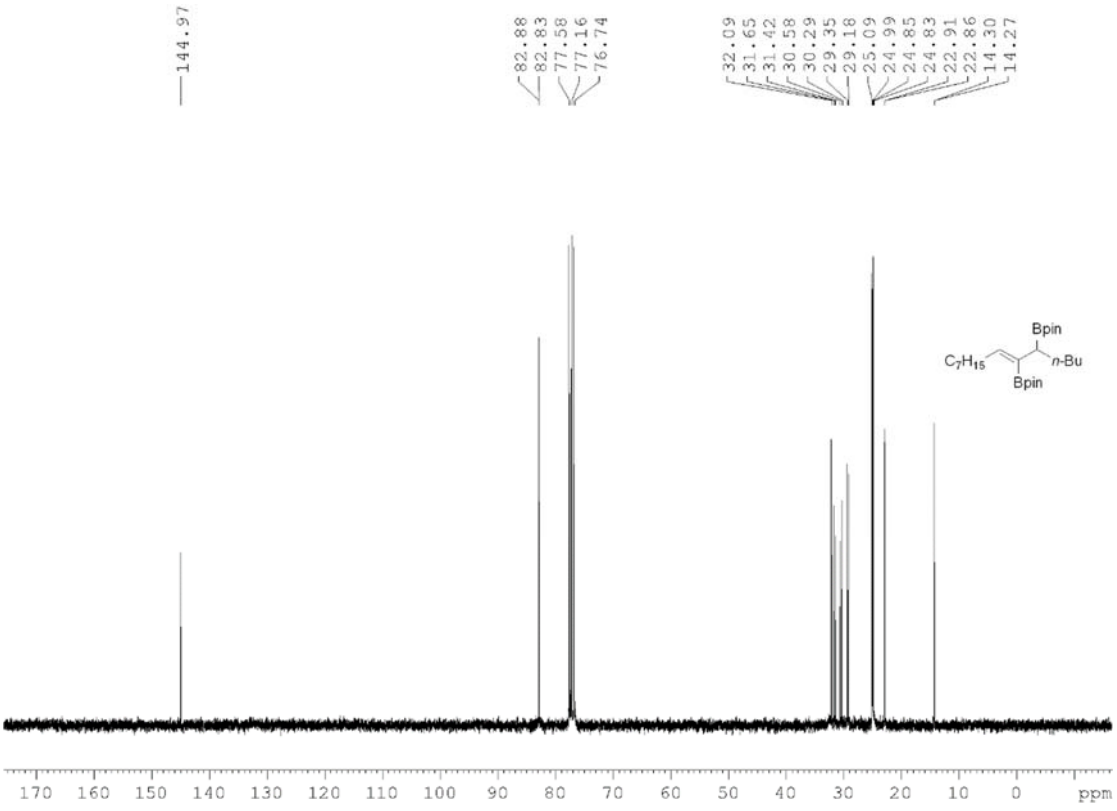


Compound (3-2)e

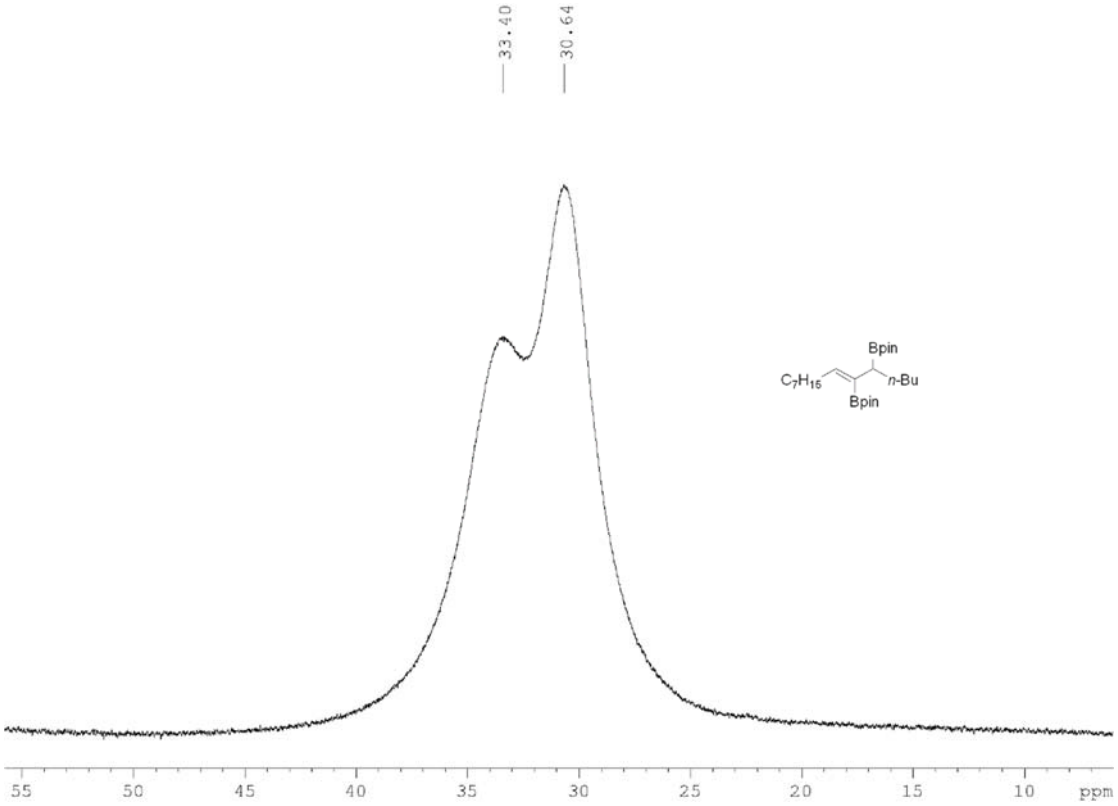
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

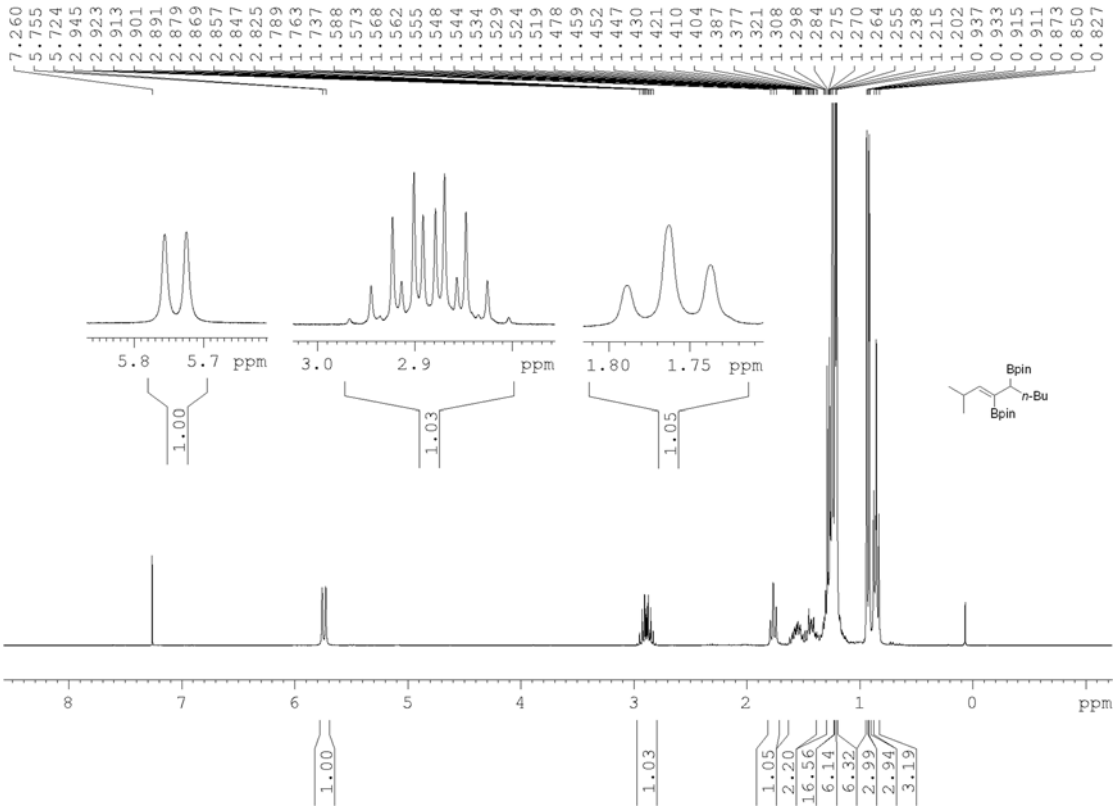


^{11}B NMR (160 MHz, $CDCl_3$)

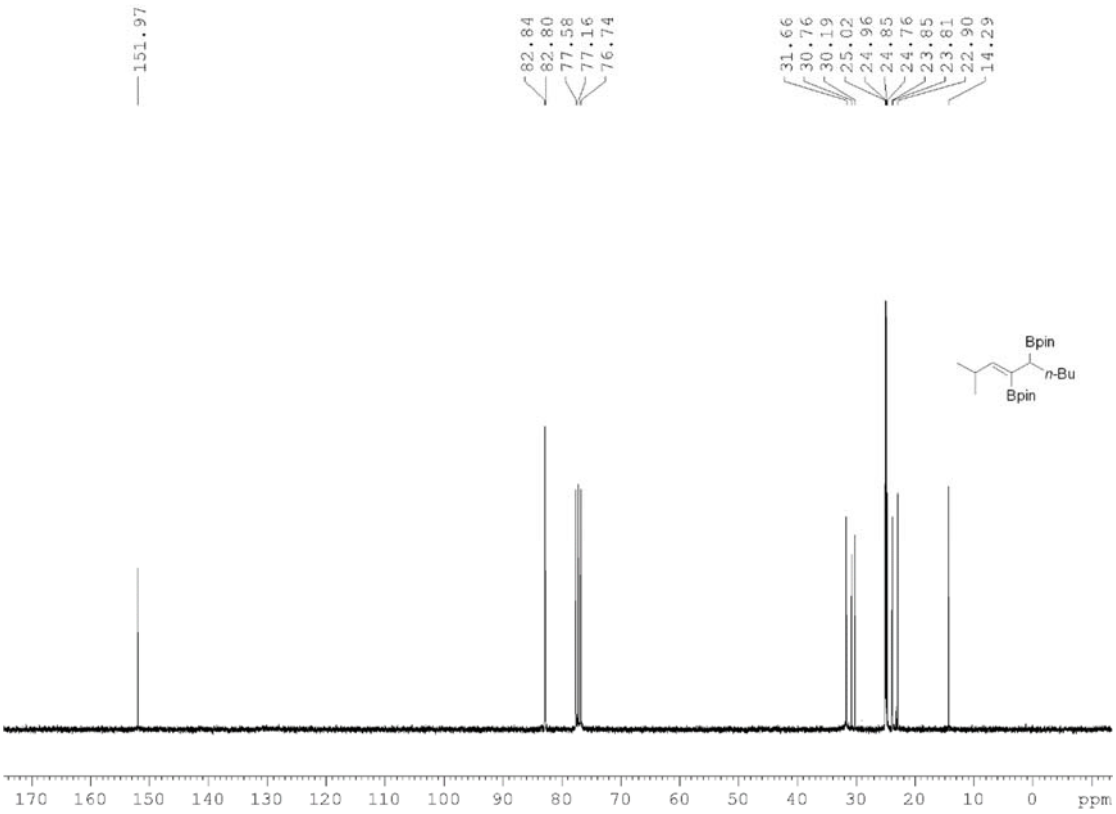


Compound (3-2)f

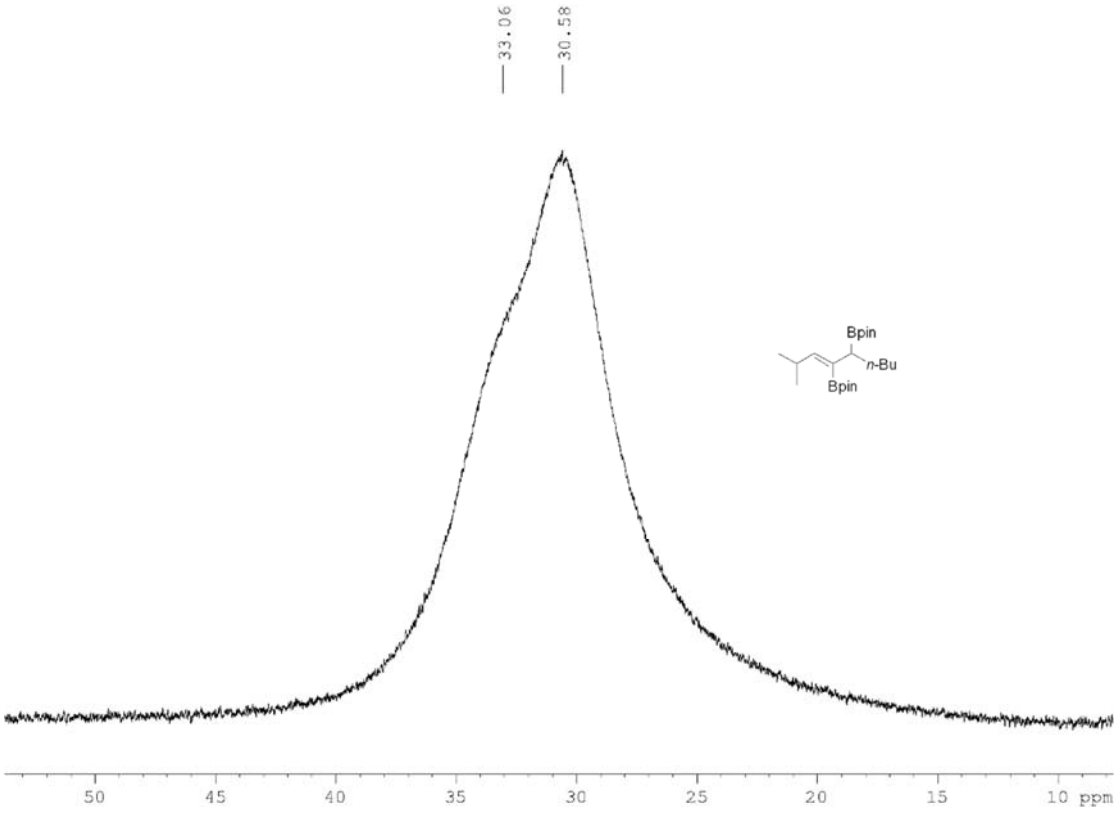
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

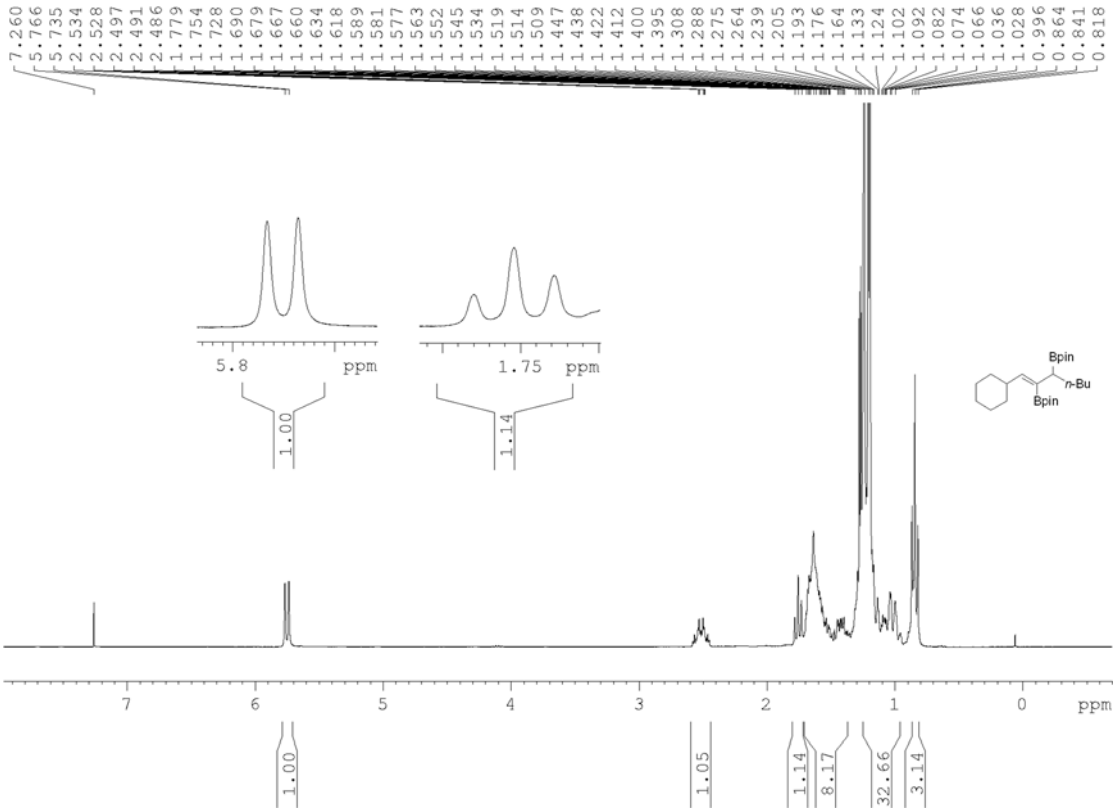


^{11}B NMR (96 MHz, $CDCl_3$)

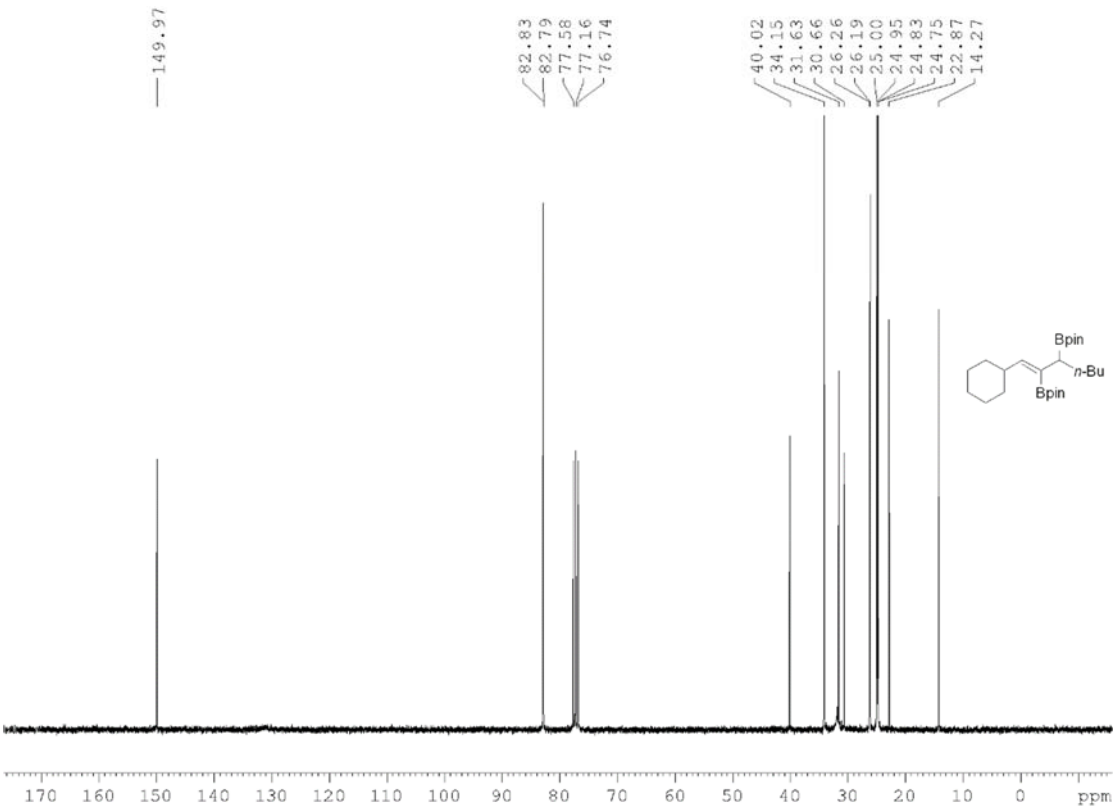


Compound (3-2)g

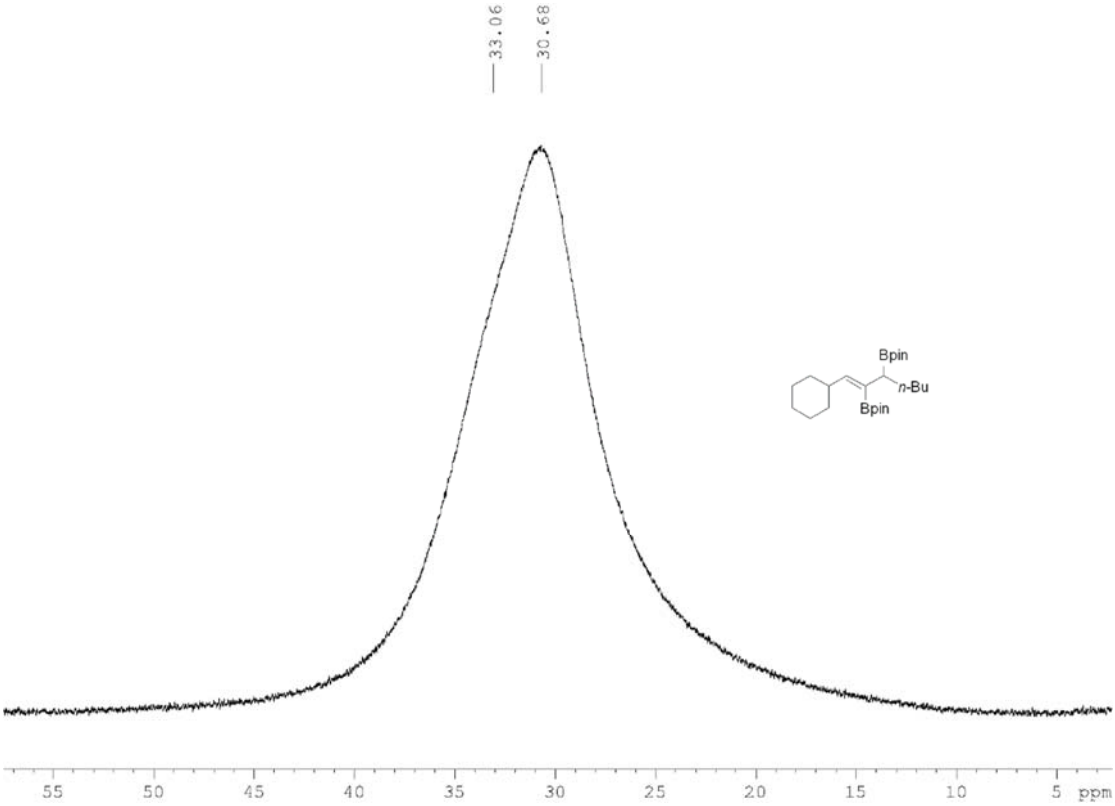
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

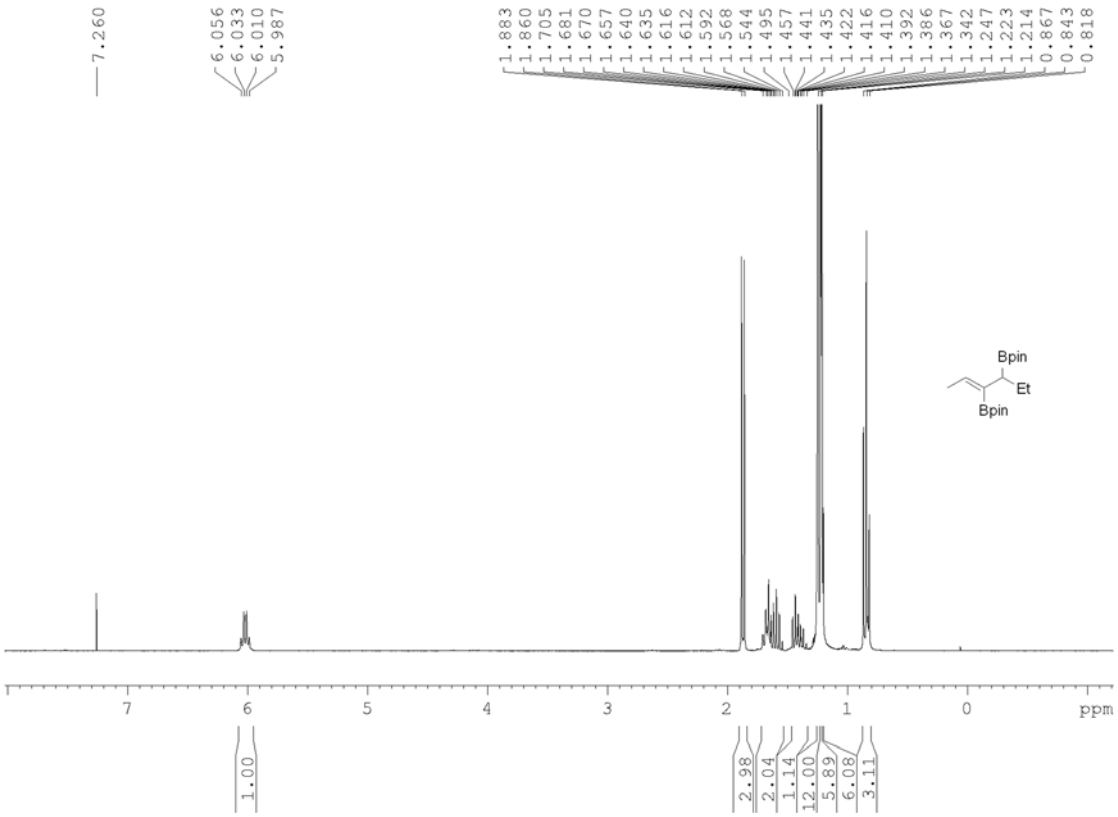


^{11}B NMR (96 MHz, $CDCl_3$)

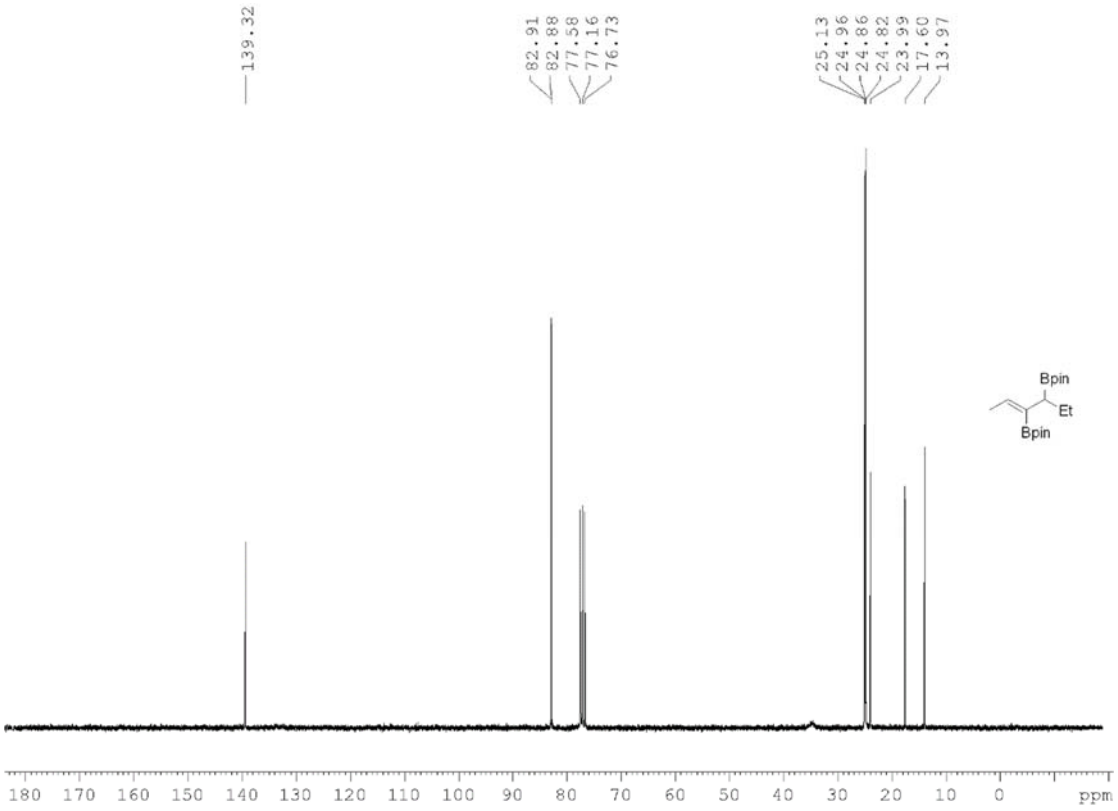


Compound (3-2)h

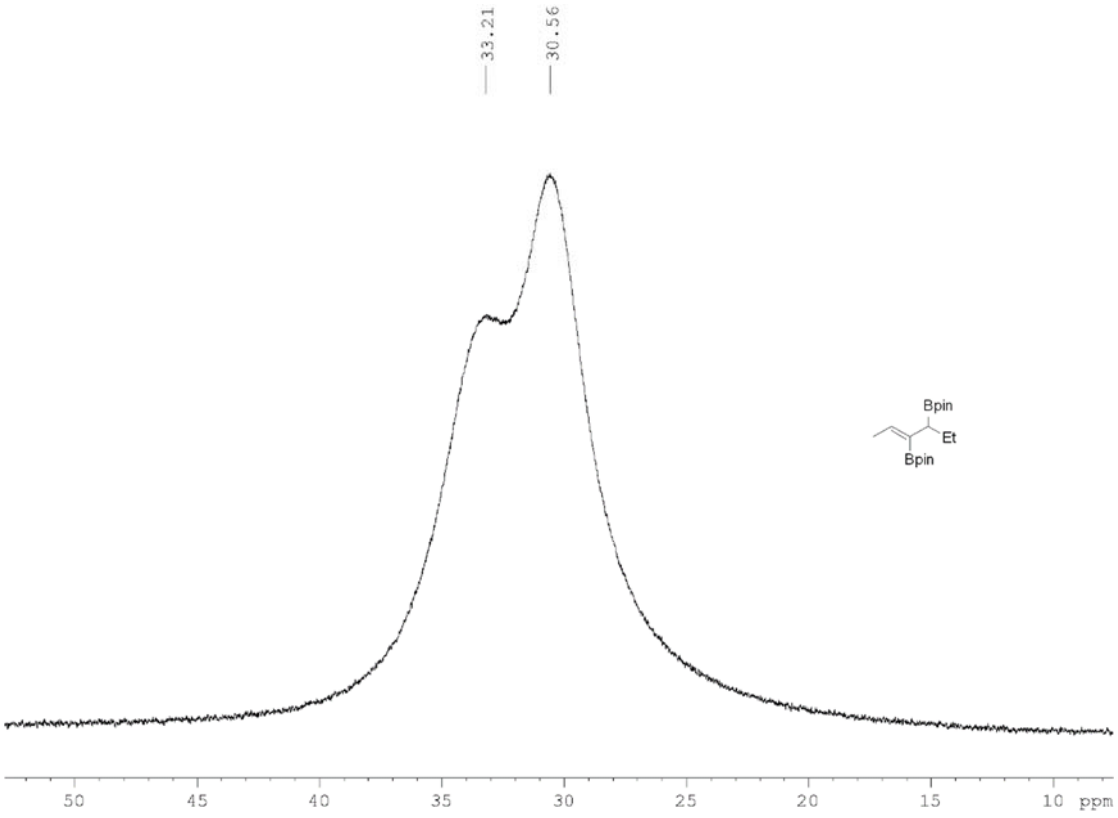
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

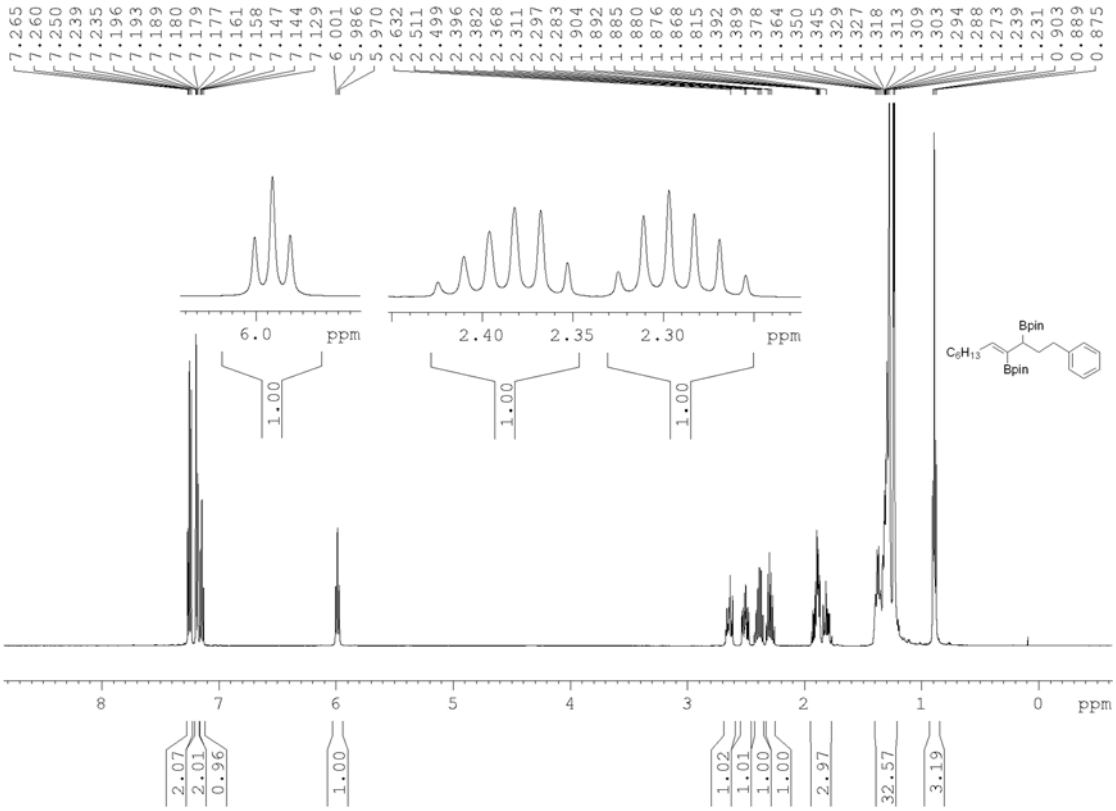


^{11}B NMR (96 MHz, $CDCl_3$)

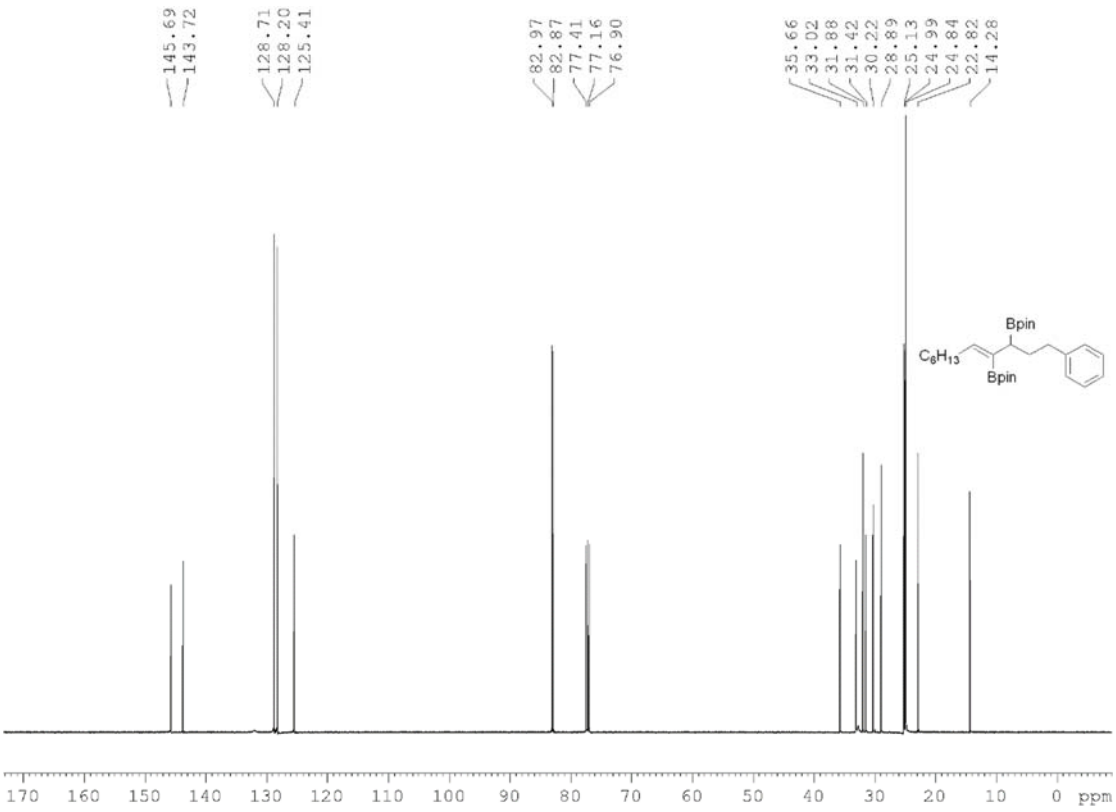


Compound (3-2)i

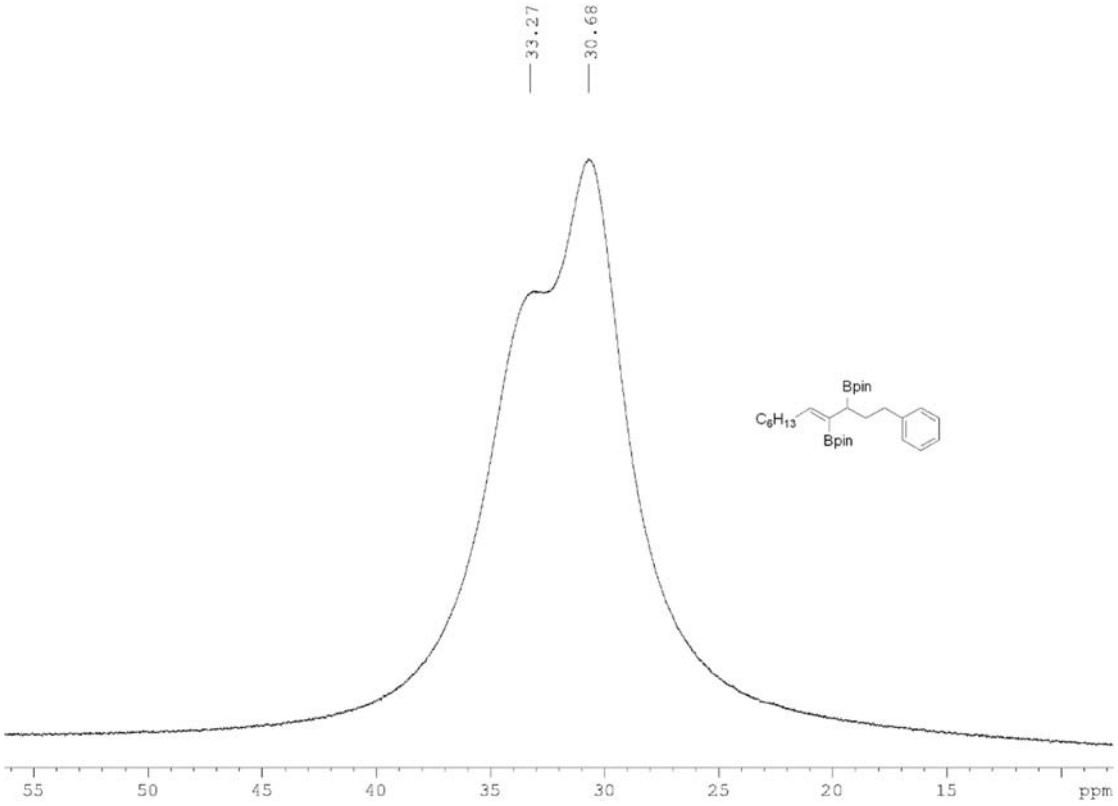
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

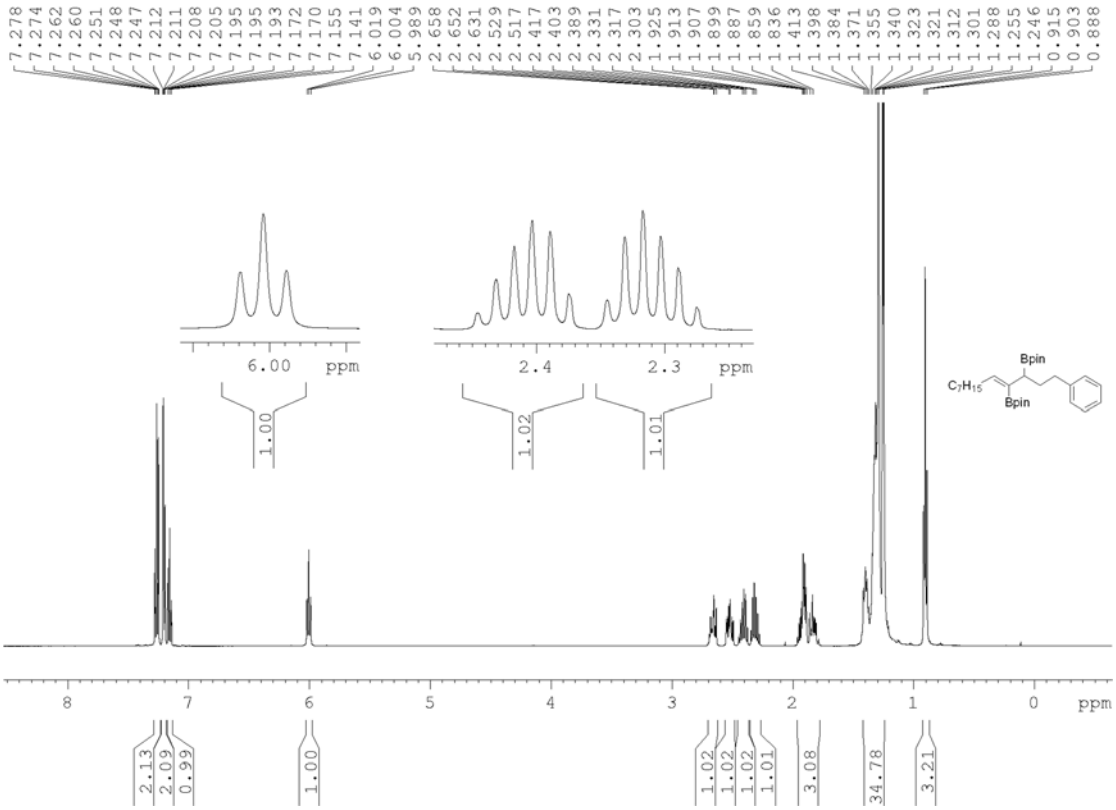


^{11}B NMR (160 MHz, $CDCl_3$)

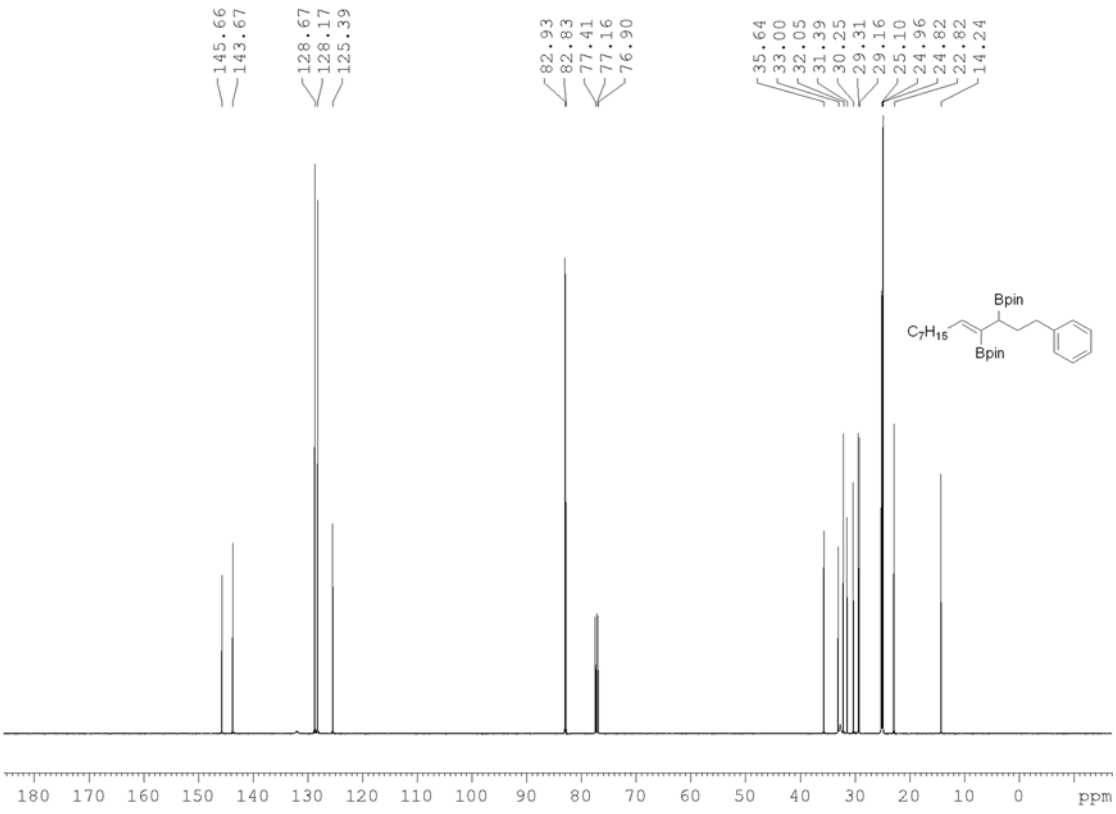


Compound (3-2)j

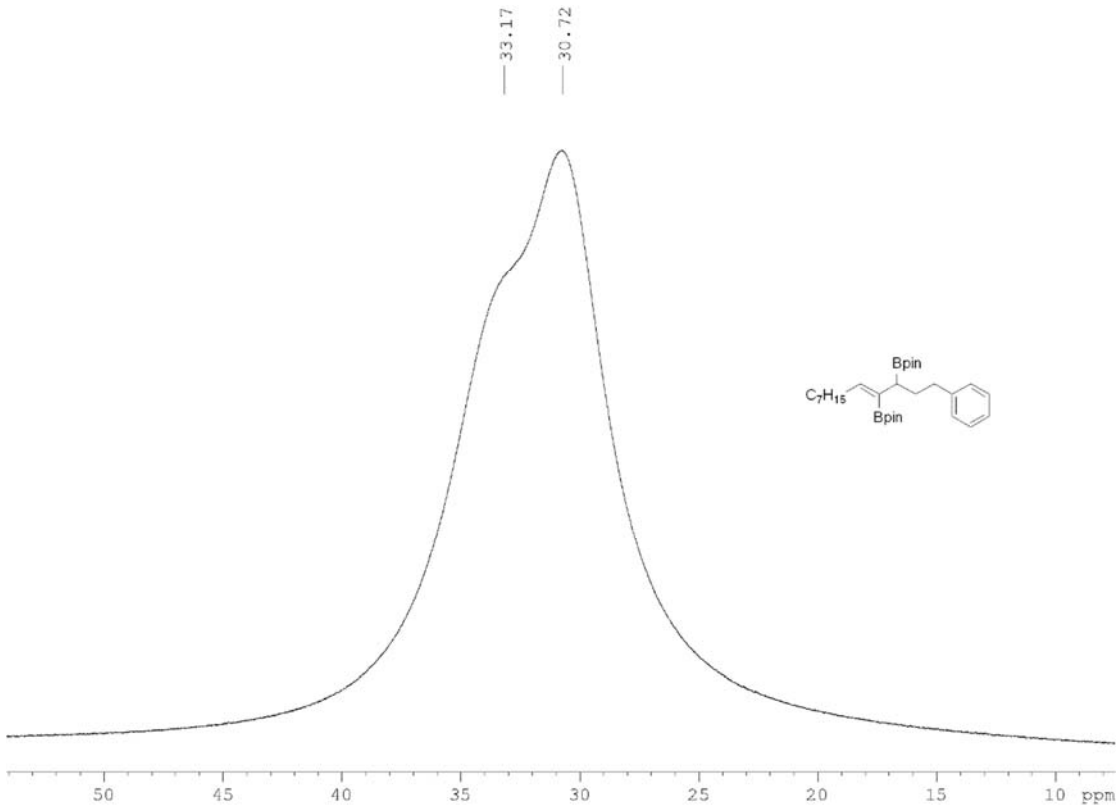
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 NMR, $CDCl_3$)

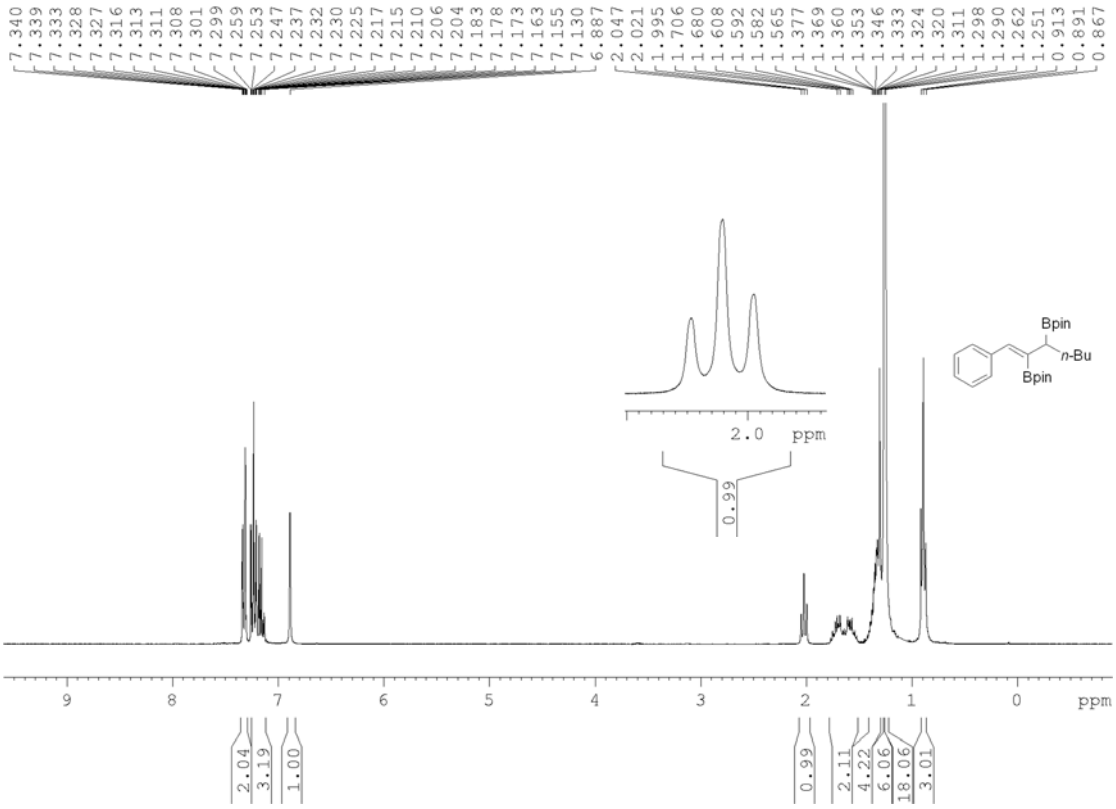


^{11}B NMR (160 NMR $CDCl_3$)

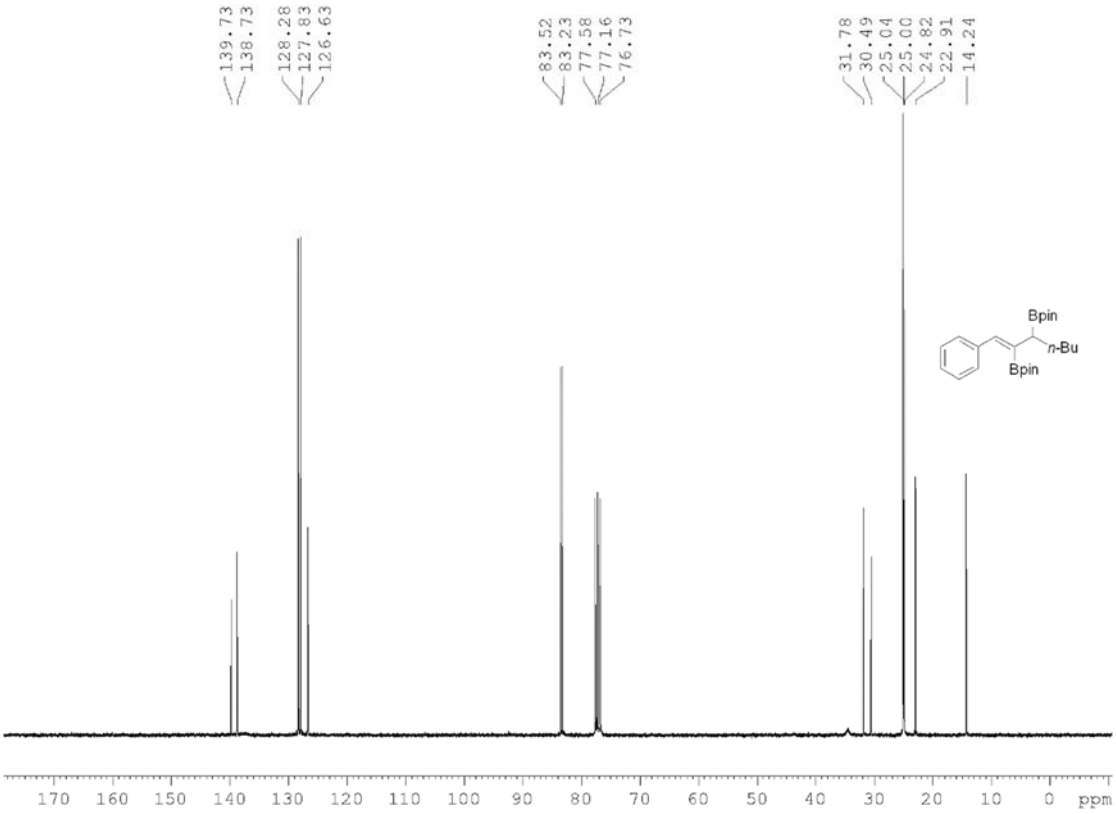


Compound (3-2)k

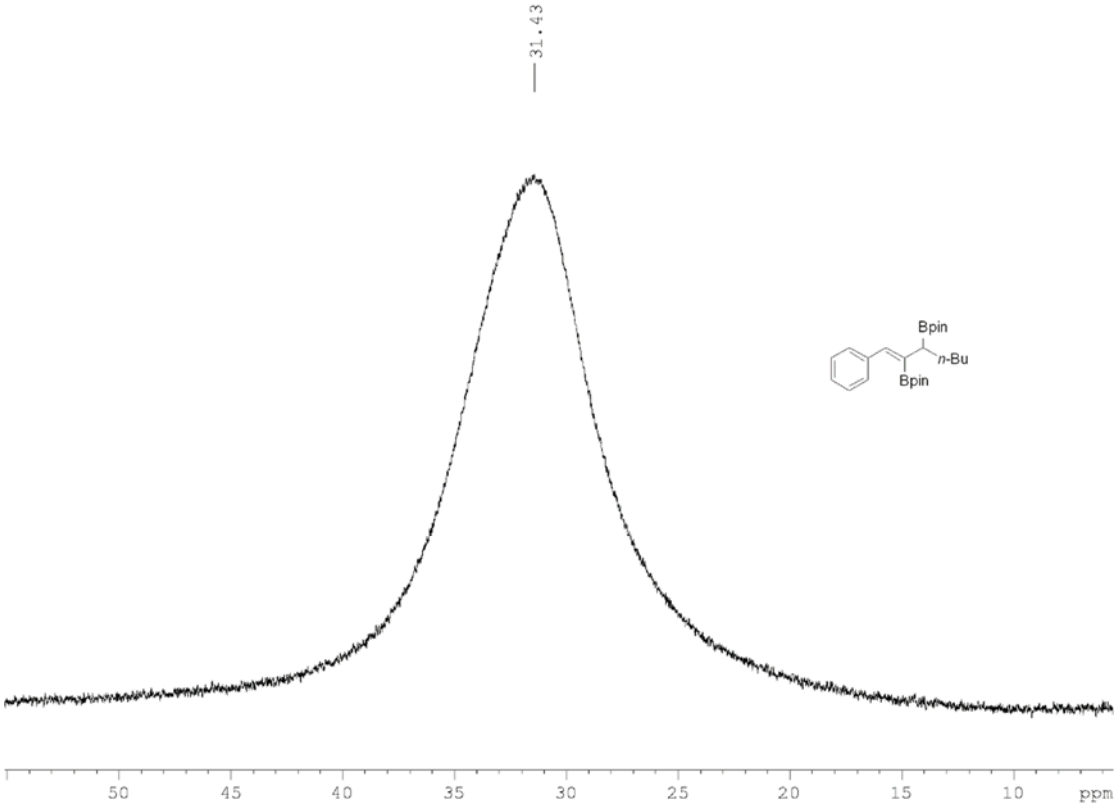
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

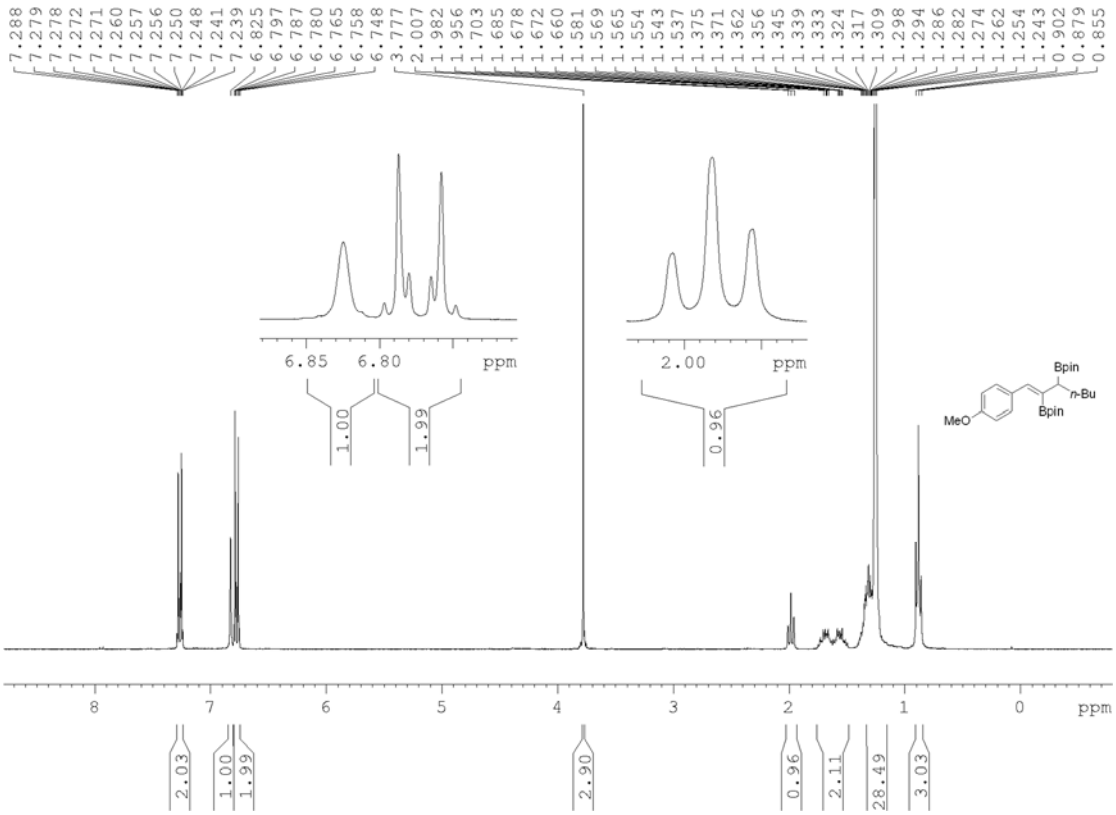


^{11}B NMR (96 MHz, $CDCl_3$)

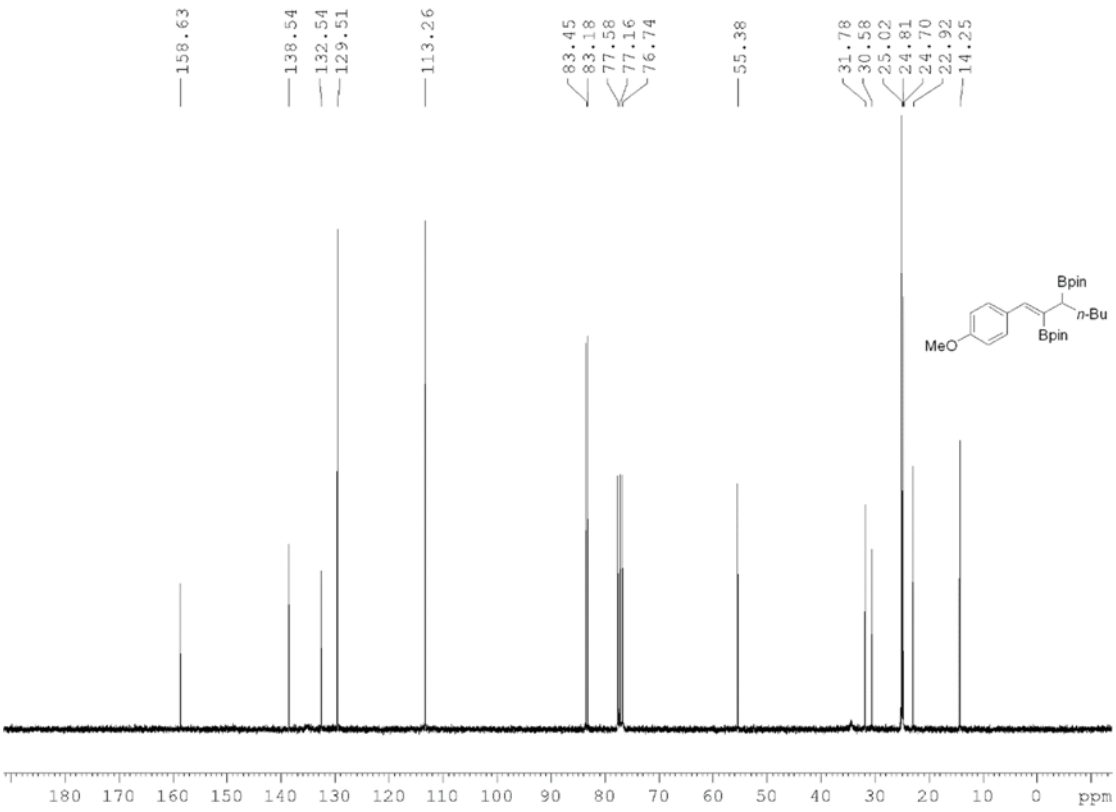


Compound (3-2)l

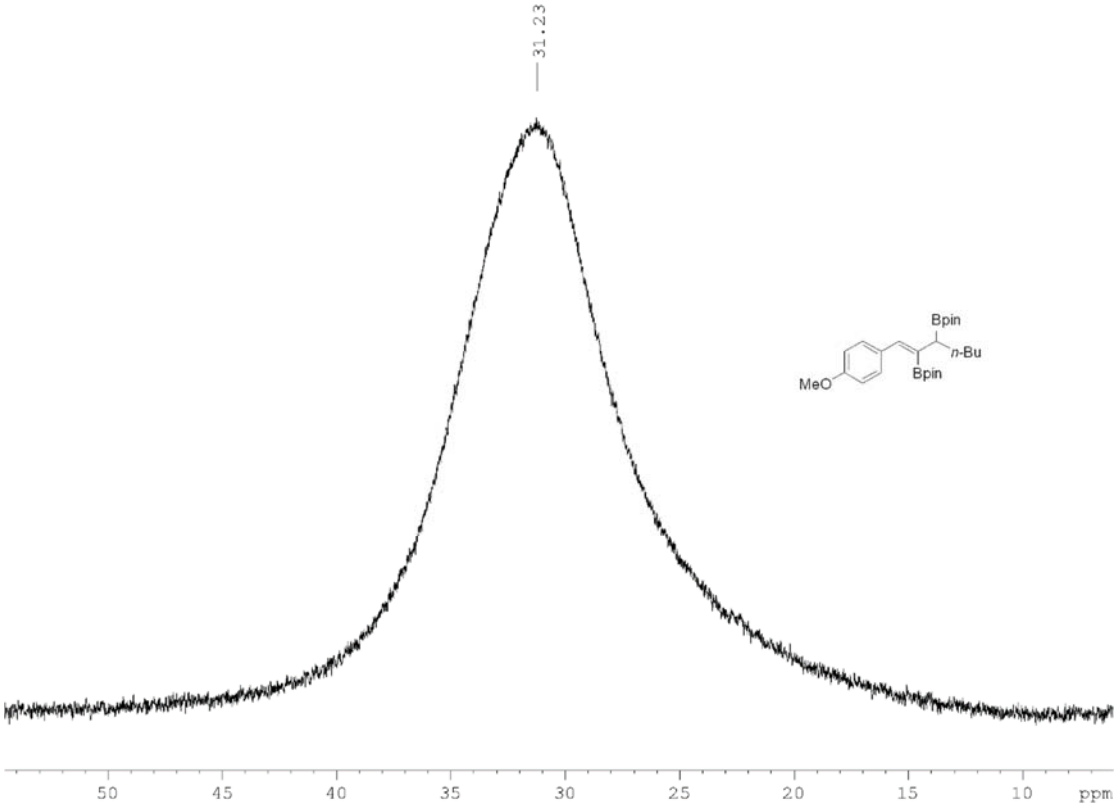
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

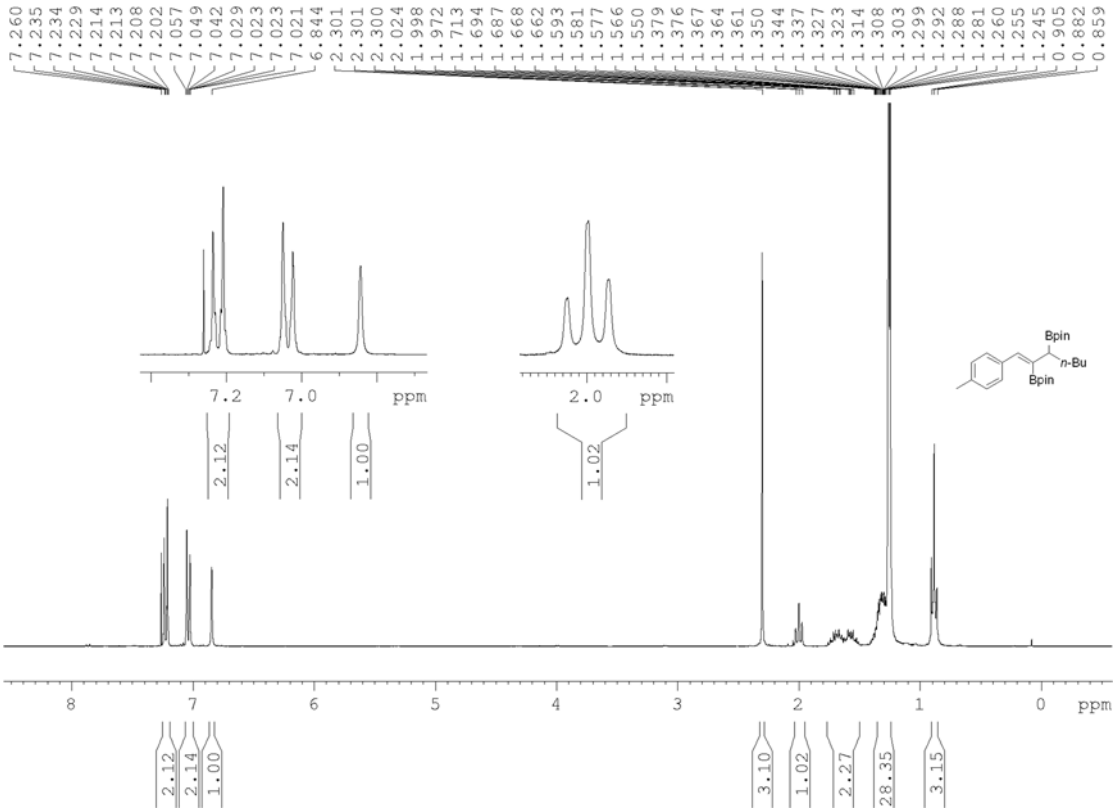


^{11}B NMR (96 MHz, $CDCl_3$)

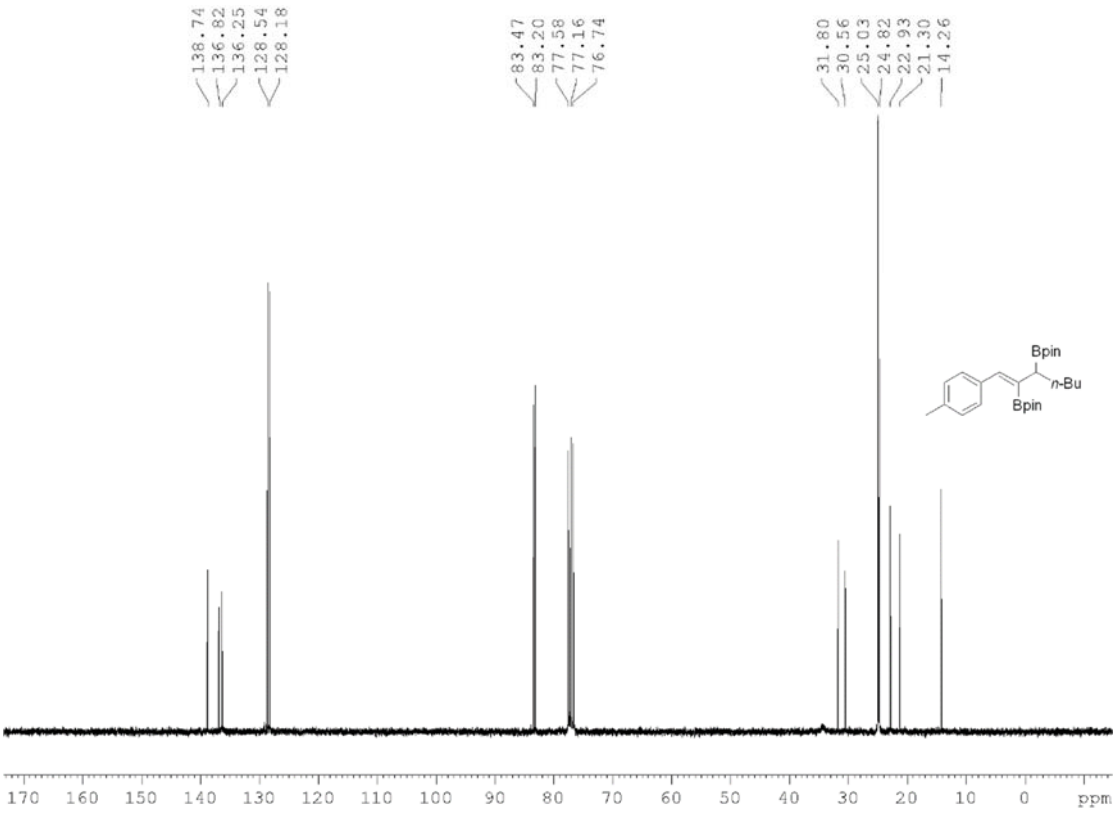


Compound (3-2)m

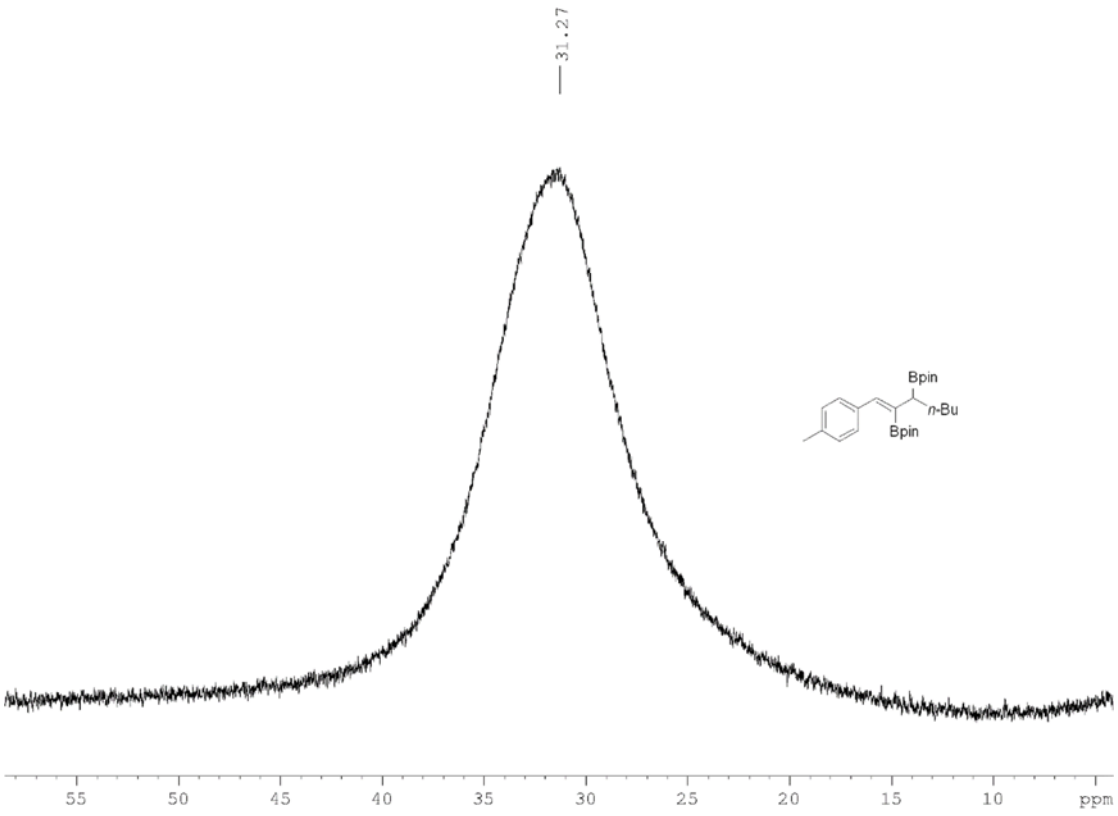
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

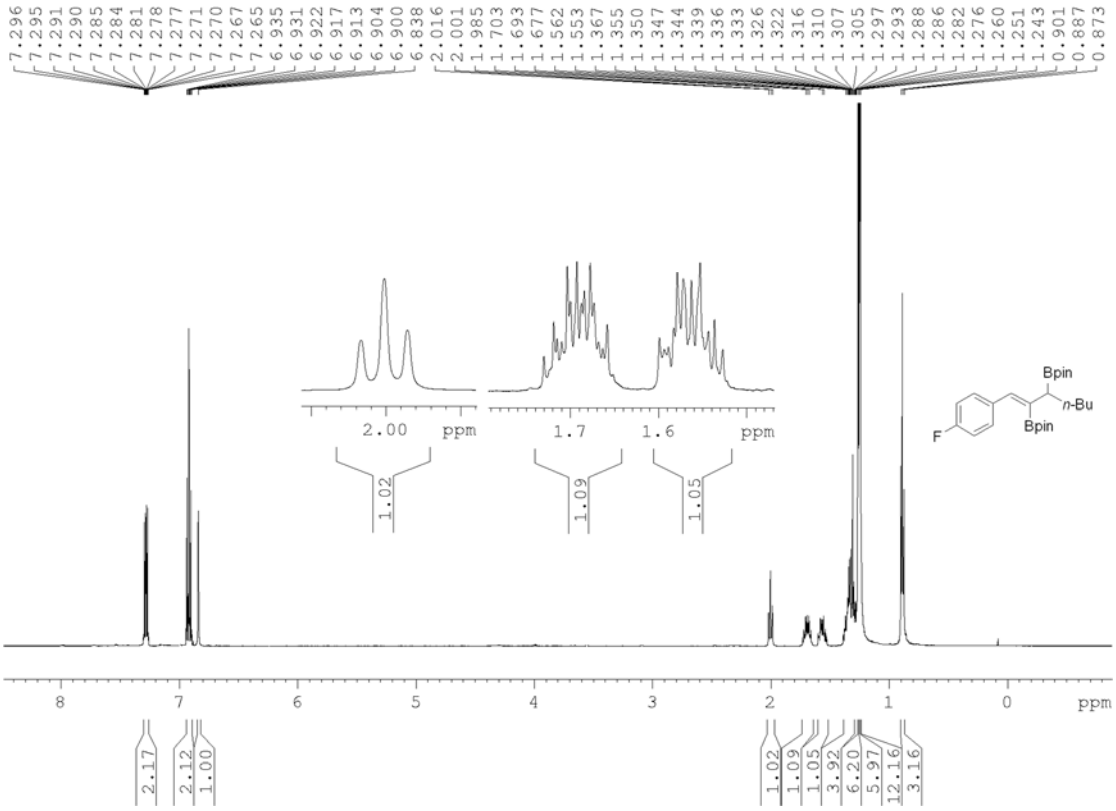


^{11}B NMR (96 MHz, $CDCl_3$)

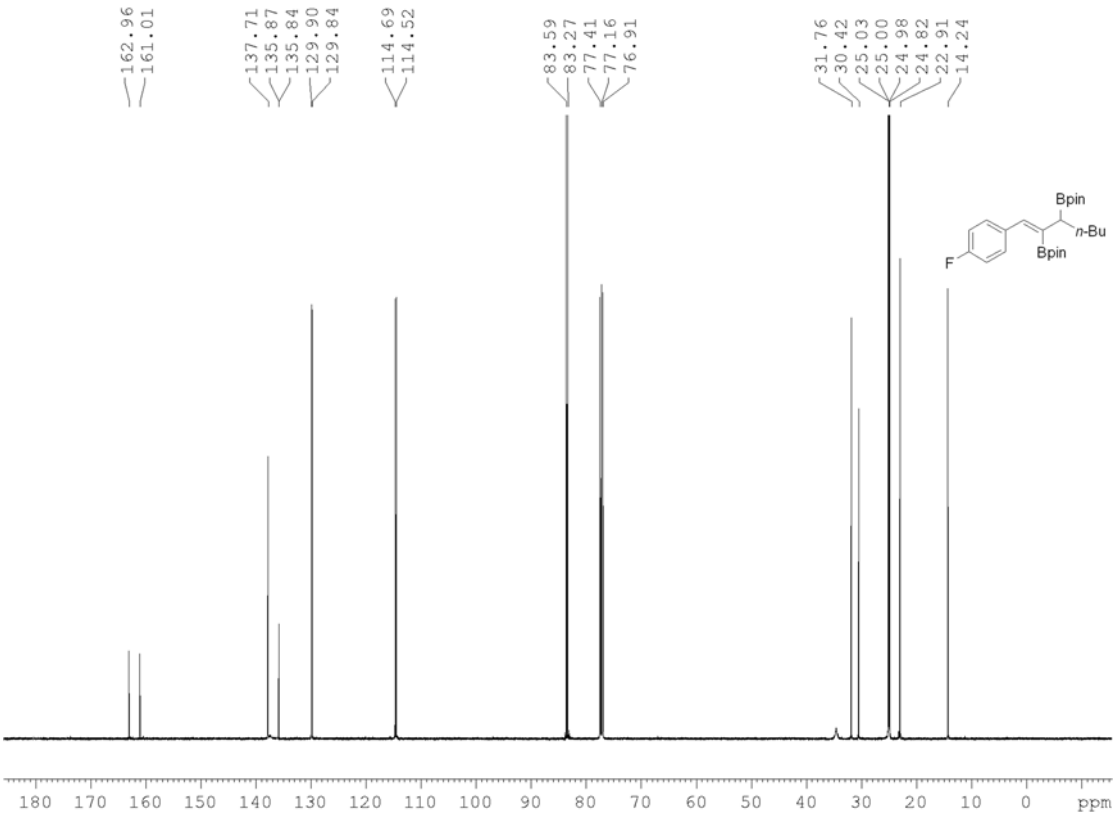


Compound (3-2)n

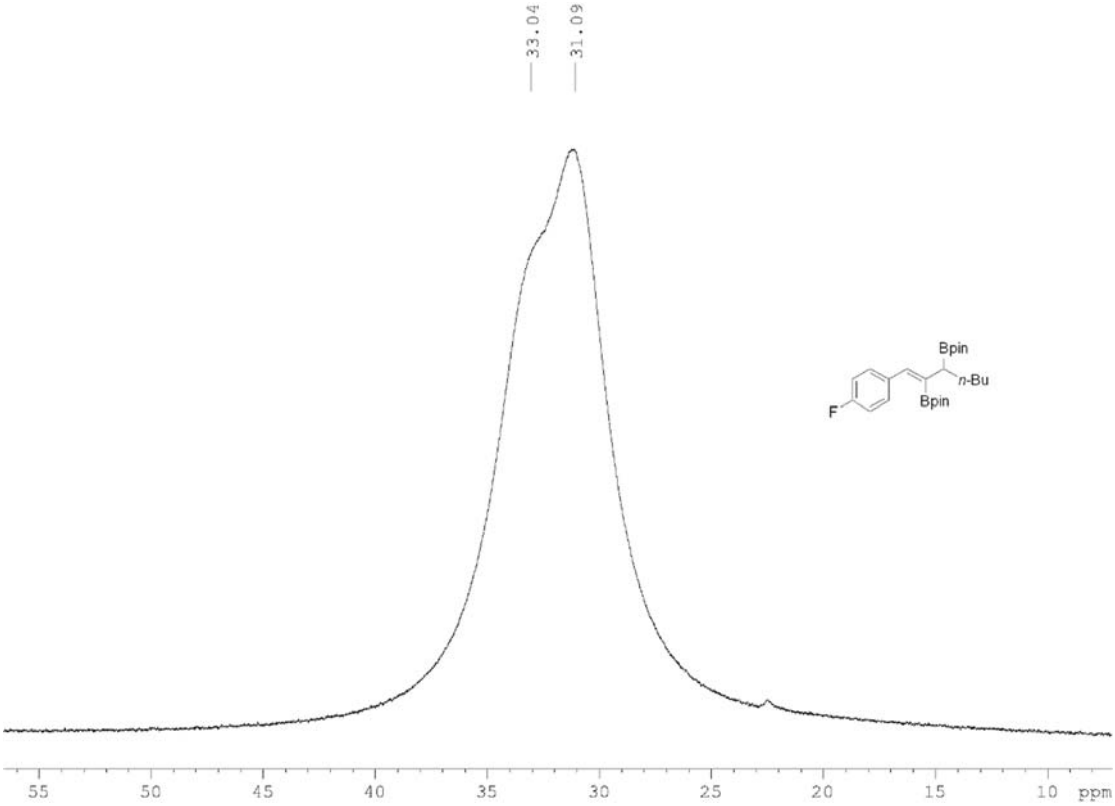
^{1}H NMR (500 MHz, $CDCl_3$)



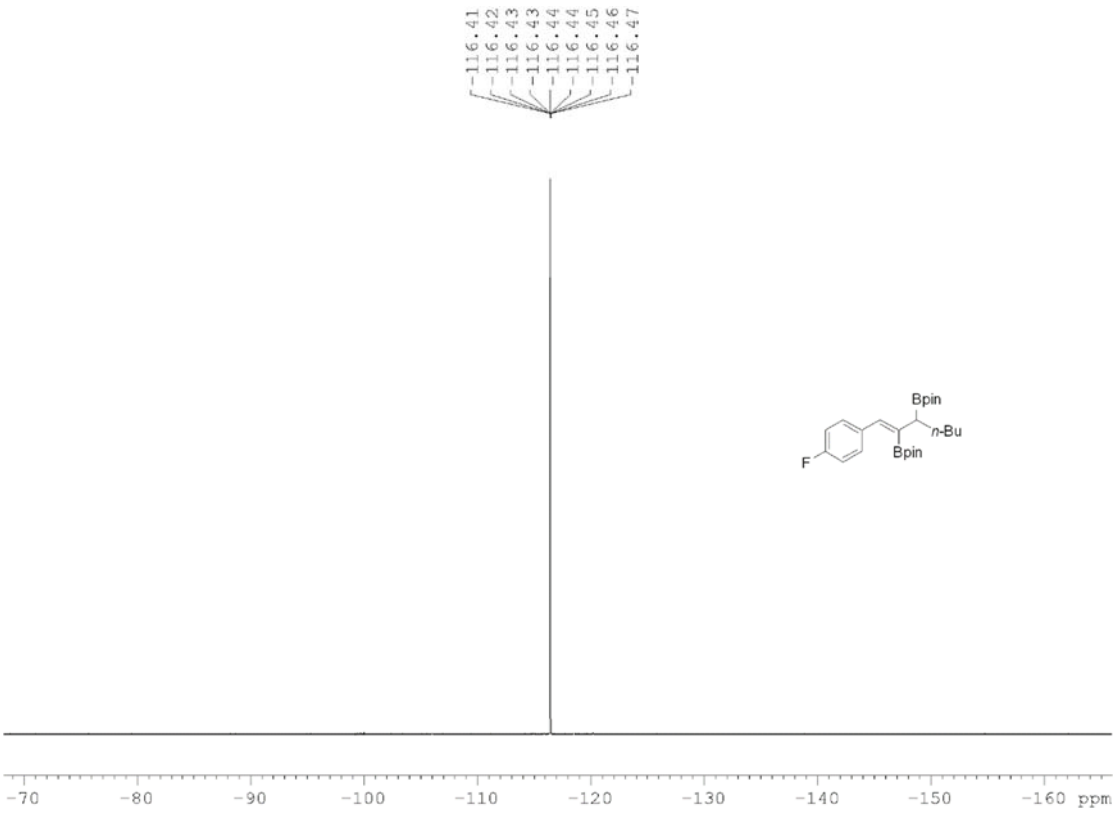
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)

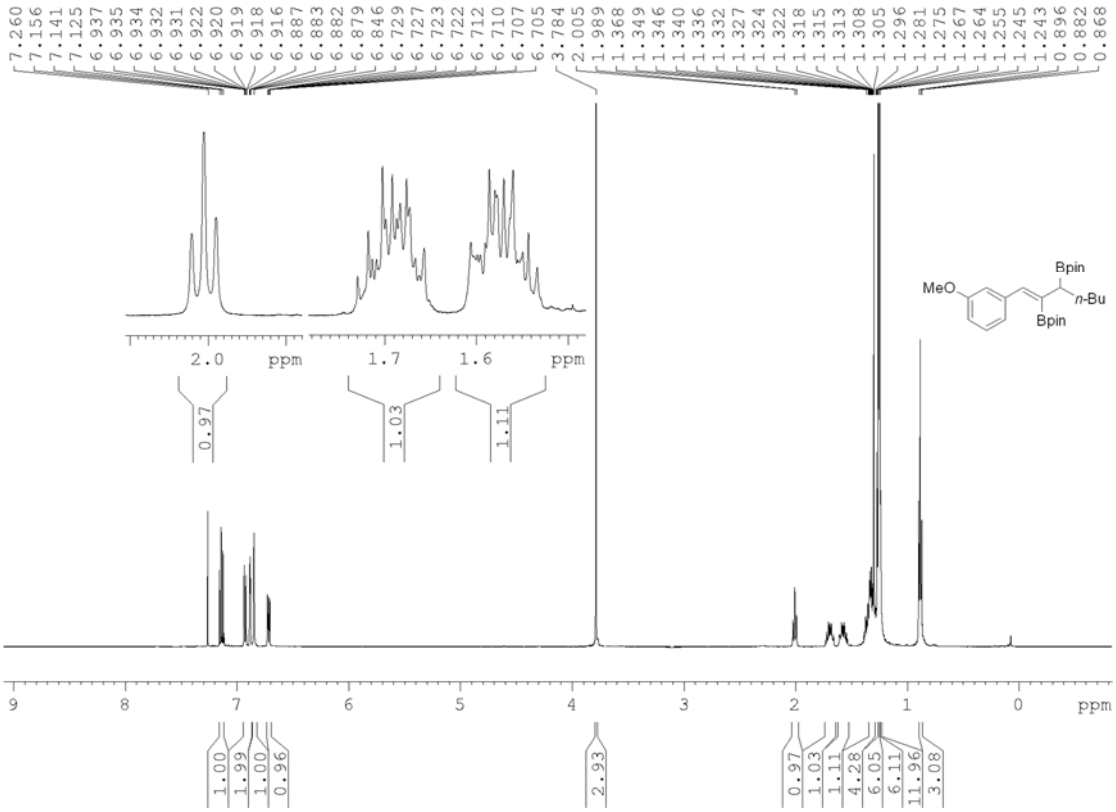


^{19}F NMR (470 MHz, $CDCl_3$)

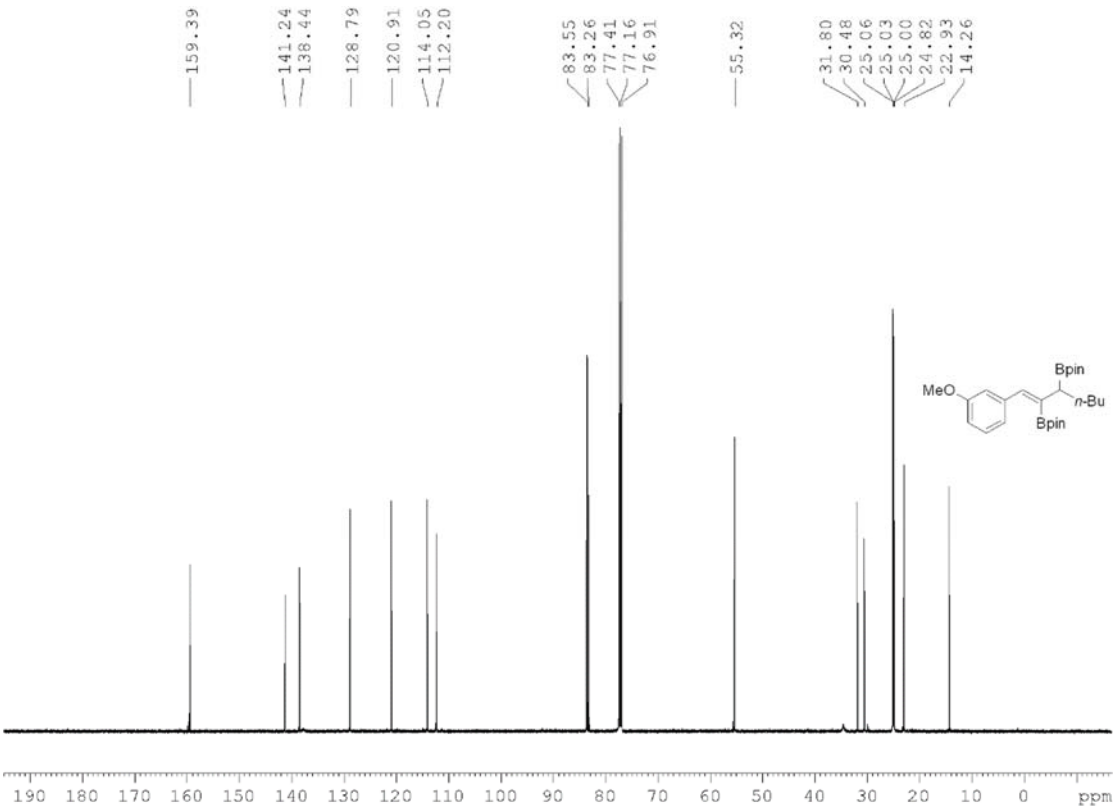


Compound (3-2)o

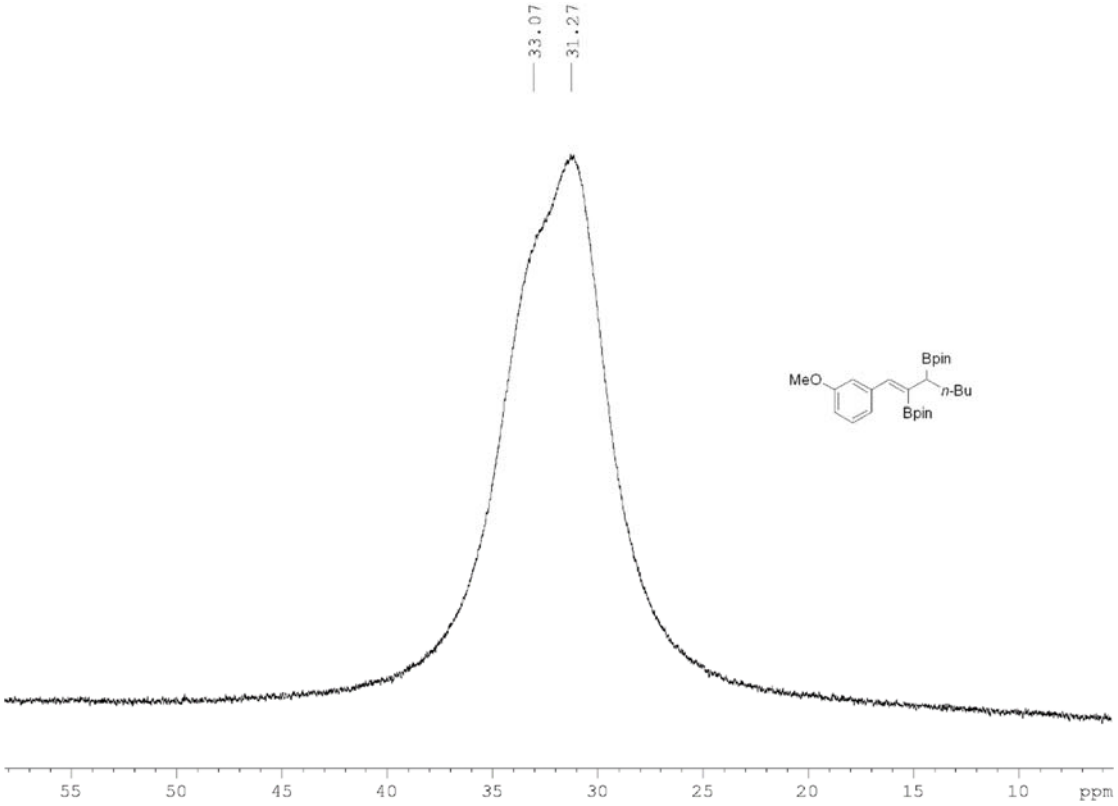
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

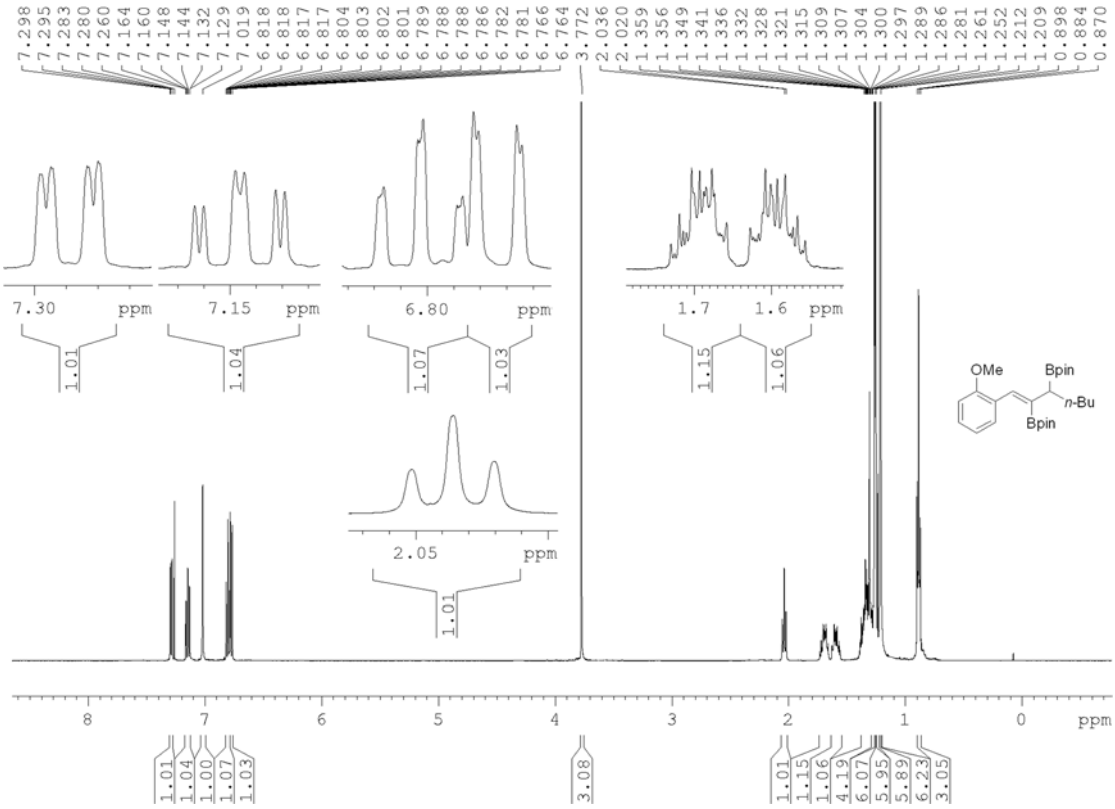


^{11}B NMR (160 MHz, $CDCl_3$)

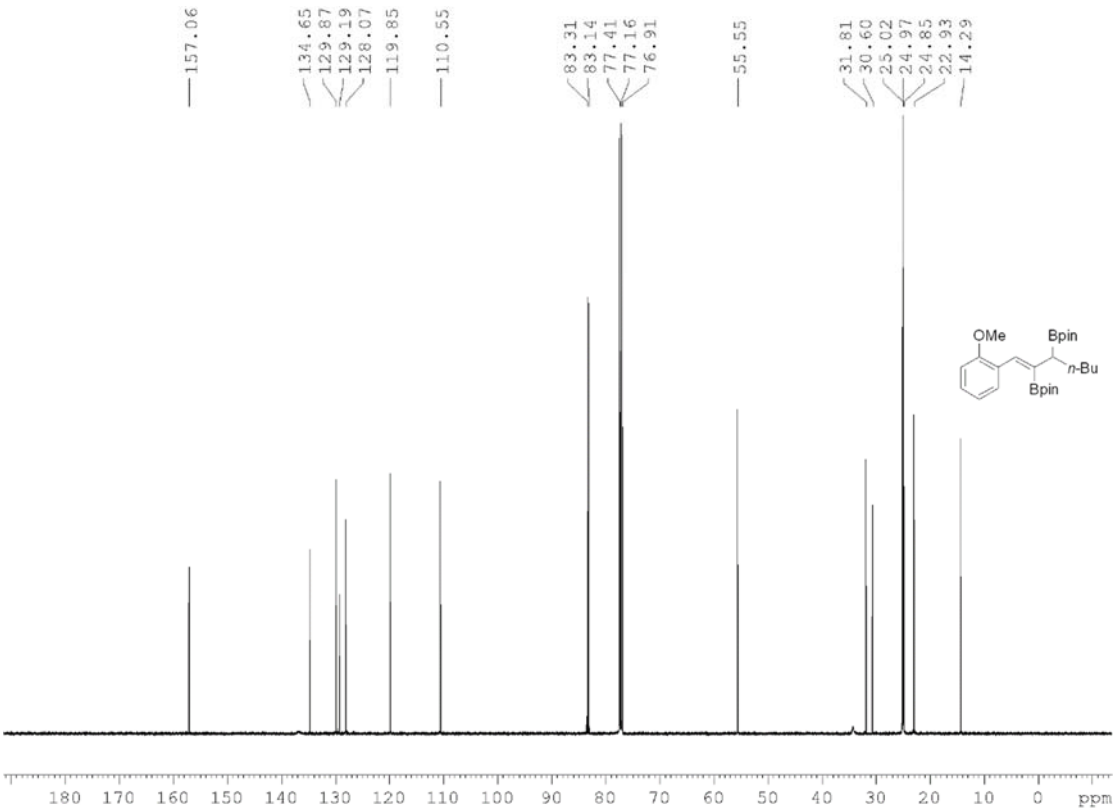


Compound (3-2)p

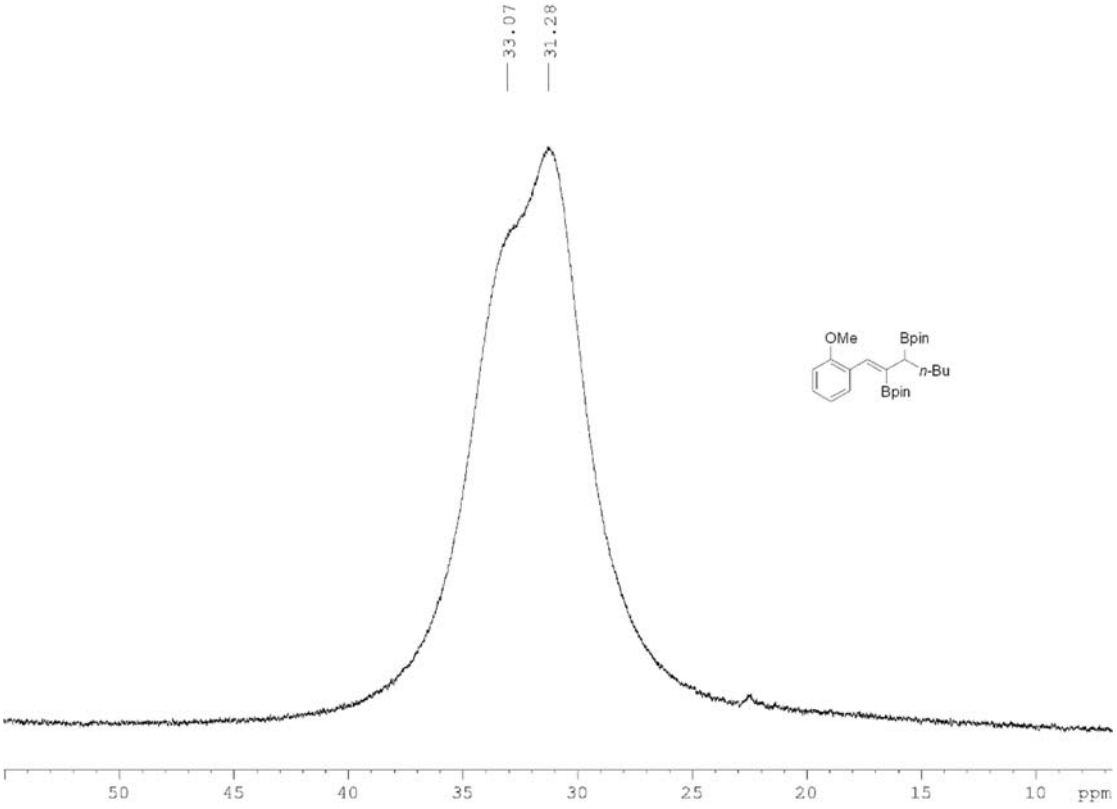
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

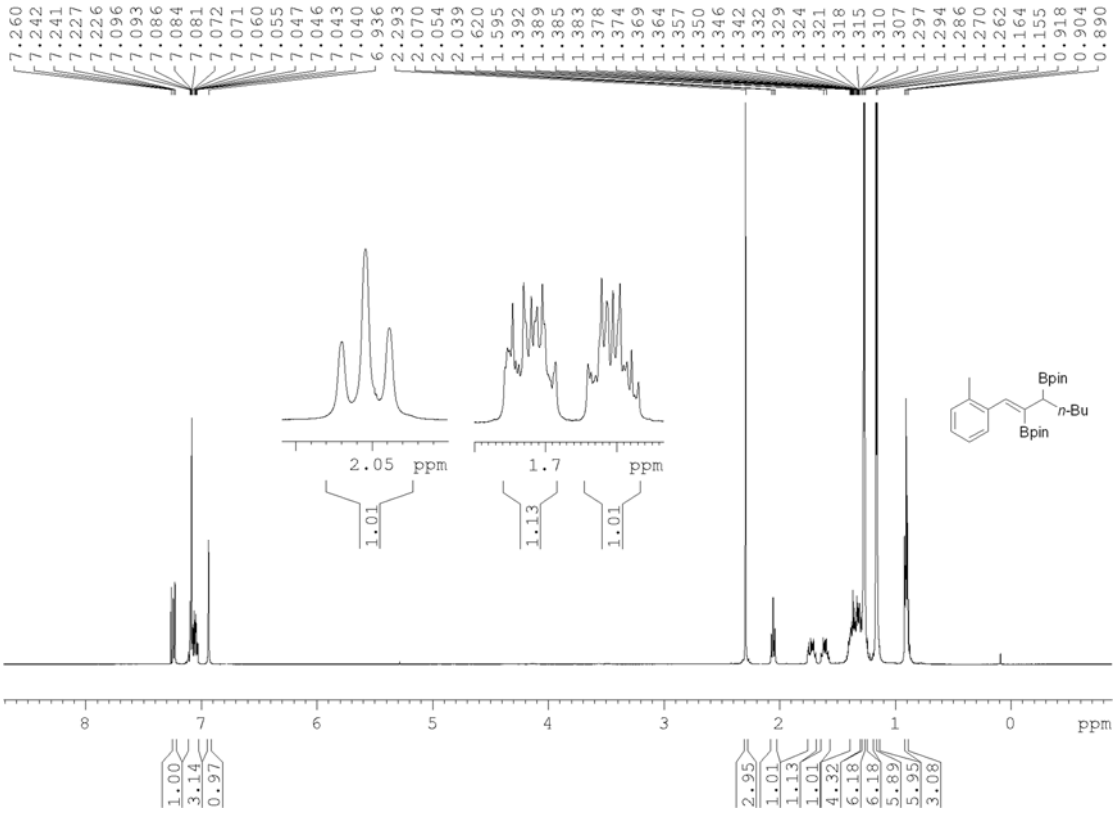


^{11}B NMR (160 MHz, $CDCl_3$)

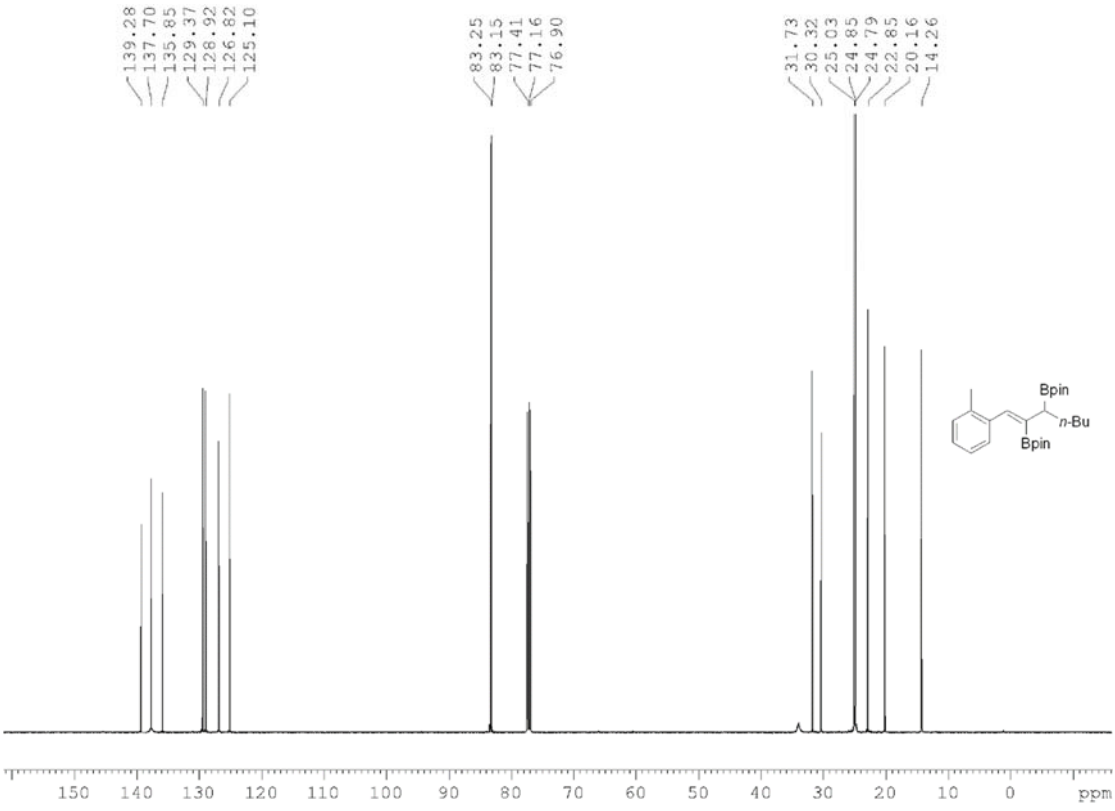


Compound (3-2)q

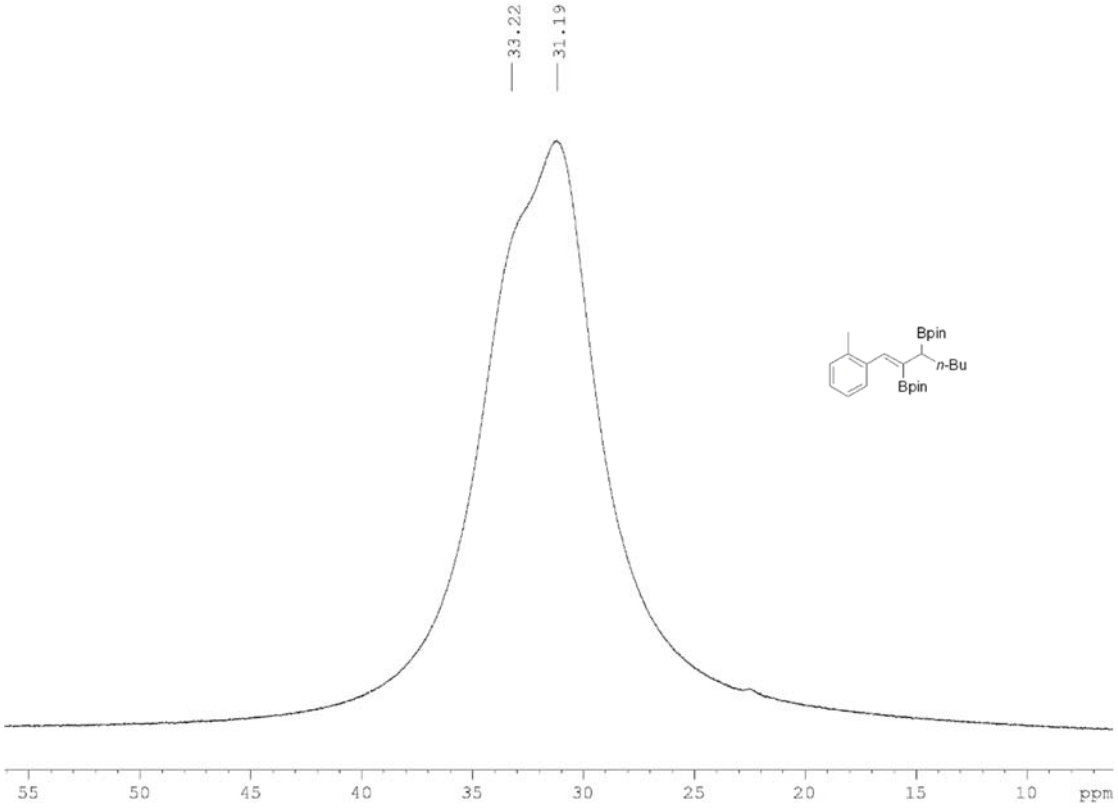
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

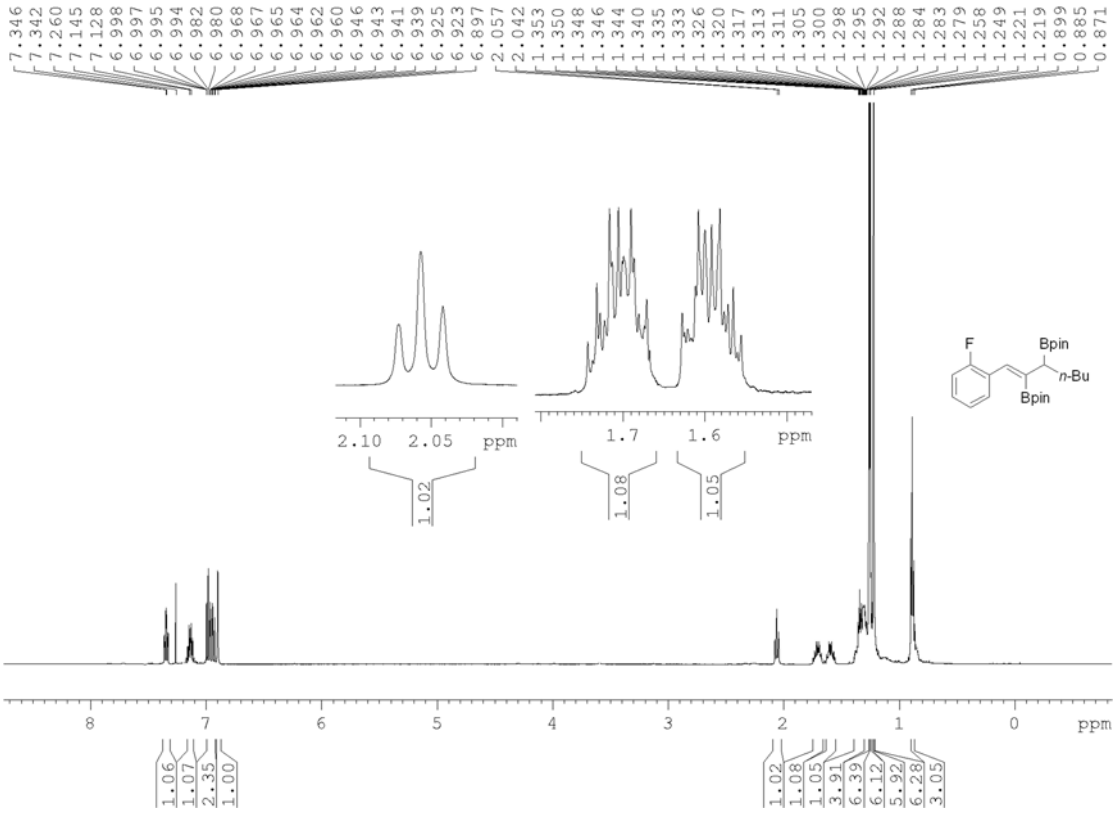


^{11}B NMR (160 MHz, $CDCl_3$)

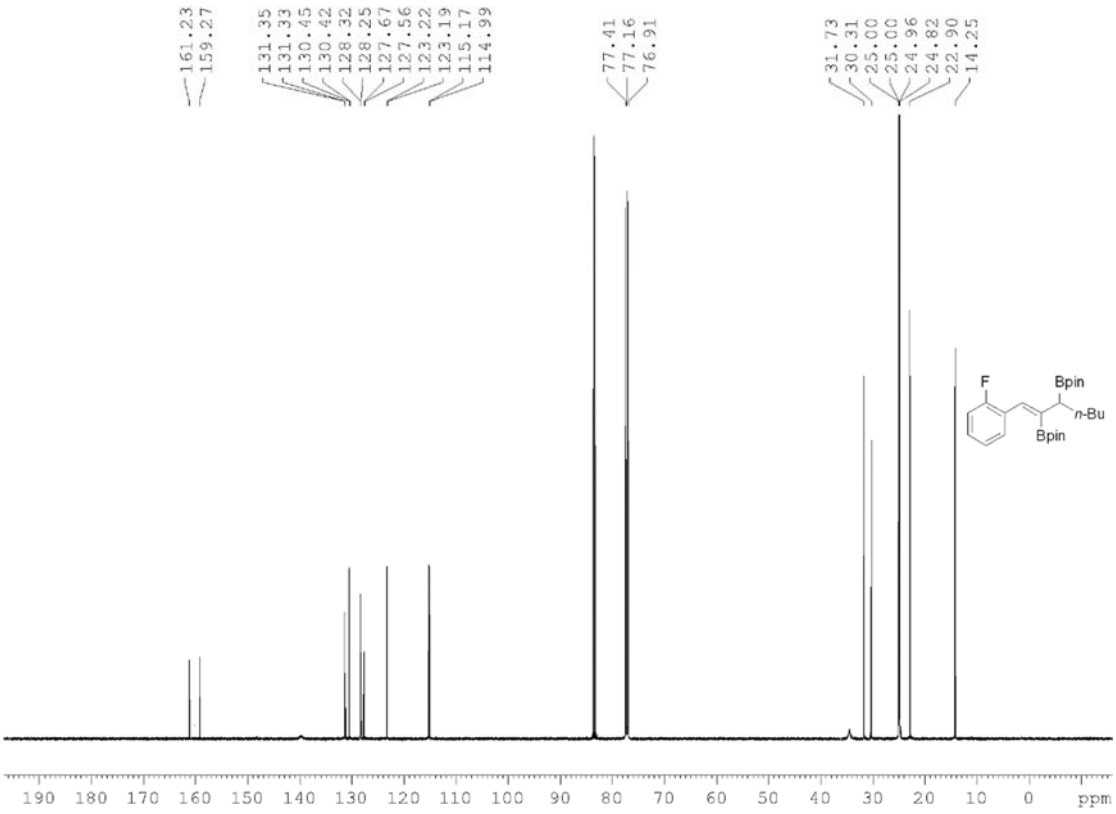


Compound (3-2)r

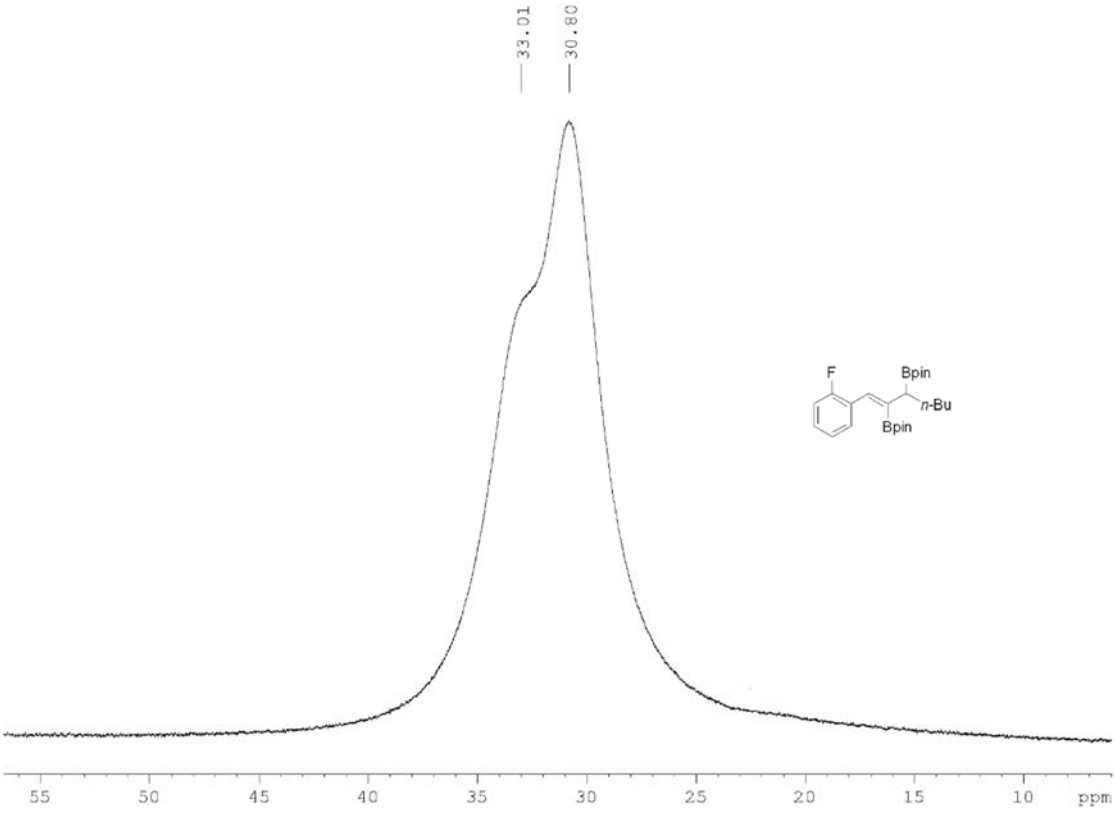
^{1}H NMR (500 MHz, $CDCl_3$)



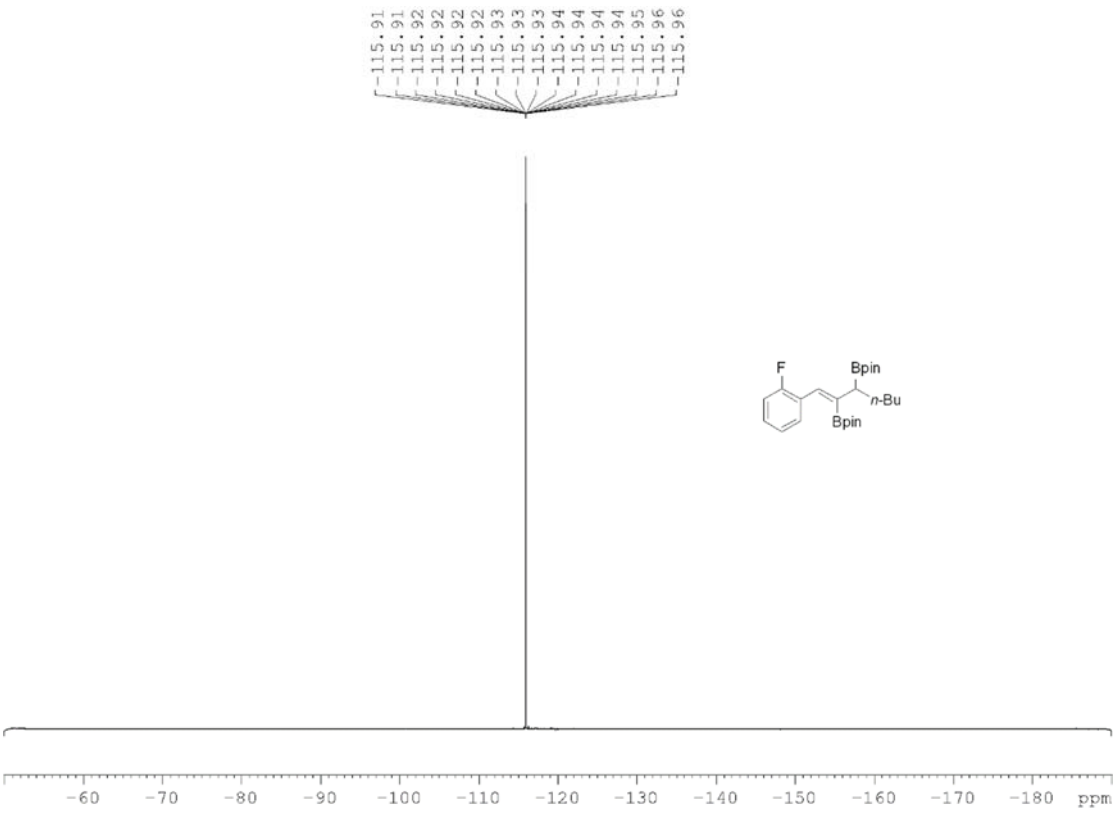
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)

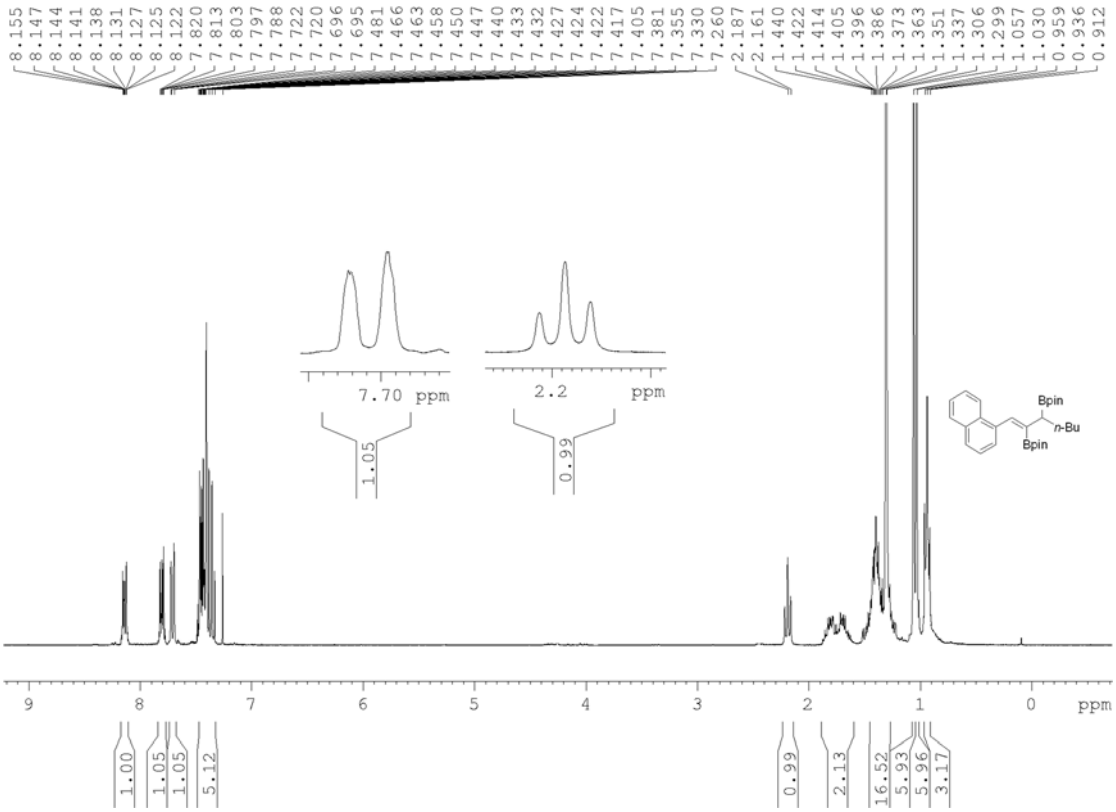


^{19}F NMR (470 MHz, $CDCl_3$)

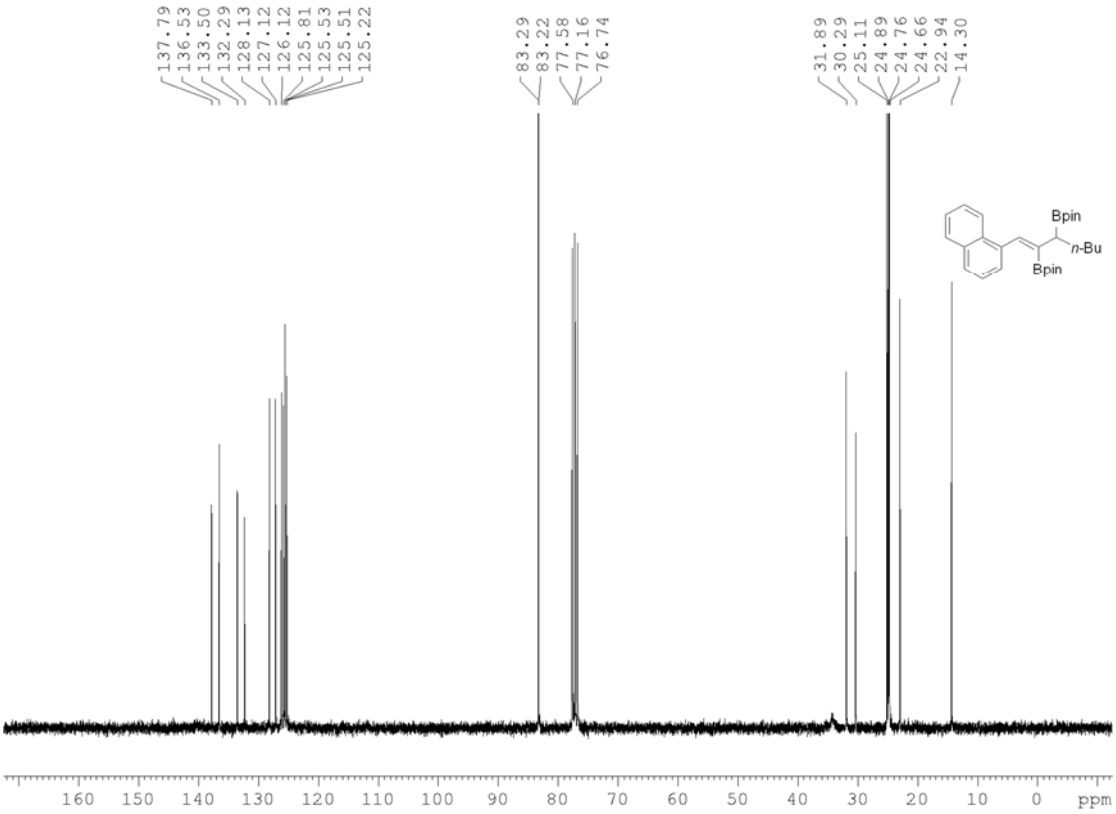


Compound (3-2)s

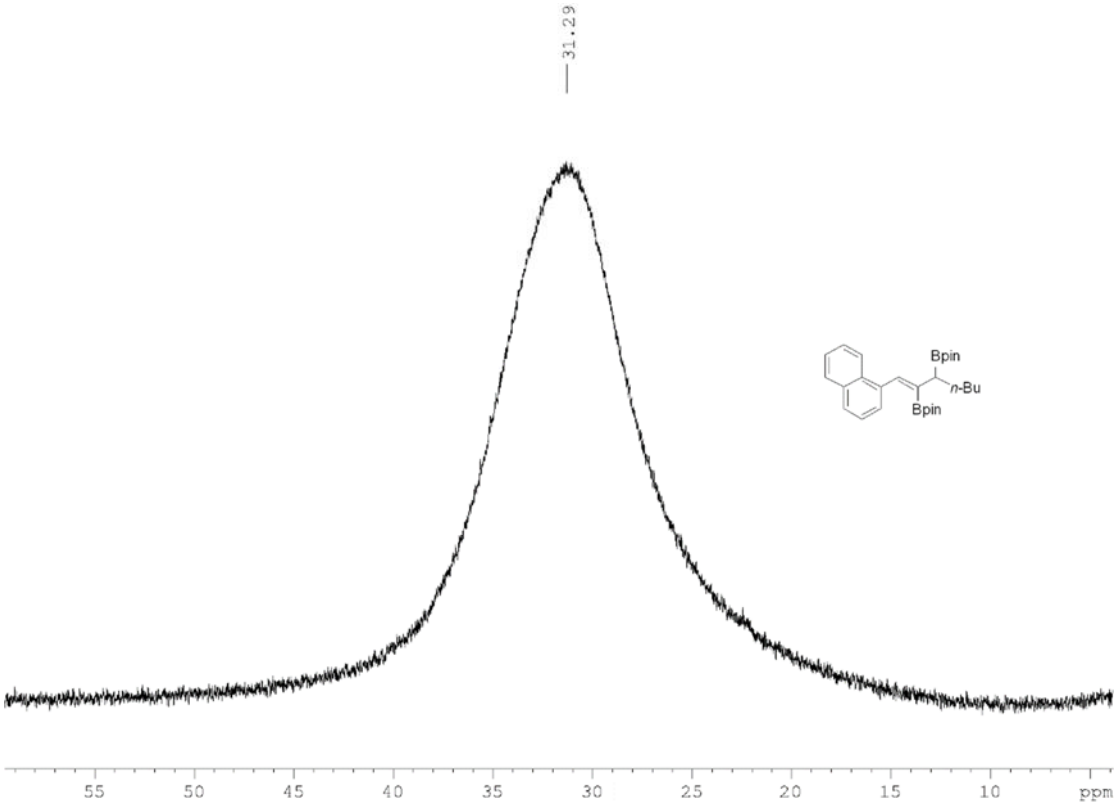
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

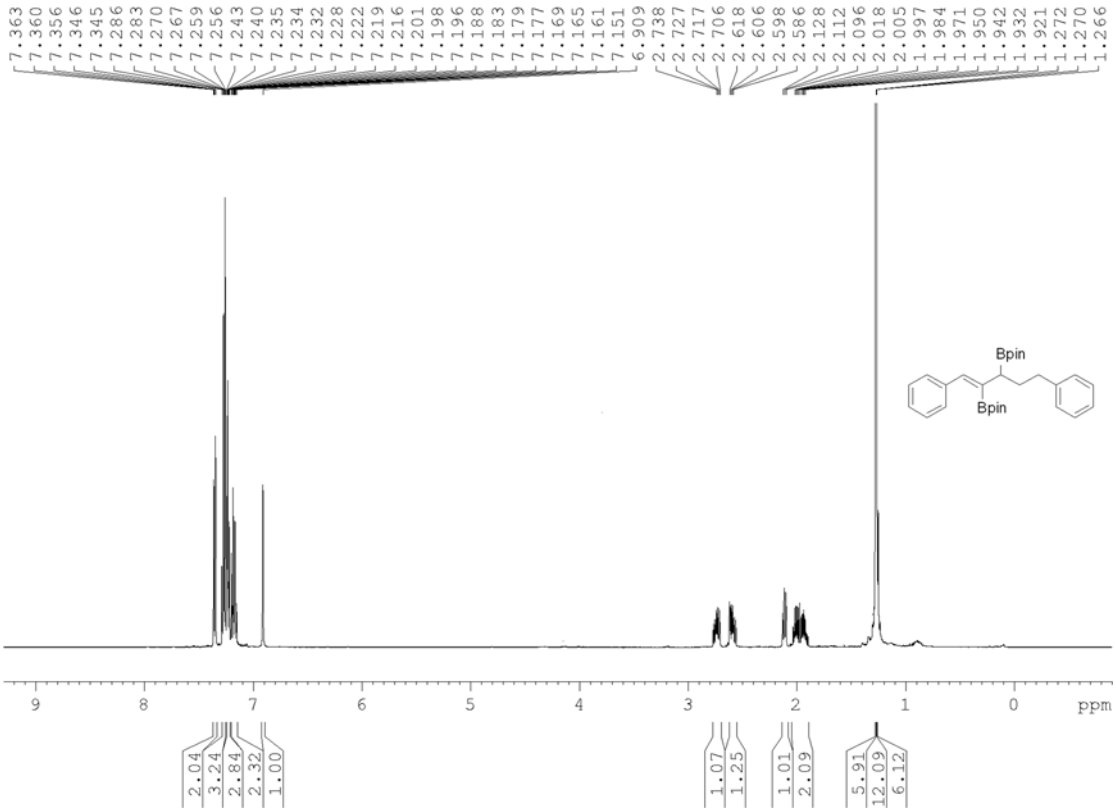


^{11}B NMR (96 MHz, $CDCl_3$)

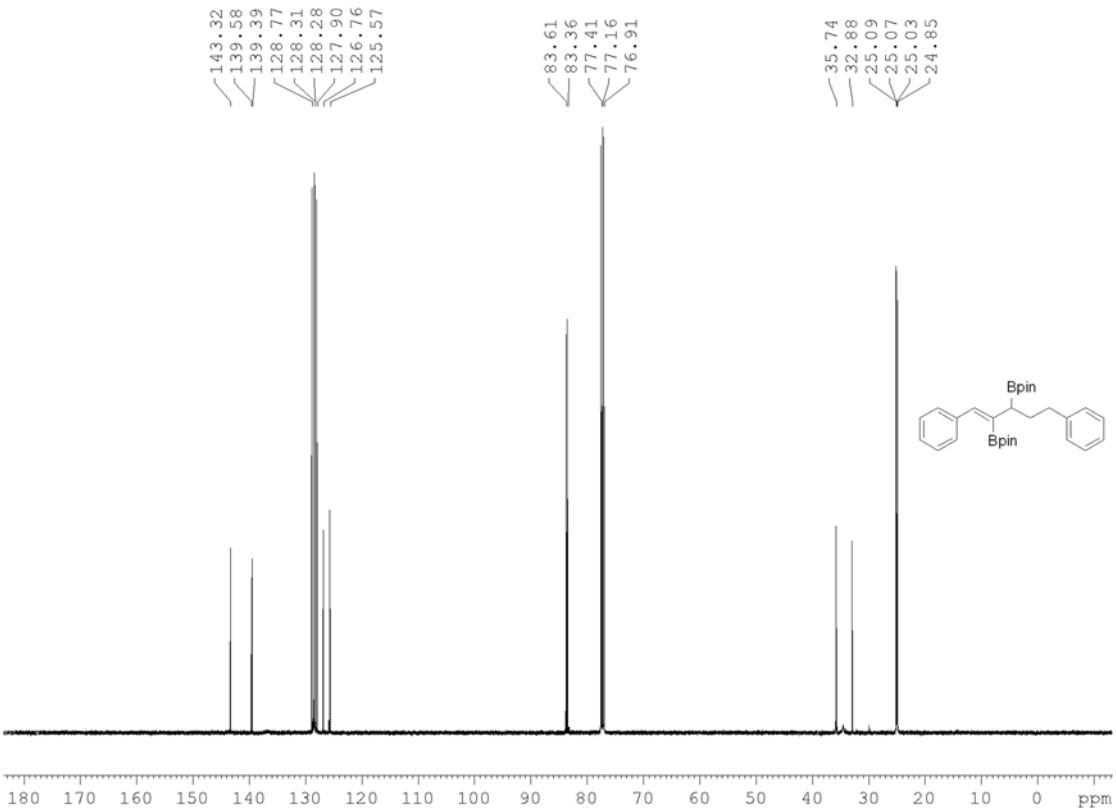


Compound (3-2)t

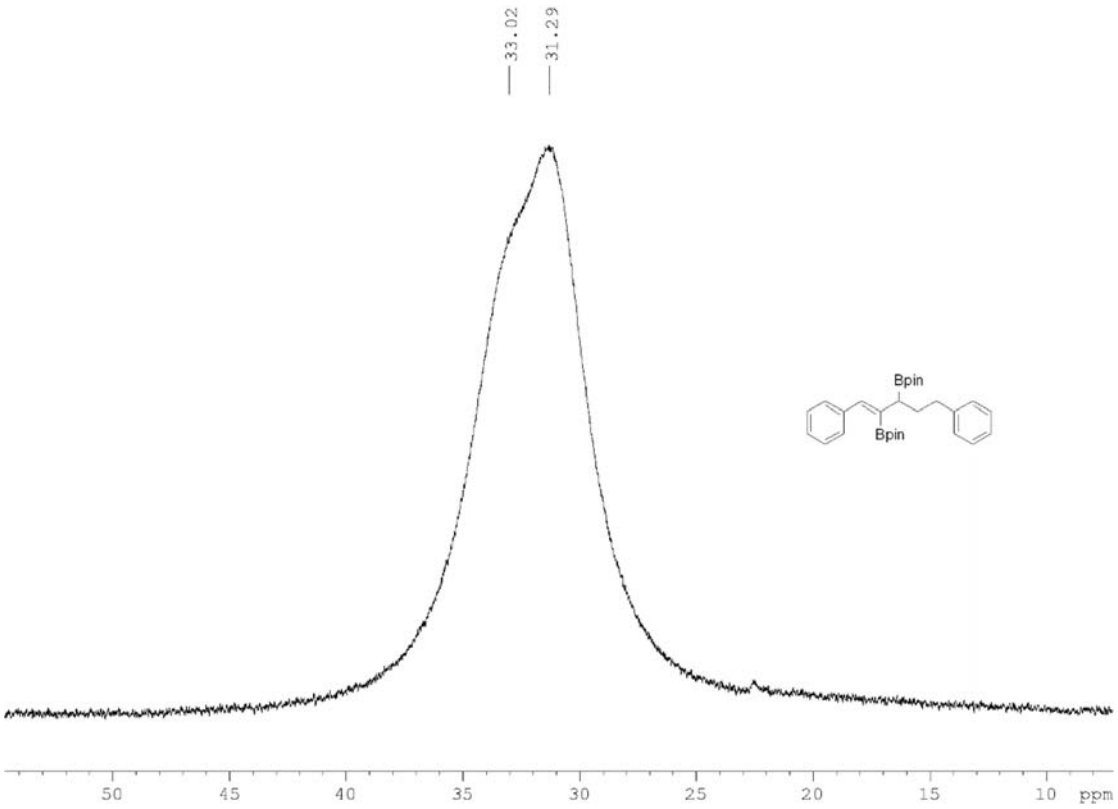
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

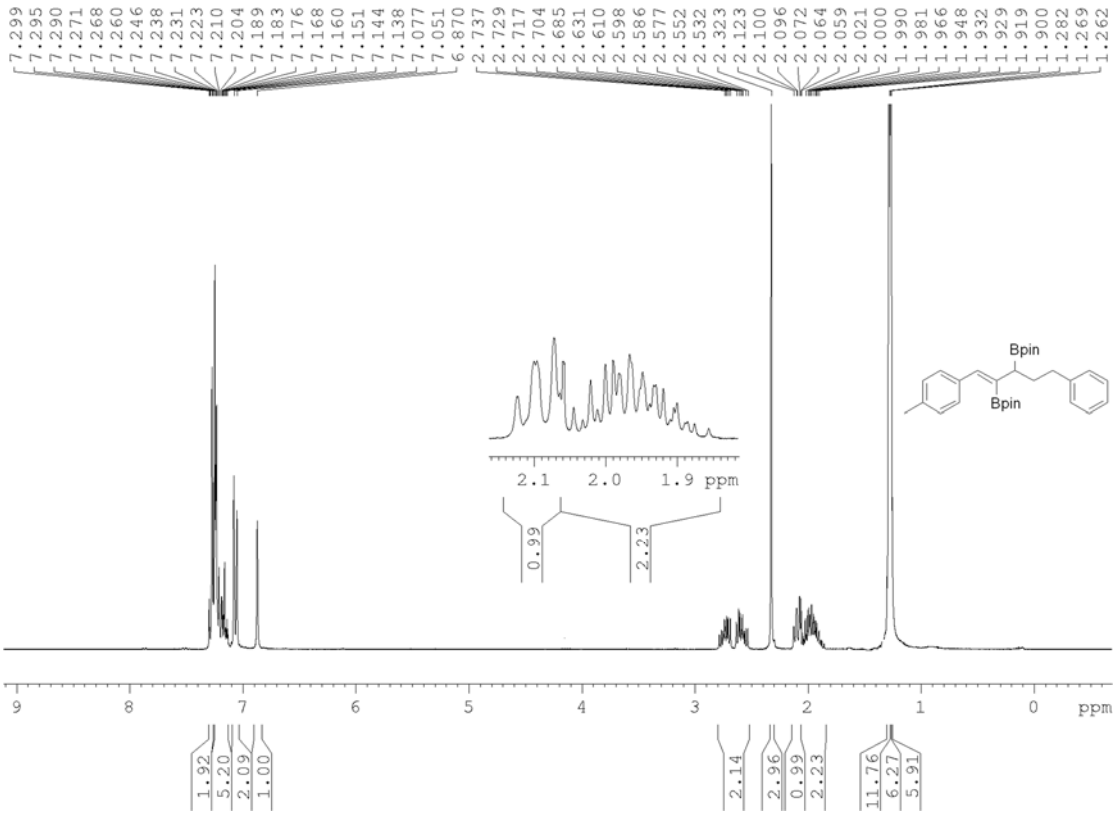


^{11}B NMR (160 MHz, $CDCl_3$)

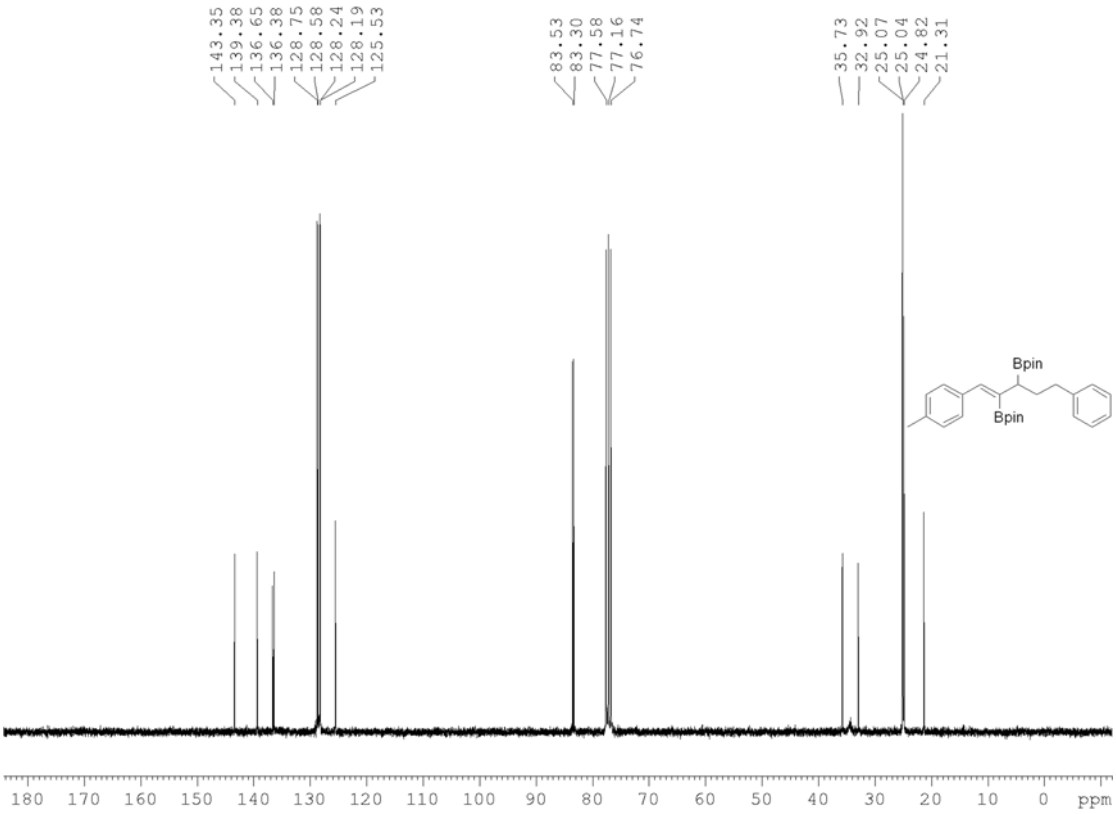


Compound (3-2)u

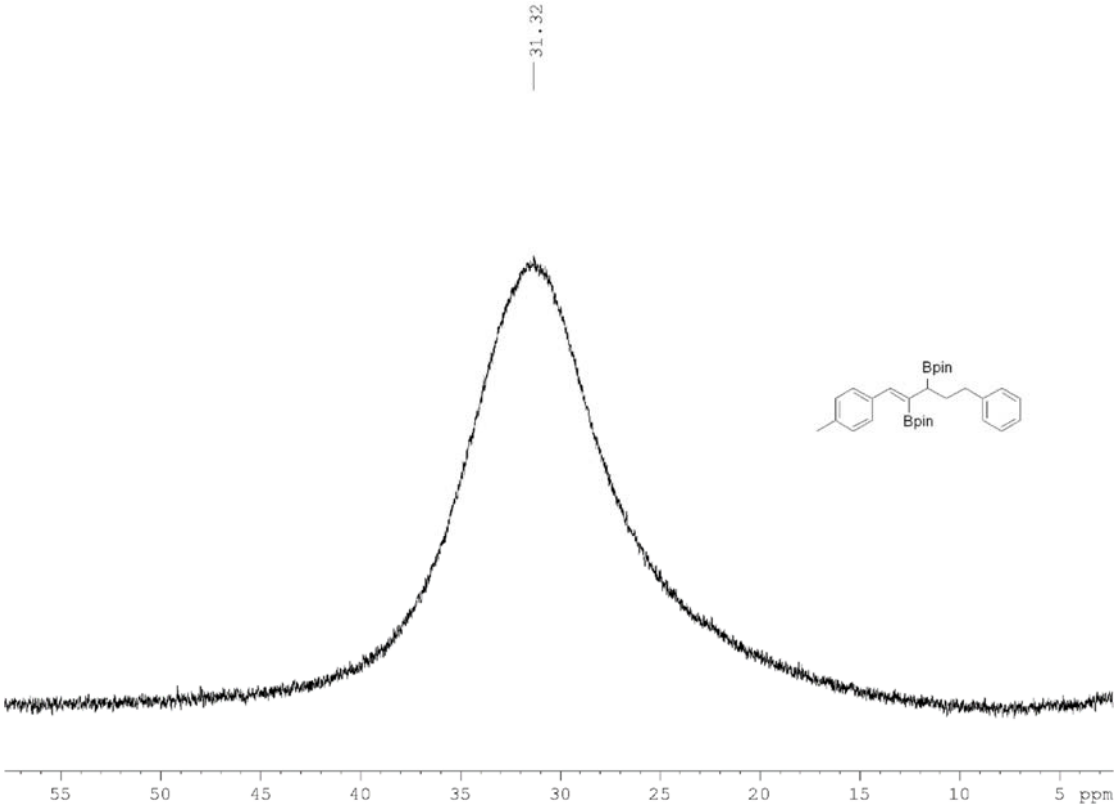
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

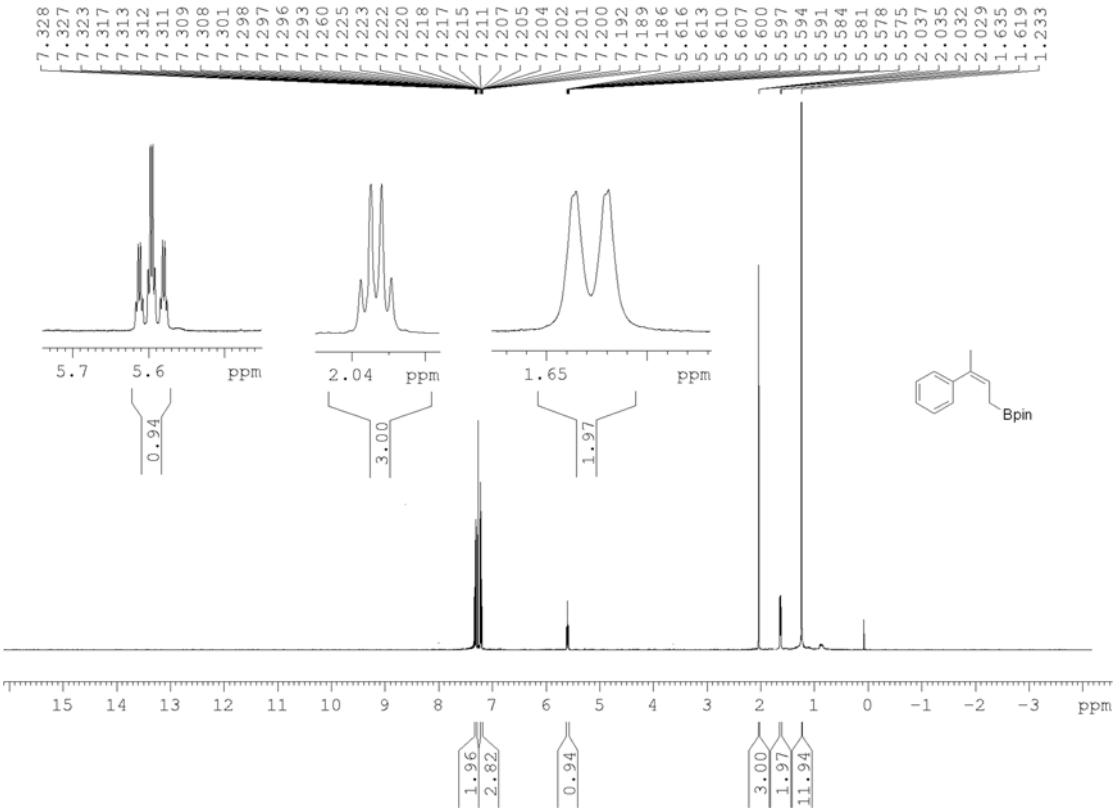


^{11}B NMR (96 MHz, $CDCl_3$)

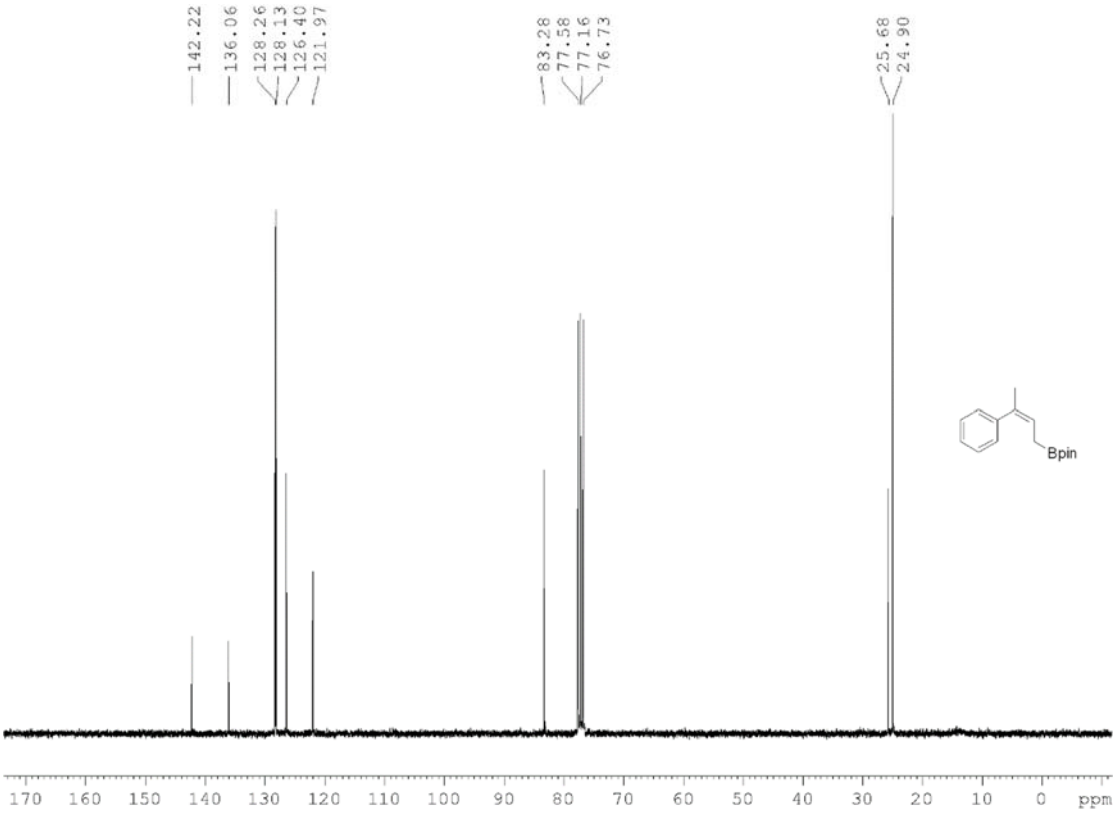


Compound (3-4)a or (4-2)l

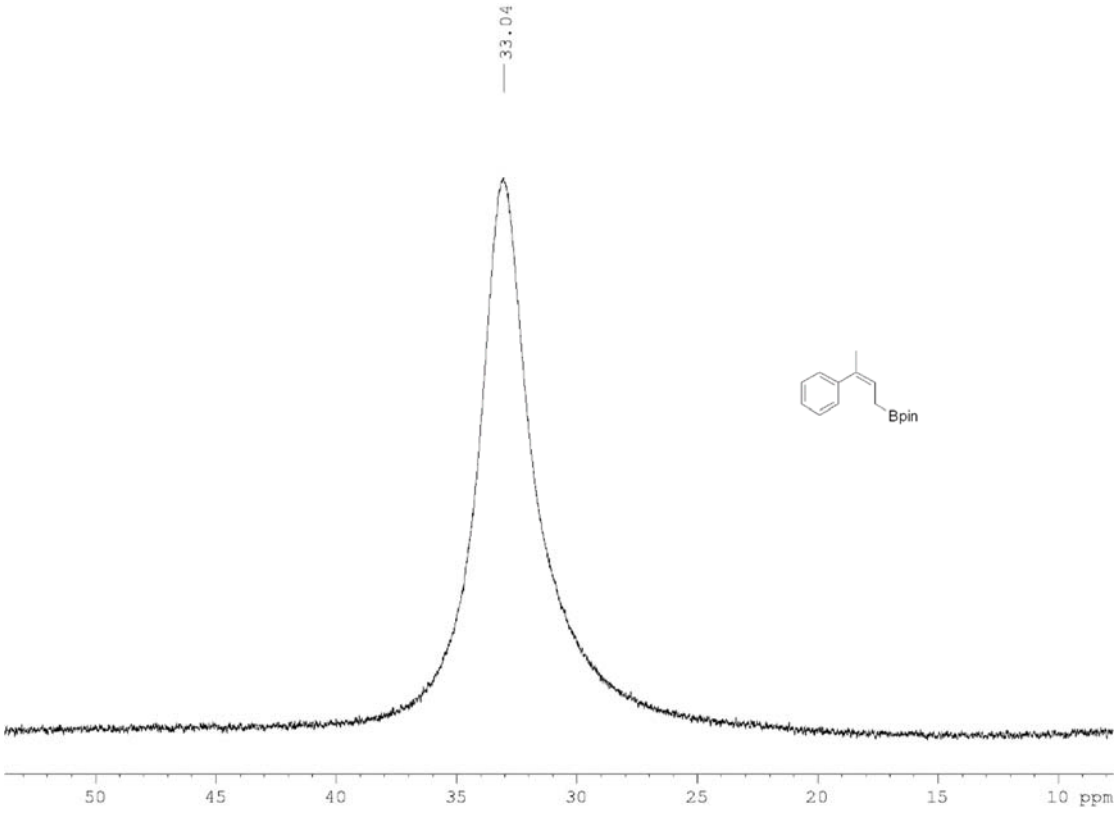
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

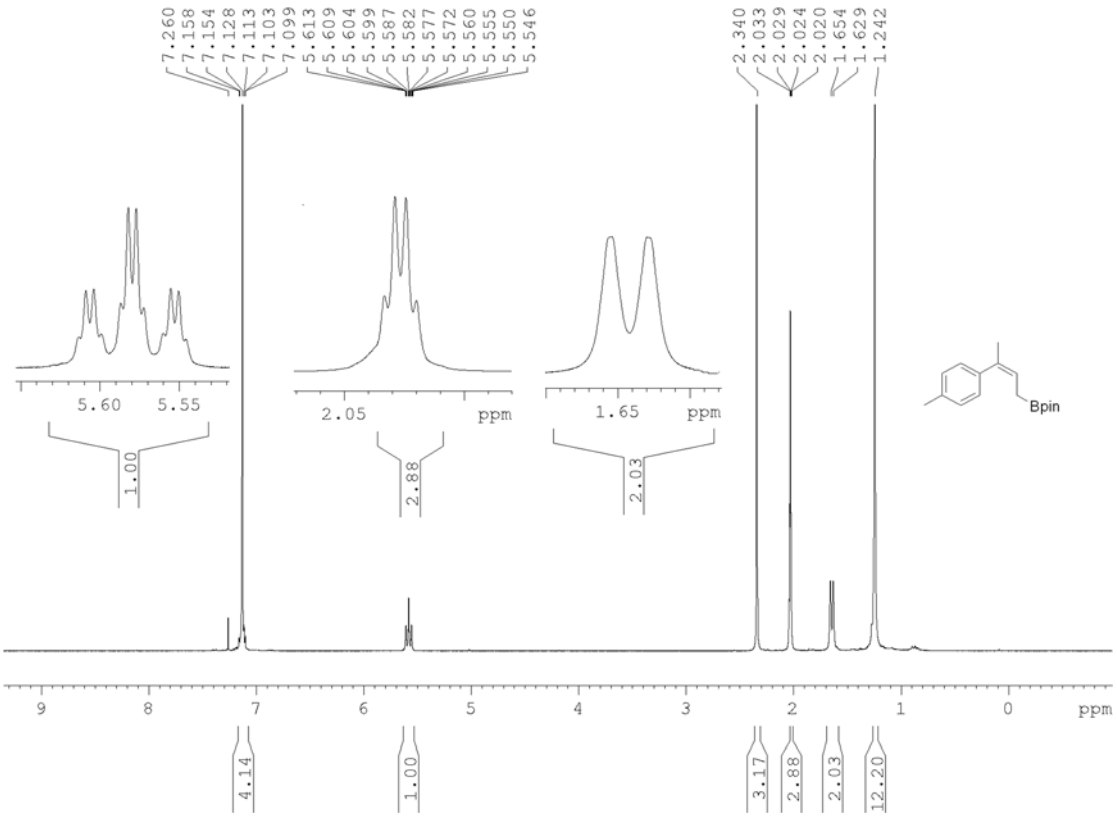


^{11}B NMR (160 MHz, $CDCl_3$)

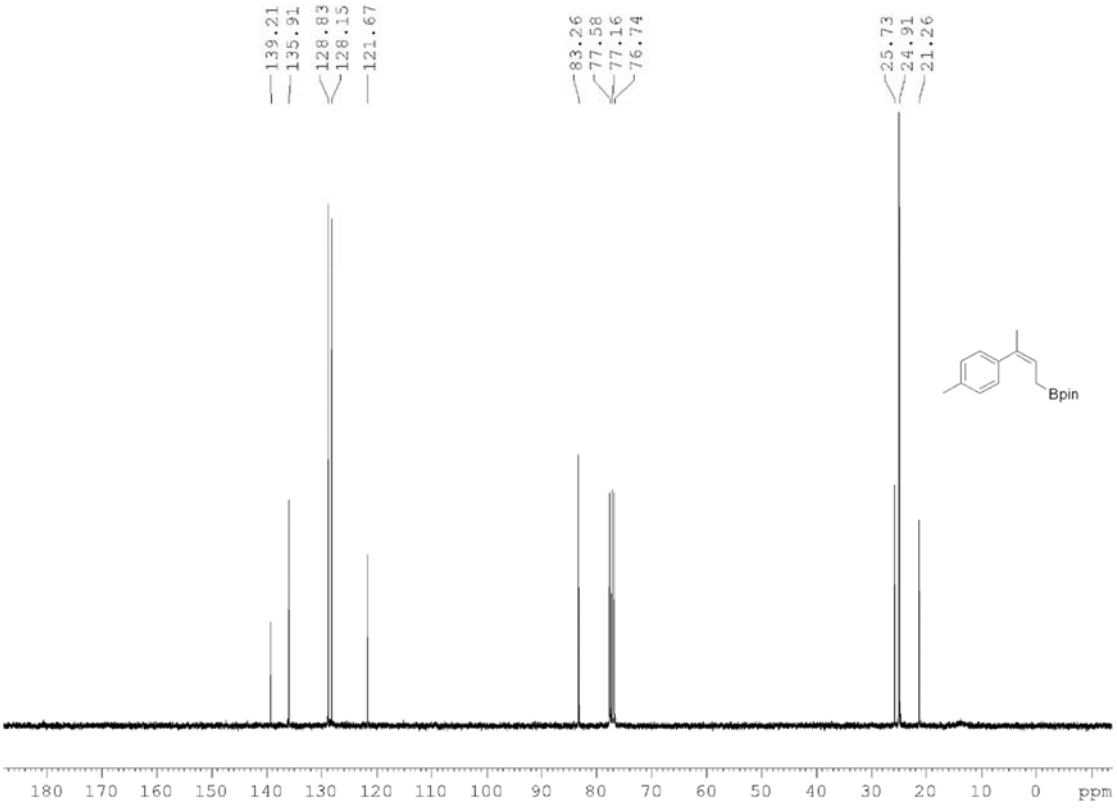


Compound (3-4)b or (4-2)m

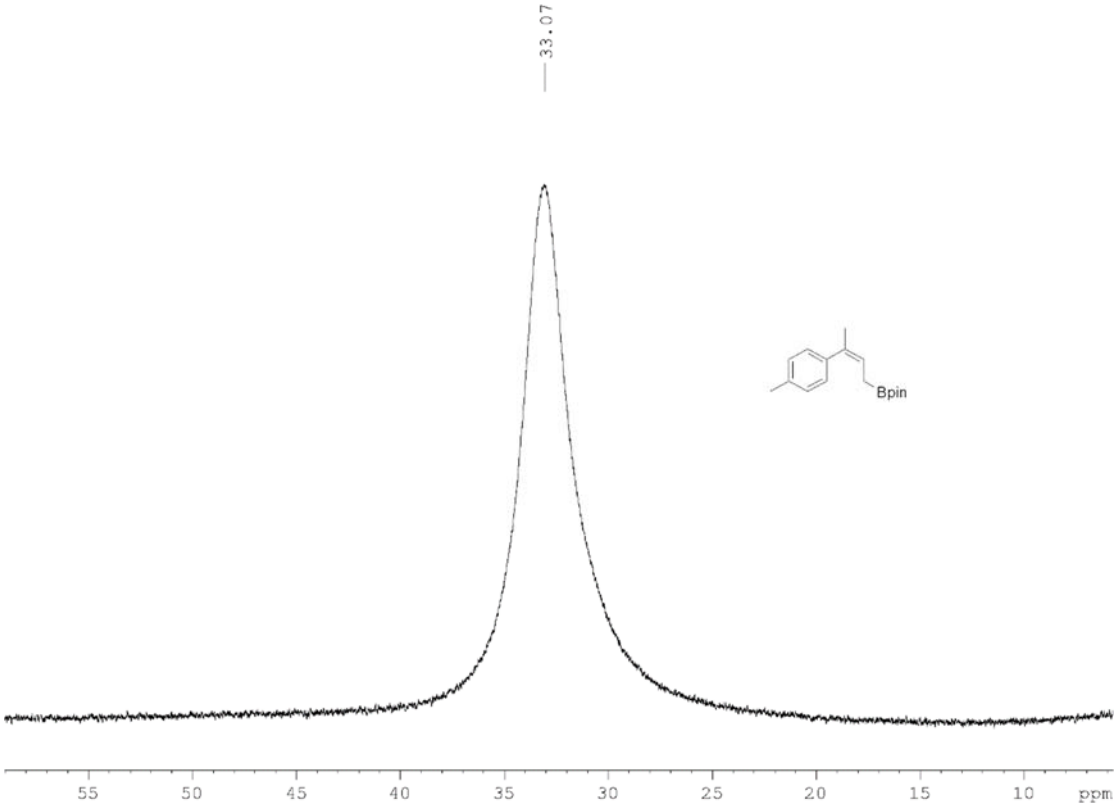
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

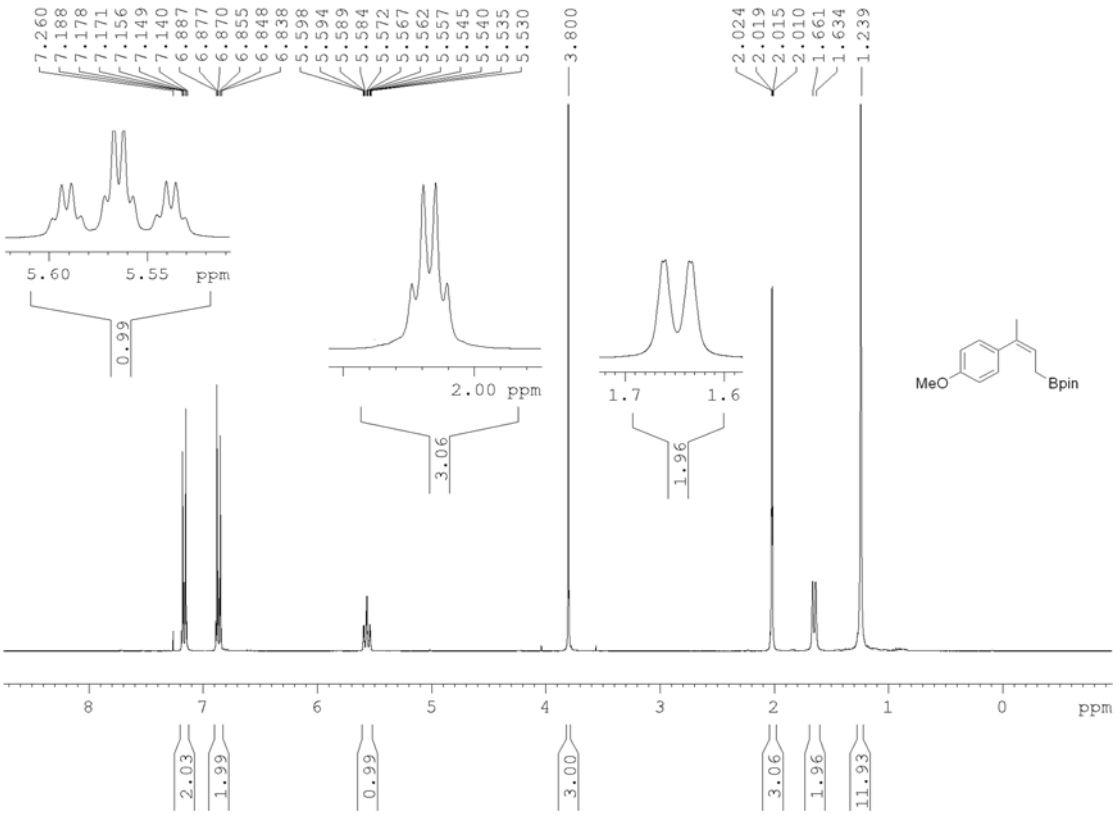


^{11}B NMR (96 MHz, $CDCl_3$)

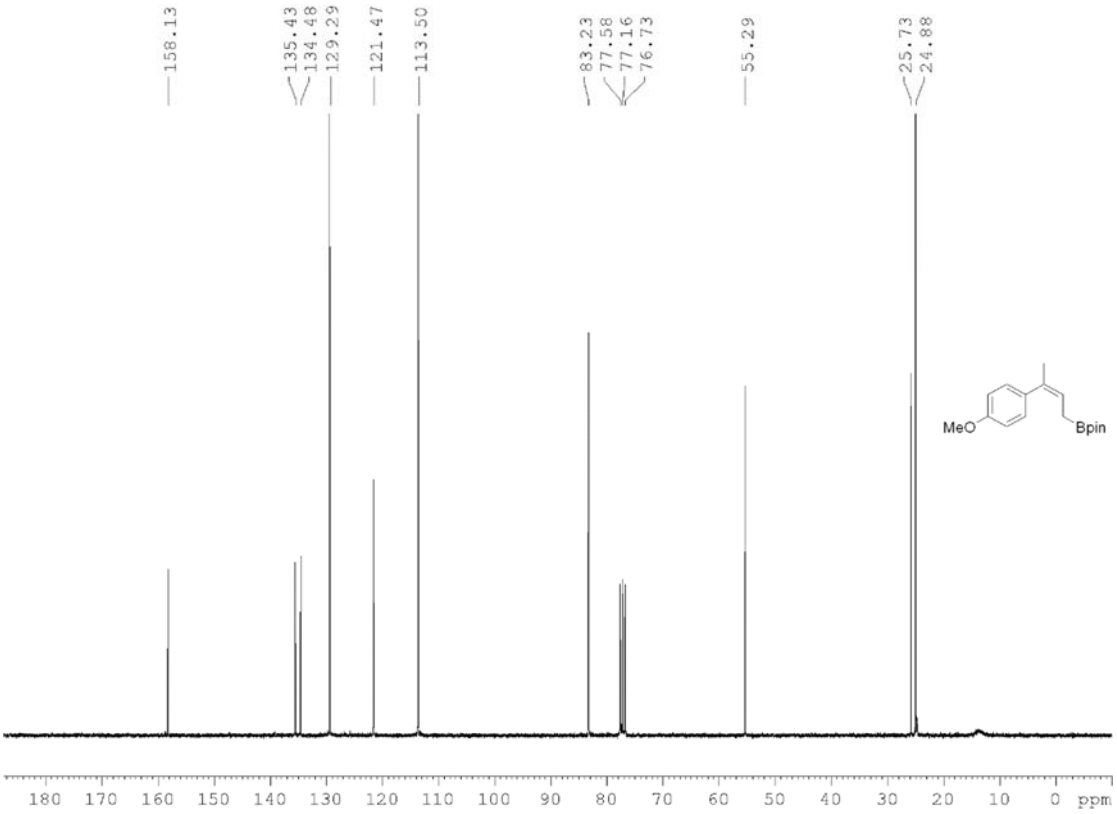


Compound (3-4)c or (4-2)n

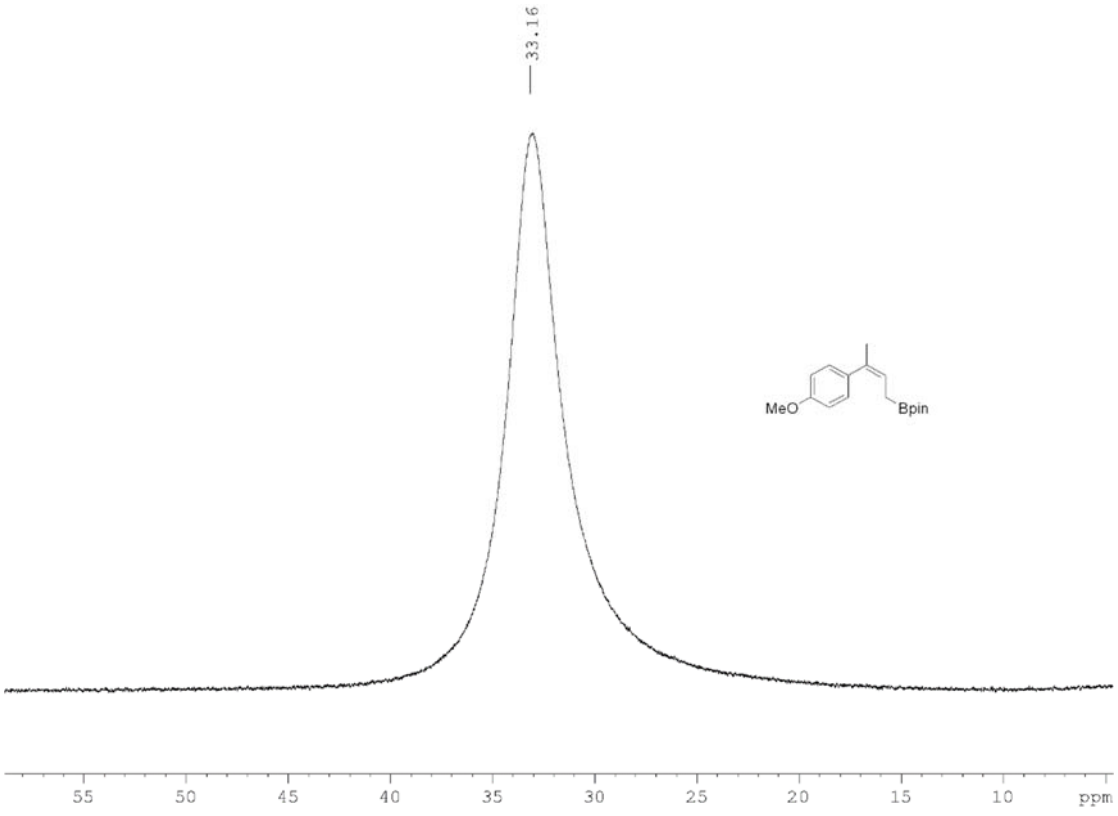
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

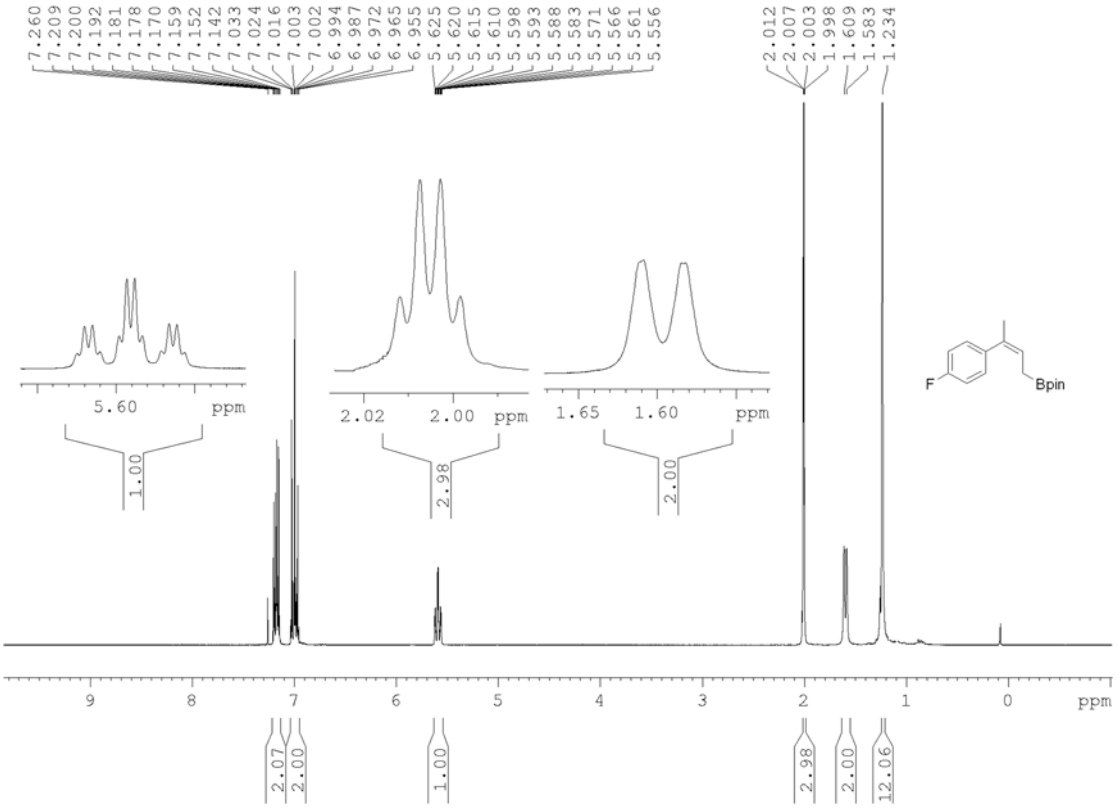


^{11}B NMR (96 MHz, $CDCl_3$)

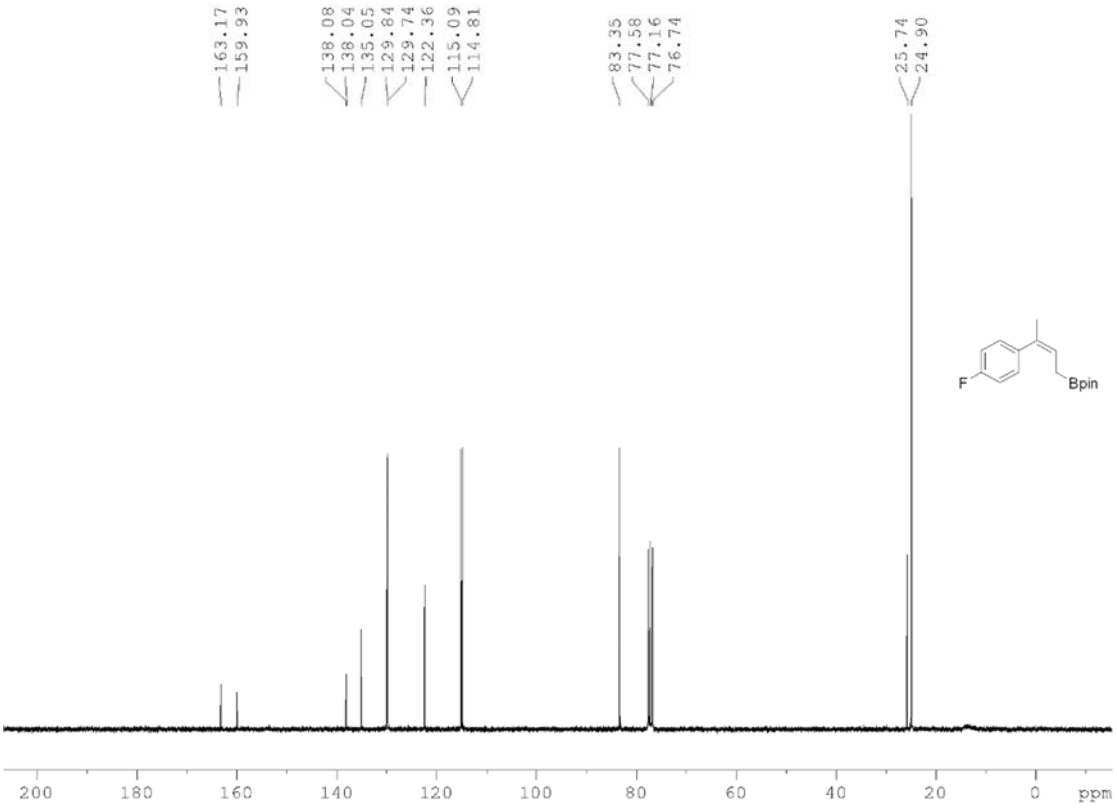


Compound (3-4)d or (4-2)o

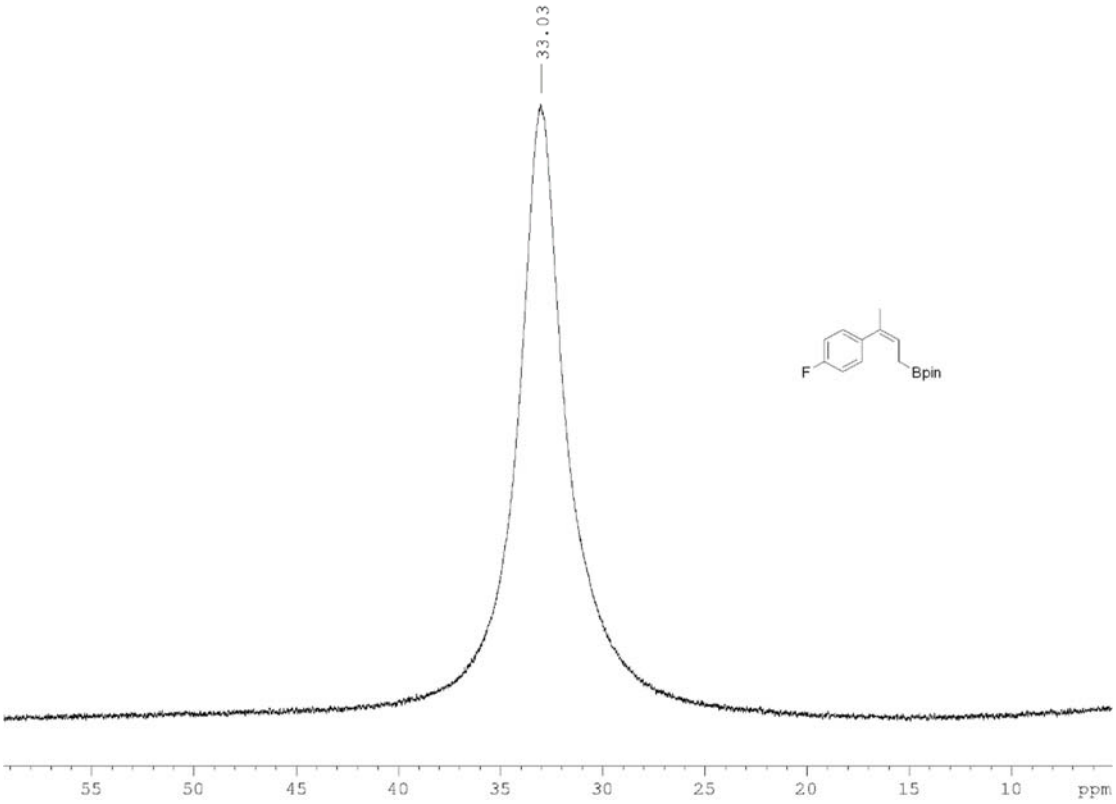
^{1}H NMR (300 MHz, $CDCl_3$)



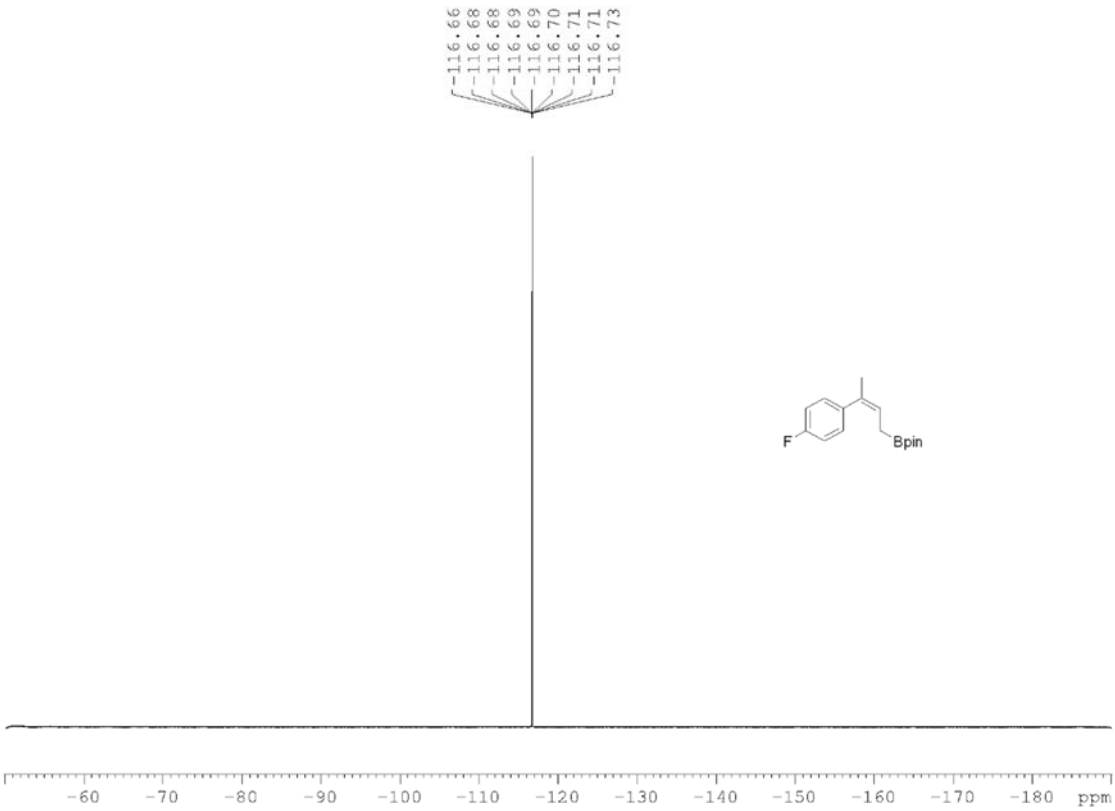
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



^{11}B NMR (96 MHz, $CDCl_3$)

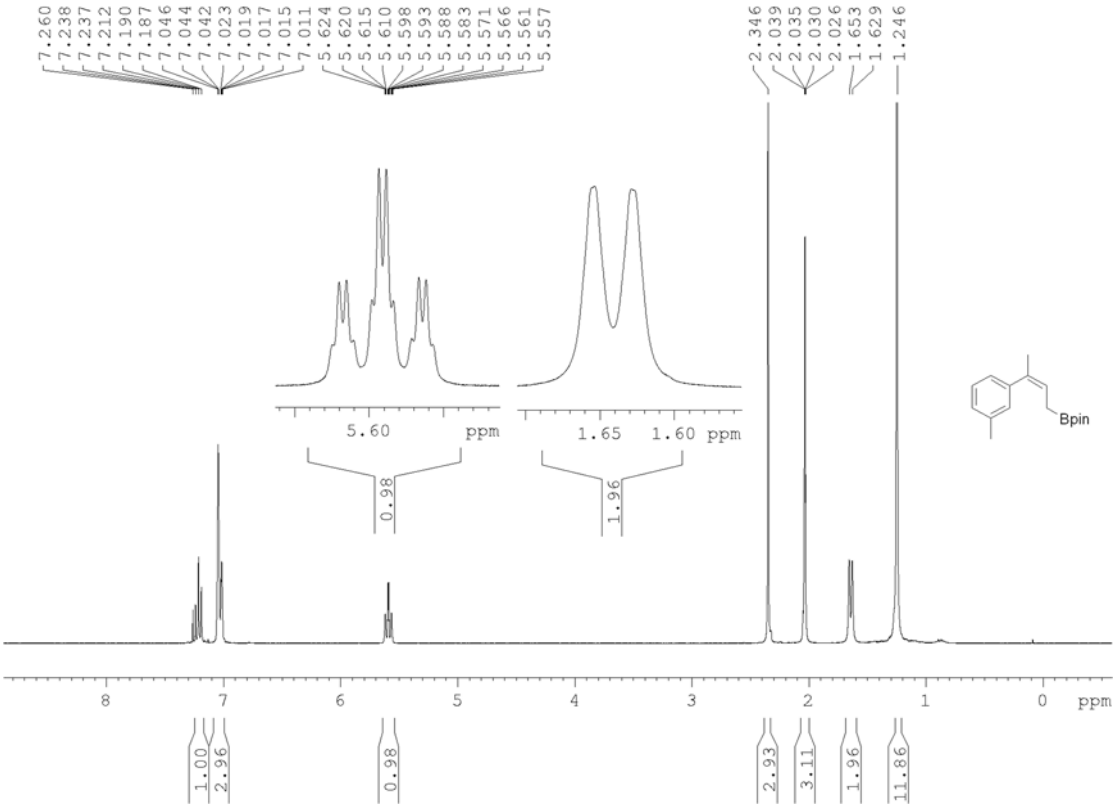


^{19}F NMR (470 MHz, $CDCl_3$)

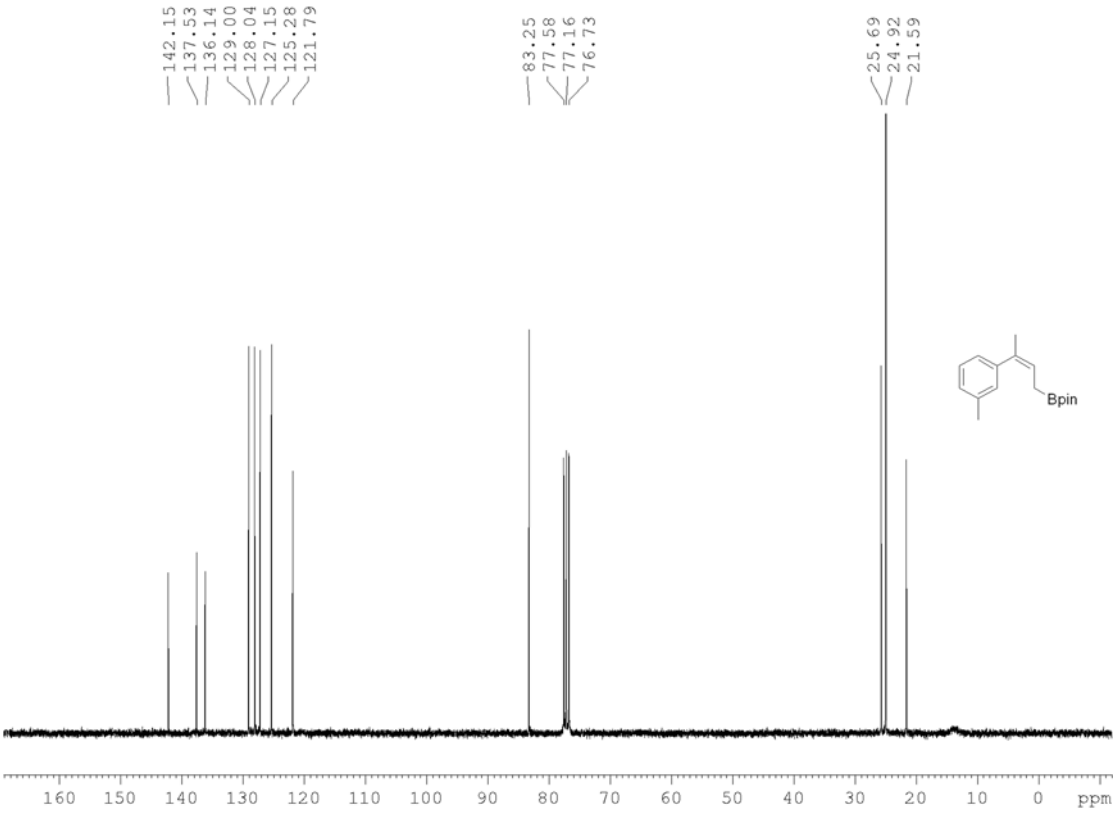


Compound (3-4)e or (4-2)p

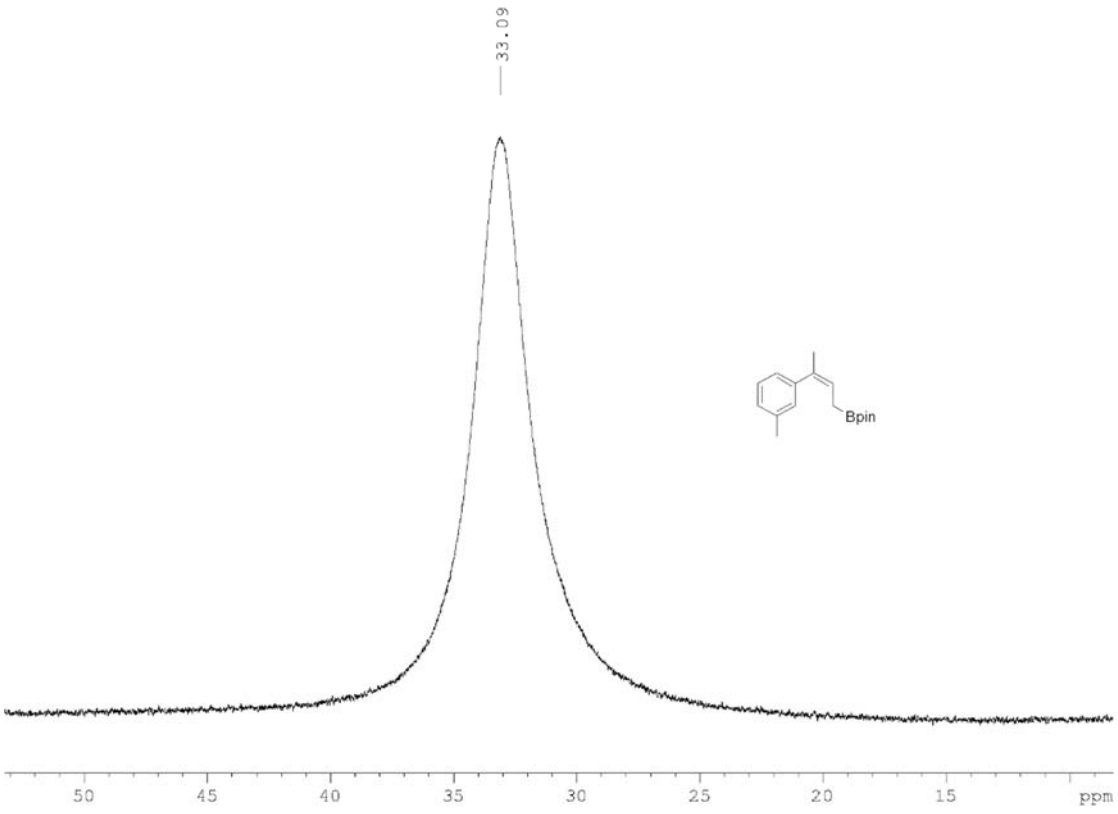
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

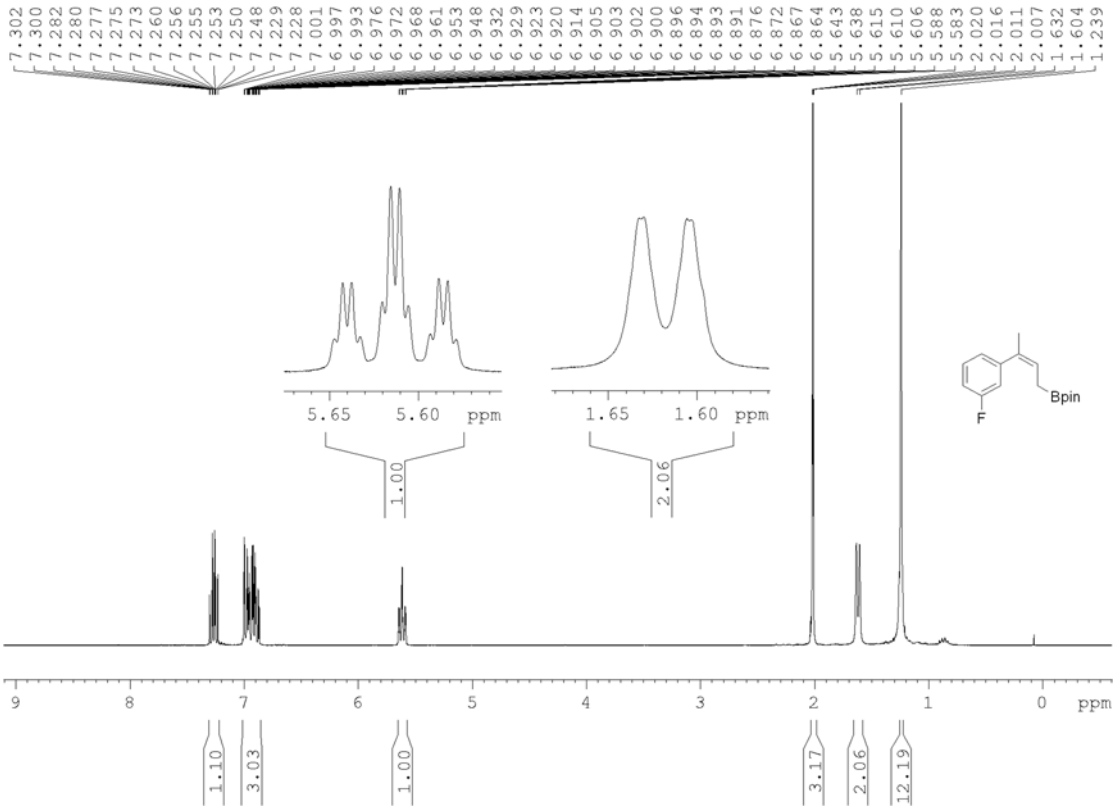


^{11}B NMR (96 MHz, $CDCl_3$)

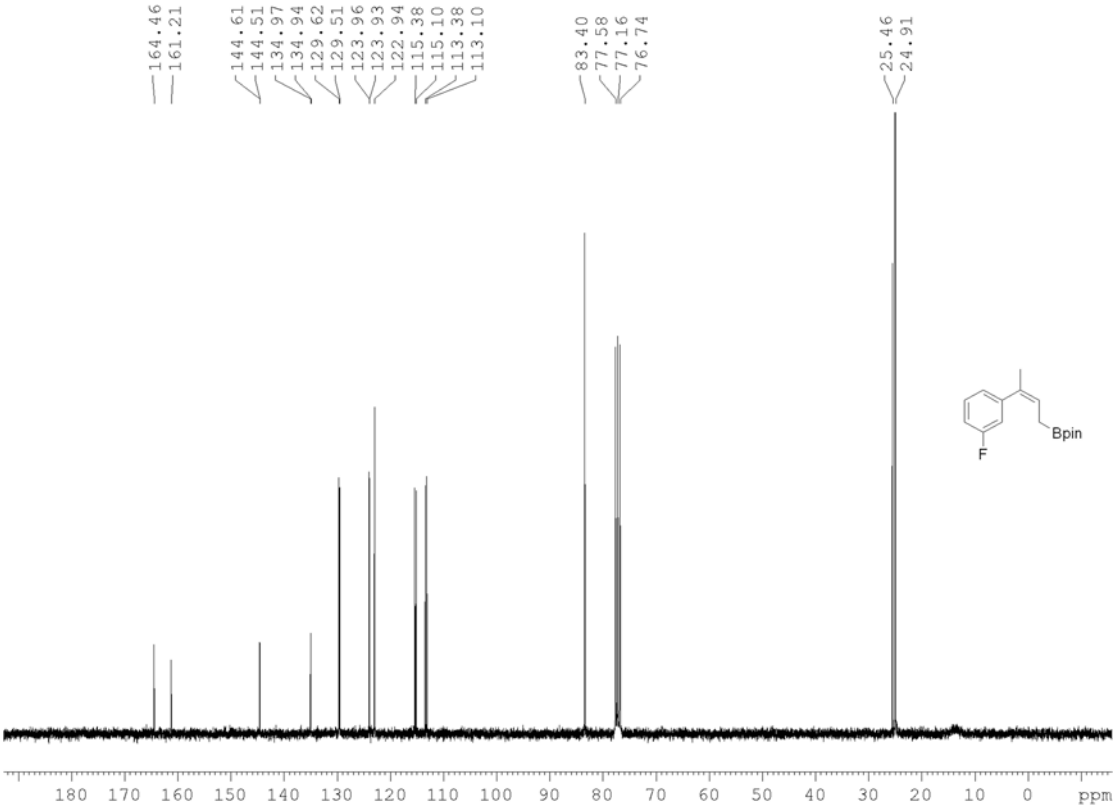


Compound (3-4)f or (4-2)q

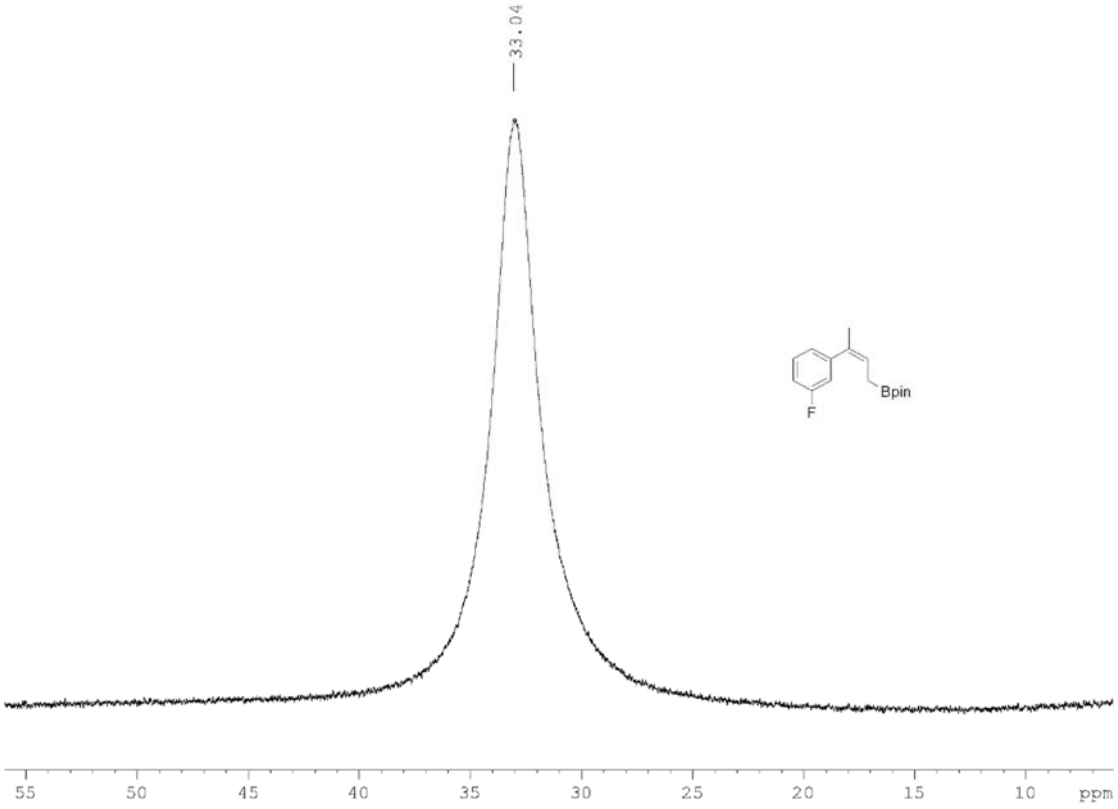
^{1}H NMR (300 MHz, $CDCl_3$)



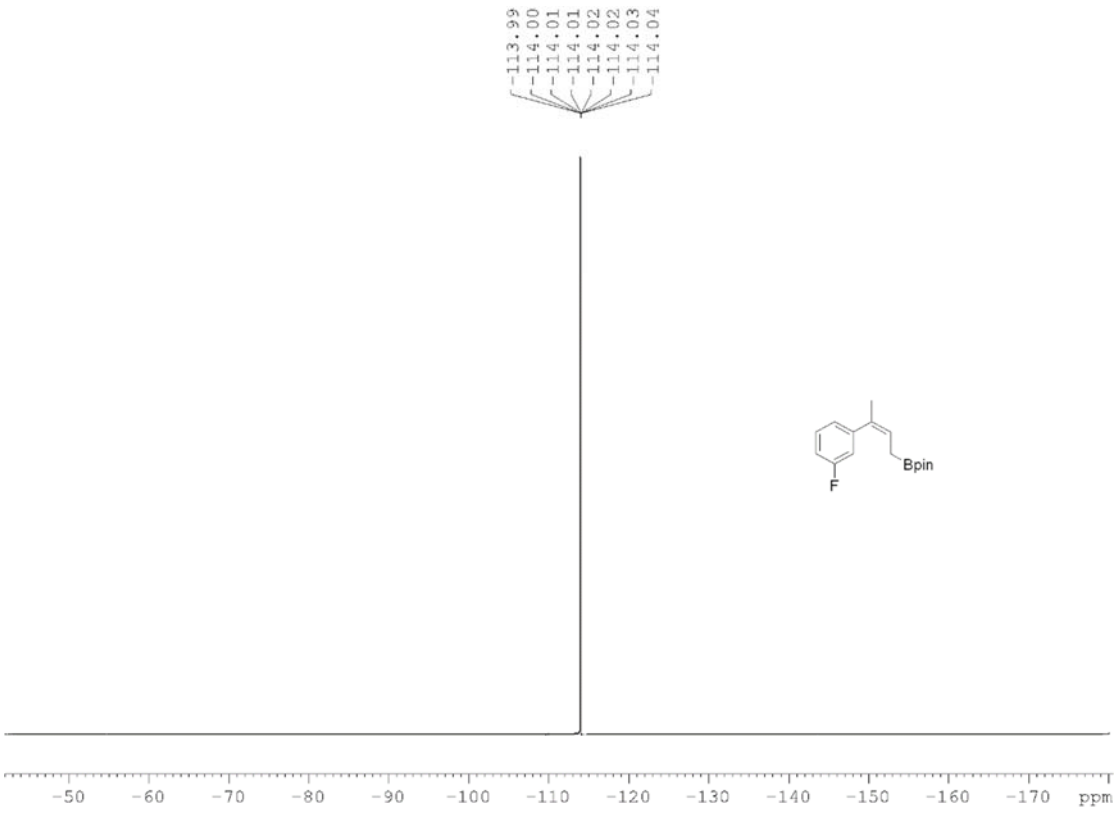
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



^{11}B NMR (96 MHz, $CDCl_3$)

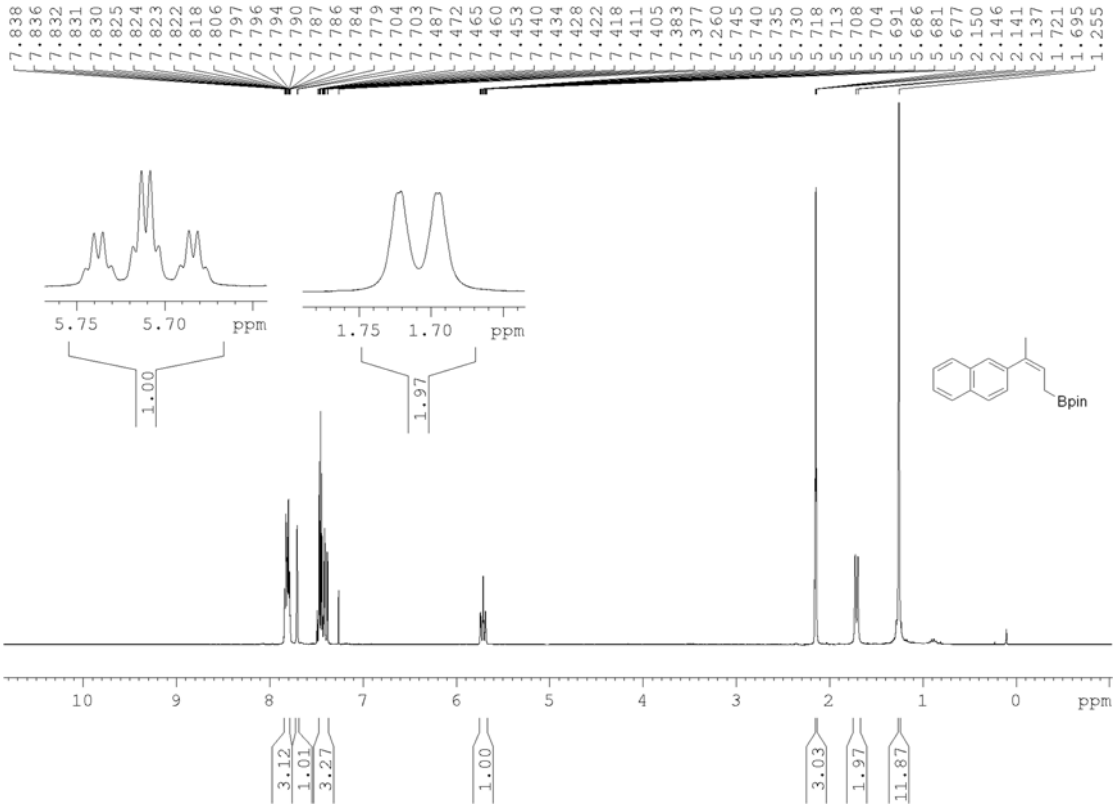


^{19}F NMR (470 MHz, $CDCl_3$)

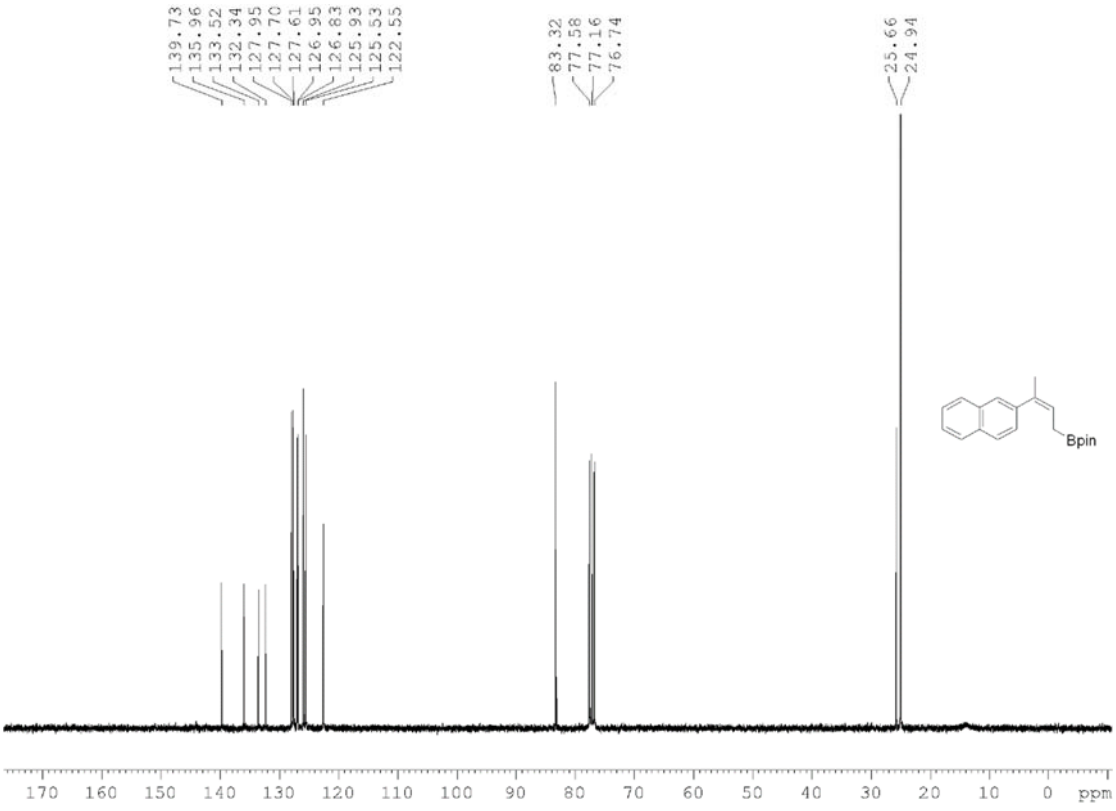


Compound (3-4)g or (4-2)r

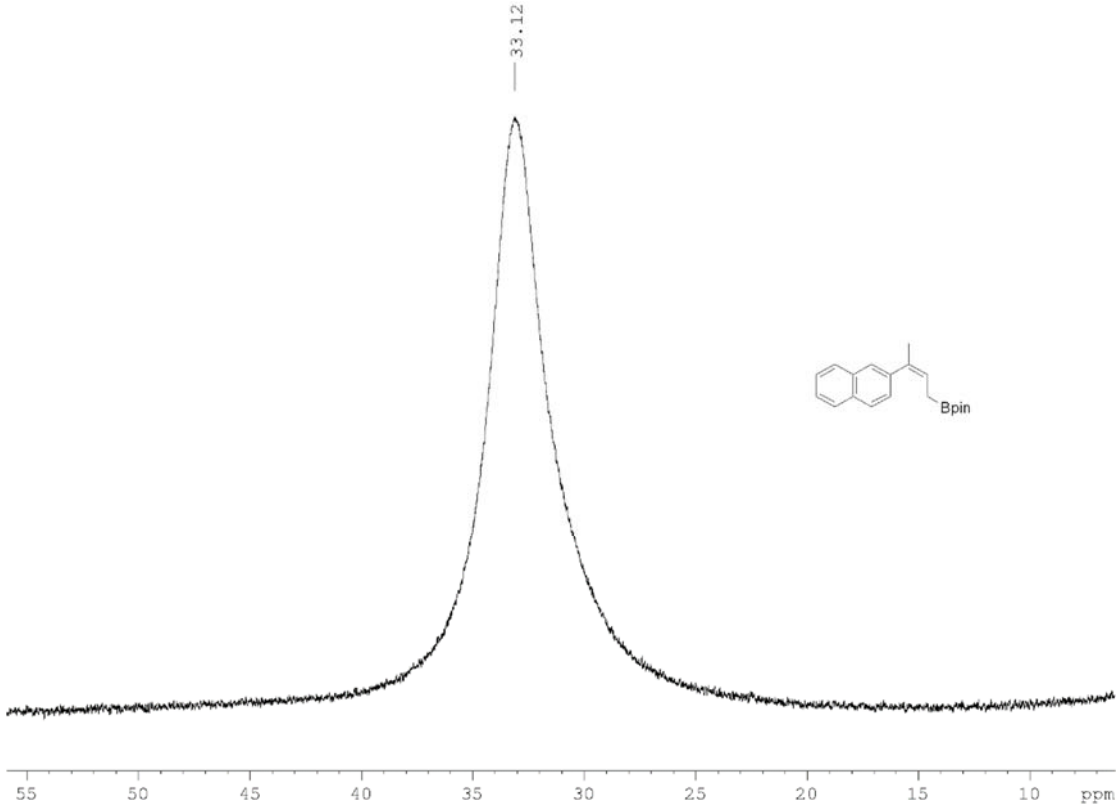
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

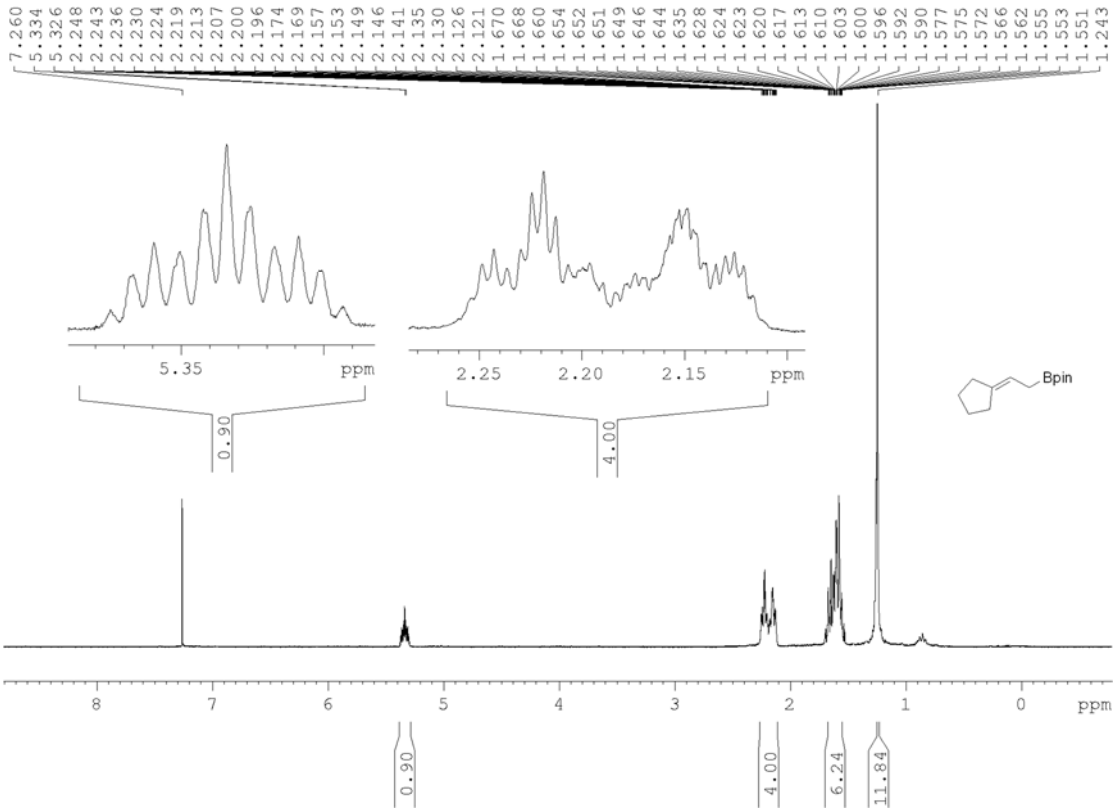


^{11}B NMR (96 MHz, $CDCl_3$)

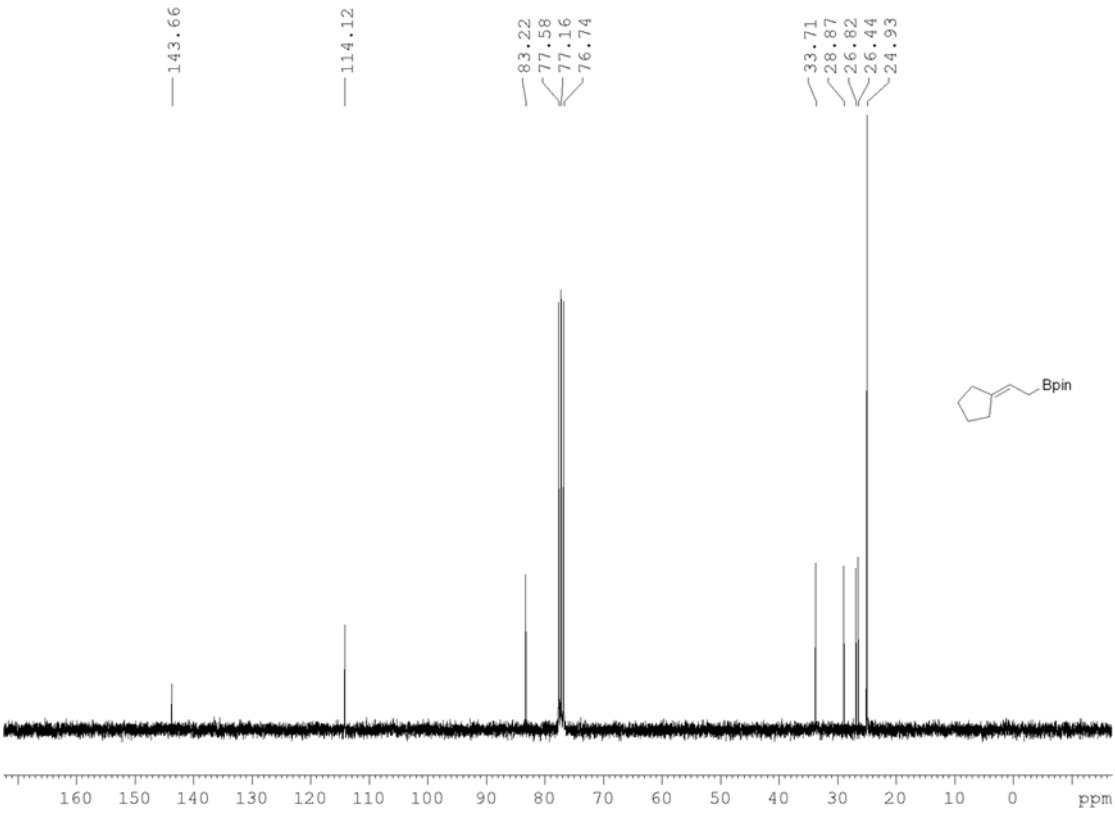


Compound (3-4)i or (4-2)e

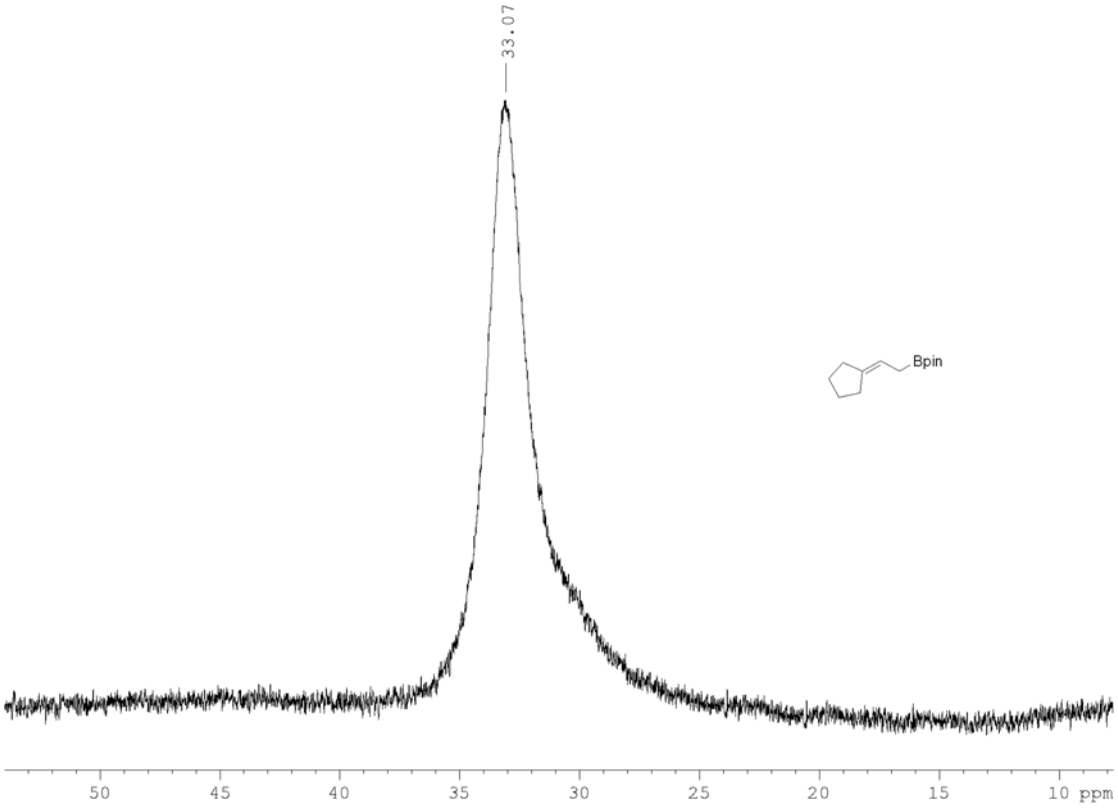
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

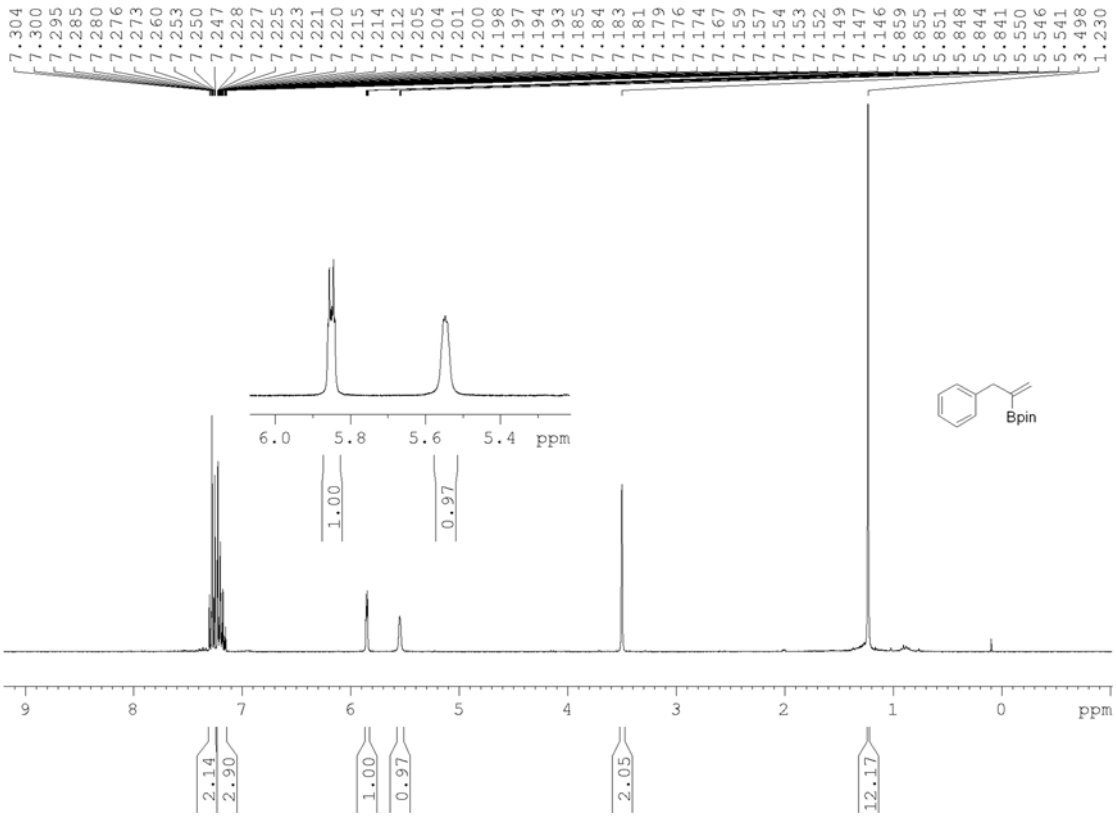


^{11}B NMR (96 MHz, $CDCl_3$)

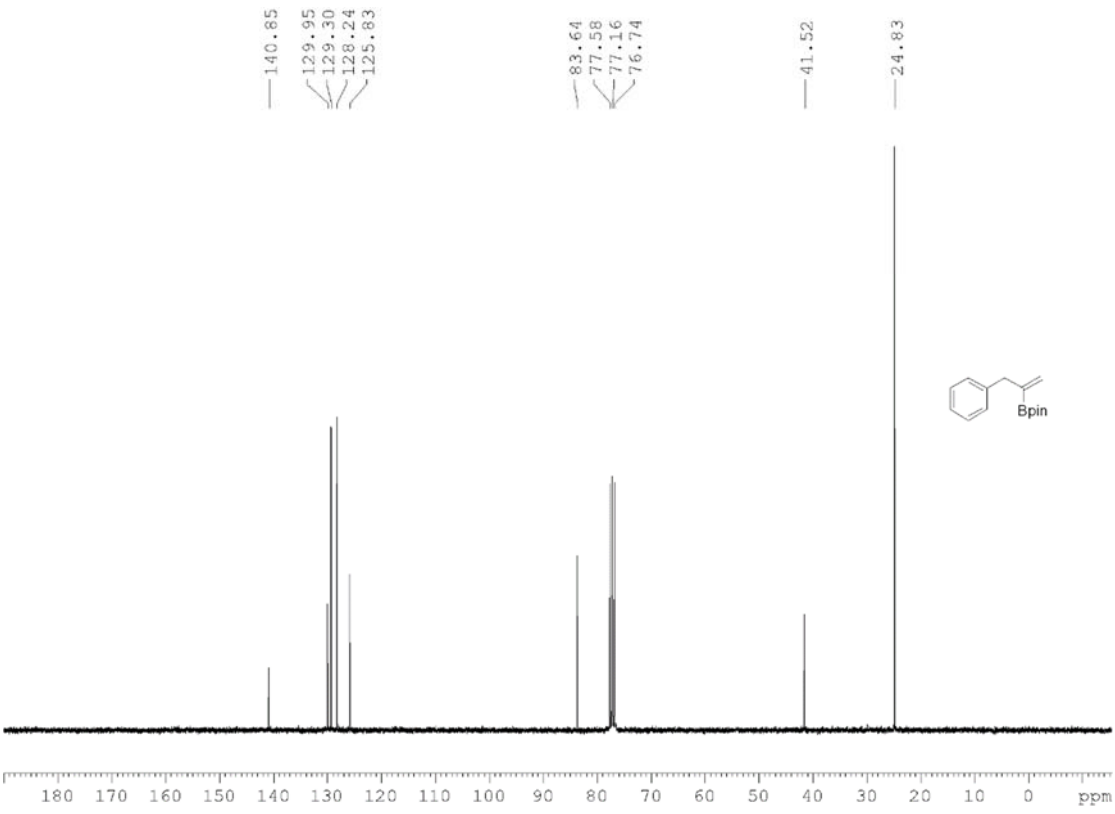


Compound (3-6)a

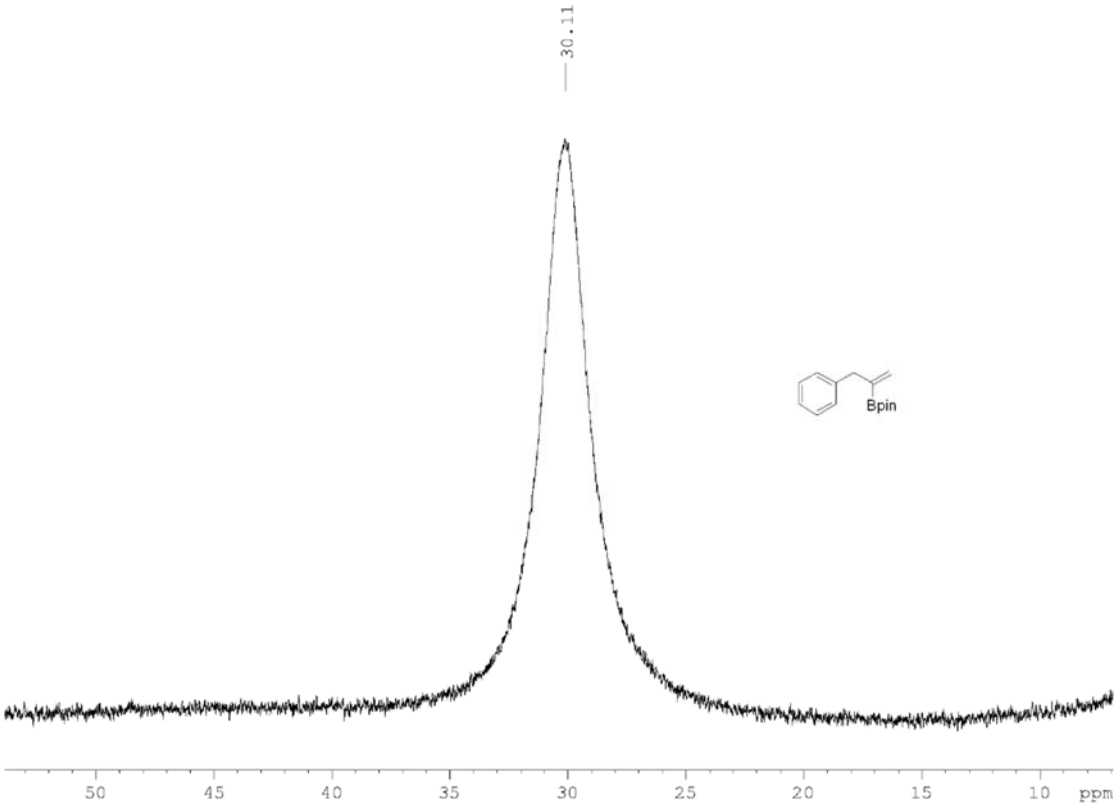
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

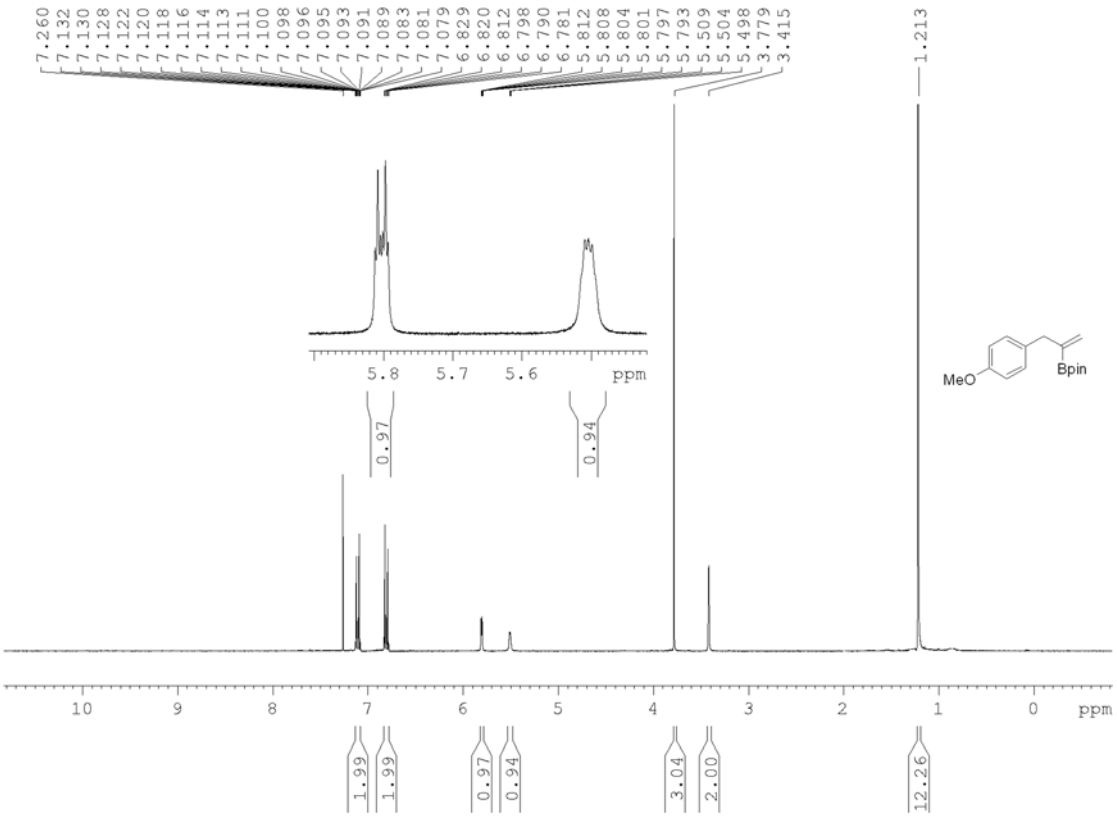


^{11}B NMR (96 MHz, $CDCl_3$)

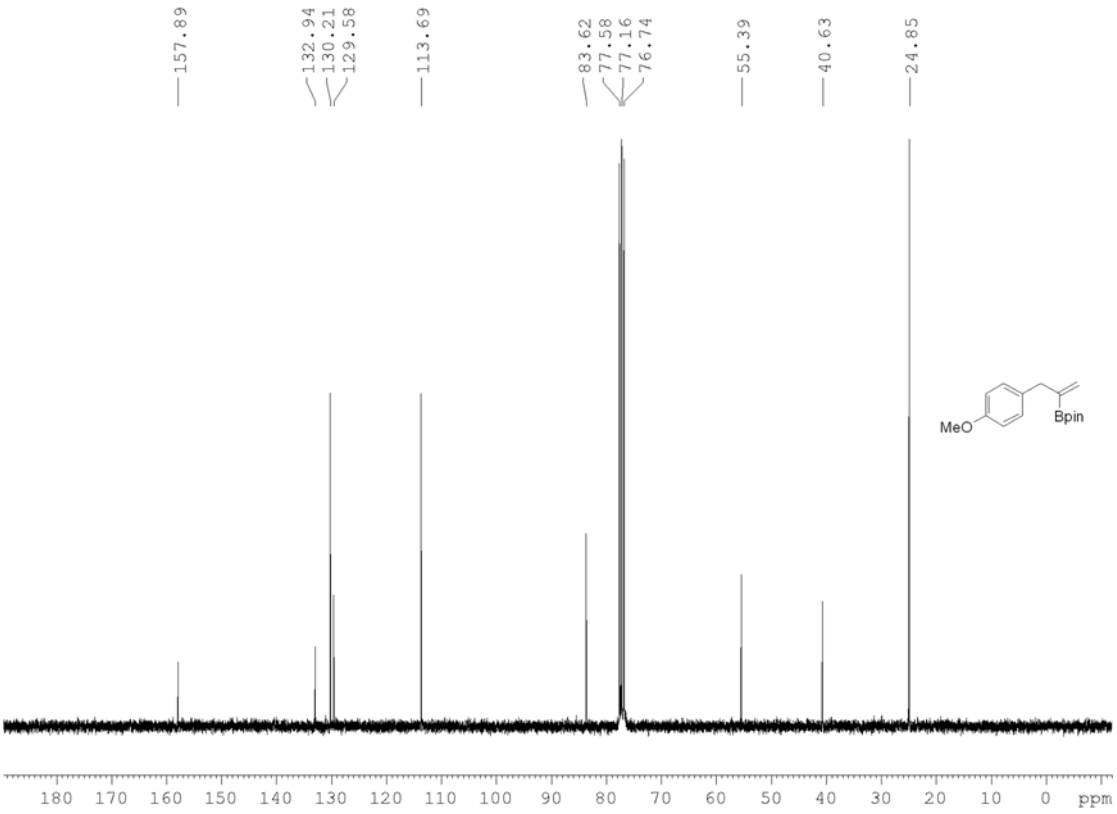


Compound (3-6)b

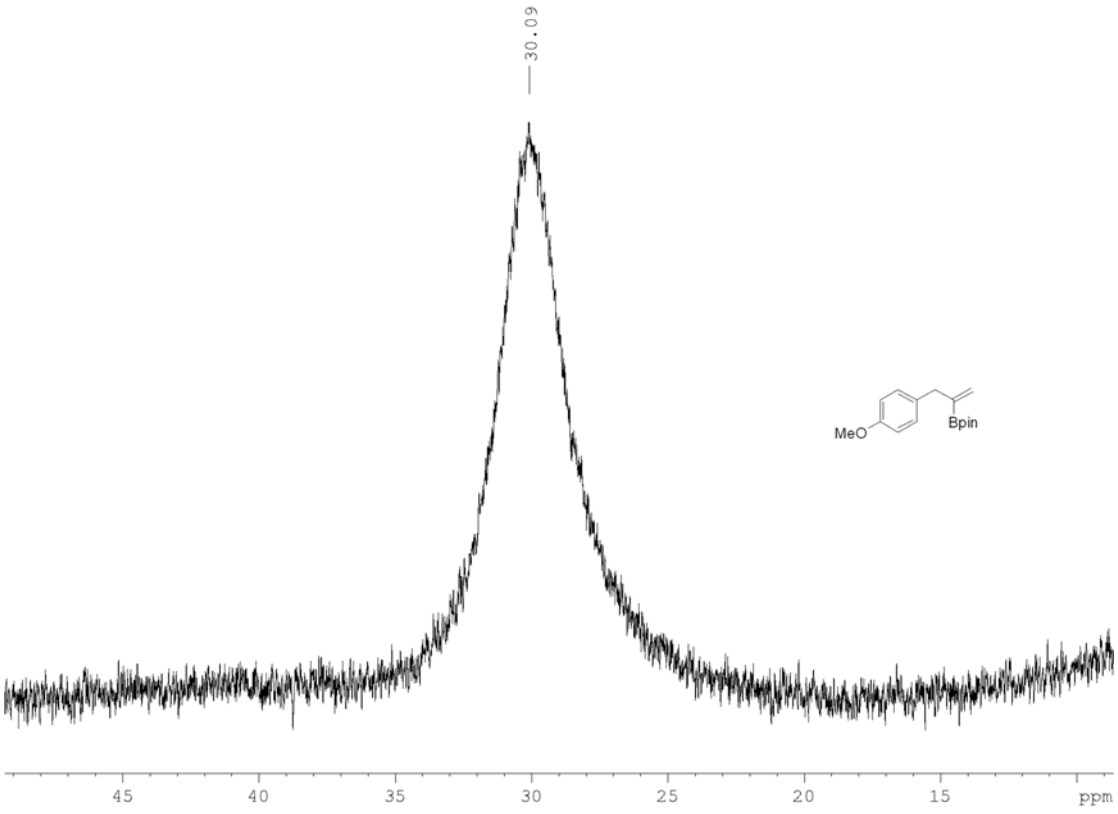
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

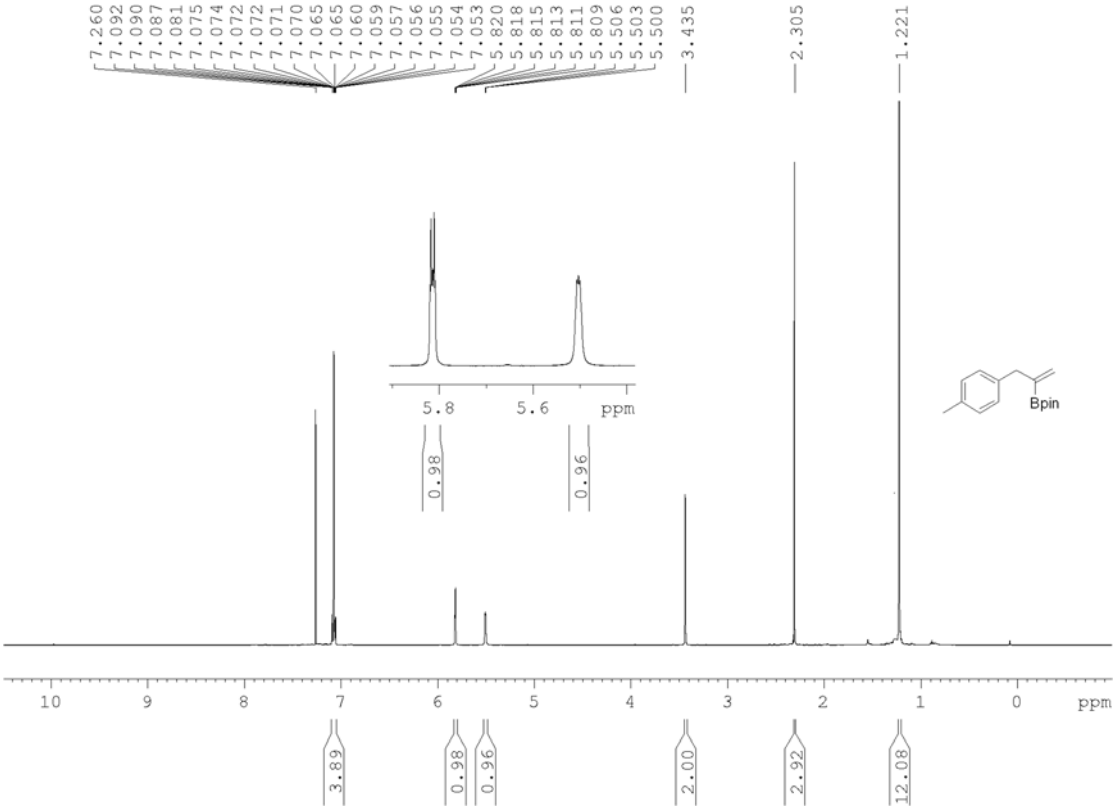


^{11}B NMR (96 MHz, $CDCl_3$)

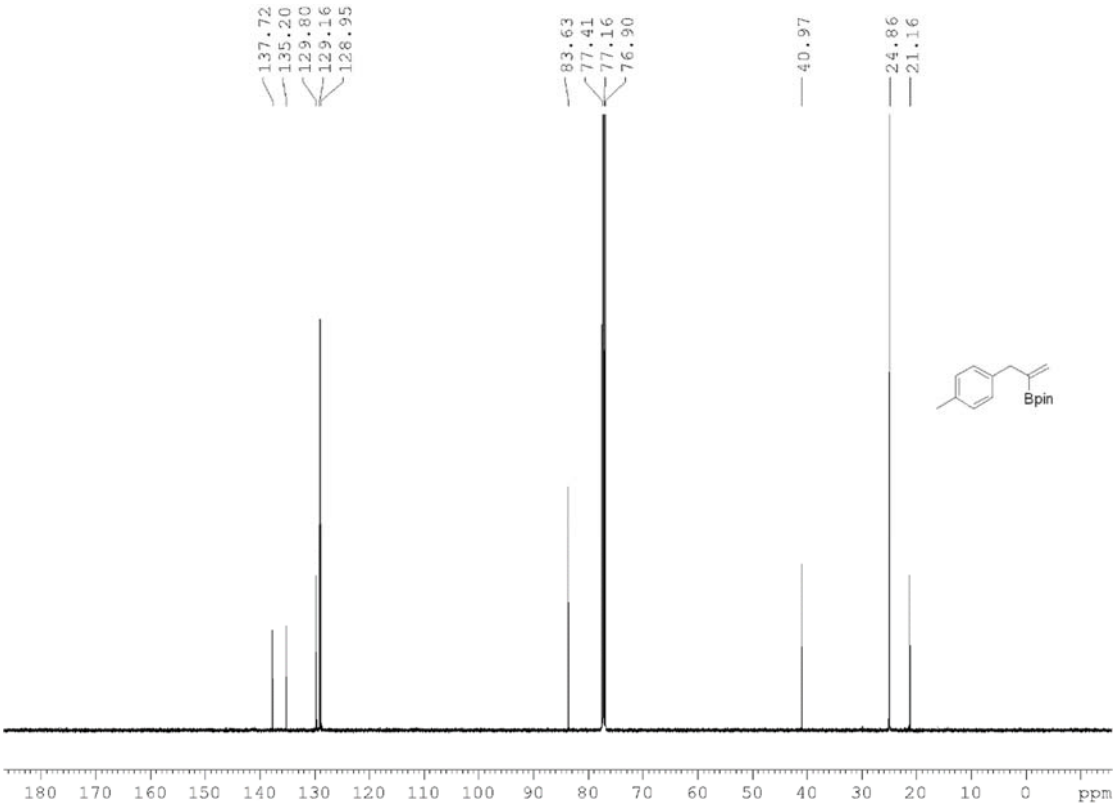


Compound (3-6)c

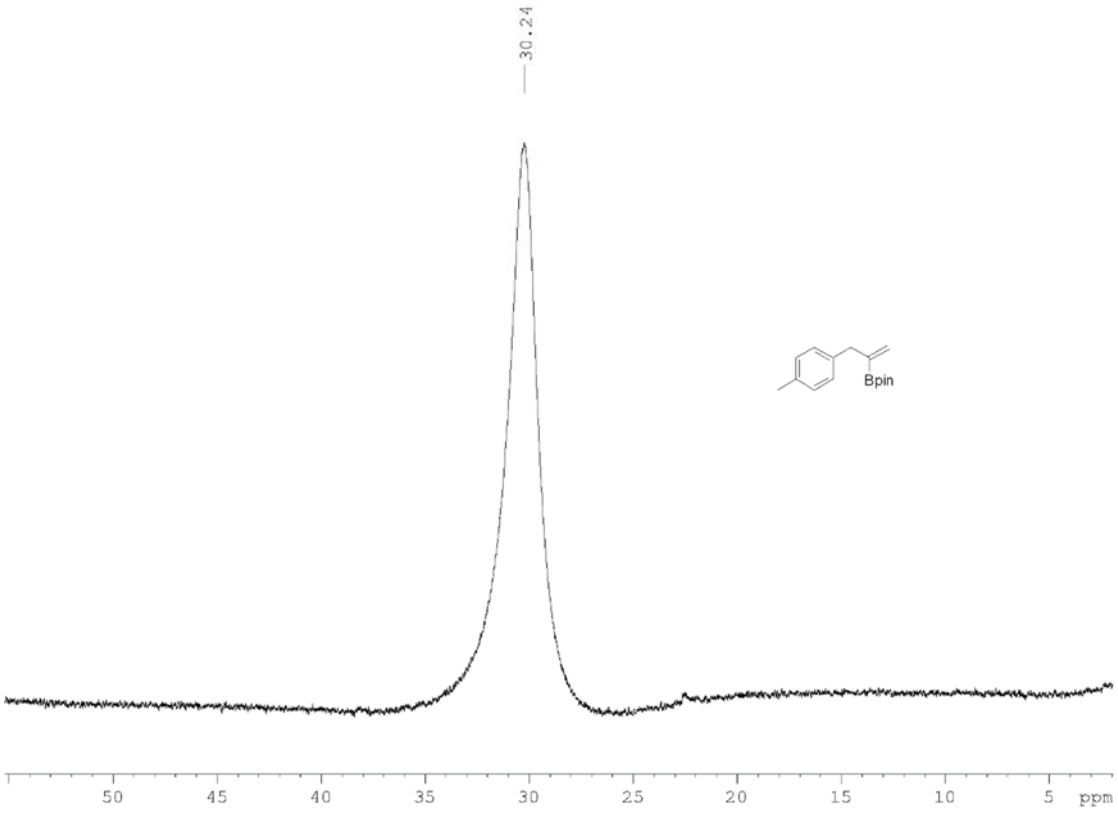
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

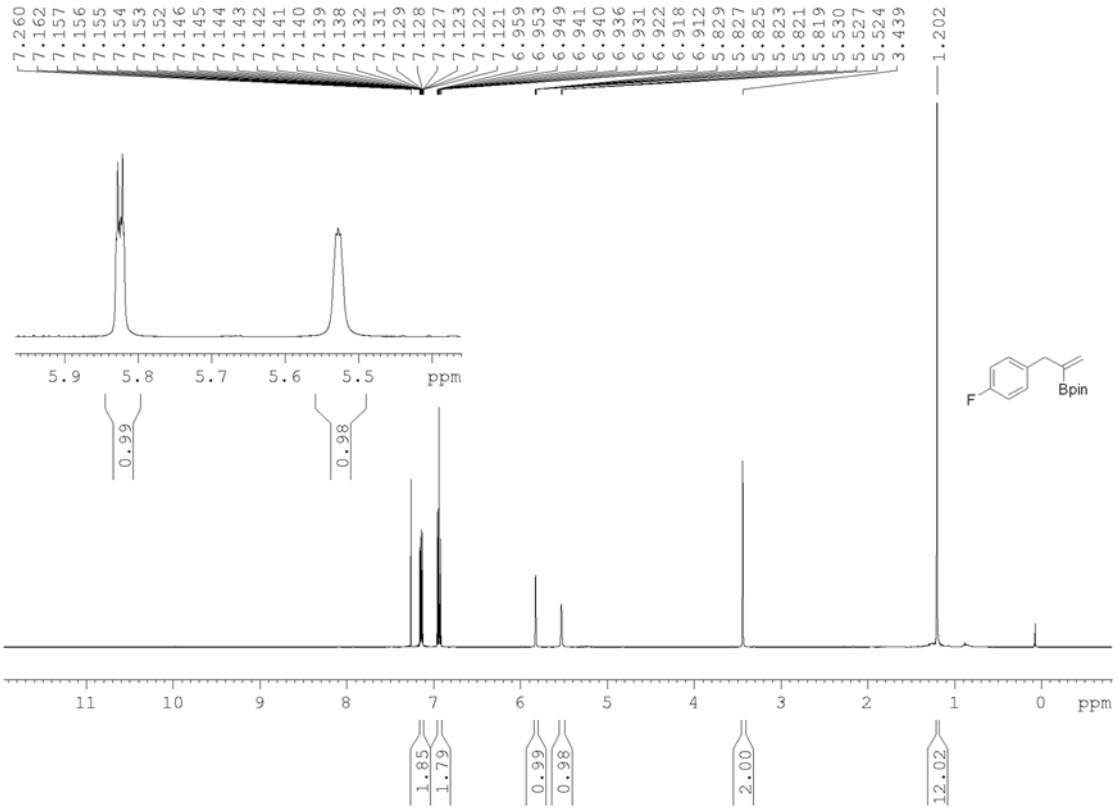


^{11}B NMR (160 MHz, $CDCl_3$)

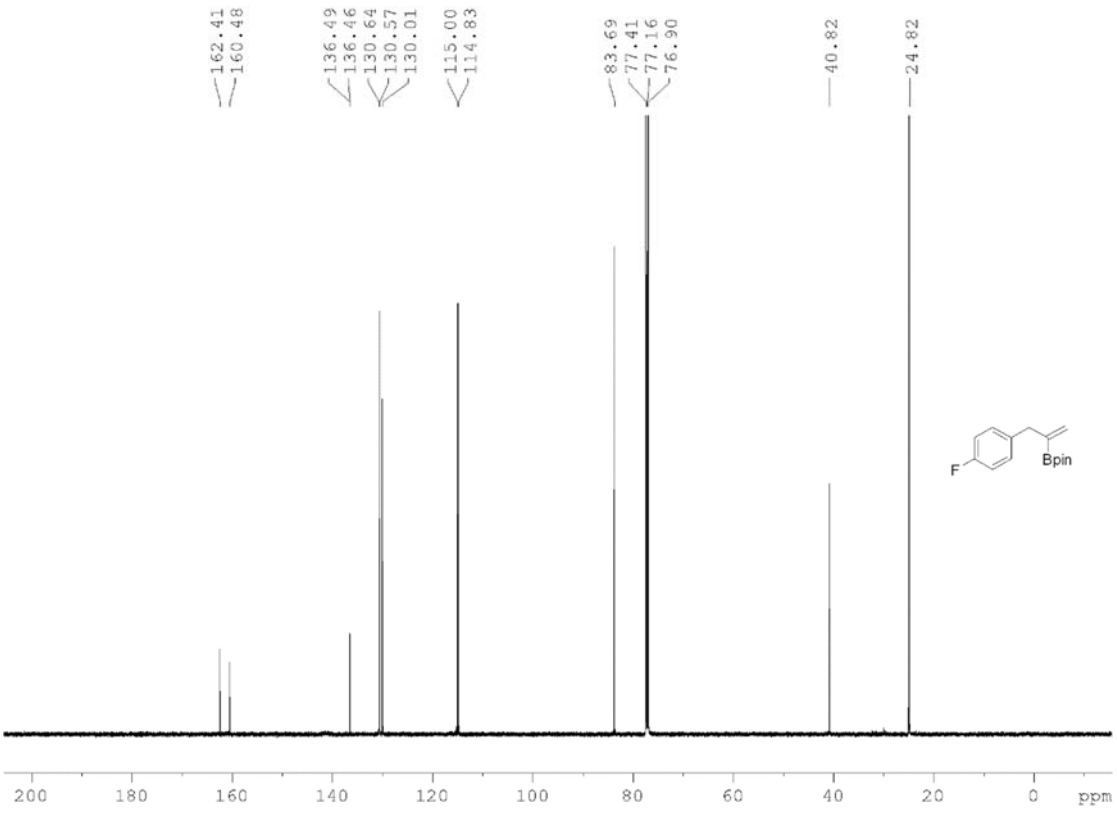


Compound (3-6)d

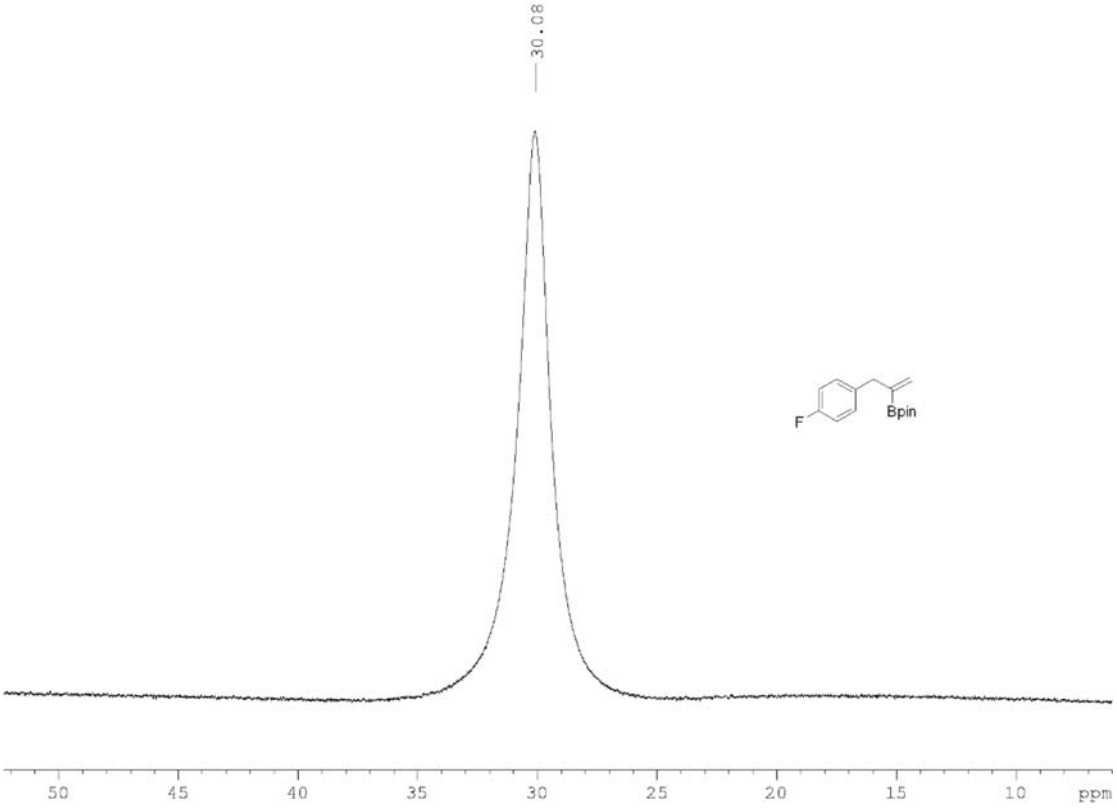
^{1}H NMR (500 MHz, $CDCl_3$)



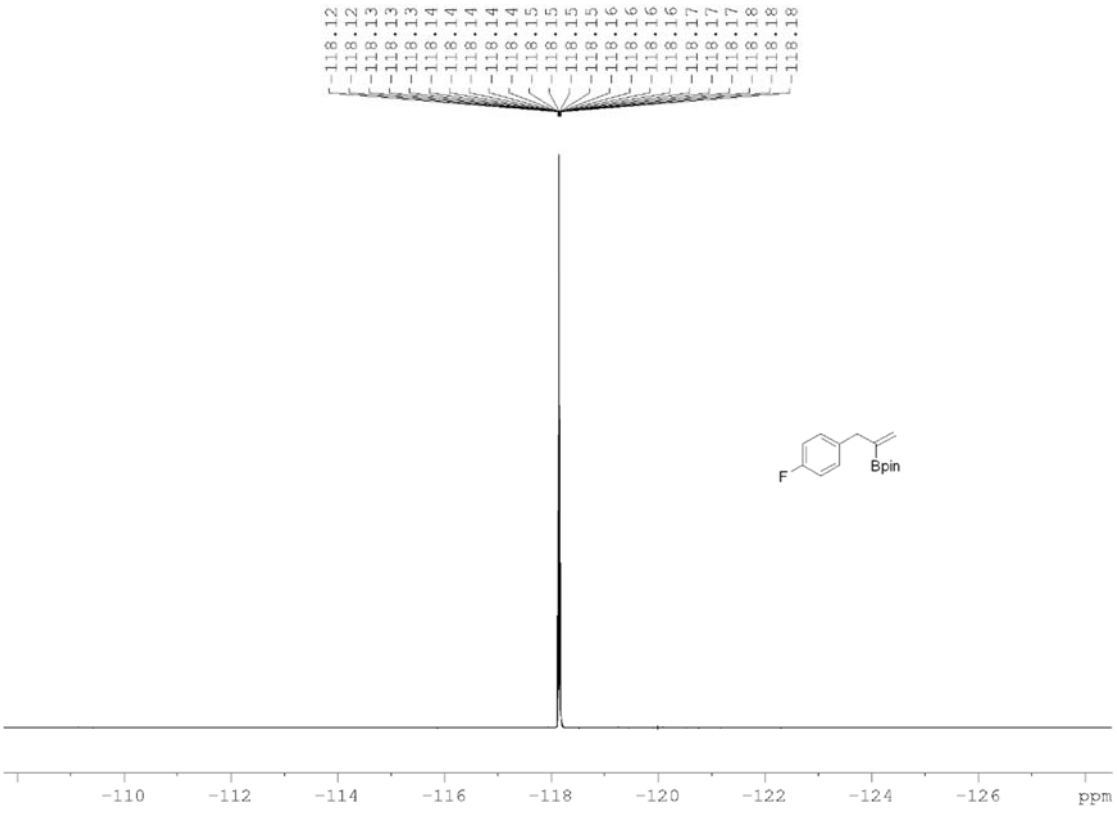
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)

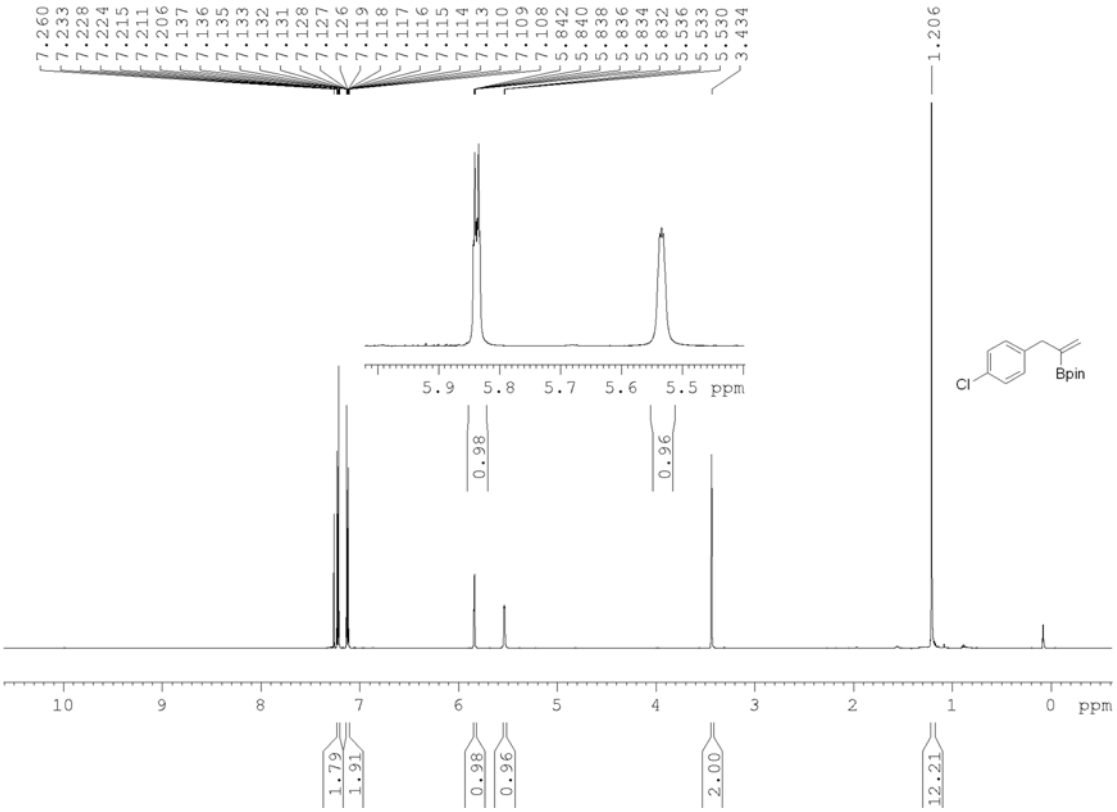


^{19}F NMR (470 MHz, $CDCl_3$)

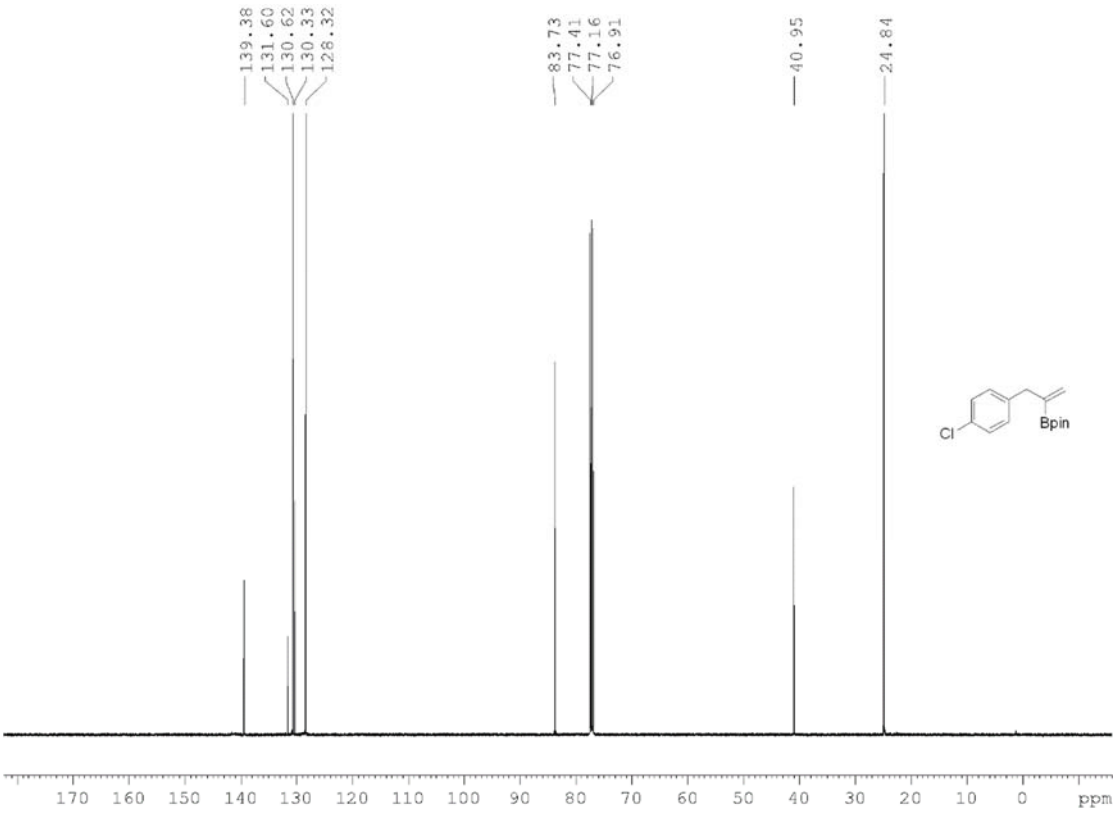


Compound (3-6)e

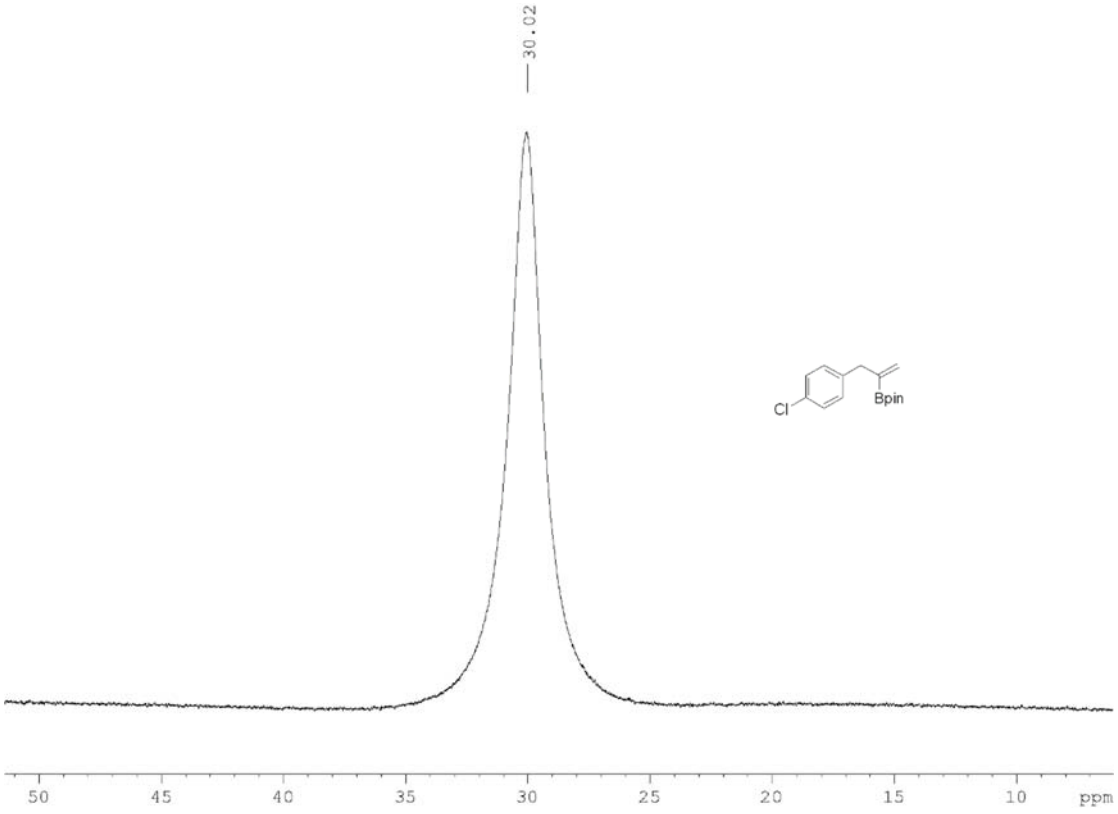
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

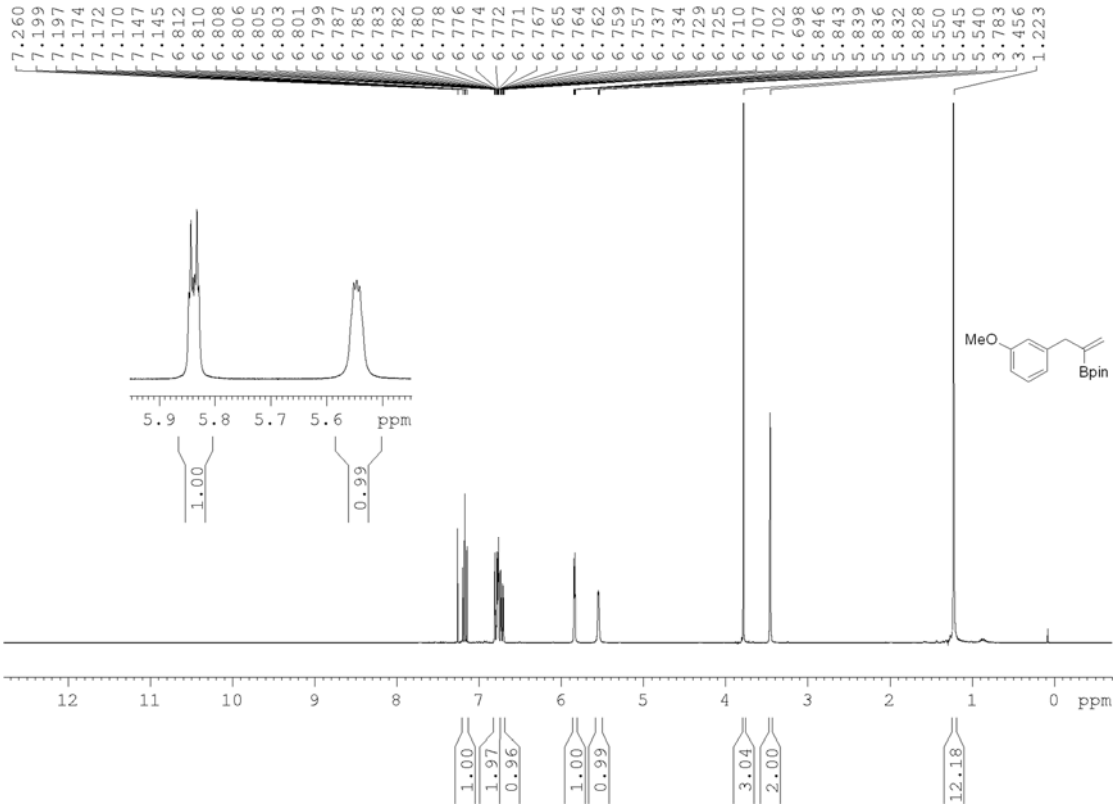


^{11}B NMR (160 MHz, $CDCl_3$)

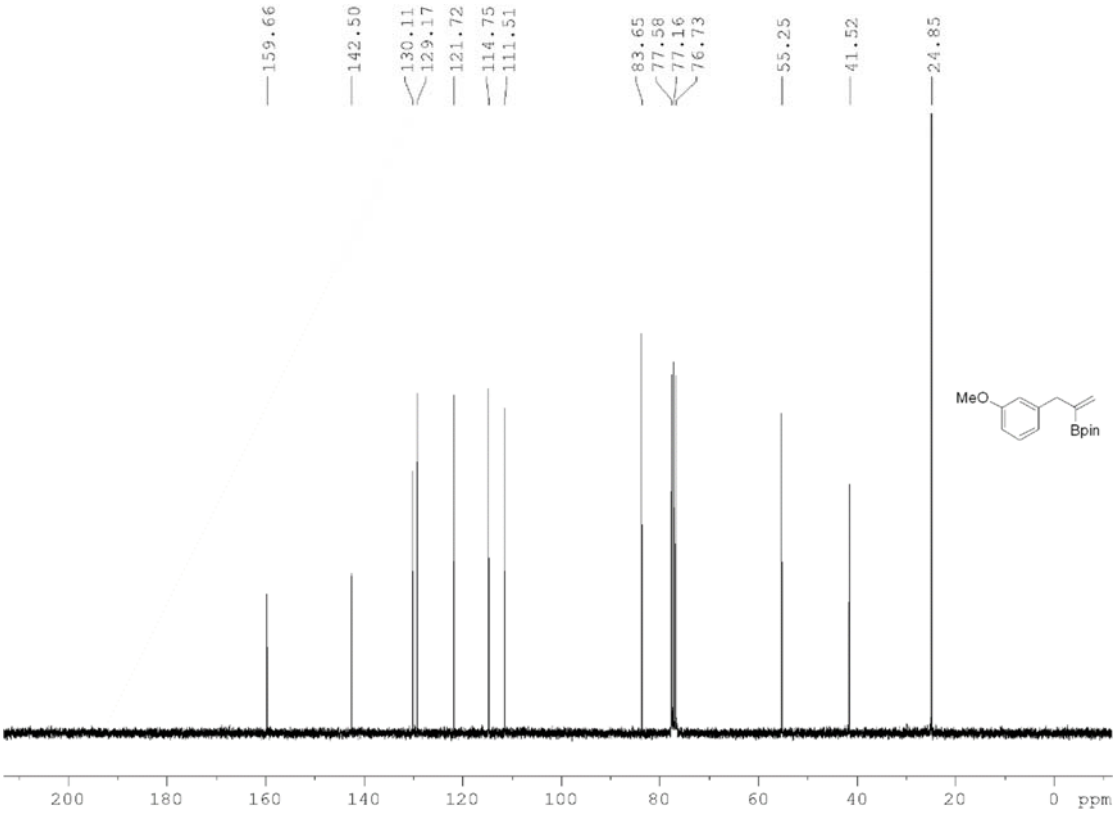


Compound (3-6)f

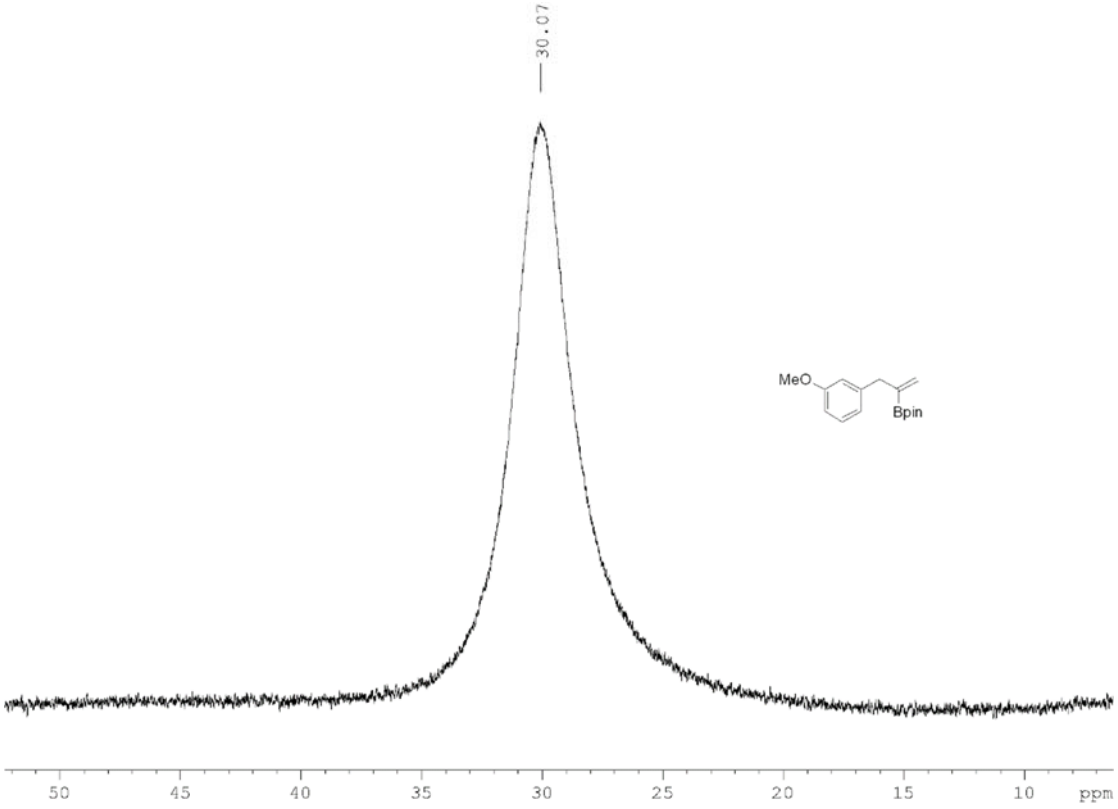
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

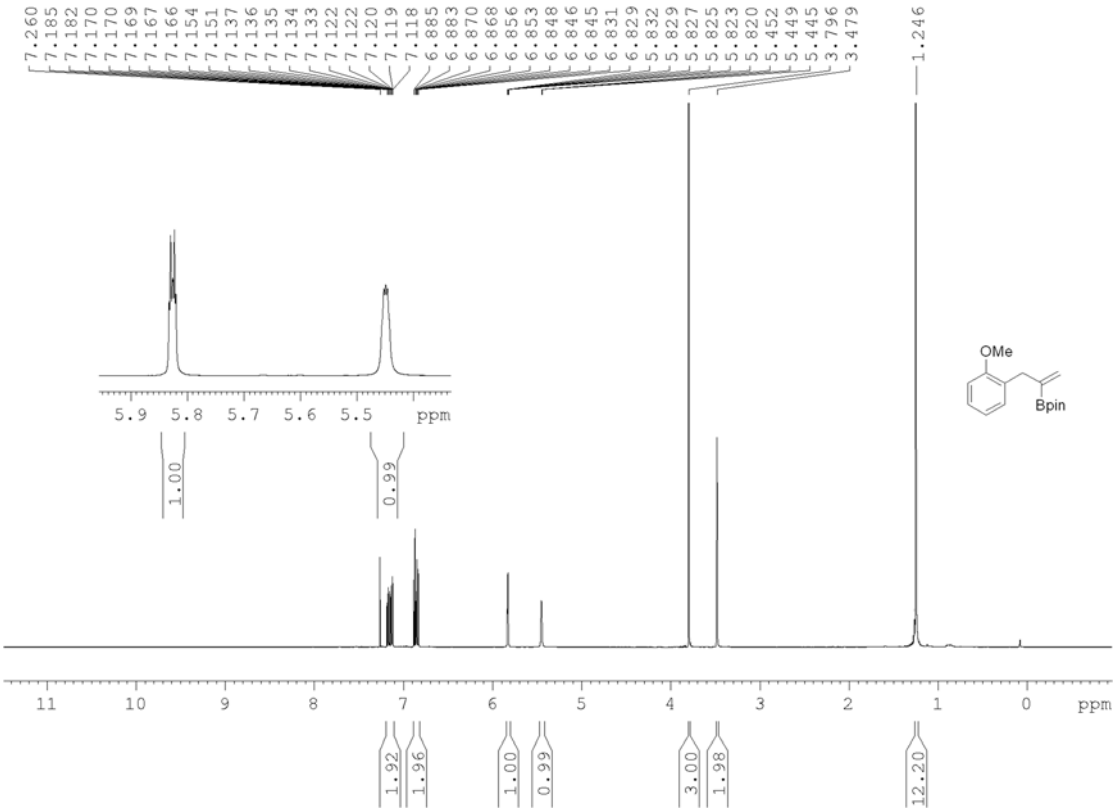


^{11}B NMR (96 MHz, $CDCl_3$)

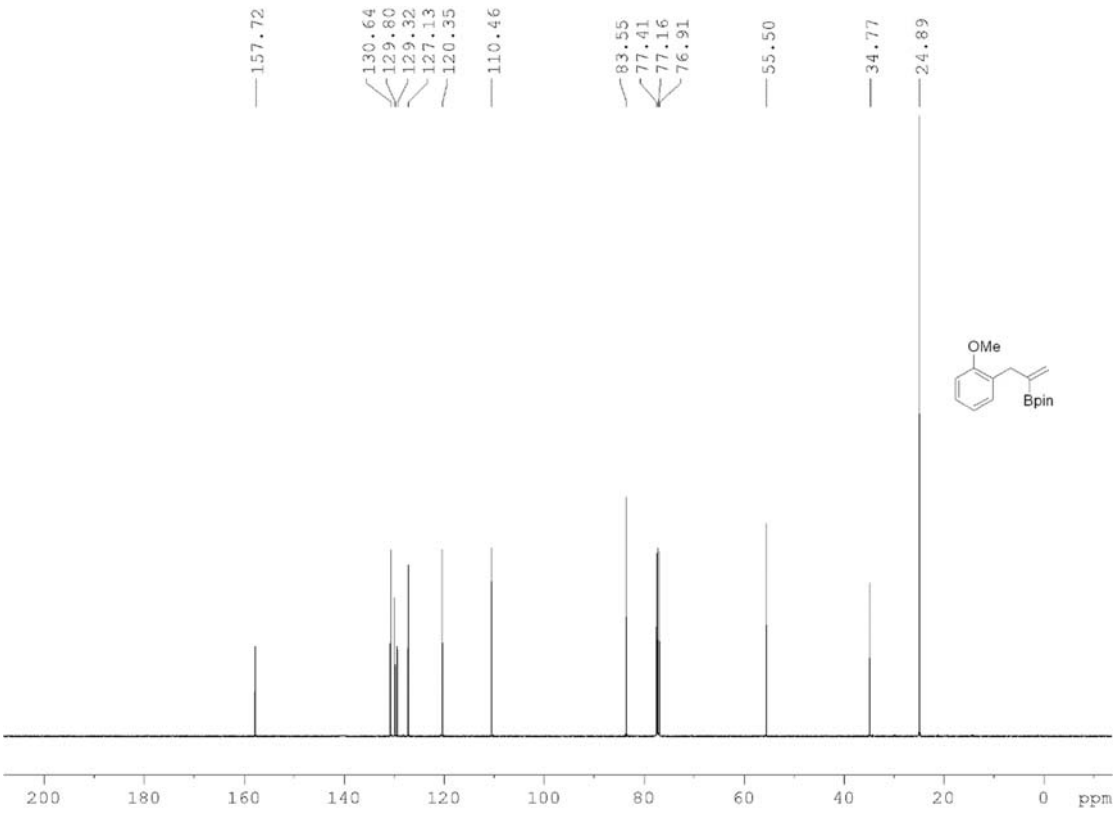


Compound (3-6)g

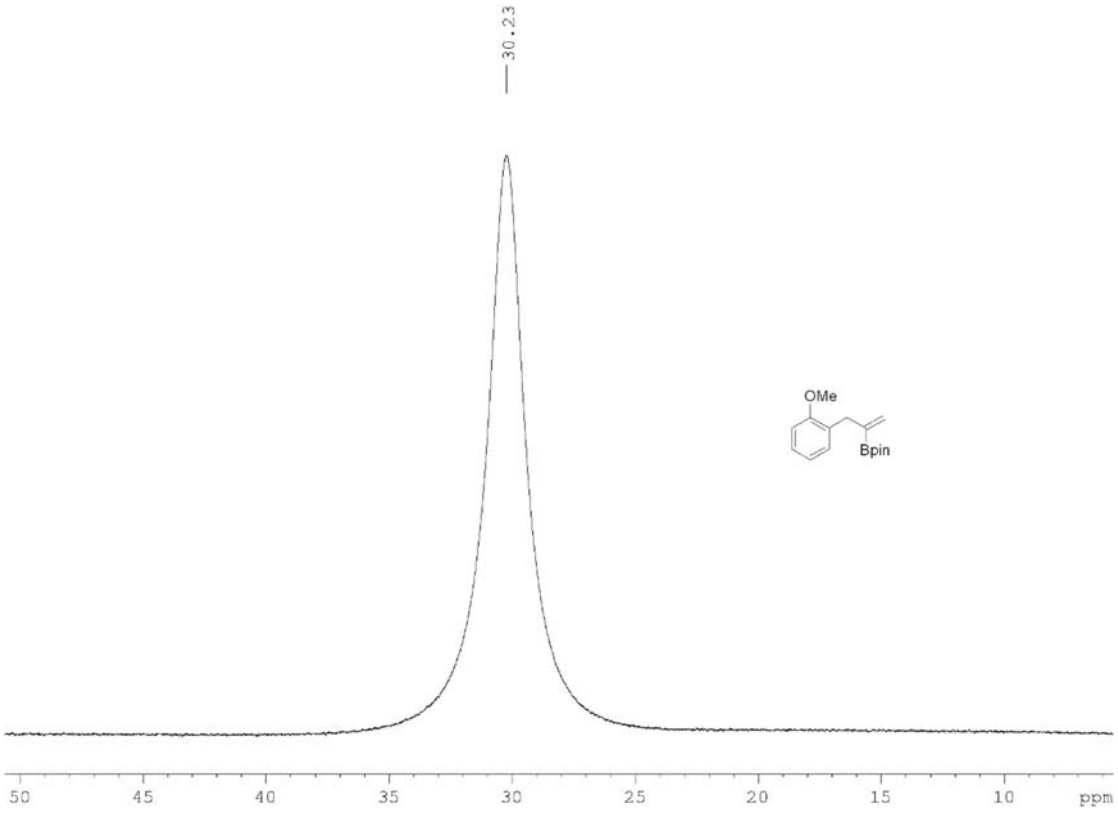
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

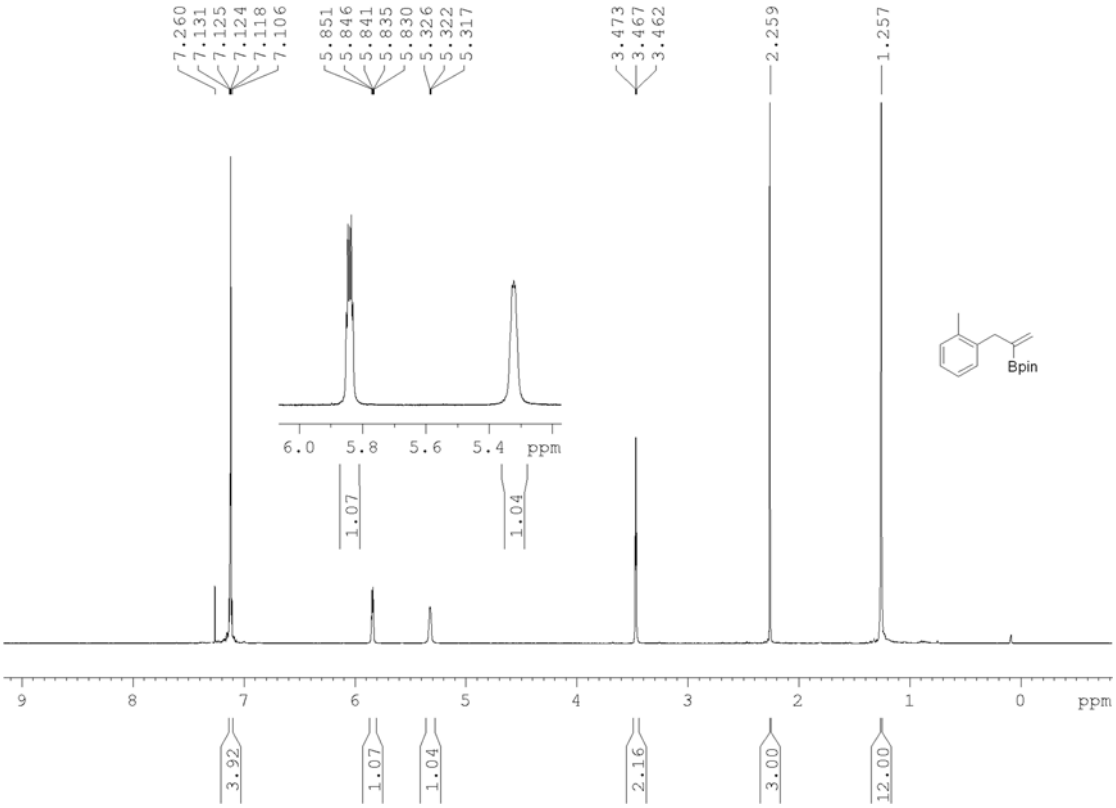


^{11}B NMR (160 MHz, $CDCl_3$)

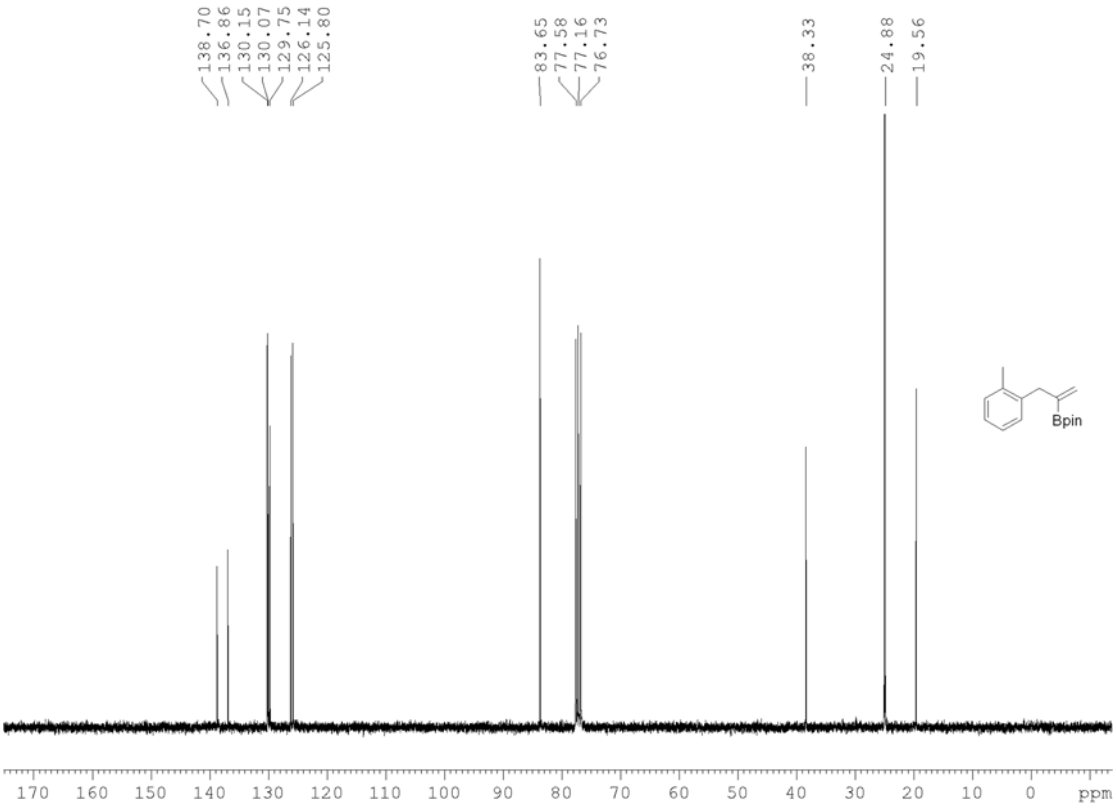


Compound (3-6)h

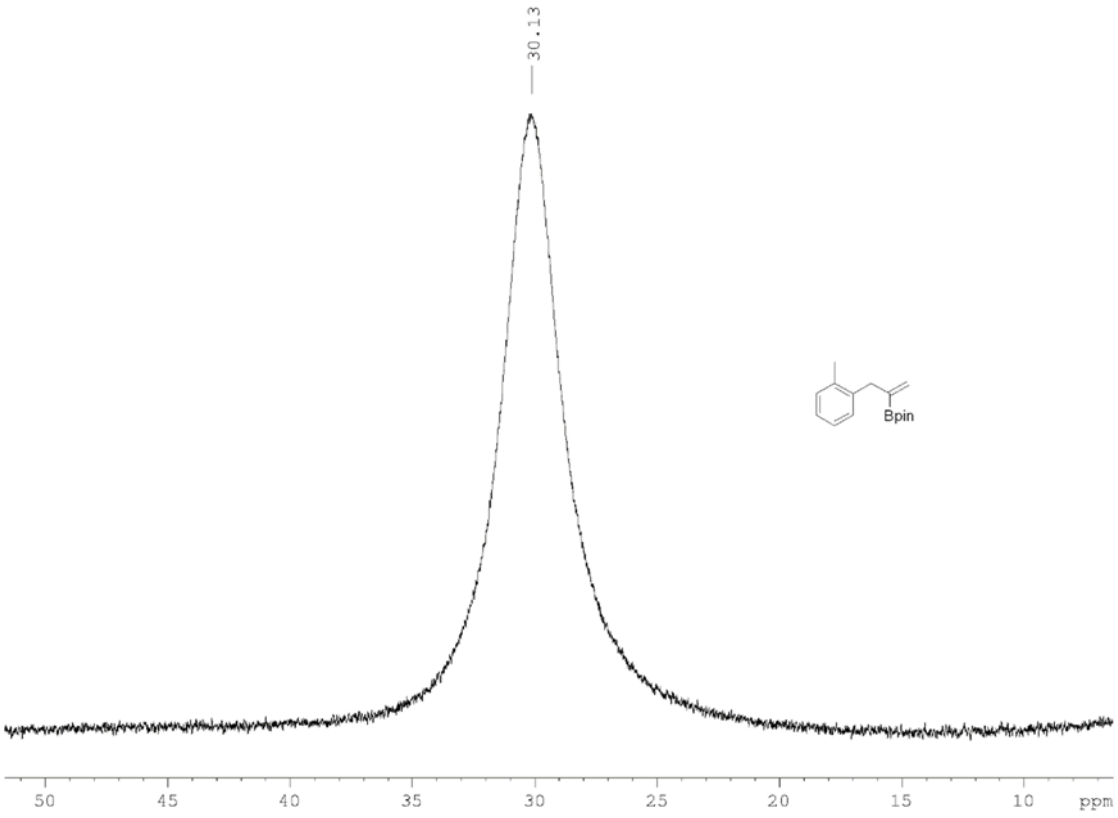
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

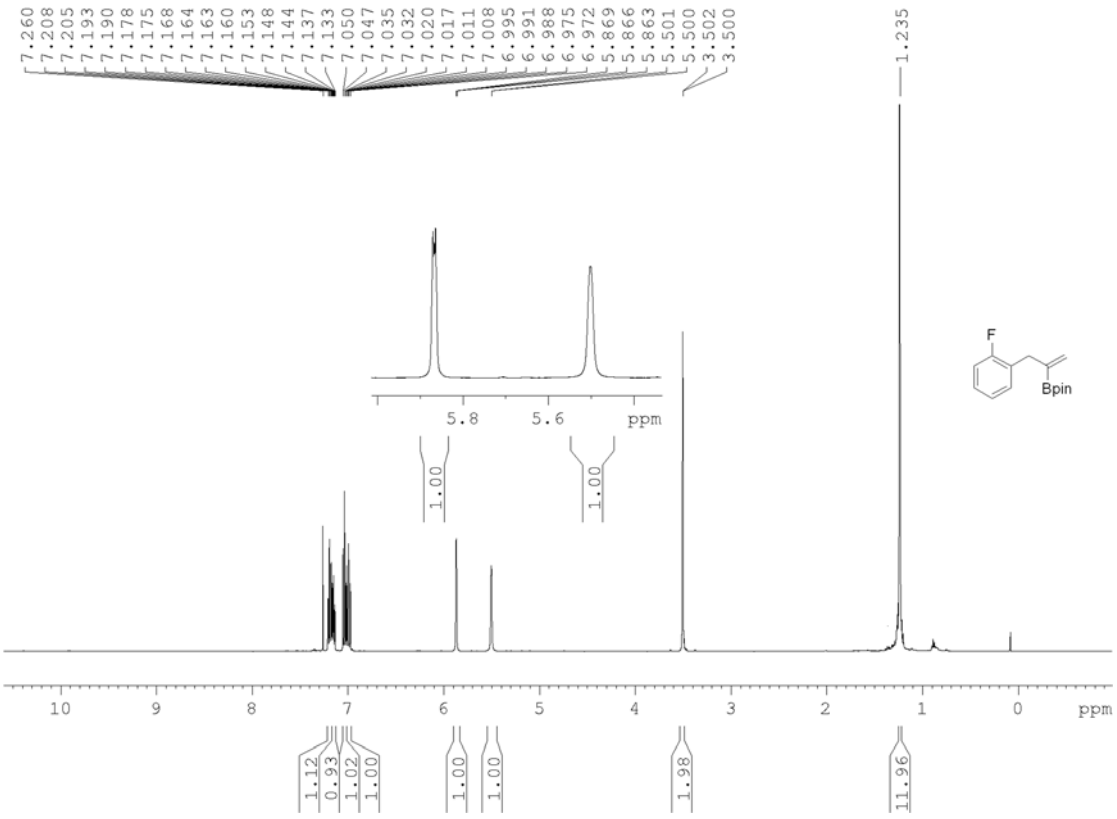


^{11}B NMR (96 MHz, $CDCl_3$)

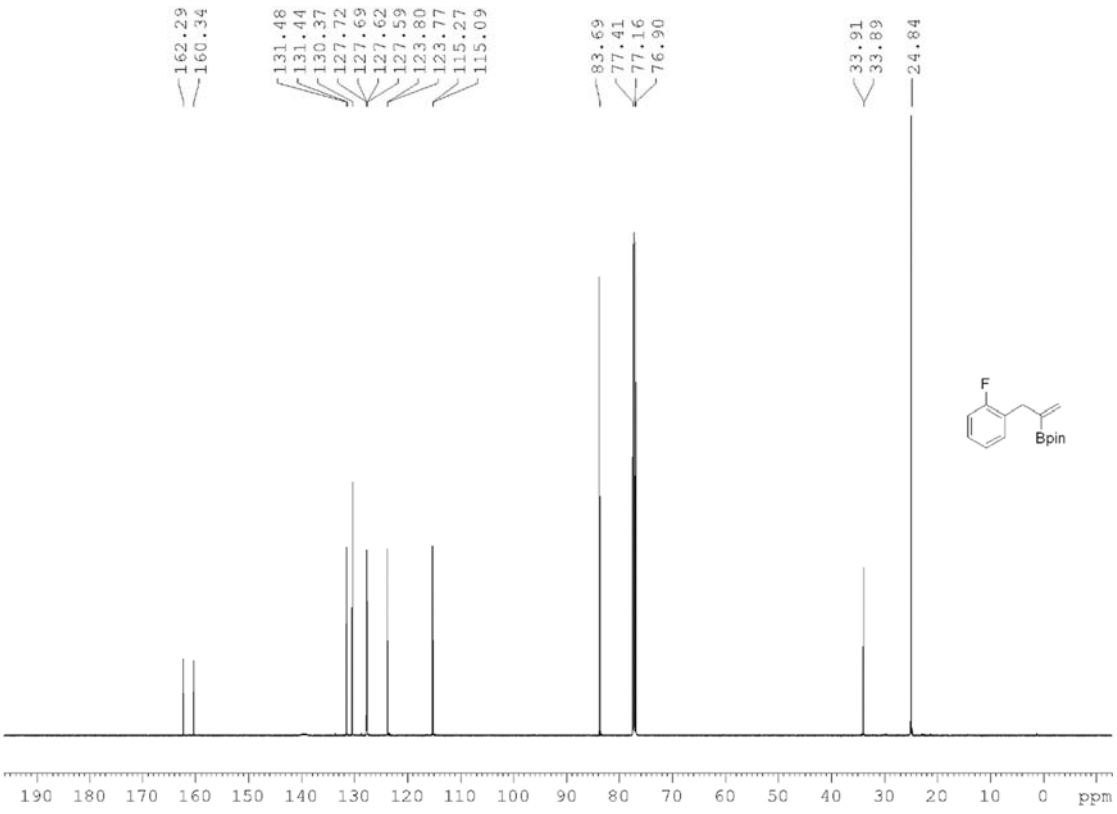


Compound (3-6)i

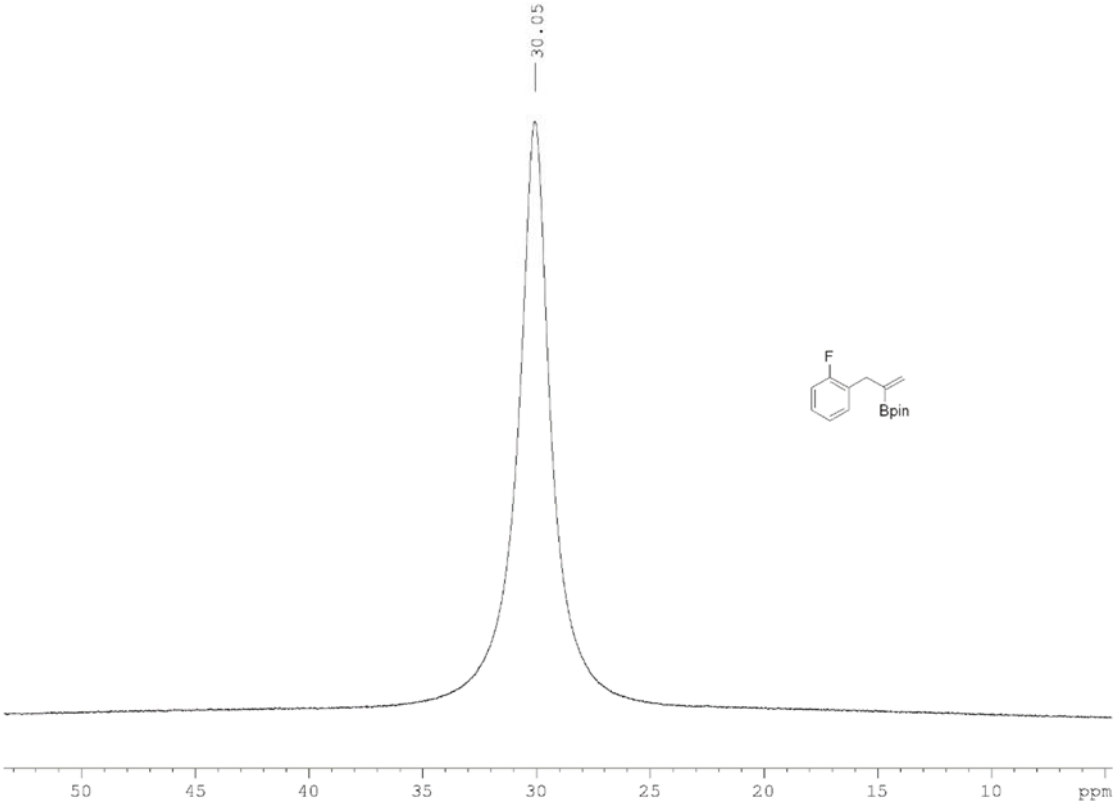
^{1}H NMR (500 MHz, $CDCl_3$)



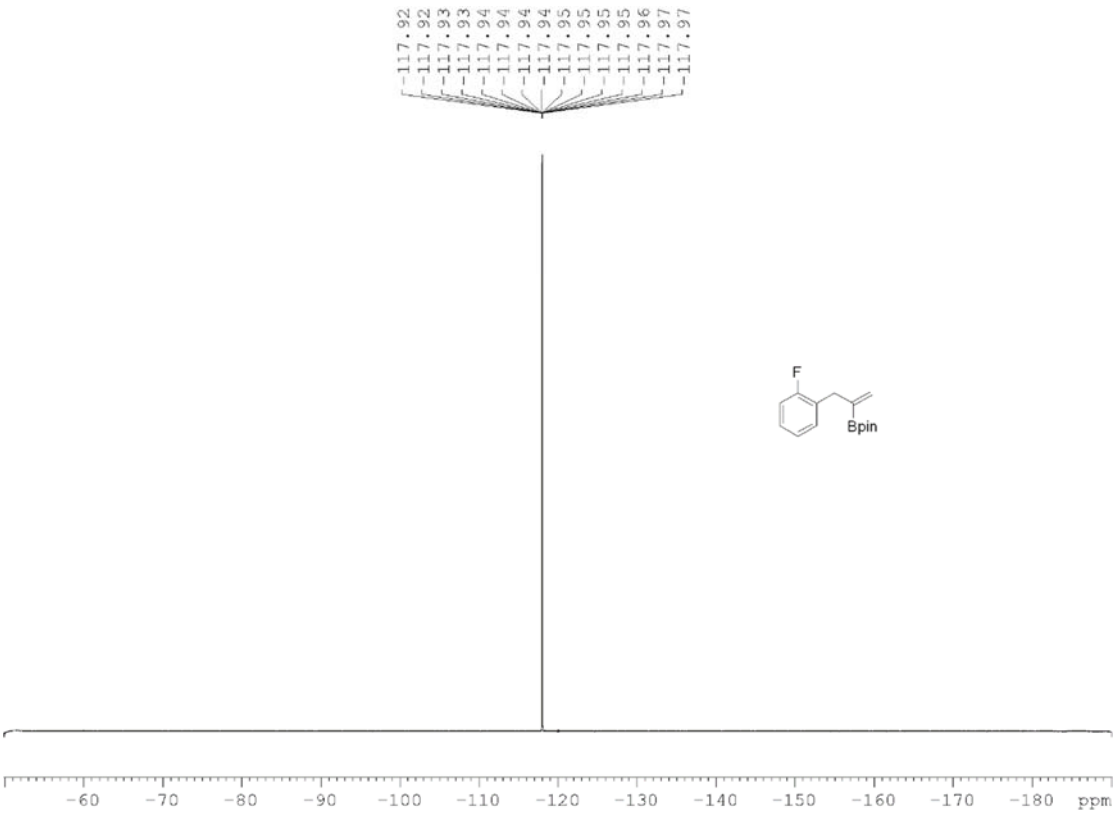
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)

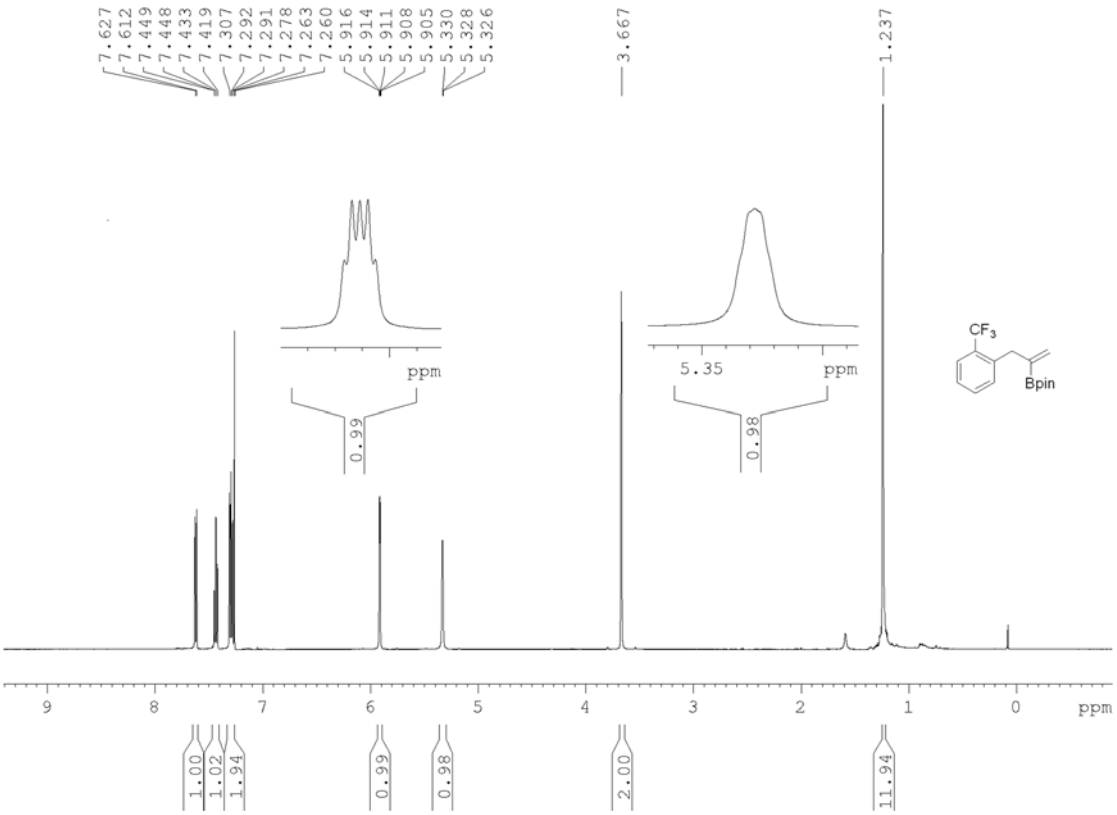


^{19}F NMR (470 MHz, $CDCl_3$)

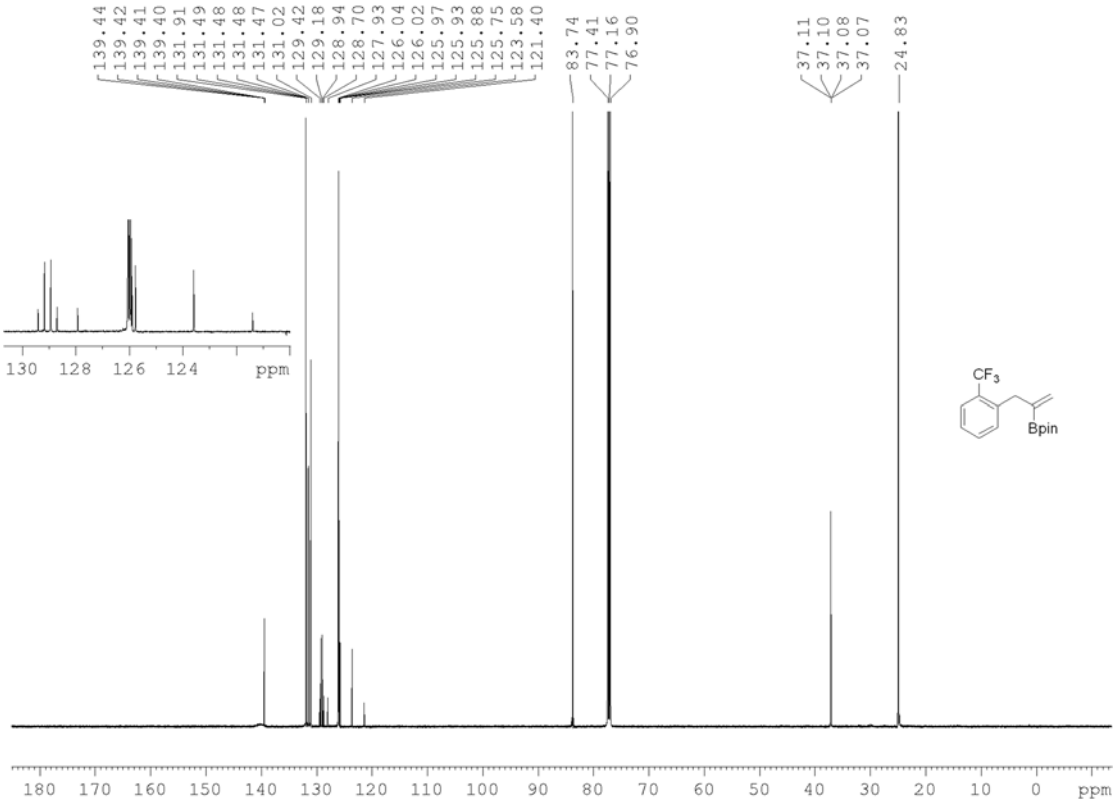


Compound (3-6)j

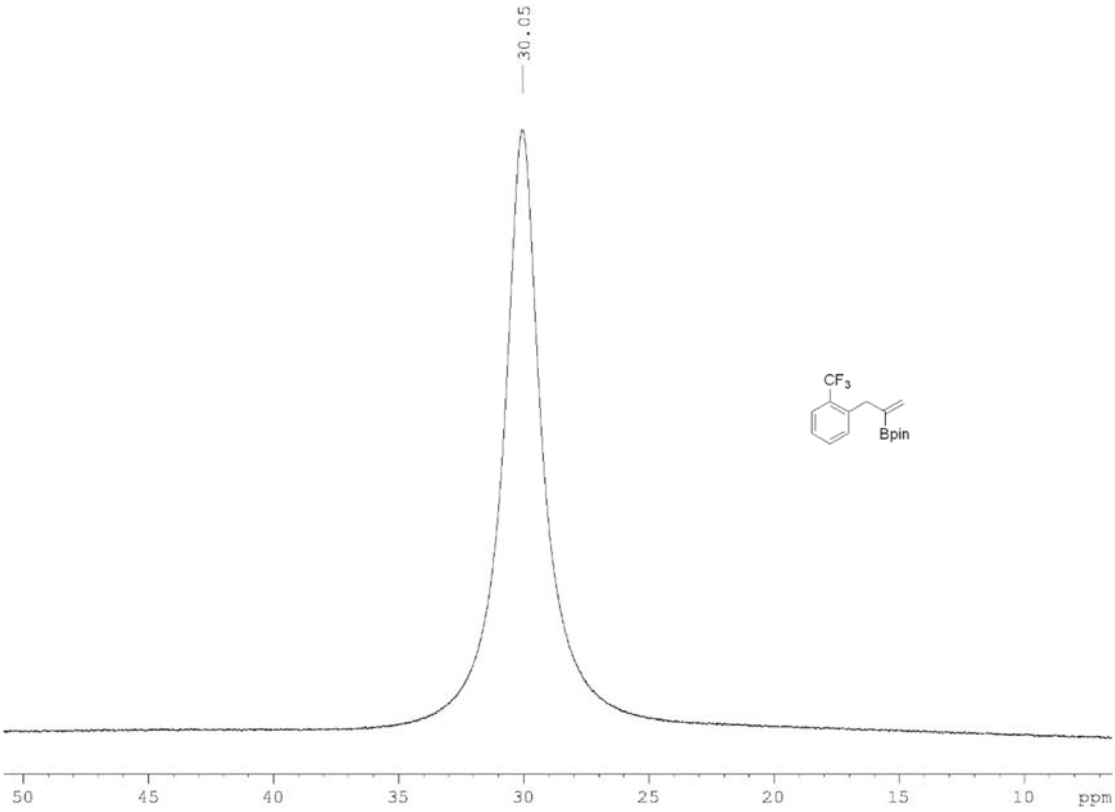
^{1}H NMR (500 MHz, $CDCl_3$)



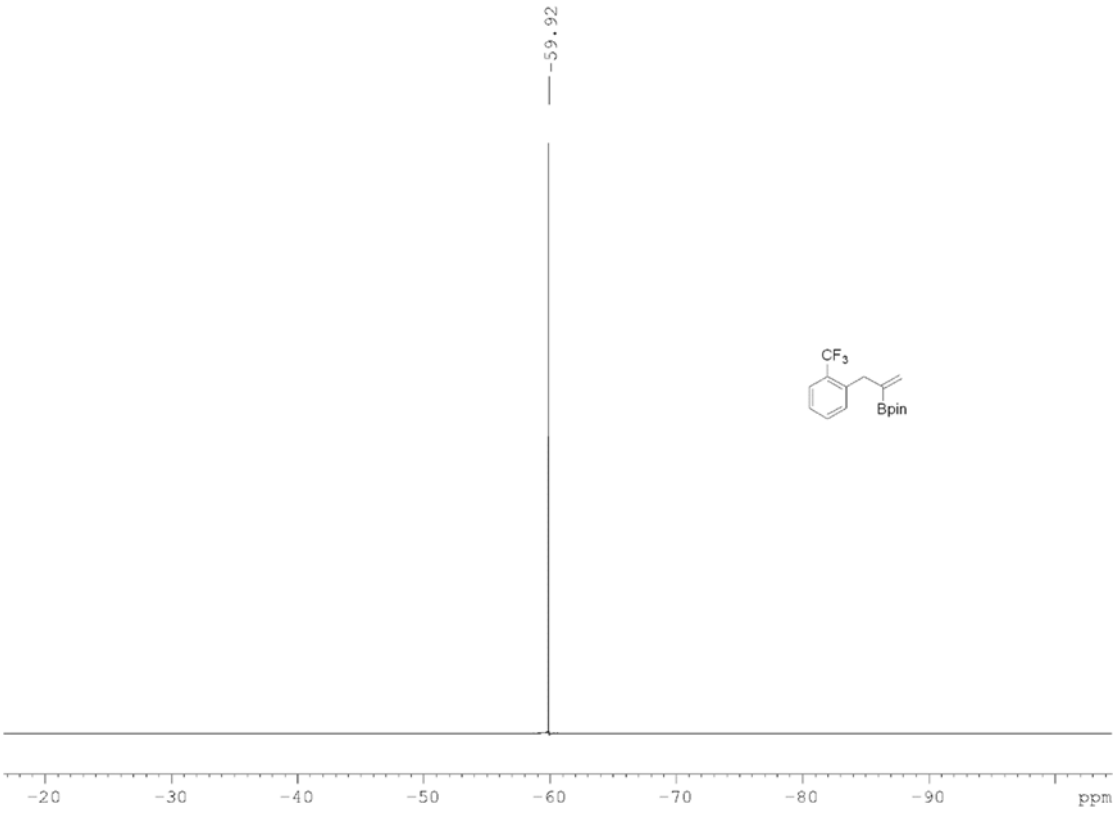
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)

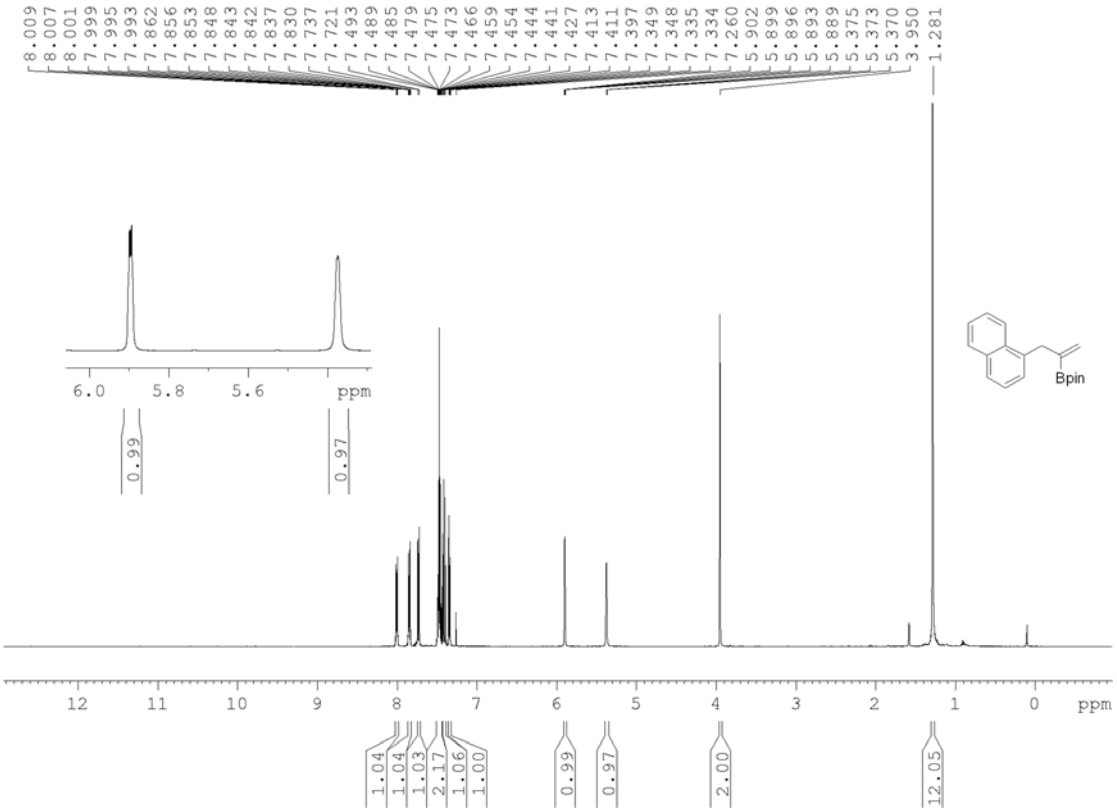


^{19}F NMR (470 MHz, $CDCl_3$)

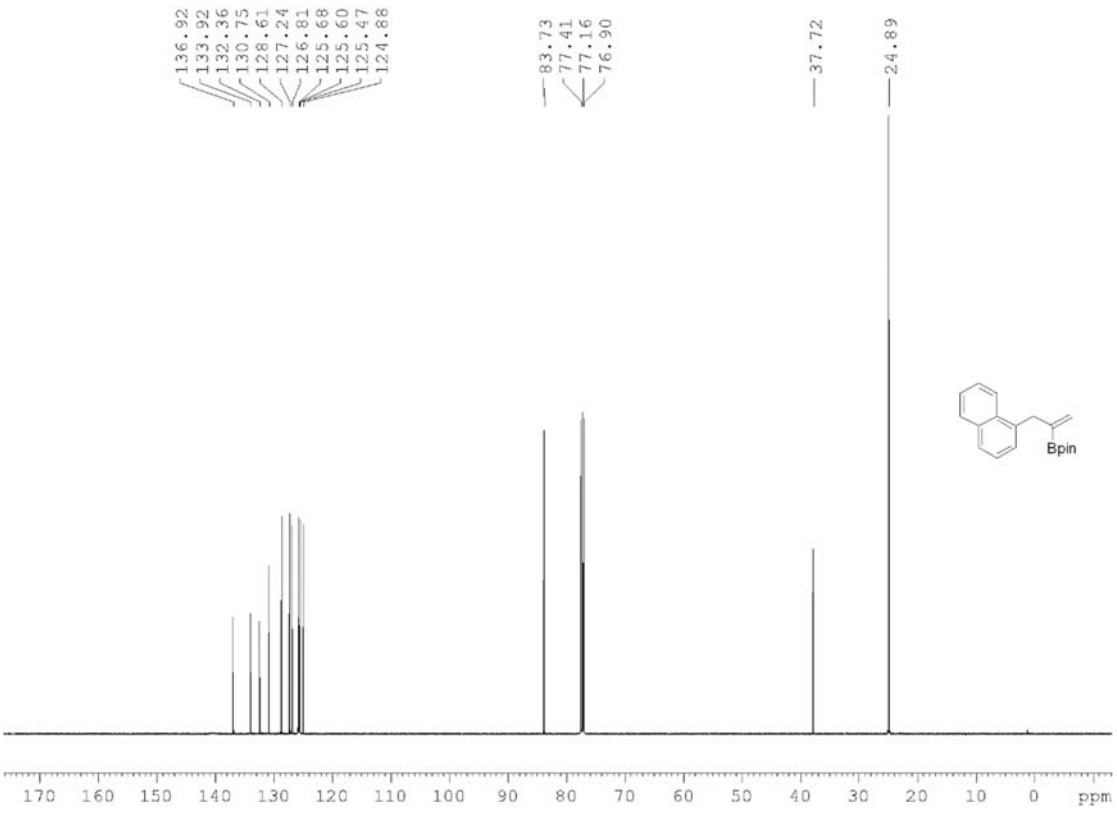


Compound (3-6)k

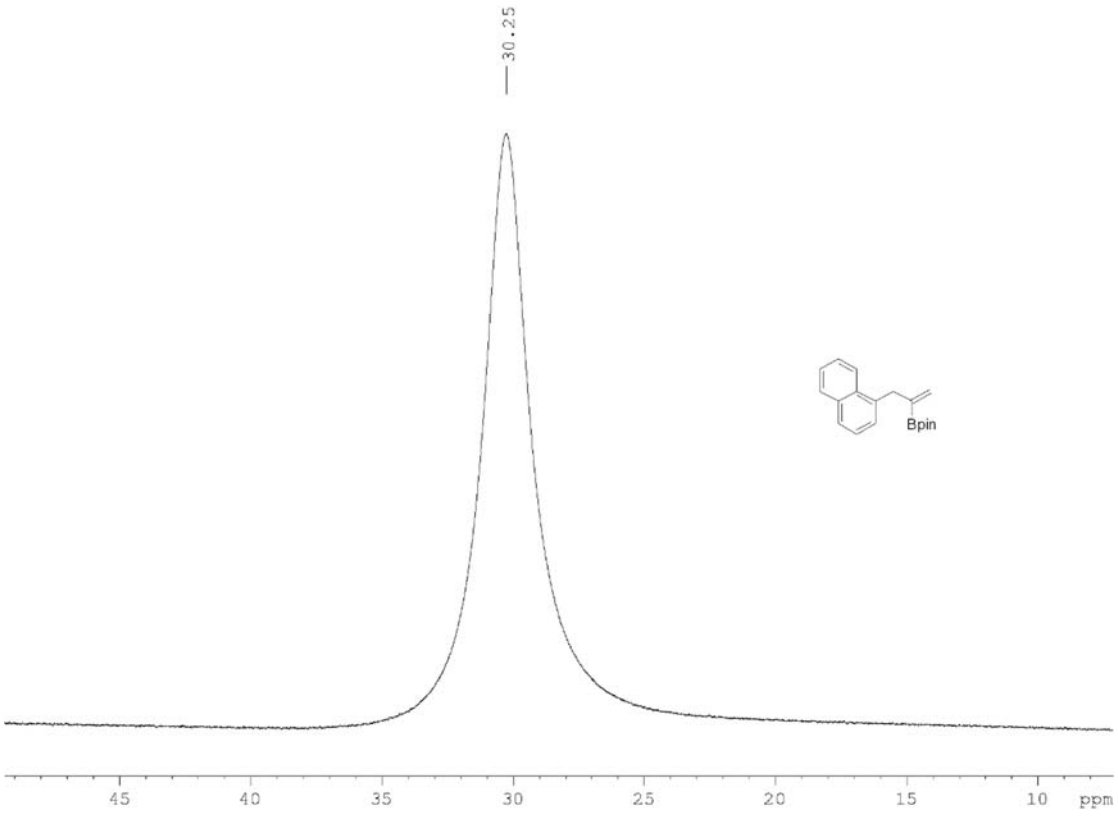
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

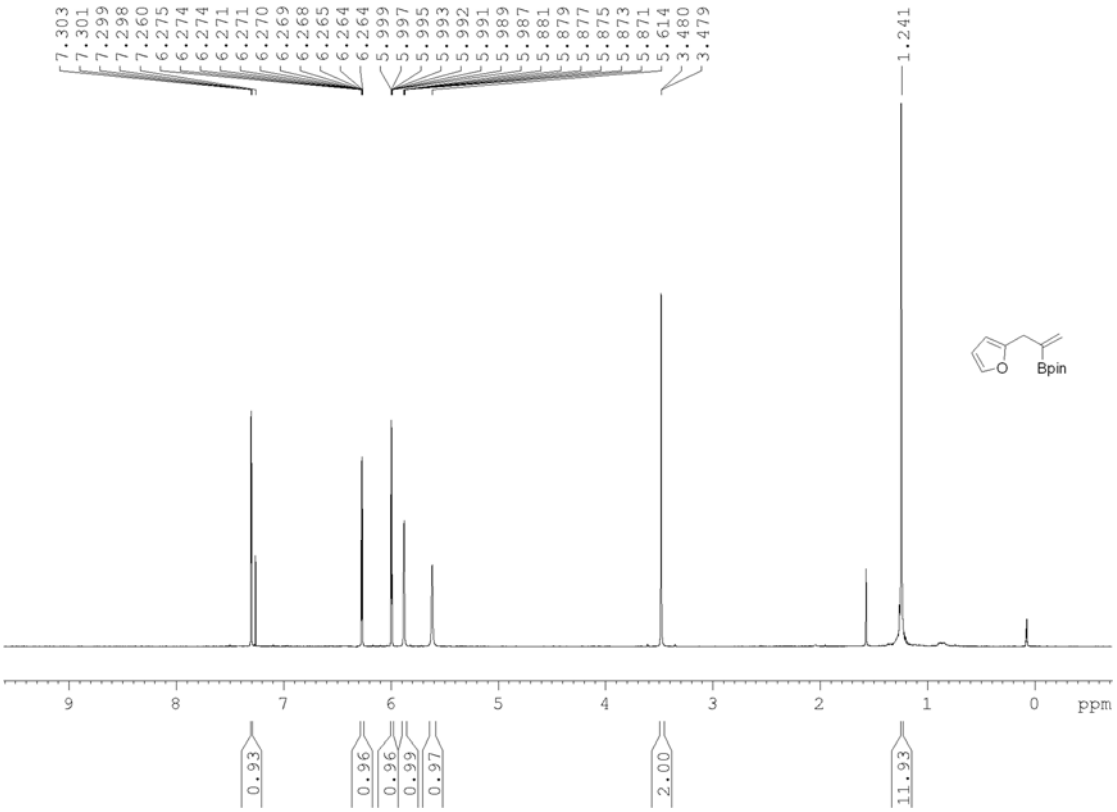


^{11}B NMR (160 MHz, $CDCl_3$)

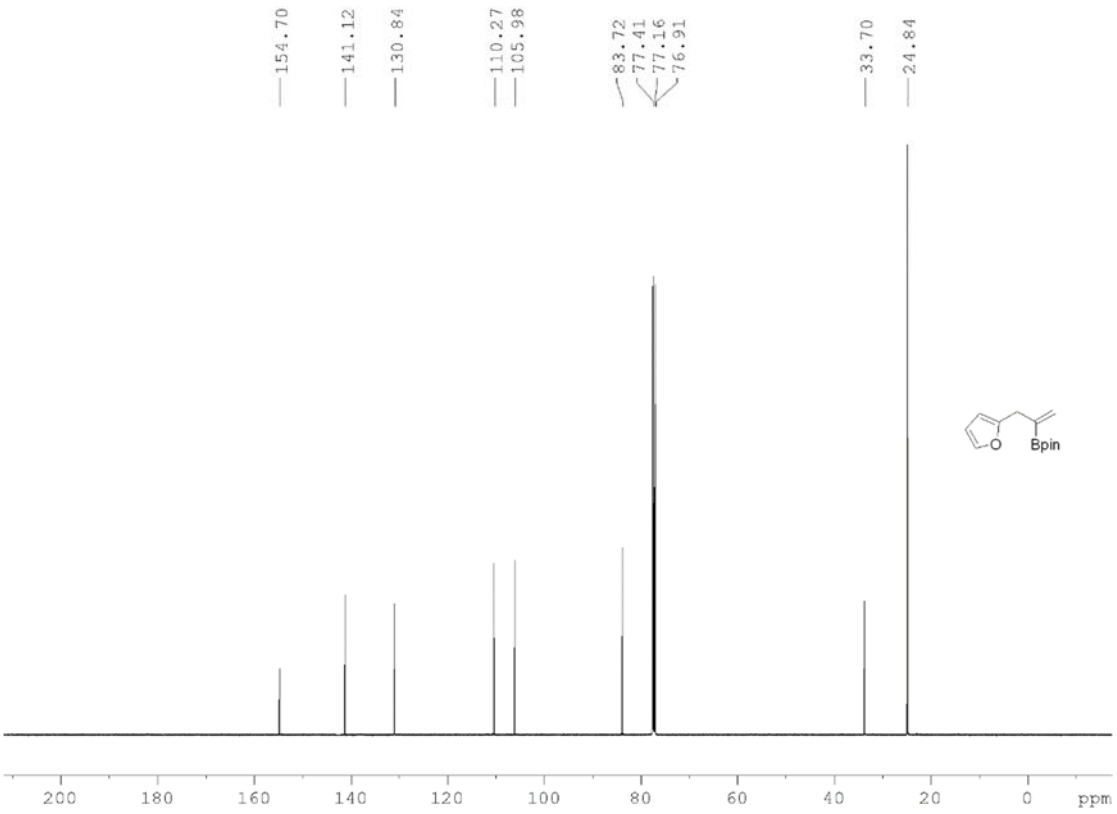


Compound (3-6)l

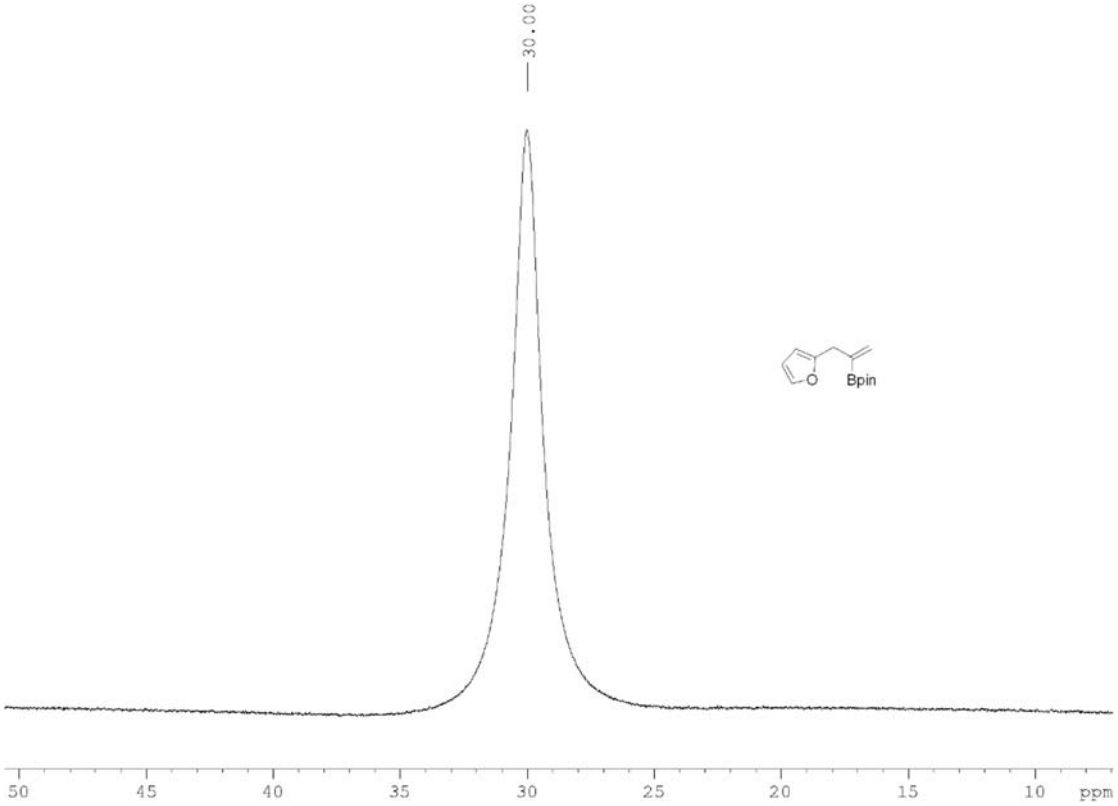
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

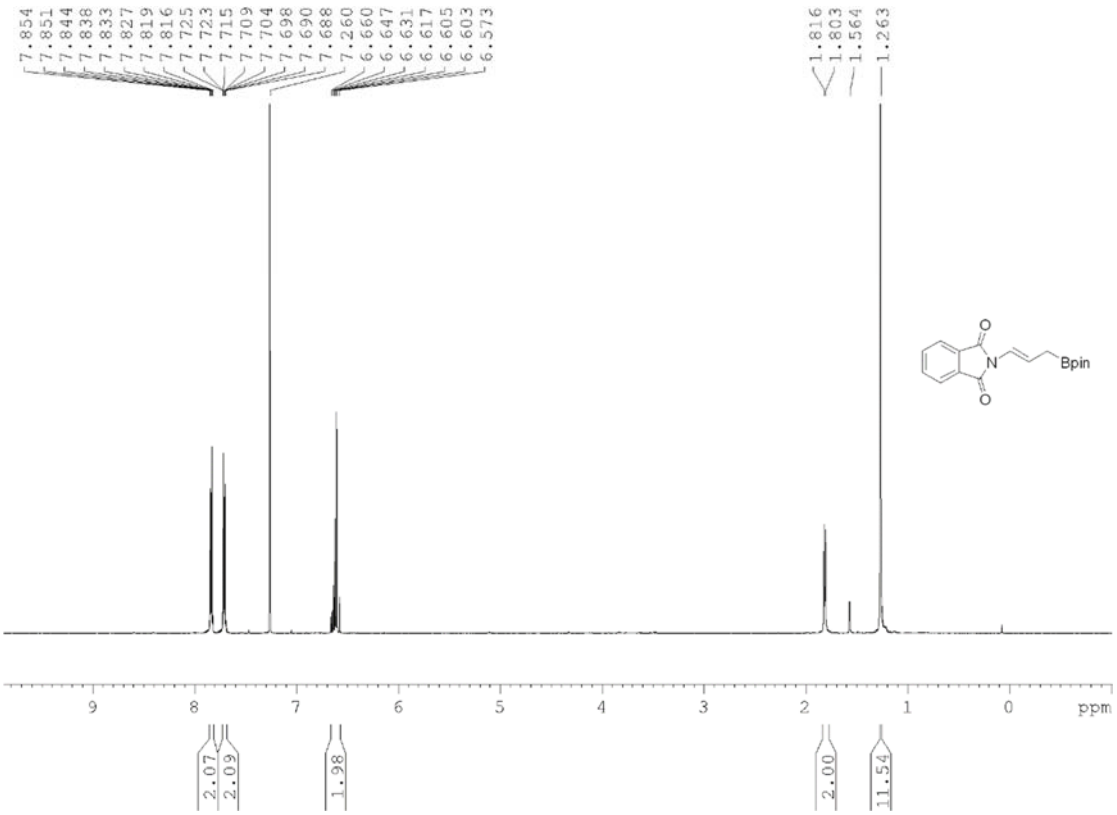


^{11}B NMR (160 MHz, $CDCl_3$)

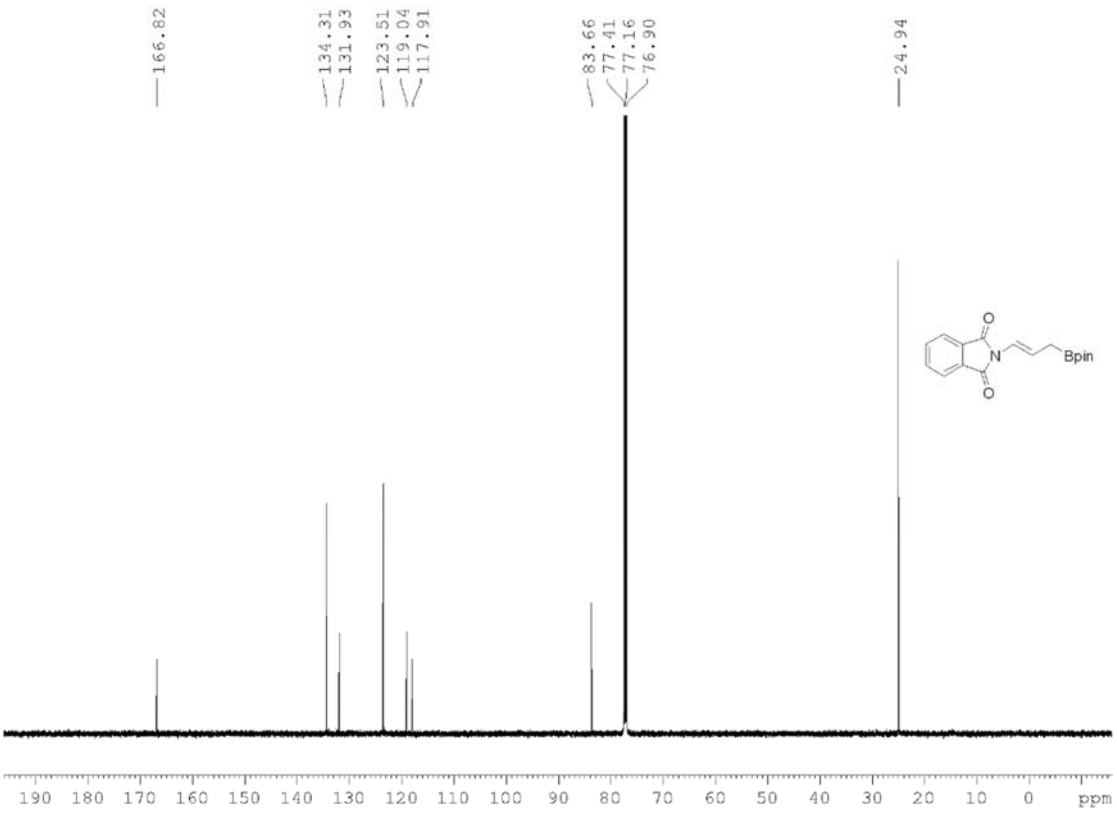


Compound (4-2)j

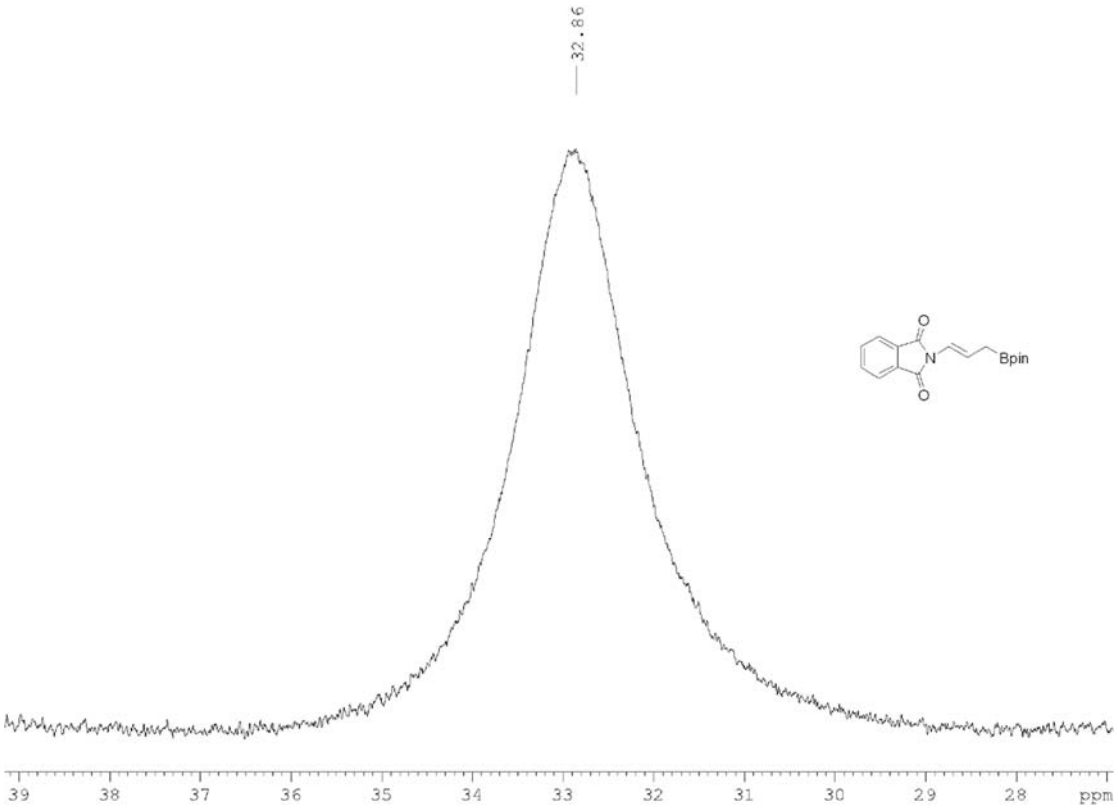
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

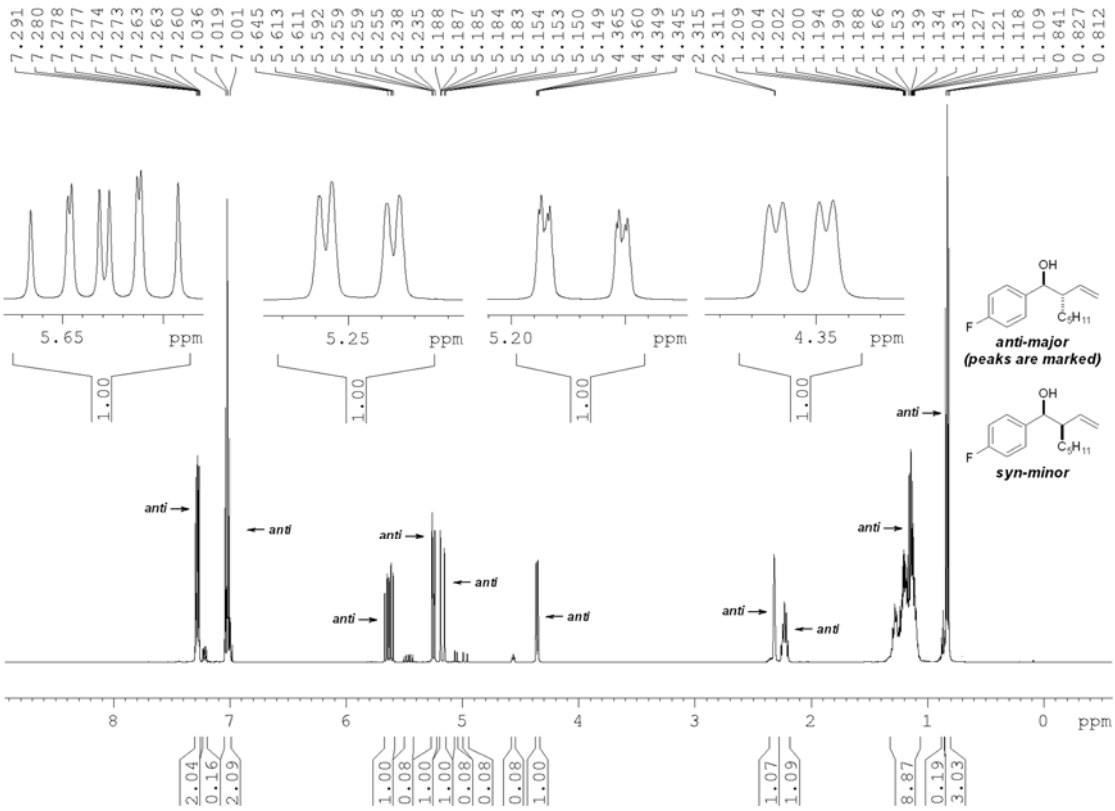


^{11}B NMR (160 MHz, $CDCl_3$)

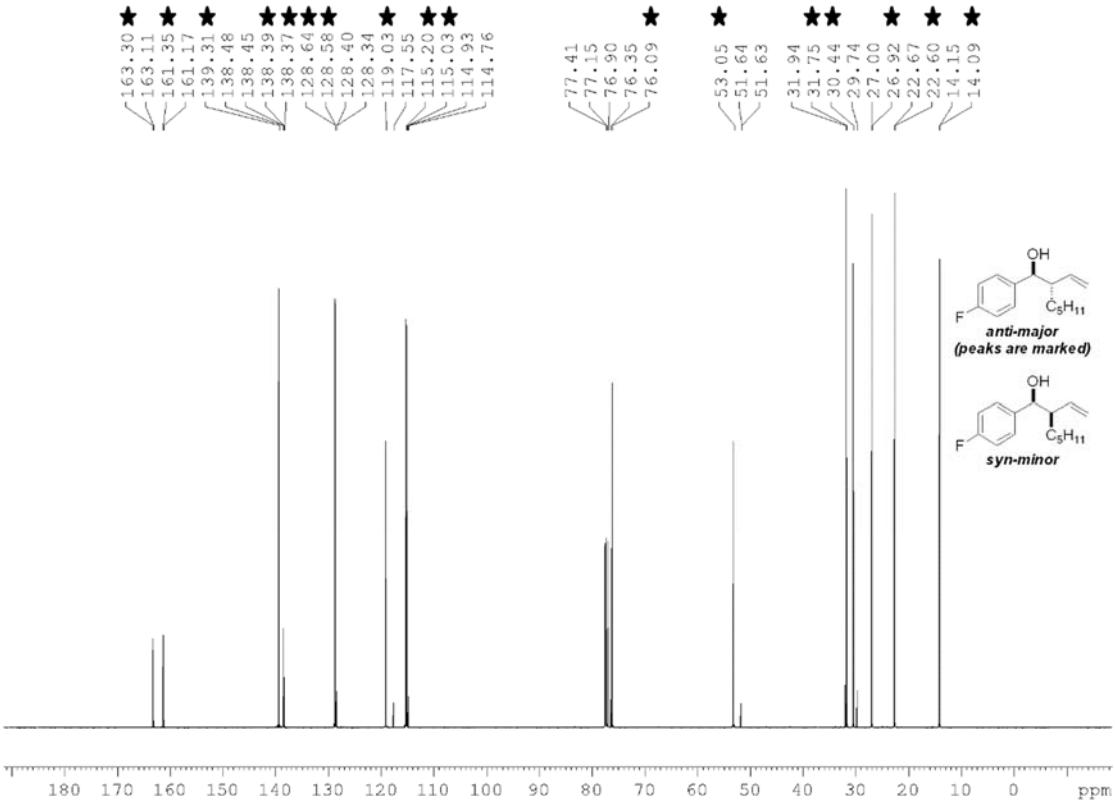


Compound (4-4)a

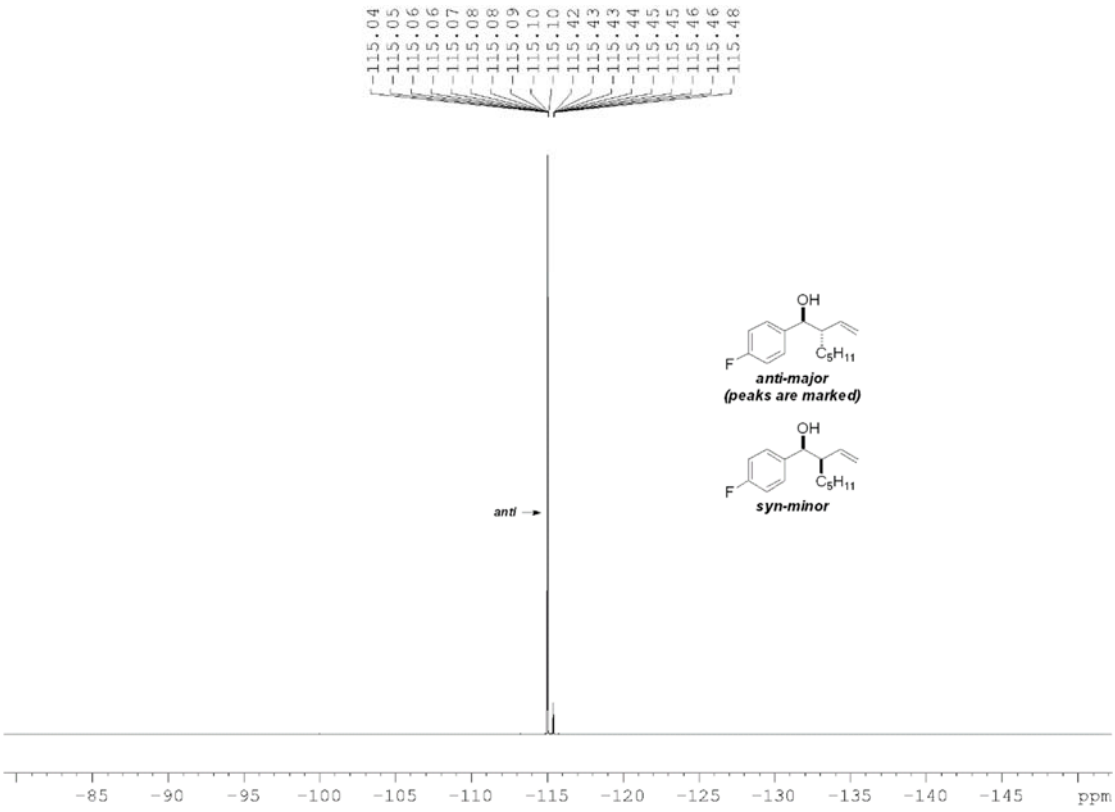
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

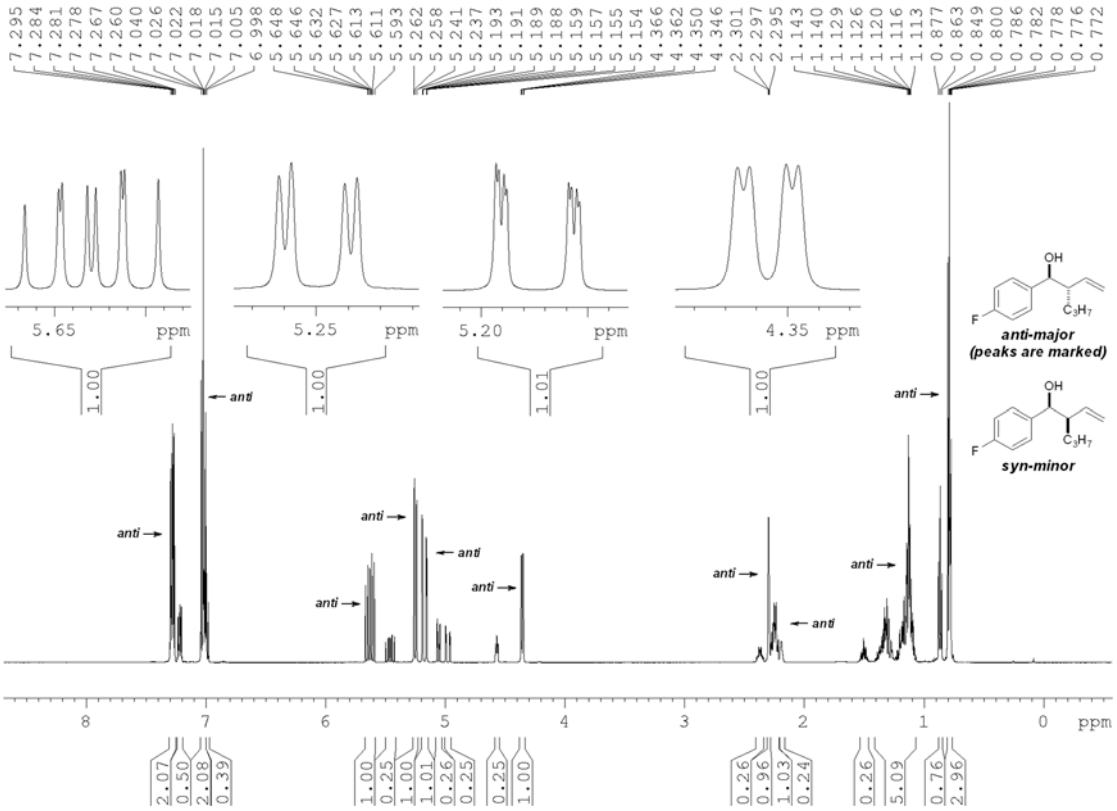


^{19}F NMR (470 MHz, $CDCl_3$)

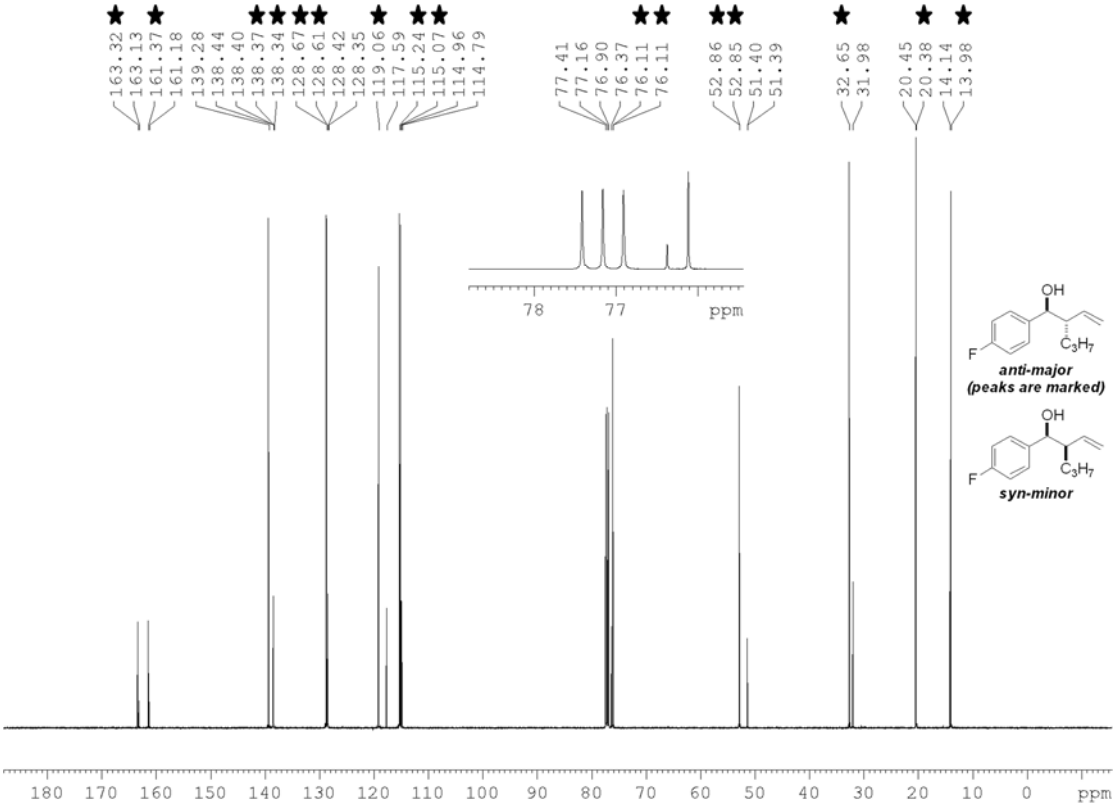


Compound (4-4)b

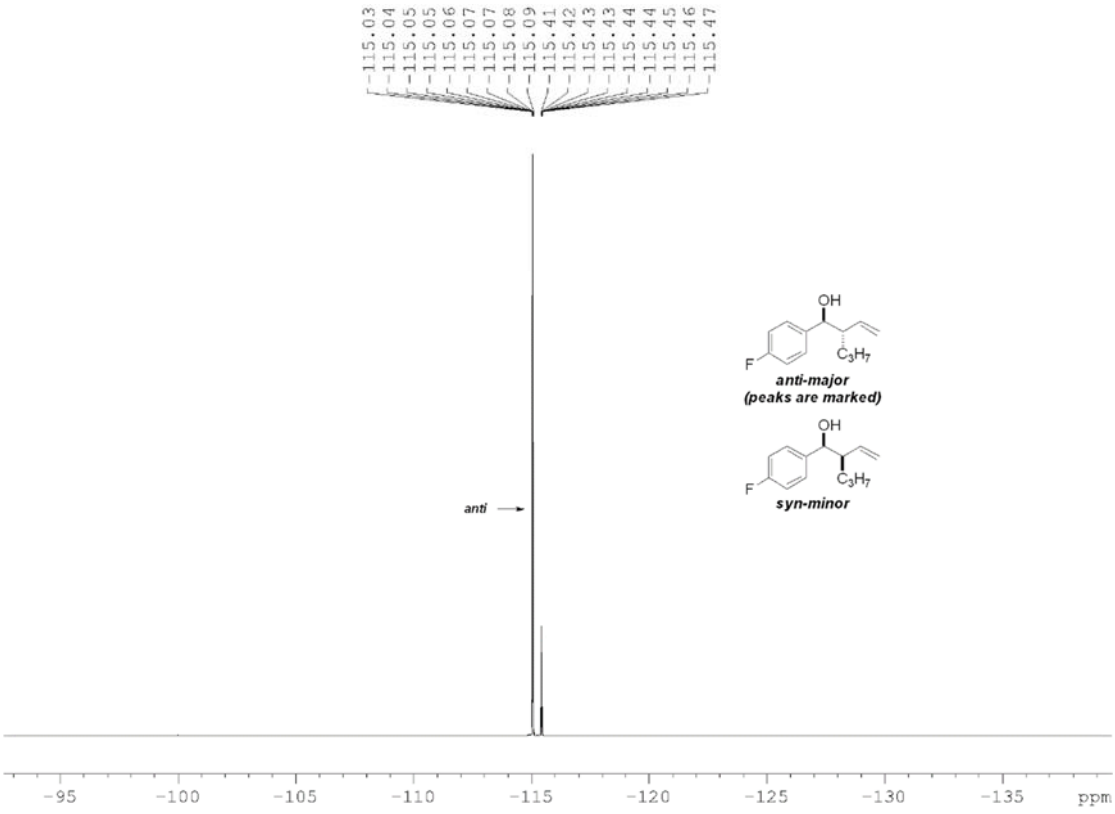
^{1}H NMR (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

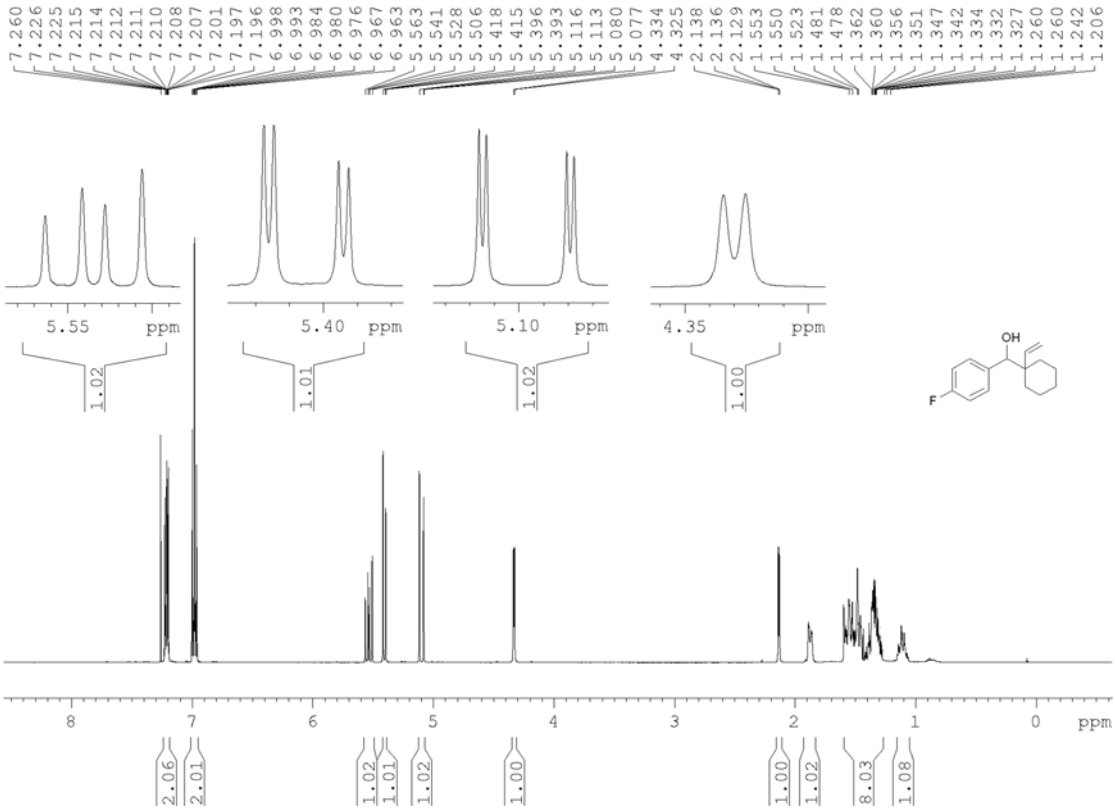


^{19}F NMR (470 MHz, $CDCl_3$)

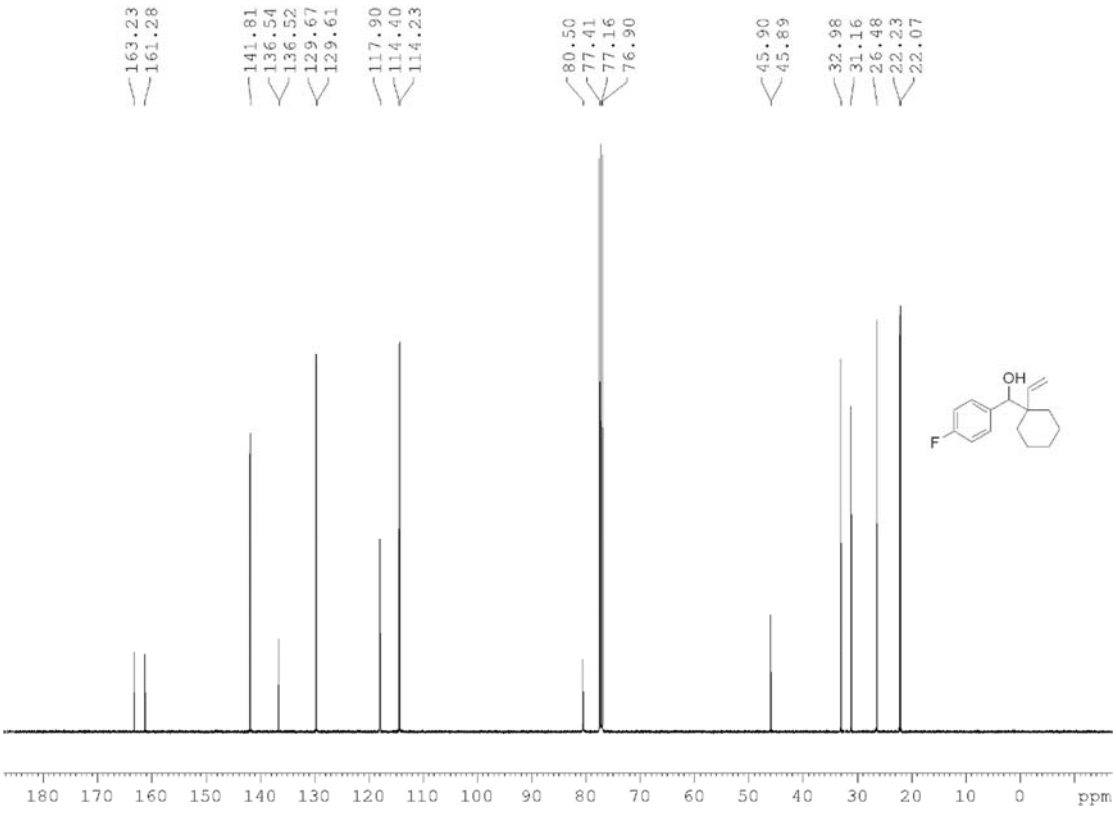


Compound (4-4)d

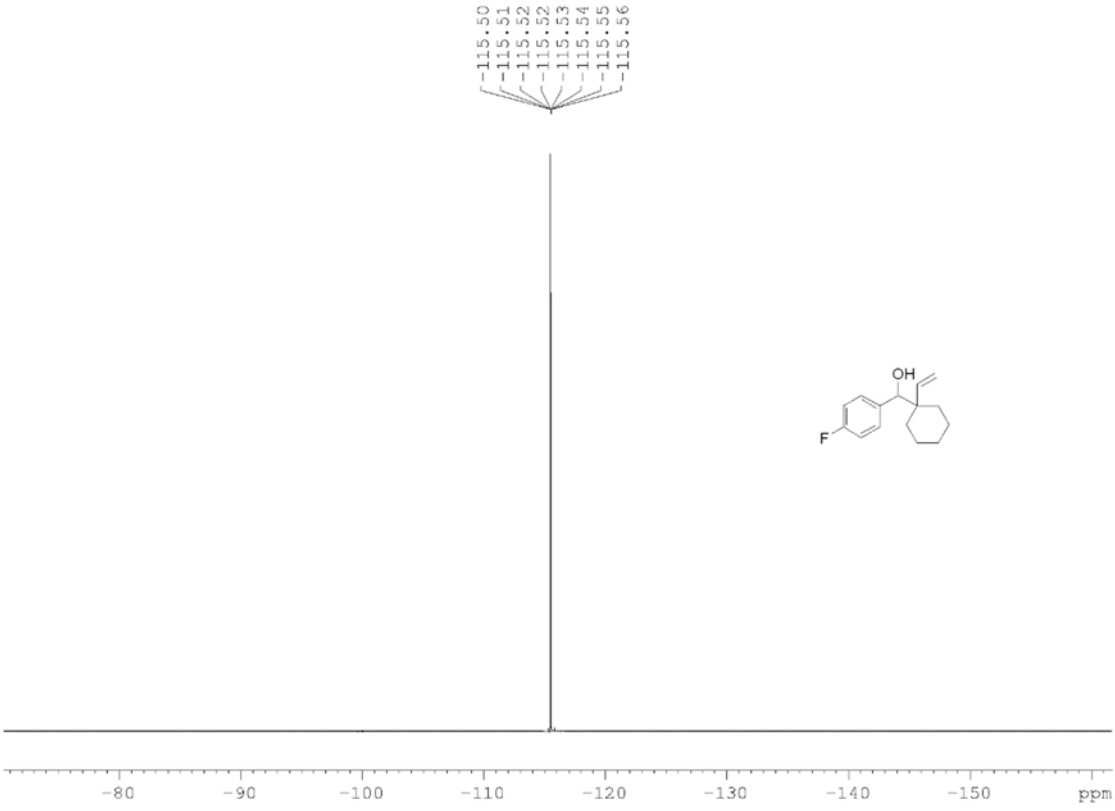
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

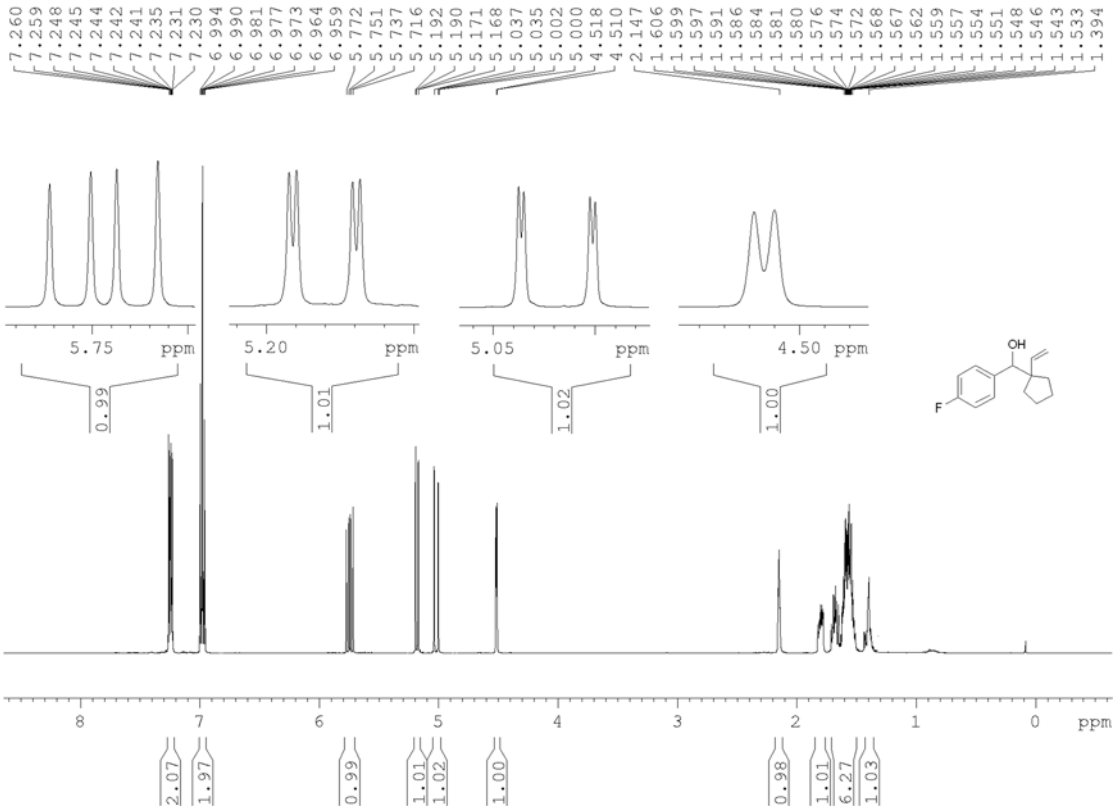


^{19}F NMR (470 MHz, $CDCl_3$)

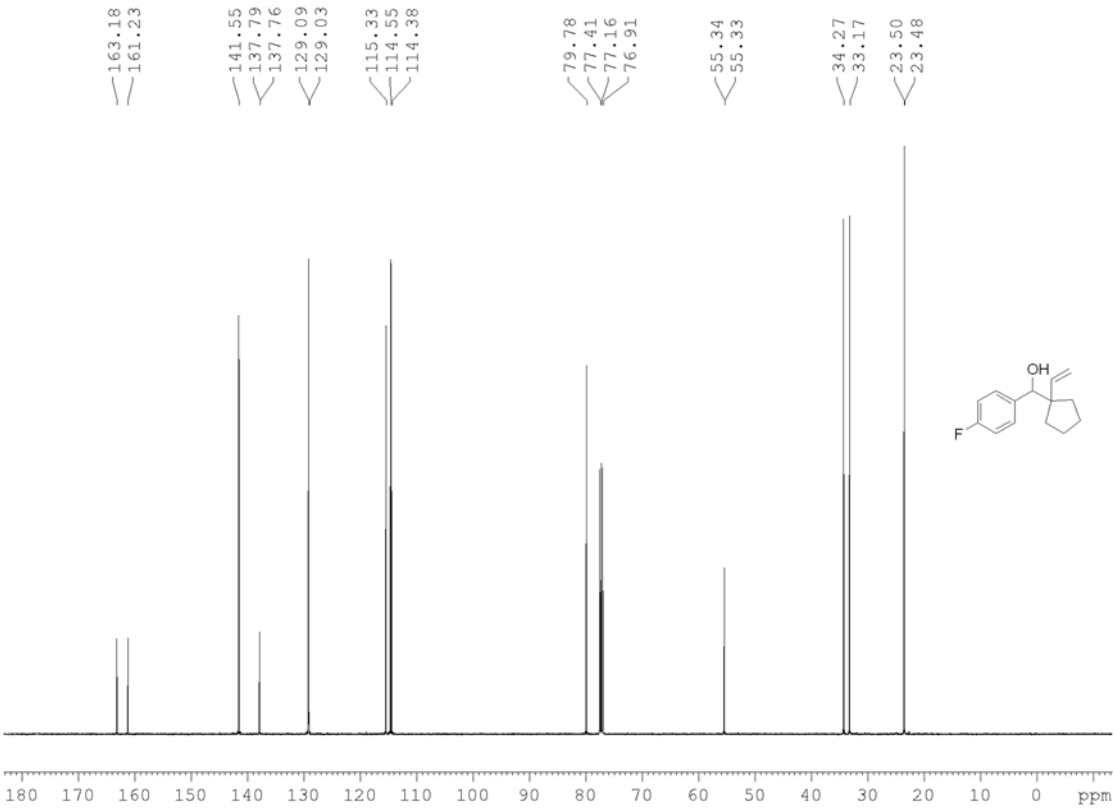


Compound (4-4)e

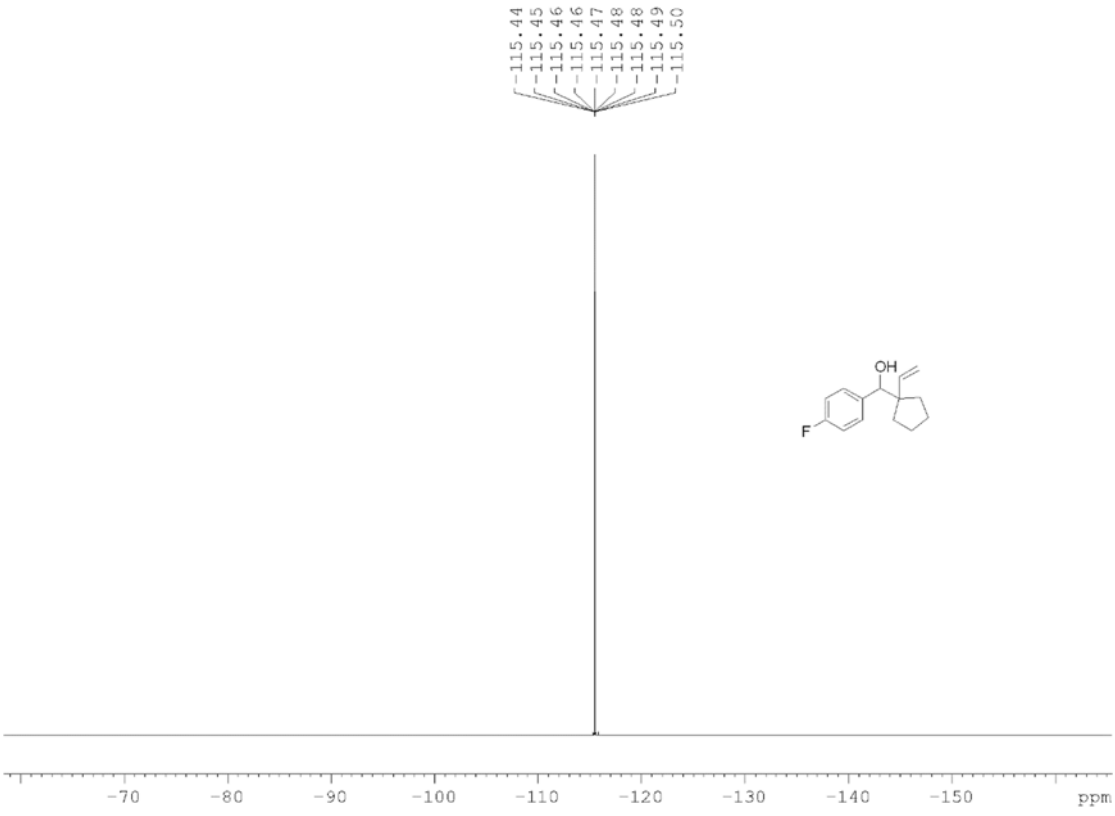
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

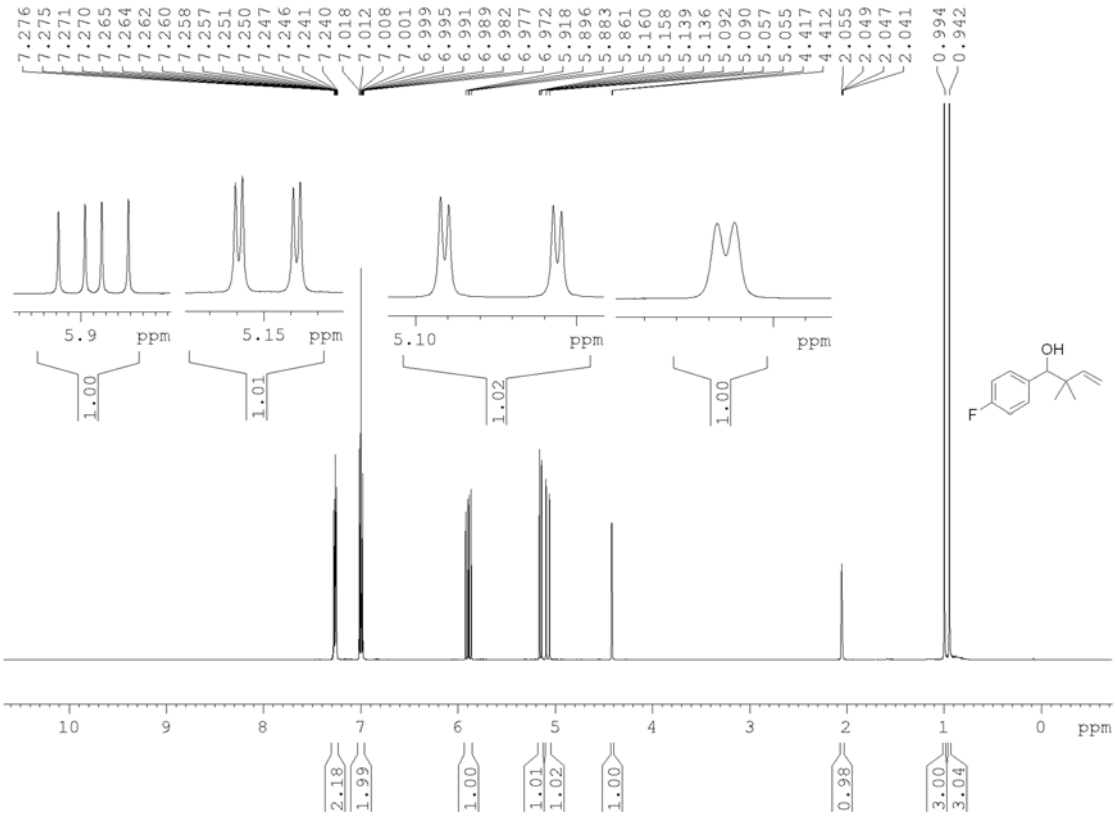


^{19}F NMR (470 MHz, $CDCl_3$)

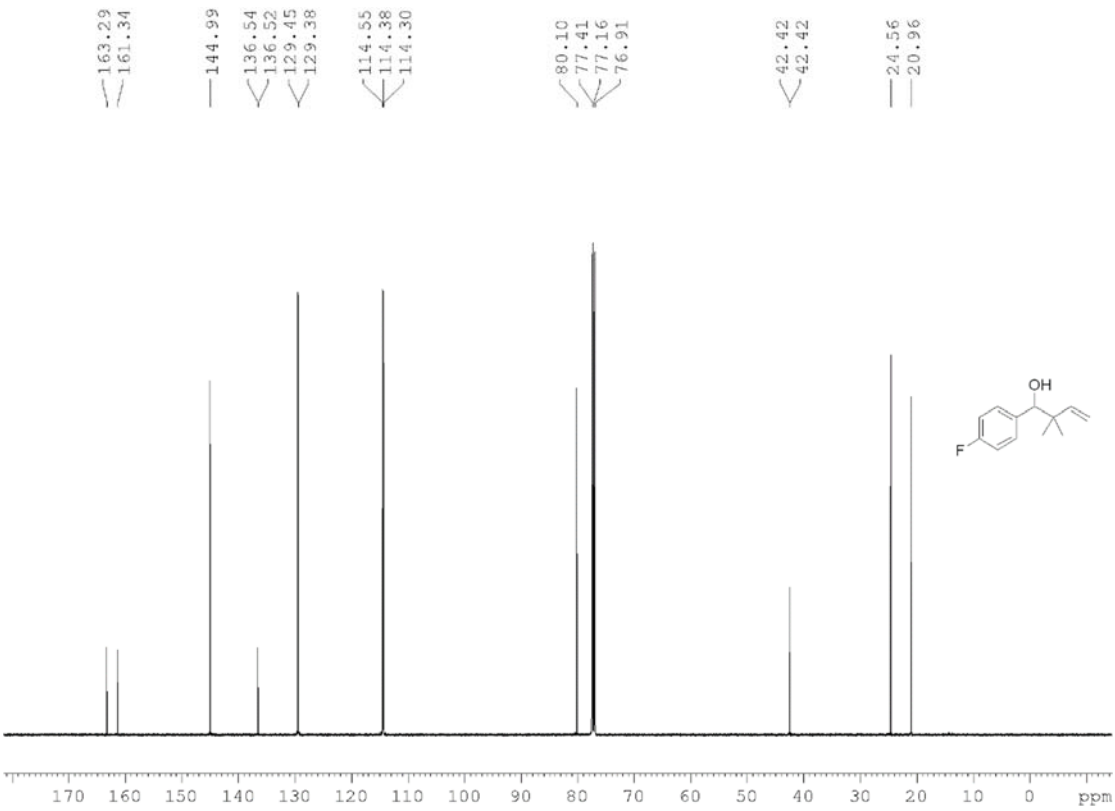


Compound (4-4)g

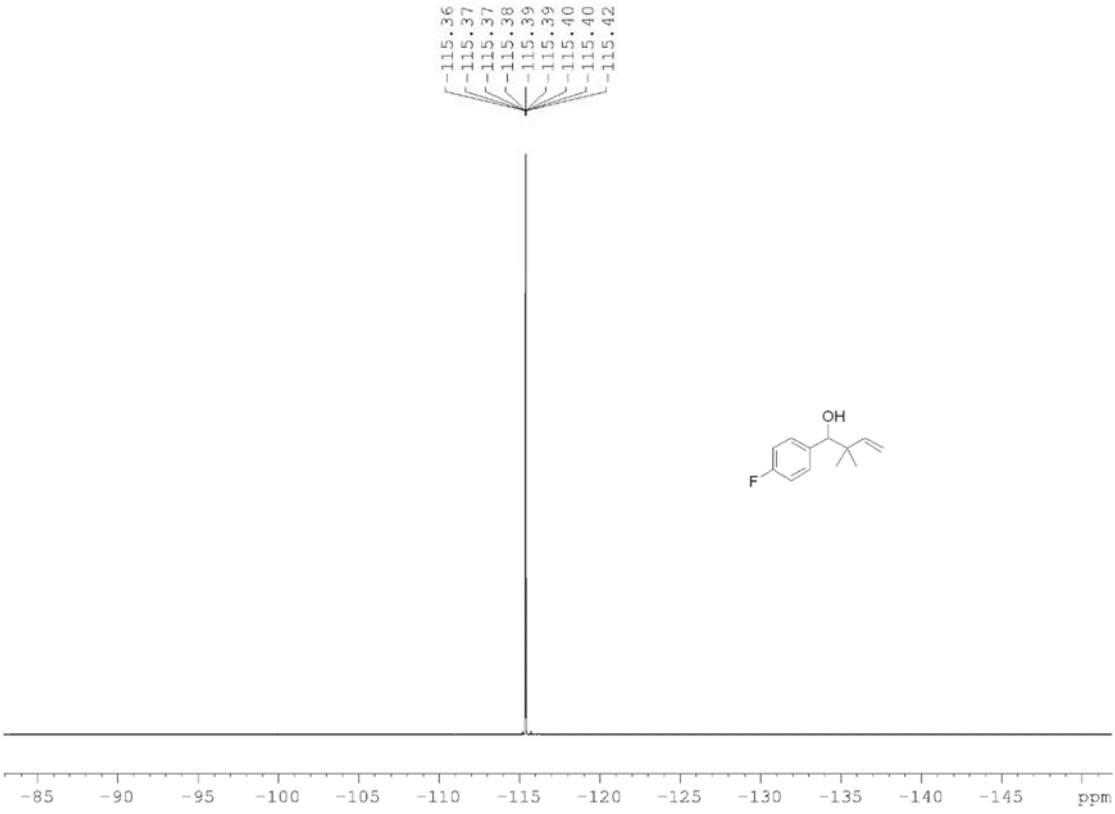
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

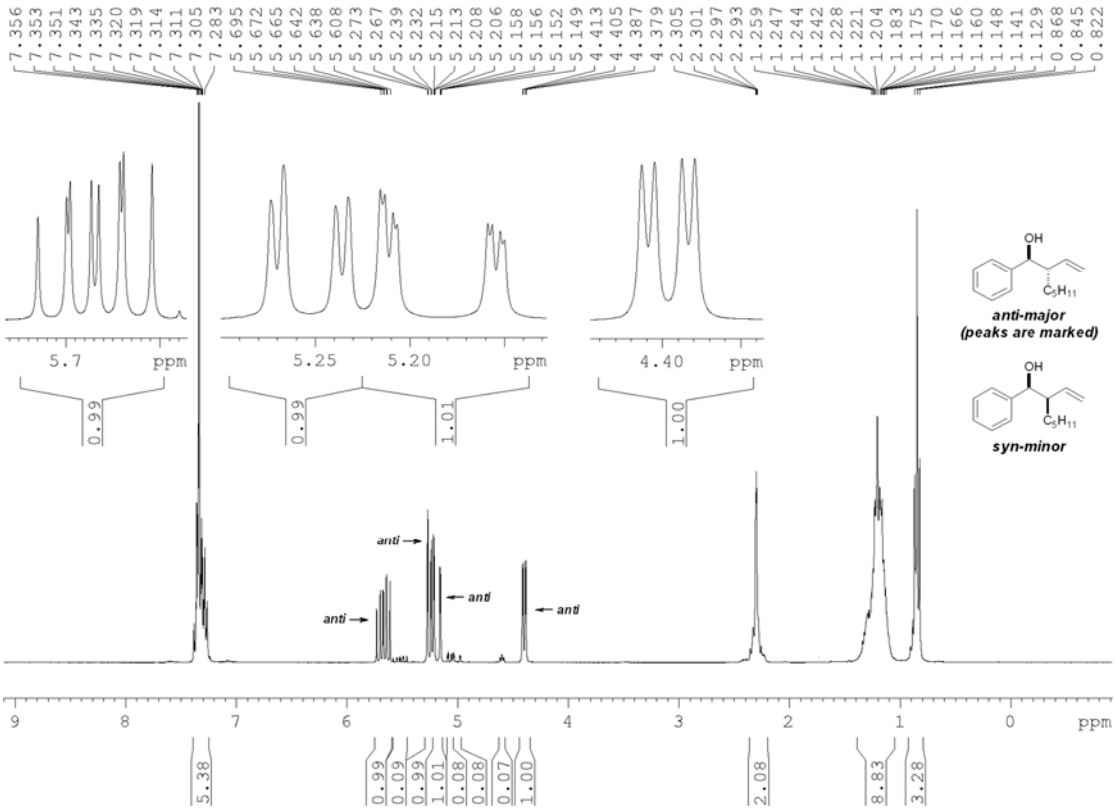


^{19}F NMR (470 MHz, $CDCl_3$)

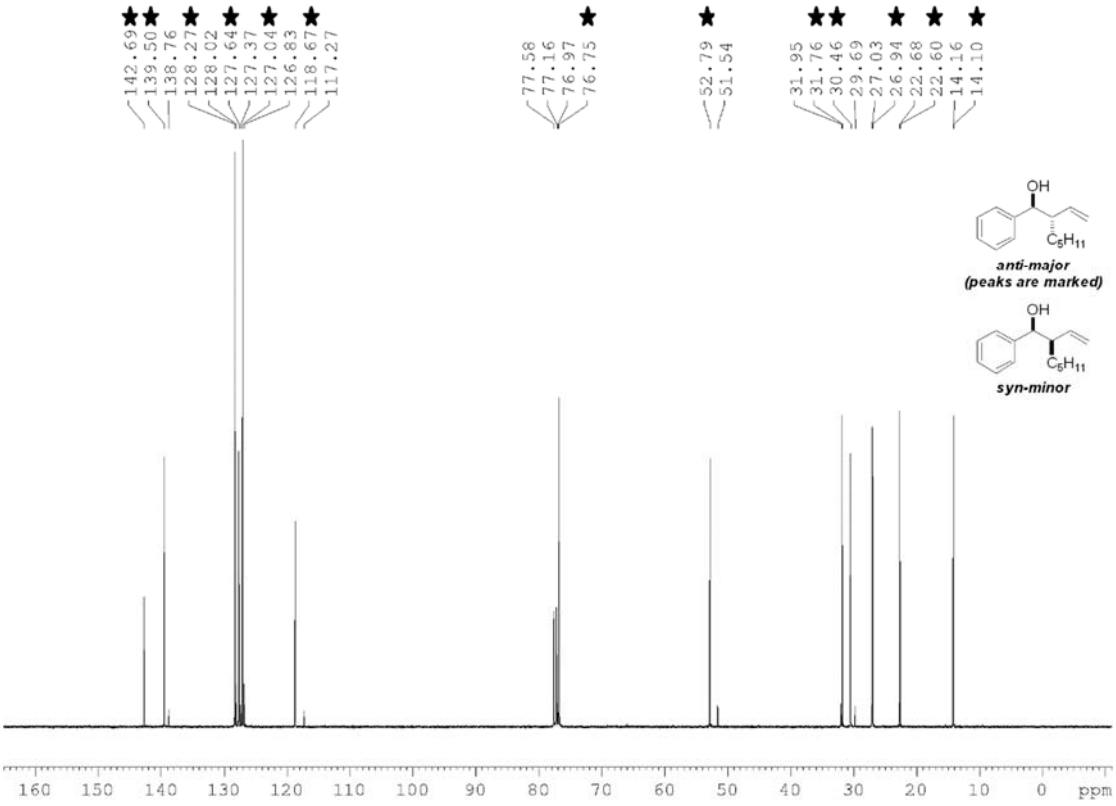


Compound (4-5)a

^{1}H NMR (300 MHz, $CDCl_3$)

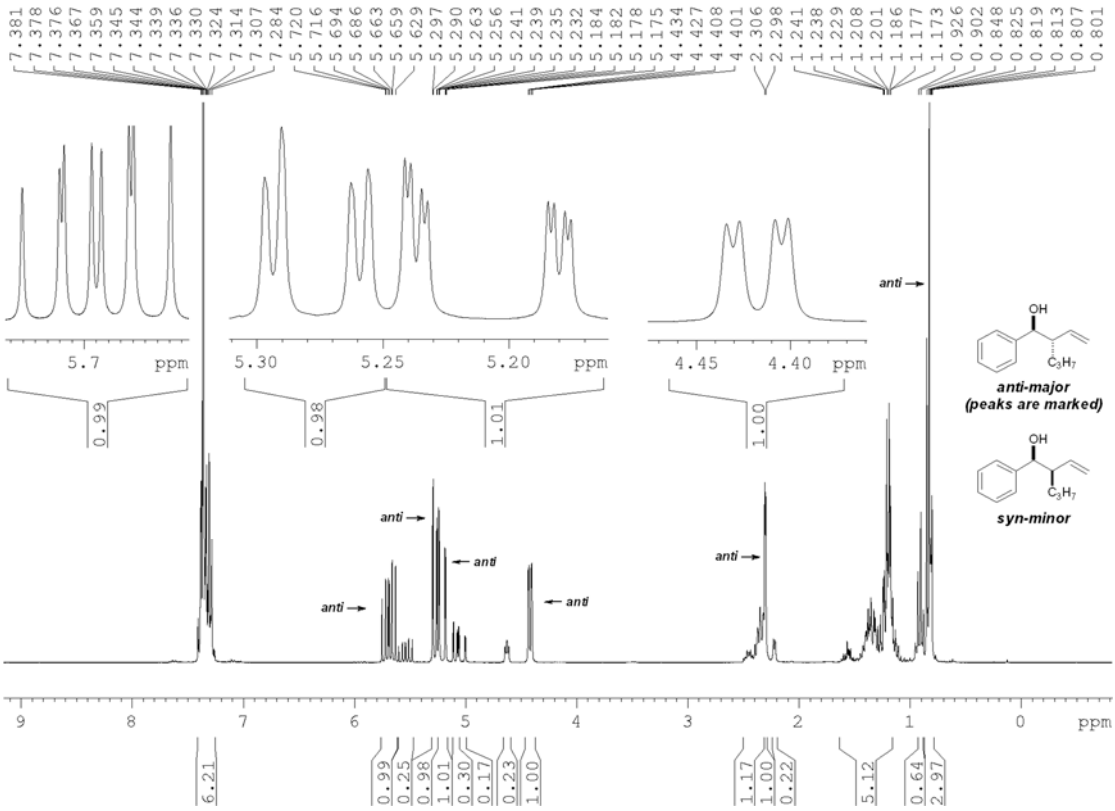


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

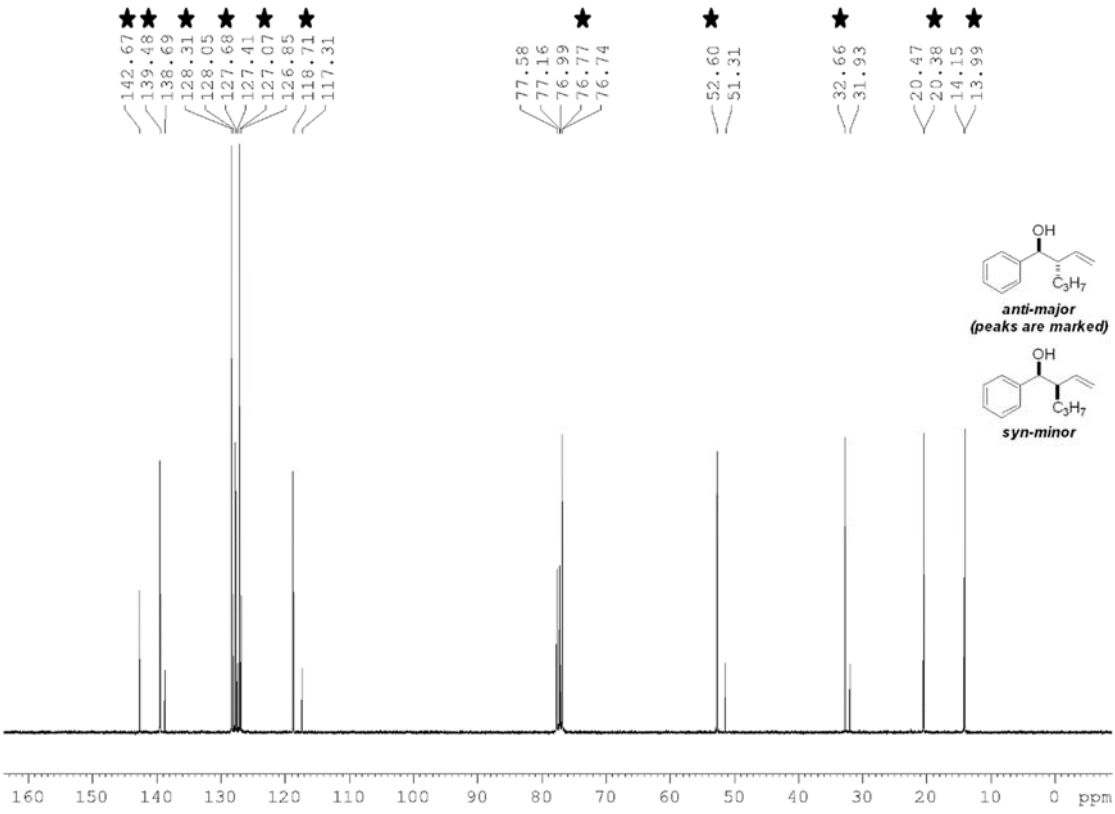


Compound (4-5)b

^{1}H NMR (300 MHz, $CDCl_3$)

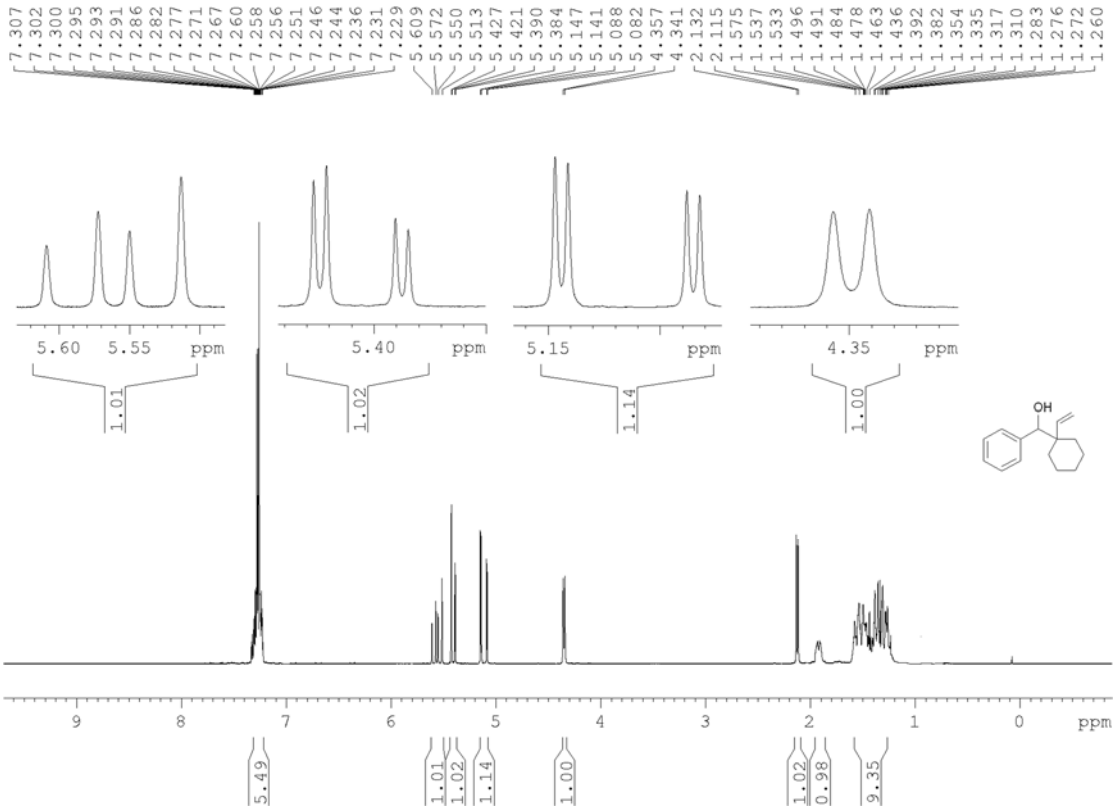


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

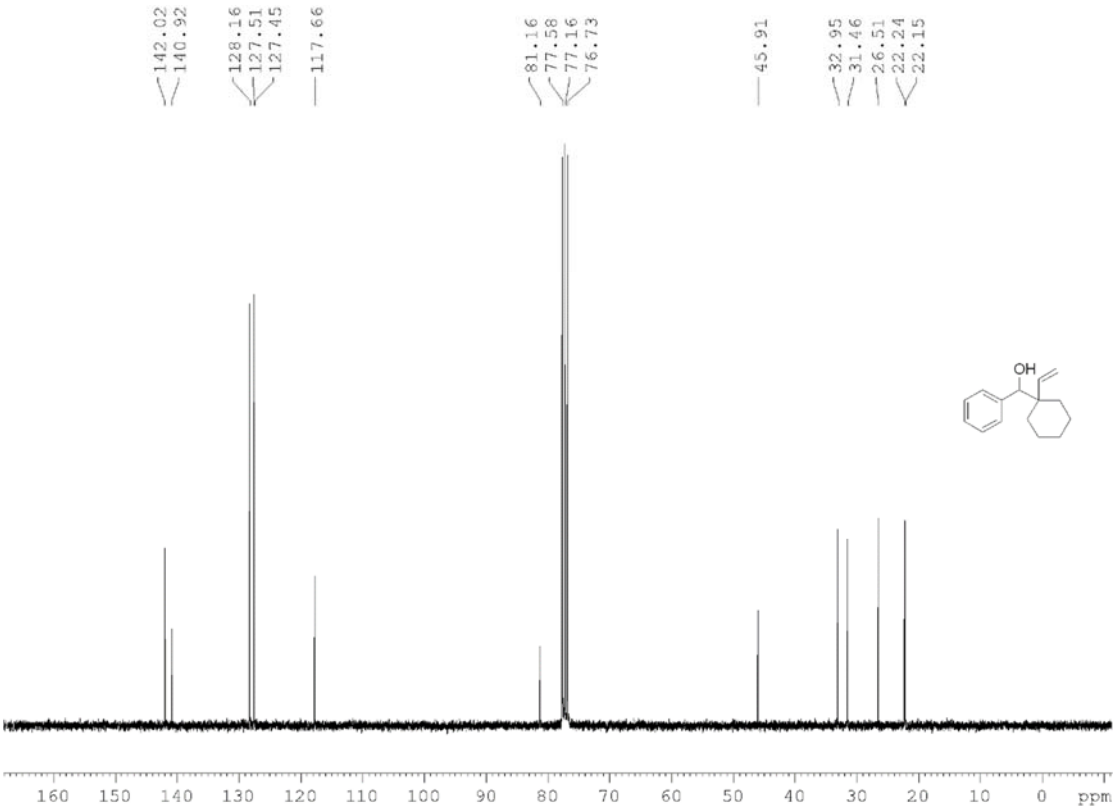


Compound (4-5)d

^{1}H NMR (300 MHz, $CDCl_3$)

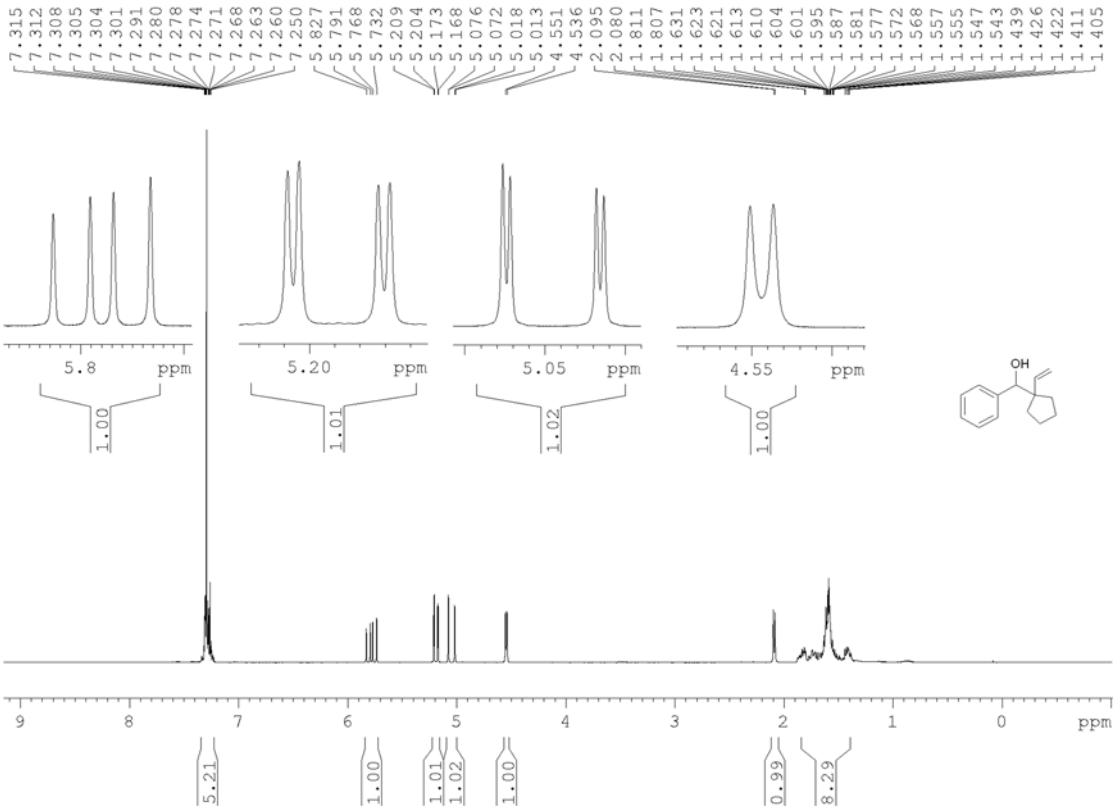


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

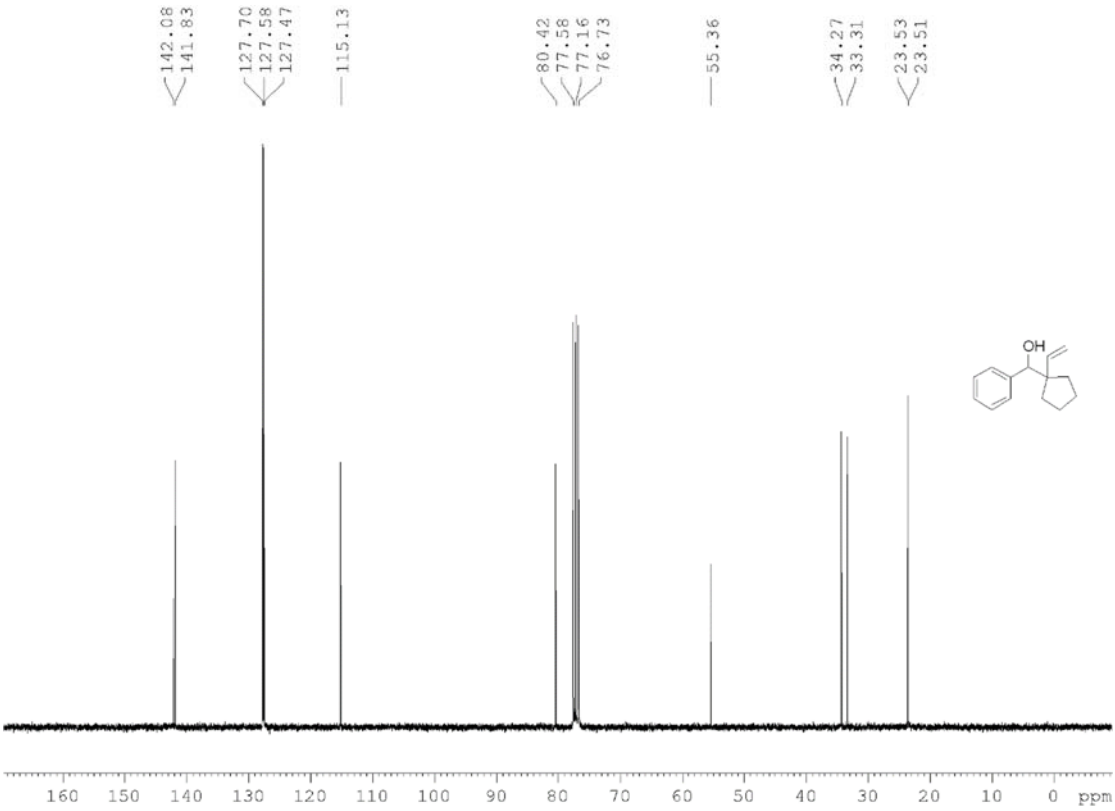


Compound (4-5)e

^{1}H NMR (300 MHz, $CDCl_3$)

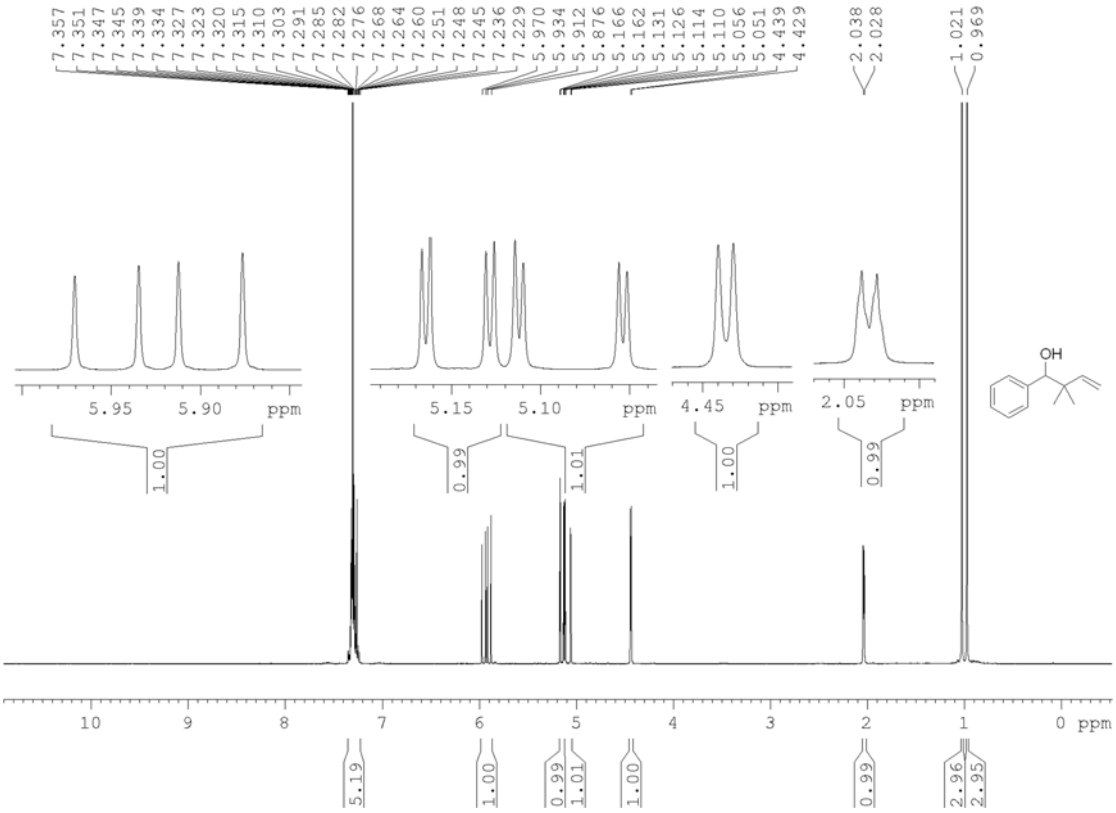


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

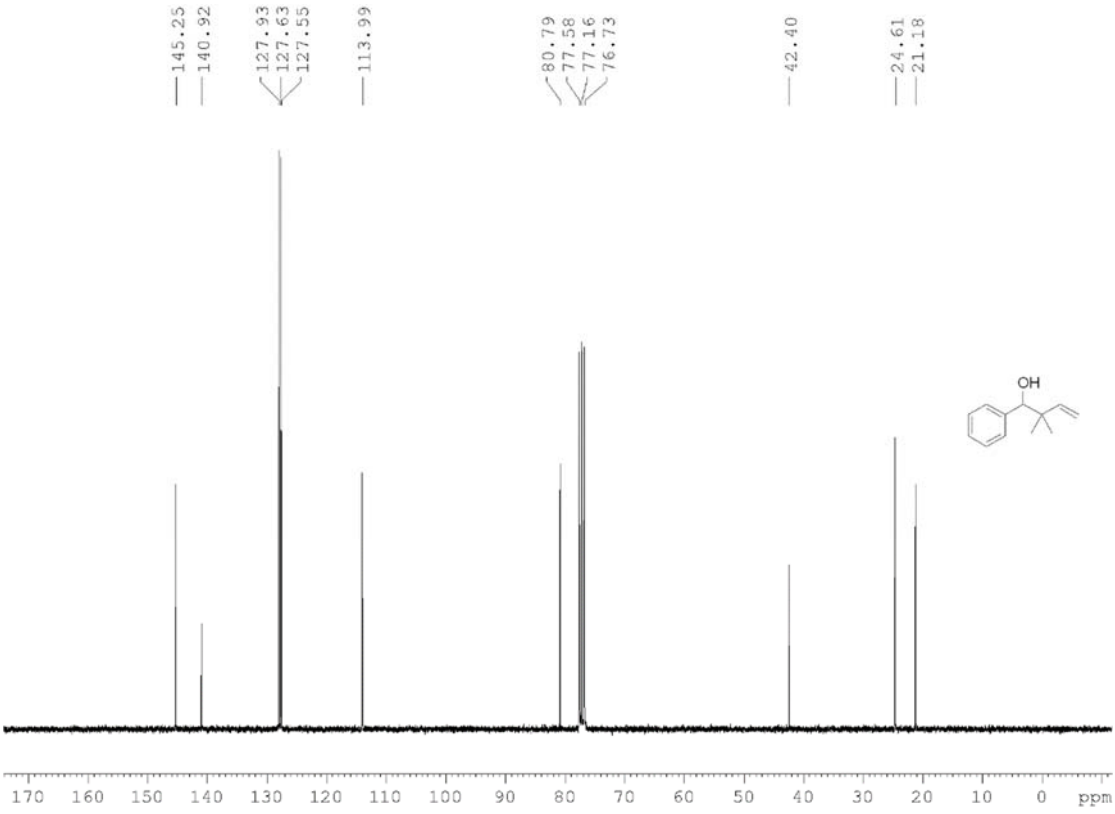


Compound (4-5)g

^{1}H NMR (300 MHz, $CDCl_3$)

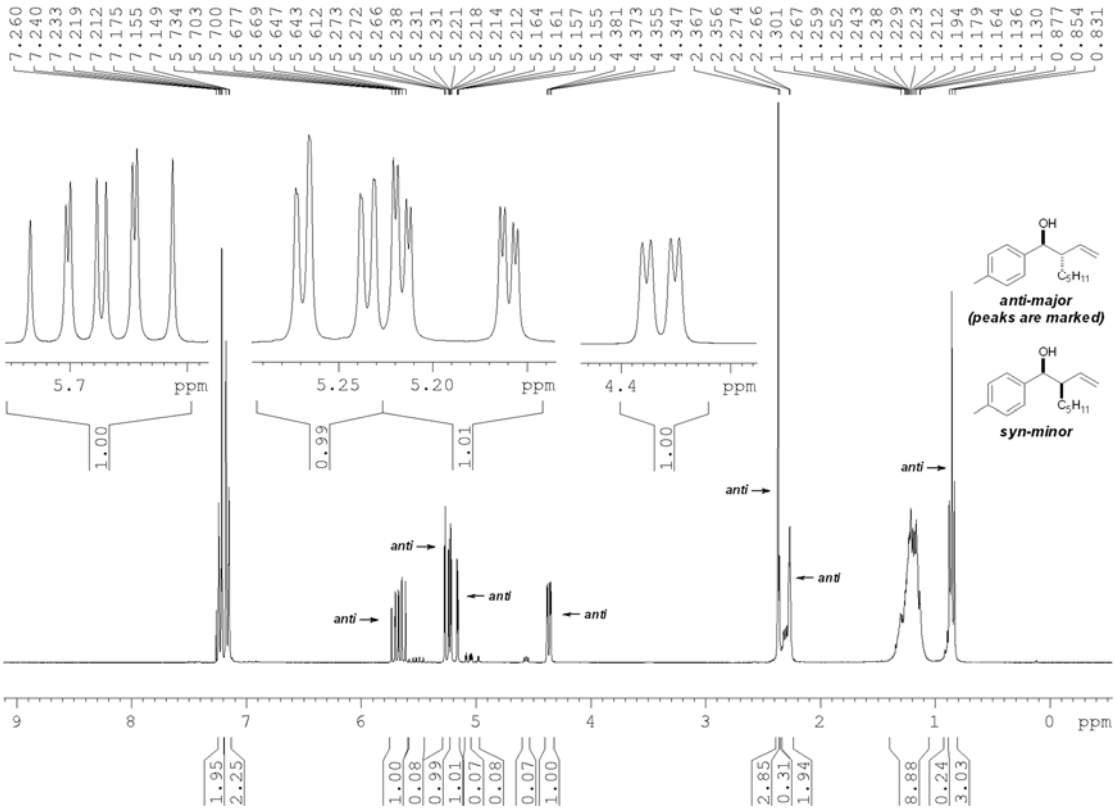


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

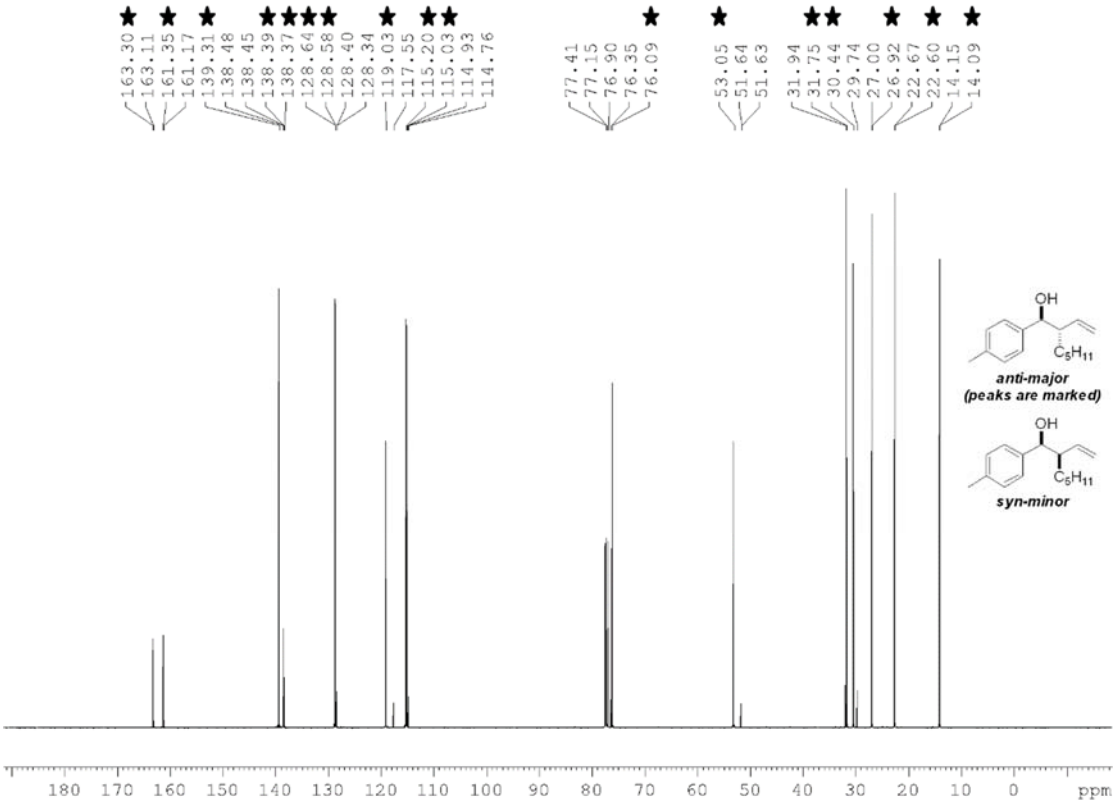


Compound (4-6)a

^{1}H NMR (300 MHz, $CDCl_3$)

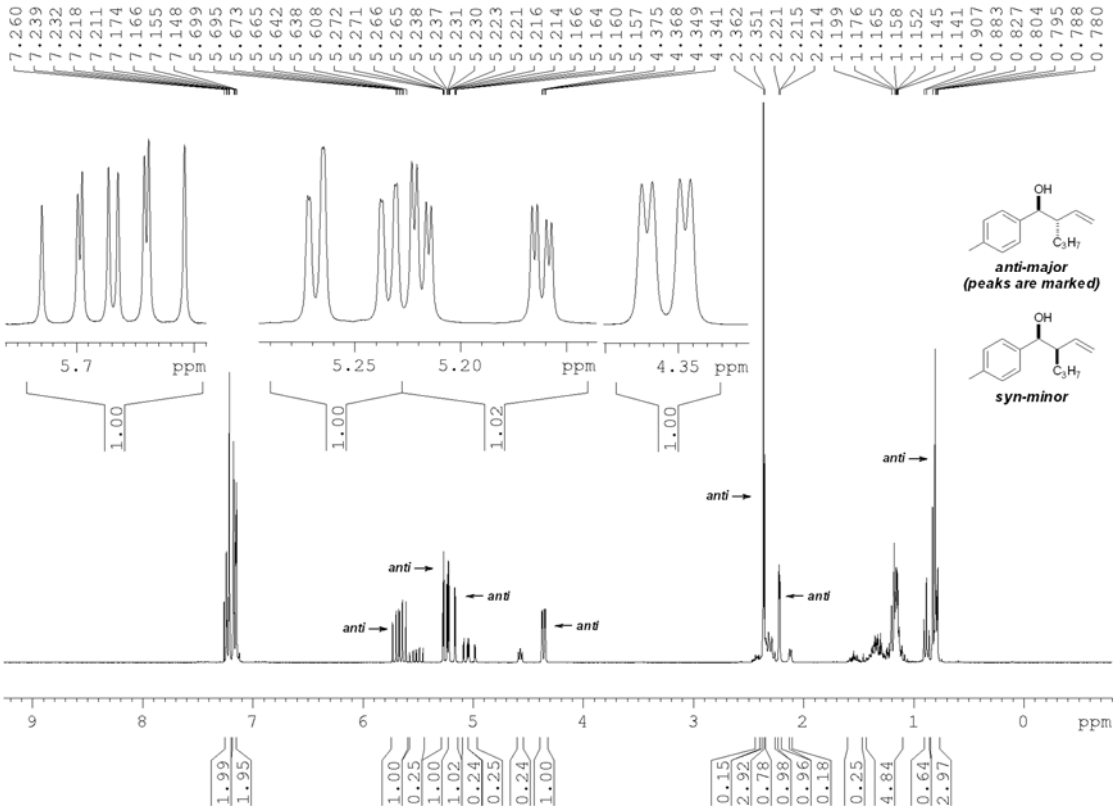


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

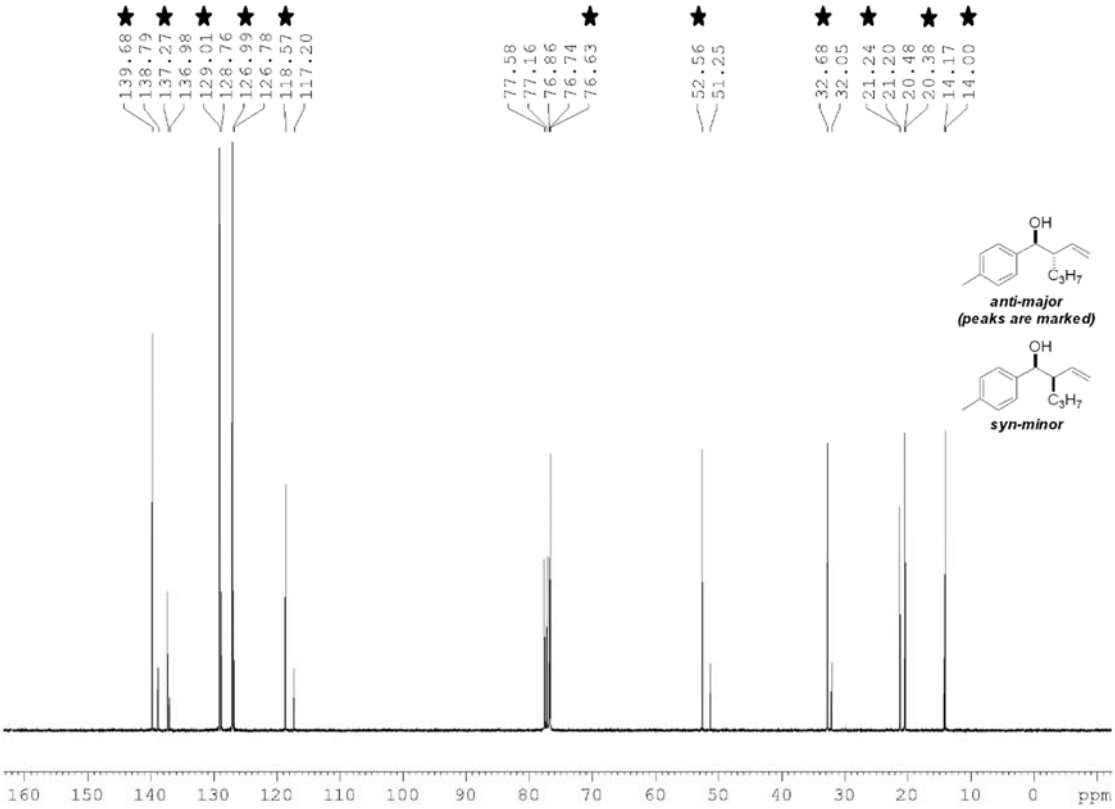


Compound (4-6)b

^{1}H NMR (300 MHz, $CDCl_3$)

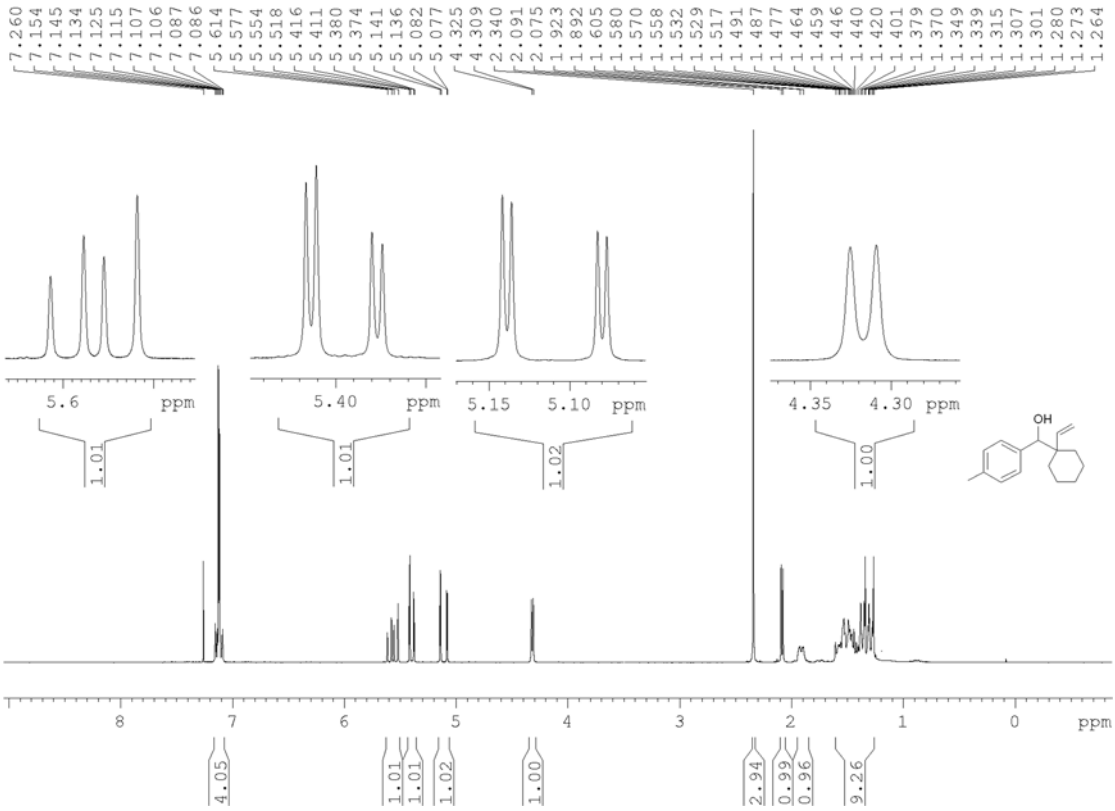


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

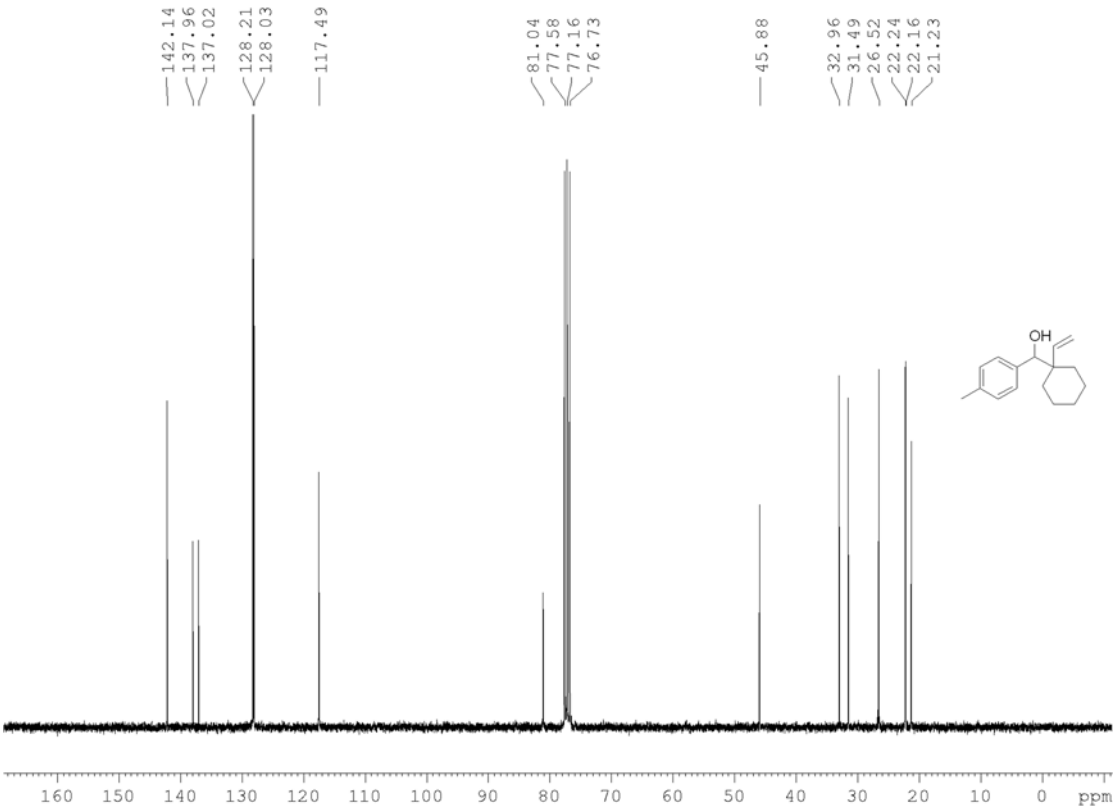


Compound (4-6)d

^{1}H NMR (300 MHz, $CDCl_3$)

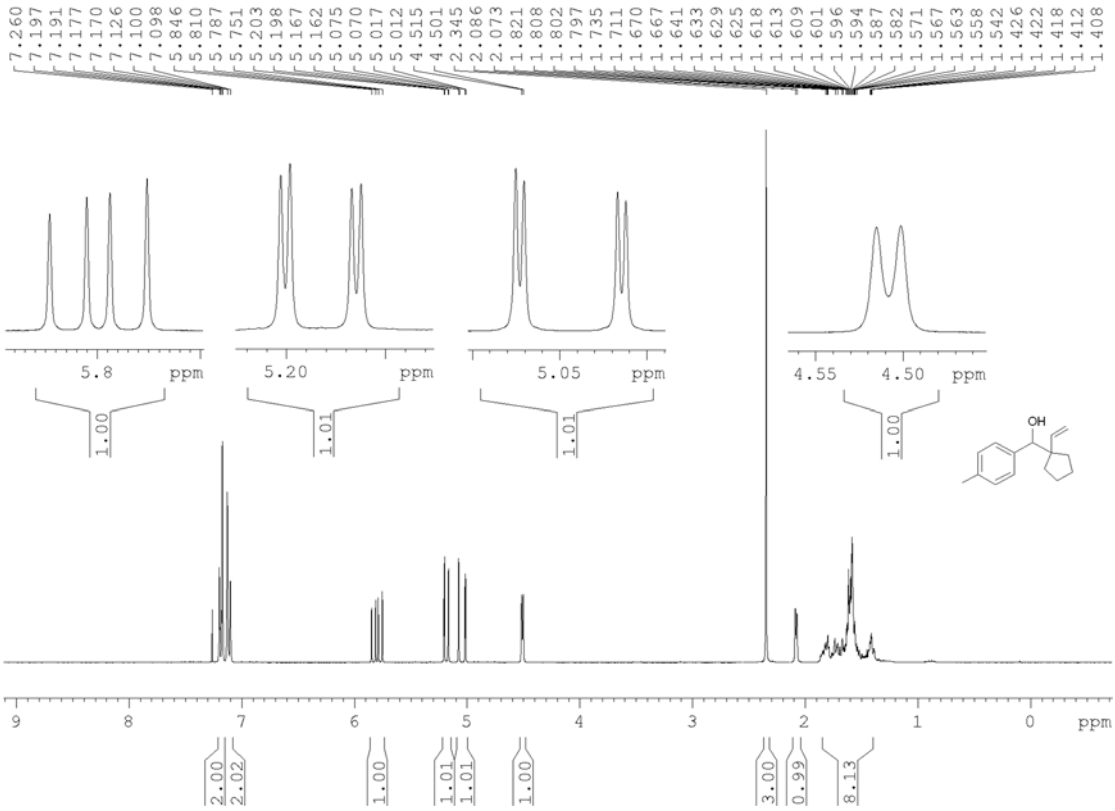


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

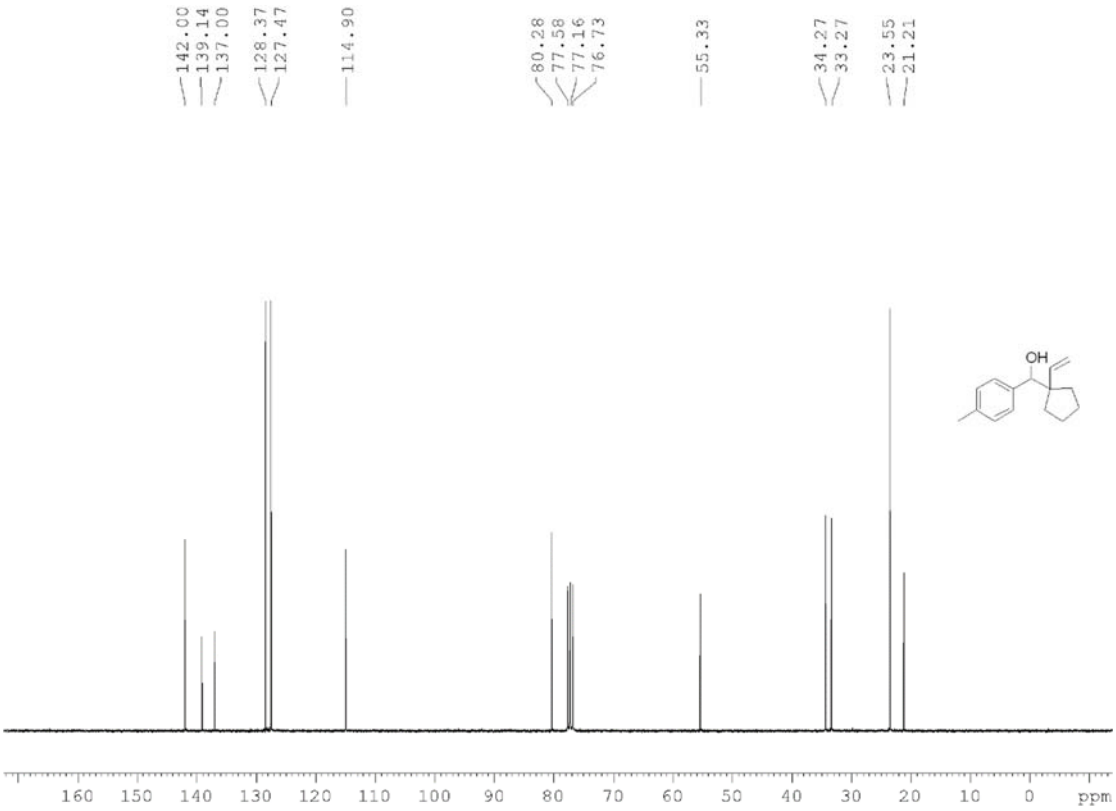


Compound (4-6)e

^{1}H NMR (300 MHz, $CDCl_3$)

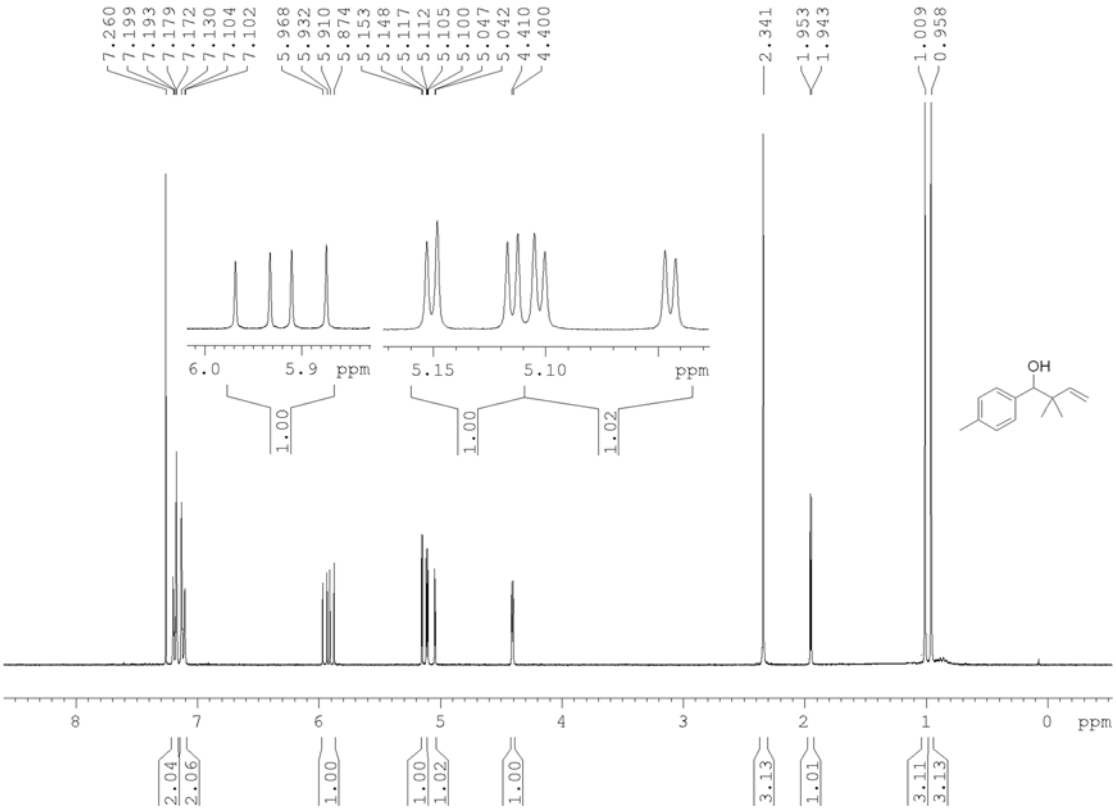


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

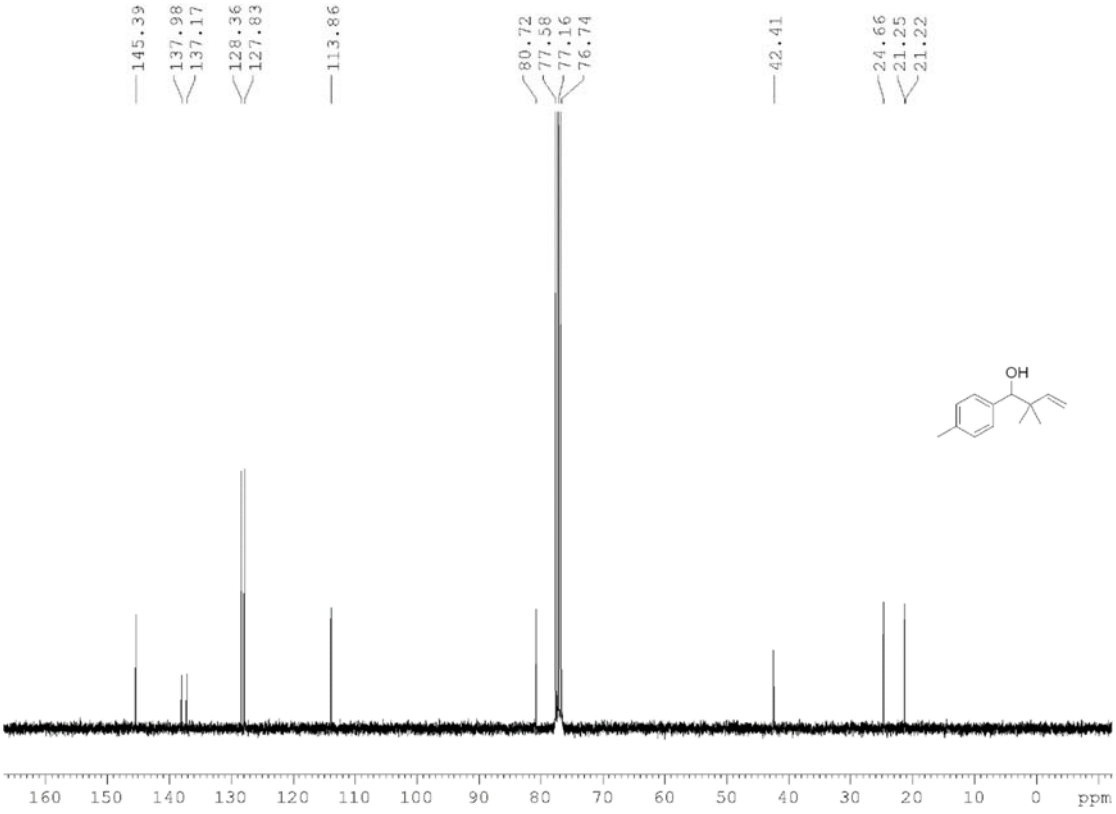


Compound (4-6)g

^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



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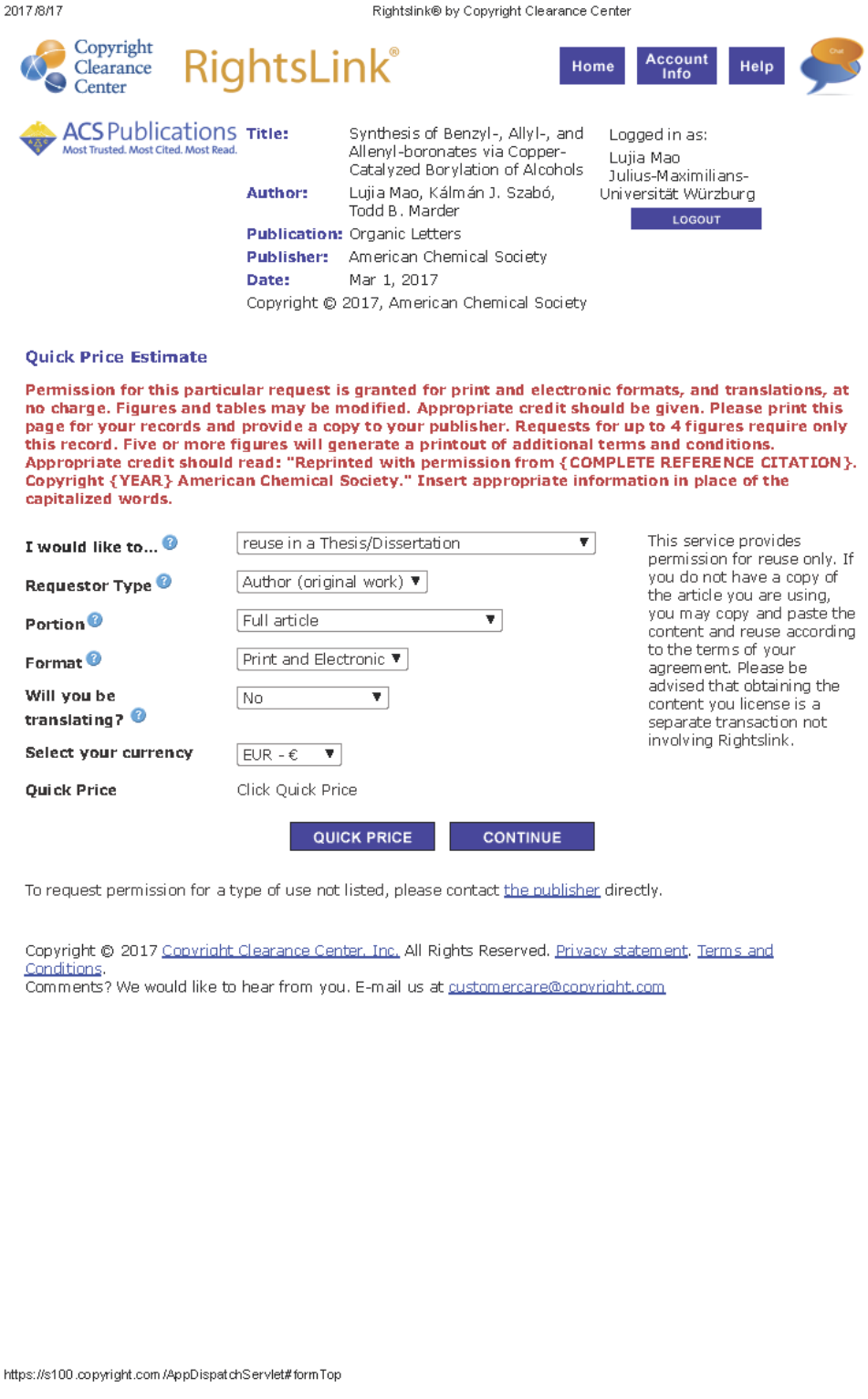

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