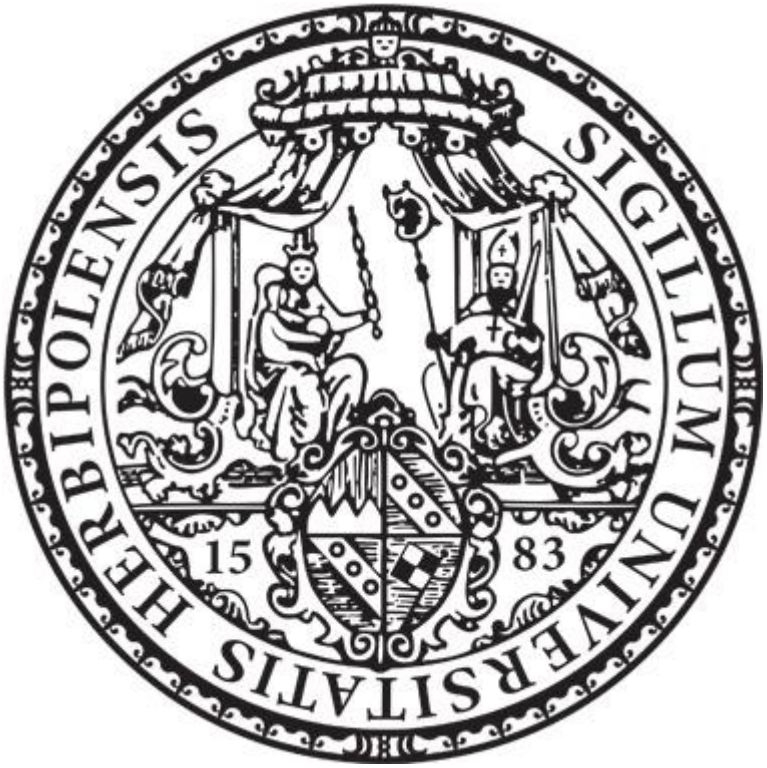
Catalytic Triboration and Diboration of Terminal Alkynes



Dissertation zur Erlangung des naturwissenschaftlichen Doktorgrades

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Xiaocui Liu

aus Chongqing, V.R. China

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1. Gutachter: Prof. Dr. Dr. h. c. Todd B. Marder

2. Gutachter: Prof. Dr. rer. nat. habil. Udo Radius

Prüfer des öffentlichen Promotionskolloquiums

1. Prüfer: Prof. Dr. Dr. h. c. Todd B. Marder

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Doktorurkunde ausgehändigt am

_____

谨此献给我的家人

Für meine Familie

The only limit to our realization of tomorrow will be our doubts of today.

Franklin D. Roosevelt

Die Experimente zur vorliegenden Arbeit wurden in der Zeit von Oktober 2015 bis Dezember 2019 am Institut für Anorganische Chemie der Julius-Maximilians-Universität Würzburg unter der Aufsicht von Prof. Dr. Dr. h. c. Todd B. Marder durchgeführt.

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appreciation to them for what they did for me. Thanks to my brother (Junwei Liu) and sister-in-law (Zhangmei Cao) for always encouraging me and having an open ear. Thanks to my little nephew (Chenchen) and niece (Yanyan) for giving me a lot of happy time. I want to thank my parents-in-law for their care and support they gave through the years I have been abroad. I want to thank my husband (Wenbo Ming) for his support and discussion in science and life. He is always there when I need him. Finally, I just want to say to the members of my family: “I love you!”

Thanks

List of Publications

The publications listed below are partly reproduced in this dissertation with permission from Wiley-VCH. The table itemizes at which position in this work the papers have been reproduced.

Publication	**Position**
X. Liu, W. Ming, A. Friedrich, F. Kerner, T. B. Marder*, *Angew. Chem. Int. Ed.*, **2019**, doi 10.1002/anie.201908466.	Chapter 2
X. Liu, W. Ming, Y. Zhang, A. Friedrich, T. B. Marder*, *Angew. Chem. Int. Ed.,* **2019**, doi 10.1002/anie.201909376.	Chapter 3

List of Abbreviations

acac	Acetylacetonate
9-BBN	9-Borabicyclo[3.3.1]nonane
dba	Dibenzylideneacetone
CAACs	Cyclic alkyl amino carbenes
cod	1,5-Cyclooctadiene
CPME	Cyclopentyl methyl ether
CuTC	Copper(I) thiophene-2-carboxylate
DABCO	1,4-Diazabicyclo[2.2.2]octane
DCM	Dichloromethane
DFT	Density functional theory
DIBALH	Diisobutylaluminumhydride
DIPEA	*N*,*N*-Diisopropylethylamine
DMAP	4-Dimethylaminopyridine
DMF	*N*,*N*-Dimethylformamide
DMSO	Dimethyl sulfoxide
DPEphos	Bis[(2-diphenylphosphino)phenyl] ether
DPPB	1,4-Bis(diphenylphosphino)butane
dppe	1,2-Bis(diphenylphosphino)ethane
DPPM	Bis(diphenylphosphino)methane
Dppp	1,3-Bis(diphenylphosphino)propane
DTBP	Di-*tert*-butyl peroxide
$Fe(OTf)_2$	Iron(II) trifluoromethanesulfonate
GC-MS	Gas chromatography-mass spectrometry
HBcat	Catecholborane
HBdan	1,8-Naphthalenediaminatoborane
HBpin	4,4,5,5-Tetramethyl-1,3,2-dioxaborolane
$HBSia_2$	9-Borabicyclo[3.3.1]nonane
IPr·HCl	1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride
LDA	Lithium diisopropylamide
MMP-2	Matrix Metalloproteinase-2
MIDA	Trivalent *N*-methyliminodiacetic acid

MTBE	Methyl *tert*-butyl ether
NBS	N-Bromosuccinimide
NCS	N-Chlorosuccinimide
NHC	*N*-Heterocyclic carbene
NMR	Nuclear magnetic resonance
PCy_3	Tricyclohexylphosphine
Phen	1,10-Phenanthroline
Piv	Pivaloy
TFP	Tri(2-furyl)phosphine
THF	Tetrahydrofuran

Table of Contents

Chapter One

Introduction

1 Introduction

1.1 Boration of alkynes

Alkynes are ideal starting materials in organic synthesis due to the fact that they are inexpensive and readily available from commercial suppliers. Uncatalyzed and catalyzed hydroboration, diboration and dehydrogenative borylation of alkynes have made organoboron compounds readily available. In the synthesis of multiborylated compounds, multiple carbon-boron bonds were formed via a sequence of hydroboration, diboration or dehydrogenative borylation of alkynes. The past few decades have seen remarkable progress in the boration of alkynes.[1] Note that the heterogeneous catalyzed boration of alkynes[2] is not widely discussed here.

1.1.1 Hydroboration of alkynes

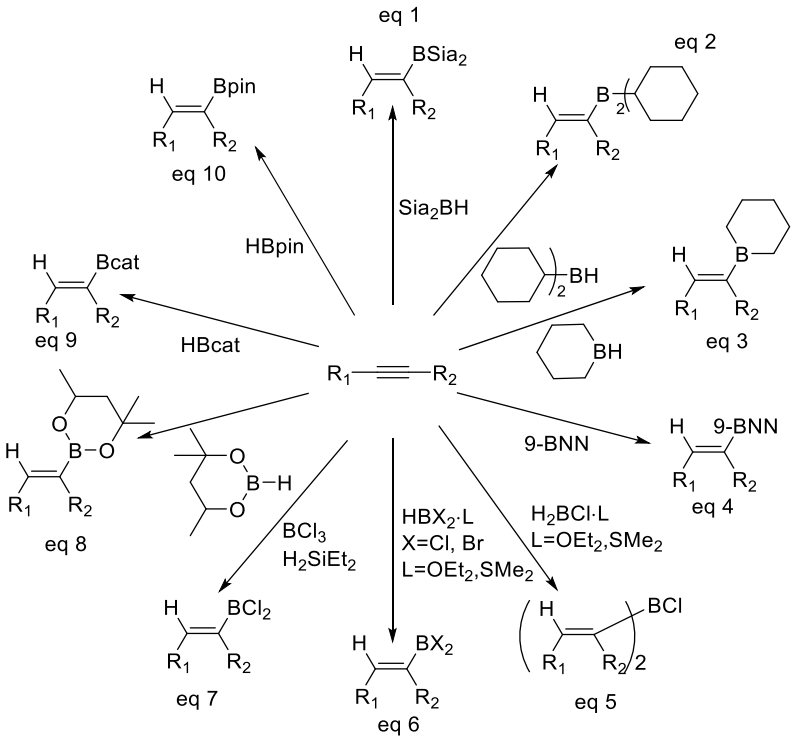
1.1.1.1 Transition metal-free hydroboration of alkynes

The hydroboration of alkynes provides a convenient route to alkenyl boron compounds via addition of B-H moiety to the C≡C bonds.

Zweifel and coworkers reported the first hydroboration of alkynes using a mixture of $NaBH_4$ and $BF_3{\cdot}Et_2O$.[3] The reaction of internal alkynes with one third of an equivalent of borane afforded the corresponding trivinylboranes. However, under the same conditions, terminal alkynes underwent dihydroboration predominantly.[4] The use of hydroborating agents with large steric requirements, $HBSia_2$ (disiamylborane) and dicyclohexylborane, resulted in a simple monohydroboration of both terminal and internal alkynes (Scheme 1-1, eq 1 and eq 2).[5]

Later on, the Brown group disclosed that internal alkynes were readily converted into the monohydroboration derivatives in high yields. This reaction was proceeded at 0 °C in THF with 1 equivalent of 9-BBN. Interestingly, *gem*-diborylalkane derivatives were obtained in high yields when terminal alkynes were used, while, using an excess of terminal alkynes gave monohydroboration derivatives in good

yields. Consequently, this method can be readily controlled to give either mono- or dihydroboration products (Scheme 1-1, eq 4).[6]



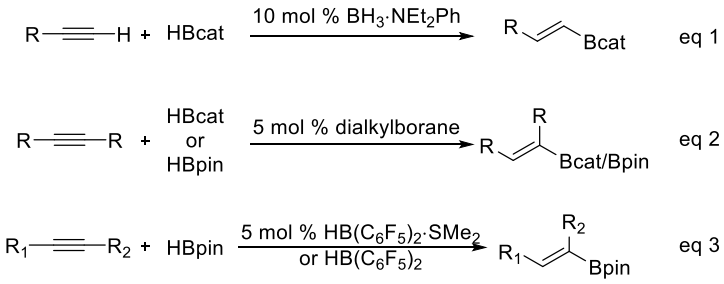
Scheme 1-1. Catalyst-free hydroboration of alkynes with boron reagents.

Alkenylhaloboranes were synthesized through a direct hydroboration of alkynes with monohaloborane complexes (Scheme 1-1, eq 5),[7] dihaloborane complexes (Scheme 1-1, eq 6)[8] and boron trichloride (Scheme 1-1, eq 7).[9]

However, when the boron is attached to heteroatoms (O and N) that lower the electron deficiency at boron, the uncatalyzed hydroboration required an elevated temperature.[10] A stable dialkoxyborane, 4,4,6-trimethyl-1,3,2-dioxaborinane, was prepared by Woods and coworkers using 2-chloro-4,4,6-trimethyl-1,3,2-dioxaborinane and sodium borohydride. Hydroboration of alkynes with this stable dialkoxyborane at 100 °C proceeded to give *cis* addition products confirmed directly by NMR spectra (Scheme 1-1, eq 8).[11]

Brown further extended this research to the hydroboration of alkynes using HBcat as a new hydroborating agent.[12] This novel protocol provided a facile, clean and highly convenient synthesis of alkenylboronates (Scheme 1-1, eq 9). The high temperature employed when dialkoxyboranes are used likely leads to disproportionation quickly BH_3 which can act as a catalyst.

These methods mentioned above using dialkoxy boranes, though useful, required harsh reaction conditions (high temperature), and dialkylalkenylboranes and alkenylcatecholboranes were sensitive to moisture, air and chromatography. Knochel *et al.* developed a new hydroborating reagent, HBpin (pinacolborane), using $BH_3 \cdot SMe_2$ and pinacol.[13] The hydroboration of alkynes with an excess of HBpin was carried out with excellent regio- and stereoselectivities (Scheme 1-1, eq 10). Most of the alkenyl pinacolboronates can be purified by silica gel column chromatography. Here again, using pure HBpin does not seem to work. Knochel likely had some unreacted $BH_3 \cdot SMe_2$ in his mixture.

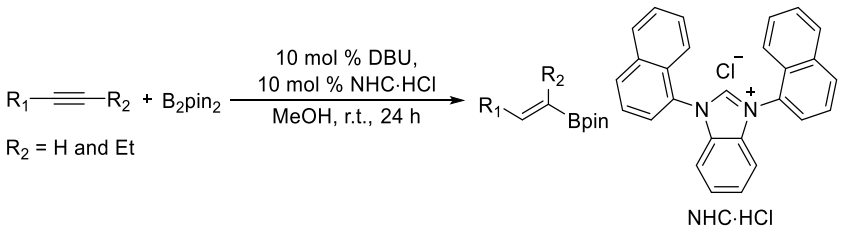


Scheme 1-2. Hydroboration of alkynes catalyzed by boranes.

The hydroboration of alkynes with HBcat without catalysts required harsh conditions due to the low reactivity of HBcat.[12] Using $BH_3 \cdot NEt_2Ph$ as catalyst, Periasamy and coworkers achieved the hydroboration with HBcat under mild reaction conditions (Scheme 1-2, eq 1).[14]

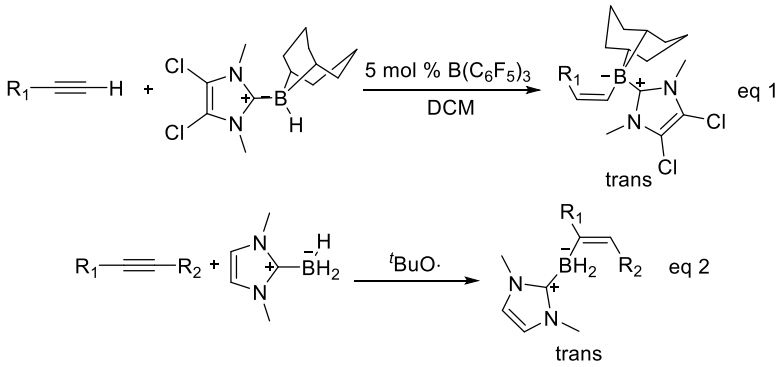
Then, Arase *et al.* and Hoshi *et al.* reported that dialkylboranes catalyzed hydroboration of alkynes with HBcat or HBpin under mild reaction conditions.[15] Hoshi proposed a mechanism in which borane-catalyzed hydroboration of alkynes proceeded via transferring an alkenyl group from one boron to another boron (Scheme 1-2, eq 2).[15b]

Hoshi further demonstrated that hydroboration of terminal alkynes with HBpin can be promoted by 5 mol % $HB(C_6F_5)_2 \cdot SMe_2$. This catalyst was also capable of transferring an alkenyl group from boron to boron.[16] Stephan later reported that direct use of 5 mol % $HB(C_6F_5)_2$ led to a quantitative hydroboration of alkynes with HBpin at room temperature (Scheme 1-2, eq 3).[17]



Scheme 1-3. Hydroboration of alkynes catalyzed by NHC.

N-Heterocyclic carbenes (NHCs) exhibit a wide range of reactivity in many typical organic transformations due to their electron richness.[18] The activation of diboron compounds for direct hydroboration of alkenes and alkynes by NHCs has been extensively studied in recent years.[19] Sun and coworkers developed an NHC-catalyzed hydroboration of alkynes with B_2pin_2 in a protic solvent (MeOH) which served as proton source (Scheme 1-3).[20]

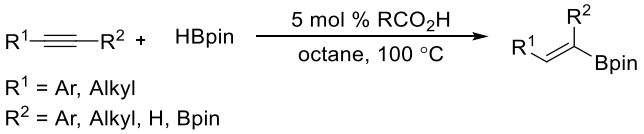


Scheme 1-4. Hydroboration of alkynes with NHC-boron reagents.

In 2016, Ingleson developed a *trans*-hydroboration of terminal alkynes with a catalytic amount of $B(C_6F_5)_3$. A boreniumion, generated from $B(C_6F_5)_3$ and an NHC-borane complex (borane = 9-BBN(H)), was proposed to be an important intermediate in this reaction (Scheme 1-4, eq 1).[21]

Recently, a radical *trans*-hydroboration of alkynes with NHC boranes was disclosed by Curran and Taniguchi. The NHC-boryl radical was formed by heating NHC boranes with DTBP (di-*tert*-butyl peroxide) (Scheme 1-4, eq 2).[22]

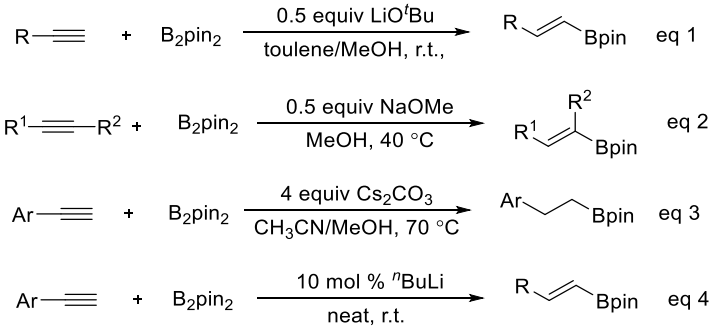
Jin and coworkers demonstrated a carboxylic acid-catalyzed direct *cis*-hydroboration of alkynes with HBpin at 100 °C. A series of alkenylboronates were obtained in excellent yields (Scheme 1-5). In addition, various alkynylboronates underwent a hydroboration under the same reaction conditions to afford synthetically important 1,1-diborylalkenes.[23]



Scheme 1-5. Carboxylic acid-catalyzed hydroboration of alkynes.

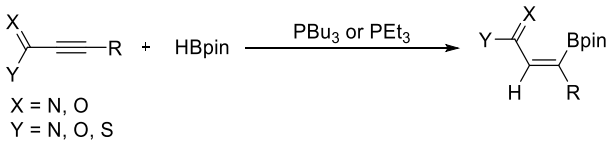
B_2pin_2 is a bifunctional Lewis acid, which interacts with Lewis bases to afford Lewis acid-base adducts without or with B-B cleavage.[24] ^{t}BuOM or MeOM (M = Na, K, Li) react with B_2pin_2 forming the Lewis acid-base adduct $[B_2pin_2OMe]^-$.[24-25] Deng and coworkers presented a transition metal-free hydroboration of terminal alkynes activated by ^{t}BuOLi (Scheme 1-6, eq 1).[26] Alternatively, Wen's research group found that transition metal-free hydroboration can also occur with alkynes using MeONa instead of ^{t}BuOLi (Scheme 1-6, eq 2).[27]

Furthermore, the synthesis of alkylboronates from terminal alkynes and B_2pin_2 through tandem boration and protodeboronation under basic conditions was reported by the Song group (Scheme 1-6, eq 3).[28] Recently, Bao and Xue discovered that ^{n}BuLi could be used as an efficient catalyst for the hydroboration of terminal alkynes with HBpin (Scheme 1-6, eq 4).[29]



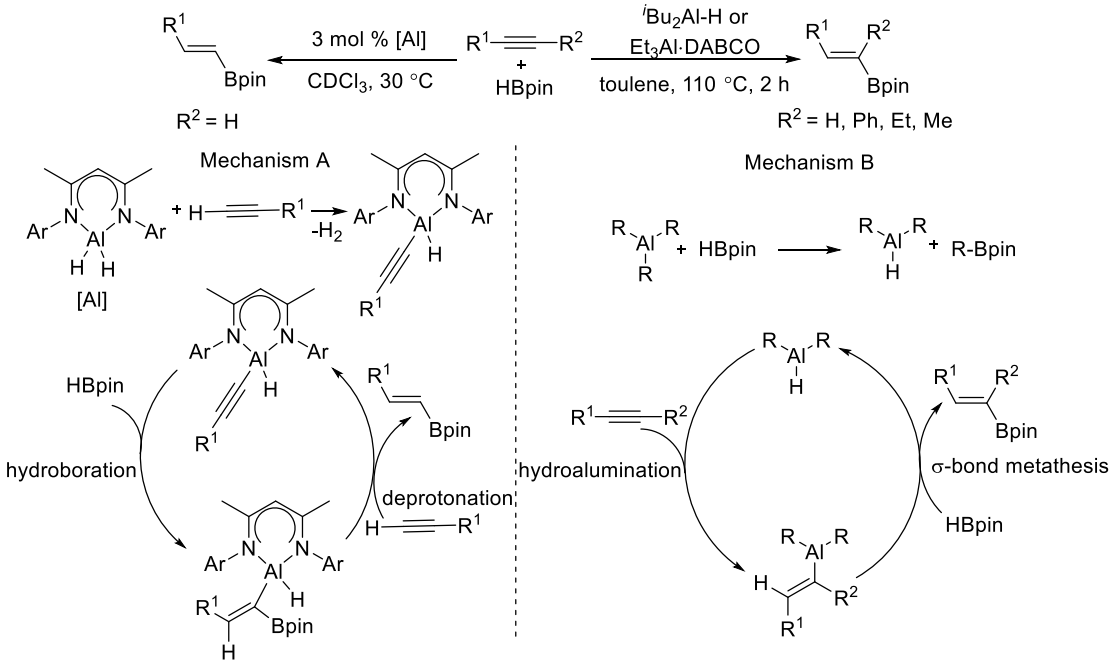
Scheme 1-6. Base-promoted hydroboration of alkynes.

Hydroboration of alkynes typically afforded alkenylboronates in a *cis* fashion, and *trans*-hydroboration of alkynes is scarce. In 2018, a regioselective *trans*-hydroboration of internal alkynes catalyzed by trialkylphosphine organocatalysts was reported by Sawamura,[30] Santos[31] and Vilotijevic[32], respectively. Interestingly, the presence of ester and amide directing groups effectively led to the *trans*-hydroboration of alkynes (Scheme 1-7).



Scheme 1-7. Trialkylphosphine catalyzed *trans*-hydroboration of alkynes.

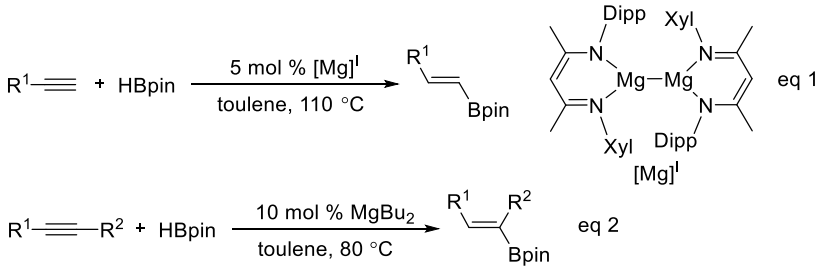
In 2016, Yang *et al.*[33] and Thomas *et al.*[34] independently developed an Al-catalyzed hydroboration of alkynes using $LAlH_2$ (L = $HC(CMeNAr)_2$, Ar = 2,6-$Et_2C_6H_3$) or R_2AlH. Yang proposed a mechanism involving a deprotonation of alkynes via *σ*-bond metathesis with Al-H. The formation of the aluminum acetylide was the overall rate-determining step based on a computational study (Scheme 1-8, left), while Thomas proposed an alternative mechanism (Scheme 1-8, right). The formation of aluminum hydride was followed by a hydroalumination of alkynes, and then the vinylaluminum intermediate underwent a *σ*-bond metathesis with HBpin to generate the products.



Scheme 1-8. Al-catalyzed hydroboration of alkynes.

Recently, Ma and coworkers successfully synthesized an unsymmetrical *β*-diketimine coordinated magnesium(I) complex which was a highly active pre-catalyst for the hydroboration of terminal alkynes (Scheme 1-9, eq 1).[35] However, this method had a problem of regioselectivity for unsymmetrical alkynes. Rueping *et al.* disclosed that Mg^nBu_2 can catalyze the hydroboration of unsymmetrical internal alkynes leading to *α*-vinyl boranes with high regioselectivities (Scheme 1-

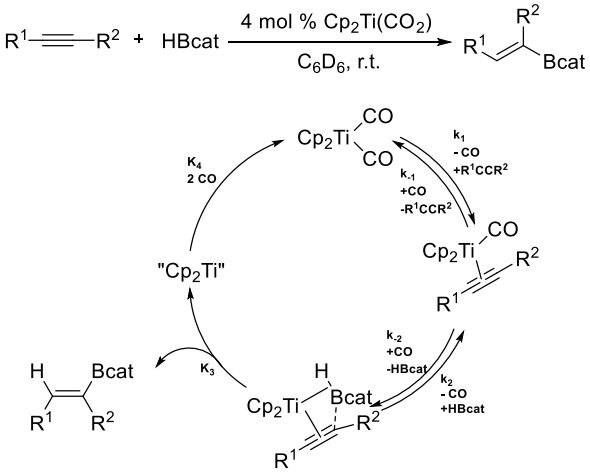
9, eq 2).[36]



Scheme 1-9. Mg-catalyzed hydroboration of alkynes.

1.1.1.2 Ti-catalyzed hydroboration of alkynes

The Hartwig group have studied the synthesis, structure and preliminary reaction chemistry of new titanocene *σ*-complexes with unusual *σ*-borane coordination of neutral HBcat.[37] In 1996, they reported the $Cp_2Ti(CO_2)$-catalyzed hydroboration of alkynes carried out in the presence of HBcat and 4 mol % $Cp_2Ti(CO_2)$ (Scheme 1-10).[38]

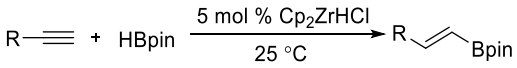


Scheme 1-10. Ti-catalyzed hydroboration of alkynes.

After a series of mechanistic studies, including kinetic studies, low temperature spectroscopic studies and stoichiometric studies, they identified the most possible catalytic cycle for this hydroboration reaction, which is shown in Scheme 1-10.[39]

1.1.1.3 Zr-catalyzed hydroboration of alkynes

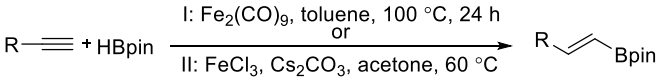
In 1995, Srebnik found that the Schwartz reagent (Cp_2ZrHCl) catalyzed the hydroboration of alkynes with HBpin giving *trans*-vinylboronic esters in excellent yields and with high regioselectivities (Scheme 1-11).[40]



Scheme 1-11. Zr-catalyzed hydroboration of alkynes.

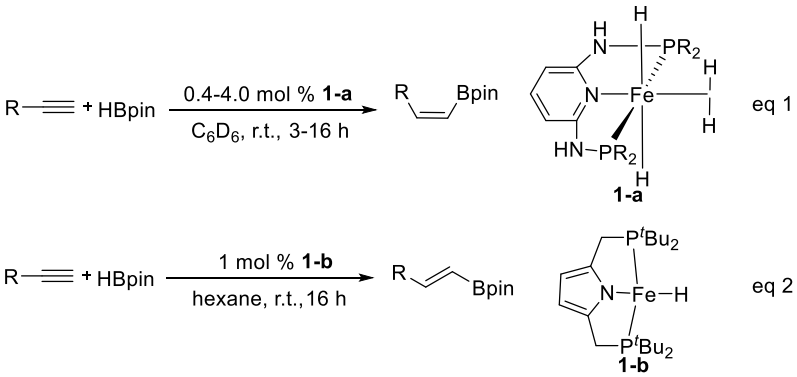
1.1.1.4 Fe-catalyzed hydroboration of alkynes

As iron salts are readily available, cheap, and environment friendly, the highly selective hydroboration of terminal alkynes catalyzed by an iron catalyst was established under conditions I or II (Scheme 1-12) by Enthaler[41] and Sreedhar.[42] Although unsymmetrical internal alkynes were feasible under condition I, poor selectivities for hydroboration were achieved (Scheme 1-12).



Scheme 1-12. Fe-catalyzed hydroboration of alkynes.

In 2017, Kirchner and coworkers synthesized a nonclassical iron(II) polyhydride pincer complex **1-a**, which was a highly active catalyst for hydroboration of terminal alkynes to give *cis*-vinylboronates (Scheme 1-13, eq 1).[43] It is noteworthy that the *cis*-selectivity could be switched by using a pyrrolide-based PNP pincer complex **1-b** to obtain the *trans*-isomers in high yields (Scheme 1-13, eq 2).[44]

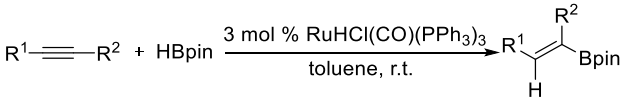


Scheme 1-13. Ligand controlled *cis*/*trans*-selective hydroboration of alkynes.

1.1.1.5 Ru-catalyzed hydroboration of alkynes

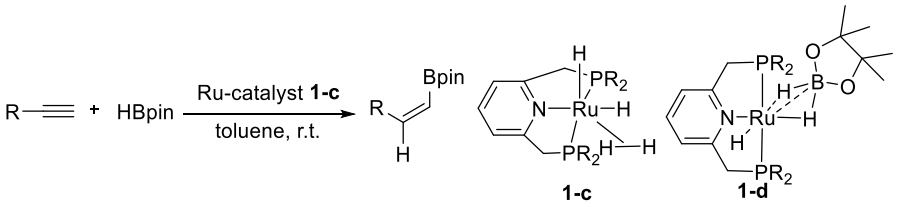
In 2002, a novel catalytic system for the hydroboration of alkynes using a ruthenium catalyst was developed by Murata and Masuda.[45] This reaction was conducted in the presence of 3 mol % $RuHCl(CO)(PPh_3)_3$ providing alkenylboronates in high

yields (Scheme 1-14). The possible mechanism included insertion of C≡C into the Ru-H bond to obtain a vinylruthenium intermediate, and *σ*-bond metathesis between HBpin and Ru-C.[46]



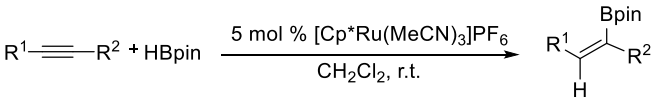
Scheme 1-14. Ru-catalyzed *cis*-hydroboration of alkynes.

In 2012, the Leitner group reported the synthesis of *cis*-vinylboronates via a regio-, chemo- and stereoselective boration of terminal alkynes catalyzed by [$RuH_2(H_2)$(PNP)] **1-c** (Scheme 1-15). They identified that complex **1-d**, obtained from a pentane solution of HBpin and catalyst **1-c** in 96% yield, played an important role in the *cis*-selectivity.[47]

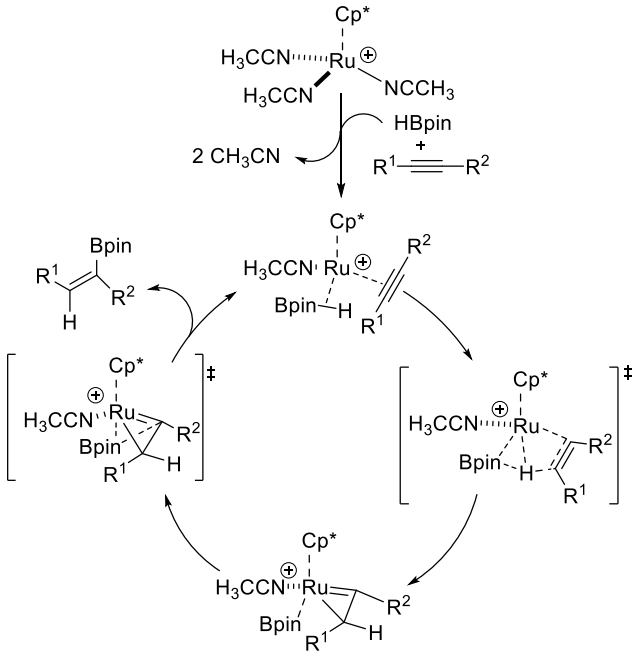


Scheme 1-15. Ru-catalyzed *trans*-hydroboration of terminal alkynes.

Leitner's method only worked with terminal alkynes,[47] and *trans*-hydroboration of internal alkynes remained basically unknown. In 2013, Fürstner successfully achieved the first general *trans*-selective hydroboration of internal alkynes using 5 mol % of [Cp*Ru(MeCN)$_3$]PF_6 instead of [$RuH_2(H_2)$(PNP)] (Scheme 1-16).[48] The corresponding *trans*-alkenylboronates were prepared in excellent yields (up to 95%) and high *trans*/*cis* selectivities (up to 98:2). Through Fürstner's combined experimental mechanistic studies[48] and Wu's DFT calculations,[49] the mechanism of cationic Ru(II)-catalyzed hydroboration of internal alkynes was proposed as outlined in Scheme 1-17.



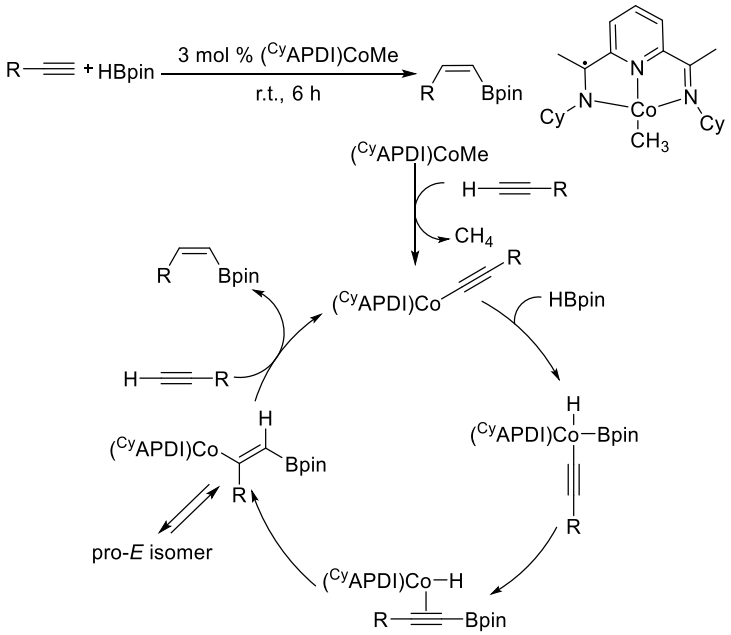
Scheme 1-16. Ru-catalyzed *trans*-hydroboration of internal alkynes.



Scheme 1-17. Mechanism of Ru-catalyzed *trans*-hydroboration of internal alkynes.

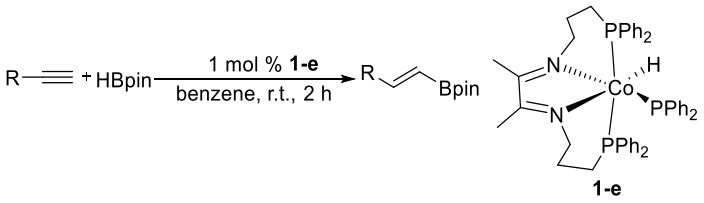
1.1.1.6 Co-catalyzed hydroboration of alkynes

In 2015, Chirik and coworkers demonstrated a bis(imino)pyridine cobalt-catalyzed hydroboration of terminal alkynes with high yields and excellent selectivities. Detailed mechanistic studies indicated that the possible mechanism involved a selective insertion of alkynylboronates into a Co-H bond (Scheme 1-18).[50]



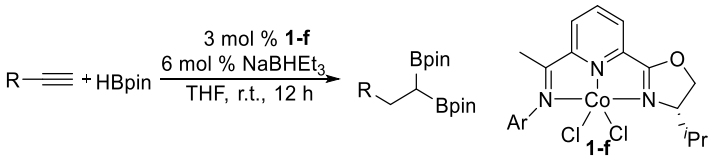
Scheme 1-18. Co-catalyzed *trans*-hydroboration of alkynes.

Later, Trovitch synthesized an *α*-diimine cobalt hydride complex. This complex promoted the hydroboration of terminal alkynes to afford *trans*-alkenylboronates in high yield (Scheme 1-19).[51] Petit and coworkers subsequently reported a low-valent Co(I)-catalyzed ($HCo(Pme_3)_4$) hydroboration of internal alkynes.[52]

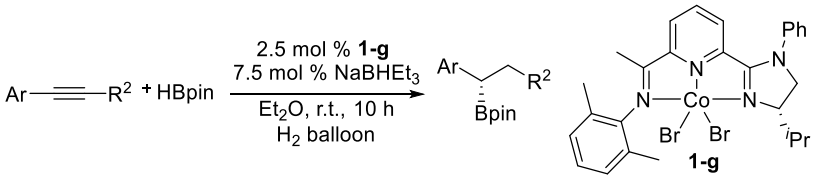


Scheme 1-19. Co-catalyzed *cis*-hydroboration of alkynes.

In 2016, the Huang group developed an attractive protocol to furnish 1,1-diboronates via a Co-catalyzed sequential hydroboration of terminal alkynes with HBpin (Scheme 1-20).[53] In 2017, Lu and coworkers introduced a new type of chiral imidazoline iminopyridine ligand, which could efficiently promote asymmetric transformations of internal alkynes to give chiral secondary organoboronates (Scheme 1-21).[54]



Scheme 1-20. Co-catalyzed double hydroboration of alkynes.

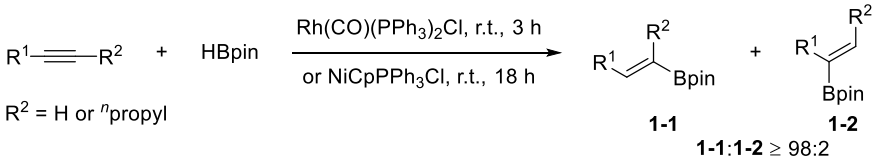


Scheme 1-21. Co-catalyzed asymmetric transformations of internal alkynes.

1.1.1.7 Rh-catalyzed hydroboration of alkynes

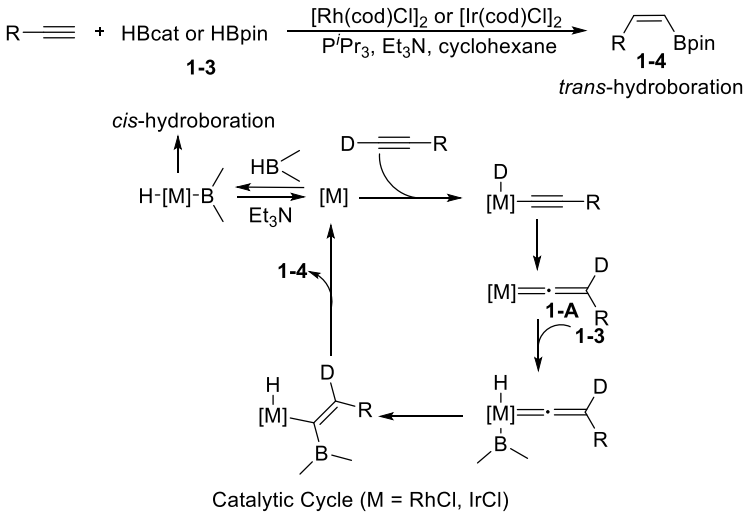
As mentioned above, hydroboration of alkynes and alkenes with less active HBcat required a high temperature in the absence of catalysts. The Nöth group found that the hydroboration could be conducted smoothly at room temperature in the presence of Wilkinson's catalyst ($[Rh(PPh_3)_3Cl]$). Application of this method to alkynes provided vinylboronic esters in a low yield of 52%.[55]

Remarkably, other catalysts such as $Rh(CO)(PPh_3)_2Cl$ and $NiCp(PPh_3)Cl$ influenced the ratio of regioisomers and gave pure *anti*-Markovnikov product **1-1** (Scheme 1-22). Fine tuning of ligands in the Rh-catalyzed hydroboration of alkynes improved the yields and regioselectivities. As a case in point, Gladysz and coworkers prepared pure vinylboronic esters in high yields (88%-90%) catalyzed by $Rh[P(CH_2CH_2R_{f6})_3]_3Cl$ (R_{f6} = $(CF_2)_5CF_3$), which represented the first recoverable hydroboration catalysts.[56] Later on, Bates improved this reaction using tri(2-furyl)phosphine as a ligand, giving better yields of pure products in shorter reaction time.[57]



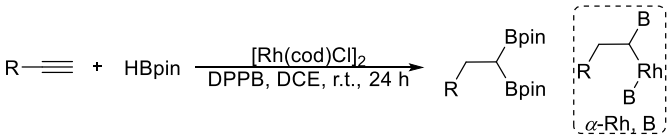
Scheme 1-22. Rh- or Ni-catalyzed hydroboration of alkynes.

In 2000, Miyaura and coworkers developed a formal *trans*-hydroboration of terminal alkynes with HBcat or HBpin.[58] The use of Et_3N was critical to achieve high *trans*-selectivities and yields. A possible mechanism, which might account for both the acetylenic hydrogen migration and the *trans*-addition of the B-H bond, is one proceeding through vinylidene complex **1-A** (Scheme 1-23).



Scheme 1-23. Rh- or Ir-catalyzed *trans*-hydroboration of alkynes.

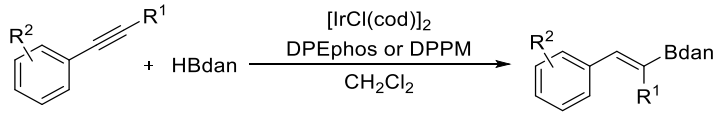
Shibata and Endo described a $[Rh(cod)Cl]_2$-catalyzed double hydroboration of terminal alkynes via the generation of *α*-Rh, B intermediate. *Gem*-diborylalkanes were synthesized in low yields in the presence of a Rh catalyst precursor and DPPB (1,4-bis(diphenylphosphino)butane) (12-68%) (Scheme 1-24).[59]



Scheme 1-24. Rh-catalyzed double hydroboration of alkynes.

1.1.1.8 Ir-catalyzed hydroboration of alkynes

In 2009, Suginome reported that masked alkenylboronates could be synthesized using HBdan in good yields (Scheme 1-25), and the products were further transformed into oligo(phenylenevinylene)s via an iterative Suzuki-Miyaura coupling.[60]

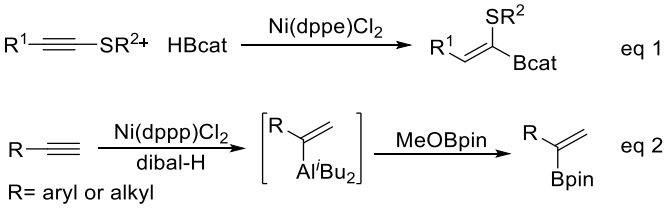


Scheme 1-25. Ir-catalyzed hydroboration of alkynes.

1.1.1.9 Ni-catalyzed hydroboration of alkynes

In 1993, Miyaura and Suzuki disclosed the first example of a Ni-catalyzed hydroboration of alkynes. Hydroboration of thioacetylenes with HBcat proceeded under mild conditions using $Ni(dppe)Cl_2$. *β*-(Alkylthio)alkenyl-1,3,2-benzodioxaboroles were obtained regio- and stereospecifically in excellent yields (Scheme 1-26, eq 1).[61]

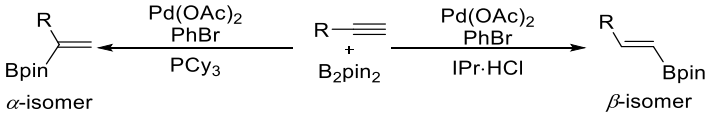
Later on, Hoveyda described a one-pot synthesis of *α*-vinyl boronates in the presence of DIBALH (diisobutylaluminumhydride) and 3 mol % of $Ni(dppp)Cl_2$. This approach furnished *α*-vinyl boronates directly with >98% *α*-selectivities and 68-94% yields via the intermediate vinylaluminums (Scheme 1-26, eq 2).[62]



Scheme 1-26. Ni-catalyzed hydroboration of alkynes.

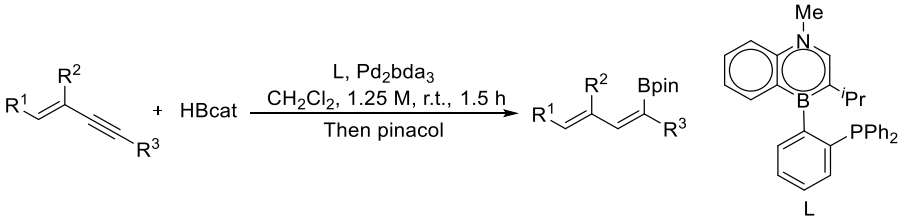
1.1.1.10 Pd-catalyzed hydroboration of alkynes

In 2016, Prabhu and coworkers presented the first Pd-catalyzed selective hydroboration of alkynes to give *α*- or *β*-vinylboronates (Scheme 1-27).[63] The use of $Pd(OAc)_2$, PCy_3, CF_3CH_2OH and PhBr in toluene afforded *α*-vinylboronates in good yields and high selectivities. Interestingly, this selectivity could be switched by using IPr·HCl to afford *β*-selectivity.



Scheme 1-27. Pd-catalyzed hydroboration of terminal alkynes.

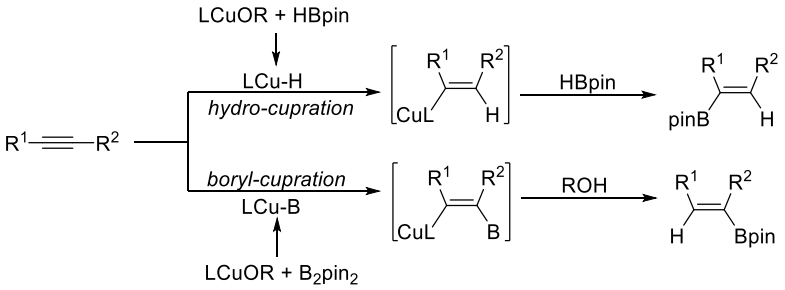
In the meantime, the Liu group designed a new phosphine ligand (Senphos) which uniquely resulted in the *trans*-selective Pd-catalyzed hydroboration of the triple bonds of 1,3-enynes. Dienylboronates were obtained with high stereoselectivities and regioselectivities under these reaction conditions (Scheme 1-28).[64]



Scheme 1-28. Pd-catalyzed hydroboration of 1,3-enynes.

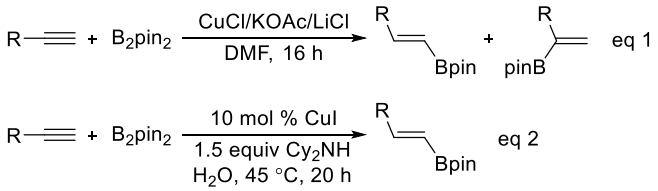
1.1.1.11 Cu-catalyzed hydroboration of alkynes

A Cu-catalyzed hydroboration of alkynes was developed as an efficient method to prepare vinylboronates. An alkenylcopper species, formed via regioselective addition of [LCuB] or [LCuH]) to alkynes, was proposed to be an important intermediate (Scheme 1-29).[65]



Scheme 1-29. General approaches of Cu-catalyzed hydroboration alkynes.

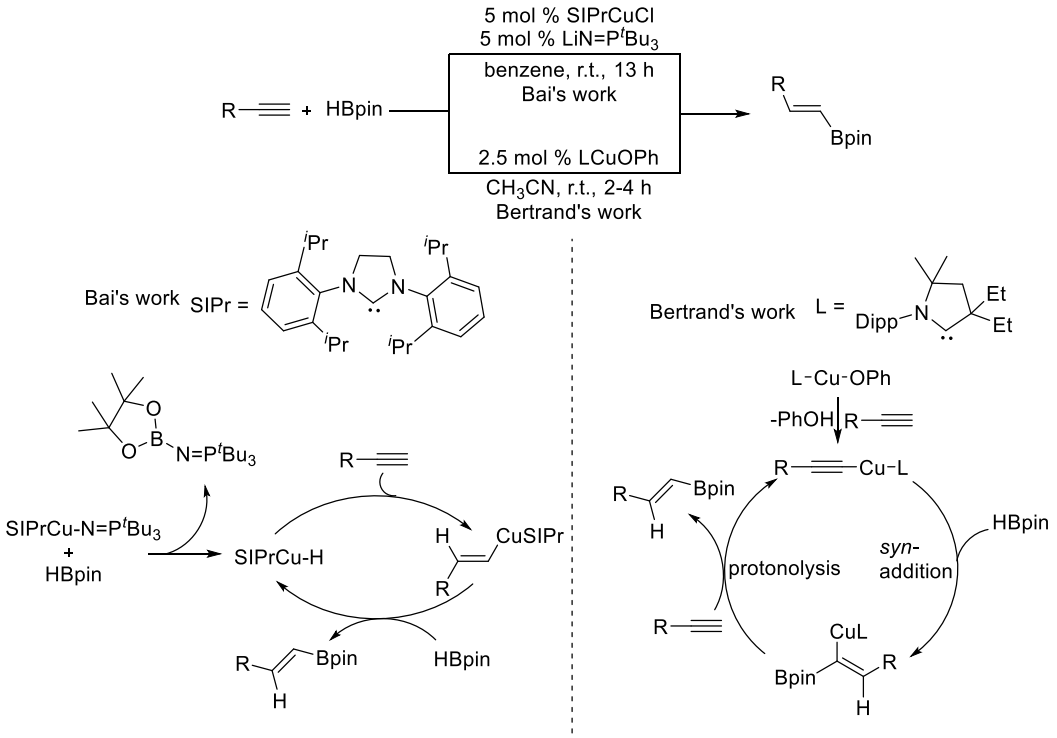
Miyaura and coworkers reported the addition of B_2pin_2 to terminal alkynes affording a mixture of 2-boryl-1-alkenes and 1-boryl-1-alkenes with a low regioselectivity (Scheme 1-30, eq 1).[66] In 2017, the Nishikata group demonstrated that hydroboration of terminal alkynes with B_2pin_2 in water could be catalyzed by CuI (Scheme 1-30, eq 2).[67]



Scheme 1-30. Cu-catalyzed hydroboration alkynes.

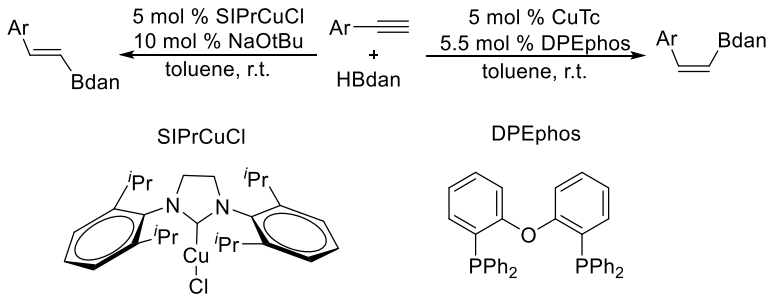
Note that the regioselectivity can be controlled by the steric and electronic effects of ligands on the copper catalysts. Bai and co-workers synthesized a novel NHC copper(I) phosphoranimide complex (NHCCuNP^{t}Bu), which was an excellent catalyst for the hydroboration of terminal alkynes using HBpin. This reaction was conducted under mild conditions furnishing the desired products in high yields (isolated yield up to 99%) and with excusive *β*-regio and *trans*-stereoselectivities.[68] A possible mechanism is shown in Scheme 1-31, left. The Cu-H intermediate, which was generated from the reaction of NHCCuNP^{t}Bu and HBpin, underwent a *syn*-addition with terminal alkynes giving an alkenylcopper species which reacted with HBpin to afford vinylboronates in a *β*-selective manner.

On the other hand, Bertrand and coworkers achieved a LCuOPh-catalyzed hydroboration of terminal alkynes with HBpin. The side reaction, dehydrogenative borylation of terminal alkynes, was successfully avoided.[69] Deuterium labeling experiments identified another catalytic pathway involving a *σ*-mono(copper)acetylide complex (Scheme 1-31, right).



Scheme 1-31. Cu-catalyzed hydroboration of alkynes with HBpin.

In 2016, Yun developed a ligand-controlled stereoselective hydroboration of terminal alkynes with HBdan.[70] In this procedure, when using a CuTc-DPEphos catalyst, *cis*-alkenylboronates were obtained in good yields and with excellent *cis*-selectivities. In contrast, the use of SIPrCuCl as catalyst furnished exclusively *trans*-alkenylboronates (Scheme 1-32).

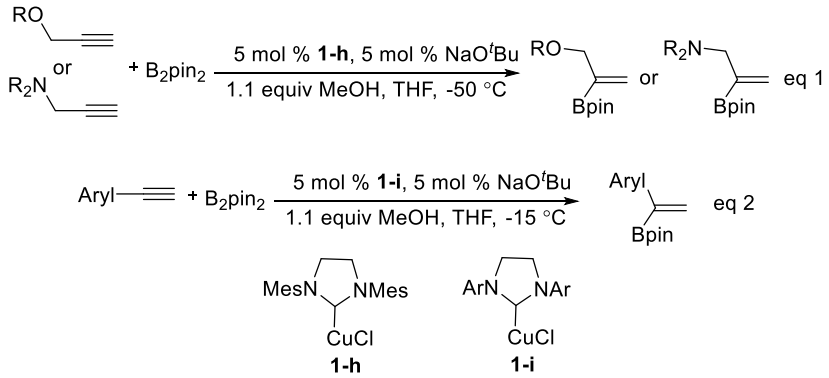


Scheme 1-32. Cu-catalyzed hydroboration alkynes with HBdan.

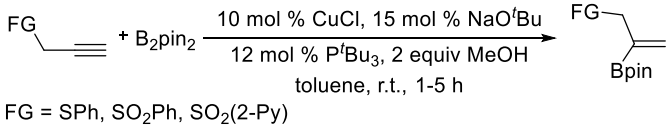
Accordingly, a number of methods have been developed to access terminal vinyl(pinacolato)boronates, while the synthesis of internal vinylboronates was significantly more limited. In 2011, Hoveyda presented a Cu-catalyzed method for the synthesis of internal or *α*-vinylboronates in up to 95% yields and with excellent site selectivities (up to > 98:2).[71] *α*-Borylated products were prepared with NHC-Cu complex **1-h** when using propargyl alcohols, amines and derivatives (Scheme

1-33, eq 1). In the case of aryl-substituted terminal alkynes, various types of *α*-vinylboronates were obtained directly in the presence of NHC-Cu complex **1-i** (Scheme 1-33, eq 2).

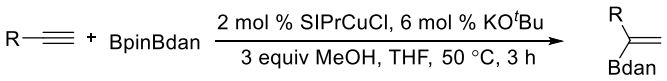
This protocol was further extended to *α*-selective hydroboration of terminal alkynes with S-functional groups (SPh, SO_2Ph and SO_2(2-Py)) by Arrayàs and Carretero (Scheme 1-34).[72] Later on, a highly *α*-selective hydroboration reaction was disclosed by Yoshida and Takaki (Scheme 1-35).[73] In addition, the stereoselective preparation of *α*-vinylboronates was carried out in an aqueous medium by Moro[74] and Yao.[75]



Scheme 1-33. NHC-Cu complex catalyzed hydroboration of alkynes.

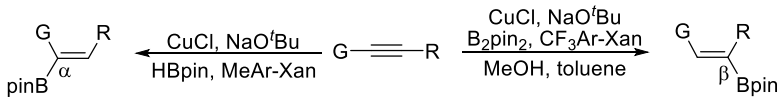


Scheme 1-34. Cu-P complex-catalyzed hydroboration of alkynes.



Scheme 1-35. Cu-catalyzed hydroboration of alkynes with BpinBdan.

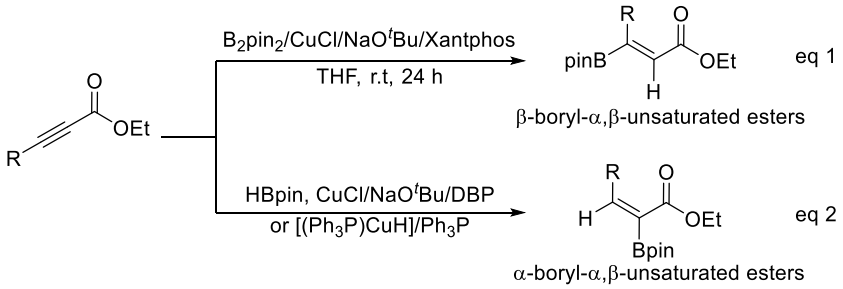
In 2011, Tsuji and coworkers reported a Cu-catalyzed highly regio- and stereoselective hydroboration of internal alkynes. The hydroboration was carried out to obtain *α* products using internal alkynes and HBpin in the presence of CuCl and MeAr-Xan. In contrast, the use of B_2pin_2/MeOH exclusively afforded *β*-selective hydroboration products (Scheme 1-36).[76] Additionally, other ligands, such as P(*p*-$C_6H_4OMe)_3$ and 1,3-dimethylimidazoline-2-thiones (IMS), were highly effective for the synthesis of *β* products.[77]



Scheme 1-36. Regio- and stereoselective hydroboration of alkynes controlled by ligands.

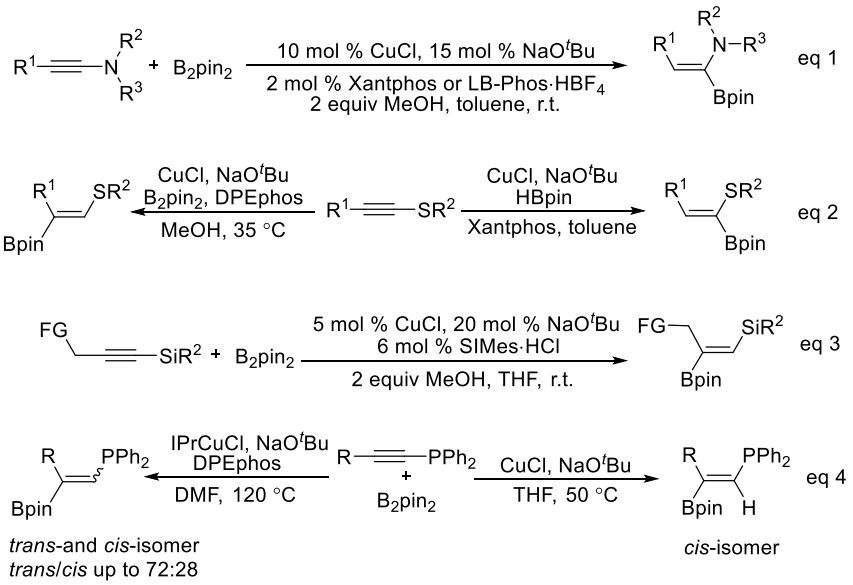
Given that general approaches for the preparation of electron-deficient alkenylboronates were not discovered before, in 2008, the Yun group developed a stereoselective hydroboration of *α,β*-acetylenic esters catalyzed by a copper-phosphine catalyst. The addition of B_2pin_2 to alkynoates provided *β*-borylated-*α,β*-ethylenic esters in excellent yields and stereoselectivities (Scheme 1-37, eq 1).[78] Then, an improved catalytic system using $CuSO_4$ and 4-picoline was developed by Santos, which allowed the reaction to occur in an aqueous medium and open to air.[79] This protocol was further extended to an addition of BpinBdan to alkynoates and alkynamides affording 1,8-diaminonaphthalene-protected *cis-β*-boryl enoates.[80]

Interestingly, the regioselectivity of the boration could be switched by employing HBpin instead of B_2pin_2. Aue and coworkers described the synthesis of *α*-borylated-*α,β*-ethylenic esters in the presence of CuCl and NaO^{t}Bu. The commercially available Stryker's reagent was also effective here. Both methods smoothly afforded the corresponding products with excellent *cis/trans* ratios (Scheme 1-37, eq 2).[81]



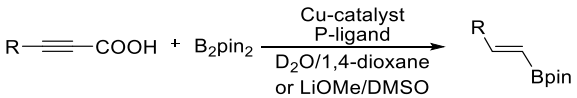
Scheme 1-37. Cu-catalyzed hydroboration of *α,β*-acetylenic esters.

Similar approaches were also utilized for the hydroboration of internal propargyl alkynes bearing heteroatom substituents (N,[82] S,[83] Si,[84] P[85]) with high regioselectivities (Scheme 1-38).



Scheme 1-38. Cu-catalyzed hydroboration of internal alkynes with heteroatom substituents.

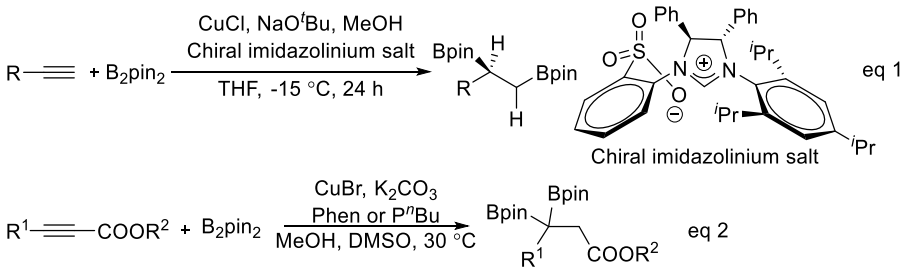
The groups of Song[86] and Lee[87] independently and almost simultaneously reported the synthesis of alkenylboronates via decarboxylation hydroboration of alkynyl carboxylic acids. Cu-catalyst and P-ligands were crucial factors for these reactions (Scheme 1-39). Later, these strategies were further extended to synthesize alkenylboronates under ligand-free, or ligand- and base-free conditions.[88]



Scheme 1-39. Cu-catalyzed decarboxylation hydroboration of alkynyl carboxylic acids.

In 2009, Hoveyda and coworkers revealed a Cu-catalyzed double hydroboration of terminal alkynes. It represented an efficient protocol for the enantioselective synthesis of 1,2-diboronates with high enantiomeric purities. A chiral bidentate NHC was used as a ligand (Scheme 1-40, eq 1).[89]

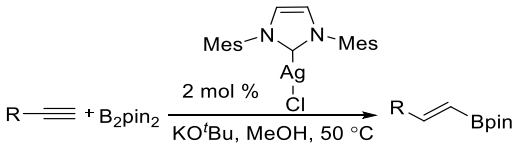
In previous studies, double hydroboration occurred mainly on terminal alkynes. Tsukada illustrated that internal conjugated alkynes could undergo double hydroboration to give the corresponding products (Scheme 1-40, eq 2),[90] while unactivated internal alkynes were still limited under these conditions.



Scheme 1-40. Cu-catalyzed double hydroboration of alkynes.

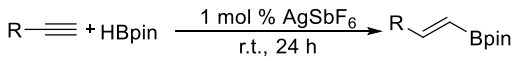
1.1.1.12 Ag-catalyzed hydroboration of alkynes

In 2014, the first Ag-catalyzed hydroboration of alkynes was disclosed by Yoshida and coworkers.[91] This reaction provided aliphatic borylalkenes in the presence of (IMes)AgCl in good yields (Scheme 1-41).



Scheme 1-41. Ag-catalyzed hydroboration of alkynes.

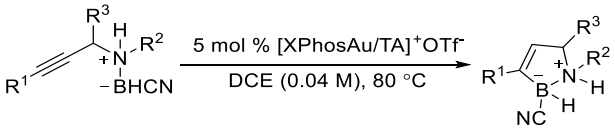
Recently, Rit reported the $AgSbF_6$-catalyzed hydroboration of terminal alkynes conducted with HBpin under solvent and ligand-free conditions.[92] Preliminary mechanistic studies indicated that this reaction follows a single electron transfer pathway (Scheme 1-42).



Scheme 1-42. Ag-catalyzed hydroboration of alkynes via a single electron transfer process.

1.1.1.13 Au-catalyzed hydroboration of alkynes

In 2009, Corma first demonstrated a gold-catalyzed hydroboration of double bonds and triple bonds with HBpin or HBcat, and alkynes are preferentially hydroborated in the presence of alkenes when using gold salts or complexes.[93] Later, Shi and coworkers developed a new strategy to furnish the cyclic amine boranes via triazole-gold(I)-catalyzed hydroboration of alkynes with high efficiency (Scheme 1-43).[94]

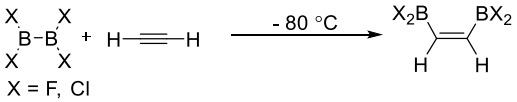


Scheme 1-43. Au-catalyzed hydroboration of alkynes.

1.1.2 Diboration of alkynes

1.1.2.1 Transition metal-free diboration of alkynes

In 1959, the first example of a diboron tetrahalide addition to alkynes under catalyst-free conditions was developed by Schlesinger. *Cis*-1,2-bis(dichloroboryl)ethene was obtained using acetylene and B_2X_4 (X = Cl, F) at –80 °C (Scheme 1-44).[95] A few years later, Rudolph found that the mechanism of this diboration involved a stereospecific *cis* addition, which was consistent with a four-center transition state.[96] The *cis* addition of B_2X_4 across triple bonds was further identified by Wartik and coworkers.[97]

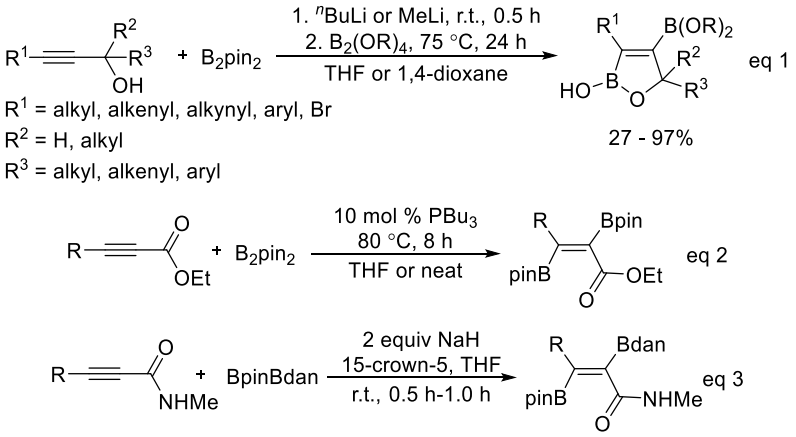


Scheme 1-44. Diboration of acetylene under the catalyst-free conditions.

In 2014, Hirano and Uchiyama established a *trans*-diboration of propargylic alcohols by designing a *pseudo*-intramolecular reaction, which was promoted by a stoichiometric amount of base. Interestingly, one of the boron moieties was deprotected to afford *trans*-vinyldiboronates after working up with aq. NH_4Cl (Scheme 1-45, eq 1).[98]

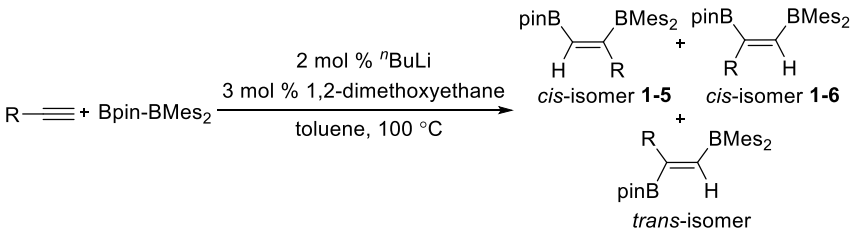
Later on, a phosphine-catalyzed *trans*-selective diboration of alkynoates with B_2pin_2 successfully furnished *α*,*β*-diborylacrylates, which was reported by Ohmiya and Sawamura. Remarkably, this *trans*-selective vicinal diboration showed excellent stereoselectivities. The possible mechanism for this diboration involved phosphonium allenolates as key intermediate (Scheme 1-45, eq 2).[99]

More recently, transition metal-free catalyzed *trans*-diboration of alkynes has been extended to NaH-promoted diboration of alkynamides with BpinBdan. This method exhibited excellent stereo- and regioselectivities, providing *trans*-1,2-vinyldiboronates in good yields (Scheme 1-45, eq 3).[100]



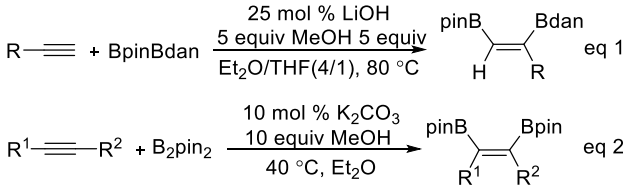
Scheme 1-45. Transition metal-free catalyzed diboration of alkynes with heteroatom substituents.

Yamashita and Lin reported the transition metal-free catalyzed diboration of alkynes using the unsymmetrical diborane(4), Bpin-$BMes_2$, to afford a mixture of two *cis*-isomers(**1-5** and **1-6**) and one *trans*-isomer. The ratio of three isomers could be controlled by solvent, temperature and additives (Scheme 1-46). They further developed a two-step synthesis of fluorescent molecules via diboration under this reaction condition and Suzuki-Miyaura coupling.[101]



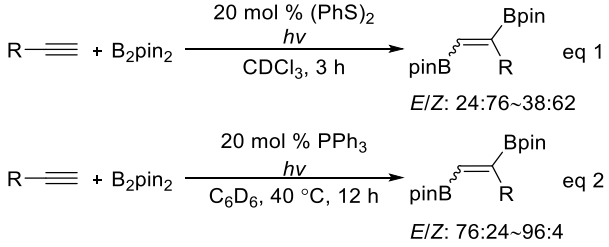
Scheme 1-46. Transition metal-free catalyzed diboration of alkynes using Bpin-$BMes_2$.

In 2018, Huang and Liu reported a mixed *cis*-diboration of terminal alkynes with BpinBdan catalyzed by LiOH in the presence of MeOH. The Bdan motif was added to the internal position of alkynes with excellent regio- and stereoselectivities (Scheme 1-47, eq 1). It was worth noting that the diboration of symmetric and asymmetric internal alkynes occurs with B_2pin_2 using NaOH instead of LiOH in moderate to good yields.[102] In the meantime, Song *et al.* also developed a similar base-catalytic system that furnished 1,2-diborylalkenes using various alkynes in good yields (Scheme 1-47, eq 2).[103]



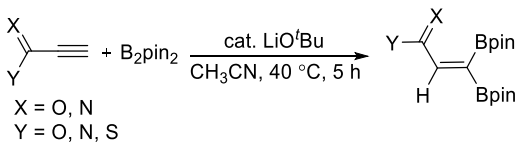
Scheme 1-47. Base-catalyzed diboration of alkynes.

Ogawa and coworkers reported a photocatalyzed diboration of terminal alkynes applying an organosulfide ($(PhS)_2$)[104] or organophosphine (PPh_3)[105] as catalysts under light irradiation. Compared with the organosulfide-catalyzed diboration, the organophosphine-catalyzed method showed much higher *trans*-selectivities, but lower yields (Scheme 1-48).



Scheme 1-48. Photocatalyzed diboration of terminal alkynes.

Although the base-catalyzed approaches to 1,2-diborylalkenes have been well established, base-catalyzed 1,1-diboration of terminal alkynes was still in its infancy, until in 2015, Ohmiya and Sawamura demonstrated the synthesis of 1,1-diborylalkenes by a ^{t}BuOLi-catalyzed diboration of terminal alkynes, including propiolates, propiolamides and 2-ethynylazoles (Scheme 1-49).[106]

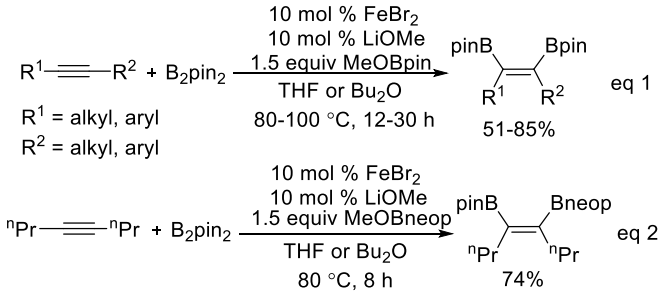


Scheme 1-49. Base-catalyzed approach to 1,1-diborylalkenes from alkynes.

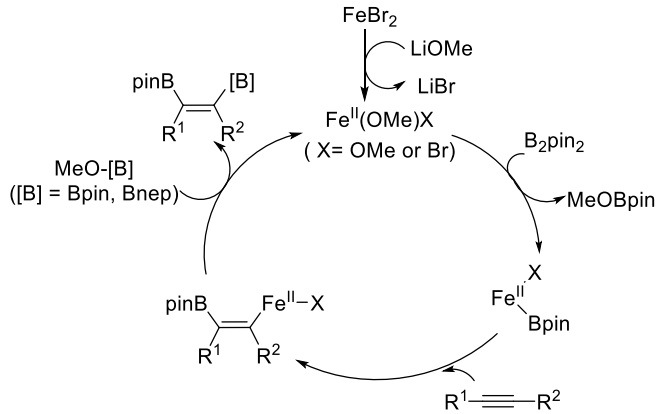
1.1.2.2 Fe-catalyzed diboration of alkynes

In 2015, Nakamura *et al.* developed a novel Fe(II)-catalyzed diboration of internal alkynes with B_2pin_2 and an additional borating agent (MeOBpin or MeOBneop) to synthesize diverse symmetrical and unsymmetrical *cis*-diborylalkenes (Scheme 1-50). The combination of $FeBr_2$, LiOMe and MeOBpin was efficient for this reaction with exclusive *cis*-selectivity and good to high yields. Unsymmetrical *cis*-

diborylalkenes were obtained as the main products using MeOBneop instead of MeOBpin (Scheme 1-50, eq 2). The two boron atoms of diborylalkenes are derived from the two different borating agents. A possible catalytic mechanism for the Fe-catalyzed diboration of internal alkynes is shown in Scheme 1-51. *In situ* trapping experiments and DFT calculations supported the formation of alkenyliron intermediate which came from a boryliron species addition to the triple bond of alkynes (Scheme 1-51).[107]



Scheme 1-50. Fe-catalyzed diboration of alkynes.



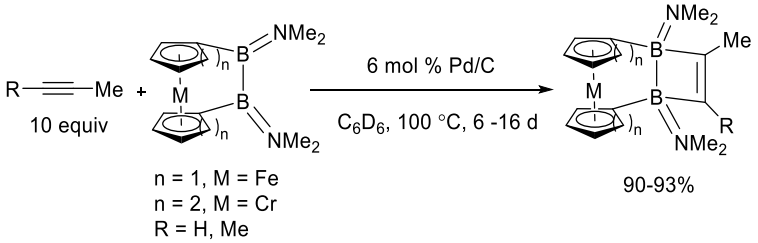
Scheme 1-51. Possible catalytic mechanism for the Fe-catalyzed diboration of alkynes.

1.1.2.3 Pd-catalyzed diboration of alkynes

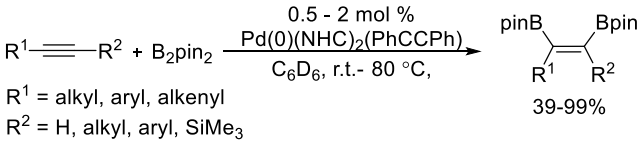
The Braunschweig group developed the first Pd-catalyzed diboration of alkynes in 2006. This process provided interesting *ansa*-bis(boryl)alkenes using Pd/C as the catalyst. However, this protocol suffered from long reaction times, high alkyne loadings and limited substrate scope (Scheme 1-52).[108] In contrast, the first homogenous Pd-catalyzed diboration of alkynes was presented by Braga and Navarro in 2016, in which Pd(0)$(NHC)_2$(PhC≡CPh) was used as the catalyst to furnish *cis*-diborylalkenes in high yields.[109] Based on DFT calculations and previous studies,[110] they proposed that the Pd-catalyzed diboration reaction

proceeded via the same mechanistic pathway as in the Pt-catalyzed alkyne diboration.[110-111] NHC ligands increased the reactivity of the Pd-catalyzed diboration compared to phosphine ligands (Scheme 1-53).

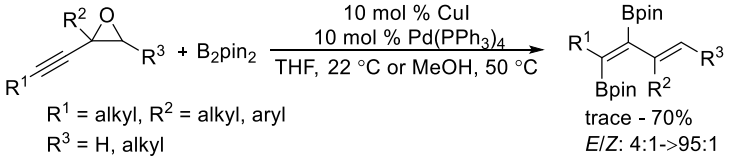
Examples of the *trans*-diboration of alkynes were achieved by Szabó in 2014. The diboration of propargyl epoxides was conducted using a bimetallic Pd/Cu catalytic system to obtain *trans*-selective diboration products via an S_N2'-type mechanism (Scheme 1-54). This reaction also occurred using a $CuCl/PCy_3/KO^tBu$ catalytic system in the absence of palladium.[112]



Scheme 1-52. Diboration of alkynes using Pd/C as the catalyst.



Scheme 1-53. Pd-catalyzed diboration of alkynes.

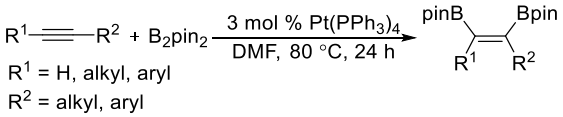


Scheme 1-54. Pd-catalyzed *trans*-diboration of alkynes.

1.1.2.4 Pt-catalyzed diboration of alkynes

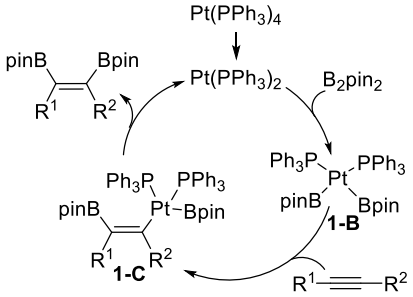
The platinum-catalyzed diboration of alkynes has been studied extensively after the Suzuki group's seminal work.[113] They developed the first Pt-catalyzed diboration of alkynes with B_2pin_2 to afford *cis*-1,2-diborylalkenes in high yields in 1993. This reaction was conducted at 80 °C in DMF for 24 h. It is worth noting that $Pt(PPh_3)_4$ played an important role, while other metal catalysts ($Pd(PPh_3)_4$, $RhCl(PPh_3)_3$ or $CoCl(PPh_3)_3$) were ineffective in this reaction (Scheme 1-55).[113] In addition, this method was also extended to other diboron reagents such as $B_2(OMe)_4$, $B_2(NMe_2)_4$,[113b] $B_2Cl_2(NMe_2)_2$[114] and B_2cat_2.[115] Miyaura further studied Suzuki-

Miyaura coupling using the 1,2-diborylalkenes products with aryl, 1-alkenyl, benzyl and allyl halides. This cross-coupling reaction furnished multisubstituted olefins in good yields.[116] In 1996, Marder and coworkers demonstrated that bis(phosphine) Pt(II)bis(boryls) and bis(phosphine) Pt(0)-ethylene complexes were more efficient than $Pt(PPh_3)_4$ for the diboration of alkynes. They also found that diboration or tetraboration of diynes could be controlled using their systems.[117]



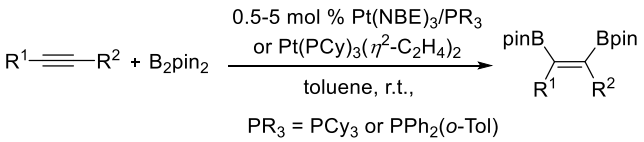
Scheme 1-55. Pt-catalyzed diboration of alkynes.

A proposed mechanism for the Pt-catalyzed diboration of alkynes is outlined in Scheme 1-56. [111a, 113b, 118] Oxidative addition of B_2pin_2 to $Pt(PPh_3)_4$ gave *cis*-$[(PPh_3)_2Pt(Bpin)_2]$ (**1-B**), which was isolated and characterized by the single-crystal X-ray diffraction analysis.[113b] After that, *cis*-insertion of alkynes to intermediate **1-B** afforded vinylplatinum species **1-C**. A following reductive elimination of **1-C** yielded diborylalkenes and regenerated the catalyst (Scheme 1-56).



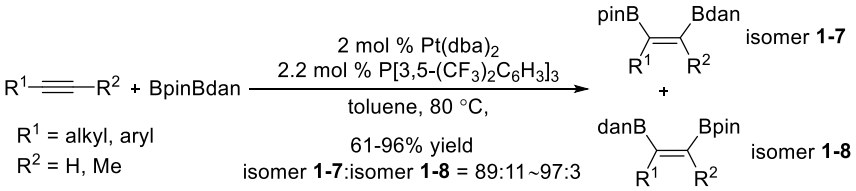
Scheme 1-56. Proposed mechanism for the Pt-catalyzed diboration of alkynes.

In 2001, the Marder group reported highly efficient monophosphine platinum catalysts for the diboration of alkynes. Screening of a series of phosphines disclosed that PCy_3 and PPh_2(*o*-tol) were identified as the best ones for this diboration. Additionally, this diboration could be conducted at room temperature (Scheme 1-57).[119] They noted that all of the above mentioned platinum-phosphine-catalyzed alkyne diboration likely proceeded via monophosphine Pt intermediates.



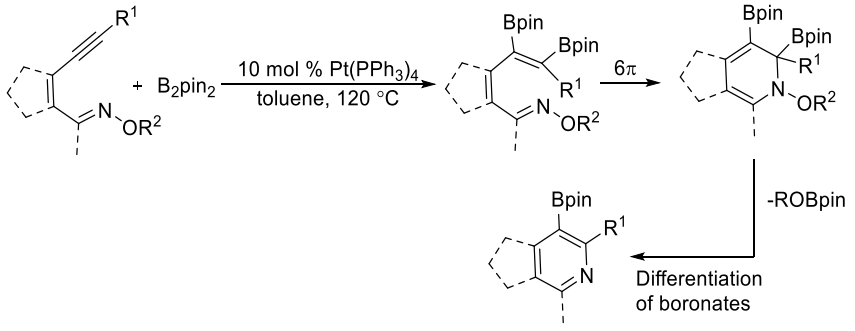
Scheme 1-57. Monophosphine platinum-catalyzed diboration of alkynes.

In 2010, Suginome and coworkers reported an efficient platinum catalyst system for diboration with an unsymmetrical diboron reagent, BpinBdan, to prepare the corresponding 1,2-diborylalkenes with high regioselectivities (Scheme 1-58). Given the sufficiently differentiable reactivities between Bpin and Bdan, the Suzuki-Miyaura coupling reaction preferentially occurred on Bpin to obtain monoborylalkenes with excellent chemoselectivities. More importantly, monoborylalkenes could undergo further conversion to furnish unsymmetrical multisubstituted olefins.[120]



Scheme 1-58. Pt-catalyzed diboration of alkynes with BpinBdan.

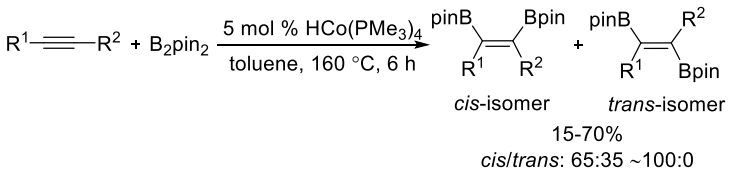
In 2016, the Harrity group developed a novel and efficient synthesis of pyridine boronic acid derivatives via the Pt-catalyzed diboration of alkynes and a 6π electrocyclization reaction. This protocol successfully furnished bicyclic pyridines, although the strategy to access monocyclic heterocycles required further studies. This is an important application of Pt-catalyzed diboration of alkynes (Scheme 1-59).[121]



Scheme 1-59. Pt-catalyzed diboration of alkynes and 6π electrocyclization reaction.

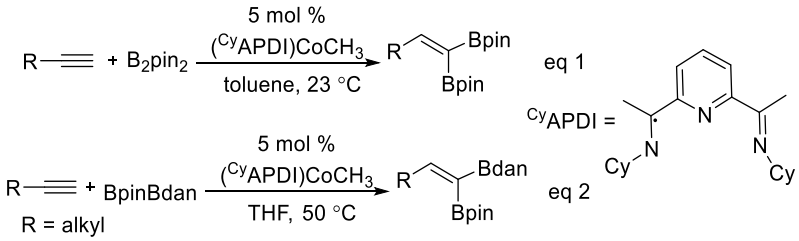
1.1.2.5 Co-catalyzed diboration of alkynes

In 2006, Lin and Marder reported the synthesis and reactivity of cobalt boryl complexes. The first example of Co-catalyzed diboration of alkynes were achieved in this research.[122] After that, Petit *et al.* applied a low-valent cobalt(I)catalyst $HCo(PMe_3)_4$ for the diboration of internal alkynes to afford *cis*/*trans*-diborylalkenes, but low yields and low stereoselectivities were obtained (Scheme 1-60).[52]



Scheme 1-60. Co-catalyzed 1,2-diboration of alkynes.

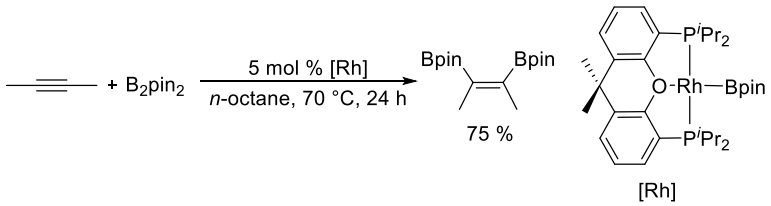
A number of methods for the synthesis of 1,2-diborylalkenes from alkynes have been developed. By contrast, the direct preparation from terminal alkynes and B_2pin_2 was limited. In 2017, Chirik and coworkers developed a cobalt-catalyzed method to synthesize 1,1-diborylalkenes with excellent selectivities directly from terminal alkynes with B_2pin_2 (Scheme 1-61, eq 1). The reaction was conducted under mild conditions with broad functional group tolerance. In addition, this catalytic system could be extended to stereoselective 1,1-diboration of terminal alkynes with BpinBdan (Scheme 1-61, eq 2).[123]



Scheme 1-61. Co-catalyzed 1,1-diboration of alkynes.

1.1.2.6 Rh-catalyzed diboration of alkynes

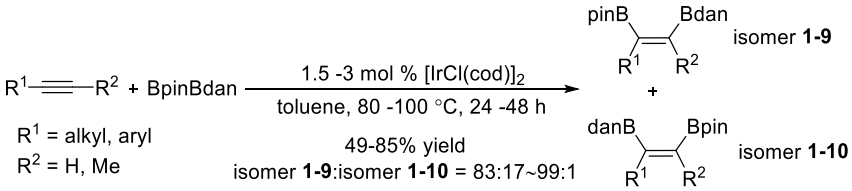
Recently, Esteruelas and coworkers tried to design a Rh-boryl complex for the *trans*-diboration of nonfunctionalized internal alkynes. A *cis*-diborylalkene was obtained using 2-butyne and B_2pin_2 at 70 °C in the presence of the Rh-boryl catalyst (Scheme 1-62).[124]



Scheme 1-62. Rh-catalyzed diboration of alkynes.

1.1.2.7 Ir-catalyzed diboration of alkynes

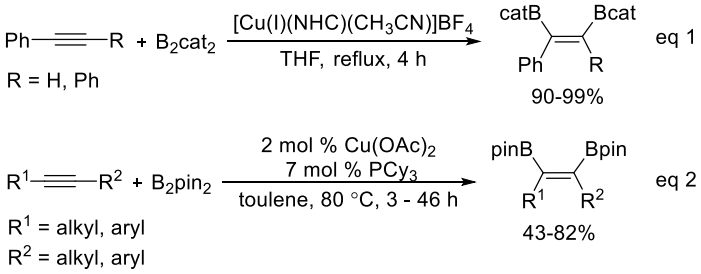
In 2010, Suginome *et al.* found that $[IrCl(cod)]_2$ showed high catalytic activity for the diboration of alkynes with BpinBdan. Notably, this Ir system (Scheme 1-63) exhibited comparable or even better regioselectivities than platinum catalysts they were examining.[120]



Scheme 1-63. Ir-catalyzed diboration of alkynes.

1.1.2.8 Cu-catalyzed diboration of alkynes

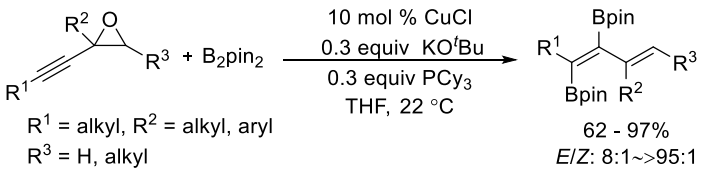
In 2007, Fernández and coworkers reported the Cu-catalyzed diboration of alkynes with B_2cat_2, using a Cu-NHC complex as the catalyst (Scheme 1-64, eq 1).[125] In 2012, Yoshida *et al.* reported an improved Cu-catalyst system, namely $Cu(OAc)_2/PCy_3$, which was more practical using readily available catalyst and ligand (Scheme 1-64, eq 2),[126] and process was applicable to various internal alkynes affording *cis*-diboryalkenes in high yields. Interestingly, this method could be further extended to the diboration of arynes and propargyl ethers.



Scheme 1-64. Cu-catalyzed diboration of alkynes.

In 2014, Szabó and coworkers reported the synthesis of *trans*-diborylalkenes using

CuCl/PCy_3/KO^tBu. This Cu-catalyzed diboration of propargyl epoxides gave higher yields and stereoselectivities than a bimetallic CuI/$Pd(PPh_3)_4$ catalytic protocol (Scheme 1-65).[112]



Scheme 1-65. Cu-catalyzed *trans*-diboration of alkynes.

1.1.3 Dehydrogenative borylation of terminal alkynes

1.1.3.1 Preparation alkynylboron compounds via lithiation and subsequent boration

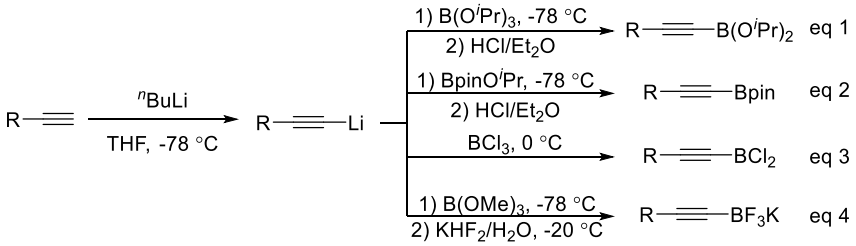
Although the chemistry of organoboron compounds containing sp^3 and sp^2 C-B bonds has been extensively developed for applications in organic synthesis,[127] alkynylboron compounds have received less attention. Traditionally,[128] terminal alkynes were deprotonated using a ^{n}BuLi and then reacted with boron reagents to give alkynylboron compounds. In 1987, Brown *et al.* successfully obtained alkynylboronates in high purities and yields via addition of alkynyllithiums to a boronic ester ($B(O^iPr)_3$), followed by treatment with anhydrous HCl/Et_2O (Scheme 1-66, eq 1).[129]

Using the same methodology, Srebnik *et al*. prepared of alkynylboronates using ^{i}PrOBpin as the boron reagent (Scheme 1-66, eq 2).[130] This protocol could then be combined with zirconium chemistry to synthesize 1,1-dimetallic compounds stereospecifically.[131]

In 1997, the Singleton group synthesized alkynyldihaloboranes *in situ* via a boron-tin exchange reaction with BBr_3 or BCl_3.[128f] Considering the toxicity of tin reagents, Kabalka and coworkers successfully obtained alkynyldichloroboranes by the sequential treatment of terminal alkynes with ^{n}BuLi followed by BCl_3 at 0 °C (Scheme 1-66, eq 3).[132]

In 1999, Genêt reported the formation of potassium alkynyltrifluoroborates for the first time.[133] Treatment of alkynylboronates with KHF_2 afforded air- and moisture-

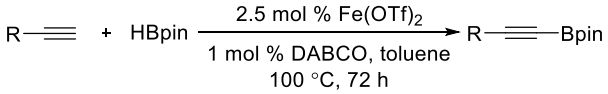
stable potassium alkynyltrifluoroborates which were easily isolated in good yields (Scheme 1-66, eq 4).



Scheme 1-66. Base promoted dehydrogenative borylation of terminal alkynes.

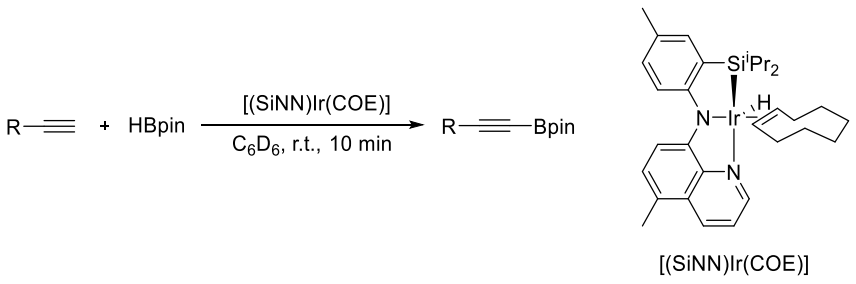
1.1.3.2 Fe-catalyzed dehydrogenative borylation of terminal alkynes

In 2018, Darcel and coworkers reported an $Fe(OTf)_2$ catalytic system for the dehydrogenative borylation of aromatic and aliphatic terminal alkynes,[134] which generated the corresponding borylated alkynes in the presence of HBpin at 100 °C for 72 h (Scheme 1-67).



Scheme 1-67. Fe-catalyzed dehydrogenative borylation of terminal alkynes.

1.1.3.3 Ir-catalyzed dehydrogenative borylation of terminal alkynes



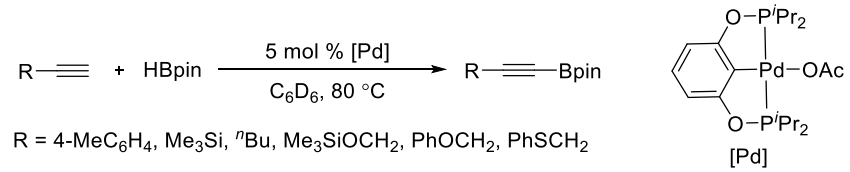
Scheme 1-68. Ir-catalyzed dehydrogenative borylation of terminal alkynes.

Iridium-catalyzed dehydrogenative borylation of aromatic C-H bonds has been well established by Smith III,[135] Hartwig,[136] Marder,[137] and others.[138] In 2013, a new iridium catalyst [(SiNN)Ir(COE)] was synthesized and characterized by Ozerov (Scheme 1-68), which was chemoselective for the dehydrogenative borylation of terminal alkynes. This iridium catalyst, featuring a new SiNN pincer ligand, exhibited a high turnover numbers at ambient temperature, and a variety of terminal alkynes

were transformed into the corresponding alkynylboronates with high yields and chemoselectivities.[139]

1.1.3.4 Pd-catalyzed dehydrogenative borylation of terminal alkynes

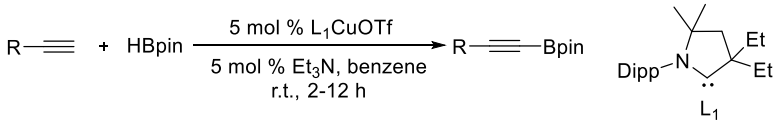
In 2015, Ozerov and coworkers studied the Pd-catalyzed dehydrogenative borylation of terminal alkynes.[139-140] They found that POCOP-supported palladium complexes could promote the dehydrogenative borylation of terminal alkynes (Scheme 1-69). Although this reaction was accompanied by hydrogenation of the alkynes, the competing side reaction was inhibited by the addition of phosphines.



Scheme 1-69. Pd-catalyzed dehydrogenative borylation of terminal alkynes.

1.1.3.5 Cu-catalyzed dehydrogenative borylation of terminal alkynes

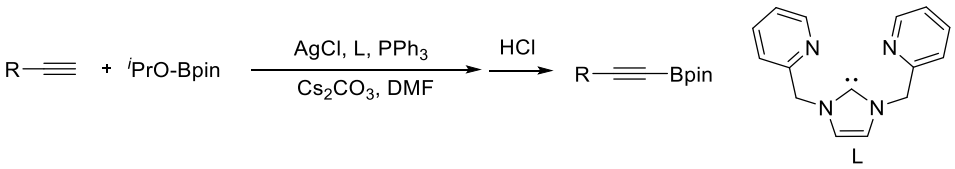
In 2017, Bertrand *et al.* reported a Cu-catalyzed dehydrogenative borylation of terminal alkynes. The dehydrogenative borylation products were obtained when terminal alkynes were reacted with HBpin in the presence of 5 mol % of L_1CuOTf when L_1 is a CAAC ligand (Scheme 1-70).[69b] Mechanistic studies indicated that a σ,π-bis(copper)acetylide intermediate protected the triple bond from hydroboration.[141]



Scheme 1-70. Cu-catalyzed dehydrogenative borylation of terminal alkynes.

1.1.3.6 Ag-catalyzed dehydrogenative borylation of terminal alkynes

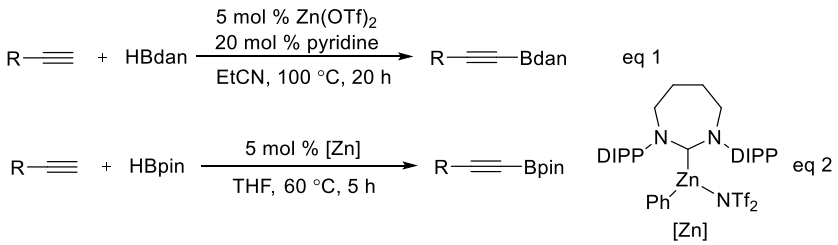
In 2014, Hu and coworkers developed an efficient Ag(I)-catalyzed dehydrogenative borylation of terminal alkynes with ^{i}PrOBpin. Various of aryl- and alkyl-substituted terminal alkynes gave the desired products in good to high yields (Scheme 1-71), and the Ag(I)-catalyst could be recycled.[142]



Scheme 1-71. Ag-catalyzed dehydrogenative borylation of terminal alkynes.

1.1.3.7 Zn-catalyzed dehydrogenative borylation of terminal alkynes

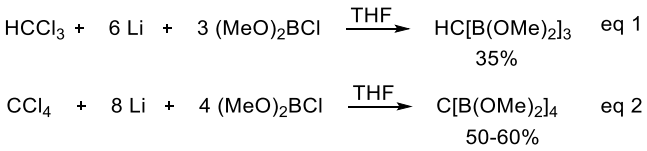
A Zn-catalyzed dehydrogenative borylation of terminal alkynes was reported by Tsuchimoto *et al.* in 2015. [143] Terminal alkynes were coupled with HBdan (1,8-naphthalenediaminatoborane) using a $Zn(OTf)_2$-pyridine system giving alkynylboranes in high yields (Scheme 1-72, eq 1). It is noteworthy that alkynylboranes with a C(*sp*)-Bdan can be easily isolated by silica gel column chromatography without any pretreatment. Unfortunately, the more widely used boron reagent, HBpin, was unsuitable under these reaction conditions. Ingleson and coworkers recently reported an alternative NHC-zinc system to prepare alkynylboronates using HBpin (Scheme 1-72, eq 2).[144]



Scheme 1-72. Zn-catalyzed dehydrogenative borylation of terminal alkynes.

1.2 Multiborylated compounds

1.2.1 1,1,1-Triborylalkanes

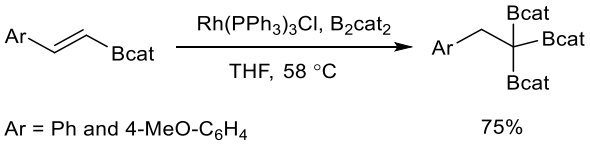


Scheme 1-73. Triboration and tetraboration of chloroform.

In 1969, Matteson and coworkers reported the triboration of chloroform using $(RO)_2BCl$ and 6 equivalents of lithium metal at low temperature (Scheme 1-73, eq 1). An extension of this approach, employing CCl_4 in place of $HCCl_3$, led to

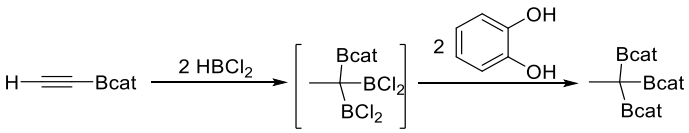
octamethyl methanetetraboronate (Scheme 1-73, eq 2).[145]

In 1995, Wester and Marder reported the synthesis of $ArCH_2C(Bcat)_3$ during their studies of the Rh-catalyzed diboration of vinylarenes.[146] The Marder group thus reported a Rh-catalyzed dehydrogenative borylation-hydroboration of (*E*)-styrylboronates, furnishing 1,1,1-tris(boronates) in 75% yield (Scheme 1-74).[147]



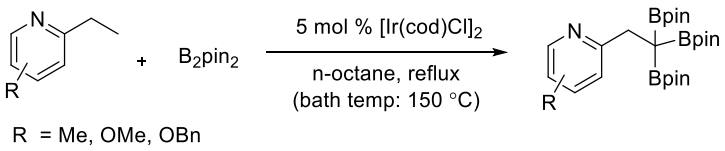
Scheme 1-74. Rh-catalyzed triboration of vinylarenes.

In 2001, Siebert prepared 1,1,1-triborylalkanes via double hydroboration of an ethynylboronate with $HBCl_2$, and subsequent substitution of the chlorine atoms by cat groups (Scheme 1-75).



Scheme 1-75. Double hydroboration of an ethynylboronate.

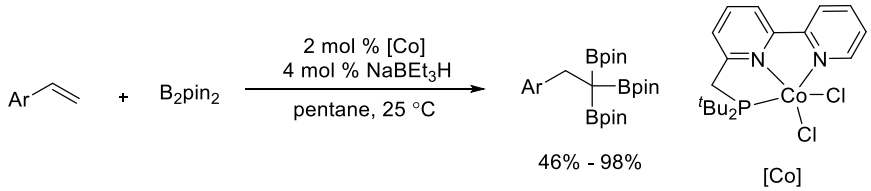
In 2013, Mita, Sato *et al.* developed an Ir-catalyzed, nitrogen-directed triple C(sp^3)-H boration of 2-ethylpyridines with B_2pin_2 using *n*-octane as the solvent under reflux conditions. However, good yields and selectivities were obtained only when small, electron-donating substituents were presented on the pyridine rings (Scheme 1-76). The products were further transformed into carboxylic acid derivatives.[148]



Scheme 1-76. Ir-catalyzed triboration of 2-ethylpyridines.

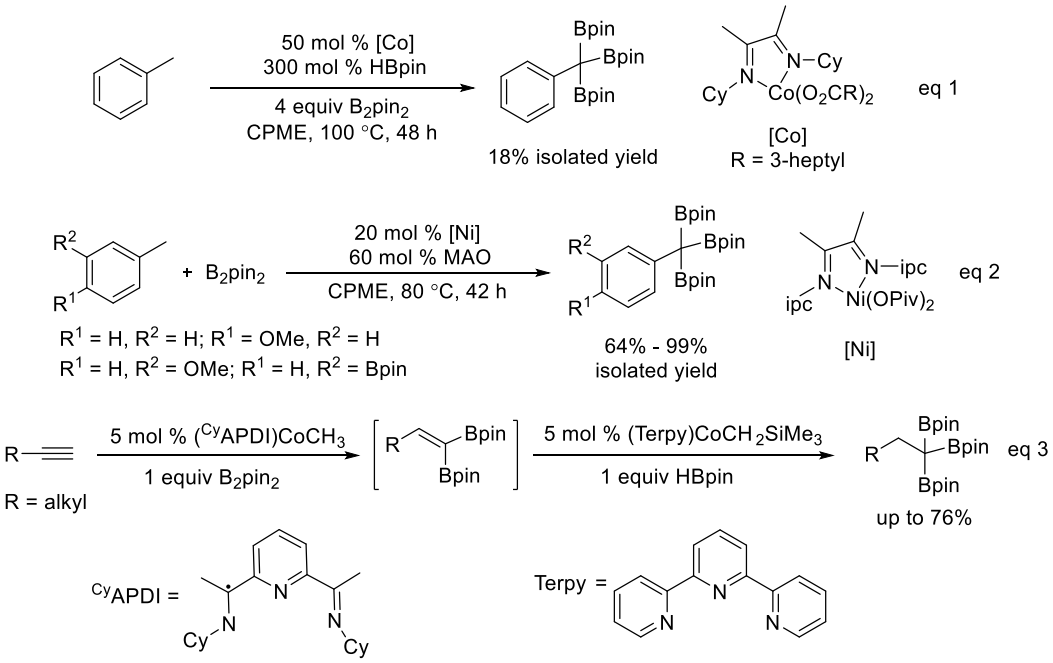
The Huang group synthesized 1,1,1-triborylalkanes from vinylarenes with B_2pin_2 using ($^{t\text{Bu}}$PNN)$CoCl_2$ as the precatalyst and $NaBEt_3H$ as the activator. The reaction proceeded under mild conditions furnishing 1,1,1-triborylalkanes with excellent selectivities and high yields, but unactivated alkenes were not suitable substrates. Mechanistic studies indicated that Co-catalyzed double dehydrogenative borylations formed a *gem*-diborylalkene intermediate, which then reacted with

HBpin, formed *in situ,* to generate the final products (Scheme 1-77).[149]



Scheme 1-77. Co-catalyzed triboration of alkenes.

In 2016, Chirik and coworkers found that 1,1,1-triborylated toluene was formed in 18% yield from toluene using high Co-catalyst loadings of 50 mol % after long reaction periods (Scheme 1-78, eq 1).[150] They then developed an α-diimine nickel catalyst which promoted the selective formation of 1,1,1-triborylated toluene in high yield via a perboration of benzylic C-H bonds, but the reported substrate scope was quite limited (only 4 examples) (Scheme 1-78, eq 2).[151] The same group achieved the synthesis of 1,1,1-triboronates in high yields via a Co-catalyzed 1,1-diboration of terminal alkynes with B_2pin_2, which underwent subsequent hydroboration with HBpin. Two different types of cobalt catalysts were used in this two-step sequence (Scheme 1-78, eq 3).[123]

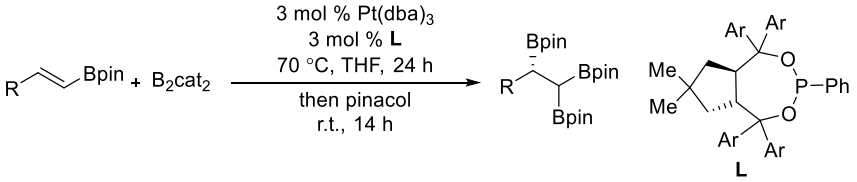


Scheme 1-78. Co-catalyzed triboration.

1.2.2 1,1,2-Triborylalkanes

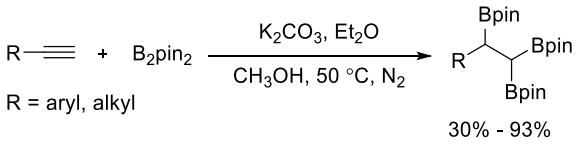
In 2014, enantiomerically enriched 1,1,2-tris(boronates) were prepared via a Pt-

catalyzed enantioselective diboration of vinyl boronic esters which are usually synthesized by transition metal-catalyzed hydroboration of terminal alkynes. The corresponding products were obtained in good yields and enantiomeric ratios when vinyl boronic esters were treated with B_2cat_2 in the presence of 3 mol % of $Pt(dba)_3$ and the chiral ligand (L) at 70 °C for 24 h (Scheme 1-79). Furthermore, the application of 1,1,2-tris(boronates) for practical asymmetric synthesis was examined via a range of deborylative alkylation both for intermolecular and intramolecular reactions.[152]



Scheme 1-79. Pt-catalyzed enantioselective diboration of vinyl boronic esters.

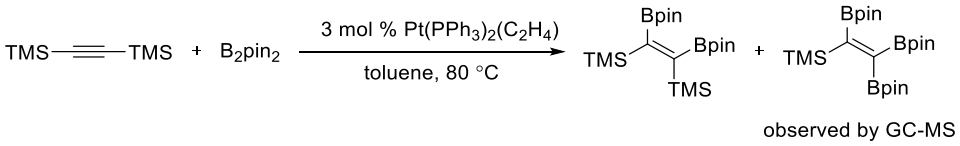
In 2017, a base-promoted synthesis of 1,1,2-tris(boronates) directly from terminal alkynes was reported by the Song group. The main products, 1,1,2-tris(boronates), were obtained in good yields using a K_2CO_3/Et_2O system in methanol (Scheme 1-80). Interestingly, 1,1,2-tris(boronates) underwent protodeboronation giving 1,2-bis(boronates) in the presence of Cs_2CO_3 and CH_3CN.[153]



Scheme 1-80. Base-promoted synthesis of 1,1,2-tris(boronates) from terminal alkynes.

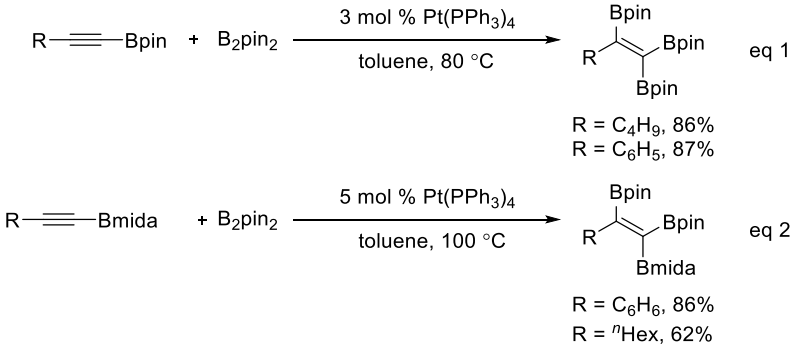
1.2.3 1,1,2-Triborylalkenes

In 1996, the Marder group observed the formation of a 1,1,2-tris(boronate) by GC-MS when they optimized the Pt-catalyzed diboration of 1,2-bis(trimethylsilyl)ethyne. This novel product arose from the diboration of trimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)silane which derived from C-Si bond cleavage in 1,2-bis(trimethylsilyl)ethyne by the platinum catalyst (Scheme 1-81).[117]



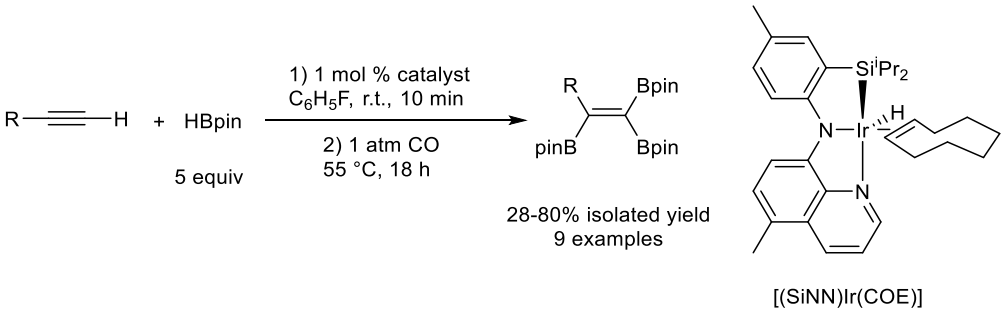
Scheme 1-81. Pt-catalyzed triboration of 1,2-bis(trimethylsilyl)ethyne.

In 2002, Srebnik and coworkers reported an efficient Pt-catalyzed diboration of 1-alkynylboronates to give1,1,2-triborylalkenes in high yields (Scheme 1-82, eq 1).[154] In 2014, Nishihara successfully synthesized 1,1,2-triboryl-2-phenylethene with two different boron groups using alkynyl mida as the starting material (Scheme 1-82, eq 2). Given that the Bpin and Bmida have different reactivities, the corresponding products underwent a selective Suzuki-Miyaura coupling to yield 1,1-diboryl-2,2-diarylethenes.[155]



Scheme 1-82. Pt-catalyzed diboration of 1-alkynylboronates.

In 2015, Ozerov disclosed an Ir-catalyzed synthesis of 1,1,2-triborylalkenes via a two-step reaction of terminal alkynes with HBpin under an atmosphere of CO. It is the first example of a sequential dehydrogenative borylation-diboration of terminal alkynes using HBpin, in contrast with additive diboration using diboron reagents (Scheme 1-83).[156]

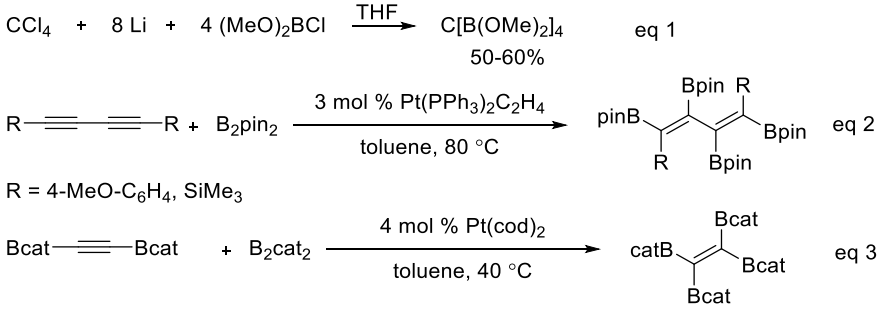


Scheme 1-83. Ir-catalyzed dehydrogenative diboration of terminal alkynes.

1.2.4 Tetrakis(boronate)s

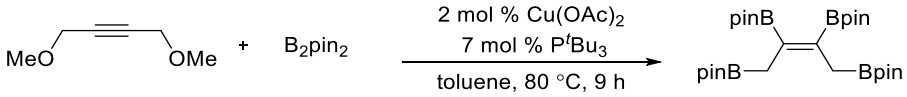
In 1969, Matteson and coworkers developed a quadruple boration of carbon tetrachloride using $(RO)_2BCl$ and 8 equivalents of lithium metal at low temperature, which was applicable to a gram-scale synthesis (Scheme 1-84, eq 1).[145a] In 1996, the Marder group reported the tetraboration of 1,3-diynes employing 2 equivalents of diboron reagents in the presence of $Pt(PPh_3)_2C_2H_4$ (Scheme 1-84, eq 2).[117] Subsequently, Siebert and Gleiter prepared tetraborylethenes by diboration of diborylacetylene under similar conditions (Scheme 1-84, eq 3).[157]

In 2016, Marder and Cabeza studied the reactivity of B_2pin_2 with $[Ru_3(CO)_{12}]$ analyzed by GC-MS and NMR spectroscopy. The results indicated the formation of various metal-free C-borylated products ($C(Bpin)_4$, $C_2(Bpin)_6$, $HC(Bpin)_3$ and $H_2C(Bpin)_2$), which were formed in this reaction in small amounts (< 5% based on initial B_2pin_2).[158] $C(Bpin)_4$ and $C_2(Bpin)_6$ were isolated and their structures were confirmed by single-crystal X-ray diffraction studies.



Scheme 1-84. Synthesis of tetrakis(boronate)s.

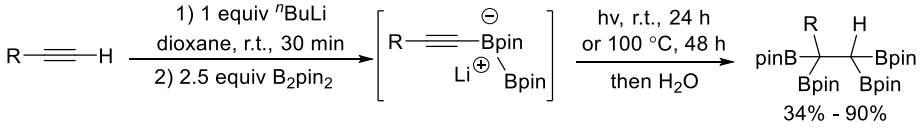
In 2012, Yoshida discovered that a propargyl ether smoothly underwent tetraboration by a formal C-O bond boration accompanied by diboration of the C-C triple bond in the presence of $Cu(OAc)_2$ and P^tBu_3 (Scheme 1-85).



Scheme 1-85. Cu-catalyzed tetraboration of a propargyl ether.

Recently, Nagashima and Uchiyama reported the first example of the quadruple boration of terminal alkynes yielding saturated 1,1,2,2-tetrakis(boronate) derivatives without a transition-metal catalyst. They found that two sets of reaction

conditions (photo-induced and thermal) were effective for aryl and alkyl alkynes, respectively (Scheme 1-86).[159]



Scheme 1-86. Quadruple boration of terminal alkynes without a transition-metal catalyst.

Multiborylated compounds are important in modern organic chemistry due to their various roles such as bio-active agents and synthetic building blocks. Monoboronates and bisboronates have been increasingly applied in organic synthesis (*vide supra*). In contrast, triboronates are relatively rare, but are potentially very interesting; thus, efficient methods for their synthesis are desirable, but few are currently available. In this thesis, readily available starting materials, catalysts and ligands were employed to synthesize 1,1,2-triborylalkenes, 1,1,1-triborylalkanes, and *gem*-diborylalkenes and their derivatives.

Chapter Two

Copper-Catalyzed Triboration of Terminal Alkynes Using B_2pin_2: Efficient Synthesis of 1,1,2-Triborylalkenes

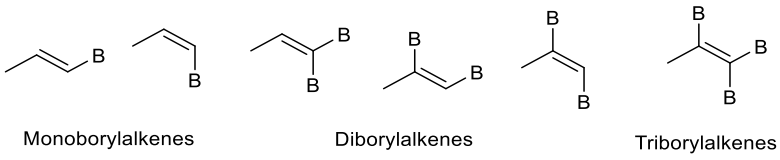
2 Copper-Catalyzed Triboration of Terminal Alkynes Using B_2pin_2: Efficient Synthesis of 1,1,2-Triborylalkenes

2.1 Abstract

Chapter two reports the catalytic triboration of terminal alkynes with B_2pin_2 using readily available $Cu(OAc)_2$ and P^nBu_3. Various 1,1,2-triborylalkenes, a class of compounds which have been demonstrated to be potential Matrix Metalloproteinase-2 (MMP-2) inhibitors, are obtained directly in moderate to good yields. The process features mild reaction conditions, broad substrate scope, and good functional group tolerance were observed. This Cu-catalyzed reaction can be conducted on a gram scale to produce the corresponding 1,1,2-triborylalkenes in modest yields. The utility of these products is demonstrated by further transformation of the C-B bonds to prepare *gem*-dihaloborylalkenes (F, Cl, Br), monohalodiborylalkenes (Cl, Br), and *trans*-diaryldiborylalkenes, which serve as important synthons and have previously been challenging to prepare.

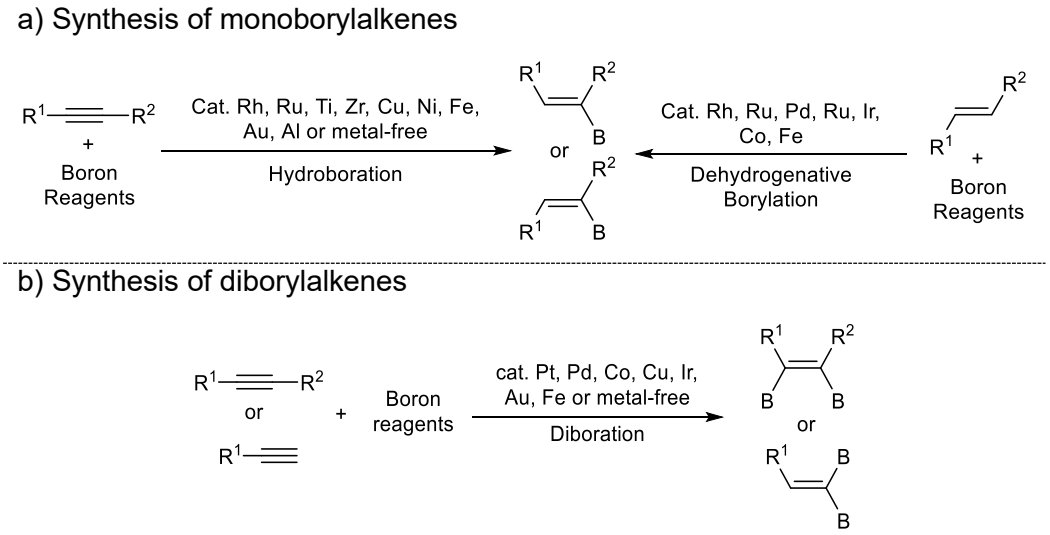
2.2 Introduction

Organoboronic acids and their derivatives (boronate esters, trifluoroborates and boroxines) play a critical role in organic synthesis, materials science, and pharmaceutical development.[137b, 160] In particular, alkenylboron compounds have been utilized for the stereodefined construction of valuable multisubstituted alkenes including natural products, biologically active molecules, and functional materials.[1f, 161] These species can be categorized into three classes, namely monoborylalkenes, diborylalkenes and triborylalkenes (Scheme 2-1).



Scheme 2-1. Classification of alkenylboron species.

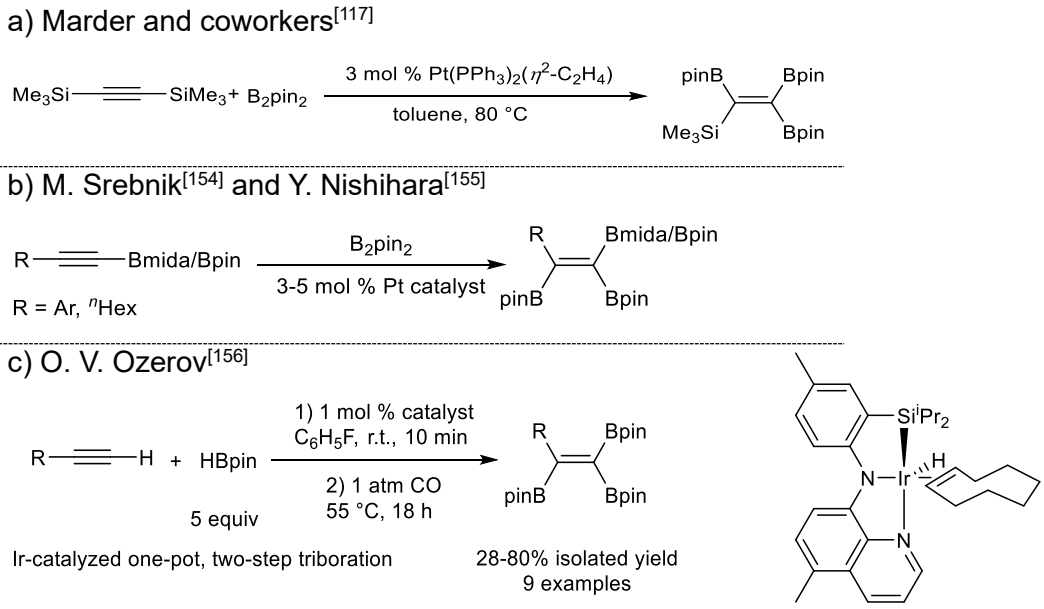
The syntheses of monoborylalkenes and diborylalkenes have been well established. Various alkenylboronates are conventionally available through hydroboration and diboration of alkynes and dehydrogenative borylation of alkenes. Synthesis of monoborylalkenes is typically accomplished by hydroboration of terminal or internal alkynes and is often promoted by metal catalysts, such as Rh,[55-59] Ru,[45, 47-48] Pd,[63-64, 162] Ti,[37-38] Ir,[58] Cu,[65, 67, 70-71, 73, 79-81, 84, 86] Ni,[55c] Fe,[41, 42b, 43-44] Au,[93-94] Al,[33-34, 163] Co,[50-52, 54] Mg,[35-36] and, in some cases, proceeds under metal-free conditions (Scheme 2-2a).[6c, 15b, 17, 20-23, 30-31, 164] In addition, metal-catalyzed dehydrogenative borylation of alkenes has been reported as a route to monoborylalkenes or *gem*-diborylalkenes (Scheme 2-2a).[137b, 144, 165] Diboration of alkynes is a particularly attractive tool for the synthesis of 1,2-diborylalkenes.[1a, 1b, 1f, 1j, 166] The first metal-catalyzed diboration of alkynes was reported by Suzuki and Miyaura in 1993 using a Pt catalyst,[113a] and significantly improved Pt catalyst systems were reported by the Marder group.[119] During the last few years, Pd,[112, 167] Cu,[125-126] Co,[52, 123] Fe[2c, 107], Zn[144] and metal-free[98-99, 104, 106, 168] systems were reported for the diboration of alkynes, which provide a practical and economic alternative to the Pt-catalyzed processes (Scheme 2-2b).[113, 117-118, 119, 121, 154] However, the availability of diverse multiborylalkenes is quite limited due to the lack of efficient and versatile synthetic methods. All of these methods, though useful, have limitations which do not provide access to certain types of multiborylalkenes.



Scheme 2-2. Synthesis of monoborylalkenes and diborylalkenes.

Interestingly, in 1996, in a previous study of the Marder group on Pt-catalyzed diboration of alkynes,[117] it was found that a novel 1,1,2-triborylalkene was formed

by desilylative boration and subsequent diboration of bis(trimethylsilyl)acetylene with B_2pin_2 (Scheme 2-3a). Since then, only two methods have been developed for the preparation of 1,1,2-triborylalkenes. One is the Pt-catalyzed diboration of alkynylboronates, which are usually synthesized using Grignard reagents or organolithium reagents (Scheme 2-3b).[154-155] Recently, Ozerov disclosed an Ir-catalyzed synthesis of 1,1,2-triborylalkenes via a two-step reaction of terminal alkynes with HBpin under an atmosphere of CO (Scheme 2-3c).[156] These methods suffer from major or minor drawbacks, such as weak functional group tolerance, tedious procedures or expensive catalysts. On the other hand, 1,1,2-triborylalkenes (**2-2a** and **2-2r**) have been shown to be potent Matrix Metalloproteinase-2 (MMP-2) inhibitors.[169] Therefore, the development of efficient and versatile chemical transformations for the synthesis of diverse multiborylated alkenes from easily available starting materials is highly desirable. This chapter reports a novel and straightforward Cu-catalyzed synthesis of 1,1,2-triborylalkenes from terminal alkynes.



Scheme 2-3. Synthesis of triborylalkenes.

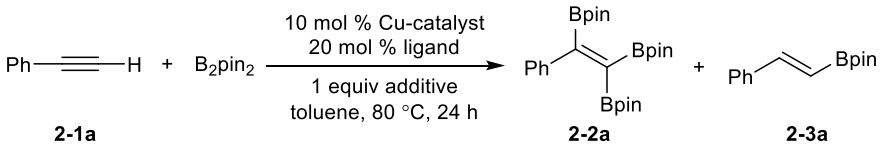
2.3 Results and discussion

2.3.1 Optimization of reaction conditions

Initial studies showed that triboration of phenylacetylene **2-1a** could be achieved in toluene at 80 °C in 38% isolated yield in the presence of $Cu(OAc)_2$, P^{n}Bu$_3$, the

diboron(4) reagent B_2pin_2, and $^iPr_2EtN$ (Hünig's base) as a stoichiometric additive, together with 32% monoborylalkene (Table 2-1), which was formed via competing hydroboration of the alkyne.

Table 2-1: Optimization of the reaction conditions.[a]



2-1a **2-2a** **2-3a**

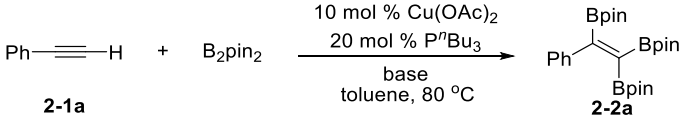
Entry	Catalyst	Ligand	Additive	Yield (2-2a)[b]	Yield (2-3a)[b]
1	$Cu(OAc)_2$	P^nBu_3	$^iPr_2EtN$	45% (38% [c])	32%
2	$Cu(OTf)_2$	P^nBu_3	$^iPr_2EtN$	0	2%
3	$CuCl_2$	P^nBu_3	$^iPr_2EtN$	0	0
4[c]	$CuCl_2$	P^nBu_3	$^iPr_2EtN$	42%	26%
5[c]	CuCl	P^nBu_3	$^iPr_2EtN$	22%	34%
6	CuOAc	P^nBu_3	$^iPr_2EtN$	29%	20%
7	$Cu(OAc)_2$	PPh_3	$^iPr_2EtN$	18%	40%
8	$Cu(OAc)_2$	PCy_3	$^iPr_2EtN$	33%	23%
9	$Cu(OAc)_2$	phen	$^iPr_2EtN$	trace	8%
10	$Cu(OAc)_2$	bpy	$^iPr_2EtN$	0	4%
11[d]	$Cu(OAc)_2$	P^nBu_3	$^iPr_2EtN$	14%	39%
12[e]	$Cu(OAc)_2$	P^nBu_3	$^iPr_2EtN$	31%	18%
13	$Cu(OAc)_2$	P^nBu_3	--	28% (16%)	28%
14	$Cu(OAc)_2$	P^nBu_3	benzophenone	48%	22%
15	$Cu(OAc)_2$	P^nBu_3	2-norbornene	59% (50%)	16%
16	$Cu(OAc)_2$	P^nBu_3	acrylonitrile	69% (66%)	12%
17[f]	$Cu(OAc)_2$	P^nBu_3	acrylonitrile	78% (73%)	11%
18[f]	$Cu(OAc)_2$	--	acrylonitrile	0	0
19[f]	--	P^nBu_3	acrylonitrile	0	0

[a] Reaction conditions: **2-1a** (0.2 mmol), B_2pin_2 (0.6 mmol), Cu-catalyst (0.02 mmol), ligand (0.04 mmol) and additive (0.2 mmol) in solvent (2 mL) at 80 °C. [b] Yields were determined by GC-MS analysis vs. *n*-dodecane as an internal calibration standard. Isolated yields are given in parentheses. [c] 20 mol % KOAc. [d] 60 °C. [e] 90 °C. [f] 4 h.

Screening of Cu catalyst precursors identified $Cu(OAc)_2$ as the most effective one (Table 2-1, entry 1). No desired product was observed using $Cu(OTf)_2$ or $CuCl_2$ (Table 2-1, entries 2 and 3). Addition of 20 mol % of KOAc to the $CuCl_2$ and CuCl systems was also effective, which indicated that AcO^- played an important role in this reaction and that the efficiency of a Cu(II) precursor was somewhat higher than Cu(I) (Table 2-1, entries 4 and 5). Further screening using other phosphine ligands, PPh_3 and PCy_3, afforded low yields of **2-2a** (Table 2-1, entries 7 and 8). Switching from phosphine ligands to nitrogen ligands, phen and bpy, gave no product (Table 2-1, entries 9 and 10). As depicted in entries 11 and 12, the yield dropped when the reaction was conducted at either 60 °C or 90 °C. In the absence of added Hünig's

base, a lower yield was obtained (Table 2-1, entry 13). To avoid the alkyne hydroboration side reaction, benzophenone, 2-norbornene and acrylonitrile, instead of Hünig's base, were used as hydrogen (B-H) acceptors.[165q, 165s, 165t] These results revealed that the desired product was formed in good yield when acrylonitrile was used (Table 2-1, entries 14-16). A high yield (73%) was obtained when the reaction time was decreased from 24 h to 4 h. As shown in entries 18 and 19, control reactions revealed that $Cu(OAc)_2$ and ligand were both essential for this reaction. Other screening details are listed in Tables 2-2 to 2-7 and Scheme 2-4.

Table 2-2: Screening of bases for the triboration of alkynes.[a]

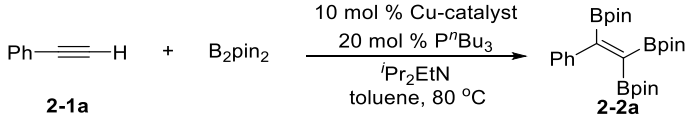


2-1a **2-2a**

Entry	Base (1 equiv)	Yield 2-2a[b]
1	4-picoline	21%
2	*N*,*N*-dimethylaniline	37%
3	DABCO	33%
4	LDA	-
5	-	28% (16%)
6	2,6-lutidine	32% (15%)
7	Et_3N	24%
9	$^{n}Pr_3N$	29%
10	$^{i}Pr_2EtN$ + *N*,*N*-dimethylaniline	36% (31%)
11	NaOAc	<10%
12	Na_2CO_3	<10%
13	Cs_2CO_3	0
14	NaOH	0
15	KOH	0
16	K_3PO_4	<10%

[a] Standard conditions: In an argon-filled glove box, **2-1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), $P^{n}Bu_3$ (20 mol %), base (1 equiv), B_2pin_2 (3 equiv), toluene (1 mL), at 80 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses.

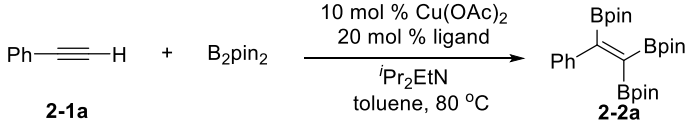
Table 2-3: Screening of Cu-catalysts for the triboration of alkynes.[a]



Entry	Catalyst (10 mol %)	Yield 2-2a[b]
1	$CuBr_2$	0
2	$Cu(NO_3)_2{\cdot}3H_2O$	0
3	$CuSO_4$	0
4	$Cu(acac)_2$	0
5[c]	$CuCl_2$	<10%
6	CuOAc	29% (31%)
7	CuI	0
8	CuCl	0
9	Cu_2O	0

[a] Standard conditions: In an argon-filled glove box, **2-1a** (0.2 mmol, 1 equiv), Cu-catalyst (10 mol %), P^{n}Bu$_3$ (20 mol %), DIPEA (1 equiv), B_2pin_2 (3 equiv), toluene (1 mL), at 80 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses. [c] 20 mol % of KOAc and 20 mol % of 18-crown-6 added.

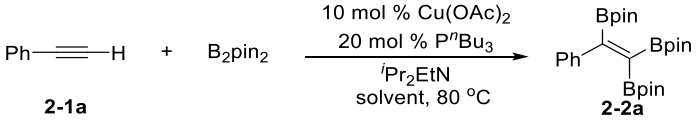
Table 2-4: Screening of ligands for the triboration of alkynes.[a]



Entry	Ligand (20 mol %)	Yield 2-2a[b]
1	TFP	25%
2	P(p-tolyl)$_3$	14%
3	P(o-tolyl)$_3$	0
4	P(1-naphthyl)$_3$	0
5	P^{t}Bu$_3$ (1M in toluene)	< 10%
6	DPPP	13%
7	Xantphos	0
8	DPPF	17%
9	TBP	0
10	Xphos	0

[a] Standard conditions: In an argon-filled glove box, **2-1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), ligand (20 mol %), DIPEA (1 equiv), B_2pin_2 (3 equiv), toluene (1 mL), at 80 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard.

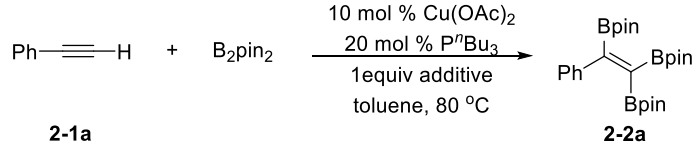
Table 2-5: Screening of solvents for the triboration of alkynes.[a]



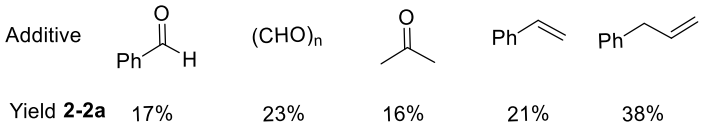
2-1a **2-2a**

Entry	Solvent (1 mL)	Yield 2-2a[b]
1	ethyl acetate	15%
2	MeCN	< 10%
3	MTBE	35%
4	THF	10%
5	hexane	16%
6	1,2-dioxane	14%
7	diethyl ether	30%
8	acetone	0

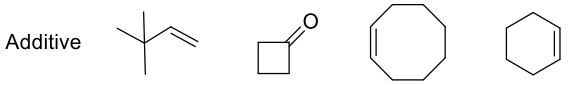
[a] Standard conditions: In an argon-filled glove box, **2-1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), P^nBu_3 (20 mol %), DIPEA (1 equiv), B_2pin_2 (3 equiv), solvent (1 mL), at 80 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard.



2-1a **2-2a**



Yield **2-2a** 17% 23% 16% 21% 38%

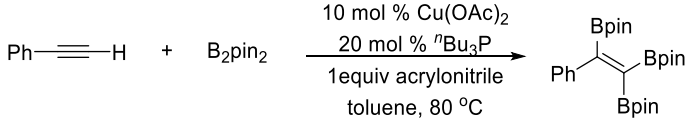


Yield **2-2a** 39% 34% 44% 57% (57%)[b]

[a] Standard conditions: In an argon-filled glove box, **2-1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), P^nBu_3 (20 mol %), B_2pin_2 (3 equiv), additives (1 equiv), toluene (1 mL), at 80 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses.

Scheme 2-4. Screening of additives for the triboration of alkynes.

Table 2-7: Screening of other conditions for the triboration of alkynes.[a]



2-1a **2-2a**

Entry	Catalyst	Ligand	Time/ h	T/ °C	Yield 2-2a[b]
1[c]	$Cu(OAc)_2$	P^nBu_3	24	80	42% (37%)
2	$Cu(OAc)_2$	P^nBu_3	14	80	49%
3	$Cu(OAc)_2$	P^nBu_3	14	r.t	0
4	$Cu(OAc)_2$	P^nBu_3	14	60	22%
5	$Cu(OAc)_2$	P^nBu_3	12	80	47% (44%)
6	$Cu(OAc)_2$	P^nBu_3	12	90	38%
7	$Cu(OAc)_2$	P^nBu_3	12	100	42%
8	$Cu(OAc)_2$	P^nBu_3	10	80	(60%)
9	$Cu(OAc)_2$	P^nBu_3	8	80	(51%)
10	$Cu(OAc)_2$	P^nBu_3	6	80	(52%)
11	$Cu(OAc)_2$	P^nBu_3	5	80	(52%)
12	$Cu(OAc)_2$	P^nBu_3	3	80	(39%)
13	$Cu(OAc)_2$	P^nBu_3	2	80	(60%)
14[d]	$Cu(OAc)_2$	P^nBu_3	4	80	(31%)
15[e]	$Cu(OAc)_2$	P^nBu_3	4	80	67% (59%)

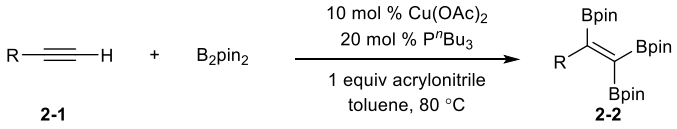
[a] Standard conditions: In an Ar-filled glove box, **2-1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), P^nBu_3 (20 mol %), B_2pin_2 (3 equiv), acrylonitrile (1 equiv), toluene (1 mL). [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses. [c] $^i Pr_2EtN$ (1 equiv). [d] Without acrylonitrile. [e] P^nBu_3 (10 mol %)

2.3.2 Investigation of reaction scope

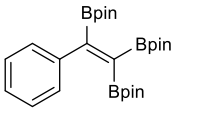
With the optimized reaction conditions in hand, the triboration of a wide variety of terminal alkynes **2-1** was tested (Table 2-8). A range of both donor- and acceptor-substituted aromatic alkynes were found to work well, affording the corresponding triborylalkenes in moderate to good yields (**2-2a** to **2-2m**). Arylalkynes bearing electron-donating functionalities such as Me, OMe and NMe_2 reacted with B_2pin_2 smoothly to yield the corresponding triborylalkenes (35-72% isolated yields). F-, Cl-, and CF_3-substituted arylalkynes were all viable substrates giving moderate to high yields (47-72%) of **2-2**. In particular, the tolerance of halide substituents, such as F and Cl, provided possibilities for further functionalization. Unfortunately, substrates bearing strong electron-withdrawing groups, e.g. CN and CO_2Me, were not well tolerated in this system (**2-2h** and **2-2i**).[170] The isolated yields obtained for *para*-substituted arylalkynes were higher than those for *meta*- and *ortho*-substituted substrates (e.g. compare **2-2b**/**2-2c**, **2-2d**/**2-2e**/**2-2f**, and **2-2j**/**2-2k**). Polyaromatic and heteroaromatic substrates, *e.g.* 2-ethynyl-6-methoxynaphthalene and 3-ethynylthiophene, reacted to give the desired products in moderate and good yields

(**2-2n** 49% and **2-2o** 61%, respectively).

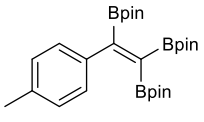
Table 2-8: Scope of the triboration of terminal alkynes.[a]



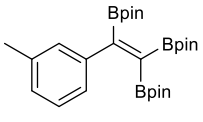
2-1 **2-2**



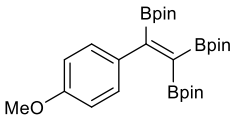
2-2a
4 h, 73% (48%)[b]



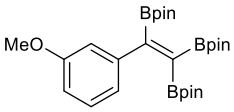
2-2b
4 h, 72%



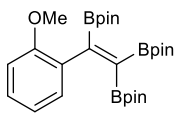
2-2c
4 h, 58%



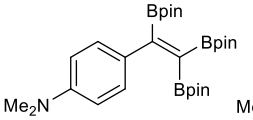
2-2d
4 h, 70%



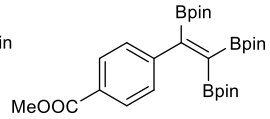
2-2e
4 h, 58%



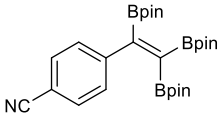
2-2f
4 h, 49%



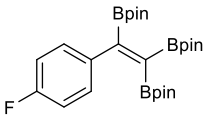
2-2g
4 h, 35%



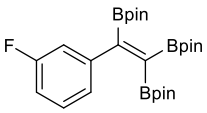
2-2h
6 h, trace



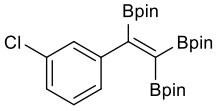
2-2i
4 h, 8 h, trace



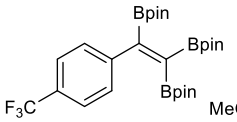
2-2j
6 h, 72%



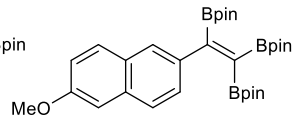
2-2k
6 h, 59%



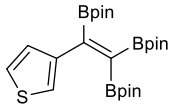
2-2l
6 h, 56%



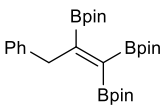
2-2m
4 h, 47%



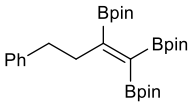
2-2n
8 h, 49%



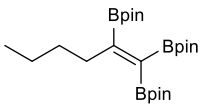
2-2o
6 h, 61%



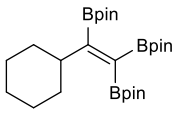
2-2p
8 h, 69%



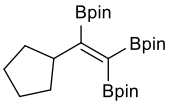
2-2q
8 h, 74%



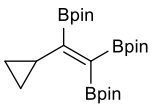
2-2r
6 h, 58%



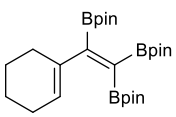
2-2s
4 h, 71%



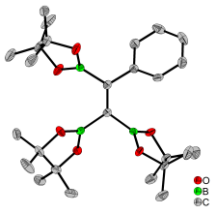
2-2t
4 h, 64%



2-2u
4 h, 54%



2-2v
4 h, 52%



Molecular structure of **2-2a**[c]

[a] Reaction conditions: **2-1** (0.2 mmol), B_2pin_2 (0.6 mmol), $Cu(OAc)_2$ (0.02 mmol), P^nBu_3 (0.04 mmol) and acrylonitrile (0.2 mmol) in toluene at 80 °C. Isolated yields. [b] The reaction was performed on a 5 mmol scale. [c] H atoms are omitted for clarity.

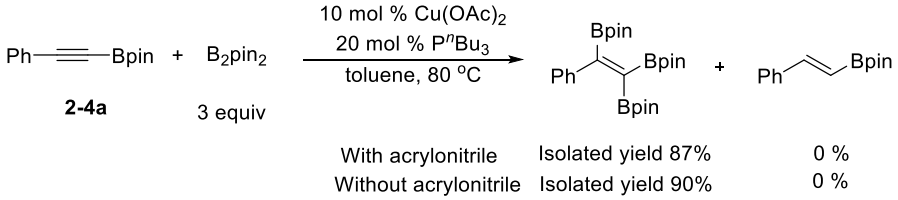
Furthermore, both linear alkyl- and cycloalkyl-substituted alkynes also afforded the desired products in good yields (**2-2p** to **2-2u**, 54-74%). Even though **2-1u** has a high degree of ring strain, the cyclopropyl moiety was retained after the reaction, providing the target product **2-2u** in a slightly lower yield (54%) than its cyclopentyl

2-2t and cyclohexyl analogues **2-2s** (64% and 71%, respectively). Conjugated 1,3-enyne 1-ethynylcyclohexene was also tested, and boration occurred only at the triple bond, giving **2-2v** in 52% yield, which indicated the high chemoselectivity of this reaction. The structure of the triborylalkene products was exemplified by a single-crystal X-ray diffraction study of **2-2a** (Table 2-8, bottom). To highlight the practicality of this method, this reaction was carried out on a gram-scale, affording **2-2a** in 48% yield.

2.4 Mechanistic study

2.4.1 Evidence for an alkynylboronate intermediate

It is proposed that an alkynylboronate is an intermediate in this reaction. Indeed, when using alkynylboronate **2-4a** as the starting material, under standard conditions (with or without added acrylonitrile), the 1,1,2-triborylalkene was isolated in 87% yield and no by-product was observed (Scheme 2-5). Monitoring a reaction by *in situ* ^{19}F NMR spectroscopy and GC-MS (Figures 2-1 to 2-3) showed that the alkyne substrate was converted into the alkynylboronate from which the final 1,1,2-triborylalkene product was subsequently formed.



Scheme 2-5: Diboration of alkynylboronate.

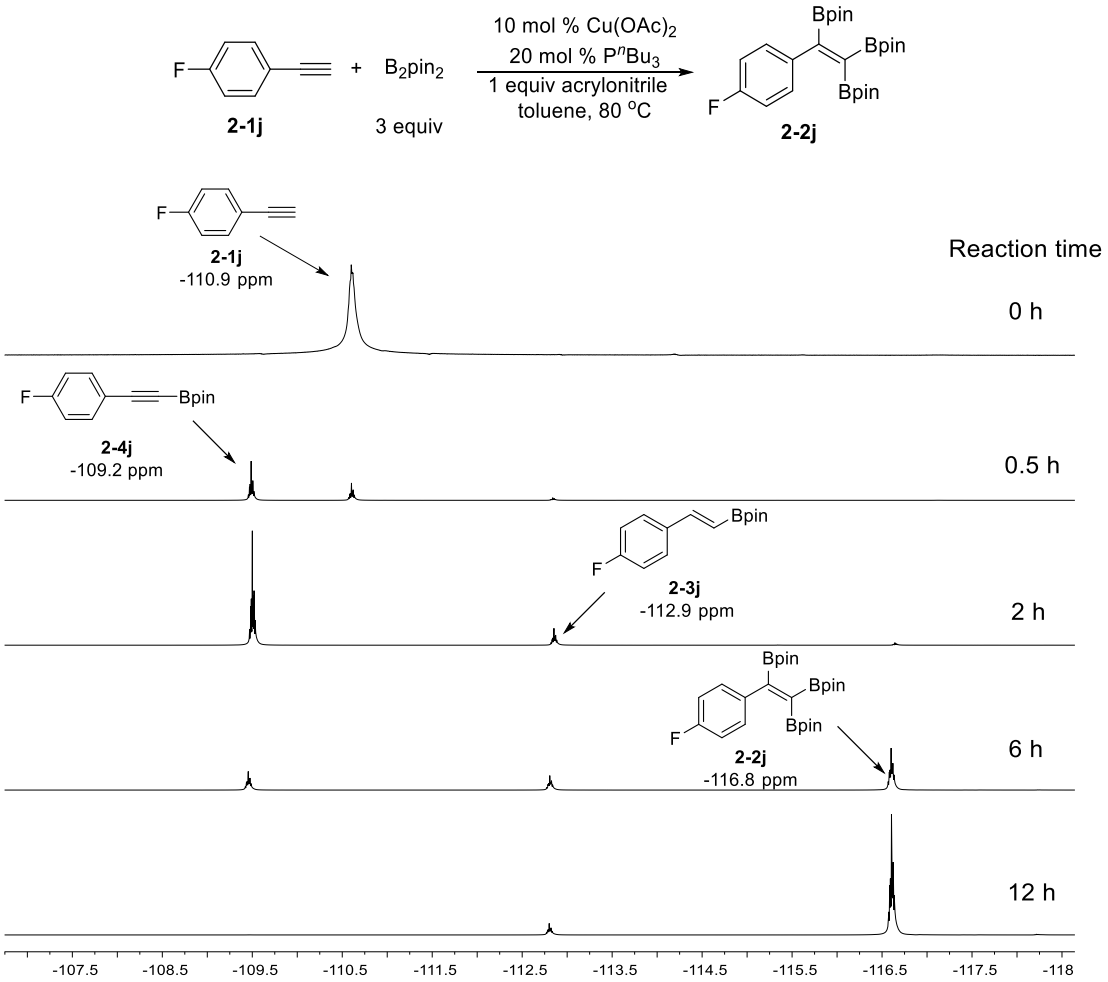


Figure 2-1. Reaction progress monitored by *in situ* ^{19}F NMR spectroscopy (471 MHz).

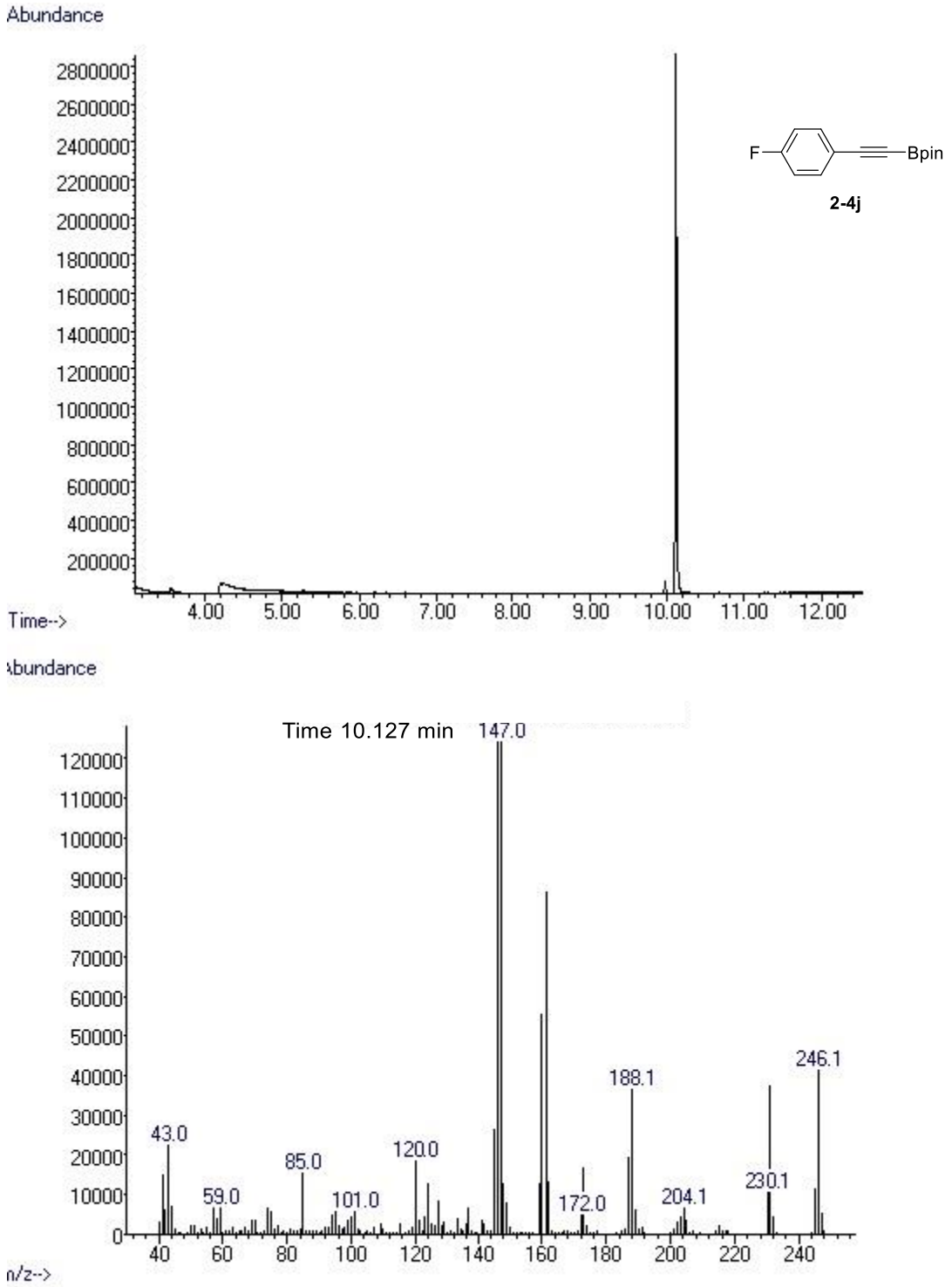
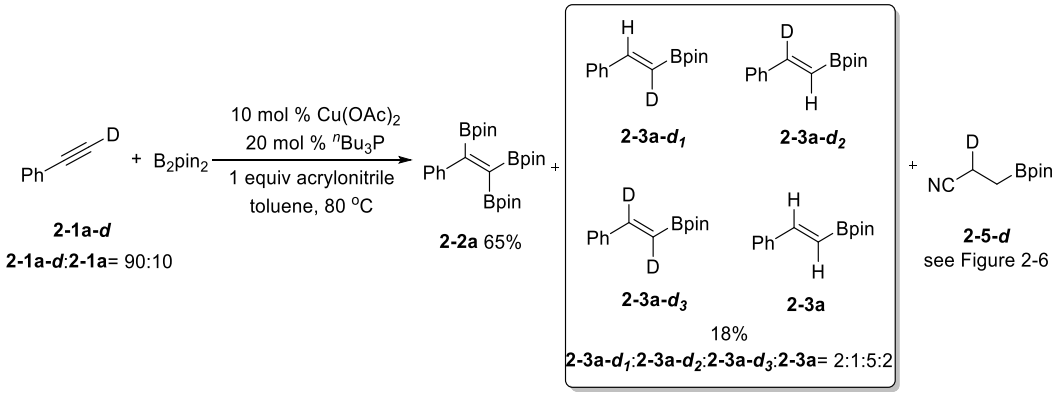


Figure 2-2. GC-MS of an authentic sample of **2-4j** (m/z for $C_{14}H_{16}BFO_2$ $[M]^+$ calcd: 246, found: 246) prepared using the method described in literature.[69b]

Figure 2-3. ^{19}F NMR (471 MHz, toluene) spectrum of authentic **2-4j** (δ -109.0; td, J = 9, 5 Hz).

2.4.2 Deuterium labeling studies

Deuterium labeling studies were conducted using 1-deutero-2-phenylethyne **2-1a-*d*** as the substrate (the level of deuterium content was 90%, as shown below in Figure 2-4) under the standard reaction conditions (Scheme 2-6).[171] The reaction gave **2-3a-*d*$_1$**, **2-3a-*d*$_2$**, **2-3a-*d*$_3$**, and **2-3a** in a 2:1:5:2 ratio (see NMR spectrum in Figure 2-5). HRMS analysis indicated the formation of **2-5-*d*** (see Figure 2-6).



Scheme 2-6. Deuterium labeling studies.

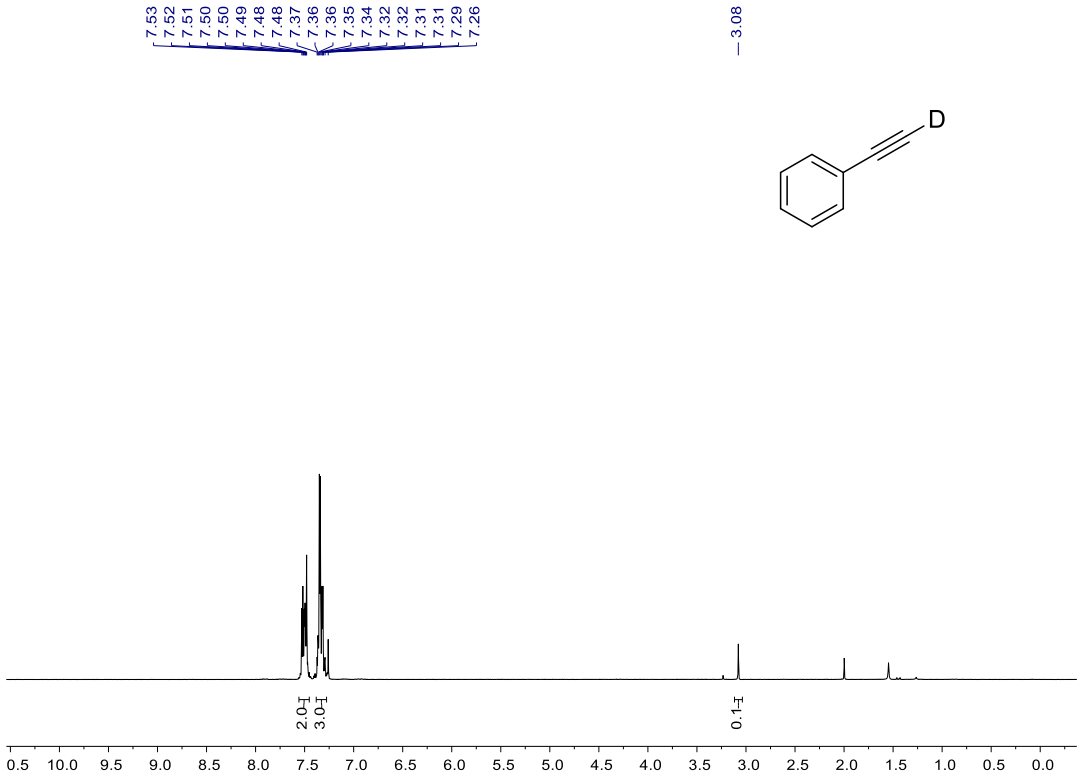


Figure 2-4. ^{1}H NMR spectrum of **2-1a-*d*** (200 MHz, $CDCl_3$).

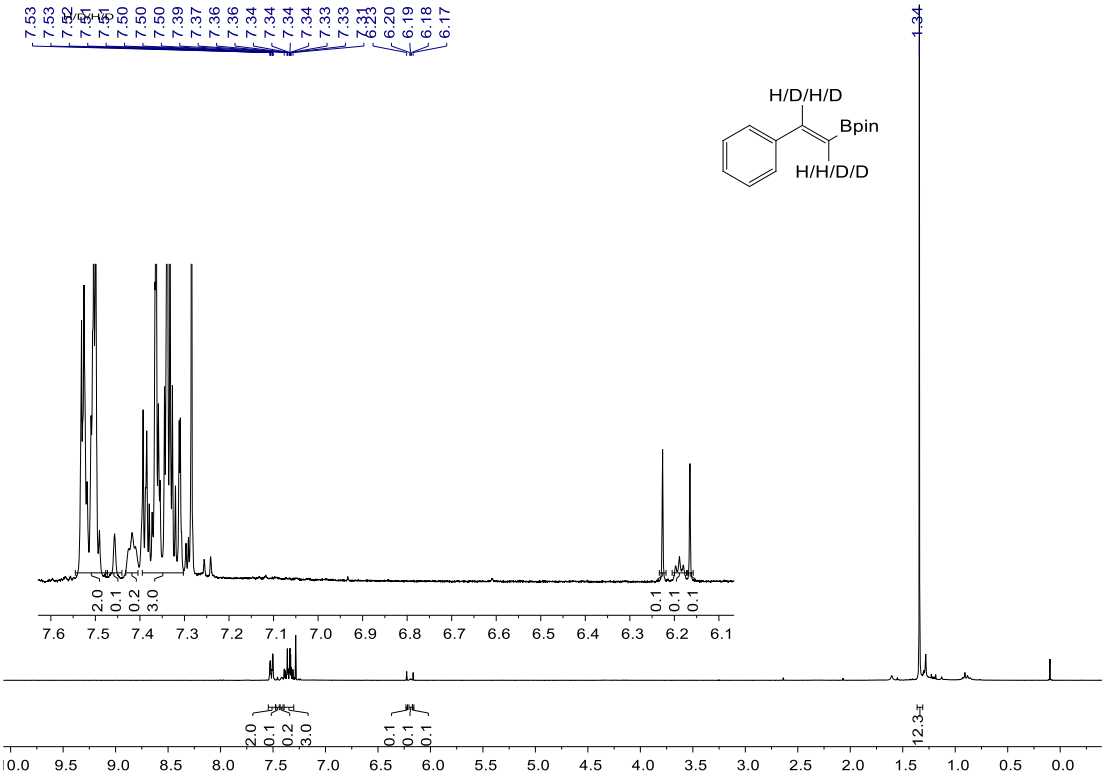


Figure 2-5. ^{1}H NMR spectrum of **2-3a** (300 MHz, $CDCl_3$).

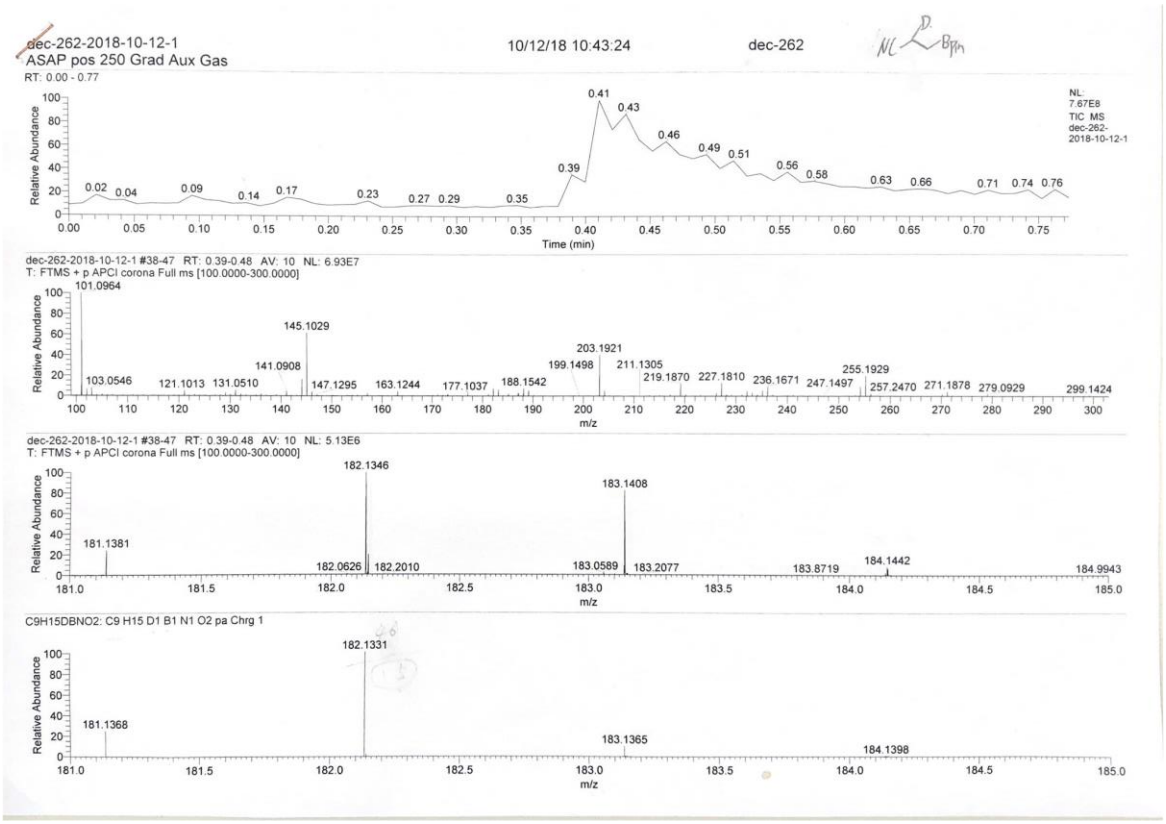


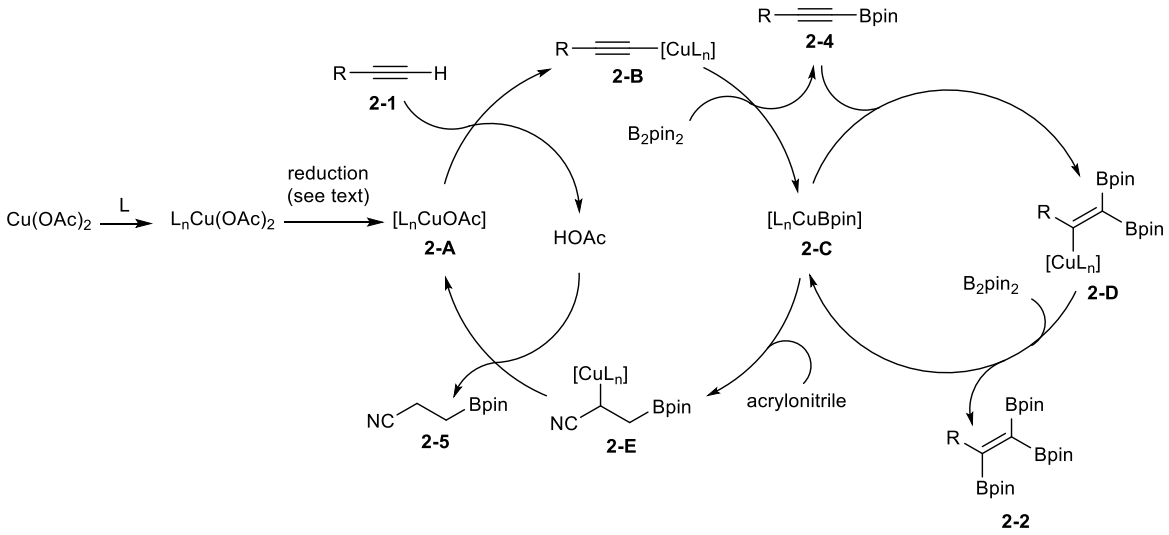
Figure 2-6. HRMS (ASAP) of **2-5-*d***: m/z for $C_9H_{15}DBNO_2$ [M^+] calcd: 182.1331, found: 182.1346.

The above result indicated that electron-deficient alkenes were more reactive than alkynes for hydroboration and acted as a sacrificial borane (HBpin) scavenger to drive catalysis toward triboration of alkynes and away from hydroboration.

2.4.3 Plausible mechanism

On the basis of the experimental observations and precedents regarding related catalytic dehydrogenative borylation processes,[69b, 134, 140, 143] a plausible mechanism is shown in Scheme 2-7. The terminal alkyne reacts with [L_nCuOAc],[172][173] which is formed from $Cu(OAc)_2$ and a phosphine ligand, followed by reduction,[126, 174] to afford the alkynylcopper intermediate **2-B**.[175] Intermediate **2-B** undergoes σ-bond metathesis with B_2pin_2 to afford the alkynylboronate **2-4**, as well as the copper-boryl complex **2-C**.[69, 176] Insertion of alkynylboronate **2-4** into a Cu-B bond in **2-C** generates alkenylcopper species **2-D**, which undergoes σ-bond metathesis with B_2pin_2 to give the desired 1,1,2-triborylalkene **2-2**.[126] Hydroboration of acrylonitrile is faster than that of alkynes, which suppresses the

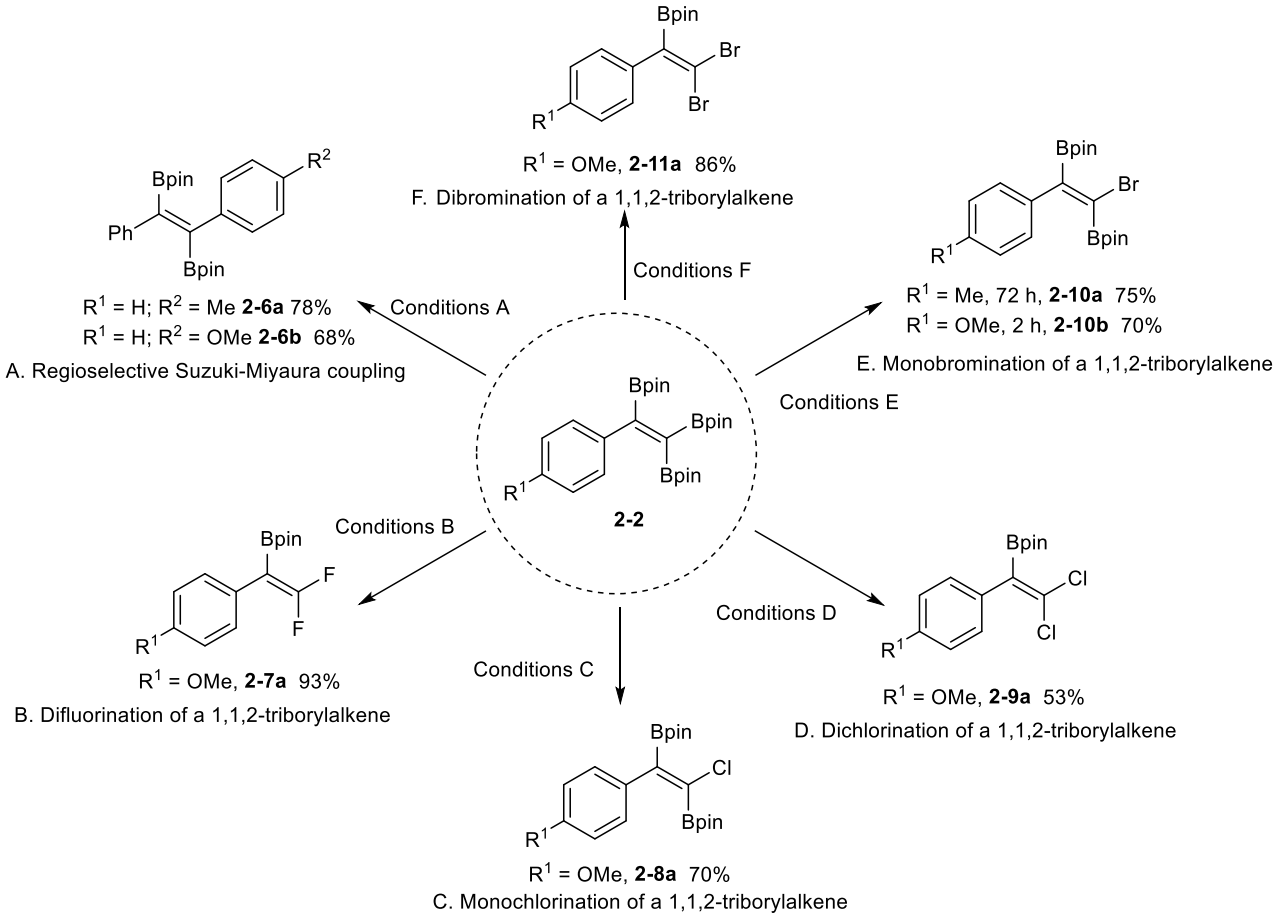
alkyne hydroboration side reaction and improves the efficiency of the triboration process. Byproduct **2-5** could be formed from alkylcopper intermediate **2-E**, which is generated by insertion of acrylonitrile into the C-B bond of **2-C**.



Scheme 2-7. Proposed mechanism of the catalytic triboration reaction.

2.5 Synthetic applications of 1,1,2-triborylalkenes

In order to explore the versatility of 1,1,2-triborylalkenes in synthesis, a Suzuki-Miyaura cross-coupling reaction of the triborated product **2-2** with aryl iodides was conducted. The 1,1,2-triborylalkene reacted selectively to form a new C-C bond providing *trans*-diaryldiborylalkene **2-6** (Scheme 2-8A). The *E*-configuration of **2-6b** was confirmed by single-crystal X-ray diffraction (Figure 2-8). Compound **2-2d** reacted selectively with Selectfluor® affording *gem*-difluoroborylalkene **2-7a** in 93% isolated yield (Scheme 2-8B). Only two examples were reported previously for the synthesis of this type of product, but small quantities of borylated fluoroalkenes were observed using polyfluoroalkenes as substrates.[177] In addition, treatment of **2-2** with *N*-chlorosuccinimide (NCS) or *N*-bromosuccinimide (NBS) furnished selectively either monohalo-diborylated alkene (Cl and Br, **2-8** and **2-10**) or dihalo-monoborylated alkene (Cl and Br, **2-9** and **2-11**) products in good yields, depending on the amount of NCS and NBS added and the reaction time. The structure of **2-10b** was confirmed by single-crystal X-ray diffraction (Figure 2-9). This is the first time that products of these types (**2-8** to **2-11**) have been prepared, which clearly have potential for further use in cross-coupling and other reactions.



Conditions A: 4-R^2-C_6H_4-I (1 equiv), $Pd(PPh_3)_4$ (10 mol %), K_3PO_4 (2 equiv), H_2O (7 equiv), THF, 70 °C, 24 h; conditions B: Selectfluor® (3 equiv), $NaHCO_3$ (2.2 equiv), CH_3CN, r.t., 6 h; conditions C: NCS (1.3 equiv), 60 °C, CH_3CN, 12 h; conditions D: NCS (2 equiv), 60 °C, CH_3CN, 48 h; conditions E: NBS (1.3 equiv), r.t., CH_3CN; conditions F: NBS (2 equiv), r.t., CH_3CN, 72 h.

Scheme 2-8. Synthetic applications of 1,1,2-triborylalkenes with isolated yields.

2.6 Summary

In conclusion, a convenient Cu-catalyzed triboration of terminal alkynes was developed. A variety of functional groups are tolerated, and diverse 1,1,2-trisborylalkenes were obtained in moderate to good yields. The products were applied in the synthesis of unsymmetrically substituted *trans*-diaryldiborylalkenes and haloborylalkenes, which are expected to serve as useful building blocks.

2.7 Experimental procedure and characterization data

2.7.1 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 AllyChem Co. Ltd. (Dalian, China). HPLC grade solvents were argon saturated and 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. All manipulations in this paper were performed in an argon-filled glove box.

Products were purified by silica gel columns using $B(OH)_3$-impregnated SiO_2 to suppress over-adsorption on the silica gel. 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 40 °C.

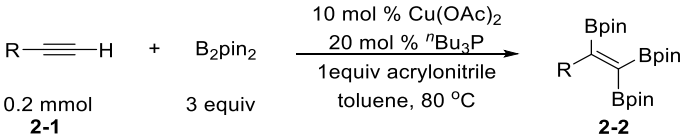
GC-MS analyses were performed using an Agilent 7890A gas chromatograph (column: HP-5MS 5% phenyl methyl siloxane, 30 m, ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 80 °C (2 min), 80 °C to 180 °C (20 °C min^{-1}), 180 °C to 280 °C (50 °C min^{-1}), 280 °C (5 min); carrier gas: He (1.2 mL min^{-1})) equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A series auto sampler/injector. Elemental analyses were performed on a Leco CHNS-932 Elemental Analyzer. High-resolution mass spectra were recorded using a Thermo Fischer Scientific Exactive Plus Orbitrap MS system (ASAP, ESI or HESI probe).

All NMR spectra were recorded at ambient temperature using Bruker DRX-300 (^{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, 471 MHz) spectrometers. ^{1}H NMR chemical shifts are reported relative to TMS and were referenced *via* the residual proton resonance of the deuterated solvent ($CDCl_3$: 7.26 ppm) whereas ^{13}C{^{1}H} NMR spectra are reported relative to TMS *via* the carbon signal of the deuterated solvent ($CDCl_3$: 77.00 ppm). ^{11}B NMR chemical shifts are quoted relative to $BF_3{\cdot}Et_2O$ as

the external standard. ^{19}F NMR chemical shifts are quoted relative to $CFCl_3$ as the external standard.

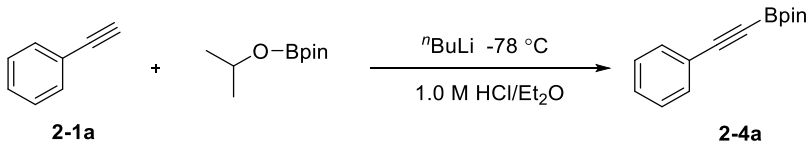
2.7.2 Experimental procedures

2.7.2.1 Synthesis of 1,1,2-triborylalkenes (2-2)



In a glove box, to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, $Cu(OAc)_2$ (10 mol %, 3.6 mg, 0.02 mmol), B_2pin_2 (3 equiv, 152.4 mg, 0.6 mmol) and toluene (1 mL) were added. Then, alkynes **2-1** (0.2 mmol), acrylonitrile (10.6 mg, 13 μL, 0.2 mmol) and P^{n}Bu$_3$ (8.1 mg, 9.9 μL, 0.04 mmol) were added in that order and the tube was sealed with a crimped septum cap. The reaction was heated at 80 °C under argon for the indicated amount of time. The reaction mixture was then diluted with Et_2O (4 mL) and filtered through a plug of celite (ø 3 mm × 8 mm) in air with copious washing (Et_2O). The solvents were removed *in vacuo*, and the residue was purified by column chromatography on silica gel (pentane: ethyl acetate = 25:1).

2.7.2.2 Synthesis of 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (2-4a)



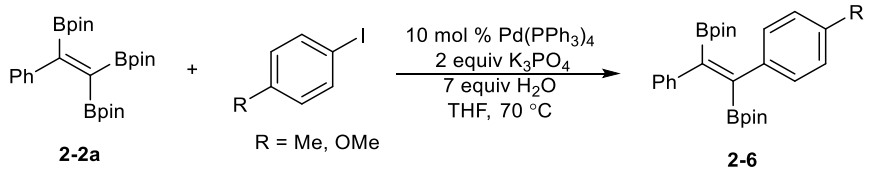
A solution of phenylacetylene (1.32 mL, 12 mmol) in THF (30 mL) in a 50 mL Schlenk tube was cooled to –78 °C and, under an argon atmosphere ^{n}BuLi (7.5 mL, 1.6 M hexane solution, 12 mmol) was added dropwise. The reaction mixture was stirred at –78 °C for 1 h. The resulting reaction mixture was then added to a solution of 4,4,5,5-tetramethyl-2-(isopropoxy)-1,3,2-dioxaborolane (2.04 mL, 10 mmol) in THF (30 mL) at –78 °C. After being stirred at –78 °C for 2 h, the reaction mixture was quenched with 1.0 M HCl/Et_2O (12.6 mL, 12.6 mmol), and the mixture was warmed to room temperature with additional stirring for 1 h. Filtration and

evaporation afforded a pale yellow oil. Bulb to bulb distillation (160 °C/2 Torr) gave **2-4a** (1.98 g, 8.7 mmol, 87% yield) as a white solid.[178]

2.7.2.3 Evidence for the formation of R-C_6H_4-C≡C-Bpin (2-4j, R = F) as a reaction intermediate

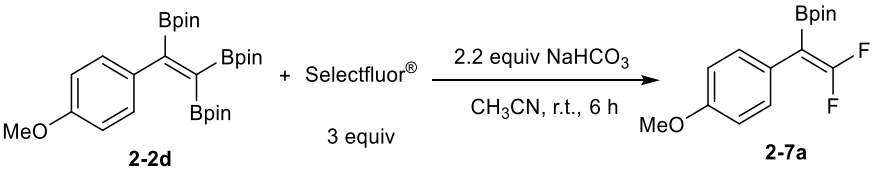
In a Young's tap NMR tube, $Cu(OAc)_2$ (10 mol %, 1.8 mg, 0.01 mmol), B_2pin_2 (3 equiv, 76.2 mg, 0.3 mmol) and toluene (0.7 mL) were added. Then, alkyne **2-1j** (12 mg, 0.1 mmol), acrylonitrile (5.3 mg, 6.5 μL, 0.1 mmol) and P^{n}Bu$_3$ (4 mg, 4.5 μL, 0.02 mmol) were added in this order. The mixture was kept under argon at 80 °C. The formation of **2-4j** was detected by *in situ* ^{19}F NMR spectroscopy and GC-MS.

2.7.2.4 Synthesis of *trans*-diaryldiborylalkenes (2-6)



In a glove box, a tube (20 mL) containing $Pd(PPh_3)_4$ (30 mg, 0.026 mol), **2-2a** (129 mg, 0.26 mmol), and aryl iodides (0.26 mmol) was capped with a septum, and the system was evacuated and purged with argon three times. Dry THF (3 mL) and degassed aqueous K_3PO_4 (520 μL, 1.5 M, 0.78 mmol) were transferred to the system via syringes, and the mixture was stirred at 70 °C for 24 h. After cooling to room temperature, the mixture was filtered through a pad of celite and washed through with Et_2O (25 mL). The filtrate was concentrated under vacuum, the residue was purified by flash column chromatography (ethyl acetate: hexanes = 1:10) to yield a white solid.

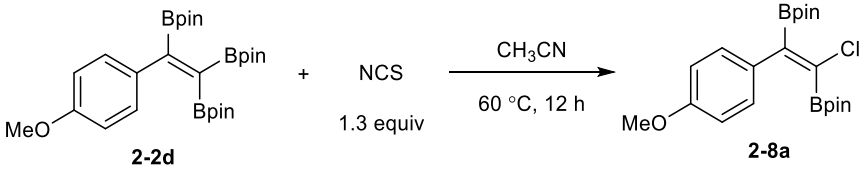
2.7.2.5 Synthesis of *gem*-difluoroborylalkene (2-7a)



To a solution of **2-2d** (102.4 mg, 0.2 mmol) in MeCN (2 mL), under argon, Selectfluor® (212.6 mg, 3 equiv) and $NaHCO_3$ (38.2 mg, 2.2 equiv) were added and the reaction mixture was stirred at r.t. for 7 h. The mixture was filtered through a

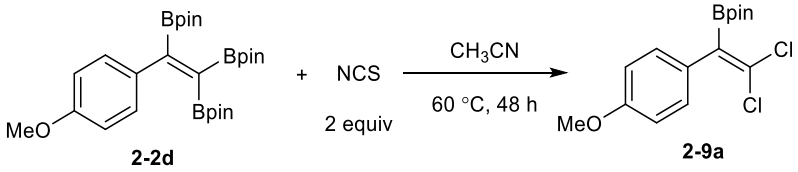
pad of celite and washed through with CH_2Cl_2 (25 mL). Then, the solvent was removed under reduced pressure at room temperature. The residue was purified by column chromatography on silica gel (*n*-pentane: ethyl acetate = 100:1) to yield 55 mg (93%) of a colorless liquid **2-7a**.

2.7.2.6 Synthesis of monochlorodiborylated alkene (2-8a)



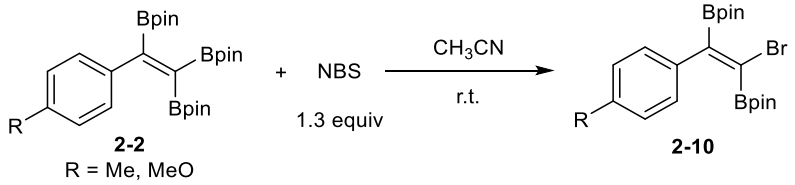
To a solution of **2-2d** (102.4 mg, 0.2 mmol) in MeCN (1 mL) under argon and protected from light was added NCS (35 mg, 1.3 equiv). The reaction mixture was stirred at 60 °C for 12 h. The mixture was filtered through a pad of celite and washed through with CH_2Cl_2 (25 mL). Then, the solvent was removed under reduced pressure at room temperature. The residue was purified quickly by column chromatography on silica gel (*n*-pentane: ethyl acetate = 50:1) to give the product **2-8a** as a white solid (59 mg, 70%).

2.7.2.7 Synthesis of *gem*-dichloroborylalkene (2-9a)



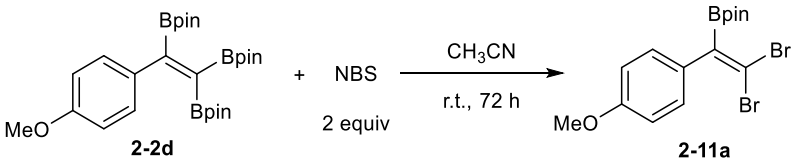
To a solution of **2-2d** (102.4 mg, 0.2 mmol) in MeCN (1 mL) under argon and protected from light was added NCS (53.4 mg, 2 equiv). The reaction mixture was stirred at 60 °C for 48 h. The mixture was filtered through a pad of celite and washed through with CH_2Cl_2 (25 mL). Then, the solvent was removed under reduced pressure at room temperature. The residue was purified quickly by column chromatography on silica gel (*n*-pentane: diethyl ether = 100:1) to yield 34 mg (53%) of a colorless liquid **2-9a**.

2.7.2.8 Synthesis of monobromodiborylated alkenes (2-10)



To a solution of **2-2** (0.2 mmol) in MeCN (1 mL) under argon and protected from light was added *N*-bromosuccinimide (46.3 mg, 1.3 equiv). The reaction mixture was stirred at r.t. for 2 h (R = MeO) or 72 h (R = Me), and then washed with a saturated solution of $Na_2S_2O_3$ (10 mL). The organic phase was extracted with CH_2Cl_2 (3 x 10 mL), dried over $MgSO_4$ and filtered. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (*n*-pentane: ethyl acetate = 50:1) to give the product **2-10**.

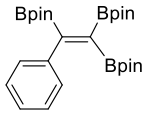
2.7.2.9 Synthesis of *gem*-dibromoborylalkene (2-11a)



To a solution of **2-2d** (102.4 mg, 0.2 mmol) in MeCN (1 mL) under argon and protected from light was added *N*-bromosuccinimide (71.2 mg, 2 equiv). The reaction mixture was stirred at r.t. for 72 h. The mixture was filtered through a pad of celite and washed through with CH_2Cl_2 (25 mL). Then the solvent was removed under reduced pressure at room temperature. The residue was purified quickly by column chromatography on silica gel (*n*-pentane: diethyl ether = 20:1) to yield 74 mg (86%) of a colorless liquid **2-11a**.

2.7.3 Characterization data for products

2,2',2''-(2-phenylethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2a)



Isolated yield: 73%.

White solid, m.p.: 244.8 °C. Its spectroscopic data are consistent with a literature report.[156]

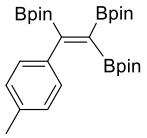
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 – 7.26 (m, 2H), 7.24 – 7.20 (m, 2H), 7.19 – 7.15 (m, 1H), 1.30 (s, 12H), 1.27 (s, 12H), 1.08 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 145.2, 127.7, 127.6, 126.6, 83.8, 83.4, 83.1, 24.9, 24.8, 24.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 30.9.

HRMS (ASAP): m/z for $C_{26}H_{42}B_3O_6$ $[M+H]^+$ calcd: 483.3255, found: 483.3245.

2,2',2''-(2-(p-tolyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2b)



Isolated yield: 72%.

White solid, m.p.: 230.9 °C. Its spectroscopic data are consistent with a literature report.[156]

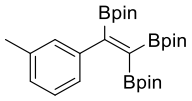
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.18 (d, J = 8 Hz, 2H), 7.03 (d, J = 8 Hz, 2H), 2.29 (s, 3H), 1.30 (s, 12H), 1.27 (s, 12H), 1.10 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 142.3, 136.3, 128.3, 127.6, 83.8, 83.4, 83.1, 24.9, 24.8, 24.5, 21.2. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{27}H_{44}B_3O_6$ $[M+H]^+$ calcd: 497.3412, found: 497.3402.

2,2',2''-(2-(m-tolyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2c)



Isolated yield: 58%.

White solid, m.p.: 230.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.1 – 7.1 (m, 1H), 7.1 – 7.1 (m, 2H), 7.0 – 7.0 (m, 1H), 2.28 (s, 3H), 1.30 (s, 12H), 1.27 (s, 12H), 1.09 (s, 12H).

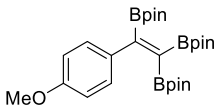
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 145.1, 136.8, 128.5, 127.5, 127.5, 124.7, 83.8, 83.4, 83.1, 24.9, 24.8, 24.5, 21.4. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{27}H_{44}B_3O_6$ $[M+H]^+$ calcd: 497.3412, found: 497.3414.

Anal. Calcd for $C_{27}H_{43}B_3O_7$: C, 65.37; H, 8.74; found: C, 65.28; H, 8.54.

2,2',2''-(2-(4-methoxyphenyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2d)



Isolated yield: 70%.

White solid, m.p.: 137.1 °C. Its spectroscopic data are consistent with a literature report.[156]

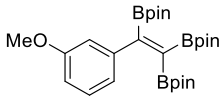
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 (d, J = 9 Hz, 2H), 6.78 (d, J = 9 Hz, 2H), 3.77 (s, 3H), 1.30 (s, 12H), 1.27 (s, 12H), 1.11 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 158.7, 137.9, 129.0, 113.1, 83.8, 83.3, 83.1, 55.2, 24.9, 24.8, 24.6. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 30.4.

HRMS (ASAP): m/z for $C_{27}H_{44}B_3O_7$ $[M+H]^+$ calcd: 513.3361, found: 513.3353.

2,2',2''-(2-(3-methoxyphenyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2e)



Isolated yield: 58%.

White solid, m.p.: 217.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.2 – 7.1 (m, 1H), 6.9 (ddd, J = 8, 2, 1 Hz, 1H), 6.8 (dd, J = 3, 2 Hz, 1H), 6.7 (ddd, J = 8, 3, 1 Hz, 1H), 3.77 (s, 3H), 1.30 (s, 12H), 1.27 (s, 12H), 1.08 (s, 12H).

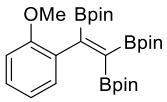
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 158.9, 146.7, 128.6, 120.1, 113.0, 112.7, 83.8, 83.4, 83.2, 55.0, 24.9, 24.8, 24.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{27}H_{44}B_3O_7$ $[M+H]^+$ calcd: 513.3361, found: 513.3362.

Anal. Calcd for $C_{27}H_{43}B_3O_7$: C, 63.33; H, 8.46; found: C, 63.45; H, 8.71.

2,2',2''-(2-(2-methoxyphenyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2f)



Isolated yield: 49%.

White solid, m.p.: 166.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17 – 7.09 (m, 2H), 6.80 (apparent td, J = 7, 1 Hz, 1H), 6.75 (dd, J = 8, 1 Hz, 1H), 3.73 (s, 3H), 1.31 (s, 12H), 1.25 (s, 12H), 1.06 (s, 12H).

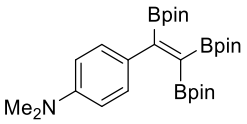
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 156.4, 135.2, 129.8, 128.1, 120.3, 109.8, 83.5, 83.3, 83.0, 55.1, 24.9, 24.7, 24.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 31.0.

HRMS (ASAP): m/z for $C_{27}H_{44}B_3O_7$ $[M+H]^+$ calcd: 513.3361, found: 513.3357.

Anal. Calcd for $C_{27}H_{43}B_3O_7$: C, 63.33; H, 8.46; found: C, 63.05; H, 8.56.

_N_,_N_-dimethyl-4-(1,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (2-2g)



Isolated yield: 35%.

White solid, m.p.: 220.3 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22 (d, J = 9 Hz, 2H), 6.62 (d, J = 9 Hz, 2H), 2.91 (s, 6H), 1.29 (s, 12H), 1.28 (s, 12H), 1.14 (s, 12H).

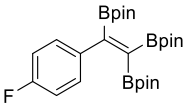
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 149.8, 134.0, 128.7, 112.0, 83.6, 83.1, 82.9, 40.7, 24.9 (2C), 24.6. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 30.4.

HRMS (ASAP): m/z for $C_{28}H_{47}B_3NO_6$ $[M+H]^+$ calcd: 526.3677, found: 526.3672.

Anal. Calcd for $C_{28}H_{46}B_3NO_6$: C, 64.05; H, 8.83; N, 2.67; found: C, 63.91; H, 9.03; N, 2.63.

2,2',2''-(2-(4-fluorophenyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2j)



Isolated yield: 72%.

White solid, m.p.: 235.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26-7.21 (m, 2H), 6.95-6.88 (m, 2H), 1.30 (s, 12H), 1.26 (s, 12H), 1.09 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 162.0 (d, J = 245 Hz), 141.2 (d, J = 4 Hz), 129.4 (d, J = 8 Hz), 114.3 (d, J = 21 Hz), 84.0, 83.5, 83.2, 24.9, 24.8, 24.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

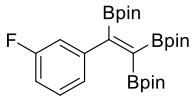
^{11}B NMR (160 MHz, $CDCl_3$): δ = 30.7.

^{19}F NMR (471 MHz, $CDCl_3$): δ = -116.7 (tt, J = 9, 6 Hz).

HRMS (ASAP): m/z for $C_{26}H_{41}B_3F_1O_6$ $[M+H]^+$ calcd: 501.3161, found: 501.3156.

Anal. Calcd for $C_{26}H_{40}B_3F_1O_6$: C, 62.45; H, 8.06; found: C, 62.96; H, 8.19.

2,2',2''-(2-(3-fluorophenyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2k)



Isolated yield: 59%.

White solid, m.p.: 196.0 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19 (td, J = 8, 6 Hz, 1H), 7.04 (ddd, J = 8, 2, 1 Hz, 1H), 6.99 (ddd, J = 10, 3, 2 Hz, 1H), 6.87 (dddd, J = 9, 8, 3, 1 Hz, 1H), 1.31 (s, 12H), 1.27 (s, 12H), 1.10 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 162.3 (d, J = 245 Hz), 147.4 (d, J = 7 Hz), 129.0 (d, J = 8 Hz), 123.5 (d, J = 3 Hz), 114.7 (d, J = 21 Hz), 113.4 (d, J = 21 Hz), 84.0, 83.5, 83.3, 24.9, 24.8, 24.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

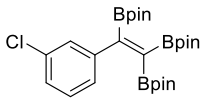
^{11}B NMR (160 MHz, $CDCl_3$): δ = 30.7.

^{19}F NMR (471 MHz, $CDCl_3$): δ = -114.6 (dddd, J = 10, 9, 6, 1 Hz).

HRMS (ASAP): m/z for $C_{26}H_{41}B_3FO_6$ $[M+H]^+$ calcd: 501.3161, found: 501.3162.

Anal. Calcd for $C_{26}H_{40}B_3FO_6$: C, 62.45; H, 8.06; found: C, 62.80; H, 8.37.

2,2',2''-(2-(3-chlorophenyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2l)



Isolated yield: 56%.

White solid, m.p.: 186.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 – 7.26 (m, 1H), 7.17 – 7.14 (m, 3H), 1.31 (s, 12H), 1.27 (s, 12H), 1.10 (s, 12H).

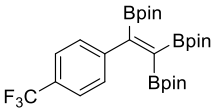
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 146.9, 133.4, 128.8, 127.9, 126.6, 125.9, 84.0, 83.6, 83.4, 24.9, 24.8, 24.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{26}H_{41}B_3Cl_1O_6$ $[M+H]^+$ calcd: 517.2865, found: 517.2870.

Anal. Calcd for $C_{26}H_{40}B_3ClO_6$: C, 60.46; H, 7.81; found: C, 60.48; H, 7.95.

2,2',2''-(2-(4-(trifluoromethyl)phenyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2m)



Isolated yield: 47%.

White solid, m.p.: 201.0 °C. Its spectroscopic data are consistent with a literature report.[156]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, J = 8 Hz, 2H), 7.35 (d, J = 8 Hz, 2H), 1.32 (s, 12H), 1.27 (s, 12H), 1.06 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 148.9, 128.5 (q, J = 32 Hz), 128.0, 124.5 (q, J = 272 Hz), 124.5 (q, J = 4 Hz), 84.1, 83.7, 83.4, 24.9, 24.7, 24.4. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

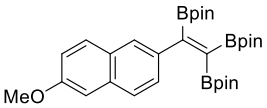
^{11}B NMR (160 MHz, $CDCl_3$): δ = 30.8.

^{19}F NMR (471 MHz, $CDCl_3$): δ = -62.3.

HRMS (ASAP): m/z for $C_{27}H_{41}B_3F_3O_6$ $[M+H]^+$ calcd: 551,3129, found: 551.3124.

Anal. Calcd for $C_{27}H_{40}B_3F_3O_6$: C, 58.96; H, 7.33; found: C, 59.31; H, 7.64.

2,2',2''-(2-(6-methoxynaphthalen-2-yl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2n)



Isolated yield: 49%.

White solid, m.p.: 190.3 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69 – 7.59 (m, 3H), 7.43 (dd, J = 8, 2 Hz, 1H), 7.11 – 7.04 (m, 2H), 3.90 (s, 3H), 1.32 (s, 12H), 1.29 (s, 12H), 1.02 (s, 12H).

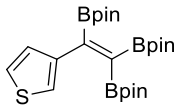
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 157.2, 141.0, 133.6, 129.6, 128.7, 127.0, 126.2, 125.9, 118.3, 105.6, 83.9, 83.4, 83.1, 55.2, 24.9, 24.8, 24.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{31}H_{46}B_3O_7$ $[M+H]^+$ calcd: 563.3517, found: 563.3514.

Anal. Calcd for $C_{31}H_{45}B_3O_7$: C, 66.24; H, 8.07; found: C, 66.46; H, 8.11.

2,2',2''-(2-(thiophen-3-yl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2o)



Isolated yield: 61%.

White solid, m.p.: 170.4 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22 (dd, J = 3, 1 Hz, 1H), 7.15 (dd, J = 5, 3 Hz, 1H), 7.10 (dd, J = 5, 1 Hz, 1H), 1.29 (s, 12H), 1.27 (s, 12H), 1.15 (s, 12H).

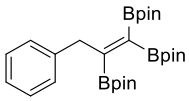
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 146.2, 128.2, 124.2, 122.1, 83.8, 83.4, 83.3, 24.9, 24.8, 24.6. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{24}H_{40}B_3O_6S_1$ $[M+H]^+$ calcd: 489.2819, found: 489.2811.

Anal. Calcd for $C_{24}H_{39}B_3O_6S$: C, 59.06; H, 8.05; S, 6.57; found: C, 59.27; H, 8.36; S, 6.01.

2,2',2''-(3-phenylprop-1-ene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2p)



Isolated yield: 69%.

White solid, m.p.: 167.2 °C. Its spectroscopic data are consistent with a literature report.[156]

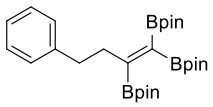
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 – 7.29 (m, 2H), 7.21 – 7.16 (m, 2H), 7.12 – 7.07 (m, 1H), 3.76 (s, 2H), 1.29 (s, 12H), 1.25 (s, 12H), 1.07 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 140.8, 129.7, 127.8, 125.4, 83.5, 83.3, 83.1, 43.6, 24.9, 24.8, 24.6. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{27}H_{44}B_3O_7$ $[M+H]^+$ calcd: 497.3412, found: 497.3412.

2,2',2''-(4-phenylbut-1-ene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2q)



Isolated yield: 74%.

White solid, m.p.: 226.8 °C. Its spectroscopic data are consistent with a literature report.[156]

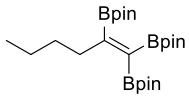
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (d, J = 1 Hz, 2H), 7.25 (s, 2H), 7.17 – 7.12 (m, 1H), 2.66 (s, 4H), 1.31 (s, 12H), 1.27 (s, 12H), 1.25 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 143.5, 128.5, 128.1, 125.3, 83.7, 83.3, 83.0, 40.2, 37.2, 24.9, 24.9, 24.8. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{28}H_{46}B_3O_6$ $[M+H]^+$ calcd: 511.3568, found: 511.3571.

2,2',2''-(hex-1-ene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2r)



Isolated yield: 58%.

White solid, m.p.: 216.2 °C. Its spectroscopic data are consistent with a literature report.[156]

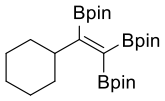
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.36 (t, J = 7 Hz, 2H), 1.38 – 1.29 (m, 4H), 1.28 (s, 12H), 1.24 (s, 12H), 1.23 (s, 12H), 0.86 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 83.5, 83.1, 82.8, 37.5, 32.7, 24.9, 24.8, 24.7, 22.8, 14.1. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{24}H_{46}B_3O_6$ $[M+H]^+$ calcd: 463.3568, found: 463.3569.

2,2',2''-(2-cyclohexylethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2s)



Isolated yield: 71%.

White solid, m.p.: 278.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.32 (tt, J = 12, 4 Hz, 1H), 1.76 – 1.58 (m, 6H), 1.48 – 1.34 (m, 2H), 1.27 (s, 12H), 1.25 (s, 12H), 1.23 (s, 12H), 1.22 – 1.06 (m, 2H).

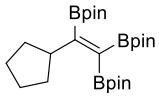
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 83.3, 83.0, 82.9, 49.9, 32.2, 26.6, 26.1, 25.1, 24.9, 24.7. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{26}H_{48}B_3O_6$ $[M+H]^+$ calcd: 489.3725, found: 489.3726.

Anal. Calcd for $C_{26}H_{47}B_3O_6$: C, 63.98; H, 9.71; found: C, 64.38; H, 9.90.

2,2',2''-(2-cyclopentylethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2t)



Isolated yield: 64%.

White solid, m.p.: 278.6 °C. Its spectroscopic data are consistent with a literature report.[156]

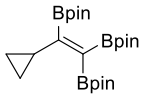
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.87 – 2.75 (apparent quintet, J = 9 Hz,1H), 1.77 – 1.44 (m, 8H), 1.26 (s, 12H), 1.24 (s, 12H), 1.23 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 83.3, 83.0, 82.9, 50.6, 32.6, 26.1, 25.1, 24.9, 24.7. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{26}H_{46}B_3O_6$ $[M+H]^+$ calcd: 487.3568, found: 487.3565.

2,2',2''-(2-cyclopropylethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2u)



Isolated yield: 54%.

White solid, m.p.: 233.4 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.94 (tt, J = 8, 5 Hz, 1H), 1.24 (s, 12H), 1.24 (s, 24H), 0.77 (m, 2H), 0.71 – 0.63 (m, 2H).

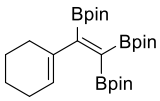
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 83.4, 82.9, 82.8, 25.0, 24.9, 24.7, 20.2, 7.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{23}H_{42}B_3O_6$ $[M+H]^+$ calcd: 447.3255, found: 447.3258.

Anal. Calcd for $C_{23}H_{41}B_3O_6$: C, 61.94; H, 9.27; found: C, 62.12; H, 9.42.

2,2',2''-(2-(cyclohex-1-en-1-yl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-2v)



Isolated yield: 52%.

White solid, m.p.: 235 °C. Its spectroscopic data are consistent with a literature report.[156]

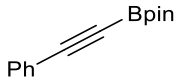
^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.48 (tt, J = 4, 2 Hz, 1H), 2.10 (m, 2H), 2.05 – 1.97 (m, 2H), 1.65 – 1.56 (m, 2H), 1.53 (m, 2H), 1.25 (s, 12H), 1.25 (s, 12H), 1.20 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 145.4, 122.4, 83.5, 83.1, 82.8, 28.0, 25.4, 24.9, 24.8, 24.7, 22.6, 22.1. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{26}H_{46}B_3O_6$ $[M+H]^+$ calcd: 487.3568, found: 487.3565.

4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (2-4a)



Isolated yield: 77%.

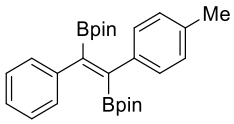
White solid, Its spectroscopic data are consistent with a literature report.[178]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 – 7.46 (m, 2H), 7.39 – 7.28 (m, 3H), 1.32 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 132.5, 129.4, 128.3, 121.8, 84.4, 24.7.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 24.2.

(*E*)-2,2'-(1-phenyl-2-(p-tolyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-6a)



Isolated yield: 78%.

White solid, m.p.: 137.4 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 – 7.32 (m, 2H), 7.31 – 7.19 (m, 5H), 7.12 – 7.06 (m, 2H), 2.33 (s, 3H), 1.10 (s, 12H), 1.08 (s, 12H).

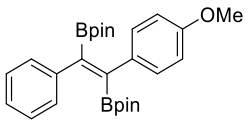
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 143.4, 140.2, 136.2, 128.6, 128.1, 128.0, 127.9, 126.5, 83.5, 24.6, 21.2. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 30.3.

HRMS (ASAP): m/z for $C_{27}H_{37}B_2O_4$ $[M+H]^+$ calcd: 447.2872, found: 447.2866.

Anal. Calcd for $C_{27}H_{37}B_2O_4$: C, 72.68; H, 8.73; found: C, 72.52; H, 8.15.

(*E*)-2,2'-(1-(4-methoxyphenyl)-2-phenylethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-6b)



Isolated yield: 68%.

White solid, m.p.: 179.0 °C.

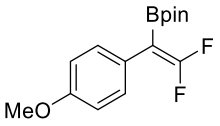
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 – 7.32 (m, 2H), 7.31 – 7.25 (m, 4H), 7.23 – 7.17 (m, 1H), 6.87 – 6.80 (m, 2H), 3.80 (s, 3H), 1.11 (s, 12H), 1.08 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ = 158.7, 143.4, 135.9, 129.3, 128.1, 127.9, 126.5, 113.4, 83.5, 83.5, 55.3, 24.6, 24.6. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{27}H_{37}B_2O_5$ $[M+H]^+$ calcd: 463.2822, found: 463.2812.

2-(2,2-difluoro-1-(4-methoxyphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-7a)



Isolated yield: 93%.

Colorless liquid

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22 (m, 2H), 6.87 (m, 2H), 3.80 (s, 3H), 1.31 (s, 12H).

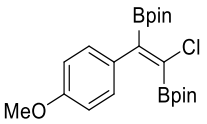
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ = 159.5 (dd, J = 306, 299 Hz), 158.3, 130.6 (t, J = 3 Hz), 124.7 (dd, J = 8, 1 Hz), 113.7, 83.9, 55.2, 24.7. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

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

^{19}F NMR (471 MHz, $CDCl_3$): δ = -70.0 (s, br), -72.0 (d, J = 5 Hz).

HRMS (ASAP): m/z for $C_{15}H_{20}B_1F_2O_3$ $[M+H]^+$ calcd: 297.1468, found: 297.1457.

(*E*)-2,2'-(1-chloro-2-(4-methoxyphenyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-8a)



Isolated yield: 70%.

White solid, m.p.: 157.4 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17 (d, J = 9 Hz, 2H), 6.81 (d, J = 9 Hz, 2H), 3.79 (s, 3H), 1.31 (s, 12H), 1.17 (s, 12H).

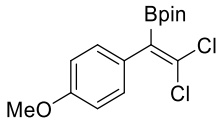
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 159.2, 131.8, 129.2, 113.5, 84.3, 84.3, 55.2, 24.7, 24.4. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 28.2.

HRMS (ASAP): m/z for $C_{21}H_{32}B_2Cl_1O_5$ $[M+H]^+$ calcd: 421.2119, found: 421.2112.

Anal. Calcd for $C_{21}H_{32}B_2Cl_1O_5$: C, 59.98; H, 7.43; found: C, 59.67; H, 7.58.

2-(2,2-dichloro-1-(4-methoxyphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-9a)



Isolated yield: 53%.

Colorless liquid.

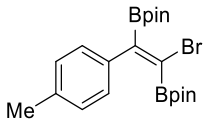
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24 (d, J = 9 Hz, 2H), 6.88 (d, J = 9 Hz, 2H), 3.81 (s, 3H), 1.30 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 158.9, 129.6, 129.5, 125.2, 113.7, 84.6, 55.2, 24.6. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 29.4.

HRMS (ASAP): m/z for $C_{15}H_{20}B_1Cl_2O_3$ $[M+H]^+$ calcd: 329.0877, found: 329.0869.

(*E*)-2,2'-(1-bromo-2-(p-tolyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-10a)



Isolated yield: 75%.

White solid, m.p.: 200.7 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.14 (d, J = 8 Hz, 2H), 7.07 (d, J = 8 Hz, 2H), 2.31 (s, 3H), 1.32 (s, 12H), 1.16 (s, 12H).

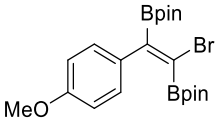
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 137.8, 137.2, 128.8, 127.4, 84.3, 84.3, 24.7, 24.3, 21.2. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 28.5.

HRMS (ASAP): m/z for $C_{21}H_{32}B_2Br_1O_4$ $[M+H]^+$ calcd: 449.1665, found: 449.1661.

Anal. Calcd for $C_{21}H_{31}B_2BrO_4$: C,56.18; H, 6.96; found: C, 56.83; H, 7.13.

(*E*)-2,2'-(1-bromo-2-(4-methoxyphenyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2-10b)



Isolated yield: 70%.

White solid, m.p.: 249.0 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19 (d, J = 9 Hz, 2H), 6.80 (d, J = 9 Hz, 2H), 3.78 (s, 3H), 1.32 (s, 12H), 1.17 (s, 12H).

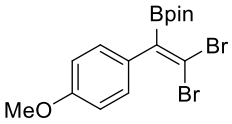
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 159.2, 133.3, 128.8, 113.6, 84.3, 84.3, 55.2, 24.8, 24.3. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 28.1.

HRMS (ASAP): m/z for $C_{21}H_{32}B_2Br_1O_5$ $[M+H]^+$ calcd: 465.1614, found: 465.1613.

Anal. Calcd for $C_{21}H_{31}B_2BrO_5$: C, 54.24; H, 6.72; found: C, 54.87; H, 6.79.

2-(2,2-dibromo-1-(4-methoxyphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-11a)



Isolated yield: 86%.

Colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22 (m, 2H), 6.88 (m, 2H), 3.81 (s, 3H), 1.29 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 158.9, 132.1, 129.0, 113.8, 94.2, 84.7, 55.2, 24.6. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 29.6.

HRMS (ASAP): m/z for $C_{15}H_{20}B_1Br_2O_3$ $[M+H]^+$ calcd: 418.9846, found: 418.9841.

2.7.4 Crystallographic data

Crystals suitable for single-crystal X-ray diffraction were selected, coated in perfluoropolyether oil, and mounted on MiTeGen sample holders. Diffraction data were collected on Bruker X8 Apex II 4-circle diffractometers with CCD area detectors using Mo-Kα radiation monochromated by graphite (**2-6b, 2-10b**) or multi-layer focusing mirrors (**2-2a**). The crystals were cooled using an Oxford Cryostreams or Bruker Kryoflex II low-temperature device. Data were collected at 100 K. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the Bruker software packages. The structures were solved using the intrinsic phasing method (SHELXT)[179] and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' in idealized positions, by full-matrix least squares against F^2 of all data, using SHELXL[180] software and the SHELXLE graphical user interface.[181] The crystal structure of **2-2a** was solved in space group $P2_1$ and transformed to higher symmetry (space group $P2_1/c$) using the PLATON program.[182] The PLATON program[182] was also used for the determination of the occurrence of twinning. The crystal structure of **2-2a** was refined as a twin applying the twin matrix (-1 0 0, 0 -1 0, 0 0 1). The twin component was refined to 47.5%. The crystal structure of **2-10b** was refined as a twin applying the twin matrix (0 2 0, 0.5 0 0, 0 0 -1). The twin component was refined to 1.9%. Diamond[183] software was used for graphical representation. Crystal data and experimental details are listed in Table 2-9; full structural information has been deposited with Cambridge Crystallographic Data Centre. CCDC-1918365 (**2-2a**), 1918366 (**2-6b**), and 1918367 (**2-10b**).

Table 2-9: Single-crystal X-ray diffraction data and structure refinements of **2-2a**, **2-6b**, and **2-10b**.

Data	**2-2a**	**2-6b**	**2-10b**
CCDC number	1918365	1918366	1918367
Empirical formula	$C_{26}H_{41}B_3O_6$	$C_{27}H_{36}B_2O_5$	$C_{21}H_{31}B_2BrO_5$
Formula weight / g·mol^{-1}	482.02	462.18	464.99
T / K	100(2)	100(2)	100(2)
λ / Å, radiation	MoKα 0.71073	MoKα 0.71073	MoKα 0.71073
Crystal size / mm³	0.15×0.30×0.40	0.21×0.32×0.70	0.19×0.30×0.34
Crystal color, habit	colorless block	colorless block	colorless block
μ / mm^{-1}	0.077	0.079	1.841
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
a / Å	13.084(7)	9.492(3)	18.711(5)
b / Å	11.994(5)	11.493(7)	9.336(2)
c / Å	17.812(7)	13.055(3)	12.982(3)
α / °	90	72.7910(10)	90
β / °	90.124(12)	74.7050(10)	90
γ / °	90	74.3700(10)	90
Volume / Å^3	2795(2)	1283.7(9)	2267.6(9)
Z	4	2	4
ρ_{calc} / g·cm^{-3}	1.145	1.196	1.362
F(000)	1040	496	968
θ range / °	1.556 - 26.053	1.667 - 26.022	1.088 - 30.039
Reflections collected	20326	23816	76146
Unique reflections	5512	5067	6647
Parameters / restraints	329 / 0	393 / 0	458 / 625
GooF on F^2	1.027	1.023	1.246
R_1 [I>2σ(I)]	0.0465	0.0387	0.0466
wR^2 (all data)	0.1091	0.0982	0.1049
Max. / min. residual electron density / e·Å^{-3}	0.591 / –0.239	0.273 / –0.233	0.543 / –1.387

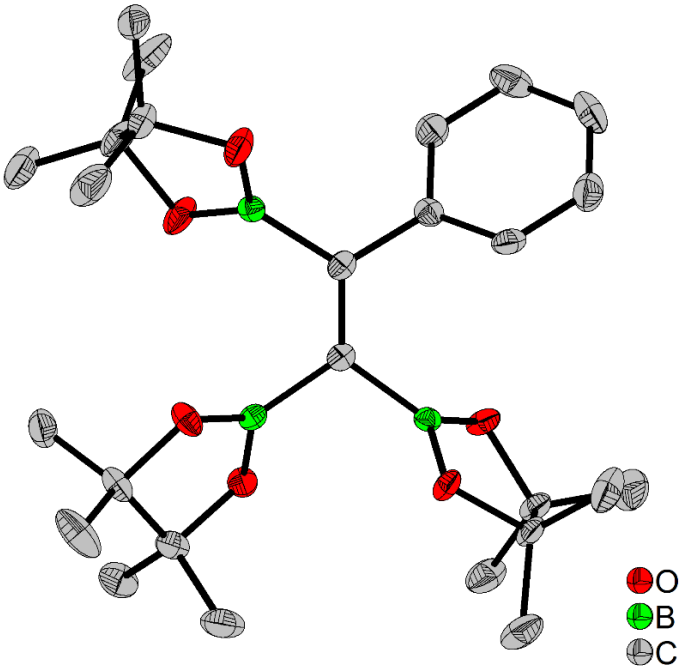


Figure 2-7. Molecular structure of **2-2a** in the solid state at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

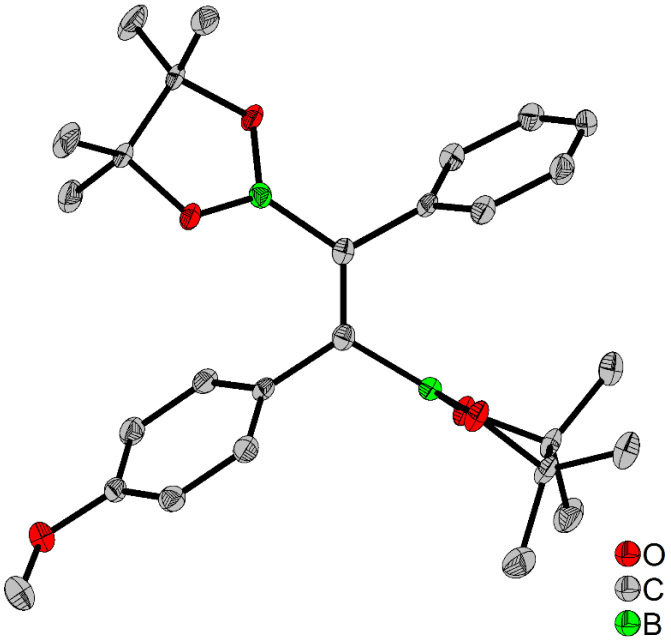


Figure 2-8. Molecular structure of **2-6b** in the solid state at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. One of the Bpin moieties is disordered and only the part with 88% occupancy is shown.

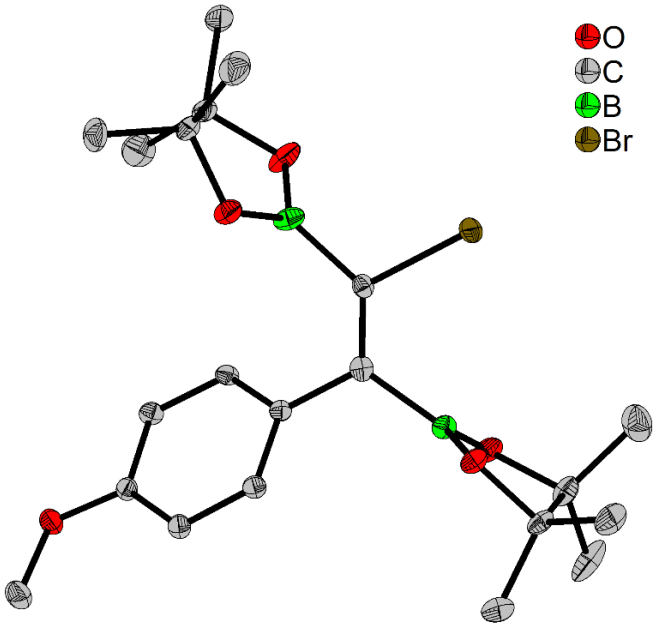


Figure 2-9. Molecular structure of **2-10b** in the solid state at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The molecule is disordered except for one Bpin moiety and only the part with 85.5% occupancy is shown.

Chapter Three

Copper-Catalyzed Triboration: Straightforward, Atom-Economical Synthesis of 1,1,1-Triborylalkanes from Terminal Alkynes and HBpin

3 Copper-Catalyzed Triboration: Straightforward, Atom-Economical Synthesis of 1,1,1-Triborylalkanes from Terminal Alkynes and HBpin

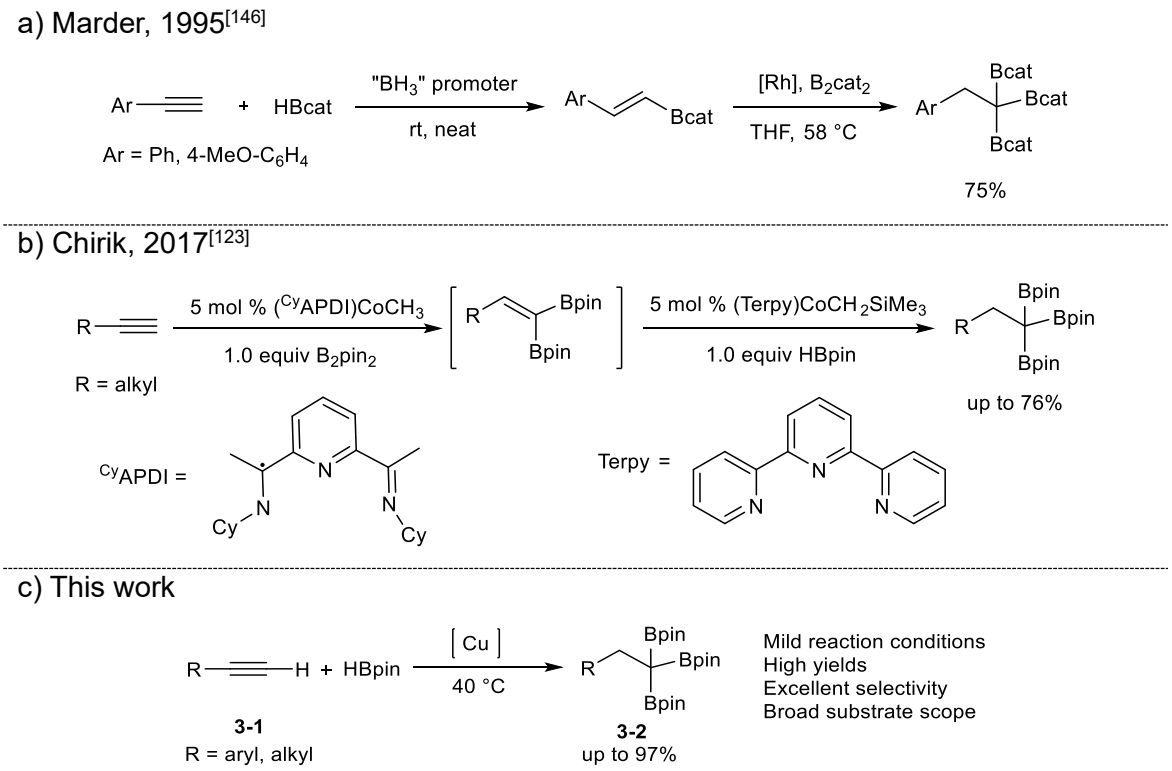
3.1 Abstract

A convenient and efficient one step synthesis of 1,1,1-triborylalkanes was achieved via sequential dehydrogenative borylation and double hydroboration of terminal alkynes with HBpin (HBpin = pinacolborane) catalyzed by inexpensive and readily available $Cu(OAc)_2$. This protocol proceeded under mild conditions, furnishing 1,1,1-tris(boronates) with wide substrate scope, excellent selectivity and good functional group tolerance, and is applicable to gram-scale synthesis without loss of yield. The 1,1,1-triborylalkanes can be used in the preparation of α-vinylboronates and borylated cyclic compounds, which are valuable but previously rare compounds. Different alkyl groups can be introduced stepwise via base-mediated deborylative alkylation to produce racemic tertiary alkyl boronates, which can be readily transformed into useful tertiary alcohols.

3.2. Introduction

Organoboron compounds have become, without doubt, among the most useful species in organic chemistry due to their ease of preparation and widespread application in synthesis, pharmaceuticals and functional materials.[160a, 160b] Multiborylated compounds are important in modern organic chemistry due to their various roles such as bio-active agents and synthetic building blocks.[117, 152-153, 155-156, 159, 160c, 167, 184] Monoboronates[137b, 185] and *gem*-bisboronates[186] have been increasingly applied in organic synthesis. In contrast, 1,1,1-triboronates analogues are relatively rare, but are very interesting due to their documented reactivity arising from the stabilization of a carbanion center by the *α*-boronate moieties;[1a, 145-146, 157-158, 187] thus, efficient methods for their synthesis are desirable, but few are currently available. The triboration of chloroform using $(RO)_2BCl$ and six equivalents of lithium metal at low temperature was developed by Matteson and coworkers.[145] Mita, Sato *et al.* reported an Ir-catalyzed, pyridine-directed triple $C(sp^3)$-H boration

of 2-ethylpyridines at 150 °C. However, good yields and selectivities resulted only when small, electron-donating substituents were present on the pyridine rings.[148] Chirik and coworkers reported a Ni-catalyzed preparation of benzyltriboronates via triboration of benzylic C-H bonds. Even though the selectivities and yields were high, the substrate scope was quite limited.[151, 188] The Huang group synthesized 1,1,1-triborylalkanes from alkenes via a Co-catalyzed double dehydrogenative borylation-hydroboration sequence, but unactivated alkenes were not suitable substrates.[149]



Scheme 3-1. Methods for the synthesis of 1,1,1-tris(boronates) from alkynes.

Terminal alkynes are very useful reagents in the synthesis of diversified organoboron compounds.[1a, 1b, 1f, 166a, 189] In 1995, Marder group reported a Rh-catalyzed 1,1-diboration of (*E*)-styrylboronates which, in turn, were prepared via hydroboration of the corresponding ethynylarenes with HBcat (HBcat = catecholborane) (Scheme 3-1a), which yielded predominantly 1,1,1-triboronates.[146-147] In 2017, Chirik *et al.* achieved the synthesis of 1,1,1-triboronates via Co-catalyzed 1,1-diboration of terminal alkynes with B_2pin_2 (Scheme 3-1b), which underwent subsequent hydroboration with HBpin. Two different types of cobalt catalysts were used in this two-step sequence (Scheme 3-

1b).[123] All of these methods, though useful, suffer from major or minor drawbacks, such as weak functional group tolerance, expensive catalysts or tedious procedures. Herein, a straightforward atom-economical synthesis of diverse 1,1,1-triborylalkanes from easily available and low-cost catalysts and starting materials under mild conditions was reported (Scheme 3-1c).

3.3 Results and discussion

3.3.1 Optimization of reaction conditions

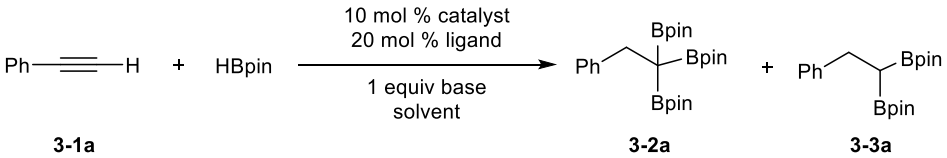
The investigation began with the triboration of phenylacetylene (**3-1a**) with HBpin in the presence of 10 mol % $Cu(OAc)_2$, 20 mol % PCy_3 and stoichiometric KF in toluene at 80 °C (Table 3-1, entry 1), giving the desired product **3-2a** in 78% yield. The effect of the ligand was investigated (Table 3-1, entries 2-4), and P^nBu_3 was found to be the optimal one among PCy_3, PPh_3 and P^tBu_3. In the presence of nitrogen ligands, no desired product was obtained (Table 3-2). There was no reaction in the absence of a ligand (Table 3-1, entry 5).

The influence of the copper precursor was studied (Table 3-1, entries 6-8 and Table 3-3), and copper (I) acetate (Table 3-1, entry 6) appeared to be slightly less effective than copper (II) acetate, but the difference is probably within experimental error (85 ± 5%). When $Cu(acac)_2$ (Table 3-1, entry 7) was used, the desired product was afforded in only 16% yield. Other copper sources such as $CuCl_2$, CuCl and $Cu(OTf)_2$ (Table 3-3, entries 1-3) were also examined, but unfortunately, no desired product was detected. In the absence of a copper source, the reaction did not occur (Table 3-1, entry 8).

When KF was omitted from the reaction mixture, only trace amounts of the 1,1,1-tris(boronates) were formed (Table 3-1, entries 9). Much lower yields were obtained when the KF loading was reduced to 20 mol % and 50 mol % (31% and 58% yield, respectively) (Table 3-7, entries 1 and 2), which indicated that KF possibly promotes this transformation. Then, a series of bases (Table 3-1, entries 10-15) were evaluated, with KOAc, K_2CO_3, KOPiv and Li_2CO_3 being slightly less effective than KF. Remarkably, as illustrated in entries 16-19, the desired product can be obtained in up to 97% yield at 40 °C, while either higher or lower temperature gave inferior

results. Other screening details are listed in Tables 3-2 to 3-7.

Table 3-1: Optimization of reaction conditions.[a]

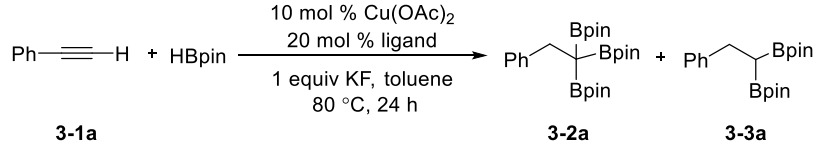


3-1a **3-2a** **3-3a**

Entry	Catalyst	Ligand	Base	Temp. (°C)	Yield 3-2a (%)[b]	Yield 3-3a (%)[b]
1	$Cu(OAc)_2$	PCy_3	KF	80	78	9
2	$Cu(OAc)_2$	PPh_3	KF	80	23	4
3	$Cu(OAc)_2$	P^tBu_3	KF	80	21	54
4	$Cu(OAc)_2$	P^nBu_3	KF	80	89 (84)	1
5	$Cu(OAc)_2$	--	KF	80	0	0
6	CuOAc	P^nBu_3	KF	80	80	4
7	$Cu(acac)_2$	P^nBu_3	KF	80	16	8
8	--	P^nBu_3	KF	40	0	0
9	$Cu(OAc)_2$	P^nBu_3	--	80	trace	trace
10	$Cu(OAc)_2$	P^nBu_3	KOAc	80	84 (78)	3
11	$Cu(OAc)_2$	P^nBu_3	K_2CO_3	80	71	6
12	$Cu(OAc)_2$	P^nBu_3	KOPiv	80	85 (80)	3
13	$Cu(OAc)_2$	P^nBu_3	Li_2CO_3	80	82 (75)	5
14	$Cu(OAc)_2$	P^nBu_3	KO^tBu	80	15	35
15	$Cu(OAc)_2$	P^nBu_3	DABCO	80	40	11
16	$Cu(OAc)_2$	P^nBu_3	KF	100	66	6
17	$Cu(OAc)_2$	P^nBu_3	KF	60	81	3
18	$Cu(OAc)_2$	P^nBu_3	KF	40	97 (93)	3
19[c]	$Cu(OAc)_2$	P^nBu_3	KF	40	62	10
20	$Cu(OAc)_2$	P^nBu_3	KF	r.t	58	3

[a] Standard conditions: In an argon-filled glove box, **3-1a** (0.2 mmol, 1 equiv), catalyst (10 mol %), ligand (20 mol %), base (1 equiv), HBpin (4 equiv), toluene (0.25 mL), 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. [c] Using 'standard conditions' except HBpin (3 equiv). Isolated yields are given in parentheses.

Table 3-2: Screening of ligands for the triboration of alkynes.[a]

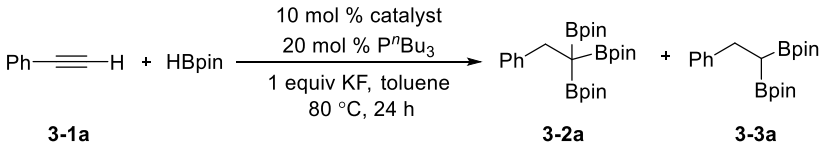


3-1a 3-2a 3-3a

Entry	Ligand	Yield 3-2a (%)[b]	Yield 3-3a (%)[b]
1	dppp	68	5
2	phen	0	0
3	2,2′-bipyridyl	0	0
4	4-picoline	0	0

[a] Standard conditions: in an argon-filled glove box, **3-1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), ligand (20 mol %), KF (1 equiv), HBpin (4 equiv), toluene (0.25 mL), at 80 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses.

Table 3-3: Screening of catalysts for the triboration of alkynes.[a]

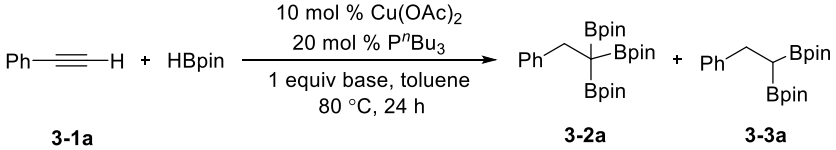


3-1a 3-2a 3-3a

Entry	Catalyst	Yield 3-2a (%)[b]	Yield 3-3a (%)[b]
1	$CuCl_2$	0	0
2	CuCl	0	0
3	$Cu(OTf)_2$	0	0
4	$FeCl_3$	0	0
5	$MgCl_2$	0	0
6	$Zn(acac)_2$	0	0
7	$CoCl_2$	0	0
8	$Fe(OAc)_2$	0	0

[a] Standard conditions: in an argon-filled glove box, **3-1a** (0.2 mmol, 1 equiv), catalyst (10 mol %), P^{n}Bu$_3$ (20 mol %), KF (1 equiv), HBpin (4 equiv), toluene (0.25 mL), at 80 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses.

Table 3-4: Screening of bases for the triboration of alkynes.[a]

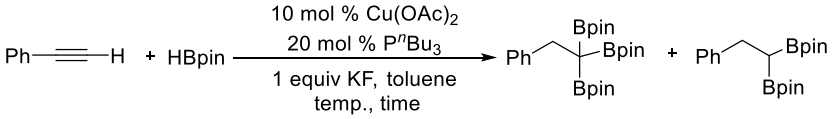


3-1a 3-2a 3-3a

Entry	Base	Yield 3-2a (%)[b]	Yield 3-3a (%)[b]
1	$NaCO_2CF_3$	72 (69)	7
2	$KHCO_3$	79	7
3	KPF_6	80	6
4	LiO^{t}Bu	57	7
5	CsPiv	59	6

[a] Standard conditions: in an argon-filled glove box, **3-1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), P^{n}Bu$_3$ (20 mol %), base (1 equiv), HBpin (4 equiv), toluene (0.25 mL), at 80 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses.

Table 3-5: Screening of temperatures and time for the triboration of alkynes.[a]

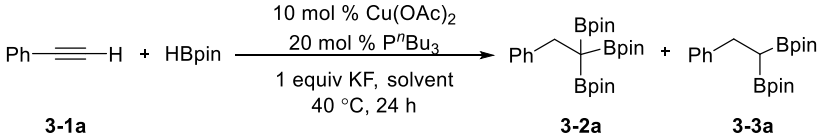


3-1a **3-2a** **3-3a**

Entry	Temp. (°C)	Time (h)	Yield 3-2a (%)[b]	Yield 3-3a (%)[b]
1	100	24	66	6
2	60	24	84	3
3	40	24	97 (93)	3
4	r.t.	24	58	3
5	40	4	0	0
6	40	8	56	3
7	40	12	59	3

[a] Standard conditions: in an argon-filled glove box, **3-1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), P^nBu_3 (20 mol %), KF (1 equiv), HBpin (4 equiv), toluene (0.25 mL). [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses.

Table 3-6: Screening of solvents for the triboration of alkynes.[a]

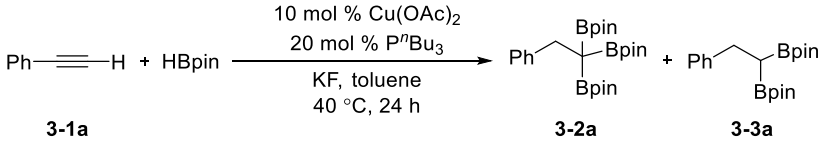


3-1a **3-2a** **3-3a**

Entry	Solvent	Yield 3-2a (%)[b]	Yield 3-3a (%)[b]
1	MTBE	66	7
2	CH_2Cl_2	33	48
3	hexane	49	8
4	Et_2O	64	6
5	acetone	0	0
6	THF	63	12
7	CH_3CN	0	0
8[c]	toluene	35	20
9[d]	toluene	59	10
10	--	60	5

[a] Standard conditions: in an argon-filled glove box, **3-1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), P^nBu_3 (20 mol %), KF (1 equiv), HBpin (4 equiv), solvent (0.25 mL), at 40 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses. [c] Toluene 1 mL. [d] Toluene 0.5 mL.

Table 3-7: Screening of the amount of KF for the triboration of alkynes.[a]



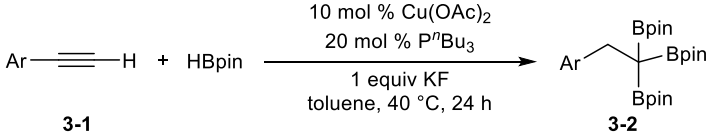
3-1a 3-2a 3-3a

Entry	Base	Yield 3-2a (%)[b]	Yield 3-3a (%)[b]
1	KF 0.2 equiv	31	33
2	KF 0.5 equiv	58	9
3	KF 1.5 equiv	65	5

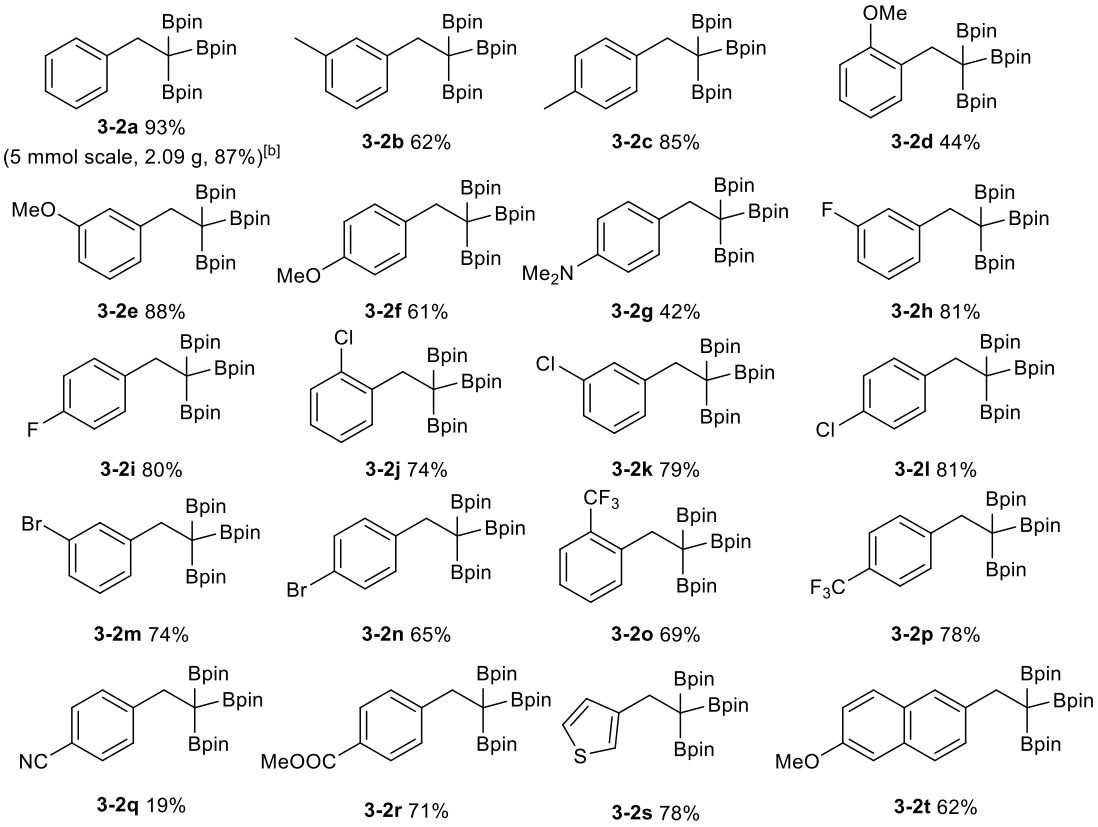
[a] Standard conditions: in an argon-filled glove box, **3-1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), P^nBu_3 (20 mol %), KF, HBpin (4 equiv), solvent (0.25 mL), at 40 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses.

3.3.2 Investigation of reaction scope

Table 3-8: Substrate scope for the Cu-catalyzed triboration of aromatic alkynes.[a]



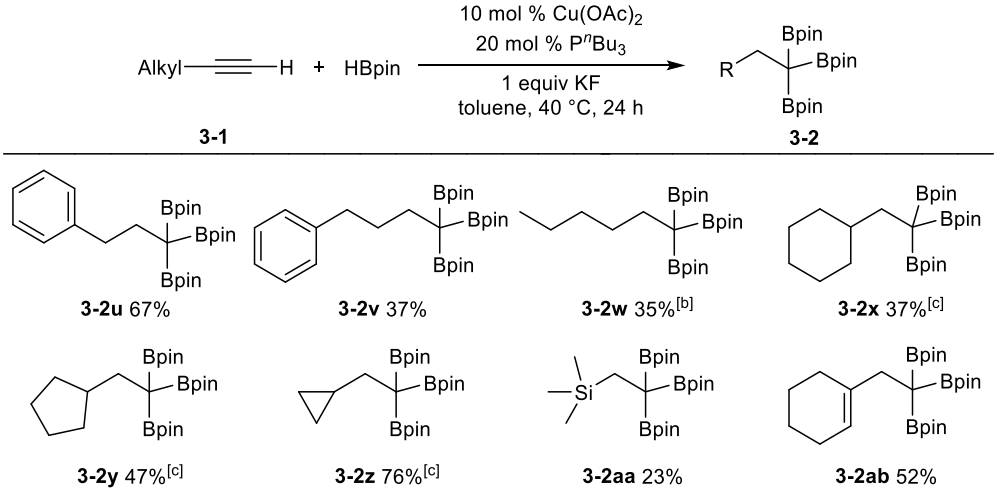
3-1 3-2



[a] Standard conditions: in an argon-filled glove box, **3-1** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), P^nBu_3 (20 mol %), KF (1 equiv), HBpin (4 equiv), toluene (0.25 mL), 40 °C, 24 h; isolated yield. [b] In an argon-filled glove box, **3-1** (5 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), P^nBu_3 (20 mol %), KF (1 equiv), HBpin (4 equiv), toluene (5 mL), 40 °C, 24 h.

With optimized reaction conditions identified, the scope of this novel Cu-catalyzed triboration reaction was examined. Generally, a wide range of both donor- and acceptor-substituted aromatic alkynes were found to work well, providing the corresponding 1,1,1-triborylated alkanes in moderate to good yields (**3-2a** to **3-2t**). Substrates containing electron-donating substituents, such as methyl (**3-2b**/**3-2c**), methoxy (**3-2d**/**3-2e**/**3-2f**), and dimethylamino (**3-2g**), afforded the corresponding products in moderate to good isolated yields ranging from 42% to 88%. This catalytic system was also efficient for substrates containing electron-withdrawing groups (up to 81% isolated yield), such as F (**3-2h**/**3-2i**), Cl (**3-2j**/**3-2k**/**3-2l**), Br (**3-2m**/**3-2n**), CF_3 (**3-2o**/**3-2p**), CN (**3-2q**) and CO_2Me (**3-2r**). It should be noted that reaction of haloaryl-substituted alkynes (**3-2h** to **3-2n**) occurred selectively to form the desired products, and no C-X (X= F, Cl, Br) bond boration was detected, opening the door for further functionalization. Furthermore, heteroaromatic and polyaromatic substrates, e.g. thienyl- (**3-2s**) and naphthyl-substituted acetylenes (**3-2t**), are suitable substrates for this sequential dehydrogenative borylation-double hydroboration reaction (78% and 62% yield, respectively). This method enables a convenient gram-scale synthesis (5 mmol) without significant loss of yield, as demonstrated for **3-1a** (**3-2a**: 2.09 g, 87%).

Table 3-9: Substrate scope for Cu-catalyzed triboration of alkyl alkynes and a 1,3-enyne.[a]



[a] Standard conditions: in an argon-filled glove box, **3-1** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), P^{n}Bu$_3$ (20 mol %), KF (1 equiv), HBpin (4 equiv), toluene (0.25 mL), at 40 °C for 24 h; isolated yield. [b] Reaction time 36 h. [c] Reaction time 12 h.

Unlike the previous synthetic method for preparing 1,1,1-triborylalkanes from alkenes which was limited to aryl alkenes,[149] this Cu-catalyzed system is not, as it

can be extended to readily available unactivated alkyl alkynes (Table 3-9). Alkynes with linear alkyl groups were converted into the corresponding 1,1,1-tris(boronates) in moderate yields (**3-2u** to **3-2w**, 35-67%). Reaction of cyclohexylacetylene and cyclopentylacetylene gave the triboration product **3-2x** in 37% and **3-2y** in 47% isolated yield, respectively, but reaction of cyclopropylacetylene afforded the product **3-2z** in higher yield (76%). Trimethylsilylacetylene **3-1aa** gave the desired product **3-2aa** in 23% yield. For the conjugated 1,3-enyne, 1-ethynylcyclohexene **3-1ab**, no boration occurred at the double bond, and **3-2ab** was isolated in 52% yield, indicating the high chemoselectivity of this reaction.

3.4 Mechanistic study

3.4.1 Evidence for FBpin formation

A mixture of $Cu(OAc)_2$ (0.1 mmol), P^nBu_3 (0.2 mmol), KF (0.1 mmol) and HBpin (0.2 mmol) was dissolved in CH_2Cl_2 (0.6 mL) in a Young's tap NMR tube. The mixture was kept under argon at 40 °C for 2 h. The formation of FBpin was detected by $^{11}B\{^1H\}$ NMR and ^{19}F spectroscopy (Figures 3-1 and 3-2).[190]

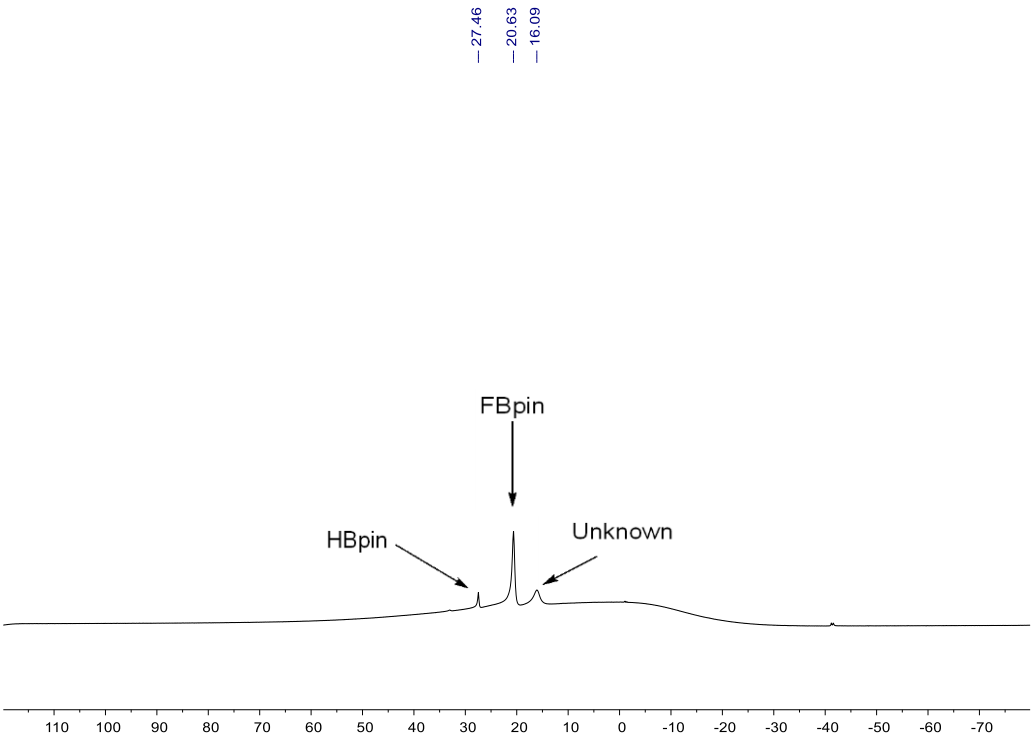


Figure 3-1. *In situ* $^{11}B\{^1H\}$ NMR spectrum of FBpin in CH_2Cl_2 (160 MHz).

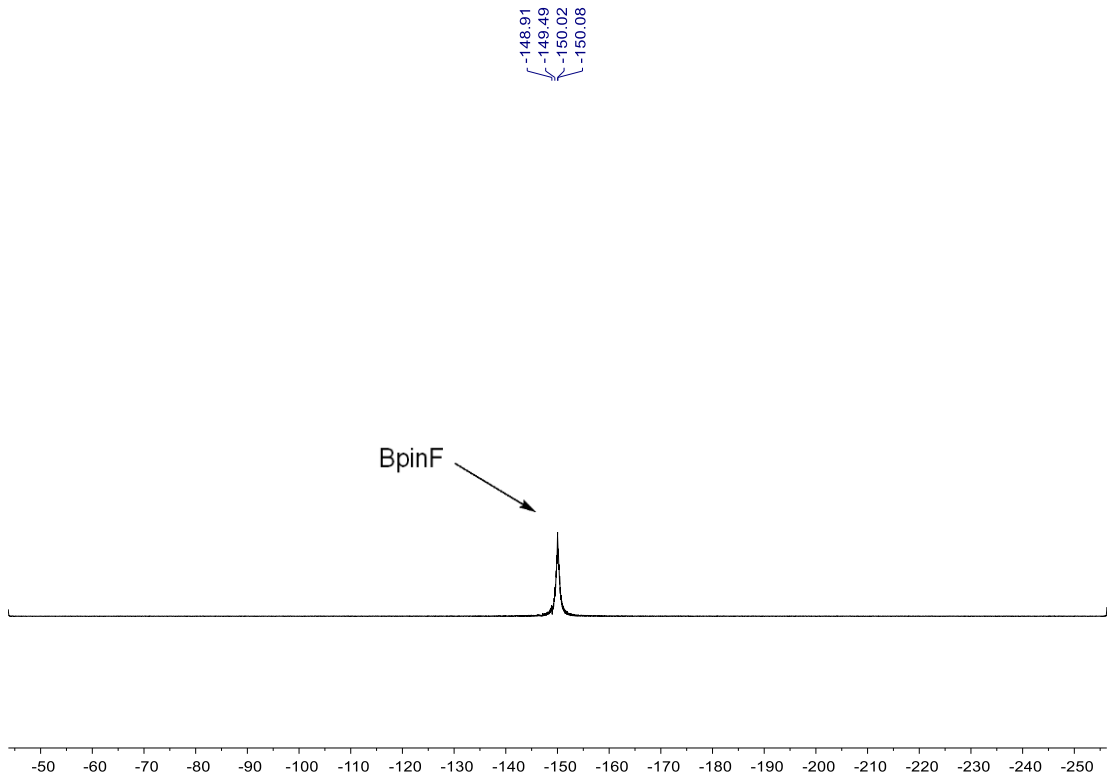
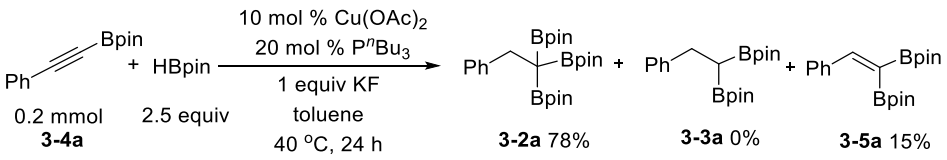


Figure 3-2. *In situ* ^{19}F NMR spectrum of FBpin in CH_2Cl_2 (471 MHz).

3.4.2 Evidence for an alkynylboronate intermediate

A series of studies were carried out to gain insight into the reaction mechanism. Alkynylboronate **3-4a** gave **3-2a** in 78% yield with the concomitant generation of side product **3-5a** in 15% yield (Scheme 3-2). This indicated that alkynylboronate **3-4a** may serve as an intermediate in the catalytic reaction.

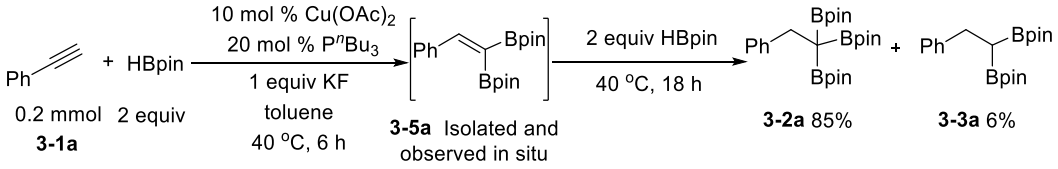


Scheme 3-2. Evidence for an alkynylboronate intermediate.

3.4.3 Evidence for a 1,1-diborylalkene intermediate 3-5a

When **3-2a** was reacted with 2 equiv of HBpin, 1,1-diborylalkene **3-5a** was observed as the major product by GC-MS after 6 h with the concomitant generation of byproduct **3-3a** via double hydroborations of terminal alkyne **3-1a** (Figure 3-3). When another 2 equiv of HBpin were added to the reaction mixture, **3-2a** was isolated in 85% yield after 18 h, and no 1,1-diborylalkene **3-5a** remained, as

evidenced by GC-MS (Figure 3-4), suggesting that the 1,1-diborylalkene is an intermediate in the catalytic cycle which undergoes hydroboration to form the final product.



Scheme 3-3. Evidence for a 1,1-diborylalkene intermediate **3-5a**.

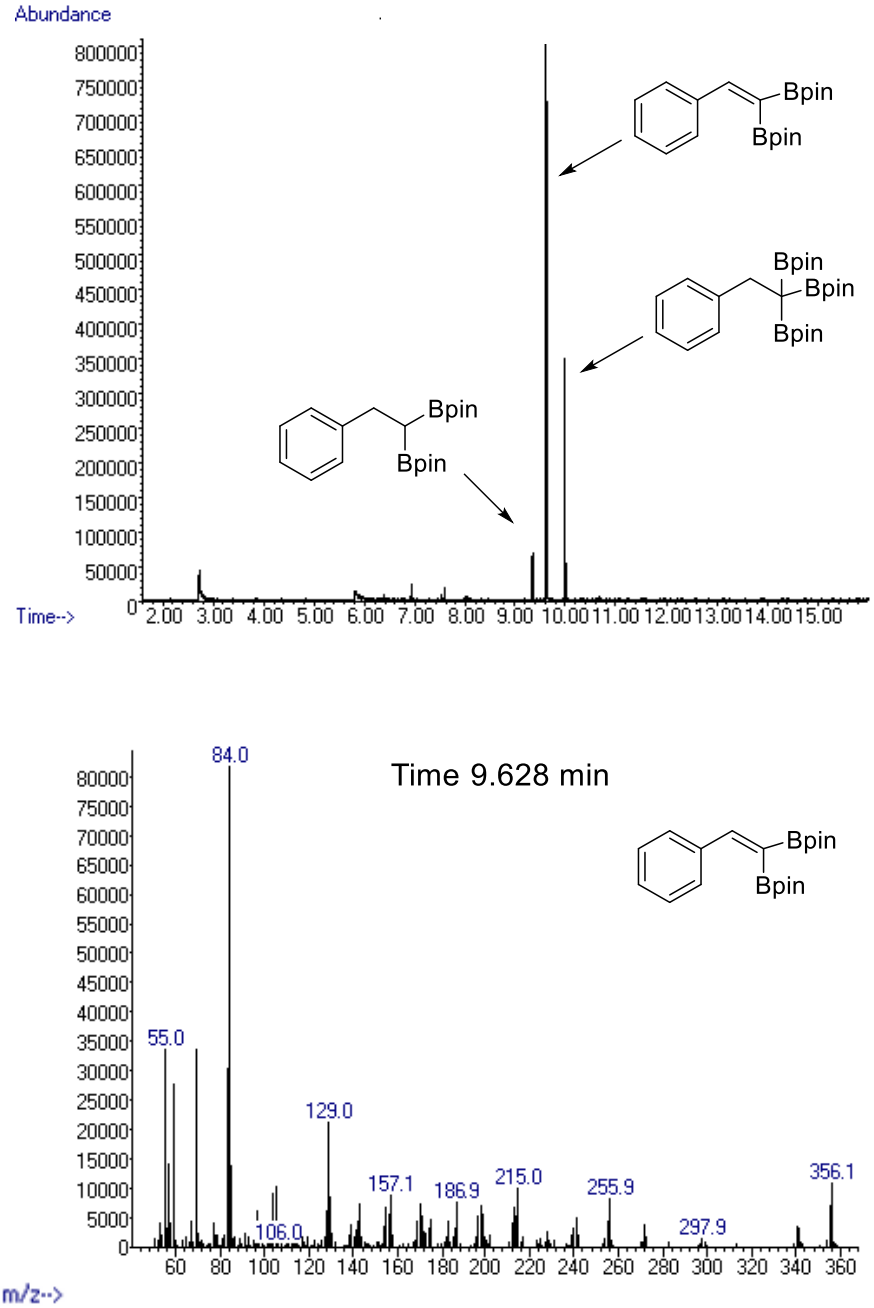


Figure 3-3. GC-MS of reaction mixture after 6 h.

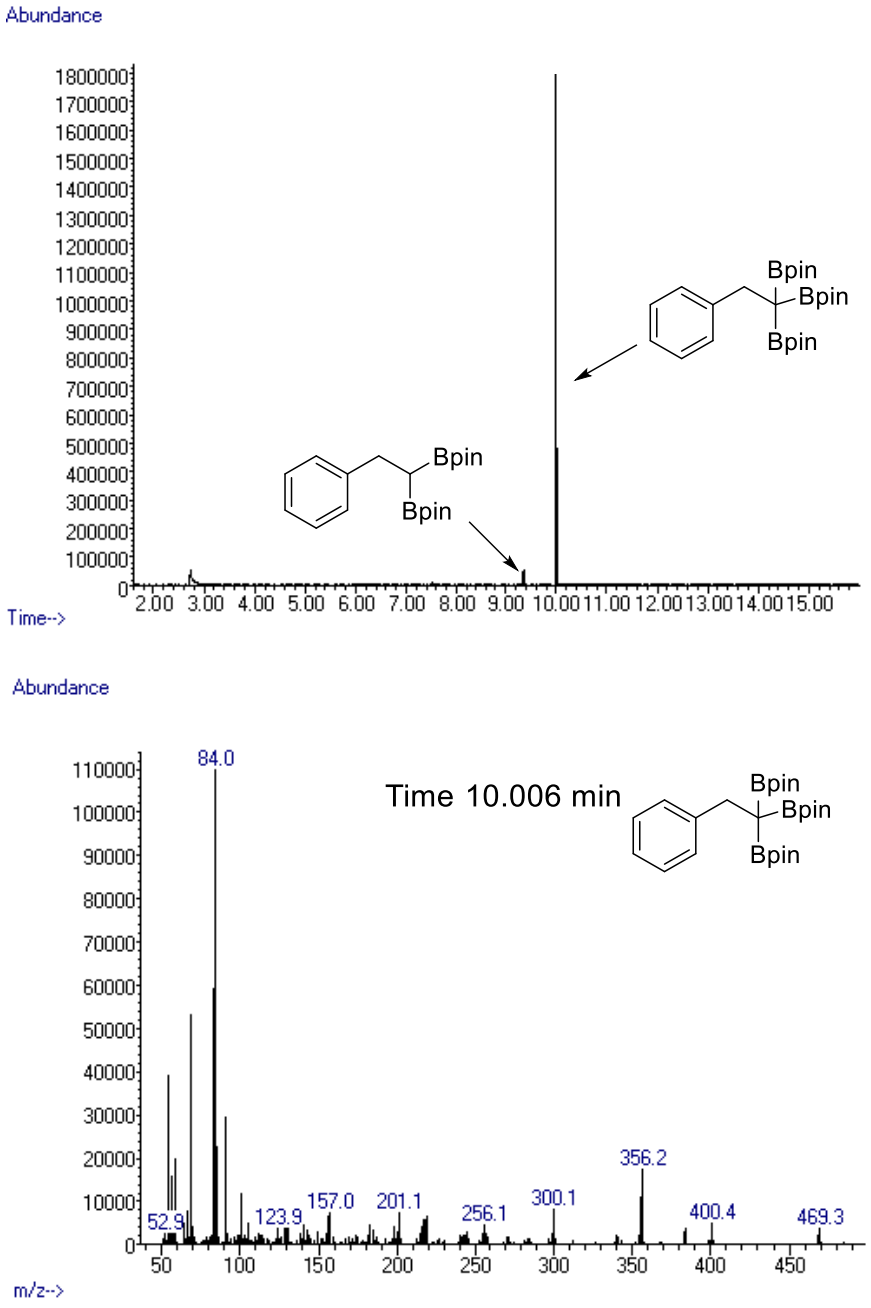
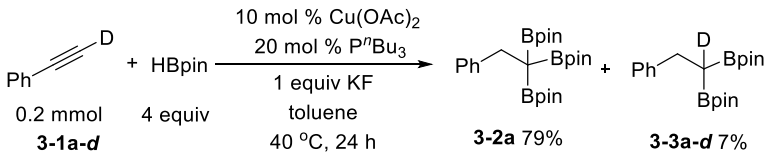


Figure 3-4. GC-MS of reaction mixture after 24 h.

3.4.4 Deuterium labeling studies

Deuterium labeling studies were conducted by using 1-deutero-2-phenylethyne **3-1a-*d*** as the substrate (the level of deuterium content was 90%, shown below in Figure 3-5) under the standard reaction conditions.[171] The reaction gave **3-2a** without deuterium incorporation (see NMR spectrum in Figure 3-6). GC-MS analysis indicated the formation of **3-3a-*d*** (see Figure 3-7 and Figure 3-8).



Scheme 3-4. Deuterium labeling studies.

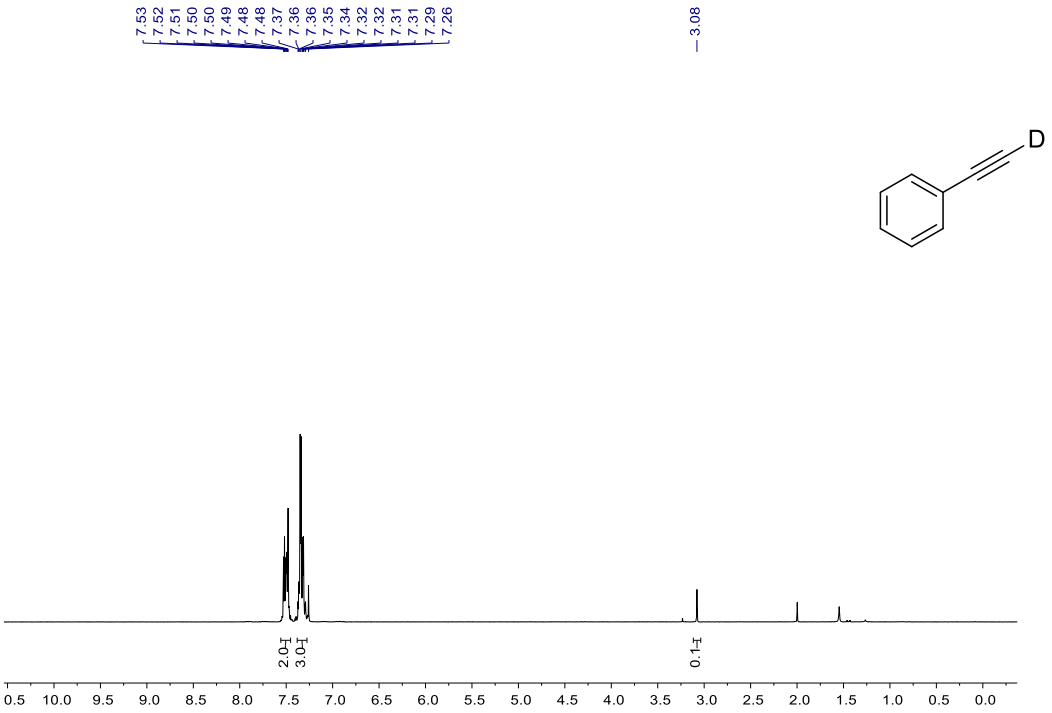


Figure 3-5. ^{1}H NMR spectrum of **3-1a-*d*** (200 MHz, $CDCl_3$).

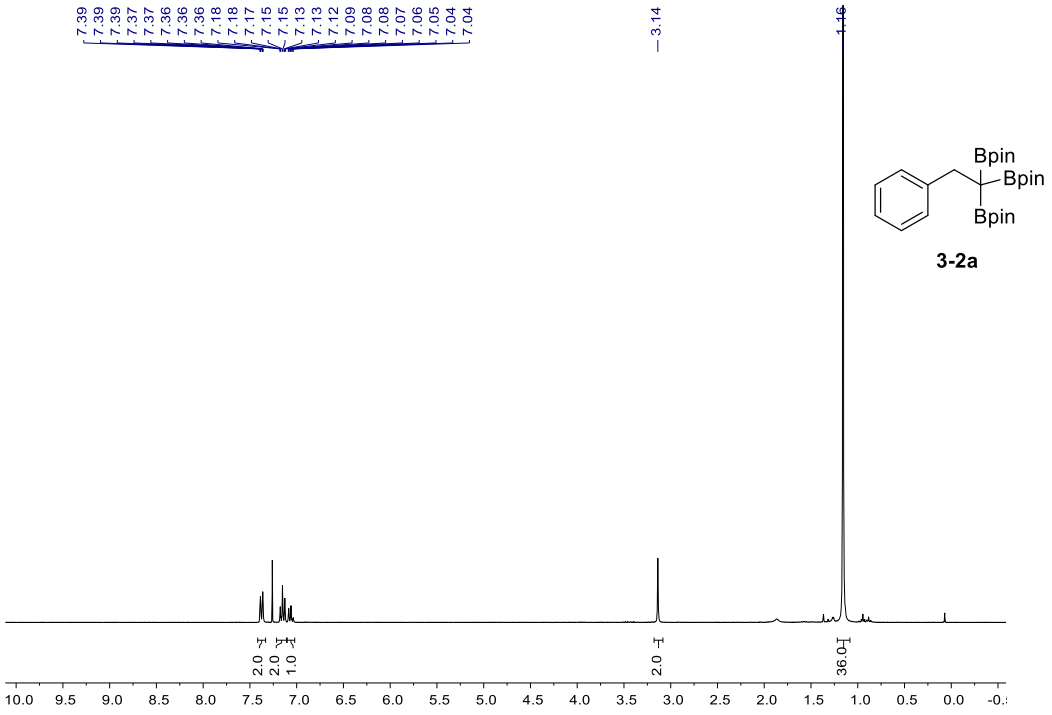


Figure 3-6. ^{1}H NMR spectrum of **3-2a** (300 MHz, $CDCl_3$).

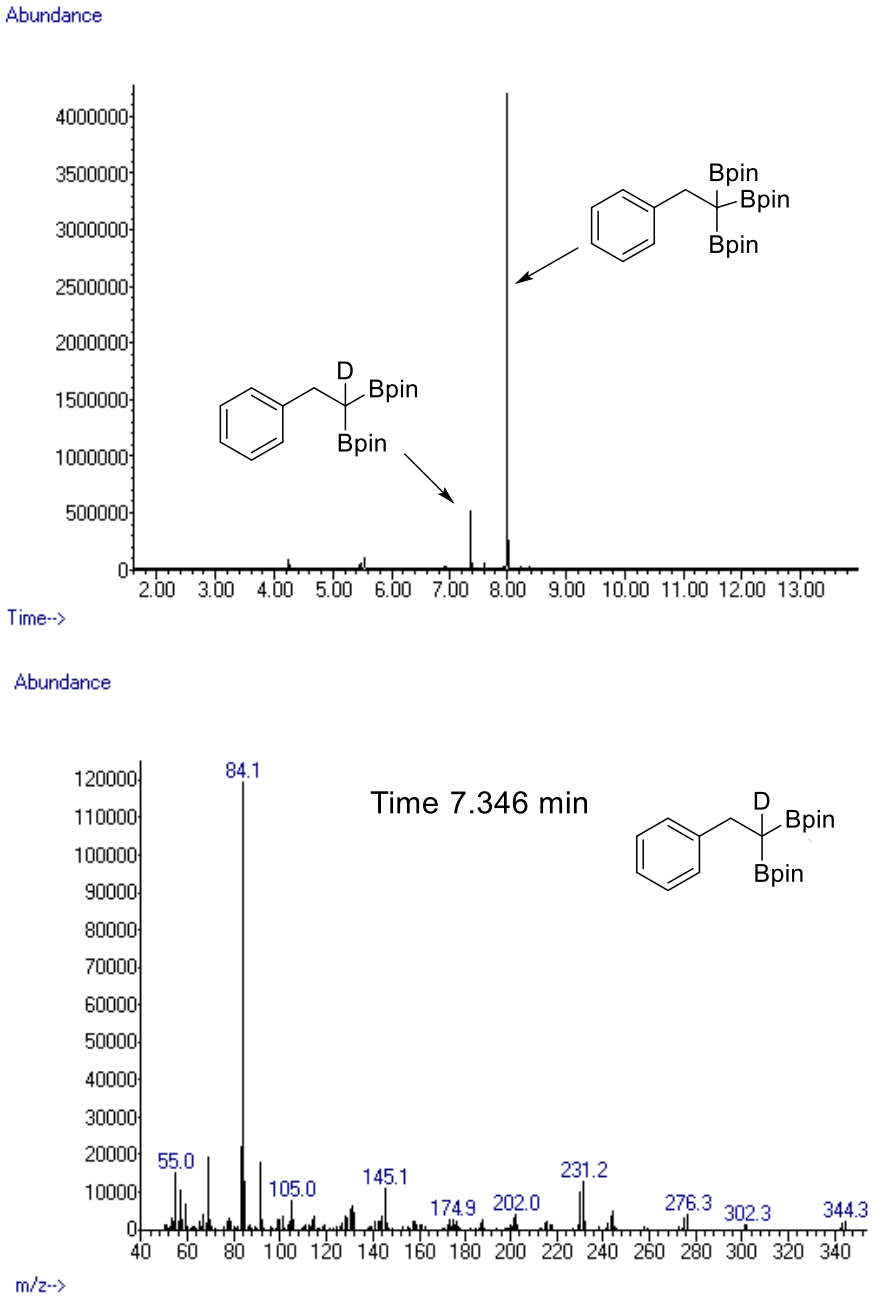


Figure 3-7. GC-MS of **3-3a-*d***: m/z: 359 $[M]^+$ (not observed), 344 $[M\text{-}CH_3]^+$.

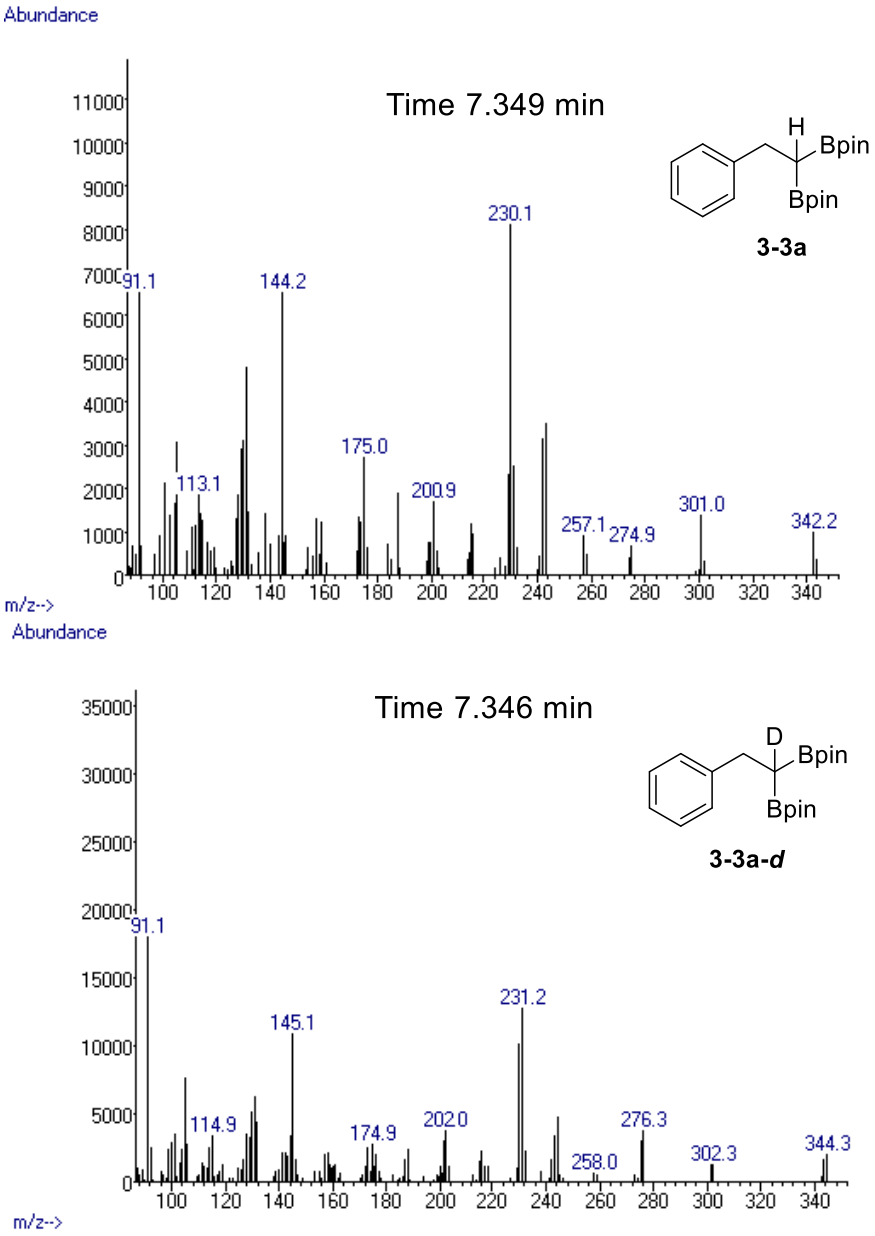
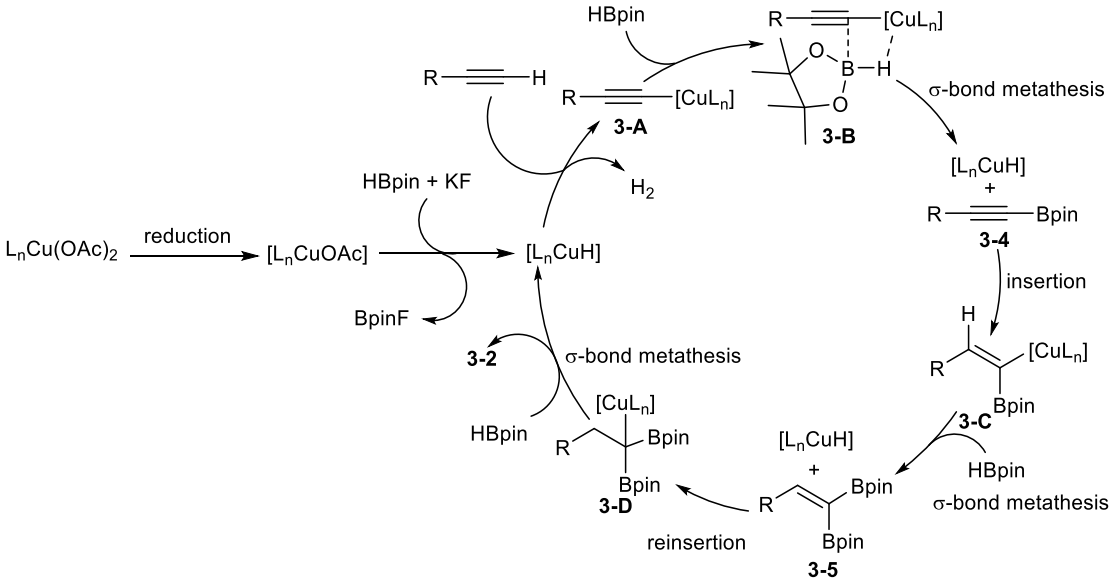


Figure 3-8. The fragmentation patterns for **3-3a** and **3-3a-*d*** (GC-MS, EI^+).

3.4.5 Plausible mechanism

Based on the experimental observations and literature precedents.[191][192] a possible catalytic cycle for the Cu-catalyzed sequential dehydrogenative borylation and hydroboration of terminal alkynes is shown in Scheme 3-5. [L_nCuOAc], generated by reduction of $Cu(OAc)_2$ in the presence of phosphine,[173-174][193] reacts with HBpin and KF to afford a copper hydride intermediate, as well as FBpin, the latter confirmed by *in situ* $^{11}B\{^1H\}$ and ^{19}F NMR studies (Figure 3-1 and 3-2).[190c] The copper hydride can react with terminal alkynes to give the alkynylcopper

intermediate **3-A**, and H_2.[194] The highly polarized copper-carbon bond could undergo a σ-bond metathesis with HBpin (**3-B**) to afford intermediate alkynyl boronic ester **3-4**, and [L_nCuH].[69, 195] *Syn* addition of [L_nCuH] to alkynyl boronic ester **3-4** would afford the alkenyl copper species **3-C**,[65, 68] which then reacts with HBpin via σ-bond metathesis to give intermediate 1,1-diborylalkene **3-5** *vide supra*.[196] Then, **3-5** undergoes Cu-catalyzed hydroboration to furnish the 1,1,1-tris(boronate), regenerating [L_nCuH].[90]

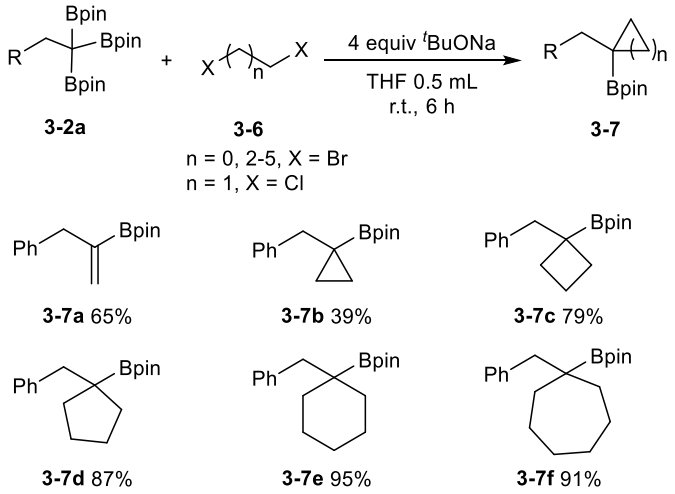


Scheme 3-5. A plausible mechanism.

3.5 Synthetic applications of 1,1,1-triborylalkanes

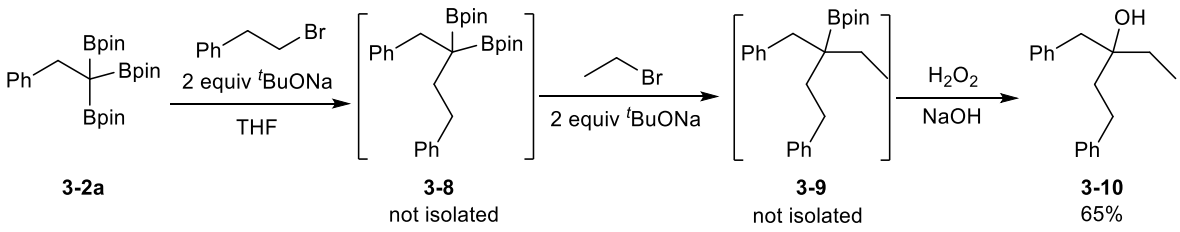
While multiple borylated compounds such as *gem*-diborylalkanes are important synthetic intermediates for preparing organoboron compounds via C-C bond formation,[186m-o, 197] by comparison, the use of 1,1,1-tris(boronates) is much less developed.[148-149, 151] Herein, an alkoxide-promoted deborylative alkylation of 1,1,1-tris(boronates) through the generation and electrophilic trapping of *α*-boryl carbanions is described. Using 1,n-dihalides as electrophiles and ^{t}BuONa as base, It was found that double deborylative alkylation of 1,1,1-tris(boronates) reliably delivered α-vinylboronates **3-7a** and carbocyclic derivatives **3-7b** to **3-7f** at room temperature in high yields within 6 h (Table 3-10). This strategy provides an efficient, straightforward route to useful α-vinylboronates and cyclic organoboronates.[186f]

Table 3-10: Deborylative alkylation for the construction of carbocyclic organoboronates.[a]



[a] Standard conditions: in an argon-filled glove box, **3-2a** (0.11 mmol, 1.1 equiv), **3-6** (0.1 mmol), ^{t}BuONa (4 equiv), THF (0.5 mL), r.t., 6 h; isolated yield.

In addition, different alkyl groups can be introduced in a stepwise manner by two sequential base-mediated deborylative alkylations to furnish tertiary boronic esters **3-9** with three different alkyl groups. Oxidation of the tertiary boronic ester with H_2O_2/NaOH proceeded with reasonable efficiency giving tertiary alcohol **3-10** in 65% isolated yield. Importantly, the transformations of 1,1,1-tris(boronates) products to tertiary alcohols can be performed in a one-pot, three-step fashion without the requirement for isolation of the intermediates (Scheme 3-6).



Scheme 3-6. Stepwise deborylative alkylation and oxidation to prepare a tertiary alcohol.

3.6 Summary

In conclusion, a general, atom-economical method for the synthesis of 1,1,1-trisboronates from terminal alkynes catalyzed using readily available and inexpensive $Cu(OAc)_2$ and phosphine ligand has been developed. A wide range of aryl and alkyl alkynes underwent this transformation producing the corresponding 1,1,1-triborylalkanes in modest to high yields. The reaction can be readily

conducted on a gram scale in high yield. It was demonstrated that 1,1,1-triborylalkanes are useful synthetic intermediates for the construction of carbocyclic organoboronates and α-vinylboronates, which were difficult to synthesize using previously reported methods. A one-pot, stepwise deborylative functionalization of 1,1,1-triborylated alkanes gave an unsymmetrical $R_1R_2R_3C(OH)$ tertiary alcohol.

3.7 Experimental procedure and characterization data

3.7.1 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. HPLC grade solvents were argon saturated and 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. All manipulations in this work were performed in an argon-filled glove box.

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 40 °C.

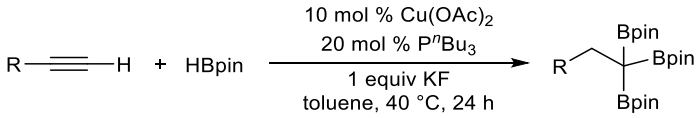
GC-MS analyses were performed using an Agilent 7890A gas chromatograph (column: HP-5MS 5 % phenyl methyl siloxane, 30 m, ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 80 °C (2 min), 80 °C to 180 °C (20 °C min^{-1}), 180 °C to 280 °C (50 °C min^{-1}), 280 °C (5 min); carrier gas: He (1.2 mL min^{-1})) equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A series auto sampler/injector. Elemental analyses were performed on a Leco CHNS-932 Elemental Analyzer. High-resolution mass spectra were recorded using a Thermo Fischer Scientific Exactive Plus Orbitrap MS system (ASAP, ESI or HESI probe).

NMR spectra were recorded at ambient temperature using Bruker Avance 200 NMR (^{1}H, 200 MHz), Bruker DRX-300 (^{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}, 126 MHz; ^{11}B, 160 MHz; ^{19}F, 471 MHz) spectrometers. ^{1}H NMR chemical shifts are reported relative to TMS and were referenced *via* the residual proton resonance of the deuterated solvent ($CDCl_3$: 7.26 ppm) whereas ^{13}C{^{1}H} NMR spectra are reported relative to TMS *via* the carbon signal of the deuterated solvent ($CDCl_3$: 77.00 ppm). ^{11}B NMR chemical shifts are quoted relative to $BF_3{\cdot}Et_2O$ as the external standard. ^{19}F NMR chemical shifts are quoted relative to $CFCl_3$ as the external standard.

3.7.2 Experimental procedure

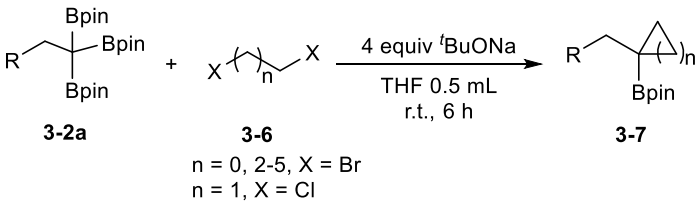
3.7.2.1 Synthesis of 1,1,1-triborylalkanes (3-2)



3-1 **3-2**

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, $Cu(OAc)_2$ (10 mol %, 3.6 mg, 0.02 mmol), KF (1 equiv, 11.6 mg, 0.2 mmol) and toluene (0.25 mL) were added. Then, P^nBu_3 (8.1 mg, 9.9 μL, 0.04 mmol), alkyne **3-1** (0.2 mmol), and HBpin (102.4 mg, 116.1 μL, 0.8 mmol) were added in this order and the tube was sealed with a crimped septum cap. The reaction was heated at 40 °C under argon for the indicated amount of time. The reaction mixture was then diluted with Et_2O (4 mL) and filtered through a plug of celite (ø 3 mm × 8 mm) in air with copious washing (Et_2O). The solvents were removed *in vacuo*, and the residue was purified by flash column chromatography on silica gel (hexane: ethyl acetate = 95:5).

3.7.2.2 Synthesis of carbocyclic organoboronates (3-7)

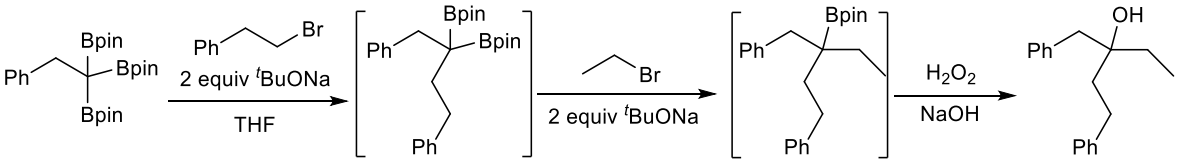


3-2a **3-6** **3-7**

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, **3-2a** (1.1 equiv, 53.3 mg, 0.11 mmol), alkyl halide (1.0 equiv, 0.1 mmol) and THF (0.5 mL) were added, then NaO^tBu (4.0 equiv, 38.4 mg, 0.4 mmol) was added

slowly and the tube was sealed with a crimped septum cap. The mixture was stirred under argon at r.t. for 6 h. The mixture was then filtered through a plug of celite (Ø 3 mm × 8 mm) in air with copious washing (Et_2O). The solvents were removed *in vacuo*, and the residue was then purified by flash column chromatography on silica gel (pentane: diethylether = 96:4).

3.7.2.3 Synthesis of tertiary alcohol (3-10)

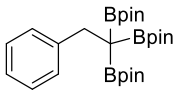


3-2a **3-8** not isolated **3-9** not isolated **3-10** 65%

In a 10 mL Schlenk tube equipped with a magnetic stirring bar, **3-2a** (1.1 equiv, 53.3 mg, 0.11 mmol), 2-phenylethyl bromide (1.0 equiv, 0.1 mmol) and THF (0.5 mL) were added, then NaO*t*Bu (2.0 equiv, 0.2 mmol) was added. The mixture was stirred under argon at ambient temperature for 3 h. GC-MS analysis of an aliquot was used to confirm that the reaction **3-2a** had gone to completion. NaO*t*Bu (2.0 equiv, 0.2 mmol) was then added to the mixture, followed by bromoethane (1.0 equiv, 0.1 mmol) via microsyringe. The mixture was stirred under argon at ambient temperature for 3 h. GC analysis of aliquots was used to monitor reaction progress. The tube was chilled with an ice water bath, and 0.1 mL of degassed mixture of 3 M aqueous NaOH and 30% H_2O_2, 1:1, was injected all at once at 0 °C. The cooling bath was removed, and the reaction mixture was stirred at ambient temperature for 3 h. Then, the mixture was extracted with diethyl ether (3 × 5 mL), and the combined organic layers were washed with water (5 mL), brine (10 mL) and dried over $MgSO_4$. The solvents were removed *in vacuo*, and the residue was then purified by flash column chromatography on silica gel (pentane: diethylether = 92:8).

3.7.3 Characterization data for products

2,2',2''-(2-phenylethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2a)



Isolated yield: 93%.

White solid, m.p.: 83.9 °C. Its spectroscopic data are consistent with a literature report.[149]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 – 7.34 (m, 2H), 7.20 – 6.99 (m, 3H), 3.14 (s, 2H), 1.16 (s, 36H).

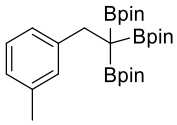
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 144.2, 129.5, 127.1, 124.9, 82.9, 33.2, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.7.

HRMS (ASAP): m/z for $C_{26}H_{44}B_3O_6$ $[M+H]^+$ calcd: 485.3412, found: 485.3400.

Anal. Calcd for $C_{26}H_{43}B_3O_6$: C, 64.51; H, 8.95; found: C, 64.57; H, 8.95.

2,2',2''-(2-(m-tolyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2b)



Isolated yield: 62%.

White solid, m.p.: 77.7 °C. Its spectroscopic data are consistent with a literature report.[149]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23 – 7.14 (m, 2H), 7.04 (apparent t, J = 8 Hz, 1H), 6.92 – 6.85 (m, 1H), 3.11 (s, 2H), 2.26 (s, 3H), 1.16 (s, 36H).

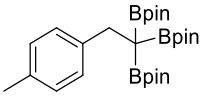
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 144.1, 136.3, 130.1, 127.1, 126.6, 125.5, 82.9, 33.1, 24.6, 21.3. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.3.

HRMS (ASAP): m/z for $C_{27}H_{46}B_3O_6$ $[M+H]^+$ calcd: 499.3568, found: 499.3561.

Anal. Calcd for $C_{27}H_{45}B_3O_6$: C, 65.11; H, 9.11; found: C, 65.05; H, 9.09.

2,2',2''-(2-(p-tolyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2c)



Isolated yield: 85%.

White solid, m.p.: 101.5 °C. Its spectroscopic data are consistent with a literature report.[149]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (d, J = 8 Hz, 2H), 6.96 (d, J = 8 Hz, 2H), 3.09 (s, 2H), 2.26 (s, 3H), 1.16 (s, 36H).

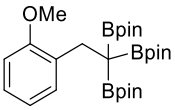
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 141.0, 134.0, 129.3, 127.8, 82.8, 32.8, 24.6, 20.9. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.8.

HRMS (ASAP): m/z for $C_{27}H_{46}B_3O_6$ $[M+H]^+$ calcd: 499.3568, found: 499.3562.

Anal. Calcd for $C_{27}H_{45}B_3O_6$: C, 65.11; H, 9.11; found: C, 65.11; H, 9.01.

2,2',2''-(2-(2-methoxyphenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2d)



Isolated yield: 44%.

White solid, m.p.: 160.1 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16 – 7.02 (m, 2H), 6.82 – 6.68 (m, 2H), 3.80 (s, 3H), 3.12 (s, 2H), 1.16 (s, 36H).

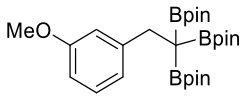
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 157.6, 132.4, 128.3, 125.5, 119.2, 109.1, 82.8, 55.1, 26.6, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.6.

HRMS (ASAP): m/z for $C_{27}H_{46}B_3O_7$ $[M+H]^+$ calcd: 515.3517, found: 515.3512.

Anal. Calcd for $C_{27}H_{45}B_3O_7$: C, 63.08; H, 8.82; found: C, 62.94; H, 8.83.

2,2',2''-(2-(3-methoxyphenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2e)



Isolated yield: 88%.

White solid, m.p.: 109.2 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15 – 6.84 (m, 3H), 6.63 (ddd, J = 8, 3, 1 Hz, 1H), 3.76 (s, 3H), 3.12 (s, 2H), 1.16 (s, 36H).

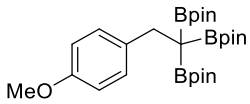
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 158.9, 145.9, 128.0, 122.0, 114.6, 111.1, 82.9, 55.1, 33.3, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.4.

HRMS (ASAP): m/z for $C_{27}H_{46}B_3O_7$ $[M+H]^+$ calcd: 515.3517, found: 515.3510.

Anal. Calcd for $C_{27}H_{45}B_3O_7$: C, 63.08; H, 8.82; found: C, 62.97; H, 8.81.

2,2',2''-(2-(4-methoxyphenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2f)



Isolated yield: 61%.

White solid, m.p.: 113.7 °C. Its spectroscopic data are consistent with a literature report.[149]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, J = 9 Hz, 2H), 6.71 (d, J = 9 Hz, 2H), 3.75 (s, 3H), 3.06 (s, 2H), 1.16 (s, 36H).

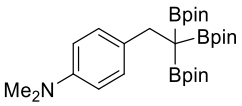
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 157.2, 136.5, 130.5, 112.5, 82.9, 55.2, 32.3, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.5.

HRMS (ASAP): m/z for $C_{27}H_{46}B_3O_7$ $[M+H]^+$ calcd: 515.3517, found: 515.3511.

Anal. Calcd for $C_{27}H_{45}B_3O_7$: C, 63.08; H, 8.82; found: C, 63.19; H, 8.77.

N, N-dimethyl-4-(2,2,2-tris (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)aniline (3-2g)



Isolated yield: 42%.

White solid, m.p.: 121.6 °C. Its spectroscopic data are consistent with a literature report.[149]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (d, J = 9 Hz, 2H), 6.63 (d, J = 9 Hz, 2H), 3.04 (s, 2H), 2.85 (s, 6H), 1.16 (s, 36H).

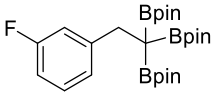
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 148.6, 133.5, 130.1, 112.8, 82.8, 41.4, 32.2, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.6.

HRMS (ASAP): m/z for $C_{28}H_{49}B_3NO_6$ $[M+H]^+$ calcd: 528.3824, found: 528.3834.

Anal. Calcd for $C_{28}H_{48}B_3NO_6$: C, 63.80; H, 9.18; N, 2.66; found: C, 63.58; H, 9.19; N,2.50.

2,2',2''-(2-(3-fluorophenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2h)



Isolated yield: 81%.

White solid, m.p.: 107.8 °C. Its spectroscopic data are consistent with a literature report.[149]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19 – 7.02 (m, 3H), 6.86 – 6.67 (m, 1H), 3.11 (s, 2H), 1.16 (s, 36H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 162.4 (d, J = 243 Hz), 147.0 (d, J = 7 Hz), 128.3 (d, J = 8 Hz), 125.3 (d, J = 3 Hz), 116.3 (d, J = 21 Hz), 111.6 (d, J = 21 Hz), 83.0, 33.0 (d, J = 2 Hz), 24.5. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

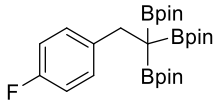
^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.7.

^{19}F NMR (471 MHz, $CDCl_3$): δ = -115.8 (ddd, J = 11, 9, 6 Hz).

HRMS (ASAP): m/z for $C_{26}H_{43}B_3FO_6$ $[M+H]^+$ calcd: 503.3317, found: 503.3311.

Anal. Calcd for $C_{26}H_{42}B_3FO_6$: C, 62.20; H, 8.43; found: C, 62.20; H, 8.63.

2,2',2''-(2-(4-fluorophenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2i)



Isolated yield: 80%.

White solid, m.p.: 101.6 °C. Its spectroscopic data are consistent with a literature report.[149]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 – 7.29 (m, 2H), 7.05 – 6.65 (m, 2H), 3.08 (s, 2H), 1.16 (s, 36H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 160.9 (d, J = 242 Hz), 139.8 (d, J = 3 Hz), 130.9 (d, J = 8 Hz), 113.6 (d, J = 21 Hz), 83.0, 32.4, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

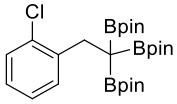
^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.4.

^{19}F NMR (471 MHz, $CDCl_3$): δ = -117.9 – -122.0 (m).

HRMS (ASAP): m/z for $C_{26}H_{43}B_3FO_6$ $[M+H]^+$ calcd: 503.3317, found: 503.3308.

Anal. Calcd for $C_{26}H_{42}B_3FO_6$: C, 62.20; H, 8.43; found: C, 62.09; H, 8.49.

2,2',2''-(2-(2-chlorophenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2j)



Isolated yield: 74%.

White solid, m.p.: 165.3 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.3 – 7.2 (m, 2H), 7.1 – 6.9 (m, 2H), 3.2 (s, 2H), 1.2 (s, 36H).

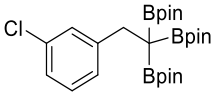
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 141.4, 134.8, 129.1, 128.5, 125.9, 125.3, 83.0, 30.7, 24.5. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.6.

HRMS (ASAP): m/z for $C_{26}H_{43}B_3ClO_6$ $[M+H]^+$ calcd: 519.3022, found: 519.3016.

Anal. Calcd for $C_{26}H_{42}B_3ClO_6$: C, 60.23; H, 8.17; found: C, 60.30; H, 8.15.

2,2',2''-(2-(3-chlorophenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2k)



Isolated yield: 79%.

White solid, m.p.: 132.7 °C. Its spectroscopic data are consistent with a literature report.[149]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 – 7.39 (m, 1H), 7.31 – 7.24 (m, 1H), 7.19 – 6.85 (m, 2H), 3.09 (s, 2H), 1.17 (s, 36H).

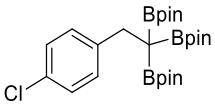
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 146.4, 133.0, 129.6, 128.3, 128.0, 125.0, 83.1, 32.9, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.4.

HRMS (ASAP): m/z for $C_{26}H_{43}B_3ClO_6$ $[M+H]^+$ calcd: 519.3022, found: 519.3017.

Anal. Calcd for $C_{26}H_{42}B_3ClO_6$: C, 60.23; H, 8.17; found: C, 60.31; H, 8.23.

2,2',2''-(2-(4-chlorophenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2l)



Isolated yield: 81%.

White solid, m.p.: 136.7 °C. Its spectroscopic data are consistent with a literature report.[149]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 – 7.28 (m, 2H), 7.21 – 6.85 (m, 2H), 3.07 (s, 2H), 1.16 (s, 32H).

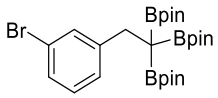
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 142.7, 131.0, 130.5, 127.1, 83.0, 32.6, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.5.

HRMS (ASAP): m/z for $C_{26}H_{43}B_3ClO_6$ $[M+H]^+$ calcd: 519.3022, found: 519.3018.

Anal. Calcd for $C_{26}H_{42}B_3ClO_6$: C, 60.23; H, 8.17; found: C, 60.23; H, 8.26.

2,2',2''-(2-(3-bromophenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2m)



Isolated yield: 74%.

White solid, m.p.: 131.3 °C. Its spectroscopic data are consistent with a literature report.[149]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (apparent t, J = 2 Hz, 1H), 7.38 – 7.28 (m, 1H), 7.20 (ddd, J = 8, 2, 1 Hz, 1H), 7.02 (apparent t, J = 8 Hz, 1H), 3.08 (s, 2H), 1.17 (s, 36H).

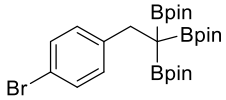
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 146.8, 132.5, 128.7, 128.5, 127.9, 121.4, 83.1, 32.9, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.7.

HRMS (ASAP): m/z for $C_{26}H_{43}B_3BrO_6$ $[M+H]^+$ calcd: 563.2517, found: 563.2510.

Anal. Calcd for $C_{26}H_{42}B_3BrO_6$: C, 55.47; H, 7.52; found: C, 55.79; H, 7.61.

2,2',2''-(2-(4-bromophenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2n)



Isolated yield: 65%.

White solid, m.p.: 138.0 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (s, 4H), 3.05 (s, 2H), 1.16 (s, 12H).

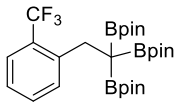
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 143.3, 131.4, 130.0, 118.6, 83.0, 32.7, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.7.

HRMS (ASAP): m/z for $C_{26}H_{43}B_3BrO_6$ $[M+H]^+$ calcd: 563.2517, found: 563.2509.

Anal. Calcd for $C_{26}H_{42}B_3BrO_6$: C, 55.47; H, 7.52; found: C, 55.56; H, 7.52.

2,2',2''-(2-(2-(trifluoromethyl)phenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2o)



Isolated yield: 69%.

White solid, m.p.: 159.8 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (d, J = 8 Hz, 1H), 7.41 (d, J = 8 Hz, 2H), 7.33 (apparent t, J = 8 Hz, 1H), 7.16 (t, J = 8 Hz, 1H), 3.33 (s, 2H), 1.12 (s, 36H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 143.4 (q, J = 2 Hz), 130.5 (q, J = 1 Hz), 129.4, 128.8 (q, J = 29 Hz), 124.8 (q, J = 274 Hz), 125.1 (q, J = 6 Hz), 124.6, 83.0, 29.0 (d, J = 3 Hz), 24.5. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

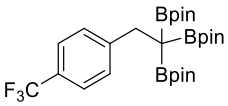
^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.5.

^{19}F NMR (471 MHz, $CDCl_3$): δ = -60.0.

HRMS (ASAP): m/z for $C_{27}H_{43}B_3F_3O_6$ $[M+H]^+$ calcd: 553.3285, found: 553.3285.

Anal. Calcd for $C_{27}H_{42}B_3F_3O_6$: C, 58.74; H, 7.67; found: C, 59.18; H, 7.67.

2,2',2''-(2-(4-(trifluoromethyl)phenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2p)



Isolated yield: 78%.

White solid, m.p.: 123.3 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 – 7.45 (m, 2H), 7.46 – 7.35 (m, 2H), 3.16 (s, 2H), 1.15 (s, 36H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 148.6 (d, J = 1 Hz), 129.8, 127.3 (q, J = 32 Hz), 124.7 (q, J = 272 Hz), 124.0 (q, J = 4 Hz), 83.1, 33.2, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

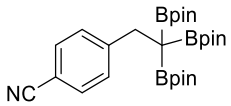
^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.5.

^{19}F NMR (471 MHz, $CDCl_3$): δ = -62.1.

HRMS (ASAP): m/z for $C_{27}H_{43}B_3F_3O_6$ $[M+H]^+$ calcd: 553.3285, found: 553.3278.

Anal. Calcd for $C_{27}H_{42}B_3F_3O_6$: C, 58.74; H, 7.67; found: C, 58.96; H, 7.96.

4-(2,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (3-2q)



Isolated yield: 19%.

White solid, m.p.: 131.4 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (aa'bb' quartet, 4H), 3.15 (s, 2H), 1.16 (s, 36H).

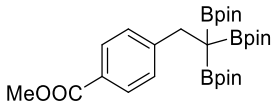
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 150.4, 131.0, 130.3, 119.7, 108.6, 83.2, 33.6, 24.5. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

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

HRMS (ASAP): m/z for $C_{27}H_{43}B_3NO_6$ $[M+H]^+$ calcd: 510.3364, found: 510.3359.

Anal. Calcd for $C_{27}H_{42}B_3NO_6$: C, 63.70; H, 8.32; N,2.75; found: C, 63.02, H, 8.43; N, 2.44.

methyl 4-(2,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (3-2r)



Isolated yield: 71%.

White solid, m.p.: 110.1 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 – 7.73 (m, 2H), 7.52 – 7.36 (m, 2H), 3.87 (s, 3H), 3.16 (s, 2H), 1.15 (s, 36H).

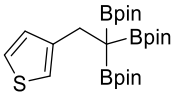
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 167.5, 150.2, 129.4, 128.5, 126.8, 83.0, 51.7, 33.4, 24.5. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.6.

HRMS (ASAP): m/z for $C_{28}H_{46}B_3O_8$ $[M+H]^+$ calcd: 543.3466, found: 543.3455.

Anal. Calcd for $C_{28}H_{45}B_3O_8$: C, 62.04; H, 8.37; found: C, 61.97; H, 8.45.

2,2',2''-(2-(thiophen-3-yl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2s)



Isolated yield: 78%.

White solid, m.p.: 91.2 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 – 6.89 (m, 3H), 3.07 (s, 2H), 1.16 (s, 36H).

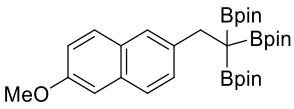
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 145.0, 130.4, 122.9, 121.0, 82.9, 27.9, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.6.

HRMS (ASAP): m/z for $C_{21}H_{42}B_3O_6S$ $[M+H]^+$ calcd: 491.2976, found: 491.2972.

Anal. Calcd for $C_{21}H_{41}B_3O_6S$: C, 58.82; H, 8.43; S, 6.54 Found: C, 58.96; H, 8.41; S, 6.21.

2,2',2''-(2-(6-methoxynaphthalen-2-yl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2t)



Isolated yield: 62%.

White solid, m.p.: 139.9 °C. Its spectroscopic data are consistent with a literature report.[149]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (dd, J = 2, 1 Hz, 1H), 7.64 – 7.44 (m, 3H), 7.05 (m, 2H), 3.89 (s, 3H), 3.28 (s, 2H), 1.16 (s, 36H).

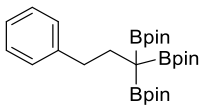
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 156.6, 139.6, 132.6, 129.6, 128.9, 128.7, 126.8, 125.3, 117.8, 105.5, 82.9, 55.2, 33.2, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.6.

HRMS (ASAP): m/z for $C_{31}H_{48}B_3O_7$ $[M+H]^+$ calcd: 565.3674, found: 565.3662.

Anal. Calcd for $C_{31}H_{47}B_3O_7$: C, 66.00; H, 8.40 Found: C, 65.93; H, 8.45.

2,2',2''- (3-phenylpropane-1,1,1-triyl)tris (4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2u)



Isolated yield: 67%.

White solid, m.p.: 145.4°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.7 – 7.6 (m, 4H), 7.5 – 7.4 (m, 1H), 3.4 – 2.9 (m, 2H), 2.5 – 2.0 (m, 2H), 1.6 (s, 36H).

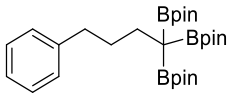
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 144.7, 128.6, 127.9, 125.1, 82.8, 37.0, 31.1, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.6.

HRMS (ASAP): m/z for $C_{27}H_{46}B_3O_6$ $[M+H]^+$ calcd: 499.3568, found: 499.3558.

Anal. Calcd for $C_{27}H_{45}B_3O_6$: C, 65.11; H, 9.11 Found: C, 65.10; H, 9.08.

2,2',2''-(4-phenylbutane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2v)



Isolated yield: 37%.

White solid, m.p.: 84.5 °C. Its spectroscopic data are consistent with a literature report.[123]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 – 7.10 (m, 5H), 2.72 – 2.47 (m, 2H), 1.88 – 1.68 (m, 4H), 1.21 (s, 36H).

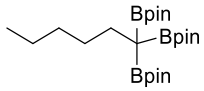
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 143.7, 128.4, 128.0, 125.1, 82.7, 37.0, 32.1, 28.4, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.7.

HRMS (ASAP): m/z for $C_{28}H_{48}B_3O_6$ $[M+H]^+$ calcd: 513.3725, found: 513.3722.

Anal. Calcd for $C_{28}H_{47}B_3O_6$: C, 65.67; H, 9.25 Found: C, 65.62; H, 9.32.

2,2',2''-(hexane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2w)



Isolated yield: 35%.

White solid, m.p.: 70.6 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.71 – 1.59 (m, 2H), 1.47 – 1.24 (m, 6H), 1.20 (s, 36H), 0.86 (t, *J* = 6 Hz, 3H).

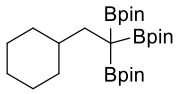
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 82.6, 32.7, 30.1, 28.1, 24.6, 22.5, 14.0. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.5.

HRMS (ASAP): m/z for $C_{24}H_{48}B_3O_6$ $[M+H]^+$ calcd: 465.3725, found: 465.3720.

Anal. Calcd for $C_{24}H_{47}B_3O_6$: C, 62.12; H, 10.21 Found: C, 62.07; H, 10.21.

2,2',2''-(2-cyclohexylethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2x)



Isolated yield: 37%.

White solid, m.p.: 168.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.75 – 1.59 (m, 7H), 1.42 (m, 1H), 1.23 (s, 36H), 1.18 – 1.06 (m, 3H), 0.98 – 0.84 (m, 2H).

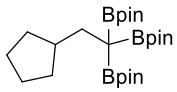
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 82.6, 38.8, 35.1, 33.7, 26.7, 24.6. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.9.

HRMS (ASAP): m/z for $C_{26}H_{50}B_3O_6$ $[M+H]^+$ calcd: 491.3881, found: 491.3877.

Anal. Calcd for $C_{26}H_{49}B_3O_6$: C, 63.72; H, 10.08 Found: C, 63.78; H, 10.08.

2,2',2''-(2-cyclopentylethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2y)



Isolated yield: 47%.

White solid, m.p.: 120.1 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.98 – 1.85 (m, 1H), 1.85 – 1.77 (m, 2H), 1.74 – 1.36 (m, 6H), 1.26 – 1.12 (m, 38H).

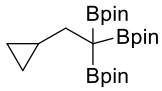
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 82.6, 42.2, 33.3, 33.2, 24.9, 24.7. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.6.

HRMS (ASAP): m/z for $C_{25}H_{48}B_3O_6$ $[M+H]^+$ calcd: 477.3725, found: 477.3719.

Anal. Calcd for $C_{25}H_{47}B_3O_6$: C, 63.07; H, 9.25 Found: C, 63.11; H, 9.32.

2,2',2''-(2-cyclopropylethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2z)



Isolated yield: 76%.

White solid, m.p.: 99.7 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.62 (d, J = 7 Hz, 2H), 1.20 (s, 36H), 1.05 – 0.87 (m, 1H), 0.37 – 0.13 (m, 4H).

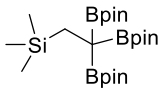
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 82.6, 33.0, 24.6, 11.8, 5.5. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.7.

HRMS (ASAP): m/z for $C_{23}H_{44}B_3O_6$ $[M+H]^+$ calcd: 449.3412, found: 449.3405.

Anal. Calcd for $C_{23}H_{43}B_3O_6$: C, 61.66; H, 9.67 Found: C, 61.71; H, 9.65.

trimethyl(2,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (3-2aa)



Isolated yield: 23%.

White solid, m.p.: 94.7 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, 36H), 0.91 (s, 2H), 0.01 (s, 9H).

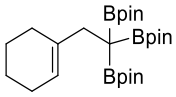
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 82.8, 24.7, 13.6, 0.8. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.5.

HRMS (ASAP): m/z for $C_{23}H_{48}B_3O_6Si$ $[M+H]^+$ calcd: 481.3494, found: 481.3483.

Anal. Calcd for $C_{23}H_{47}B_3O_6Si$: C, 57.54; H, 9.87 Found: C, 57.84; H, 10.00.

2,2',2''-(2-(cyclohex-1-en-1-yl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3-2ab)



Isolated yield: 52%.

White solid, m.p.: 140.0 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.48 – 5.09 (m, 1H), 2.37 (d, J = 2 Hz, 2H), 2.01 – 1.75 (m, 4H), 1.68 – 1.38 (m, 4H), 1.18 (s, 36H).

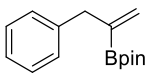
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 139.2, 118.6, 82.6, 35.4, 29.8, 25.0, 24.6, 23.1, 22.7. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.8.

HRMS (ASAP): m/z for $C_{26}H_{48}B_3O_6$ $[M+H]^+$ calcd: 489.3725, found: 489.3712.

Anal. Calcd for $C_{26}H_{47}B_3O_6$: C, 63.98; H, 9.71 Found: C, 64.01; H, 9.76.

4,4,5,5-tetramethyl-2-(3-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (3-7a)



Isolated yield: 65%.

Colorless oil. Its spectroscopic data are consistent with a literature report.[198]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 – 7.05 (m, 5H), 5.83 (d, J = 3 Hz, 1H), 5.53 (s,

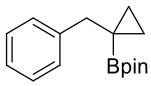
1H), 3.48 (s, 2H), 1.21 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 140.7, 129.8, 129.1, 128.1, 125.7, 83.5, 41.4, 24.7. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 30.0.

HRMS (ASAP): m/z for $C_{15}H_{22}BO_2$ $[M+H]^+$ calcd: 245.1707, found: 245.174.

2-(1-benzylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-7b)



Isolated yield: 39.0%.

Colorless oil.

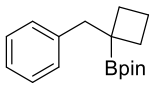
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 – 7.19 (m, 4H), 7.19 – 7.11 (m, 1H), 2.63 (s, 2H), 1.16 (s, 12H), 0.81 – 0.70 (m, 2H), 0.51 – 0.41 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 142.1, 129.0, 127.8, 125.5, 83.1, 41.1, 24.5, 11.3. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 33.7.

HRMS (ASAP): m/z for $C_{16}H_{23}BO_2$ [M] calcd: 258.1786, found: 258.1780.

2-(1-benzylcyclobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-7c)



Isolated yield: 79%.

Colorless oil.

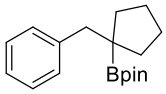
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.01 (m, 5H), 2.88 (s, 2H), 2.21 – 2.04 (m, 2H), 2.01 – 1.76 (m, 4H), 1.17 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 141.1, 129.0, 127.8, 125.6, 83.1, 45.0, 30.4, 24.6, 18.2. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 34.8.

HRMS (ASAP): m/z for $C_{17}H_{25}BO_2$ [M] calcd: 272.1942, found: 272.1938.

2-(1-benzylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-7d)



Isolated yield: 87%.

Colorless oil.

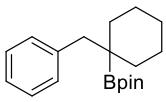
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 – 7.05 (m, 5H), 2.71 (s, 2H), 1.88 – 1.70 (m, 2H), 1.70 – 1.48 (m, 4H), 1.47 – 1.33 (m, 2H), 1.17 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 141.5, 129.7, 127.7, 125.6, 83.0, 43.4, 35.2, 24.8, 24.7. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 35.0.

HRMS (ASAP): m/z for $C_{18}H_{27}BO_2$ [M] calcd: 286.2099, found: 286.2095.

2-(1-benzylcyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-7e)



Isolated yield: 95%.

Colorless oil.

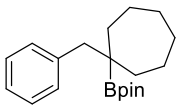
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.19 (m, 2H), 7.19 – 7.12 (m, 3H), 2.60 (s, 2H), 1.86 (s, 2H), 1.68 – 1.51 (m, 3H), 1.40 – 1.23 (m, 2H), 1.20 (s, 12H), 1.15 – 0.91 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 139.6, 130.3, 127.6, 125.7, 83.0, 46.3, 35.0, 26.4, 25.0. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 34.8.

HRMS (ASAP): m/z for $C_{19}H_{29}BO_2$ $[M+H]^+$ calcd: 301.2333, found: 301.2324.

2-(1-benzylcycloheptyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-7f)



Isolated yield: 91%.

Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 – 7.18 (m, 4H), 7.18 – 7.10 (m, 1H), 2.63 (s,

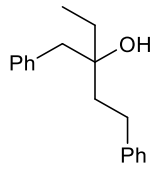
2H), 1.81 (dd, *J* = 13, 8 Hz, 2H), 1.61 – 1.31 (m, 10H), 1.21 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): *δ* = 130.30, 127.59, 125.60, 82.99, 45.53, 35.99, 29.96, 24.93, 24.09.

^{11}B NMR (128 MHz, $CDCl_3$): *δ* = 34.99.

HRMS (ASAP): m/z for $C_{20}H_{32}BO_2$ $[M+H]^+$ calcd: 315.2490, found: 315.2484.

3-benzyl-1-phenylpentan-3-ol (3-10)



Isolated yield: 65%.

Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.4 – 7.2 (m, 7H), 7.2 – 7.2 (m, 3H), 2.8 (s, 2H), 2.7 (dd, J = 10, 8 Hz, 2H), 1.9 – 1.6 (m, 2H), 1.6 – 1.4 (m, 2H), 1.3 (s, 1H), 1.0 (t, J = 8 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): *δ* = 142.5, 137.1, 130.5, 128.4, 128.3, 128.3, 126.5, 125.7, 74.2, 45.1, 40.1, 31.0, 30.0, 8.2.

HRMS (ASAP): m/z for $C_{11}H_{15}O$ $[M-Bn]^+$ calcd: 163.1117, found: 163.1114.

3.7.4 Crystallographic data

A crystal of **3-2m** suitable for single-crystal X-ray diffraction was selected, coated in perfluoropolyether oil, and mounted on a MiTeGen sample holder. Diffraction data were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector using Mo-Kα radiation monochromated by multi-layer focusing mirrors. The crystal was cooled using an Oxford Cryostream low-temperature device. Data were collected at 100 K. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the Bruker software packages. The structure was solved using the intrinsic phasing method (SHELXT)[179] and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' in idealized positions, by full-matrix least squares against F^2 of all data, using SHELXL[180] software and the SHELXLE graphical user interface.[181] Diamond[183] software was used for graphical representation. Crystal data and experimental details are listed

in Table 3-11; full structural information has been deposited with Cambridge Crystallographic Data Centre. CCDC-1936608 (**3-2m**).

Table 3-11: Single-crystal X-ray diffraction data and structure refinements of compound **3-2m**.

Data	**3-2m**
CCDC number	1936608
Empirical formula	$C_{26}H_{42}B_3BrO_6$
Formula weight / g·mol^{-1}	562.93
T / K	100(2)
λ / Å, radiation	MoKα 0.71073
Crystal size / mm³	0.256×0.310×0.489
Crystal color, habit	colorless block
μ / mm^{-1}	1.453
Crystal system	Monoclinic
Space group	$P2_1/n$
a / Å	12.490(4)
b / Å	11.208(4)
c / Å	21.524(5)
α / °	90
β / °	105.706(12)
γ / °	90
Volume / Å^3	2900.8(15)
Z	4
ρ_{calc} / g·cm^{-3}	1.289
F(000)	1184
θ range / °	1.713 - 30.682
Reflections collected	73147
Unique reflections	8932
Parameters / restraints	414 / 132
GooF on F^2	1.018
R_1 [I>2σ(I)]	0.0393
wR^2 (all data)	0.1025
Max. / min. residual electron density / e·Å^{-3}	0.709 / –0.420

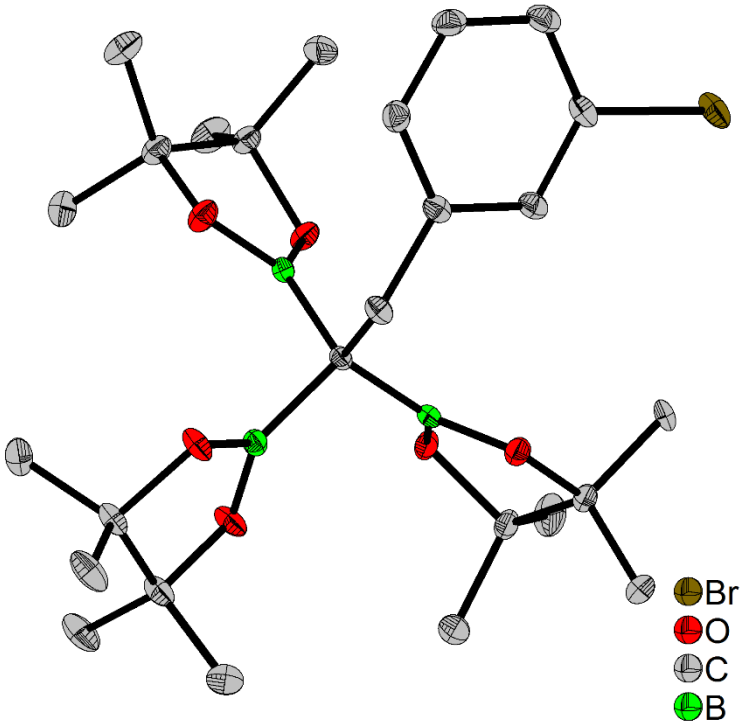


Figure 3-9. Molecular structure of **3-2m** in the solid state at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. One of the Bpin moieties is slightly disordered and only the part with the higher occupancy (94%) is shown here.

Chapter Four

Regio- and Stereoselective Synthesis of 1,1-Diborylalkenes via Brønsted Base-Catalyzed Mixed Diboration of Alkynes with BpinBdan

4 Regio- and Stereoselective Synthesis of 1,1-Diborylalkenes via Brønsted Base-Catalyzed Mixed Diboration of Alkynes with BpinBdan

4.1 Abstract

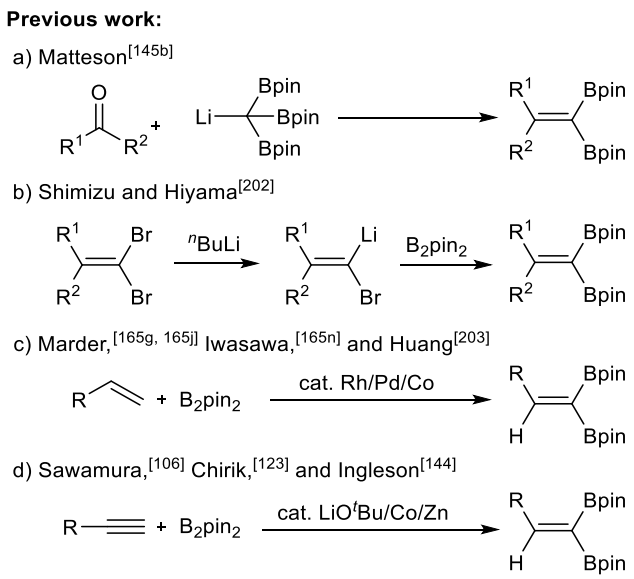
Chapter 4 reported a NaO*t*Bu-catalyzed mixed 1,1-diboration of terminal alkynes with an unsymmetrical diboron reagent BpinBdan. This Brønsted base-catalyzed reaction proceeds in a regio- and stereoselective fashion affording 1,1-diborylalkenes with two different boryl moieties in moderate to high yields, and is applicable to gram-scale synthesis without loss of yield or selectivity. Hydrogen bonding between the Bdan group and *t*BuOH is proposed to be responsible for the observed stereoselectivity. The mixed 1,1-diborylalkenes can be utilized in stereoselective Suzuki-Miyaura cross-coupling reactions.

4.2 Introduction

Organoboronic acids and derivatives have become increasingly of interest due to their widespread applications in organic synthesis, materials science, and pharmaceuticals.[1i, 127, 160, 185d, 185e, 186b, 199] Alkenylboron compounds have been employed in the stereodefined construction of valuable multisubstituted alkenes including natural products, biologically active molecules, and functional materials.[1i, 200] 1,2-Diborylalkenes are well established and are typically synthesized by catalytic diboration of alkynes using Pt catalysts.[1a, 1b, 1f, 1j, 113, 117-119, 154, 166a] Recently, 1,1-diborylalkenes have emerged as versatile building blocks for the synthesis of multisubstituted alkenes, *e.g.* the anticancer agent tamoxifen, via selective and stepwise Suzuki-Miyaura couplings.[1l, 201]

Several approaches have been developed for the synthesis of 1,1-diborylalkenes. As early as 1945, Matteson *et al.* described a condensation of carbonyl compounds with triborylmethylithium, which was prepared by treatment of tetraborylmethane with methyllithium (Scheme 4-1a).[145b] Shimizu and Hiyama reported that B_2pin_2 reacted with alkenylidene-type lithium carbenoids to afford 1,1-diborylalkenes via a boron-based 1,2-migration. Alkenylidene-type lithium carbenoids were formed from

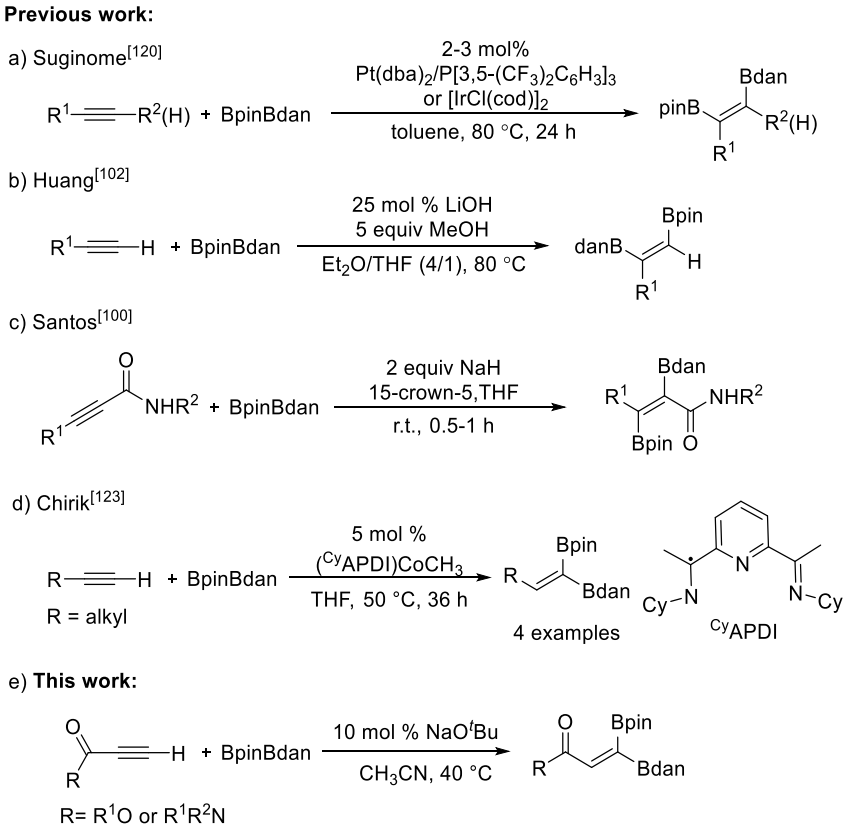
1,1-dibromoalkenes through Li-Br exchange (Scheme 4-1b).[202] Later, several transition metal-catalyzed methods were reported for the synthesis of 1,1-diborylalkenes using alkenes as the starting materials (Scheme 4-1c). In 2003, during the study of the Rh-catalyzed dehydrogenative borylation of alkenes, the Marder group found that a 1,1-diborylalkene was formed via a double dehydrogenative borylation of 4-vinyl anisole with 2 equivalents of B_2pin_2.[165g, 165j] Subsequently, the Iwasawa and Huang groups reported the use of palladium or cobalt catalysts for the geminal diboration of terminal alkenes.[165n, 203] The synthesis of 1,1-diborylalkenes from terminal alkynes is of great interest (Scheme 4-1d). In 2015, Sawamura developed a Brønsted base (LiO^tBu)-catalyzed 1,1-diboration of terminal alkynes bearing electron-withdrawing substituents.[106] Very recently, more general routes to 1,1-diborylalkenes from terminal alkynes were developed by the groups of Chirik and Ingleson using cobalt or zinc catalysts.[123, 144]



Scheme 4-1. Synthesis of 1,1-diborylalkenes.

Unsymmetrical diboron reagents have been developed and applied in many boration reactions.[1m, 24a, 24c, 73, 80, 101, 160c, 185g, 204] In 2010, Suginome and coworkers reported the Pt-catalyzed regioselective 1,2-diboration of alkynes[1a, 1b, 1f, 1j, 113, 117-119, 154, 166a] with the unsymmetrical diboron(4) reagent BpinBdan (pin = pinacolato; dan = 1,8-diaminonaphthalene) in which the Bdan moiety ends up on the terminal carbon (Scheme 4-2a).[120] Later, Huang and Liu reported the diboration of alkyl alkynes with BpinBdan using LiOH as the catalyst in the presence of MeOH. Unlike

Suginome's protocol, the Bdan moiety was incorporated at the internal position (Scheme 4-2b).[102] Diboration of alkynes to generate the *trans*-configured products are scarce.[98, 112, 122, 168, 205] The Santos group developed a transition metal-free *trans*-diboration of alkynamides with BpinBdan promoted by NaH. The amide group in the substrates acted as a directing group to assist this *trans*-diboration with excellent selectivities. Bdan and Bpin were exclusively installed on the *α*- and *β*-carbon atoms, respectively (Scheme 4-2c).[100]



Scheme 4-2. Diboration of alkynes with unsymmetrical diboron reagent BpinBdan.

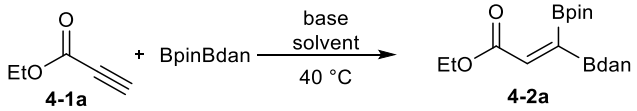
The only report on 1,1-diboration of alkyl alkynes with BpinBdan was achieved by Chirik and coworkers, who synthesized 1,1-diborylalkenes using 5 mol % of (^{Cy}APDI)$CoCH_3$ as the catalyst (Scheme 4-2d).[123] Only 4 examples were reported. Herein, the stereoselective 1,1-diboration of terminal alkynes with BpinBdan catalyzed by NaO^{t}Bu affording 1,1-diborylalkenes containing two different boryl groups was reported (Scheme 4-2e).

4.3 Results and discussion

4.3.1 Optimization of reaction conditions

Initially, the reaction using ethyl propiolate **4-1a** and BpinBdan, under a range of conditions was studied (Table 4-1). Encouragingly, 1,1-diboryalkene **4-2a** was obtained in 62% yield when the reaction was performed in CH_3CN at 40 °C using Li*O*^{t}Bu as the base catalyst (Entry 1). Analysis of the reaction mixture by GC-MS showed the presence of a trace amount of byproduct, which might be the *E*-isomer or 1,2-isomer, with the same mass and similar fragmentation pattern as **4-2a**. A screen of the Brønsted base catalysts revealed that Na*O*^{t}Bu was superior to other catalysts, namely Li*O*^{t}Bu, K*O*^{t}Bu, and Cs_2CO_3 (Entries 1-4). Using organic bases, such as DABCO or Hünig's base (^{i}Pr$_2$EtN), as catalysts were inefficient in this reaction (Entries 5 and 6), indicating that weak bases are not suitable for this transformation. As shown in Entry 7, a control reaction revealed that Na^{t}OBu was essential for this diboration.

Table 4-1: Optimization of reaction conditions.[a]



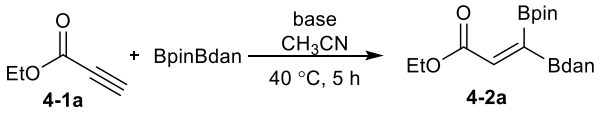
Entry	Base (mol %)	Solvent	Yield of 4-2a (%)[b]
1	Li*O*^{t}Bu (10)	CH_3CN	62 (56)
2	Na*O*^{t}Bu (10)	CH_3CN	88 (76)
3	K*O*^{t}Bu (10)	CH_3CN	60 (55)
4	Cs_2CO_3 (10)	CH_3CN	42
5	DABCO (10)	CH3CN	< 5
6	DIPEA (10)	CH_3CN	< 5
7	-	CH_3CN	0
8	Na*O*^{t}Bu (2)	CH_3CN	54
9	Na*O*^{t}Bu (5)	CH_3CN	72 (45)
10	Na*O*^{t}Bu (20)	CH_3CN	64 (51)
11	Na*O*^{t}Bu (100)	CH_3CN	< 5
12	Na*O*^{t}Bu (10)	1,4-dioxane	72 (61)
13	Na*O*^{t}Bu (10)	Et_2O	65 (52)
14	Na*O*^{t}Bu (10)	MTBE	52 (40)
15	Na*O*^{t}Bu (10)	toluene	60 (51)

[a] Reaction conditions: In an argon-filled glove box, **4-1a** (0.24 mmol, 1.2 equiv), base (10 mol %), BpinBdan (0.2 mmol), solvent (2 mL), at 40 °C for 5 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses.

Further screening of the amount of Na*O*^{t}Bu (2 mol %, 5 mol % and 20 mol %), afforded lower yields of **4-2a** (Entries 8-10). Only trace amount of desired product

was obtained when 1 equivalent of NaO^{t}Bu was used (Entry 11). A survey of solvents revealed that CH_3CN was the optimal reaction medium (Entries 12-15). It is worth noting that GC-MS analysis of the crude reaction mixture showed that **4-2a** was the main product, which indicated that this base catalysis enabled the mixed 1,1-diboration with excellent regio- and stereoselectivities. Other screening details are listed in Table 4-2 to 4-4.

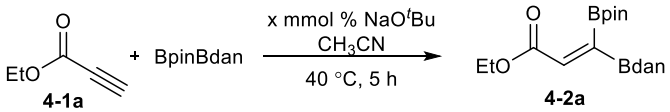
Table 4-2: Screening of bases for the mixed 1,1-diboration of alkynes.[a]



Entry	Base	Yield 4-2a (%)[b]
1	LiOMe	0
2	LiOAc	0
3	DMAP	5
4	K_2CO_3	0
5	Li_2CO_3	0

[a] Standard conditions: in an argon-filled glove box, BpinBdan (0.2 mmol), **4-1a** (0.24 mmol, 1.2 equiv), base (10 mmol %), CH_3CN (2 mL), at 40 °C for 5 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses.

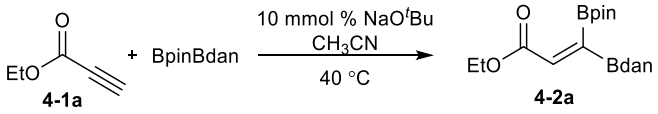
Table 4-3: Screening of the amount of base for the mixed 1,1-diboration of alkynes.[a]



Entry	NaO^{t}Bu (x mmol %)	Yield 4-2a (%)[b]
1	40	40
2	60	24

[a] Standard conditions: in an argon-filled glove box, BpinBdan (0.2 mmol), **4-1a** (0.24 mmol, 1.2 equiv), base (x mmol %), CH_3CN (2 mL), at 40 °C for 5 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses.

Table 4-4: Screening of time for the mixed 1,1-diboration of alkynes.[a]

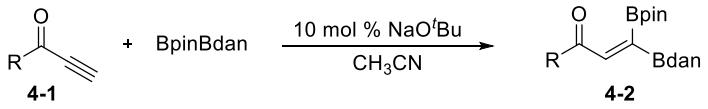


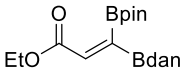
Entry	Time (h)	Yield 4-2a (%)[b]
1	1	53
2	2	56 (54)
3	3	64 (60)
4	4	70
5	10	86 (72)

[a] Standard conditions: in an argon-filled glove box, BpinBdan (0.2 mmol), **4-1a** (0.24 mmol, 1.2 equiv), NaO^{t}Bu (10 mmol %), CH_3CN (2 mL), at 40 °C. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses.

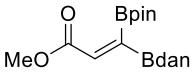
4.3.2 Investigation of reaction scope

Table 4-5: Scope of the mixed 1,1-diboration of terminal alkynes.[a]

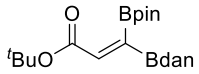




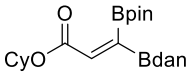
4-2a 76% 5 h
5 mmol scale, 1.47 g, 75%



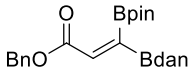
4-2b 75%, 5 h



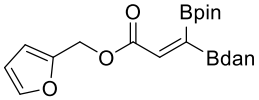
4-2c 78%, 5 h



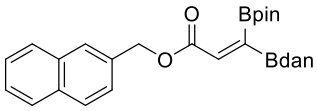
4-2d 74%, 5 h



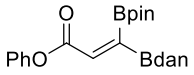
4-2e 78%, 10 h



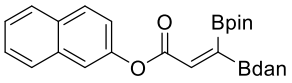
4-2f 43%, 5 h
50%, 10 h



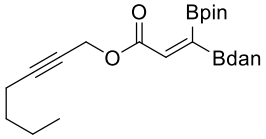
4-2g 63%, 5 h



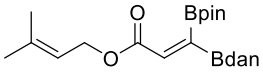
4-2h 65%, 10 h



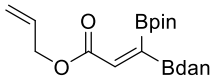
4-2i 75%, 5 h



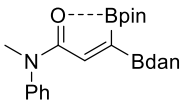
4-2j 62%, 5 h



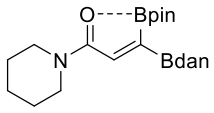
4-2k 72%, 5 h



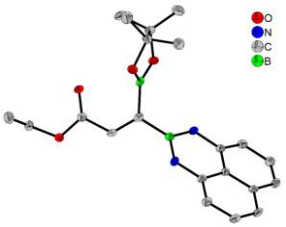
4-2l 75%. 5 h



4-2m 63%, 5 h
87%, 10 h



4-2n 29%, 5 h
50%, 10 h



Molecular structure of **4-2a**[b]

[a] Standard conditions: **4-1** (0.24 mmol), BpinBdan (0.2 mmol), and NaO^{t}Bu (10 mol %) in CH_3CN (2 mL) at 40 °C. Isolated yields. [b] H atoms are omitted for clarity.

With the optimized reaction conditions in hand, the mixed 1,1-diboration of a variety of alkynoates **4-1** was tested (Table 4-5). The model reaction with **4-1a** afforded **4-2a** in 76% isolated yield. Alkoxy substituents ranging from a small methoxy group (**4-2b**) to much larger *tert*-butyoxy group (**4-2c**) provided the desired products in high yields. Substrates with cyclohexyloxy (**4-2d**), benzyloxy (**4-2e**), furan-2-ylmethoxy (**4-2f**), and naphthalen-2-ylmethoxy (**4-2g**) carbonyl groups, afforded the corresponding products in moderated to high yields (43%-78%). The 1,1-diboration of phenyl propiolate (**4-1h**) and naphthalen-2-yl propiolate (**4-1i**) gave products in good yields of 65% and 75%, respectively. Notably, in the presence of competing internal alkyne (**4-2j**) or alkenes (**4-2k** and **4-2l**) substituents, excellent regio- and

chemoselective 1,1-diboration proceeded at the terminal C≡C bond in good yields. Propiolamides **4-1m** and **4-1n** were also compatible with this diboration protocol. Increasing the reaction time to 10 h resulted in increased conversion, and the corresponding products were isolated in 87% and 50% yield, respectively. The formation of five-membered rings via O-B coordination was observed in **4-2m** and **4-2n** (^{11}B NMR spectroscopy of **4-2m**, δ = 29.15, 17.25 ppm; **4-2n**, δ = 29.88, 15.38 ppm). This method enables a convenient gram-scale synthesis (5 mmol) without loss of yield, as demonstrated for **4-1a** (**4-2a**: 1.47 g, 75%). The structure and stereochemistry of the 1,1-diborylalkene products was exemplified by a single-crystal X-ray diffraction study of **4-2a** (Table 4-5, bottom).

4.4 Mechanistic study

4.4.1 Sequential stoichiometric reaction

A mixture of **4-1a** (19.6 mg, 0.2 mmol) in THF (1 mL) was cooled to –78 °C. Then ^{n}BuLi (80 μL, 2.5 M in hexane, 0.2 mmol) was added dropwise at –78 °C. After stirring for 30 min at the same temperature, BpinBdan (58.8 mg, 0.2 mmol) in THF (1 mL) was added dropwise at –78 °C. Then, the mixture was warmed to the ambient temperature with stirring for 1 h. Subsequently, ^{t}BuOH (19 μL, 0.2 mmol) was added and the mixture was stirred for another 1 h. The solvent was removed under reduced pressure to give a brown oil. The yield of **4-2a** was determined to be 23% by ^{1}H NMR analysis using 1,3,5-trioxacyclohexane (0.09 mmol) as an internal standard (Figure 4-1). This sequential stoichiometric reaction indicated that intermediate acetylide **4-A** was generated via deprotonation of the terminal alkyne with NaO^{t}Bu.

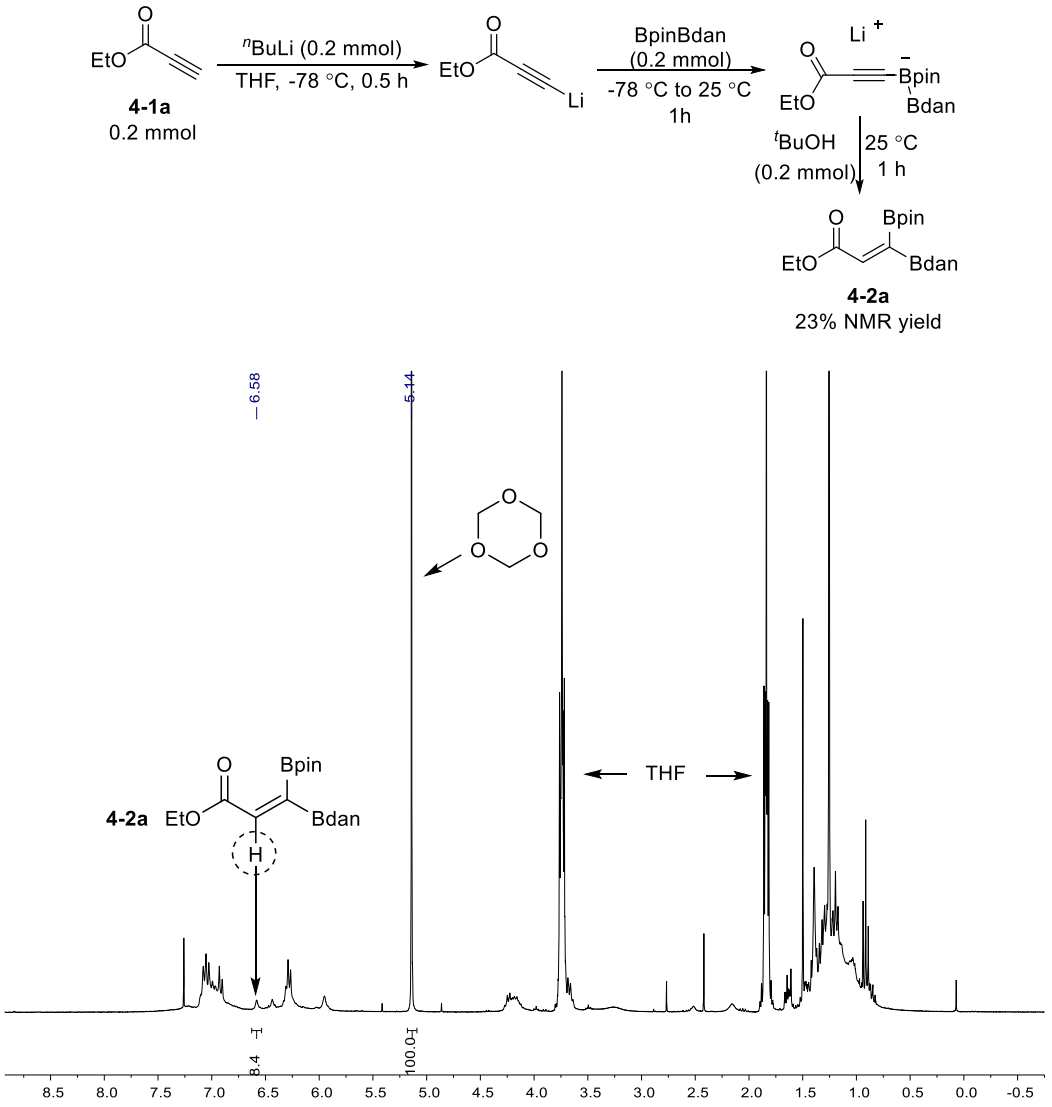


Figure 4-1. ^{1}H NMR spectrum of the crude material including **4-2a** (300 MHz, $CDCl_3$); 1,3,5-trioxacyclohexane (0.09 mmol) was used as an internal standard.

4.4.2 Deuterium labelling experiment

Deuterium labeling studies were conducted by using deuterated ethyl propiolate **4-1a-*d*** as the substrate (the level of deuterium content was 90%, shown below in Figure 4-2) under the standard reaction conditions. The alkenyl C-H of product **4-2a-*d*** is incorporated with 50% deuterium, and there are 45% deuterium on the N-H of Bdan (Figures 4-3 and 4-4). Given the possibility of H/D exchange between ^{t}BuOD and N-H of Bdan, whether the proton on the alkene comes from N-H of Bdan, or from ^{t}BuOH directly cannot be confirmed.

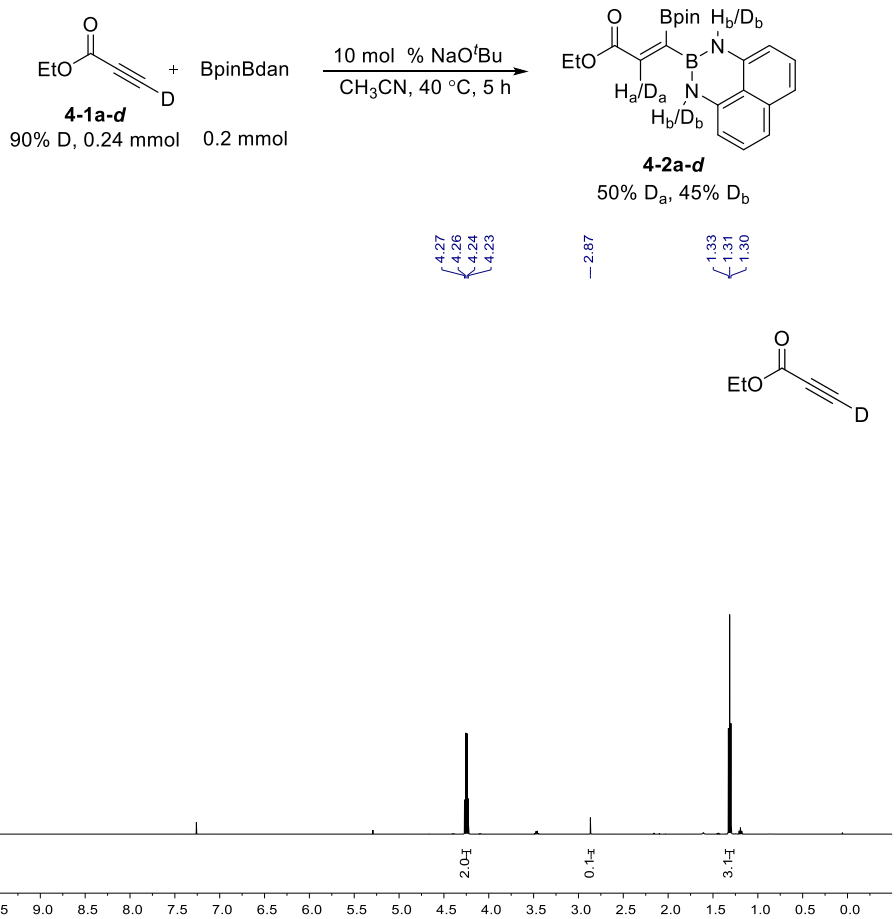


Figure 4-2. ^{1}H NMR spectrum of **4-1a-*d***. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.25 (q, J = 7 Hz, 2H), 2.87 (s, 0.1H), 1.31 (t, J = 7 Hz, 3H).

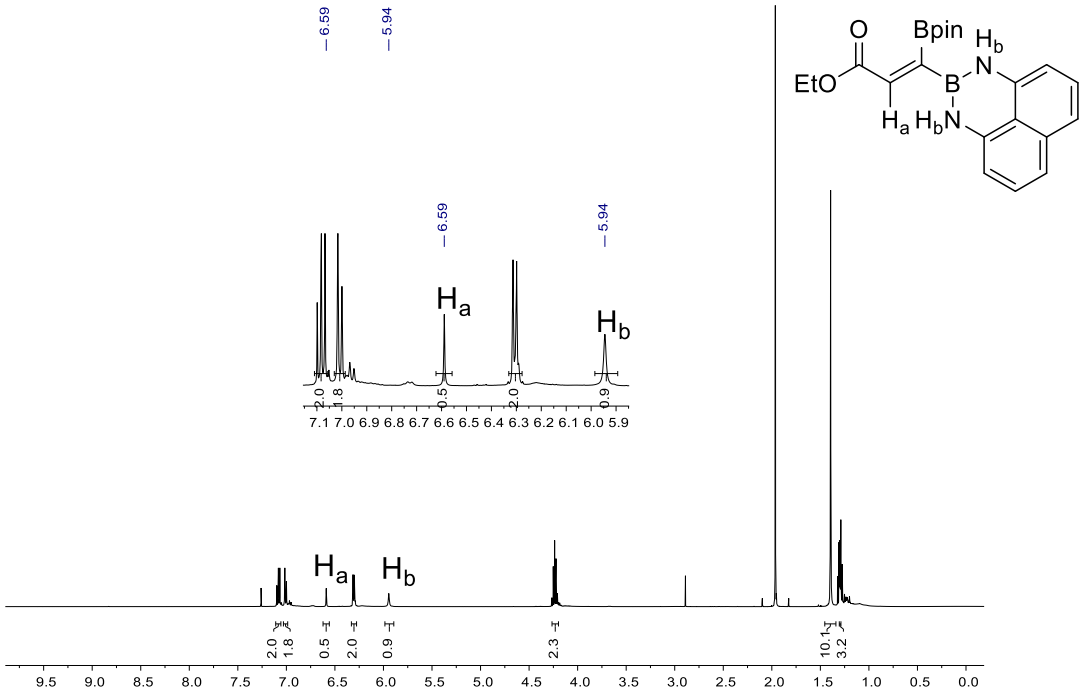


Figure 4-3. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2a-*d*** (reaction mixture).

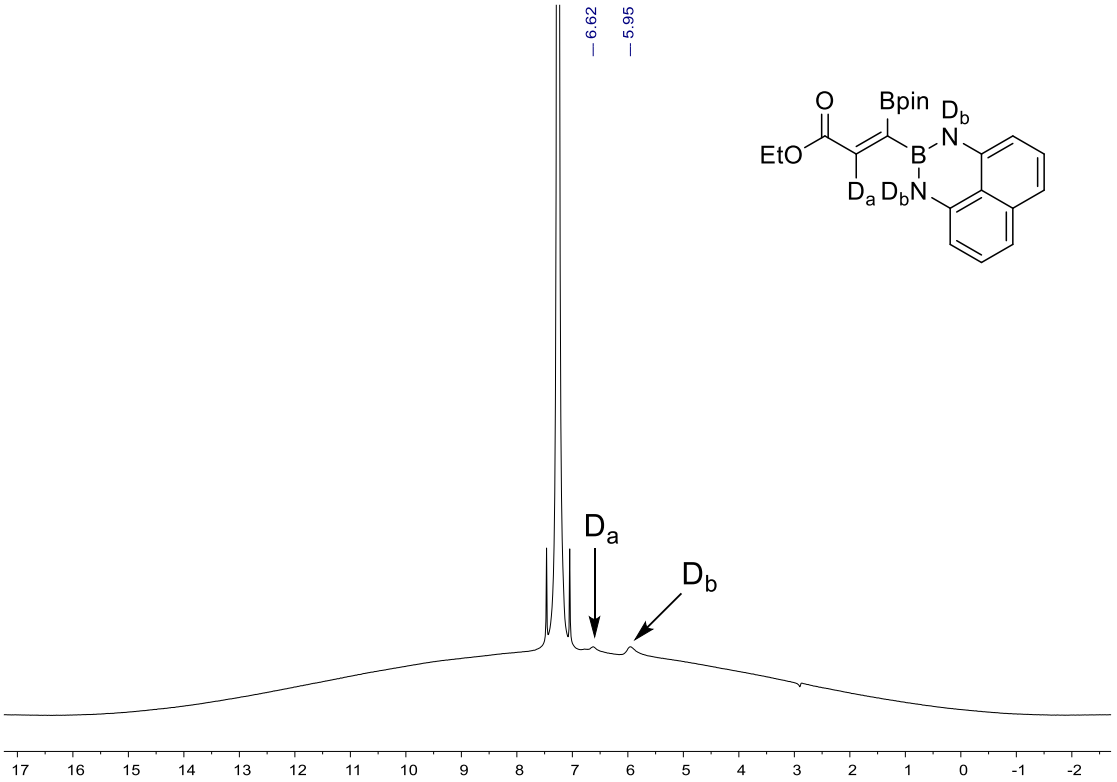
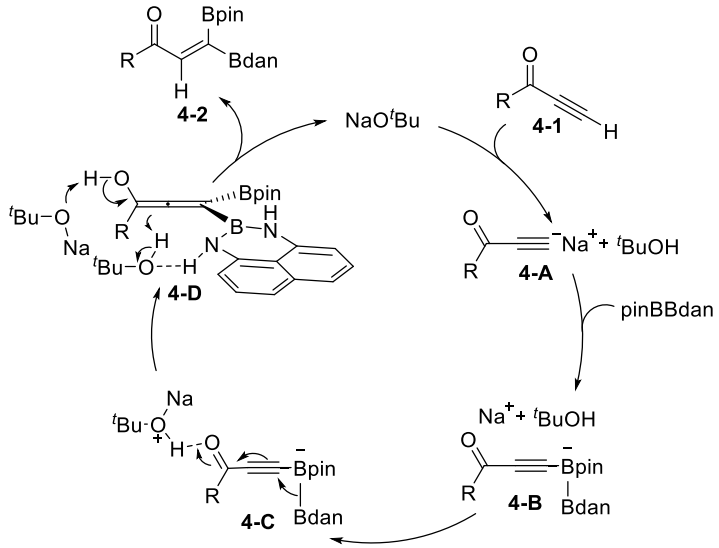


Figure 4-4. ^{2}D NMR spectrum (500 MHz, $CDCl_3$) of **4-2a-*d*** (reaction mixture).

4.4.3 Plausible mechanism

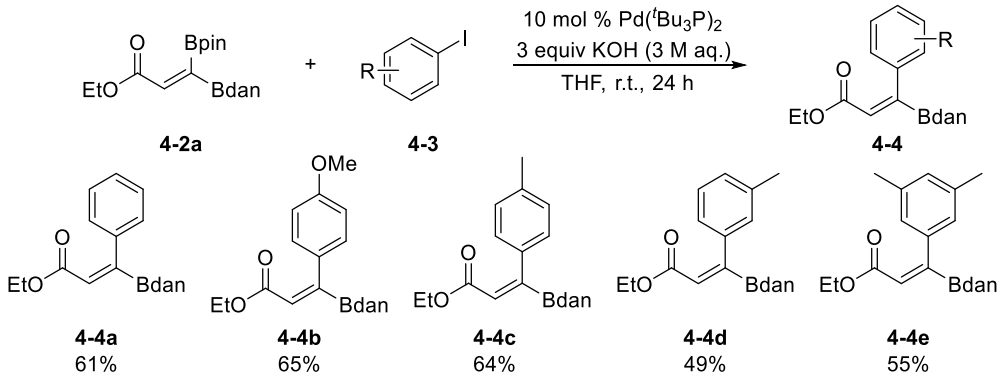
A plausible catalytic cycle for the NaO^{t}Bu-catalyzed mixed 1,1-diboratoin of alkynes is shown in Scheme 4-3. Deprotonation of the terminal alkyne with NaO^{t}Bu generates acetylide **4-A**, which was evidenced by the stoichiometric reaction with ^{n}BuLi. Specie **4-A** reacts with BpinBdan, in which the carbanion attacks the Bpin moiety selectively versus the less electrophilic Bdan group, to form an sp^2-sp^3 alkynyl borate intermediate **4-B**.[24d, 160c, 173a, 206] Then, 1,2-migration of the Bdan moiety in **4-B** to the terminal carbon atom of the alkyne occurs concomitantly with protonation of the carbonyl oxygen atom by ^{t}BuOH to generate allenol intermediate **4-D** and regenerates NaO^{t}Bu. With the assistance of ^{t}BuOH and NaO^{t}Bu, **4-D** isomerizes to the desired product **4-2**. Hydrogen bonding between Bdan and ^{t}BuOH is proposed to result in the high stereoselectivity.



Scheme 4-3. Proposed mechanism.

4.5 Synthetic applications of 1,1-diborylalkenes

The synthesis of 1,1-diborylalkenes bearing two different boryl groups (Bpin and Bdan) is particularly attractive, because their differing reactivities allows selective and stepwise Suzuki-Miyaura cross-couplings.[100, 102, 120, 123] Thus, Suzuki-Miyaura coupling of **4-2a** with aryl iodides **4-3**, gave the corresponding (*Z*)-alkenylboronates **4-4** as single isomers in moderate yields (Scheme 4-4).



Scheme 4-4. Chemoselective Suzuki-Miyaura cross-coupling reactions of **4-2a** with aryl iodides.

4.6 Summary

In conclusion, this chapter reports a simple and highly selective mixed diboration of terminal alkynes with BpinBdan catalyzed by inexpensive and readily available NaO^{t}Bu. Diverse 1,1-diborylacrylates and 1,1-diborylacrylamides with two different

boron substituents, which were difficult to prepare previously, were obtained in moderate to high yields with excellent atom-economy. Suzuki-Miyaura cross-coupling reactions of the products occurred exclusively at the Bpin position.

4.7 Experimental procedure and characterization data

4.7.1 General information

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. BpinBdan was synthesized from B_2pin_2 according to a literature procedure.[207] HPLC grade solvents were argon saturated and 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. All manipulations in this paper were performed in an argon-filled glove box.

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 40 °C.

GC-MS analyses were performed using an Agilent 7890A gas chromatograph (column: HP-5MS 5 % phenyl methyl siloxane, 30 m, ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 80 °C (2 min), 80 °C to 180 °C (20 °C min^{-1}), 180 °C to 280 °C (50 °C min^{-1}), 280 °C (5 min); 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. Elemental analyses were performed on a Leco CHNS-932 Elemental Analyzer. High-resolution mass spectra were recorded using a Thermo Fischer Scientific Exactive Plus Orbitrap MS system (ASAP, ESI or HESI probe).

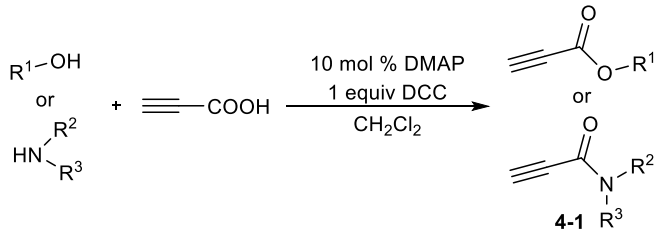
NMR spectra were recorded at ambient temperature using Bruker DRX-300 (^{1}H, 300 MHz; ^{13}C{^{1}H}, 75 MHz; ^{11}B, 96 MHz) or Bruker Avance 500 NMR (^{1}H, 500 MHz; ^{13}C{^{1}H}, 126 MHz; ^{11}B, 160 MHz; ^{19}F, 471 MHz) spectrometers. ^{1}H NMR chemical

shifts are reported relative to TMS and were referenced via the residual proton resonance of the deuterated solvent ($CDCl_3$: 7.26 ppm) whereas $^{13}C\{^1H\}$ NMR spectra are reported relative to TMS via the carbon signal of the deuterated solvent ($CDCl_3$: 77.00 ppm). ^{11}B NMR chemical shifts are quoted relative to $BF_3{\cdot}Et_2O$ as the external standard. ^{19}F NMR chemical shifts are quoted relative to $CFCl_3$ as the external standard.

4.7.2 Experimental procedures

4.7.2.1 Preparation of propiolates and propiolamides (4-1)

The propiolates and propiolamides were synthesized according to literature procedures[208] and their ^1H and ^{13}C NMR spectra are in accordance with those in the literature (**4-1d**,[209] **4-1e**,[209] **4-1i**[210] and **4-1l**[211]).



4.7.2.2 Synthesis of 1,1-diborylalkenes (4-2)

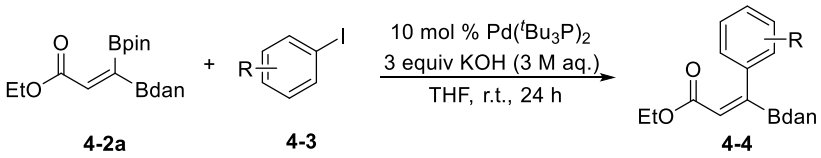
In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, BpinBdan (58.8 mg, 0.2 mmol), base (1.9 mg, 0.02 mmol) and CH_3CN (2 mL) were added. Then, alkynes **4-1** (0.24 mmol) were added and the tube was sealed with a crimped septum cap. The reaction was heated at 40 °C under argon for 5 h. The reaction mixture was then diluted with Et_2O (4 mL) and filtered through a plug of celite (ø 3 mm × 8 mm) in air with copious washing (Et_2O). The solvents were removed *in vacuo*, and the residue was purified by flash chromatography on silica gel (hexane: ethyl acetate = 90:10).

4.7.2.3 Experiments of sequential stoichiometric reaction

The mixture of **4-1a** (19.6 mg, 0.2 mmol) in THF (1 mL) was cooled to –78 °C. Then ^{n}BuLi (80 μL, 2.5 M in hexane, 0.2 mmol) was added dropwise at –78 °C. After stirring for 30 min at the same temperature, BpinBdan (58.8 mg, 0.2 mmol) in THF

(1 mL) was added dropwise at –78 °C. Then, the mixture was warmed to the ambient temperature with stirring for 1 h. Subsequently, ^{t}BuOH (19 μL, 0.2 mmol) was added and stirred for another 1 h. The solvent was removed under reduced pressure to give a brown oil. The yield of **4-2a** was determined to be 23% by ^{1}H NMR analysis using 1,3,5-trioxacyclohexane (0.09 mmol) as an internal standard.

4.7.2.4 Synthetic applications of the mixed 1,1-diborylalkene

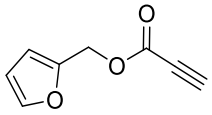


4-2a **4-3** **4-4**

In a glove box, a tube (20 mL) containing Pd(^{t}Bu$_3$P)$_2$ (5.1 mg, 0.01 mol), **4-2a** (39.2 mg, 0.1 mmol), aryl iodides **4-3** (1.1 equiv) and dry THF (1 mL) was capped with a septum. Degassed aqueous KOH (100 μL, 3 M, 0.3 mmol) was added to the system via syringe, and the mixture was stirred at room temperature for 24 h. Then the mixture was filtered through a pad of celite and washed through with Et_2O (20 mL). The filtrate was concentrated under vacuum, and the residue was purified by flash column chromatography (ethyl acetate: hexanes = 1:10) to yield a yellow liquid.

4.7.3 Characterization data for products

furan-2-ylmethyl propiolate (4-1f)



Isolated yield: 66%.

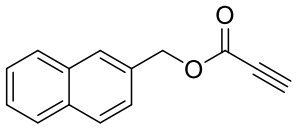
Pale yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (dd, J = 2, 1 Hz, 1H), 6.47 – 6.44 (m, 1H), 6.36 (dd, J = 3, 2 Hz, 1H), 5.16 (s, 2H), 2.91 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.2, 148.0, 143.6, 111.6, 110.6, 75.4, 74.2, 59.3.

HRMS (ASAP): m/z for $C_8H_6O_3$ $[M+H]^+$ calcd: 151.0345, found: 151.0344.

naphthalen-2-ylmethyl propiolate (4-1g)



Isolated yield: 76%.

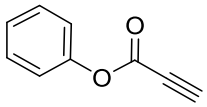
White solid, m.p.: 124.4 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = = 7.96 – 7.71 (m, 4H), 7.57 – 7.43 (m, 3H), 5.39 (s, 2H), 2.91 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.5, 133.3, 133.1, 131.9, 128.5, 128.0, 127.9, 127.7, 126.5, 126.4, 125.9, 75.1, 74.5, 68.0.

HRMS (ASAP): m/z for $C_{14}H_{10}O_2$ $[M+H]^+$ calcd: 211.0709, found: 211.0706.

phenyl propiolate (4-1h)



Isolated yield: 73%.

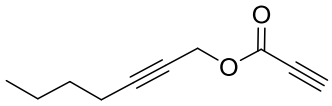
Pale yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 – 7.37 (m, 2H), 7.32 – 7.23 (m, 1H), 7.20 – 7.11 (m, 2H), 3.08 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 150.9, 149.8, 129.6, 126.6, 121.2, 76.8, 74.2.

HRMS (ASAP): m/z for $C_9H_6O_2$ $[M+H]^+$ calcd: 147.0441, found: 147.0438.

hept-2-yn-1-yl propiolate (4-1j)



Isolated yield: 65%.

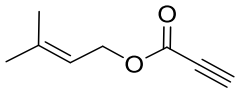
Colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.76 (s, 2H), 2.92 (s, 1H), 2.22 (tt, J = 7, 2 Hz, 2H), 1.60 – 1.32 (m, 4H), 0.90 (t, J = 7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.0, 88.9, 75.4, 74.1, 72.6, 54.5, 30.3, 21.9, 18.4, 13.5.

HRMS (ASAP): m/z for $C_{10}H_{12}O_2$ $[M+H]^+$ calcd: 165.0910, found: 165.0908.

3-methylbut-2-en-1-yl propiolate (4-1k)



Isolated yield: 55%.

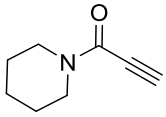
Pale yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.34 (ddq, J = 9, 6, 1 Hz, 1H), 4.67 (dt, J = 7, 1 Hz, 2H), 2.86 (s, 1H), 1.75 (s, 3H), 1.71 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.7, 140.7, 117.3, 74.7, 74.4, 63.0, 25.7, 18.0.

HRMS (ASAP): m/z for $C_8H_{10}O_2$ [M] calcd: 138.0675, found: 138.0674.

1-(piperidin-1-yl)prop-2-yn-1-one (4-1n)



Isolated yield: 77%.

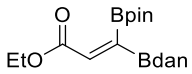
Pale yellow solid, m.p.: 104.4 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (t, J = 6 Hz, 2H), 3.52 (t, J = 6 Hz, 2H), 3.10 (s, 1H), 1.68-1.40 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.5, 78.9, 75.5, 48.0, 42.2, 26.2, 25.1, 24.3.

HRMS (ASAP): m/z for $C_8H_{11}NO$ $[M+H]^+$ calcd: 138.0913, found: 138.0911.

ethyl(*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (4-2a)



Isolated yield: 76%.

Yellow solid, m.p.: 174.4 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10 (dd, J = 8, 7 Hz, 2H), 7.03 (dd, J = 8, 1 Hz, 2H), 6.59 (s, 1H), 6.31 (dd, J = 7, 1 Hz, 2H), 5.89 (s, 2H), 4.25 (q, J = 7 Hz, 2H), 1.40 (s, 12H), 1.31 (t, J = 7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.9, 140.6, 136.3, 163.3, 127.5, 120.1, 118.0, 106.1, 84.2, 61.0, 24.9, 14.2.

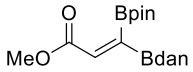
^{11}B NMR (160 MHz, $CDCl_3$): δ = 31.6, 28.7.

HRMS (ASAP): m/z for $C_{21}H_{27}B_2N_2O_4$ $[M+H]^+$ calcd: 393.2151, found: 393.2142.

Anal. Calcd for $C_{21}H_{26}B_2N_2O_4$: C, 64.33; H, 6.68; N, 7.39; found: C, 64.10; H, 6.78;

N, 7.16.

methyl(*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (4-2b)



Isolated yield: 75%.

Yellow solid, m.p.: 177.0 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10 (dd, *J* = 8, 7 Hz, 2H), 7.03 (dd, *J* = 8, 1 Hz, 2H), 6.59 (s, 1H), 6.32 (dd, *J* = 7, 1 Hz, 2H), 5.90 (s, 2H), 3.79 (s, 3H), 1.41 (s, 12H).

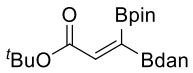
^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.3, 140.6, 136.3, 135.7, 127.5, 120.1, 118.0, 106.1, 84.3, 52.0, 24.9.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 31.8, 28.7.

HRMS (ASAP): m/z for $C_{20}H_{25}B_2N_2O_4$ $[M+H]^+$ calcd: 379.1995, found: 379.1992.

Anal. Calcd for $C_{20}H_{24}B_2N_2O_4$: C, 63.54; H, 6.40; N, 7.41; found: C, 63.33; H, 6.60; N, 7.65.

tert-butyl(*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (4-2c)



Isolated yield: 78%.

Yellow solid, m.p.: 181.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09 (dd, *J* = 8, 7 Hz, 2H), 7.02 (dd, *J* = 8, 1 Hz, 2H), 6.54 (s, 1H), 6.30 (dd, *J* = 7, 1 Hz, 2H), 5.88 (s, 2H), 1.50 (s, 9H), 1.40 (s, 12H).

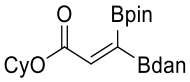
^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.4, 140.7, 138.5, 136.3, 127.5, 120.0, 117.9, 106.0, 84.0, 81.2, 28.1, 24.9.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 32.2, 28.8.

HRMS (ASAP): m/z for $C_{23}H_{31}B_2N_2O_4$ $[M+H]^+$ calcd: 421.2464, found: 421.2473.

Anal. Calcd for $C_{23}H_{30}B_2N_2O_4$: C, 65.76; H, 7.20; N, 6.67; found: C, 65.72; H, 7.39; N, 6.71.

cyclohexyl(*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (4-2d)



Isolated yield: 74%.

Yellow solid, m.p.: 244.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.13 – 7.06 (m, 2H), 7.02 (dd, *J* = 8, 1 Hz, 2H), 6.59 (s, 1H), 6.31 (dd, *J* = 7, 1 Hz, 2H), 5.90 (s, 2H), 4.86 (tt, *J* = 9, 4 Hz, 1H), 1.94 – 1.82 (m, 2H), 1.79 – 1.69 (m, 2H), 1.60 – 1.17 (m, 18H).

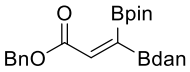
^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.4, 140.7, 137.0, 136.3, 127.5, 120.1, 118.0, 106.1, 84.2, 73.3, 31.6, 25.4, 24.9, 23.7.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 32.5, 28.7

HRMS (ASAP): m/z for $C_{25}H_{32}B_2N_2O_4$ $[M+H]^+$ calcd: 447.2621, found: 447.2605.

Anal. Calcd for $C_{25}H_{32}B_2N_2O_4$: C, 67.30; H, 7.23; N, 6.28; found: C, 67.72; H, 7.39; N, 6.51.

benzyl(*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (4-2e)



Isolated yield: 78%.

Yellow solid, m.p.: 221.7 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 – 7.30 (m, 5H), 7.10 (dd, *J* = 8, 7 Hz, 2H), 7.03 (dd, *J* = 8, 1 Hz, 2H), 6.65 (s, 1H), 6.31 (dd, *J* = 7, 1 Hz, 2H), 5.90 (s, 2H), 5.23 (s, 2H), 1.41 (s, 12H).

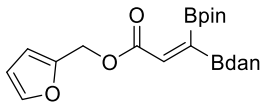
^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.7, 140.6, 136.3, 135.8, 135.5, 128.5, 128.3, 128.3, 127.5, 120.1, 118.0, 106.1, 84.3, 66.9, 24.9.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 32.4, 28.7.

HRMS (ASAP): m/z for $C_{26}H_{29}B_2N_2O_4$ $[M+H]^+$ calcd: 455.2308, found: 455.2321.

Anal. Calcd for $C_{26}H_{28}B_2N_2O_4$: C, 68.76; H, 6.21; N, 6.17; found: C, 68.73; H, 6.35; N, 6.23.

furan-2-ylmethyl(*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (4-2f)



Isolated yield: 43% (5 h), 50% (10 h).

Yellow solid, m.p.: 181.0 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (dd, *J* = 2, 1 Hz, 1H), 7.09 (dd, *J* = 8, 7 Hz, 2H), 7.02 (dd, *J* = 8, 1 Hz, 2H), 6.60 (s, 1H), 6.42 (dd, *J* = 3, 1 Hz, 1H), 6.37 (dd, *J* = 3, 2 Hz, 1H), 6.30 (dd, *J* = 7, 1 Hz, 2H), 5.88 (s, 2H), 5.17 (s, 2H), 1.41 (s, 12H).

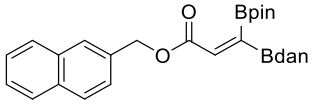
^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.3, 149.1, 143.3, 140.5, 136.3, 135.6, 127.5, 120.1, 118.1, 110.9, 110.6, 106.1, 84.3, 58.6, 24.9.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 30.9, 28.6

HRMS (ASAP): m/z for $C_{24}H_{26}B_2N_2O_5$ $[M+H]^+$ calcd: 445.2101, found: 445.2087

Anal. Calcd for $C_{24}H_{26}B_2N_2O_5$: C, 64.91; H, 5.90; N, 6.31; found: C, 64.28; H, 5.93; N, 6.07.

naphthalen-2-ylmethyl(*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (4-2g)



Isolated yield: 63% (5 h).

White solid, m.p.: 256.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 9, 3 Hz, 4H), 7.57 – 7.39 (m, 3H), 7.10 (dd, *J* = 8, 7 Hz, 2H), 7.03 (dd, *J* = 8, 1 Hz, 2H), 6.68 (s, 1H), 6.31 (dd, *J* = 7, 1 Hz, 2H), 5.91 (s, 2H), 5.39 (s, 2H), 1.41 (s, 12H).

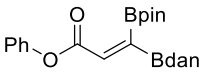
^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.7, 140.6, 136.3, 135.8, 133.2, 133.1, 133.0, 128.4, 128.0, 127.7, 127.5, 127.4, 126.3, 126.3, 125.8, 120.1, 118.1, 106.2, 84.3, 67.0, 24.9.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 32.0, 28.5.

HRMS (ASAP): m/z for $C_{30}H_{30}B_2N_2O_4$ $[M+H]^+$ calcd: 505.2464, found: 505.2452.

Anal. Calcd for $C_{30}H_{30}B_2N_2O_4$: C, 71.47; H, 6.00; N, 5.56; found: C, 70.94; H, 5.98; N, 5.56.

phenyl(*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (4-2h)



Isolated yield: 65% (10 h).

Yellow solid, m.p.: 220.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$): *δ* = 7.43 – 7.34 (m, 2H), 7.27 – 7.21 (m, 1H), 7.18 – 7.09 (m, 4H), 7.05 (dd, *J* = 8, 1 Hz, 2H), 6.80 (s, 1H), 6.34 (dd, *J* = 7, 1 Hz, 2H), 5.96 (s, 2H), 1.35 (s, 12H).

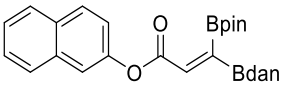
^{13}C NMR (126 MHz, $CDCl_3$): *δ* = 164.8, 150.6, 140.5, 136.3, 135.5, 129.4, 127.5, 125.9, 121.5, 120.1, 118.2, 106.2, 84.5, 24.9.

^{11}B NMR (160 MHz, $CDCl_3$): *δ* = 31.5, 28.6.

HRMS (ASAP): m/z for $C_{25}H_{26}B_2N_2O_4$ $[M+H]^+$ calcd: 441.2151, found:441.2136.

Anal. Calcd for $C_{25}H_{26}B_2N_2O_4$: C, 68.23; H, 5.95; N, 6.37; found: C, 68.04; H, 5.95; N, 6.43.

naphthalen-2-yl(*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (4-2i)



Isolated yield: 75% (5 h).

Yellow solid, m.p.: 222.8 °C.

^{1}H NMR (500 MHz, $CDCl_3$): *δ* = 7.97 – 7.76 (m, 3H), 7.63 (d, *J* = 2 Hz, 1H), 7.49 (pd, *J* = 7, 2 Hz, 2H), 7.30 (dd, *J* = 9, 2 Hz, 1H), 7.12 (dd, *J* = 8, 7 Hz, 2H), 7.06 (dd, *J* = 8, 1 Hz, 2H), 6.86 (s, 1H), 6.36 (dd, *J* = 7, 1 Hz, 2H), 5.99 (s, 2H), 1.35 (s, 12H).

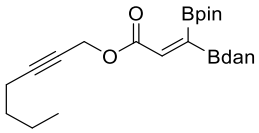
^{13}C NMR (126 MHz, $CDCl_3$): *δ* = 165.0, 148.2, 140.5, 136.3, 135.4, 133.7, 131.5, 129.4, 127.7, 127.7, 127.5, 126.5, 125.7, 121.1, 120.1, 118.6, 118.2, 106.2, 84.5, 24.9.

^{11}B NMR (160 MHz, $CDCl_3$): *δ* = 31.7, 28.7.

HRMS (ASAP): m/z for $C_{29}H_{28}B_2N_2O_4$ $[M+H]^+$ calcd: 491.2308, found:491.2311

Anal. Calcd for $C_{29}H_{28}B_2N_2O_4$: C, 71.06; H, 5.76; N, 5.72; found: C, 70.54; H, 5.81; N, 5.74.

hept-2-yn-1-yl(*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (4-2j)



Isolated yield: 62% (5 h).

Yellow solid, m.p.: 152.1 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10 (dd, *J* = 8, 7 Hz, 2H), 7.03 (dd, *J* = 8, 1 Hz, 2H), 6.62 (s, 1H), 6.31 (dd, *J* = 7, 1 Hz, 2H), 5.89 (s, 2H), 4.78 (t, *J* = 2 Hz, 2H), 2.30 – 2.14 (m, 2H), 1.57 – 1.46 (m, 2H), 1.40 (s, 14H), 0.92 (t, *J* = 7 Hz, 3H).

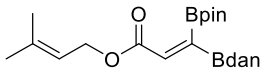
^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.1, 140.5, 136.3, 135.5, 127.5, 120.1, 118.1, 106.2, 88.1, 84.3, 73.6, 53.4, 30.4, 24.9, 21.9, 18.4, 13.6.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 32.2, 28.5.

HRMS (ASAP): m/z for $C_{26}H_{32}B_2N_2O_4$ $[M+H]^+$ calcd: 459.2621, found:459.2606.

Anal. Calcd for $C_{26}H_{32}B_2N_2O_4$: C, 68.16; H, 7.04; N, 6.11; found: C, 68.16; H, 7.08; N, 6.18.

3-methylbut-2-en-1-yl(*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (4-2k)



Isolated yield: 72% (5 h).

Yellow solid, m.p.: 155.1 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09 (ddd, *J* = 8, 7, 2 Hz, 2H), 7.02 (dd, *J* = 7, 1 Hz, 2H), 6.59 (d, *J* = 2 Hz, 1H), 6.30 (dd, *J* = 7, 1 Hz, 2H), 5.88 (s, 2H), 5.38 (dddd, *J* = 7, 6, 2, 1 Hz, 1H), 4.68 (d, *J* = 7 Hz, 2H), 1.77 (s, 3H), 1.72 (s, 3H), 1.41 (s, 12H).

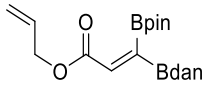
^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.9, 140.6, 139.5, 136.3, 136.2, 127.5, 120.1, 118.3, 118.0, 106.1, 84.2, 62.0, 25.8, 24.9, 18.0.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 32.5, 29.1.

HRMS (ASAP): m/z for $C_{24}H_{30}B_2N_2O_4$ $[M+H]^+$ calcd: 433.2464, found:433.2447.

Anal. Calcd for $C_{24}H_{30}B_2N_2O_4$: C, 66.71; H, 7.00; N, 6.48; found: C, 66.84; H, 7.21; N, 6.39.

allyl(*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (4-2l)



Isolated yield: 75% (5 h).

Yellow solid, m.p.: 181.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10 (dd, *J* = 8, 7 Hz, 2H), 7.03 (dd, *J* = 8, 1 Hz, 2H), 6.62 (s, 1H), 6.32 (dd, *J* = 7, 1 Hz, 2H), 6.06 – 5.86 (m, 3H), 5.35 (dq, *J* = 17, 2 Hz, 1H), 5.26 (dq, *J* = 10, 1 Hz, 1H), 4.69 (dt, *J* = 6, 1 Hz, 2H), 1.41 (s, 12H).

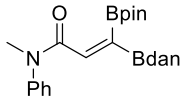
^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.5, 140.6, 136.3, 135.8, 131.9, 127.5, 120.1, 118.5, 118.0, 106.1, 84.3, 65.7, 24.9.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 32.2, 28.9.

HRMS (ASAP): m/z for $C_{22}H_{26}B_2N_2O_4$ $[M+H]^+$ calcd: 405.2151, found:405.2137.

Anal. Calcd for $C_{22}H_{26}B_2N_2O_4$: C, 65.39; H, 6.49; N, 6.93; found: C, 65.22; H, 6.59; N, 6.98.

(*Z*)-N-methyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-N-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylamide (4-2m)



Isolated yield: 63% (5 h); 87% (10 h).

Yellow solid, m.p.: 256.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 – 7.35 (m, 3H), 7.10 (dd, *J* = 8, 7 Hz, 2H), 7.01 – 6.93 (m, 4H), 6.53 (s, 2H), 6.35 (dd, *J* = 7, 1 Hz, 2H), 6.24 (s, 1H), 3.25 (s, 3H), 1.31 (s, 12H).

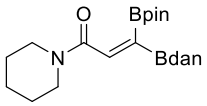
^{13}C NMR (126 MHz, $CDCl_3$): δ = 172.5, 141.4, 140.7, 136.4, 130.0, 129.0, 128.9, 127.5, 126.4, 120.2, 117.1, 105.7, 80.9, 39.2, 25.7.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 29.2, 17.2.

HRMS (ASAP): m/z for $C_{26}H_{29}B_2N_3O_3$ $[M+H]^+$ calcd: 454.2468, found:454.2456.

Anal. Calcd for $C_{26}H_{29}B_2N_3O_3$: C, 68.91; H, 6.45; N, 9.27; found: C, 68.88; H, 6.51; N, 9.25.

(*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-1-(piperidin-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-one (4-2n)



Isolated yield: 29% (5 h); 50% (10 h).

Yellow solid, m.p.: 154.0 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.11 – 7.03 (m, 2H), 6.97 (dd, *J* = 8, 1 Hz, 2H), 6.78 (s, 1H), 6.41 (s, 2H), 6.32 (dd, *J* = 7, 1 Hz, 2H), 3.55 (dt, *J* = 11, 5 Hz, 4H), 1.67 – 1.47 (m, 6H), 1.32 (s, 12H).

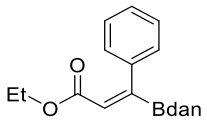
^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.0, 141.4, 136.4, 127.6, 126.5, 120.2, 117.2, 105.7, 80.6, 46.9, 46.3, 26.1, 25.7, 25.0, 23.7.

^{11}B NMR (160 MHz, $CDCl_3$): δ = 29.9, 15.4.

HRMS (ASAP): m/z for $C_{24}H_{31}B_2N_3O_3$ $[M+H]^+$ calcd: 432.2624, found:432.2610.

Anal. Calcd for $C_{24}H_{31}B_2N_3O_3$: C, 66.86; H, 7.25; N, 9.75; found: C, 66.19; H, 7.38; N, 9.55.

ethyl (*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-phenylacrylate (4-4a)



Isolated yield: 61%.

Yellow liquid.

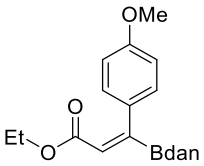
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 – 7.31 (m, 3H), 7.21 – 7.14 (m, 2H), 7.13 – 7.00 (m, 4H), 6.42 (s, 1H), 6.28 (dd, *J* = 7, 1 Hz, 2H), 5.66 (s, 2H), 4.05 (q, *J* = 7 Hz, 2H), 1.10 (t, *J* = 7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.6, 140.4, 139.3, 136.2, 128.3, 127.5, 127.4, 127.2, 126.8, 120.0, 118.2, 106.3, 60.3, 13.9.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 28.0.

HRMS (ASAP): m/z for $C_{21}H_{19}B_1N_2O_2$ $[M+H]^+$ calcd: 343.1612, found:343.1598.

ethyl (*Z*)-3-(4-methoxyphenyl)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)acrylate (4-4b)



Isolated yield: 65%.

Yellow liquid.

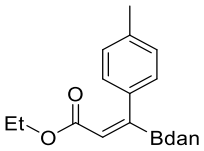
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20 – 7.00 (m, 6H), 6.96 – 6.90 (m, 2H), 6.36 (s, 1H), 6.28 (dd, *J* = 7, 1 Hz, 2H), 5.67 (s, 2H), 4.09 (q, *J* = 7 Hz, 2H), 3.85 (s, 3H), 1.16 (t, *J* = 7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.8, 159.2, 140.5, 136.3, 131.1, 129.1, 127.5, 125.9, 120.0, 118.1, 113.7, 106.2, 60.2, 55.2, 14.0.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 27.8.

HRMS (ASAP): m/z for $C_{22}H_{21}B_1N_2O_3$ $[M+H]^+$ calcd: 373.1718, found: 373.1704.

ethyl (*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-(p-tolyl)acrylate (4-4c)



Isolated yield: 64%.

Yellow liquid.

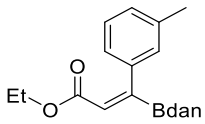
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (dq, *J* = 8, 1 Hz, 2H), 7.12 – 7.00 (m, 6H), 6.38 (s, 1H), 6.27 (dd, *J* = 7, 1 Hz, 2H), 5.67 (s, 2H), 4.08 (q, *J* = 7 Hz, 2H), 2.40 (s, 3H), 1.14 (t, *J* = 7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.7, 140.5, 137.2, 136.2, 136.1, 129.0, 127.5, 127.3, 126.3, 120.0, 118.1, 106.2, 60.2, 21.3, 14.0.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 27.5.

HRMS (ASAP): m/z for $C_{22}H_{21}B_1N_2O_3$ $[M+H]^+$ calcd: 357.1769, found: 357.1760.

ethyl (*Z*)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-3-(m-tolyl)acrylate (4-4d)



Isolated yield: 49%.

Yellow liquid.

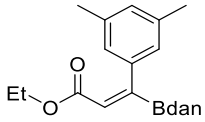
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8 Hz, 1H), 7.15 (d, *J* = 8 Hz, 1H), 7.15 – 6.98 (m, 4H), 7.02 – 6.92 (m, 2H), 6.39 (s, 1H), 6.28 (dd, *J* = 7, 1 Hz, 2H), 5.66 (s, 2H), 4.05 (q, *J* = 7 Hz, 2H), 2.38 (s, 3H), 1.10 (t, *J* = 7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.7, 140.5, 139.2, 137.8, 136.3, 128.2, 127.8, 127.5, 126.6, 124.3, 120.0, 118.2, 106.2, 60.2, 21.5, 13.9.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 28.3.

HRMS (ASAP): m/z for $C_{22}H_{21}B_1N_2O_2$ $[M+H]^+$ calcd: 357.1769, found: 357.1754.

ethyl (*Z*)-3-(3,5-dimethylphenyl)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)acrylate (4-4e)



Isolated yield: 55%.

Yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15 – 6.99 (m, 4H), 6.97 (dd, *J* = 2, 1 Hz, 1H), 6.77 (s, 2H), 6.38 (s, 1H), 6.28 (dd, *J* = 7, 1 Hz, 2H), 5.67 (s, 2H), 4.06 (q, *J* = 7 Hz, 2H), 2.34 (s, 6H), 1.11 (t, *J* = 7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.8, 140.5, 139.2, 137.7, 136.3, 129.1, 127.5, 126.5, 124.9, 120.0, 118.1, 106.2, 60.2, 21.4, 13.9.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 27.8.

HRMS (ASAP): m/z for $C_{23}H_{24}B_1N_2O_2$ $[M+H]^+$ calcd: 371.1925, found: 371.1913.

4.7.4 Crystallographic data

A crystal of **4-2a** suitable for single-crystal X-ray diffraction was selected, coated in perfluoropolyether oil, and mounted on a MiTeGen sample holder. Diffraction data were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector using graphite-monochromated Mo-Kα radiation. The crystal was cooled using an

Oxford Cryostream low-temperature device. Data were collected at 100 K. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the Bruker software packages. The structure was solved using the intrinsic phasing method (SHELXT)[179] and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' in idealized positions, by full-matrix least squares against F^2 of all data, using SHELXL[180] software and the SHELXLE graphical user interface.[181] Diamond[183] software was used for graphical representation. Crystal data and experimental details are listed in Table 4-6; full structural information has been deposited with Cambridge Crystallographic Data Centre. CCDC-1959477 (**4-2a**).

Table 4-6: Single-crystal X-ray diffraction data and structure refinements of compound **4-2a**.

Data	**4-2a**
CCDC number	1959477
Empirical formula	$C_{21}H_{26}B_2N_2O_4$
Formula weight / g·mol^{-1}	392.06
T / K	100(2)
γ / Å, radiation	MoKα 0.71073
Crystal size / mm³	0.152×0.300×0.423
Crystal color, habit	colorless plate
μ / mm^{-1}	0.084
Crystal system	Monoclinic
Space group	$P2_1/c$
a / Å	11.033(3)
b / Å	8.345(2)
c / Å	22.965(8)
α / °	90
β / °	99.702(19)
γ / °	90
Volume / Å³	2084.2(11)
Z	4
ρ_{calc} / g·cm^{-3}	1.249
F(000)	832
θ range / °	2.601 - 26.767
Reflections collected	22419
Unique reflections	4432
Parameters / restraints	267 / 0
GooF on F^2	1.026
R_1 [I>2σ(I)]	0.0442
wR^2 (all data)	0.1097
Max. / min. residual electron density / e·Å^{-3}	0.296 / –0.252

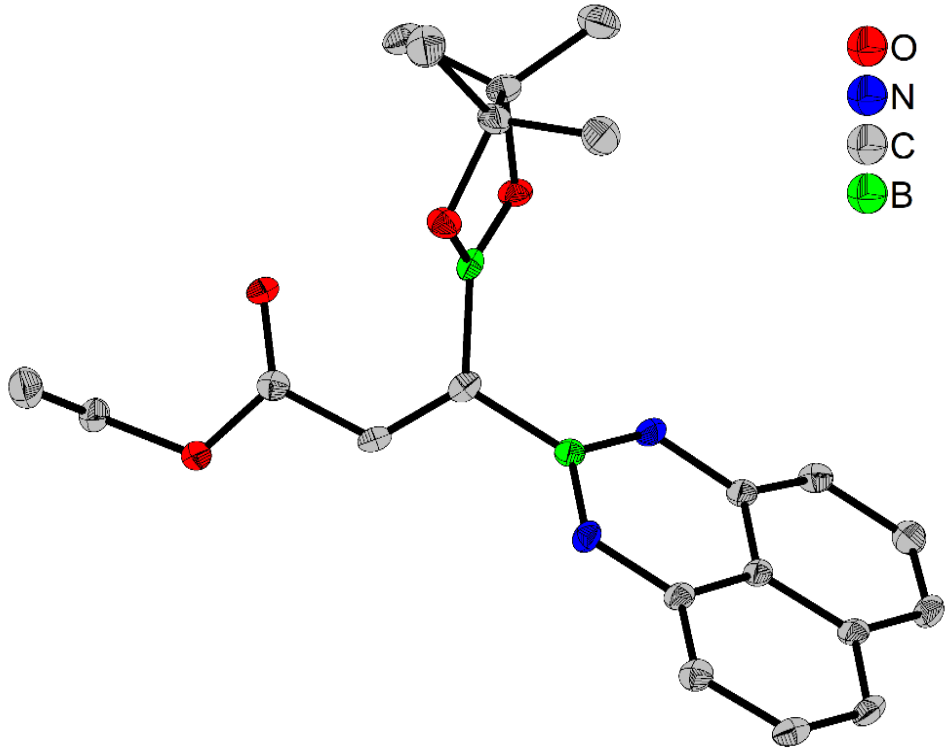


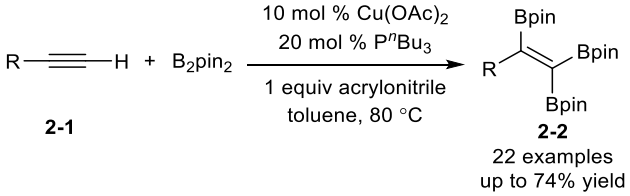
Figure 4-5. Molecular structure of **4-2a** in the solid state at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

Summary

Multiborylated compounds are important in modern chemistry due to their various roles as bio-active agents and synthetic building blocks. Monoboronates and bisboronates have been increasingly applied in organic synthesis. In contrast, triboronates are relatively rare, but are potentially very interesting. Efficient methods for the synthesis of 1,1,2-triborylalkenes and 1,1,1-triborylalkanes are presented in Chapter 2 and Chapter 3. In addition, mixed 1,1-diborylalkenes are an important building block in stereoselective Suzuki-Miyaura cross-coupling reactions. A simple and efficient method for the synthesis of mixed 1,1-diborylalkenes via the diboration of terminal alkynes with BpinBdan are reported in Chapter 4.

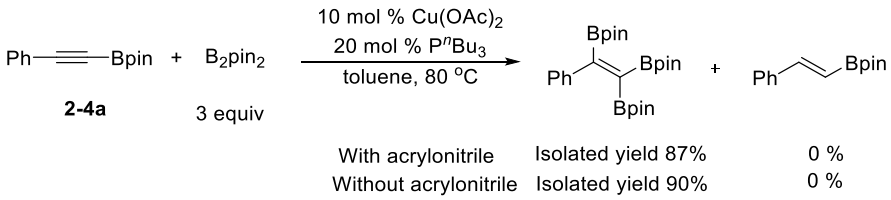
Chapter 2

Chapter 2 reports the catalytic triboration of terminal alkynes with B_2pin_2 using readily available $Cu(OAc)_2$ and P^nBu_3 (Scheme S-1). Various 1,1,2-tris(boryl)alkenes were obtained in moderate to good yields (22 examples, up to 74% yield). The process features mild reaction conditions, broad substrate scope, and good functional group tolerance. This Cu-catalyzed reaction was conducted on a gram scale to produce the corresponding 1,1,2-triborylalkene in modest yields (48% yield).



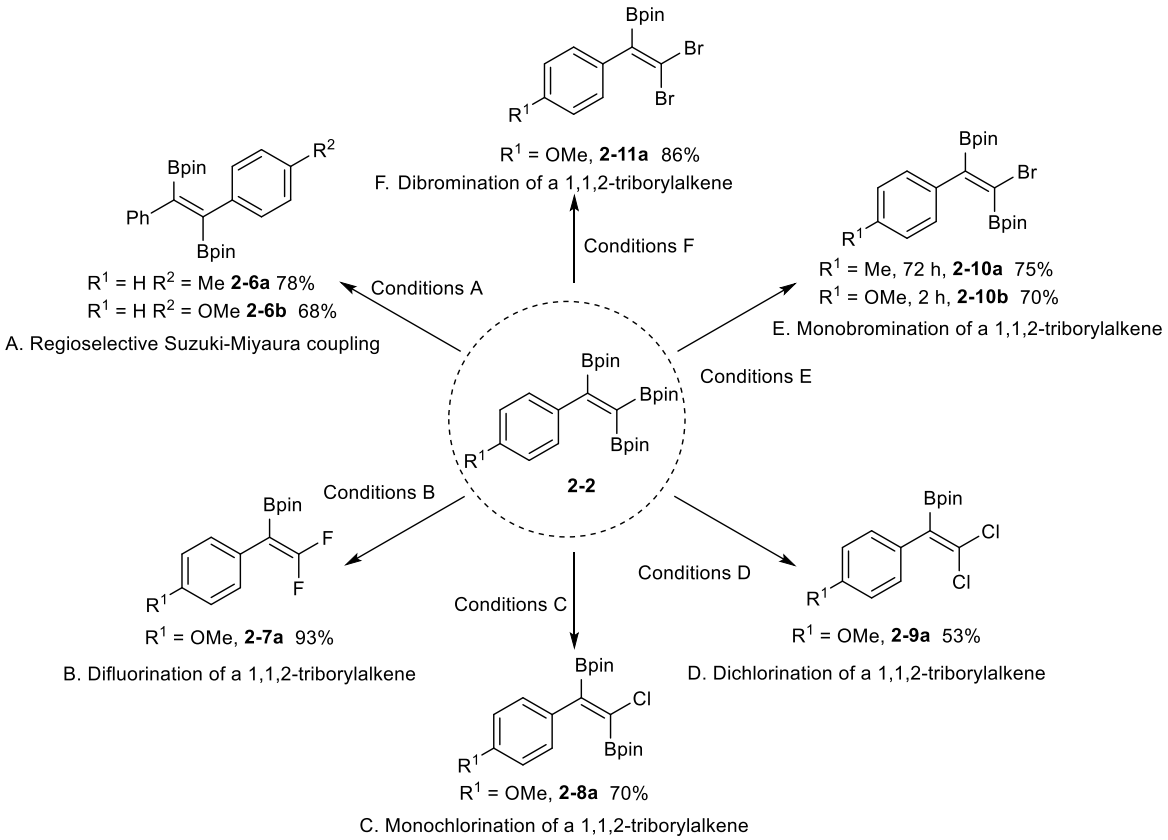
Scheme S-1. Synthesis of 1,1,2-triborylalkenes from terminal alkynes.

Control experiments were carried out to gain insight into the reaction mechanism. The control experiment and monitoring a reaction by *in situ* ^{19}F NMR spectroscopy indicated that alkynylboronate (**2-4**) may serve as an intermediate in the catalytic cycle (Scheme S-2). The possible mechanism of this copper-catalyzed triboration of terminal alkynes involves two processes: dehydrogenative borylation of terminal alkynes and diboration of alkynylboronates.



Scheme S-2. Diboration of alkynylboronate.

The utility of these products was demonstrated by further transformation of the C-B bonds to prepare *gem*-dihaloborylalkenes (**2-7**, **2-9**, and **2-11**), monohaloborylalkenes (**2-8** and **2-10**), and transdiaryldiborylalkenes (**2-6**) (Scheme S-3), which serve as important synthons and have previously been challenging to prepare.

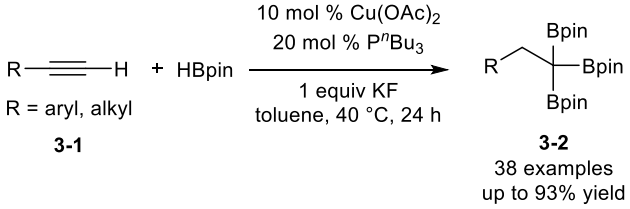


Conditions A: 4-R^2-C_6H_4-I (1 equiv), $Pd(PPh_3)_4$ (10 mol %), K_3PO_4 (2 equiv), H_2O (7 equiv), THF, 70 °C; conditions B: Selectfluor® (3 equiv), $NaHCO_3$ (2.2 equiv), CH_3CN, r.t., 6 h; conditions C: NCS (1.3 equiv), 60 °C, CH_3CN, 12 h; conditions D: NCS (2 equiv), 60 °C, CH_3CN, 48 h; conditions E: NBS (1.3 equiv), r.t., CH_3CN; conditions F: NBS (2 equiv), r.t., CH_3CN, 72 h; isolated yields.

Scheme S-3. Synthetic applications of 1,1,2-triborylalkenes.

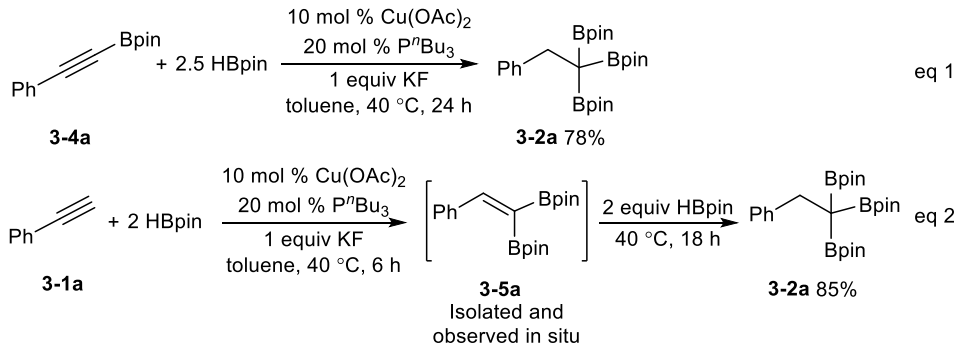
Chapter 3

In Chapter 3, a convenient and efficient one-step synthesis of 1,1,1-triborylalkanes was achieved by triboration of terminal alkynes with HBpin catalyzed by 10 mol % of $Cu(OAc)_2$ (Scheme S-4). A wide range of aryl and alkyl alkynes underwent this transformation producing the corresponding 1,1,1-triborylalkanes in modest to high yield (38 examples, up to 93% yield). The reaction was conducted on a gram scale (87% yield).



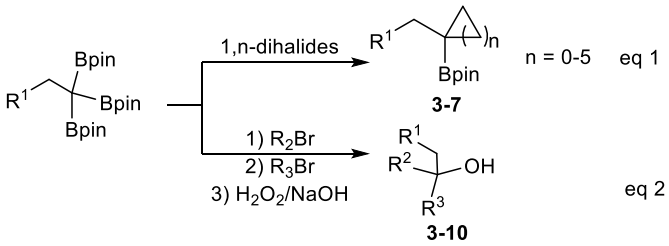
Scheme S-4. Synthesis of 1,1,1-triborylalkanes from terminal alkynes.

The catalytic process most likely involves the Cu-catalyzed sequential dehydrogenative borylation and double hydroboration of terminal alkynes. The role of alkynylboronate (**3-4a**) resulting from dehydrogenative borylation as a key intermediate, was demonstrated by the control experiment shown in Scheme S-5, eq 1. In addition, *in situ* monitoring of the reaction using 2 equivalents of HBpin by GCMS revealed the formation of intermediate **3-5a** at the early stage of the reaction (6 h). When another 2 equivalents of HBpin were added to the reaction mixture, **3-2a** was obtained in 85% yield via hydroboration of intermediate **3-5a** after 18 h (Scheme S-5, eq 2). This result indicated that the 1,1-diborylalkene (**3-5a**) is an intermediate in the catalytic cycle.



Scheme S-5. Mechanistic investigations.

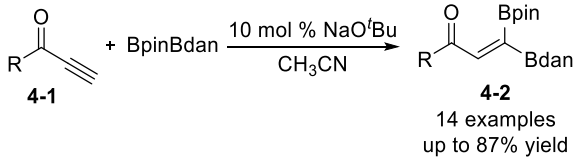
1,1,1-Triborylalkanes are demonstrated to be useful synthetic intermediates for the construction of carbocyclic organoboronates and α-vinylboronates (Scheme S-6, eq 1), which were difficult to synthesize using previously reported methods. A one-pot, stepwise deborylative functionalization of 1,1,1-triborylated alkanes gave an unsymmetrical tertiary alcohol (Scheme S-6, eq 2).



Scheme S-6. Synthetic applications of 1,1,1-triborylalkanes.

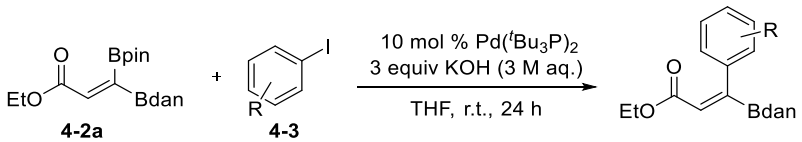
Chapter 4

Chapter 4 presents a simple and atom-economical method for the mixed diboration of terminal alkynes with the unsymmetrical diboron reagent, BpinBdan, catalyzed by inexpensive and readily available NaO^{t}Bu (Scheme S-7). Diverse 1,1-diborylacrylates and 1,1-diborylacrylamides with two different boron substituents, which were difficult to prepare previously, were obtained in moderate to high yields and with high stereoselectivities (14 examples). Hydrogen bonding between Bdan and ^{t}BuOH was proposed to be responsible for the observed stereoselectivity.



Scheme S-7. The mixed 1,1-diboration of terminal alkynes with BpinBdan.

The products were applied in the stereoselective synthesis of trisubstituted olefins. Suzuki-Miyaura cross-coupling reactions exclusively occurred at the Bpin position (Scheme S-8).



Scheme S-8. Chemoselective Suzuki-Miyaura cross-coupling reaction.

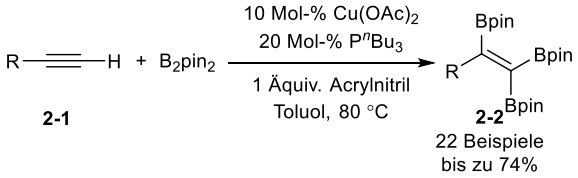
In summary, a variety of boration reactions were developed to prepare 1,1,2-triborylalkenes, 1,1,1-triborylalkanes, and mixed 1,1-diborylalkenes via Cu- or base-catalyzed boration of terminal alkynes, which are easily accessible starting materials. The synthetic utility of di- or triboronates have been applied to highly concise syntheses of certain interesting target compounds.

Zusammenfassung

Multiboryl-Verbindungen sind von entscheidender Bedeutung für die moderne Chemie in Form von bioaktiven Wirkstoffen und Synthesebausteinen. Der Einsatz von Monoboronaten und Bisboronaten in der organischen Synthese ist von steigendem Interesse. Triboronate hingegeben werden eher selten verwendet, sind aber von potentiellem Interesse. Effiziente Methoden zur Darstellung von 1,1,2-Triborylalkenen und 1,1,1-Triborylalkanen sind in Kapitel 2 und Kapitel 3 gezeigt. Außerdem stellen gemischte 1,1-Diborylalkene einen wichtigen Synthesebaustein in der stereoselektiven Suzuki-Miyaura-Kreuzkupplung dar. Eine einfache und effiziente Methode für die Synthese von gemischten 1,1-Diborylalkenen durch Diborierung terminaler Alkine mit BpinBdan ist in Kapitel 4 vorgestellt.

Kapitel 2

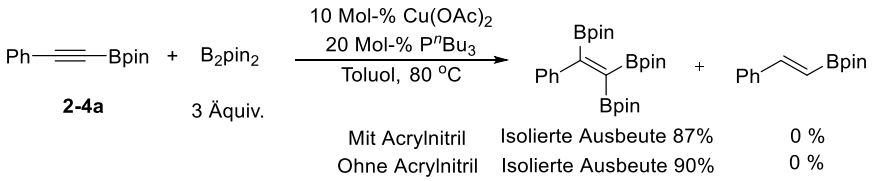
Kapitel 2 zeigt die katalytische Triborierung von terminalen Alkinen mit B_2pin_2 in Anwesenheit von einfach zugänglichem $Cu(OAc)_2$ and P^nBu_3 (Schema S-1). Verschiedene 1,1,2-Tris(boryl)alkene konnten in mäßigen bis guten Ausbeuten erhalten werden (22 Beispiele, bis zu 74% Ausbeute). Die Syntheseroute zeichnet sich durch milde Reaktionsbedingungen, ein breites Substratspektrum und eine gute Toleranz gegenüber funktionellen Gruppen aus. Diese Cu-katalysierte Reaktion kann außerdem im Gramm- Maßstab durchgeführt werden, wobei das entsprechende 1,1,2-Triborylalken in mäßigen Ausbeuten (48% Ausbeute) erhalten wurde.



Schema S-1. Synthese von 1,1,2-Triborylalkenen ausgehend von terminalen Alkinen.

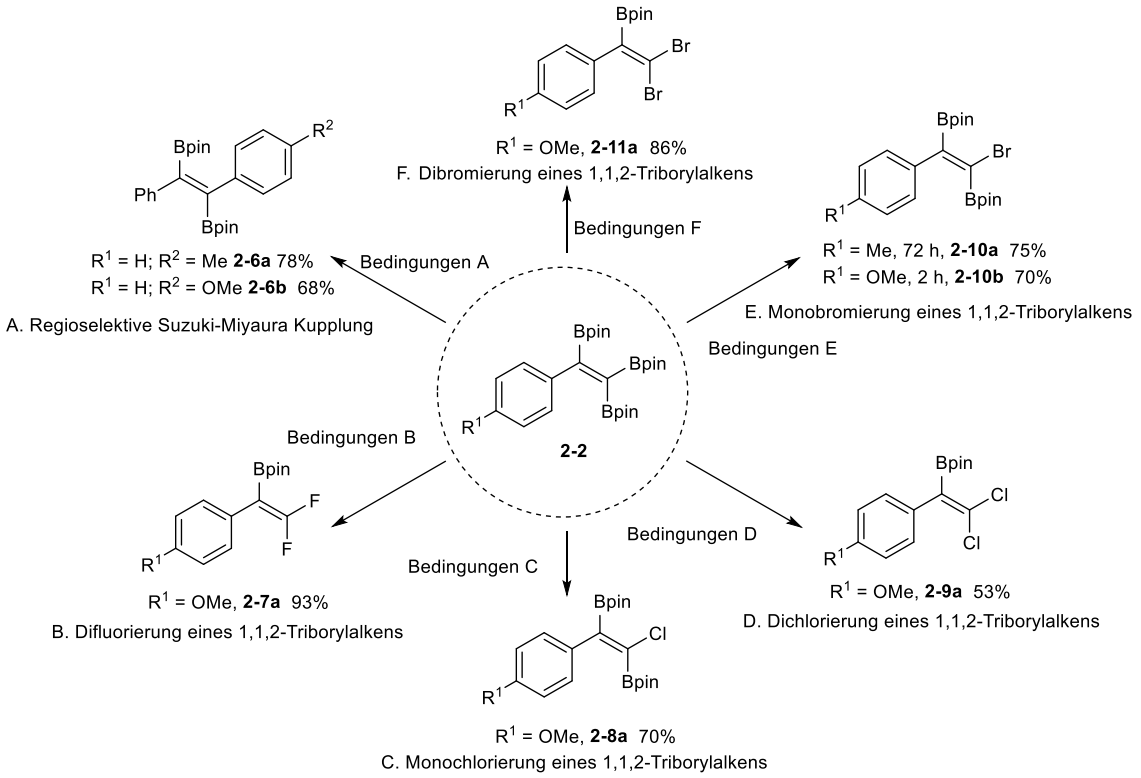
Um Einblick in den Reaktionsmechanismus zu erhalten, wurden Kontrollexperimente durchgeführt. Das Kontrollexperiment und die Verfolgung des Reaktionsverlaufs mittels *in situ* ^{19}F NMR Spektroskopie deuten darauf hin, dass es sich bei dem Alkinylboronat (**2-4**) um ein Zwischenprodukt im Katalysezyklus handelt (Schema S-2). Der mögliche Mechanismus dieser Kupfer-katalysierten Triborierung von terminalen Alkinen umfasst zwei Prozesse: Die dehydrierende

Borierung terminaler Alkine and die Diborierung von Alkinylboronaten.



Schema S-2. Diborierung von Alkinylboronaten.

Der synthetische Nutzen dieser Verbindungen ist anhand weiterer Transformationen der C-B-Bindungen zur Darstellung geminaler Dihalogenborylalkene (**2-7**, **2-9** und **2-11**), Monohalogenborylalkene (**2-8** und **2-10**) und *trans*-Diaryldiborylalkene (**2-6**) demonstriert (Schema S-3), welche bedeutende Synthesebausteine darstellen und bislang nur schwer zugänglich waren.

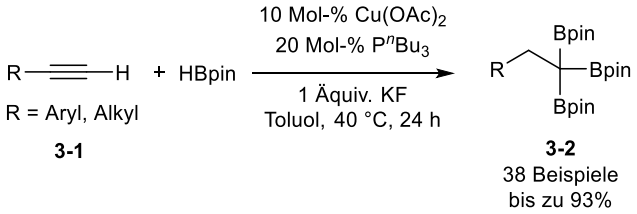


Bedingungen A: 4-R^2-C_6H_4-I (1 Äquiv.), $Pd(PPh_3)_4$ (10 Mol-%), K_3PO_4 (2 Äquiv.), H_2O (7 Äquiv.), THF, 70 °C; Bedingungen B: Selectfluor® (3 Äquiv.), $NaHCO_3$ (2.2 Äquiv.), CH_3CN, RT, 6 h; Bedingungen C: NCS (1.3 Äquiv.), 60 °C, CH_3CN, 12 h; Bedingungen D: NCS (2 Äquiv.), 60 °C, CH_3CN, 48 h; Bedingungen E: NBS (1.3 Äquiv.), RT, CH_3CN; Bedingungen F: NBS (2 Äquiv.), RT, CH_3CN, 72 h.

Schema S-3. Syntheseanwendungen von 1,1,2-Triborylalkenen mit isolierten Ausbeuten.

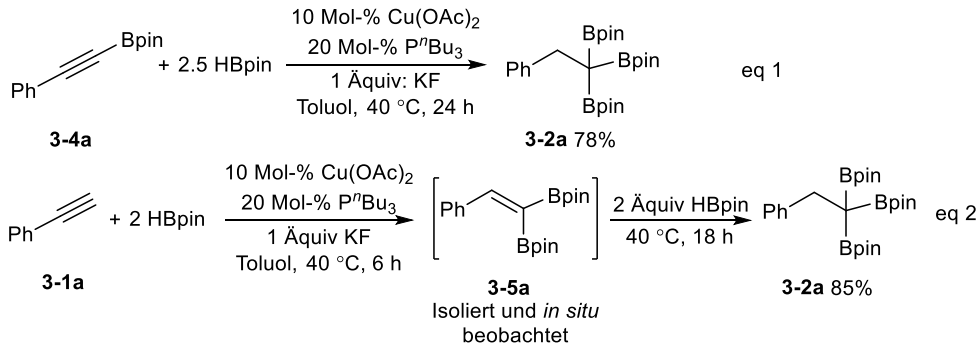
Kapitel 3

In Kapitel 3 wurde eine praktische und effiziente Eintopf-Synthese zur Darstellung von 1,1,1-Triborylalkanen, durch Triborierung von terminalen Alkinen mit HBpin in Anwesenheit von 10 mol-% $Cu(OAc)_2$, demonstriert (Schema S-4). Ein großes Spektrum an Aryl- und Alkylalkinen konnte in mäßigen bis hohen Ausbeuten (38 Beispiele, bis zu 93% Ausbeute) in die entsprechenden 1,1,1-Triborylalkane überführt werden. Die Reaktion lässt sich außerdem erfolgreich im Gramm-Maßstab durchführen (87% Ausbeute).



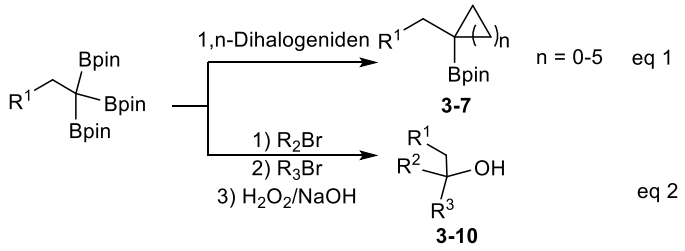
Schema S-4. Synthese von 1,1,1-Triborylalkanen ausgehend von terminalen Alkinen.

Der Katalysezyklus umfasst höchstwahrscheinlich eine Cu-katalysierte sequenzielle, dehydrierende Borierung und zweifache Hydroborierung von terminalen Alkinen. Die Rolle des Alkinylboronats (**3-4a**), welches aus der dehydrierenden Borierung als Schlüsselintermediat hervorgeht, wurde mithilfe des in Schema S-5 (eq 1) gezeigten Kontrollexperiments demonstriert. Desweiteren zeigte die *in situ* Verfolgung der Reaktion mit 2 Äquivalenten HBpin mittels GCMS die Bildung von Zwischenprodukt **3-5a** im Anfangsstadium der Reaktion (6 h). Bei Zugabe von 2 weiteren Äquivalenten HBpin zur Reaktion, konnte **3-2a** in 85% Ausbeute, durch Hydroborierung von Zwischenprodukt **3-5a** nach 18 h, erhalten werden (Schema S-5, eq 2). Dies deutet darauf hin, dass es sich bei dem 1,1-Diborylalken (**3-5a**) um ein Zwischenprodukt im Katalysezyklus handelt.



Schema S-5. Untersuchungen zum Reaktionsmechanismus.

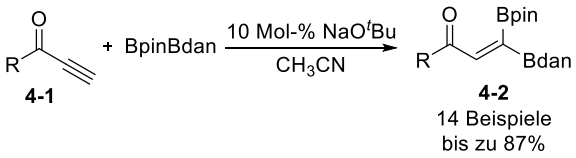
Wir konnten zeigen, dass 1,1,1-Triborylalkane bedeutende Syntheseintermediate zur Ausbildung von carbozyklischen Organoboronaten und α-Vinylboronaten (Schema S-6, eq 1) repräsentieren, welche mit den bislang bekannten Methoden nur schwer zugänglich waren. Eine stufenweise, deborylierende Funktionalisierung von 1,1,1-Triborylalkanen ergab einen unsymmetrischen tertiären Alkohol (Schema S-6, eq 2).



Schema S-6. Synthetische Anwendungen von 1,1,1-Triborylalkanen.

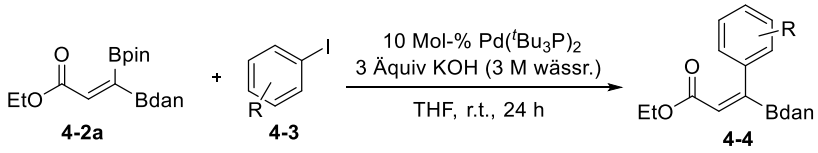
Kapitel 4

In Kapitel 4 ist eine einfache und atomökonomische Route für die gemischte Borierung von terminalen Alkinen mit dem unsymmetrischen Diboran BpinBdan demonstriert, katalysiert durch kostengünstiges und einfach zugängliches NaO^{t}Bu (Schema S-7). Verschiedene 1,1-Diborylacrylate und 1,1-Diborylacrylamide mit zwei unterschiedlichen Bor-Substituenten, welche bislang schwer darzustellen waren, konnten in mäßigen bis hohen Ausbeuten und mit hohen Stereoselektivitäten erhalten werden (14 Beispiele). Die beobachtete Stereoselektivität ist vermutlich auf Wasserstoffbrückenbindungen zwischen Bdan und ^{t}BuOH zurückzuführen.



Schema S-7. Die gemischte 1,1-Diborierung von terminalen Alkinen mit BpinBdan.

Die Produkte fanden weiter Anwendung in der stereoselektiven Synthese von trisubstituierten Olefinen. Suzuki-Miyaura Kreuzkupplungen wurden ausschließlich an der Bpin-Position beobachtet (Schema S-8).



Schema S-8. Chemoselektive Suzuki-Miyaura Kreuzkupplung.

Zusammenfassend, konnte eine Vielzahl an Borierungen zur Darstellung von 1,1,2-Triborylalkenen, 1,1,1-Triborylalkanen und gemischten 1,1-Diborylalkenen durch Cu- oder Basen-katalysierte Borierung von terminalen Alkinen vorgestellt werden, welche einfach zugängliche Startmaterialien darstellen. Der synthetische Nutzen von Di- oder Triboronaten konnte anhand sehr präziser Synthesen von gewissen interessanten Zielverbindungen verdeutlicht werden.

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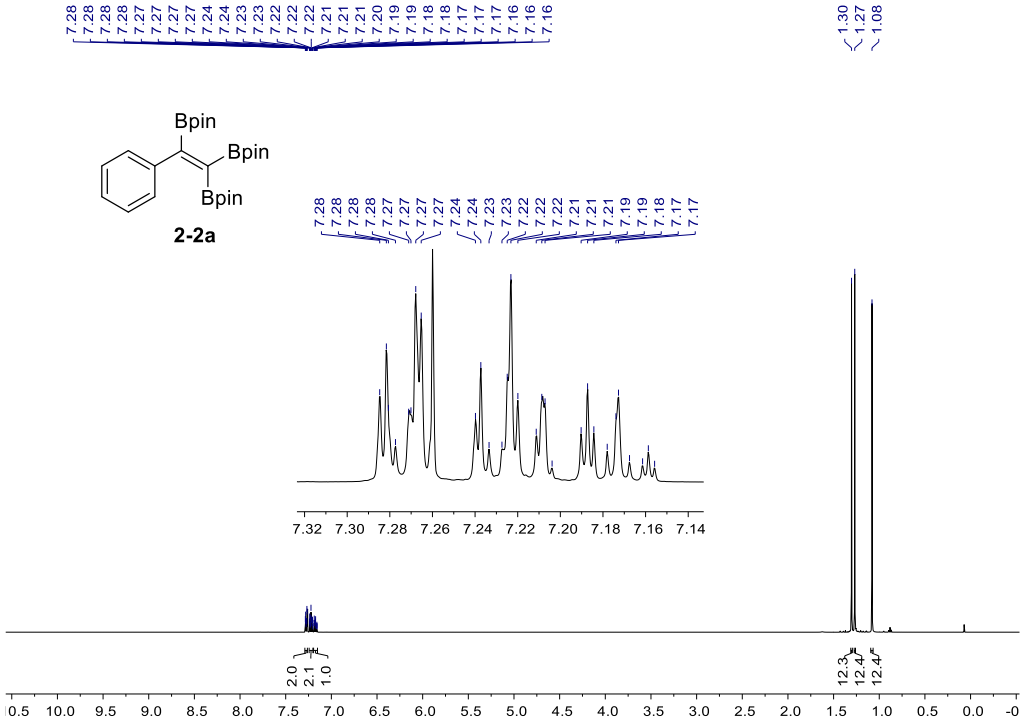
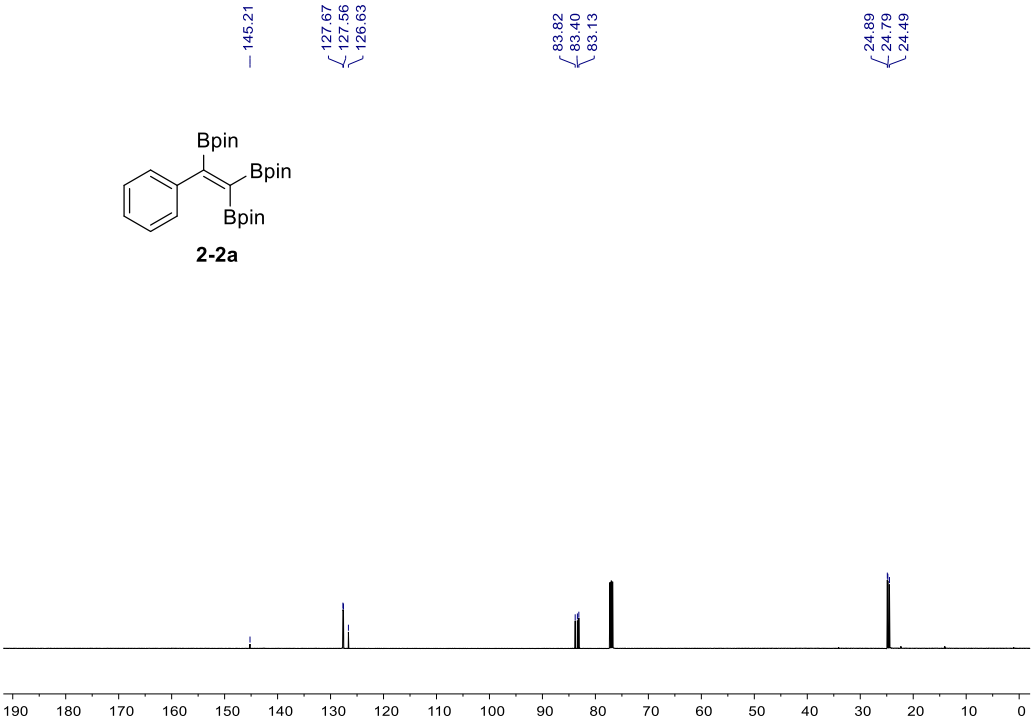
Appendix

NMR spectra

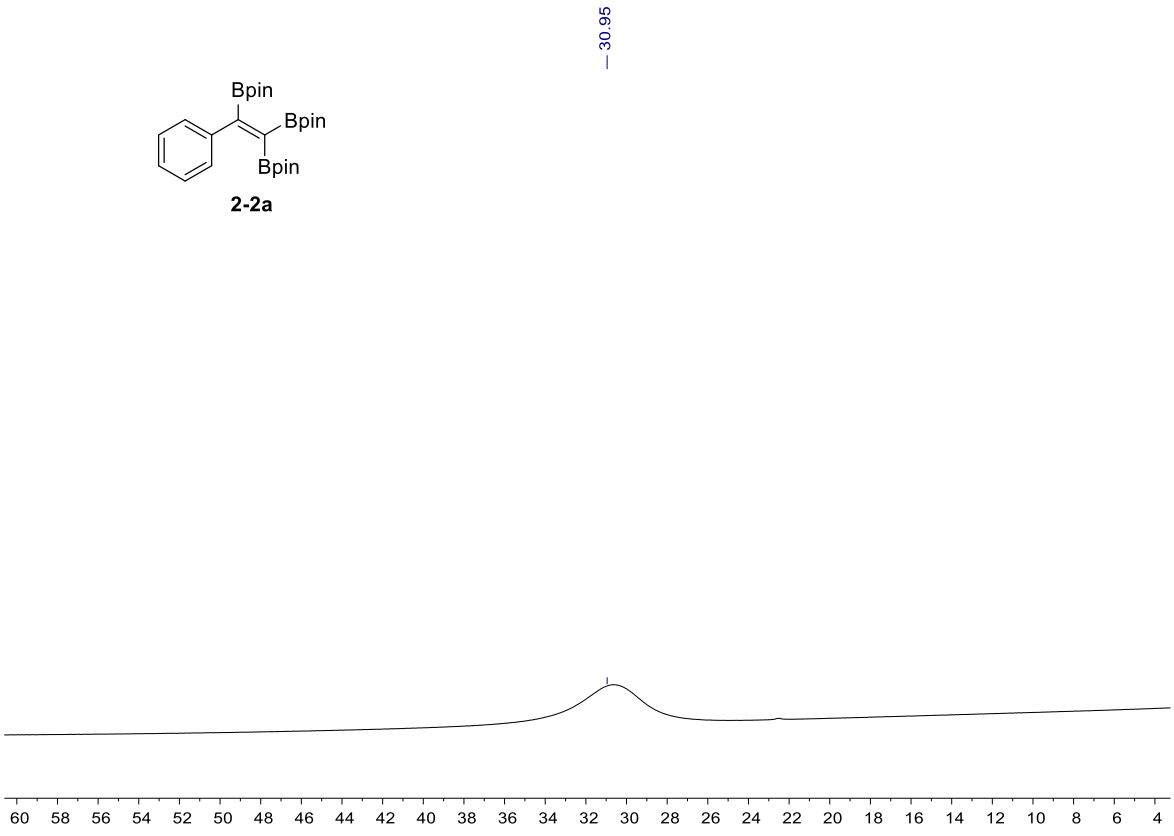
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2a**



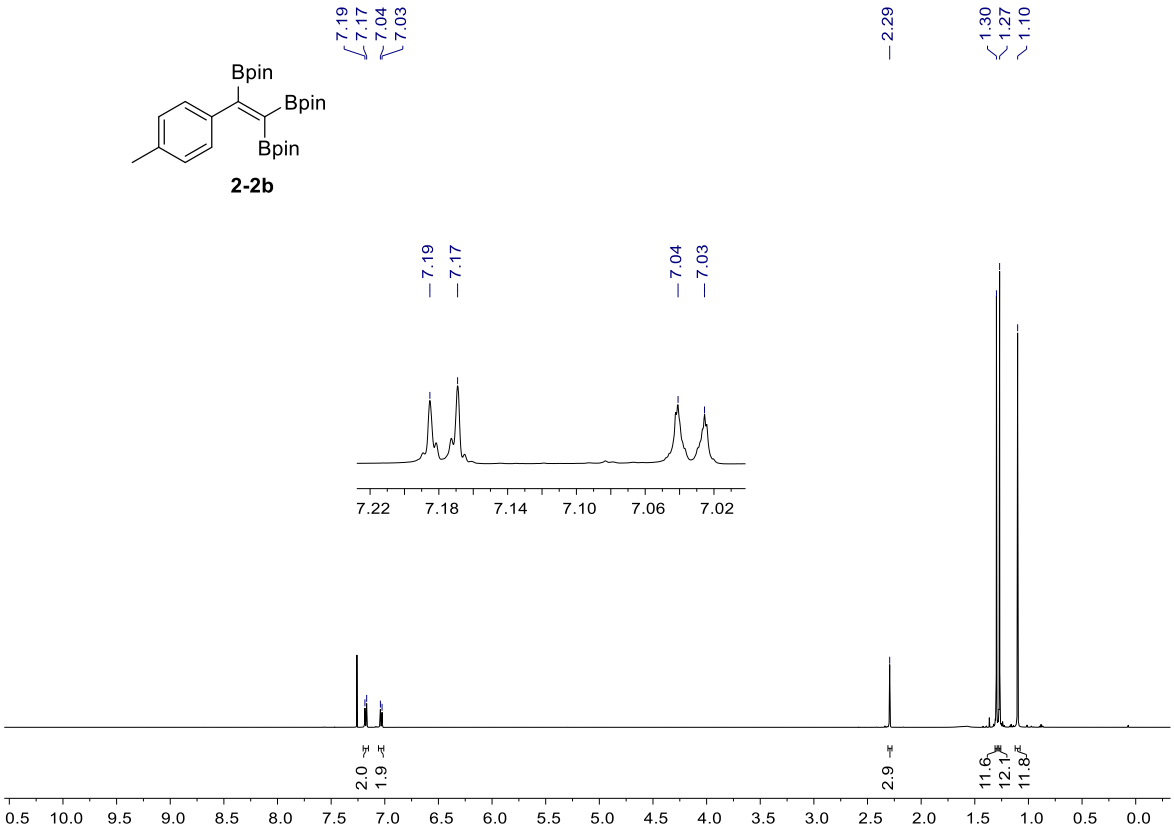
^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2-2a**



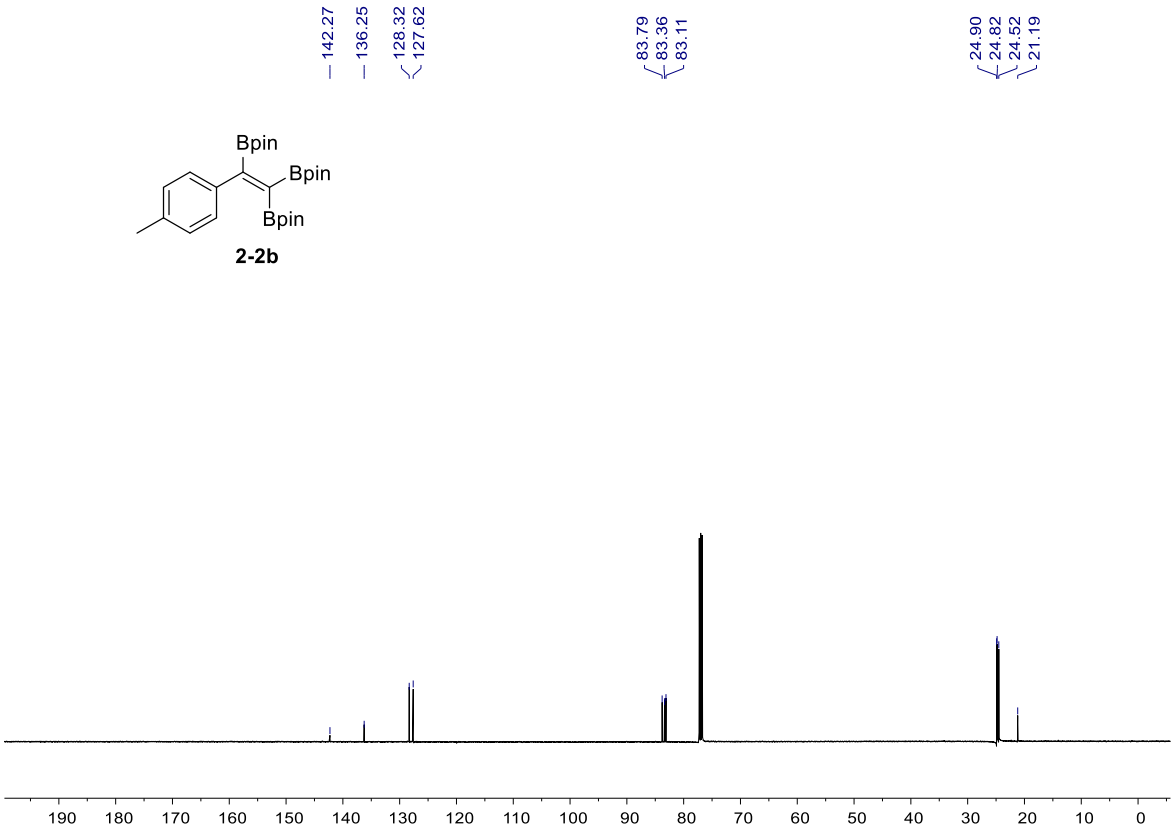
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2a**



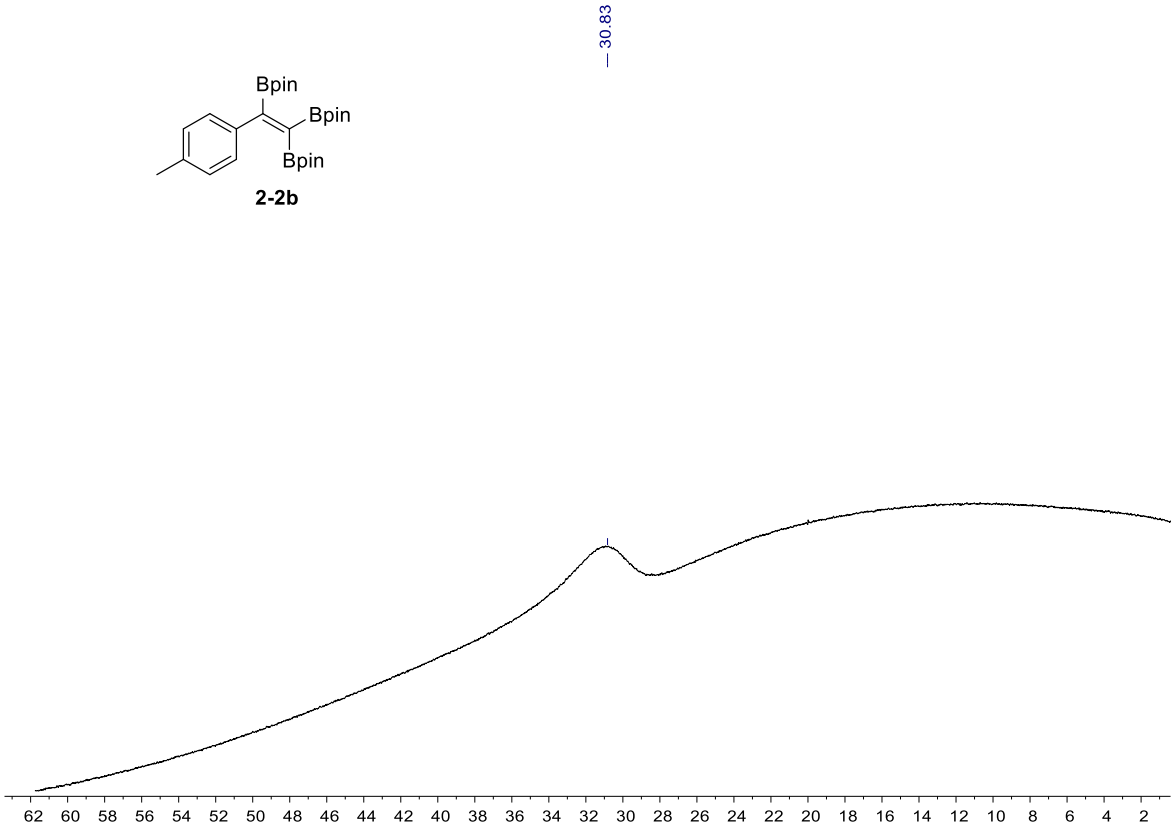
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2b**



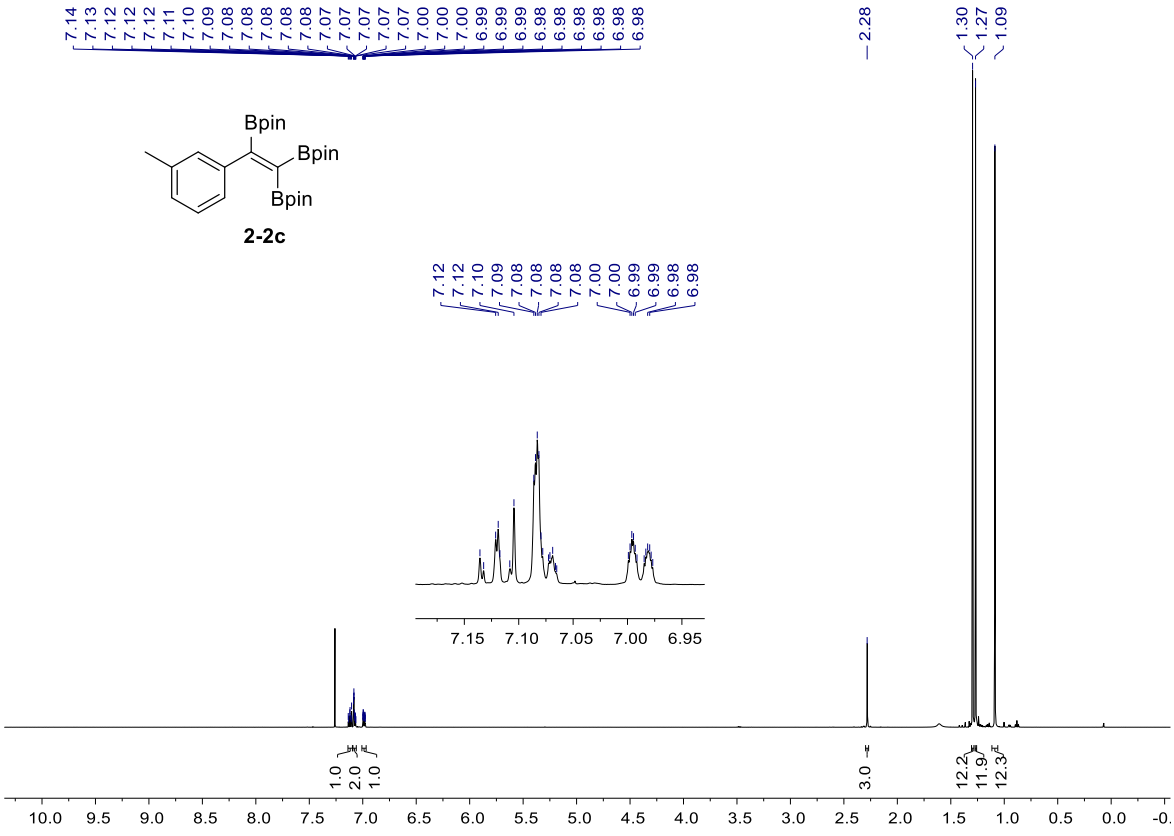
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2-2b**



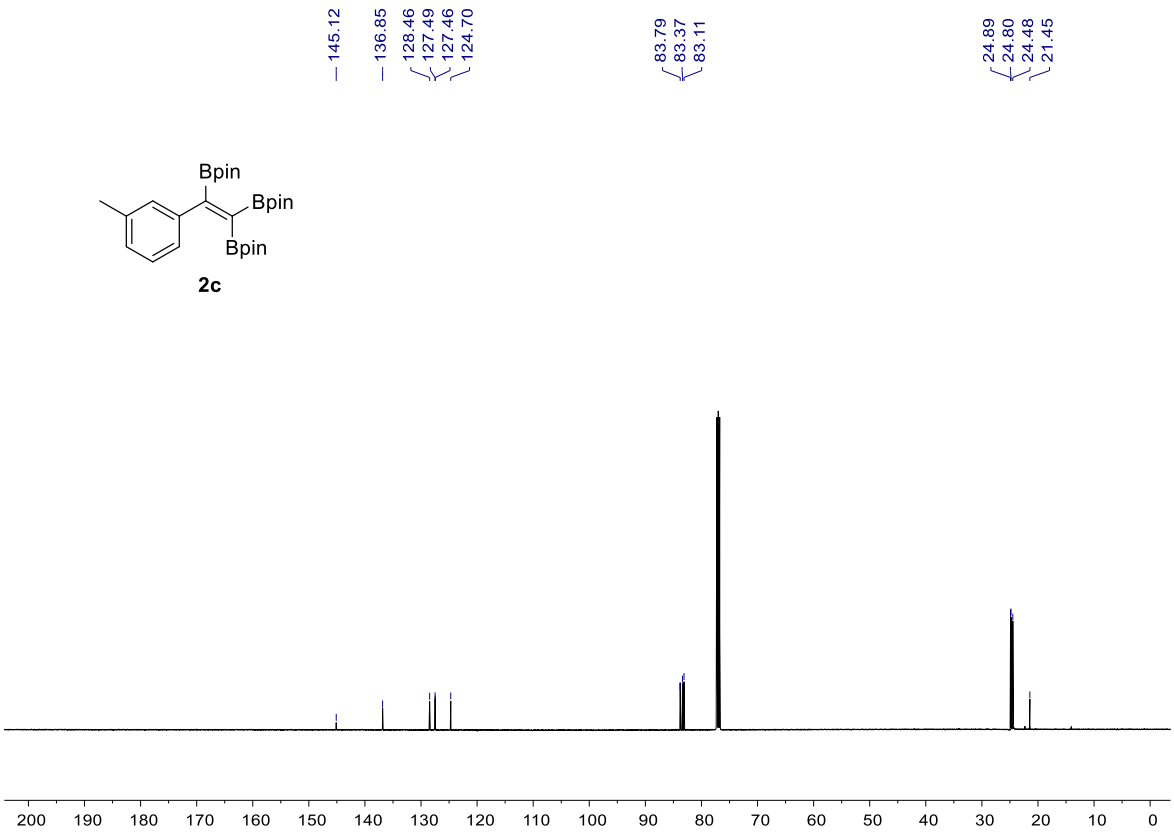
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2b**



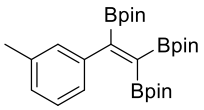
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2c**



^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2-2c**

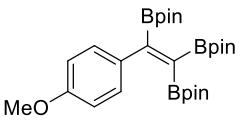


^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2c**



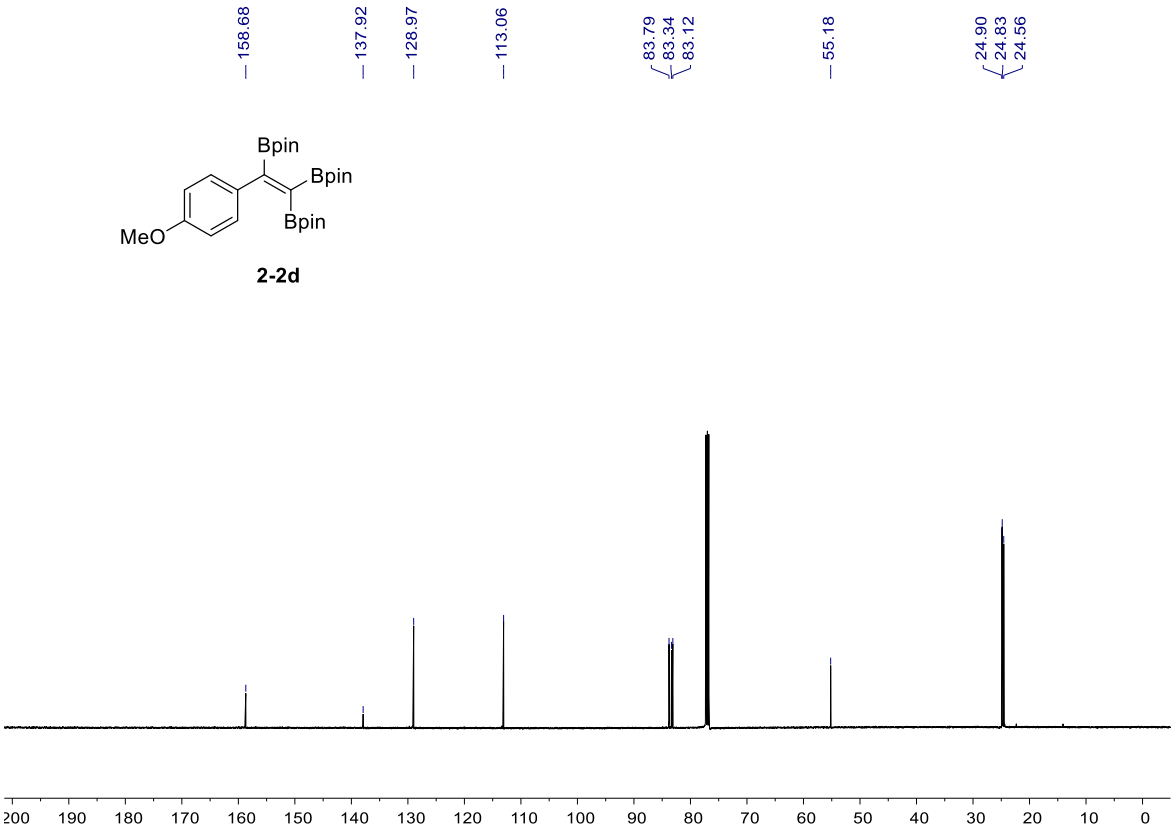
2-2c

^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2d**



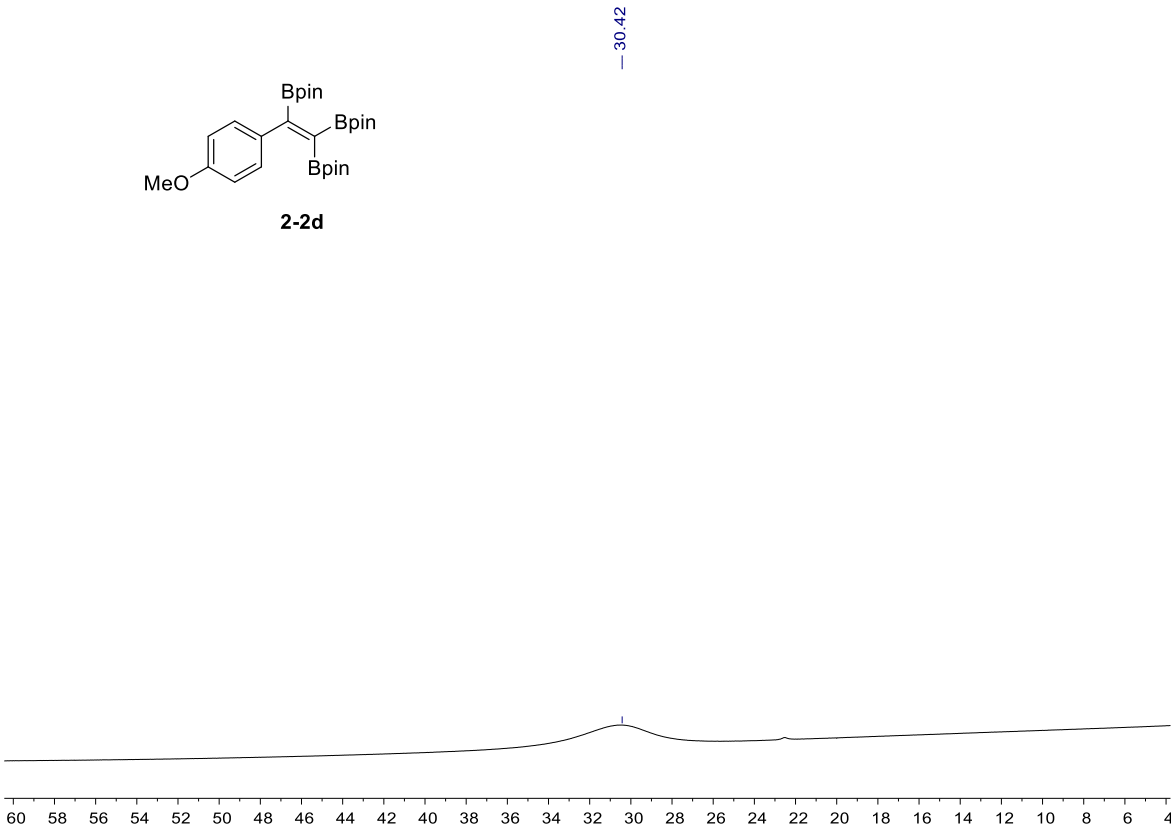
2-2d

$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2-2d**



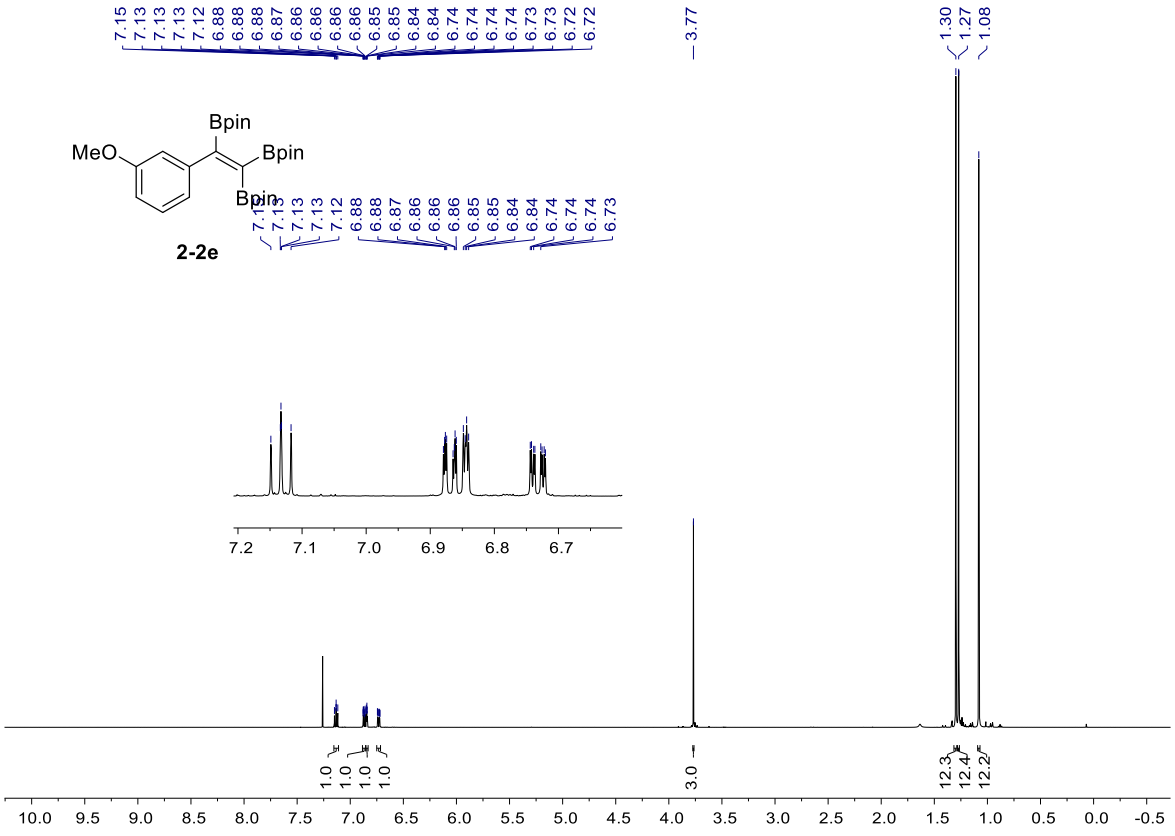
2-2d

^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2d**

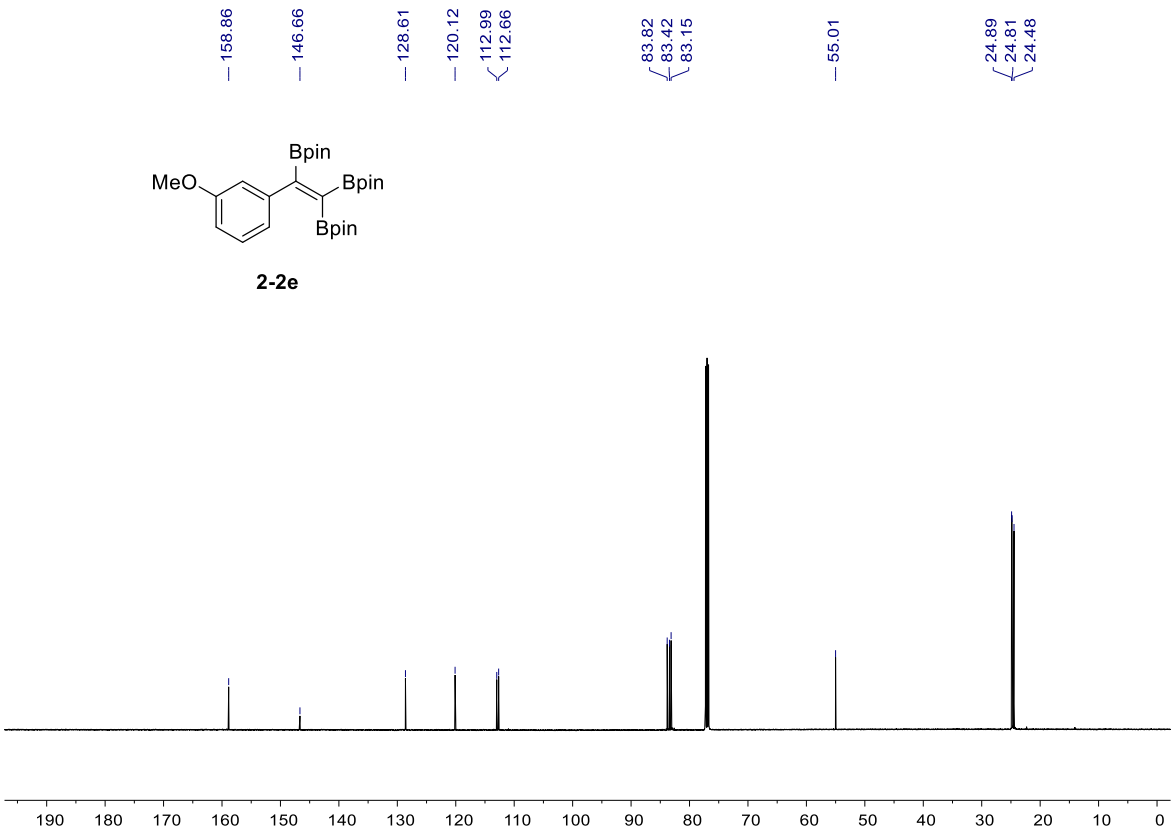


2-2d

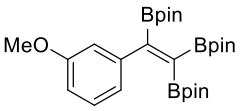
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2e**



^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2-2e**



^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2e**

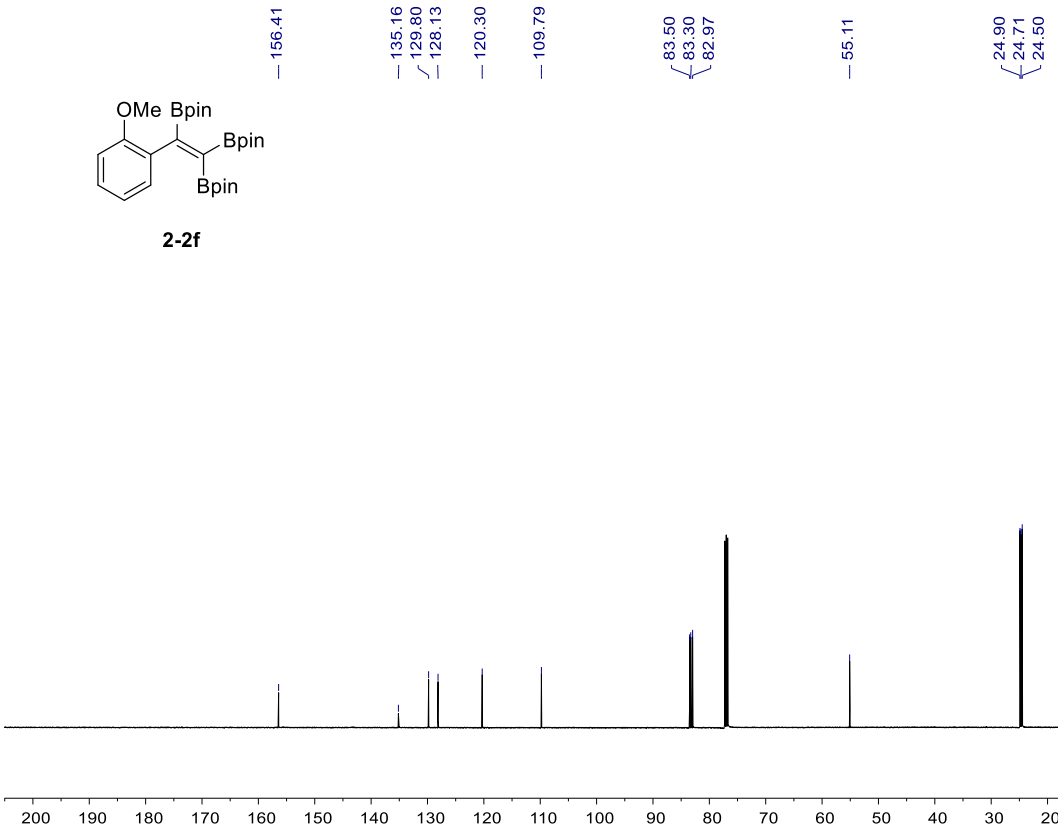


2-2e

^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2f**

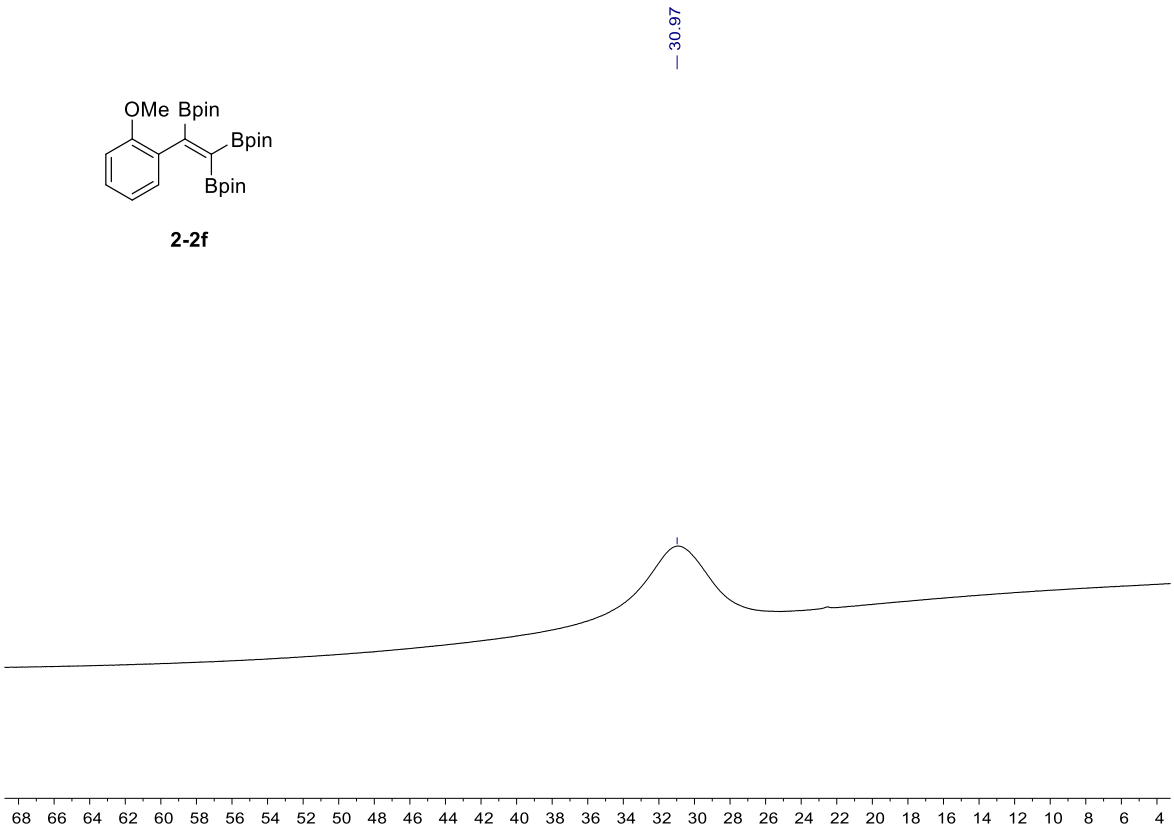
2-2f

$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2-2f**



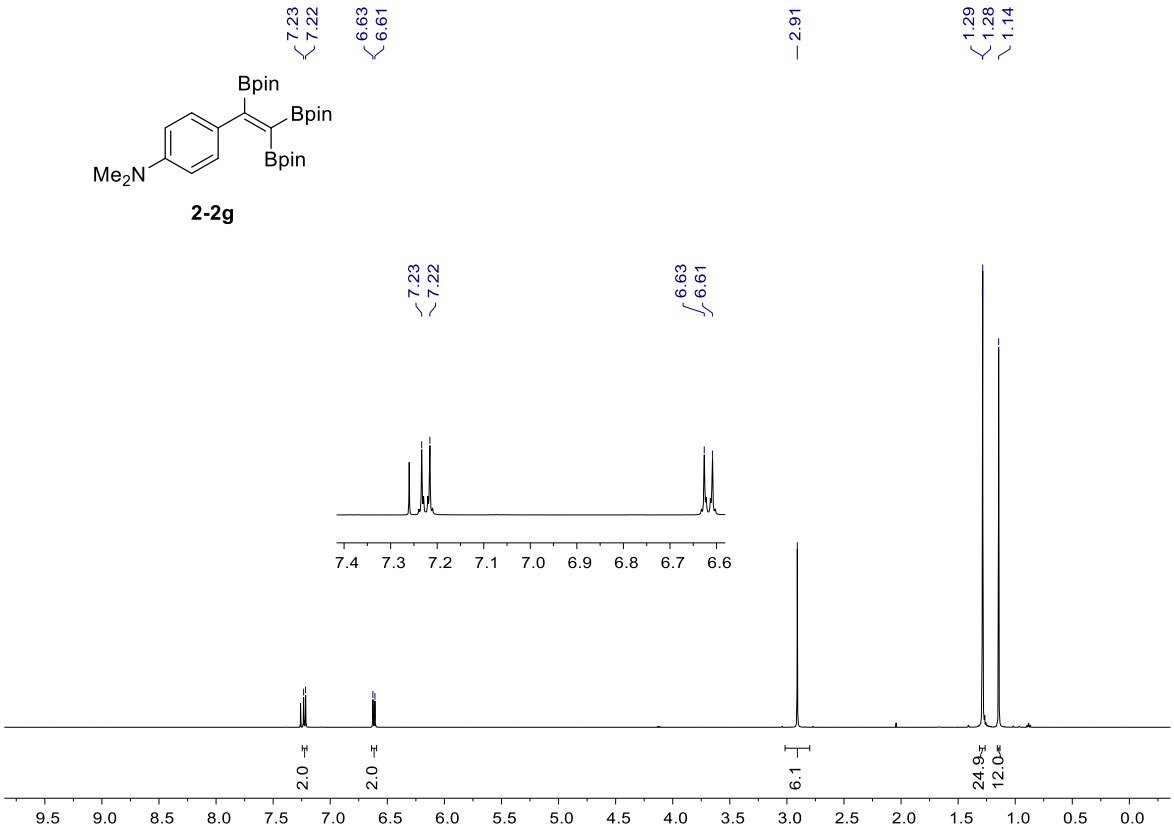
2-2f

^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2f**

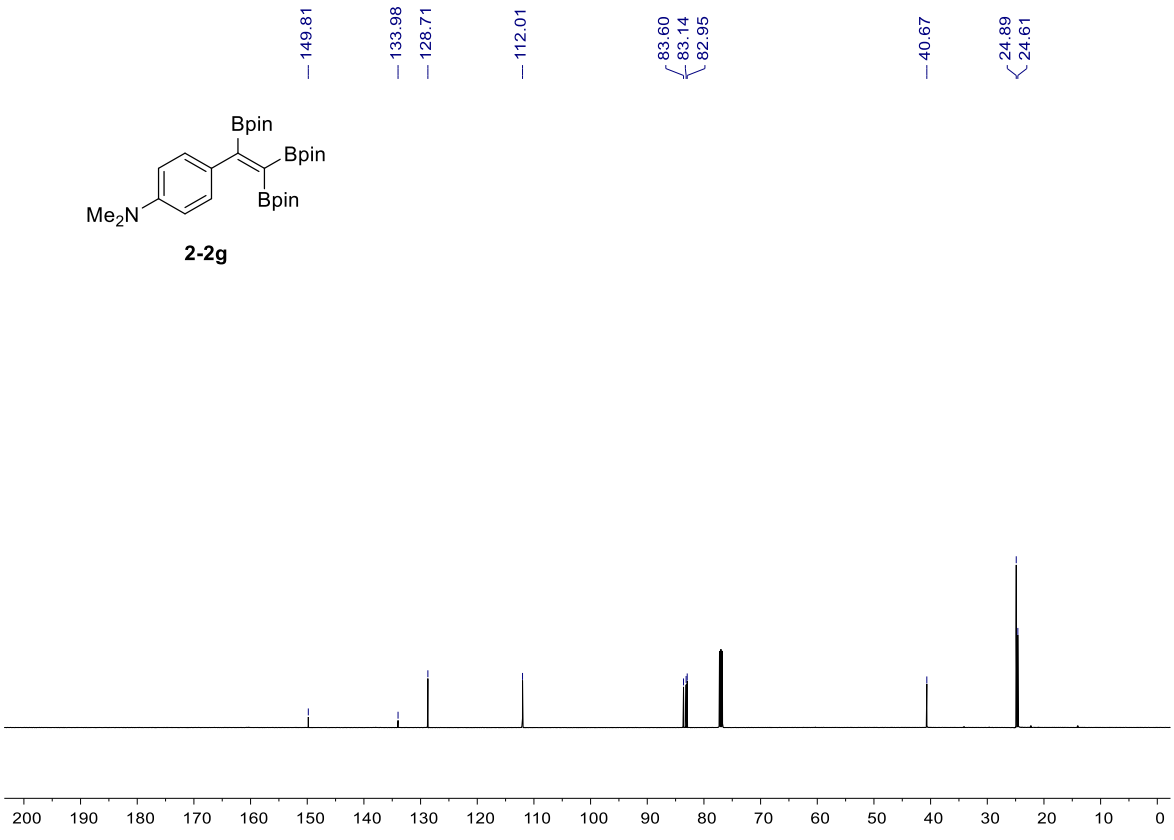


2-2f

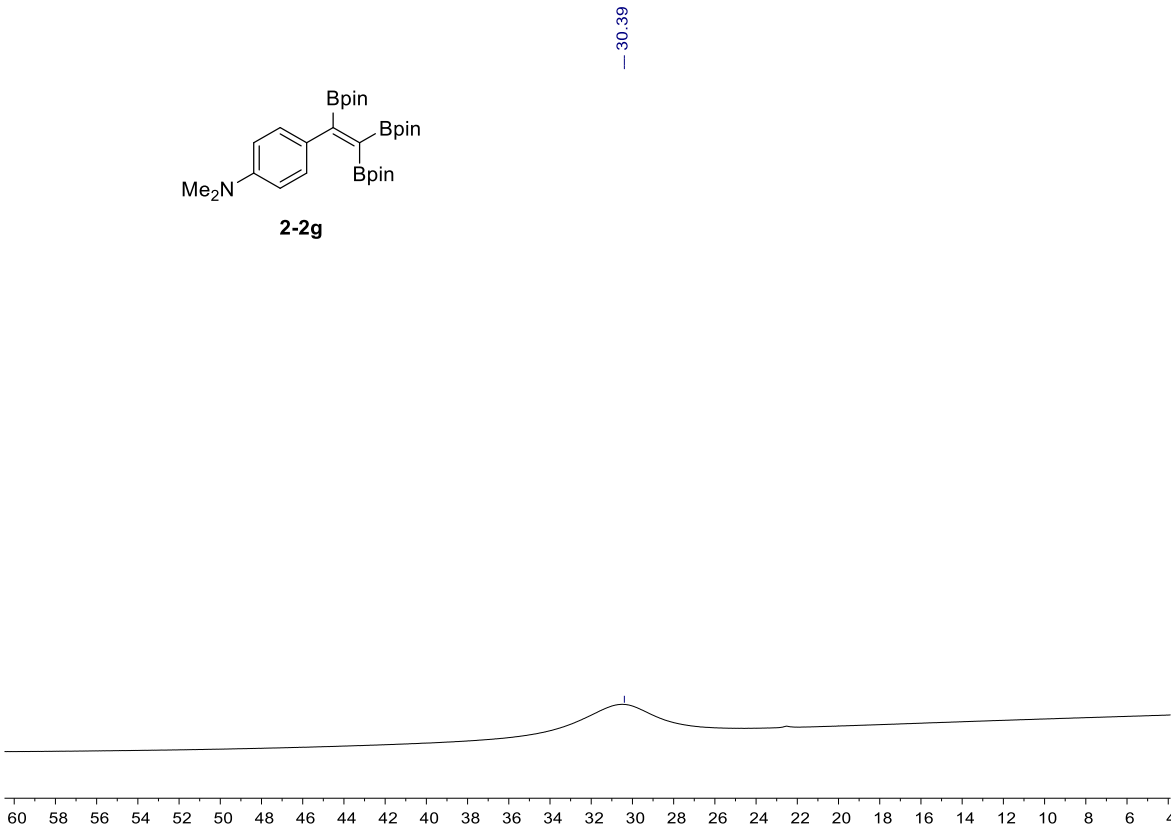
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2g**



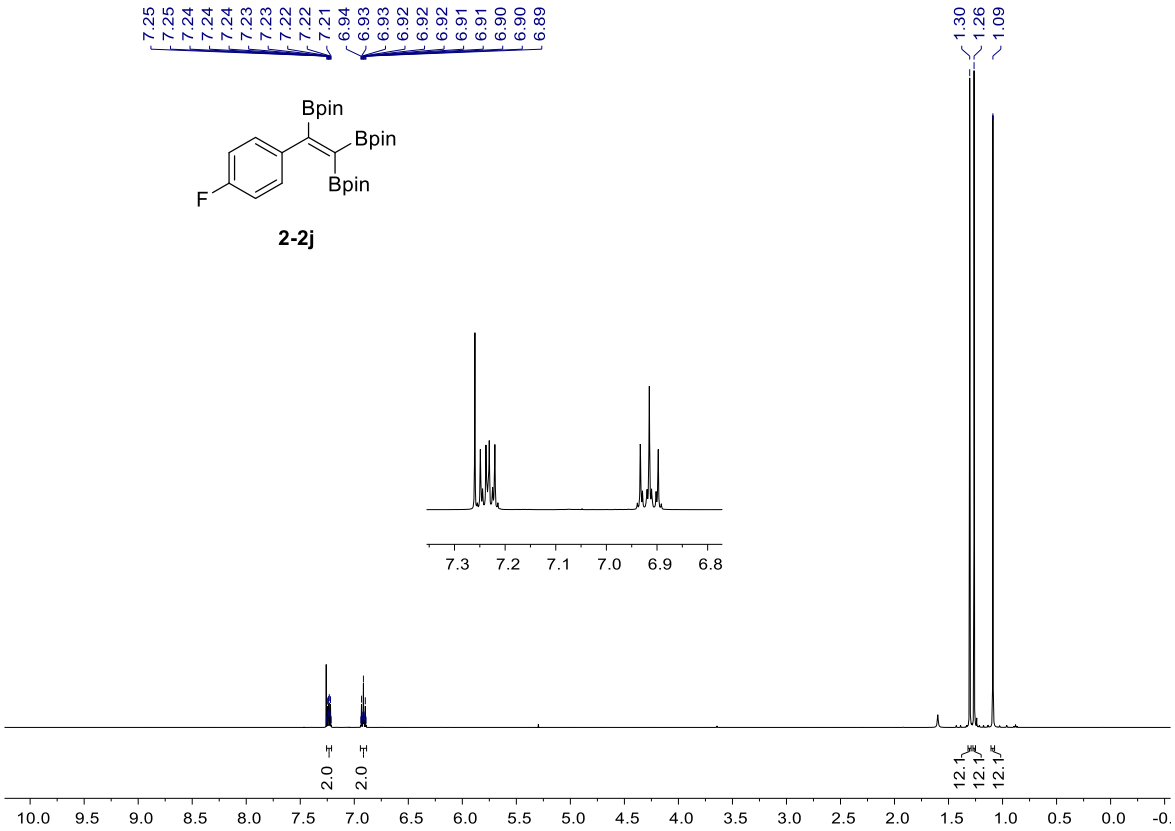
^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2-2g**



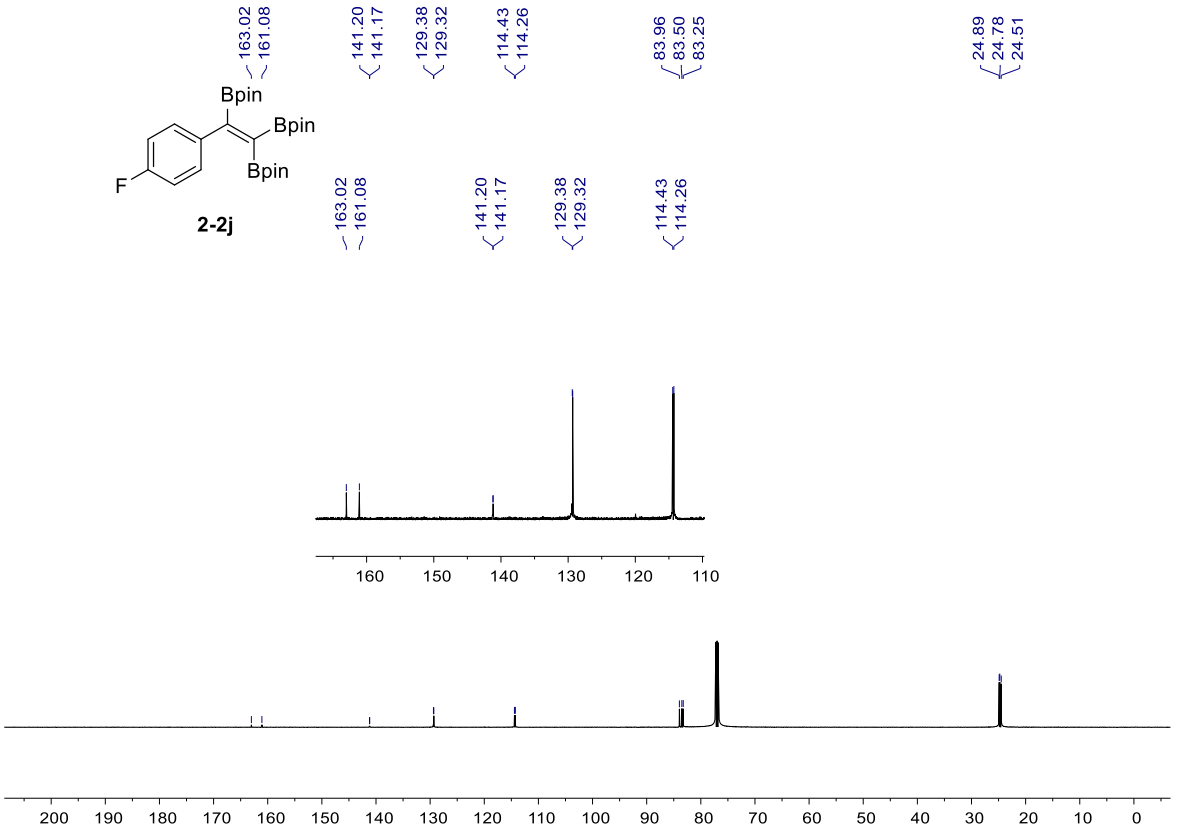
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2g**



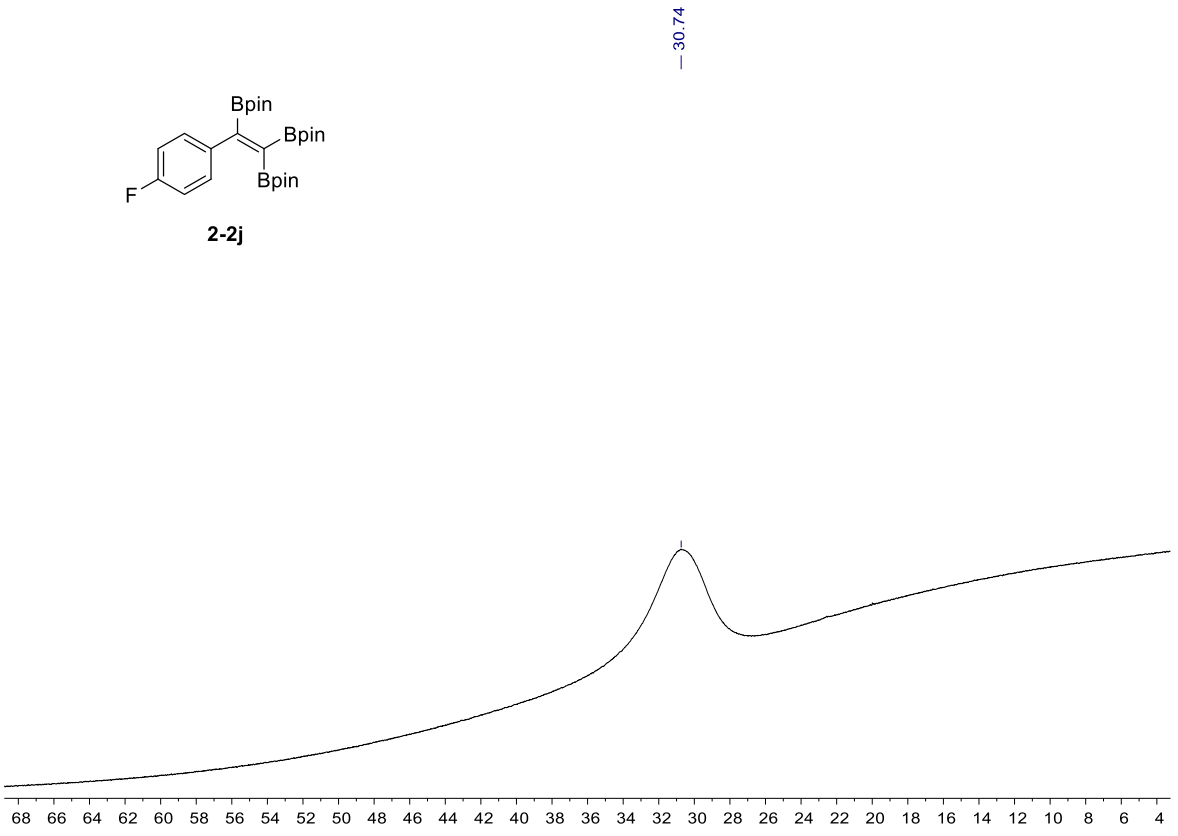
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2j**



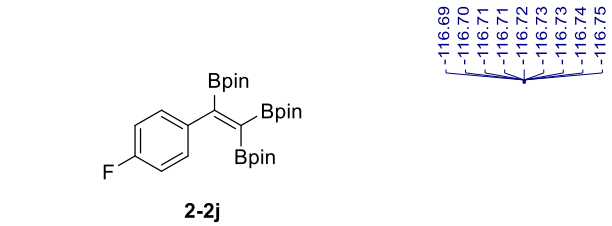
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2-2j**



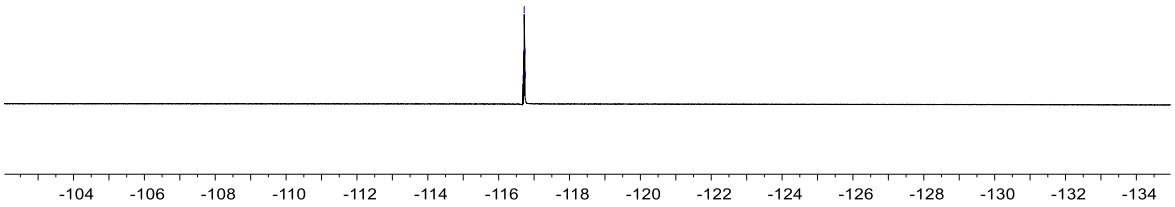
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2j**



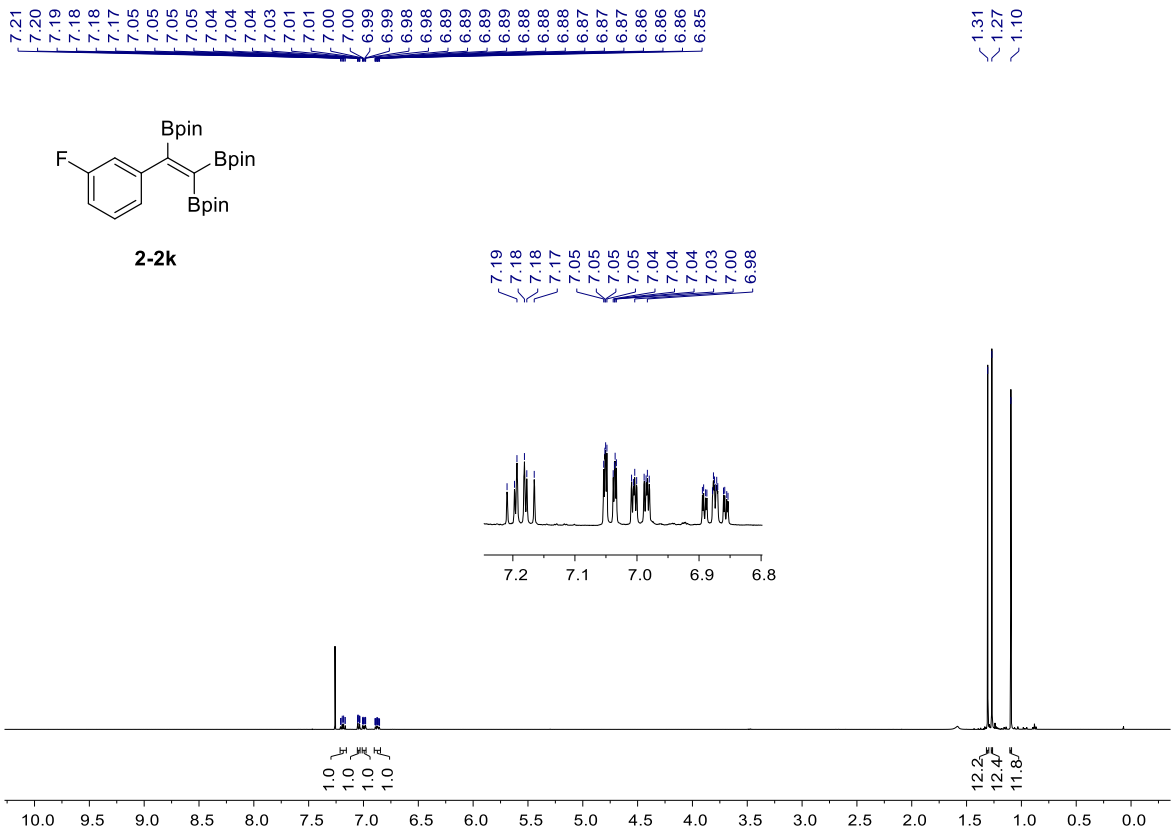
^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **2-2j**



2-2j

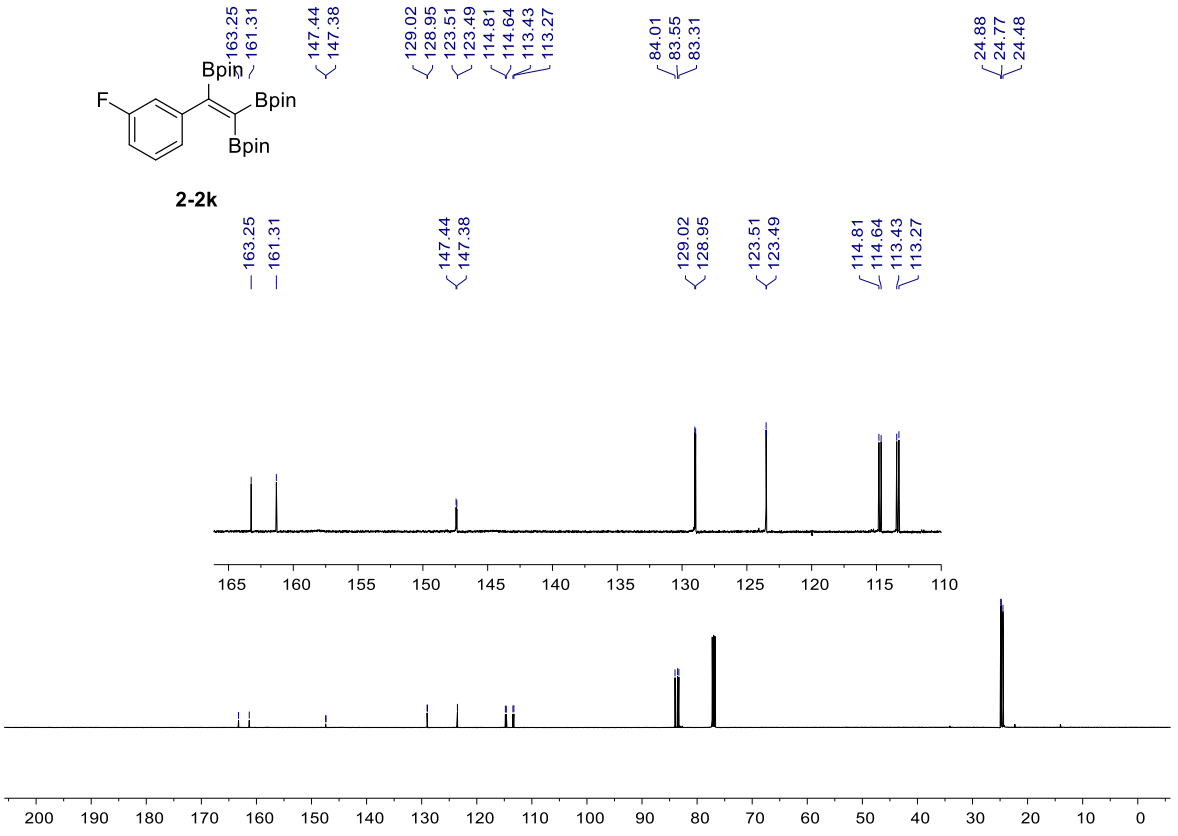


^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2k**

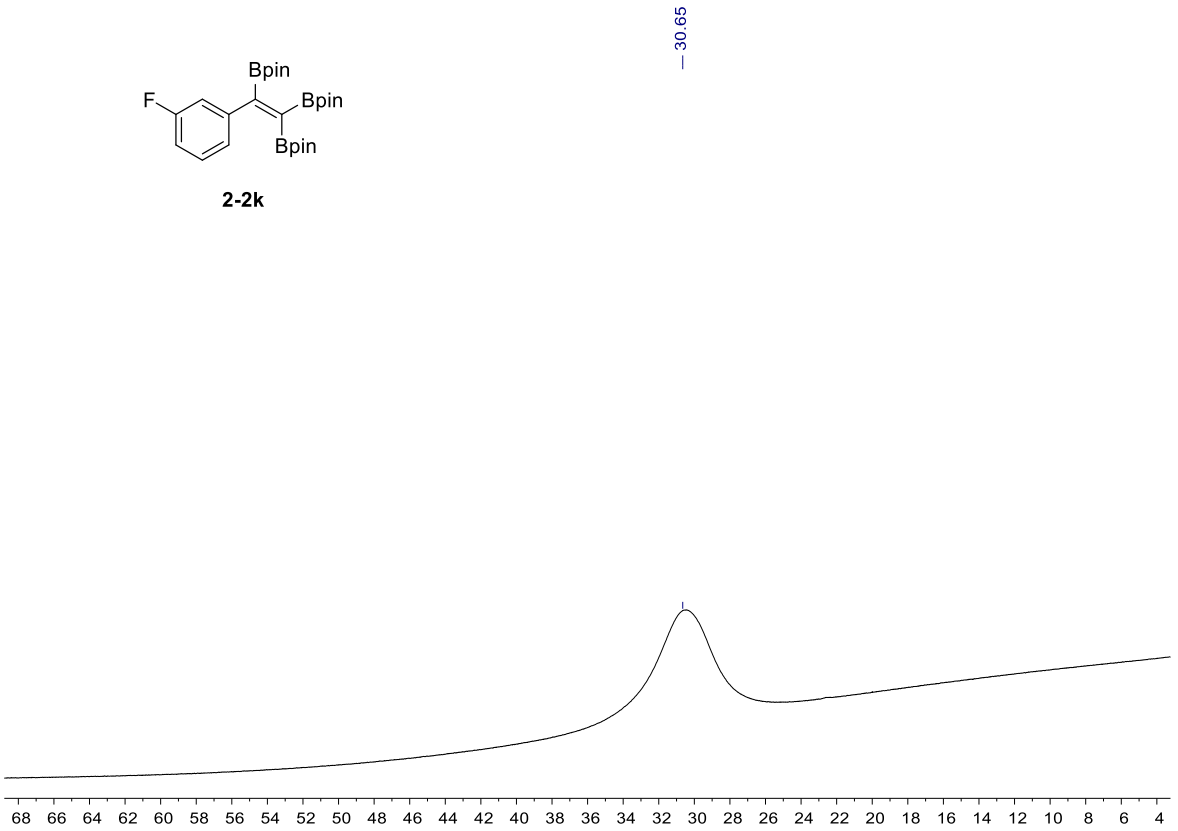


2-2k

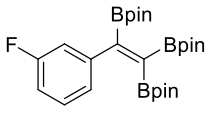
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2-2k**



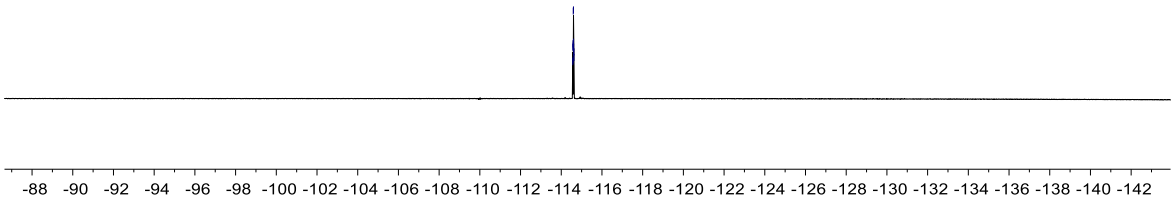
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2k**



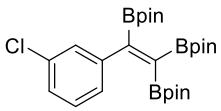
^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **2-2k**



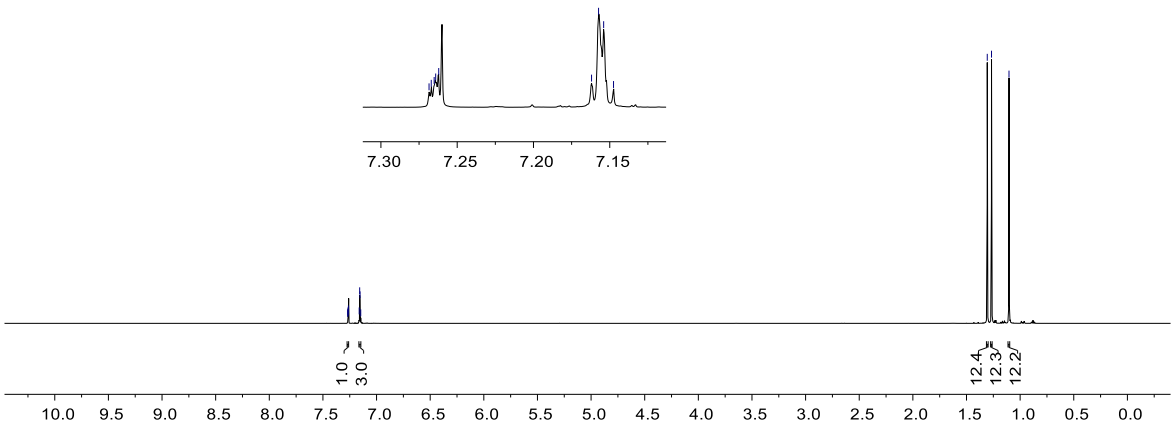
2-2k



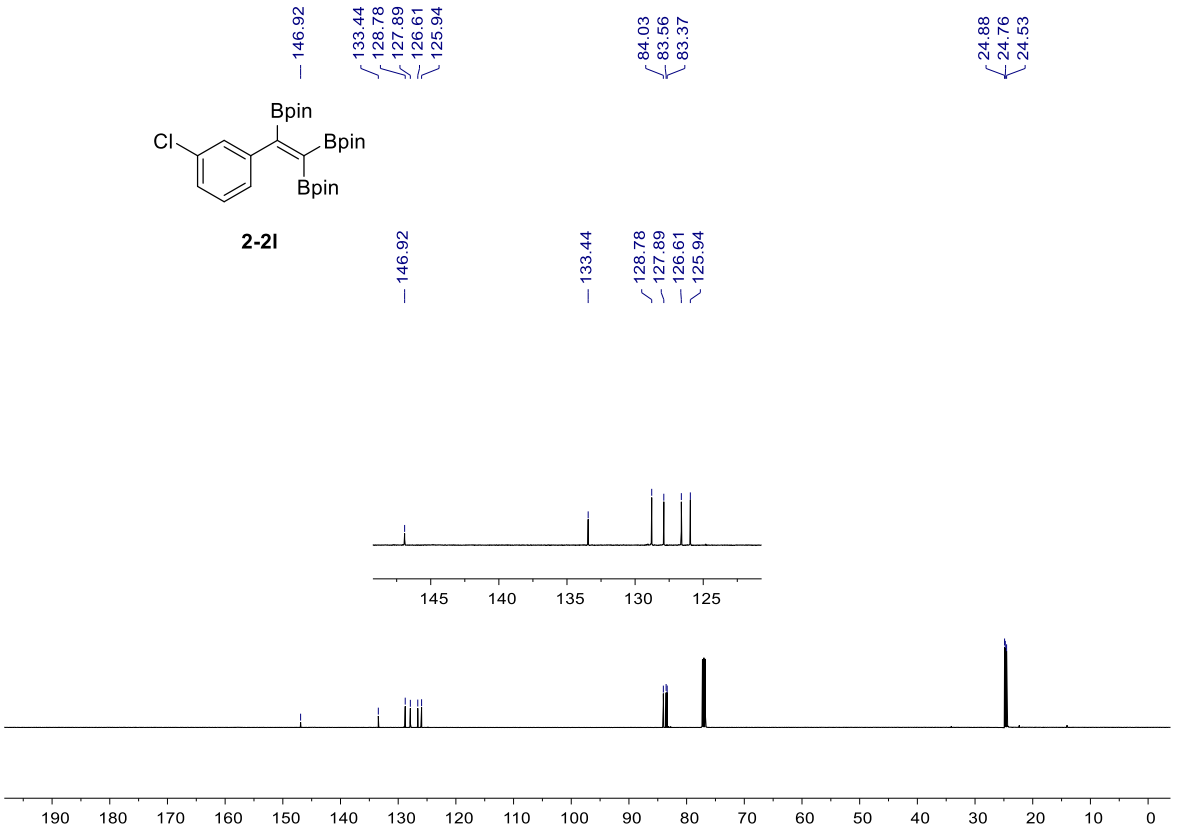
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2l**



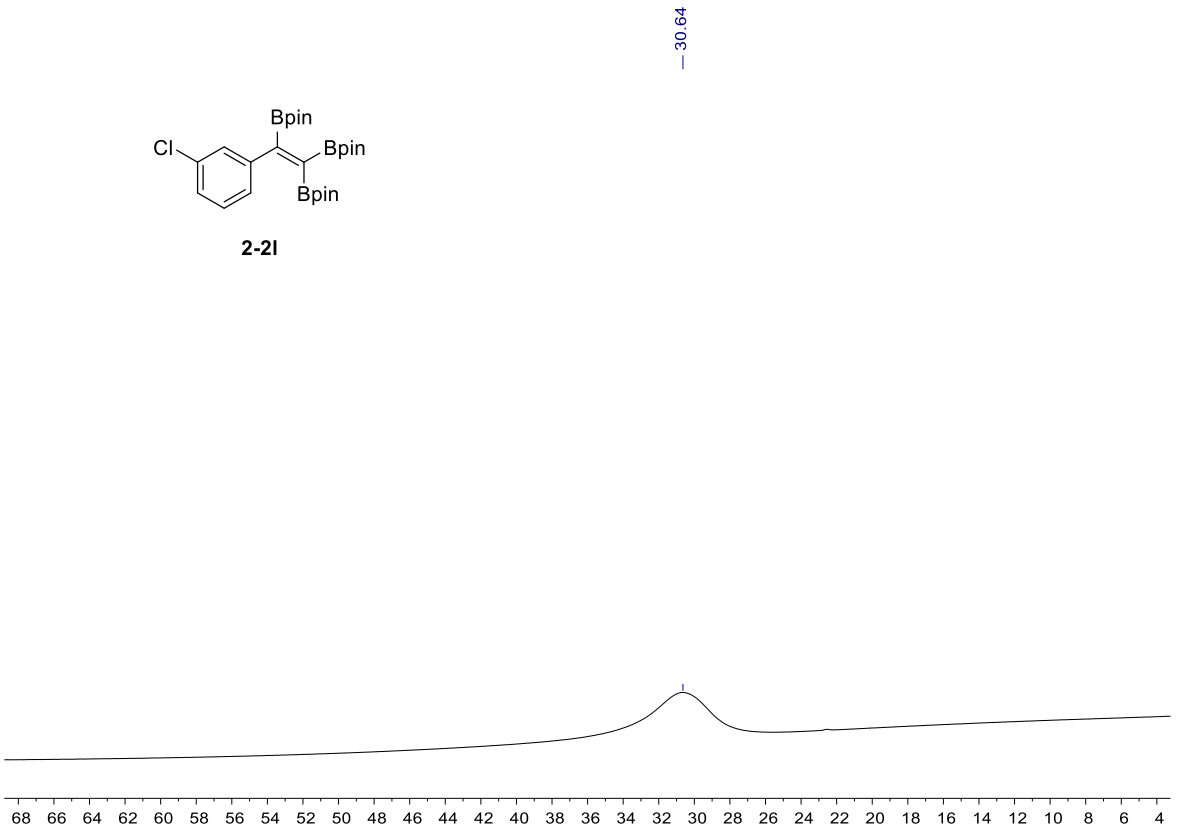
2-2l



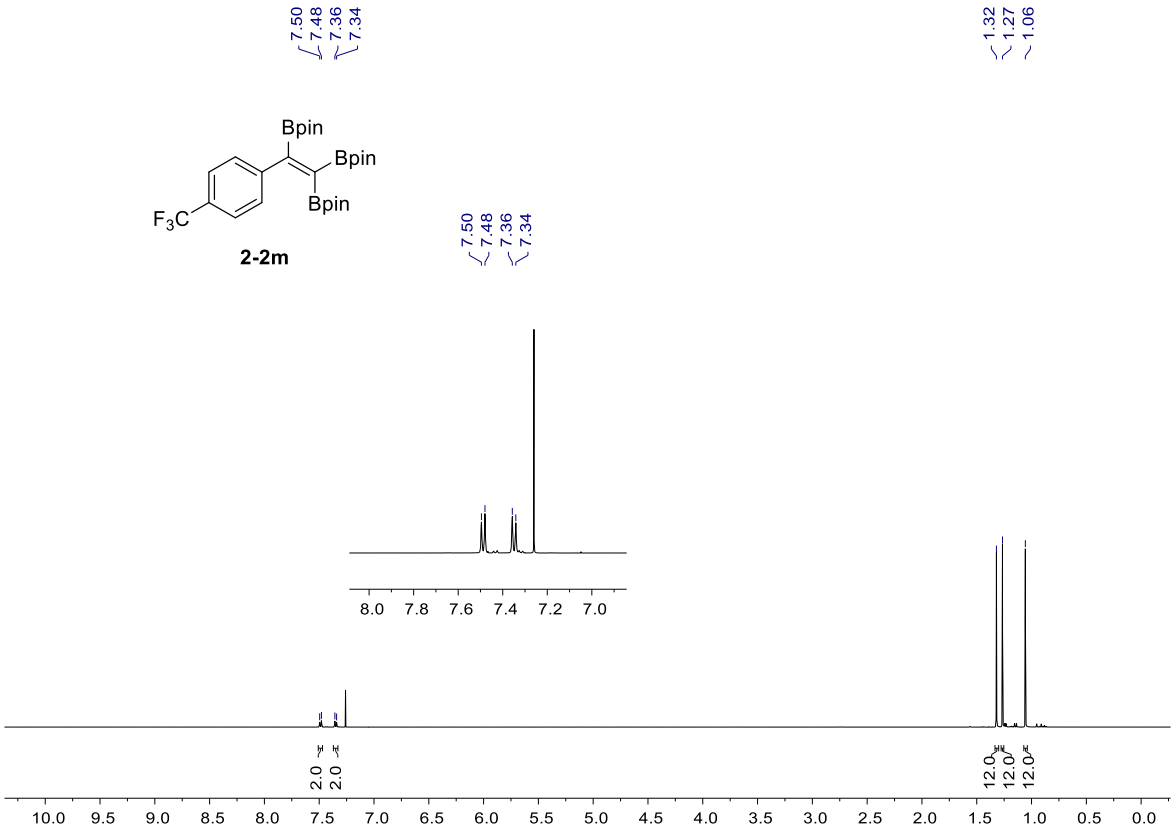
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2-2l**



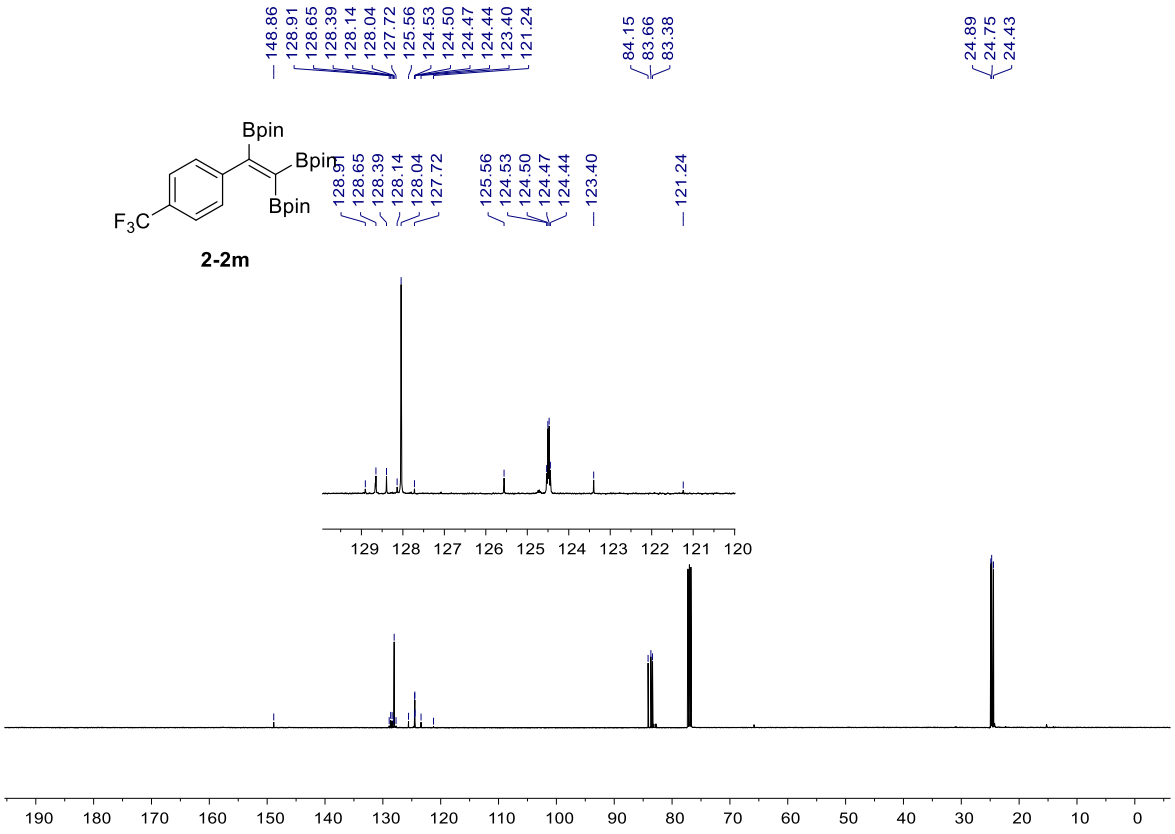
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2l**



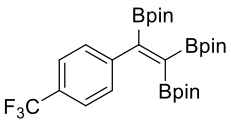
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2m**



^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2-2m**

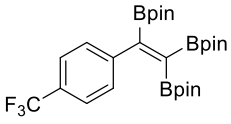


^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2m**



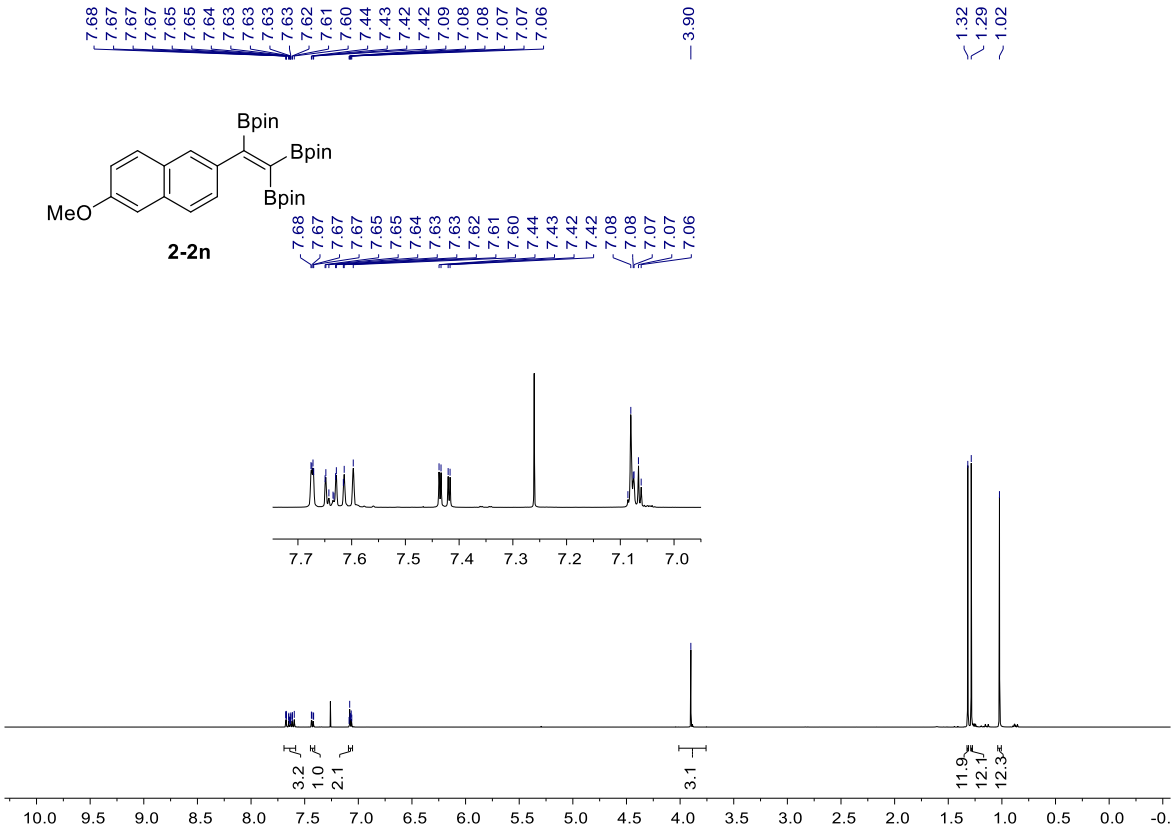
2-2m

^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **2-2m**

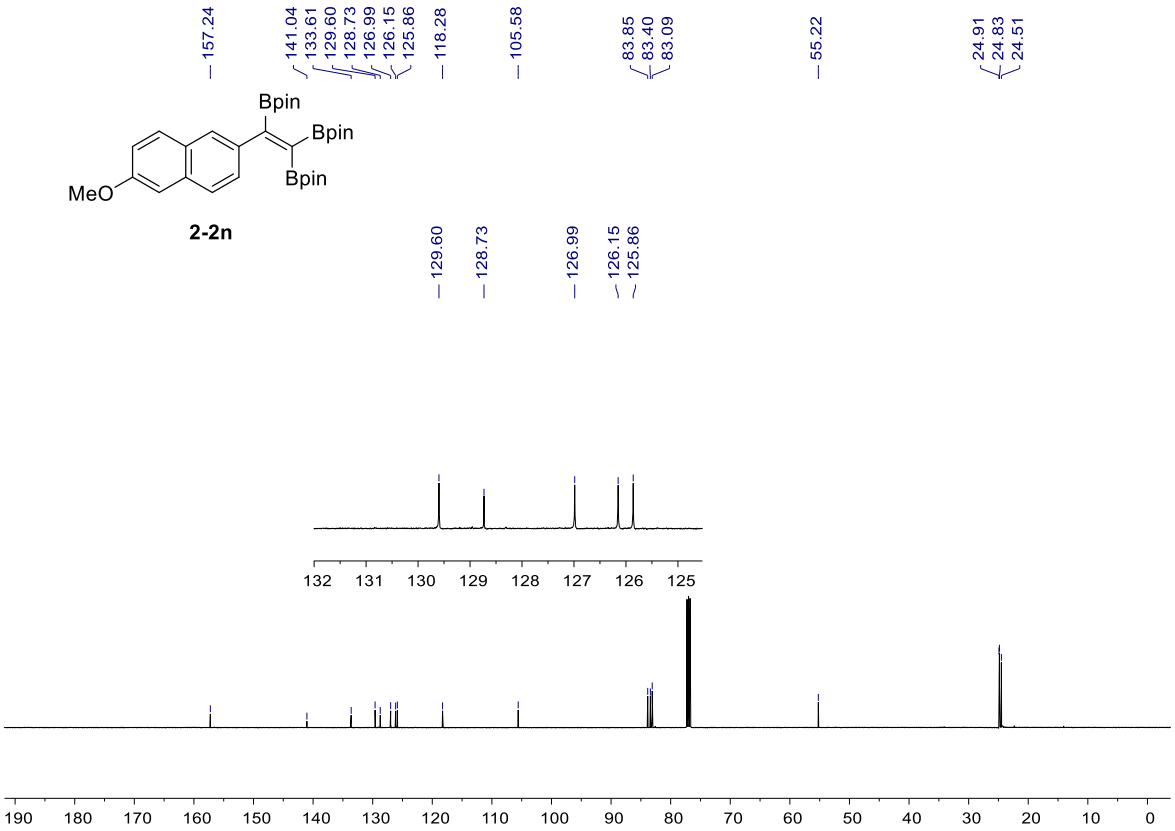


2-2m

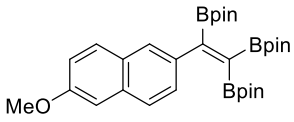
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2n**



^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2-2n**



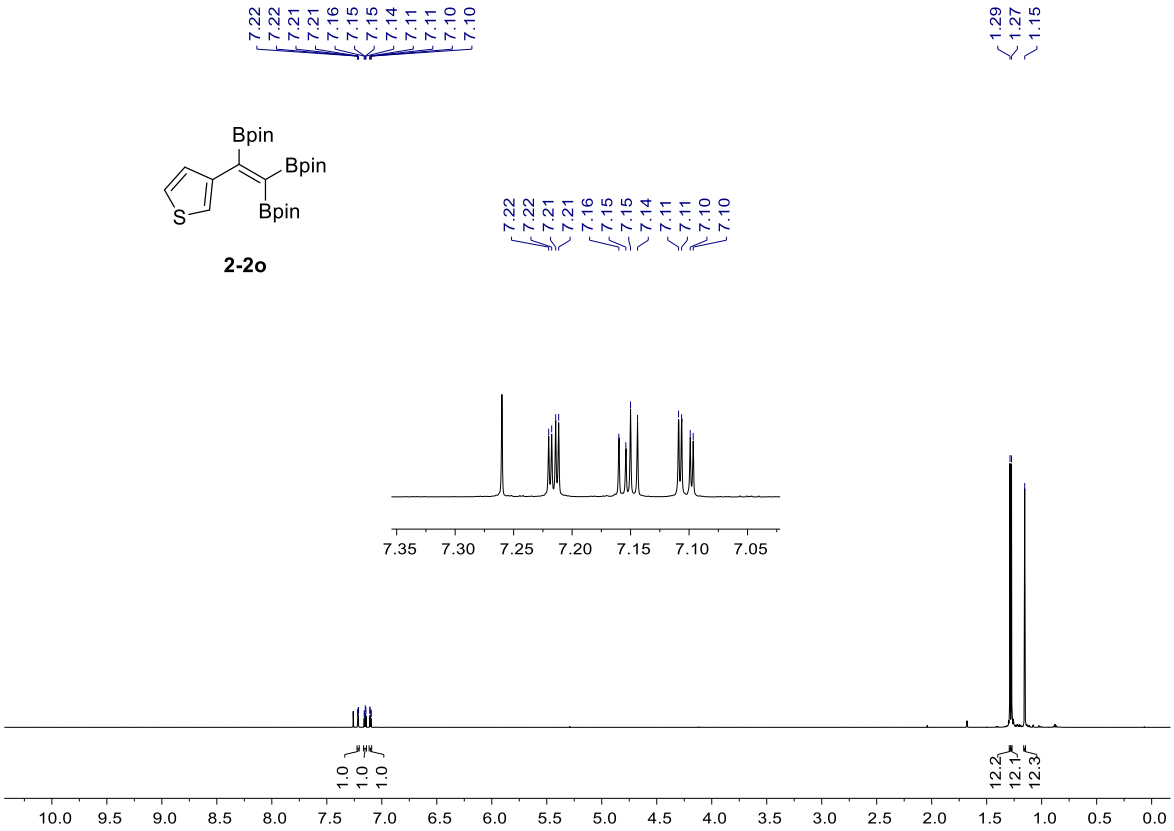
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2n**



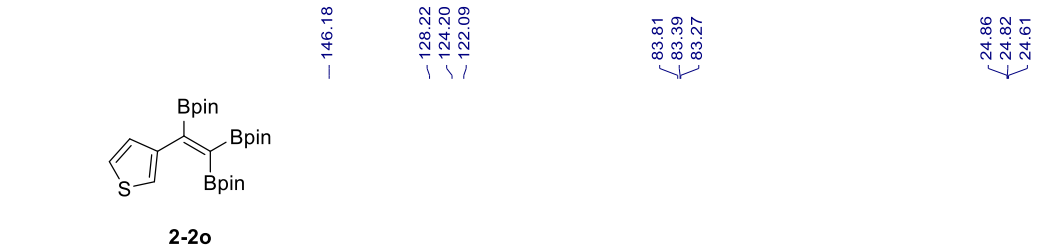
2-2n

^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2o**

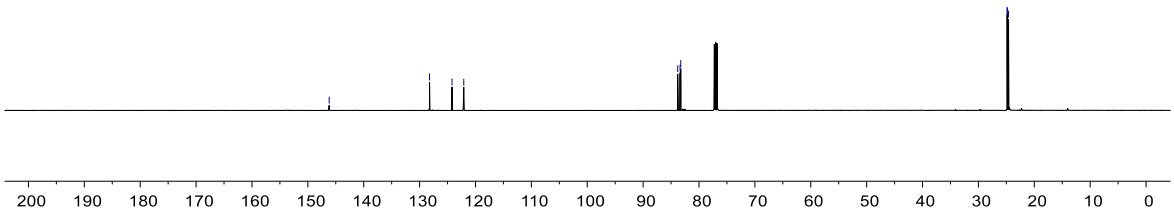
2-2o



$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2-2o**

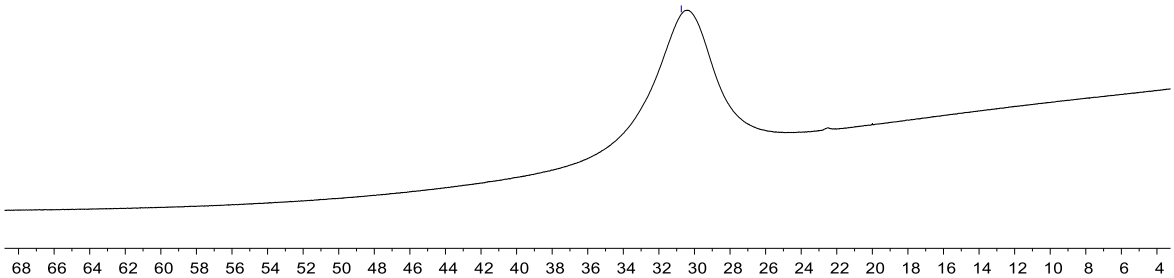


2-2o

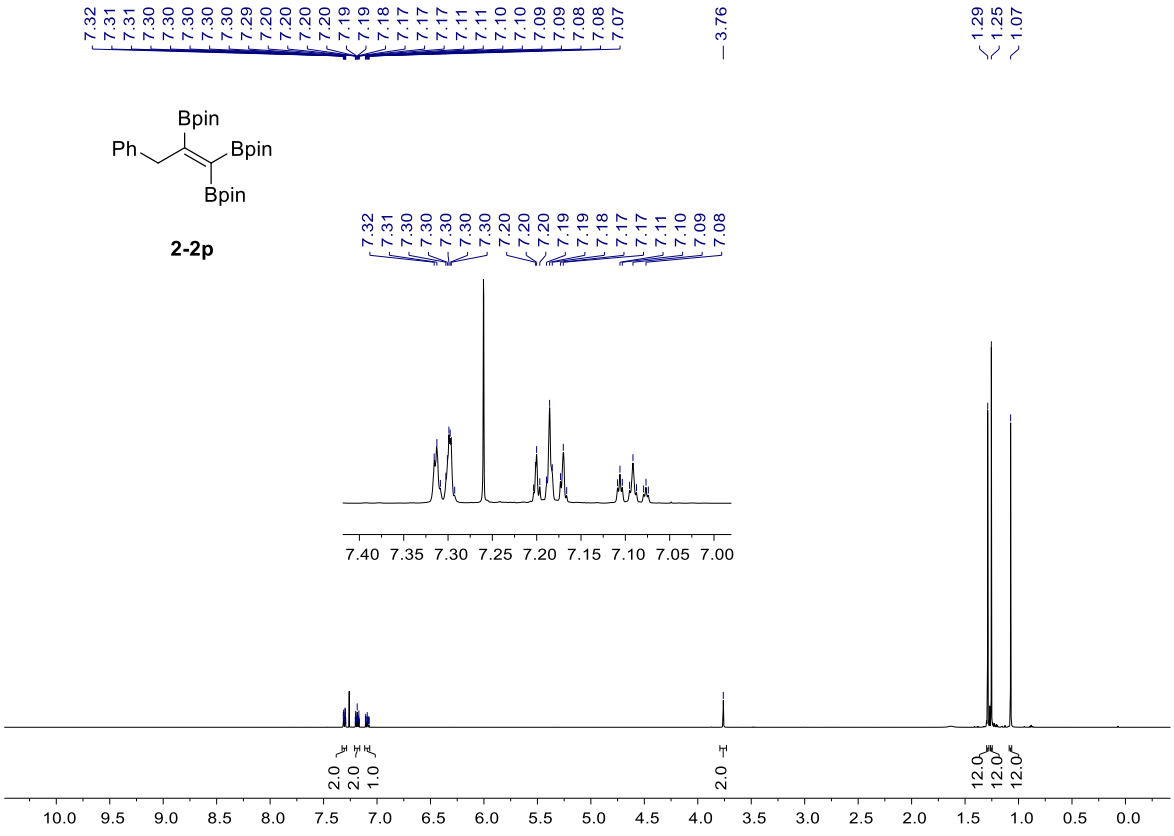


^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2o**

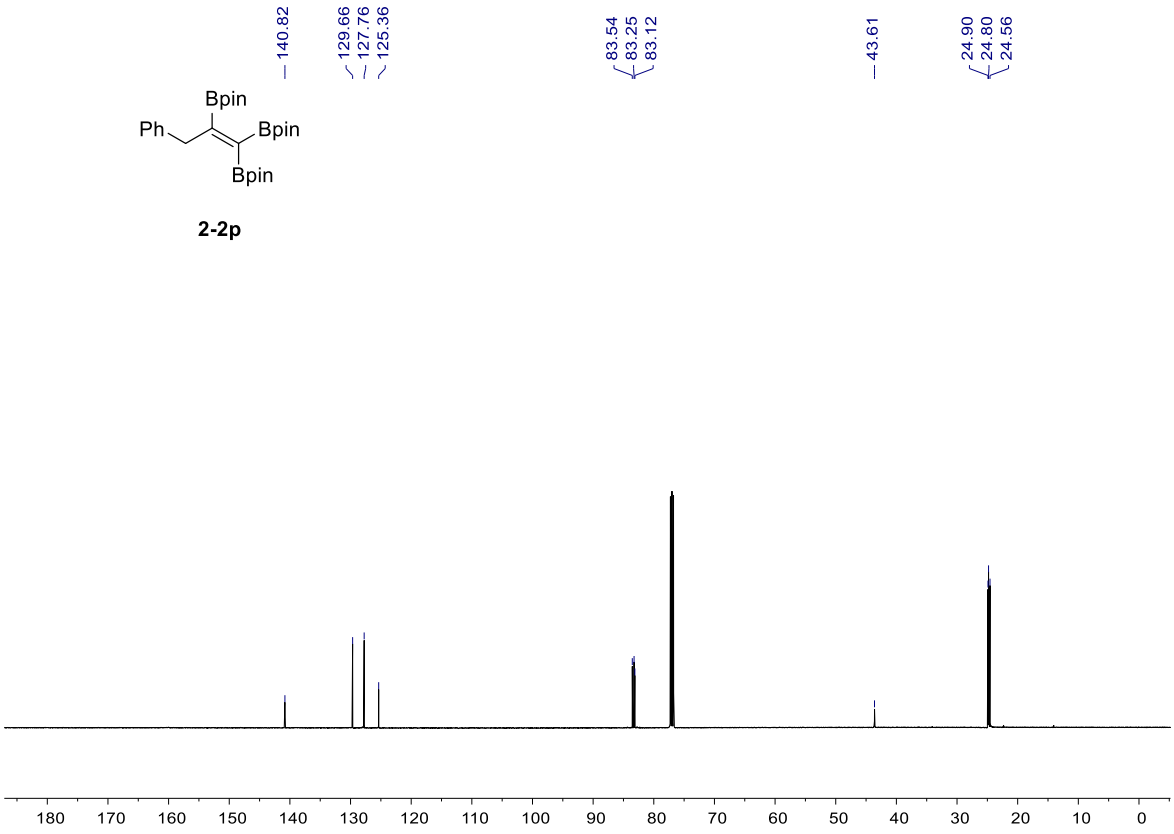
2-2o



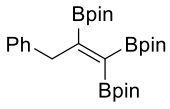
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2p**



^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2-2p**

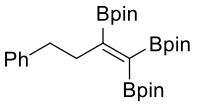


^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2p**



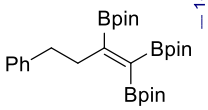
2-2p

^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2q**



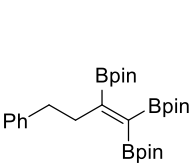
2-2q

$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2-2q**



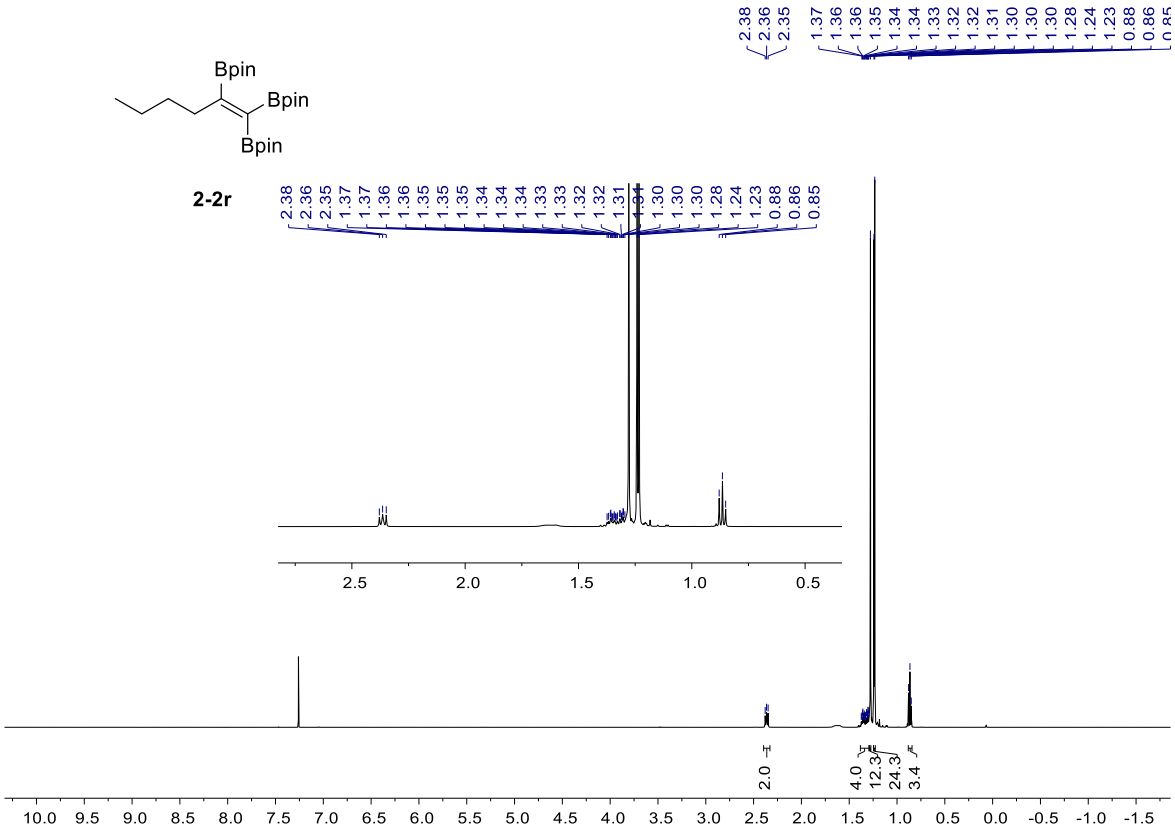
2-2q

^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2q**

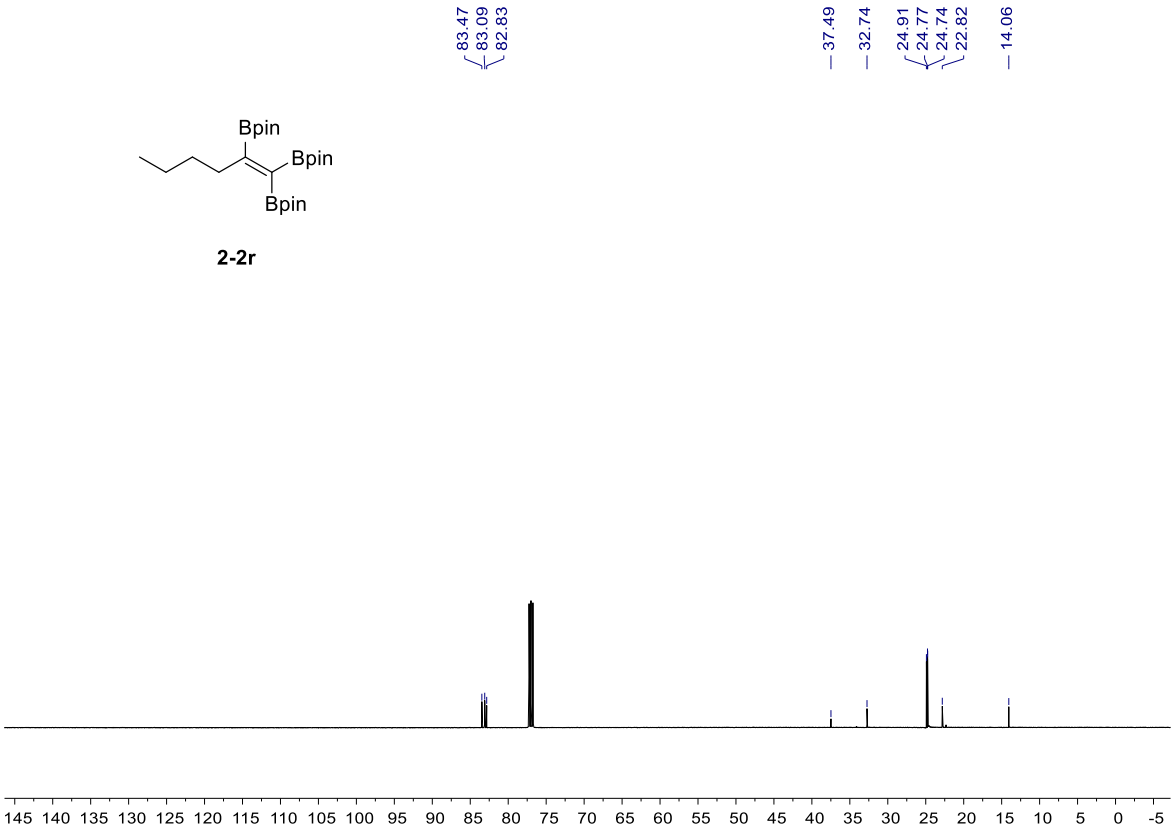


2-2q

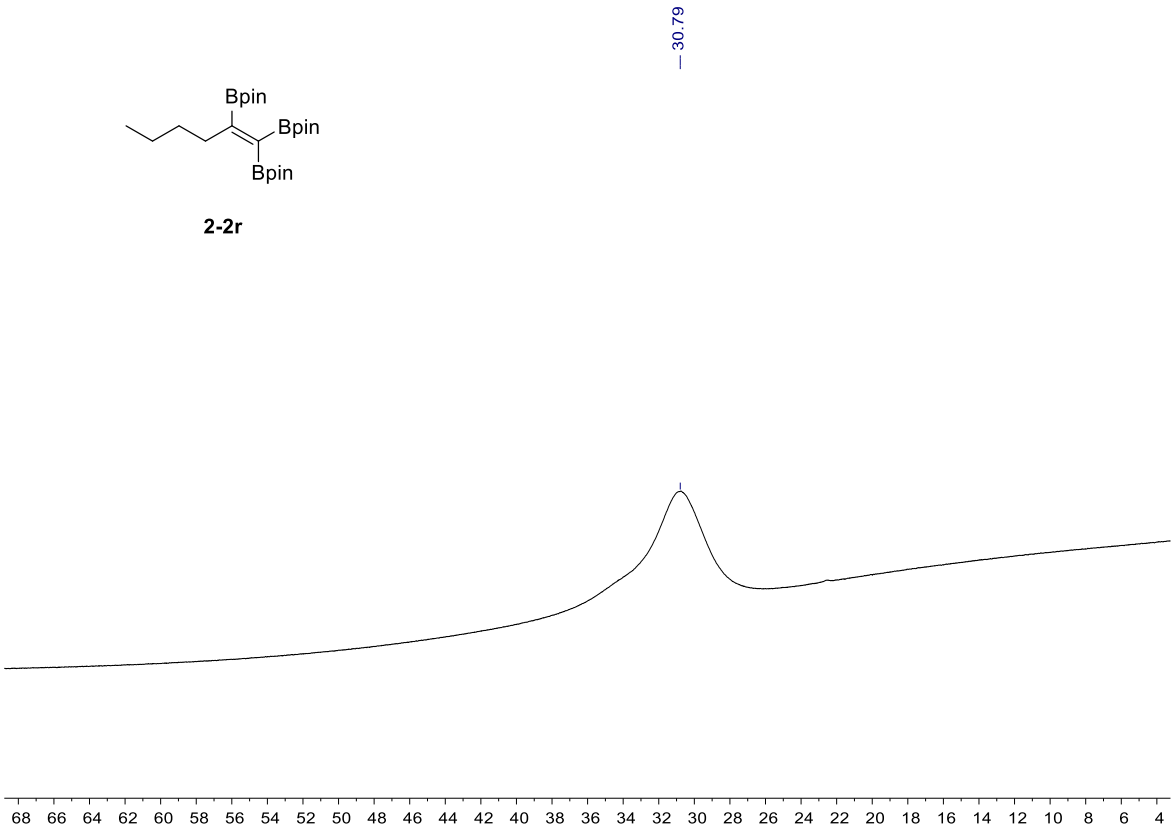
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2r**



^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2-2r**

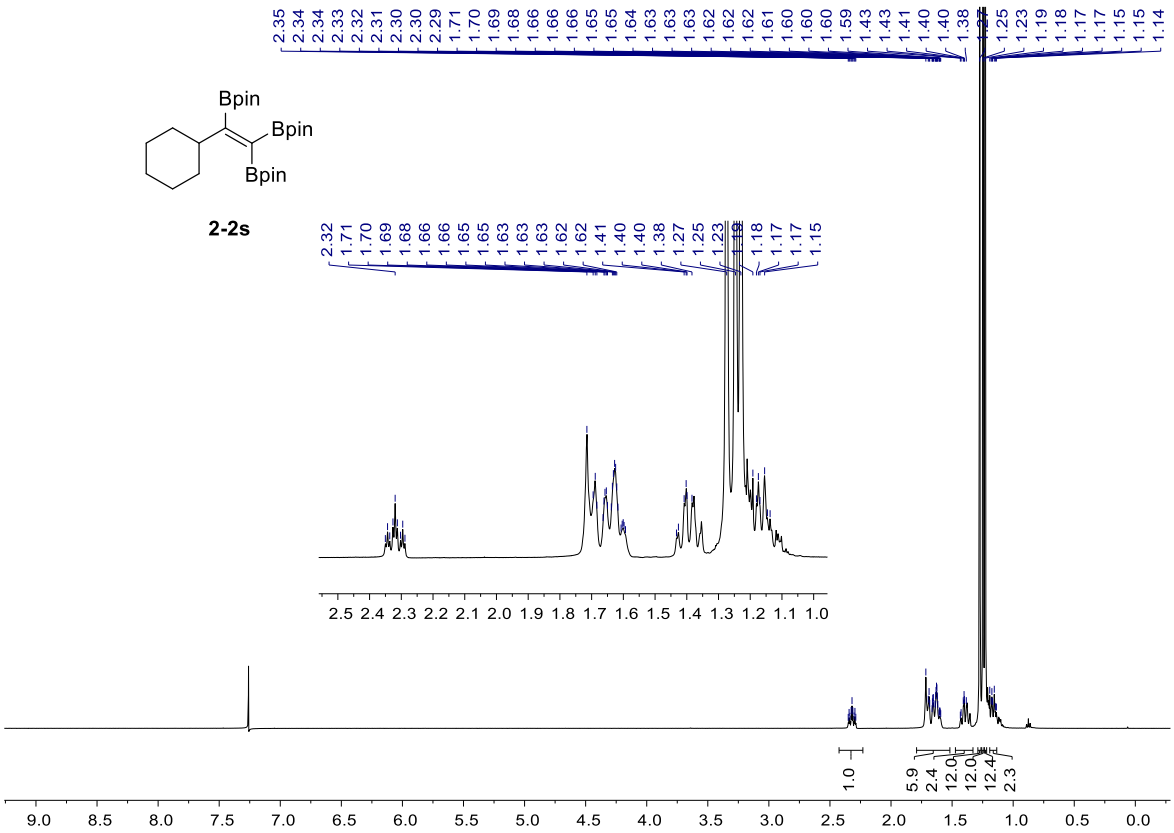


^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2r**



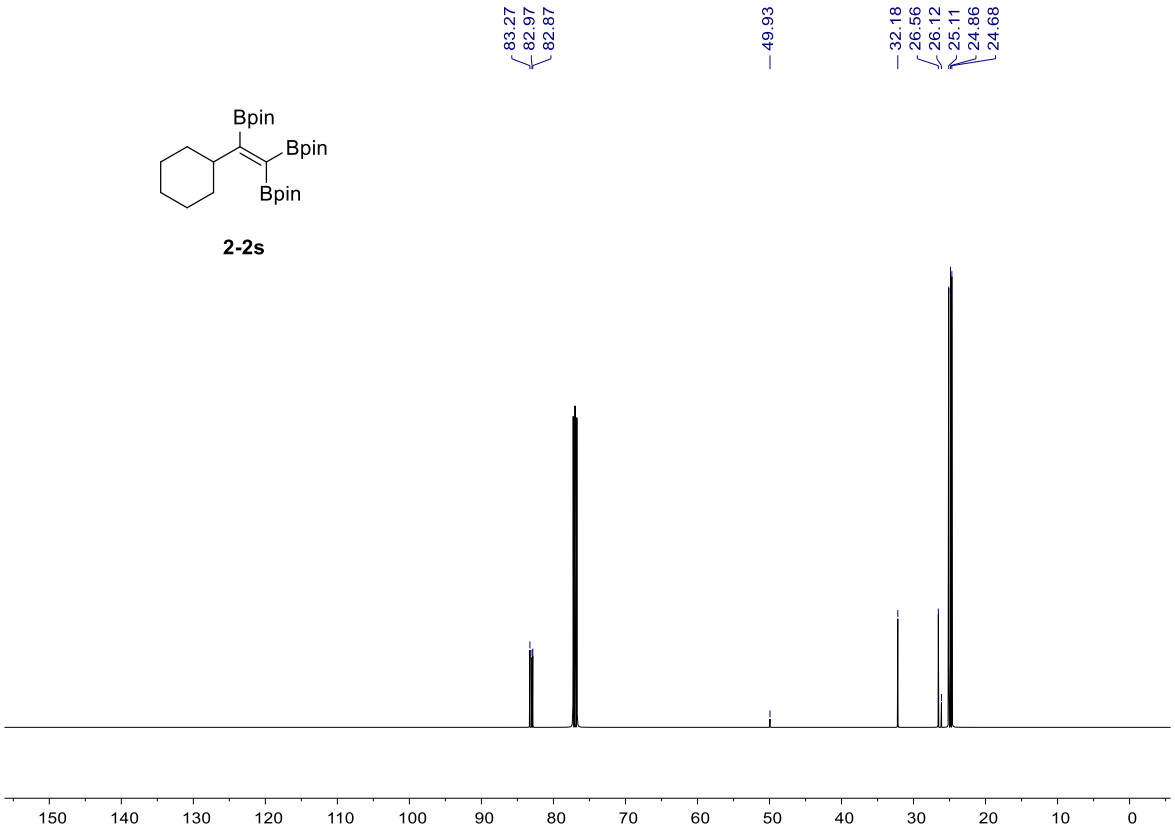
2-2r

^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2s**



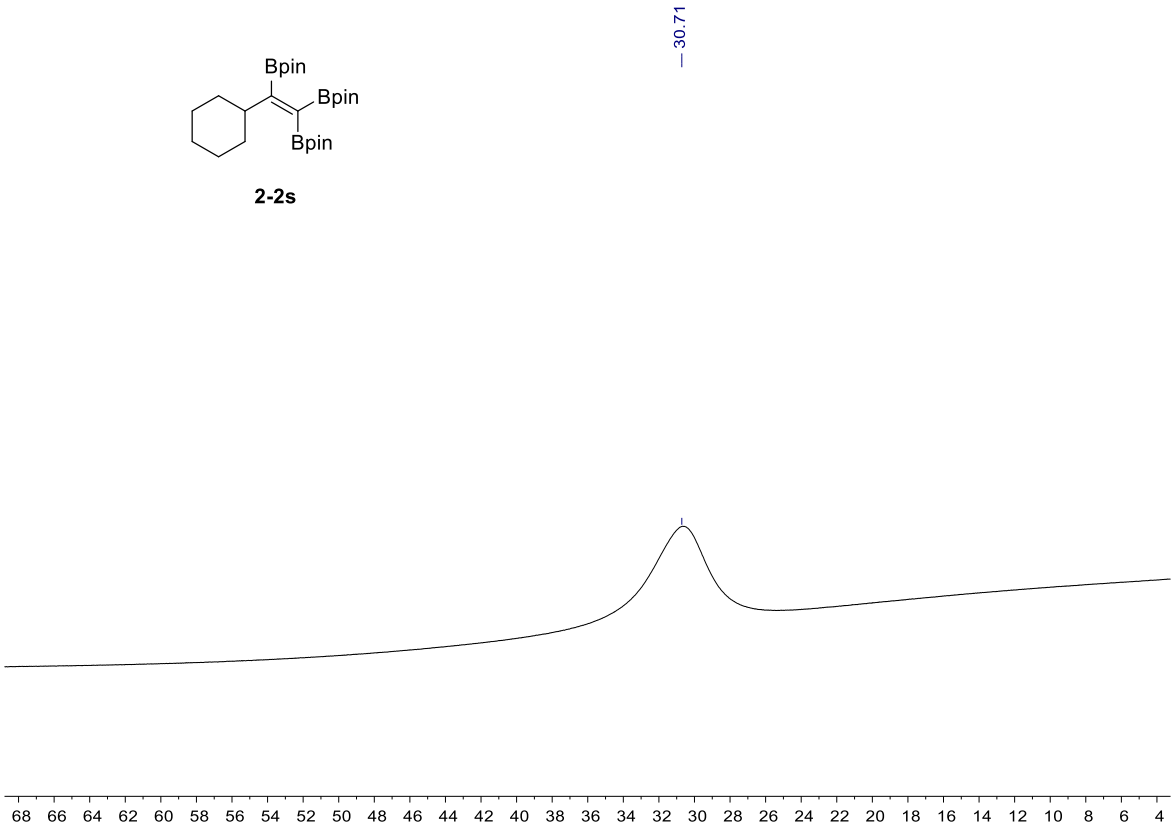
2-2s

$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2-2s**



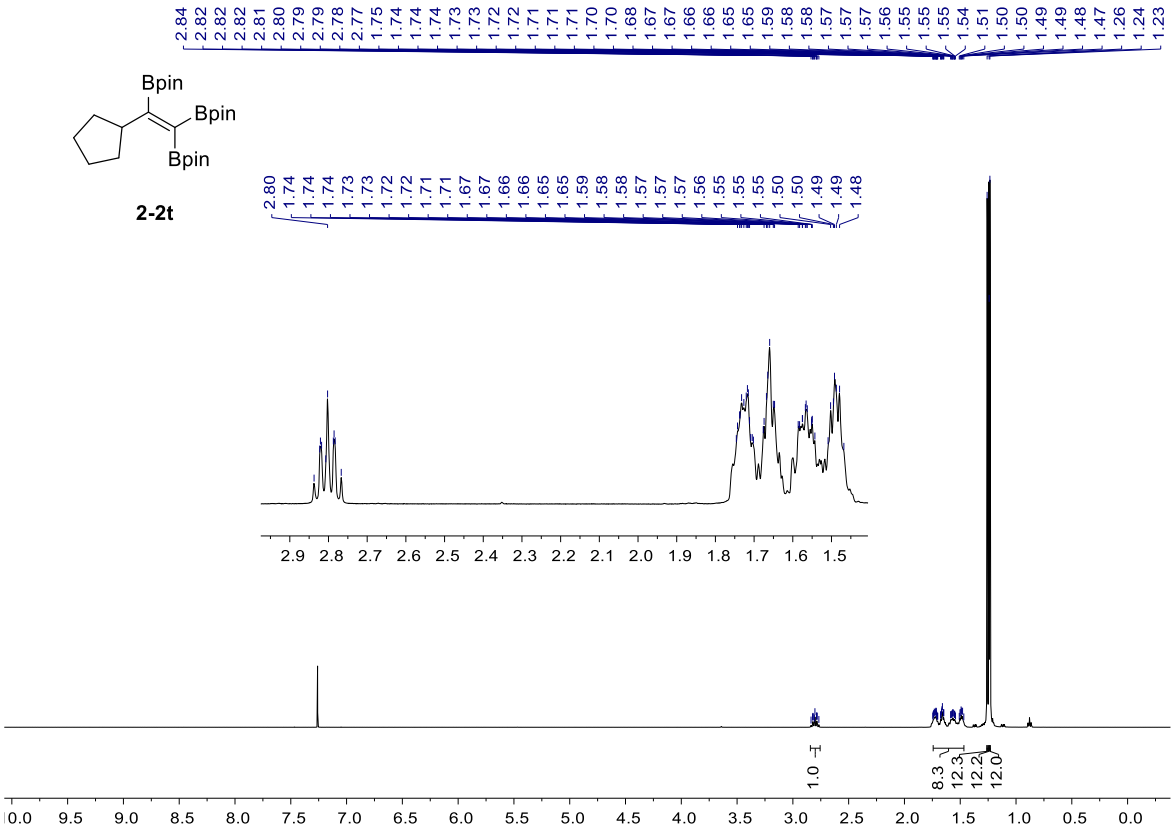
2-2s

^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2s**

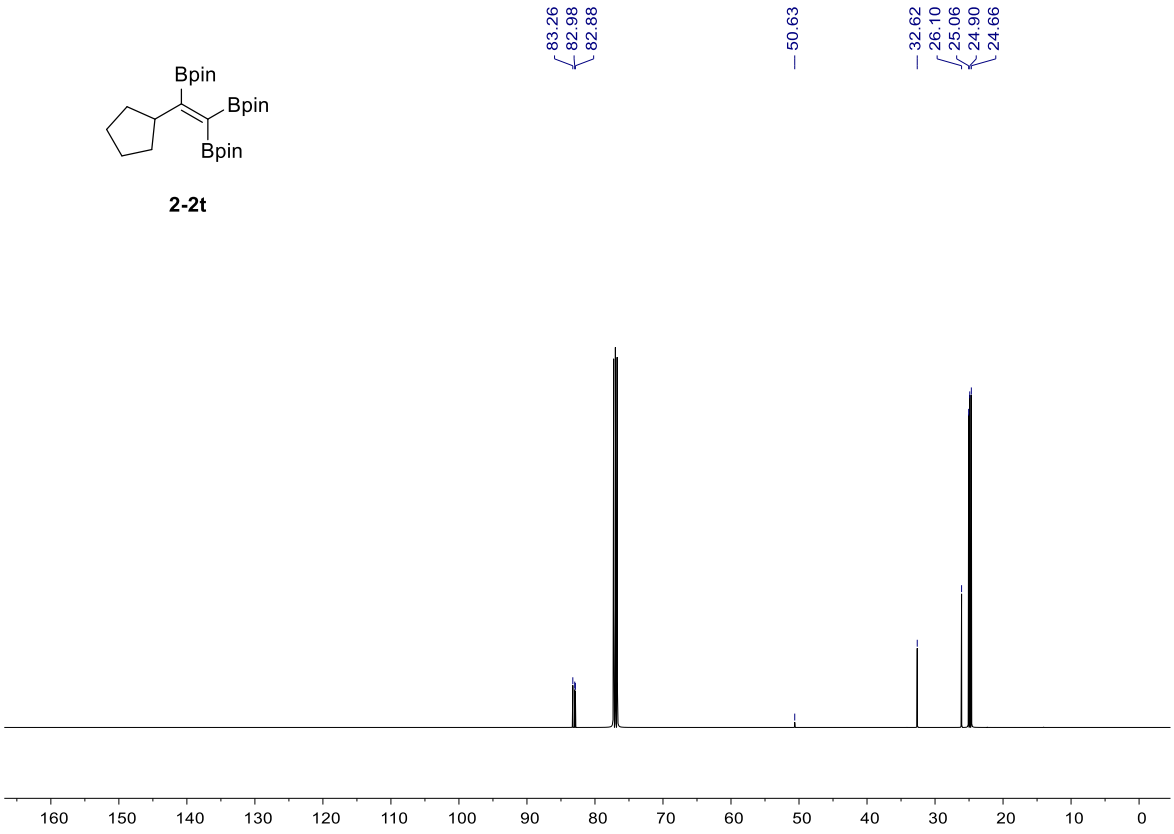


2-2s

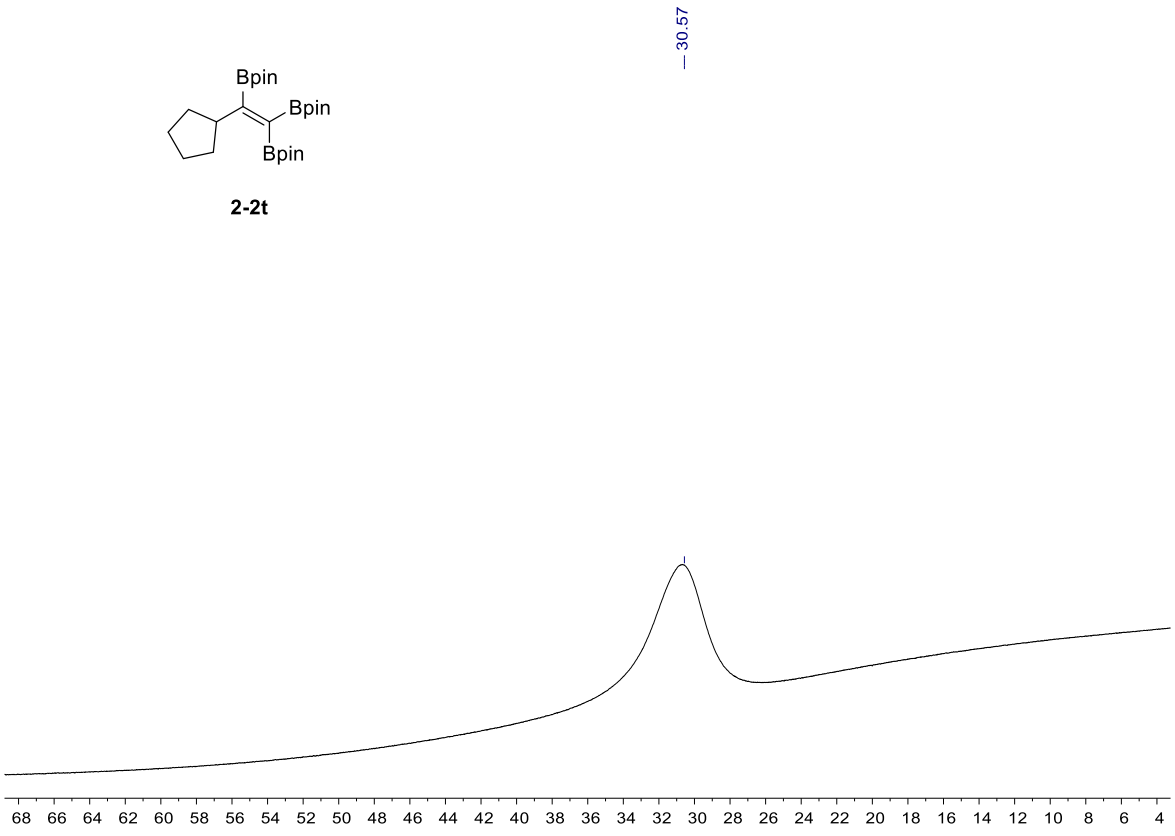
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2t**



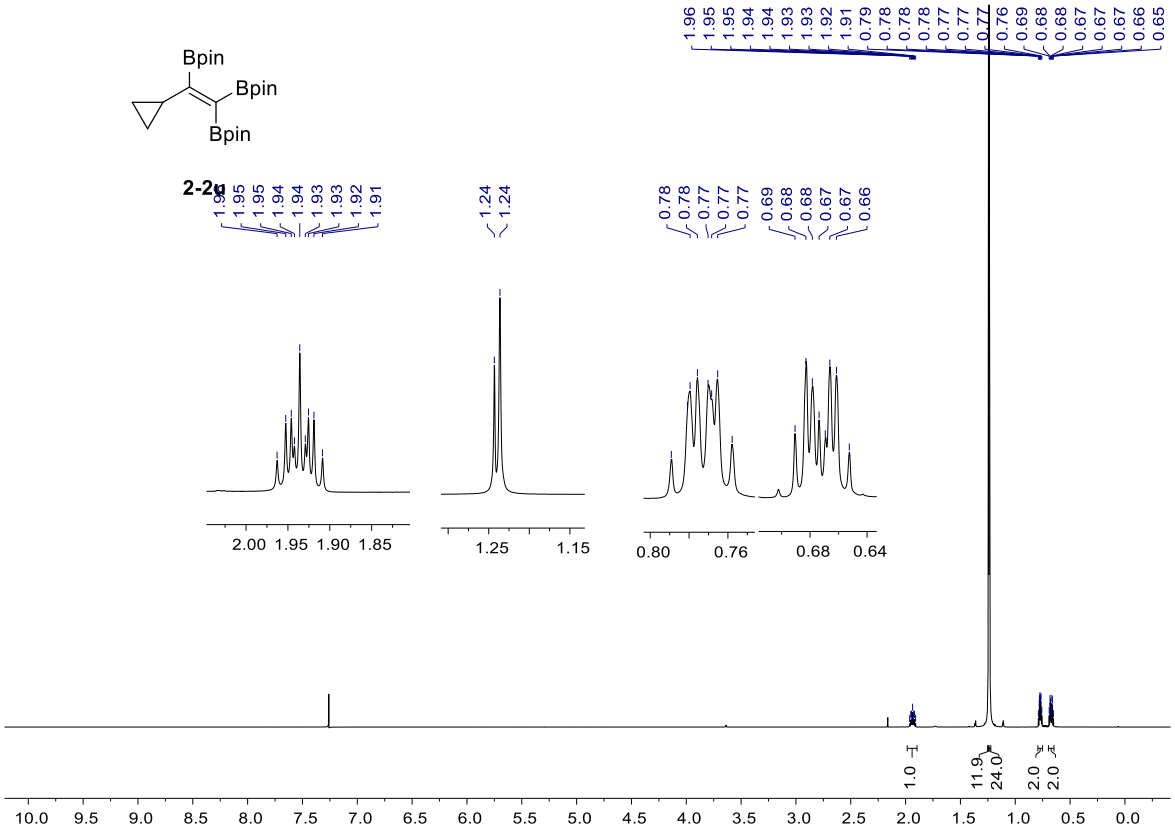
^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2-2t**



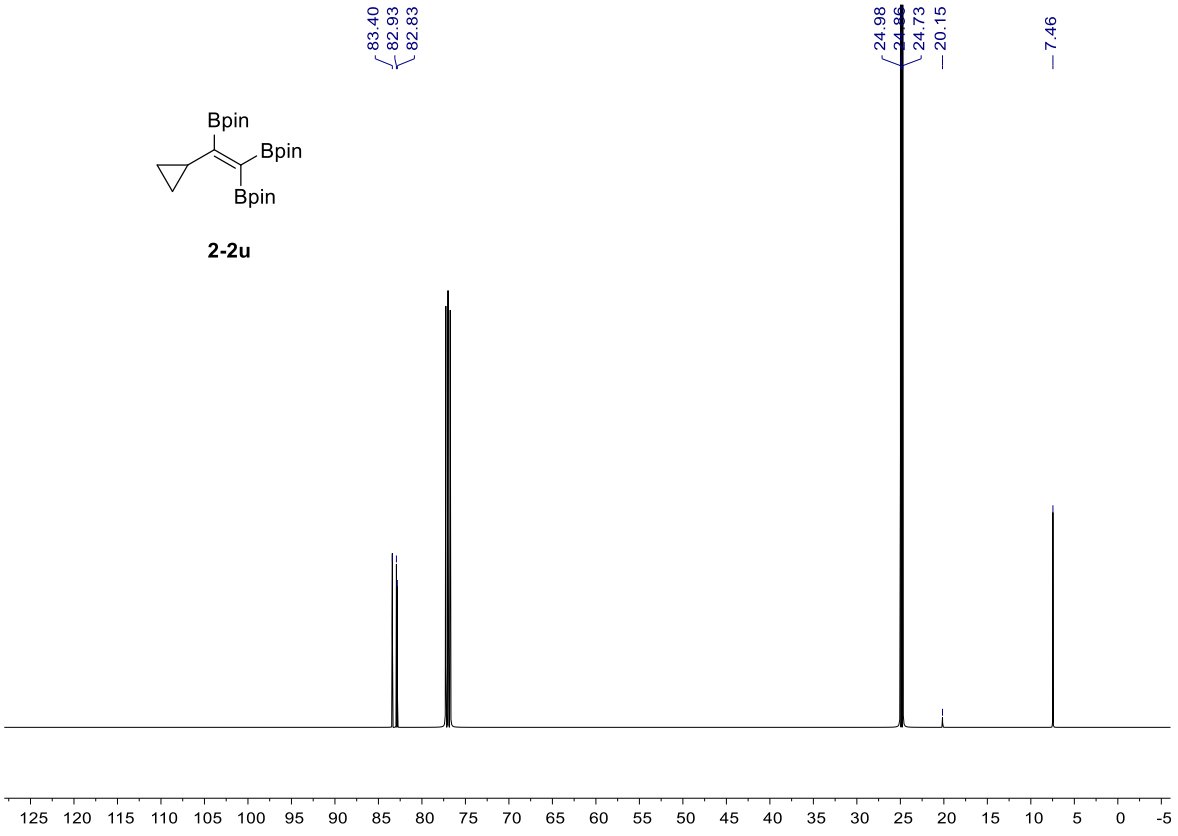
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2t**



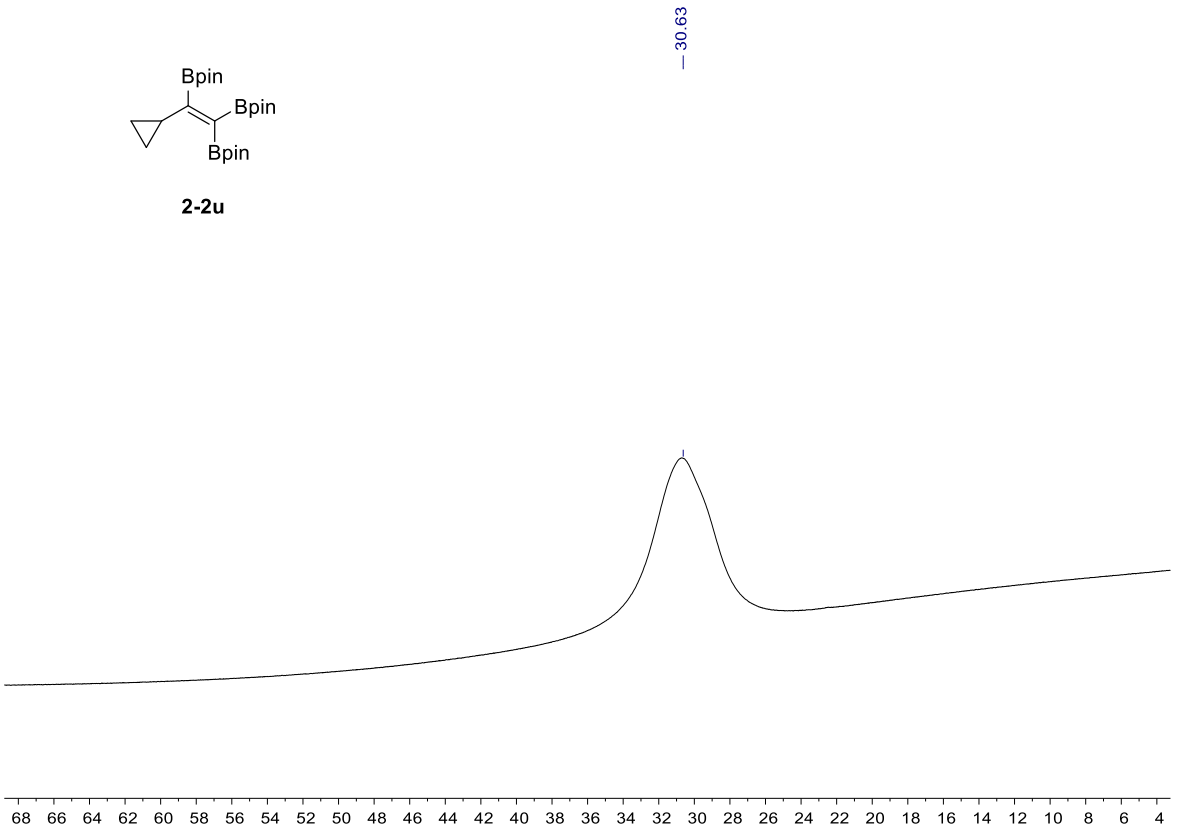
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2u**



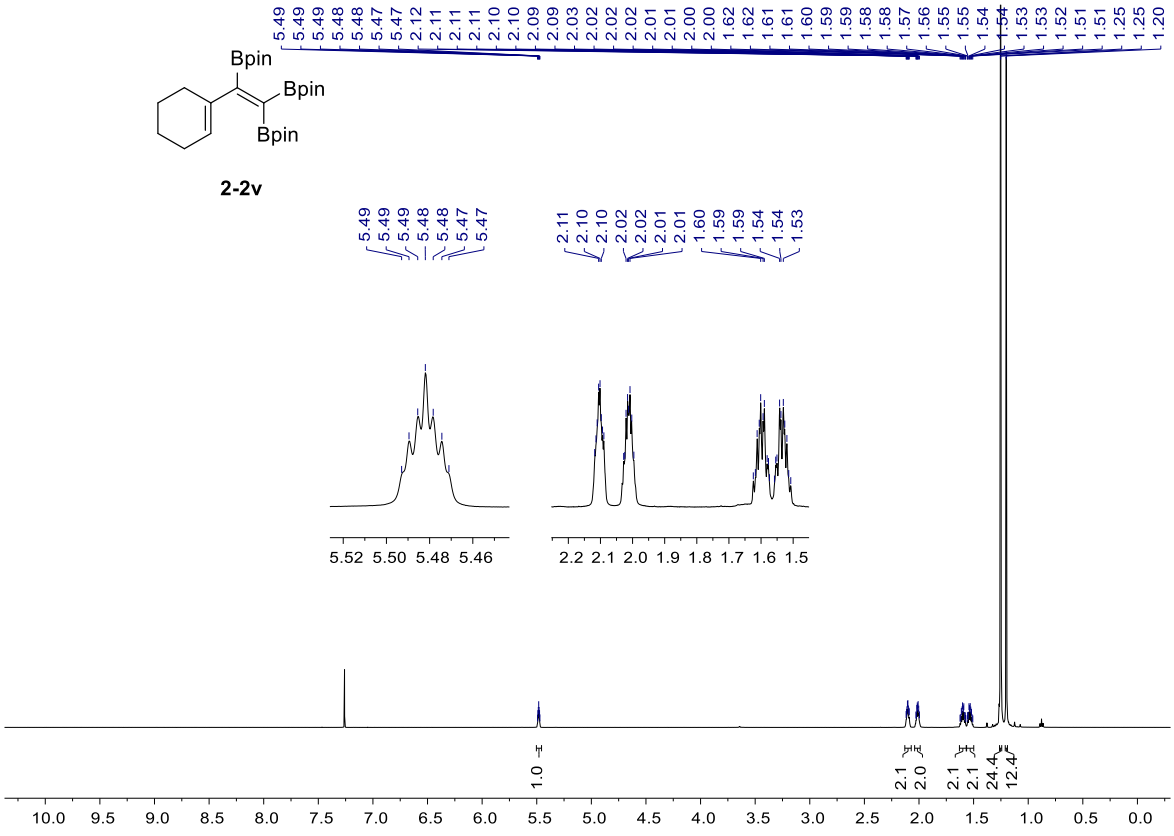
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2-2u**



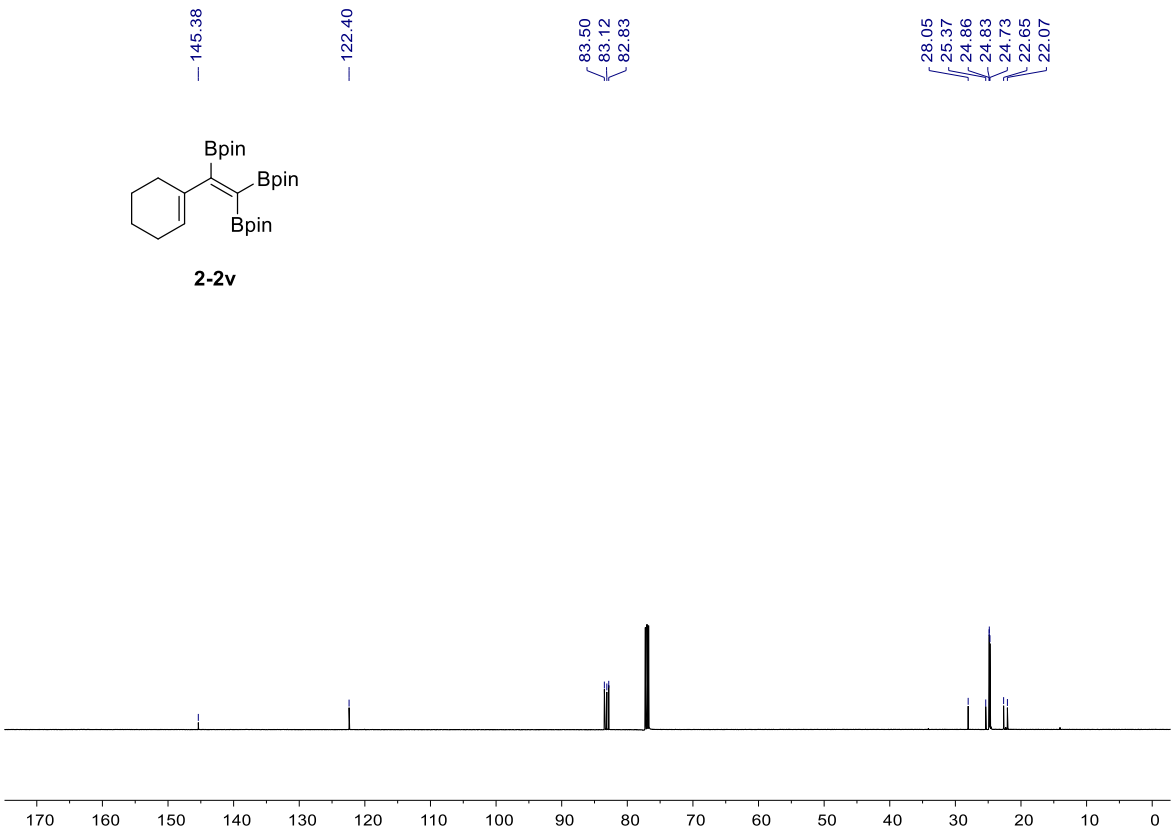
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2u**



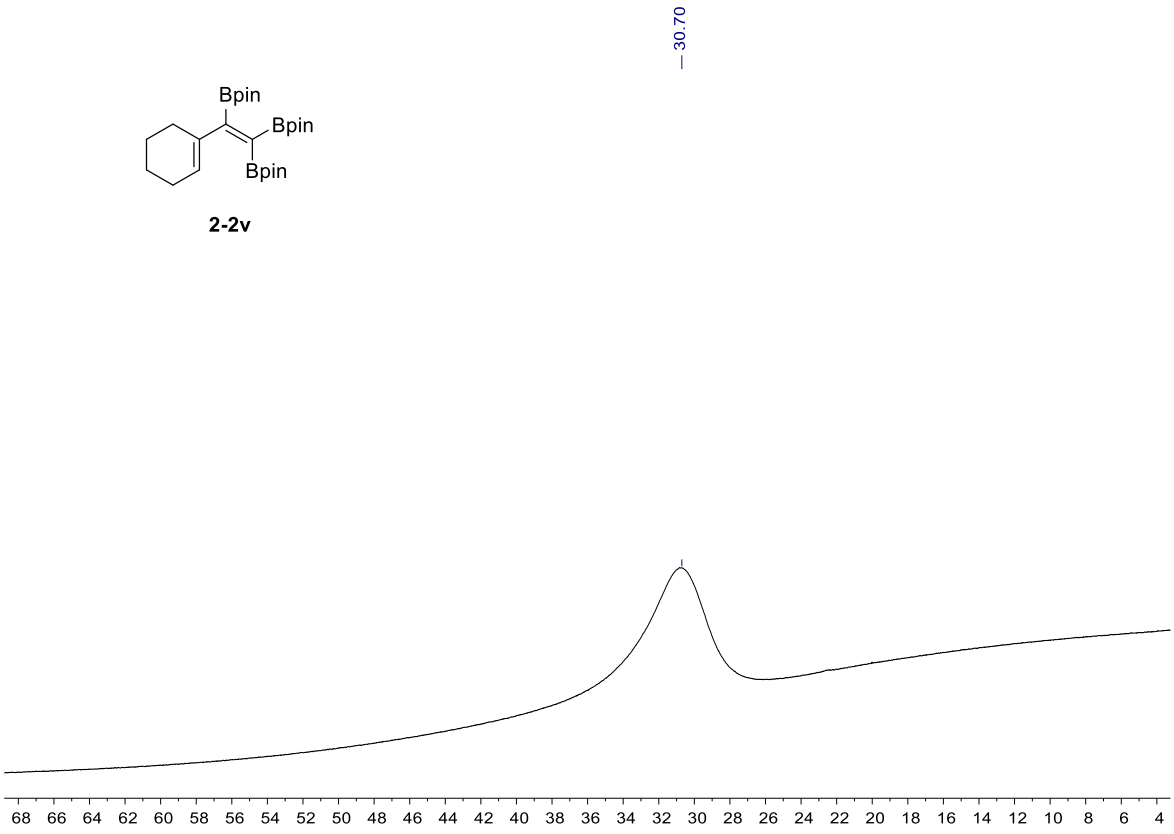
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-2v**



^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2-2v**

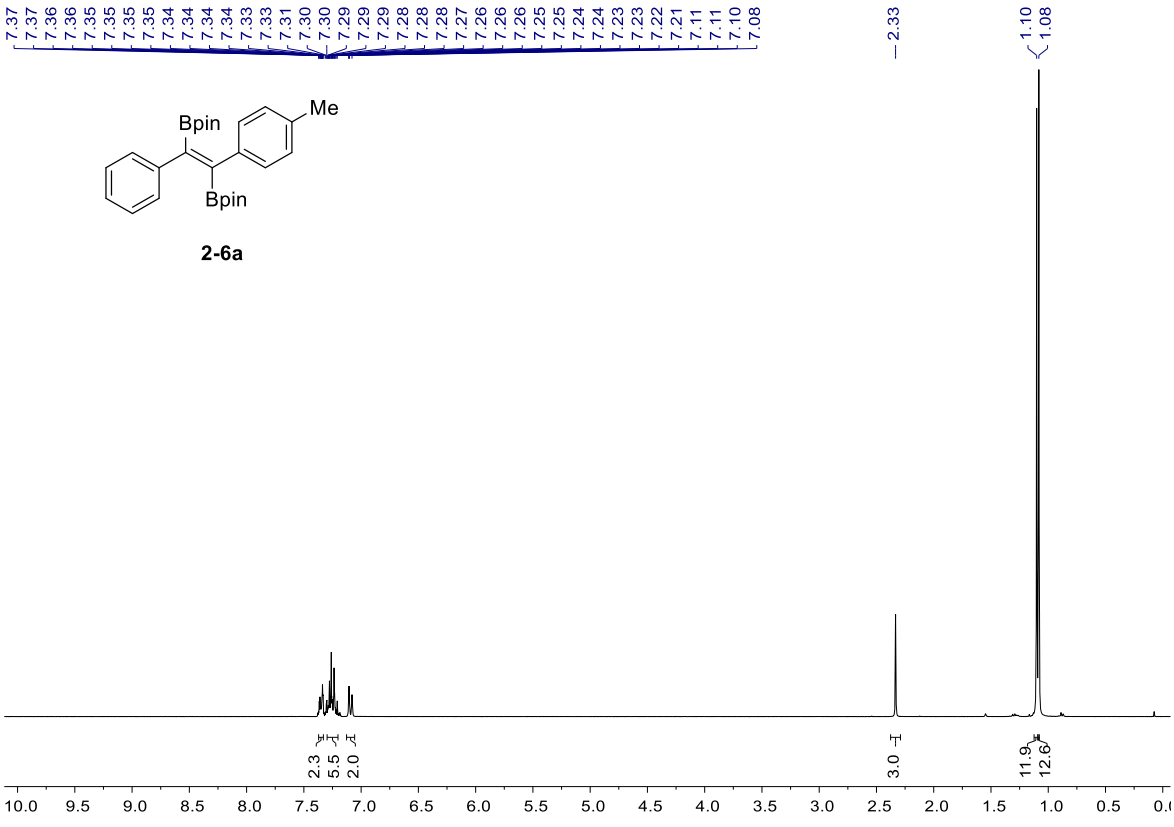


^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-2v**



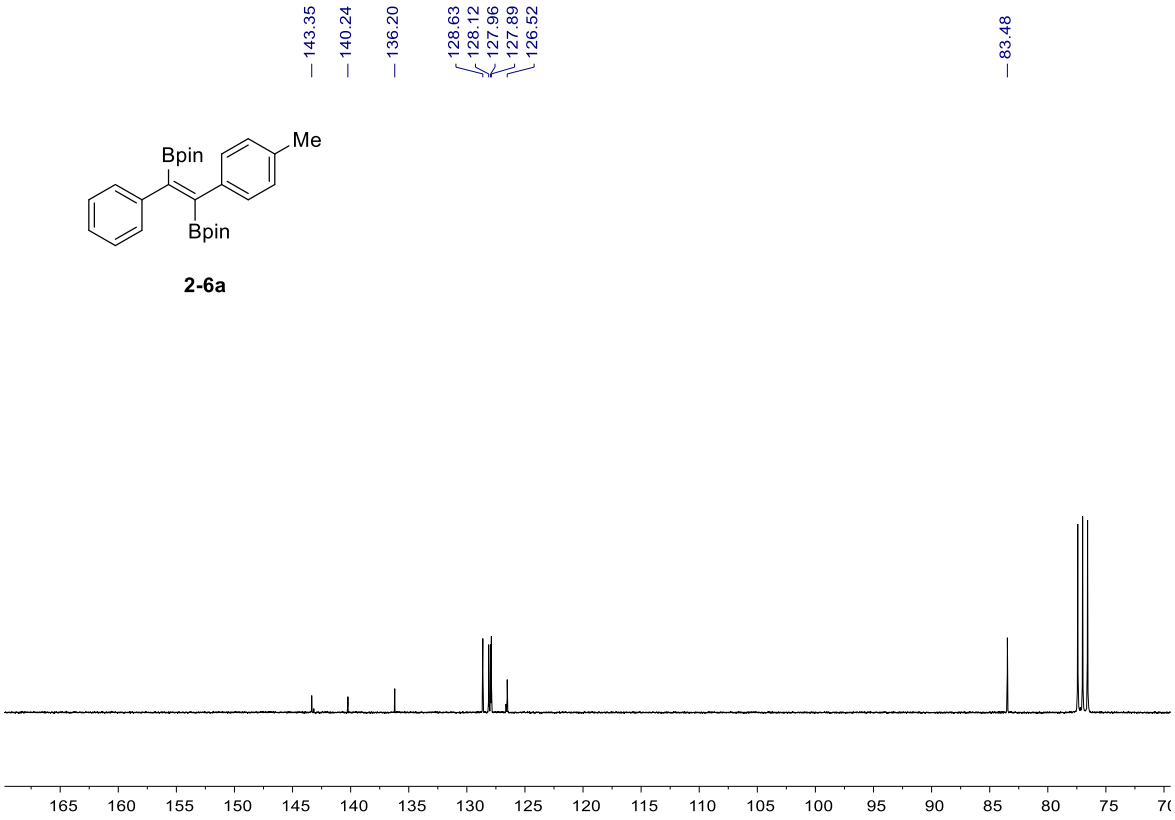
2-2v

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2-6a**

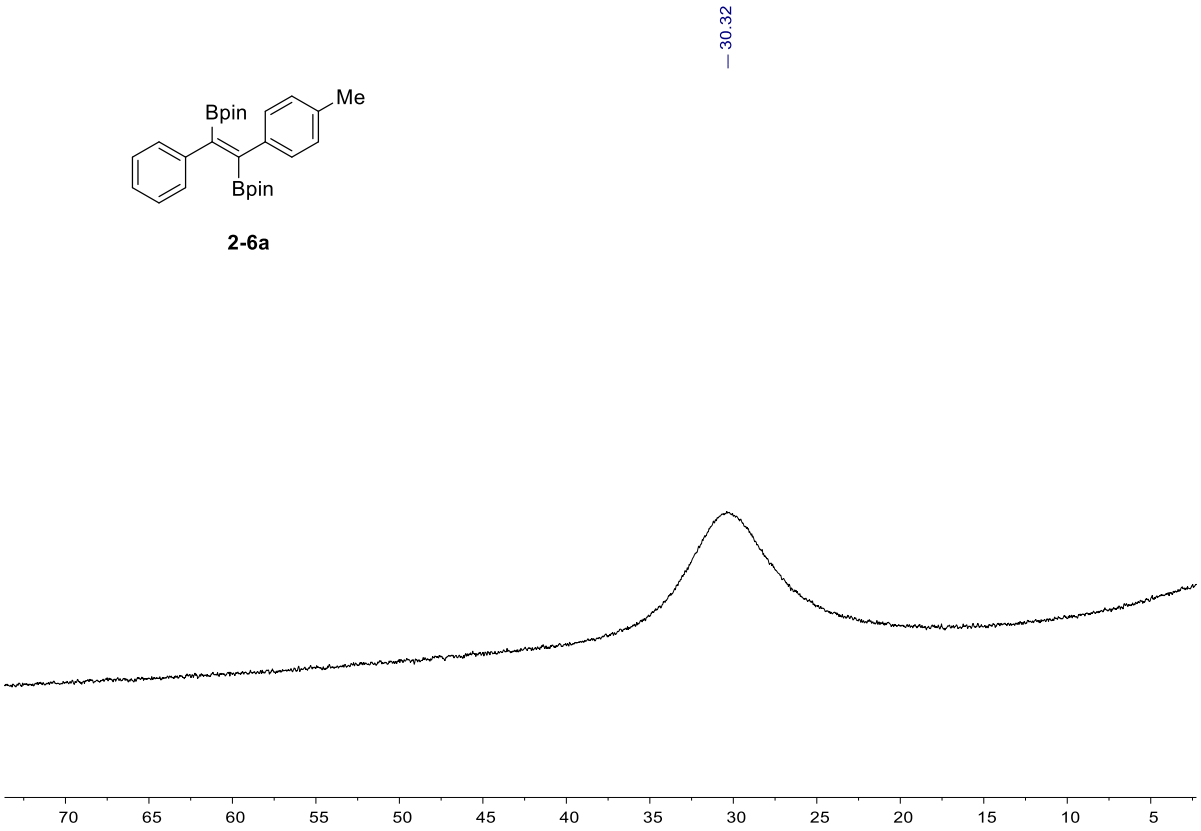


2-6a

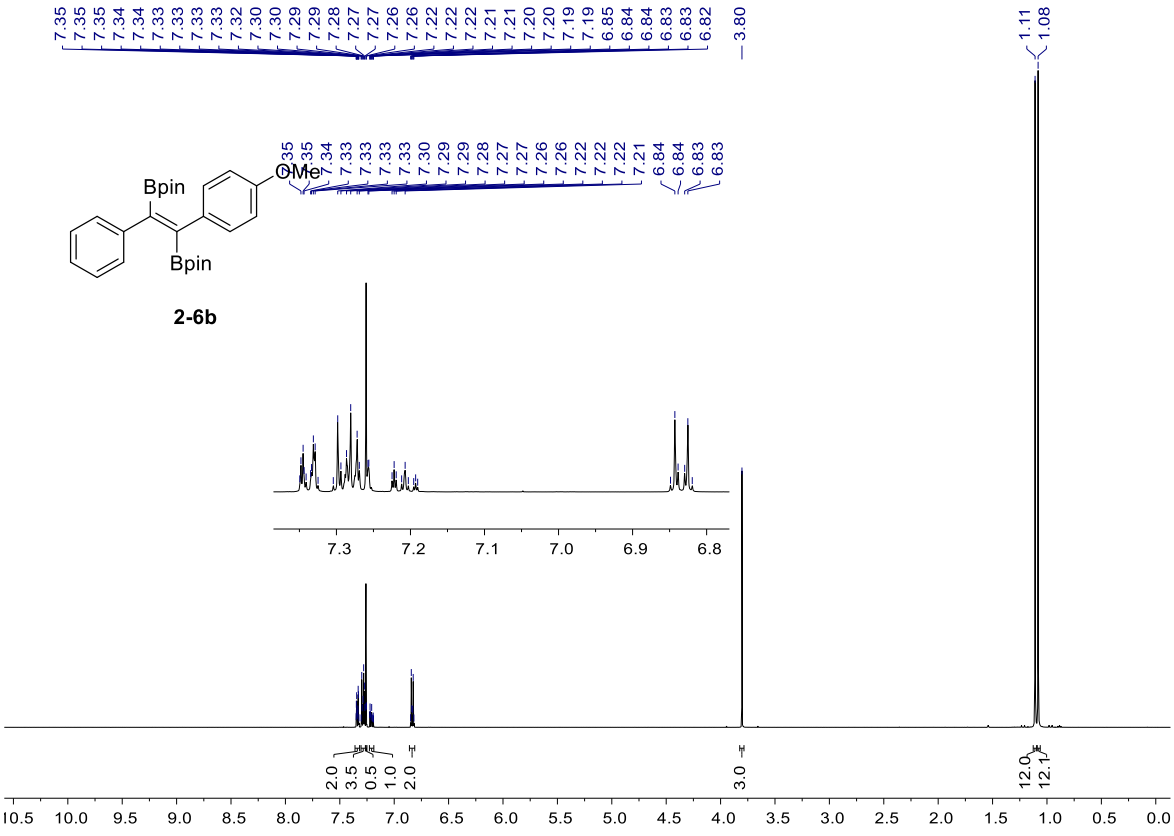
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **2-6a**



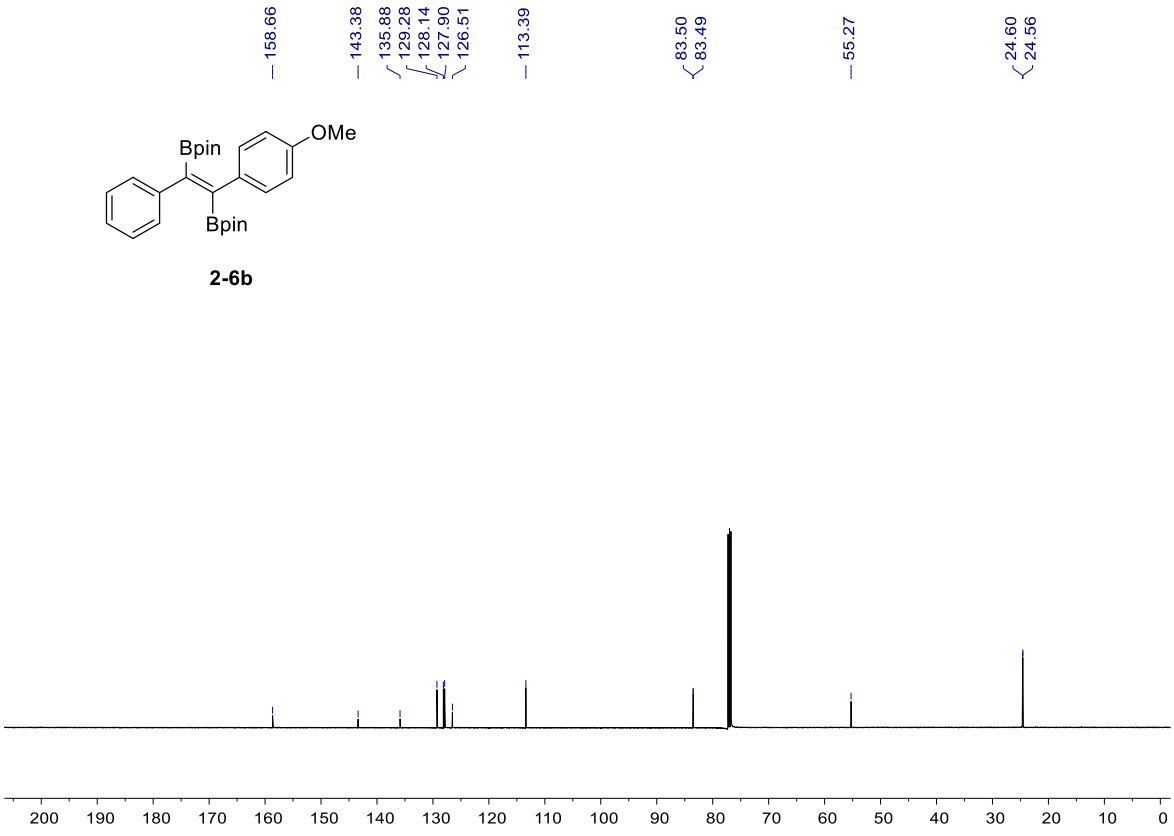
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **2-6a**



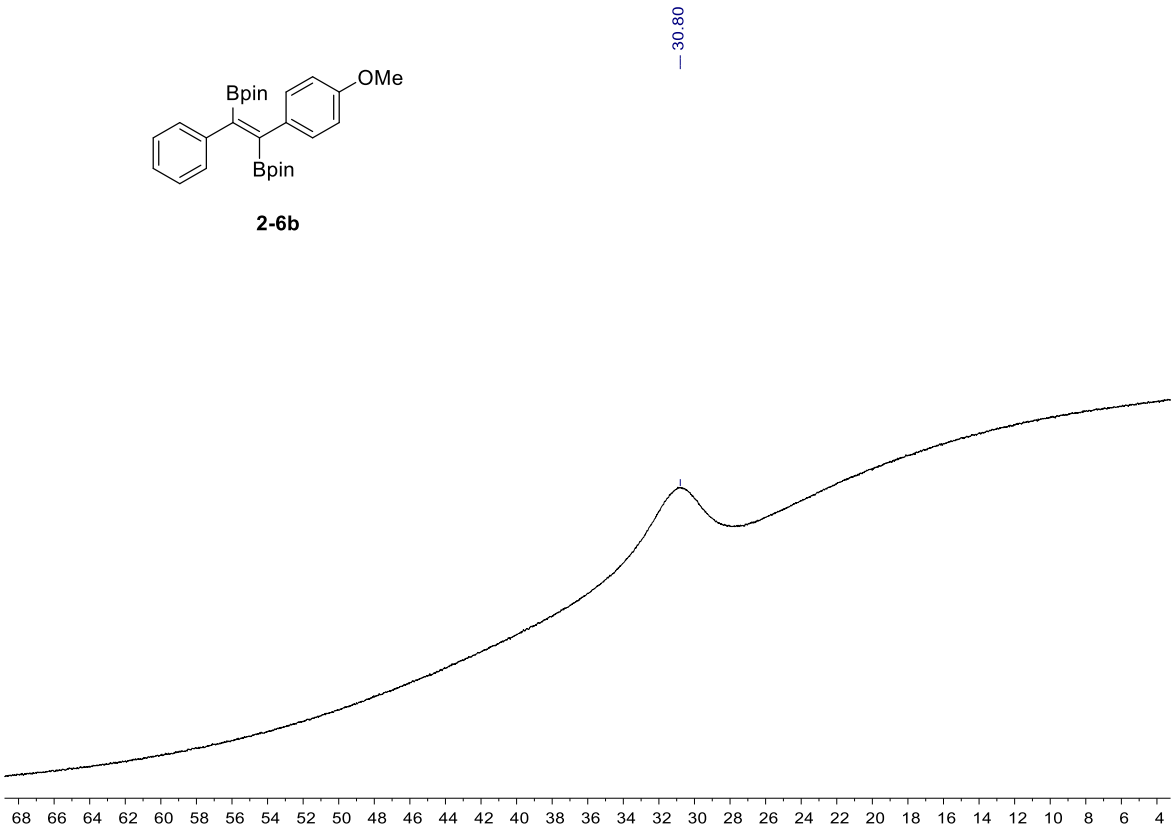
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-6b**



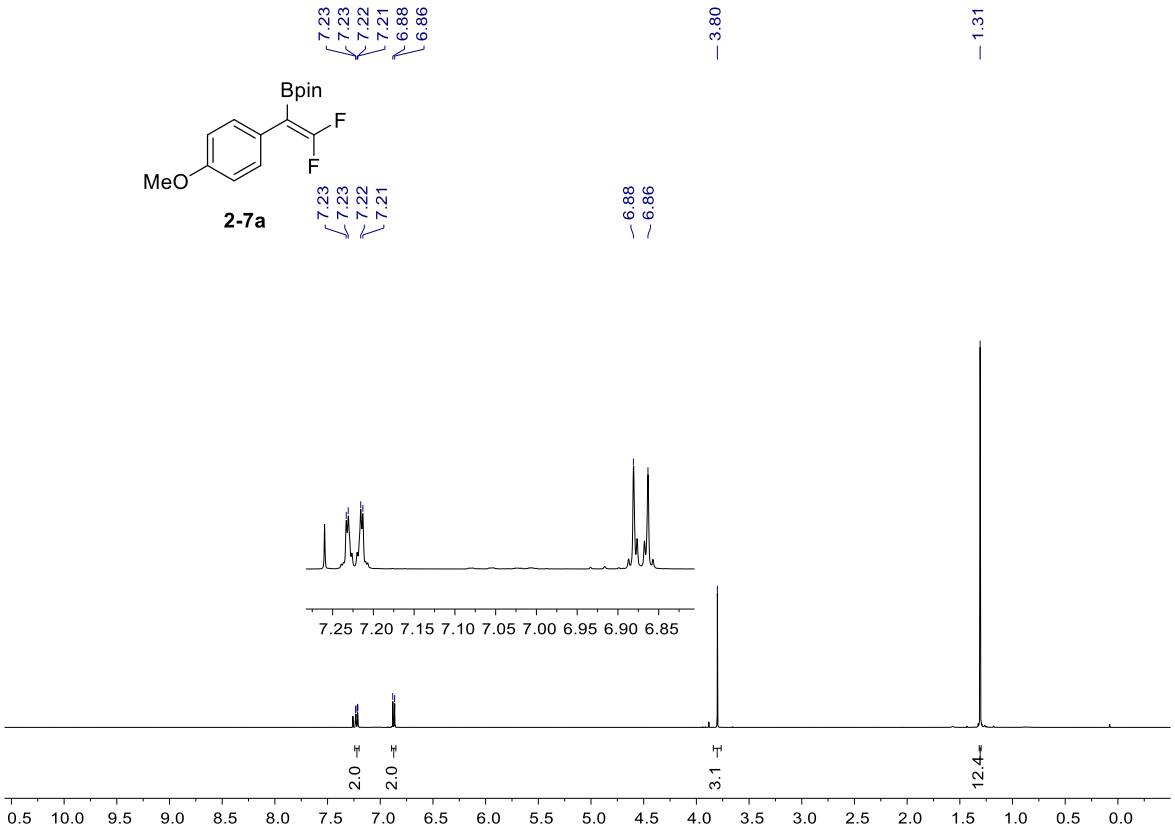
^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2-6b**



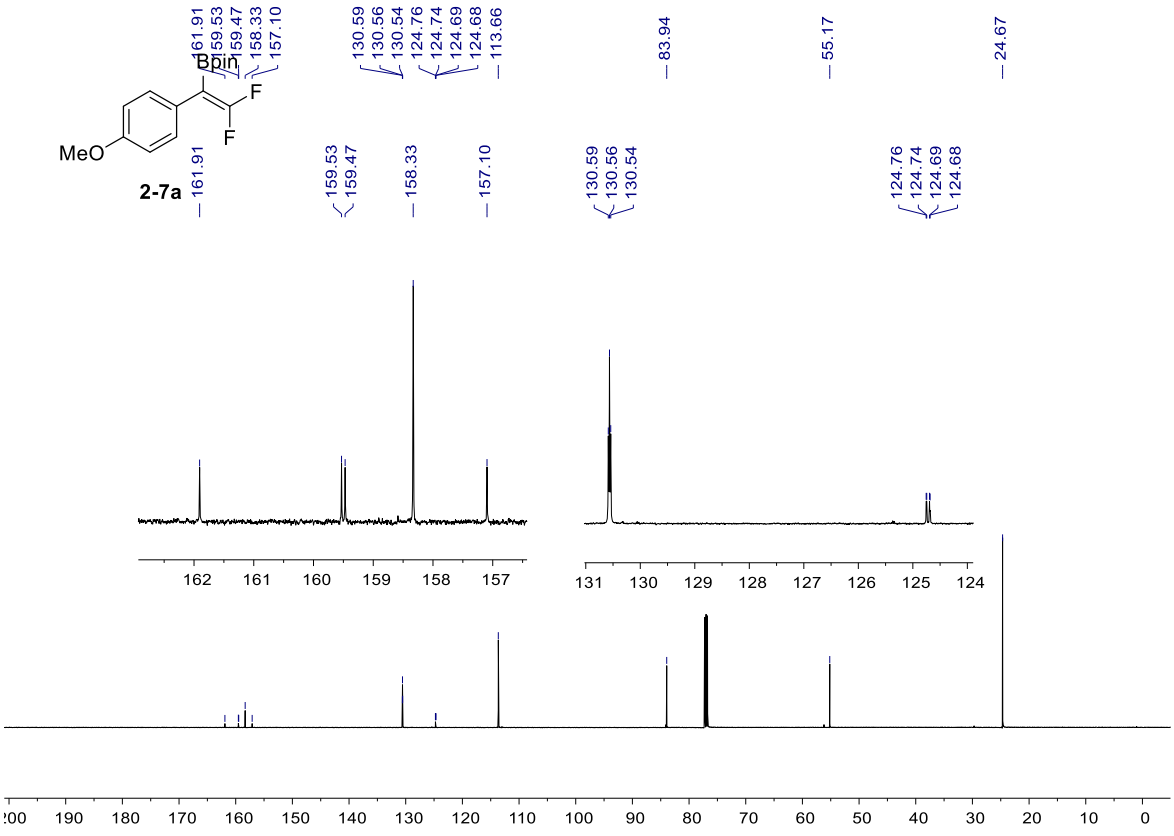
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-6b**



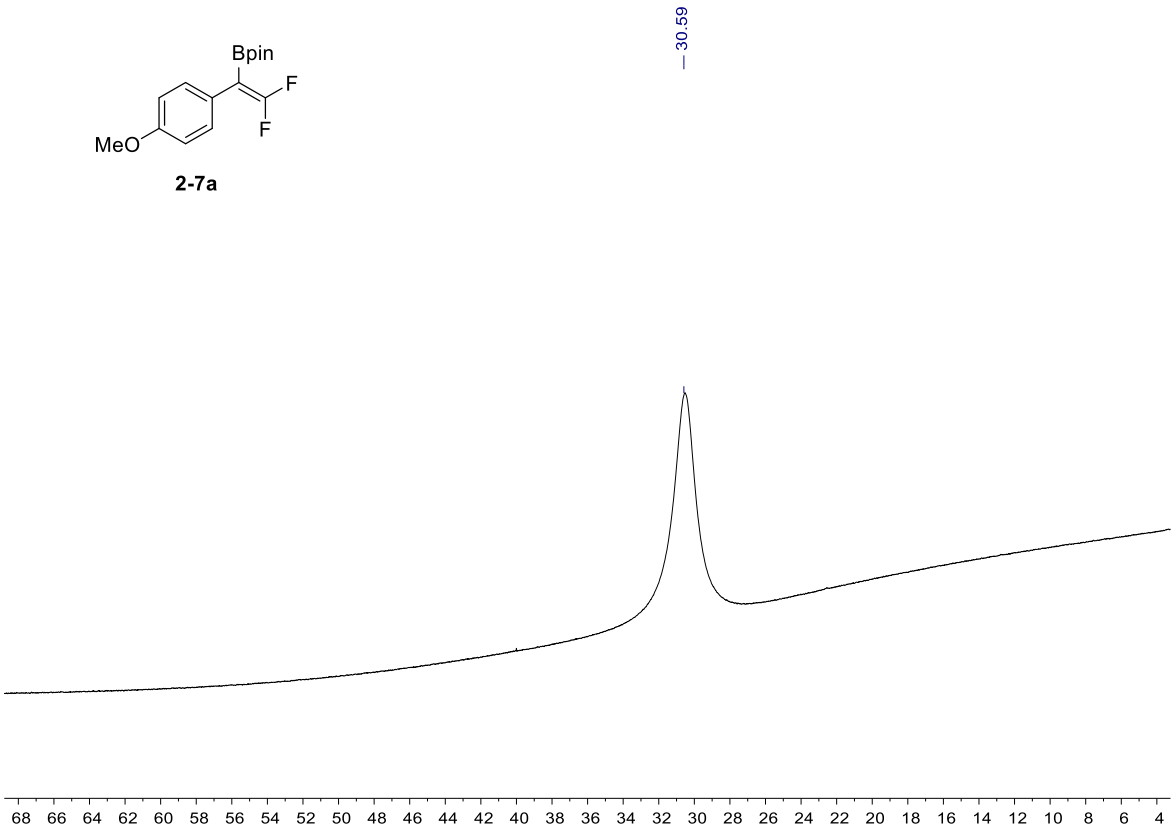
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-7a**



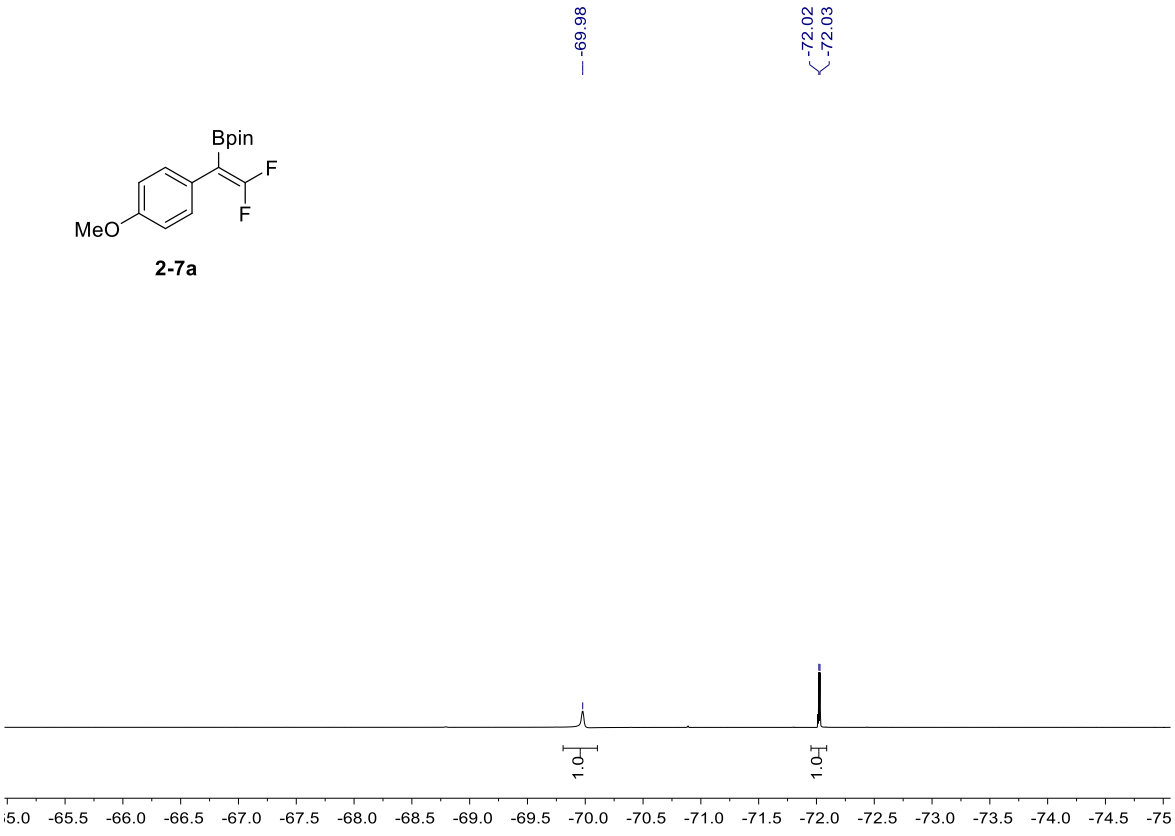
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2-7a**



^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-7a**

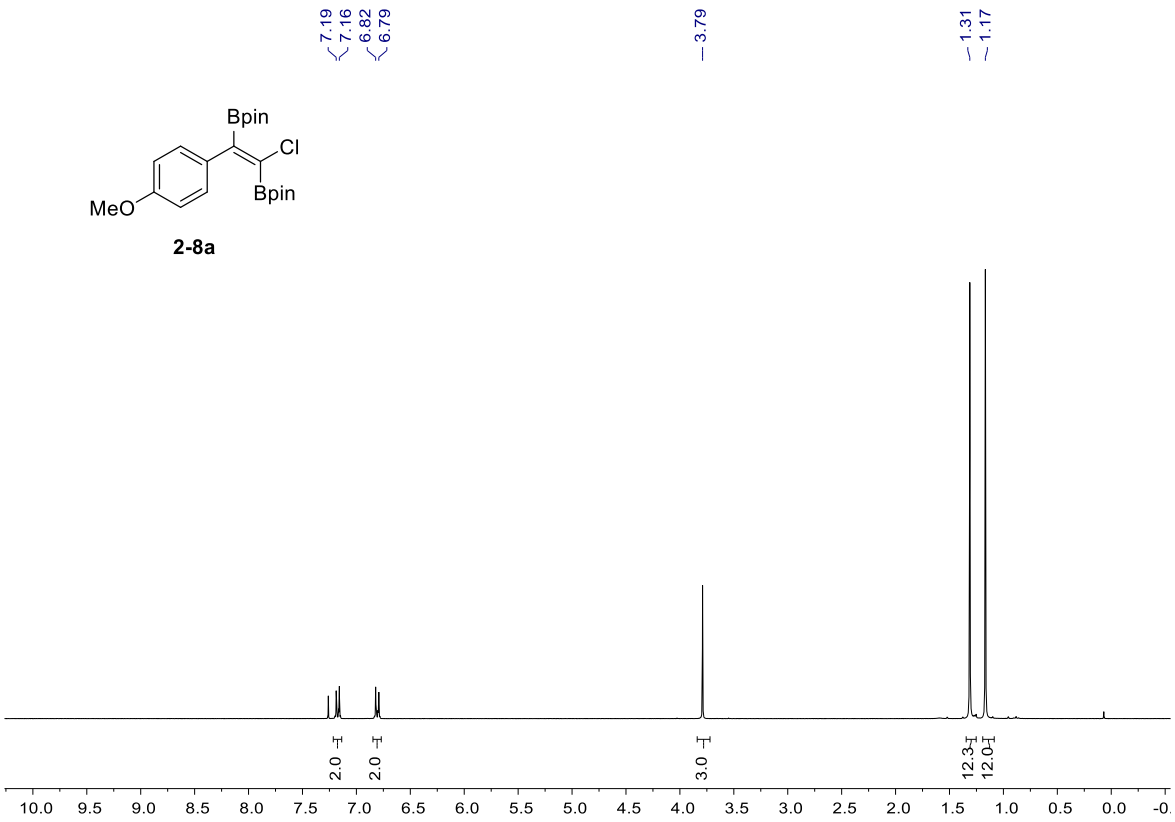


^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **2-7a**



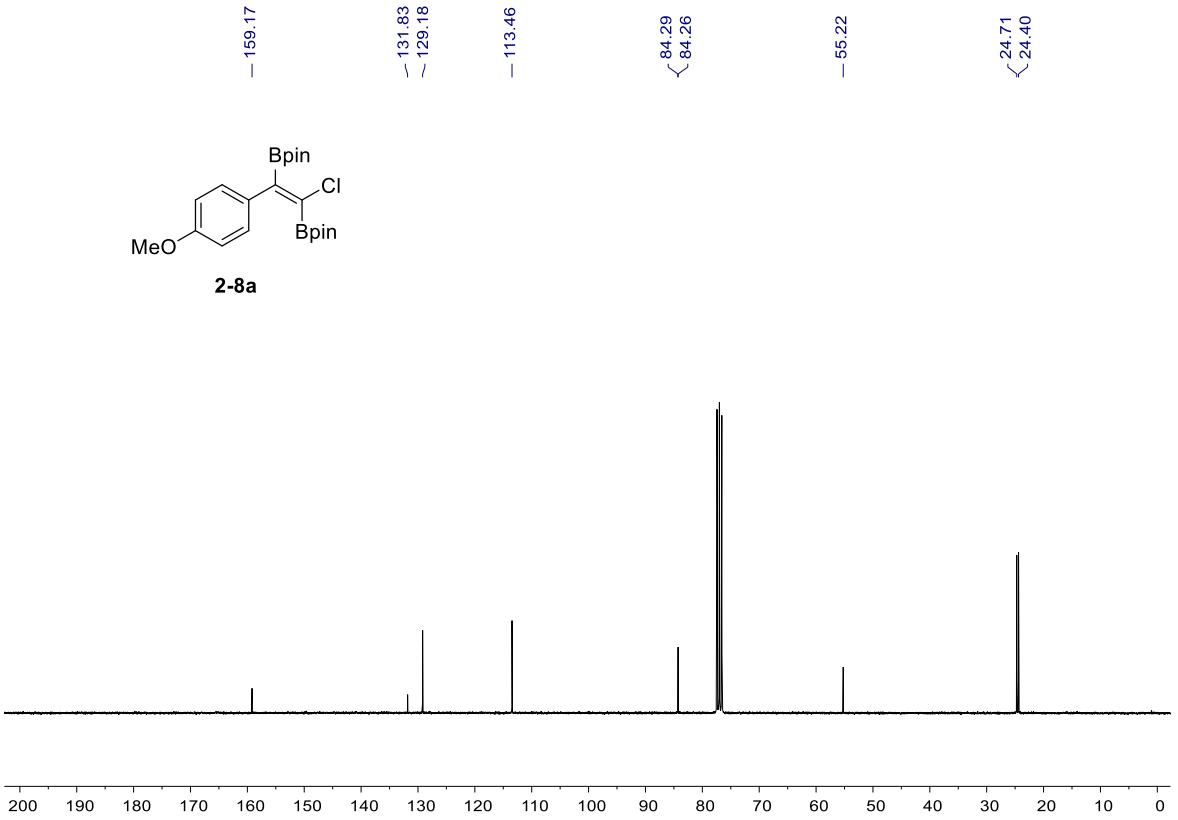
2-7a

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2-8a**

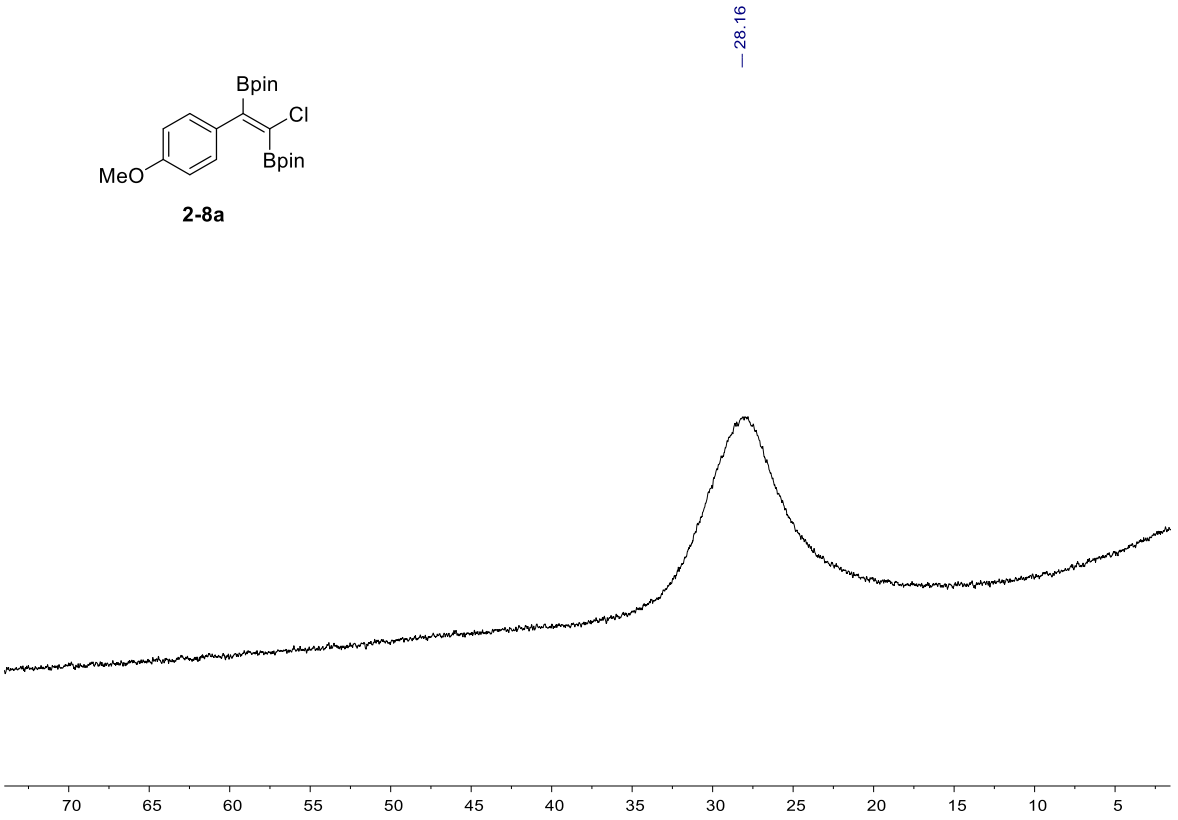


2-8a

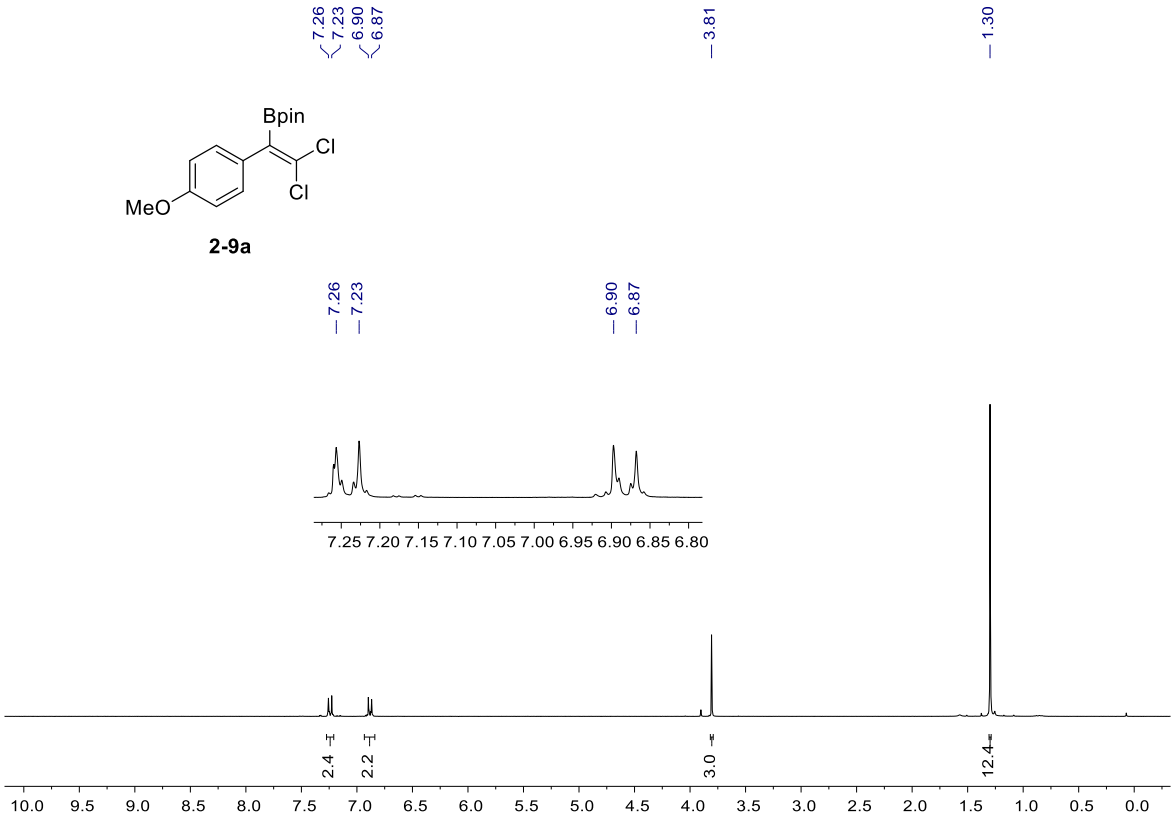
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **2-8a**



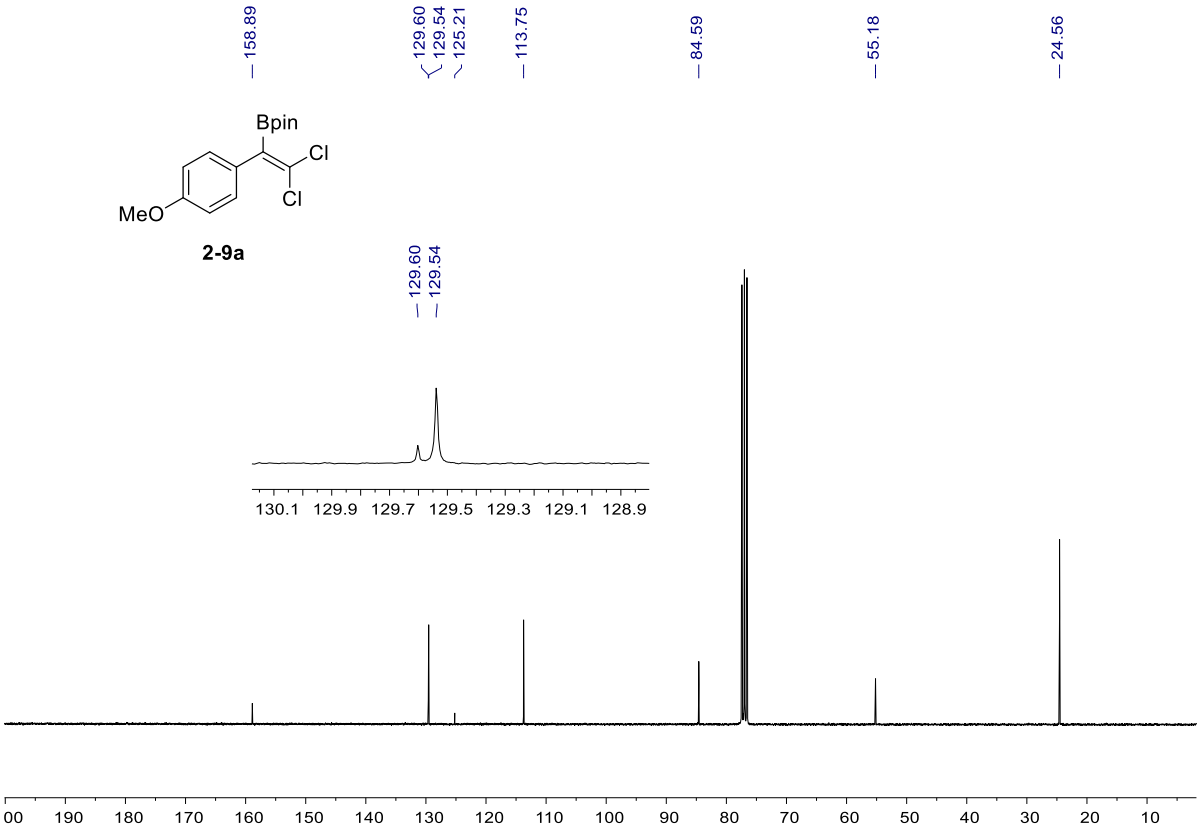
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **2-8a**



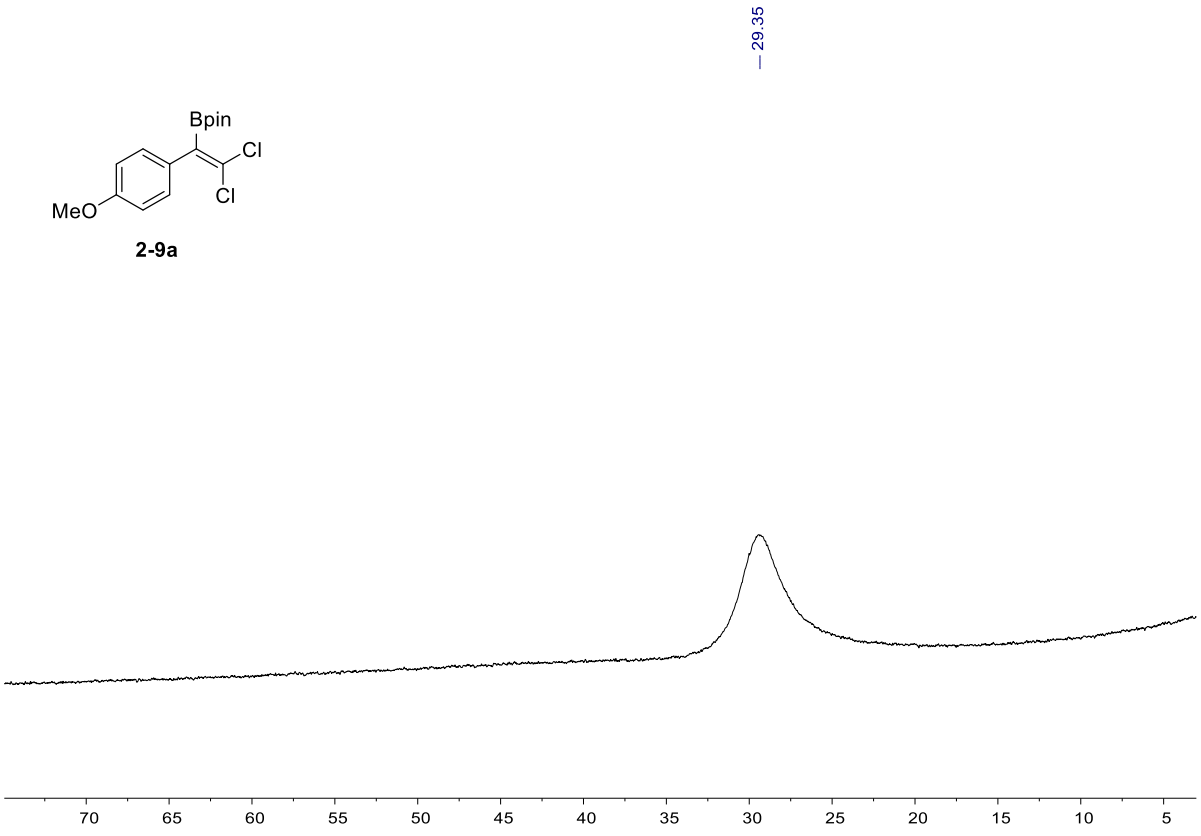
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2-9a**



^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **2-9a**

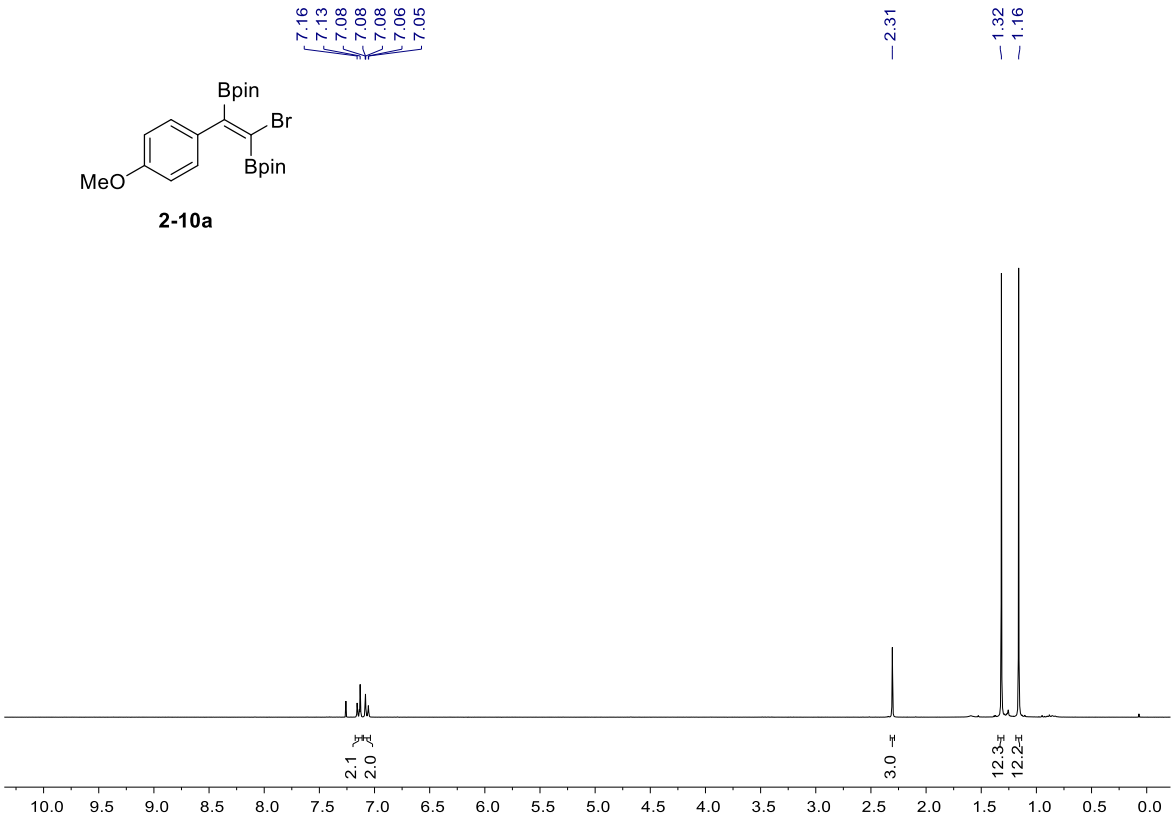


^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **2-9a**



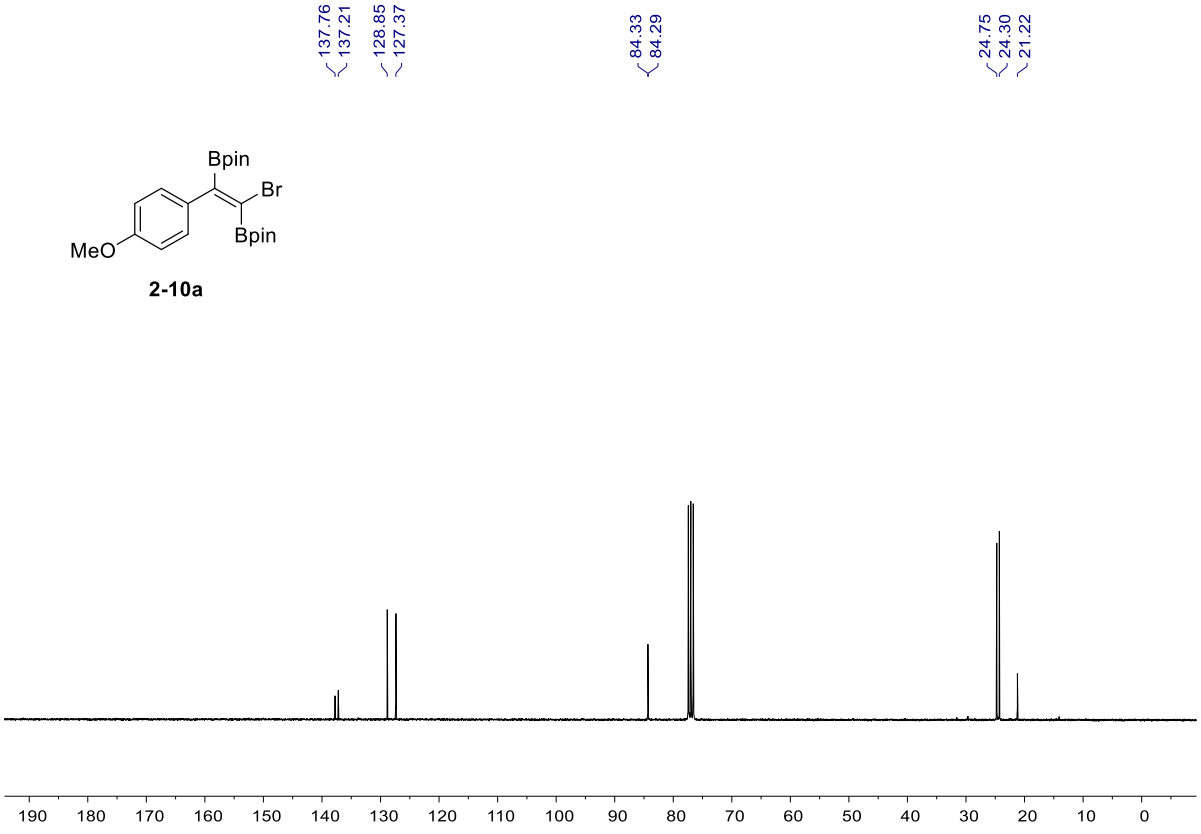
2-9a

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2-10a**



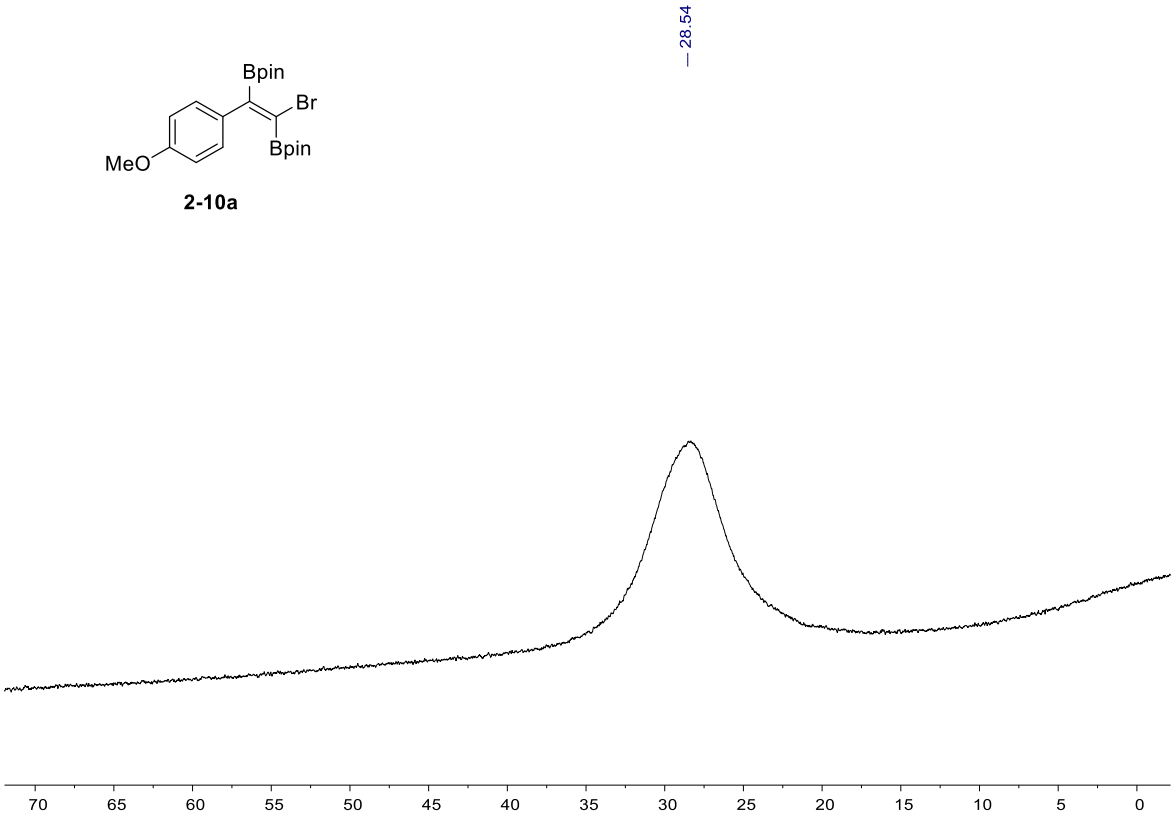
2-10a

$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **2-10a**



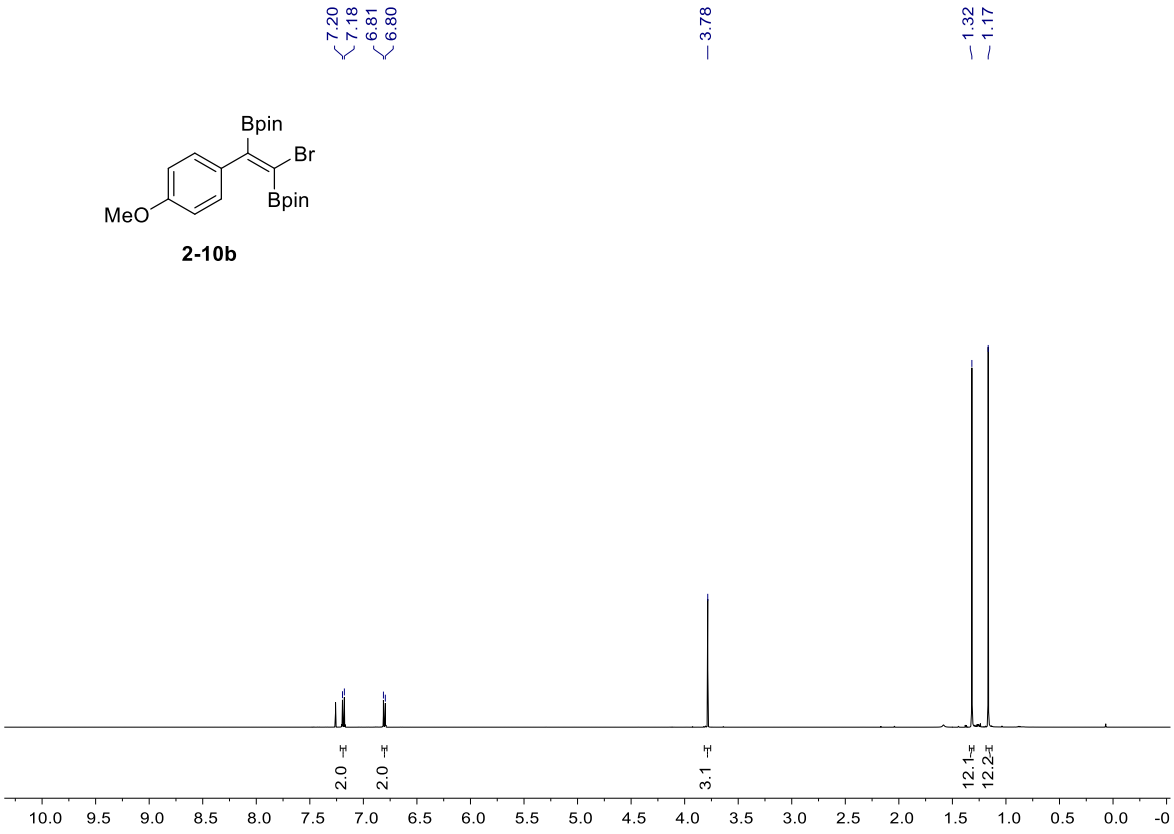
2-10a

^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **2-10a**

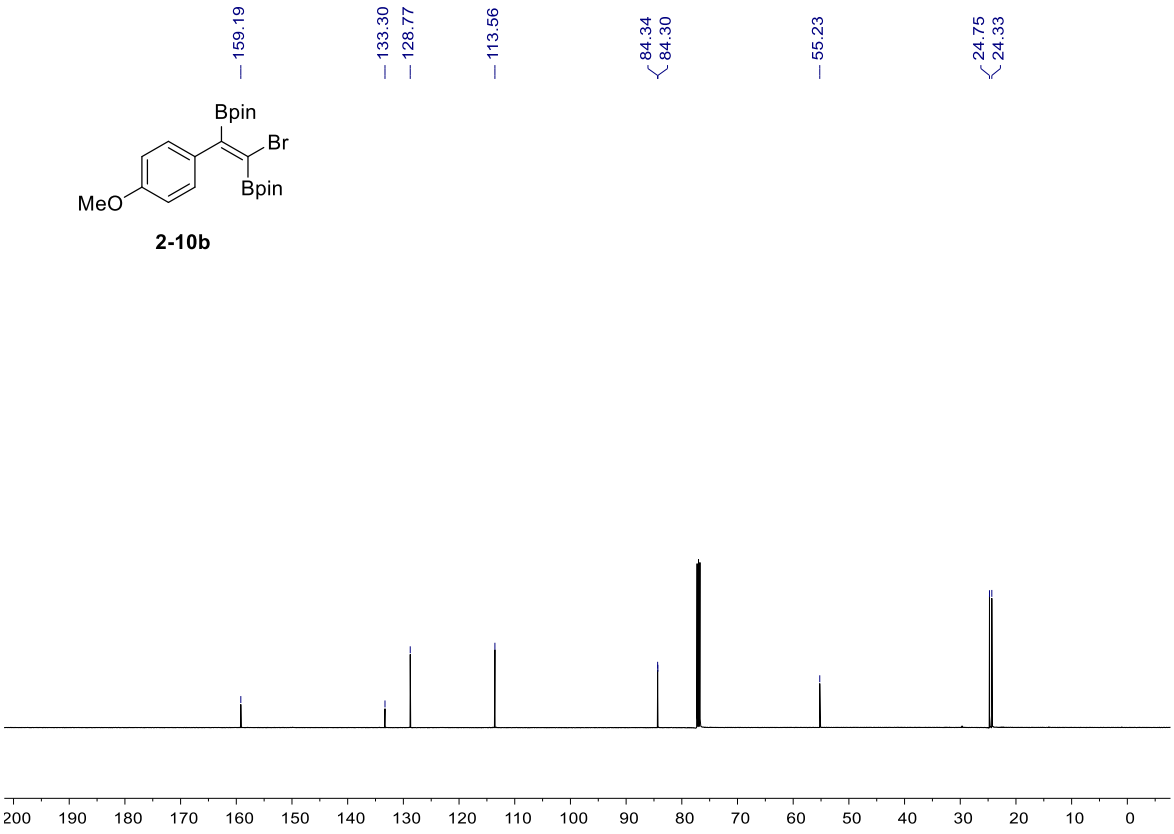


2-10a

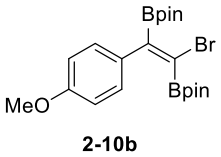
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-10b**



^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2-10b**

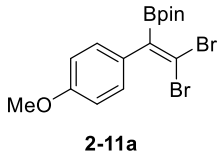


^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-10b**



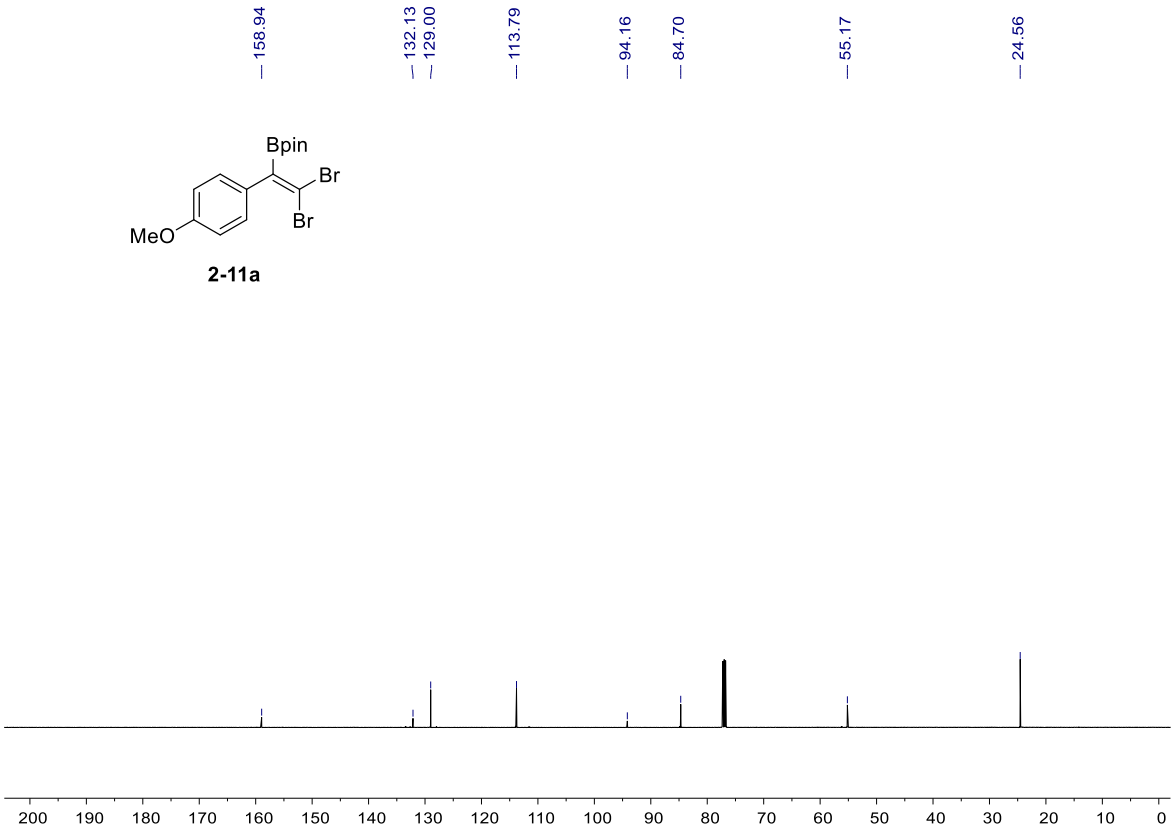
2-10b

^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2-11a**



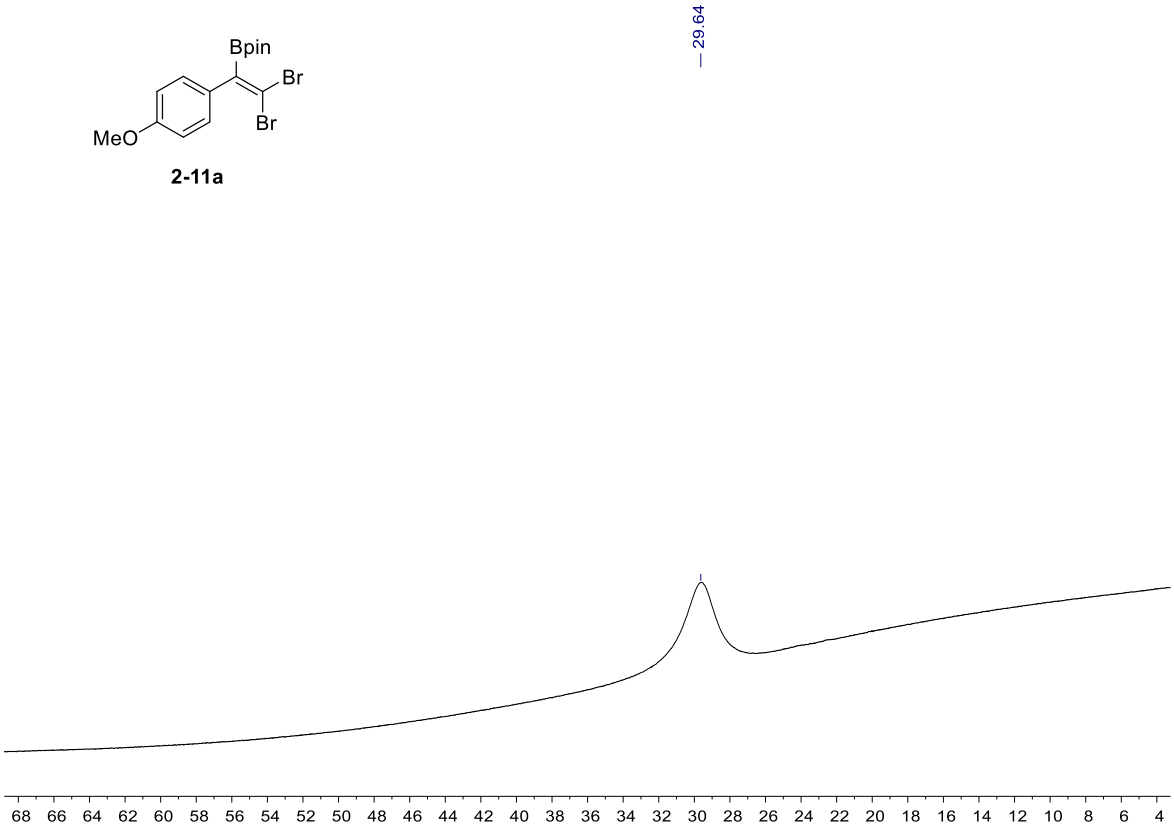
2-11a

$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2-11a**



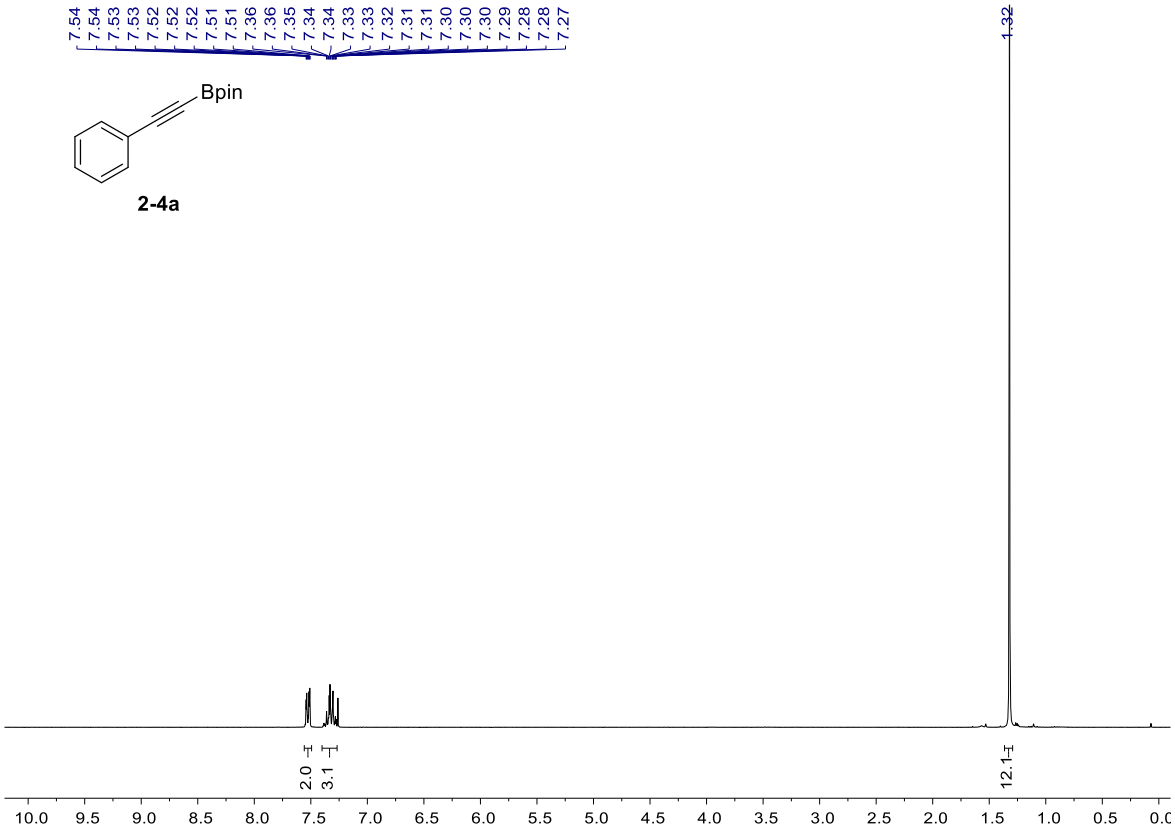
2-11a

^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2-11a**

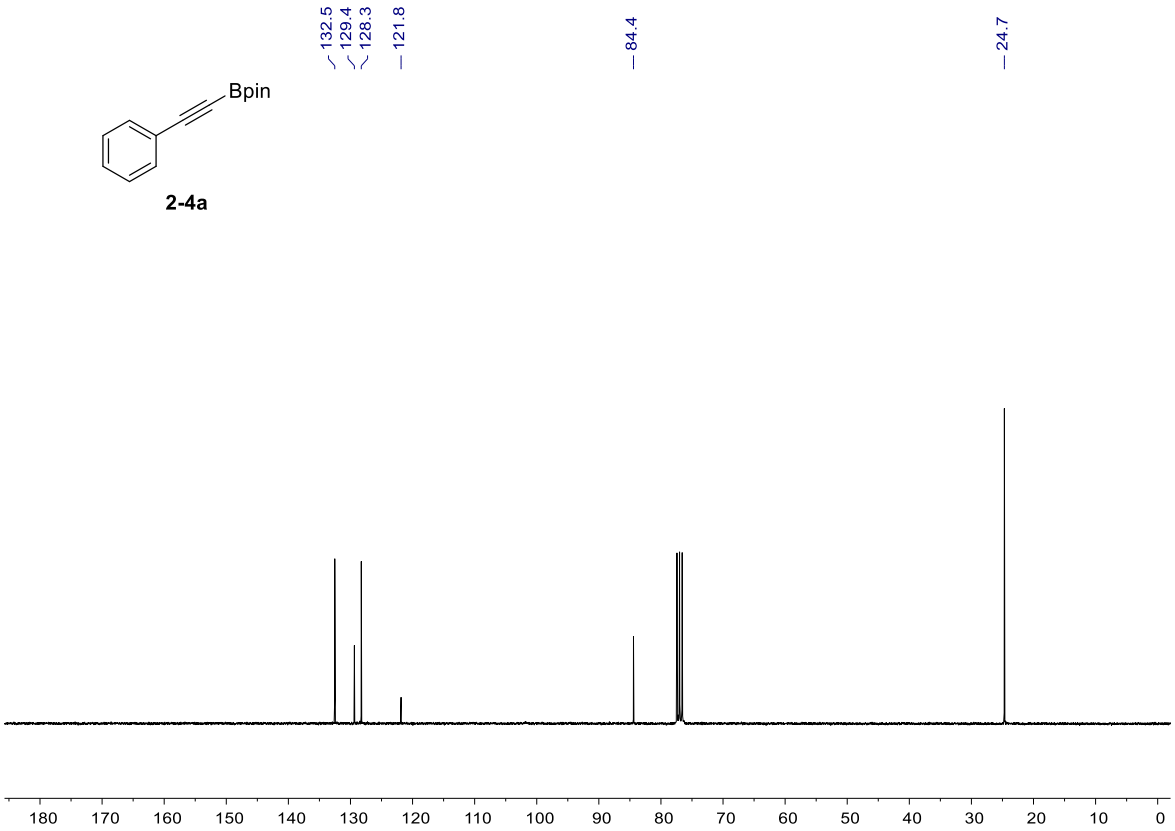


2-11a

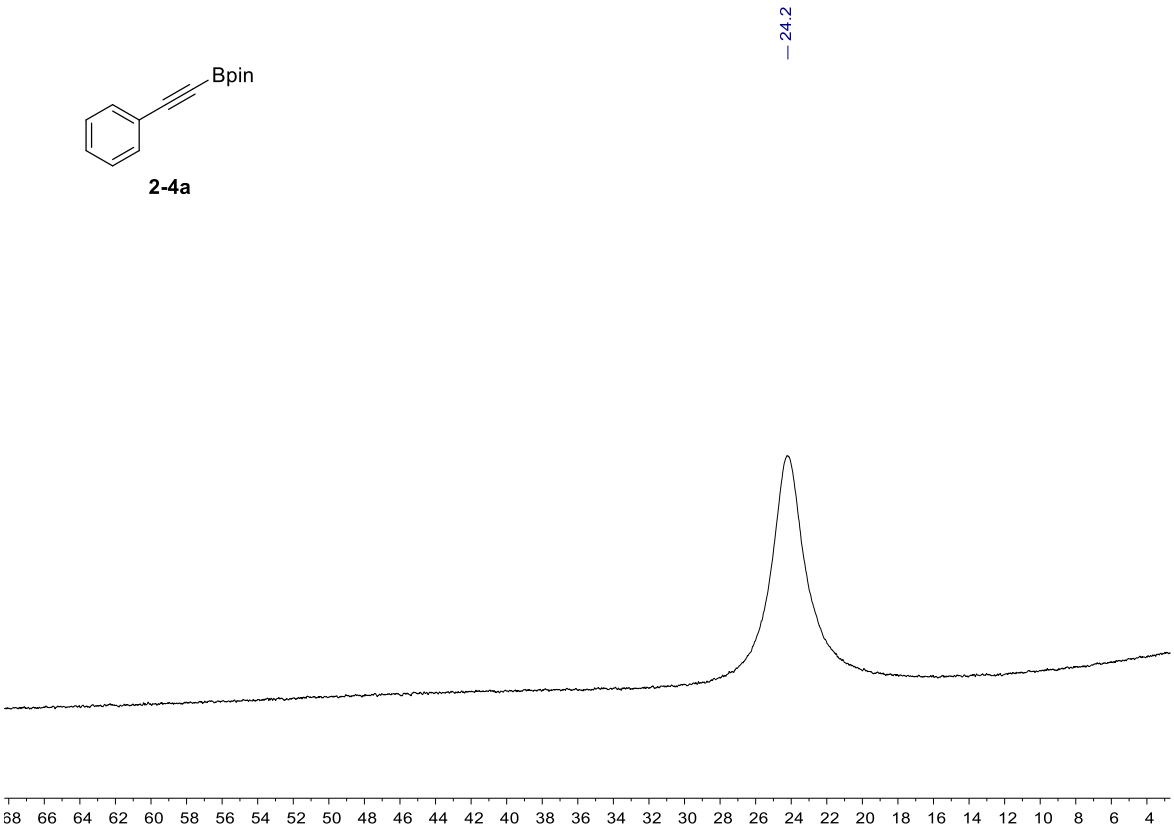
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2-4a**



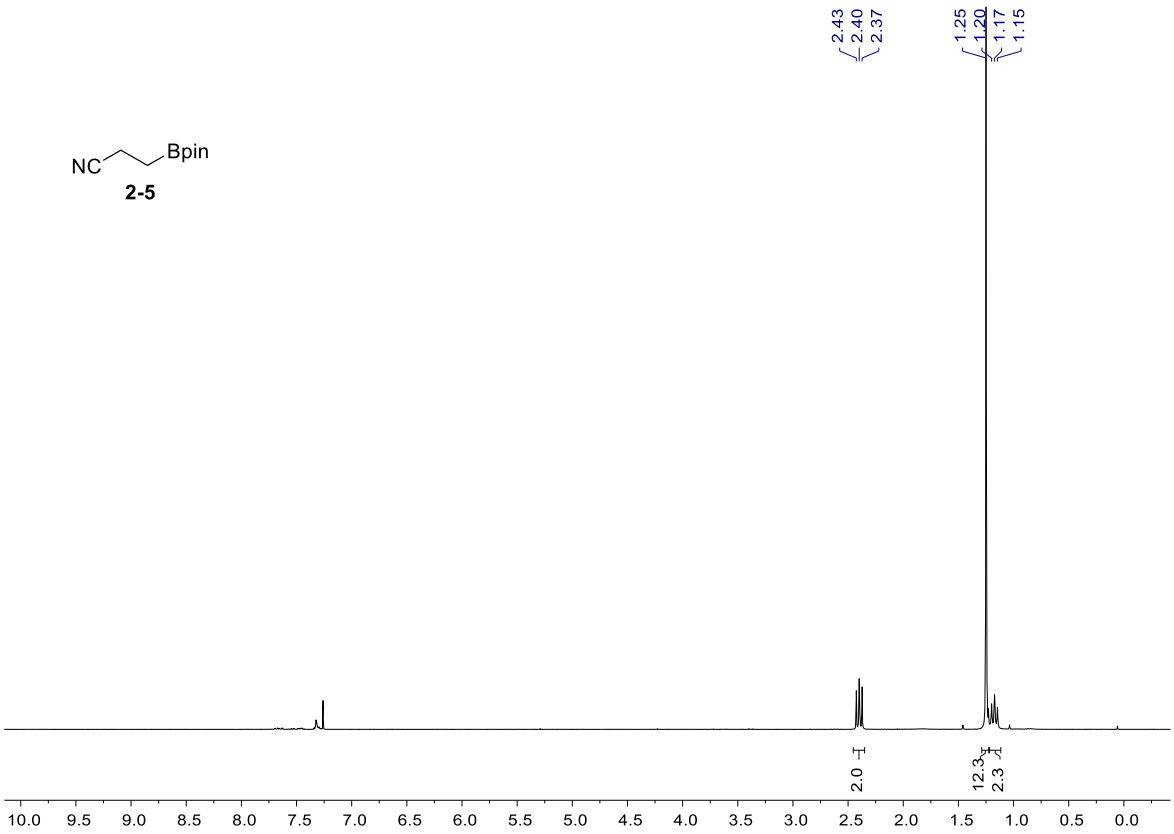
^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **2-4a**



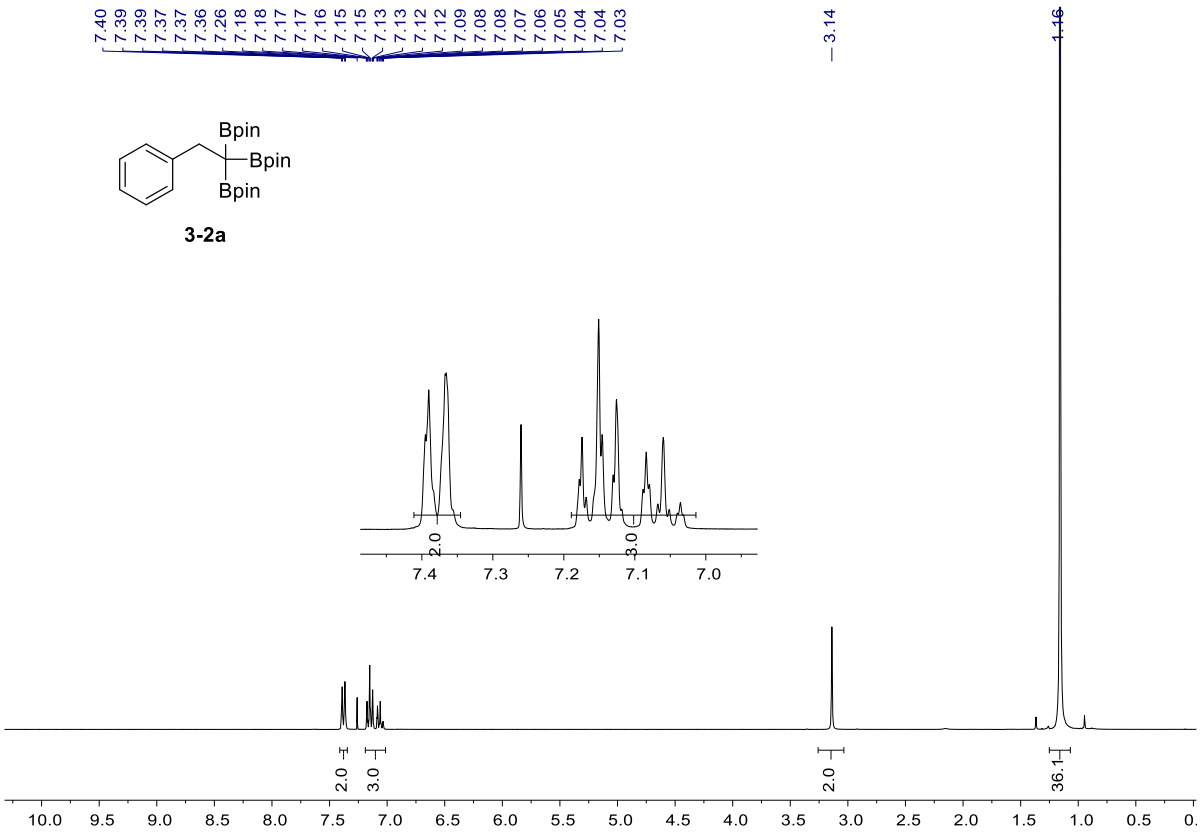
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **2-4a**



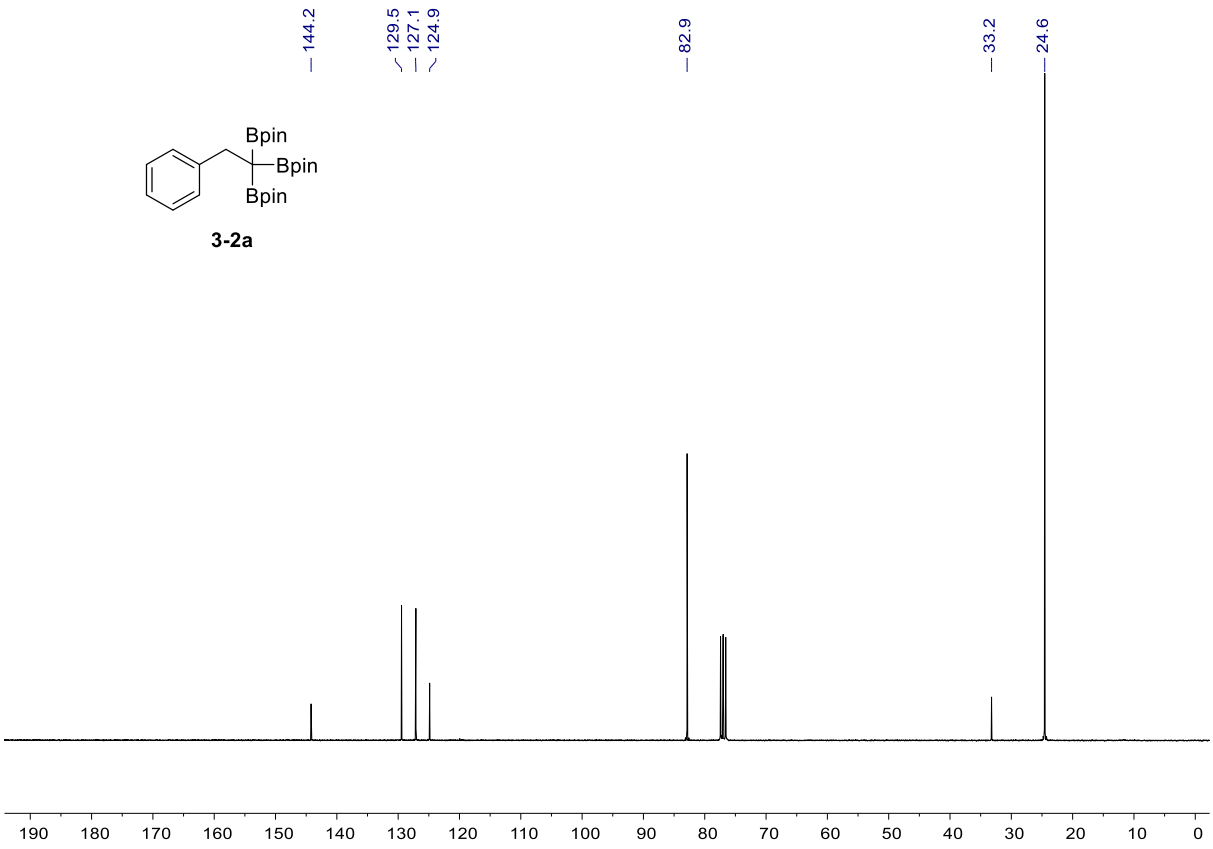
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2-5**



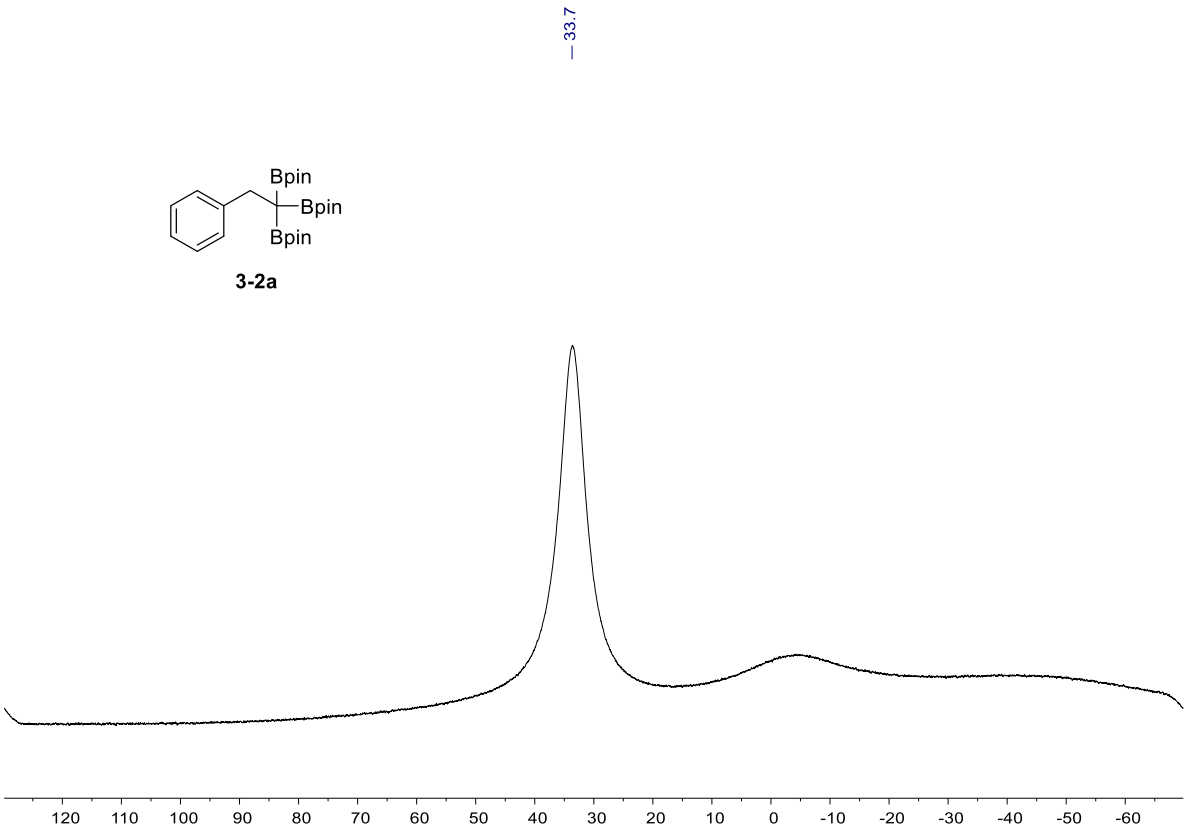
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2a**



^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **3-2a**

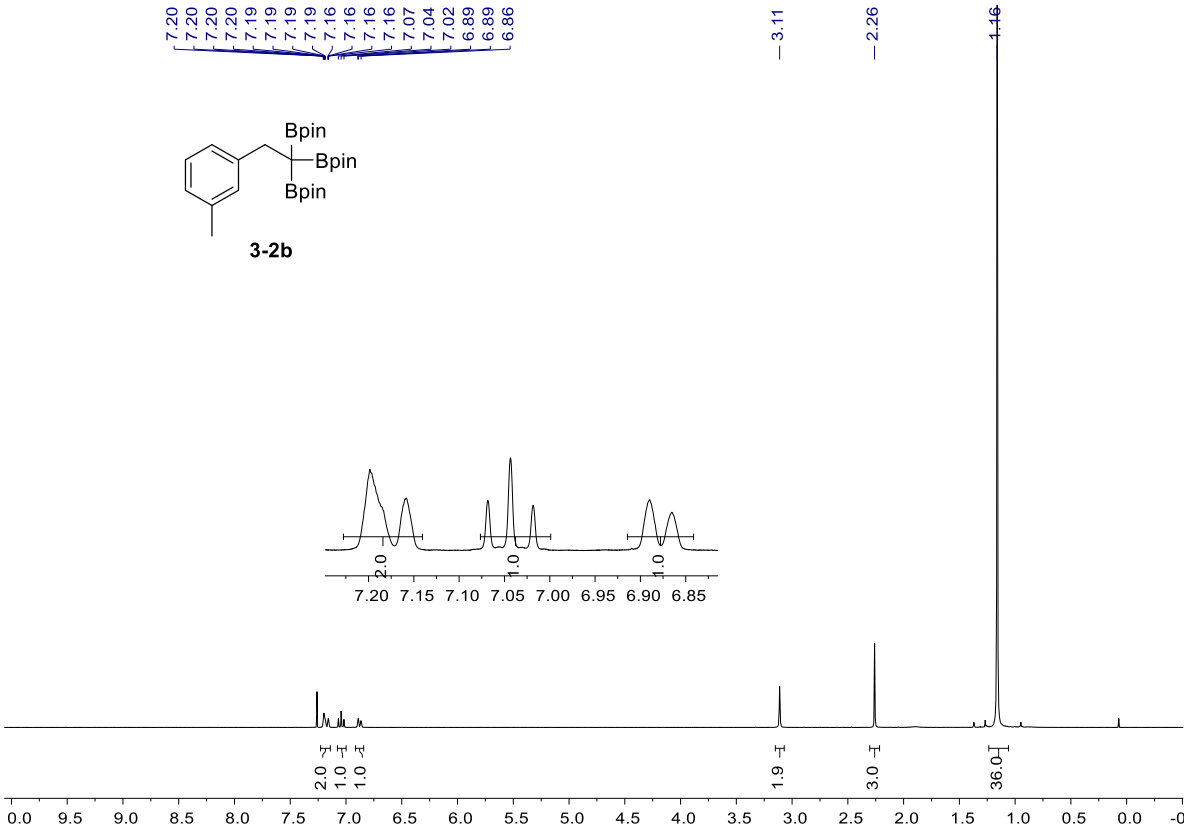


^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2a**



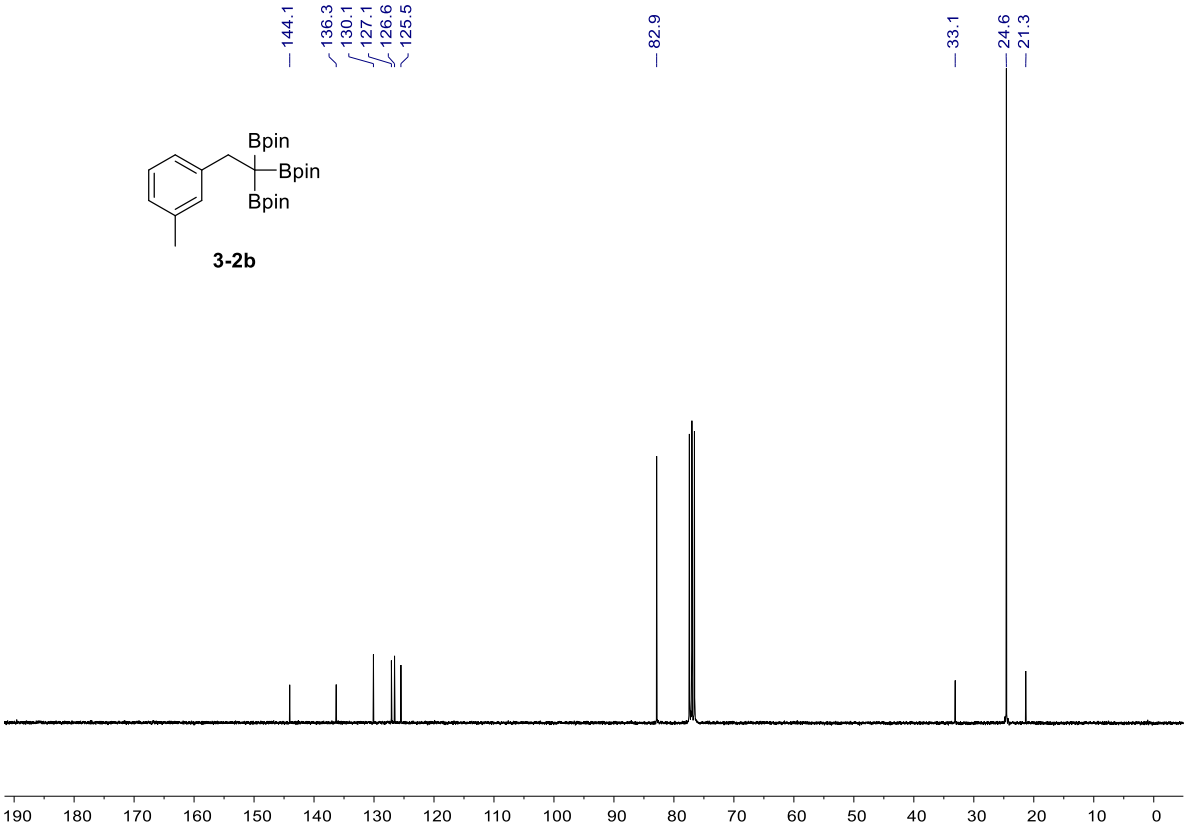
3-2a

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2b**

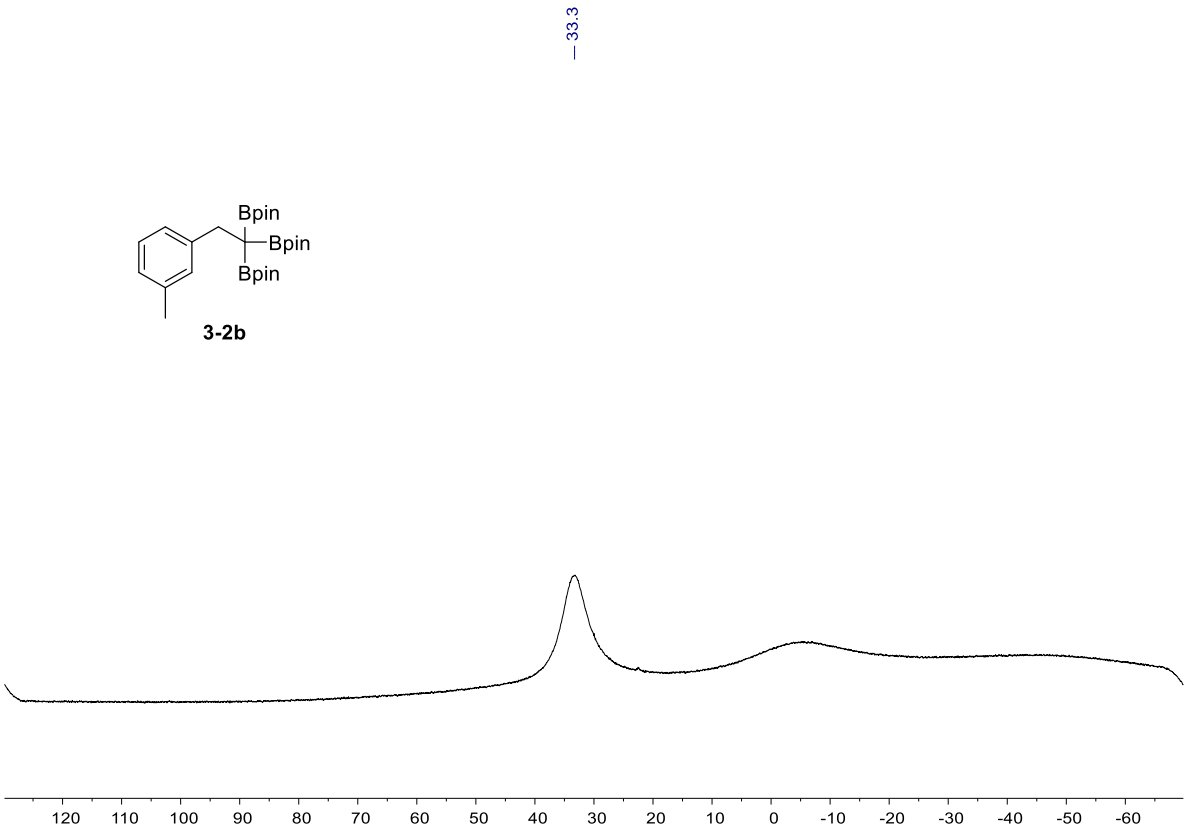


3-2b

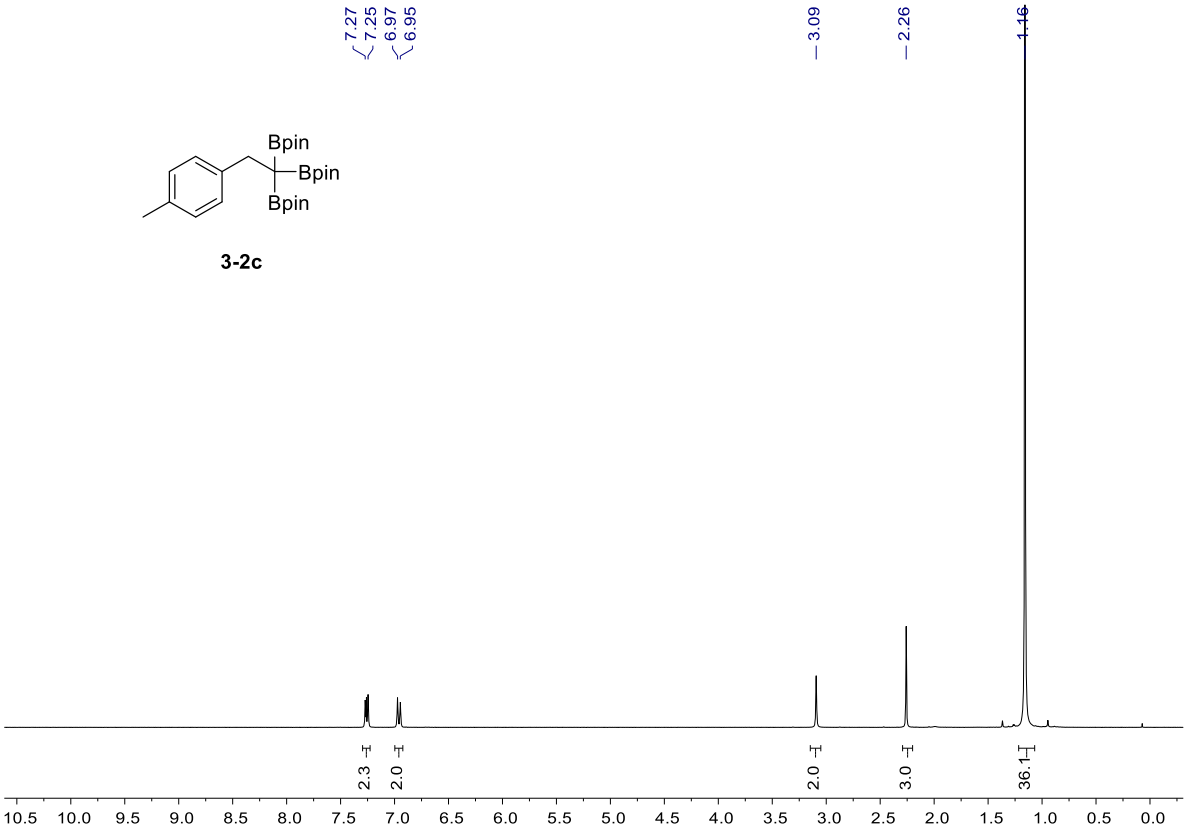
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-2b**



^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2b**

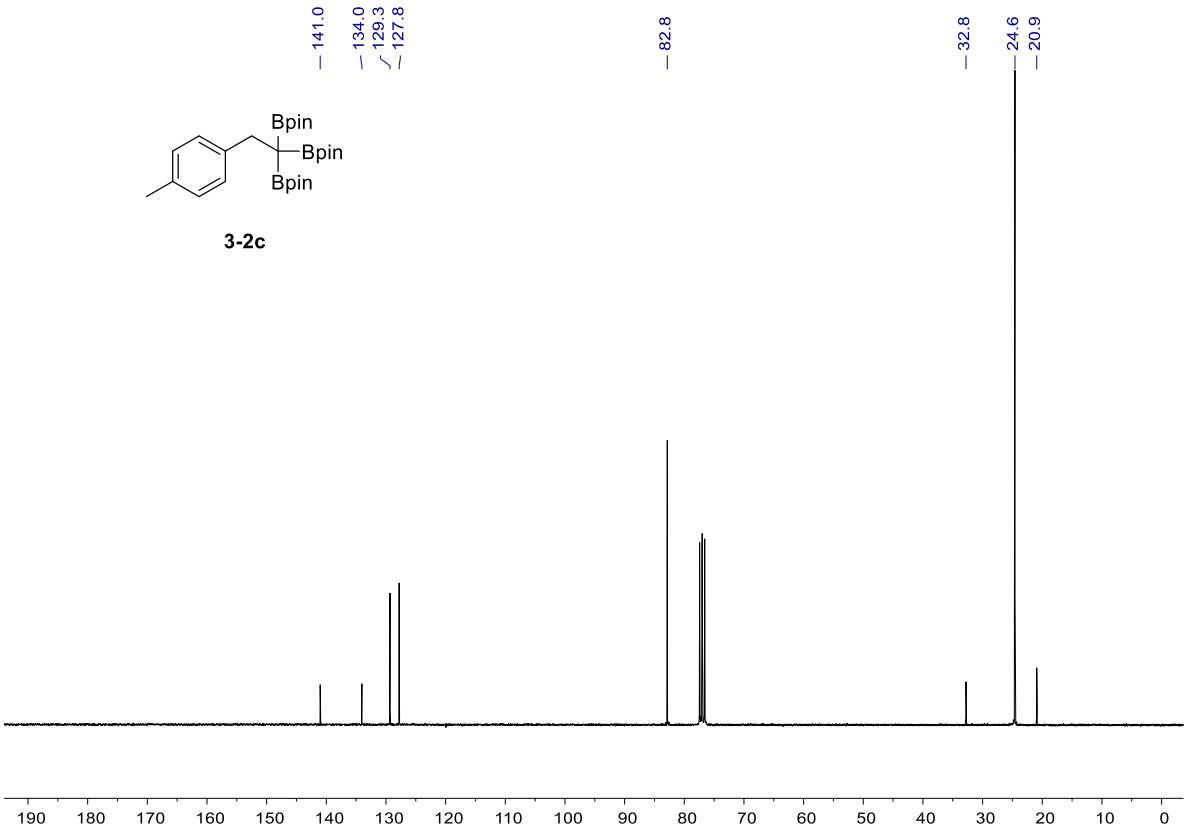


^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2c**



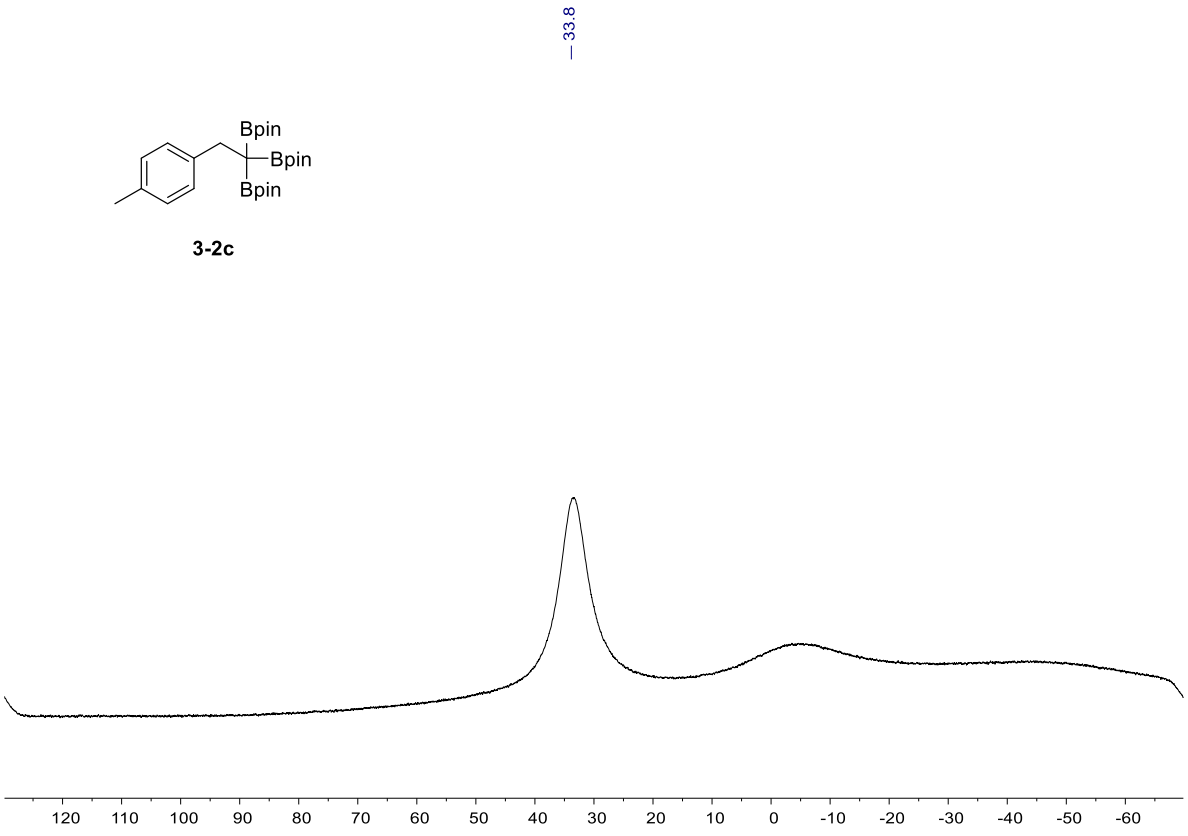
3-2c

^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **3-2c**



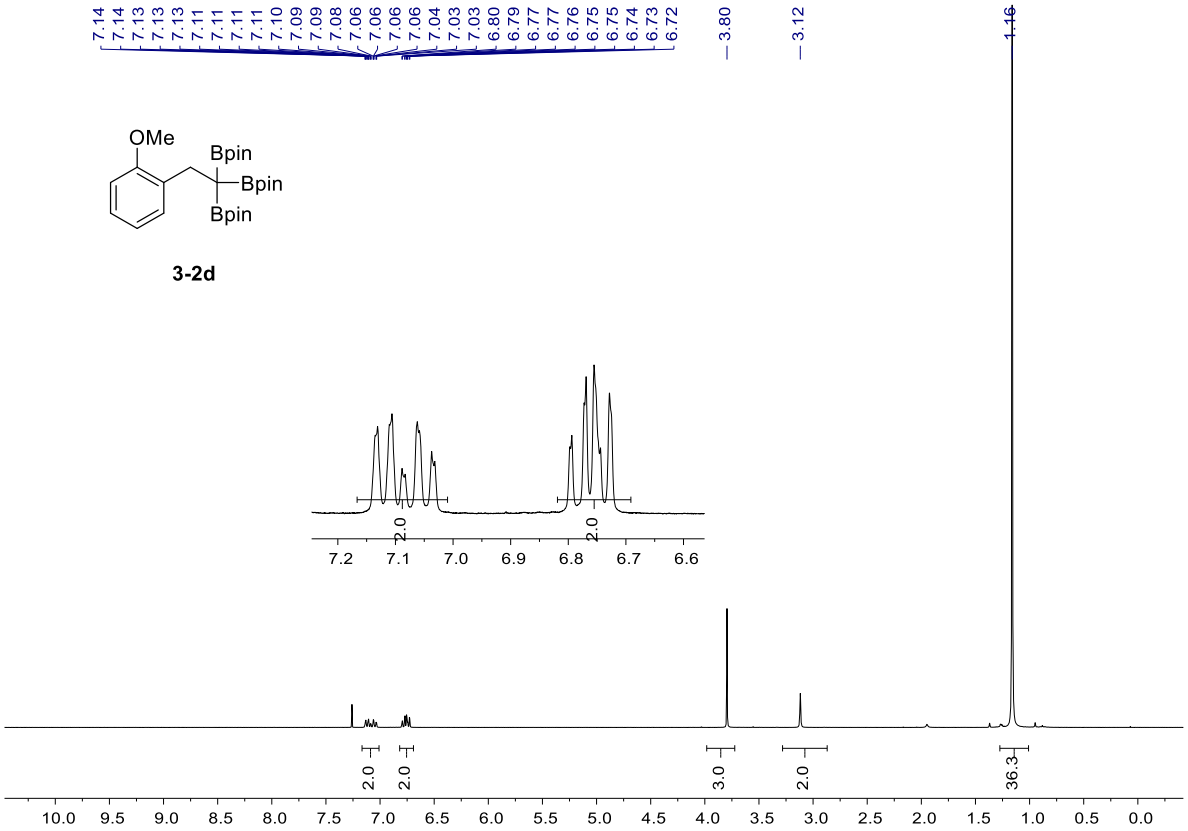
3-2c

^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2c**



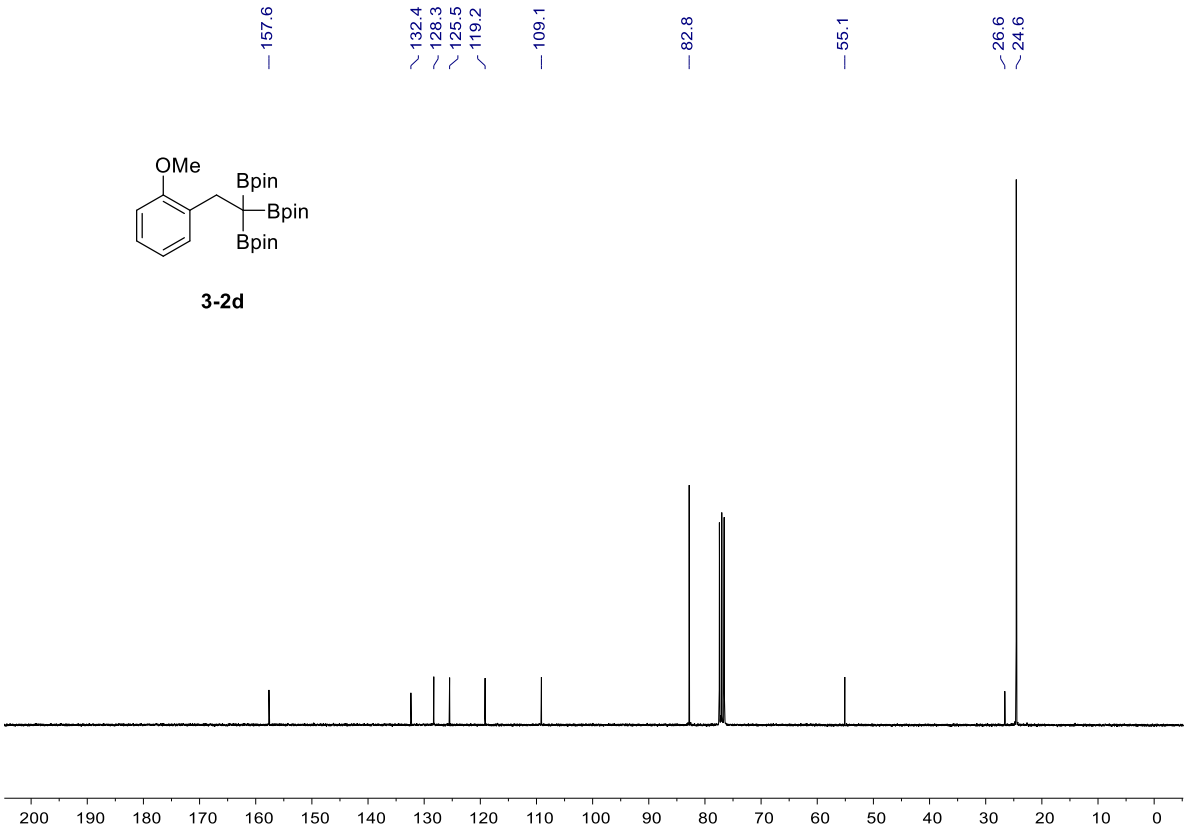
3-2c

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2d**



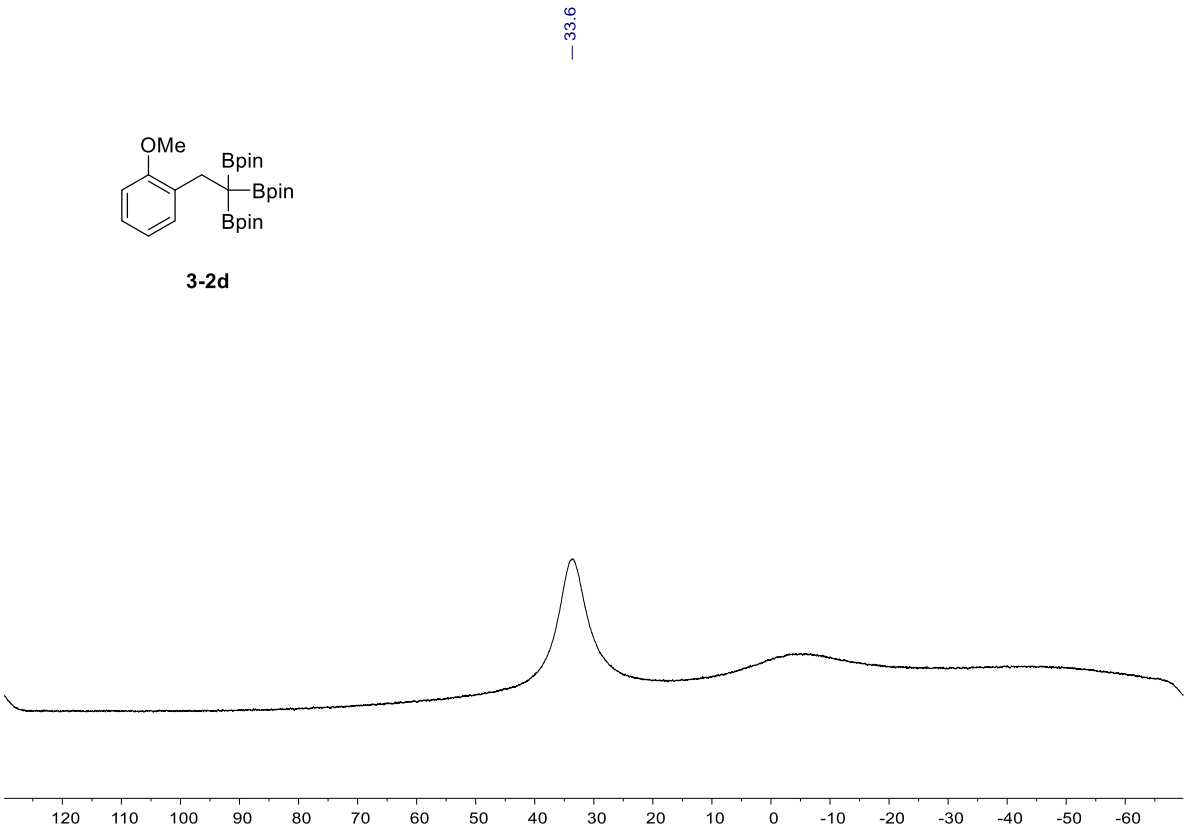
3-2d

$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-2d**



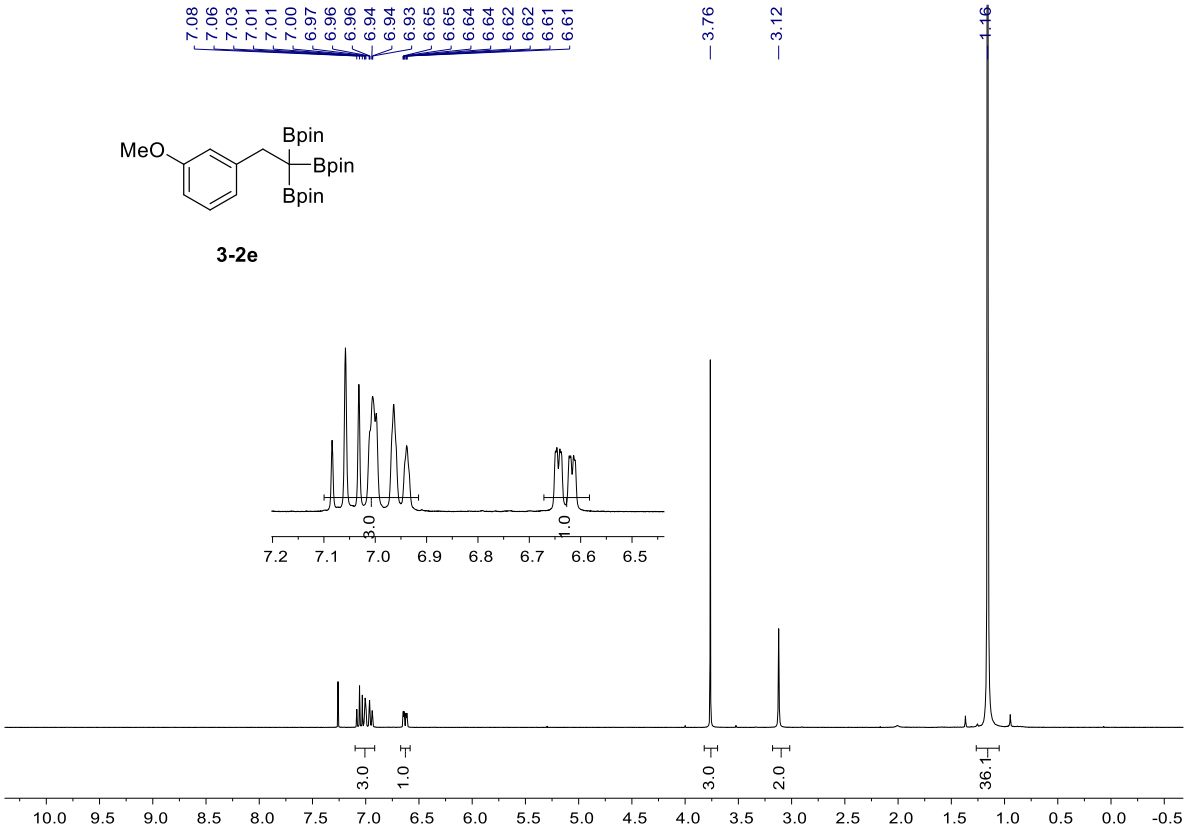
3-2d

^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2d**

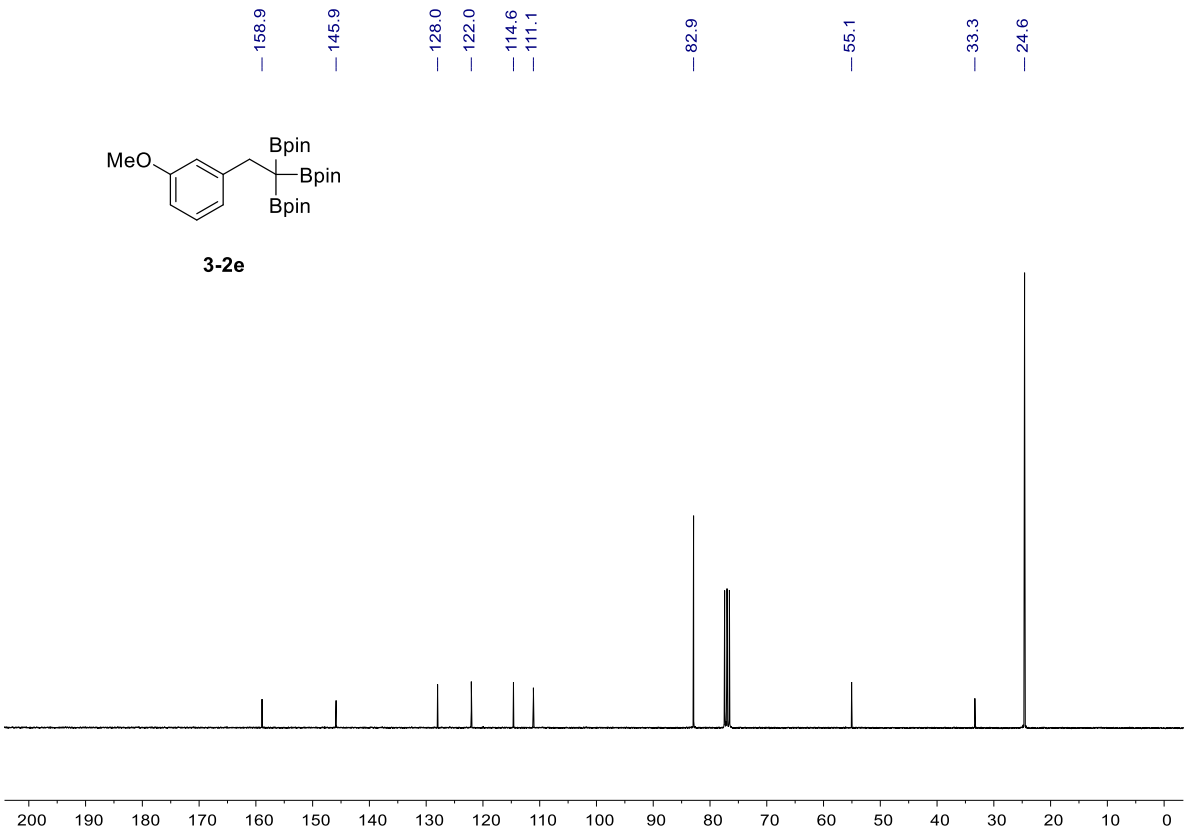


3-2d

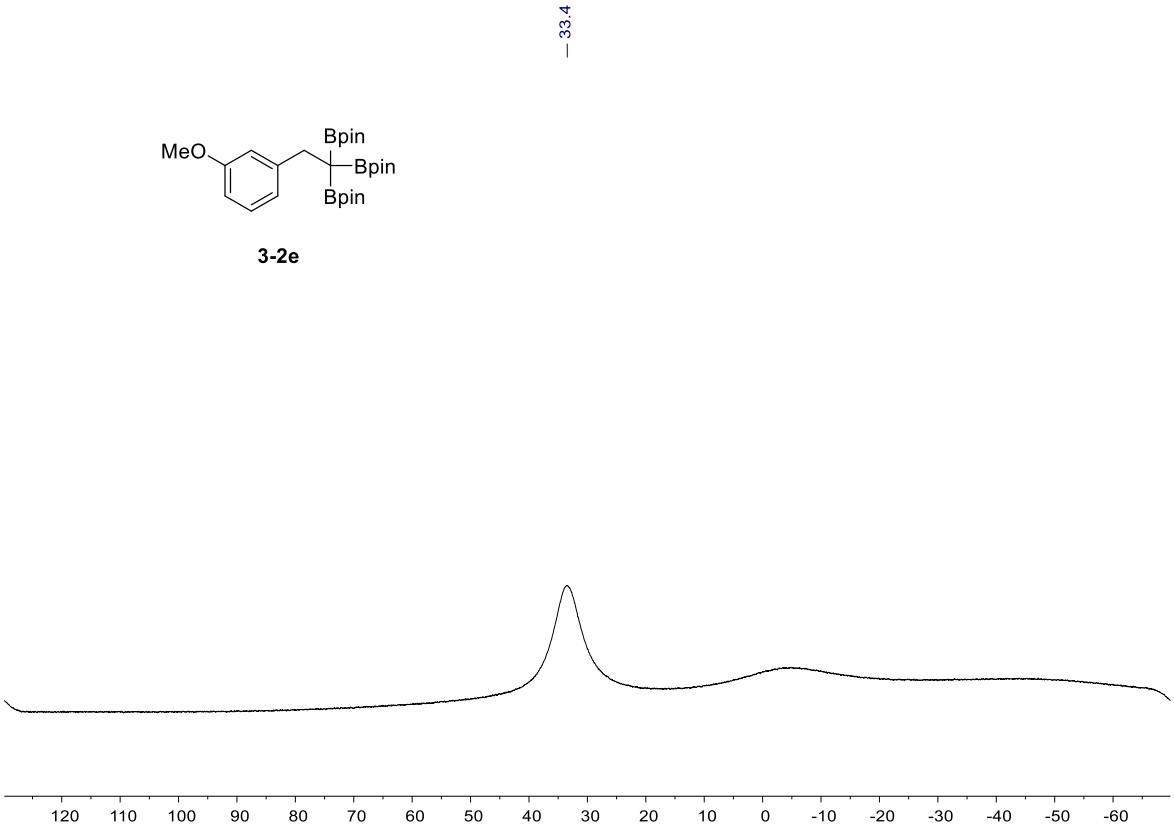
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2e**



^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **3-2e**

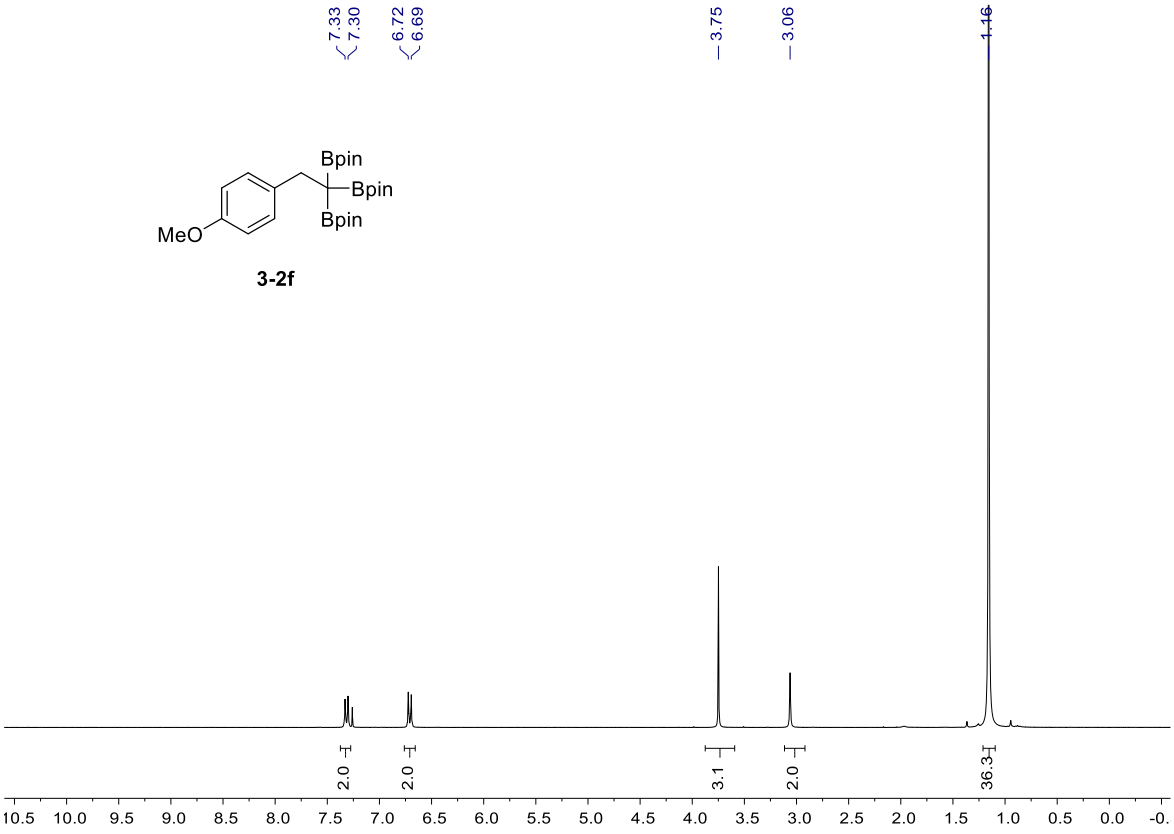


^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2e**



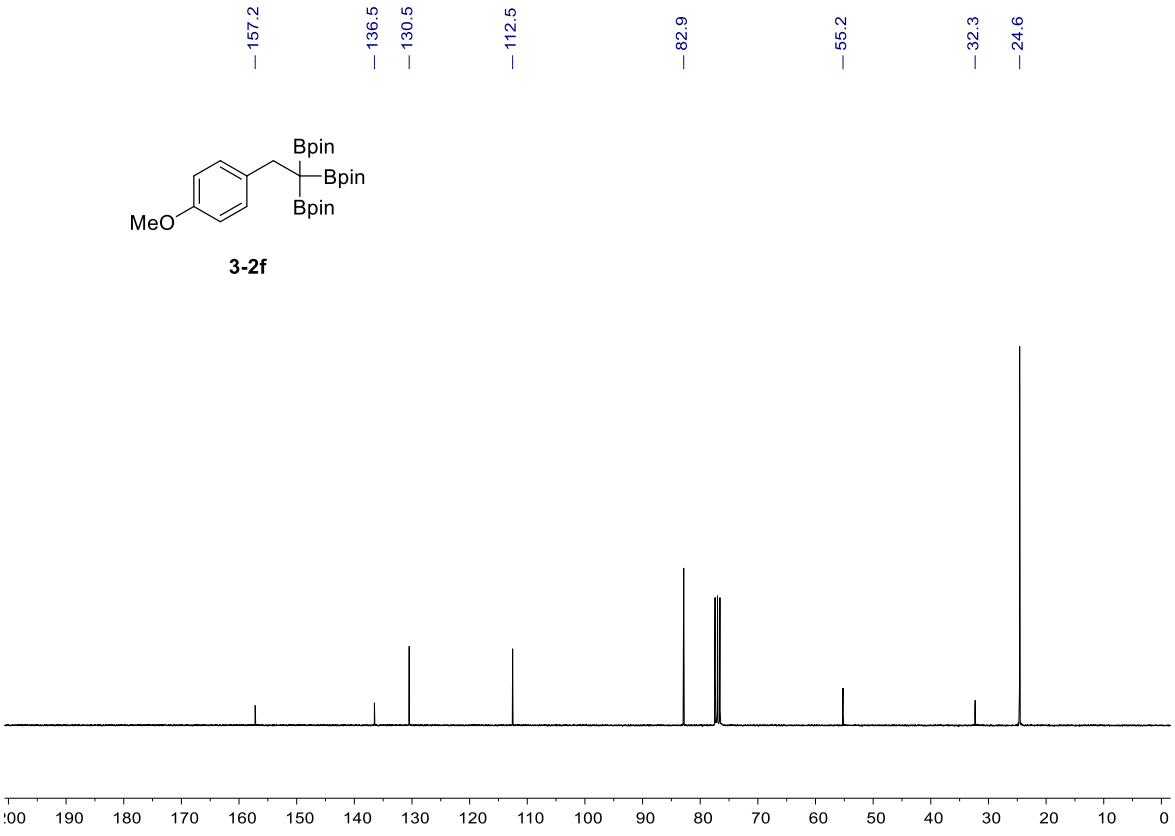
3-2e

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2f**



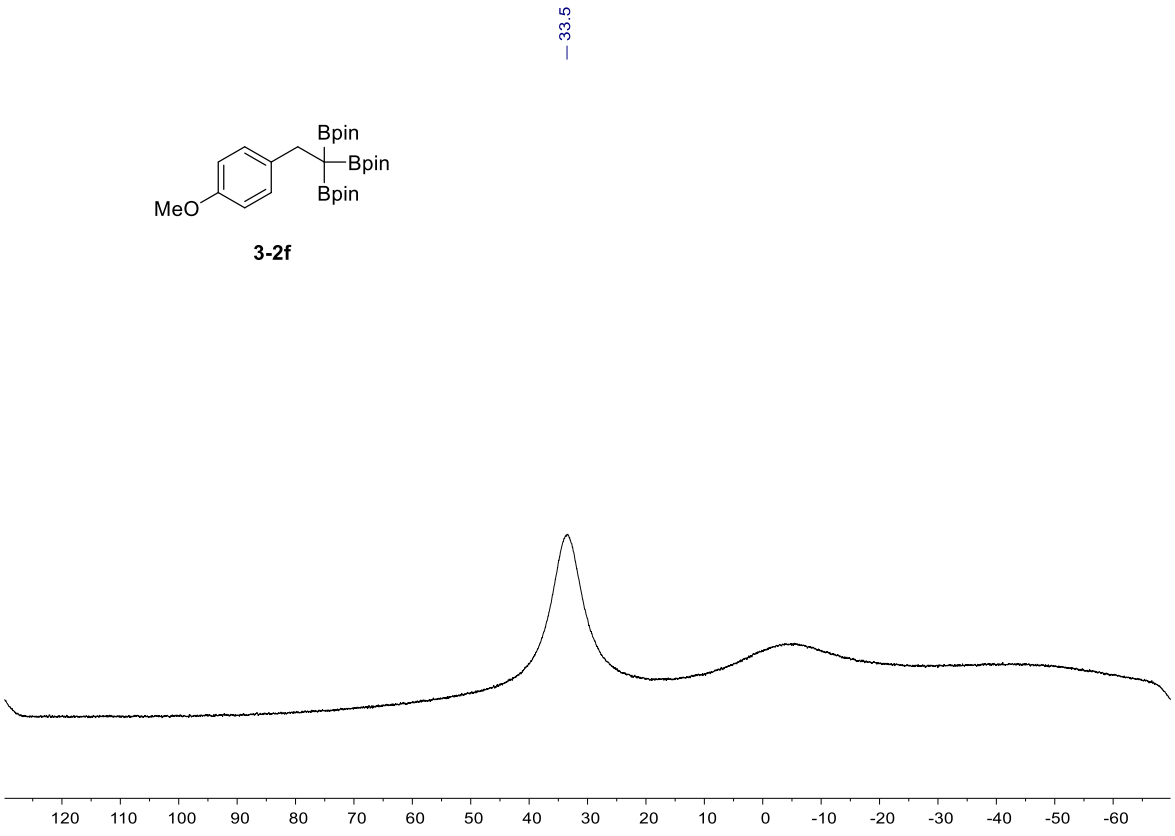
3-2f

$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-2f**



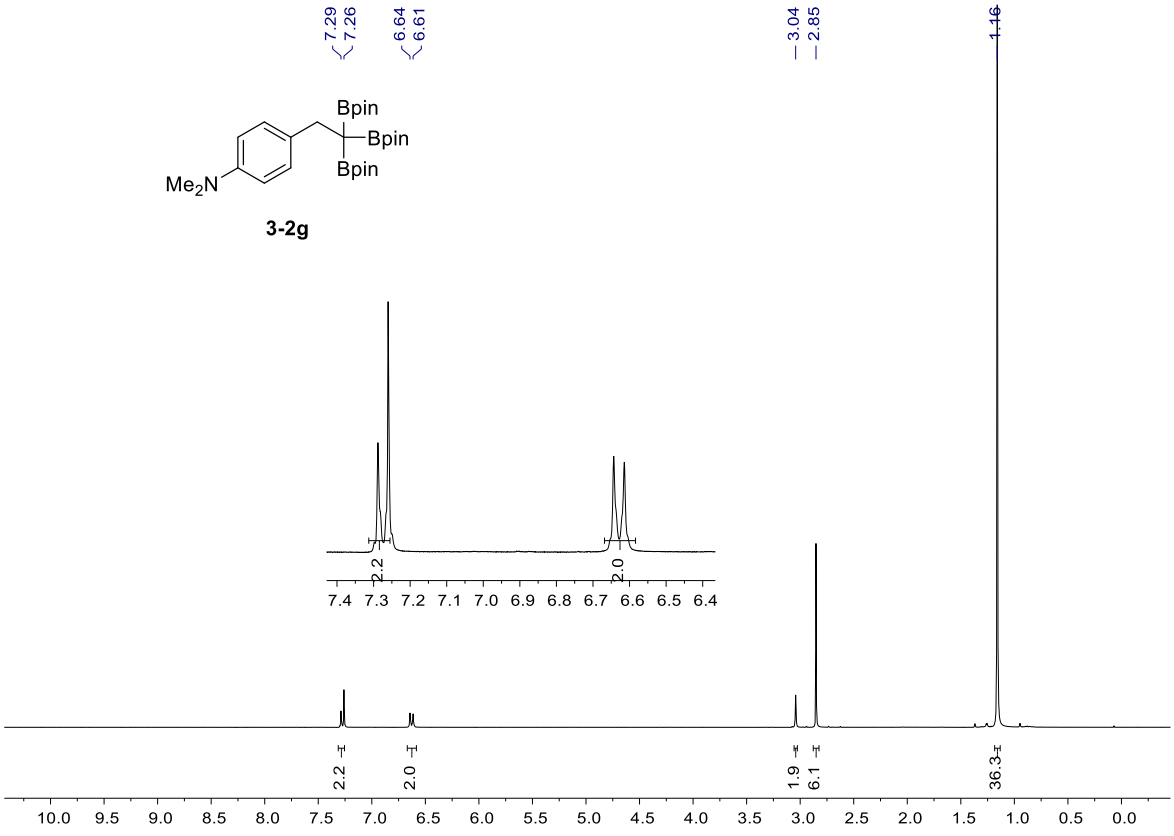
3-2f

^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2f**

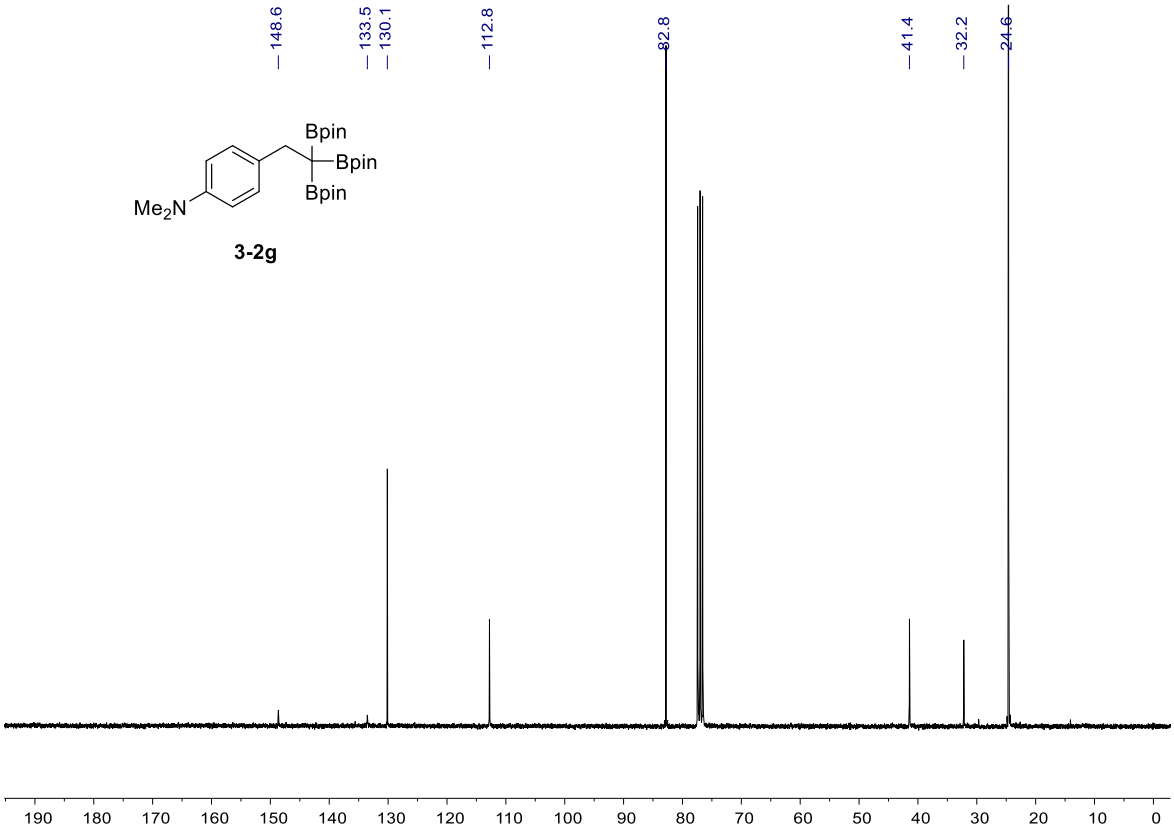


3-2f

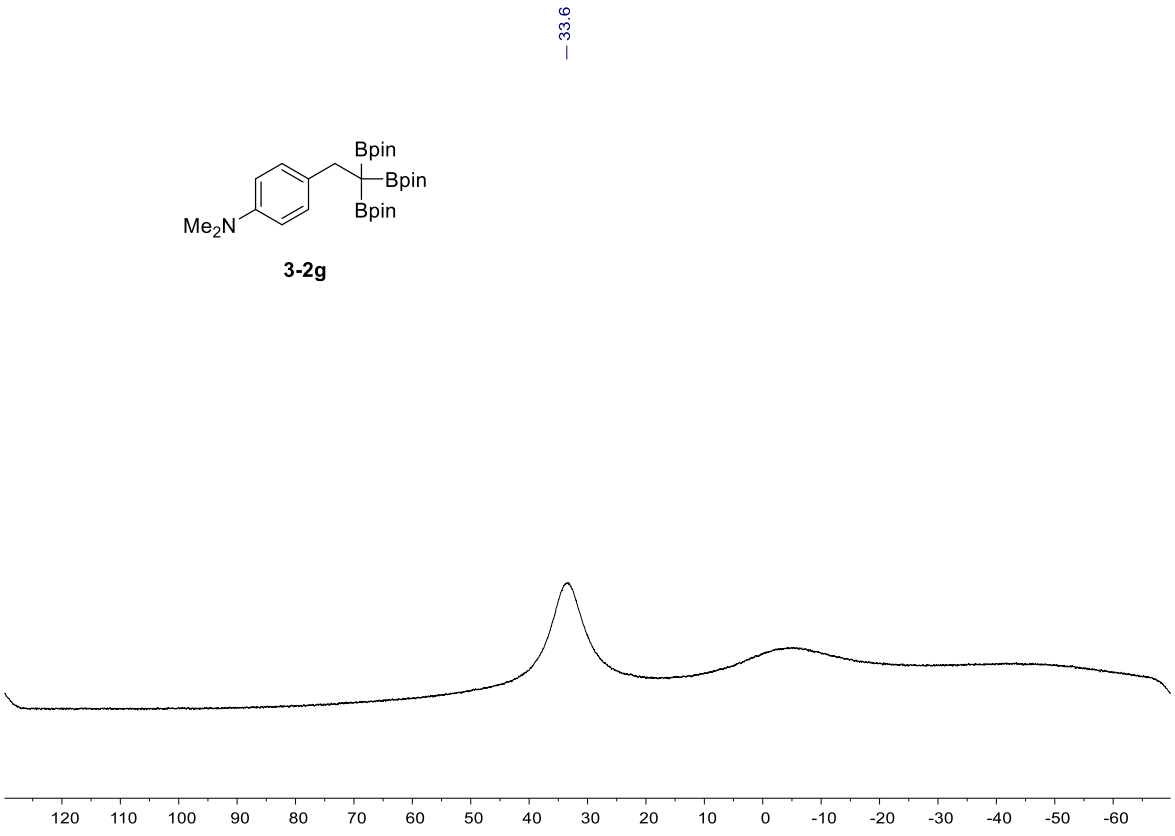
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2g**



^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **3-2g**

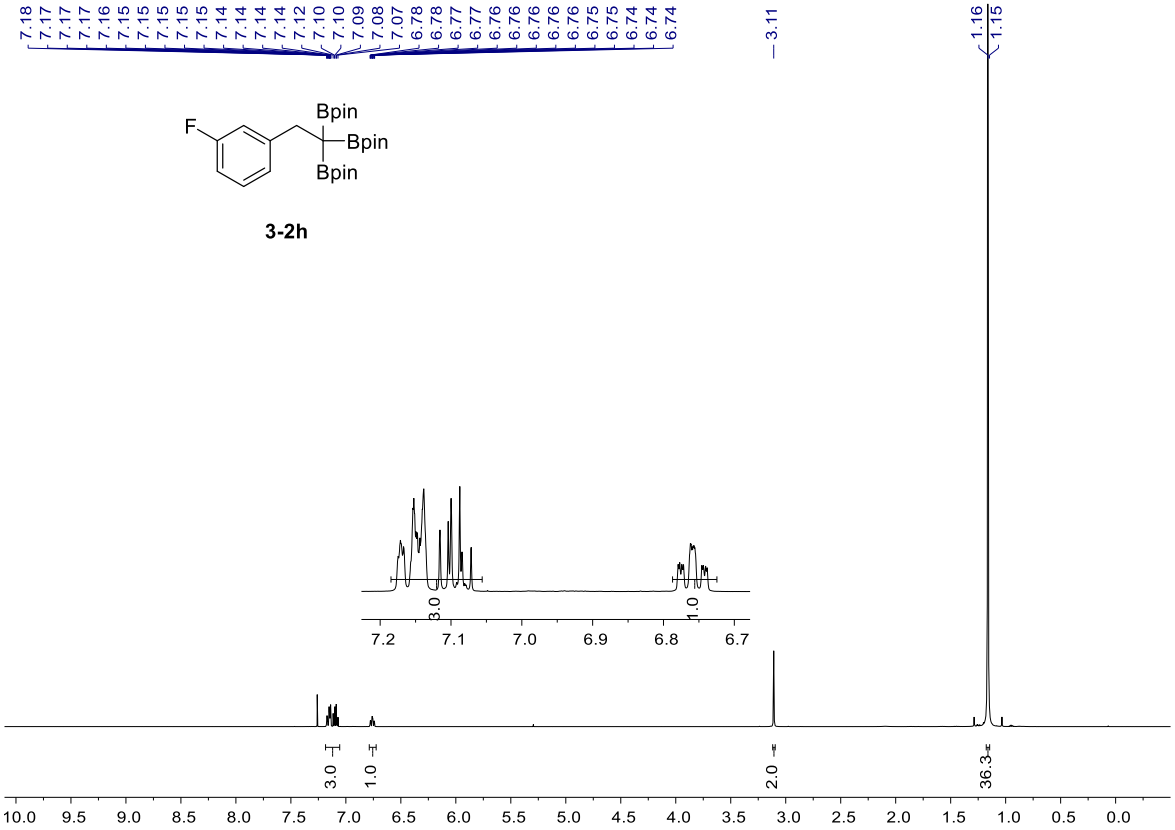


^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2g**



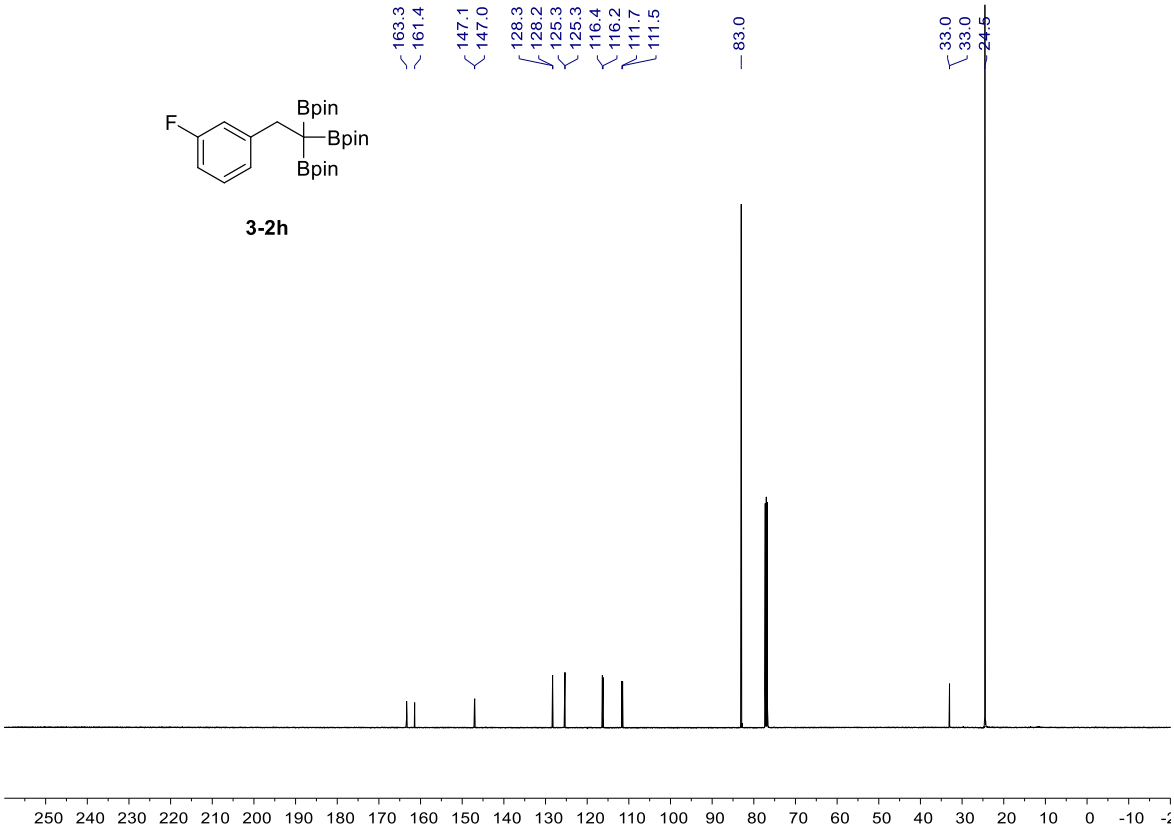
3-2g

^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3-2h**



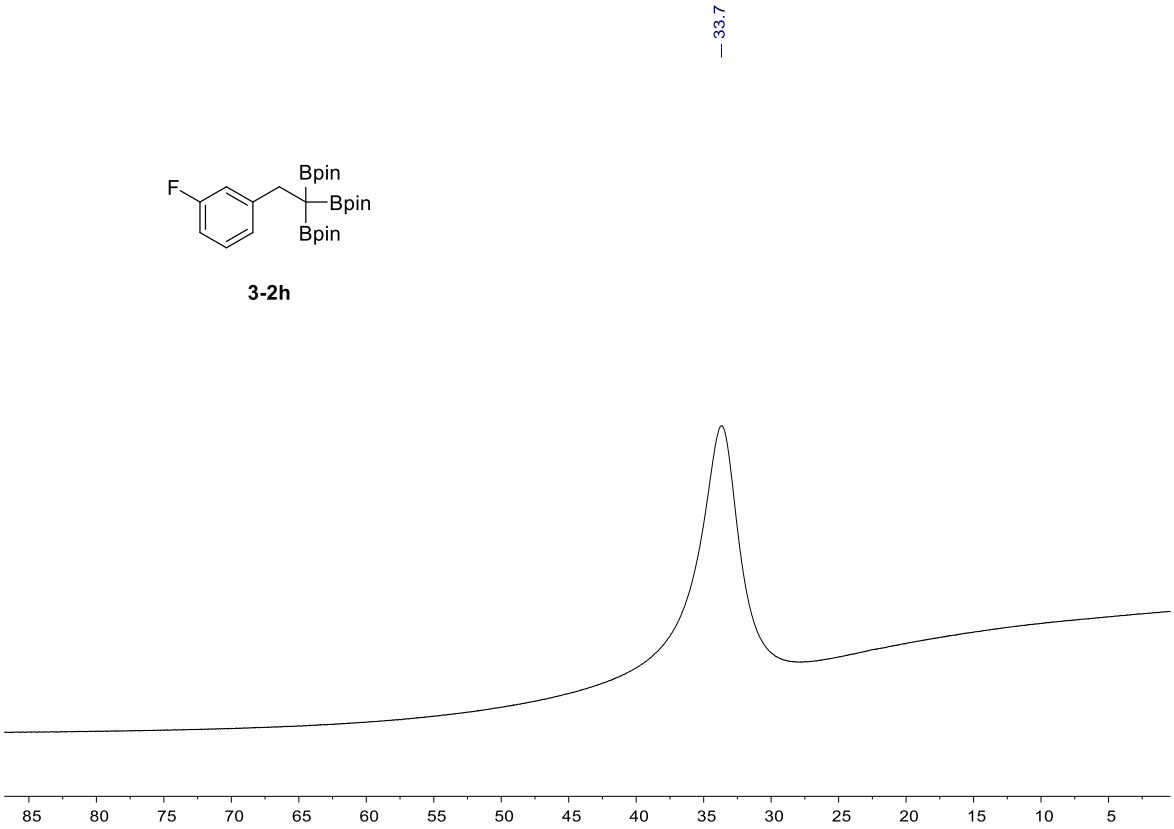
3-2h

$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **3-2h**



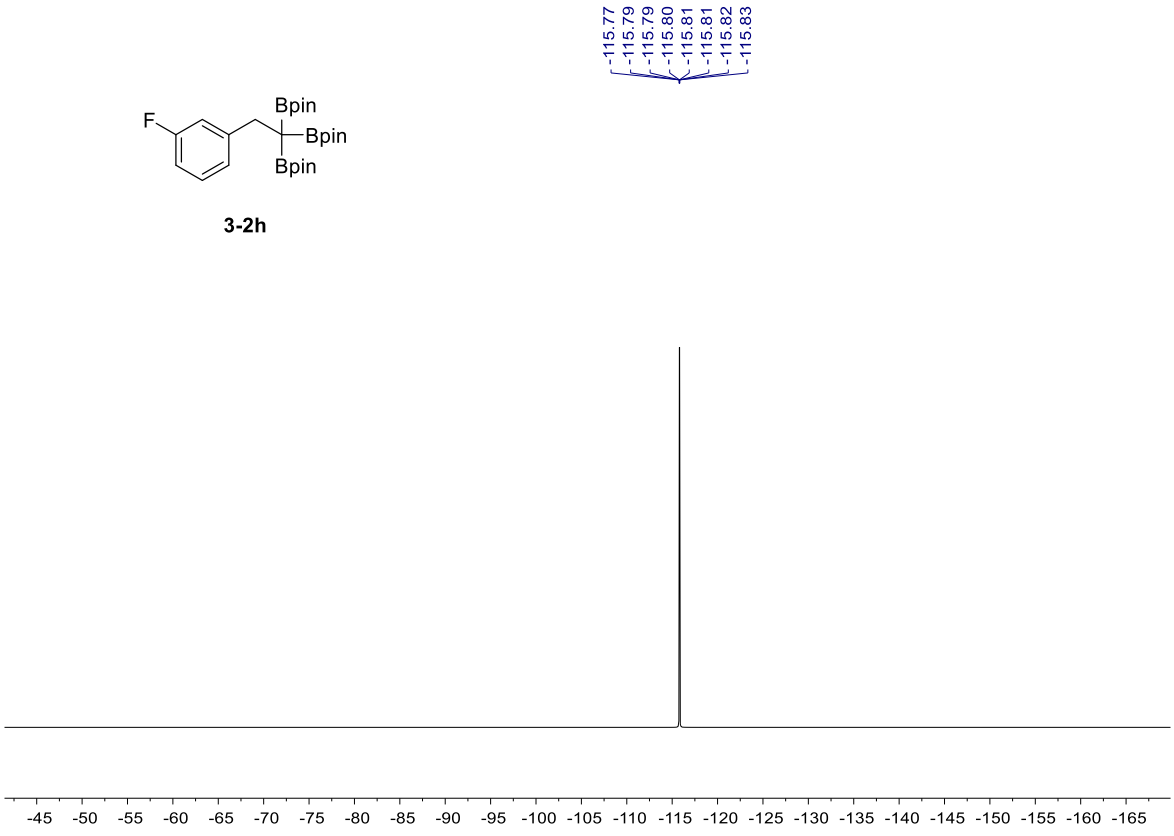
3-2h

^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **3-2h**



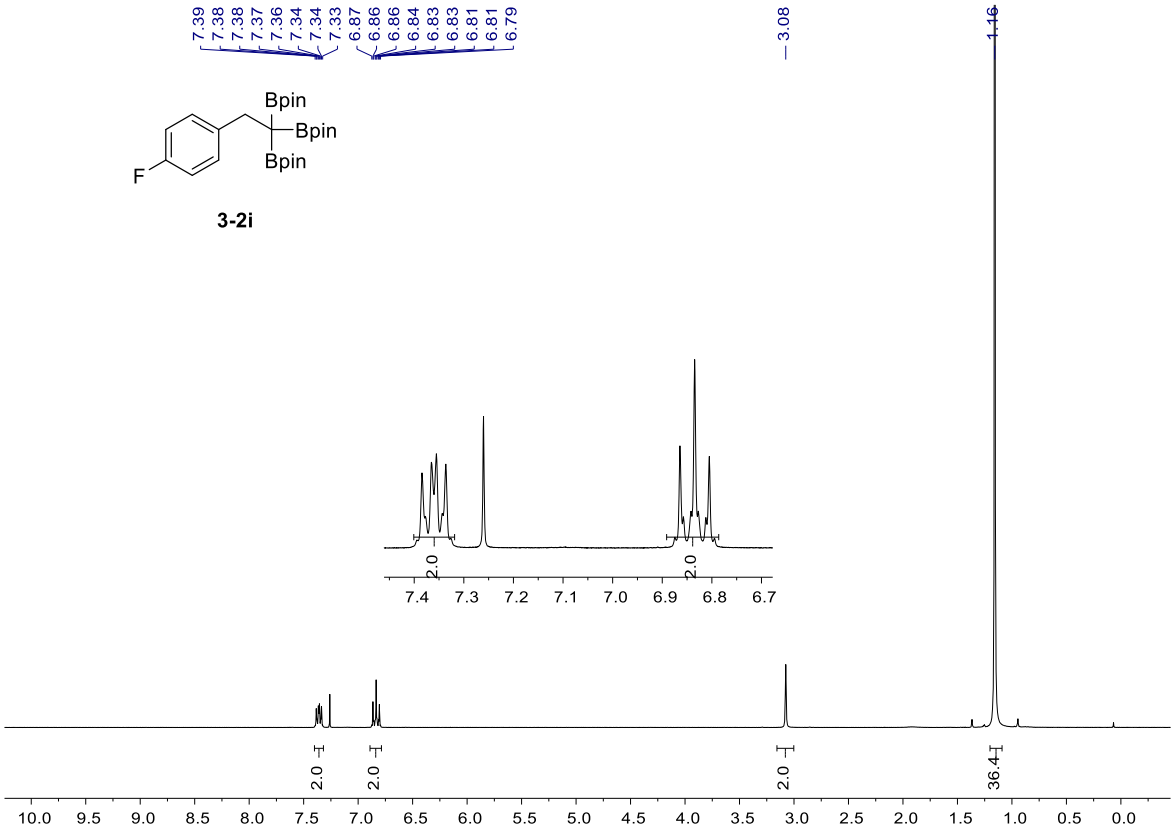
3-2h

^{19}F NMR spectrum (471 MHz, $CDCl_3$) of **3-2h**



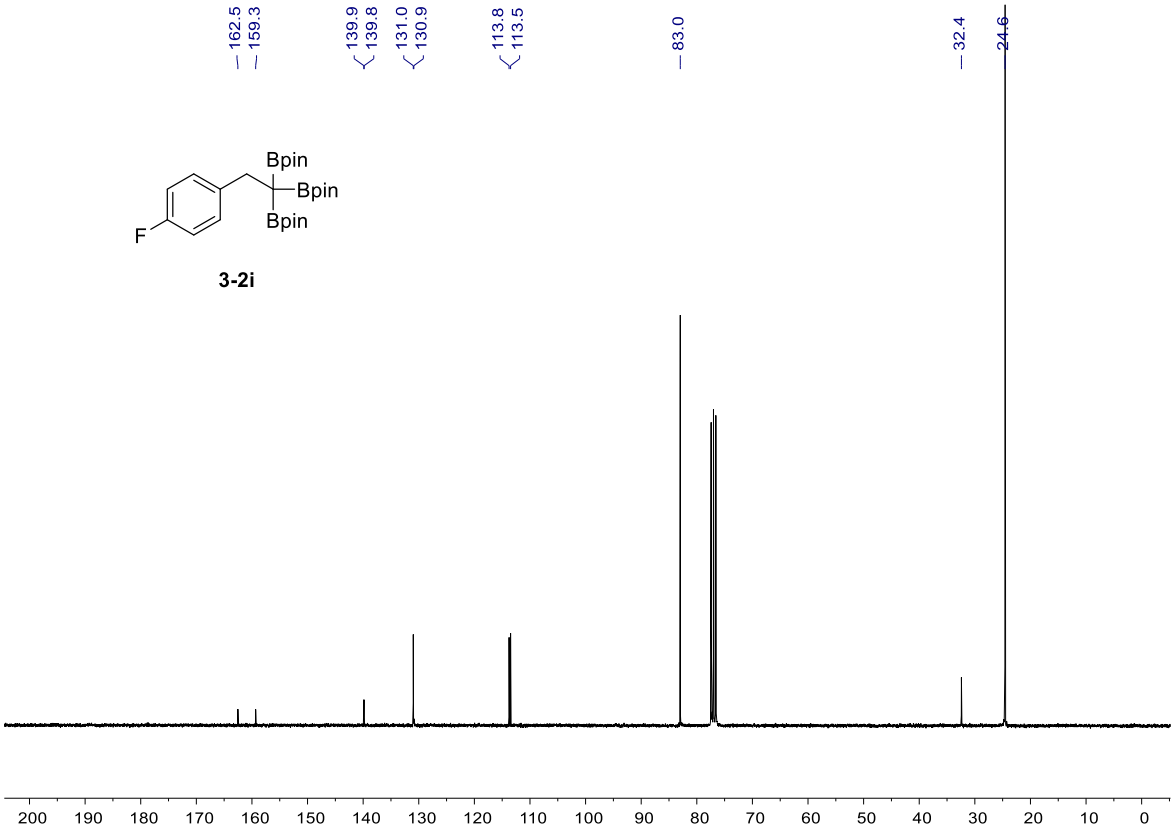
3-2h

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2i**



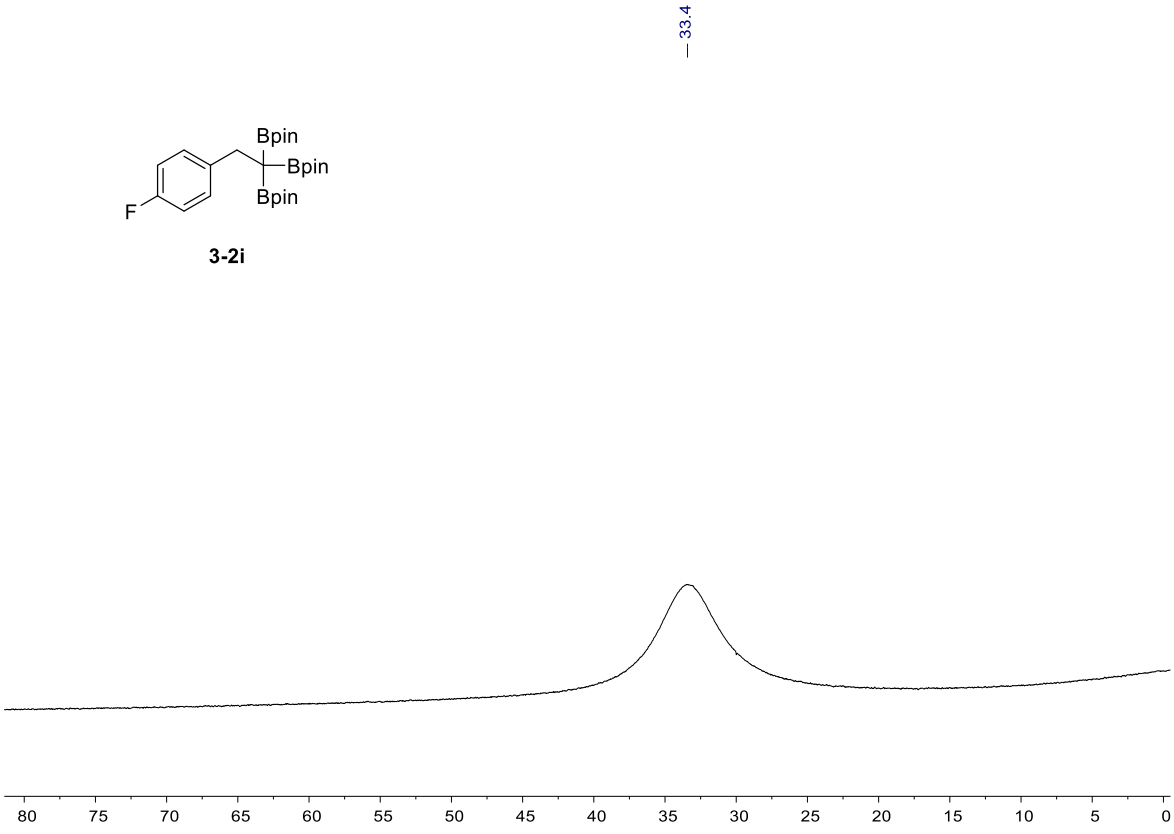
3-2i

$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-2i**



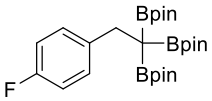
3-2i

^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2i**

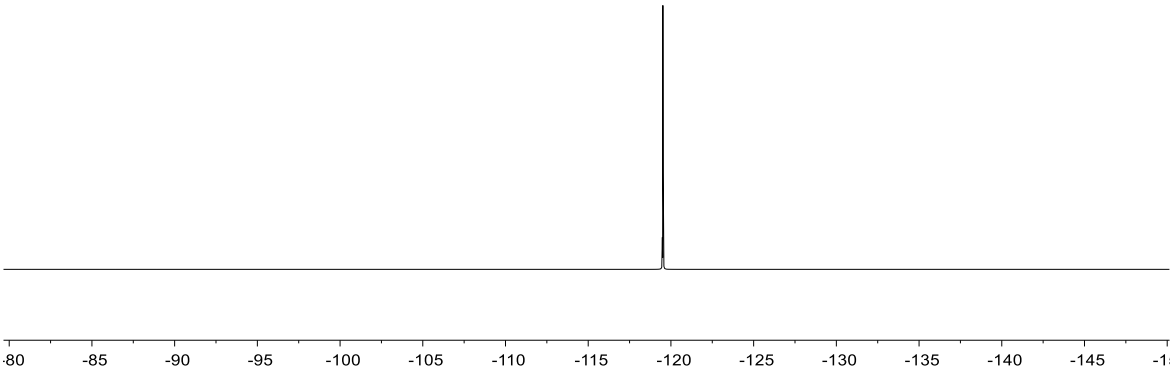


3-2i

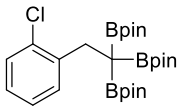
^{19}F NMR spectrum (471 MHz, $CDCl_3$) of **3-2i**



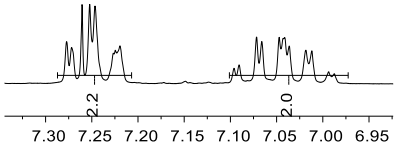
3-2i

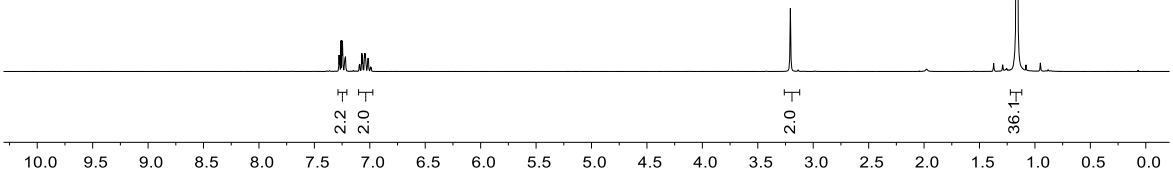


^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2j**

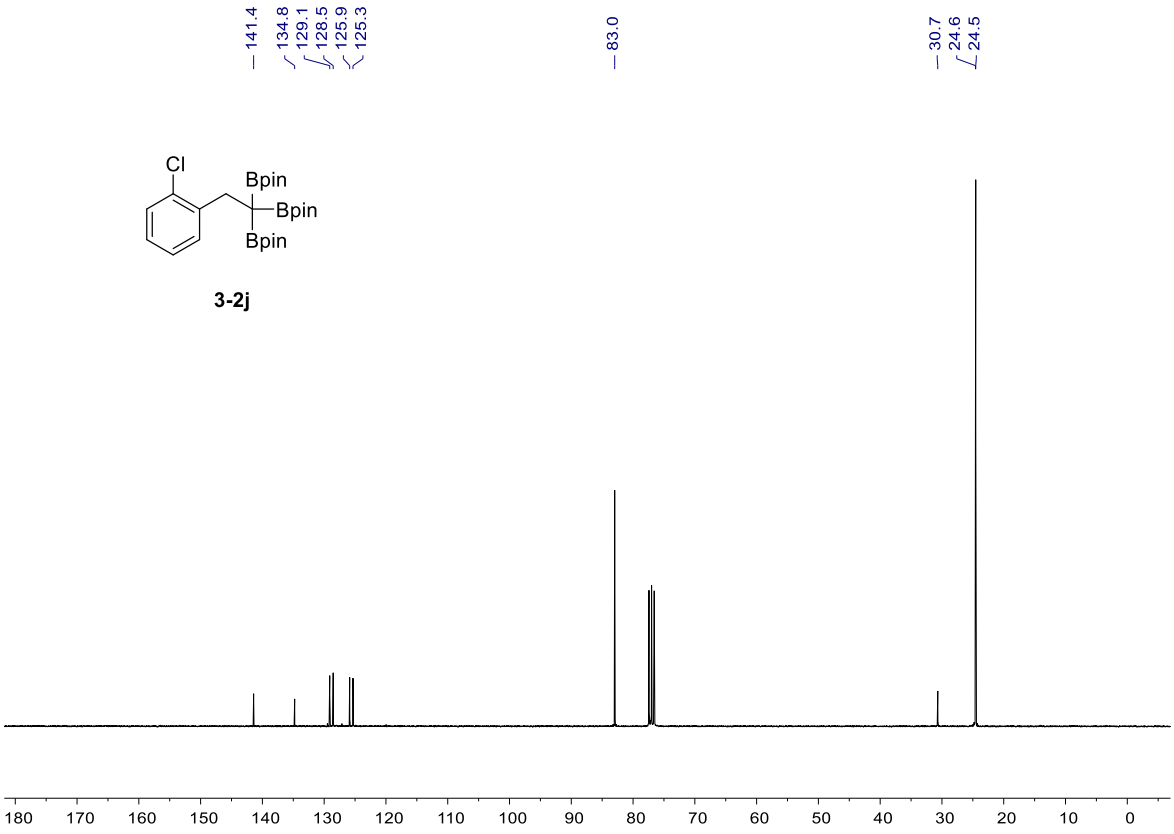


3-2j



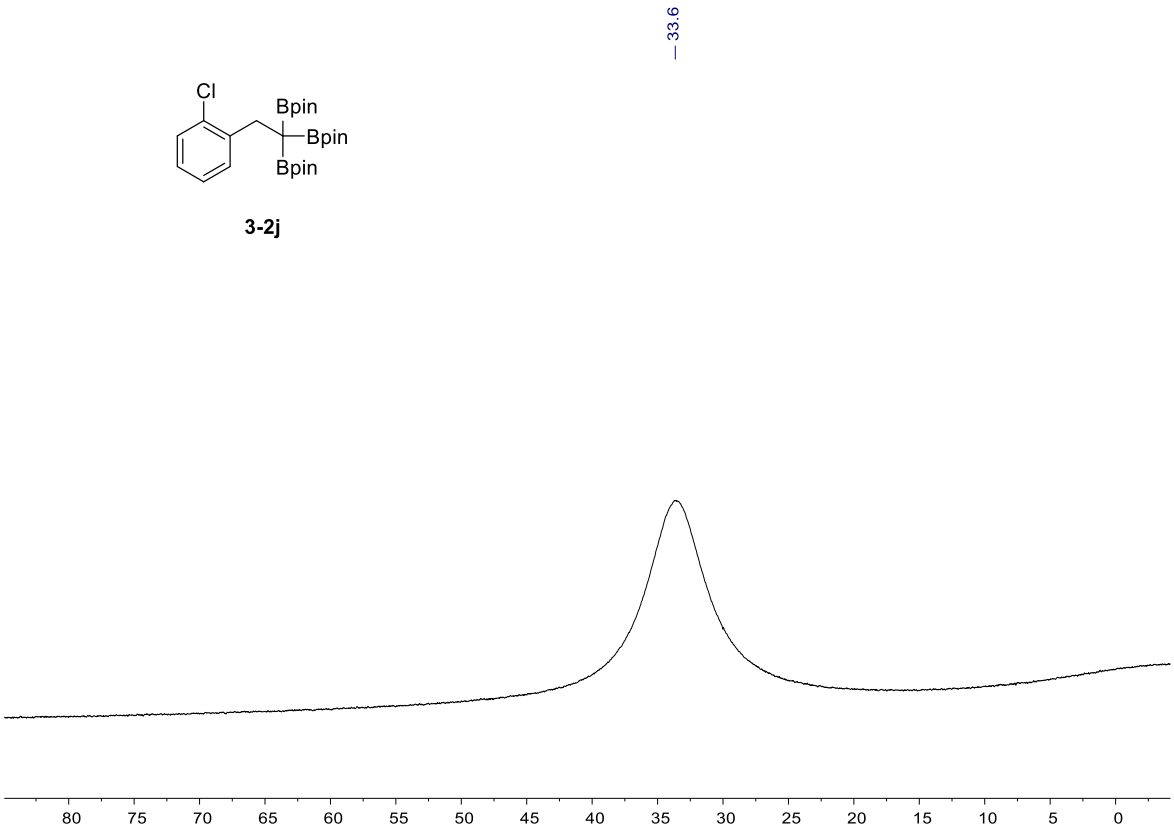


$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-2j**



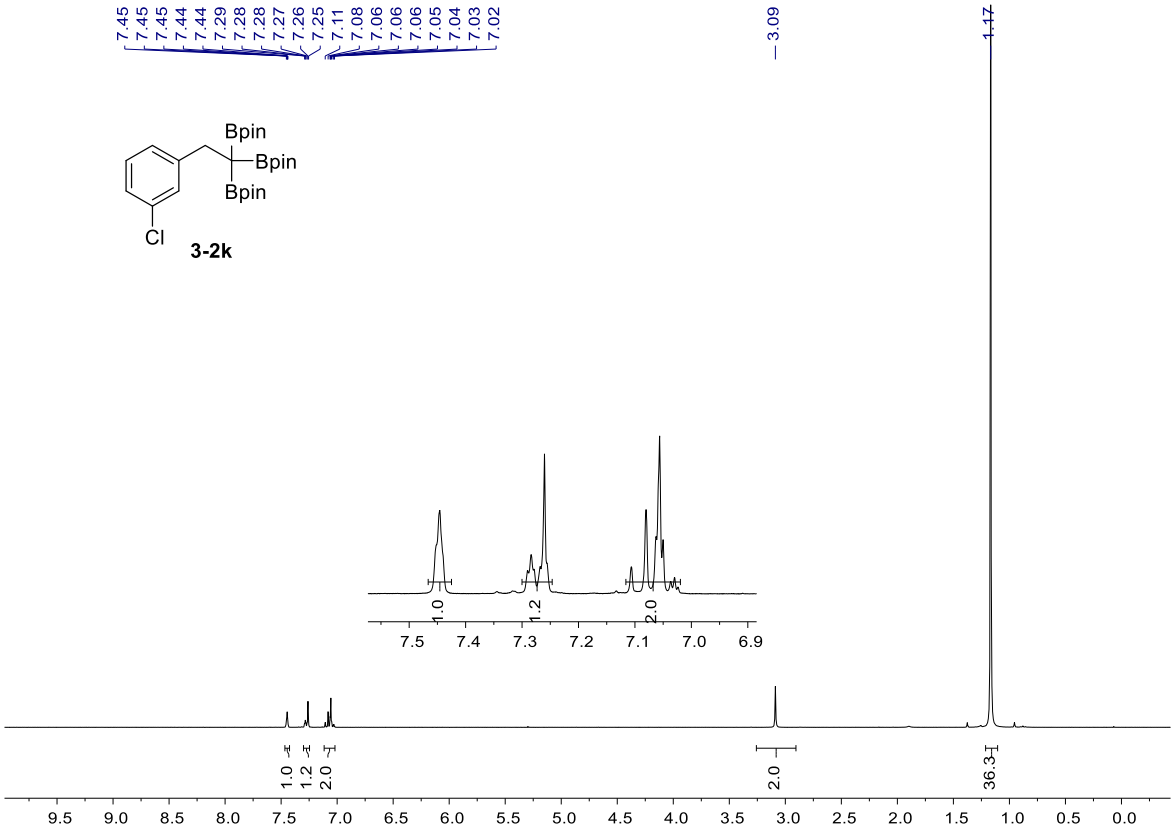
3-2j

^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2j**

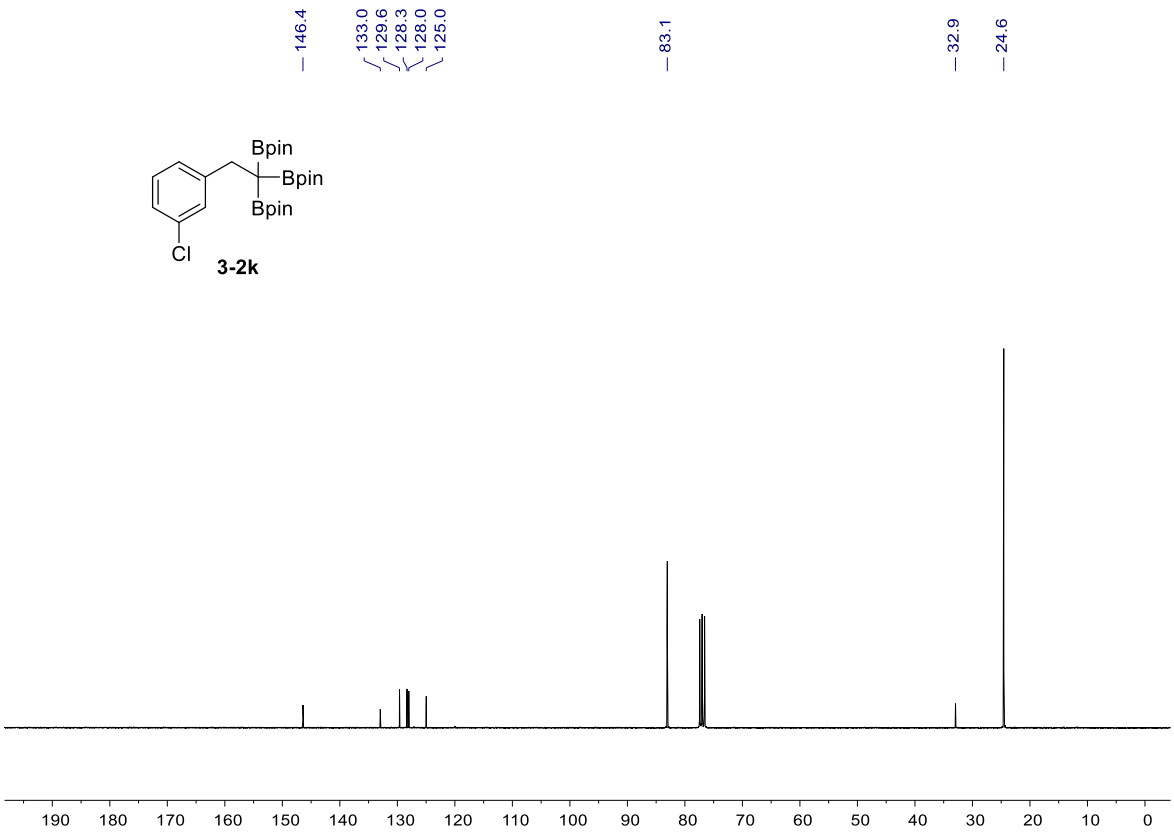


3-2j

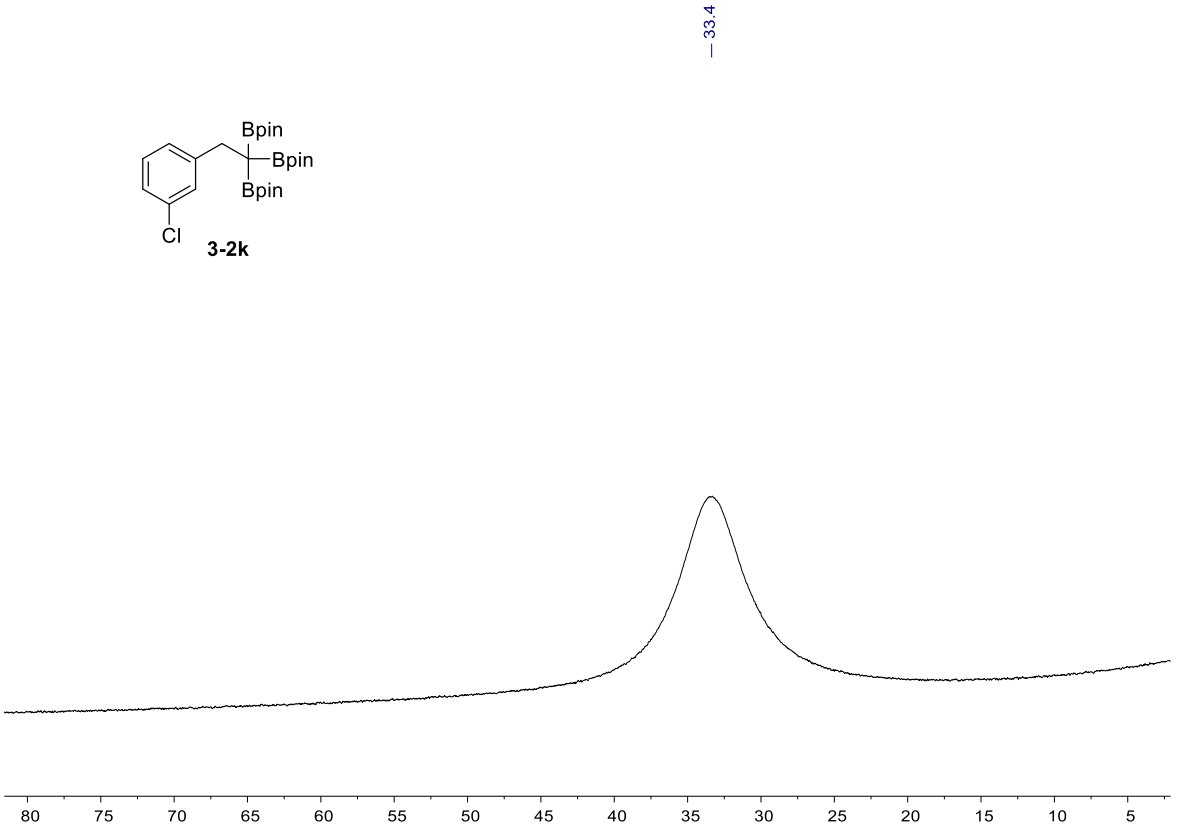
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2k**



^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **3-2k**

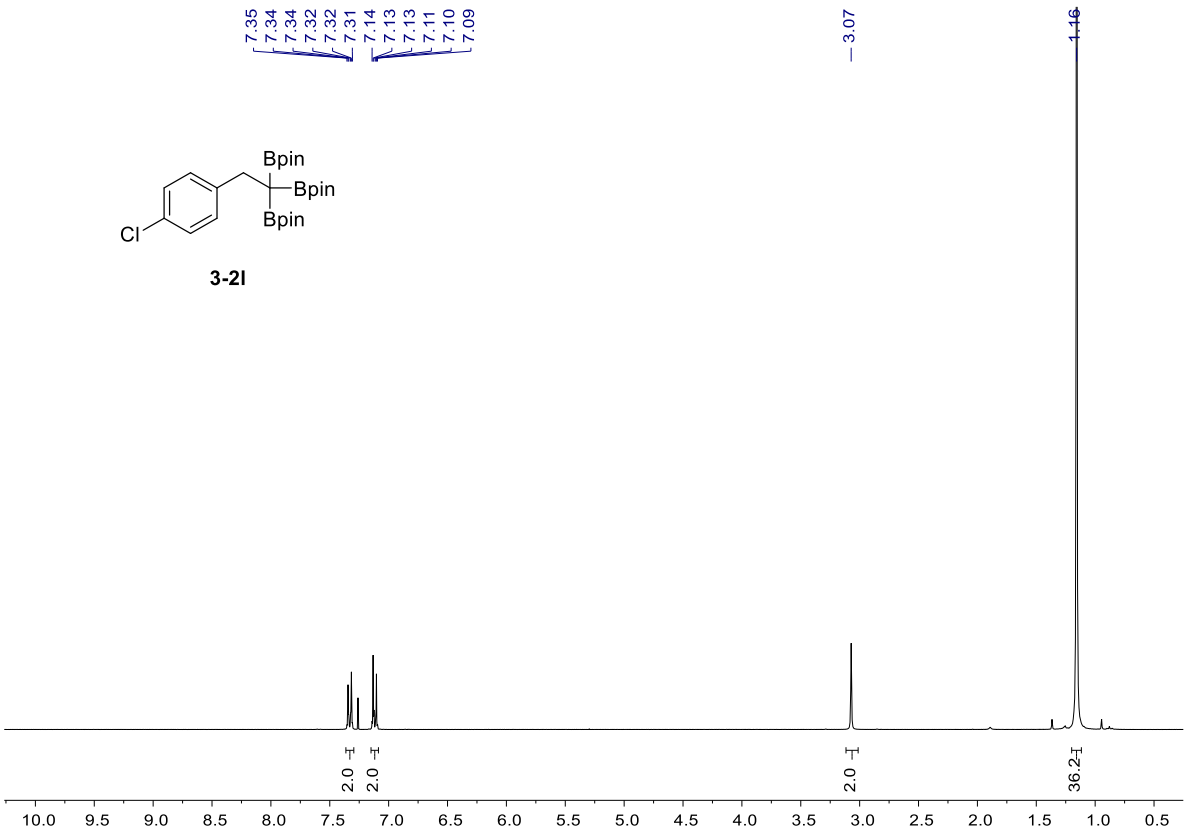


^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2k**



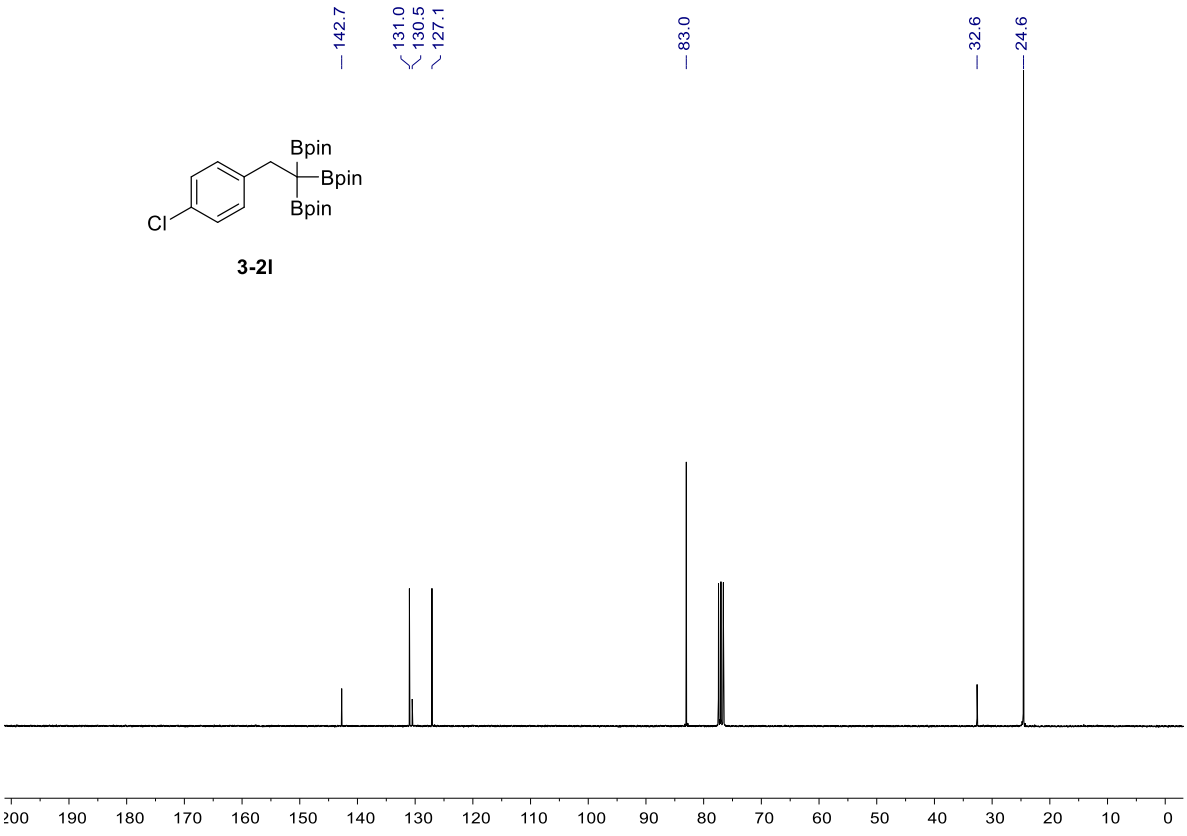
3-2k

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2l**



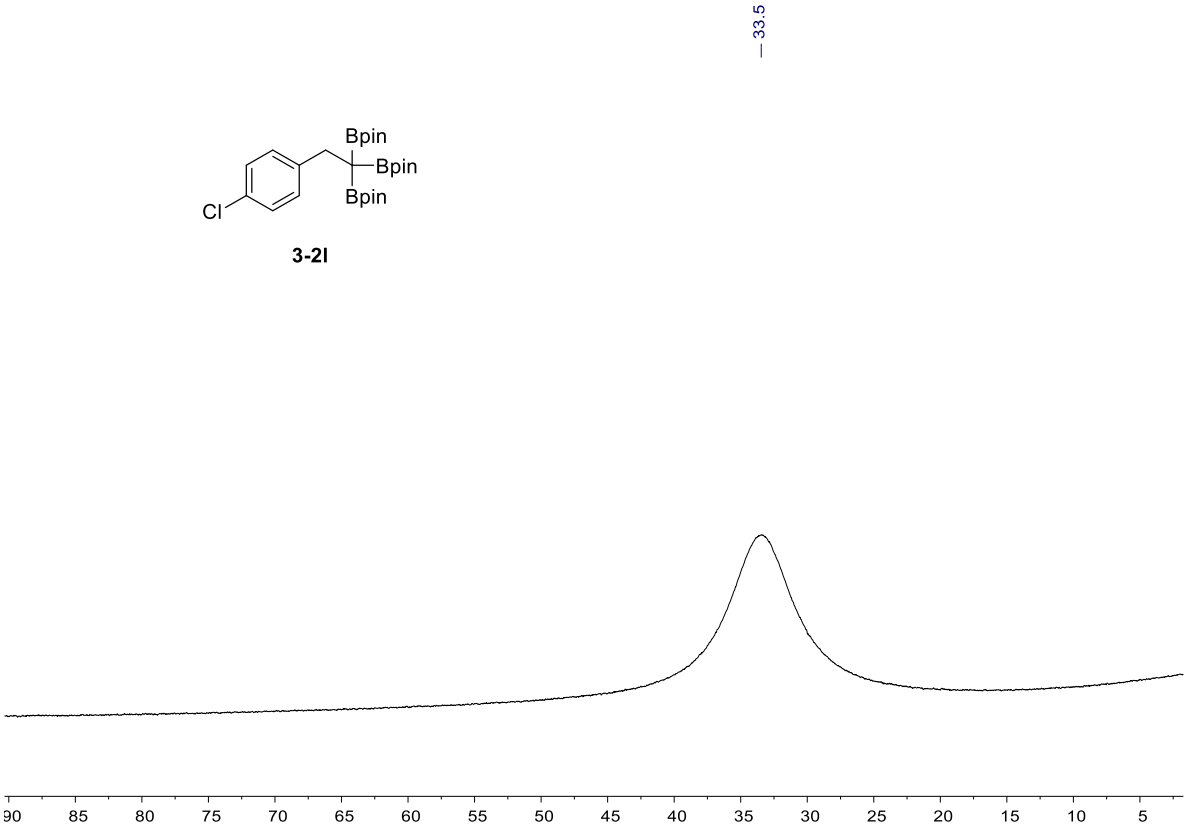
3-2l

$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-2l**



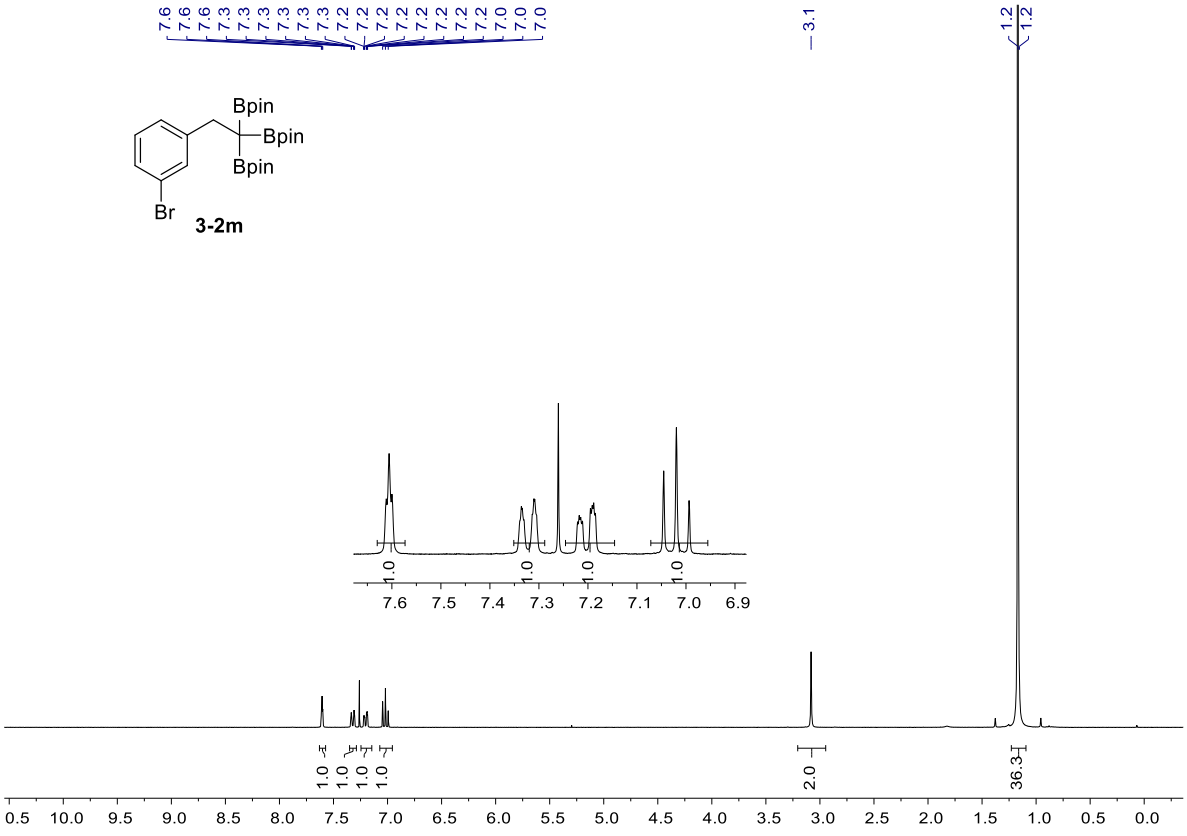
3-2l

^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2l**

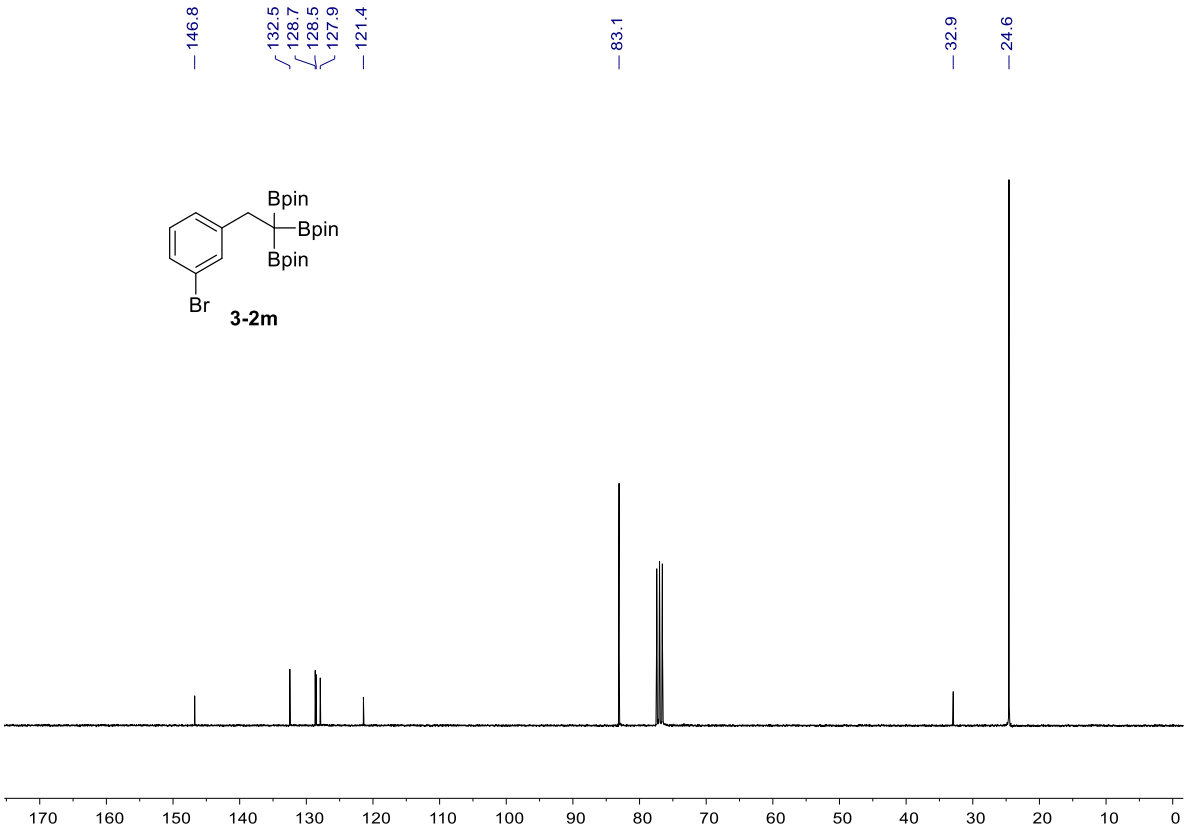


3-2l

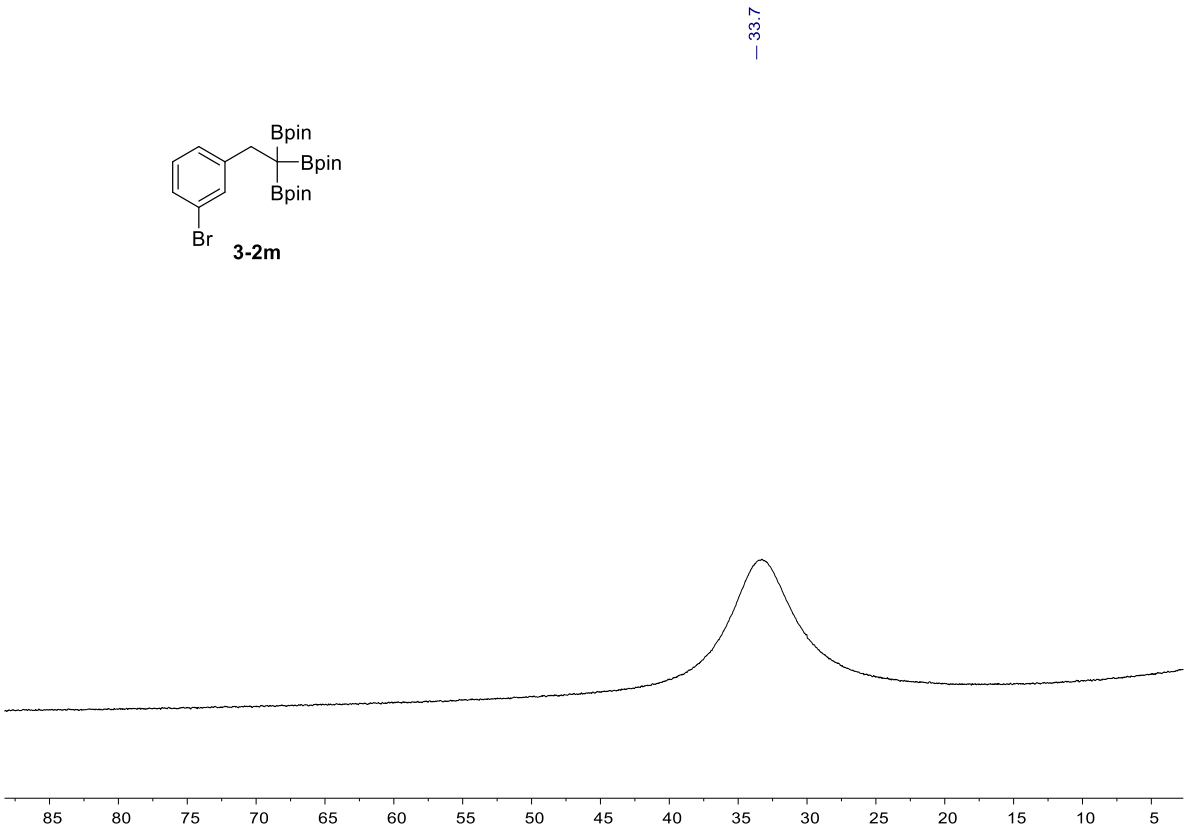
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2m**



$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-2m**

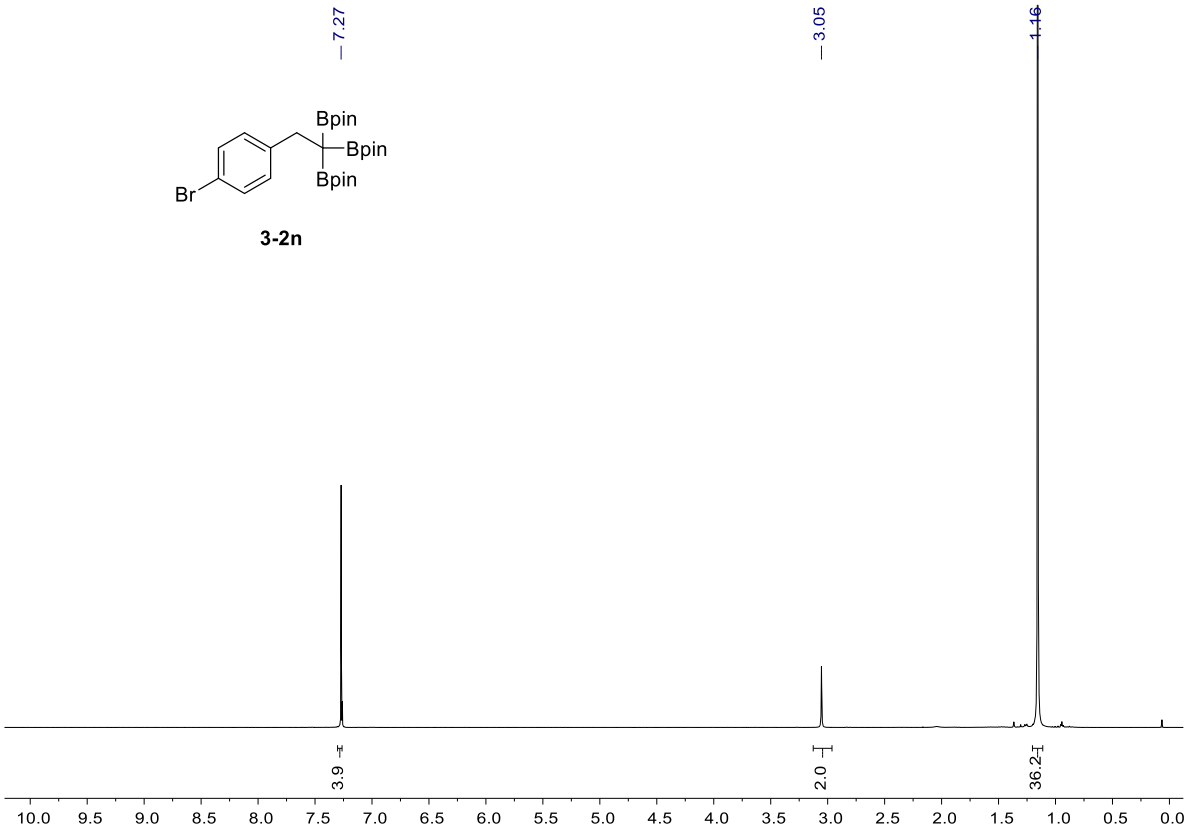


^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2m**



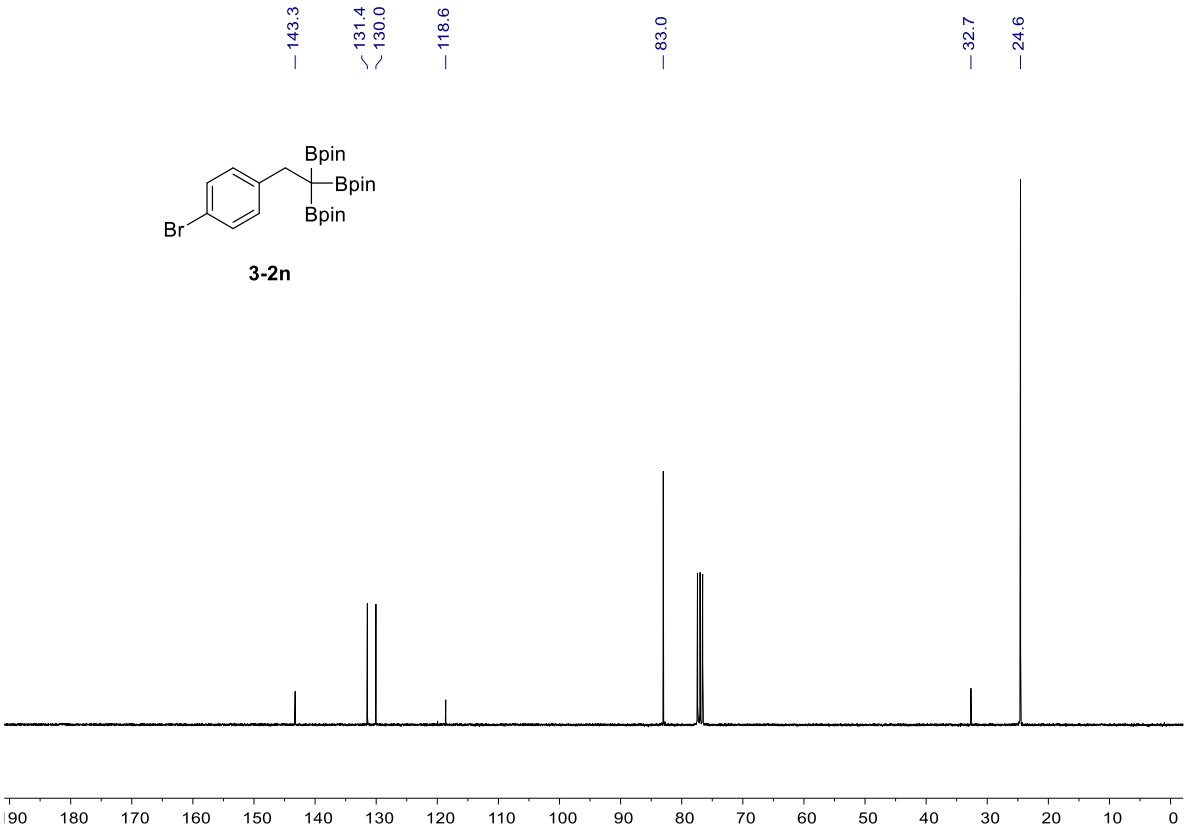
3-2m

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2n**

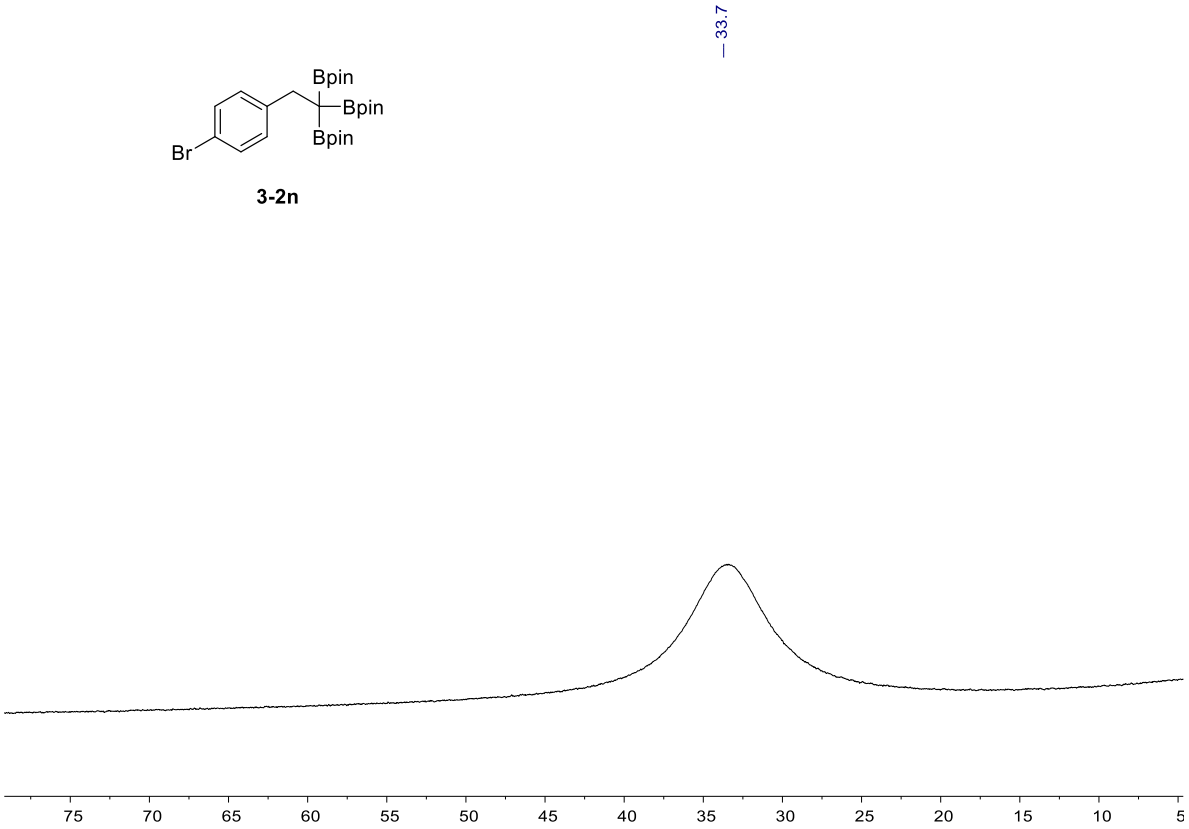


3-2n

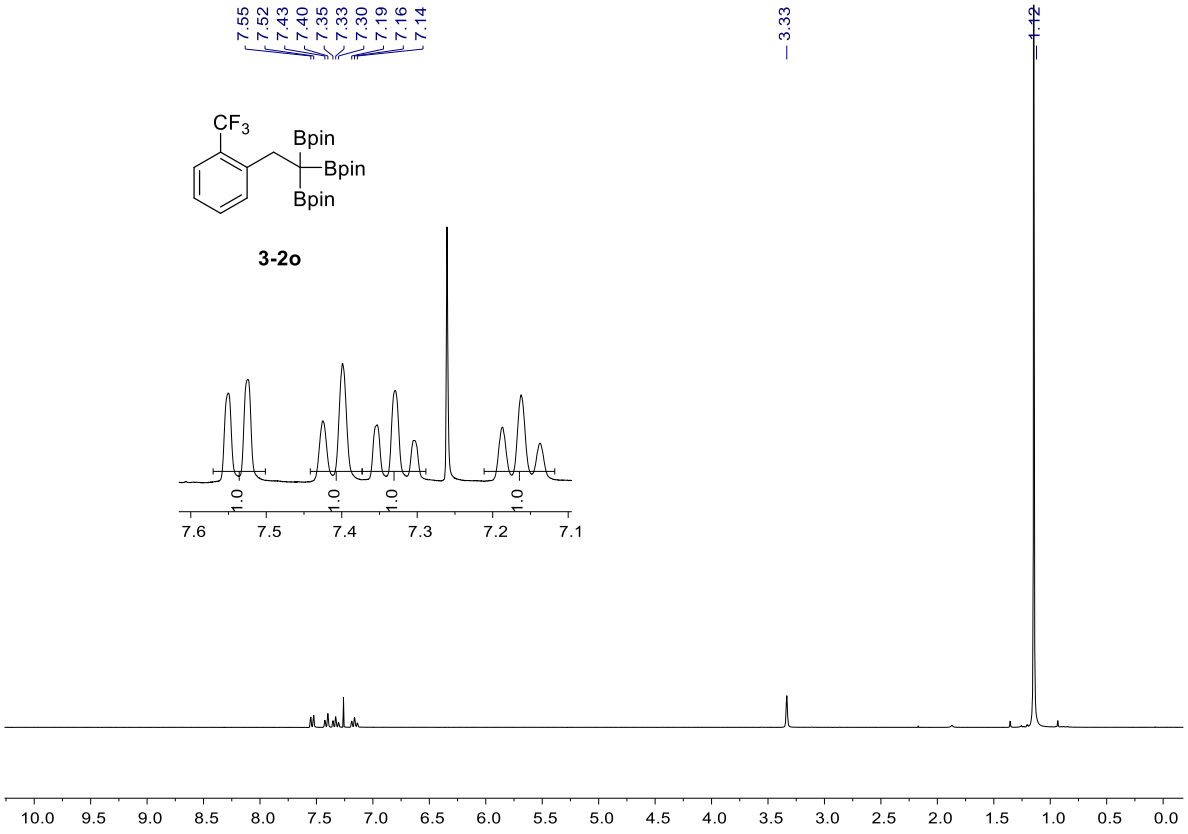
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-2n**



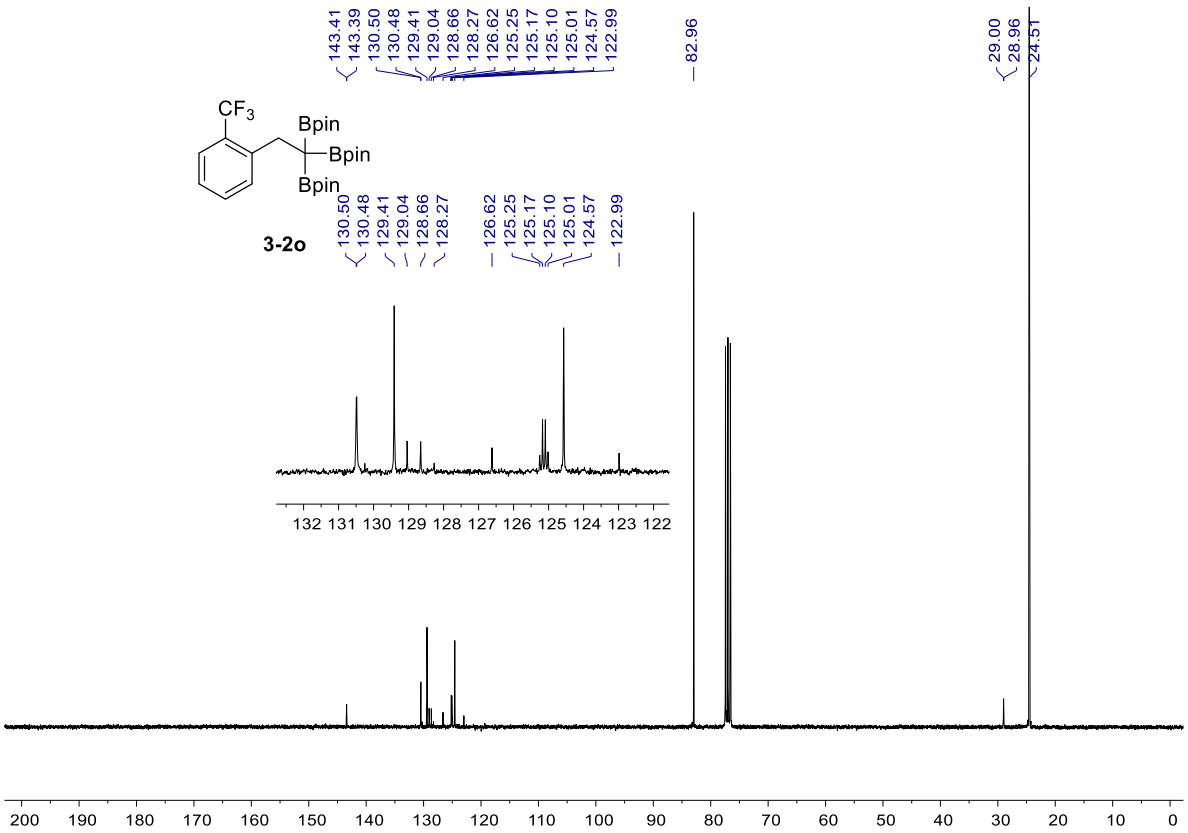
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2n**



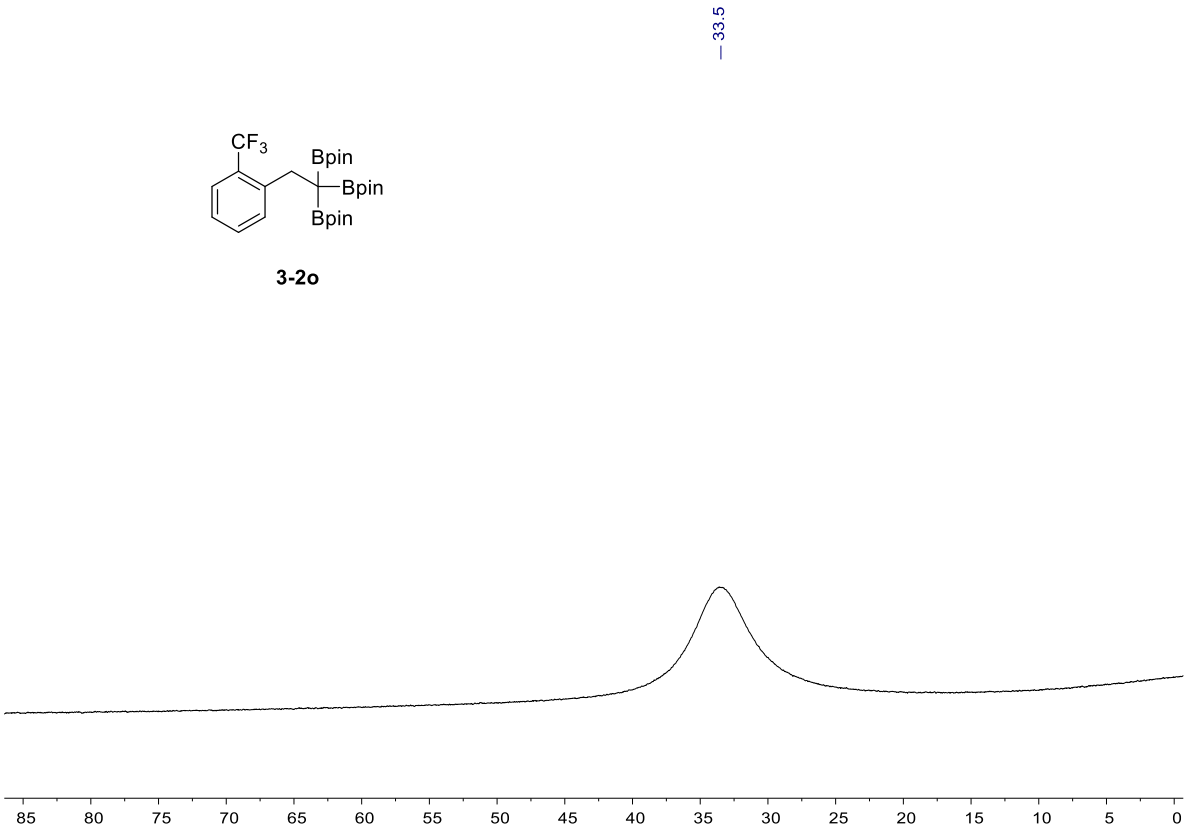
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2o**



^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **3-2o**

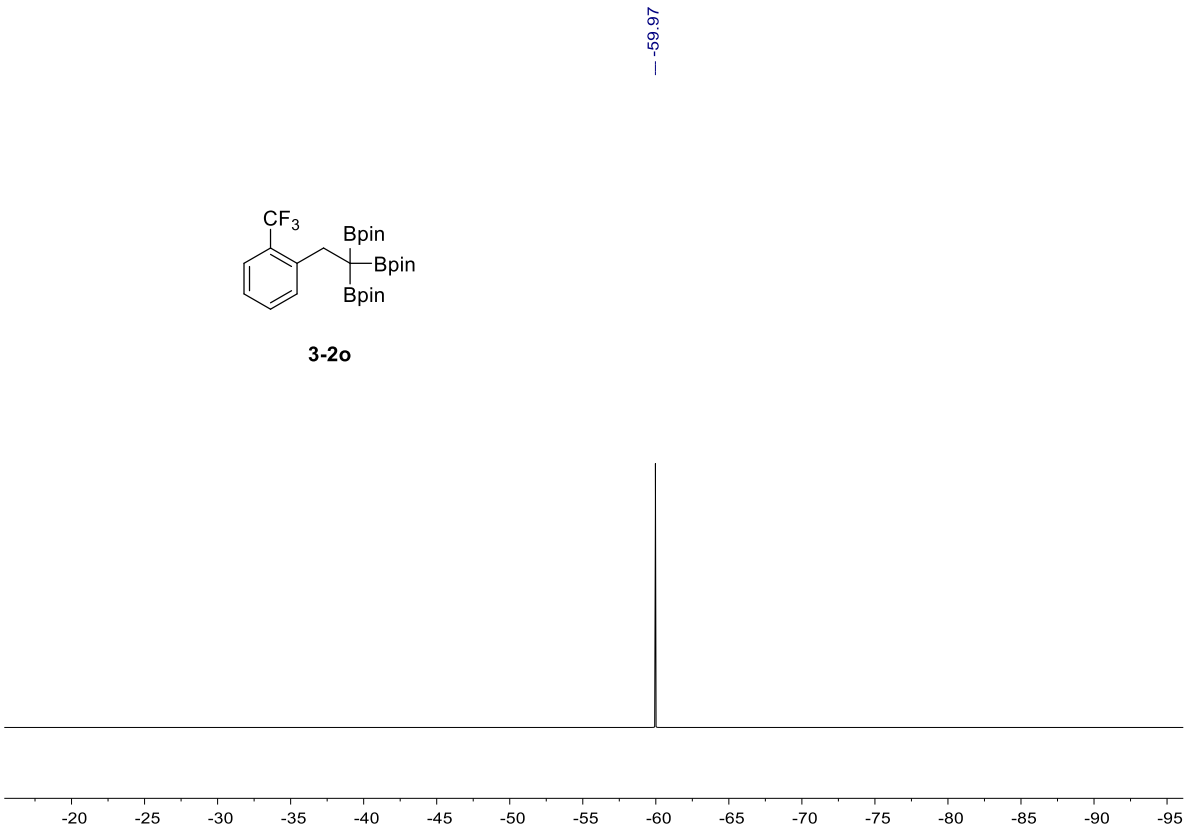


^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2o**



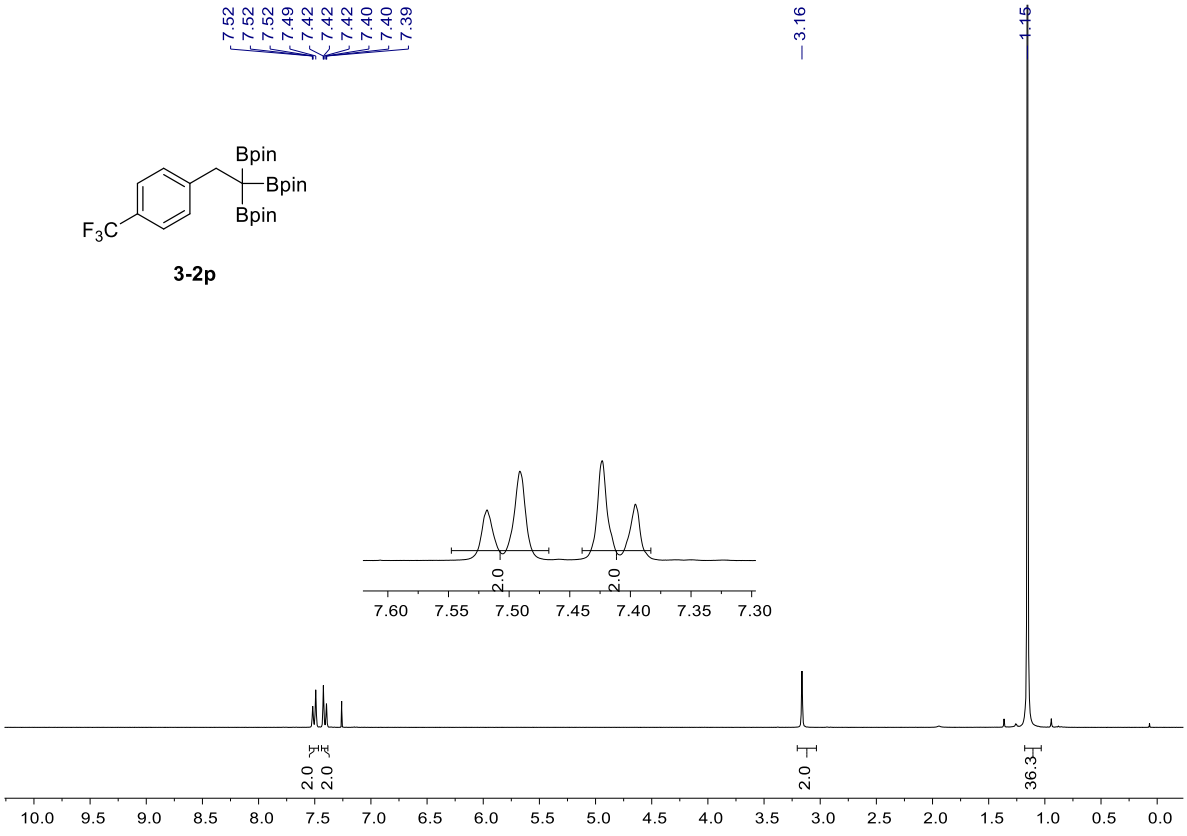
3-2o

^{19}F NMR spectrum (471 MHz, $CDCl_3$) of **3-2o**

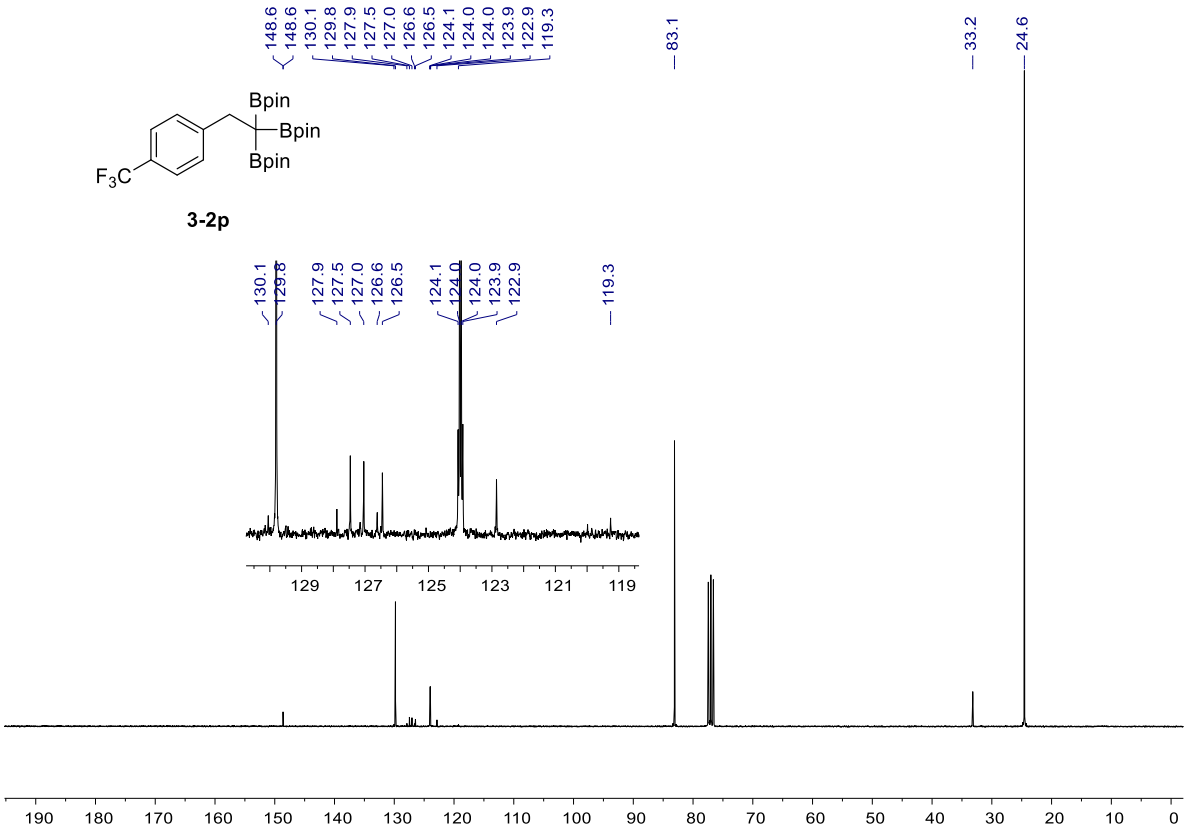


3-2o

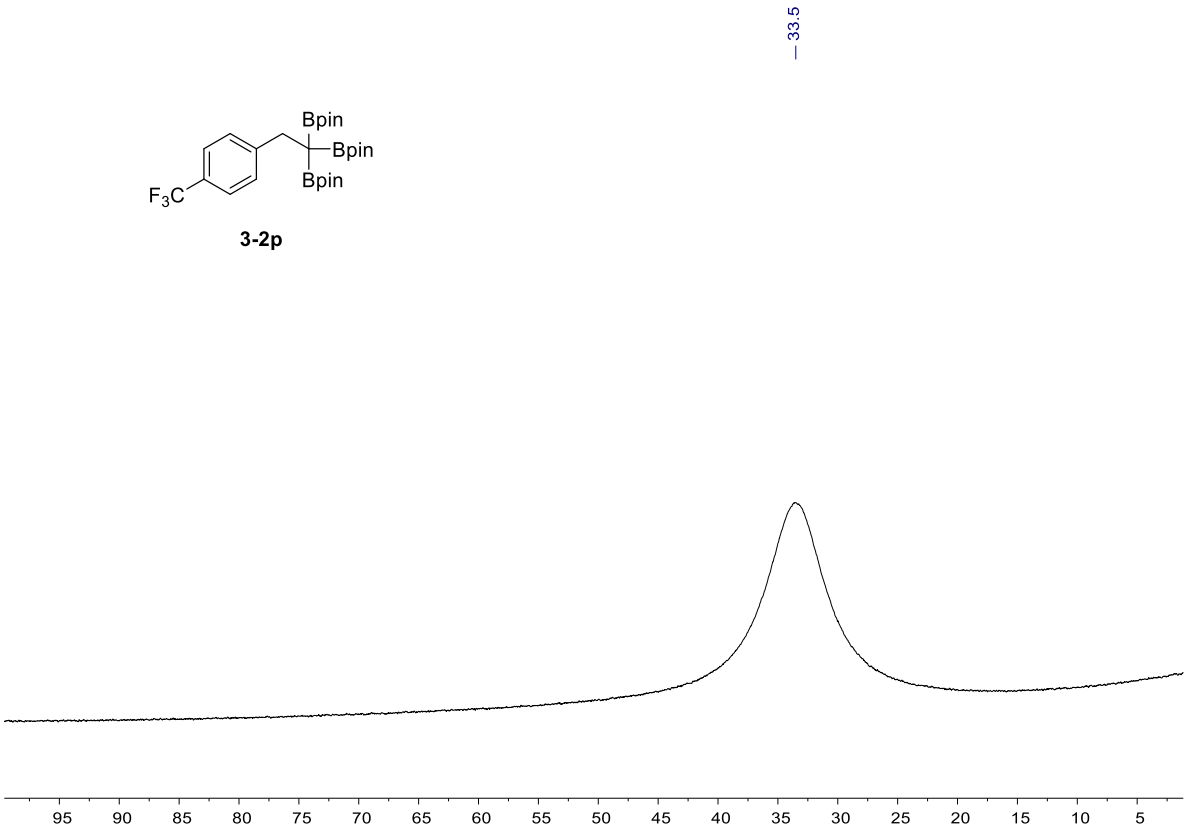
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2p**



^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **3-2p**

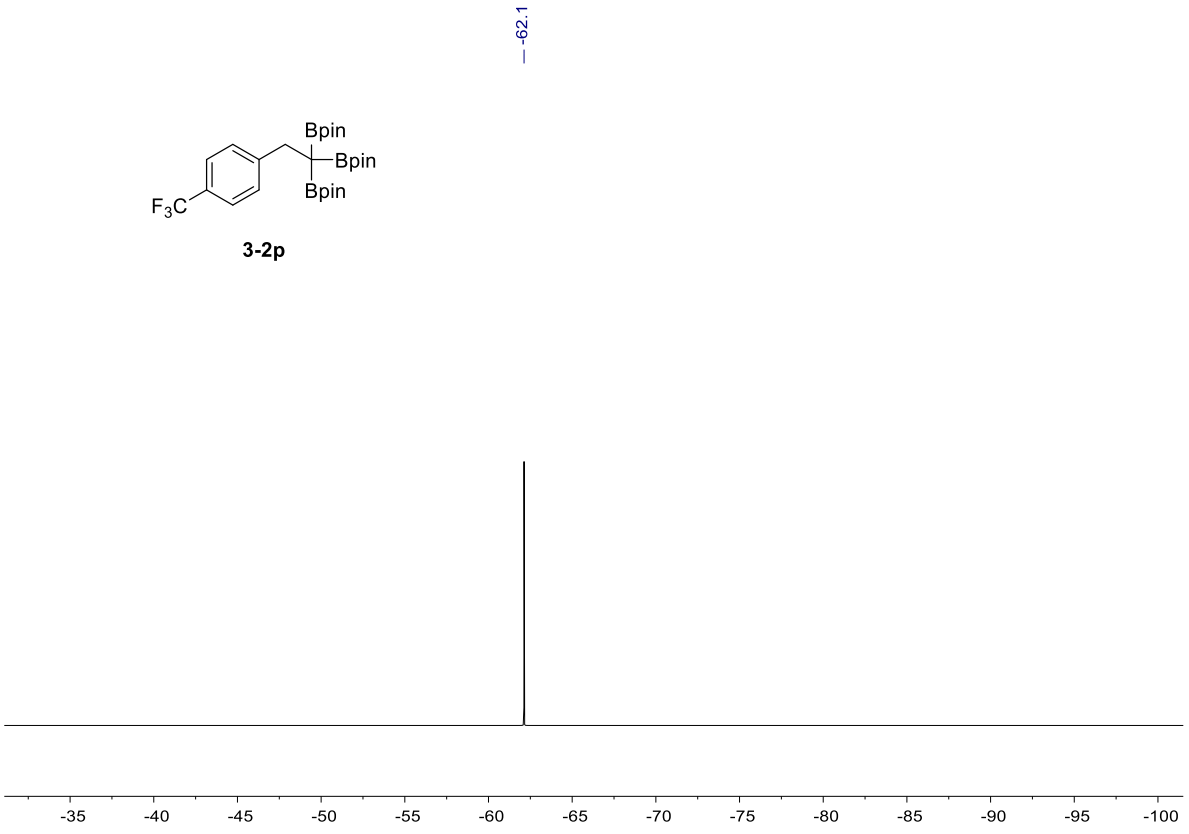


^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2p**



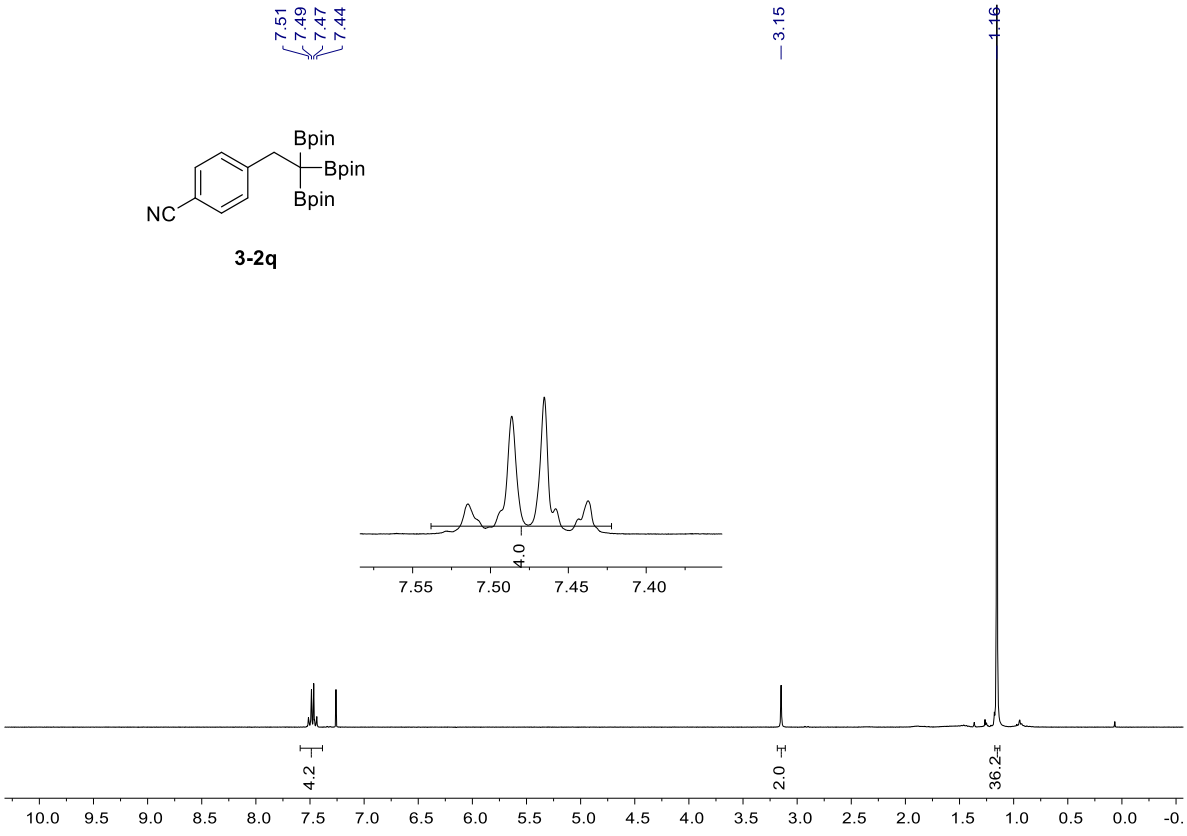
3-2p

^{19}F NMR spectrum (471 MHz, $CDCl_3$) of **3-2p**

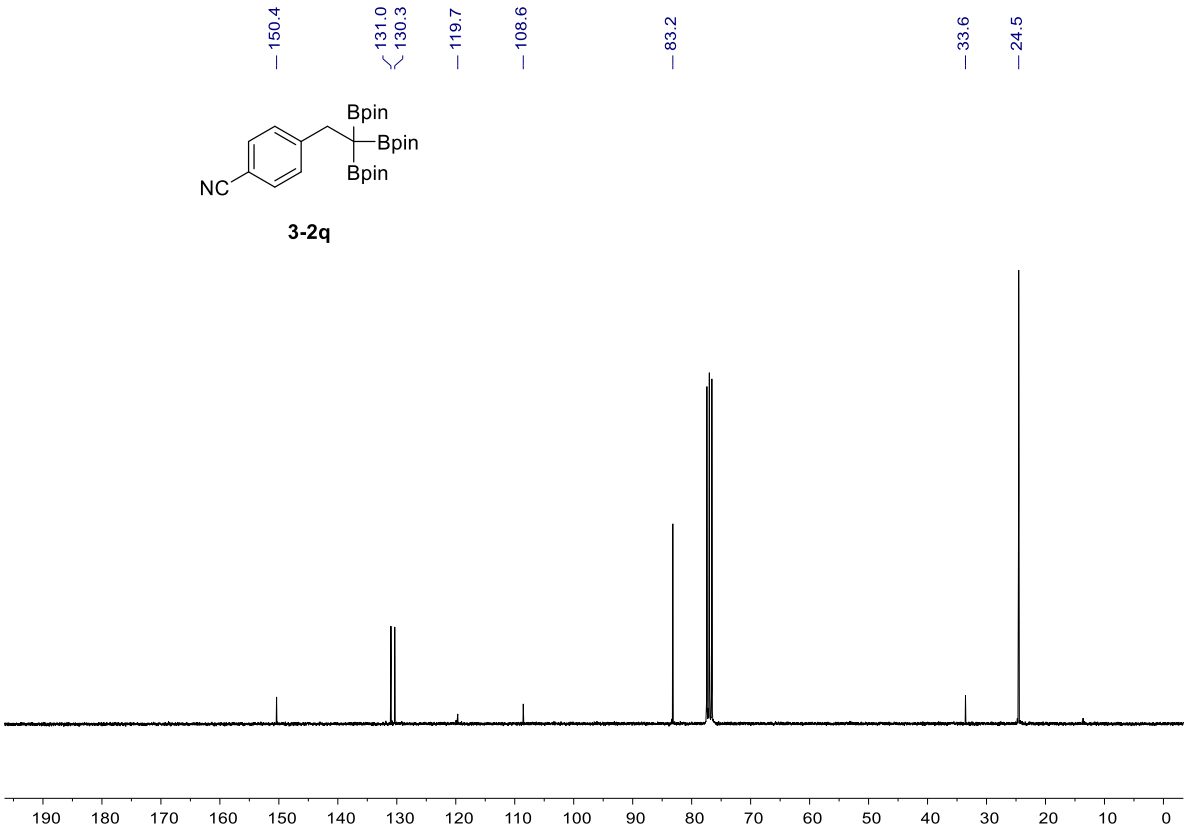


3-2p

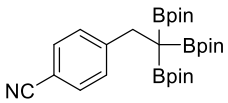
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2q**



^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **3-2q**

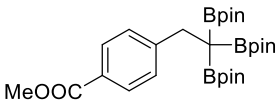


^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2q**



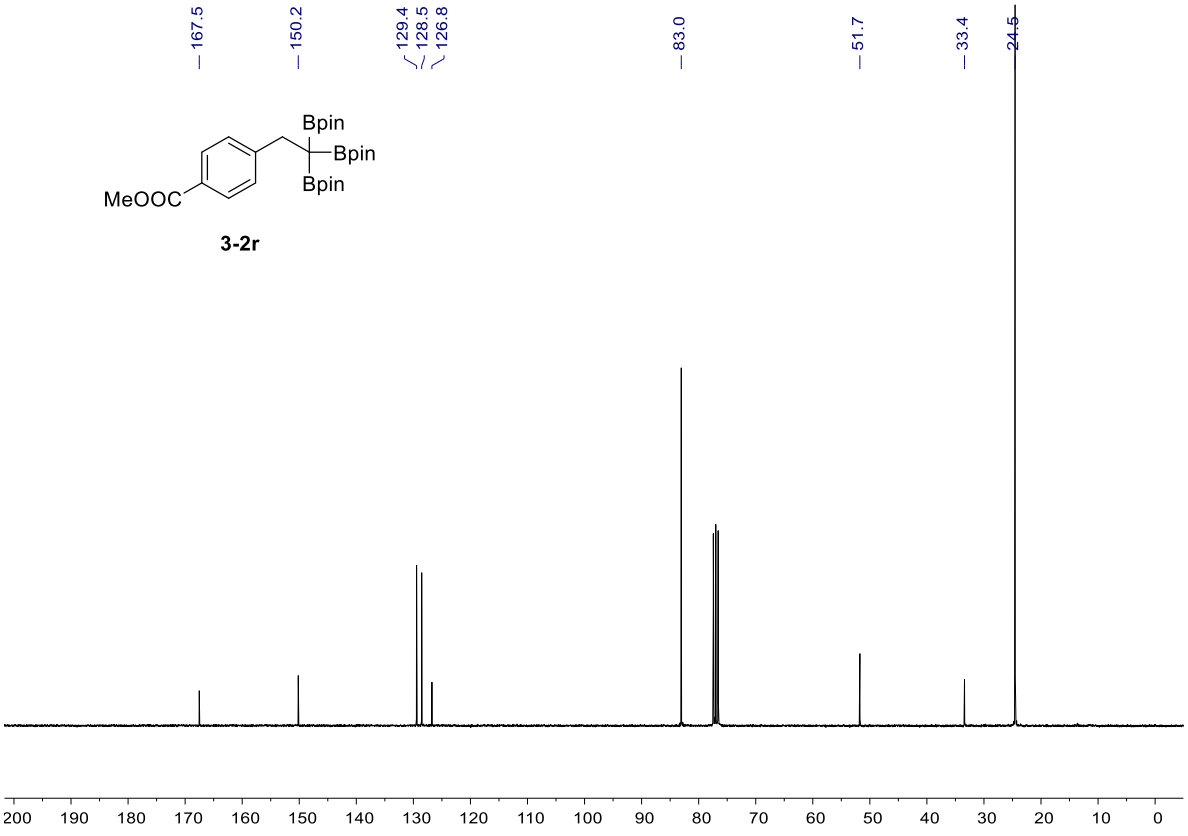
3-2q

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2r**



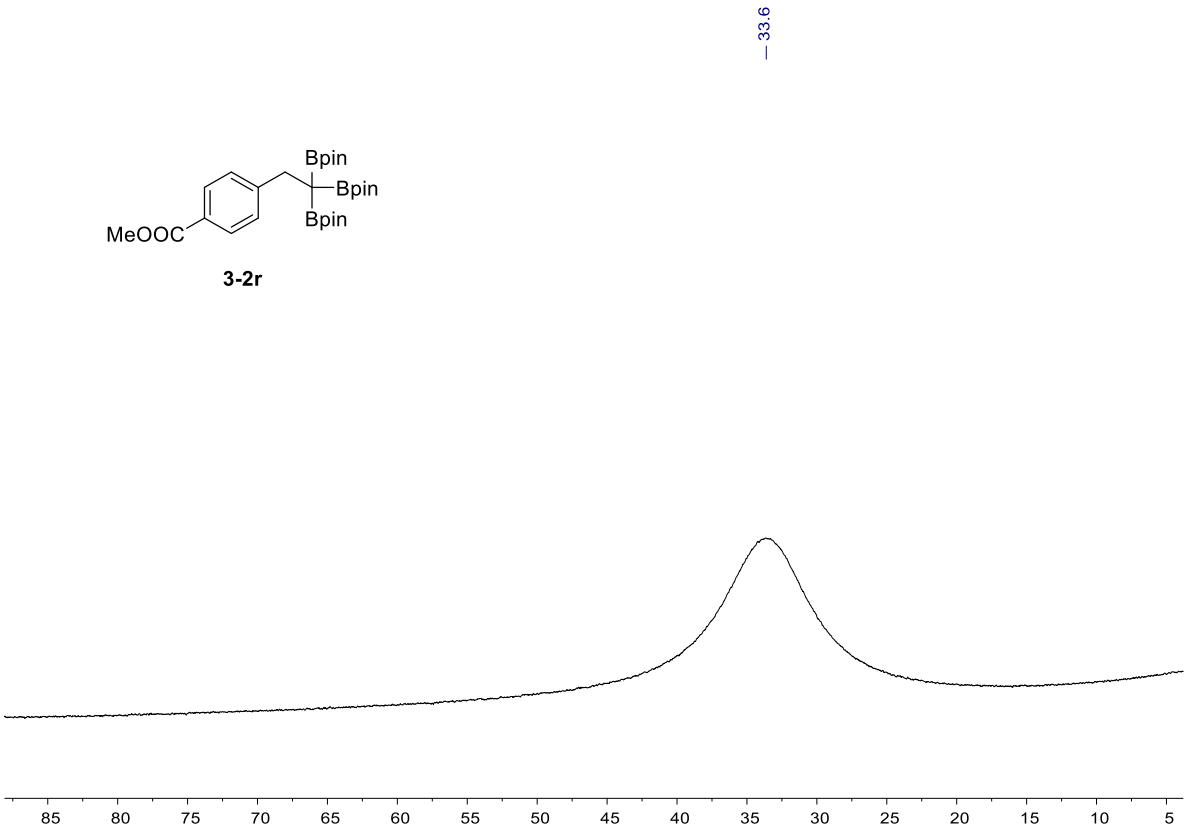
3-2r

$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-2r**



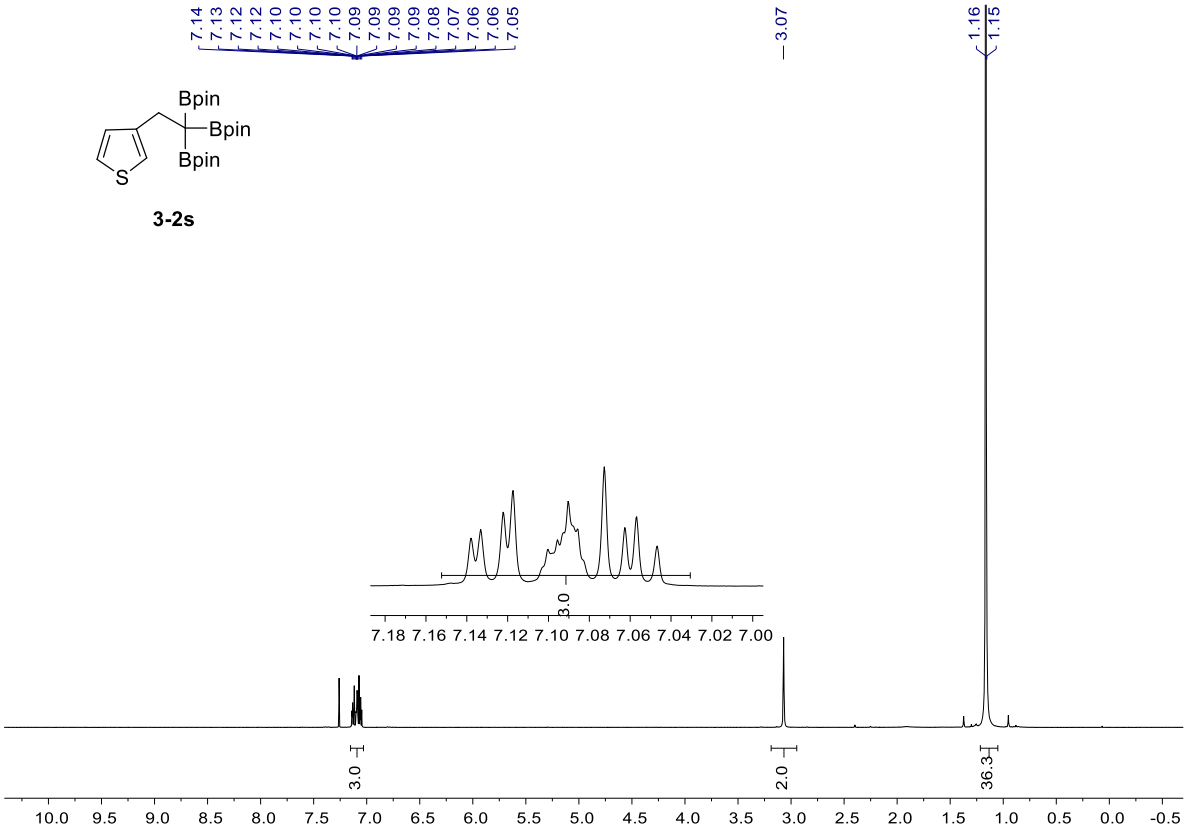
3-2r

^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2r**

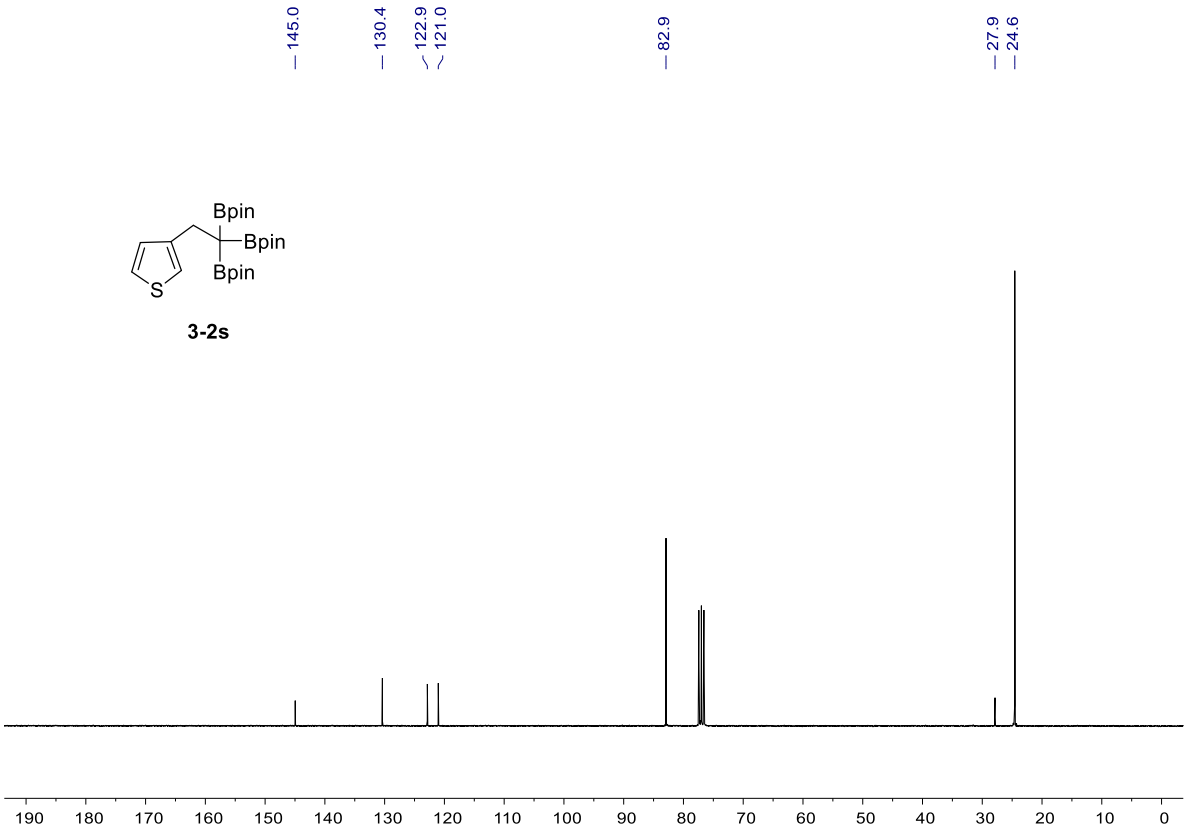


3-2r

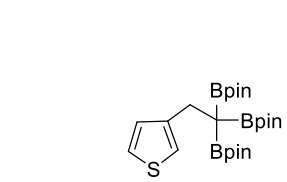
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2s**



^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **3-2s**

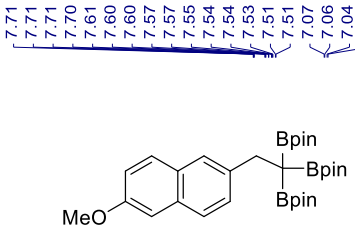


^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2s**



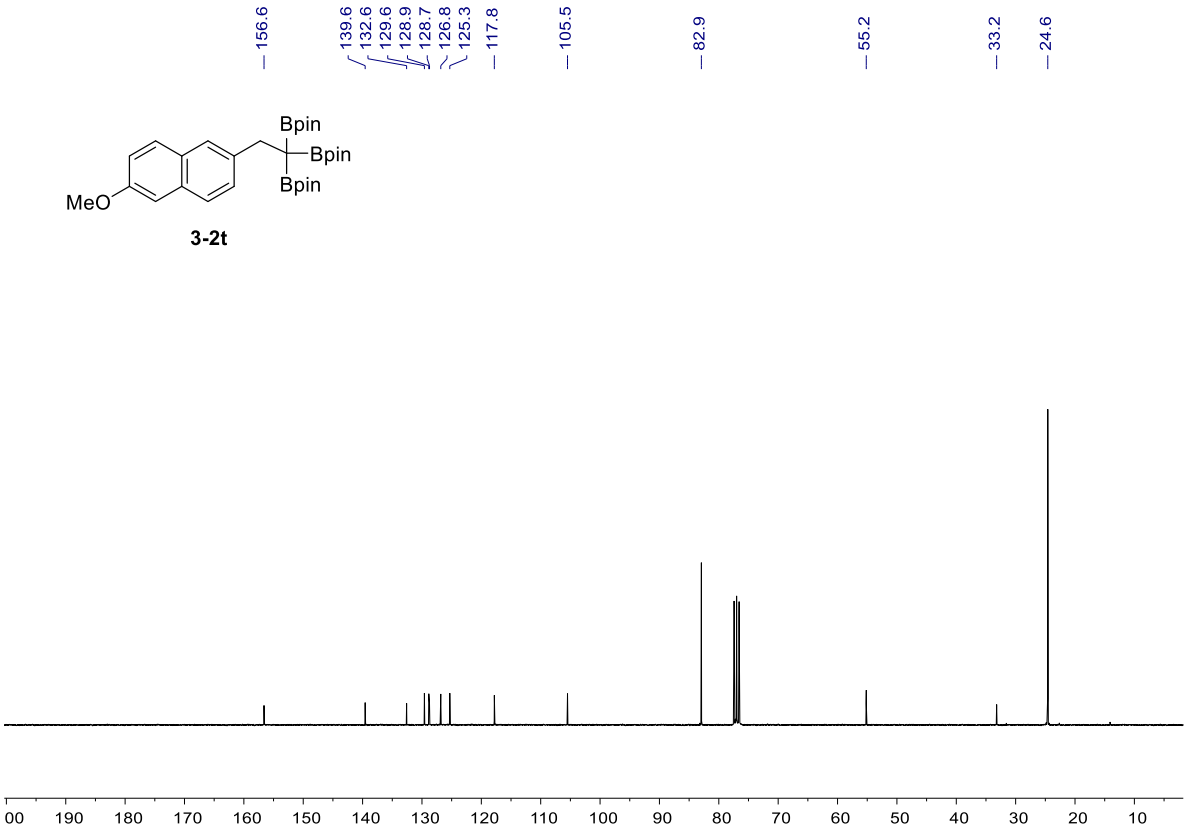
3-2s

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2t**

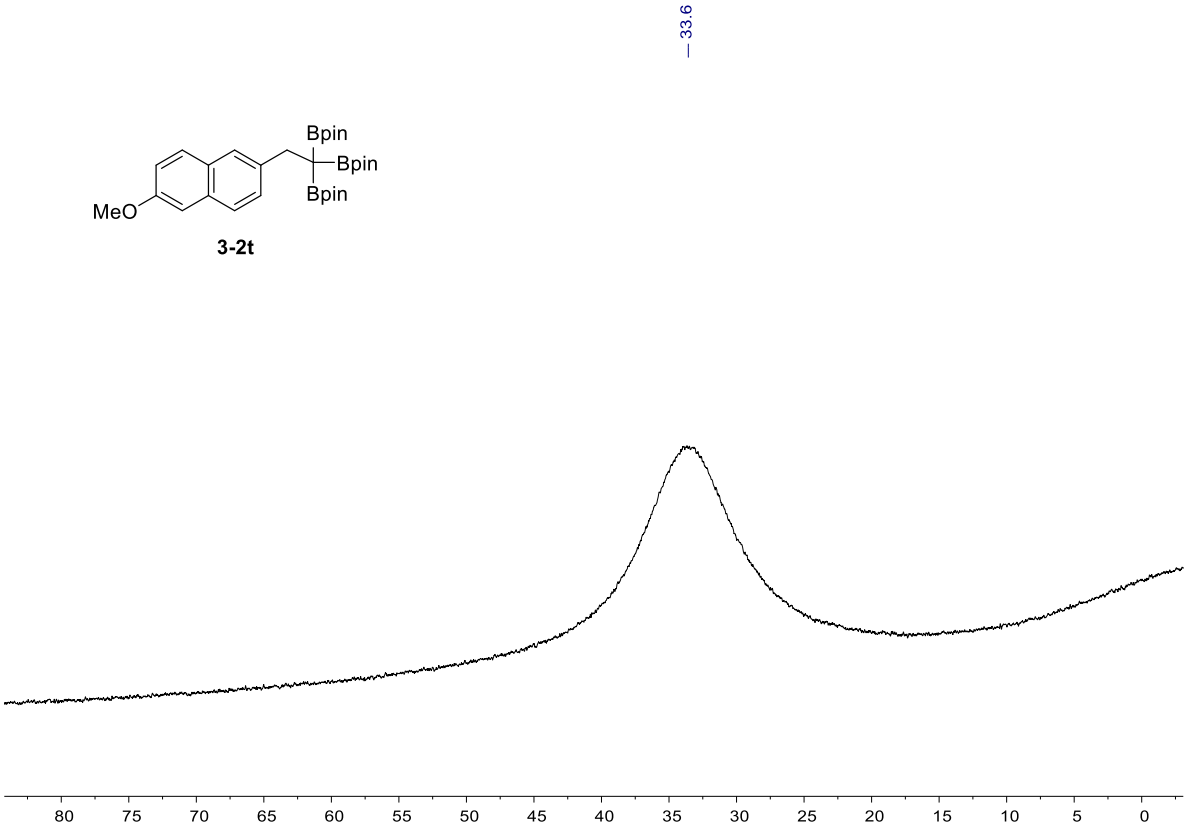


3-2t

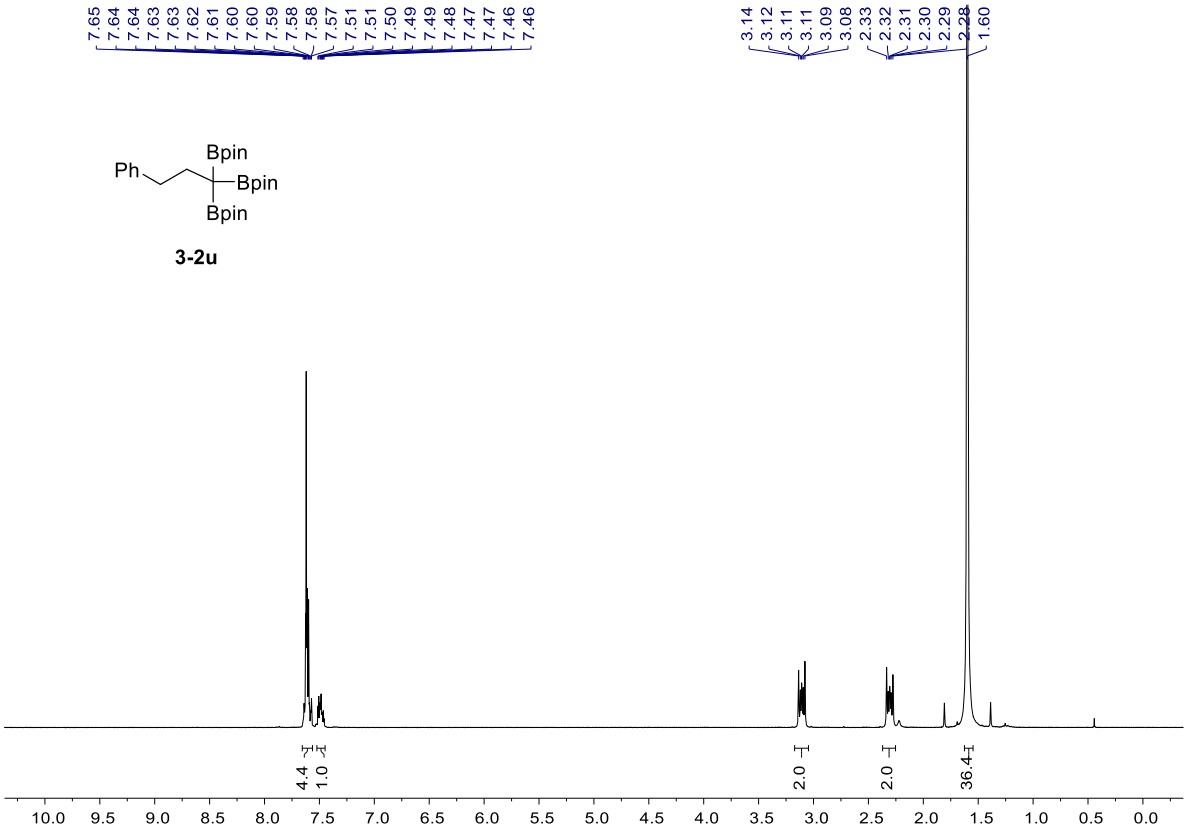
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-2t**



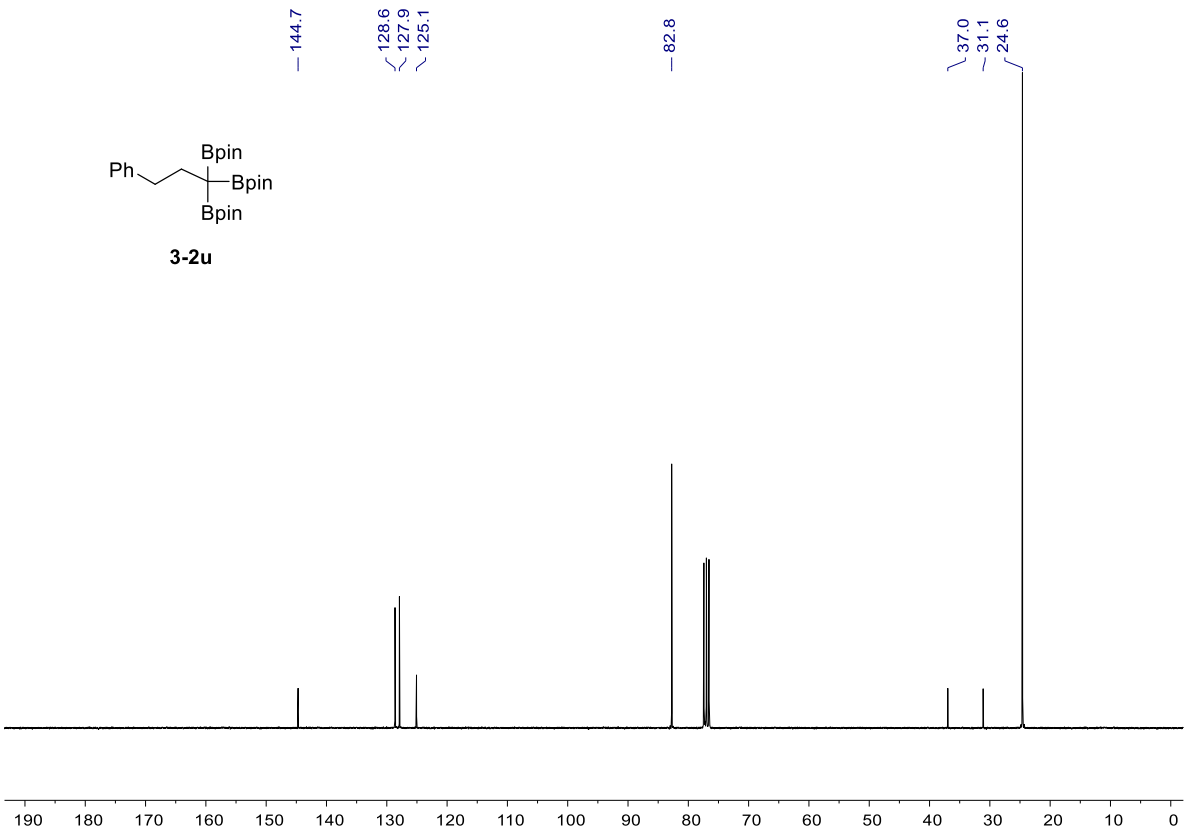
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2t**



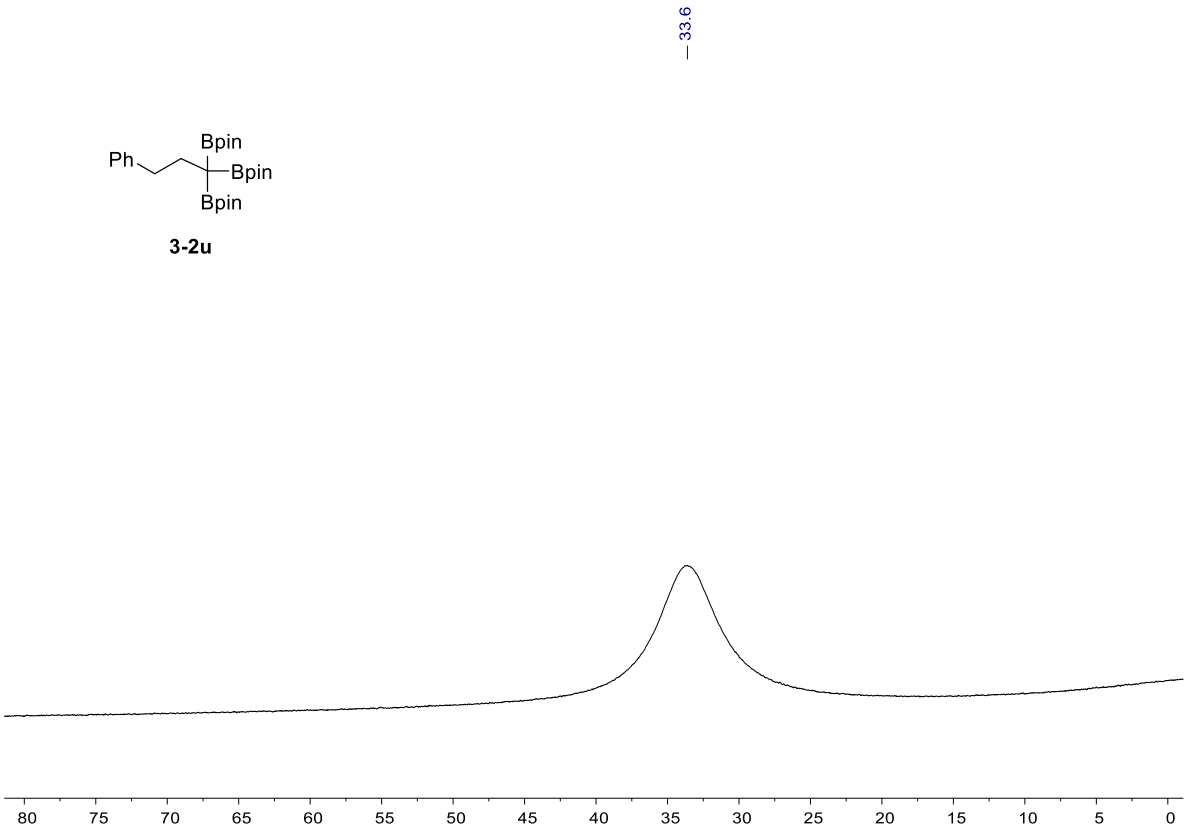
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2u**



^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **3-2u**

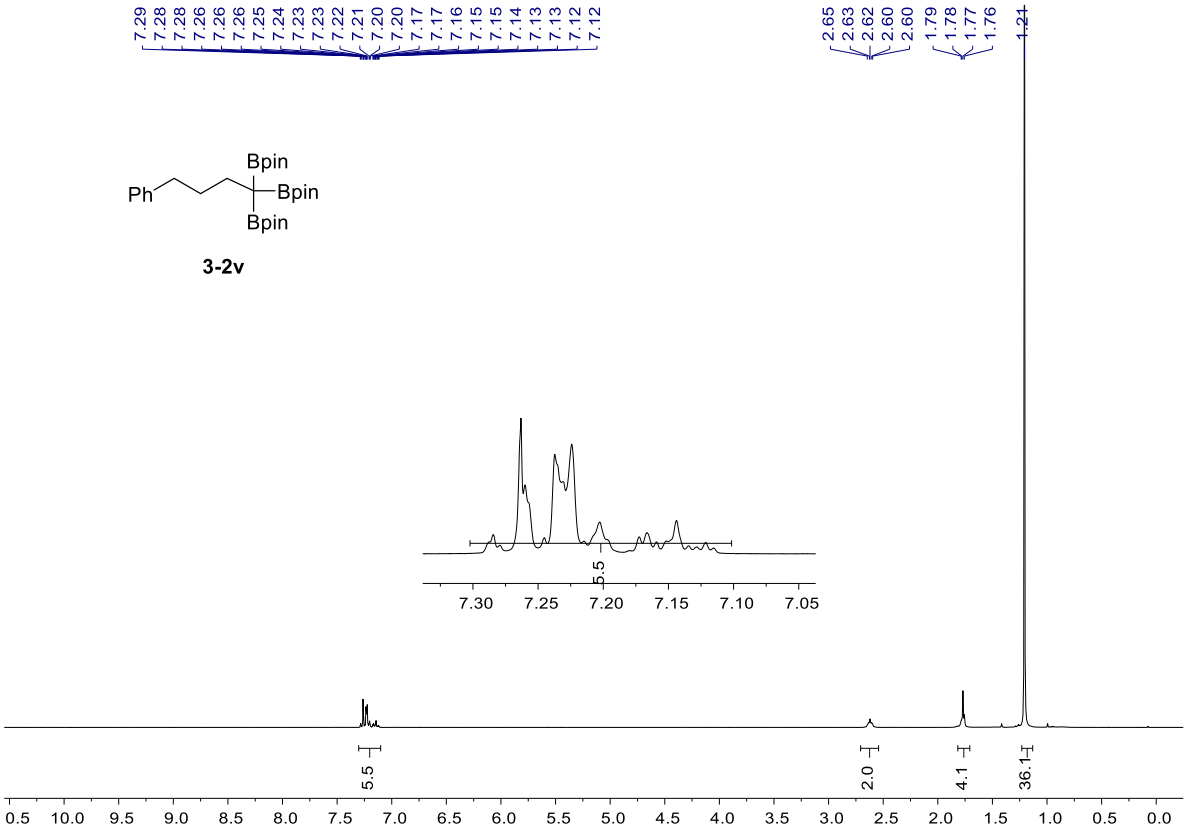


^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2u**



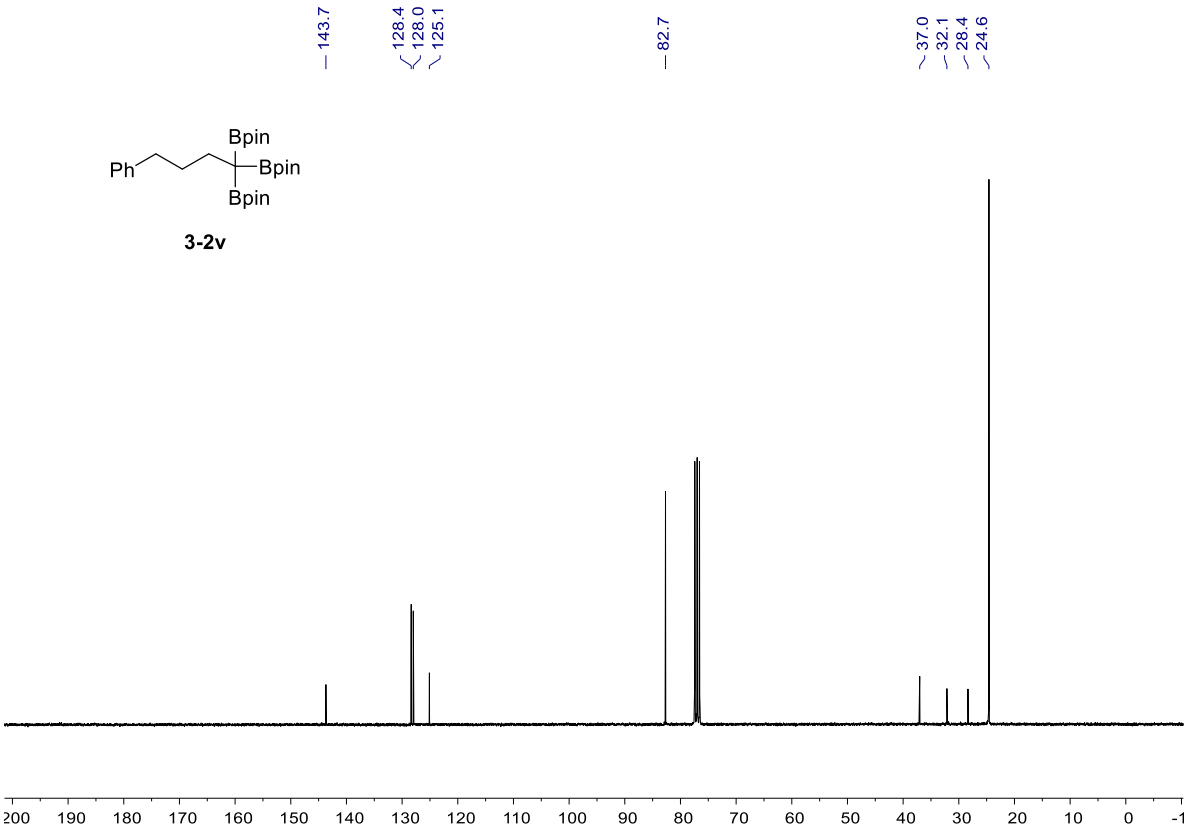
3-2u

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2v**

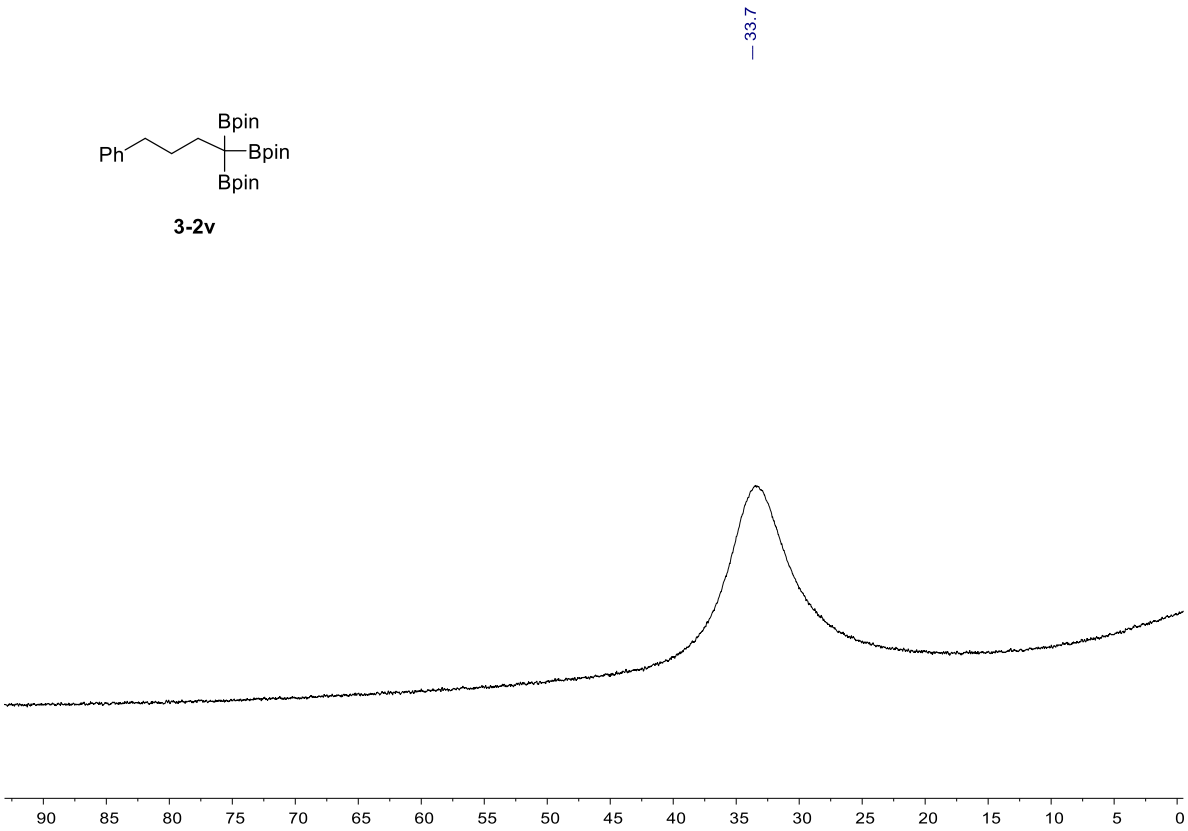


3-2v

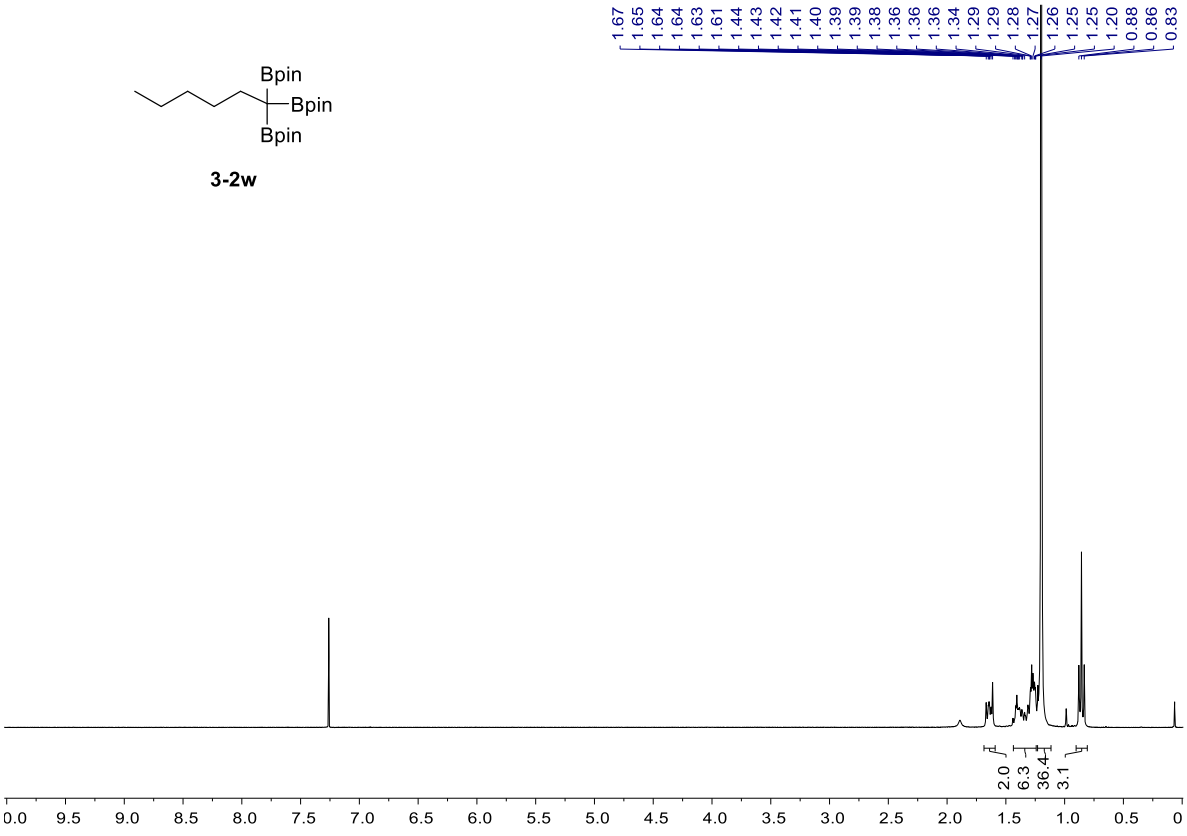
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-2v**



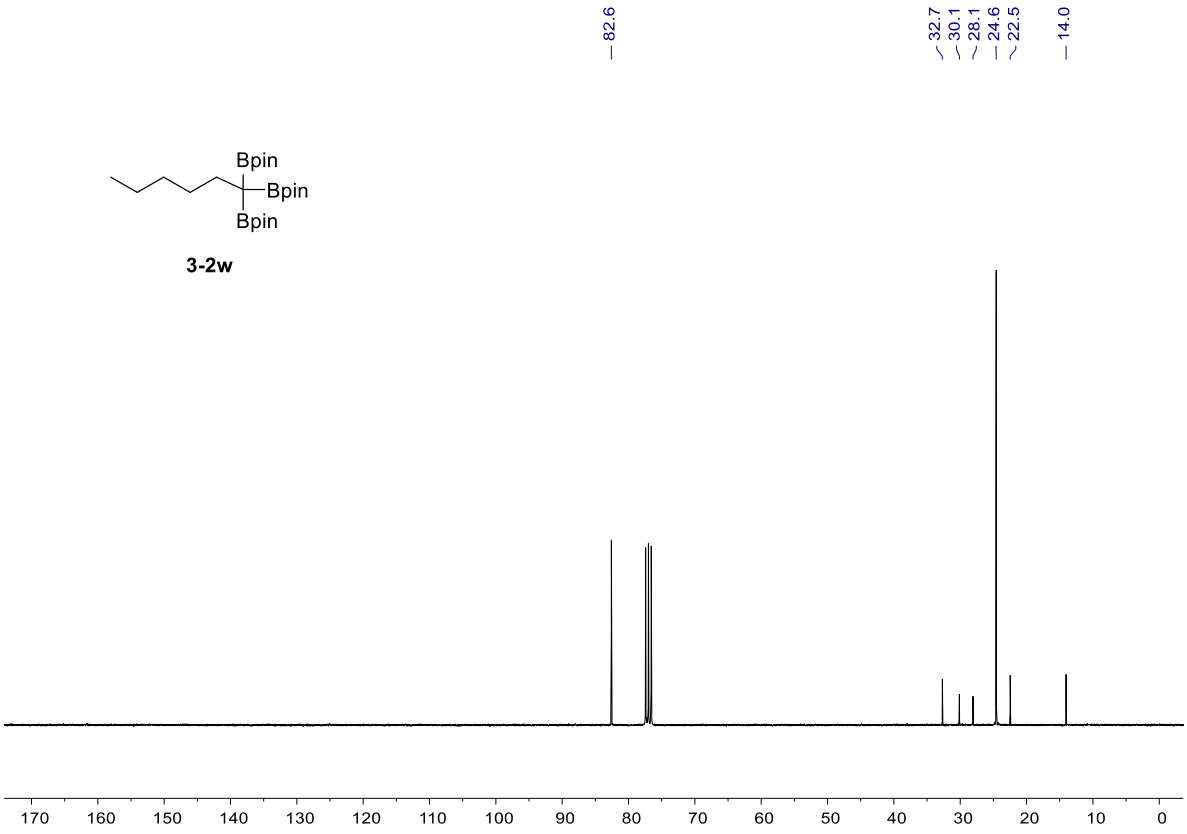
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2v**



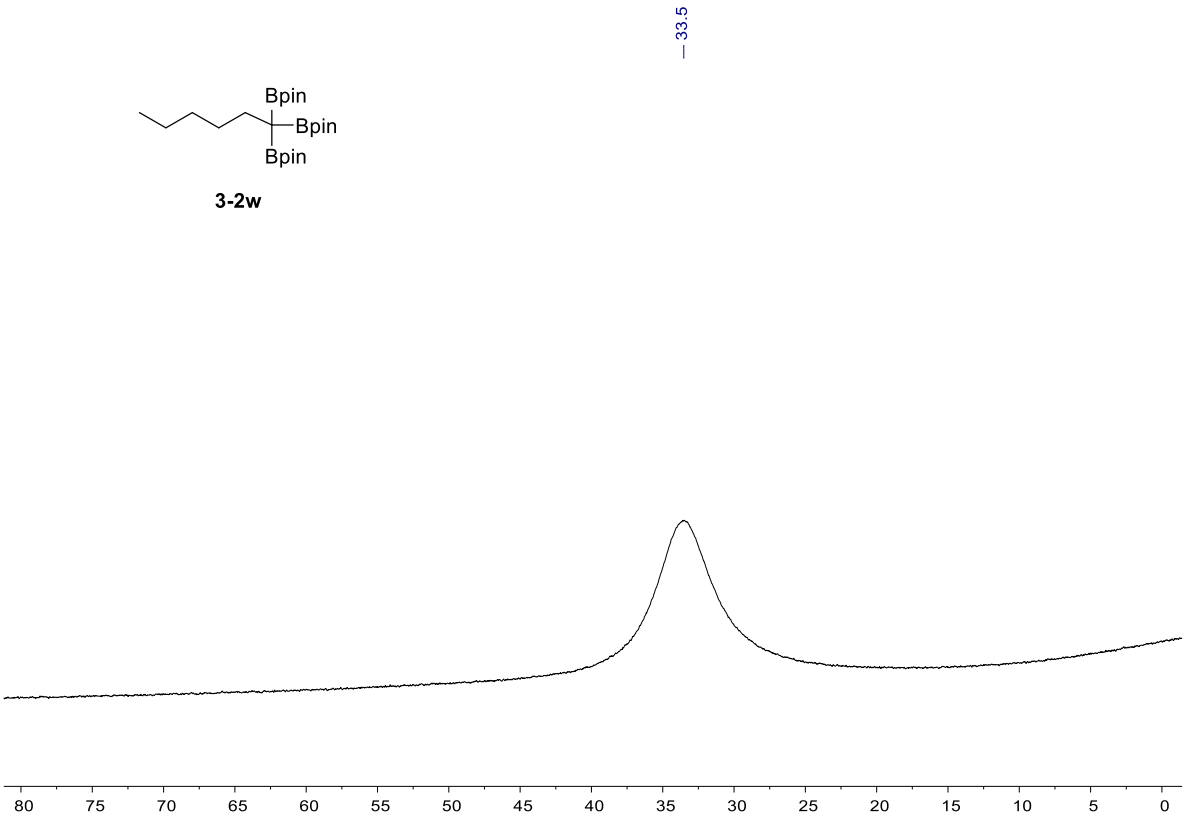
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2w**



^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **3-2w**

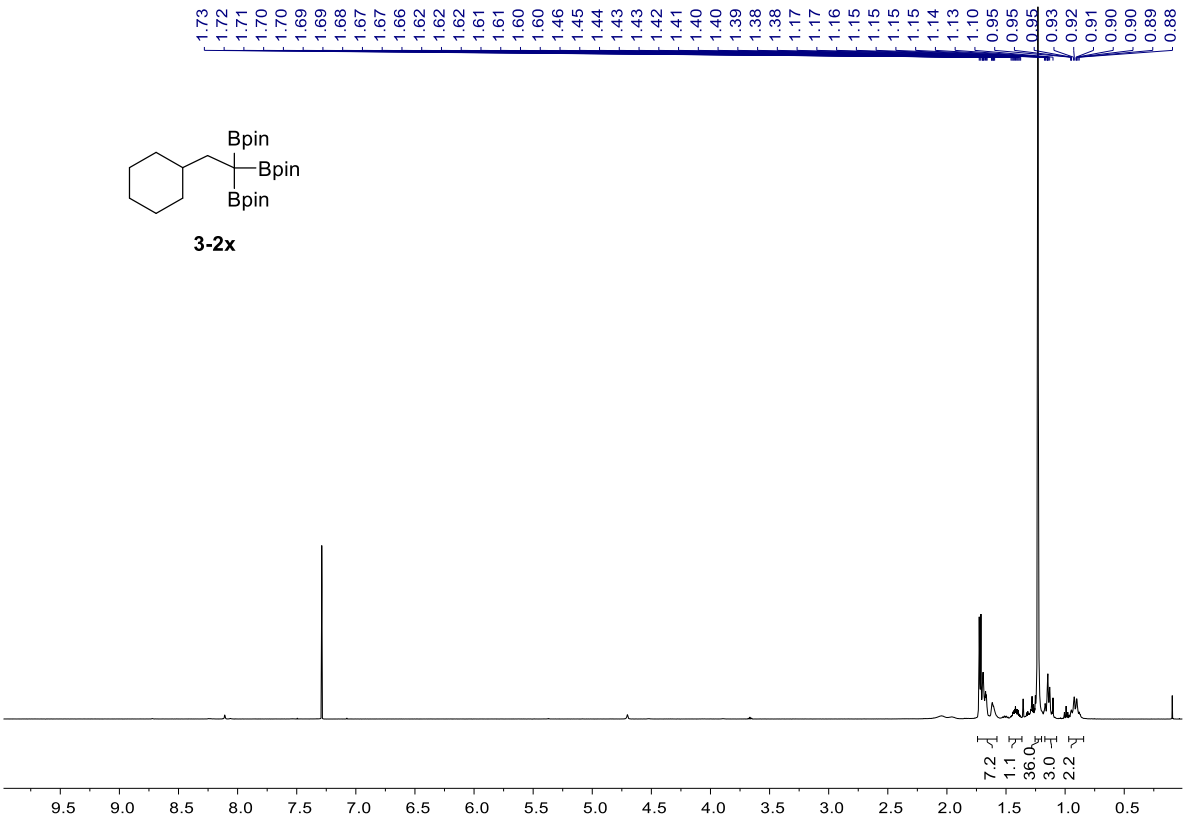


^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2w**



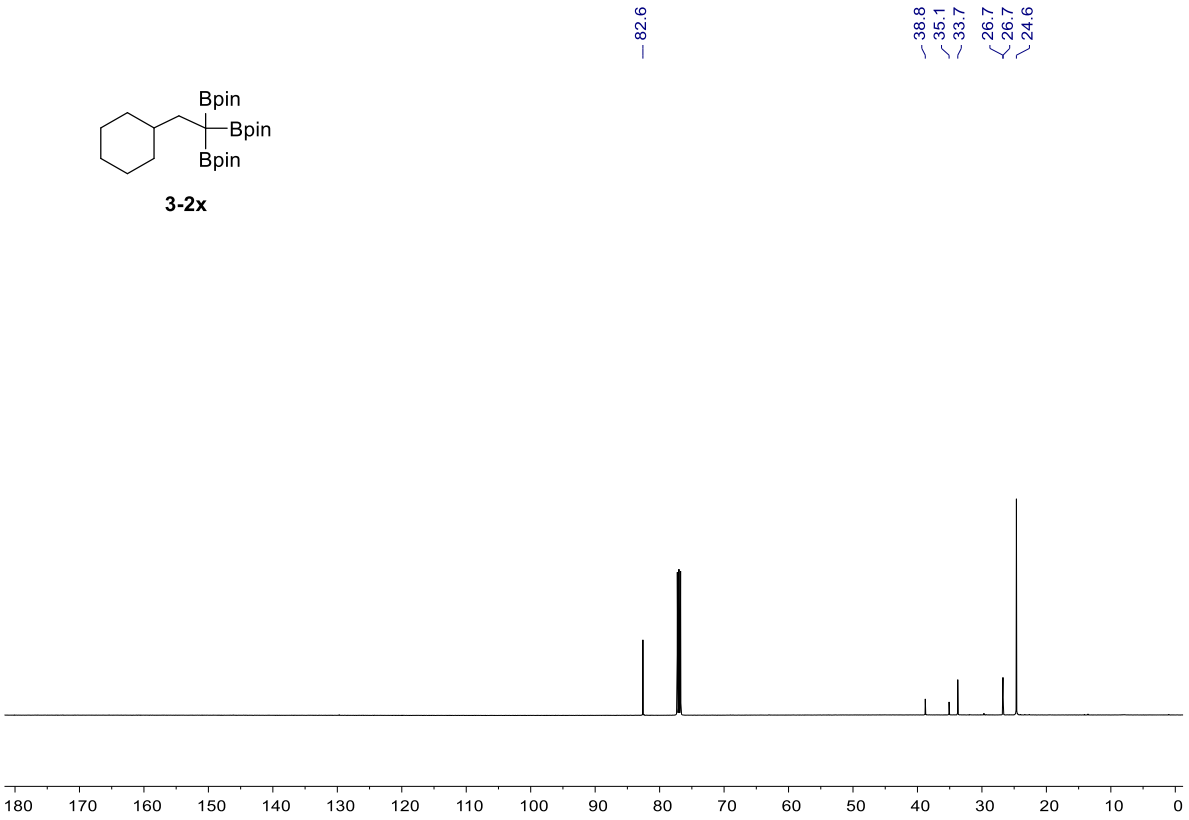
3-2w

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2x**



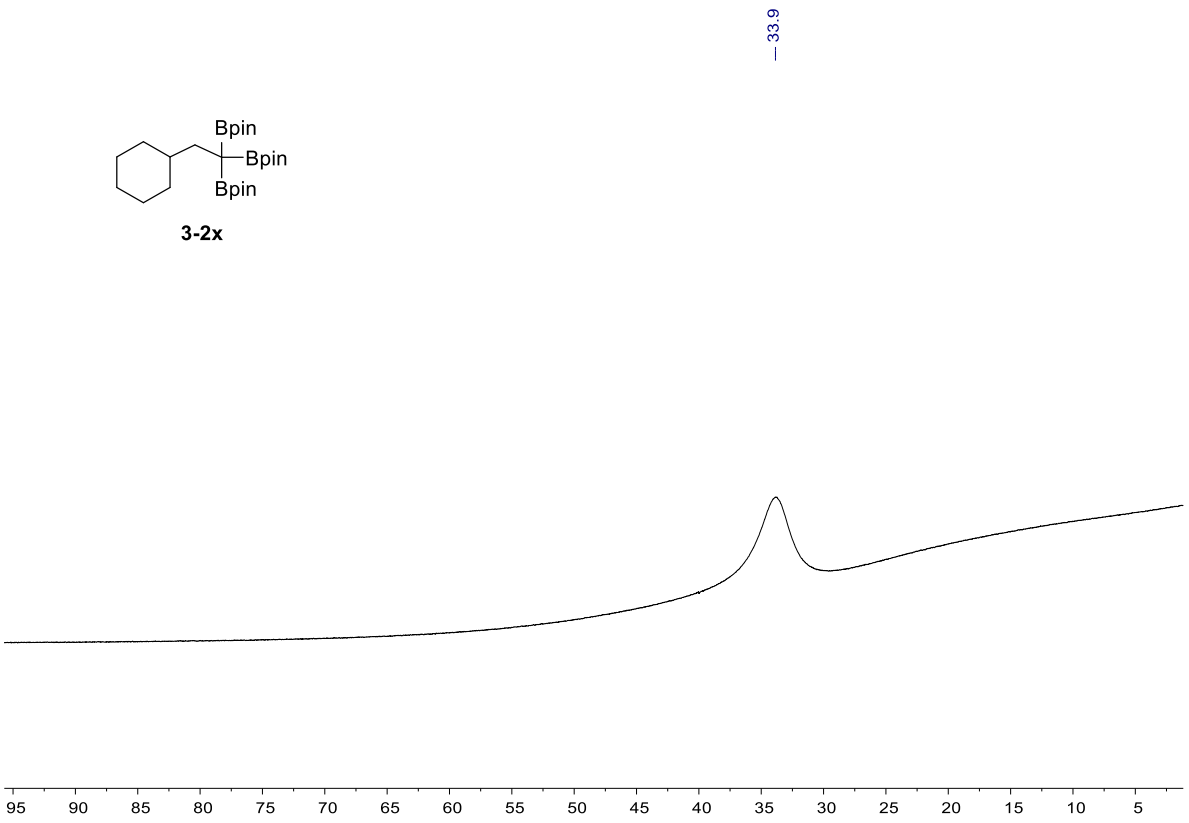
3-2x

$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-2x**



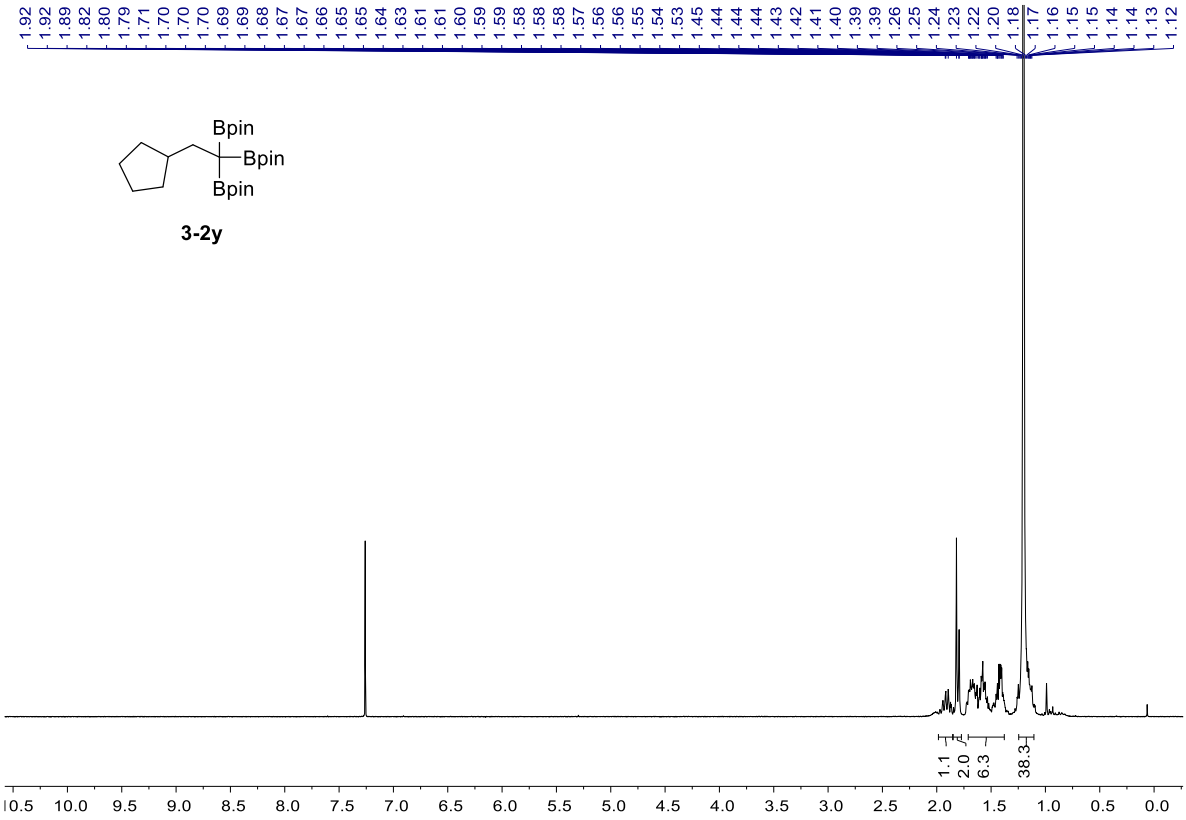
3-2x

^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2x**

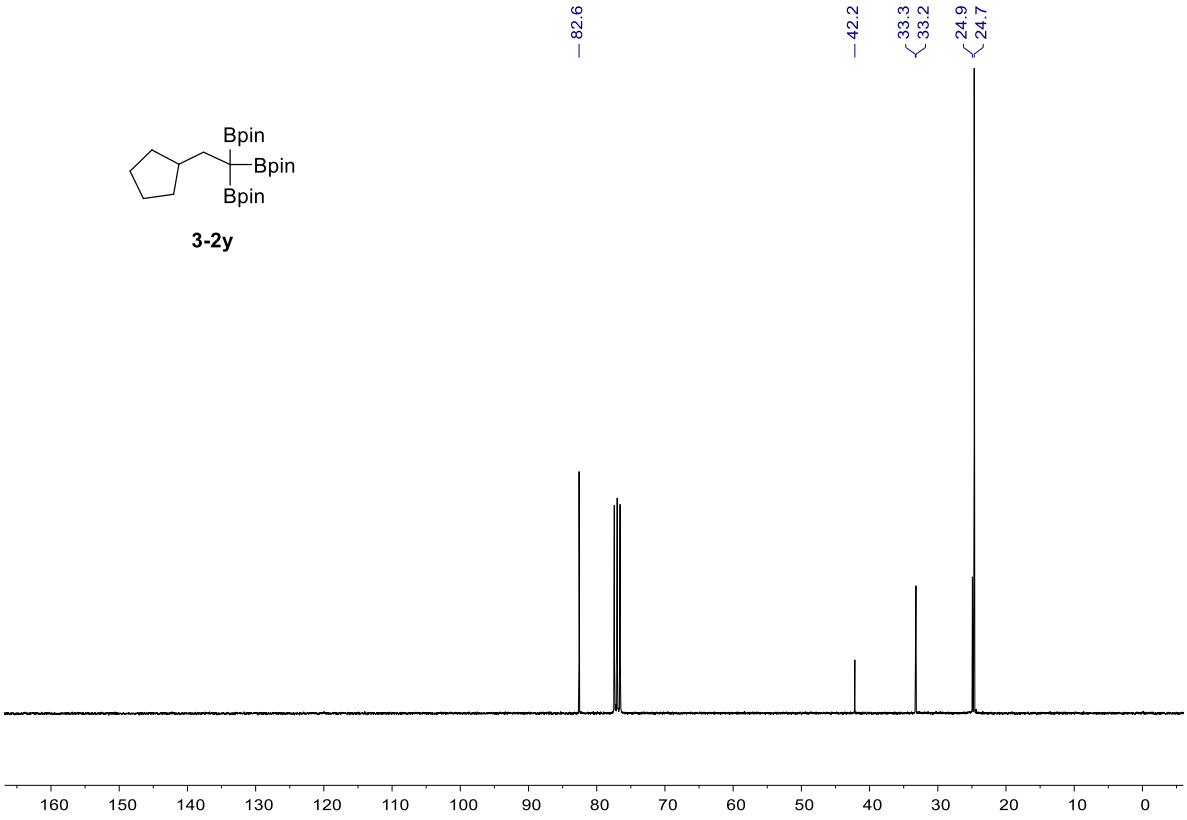


3-2x

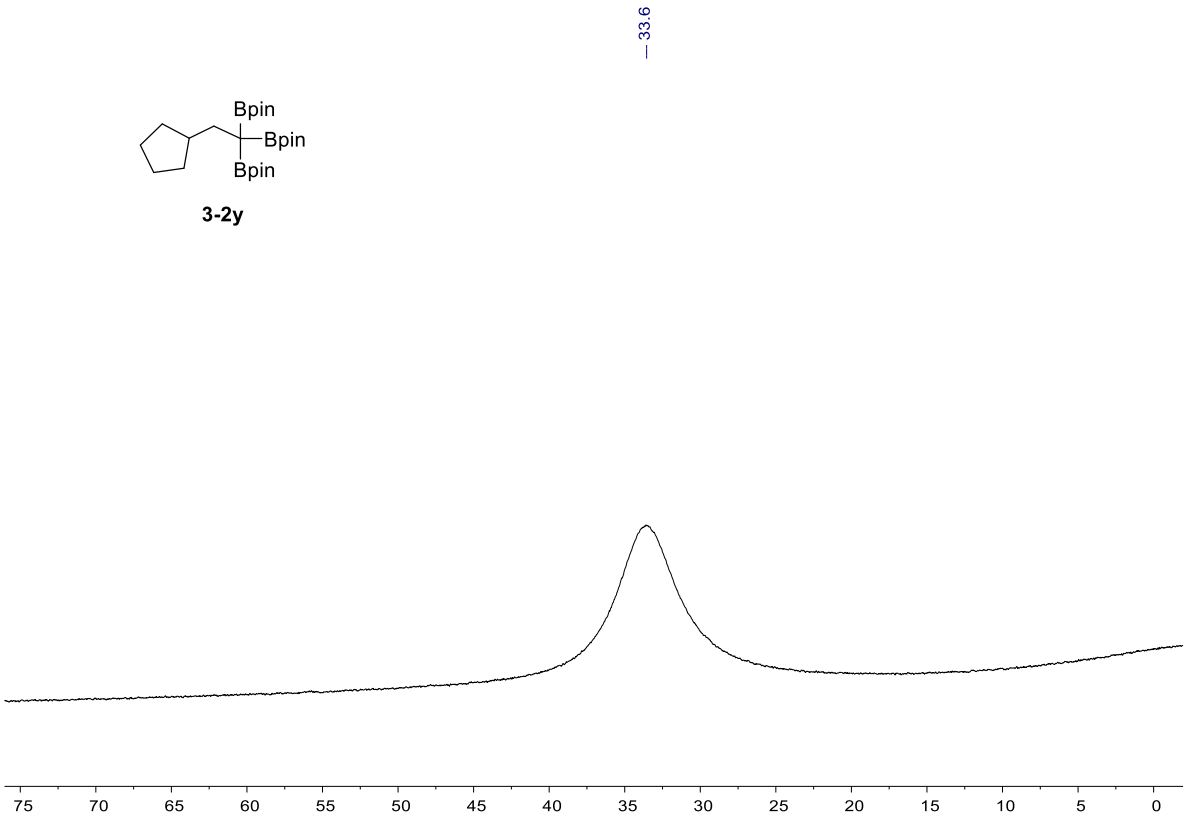
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2y**



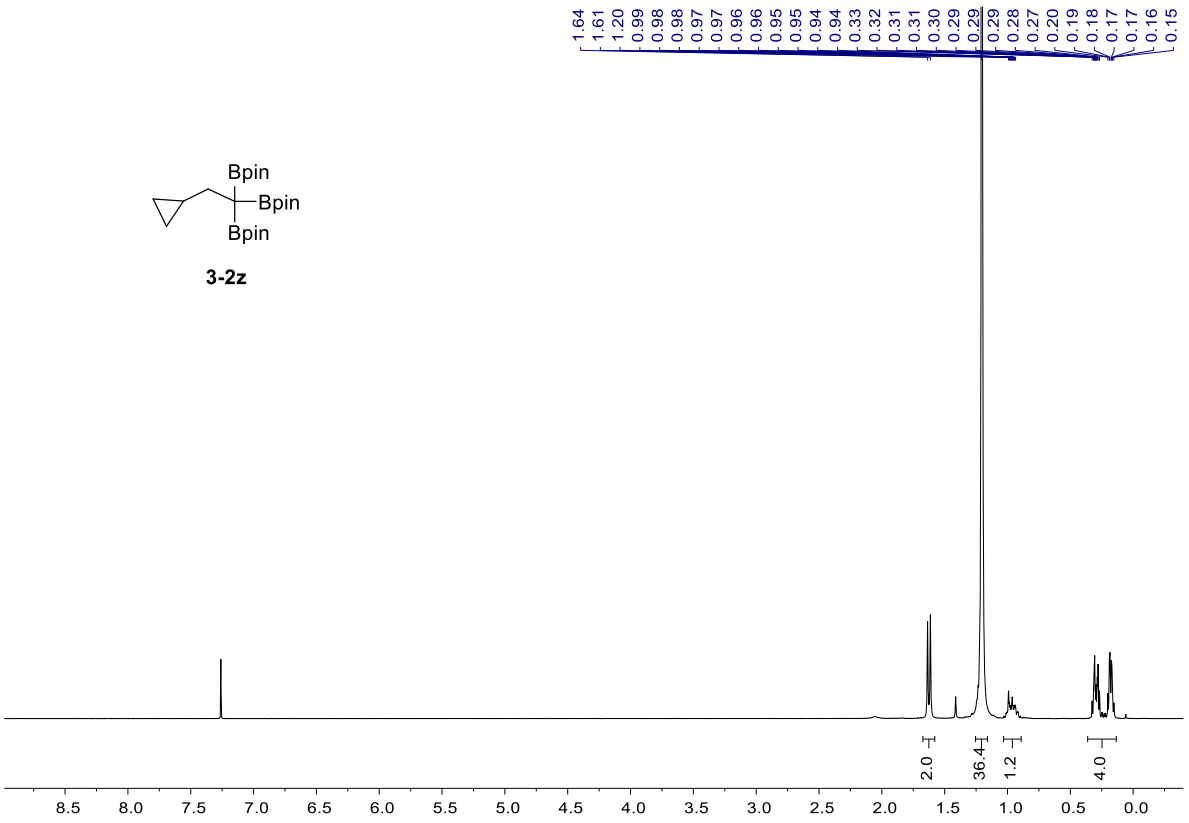
^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **3-2y**



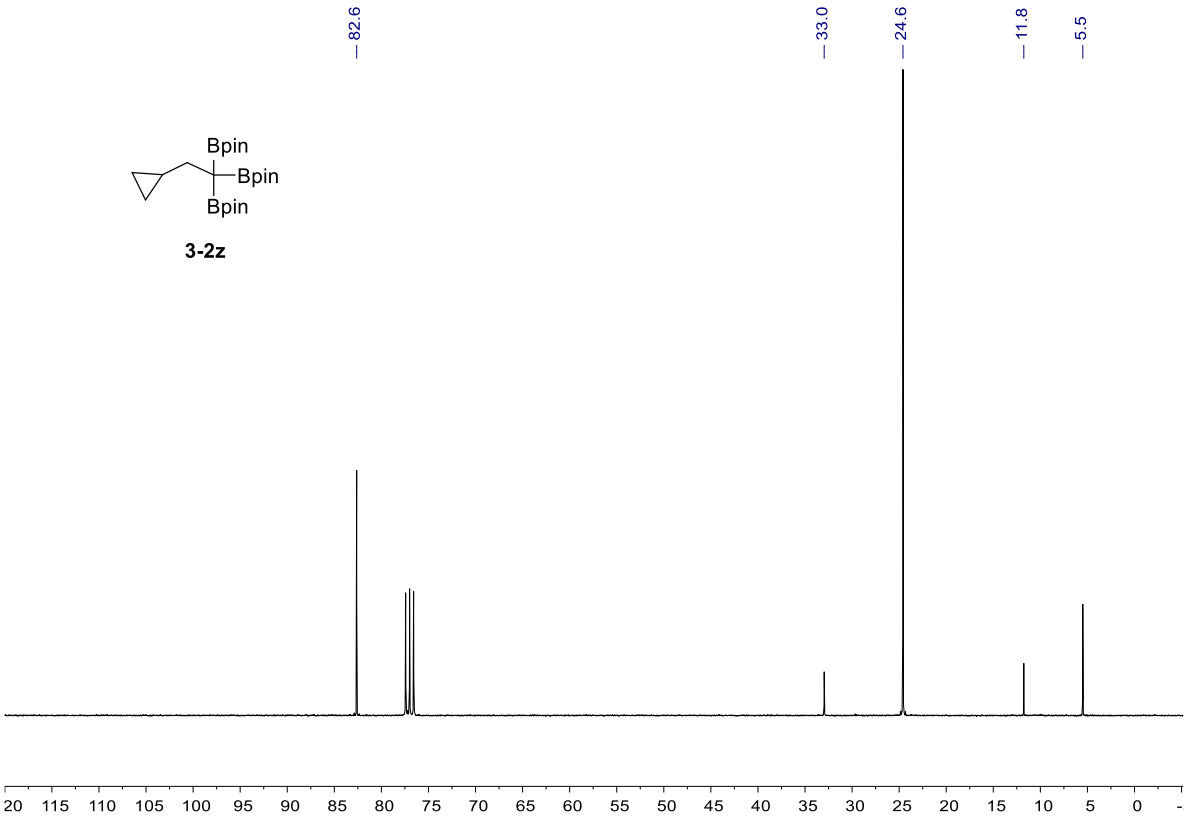
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2y**



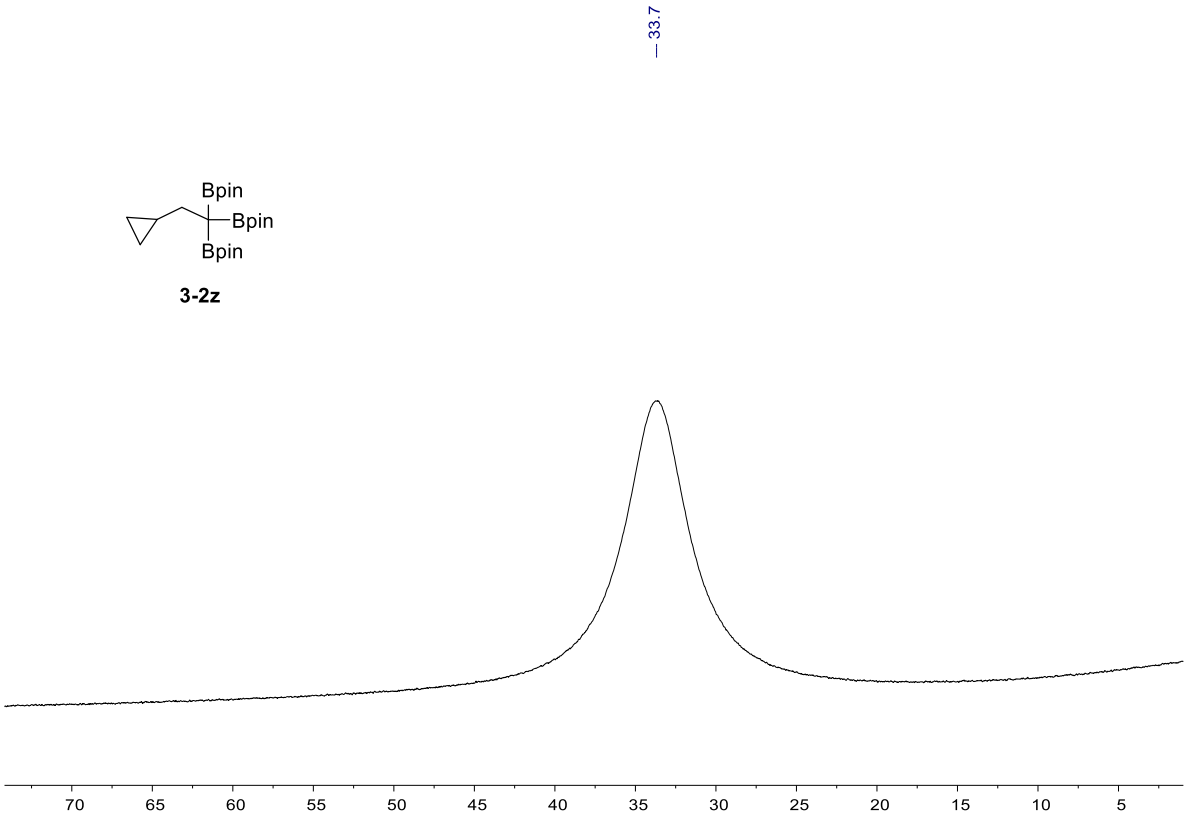
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2z**



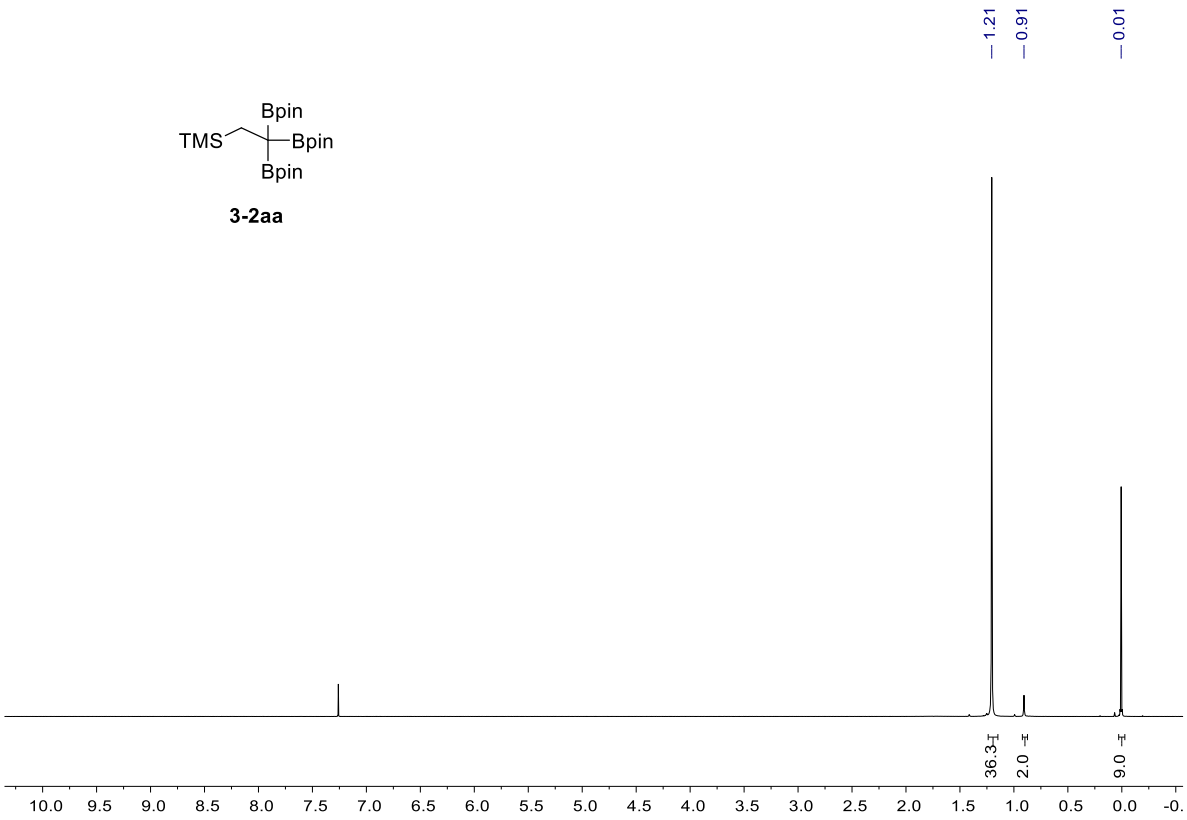
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-2z**



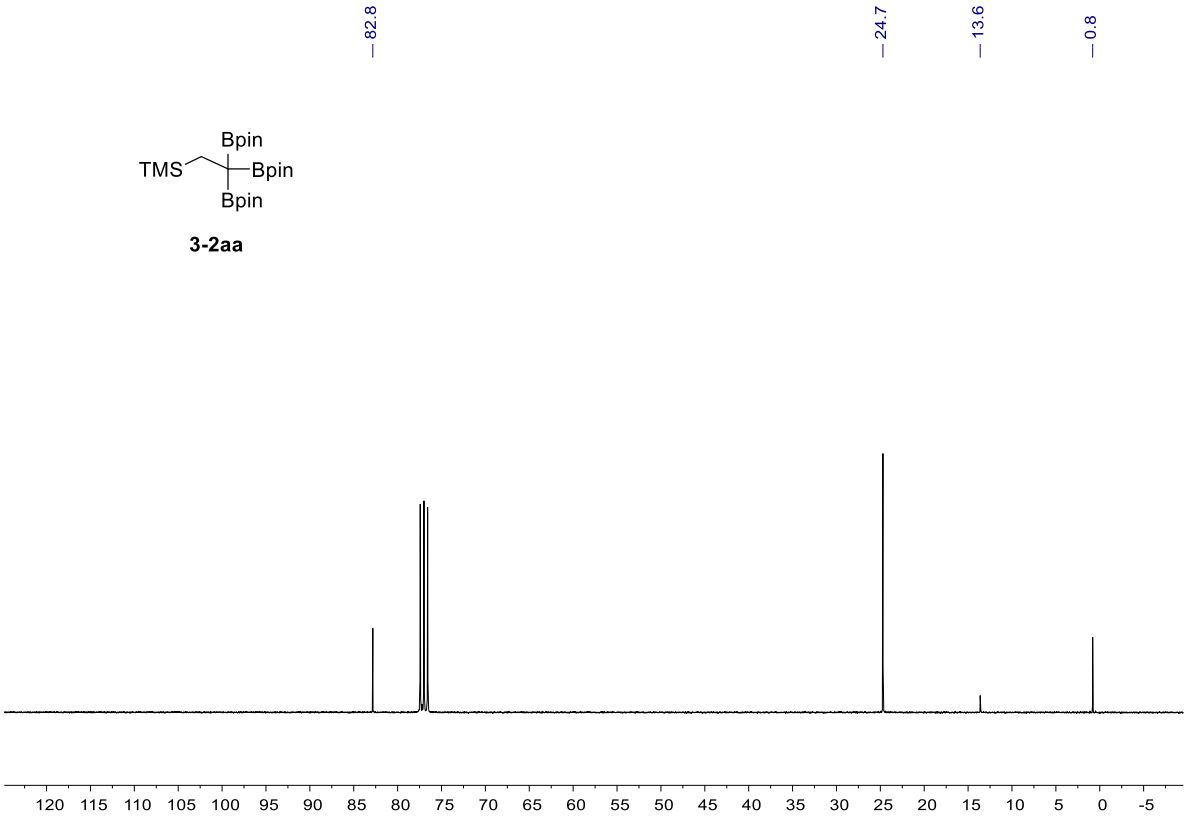
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2z**



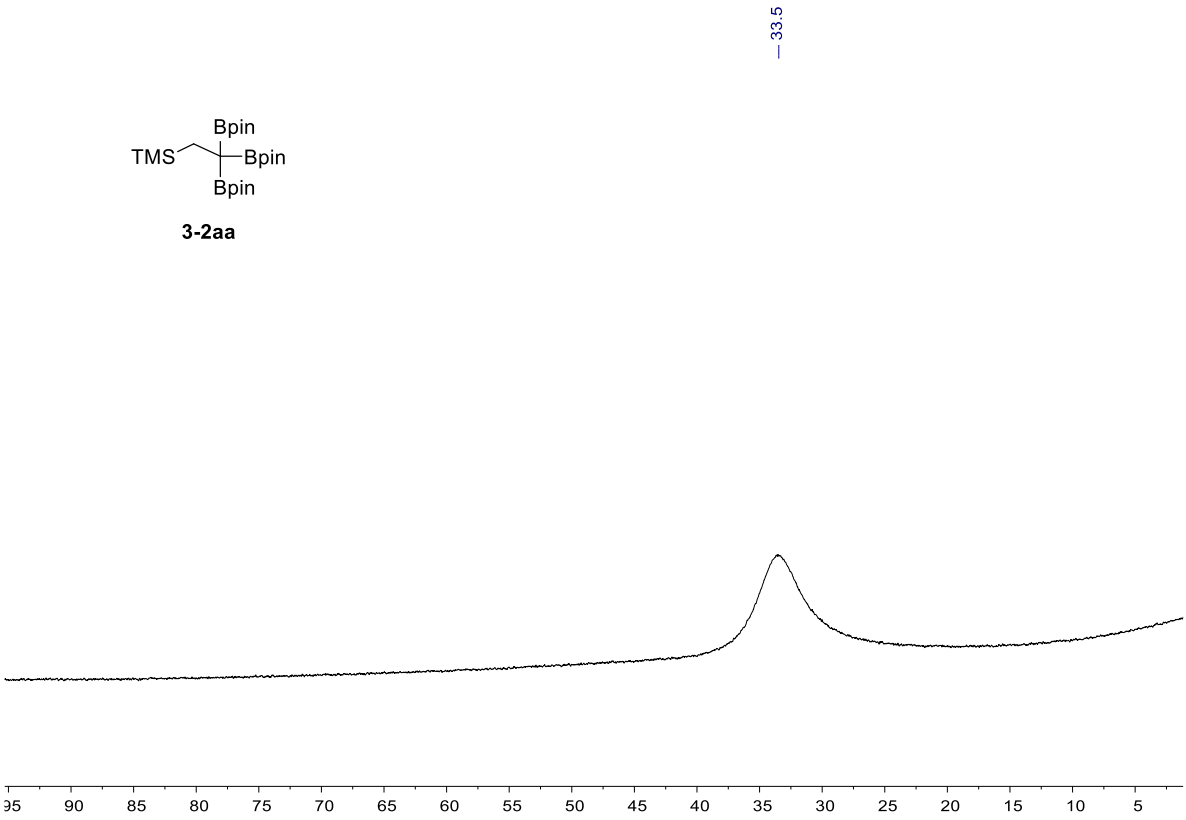
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2aa**



^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **3-2aa**

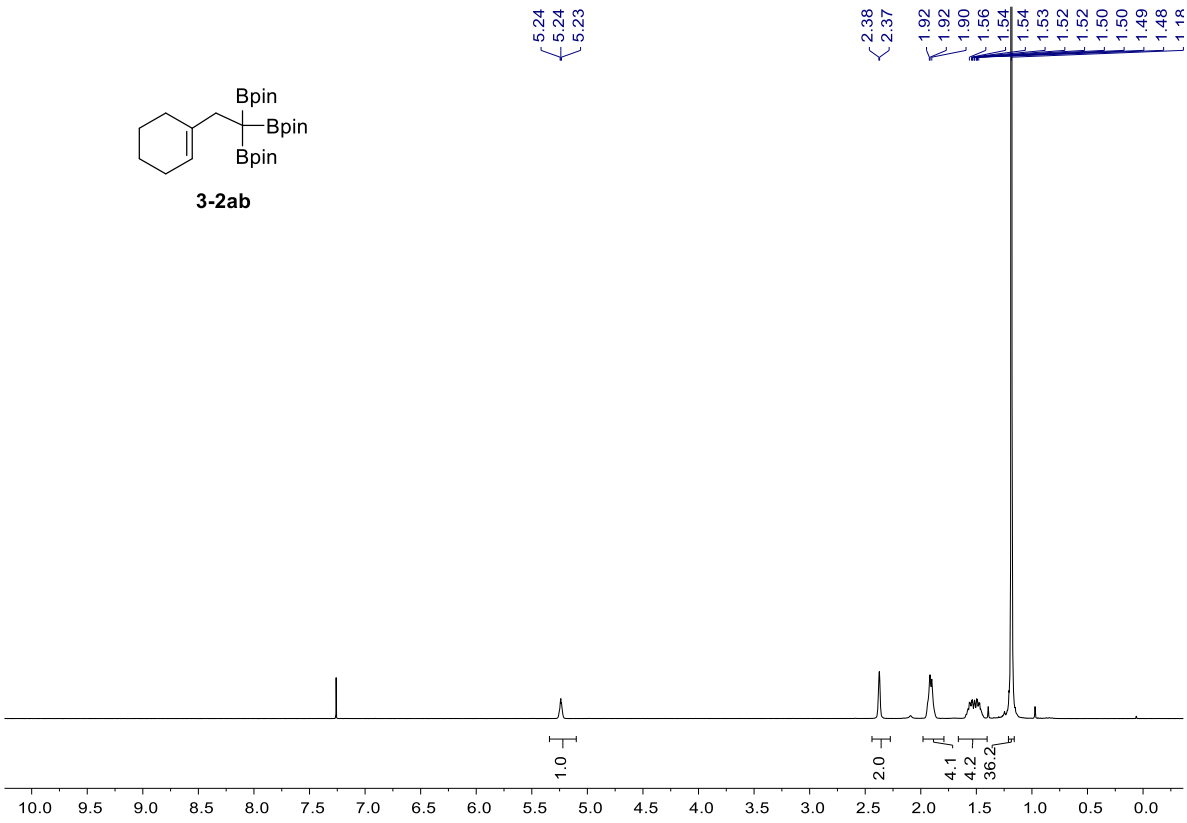


^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2aa**



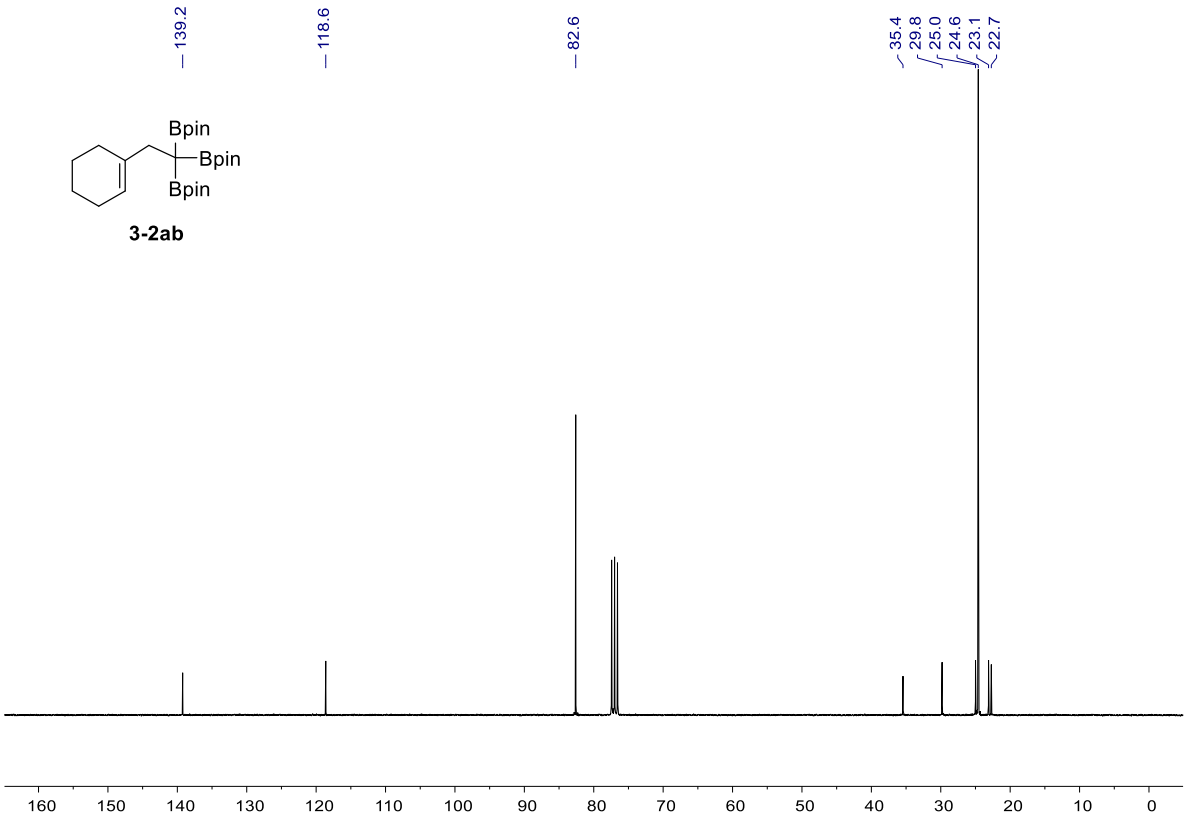
3-2aa

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-2ab**

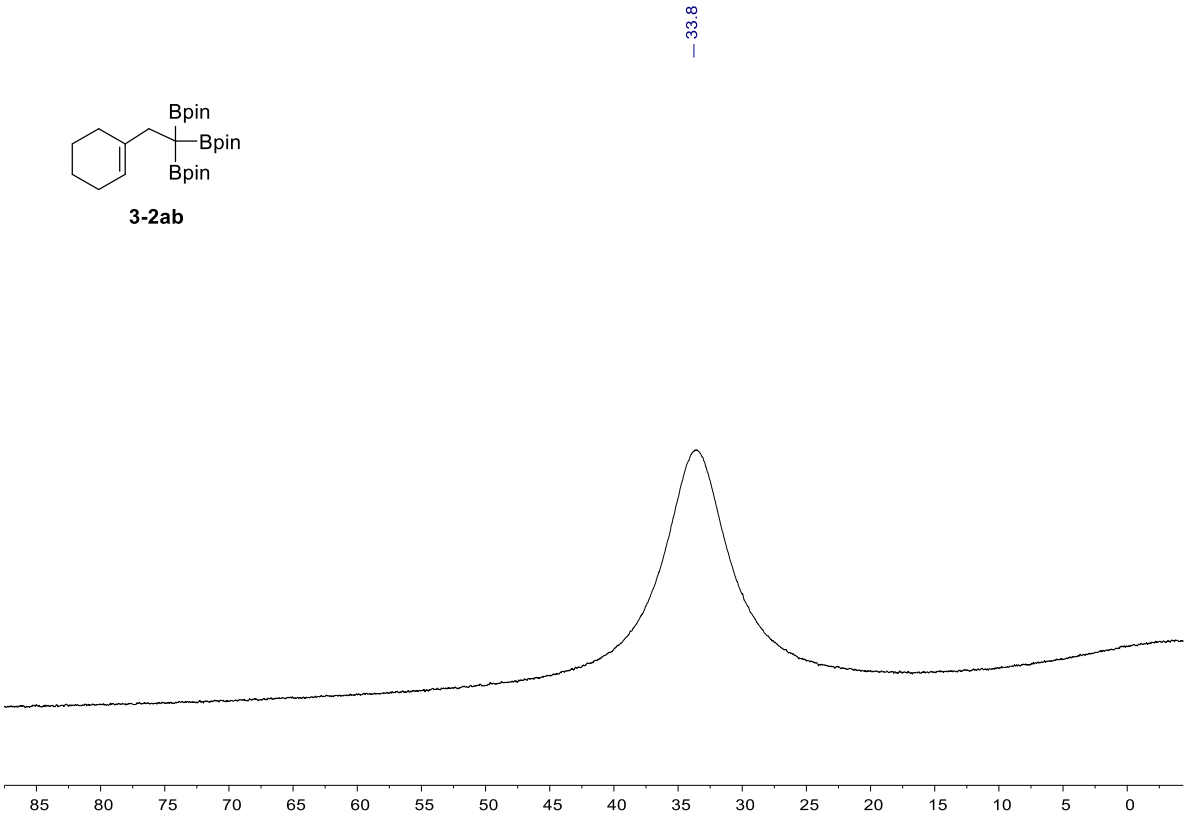


3-2ab

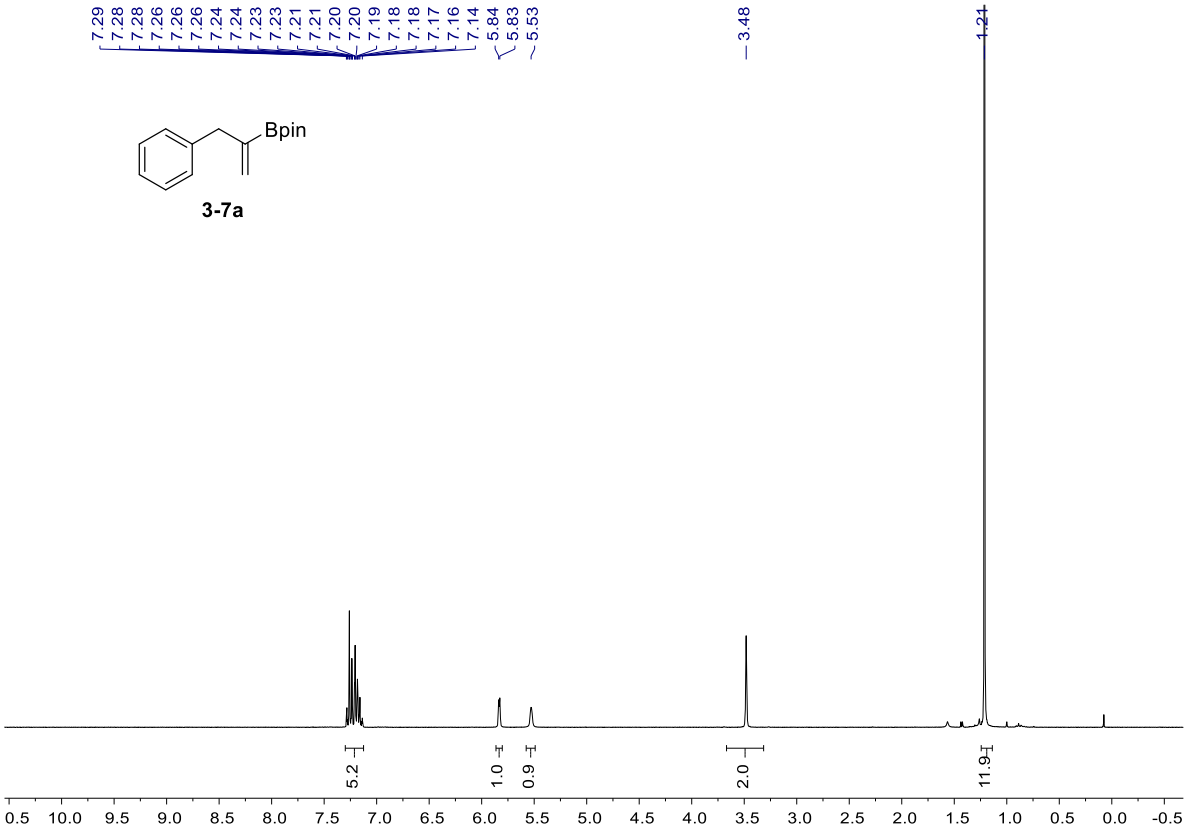
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-2ab**



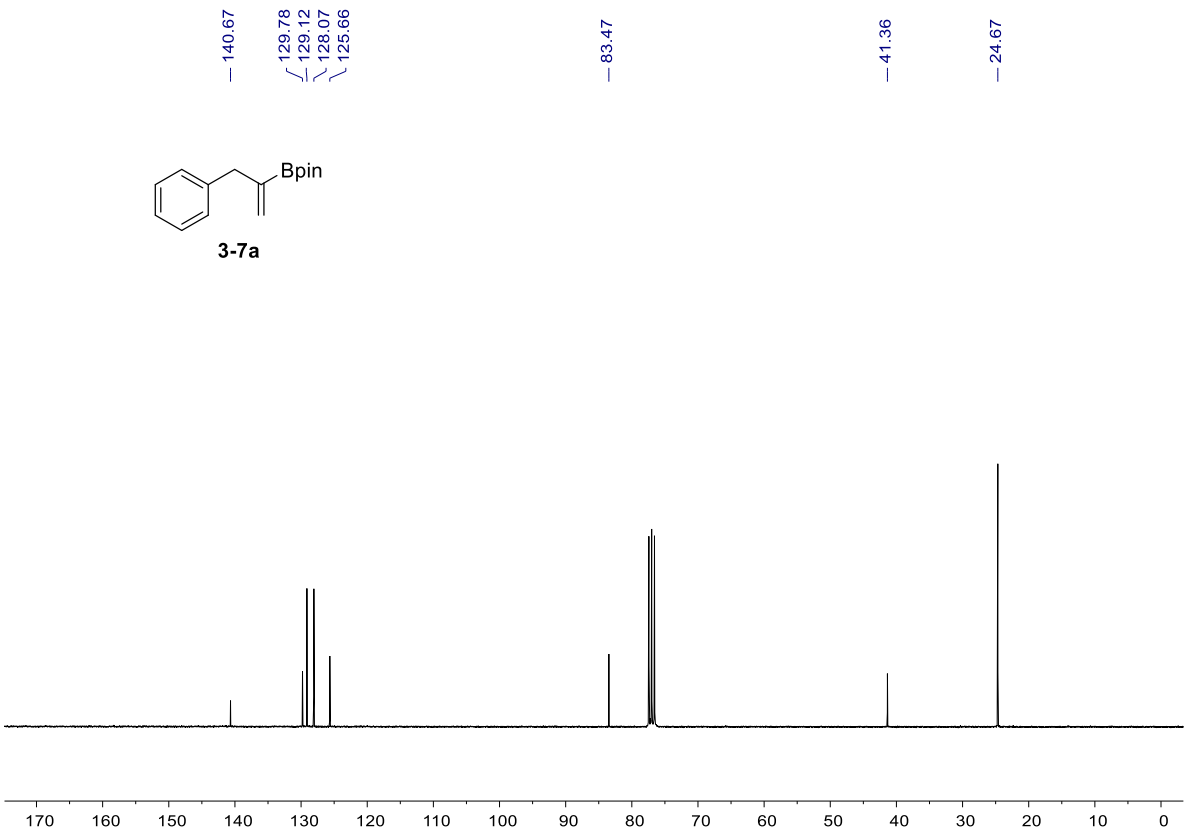
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-2ab**



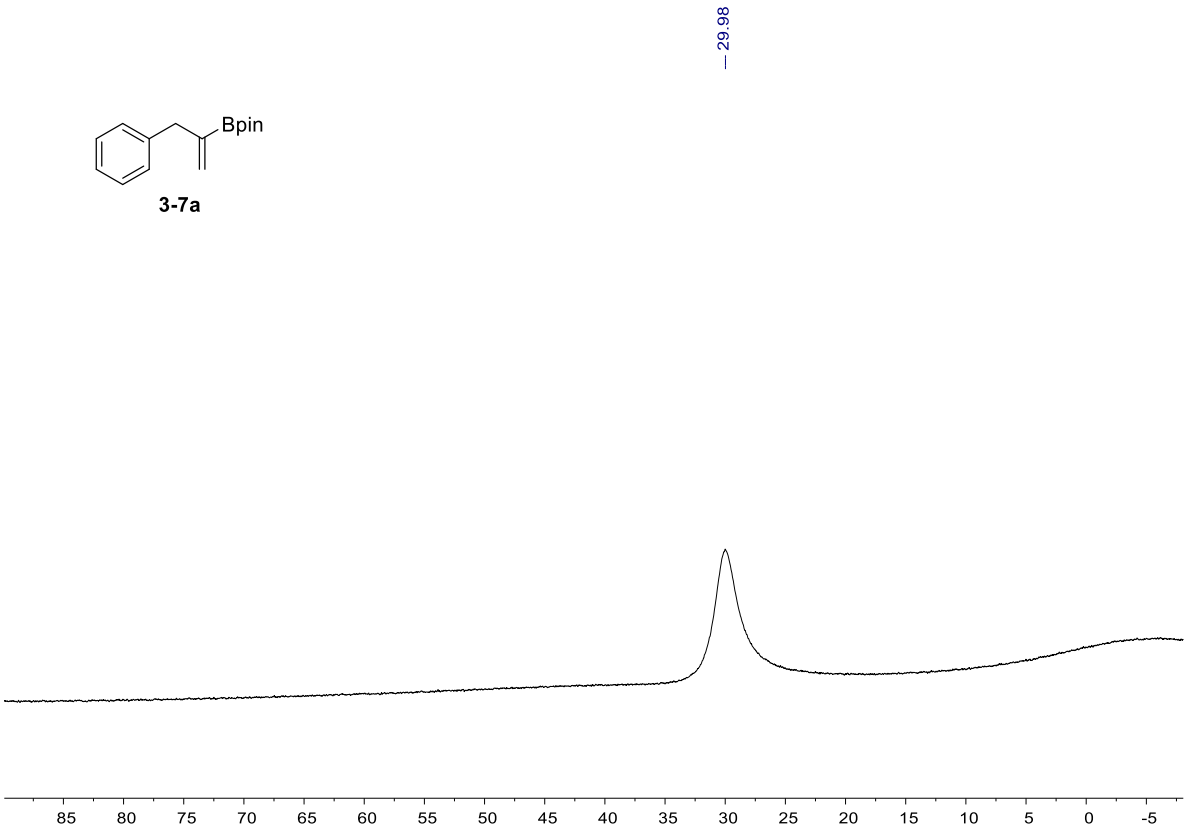
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-7a**



^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **3-7a**

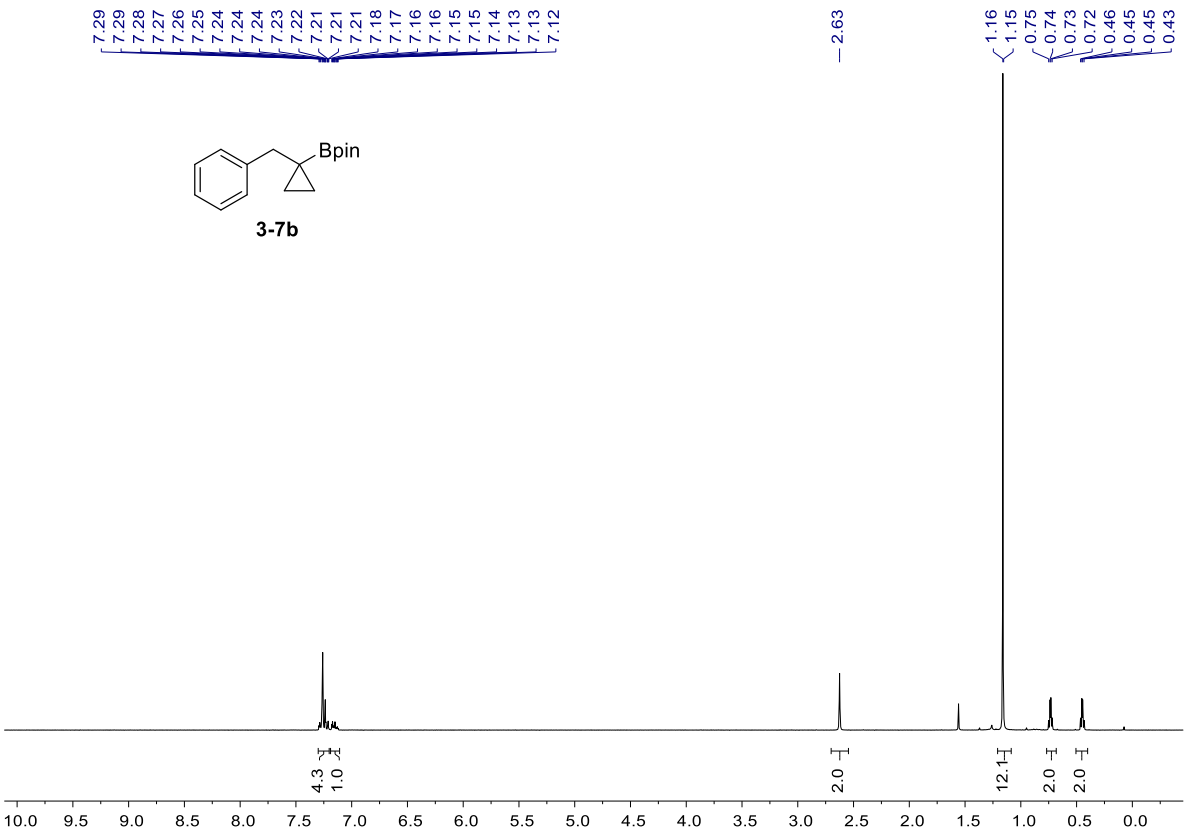


^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-7a**



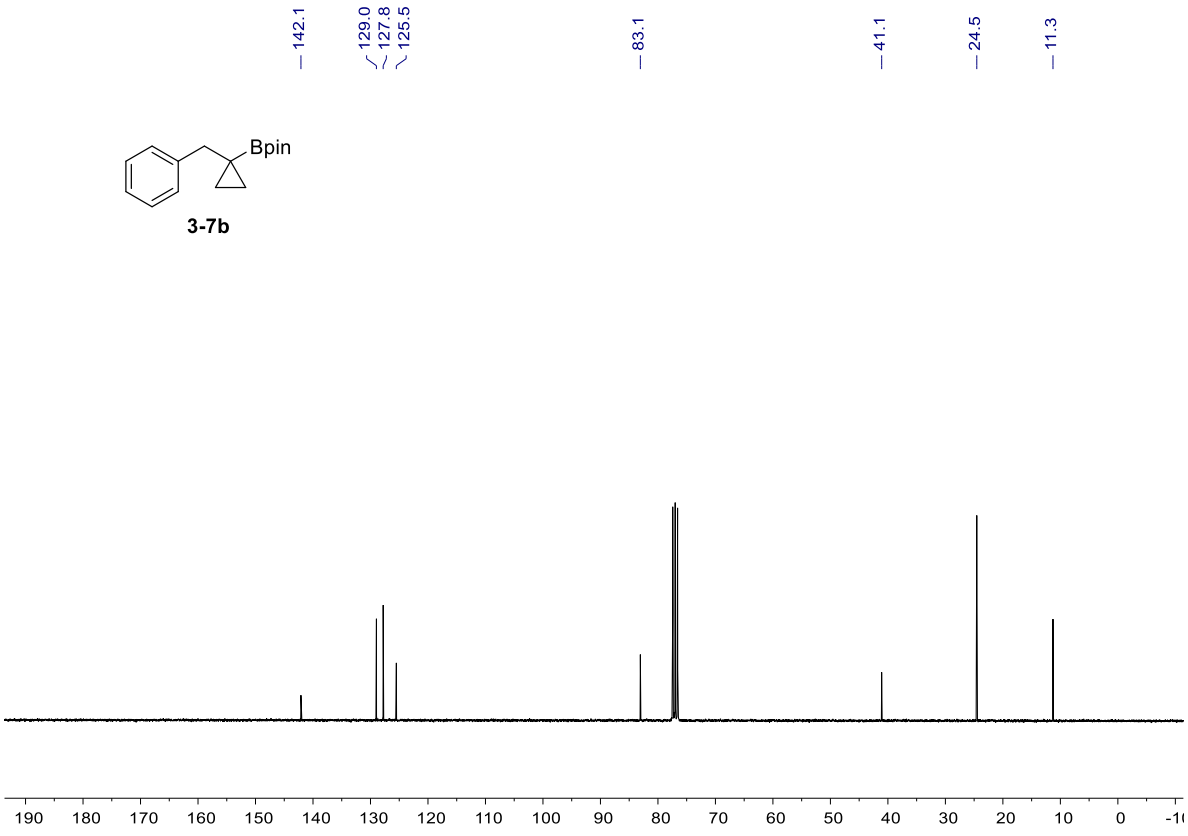
3-7a

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-7b**

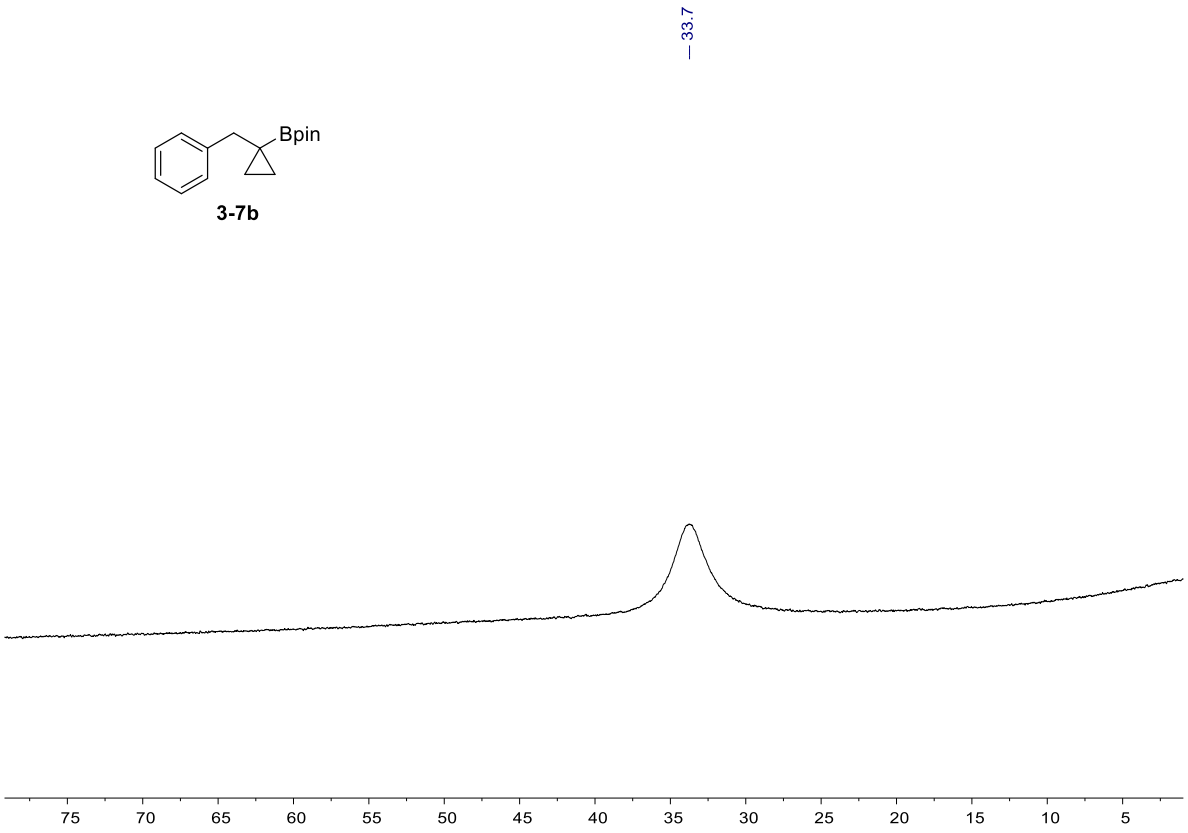


3-7b

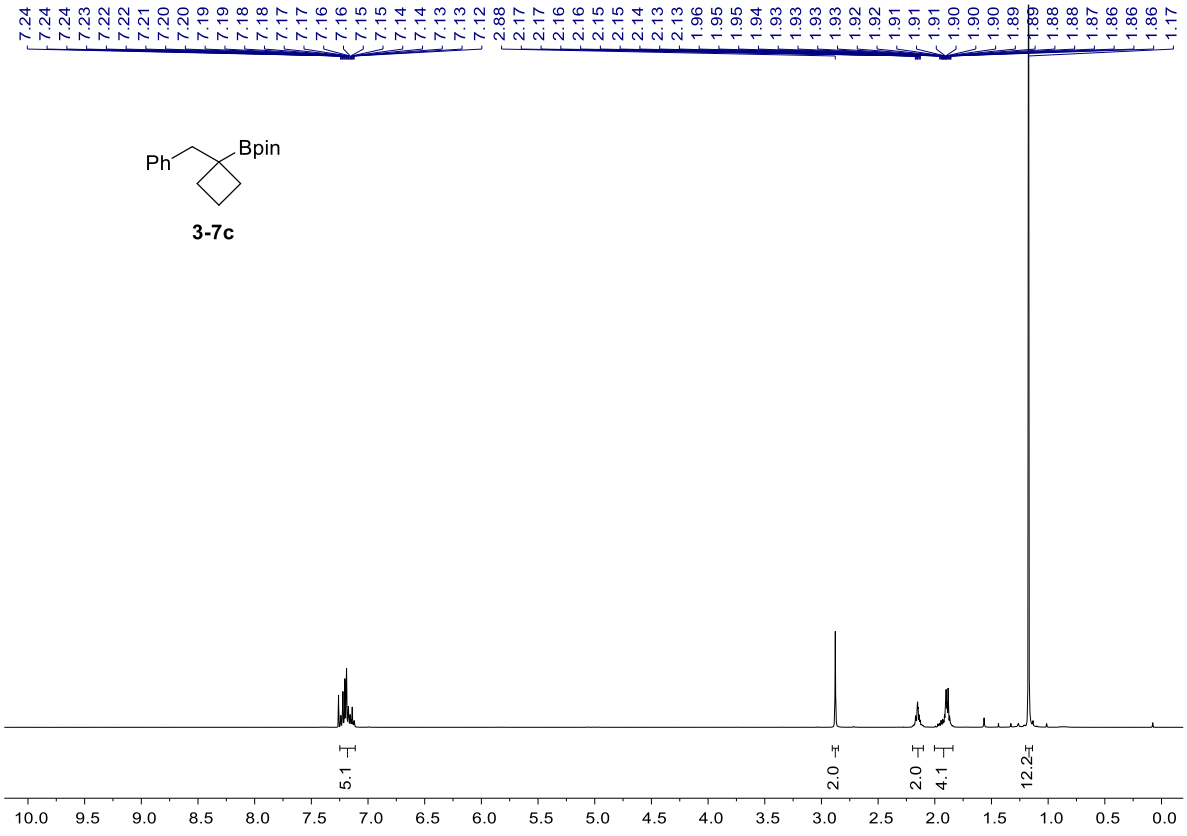
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-7b**



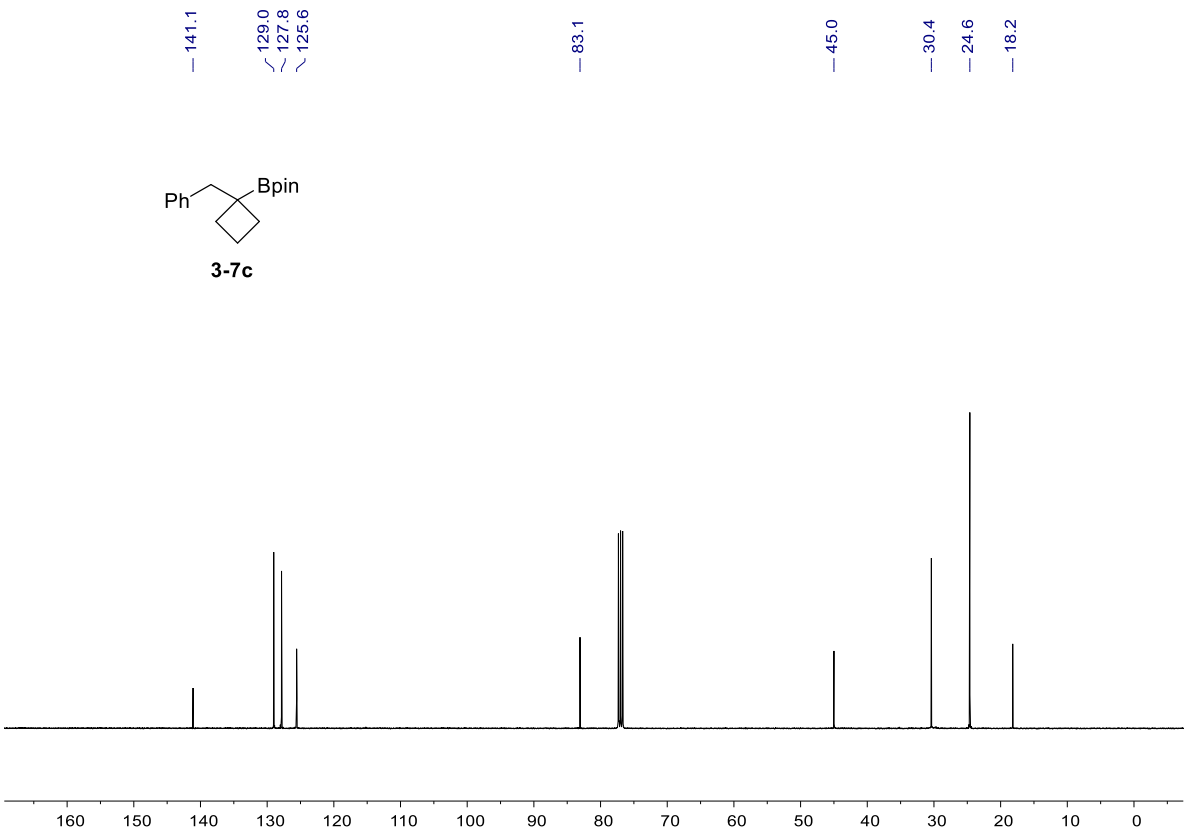
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-7b**



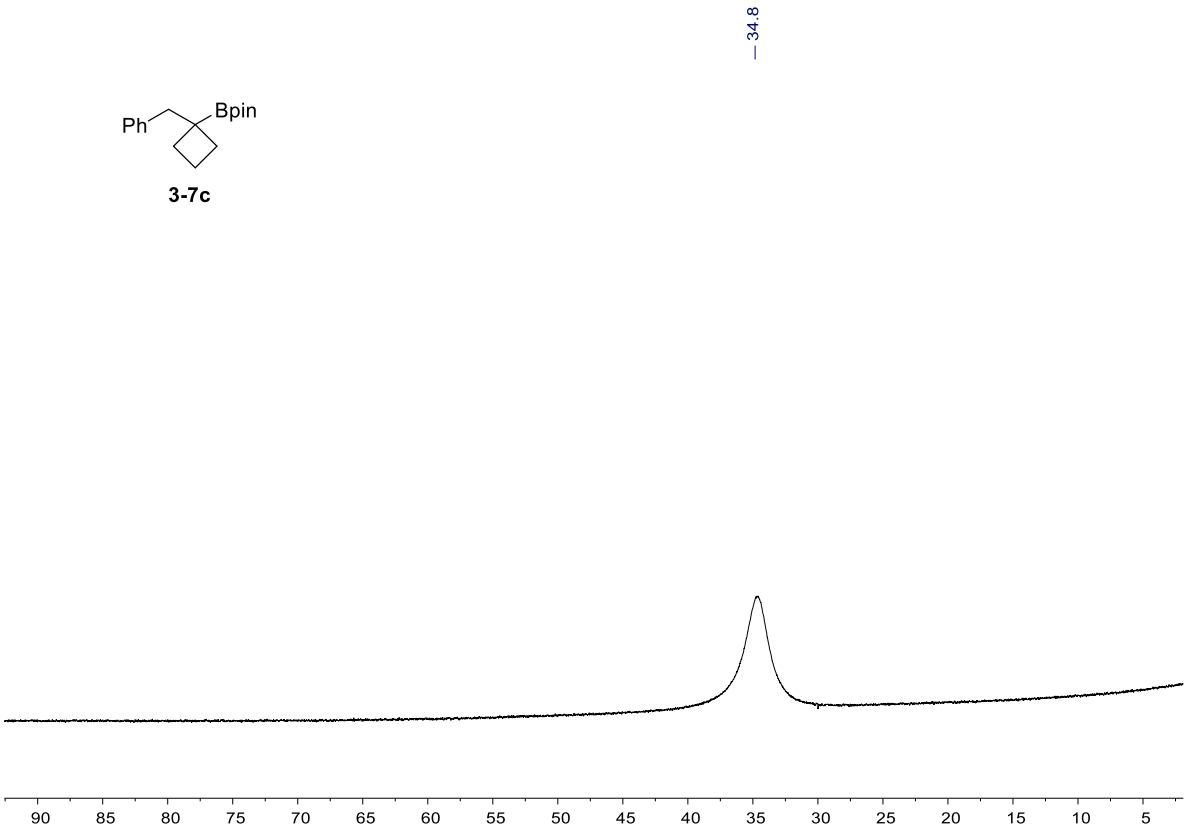
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3-7c**



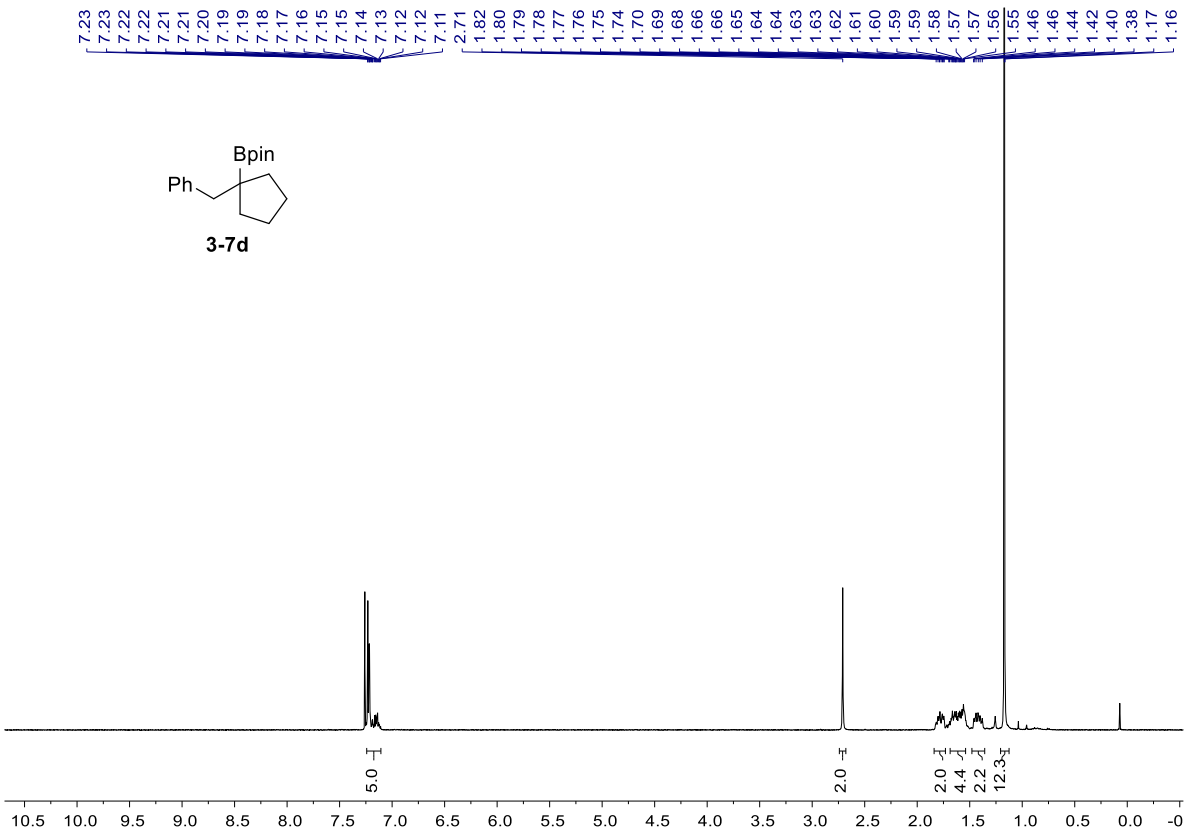
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **3-7c**



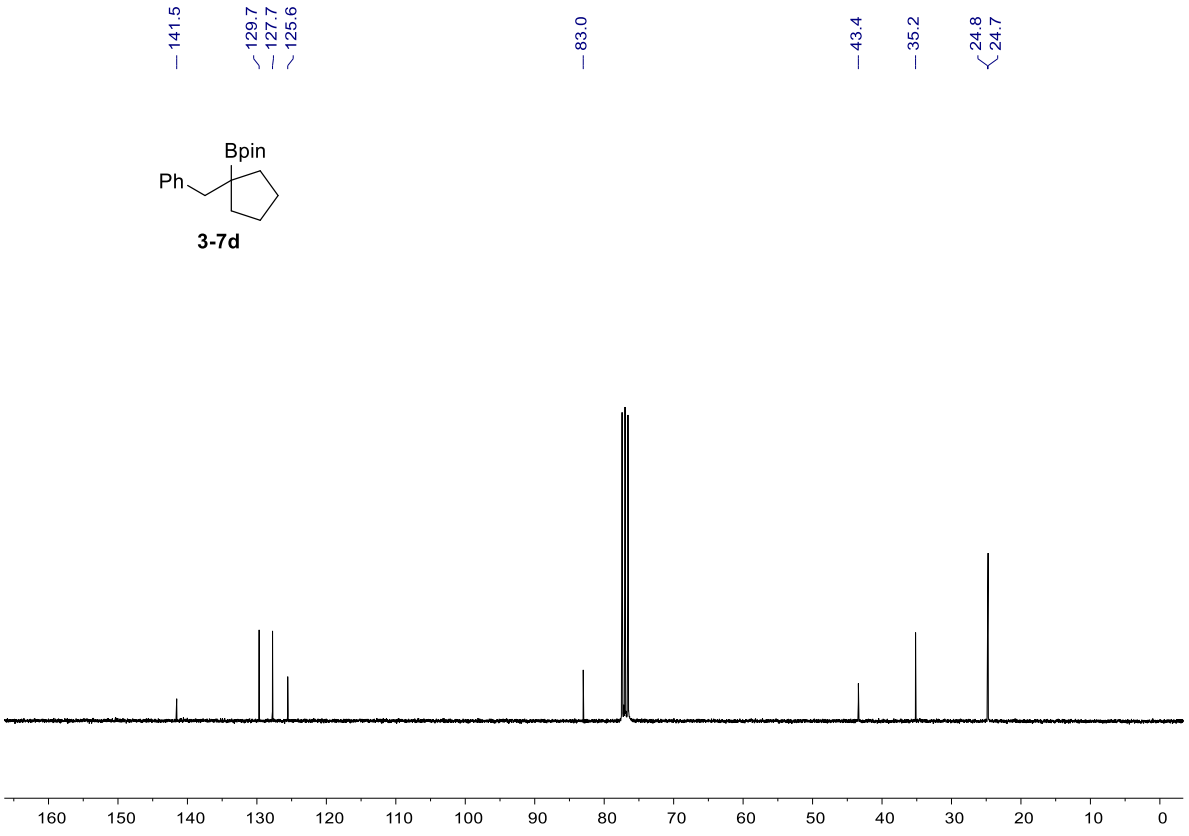
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **3-7c**



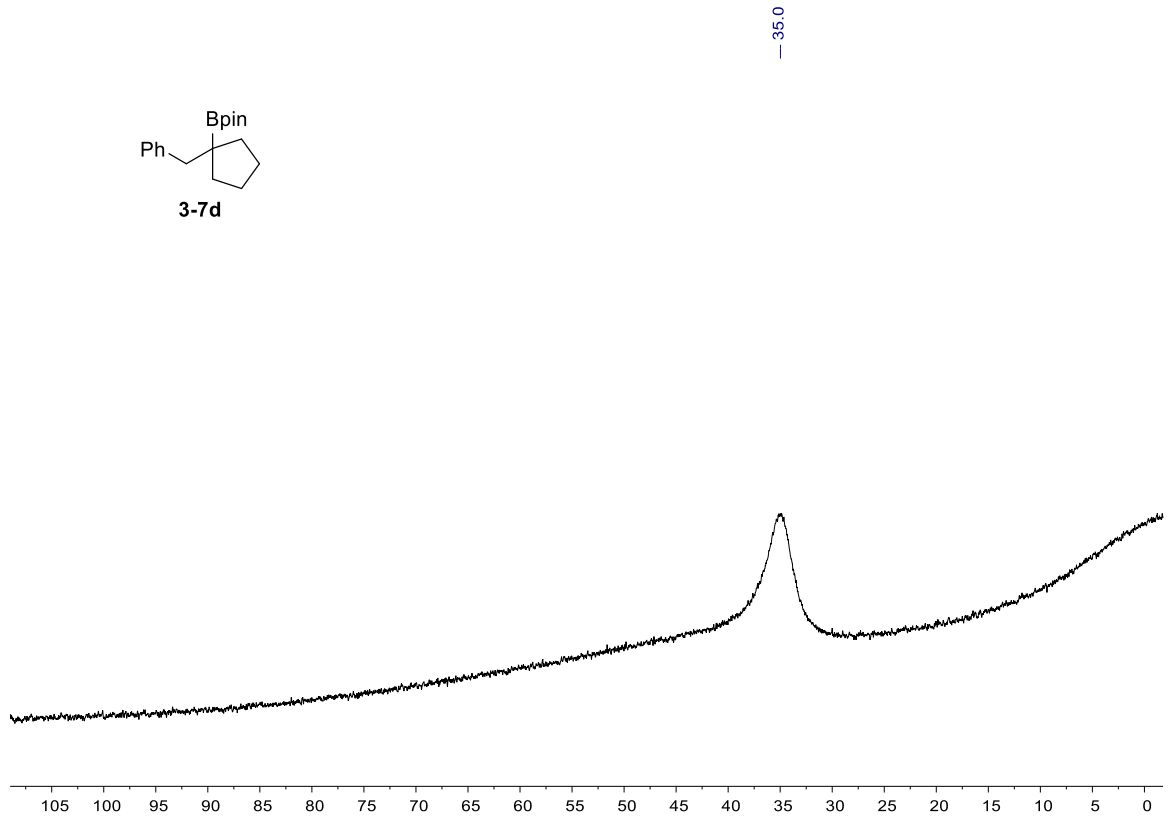
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3-7d**



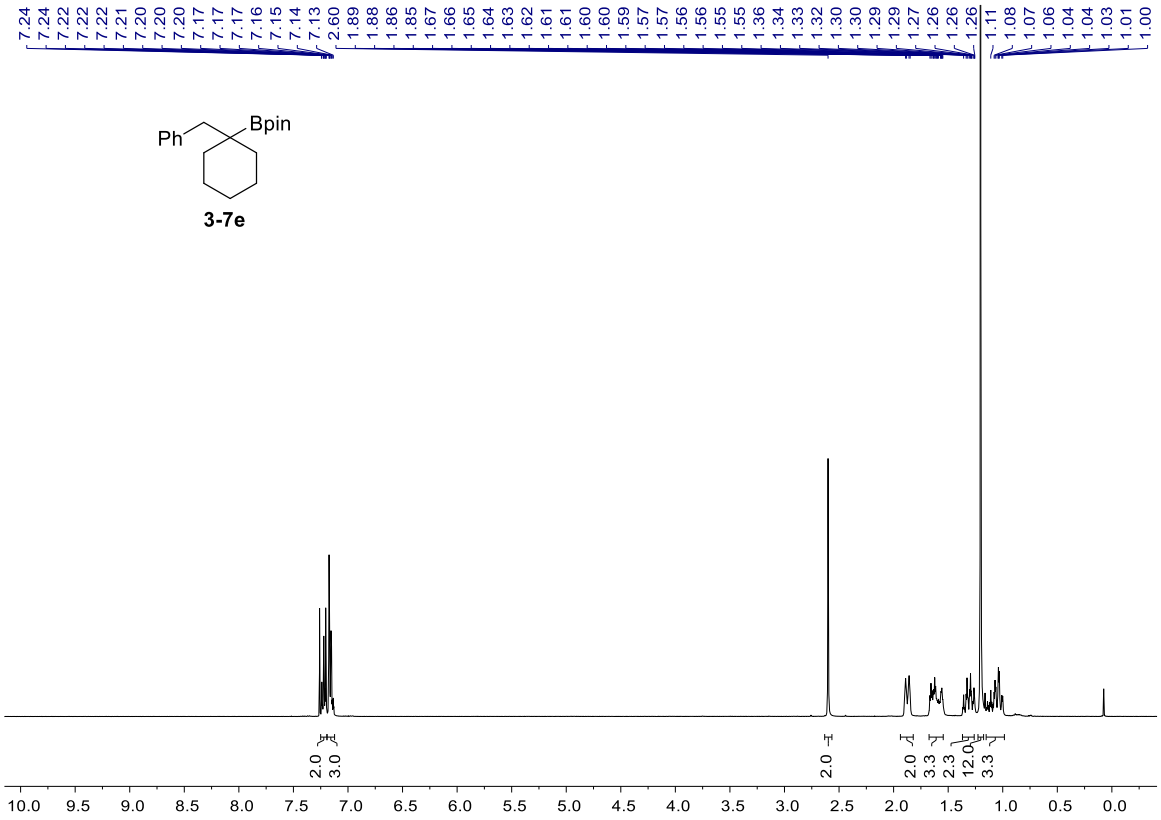
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3-7d**



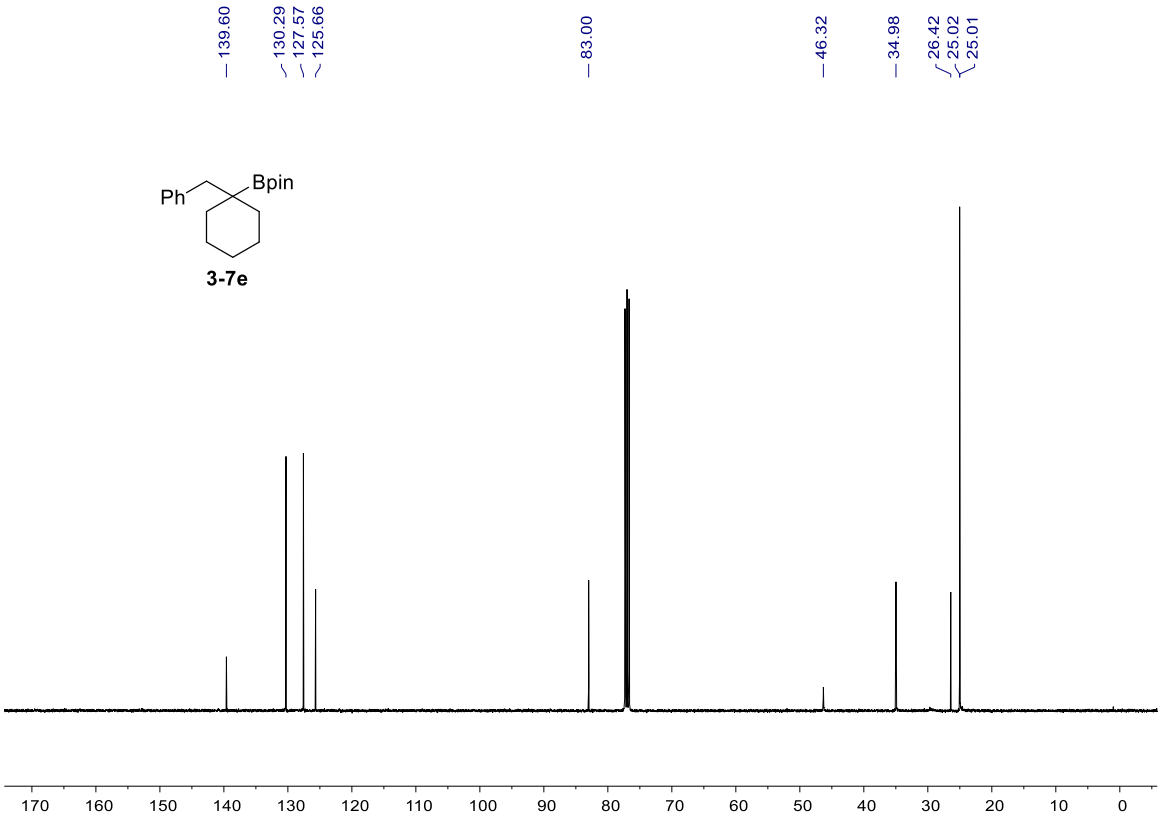
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **3-7d**



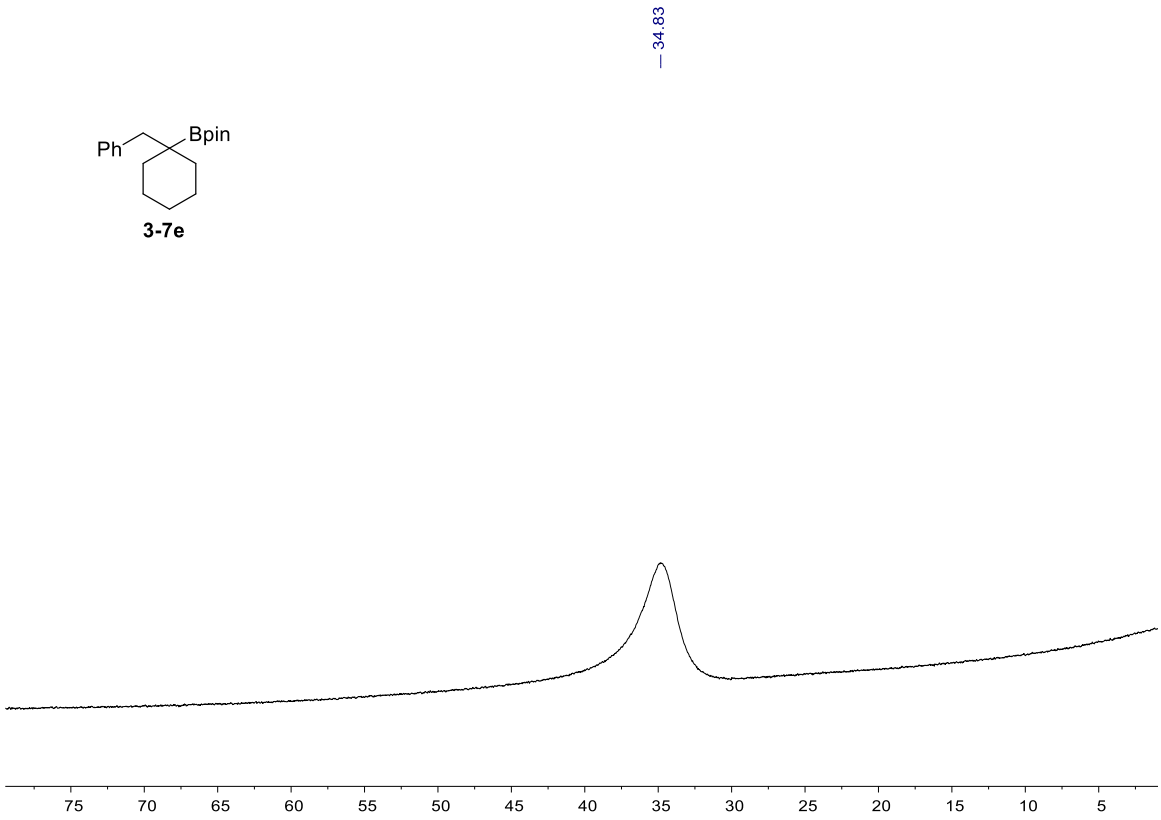
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3-7e**



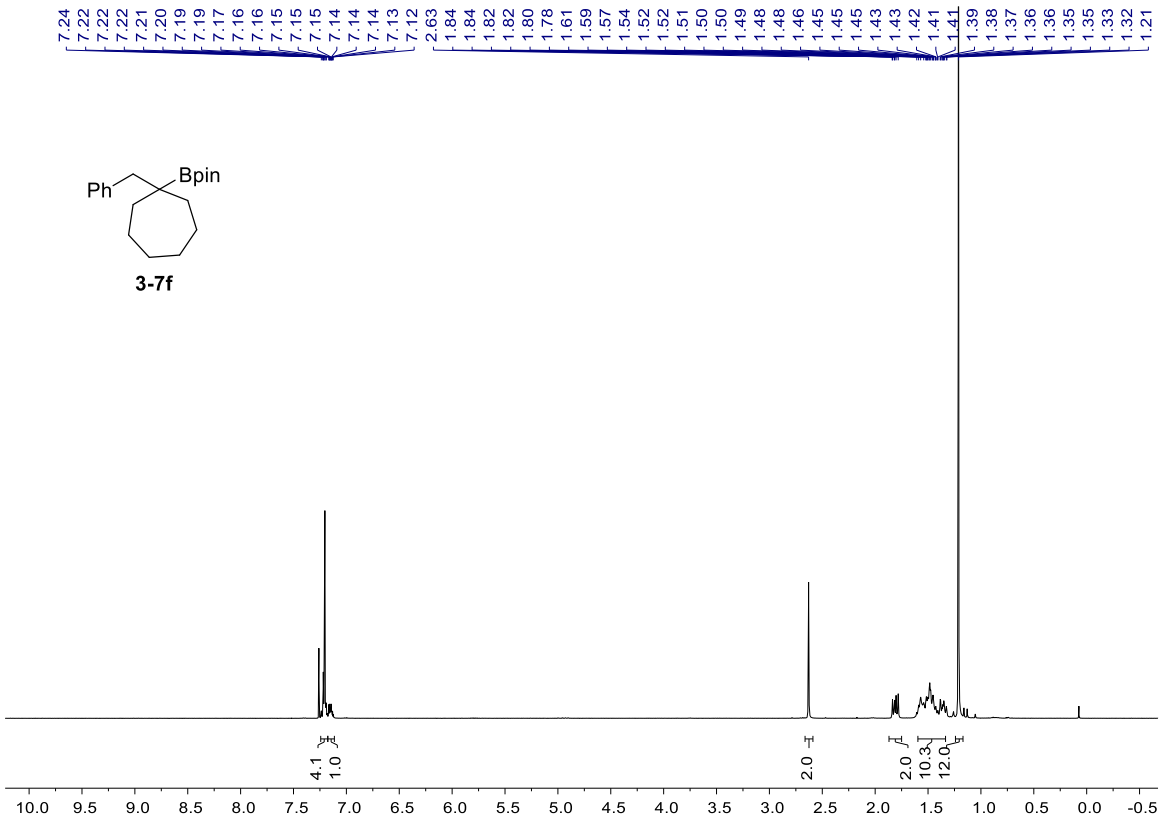
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **3-7e**



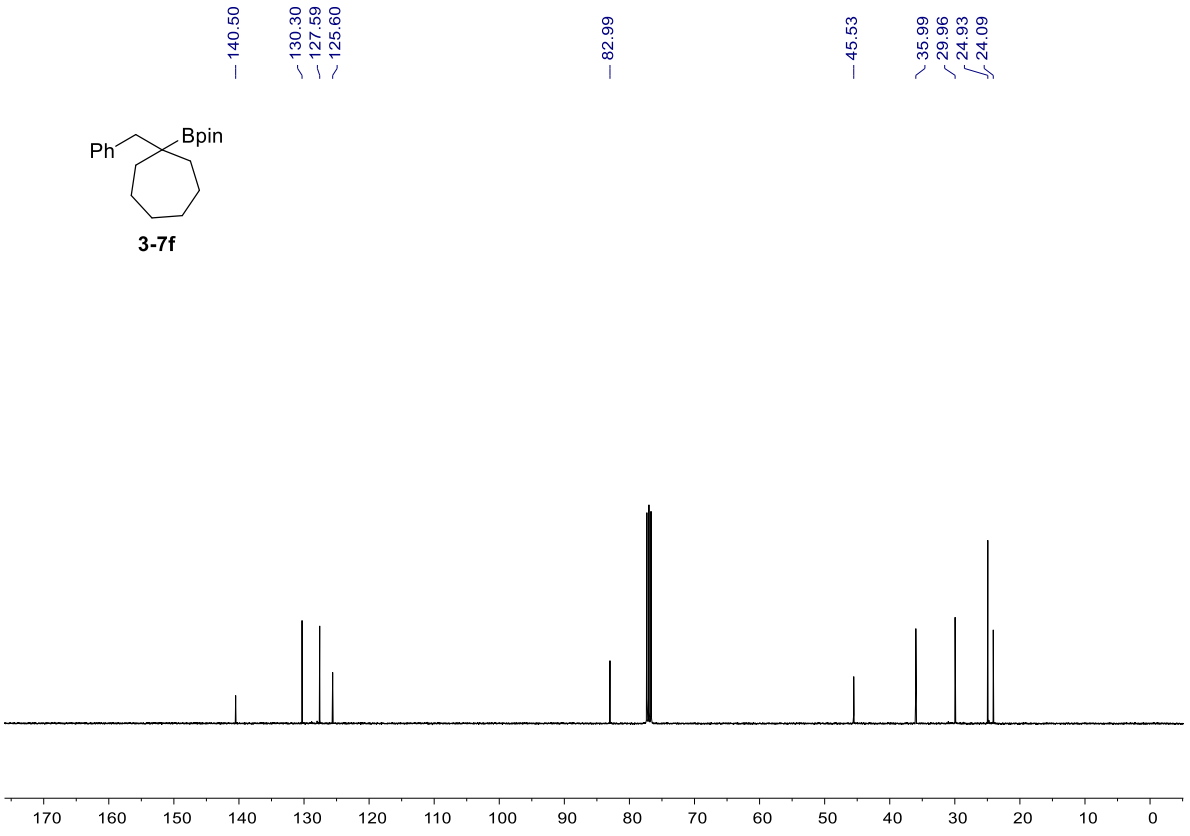
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **3-7e**



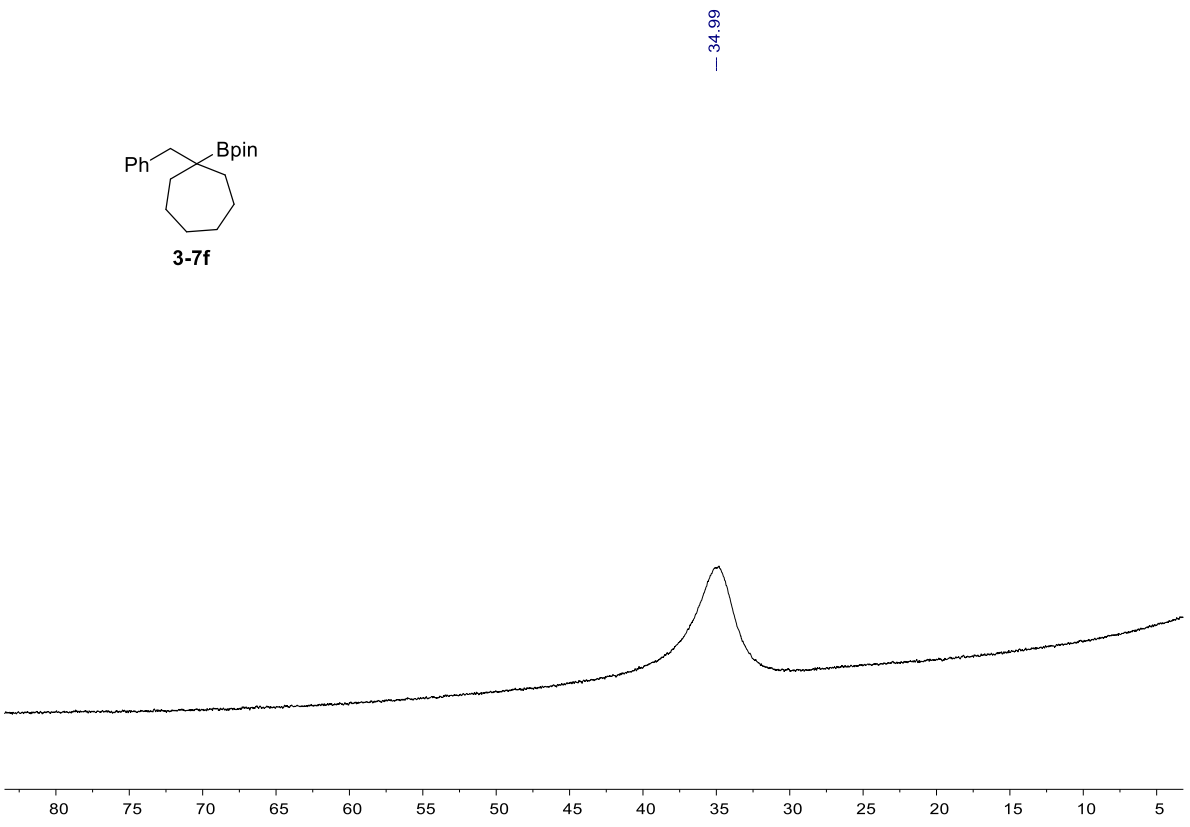
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3-7f**



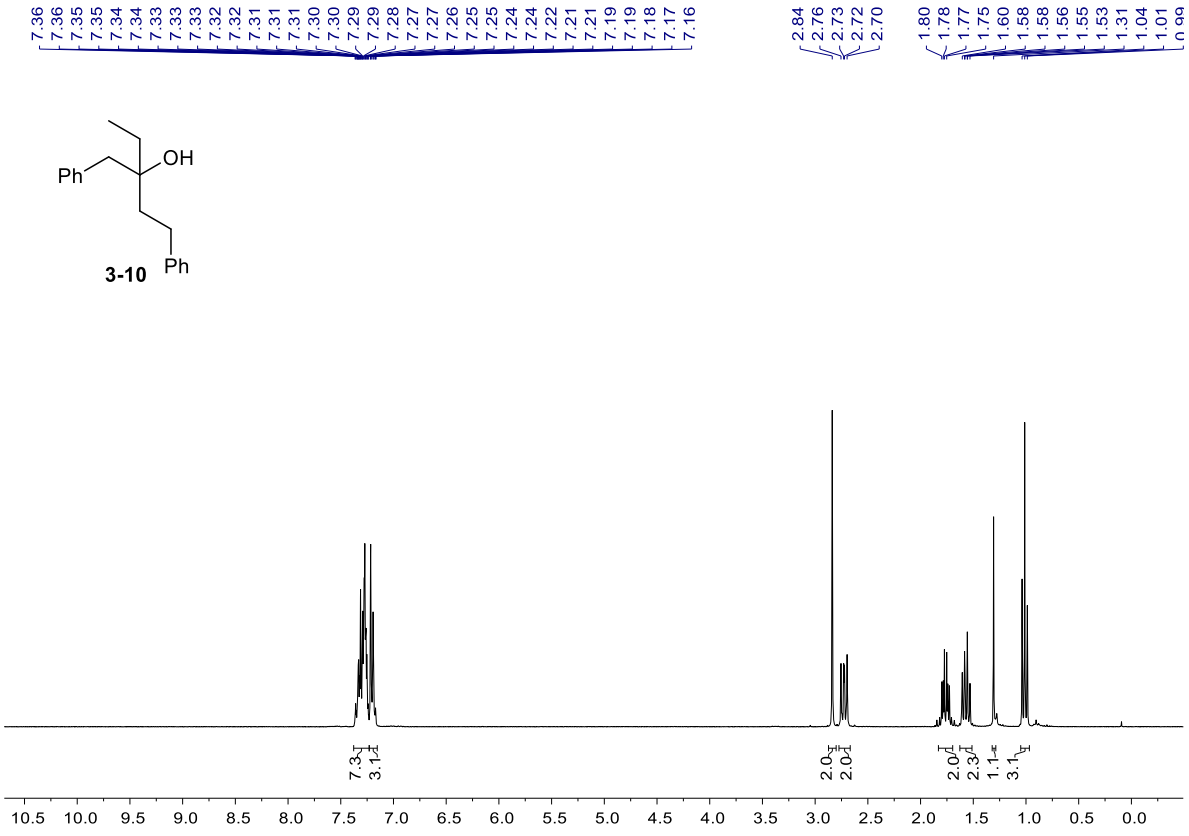
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3-7f**



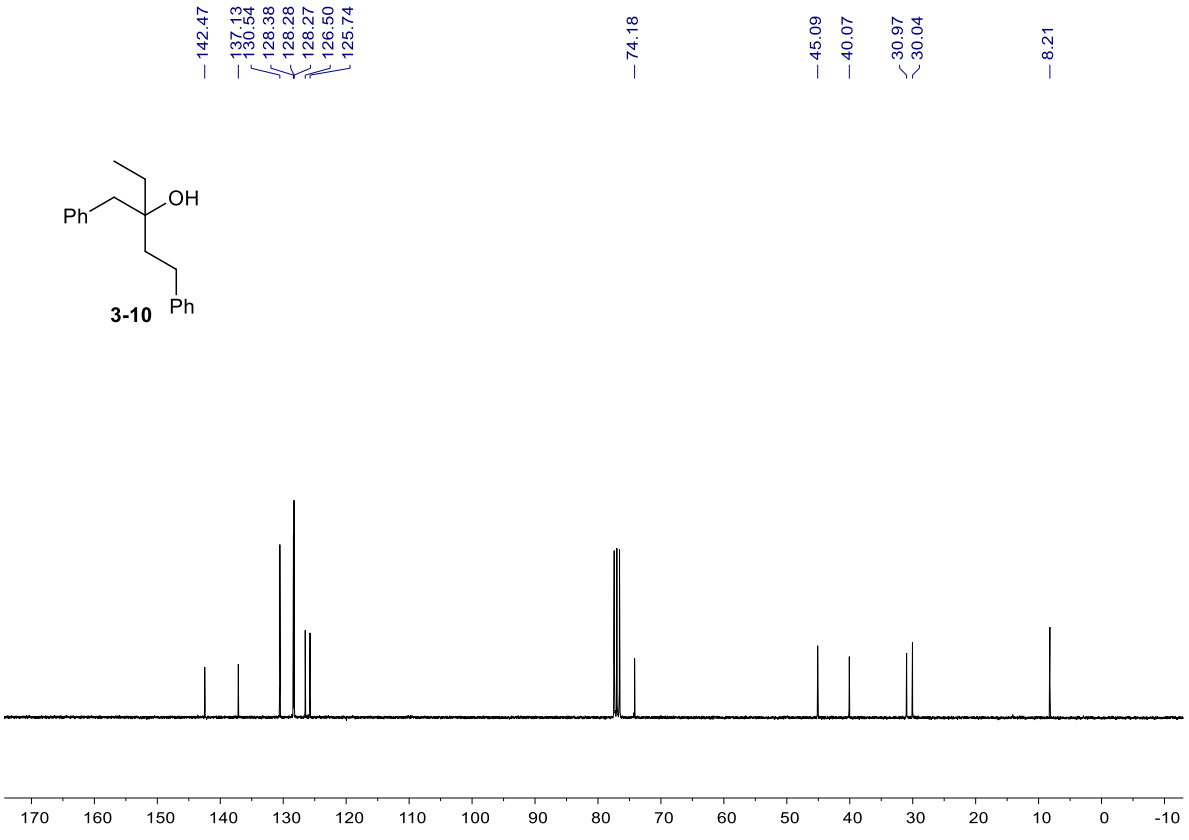
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **3-7f**



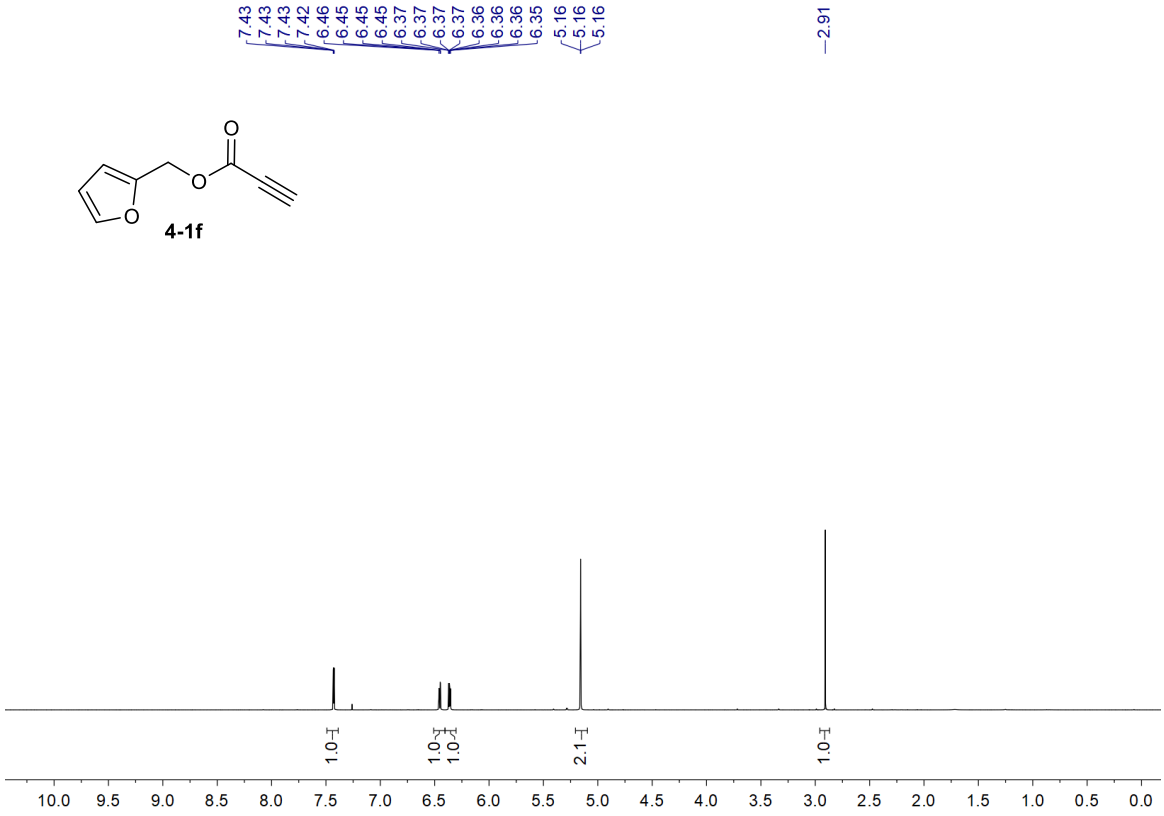
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3-10**



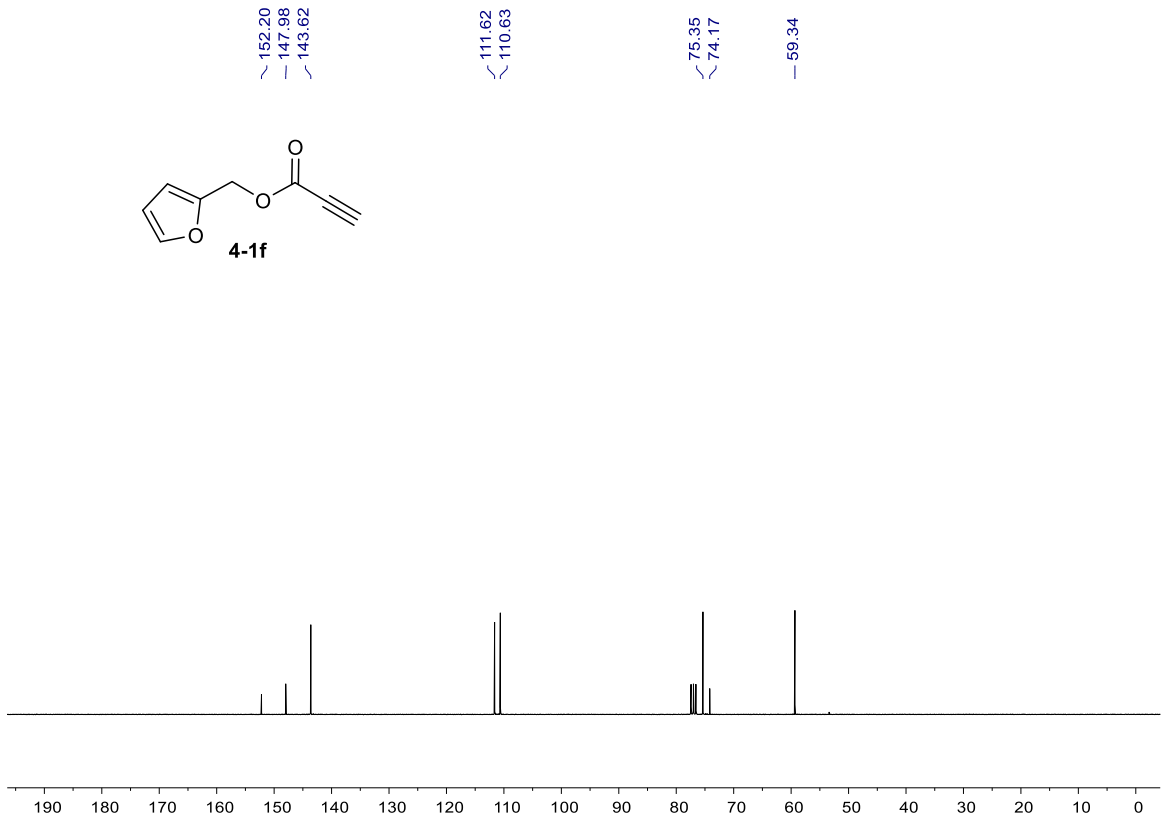
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **3-10**



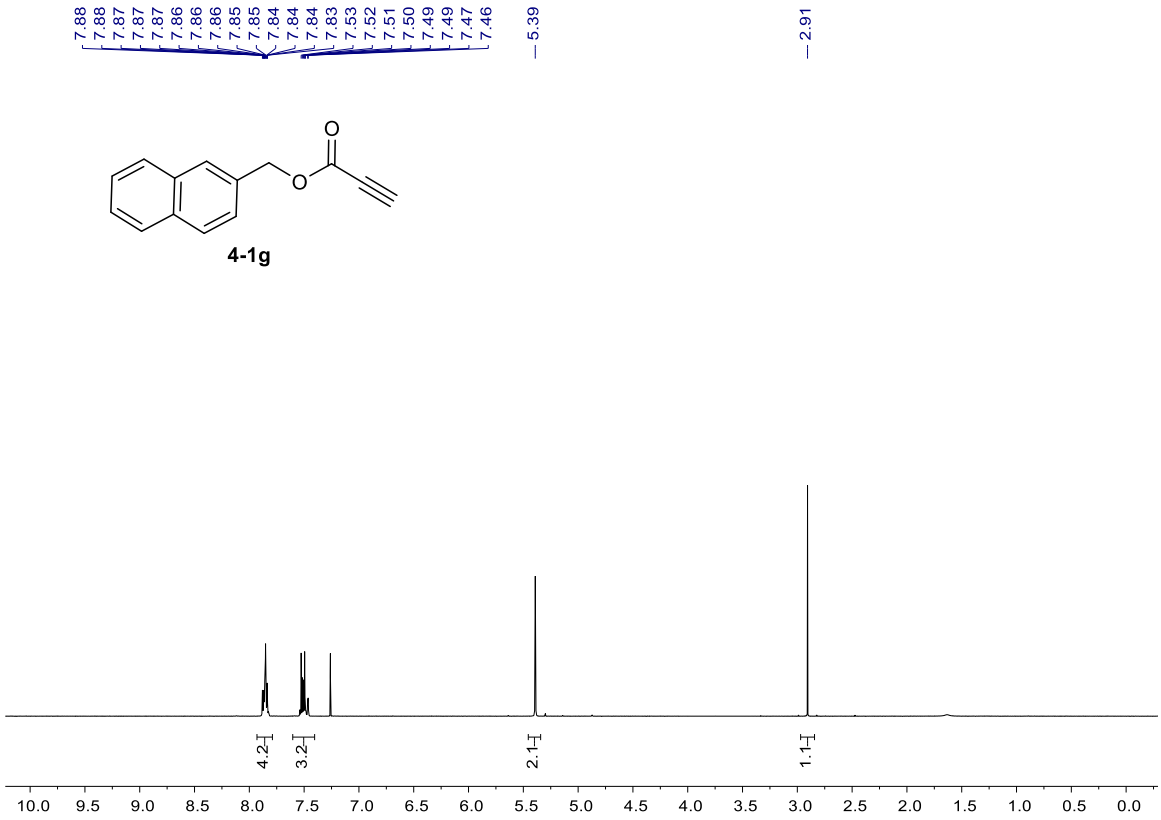
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4-1f**



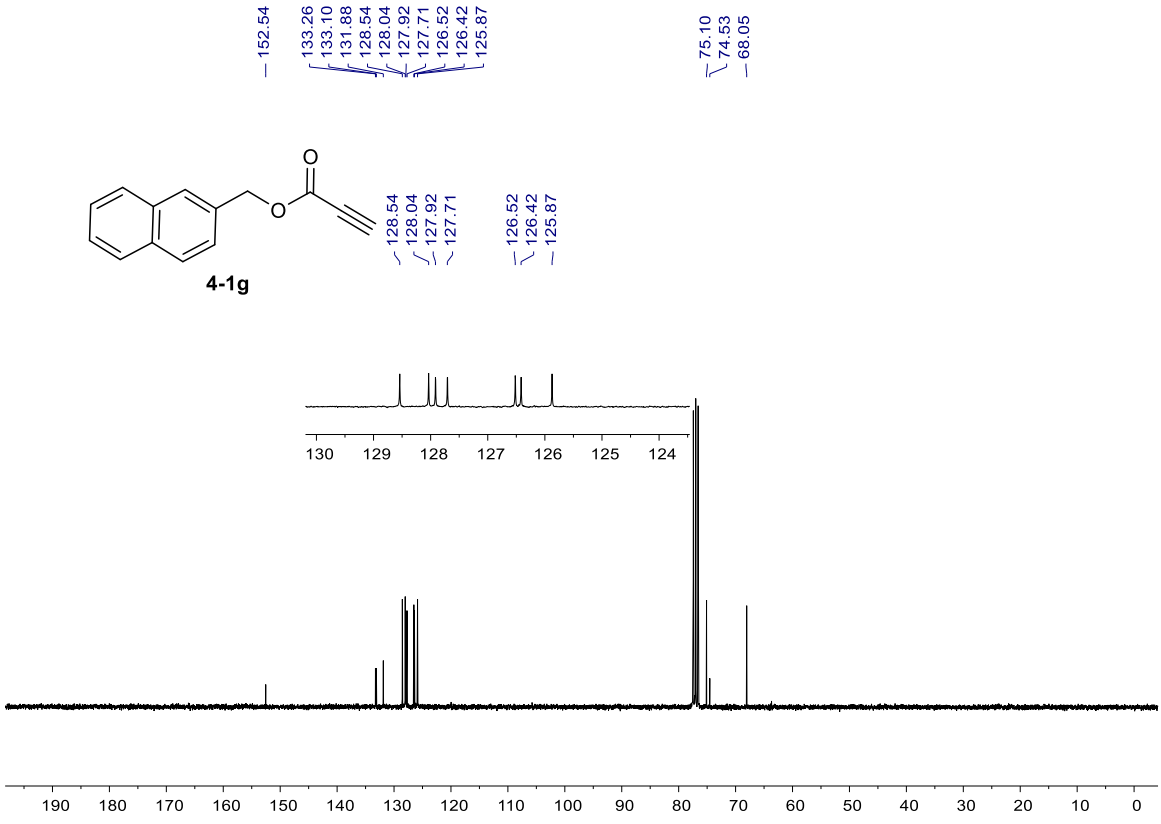
^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **4-1f**



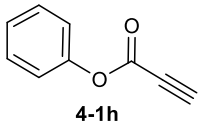
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4-1g**



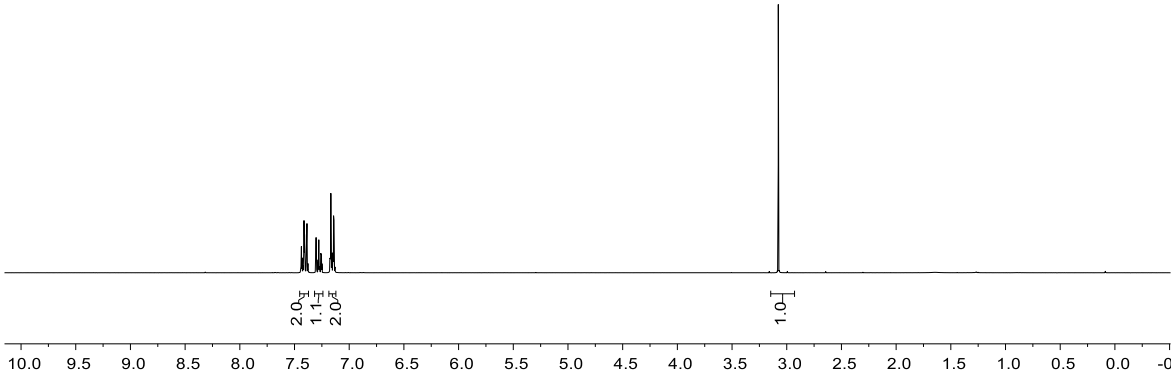
^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **4-1g**



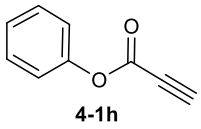
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4-1h**



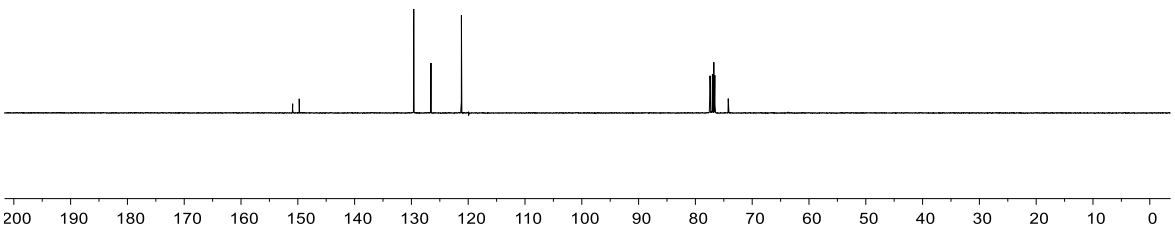
4-1h



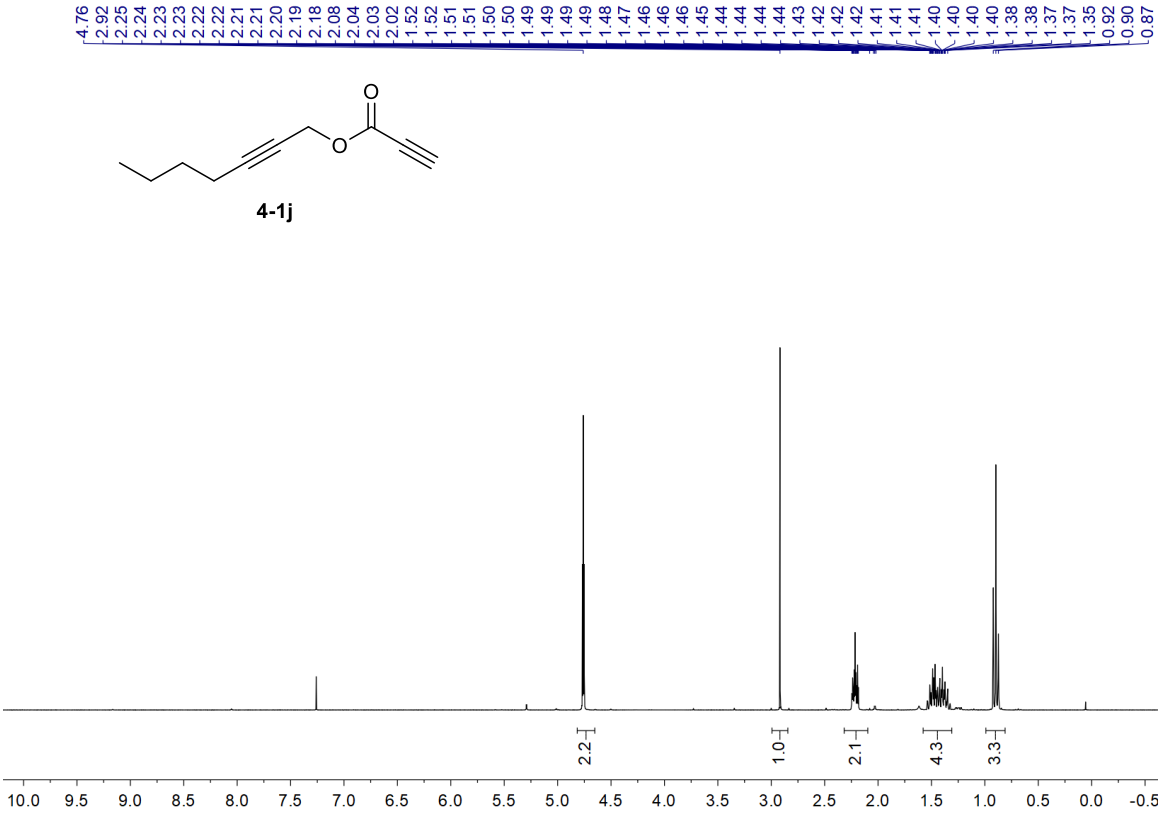
^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **4-1h**



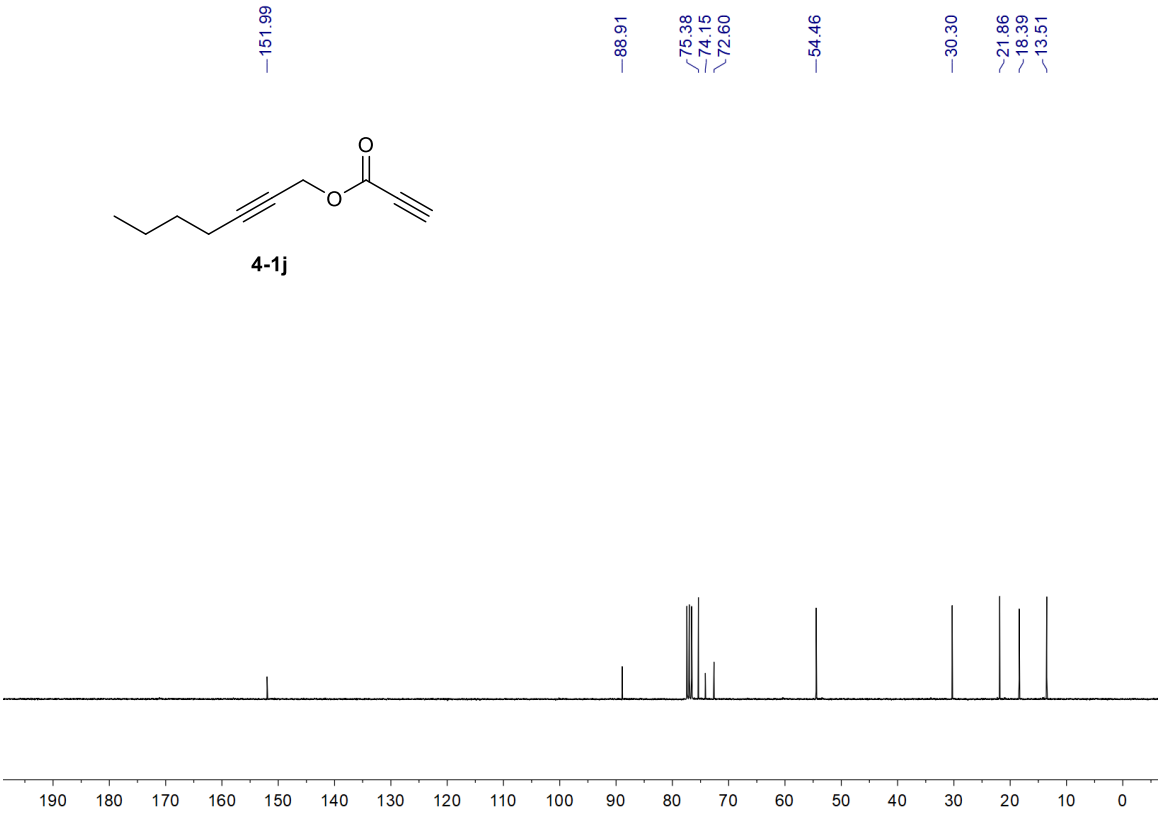
4-1h



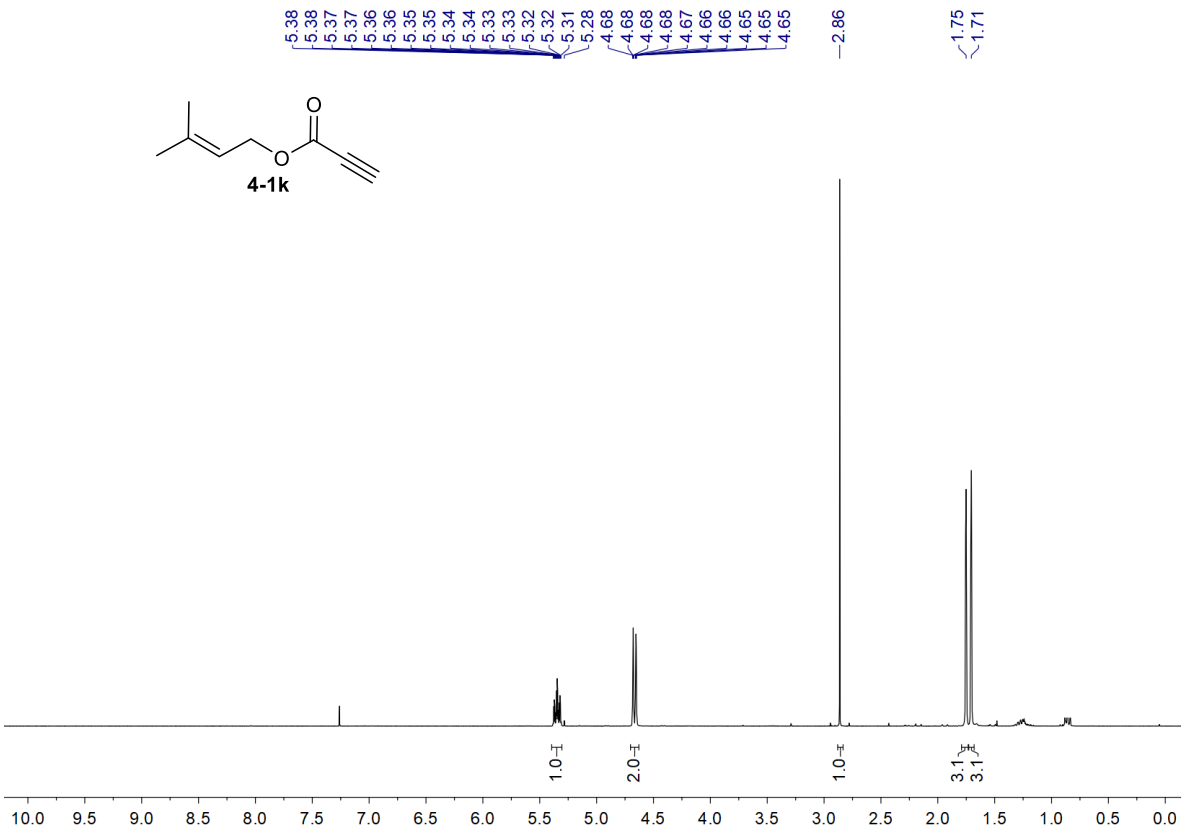
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4-1j**



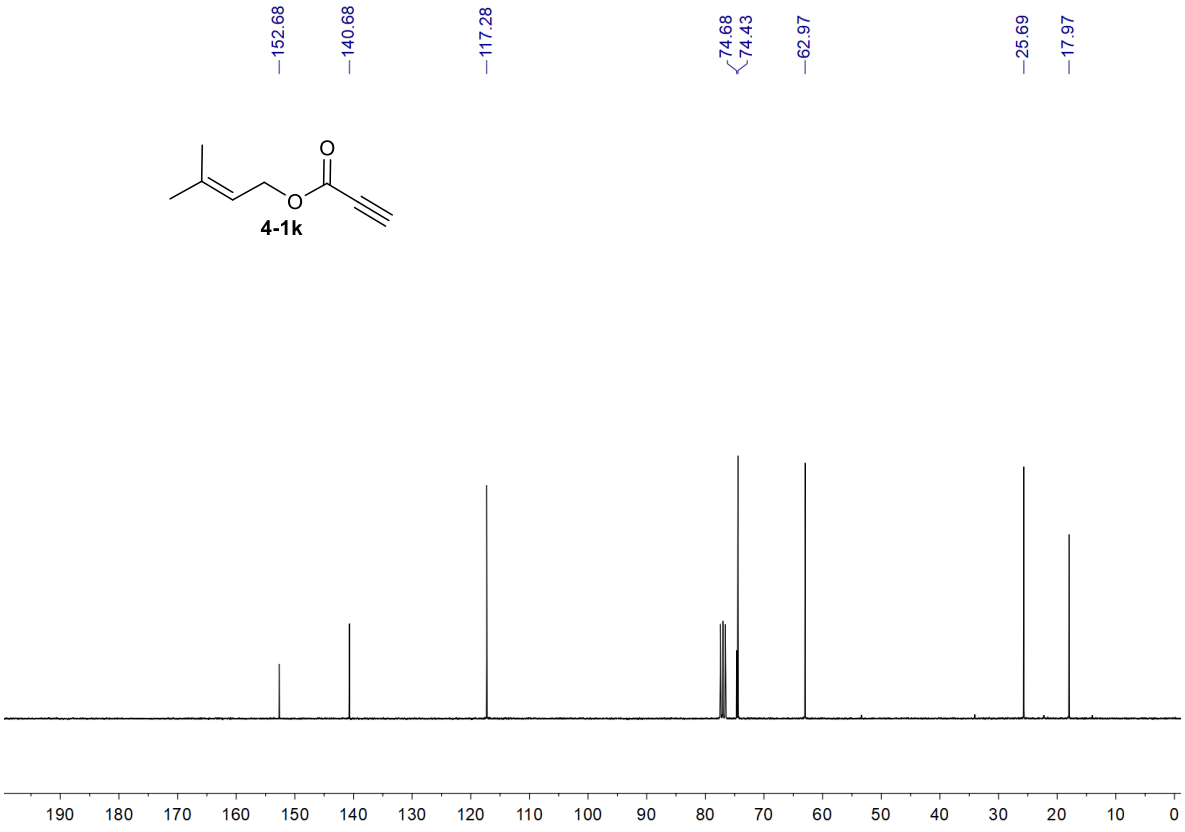
^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **4-1j**



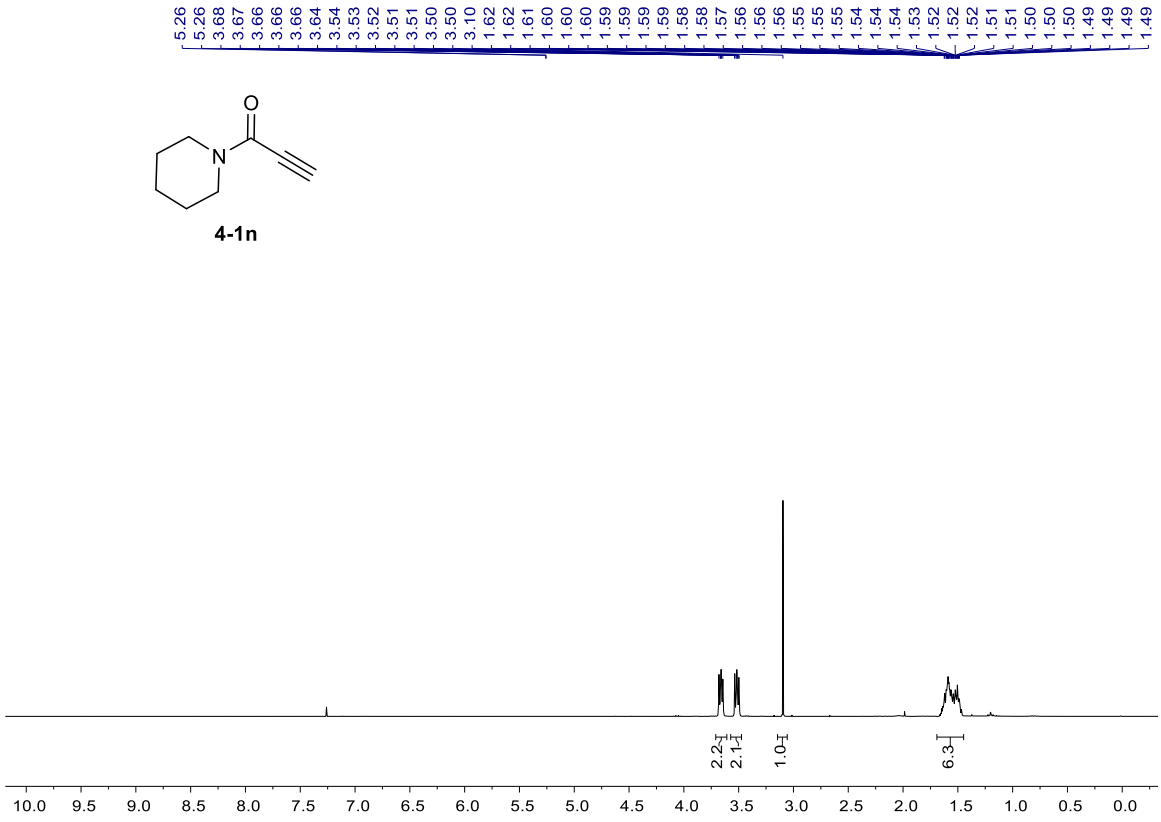
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4-1k**



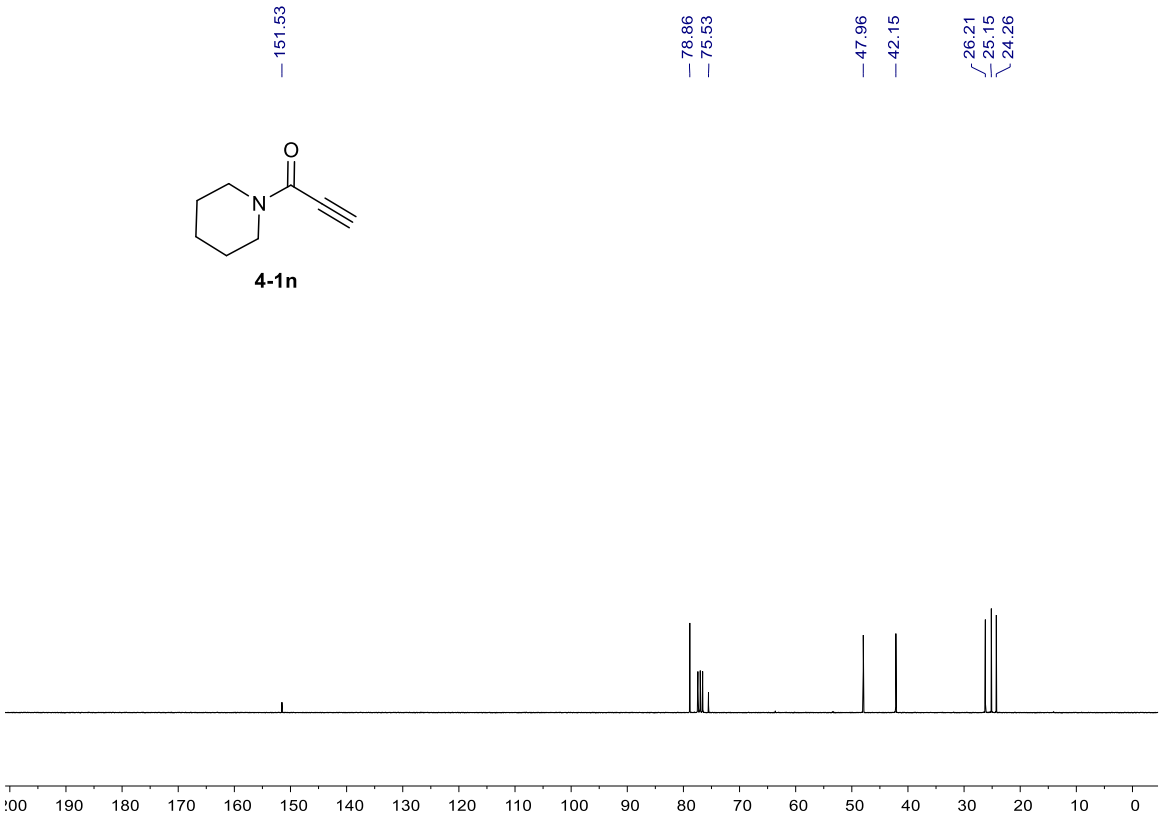
^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **4-1k**



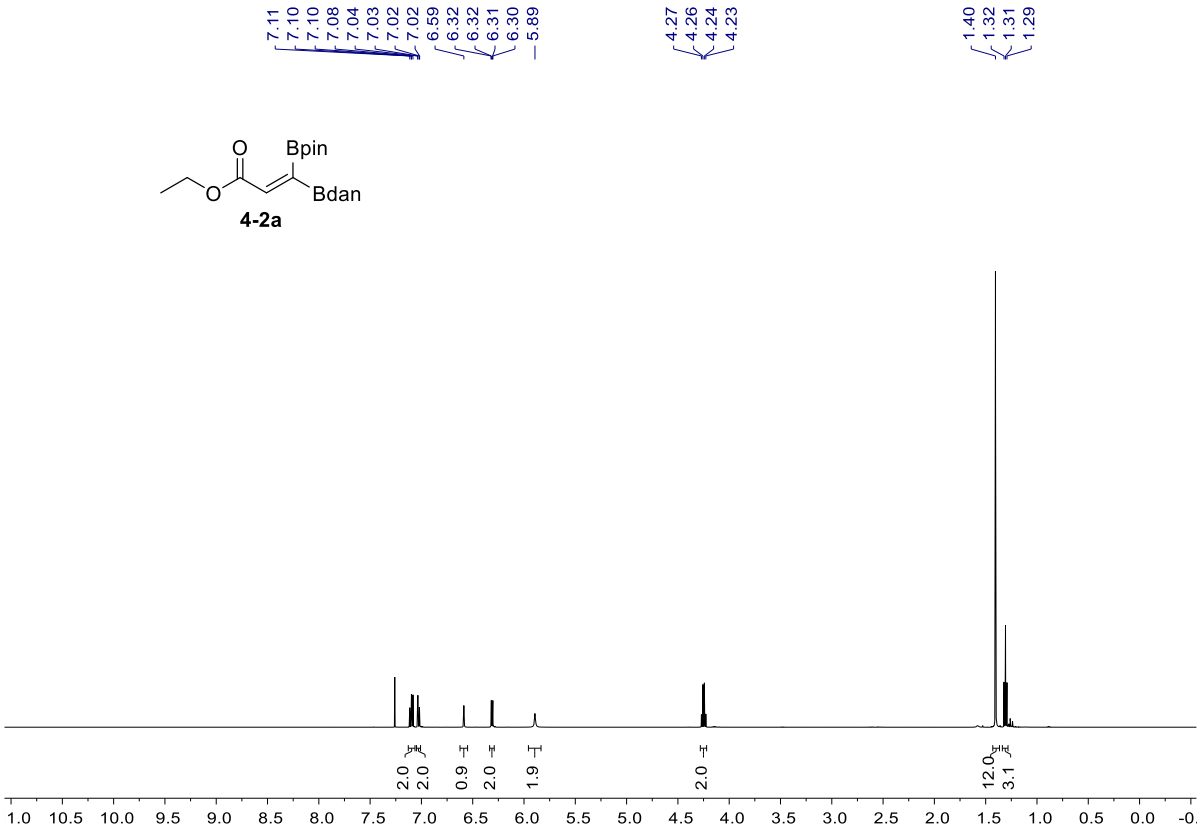
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4-1n**



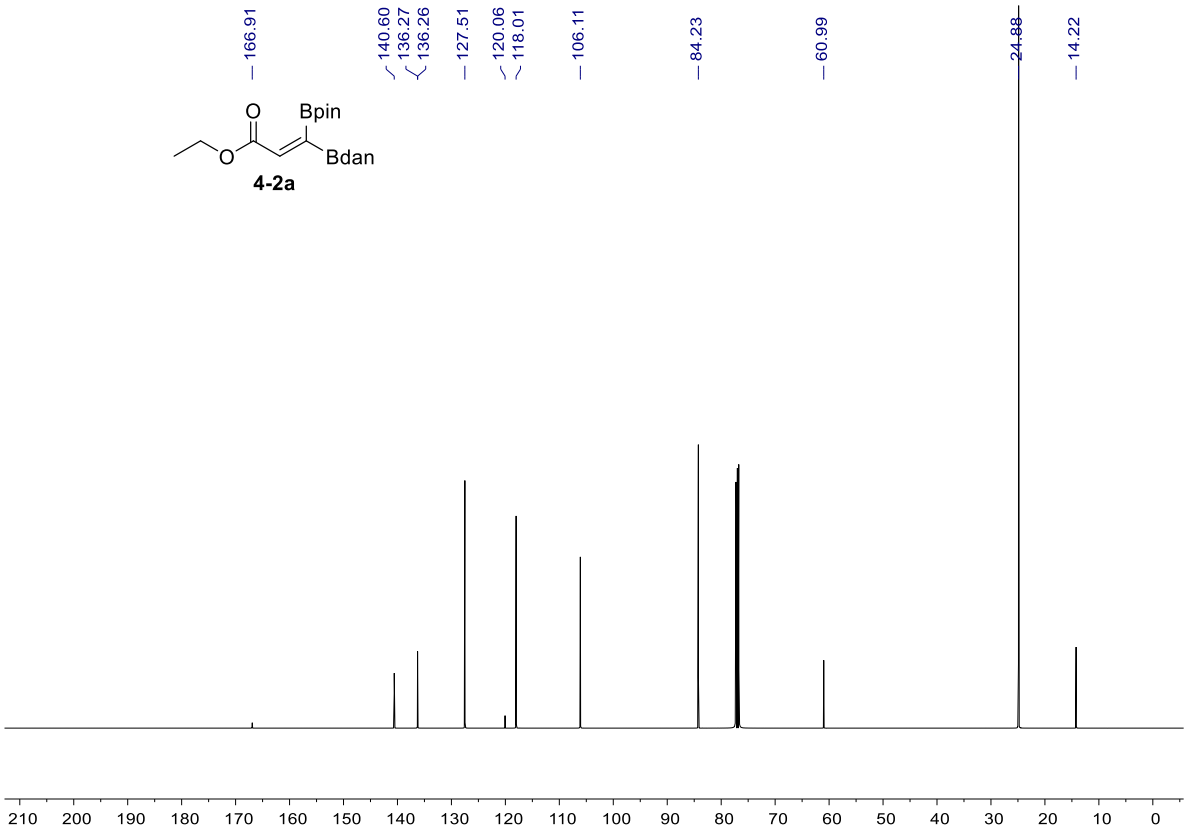
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **4-1n**



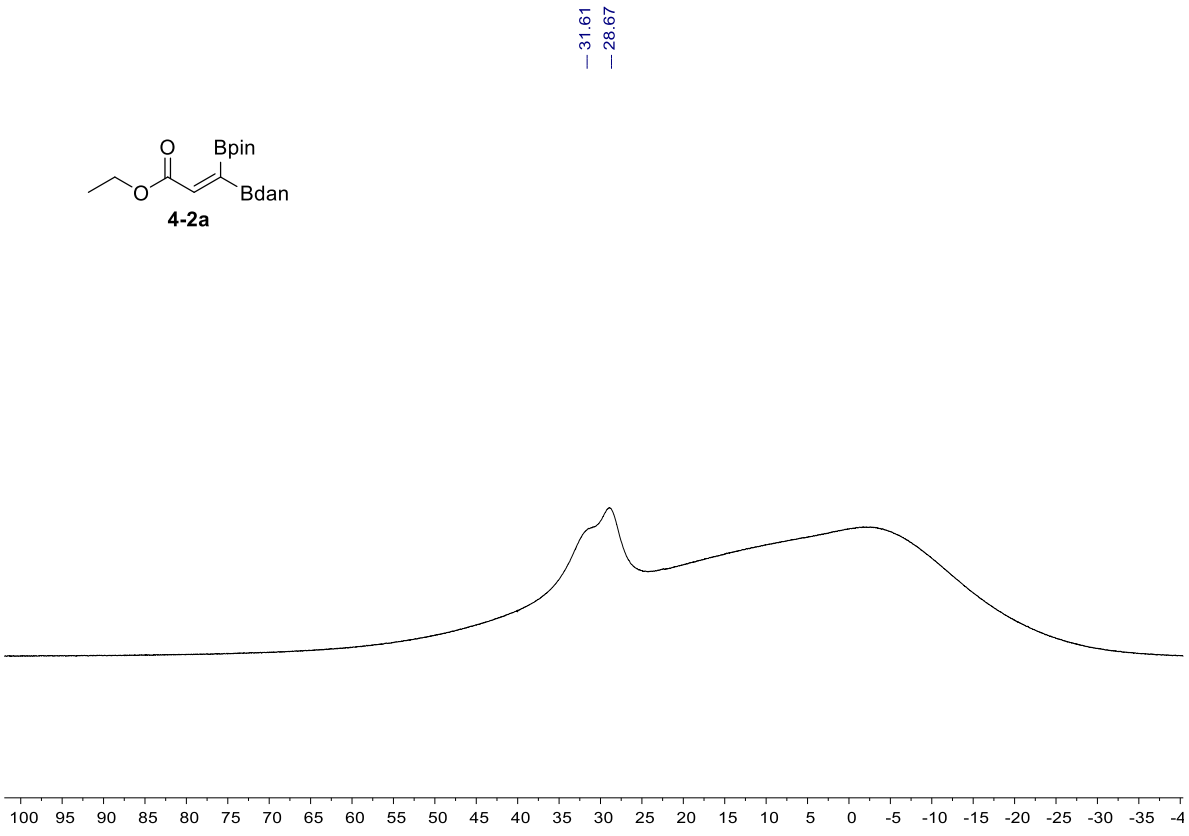
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2a**



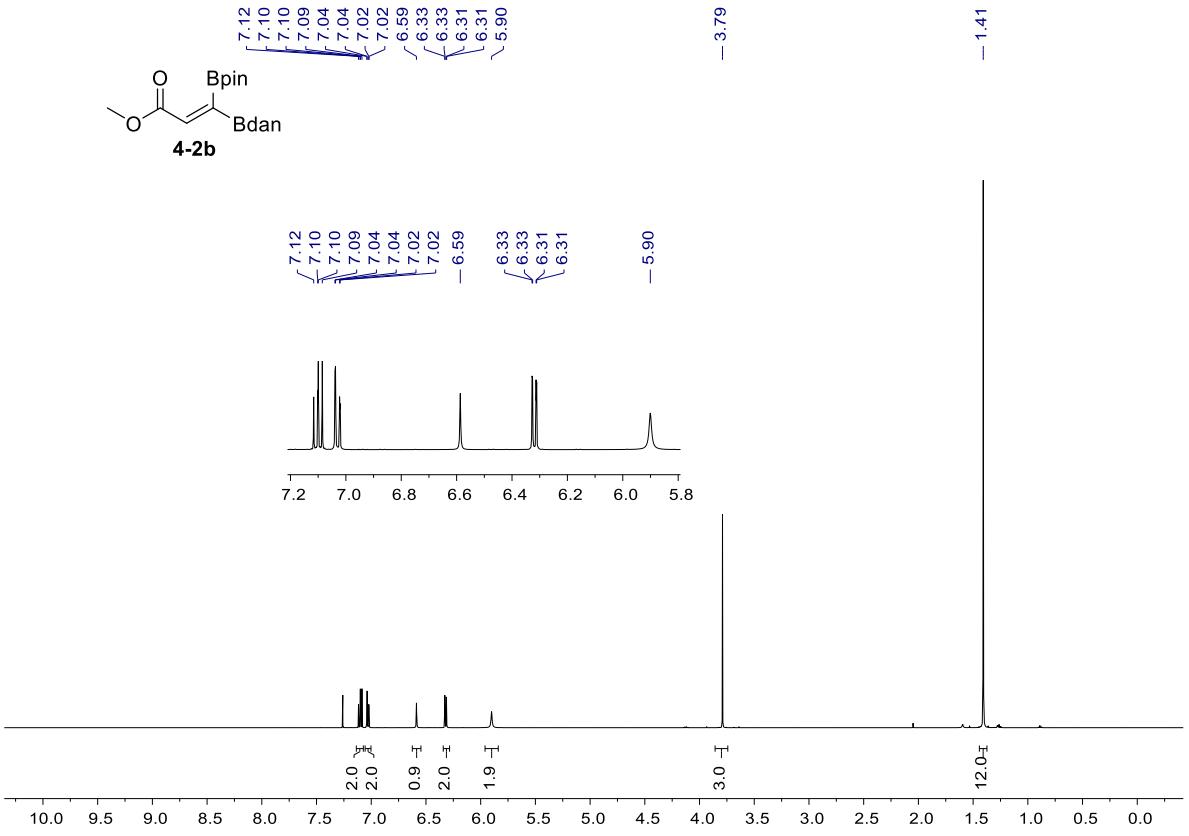
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **4-2a**



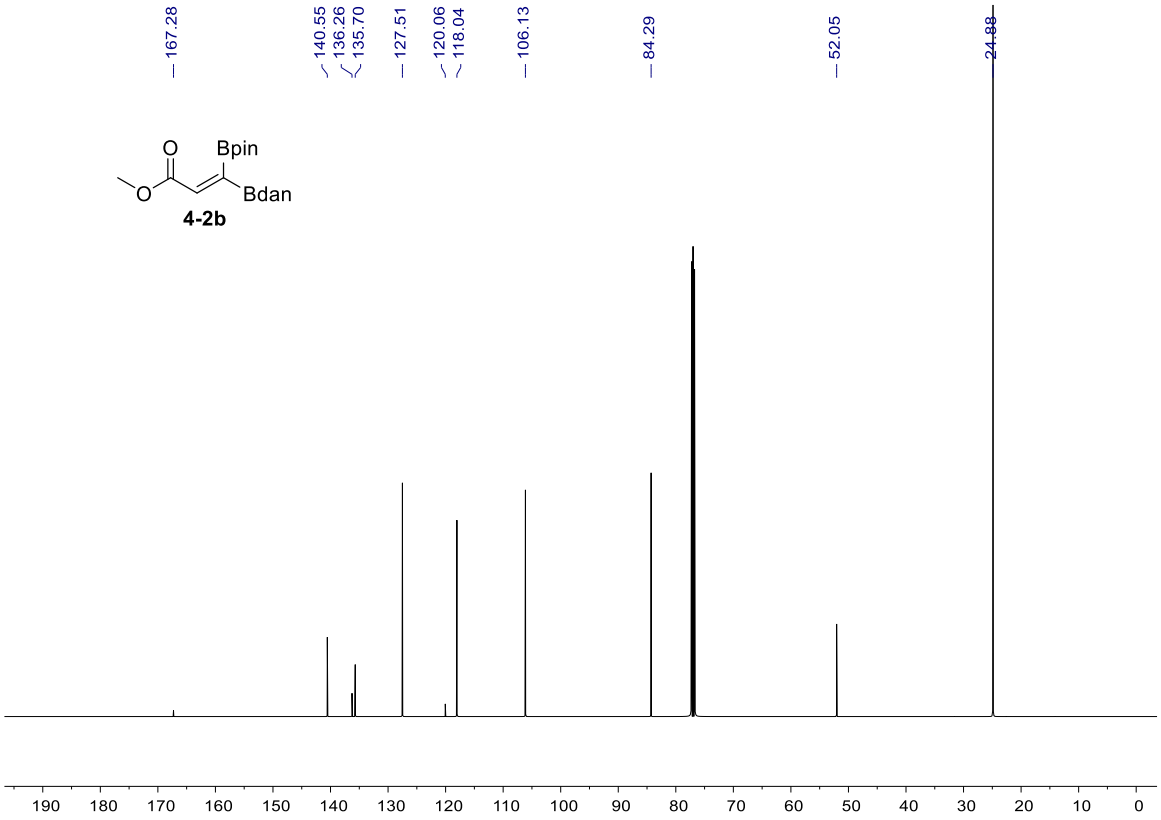
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **4-2a**



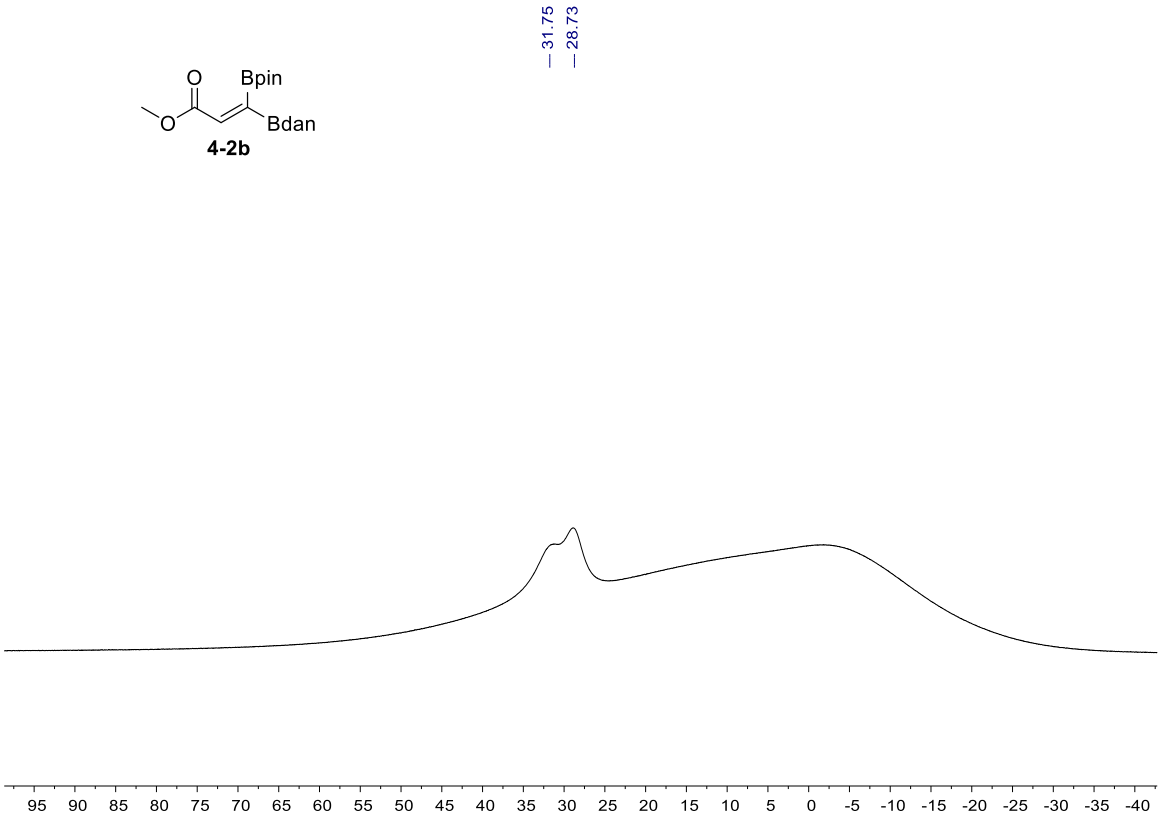
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2b**



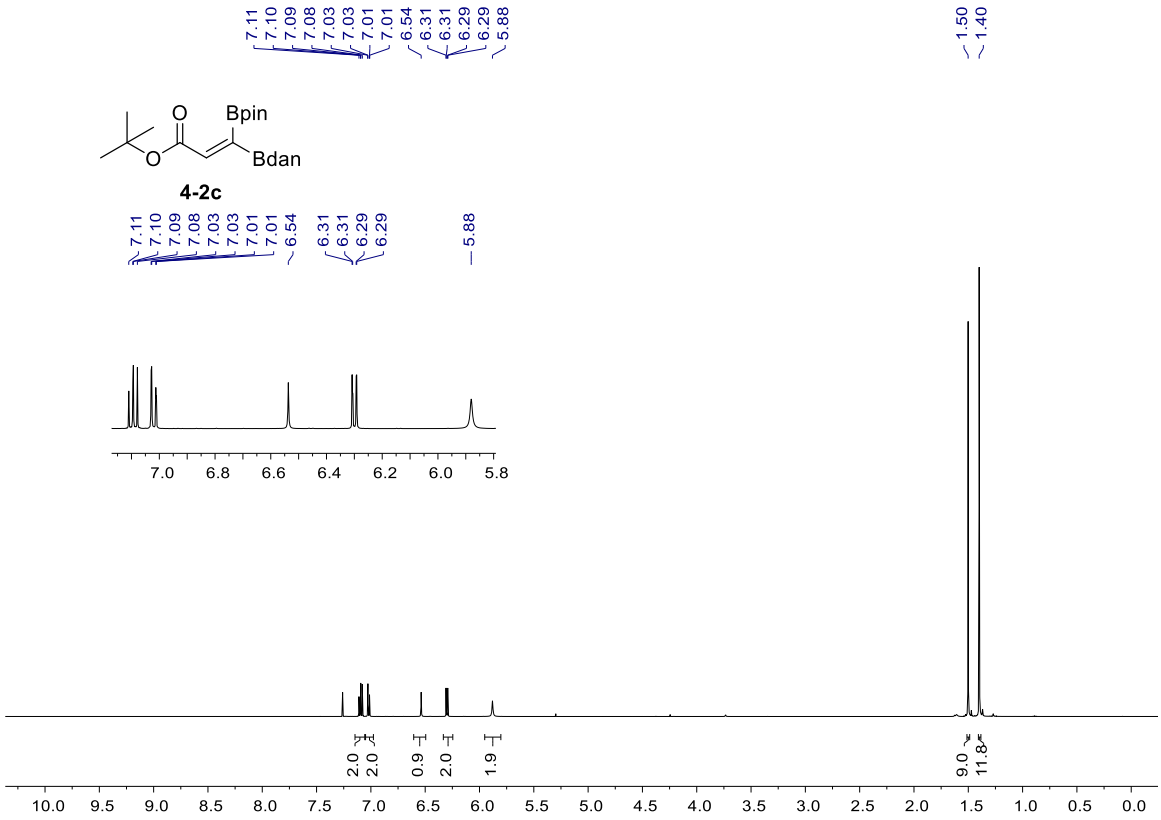
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **4-2b**



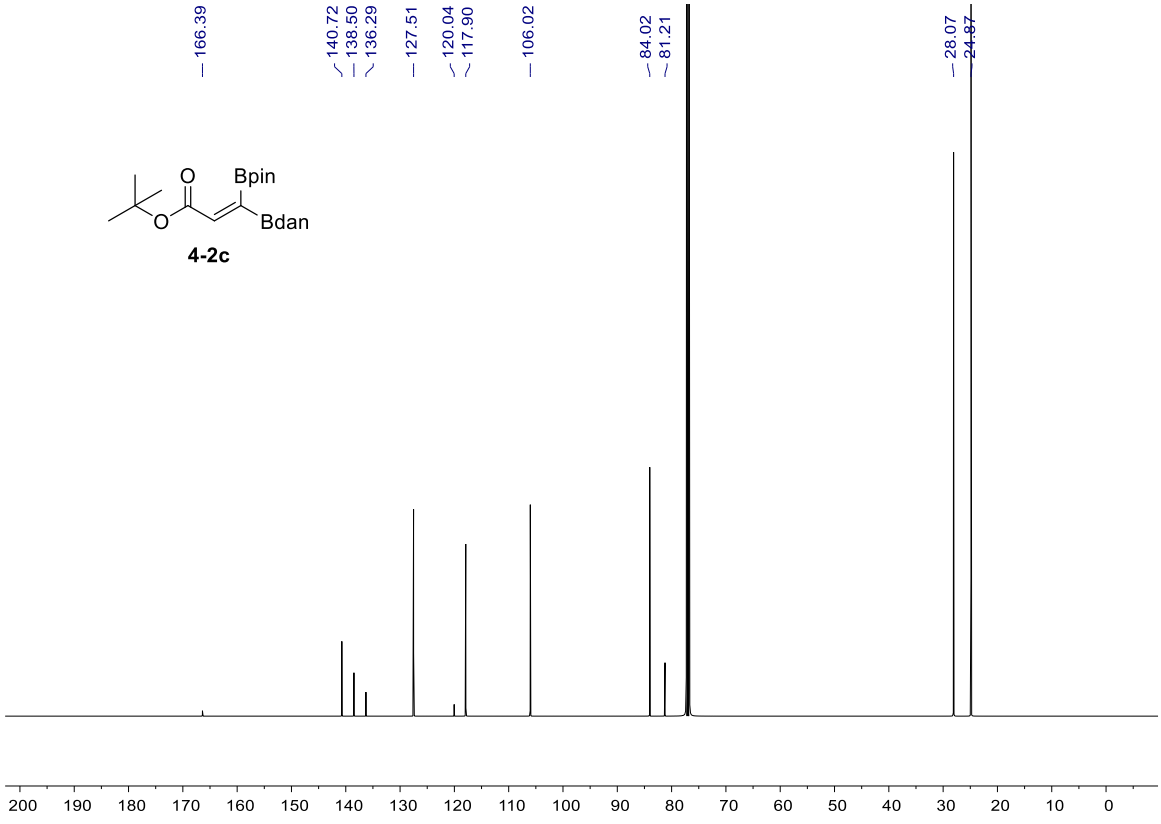
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **4-2b**



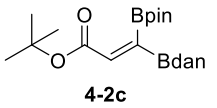
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2c**



^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **4-2c**

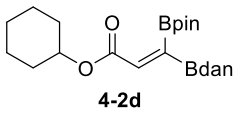


^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **4-2c**

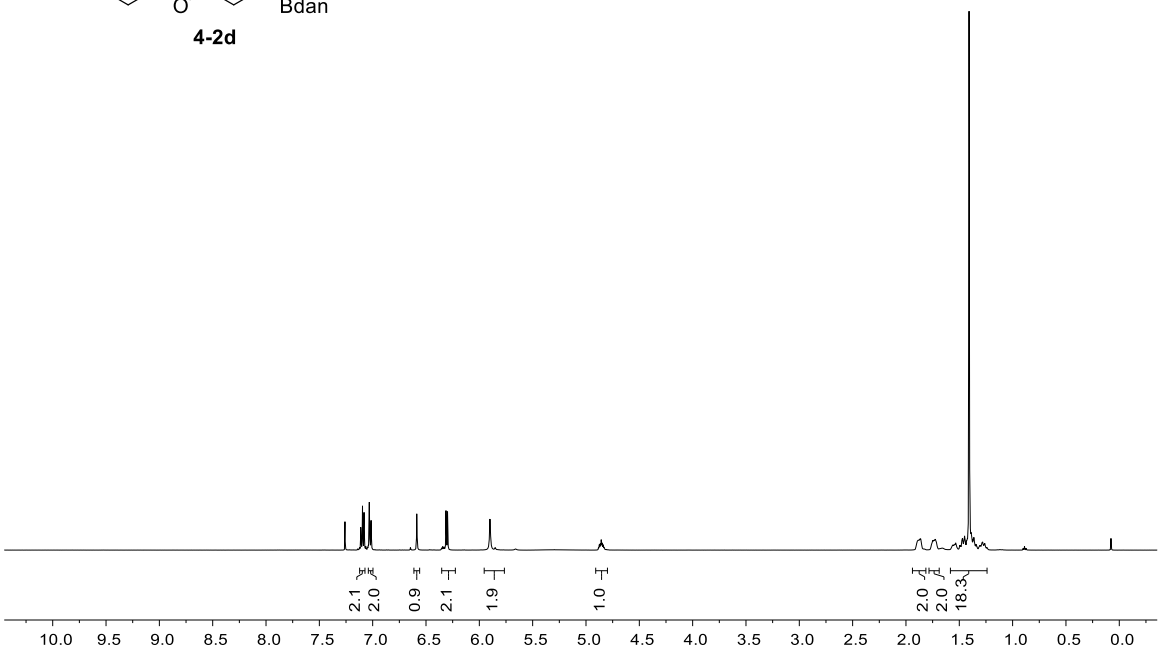


4-2c

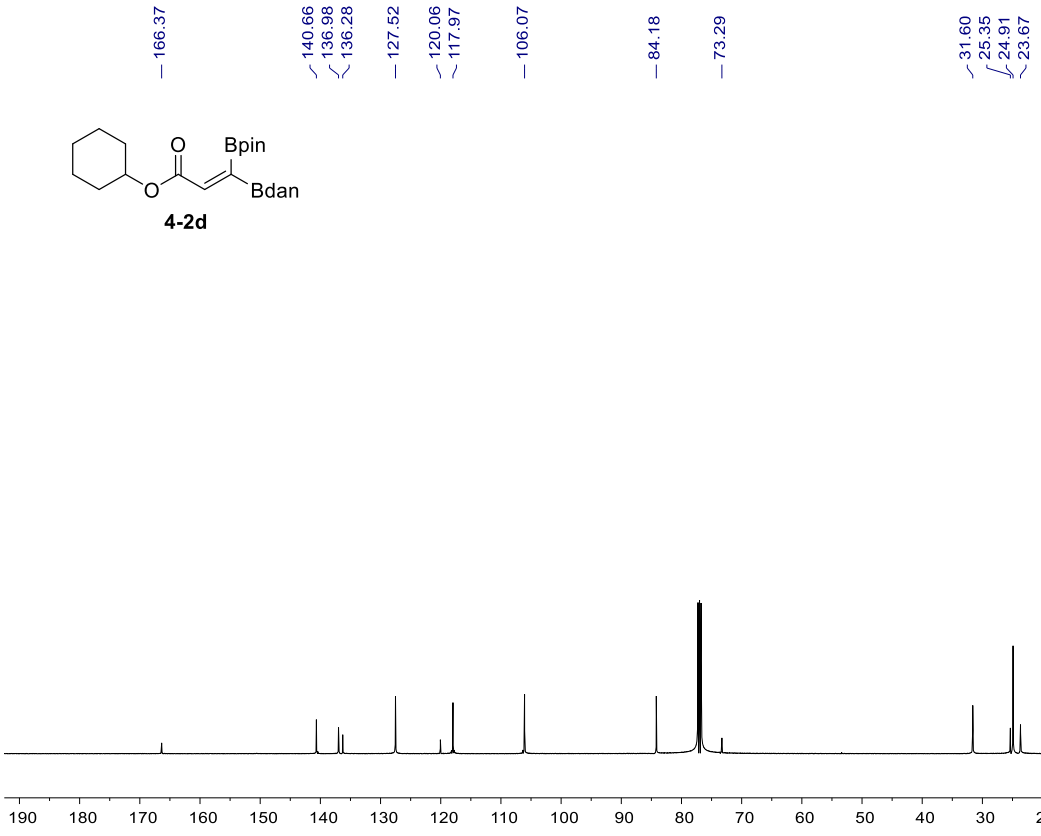
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2d**



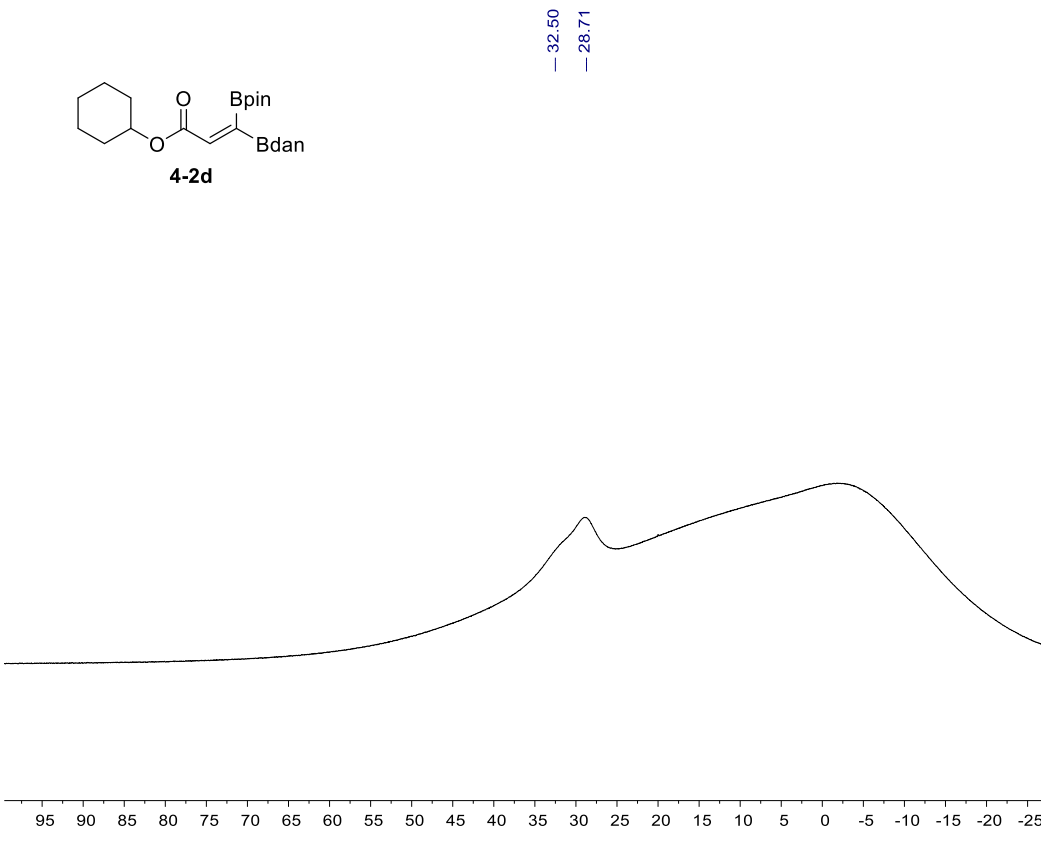
4-2d



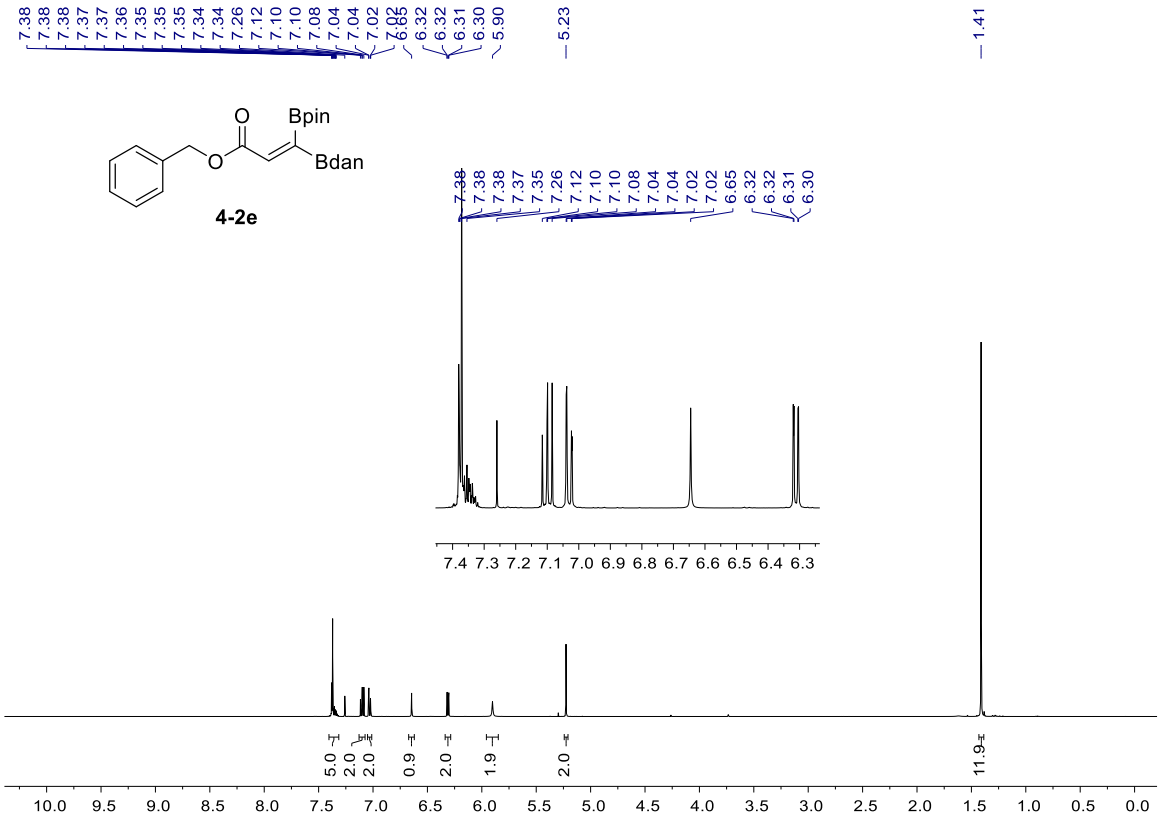
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **4-2d**



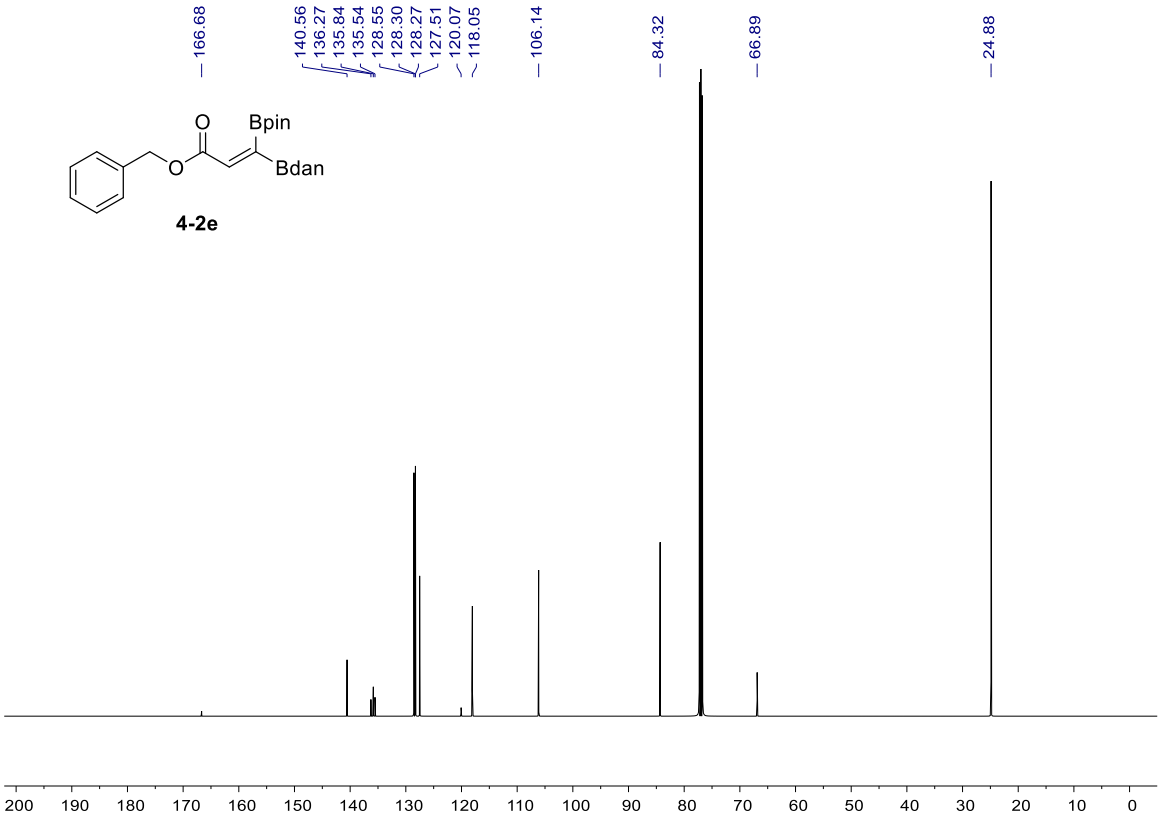
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **4-2d**



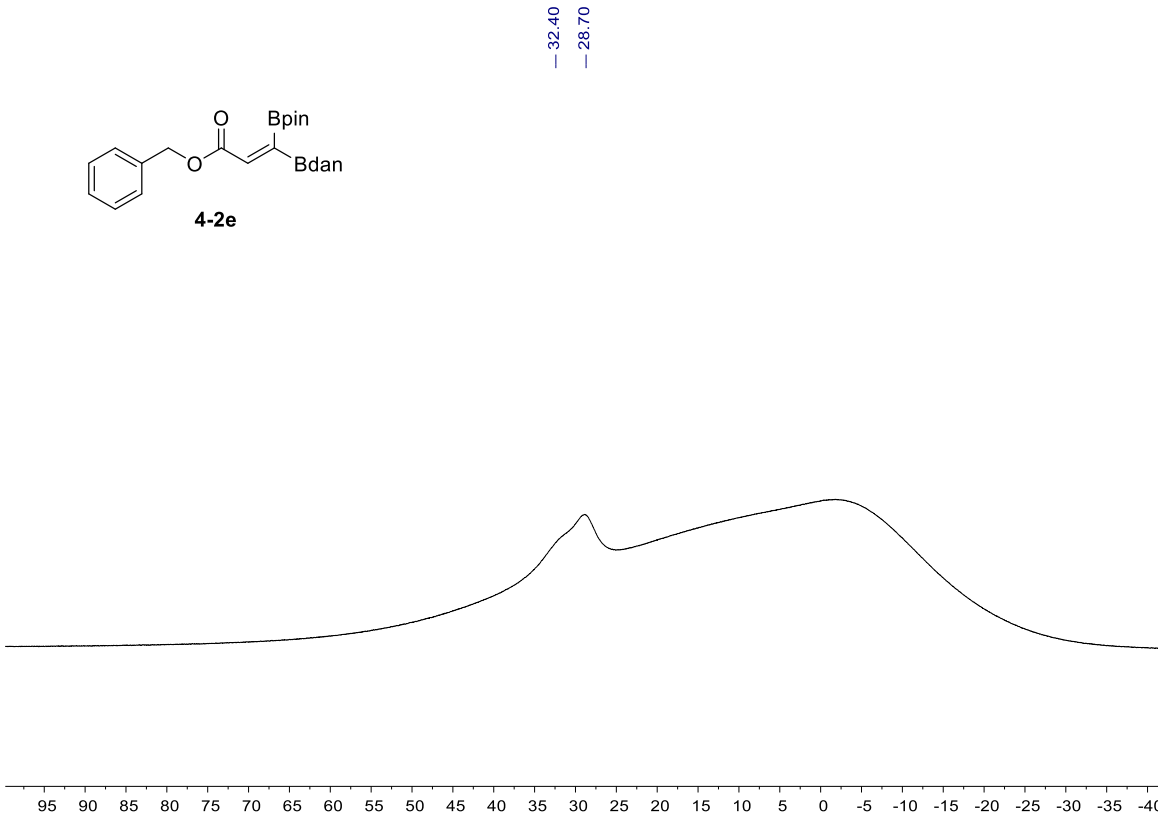
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2e**



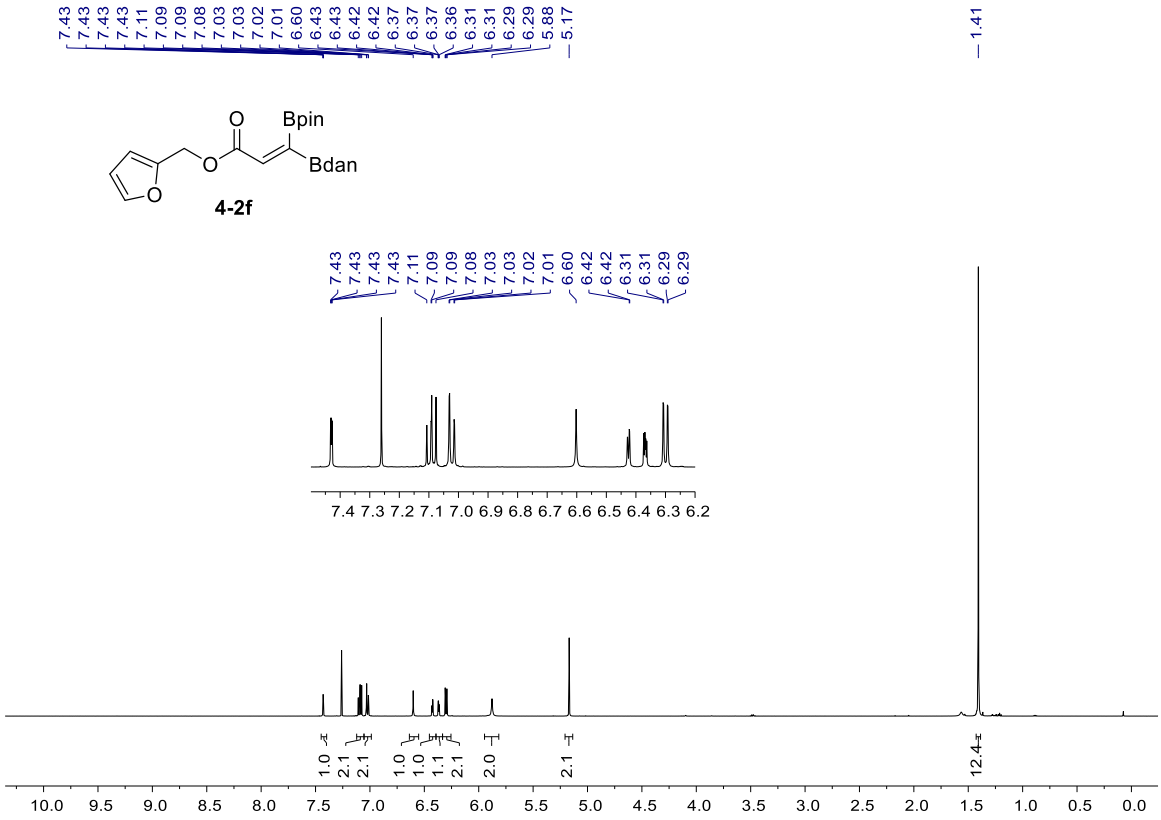
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **4-2e**



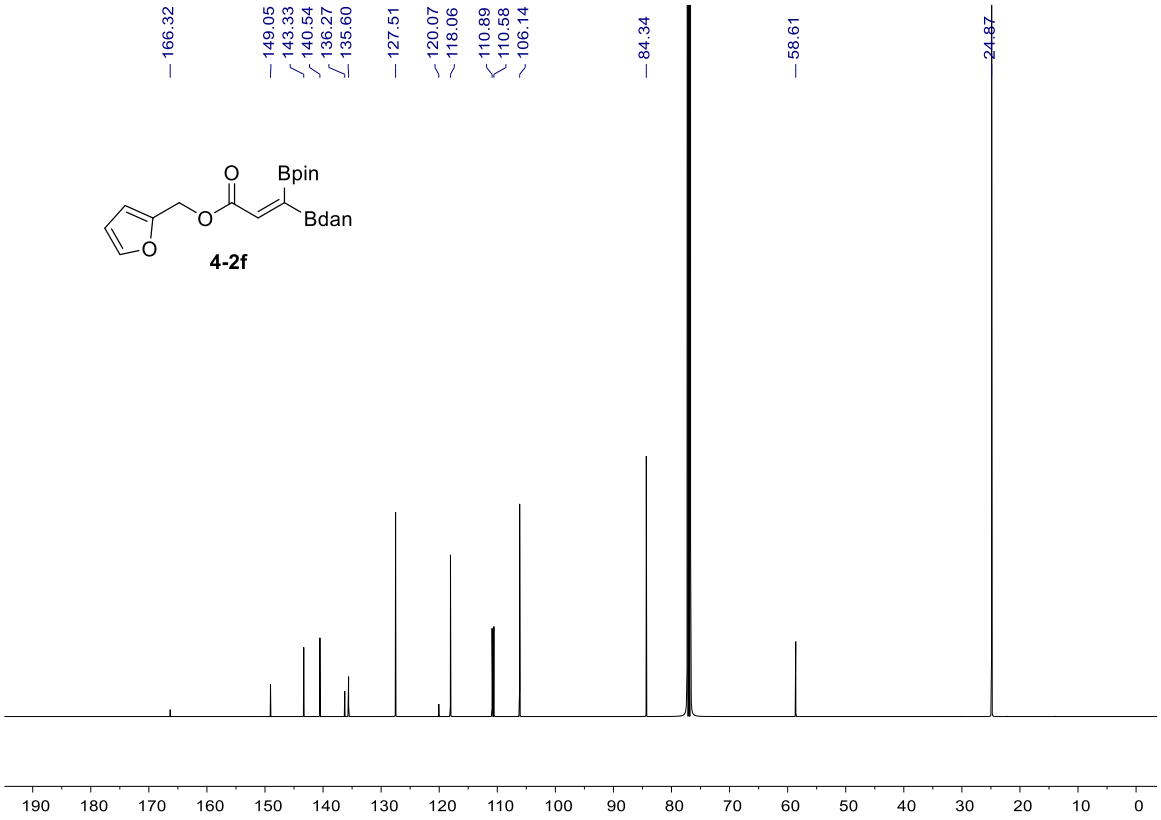
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **4-2e**



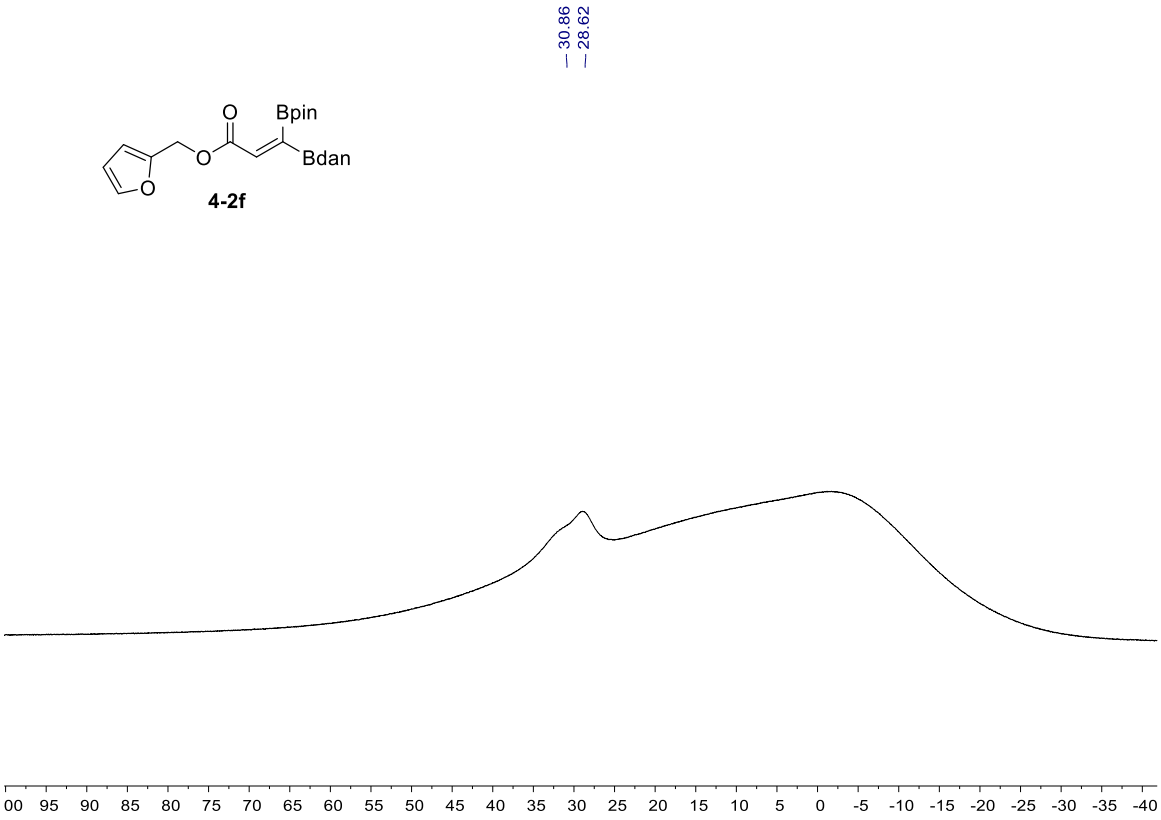
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2f**



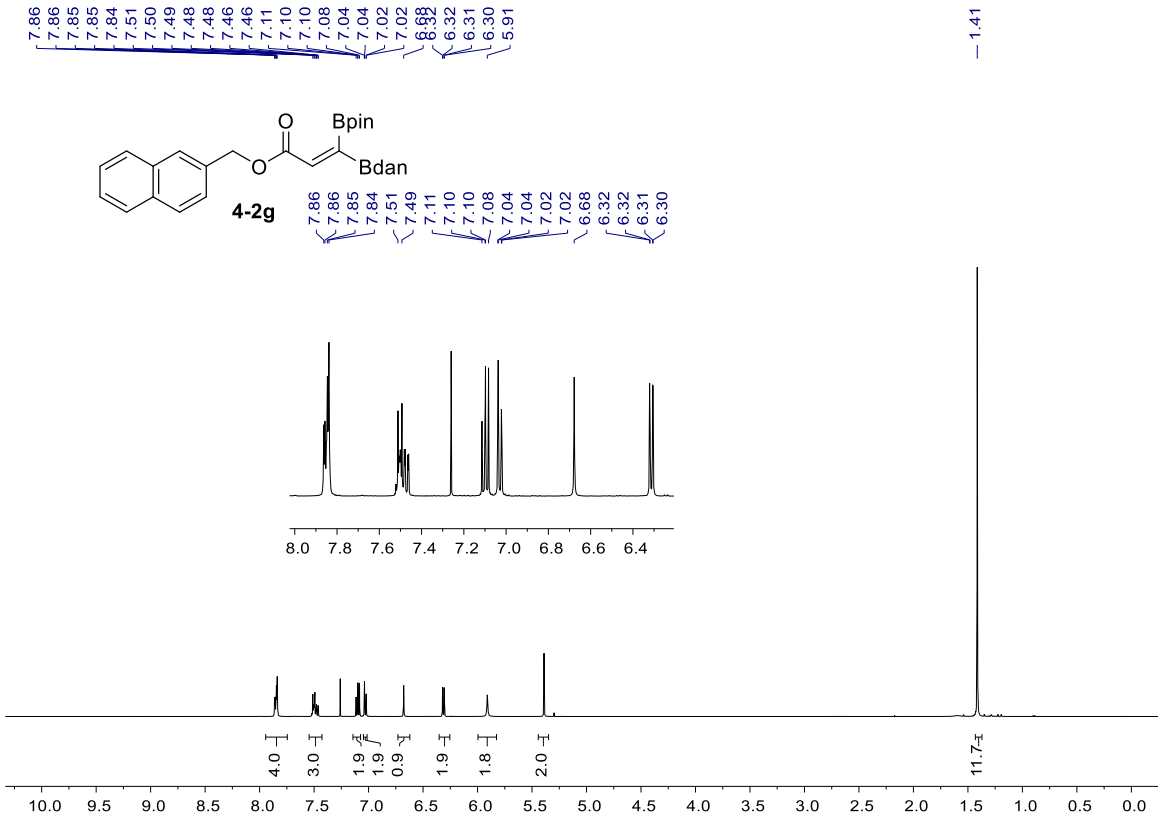
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **4-2f**



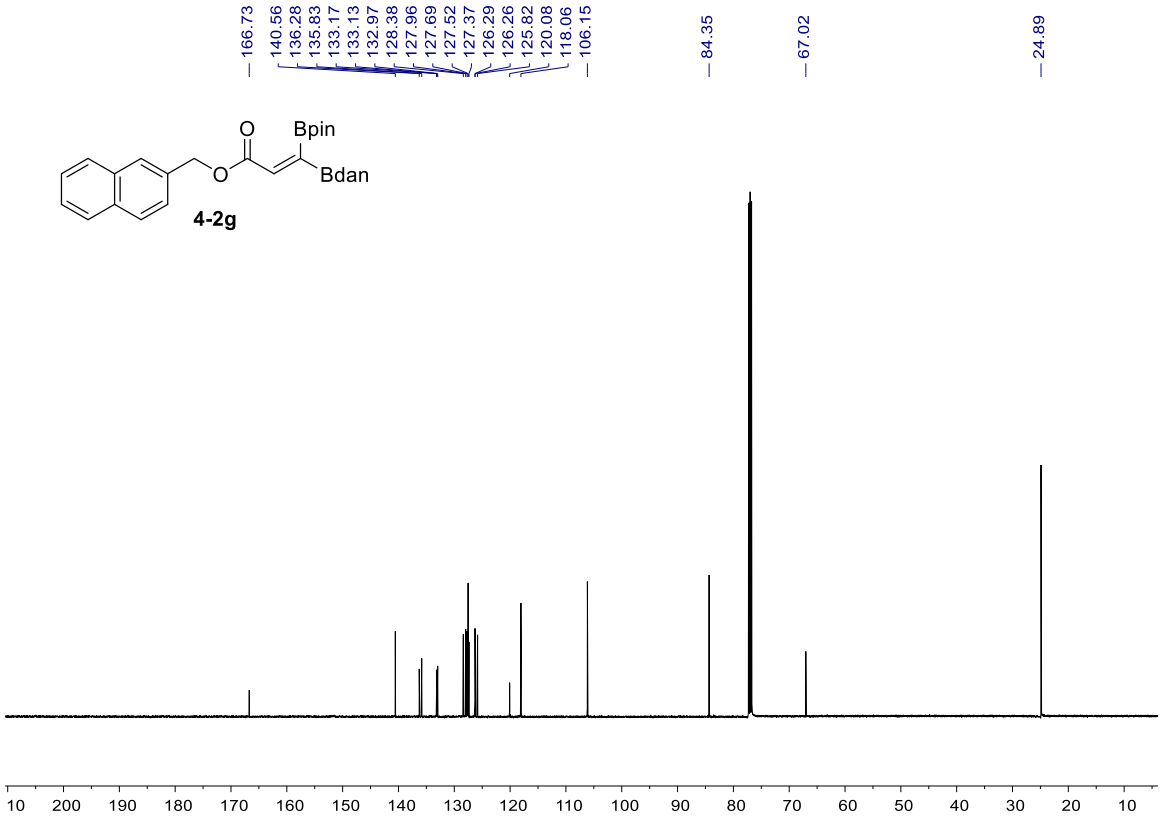
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **4-2f**



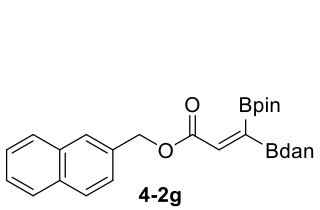
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2g**



^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **4-2g**

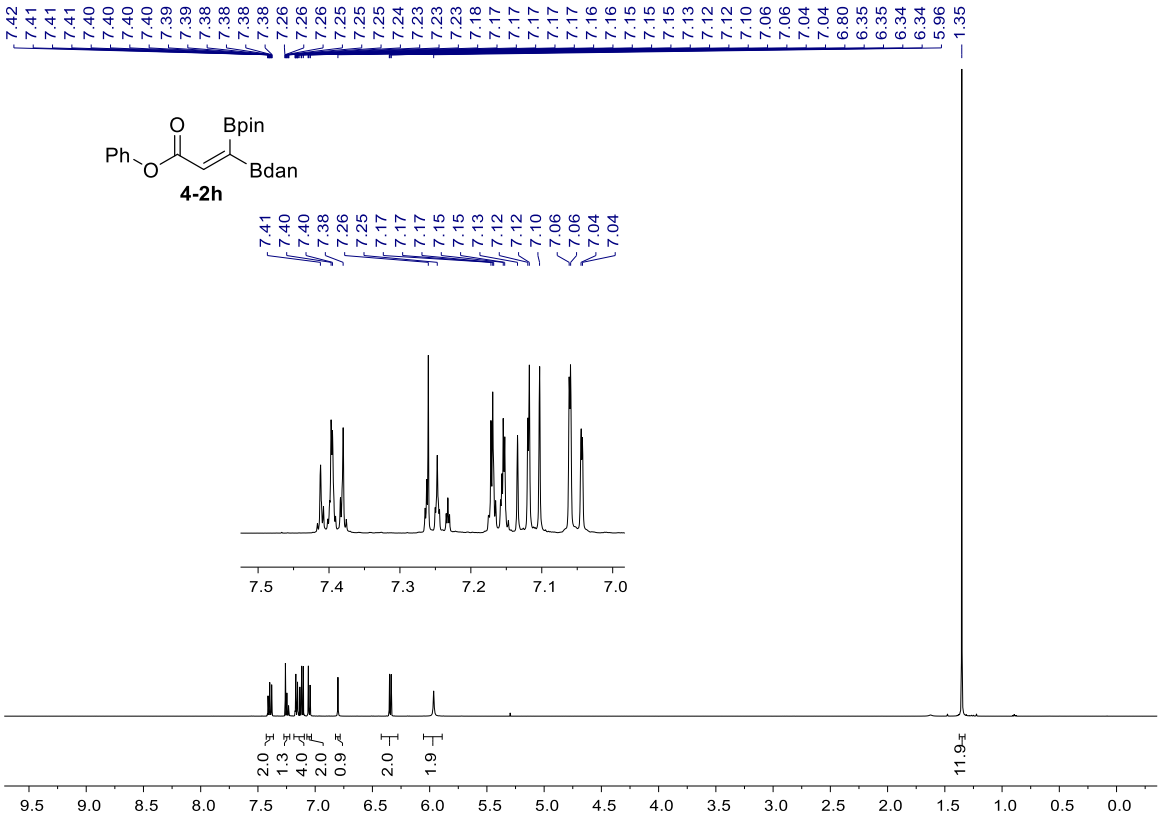


^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **4-2g**

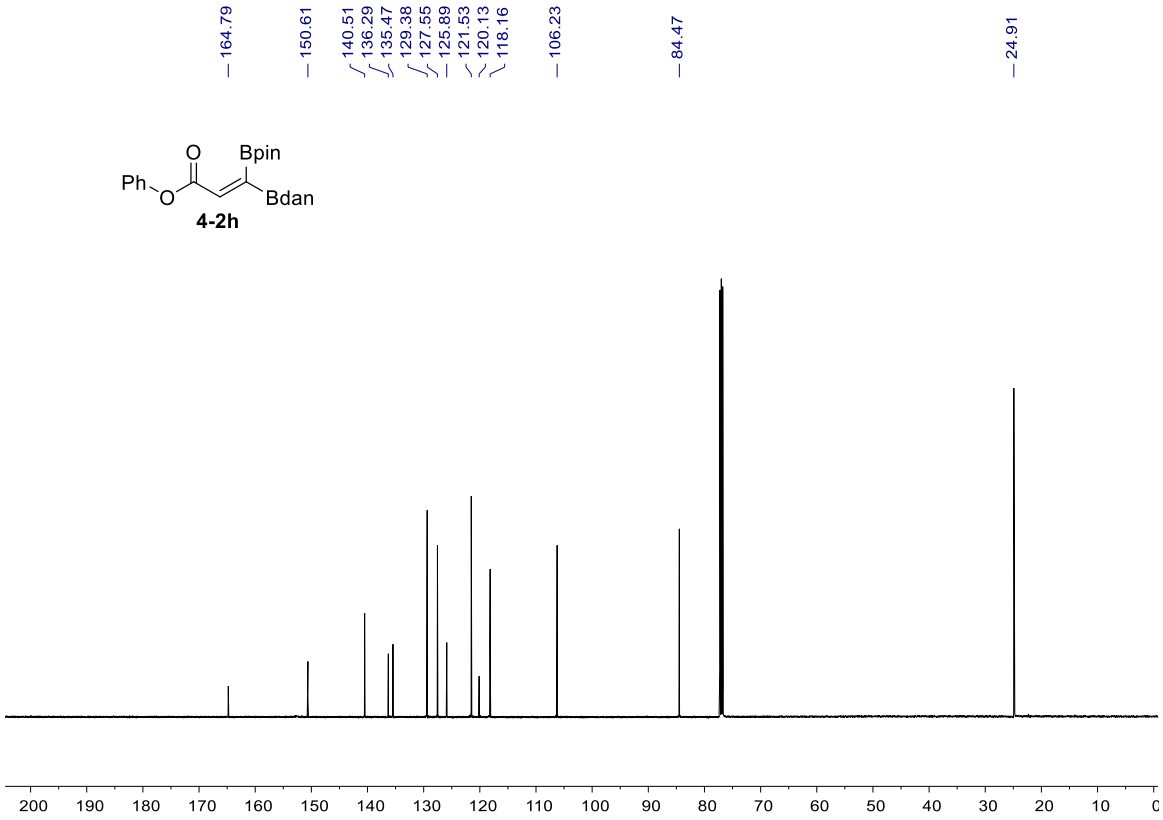


4-2g

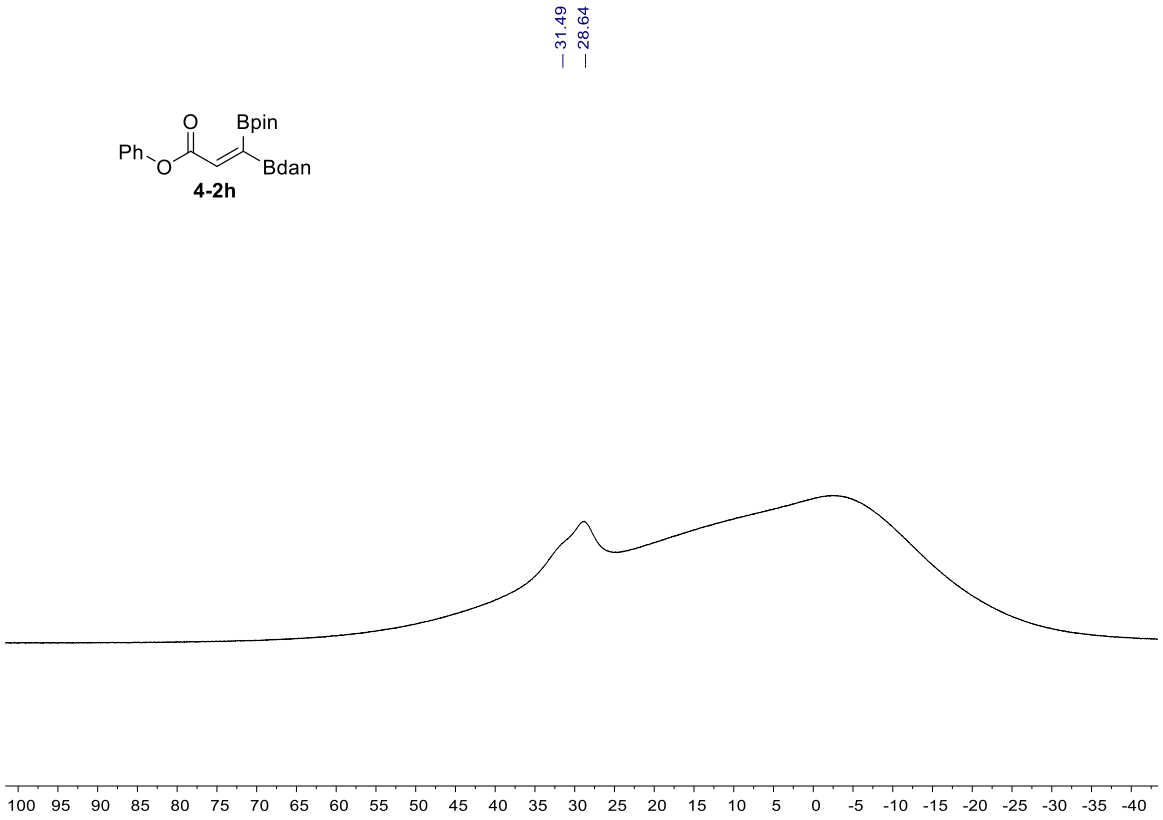
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2h**



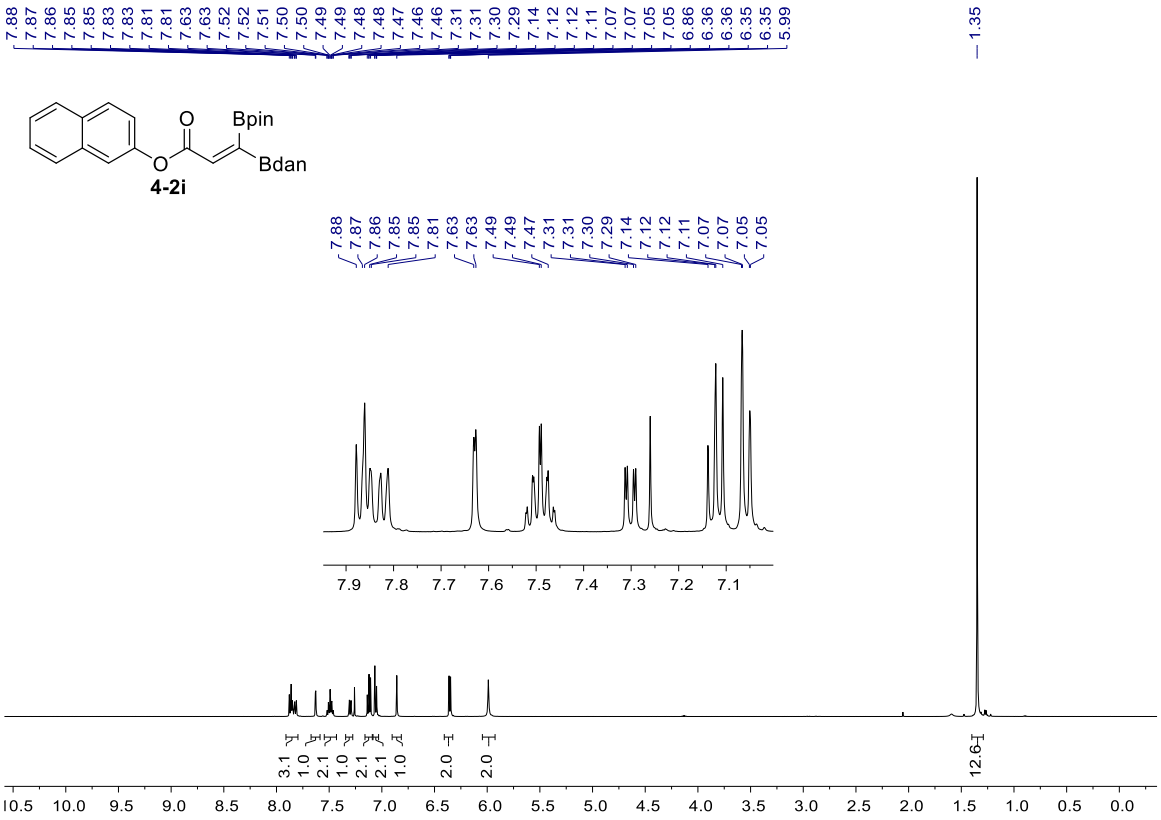
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **4-2h**



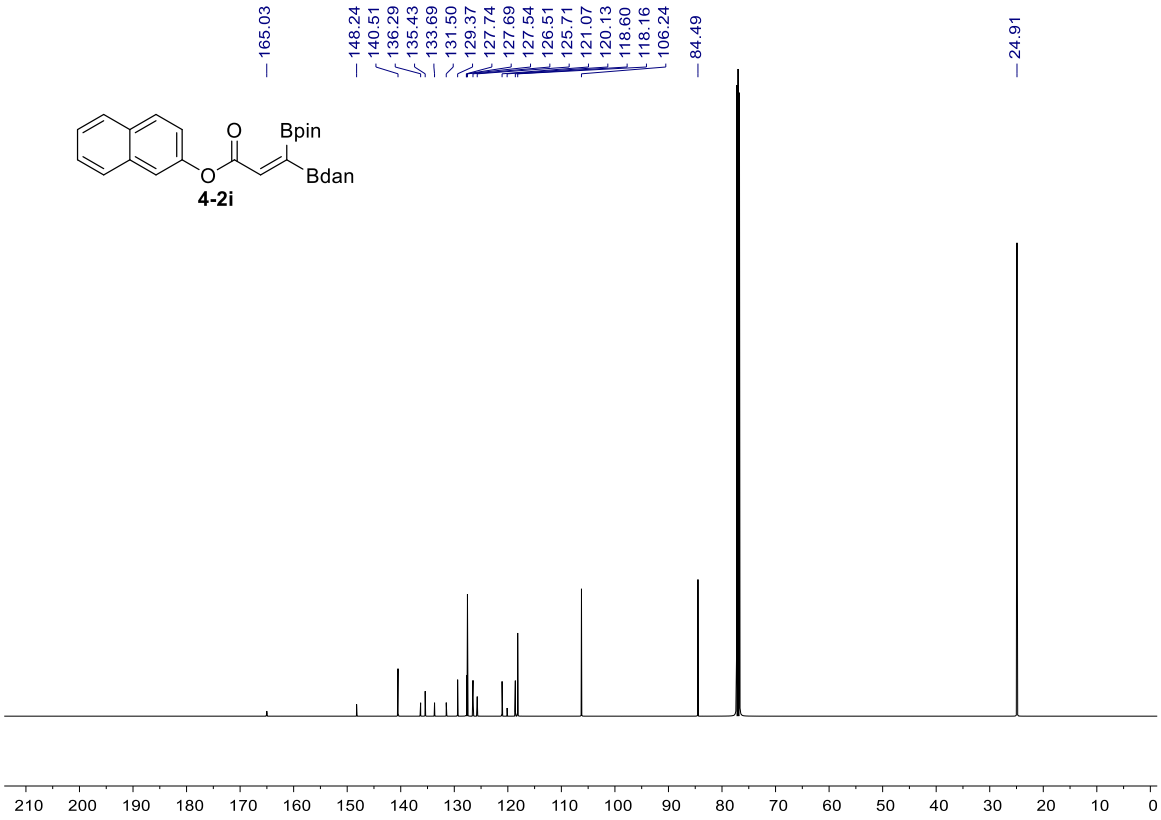
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **4-2h**



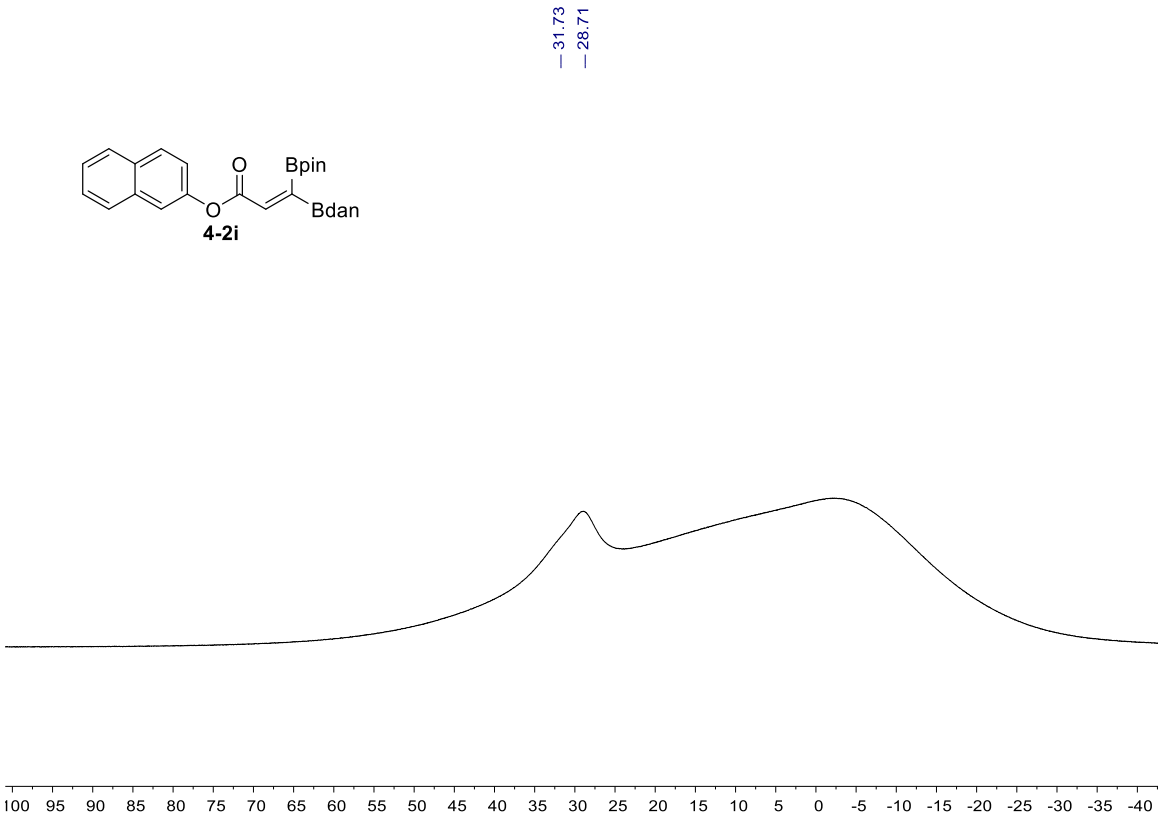
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2i**



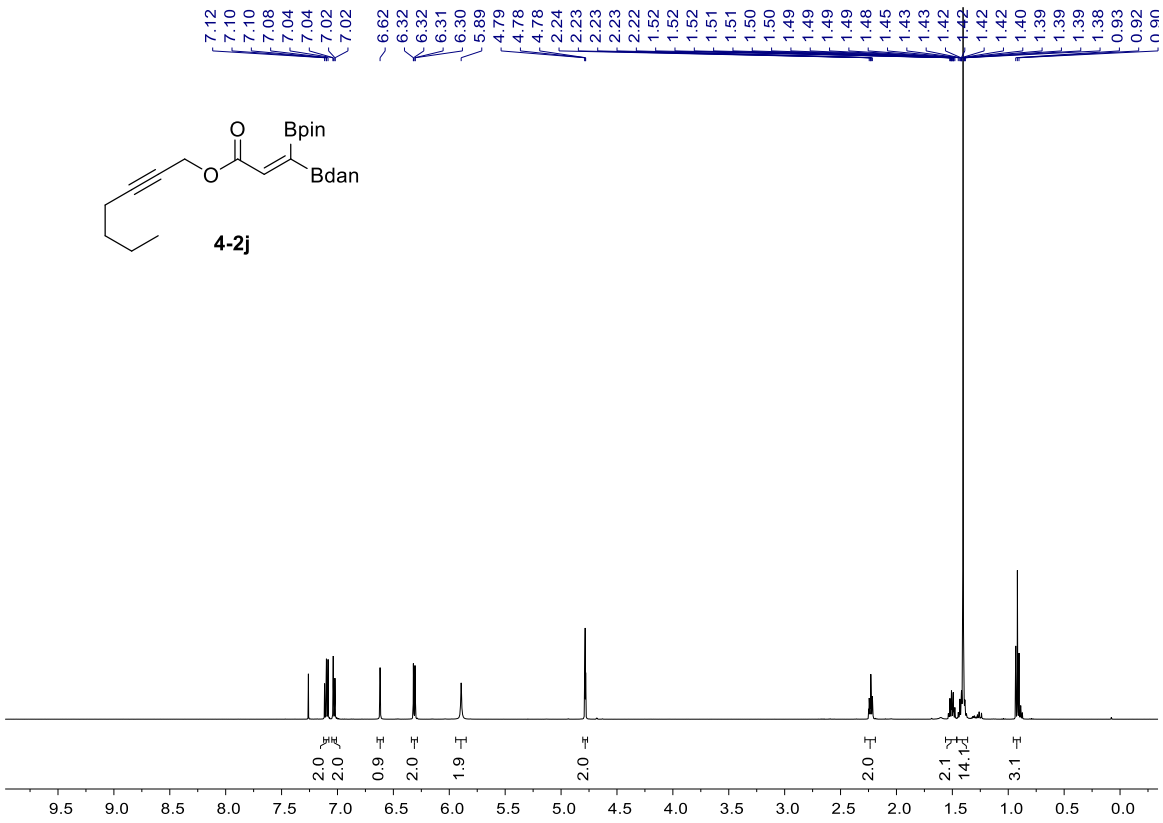
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **4-2i**



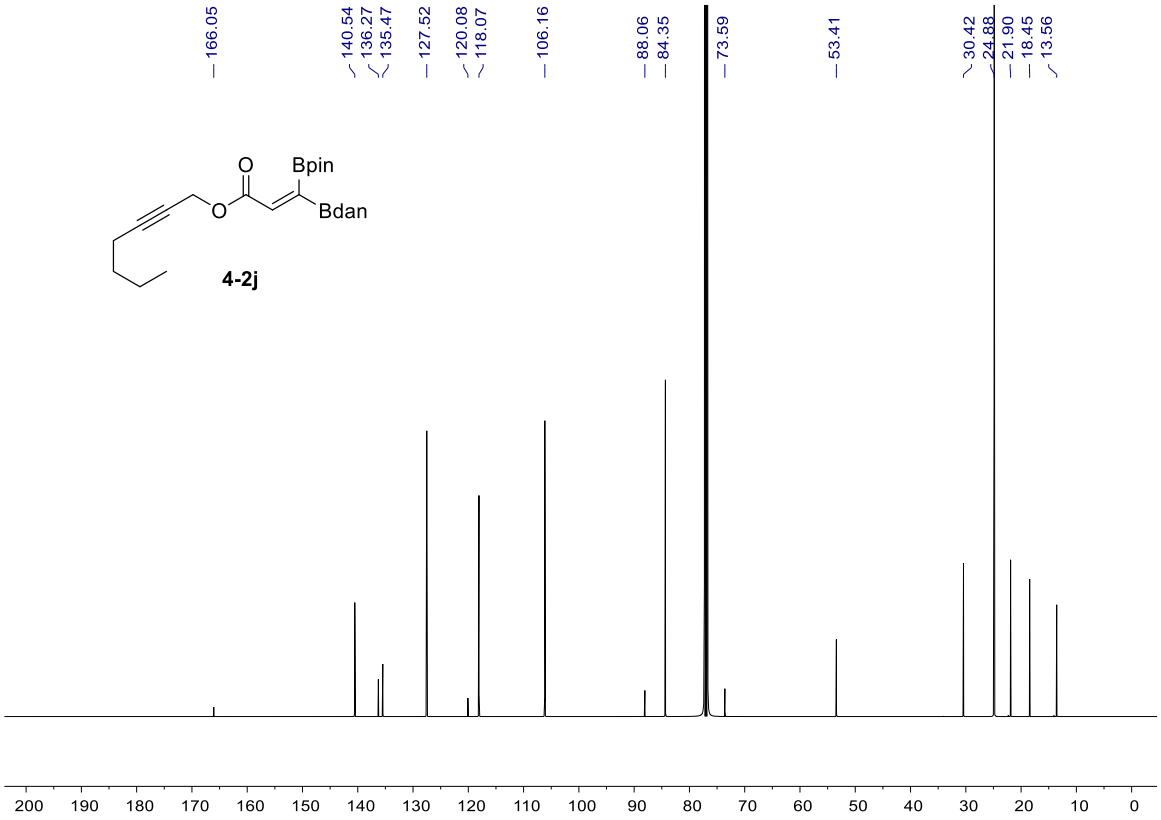
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **4-2i**



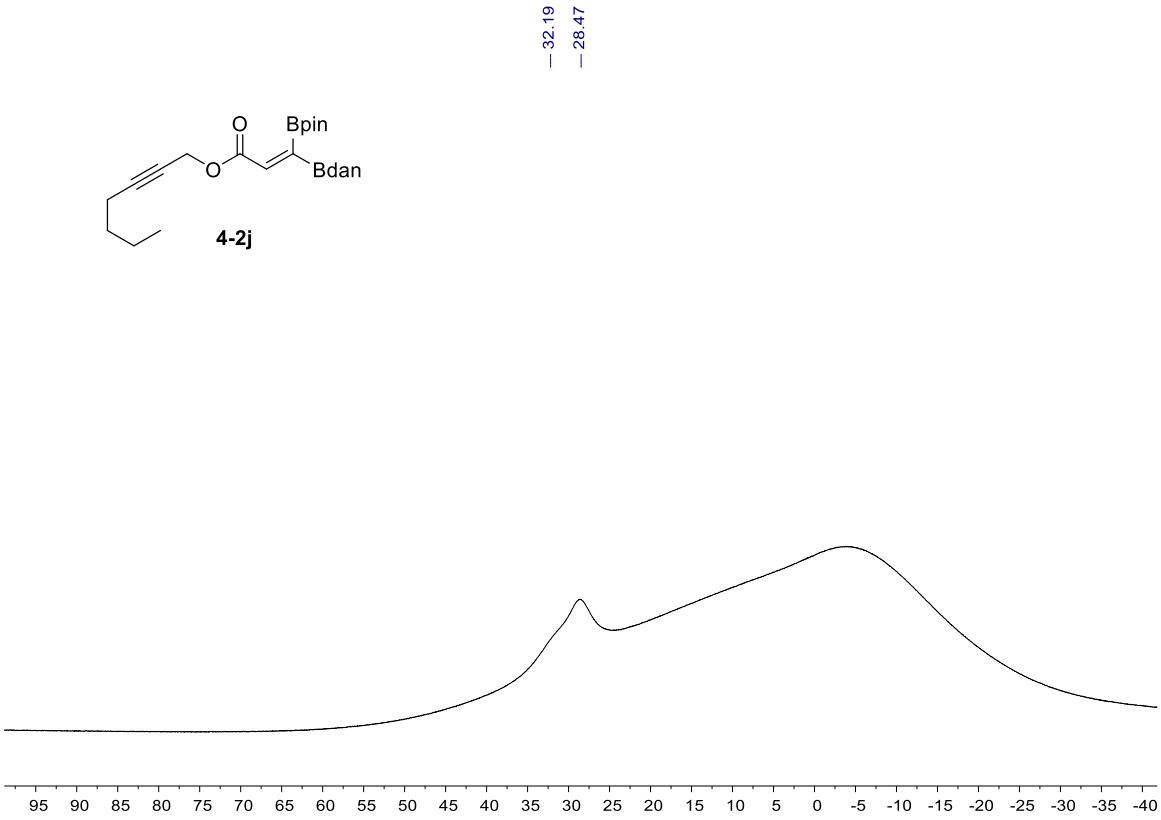
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2j**



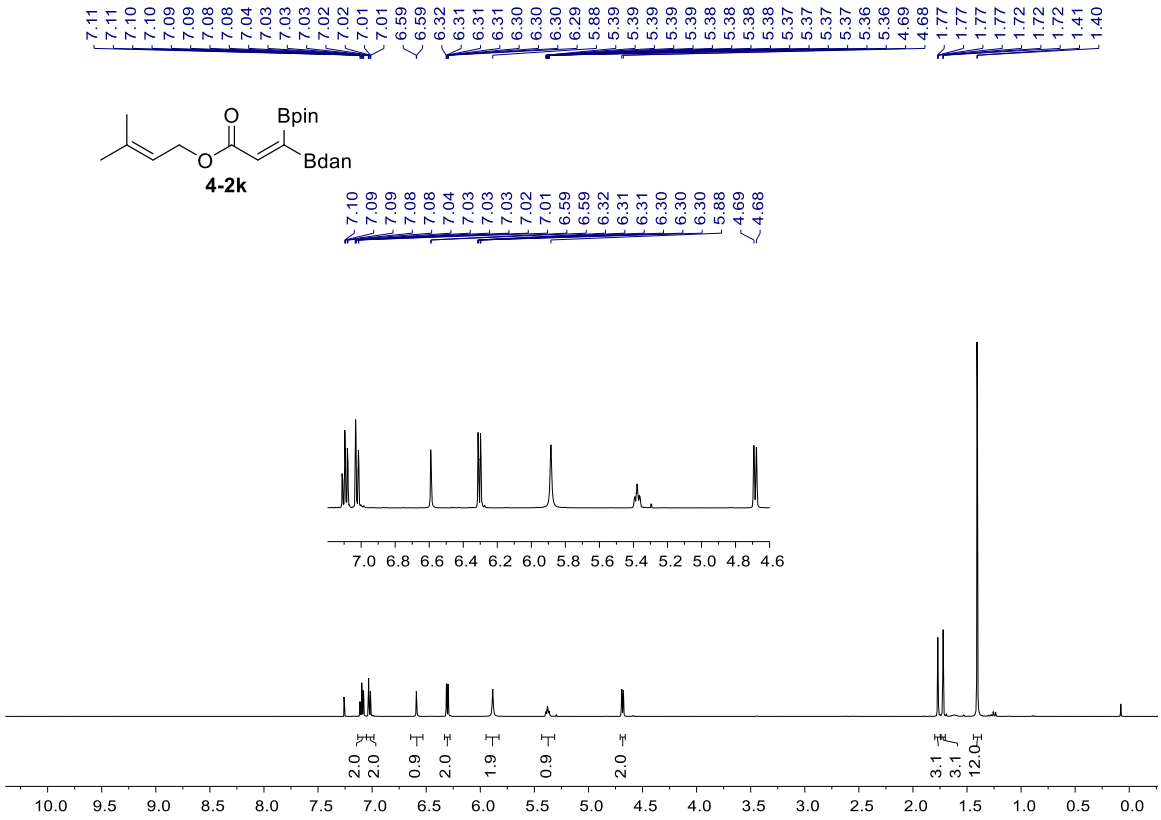
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **4-2j**



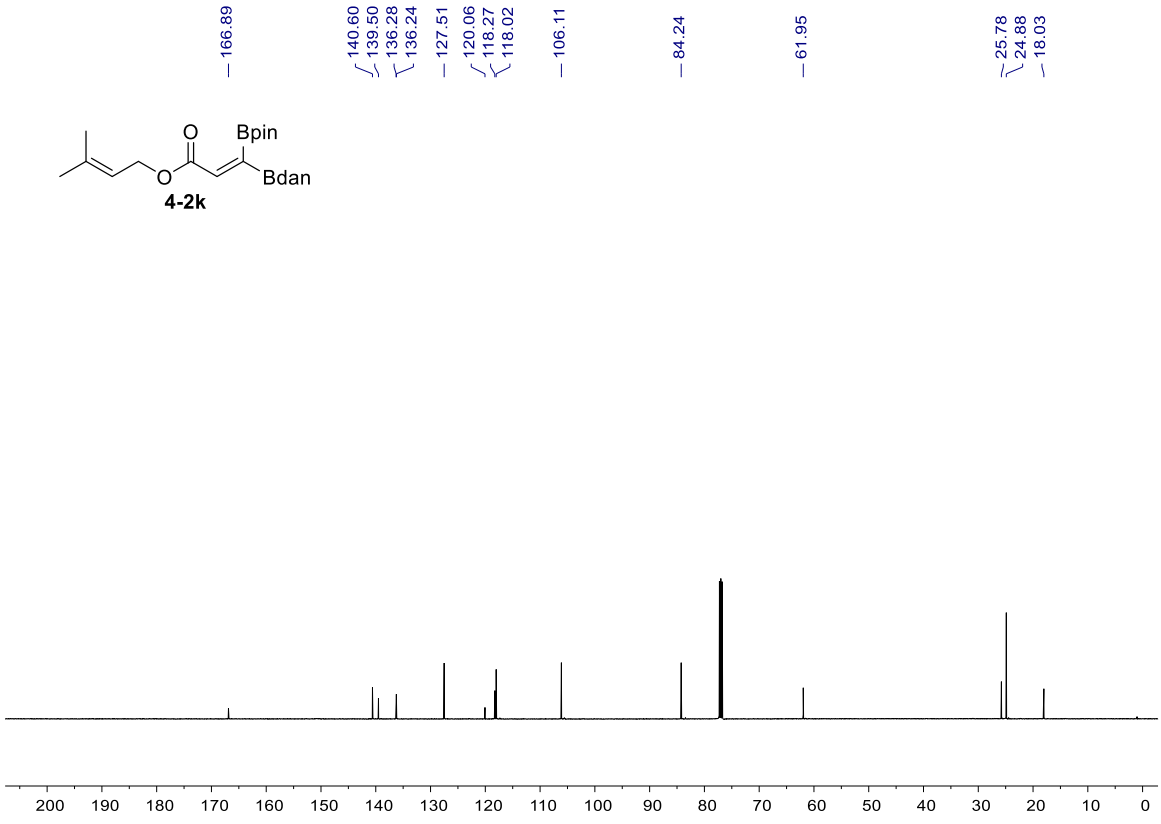
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **4-2j**



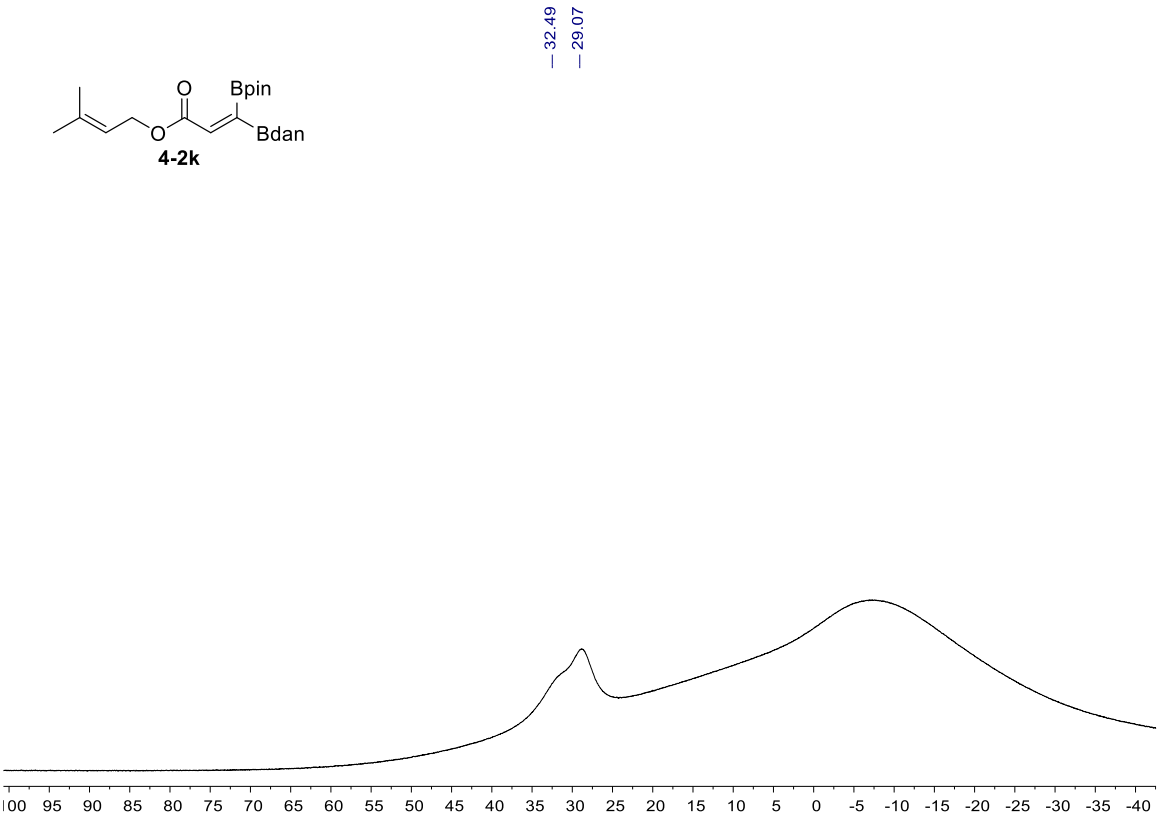
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2k**



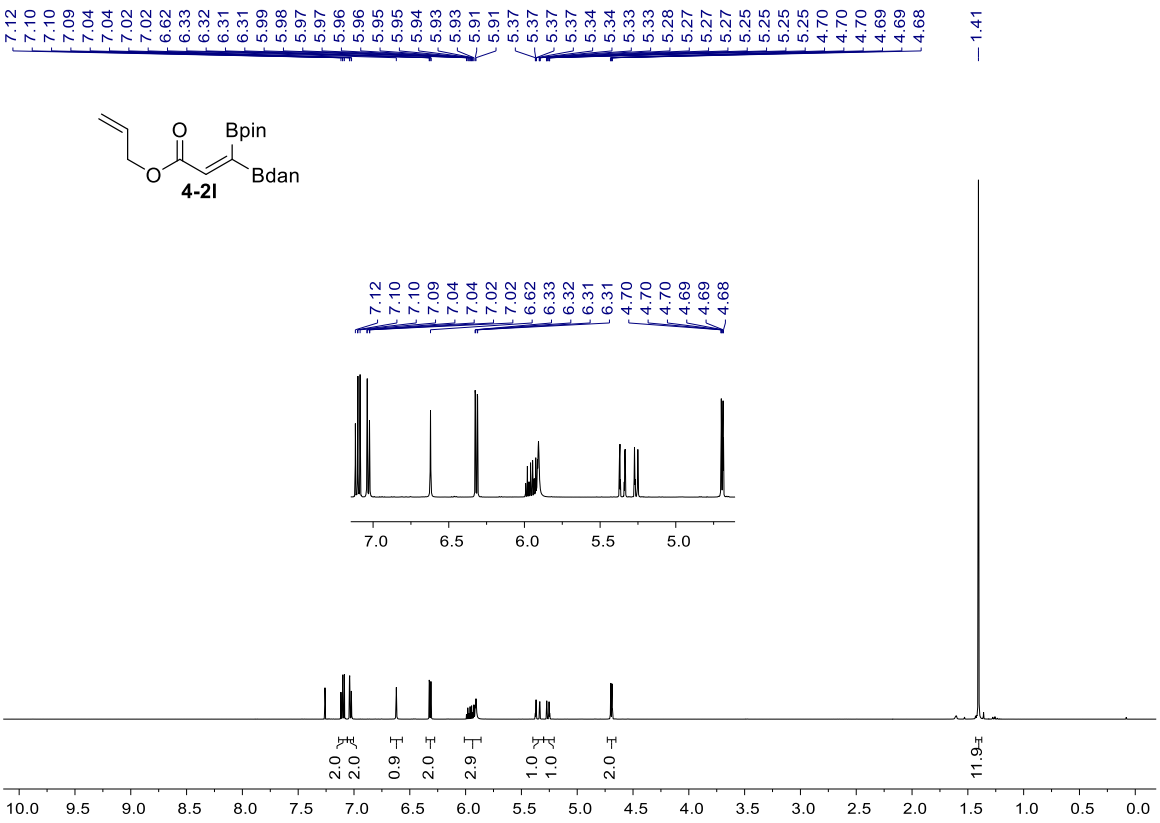
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **4-2k**



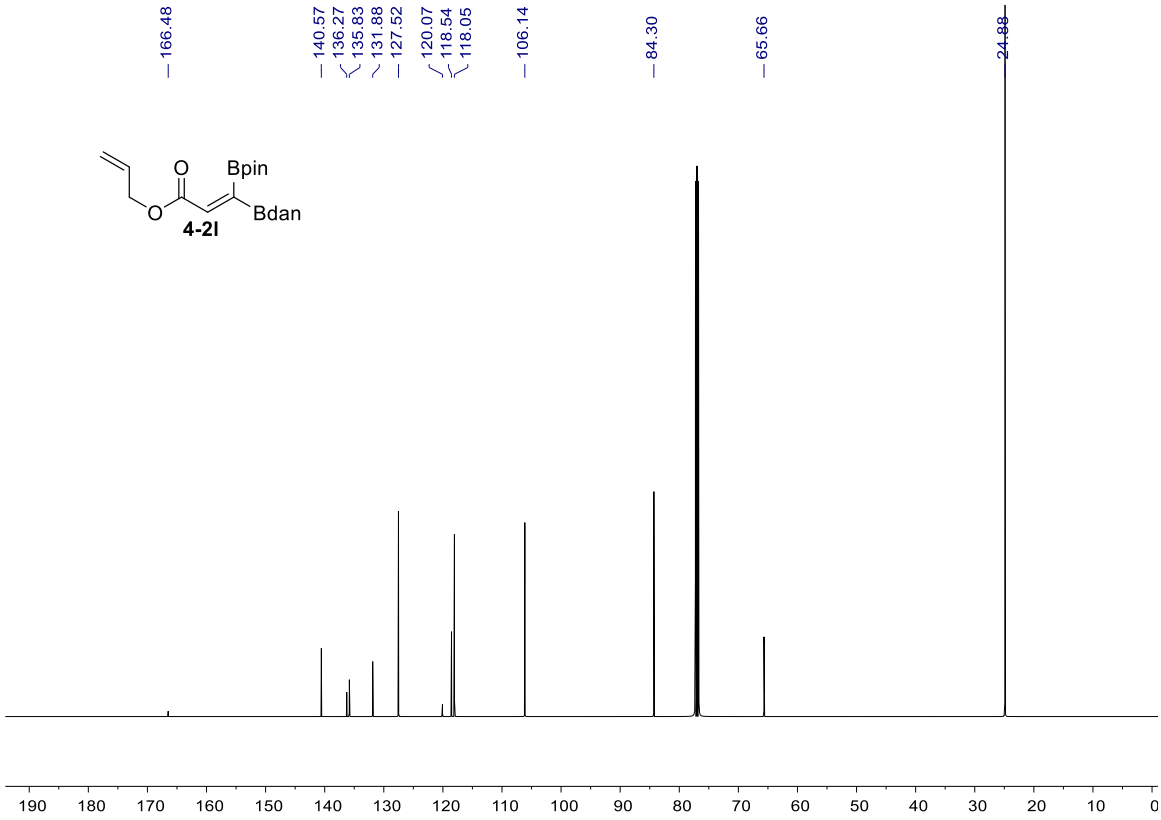
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **4-2k**



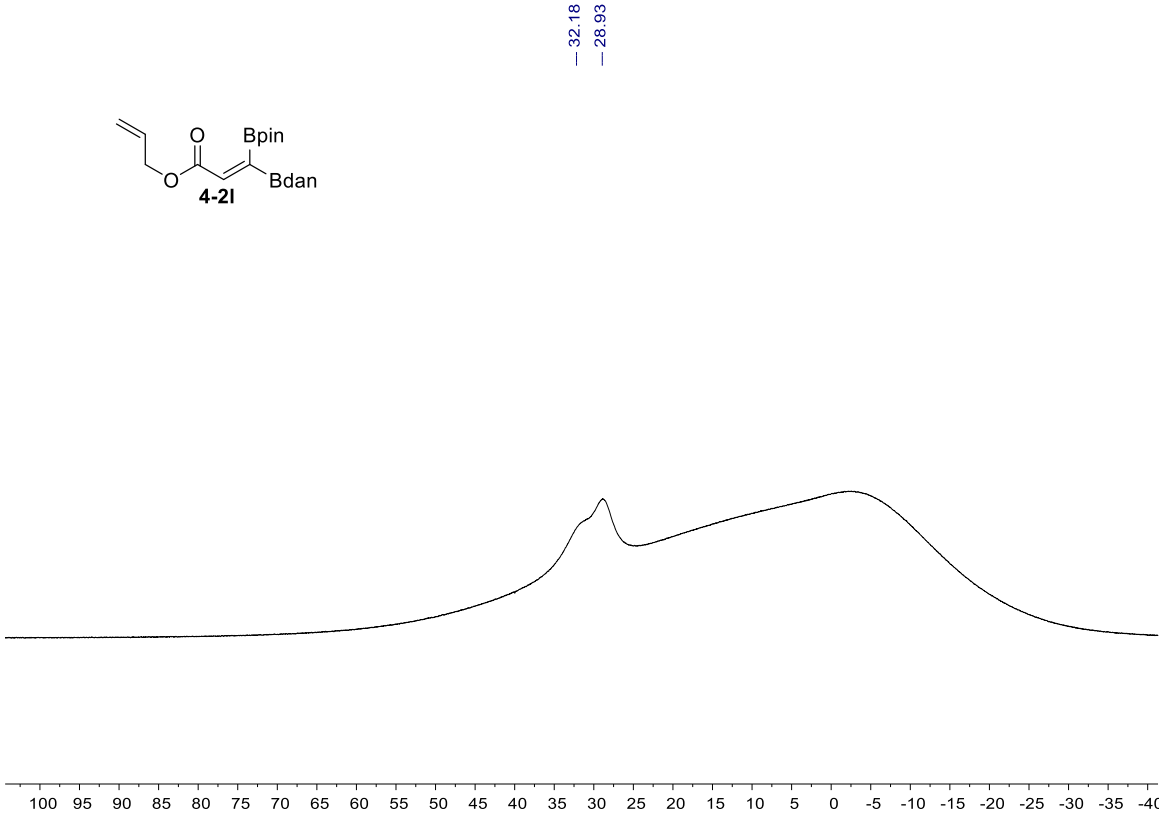
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2l**



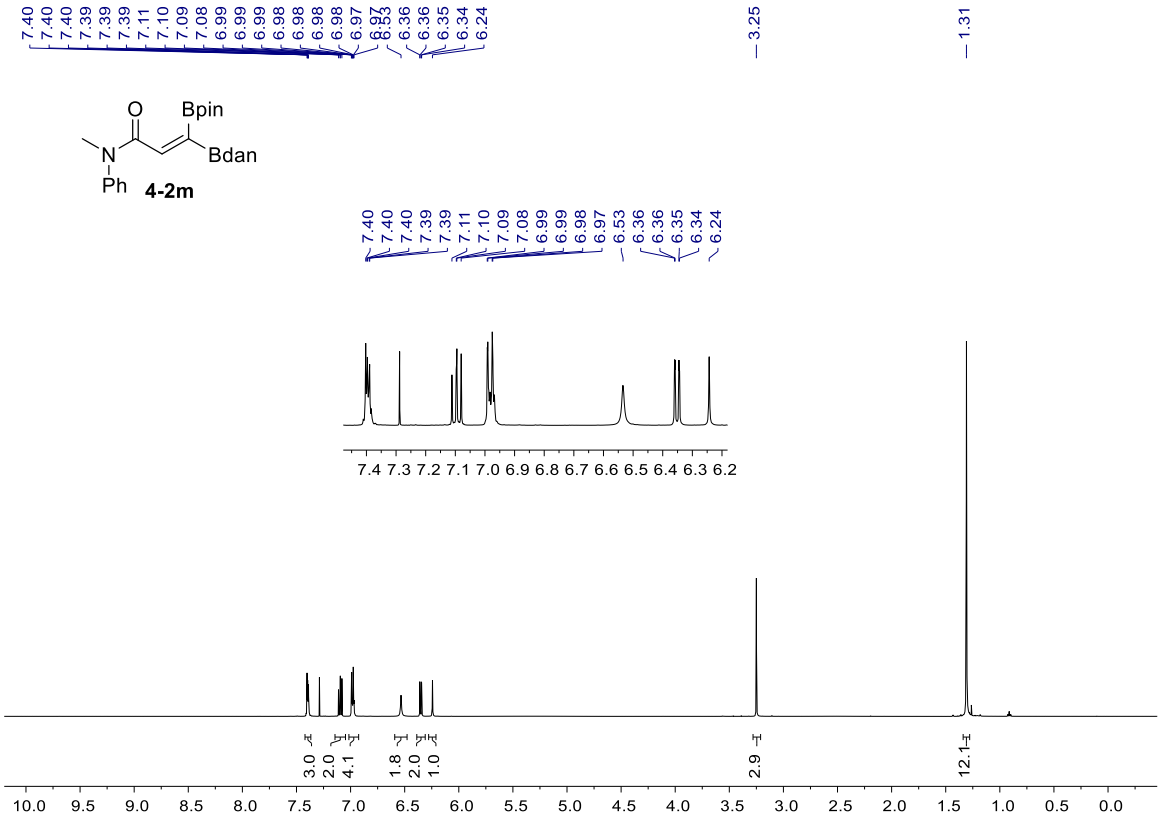
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **4-2l**



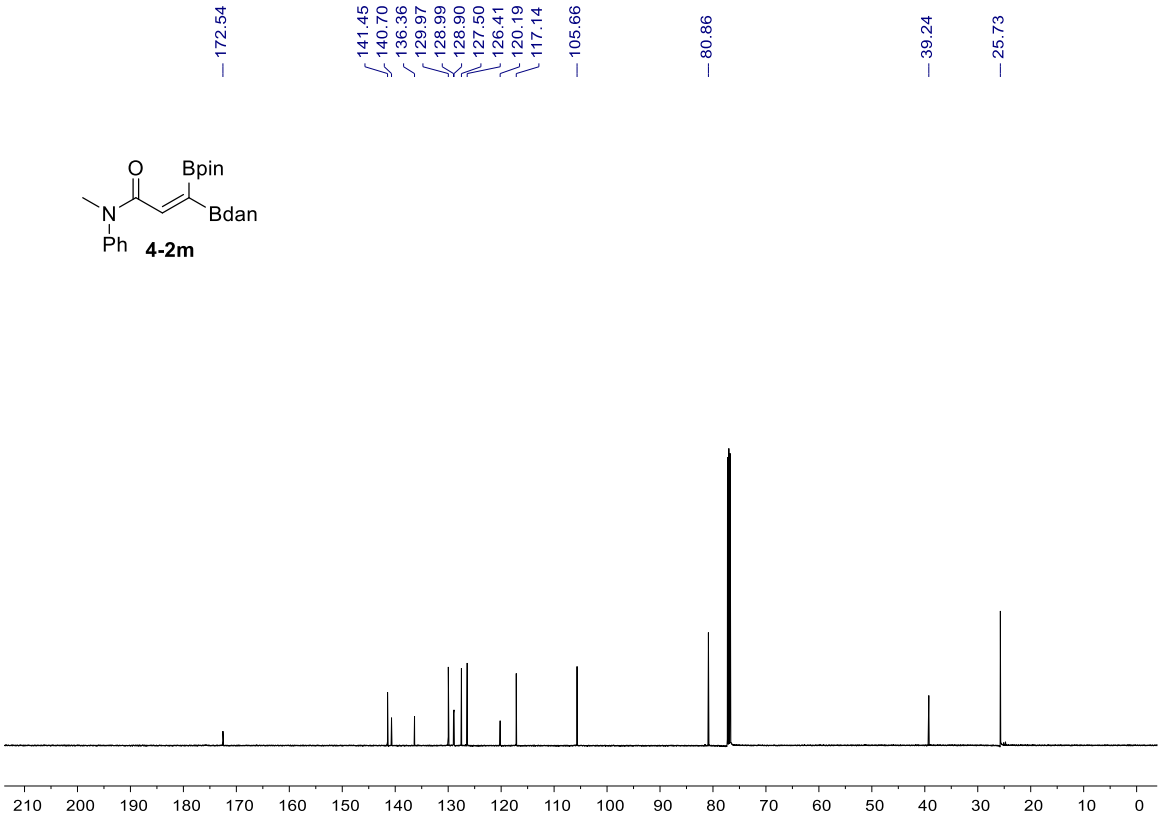
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **4-2l**



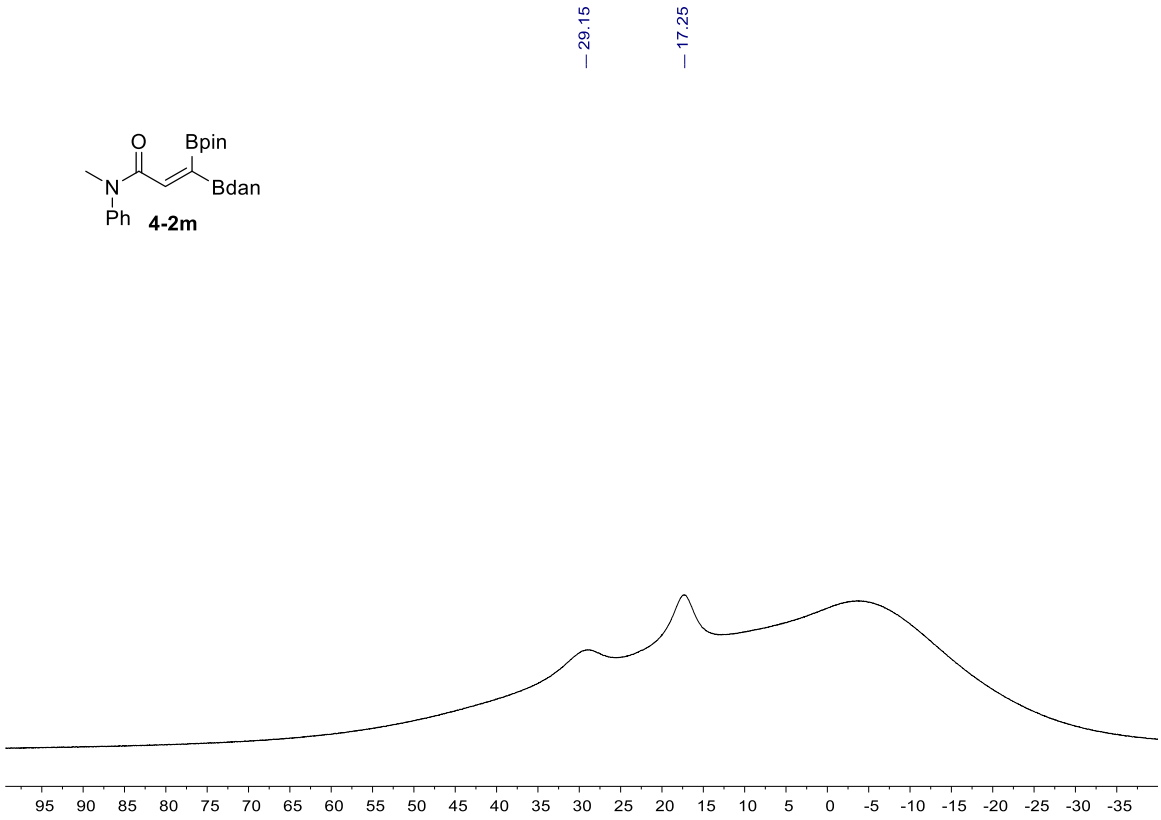
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2m**



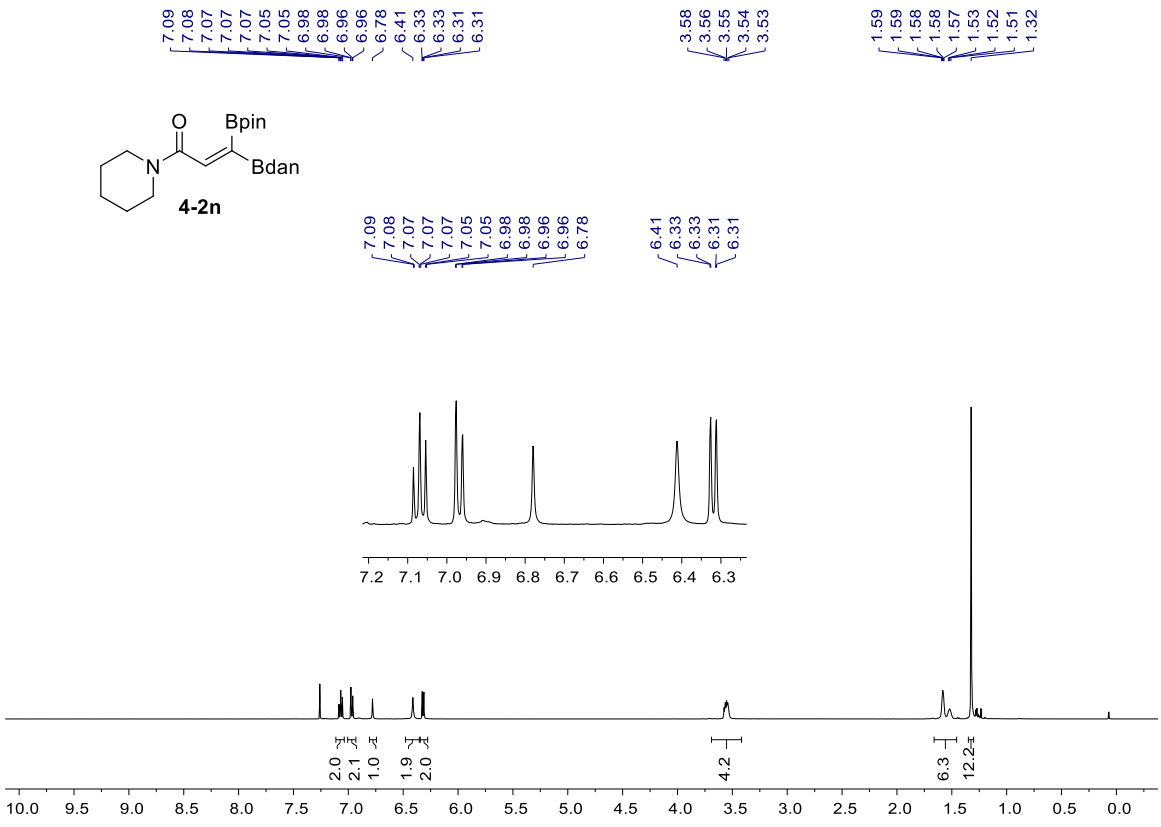
^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of **4-2m**



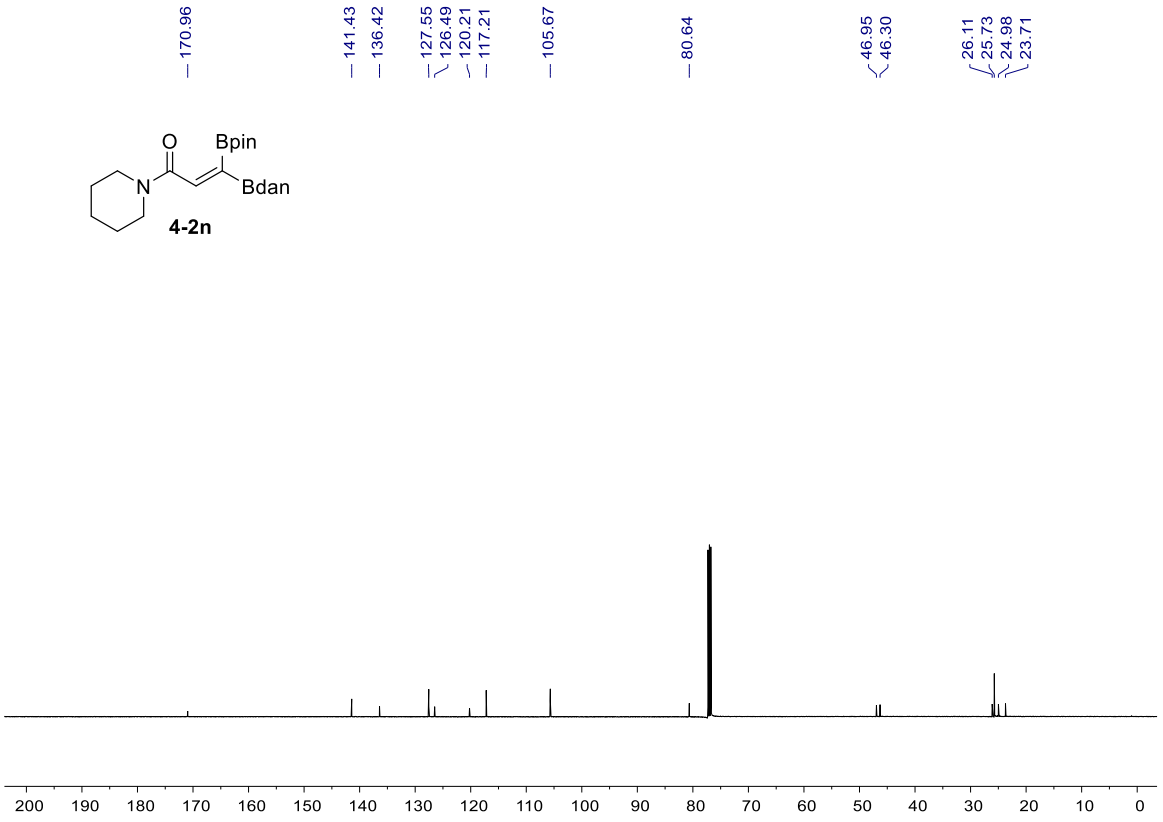
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **4-2m**



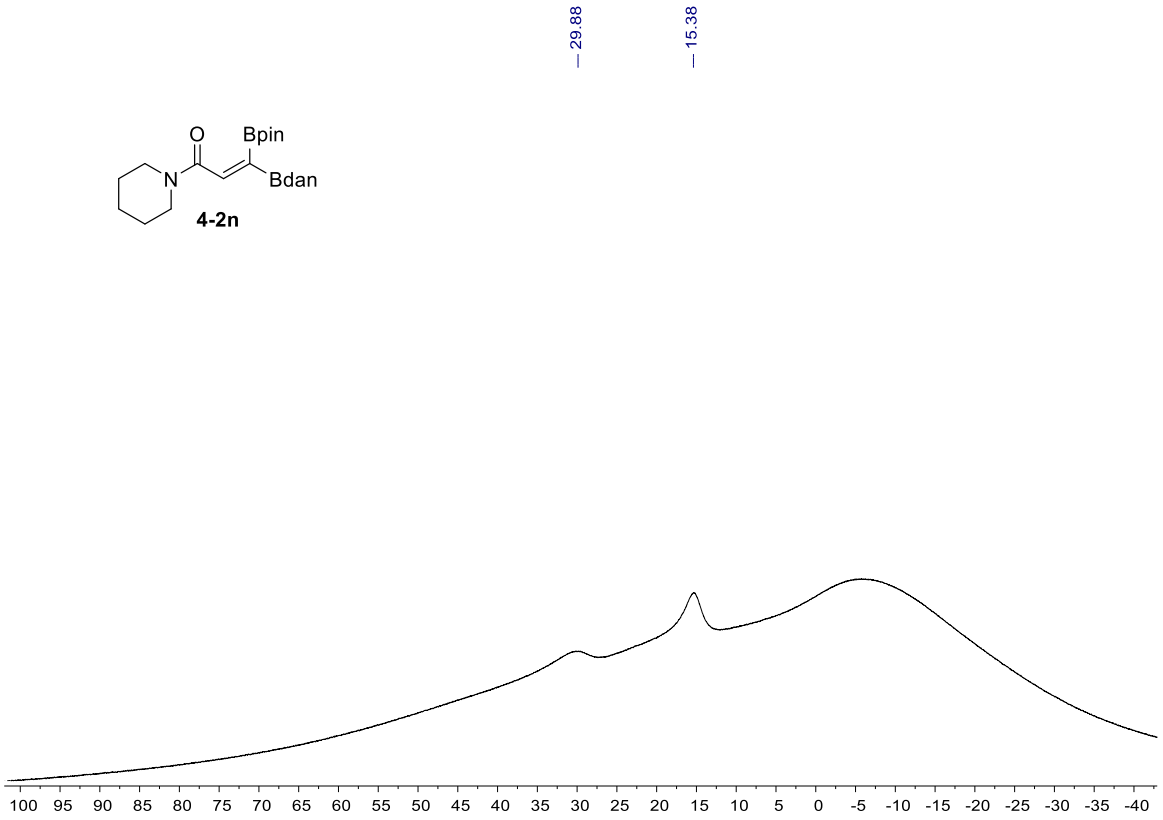
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4-2n**



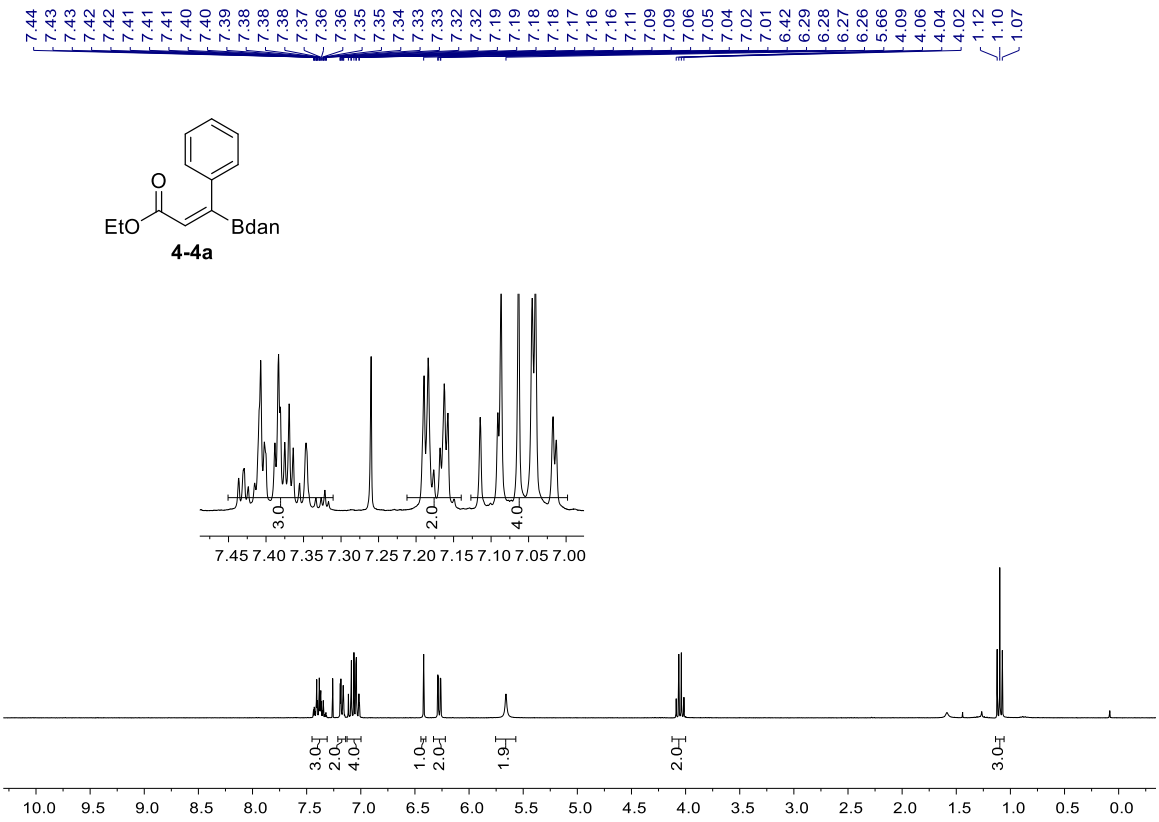
$^{13}C\{^1H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **4-2n**



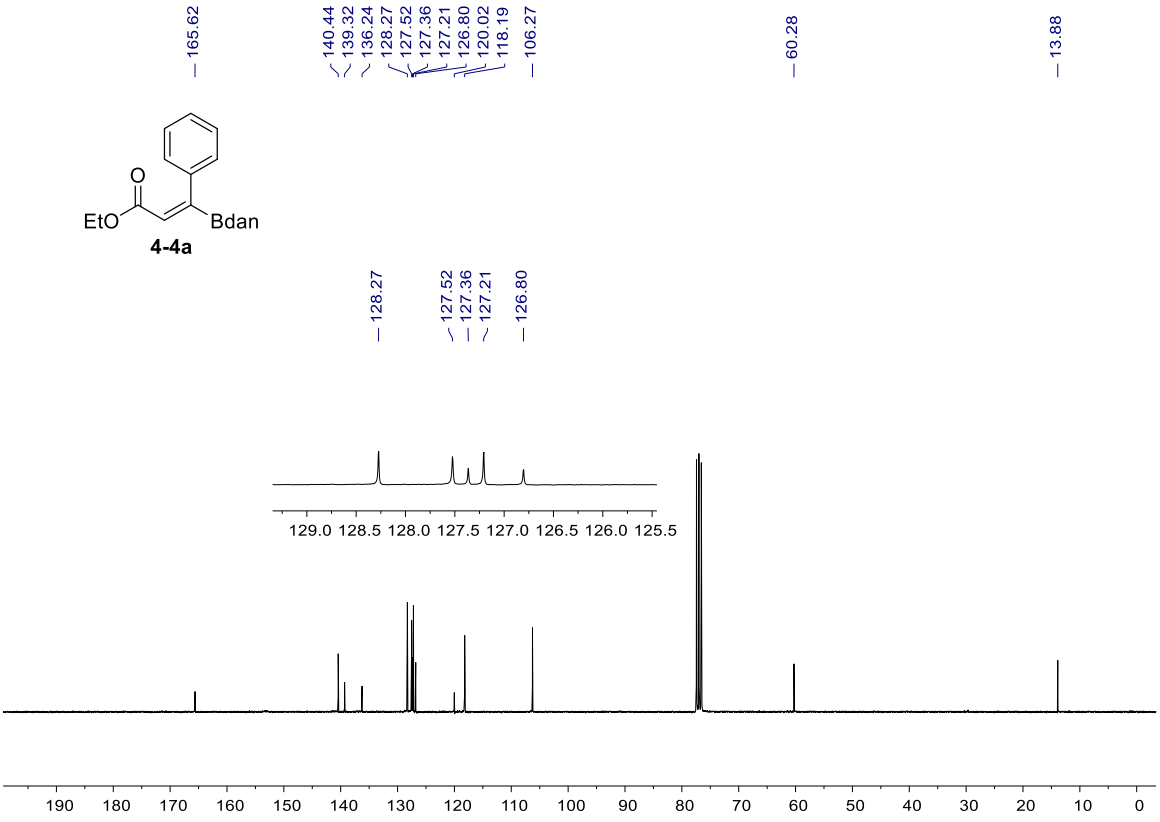
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **4-2n**



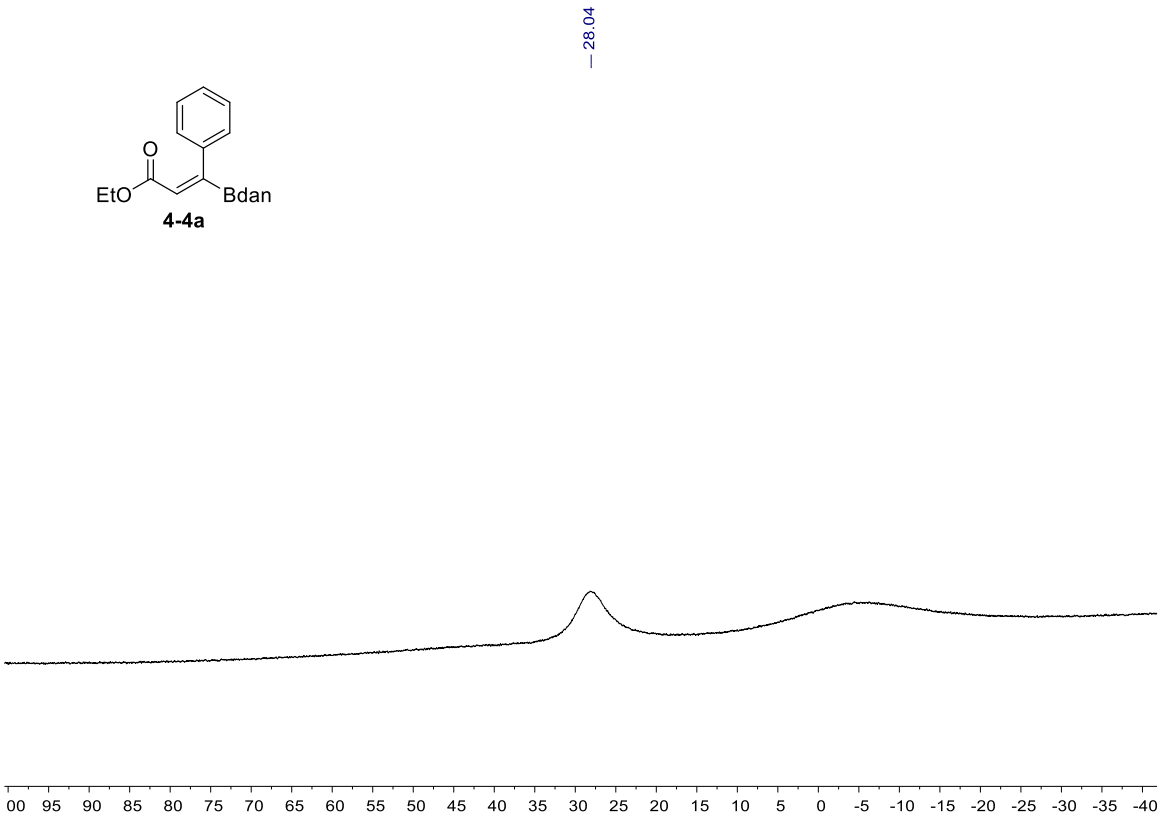
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4-4a**



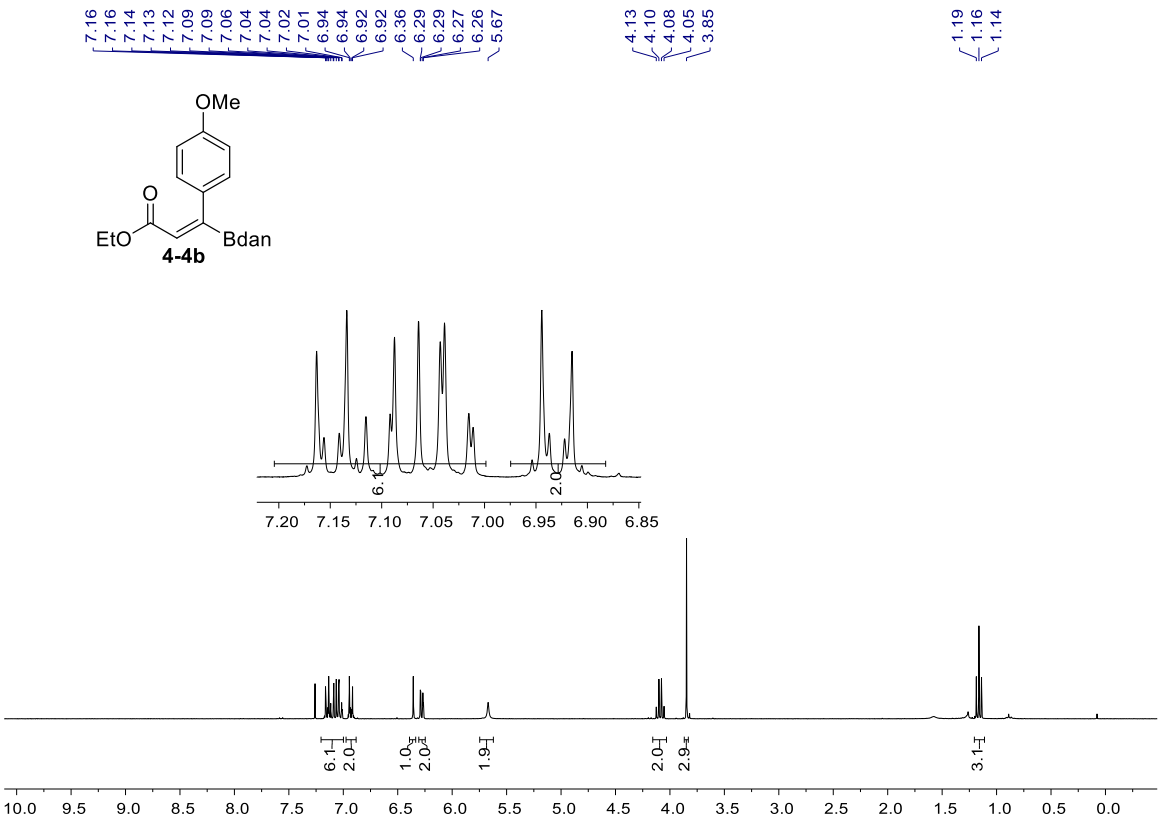
^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **4-4a**



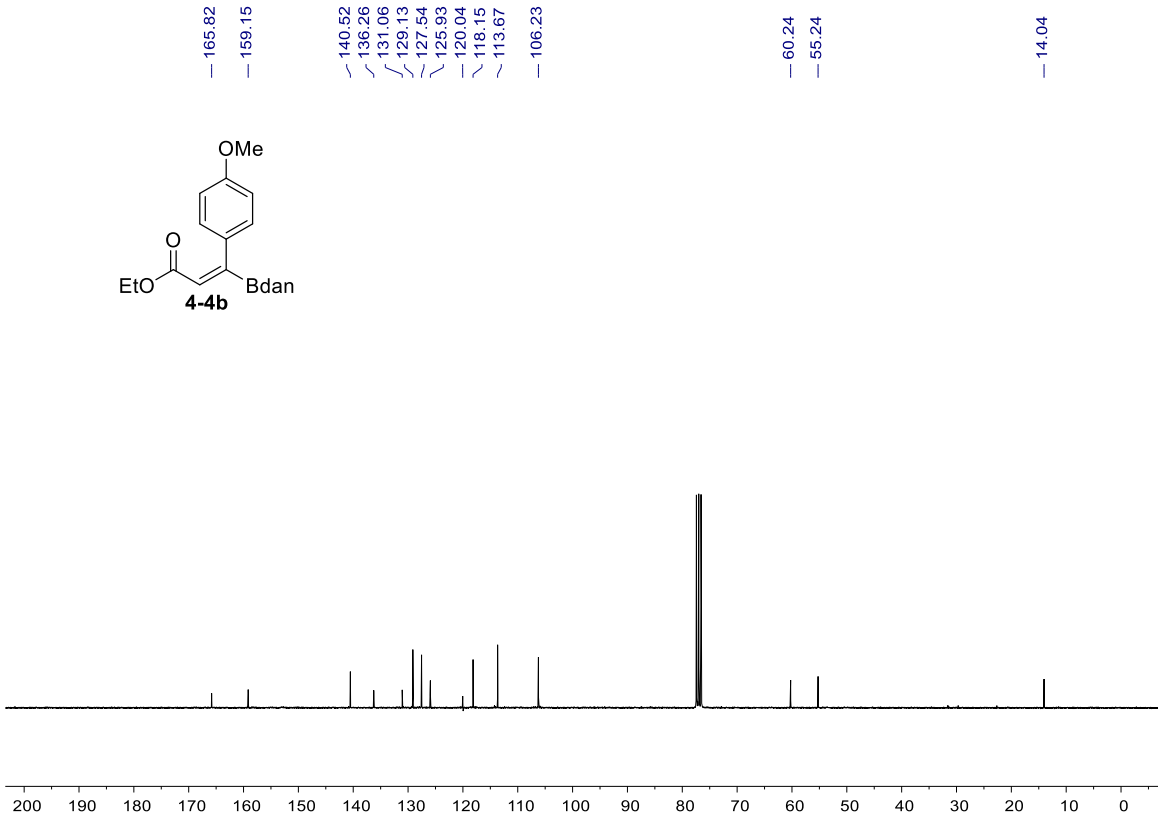
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **4-4a**



^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4-4b**



$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **4-4b**



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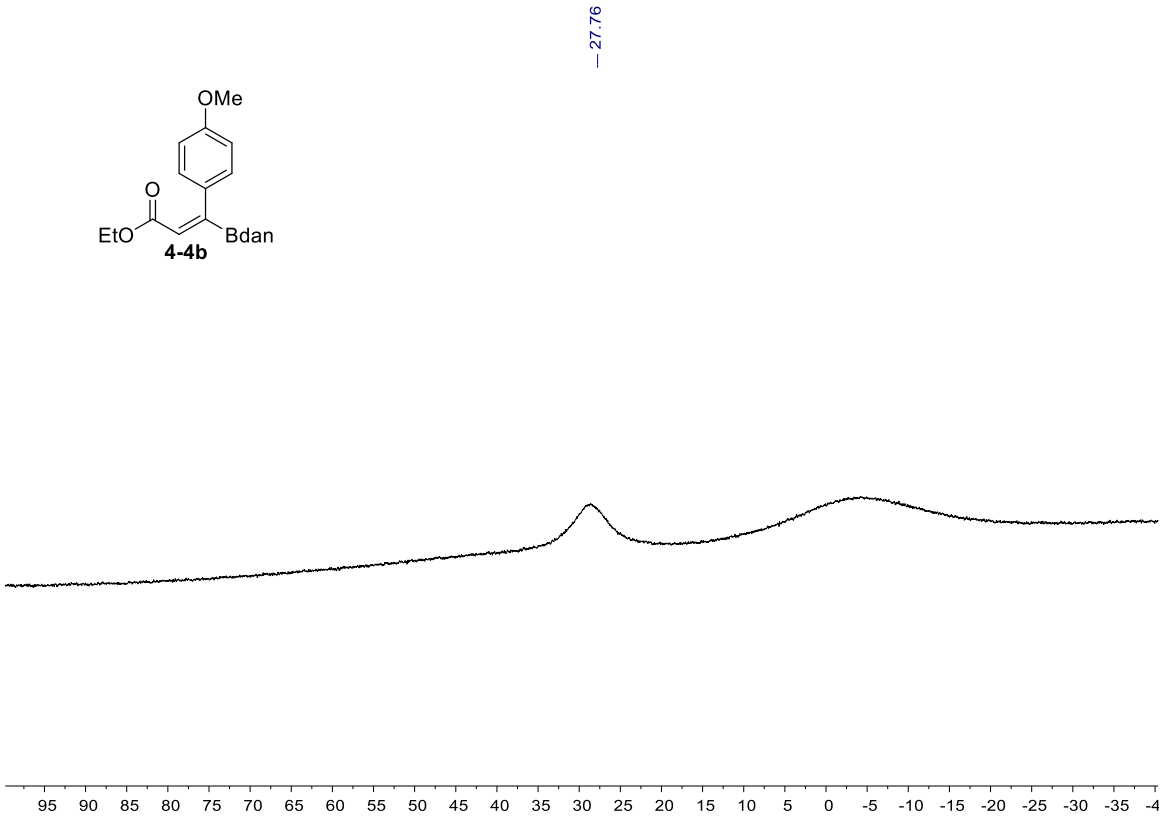

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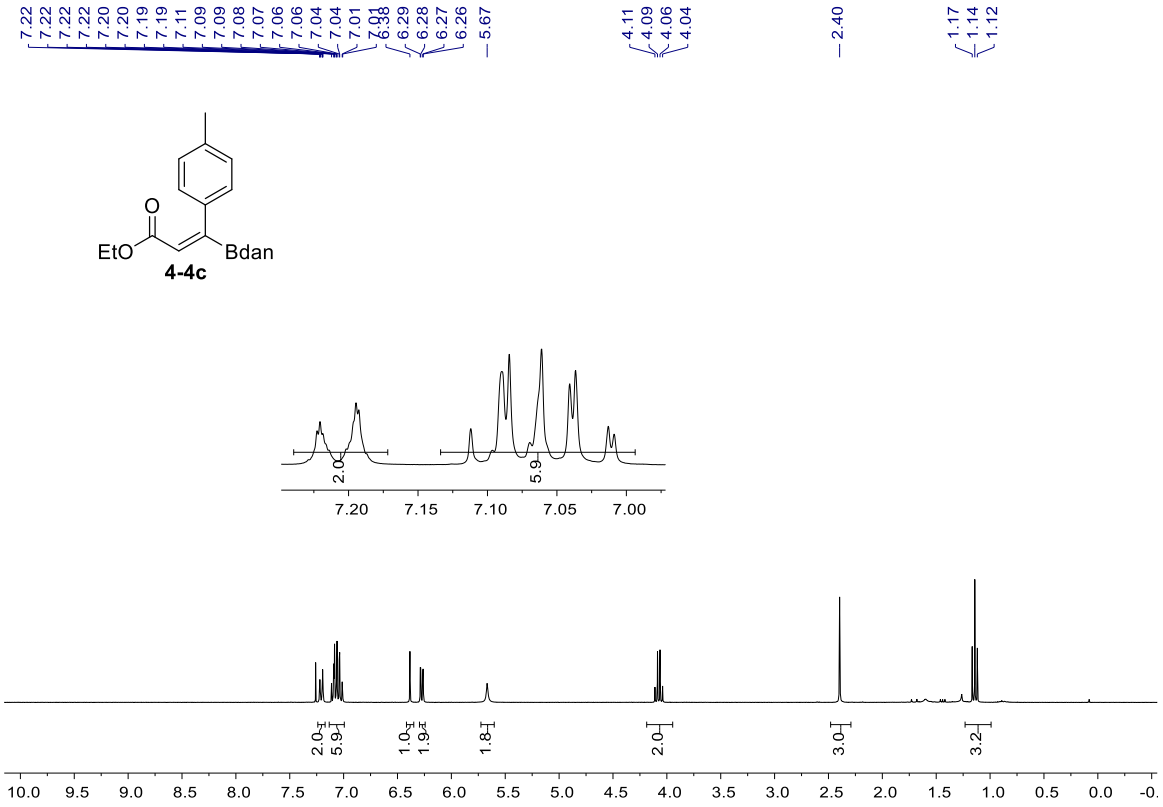
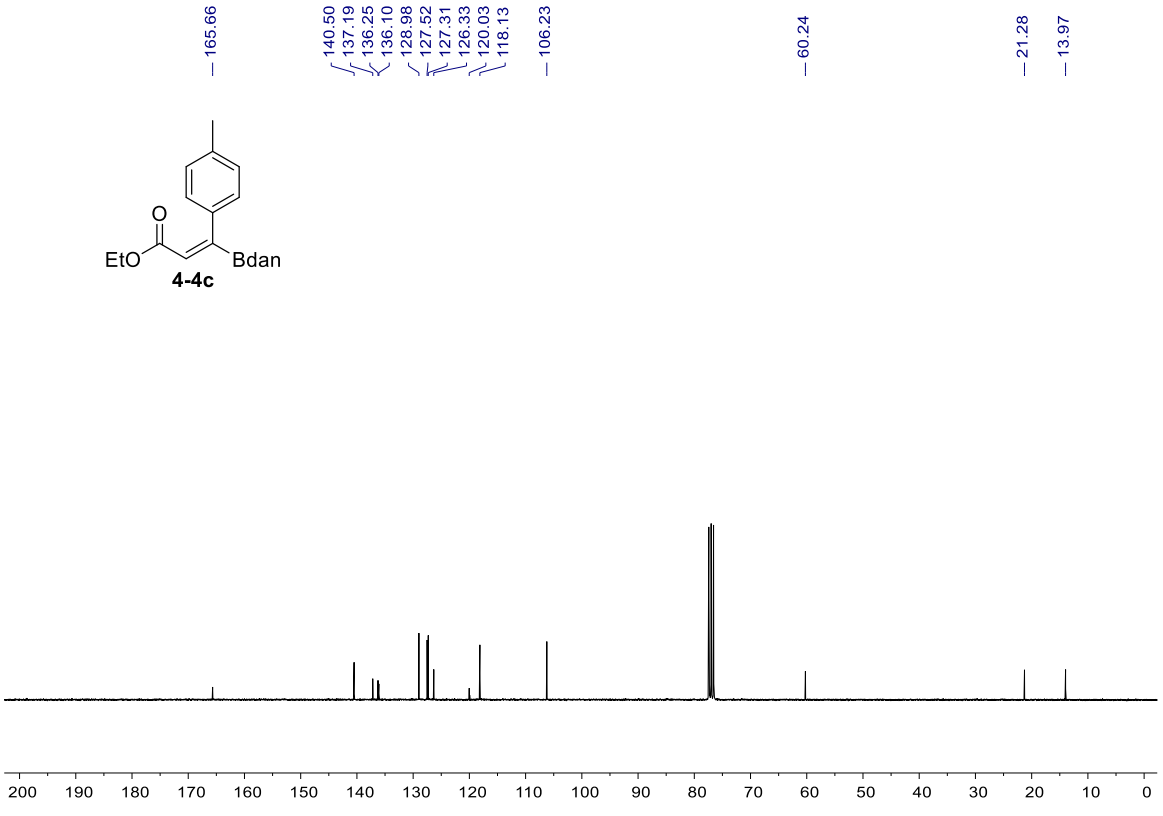


^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **4-4c**



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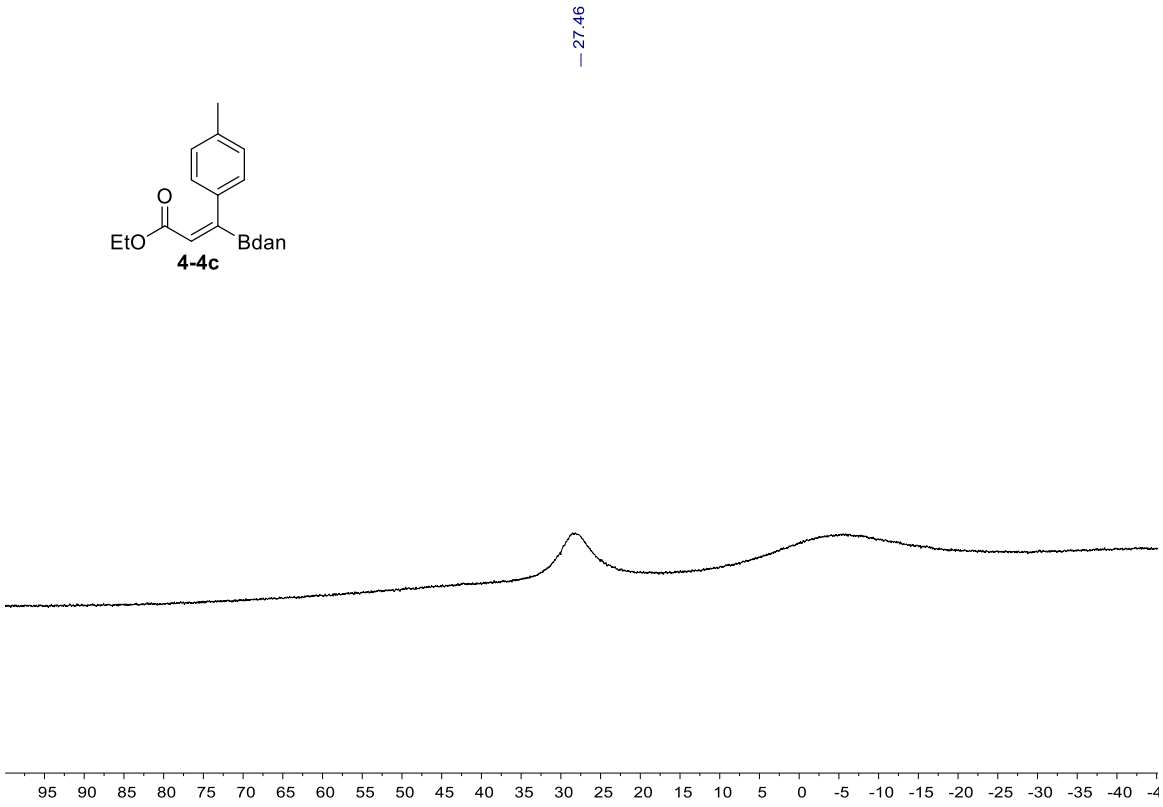
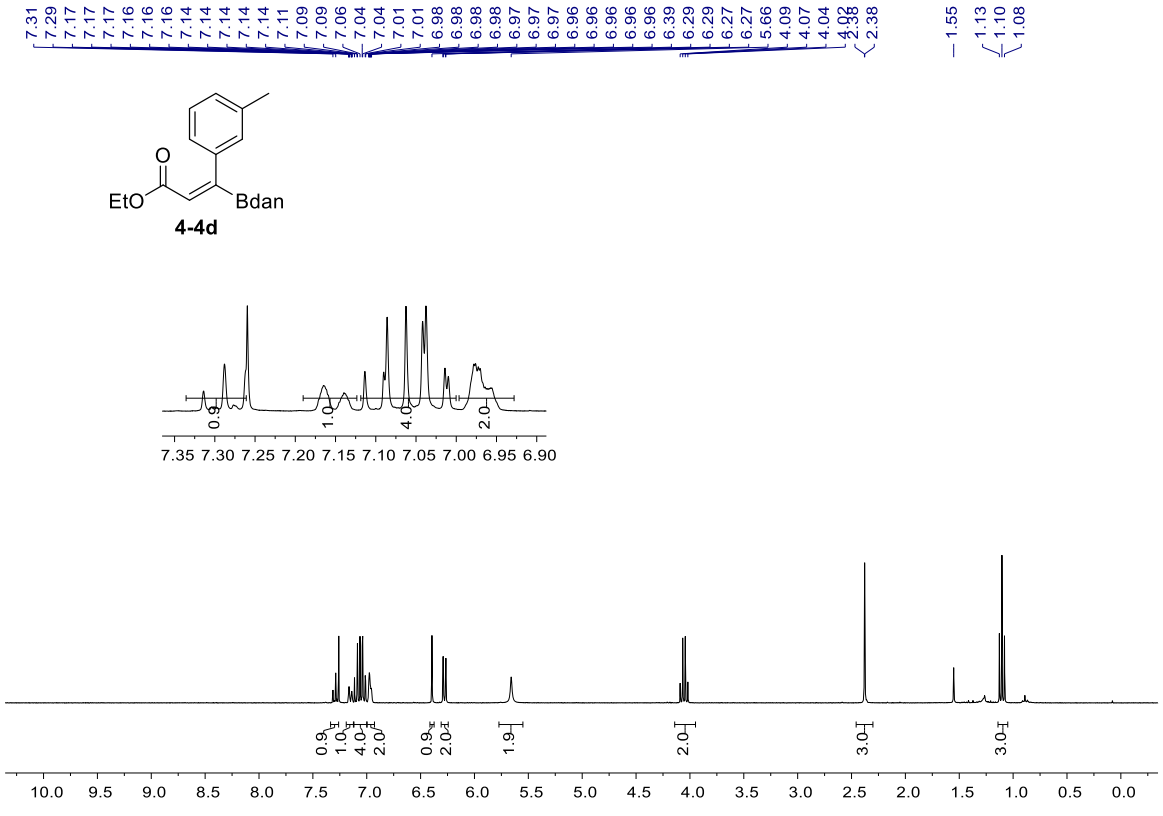
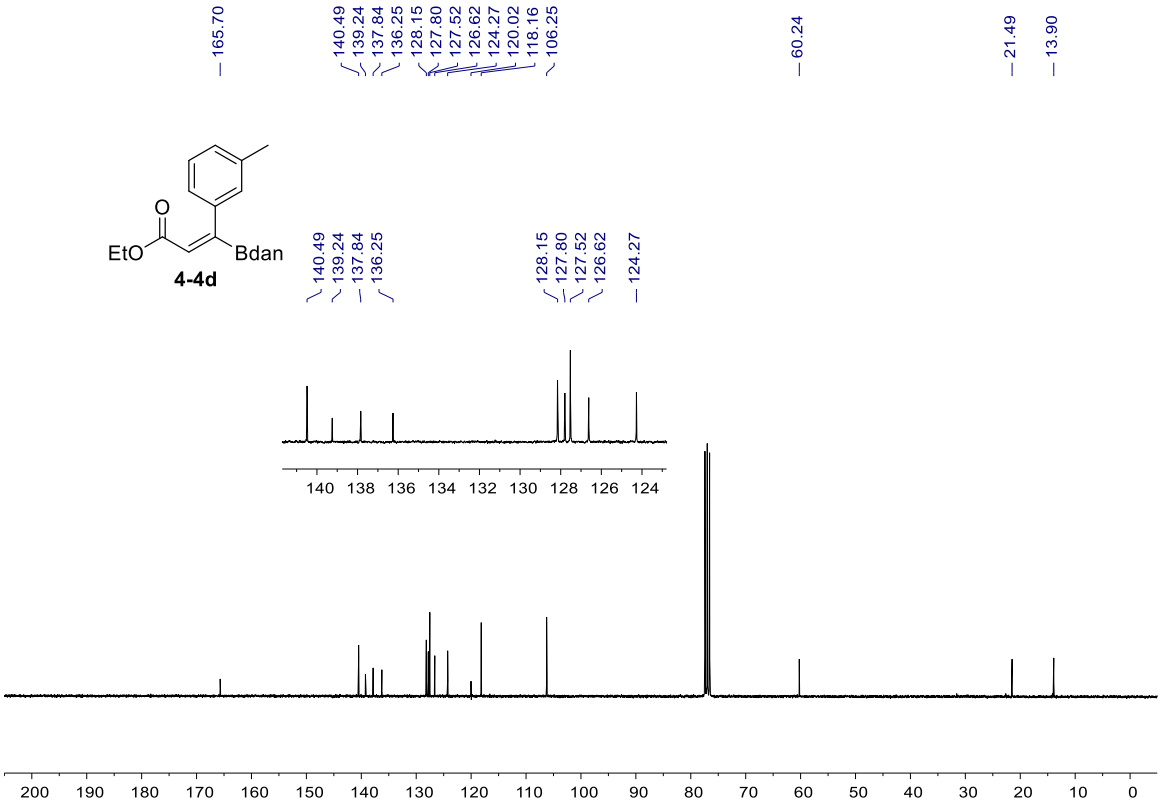


^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4-4d**



$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **4-4d**



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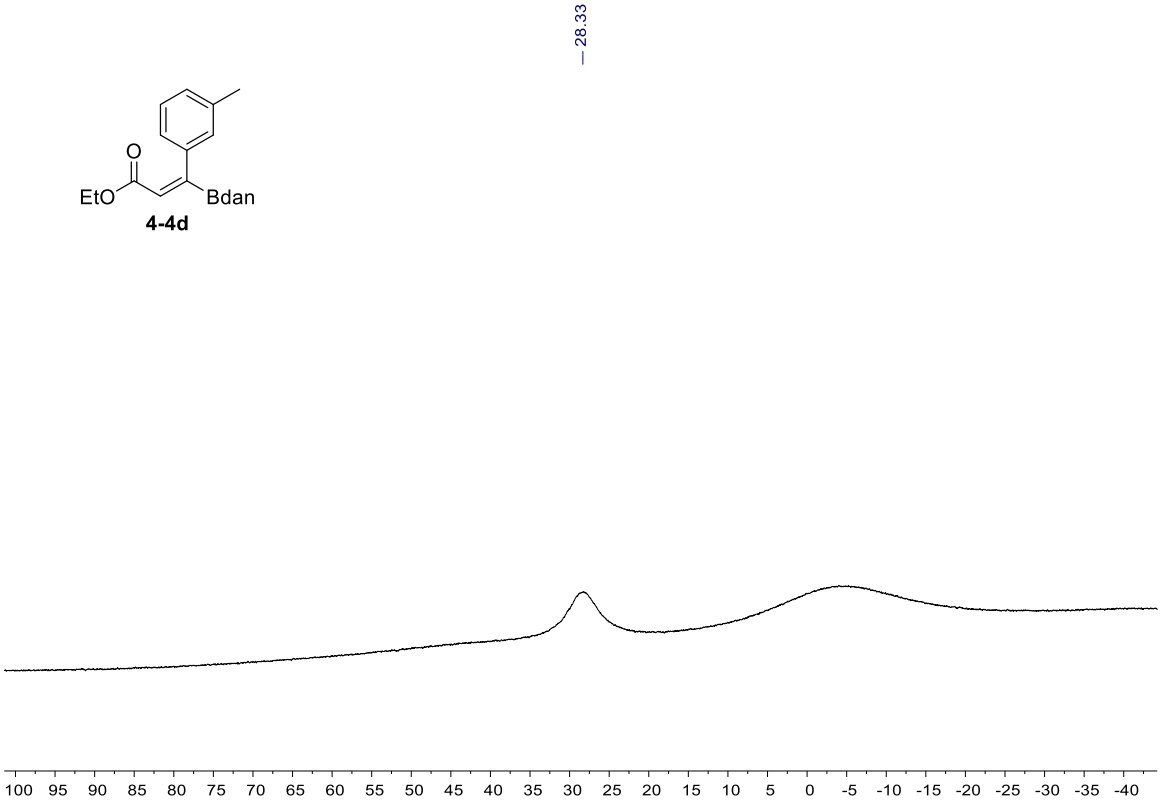
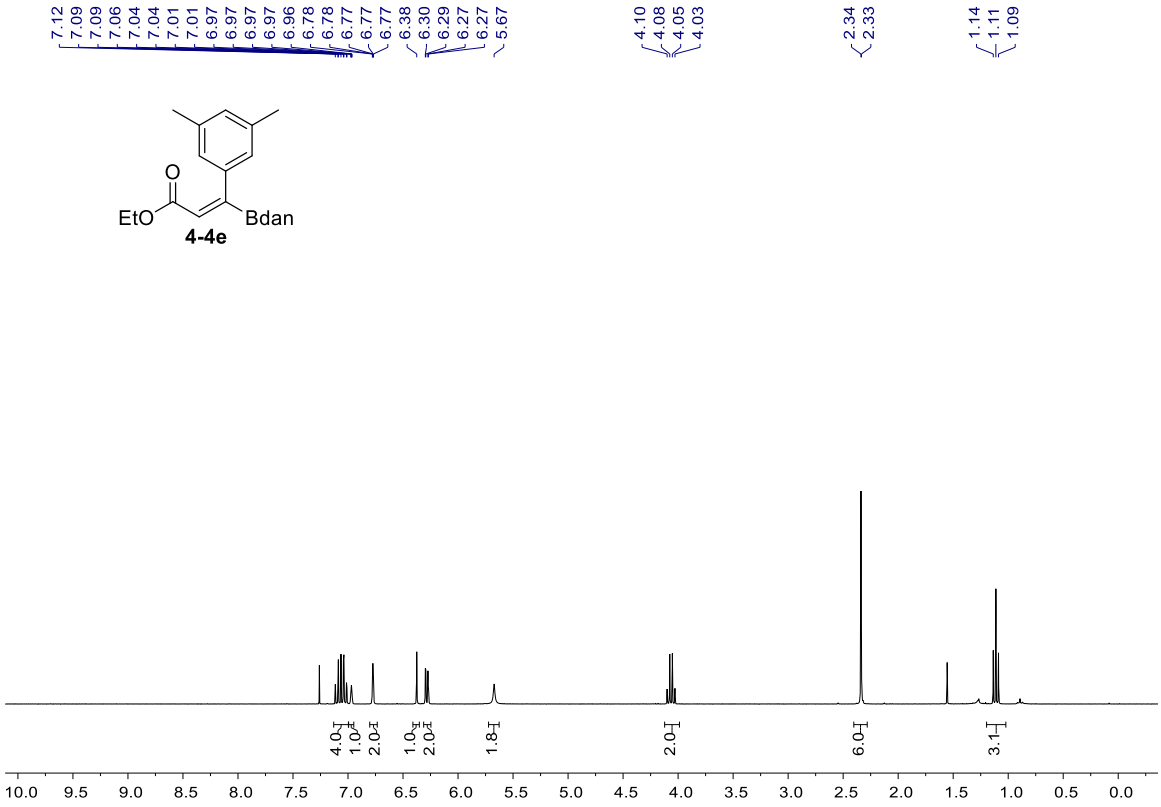


^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4-4e**



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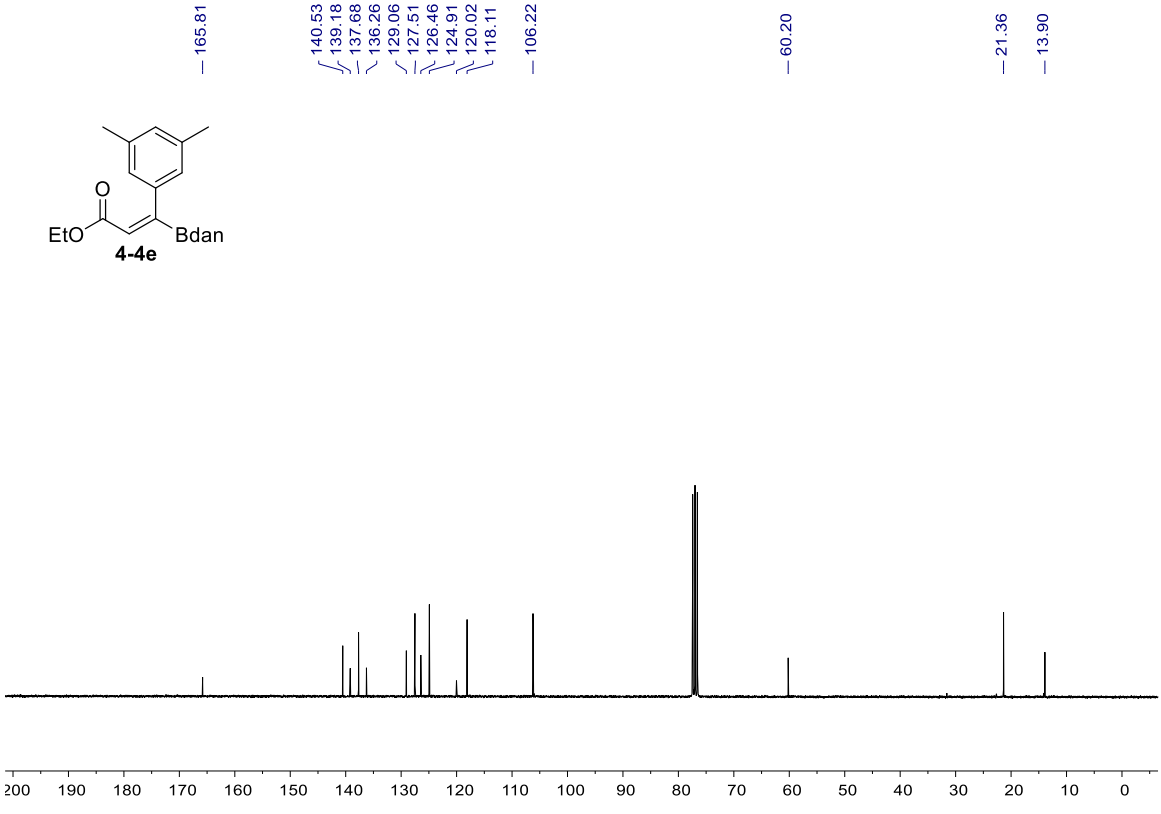

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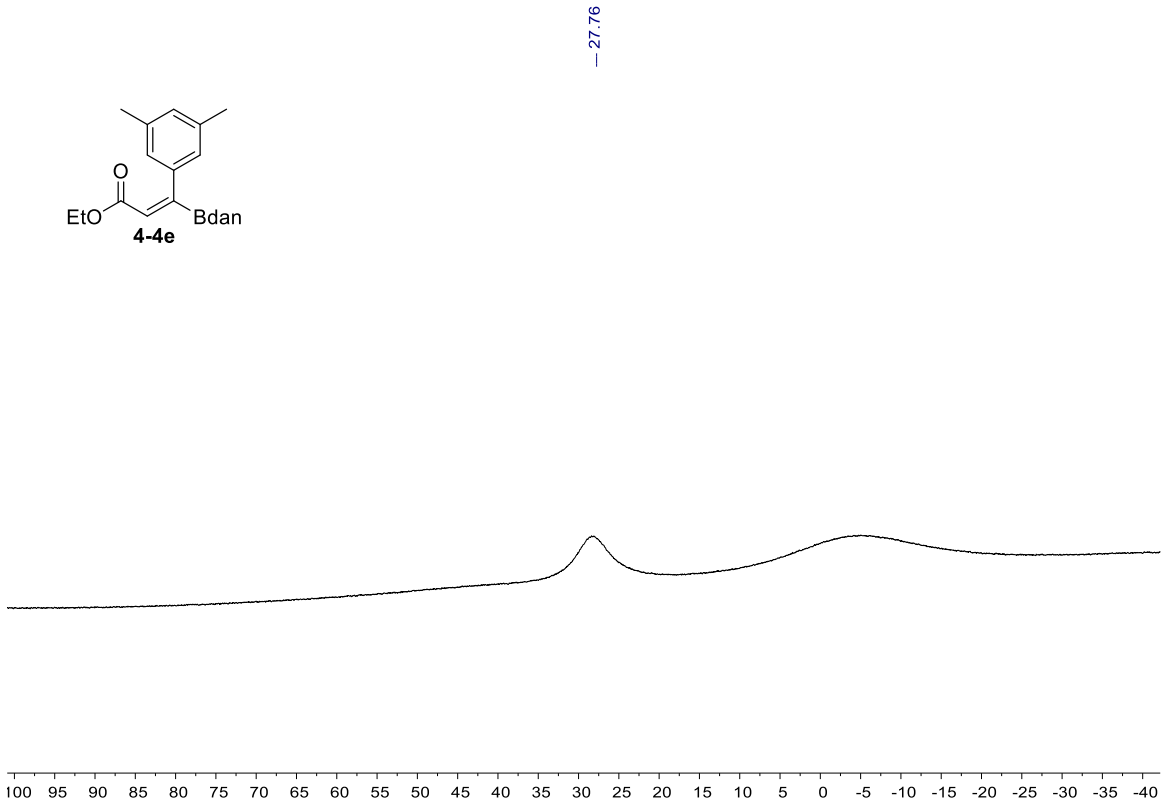

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