Borylative Transition Metal-Free Couplings of Vinyl Iodides with Various Nucleophiles, Alkenes or Alkynes

Gesa Seidler, Max Schwenzer, Florian Clausen, Constantin G. Daniliuc, and Armido Studer*

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, 48149 Münster, Germany.

Email: studer@uni-muenster.de

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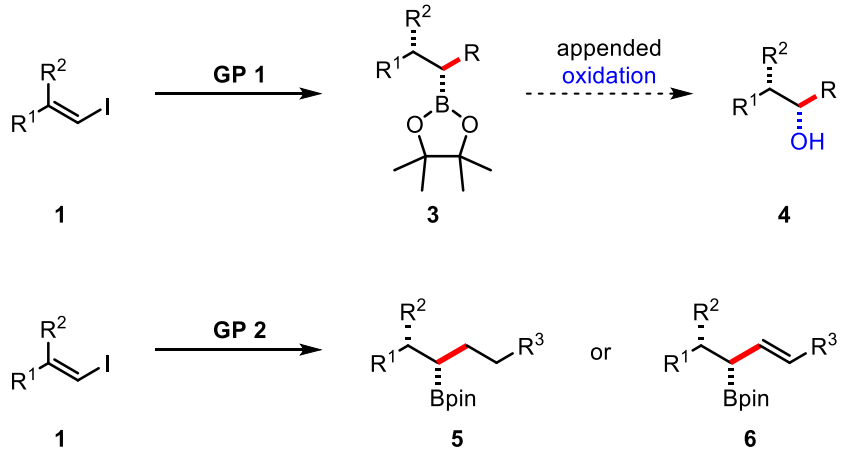
1 General Information

All reactions containing air or moisture sensitive reagents were carried out under argon atmosphere using *Schlenk* technique. Glassware for these reactions was dried in an oven for at least 12 h at 100–110 °C prior to use. Solvents for extractions or flash column chromatography were distilled before use (EtOAc, Et_2O, CH_2Cl_2, and pentane). Solvents for air and moisture sensitive reactions were dried according to standard procedures (THF over potassium, Et_2O over potassium-sodium alloy (4:1), CH_2Cl_2 over P_2O_5) and were freshly distilled under argon atmosphere before use. DMS was dried over sodium, distilled, and stored over molecular sieves (4 Å) under argon in the dark at 5 °C. Triethylsilane was heated to reflux briefly over molecular sieves (4 Å) then distilled and stored over molecular sieves (4 Å) under argon. Two commercial samples of Et_3SiH from two suppliers with different bottle age showed only 80–85% of Si-H by NMR using an internal standard, which was improved to about 95% by the distillation. BCl_3 solutions were bought from Sigma Aldrich (25 mL) and were used as received, applying a minimal stream of argon when taking the reagent by syringe. Only marginal losses in the reaction yields were observed when using older bottles (over 1 month). Titrations of organometallic reagents were carried out with 0.1 N HCl after addition of H_2O using phenolphthalein as an indicator.[1] All other chemicals were purchased from *ABCR*, *Acros Organics*, *Alfa Aesar*, *BLDpharm*, *Enamine*, *fluorochem*, *FisherScientific*, *Merck*, *Sigma Aldrich*, or *TCI* and were used in the reactions without further purification (unless noted otherwise). A sodium borate buffer solution (10 mM sodium borate, 150 mM NaCl in H_2O) was used for oxidation of the boronic esters to alcohols. Thin layer chromatography was conducted on *Merck Silica Gel 60 F-254* plates. UV-fluorescence or fluorescence quenching at 254 nm or $KMnO_4$ staining (1.5 g $KMnO_4$, 5 g $NaHCO_3$ in 200 mL H_2O) were used for detection. For flash column chromatography *Merck or VWR Silica Gel 60* (40–63 μm) was used. Whenever stated, the silica was deactivated by vigorously stirring a slurry in aqueous sodium acetate (3 wt%) for one hour before removing the water *in vacuo* and drying in the oven overnight.[2] The overpressure of air applied to the column did not exceed 0.5 bar. *Celite*® was used as filter aid. A *Büchi B-585* glass oven was used for bulb-to-bulb distillations. For prolonged periods of time (e.g. overnight) the cooling bath temperature was controlled by a *Julabo FT902* cryostat. The isolated vinyl iodides were stored under argon in the dark at -20 °C for prolonged periods of time. ^{1}H NMR, ^{13}C NMR, $^{13}C\{^{1}H, ^{19}F\}$ NMR, ^{11}B NMR, ^{19}F NMR, ^{29}Si NMR and ^{31}P NMR spectra were measured at the NMR spectrometry department of the Organic Chemistry institute of the Westfälische Wilhelms-Universität Münster. The spectra

were recorded on a *Bruker Avance II 300*, a *Bruker NEO 400*, an *Agilent DD2 500* and an *Agilent DD2 600* at 300 K. The chemical shift (δ) of the signals is reported in parts per million (ppm) and was calibrated to the respective solvent residual peak ($CDCl_3$: ^1H: δ = 7.26 ppm, ^{13}C: δ = 77.2 ppm, DMSO-d_6: ^1H: δ = 2.50 ppm, ^{13}C: δ = 39.5 ppm).[3] ^{11}B, ^{19}F, ^{29}Si and ^{31}P NMR spectra are referenced according to the proton signal of TMS as the primary reference for the unified chemical shift scale.[4] Multiplicities of the signals are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and combinations thereof. The Coupling constants (*J*) are given in Hertz. For some of the ^{11}B spectra large broad peaks are observed due to the borosilicate NMR tubes used. *MestReNova* (version 14.3.1-31739) was used for data analysis and visualization. High resolution mass spectra (HRMS) data was recorded on a *Bruker MicroTof*, a *Thermo-Fisher Scientific Orbitrap LTQ XL*, *Orbitrap Velos Pro* or *Exploris 120 Orbitrap* with electrospray ionization (ESI). HRMS spectra with electron impact ionization (EI) were measured on a Thermo-Fischer Scientific Exactive GC Orbitrap GC-MS System or as pushrod measurements. The data was analyzed with *Thermo Xcalibur Qual Browser* (v4.5.474.0) and degree of deuteration determined with *Universal Mass Calculator* (v3.11.0.27). Reaction control was routinely carried out using *Agilent 6890N*, *7890A* or *8860* gas chromatographs equipped with *HP-5* columns (30m x 0.32 mm, film thickness 0.2 µm) utilizing H_2 as carrier gas and flame ionization detection (FID) aswell as an *Agilent 7820A* using a *HP-5* column with He as carrier gas connected to a *Waters Micromass QuattroMicro* system (EI at 70 eV). Pre-installed temperature programs were used for all measurements (50 °C to 300 °C, heating at 10 °C/min or 30 °C/min) and the collected chromatographs were analyzed with *OpenLab* (version 2.7). All mass/charge ratios (*m*/*z*) are given in the atomic mass unit u. IR spectra were measured on a *Digilab 3100 FT-IR Excalibur Series* processing with *Varian Resolutions Pro* (v4.0.5.009) and a *Jasco FT/IR-4600* spectrometer using at least 20 scans and processing with *Jasco Spectra Manager* (v2.15.03). The wave numbers of the absorption bands are reported in cm^{-1}. Melting points of the prepared compounds were measured on a *Stuart SMP10* or a *Büchi Melting Point M-560* device and are uncorrected. Graphics were created in *PerkinElmer ChemDraw Professional* (version 22.2.0.3300), literature was managed with *Citavi* (v6.15) and the text edited with *Microsoft Word (v*1808*)*. X-Ray diffraction data sets were collected with a *Bruker D8 Venture Photon III* diffractometer. Details on the programs used are given in chapter 11.

2 General Procedures

2.1. Reactions



General Procedure 1 (GP1): Borylative coupling of vinyl iodide **1a** with organometallic nucleophiles

To a cooled (0 °C) solution of BCl_3 (1.0 M in CH_2Cl_2, 0.28 mL, 0.28 mmol, 1.1 equiv.) a preformed solution of vinyl iodide **1a** (61 mg, 0.25 mmol, 1.0 equiv.) and triethylsilane (44 µL, 0.28 mmol, 1.1 equiv.) in CH_2Cl_2 (0.10 M) is added *via* syringe. The solution is stirred for 30 min at 0 °C and is then allowed to warm to room temperature over 30 min. Pinacol (33 mg, 0.28 mmol, 1.1 equiv.) is added at once at which point a slight gas evolution can be observed and the solution is stirred for 15 min. The volatiles are removed under reduced pressure, the residue dissolved in the indicated solvent (THF/Et_2O/DMS, 2.5 mL, 0.10 M) and cooled to -78 °C. A solution of the nucleophile (usually 1.5–3.0 equiv.) is added dropwise and the cooling bath removed after 15 min. After 1 h, unless noted otherwise (progress is usually monitored by GC analysis after 40 min), either 0.1 N HCl is added for isolation of the boronic pinacol ester **3** or the reaction mixture is concentrated *in vacuo* (for appended oxidation to the corresponding alcohol **4**, continue with procedure below). The aqueous phase is extracted with CH_2Cl_2 and the combined organic layers are dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue is purified by flash column chromatography on normal or NaOAc-deactivated (whenever stated) silica gel usually using pentane/Et_2O as the eluent or bulb-to-bulb distillation yielding the desired boronic pinacol esters **3**.

In case of appended oxidation:

The concentrated reaction mixture is dissolved in THF (2.5 mL, 0.10 M) followed by the addition of a sodium borate buffer solution (2.5 mL), a sodium hydroxide solution (3.0 M, 0.09 mL, 0.3 mmol, 1 equiv.) and H_2O_2 (35%, 0.20 mL, 2.3 mmol, 10 equiv.). The reaction mixture is stirred at ambient temperature overnight and extracted with CH_2Cl_2. The combined organic phases are dried over $MgSO_4$ and mixture is concentrated *in vacuo*. The product alcohols **4** are obtained after purification *via* flash column chromatography using pentane/Et_2O as the eluent.

General Procedure 2 (GP2): Borylative coupling of vinyl iodides with alkenes or alkynes

Et_3SiH (44 µL, 0.28 mmol, 1.1 equiv.) and vinyl iodide (0.25 mmol, 1.0 equiv.) are dissolved in CH_2Cl_2 (2.0 mL, 0.13 M). BCl_3 (1.0 M in CH_2Cl_2, 0.28 mL, 0.28 mmol, 1.1 equiv.) is cooled to 0 °C and after five minutes the premixed solution of vinyl iodide and silane is added dropwise (over ca. 3 min, through septum cap, flushing with another 0.5 mL CH_2Cl_2). The reaction mixture is stirred for 30 min at 0 °C at which point the cooling bath is removed and the reaction mixture is allowed to warm to room temperature. A premixed solution of Et_3SiH (44 µL, 0.28 mmol, 1.1 equiv.) and alkene or alkyne (0.25 mmol, 1.0 equiv.) in CH_2Cl_2 (1.0 mL, 0.25 M) is added at once by syringe (flushing with another 0.5 mL CH_2Cl_2) and stirring is continued overnight. The volatiles are removed *in vacuo* over the course of an hour and the residue is redissolved in THF (2.0 mL, 0.13 M) and cooled to -78 °C. In another vial, ^{n}BuLi (1.6 M in hexanes, 0.47 mL, 0.75 mmol, 3.0 equiv.) is added to a solution of pinacol (89 mg, 0.75 mmol, 3.0 equiv.) in THF (1.0 mL, 0.75 M) and the resulting solution is stirred for 5 min before being transferred dropwise *via* syringe to the cooled reaction mixture. Stirring is continued for 30 min at -78 °C, the cooling bath is removed and the reaction mixture is stirred at room temperature for 2-3 h (progress monitored by GC analysis) before addition of 0.1 N HCl. The aqueous phase is extracted with CH_2Cl_2, the combined organic layers are dried over $MgSO_4$ and concentrated under reduced pressure. The crude product is then purified *via* flash column chromatography using pentane/Et_2O as the eluent to obtain the target boronic esters **5** or allylboronic esters **6**.

2.2. Generation of Organometallic Reagents

Alkyl and aryl Grignards (RMgX):

The procedure is given for generation of 2.0 equiv. of reagent and was scaled if needed: To a suspension of magnesium turnings (12 mg, 0.49 mmol, 2.0 equiv.) in Et_2O (0.5 mL, usually 1 M) is added the alkyl or aryl halide (X = Br or I, 0.50 mmol, 2.0 equiv.) at room temperature. 1,2-dibromoethane (2 µL, 0.02 mmol, 8 mol%) is added and the mixture stirred until almost all the Mg has been consumed. If low conversion is observed within 30 min, the reaction mixture is heated to reflux for 1 . The formed Grignard reagent is allowed to reach room temperature and transferred to the reaction mixture dropwise *via* syringe.

Aryllithium generation (ArLi):

The aryl bromide or iodide (0.38 mmol. 1.5 equiv.) is dissolved in DMS (0.5 mL, 0.8 M) and cooled to -78 °C. ^{t}BuLi (1.7 M in pentane, 0.41 mL, 0.70 mmol, 2.8 equiv.) is added dropwise and stirring is continued for 15 min. The mixture is allowed to reach room temperature, stirred for 1 h and then transferred to the reaction mixture dropwise *via* syringe.

Alkynyllithium generation (RC≡CLi):

The alkyne (0.50 mmol, 2.0 equiv.) is dissolved in Et_2O (1.0 mL, 0.50 M) and cooled to -78 °C. ^{n}BuLi (1.6 M in hexanes, 0.27 mL, 0.43 mmol, 1.7 equiv.) is added dropwise and stirring is continued for 15 min at -78 °C. The mixture is allowed to reach room temperature, stirred for 1 h and transferred to the reaction mixture dropwise *via* syringe.

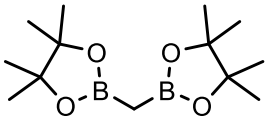
Vinyllithium generation ($R^1R^2C=CR^3Li$):

The vinyl iodide (0.38 mmol, 1.5 equiv.) is dissolved in DMS (0.5 mL, 0.8 M) and ^{n}BuLi (1.6 M in hexanes, 0.20 mL, 0.32 mmol, 1.3 equiv.) is added dropwise at room temperature and stirring is continued for 10 min. The formed reagent is transferred to the reaction mixture dropwise *via* syringe.

3 Synthesis of Starting Materials

3.1 Synthesis of Precursors and Reagents

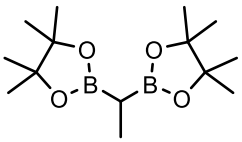
bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (S1a)



$(Bpin)_2CH_2$ **S1a** was synthesized according to a modified literature protocol:[5] To a solution of diiodomethane (4.2 mL, 52 mmol, 4.0 equiv.) in THF (180 mL) was added isopropylmagnesium chloride (2.0 M in THF, 24 mL, 48 mol, 3.7 equiv.) dropwise at -78 °C over 15 min. After 30 min bis(pinacolato) diboron (3.3 g, 13 mmol, 1.0 equiv.) in THF (60 mL) was added and stirring was continued for 30 min after which the reaction was stirred at -55 °C overnight. After addition of sat. aq. NH_4Cl the mixture was allowed to warm to room temperature. The phases were separated, and the aqueous phase was extracted with Et_2O. The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The product was isolated *via* flash column chromatography (pentane/EtOAc) as a colorless crystalline solid (2.7 g, 9.9 mmol, 76%).[i]

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 24H), 0.34 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 83.1, 24.9. The carbon in the α-position to the boron atoms could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.5. **HRMS (ESI)**: Calculated for $C_{13}H_{26}O_4{}^{11}B_2Na^+$: m/z = 291.19094 ($[M+Na]^+$), found: 291.19089. The NMR data is in accordance with that reported in the literature.[6]

2,2'-(ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S1b)



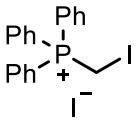
$(Bpin)_2CHMe$ **S1b** was synthesized according to a modified literature protocol:[5] A solution of 2,2,6,6-tetramethylpiperidine (3.0 mL, 18 mmol, 1.2 equiv.) in THF (60 mL) was cooled to 0 °C and ^{n}BuLi (1.6 M in hexanes, 10 mL, 16 mmol, 1.1 equiv.) was added. The mixture was allowed to warm to room temperature over 30 min then cooled to 0 °C. $(Bpin)_2CH_2$ **S1a** (4.0 g, 15 mmol, 1.0 equiv.) was added and stirring continued for 5 min before methyl iodide (1.2 mL, 19 mmol, 1.3 equiv.) was added dropwise. After stirring for 10 min, the reaction mixture was allowed to warm to room temperature over 30 min. Sat. aq. NH_4Cl was added, the phases separated and the aqueous phase was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and

[i] Apart from this transition metal-free approach, the reagent **S1a** can also conveniently be prepared in large batches (ca. 15 g) by a copper-catalyzed approach[6] and purifying by distillation and is also commercially available (<$5/g).

concentrated *in vacuo*. The product was isolated *via* flash column chromatography (pentane/EtOAc) as a colorless oil (3.8 g, 14 mmol, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 – 1.17 (m, 24H), 1.03 (d, *J* = 7.3 Hz, 3H), 0.70 (q, *J* = 7.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 83.0, 25.0, 24.7, 9.2. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.0. **HRMS (ESI)**: Calculated for $C_{14}H_{28}O_4{}^{11}B_2Na^+$: m/z = 305.20659 ($[M+Na]^+$), found: 305.20609. The NMR data is in accordance with that reported in the literature.[7]

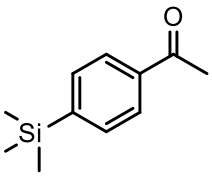
(iodomethyl)triphenylphosphonium iodide (S2)



STORK-ZHAO salt **S2** was synthesized according to a literature protocol:[8] A mixture of diiodomethane (16 mL, 0.20 mol, 1.4 equiv.) and triphenylphosphine (36 g, 0.14 mmol, 1.0 equiv.) in toluene (120 mL) was stirred at 100 °C overnight. The precipitate was filtered and then washed with cold toluene followed by CH_2Cl_2. Drying under reduced pressure yielded the product as a pale-yellow solid (57 g, 0.11 mol, 78%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95 – 7.75 (m, 15H), 5.06 (d, *J* = 8.7 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 135.2 (d, *J* = 3.0 Hz), 133.8 (d, *J* = 10.2 Hz), 130.1 (d, *J* = 12.7 Hz), 118.3 (d, *J* = 88.7 Hz), -16.1 (d, *J* = 52.3 Hz). **^{31}P NMR** (162 MHz, DMSO-d_6) δ 23.7. **HRMS (ESI)**: Calculated for $C_{19}H_{17}I^{31}P^+$: m/z = 403.01071 ($[M-I]^+$), found: 403.00921. The NMR data is in accordance with that reported in the literature.[9]

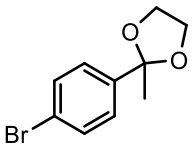
1-(4-(trimethylsilyl)phenyl)ethan-1-one (S3)



Acetophenone derivative **S3** was synthesized according to a modified literature protocol:[10] To a mixture of 4'-bromoacetophenone (2.0 g, 10 mmol, 1.0 equiv.), KF (2.9 g, 50 mmol, 5.0 equiv.), tris-(dibenzylideneacetone)dipalladium(0) (0.14 g, 0.15 mmol, 1.5 mol%) and 2-(di-t-butylphosphino)biphenyl (0.27 g, 0.90 mmol, 9.0 mol%) in argon-purged 1,3-dimethyl-1,3-diazinan-2-one (DMPU, 30 mL) was added H_2O (0.36 mL, 20 mmol, 2.0 equiv.) and hexamethyldisilane (2.5 mL, 12 mmol, 1.2 equiv.). The reaction mixture was stirred at 100 °C for 2 h. Pentane (300 mL) was added and the phases were separated. The organic phase was washed with H_2O (4x200 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The product was isolated *via* flash column chromatography (pentane/Et_2O) as a colorless oil (1.1 g, 5.7 mmol, 57%).

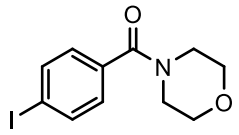
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.65 – 7.60 (m, 2H), 2.60 (s, 3H), 0.30 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.5, 147.4, 137.4, 133.7, 127.4, 26.8, -1.19. **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -3.3. **MS (EI)**: Calculated for $C_{11}H_{16}OSi^{\bullet+}$: *m*/z = 192.1 ($[M]^{\bullet+}$), found: 192.1. The NMR data is in accordance with that reported in the literature.[11]

2-(4-bromophenyl)-2-methyl-1,3-dioxolane (S4)



Aryl bromide **S4** was synthesized according to a modified literature protocol:[12] A mixture of 4'-bromoacetophenone (5.0 g, 25 mmol, 1.0 equiv.), ethylene glycol (14 mL, 0.25 mol, 10 equiv.), *p*-toluenesulfonic acid monohydrate (0.47 g, 2.5 mmol, 10 mol%) and $MgSO_4$ (6.0 g) in toluene (70 mL) was heated to reflux for three days. The mixture was allowed to cool to room temperature, washed with sat. aq. $NaHCO_3$ and the phases were separated. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The product was obtained *via* flash column chromatography (pentane/Et_2O) as a colorless crystalline solid (0.52 g, 2.1 mmol, 9%).**^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 2H), 7.39 – 7.32 (m, 2H), 4.10 – 3.97 (m, 2H), 3.82 – 3.68 (m, 2H), 1.63 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6, 131.5, 127.3, 122.0, 108.6, 64.6, 27.7. **HRMS (ESI)**: Calculated for $C_{10}H_{11}O_2{}^{79}BrNa^+$: m/z = 264.98346 ($[M+Na]^+$), found: 264.98348. NMR data is in accordance with that reported in the literature.[13]

(4-iodophenyl)(morpholino)methanone (S5)



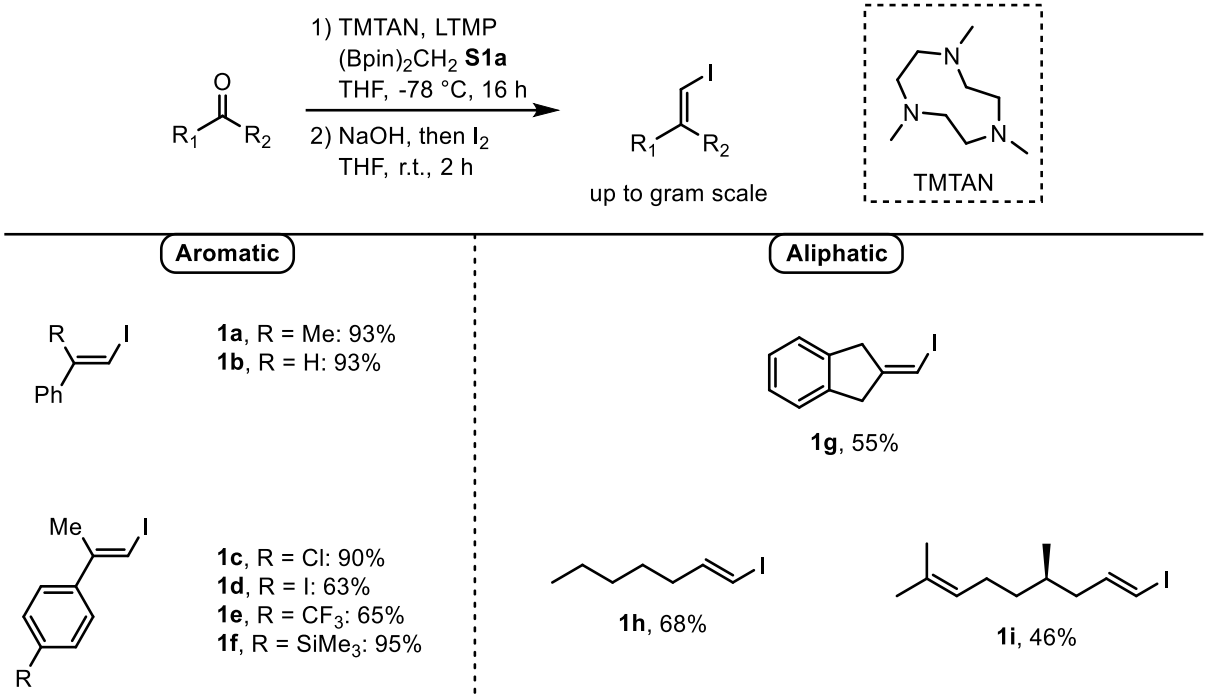
Aryl iodide **S5** was synthesized according to a modified literature protocol:[14] To a mixture of 4-iodobenzoic acid (2.5 g, 10 mmol, 1.0 equiv.), morpholine (1.1 mL, 13 mmol, 1.3 equiv.) and triethylamine (2.1 mL, 15 mmol, 1.5 equiv.) in DMF (20 mL) and CH_2Cl_2 (12 mL) was added 3-(Ethyliminomethylidenamino)-*N*,*N*-dimethylpropan-1-amine hydrochloride (EDCI•HCl, 2.9 g, 15 mmol, 1.5 equiv.) and 1-Hydroxy-1*H*-benzotriazole hydrate (HOBt, 0.68 g, 5.0 mmol, 0.50 equiv.). The mixture was stirred at room temperature overnight, diluted with H_2O and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The product was obtained *via* flash column chromatography (pentane/EtOAc) followed by bulb-to-bulb distillation as a pale-yellow crystalline solid (1.0 g, 3.2 mmol, 32%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.19 – 7.10 (m, 2H), 3.94 – 3.33 (m, 8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 137.9, 134.8, 129.0, 96.2, 66.9. **HRMS (ESI)**:

Calculated for $C_{11}H_{12}O_2NINa^+$: m/z = 339.98049 ([M+Na]$^+$), found: 339.98044. NMR data is in accordance with that reported in the literature.[15]

3.2 Synthesis of Vinyl Iodides (*E*-selective)

3.2.1 From Ketones or Aldehydes *via* Boron-WITTIG/Iodinolysis One-pot



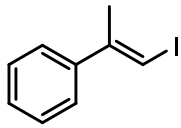
The procedure was developed based on literature protocols for Boron-WITTIG reactions of ketones[16] and aldehydes[17] as well as for the iodinolysis of vinyl boronates[18] and only briefly optimized.[ii]

A solution of 2,2,6,6-tetramethylpiperidine (1.5 equiv.) in THF (0.15 M) is cooled to 0 °C and ^{n}BuLi (1.6 M in hexanes, 1.4 equiv.) is added. The mixture is allowed to warm to room temperature over 30 min, then 1,4,7-trimethyl-1,4,7-triazonane (TMTAN, 0.5 equiv.) is added and stirring continued for 5 min before cooling to 0 °C. $(Bpin)_2CH_2$ **S1a** (1.5 equiv.) is added at once and the resulting suspension stirred at 0 °C for 5 min. The solution is placed in a cooling bath at -78 °C and stirred for 30 min after which the ketone or aldehyde is added dropwise. The reaction mixture is stirred at -78 °C for 16 h, then opened to air and allowed to warm to ambient temperature. NaOH (3.0 M in H_2O, 6 equiv.) is added and stirring continued for 10 min at which point I_2 (4 equiv.) is added at once.[iii] After 2 h sat. aq. $Na_2S_2O_3$ is added and the aqueous phase

[ii] The amount of reagent **S1a** was reduced from 2.0 equiv. to 1.5 equiv. The amounts of NaOH and iodine were doubled to guarantee full conversion to the vinyl iodide which was usually but not always the case otherwise. Increasing the amount of TMTAN did not lead to improved selectivity or yield but small amounts of the *Z*-isomer were removed by flash column chromatograph for acetophenone-derived vinyl iodides.
[iii] Heat formation is observed but no additional precautions had to be taken up to 14 mmol scale.

extracted with Et_2O. The combined organic layers are washed with sat. aq. $NaHCO_3$ and brine successively, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product is then purified by flash column chromatography (pentane) to obtain the target vinyl iodide **1**.

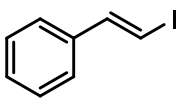
(*E*)-(1-iodoprop-1-en-2-yl)benzene (1a)



Vinyl iodide **1a** was prepared using acetophenone (1.2 mL, 10 mmol, 1.0 equiv.), $(Bpin)_2CH_2$ **S1a** (4.0 g, 15 mmol, 1.5 equiv.), 2,2,6,6-tetramethylpiperidine (2.5 mL, 15 mmol, 1.5 equiv.), ^{n}BuLi (1.6 M in hexanes, 8.5 mL, 14 mmol, 1.4 equiv.), 1,4,7-trimethyl-1,4,7-triazonane (1.0 mL, 5.2 mmol, 0.52 equiv.), NaOH (3.0 M in H_2O, 20 mL, 60 mmol, 6.0 equiv.), iodine (10.1 g, 39.8 mmol, 4.0 equiv.) and THF (100 mL). The product was isolated as a colorless oil (2.3 g, 9.3 mmol, 93%) which turned orange over time.[iv]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 6.53 – 6.51 (m, 1H), 2.30 – 2.27 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.4, 141.6, 128.6, 128.0, 126.2, 79.3, 24.5. **MS (EI)**: Calculated for $C_9H_9I^{\bullet+}$: *m*/z = 244.0 ($[M]^{\bullet+}$), found: 244.0. The NMR data is in accordance with that reported in the literature.[19]

(*E*)-(2-iodovinyl)benzene (1b)



Vinyl iodide **1b** was prepared using benzaldehyde (1.4 mL, 14 mmol, 1.0 equiv.), $(Bpin)_2CH_2$ **S1a** (5.8 g, 22 mmol, 1.6 equiv.), 2,2,6,6-tetramethylpiperidine (3.6 mL, 21 mmol, 1.5 equiv.), ^{n}BuLi (1.6 M in hexanes, 12 mL, 18 mmol, 1.3 equiv.), 1,4,7-trimethyl-1,4,7-triazonane (0.14 mL, 0.72 mmol, 5.2 mol%)[v], NaOH (3.0 M in H_2O, 28 mL, 84 mmol, 6.0 equiv.), iodine (14.4 g, 56.7 mmol, 4.1 equiv.) and THF (120 mL). The product was isolated as a pale-yellow liquid (3.0 g, 13 mmol, 94%) which turned orange over time.

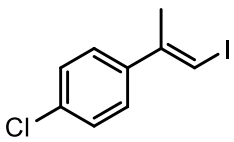
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 14.9 Hz, 1H), 7.38 – 7.26 (m, 5H), 6.84 (d, *J* = 14.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.1, 137.8, 128.8, 128.5, 126.1, 76.8. **MS (EI)**:

[iv] Reaction was run under these conditions multiple times: 91%, 91%, 84%, 88%, 93%, 93%; average yield: 90%. With 2.0 equiv. LTMP and reagent **S1a** 93% yield (7 mmol scale) was obtained with 3 equiv. of NaOH and 1.3 equiv. of I_2 and 95% yield (8 mmol scale) with 6.0 equiv. of NaOH and 4.0 equiv. of I_2. Adding 3 equiv. of anhydrous LiCl instead of TMTAN leads to complete loss of selectivity (*E*:*Z* = 1:1) allowing for isolation of both conformers at once (if desired) as they are separable by column chromatography.

[v] While full *E*-selectivity was observed when running the reaction without TMTAN, a catalytic amount improved the yield to some extent (without: 84%, 71%, 72% on 10 mmol scale). The reaction may also be run for a shorter duration (4 h) or at 0 °C[17].

Calculated for $C_8H_7I^{\bullet+}$: *m*/z = 230.0 ($[M]^{\bullet+}$), found: 230.0. The NMR data is in accordance with that reported in the literature.[20]

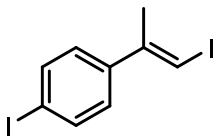
(*E*)-1-chloro-4-(1-iodoprop-1-en-2-yl)benzene (1c)



Vinyl iodide **1c** was prepared using 4'-chloroacetophenone (0.52 mL, 4.0 mmol, 1.0 equiv.), $(Bpin)_2CH_2$ **S1a** (1.6 g, 6.0 mmol, 1.5 equiv.), 2,2,6,6-tetramethylpiperidine (1.0 mL, 5.9 mmol, 1.5 equiv.), ^{n}BuLi (1.6 M in hexanes, 3.4 mL, 5.4 mmol, 1.4 equiv.), 1,4,7-trimethyl-1,4,7-triazonane (0.39 mL, 2.0 mmol, 0.50 equiv.), NaOH (3.0 M in H_2O, 8.0 mL, 24 mol, 6.0 equiv.), iodine (4.1 g, 16 mmol, 4.0 equiv.) and THF (40 mL). The product was isolated as a pink liquid (1.0 g, 3.6 mmol, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 4H), 6.54 (q, *J* = 1.1 Hz, 1H), 2.25 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.2, 140.0, 133.9, 128.7, 127.4, 79.9, 24.4. **MS (EI)**: Calculated for $C_9H_8{}^{35}ClI^{\bullet+}$: *m*/z = 277.9 ($[M]^{\bullet+}$), found: 277.9. The NMR data is in accordance with that reported in the literature.[21]

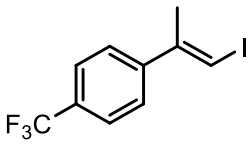
(*E*)-1-iodo-4-(1-iodoprop-1-en-2-yl)benzene (1d)



Vinyl iodide **1d** was prepared using 4'-iodoacetophenone (0.99 g, 4.0 mmol, 1.0 equiv.), $(Bpin)_2CH_2$ **S1a** (1.6 g, 6.0 mmol, 1.5 equiv.), 2,2,6,6-tetramethylpiperidine (1.0 mL, 5.9 mmol, 1.5 equiv.), ^{n}BuLi (1.6 M in hexanes, 3.4 mL, 5.4 mmol, 1.4 equiv.), 1,4,7-trimethyl-1,4,7-triazonane (0.39 mL, 2.0 mmol, 0.50 equiv.), NaOH (3.0 M in H_2O, 8.0 mL, 24 mmol, 6.0 equiv.), iodine (4.1 g, 16 mmol, 4.0 equiv.) and THF (40 mL). The product was isolated as a yellow crystalline solid (0.91 g, 2.5 mmol, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.10 – 7.06 (m, 2H), 6.55 (q, *J* = 1.1 Hz, 1H), 2.24 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.4, 141.0, 137.7, 128.0, 93.5, 80.1, 24.3. **HRMS (EI)**: Calculated for $C_9H_8I_2^{\bullet+}$: *m*/z =369.87099 ($[M]^{\bullet+}$), found: 369.87093. **IR** 3840, 3393, 1591, 1543, 1487, 1390, 1065, 1003, 827, 773, 680, 523. **mp**: 53–55 °C.

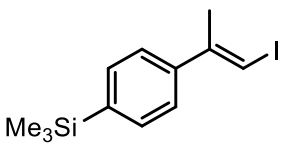
(*E*)-1-(1-iodoprop-1-en-2-yl)-4-(trifluoromethyl)benzene (1e)



Vinyl iodide **1e** was prepared using 4'-(trifluoromethyl) acetophenone (1.1 mL, 5.4 mmol, 1.0 equiv.), $(Bpin)_2CH_2$ **S1a** (2.2 g, 8.2 mmol, 1.5 equiv.), 2,2,6,6-tetramethylpiperidine (1.4 mL, 8.3 mmol, 1.5 equiv.), ^{n}BuLi (1.6 M in hexanes, 5.0 mL, 8.0 mmol, 1.5 equiv.), 1,4,7-trimethyl-1,4,7-triazonane (0.54 mL, 2.8 mmol, 0.52 equiv.), NaOH (3.0 M in H_2O, 11 mL, 33 mol, 6.1 equiv.), iodine (5.5 g, 22 mmol, 4.1 equiv.) and THF (55 mL). The product was isolated as an orange liquid (1.1 g, 3.5 mmol, 65%).[vi]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.48 – 7.42 (m, 2H), 6.65 (q, *J* = 1.1 Hz, 1H), 2.29 (d, *J* = 1.1 Hz, 3H). **^{13}C{^{1}H, ^{19}F} NMR** (126 MHz, $CDCl_3$) δ 146.3, 144.9, 130.0, 126.5, 125.6, 124.2, 81.6, 24.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.6. **HRMS (EI)**: Calculated for $C_{10}H_8F_3I^{\bullet+}$: *m*/z =311.96173 ($[M]^{\bullet+}$), found: 311.96178. **IR** 3065, 1617, 1596, 1566, 1405, 1377, 1320, 1164, 1111, 1069, 1014, 972, 844, 786, 730, 677, 605, 534.

(*E*)-(4-(1-iodoprop-1-en-2-yl)phenyl)trimethylsilane (1f)

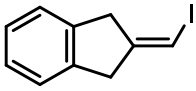


Vinyl iodide **1f** was prepared using 1-(4-(trimethylsilyl)phenyl) ethan-1-one **S3** (1.1 g, 5.5 mmol, 1.0 equiv.), $(Bpin)_2CH_2$ **S1a** (2.2 g, 8.2 mmol, 1.5 equiv.), 2,2,6,6-tetramethylpiperidine (1.4 mL, 8.3 mmol, 1.5 equiv.), ^{n}BuLi (1.6 M in hexanes, 5.0 mL, 8.0 mmol, 1.5 equiv.), 1,4,7-trimethyl-1,4,7-triazonane (0.54 mL, 2.8 mmol, 0.51 equiv.), NaOH (3.0 M in H_2O, 11 mL, 33 mmol, 6.1 equiv.), iodine (5.6 g, 22 mmol, 4.0 equiv.) and THF (55 mL). The product was isolated as an orange liquid (1.6 g, 5.2 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.35 – 7.31 (m, 2H), 6.54 (q, *J* = 1.1 Hz, 1H), 2.28 (d, *J* = 1.1 Hz, 3H), 0.28 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.4, 141.9, 140.4, 133.6, 125.5, 79.5, 24.4, -1.0. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -4.0. **HRMS (EI)**: Calculated for $C_{12}H_{17}ISi^{\bullet+}$: *m*/z =316.01387 ($[M]^{\bullet+}$), found: 316.01389. **IR** 3062, 2953, 1590, 1383, 1309, 1292, 1247, 1202, 113, 1055, 836, 823, 779, 753, 719, 691, 678, 638, 596, 547.

[vi] A mixed fraction (0.7 g, 2 mmol, ca. 40%, *E*:*Z* = 8:1) was also obtained.

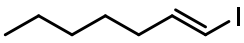
2-(iodomethylene)-2,3-dihydro-1*H*-indene (1g)



Vinyl iodide **1g** was prepared using 2-indanone (0.27 g, 2.0 mmol, 1.0 equiv.), $(Bpin)_2CH_2$ **S1a** (0.81 g, 3.0 mmol, 1.5 equiv.), 2,2,6,6-tetramethylpiperidine (0.50 mL, 3.0 mmol, 1.5 equiv.), ^{n}BuLi (1.6 M in hexanes, 1.7 mL, 2.7 mmol, 1.4 equiv.), 1,4,7-trimethyl-1,4,7-triazonane (0.20 mL, 1.0 mmol, 0.50 equiv.), NaOH (3.0 M in H_2O, 4.0 mL, 12 mmol, 6.0 equiv.), iodine (2.0 g, 7.9 mmol, 4.0 equiv.) and THF (20 mL). The product was isolated as a red oil (0.27 g, 1.1 mmol, 55%) containing a small but slowly increasing amount of a decomposition product. Substrate **1g** was therefore used directly.

MS (EI): Calculated for $C_{10}H_9I^{\bullet+}$: *m*/z = 256. 0 ($[M]^{\bullet+}$), found: 256.0. The crude NMR data is in accordance with that reported in the literature.[22]

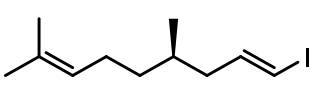
(*E*)-1-iodohept-1-ene (1h)



Vinyl iodide **1h** was prepared using hexanal (0.49 mL, 4.0 mmol, 1.0 equiv.), $(Bpin)_2CH_2$ **S1a** (1.6 g, 6.0 mmol, 1.5 equiv.), 2,2,6,6-tetramethylpiperidine (1.0 mL, 5.9 mmol, 1.5 equiv.), ^{n}BuLi (1.6 M in hexanes, 3.4 mL, 5.4 mmol, 1.4 equiv.), 1,4,7-trimethyl-1,4,7-triazonane (0.39 mL, 2.0 mmol, 0.50 equiv.), NaOH (3.0 M in H_2O, 8.0 mL, 24 mmol, 6.0 equiv.), iodine (4.0 g, 16 mmol, 4.0 equiv.) and THF (40 mL). The product was isolated as a colorless liquid (0.61 g, 2.7 mmol, 68%) which turned pink over time.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 (dt, *J* = 14.3, 7.1 Hz, 1H), 5.97 (dt, *J* = 14.3, 1.5 Hz, 1H), 2.08 – 2.00 (m, 2H), 1.44 – 1.34 (m, 2H), 1.34 – 1.22 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.0, 74.4, 36.2, 31.3, 28.2, 22.6, 14.1. **MS (EI)**: Calculated for $C_7H_{13}I^{\bullet+}$: *m*/z = 224.0 ($[M]^{\bullet+}$), found: 224.0. The NMR data is in accordance with that reported in the literature.[23]

(*R*,*E*)-1-iodo-4,8-dimethylnona-1,7-diene (1i)

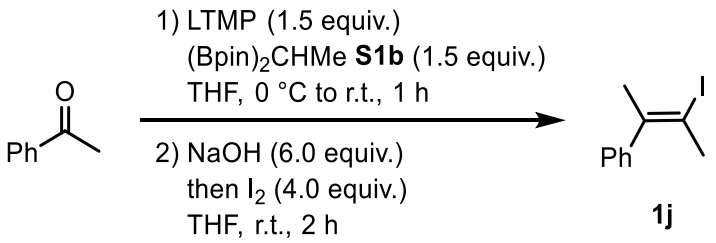


Vinyl iodide **1i** was prepared using (+)-citronellal (1.1 mL, 6.1 mmol, 1.0 equiv.), $(Bpin)_2CH_2$ **S1a** (2.5 g, 9.3 mmol, 1.5 equiv.), 2,2,6,6-tetramethylpiperidine (1.5 mL, 8.9 mmol, 1.5 equiv.), ^{n}BuLi (1.6 M in hexanes, 5.0 mL, 8.0 mmol, 1.3 equiv.), 1,4,7-trimethyl-1,4,7-triazonane (0.60 mL, 3.1 mmol, 0.51 equiv.), NaOH (3.0 M in H_2O, 12 mL, 36 mmol, 5.9 equiv.), iodine (6.1 g, 24 mmol,

3.9 equiv.) and THF (60 mL) with a reaction time of 20 h. The product was isolated as a pale-yellow liquid (0.77 g, 2.8 mmol, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (dt, *J* = 14.3, 7.6 Hz, 1H), 5.96 (dt, *J* = 14.3, 1.4 Hz, 1H), 5.12 – 5.04 (m, 1H), 2.11 – 1.83 (m, 4H), 1.70 – 1.66 (m, 3H), 1.60 (s, 3H), 1.58 – 1.48 (m, 1H), 1.38 – 1.27 (m, 1H), 1.20 – 1.09 (m, 1H), 0.88 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 131.6, 124.6, 75.2, 43.5, 36.5, 32.2, 25.9, 25.6, 19.4, 17.8. **MS (EI)**: Calculated for $C_{11}H_{19}I^{\bullet+}$: *m*/z = 278.1 ($[M]^{\bullet+}$), found: 278.0. The NMR data is in accordance with that reported in the literature.[24]

(*E*)-(3-iodobut-2-en-2-yl)benzene (1j)



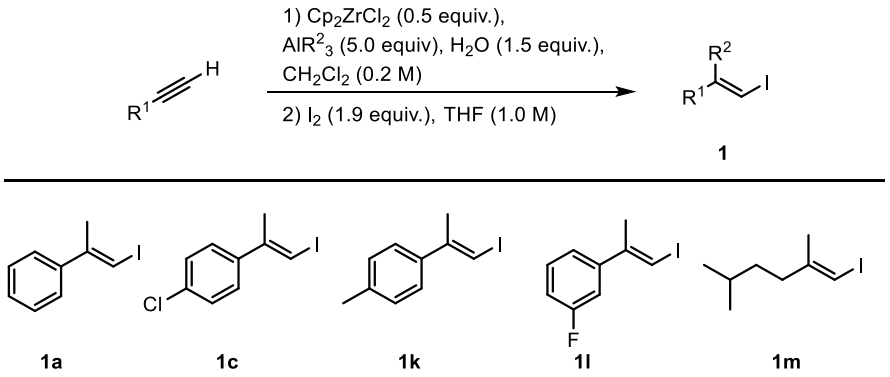
Vinyl iodide **1j** was prepared following a modified literature protocol:[7] A solution of 2,2,6,6-tetramethylpiperidine (1.5 mL, 8.9 mmol, 1.5 equiv.) in THF (24 mL) was cooled to 0 °C and ^{n}BuLi (1.6 M in hexanes, 5.0 mL, 8.0 mmol, 1.3 equiv.) was added. The mixture was allowed to warm to room temperature over 30 min before cooling to 0 °C. $(Bpin)_2CHMe$ **S1b** (2.6 g, 9.1 mmol, 1.5 equiv.) was added at once and the resulting suspension stirred at 0 °C for 5 min after which acetophenone (0.70 mL, 6.0 mmol, 1.0 equiv.) was added dropwise and the reaction mixture was stirred at room temperature for 1 h. NaOH (3.0 M in H_2O, 12 mL, 36 mmol, 6.0 equiv.) was added and stirring continued for 10 min at which point iodine (6.0 g, 24 mmol, 4.0 equiv.) was added at once. After 2 h[vii] sat. aq. $Na_2S_2O_3$ was added and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with sat. saq. $NaHCO_3$ and brine successively, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by flash column chromatography (pentane) yielding a pale orange liquid (0.36 g, 1.4 mmol, 23%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.31 – 7.26 (m, 1H), 7.17 – 7.12 (m, 2H), 2.67 (q, *J* = 1.1 Hz, 3H), 2.11 (q, *J* = 1.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.6, 142.4, 128.3, 127.8,

[vii] GC analysis showed low conversion of the vinyl boronate after 2 h (likely due to the larger steric hindrance compared to trisubstituted vinyl iodides). Running the iodinolysis overnight to improve the yield was not tested.

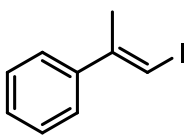
127.1, 95.9, 30.8, 20.8. **HRMS (EI)**: Calculated for $C_{10}H_{11}I^{\bullet+}$: *m*/z =257.98999 ($[M]^{\bullet+}$), found: 257.99000. **IR** 3054, 3020, 2915, 2851, 1597, 1490, 1438, 1380, 1264, 1105, 1067, 1042, 1025, 910, 762, 697, 617.

3.2.2 From Alkynes



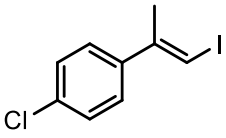
The synthetic steps for the preparation of (*E*)-vinyl iodides were conducted according to a literature procedure:[25] To a solution of zirconocene dichloride (1.2 g, 4.0 mmol, 0.50 equiv.) in CH_2Cl_2 (20 mL, 0.2 M), trialkylaluminum (neat, 3.8 mL, 40 mmol, 5.0 equiv.) was added at -23 °C the resulting solution was stirred for 15 minutes. Water (0.22 mL, 12 mmol, 1.5 equiv.) was added very slowly upon which gas evolution was observed. After stirring for 15 minutes, the corresponding alkyne (8.0 mmol, 1.0 equiv.) was added and the solution was stirred for additional 15 minutes. A solution of iodine (3.9 g, 15 mmol, 1.9 equiv.) in THF (15 mL, 1.0 M) was then added to the reaction mixture which was then allowed to warm to room temperature. The crude mixture was carefully poured into ice water while stirring the receiving flask. HCl (1 M) was added to dissolve precipitating aluminium hydroxides. The mixture was extracted with ether and the combined organic phases were dried over $MgSO_4$. The mixture was concentrated *in vacuo* and the desired vinyl iodides were obtained after purification via flash column chromatography using pentane as the eluent.

(*E*)-(1-iodoprop-1-en-2-yl)benzene (1a)



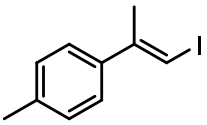
Vinyl iodide **1a** was prepared using phenyl acetylene (0.82 g, 8.0 mmol, 1.0 equiv.). The product was isolated as a colorless oil (1.8 g, 7.5 mmol, 94%). The analytical data are in accordance with those reported in section 3.2.1 and in the literature.[6]

(*E*)-1-chloro-4-(1-iodoprop-1-en-2-yl)benzene (1c)



Vinyl iodide **1c** was prepared using 4-ethynylchlorobenzene (1.1 g, 8.0 mmol, 1.0 equiv.). The product was isolated as a colorless oil (1.1 g, 3.8 mmol, 48%). Analytical data is accordance with those reported in section 3.2.1.

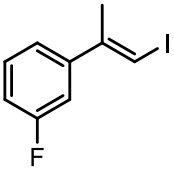
(*E*)-1-(1-iodoprop-1-en-2-yl)-4-methylbenzene (1k)



Vinyl iodide **1k** was prepared using 4-ethynyltoluene (1.0 mL, 8.0 mmol, 1.0 equiv.). The product was isolated as a colorless oil (1.5 g, 5.7 mmol, 72%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 7.19 – 7.09 (m, 2H), 6.48 (t, *J* = 1.2 Hz, 1H), 2.35 (s, 3H), 2.27 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 147.13, 138.75, 137.84, 129.25, 126.02, 78.40, 24.50, 21.26. **HRMS (EI)**: Calculated for $C_{10}H_{11}I^{\bullet+}$: m/z = 257.98999 ($[M]^{\bullet+}$), found: 257.98991. **IR** 3665, 3024, 2916, 1900, 1594, 1561, 1510, 1439, 1406, 1373, 1293, 1196, 1116, 1058, 1017, 969, 822, 772, 715, 671.

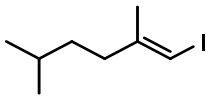
(*E*)-1-fluoro-3-(1-iodoprop-1-en-2-yl)benzene (1l)



Vinyl iodide **1l** was prepared using 3-fluorophenylacetylene (0.92 mL, 8.0 mmol, 1.0 equiv.). The product was isolated as a colorless oil (0.76 g, 2.9 mmol, 36%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 1H), 7.13 (ddd, *J* = 7.7, 1.8, 0.8 Hz, 1H), 7.09 – 6.95 (m, 2H), 6.60 (s, 1H), 2.27 (s, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 162.85 (d, *J* = 246.2 Hz), 146.22, 143.61 (d, *J* = 7.4 Hz), 130.01 (d, *J* = 8.5 Hz), 121.83 (d, *J* = 2.9 Hz), 114.80 (d, *J* = 21.2 Hz), 113.20 (d, *J* = 22.2 Hz), 80.54, 24.41. **HRMS (EI)**: Calculated for $C_9H_8FI^{\bullet+}$: m/z = 261.96492 ($[M]^{\bullet+}$), found: 261.96496. **IR** 3066, 2460, 1933, 1856, 1611, 1597, 1573, 1486, 1431, 1375, 1293, 1266, 1226, 1157, 1055, 977, 890, 869, 770, 715, 691, 603.

(*E*)-1-iodo-2,5-dimethylhex-1-ene (1m)



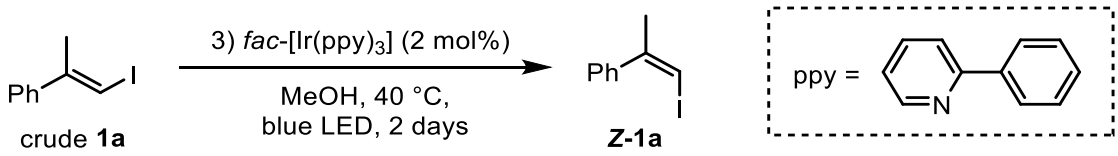
Vinyl iodide **1m** was prepared on an 8.0 mmol scale using 5-methyl-1-hexyne (1.1 mL, 8.0 mmol, 1.0 equiv.), trimethyl aluminium (neat, 7.7 mL, 40 mmol, 5.0 equiv.), zirconocene dichloride (1.2 g, 4.0 mmol, 0.5 equiv.), H_2O (0.22 mL, 12 mmol, 1.5 equiv.), CH_2Cl_2 (20 mL), iodine (3.9 g, 15 mmol, 1.9 equiv.) and THF (15 mL). The product was isolated as a colorless oil (1.4 g, 3.8 mmol, 72%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (q, *J* = 1.1 Hz, 1H), 2.20 (ddd, *J* = 9.3, 6.1, 1.2 Hz, 2H), 1.83 (d, *J* = 1.1 Hz, 3H), 1.59 – 1.43 (m, 1H), 1.37 – 1.25 (m, 2H), 0.90 (s, 3H), 0.88 (s, 3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 148.6, 74.4, 37.7, 37.1, 27.7, 24.1, 22.6. **HRMS (ESI)**: Calculated for $C_8H_{15}I^{\bullet+}$: *m/z* = 238.02130 ($[M]^{\bullet+}$), found: 238.02131. **IR** 2953, 2925, 2869, 1616, 1467, 1384, 1366, 1268, 1170, 1143, 1121, 1008, 772, 667, 563, 539, 507.

3.3 Synthesis of Vinyl Iodides (*Z*-selective)

3.3.1 From Ketones or Aldehydes (Boron-WITTIG, Photoisomerization, STORK-ZHAO)

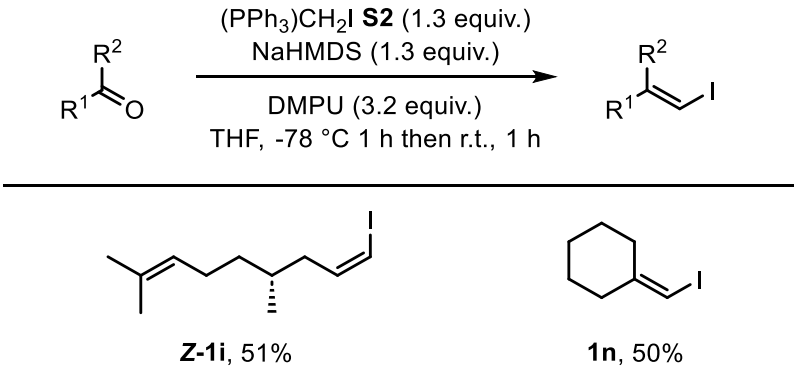
(*Z*)-(1-iodoprop-1-en-2-yl)benzene (*Z*-1a)



Photoisomerization of crude (1-iodoprop-1-en-2-yl)benzene to isomer ***Z*-1a** was tested according to a modified literature protocol:[26] After running the procedure from section **3.1.1** using acetophenone (0.70 mL, 6.0 mmol, 1.0 equiv.), $(Bpin)_2CH_2$ **S1a** (2.4 g, 9.0 mmol, 1.5 equiv.), 2,2,6,6-tetramethylpiperidine (1.5 mL, 8.9 mmol, 1.5 equiv.), ^{n}BuLi (1.6 M in hexanes, 5.0 mL, 8.0 mmol, 1.3 equiv.) without 1,4,7-trimethyl-1,4,7-triazonane (TMTAN), then NaOH (3.0 M in H_2O, 12 mL, 36 mmol, 6.0 equiv.), iodine (6.1 g, 24 mmol, 4.0 equiv.) and THF (60 mL), the crude vinyl iodide was dissolved in MeOH (24 mL, 0.25 M), which had been purged for 15 min with argon for degassing, and tris(2-phenylpyridinato)iridium(III) (76 mg, 0.12 mmol, 1.9 mol%) was added. The reaction mixture was then irradiated with a *Kessil* lamp (40 W, 456 nm) placed periplanar to the tube at a distance of 2 cm under fan cooling (ca. 40 °C) until a stationary *Z*:*E* ratio (≈ 3:1) was observed by NMR analysis (2 days). The crude mixture was concentrated and the *Z*-isomer was isolated *via* flash column

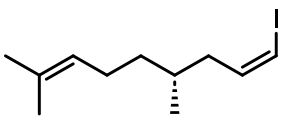
chromatography (pentane) as a pale-yellow liquid (0.50 g, 2.1 mmol, 35%)[viii] that turned pink over time.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.36 – 7.31 (m, 1H), 7.30 – 7.26 (m, 2H), 6.29 (q, *J* = 1.5 Hz, 1H), 2.24 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.4, 143.1, 128.4, 127.8, 127.5, 75.1, 26.7. **MS (EI)**: Calculated for $C_9H_9I^{\bullet+}$: *m*/z = 244.0 ($[M]^{\bullet+}$), found: 244.0. The NMR data is in accordance with that reported in the literature.[28]



The reactions were run according to a modified literature protocol:[29] To a suspension of $(PPh_3)CH_2I$ **S2** (1.3 equiv.) in THF was added a solution of sodium bis(trimethylsilyl)amide (NaHMDS, 1.3 equiv) in THF dropwise and stirring of the resulting reaction mixture (0.27 M in THF) was continued for 5 min at room temperature. The reaction was cooled to -78 °C and 1,3-dimethyl-1,3-diazinan-2-one (DMPU, 3.2 equiv.) was added. After 5 min the aldehyde or ketone (1.0 equiv.) was added dropwise and stirring was continued for 1 h. The cooling bath was removed and stirring continued for 1 h after which sat. aq. NH_4Cl was added. The aqueous phase was extracted with Et_2O, the combined organic layers washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The desired vinyl iodides were obtained after purification *via* flash column chromatography using pentane as the eluent.

(*R*,*Z*)-1-iodo-4,8-dimethylnona-1,7-diene (*Z*-1i)



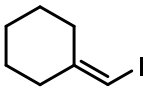
Vinyl iodide ***Z*-1i** was prepared using (+)-citronellal (1.1 mL, 6.1 mmol, 1.0 equiv.), $(PPh_3)CH_2I$ **S2** (4.1 g, 7.8 mmol, 1.3 equiv.), NaHMDS (40% in THF, 3.6 mL, 7.2 mmol, 1.2 equiv.), DMPU

[viii] A mixted fraction (0.28 g, 1.0 mmol, 25%, *E*:*Z* = 1:5) was also obtained. This approach was not further optimized (time, temperature, wattage). Photoisomerizations of vinyl boronic esters are also known (even in transition metal-free manner).[27].

(2.3 mL, 19 mmol, 3.1 equiv.) and THF (22 mL) adding sat. aq. NH_4Cl at -78 °C after 4 h. The product was isolated as colorless liquid (0.85 g, 3.1 mmol, 51%) which turned pink over time.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.26 – 6.14 (m, 2H), 5.13 – 5.05 (m, 1H), 2.19 – 2.11 (m, 1H), 2.07 – 1.95 (m, 3H), 1.70 – 1.59 (m, 7H), 1.41 – 1.30 (m, 1H), 1.29 – 1.15 (m, 1H), 0.93 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.4, 131.5, 124.7, 83.2, 41.8, 36.8, 32.3, 25.9, 25.7, 19.7, 17.9. **HRMS (ESI)**: Calculated for $C_{11}H_{19}I^{107}Ag^+$: *m*/z =384.95769 ([M+^{107}Ag]$^+$), found: 384.95815. **IR** 2961, 2911, 1608, 1454, 1377, 1303, 1269, 1109, 1079, 983, 948, 824, 741, 683, 625.

(iodomethylene)cyclohexane (1n)

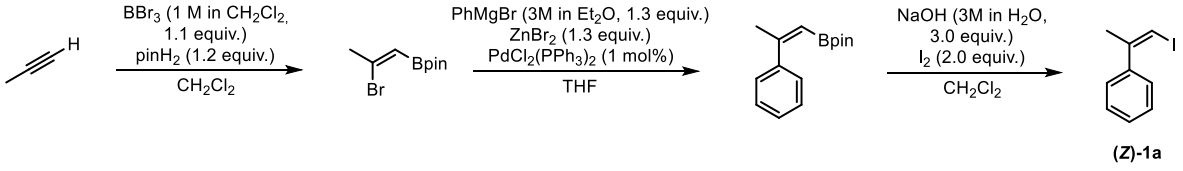


Vinyl iodide **1n** was prepared using cyclohexanone (0.83 mL, 8.0 mmol, 1.0 equiv.), $(PPh_3)CH_2I$ **S2** (5.3 g, 10 mmol, 1.3 equiv.), NaHMDS (1.0 M in THF, 10 mL, 10 mmol, 1.3 equiv.) and THF (23 mL) running the reaction without DMPU directly at room temperature for 2 h. The product was isolated as colorless liquid (0.89 g, 4.0 mmol, 50%)[ix] which turned pink over time.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79 – 5.75 (m, 1H), 2.33 – 2.23 (m, 4H), 1.62 – 1.44 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.5, 71.2, 37.4, 36.1, 28.2, 27.1, 26.2. **MS (EI)**: Calculated for $C_7H_{11}I^{\bullet+}$: *m*/z = 222.0 ([M]$^{\bullet+}$), found: 222.0. The NMR data is in accordance with that reported in the literature.[22]

3.3.2 From Alkynes

(*Z*)-(1-iodoprop-1-en-2-yl)benzene ((*Z*)-1a)

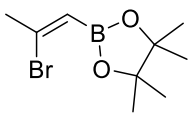


(*Z*)-1a

The synthesis of vinyl iodides (*Z*)-1a was conducted in three steps according to a literature procedure.[18]

[ix] The NMR yield could be improved to 78% running the reaction with DMPU and at -78 °C on a 0.8 mmol scale compared to 48% before.

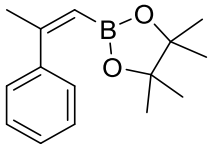
(*Z*)-2-(2-bromoprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



Methyl acetylene (2.0 mL, 35 mmol, 1.0 equiv.) was condensed into a Schlenk tube at -78°C. CH_2Cl_2 (18 mL, 2.0 M) was slowly added at -78 °C followed by BBr_3 (1M in CH_2Cl_2, 39 mL, 39 mmol, 1.1 equiv.). The reaction mixture was stirred for 1 hour at -78 °C, was then allowed to warm to room temperature and was stirred for an additional hour. In a second flask, pinacol (5.0 g, 42 mmol, 1.2 equiv.) was dissolved in CH_2Cl_2 (35 mL, 1.2 M) and cooled to 0 °C. The solution of the boronic acid bromide was added to the pinacol solution, the mixture was stirred for 1 hour at room temperature. The reaction mixture was diluted with ether, washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo and the vinyl bromide was obtained as a colorless liquid (7.5 g, 30 mmol, 87%) after purification by flash column chromatography (pentane/Et_2O = 50:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 (q, *J* = 1.2 Hz, 1H), 2.41 (d, *J* = 1.2 Hz, 3H), 1.29 (s, 12H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 139.5, 83.6, 33.0, 24.8. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (96 MHz, $CDCl_3$) δ 29.01. The analytical data are in accordance with those reported in the literature.[18]

(*Z*)-4,4,5,5-tetramethyl-2-(2-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane

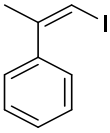


Zinc bromide (2.0 g, 9.1 mmol, 1.3 equiv.) was flame-dried in vacuo at 300 °C for 1 hour. It was then dissolved in THF (15 mL, 0.6 M) and added to phenyl magnesium bromide solution (3 M in Et_2O, 3.0 mL, 9.1 mmol, 1.3 equiv.) at 0 °C. The resulting suspension was stirred for 30 minutes at 0 °C. In a second flask, (*Z*)-2-(2-bromoprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.7 g, 7.0 mmol, 1.0 equiv.) and $PdCl_2(PPh_3)_2$ (52 mg, 0.07 mmol, 1.0 mol%) were dissolved in THF (15 mL, 0.5 M). The solution was cooled to 0 °C and the solution of the organozinc reagent was added. The reaction mixture was stirred at room temperature overnight. The reaction was quenched by addition of HCl (0.5 M), extracted with ether and the combined organic phases were washed with sat. aq. $NaHCO_3$ solution and brine. The organic phase was dried over $MgSO_4$, the solvent was removed in vacuo and the cross-coupling product was obtained as a colorless liquid (1.1 g, 4.5 mmol, 63%) after purification by flash column chromatography with pentane/Et_2O = 50:1 as the eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 5H), 5.47 (q, *J* = 1.4 Hz, 1H), 2.22 (d, *J* = 1.4 Hz, 3H), 1.15 (s, 12H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 157.8, 143.3, 127.7, 127.6, 83.1, 27.9,

24.7. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (96 MHz, $CDCl_3$) δ 30.09. The analytical data are in accordance with those reported in the literature.[18]

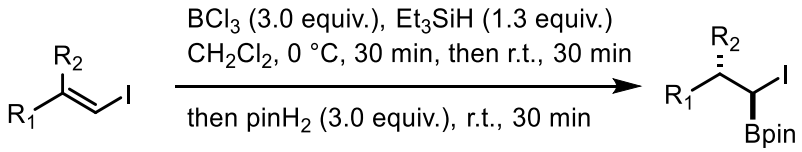
(*Z*)-(1-iodoprop-1-en-2-yl)benzene ((*Z*)-**1a**)



(*Z*)-4,4,5,5-tetramethyl-2-(2-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (0.96 g, 4.0 mmol, 1.0 equiv.) was dissolved in THF (8 mL, 0.5 M). NaOH (3 M in H_2O, 4.0 mL, 12 mmol, 3.0 equiv.) was added followed by slow addition of an iodine (2.0 g, 8.0 mmol, 2.0 equiv.) solution in THF (40 mL). The reaction mixture was stirred for 1 hour at room temperature, quenched by addition of sat. aq. $Na_2S_2O_3$ solution and extracted with ether. The combined organic phases were washed with sat. aq. $NaHCO_3$ solution and brine. The solvent was removed in vacuo and the vinyl iodide product was obtained as a slightly orange oil (0.87 g, 3.6 mmol, 89%) after purification by flash column chromatography with pentane as the eluent.

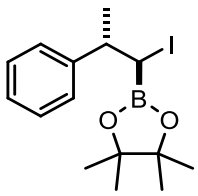
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.24 (m, 5H), 6.28 (q, *J* = 1.5 Hz, 1H), 2.22 (d, *J* = 1.5 Hz, 3H).**^{13}C NMR** (76 MHz, $CDCl_3$) δ 148.5, 143.1, 128.4, 127.8, 127.6, 75.1, 26.7. The analytical data are in accordance with those reported in the literature.[18]

4 Preparation of α-Iodo Pinacol Boronic Esters



To a cooled (0 °C) solution of BCl_3 (1.0 M in CH_2Cl_2, 0.75 mL, 0.75 mmol, 3.0 equiv.) a preformed solution of vinyl iodide (0.25 mmol, 1.0 equiv.) and triethylsilane (50 µL, 0.31 mmol, 1.3 equiv.) in CH_2Cl_2 (0.10 M) is added *via* syringe. The solution is stirred for 30 min at 0 °C and is then allowed to warm to room temperature over 30 min. Pinacol (89 mg, 0.75 mmol, 3.0 equiv.) is added at once at which point a slight gas evolution can be observed and the solution is stirred for 30 min. H_2O is added and the aqueous phase is extracted with CH_2Cl_2. The combined organic layers are dried over $MgSO_4$ and concentrated under reduced pressure. The crude product is then purified by bulb-to-bulb distillation or *via* flash column chromatography on NaOAc-deactivated silica gel.[x]

2-((1*S,2*S**)-(±)-1-iodo-2-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)**

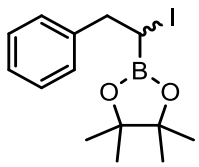


α-Iodoboronic ester **2a** was prepared using vinyl iodide **1a** (61 mg, 0.25 mmol, 1.0 equiv). The product was purified by bulb-to-bulb distillation and was obtained as a colorless crystalline solid (88 mg, 0.24 mmol, 95%).[xi]

^{1}H NMR (300 MHz, CDCl3) δ 7.32 – 7.14 (m, 5H), 3.37 (d, J = 11.6 Hz, 1H), 3.10 (dq, J = 11.6, 6.8 Hz, 1H), 1.51 (d, J = 6.8 Hz, 3H), 1.01 (s, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.8, 128.4, 127.3, 126.9, 83.7, 43.2, 24.0. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, CDCl3) δ 30.8. **HRMS (ESI)**: Calculated for $C_{15}H_{22}O_2BINa^+$: m/z = 395.06498 ($[M+Na]^+$), found: 395.06490. **IR** 3028, 2976, 2927, 1600, 1493, 1452, 1402, 1367, 1335, 1313, 1268, 1212, 1166, 1142, 1083, 1009, 967, 921, 873, 846, 824, 762, 699, 678, 642, 609, 578. **mp**: 42–44 °C.

[x] As evidenced by the yields obtained in the one-pot procedure, the hydroborations may as well be run with 1.1 equiv. BCl_3 and 1.1 equiv. pinacol with only a small loss in the obtained yields.
[xi] Isolation by column chromatography yielded 75%, 74%, 75% on normal silica and 83% on NaOAc-deactivated silica (1 mmol scale).

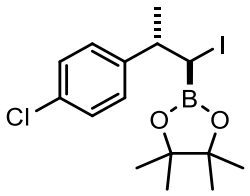
(±)-2-(1-iodo-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)



α-Iodoboronic ester **2b** was prepared using vinyl iodide **1b** (57 mg, 0.25 mmol, 1.0 equiv.). The product was purified by bulb-to-bulb distillation and obtained as a pale-yellow oil (80 mg, 0.22 mmol, 90%).[xii]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.25 – 7.20 (m, 3H), 3.40 (dd, *J* = 10.2, 7.4 Hz, 1H), 3.29 – 3.15 (m, 2H), 1.21 (s, 6H), 1.20 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.2, 128.9, 128.6, 126.9, 84.2, 41.4, 24.5, 24.3. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 31.6. **HRMS (ESI)**: Calculated for $C_{14}H_{20}O_2BINa^+$: m/z = 381.04933 ($[M+Na]^+$), found: 381.04900. The NMR data is in accordance with that reported in the literature.[30]

2-((1*S,2*S**)-(±)-2-(4-chlorophenyl)-1-iodopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)**



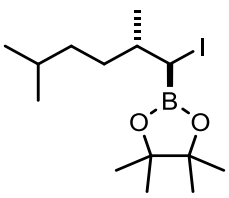
α-Iodoboronic ester **2c** was prepared on a 1.8 mmol scale under slightly different conditions: To a cooled (0 °C) solution of BCl_3 (1.0 M in CH_2Cl_2, 5.4 mL, 5.4 mmol, 3.0 equiv.) a preformed solution of vinyl iodide **1c** (0.50 g, 1.8 mmol, 1.0 equiv.) and triethylsilane (0.29 mL, 1.8 mmol, 1.0 equiv.) in dichloromethane (18 mL) was added via a syringe. The solution was stirred for 5 minutes at 0 °C and was then allowed to warm to room temperature. After an additional 30 minutes of stirring pinacol (0.64 g, 5.4 mmol, 3.0 equiv.) was added at once upon which gas evolution is observed. The solution was stirred for 30 minutes and was then washed with water. The organic phase was dried over magnesium sulfate and the solvent was removed in vacuo. The product was purified by bulb-to-bulb distillation and was obtained as a colorless solid (0.48 g, 1.2 mmol, 65%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 2H), 7.23 – 7.09 (m, 2H), 3.33 (d, *J* = 11.4 Hz, 1H), 3.09 (dq, *J* = 11.4, 6.8 Hz, 1H), 1.50 (d, *J* = 6.8 Hz, 3H), 1.07 (s, 6H), 1.06 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 142.4, 132.5, 128.7, 128.5, 83.9, 42.5, 24.1, 24.0, 23.9. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 31.0. **HRMS (ESI)**: Calculated for $C_{15}H_{21}O_2{}^{11}BI^{35}ClNa^+$: *m/z* = 429.0263 ($[M+Na]^+$), found: 429.0258. **IR**

[xii] The reaction was repeated in gram-scale using vinyl iodide **1b** (1.4 g, 6.0 mmol, 1.0 equiv.), BCl_3 (1.0 M in CH_2Cl_2, 18 mL, 18 mmol, 3.0 equiv.), triethylsilane (1.2 mL, 7.5 mmol, 1.3 equiv.), pinacol (2.1 g, 18 mmol, 3.0 equiv.) and CH_2Cl_2 (60 mL) yielding 1.73 g (4.8 mmol, 81%) of product **2b**.

2975, 1592, 1491, 1478, 1402, 1369, 1336, 1265, 1213, 1165, 1141, 1093, 1082, 1012, 966, 923, 873, 845, 830, 782, 738, 704, 677, 649, 564. **mp:** 106–108 °C.

2-((1*S,2*S**)-(±)-1-iodo-2,5-dimethylhexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)**

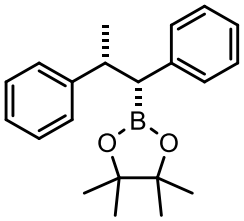


α-Iodoboronic ester **2d** was prepared under slightly different conditions: Vinyl iodide **1m** (60 mg, 0.25 mmol, 1.0 equiv) and the unoptimized amount of triethylsilane (40 µL, 0.25 mmol, 1.0 equiv.) were used. The product was purified *via* flash column chromatography and obtained as a pale pink oil (56 mg, 0.15 mmol, 60%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.18 (d, *J* = 8.2 Hz, 1H), 1.54 – 1.45 (m, 2H), 1.45 – 1.37 (m, 1H), 1.27 (s, 6H), 1.27 (s, 6H), 1.22 – 1.13 (m, 3H), 1.06 (d, *J* = 6.4 Hz, 3H), 0.88 (d, *J* = 1.9 Hz, 3H), 0.86 (d, *J* = 1.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 84.0, 36.7, 35.9, 34.2, 28.2, 24.6, 24.4, 22.9, 22.6, 21.4. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 31.5. **HRMS (ESI)**: Calculated for $C_{14}H_{28}O_2{}^{11}BINa^+$: *m/z* = 389.11192 ($[M+Na]^+$), found: 389.11182. **IR** 2955, 2927, 2871, 1467, 1371, 1334, 1214, 1144, 1076, 970, 887, 849, 678.

5 Coupling Reactions with Organometallics

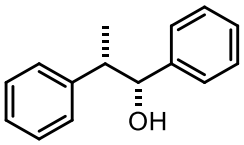
2-((1*R**,2*R**)-1,2-diphenylpropyl)-(±)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ba)



Boronic ester **3ba** was prepared according to **GP1** using phenylmagnesium bromide (3 M in Et_2O, 0.13 mL, 0.4 mmol, 2 equiv.) in DMS. The product was isolated *via* bulb-to-bulb distillation as a colorless crystalline solid (70 mg, 0.22 mmol, 87%).[xiii]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 – 6.96 (m, 10H), 3.33 – 3.25 (m, 1H), 2.61 (d, *J* = 11.2 Hz, 1H), 1.41 (d, *J* = 6.9 Hz, 3H), 1.25 (s, 6H), 1.22 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.6, 141.3, 129.2, 128.0, 127.4, 125.7, 125.2, 83.6, 42.8, 41.2, 24.7, 22.9. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 33.6. **HRMS (ESI)**: Calculated for $C_{21}H_{27}O_2{}^{11}BNa^+$: *m/z* = 345.19963 ($[M+Na]^+$), found: 345.19955. **IR** 3026, 2977, 1602, 1493, 1451, 1371, 1358, 1318, 1269, 1214, 1165, 1140, 1108, 1071, 1032, 1010, 969, 888, 850, 769, 698, 598, 555, 539. **mp**: 62–64 °C.

(1*R**,2*S**)-(±)-1,2-diphenylpropan-1-ol (4ba)



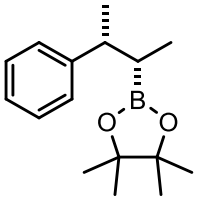
Alcohol **4ba** was prepared according to **GP1** with appended oxidation using isolated α-iodoboronic ester **2a** (74 mg, 0.20 mmol, 1.0 equiv.) and phenyllithium (1.9 M in $^nBu_2O$, 0.11 mL, 0.21 mmol, 1.0 equiv.) in DMS overnight. Instead of the aqueous work-up, the reaction mixture was concentrated *in vacuo* and the crude reaction mixture suspended in CH_2Cl_2 and hexanes. The suspension was filtered through a short plug of filter aid to remove the insoluble residue. The solution was concentrated *in vacuo* and the appended oxidation was run as usual. The product was isolated as a colorless oil (38 mg, 0.18 mmol, 90%, (86% over two steps)).[xiv] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.14 (m, 10H), 4.84 (dd, *J* = 5.7, 3.3 Hz, 1H), 3.19 – 3.09 (m, 1H), 1.89 (d, *J* = 3.3 Hz, 1H), 1.34 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 143.0, 128.4, 128.2, 128.1, 127.4, 126.6, 126.4, 78.9, 47.4, 15.0. **HRMS (ESI)**: Calculated for $C_{15}H_{16}ONa^+$: *m/z* =

[xiii] The reaction was run again with a matching yield (87%). The reaction was also run according to **GP1** using vinyl iodide **1a** (61 mg, 0.25 mmol) and PhMgBr (3 M in Et_2O, 0.13 mL, 0.4 mmol, 2 equiv.) in Et_2O for 2 h giving product **3ba** (65 mg, 0.20 mmol, 81%, NaOAc silica purification) and as a stepwise protocol (**2a**, 76 mg, 0.20 mmol) with PhMgBr (3 M in Et_2O, 0.07 mL, 0.2 mmol, 1 equiv.) in DMS overnight giving product **3ba** (62 mg, 0.19 mmol, 94%, 89% over two steps).

[xiv] The reaction was also run according to **GP1** with appended oxidation using vinyl iodide **1a** (61 mg, 0.25 mmol), BCl_3 (1.0 M in CH_2Cl_2, 0.25 mL, 0.25 mmol, 1.0 equiv.), Et_3SiH (40 µL, 0.25 mmol, 1.0 equiv.), $pinH_2$ (30 mg, 0.25 mmol, 1.0 equiv.) and PhLi (1.9 M in $^nBu_2O$, 0.13 mL, 0.25 mmol, 1.0 equiv.) in DMS (2.5 mL) overnight to give alcohol **4ba** (44 mg, 0.21 mmol, 84%).

235.10934 ([M+Na]$^+$), found: 235.10933. The NMR data is in accordance with that reported in the literature.[31]

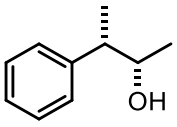
4,4,5,5-tetramethyl-2-((2*S,3*R**)-(±)-3-phenylbutan-2-yl)-1,2-oxaborolane (3aa)**



Boronic ester **3aa** was prepared according to **GP1** using methylmagnesium bromide (3.0 M in Et_2O, 0.13 mL, 0.39 mmol, 1.6 equiv.) in Et_2O for 2 h. The product was isolated *via* flash column chromatography as a pale pink oil (49 mg, 0.19 mmol, 76%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.19 – 7.14 (m, 3H), 2.71 (dq, *J* = 10.6, 7.0 Hz, 1H), 1.30–1.24 (m, 16H), 0.75 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.5, 128.3, 127.4, 125.9, 83.2, 42.9, 25.0, 24.8, 23.0, 14.5. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 34.4. **HRMS (ESI)**: Calculated for $C_{16}H_{25}O_2{}^{11}BNa^+$: *m/z* = 283.18398 ([M+Na]$^+$), found: 283.18404. The NMR data is in accordance with that reported in the literature.[32]

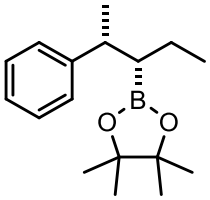
(2*S,3*S**)-(±)-3-phenylbutan-2-ol (4aa)**



Alcohol **4aa** was prepared according to **GP1** with appended oxidation using methylmagnesium bromide (3.0 M in Et_2O, 0.13 mL, 0.39 mmol, 1.6 equiv.) in Et_2O. The product was isolated *via* flash column chromatography as a pale-yellow oil (27 mg, 0.18 mmol, 72%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.25 – 7.19 (m, 3H), 3.92 – 3.85 (m, 1H), 2.78 – 2.71 (m, 1H), 1.46 (s, 1H), 1.34 (d, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.4, 128.6, 128.0, 126.6, 72.5, 47.3, 21.2, 16.1. **HRMS (ESI)**: Calculated for $C_{10}H_{13}O^-$: *m/z* = 149.09719 ([M-H]$^-$), found: 149.09714. The NMR data is in accordance with that reported in the literature.[33]

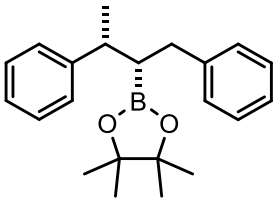
4,4,5,5-tetramethyl-2-((2*R,3*S**)-(±)-2-phenylpentan-3-yl)-1,3,2-dioxaborolane (3ab)**



Boronic ester **3ab** was prepared according to **GP1** using ethylmagnesium bromide (3 M in Et_2O, 0.13 mL, 0.4 mmol, 2 equiv.) in Et_2O. The product was isolated *via* flash column chromatography as a colorless oil (48 mg, 0.18 mmol, 71%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.23 – 7.18 (m, 3H), 2.80 (dq, *J* = 10.2, 6.9 Hz, 1H), 1.33 (s, 12H), 1.28 (d, *J* = 6.9 Hz, 3H), 1.27 – 1.16 (m, 3H), 0.84 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.9, 128.3, 127.4, 125.8, 83.2, 41.6, 34.1, 25.1, 25.1, 23.3, 23.1, 13.7. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 34.3. **HRMS (ESI)**: Calculated for $C_{17}H_{27}O_2{}^{11}BNa^+$: *m/z* = 297.19963 ($[M+Na]^+$), found: 297.19948. **IR** 3026, 2977, 2926, 1603, 1493, 1453, 1376, 1321, 1253, 1212, 1143, 1109, 1063, 970, 861, 837, 764, 744, 699, 587, 557, 522.

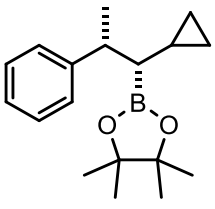
2-((2*S,3*R**)-(±)-1,3-diphenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ac)**



Boronic ester **3ac** was prepared according to **GP1** using freshly prepared benzylmagnesium bromide (0.8 M in Et_2O, 1.3 mL, 1 mmol, 4 equiv.) in Et_2O (5 mL) without stirring[xv] while warming up to room temperature over 2 h. The product was isolated *via* flash column chromatography as a colorless crystalline solid (73 mg, 0.22 mmol, 88%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.29 – 7.25 (m, 2H), 7.22 – 7.17 (m, 3H), 7.15 – 7.08 (m, 3H), 2.84 (dq, *J* = 10.7, 7.0 Hz, 1H), 2.53 – 2.42 (m, 2H), 1.73 (td, *J* = 10.7, 5.9 Hz, 1H), 1.32 (d, *J* = 7.0 Hz, 3H), 1.13 (s, 6H), 1.05 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.5, 142.1, 128.9, 128.5, 128.1, 127.3, 126.1, 125.7, 83.2, 42.3, 36.8, 34.2, 25.1, 24.8, 22.8. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 33.9. **HRMS (ESI)**: Calculated for $C_{22}H_{29}O_2{}^{11}BNa^+$: *m/z* = 359.21528 ($[M+Na]^+$), found: 359.21503. **IR** 3061, 3026, 2977, 2926, 1747, 1648, 1603, 1542, 1493, 1453, 1407, 1376, 1321, 1253, 1212, 1143, 1109, 1063, 1030, 1006, 970, 906, 861, 837, 764, 744, 699, 681, 587, 557, 522. **mp**: 53–55 °C.

2-((1*S,2*R**)-(±)-1-cyclopropyl-2-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ad)**

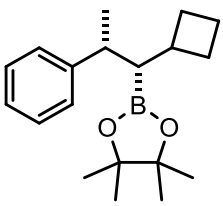


Boronic ester **3ad** was prepared according to **GP1** using freshly prepared cyclopropylmagnesium bromide (0.7 M in Et_2O, 0.71 mL, 0.5 mmol, 2 equiv.) in Et_2O for 2 h. The product was isolated *via* flash column chromatography as a pale-yellow oil (49 mg, 0.17 mmol, 69%).

[xv] When stirring the reaction during warm-up some epimerization product was observed. Using BnLi works but a bad diastereoselectivity was observed and the reaction is overall a bit messier (GC analysis).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.22 – 7.18 (m, 2H), 7.18 – 7.13 (m, 1H), 2.92 (dq, *J* = 10.1, 7.0 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 3H), 1.27 (s, 6H), 1.27 (s, 6H), 0.78 – 0.71 (m, 1H), 0.56 – 0.48 (m, 1H), 0.27 – 0.20 (m, 1H), 0.14 – 0.08 (m, 1H), 0.05 – -0.01 (m, 1H), -0.32 – -0.39 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.0, 128.1, 127.6, 125.8, 83.2, 42.3, 37.4, 25.0, 24.9, 21.9, 11.7, 6.2, 2.6. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 33.8. **HRMS (ESI)**: Calculated for $C_{18}H_{27}O_2{}^{11}BNa^+$: *m/z* = 309.19996 ($[M+Na]^+$), found: 309.19947. **IR** 3076, 3026, 2977, 2929, 2871, 1603, 1494, 1453, 1369, 1343, 1314, 1271, 1213, 1165, 1142, 1107, 1076, 1042, 1014, 970, 892, 874, 850, 818, 761, 699, 667, 567, 537, 511.

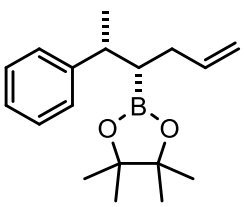
2-((1*S,2*R**)-(±)-1-cyclobutyl-2-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ae)**



Boronic ester **3ae** was prepared according to **GP1** using cyclobutylmagnesium bromide from bromocyclobutane (47 µL, 0.50 mmol, 2.0 equiv.) in Et_2O. The product was isolated *via* flash column chromatography as a colorless crystalline solid (51 mg, 0.17 mmol, 68%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 7.20 – 7.17 (m, 2H), 7.16 – 7.12 (m, 1H), 2.74 (dq, *J* = 9.9, 7.0 Hz, 1H), 2.27 – 2.18 (m, 1H), 1.92 – 1.85 (m, 1H), 1.75 – 1.67 (m, 1H), 1.67 – 1.60 (m, 1H), 1.60 – 1.53 (m, 1H), 1.43 – 1.29 (m, 3H), 1.27 (s, 6H), 1.27 (s, 6H), 1.23 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.0, 128.2, 127.4, 125.8, 83.2, 40.9, 40.2, 37.5, 30.7, 28.2, 25.1, 25.1, 22.0, 18.8. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 33.5. **HRMS (ESI)**: Calculated for $C_{19}H_{29}O_2{}^{11}BNa^+$: *m/z* = 323.21528 ($[M+Na]^+$), found: 323.21497. **IR** 2974, 2866, 1603, 1494, 1452, 1370, 1312, 1268, 1213, 1165, 1142, 1110, 1083, 1008, 969, 908, 849, 762, 699, 627, 562, 537. **mp**: slightly above room temperature.

4,4,5,5-tetramethyl-2-((2*R,3*S**)-(±)-2-phenylhex-5-en-3-yl)-1,3,2-dioxaborolane (3af)**

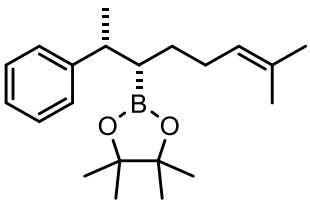


Boronic ester **3af** was prepared according to **GP1** using allylmagnesium bromide (0.7 M in Et_2O, 0.54 mL, 0.4 mmol, 2 equiv.) in Et_2O. The product was isolated *via* flash column chromatography as a colorless crystalline solid (59 mg, 0.20 mmol, 82%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.19 – 7.14 (m, 3H), 5.76 – 5.66 (m, 1H), 4.95 – 4.84 (m, 2H), 2.76 (dq, *J* = 10.7, 7.0 Hz, 1H), 2.00 – 1.85 (m, 2H), 1.38 (td, *J* = 10.7, 4.7

Hz, 1H), 1.29 – 1.24 (m, 15H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.4, 138.3, 128.4, 127.4, 126.0, 115.0, 83.4, 41.5, 34.8, 31.7, 25.2, 25.1, 22.9. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 34.4. **HRMS (ESI)**: Calculated for $C_{18}H_{27}O_2{}^{11}BNa^+$: *m/z* = 309.19963 ($[M+Na]^+$), found: 309.19936. The NMR data is in accordance with that reported in the literature.[34]

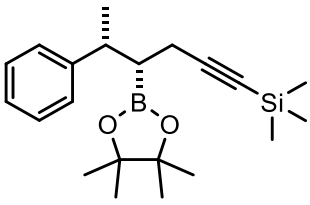
4,4,5,5-tetramethyl-2-((2*R,3*S**)-(±)-7-methyl-2-phenyloct-6-en-3-yl)-1,3,2-dioxaborolane (3ag)**



Boronic ester **3ag** was prepared according to **GP1** using (4-methylpent-3-en-1-yl)magnesium bromide from 5-bromo-2-methylpent-2-ene (0.14 mL, 1.0 mmol, 4.0 equiv.) and magnesium turnings (18 mg, 0.74 mmol, 3.0 equiv.) in Et_2O. The product was isolated *via* flash column chromatography as a pale-yellow oil (72 mg, 0.22 mmol, 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 7.17 – 7.11 (m, 3H), 4.97 – 4.92 (m, 1H), 2.75 (dq, *J* = 10.1, 6.9 Hz, 1H), 1.97 – 1.87 (m, 1H), 1.82 – 1.71 (m, 1H), 1.61 – 1.58 (m, 3H), 1.51 – 1.48 (m, 3H), 1.31 – 1.20 (m, 17H), 1.17 – 1.07 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.8, 131.2, 128.3, 127.4, 125.8, 124.9, 83.2, 41.7, 32.0, 30.5, 28.0, 25.8, 25.2, 25.1, 23.1, 17.7. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 34.7. **HRMS (ESI)**: Calculated for $C_{21}H_{33}O_2{}^{11}BNa^+$: *m/z* = 351.24658 ($[M+Na]^+$), found: 351.24653. **IR** 2977, 2925, 1602, 1493, 1451, 1372, 1314, 1264, 1241, 1212, 1142, 1109, 1007, 966, 905, 848, 763, 699, 567, 527.

trimethyl((4*S,5*R**)-(±)-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-yn-1-yl)silane (3ah)**

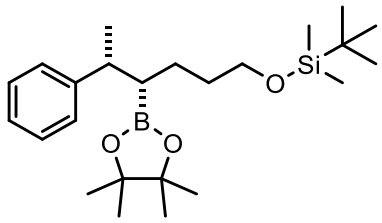


Boronic ester **3ah** was prepared according to **GP1** using (3-(trimethylsilyl)prop-2-yn-1-yl)magnesium bromide in Et_2O for 2 h. The Grignard reagent was prepared from (3-bromoprop-1-yn-1-yl)trimethylsilane (82 µL, 0.50 mmol, 2.0 equiv.). The product was isolated *via* flash column chromatography as a colorless crystalline solid (84 mg, 0.24 mmol, 94%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.19 – 7.14 (m, 3H), 2.78 (dq, *J* = 11.0, 7.0 Hz, 1H), 2.08 – 1.98 (m, 2H), 1.51 – 1.43 (m, 1H), 1.32 (s, 12H), 1.28 (d, *J* = 7.0 Hz, 3H), 0.11 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.6, 128.5, 127.3, 126.2, 107.2, 84.7, 83.6, 41.2,

31.9, 25.1, 25.0, 22.5, 20.8, 0.3. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 34.0. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -19.6. **HRMS (ESI)**: Calculated for $C_{21}H_{33}O_2{}^{11}BSiNa^+$: *m/z* = 379.22351 ($[M+Na]^+$), found: 379.22336. **IR** 2978, 2961, 2928, 2173, 1453, 1379, 1327, 1249, 1214, 1144, 1045, 1011, 970, 842, 762, 701, 639, 577. **mp**: 41–43 °C.

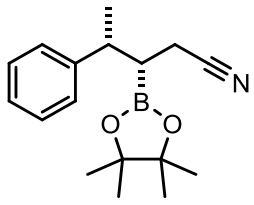
tert-butyldimethyl(((4*S,5*R**)-(±)-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)silane (3ai)**



Boronic ester **3ai** was prepared according to **GP1** in Et_2O. The Grignard reagent was generated from (3-bromopropoxy)(*tert*-butyl)dimethylsilane (0.27 mL, 1.2 mmol, 4.7 equiv.) and magnesium turnings (18 mg, 0.74 mmol, 3.0 equiv.) in THF[xvi] (1.0 mL). After addition of H_2O instead of HCl and applying the otherwise unchanged work-up, the product was isolated *via* flash column chromatography as a pale-yellow oil (29 mg, 69 µmol, 28%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.17 – 7.13 (m, 3H), 3.47 – 3.40 (m, 2H), 2.75 (dq, *J* = 10.4, 6.9 Hz, 1H), 1.52 – 1.44 (m, 1H), 1.39 – 1.30 (m, 2H), 1.28 (s, 6H), 1.28 (s, 6H), 1.24 (d, *J* = 6.9 Hz, 3H), 1.22 – 1.11 (m, 2H), 0.82 (s, 9H), -0.05 (d, *J* = 4.6 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.7, 128.4, 127.4, 125.9, 83.3, 63.5, 41.8, 32.6, 31.9, 26.5, 26.1, 25.2, 25.1, 23.0, 18.4, -5.2, -5.2. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 34.4. **^{29}Si NMR** (119 MHz, $CDCl_3$) δ 18.0. **HRMS (ESI)**: Calculated for $C_{24}H_{43}O_3{}^{11}BSiNa^+$: *m/z* = 441.29667 ($[M+Na]^+$), found: 441.29658. **IR** 2955, 2928, 2857, 1494, 1461, 1379, 1318, 1254, 1211, 1144, 1097, 1007, 969, 835, 774, 700, 567.

(3*S,4*R**)-(±)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanenitrile (3aj)**



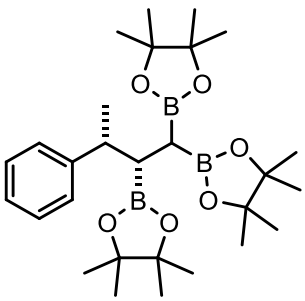
Boronic ester **3aj** was prepared according to **GP1** in THF overnight.[xvii] The lithium reagent was generated according to a modified literature procedure:[35] lithium diisopropylamide (LDA) was formed from diisopropylamine (72 µL, 0.51 mmol, 2.1 equiv.) and ^{n}BuLi (1.6 M in hexanes, 0.27 mL, 0.43 mmol, 1.7 equiv.) in THF (1.0 mL) at -78 °C. After 5 min, acetonitrile

[xvi] No product formation was observed when running the reaction in Et_2O.
[xvii] GC indicated almost complete conversion of the intermediate after 1 h.

(25 µL, 0.48 mmol, 1.9 equiv.) was added and stirring continued for 1 h. The product was isolated *via* flash column chromatography as a colorless oil (32 mg, 0.11 mmol, 45%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.24 – 7.16 (m, 3H), 2.84 (dq, *J* = 10.8, 6.9 Hz, 1H), 2.11 (s, 1H), 2.09 (d, *J* = 2.4 Hz, 1H), 1.60 – 1.53 (m, 1H), 1.34 – 1.30 (m, 15H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.2, 128.9, 127.2, 126.8, 119.7, 84.3, 40.9, 28.7, 25.0, 24.9, 22.2, 17.8. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 33.2. **HRMS (ESI)**: Calculated for $C_{17}H_{24}O_2N^{11}BNa^+$: *m/z* = 308.17923 ($[M+Na]^+$), found: 308.17858. **IR** 3028, 2978, 2930, 2245, 1603, 1494, 1453, 1372, 1333, 1253, 1215, 1167, 1140, 1110, 1086, 1007, 970, 914, 858, 848, 833, 765, 701, 672, 564, 527.

2,2',2''-((2*S,3*R**)-(±)-3-phenylbutane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3ak)**

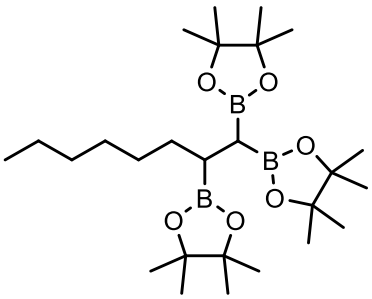


Boronic ester **3ak** was prepared according to **GP1** in THF. The lithium reagent was generated as follows: lithium tetramethylpiperidide (LTMP) was formed by addition of ^{n}BuLi (1.6 M in hexanes, 0.41 mL, 0.66 mmol, 2.6 equiv.) to 2,2,6,6-tetramethylpiperidine (0.13 mL, 0.77 mmol, 3.1 equiv.) in THF (2.5 mL) at 0 °C. The mixture was stirred allowed to warm to room temperature over 1 h before cooling to 0 °C, adding $(Bpin)_2CH_2$ (0.20 g, 0.75 mmol, 3.0 equiv.) at once and stirring for 5 min. The product was isolated *via* flash column chromatography on NaOAc-deactivated silica followed by bulb-to-bulb distillation as a colorless crystalline solid (44 mg, 86 µmol, 34%).[xviii]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 4H), 7.12 – 7.07 (m, 1H), 3.04 – 2.96 (m, 1H), 1.63 – 1.57 (m, 1H), 1.29 (d, *J* = 7.1 Hz, 3H), 1.23 – 1.18 (m, 36H), 0.72 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.1, 128.0, 127.8, 125.5, 82.8, 82.8, 41.9, 28.4, 25.3, 25.1, 25.1, 25.0, 24.9, 24.7, 19.9, 10.8. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 34.2. **HRMS (ESI)**: Calculated for $C_{28}H_{47}O_6{}^{11}B_3Na^+$: *m/z* = 535.35440 ($[M+Na]^+$), found: 535.35413. **IR** 2977, 2929, 1453, 1369, 1349, 1316, 1266, 1213, 1140, 970, 849, 763, 700, 671. **mp**: 80–82 °C.

[xviii] The reaction does not work in DMS.

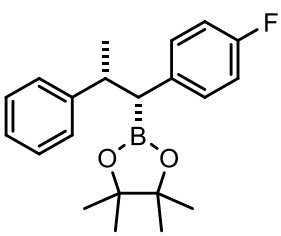
(±)-2,2',2''-(octane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3ak')



Boronic ester **3ak'** was prepared according to **GP1** using vinyl iodide **1h** (55 mg, 0.25 mmol, 1.0 equiv.) in THF. The lithium reagent was generated as follows: lithium tetramethylpiperidide (LTMP) was formed by addition of ^{n}BuLi (1.6 M in hexanes, 0.41 mL, 0.66 mmol, 2.6 equiv.) to 2,2,6,6-tetramethylpiperidine (0.13 mL, 0.77 mmol, 3.1 equiv.) in THF (1.5 mL) at 0 °C. The mixture was stirred at room temperature for 30 min before cooling to 0 °C, adding $(Bpin)_2CH_2$ (0.20 g, 0.76 mmol, 3.1 equiv.) at once and stirring for 5 min. The product was isolated *via* flash column chromatography on NaOAc-deactivated silica followed by bulb-to-bulb distillation as a colorless crystalline solid (0.11 g, 0.22 mmol, 90%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 1.44 – 1.36 (m, 2H), 1.36 – 1.29 (m, 2H), 1.29 – 1.14 (m, 43H), 0.87 – 0.82 (m, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 82.8, 82.8, 82.7, 33.5, 31.9, 29.8, 28.7, 25.2, 25.0, 25.0, 24.8, 24.8, 22.7, 20.0, 14.2, 11.7. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 34.0. **HRMS (ESI)**: Calculated for $C_{26}H_{51}O_6{}^{11}B_3Na^+$: *m/z* = 515.38570 ($[M+Na]^+$), found: 515.38451. The NMR data is in accordance with that reported in the literature.[36]

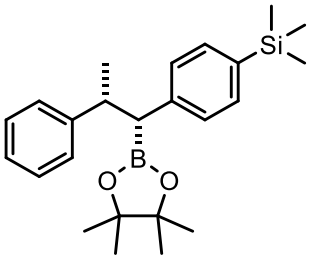
2-((1*R,2*R**)-(±)-1-(4-fluorophenyl)-2-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3bb)**



Boronic ester **3bb** was prepared according to **GP1** using (4-fluorophenyl)magnesium bromide from 1-bromo-4-fluorobenzene (55 µL, 0.50 mmol, 2.0 equiv.) in Et_2O for 2 h. The product was isolated *via* flash column chromatography using NaOAc-deactivated silica as a colorless crystalline solid (69 mg, 0.20 mmol, 82%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 2H), 7.05 – 7.01 (m, 1H), 7.01 – 6.96 (m, 4H), 6.79 – 6.73 (m, 2H), 3.22 (dq, *J* = 11.3, 6.9 Hz, 1H), 2.57 (d, *J* = 11.3 Hz, 1H), 1.39 (d, *J* = 6.9 Hz, 3H), 1.24 (s, 6H), 1.22 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.9 (d, *J* = 242.5 Hz), 146.4, 137.0 (d, *J* = 3.1 Hz), 130.4 (d, *J* = 7.7 Hz), 128.1, 127.4, 125.8, 114.7 (d, *J* = 21.0 Hz, 83.7, 43.0, 40.4, 24.7, 22.9. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 33.6. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -118.6. **HRMS (ESI)**: Calculated for $C_{21}H_{26}O_2{}^{11}BFNa^+$: *m/z* = 363.19021 ($[M+Na]^+$), found: 363.18989. **IR** 3028, 2977, 2929, 1602, 1505, 1452, 1417, 1371, 1358, 1321, 1269, 1219, 1139, 1108, 1085, 1011, 968, 888, 850, 830, 762, 731, 699, 664. **mp**: 45–47 °C.

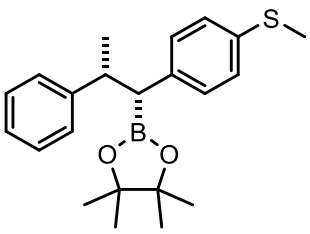
trimethyl(4-((1*R,2*R**)-(±)-2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)silane (3bc)**



Boronic ester **3bc** was prepared according to **GP1** using (4-(trimethylsilyl)phenyl)magnesium bromide from (4-bromophenyl)trimethylsilane (0.15 mL, 0.77 mmol, 3.1 equiv.) in Et_2O. The product was isolated *via* flash column chromatography using NaOAc-deactivated silica as a colorless crystalline solid (79 mg, 0.20 mmol, 80%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.25 – 7.22 (m, 2H), 7.14 – 7.10 (m, 2H), 7.07 – 7.02 (m, 5H), 3.28 (dq, *J* = 10.9, 6.9 Hz, 1H), 2.63 (d, *J* = 10.9 Hz, 1H), 1.40 (d, *J* = 6.9 Hz, 3H), 1.24 (s, 6H), 1.22 (s, 6H), 0.19 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.7, 141.9, 136.3, 133.1, 128.6, 128.0, 127.4, 125.7, 83.5, 42.7, 41.0, 24.8, 24.8, 22.7, -0.9. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.3. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -4.8. **HRMS (ESI)**: Calculated for $C_{24}H_{35}O_2{}^{11}BSiNa^+$: *m/z* = 417.23916 ($[M+Na]^+$), found: 417.23908. **IR** 2977, 2957, 1598, 1494, 1452, 1358, 1319, 1262, 1248, 1214, 1141, 1109, 1010, 969, 849, 836, 819, 760, 730, 698, 641, 564, 540, 524. **mp**: 79–81 °C.

4,4,5,5-tetramethyl-2-((1*R,2*R**)-(±)-1-(4-(methylthio)phenyl)-2-phenylpropyl)-1,3,2-dioxaborolane (3bd)**

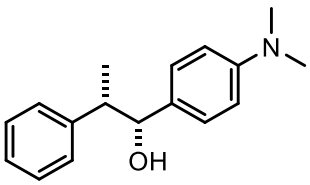


Boronic ester **3bd** was prepared according to **GP1** using (4-(methylthio)phenyl)magnesium bromide from 4-bromothioanisole (158 mg, 0.78 mmol, 3.1 equiv.) in Et_2O. The product was isolated *via* flash column chromatography using NaOAc-deactivated silica as a colorless crystalline solid (67 mg, 0.18 mmol, 73%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 2H), 7.05 – 7.00 (m, 3H), 7.00 – 6.95 (m, 4H), 3.24 (dq, *J* = 11.2, 6.9 Hz, 1H), 2.57 (d, *J* = 11.2 Hz, 1H), 2.38 (s, 3H), 1.38 (d, *J* = 6.9 Hz, 3H), 1.23 (s, 6H), 1.21 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.5, 138.5, 134.3, 129.7, 128.0, 127.4, 126.7, 125.7, 83.6, 42.7, 40.6, 24.8, 23.0, 16.2. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.6. **HRMS (ESI)**: Calculated for $C_{22}H_{29}O_2{}^{11}BSNa^+$: *m/z* = 391.18735 ($[M+Na]^+$), found:

391.18725. **IR** 3022, 2968, 2923, 2867, 1599, 1492, 1449, 1323, 1267, 1211, 1166, 1137, 1092, 1012, 969, 892, 850, 818, 760, 735, 695, 634, 565, 536, 523. **mp**: 118–120 °C.

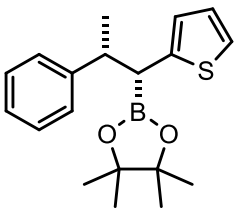
(1*R,2*S**)-(±)-1-(4-(dimethylamino)phenyl)-2-phenylpropan-1-ol (4be)**



Alcohol **4be** was prepared according to **GP1** with appended oxidation[xix] using (4-(dimethylamino)phenyl)lithium from 4-bromo-*N*,*N*-dimethylaniline (76 mg, 0.38 mmol, 1.5 equiv.) in DMS. The product was isolated *via* flash column chromatography as a pale-yellow oil (41 mg, 0.16 mmol, 64%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 7.10 – 7.06 (m, 2H), 6.67 – 6.63 (m, 2H), 4.75 (d, *J* = 6.1 Hz, 1H), 3.15 – 3.09 (m, 1H), 2.93 (s, 6H), 1.82 (s, 1H), 1.35 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.0, 144.1, 131.1, 128.3, 128.2, 127.3, 126.3, 112.3, 78.7, 47.3, 40.8, 15.7. **HRMS (ESI)**: Calculated for $C_{17}H_{21}ONNa$: *m/z* = 278.15153 ($[M+Na]^+$), found: 278.15167. **IR** 3402, 3026, 2961, 2801, 1656, 1609, 1519, 1494, 1444, 1350, 1191, 1165, 1130, 1063, 1026, 947, 909, 872, 814, 763, 699.

4,4,5,5-tetramethyl-2-((1*R,2*R**)-(±)-2-phenyl-1-(thiophen-2-yl)propyl)-1,3,2-dioxaborolane (3bf)**



Boronic ester **3bf** was prepared according to **GP1** using thiophen-2-yllithium in Et_2O. The lithium reagent was generated as follows: to thiophene (30 µL, 0.38 mmol, 1.5 equiv.) in Et_2O (0.5 mL) was added ^{n}BuLi (1.6 M in hexanes, 0.20 mL, 0.32 mmol, 1.3 equiv.) dropwise at -78 °C. After stirring for 15 min the mixture was allowed to warm to room temperature and stirred for 1 h. The product was isolated *via* flash column chromatography using NaOAc-deactivated silica as a pale-yellow crystalline solid (49 mg, 0.15 mmol, 60%).[xx]

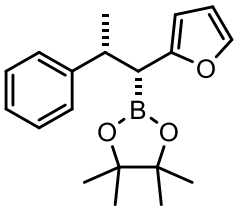
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.15 (m, 2H), 7.12 – 7.07 (m, 3H), 6.93 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.74 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.62 – 6.59 (m, 1H), 3.20 (dq, *J* = 10.8, 6.9 Hz, 1H), 2.90 (d, *J* = 10.8 Hz, 1H), 1.39 (d, *J* = 6.9 Hz, 3H), 1.27 (s, 6H), 1.25 (s, 6H). **^{13}C NMR** (126

[xix] The parent boronic ester quickly decomposed after purification (45% yield, characterized by ^{1}H NMR and HRMS).

[xx] Using a too large excess of the lithium reagent will decompose the desired product forming 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane which may be removed by bulb-to-bulb distillation. No product formation is observed in DMS.

MHz, $CDCl_3$) δ 146.4, 144.1, 128.1, 127.4, 126.5, 126.0, 125.0, 123.0, 83.9, 44.1, 35.4, 24.8, 24.8, 22.3. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.7. **HRMS (ESI)**: Calculated for $C_{19}H_{25}O_2{}^{11}BSNa^+$: *m/z* = 351.15605 ([M+Na]$^+$), found: 351.15581. **IR** 2978, 1452, 1371, 1327, 1272, 1213, 1142, 968, 849, 763, 699. **mp**: 77–79 °C.

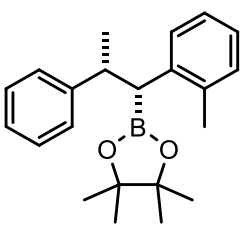
2-((1*R,2*R**)-(±)-1-(furan-2-yl)-2-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3bg)**



Boronic ester **3bg** was prepared according to **GP1** using furan-2-yllithium in Et_2O. The lithium reagent was generated as follows: to furan (27 µL, 0.37 mmol, 1.5 equiv.) in Et_2O (0.5 mL) was added ^{n}BuLi (1.6 M in hexanes, 0.20 mL, 0.32 mmol, 1.3 equiv.) dropwise at -78 °C. After stirring for 1 h the mixture was allowed to warm to room temperature and stirred for 30 min. The product was isolated *via* flash column chromatography using NaOAc-deactivated silica as a pale-yellow oil (43 mg, 0.14 mmol, 56%) containing a mixture of diastereomers (d.r. = 17:1).

^{1}H NMR (599 MHz, $CDCl_3$) **major diastereomer**: δ 7.22 – 7.17 (m, 3H), 7.14 – 7.09 (m, 3H), 6.13 – 6.10 (m, 1H), 5.79 – 5.76 (m, 1H), 3.30 (dq, *J* = 10.1, 7.0 Hz, 1H), 2.77 (d, *J* = 10.1 Hz, 1H), 1.36 (d, *J* = 7.0 Hz, 3H), 1.26 (s, 6H), 1.25 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) **major diastereomer**: δ 155.1, 146.6, 140.7, 128.1, 127.2, 126.0, 110.1, 106.3, 83.8, 41.1, 33.8, 24.8, 24.8, 21.6. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 32.5. **HRMS (ESI)**: Calculated for $C_{19}H_{25}O_3{}^{11}BNa^+$: *m/z* = 335.17890 ([M+Na]$^+$), found: 335.17893. **IR** 3385, 3062, 2977, 2931, 1604, 1474, 1453, 1372, 1329, 1272, 1215, 1142, 1075, 1009, 982, 968, 849, 762, 733, 699, 673.

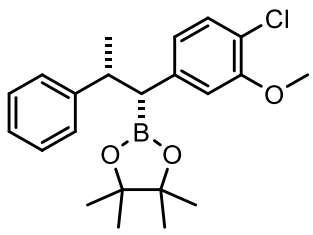
4,4,5,5-tetramethyl-2-((1*R,2*R**)-(±)-2-phenyl-1-(*o*-tolyl)propyl)-1,3,2-dioxaborolane (3bh)**



Boronic ester **3bh** was prepared according to **GP1** using *o*-tolyllithium from 2-bromotoluene (45 µL, 0.37 mmol, 1.5 equiv.) in DMS. The product was isolated *via* flash column chromatography using NaOAc-deactivated silica as a colorless crystalline solid (78 mg, 0.23 mmol, 92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 1H), 7.12 – 7.07 (m, 2H), 7.06 – 7.00 (m, 4H), 6.94 – 6.88 (m, 2H), 3.35 (dq, *J* = 11.0, 6.9 Hz, 1H), 2.88 (d, *J* = 11.0 Hz, 1H), 2.12 (s, 3H), 1.44 (d, *J* = 6.9 Hz, 3H), 1.22 (s, 6H), 1.19 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.8, 139.7, 136.3, 130.0, 128.8, 127.9, 127.3, 125.7, 125.6, 124.9, 83.4, 42.1, 36.4, 24.7, 24.7, 22.5, 20.2. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.7. **HRMS (ESI)**: Calculated for $C_{22}H_{29}O_2{}^{11}BNa^+$: *m/z* = 359.21528 ($[M+Na]^+$), found: 359.21523. **IR** 3061, 3027, 2977, 2931, 1603, 1491, 1454, 1372, 1356, 1339, 1320, 1270, 1214, 1143, 1010, 969, 850, 767, 730, 700. **mp**: 76–78 °C.

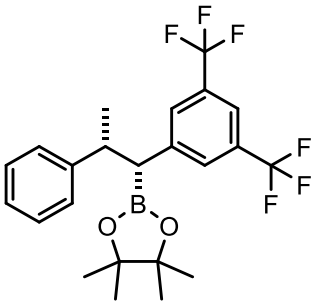
2-((1*R,2*R**)-(±)-1-(4-chloro-3-methoxyphenyl)-2-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3bi)**



Boronic ester **3bi** was prepared according to **GP1** using (4-chloro-3-methoxyphenyl)lithium from 5-bromo-2-chloroanisole (87 mg, 0.39 mmol, 1.6 equiv.) in DMS. The product was isolated *via* flash column chromatography using NaOAc-deactivated silica as a pale yellow crystalline solid (62 mg, 0.16 mmol, 65%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.14 – 7.10 (m, 2H), 7.06 – 7.02 (m, 2H), 7.01 – 6.98 (m, 2H), 6.60 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.55 (d, *J* = 1.9 Hz, 1H), 3.71 (s, 3H), 3.22 (dq, *J* = 11.3, 6.9 Hz, 1H), 2.55 (d, *J* = 11.3 Hz, 1H), 1.39 (d, *J* = 6.9 Hz, 3H), 1.25 (s, 6H), 1.23 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 154.4, 146.2, 141.6, 129.5, 128.1, 127.3, 125.9, 122.1, 119.1, 113.4, 83.8, 56.0, 43.0, 41.2, 24.8, 24.8, 22.8. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 33.0. **HRMS (ESI)**: Calculated for $C_{22}H_{28}O_3{}^{11}B^{35}ClNa^+$: *m/z* = 409.17122 ($[M+Na]^+$), found: 409.17118. **IR** 3366, 2977, 1591, 1578, 1491, 1455, 1413, 1359, 1322, 1281, 1214, 1166, 1142, 1065, 1032, 969, 850, 815, 763, 700. **mp**: 86–88 °C.

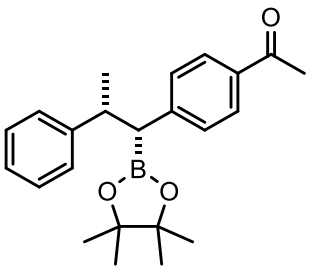
2-((1*R,2*R**)-(±)-1-(3,5-bis(trifluoromethyl)phenyl)-2-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3bj)**



Boronic ester **3bj** was prepared according to **GP1** using (3,5-bis(trifluoromethyl)phenyl)lithium from 1-iodo-3,5-bis (trifluoromethyl)benzene (66 µL, 0.37 mmol, 1.5 equiv.) in DMS. The product was isolated *via* bulb-to-bulb distillation as a pale-yellow oil (95 mg, 0.21 mmol, 84%).[xxi]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 1H), 7.45 – 7.42 (m, 2H), 7.14 – 7.09 (m, 2H), 7.06 – 7.02 (m, 1H), 6.95 – 6.91 (m, 2H), 3.24 (dq, *J* = 11.1, 6.9 Hz, 1H), 2.67 (d, *J* = 11.1 Hz, 1H), 1.43 (d, *J* = 6.9 Hz, 3H), 1.25 (s, 6H), 1.24 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.1, 144.2, 130.9 (q, *J* = 32.9 Hz), 129.6 – 129.4 (m), 128.4, 127.2, 126.3, 123.6 (q, *J* = 272.6 Hz), 119.3 – 119.1 (m), 84.2, 43.3, 41.5, 24.9, 24.6, 22.4. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.1. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -63.1. **HRMS (ESI)**: Calculated for $C_{23}H_{25}O_2{}^{11}BF_6Na^+$: *m/z* = 481.17440 ($[M+Na]^+$), found: 481.17475. **IR** 3030, 2979, 2932, 1455, 1371, 1328, 1275, 1167, 1127, 1010, 969, 935, 890, 849, 764, 741, 700, 681.

1-(4-((1*R,2*R**)-(±)-2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)ethan-1-one (3bk)**



Boronic ester **3bk** was prepared according to a modified **GP1** using (4-(2-methyl-1,3-dioxolan-2-yl)phenyl)lithium from 2-(4-bromophenyl)-2-methyl-1,3-dioxolane **S4** (92 mg, 0.38 mmol, 1.5 equiv.) in DMS. After 1 h the reaction mixture is concentrated *in vacuo*, then redissolved in THF (2.5 mL) and HCl (0.1 N in H_2O, 0.5 mL, 0.5 mmol, 2 equiv.). After stirring for 1 h the usual work-up was applied. The product was isolated *via* bulb-to-bulb distillation[xxii] as a pale-yellow crystalline solid (59 mg, 0.16 mmol, 66%).

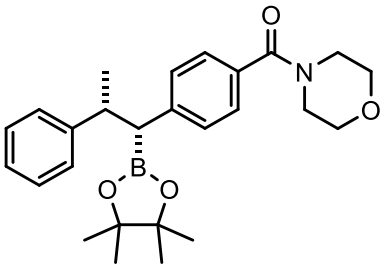
^{1}H NMR (599 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 2H), 7.15 – 7.12 (m, 2H), 7.12 – 7.07 (m, 2H), 7.03 – 6.98 (m, 3H), 3.33 (dq, *J* = 11.4, 6.8 Hz, 1H), 2.70 (d, *J* = 11.4 Hz, 1H), 2.48 (s, 3H),

[xxi] The reaction was also run with bis(trifluoromethyl)phenyl)magnesium iodide from 1-iodo-3,5-bis(trifluoromethyl)benzene (0.13 mL, 0.73 mmol, 2.9 equiv.) in Et_2O which required prolonged reaction times (overnight) and provided the product **3bj** (67 mg, 0.15 mmol, 60%) in lower yields.

[xxii] Almost full protodeboronation was observed when trying to isolate the product on NaOAc-deactivated silica gel.

1.40 (d, *J* = 6.9 Hz, 3H), 1.23 (s, 6H), 1.20 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.1, 147.7, 146.1, 134.5, 129.2, 128.2, 127.3, 125.9, 83.9, 42.6, 41.6, 26.6, 24.7, 23.2. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 32.8. **HRMS (ESI)**: Calculated for $C_{23}H_{29}O_3{}^{11}BNa^+$: *m/z* = 387.21020 ($[M+Na]^+$), found: 387.20908. **IR** 3366, 2978, 1747, 1681, 1647, 1604, 1543, 1455, 1361, 1323, 1269, 1142, 969, 851, 765, 701. **mp**: 79–81 °C.

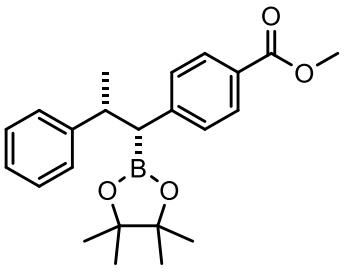
morpholino(4-((1*R,2*R**)-(±)-2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)methanone (3bl)**



Boronic ester **3bl** was prepared according to **GP1** using (4-(morpholine-4-carbonyl)phenyl)magnesium bromide in THF overnight. The Grignard reagent was prepared according to a literature-inspired procedure:[37] to (4-iodophenyl)(morpholino)methanone **S5** (0.24 g, 0.75 mmol, 3.0 equiv.) in THF (2.0 mL) was added ^{i}PrMgBr (1.0 M in THF, 0.67 mL, 0.67 mmol, 2.7 equiv.) dropwise 0 °C and the mixture was stirred for 1 . The product was isolated *via* bulb-to-bulb distillation as a colorless crystalline solid (57 mg, 0.13 mmol, 53%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 – 7.03 (m, 6H), 7.02 – 6.95 (m, 3H), 3.63 (s, 7H), 3.36 – 3.15 (m, 2H), 2.61 (d, *J* = 11.3 Hz, 1H), 1.39 (d, *J* = 6.9 Hz, 3H), 1.23 (s, 6H), 1.21 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.9, 146.3, 143.9, 131.9, 129.3, 128.0, 127.4, 127.0, 125.8, 83.8, 67.0, 42.9, 41.4, 24.8, 24.8, 22.9. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 31.8. **HRMS (ESI)**: Calculated for $C_{26}H_{34}O_4{}^{11}BNNa^+$: *m/z* = 458.24731 ($[M+Na]^+$), found: 458.24707. **IR** 2974, 2924, 2857, 1632, 1494, 1453, 1425, 1359, 1322, 1301, 1275, 1258, 1214, 1141, 1114, 1067, 1011, 969, 894, 851, 764, 733, 701, 566. **mp**: 139–141 °C.

methyl 4-((1*R,2*R**)-(±)-2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl) benzoate (3bm)**

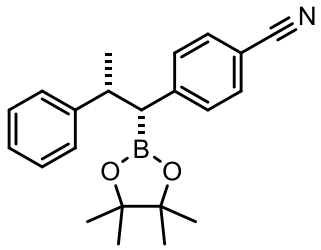


Boronic ester **3bm** was prepared according to **GP1** using (4-(methoxycarbonyl)phenyl)magnesium bromide in THF overnight. The Grignard reagent was prepared according to a literature-inspired procedure:[38] to methyl 4-iodobenzoate (0.33 g, 1.3 mmol, 5.1 equiv.) in THF (1.5 mL) was added ^{i}PrMgBr (1.0 M in THF,

1.1 mL, 1.1 mmol, 4.4 equiv.) dropwise at -20 °C and the mixture was stirred for 1 h. The product was isolated *via* flash column chromatography using NaOAc-deactivated silica as a pale-yellow crystalline solid (41 mg, 0.11 mmol, 44%).[xxiii]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.14 – 7.05 (m, 4H), 7.04 – 6.95 (m, 3H), 3.83 (s, 3H), 3.37 – 3.25 (m, 1H), 2.68 (d, *J* = 11.5 Hz, 1H), 1.39 (d, *J* = 6.9 Hz, 3H), 1.22 (s, 6H), 1.20 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.4, 147.4, 146.1, 129.4, 129.1, 128.1, 127.3, 127.1, 125.9, 83.8, 51.9, 42.6, 41.6, 24.7, 23.2. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 32.9. **HRMS (ESI)**: Calculated for $C_{23}H_{29}O_4{}^{11}BNa^+$: *m/z* = 403.20511 ($[M+Na]^+$), found: 403.20503. **IR** 2976, 1719, 1607, 1452, 1435, 1359, 1322, 1274, 1214, 1179, 1140, 1108, 1020, 1009, 968, 855, 777, 762, 716, 699, 565, 542, 524. **mp**: 109–111 °C.

4-((1*R,2*R**)-(±)-2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl) benzonitrile (3bn)**

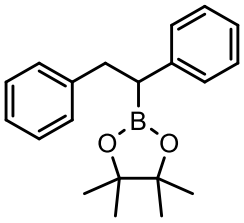


Boronic ester **3bn** was prepared according to **GP1** using (4-cyanophenyl)magnesium bromide in THF overnight. The Grignard reagent was prepared according to a literature-inspired protocol:[37] to 4-iodobenzonitrile (0.17 g, 0.75 mmol, 3.0 equiv.) in THF (1.0 mL) was added ^{i}PrMgBr (1.0 M in THF, 0.67 mL, 0.67 mmol, 2.7 equiv.) dropwise at -20 °C and the mixture was stirred for 1 h. The product was isolated *via* flash column chromatography using NaOAc-deactivated silica as a colorless crystalline solid (68 mg, 0.20 mmol, 79%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.15 – 7.08 (m, 4H), 7.05 – 7.00 (m, 1H), 6.99 – 6.94 (m, 2H), 3.28 (dq, *J* = 11.4, 6.9 Hz, 1H), 2.67 (d, *J* = 11.4 Hz, 1H), 1.40 (d, *J* = 6.9 Hz, 3H), 1.23 (s, 6H), 1.21 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.6, 145.7, 131.8, 129.8, 128.2, 127.2, 126.1, 119.4, 109.0, 84.0, 42.7, 41.9, 24.7, 23.1. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.5. **HRMS (ESI)**: Calculated for $C_{22}H_{26}O_2{}^{11}BNNa^+$: *m/z* = 370.19488 ($[M+Na]^+$), found: 370.19465. **IR** 2978, 2225, 1605, 1499, 1454, 1360, 1325, 1271, 1214, 1141, 851, 764, 701, 573. **mp**: 87–89 °C.

[xxiii] Slow decomposition of the Grignard reagent was observed. Using a large excess of the reagent proved insufficient to achieve full conversion of the intermediate α-iodoboronic ester (observed ca. 60% conversion by GC-FID). Adding freshly prepared reagent portionwise until full conversion was also tested but could not improve the isolated yield because purification was more challenging.

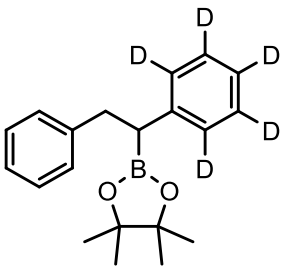
(±)-2-(1,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3bo')



Boronic ester **3bo'** was prepared according to **GP1** using vinyl iodide **1b** (57 mg, 0.25 mmol, 1.0 equiv.) and PhMgBr (3 M in Et_2O, 0.13 mL, 0.4 mmol, 2 equiv.) in Et_2O. The product was isolated *via* flash column chromatography as a colorless oil (34 mg, 0.11 mmol, 45%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 8H), 7.16 – 7.12 (m, 2H), 3.18 – 2.93 (m, 2H), 2.68 (dd, *J* = 9.8, 6.9 Hz, 1H), 1.11 (s, 6H), 1.10 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.7, 141.9, 129.0, 128.6, 128.5, 128.2, 125.9, 125.5, 83.5, 39.0, 24.7, 24.7. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 33.1. **MS (EI)**: Calculated for $C_{20}H_{25}O_2{}^{11}B^{\bullet+}$: *m*/z = 308.2 ($[M]^{\bullet+}$), found: 308.2. The NMR data is in accordance with that reported in the literature.[39]

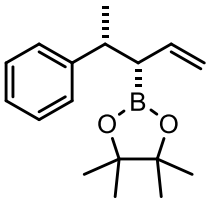
(±)-4,4,5,5-tetramethyl-2-(2-phenyl-1-(phenyl-*d*$_5$)ethyl)-1,3,2-dioxaborolane (3bp')



Boronic ester **3bp'** was prepared according to **GP1** using vinyl iodide **1b** (58 mg, 0.25 mmol, 1.0 equiv.) and C_6D_5MgBr from bromobenzene-*d*$_5$ (80 µL, 0.76 mmol, 3.0 equiv.) in Et_2O. The product was isolated *via* flash column chromatography using NaOAc-deactivated silica as a colorless oil (34 mg, 0.11 mmol, 46%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 4H), 7.17 – 7.12 (m, 1H), 3.17 (dd, *J* = 13.5, 9.8 Hz, 1H), 2.98 (dd, *J* = 13.5, 6.9 Hz, 1H), 2.70 (dd, *J* = 9.8, 6.9 Hz, 1H), 1.12 (s, 6H), 1.11 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.5, 141.9, 129.0, 128.2, 125.9, 83.5, 39.0, 24.7, 24.6. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 33.5. **HRMS (ESI)**: Calculated for $C_{20}H_{20}O_2{}^{11}BD_5Na^+$: *m/z* = 336.21573 ($[M+Na]^+$), found: 336.21589. **IR** 3061, 3028, 2978, 2928, 2274, 1604, 1567, 1495, 1438, 1369, 1327, 1272, 1247, 1214, 1142, 1076, 1030, 1010, 968, 852, 780, 741, 698, 673.

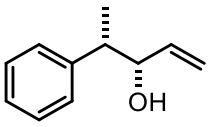
4,4,5,5-tetramethyl-2-((3*S,4*R**)-(±)-4-phenylpent-1-en-3-yl)-1,3,2-dioxaborolane (3ca)**



Boronic ester **3ca** was prepared according to **GP1** using vinylmagnesium bromide (1 M in THF, 0.38 mL, 0.4 mmol, 2 equiv.) in Et_2O. The product was isolated *via* flash column chromatography as a pink oil (40 mg, 0.15 mmol, 60%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.17 – 7.13 (m, 3H), 5.57 (ddd, *J* = 17.2, 10.2, 9.2 Hz, 1H), 4.85 (ddd, *J* = 17.2, 1.9, 1.0 Hz, 1H), 4.79 (ddd, *J* = 10.2, 1.9, 0.7 Hz, 1H), 3.01 (dq, *J* = 10.5, 7.0 Hz, 1H), 2.20 – 2.14 (m, 1H), 1.28 – 1.26 (m, 15H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.9, 138.2, 128.2, 127.6, 125.9, 115.1, 83.5, 41.2, 38.6, 24.9, 24.7, 22.9. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 32.8. **MS (EI)**: Calculated for $C_{17}H_{25}O_2{}^{11}B^{\bullet+}$: *m*/z = 272.2 ($[M]^{\bullet+}$), found: 272.1. The NMR data is in accordance with that reported in the literature.[40]

(3*S,4*S**)-(±)-4-phenylpent-1-en-3-ol (4ca)**

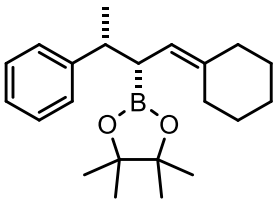


Alcohol **4ca** was prepared according to **GP1** with appended oxidation using vinylmagnesium bromide (1 M in THF, 0.38 mL, 0.4 mmol, 2 equiv.) in Et_2O. The product was isolated *via* flash column chromatography as a pale-yellow oil (21 mg, 0.13 mmol, 53%).[xxiv]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.26 – 7.19 (m, 3H), 5.79 (ddd, *J* = 17.2, 10.5, 5.8 Hz, 1H), 5.24 – 5.15 (m, 1H), 5.13 – 5.06 (m, 1H), 4.28 – 4.19 (m, 1H), 2.90 (qd, *J* = 7.1, 5.0 Hz, 1H), 1.53 (d, *J* = 5.0 Hz, 1H), 1.33 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.4, 139.2, 128.5, 128.3, 126.7, 115.6, 77.3, 45.8, 15.9. **HRMS (ESI)**: Calculated for $C_{11}H_{13}O^-$: *m/z* = 161.09719 ($[M-H]^-$), found: 161.09712. **IR** 3400, 3061, 3028, 2966, 2931, 2875, 1602, 1494, 1452, 1424, 1376, 1235, 1123, 991, 921, 761, 698, 535.

[xxiv] Alcohol **4ca** (31 mg, 0.19 mmol, 95%, 90% over two steps) was also prepared according to **GP1** with appended oxidation using isolated α-iodoboronic ester **2a** (74 mg, 0.20 mmol, 1.0 equiv.) and vinylmagnesium bromide (1 M in THF, 0.22 mL, 0.2 mmol, 1 equiv.) in THF overnight.

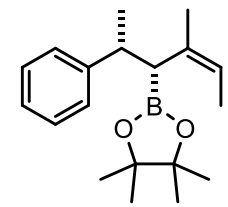
2-((2*S,3*R**)-(±)-1-cyclohexylidene-3-phenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3cb)**



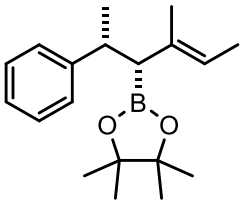
Boronic ester **3cb** was prepared according to **GP1** using (cyclohexylidenemethyl)lithium from (iodomethylene)cyclohexane **1n** (0.11 g, 0.49 mmol, 2.0 equiv.) in DMS. The product was isolated *via* flash column chromatography as a colorless crystalline solid (62 mg, 0.18 mmol, 74%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 7.15 – 7.09 (m, 3H), 4.84 – 4.80 (m, 1H), 2.92 (dq, *J* = 10.7, 6.9 Hz, 1H), 2.34 – 2.29 (m, 1H), 2.01 – 1.93 (m, 2H), 1.93 – 1.83 (m, 2H), 1.42 – 1.32 (m, 4H), 1.29 – 1.20 (m, 16H), 1.15 – 1.06 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.5, 139.5, 128.0, 127.6, 125.6, 120.6, 83.1, 41.8, 37.4, 32.4, 29.2, 28.9, 27.7, 27.0, 25.0, 24.7, 22.9. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 32.6. **HRMS (ESI)**: Calculated for $C_{22}H_{33}O_2{}^{11}BNa^+$: *m/z* = 363.24658 ($[M+Na]^+$), found: 363.24633. **IR** 3400, 3061, 2966, 2931, 2875, 1948, 1874, 1701, 1643, 1494, 1452, 1424, 1376, 1328, 1235, 1123, 1085, 1051, 991, 921, 867, 761, 698, 611, 588, 562, 535, 510. **mp:** slightly above room temperature.

(*Z*)- and (*E*)-4,4,5,5-tetramethyl-2-((2*R,3*R**)-(±)-4-methyl-2-phenylhex-4-en-3-yl)-1,3,2-dioxaborolane (3cc)**



and



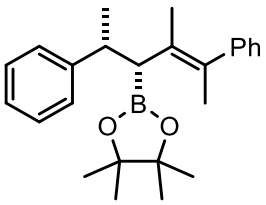
Boronic ester **3cc** was prepared according to **GP1** using but-2-en-2-yllithium in DMS. The lithium reagent was prepared as follows: to (*Z*)-2-bromobut-2-ene[xxv] (51 µL, 0.50 mmol, 2.0 equiv.) in DMS (0.5 mL) was added ^{t}BuLi (1.7 M in pentane, 0.41 mL, 0.70 mmol, 2.8 equiv.) at -78 °C. After stirring for 1 h the mixture was allowed to warm to room temperature and stirred for 1 . The product was isolated *via* flash column chromatography as an orange oil (48 mg, 0.16 mmol, 64%) containing a mixture of isomers (*E*:*Z* = 1:7).

^{1}H NMR (500 MHz, $CDCl_3$) **major diastereomer**: δ 7.26 – 7.20 (m, 2H), 7.17 – 7.10 (m, 3H), 5.07 – 4.99 (m, 1H), 3.17 (dq, *J* = 11.9, 6.9 Hz, 1H), 2.66 (d, *J* = 11.9 Hz, 1H), 1.56 – 1.52 (m, 6H), 1.29 – 1.24 (m, 15H). **^{13}C NMR** (126 MHz, $CDCl_3$) **major**

[xxv]The vinyl bromide seems to be of moderate isomeric purity. Compared to internal bromides, terminal bromides can't be employed as easily as temperatures below -110 °C are needed to avoid alkyne formation, but DMS freezes at -98°C. Solvent change from THF or Et_2O was not tested. Adding $MgBr_2$ to the lithium reagent to form the Grignard reagent did not provide satisfactory results.

diastereomer: δ 147.3, 134.6, 128.1, 127.1, 125.8, 120.1, 83.2, 39.0, 35.1, 24.9, 24.6, 24.5, 21.9, 13.6. **^{11}B NMR** (160 MHz, $CDCl_3$) **major diastereomer**: δ 32.5. **HRMS (ESI)**: Calculated for $C_{19}H_{29}O_2{}^{11}BNa^+$: *m/z* = 323.21528 ($[M+Na]^+$), found: 323.21509. **IR** 3026, 2976, 2924, 2867, 1603, 1451, 1371, 1314, 1271, 1213, 1142, 1108, 1073, 1010, 969, 927, 885, 850, 802, 761, 698, 672, 578, 555.

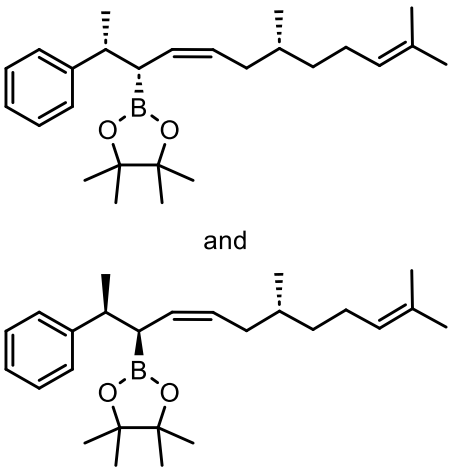
4,4,5,5-tetramethyl-2-((2*R,3*R**,*E*)-(±)-4-methyl-2,5-diphenylhex-4-en-3-yl)-1,3,2-dioxaborolane (3cd)**



Boronic ester **3cd** was prepared according to **GP1** using (*Z*)-(3-phenylbut-2-en-2-yl)lithium from (*E*)-(3-iodobut-2-en-2-yl)benzene **1j** (0.13 g, 0.50 mmol, 2.0 equiv.) in DMS. The product was isolated *via* flash column chromatography as a colorless oil (30 mg, 80 µmol, 32%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.10 (m, 4H), 7.00 – 6.94 (m, 2H), 6.87 – 6.82 (m, 2H), 3.08 (dq, *J* = 11.7, 6.9 Hz, 1H), 2.43 (d, *J* = 11.7 Hz, 1H), 1.69 – 1.66 (m, 6H), 1.30 (s, 6H), 1.30 (s, 6H), 1.07 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.2, 145.4, 131.9, 129.5, 129.2, 127.8, 127.7, 127.6, 125.8, 125.5, 83.2, 39.8, 38.4, 30.5, 25.1, 24.7, 23.8, 21.4, 16.2. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 33.1. **HRMS (ESI)**: Calculated for $C_{25}H_{33}O_2{}^{11}BNa^+$: *m/z* = 399.24658 ($[M+Na]^+$), found: 399.24601. **IR** 3058, 3025, 2977, 2925, 2868, 1599, 1492, 1452, 1338, 1311, 1271, 1212, 1165, 1142, 1111, 1071, 1027, 1010, 967, 909, 887, 850, 764, 735, 698, 555, 532.

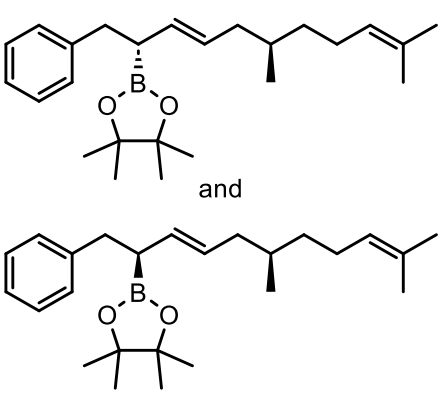
2-((2*R*,3*S*,7*R*,*Z*)-7,11-dimethyl-2-phenyldodeca-4,10-dien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2-((2*S*,3*R*,7*R*,*Z*)-7,11-dimethyl-2-phenyldodeca-4,10-dien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ce)



Boronic ester **3ce** was prepared according to **GP1** using (*R*,*Z*)-(4,8-dimethylnona-1,7-dien-1-yl)lithium from vinyl iodide (*Z*)-**1i** **(**0.14 g, 0.50 mmol, 2.0 equiv.) in DMS. The product was isolated *via* flash column chromatography as a pale orange oil (80 mg, 0.20 mmol, 82%) containing a mixture of diastereomers (d.r. = 1:1).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 7.16 – 7.11 (m, 3H), 5.21 – 5.15 (m, 2H), 5.11 – 5.05 (m, 1H), 3.01 – 2.94 (m, 1H), 2.46 – 2.40 (m, 1H), 2.03 – 1.84 (m, 3H), 1.83 – 1.75 (m, 1H), 1.71 – 1.67 (m, 3H), 1.63 – 1.57 (m, 3H), 1.38 – 1.20 (m, 16H), 1.12 – 1.01 (m, 1H), 0.99 – 0.88 (m, 1H), 0.81 and 0.74 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.2, 130.9, 129.9, 129.8, 128.4, 128.1, 127.5, 125.8, 125.2, 83.3, 41.7, 37.0, 36.9, 35.0, 33.1, 25.9, 25.8, 24.9, 24.6, 23.0, 19.6, 19.5, 17.8. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 32.5. The carbon in the α-position to boron could not be observed. **HRMS (ESI)**: Calculated for $C_{26}H_{41}O_2{}^{11}BNa^+$: *m/z* = 419.30965 ([M+Na]$^+$), found: 419.31006. **IR** 2962, 2924, 1452, 1371, 1357, 1339, 1316, 1270, 1214, 1165, 1142, 1107, 1010, 968, 873, 849, 762, 698, 672, 568.

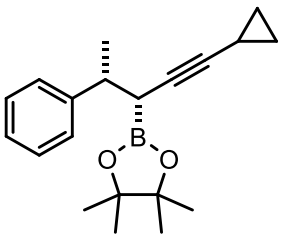
2-((2*R*,6*R*,*E*)-6,10-dimethyl-1-phenylundeca-3,9-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2-((2*S*,6*R*,*E*)-6,10-dimethyl-1-phenylundeca-3,9-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3cf')



Boronic ester **3cf'** was prepared according to **GP1** using vinyl iodide **1b** (58 mg, 0.25 mmol, 1.0 equiv.) and (*R*,*E*)-(4,8-dimethylnona-1,7-dien-1-yl)lithium from vinyl iodide **1i (**0.10 g, 0.37 mmol, 1.5 equiv.) in DMS. The product was isolated *via* flash column chromatography as a pink oil (64 mg, 0.17 mmol, 66%) containing a mixture of diastereomers (d.r. = 1:1).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 4H), 7.16 – 7.12 (m, 1H), 5.46 – 5.33 (m, 2H), 5.11 – 5.06 (m, 1H), 2.85 (ddd, *J* = 13.7, 8.8, 2.0 Hz, 1H), 2.74 (dd, *J* = 13.7, 7.6 Hz, 1H), 2.20 – 2.14 (m, 1H), 2.03 – 1.87 (m, 3H), 1.85 – 1.78 (m, 1H), 1.70 – 1.67 (m, 3H), 1.62 – 1.59 (m, 3H), 1.45 – 1.38 (m, 1H), 1.35 – 1.25 (m, 1H), 1.17 (s, 6H), 1.15 (s, 6H), 1.11 – 1.05 (m, 1H), 0.81 (dd, *J* = 8.2, 6.7 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.1, 131.4, 131.3, 131.0, 129.0, 128.1, 125.7, 125.2, 83.3, 40.4, 40.3, 37.3, 36.7, 36.6, 32.9, 30.8, 25.9, 25.8, 25.7, 24.8, 24.7, 19.4, 17.8. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 32.8. **HRMS (ESI)**: Calculated for $C_{25}H_{39}O_2{}^{11}BNa^+$: *m/z* = 405.29353 ($[M+Na]^+$), found: 405.29362. **IR** 3373, 2976, 2925, 1709, 1638, 1603, 1451, 1372, 1326, 1272, 1218, 1145, 1077, 1009, 980, 850, 746, 698, 672, 577, 517.

2-((3*R,4*R**)-(±)-1-cyclopropyl-4-phenylpent-1-yn-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3da)**



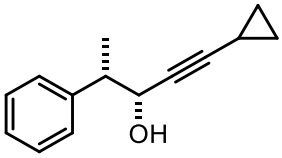
Boronic ester **3da** was prepared according to **GP1** using (cyclopropylethynyl)lithium from ethynylcyclopropane (42 µL, 0.50 mmol, 2.0 equiv.) in Et_2O for 2 h. The product was isolated *via* flash column chromatography using NaOAc-deactivated silica a pale-yellow crystalline solid (48 mg, 0.16 mmol, 62%).[xxvi]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 4H), 7.19 – 7.15 (m, 1H), 3.02 (dq, *J* = 8.7, 7.0 Hz, 1H), 2.22 (dd, *J* = 8.7, 1.9 Hz, 1H), 1.32 (d, *J* = 7.0 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H), 1.14

[xxvi] The product can also be purified using normal silica gel (35%) or by bulb-to-bulb distillation (42%).

– 1.08 (m, 1H), 0.63 – 0.55 (m, 2H), 0.47 – 0.40 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.3, 128.0, 127.6, 126.2, 85.3, 83.9, 74.4, 40.9, 24.8, 24.7, 21.4, 8.2, 0.1. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.3. **HRMS (ESI)**: Calculated for $C_{20}H_{27}O_2{}^{11}BNa^+$: *m/z* = 333.19963 ($[M+Na]^+$), found: 333.19916. **IR** 2978, 2933, 2205, 1701, 1664, 1475, 1452, 1372, 1329, 1272, 1217, 1142, 1056, 1029, 1009, 981, 952, 927, 850, 814, 760, 698, 672, 636, 578, 542, 516. **mp:** slightly above room temperature.

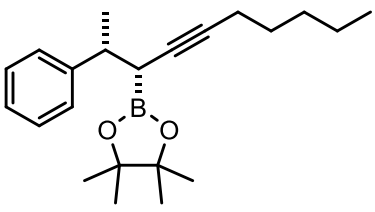
(3*R,4*S**)-(±)-1-cyclopropyl-4-phenylpent-1-yn-3-ol (4da)**



Alcohol **4da** was prepared according to **GP1** with appended oxidation using (cyclopropylethynyl)lithium from ethynylcyclopropane (42 µL, 0.50 mmol, 2.0 equiv.) in Et_2O for 2 h. The product was isolated *via* flash column chromatography as a pale-yellow oil (28 mg, 0.14 mmol, 56%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 4H), 7.26 – 7.23 (m, 1H), 4.42 (ddd, *J* = 7.1, 5.2, 1.8 Hz, 1H), 3.01 (qd, *J* = 7.1, 5.2 Hz, 1H), 1.67 (d, *J* = 7.1 Hz, 1H), 1.38 (d, *J* = 7.1 Hz, 3H), 1.24 – 1.18 (m, 1H), 0.75 – 0.71 (m, 2H), 0.63 – 0.59 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.0, 128.6, 128.3, 127.0, 90.4, 74.9, 67.5, 46.1, 16.2, 8.3, 8.3, -0.5. **HRMS (ESI)**: Calculated for $C_{14}H_{16}ONa^+$: *m/z* = 223.10934 ($[M+Na]^+$), found: 223.10929. **IR** 3374, 3087, 3061, 3028, 2967, 2931, 2905, 2875, 2240, 1603, 1494, 1452, 1376, 1234, 1157, 1090, 1008, 963, 908, 863, 812, 758, 697, 632, 541.

4,4,5,5-tetramethyl-2-((2*R,3*R**)-(±)-2-phenyldec-4-yn-3-yl)-1,3,2-dioxaborolane (3db)**

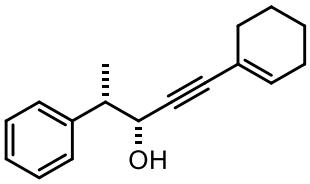


Boronic ester **3db** was prepared according to **GP1** using hept-1-yn-1-yllithium from hept-1-yne (65 µL, 0.50 mmol, 2.0 equiv.)[xxvii] in Et_2O for 2 h. The product was isolated *via* flash column chromatography as a pale-yellow oil (42 mg, 0.12 mmol, 50%).

[xxvii] Full conversion of the intermediate α-iodoboronic ester was sometimes observed when using only 1.5 equiv. of alkyne (1.3 equiv. of ^{n}BuLi) but a larger excess of the reagent was more reliable.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.19 – 7.14 (m, 3H), 4.99 – 4.94 (m, 1H), 1.99 – 1.90 (m, 1H), 1.84 – 1.73 (m, 1H), 1.63 – 1.61 (m, 3H), 1.52 (s, 3H), 1.30 (s, 14H), 1.28 – 1.23 (m, 4H), 1.18 – 1.09 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.8, 131.2, 128.3, 127.4, 125.8, 124.9, 83.2, 41.7, 32.0, 30.5, 28.0, 25.8, 25.2, 25.1, 24.9, 23.1, 17.7. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 34.7. **HRMS (ESI)**: Calculated for $C_{22}H_{33}O_2{}^{11}BNa^+$: *m/z* = 363.24658 ($[M+Na]^+$), found: 363.24653. **IR** 3386, 2976, 2931, 2872, 2211, 1714, 1672, 1603, 1475, 1453, 1373, 1330, 1272, 1219, 1145, 1010, 982, 851, 760, 699, 672.

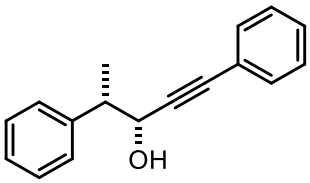
(3*R,4*S**)-(±)-1-(cyclohex-1-en-1-yl)-4-phenylpent-1-yn-3-ol (4dc)**



Alcohol **4dc** was prepared according to **GP1** with appended oxidation[xxviii] using (cyclohex-1-en-1-ylethynyl)lithium from 1-ethynylcyclohex-1-ene (58 µL, 0.49 mmol, 2.0 equiv.) in Et_2O for 2 h. The product was isolated *via* flash column chromatography as a pale-yellow oil (29 mg, 0.12 mmol, 49%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H), 6.08 – 6.04 (m, 1H), 4.58 (dd, *J* = 7.3, 5.3 Hz, 1H), 3.08 (qd, *J* = 7.1, 5.3 Hz, 1H), 2.10 – 2.04 (m, 4H), 1.69 (d, *J* = 7.3 Hz, 1H), 1.65 – 1.53 (m, 4H), 1.41 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.9, 135.4, 128.8, 128.3, 127.1, 120.3, 88.4, 85.9, 67.8, 46.0, 29.2, 25.7, 22.4, 21.6, 16.3. **HRMS (ESI)**: Calculated for $C_{17}H_{20}ONa^+$: *m/z* = 263.14064 ($[M+Na]^+$), found: 263.14059. **IR** 3379, 3060, 3028, 2929, 2858, 2218, 1603, 1495, 1452, 1435, 1376, 1270, 1208, 1136, 1090, 1009, 965, 919, 843, 800, 782, 758, 699.

(3*R,4*S**)-(±)-1,4-diphenylpent-1-yn-3-ol (4dd)**



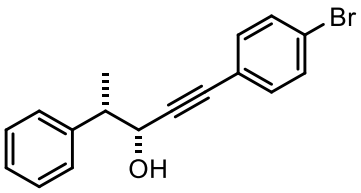
Alcohol **4dd** was prepared according to **GP1** with appended oxidation using (phenylethynyl)lithium from phenylacetylene (55 µL, 0.50 mmol, 2.0 equiv.) in THF. The product

[xxviii] Isolation of the parent boronic ester could not be achieved via flash column chromatography or bulb-to-bulb distillation (decomposition).

was isolated *via* flash column chromatography as a colorless oil (27 mg, 0.11 mmol, 46%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 6H), 7.32 – 7.27 (m, 4H), 4.73 – 4.68 (m, 1H), 3.18 (qd, *J* = 7.1, 5.3 Hz, 1H), 1.87 (d, *J* = 7.1 Hz, 1H), 1.49 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.7, 131.8, 128.7, 128.6, 128.4, 127.2, 122.8, 88.7, 86.6, 67.9, 46.1, 16.4. **HRMS (ESI)**: Calculated for $C_{17}H_{16}ONa^+$: *m/z* = 259.10934 ($[M+Na]^+$), found: 259.10933. **IR** 3402, 3060, 3029, 2970, 2929, 1599, 1491, 1453, 1376, 1091, 1068, 1010, 966, 913, 790, 756, 692.

(3*R,4*S**)-(±)-1-(4-bromophenyl)-4-phenylpent-1-yn-3-ol (4de)**

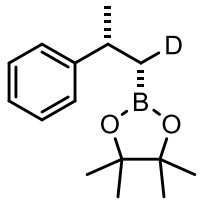


Alcohol **4de** was prepared according to **GP1** with appended oxidation[xxix] using (4-bromophenyl)ethynyl)lithium in THF. The lithium reagent was prepared as follows: lithium diisopropylamide (LDA) was formed from diisopropylamine (70 µL, 0.50 mmol, 2.0 equiv.) and ^{n}BuLi (1.6 M in hexanes, 0.27 mL, 0.43 mmol, 1.7 equiv.) in THF (1.0 mL) at -78 °C. After 5 min, (4-bromophenyl)acetylene (91 mg, 0.50 mmol, 2.0 equiv.) was added and the mixture was stirred for 15 min before warming to room temperature and stirring for 1 h. The product was isolated *via* flash column chromatography as a colorless oil (27 mg, 86 µmol, 35%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 2H), 7.38 – 7.33 (m, 4H), 7.30 – 7.27 (m, 1H), 7.23 – 7.20 (m, 2H), 4.68 (dd, *J* = 7.4, 5.5 Hz, 1H), 3.16 (qd, *J* = 7.1, 5.5 Hz, 1H), 1.85 (d, *J* = 7.4 Hz, 1H), 1.47 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.6, 133.2, 131.7, 128.7, 128.5, 127.3, 122.8, 121.7, 89.9, 85.5, 67.9, 46.0, 16.3. **HRMS (ESI)**: Calculated for $C_{17}H_{14}O^{79}Br^-$: *m/z* = 313.02335 ($[M-Na]^-$), found: 313.02319. **IR** 3378, 3060, 3028, 2968, 2930, 1485, 1453, 1392, 1254, 1095, 1069, 1010, 963, 823, 791, 758, 699, 665.

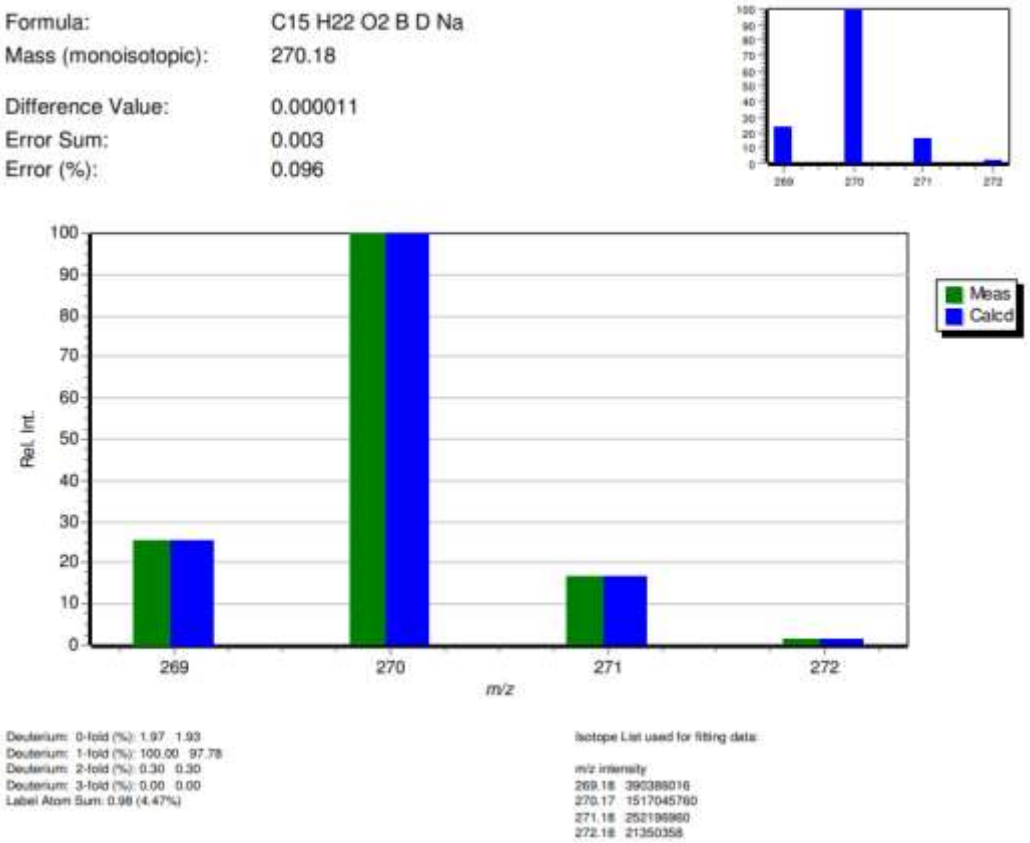
[xxix] The parent boronic ester rapidly decomposed on NaOAc-deactivated silica gel.

4,4,5,5-tetramethyl-2-((1*R,2*R**)-(±)-2-phenylpropyl-1-*d*$_1$)-1,3,2-dioxaborolane (3e)**



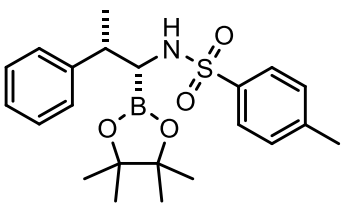
Boronic ester **3e** was prepared according to a literature-inspired[41] modified **GP1** using LiDBEt$_3$ in THF for 2 h keeping the reaction temperature constant at 0 °C. The reagent was prepared following a modified literature procedure:[42] to lithium deuteride (99 atom%D, 44 mg, 4.5 mmol, 18 equiv.) was added triethylborane (1 M in THF, 5.0 mL, 5 mmol, 20 equiv.) and the mixture was heated to reflux overnight. The product was isolated *via* flash column chromatography as a pale-yellow oil (32 mg, 0.13 mmol, 52%).[xxx]

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 4H), 7.15 – 7.11 (m, 1H), 3.05 – 2.98 (m, 1H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.15 (s, 12H), 1.12 – 1.09 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.4, 128.3, 126.8, 125.8, 83.1, 35.9, 25.0, 24.9, 24.8, 21.0. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 33.5. **HRMS (ESI)**: Calculated for $C_{15}H_{22}O_2{}^{11}BDNa^+$: *m/z* = 270.17461 ([M+Na]$^+$), found: 270.17450. **IR** 2978, 1494, 1452, 1362, 1316, 1273, 1214, 1146, 1111, 973, 876, 854, 761, 699. **Mono-D-incorporation**: 98%.



[xxx] Using 3 equiv. of superdeuteride full conversion was observed overnight but the final D-incorporation was low.

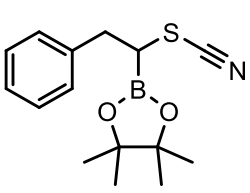
4-methyl-*N*-((1*R,2*S**)-(±)-2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzenesulfonamide (3f)**



Boronic ester **3f** was prepared according to a modified **GP1** using lithium bis(trimethylsilyl)amide (LiHMDS, 1.3 M in THF, 0.38 mL, 0.49 mmol, 2.0 equiv.) in THF. Instead of the usual work-up and according to a modified literature procedure,[43] H_2O was added and the aqueous phase extracted with pentane. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue is dissolved in THF (1.0 mL) and methanol (10 µL, 0.25 mmol, 1.0 equiv.) was added at -10 °C. After 15 min the reaction mixture was allowed to warm to room temperature over 1 h. 4-methylbenzenesulfonyl chloride (54 mg, 0.28 mmol, 1.1 equiv.) in THF (0.50 mL) was added dropwise and the reaction mixture was stirred overnight after which it was concentrated *in vacuo*. The product was isolated *via* flash column chromatography (pentane/EtOAc) as a colorless crystalline solid (34 mg, 83 µmol, 33%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H), 7.24 – 7.15 (m, 5H), 7.10 – 7.07 (m, 2H), 4.28 (d, *J* = 6.2 Hz, 1H), 3.07 – 2.99 (m, 1H), 2.90 – 2.84 (m, 1H), 2.39 (s, 3H), 1.31 (d, *J* = 7.1 Hz, 3H), 1.11 (s, 6H), 1.05 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.4, 143.1, 136.9, 129.5, 128.6, 127.8, 127.5, 127.0, 84.6, 46.9, 41.4, 25.0, 24.7, 21.6, 19.2. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 31.4. **HRMS (ESI)**: Calculated for $C_{22}H_{30}O_4{}^{11}BNSNa^+$: *m/z* = 438.18808 ($[M+Na]^+$), found: 438.18753. **IR** 3290, 2978, 2929, 1599, 1494, 1453, 1324, 1264, 1211, 1161, 1140, 1091, 1026, 968, 901, 973, 844, 814, 772, 723, 701, 660. **mp**: 111–113 °C.

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

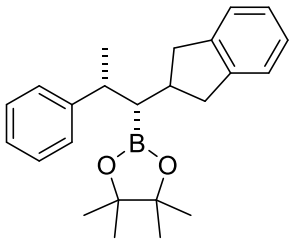


Boronic ester **3g** was prepared according to a modified **GP1** inspired by the literature,[44] using vinyl iodide **1b** (57 mg, 0.25 mmol, 1.0 equiv.) and adding KSCN (49 mg, 0.50 mmol, 2.0 equiv.) and DMF (2.5 mL) at room temperature then stirring at 60 °C for 4 h. After addition of H_2O instead of HCl and applying the otherwise unchanged work-up, the product was isolated *via* flash column chromatography (pentane/EtOAc) as a colorless crystalline solid (21 mg, 73 µmol, 30%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.28 – 7.23 (m, 3H), 3.24 – 3.11 (m, 2H), 2.91 – 2.86 (m, 1H), 1.23 (s, 6H), 1.23 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.2, 129.4, 128.7, 127.2, 112.3, 85.3, 37.5, 24.8, 24.8. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (192 MHz, $CDCl_3$) δ 31.2. **HRMS (ESI)**: Calculated for $C_{15}H_{20}O_2{}^{11}BNSNa^+$: *m/z* = 312.12000 ($[M+Na]^+$), found: 312.11982. **IR** 2982, 2922, 2148, 1493, 1453, 1389, 1367, 1345, 1310, 1272, 1247, 1213, 1167, 1140, 1108, 1072, 1018, 967, 929, 893, 848, 761, 710. **mp**: 90–92 °C.

6 Coupling Reactions with Olefins or Alkynes

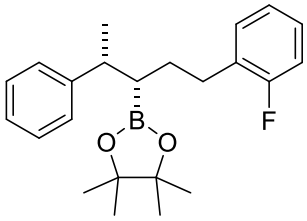
2-((1*S,2*R**)-(±)-1-(2,3-dihydro-1H-inden-2-yl)-2-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5aa)**



Boronic ester **5aa** was prepared according to **GP2** using (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and indene (29 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless crystalline solid (76 mg, 0.21 mmol, 84%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 4H), 7.19 – 7.01 (m, 5H), 3.05 – 2.76 (m, 4H), 2.72 – 2.57 (m, 1H), 2.27 (td, *J* = 8.8, 5.9 Hz, 1H), 1.61 (dd, *J* = 10.6, 5.9 Hz, 1H), 1.30 (d, *J* = 6.9 Hz, 3H), 1.23 – 1.12 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.7, 143.9, 143.6, 128.5, 127.3, 126.0, 126.0, 125.9, 124.5, 124.4, 83.3, 40.6, 39.9, 39.4, 36.7, 25.2, 25.1, 22.6. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.7. **HRMS (ESI)**: Calculated for $C_{24}H_{31}O_2BNa^+$: m/z = 385.23136 ($[M+Na]^+$), found: 385.23101. **IR** 3410, 3024, 2977, 2929, 1603, 1783, 1455, 1381, 1322, 1267, 1211, 1143, 1109, 1007, 967, 875,851, 764, 743, 701. **mp**: 101–103 °C.

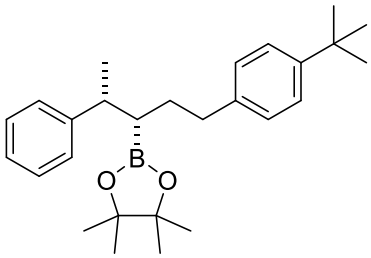
2-((3*S,4*R**)-(±)-1-(2-fluorophenyl)-4-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5ab)**



Boronic ester **5ab** was prepared according to **GP2** using (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and 2-fluorostyrene (30 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless oil (80 mg, 0.22 mmol, 87%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.21 – 6.88 (m, 7H), 2.85 (dq, *J* = 10.7, 6.9 Hz, 1H), 2.71 – 2.57 (m, 1H), 2.54 – 2.40 (m, 1H), 1.64 – 1.24 (m, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.1 (d, *J* = 244.7 Hz), 147.4, 130.5 (d, *J* = 5.1 Hz), 129.5 (d, *J* = 16.0 Hz), 128.4, 127.3, 127.3 (d, *J* = 7.9 Hz), 125.9, 123.8 (d, *J* = 3.5 Hz), 115.1 (d, *J* = 22.3 Hz), 83.4, 41.5, 31.9, 30.7 (d, *J* = 1.1 Hz), 28.4 (d, *J* = 2.5 Hz), 25.1, 25.1, 23.0. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.0. **HRMS (ESI)**: Calculated for $C_{23}H_{30}O_2BFNa^+$: m/z = 391.22151 ($[M+Na]^+$), found: 391.22155. **IR** 2978, 1585, 1493, 1454, 1379, 1321, 1265, 1230, 1144, 966, 852, 753, 702.

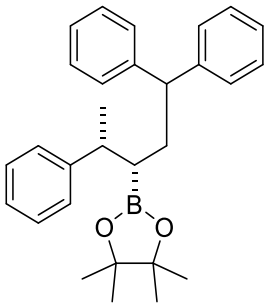
2-((3*S,4*R**)-(±)-1-(4-(tert-butyl)phenyl)-4-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5ac)**



Boronic ester **5ac** was prepared according to **GP2** using (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and 4-*tert*-butylstyrene (46 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless oil (83 mg, 0.20 mmol, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 4H), 7.17 – 7.10 (m, 3H), 7.01 – 6.94 (m, 2H), 2.81 (dq, *J* = 10.7, 6.9 Hz, 1H), 2.57 (ddd, *J* = 13.6, 11.2, 4.9 Hz, 1H), 2.37 (ddd, *J* = 13.6, 10.8, 6.3 Hz, 1H), 1.65 – 1.51 (m, 1H), 1.50 – 1.23 (m, 26H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.3, 147.5, 139.7, 128.3, 128.0, 127.3, 125.8, 125.1, 83.2, 41.5, 35.0, 34.3, 32.0, 31.5, 25.1, 25.1, 23.0. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.8. **HRMS (ESI)**: Calculated for $C_{27}H_{39}O_2BNa^+$: m/z = 429.29402 ($[M+Na]^+$), found: 429.29374. **IR** 3025, 2961, 2867, 1602, 1514, 1493, 1453, 1371, 1316, 1267, 1238, 1211, 1142, 1109, 1008, 966, 851, 825, 763, 700, 673.

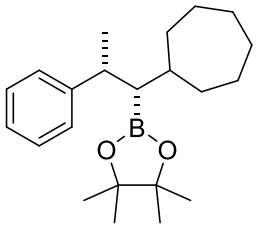
4,4,5,5-tetramethyl-2-((3*S,4*R**)-(±)-1,1,4-triphenylpentan-3-yl)-1,3,2-dioxaborolane (5ad)**



Boronic ester **5ad** was prepared according to **GP2** using (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and 1,1-diphenylethylene (44 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless oil (58 mg, 0.14 mmol, 54%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 6.94 (m, 15H), 3.84 (dd, *J* = 11.5, 4.3 Hz, 1H), 2.80 (dq, *J* = 10.8, 7.0 Hz, 1H), 1.95 (m, 2H), 1.41 – 1.26 (m, 13H), 1.21 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.2, 148.0, 145.3, 130.2, 130.1, 130.1, 130.0, 129.4, 129.3, 128.0, 127.7, 127.6, 85.1, 52.7, 43.7, 38.3, 31.6, 27.0, 26.8, 24.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.67 **HRMS (ESI)**: Calculated for $C_{29}H_{35}O_2BNa^+$: m/z = 449.26223 ($[M+Na]^+$), found: 449.26225. **IR** 3026, 2997, 2926, 1601, 1494, 1451, 1379, 1319, 1236, 1212, 1143, 969, 867, 846, 764, 700, 577.

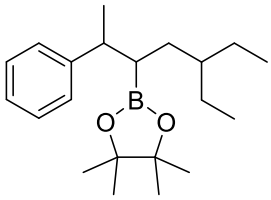
2-((1*S,2*R**)-(±)-1-cycloheptyl-2-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5ae)**



Boronic ester **5ae** was prepared according to **GP2** using (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and cycloheptene (29 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless oil (52 mg, 0.15 mmol, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 2H), 7.19 – 7.12 (m, 3H), 2.93 (dq, *J* = 11.3, 6.8 Hz, 1H), 1.87 – 1.73 (m, 1H), 1.70 – 1.10 (m, 28H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.9, 128.3, 127.3, 125.8, 83.1, 39.6, 39.3, 36.1, 30.8, 28.3, 27.6, 27.6, 27.4, 25.3, 25.1, 23.2. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.7. **HRMS (ESI)**: Calculated for $C_{22}H_{35}O_2BNa^+$: m/z = 365.26263 ($[M+Na]^+$), found: 365.26240. **IR** 2976, 2922, 2854, 1454, 1375, 1313, 1257, 1211, 1144, 966, 852, 764, 700.

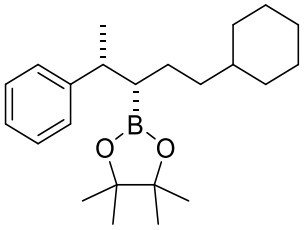
2-(5-ethyl-2-phenylheptan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5af)



Boronic ester **5af** was prepared according to **GP2** using (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and 2-ethyl-1-butene (31 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless oil (62 mg, 0.19 mmol, 75%). The product was obtained as a mixture of the (2*R**,3*S**)-(±)- and (2*S**,3*S**)-(±)-diastereomers (d.r. = 1: 0.2). Integrals in the ^{1}H-NMR spectrum therefore account for 1.2 molecules.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.12 (m, 6H), 3.11 – 2.98 (m, 0.2H), 2.72 (dq, *J* = 7.5, 5.8 Hz, 1H), 1.41 – 0.74 (m, 4H), 0.64 (t, *J* = 7.3 Hz, 31.8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.1, 148.0, 128.3, 128.2, 127.5, 127.4, 125.8, 125.7, 83.2, 82.9, 42.5, 40.4, 38.2, 36.1, 34.0, 33.6, 29.9, 29.3, 26.5, 25.4, 25.3, 25.2, 25.1, 24.9, 24.5, 23.2, 23.1, 13.6, 12.4, 11.6, 9.9. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.8. **HRMS (ESI)**: Calculated for $C_{21}H_{35}O_2BNa^+$: m/z = 353.26223 ($[M+Na]^+$), found: 353.26195. **IR** 3027, 2961, 2926, 2873, 1603, 1494, 1454, 1379, 1318, 1258, 1212, 1144, 1008, 971, 864, 764, 700.

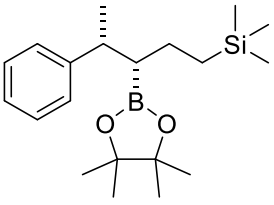
2-((3*S,4*R**)-(±)-1-cyclohexyl-4-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5ag)**



Boronic ester **5ag** was prepared according to **GP2** using (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and vinylcyclohexane (34 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless oil (74 mg, 0.21 mmol, 83%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.11 (m, 5H), 2.73 (dq, *J* = 10.1, 6.8 Hz, 1H), 1.65 – 1.47 (m, 5H), 1.32 – 1.00 (m, 24H), 0.82 – 0.61 (m, 2H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 147.9, 128.3, 127.4, 125.8, 83.2 41.8, 37.8, 37.1, 33.9, 33.0, 27.6, 26.8, 26.5, 26.4, 25.1, 25.1, 23.2. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.5. **HRMS (ESI)**: Calculated for $C_{23}H_{37}O_2BNa^+$: m/z = 379.27788 ($[M+Na]^+$), found: 353.27785. **IR** 2978, 2922, 2851, 1450, 1379, 1317, 1262, 1212, 1144, 965, 861, 763, 701, 572.

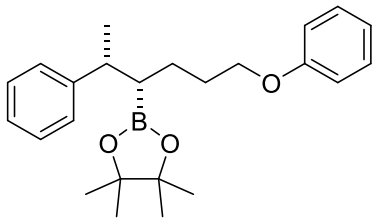
trimethyl((3*S,4*R**)-(±)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)silane (5ah)**



Boronic ester **5ah** was prepared according to **GP2** using (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and vinyltrimethylsilane (37 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless oil (58 mg, 0.17 mmol, 67%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 7.19 – 7.10 (m, 3H), 2.77 (dq, *J* = 10.2, 6.9 Hz, 1H), 1.33 – 1.15 (m, 18H), 0.55 – 0.23 (m, 2H), -0.17 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 128.3, 127.4, 125.8, 83.2, 41.3, 25.1, 25.1, 24.1, 22.9, 16.0, -1.7. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.0. **HRMS (ESI)**: Calculated for $C_{20}H_{35}O_2BSiNa^+$: m/z = 369.23916 ($[M+Na]^+$), found: 369.23920. **IR** 3026, 2954, 2924, 1603, 1452, 1375, 1313, 1248, 1213, 1144, 1032, 1007, 970, 860, 829, 762, 698.

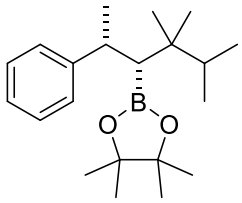
4,4,5,5-tetramethyl-2-((2*R,3*S**)-(±)-6-phenoxy-2-phenylhexan-3-yl)-1,3,2-dioxaborolane (5ai)**



Boronic ester **5ai** was prepared according to **GP2** using (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and allyl phenyl ether (34 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless crystalline solid (52 mg, 0.14 mmol, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.14 (m, 7H), 6.90 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.85 – 6.78 (m, 2H), 3.88 – 3.74 (m, 2H), 2.81 (dq, *J* = 9.9, 6.9 Hz, 1H), 1.77 (dddd, *J* = 13.8, 11.4, 6.8, 4.2 Hz, 1H), 1.69 – 1.56 (m, 1H), 1.48 – 1.22 (m, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1, 147.6, 129.4, 128.4, 127.4, 126.0, 120.5, 114.7, 83.4, 67.9, 41.7, 31.8, 28.8, 26.5, 25.1, 25.1, 23.0. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.8. Calculated for $C_{24}H_{33}O_3BNa^+$: m/z = 403.24150 ($[M+Na]^+$), found: 403.24199. **IR** 2929, 1601, 1496, 1379, 1319, 1246, 1144, 1080, 968, 854, 754, 698. **mp**: 88–90 °C.

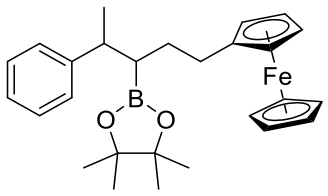
4,4,5,5-tetramethyl-2-((2*R,3*R**)-(±)-4,4,5-trimethyl-2-phenylhexan-3-yl)-1,3,2-dioxaborolane (5aj)**



Boronic ester **5aj** was prepared according to **GP2** using (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and tetramethylethylene (30 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless oil (34 mg, 0.10 mmol, 41%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 4H), 7.16 – 7.10 (m, 1H), 3.05 – 2.93 (m, 1H), 1.70 (d, *J* = 6.6 Hz, 1H), 1.56 – 1.47 (m, 1H), 1.29 (m, 15H), 0.88 (s, 3H), 0.79 – 0.76 (m, 6H), 0.70 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.8, 128.3, 127.4, 125.5, 83.0, 38.2, 37.9, 35.2, 25.6, 25.3, 23.8, 22.8, 22.6, 17.7, 17.5. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.4. **HRMS (ESI)**: Calculated for $C_{21}H_{35}O_2BNa^+$: m/z = 353.26223 ($[M+Na]^+$), found: 353.26215. **IR** 2964, 2927, 1601, 1452, 1373, 1315, 1252, 1211, 1144, 1009, 970, 908, 852, 762, 700.

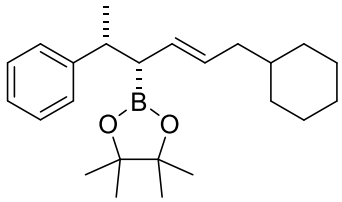
(4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)ferrocene (5ak)



Boronic ester **5ak** was prepared according to **GP2** using (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and vinyl ferrocene (53 mg, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as an orange crystalline solid (62 mg, 0.14 mmol, 54%). The product was obtained as a mixture of the (3*S**,4*R**)-(±)- and (3*S**,4*S**)-(±)-diastereomers (d.r = 1: 0.6). Integrals in the ^{1}H-NMR spectrum therefore account for 1.6 molecules.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.11 (m, 8H), 4.17 – 3.86 (m, 14.4H), 2.87 – 2.74 (m, 1.6H), 2.47 – 2.19 (m, 2.6H), 2.06 (ddd, *J* = 14.5, 11.4, 5.4 Hz, 1H), 1.86 – 1.63 (m, 1.2H), 1.53 – 1.25 (m, 20H), 1.08 – 0.99 (m, 7.2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 147.7, 128.5, 128.2, 127.7, 127.4, 126.0, 126.0, 83.3, 83.0, 68.6, 68.6, 68.3, 67.9, 67.2, 67.0, 41.8, 41.4, 32.4, 31.0, 30.6, 29.4, 28.8, 25.2, 25.1, 24.9, 24.7, 23.1, 21.5. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.4. **HRMS (ESI)**: Calculated for $C_{27}H_{35}O_2BFeNa^+$: m/z = 481.19659 ($[M+Na]^+$), found: 481.19701. **IR** 3092, 2976, 2926, 1603, 1493, 1453, 1378, 1317, 1275, 1213, 1143, 1105, 1023, 1001, 965, 846, 817, 764, 750, 701, 673, 568. **mp:** 90–93 °C.

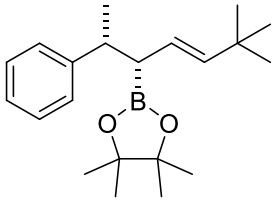
2-((2*R*,3*S*,*E*)-(±)-6-cyclohexyl-2-phenylhex-4-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6aa)



Boronic ester **6aa** was prepared according to **GP2** using (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and 3-cyclohexyl-1-propyne (36 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless oil (48 mg, 0.13 mmol, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 3H), 7.31 – 7.18 (m, 2H), 5.36 – 5.14 (m, 2H), 3.06 (dq, *J* = 10.8, 6.9 Hz, 1H), 2.20 (dd, *J* = 10.8, 8.7 Hz, 1H), 1.89 – 1.62 (m, 6H), 1.62 – 1.52 (m, 1H), 1.45 – 1.32 (m, 15H), 1.27 – 1.03 (m, 4H), 0.84 – 0.68 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.2, 130.2, 129.9, 128.1, 127.6, 125.7, 83.3, 41.6, 40.7, 38.2, 33.0, 32.8, 26.7, 26.5, 24.9, 24.7, 22.9. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.3. **HRMS (ESI)**: Calculated for $C_{24}H_{37}O_2BNa^+$: m/z = 391.27788 ($[M+Na]^+$), found: 391.27775. **IR** 2978, 2922, 2850, 1450, 1369, 1321, 1269, 1213, 1144, 970, 850, 760, 700.

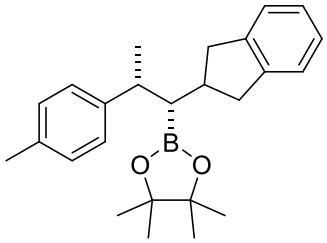
2-((2*R*,3*S*,*E*)-(±)-6,6-dimethyl-2-phenylhept-4-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6ab)



Boronic ester **6ab** was prepared according to **GP2** using (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and 3,3-dimethyl-1-butyne (31 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless oil (20.6 mg, 0.063 mmol, 25%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 7.11 (dt, *J* = 7.8, 1.1 Hz, 3H), 5.21 (dd, *J* = 15.7, 0.8 Hz, 1H), 5.03 (dd, *J* = 15.7, 9.2 Hz, 1H), 2.91 (dq, *J* = 10.7, 6.9 Hz, 1H), 1.97 (dd, *J* = 10.7, 9.2 Hz, 1H), 1.33 – 1.22 (m, 15H), 0.77 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.1, 142.6, 128.0, 127.7, 125.6, 123.9, 83.3, 41.8, 32.9, 29.7, 24.8, 24.7, 22.5. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.7. **HRMS (ESI)**: Calculated for $C_{21}H_{33}O_2BNa^+$: m/z = 351.24697 ($[M+Na]^+$), found: 351.24635. **IR** 3398, 3027, 2957, 2867, 1603, 1453, 1361, 1318, 1267, 1213, 1142, 1107, 1008, 969, 925, 850, 761, 698, 674.

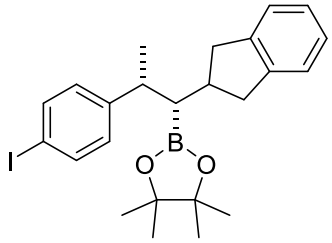
2-((1*S,2*R**)-(±)-1-(2,3-dihydro-1H-inden-2-yl)-2-(p-tolyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5ba)**



Boronic ester **5ba** was prepared according to a modified version of **GP2** using (*E*)-1-(1-iodoprop-1-en-2-yl)-4-methylbenzene (**1k**) (65 mg, 0.25 mmol, 1.0 equiv.) and indene (29 µL, 0.25 mmol, 1.0 equiv.). The reaction temperature was held at -78°C throughout both hydroboration steps. The product was isolated *via* flash column chromatography as a colorless crystalline solid (60 mg, 0.16 mmol, 64%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 – 6.99 (m, 8H), 3.11 – 2.74 (m, 4H), 2.63 (dd, *J* = 15.8, 9.3 Hz, 1H), 2.34 – 2.16 (m, 4H), 1.63 – 1.52 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 3H), 1.17 (d, *J* = 5.3 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 144.0, 143.6, 135.4, 129.2, 127.2, 126.0, 125.9, 124.5, 124.3, 83.3, 40.2, 39.9, 39.4, 36.6, 25.2, 25.1, 22.8, 21.1. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.7. **HRMS (ESI)**: Calculated for $C_{25}H_{33}O_2BNa^+$: m/z = 399.24658 ($[M+Na]^+$), found: 399.24650. **IR** 2976, 2926, 1514, 1483, 1459, 1407, 1379, 1321, 1255, 1211, 1164, 1141, 1107, 1007, 966, 876, 851, 818, 742, 722, 673, 625, 579, 557. **mp**:139–141 °C.

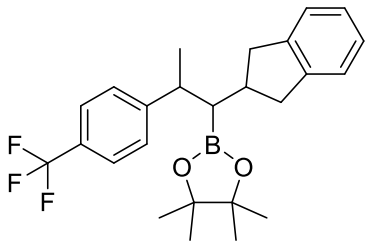
2-((1*S,2*R**)-(±)-1-(2,3-dihydro-1H-inden-2-yl)-2-(4-iodophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5ca)**



Boronic ester **5ca** was prepared according to **GP2** using (*E*)-1-iodo-4-(1-iodoprop-1-en-2-yl)benzene (**1d**) (93 mg, 0.25 mmol, 1.0 equiv.) and indene (29 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless crystalline solid (81 mg, 0.17 mmol, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.14 – 6.96 (m, 6H), 2.95 – 2.78 (m, 4H), 2.68 – 2.59 (m, 1H), 2.24 (pd, *J* = 8.7, 5.9 Hz, 1H), 1.60 – 1.49 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 3H), 1.17 (s, 6H), 1.15 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.5, 143.7, 143.4, 137.5, 129.5, 126.1, 126.0, 124.5, 124.4, 90.9, 83.4, 40.3, 39.9, 39.4, 36.6, 25.2, 25.1, 22.4. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.5. **HRMS (ESI)**: Calculated for $C_{24}H_{30}O_2BINa^+$: m/z = 511.12801 ($[M+Na]^+$), found: 511.12779. **IR** 2975, 2927, 1585, 1483, 1402, 1379, 1322, 1264, 1211, 1140, 1100, 1061, 1004, 965, 875, 850, 820, 742, 716, 673, 642. **mp**: 174–176 °C.

2-(1-(2,3-dihydro-1H-inden-2-yl)-2-(4-(trifluoromethyl)phenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5da)



Boronic ester **5da** was prepared according to **GP2** using (*E*)-1-(1-iodoprop-1-en-2-yl)-4-(trifluoromethyl)benzene (**1e**) (78 mg, 0.25 mmol, 1.0 equiv.) and indene (29 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless crystalline solid (86 mg, 0.20 mmol, 80%). The product was obtained as a mixture of the (1*S**,2*R**)-(±)- and (1*S**,2*S**)-(±)-diastereomers (d.r. = 1: 0.5). Integrals in the ^{1}H-NMR spectrum therefore account for 1.5 molecules.

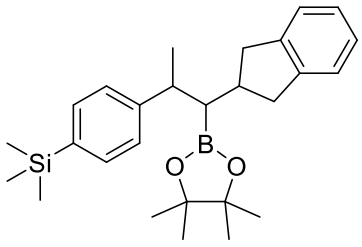
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 3H), 7.42 – 7.32 (m, 3H), 7.22 – 7.04 (m, 6H), 3.15 – 2.60 (m, 8H), 2.23 (qd, *J* = 8.8, 6.2 Hz, 1H), 1.67 – 1.59 (m, 1.5H), 1.35 – 1.29 (m, 4.5H), 1.17 (m, 12H), 0.87 (s, 3H), 0.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.3, 151.9, 143.7, 143.6, 143.4, 143.3, 128.3, 127.6, 126.2, 126.1, 126.1, 126.1, 125.5 (q, *J* = 3.8 Hz), 125.3 – 125.1 (m), 124.6, 124.5, 124.4, 124.4, 83.5, 83.2, 40.6, 40.5, 39.9, 39.8, 39.5, 39.4, 37.0, 36.7, 36.6, 25.2, 25.1, 24.8, 24.6, 22.2, 22.1. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.8. **HRMS (ESI)**:

Calculated for $C_{25}H_{30}O_2BF_3Na^+$: m/z = 453.21832 ([M+Na]$^+$), found: 453.21831. **IR** 2978, 2930, 1618, 1483, 1460, 1409, 1381, 1323, 1259, 1212, 1163, 1141, 1122, 1068, 1016, 967, 841, 745, 609. **mp:** 120–123 °C.

Boronic ester **5da** (65.1 mg, 0.21 mmol) was recrystallized from diethylether to give the product with an improved diastereomeric ratio of d.r. = 1: 0.2 (15.3 mg, 0.050 mmol, 24%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2.4H), 7.41 – 7.32 (m, 2.4H), 7.20 – 7.03 (m, 4.8H), 3.11 – 2.59 (m, 6.2H), 2.32 – 2.11 (m, 1H), 1.67 – 1.58 (m, 1.2H), 1.36 – 1.27 (m, 3.6H), 1.17 (d, *J* = 5.8 Hz, 12H), 0.87 (s, 1.2H), 0.83 (s, 1.2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.3, 151.9, 143.7, 143.6, 143.4, 143.3, 128.3, 127.6, 126.2, 126.1, 126.1, 125.5 (q, *J* = 3.8 Hz), 125.3 – 125.1 (m), 124.6, 124.5, 124.4, 124.4, 83.5, 83.2, 40.6, 40.5, 39.9, 39.8, 39.5, 39.4, 36.7, 36.6, 25.2, 25.1, 24.9, 24.6, 22.2, 22.1. The carbons in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.2. **HRMS (ESI)**: Calculated for $C_{25}H_{30}O_2BF_3Na^+$: m/z = 453.21832 ([M+Na]$^+$), found: 453.21817. **IR** 2978, 1618, 1381, 1326, 1165, 1142, 1124, 1068, 1016, 967, 842, 746. **mp:** 122–125 °C.

(4-(1-(2,3-dihydro-1H-inden-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)phenyl)trimethylsilane (5ea)



Boronic ester **5ea** was prepared according to **GP2** using (*E*)-(4-(1-iodoprop-1-en-2-yl)phenyl)trimethylsilane (**1f**) (79 mg, 0.25 mmol, 1.0 equiv.) and indene (29 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless crystalline solid (96 mg, 0.22 mmol, 89%). The product was obtained as a mixture of the (1*S**,2*R**)-(±)- and (1*S**,2*S**)-(±)-diastereomers (d.r. = 1: 0.7). Integrals in the ^{1}H-NMR spectrum therefore account for 1.7 molecules.

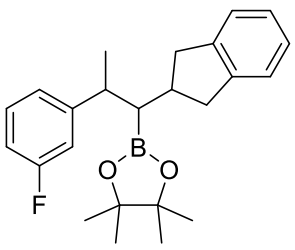
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 3.4H), 7.32 – 7.02 (m, 10.2H), 3.20 – 2.60 (m, 9.2H), 2.29 (qd, *J* = 8.7, 5.7 Hz, 1H), 1.70 – 1.60 (m, 1.7H), 1.39 – 1.30 (m, 5.1H), 1.24 – 1.14 (m, 12H), 0.89 (s, 4.2H), 0.81 (s, 4.2H), 0.27 – 0.24 (m, 15.3H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 148.7, 148.2, 144.0, 144.0, 143.6, 143.6, 137.6, 137.5, 133.6, 133.3, 127.4, 126.8, 126.1, 126.0, 125.9, 124.5, 124.5, 124.4, 124.3, 83.3, 82.9, 40.6, 40.5, 40.0, 39.9, 39.7, 39.4, 36.8, 36.6, 25.2, 25.1, 24.9, 24.5, 22.5, 22.2, -0.9, -1.0. The carbons in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.4. **HRMS (ESI)**: Calculated for $C_{27}H_{39}O_2BSiNa^+$:

m/z = 457.27046 ([M+Na]$^+$), found: 457.27060. **IR** 2955, 1600, 1482, 1459, 1379, 1323, 1248, 1212, 1142, 1116, 1006, 967, 838, 822, 743, 728, 692, 628, 579, 553. **mp:** 129–134 °C.

Boronic ester **5ea** (20.6 mg, 0.070 mmol) was recrystallized from diethylether to give the product with an improved diastereomeric ratio of d.r. = 1: 0.2 (5.5 mg, 0.018 mmol, 27%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2.4H), 7.24 – 7.02 (m, 7.2H), 3.18 – 2.59 (m, 6.2H), 2.33 – 2.20 (m, 1H), 1.70 – 1.60 (m, 1.2H), 1.36 – 1.28 (m, 3.6H), 1.20 – 1.14 (m, 12H), 0.86 (s, 1.2H), 0.79 (s, 1.2H), 0.27 – 0.20 (m, 10.8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.7, 148.2, 144.0, 144.0, 143.6, 137.7, 137.6, 133.6, 133.3, 127.4, 126.8, 126.1, 126.0, 125.9, 124.6, 124.5, 124.4, 124.4, 83.3, 82.9, 40.6, 40.0, 39.9, 39.7, 39.4, 36.8, 36.6, 25.2, 25.1, 24.9, 24.6, 22.5, 22.2, -0.9, -1.0. The carbons in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.6. **HRMS (ESI)**: Calculated for $C_{27}H_{39}O_2BSiNa^+$: m/z = 457.27046 ([M+Na]$^+$), found: 457.27047. **IR** 2957, 2928, 1600, 1459, 1380, 1323, 1248, 1212, 1144, 967, 849, 744, 626. **mp:** 144–146 °C.

2-(1-(2,3-dihydro-1H-inden-2-yl)-2-(3-fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5fa)



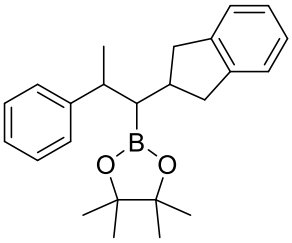
Boronic ester **5fa** was prepared according to **GP2** using (*E*)-1-fluoro-3-(1-iodoprop-1-en-2-yl)benzene (**1l**) (66 mg, 0.25 mmol, 1.0 equiv.) and indene (29 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless crystalline solid (62 mg, 0.16 mmol, 65%). The product was obtained as a mixture of the (1*S**,2*R**)-(±)- and (1*S**,2*S**)-(±)-diastereomers (d.r. = 1: 0.7).[xxxi] Integrals in the ^{1}H-NMR spectrum therefore account for 1.7 molecules.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 – 6.78 (m, 13.6H), 3.18 – 2.58 (m, 9.9H), 2.29 (qd, *J* = 8.7, 6.0 Hz, 1H), 1.63 – 1.52 (m, 1H), 1.34 – 1.27 (m, 5.1H), 1.20 – 1.15 (m, 12H), 0.93 – 0.86 (m, 8.4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2 (d, *J* = 245.0 Hz), 162.9 (d, *J* = 244.6 Hz), 150.8 (d, *J* = 6.7 Hz), 150.5 (d, *J* = 6.6 Hz), 143.8, 143.7, 143.5, 143.4, 129.8 (d, *J* = 8.3 Hz), 129.6 (d, *J* = 8.2 Hz), 126.2, 126.1, 126.0, 124.6, 124.5, 124.4, 124.4, 123.5 (d, *J* = 2.7 Hz), 123.1 (d,

[xxxi] The reaction was repeated, but lithium iodide (3.0 equivalents) was added to the solution of the intermediate borinic acid chloride in THF before generating the ate complex. As one would expect if iodide causes epimerization, the product was formed with a decreased d.r. of 1:1 (34% yield).

J = 2.6 Hz), 114.8 (d, *J* = 20.8 Hz), 114.0 (d, *J* = 20.8 Hz), 112.8 (d, *J* = 21.1 Hz), 112.8 (d, *J* = 21.0 Hz), 83.4, 83.1, 40.5 (d, *J* = 1.7 Hz), 40.3 (d, *J* = 1.7 Hz), 39.9, 39.8, 39.5, 39.4, 36.7, 36.7, 25.2, 25.1, 24.9, 24.7, 22.1, 22.1. The carbons in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.9. **HRMS (ESI)**: Calculated for $C_{24}H_{30}O_2BFNa^+$: m/z = 403.22151 ($[M+Na]^+$), found: 403.22140. **IR** 2977, 2930, 1613, 1589, 1482, 1447, 1380, 1324, 1248, 1212, 1142, 1111, 967, 933, 892, 869, 851, 785, 743, 699. **mp:** 108–110 °C.

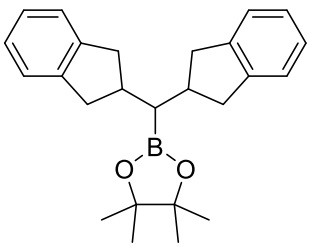
2-(1-(2,3-dihydro-1H-inden-2-yl)-2-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a*a)



Boronic ester **5a*a** was prepared according to **GP2** using (*Z*)-(1-iodoprop-1-en-2-yl)benzene (**(*Z*)-1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and indene (29 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless oil (64 mg, 0.18 mmol, 70%). The product was obtained as a mixture of the (1R*,2*R**)-(±)- and (1*S**,2R*)-(±)-diastereomers (d.r. = 1: 0.6). Integrals in the ^{1}H-NMR spectrum therefore account for 1.6 molecules.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.04 (m, 14.4H), 3.18 – 2.61 (m, 9H), 2.37 – 2.23 (m, 0.6H), 1.68 – 1.60 (m, 1.6H), 1.37 – 1.30 (m, 4.8H), 1.23 – 1.16 (m, 7.2H), 0.89 (s, 6H), 0.85 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.1, 147.7, 144.0, 143.9, 143.6, 143.6, 128.4, 128.2, 127.9, 127.3, 126.1, 126.0, 126.0, 125.9, 124.5, 124.5, 124.4, 124.3, 83.3, 82.9, 40.6, 40.5, 39.9, 39.9, 39.6, 39.4, 36.7, 36.6, 25.2, 25.1, 24.9, 24.7, 22.5, 22.4. The carbons in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.0. **HRMS (ESI)**: Calculated for $C_{24}H_{31}O_2BNa^+$: m/z = 385.23136 ($[M+Na]^+$), found: 385.23078. **IR** 2977, 1455, 1382, 1325, 1214, 1143, 967, 851, 744, 701.

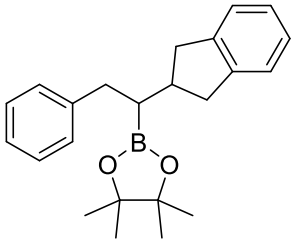
2-(bis(2,3-dihydro-1H-inden-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5ga)



Boronic ester **5ga** was prepared according to **GP2** using 2-(iodomethylene)-2,3-dihydro-1*H*-indene (**1g**) (64 mg, 0.25 mmol, 1.0 equiv.) and indene (29 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless crystalline solid (56 mg, 0.15 mmol, 59%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 4H), 7.18 – 7.12 (m, 4H), 3.22 – 3.03 (m, 4H), 2.88 – 2.71 (m, 6H), 1.51 – 1.46 (t, *J* = 7.1 Hz, 1H), 1.20 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.8, 143.6, 126.1, 126.1, 124.4, 124.4, 83.2, 41.4, 39.7, 38.2, 35.1, 25.1. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.2. **HRMS (ESI)**: Calculated for $C_{25}H_{31}O_2BNa^+$: m/z = 397.23138 ($[M+Na]^+$), found: 397.23054. **IR** 3401, 2978, 2930, 2838, 1648, 1483, 1408, 1384, 1323, 1275, 1261, 1226, 1142, 1103, 966, 886, 853, 747. **mp**: 129–132 °C.

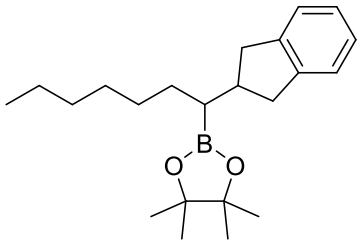
2-(1-(2,3-dihydro-1H-inden-2-yl)-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5ha)



Boronic ester **5ha** was prepared according to **GP2** using (*E*)-(2-iodovinyl)benzene (**1b**) (58 mg, 0.25 mmol, 1.0 equiv.) and indene (29 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless crystalline solid (63 mg, 0.18 mmol, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.13 (m, 9H), 3.16 (dd, *J* = 15.5, 7.9 Hz, 1H), 3.06 (dd, *J* = 15.4, 8.0 Hz, 1H), 2.96 – 2.74 (m, 4H), 2.63 (ddt, *J* = 17.4, 9.2, 8.0 Hz, 1H), 1.72 – 1.60 (m, 1H), 1.12 (s, 6H), 1.08 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 143.6, 142.3, 129.0, 128.2, 126.1, 126.1, 125.8, 124.4, 83.1, 42.1, 39.5, 38.3, 36.7, 24.9, 24.8. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.5. **HRMS (ESI)**: Calculated for $C_{23}H_{29}O_2BNa^+$: m/z = 371.21570 ($[M+Na]^+$), found: 371.21525. **IR** 2978, 2927, 1603, 1455, 1378, 1323, 1260, 1213, 1142, 1109, 966, 862, 748, 698. **mp**: 80–82 °C.

2-(1-(2,3-dihydro-1H-inden-2-yl)heptyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5ia)



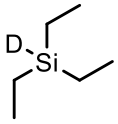
Boronic ester **5ia** was prepared according to **GP2** using (*E*)-1-iodohept-1-ene (**1h**) (56 mg, 0.25 mmol, 1.0 equiv.) and indene (29 µL, 0.25 mmol, 1.0 equiv.). The product was isolated *via* flash column chromatography as a colorless oil (66 mg, 0.19 mmol, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.15 (m, 2H), 7.13 – 7.07 (m, 2H), 3.09 (dd, *J* = 15.4, 7.7 Hz, 1H), 3.00 (dd, *J* = 15.5, 7.8 Hz, 1H), 2.73 – 2.61 (m, 2H), 2.60 – 2.47 (m, 1H), 1.54 – 1.47 (m, 1H), 1.38 – 1.21 (m, 10H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 143.8, 126.0, 126.0,

124.4, 124.4, 83.1, 42.3, 39.4, 38.8, 32.0, 30.7, 29.8, 29.6, 25.0, 22.8, 14.2. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.0. **HRMS (ESI)**: Calculated for $C_{22}H_{35}O_2BNa^+$: m/z = 365.26263 ($[M+Na]^+$), found: 365.26219. **IR** 2977, 2955, 2925, 2855, 1460, 1379, 1317, 1259, 1222, 1144, 967, 868, 742.

7 Deuteroboration Reactions

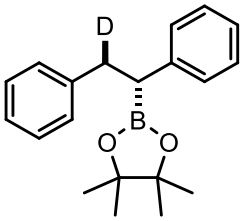
triethylsilane-d_1 (Et_3SiD)



Et_3SiD was prepared according to a modified literature protocol:[45] To $LiAlD_4$ (97 atom%D, 0.42 g, 10 mmol, 1.0 equiv.) in Et_2O (10 mL) was added Et_3SiCl (2.1 mL, 13 mmol, 1.3 equiv.) dropwise at 0 °C. The reaction mixture was heated to reflux overnight and cooled to 0 °C before H_2O (2.5 mL) and then HCl (1 N in H_2O, 12 mL) were slowly added. The phases were separated and the aqueous phase was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The product was isolated *via* bulb-to-bulb distillation as a colorless liquid (0.55 g, 4.7 mmol, 47%).[xxxii]

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.9 Hz, 9H), 0.58 (q, *J* = 7.9 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 8.31, 2.6 – 2.5 (m). **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -0.3 (m, *J* = 27.0 Hz). **HRMS (EI)**: Calculated for $C_6H_{15}SiD^{\bullet+}$: *m*/z = 117.10786 ($[M]^{\bullet+}$), found: 117.10777. The NMR data is in accordance with that reported in the literature.[45]

2-((1*R*,2*S*)-1,2-diphenylethyl-2-d_1)-(±)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7a)

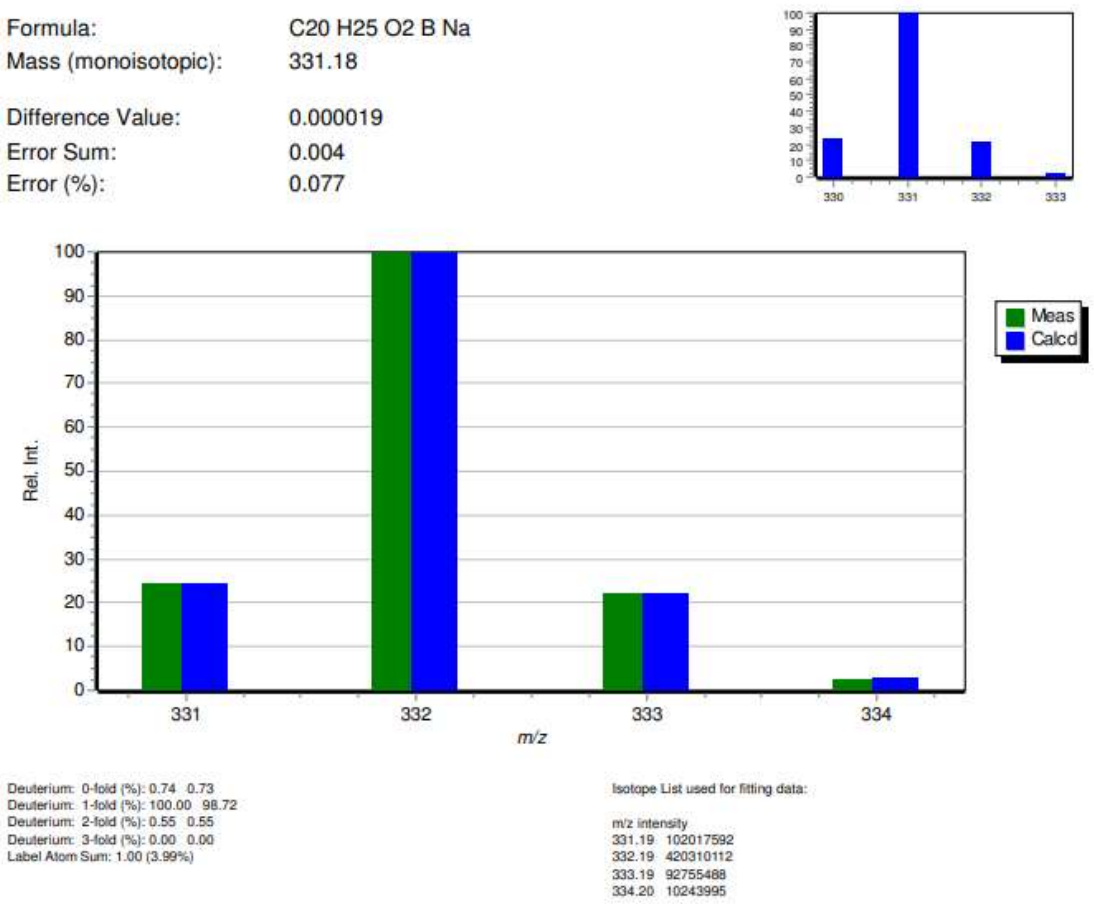


Boronic ester **7a** was prepared according to **GP1** using vinyl iodide **1b** (57 mg, 0.25 mmol, 1.0 equiv.), Et_3SiD (34 mg, 0.29 mmol, 1.1 equiv.) and phenylmagnesium bromide (3 M in Et_2O, 0.13 mL, 0.4 mmol, 2 equiv.) in Et_2O. The product was isolated *via* flash column chromatography using NaOAc-deactivated silica as a pale pink crystalline solid (43 mg, 0.14 mmol, 56%).

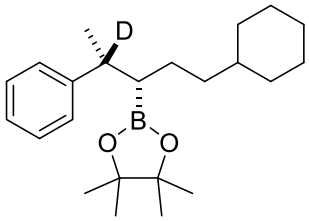
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 4H), 7.24 – 7.19 (m, 4H), 7.18 – 7.13 (m, 2H), 3.18 – 2.94 (m, 1H), 2.72 – 2.67 (m, 1H), 1.15 – 1.11 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.7, 141.8, 129.0, 128.5, 128.5, 128.2, 125.9, 125.5, 83.5, 38.8 – 38.4 (m), 34.5, 24.7, 24.6. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.8. **HRMS (ESI)**: Calculated for $C_{20}H_{24}O_2{}^{11}BDNa^+$: *m/z* = 332.19026 ($[M+Na]^+$), found: 332.19008. **IR** 3026, 2979, 1600, 1494, 1451, 1361, 1325, 1271,

[xxxii] Et_3SiD is also commercially available (ca. $500/g). The synthesized Et_3SiD was used after distillation but not dried like Et_3SiH because of the small available quantity.

1215, 1142, 1109, 1032, 969, 852, 760, 700. **mp:** slightly above room temperature. **Mono-D-incorporation**: 99%.



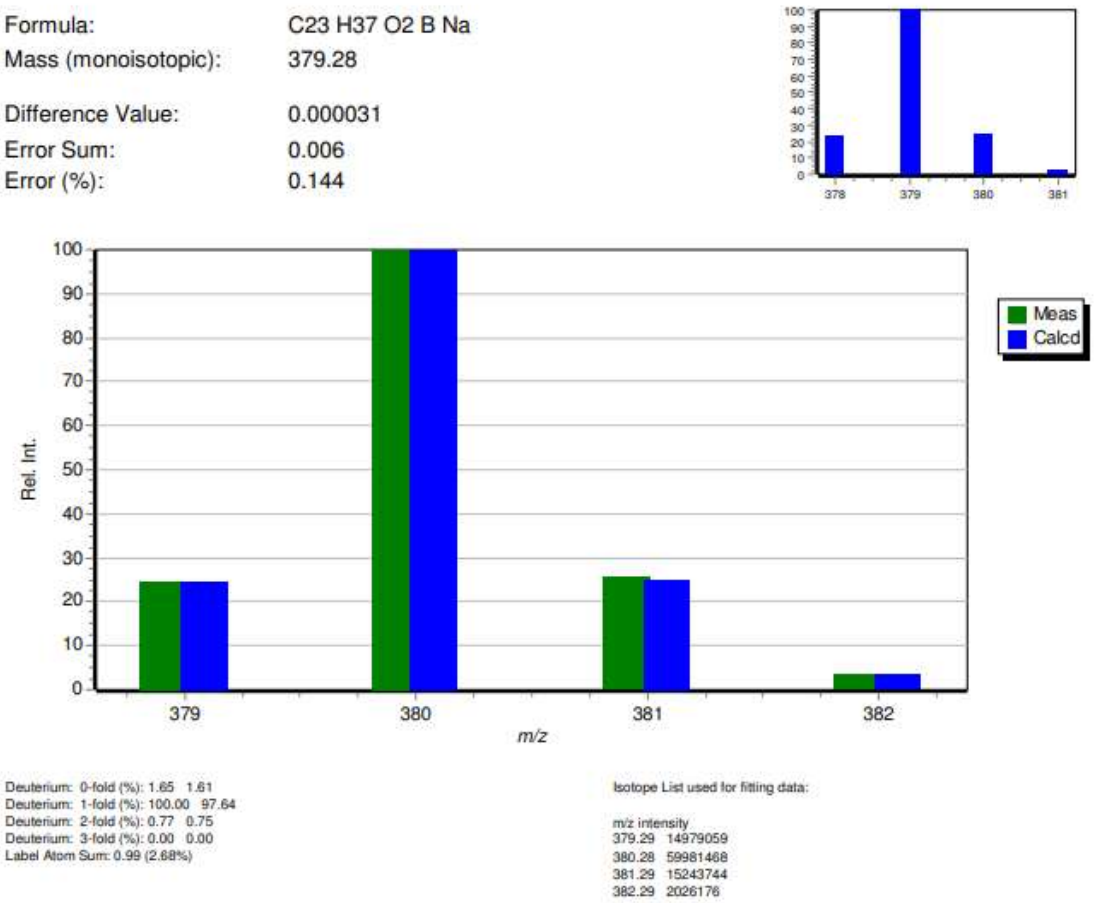
2-((3*S,4*R**)-(±)-1-cyclohexyl-4-phenylpentan-3-yl-4-d)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7b)**



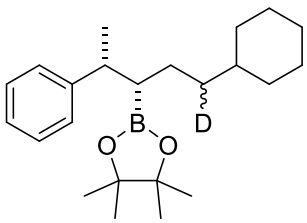
Boronic ester 7**b** was prepared according to a modified version of **GP2.** (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and vinylcyclohexane (34 µL, 0.25 mmol, 1.0 equiv.) were used as the coupling partners. Instead of using Et_3SiH for the first hydroboration step, Et_3SiD (44 µL, 0.28 mmol, 1.1 equiv.) was used to form a solution with vinyl iodide **1a**. The product was isolated *via* flash column chromatography as a colorless oil (65 mg, 0.18 mmol, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 2H), 7.19 – 7.11 (m, 3H), 1.65 – 1.50 (m, 5H), 1.34 – 1.22 (m, 17H), 1.19 – 1.03 (m, 7H), 0.84 – 0.64 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.9, 128.3, 127.3, 125.8, 83.2, 41.3 (t, *J* (^{13}C-^{2}H) = 19.6 Hz), 37.8, 37.1, 33.9, 33.0, 32.1,

27.6, 26.8, 26.5, 26.4, 25.1, 25.1, 23.0. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.0. **HRMS (ESI)**: Calculated for $C_{23}H_{36}O_2BDNa^+$: m/z = 380.28458 ($[M+Na]^+$), found: 380.28398. **IR** 2978, 2922, 2850, 1447, 1372, 1316, 1260, 1211, 1144, 966, 847, 755, 700. **Mono-D-incorporation**: 98%.

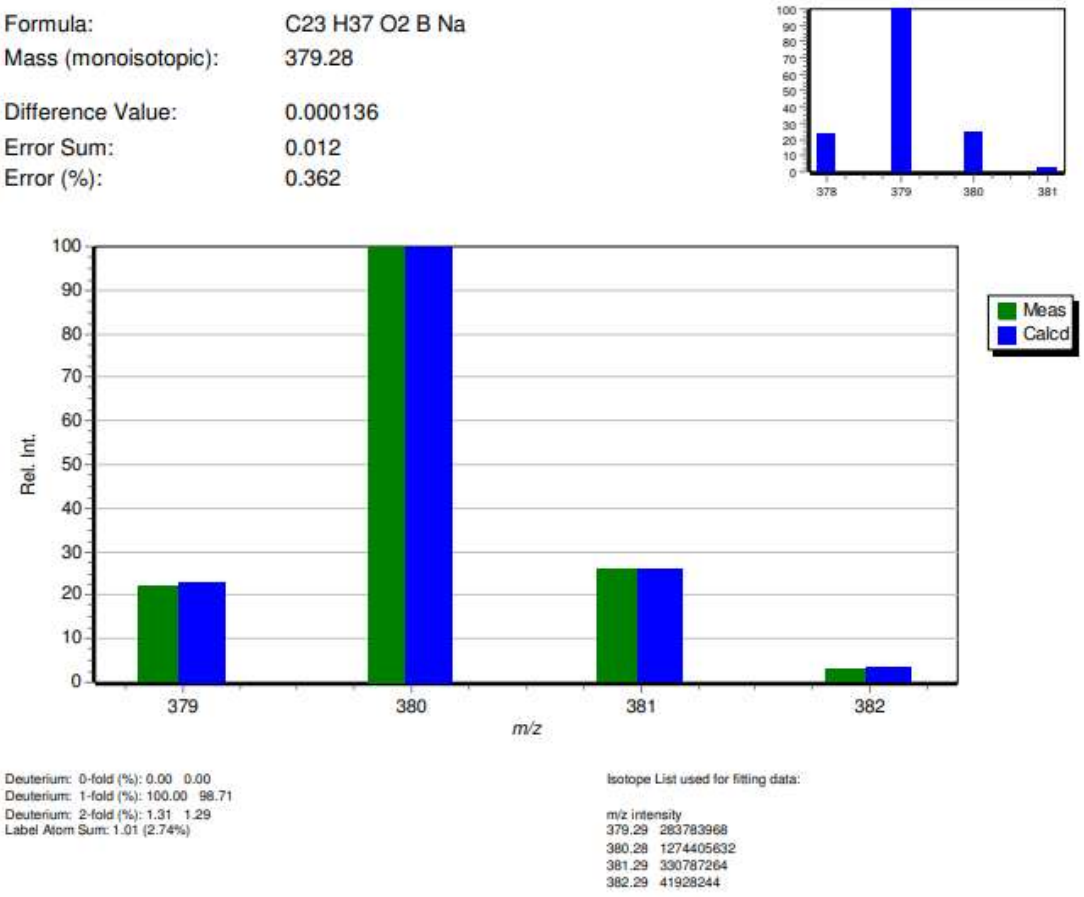


2-((3*S,4*R**)-(±)-1-cyclohexyl-4-phenylpentan-3-yl-1-d)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7c)**

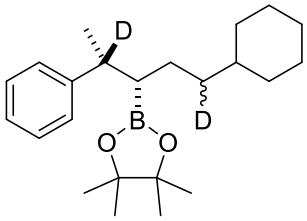


Boronic ester 7**c** was prepared according to a modified version of **GP2.** (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and vinylcyclohexane (34 µL, 0.25 mmol, 1.0 equiv.) were used as the coupling partners. Instead of using Et_3SiH for the second hydroboration step, Et_3SiD (44 µL, 0.28 mmol, 1.1 equiv.) was used to form a solution with vinylcyclohexane. The product was isolated *via* flash column chromatography as a colorless oil (69 mg, 0.19 mmol, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 2H), 7.19 – 7.11 (m, 3H), 2.75 (dq, *J* = 10.0, 6.9 Hz, 1H), 1.65 – 1.49 (m, 5H), 1.32 – 1.21 (m, 17H), 1.18 – 1.02 (m, 6H), 0.83 – 0.63 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.9, 128.3, 127.3, 125.8, 83.2, 41.8, 37.7, 36.9 – 36.4 (m), 33.9, 33.0, 32.2, 27.5, 26.8, 26.5, 26.4, 25.1, 25.1, 23.1. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.9. **HRMS (ESI)**: Calculated for $C_{23}H_{36}O_2BDNa^+$: m/z = 380.28458 ($[M+Na]^+$), found: 380.28281. **IR** 2978, 2921, 2850, 1493, 1449, 1378, 1318, 1260, 1213, 1144, 1110, 965, 853, 764, 750, 700. **Mono-D-incorporation**: 99%.

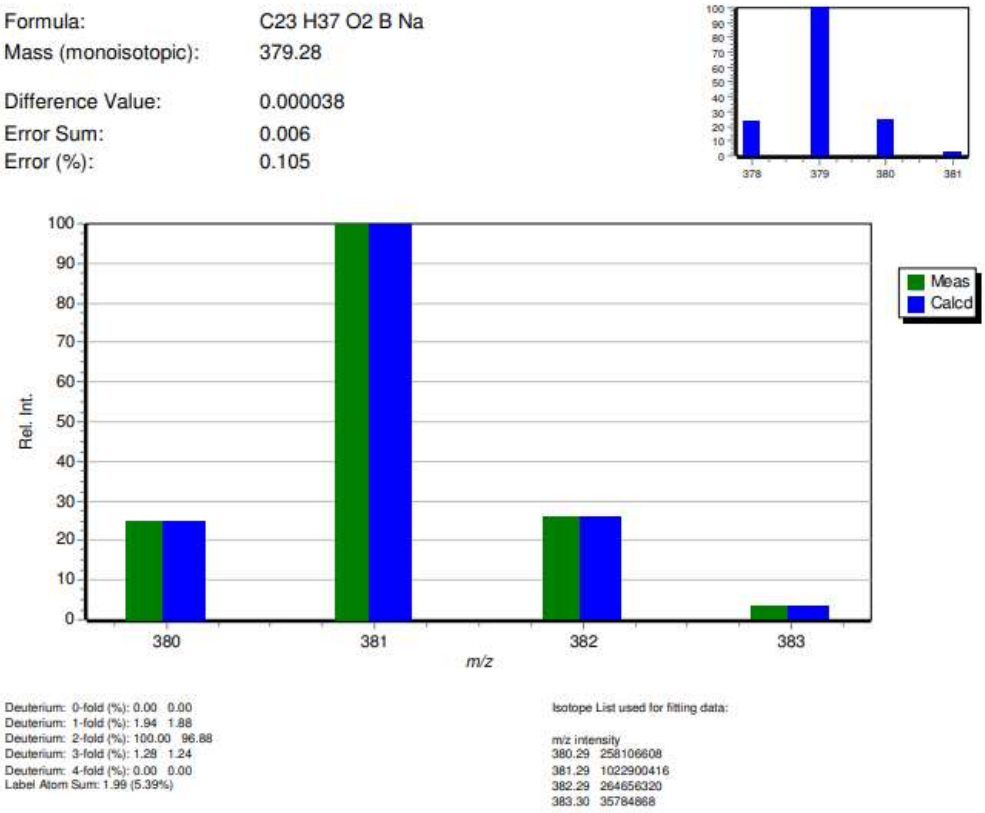


2-((1*S,2*S**)-(±)-4-cyclohexyl-1-phenylbutan-2-yl-1,4-d2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7d)**



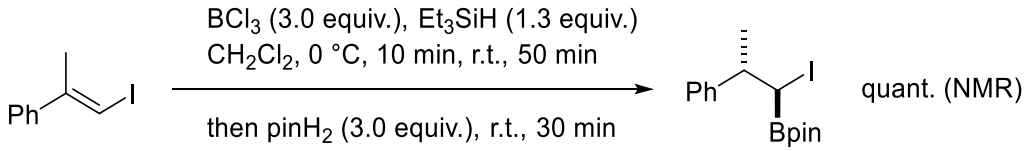
Boronic ester **7d** was prepared according to a modified version of **GP2.** (*E*)-(1-iodoprop-1-en-2-yl)benzene (**1a**) (61 mg, 0.25 mmol, 1.0 equiv.) and vinylcyclohexane (34 µL, 0.25 mmol, 1.0 equiv.) were used as the coupling partners. Instead of using Et_3SiH, Et_3SiD (2 x 44 µL, 2 x 0.28 mmol, 2 x 1.1 equiv.) was used for both hydroboration steps. The product was isolated *via* flash column chromatography as a colorless oil (66 mg, 0.18 mmol, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.20 – 7.12 (m, 3H), 1.66 – 1.49 (m, 5H), 1.32 – 1.27 (m, 12H), 1.25 – 1.20 (m, 5H), 1.16 – 0.98 (m, 6H), 0.82 – 0.62 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.9, 128.3, 127.4, 125.8, 83.2, 41.6 – 41.0 (m), 37.7, 37.0 – 36.4 (m), 33.9, 33.0, 27.5, 26.9, 26.5, 26.4, 25.1, 25.1, 23.0. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.3. **HRMS (ESI)**: Calculated for $C_{23}H_{35}O_2BD_2Na^+$: m/z = 381.29043 ([M+Na]$^+$), found: 381.29020. **IR** 2978, 2920, 2850, 2134, 1602, 1493, 1446, 1371, 1316, 1250, 1213, 1142, 1111, 1080, 1007, 965, 848, 756, 699, 678, 579, 560. **Bis-D-incorporation**: 97%.



8 Optimization

8.1 Isolation of α-Iodoboronic Esters:

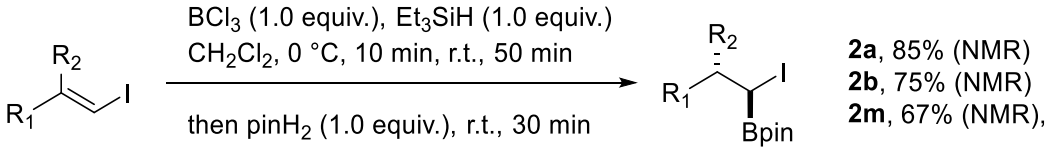


Reactions run according to the procedure from chapter **4**. Isolated yields: 75% (quick silica column), 68% (neutral EcoChrom™ alumina, deactivation grade IV: heavy tailing), 80% (neutral EcoChrom™ alumina, deactivation grade III: with impurities), 73% (NaOAc-deactivated silica), crystallization failed. The best yield was obtained *via* bulb-to-bulb distillation: 94% product with 7% (NMR) found in the mixed fractions.

8.2 Hydroboration (One-Pot Sequence):

Using a commercial $HBBr_2$ dimethylsulfide complex solution instead of generating $HBCl_2$ *in situ* gave a complex mixture of products with vinyl iodide **1a**. Messy reactions were also observed when using commercial $HBCl_2$ solution which is in equilibrium with BCl_3 and H_2BCl.[46]

For the desired one-pot sequence one equivalent BCl_3, Et_3SiH and $pinH_2$ each were initially used.



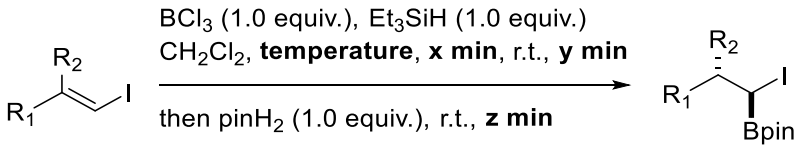
1a, R_1 = Ph, R_2 = Me
1b, R_1 = Ph, R_2 = H
1m, R_1 = Me, R_2 = ^{i}Pent

The yields were significantly lower than under the conditions given in chapter 4 (for comparision: **2m**, 87% (NMR, 3.0 equiv. BCl_3 and $pinH_2$). Therefore, the hydroboration for the one-pot process was further optimized with regard to reaction time, concentration, temperature, addition order and addition time. Some selected experiments are shown below (Table 1):

We found low temperatures are required to achieve consistent yields while too long reaction times decrease yields. Two protocols provided satisfactory results proceeding either at 0 °C or at -78 °C. Full conversion was not achieved at elevated temperatures, though the amount of BCl_3/Et_3SiH was only increased at a later point of the optimization. Another bisaliphatic vinyl

iodide **1n** was tested to compare the general applicability of this approach to related substrates. Model substrate **1a** was also applied.

Table 1: Initial optimization with stoichiometric reagents and different vinyl iodides.



entry	vinyl iodide	temperature	x	y	z	conversion /%[a]	yield /%[a]
1[b]	**1m**	0 °C	10	50	30	92	67
2[c]				30		93	71
3				40		96	75
4[d]				50		97	69
5[e]		0° C	30	0	30	93	78
6[f]						86	74
7			0	30		72	38
8		-78 °C	1000	0		98	78
9		-78 °C	180	0	30	100	87
10	**1n**	0 °C	30	0		93	79
11					60	89	70
12		0 °C	30	30	30	91	85
13		-78 °C	1000	0		85	64
14			300			84	70
15			120			93	70
16	**1a**	0 °C	30			89	68
17						85	76
18						84	69
19		**0° C**	**30**	**30**	**30**	**90**	**81**
20[e]						89	77
21[f]						89	72
22					60	79	72
23			60	0	30	86	71
24			30	60		87	84
25[e]		-78 °C	180	0		85	76
26[f]						84	69
27[d]						70	48
28			60			78	42
29	**1b**	0 °C	30	30	30	85	79
30				60		87	84
31			120	0		86	70
32			60	60		83	74
33			10	50		83	79
34[g]			30	30		79	77
35[g,h]		**0 °C**	**30**	**30**	**30**	**100**	**98**

Reactions run at 0.25 mmol scale adding the premix dropwise over 3 min. [a]Determined by ^{1}H-NMR using dibromomethane as internal standard. [b]Addition at once. [c]Addition over 20 min. [d]Only Et_3SiH added dropwise to BCl_3/vinyl iodide over 3 min. [e]BCl_3 and 2.0 mL CH_2Cl_2. [f]Et_3SiH/vinyl iodide and 2.0 mL CH_2Cl_2. [g]3.0 equiv. BCl_3. [h]1.3 equiv. Et_3SiH.

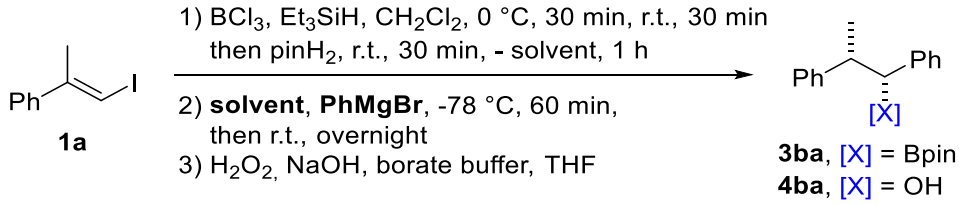
The above conditions were generally well-applicable and a low influence of solvent amount and reaction temperature was observed. When using vinyl iodide **1b** lower conversions were observed and no significant influence of the reaction time on the yield could be found. Interestingly, an increase of the amount of BCl_3 alone could not increase the conversion without

an increase in the amount of Et_3SiH which was used in the final procedure for the isolation of α-iodoboronic esters **2** (two-step sequence, see chapter **4**). The final hydroboration procedure (entry 35) was used for the following optimization of the one-pot coupling.

8.3 Borylative Coupling with PhMgBr (One-Pot Sequence)

The one-pot sequence was initially tested with 1.0 equiv. of PhMgBr as the nucleophile employing different solvents (Table 2). The obtained NMR yields matched well with the NMR yields obtained for the corresponding alcohols after oxidation. THF performed much worse than expected, as THF was well tolerated when running the reaction stepwise.[xxxiii] DMS gave the best results albeit Et_2O was almost as suitable and was chosen as the solvent of choice for further optimization due to its better availability and more pleasant odour. At first the amount of PhMgBr was increased to increase conversion of intermediate **2a** to product **3ba**.[xxxiv]

Table 2: Solvent screening for the one-pot coupling with different amounts of PhMgBr as the nucleophile.



entry	solvent	PhMgBr (3 M in Et_2O) /mL	conversion 1a /%[a]	yield 2a /%[a]	yield 3ba /%[a]	yield 4ba /%[a,b]
1	DMS	0.08	85	26	57	—
2	THF		84	25	25	22
3	Et_2O		86	29	48	43
4		0.10	85	25	50	—
5	**Et_2O**	**0.13**	**86**	**14**	**64**	**—**
6		0.17	86	0	65	—

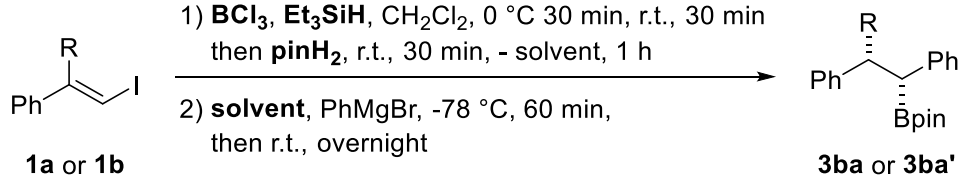
Vinyl iodide **1a** (0.25 mmol, 1.0 equiv.), BCl_3 (1.0 equiv.), Et_3SiH (1.0 equiv.) and $pinH_2$ (1.0 equiv.). Dropwise addition of reagents over 3 min for all steps. [a]Determined by ^{1}H-NMR using dibromomethane as internal standard. [b]After oxidation with H_2O_2, NaOH and borate buffer in THF (see **GP1**).

Next the reaction was run varying the stoichiometry of BCl_3/Et_3SiH and $pinH_2$ (Table 3). As expected, an excess of BCl_3 with stoichiometric Et_3SiH inhibited conversion of the intermediate **2a** to the product **3ba**. Using substoichiometric BCl_3 reaffirmed us in that the overall conversion is not heavily affected by small decreases in molarity of the commercial solution over time. Using an excess of BCl_3 as in the two-step procedure in combination with an aqueous work-up did not help to reduce the expectedly large amount of nucleophile needed for full conversion. In the following, the ratio between BCl_3 and Et_3SiH and their amounts were optimized. Further

[xxxiii] Reaction with α-iodoboronic ester **2a** and 1 equiv. of Nu. With VinylMgBr: **4ca**, 96% isolated. With AllylMgBr: 87% conversion, **3af**, 77% by NMR, after oxidation: **4af**, 72% by NMR.
[xxxiv] Apart from improving the yield, achieving full conversion of the intermediate **2** is relevant, as separation from the desired product proved difficult unless some polar group was present in the coupled compound **3**.

variations led DMS to no longer outperform Et_2O as the solvent and the absolute stoichiometry of BCl_3/Et_3SiH/$pinH_2$ was finalized (1.1/1.1/1.1 equiv.).

Table 3: Optimization of the stoichiometry of BCl_3, Et_3SiH and $pinH_2$.

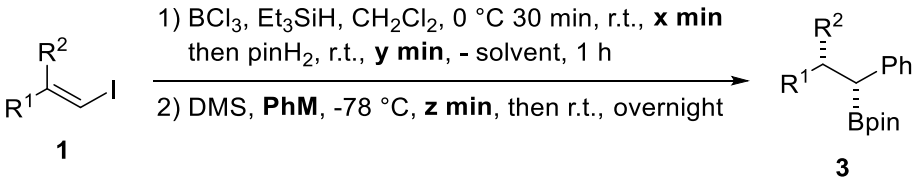


entry	vinyl iodide	solvent	BCl_3 /equiv.	Et_3SiH /equiv.	$pinH_2$ /equiv.	conversion 1 /%[a]	yield 2 /%[a]	yield 3 /%[a]
1[b]	**1a**	THF	1.1	1.0	1.0	89	28	15
2[b]			1.2			89	28	12
3[b]			1.3			86	29	1
4	**1b**	Et_2O	0.9	1.0		89	12	59
5[c]			3.0	1.3	3.0	97	41	50
6[c]					1.0	—	—	<5
7[c]					4.0	100	41	34
8			1.0		1.0	91	<5	65
9				1.1		94	<5	70
10				1.3		99	<5	69
11			1.1			100	<5	78
12		**Et_2O**	**1.1**	**1.3**	**1.1**	**97**	**<5**	**83**
13					1.2	100	0	73
14			1.2	1.4		100	8	86
15			1.3	1.5	1.3	100	17	72
16		DMS	1.1	1.3	1.1	95	<5	83
17[d]						100	22	64
18[d]			1.0	1.1	1.0	100	8	74
19[d]					1.1	96	34	56
20					1.0	100	0	68
21	**1a**	Et_2O				100	<5	80
22					1.1	98	11	65
23			1.2	1.4	1.2	100	0	73
24				1.5		100	0	79
25		**Et_2O**	**1.1**	**1.1**	**1.1**	**100**	**0**	**85**
26				1.3	1.0	100	0	81

Vinyl iodide (0.25 mmol, 1.0 equiv.) and PhMgBr (3 M in Et_2O, 0.13 mL, 0.4 mmol, 2 equiv.). Dropwise addition of reagents over 3 min for all steps. [a]Determined by ^{1}H-NMR using dibromomethane as internal standard. [b]1 equiv. PhMgBr (3 M in Et_2O, 0.07 mL, 0.2 mmol, 1 equiv.). [c]Aqueous work-up between step one and step two. [d] PhMgBr (3 M in Et_2O, 0.10 mL, 0.3 mmol, 1 equiv.).

The last parameters were then finalized (Table 4). The time after addition of $pinH_2$ could be halved without an influence on the yield, whereas the optimized reaction times of the hydroboration step proved to be best fit also in the one-pot procedure. Notably, undistilled Et_3SiH delivered worse yields when using an equal amount. Lastly, the optimized reaction conditions were applied to PhLi as the nucleophile. When lowering the amount of PhLi to 1.2 equiv. the yield did not drop by much showing that the use of more reactive nucleophiles could be more economic albeit the overall yield was lower than with PhMgBr.

Table 4: Finalization of reaction parameters, application to a bisaliphatic vinyl iodide as well as comparision of aryl Grignard with aryllithium reagent.



1 **3**

entry	M	x	y	z	yield 3 /%[a]	yield 4 /%[a,b]
1	MgBr	30	30	15	87	—
2[c]					65	—
3		60	60		76	—
4		30	10	15	88	—
5[d]	MgBr	**30**	**15**	**15**	**96 (87)**	**—**
6[e]					69	—
7	Li				69	58
8[f]					62	50

Vinyl iodide **1b** (0.25 mmol, 1.0 equiv.), BCl_3 (1.1 equiv.), Et_3SiH (1.1 equiv.), $pinH_2$ (1.1 equiv.) and PhM (M = MgBr: 2 equiv.; M = Li: 1.5 equiv.). Dropwise addition of reagents over 3 min for all steps. [a]Determined by ^{1}H-NMR using dibromomethane as internal standard. Isolated yield in parentheses. [b]After oxidation with H_2O_2, NaOH and borate buffer in THF (see **GP1**). [c]Undistilled, commercial Et_3SiH. [d]1 h at room temperature for the rearrangement. [e]Vinyl iodide **1n** was used. [f]1.2 equiv. PhLi (freshly titrated).

8.4 Isolation of Benzylic Boronic Esters

Different purification methods for the isolation of the benzylic boronic ester **3ba** and **3bo'** (Nu = PhMgBr) were tested next. Bulb-to-bulb distillation: **3ba**: 78% (Et_2O, aqueous work-up), 78% (Et_2O, concentrated crude), 87% (DMS, aqueous work-up); **3bo'**: 87% (DMS, concentrated crude) with minor impurities. Distillation is not as generally applicable and easy to get completely pure products, so column chromatography was chosen: **3ba**: 74% (Et_2O, 2 h, NEt_3-deactivated silica), 71% (Et_2O, 1 h, NEt_3-deactivated silica), **81% (Et_2O, 2 h, NaOAc-deactivated silica)**, 80% with minor impurities (Et_2O, 1 h, $B(OH)_3$-doped silica). Alumina was not tested as stationary phase as strong tailing was observed when tested for the isolation of α-iodoboronic ester **2a** and the same deactivation grade is not easily applicable for substrate classes of different polarities.

8.5 Isolation of Alkylboronic Esters

Next, different purification methods for the isolation of the alkyl boronic ester **3aa** (Nu = MeMgBr)[xxxv] were tested. Bulb-to-bulb distillation: **3aa**: 61% (Et_2O). Column chromatography: 68% (DMS), 71% (Et_2O, concentrated crude), 70% (Et_2O, aqueous work-up), 73% (Et_2O, short and rapid column), **76% (Et_2O, 2 h, rapid column)**, 62% (Et_2O, NaOAc-deactivated silica), 69% (Et_2O, HCO_2H-doped silica), 77% with minor impurities (Et_2O, $B(OH)_3$-doped silica). Flash RPLC also did not work well due to strong tailing. Alumina was

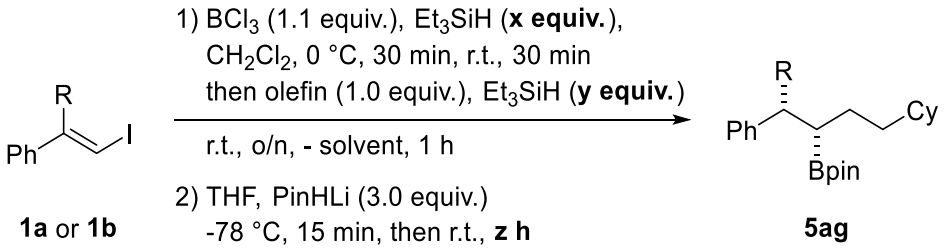
[xxxv] NMR yield of **3aa**: >90% in Et_2O and in DMS, NMR yield of **4aa** after oxidation: 88% in Et_2O and in DMS, 72% isolated.

again not tested as stationary phase (see above). The NMR yields could not be matched during isolation but the isolated yields match with the isolated yields of the corresponding alcohol **4aa** (72%).

8.6 Optimization of the Borylative Olefin Coupling

The above conditions for the hydroboration step were successfully applied to the olefin coupling reaction and briefly optimized (Table 5).

Table 5: Finalization of the reaction parameters for the olefin coupling.



entry	vinyl iodide	x	y	z	yield 5 /%[a]	yield 5-ox /%[a,b]
1	**1b**	1.1	1.1	1	83	88 (79)
2				2	84 (81)	—
3[c]					80	—
4	**1a**				89 (83)[d]	—
5[e]					66	—
6[f]					45	—
7				18	57	—
8			1.0		68	

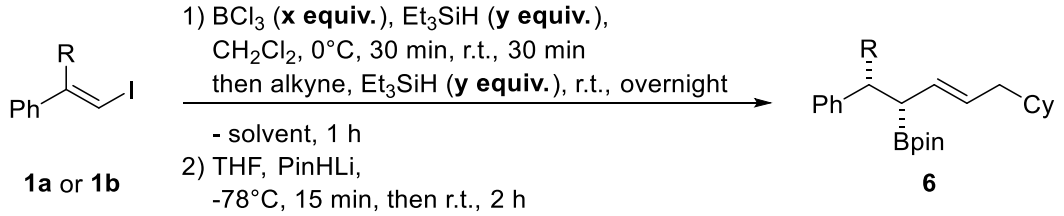
Vinyl iodide (0.25 mmol, 1.0 equiv.), BCl_3 (1.1 equiv.), olefin (1.0 equiv.) and PinHLi (3.0 equiv.). Dropwise addition of reagents except for olefin over 3 min for all steps. [a]Determined by ^{1}H-NMR using dibromomethane as internal standard. Isolated yields in parentheses. [b]After oxidation with H_2O_2, NaOH and borate buffer in THF (see **GP1**). [c]Et_2O replacing THF as the solvent. [d]Corrected yield of product **5ag** containing 10 mol% α-iodoboronic ester **2a** as an inseparable impurity (by column). [e]1.2 equiv. of olefin. [f]1.5 equiv. of PinHLi.

The initial conditions were well applicable to vinyl iodides **1a** and **1b** with a migration time of one or two hours. Increasing the amount of olefin or decreasing the amount of PinHLi led to decreased yields. Et_2O was also applicable to the reaction but PinHLi is less soluble and thus harder to transfer in Et_2O. Additionally (not shown), the time before allowing the boron-ate to reach room temperature was reduced from 30 min to 15 min as for the other sequence with no noticeable impact (even at 5 min). The same acidic work-up could be applied to aid phase separation (see above). Using 3.3 or 2.7 equivalents of ^{n}BuLi for deprotonation had no noticeable effect on the yields, so did decreasing the molarity for the 1,2-metallate rearrangement (not shown). Dropwise addition of olefin/Et_3SiH also gave the same results as adding the premix at once. Using less Et_3SiH than two times 1.1 equiv. also proved inferior.

8.7 Optimization of the Borylative Alkyne Coupling

Lastly, the optimized conditions were also applied to the coupling reaction with alkynes and the reaction parameters were finalized (Table 6). Once again, the previously optimized stoichiometry proved best.

Table 6: Finalization of the reaction parameters for the alkyne coupling.



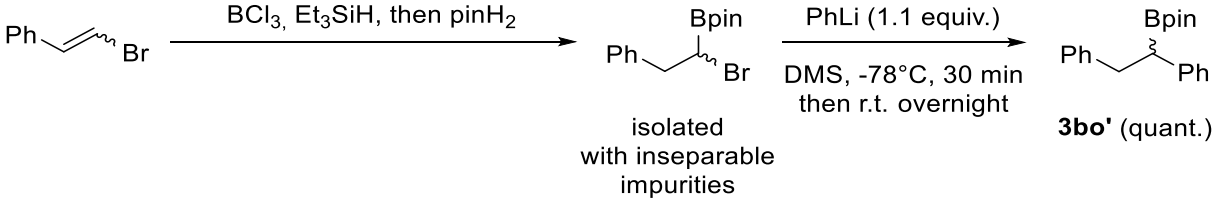
entry	x	y	temperature	yield 6 /%[a]
1	1.0	1.0	r.t.	40
2	1.1	1.1	r.t.	69 (40)[b]
3[c]			r.t.	63

Vinyl iodide **1a** (0.25 mmol, 1.0 equiv.), BCl_3 (1.1 equiv.), alkyne (1.0 equiv.) and PinHLi (3.0 equiv.). Dropwise addition of reagents except for the alkyne over 3 min for all steps. [a]Determined by ^{1}H-NMR using dibromomethane as internal standard. Isolated yields in parentheses. [b]Corrected yield of product **6aa** containing 18 mol% α-iodoboronic ester **2a** as an inseparable impurity (by column). [c]Reaction run with vinyl iodide **1b**.

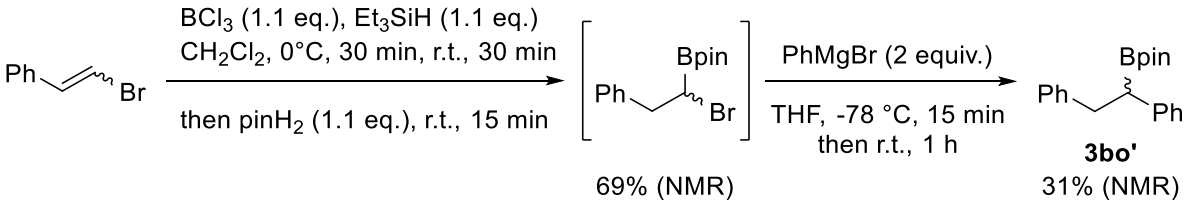
9 Reaction Limitations

9.1 Hydroboration of Vinyl Bromides and Vinyl Chlorides

The application of the developed protocol to vinyl bromides and chlorides, which could likely be synthesized via a Boron-WITTIG reaction too, would broaden the scope significantly and was therefore briefly studied. Commercial *β*-bromostyrene was successfully employed in a two-step approach, though complete purification of the intermediate α-bromoboronic ester was not achieved.



The one-pot reaction gave product **3bo'** only in acceptable yield and a less defined crude mixture with the same reaction conditions employed for vinyl iodides at near full conversion of substrate and intermediate:

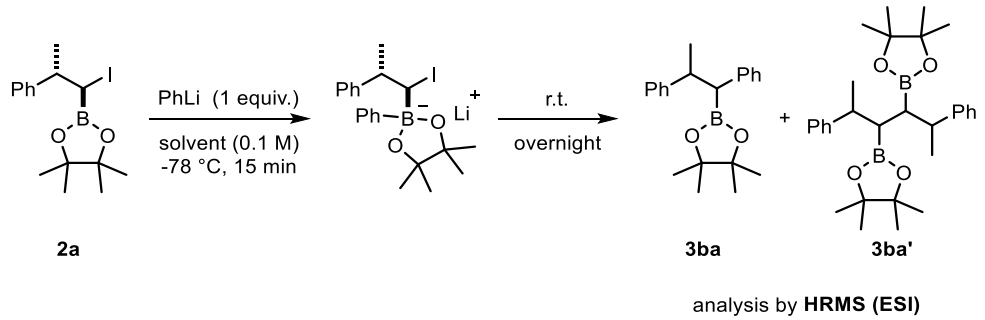


Generally, vinyl bromides and the produced intermediate α-iodoboronic esters are more volatile than their respective iodo- analogues which makes them less suited for the one-pot protocol requiring a solvent exchange[xxxvi]. Substituted vinyl chlorides and bromides also seem to be less activated towards the hydroboration step giving rise to several issues.

9.2 1,2-Metallate Rearrangements with Organolithium Compounds in Different Solvents

α-iodoboronic esters are more prone to lithium-halide exchange than the respective bromo- and common chloro- analogues that undergo facile coupling with organolithiums like *tert*-BuLi.[47] In fact, the exchange reaction and homocoupling is so fast that the intermediate anion could not be captured by other electrophiles (e.g. MeI,[47] PhCHO).

[xxxvi] No product was observed employing 1-bromo-2-methylprop-1-ene to the cascade.



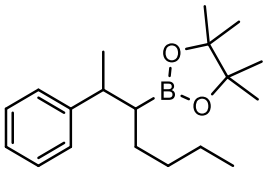
To a cooled (-78 °C) solution of the (*S**,*S**)-(±)-α-iodo pinacol boronic ester **2a** (74 mg, 0.20 mmol, 1.0 equiv.) in Et_2O or THF (2.0 mL, 0.1 M) phenyllithium in di-*n*-butyl ether (1.9 M, 0.11 mL, 0.20 mmol, 1.0 equiv.) was added. The solution was stirred for 15 min, was then allowed to warm to room temperature and was stirred overnight. An aliquot of the crude reaction mixture was diluted with EtOAc and filtered through a plug of silica. This solution revealed the presence of products **3ba** and **3ba'** as analyzed by **HRMS(ESI)**.

For the reaction in **Et_2O**: Calculated for $C_{21}H_{27}BO_2Na^+$: *m/z* = 345.19963 ([**3ba**+Na]$^+$), found: 345.19968. Calculated for $C_{30}H_{44}B_2O_4Na^+$: *m/z* = 513.33179 ([**3ba'**+Na]$^+$), found: 513.33224.

For the reaction in **THF**: Signals for [**3ba**+Na]$^+$ were not observed. Calculated for $C_{30}H_{44}B_2O_4Na^+$: *m/z* = 513.33179 ([**3ba'**+Na]$^+$), found: 513.33211.

No desired product could be isolated when using MeLi, *sec*-BuLi or *tert*-BuLi in place of PhLi. Even in DMS, HRMS analysis revealed exclusively the formation of homocoupling product **3ba'**. In case of ^{n}BuLi (1.6 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) an isolable amount of the desired product **3al** was observed albeit **3ba'** was still formed as the dominant product.

4,4,5,5-tetramethyl-2-(2-phenylheptan-3-yl)-1,3,2-dioxaborolane (3al)



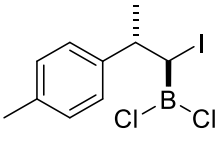
The desired product was isolated as a mixture of diastereomers (d.r. = 1:1.5) *via* flash column chromatography (pentane/Et_2O) as a colorless oil (13 mg, 42 µmol, 21%). The integrals in the ^{1}H-NMR spectrum therefore account for 2.5 molecules.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.18 (m, 6.8H), 7.19 – 7.09 (m, 5.7H), 2.78 – 2.70 (m, 2.5H), 1.37 – 1.06 (m, 43H), 0.99 (s, 6H), 0.94 (s, 6H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.76 (t, *J* = 6.7 Hz, 4.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.4, 148.0, 128.3, 128.2, 127.8, 127.4, 125.9, 125.8, 83.2, 82.8, 41.8, 41.7, 31.9, 31.6, 30.0, 29.5, 25.2, 25.1, 24.9, 24.7, 23.2, 23.1, 22.9, 21.8, 14.2, 14.1. The carbon atoms in the α-position to the boron atoms could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.94. **HRMS(ESI)**. Calculated for $C_{19}H_{31}BO_2Na^+$: *m/z* =

325.23128 ([**3al**+Na]$^+$), found: 325.23112. **IR** 3060, 3026, 2958, 2925, 2866, 1601, 1491, 1454, 1375, 1315, 1267, 1240, 1213, 1144, 1011, 970, 856, 762, 700, 544.

10 NMR Studies of Proposed Intermediates

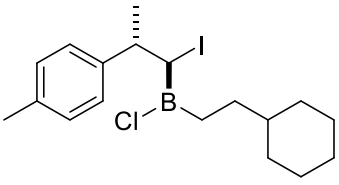
dichloro((1*S,2*S**)-(±)-1-iodo-2-(*p*-tolyl)propyl)borane (8a)**



Intermediate **8a** was prepared according to a modified version of **GP2.** (*E*)-1-(1-iodoprop-1-en-2-yl)-4-methylbenzene (**1k**) (65 mg, 0.25 mmol, 1.0 equiv.) was used as the vinyl iodide. After the first hydroboration step all volatiles were removed from the reaction mixture under reduced pressure and the residue was redissolved in dried and degassed $CDCl_3$. NMR analysis under inert conditions showed dichloroborane **8a** as a fairly clean compound.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.06 (m, 4H), 4.23 (d, *J* = 11.7 Hz, 1H), 3.26 (dq, *J* = 11.7, 6.9 Hz, 1H), 2.33 (s, 3H), 1.58 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.9, 137.2, 129.7, 127.1, 42.8, 24.6, 21.2. The carbon in the α-position to boron could not be observed. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 51.8.

chloro(2-cyclohexylethyl)((1*S,2*S**)-(±)-1-iodo-2-(*p*-tolyl)propyl)borane (8b)**



Intermediate **8b** was prepared according to a modified version of **GP2.** (*E*)-1-(1-iodoprop-1-en-2-yl)-4-methylbenzene (**1k**) (65 mg, 0.25 mmol, 1.0 equiv.) and vinylcyclohexane (34 µL, 0.25 mmol, 1.0 equiv.) were used as the coupling partners. After the second hydroboration step all volatiles were removed from the reaction mixture under reduced pressure and the residue was redissolved in dried and degassed $CDCl_3$. NMR analysis under inert conditions showed chloroborane **8b** as a fairly clean compound.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.04 (m, 4H), 4.27 (d, *J* = 11.6 Hz, 1H), 3.32 (dq, *J* = 11.6, 6.8 Hz, 1H), 2.31 (s, 3H), 1.74 – 0.71 (m, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.8, 136.8, 129.6, 127.1, 43.4, 42.0, 39.4, 33.2, 33.1, 33.1, 26.9, 26.5, 25.1, 22.5, 21.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 62.6.

11 X-ray Crystal Structure Analysis

X-Ray diffraction: Data sets for compound **2c** were collected with a Bruker D8 Venture Photon III Diffractometer. Programs used: data collection: APEX3 V2019.1-0[48] (Bruker AXS Inc., **2019**); cell refinement: SAINT V8.40A (Bruker AXS Inc., **2019**); data reduction: SAINT V8.40A (Bruker AXS Inc., **2019**); absorption correction, SADABS V2016/2 (Bruker AXS Inc., **2019**); structure solution *SHELXT-2015*[49] (Sheldrick, G. M. *Acta Cryst.*, **2015**, *A71*, 3-8); structure refinement *SHELXL-2015*[50] (Sheldrick, G. M. *Acta Cryst.*, **2015**, *C71* (1), 3-8) and graphics, *XP*[51] (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). Data sets for compounds **3ah**, **3bc**, **3bm, 5aa and 5aj** were collected with a Bruker D8 Venture Photon III Diffractometer. Programs used: data collection: *APEX4* Version 2021.4-0[52] (Bruker AXS Inc., **2021**); cell refinement: *SAINT* Version 8.40B (Bruker AXS Inc., **2021**); data reduction: *SAINT* Version 8.40B (Bruker AXS Inc., **2021**); absorption correction, *SADABS* Version 2016/2 (Bruker AXS Inc., **2021**); structure solution *SHELXT*-Version 2018-3[49] (Sheldrick, G. M. *Acta Cryst.*, **2015**, *A71*, 3-8); structure refinement *SHELXL*- Version 2018-3[50] (Sheldrick, G. M. *Acta Cryst.*, **2015**, *C71* (1), 3-8). *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Exceptions and special features: Entire compounds **2c**, **3bm** and **5aj** were found disordered over two positions in the asymmetric unit. For compound **3ah** both Bpin substituents were found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability.

For **2c** (STU10009)

A colorless prism-like specimen of $C_{15}H_{21}BClIO_2$, approximate dimensions 0.078 mm x 0.107 mm x 0.267 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube MoKα (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 211 frames were collected. The total exposure time was 1.76 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 11246 reflections to a maximum θ angle of 25.37° (0.83 Å resolution), of which 3208 were independent (average redundancy 3.506, completeness = 99.6%, R_{int} = 3.46%, R_{sig} = 3.33%) and 2875 (89.62%) were greater than $2\sigma(F^2)$. The final cell constants of a = 14.7648(5) Å,

b = 11.9997(5) Å, c = 9.9650(5) Å, volume = 1765.53(13) $Å^3$, are based upon the refinement of the XYZ-centroids of 5279 reflections above 20 σ(I) with 5.313° < 2θ < 50.66°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.918. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6220 and 0.8620. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *Pna*2_1, with Z = 4 for the formula unit, $C_{15}H_{21}BClIO_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 362 variables converged at R1 = 2.37%, for the observed data and *w*R2 = 4.48% for all data. The goodness-of-fit was 1.055. The largest peak in the final difference electron density synthesis was 0.338 $e^-/Å^3$ and the largest hole was -0.453 $e^-/Å^3$ with an RMS deviation of 0.049 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.529 g/cm^3 and F(000), 808 e^-. CCDC Nr.: 2167695.

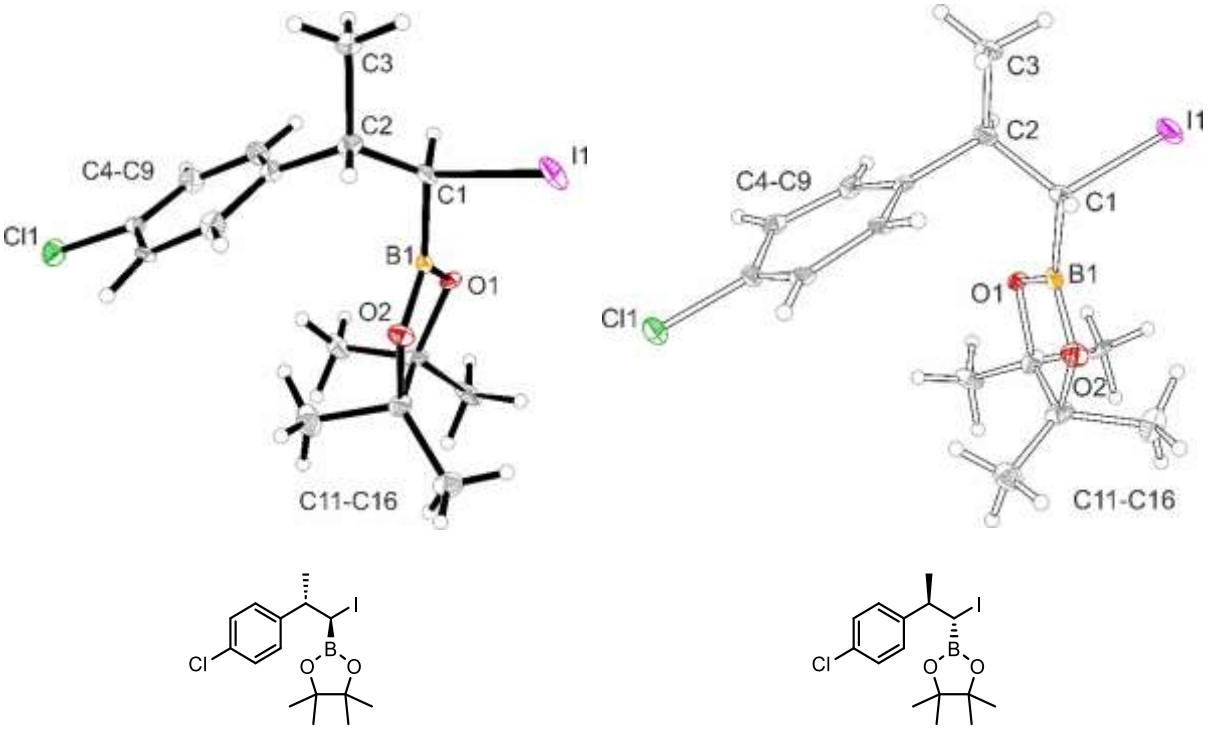


Figure S1: Crystal structure of compound **2c**.

The structure was solved using the non-centrosymmetric space group *Pna*2_1 (Z = 4) and presents one molecule of compound **2c** disordered over two positions in the asymmetric unit. Therefore, the asymmetric unit of compound **2c** contains a mixture of two enantiomers (*S*,*S* and *R*,*R* at the chiral centres C1 and C2) in ratio 51/49. Thermal ellipsoids are shown at 30% probability.

For **3ah** (STU10504)

A colorless, prism-like specimen of $C_{21}H_{33}BO_2Si$, approximate dimensions 0.113 mm x 0.185 mm x 0.209 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 1.54178 Å). A total of 1688 frames were collected. The total exposure time was 23.61 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 32918 reflections to a maximum θ angle of 66.63° (0.84 Å resolution), of which 7881 were independent (average redundancy 4.177, completeness = 99.5%, R_{int} = 6.56%, R_{sig} = 5.08%) and 5696 (72.28%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.2744(3) Å, b = 11.9893(4) Å, c = 21.6544(9) Å, α = 98.330(3)°, β = 102.067(2)°, γ = 103.257(2)°, volume = 2244.36(14) $Å^3$, are based upon the refinement of the XYZ-centroids of 9862 reflections above 20 σ(I) with 7.736° < 2θ < 133.1°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.837. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8210 and 0.8970. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 4 for the formula unit, $C_{21}H_{33}BO_2Si$. The final anisotropic full-matrix least-squares refinement on F^2 with 630 variables converged at R1 = 5.22%, for the observed data and wR2 = 13.42% for all data. The goodness-of-fit was 1.029. The largest peak in the final difference electron density synthesis was 0.557 $e^-/Å^3$ and the largest hole was -0.330 $e^-/Å^3$ with an RMS deviation of 0.044 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.055 g/cm^3 and F(000), 776 e^-. CCDC Nr.: 2293538.

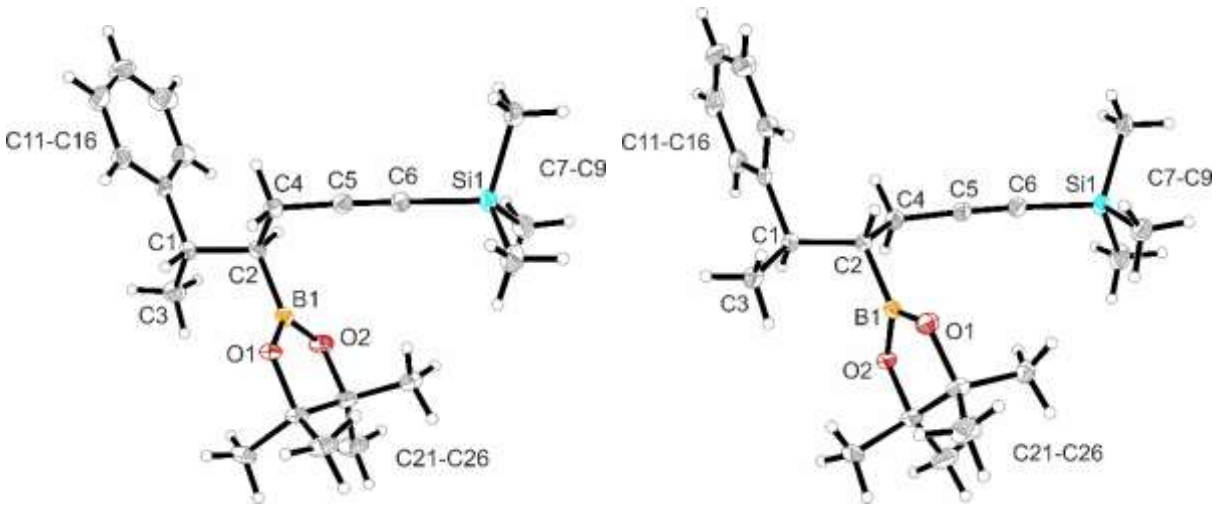


Figure S2: Crystal structure of compound **3ah**.

The structure was solved using the centrosymmetric space group *P*-1 (Z = 4) with two independent molecules in the asymmetric unit. Therefore, the asymmetric unit of compound **3ah** contains both enantiomers (*S,R* and *R,S* at the chiral centres C1 and C2) in ratio 1:1. Thermal ellipsoids are shown at 30% probability.

For **3bc** (STU10505)

A colorless, plate-like specimen of $C_{24}H_{35}BO_2Si$, approximate dimensions 0.101 mm x 0.131 mm x 0.193 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1921 frames were collected. The total exposure time was 21.96 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 30122 reflections to a maximum θ angle of 66.67° (0.84 Å resolution), of which 4171 were independent (average redundancy 7.222, completeness = 99.8%, R_{int} = 7.15%, R_{sig} = 3.79%) and 3325 (79.72%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.8688(2) Å, b = 17.6865(3) Å, c = 12.6092(3) Å, β = 116.4070(10)°, volume = 2370.71(8) $Å^3$, are based upon the refinement of the XYZ-centroids of 9973 reflections above 20 σ(I) with 8.317° < 2θ < 133.2°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.873. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8340 and 0.9080. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{24}H_{35}BO_2Si$. The final anisotropic full-matrix least-squares refinement on F^2 with 261 variables converged at R1 = 4.32%, for the observed data and wR2 = 10.91% for all data. The goodness-of-fit was 1.034. The largest peak in the final difference electron density synthesis was 0.484 $e^-/Å^3$ and the largest hole was -0.232 $e^-/Å^3$ with an RMS deviation

of 0.043 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.105 g/cm^3 and F(000), 856 e^-. CCDC Nr.: 2293539.

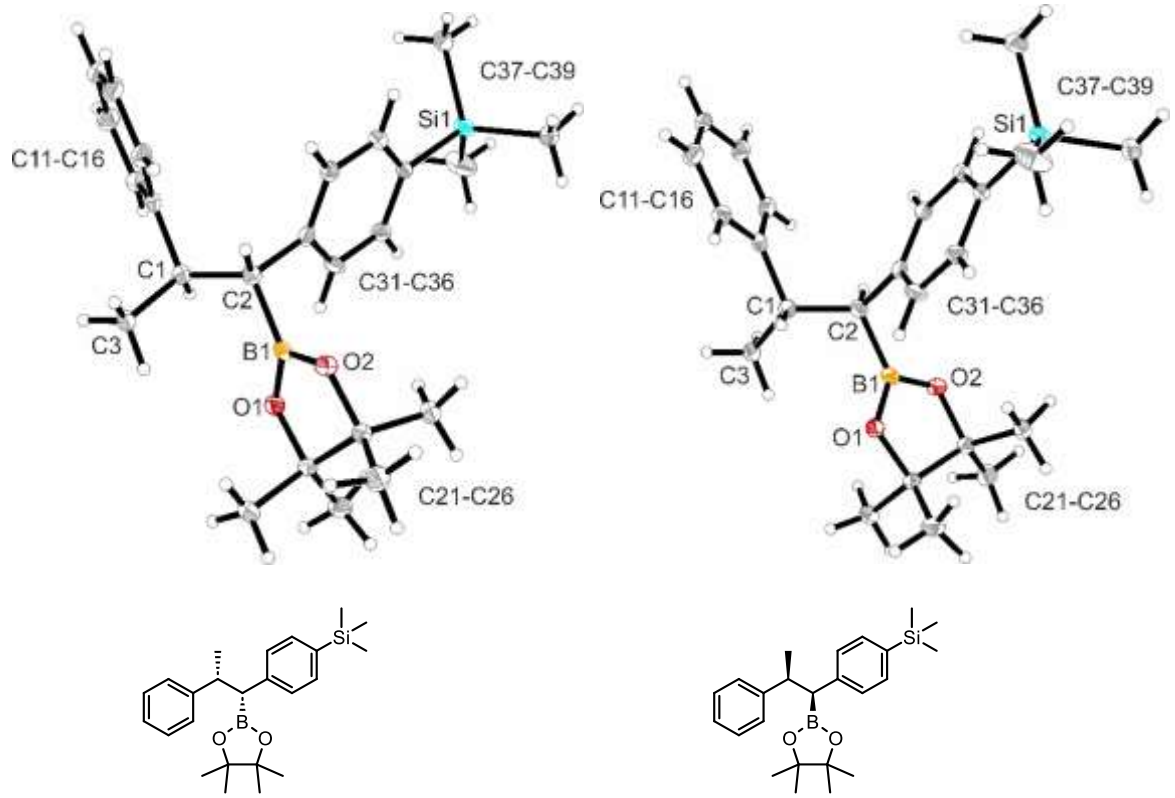


Figure S3: Crystal structure of compound **3bc**.

The structure was solved using the centrosymmetric space group $P2_1/c$ (Z = 4). The asymmetric unit of compound **3bc** contains only one enantiomer (for example *R*,*R* at the chiral centres C1 and C2). Therefore overall a mixture in ration 1:1 of both enantiomers (*S*,*S* and *R*,*R* at the chiral centres C1 and C2) is present in the elementary cell. Thermal ellipsoids are shown at 30% probability.

For **3bm** (STU10506)

A colorless, plate-like specimen of $C_{23}H_{29}BO_4$, approximate dimensions 0.079 mm x 0.084 mm x 0.217 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1447 frames were collected. The total exposure time was 19.08 hours. The frames were integrated with the Bruker SAINT software package using a wide-

frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 36792 reflections to a maximum θ angle of 66.90° (0.84 Å resolution), of which 3698 were independent (average redundancy 9.949, completeness = 97.4%, R_{int} = 14.83%, R_{sig} = 5.71%) and 2030 (54.89%) were greater than $2\sigma(F^2)$. The final cell constants of a = 6.3808(7) Å, b = 12.5531(10) Å, c = 26.558(3) Å, β = 91.822(8)°, volume = 2126.2(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 4373 reflections above 20 σ(I) with 6.659° < 2θ < 133.0°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.839. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8760 and 0.9520. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{23}H_{29}BO_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 517 variables converged at R1 = 9.03%, for the observed data and wR2 = 27.77% for all data. The goodness-of-fit was 1.028. The largest peak in the final difference electron density synthesis was 0.599 $e^-/Å^3$ and the largest hole was -0.254 $e^-/Å^3$ with an RMS deviation of 0.057 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.188 g/cm^3 and F(000), 816 e^-. CCDC Nr.: 2293540.

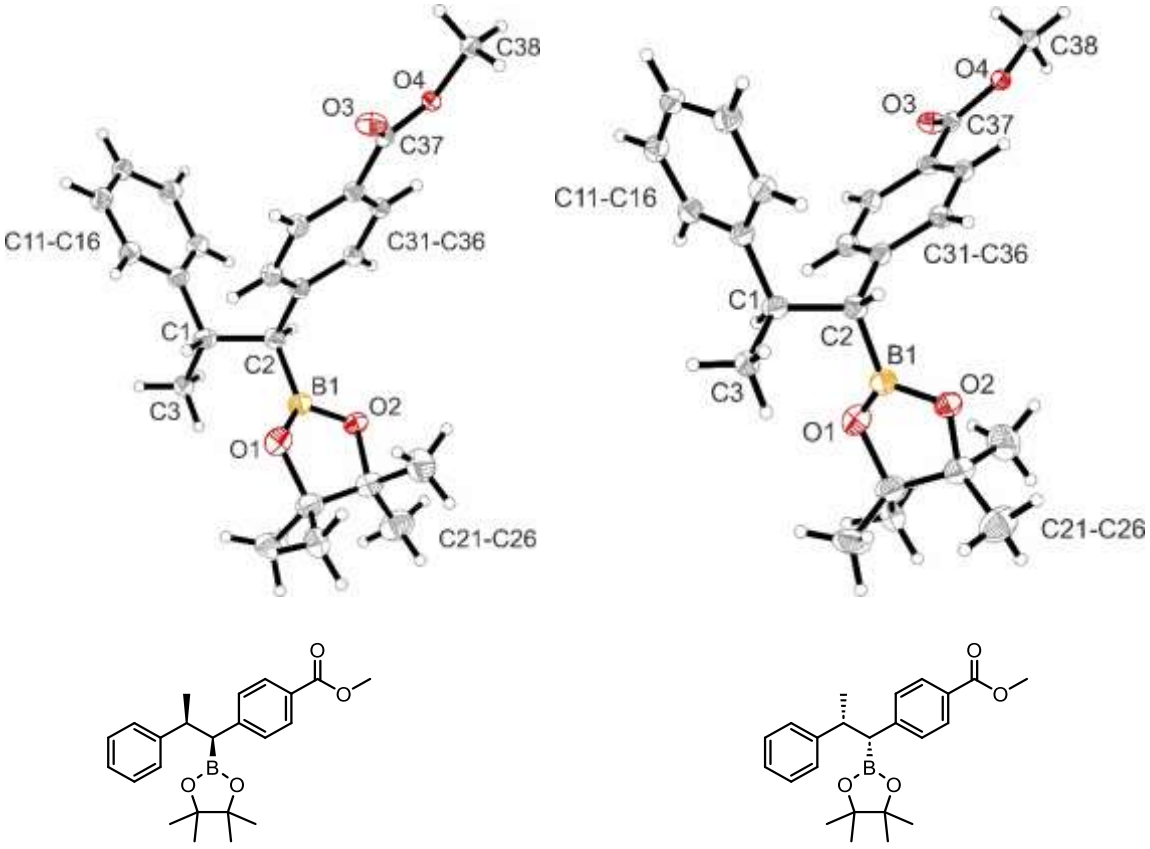
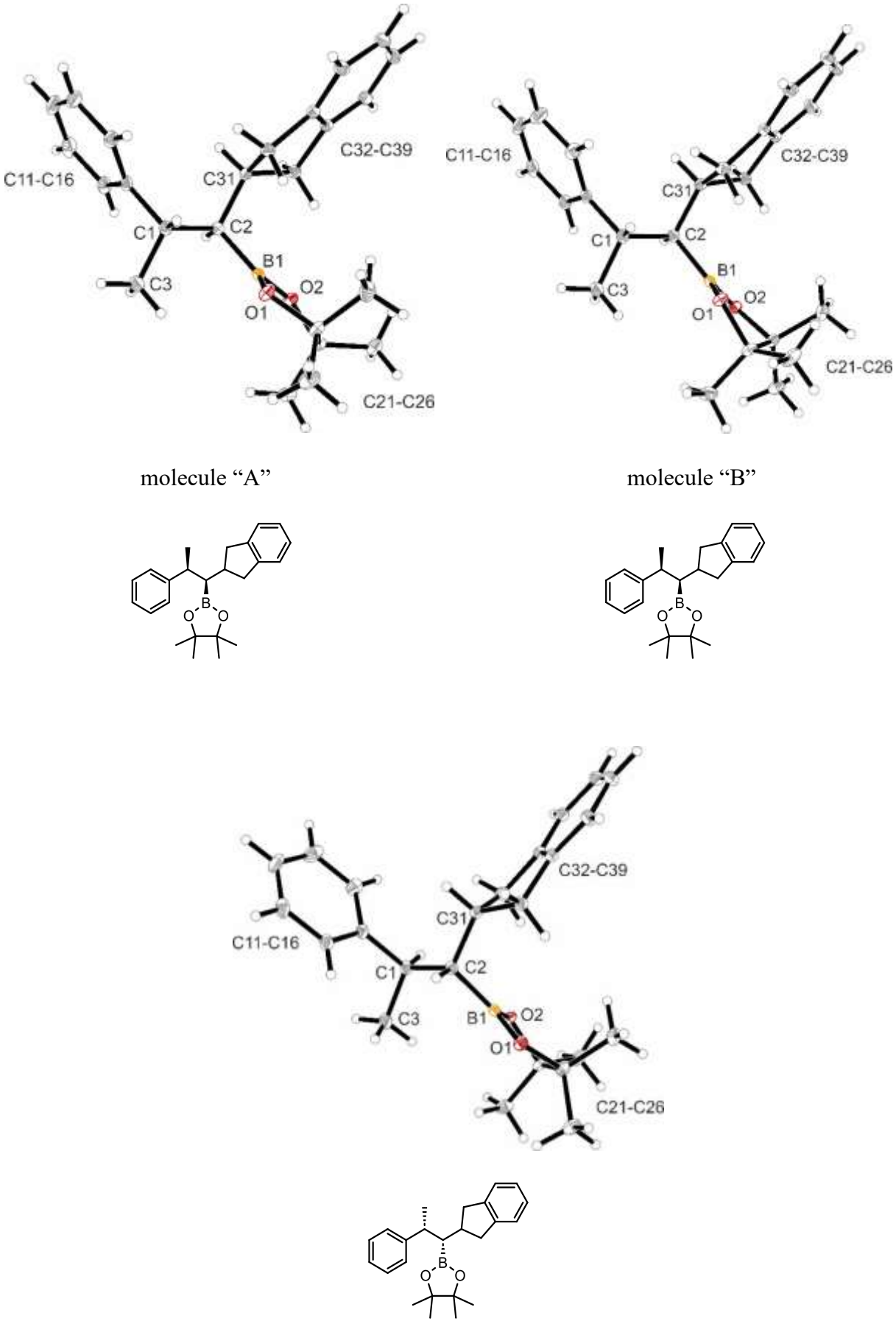


Figure S4: Crystal structure of compound **3bm**.

The structure was solved using the centrosymmetric space group $P2_1/n$ (Z = 4) and presents one molecule of compound **3bm** disordered over two positions in the asymmetric unit. Therefore, the asymmetric unit of compound **3bm** contains both enantiomers (*S,S* and *R,R* at the chiral centres C1 and C2) in ratio 65/35. Thermal ellipsoids are shown at 30% probability.

For **5aa** (STU10509)

A colorless, prism-like specimen of $C_{24}H_{31}BO_2$, approximate dimensions 0.111 mm x 0.158 mm x 0.192 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1752 frames were collected. The total exposure time was 22.62 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 86706 reflections to a maximum θ angle of 66.78° (0.84 Å resolution), of which 7501 were independent (average redundancy 11.559, completeness = 99.6%, R_{int} = 8.47%, R_{sig} = 3.37%) and 5725 (76.32%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 12.9545(5) Å, $\underline{b}$ = 20.8834(8) Å, $\underline{c}$ = 16.8105(7) Å, β = 110.893(2)°, volume = 4248.8(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9990 reflections above 20 σ(I) with 7.042° < 2θ < 133.4°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.899. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9050 and 0.9430. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 8 for the formula unit, $C_{24}H_{31}BO_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 497 variables converged at R1 = 4.29%, for the observed data and wR2 = 10.63% for all data. The goodness-of-fit was 1.028. The largest peak in the final difference electron density synthesis was 0.233 $e^-/Å^3$ and the largest hole was -0.201 $e^-/Å^3$ with an RMS deviation of 0.040 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.133 g/cm^3 and F(000), 1568 e^-. CCDC Nr.: 2293541.



molecule “A” molecule “B”

Figure S5: Crystal structure of compound **5aa**.

The structure was solved using the centrosymmetric space group $P2_1/c$ (Z = 8). The asymmetric unit of compound **5aa** contains two crystallographically independent molecules of one enantiomer (for example *S,R* at the chiral centres C1 and C2). Therefore overall a mixture in ratio 1:1 of both enantiomers (*S,R* and *R,S* at the chiral centres C1 and C2) is present in the elementary cell. Thermal ellipsoids are shown at 30% probability.

For **5ak** (STU10510)

A yellow, prism-like specimen of $C_{27}H_{35}BFeO_2$, approximate dimensions 0.078 mm x 0.154 mm x 0.335 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1167 frames were collected. The total exposure time was 6.65 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 20319 reflections to a maximum θ angle of 66.65° (0.84 Å resolution), of which 4219 were independent (average redundancy 4.816, completeness = 98.9%, R_{int} = 5.80%, R_{sig} = 4.04%) and 3629 (86.02%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.8635(5) Å, b = 11.6173(6) Å, c = 12.5223(7) Å, α = 100.723(3)°, β = 106.987(3)°, γ = 111.523(3)°, volume = 1205.26(11) $Å^3$, are based upon the refinement of the XYZ-centroids of 7164 reflections above 20 σ(I) with 7.819° < 2θ < 133.3°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.619. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2770 and 0.6890. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{27}H_{35}BFeO_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 486 variables converged at R1 = 8.00%, for the observed data and wR2 = 22.11% for all data. The goodness-of-fit was 1.065. The largest peak in the final difference electron density synthesis was 1.242 $e^-/Å^3$ and the largest hole was -1.573 $e^-/Å^3$ with an RMS deviation of 0.087 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.263 g/cm^3 and F(000), 488 e^-. CCDC Nr.: 2293542.

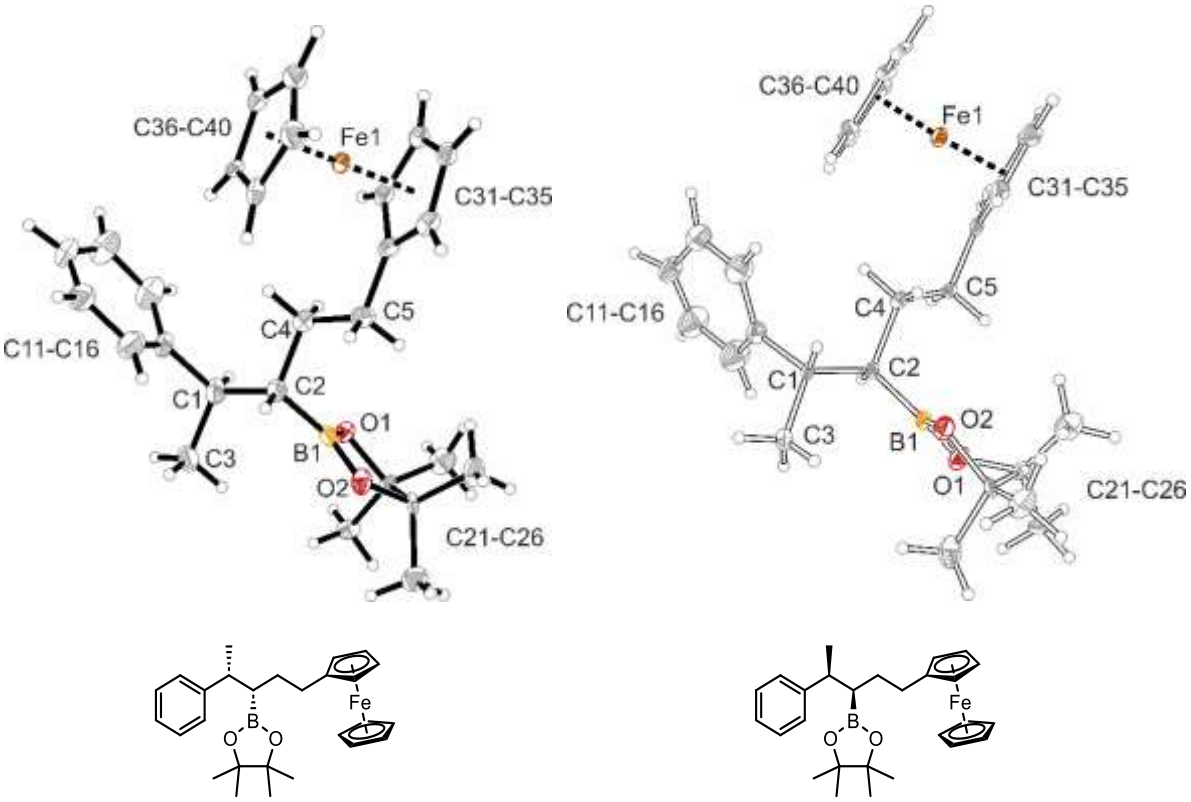
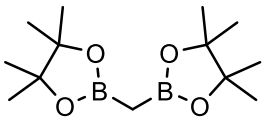


Figure S6: Crystal structure of compound **5ak**.

The structure was solved using the centrosymmetric space group *P*-1 (Z = 2) and presents one molecule of compound **5ak** disordered over two positions in the asymmetric unit. Therefore, the asymmetric unit of compound **5ak** contains a mixture of two enantiomers (*S*,*R* and *R*,*S* at the chiral centres C1 and C2) in ratio 69/31. Thermal ellipsoids are shown at 30% probability.

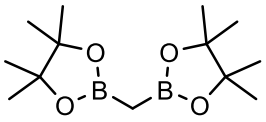
12 NMR Spectra

^{1}H-NMR (400 MHz, $CDCl_3$):



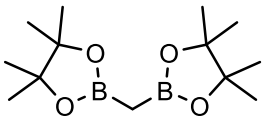
S1a

^{13}C-NMR (101 MHz, $CDCl_3$):



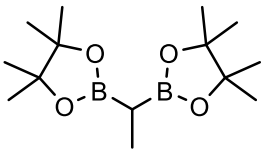
S1a

^{11}B-NMR (128 MHz, $CDCl_3$):



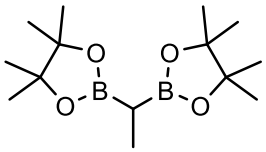
S1a

^{1}H-NMR (400 MHz, $CDCl_3$):



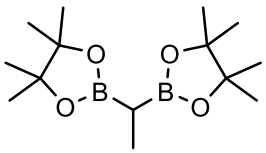
S1b

^{13}C-NMR (101 MHz, $CDCl_3$):



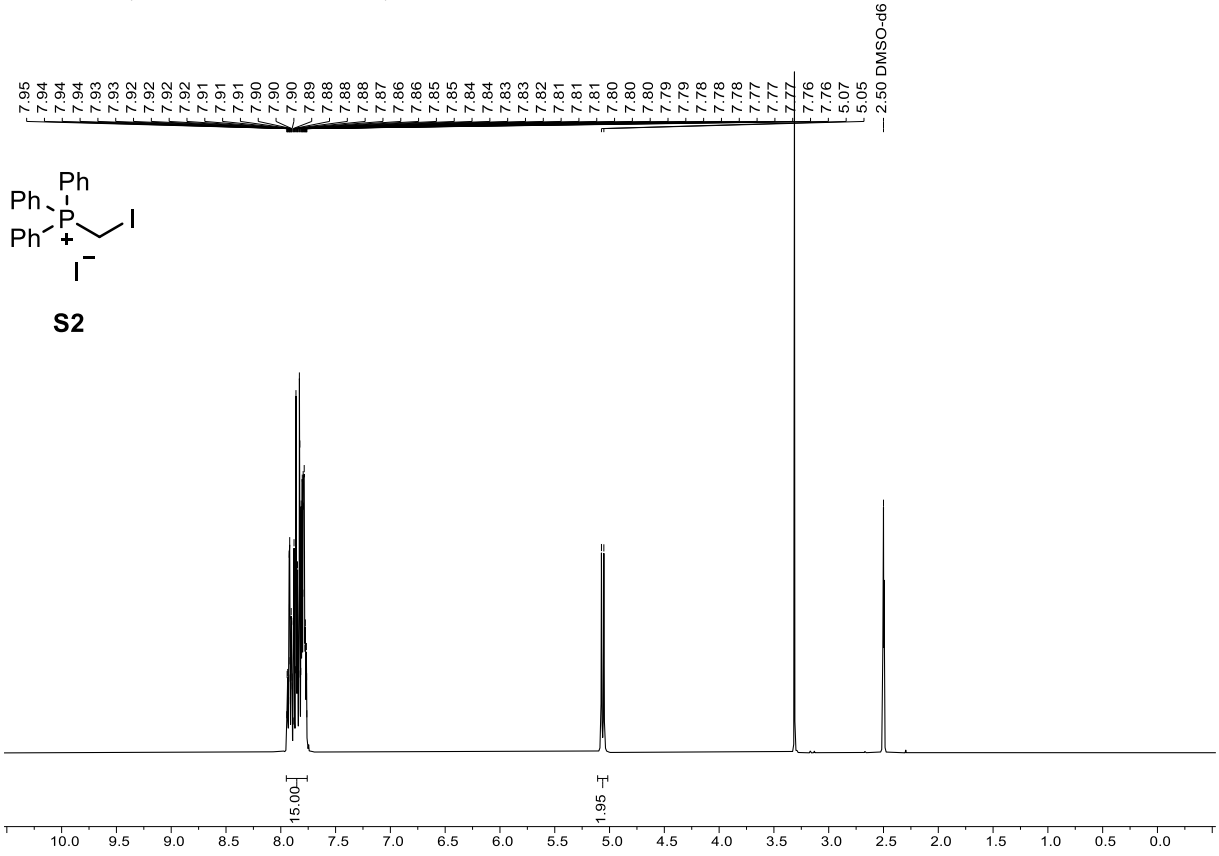
S1b

^{11}B-NMR (128 MHz, $CDCl_3$):

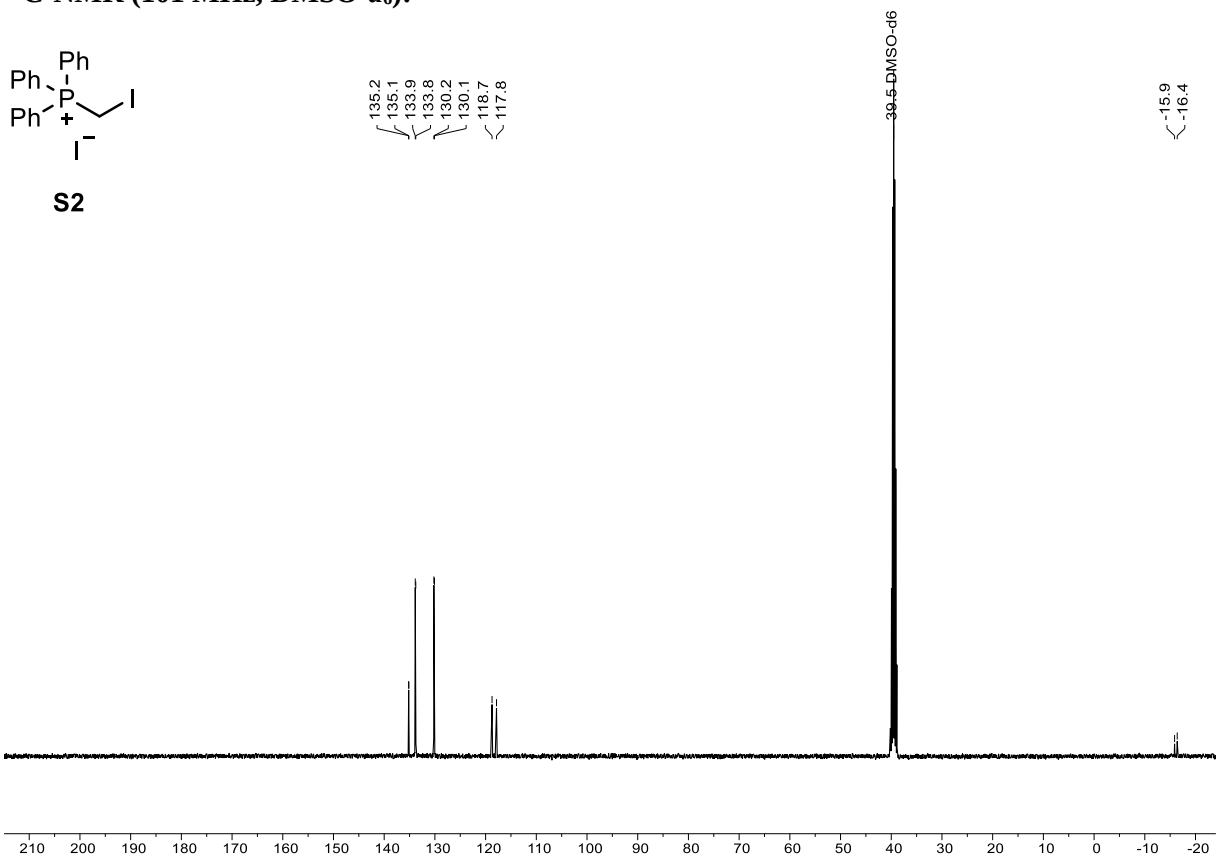


S1b

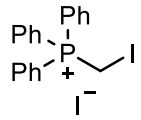
^{1}H-NMR (400 MHz, DMSO-d_6):



^{13}C-NMR (101 MHz, DMSO-d_6):

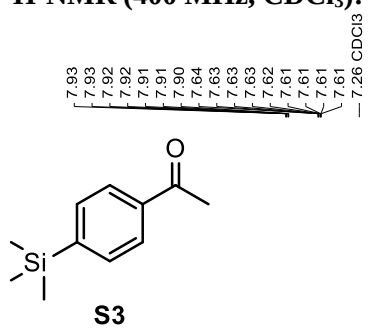


^{31}P-NMR (162 MHz, DMSO-d_6):



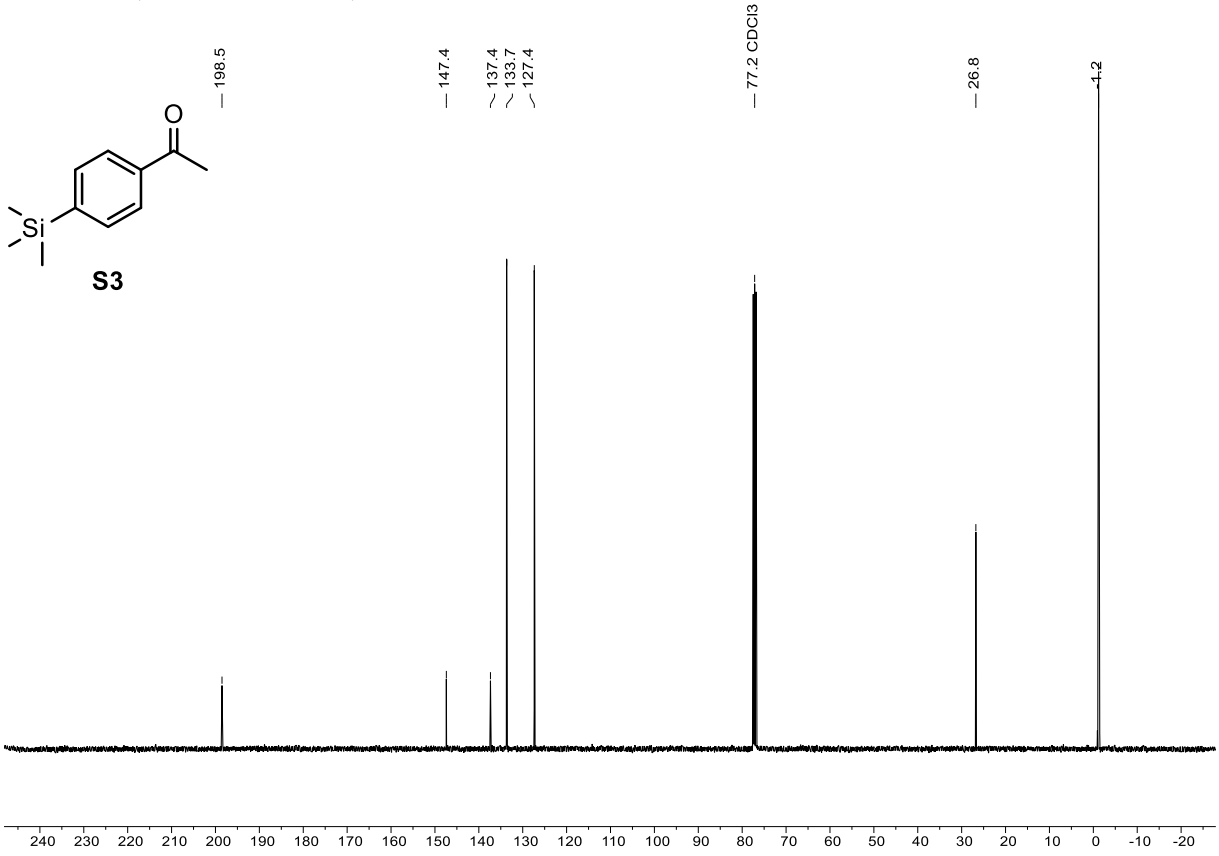
S2

^{1}H-NMR (400 MHz, $CDCl_3$):

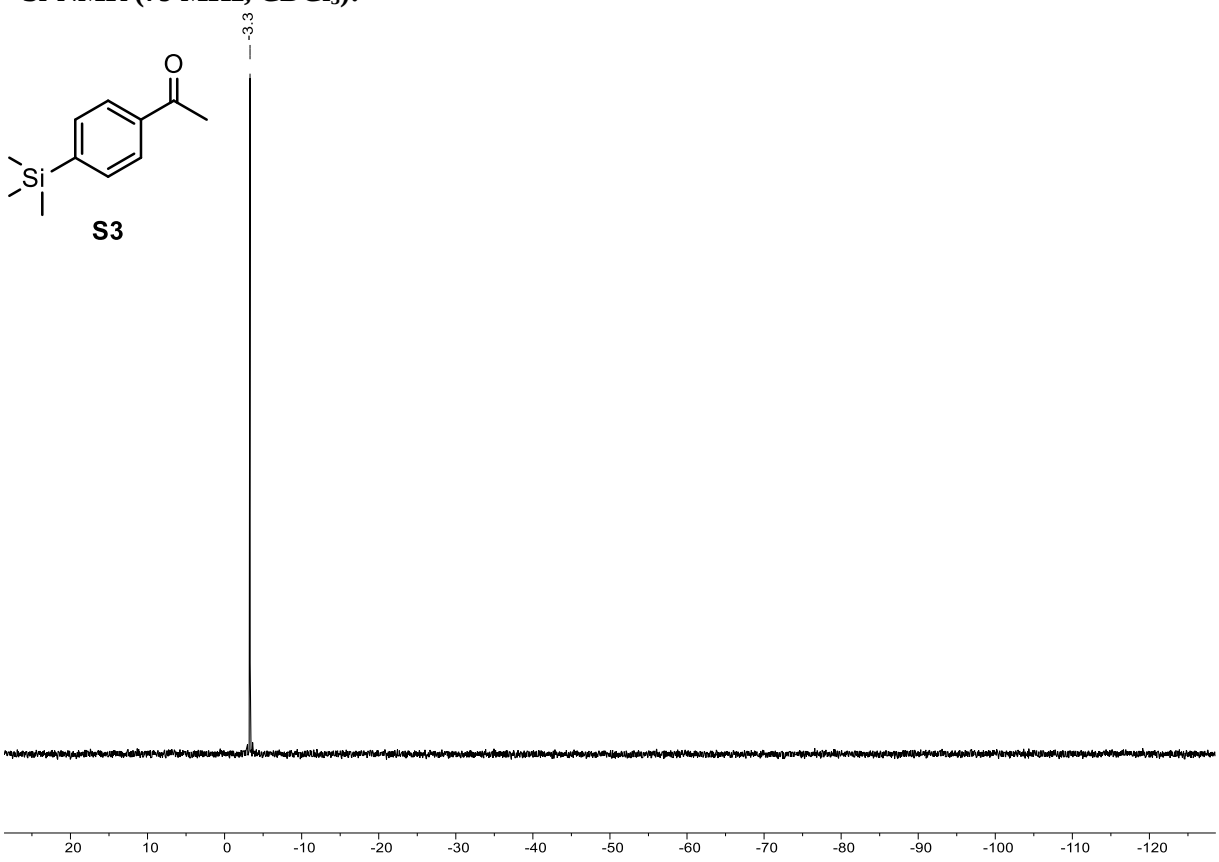


S3

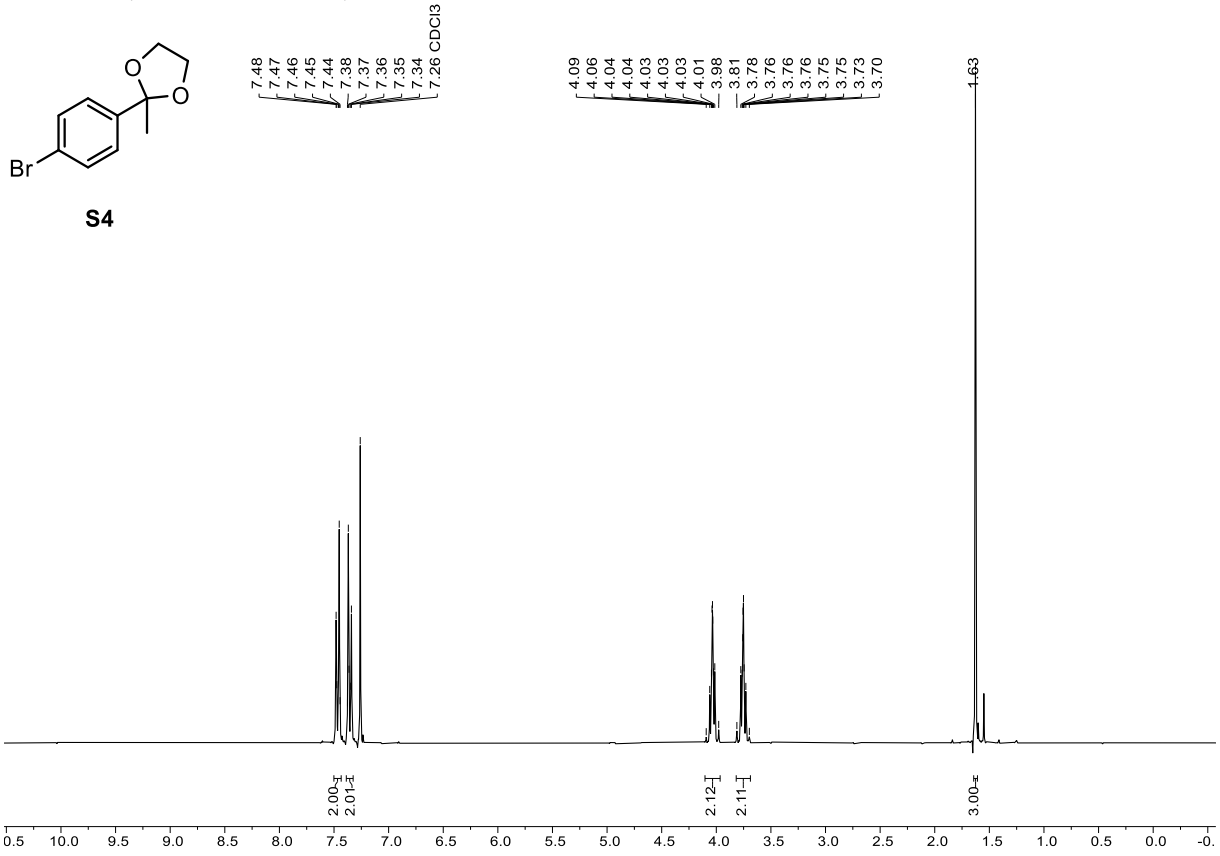
^{13}C-NMR (101 MHz, $CDCl_3$):



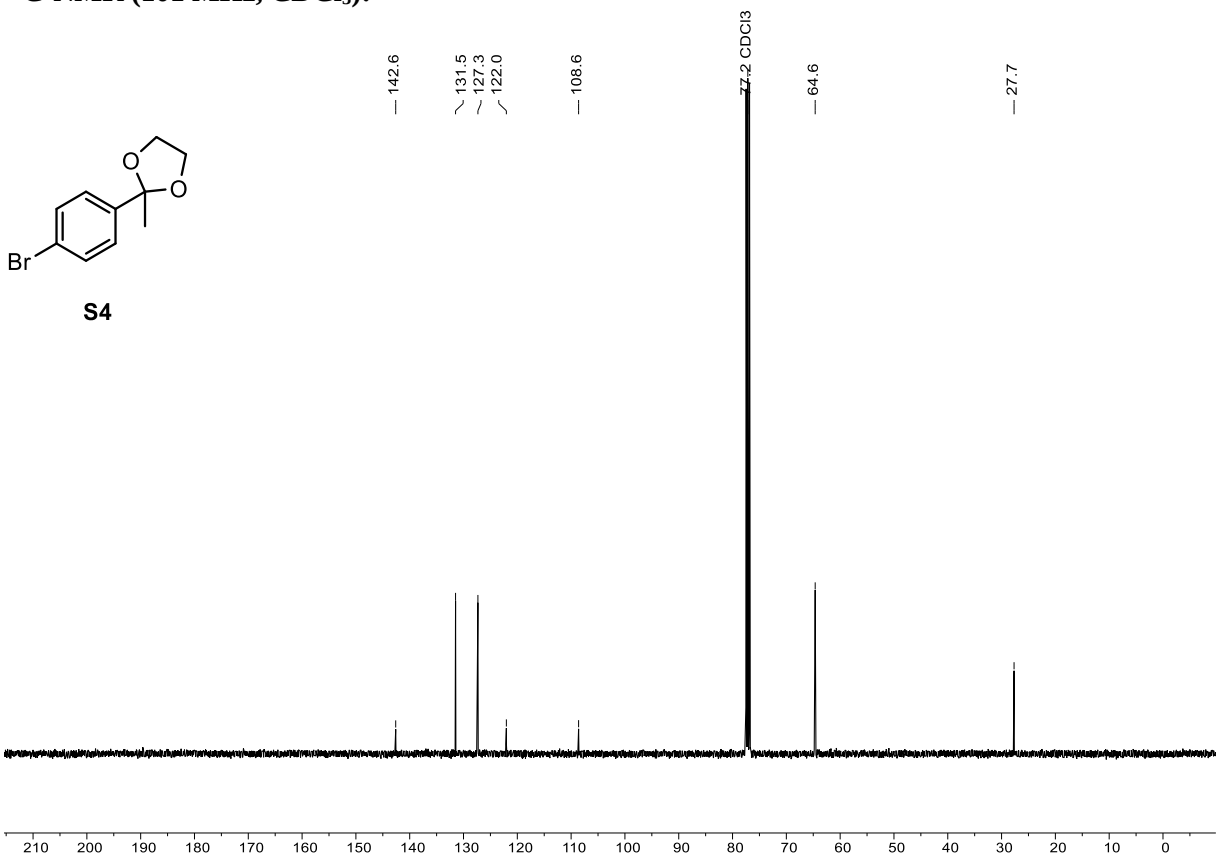
^{29}Si-NMR (79 MHz, $CDCl_3$):



^{1}H-NMR (300 MHz, $CDCl_3$):



^{13}C-NMR (101 MHz, $CDCl_3$):



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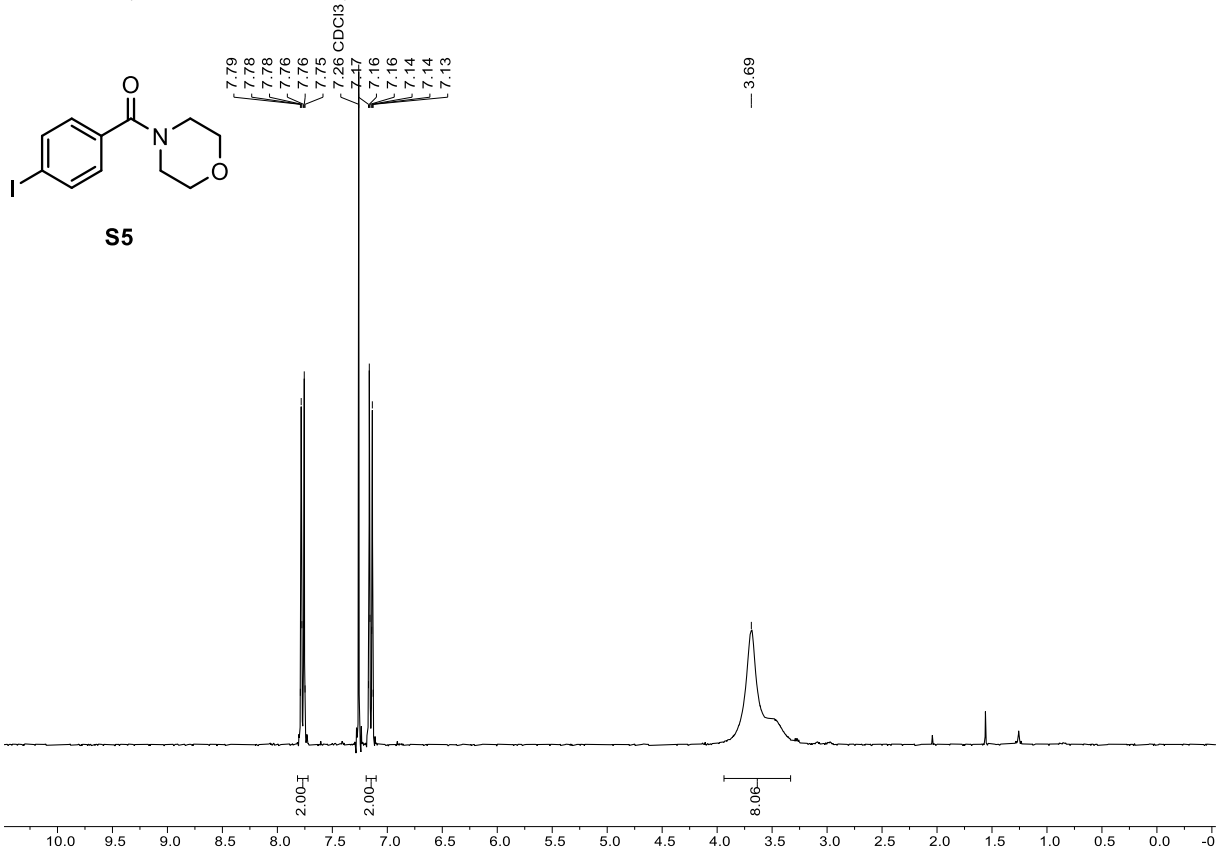
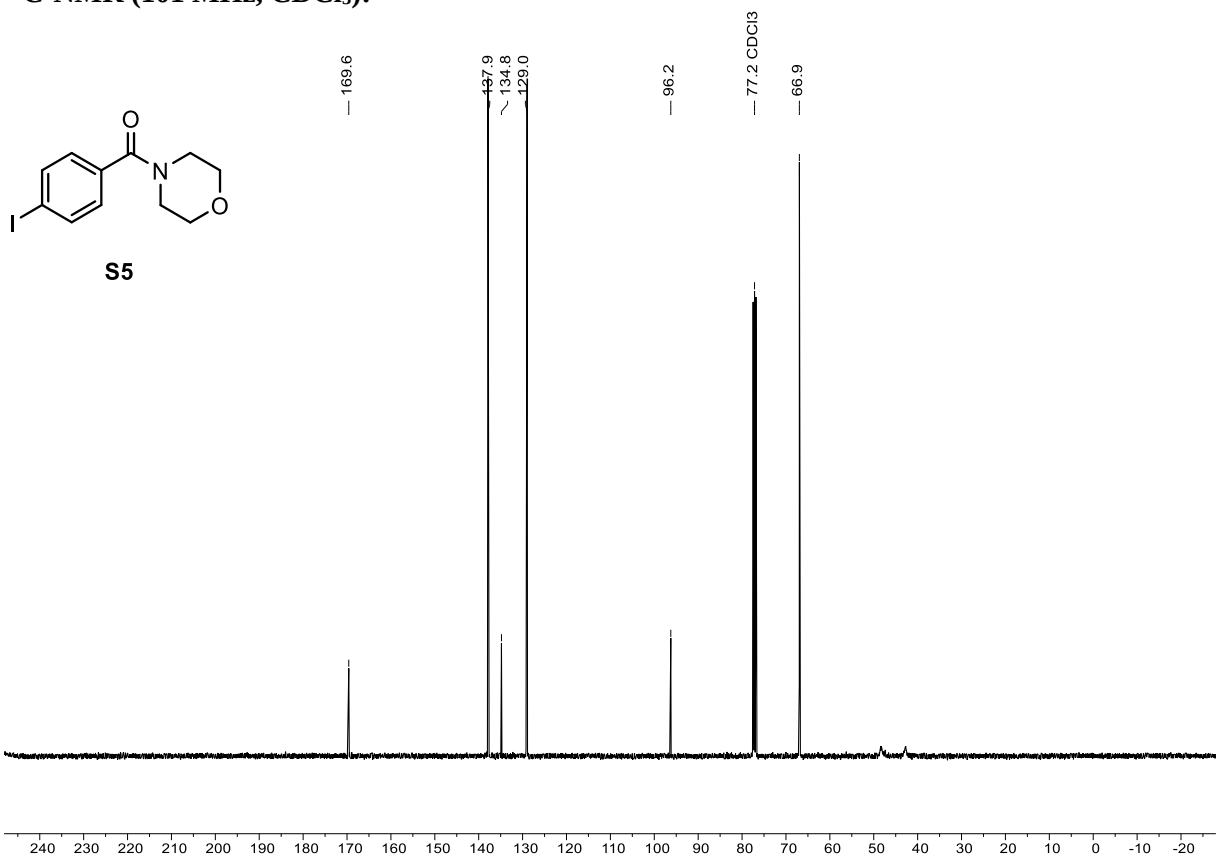
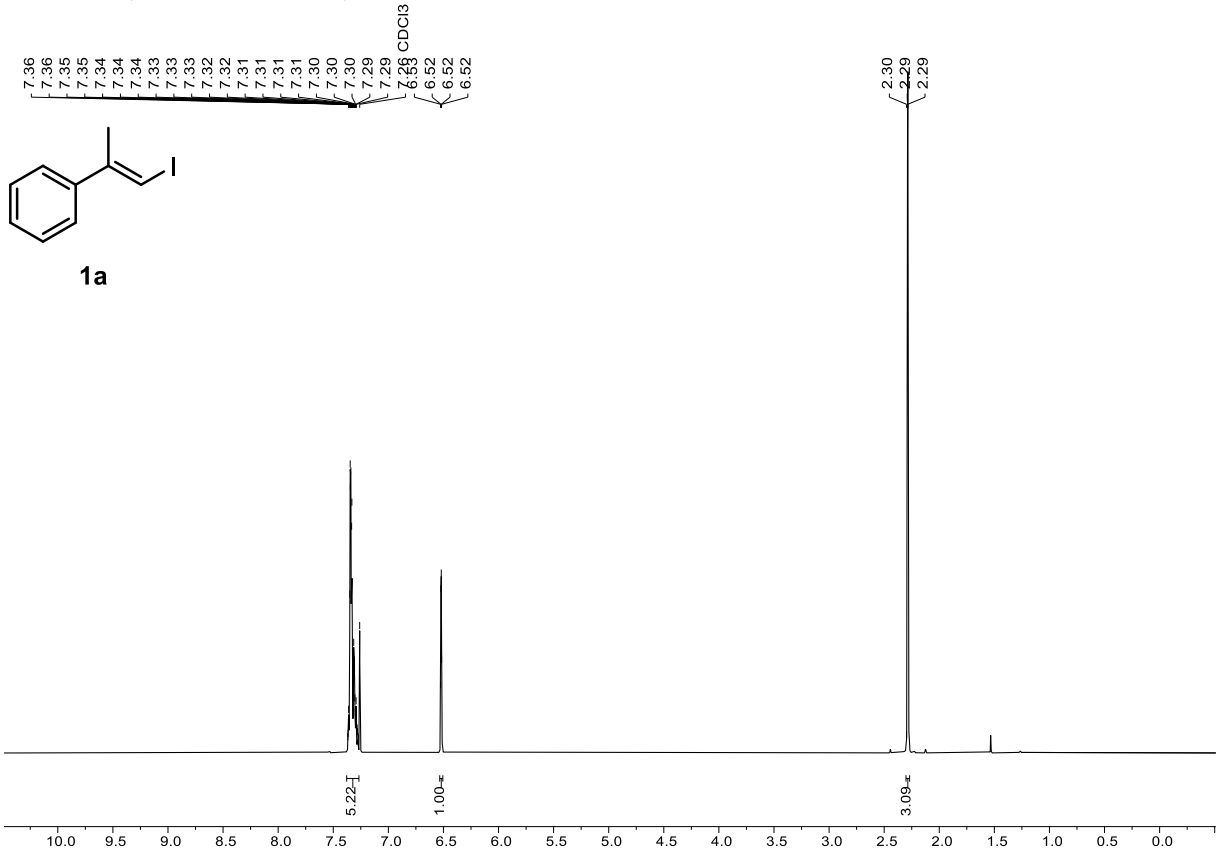


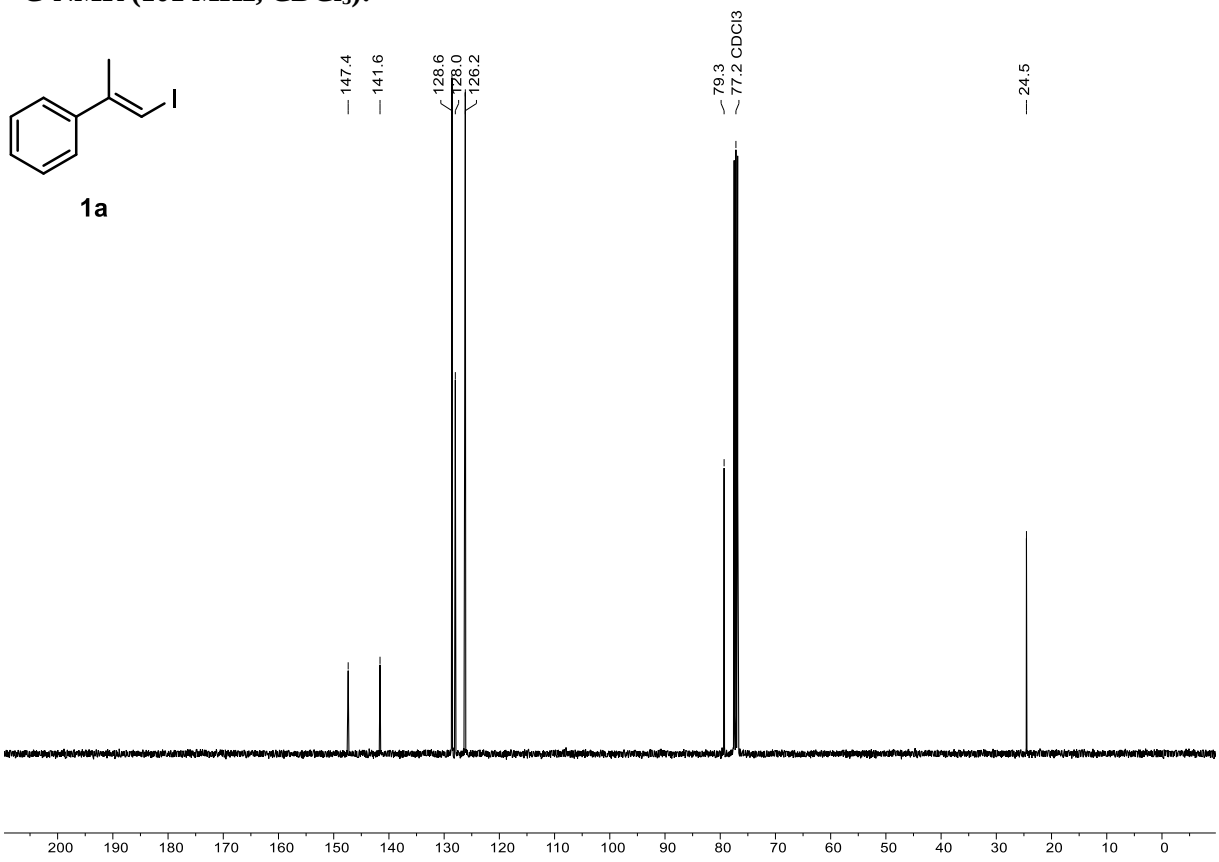
^{13}C-NMR (101 MHz, $CDCl_3$):



^{1}H-NMR (400 MHz, $CDCl_3$):



^{13}C-NMR (101 MHz, $CDCl_3$):



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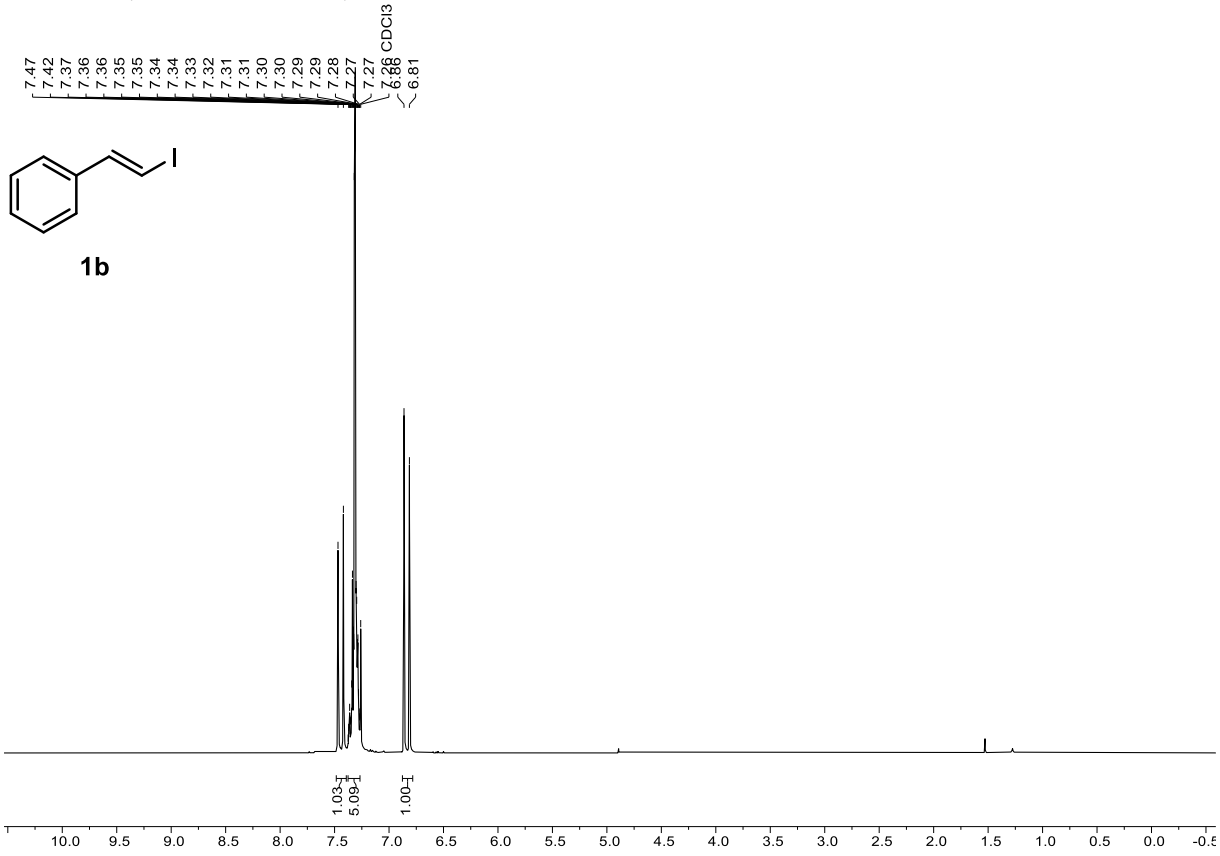
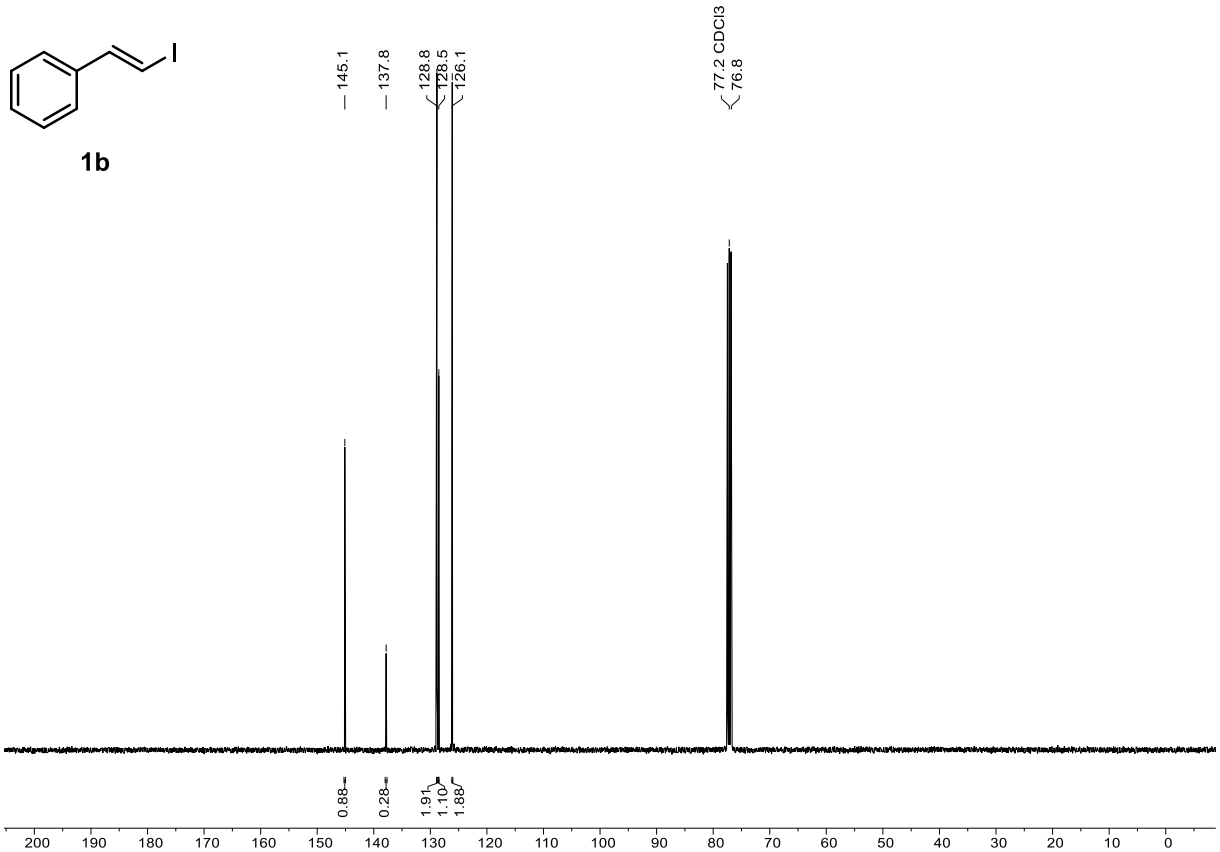
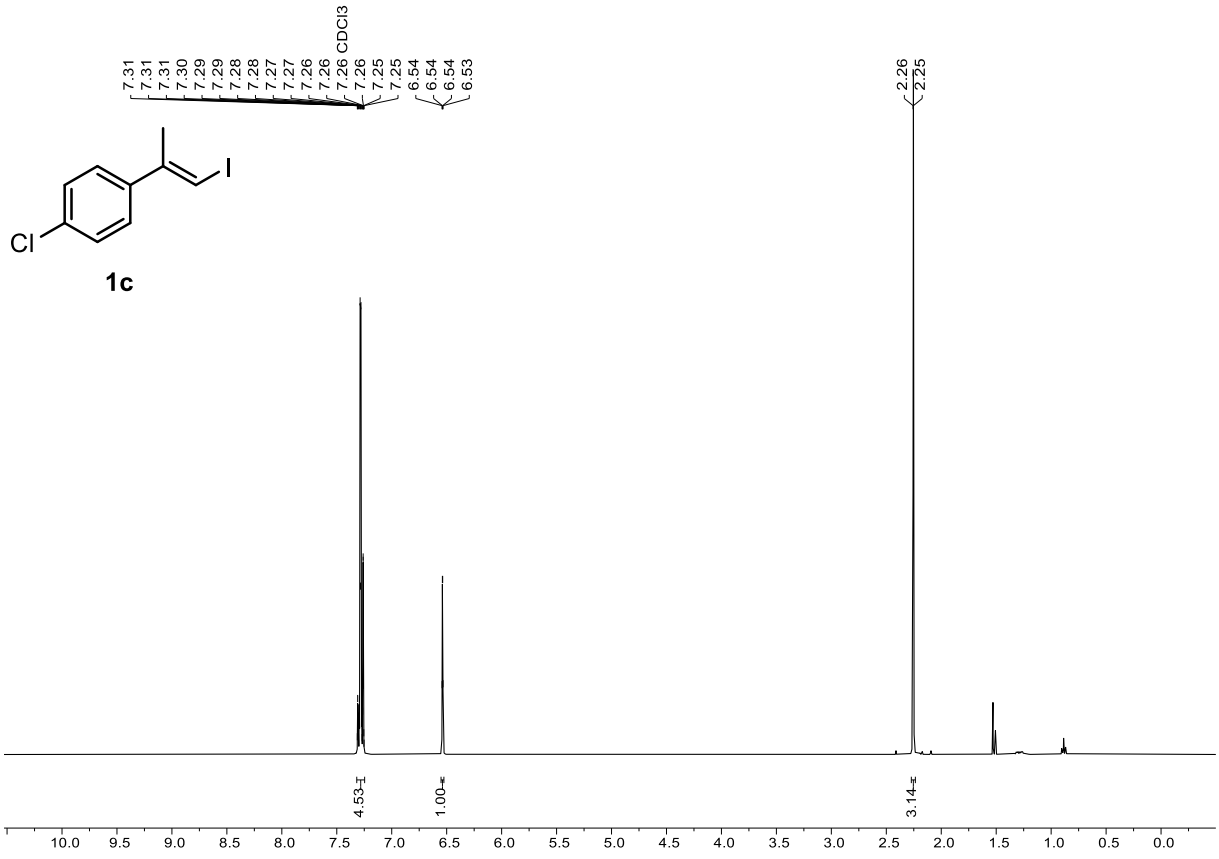


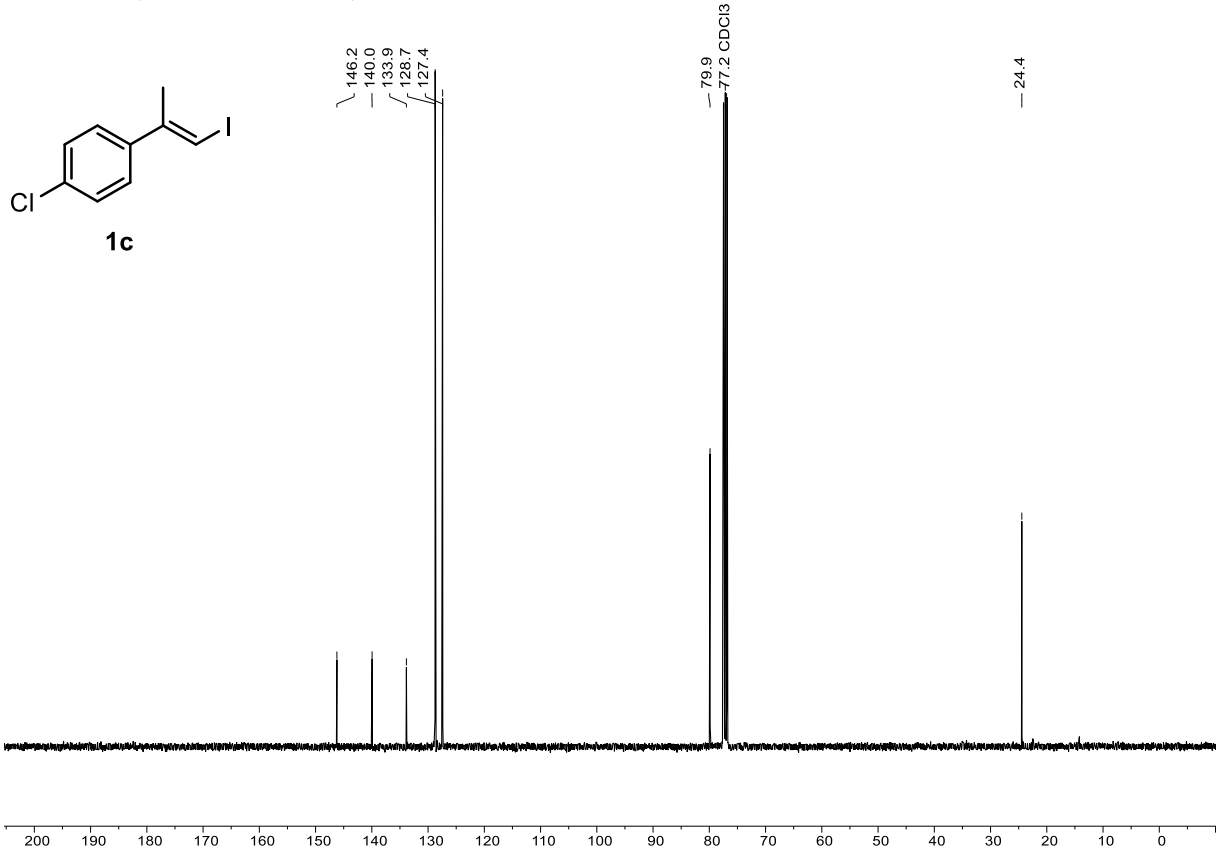
^{13}C-NMR (101 MHz, $CDCl_3$):



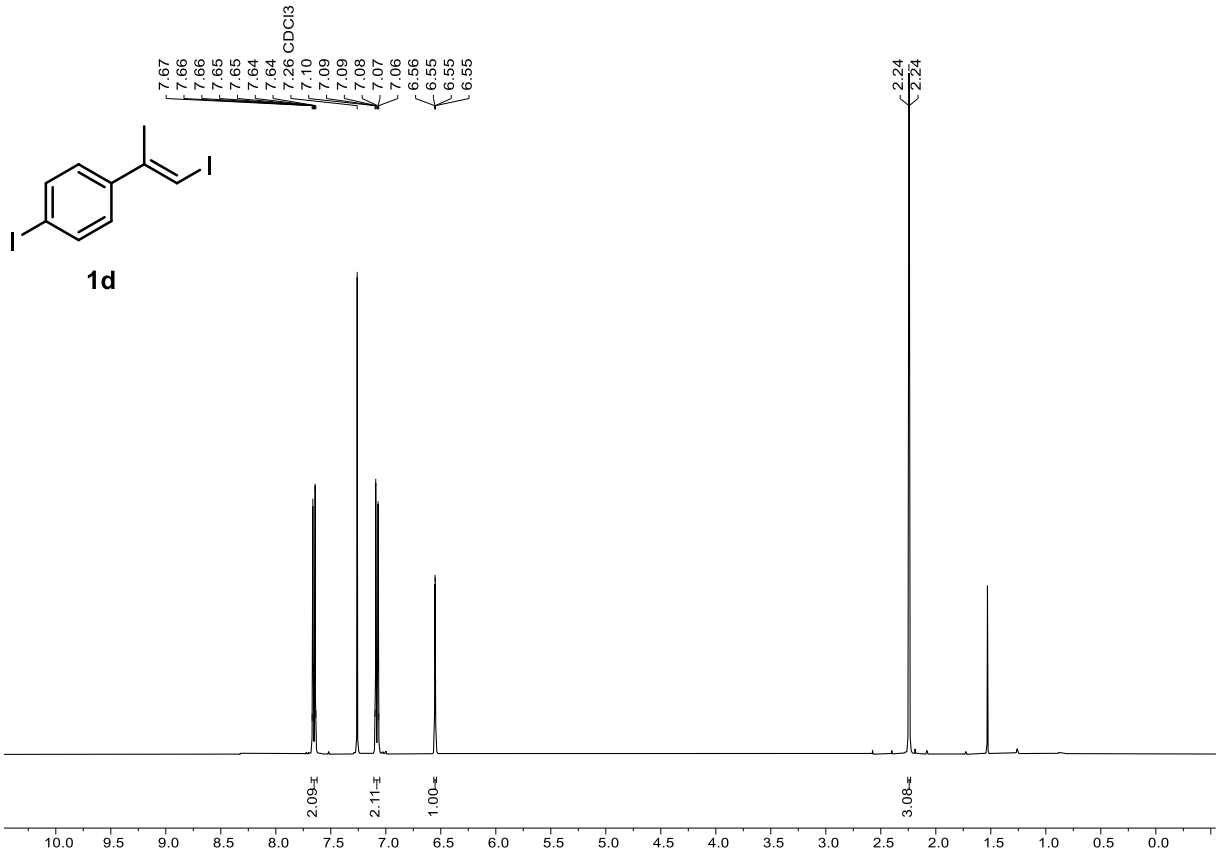
^{1}H-NMR (400 MHz, $CDCl_3$):



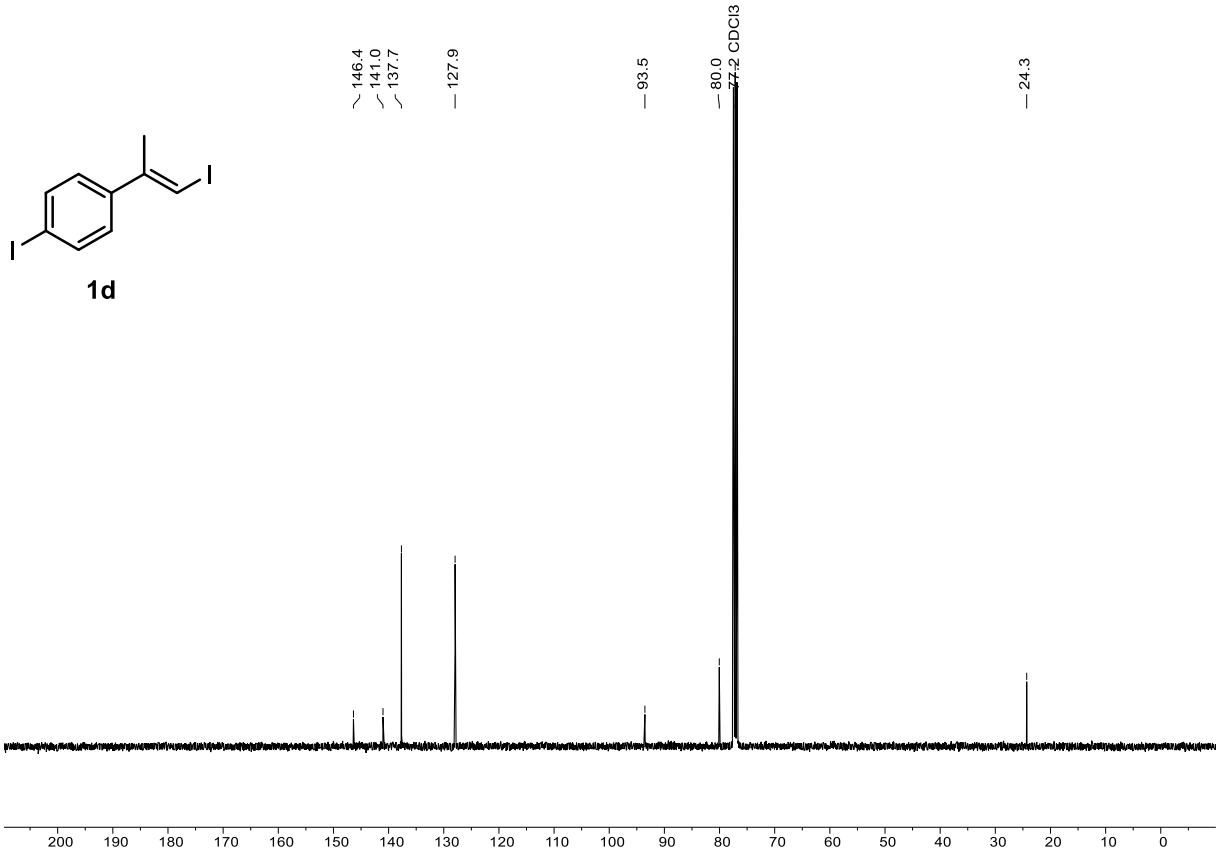
^{13}C-NMR (101 MHz, $CDCl_3$):



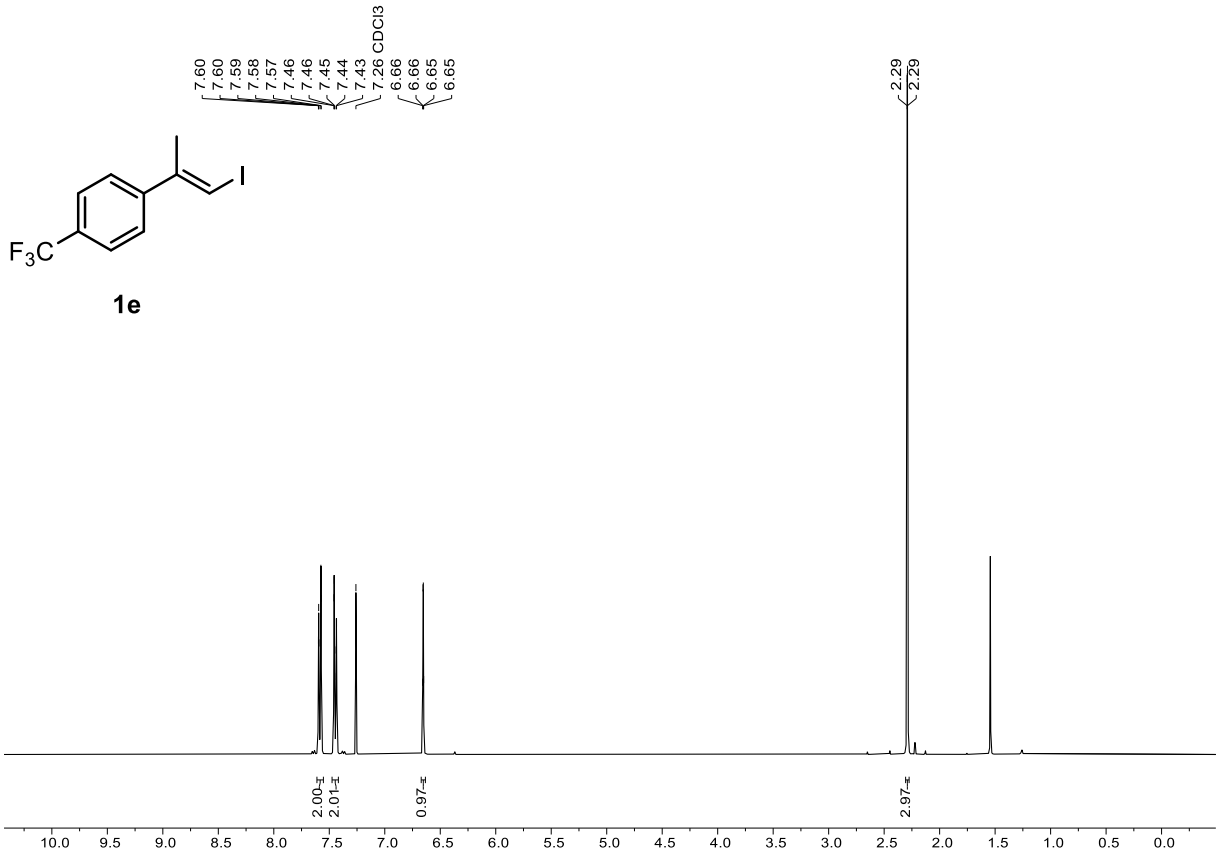
^{1}H-NMR (400 MHz, $CDCl_3$):



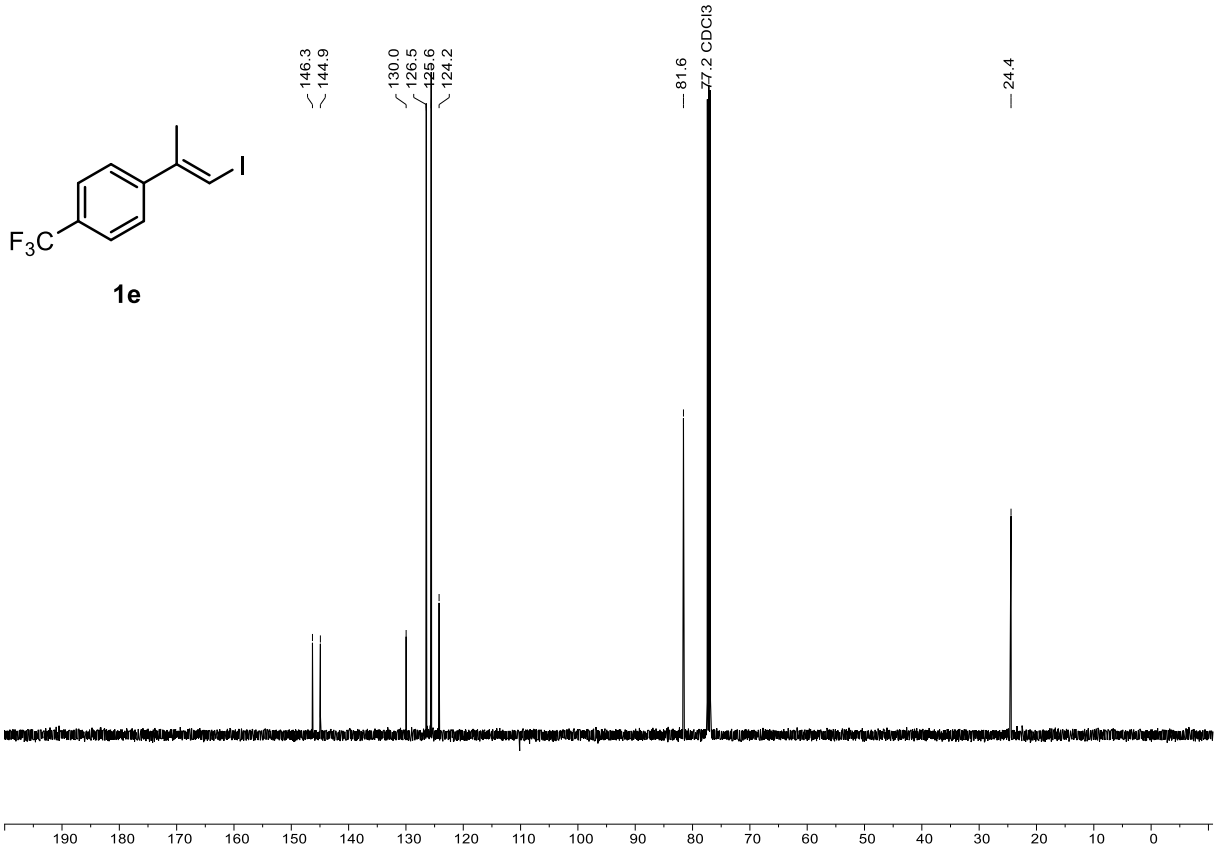
^{13}C-NMR (101 MHz, $CDCl_3$):



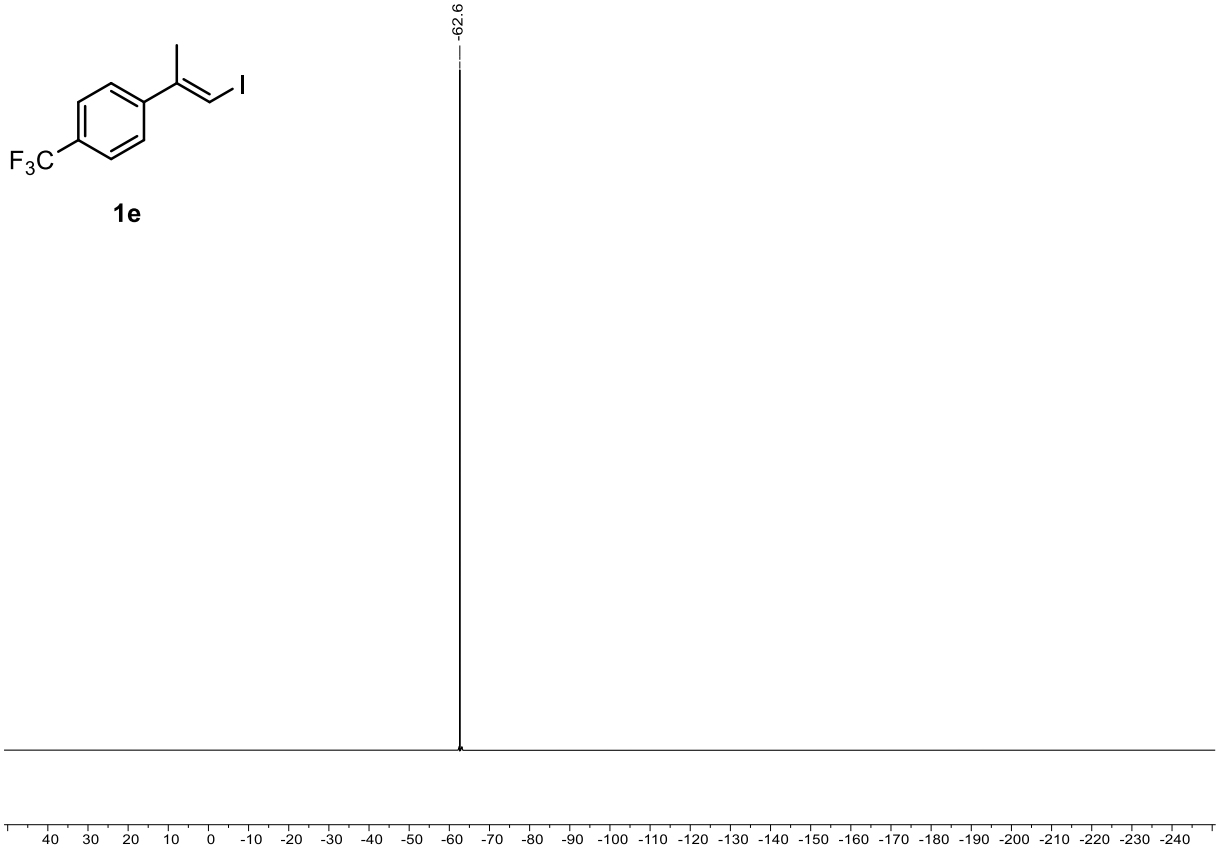
^{1}H-NMR (400 MHz, $CDCl_3$):



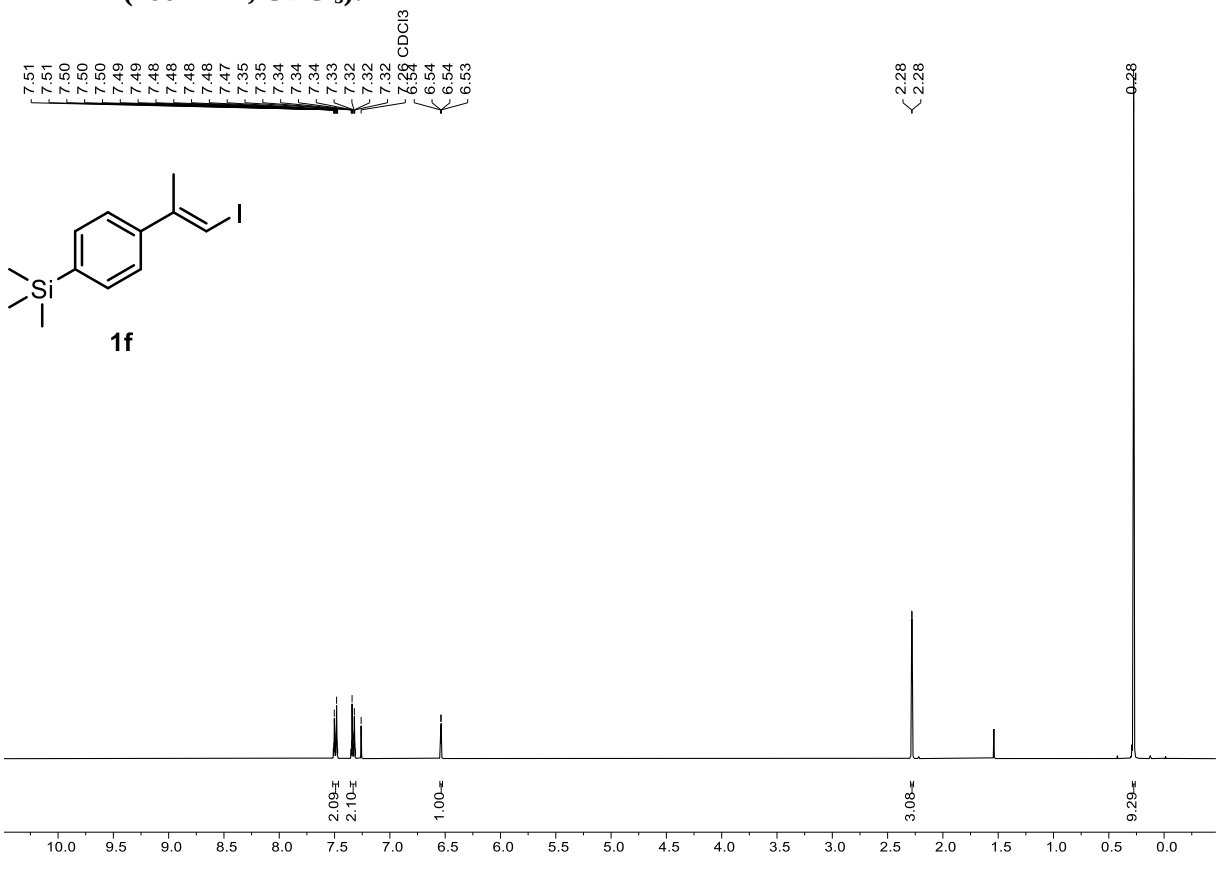
^{13}C-NMR (101 MHz, $CDCl_3$):



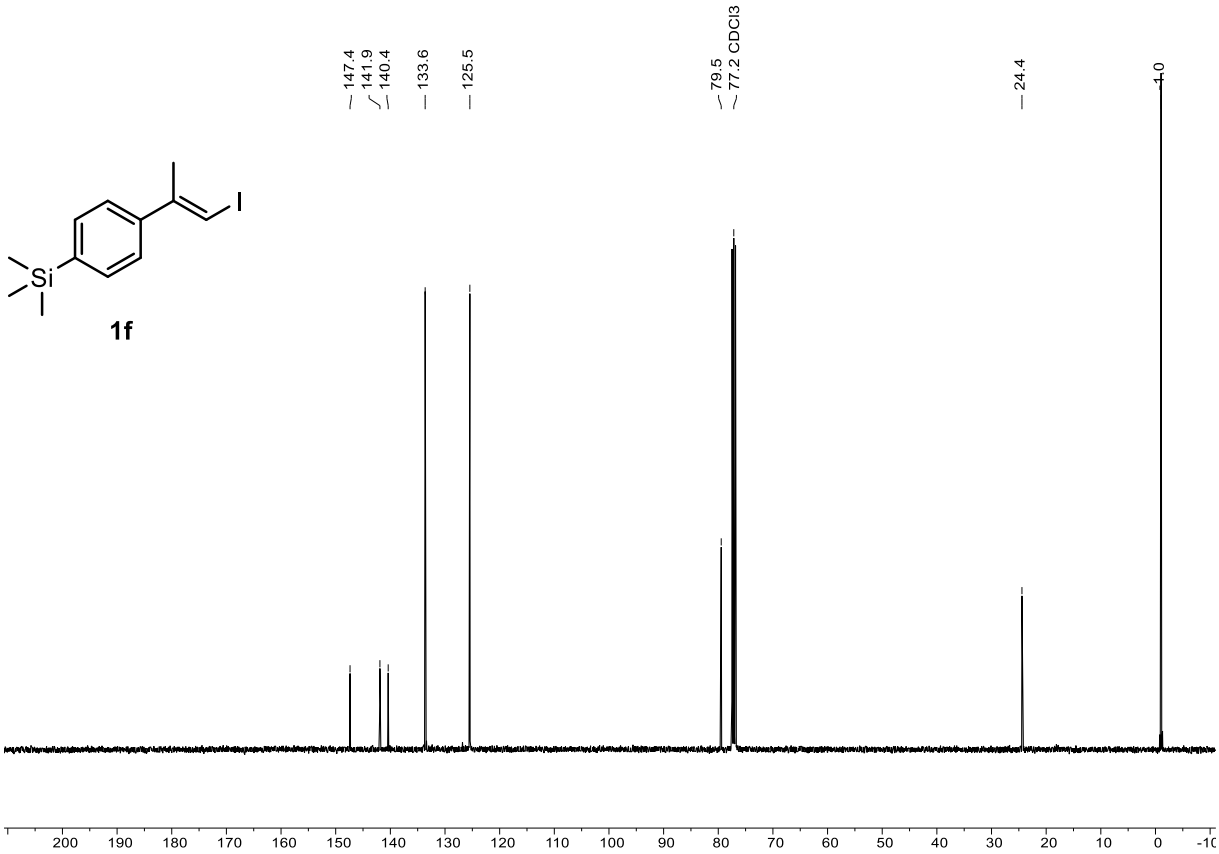
^{19}F-NMR (376 MHz, $CDCl_3$):



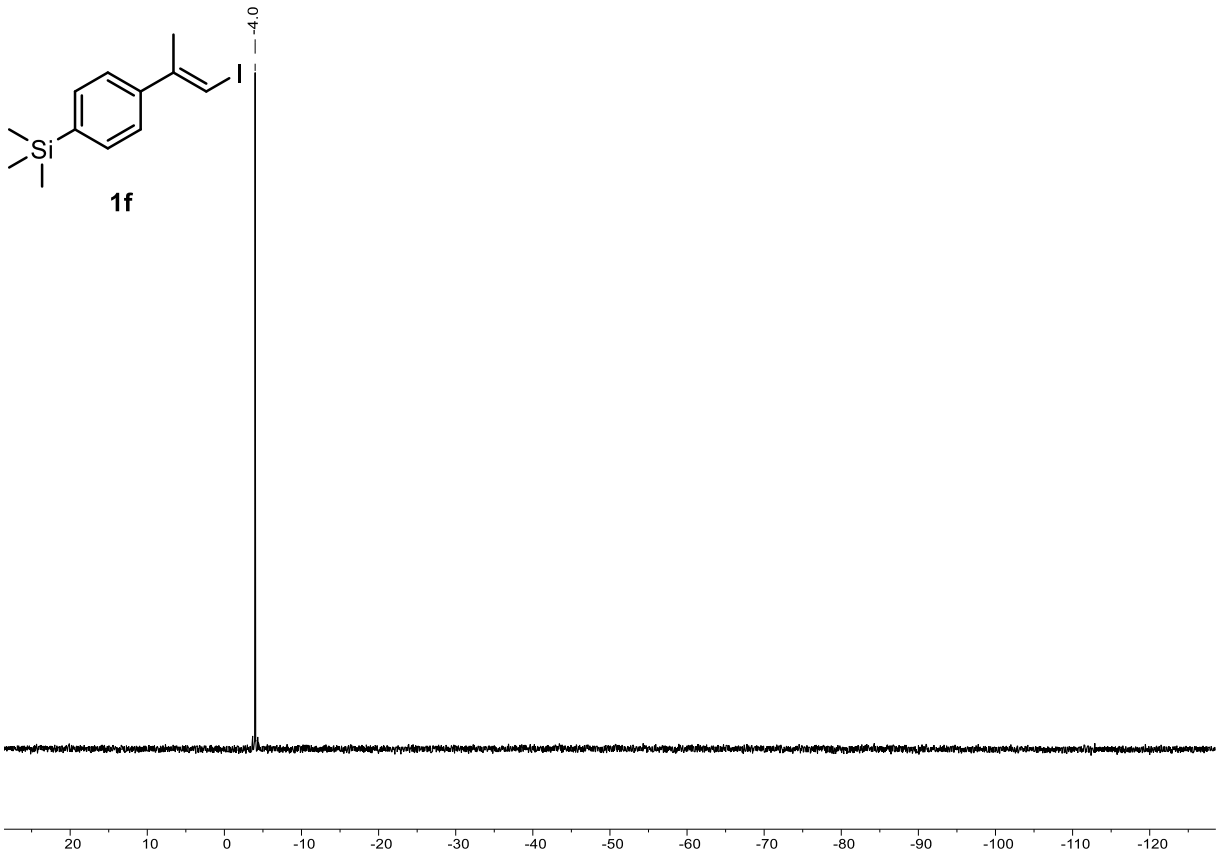
^{1}H-NMR (400 MHz, $CDCl_3$):



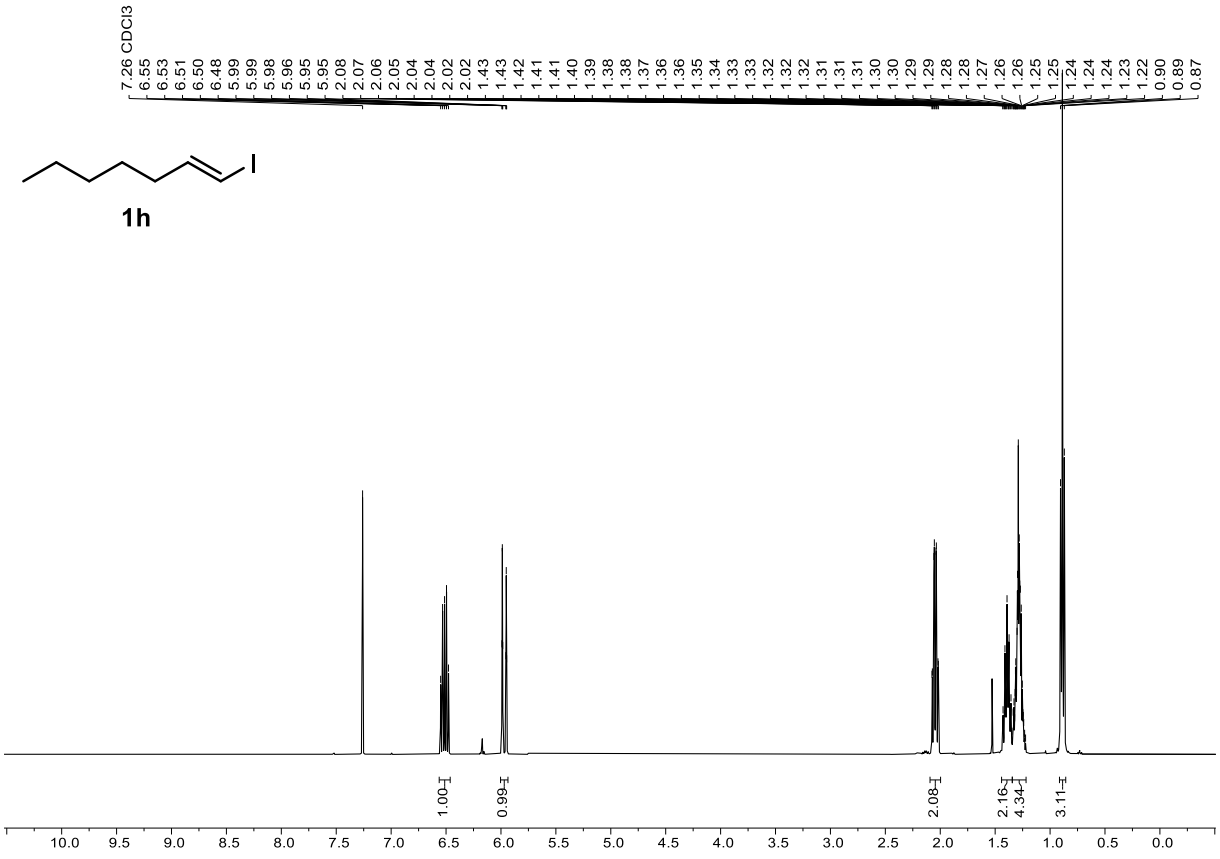
^{13}C-NMR (101 MHz, $CDCl_3$):



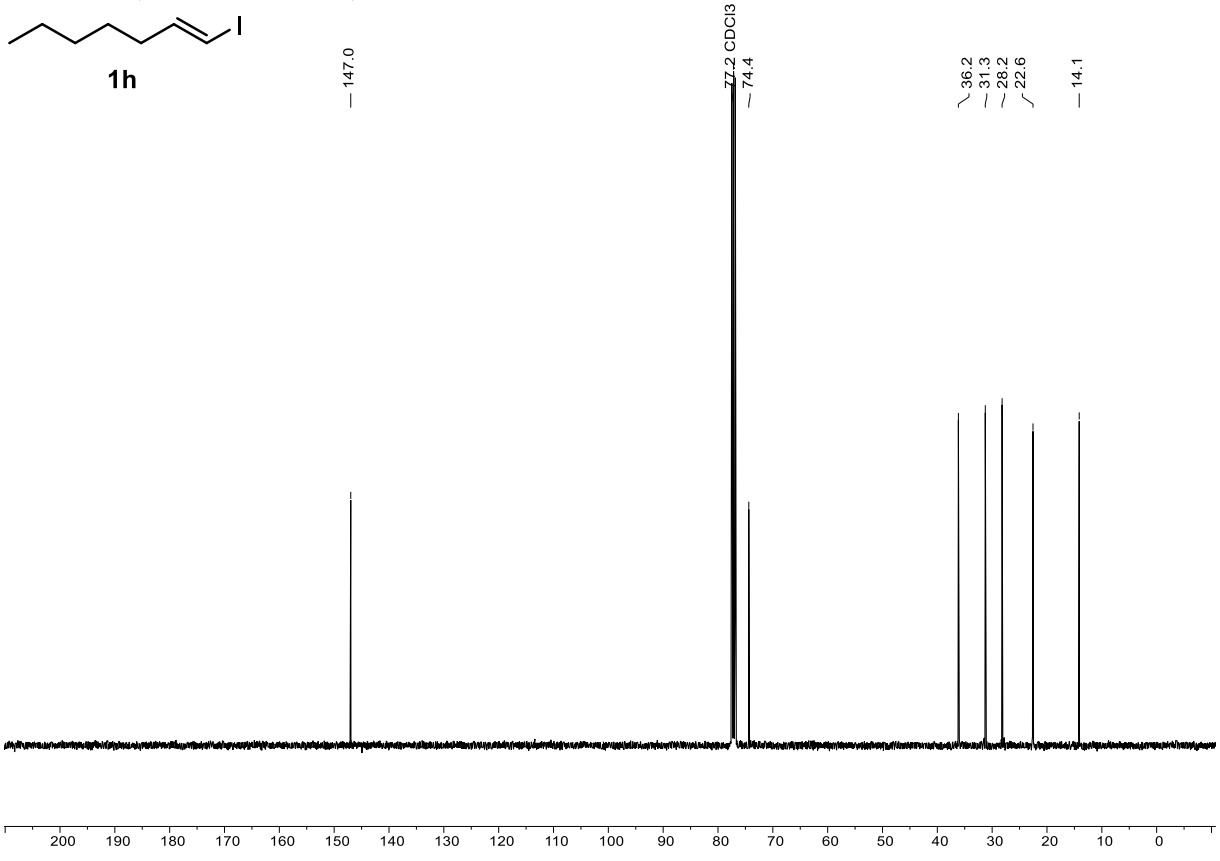
^{29}Si-NMR (80 MHz, $CDCl_3$):



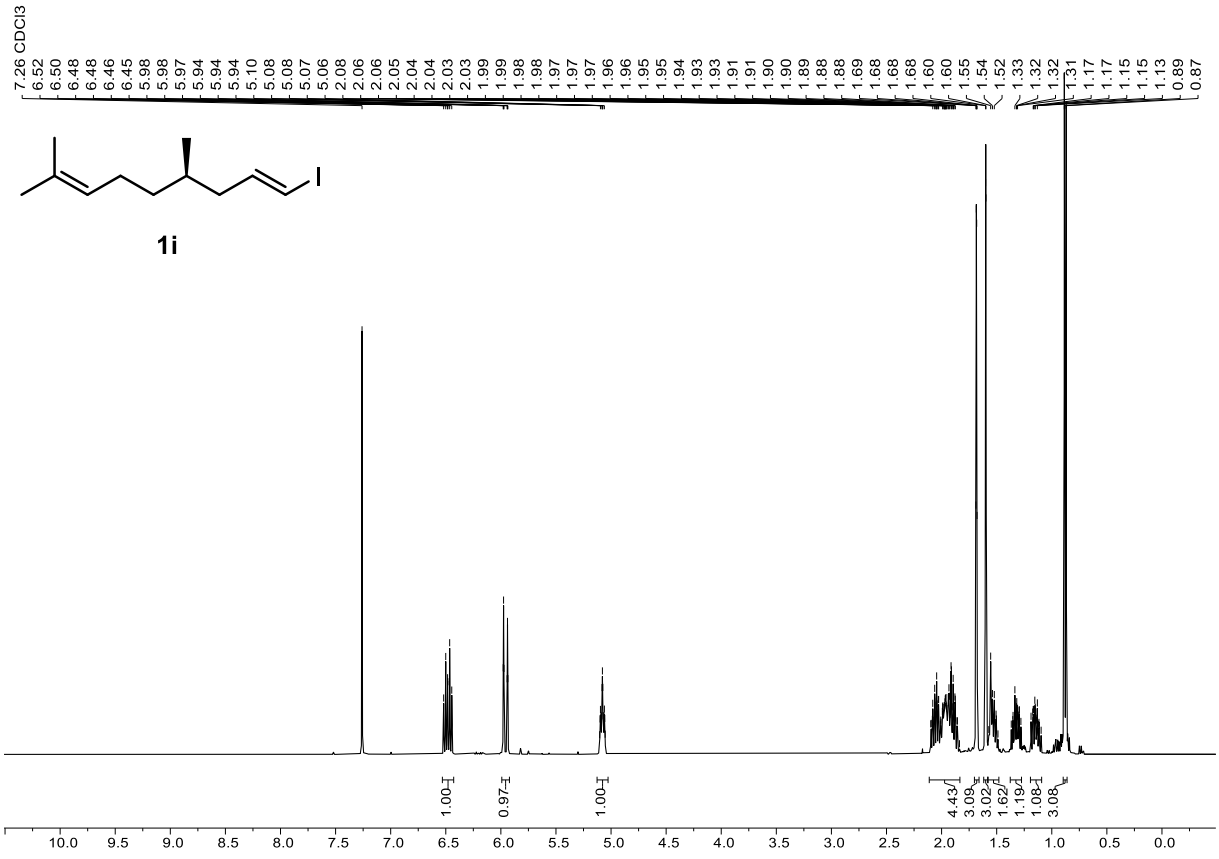
^{1}H-NMR (400 MHz, $CDCl_3$):



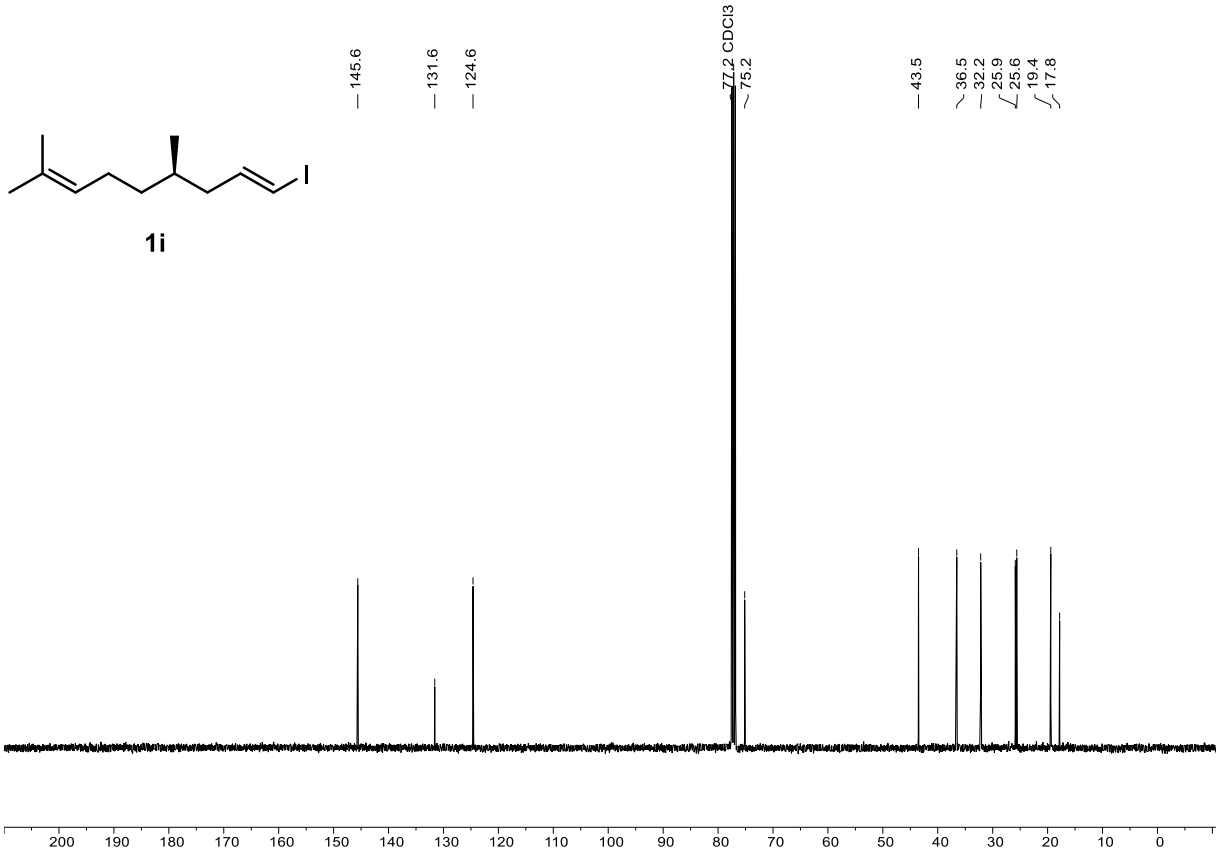
^{13}C-NMR (101 MHz, $CDCl_3$):



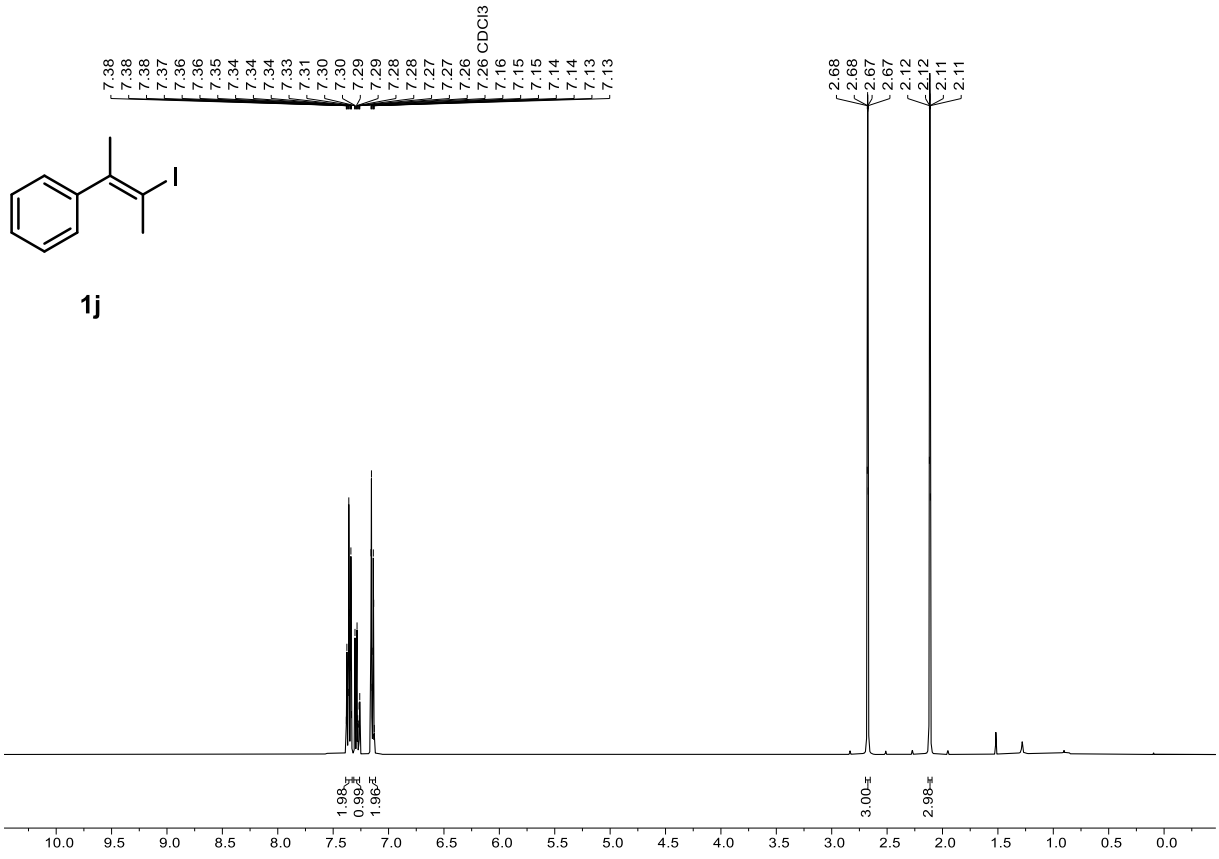
^{1}H-NMR (400 MHz, $CDCl_3$):



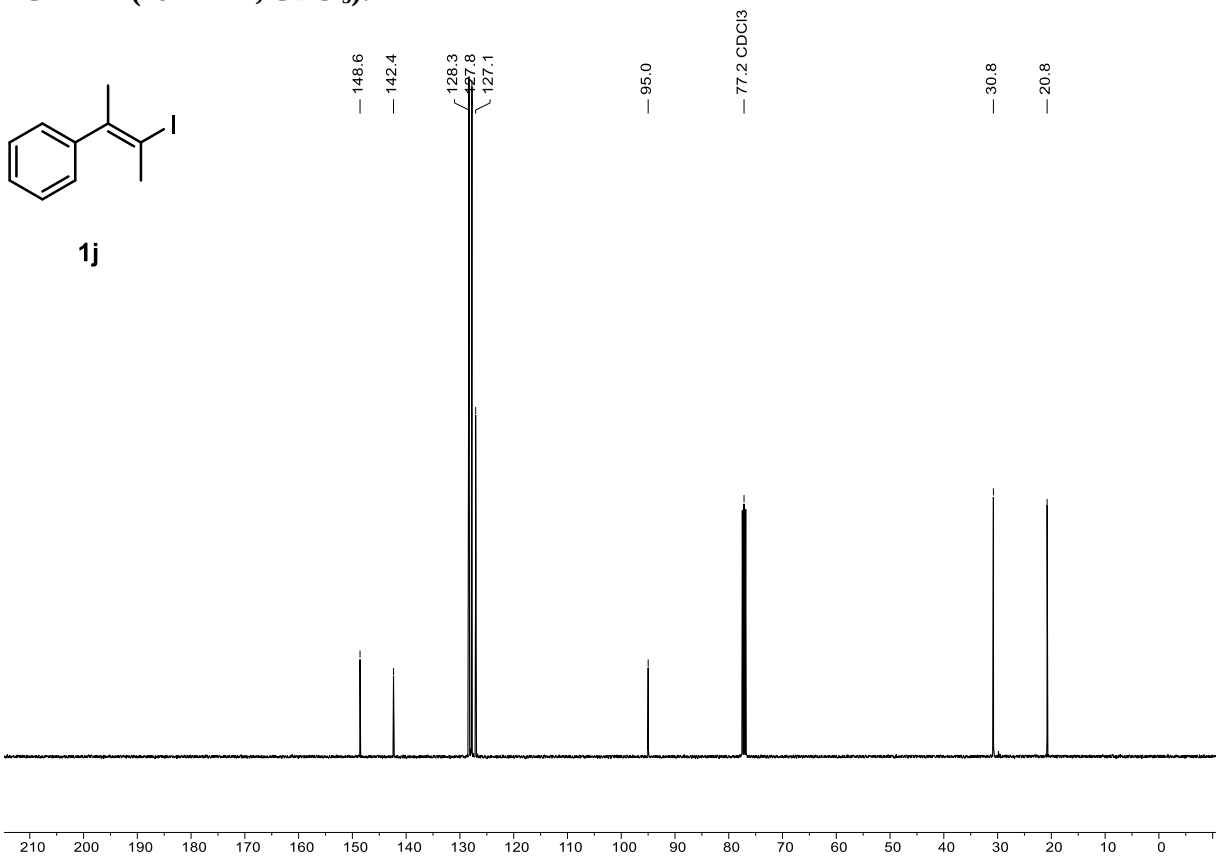
^{13}C-NMR (101 MHz, $CDCl_3$):



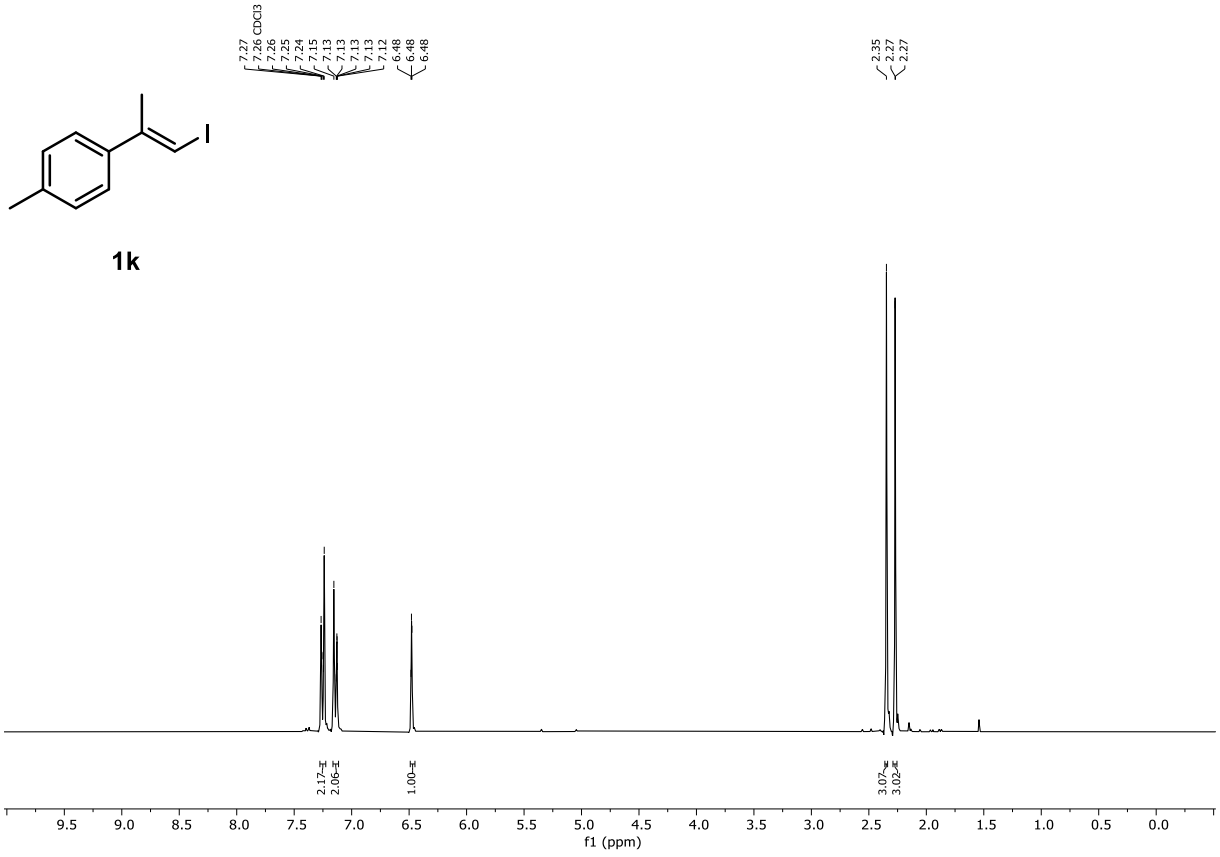
^{1}H-NMR (400 MHz, $CDCl_3$):



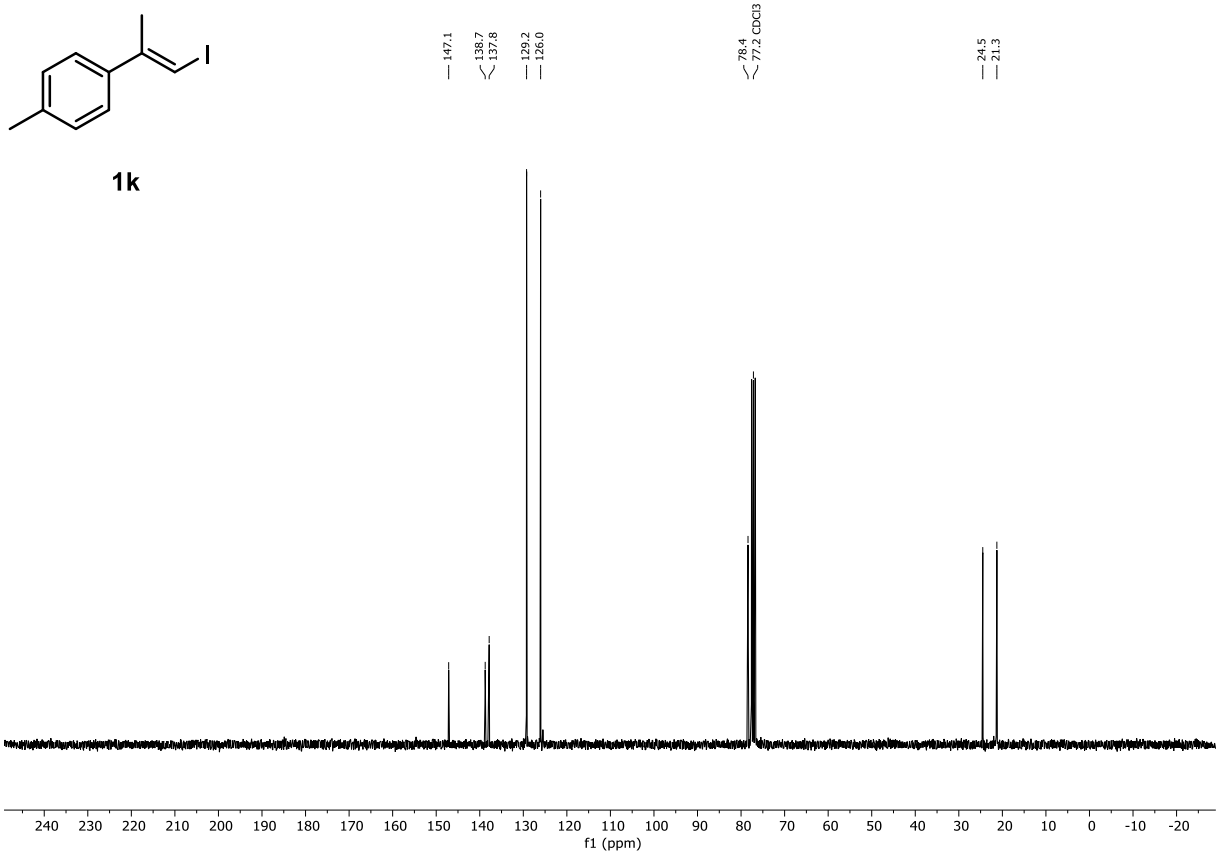
^{13}C-NMR (101 MHz, $CDCl_3$):



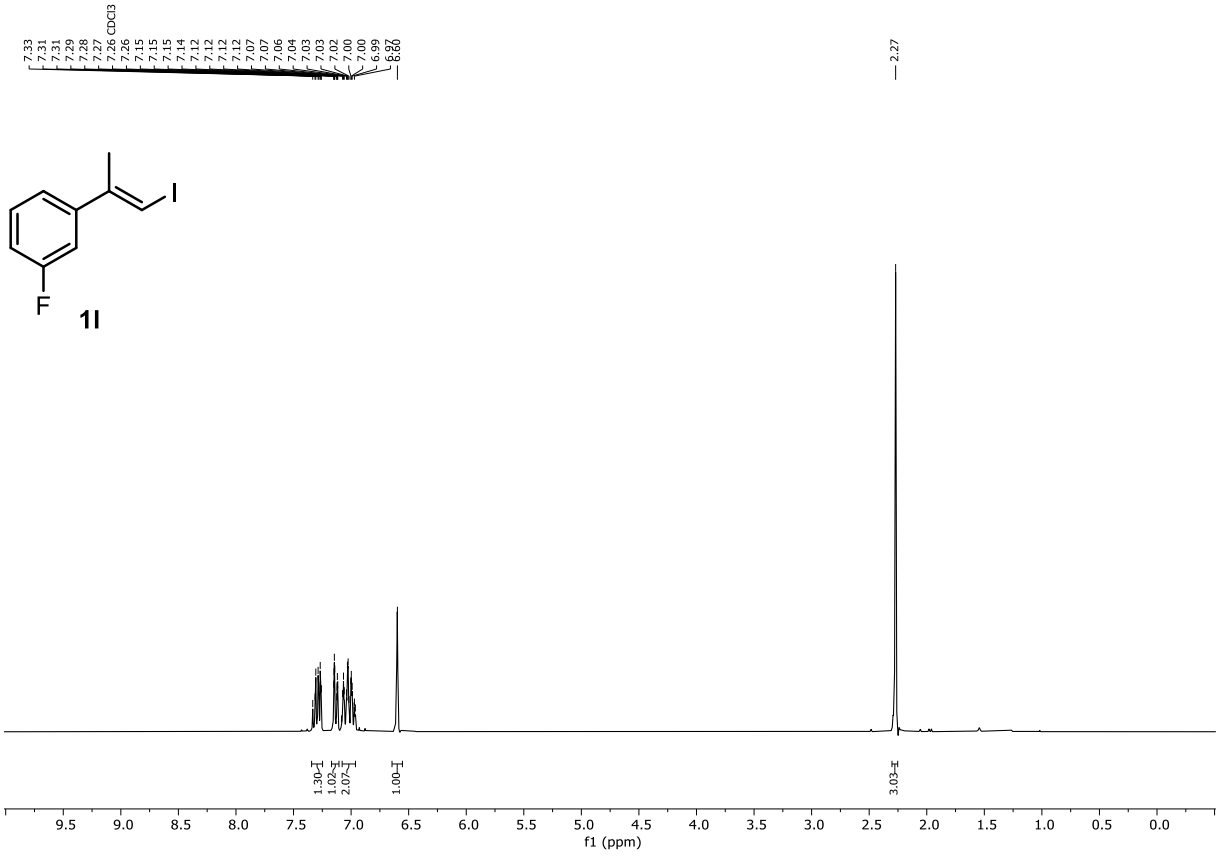
^{1}H-NMR (300 MHz, $CDCl_3$):



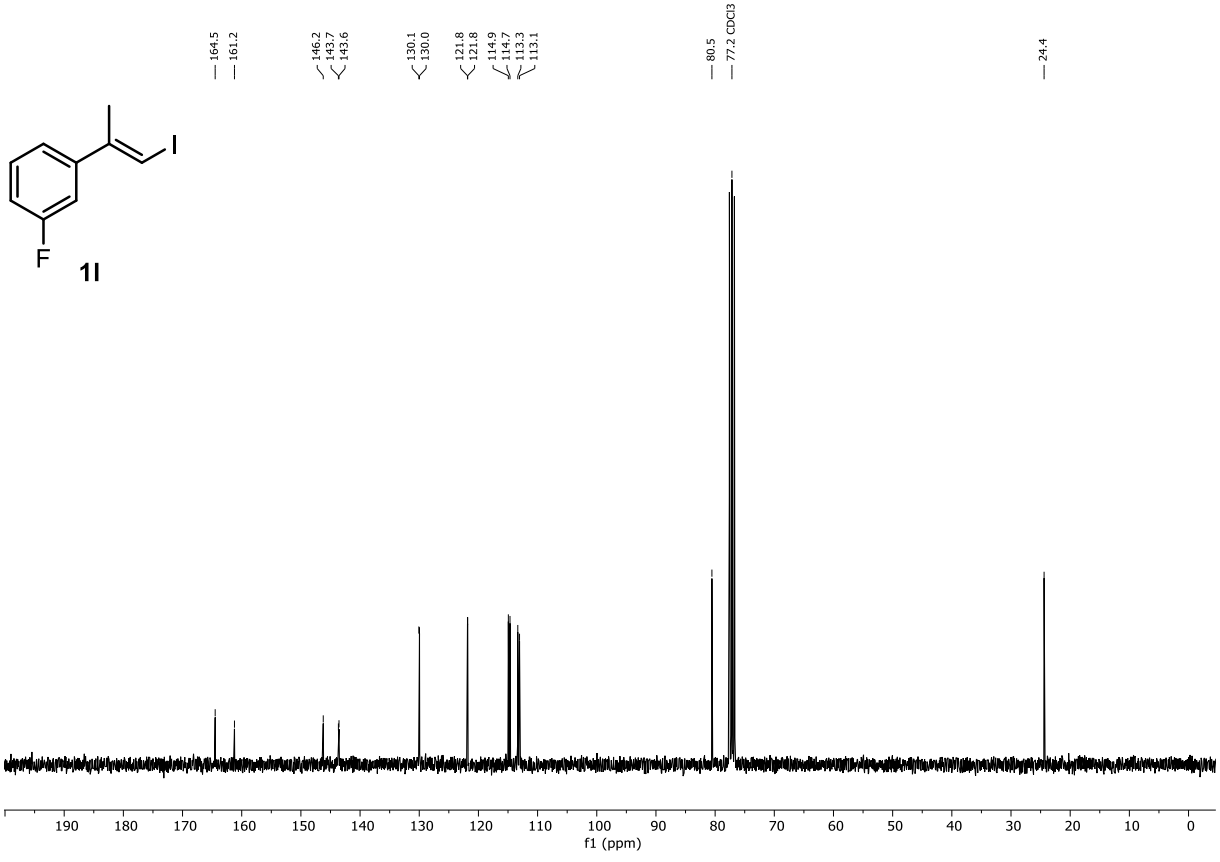
^{13}C-NMR (76 MHz, $CDCl_3$):



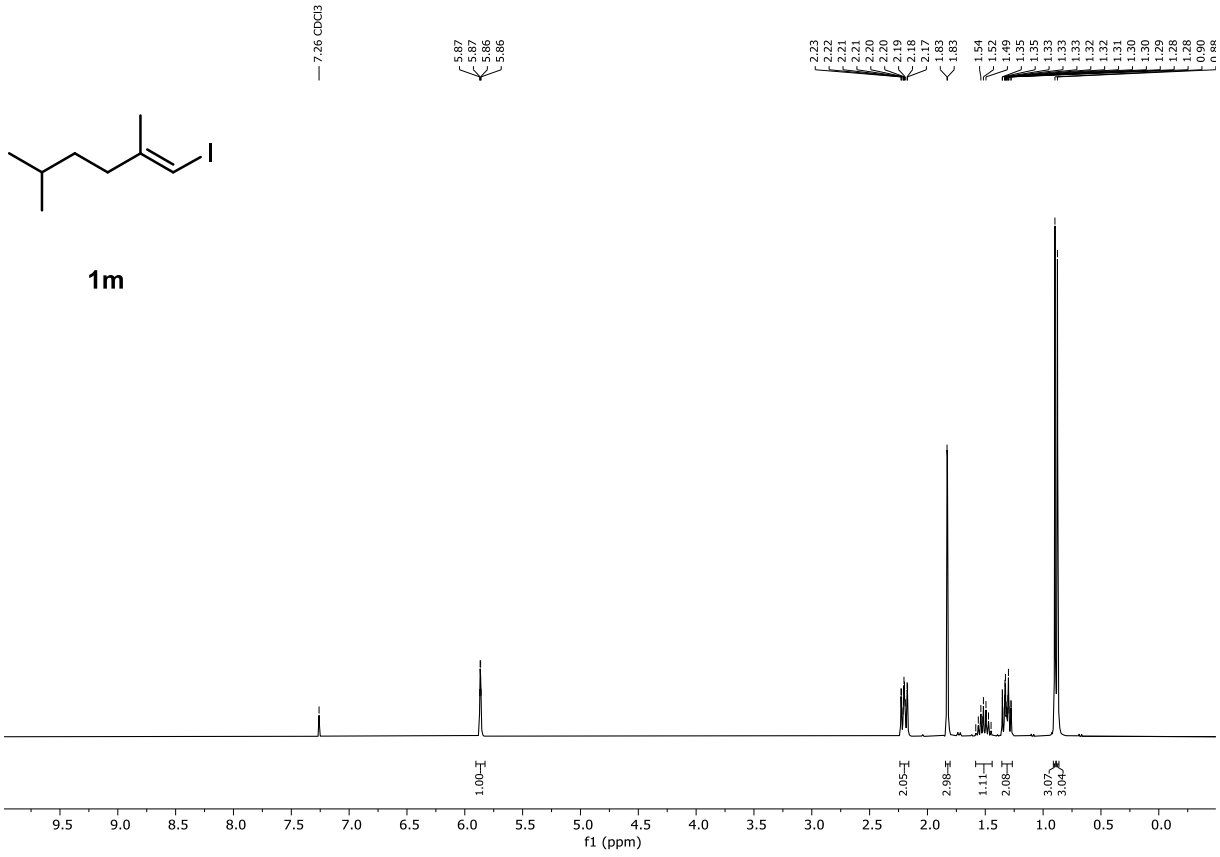
^{1}H-NMR (300 MHz, $CDCl_3$):



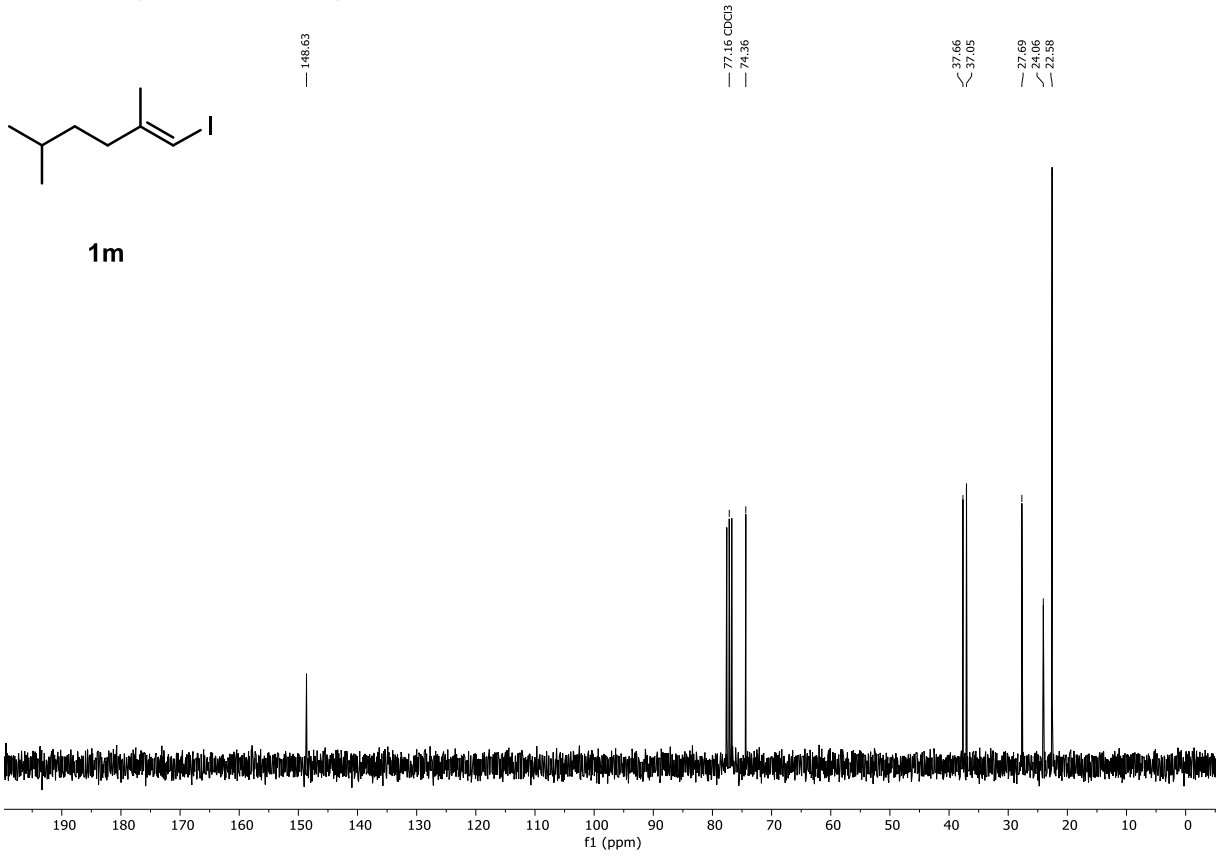
^{13}C-NMR (76 MHz, $CDCl_3$):



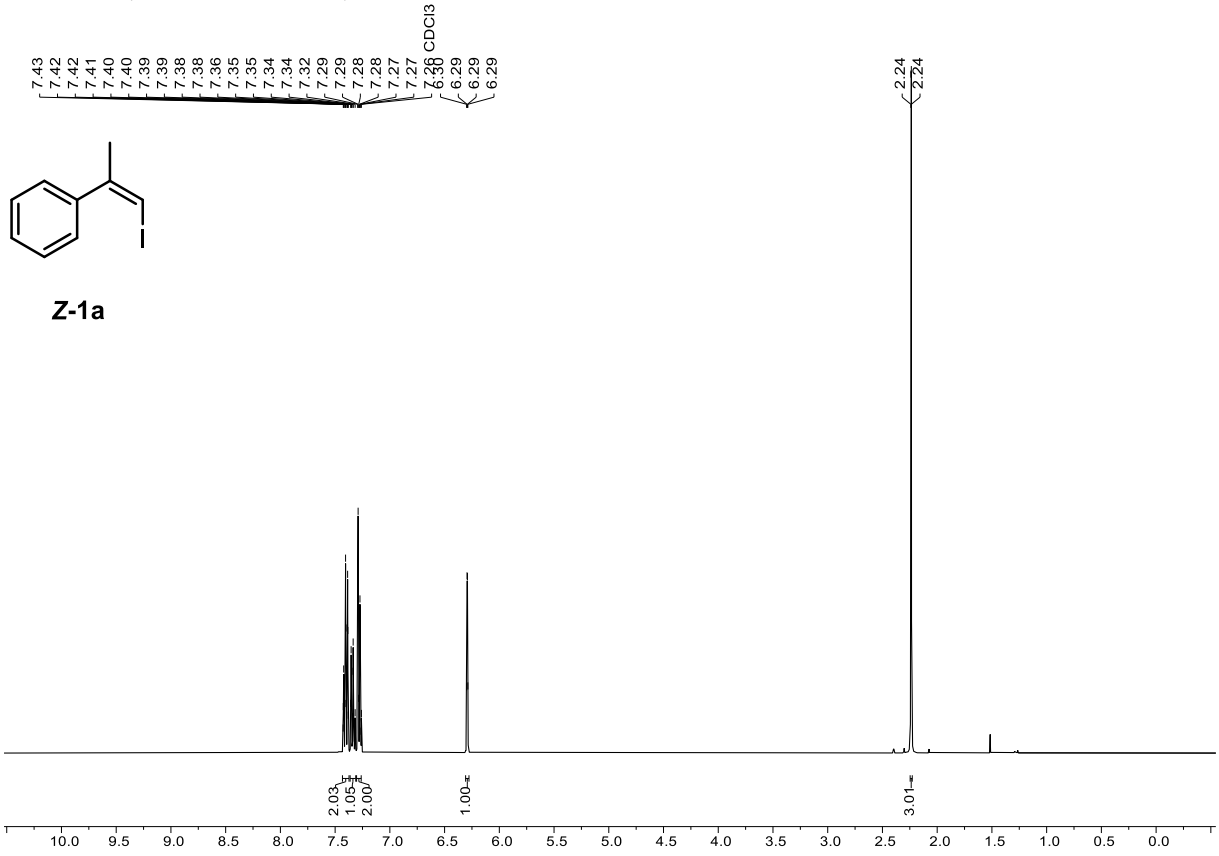
^{1}H-NMR (300 MHz, $CDCl_3$):



^{13}C-NMR (76 MHz, $CDCl_3$):

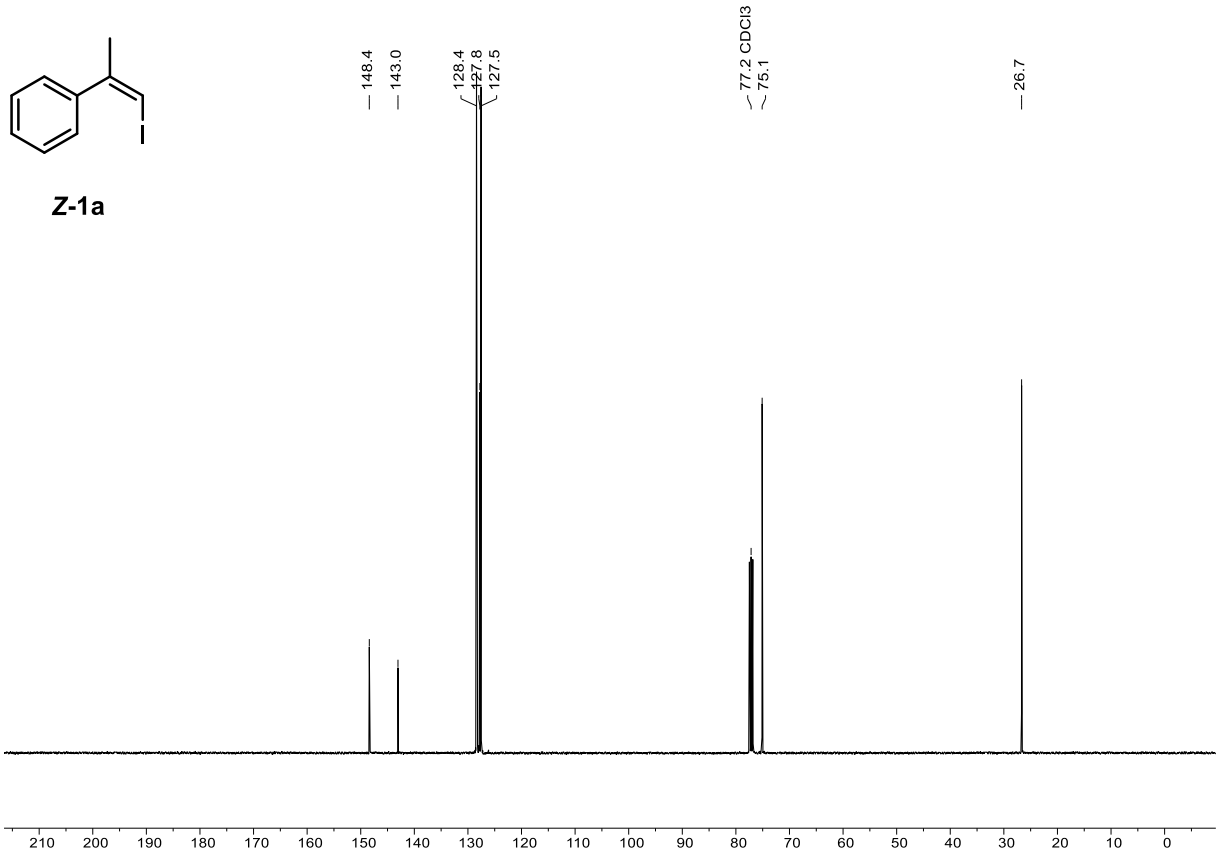


^{1}H-NMR (400 MHz, $CDCl_3$):



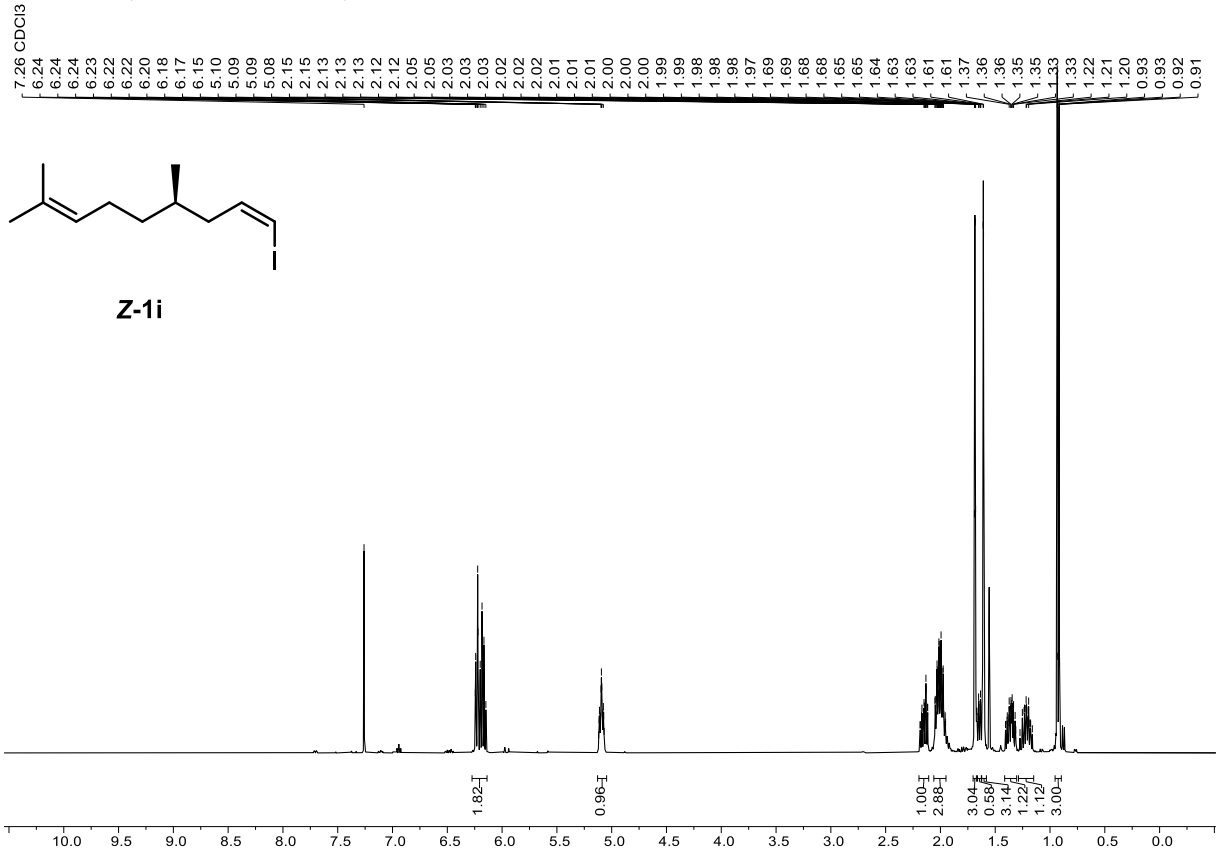
***Z*-1a**

^{13}C-NMR (101 MHz, $CDCl_3$):



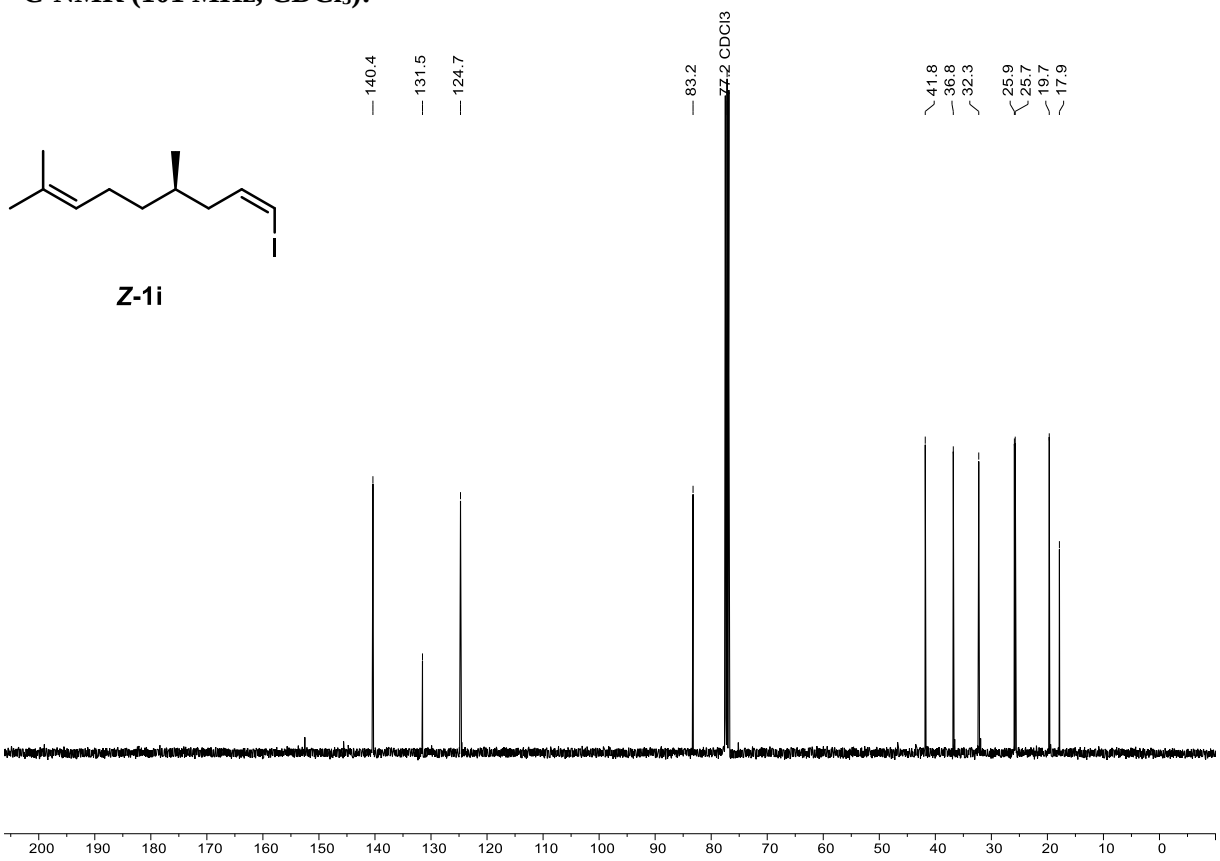
***Z*-1a**

^{1}H-NMR (400 MHz, $CDCl_3$):



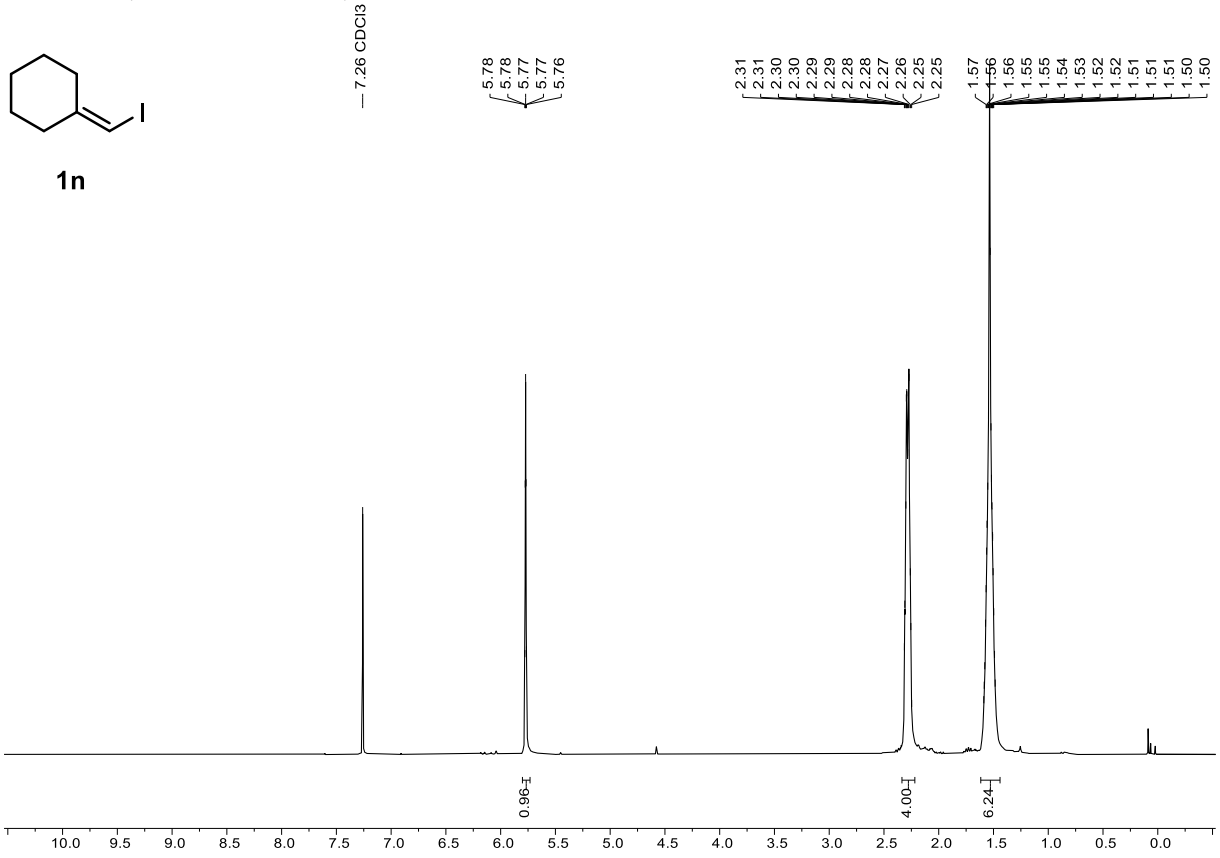
***Z*-1i**

^{13}C-NMR (101 MHz, $CDCl_3$):

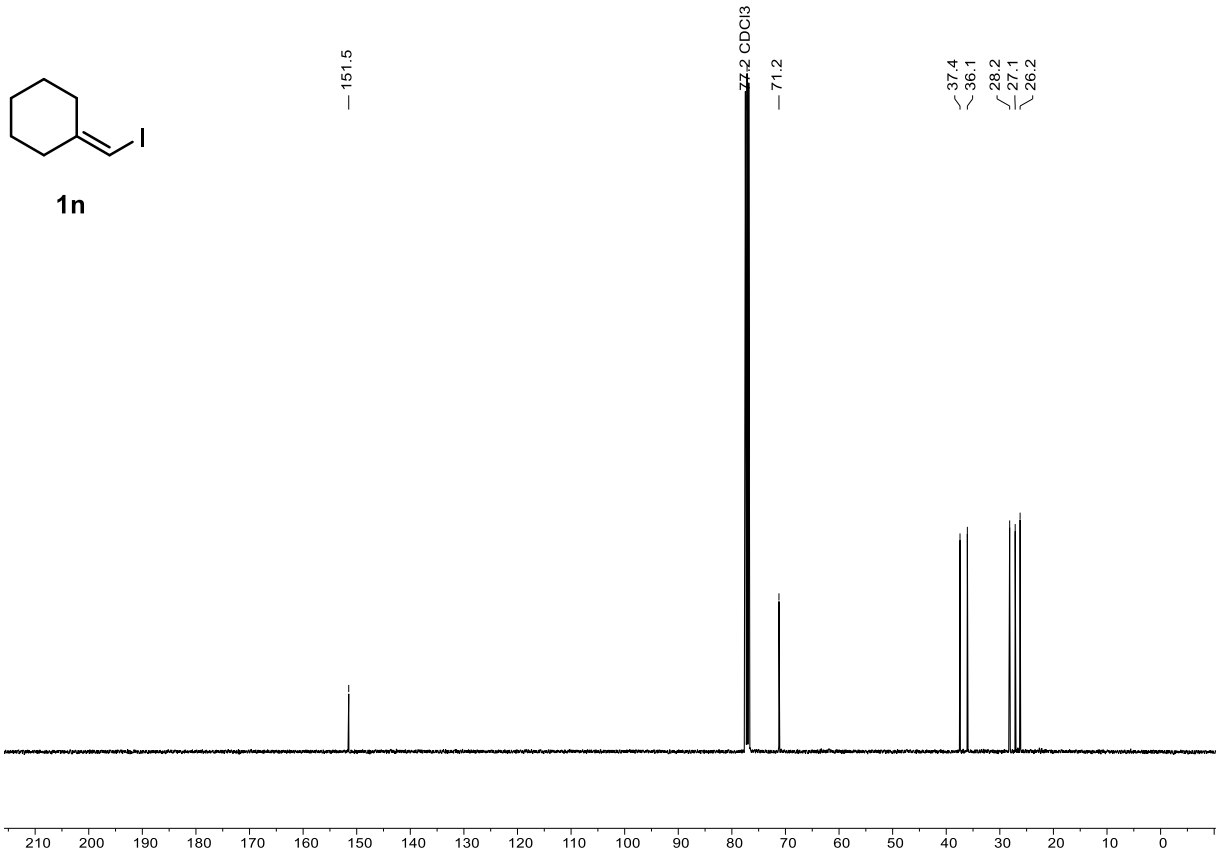


***Z*-1i**

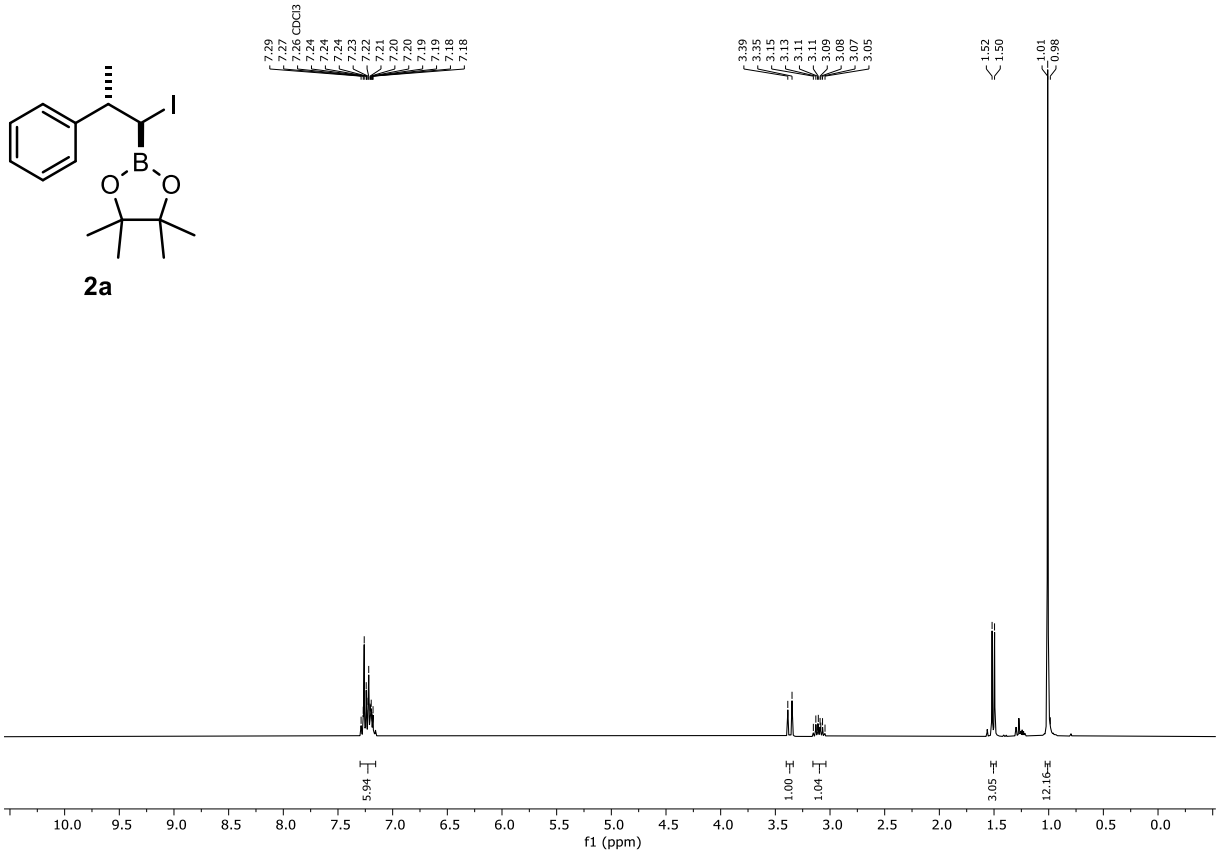
^{1}H-NMR (300 MHz, $CDCl_3$):



^{13}C-NMR (101 MHz, $CDCl_3$):

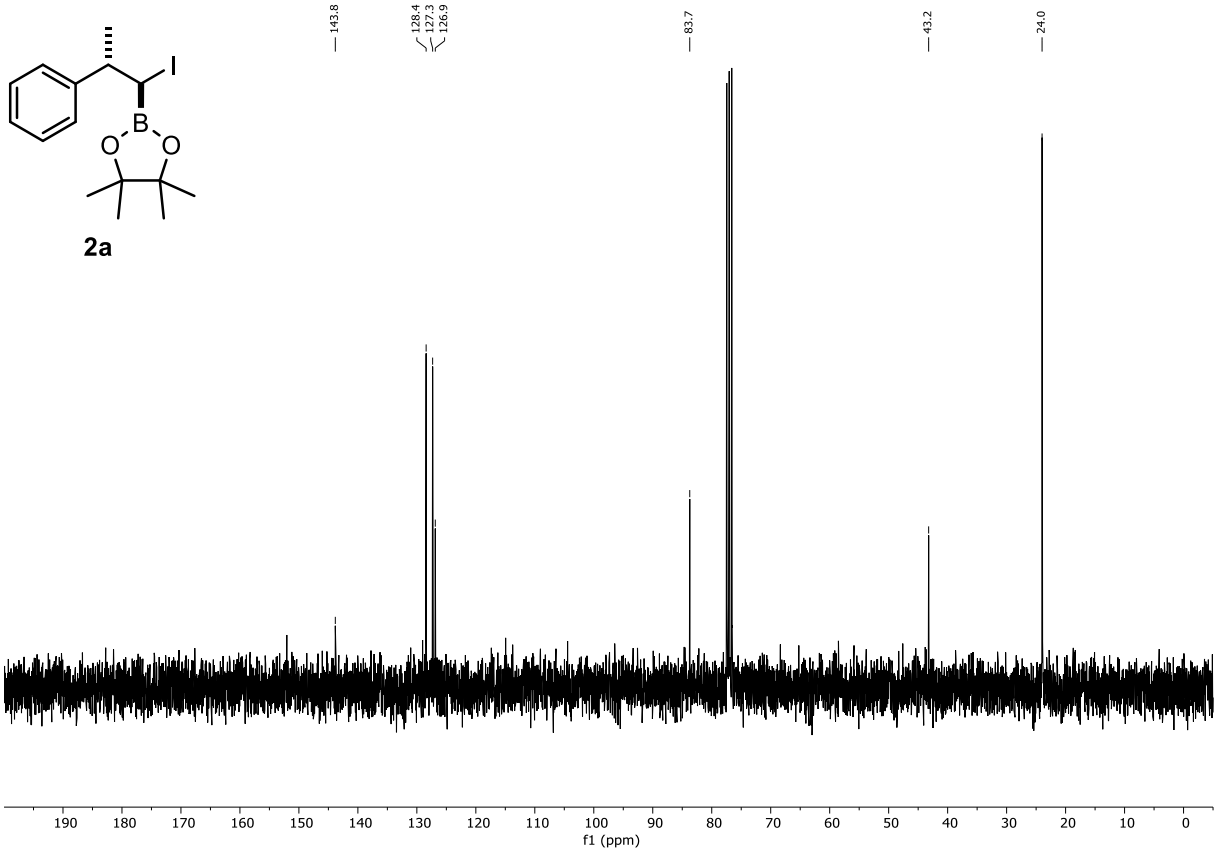


^{1}H-NMR (300 MHz, $CDCl_3$):



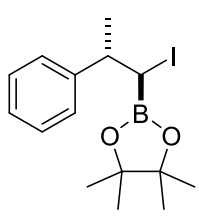
2a

^{13}C-NMR (76 MHz, $CDCl_3$):



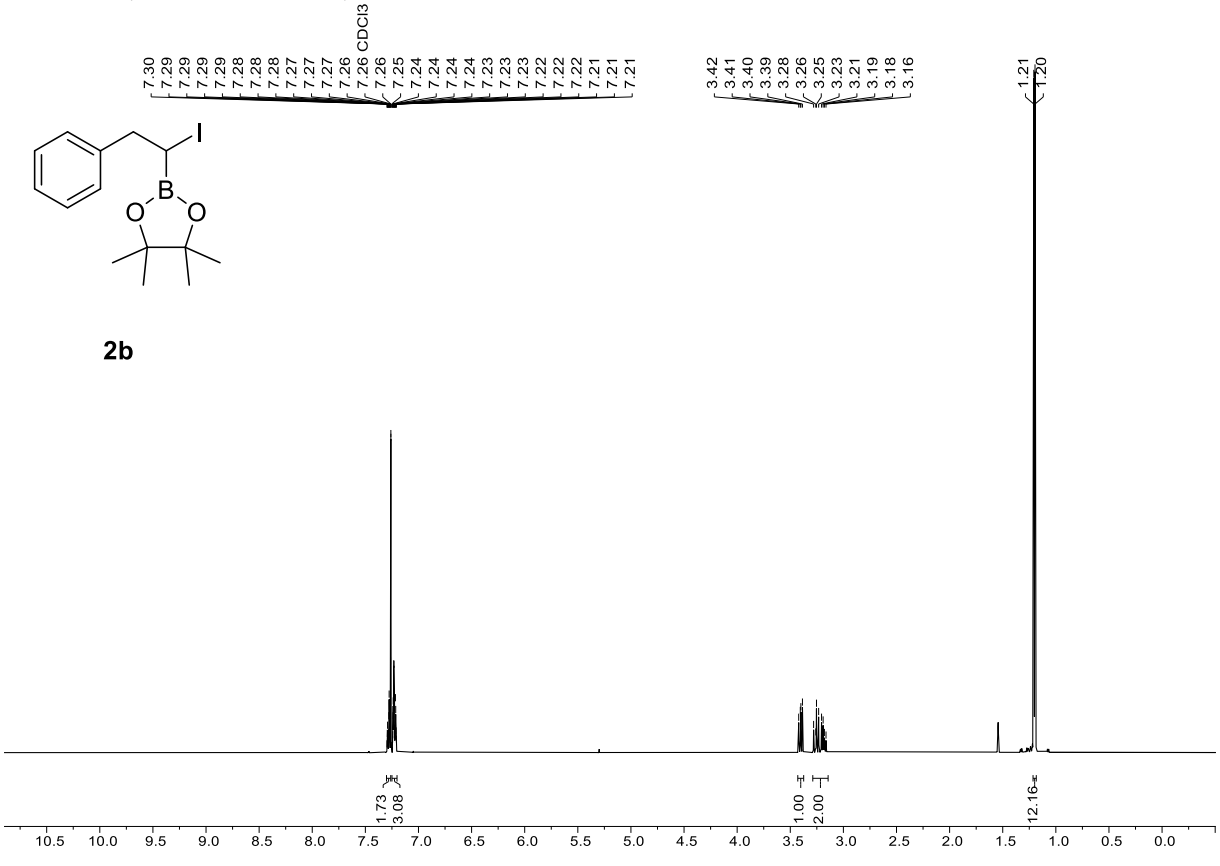
2a

^{11}B NMR (128 MHz, $CDCl_3$):



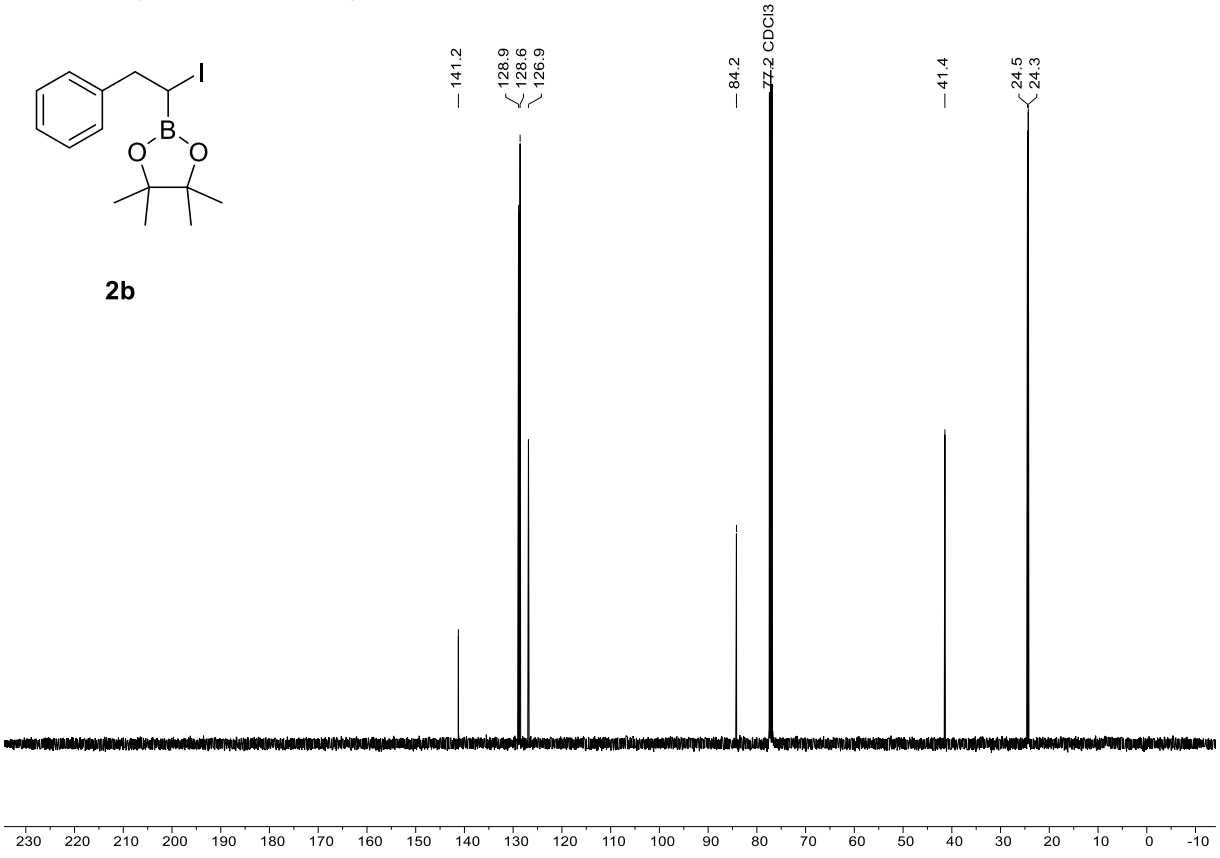
2a

^{1}H-NMR (300 MHz, $CDCl_3$):



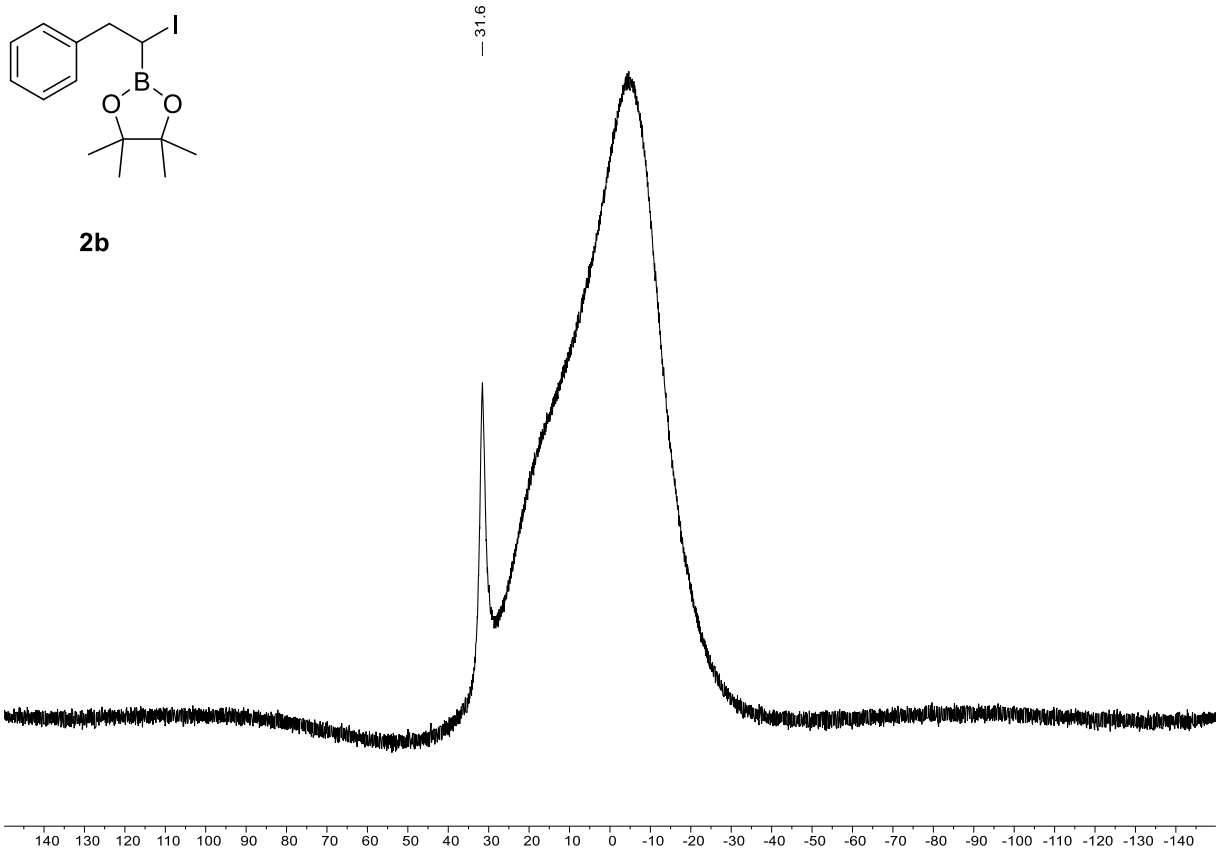
2b

^{13}C-NMR (126 MHz, $CDCl_3$):



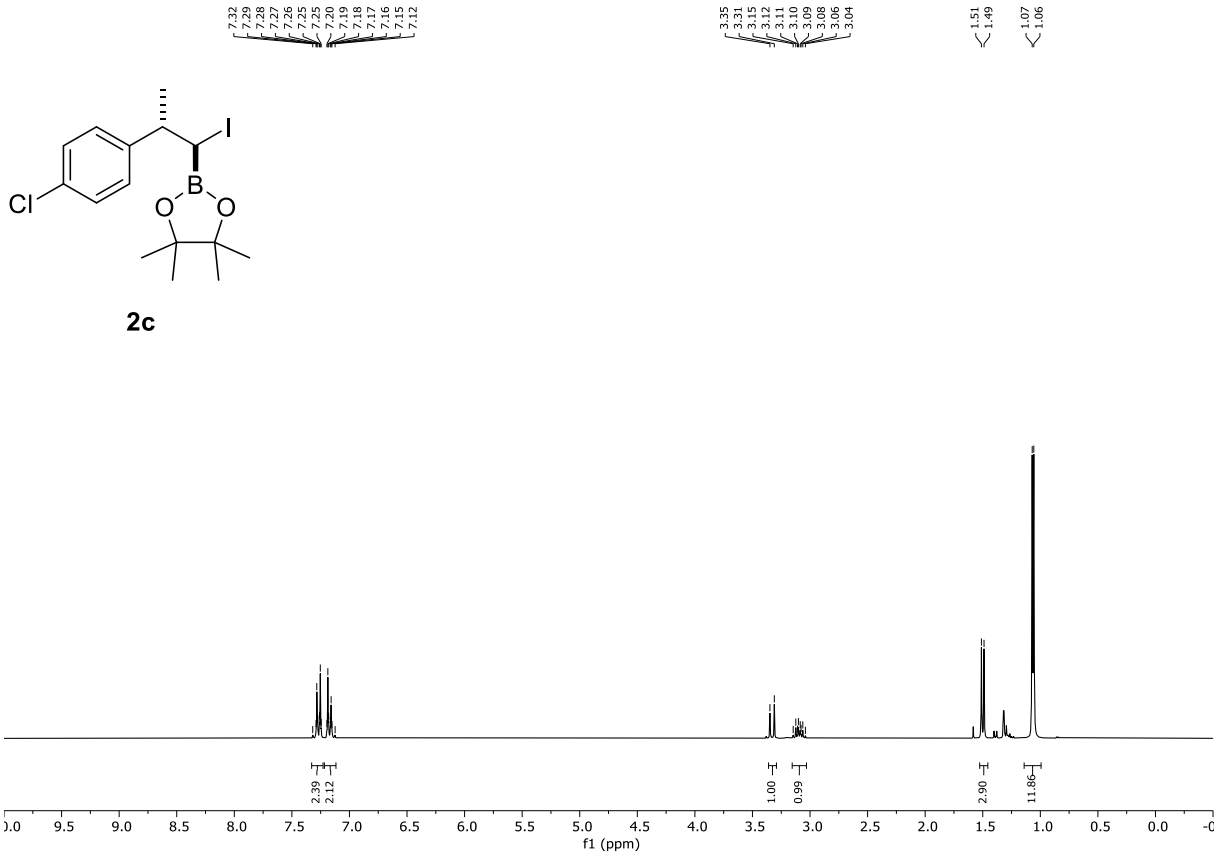
2b

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



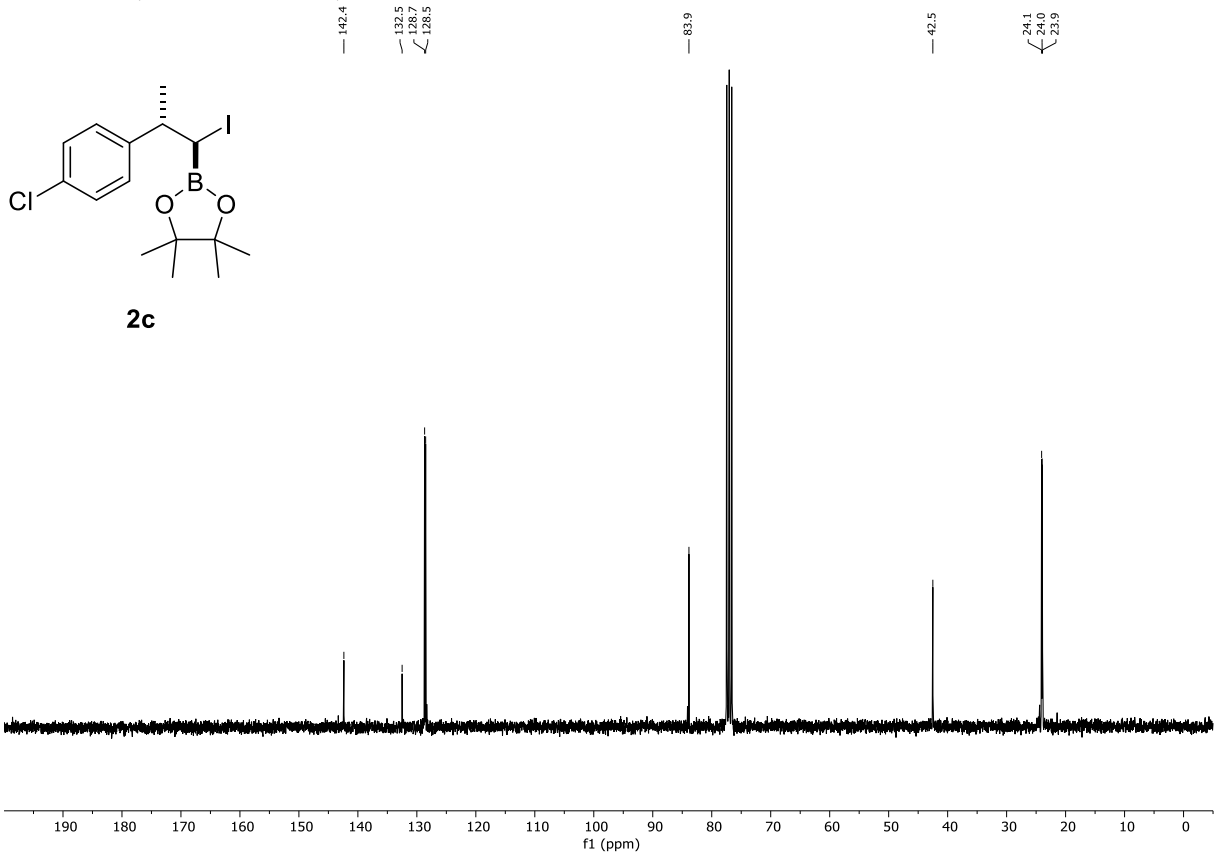
2b

^{1}H-NMR (300 MHz, $CDCl_3$):



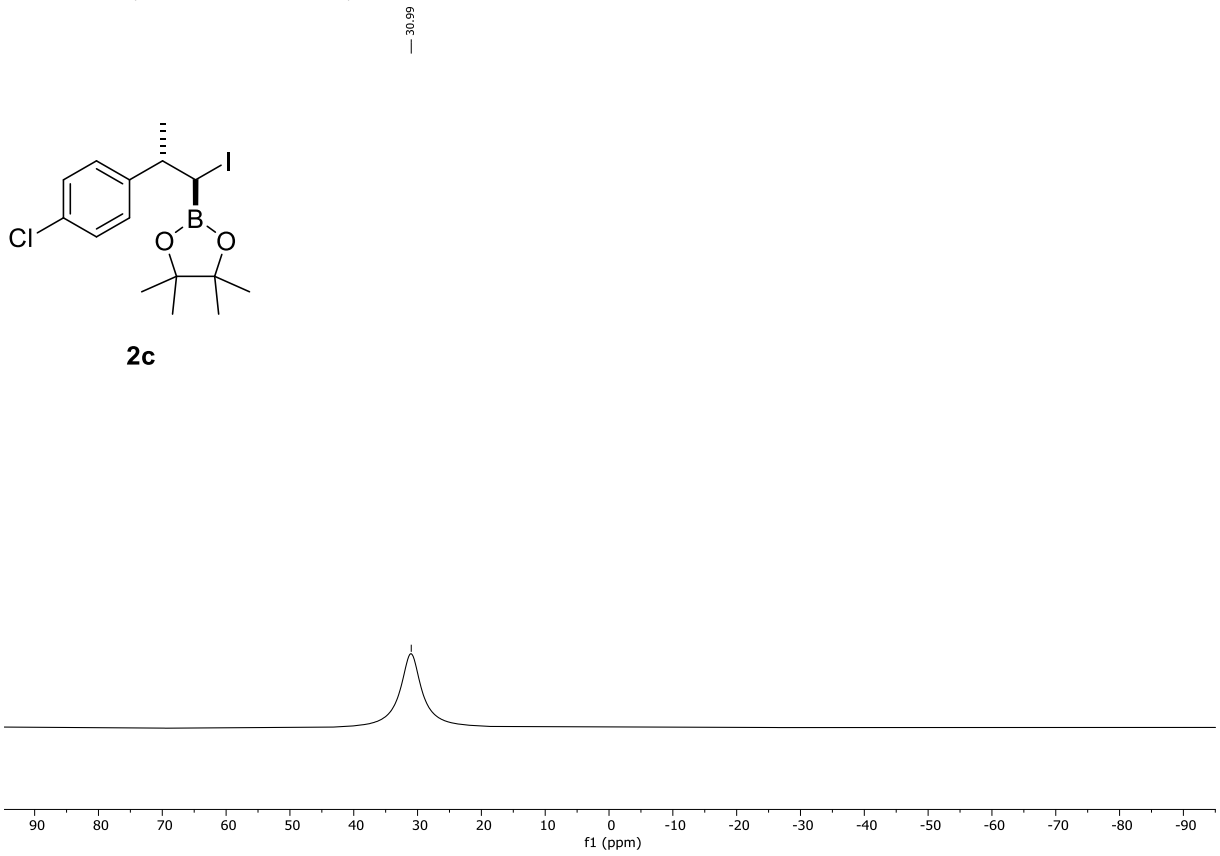
2c

^{13}C-NMR (76 MHz, $CDCl_3$):



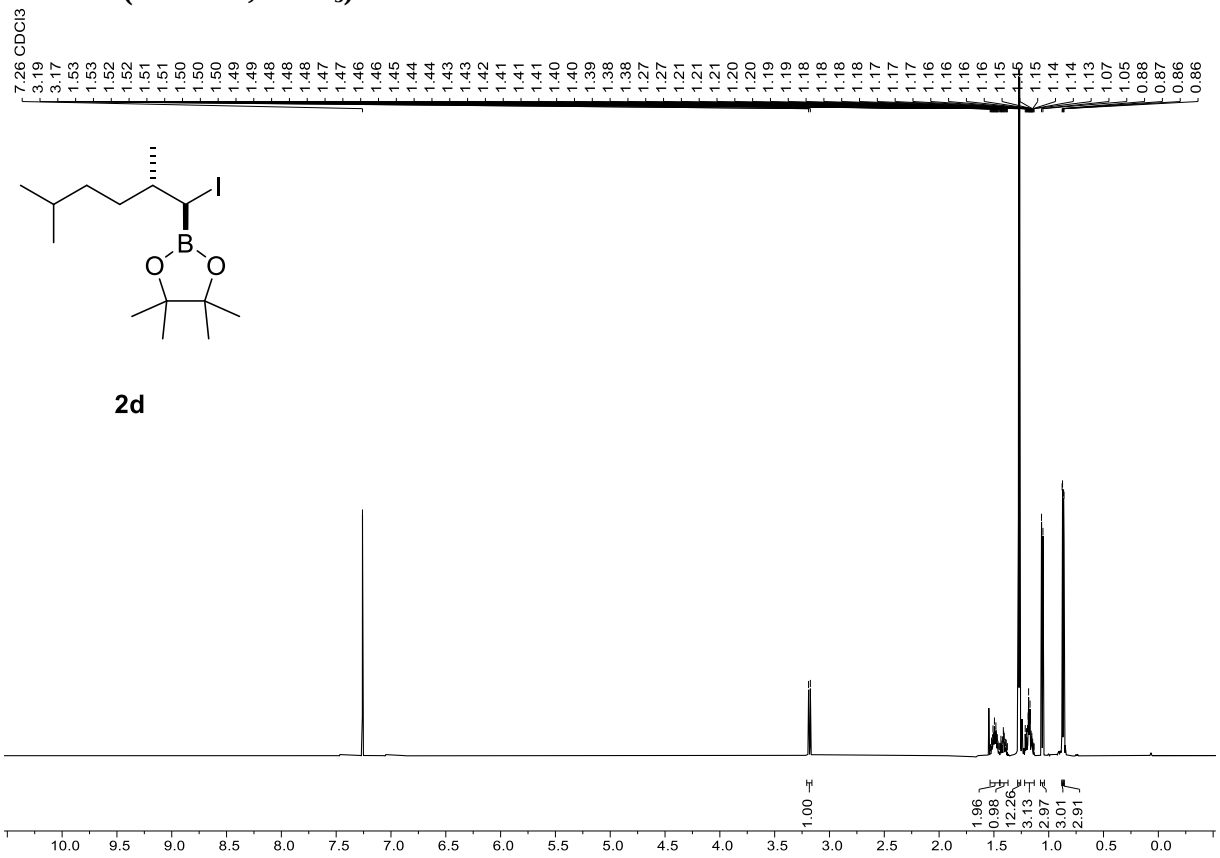
2c

^{11}B NMR (128 MHz, $CDCl_3$):



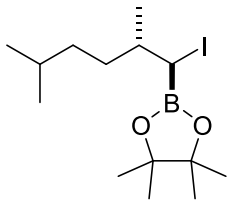
2c

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



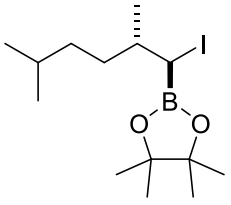
2d

^{13}C-NMR (126 MHz, $CDCl_3$):



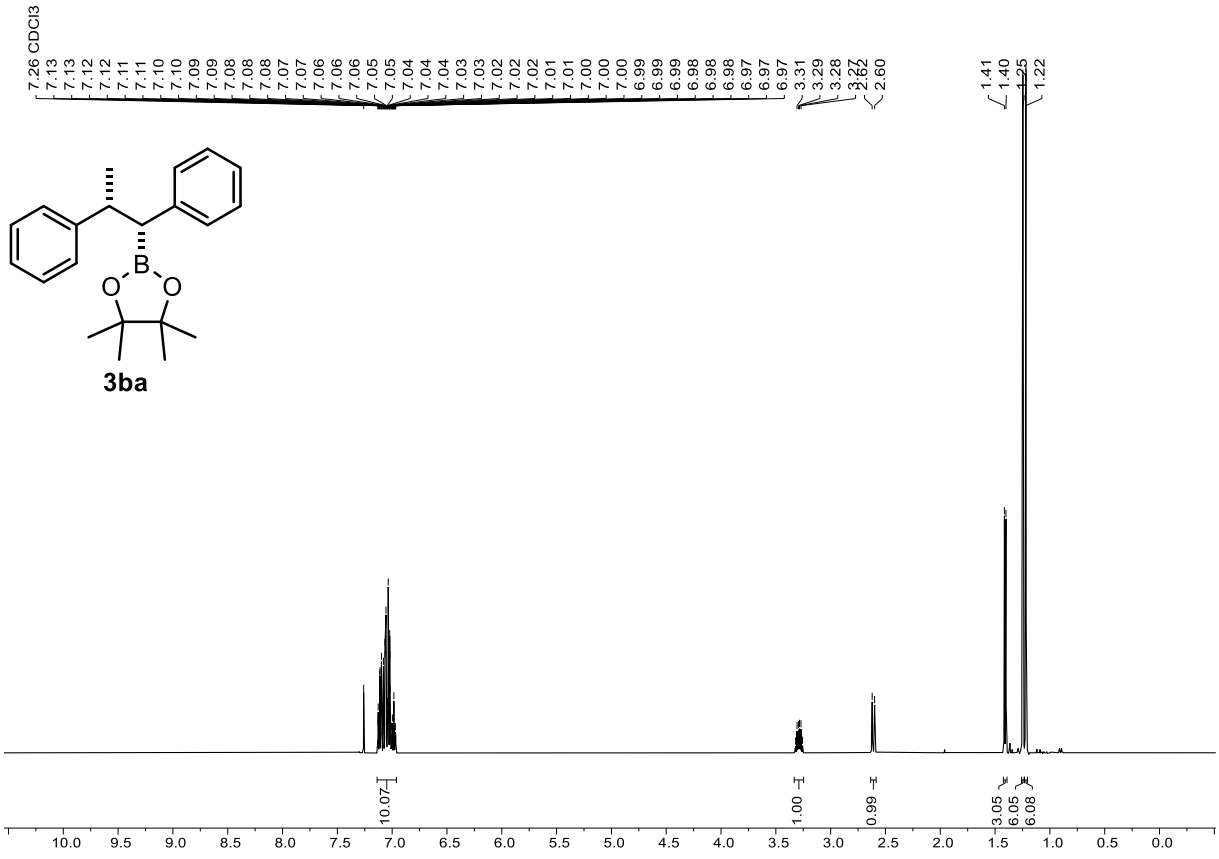
2d

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

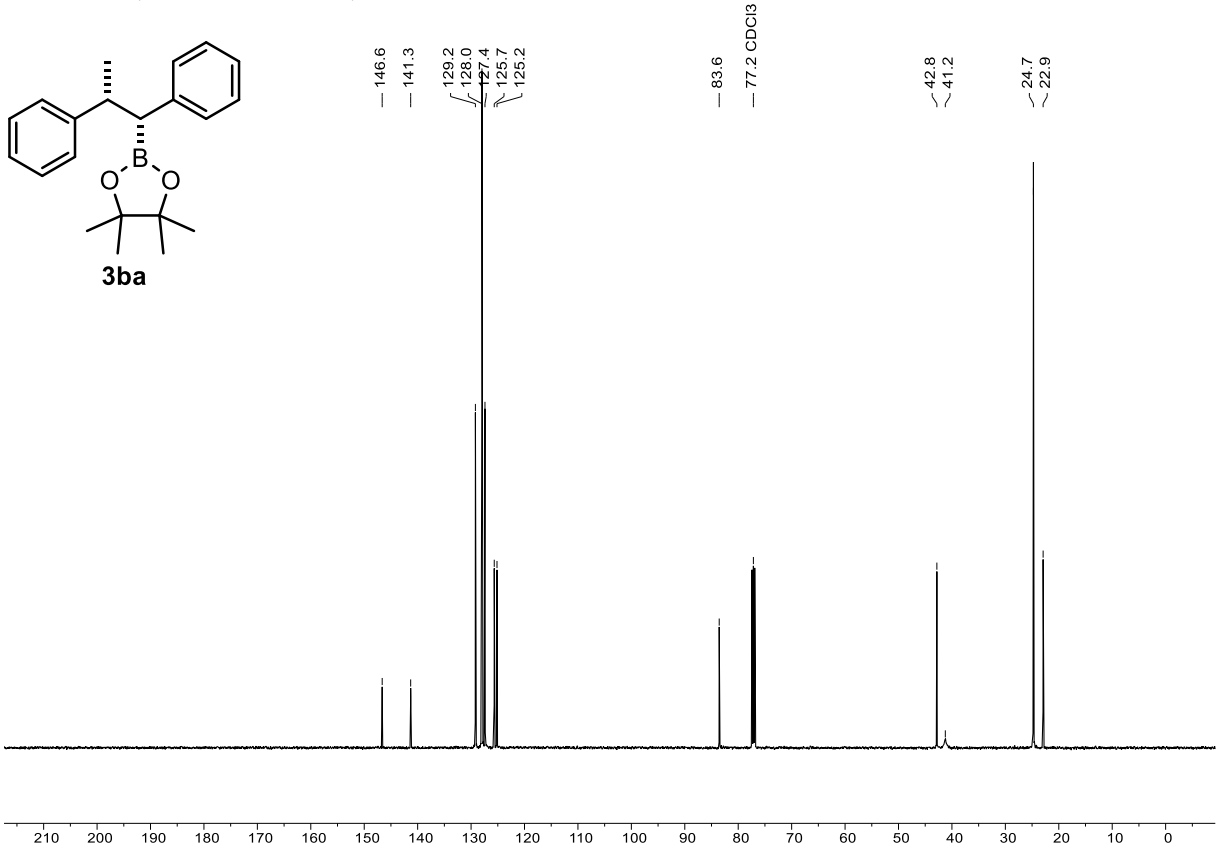


2d

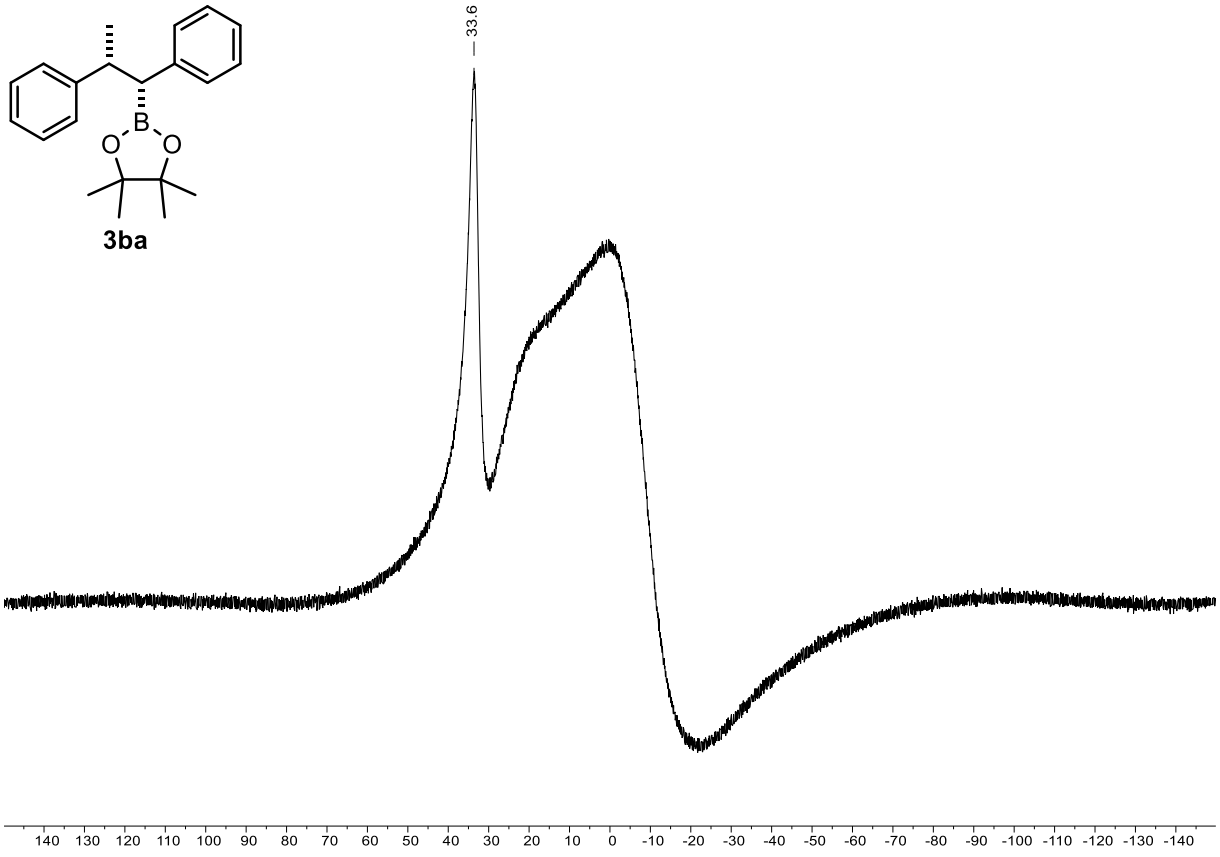
^{1}H-NMR (500 MHz, $CDCl_3$):



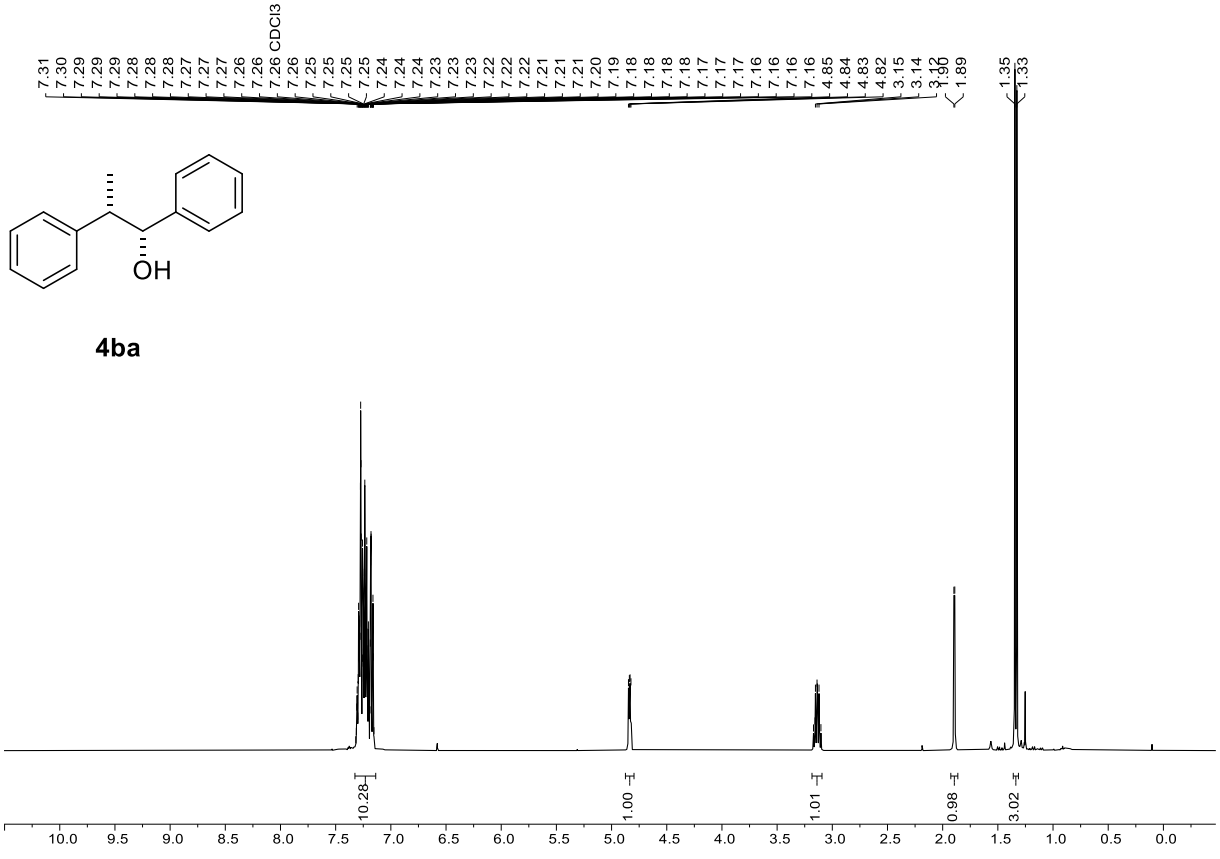
^{13}C-NMR (126 MHz, $CDCl_3$):



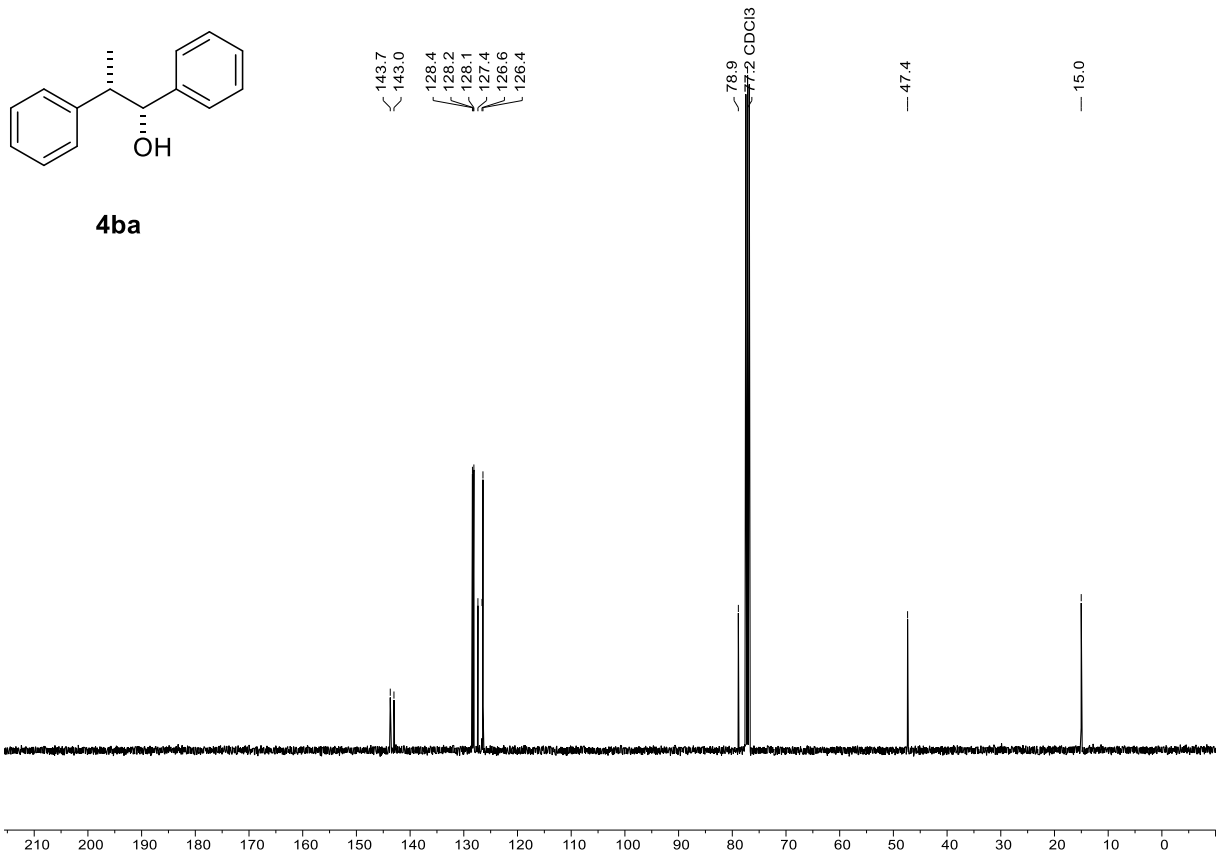
^{11}B-NMR (160 MHz, $CDCl_3$):



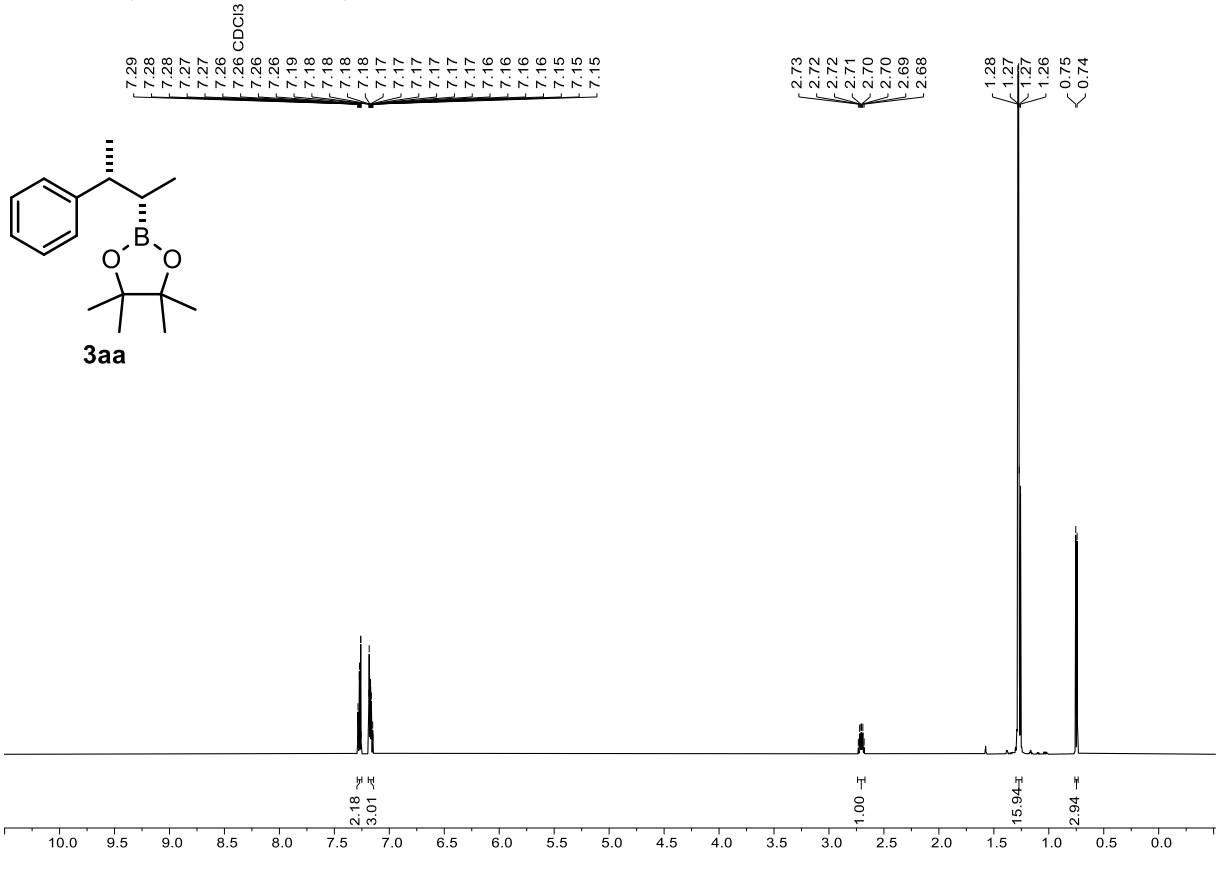
^{1}H-NMR (400 MHz, $CDCl_3$):



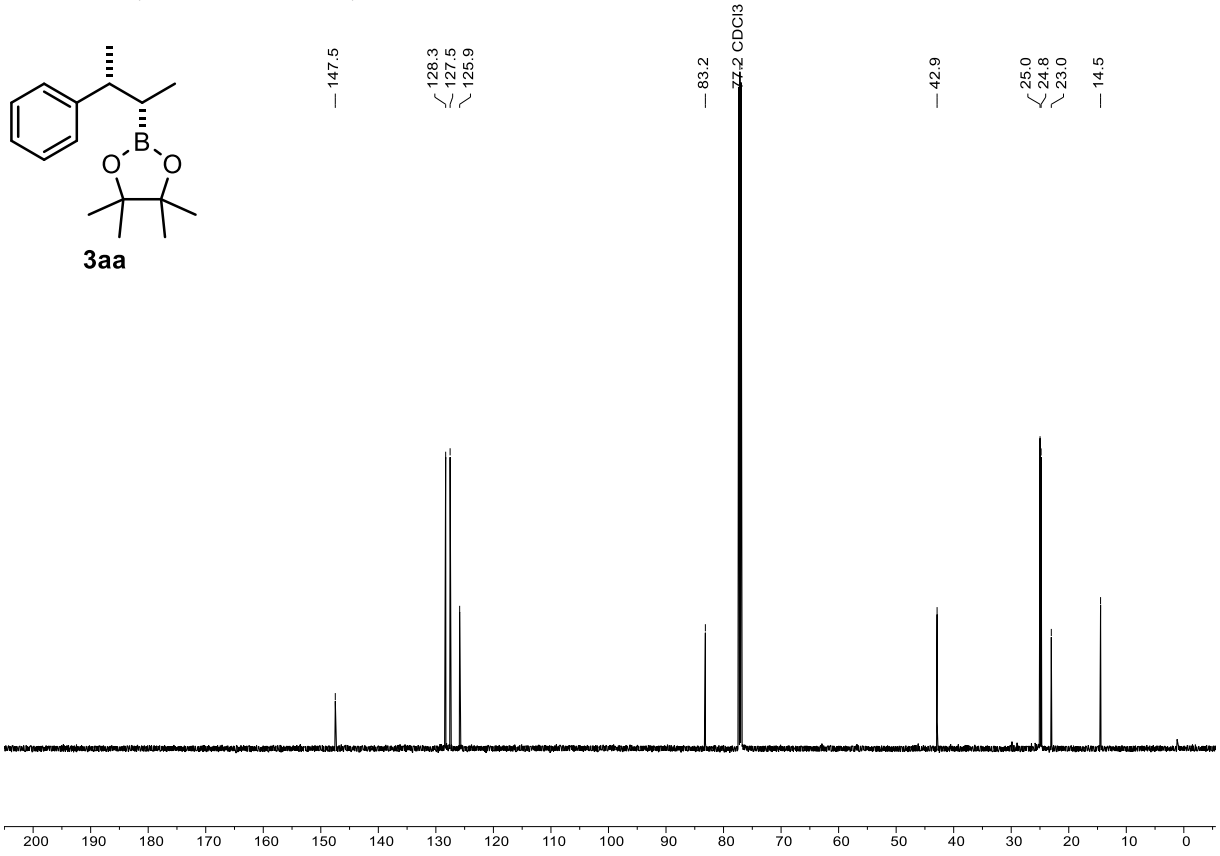
^{13}C-NMR (101 MHz, $CDCl_3$):



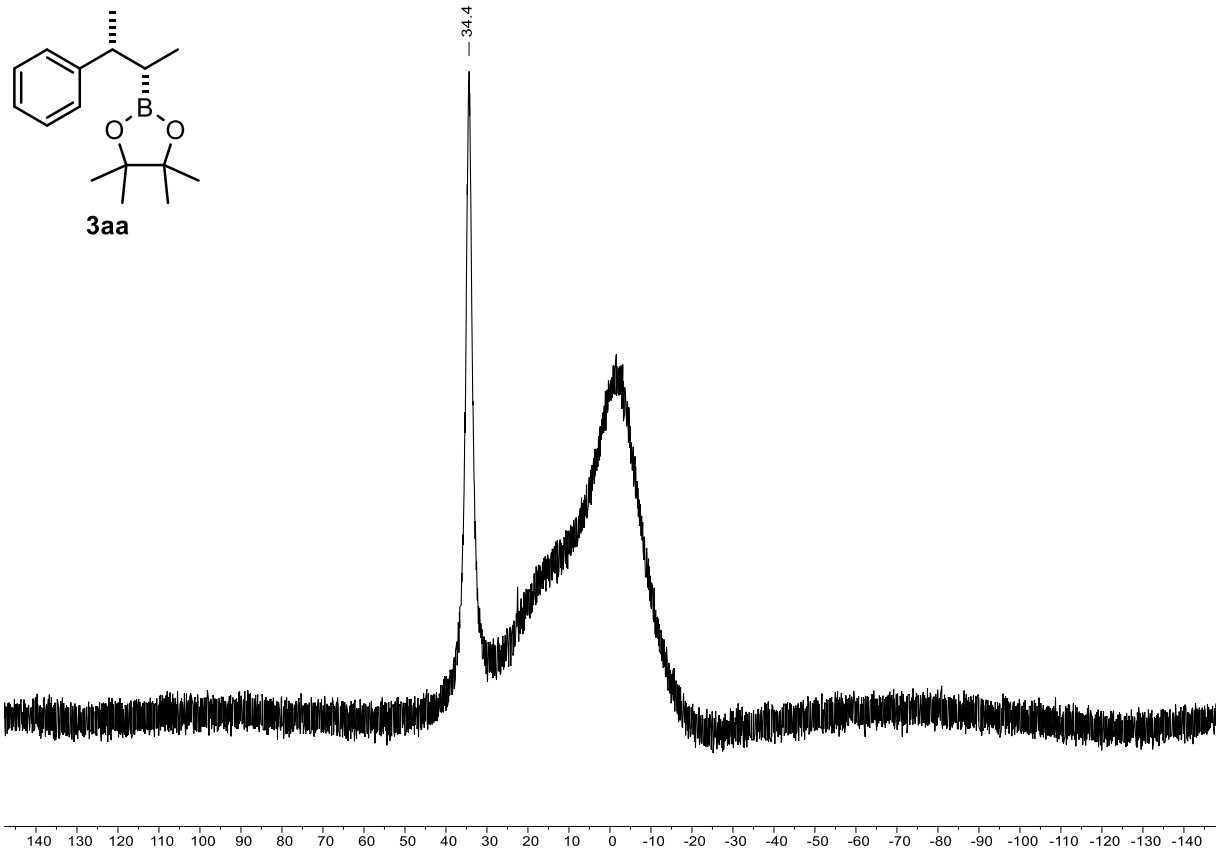
^{1}H-NMR (599 MHz, $CDCl_3$):



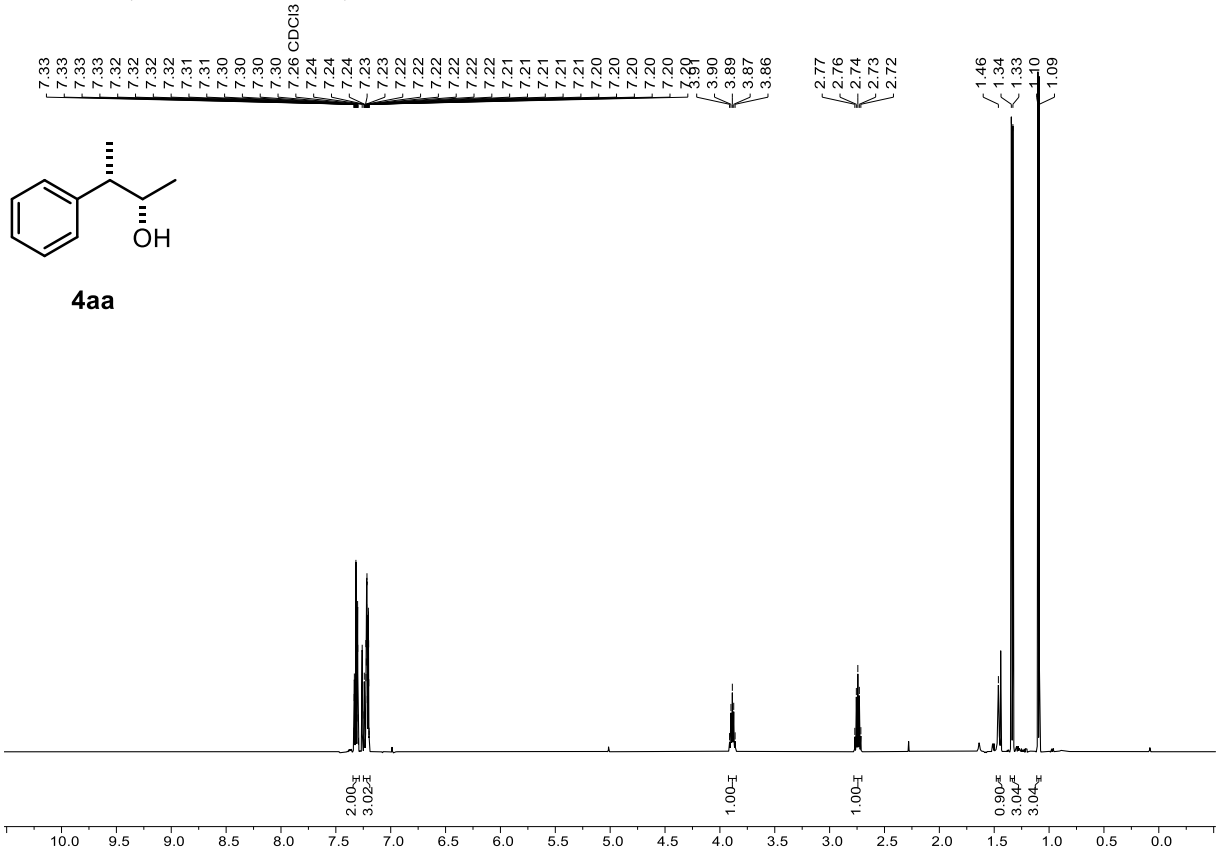
^{13}C-NMR (151 MHz, $CDCl_3$):



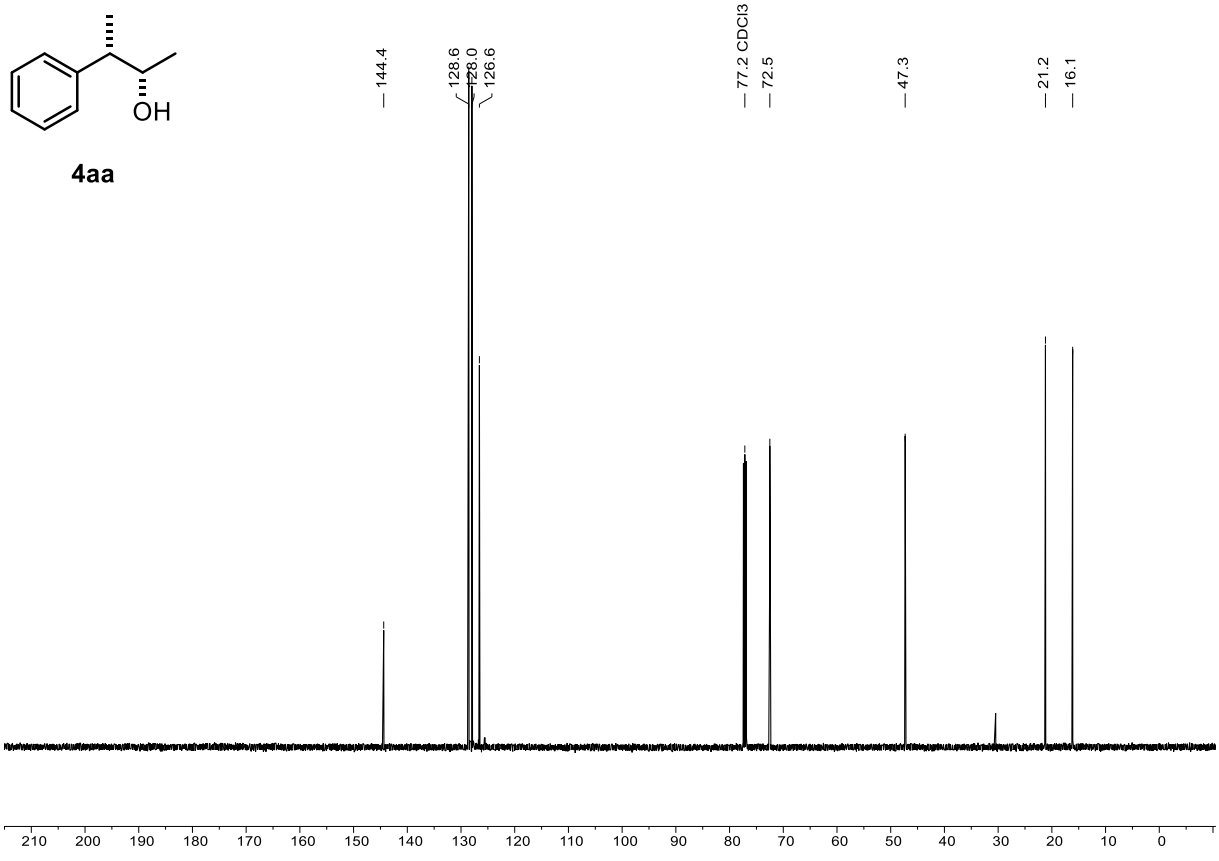
^{11}B-NMR (192 MHz, $CDCl_3$):



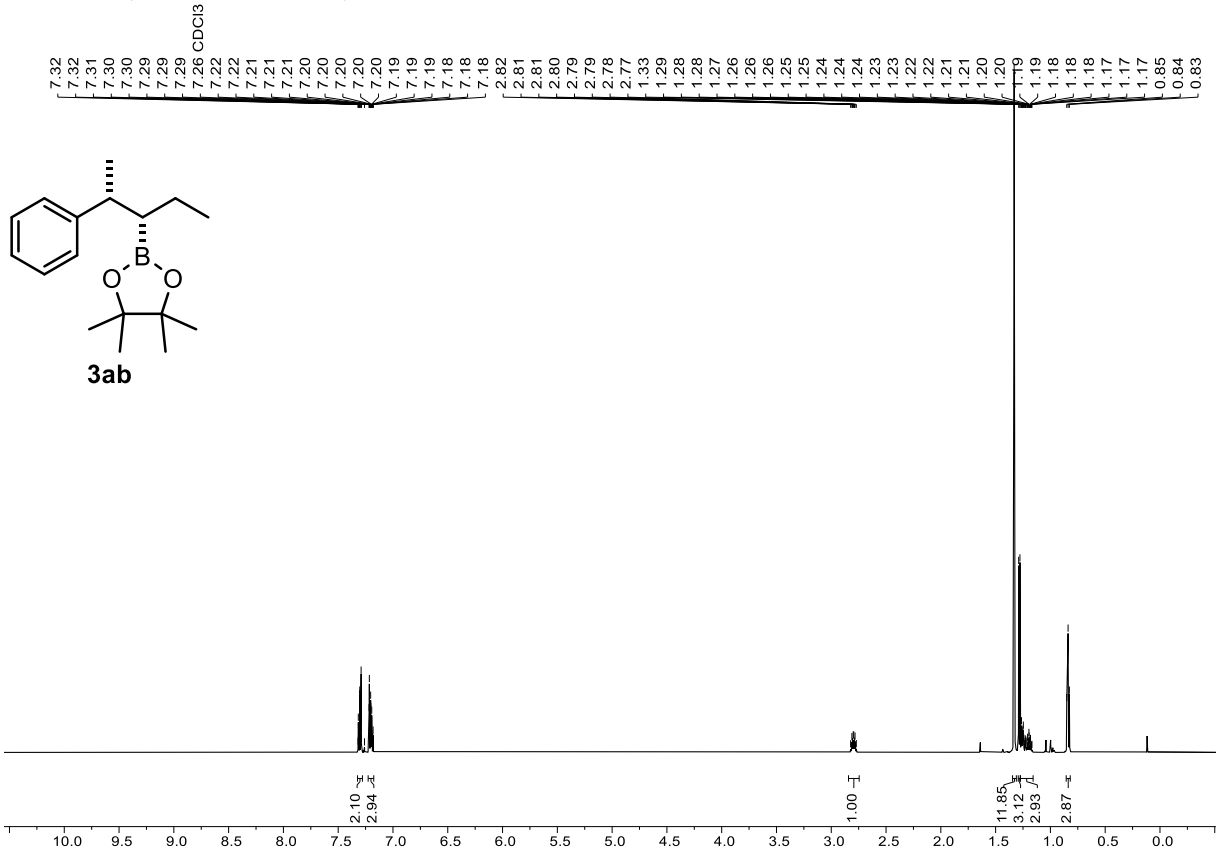
^{1}H-NMR (500 MHz, $CDCl_3$):



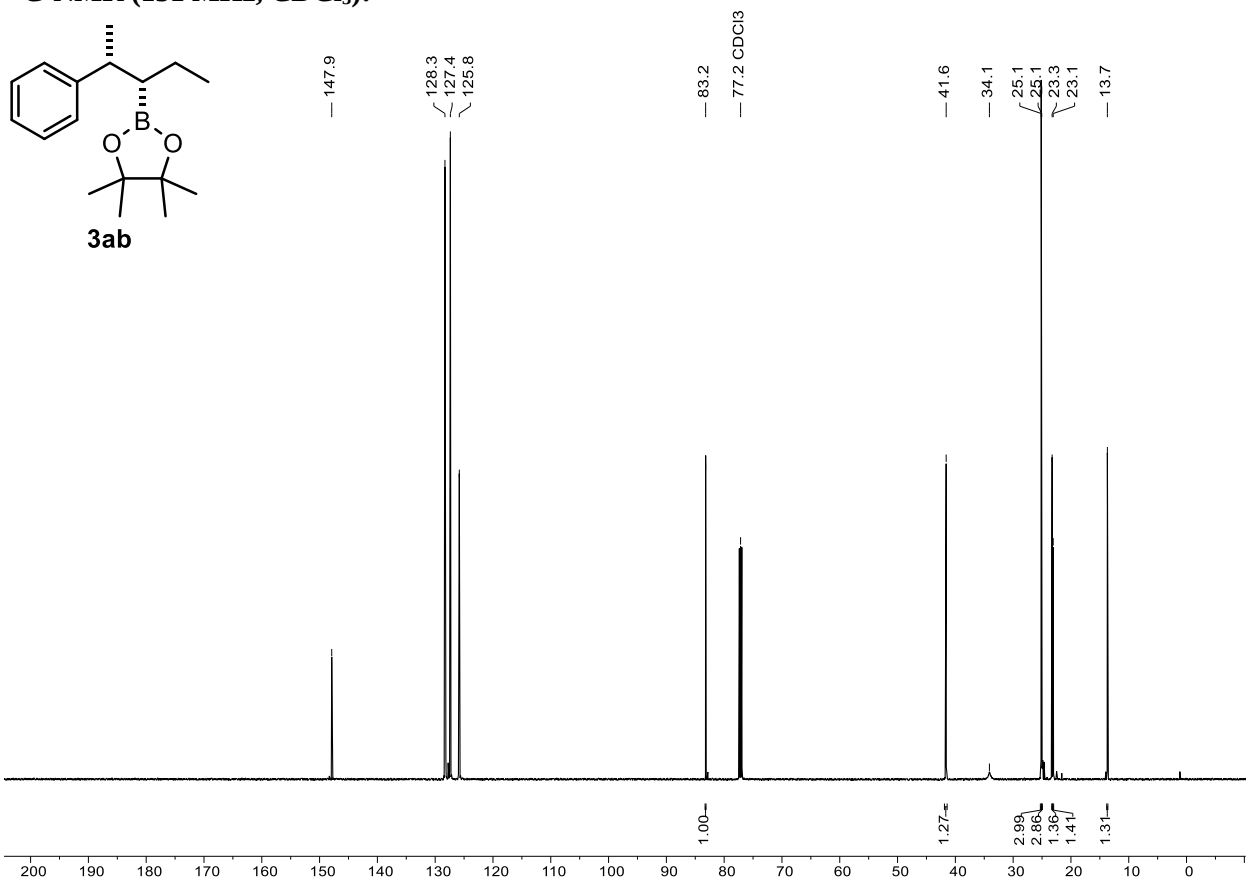
^{13}C-NMR (126 MHz, $CDCl_3$):



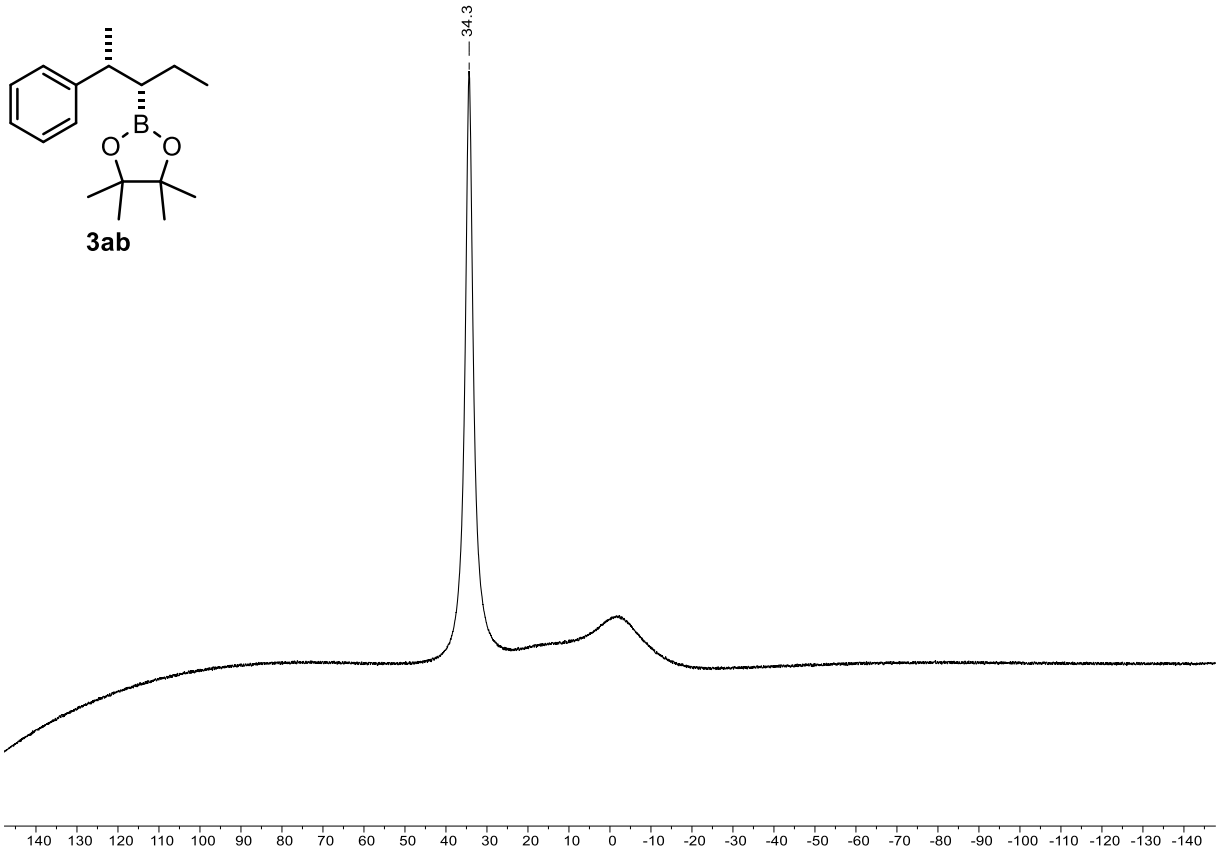
^{1}H-NMR (599 MHz, $CDCl_3$):



^{13}C-NMR (151 MHz, $CDCl_3$):

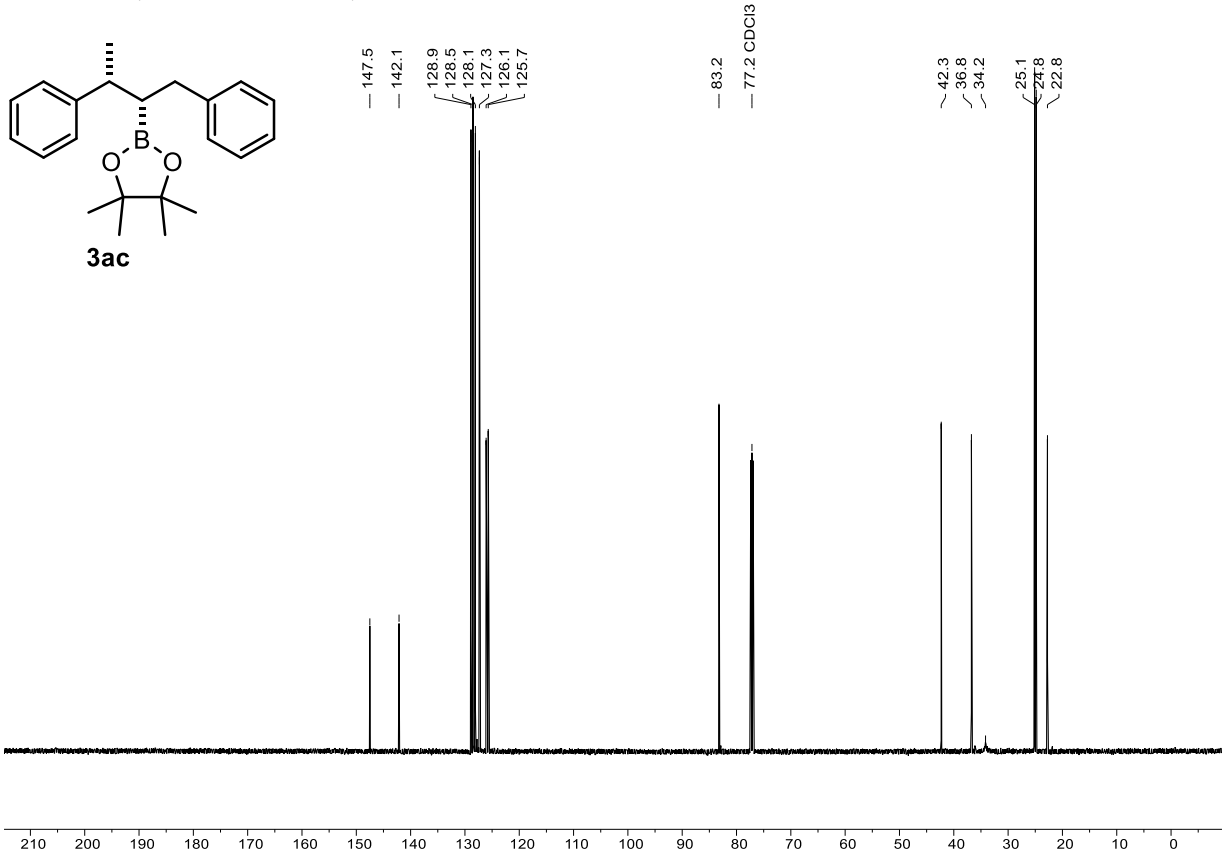


^{11}B-NMR (192 MHz, $CDCl_3$):

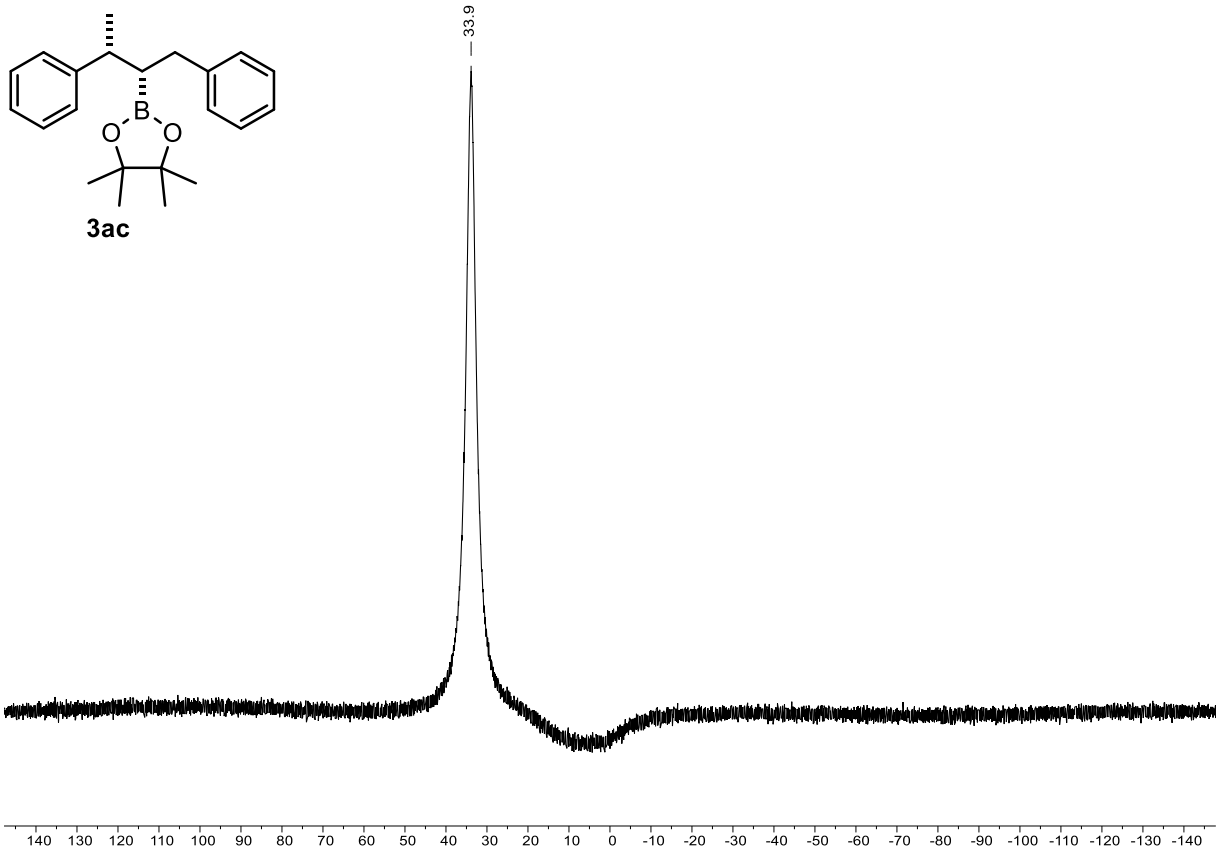


^{1}H-NMR (599 MHz, $CDCl_3$):

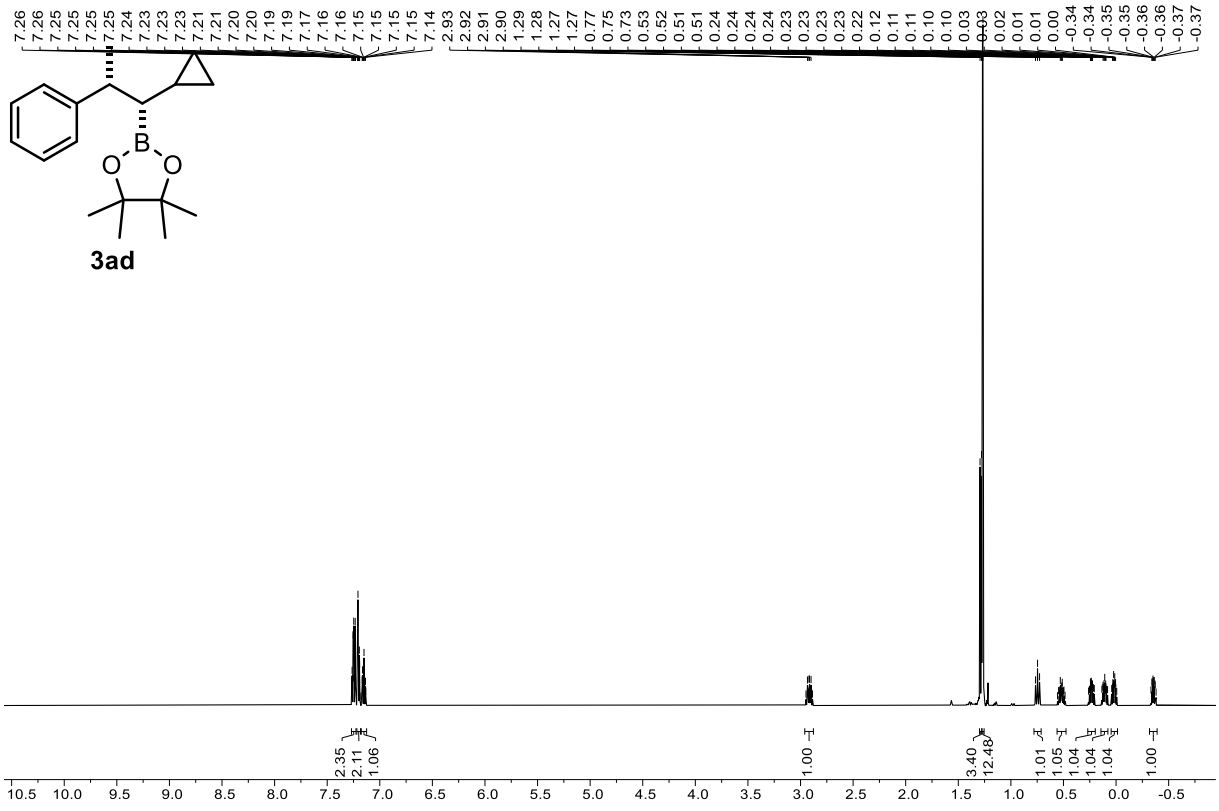
^{13}C-NMR (151 MHz, $CDCl_3$):



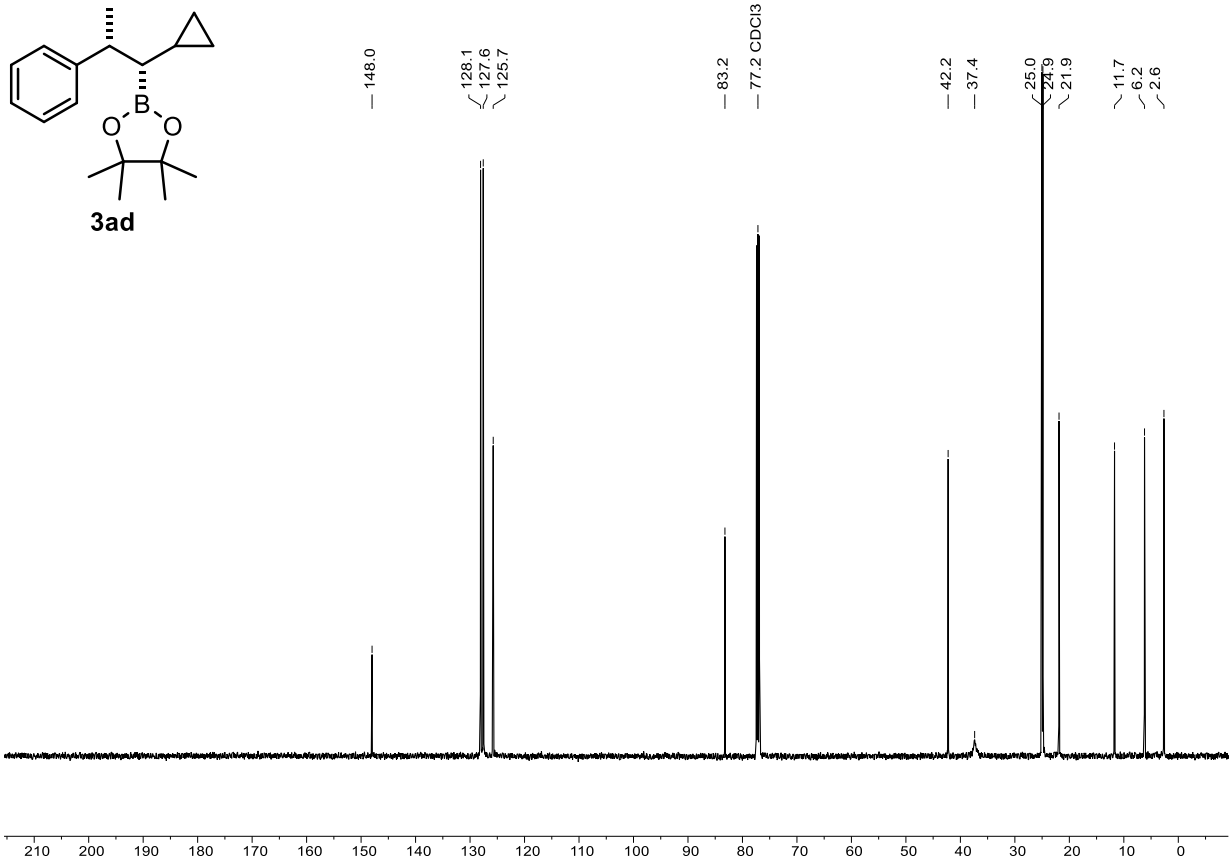
^{11}B-NMR (192 MHz, $CDCl_3$):



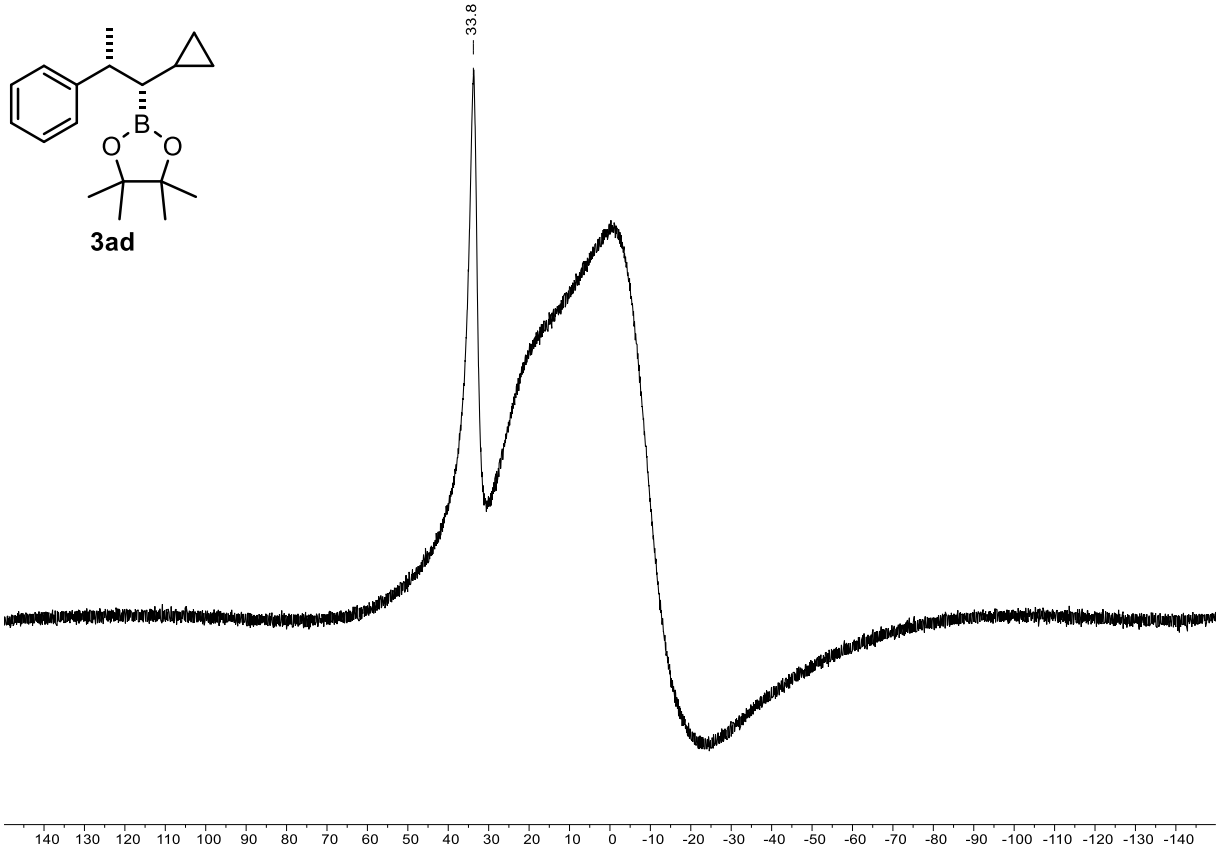
^{1}H-NMR (500 MHz, $CDCl_3$):



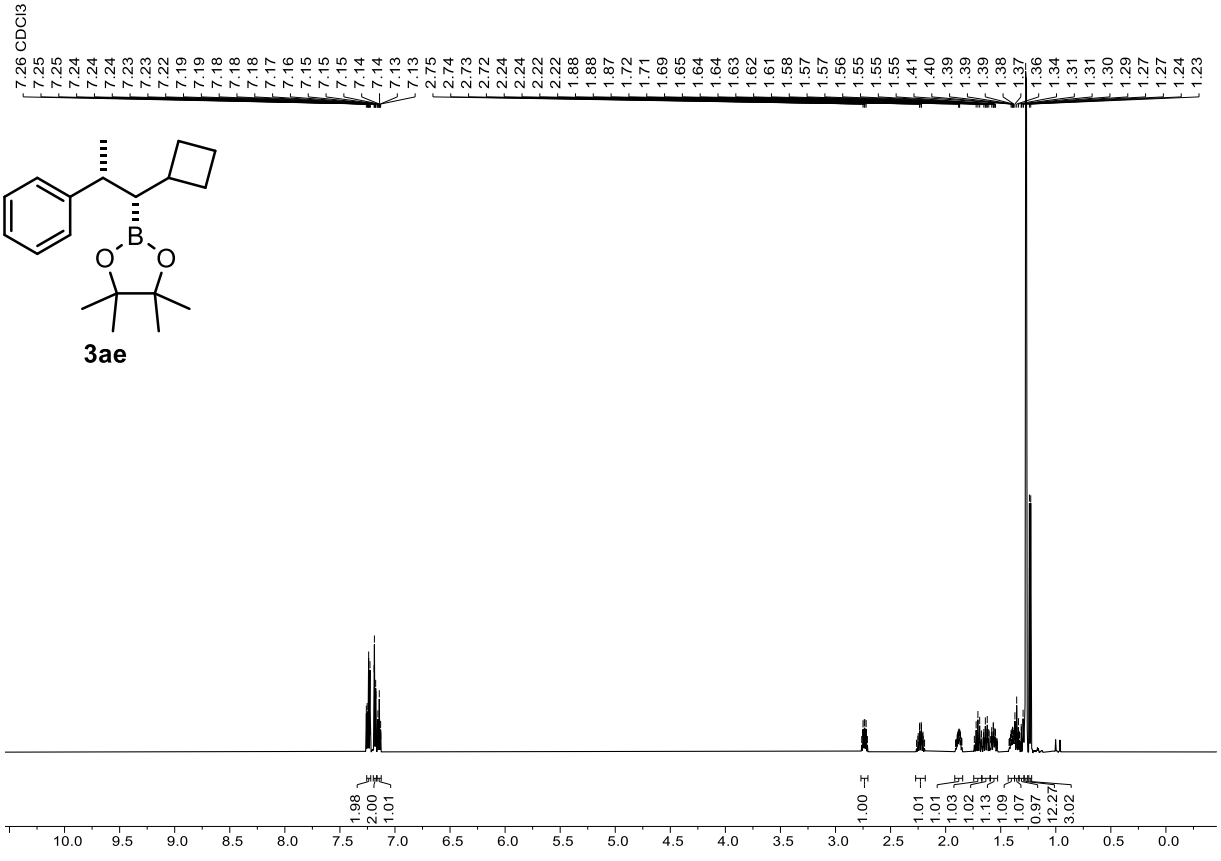
^{13}C-NMR (126 MHz, $CDCl_3$):



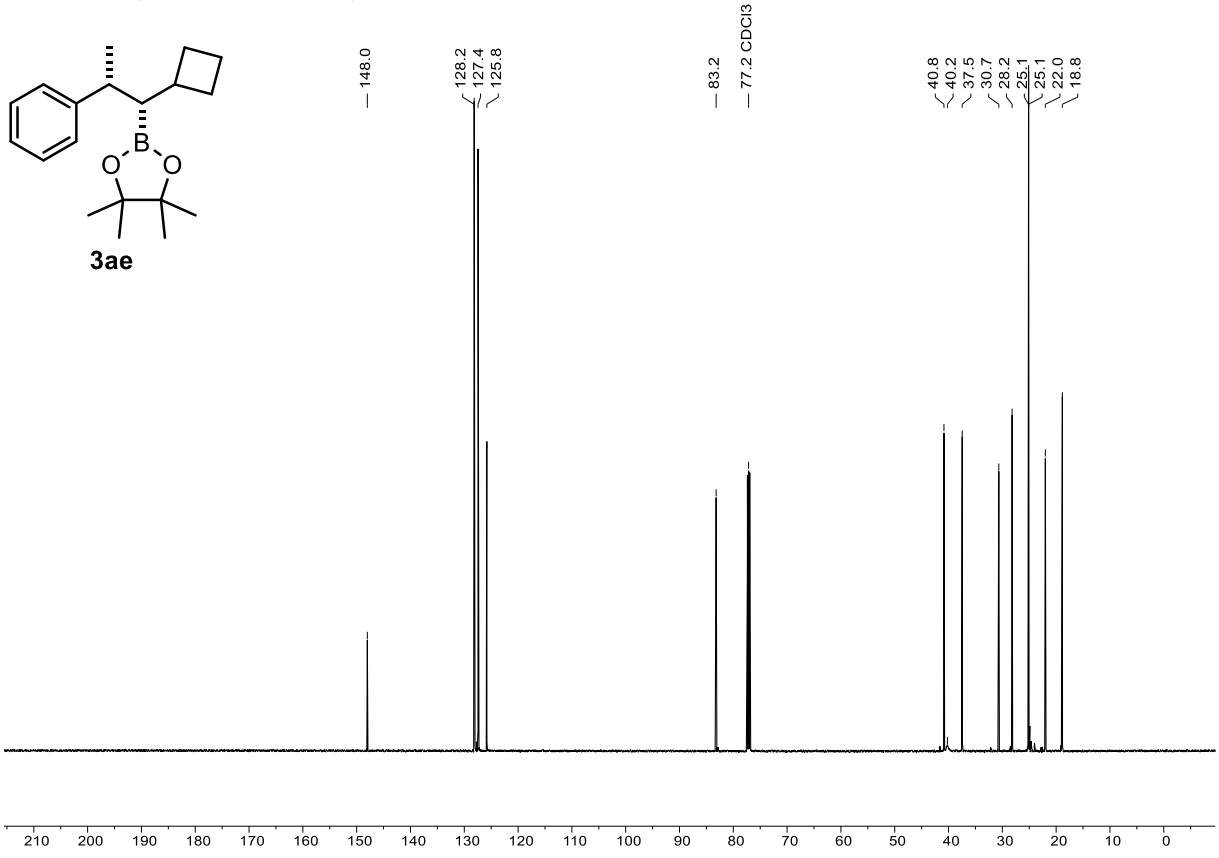
^{11}B-NMR (160 MHz, $CDCl_3$):



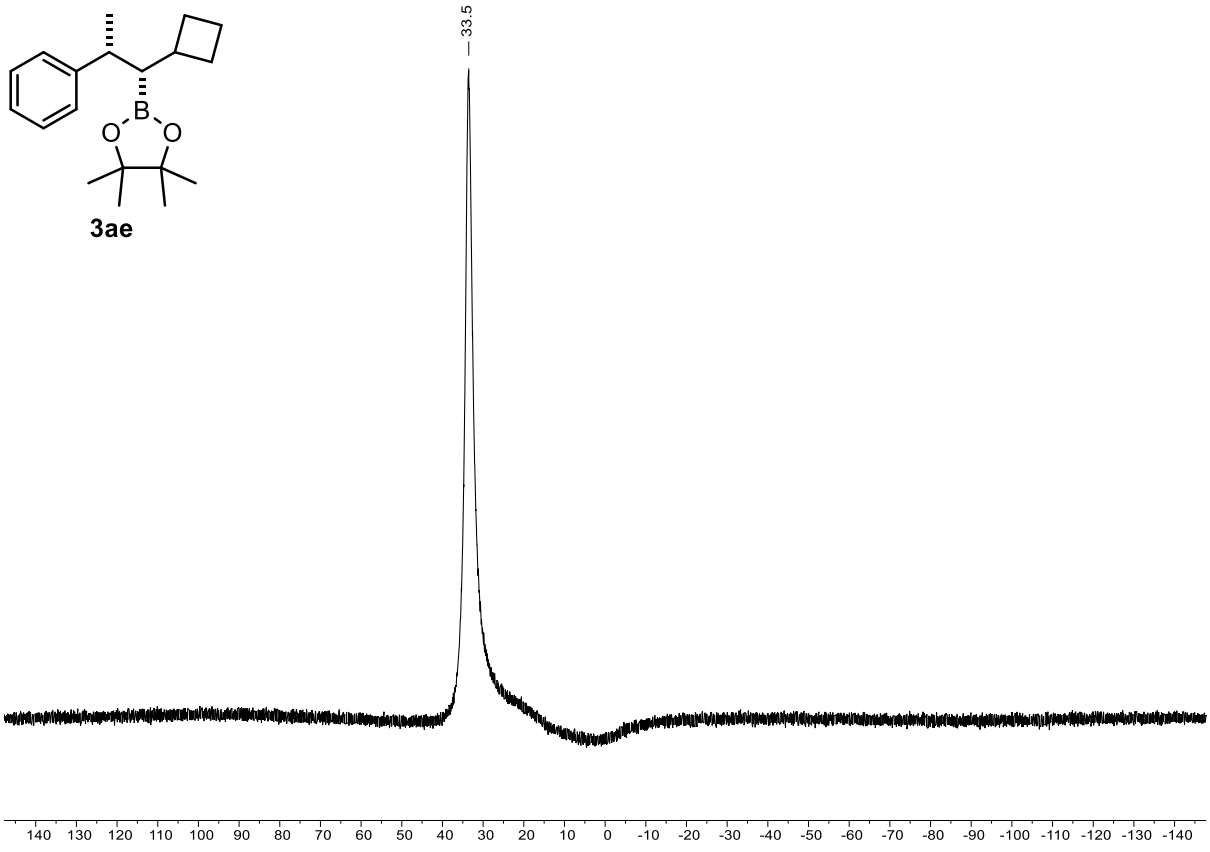
^{1}H-NMR (599 MHz, $CDCl_3$):



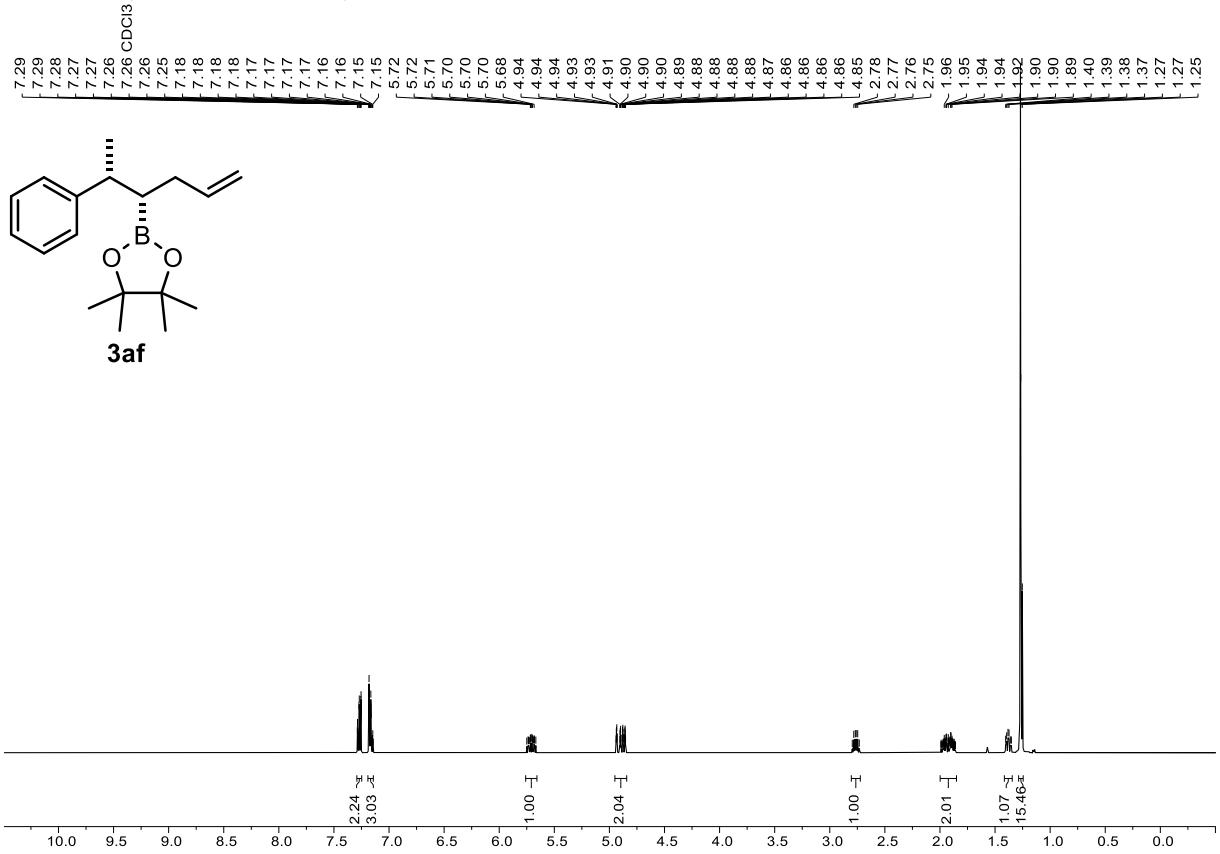
^{13}C-NMR (151 MHz, $CDCl_3$):



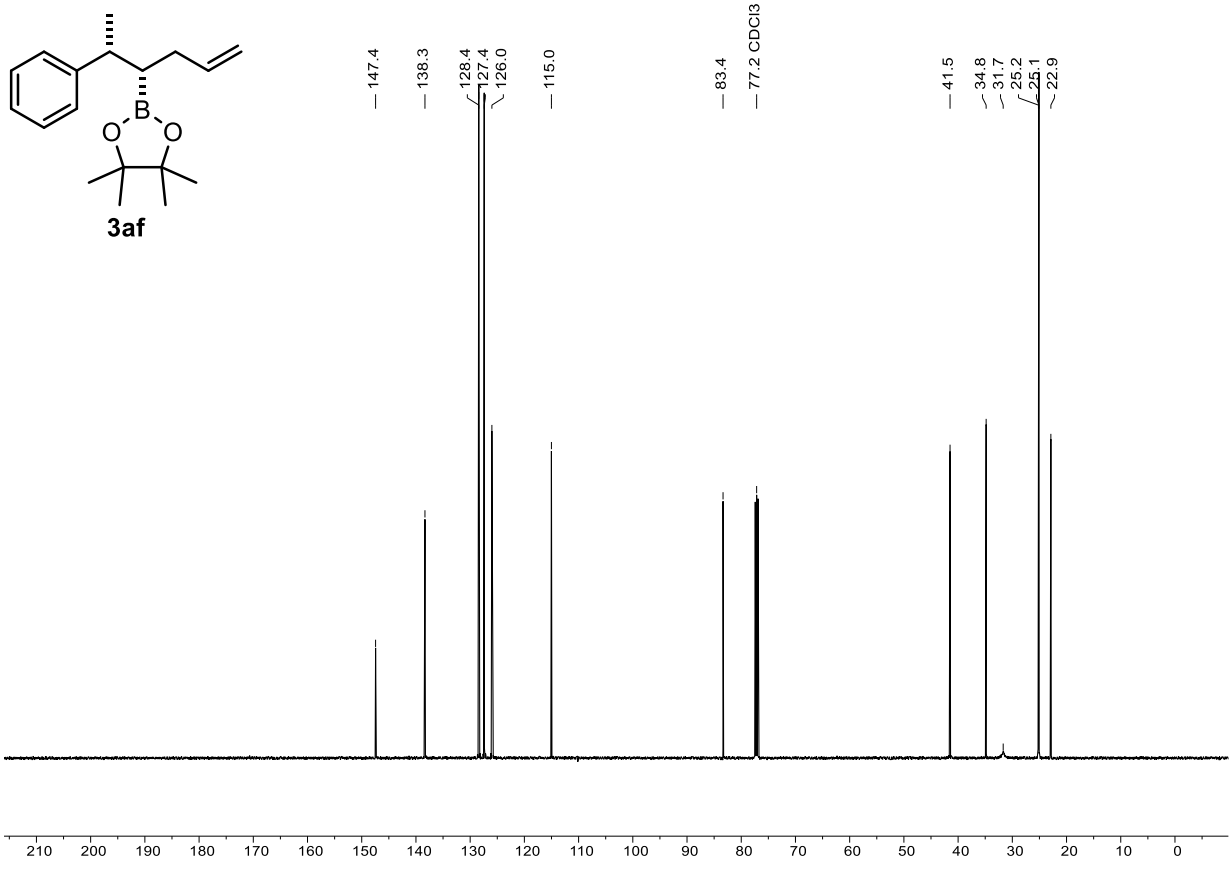
^{11}B-NMR (192 MHz, $CDCl_3$):



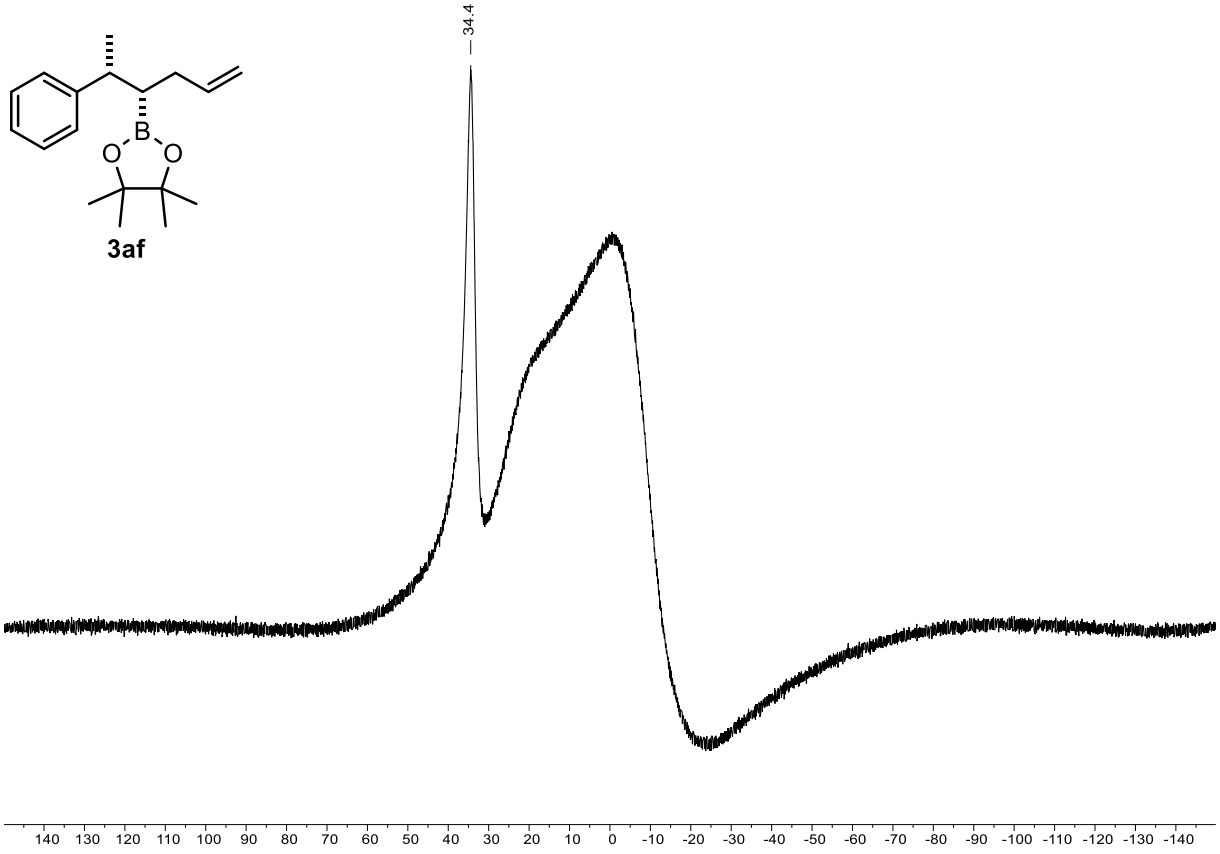
^{1}H-NMR (500 MHz, $CDCl_3$):



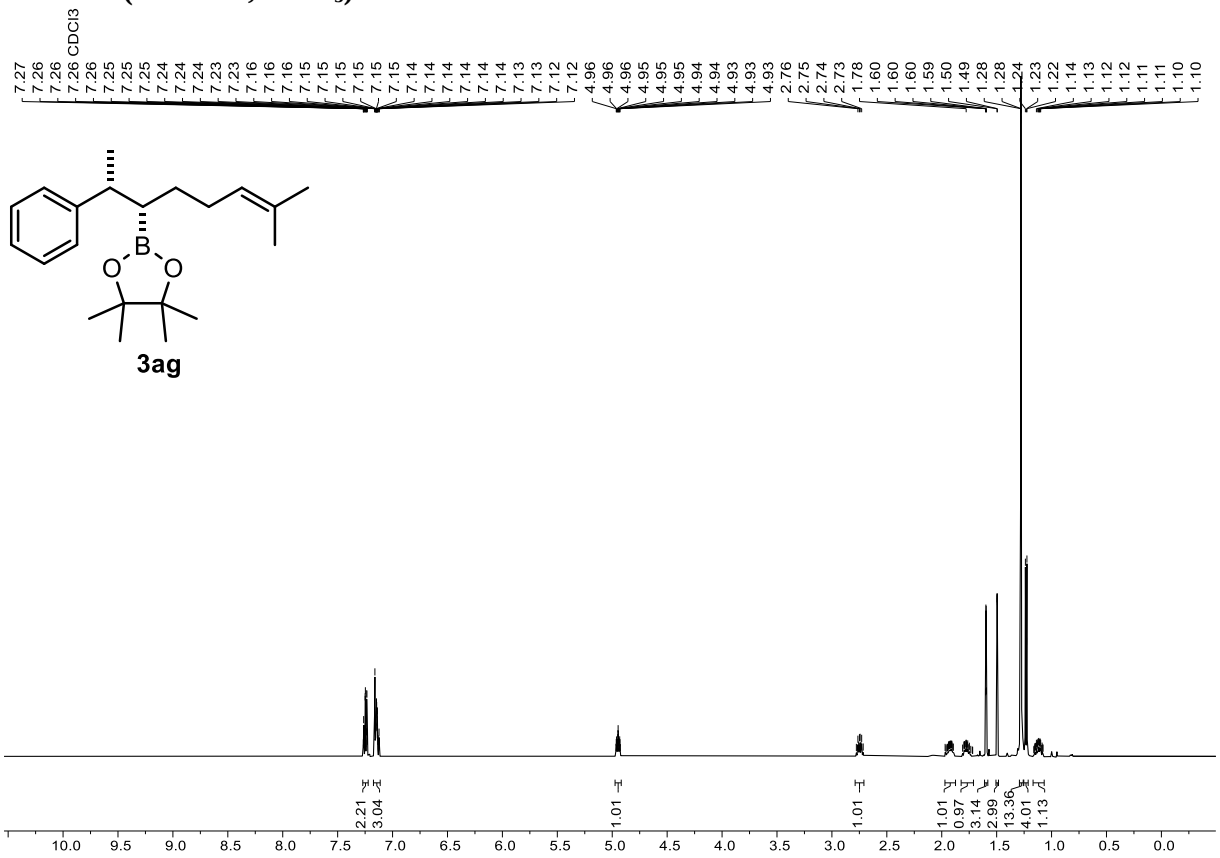
^{13}C-NMR (126 MHz, $CDCl_3$):



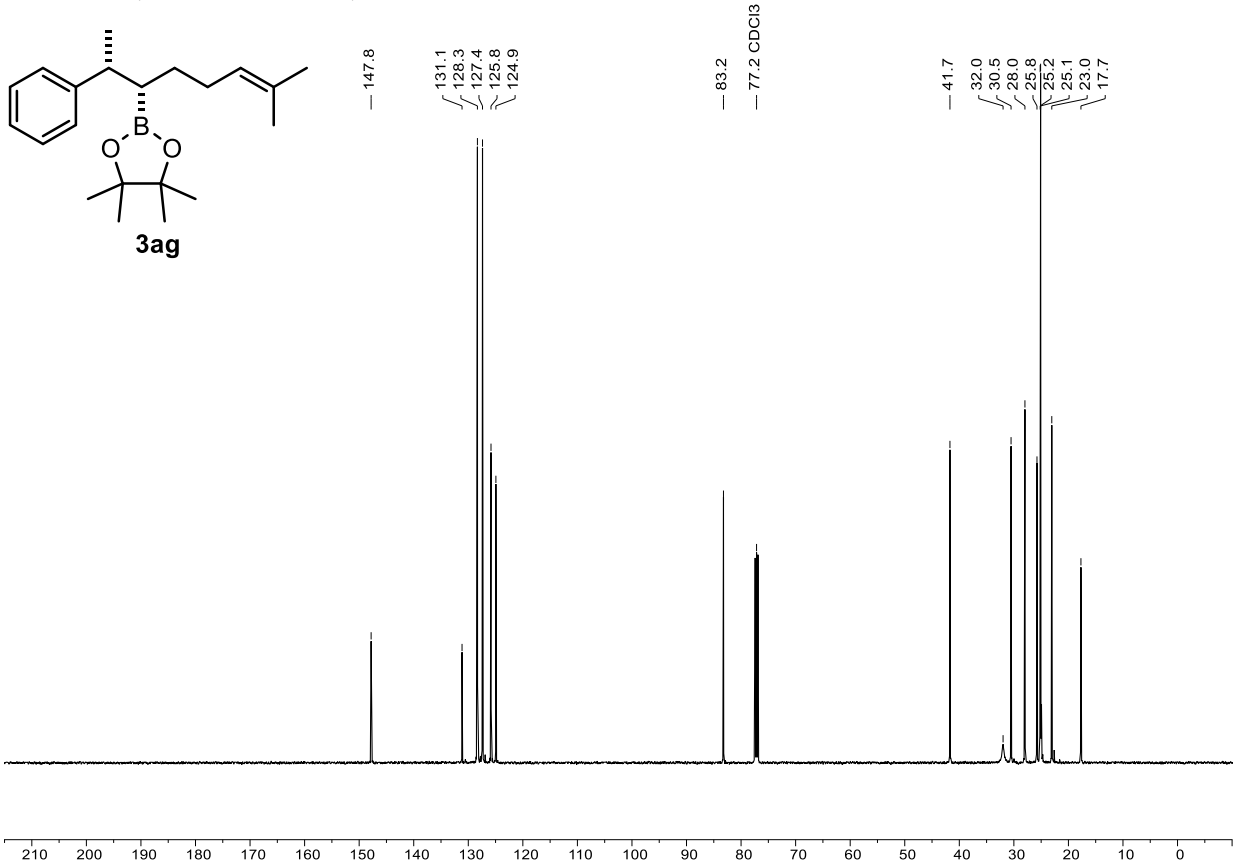
^{11}B-NMR (160 MHz, $CDCl_3$):



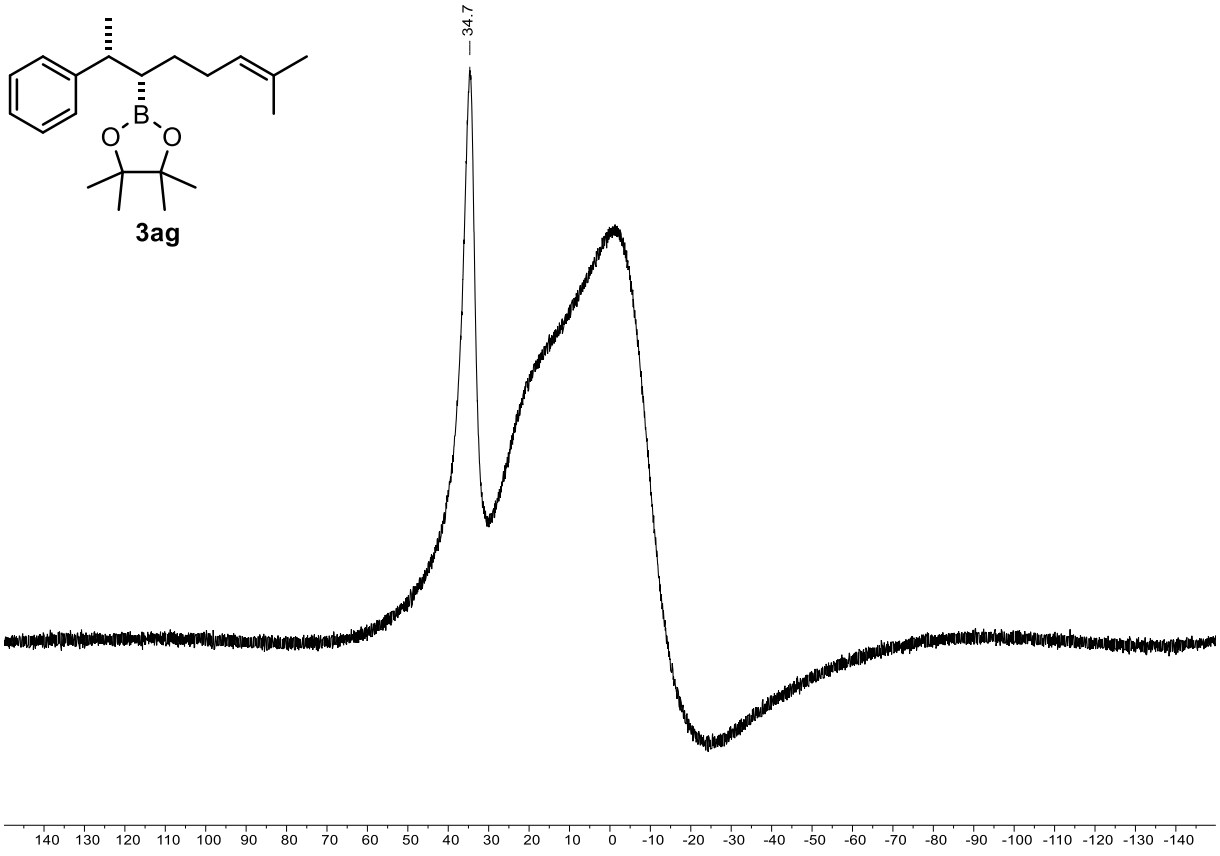
^{1}H-NMR (500 MHz, $CDCl_3$):



^{13}C-NMR (126 MHz, $CDCl_3$):



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



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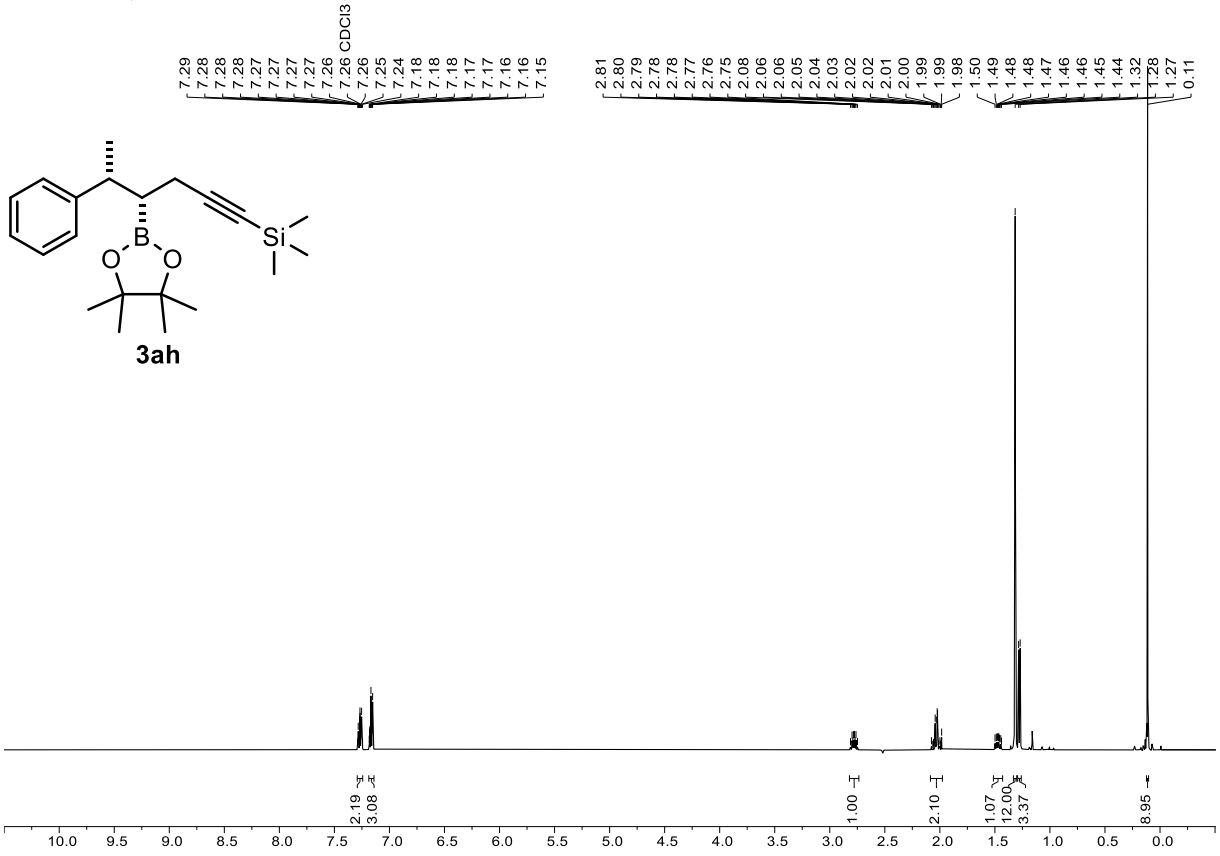
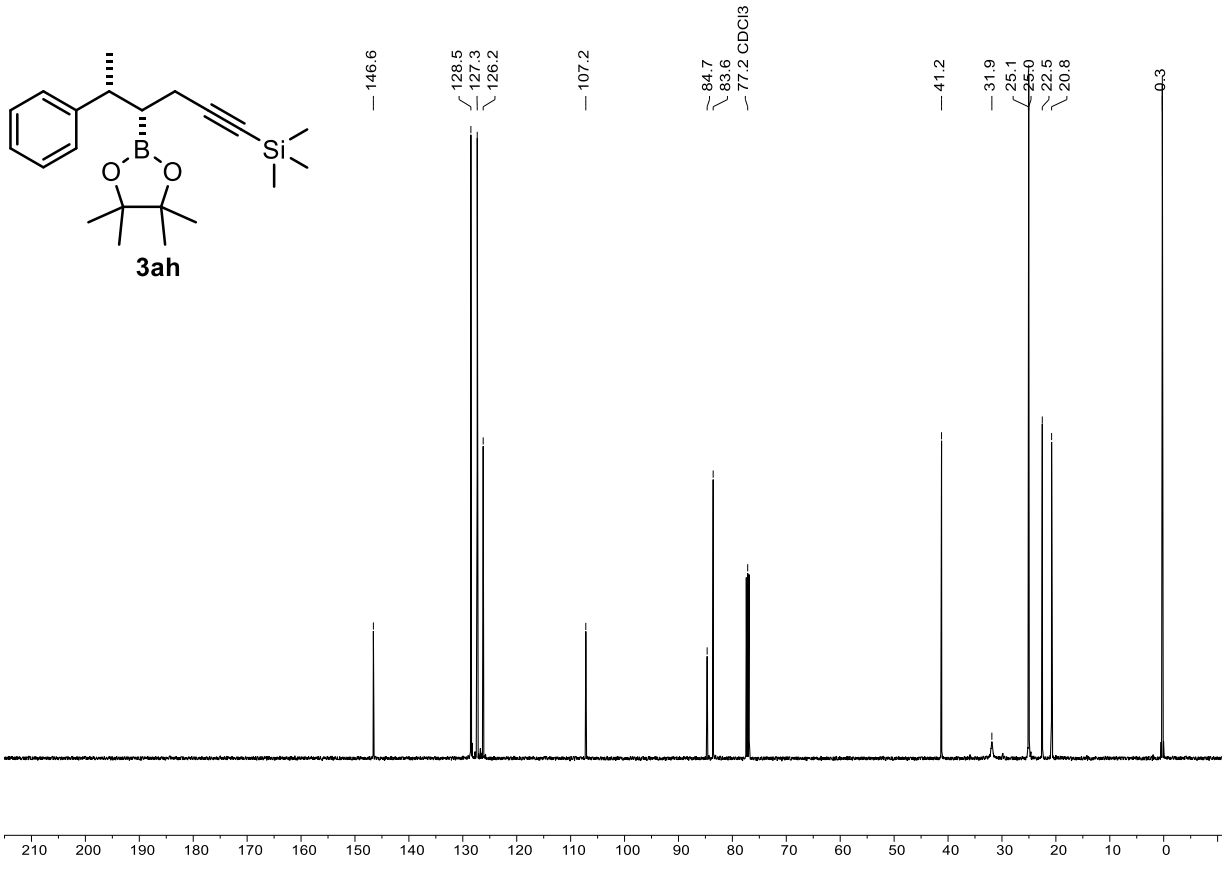
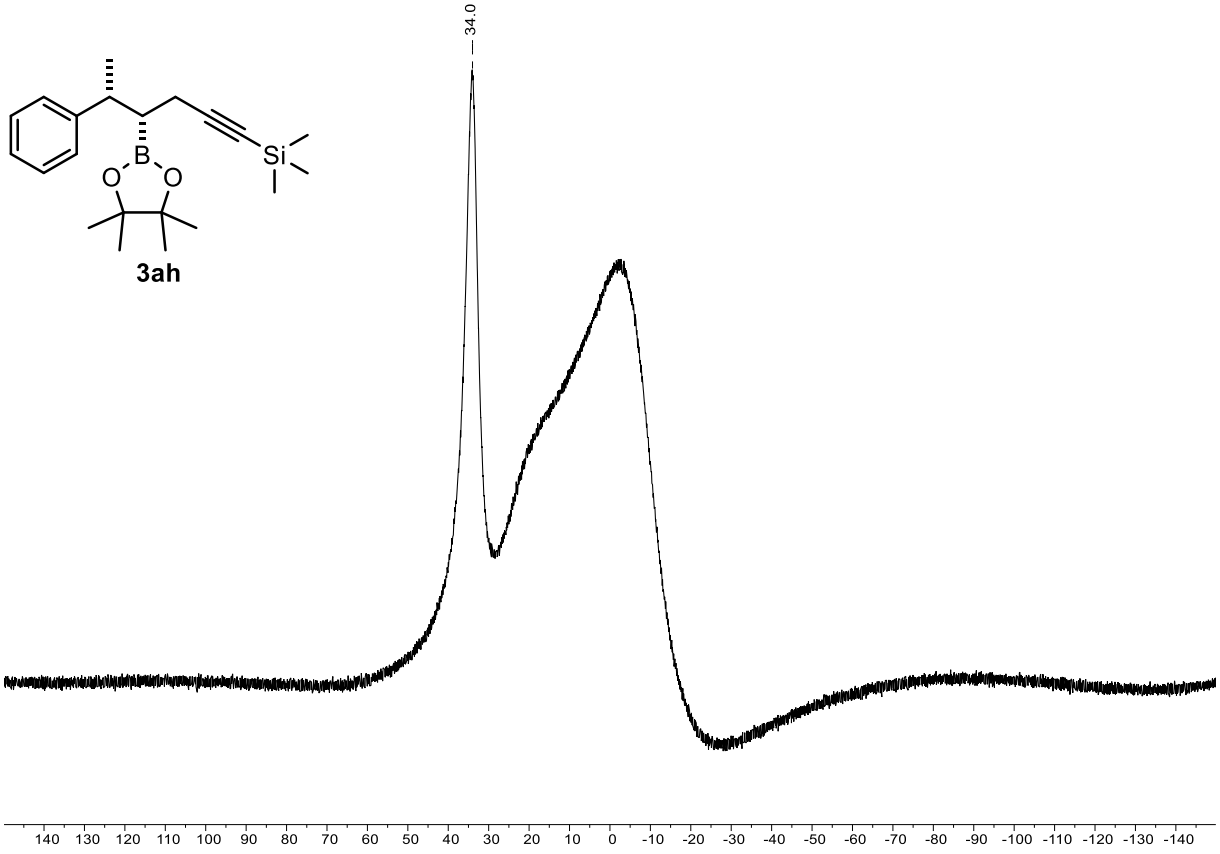


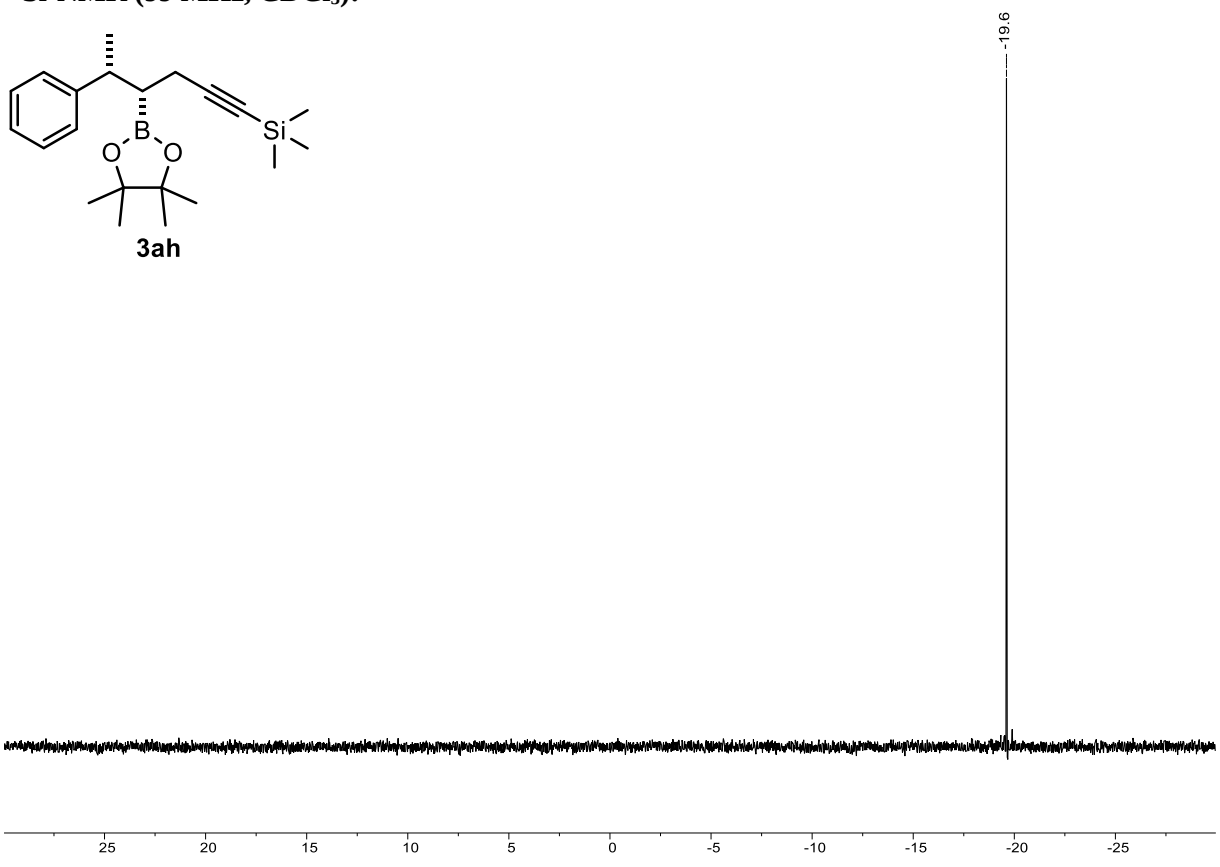
^{13}C-NMR (126 MHz, $CDCl_3$):



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

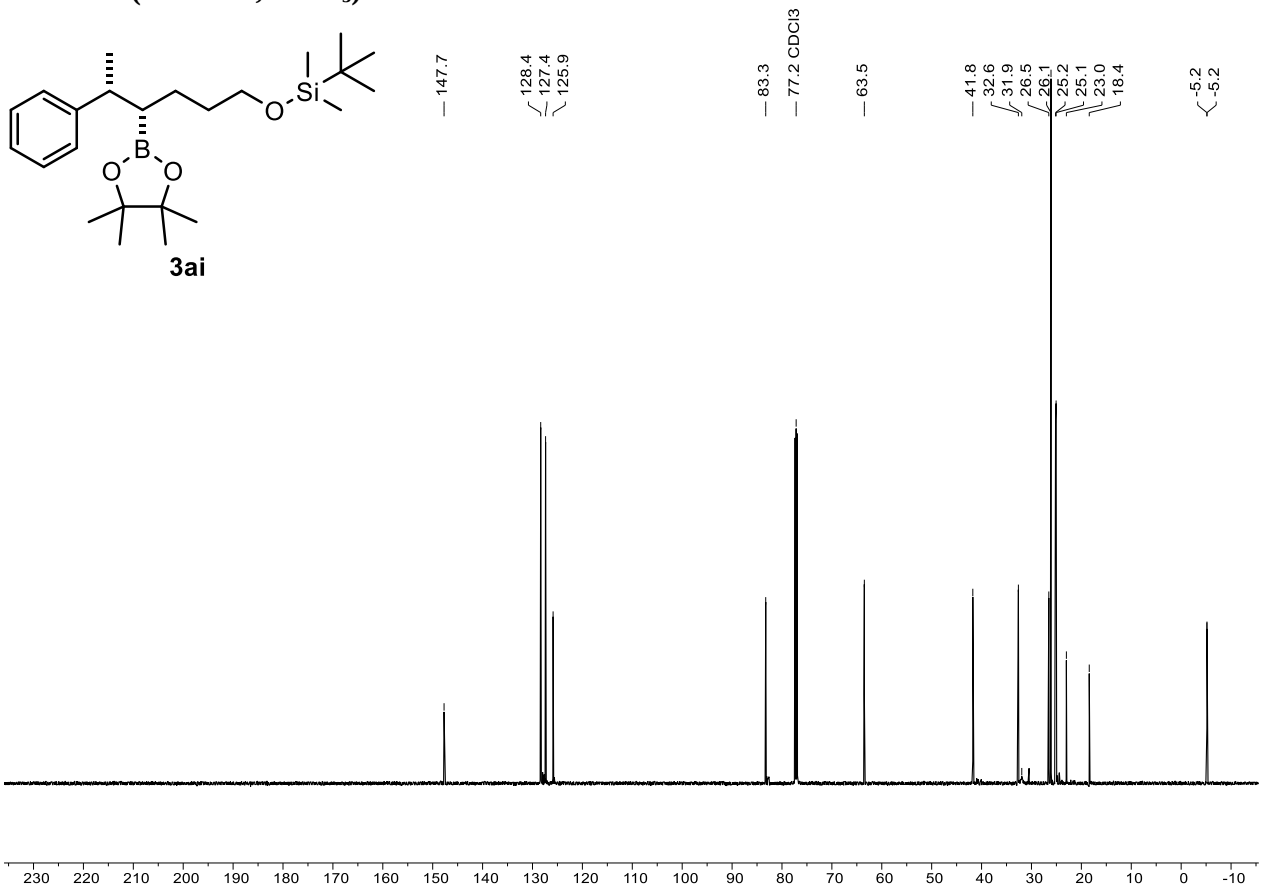


^{29}Si-NMR (99 MHz, $CDCl_3$):

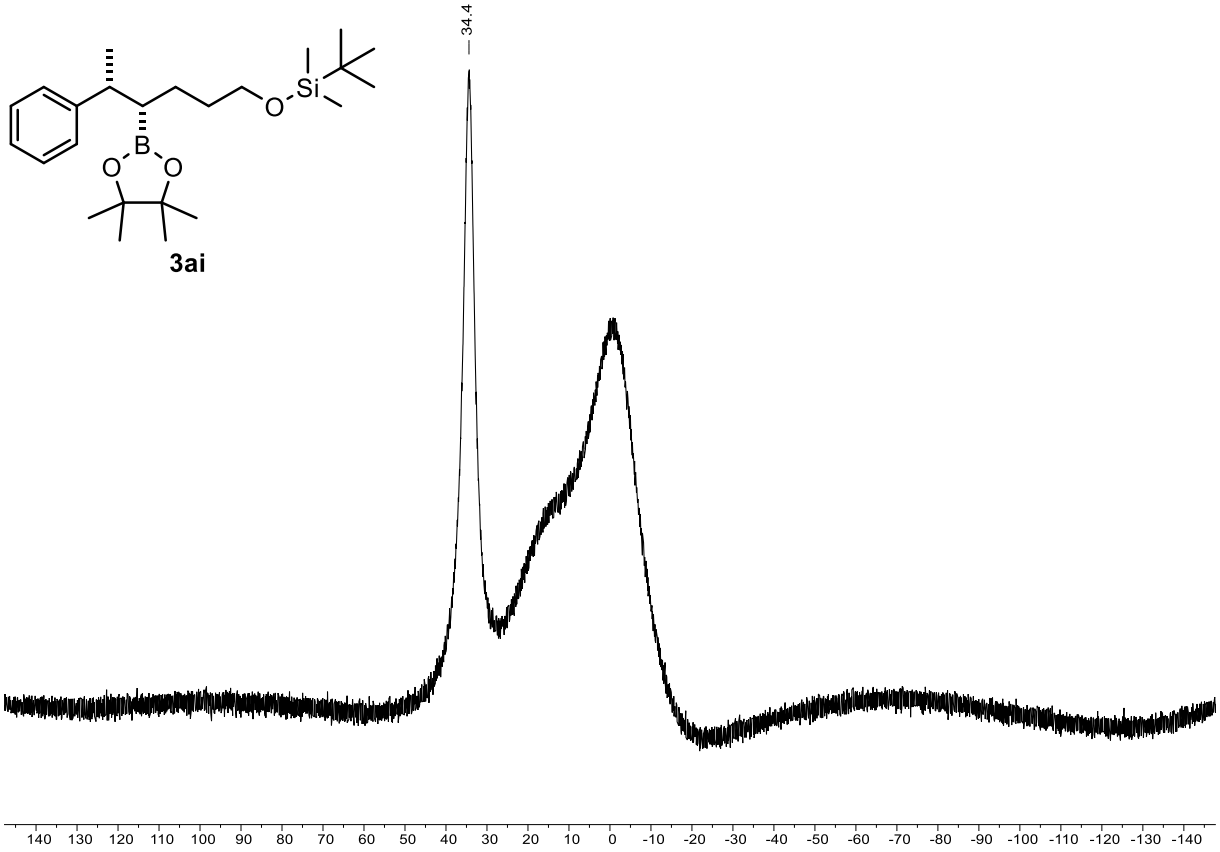


^{1}H-NMR (599 MHz, $CDCl_3$):

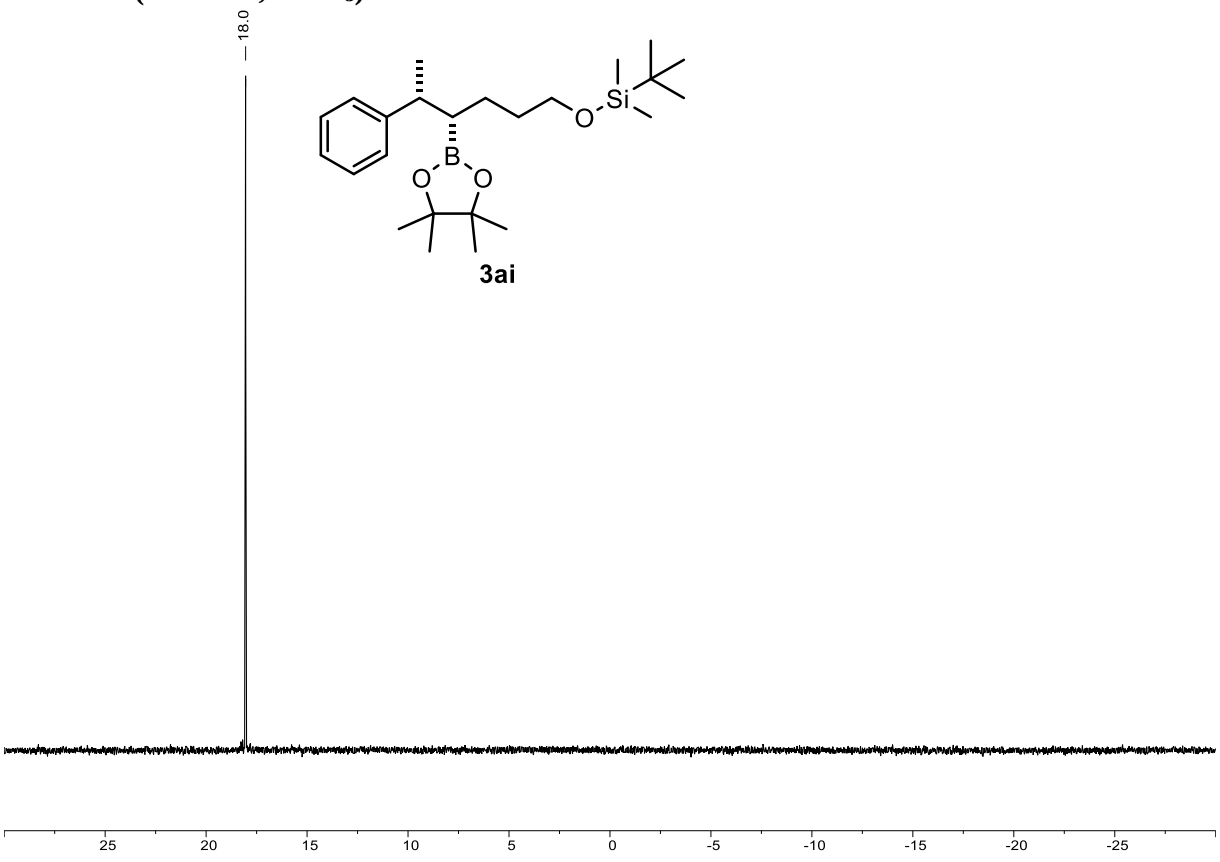
^{13}C-NMR (151 MHz, $CDCl_3$):



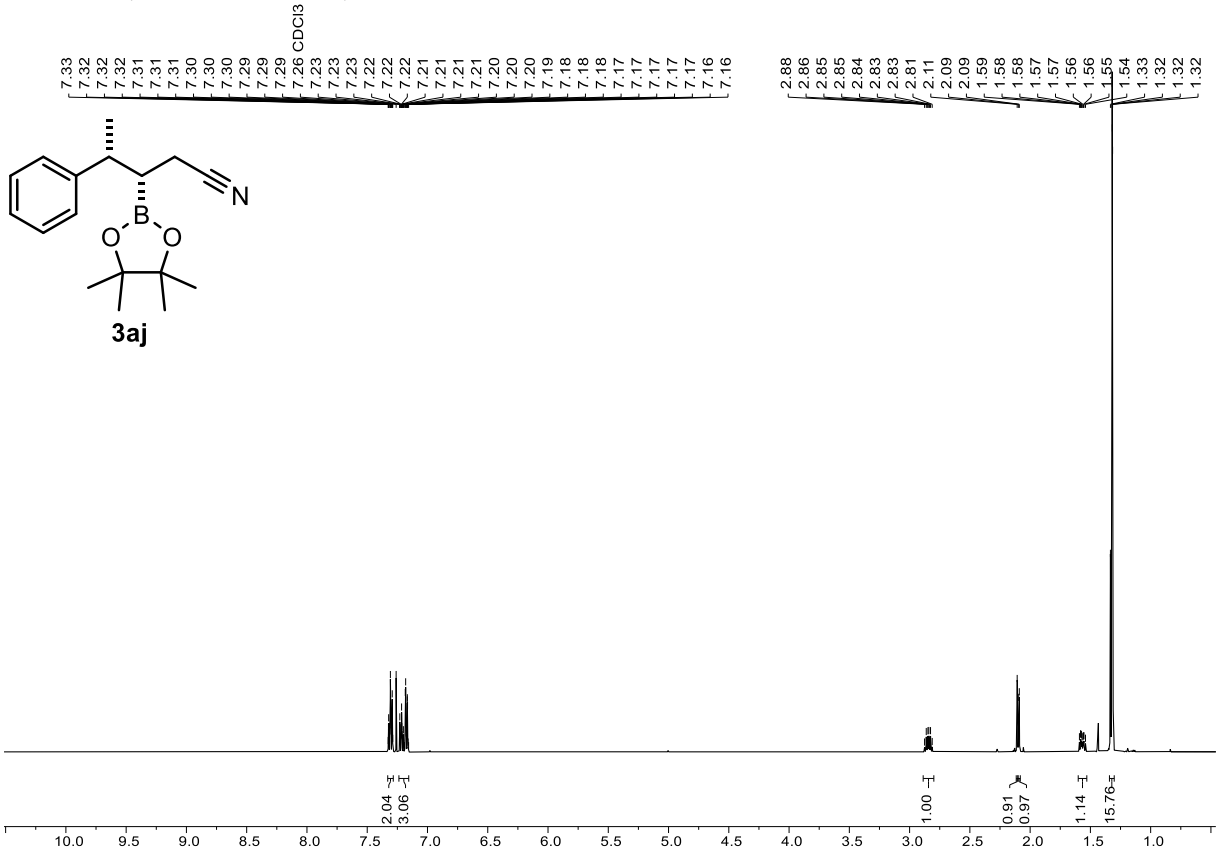
^{11}B-NMR (192 MHz, $CDCl_3$):



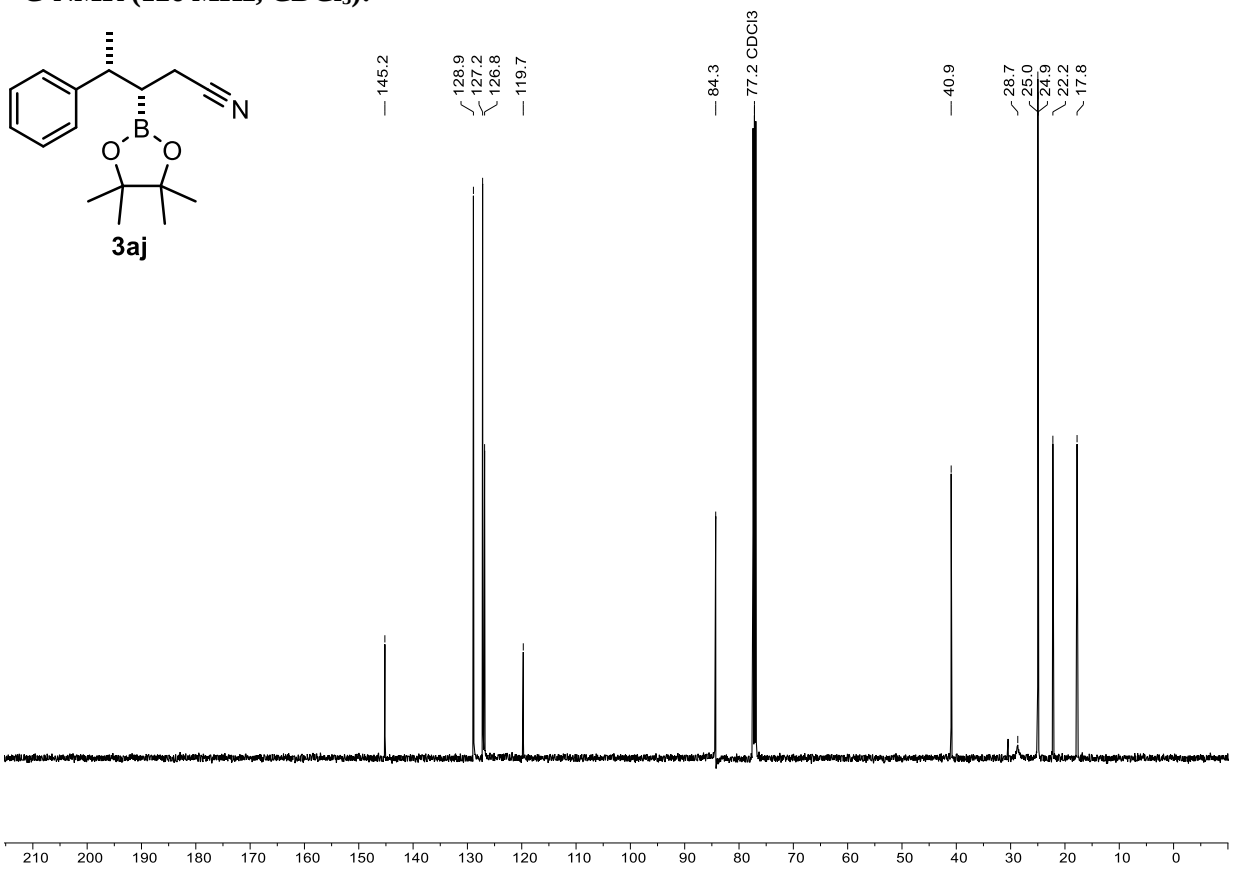
^{29}Si-NMR (119 MHz, $CDCl_3$):



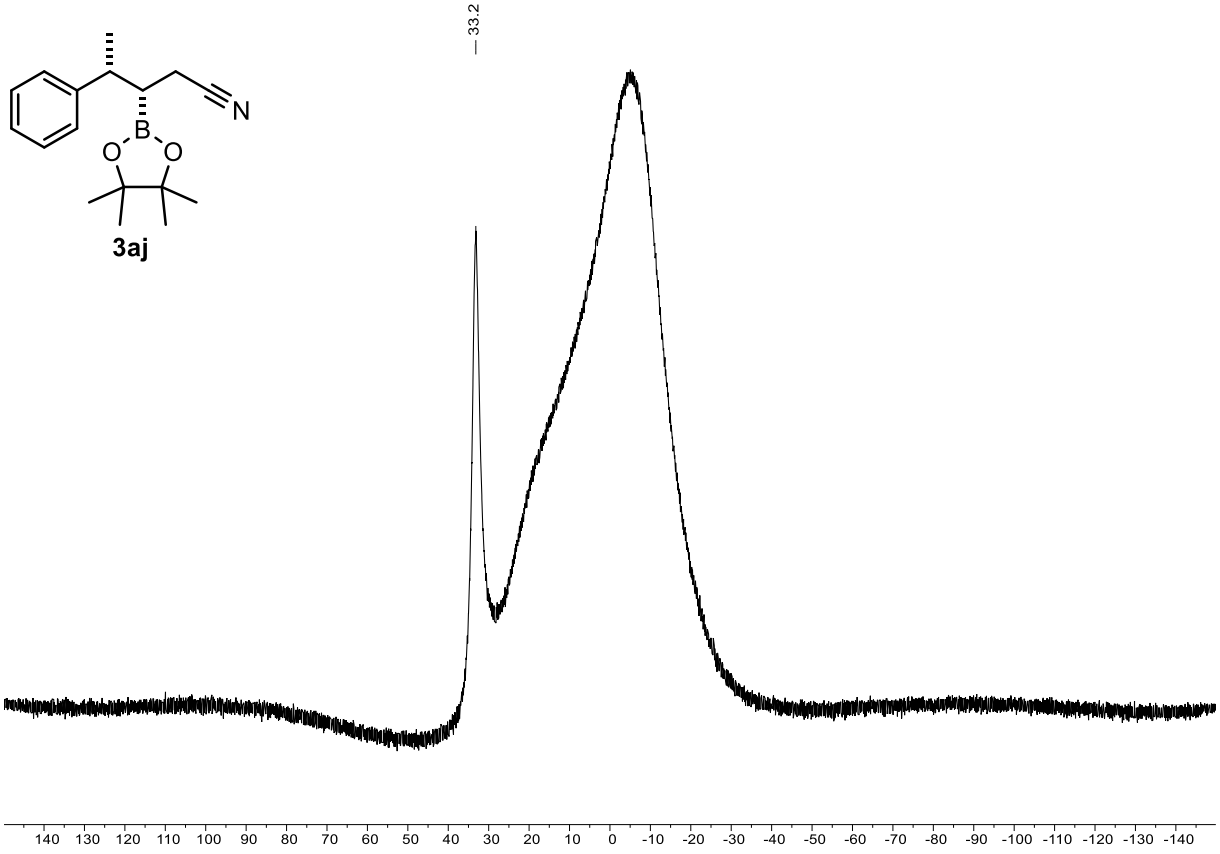
^{1}H-NMR (500 MHz, $CDCl_3$):



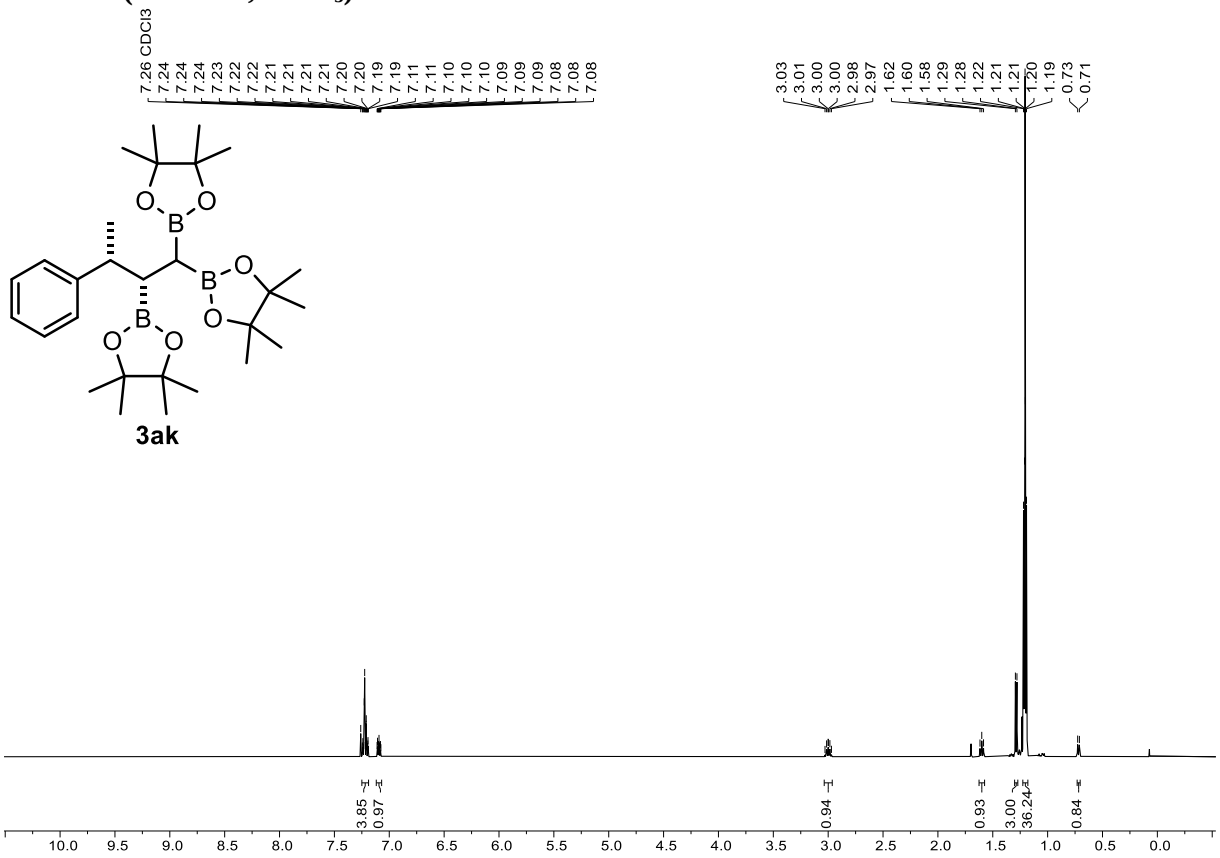
^{13}C-NMR (126 MHz, $CDCl_3$):



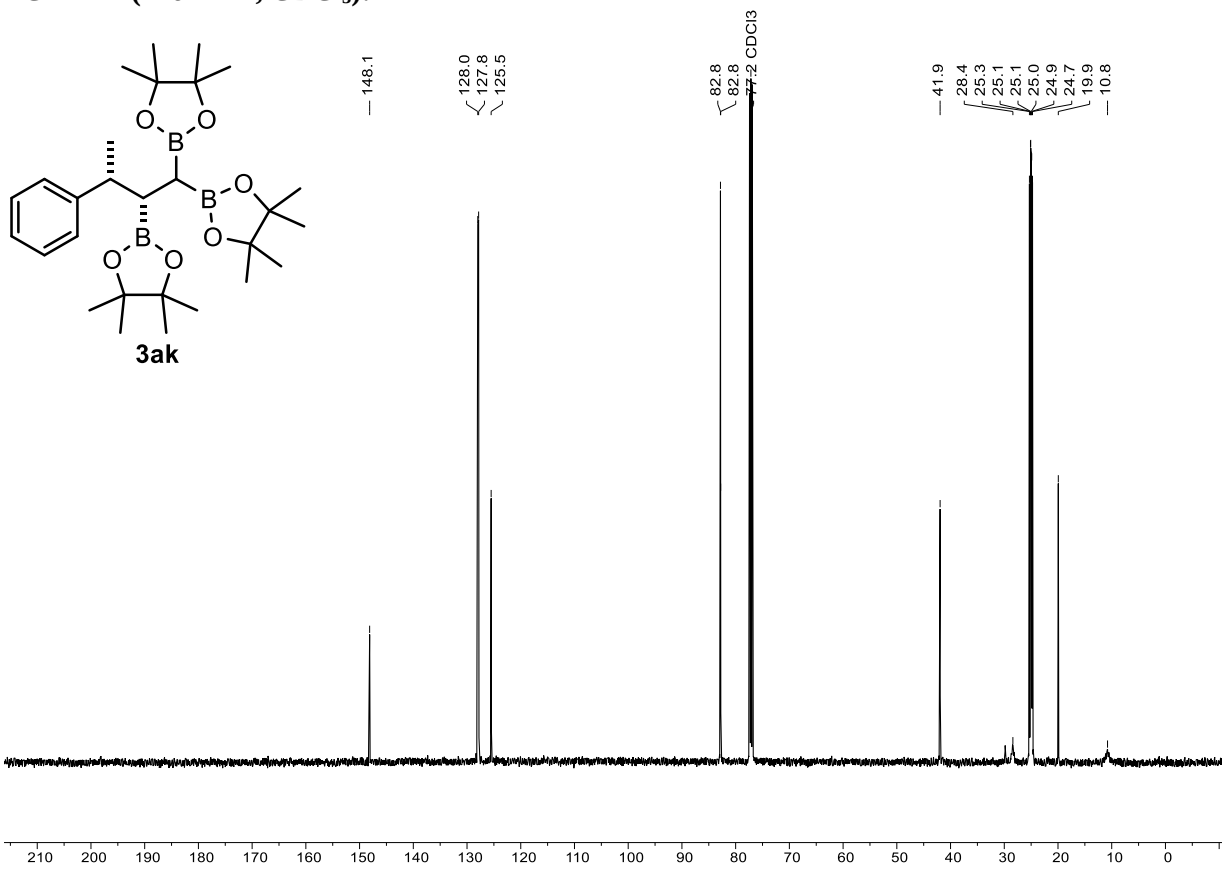
^{11}B-NMR (160 MHz, $CDCl_3$):



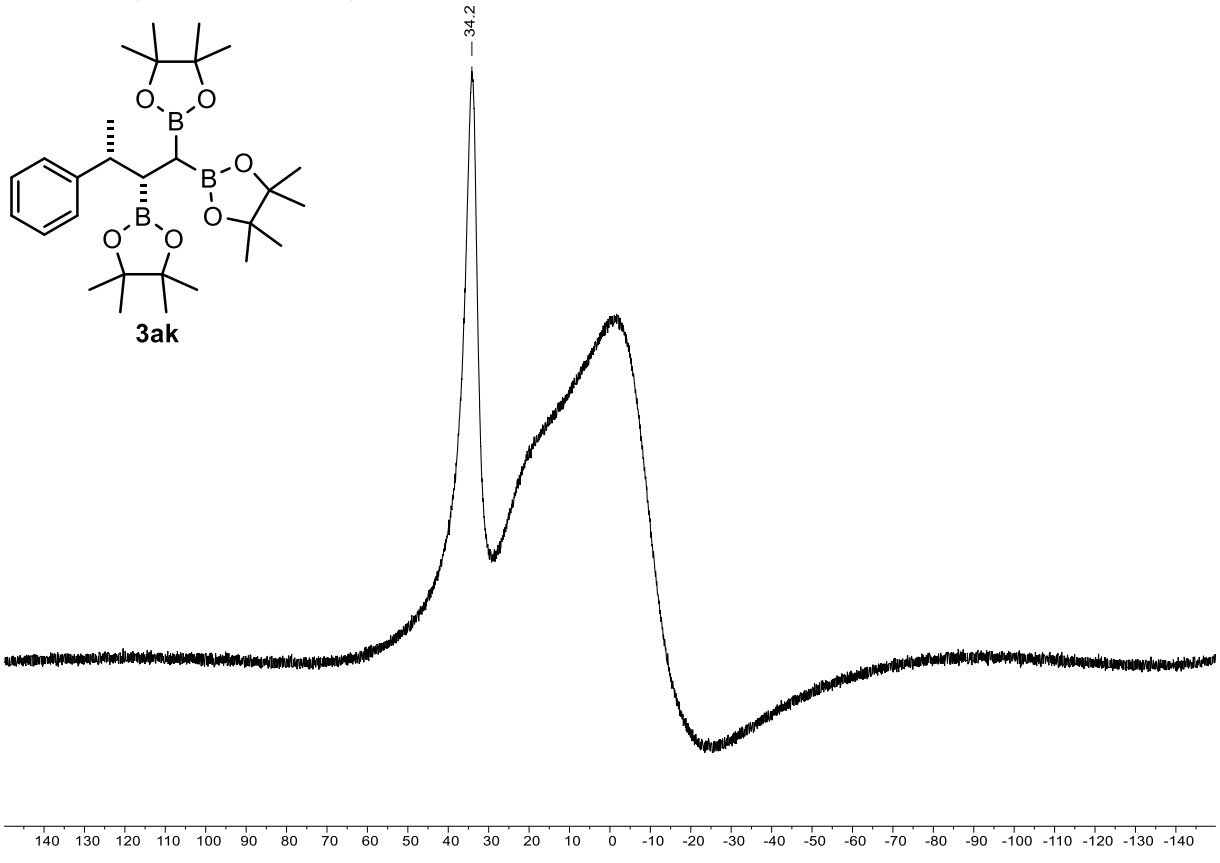
^{1}H-NMR (500 MHz, $CDCl_3$):



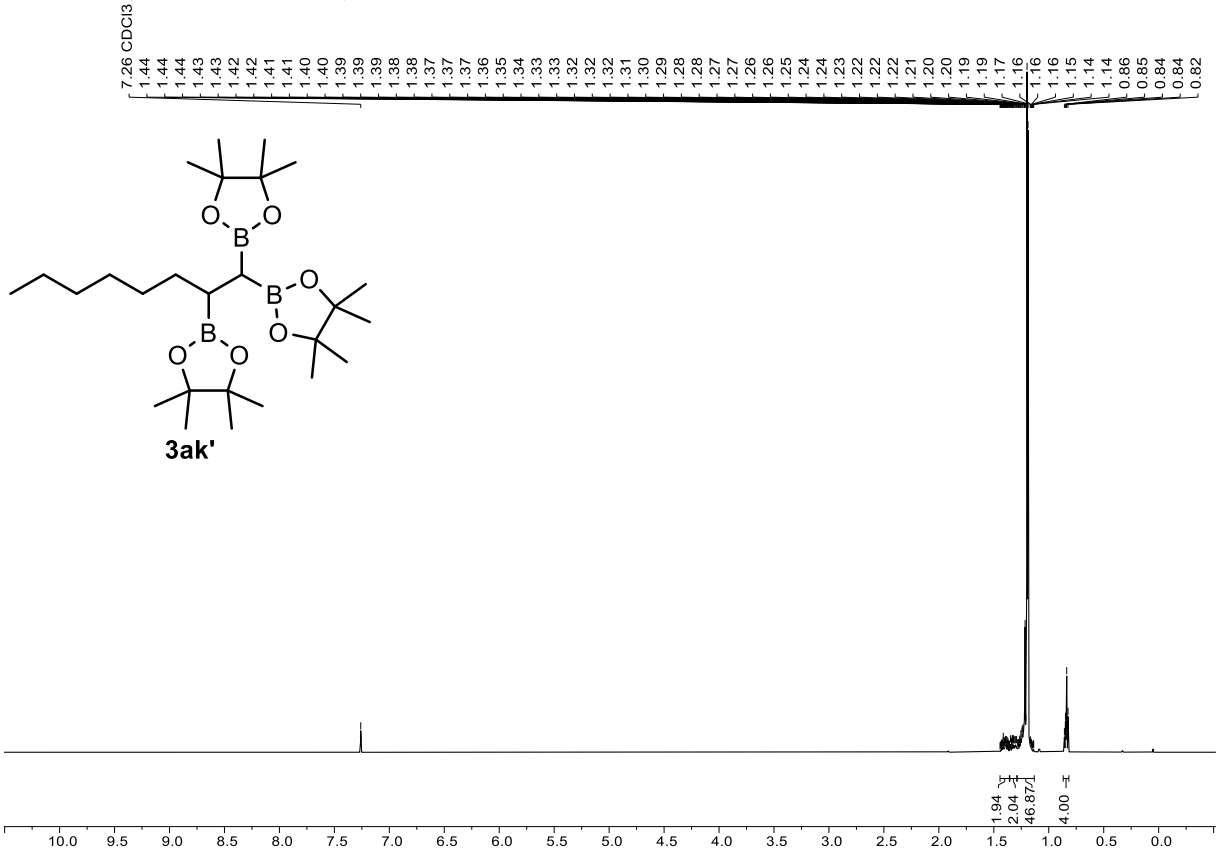
^{13}C-NMR (126 MHz, $CDCl_3$):



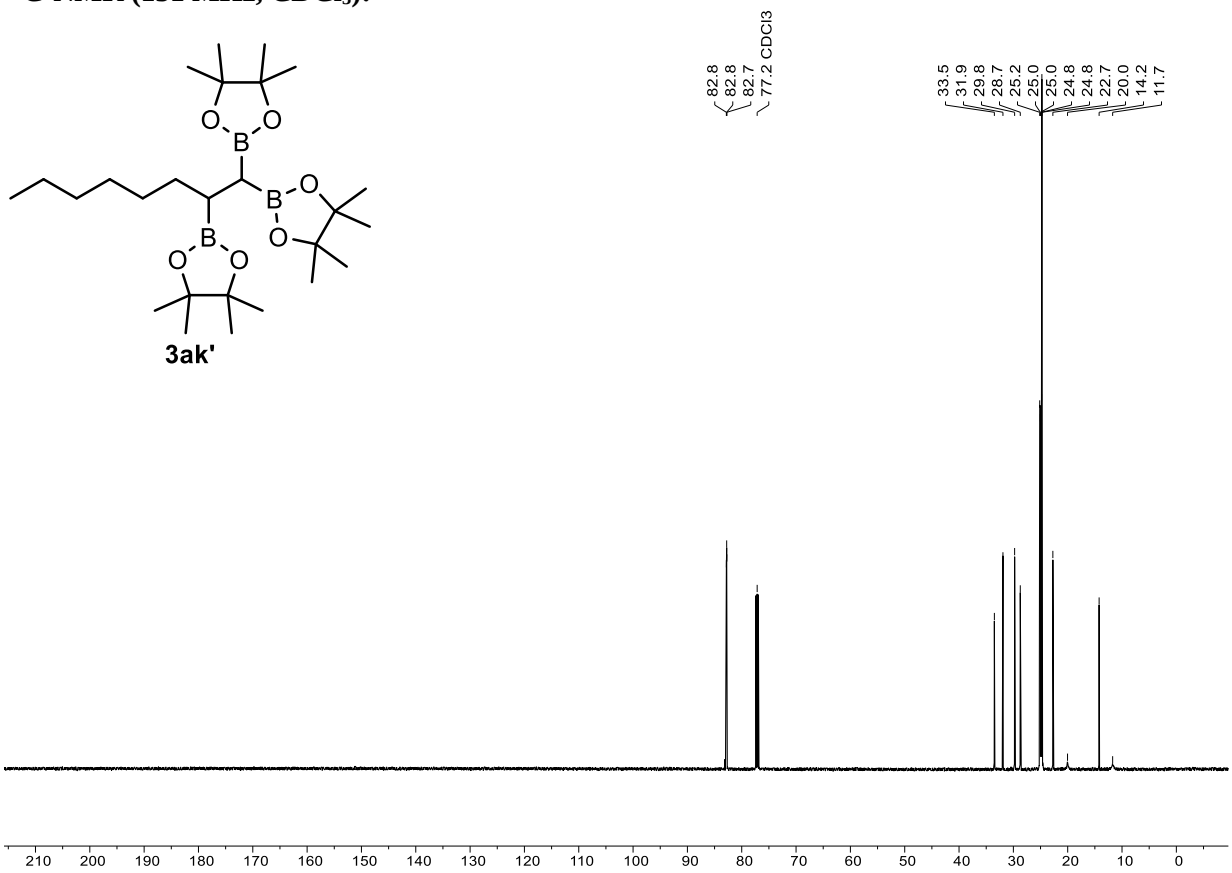
^{11}B-NMR (160 MHz, $CDCl_3$):



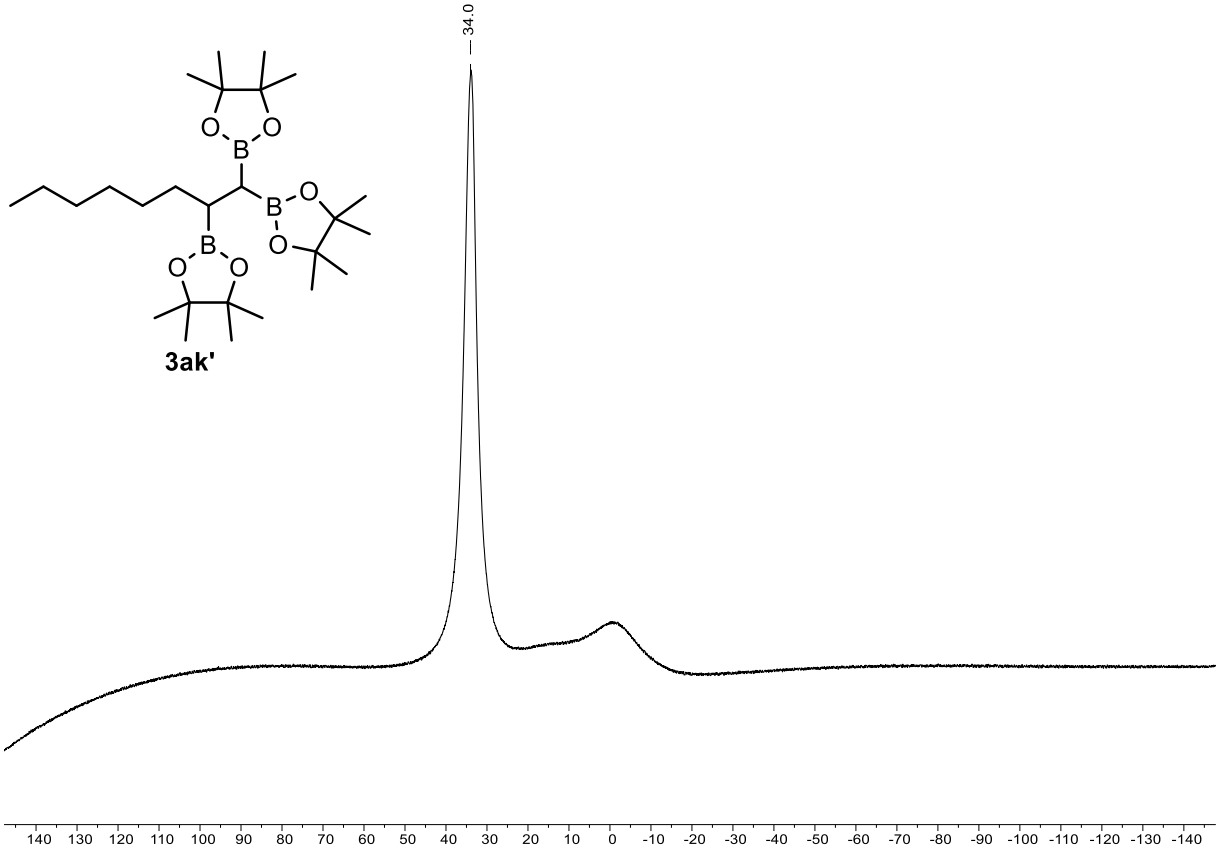
^{1}H-NMR (599 MHz, $CDCl_3$):



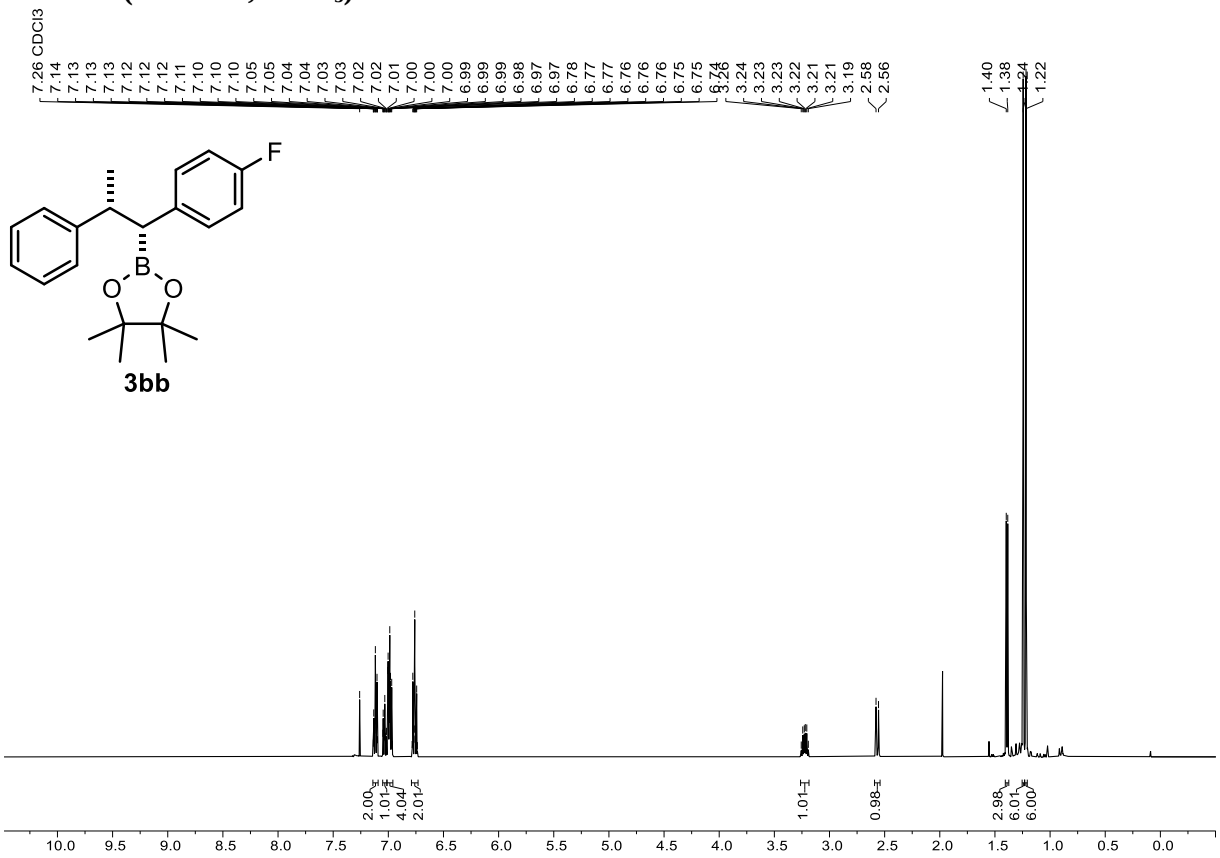
^{13}C-NMR (151 MHz, $CDCl_3$):



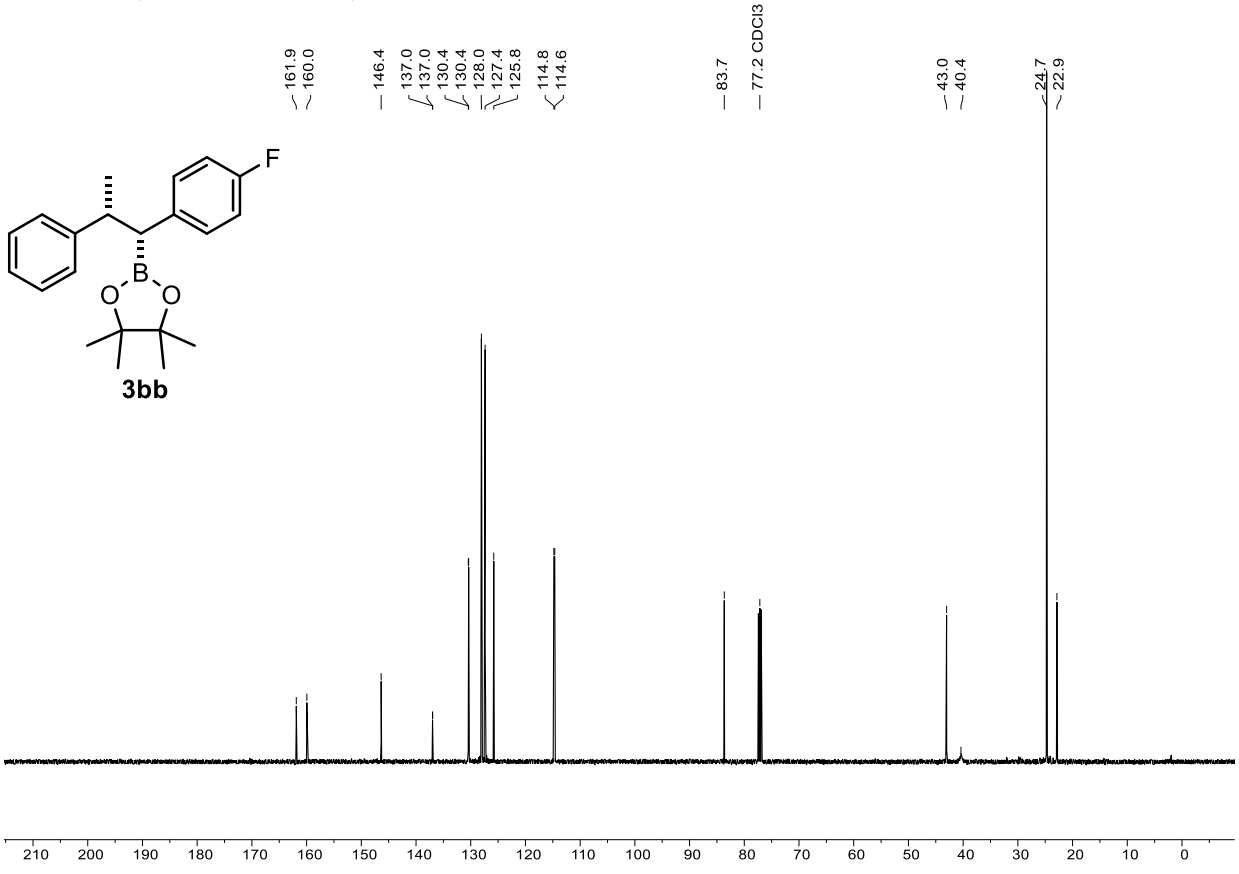
^{11}B-NMR (192 MHz, $CDCl_3$):



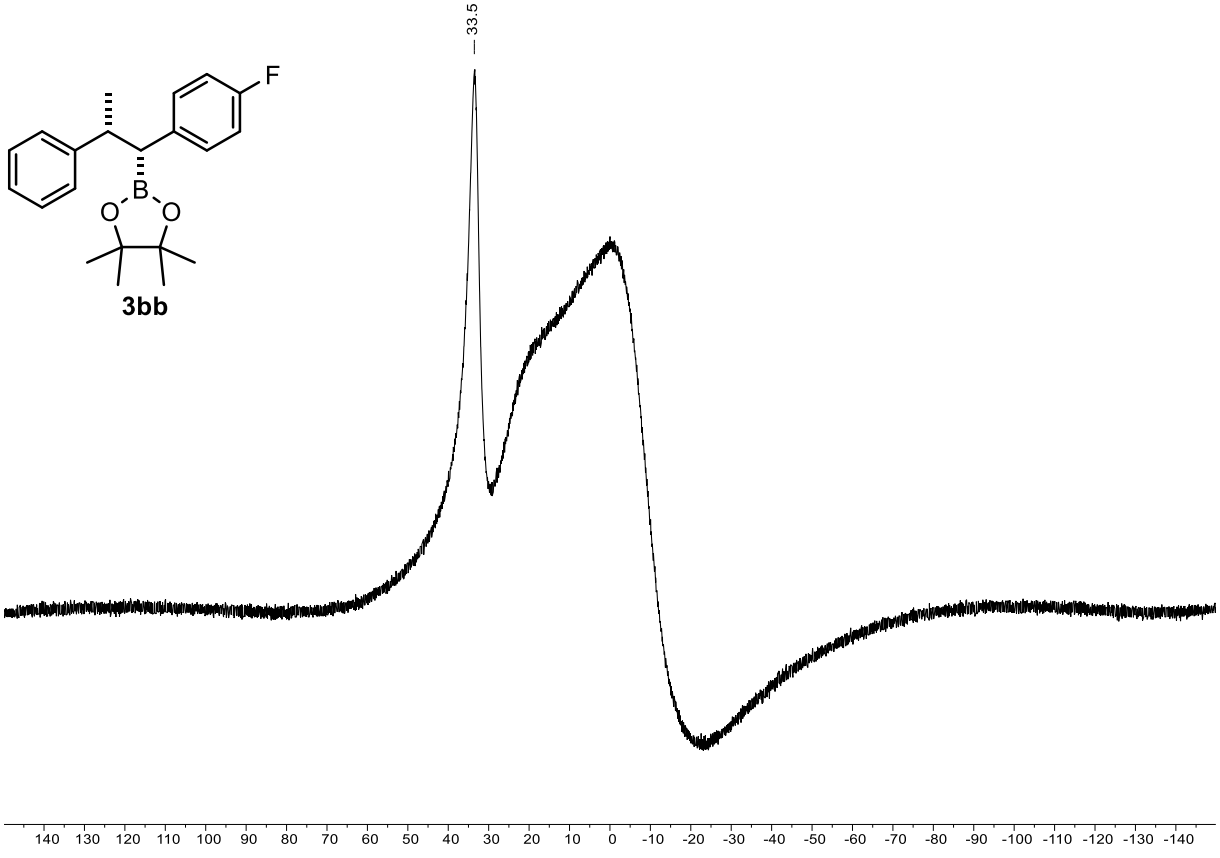
^{1}H-NMR (500 MHz, $CDCl_3$):



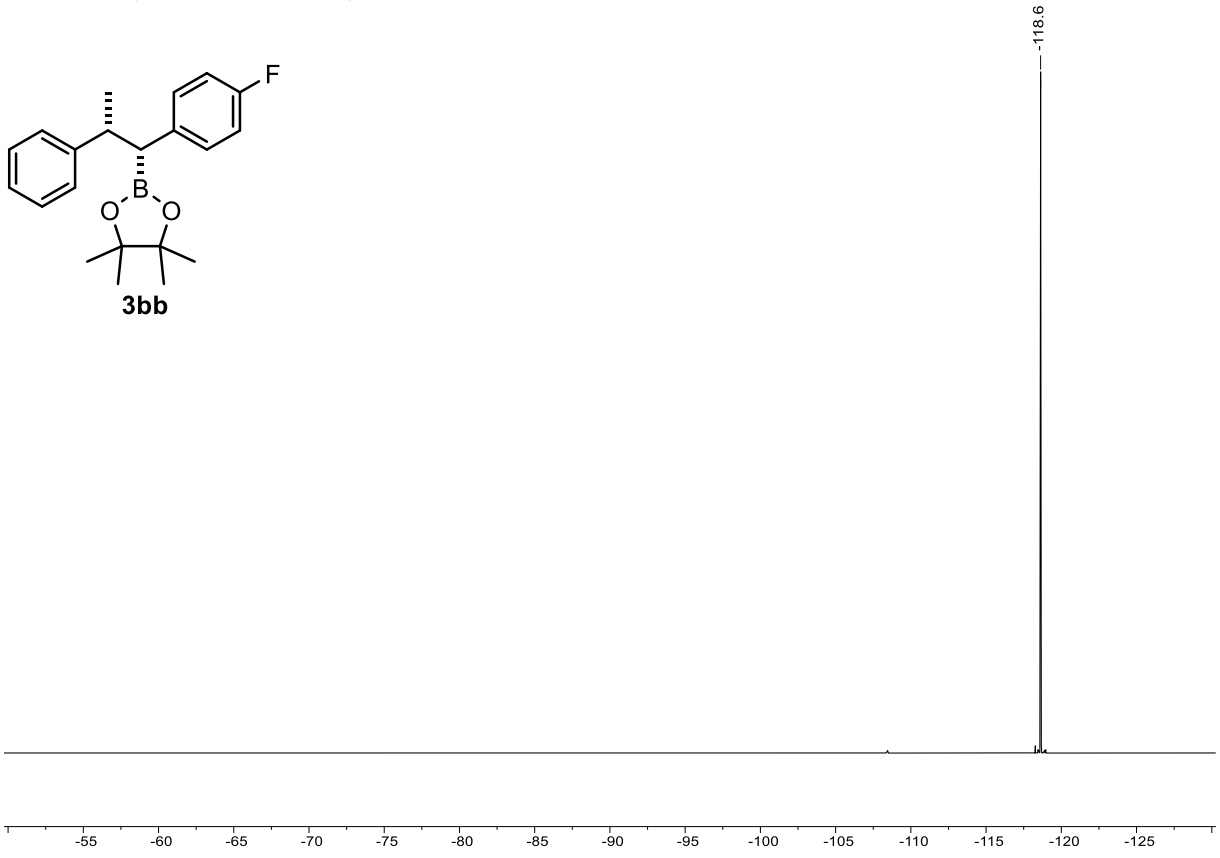
^{13}C-NMR (126 MHz, $CDCl_3$):



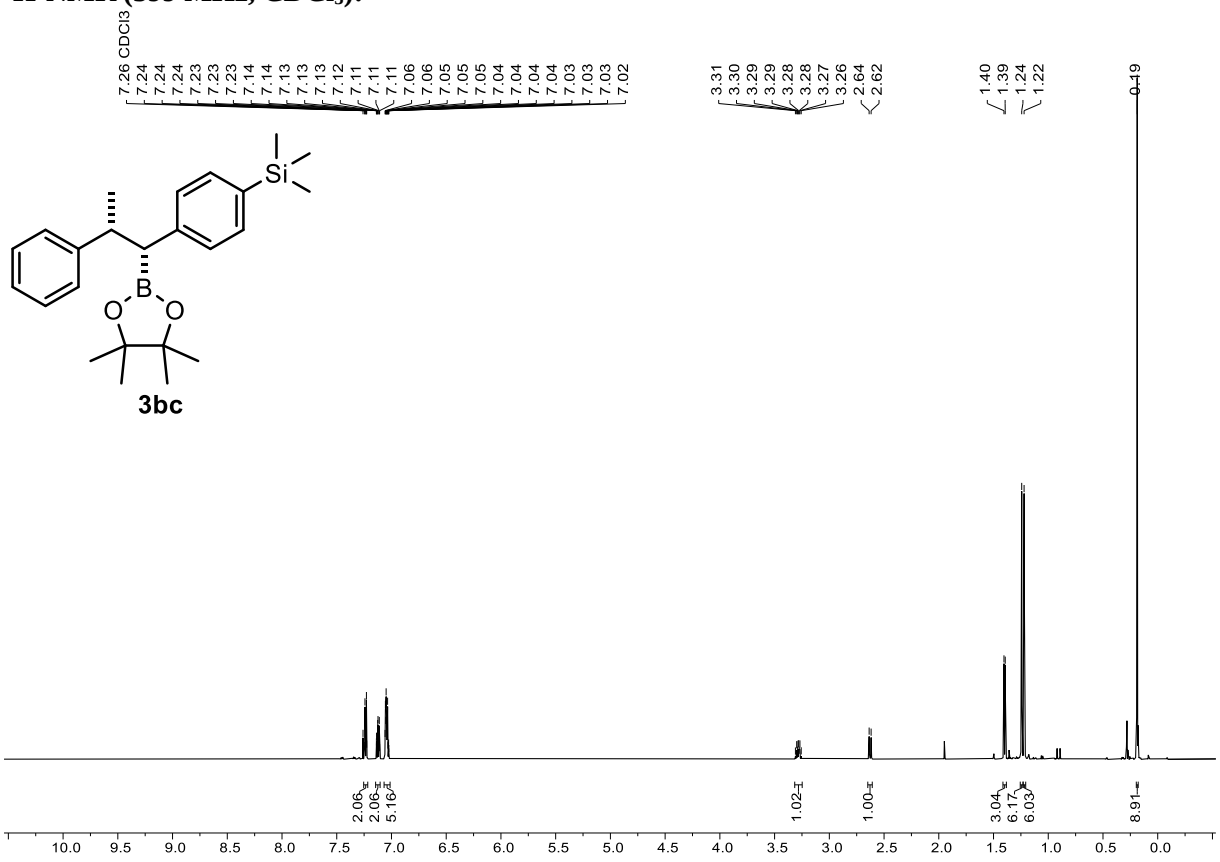
^{11}B-NMR (160 MHz, $CDCl_3$):



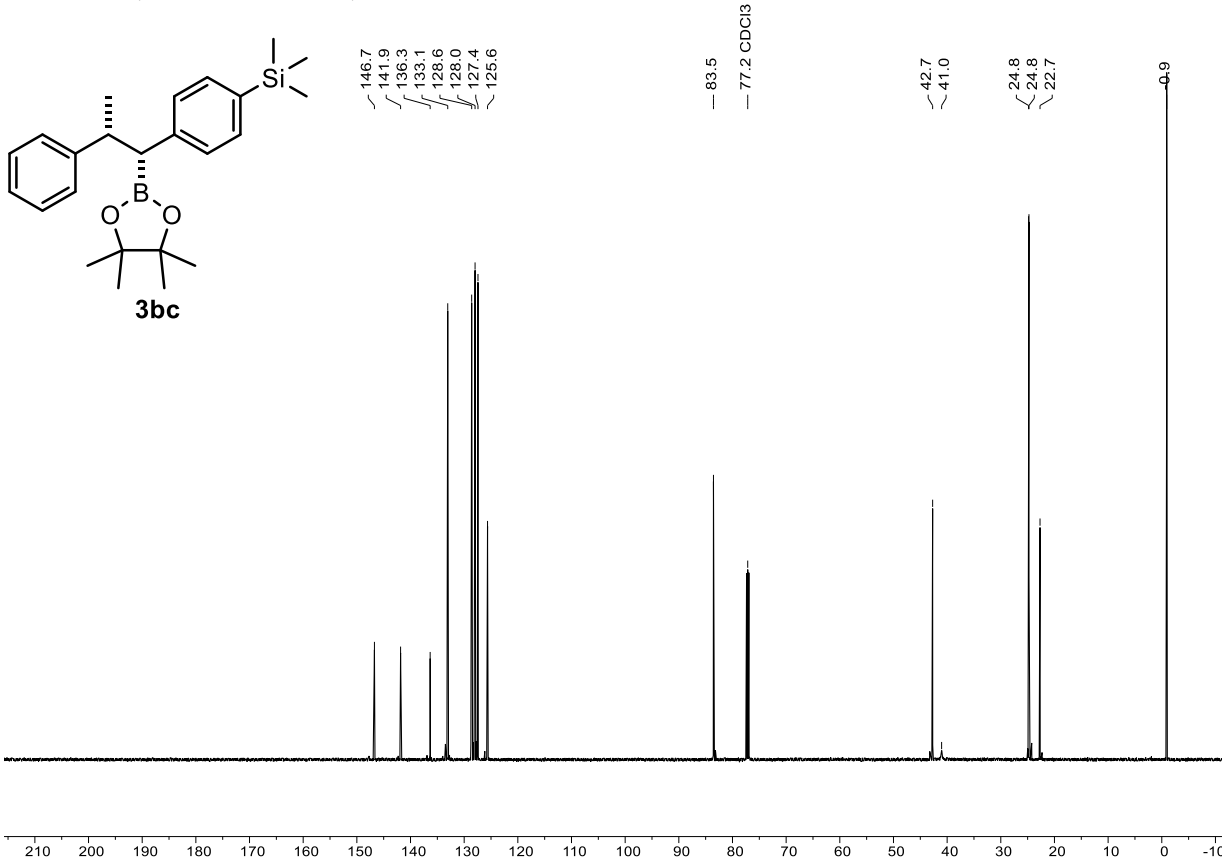
^{19}F-NMR (470 MHz, $CDCl_3$):



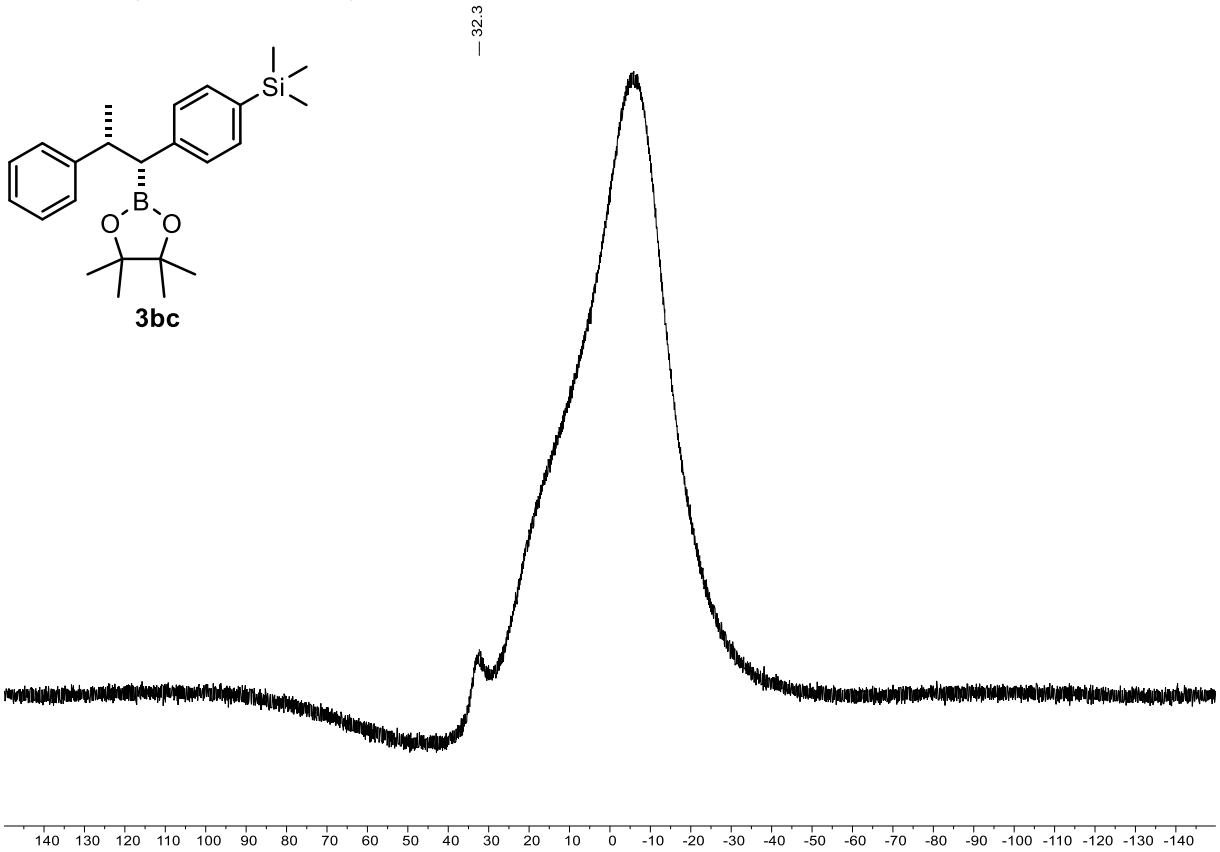
^{1}H-NMR (599 MHz, $CDCl_3$):



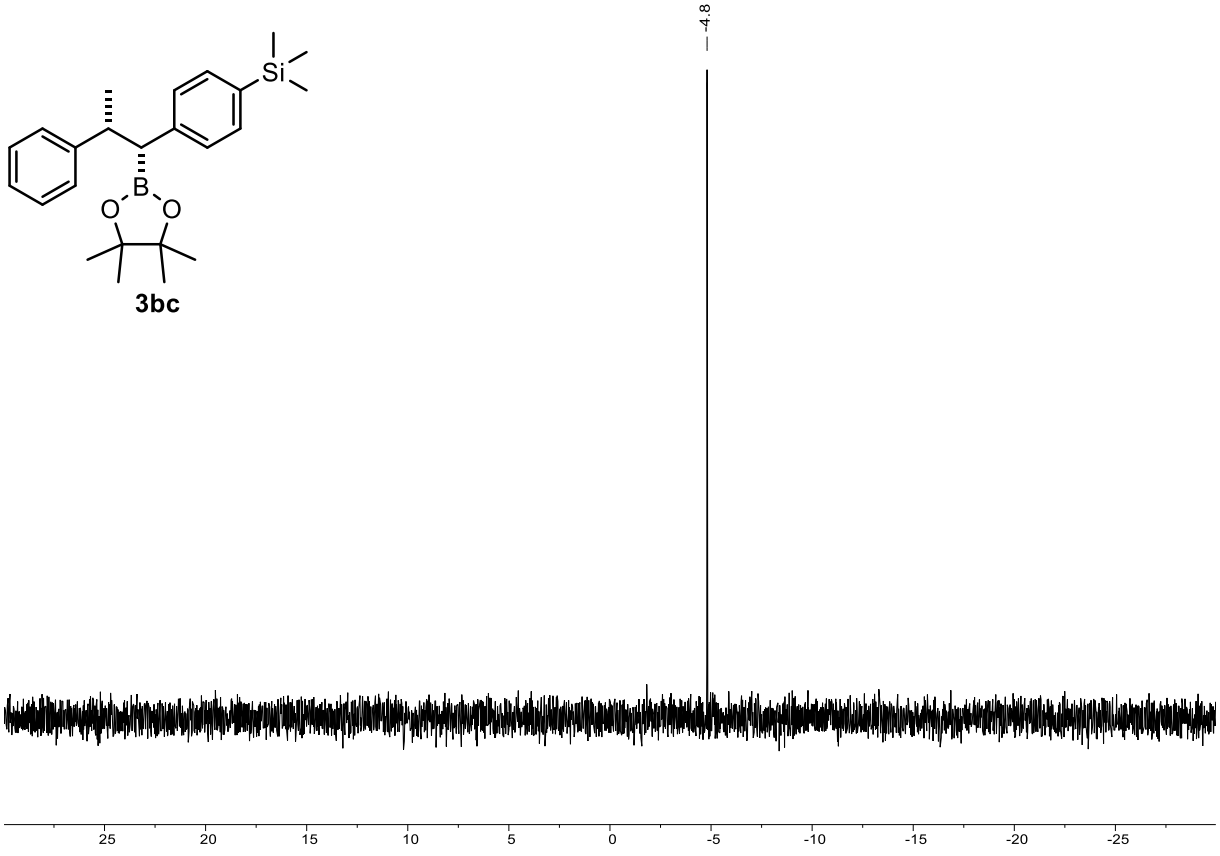
^{13}C-NMR (151 MHz, $CDCl_3$):



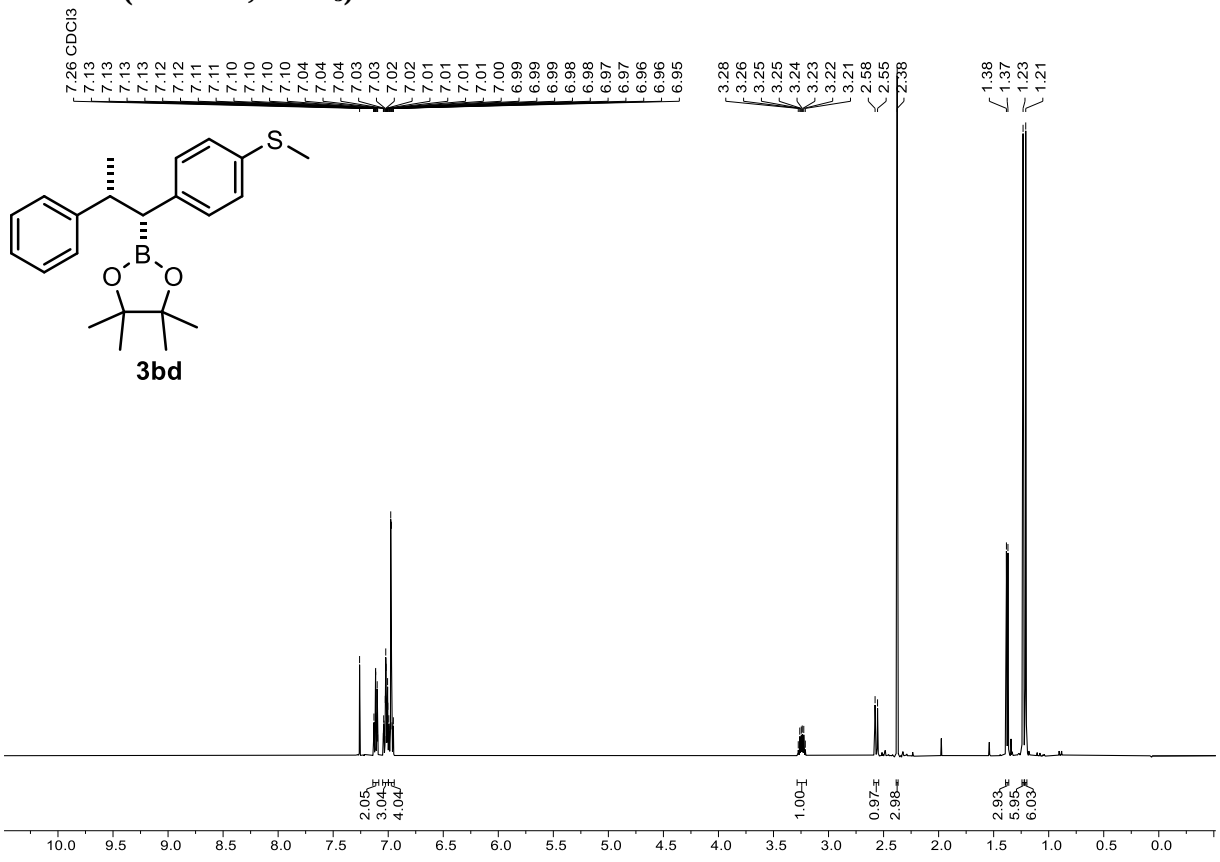
^{11}B-NMR (160 MHz, $CDCl_3$):



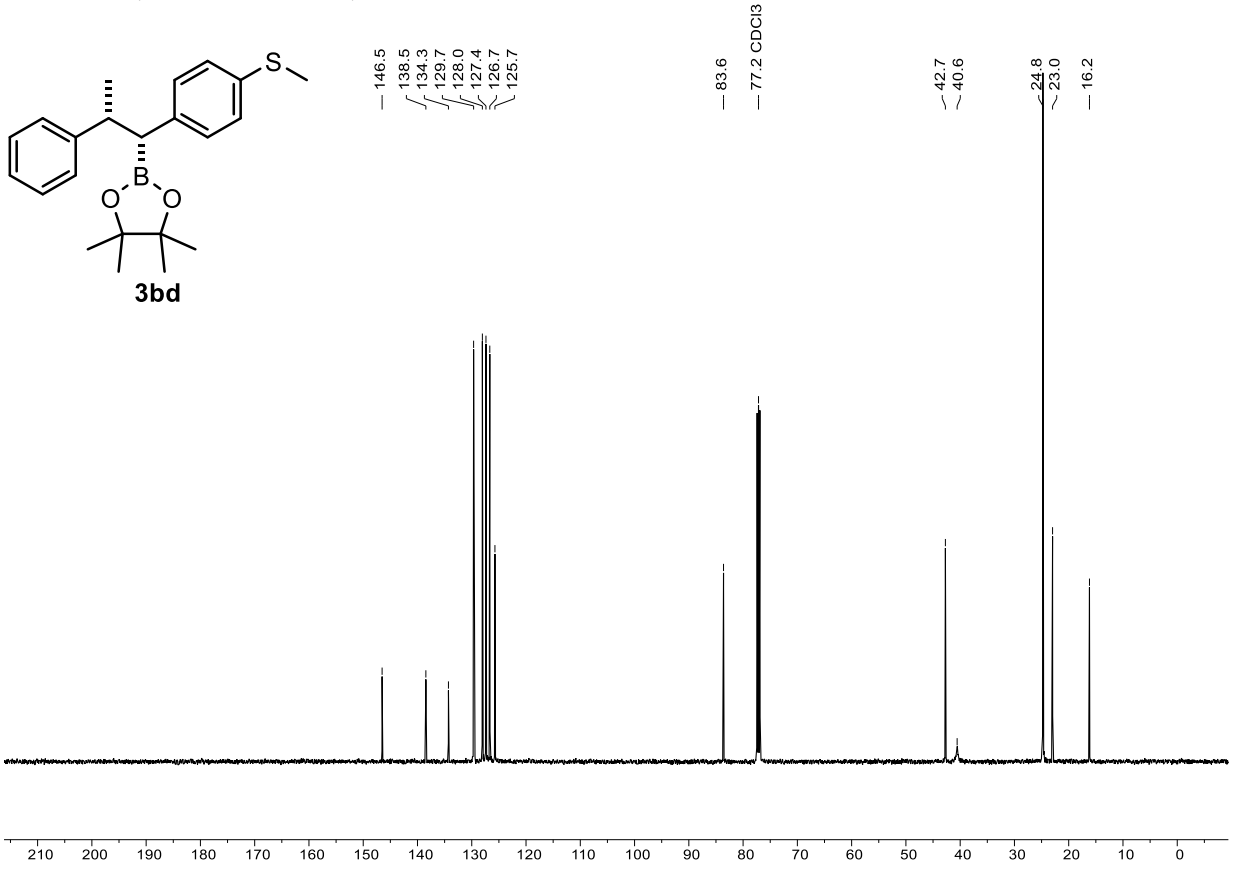
^{29}Si-NMR (90 MHz, $CDCl_3$):



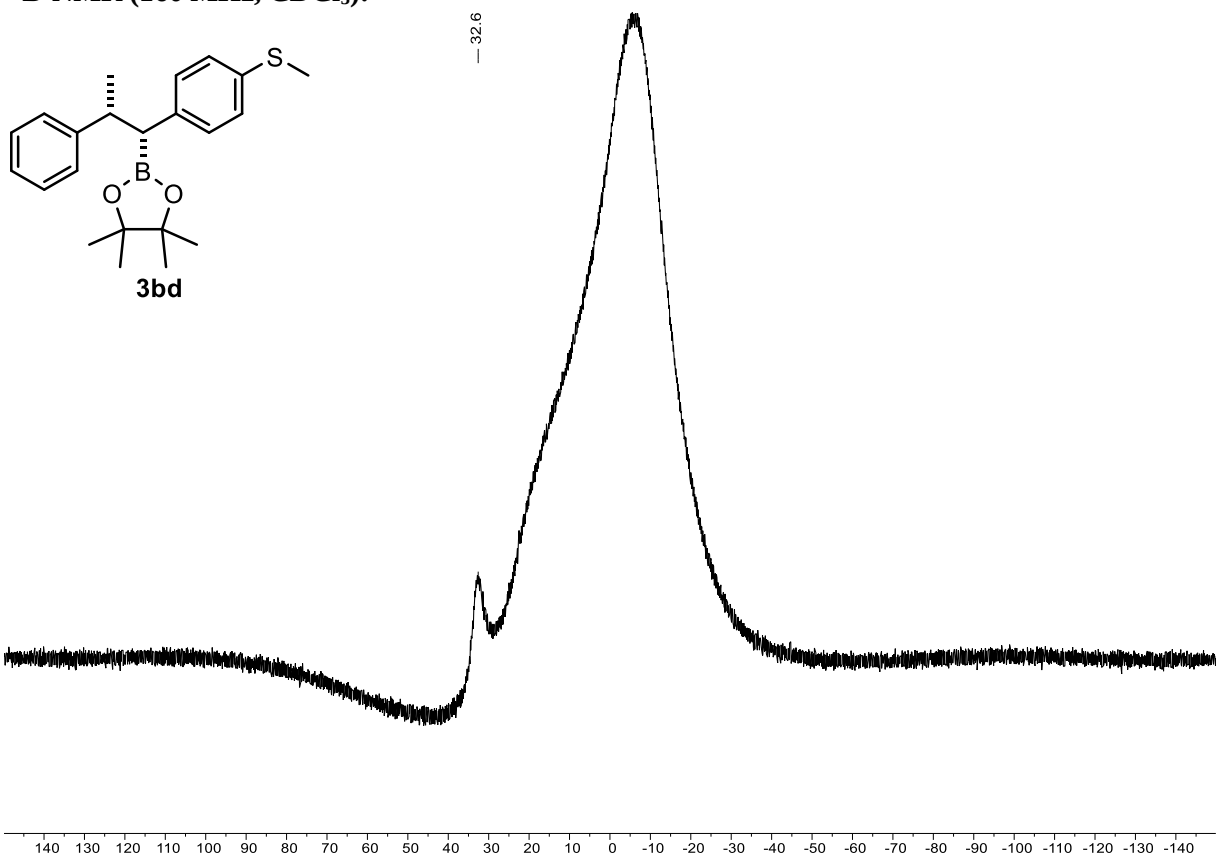
^{1}H-NMR (500 MHz, $CDCl_3$):



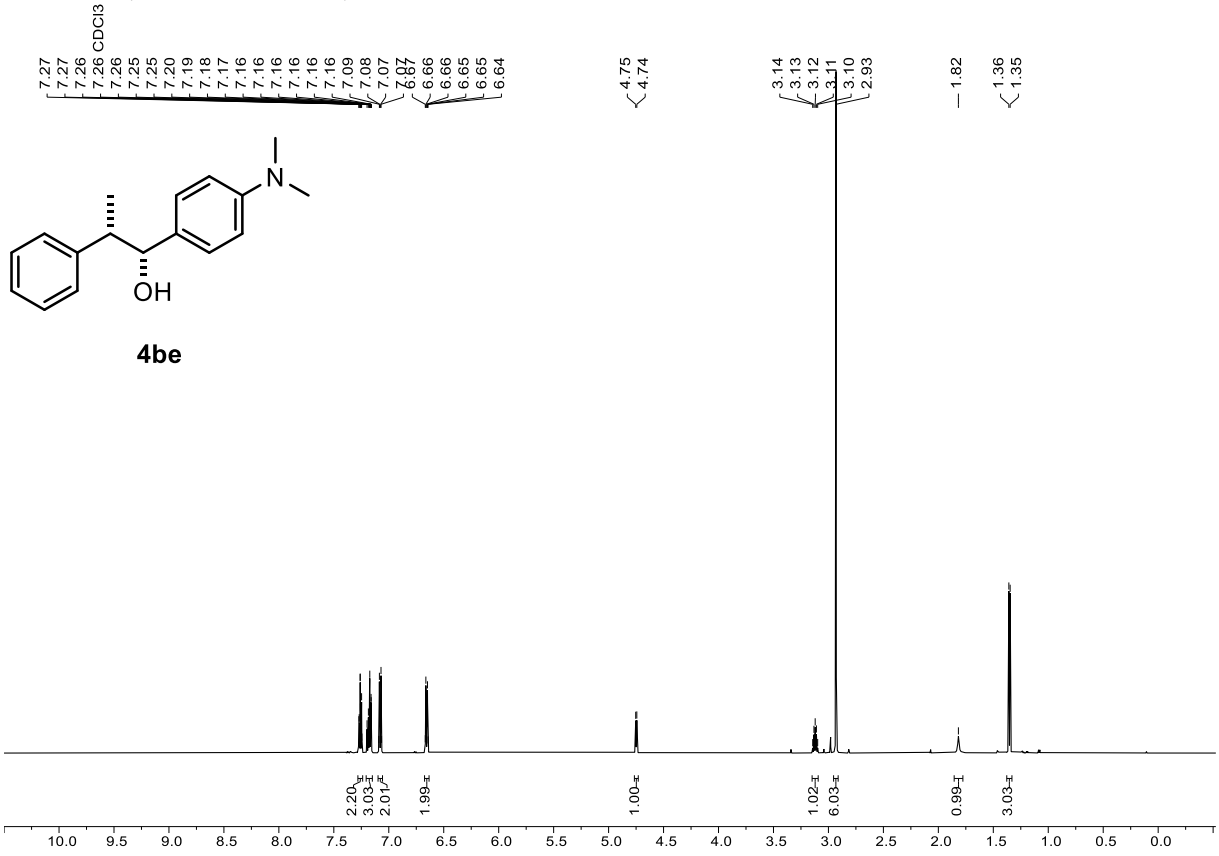
^{13}C-NMR (126 MHz, $CDCl_3$):



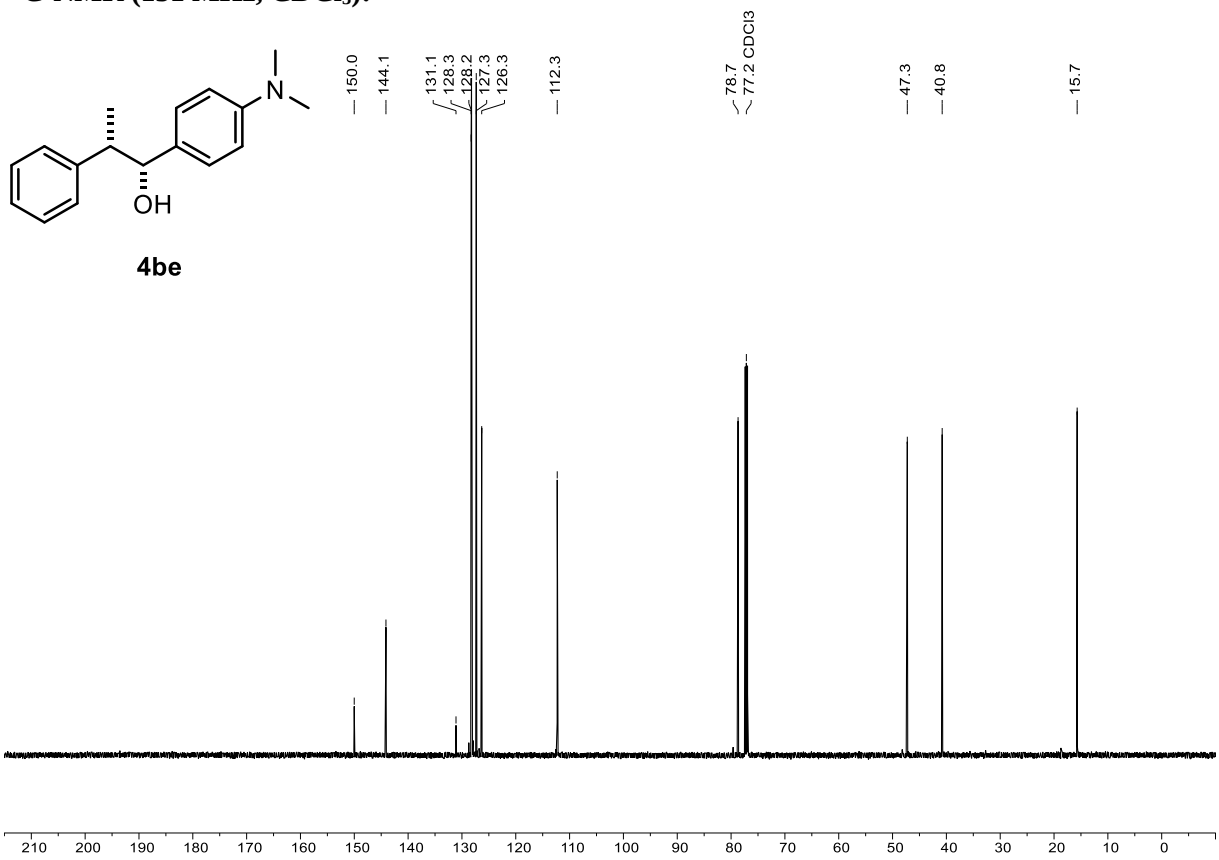
^{11}B-NMR (160 MHz, $CDCl_3$):



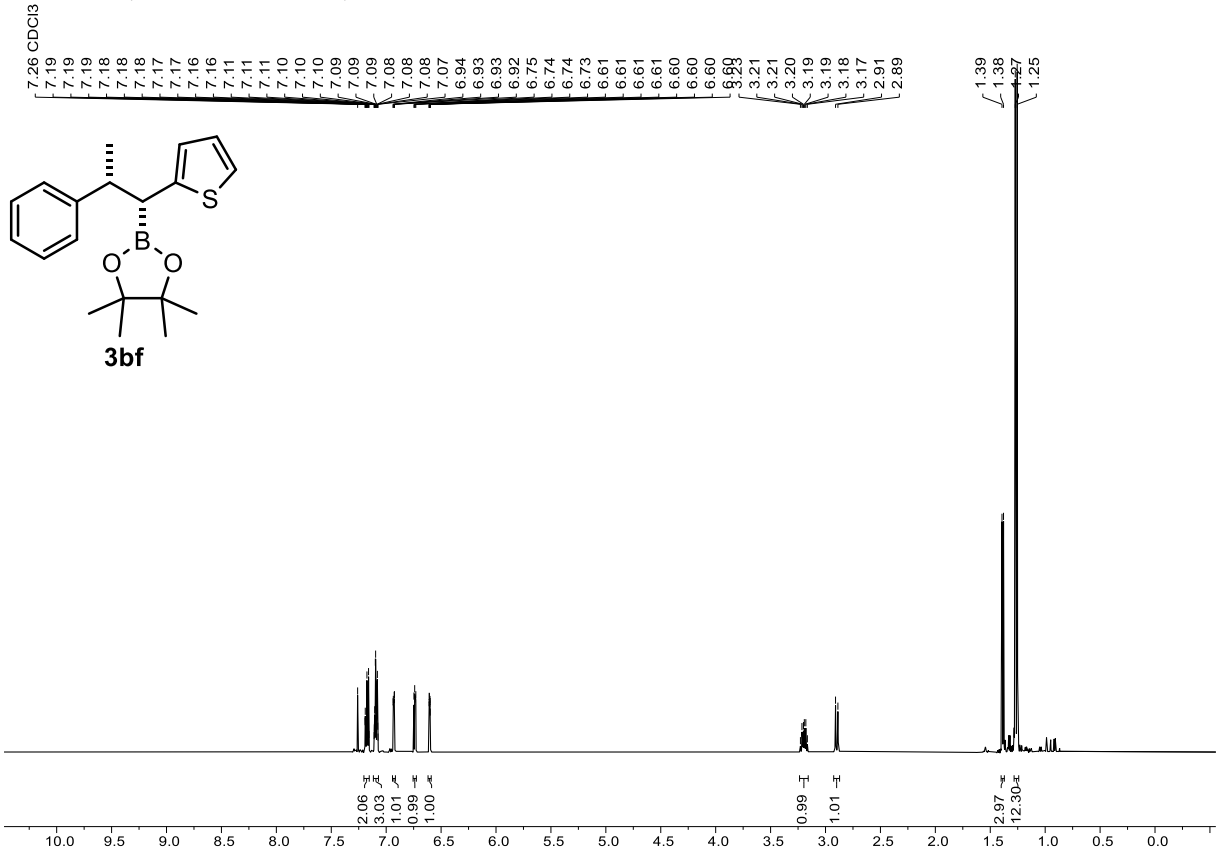
^{1}H-NMR (599 MHz, $CDCl_3$):



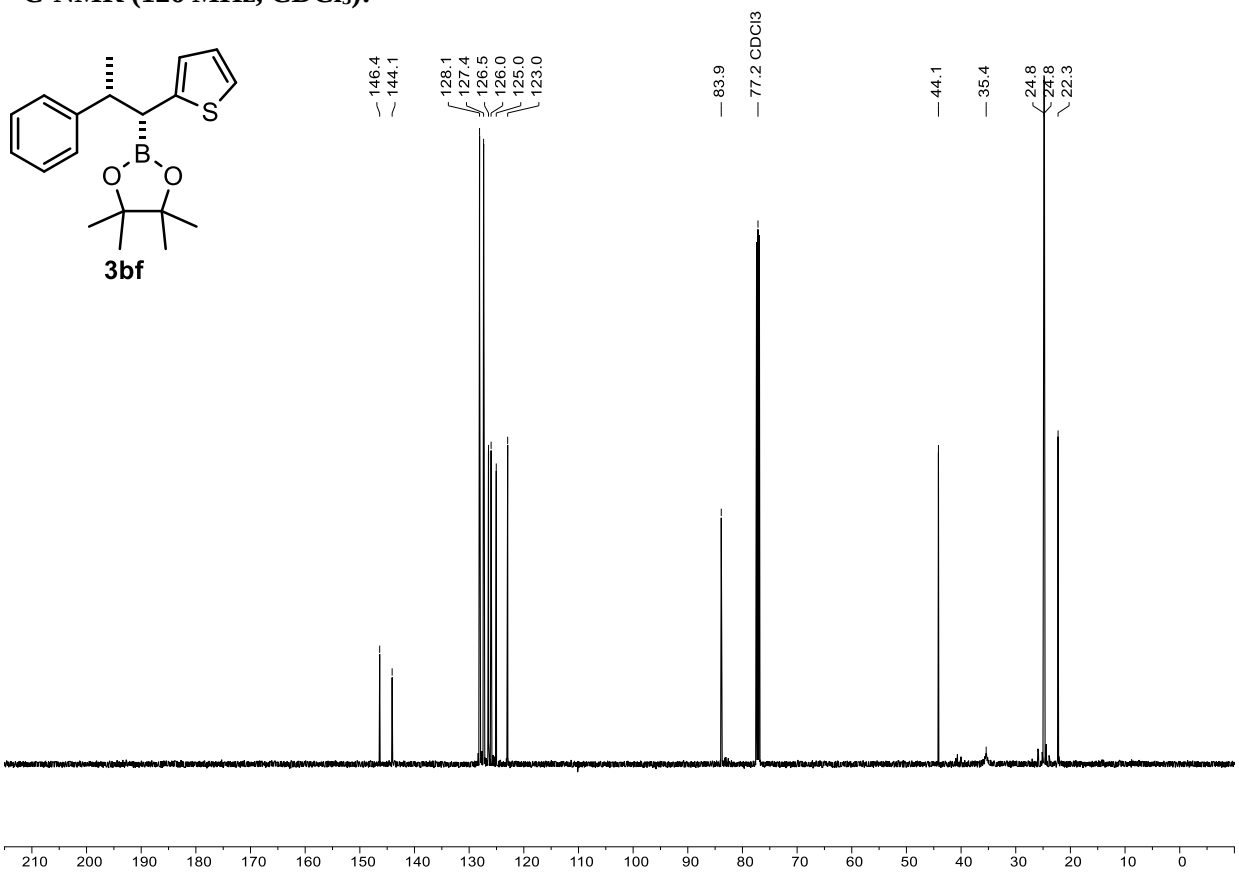
^{13}C-NMR (151 MHz, $CDCl_3$):



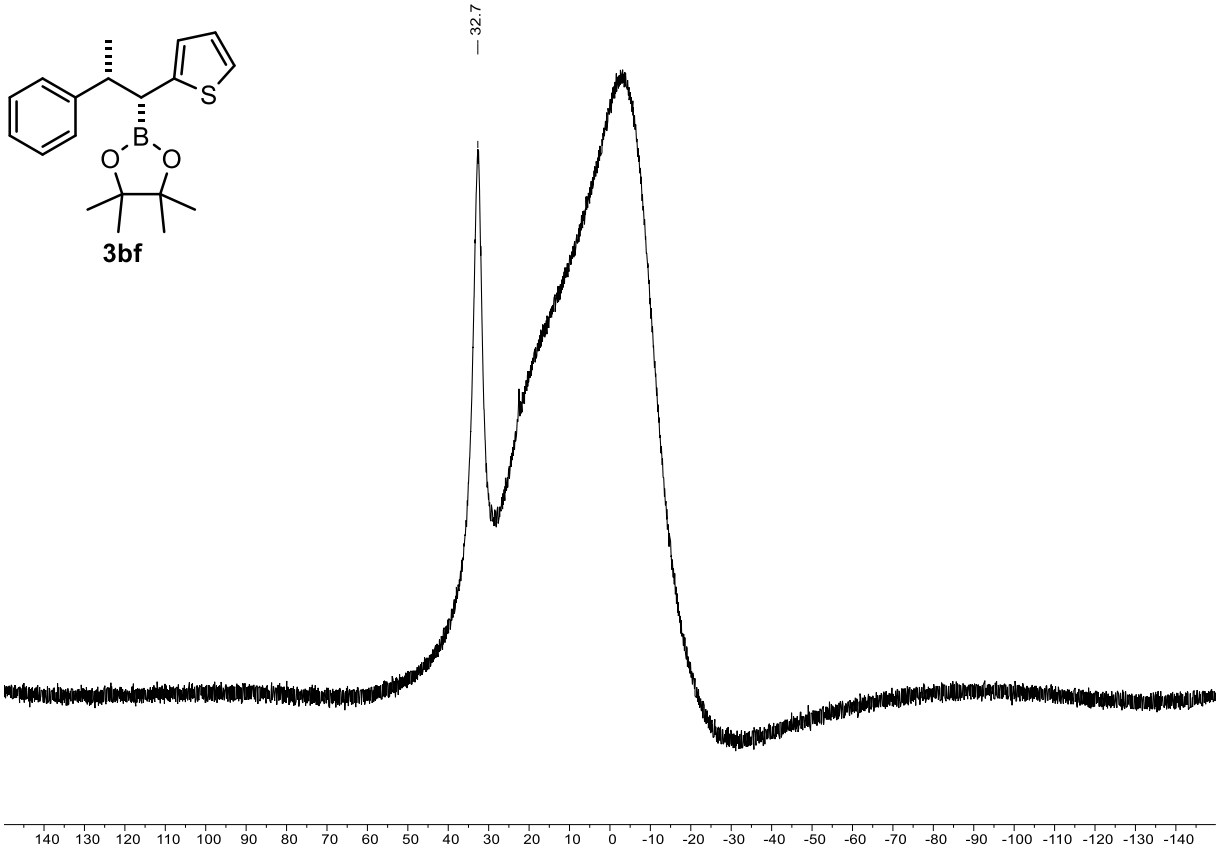
^{1}H-NMR (500 MHz, $CDCl_3$):



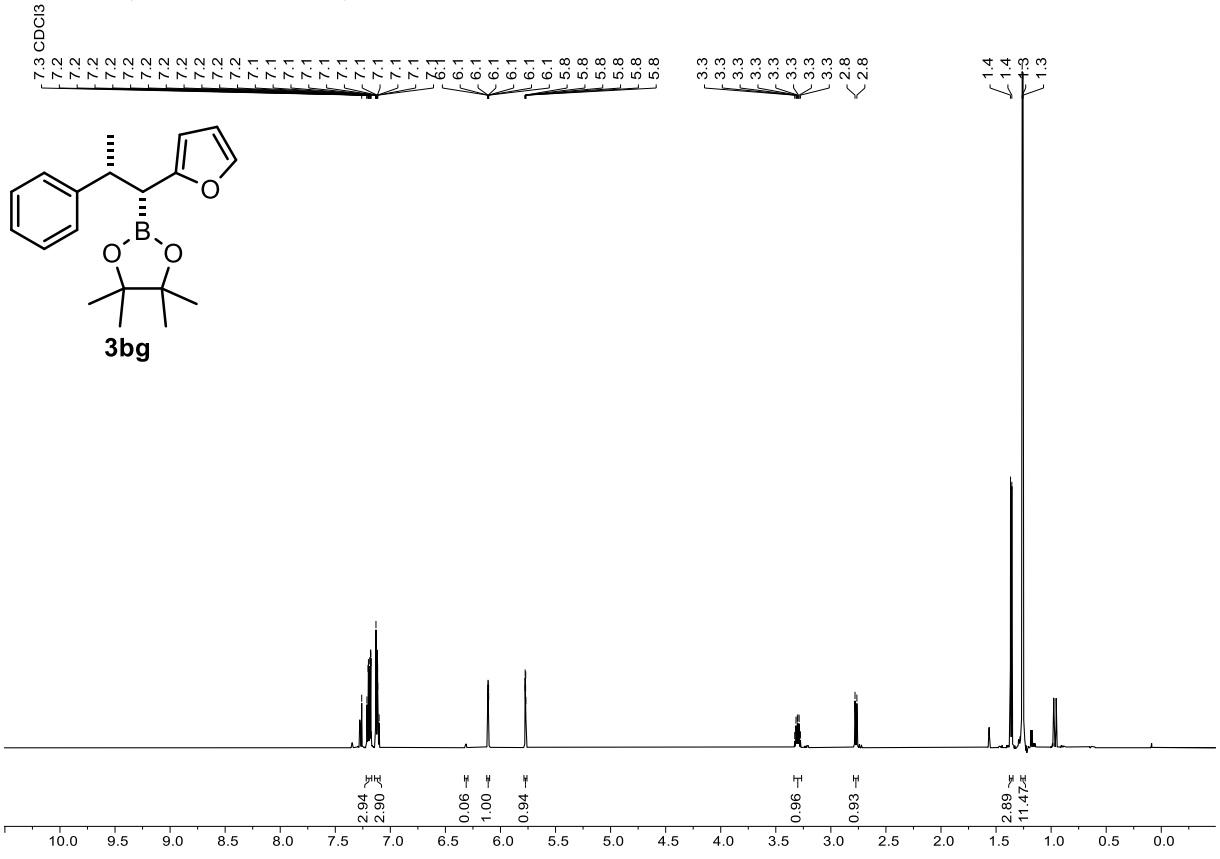
^{13}C-NMR (126 MHz, $CDCl_3$):



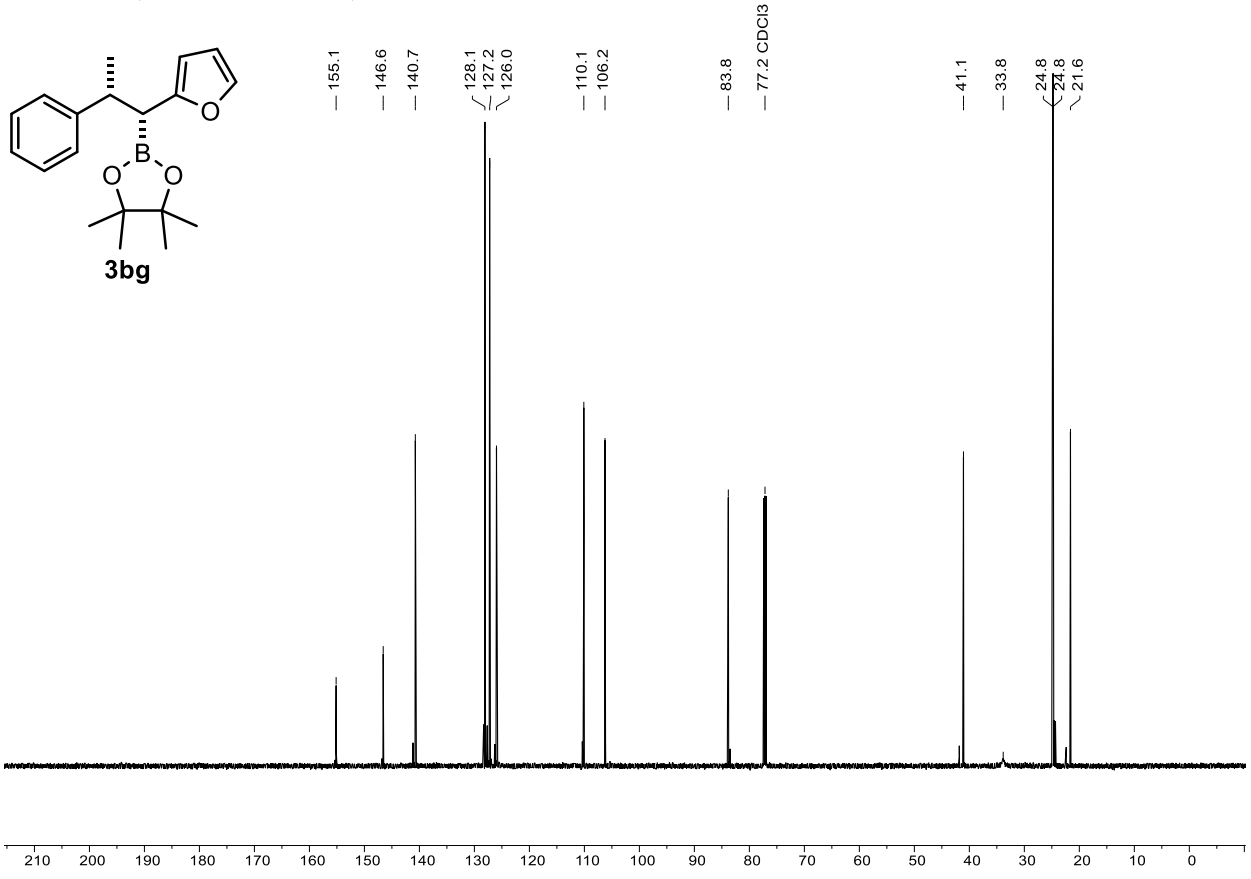
^{11}B-NMR (160 MHz, $CDCl_3$):



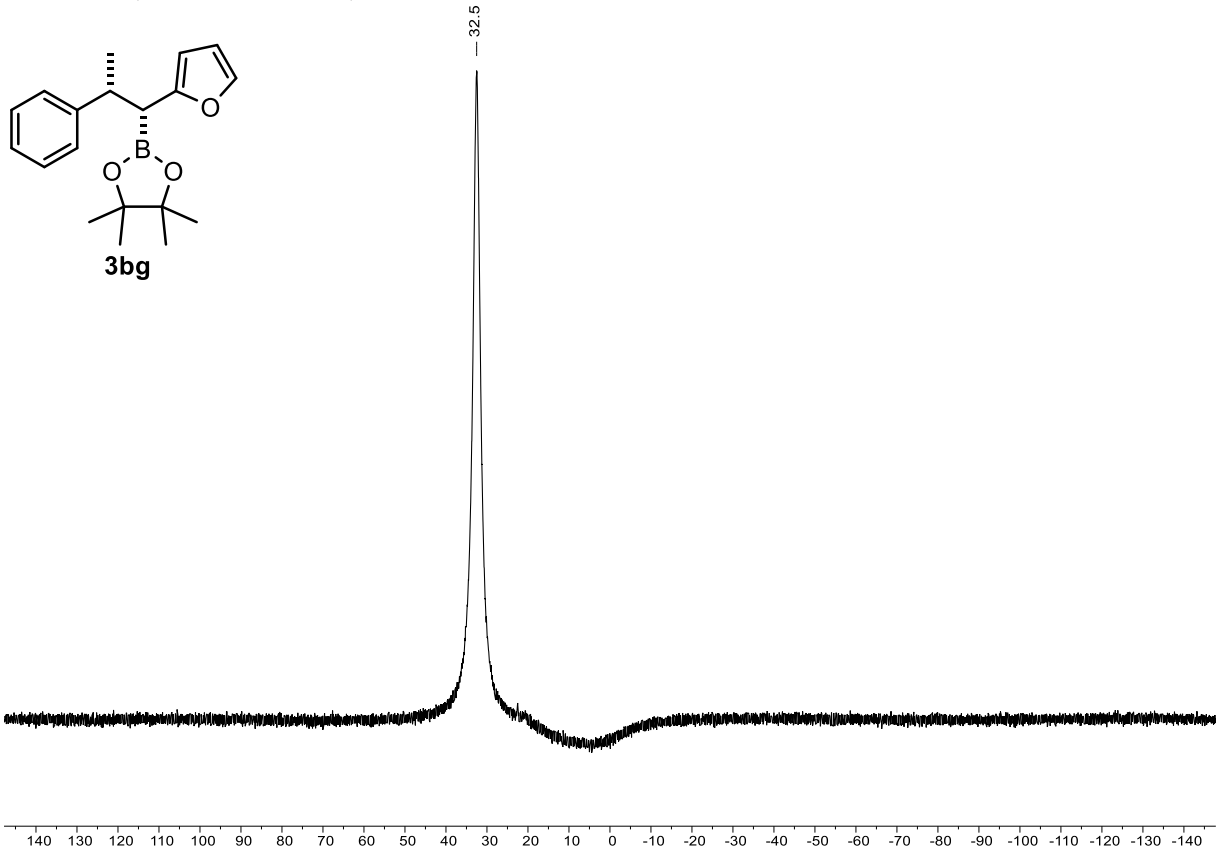
^{1}H-NMR (599 MHz, $CDCl_3$):



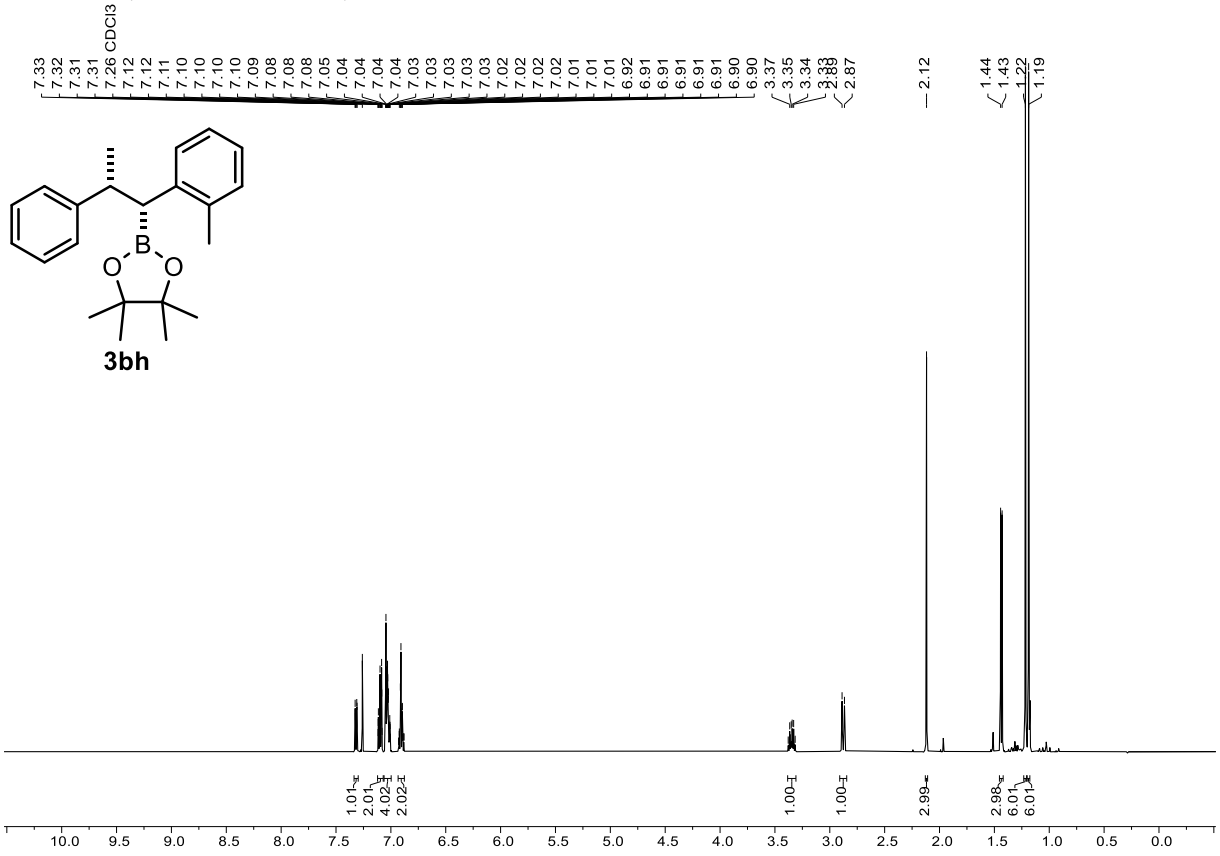
^{13}C-NMR (151 MHz, $CDCl_3$):



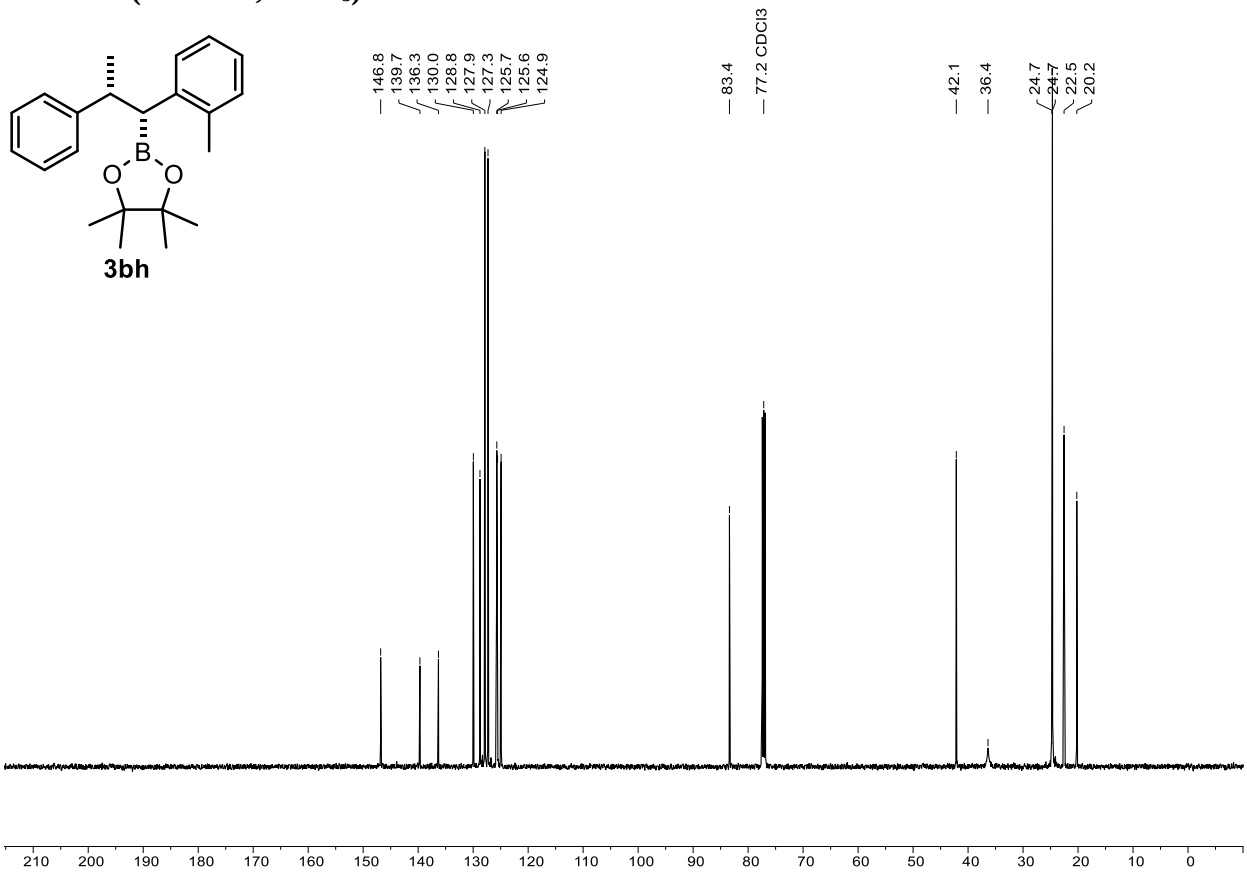
^{11}B-NMR (192 MHz, $CDCl_3$):



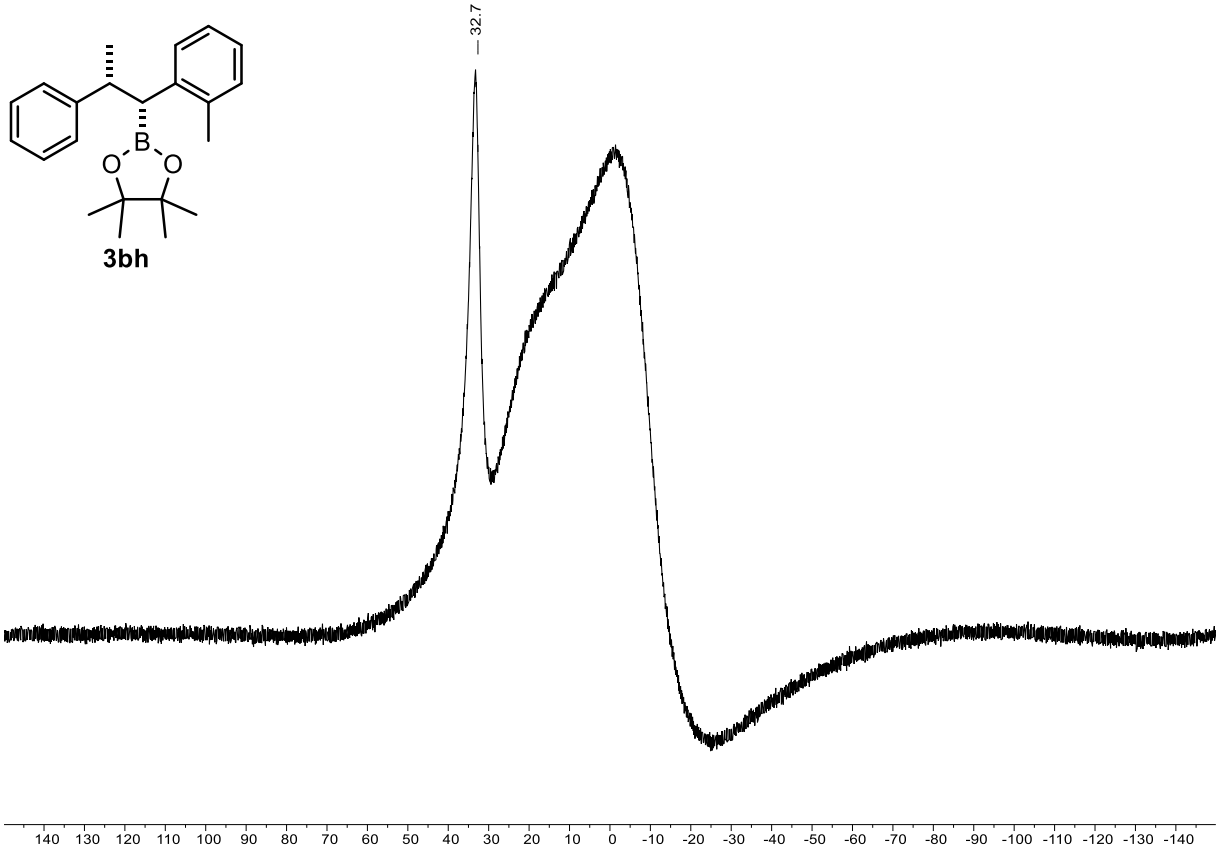
^{1}H-NMR (500 MHz, $CDCl_3$):



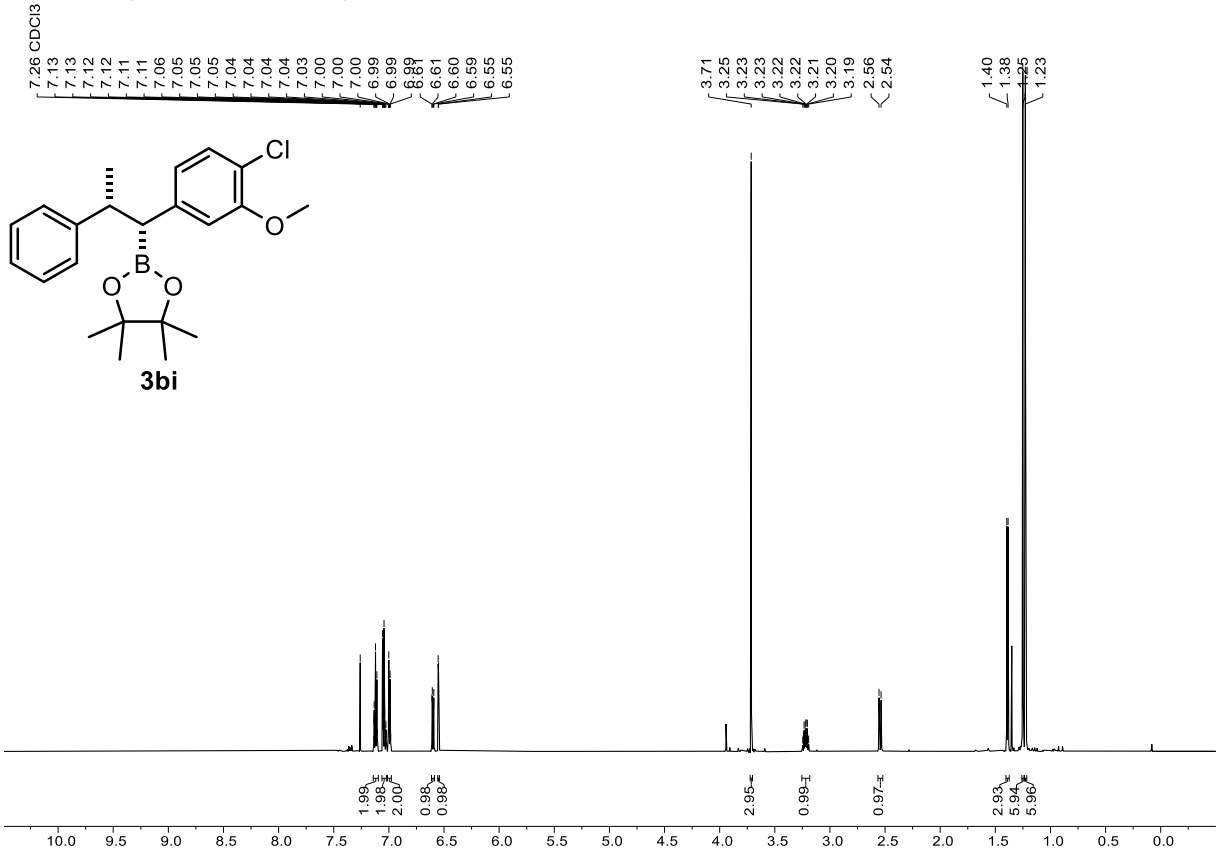
^{13}C-NMR (126 MHz, $CDCl_3$):



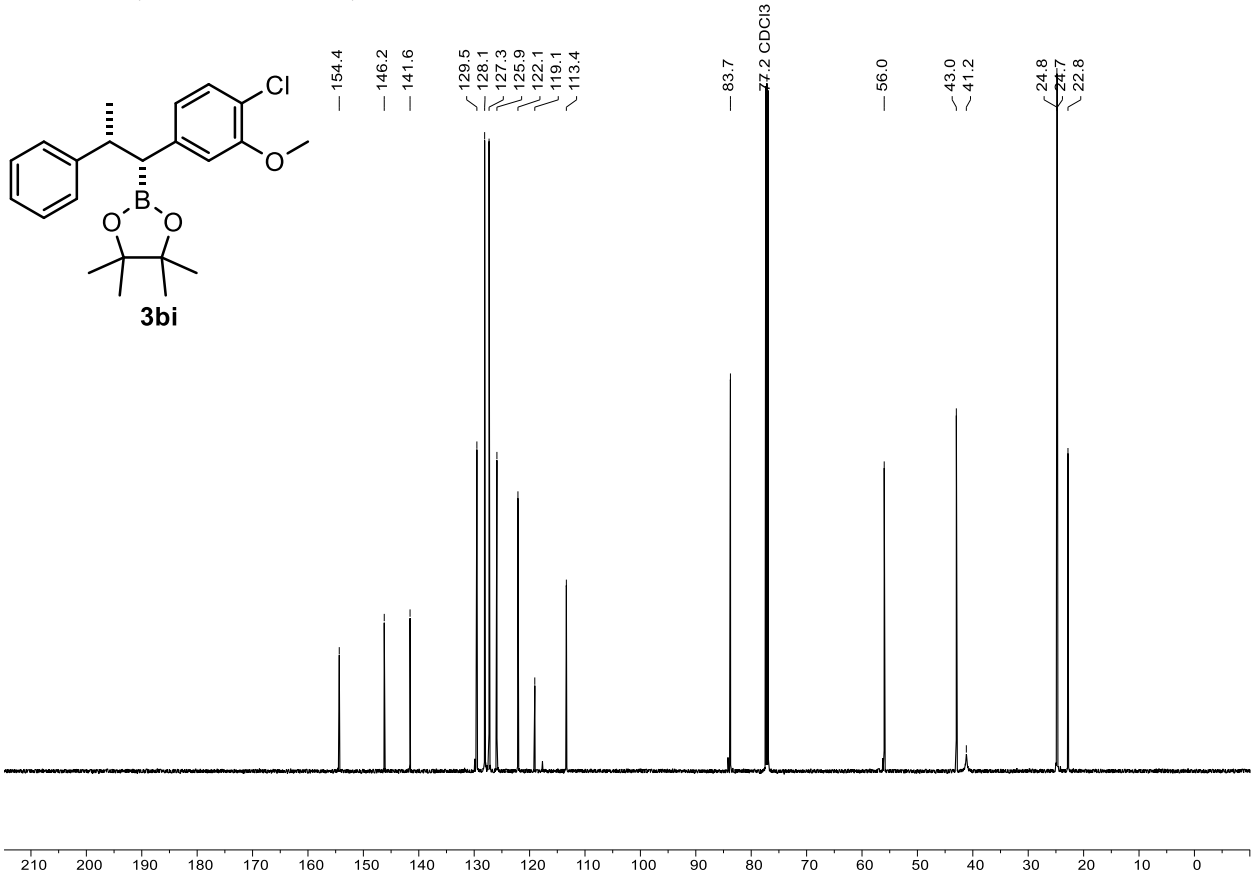
^{11}B-NMR (160 MHz, $CDCl_3$):



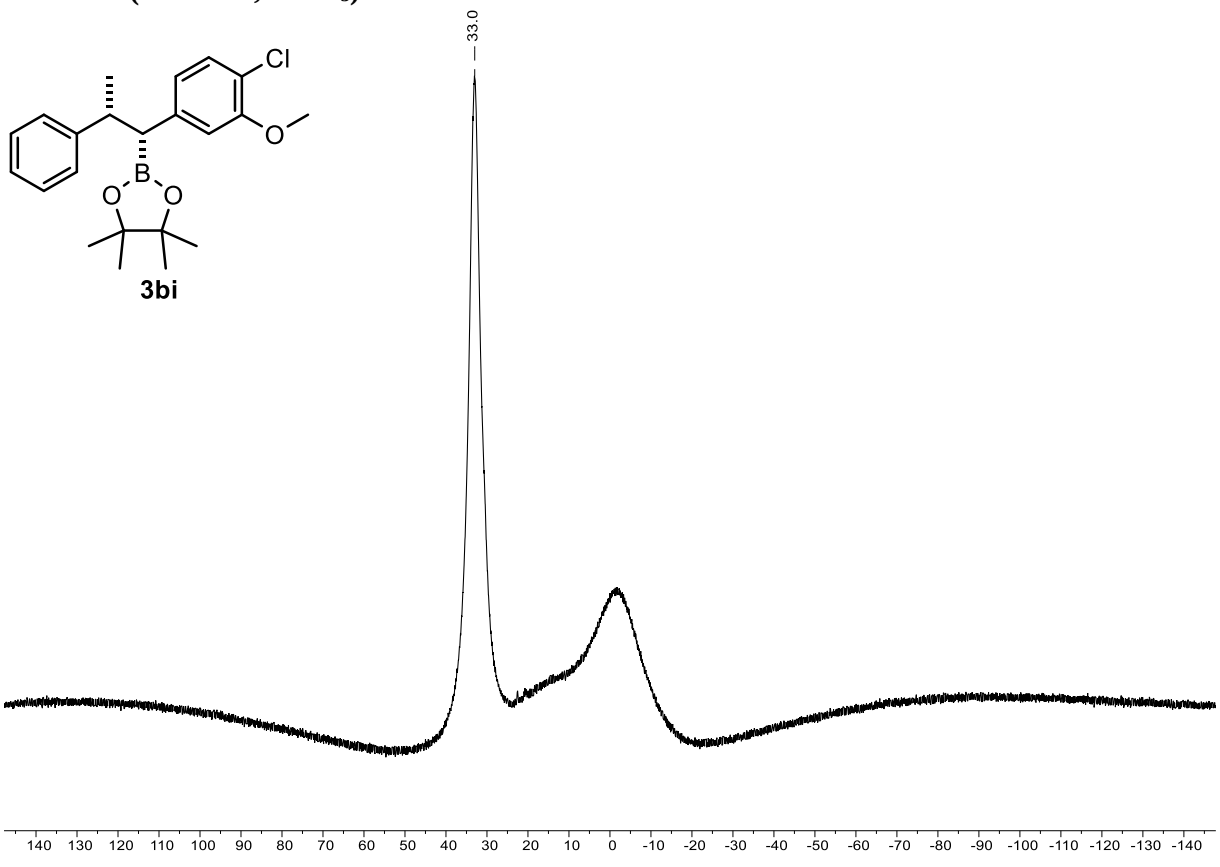
^{1}H-NMR (599 MHz, $CDCl_3$):



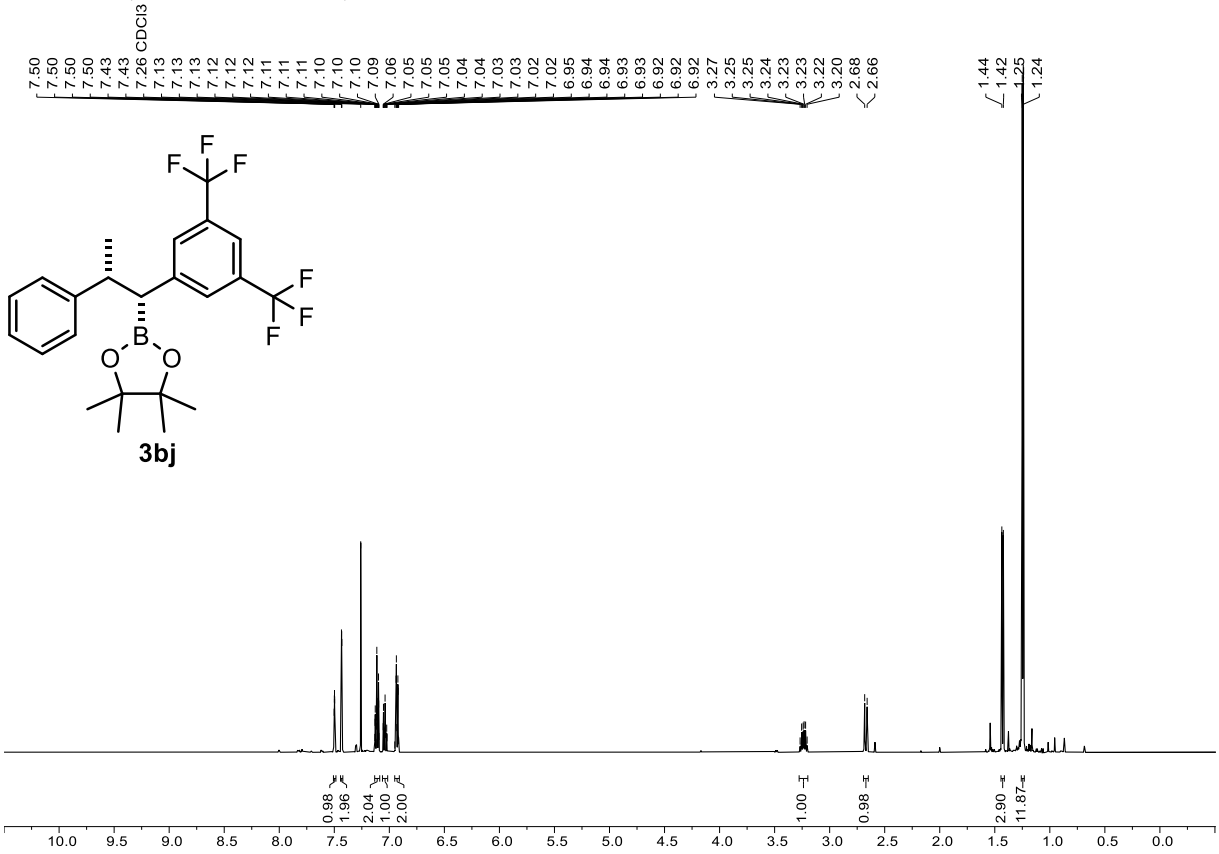
^{13}C-NMR (151 MHz, $CDCl_3$):



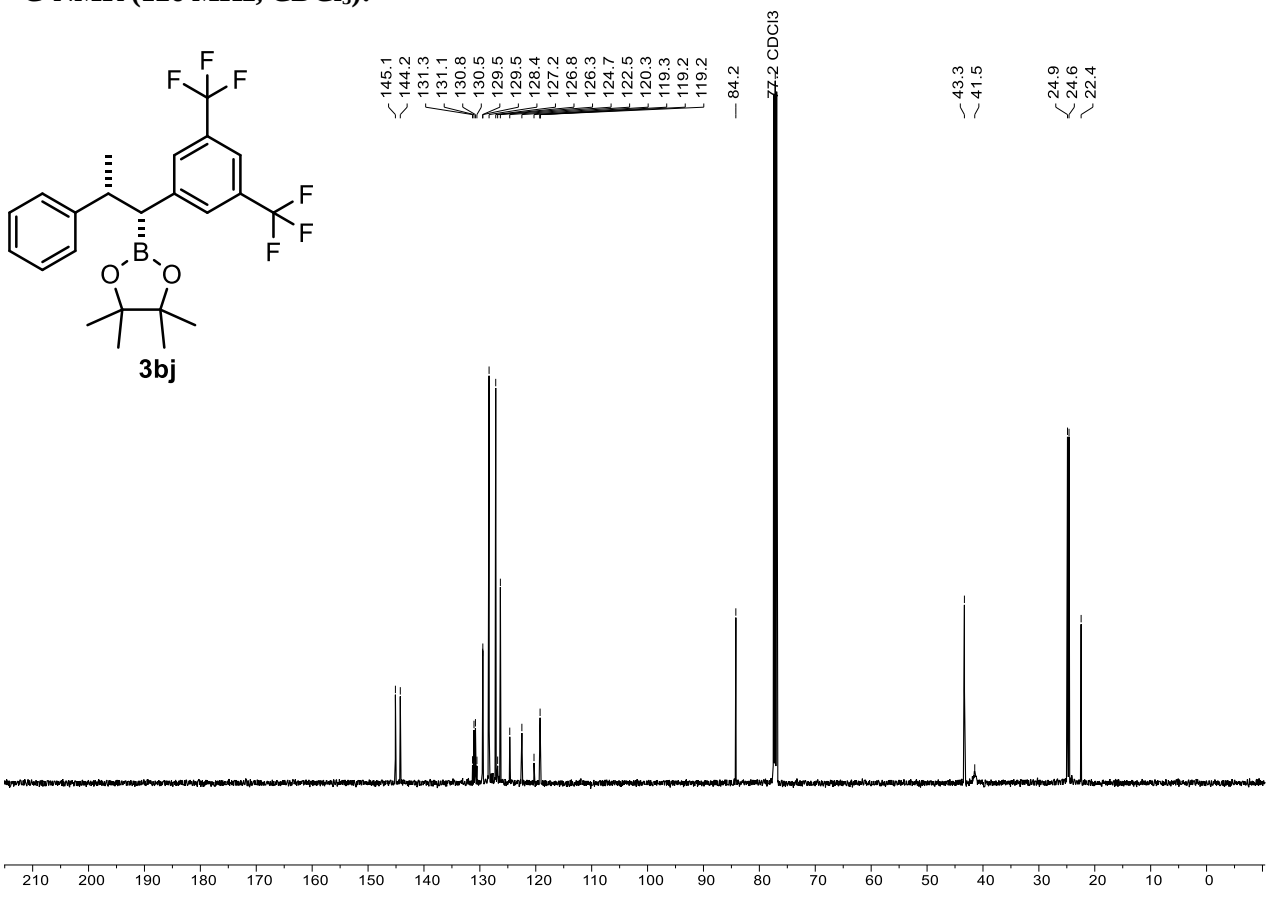
^{11}B-NMR (192 MHz, $CDCl_3$):



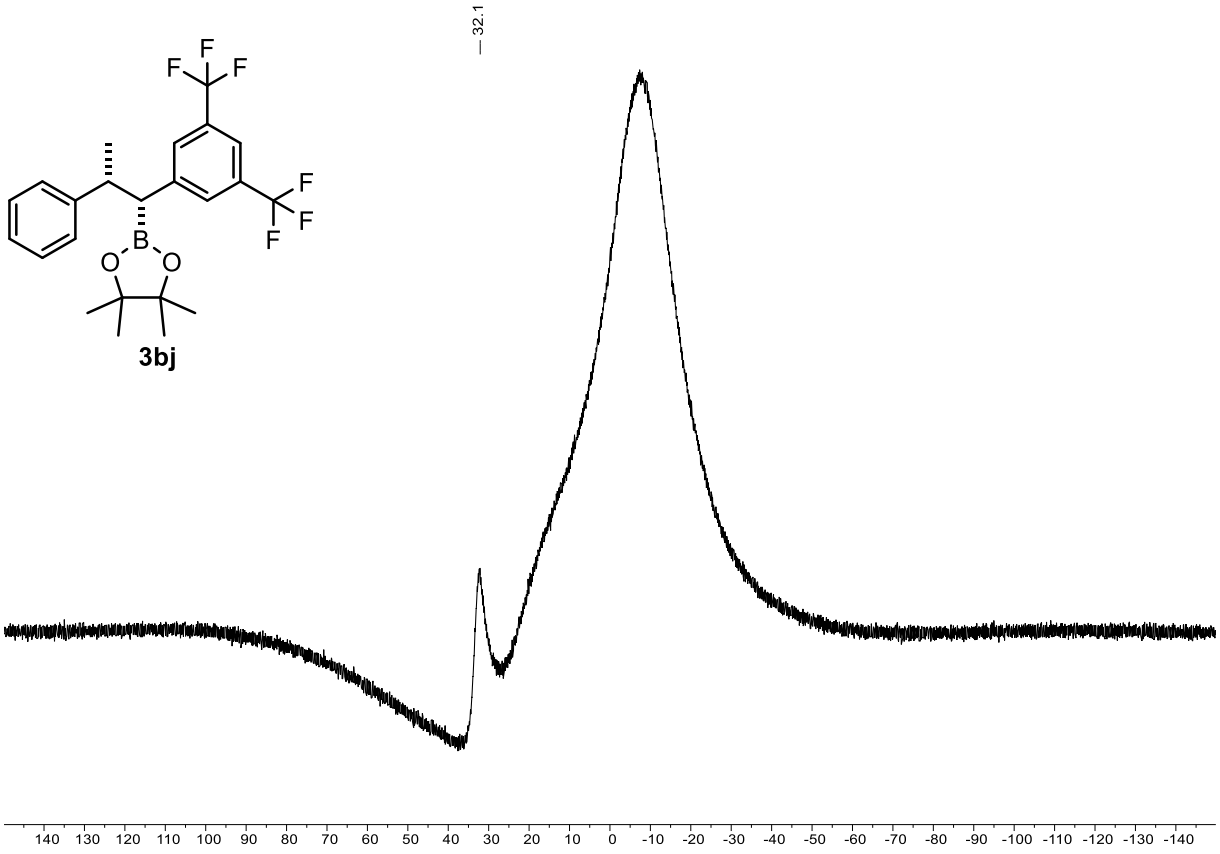
^{1}H-NMR (500 MHz, $CDCl_3$):



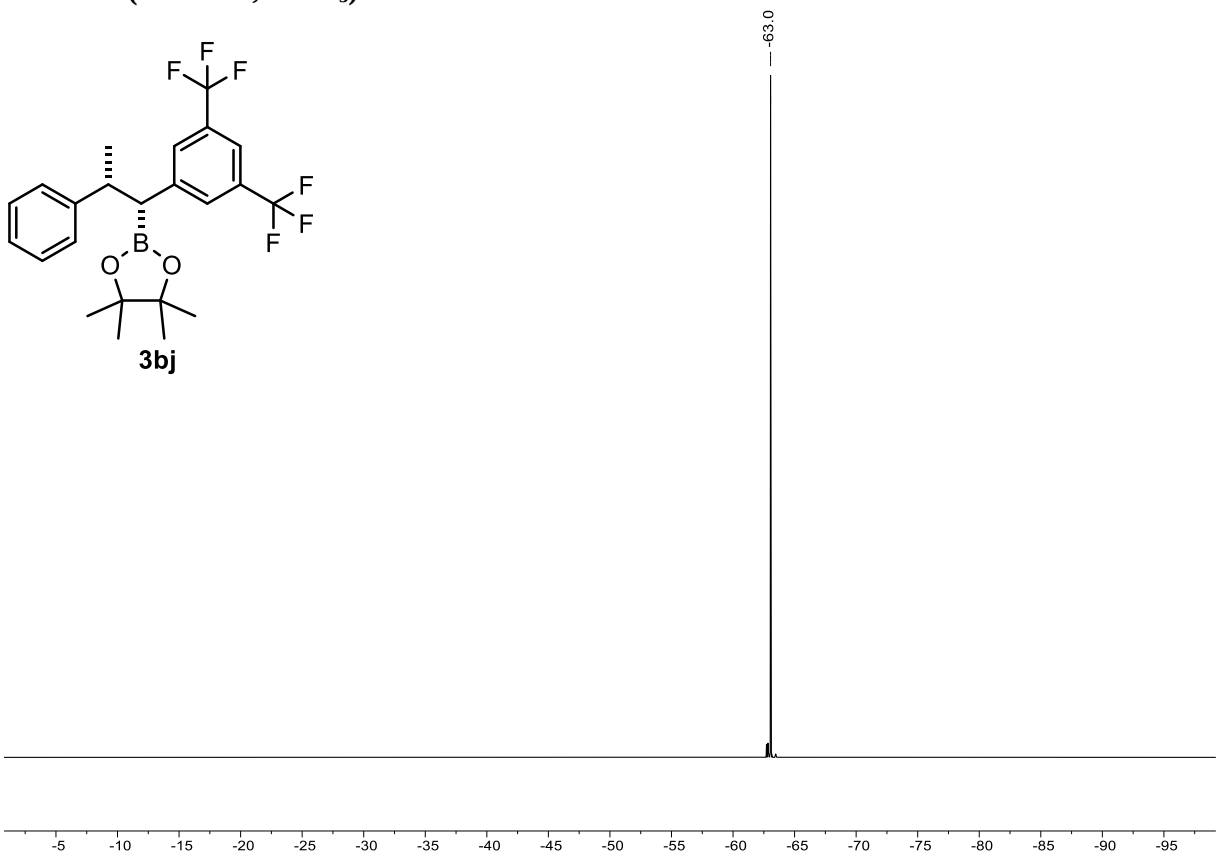
^{13}C-NMR (126 MHz, $CDCl_3$):



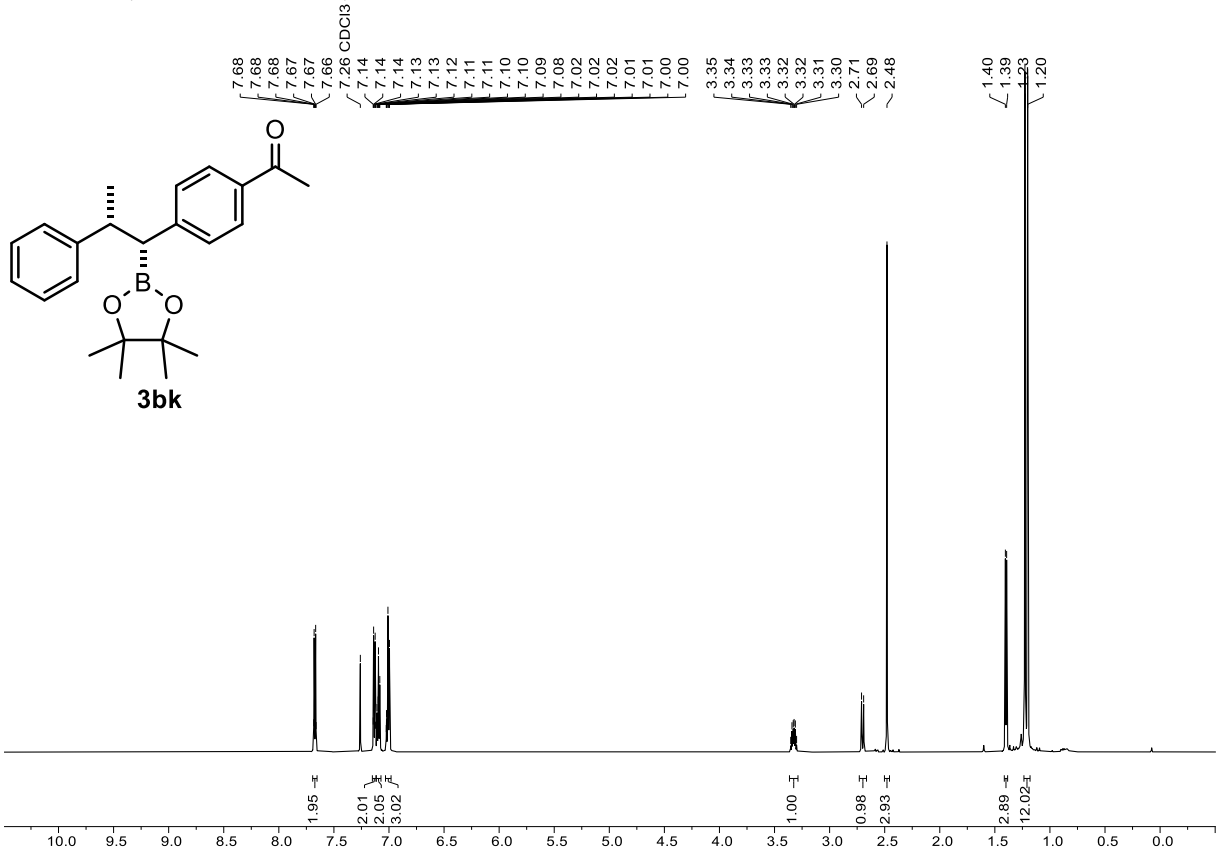
^{11}B-NMR (160 MHz, $CDCl_3$):



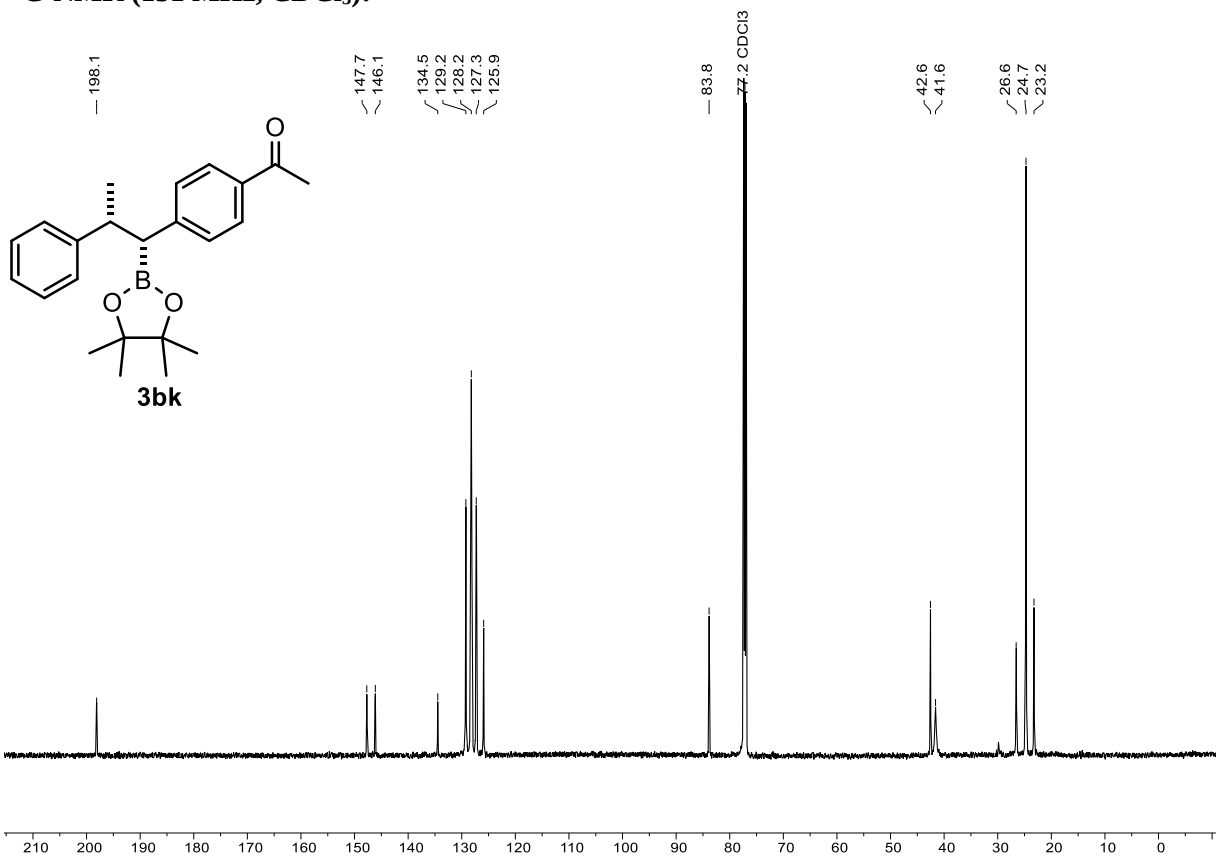
^{19}F-NMR (470 MHz, $CDCl_3$):



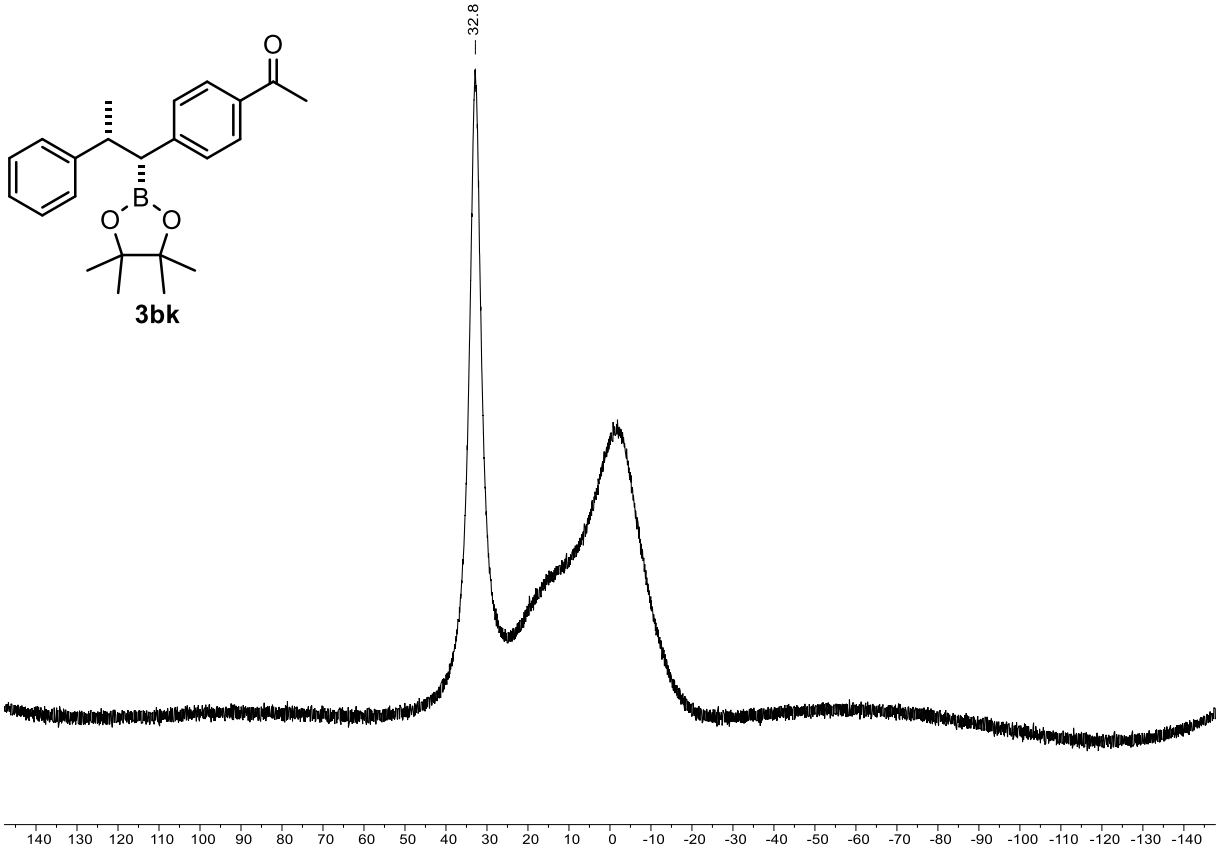
^{1}H-NMR (599 MHz, $CDCl_3$):



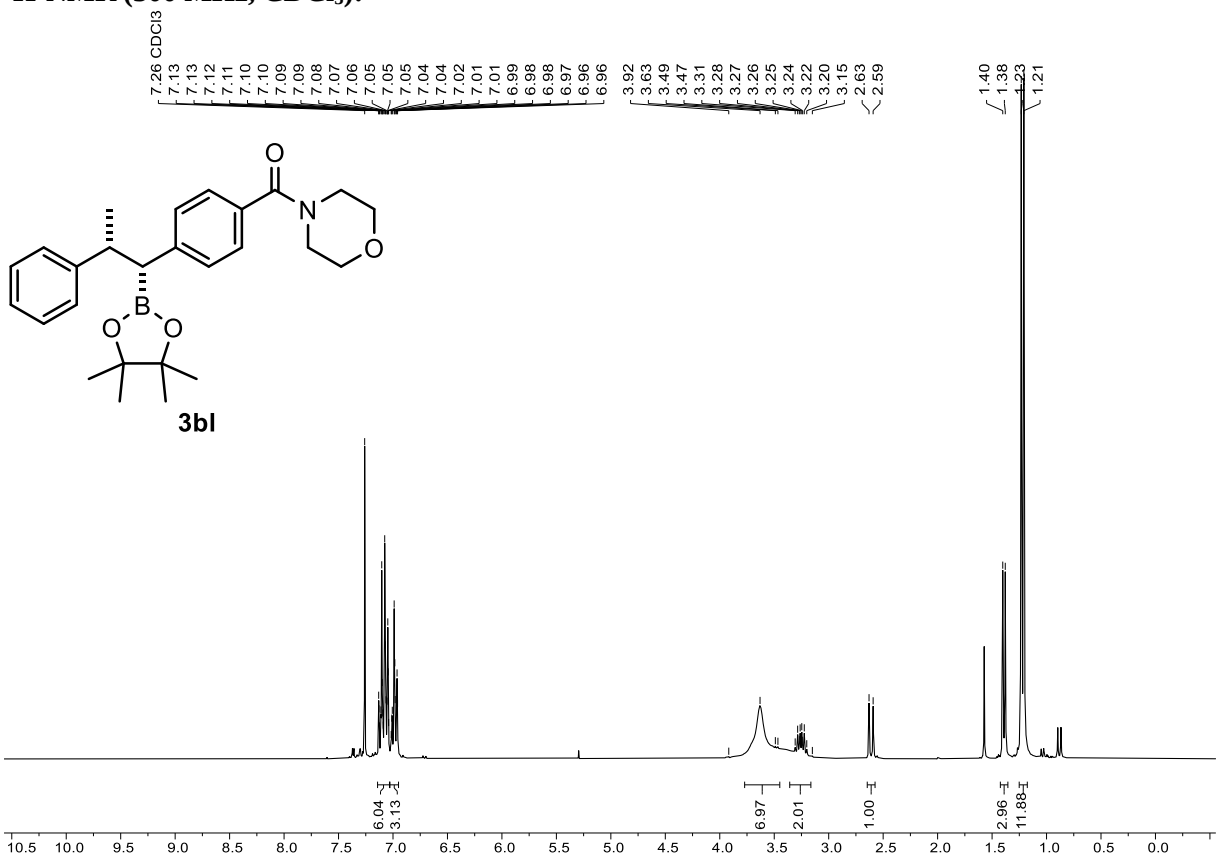
^{13}C-NMR (151 MHz, $CDCl_3$):



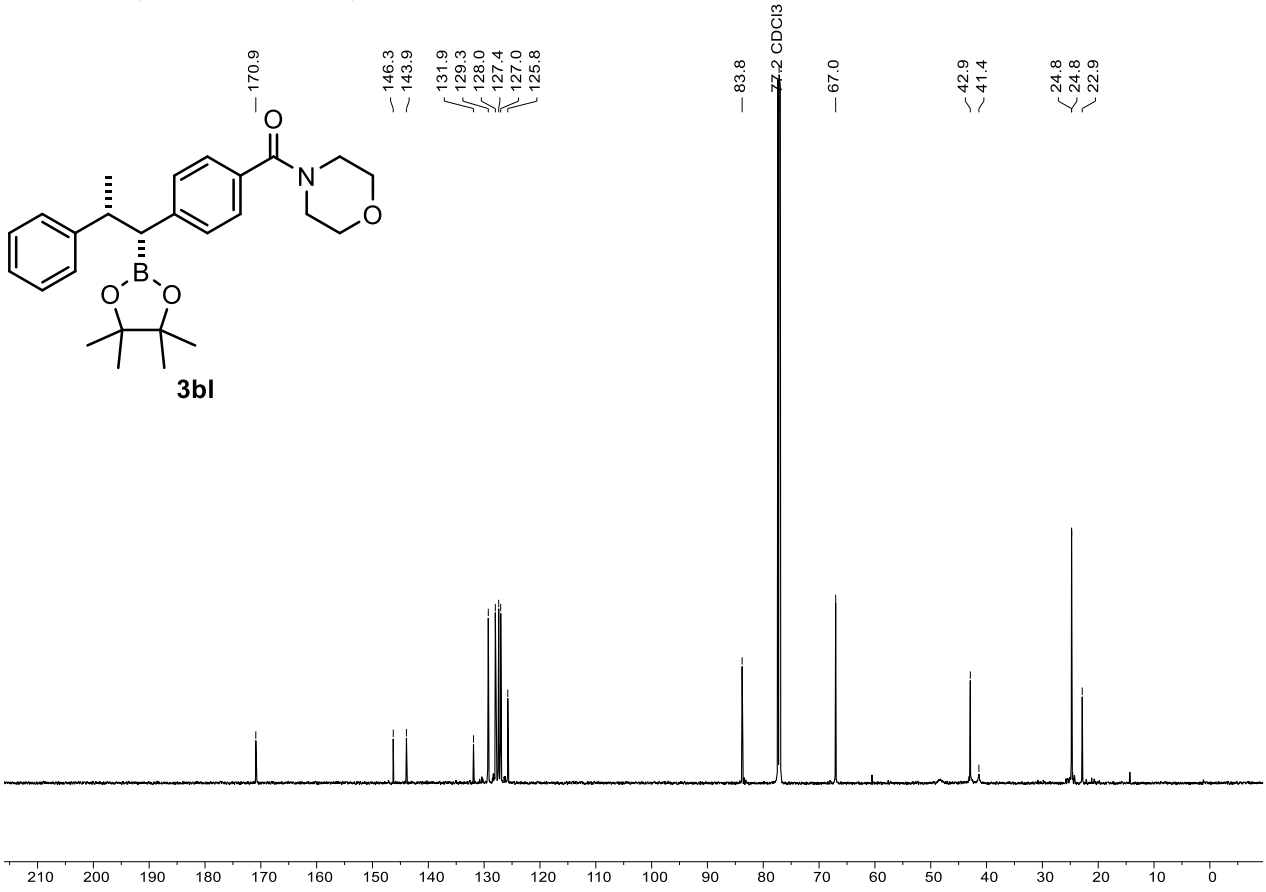
^{11}B-NMR (192 MHz, $CDCl_3$):



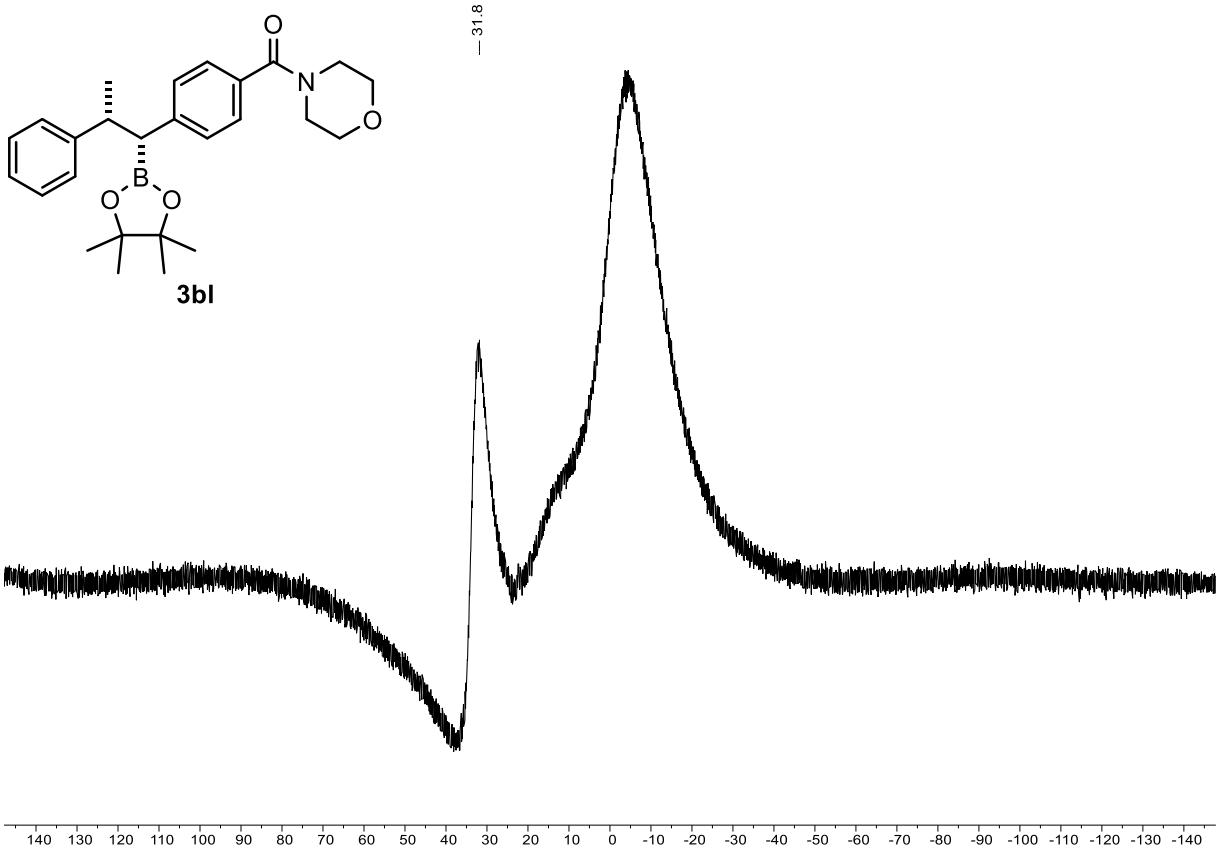
^{1}H-NMR (300 MHz, $CDCl_3$):



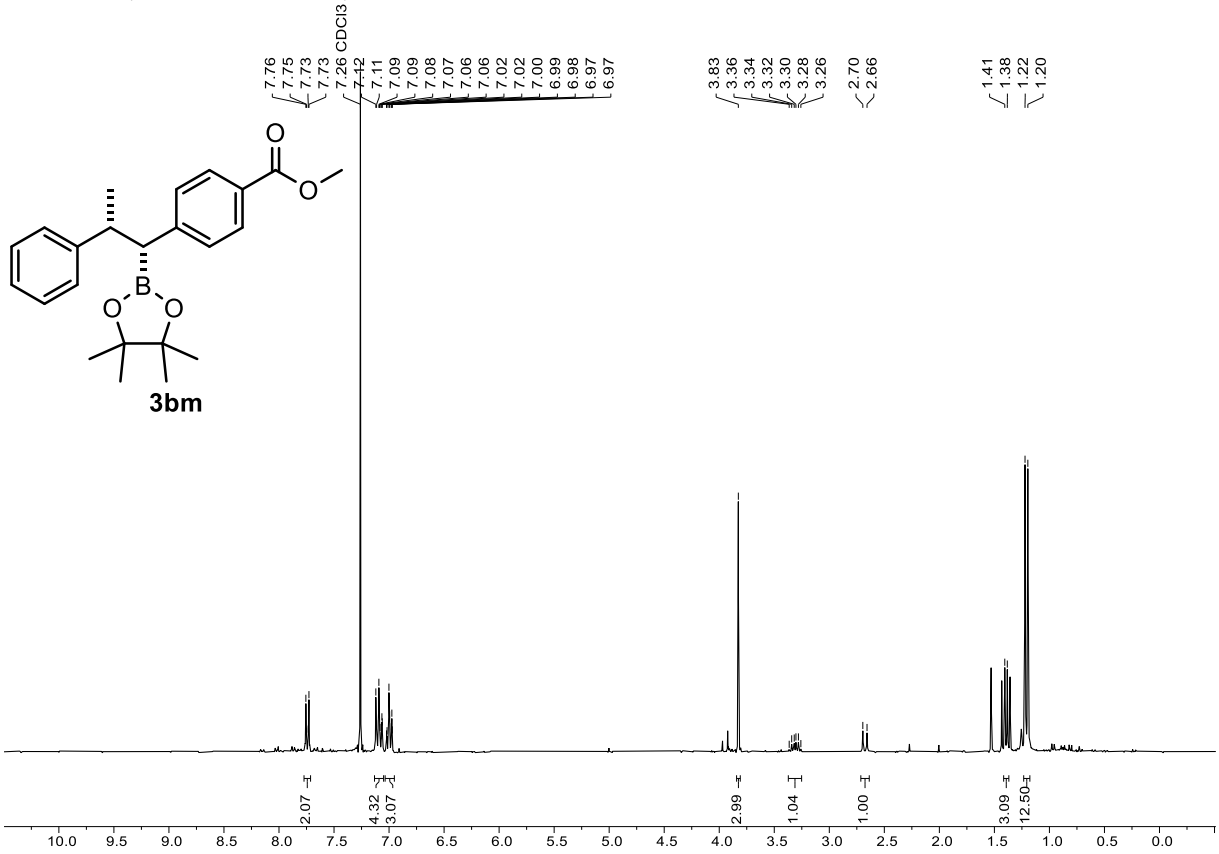
^{13}C-NMR (151 MHz, $CDCl_3$):



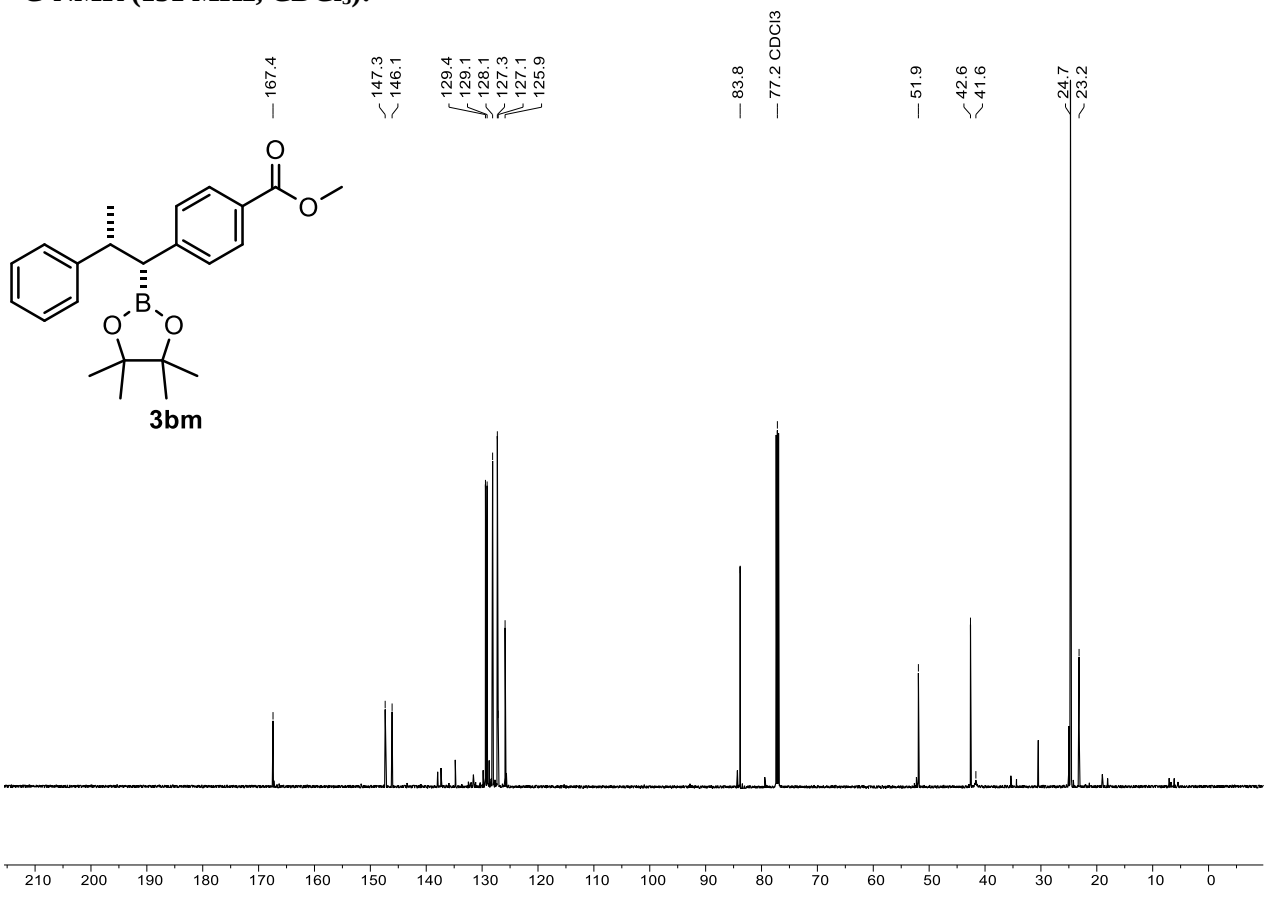
^{11}B-NMR (192 MHz, $CDCl_3$):



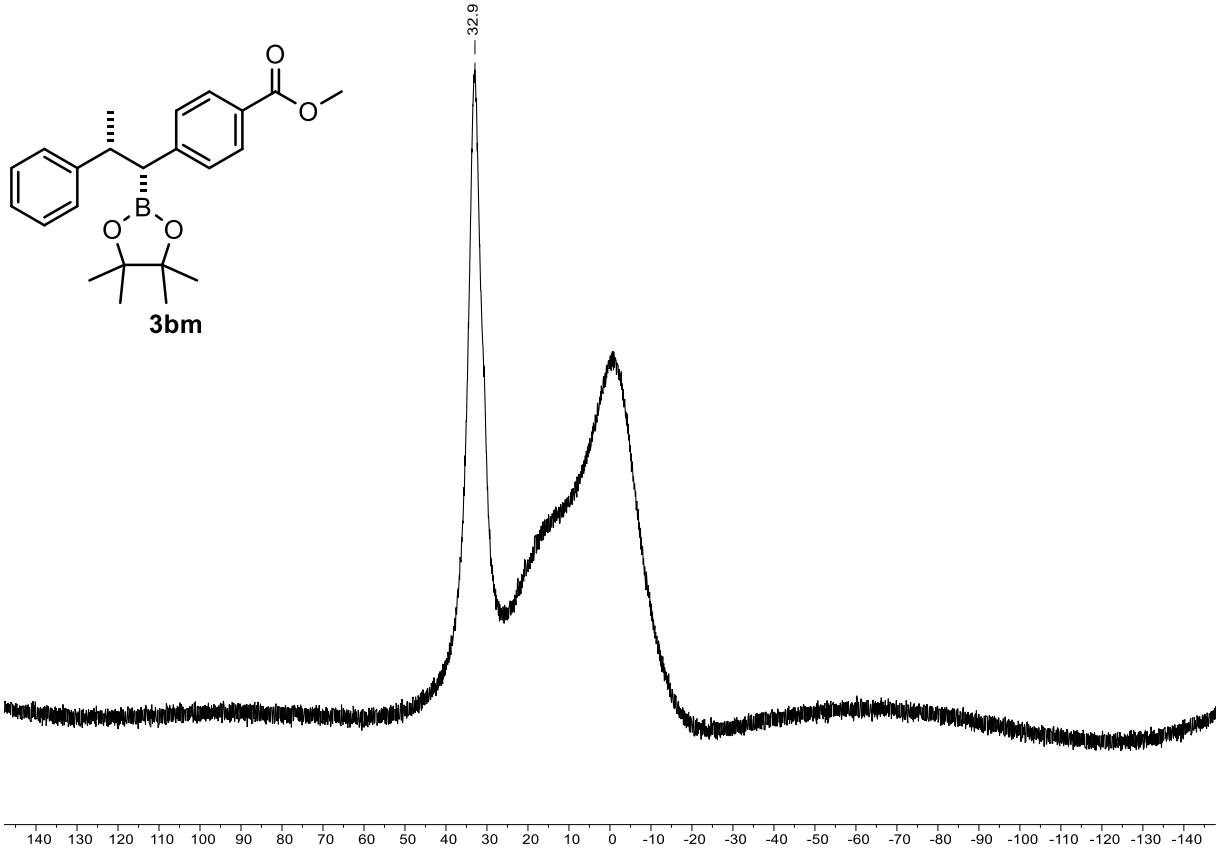
^{1}H-NMR (300 MHz, $CDCl_3$):



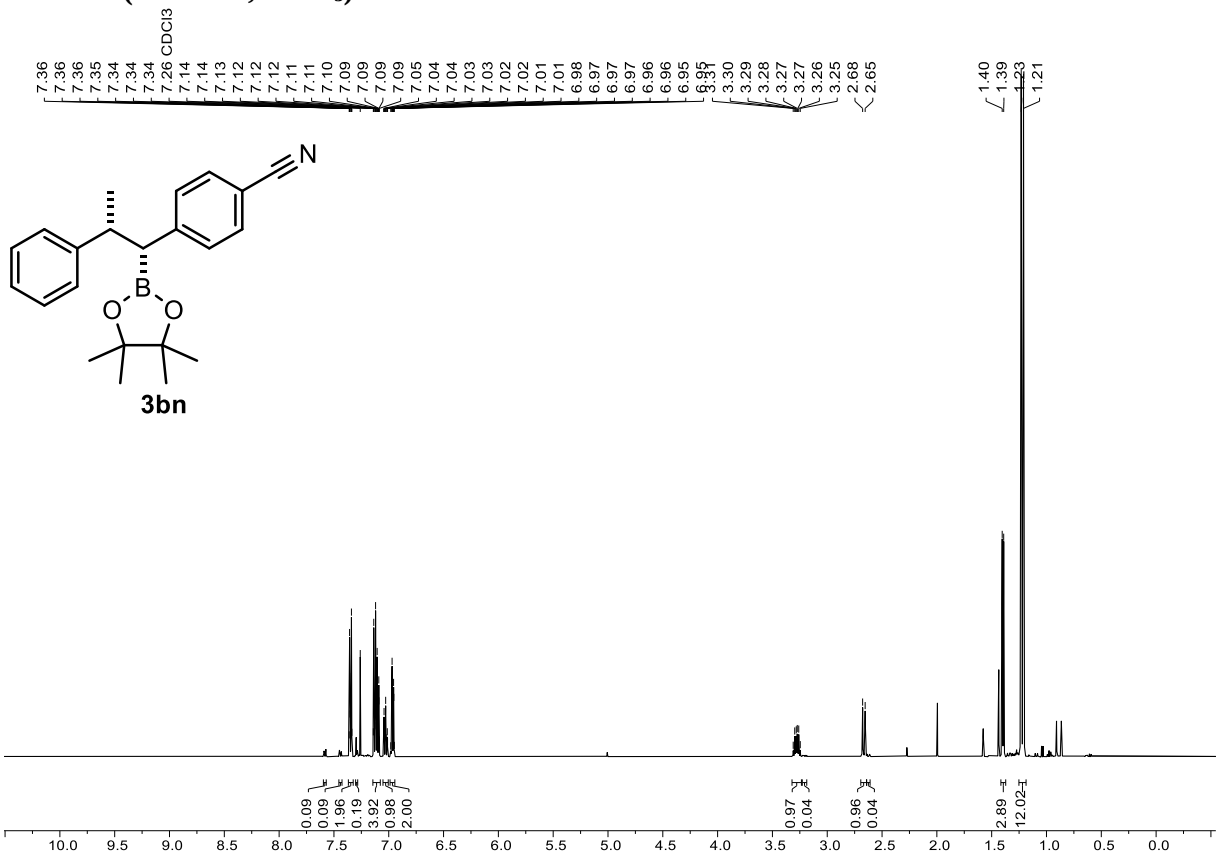
^{13}C-NMR (151 MHz, $CDCl_3$):



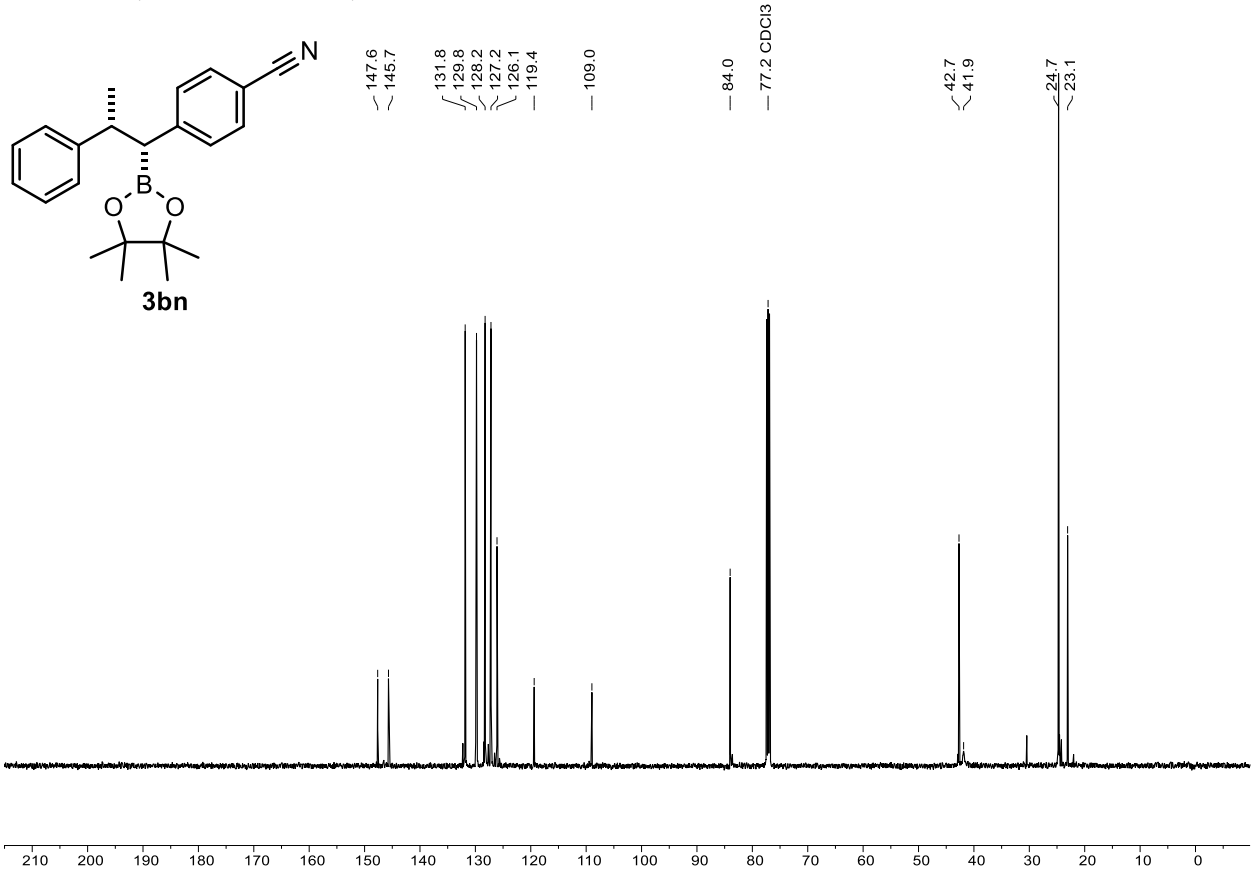
^{11}B-NMR (192 MHz, $CDCl_3$):



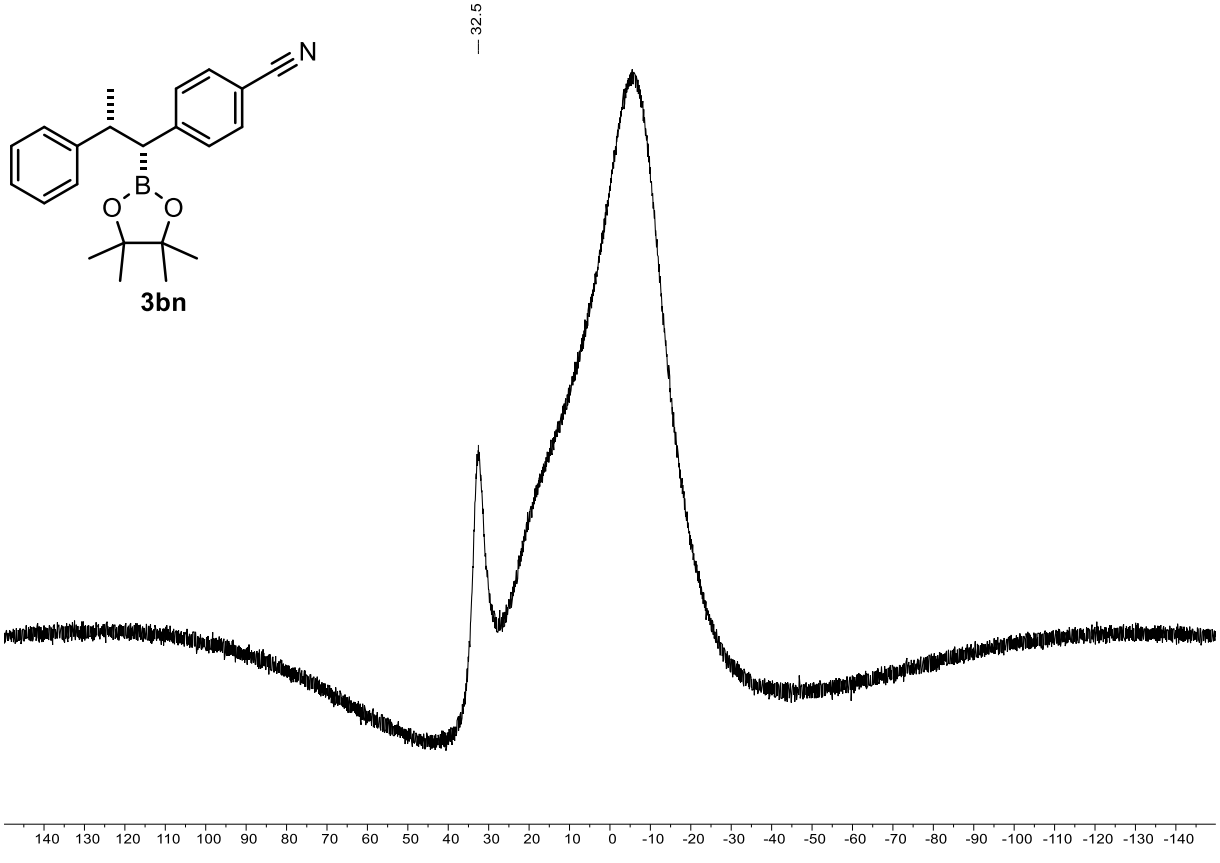
^{1}H-NMR (500 MHz, $CDCl_3$):



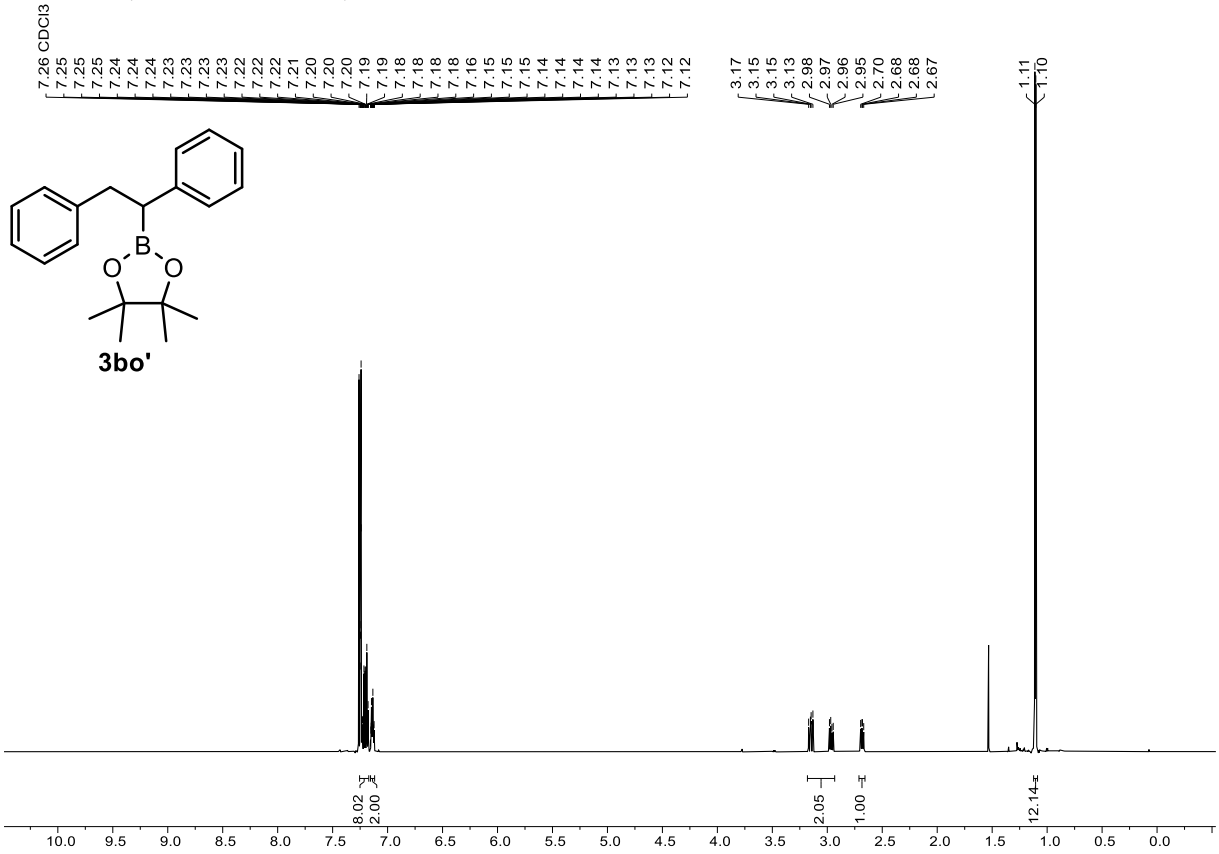
^{13}C-NMR (126 MHz, $CDCl_3$):



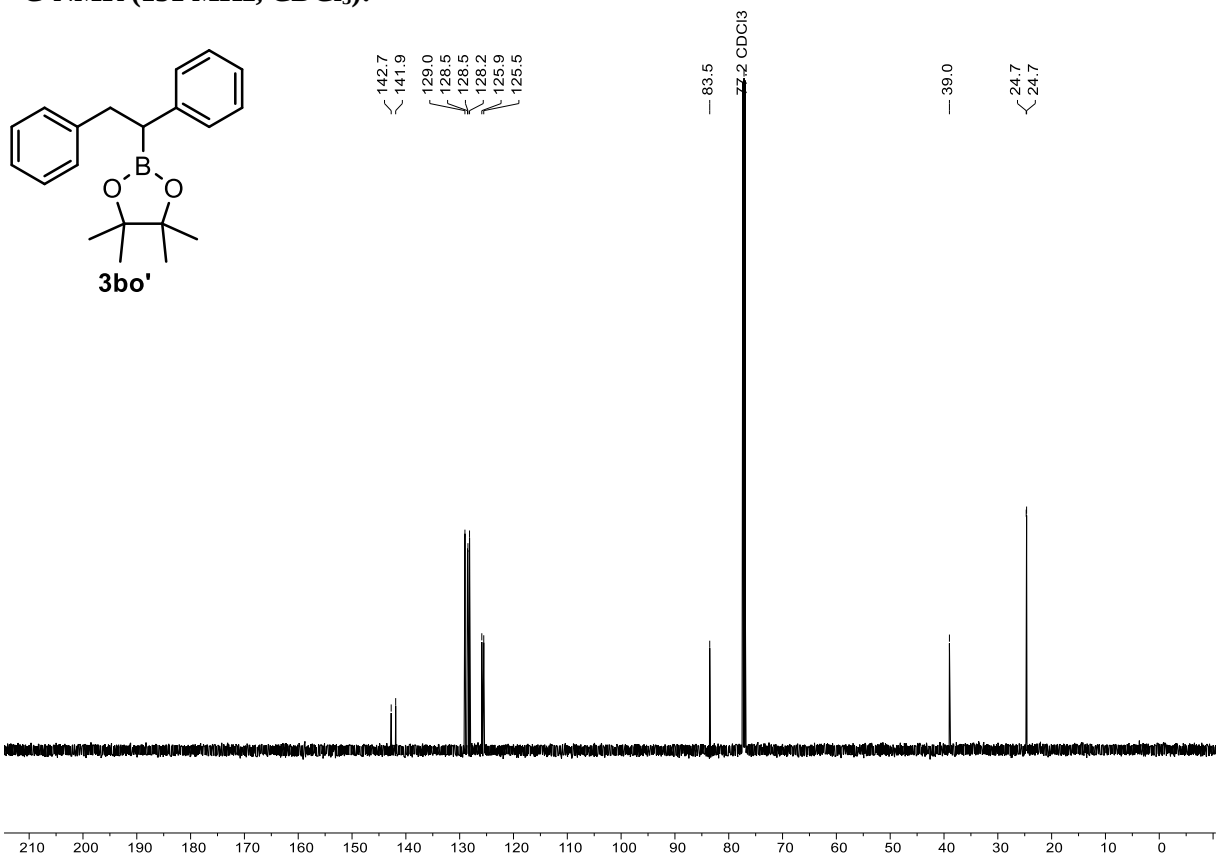
^{11}B-NMR (160 MHz, $CDCl_3$):



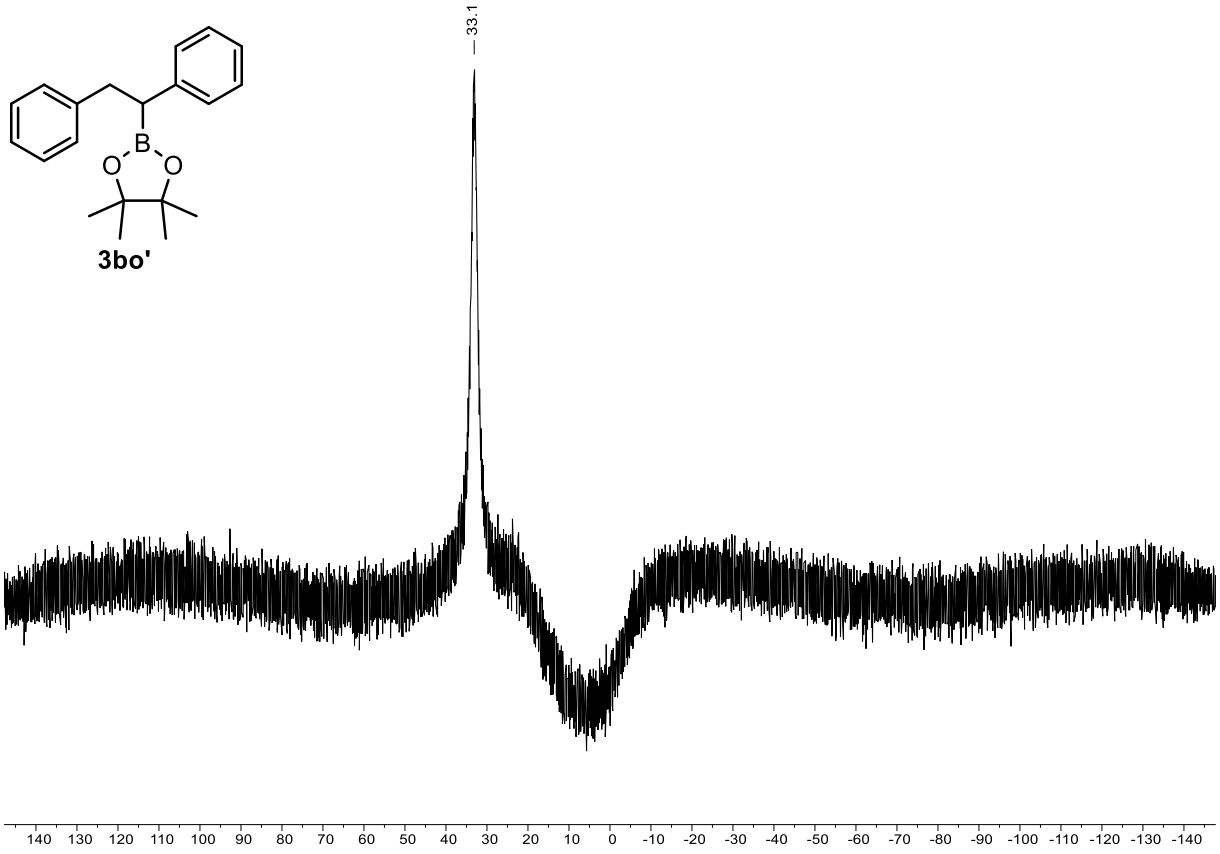
^{1}H-NMR (599 MHz, $CDCl_3$):



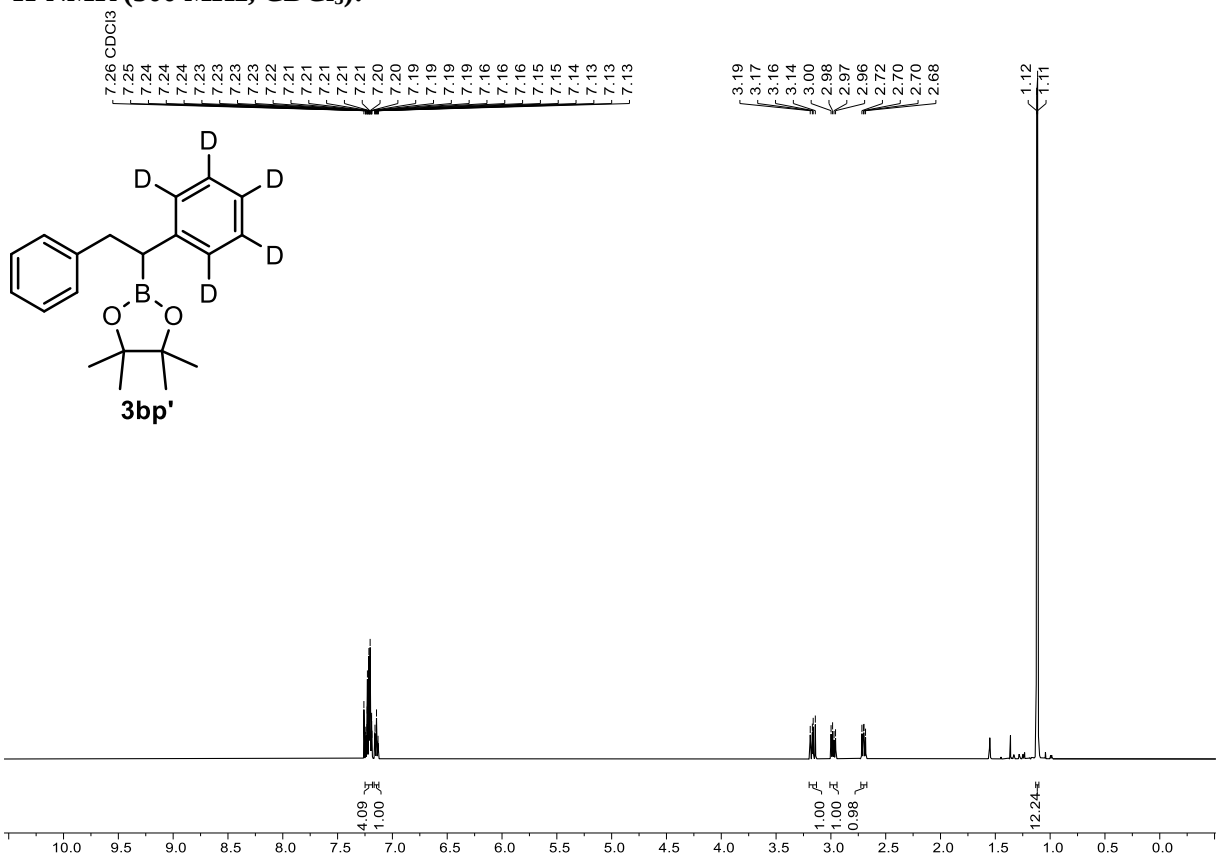
^{13}C-NMR (151 MHz, $CDCl_3$):



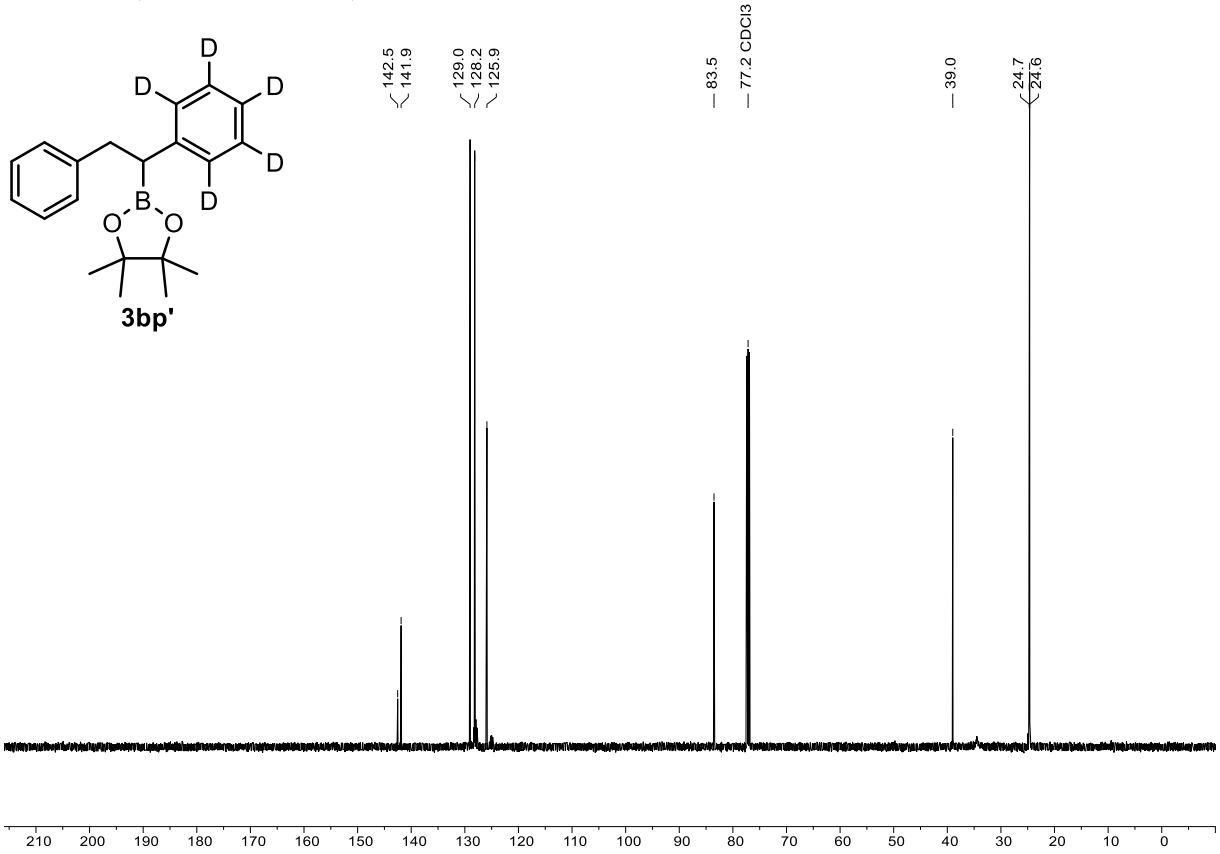
^{11}B-NMR (192 MHz, $CDCl_3$):



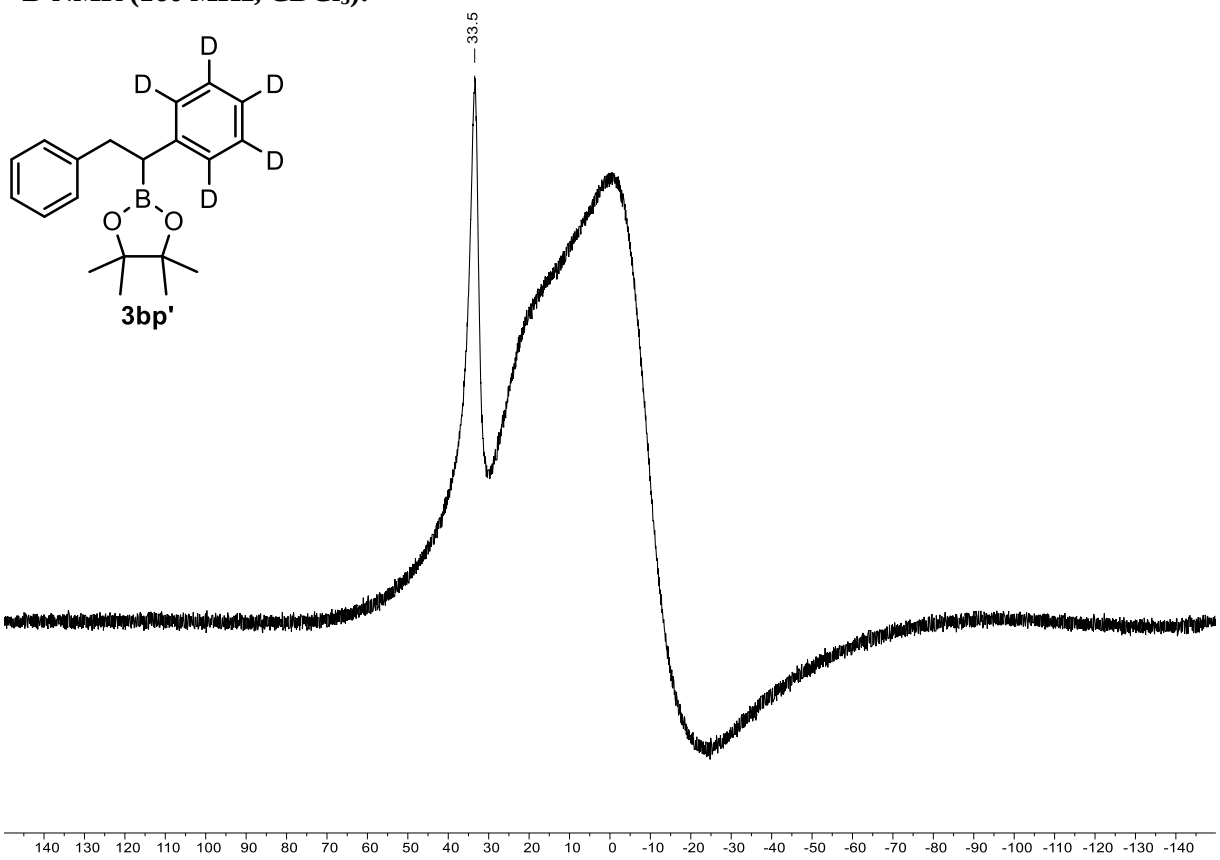
^{1}H-NMR (500 MHz, $CDCl_3$):



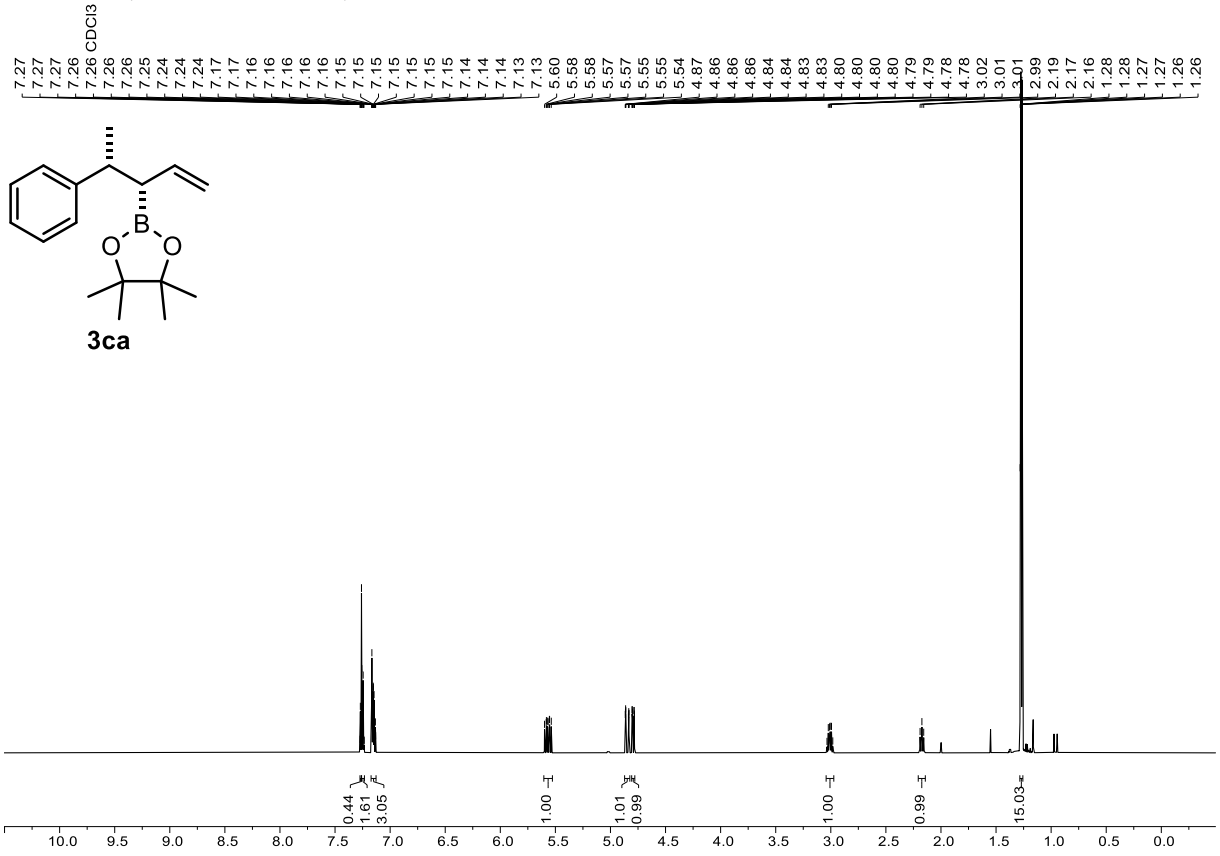
^{13}C-NMR (126 MHz, $CDCl_3$):



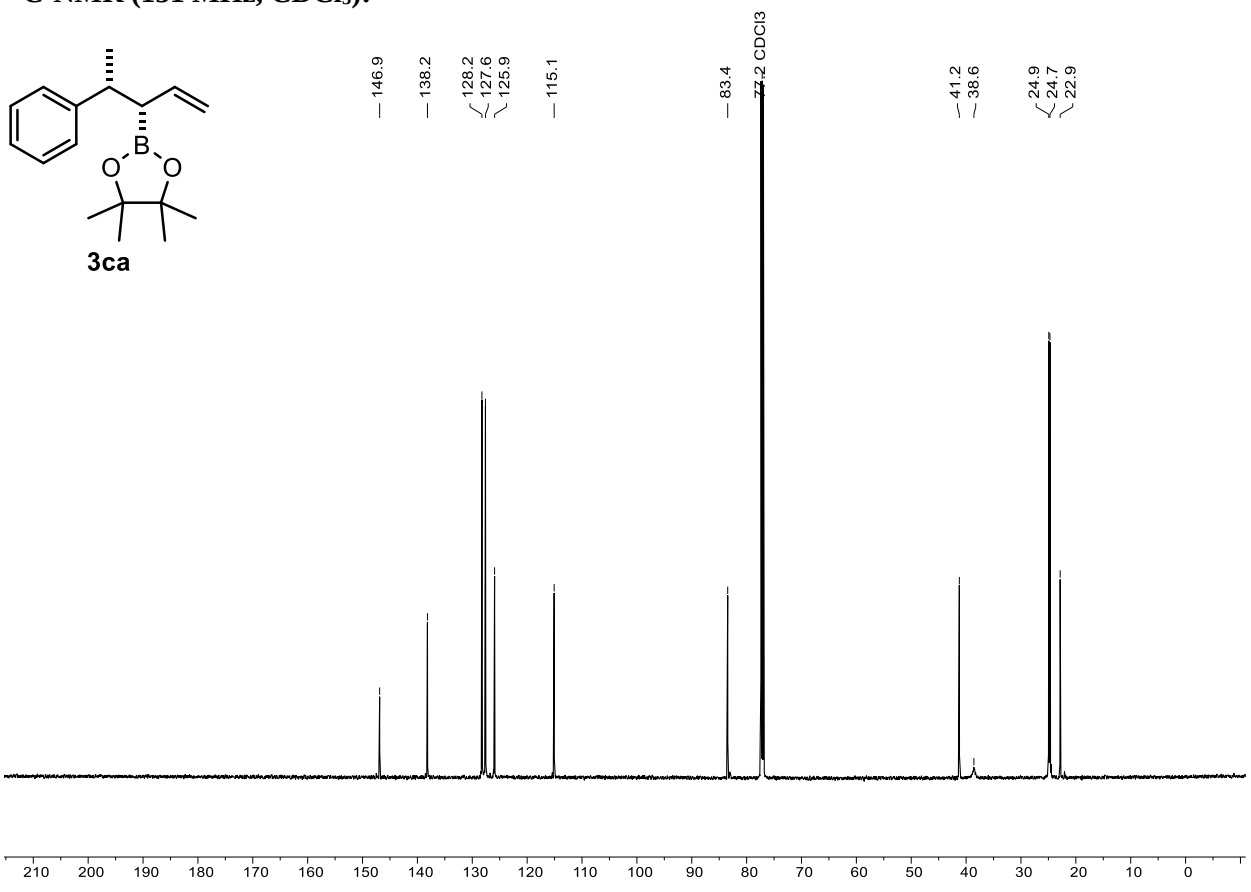
^{11}B-NMR (160 MHz, $CDCl_3$):



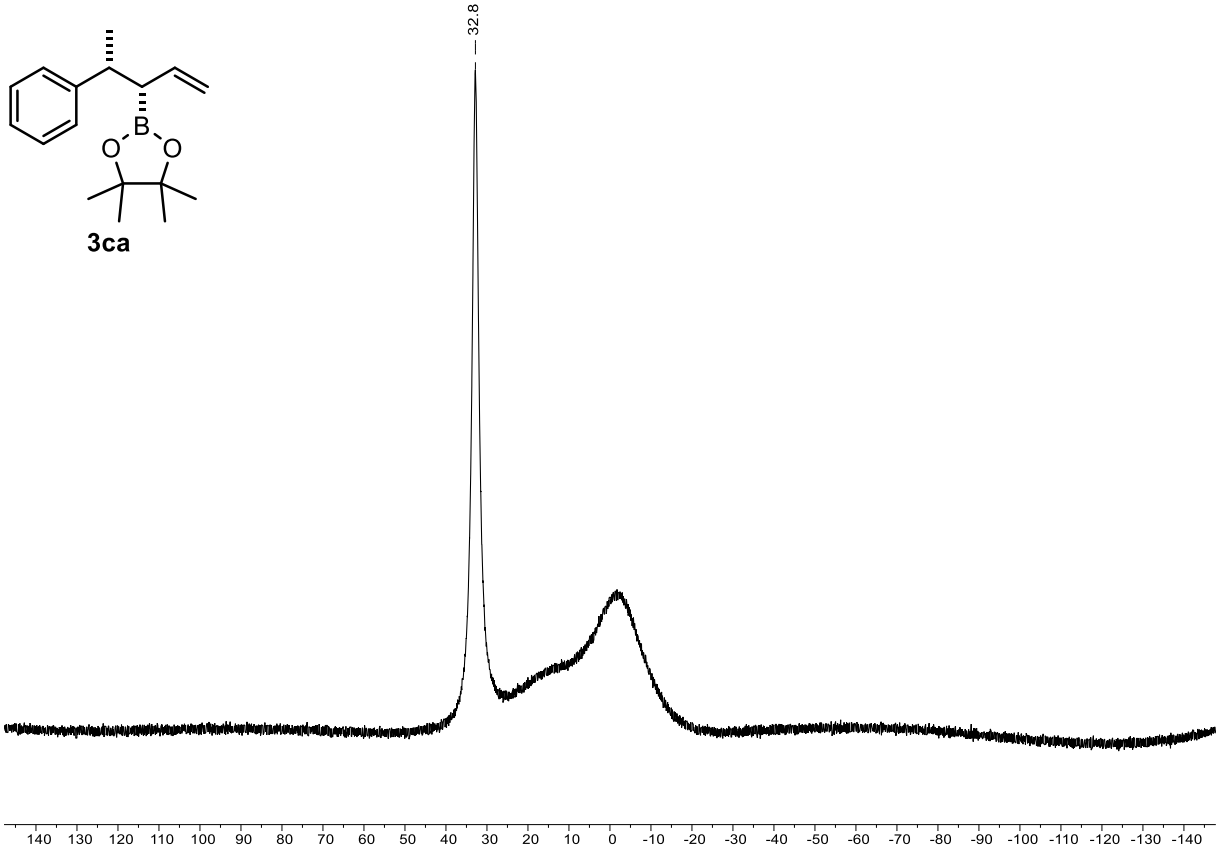
^{1}H-NMR (599 MHz, $CDCl_3$):



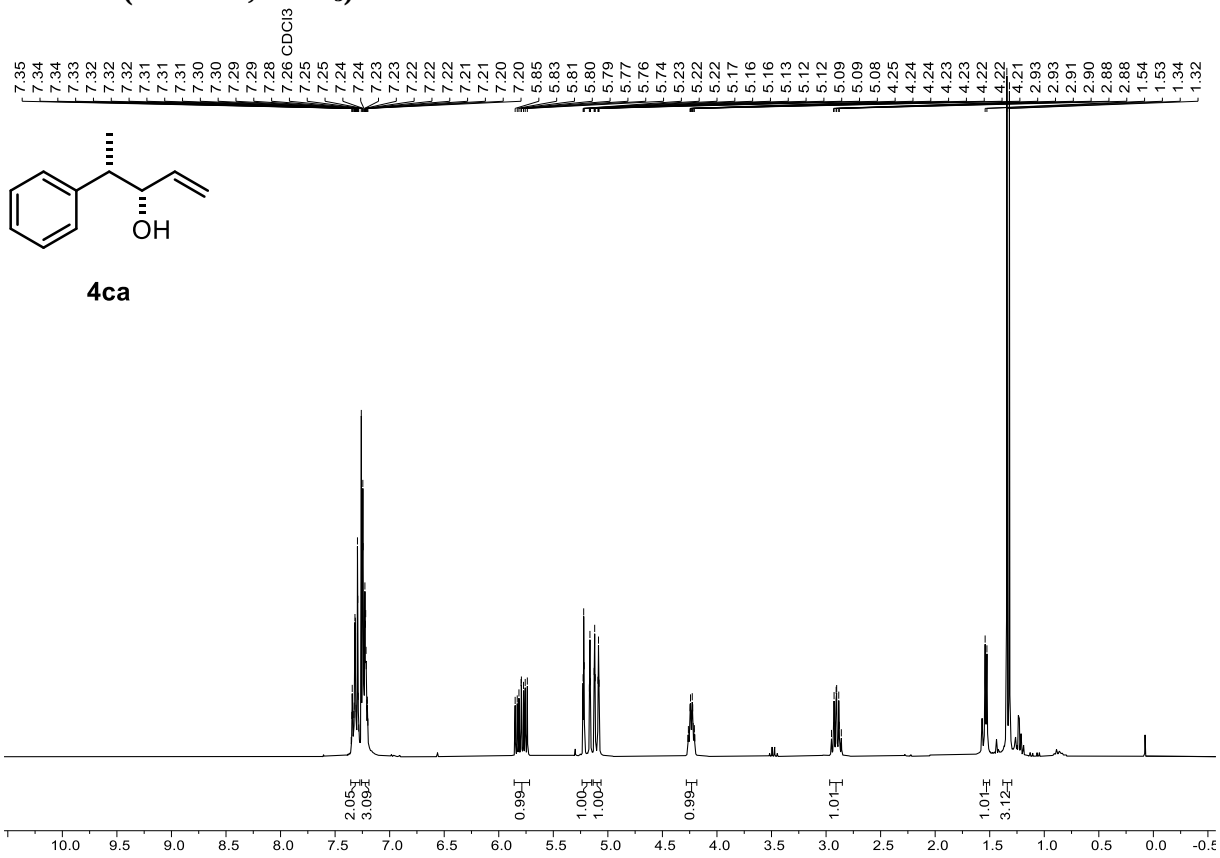
^{13}C-NMR (151 MHz, $CDCl_3$):



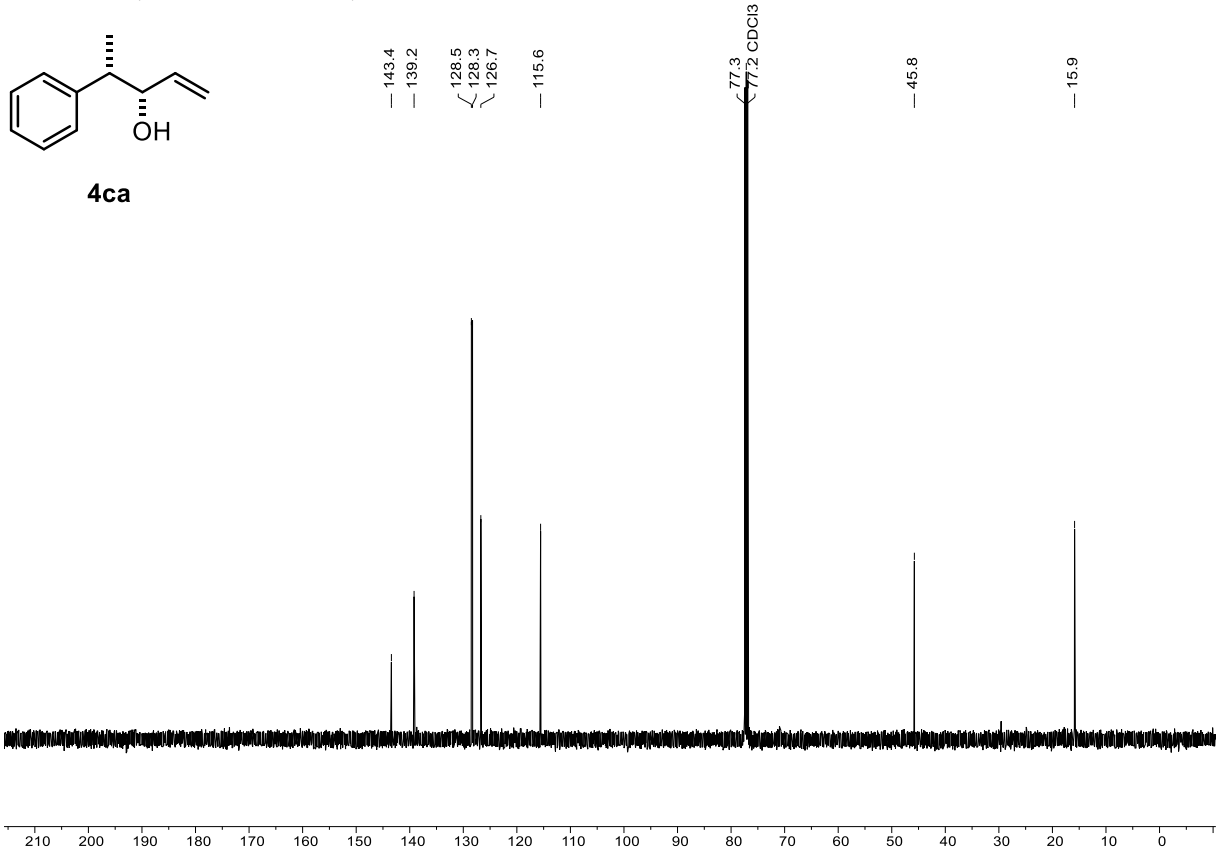
^{11}B-NMR (192 MHz, $CDCl_3$):



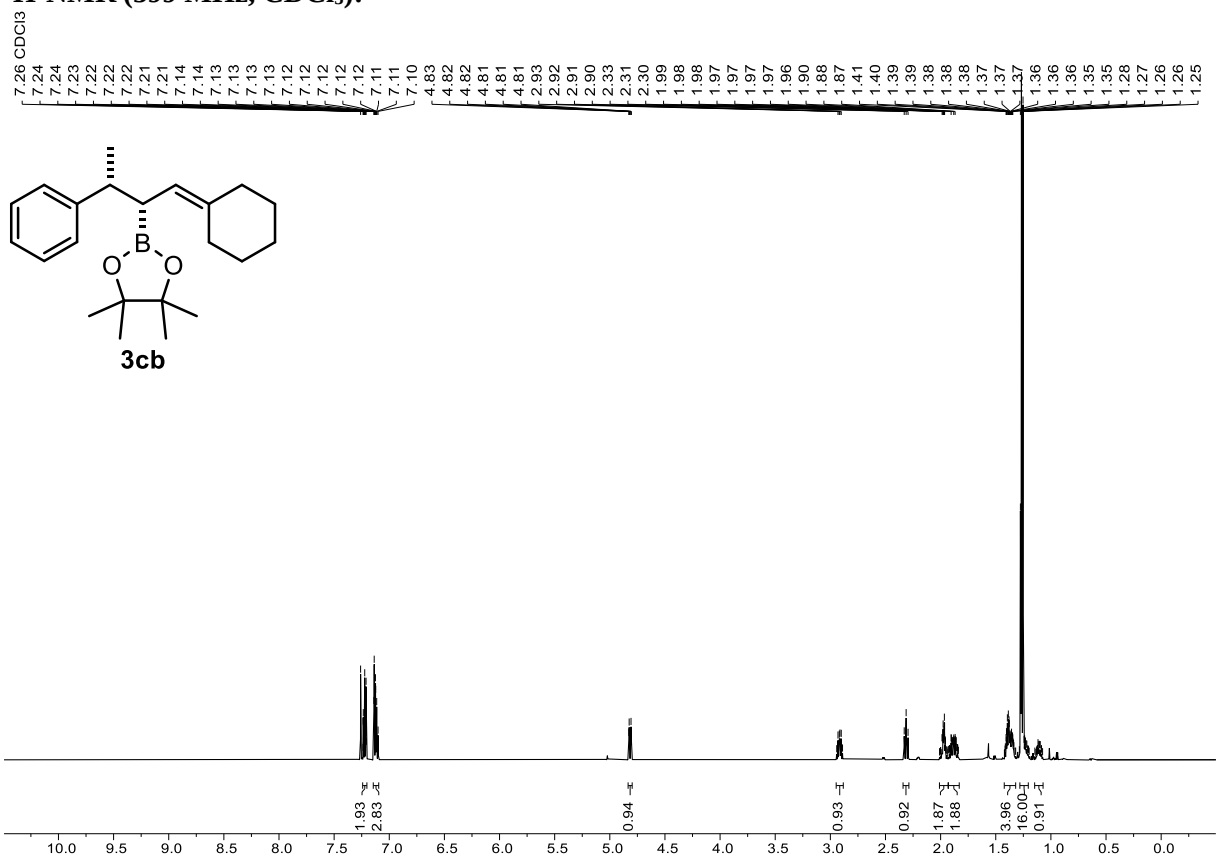
^{1}H-NMR (300 MHz, $CDCl_3$):



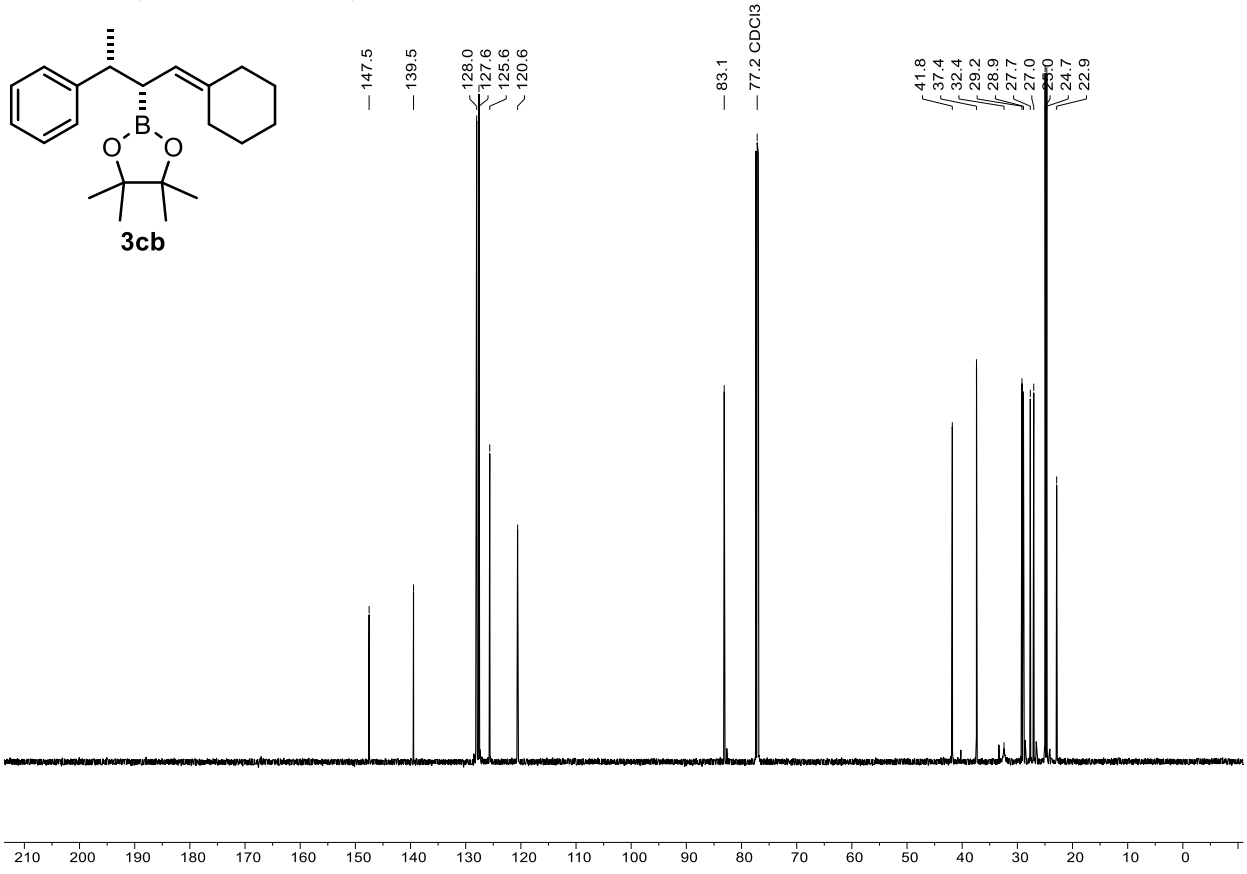
^{13}C-NMR (126 MHz, $CDCl_3$):



^{1}H-NMR (599 MHz, $CDCl_3$):



^{13}C-NMR (151 MHz, $CDCl_3$):



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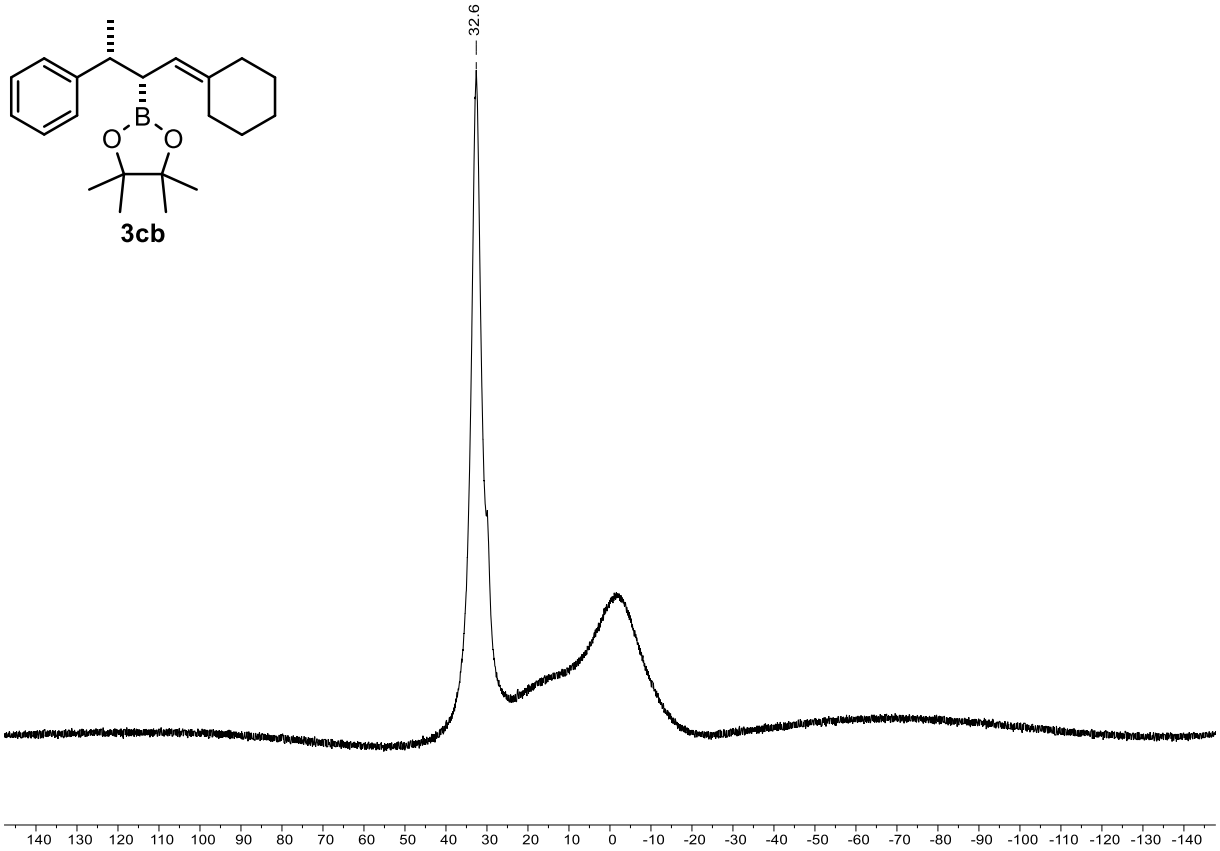
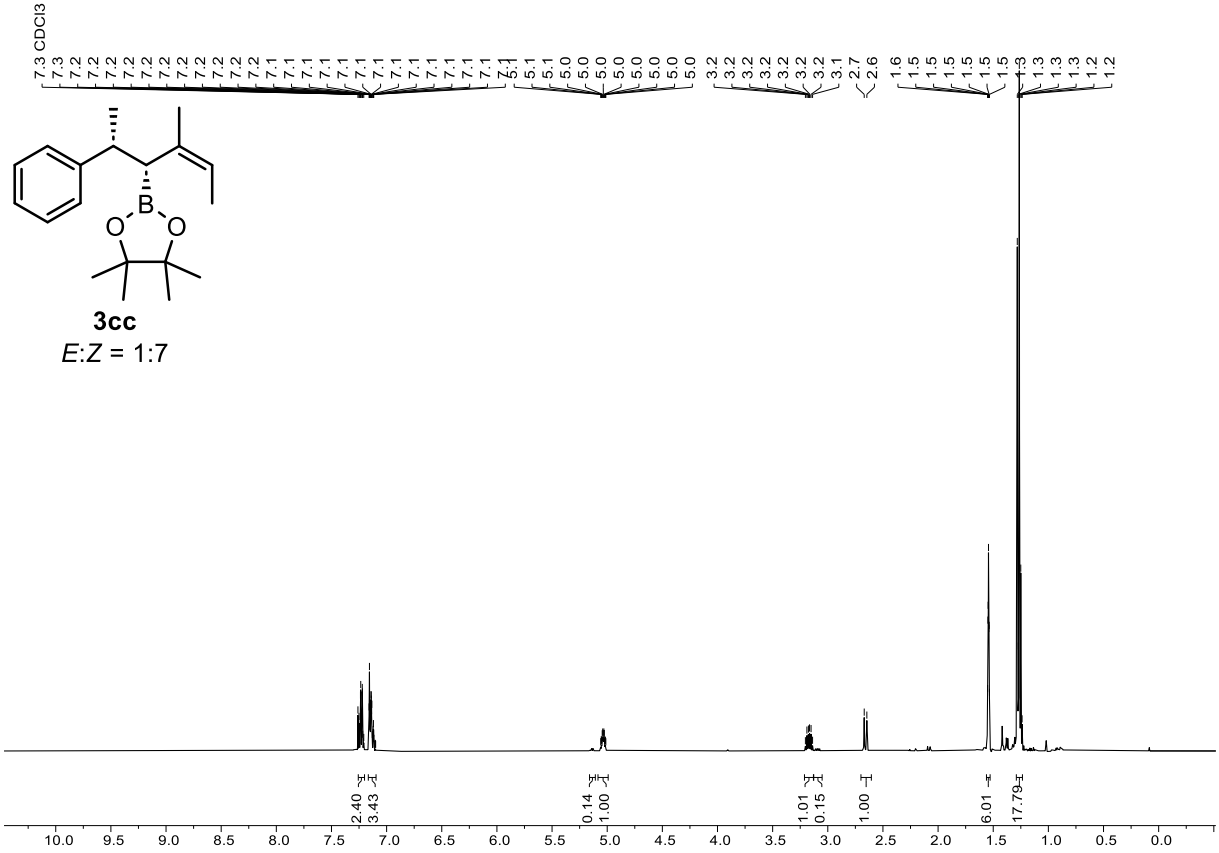
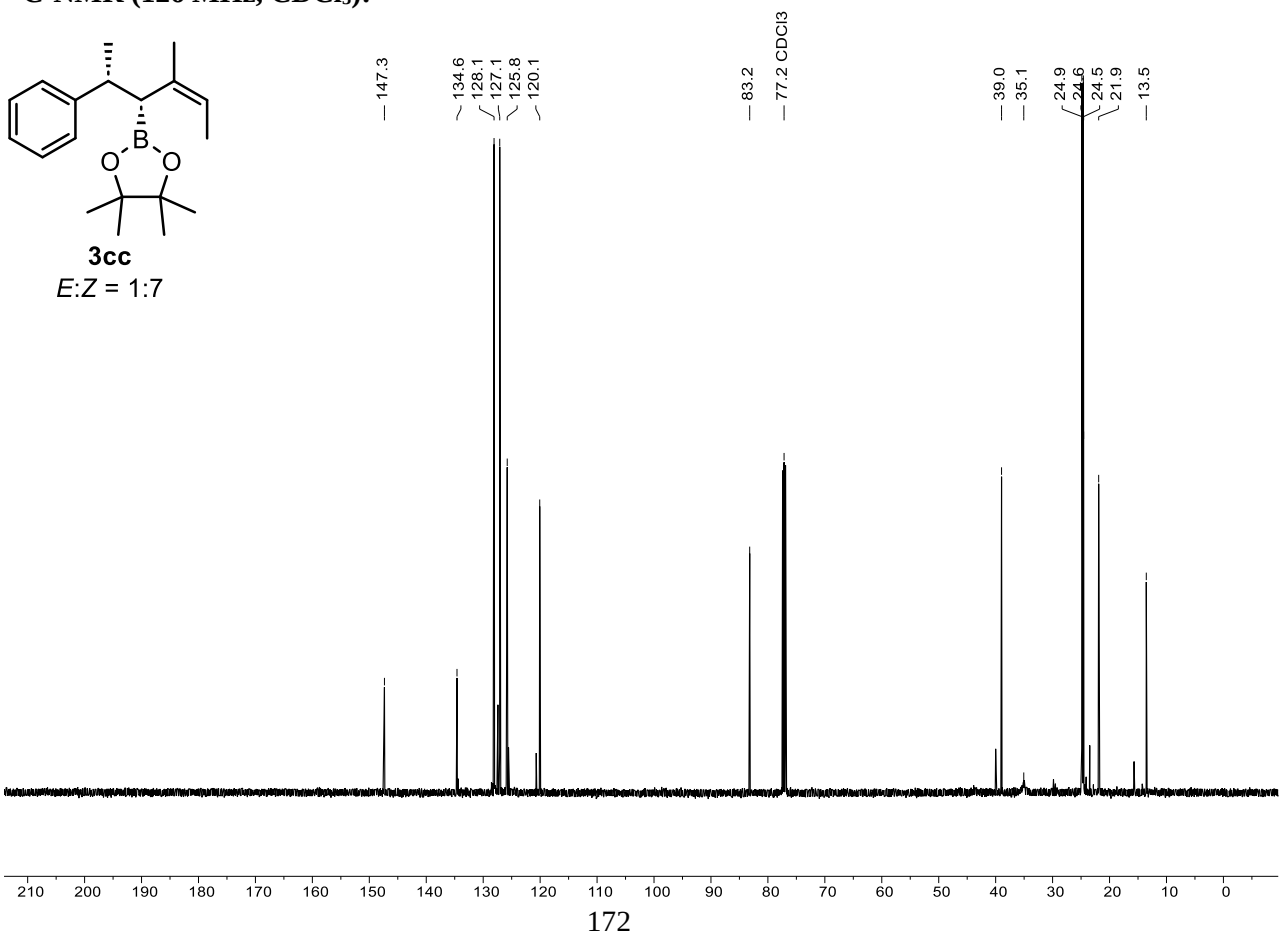


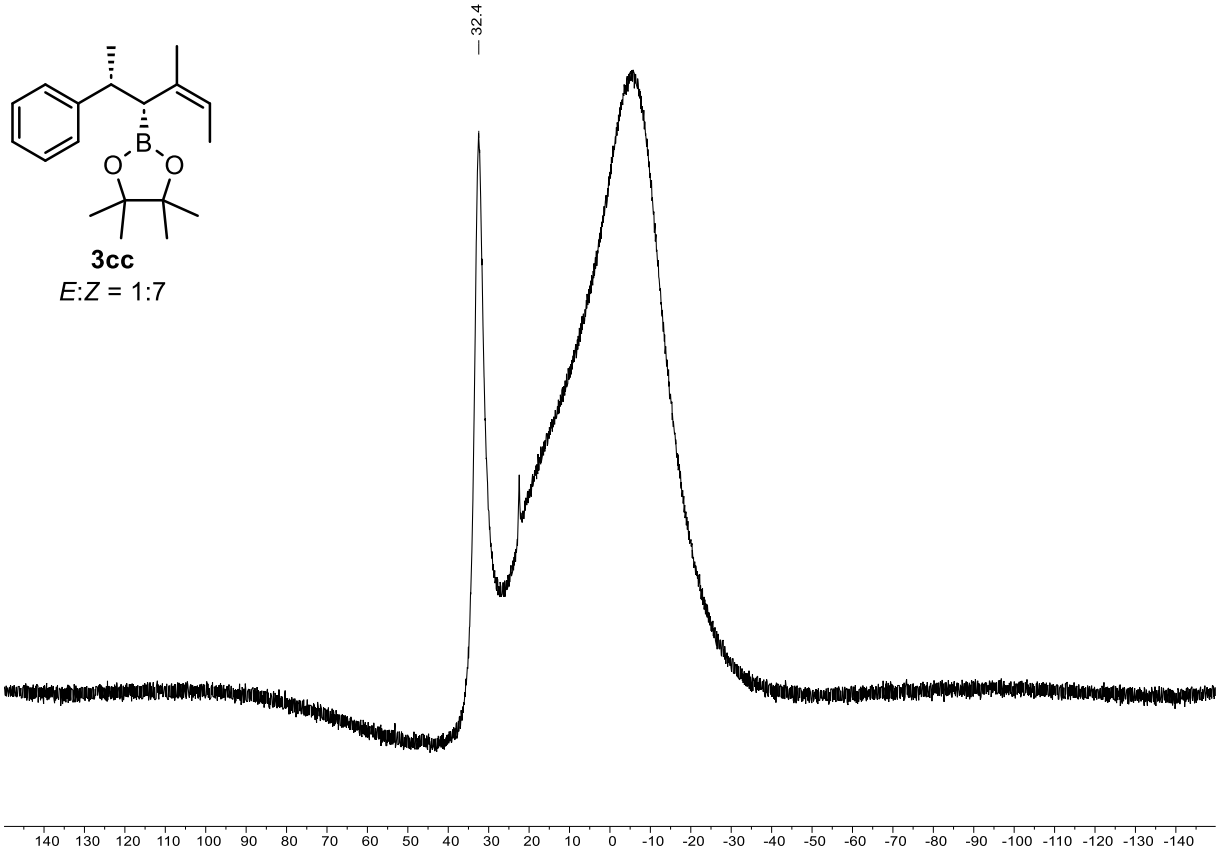
^{1}H-NMR (500 MHz, $CDCl_3$):



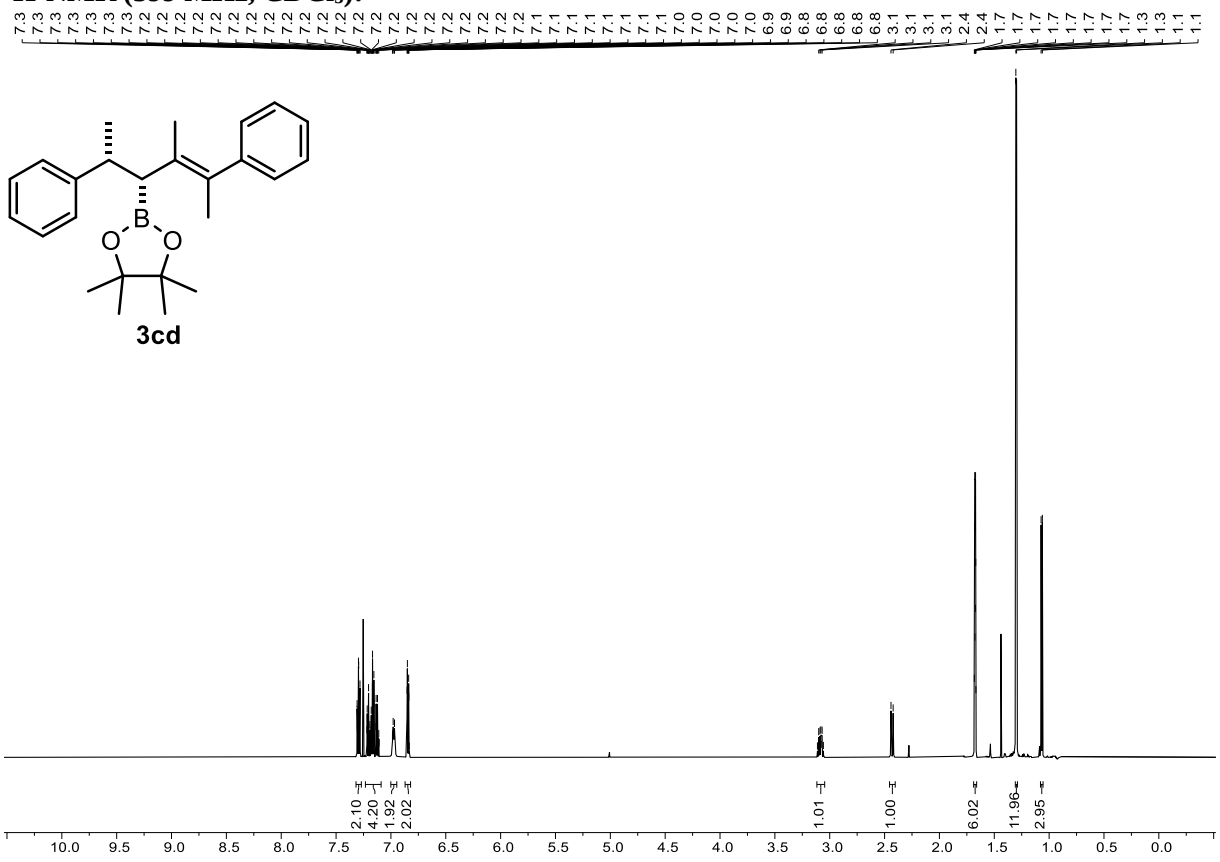
^{13}C-NMR (126 MHz, $CDCl_3$):



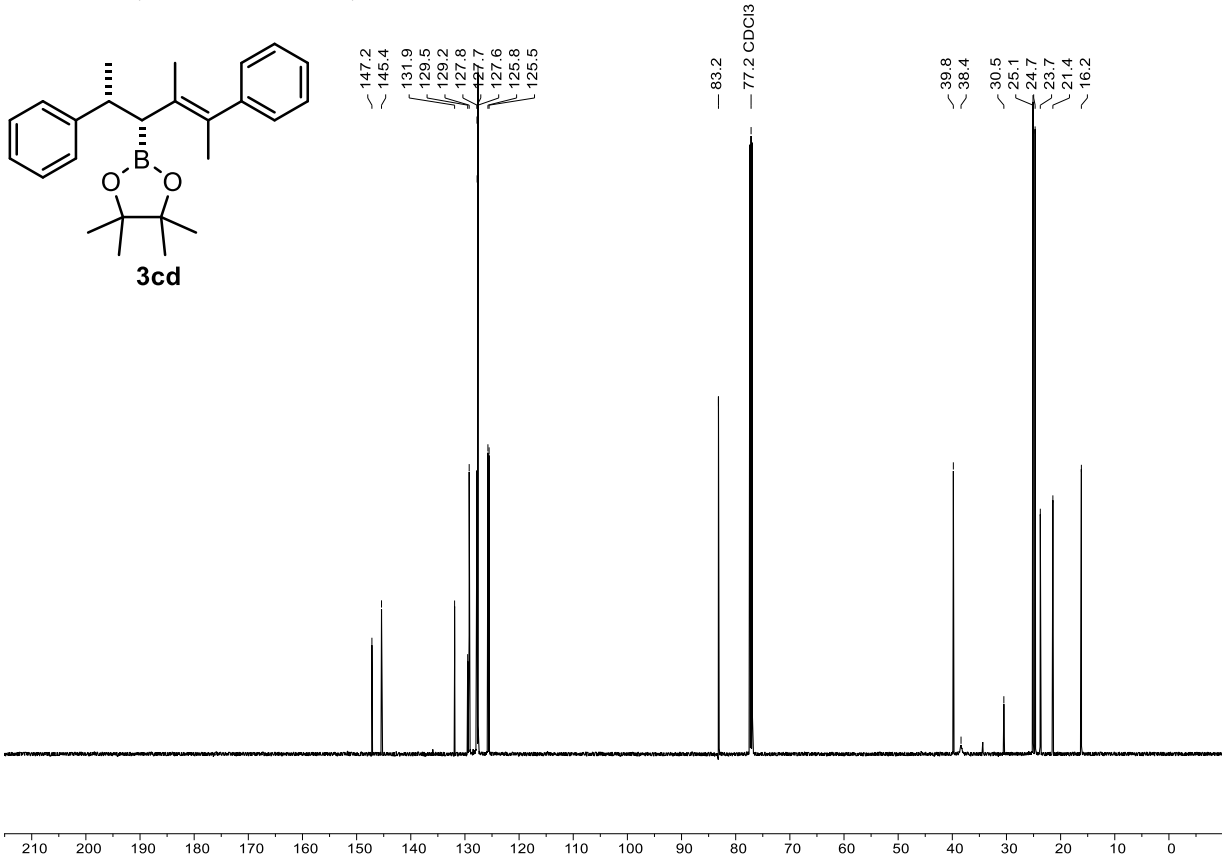
^{11}B-NMR (160 MHz, $CDCl_3$):



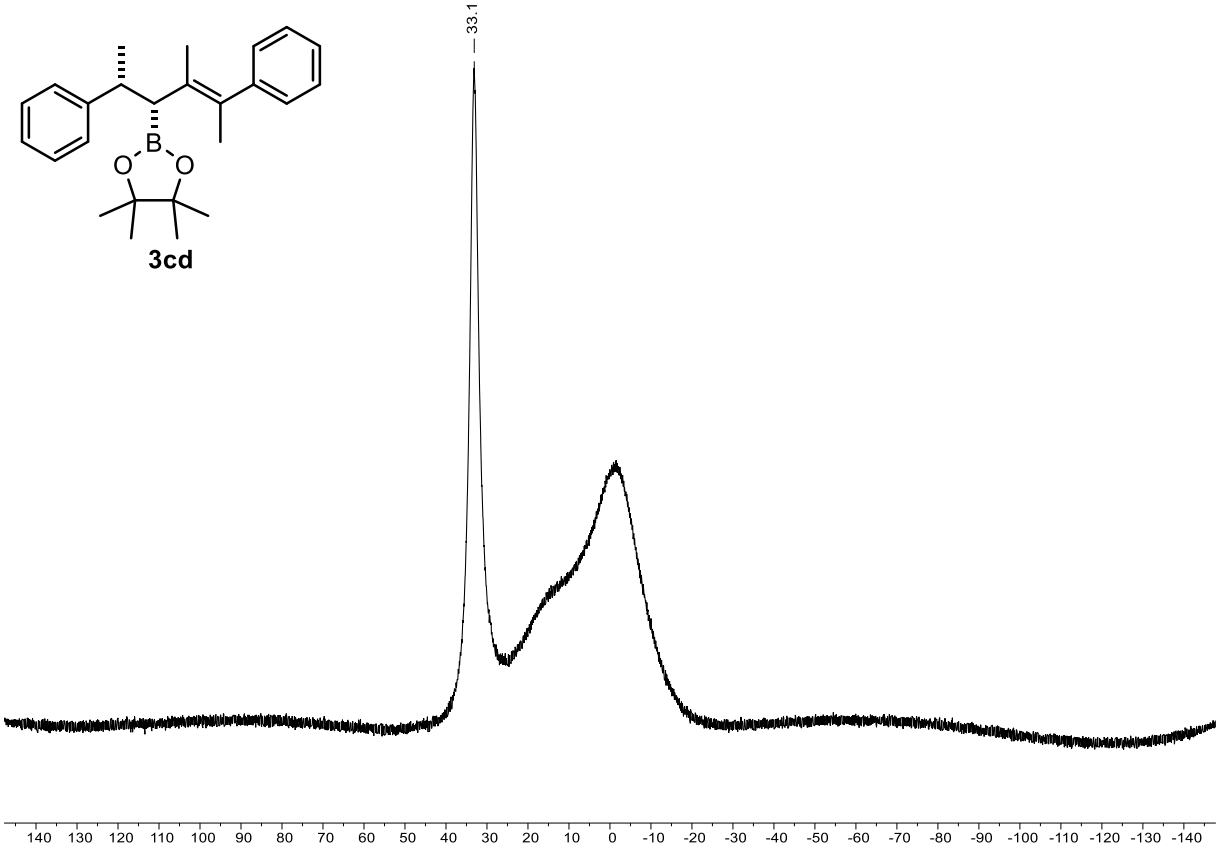
^{1}H-NMR (599 MHz, $CDCl_3$):



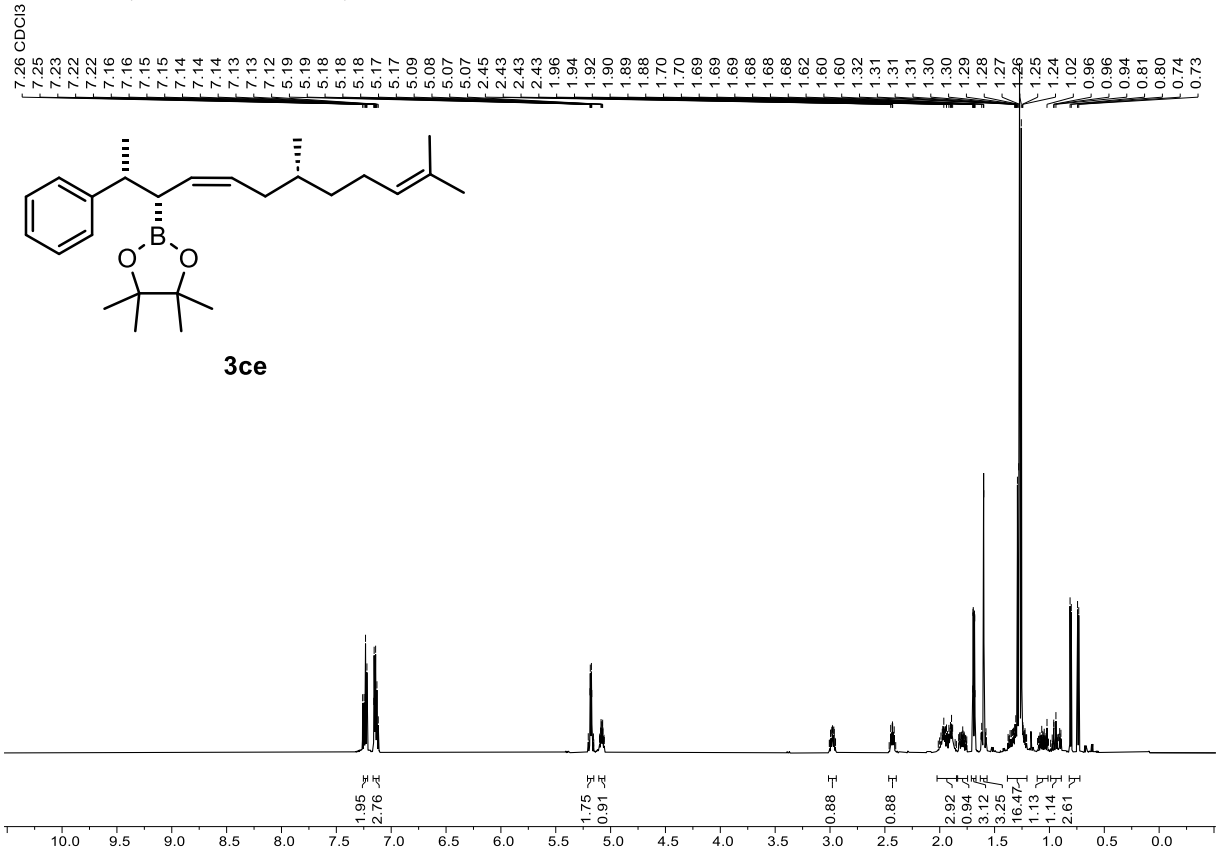
^{13}C-NMR (151 MHz, $CDCl_3$):



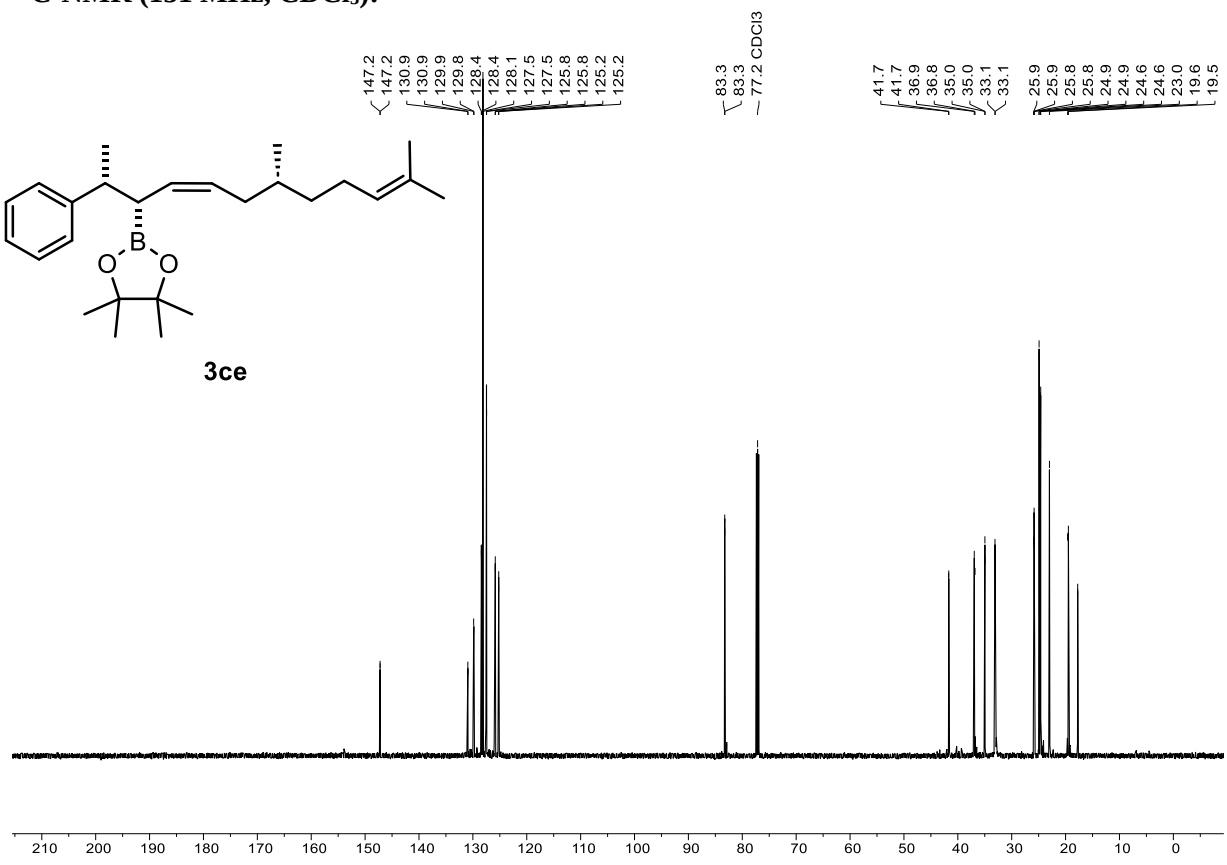
^{11}B-NMR (192 MHz, $CDCl_3$):



^{1}H-NMR (599 MHz, $CDCl_3$):



^{13}C-NMR (151 MHz, $CDCl_3$):



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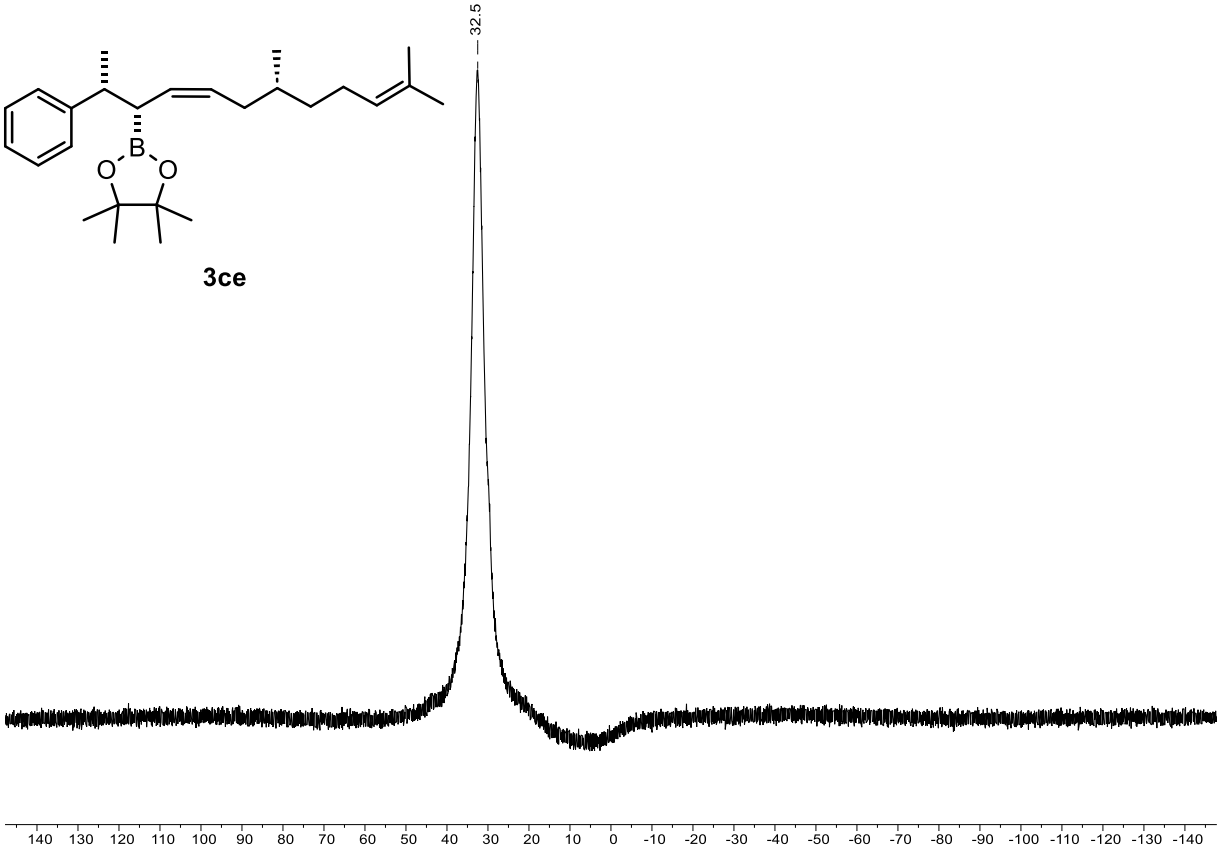

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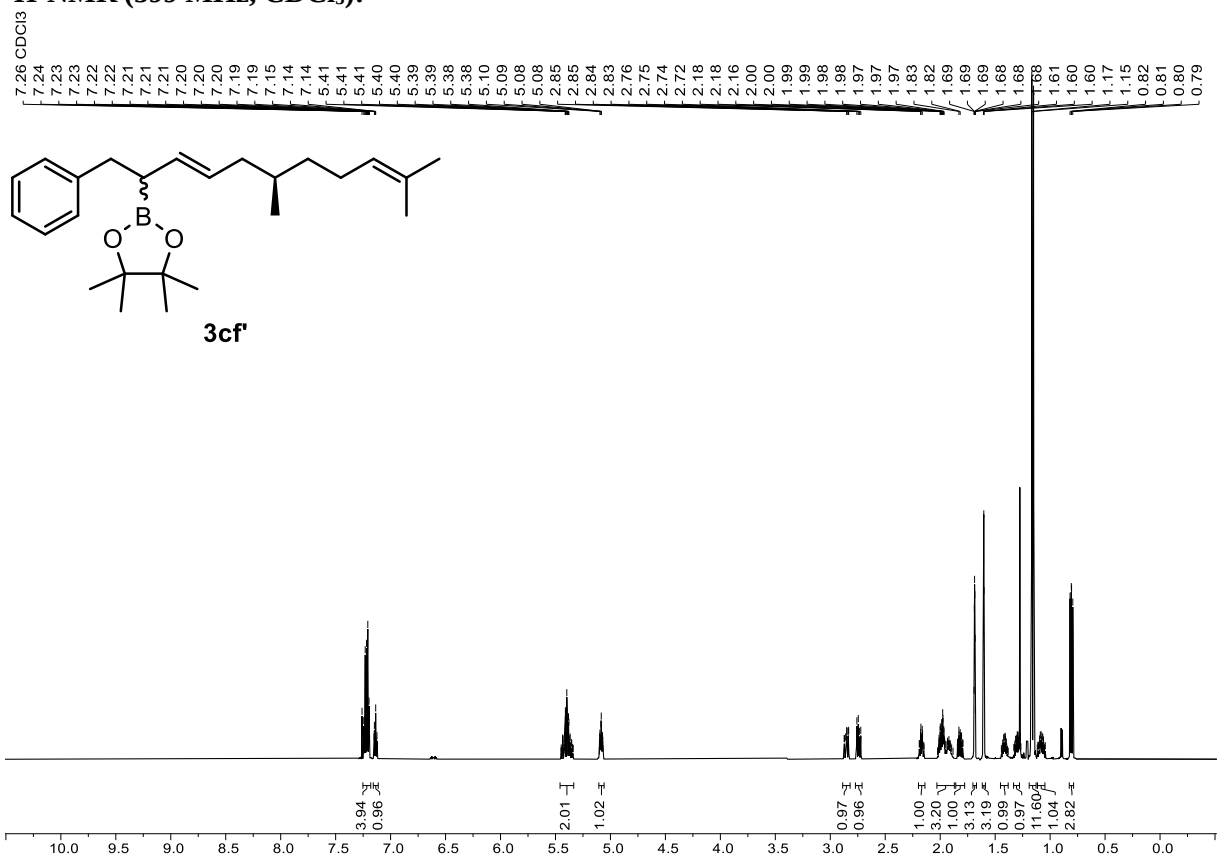

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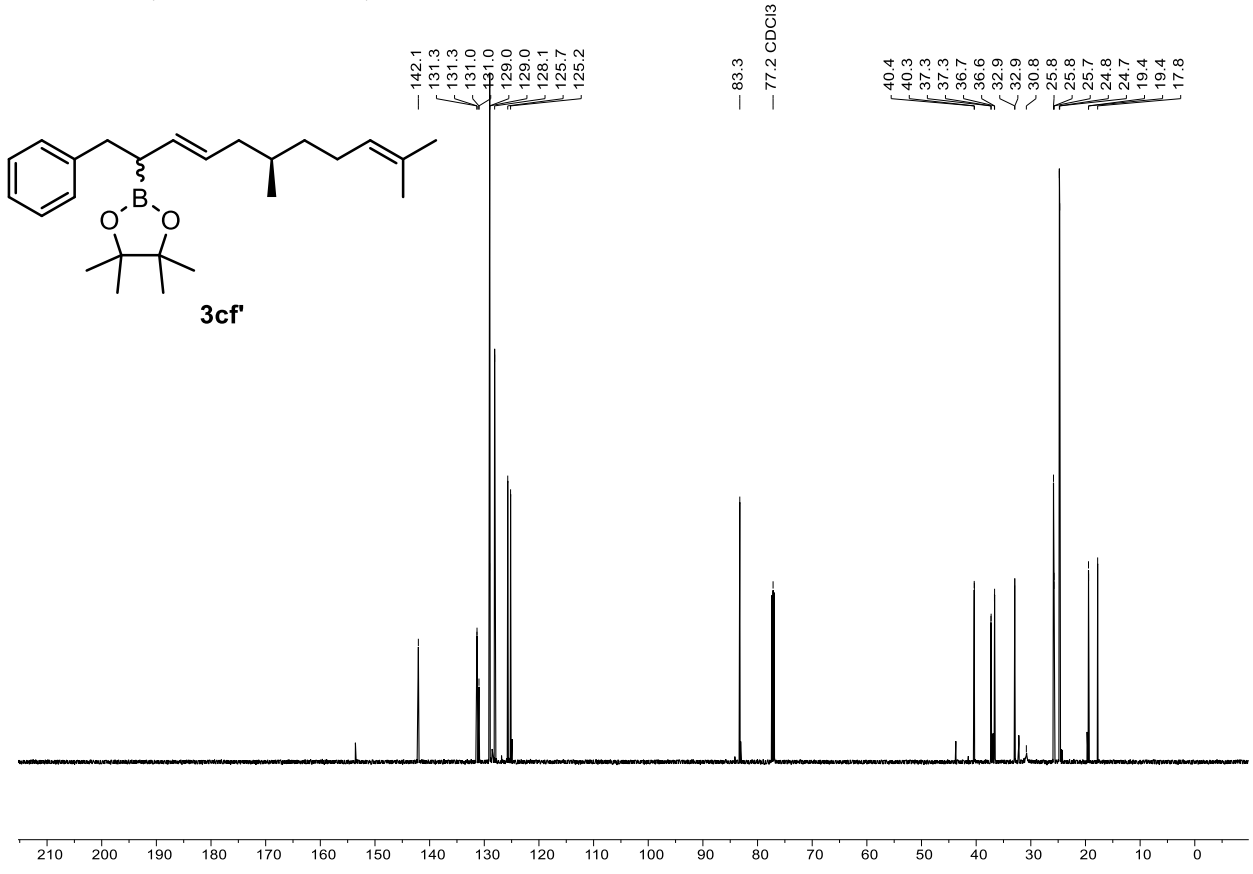

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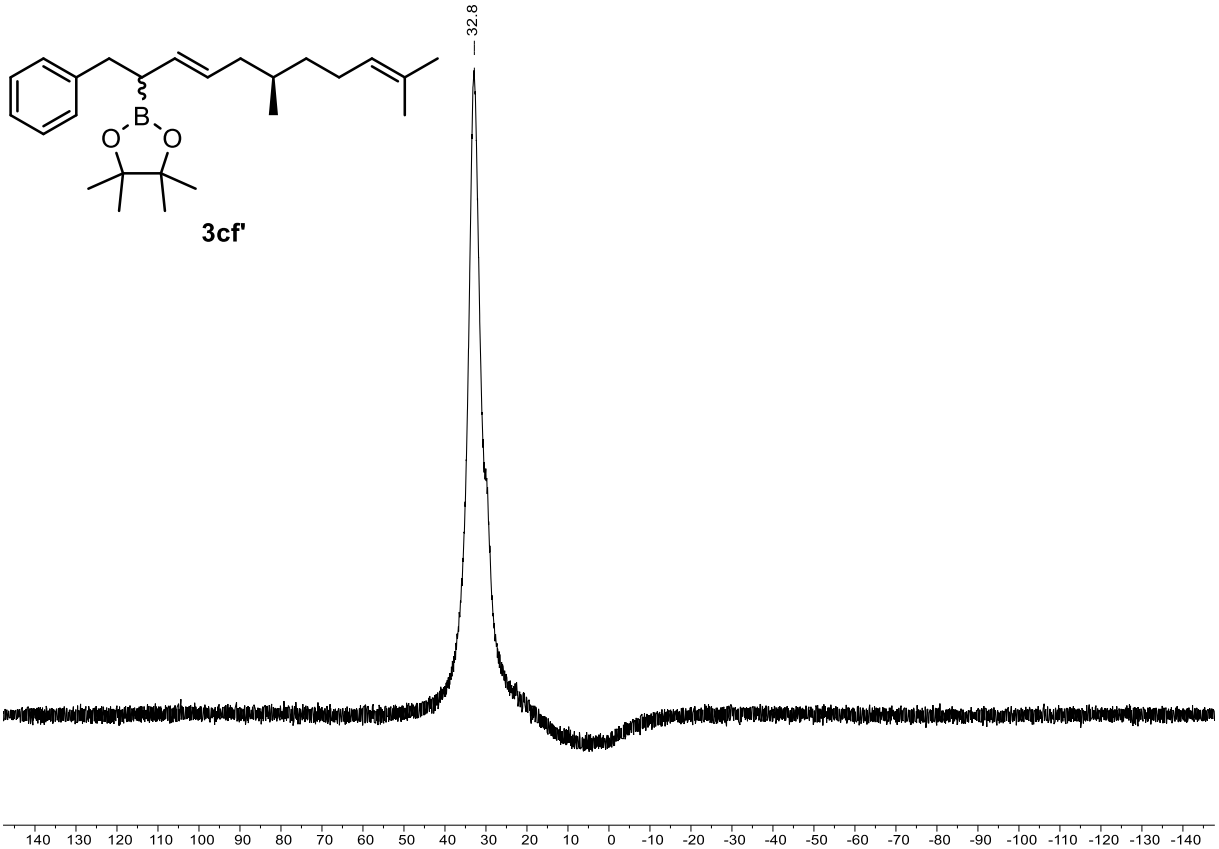
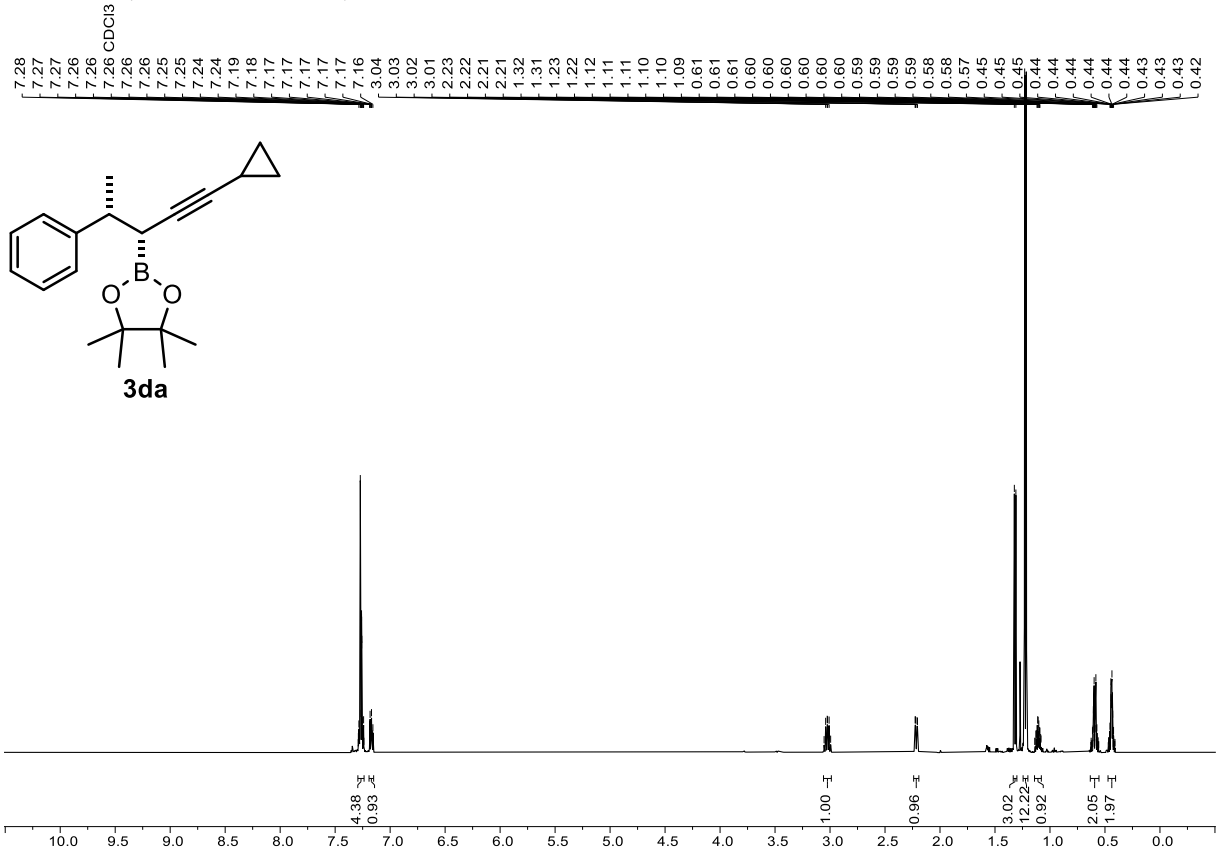
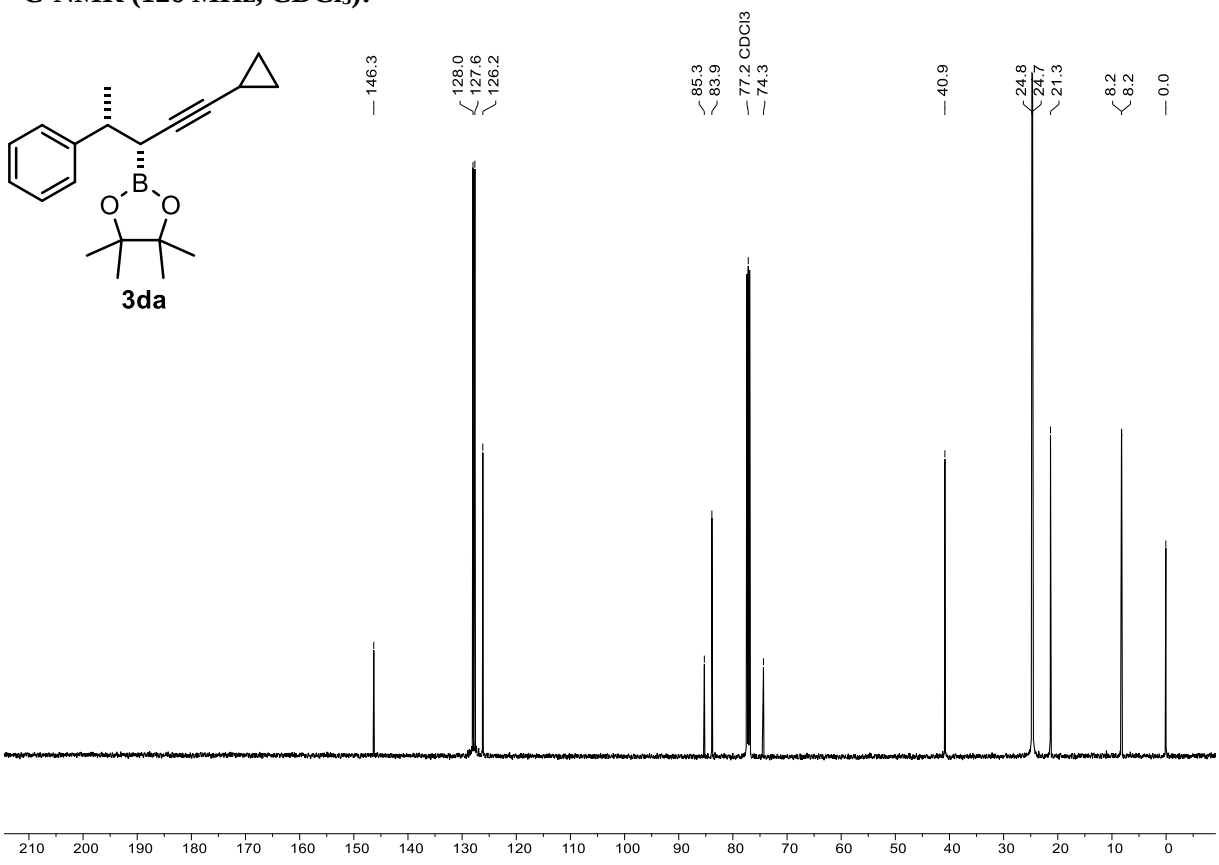


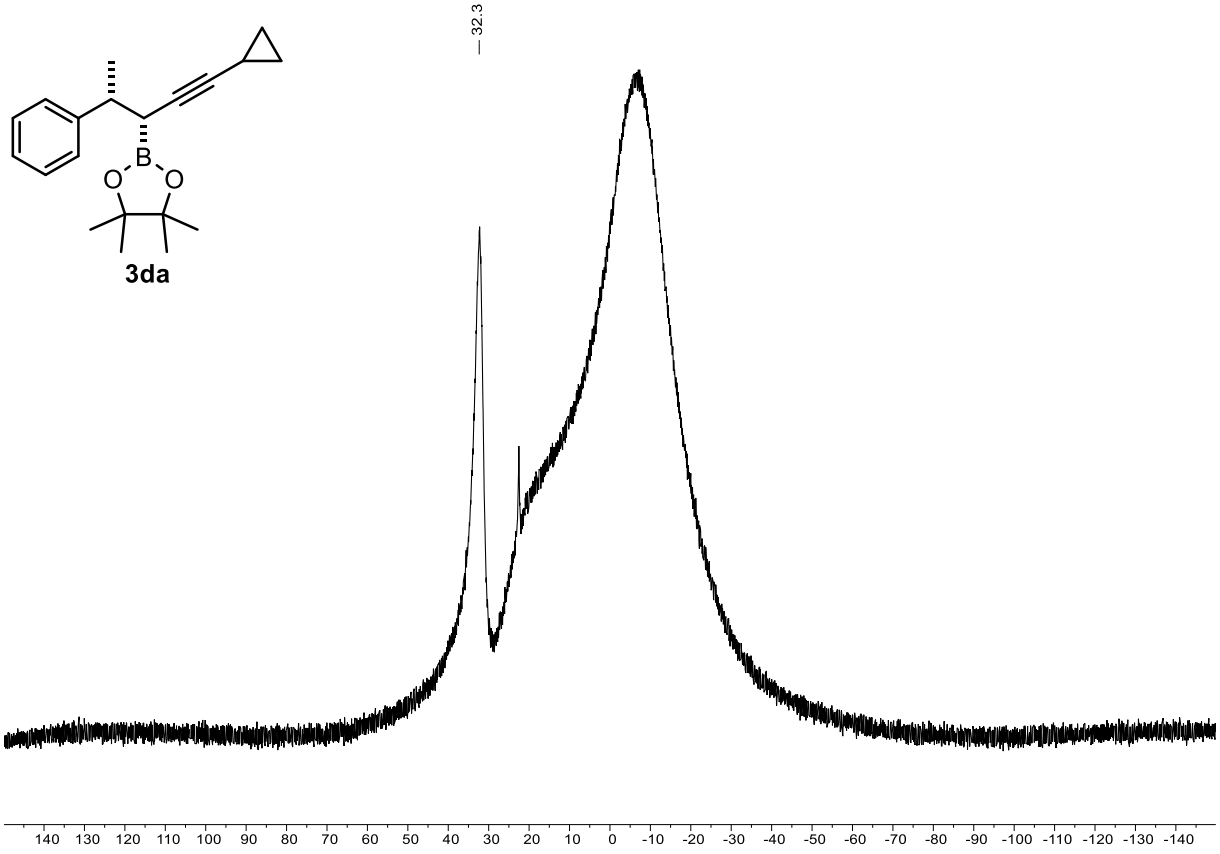
^{1}H-NMR (500 MHz, $CDCl_3$):



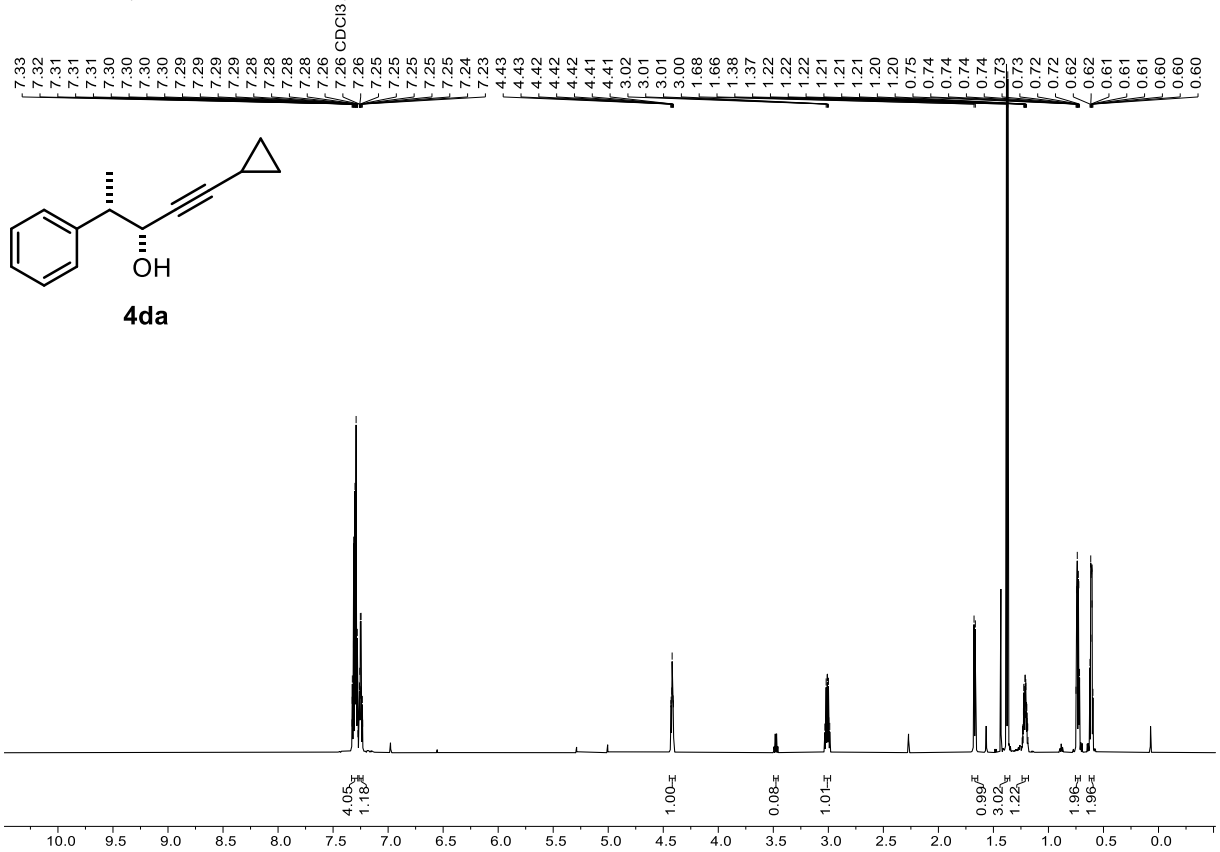
^{13}C-NMR (126 MHz, $CDCl_3$):



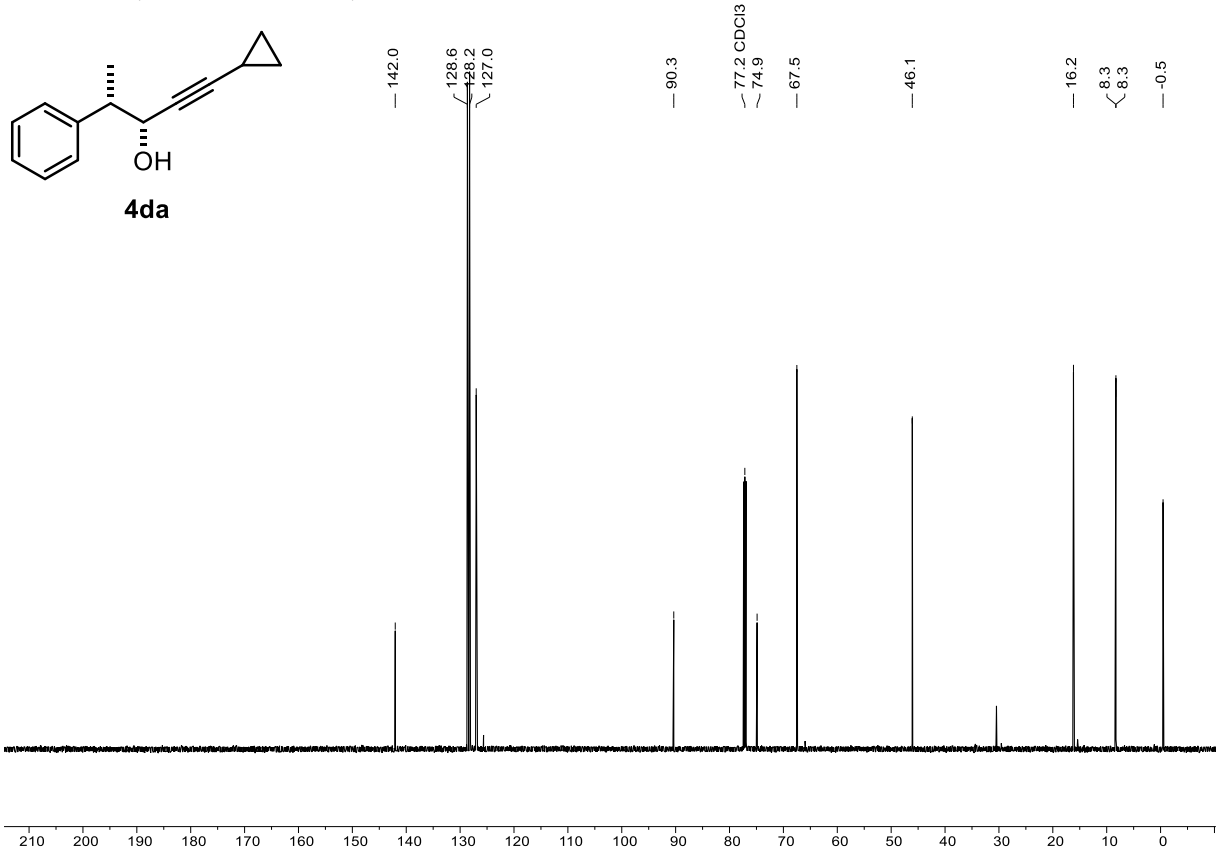
^{11}B-NMR (160 MHz, $CDCl_3$):



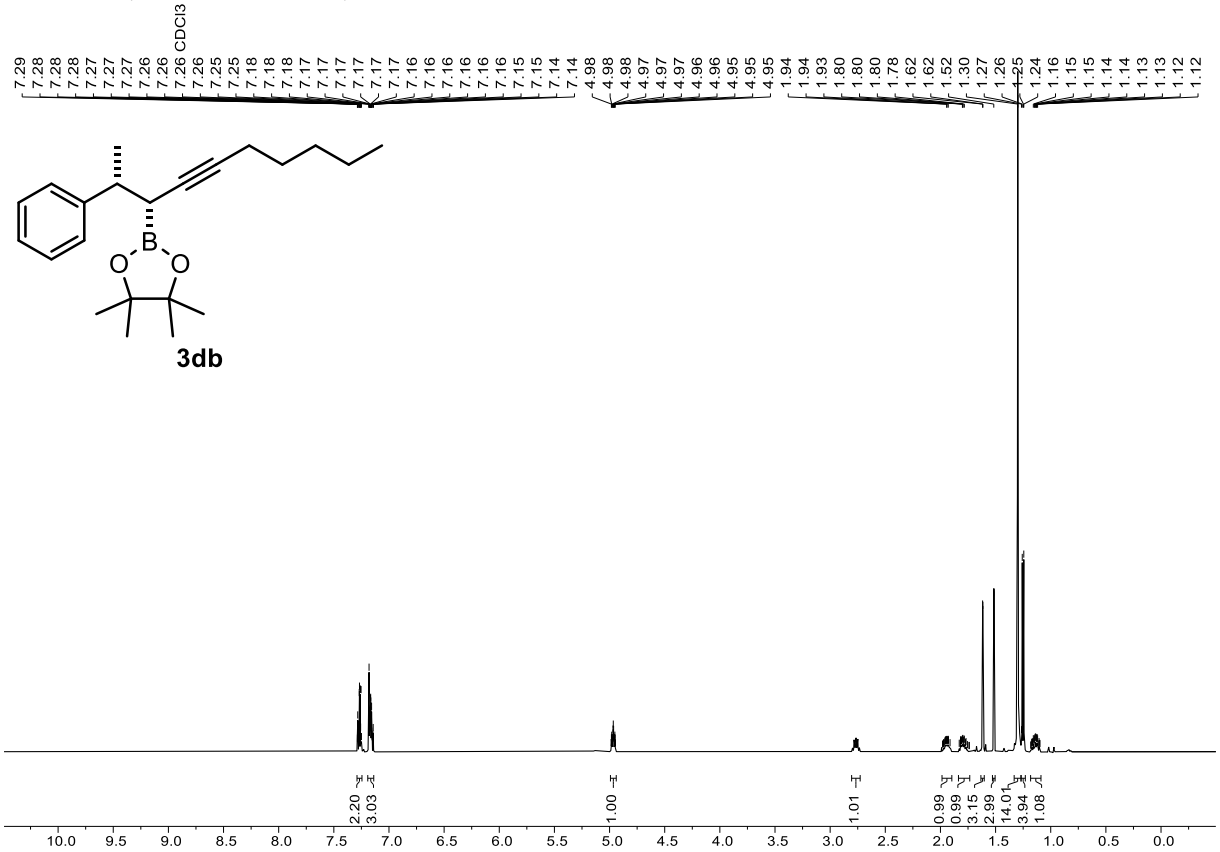
^{1}H-NMR (599 MHz, $CDCl_3$):



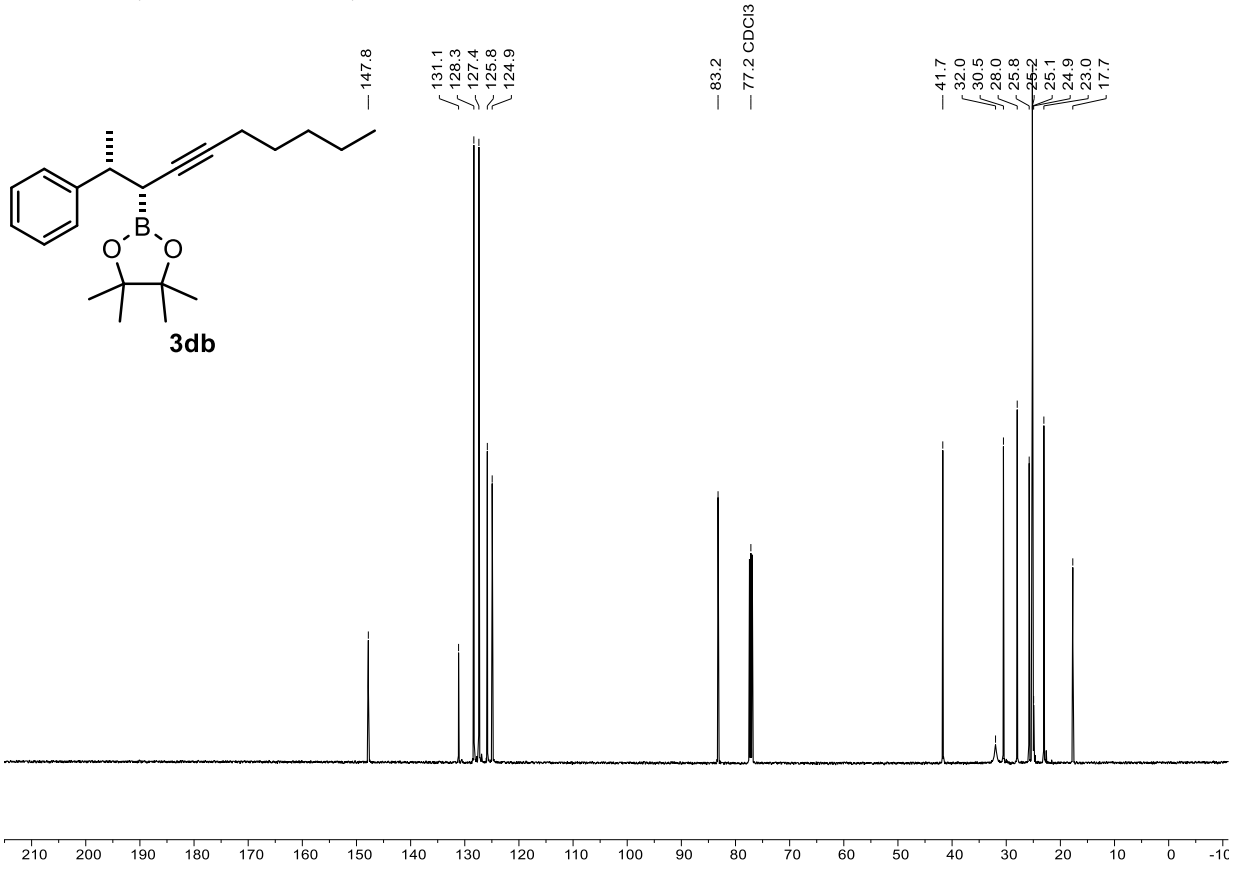
^{13}C-NMR (151 MHz, $CDCl_3$):



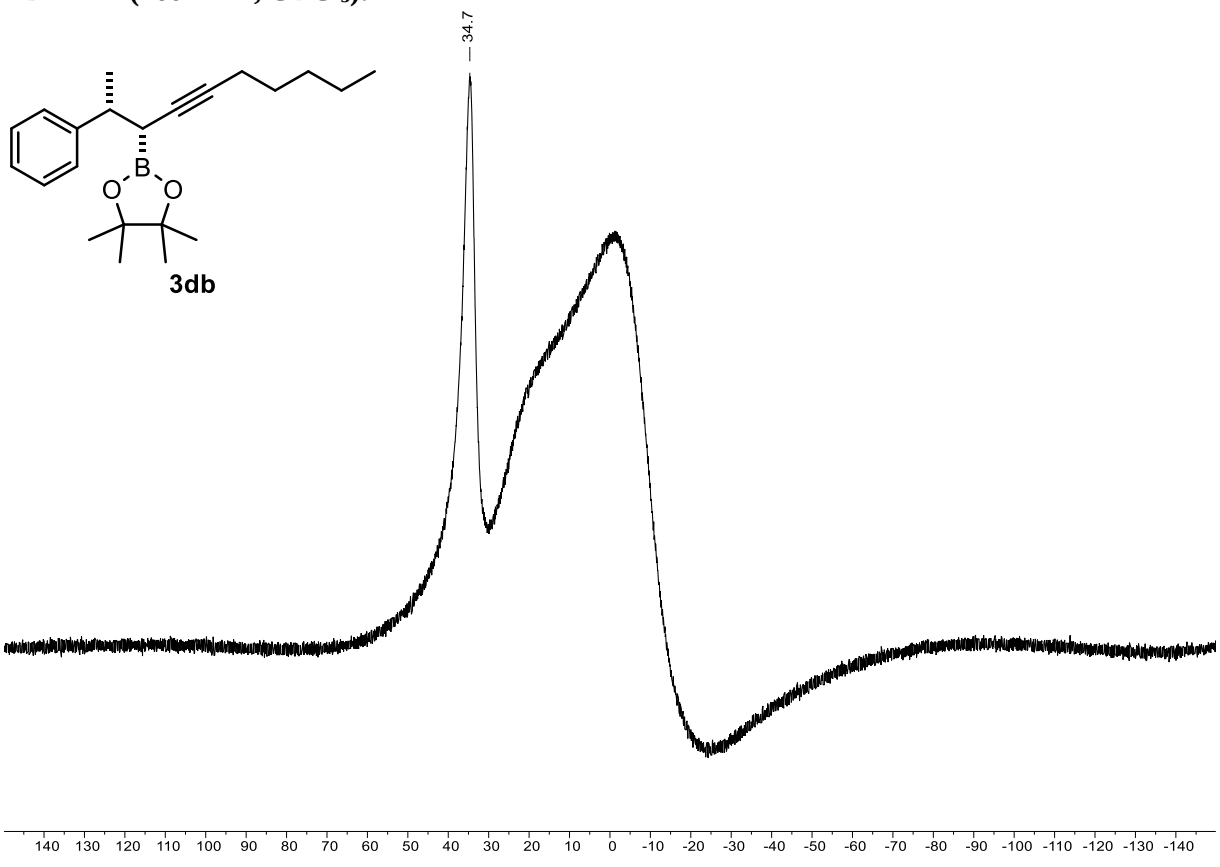
^{1}H-NMR (500 MHz, $CDCl_3$):



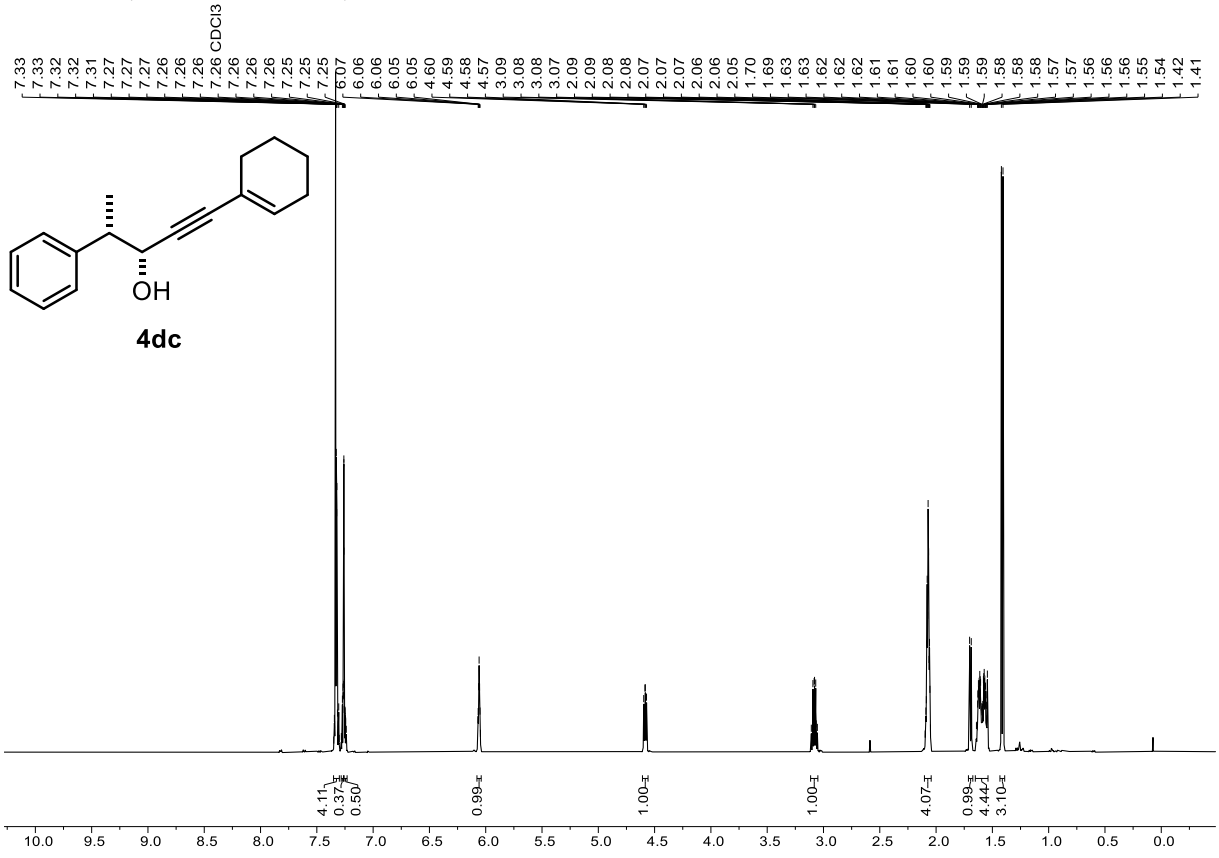
^{13}C-NMR (126 MHz, $CDCl_3$):



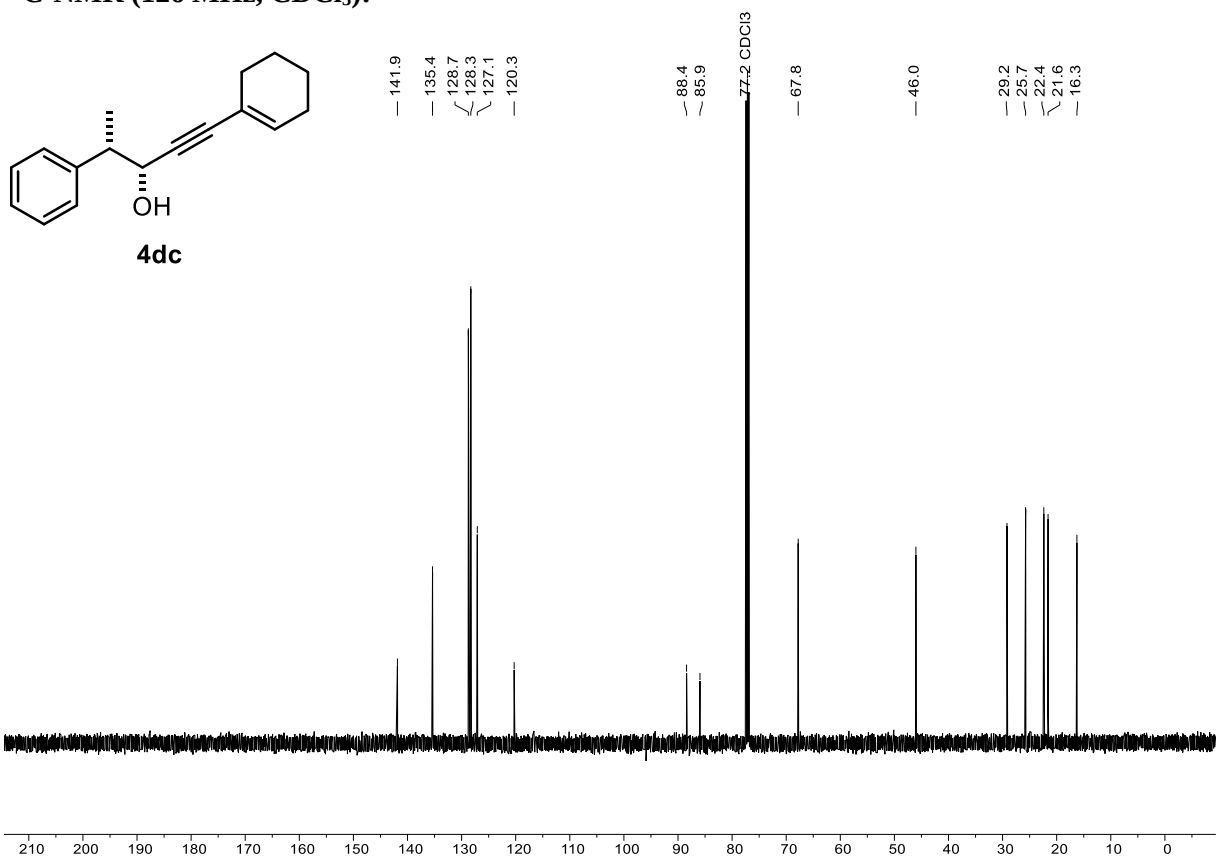
^{11}B-NMR (160 MHz, $CDCl_3$):



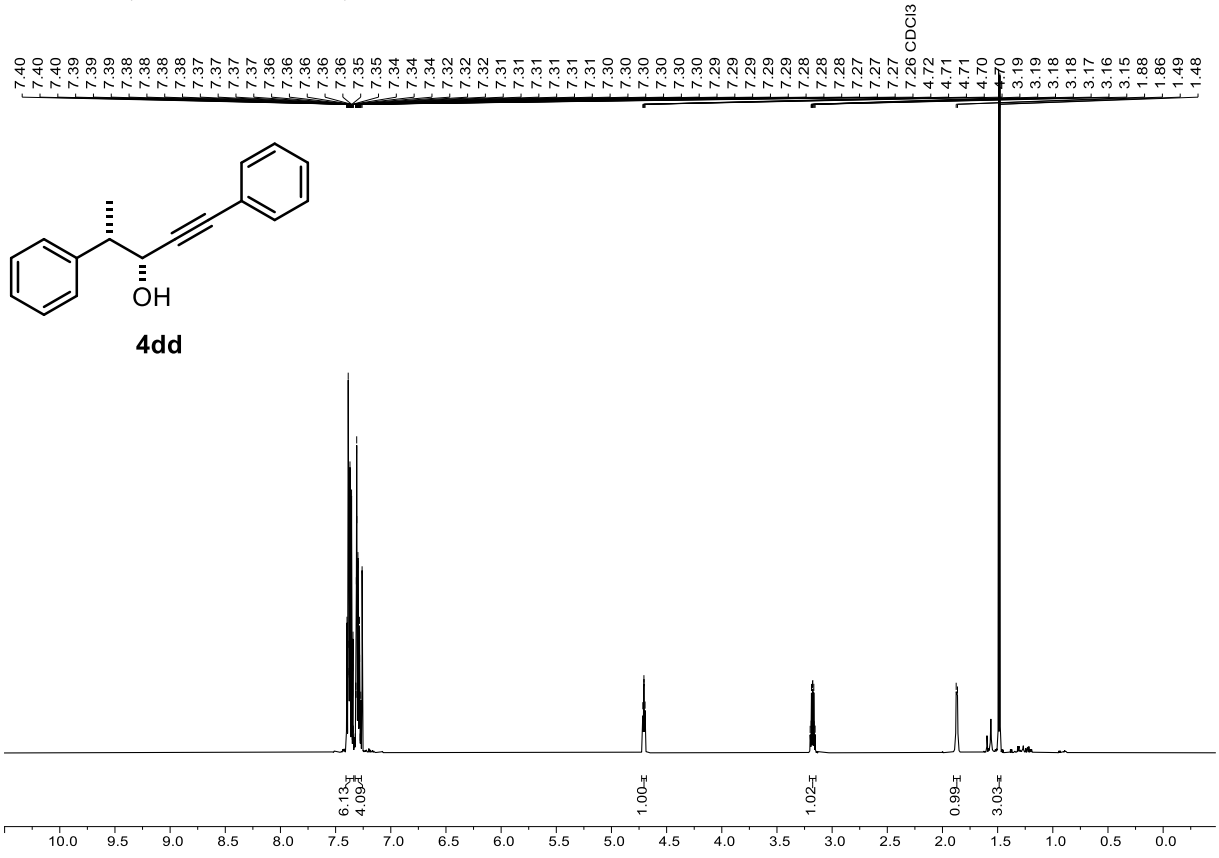
^{1}H-NMR (500 MHz, $CDCl_3$):



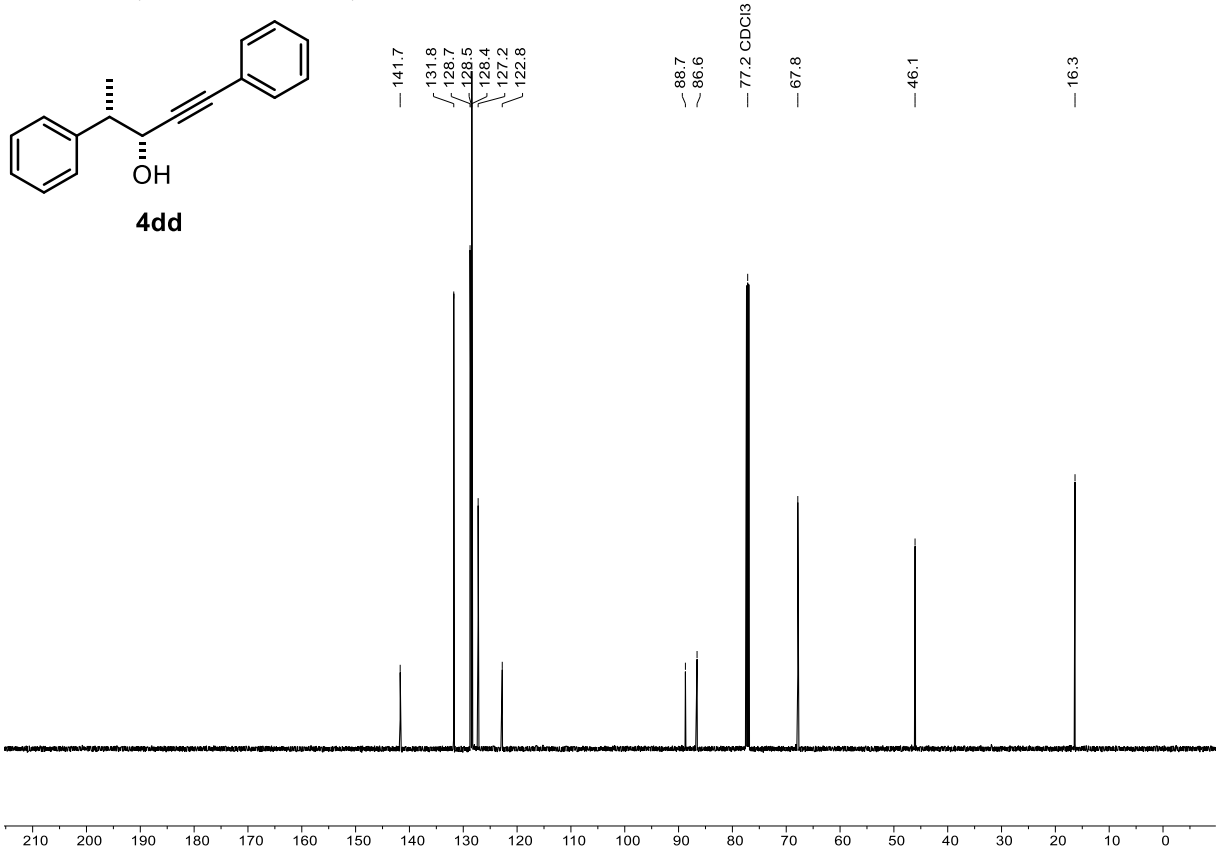
^{13}C-NMR (126 MHz, $CDCl_3$):



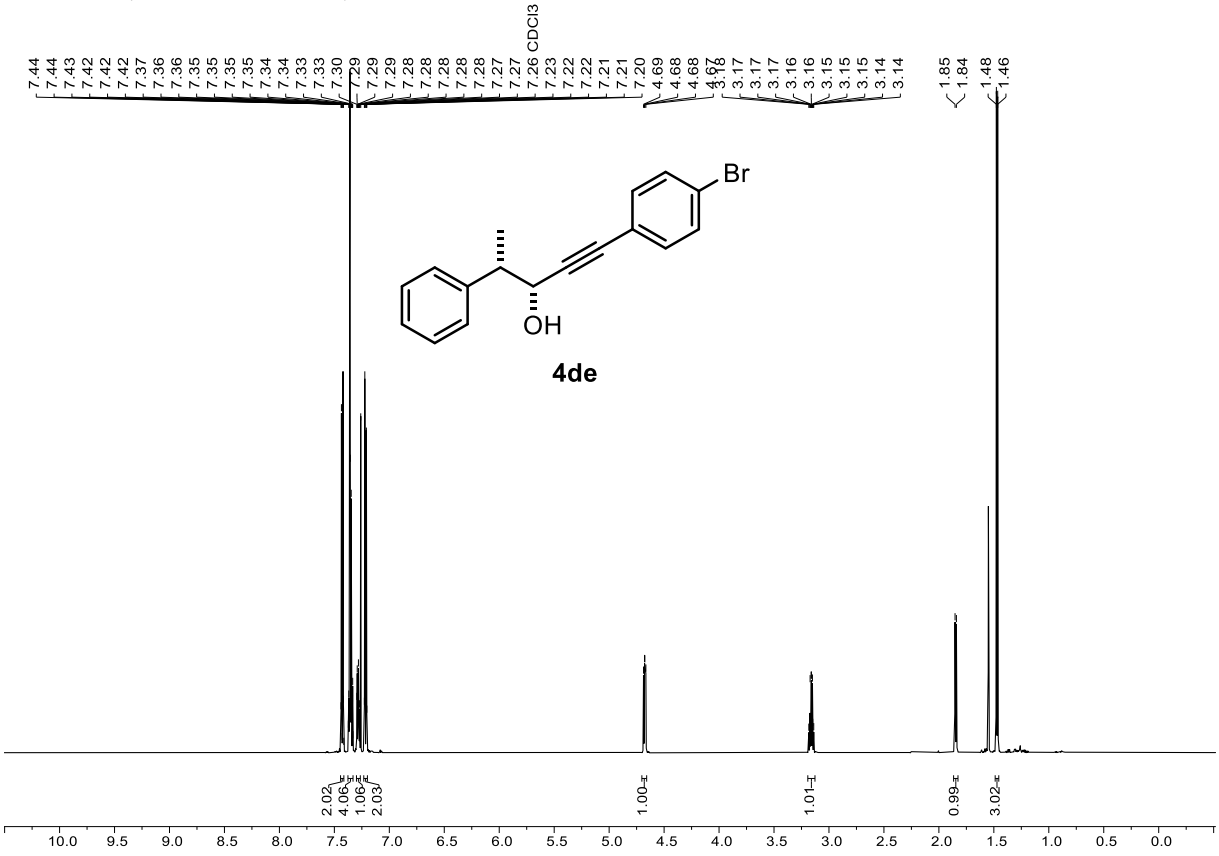
^{1}H-NMR (599 MHz, $CDCl_3$):



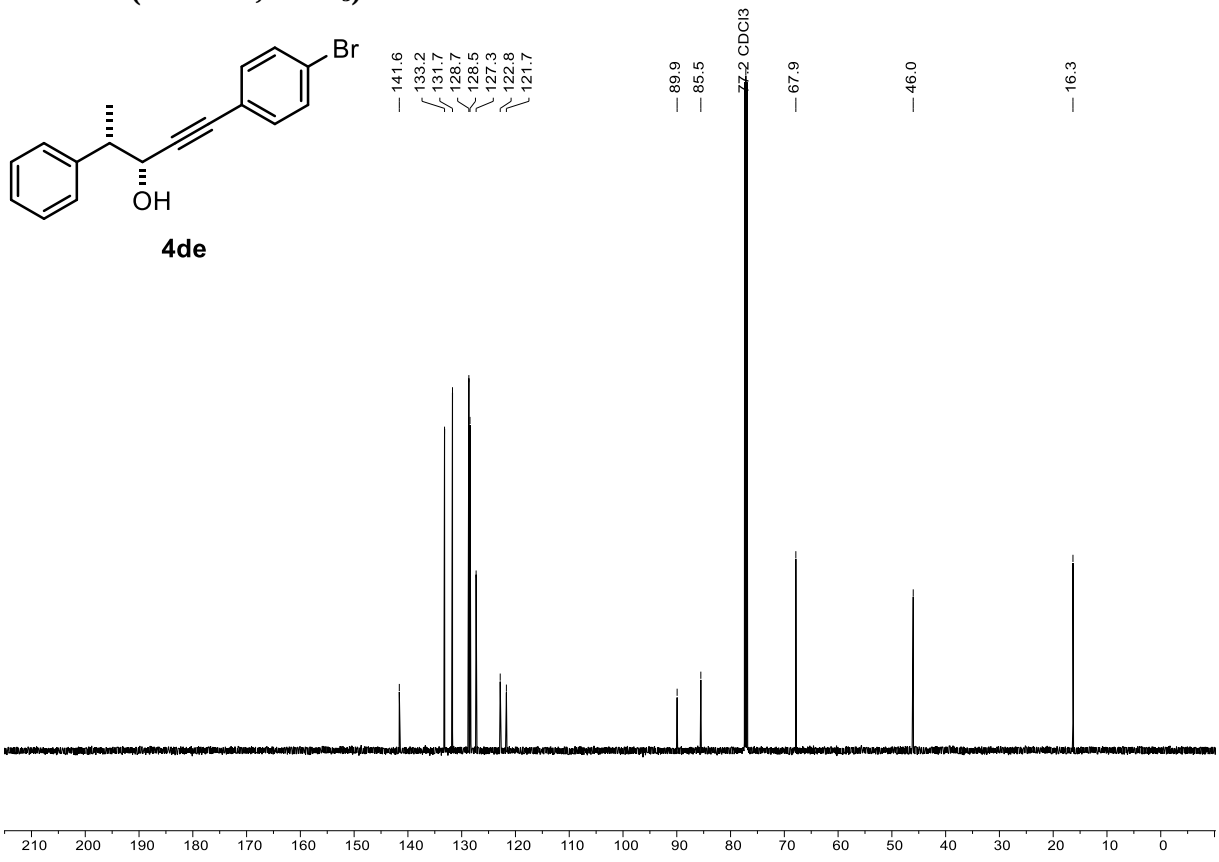
^{13}C-NMR (151 MHz, $CDCl_3$):



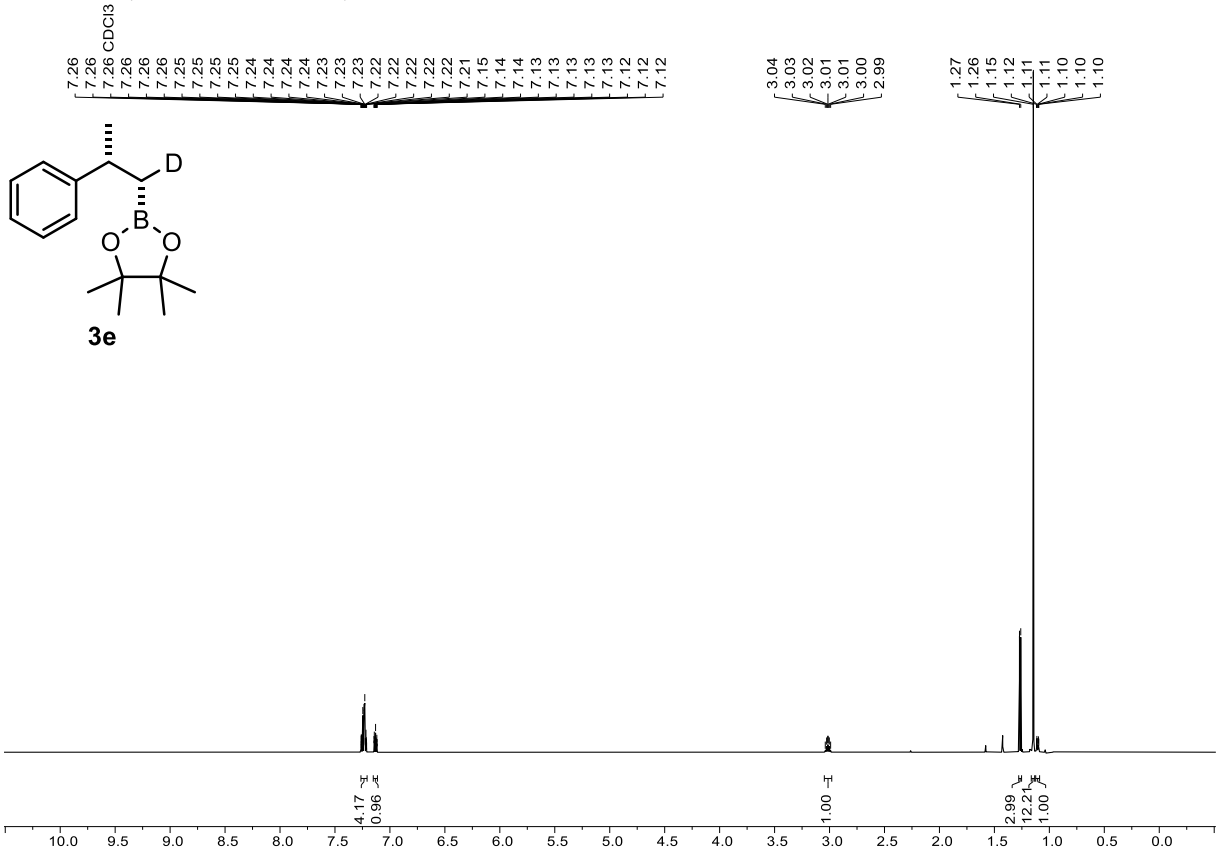
^{1}H-NMR (599 MHz, $CDCl_3$):



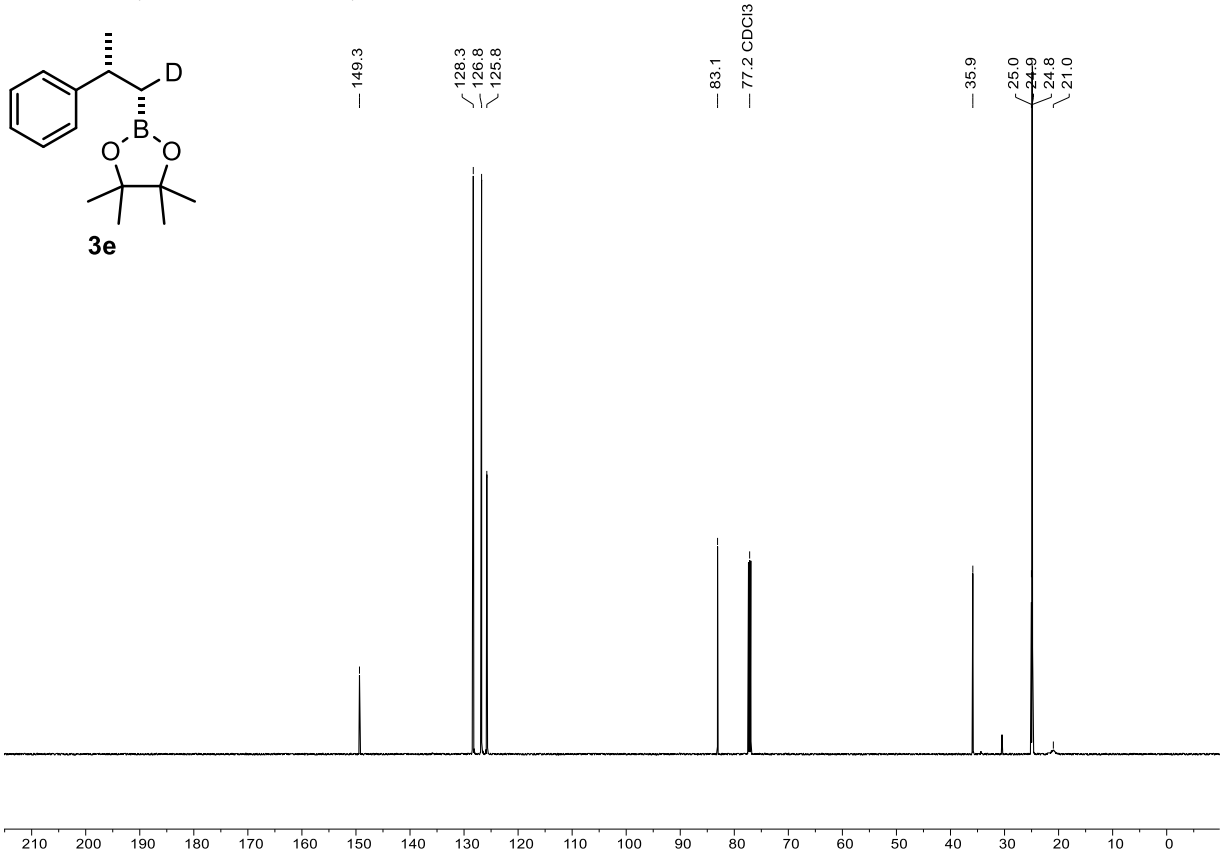
^{13}C-NMR (151 MHz, $CDCl_3$):



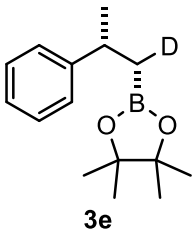
^{1}H-NMR (599 MHz, $CDCl_3$):



^{13}C-NMR (151 MHz, $CDCl_3$):

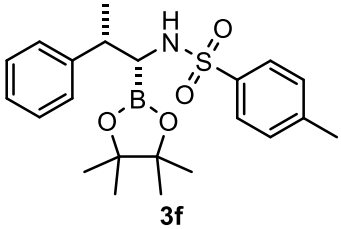


^{11}B-NMR (192 MHz, $CDCl_3$):



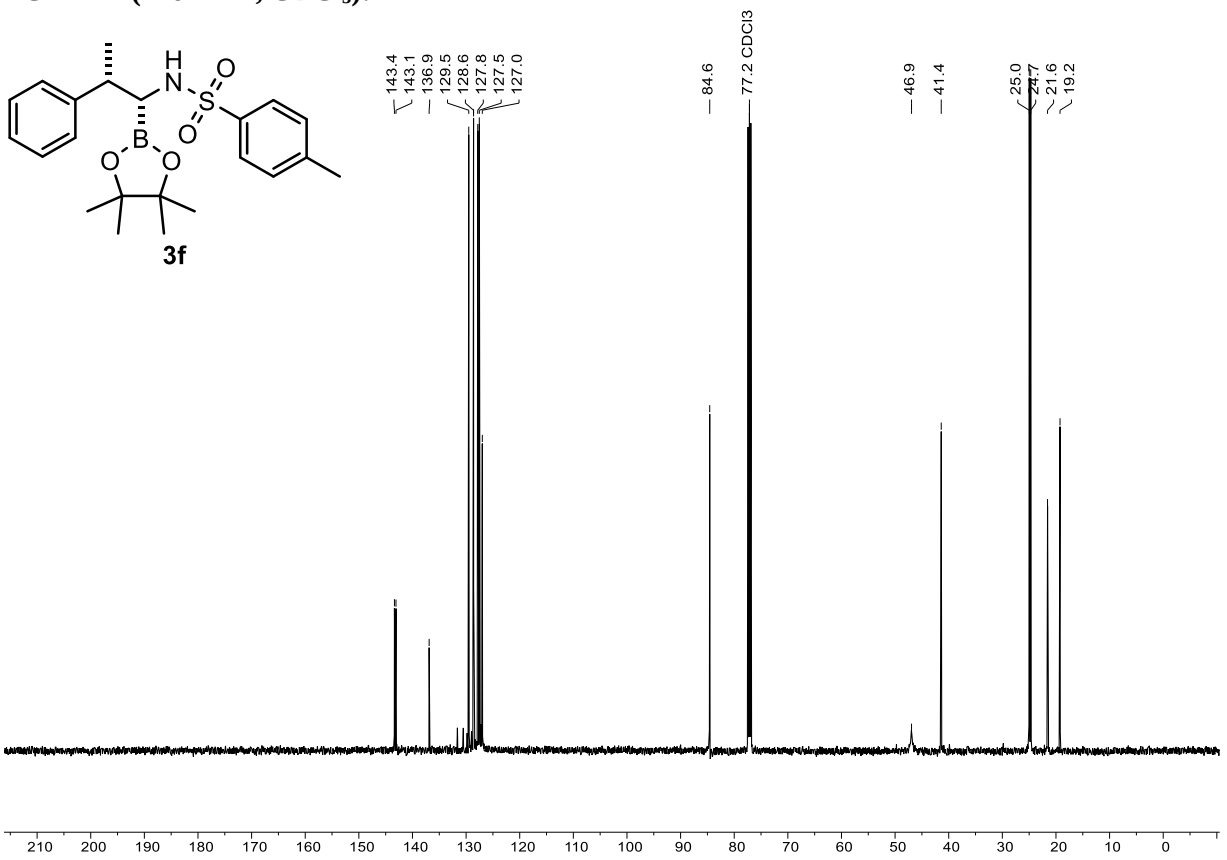
3e

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

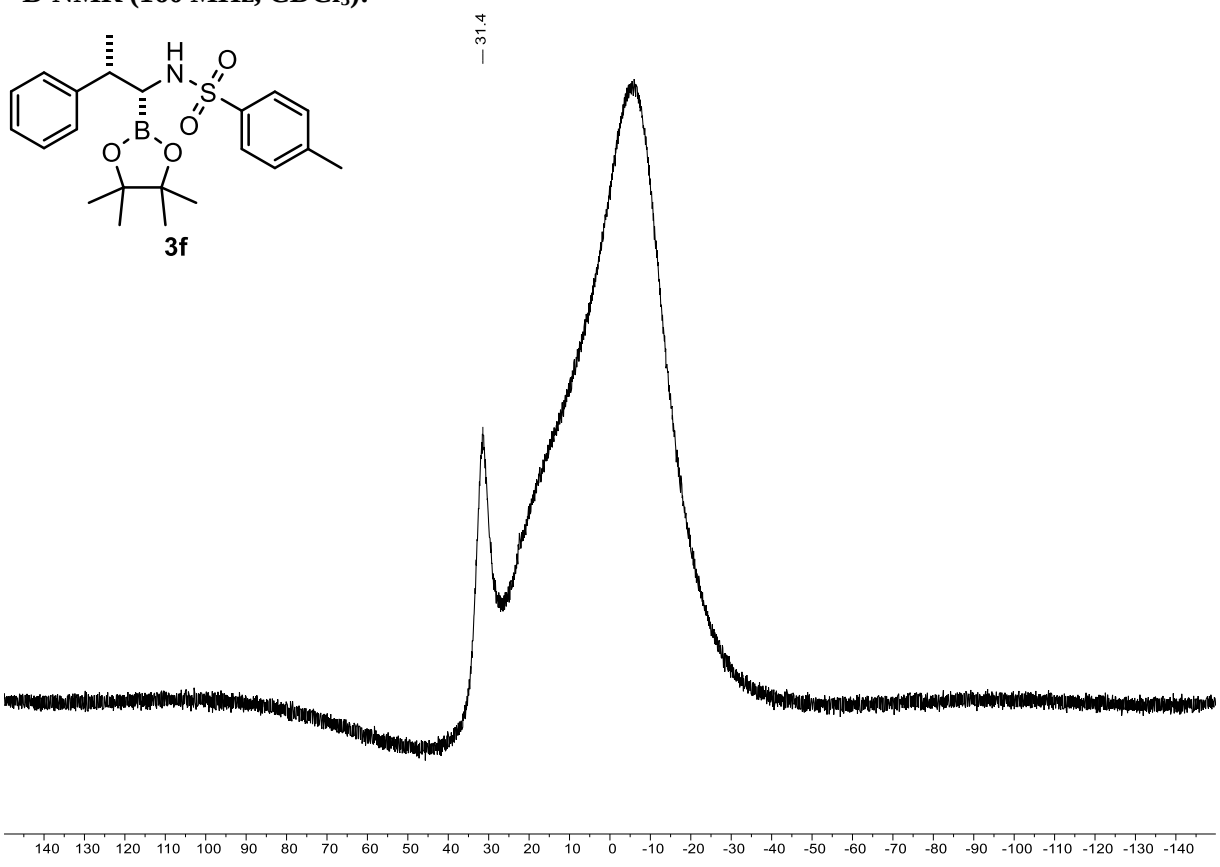


3f

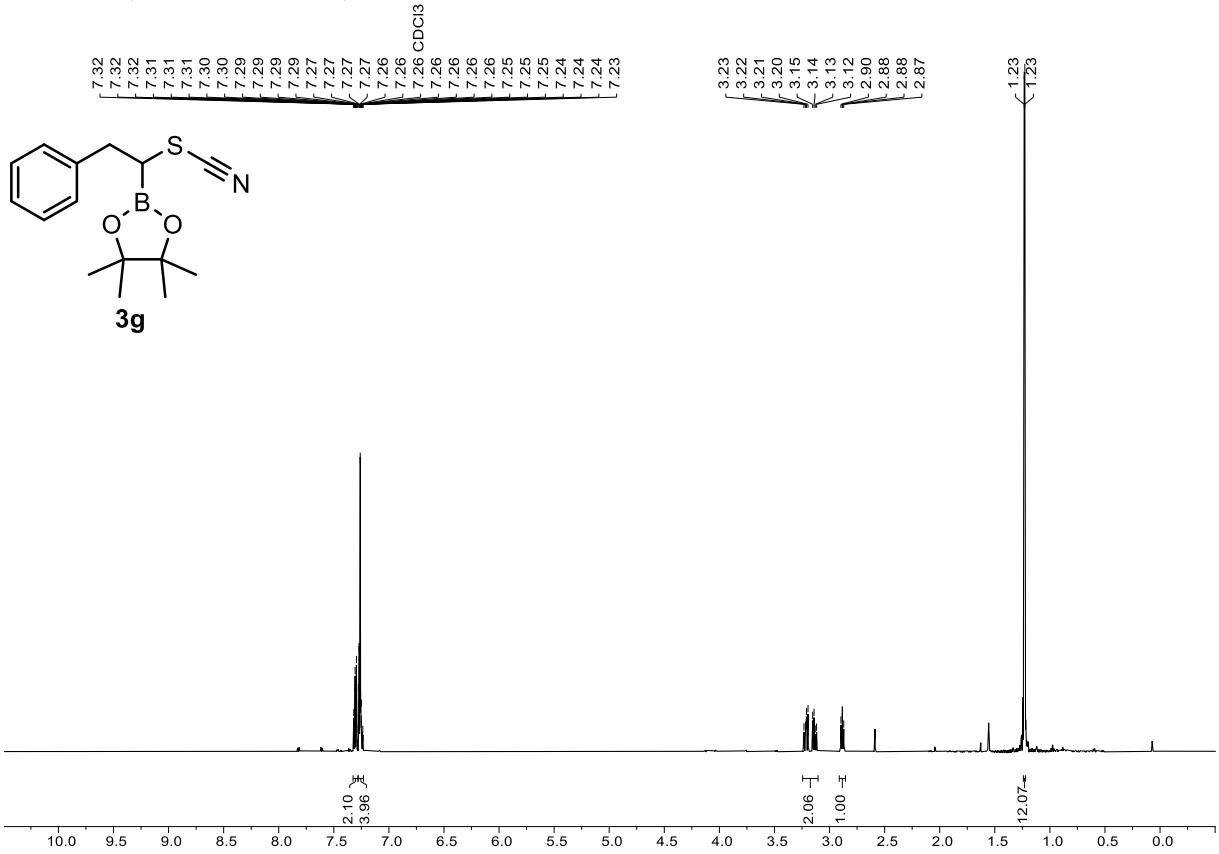
^{13}C-NMR (126 MHz, $CDCl_3$):



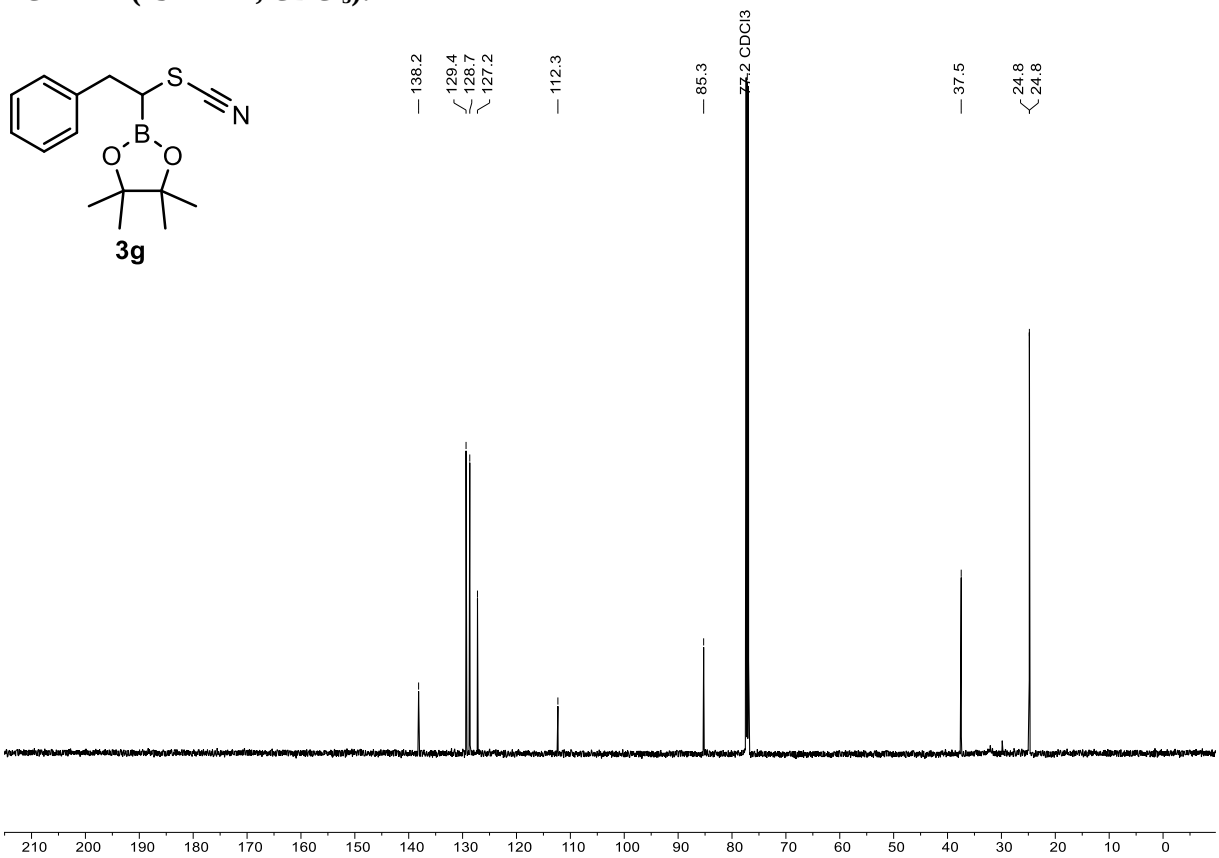
^{11}B-NMR (160 MHz, $CDCl_3$):



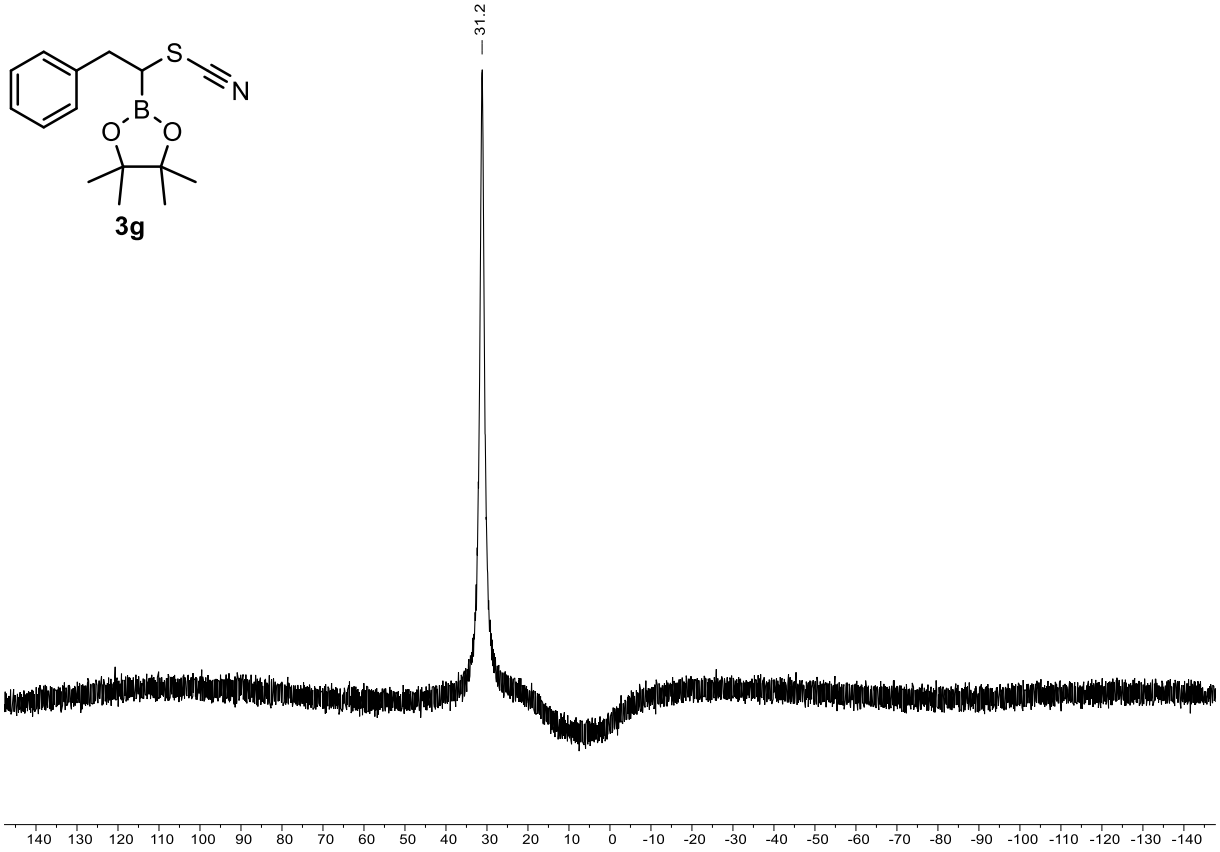
^{1}H-NMR (599 MHz, $CDCl_3$):



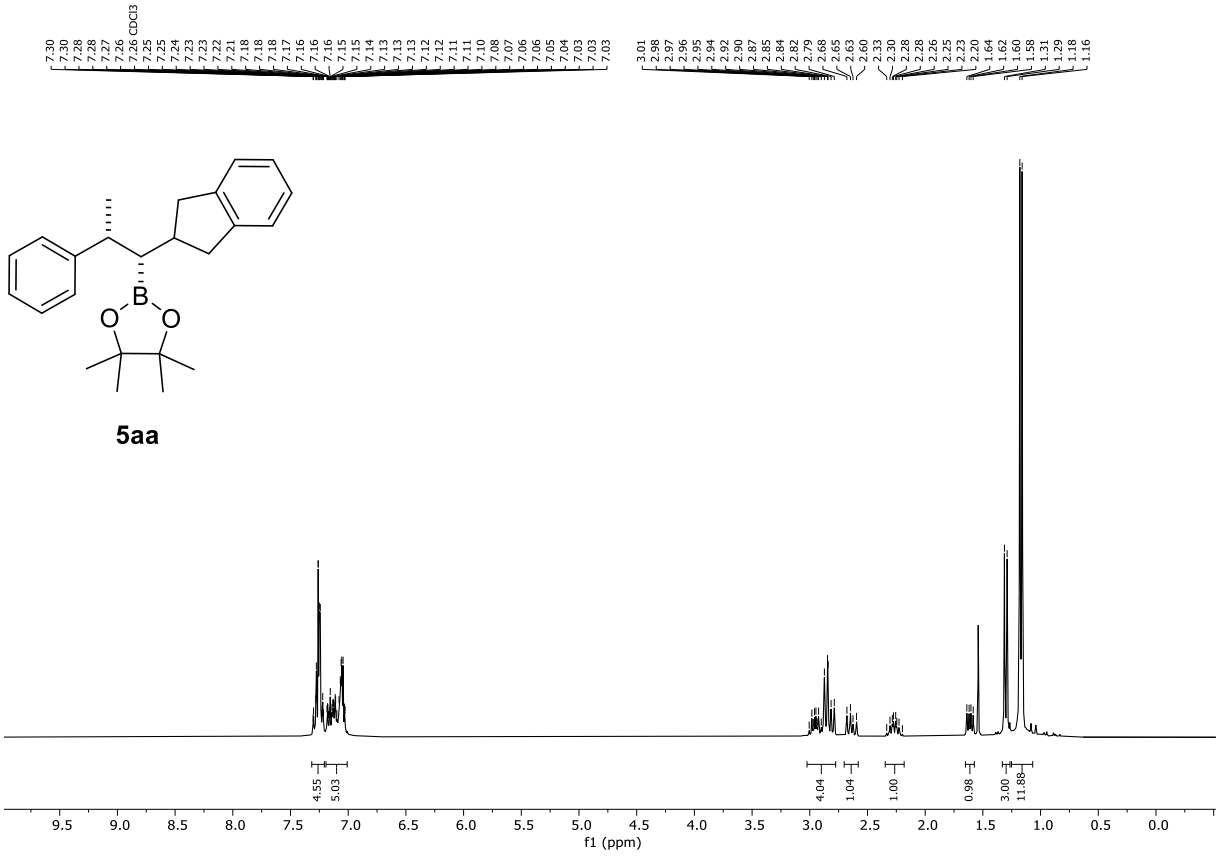
^{13}C-NMR (151 MHz, $CDCl_3$):



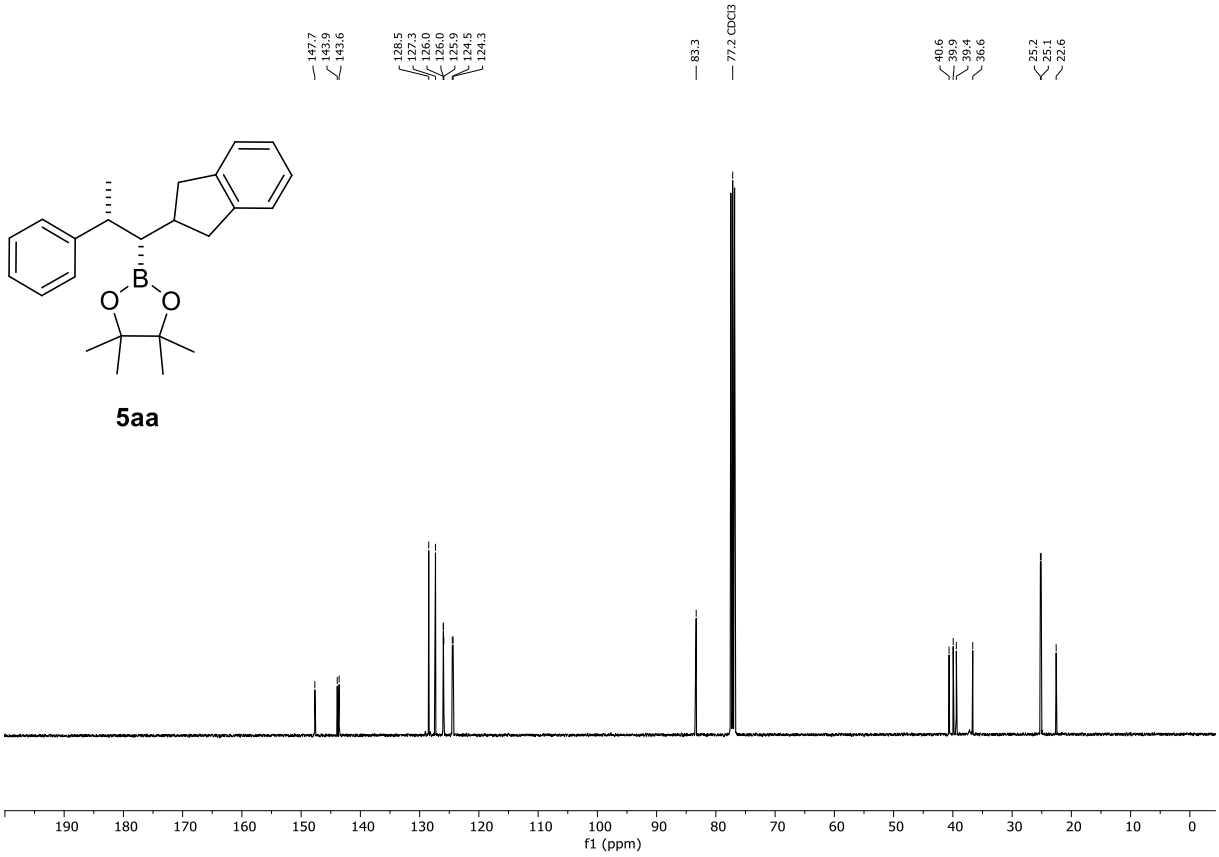
^{11}B-NMR (192 MHz, $CDCl_3$):



^{1}H-NMR (400 MHz, $CDCl_3$):

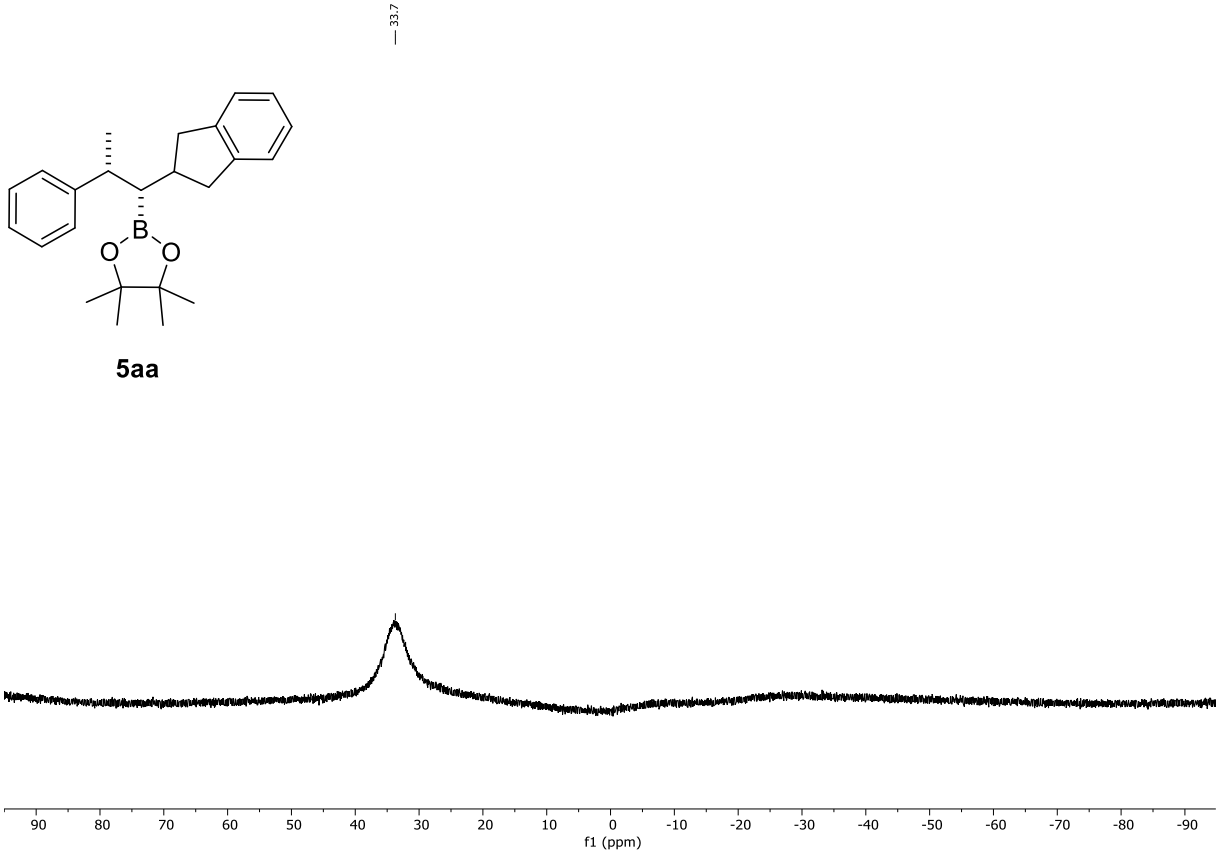


^{13}C-NMR (101 MHz, $CDCl_3$):



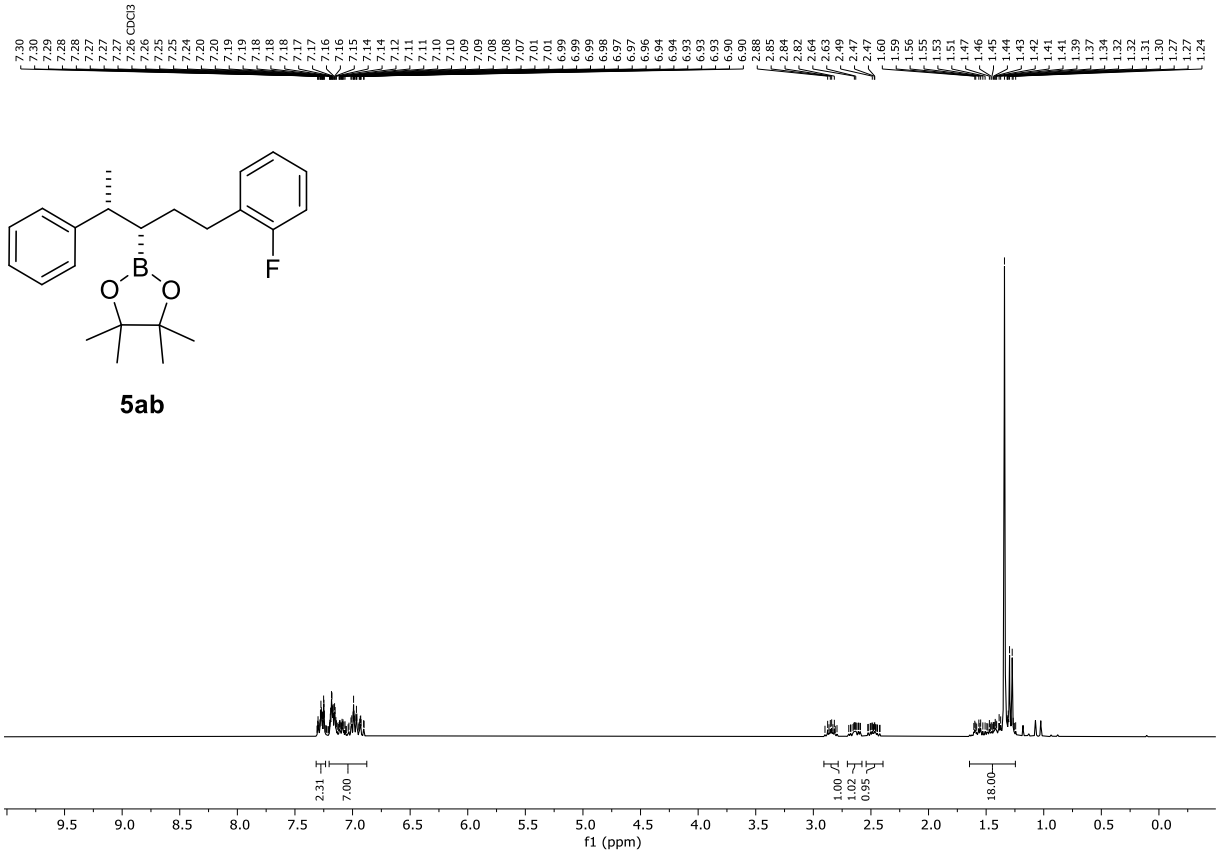
5aa

^{11}B NMR (128 MHz, $CDCl_3$):

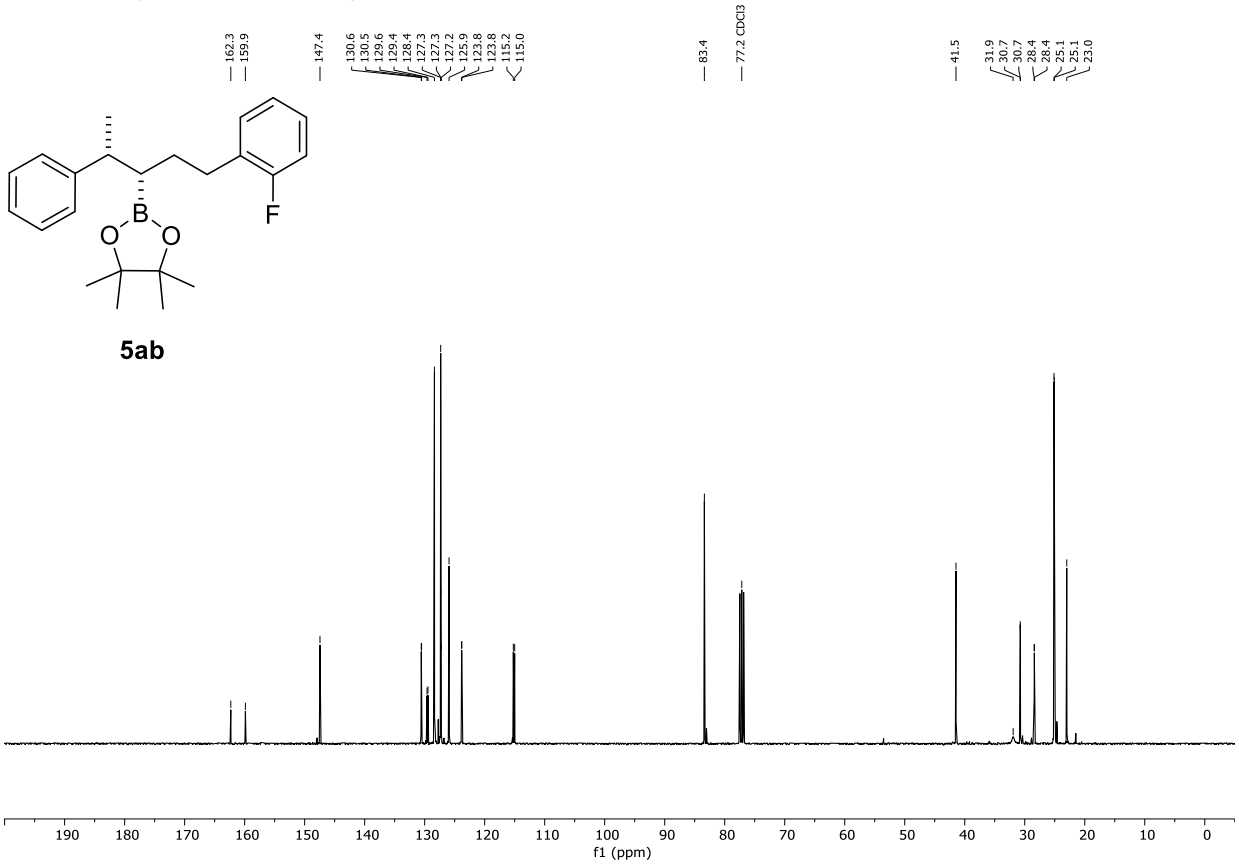


5aa

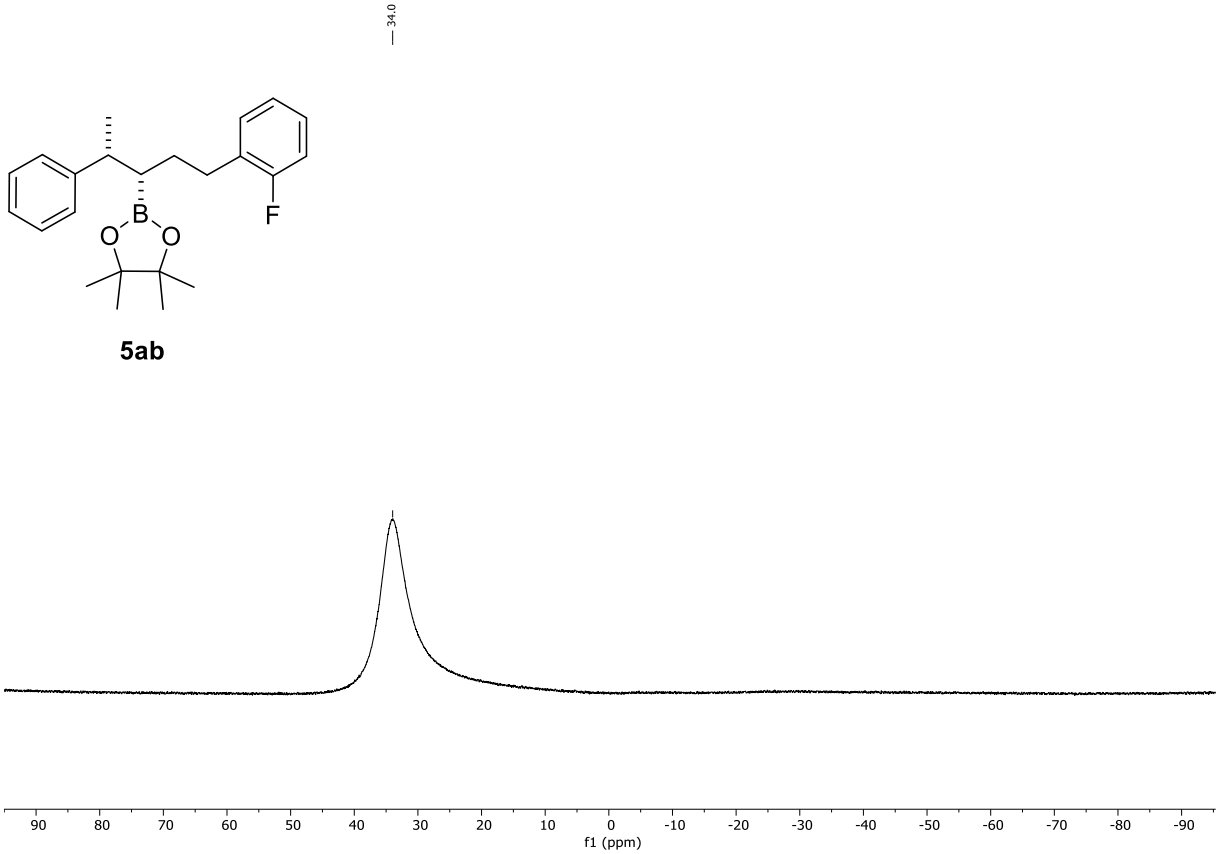
^{1}H-NMR (300 MHz, $CDCl_3$):



^{13}C-NMR (101 MHz, $CDCl_3$):

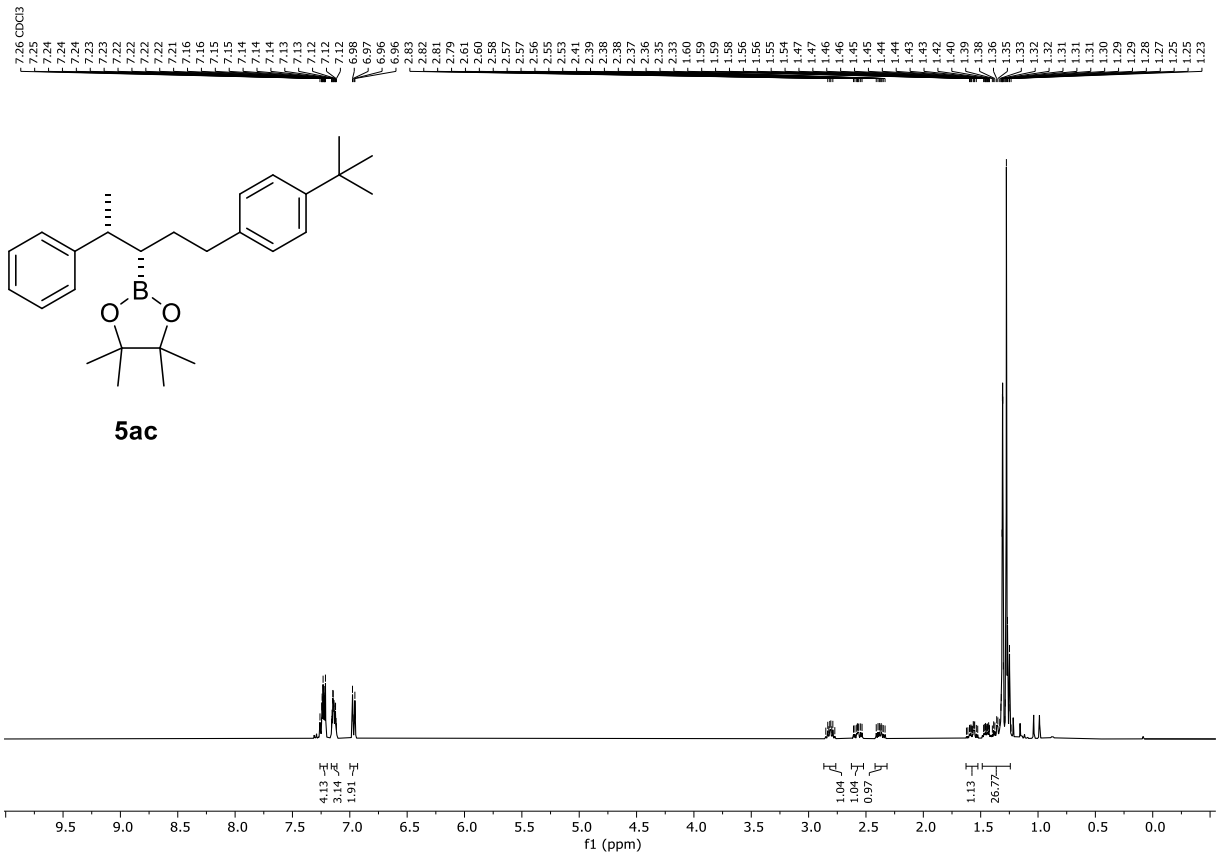


^{11}B NMR (128 MHz, $CDCl_3$):



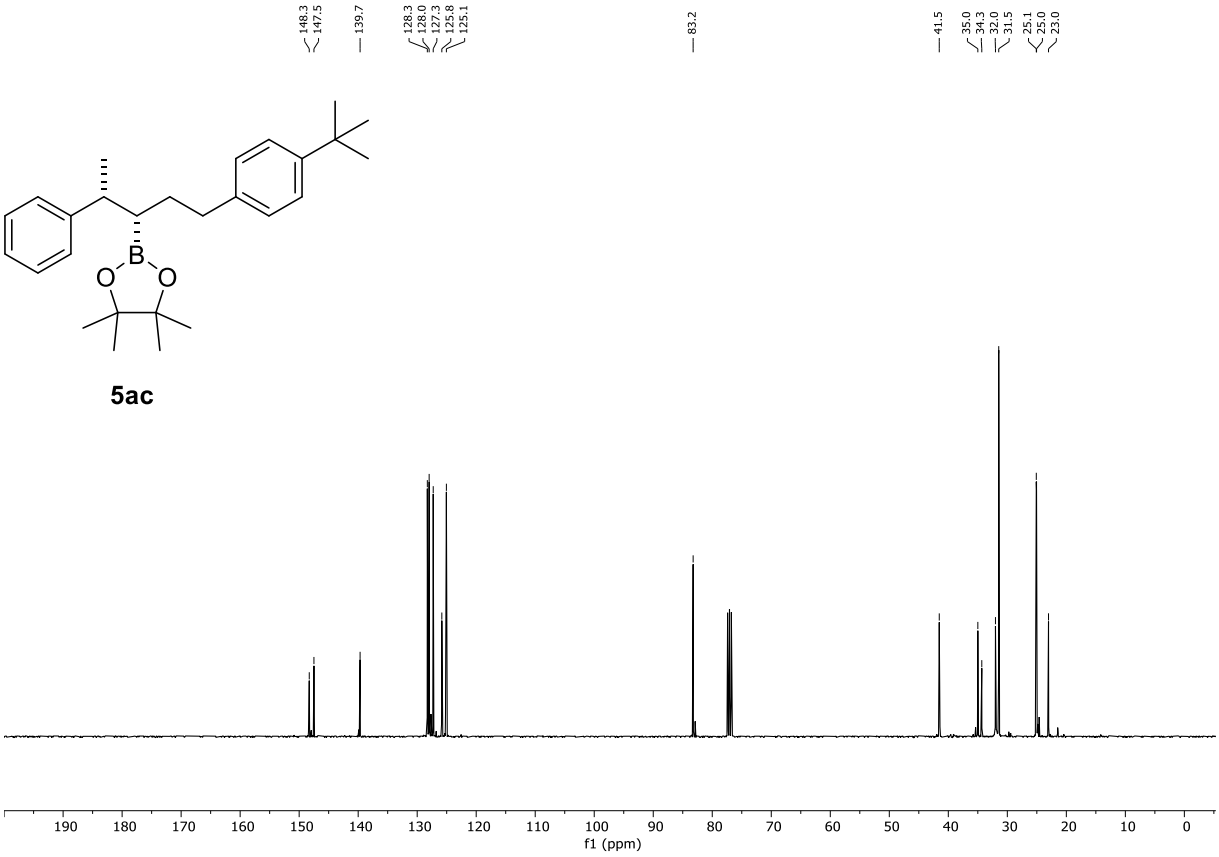
5ab

^{1}H-NMR (400 MHz, $CDCl_3$):



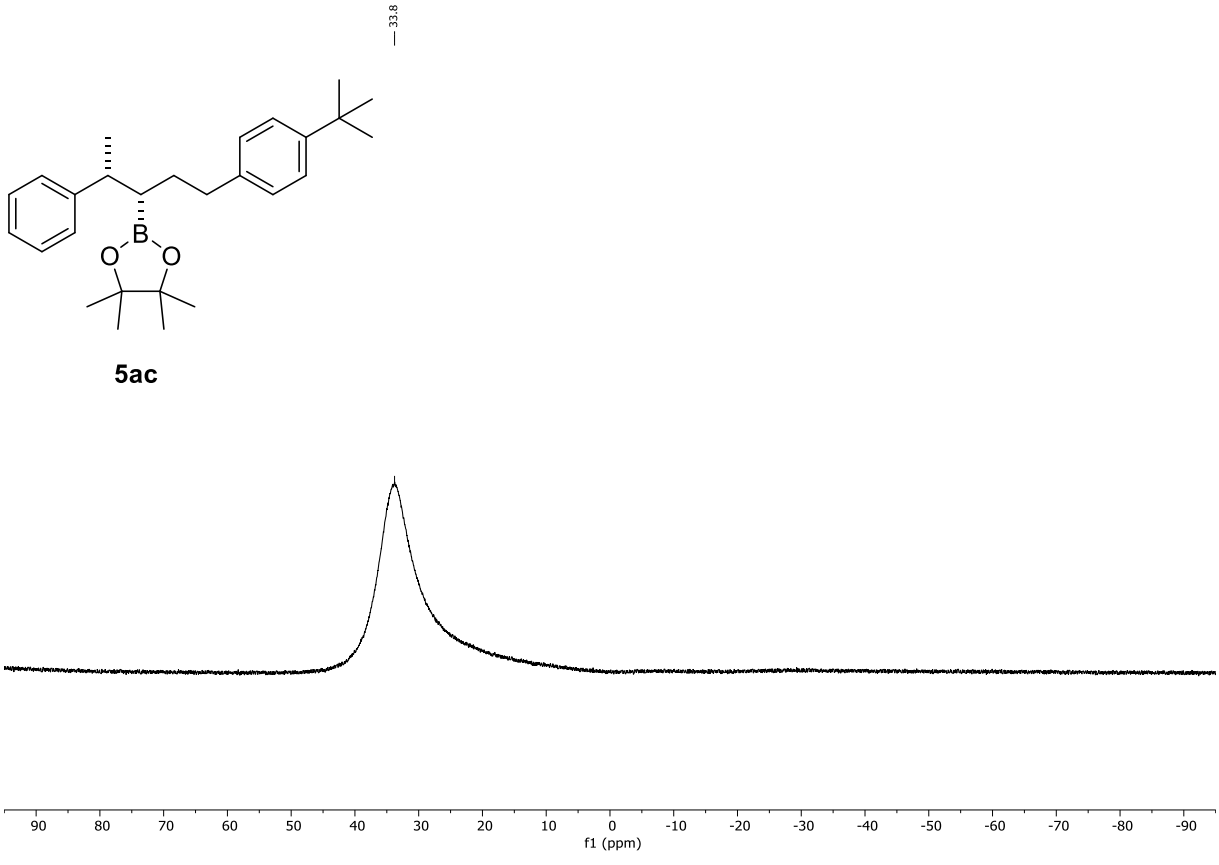
5ac

^{13}C-NMR (101 MHz, $CDCl_3$):



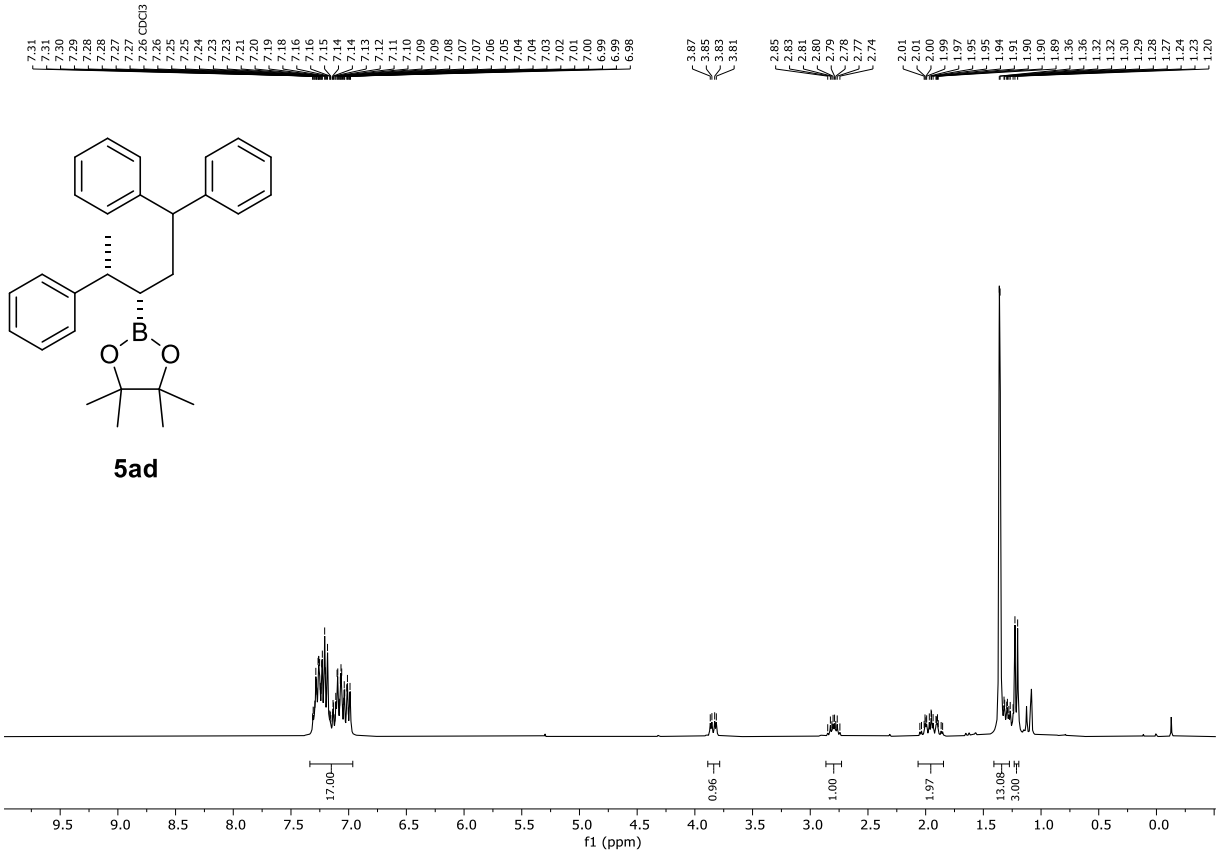
5ac

^{11}B NMR (128 MHz, $CDCl_3$):



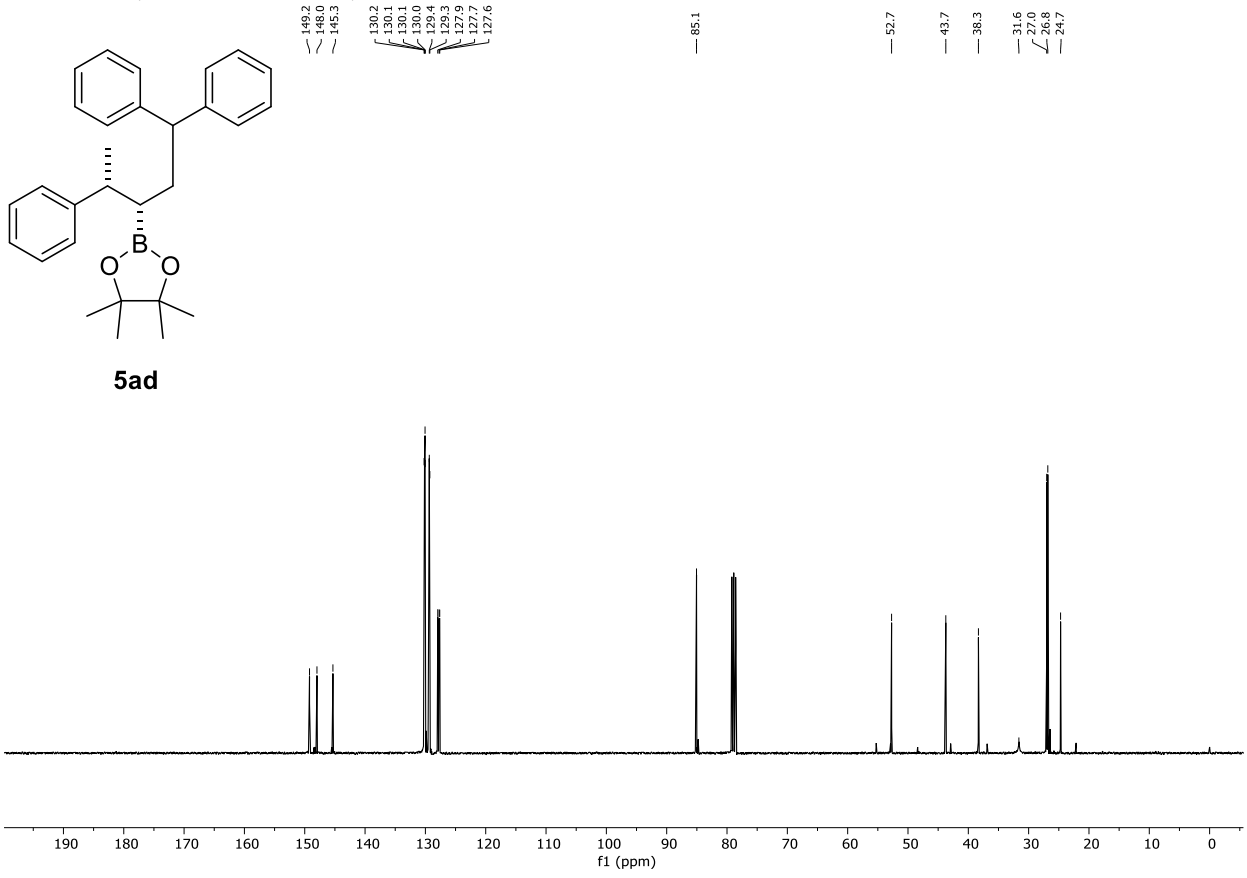
5ac

^{1}H-NMR (400 MHz, $CDCl_3$):



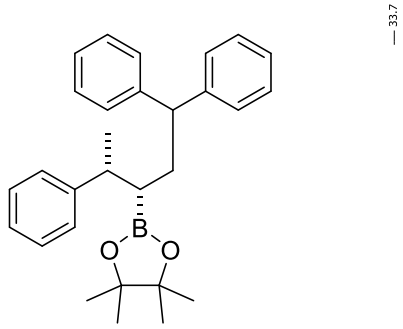
5ad

^{13}C-NMR (101 MHz, $CDCl_3$):



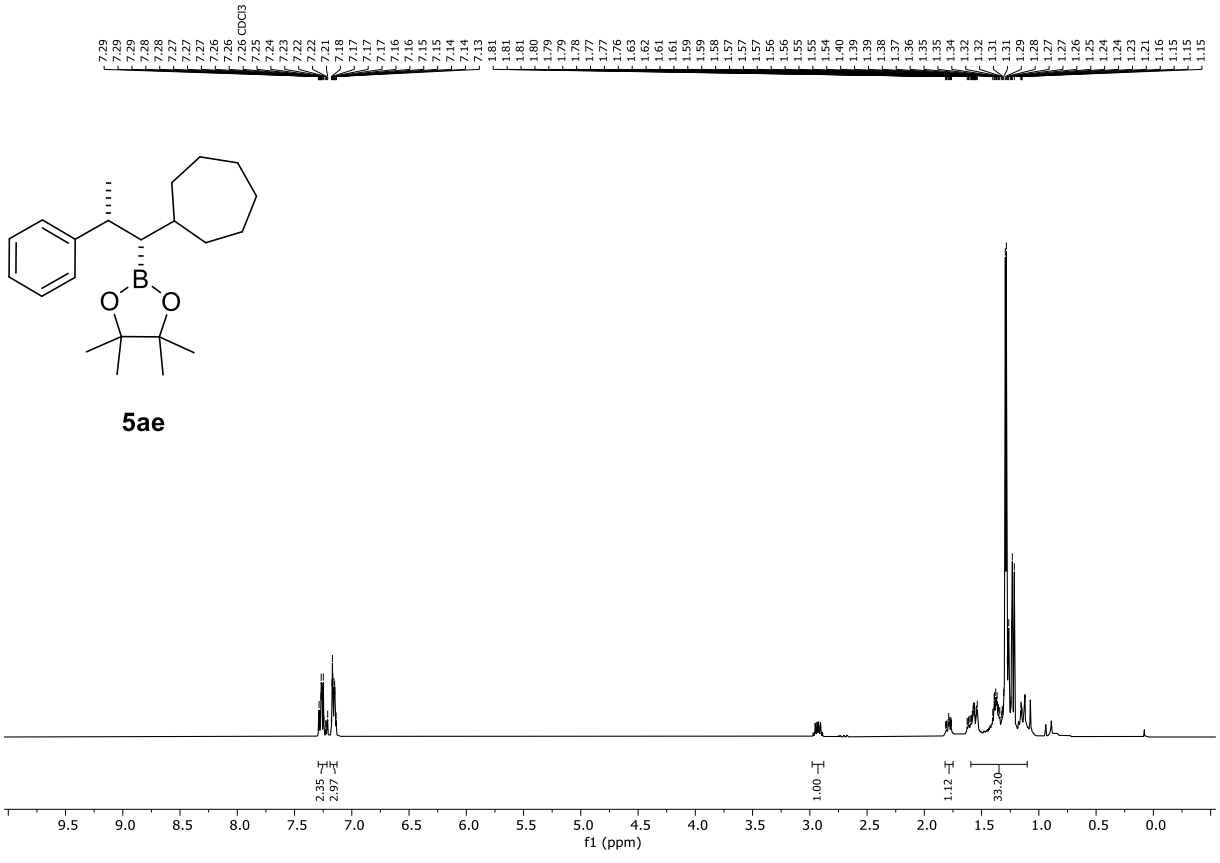
5ad

^{11}B NMR (128 MHz, $CDCl_3$):



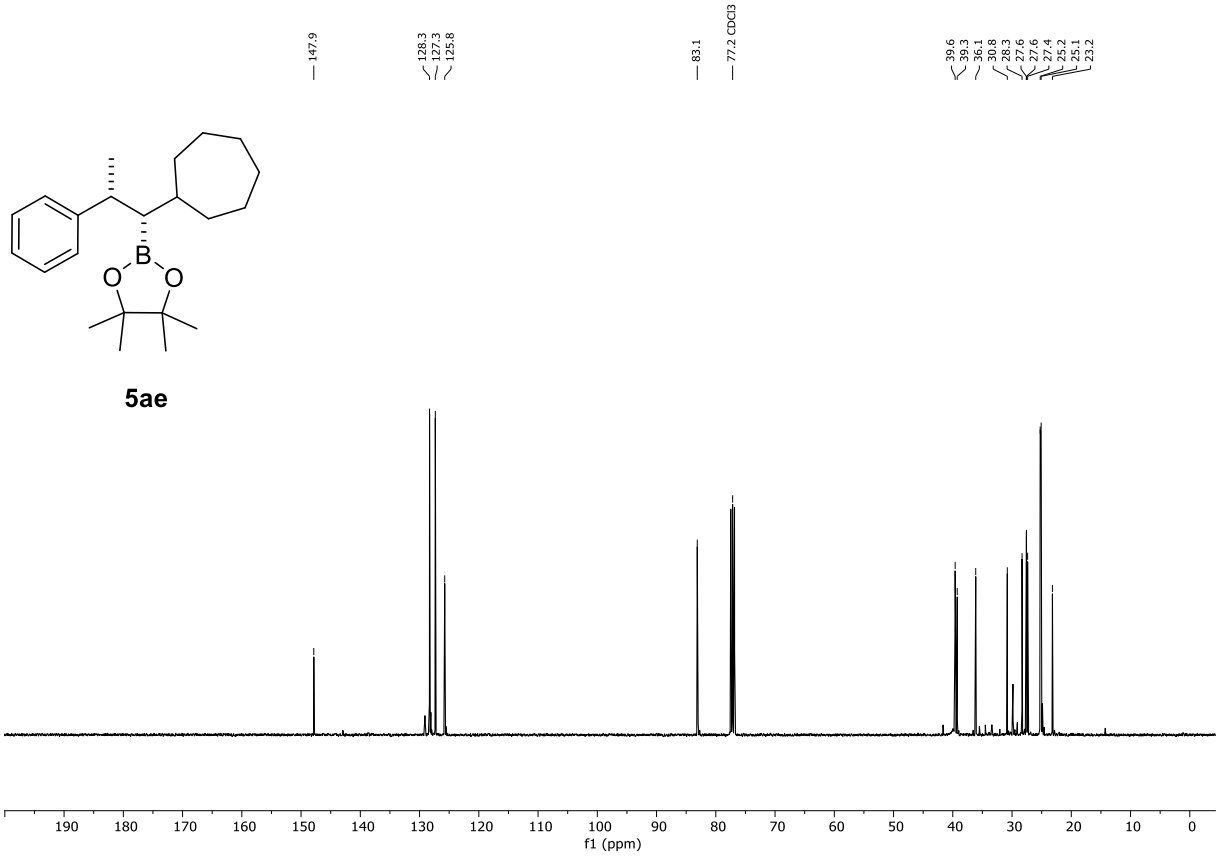
5ad

^{1}H-NMR (400 MHz, $CDCl_3$):

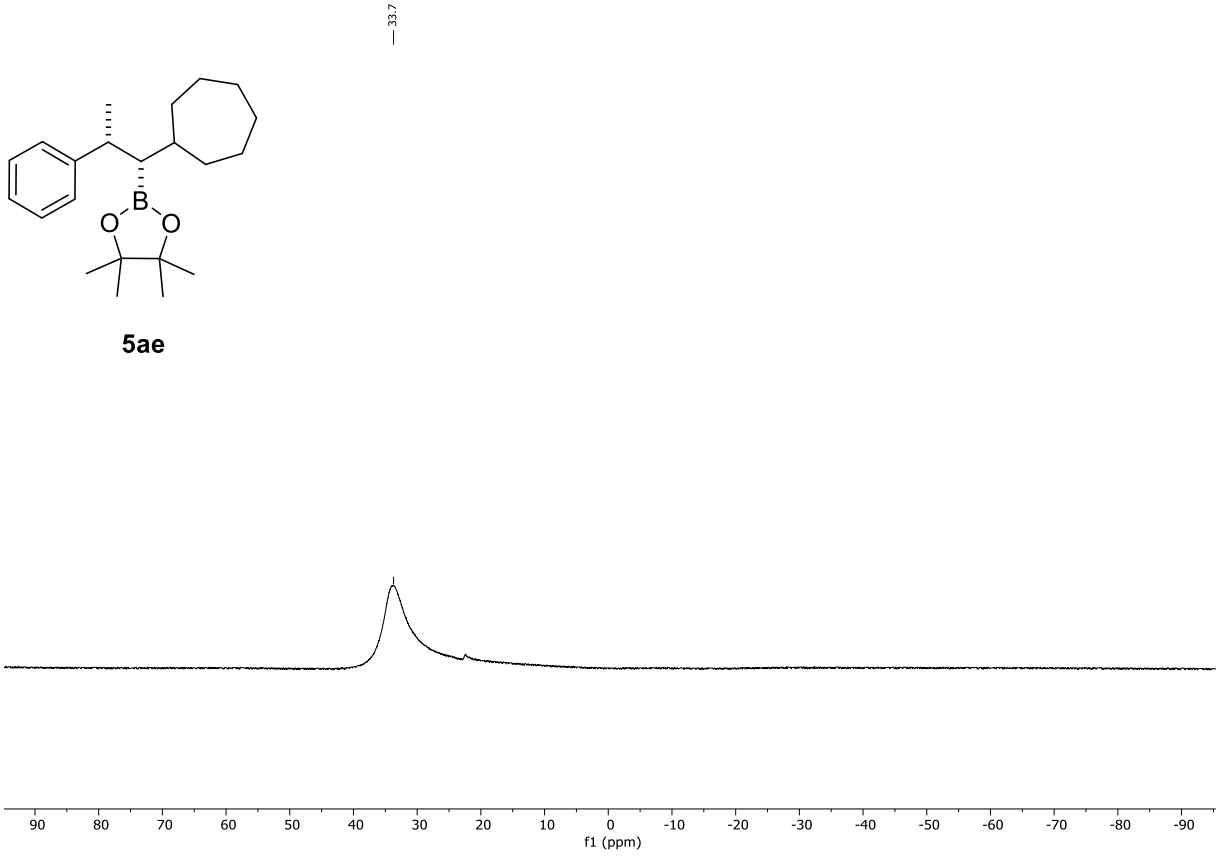


5ae

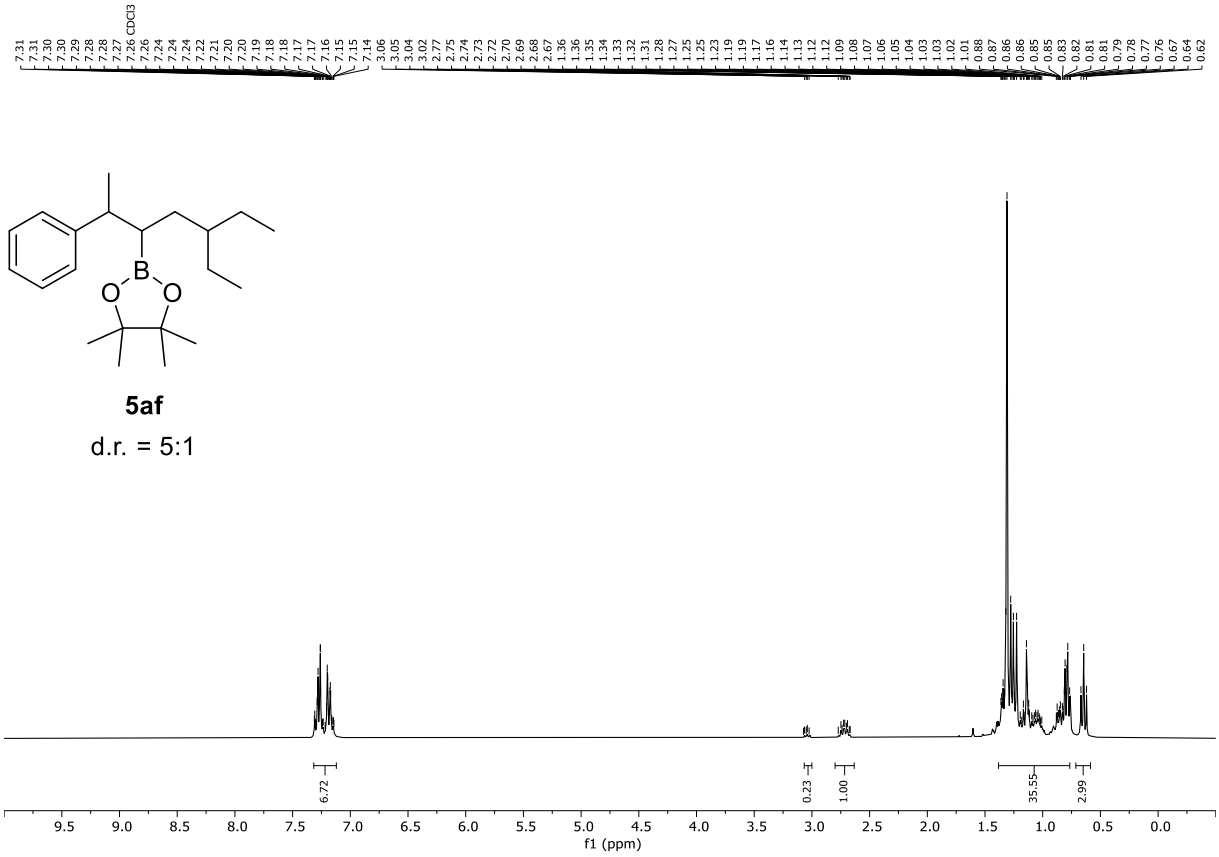
^{13}C-NMR (101 MHz, $CDCl_3$):



^{11}B NMR (128 MHz, $CDCl_3$):



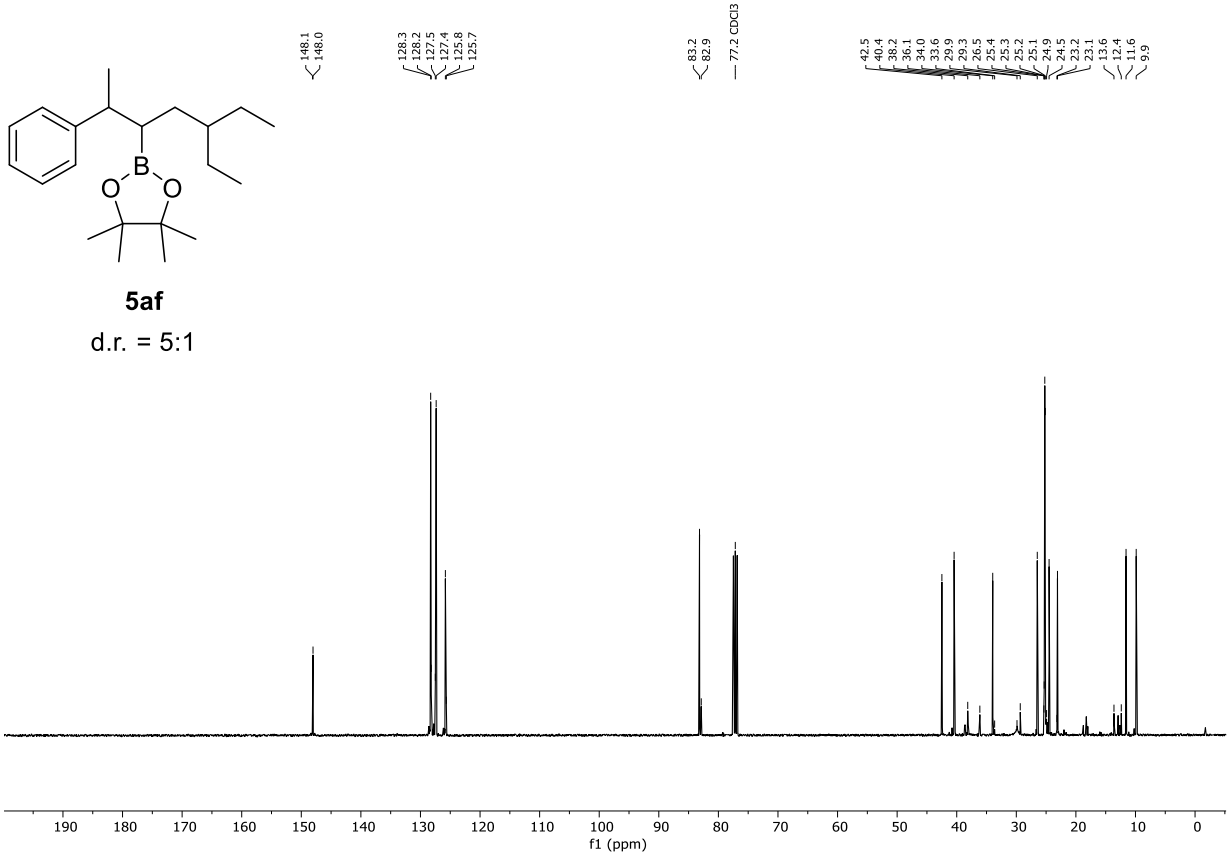
^{1}H-NMR (400 MHz, $CDCl_3$):



5af

d.r. = 5:1

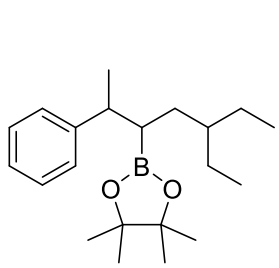
^{13}C-NMR (101 MHz, $CDCl_3$):



5af

d.r. = 5:1

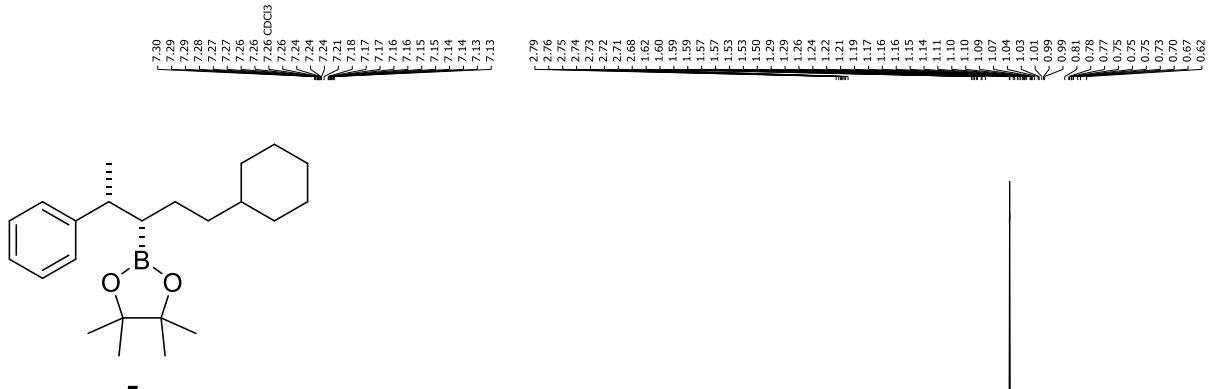
^{11}B NMR (128 MHz, $CDCl_3$):



5af

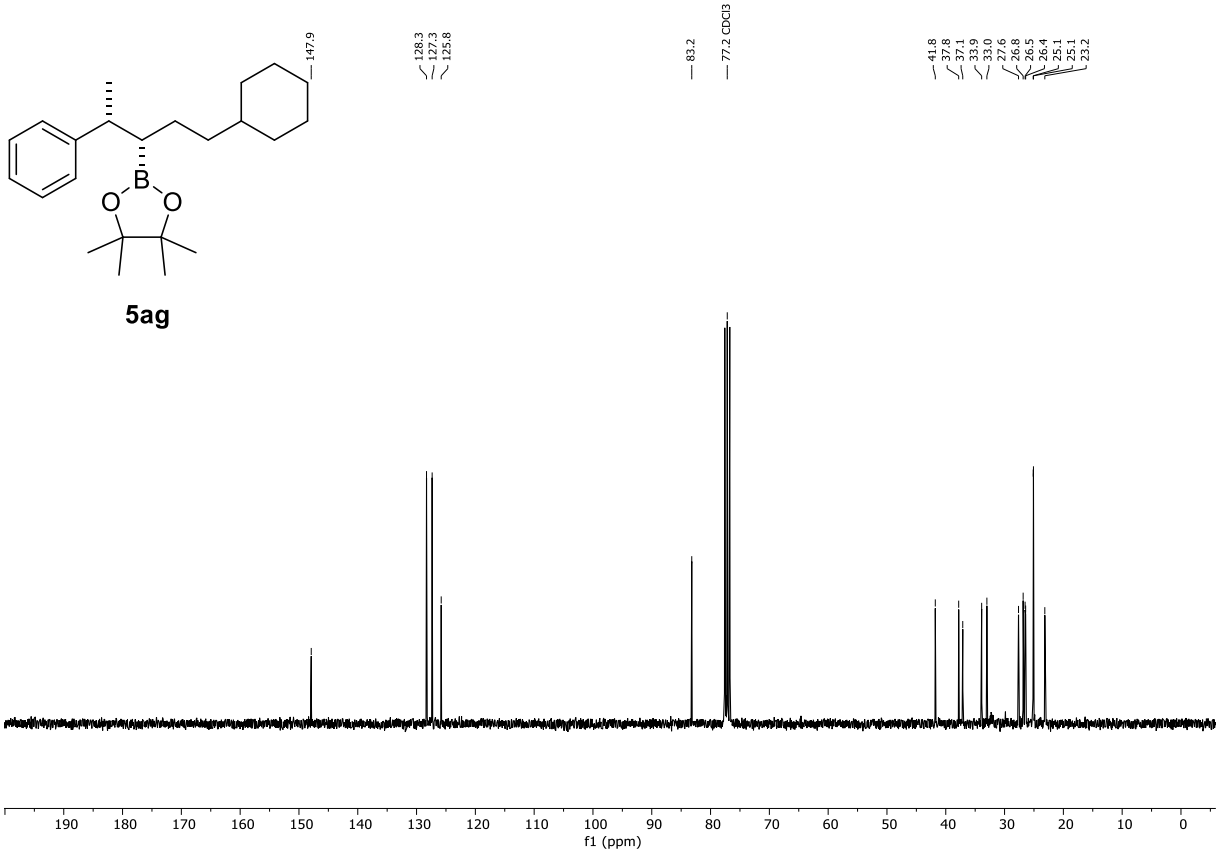
d.r. = 5:1

^{1}H-NMR (400 MHz, $CDCl_3$):

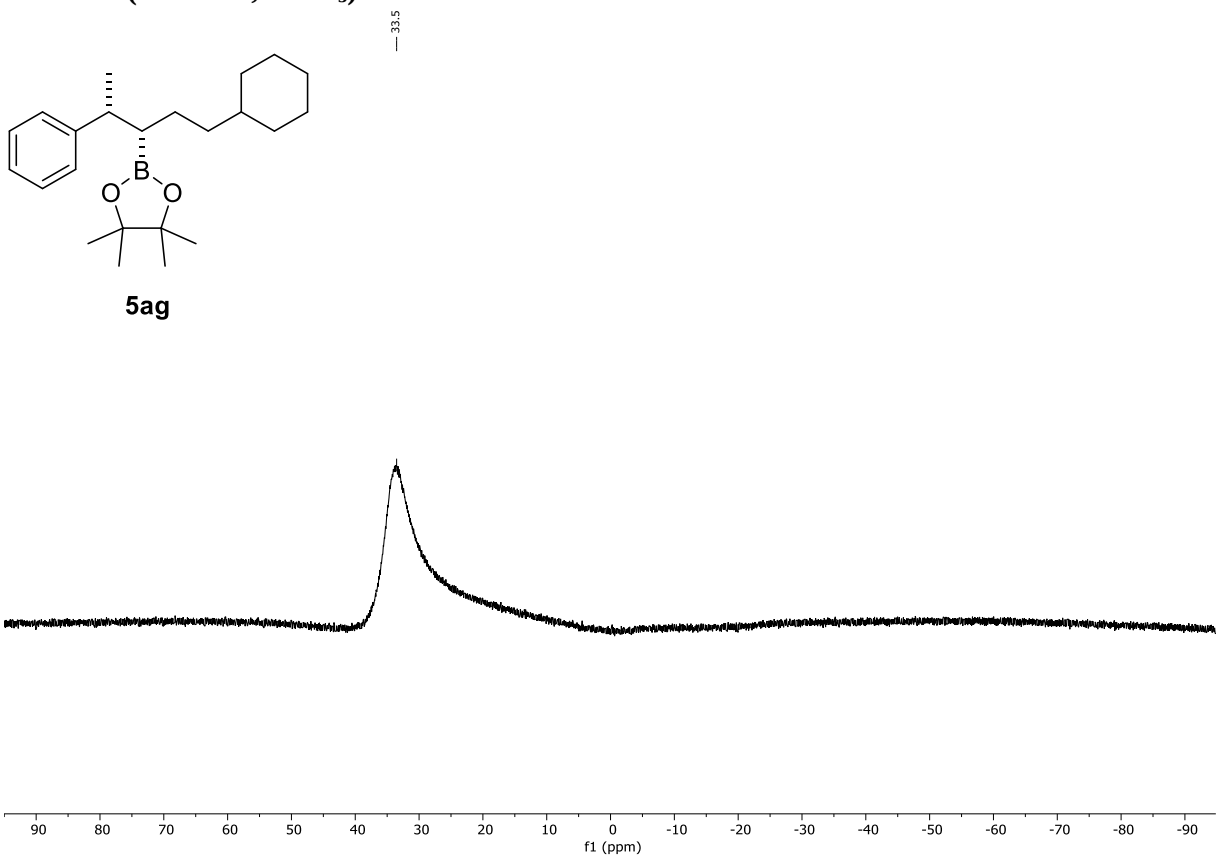


5ag

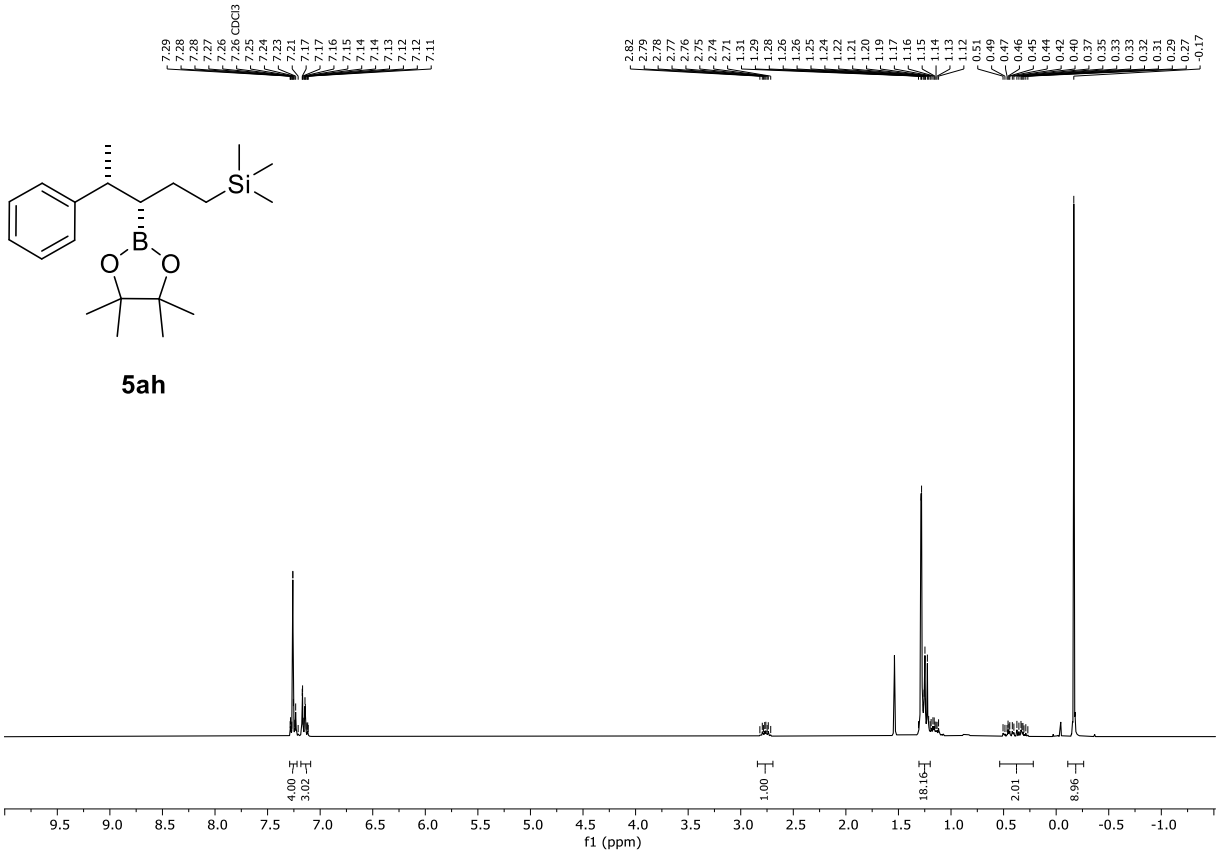
^{13}C-NMR (101 MHz, $CDCl_3$):



^{11}B NMR (128 MHz, $CDCl_3$):

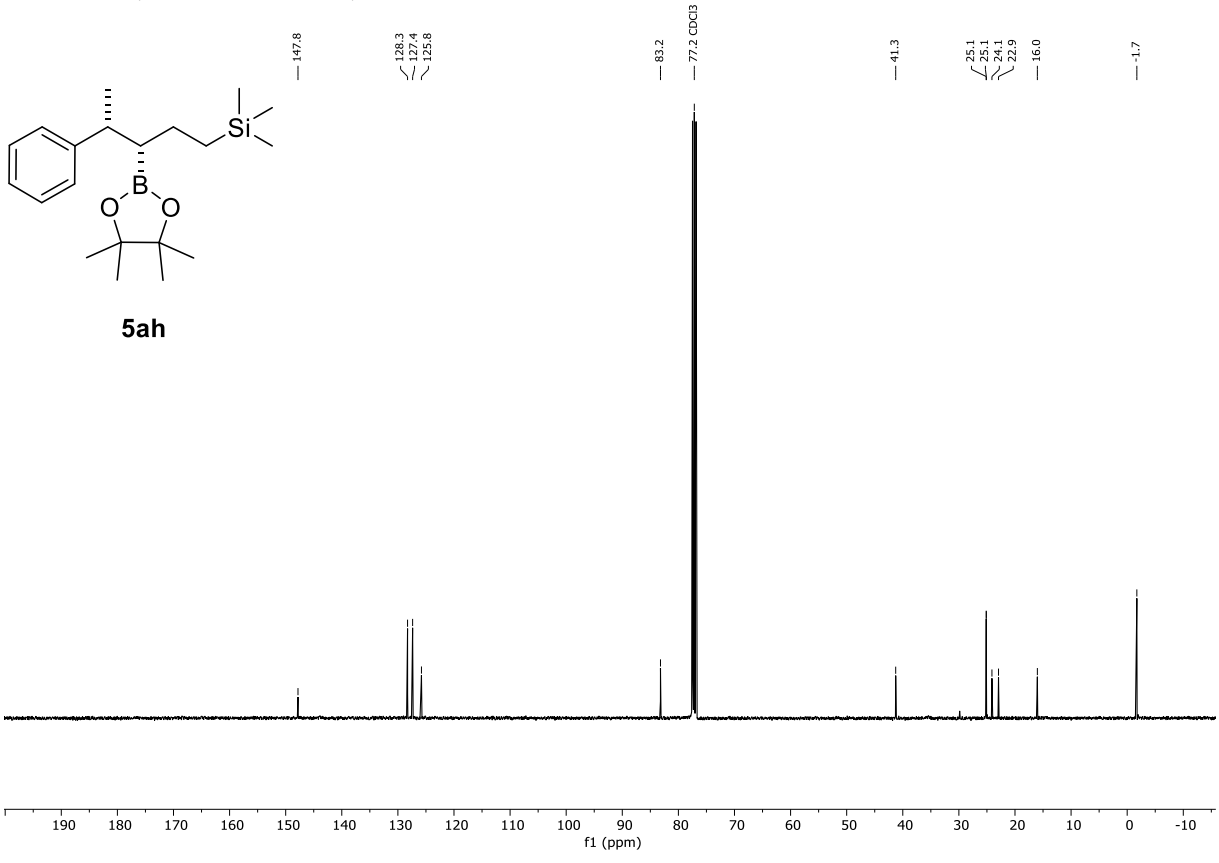


^{1}H-NMR (400 MHz, $CDCl_3$):



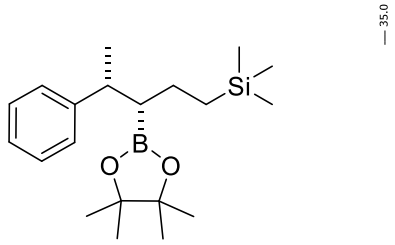
5ah

^{13}C-NMR (101 MHz, $CDCl_3$):

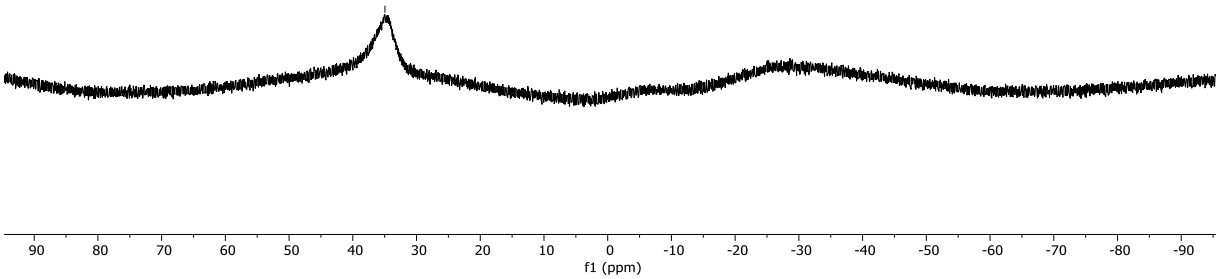


5ah

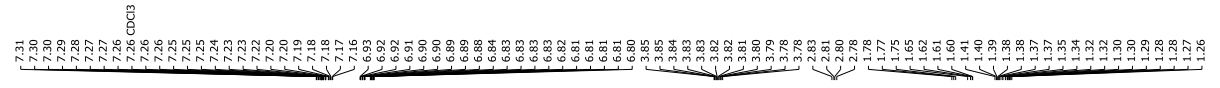
^{11}B NMR (128 MHz, $CDCl_3$):

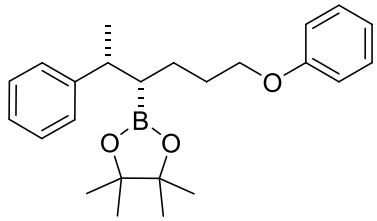


5ah



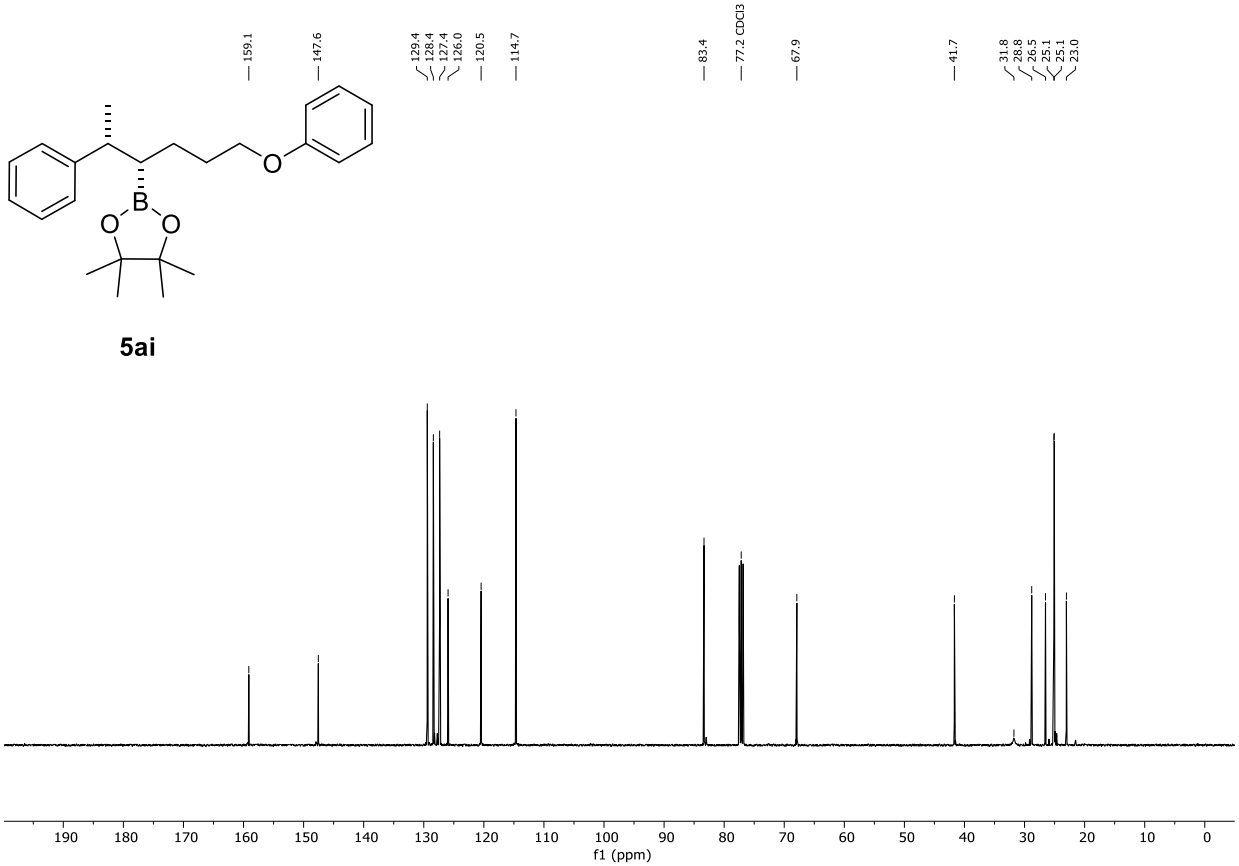
^{1}H-NMR (400 MHz, $CDCl_3$):





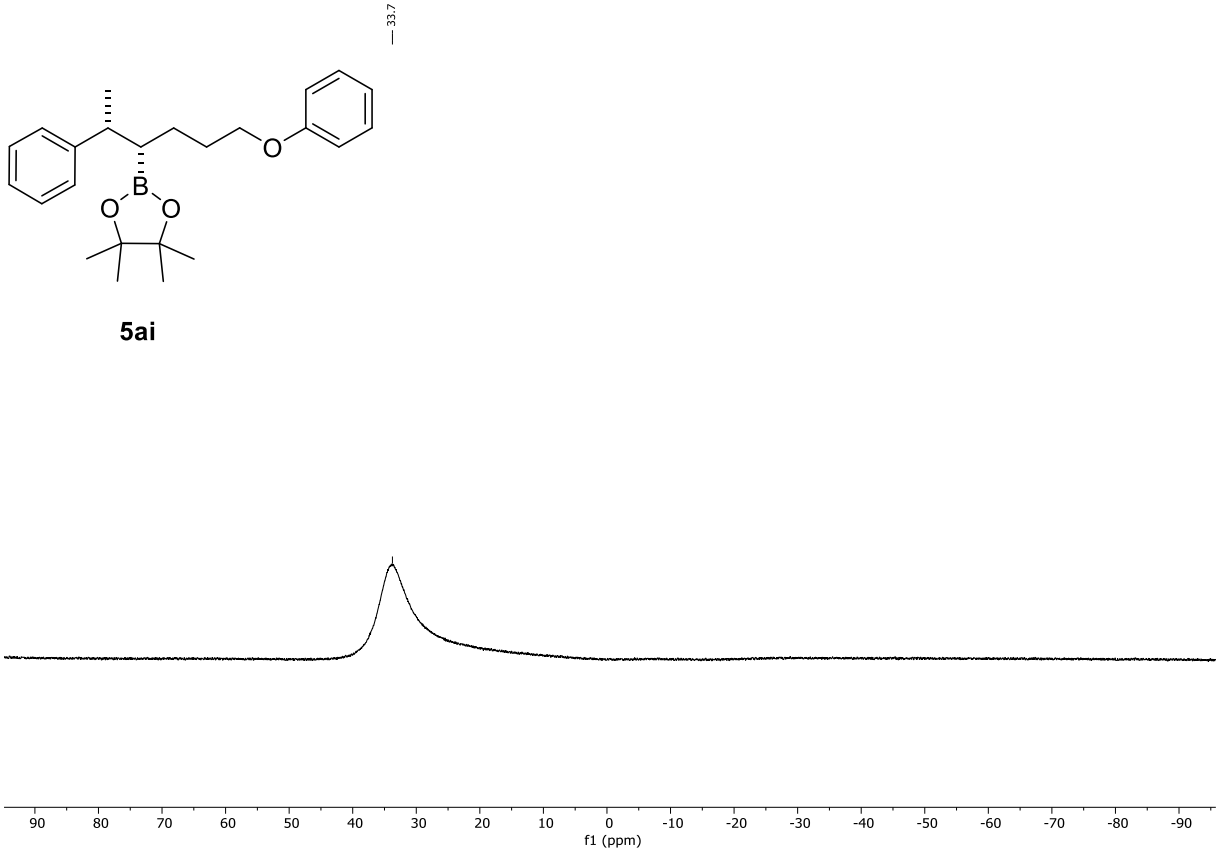
5ai

^{13}C-NMR (101 MHz, $CDCl_3$):



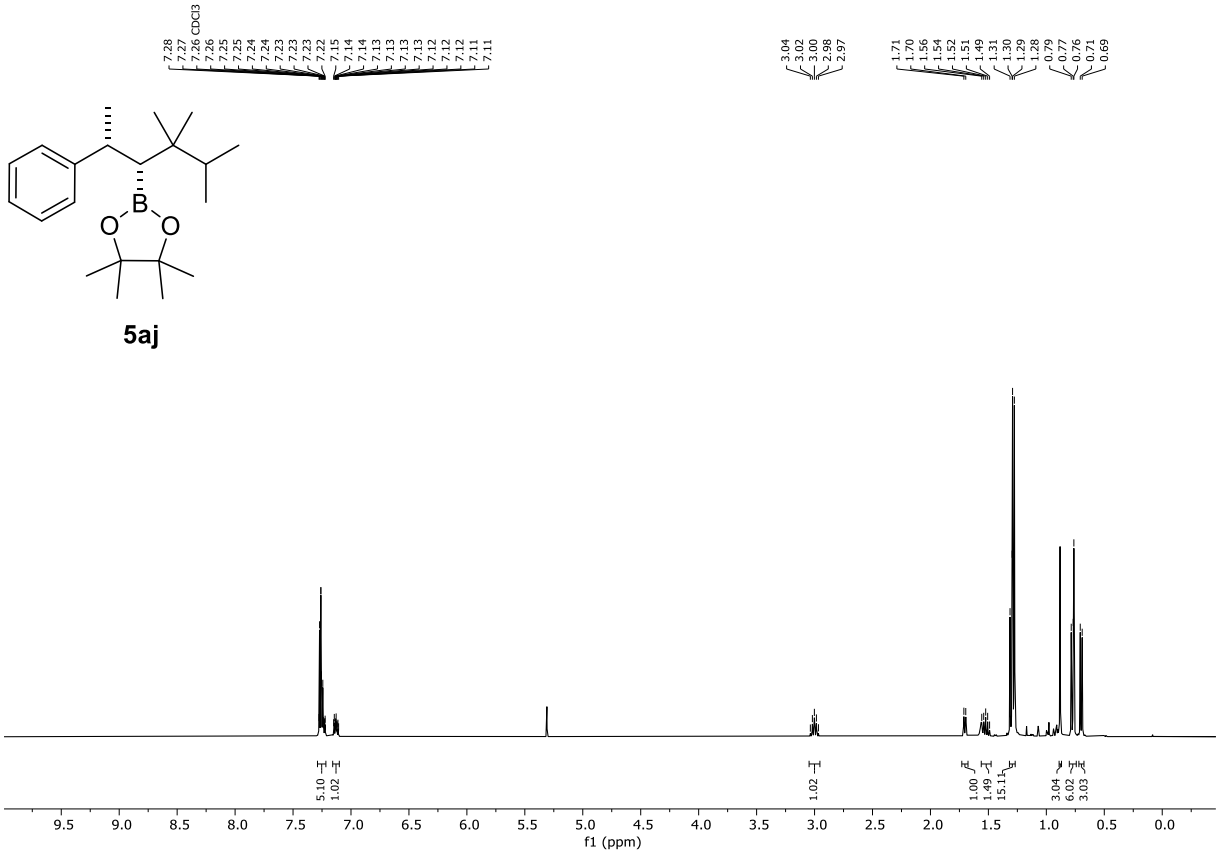
5ai

^{11}B NMR (128 MHz, $CDCl_3$):

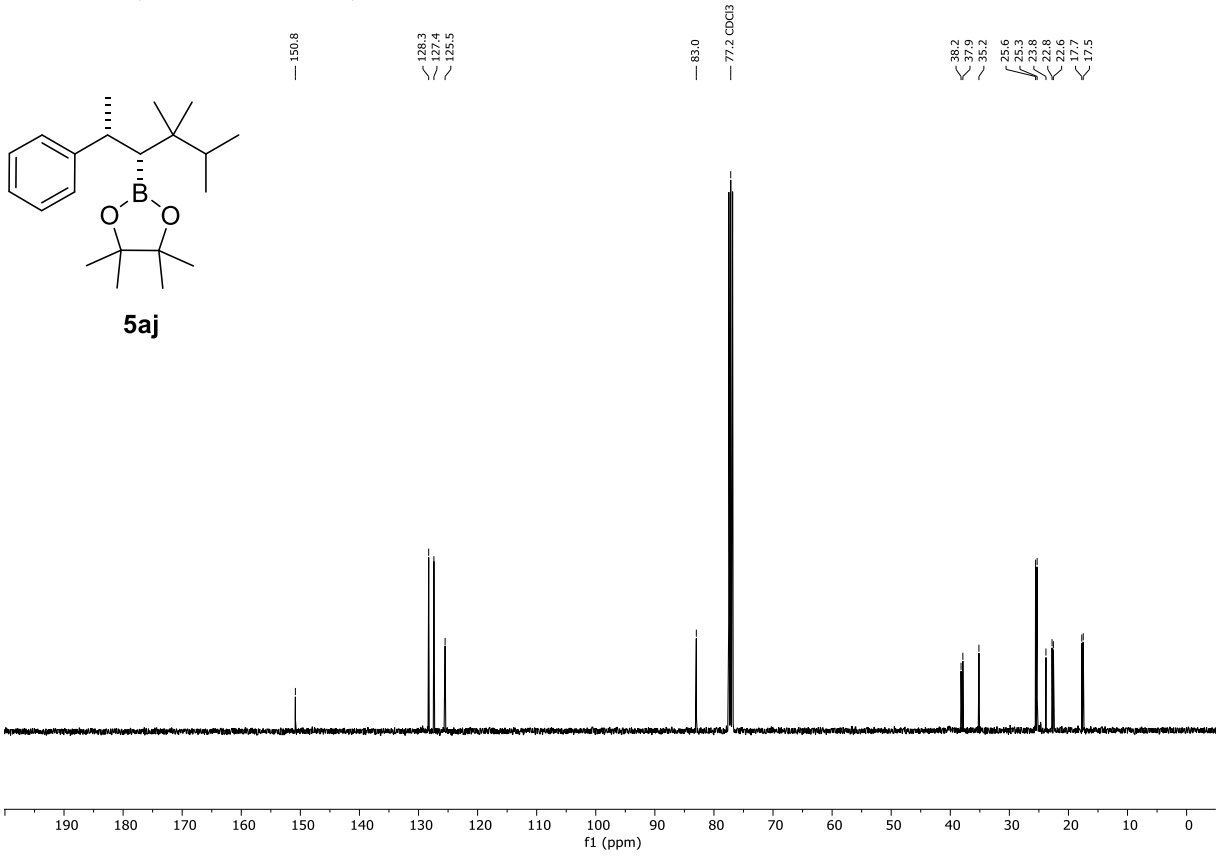


5ai

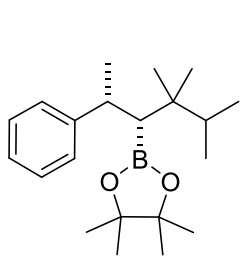
^{1}H-NMR (400 MHz, $CDCl_3$):



^{13}C-NMR (101 MHz, $CDCl_3$):

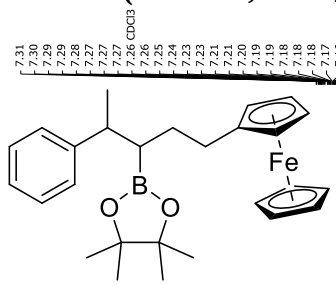


^{11}B NMR (128 MHz, $CDCl_3$):



5aj

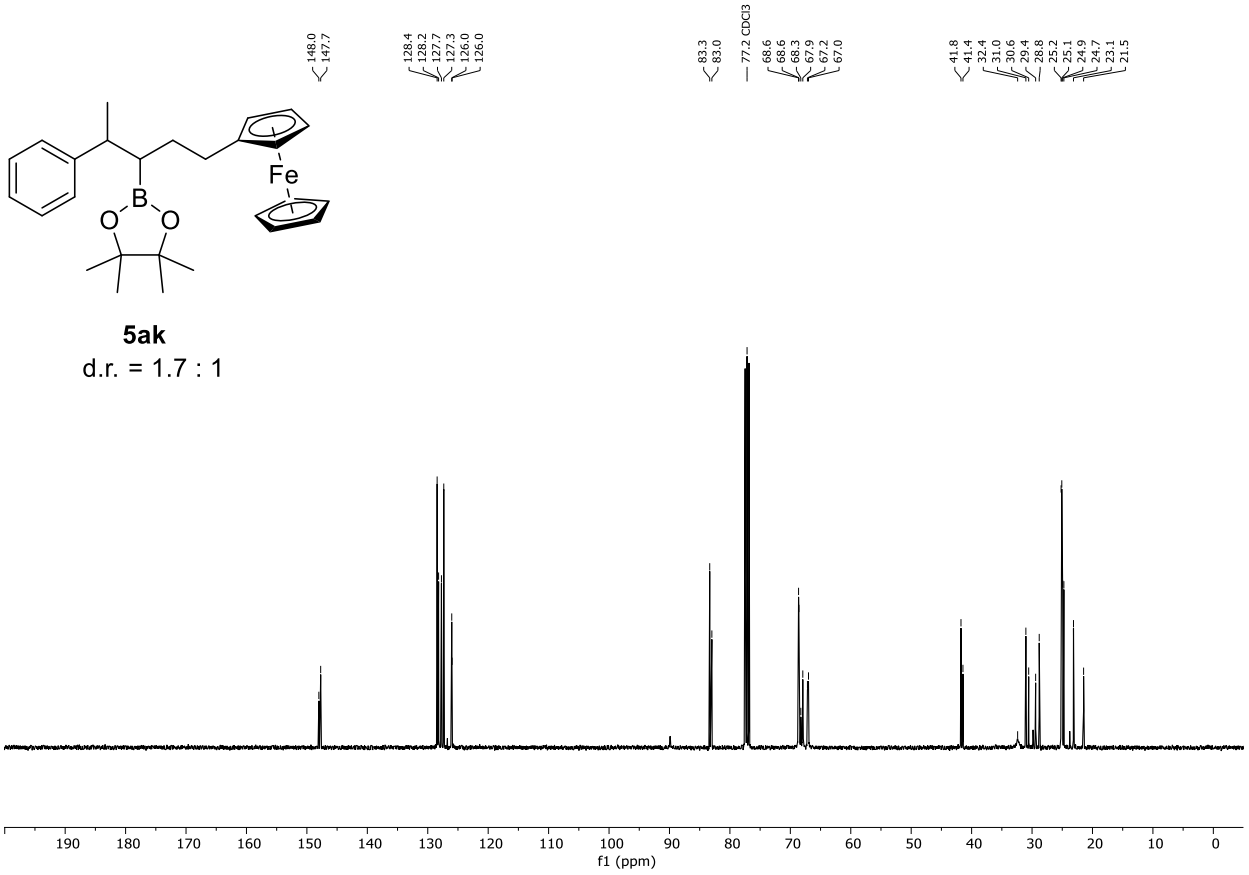
^{1}H-NMR (400 MHz, $CDCl_3$):



5ak

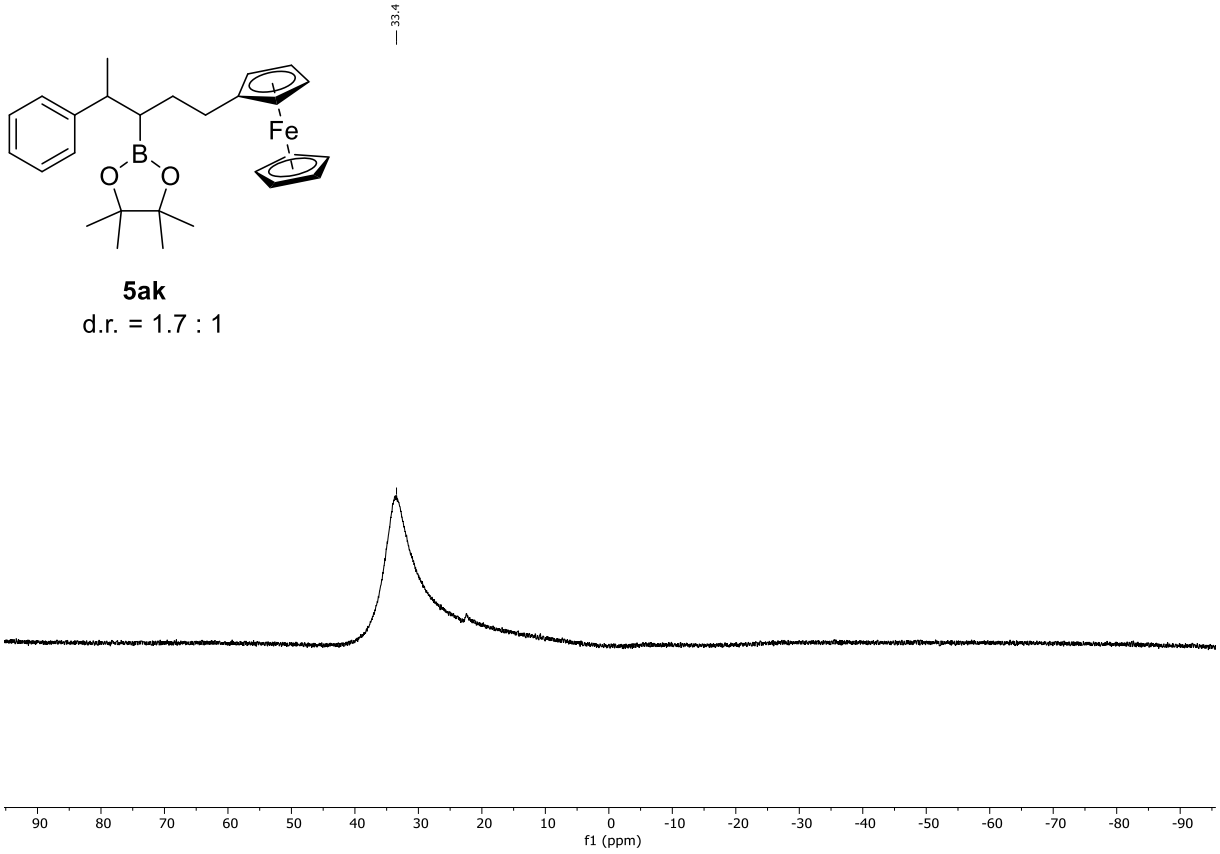
d.r. = 1.7 : 1

^{13}C-NMR (101 MHz, $CDCl_3$):



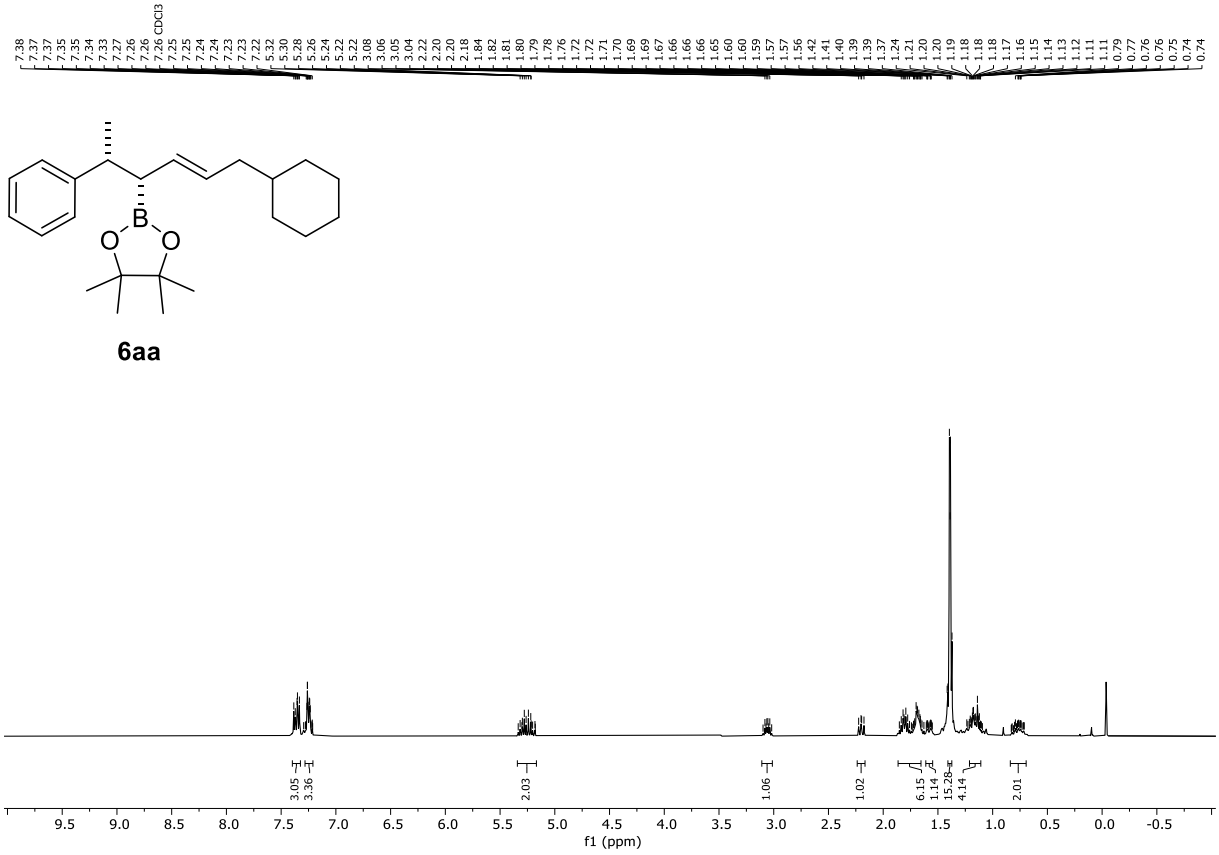
5ak
d.r. = 1.7 : 1

^{11}B NMR (128 MHz, $CDCl_3$):

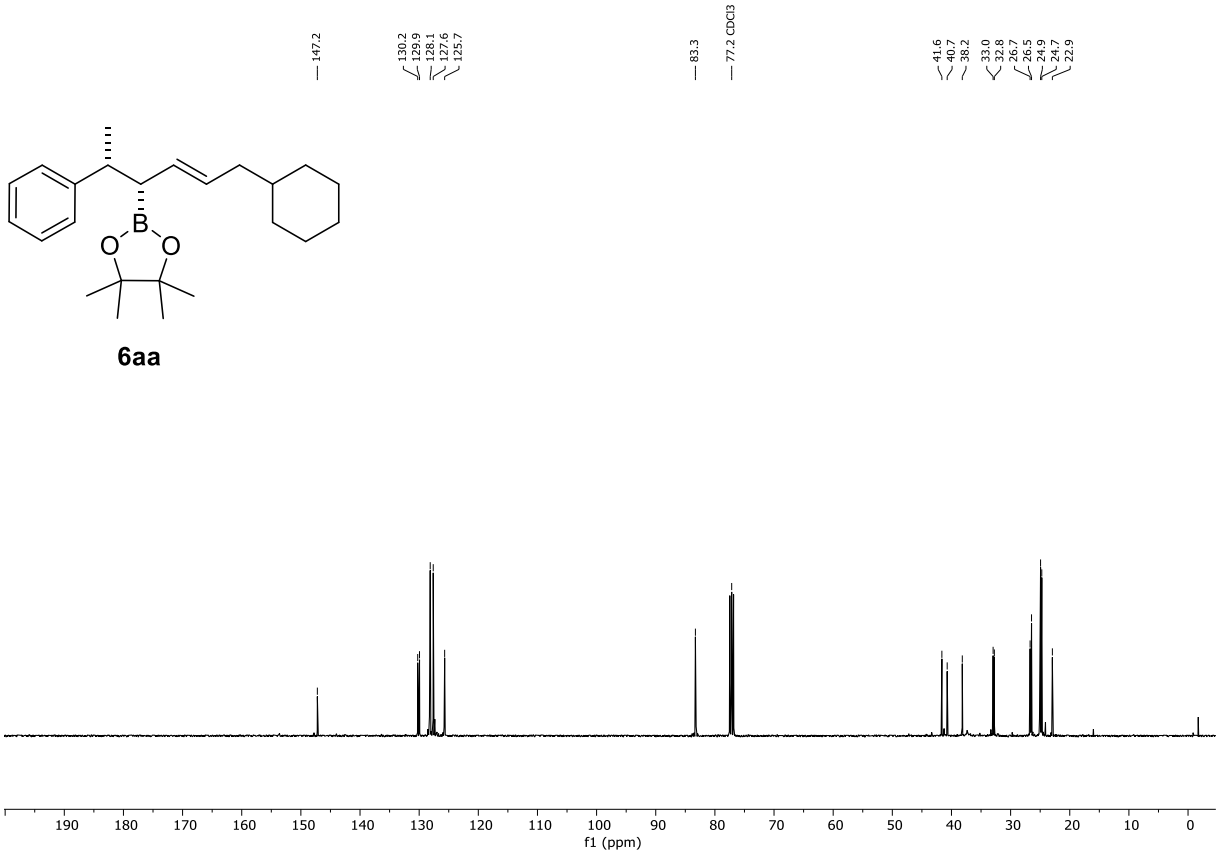


5ak
d.r. = 1.7 : 1

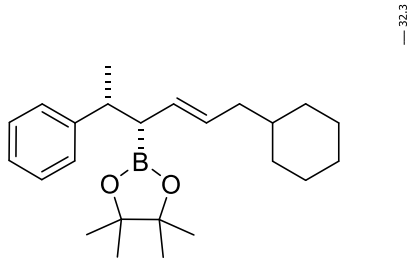
^{1}H-NMR (400 MHz, $CDCl_3$):



^{13}C-NMR (101 MHz, $CDCl_3$):

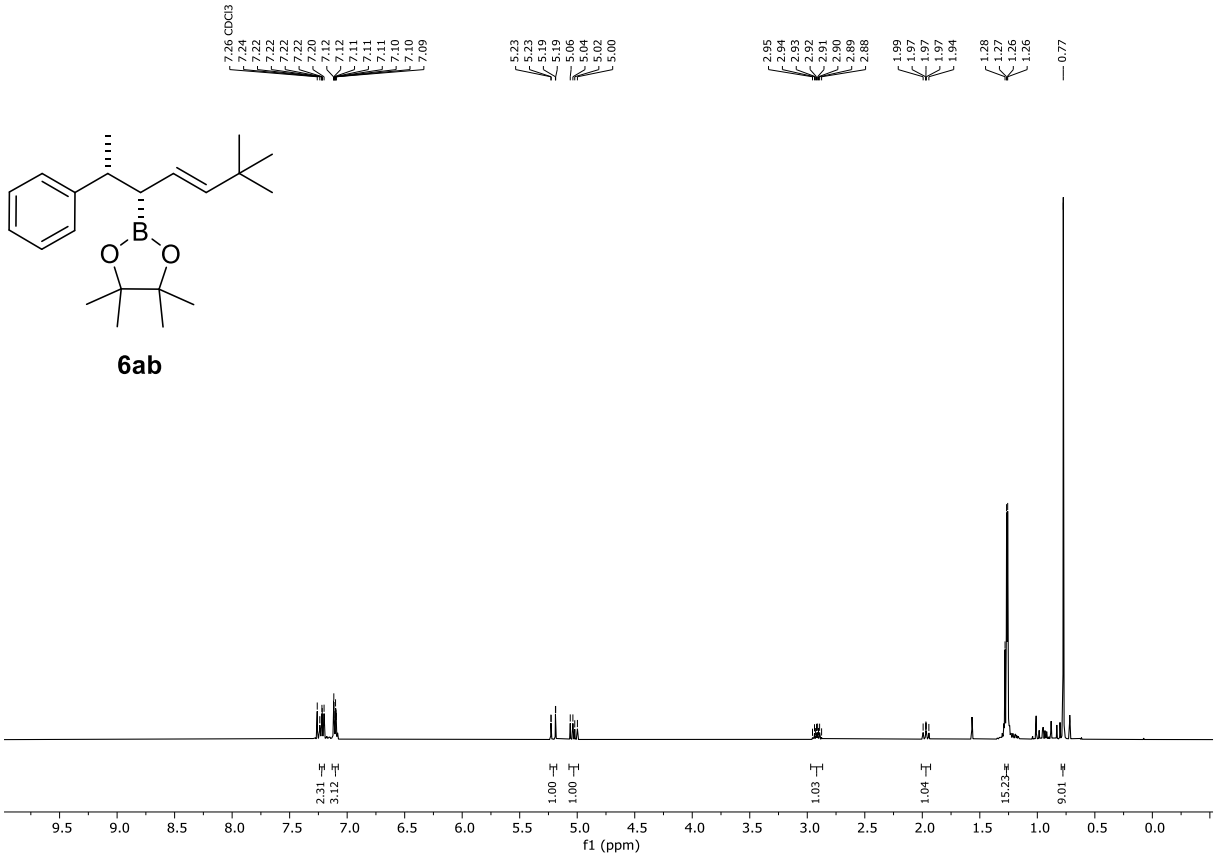


^{11}B NMR (128 MHz, $CDCl_3$):



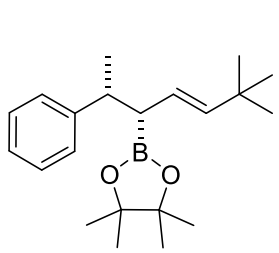
6aa

^{1}H-NMR (400 MHz, $CDCl_3$):



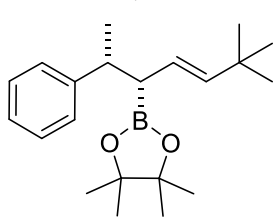
6ab

^{13}C-NMR (101 MHz, $CDCl_3$):



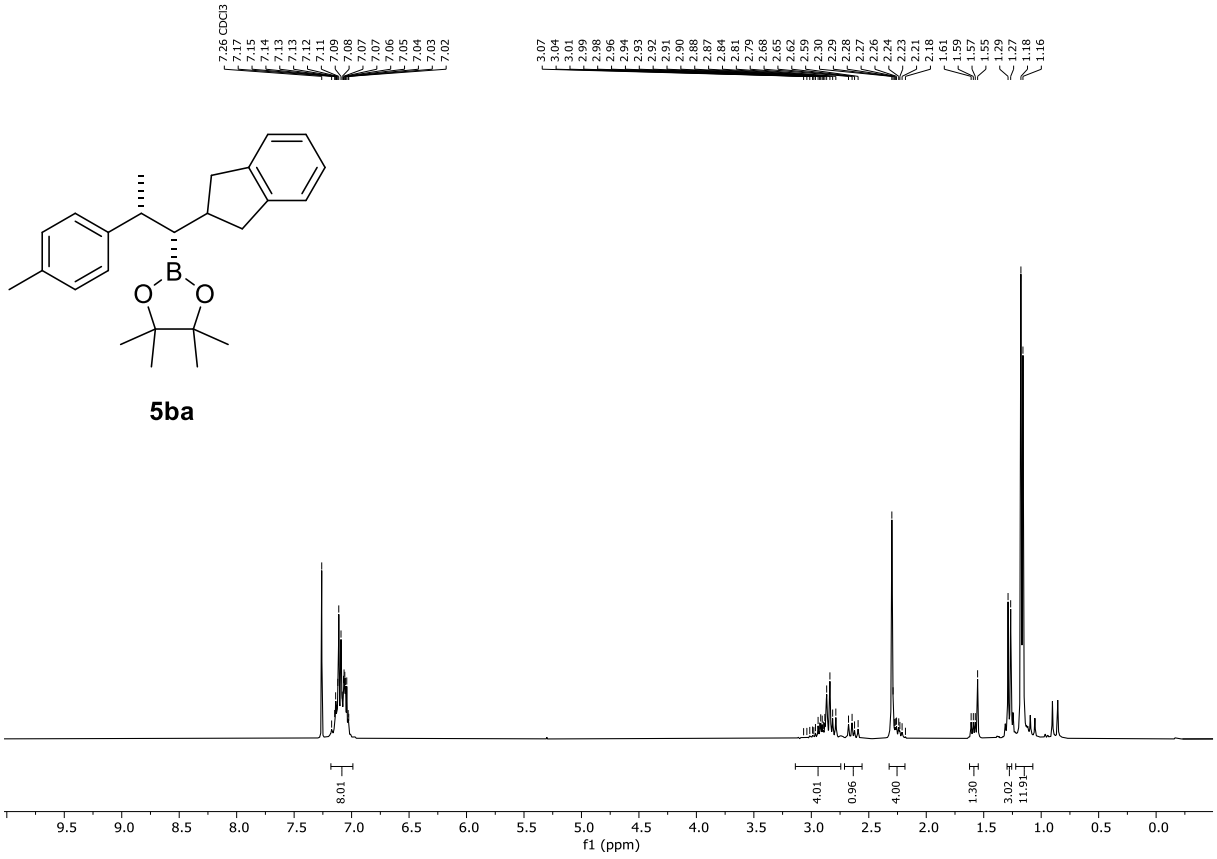
6ab

^{11}B NMR (128 MHz, $CDCl_3$):



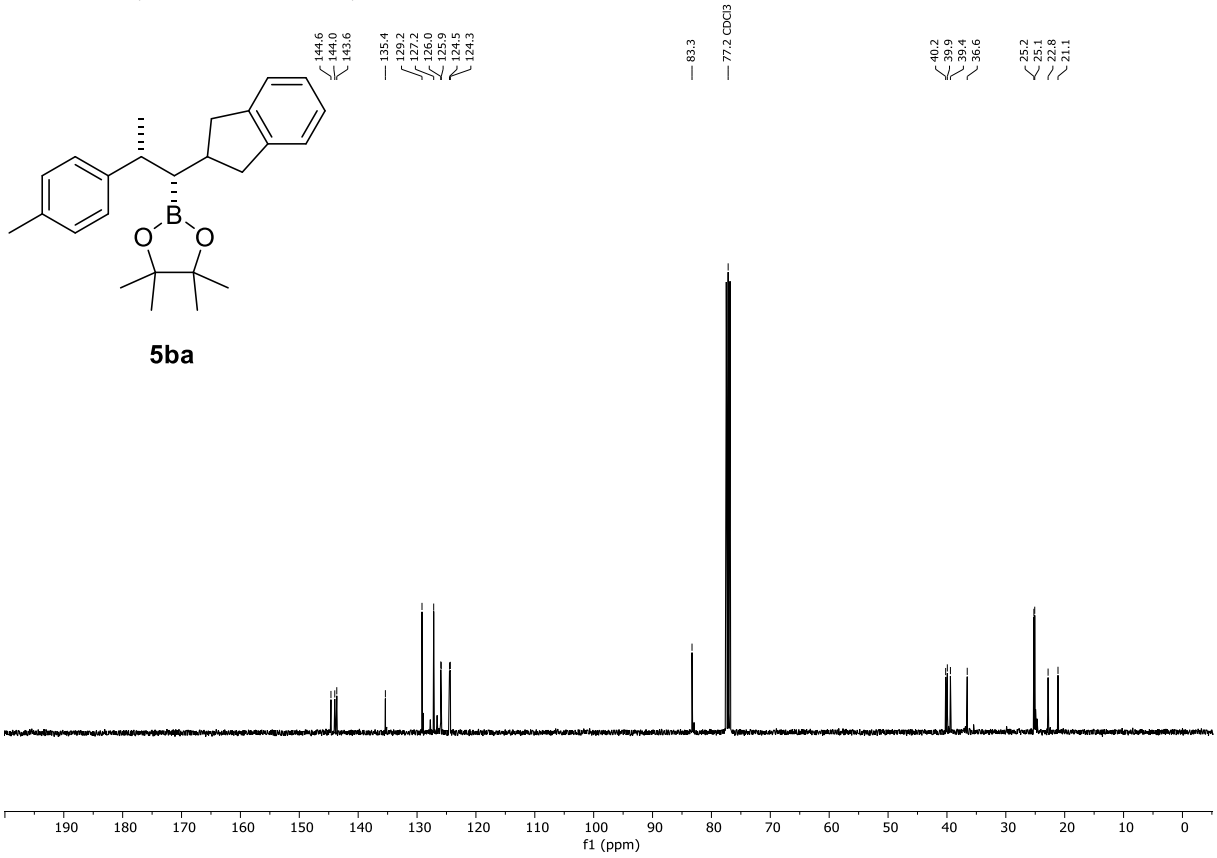
6ab

^{1}H-NMR (400 MHz, $CDCl_3$):



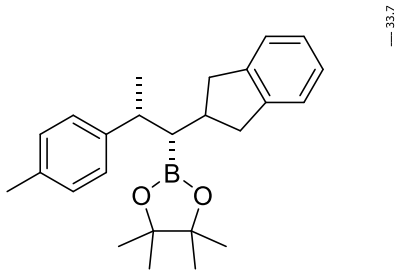
5ba

^{13}C-NMR (101 MHz, $CDCl_3$):



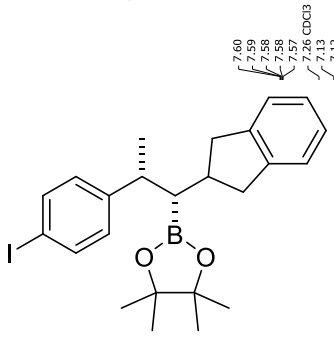
5ba

^{11}B NMR (128 MHz, $CDCl_3$):



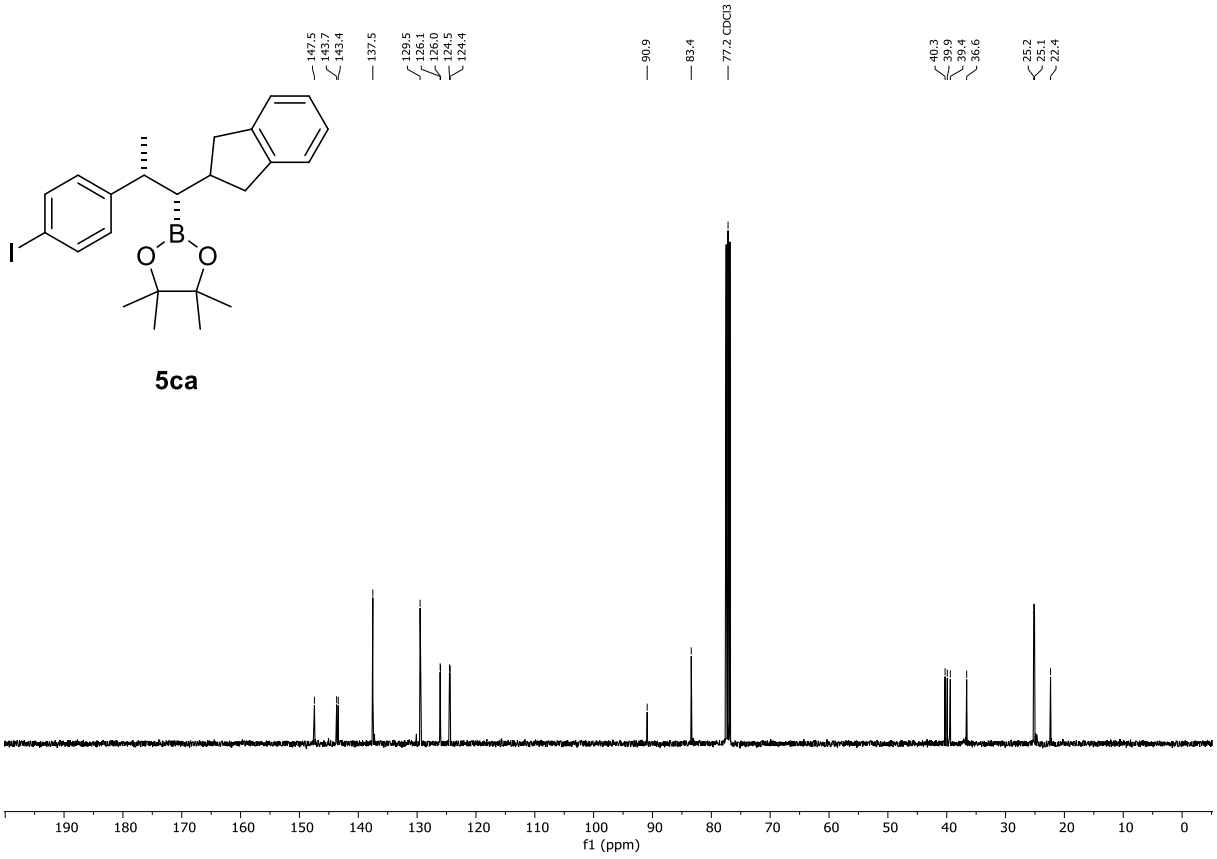
5ba

^{1}H-NMR (400 MHz, $CDCl_3$):



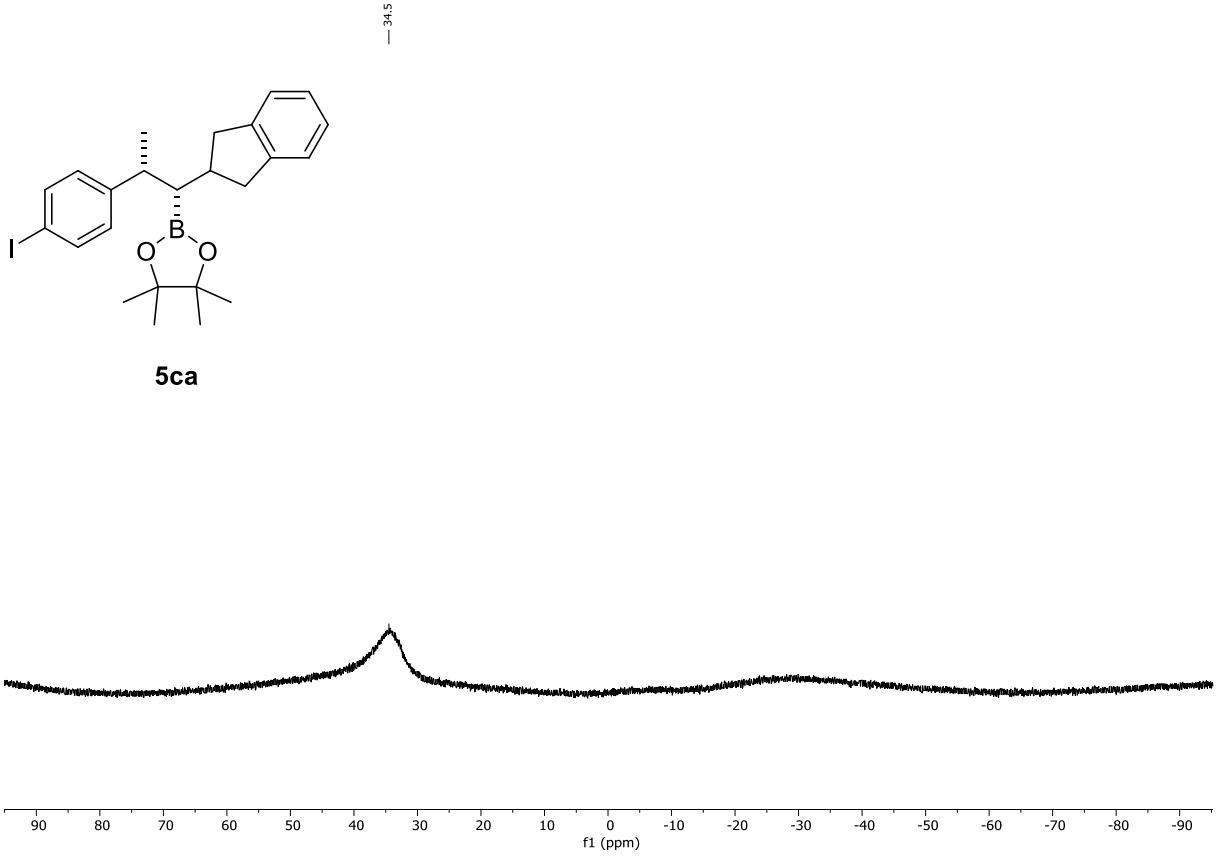
5ca

^{13}C-NMR (101 MHz, $CDCl_3$):



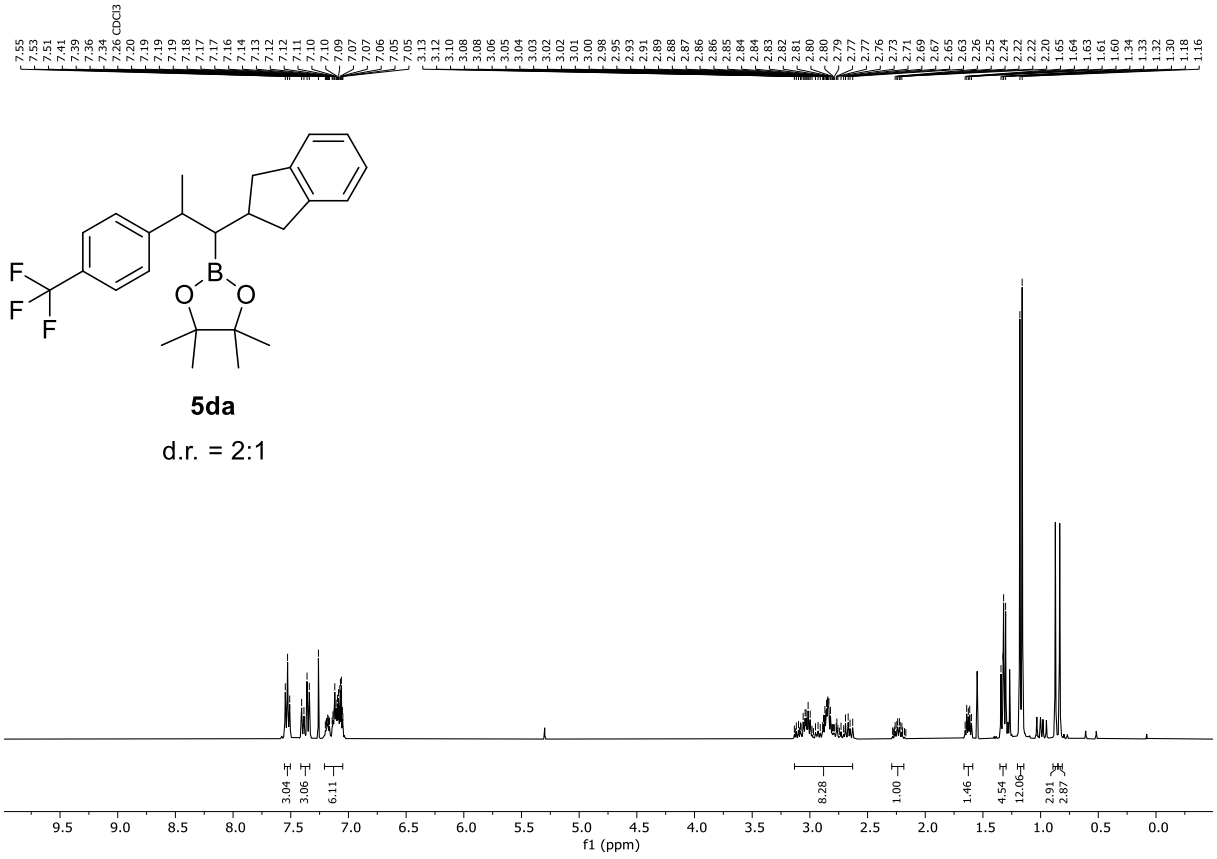
5ca

^{11}B NMR (128 MHz, $CDCl_3$):

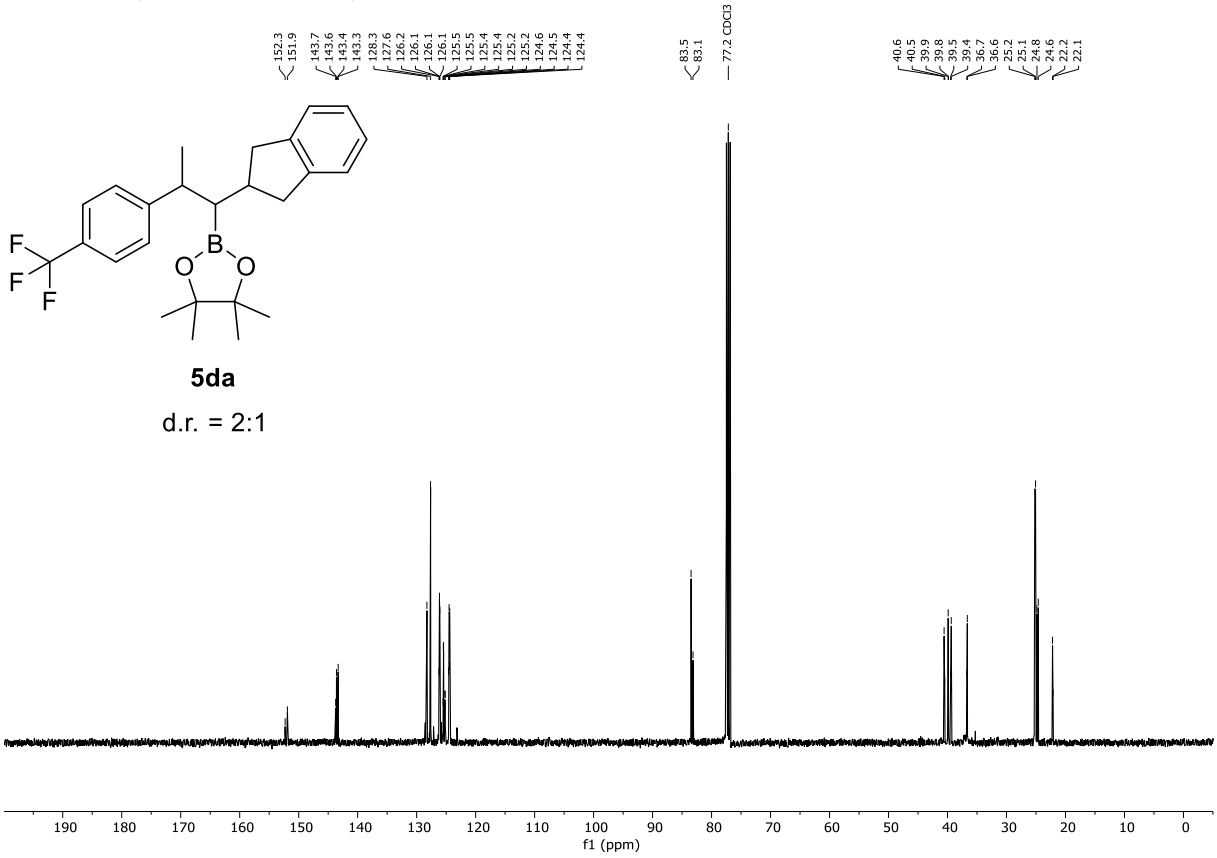


5ca

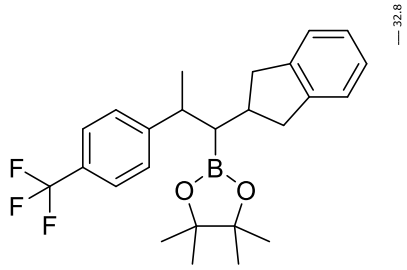
^{1}H-NMR (400 MHz, $CDCl_3$):



^{13}C-NMR (101 MHz, $CDCl_3$):

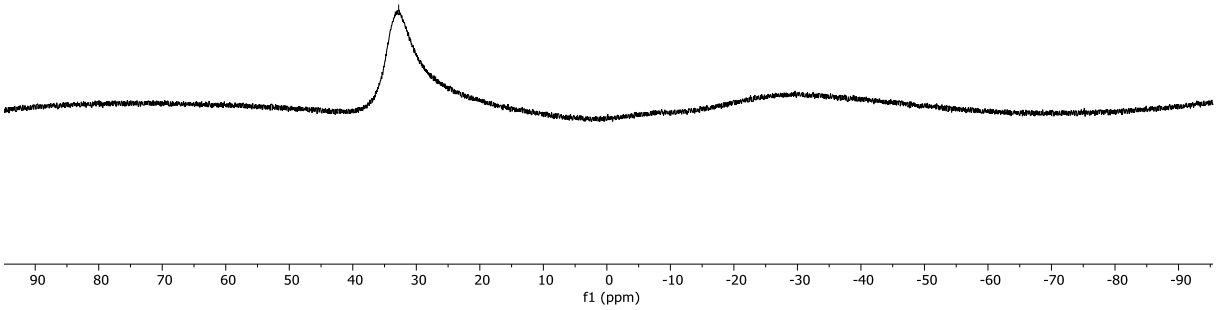


^{11}B NMR (128 MHz, $CDCl_3$):

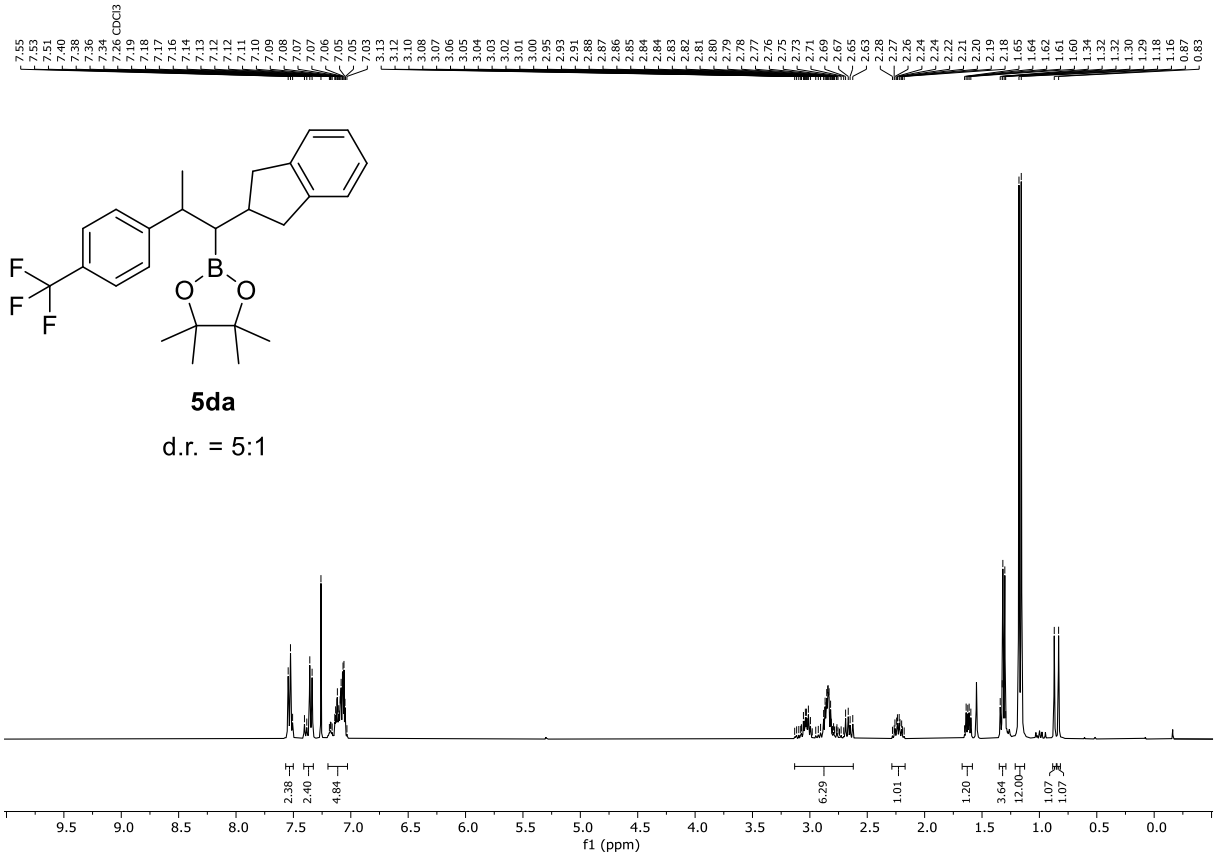


5da

d.r. = 2:1



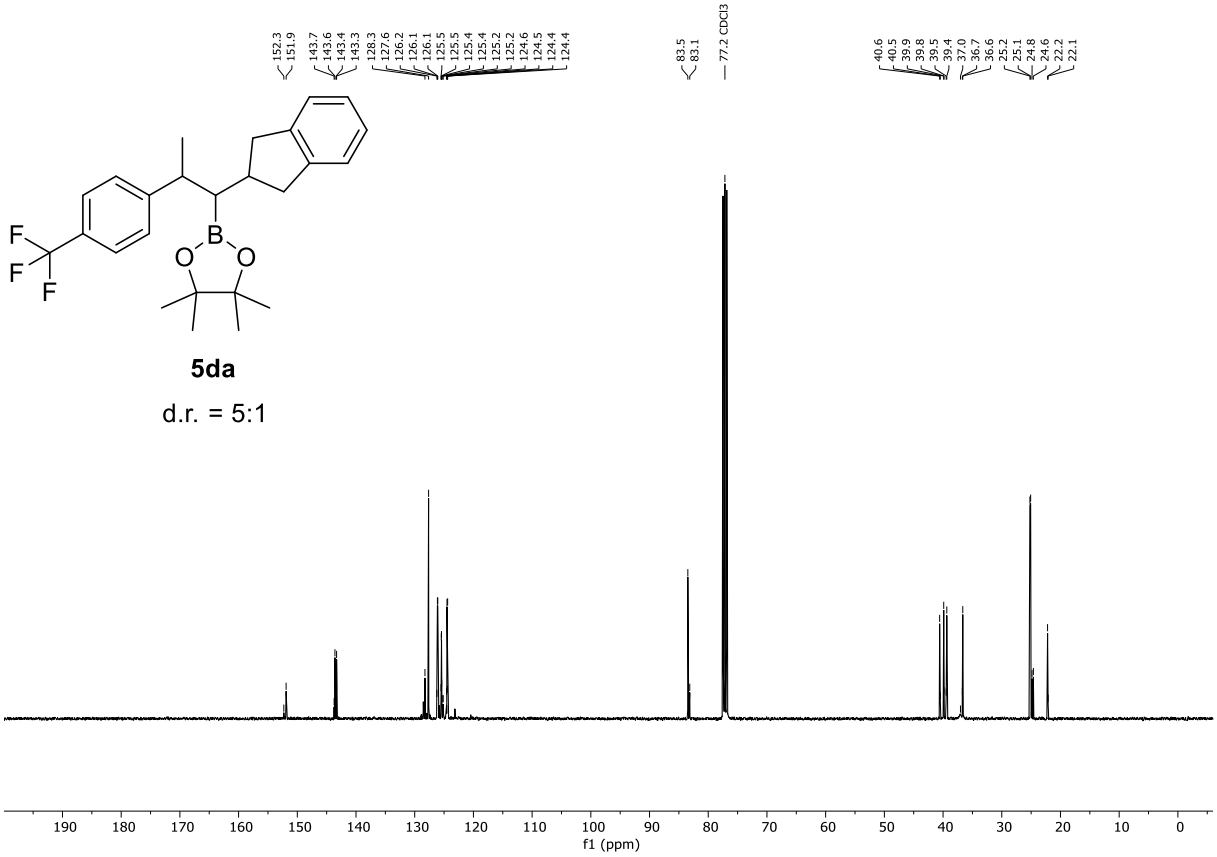
^{1}H-NMR (400 MHz, $CDCl_3$):



5da

d.r. = 5:1

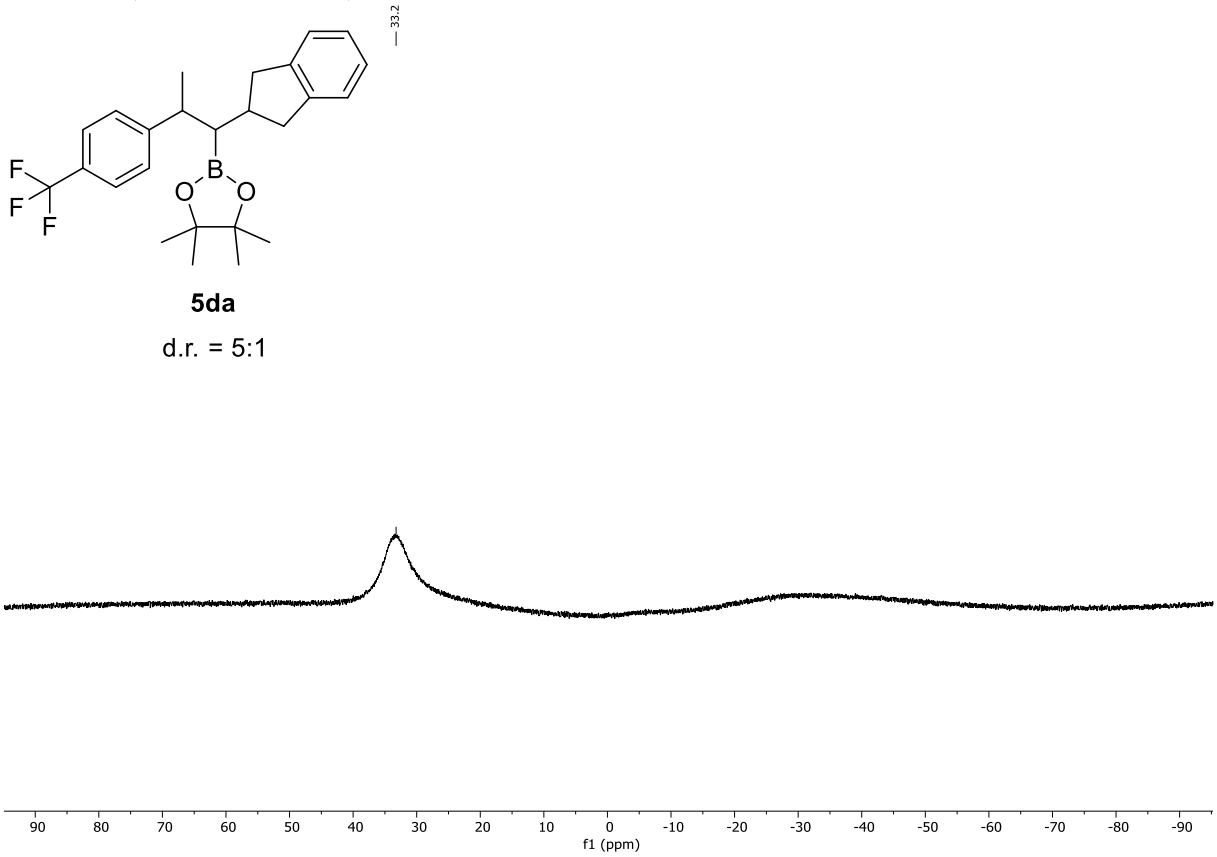
^{13}C-NMR (101 MHz, $CDCl_3$):



5da

d.r. = 5:1

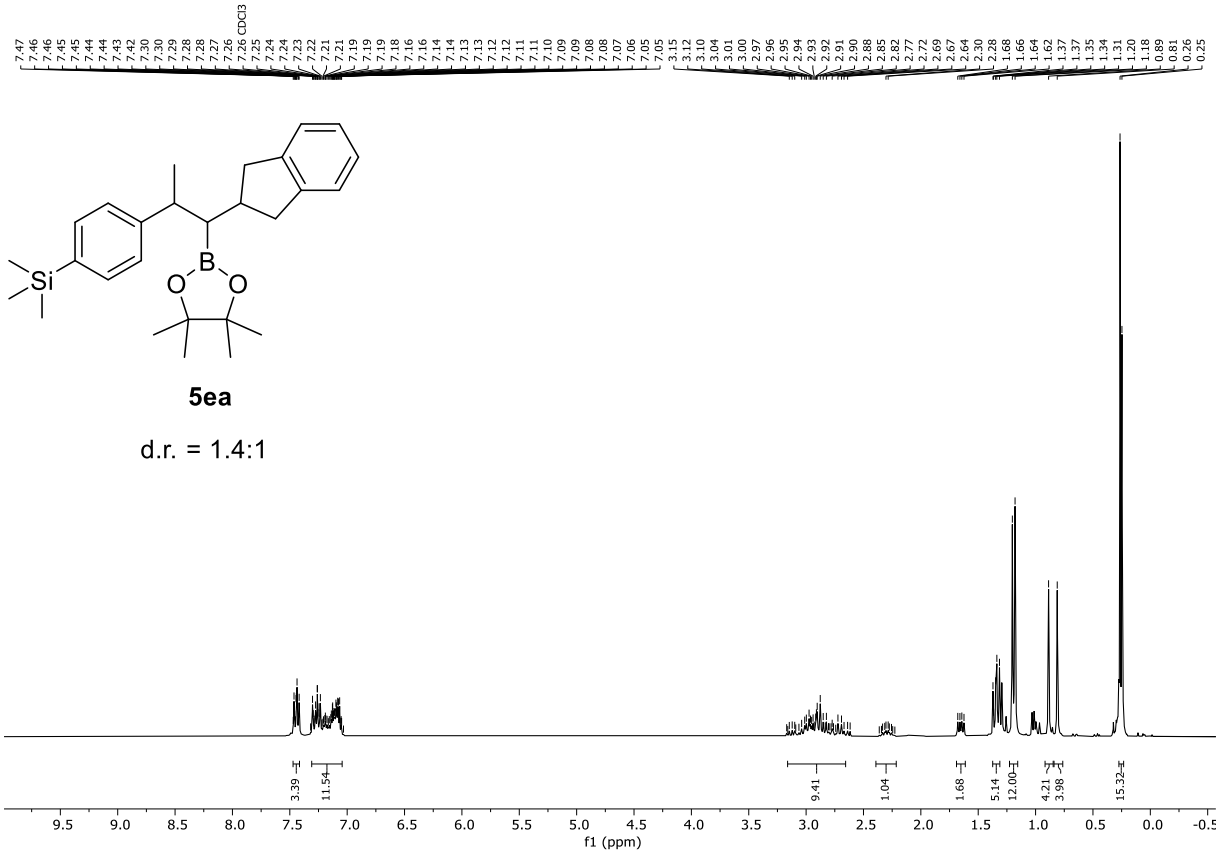
^{11}B NMR (128 MHz, $CDCl_3$):



5da

d.r. = 5:1

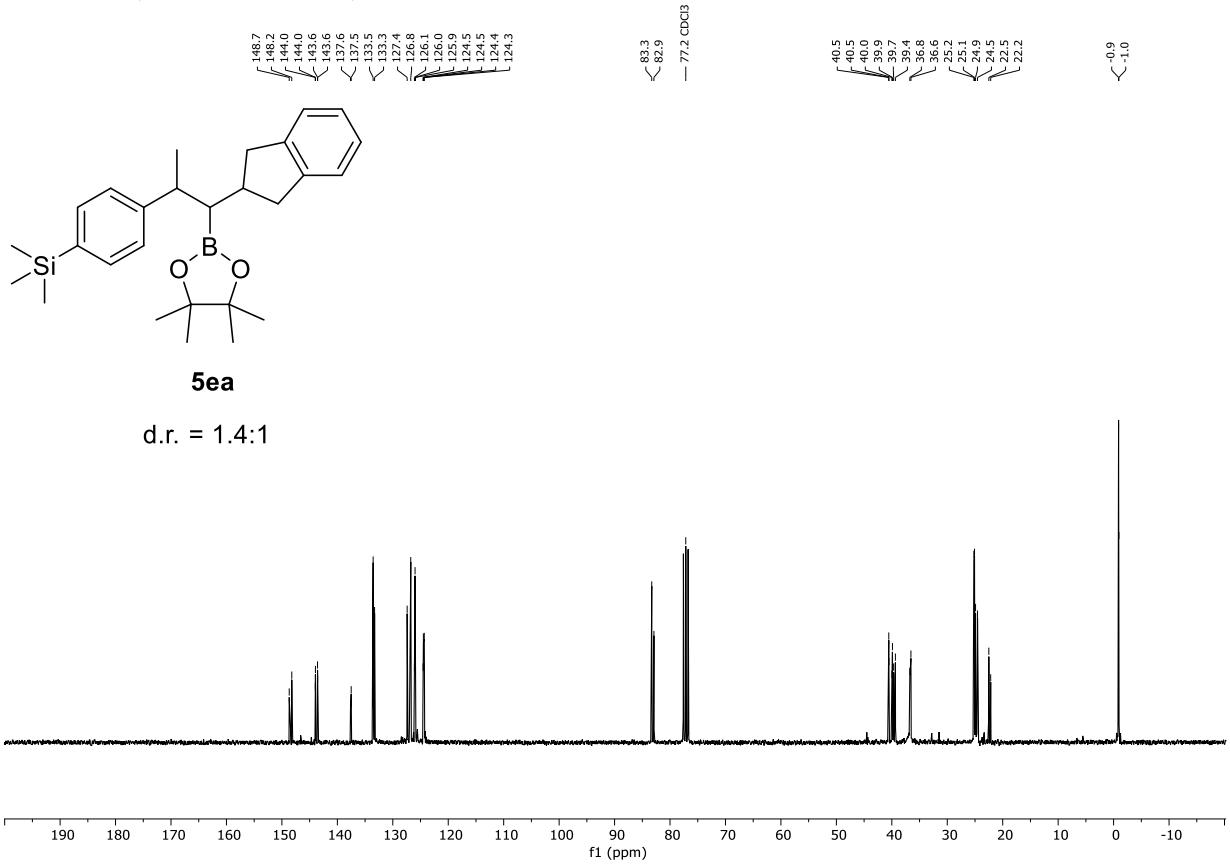
^{1}H-NMR (400 MHz, $CDCl_3$):



5ea

d.r. = 1.4:1

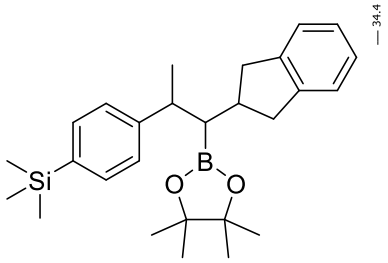
^{13}C-NMR (101 MHz, $CDCl_3$):



5ea

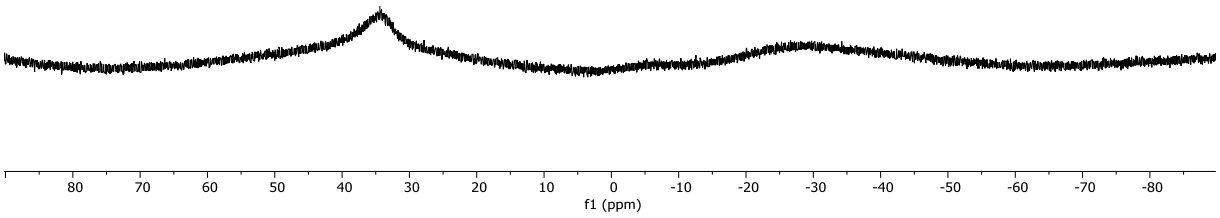
d.r. = 1.4:1

^{11}B NMR (128 MHz, $CDCl_3$):

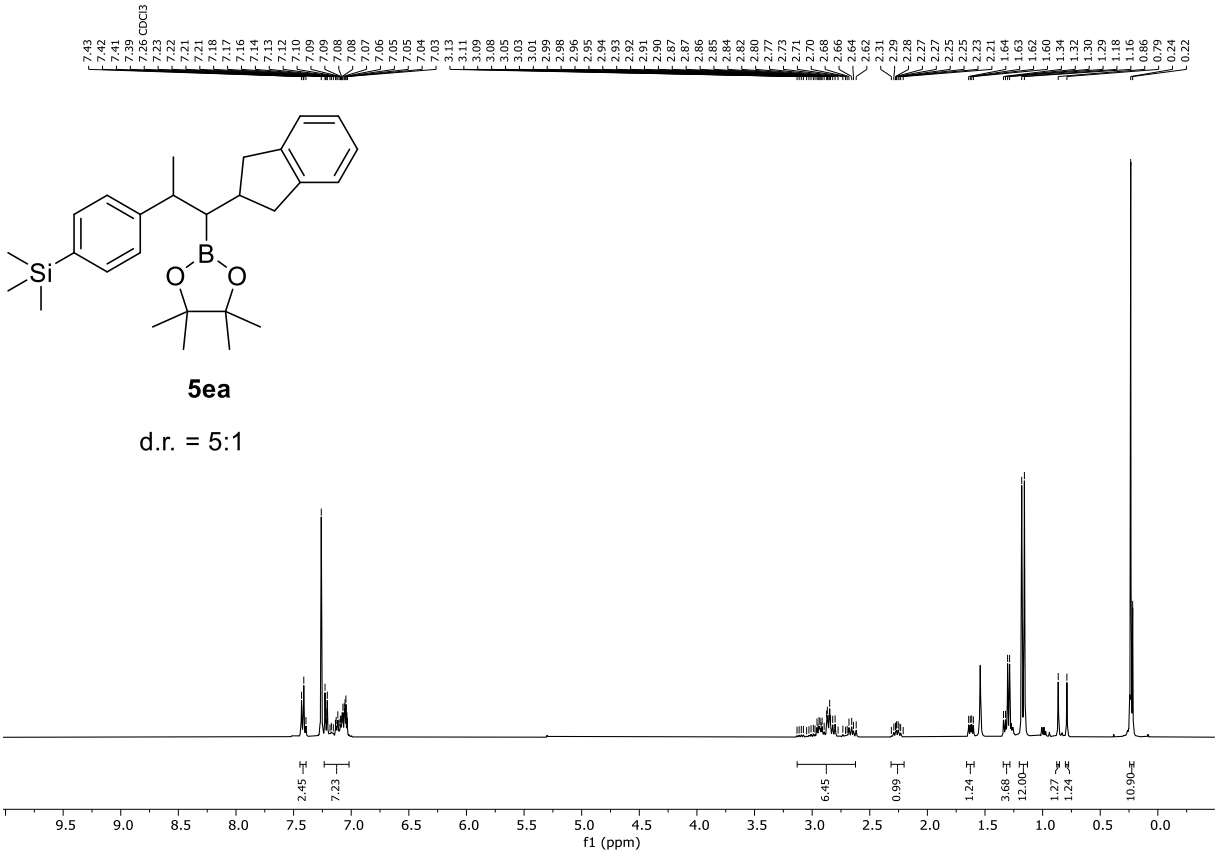


5ea

d.r. = 1.4:1



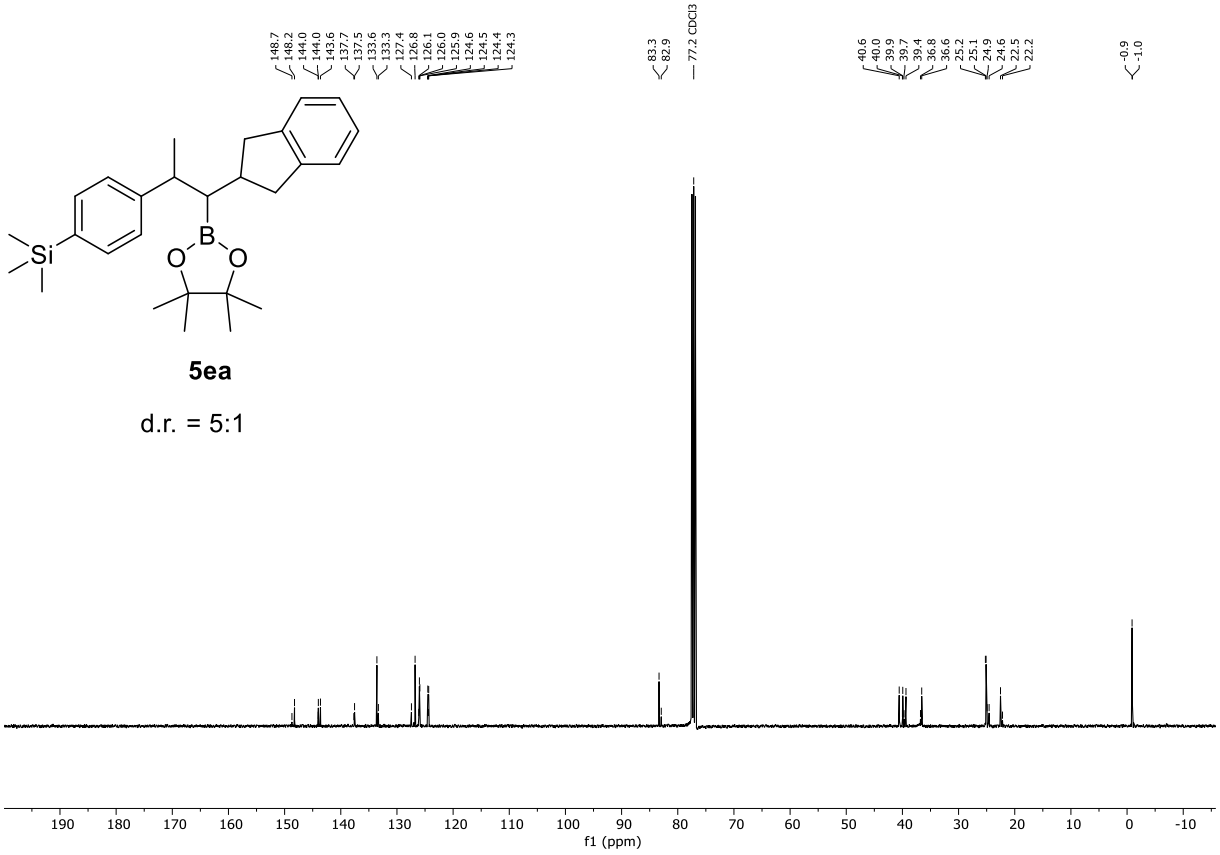
^{1}H-NMR (400 MHz, $CDCl_3$):



5ea

d.r. = 5:1

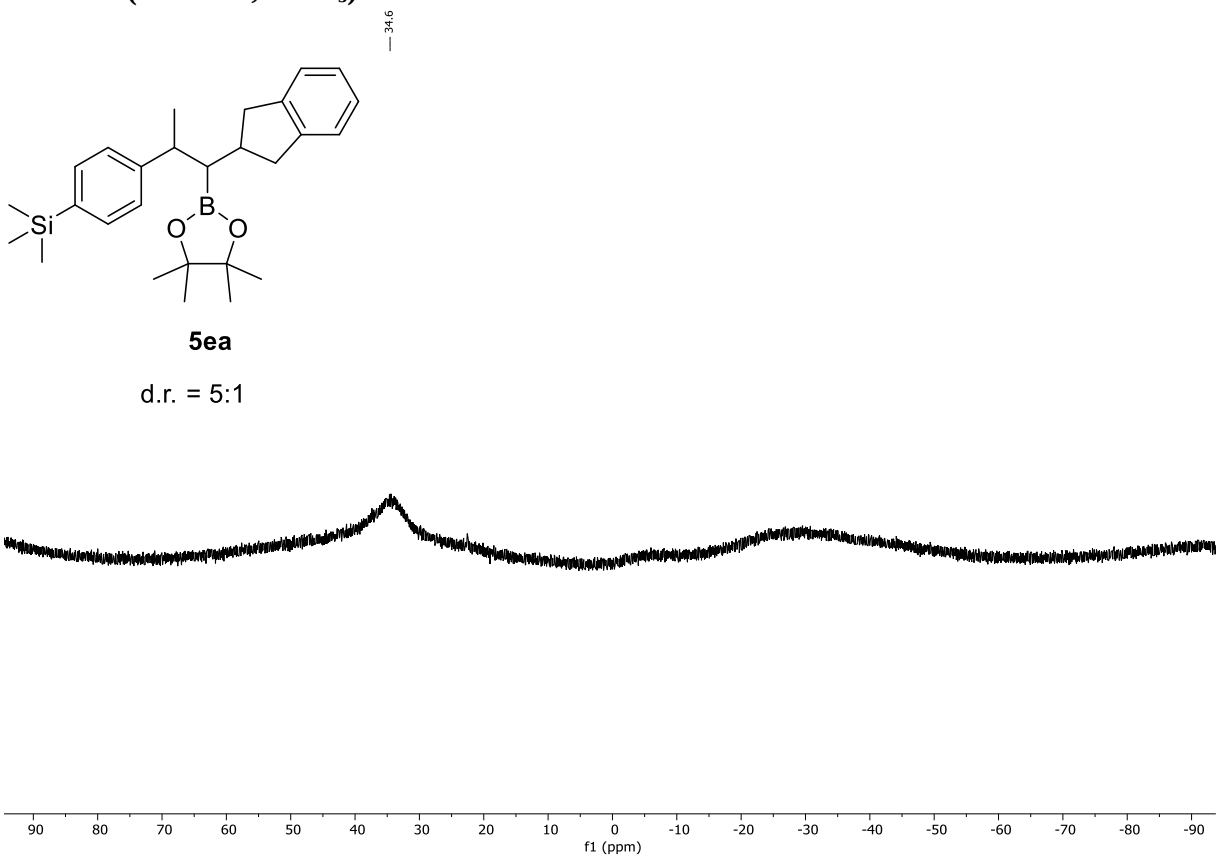
^{13}C-NMR (101 MHz, $CDCl_3$):



5ea

d.r. = 5:1

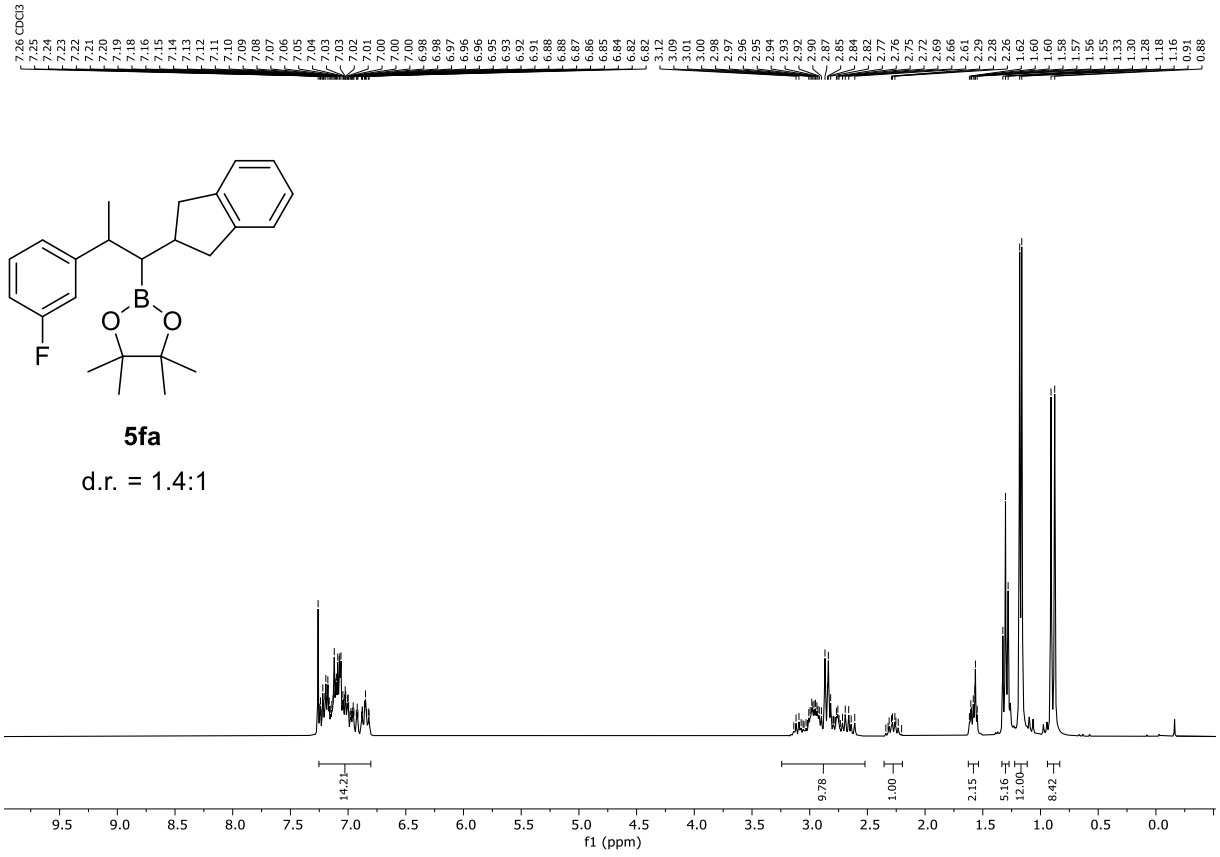
^{11}B NMR (128 MHz, $CDCl_3$):



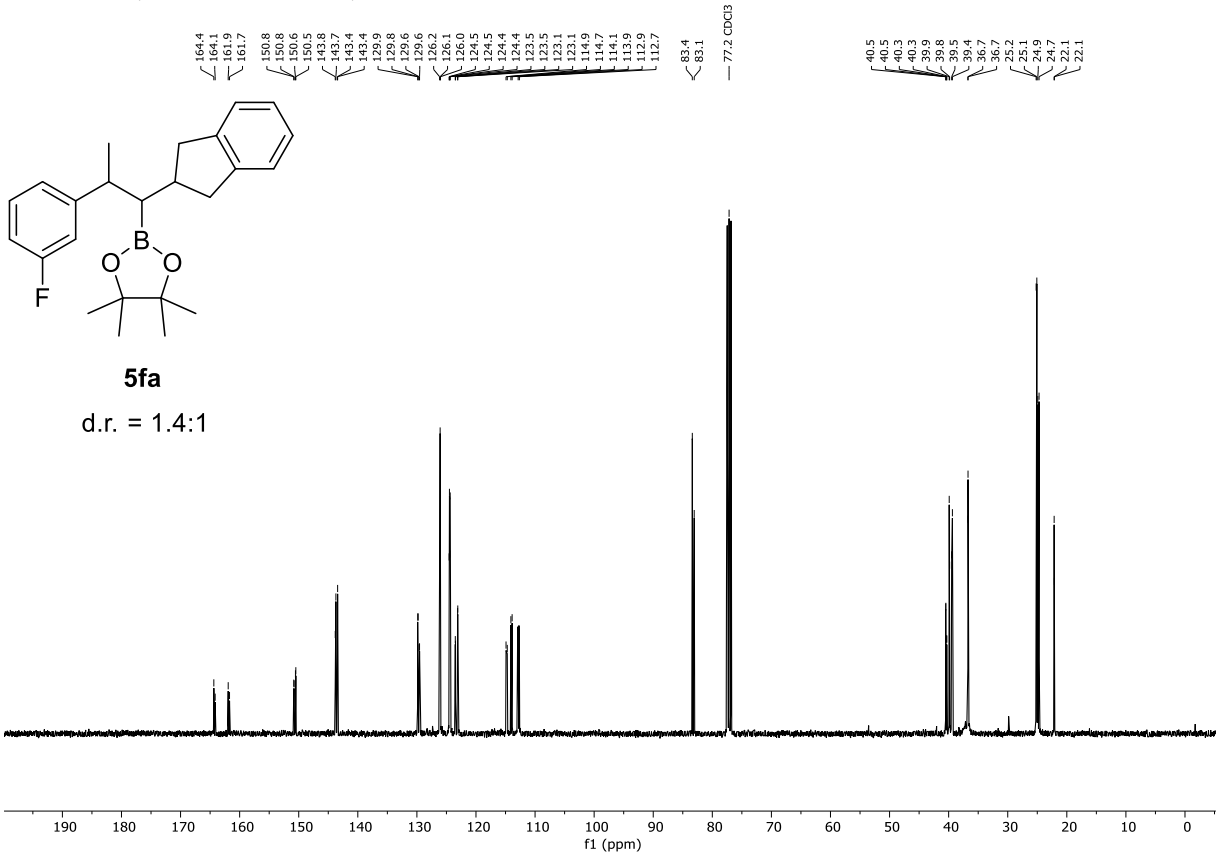
5ea

d.r. = 5:1

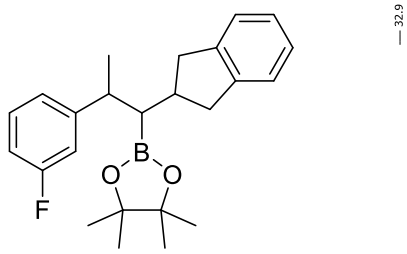
^{1}H-NMR (400 MHz, $CDCl_3$):



^{13}C-NMR (101 MHz, $CDCl_3$):

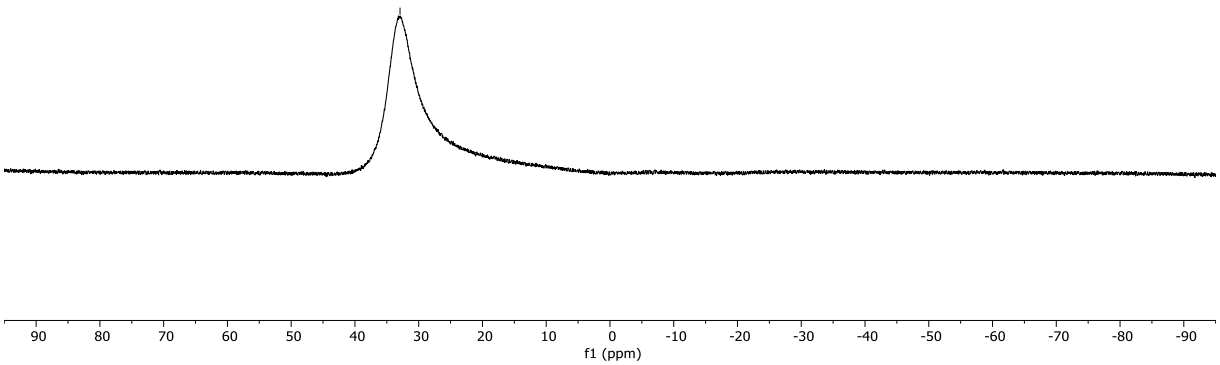


^{11}B NMR (128 MHz, $CDCl_3$):

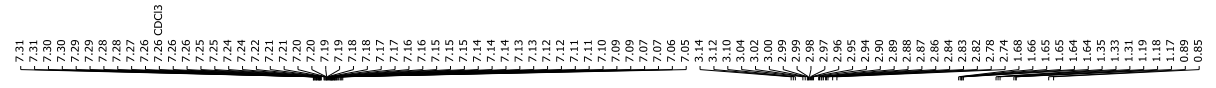


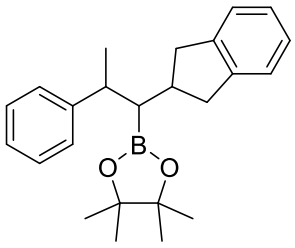
5fa

d.r. = 1.4:1



^{1}H-NMR (400 MHz, $CDCl_3$):

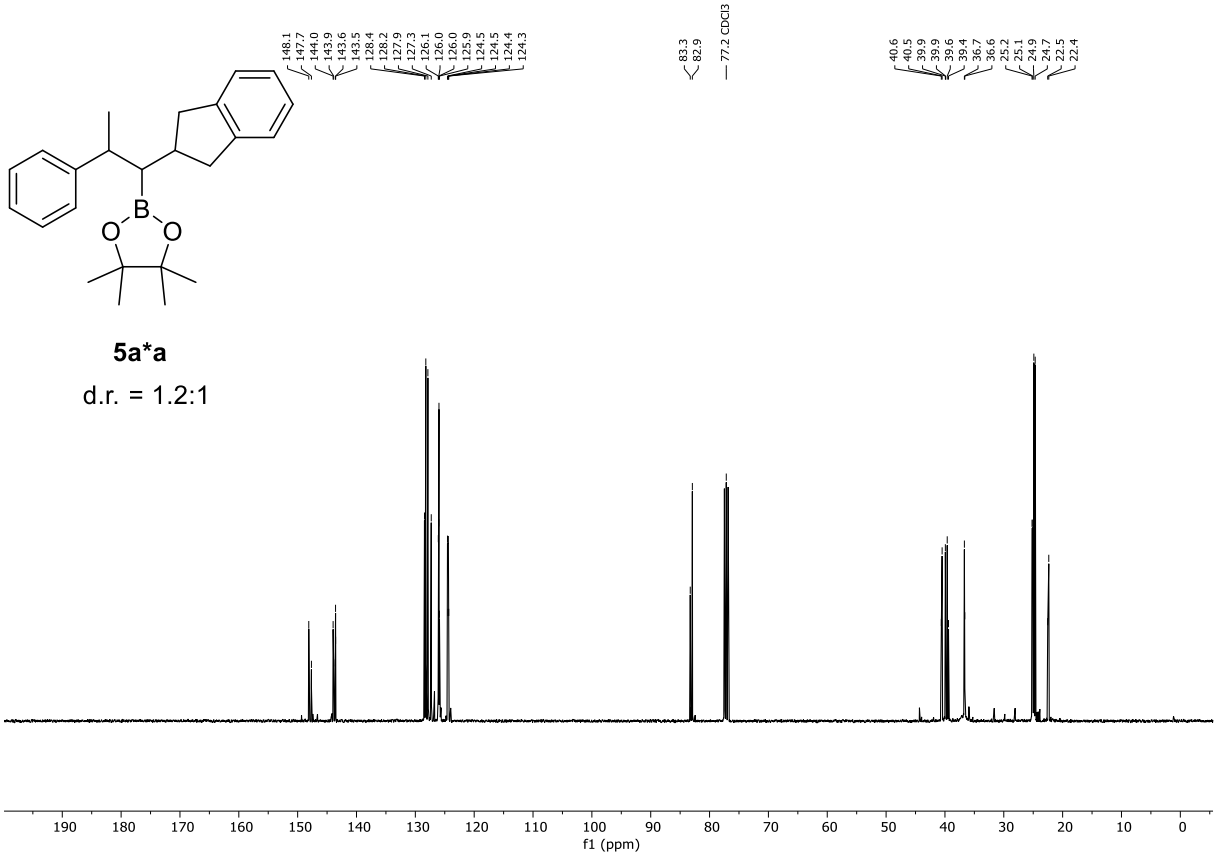




5a*a

d.r. = 1.2:1

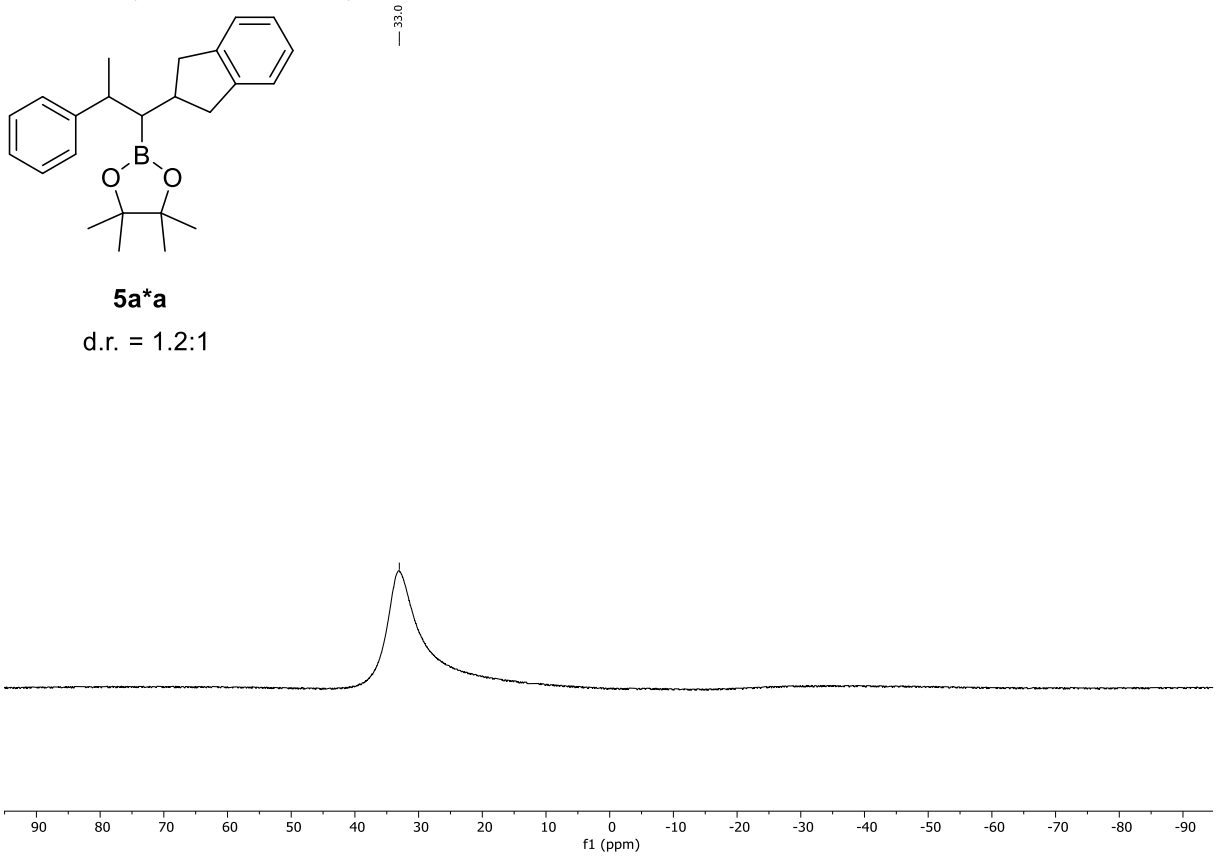
^{13}C-NMR (101 MHz, $CDCl_3$):



5a*a

d.r. = 1.2:1

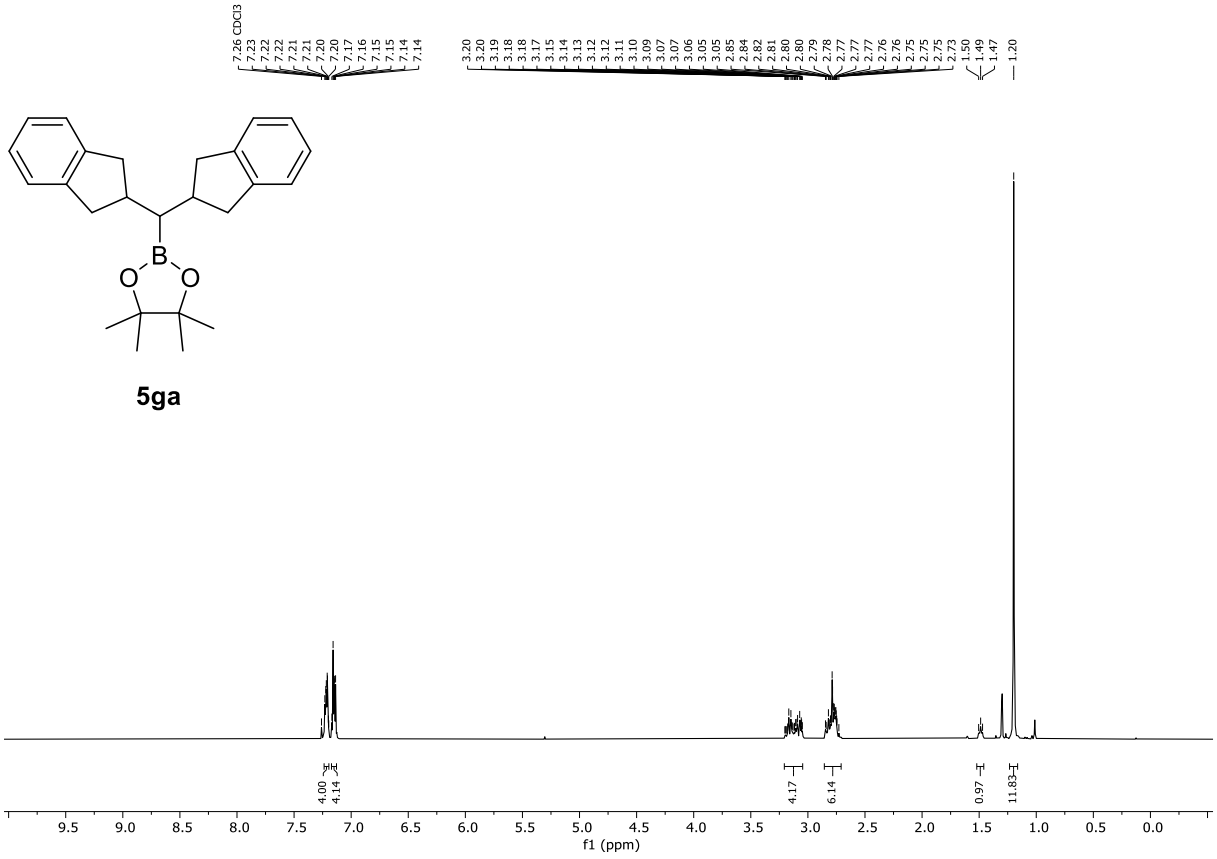
^{11}B NMR (128 MHz, $CDCl_3$):



5a*a

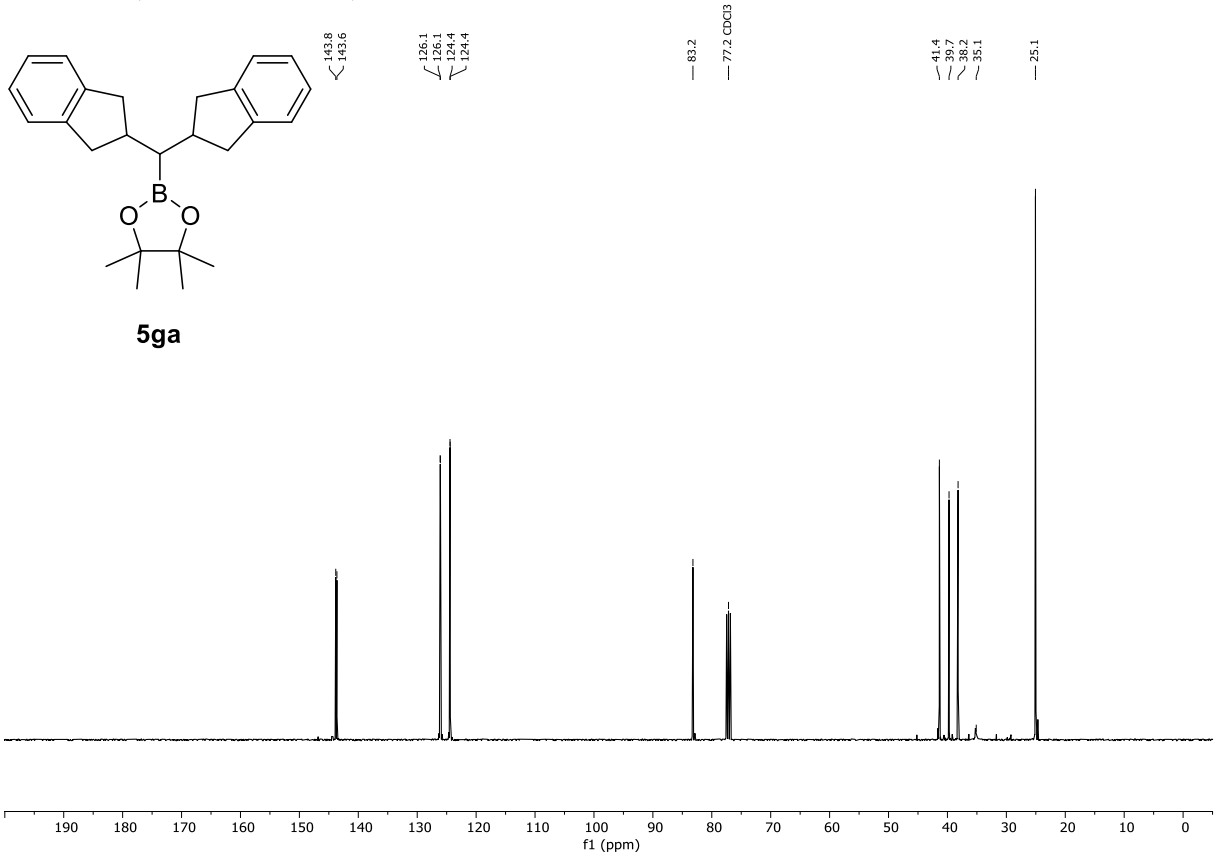
d.r. = 1.2:1

^{1}H-NMR (400 MHz, $CDCl_3$):



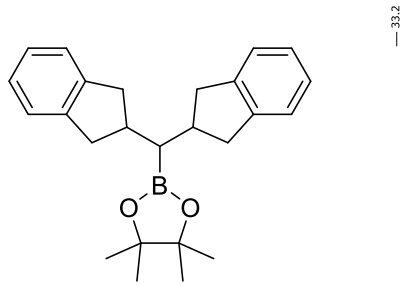
5ga

^{13}C-NMR (101 MHz, $CDCl_3$):

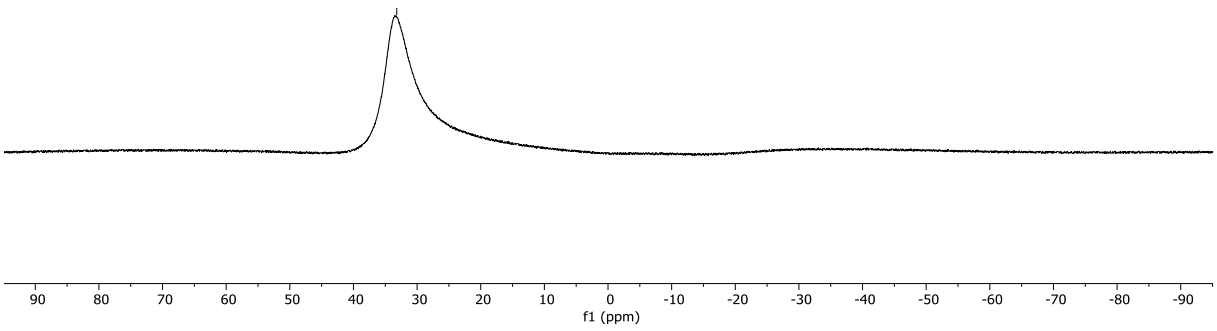


5ga

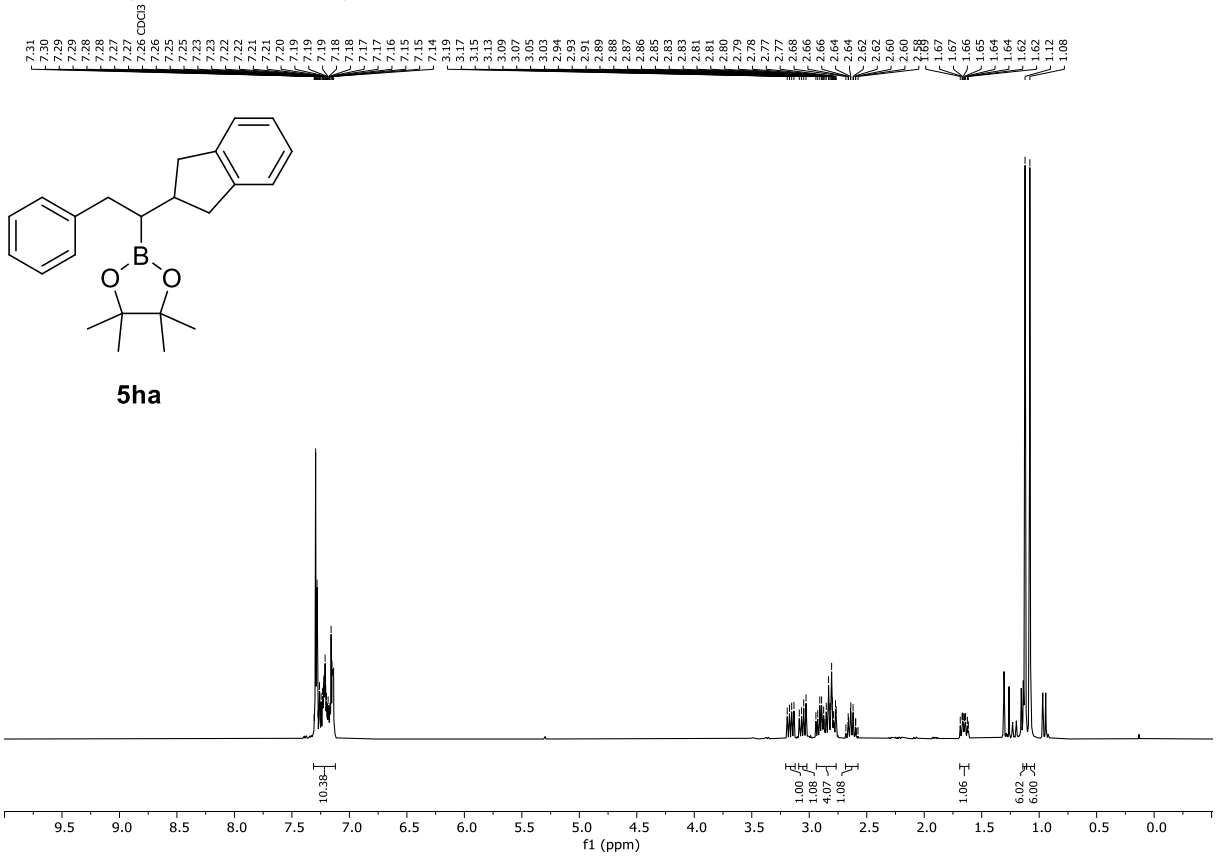
^{11}B NMR (128 MHz, $CDCl_3$):



5ga

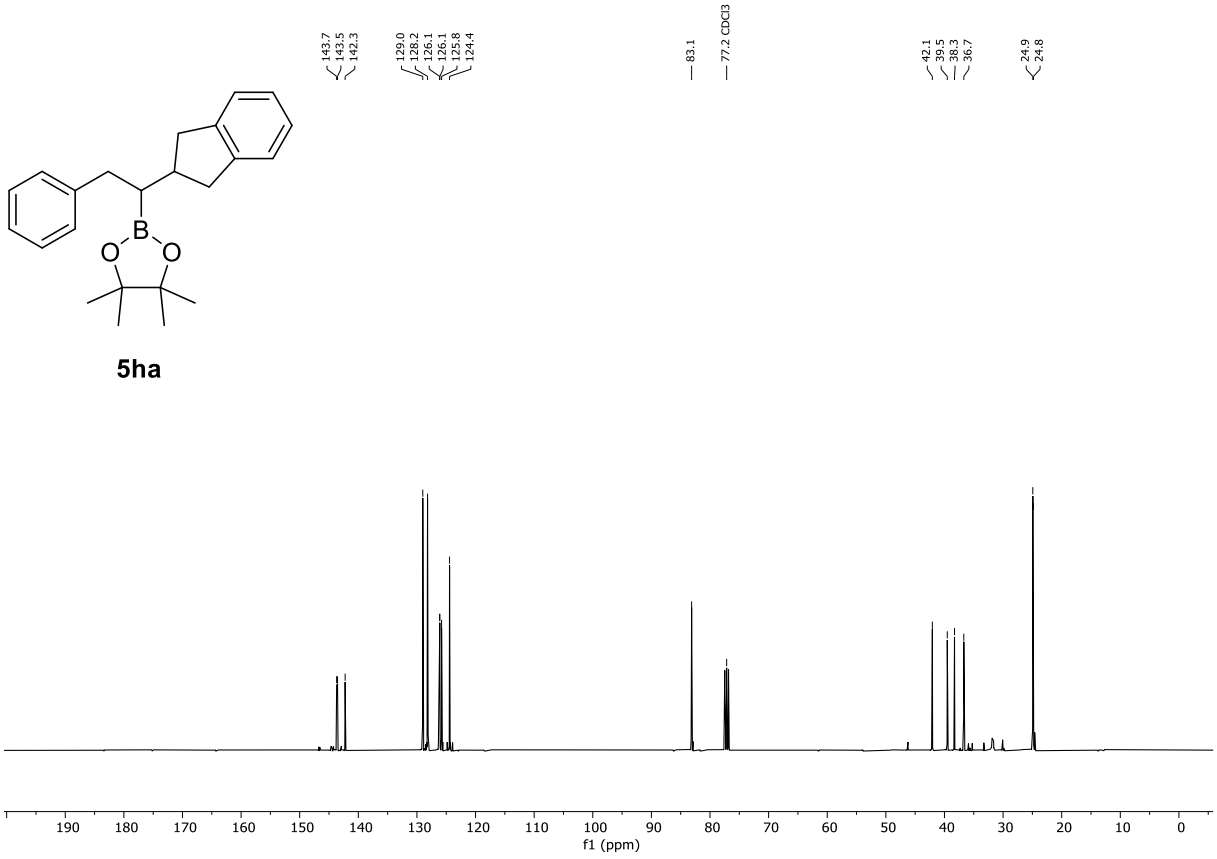


^{1}H-NMR (400 MHz, $CDCl_3$):



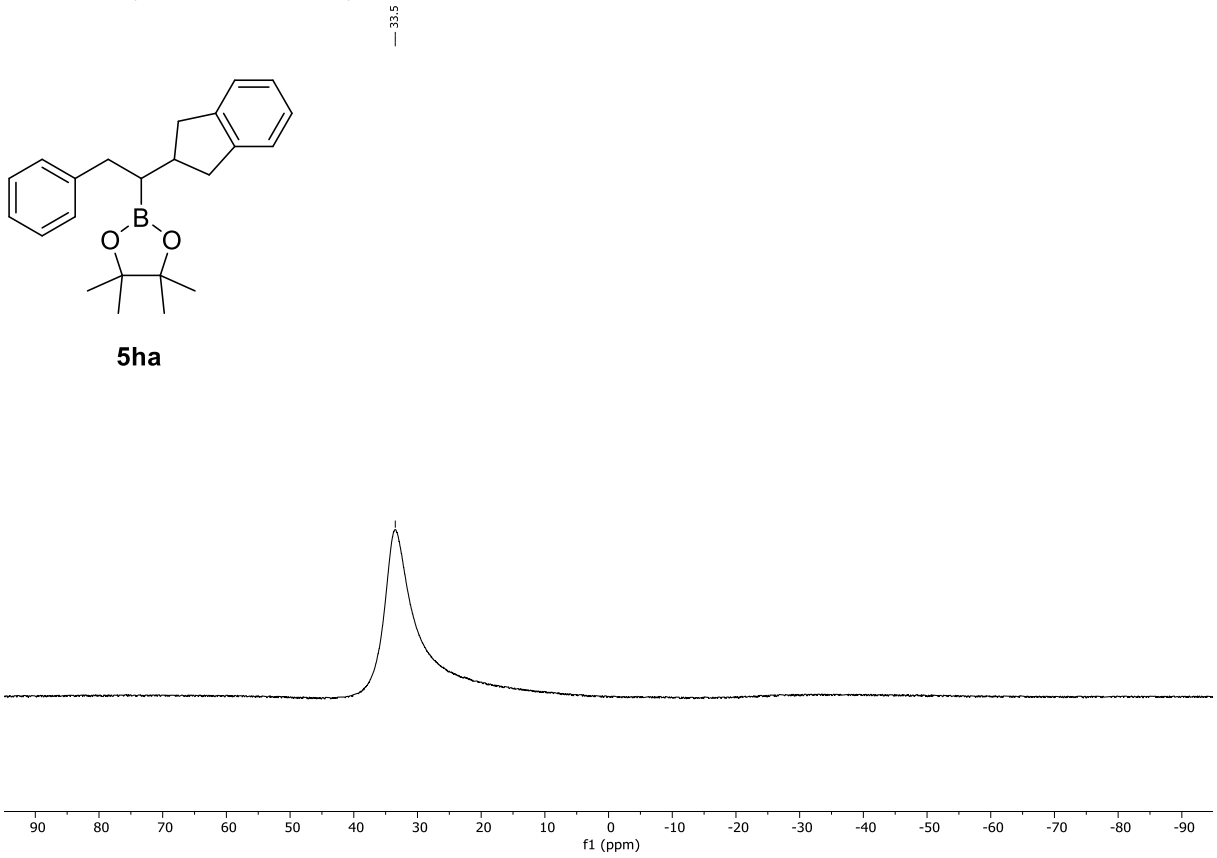
5ha

^{13}C-NMR (101 MHz, $CDCl_3$):



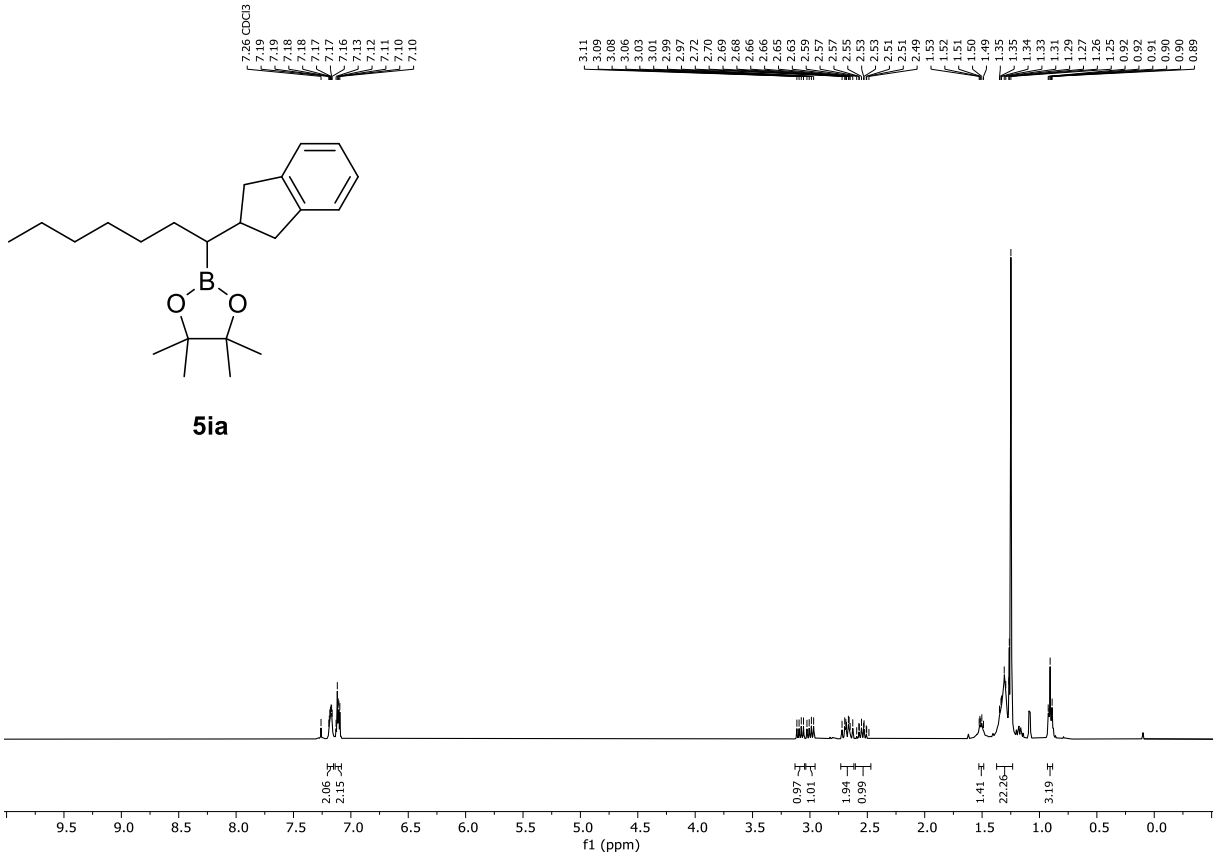
5ha

^{11}B NMR (128 MHz, $CDCl_3$):



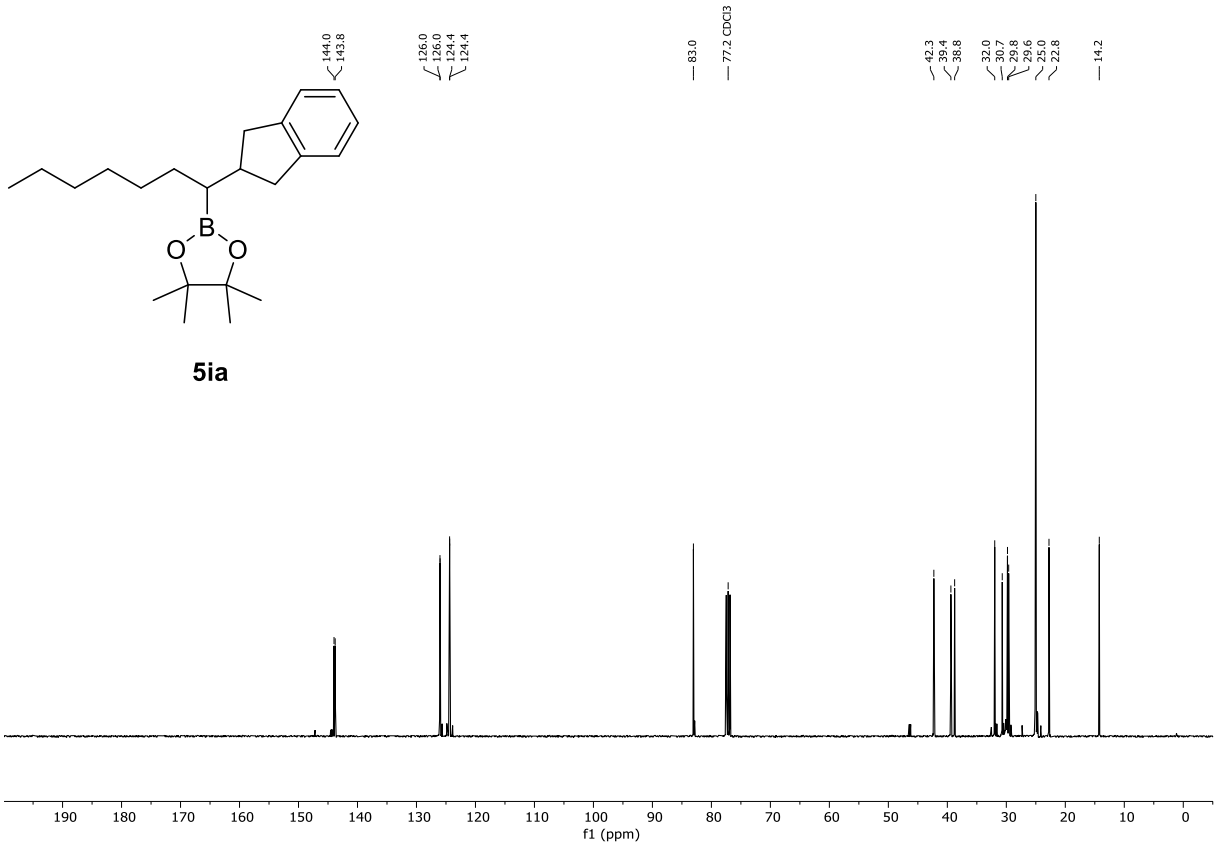
5ha

^{1}H-NMR (400 MHz, $CDCl_3$):



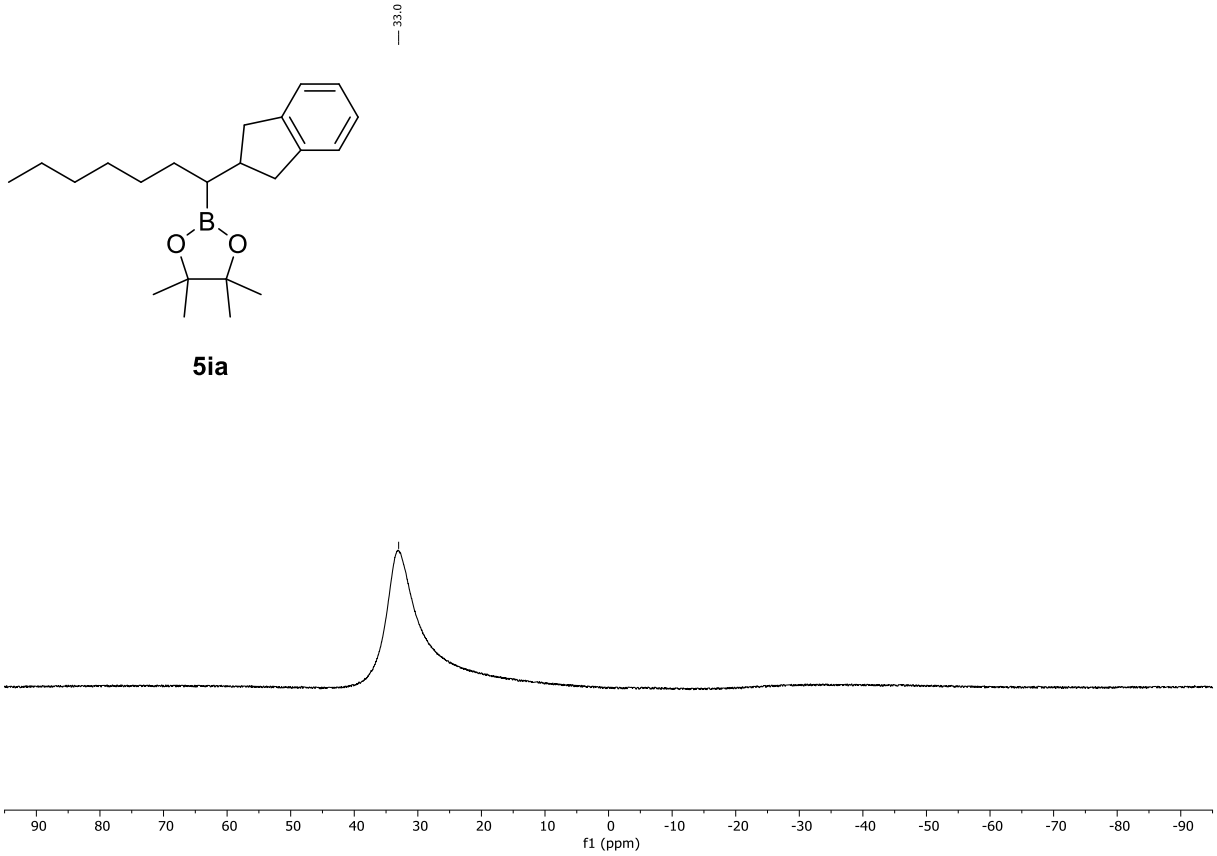
5ia

^{13}C-NMR (101 MHz, $CDCl_3$):



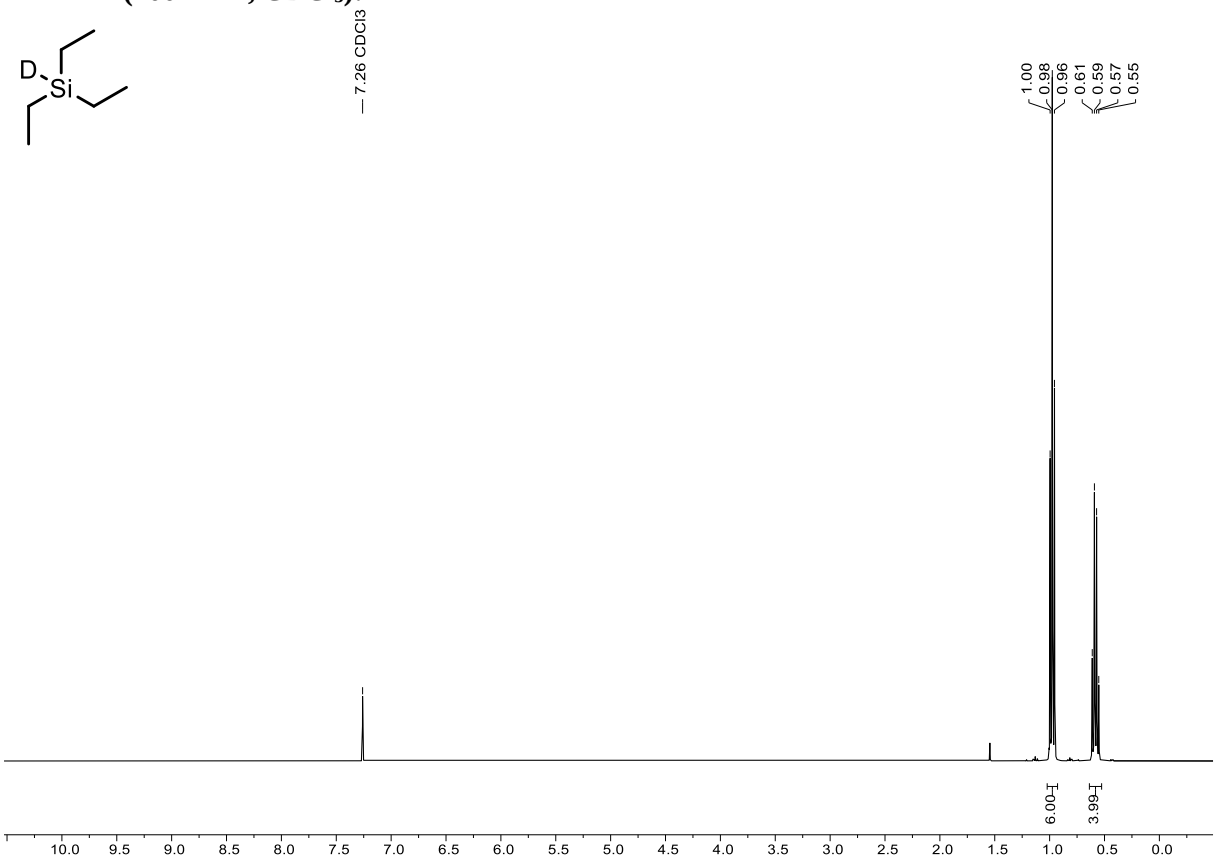
5ia

^{11}B NMR (128 MHz, $CDCl_3$):

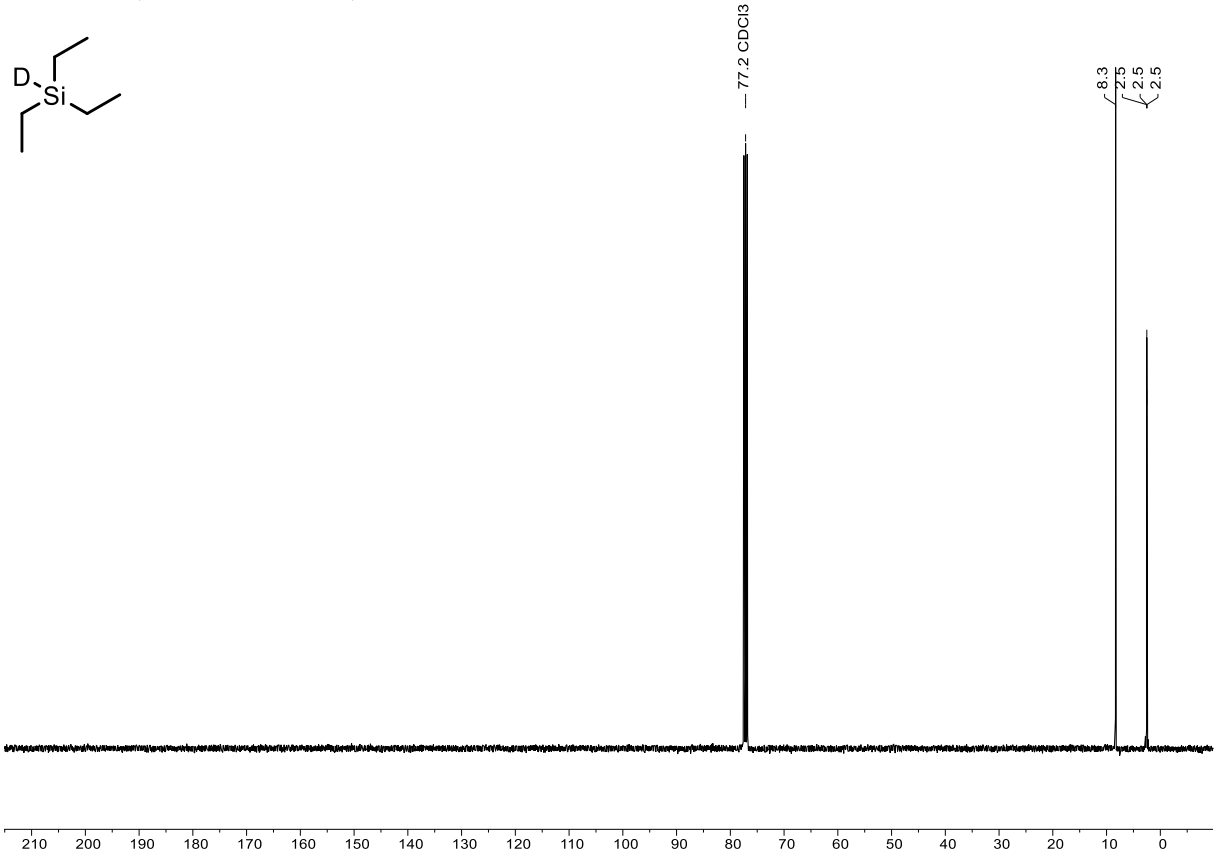


5ia

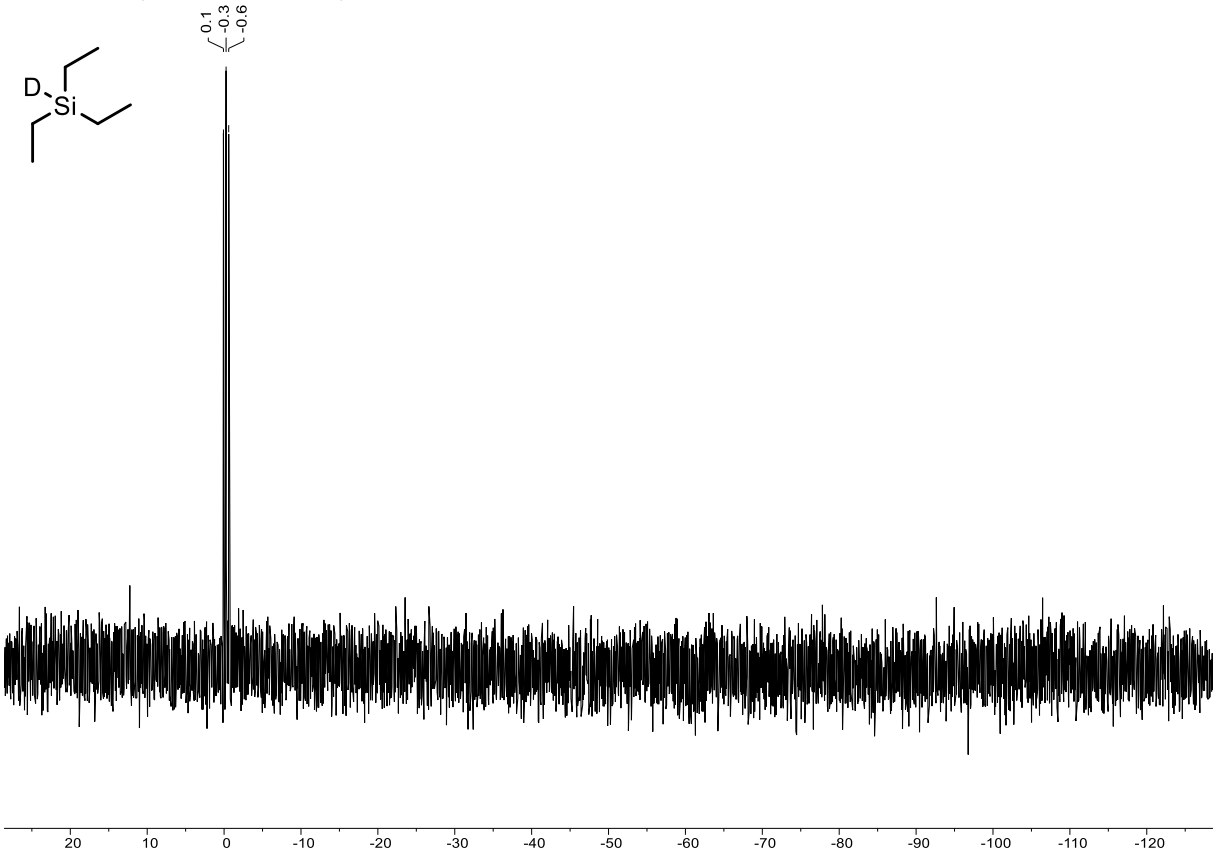
^{1}H-NMR (400 MHz, $CDCl_3$):



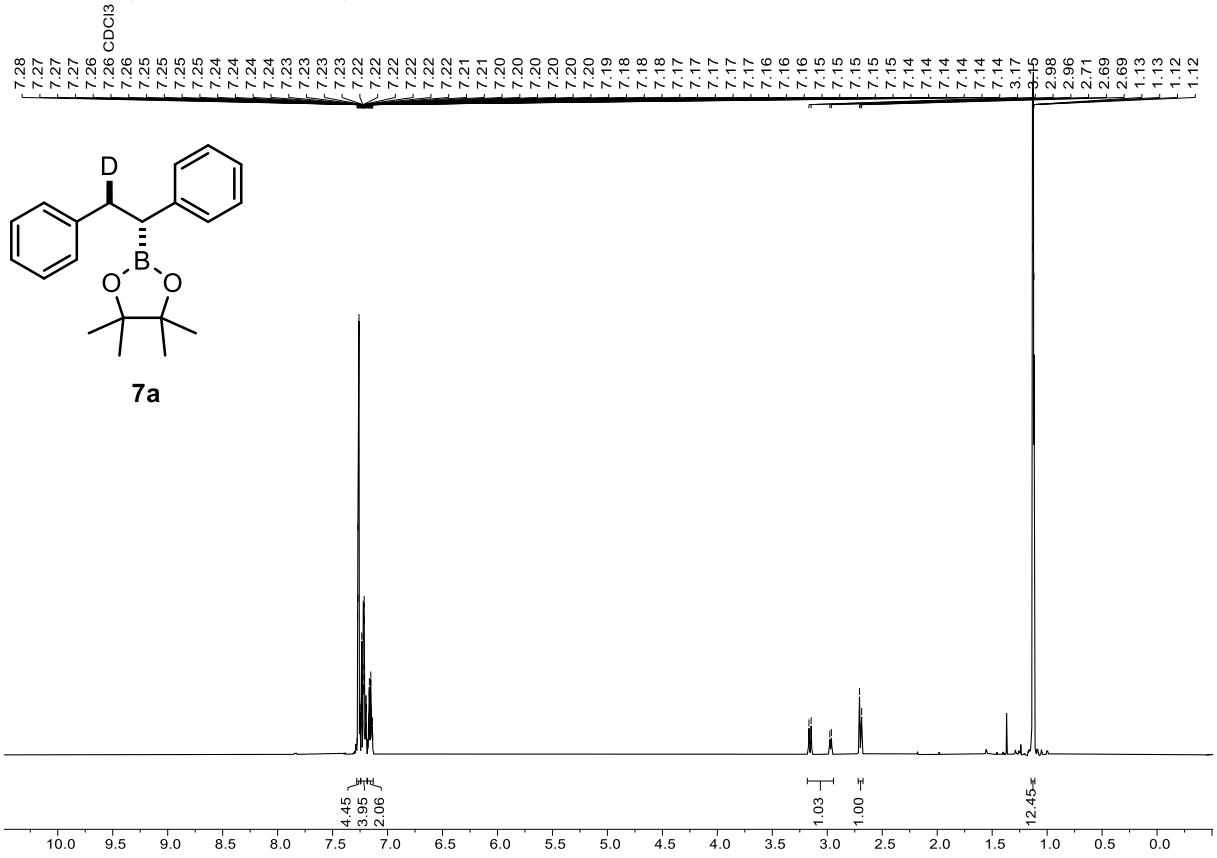
^{13}C-NMR (101 MHz, $CDCl_3$):



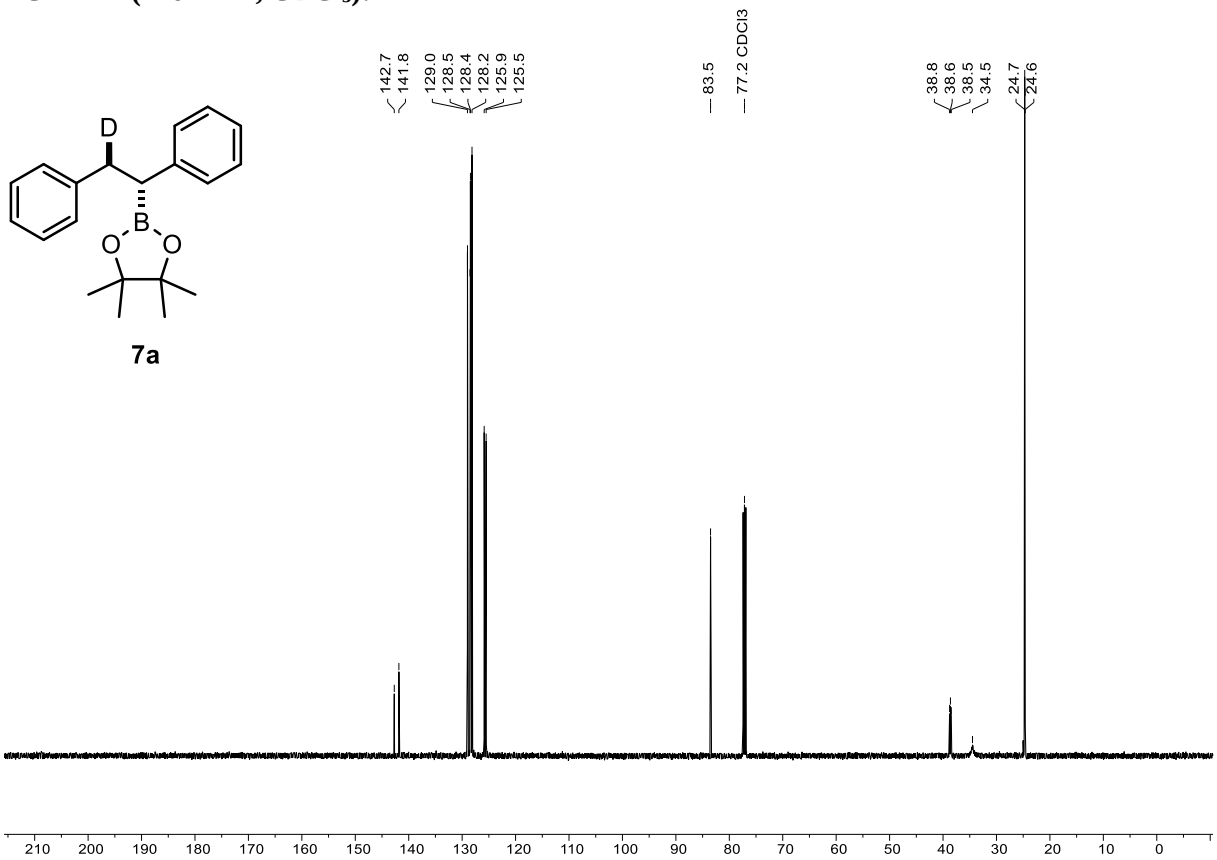
^{29}Si-NMR (79 MHz, $CDCl_3$):



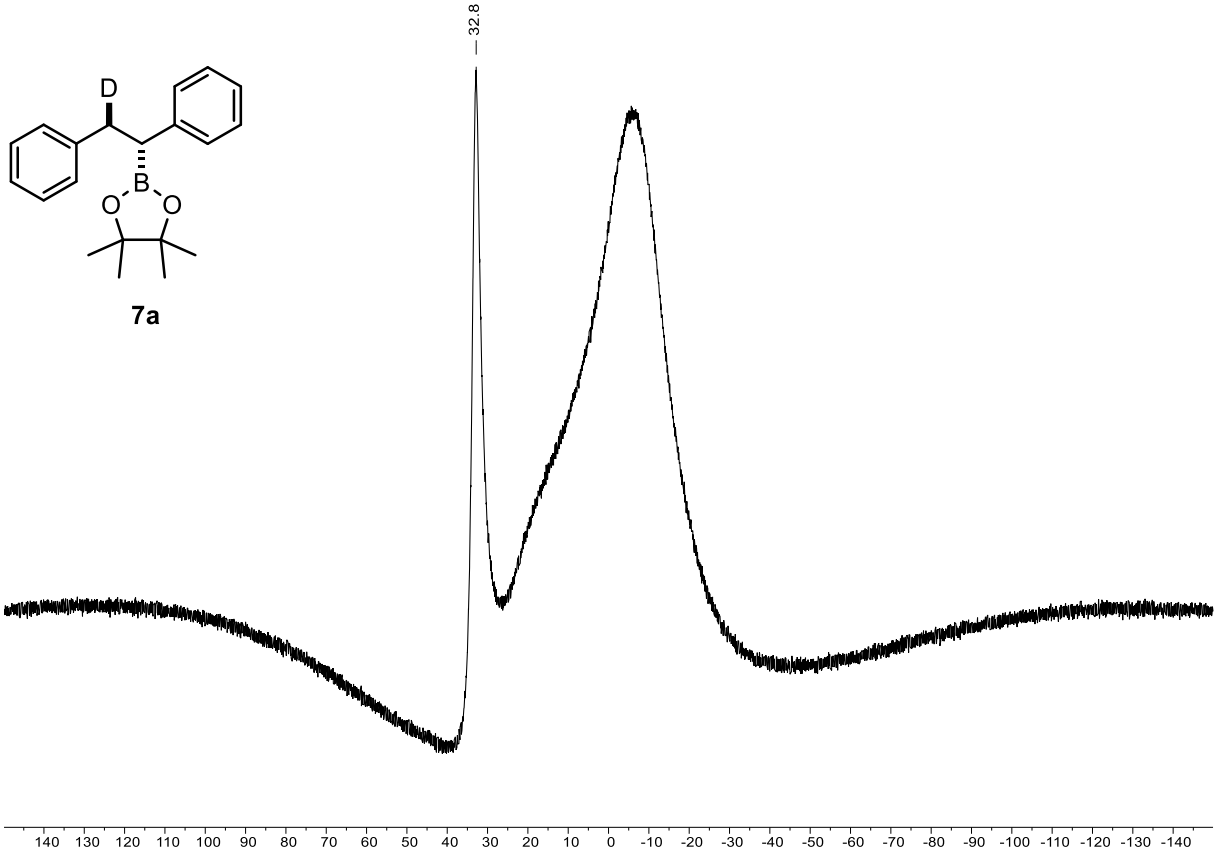
^{1}H-NMR (500 MHz, $CDCl_3$):



^{13}C-NMR (126 MHz, $CDCl_3$):

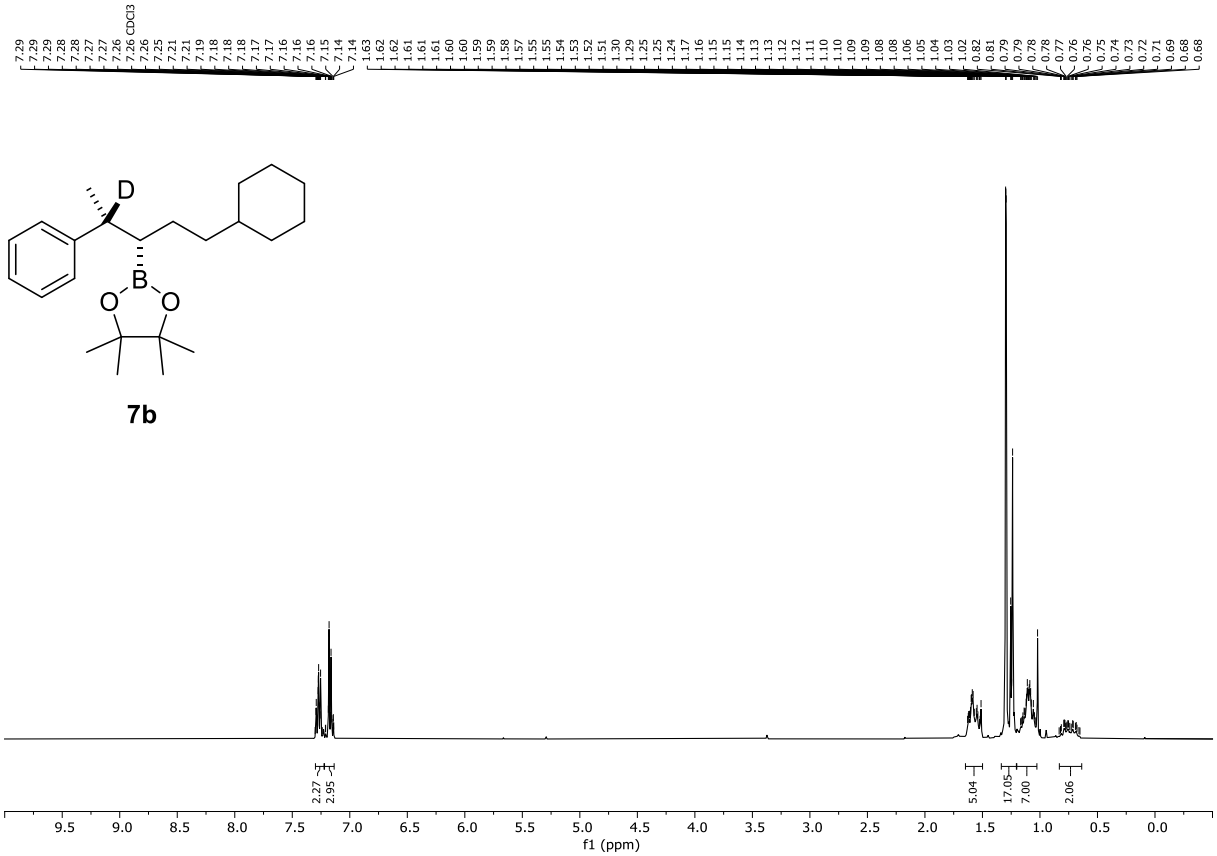


^{11}B-NMR (160 MHz, $CDCl_3$):



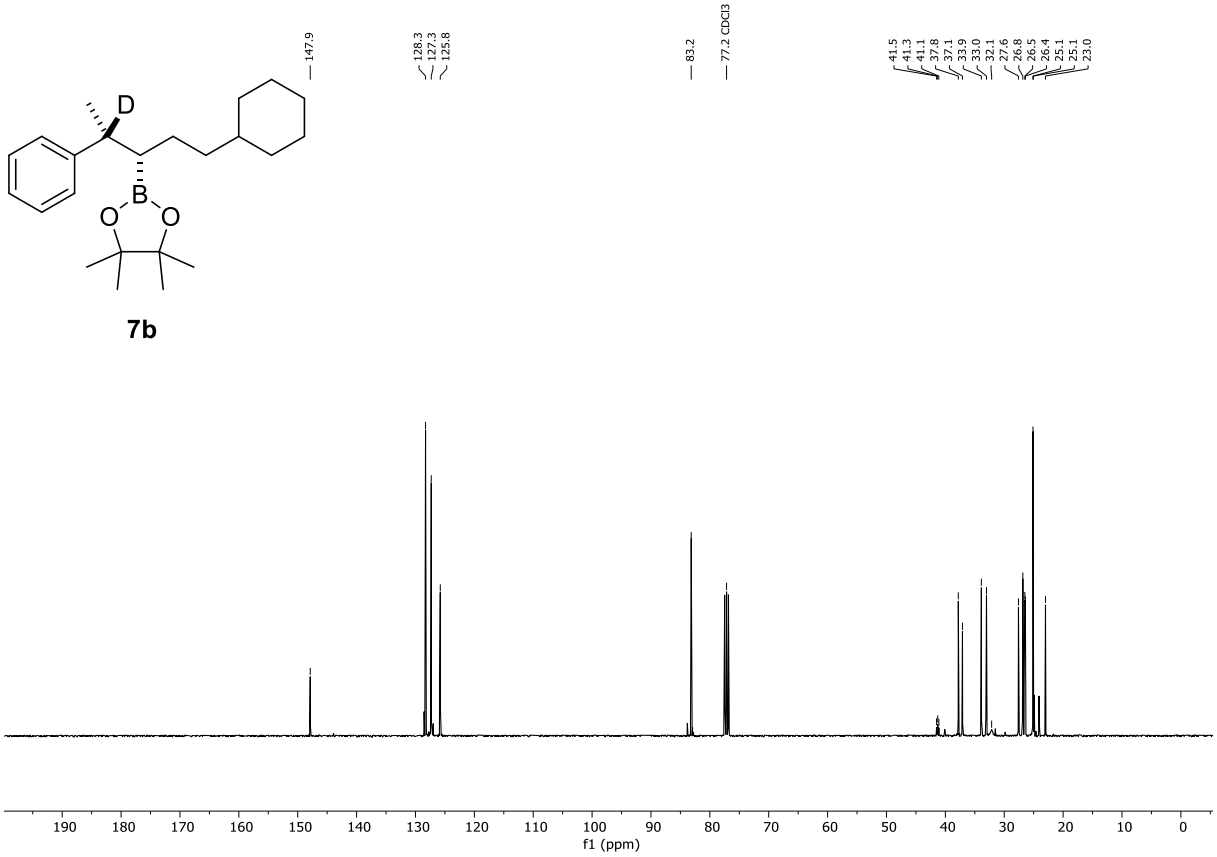
7a

^{1}H-NMR (400 MHz, $CDCl_3$):



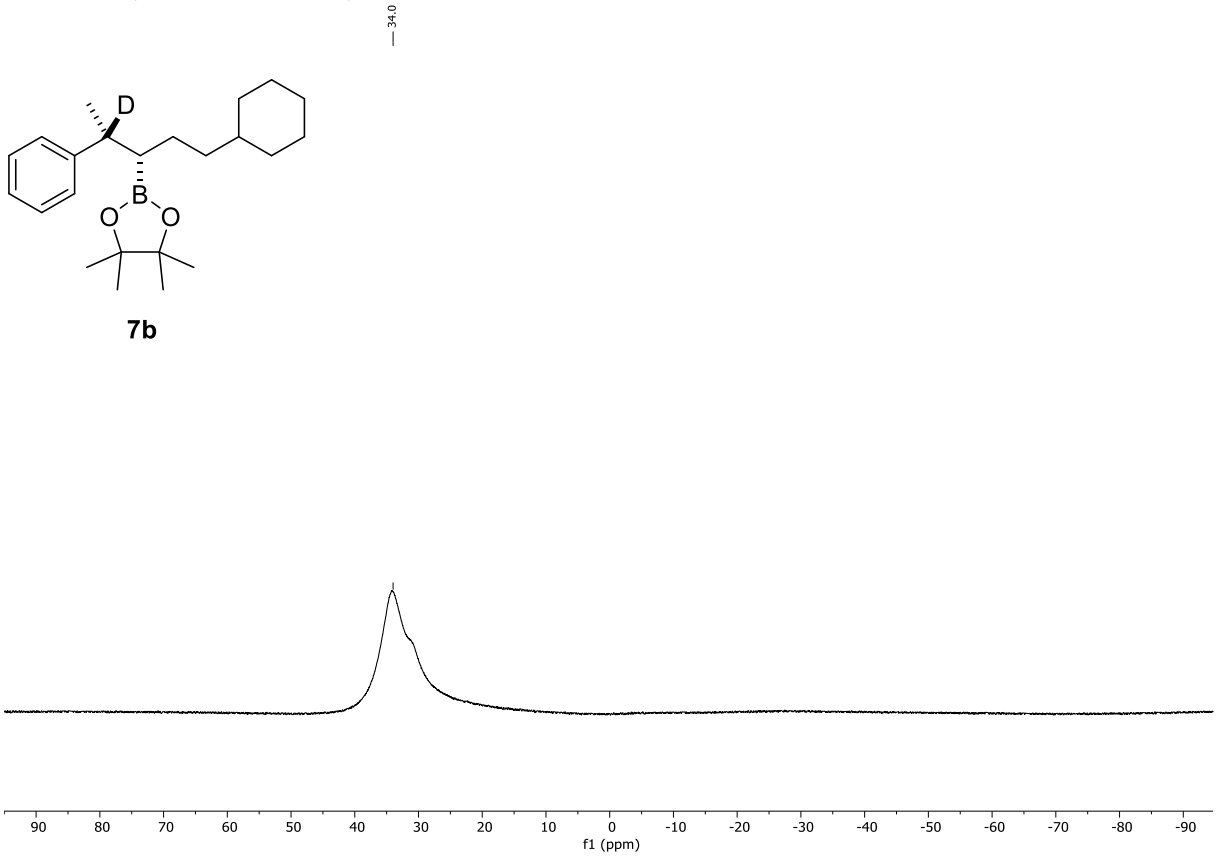
7b

^{13}C-NMR (101 MHz, $CDCl_3$):



7b

^{11}B NMR (128 MHz, $CDCl_3$):

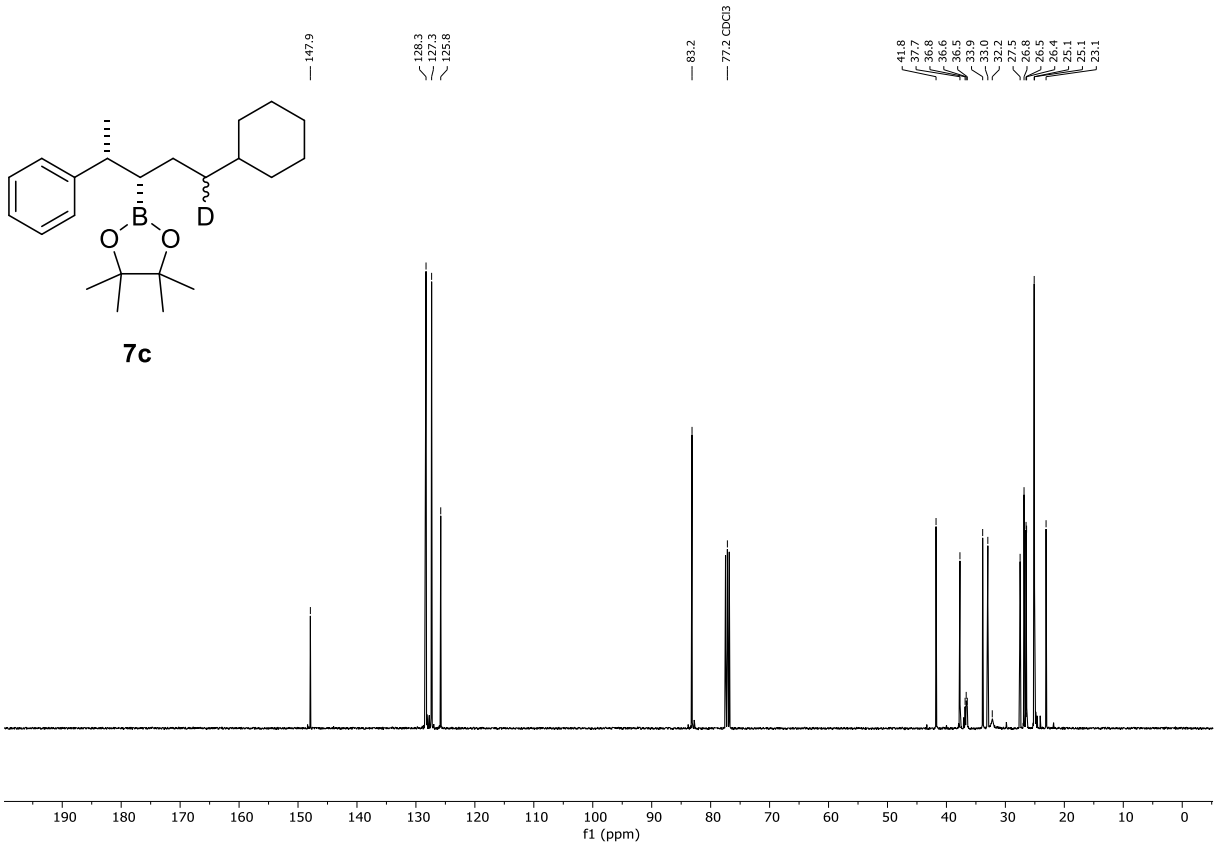


7b

^{1}H-NMR (400 MHz, $CDCl_3$):

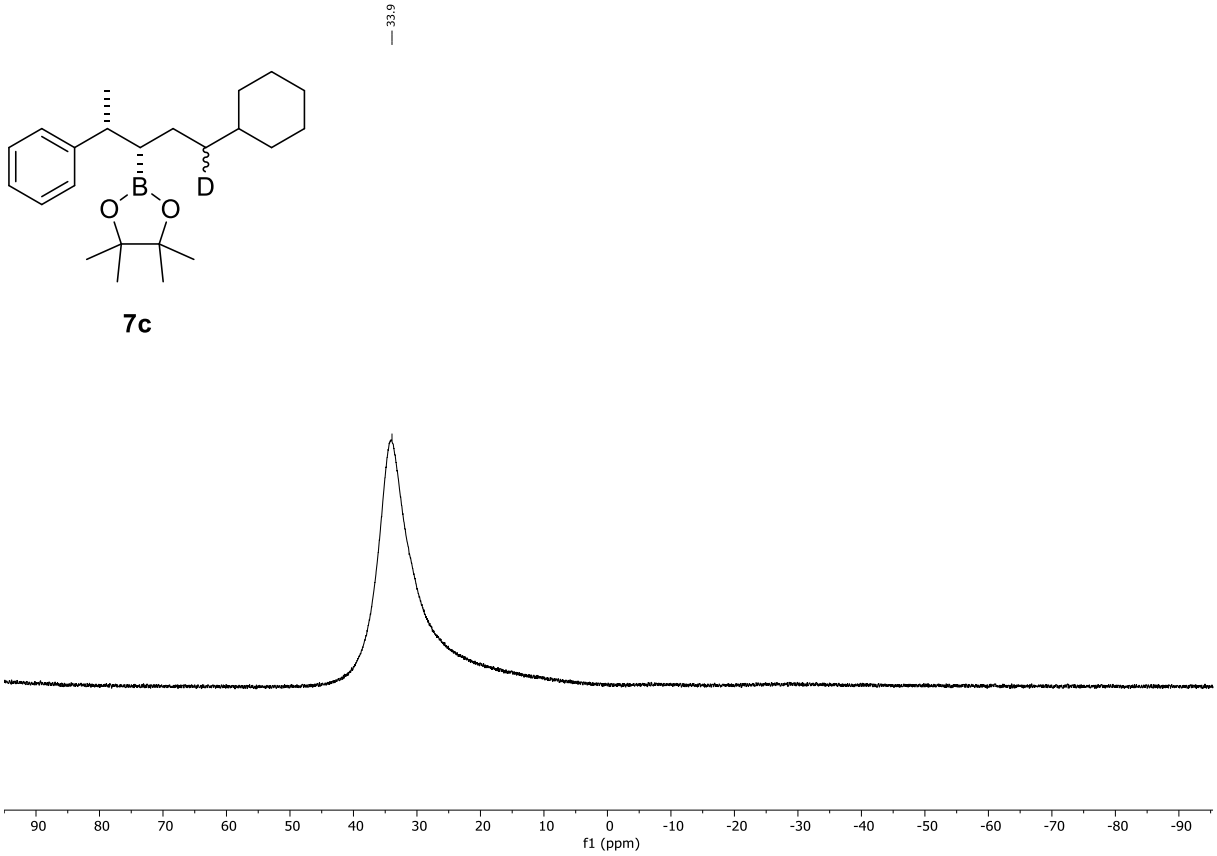
7c

^{13}C-NMR (101 MHz, $CDCl_3$):



7c

^{11}B NMR (128 MHz, $CDCl_3$):

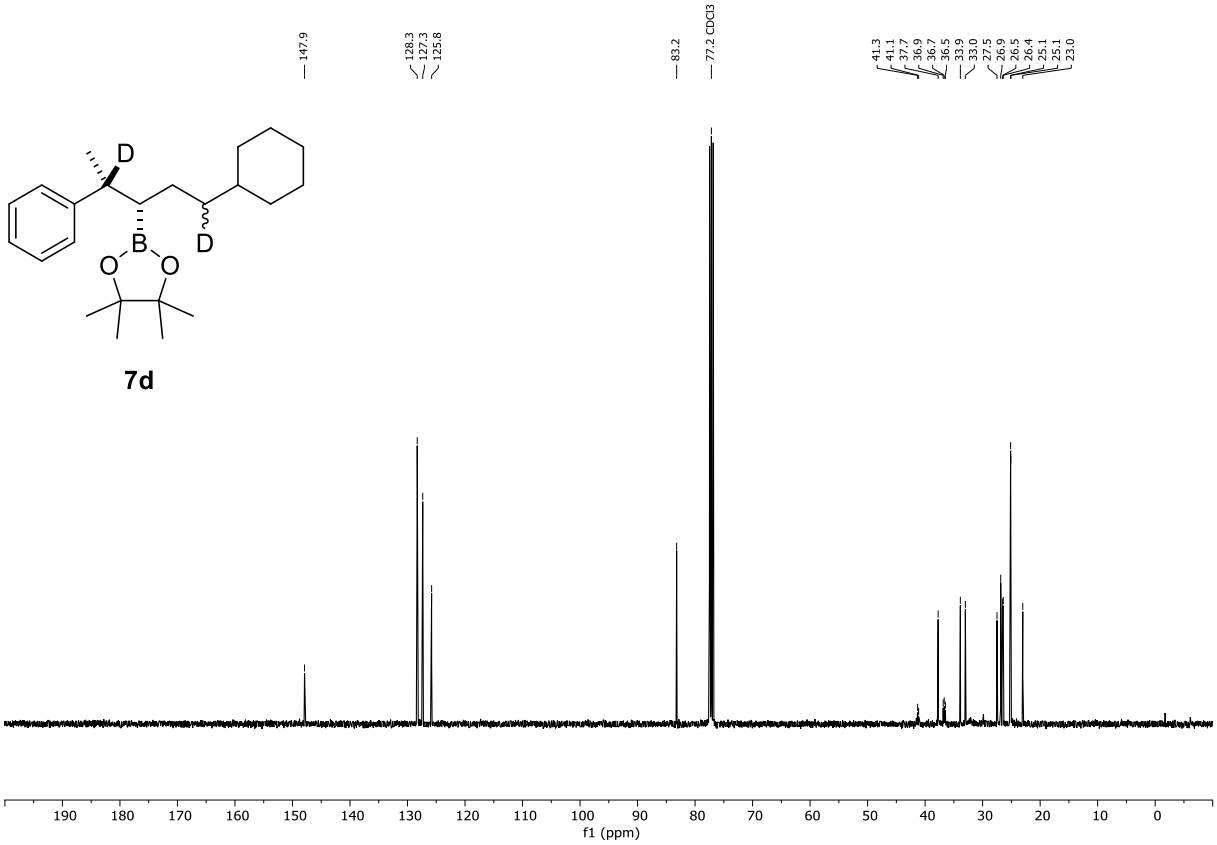


7c

^{1}H-NMR (400 MHz, $CDCl_3$):

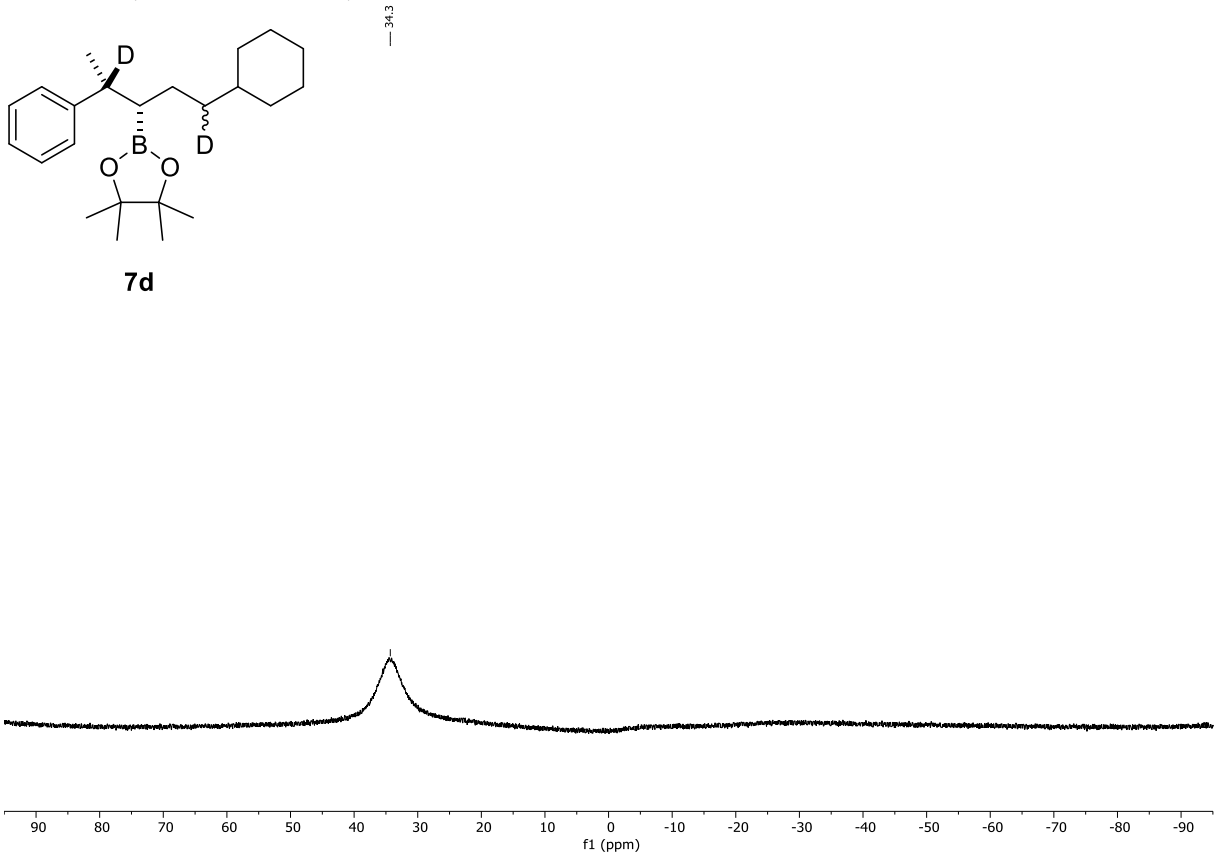
7d

^{13}C-NMR (101 MHz, $CDCl_3$):



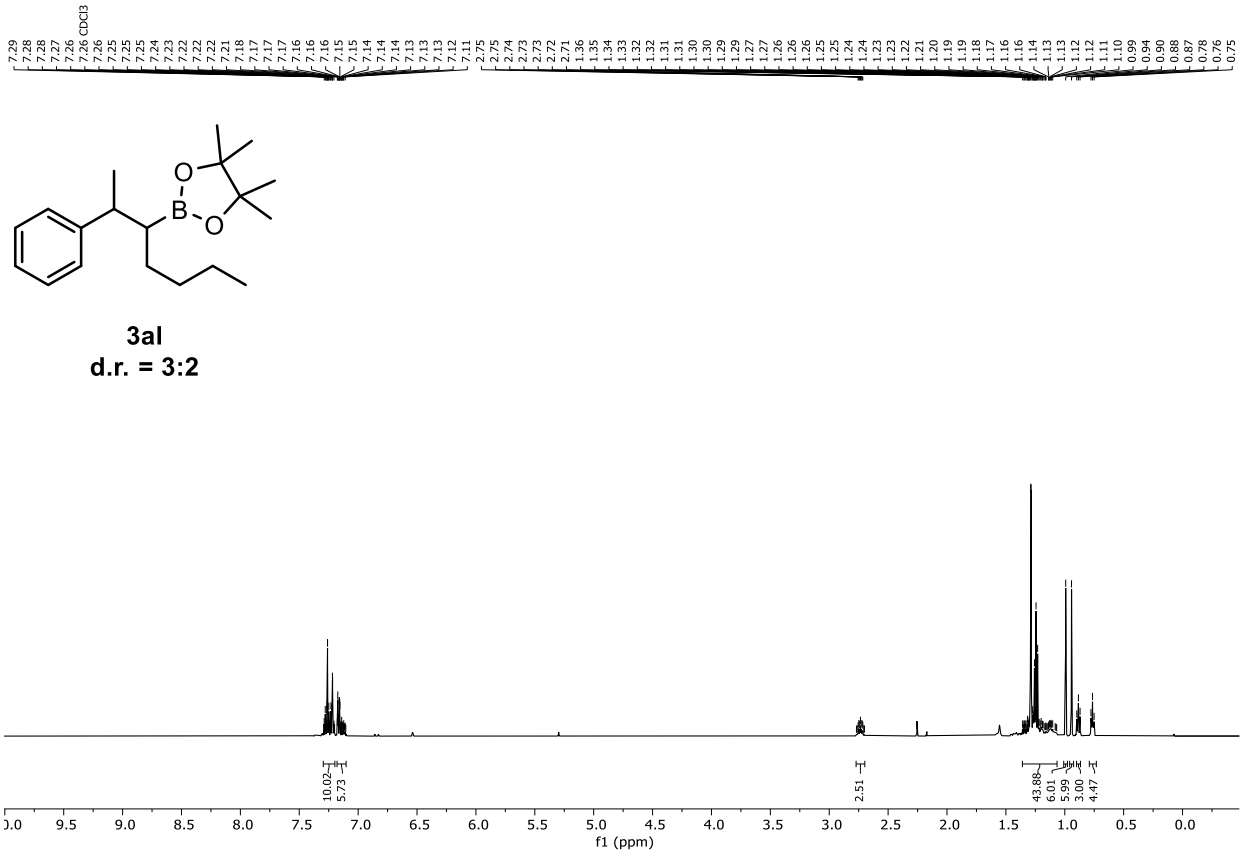
7d

^{11}B NMR (128 MHz, $CDCl_3$):



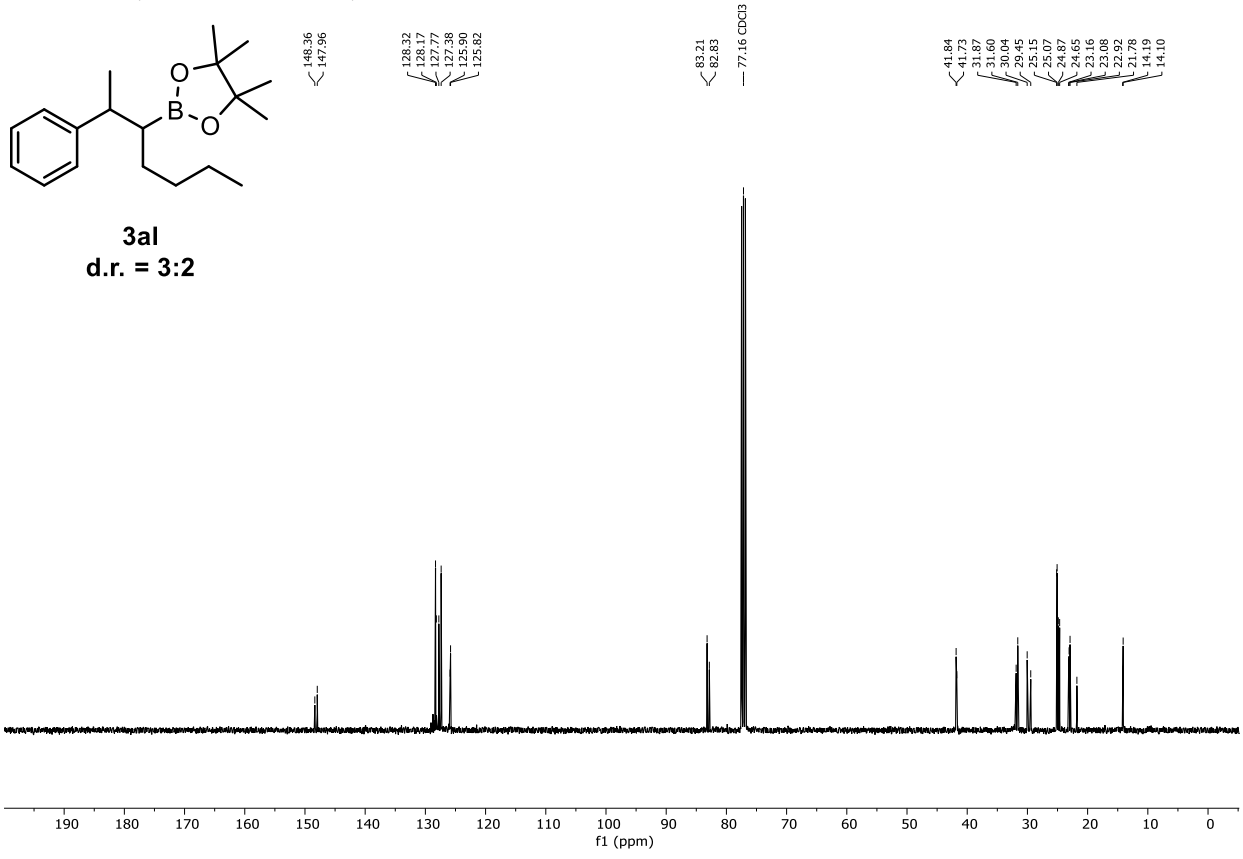
7d

^{1}H-NMR (300 MHz, $CDCl_3$):



3al
d.r. = 3:2

^{13}C-NMR (101 MHz, $CDCl_3$):



3al
d.r. = 3:2

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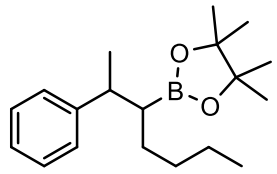

3al
d.r. = 3:2

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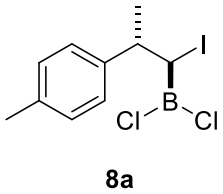
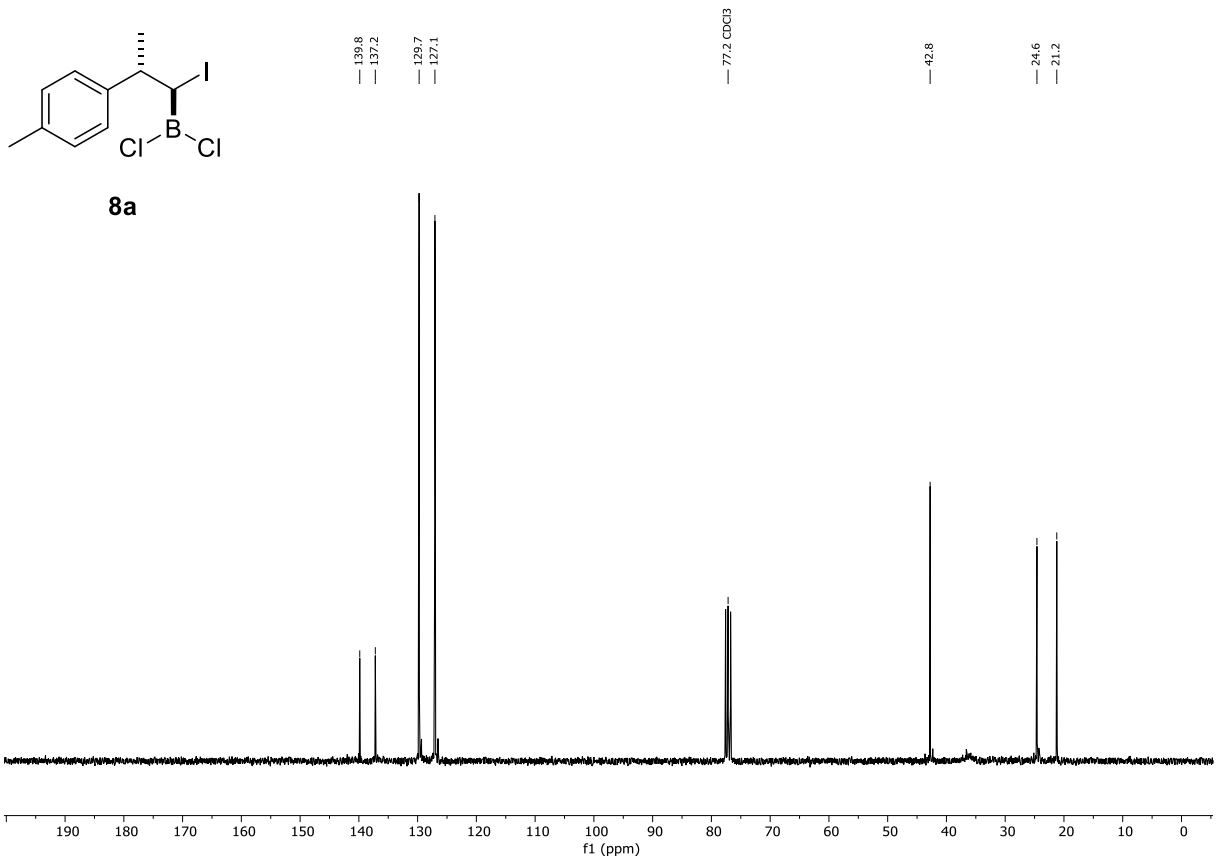


8a

^{13}C-NMR (101 MHz, $CDCl_3$):



8a

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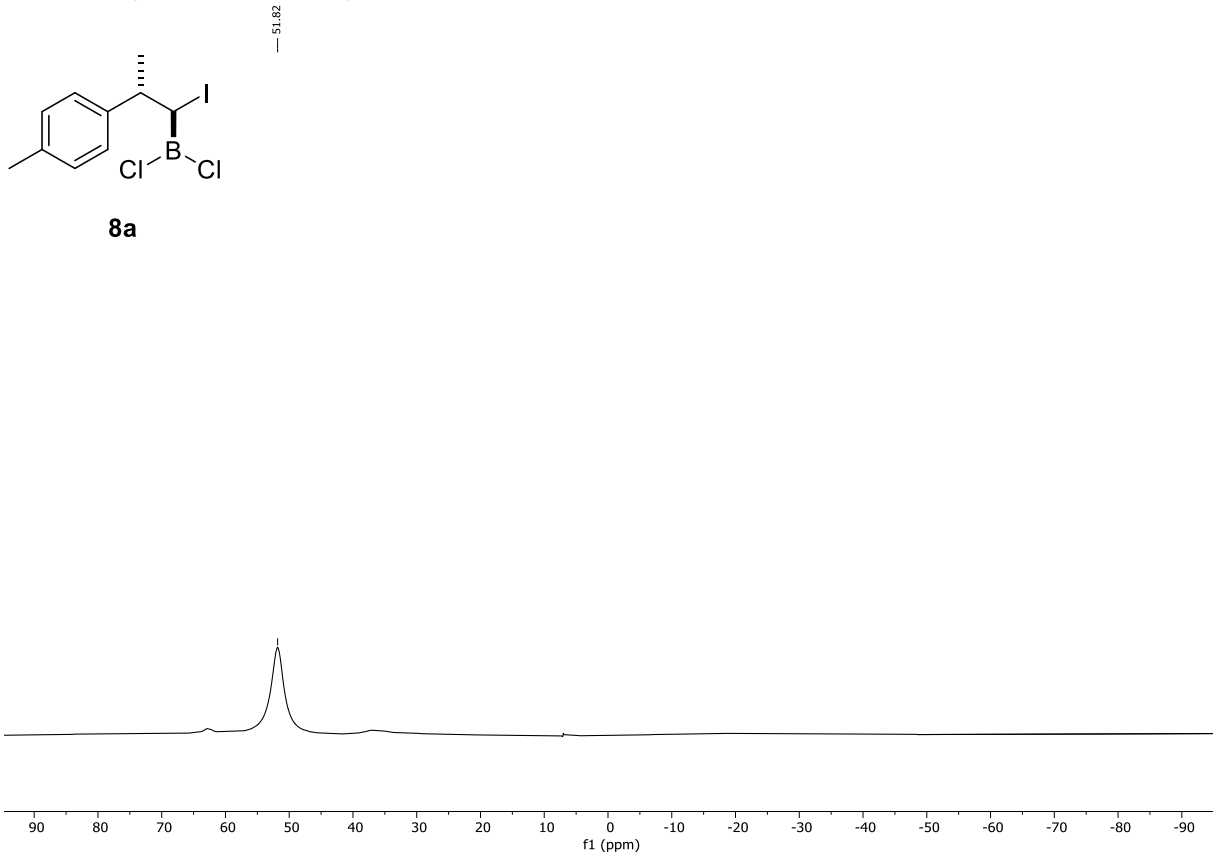
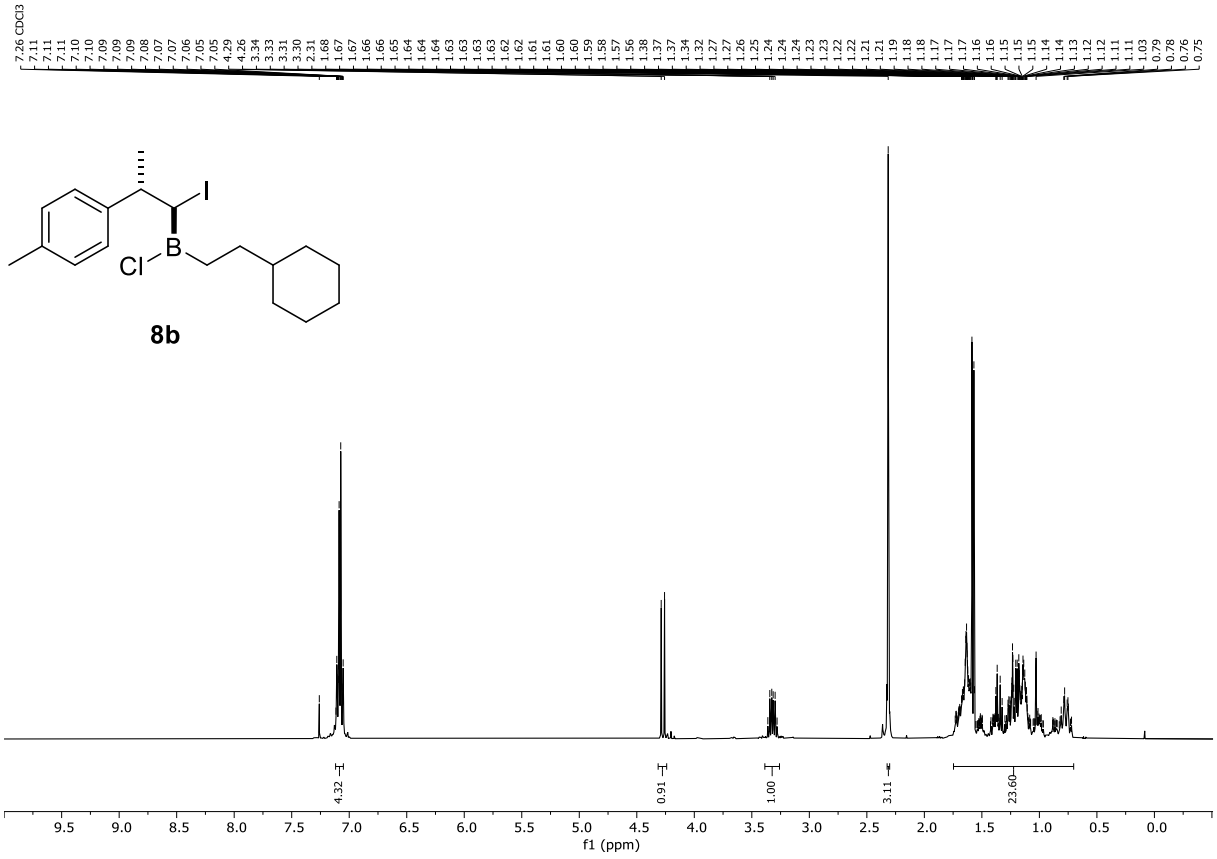


8a

^{1}H-NMR (400 MHz, $CDCl_3$):



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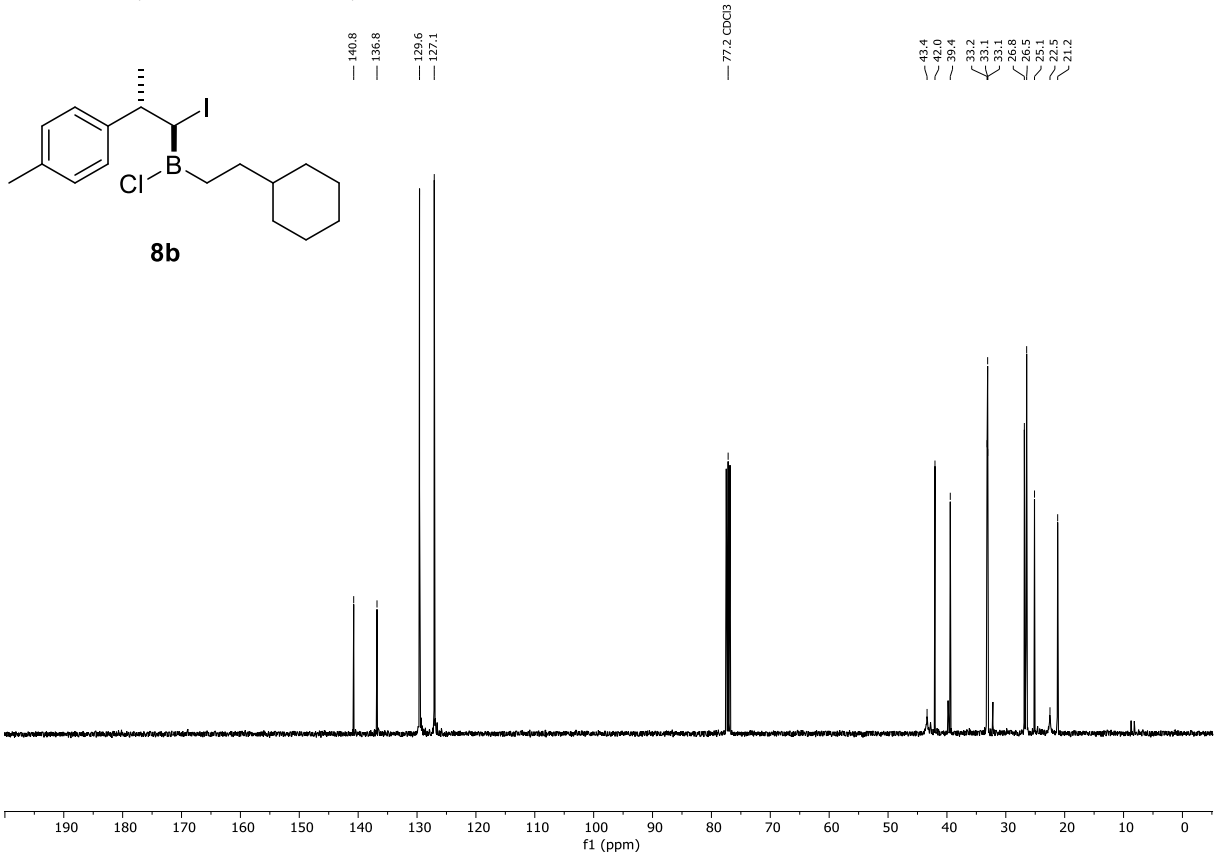

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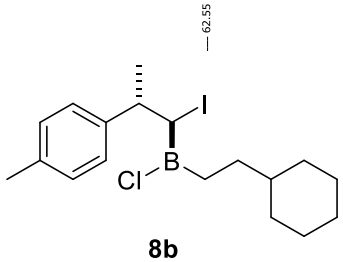
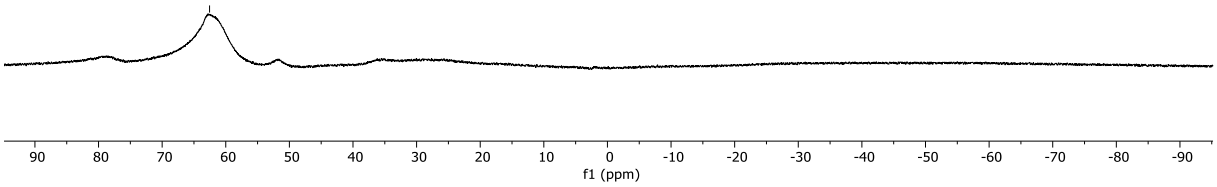


8b



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