Electronic Supplementary Material (ESI) for ChemComm.

Cobalt-Catalysed Markovnikov Selective Hydroboration of Vinylarenes

Supporting Information

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General experimental

Reaction Setup: All reactions were performed in oven (185 °C) and/or flamed-dried glassware under an atmosphere of anhydrous nitrogen or argon, unless otherwise indicated. All air- and moisture sensitive reactions were carried out using standard vacuum line and Schlenk techniques, or in a glovebox with a purified argon atmosphere. All glassware were cleaned using base (KOH, ^{i}PrOH) and acid (HCl_{aq}) baths. All reported reaction temperatures correspond to external bath temperatures. Room temperature (r.t) was approximately 22 °C. "Brine" refers to a saturated solution of sodium chloride in H_2O.

NMR Spectroscopy: ^{1}H, ^{11}B, ^{13}C, ^{19}F and ^{29}Si NMR spectra were recorded on Bruker Avance III 400 and 500 MHz; Bruker AVI 400 MHz; Bruker Avance I 600 MHz spectrometers. Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C NMR spectra were referenced to the residual deuterated solvent peak ($CHCl_3$: 7.28 ppm, CH_2Cl_2: 5.32 ppm, d_8-THF: 1.73 ppm). Multiplicities are indicated by app. (apparent), br. (broad), s (singlet), d (doublet), t (triplet), q (quartet), quin. (quintet), sext. (sextet), sept. (septet), non. (nonet). Coupling constants, *J*, are reported in Hertz and rounded to the nearest 0.1 Hz. Integration is provided and assignments are indicated.

Infrared Spectroscopy: Infra-red (IR) spectra were recorded on a Shimadzu IRAffinity-1 spectrometer (serial no. A213749) spectrometer. Relevant peaks are reported in cm^{-1}.

Mass Spectrometry: Mass spectrometry (MS) was performed by the University of Edinburgh, School of Chemistry, Mass Spectrometry Laboratory. High-resolution mass spectra were recorded on a VG autospec, or Thermo/Finnigan MAT 900, mass spectrometer. Electron Impact (EI^+) spectra were performed at 70 eV using methane as the carrier gas, with either a double focusing sector field (DFSF) or time-of-flight (TOF) mass analyzer. Electrospray Ionization (ESI^+) spectra were performed using a time-of-flight (TOF) mass analyzer. Data are reported in the form of m/z (intensity relative to the base peak = 100).

Melting Points: Melting points (mp) were determined on a Stuart Scientific SMP10, or Griffin Gallankamp, melting point apparatus in capillary tubes and are uncorrected.

Chromatography: Analytical thin-layer chromatography was performed on aluminium-backed silica plates (Merck 60 F_{254}). Product spots were visualised by UV light at 254 nm, and subsequently developed using potassium permanganate solution if appropriate. Flash column chromatography was performed on silica gel (Merck Kielselgel 60, 40-63 μm) unless otherwise stated.

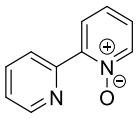
Solvents: All solvents for air- and moisture sensitive techniques were obtained from an anhydrous solvent system (Innovative Technology). Anhydrous d_8-tetrahydrofuran was distilled from sodium/benzophenone. Reaction solvents tetrahydrofuran (THF) (Fisher, HPLC grade), ether (Et_2O)

(Fisher, BHT stabilized ACS grade), and dichloromethane (CH_2Cl_2) (Fisher, unstabilized HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvent toluene (ACS grade) was dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant (supported copper catalyst for scavenging oxygen) under a positive pressure of argon. Solvents for filtration, transfers, chromatography, and recrystallization were dichloromethane (CH_2Cl_2) (ACS grade, amylene stabilized), ether (Et_2O) (Fisher, BHT stabilized ACS grade), ethyl acetate (EtOAc) (Fisher, ACS grade), hexane (Optima), methanol (MeOH) (ACS grade), pentane (ACS grade), and petroleum ether (40–60°C, ACS grade).

Chemicals: All reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros organics, Tokyo Chemical Industries UK, Fluorochem and Apollo Scientific or synthesised within the laboratory. Anhydrous cobalt chloride 99%+ (product number 93-2721. Lot A6262018). Sodium *tert*-butoxide (97%) was purchased from Sigma Aldrich (UK).

Ligand Synthesis

2,2'-Bipyridine-1-oxide



2,2'-Bipyridine (2.0 g, 12.8 mmol) was dissolved in trifluoroacetic acid (15.0 mL) at 10°C, then 30% solution hydrogen peroxide (2.0 mL, 15.5 mmol) was added and the mixture was stirred at room temperature for 3 h. The solution was diluted with chloroform (25 mL) and washed with aqueous sodium hydroxide solution (3M, 3 x 20 mL). The aqueous phase was extracted twice with chloroform (2 x 10 mL), and the combined organic phases were dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude reaction product was purified by flash column chromatography (40 g SiO_2, 30 mm Ø, petroleum ether/dichloromethane 10:1) to give 2,2'-bipyridine-1-oxide (1.76 g, 10.2 mmol, 80%) as pale yellow solid.

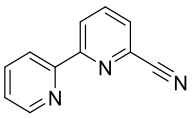
TLC: R_f = 0.26 (DCM/methanol, 1:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$) 8.92 (d, *J* = 8.1 Hz, 1H), 8.74 (d, *J* = 4.0 Hz, 1H), 8.32 (d, *J* = 6.3 Hz, 1H), 8.20 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.84 (td, *J* = 7.9, 1.8 Hz, 1H), 7.41-7.34 (m, 2H), 7.30-7.25 (m, 1H).

^{13}C NMR: (125 MHz, $CDCl_3$) 149.7, 149.4, 147.4, 140.7, 136.2, 127.9, 125.6, 125.5, 125.2, 124.3.

The spectroscopic data were in accordance with those reported in the literature.[1]

2,2'-Bipyridyl-6-carbonitrile



Trimethylsilylcyanide (3.3 mL, 26.3 mmol) was added to a stirred mixture of 2,2'-bipyridine-1-oxide (1.76 g, 10.2 mmol) in anhydrous dichloromethane (30 mL) at 0°C. Benzoyl chloride (1.23 mL, 10.2 mmol) was added dropwise (over *ca.* 1 minute) and the mixture warmed to room temperature, and stirred for 20 hours under nitrogen. Aqueous sodium carbonate solution (10 % v/v, 10 mL) was added, and the resulting mixture extracted with dichloromethane (3 x 10 mL), dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography (30 g SiO_2, 30 mm Ø, dichloromethane/ethyl acetate 7:1) to give 2,2'-bipyridyl-6-carbonitrile (1.31 g, 7.24 mmol, 71%) as a white amorphous solid.

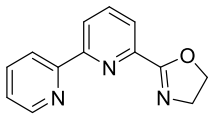
TLC: R_f= 0.73 (DCM/methanol 9:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$) 8.71-8.66 (m, 2H), 8.46 (d, *J* = 8.0 Hz, 1H), 7.95 (t, *J* = 7.9 Hz, 1H), 7.85 (td, *J* = 7.8, 1.8 Hz, 1H), 7.70 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.37 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H).

^{13}C NMR: (125 MHz, $CDCl_3$) 157.8, 154.1, 149.3, 137.9, 137.2, 133.5, 128.2, 124.2, 124.2, 121.6, 117.4.

The spectroscopic data were in accordance with those reported in the literature.[1]

2,2'-Bipyridyl-6-oxazoline (4a)



To an oven-dried 50 mL two-necked flask fitted with a reflux condenser was charged with 2,2'-bipyridyl-6-carbonitrile (300 mg, 1.64 mmol) and zinc triflate (16.0 mg, 0.05 mmol). The system was purged with argon and anhydrous toluene (5 mL) was added. The solution was stirred during 5 min and a solution of ethanolamine (150 mg, 2.46 mmol) in anhydrous toluene (10 ml). The resulting mixture was set to reflux for 48 hours, cooled to room temperature, diluted with ethyl acetate (20 mL) and then washed with saturated aqueous sodium hydrogen carbonate (3 x 10 mL) and water (20 mL), dried over Na_2SO_4,filtered, and the solvent removed *in vacuo*. The crude mixture was purified by flash column chromatography (40 g SiO_2, 30 mm Ø, petroleum ether/EtOAc 10:1) to give 2,2'-bipyridyl-6-[(*S*)-*iso*-butyloxazoline] (222 mg, 0.99 mmol, 61%) as a colourless amorphous solid.

m.p: 89 °C (petroleum ether/EtOAc)

IR: *vmax* (neat): 3055, 1712, 1699, 1612, 1511, 911.

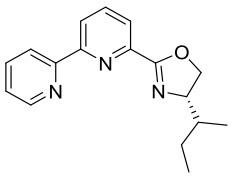
MS: (HRMS - EI^+) Found 225.25617 ($C_{13}H_{11}O_1N_3$), requires 225.25673

TLC: R_f = 0.42 (petroleum ether/EtOAc 1:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$) 8.76-8.71 (m, 1H), 8.55 (dd, *J* = 7.9, 1.0 Hz, 1H), 8.38-8.35 (m, 1H), 8.24 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.99 (t, *J* = 7.8 Hz, 1H), 7.85 (td, *J* = 7.6, 1.8 Hz, 1H), 7.37 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 3.94-3.90 (m, 2H), 3.76-3.71 (m, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$) 167.6, 156. 3, 155.9, 146. 9, 146.6, 140.0, 137.9, 126.1, 124.0, 123.5, 122.0, 68.8, 55.1.

2,2'-Bipyridyl-6-[(*S*)-*iso*-butyloxazoline] (4b)



To an oven-dried 50 mL two-necked flask fitted with a reflux condenser was charged with 2,2'-bipyridyl-6-carbonitrile (300 mg, 1.64 mmol) and zinc triflate (16.0 mg, 0.05 mmol). The system was purged with argon and anhydrous toluene (5 mL) was added. The solution was stirred during 5 min and a solution of (*S*)-(+)-isoleucinol (290 mg, 2.46 mmol) in anhydrous toluene (10 mL). The resulting mixture was set to reflux for 48 hours, cooled to room temperature, diluted with ethyl acetate (20 mL) and then washed with saturated aqueous sodium hydrogen carbonate (3 x 10 mL) and water (20 mL), dried over Na_2SO_4,filtered, and the solvent removed *in vacuo*. The crude mixture was purified by flash column chromatography (40 g SiO_2, 30 mm Ø, petroleum ether/EtOAc 10:1) to give 2,2'-bipyridyl-6-[(*S*)-*sec*-butyloxazoline] (248 mg, 0.98 mmol, 54%) as a colourless amorphous solid.

m.p: 110 °C (petroleum ether/EtOAc)

IR: *vmax* (neat): 3055, 1612, 1499, 1457, 1433, 1111, 1022.

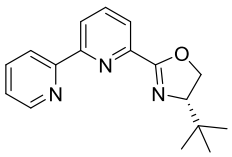
MS: (HRMS - EI^+) Found 281.15277 ($C_{17}H_{19}O_1N_3$), requires 281.15228

TLC: R_f = 0.37 (petroleum ether/EtOAc 1:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$) 8.71-8.68 (m, 1H), 8.57-8.52 (m, 2H), 8.13 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.92 (t, *J* = 7.9 Hz, 1H), 7.84 (td, *J* = 7.8, 1.8 Hz, 1H), 7.37 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 4.55 (dd, *J* = 9.0, 7.4 Hz, 1H), 4.38-4.25 (m, 2H), 1.86-1.77 (m, 1H), 1.74-1.65 (m, 1H), 1.61-1.52 (m, 1H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.92 (d, *J* = 7.5 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) 164.9, 156.1, 155.8, 147.9, 146.1, 139.4, 138.9, 124.7, 124.4, 123.8, 121.7, 76.9, 73.0, 33.8, 25.8, 15.7, 12.6.

2,2'-Bipyridyl-6-[(*S*)-*tert*-butyloxazoline] (4c)



To an oven-dried 50 mL two-necked flask fitted with a reflux condenser was charged with 2,2'-bipyridyl-6-carbonitrile (300 mg, 1.64 mmol) and zinc triflate (16.0 mg, 0.05 mmol). The system was purged with argon and anhydrous toluene (5 mL) was added. The solution was stirred during 5 min and a solution of L-*tert*-leucinol (290 mg, 2.46 mmol) in anhydrous toluene (10 ml). The resulting mixture was set to reflux for 48 hours, cooled to room temperature, diluted with ethyl acetate (20 mL) and then washed with saturated aqueous sodium hydrogen carbonate (3 x 10 mL) and water (20 mL), dried over Na_2SO_4,filtered, and the solvent removed *in vacuo*. The crude mixture was purified by flash column chromatography (40 g SiO_2, 30 mm Ø, petroleum ether/EtOAc 10:1) to give 2,2'-bipyridyl-6-[(*S*)-*tert*-butyloxazoline] (276mg, 0.98 mmol, 60%) as a colourless amorphous solid.

m.p: 138 °C (petroleum ether/EtOAc)

IR: *vmax* (neat): 3013, 1640, 1524, 1497, 1433, 1250, 1059.

MS: (HRMS - EI^+) Found 281.15264 ($C_{17}H_{19}O_1N_3$), requires 281.15226

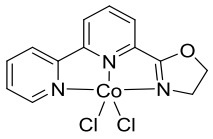
TLC: R_f = 0.37 (petroleum ether/EtOAc 1:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$) 8.70-8.68 (m, 1H), 8.65-8.52 (m, 2H), 8.16 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.91 (t, *J* = 7.9 Hz, 1H), 7.84 (td, *J* = 7.5, 1.8 Hz, 1H), 7.33 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 4.52 (dd, *J* = 10.2, 8.7 Hz, 1H), 4.38 (t, *J* = 8.43 Hz, 1H), 4.17 (dd, *J* = 10.1, 8.4 Hz, 1H), 1.02 (s, 9H).

^{13}C NMR: (125 MHz, $CDCl_3$) 162.7, 156.1, 155.5, 149.1, 146.6, 137.4, 136.9, 124.2, 124.0, 122.8, 121.7, 76.4, 69.4, 34.1, 26.0.

Complex Synthesis

^{H}BPOCoCl$_2$ (2,2'-Bipyridyl-6-oxazoline)cobalt dichloride (5a)



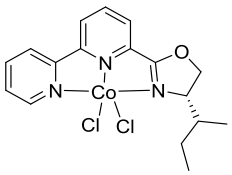
2,2'-Bipyridyl-6-oxazoline (79 mg, 0.35 mmol) and anhydrous cobalt (II) chloride (32 mg, 0.35 mmol) were stirred in anhydrous tetrahydrofuran (15 mL) for 24 hours. The mixture was concentrated *in vacuo* (to *ca.* 3 mL), diethyl ether (10 mL) was added, the precipitate collected by filtration and washed with diethyl ether (15 mL) to give (2,2'-bipyridyl-6-oxazoline)cobalt dichloride (111 mg, 0.32 mmol, 90%) as a light blue amorphous solid.

m.p: 157 °C (tetrahydrofuran)

MS: (HRMS - EI$^+$) Found 355.08456 ($C_{13}H_{11}O_1N_3CoCl_2$), requires 355.08581

^{1}H NMR: (500 MHz, CD_2Cl_2) 39.95, 8.20, 5.55, 5.37, 3.71, 2.13, 1.61, -9.85, -18.86.

^{sBu}BPOCoCl$_2$ {2,2'-Bipyridyl-6-[(*S*)-*sec*-butyloxazoline]}cobalt dichloride (5b)



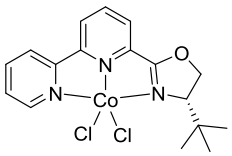
2,2'-Bipyridyl-6-[(*S*)-*sec*-butyloxazoline] (100 mg, 0.35 mmol) and anhydrous cobalt (II) chloride (32 mg, 0.35 mmol) were stirred in anhydrous tetrahydrofuran (15 mL) for 24 hours. The mixture was concentrated *in vacuo* (to *ca.* 3 mL), diethyl ether (10 mL) was added, the precipitate collected by filtration and washed with diethyl ether (15 mL) to give {2,2'-bipyridyl-6-[(*S*)-*sec*-butyloxazoline]}cobalt dichloride (117 mg, 0.32 mmol, 90%) as a dark blue amorphous solid.

m.p: 187 °C (tetrahydrofuran)

MS: (HRMS - EI$^+$) Found 410.02499 ($C_{17}H_{19}O_1N_3CoCl_2$), requires 410.02426

^{1}H NMR: (500 MHz, CD_2Cl_2) 24.41, 20.08, 11.6, 8.77, 8.13, 5.60, 5.26, 4.86, -14.06

^{tBu}BPOCoCl$_2$ {2,2'-Bipyridyl-6-[(S)-*tert*-butyloxazoline]}cobalt dichloride (5c)



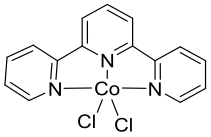
2,2'-Bipyridyl-6-[(*S*)-*tert*-butyloxazoline] (100 mg, 0.35 mmol) and anhydrous cobalt (II) chloride (32 mg, 0.35 mmol) were stirred in anhydrous tetrahydrofuran (15 mL) for 24 hours. The mixture was concentrated *in vacuo* (to *ca.* 3 mL), diethyl ether (10 mL) was added, the precipitate collected by filtration and washed with diethyl ether (15 mL) to give {2,2'-bipyridyl-6-[(*S*)-*tert*-butyloxazoline] }cobalt dichloride (117 mg, 0.32 mmol, 90%) as a light blue amorphous solid.

m.p: 191 °C (tetrahydrofuran)

MS: (HRMS - EI^+) Found 410.02248 ($C_{17}H_{19}O_1N_3CoCl_2$), requires 410.02426

^{1}H NMR: (500 MHz, CD_2Cl_2) 87.3, 73.4, 66.5, 29.57, 13.15, 9.54, -5.66, -7.46, -17.64, -20.61

TPY$CoCl_2$Terpyridine cobalt dichloride (5d)



Terpyridine (82 mg, 0.35 mmol) and anhydrous cobalt (II) chloride (32 mg, 0.35 mmol) were stirred in anhydrous tetrahydrofuran (15 mL) for 24 hours. The mixture was concentrated *in vacuo* (to *ca.* 3 mL), diethyl ether (10 mL) was added, the precipitate collected by filtration and washed with diethyl ether (15 mL) to give terpyridine cobalt dichloride (107 mg, 0.32 mmol, 95%) as a light blue solid.

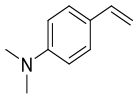
m.p: 169 °C (tetrahydrofuran)

MS: (HRMS - EI^+) Found 363.11214 ($C_{15}H_{11}O_1N_3CoCl_2$), requires 363.11287

^{1}H NMR: (500 MHz, CD_2Cl_2) 8.92, 7.30, 4.09, 3.48, 3.25, 2.05

Substrate Synthesis

N,N-Dimethylamino-4-vinylbenzene (1p)



n-BuLi (1.6 M in hexanes, 5.60 mL, 8.95 mmol), was added dropwise to a solution of methyltriphenylphosphonium bromide (3.20 g, 8.95 mmol) in THF (20 mL) at room temperature under the atmosphere of nitrogen. After stirring for 15 min, a solution of 4-dimethylaminobenzaldehyde (1.14 g, 7.65 mmol) in THF (10 mL) was added dropwise and the resulting mixture was stirred at room temperature for 16h. After that, water (30 mL) and diethyl ether (30 mL) were added and two layers were separated. The aqueous solution was extracted with ethyl ether for three times and the combined organic extracts were dried over $MgSO_4$ filtered, and concentrated *in vacuo*. The crude reaction product was purified by flash column chromatography (SiO_2 50 g, 30 mm Ø, petroleum ether/diethyl ether 10:1) to provide *N,N*-dimethylamino-4-vinylbenzene as a pale yellow oil (920 mg, 6.35 mmol, 71%).

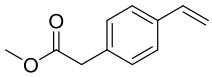
TLC: R_f = 0.49 (petroleum ether/diethyl ether, 1:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$) 7.34 (d, *J* = 8.5 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.65 (dd, *J* = 10.9, 17.5 Hz, 1H), 5.56 (d, *J* = 17.5 Hz, 1H), 5.04 (d, *J* = 10.8 Hz, 1H), 3.0 (s, 6H).

^{13}C NMR: (125 MHz, $CDCl_3$) 150.3, 136.3, 127.2, 126.3, 112.4, 109.4, 40.5

The spectroscopic data were in accordance with those reported in the literature.[2]

4-Vinyl(phenyl)acetic acid methyl ester (1s)



1,8-Diazabicycloundec-7-ene (1.707 g, 7.69 mmol) was added to a magnetically stirred solution of 2-(4-vinylphenyl)acetic acid (0.95 g, 5.92 mmol) in THF (10 mL) at 0 °C. The solution was treated in one portion with MeI (0.47 mL, 1.09 g, 7.69 mmol) and the mixture was stirred at room temperature for 3h before being diluted with diethyl ether (20 mL). The mixture was then washed with H_2O (10 mL), HCl (1M, 10 mL), NaOH (1M, 10 mL), HCl (1M, 10 mL), and H_2O (10 mL). The organic phase was then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude reaction product was purified by flash column chromatography (SiO_2 30 g, 30 mm Ø, petroleum ether/diethyl ether 20:1) to provide 4-vinyl(phenyl)acetic acid methyl ester as a white solid (51.3 mg, 3.84 mmol, 50%).

TLC: R_f = 0.38 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$) 7.39 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.76 (d, *J* = 17.6 Hz, 1H), 5.26 (d, *J* = 17.6 Hz, 1H), 3.72 (s, 3H), 3.64 (s, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$) 171.9, 136.4, 133.5, 129.5, 126.4, 113.9, 52.1, 40.9.

The spectroscopic data were in accordance with those reported in the literature.[3]

General Procedures for Hydroboration Reactions

Markovnikov hydroboration of alkenes using cobalt complexes

A reaction vial was charged with cobalt pre-catalyst (5.0 μmol, 1 mol%) and activator (10.0 μmol, 2 mol%) in an anhydrous atmosphere glovebox and the vial sealed with parafilm. The vial was removed from the glovebox and anhydrous tetrahydrofuran (3 mL), pinacolborane (80 μL, 0.55 mmol, 1.1 equiv) and olefin (0.5 mmol, 1 equiv.) were sequentially added and the resulting mixture was stirred at 25°C for 1 hour, diluted with diethyl ether (2 mL) and water (2 mL). 1,3,5-Trimethoxybenzene, as an internal standard, was added and the organic phase of the mixture was sampled. The yield and regioselectivity for the reaction were determined by integration of product ^{1}H NMR resonances.

Product Characterisation

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

Using the general procedure, styrene (57 μL, 0.5 mmol), pinacolborane (80 μL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 μmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 μmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The mixture was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-(1-phenylthyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (104 mg, 0.45 mmol, 90%) as a colourless oil, with the regioselectivity of 97:3 (B/L).

TLC: R_f = 0.28 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

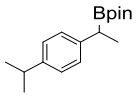
^{1}H NMR (500 MHz, $CDCl_3$) 7.30-7.22 (m, 3H), 7.18-6.13 (m, 2H), 2.46 (q, *J* = 7.48 Hz, 1H), 1.35 (d, *J* = 7.48 Hz, 3H), 1.24 (s, 6H), 1.23 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): 145.0, 128.3, 127.8, 125.1, 83.3, 24.8, 24.6, 24.6, 16.9

^{11}B NMR (160 MHz, $CDCl_3$): 33.5

The spectroscopic data were in accordance with those reported in the literature.[4]

2-(1-(4-*iso*-Propylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)



Using the general procedure, 4-*iso*-propylstyrene (73 mg, 0.5 mmol), pinacolborane (80 μL, 0.55 mmol), bipyridiyl-oxazoline cobalt dichloride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 μmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 μmol, 2 mol%) were reacted in THF (3 mL) to give the crude product

mixture which was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-(1-(4-*iso*-propylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (111 mg, 0.41 mmol, 81%) as a colourless oil, with the regioselectivity of 99:1 (B/L).

IR: *vmax* (neat): 2958, 1512, 1458, 1371, 1352, 1317, 1120, 844

MS: (HRMS - EI^+) Found 274.20977 ($C_{17}H_{27}B_1O_2$), requires 274.20986

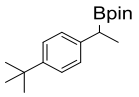
TLC: R_f = 0.29 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

^{1}H NMR (500 MHz, $CDCl_3$): 7.18-7.13 (m, 4H), 2.88 (sept, J= 6.91 Hz, 1H), 2.42 (q, *J* = 7.48 Hz, 1H), 1.34 (d, *J* = 7.48 Hz, 3H), 1.26 (s, 3H), 1.25 (s, 3H), 1.24 (s, 6H), 1.23 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$): 145.4, 142.1, 127.6, 126.3, 83.2, 33.6, 24.8, 24.6, 24.0, 17.3

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

2-(1-(4-*tert*-Butylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)



Using the general procedure, 4-*tert*-butylstyrene (92 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl_2] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The mixture was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-(1-(4-*tert*-butylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (127 mg, 0.44 mmol, 87%) as a colourless oil, with the regioselectivity of 97:3 (B/L).

TLC: R_f = 0.29 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

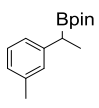
^{1}H NMR (500 MHz, $CDCl_3$): 7.32-7.27 (m, 2H), 7.19-7.14 (m, 2H), 2.43 (q, *J* = 7.49 Hz, 1H) 1.34 (d, *J* = 7.49 Hz, 3H), 1.33 (s, 9H), 1.25 (s, 6H), 1.24 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): 147.6, 141.7, 127.4, 125.2, 83.2, 34.2, 31.5, 24.8, 24.7, 24.6, 17.2

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

The spectroscopic data were in accordance with those reported in the literature.[4]

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



Using the general procedure, 3-methylstyrene (66 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl_2] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-

butoxide (1.0 mg, 10.0 μmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture which was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-(1-(3-methylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (97 mg, 0.40 mmol, 79%) as a colourless oil, with the regioselectivity of 97:3 (B/L).

IR: *vmax* (neat): 2999, 1371, 1350, 1319, 1100

MS: (HRMS - EI^+) Found 246.18590 ($C_{15}H_{23}B_1O_2$), requires 246.18639

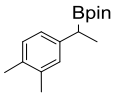
TLC: R_f = 0.25 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

^{1}H NMR (500 MHz, $CDCl_3$): 7.19-7.15 (m, 1H), 7.07-7.02 (m, 2H), 6.99-6.95 (m, 1H), 2.42 (q, *J* = 7.49 Hz, 1H), 2.23 (s, 3H), 1.34 (d, *J* = 7.57 Hz, 3H), 1.24 (s, 6H), 1.23 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$): 144.9, 137.7, 128.6, 128.1, 125.8, 124.8, 83.4, 83.3, 24.6, 21.5, 17.1

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

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



With modification to general procedure, 3,4-dimethylstyrene (73 μL, 0.5 mmol), pinacolborane (80 μL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl_2] (2.0 mg, 5.0 μmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 μmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture which was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-(1-(3,4-dimethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (94 mg, 0.36 mmol, 72%) as a colourless oil, with the regioselectivity of 95:5 (B/L).

IR: *vmax* (neat): 2922, 1472, 1411, 1369, 1287, 1171, 1120.

MS: (HRMS - EI^+) Found 260.19113 ($C_{16}H_{25}B_1O_2$), requires 260.19563

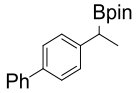
TLC: R_f = 0.27 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

^{1}H NMR (500 MHz, $CDCl_3$): 6.83-6.76 (m, 3H), 3.89 (s, 3H), 3.87 (s, 3H), 2.39 (q, *J* = 7.49 Hz, 1H), 1.33 (d, *J* = 7.49 Hz, 3H), 1.24 (s, 6H), 1.23 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): 148.7, 146.7, 137.6, 119.4, 111.4, 111.3, 83.2, 55.9, 55.7, 24.6, 17.3

^{11}B NMR (160 MHz, $CDCl_3$): 33.5

2-(1-(1,1'-Biphenyl)-4-ylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)



With modification to general procedure, 4-vinylbiphenyl (90 mg, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium tert-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture which was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 10:1) to give 2-(1-(1,1'-biphenyl)-4-ylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (136 mg, 0.44 mmol, 88%) as a colourless oil, with the regioselectivity of 98:2 (B/L).

TLC: R_f = 0.31 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

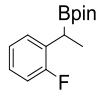
^{1}H NMR (500 MHz, $CDCl_3$): 7.63-7.58 (m, 2H), 7.55-7.51 (m, 2H), 7.46-7.41 (m, 2H), 7.35-7.29 (m, 3H), 2.51 (q, *J* = 7.49 Hz, 1H), 1.39 (d, *J* = 7.49 Hz, 3H), 1.25 (s, 6H), 1.24 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): 144.1, 141.2, 137.9, 128.6, 128.2, 127.0, 126.9, 126.8, 83.4, 24.7, 24.6, 17.08,

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

The spectroscopic data were in accordance with those reported in the literature.[5]

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



Using the general procedure, 2-fluorostyrene (60 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The crude was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-(1-(2-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (114 mg, 0.46 mmol, 91%) as a colourless oil, with the regioselectivity of 95:5 (B/L).

IR: *vmax* (neat): 2978, 1489, 1452, 1321, 1167, 846

MS: (HRMS - EI$^+$) Found 250.14530 ($C_{14}H_{20}O_2B_1F_1$), requires 250.14326

TLC: R_f = 0.26 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

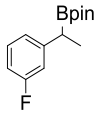
^{1}H NMR (500 MHz, $CDCl_3$): 7.27-7.23 (m, 1H), 7.17-7.11 (m, 1H), 7.10-7.05 (m, 1H), 7.03-6.97 (m, 1H), 2.59 (q, *J* = 7.57 Hz, 1H), 1.34 (d, *J* = 7.57 Hz, 3H), 1.26 (s, 6H), 1.25 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): 160.8 (d, *J* = 243.8 Hz), 132.2 (d, *J* = 15.46 Hz), 129.5 (d, *J* = 4.99 Hz), 126.6 (d, *J* = 7.98 Hz), 124.0 (d, *J* = 3.49 Hz), 114.9 (d, *J* = 22.44 Hz), 83.4, 24.7, 24.6, 15.9

^{19}F NMR (470 MHz, $CDCl_3$): -117.5

^{11}B NMR (160 MHz, $CDCl_3$): 33.5

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



Using the general procedure, 3-fluorostyrene (60 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The crude mixture was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-(1-(3-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (113 mg, 0.45 mmol, 90%) as a colourless oil, with the regioselectivity of 99:1 (B/L).

TLC: R_f = 0.26 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

^{1}H NMR (500 MHz, $CDCl_3$): 7.26-7.20 (m, 1H), 7.03-6.99 (m, 1H), 6.98-6.93 (m, 1H), 6.87-6.81 (m, 1H), 2.47 (q, *J* = 7.41 Hz, 1H), 1.35 (d, *J* = 7.49 Hz, 3H), 1.24 (s, 6H), 1.23 (s, 6H)

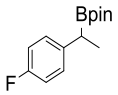
^{13}C NMR (125 MHz, $CDCl_3$): 163.2 (d, *J* = 244.8 Hz), 147.7 (d, *J* = 6.98 Hz), 129.5 (d, *J* = 8.48 Hz), 123.5 (d, *J* = 2.49 Hz), 114.5 (d, *J* = 21.44 Hz), 111.9 (d, *J* = 20.94 Hz), 83.4, 24.7, 24.6, 15.9

^{19}F NMR (470 MHz, $CDCl_3$): -114.3

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

The spectroscopic data were in accordance with those reported in the literature.[6]

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



Using the general procedure, 4-fluorostyrene (60 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The mixture was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (115 mg, 0.46 mmol, 92%) as a colourless oil, with the regioselectivity of 96:4 (B/L).

TLC: R_f = 0.26 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

^{1}H NMR (500 MHz, $CDCl_3$): 7.21-7.16 (m, 2H), 6.99-6.94 (m, 2H), 2.43 (q, *J* = 7.49 Hz, 1H), 1.33 (d, *J* = 7.57 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H)

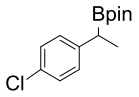
^{13}C NMR (125 MHz, $CDCl_3$): 160.9 (d, *J* = 242.3 Hz), 140.5 (d, *J* = 2.99 Hz), 129. 0 (d, *J* = 7.48 Hz), 114.9 (d, *J* = 20.94 Hz), 83.4, 24.8, 24.6, 24.5, 17.2

^{19}F NMR (470 MHz, $CDCl_3$): -119.1

^{11}B NMR (160 MHz, $CDCl_3$): 33.5

The spectroscopic data were in accordance with those reported in the literature.[6]

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



Using the general procedure, 4-chlorostyrene (60 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The mixture was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (105 mg, 0.40 mmol, 79%) as a colourless oil, with the regioselectivity of 85:15 (B/L).

TLC: R_f = 0.26 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

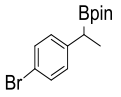
^{1}H NMR (500 MHz, $CDCl_3$): 7.26-7.22 (m, 2H), 7.18-7.15 (m, 2H), 2.42 (q, J = 7.49 Hz, 1H), 1.33 (d, J = 7.49 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): 143.6, 130.8, 129.2, 128.5, 83.6, 24.8, 24.7, 17.1.

^{11}B NMR (160 MHz, $CDCl_3$): 33.5

The spectroscopic data were in accordance with those reported in the literature.[6]

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



Using the general procedure, 4-bromostyrene (65 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The mixture was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-(1-(4-brophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (34 mg, 0.11 mmol, 45%) as a colourless oil, with the regioselectivity of 96:4 (B/L).

TLC: R_f = 0.27 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

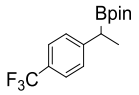
^{1}H NMR (500 MHz, $CDCl_3$): 7.41-7.37 (m, 2H), 7.13-7.09 (m, 2H), 2.41 (q, J = 7.49 Hz, 1H), 1.32 (d, J = 7.49 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): 144.0, 131.3, 129.5, 118.7, 83.46, 24.6, 24.5, 16.8.

^{11}B NMR (160 MHz, $CDCl_3$): 33.4

The spectroscopic data were in accordance with those reported in the literature.[6]

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



Using the general procedure, 4-(trifluoromethyl)styrene (74 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The mixture was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-(1-(4-trifluoromethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (120 mg, 0.4 mmol, 80%) as a colourless oil, with the regioselectivity of 94:6 (B/L).

TLC: R_f = 0.20 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

^{1}H NMR (500 MHz, $CDCl_3$): 7.53 (d, J = 8.12 Hz, 2H), 7.34 (d, J = 8.35 Hz, 2H), 2.53 (q, J = 7.41 Hz, 1H), 1.37 (d, J = 7.57 Hz, 3H), 1.24 (s, 6H), 1.23 (s, 6H)

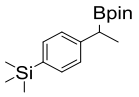
^{13}C NMR (125 MHz, $CDCl_3$): 149.3, 127.9, 125.1 (q, J = 3.49 Hz), 83.3, 24.6, 24.5, 16.7

^{19}F NMR (470 MHz, $CDCl_3$): -62.3

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

The spectroscopic data were in accordance with those reported in the literature.[6]

2-(1-(4-Trimethylsilylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m)



Using the general procedure, 4-trimethylsilylstyrene (88 mg, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The mixture was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 10:1) to give 2-(1-(4-trimethylsilylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (132 mg, 0.43 mmol, 80%) as a colourless oil, with the regioselectivity of 97:3 (B/L).

TLC: R_f = 0.7 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

^{1}H NMR (500 MHz, $CDCl_3$): 7.46-7.42 (m, 2H), 7.25-7.21 (m, 2H), 2.44 (q, *J* = 7.49 Hz, 1H), 1.35 (d, *J* = 7.57 Hz, 3H), 1.25 (s, 6H), 1.23 (s, 6H), 0.27 (s, 9H)

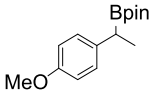
^{13}C NMR (125 MHz, $CDCl_3$): 145.6, 136.3, 133.4, 127.8, 83.29, 24.6, 17.1, -1.02

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

^{29}Si NMR (99 MHz, $CDCl_3$): -4.56

The spectroscopic data were in accordance with those reported in the literature.[4]

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



Using the general procedure, 4-methoxylstyrene (67 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture which was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-(1-(4-methoxylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (97 mg, 0.37 mmol, 74%) as a colourless oil, with the regioselectivity of 88:12 (B/L).

TLC: R_f = 0.17 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

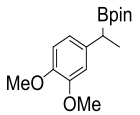
^{1}H NMR (500 MHz, $CDCl_3$): 7.19-7.15 (m, 1H), 7.07-7.02 (m, 2H), 6.99-6.95 (m, 1H), 2.42 (q, *J* = 7.49 Hz, 1H), 2.23 (s, 3H), 1.34 (d, *J* = 7.57 Hz, 3H), 1.24 (s, 6H), 1.23 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): 148.8, 146.7, 137.6, 119.4, 111.4, 111.3, 83.2, 55.8, 24.6, 17.2

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

The spectroscopic data were in accordance with those reported in the literature.[6]

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



Using the general procedure, 3,4-dimethoxystyrene (74 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture which was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 10:1) to give 2-(1-(3,4-dimethoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (102 mg, 0.35 mmol, 70%) as a colourless oil, with the regioselectivity of 94:6 (B/L).

IR: *vmax* (neat): 3000, 1514, 1456, 1370, 1351, 1249, 1234, 1169, 1028.

MS: (HRMS - EI^+) Found 292.18539 ($C_{16}H_{25}O_4B_1$), requires 292.18404

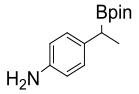
TLC: R_f = 0.14 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

^{1}H NMR (500 MHz, $CDCl_3$): 6.82-6.75 (m, 3H), 3.88 (s, 3H), 3.86 (s, 3H), 2.39 (q, *J* = 7.49 Hz, 1H), 1.33 (d, *J* = 7.49 Hz, 3H), 1.24 (s, 6H), 1.22 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): 145.1, 144.2, 125.9, 125.5, 124.3, 124.2, 83.3, 33.3, 27.8, 24.8, 24.7

^{11}B NMR (160 MHz, $CDCl_3$): 33.5

4-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzenamine (3p)



Using the general procedure, 4-aminostyrene (74 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl_2] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The crude mixture was extracted with ether (5 mL), and the organic phase were dried over $MgSO_4$, filtered and evaporated *in vacuo* to give 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzenamine (103 mg, 0.42 mmol, 83%) as a colourless oil, with the regioselectivity of 75:25 (B/L).

TLC: R_f =0.47 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

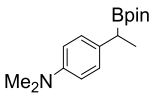
^{1}H NMR (500 MHz, $CDCl_3$): 7.05-7.01 (m, 2H), 6.67-6.62 (m, 2H), 3.56 (s, 2H), 2.33 (q, *J* = 7.49 Hz, 1H), 1.30 (d, *J* = 7.49 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): 143.5, 135.1, 128.5, 115.5, 83.1, 24.6, 24.5, 17.3.

^{11}B NMR (160 MHz, $CDCl_3$): 33.8

The spectroscopic data were in accordance with those reported in the literature.[7]

4-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-*N*, *N*-dimethylbenzenamine (3q)



Using the general procedure, *N*,*N*-dimethylamino-4-vinylbenzene (74 mg, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl_2] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The crude mixture was extracted with ether (5 mL), and the organic phase were

dried over $MgSO_4$, filtered and evaporated *in vacuo* to give 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-*N*, *N*-dimethylbenzenamine (113 mg, 0.42 mmol, 83%) as a colourless oil, with the regioselectivity of 86:14 (B/L).

IR: *vmax* (neat): 2976, 1517, 1452, 1321, 1217,

MS: (HRMS - EI^+) Found 275.20540 ($C_{16}H_{26}O_2B_1N_1$), requires 275.20511

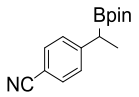
TLC: R_f =0.51 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

^{1}H NMR (500 MHz, $CDCl_3$): 7.16-7.05 (m, 2H), 6.76-6.67 (m, 2H), 2.91 (s, 6H), 2.34 (q, *J* = 7.49 Hz, 1H), 1.30 (d, *J* = 7.57 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): 155.2, 139. 8, 117.1, 109.13, 83.74, 41.91, 24.8, 24.7, 19.1.

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

2-(1-(4-Cyanophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3r)



Using the general procedure, 4-cyanostyrene (64 mg, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl_2] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The mixture was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-(1-(4-cyanophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (85 mg, 0.34 mmol, 69%) as a colourless oil, with the regioselectivity of 99:1 (B/L).

IR: *vmax* (neat): 2225, 1373, 1346, 1144, 876.

MS: (HRMS - EI^+) Found 257. 15899 ($C_{15}H_{20}B_1O_2N_1$), requires 257.15816

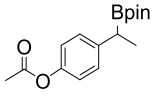
TLC: R_f = 0.29 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

^{1}H NMR (500 MHz, $CDCl_3$): 7.58-7.54 (m, 2H), 7.35-7.30 (m, 2H), 2.53 (q, *J* = 7.41 Hz, 1H), 1.36 (d, *J* = 7.41 Hz, 3H), 1.22 (s, 6H), 1.21 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): 150.9, 132.0, 128.5, 119.3, 108.9, 83.7, 24.6, 24.5, 16.3

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

2-(1-(4-Acetoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3s)



Using the general procedure, 4-acetoxystyrene (76 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The mixture was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 10:1) to give 2-(1-(4-acetoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (114 mg, 0.39 mmol, 79%) as a colourless oil, with the regioselectivity of 98:2 (B/L).

TLC: R_f = 0.44 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

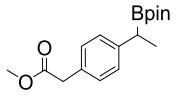
^{1}H NMR (500 MHz, $CDCl_3$): 7.26-7.21 (m, 2H), 7.02-6.97 (m, 2H), 2.45 (q, *J* = 7.49 Hz, 1H), 2.30 (s, 3H), 1.34 (d, *J* = 7.57 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): 169.8, 148.2, 142.5, 128.6, 121.2, 83.4, 24.7, 24.6, 21.2, 17.1

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

The spectroscopic data were in accordance with those reported in the literature.[6]

2-(1-(4-(Acetic acid methyl ester)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t)



Using the general procedure, 4-vinyl(phenyl)acetic acid methyl ester (88 mg, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The mixture was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 10:1) to give 2-(1-(4-(acetic acid methyl ester)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (122 mg, 0.4 mmol, 80%) as a colourless oil, with the regioselectivity of 95:5 (B/L).

IR: *vmax* (neat): 1735, 1319, 1255, 1160, 1018, 844

MS: (HRMS - EI$^+$) Found 304. 18448 ($C_{17}H_{25}B_1O_4$), requires 304. 18404

TLC: R_f = 0.48 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

^{1}H NMR (500 MHz, $CDCl_3$): 7.19 (s, 4H), 3.70 (s, 3H), 3.60 (s, 2H), 2.44 (q, *J* = 7.57 Hz, 1H), 1.34 (d, *J* = 7.57 Hz, 3H), 2.30 (s, 3H), 1.23 (s, 6H), 1.22 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): 172.3, 143.82, 130.54, 129.15, 128.0, 83.3, 51.9, 40.8, 24.7, 24.6, 17.1, 15.3

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

4, 4, 5, 5-Tetramethyl-2-(1-phenyl-propyl)-1,3,2-dioxaborolane (3u)

Using the general procedure, trans-β-methylstyrene (65 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture which was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give the single regioisomer 4, 4, 5, 5-tetramethyl-2-(1-phenyl-propyl)-1,3,2-dioxaborolane (110 mg, 0.45 mmol, 90%) as a colourless oil.

TLC: R_f = (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

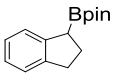
^{1}H NMR (500 MHz, $CDCl_3$): 7.30-7.21 (m, 4H), 7.17-7.13 (m, 1H), 2.24 (t, *J* = 7.88 Hz, 1H), 1.95-1.85 (m, 1H), 1.75-1.65 (m, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 0.93 (t, *J* = 7.33 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): 143.4, 128.4, 128.2, 125.1, 83.2, 25.8, 24.7, 24.6, 13.9

^{11}B NMR (160 MHz, $CDCl_3$): 33.5

The spectroscopic data were in accordance with those reported in the literature.[8]

2-(2,3-Dihydro-1*H*-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3v)



Using the general procedure, indene (58 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture which was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give the single regioisomer 2-(2,3-dihydro-1*H*-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (96 mg, 0.39 mmol, 79%) as a colourless oil.

TLC: R_f = 0.30 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

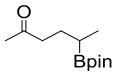
^{1}H NMR (500 MHz, $CDCl_3$): 7.33-7.29 (m, 1H), 7.25-7.21 (m, 1H), 7.16-7.09 (m, 2H), 3.03-2.89 (m, 2H), 2.75 (t, *J* = 8.51 Hz, 1H), 2.29-2.21 (m, 1H), 2.17-2.07 (m, 1H), 1.28 (s, 6H), 1.27 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): 145.1, 144.2, 125.9, 125.5, 124.4, 124.2, 83.3, 33.3, 27.8, 24.9, 24.7.

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

The spectroscopic data were in accordance with those reported in the literature.[6]

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (3w)



Using the general procedure, 5-hexen-2-one (58 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture which was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 10:1) to give 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (78 mg, 0.34 mmol, 69%) as a colourless oil, with the regioselectivity of 75:25 (B/L).

TLC: R_f = 0.38 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

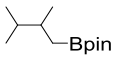
^{1}H NMR (500 MHz, $CDCl_3$): 2.43 (t, *J* = 7.6 Hz, 2H), 2.12 (s, 3H), 1.71-1.53 (m, 2H), 1.64-1.38 (m, 2H), 1.25 (s, 12H), 1.01−0.97 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): 209.5, 83.0, 43.2, 29.8, 27.2, 24.8, 24.7, 15.4

^{11}B NMR (160 MHz, $CDCl_3$): 34.0

The spectroscopic data were in accordance with those reported in the literature.[9]

2-(2,3-Dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3x)



Using the general procedure, 2,3-dimethyl-1-butene (62 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [$^{t\text{Bu}}$BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture which was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 10:1) to give 2-(2,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (78 mg, 0.34 mmol, 69%) as a colourless oil.

TLC: R_f = 0.35 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

^{1}H NMR (500 MHz, $CDCl_3$): 1.64-1.56 (m, 1H), 1.53-1.45 (m, 1H), 1.24 (2 overlapping singlets, 12H), 0.85-0.79 (overlapping doublets, 10H), 0.61 (dd, *J* = 15.2, 9.8 Hz, 1H).

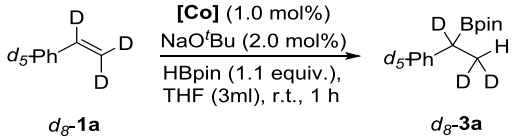
^{13}C NMR (125 MHz, $CDCl_3$): 82.9, 35.2, 34.3, 25.1, 24.8, 19.9, 18.8, 18.7.

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

The spectroscopic data were in accordance with those reported in the literature.[10]

Deuterium Labelling Experiments

2-[1-(d_5-Phenyl)-1-d_1-2-d_2-ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (d_8-3a)



d_8-**1a** d_8-**3a**

Using the general procedure, d_8-styrene (57 mg, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), bipyridiyl-oxazoline cobalt dicholoride [^{tBu}BPOCoCl$_2$] (2.0 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) were reacted in THF (3 mL) to give the crude product mixture. The mixture was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-[1-(d_5-phenyl)-1-d_1-2-d_2-ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (89 mg, 0.37 mmol, 75%) as a colourless oil, with the regioselectivity of 97:3 (B/L).

TLC: R_f = 0.28 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

^{1}H NMR (500 MHz, $CDCl_3$): 1.34-1.30 (br. m, 1H), 1.24 (s, 6H), 1.22 (s, 6H).

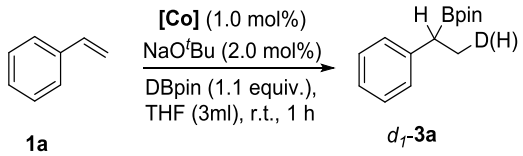
^{13}C NMR (125 MHz, $CDCl_3$): 144.8 (C), 127.8 (t, J = 24.2 Hz), 127.3 (t, J = 23.7 Hz), 124.5 (t, J = 24.2 Hz), 83.3, 24.8, 24.5, 24.6, 16.3 (quint., J = 19.3 Hz)

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

^{2}H NMR (77 MHz, $CHCl_3$): 7.31 (s), 7.28 (s), 7.19 (s), 2.42 (s), 1.32 (d, J = 1.78 Hz).

The spectroscopic data were in accordance with those reported in the literature.[4]

2-(1-Phenyl-2-d_1-ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (d_1-3a)



1a d_1-**3a**

88:12 d_1-**3a**/**3a**
98:2 b/l, 70%

Deuterated pinacolborane (d_1-pinacolborane) was prepared according to literature procedure[11] and the reaction was performed in a glovebox under a purified argon atmosphere.

Using the general procedure, the reaction mixture was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 15:1) to give 2-[1-(d_5-Phenyl)-1-d_1-2-d_2-ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (77 mg, 0.35 mmol, 70%) as a colourless oil, in a 88:12 mixture with fully protio-boronic ester, with the regioselectivity of 98:2 (B/L).

TLC: R_f = 0.28 (petroleum ether/diethylether, 15:1) [UV/$KMnO_4$]

^{1}H NMR (500 MHz, $CDCl_3$): 7.30-7.22 (m, 3H), 7.18-6.13 (m, 2H), 2.46 (q, *J* = 7.48 Hz, 1H), 1.35 (d, *J* = 7.48 Hz, 2.27 H), 1.24 (s, 6H), 1.23 (s, 6H)

^{13}C NMR (125 MHz, CD_2Cl_2): 145.0, 128.0, 128.4, 125.1, 83.3, 25.0 (CH_3), 17.4 (s, CH_3, from protonated product), 17.2 (t, *J* = 19.5 Hz, CH_2D from mono-deuterated product).

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

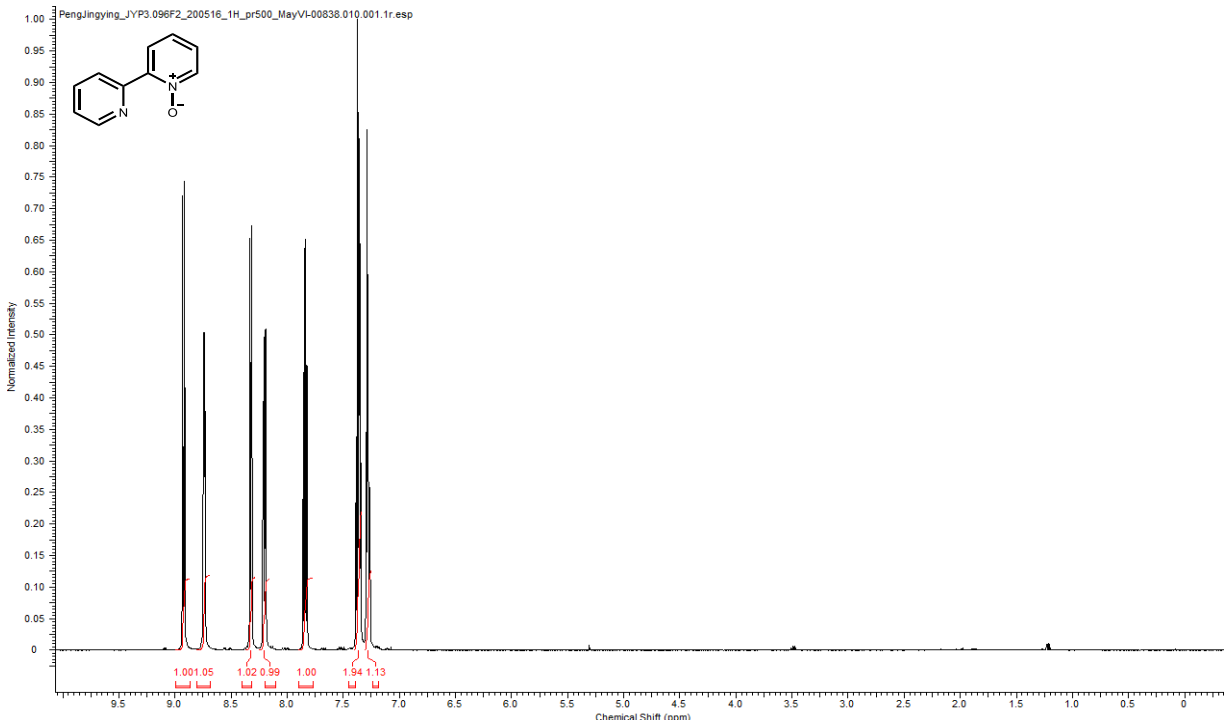
^{2}H NMR (77 MHz, CD_2Cl_2): 1.37-1.25 (br, m)

The spectroscopic data were in accordance with those reported in the literature.[4]

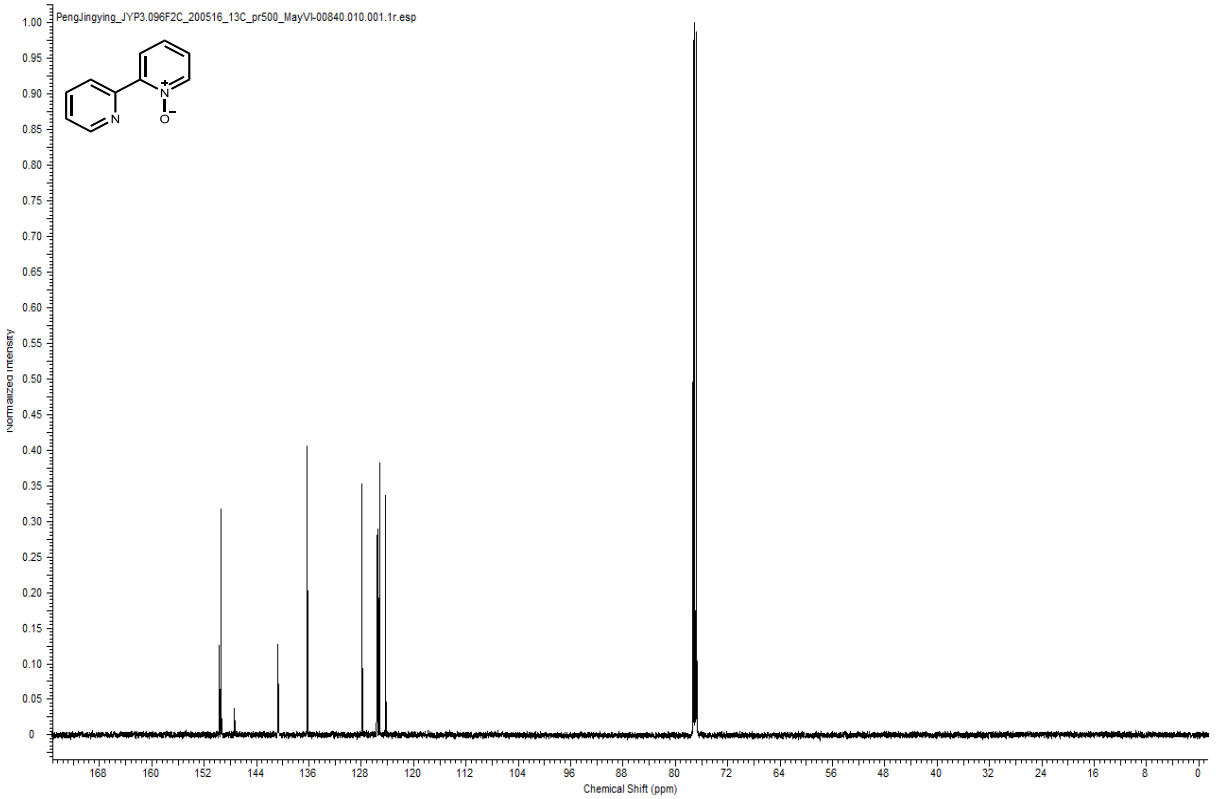
References

1. M. C. Young, E. Liew, J. Ashby, K. E. McCoy and R. J. Hooley, *Chem. Commun.*, 2013, **49**, 6331.
2. C. A. Faler and M. M. Joullié, *Org. Lett.*, 2007, **9**, 1987.
3. R. A. Boulos, N. Y. T. Man, N. A. Lengkeek, K. A. Hammer, N. F. Foster, N. A. Stemberger, B W. Skelton, P. Y. Wong, B. Martinac, T. V. Riley, A. J. McKinley and S. G. Stewart, *Chem. Eur. J.*, 2013, **19**, 17980.
4. A. J. MacNair, C. R. P. Millet, G. S. Nichol, A. Ironmonger and S. P. Thomas, *ACS Catal.*, 2016, **6**, 7217.
5. E. E. Touney, R. Van Hoveln, C. T. Buttke, M. D. Freidberg, I. A. Guzei, and J. M. Schomaker *Organometallics*, 2016, **35**, 3436.
6. G. Zhang, H. Zeng, J. Wu, Z. Yin, S. Zheng and J. C. Fettinger, *Angew. Chem. Int. Ed.*, 2016, **55**, 14369.
7. C. M. Vogelsa, A. Deckenb and S. A. Westcotta, *Tetrahedron Lett.*, 2006, **47**, 2419.
8. M. Espinal-Viguri, C. R. Woof and R. L. Webster, *Chem. Eur. J.*, 2016, **22**, 11605.
9. Y. Wen, J. Xie, C. Deng and C. Li, *J. Org. Chem.*, 2015, **80**, 4142.
10. J. V. Obligacion and P. J. Chirik, *J. Am. Chem. Soc.*, 2013, **135**, 19107.
11. F. Labre, Y. Gimbert, P. Bannwarth, S. Olivero, E. Duñach, P. Y. Chavant, *Org. Lett.*, 2014, **16**, 2366.

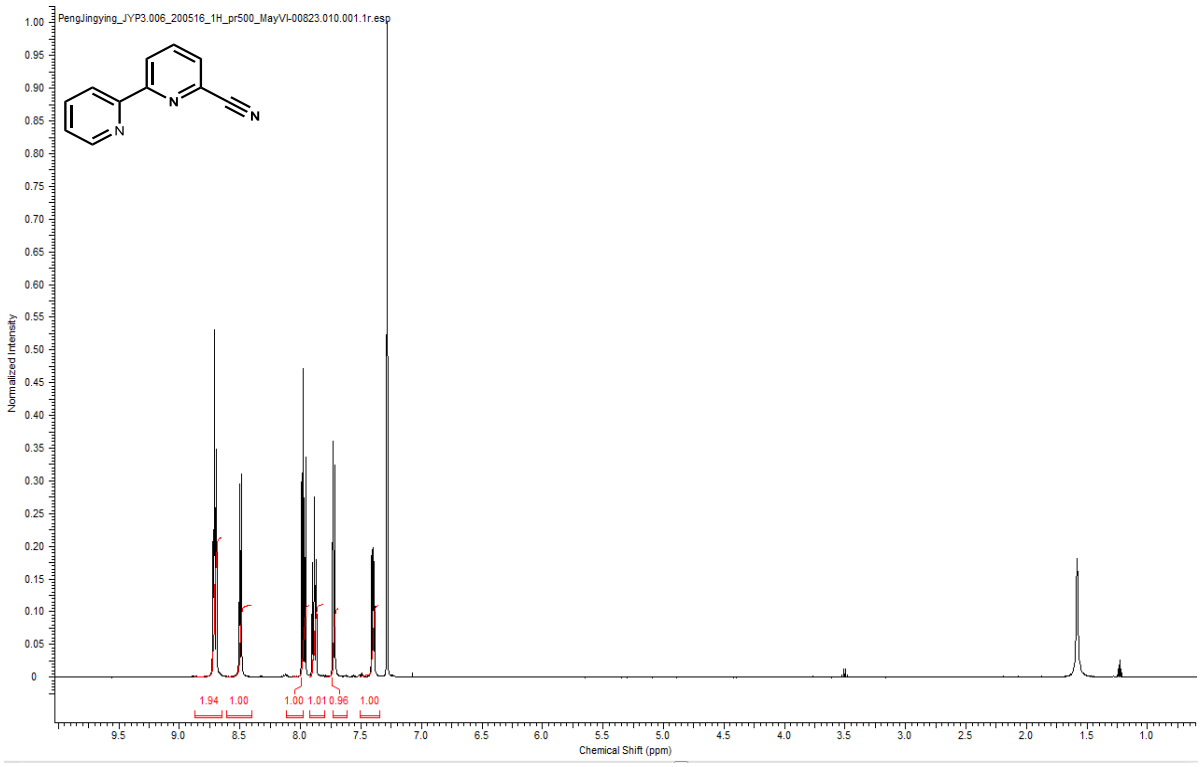
NMR Spectra



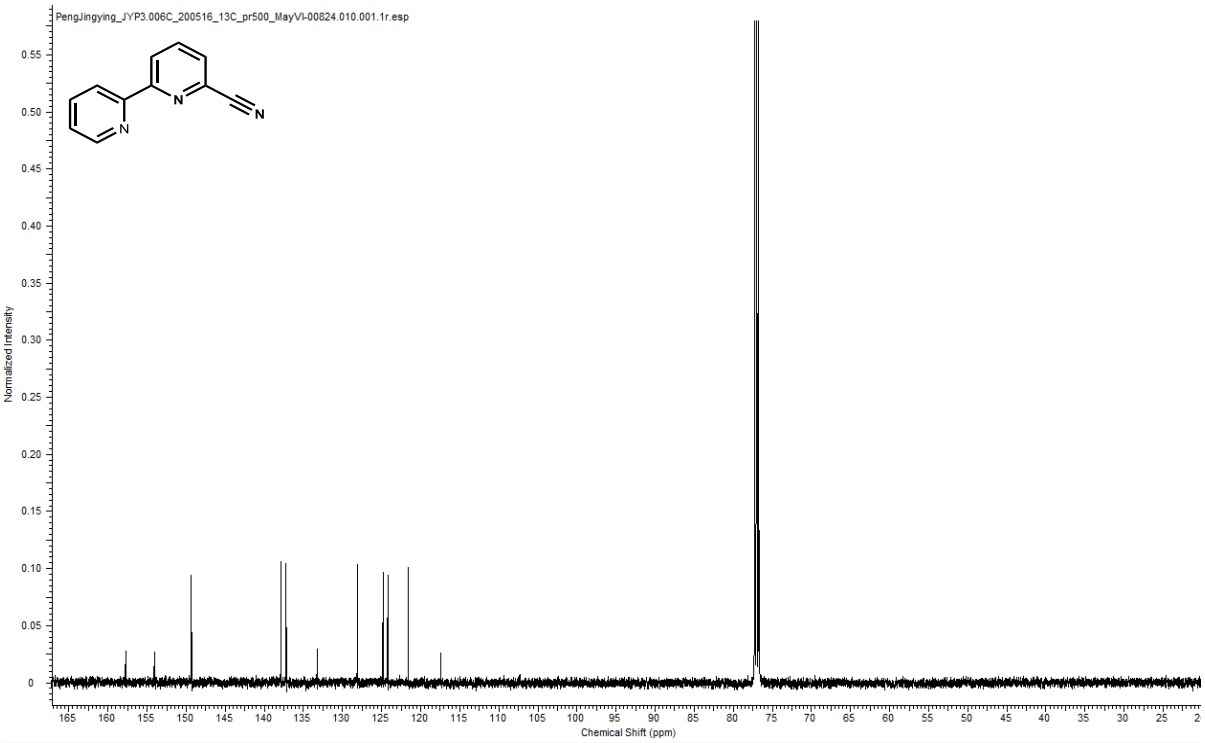
^{1}H NMR (500 MHz, $CDCl_3$) of 2,2'-bipyridyl-1-oxide.



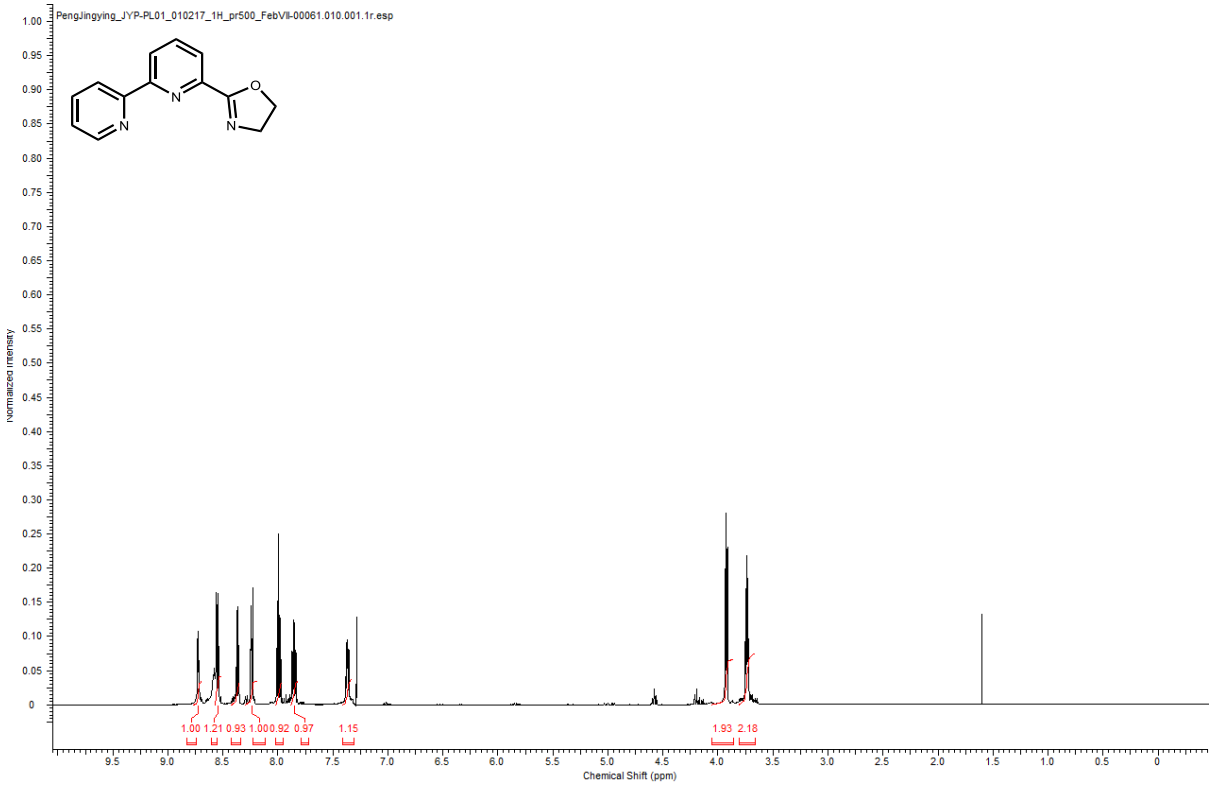
^{13}C NMR (125 MHz, $CDCl_3$) of 2,2'-bipyridyl-1-oxide



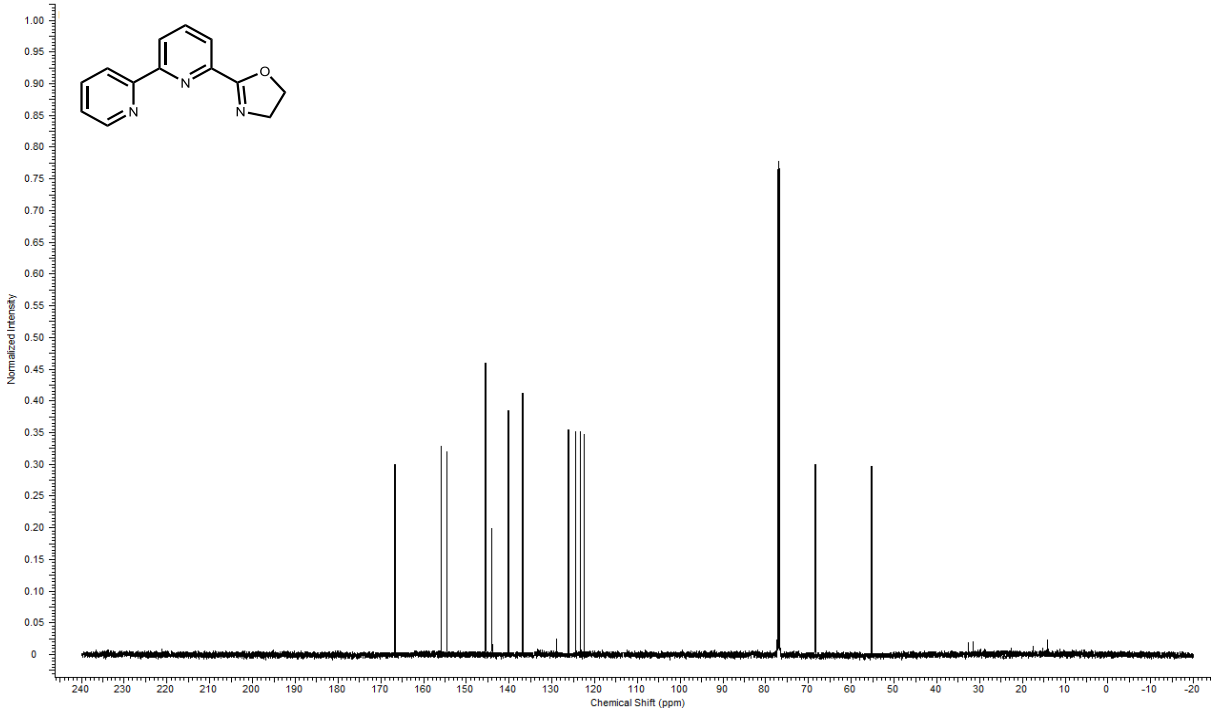
^{1}H NMR (500 MHz, $CDCl_3$) of 2,2'-bipyridyl-6-carbonitrile.



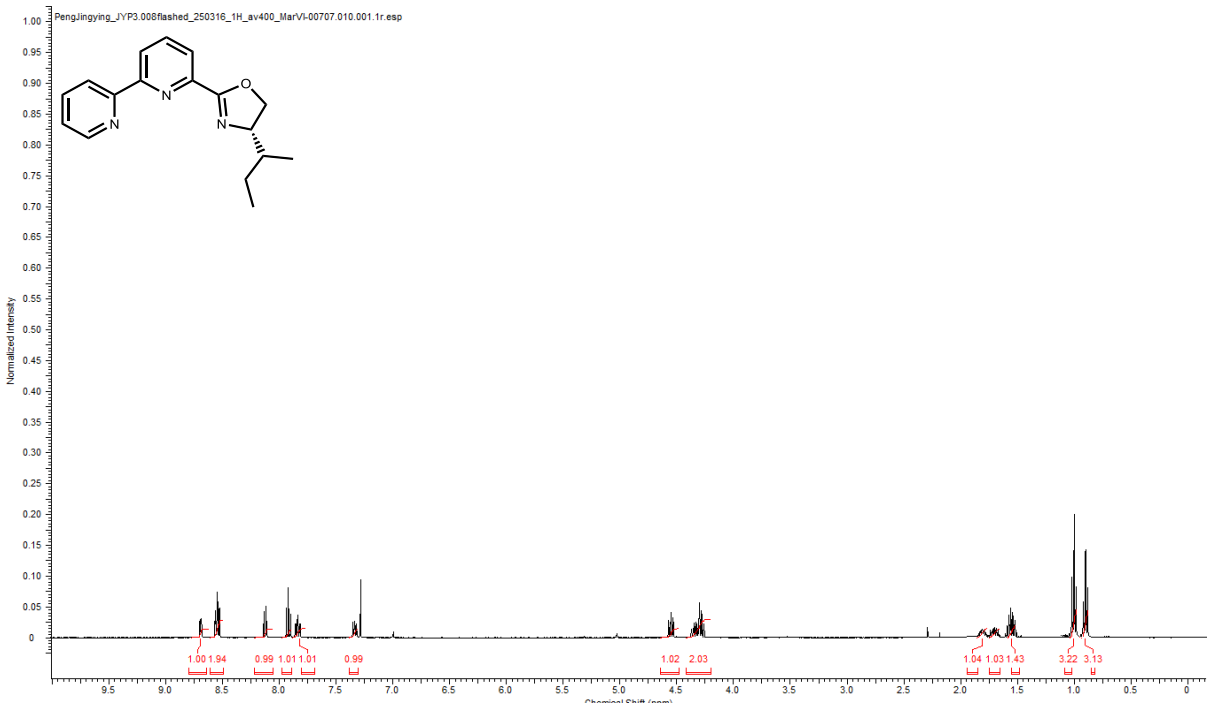
^{13}C NMR (125 MHz, $CDCl_3$) of 2,2'-bipyridyl-6-carbonitrile



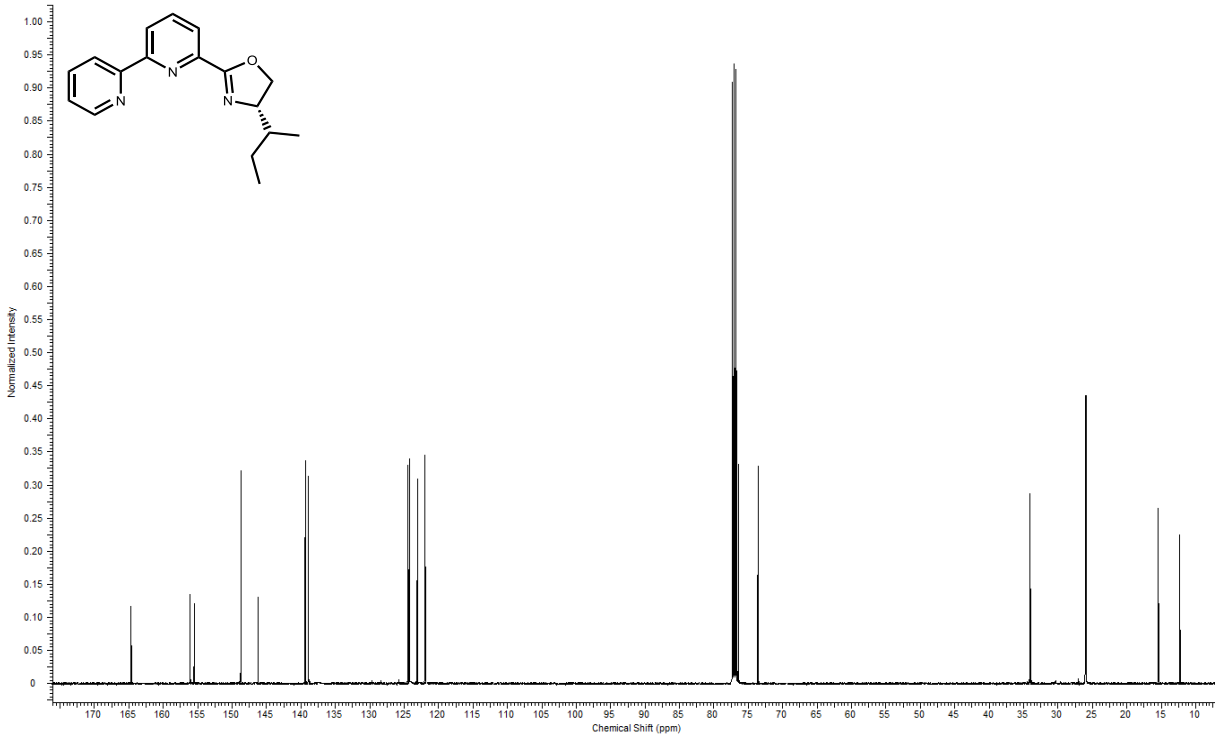
^{1}H NMR (500 MHz, $CDCl_3$) of 2,2'-bipyridyl-6-oxazoline (**4a**)



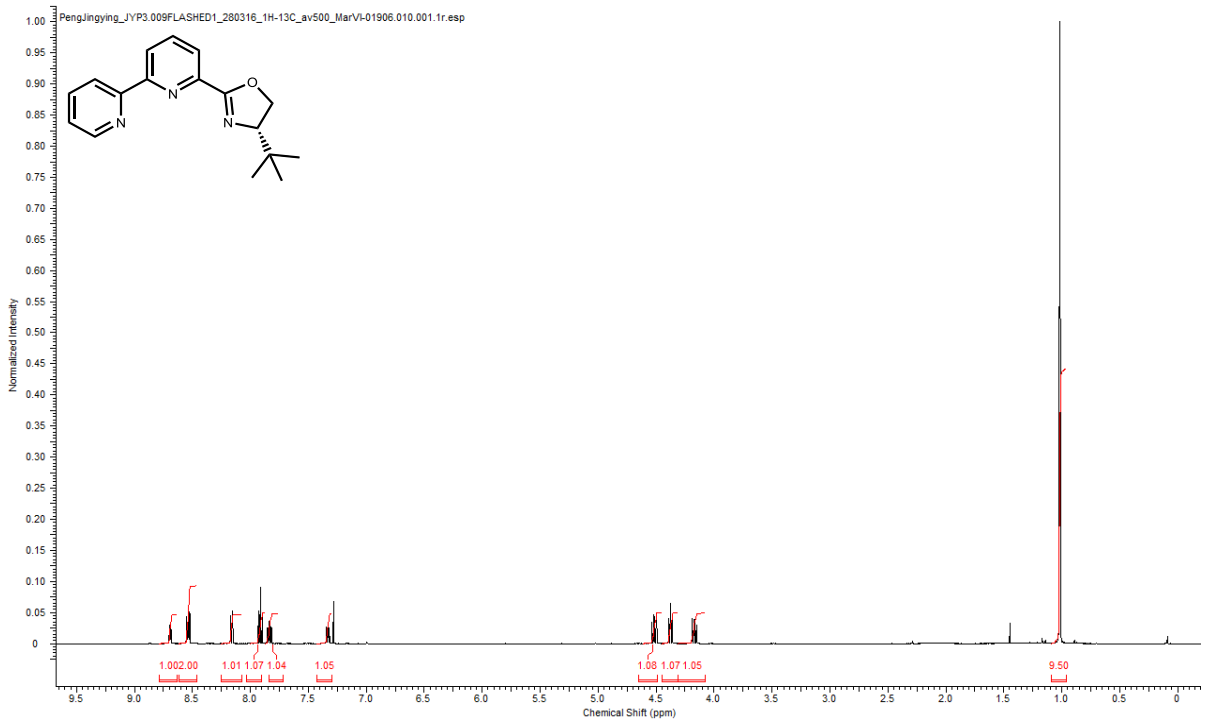
^{13}C NMR (125 MHz, $CDCl_3$) of 2,2'-bipyridyl-6-oxazoline (**4a**)



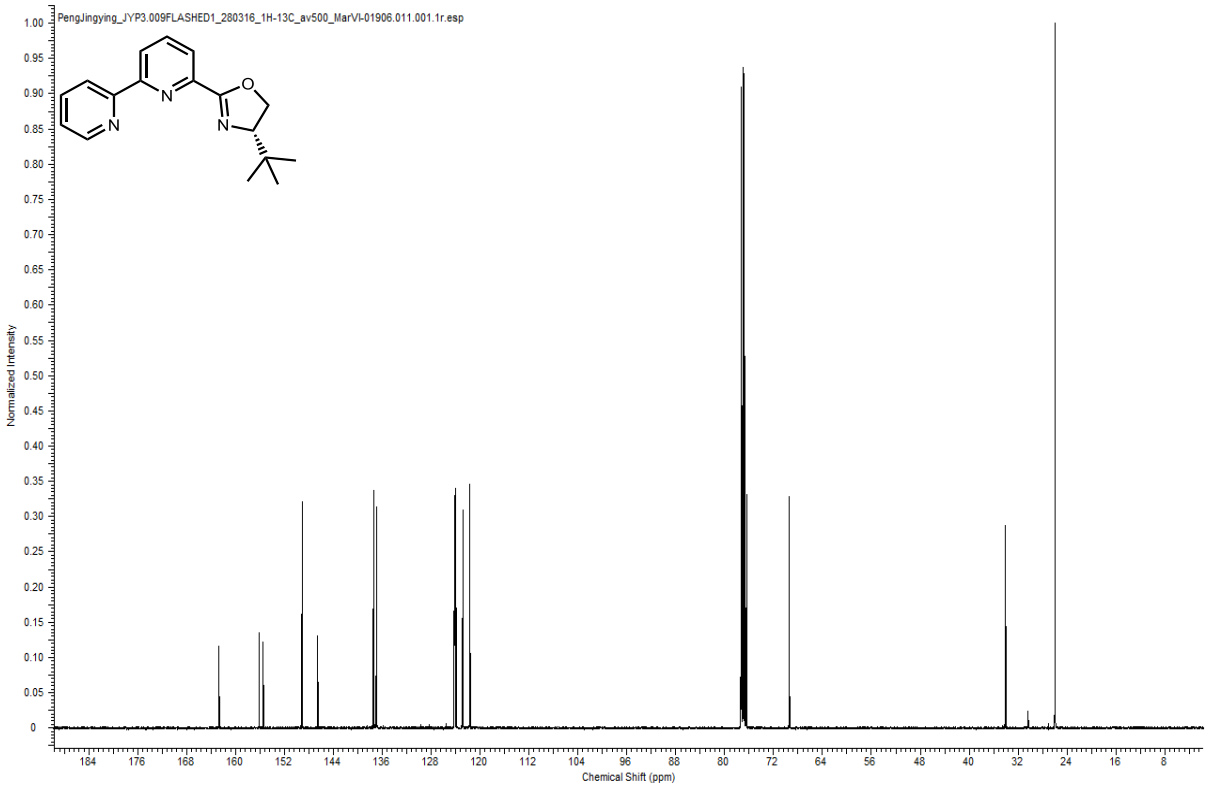
^{1}H NMR (500 MHz, $CDCl_3$) of 2,2'-bipyridyl-6-[*(S)-iso*-butyloxazoline] (**4b**)



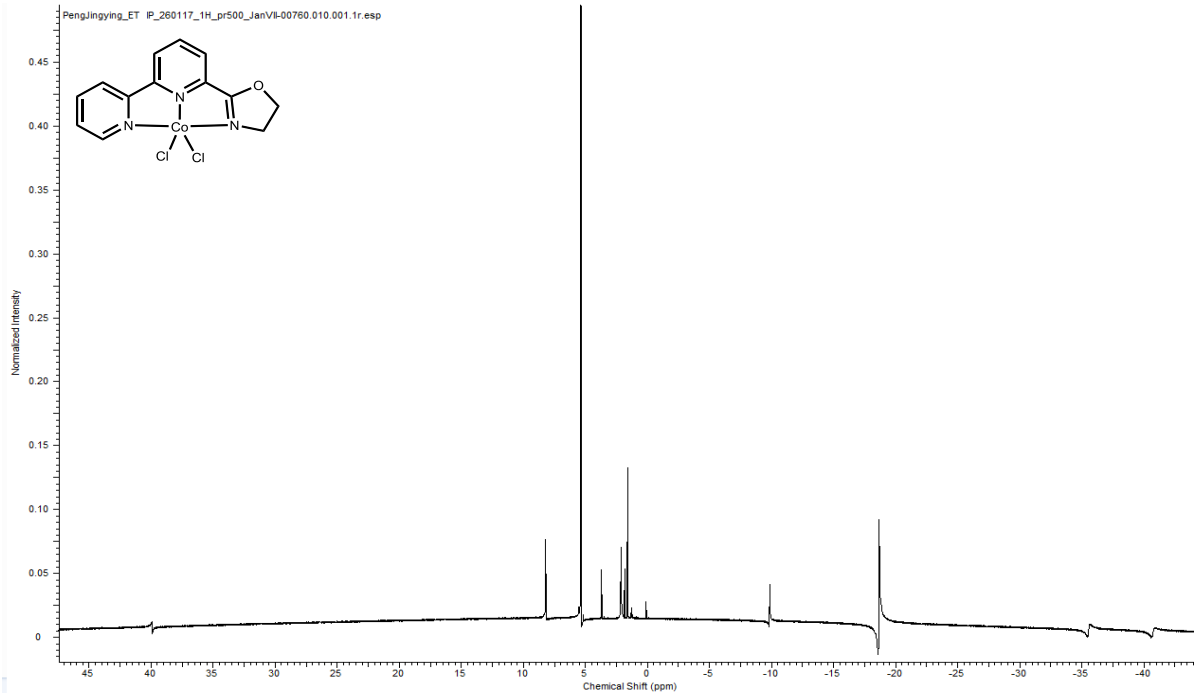
^{13}C NMR (125 MHz, $CDCl_3$) of 2,2'-bipyridyl-6-[*(S)-iso*-butyloxazoline] (**4b**)



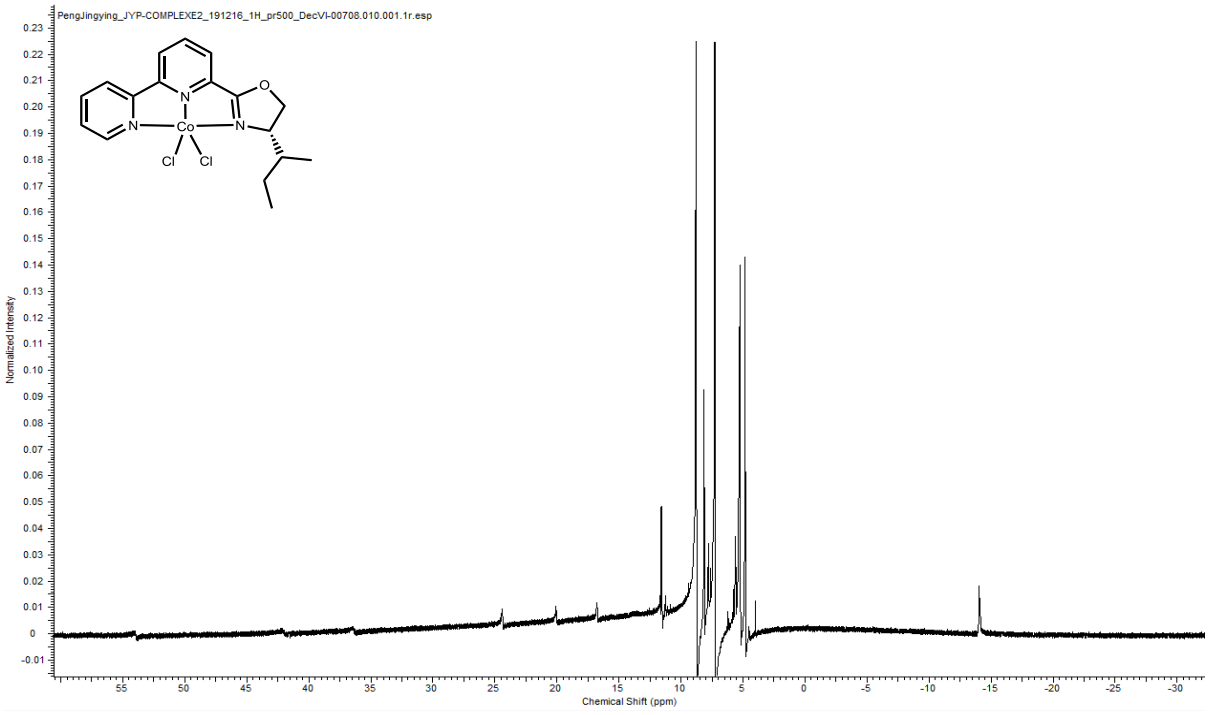
^{1}H NMR (500 MHz, $CDCl_3$) of 2,2'-bipyridyl-6-[*(S)-tert*-butyloxazoline] (**4c**)



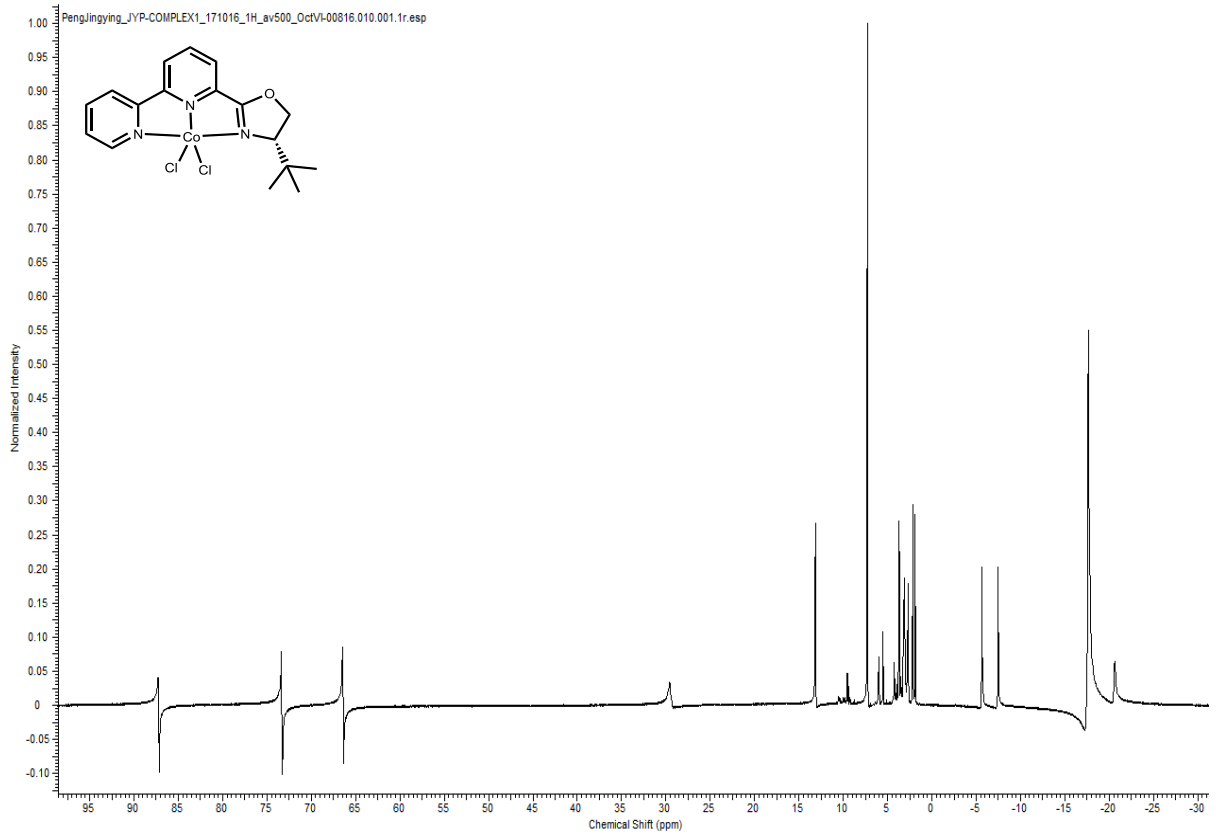
^{13}C NMR (125 MHz, $CDCl_3$) of 2,2'-bipyridyl-6-[*(S)-tert*-butyloxazoline] (**4c**)



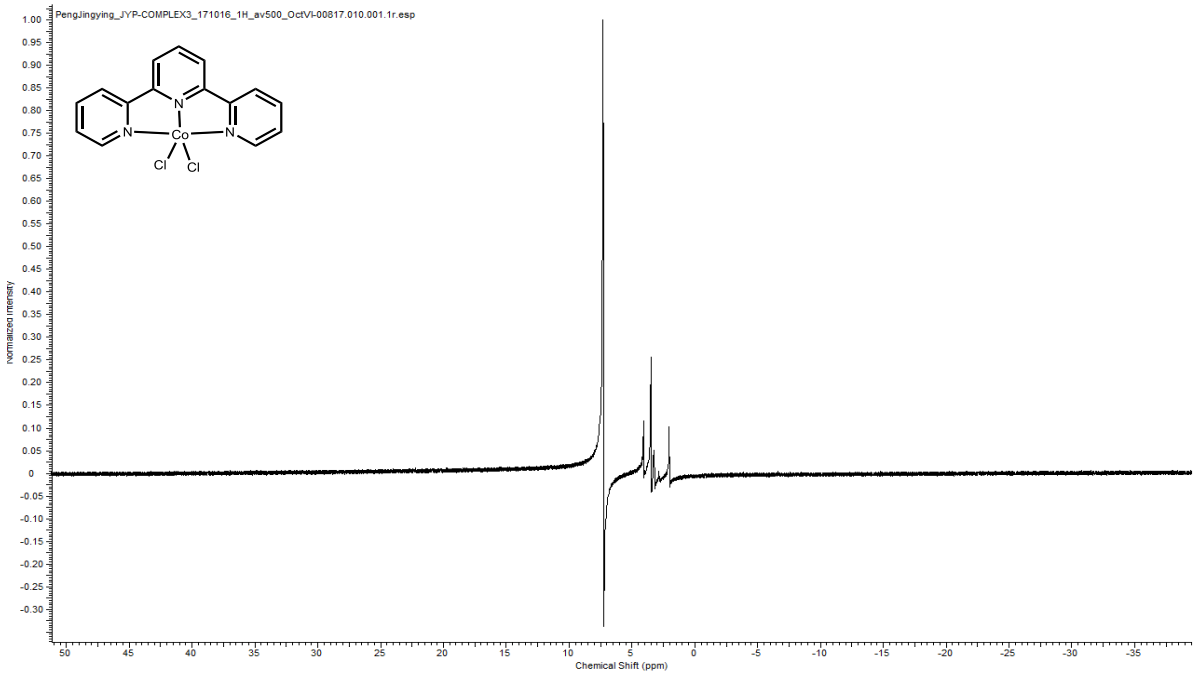
^{1}H NMR (500 MHz, CD_2Cl_2) of (2,2'-bipyridyl-6-oxazoline)$CoCl_2$ (**5a**)



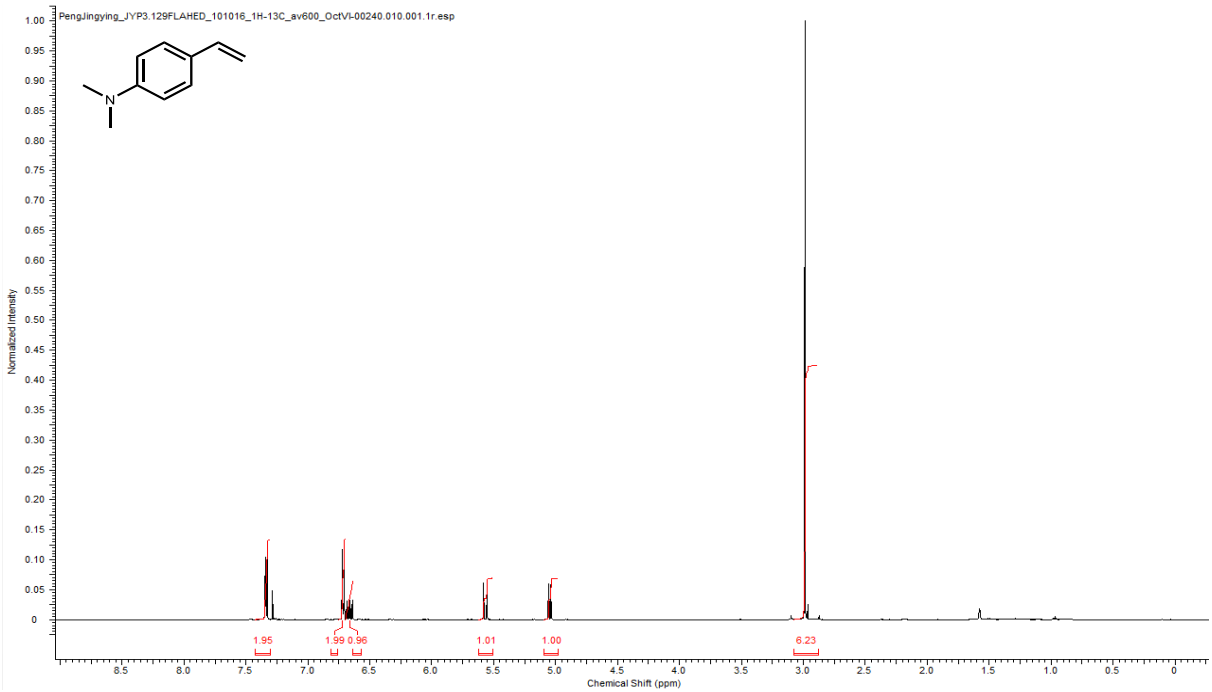
^{1}H NMR (500 MHz, CD_2Cl_2) of {2,2'-bipyridyl-6-[*(S)-iso*-butyloxazoline]}$CoCl_2$ (**5b**)



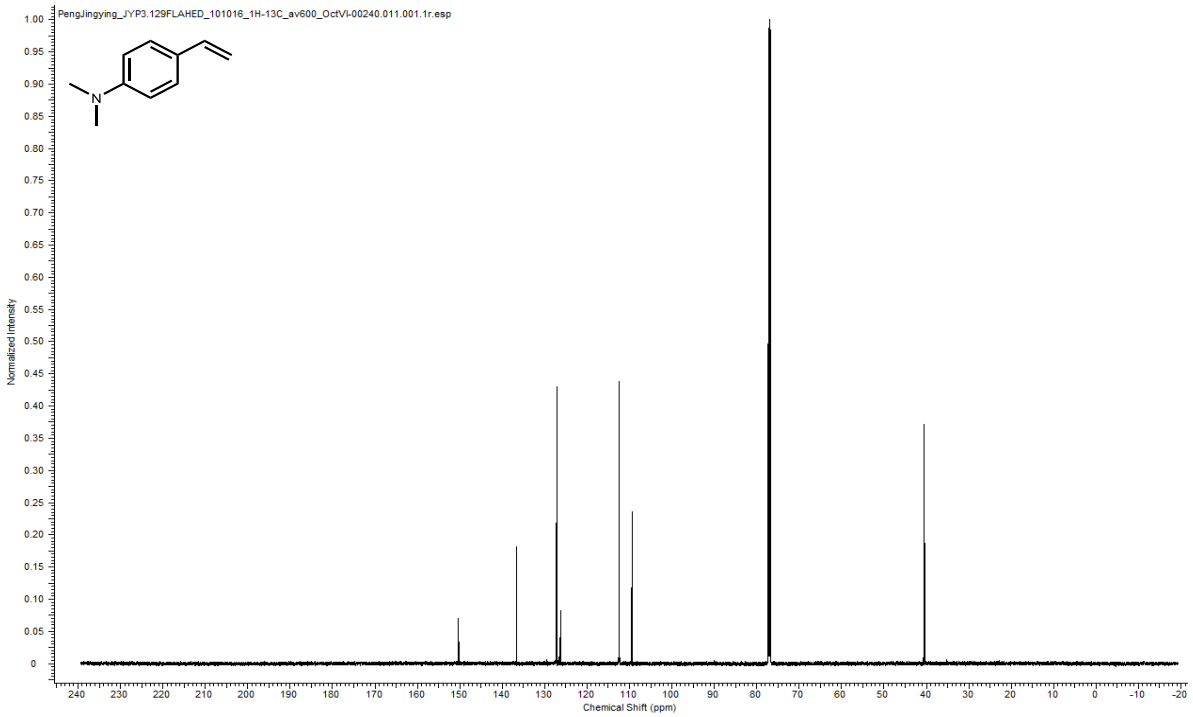
^{1}H NMR (500 MHz, CD_2Cl_2) of {2,2'-bipyridyl-6-[*(S)-tert*-butyloxazoline]}$CoCl_2$ (**5c**)



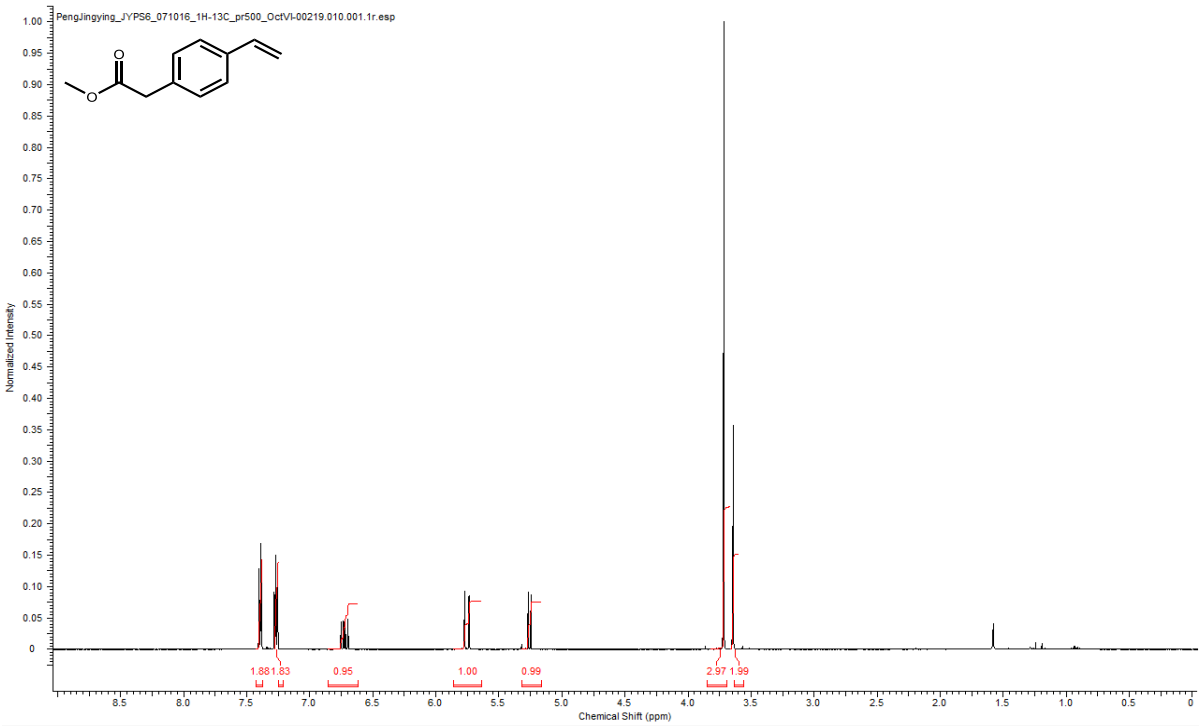
^{1}H NMR (500 MHz, CD_2Cl_2) of terpyridine $CoCl_2$ (**5d**)



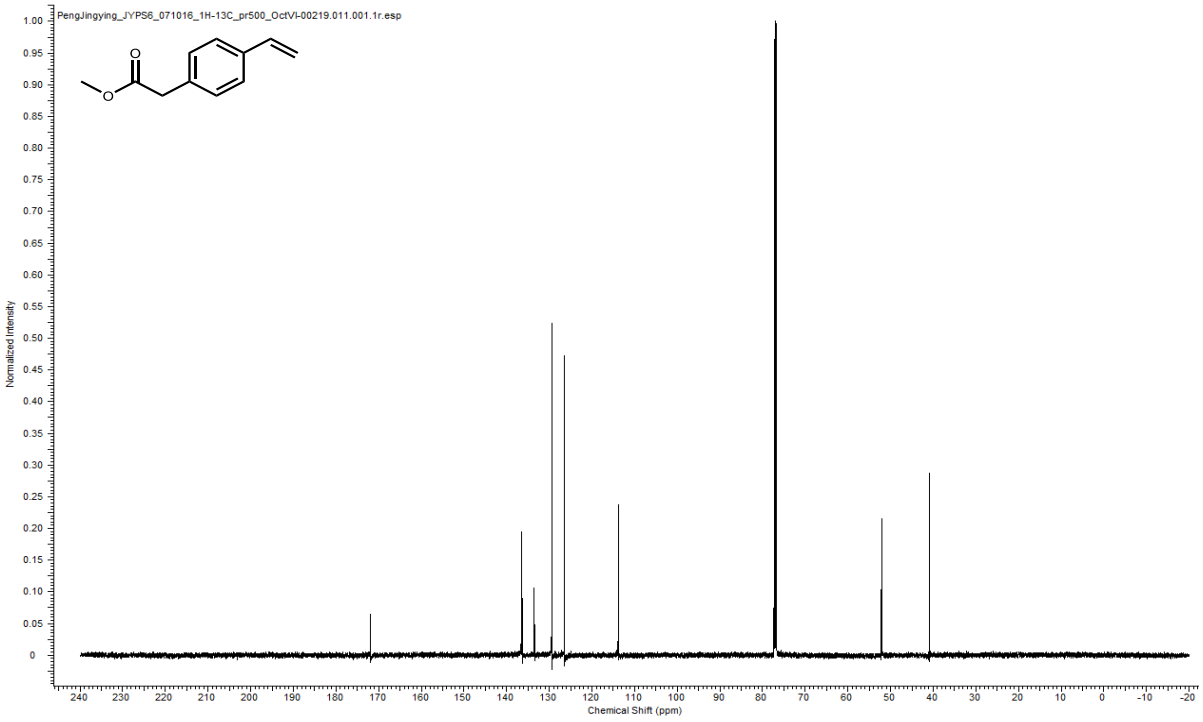
^{1}H NMR (500 MHz, $CDCl_3$) of *N,N*-Dimethylamino-4-vinylbenzene (**1q**)



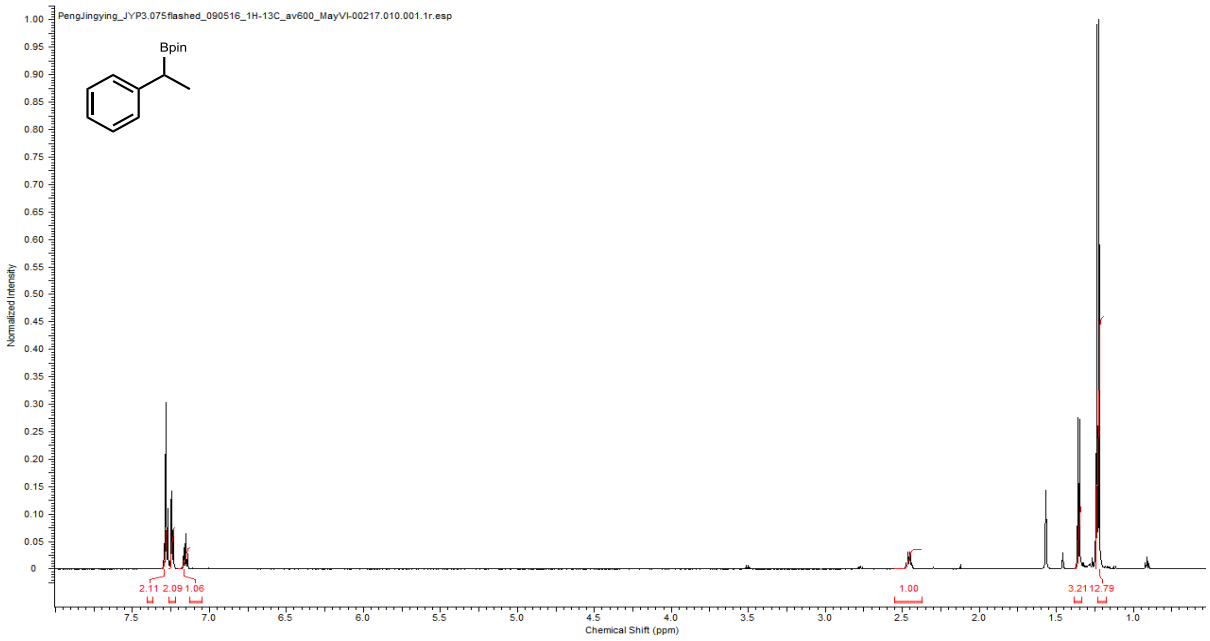
^{13}C NMR (125 MHz, $CDCl_3$) of *N,N*-Dimethylamino-4-vinylbenzene (**1q**)



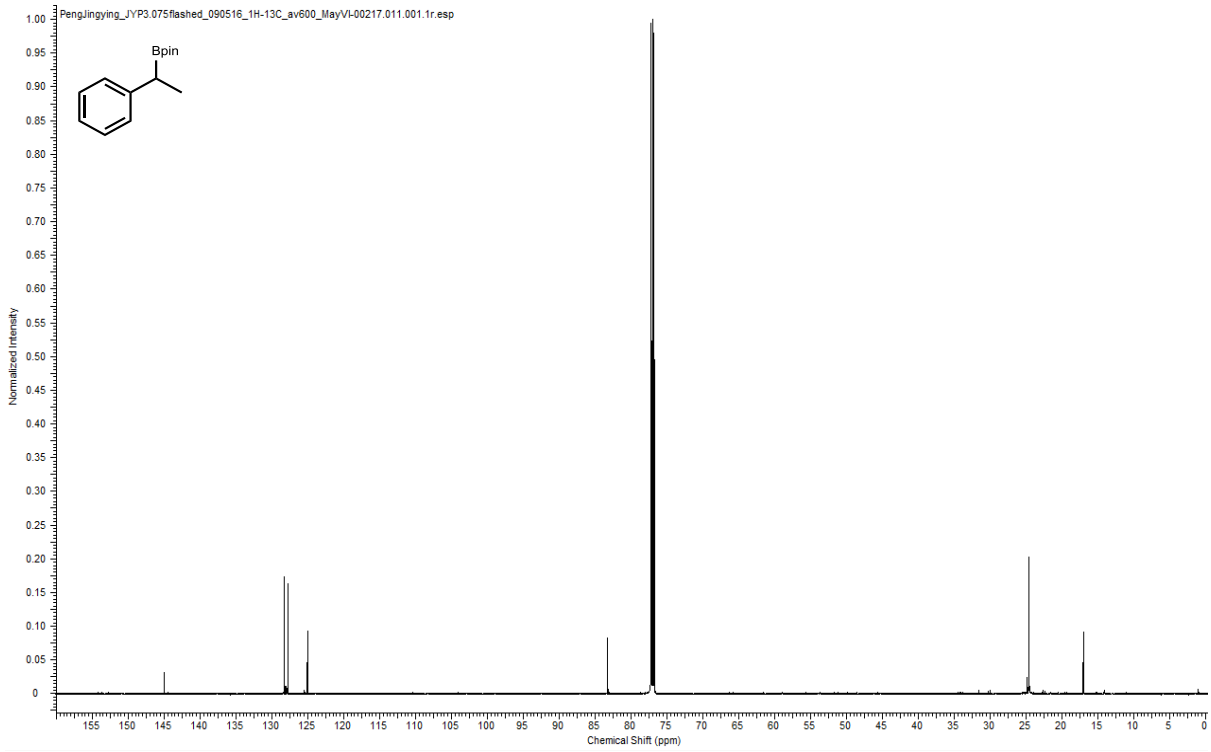
^{1}H NMR (500 MHz, $CDCl_3$) of 4-vinyl(phenyl)acetic acid methyl ester(**1t**)



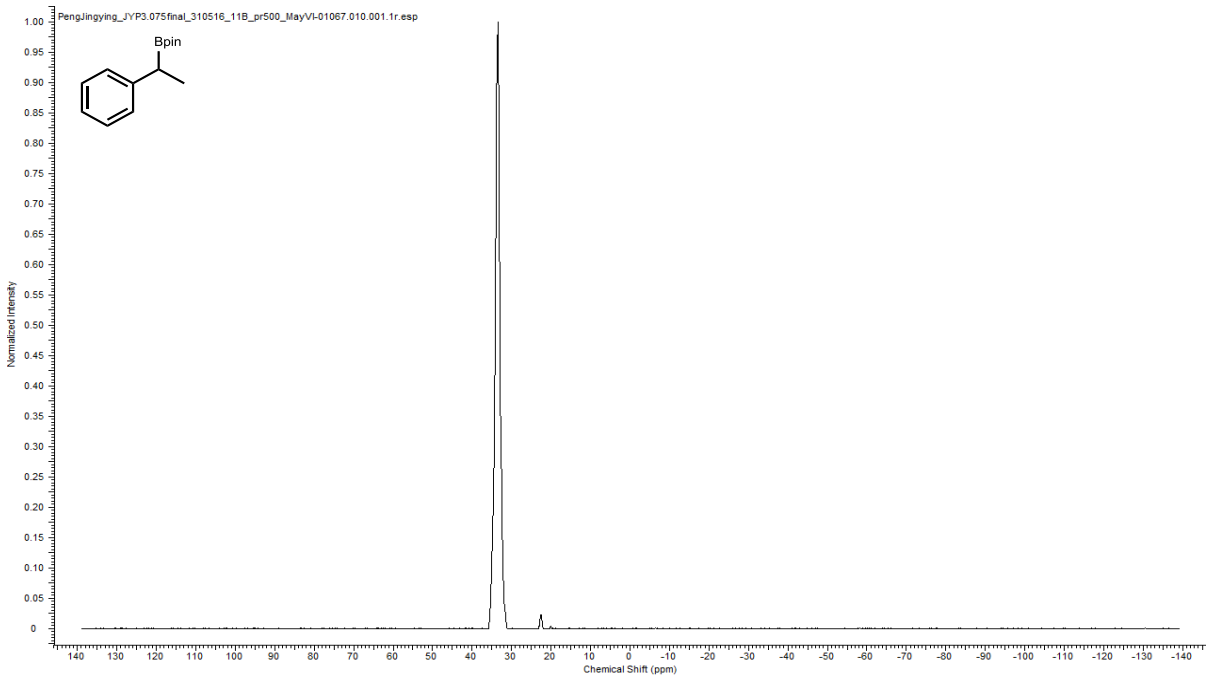
^{13}C NMR (125 MHz, $CDCl_3$) of 4-vinyl(phenyl)acetic acid methyl ester (**1t**)



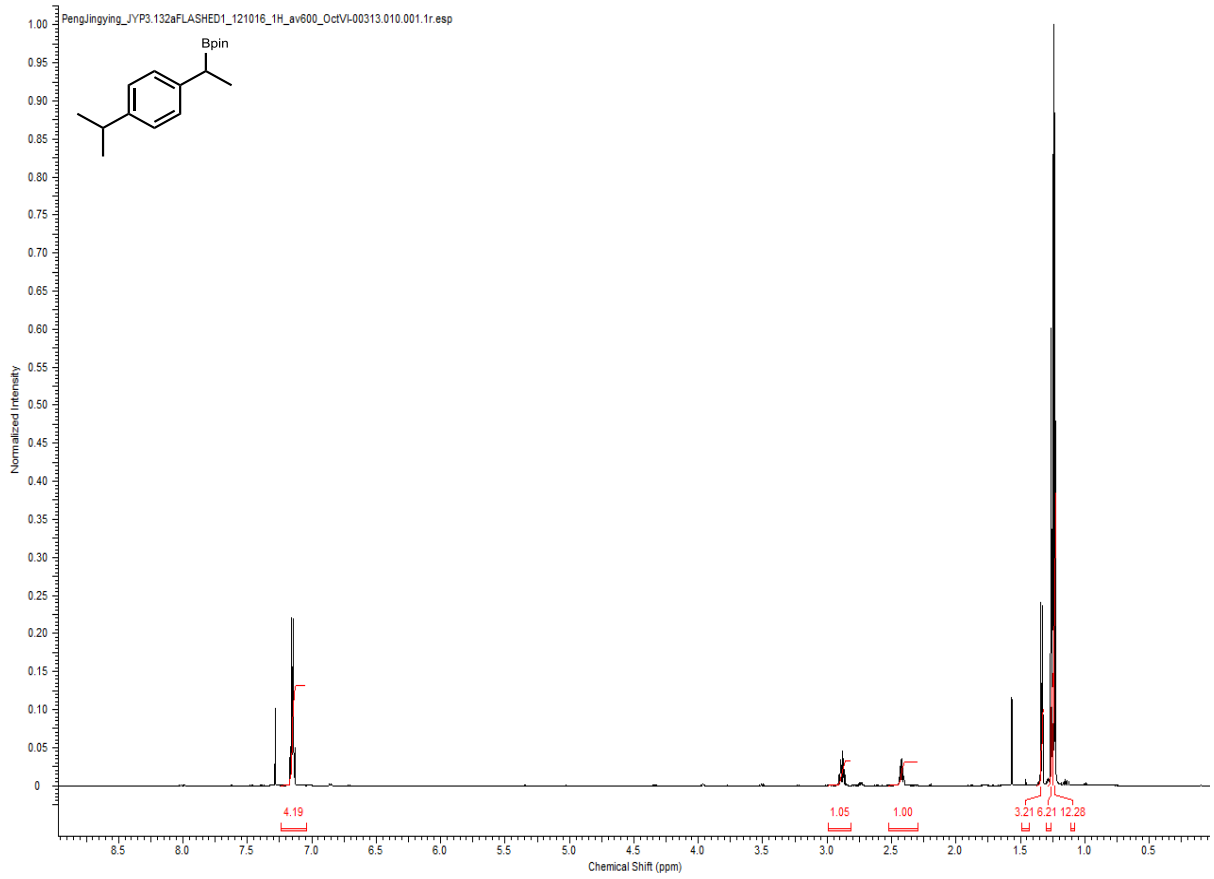
^{1}H NMR (600 MHz, $CDCl_3$) of 2-(1-phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a**)



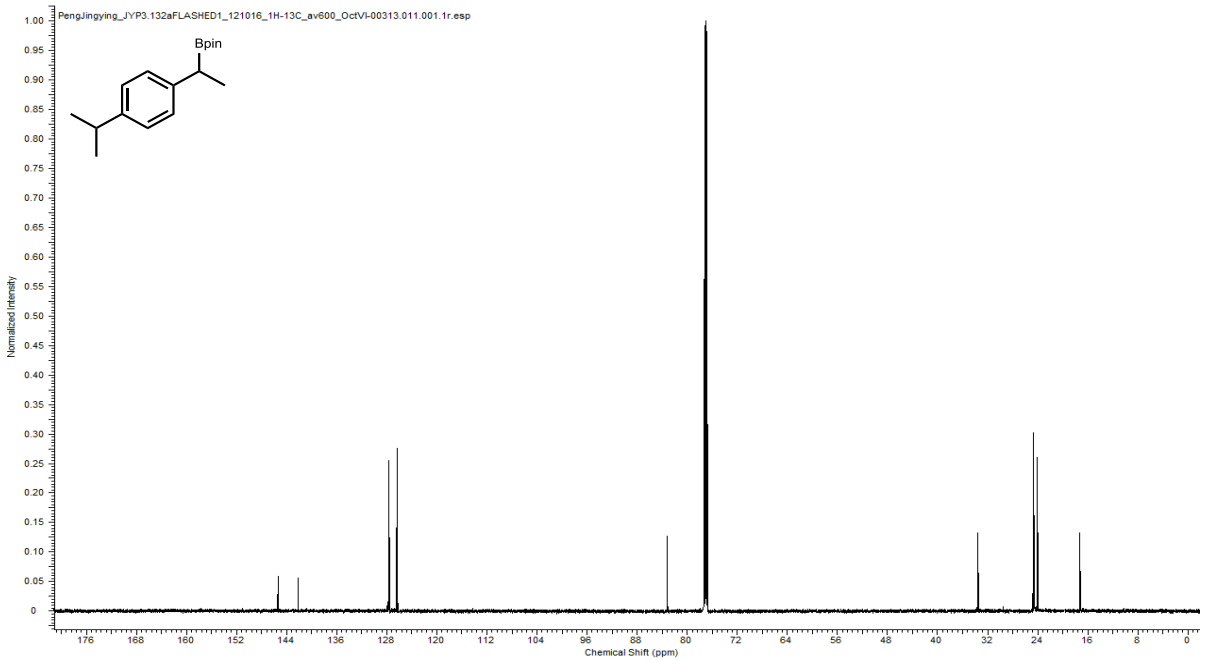
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a**)



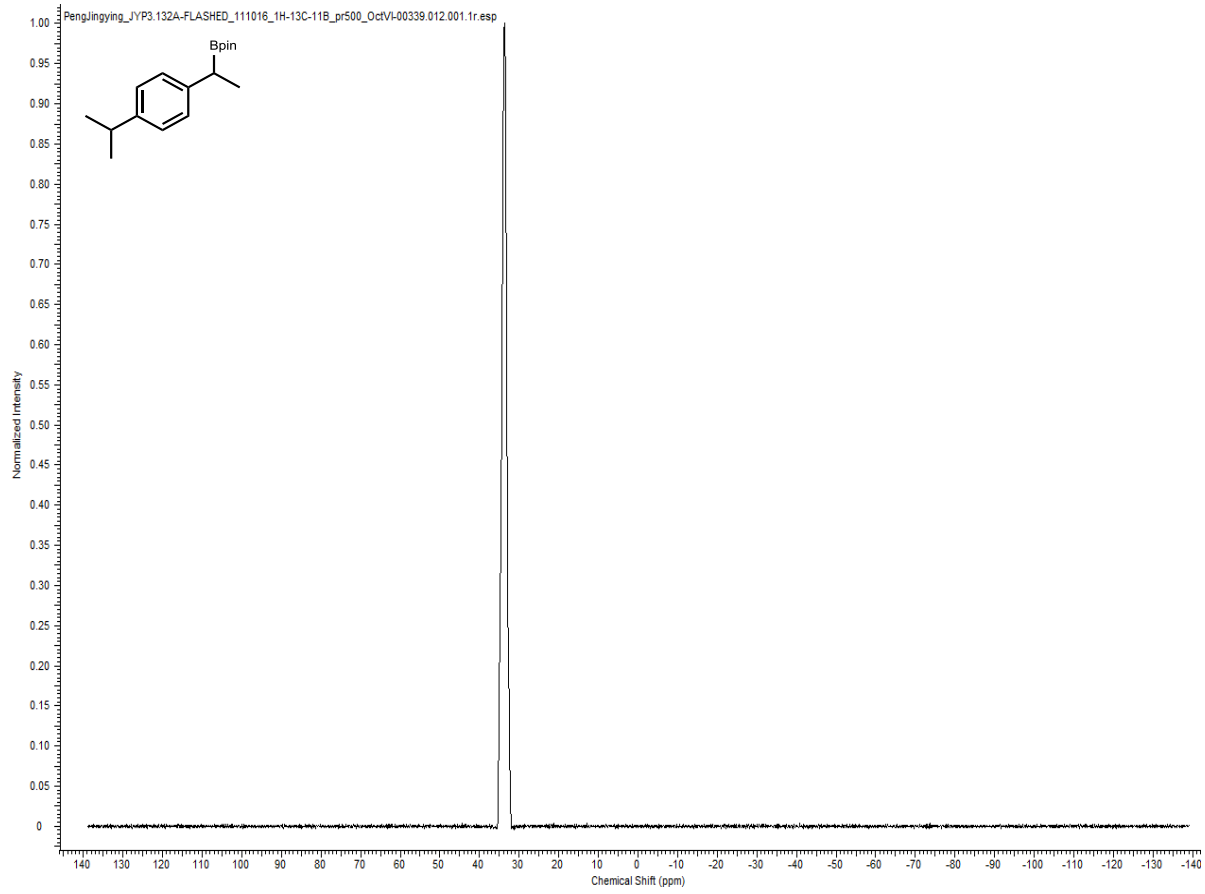
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a**)



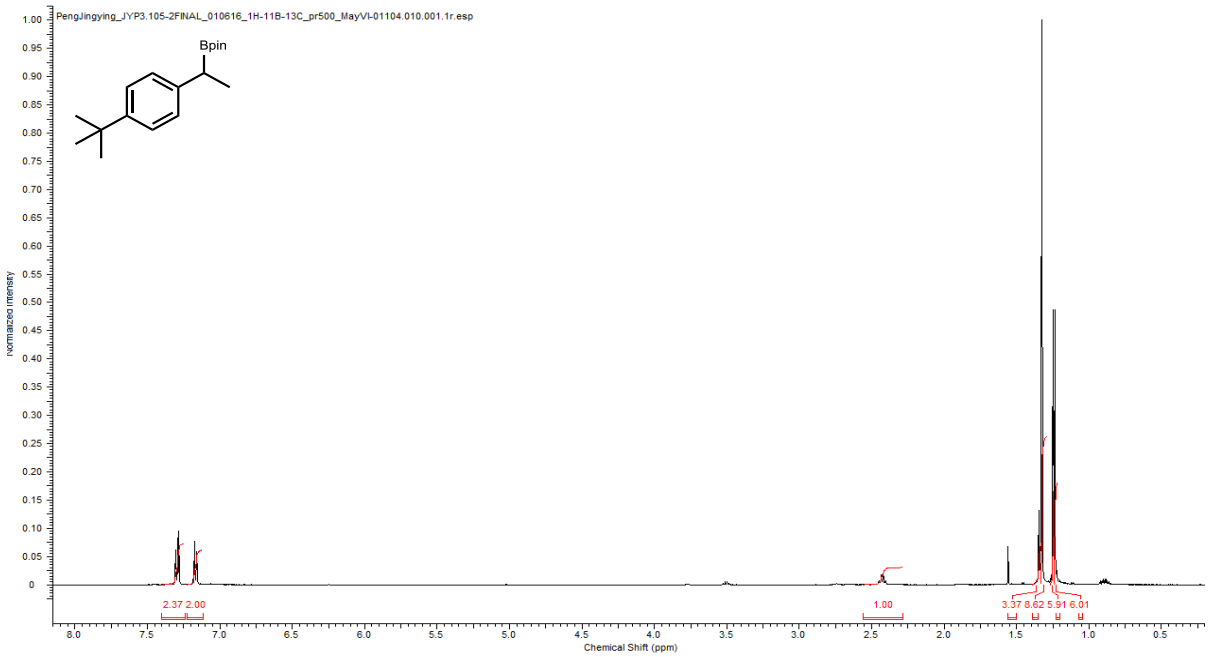
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(4-*iso*-propylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**)



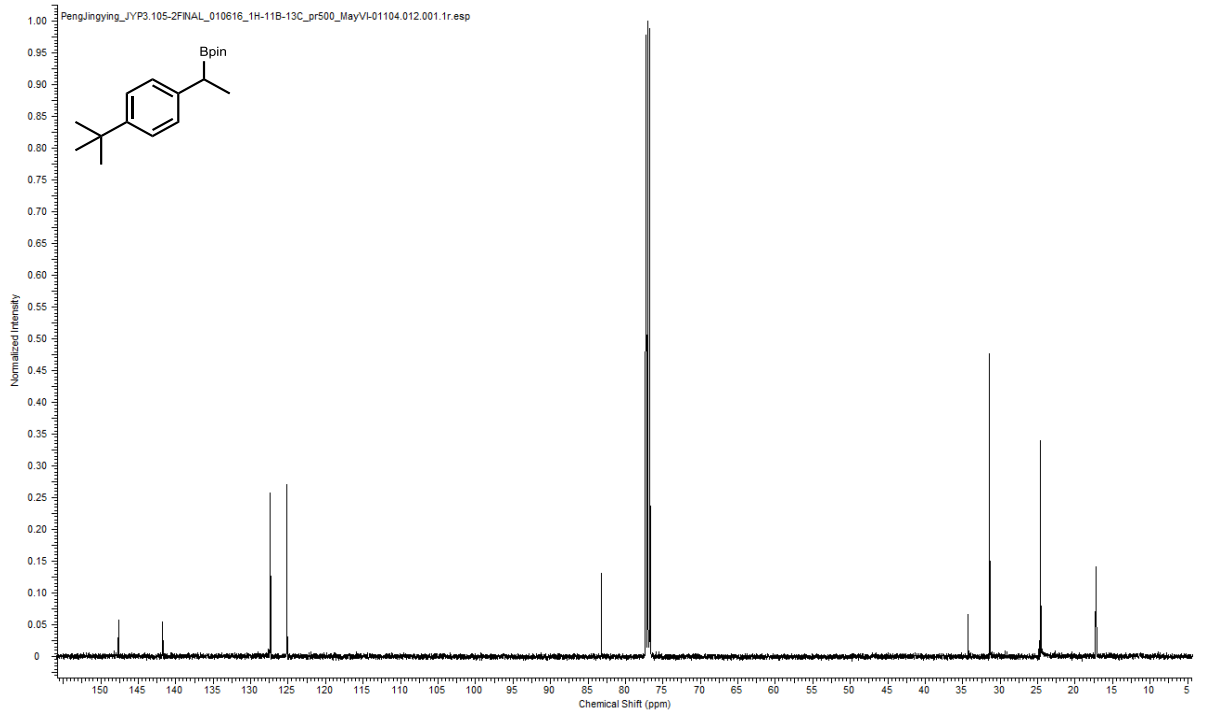
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(4-iso-propylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**)



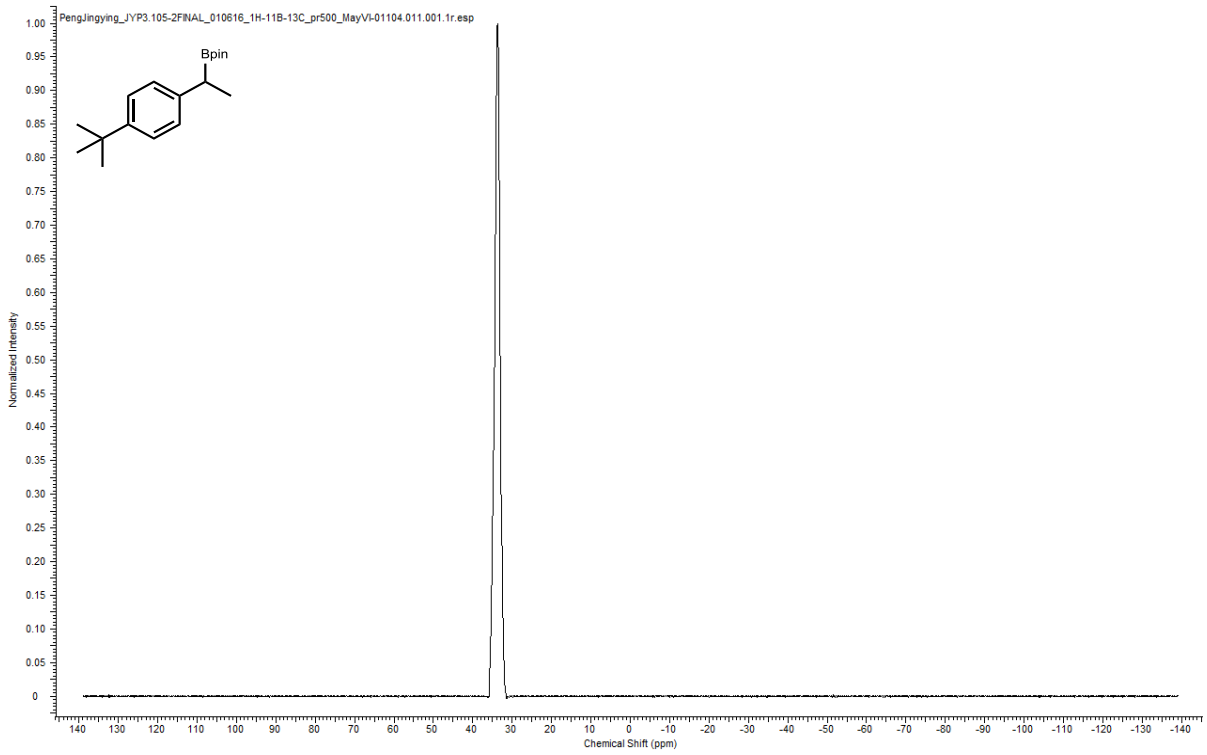
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(4-iso-propylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**)



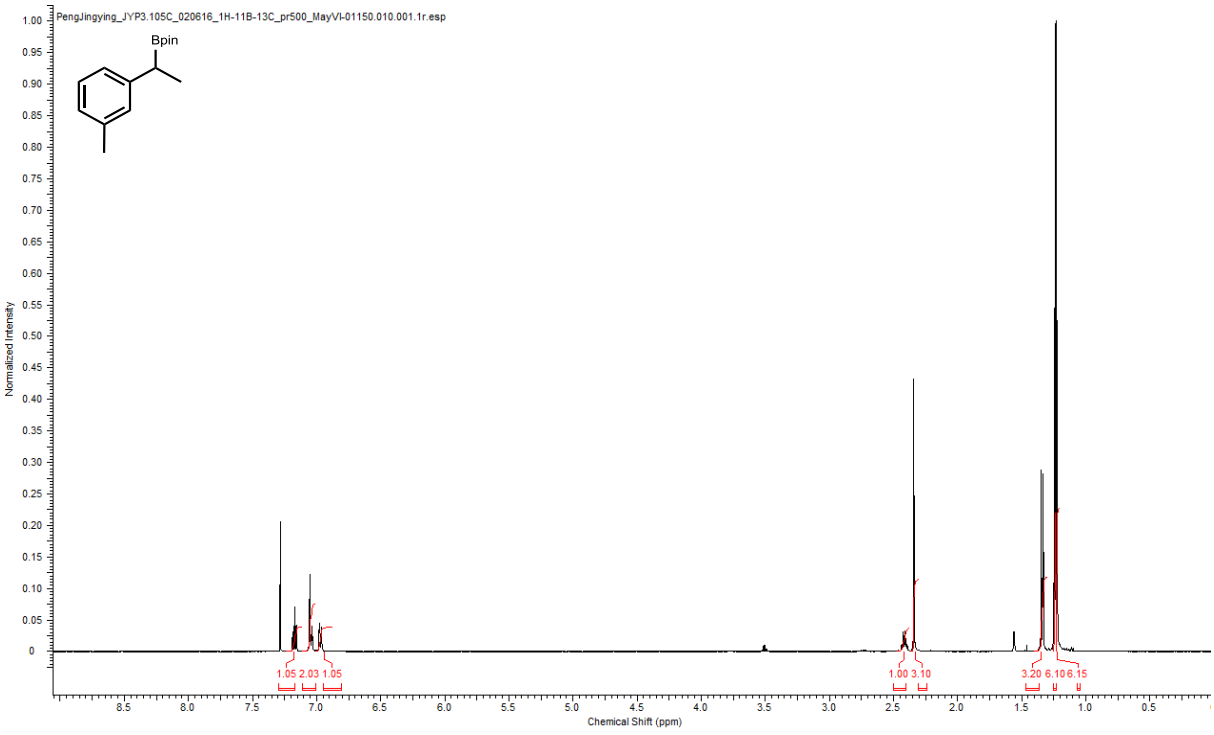
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(4-*tert*-butylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c**)



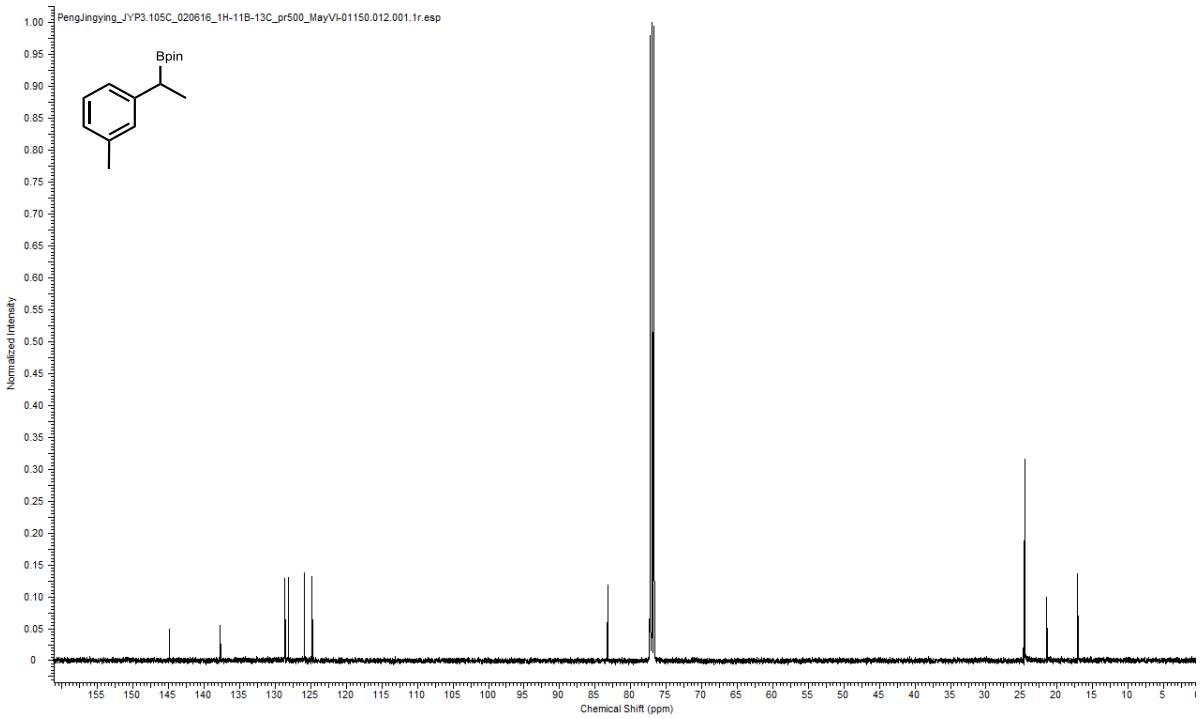
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(4-*tert*-butylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2 dioxaborolane (**3c**)



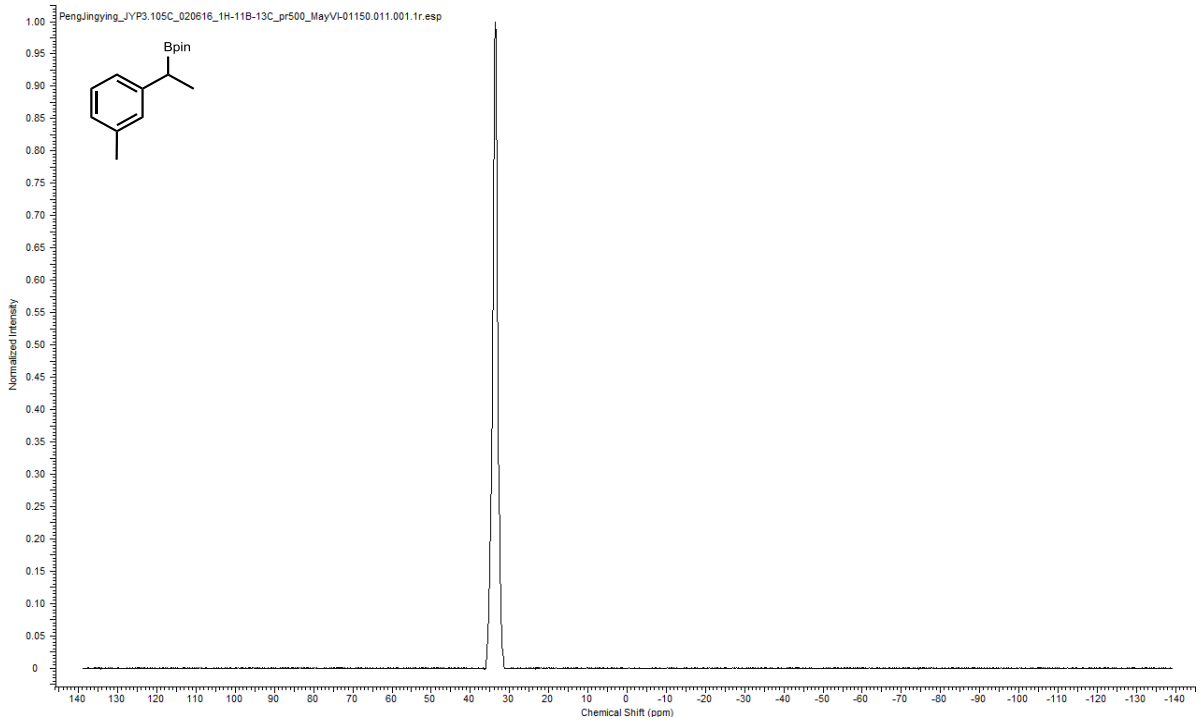
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(4-*tert*-Butylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c**)



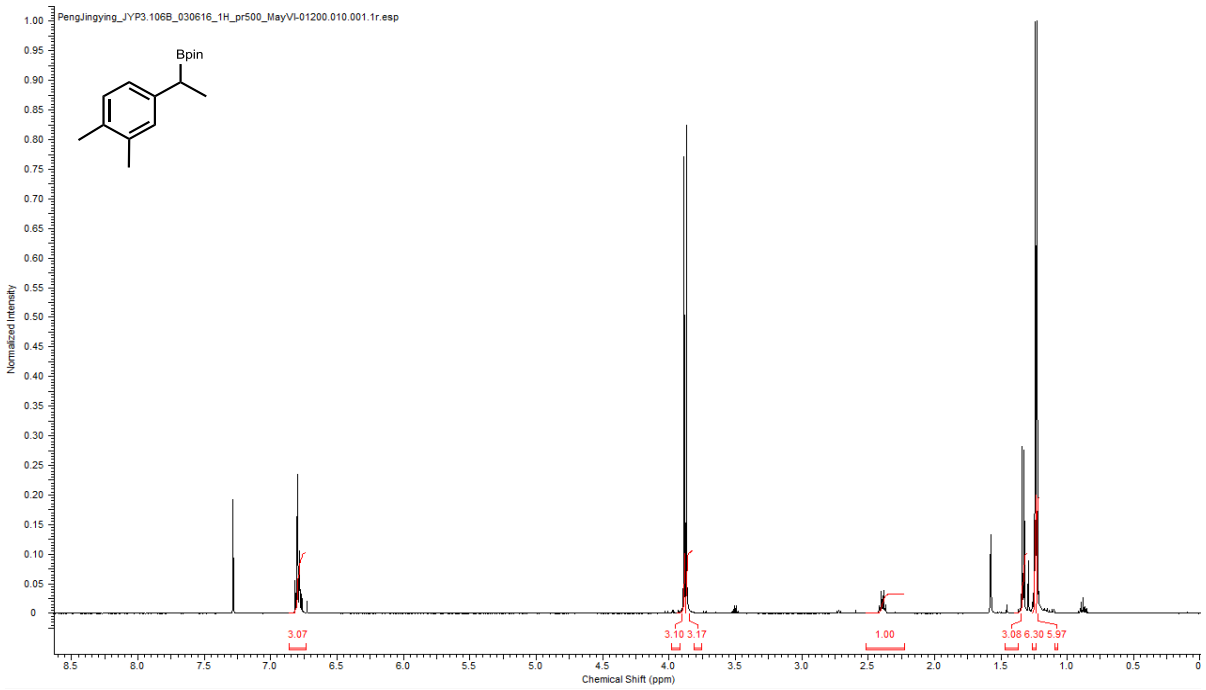
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(3-methylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**)



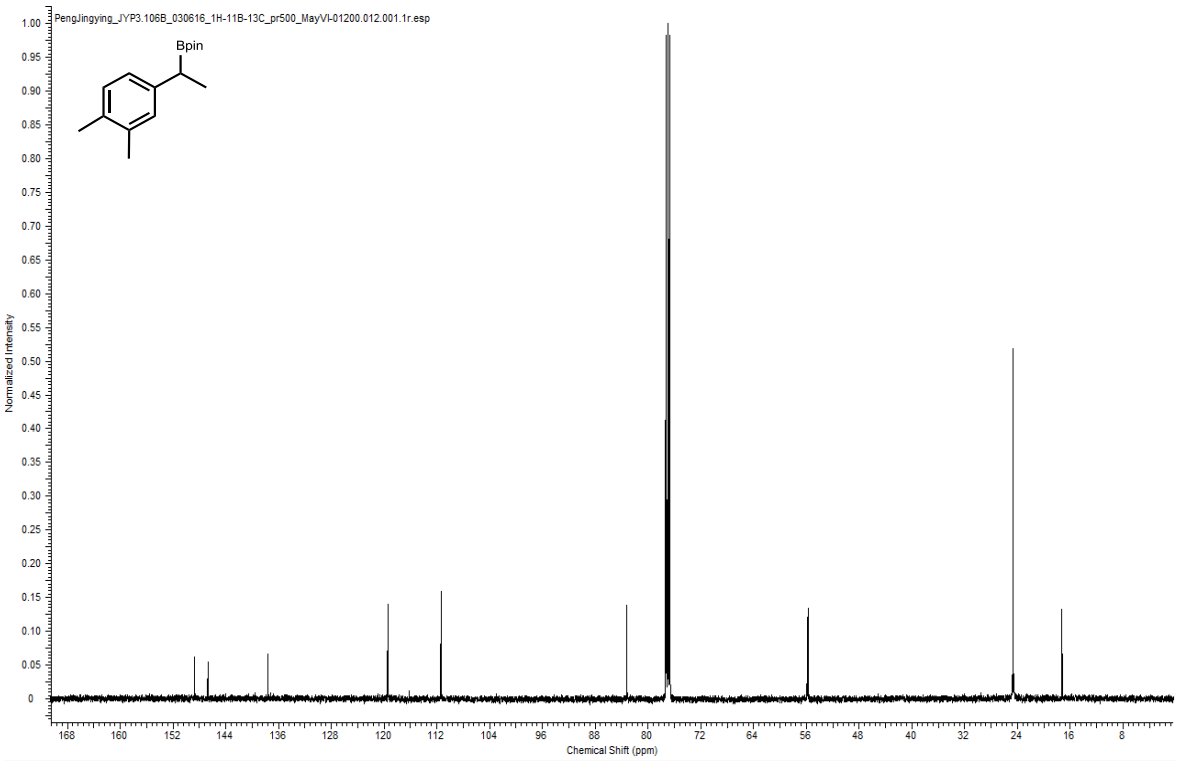
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(3-methylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**)



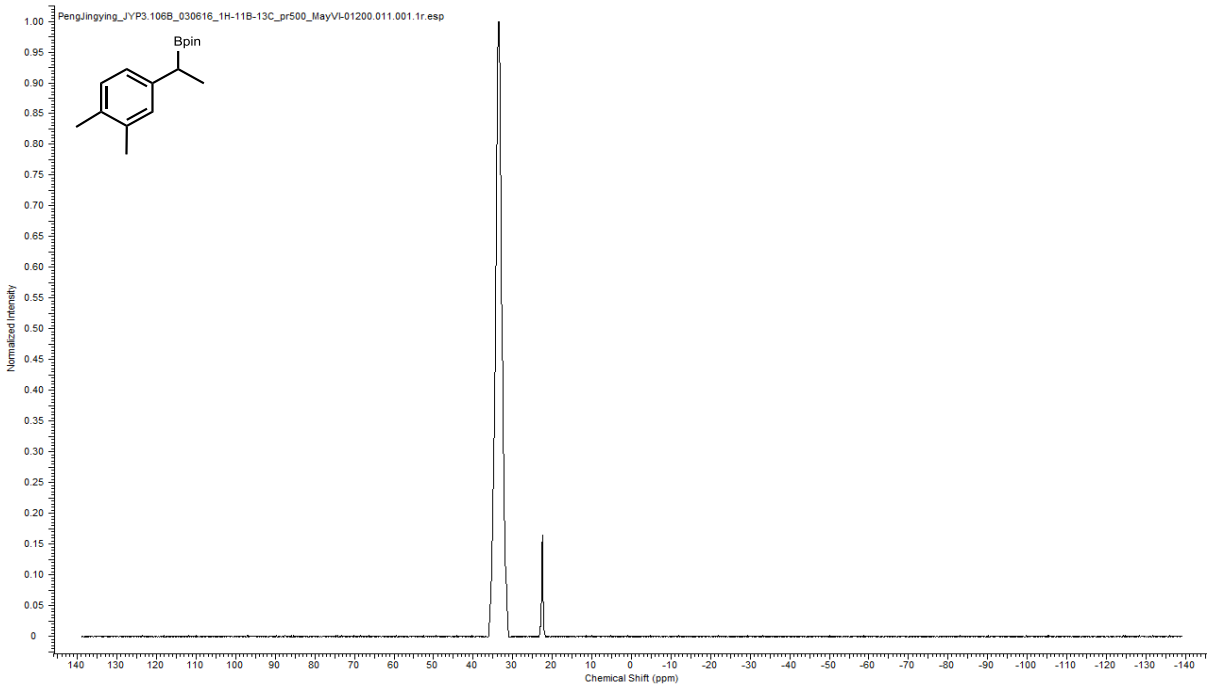
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(3-methylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**)



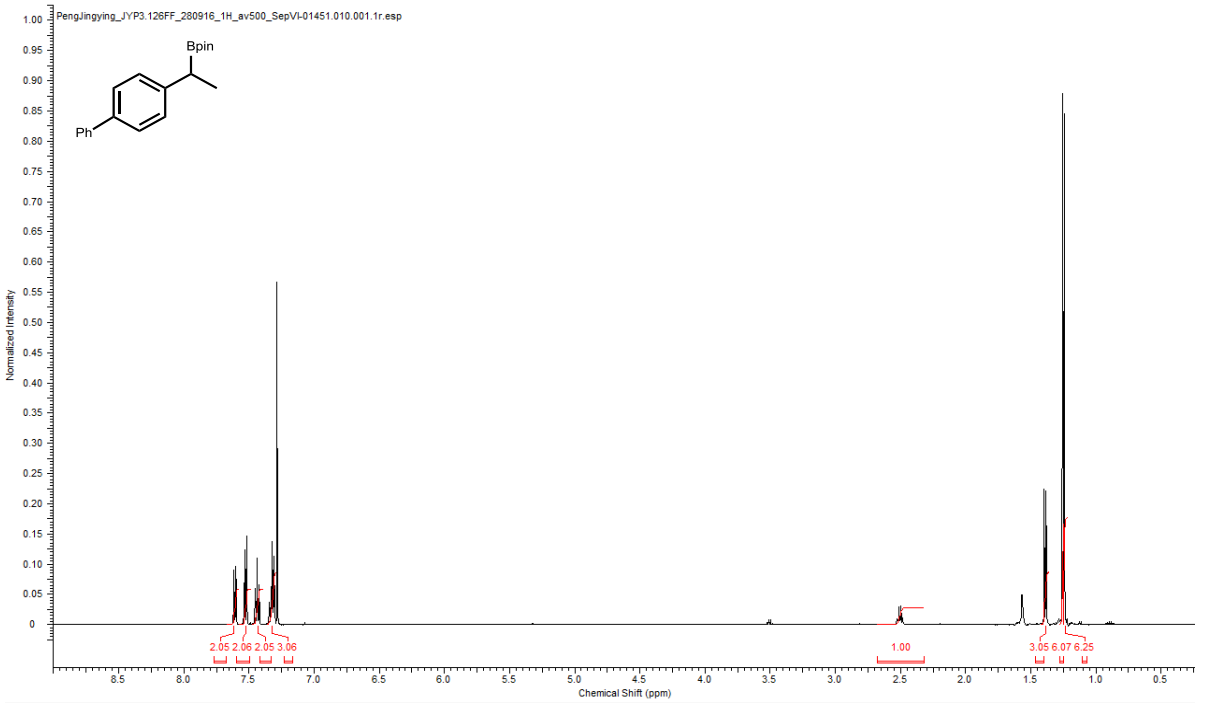
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(3,4-dimethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**)



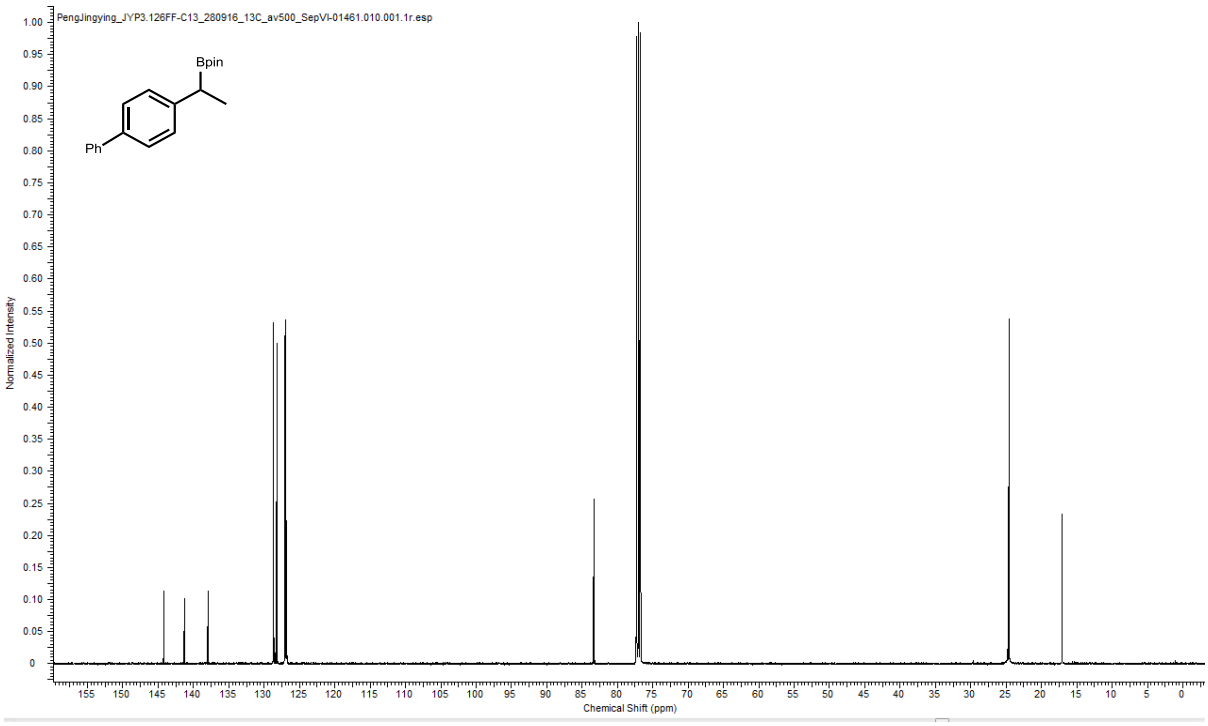
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(3,4-dimethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**)



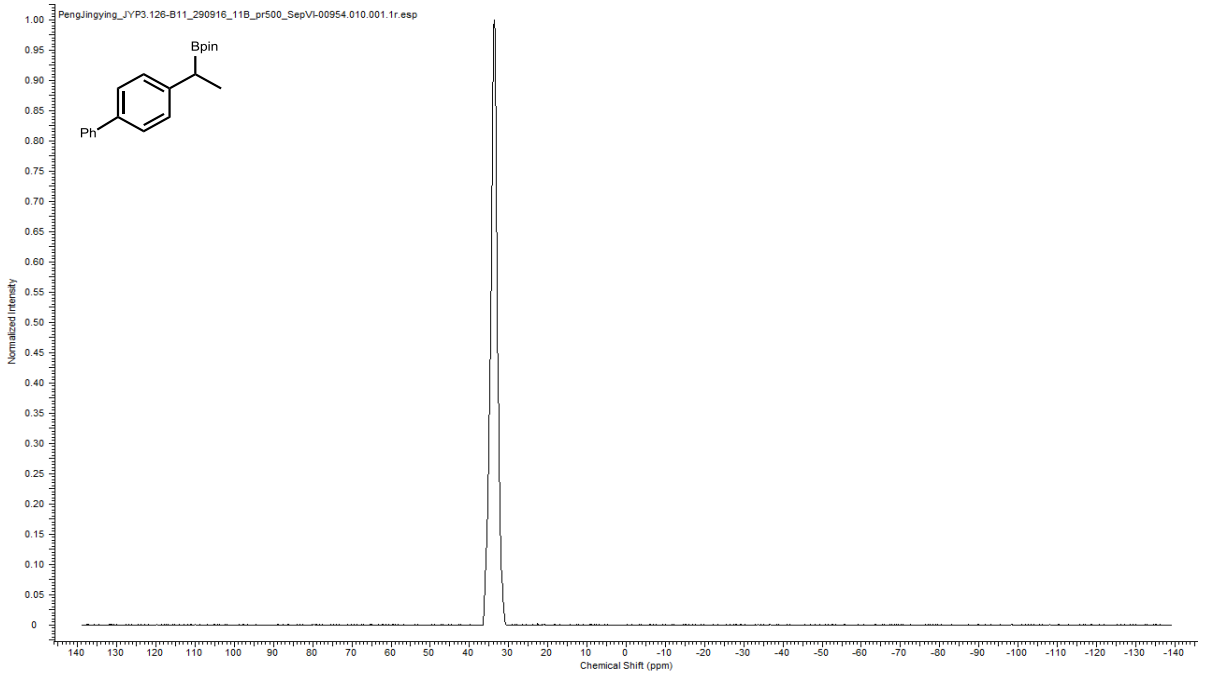
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(3,4-dimethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**)



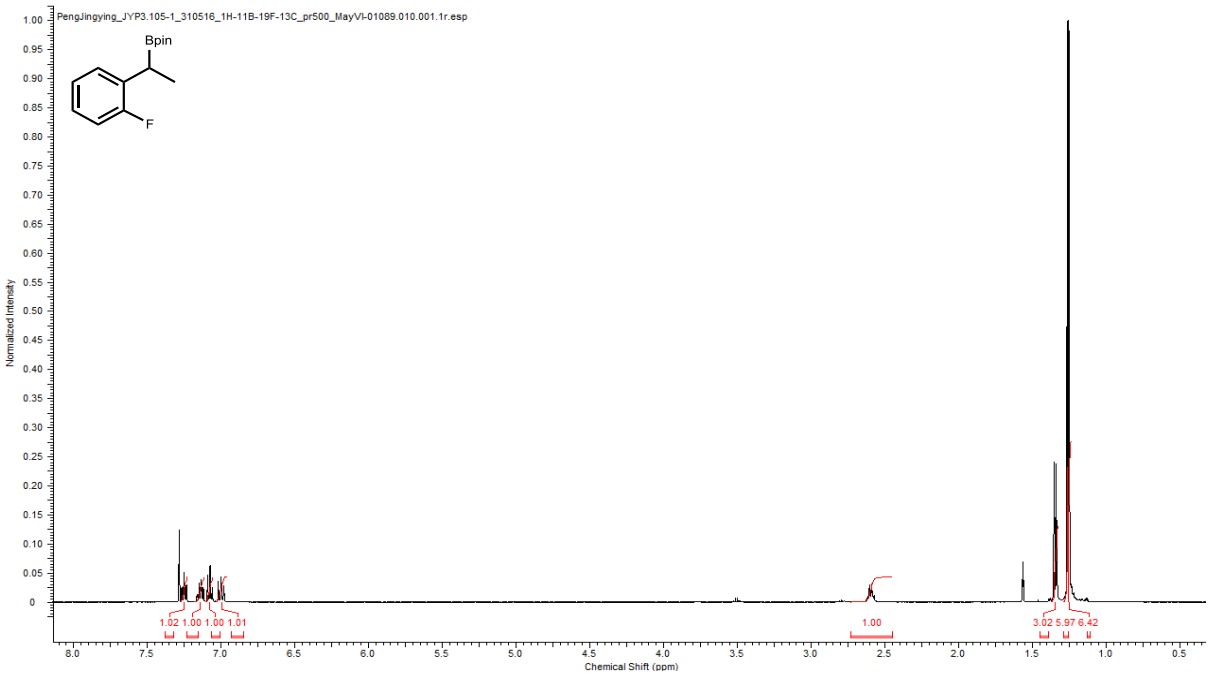
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(1,1'-biphenyl)-4-ylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**)



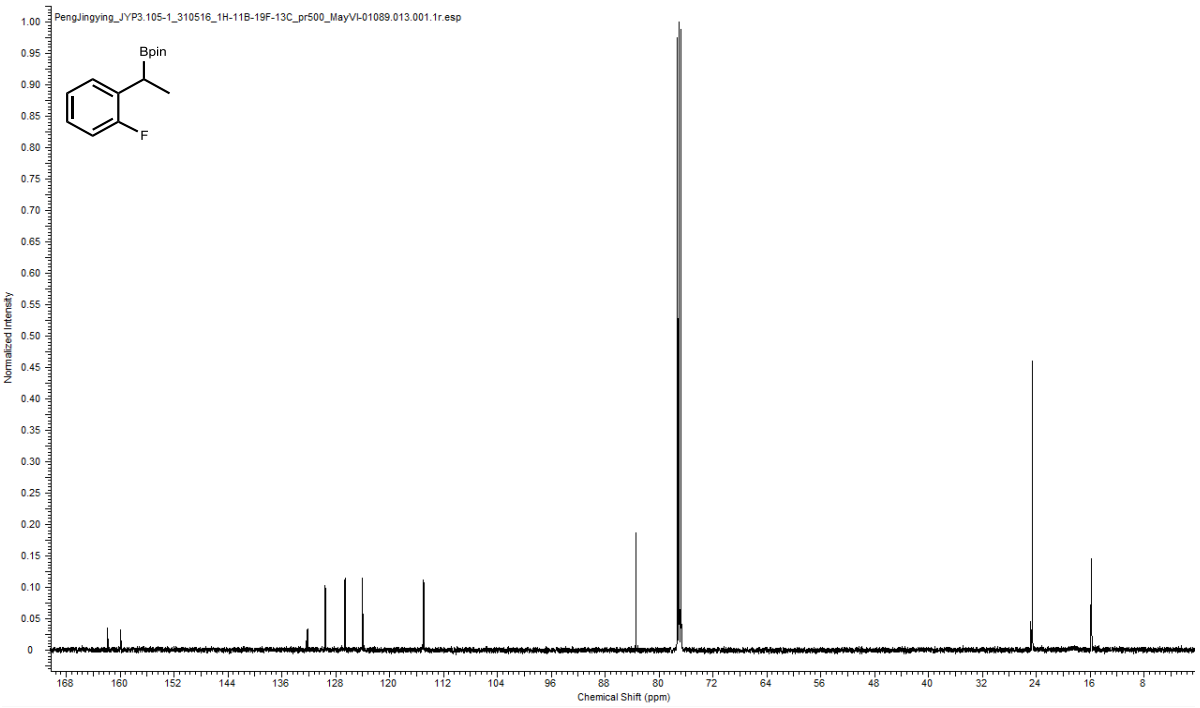
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(1,1'-biphenyl)-4-ylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**)



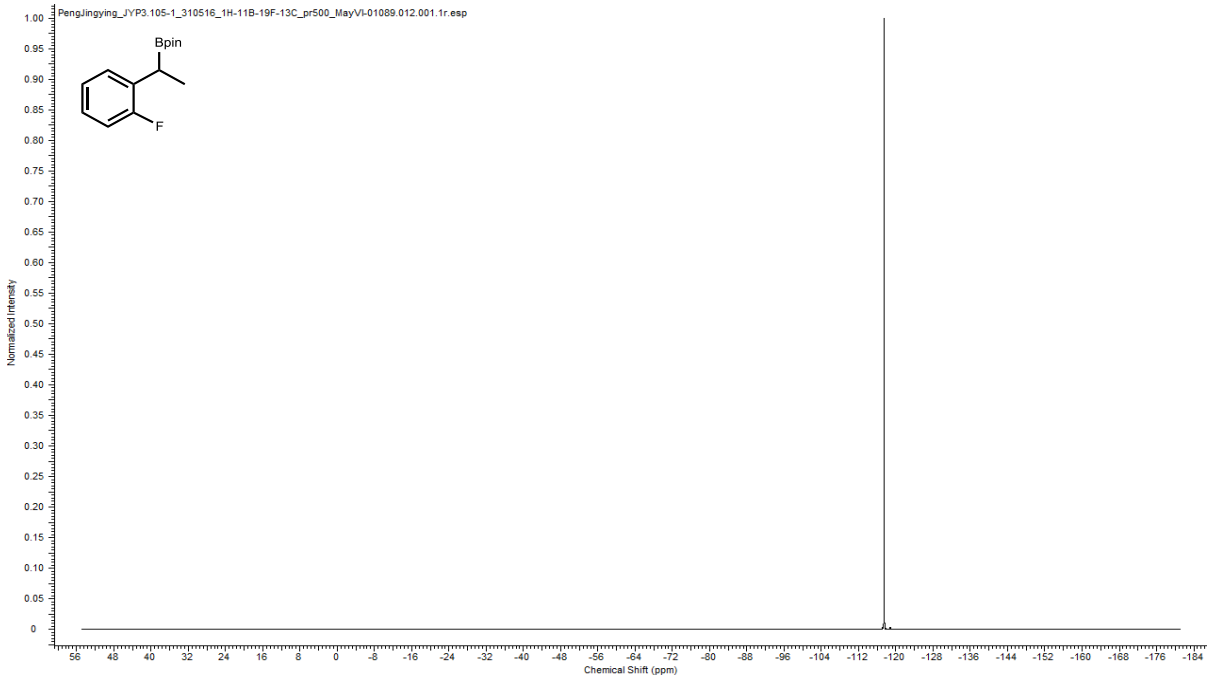
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(1,1'-biphenyl)-4-ylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**)



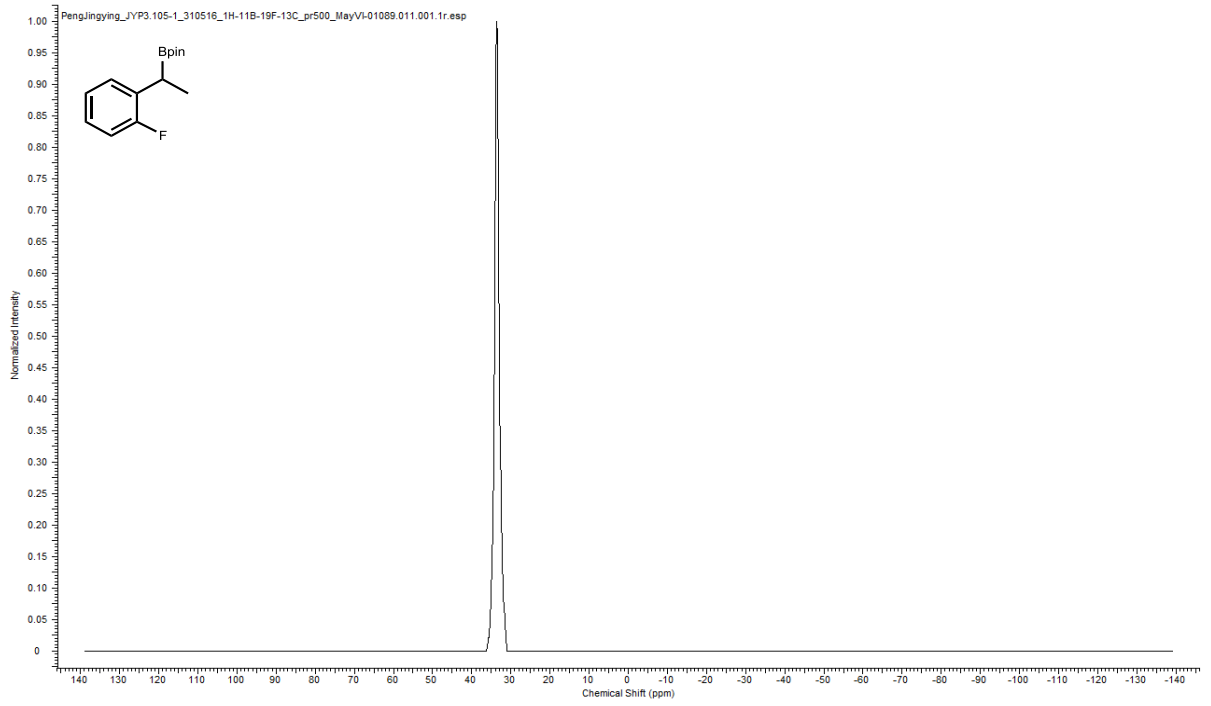
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(2-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3g**)



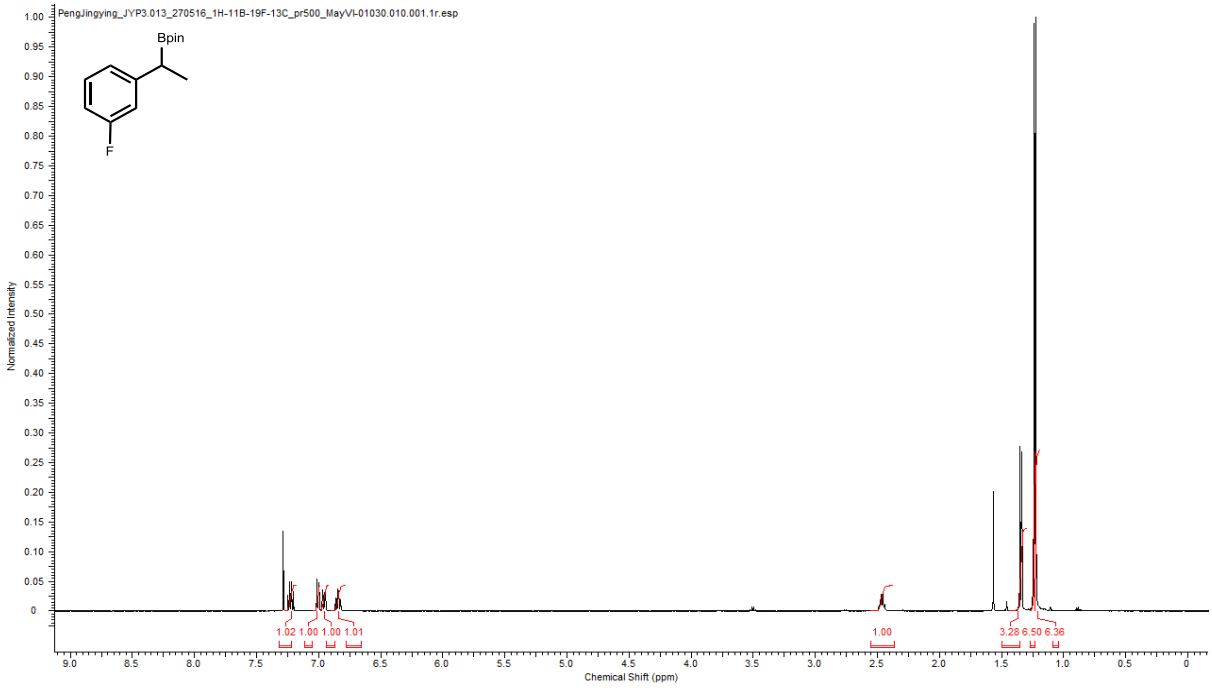
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(2-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3g**)



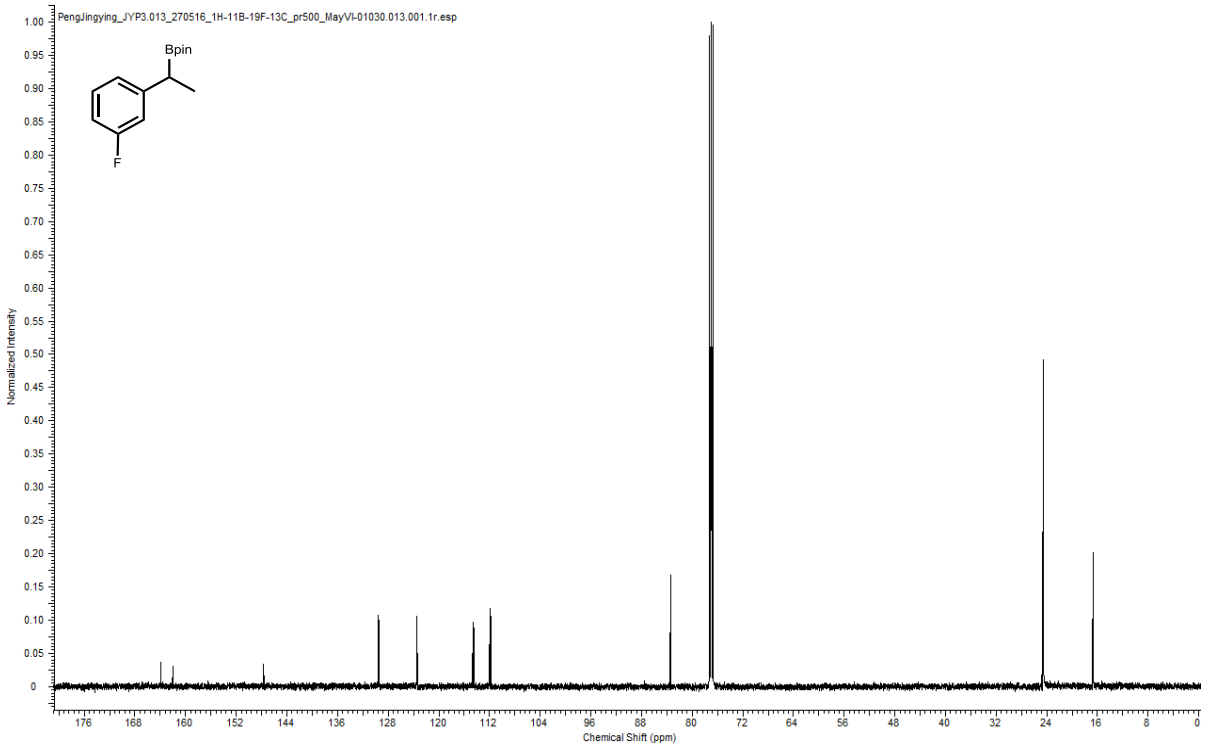
^{19}F NMR (470 MHz, $CDCl_3$) of 2-(1-(2-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3g**)



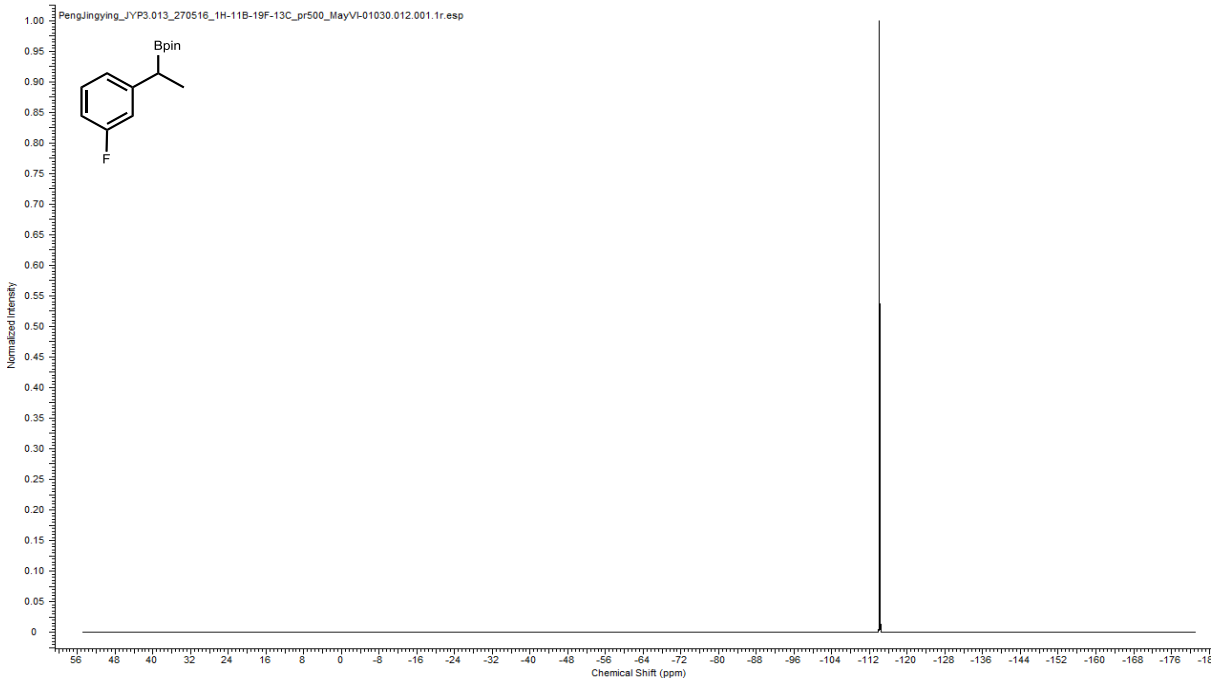
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(3-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3g**)



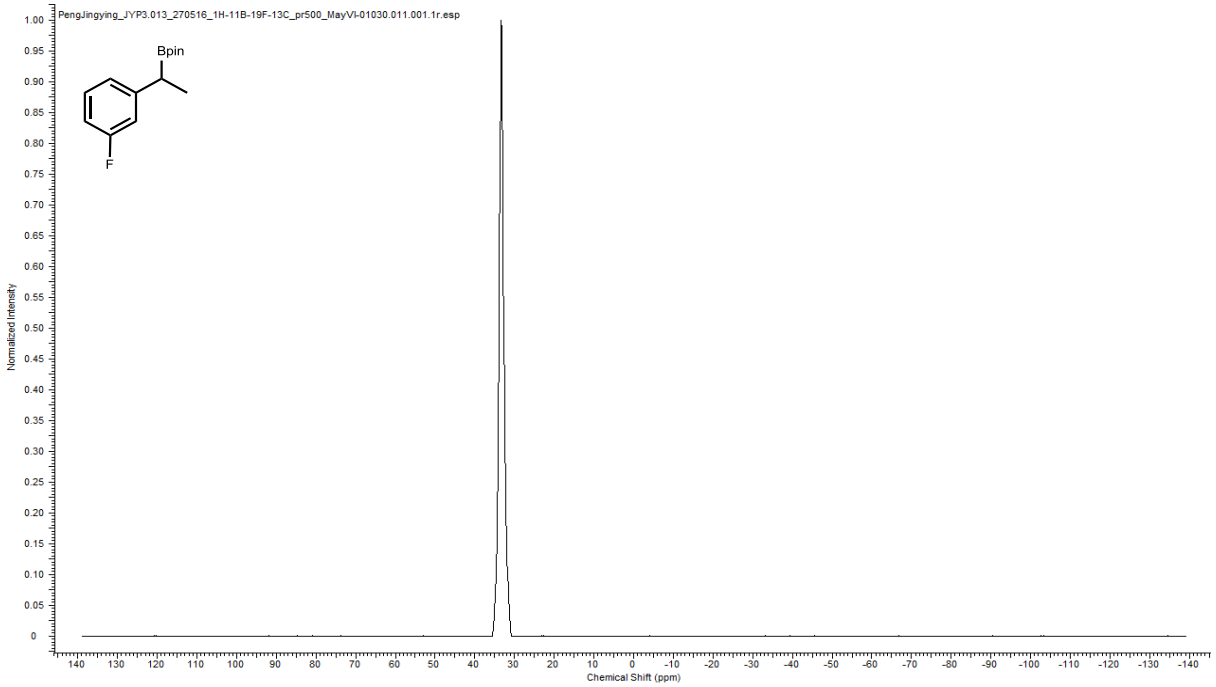
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(3-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3h**)



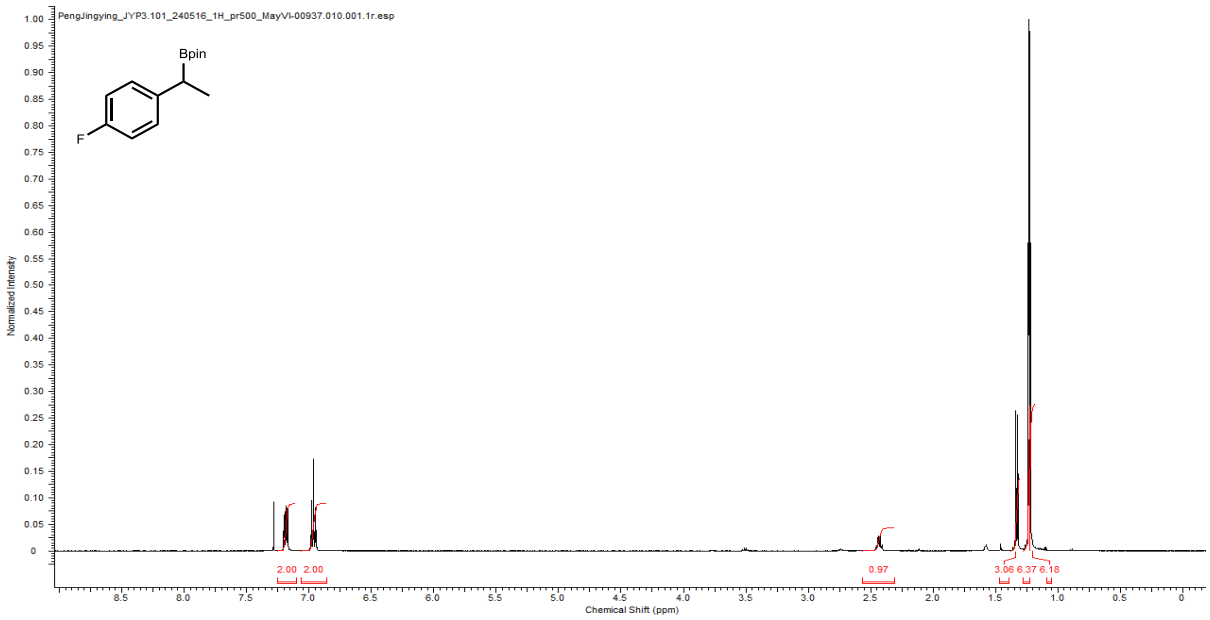
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(3-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3h**)



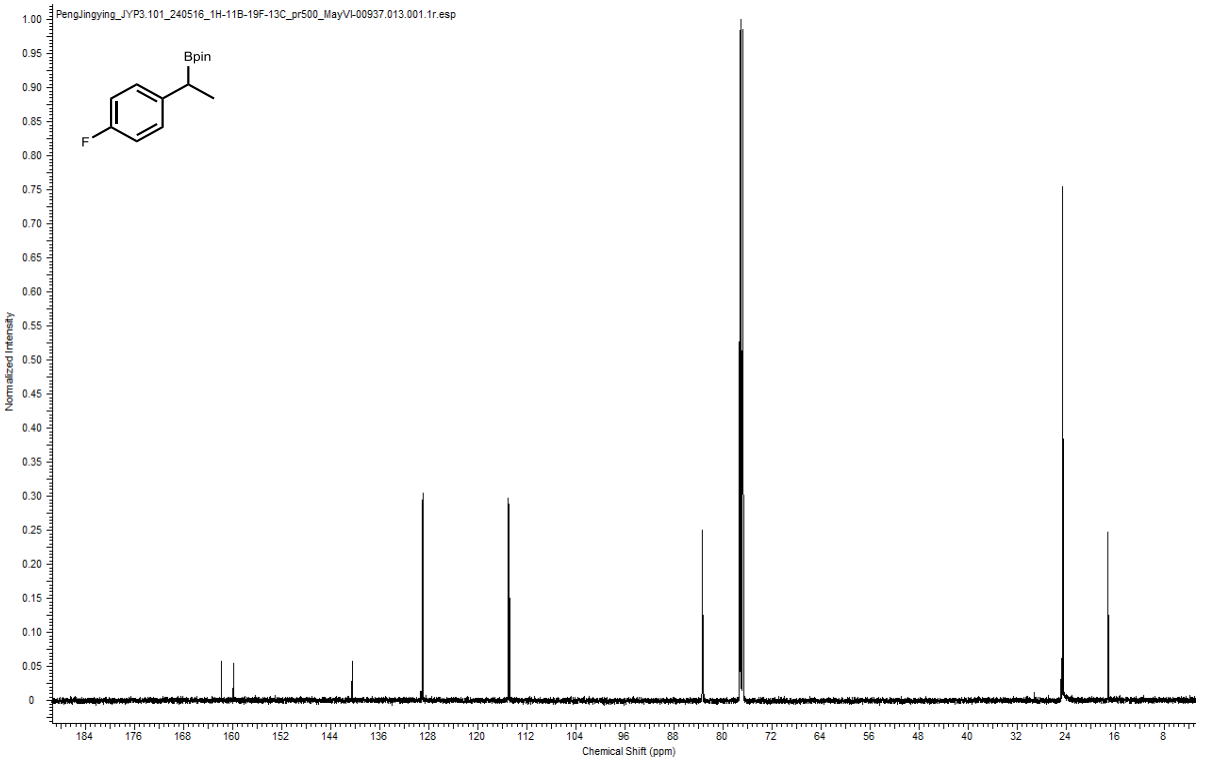
^{19}F NMR (470 MHz, $CDCl_3$) of 2-(1-(3-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3h**)



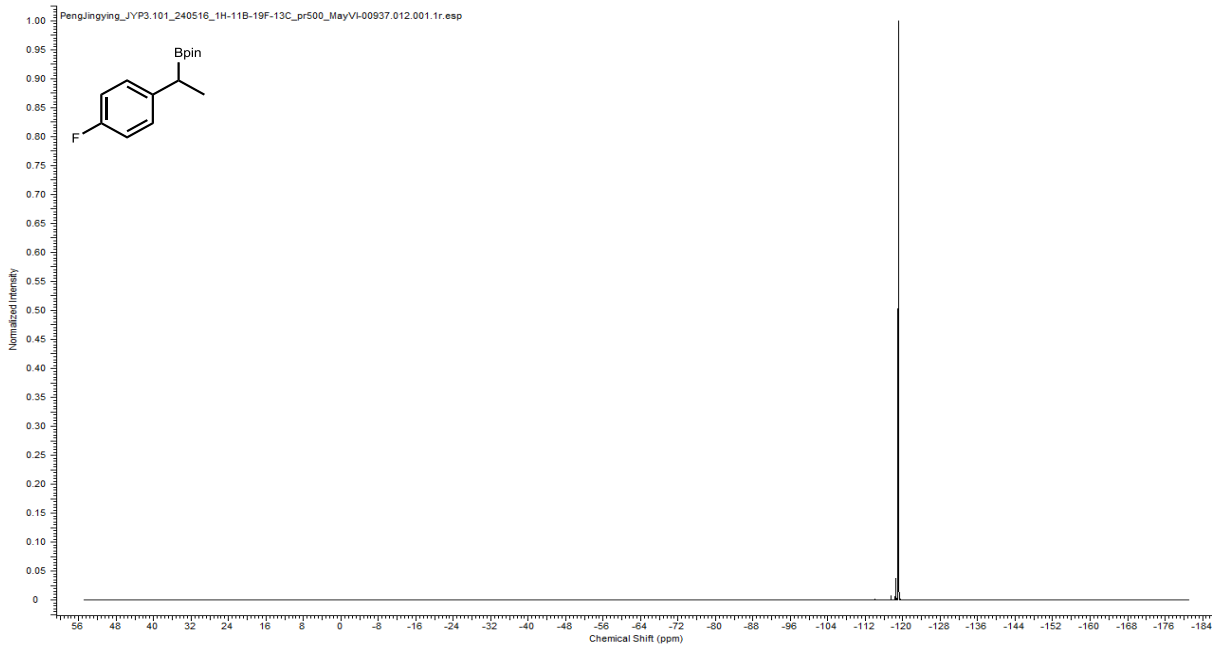
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(3-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3h**)



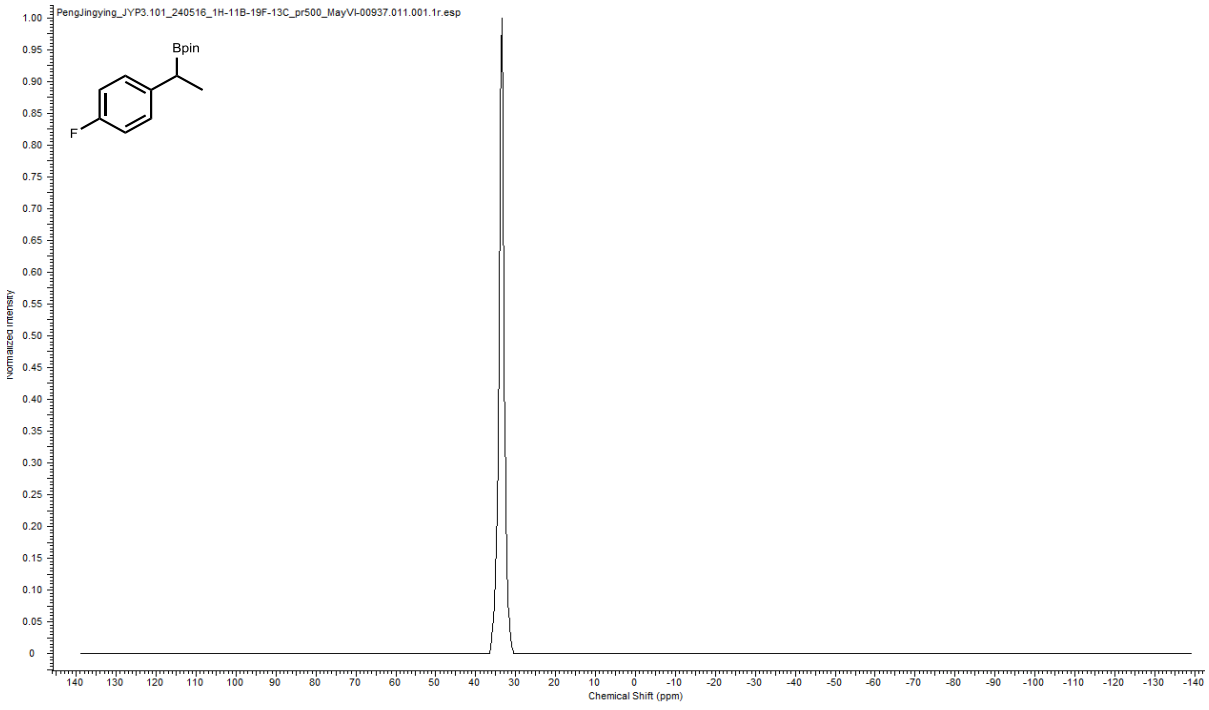
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**)



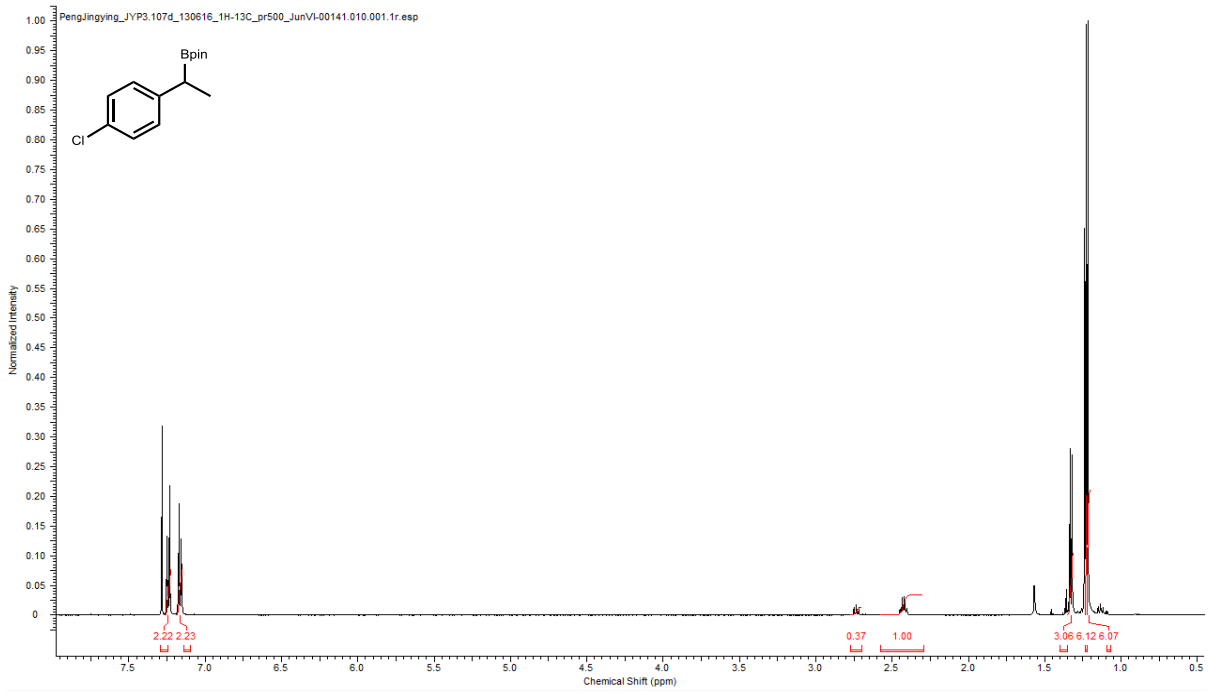
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**)



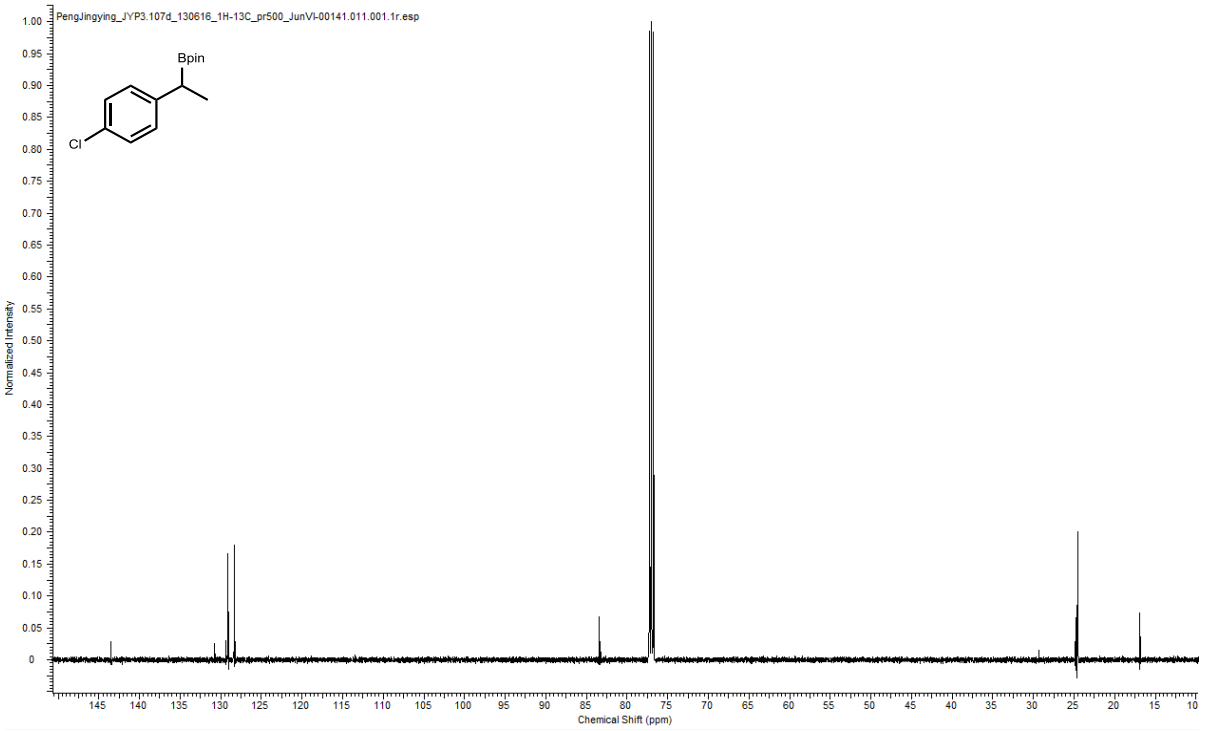
^{19}F NMR (470 MHz, $CDCl_3$) of 2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**)



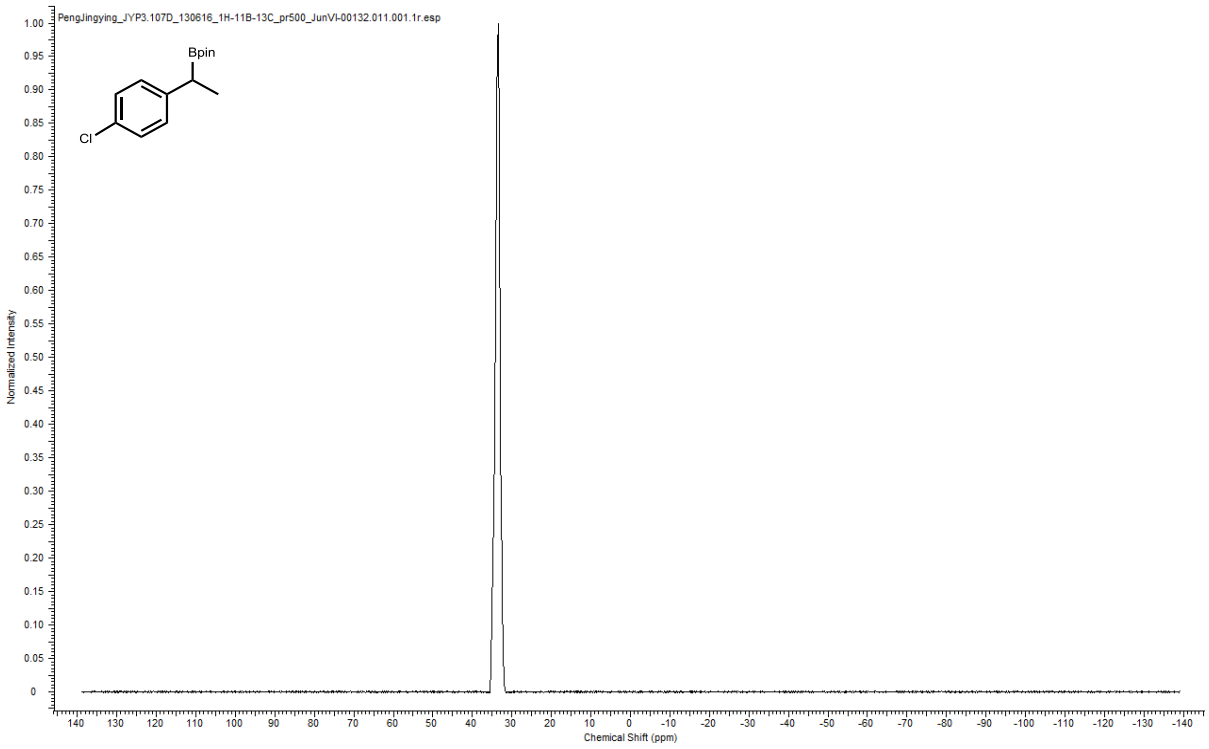
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**)



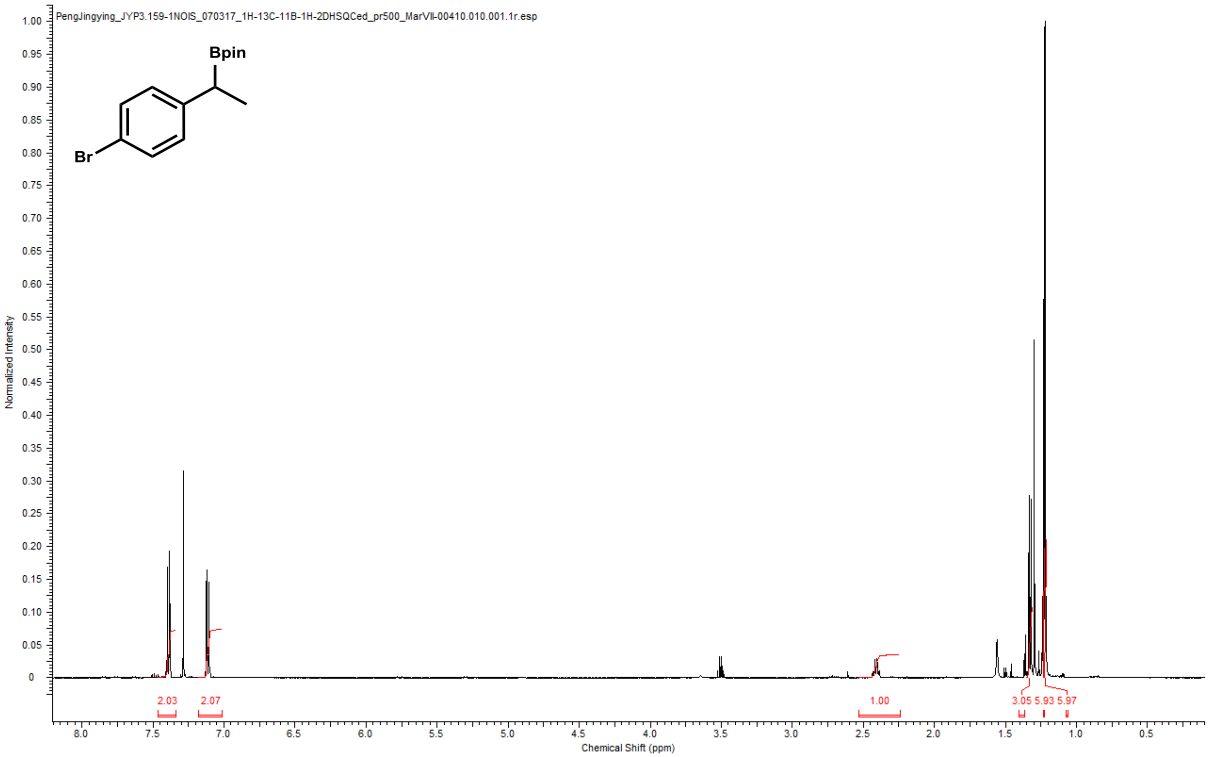
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(4-chloromethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3j**)



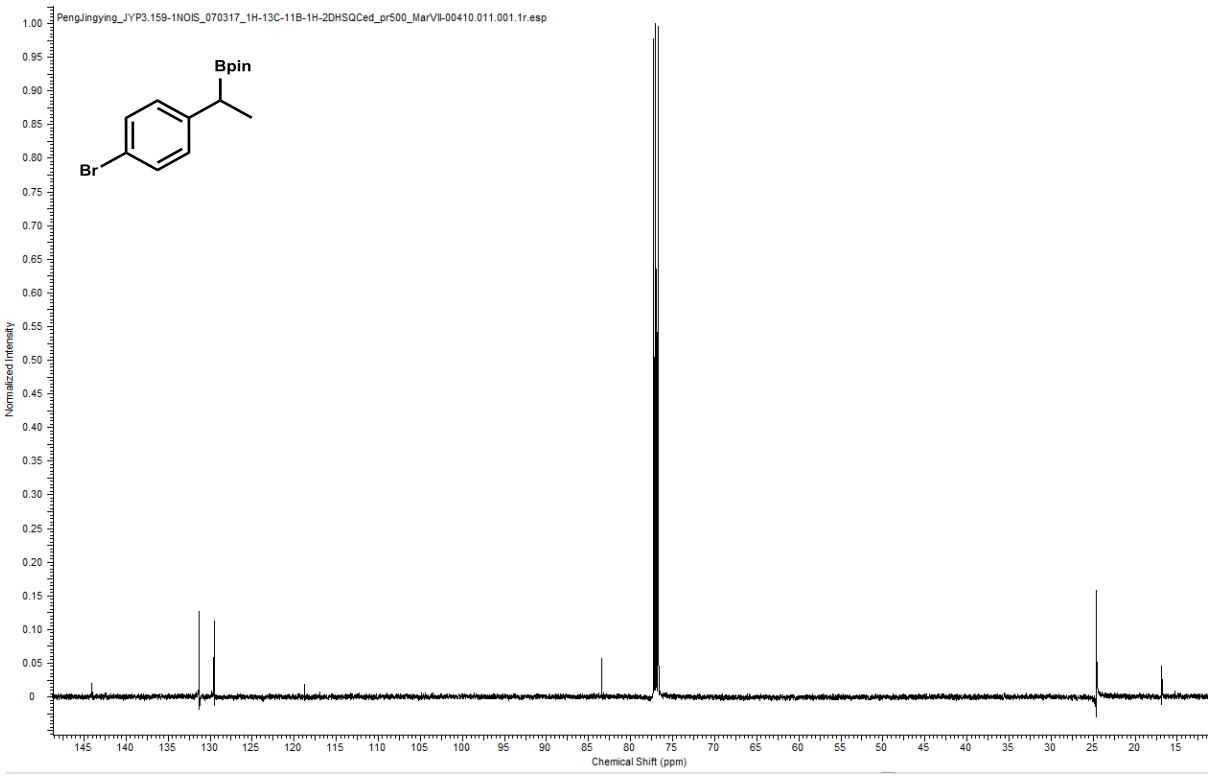
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(4-trifluromethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3j**)



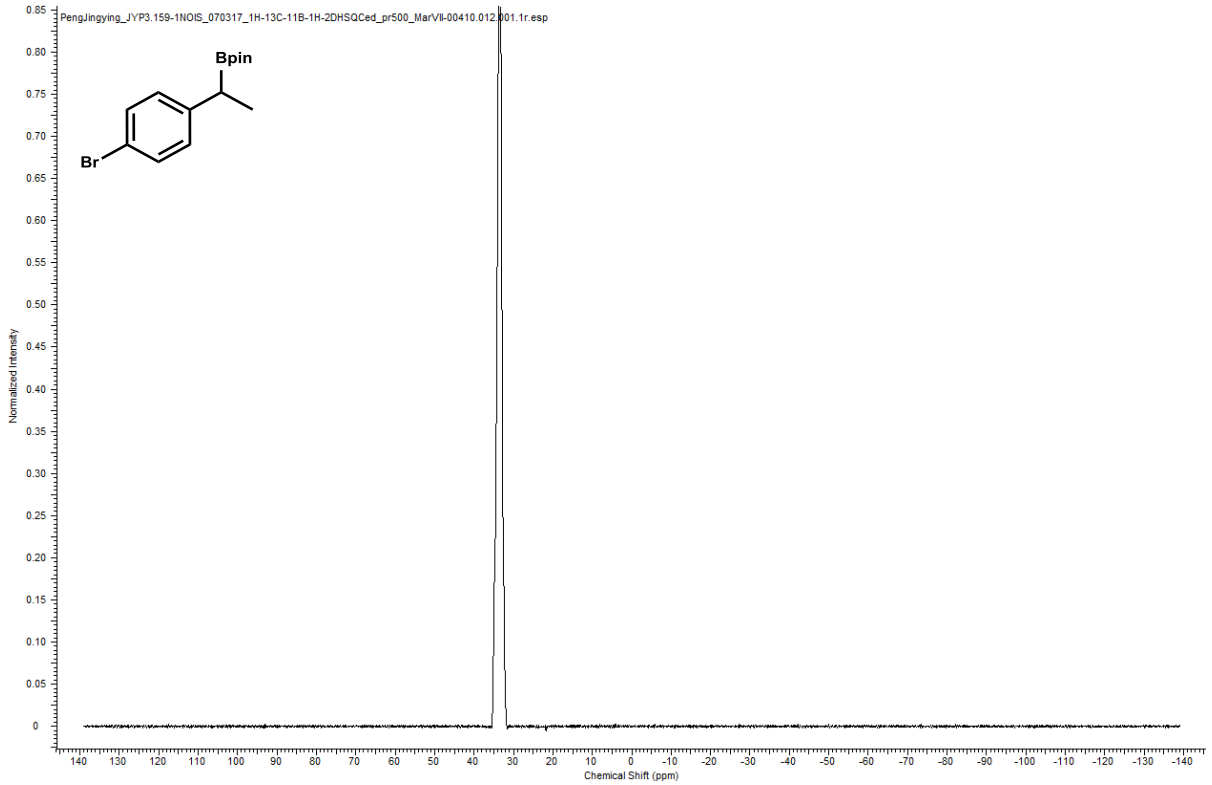
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(4-chloromethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3j**)



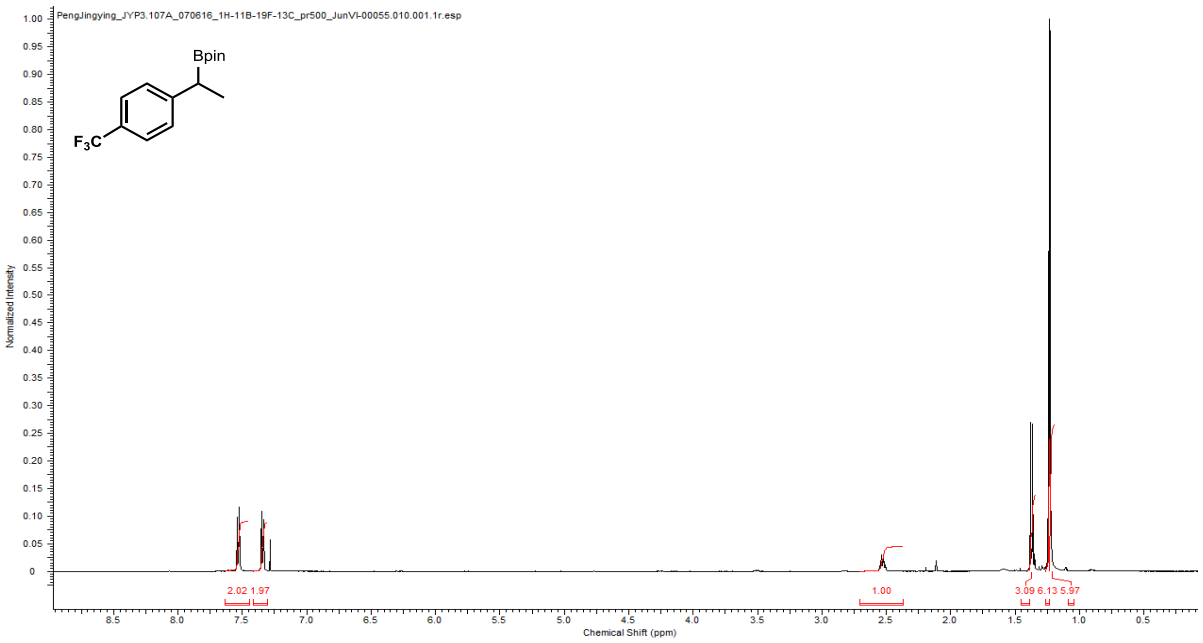
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(4-bromophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3k**)



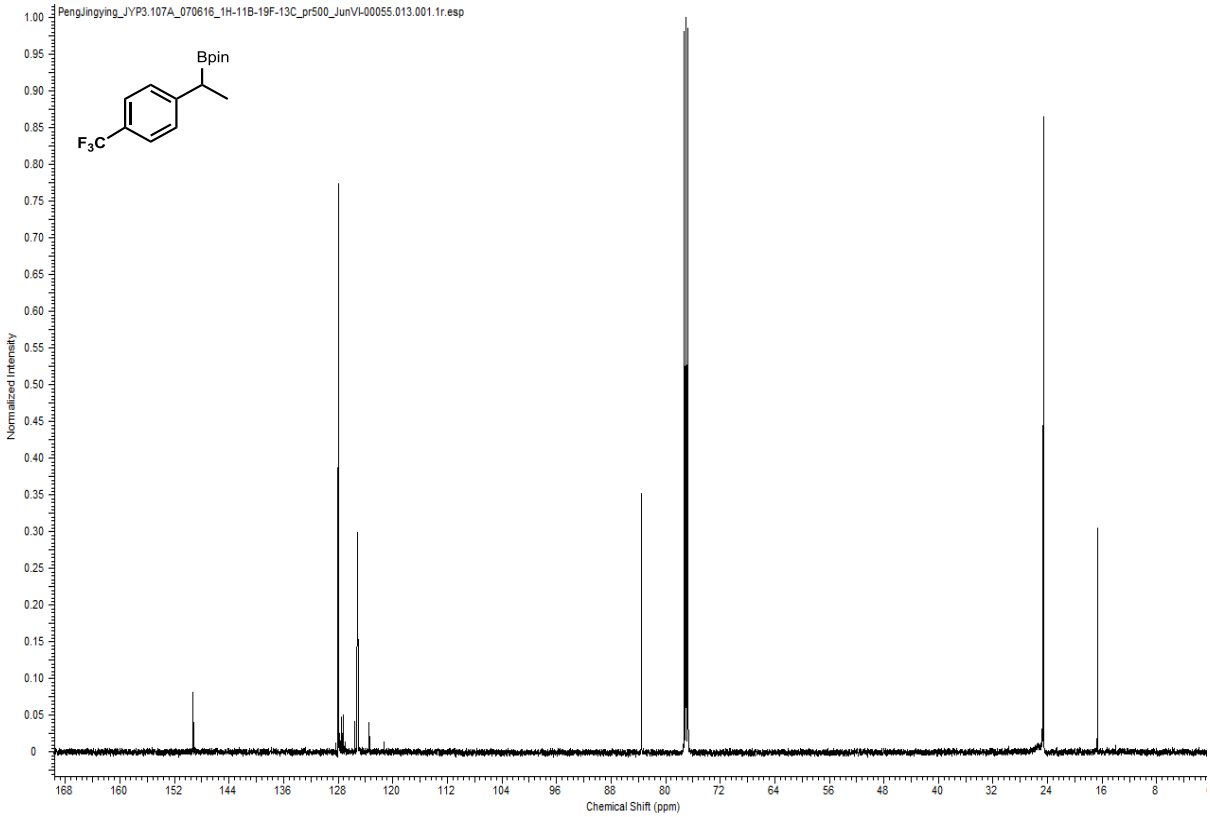
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(4-bromophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3k**)



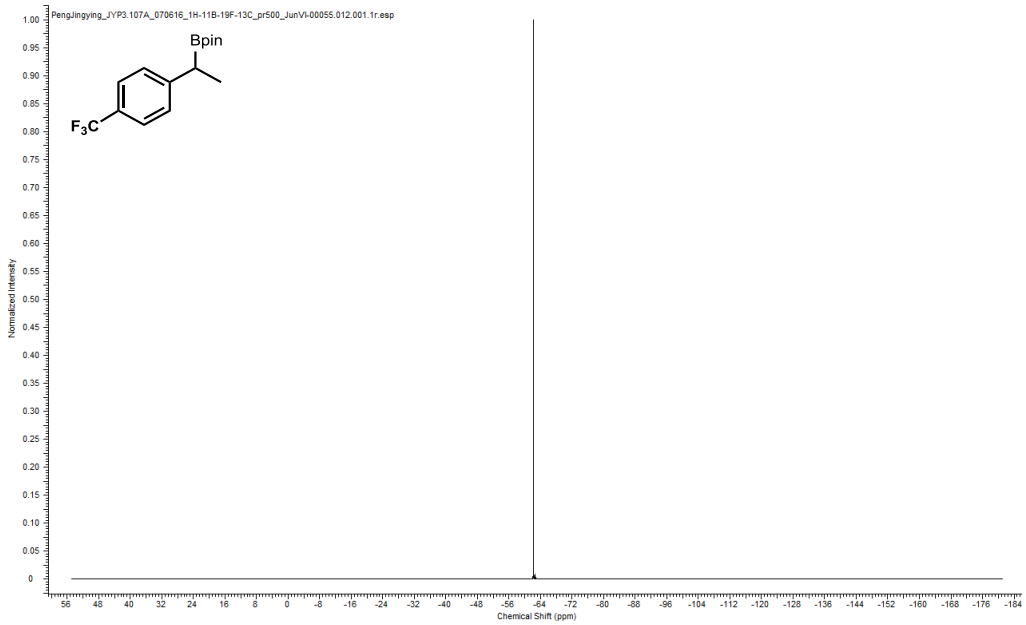
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(4-bromophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3k**)



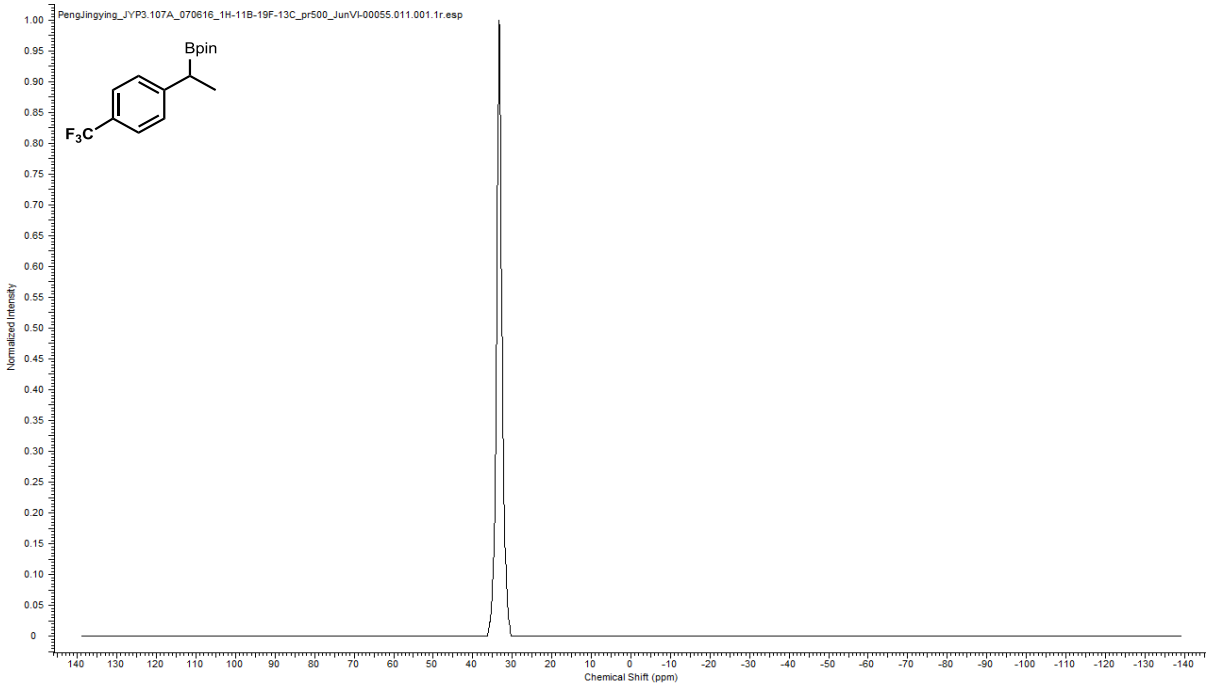
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(4-trifluromethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3l**)



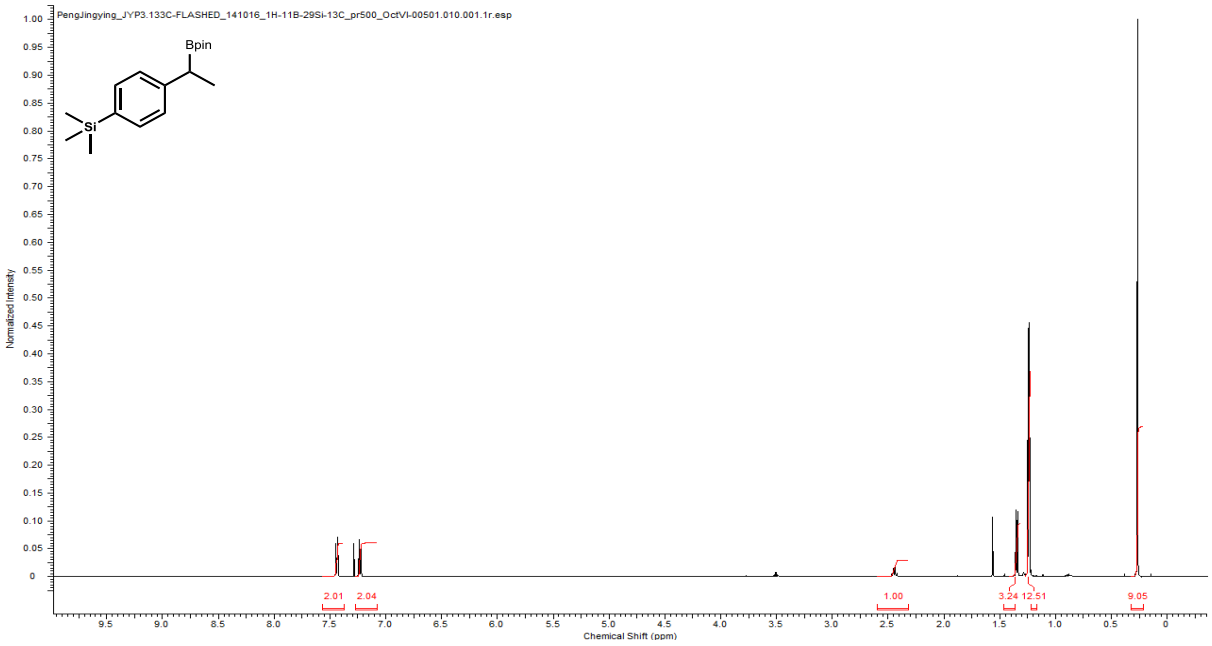
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(4-trifluromethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3l**)



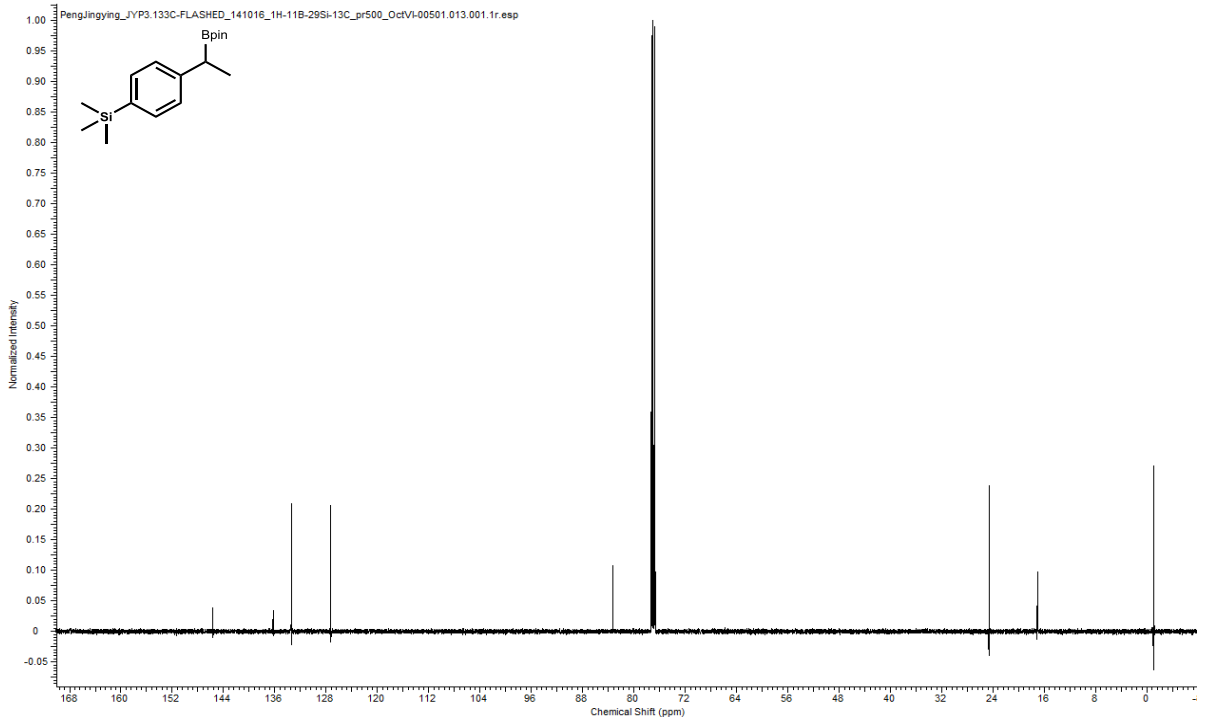
^{19}F NMR (470 MHz, $CDCl_3$) of 2-(1-(4-trifluromethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3l**)



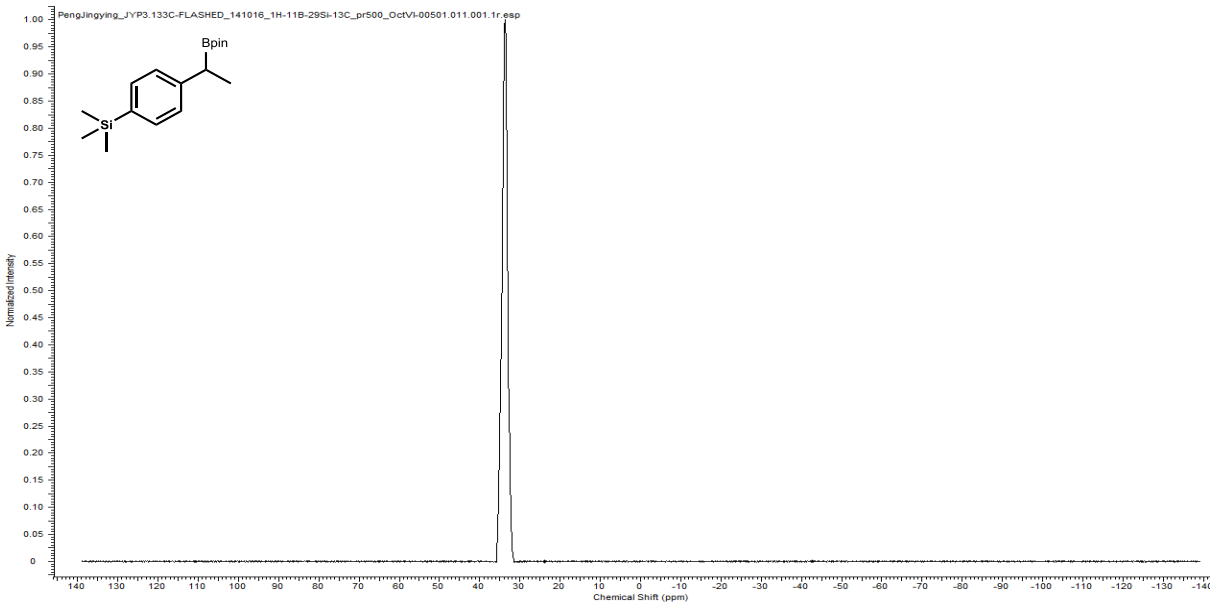
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(4-trifluromethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3l**)



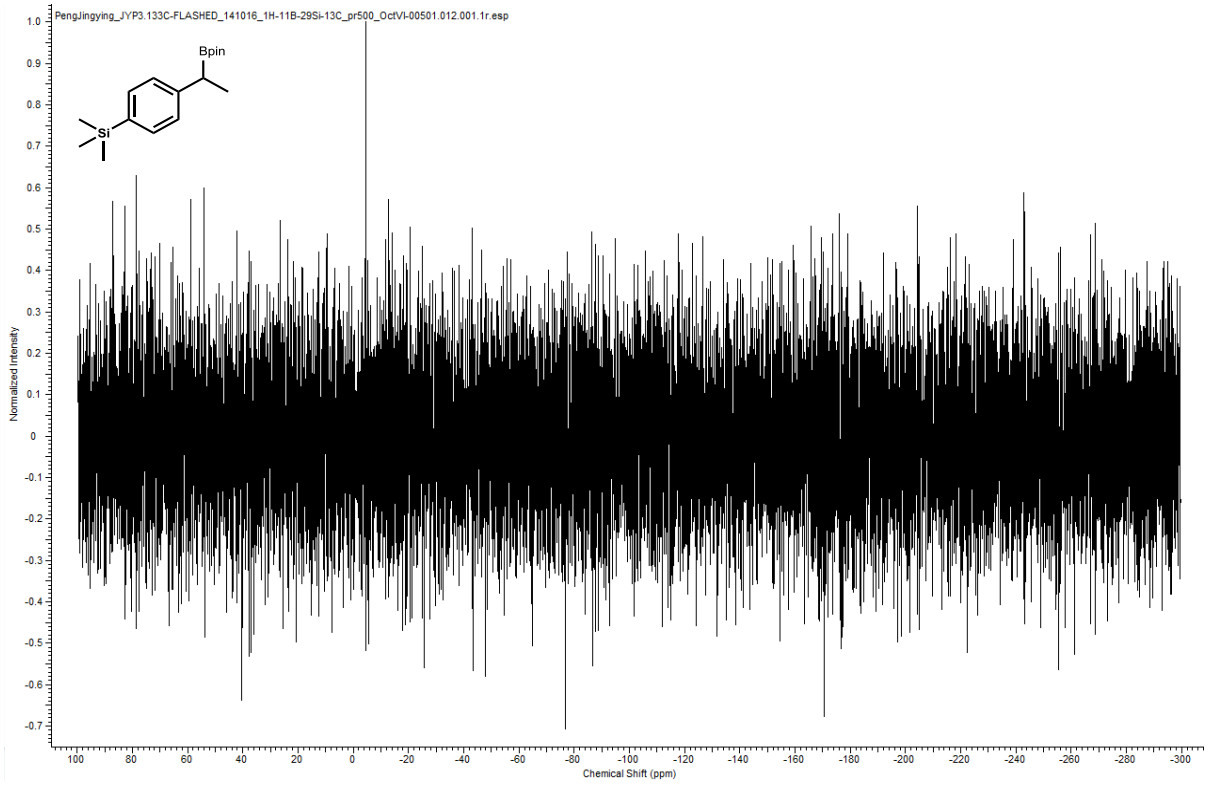
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(4-trimethylsilylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3m**)



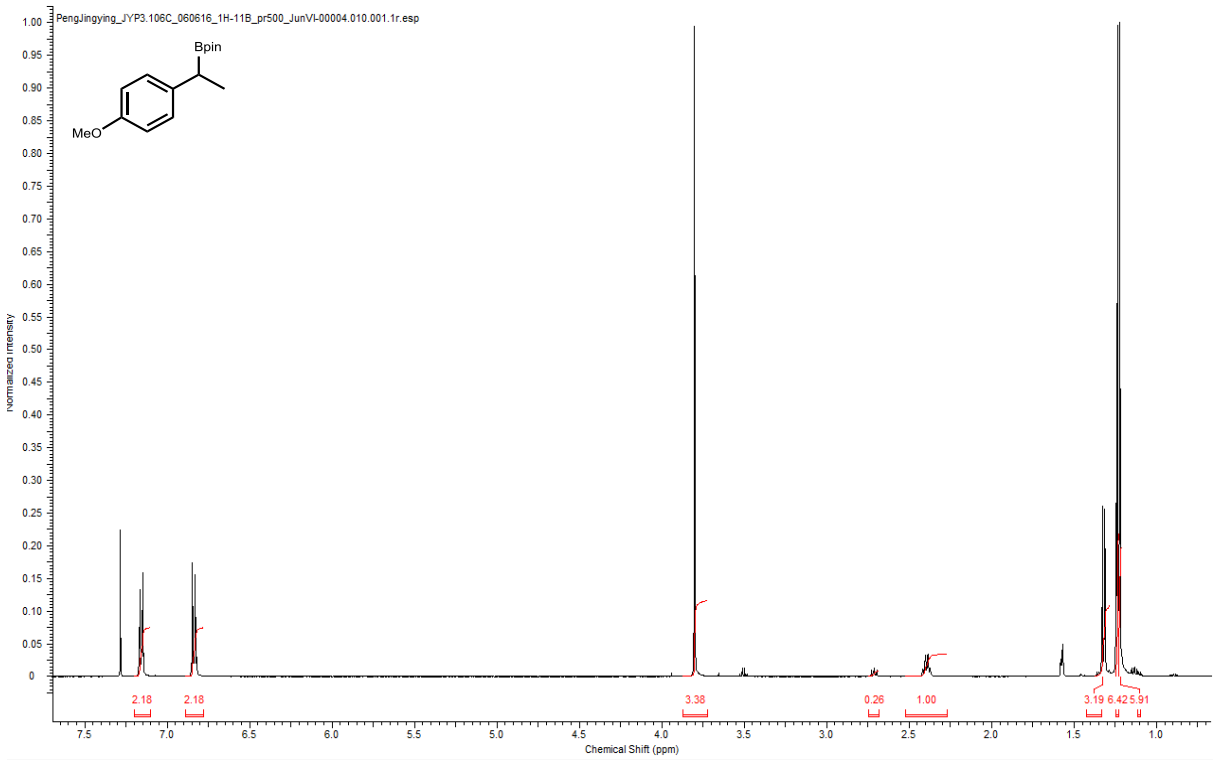
^{13}C NMR (125 MHz, $CDCl_3$)of 2-(1-(4-trimethylsilylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3m**)



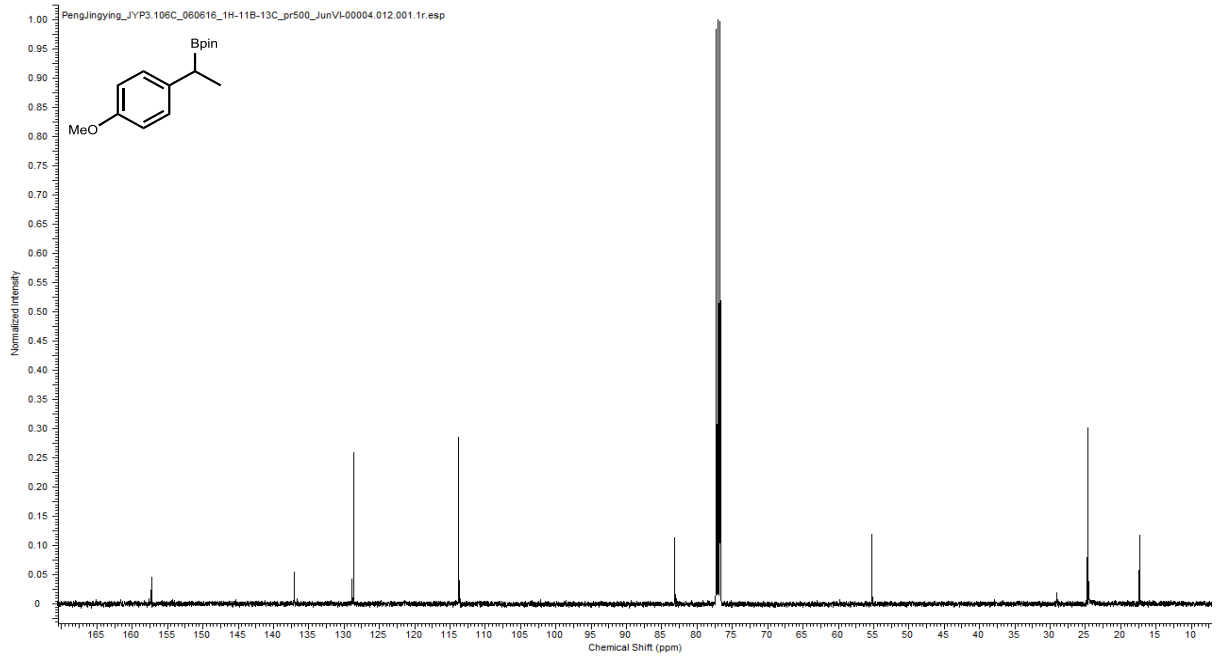
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(4-trimethylsilylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3m**)



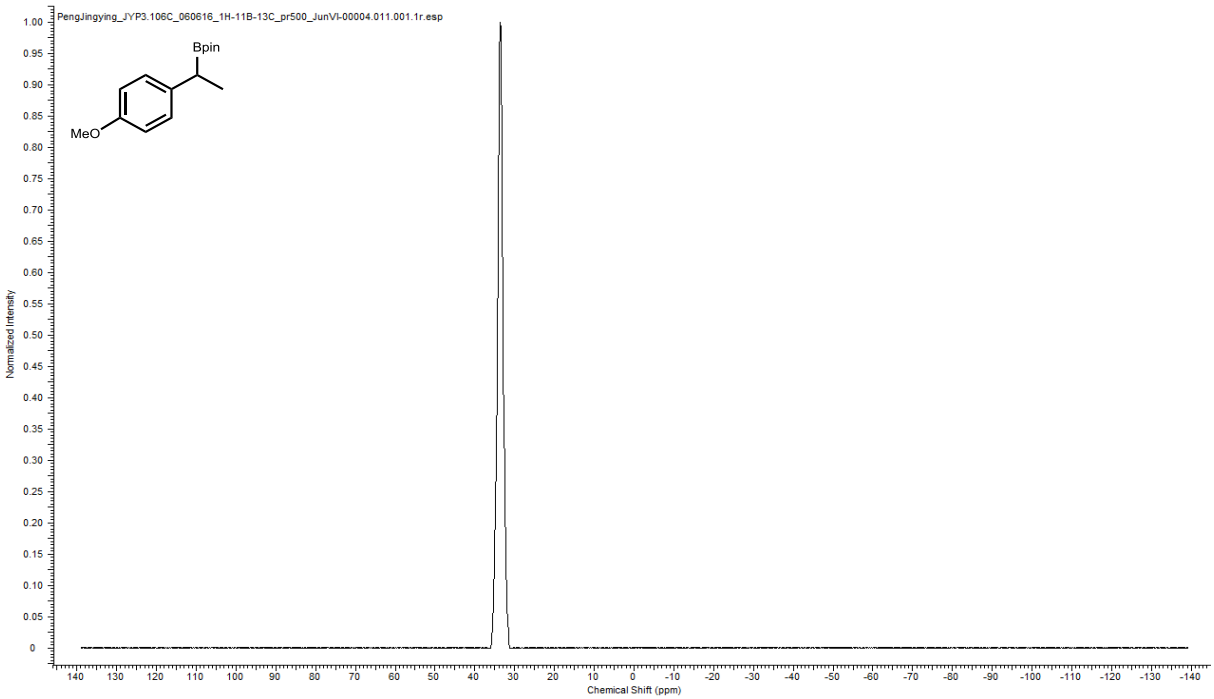
^{29}Si NMR (99 MHz, $CDCl_3$) of 2-(1-(4-trimethylsilylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3m**)



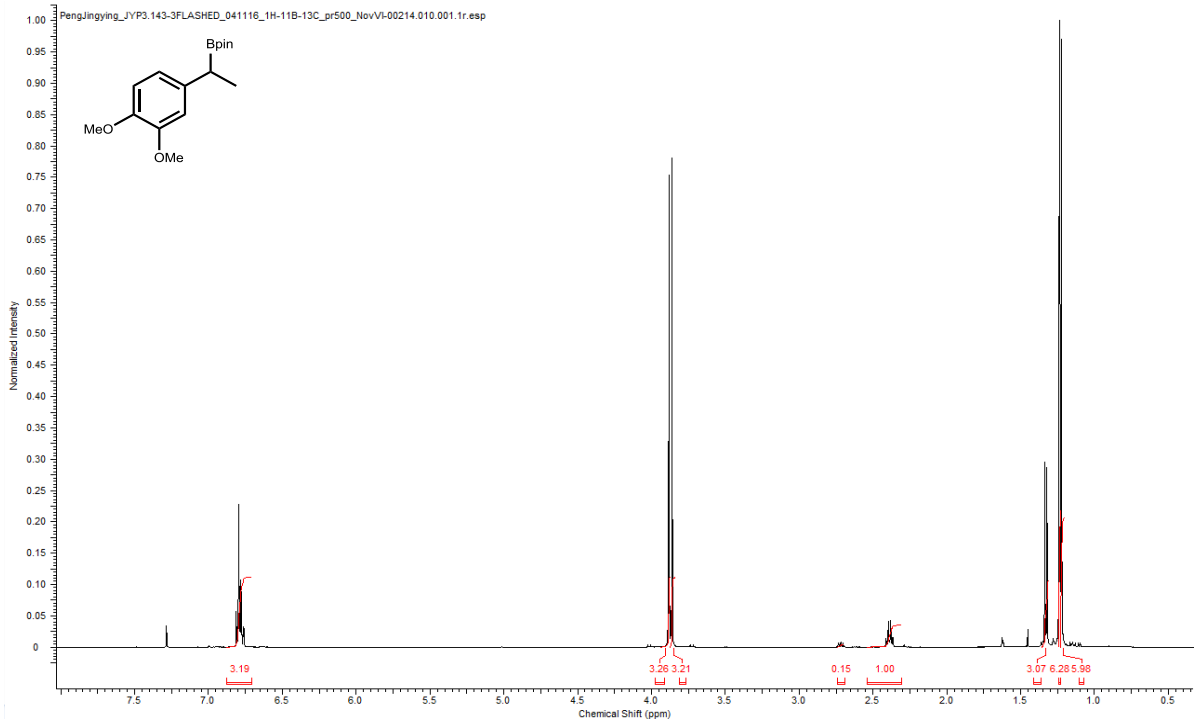
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3n**)



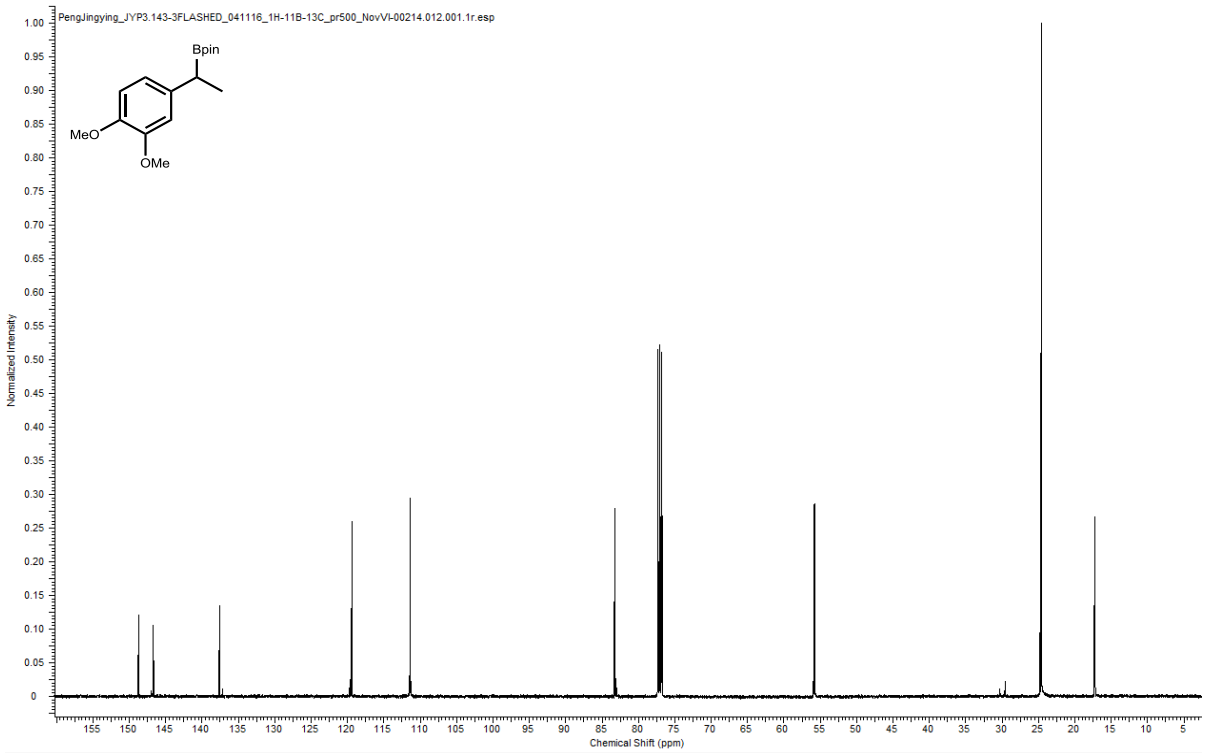
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3n**)



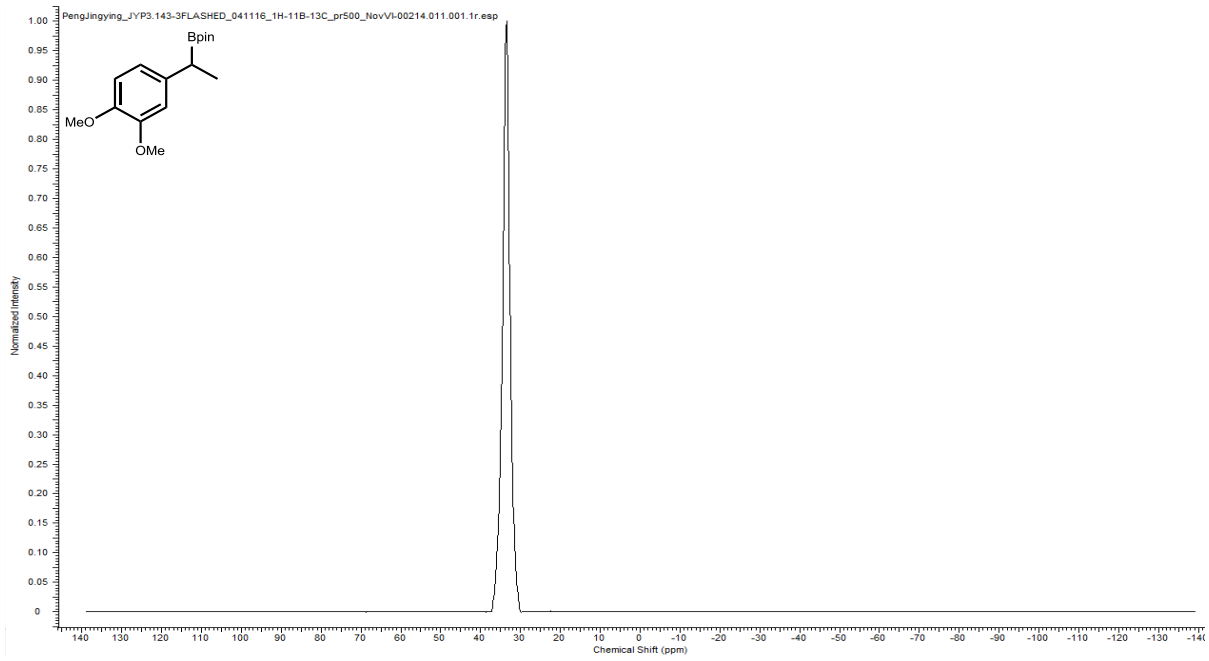
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3n**)



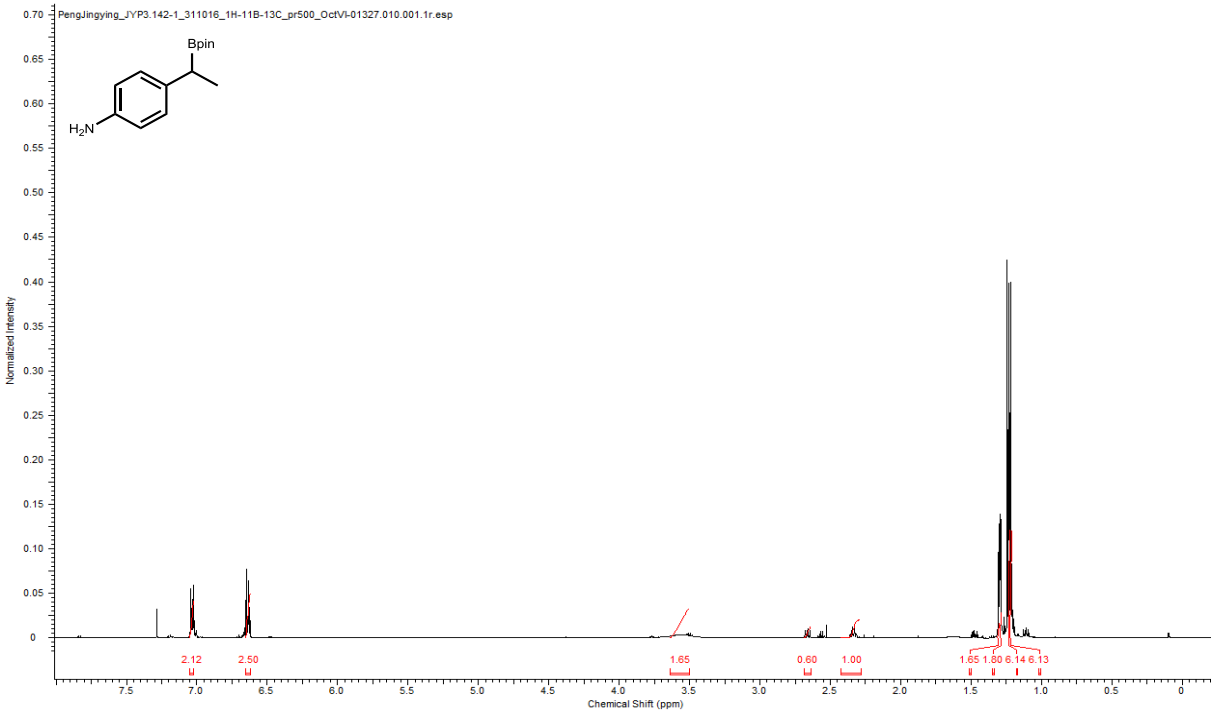
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(3,4-dimethoxylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3o**)



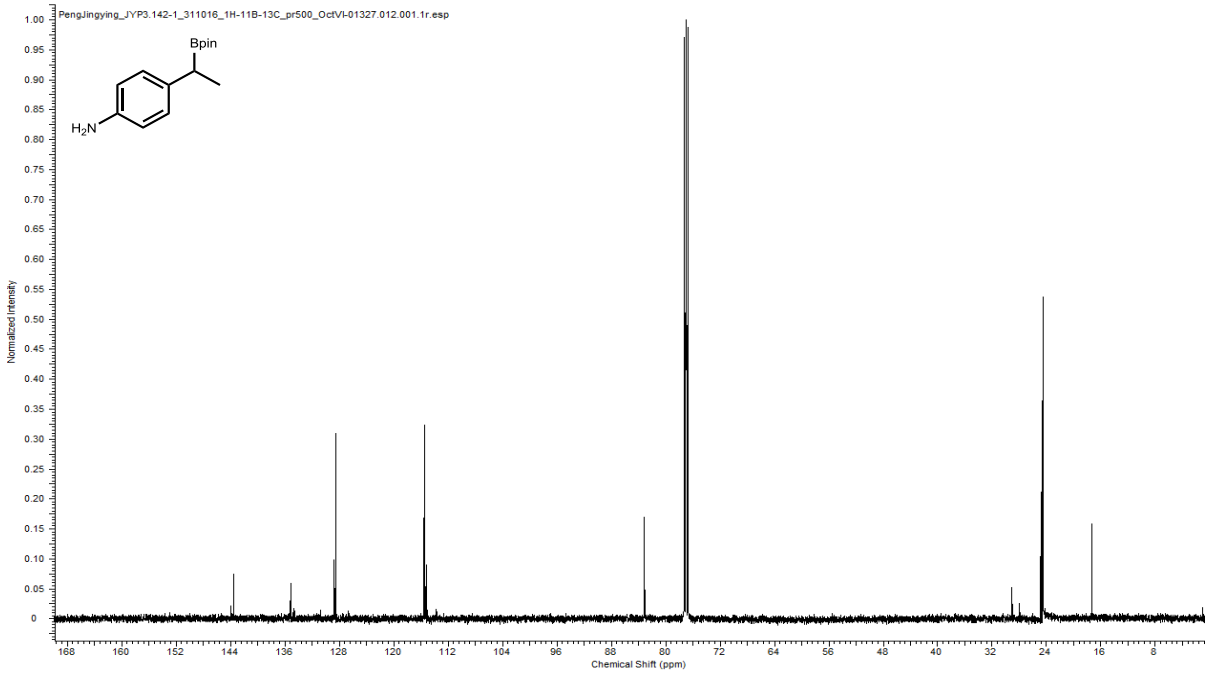
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(3,4-dimethoxylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3o**)



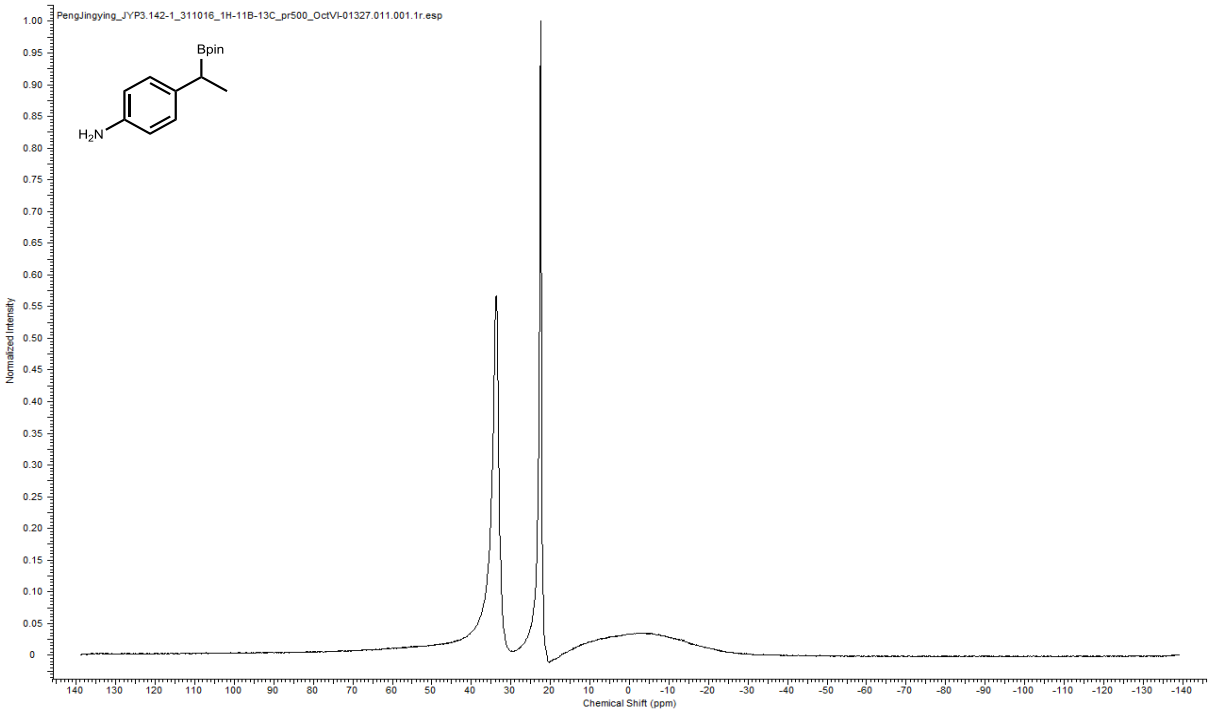
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(3,4-dimethoxylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3o**)



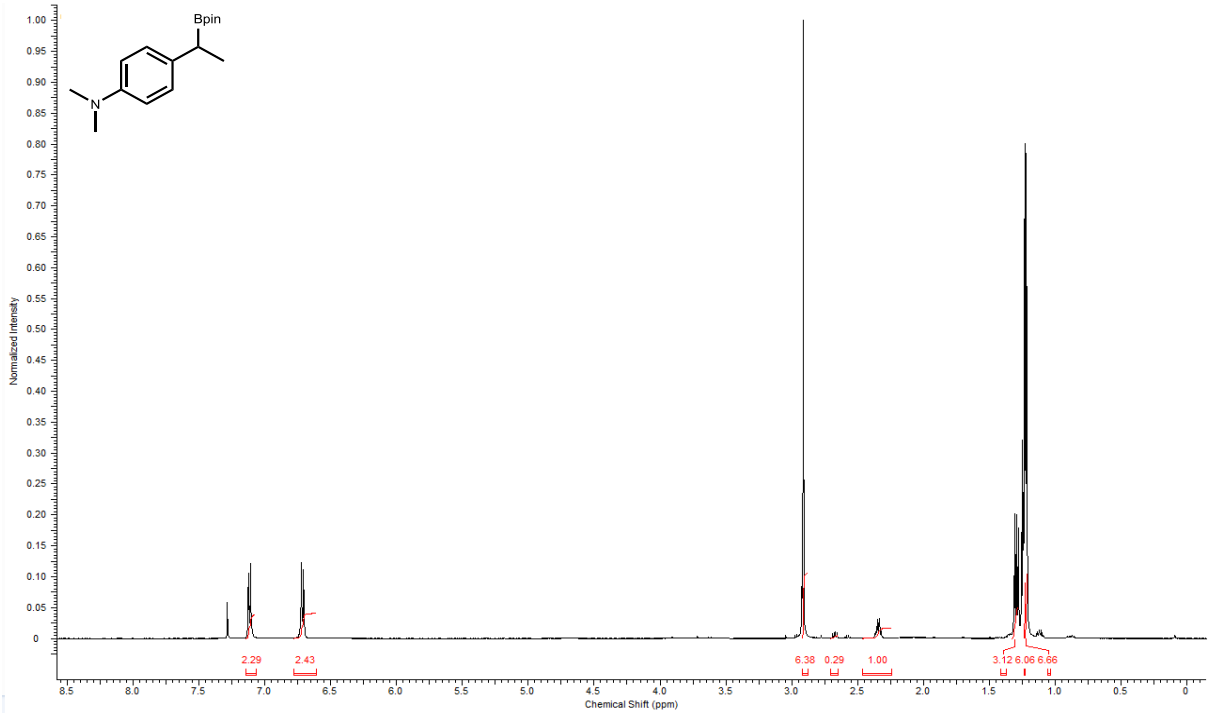
^{1}H NMR (500 MHz, $CDCl_3$) of 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzenamine (**3p**)



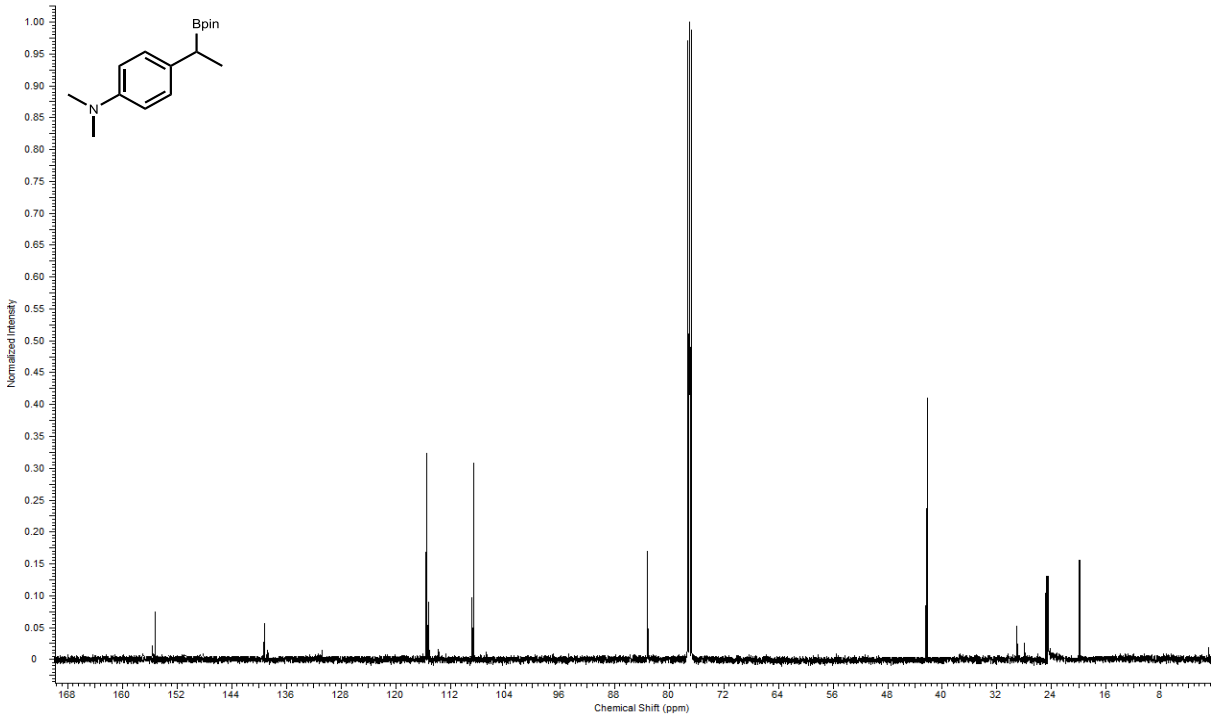
^{13}C NMR (125 MHz, $CDCl_3$) of 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)ethyl) benzenamine (**3p**)



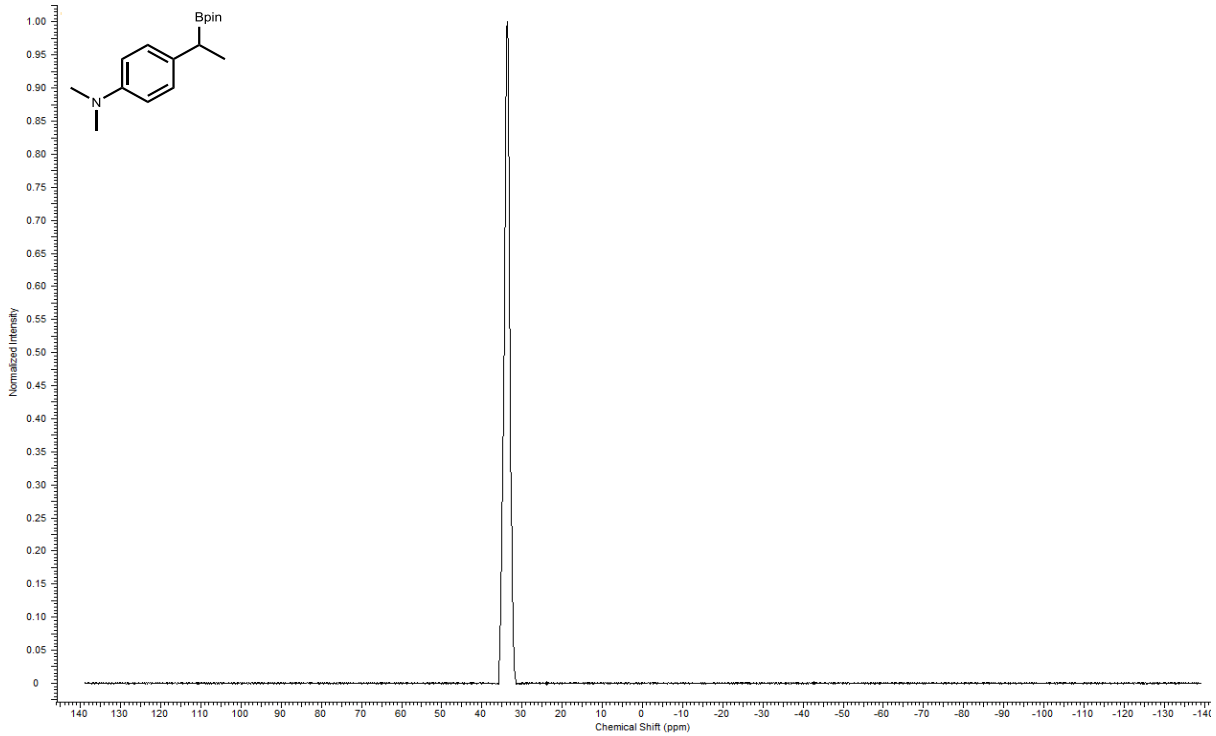
^{11}B NMR (160 MHz, $CDCl_3$) of 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)ethyl)benzenamine (**3p**)



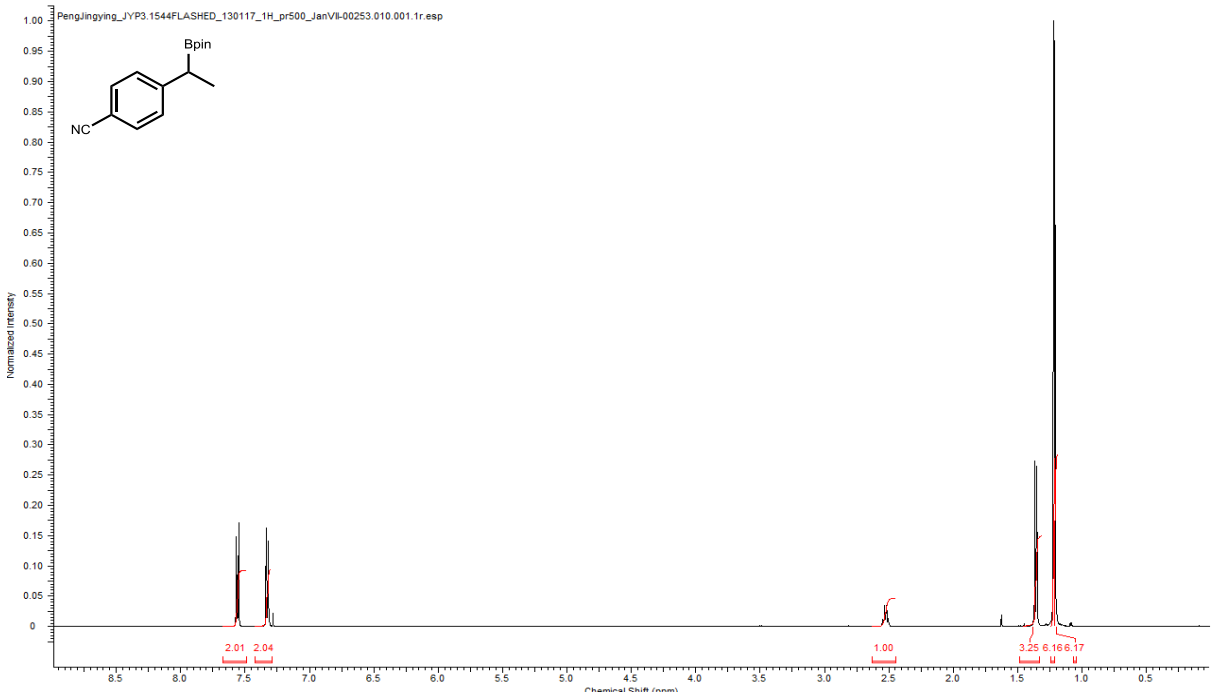
^{1}H NMR (500 MHz, $CDCl_3$) of 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-*N*, *N*-dimethylbenzenamine (**3q**)



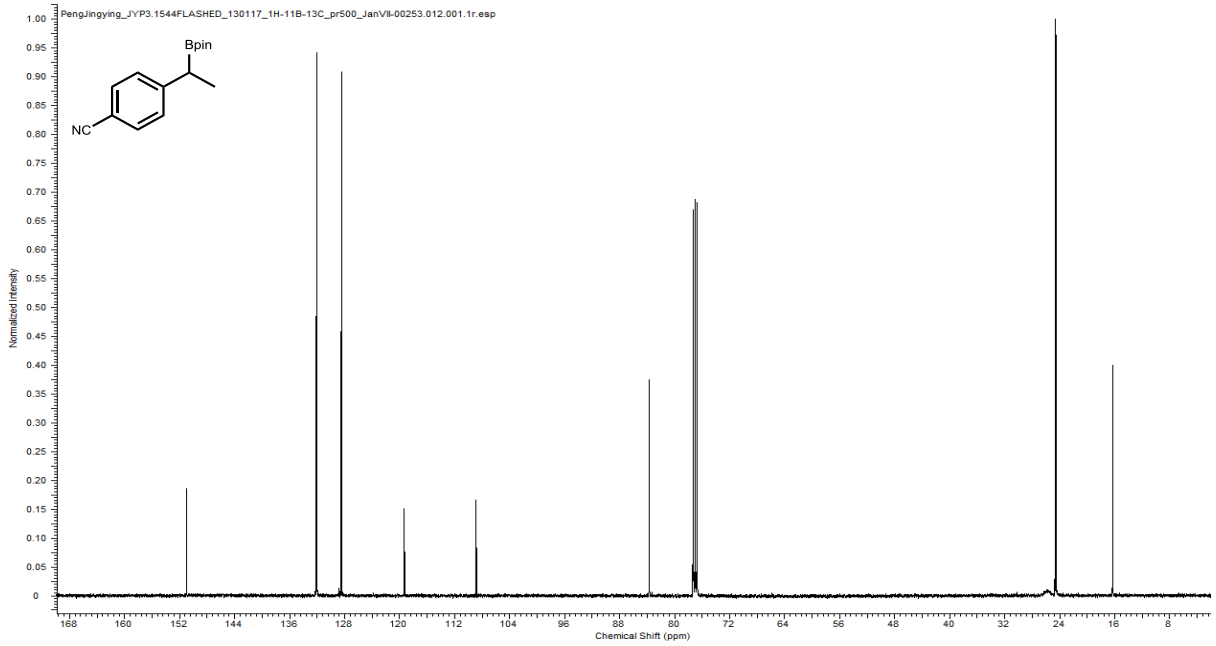
^{13}C NMR (125 MHz, $CDCl_3$) of 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-*N*, *N*-dimethylbenzenamine (**3q**)



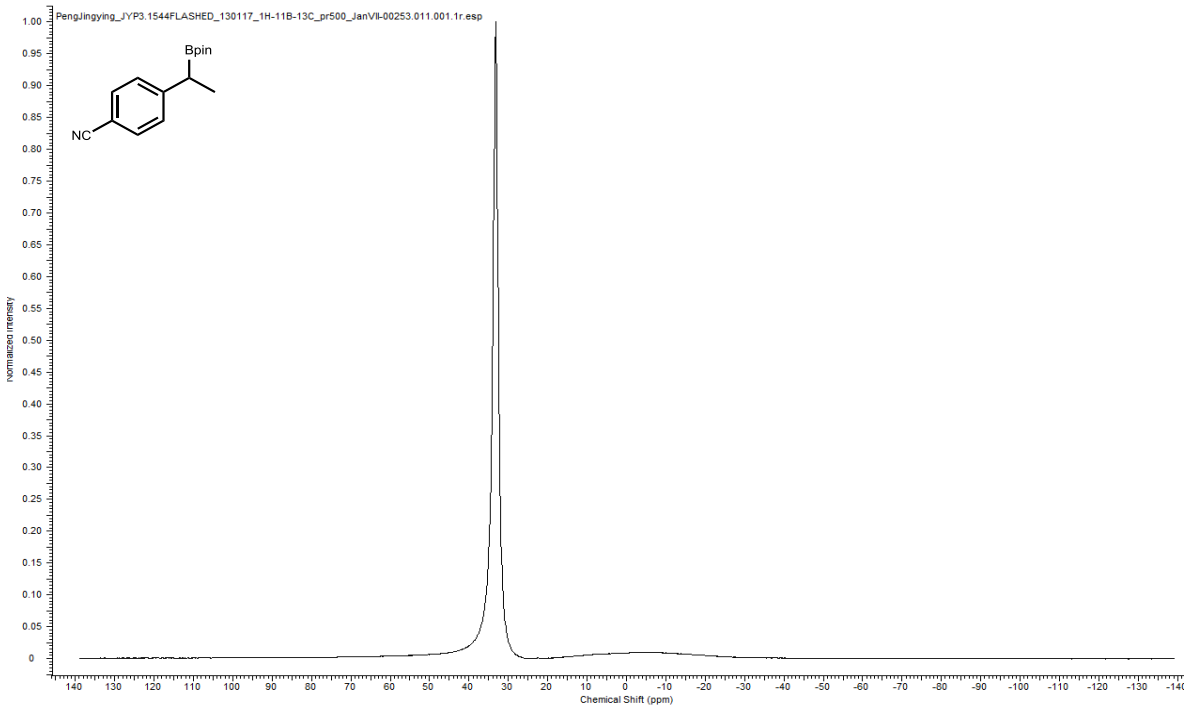
^{11}B NMR (160 MHz, $CDCl_3$) of 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-*N*, *N*-dimethylbenzenamine (**3q**)



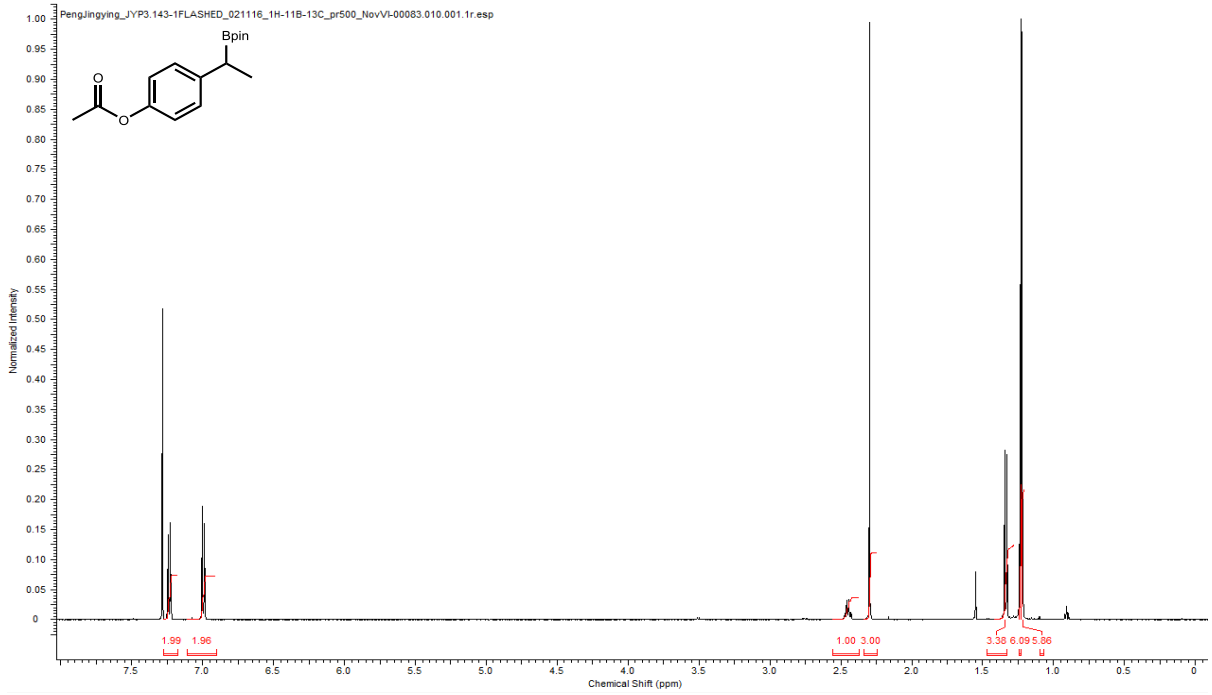
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(4-cyanophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3r**)



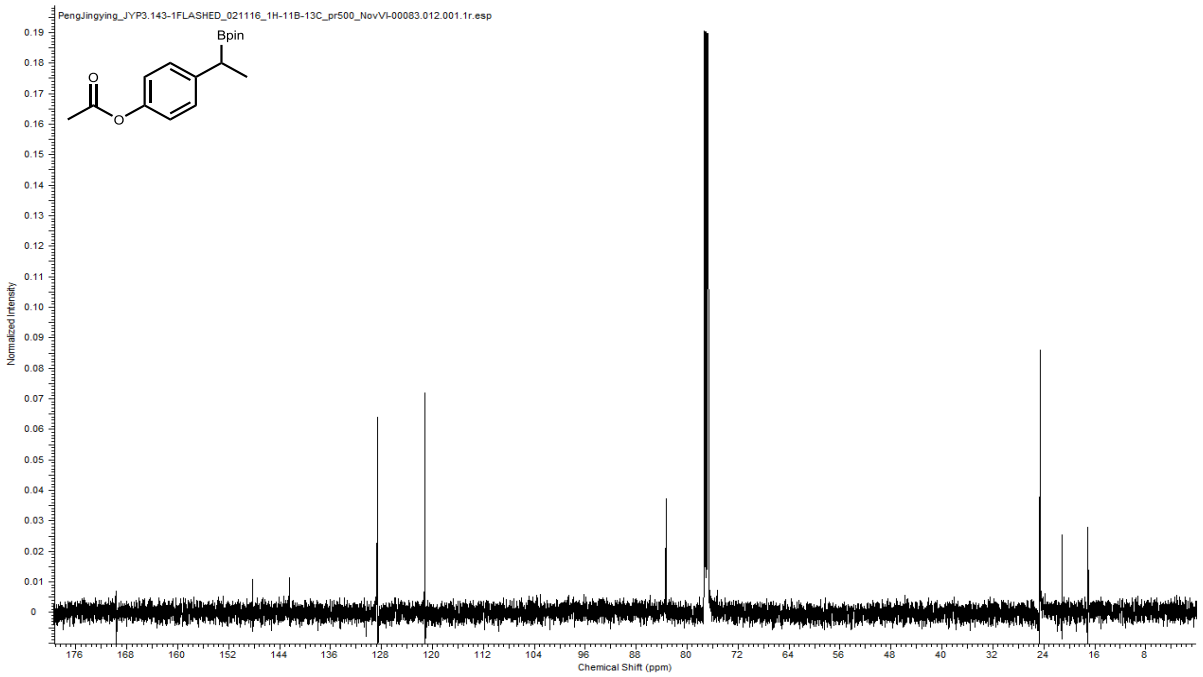
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(4-cyanophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3r**)



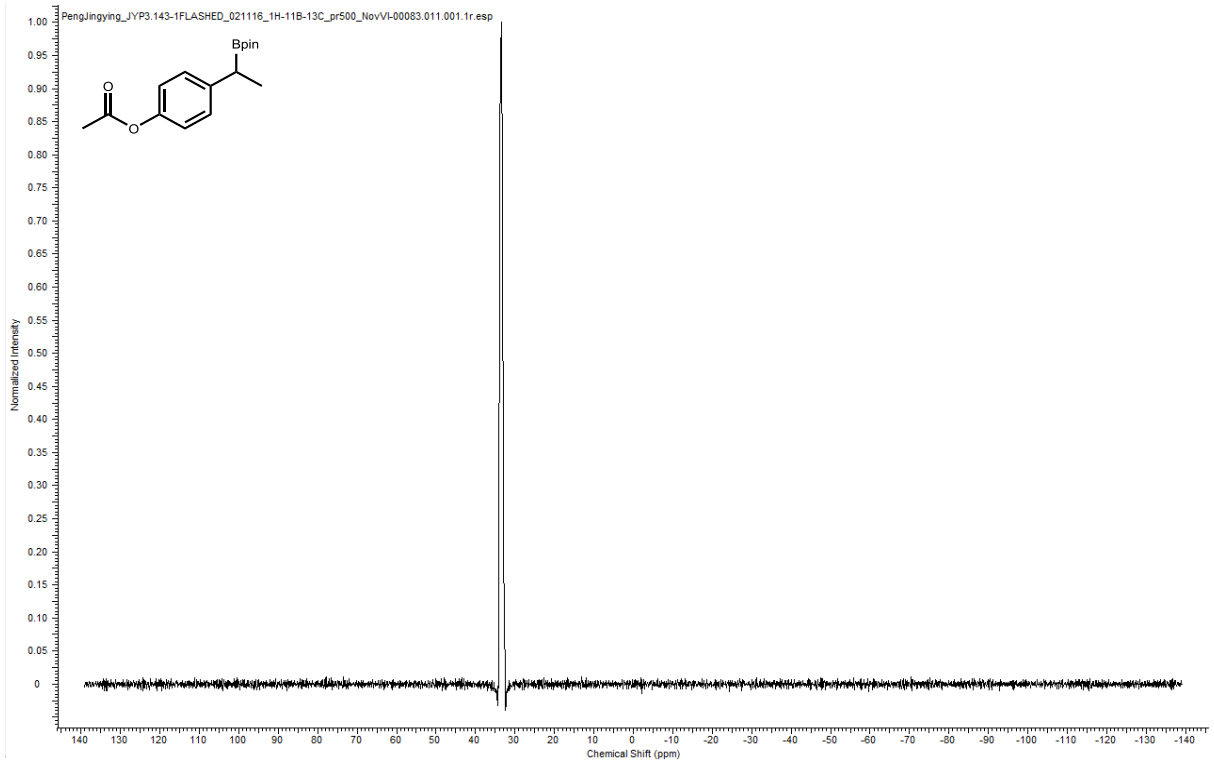
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(4-cyanophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3r**)



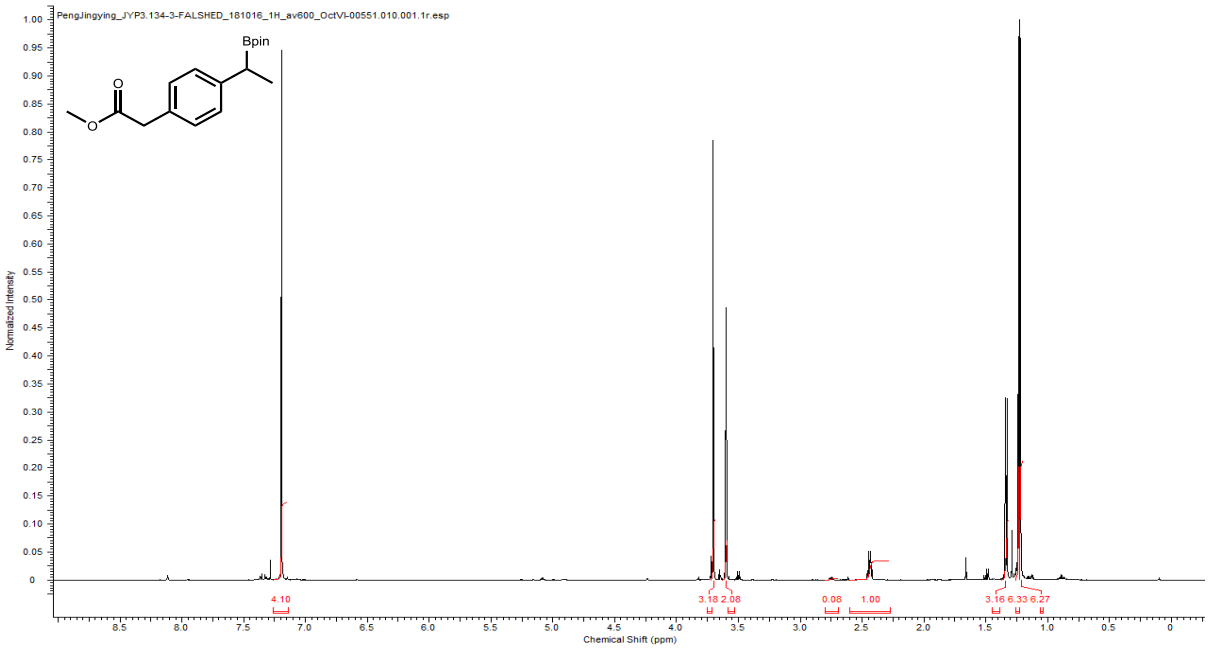
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(4-acetoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3s**)



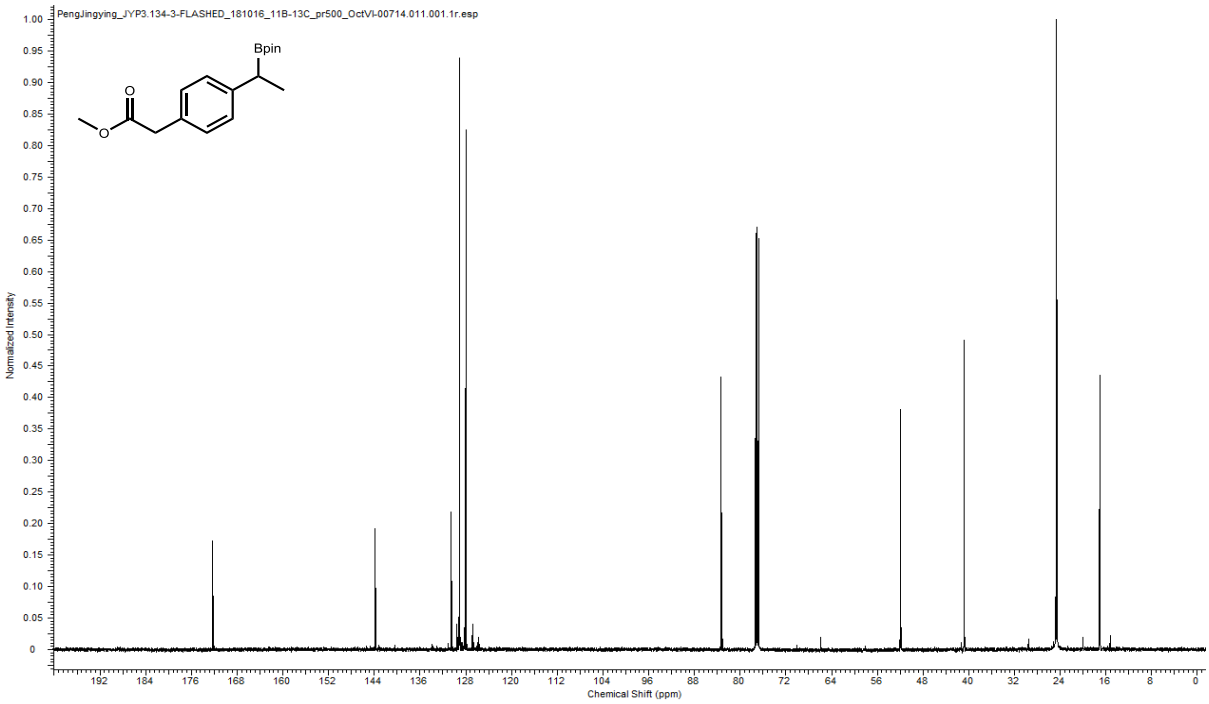
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(4-acetoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3s**)



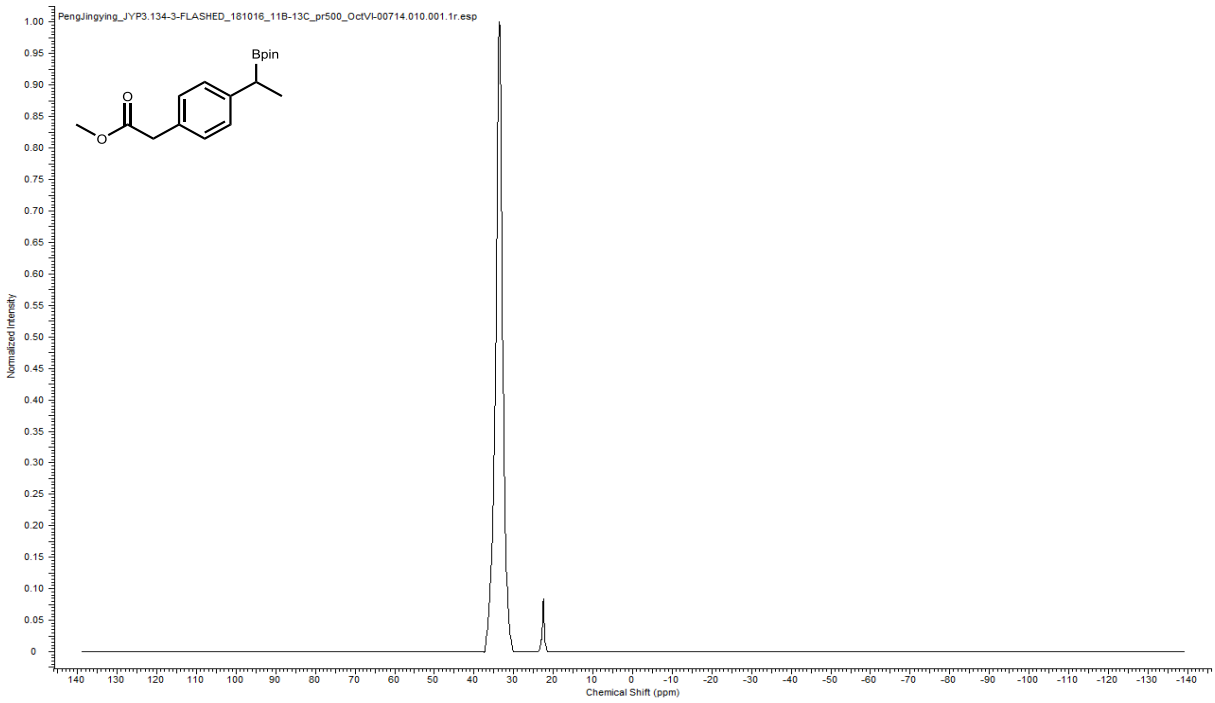
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(4-acetoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3s**)



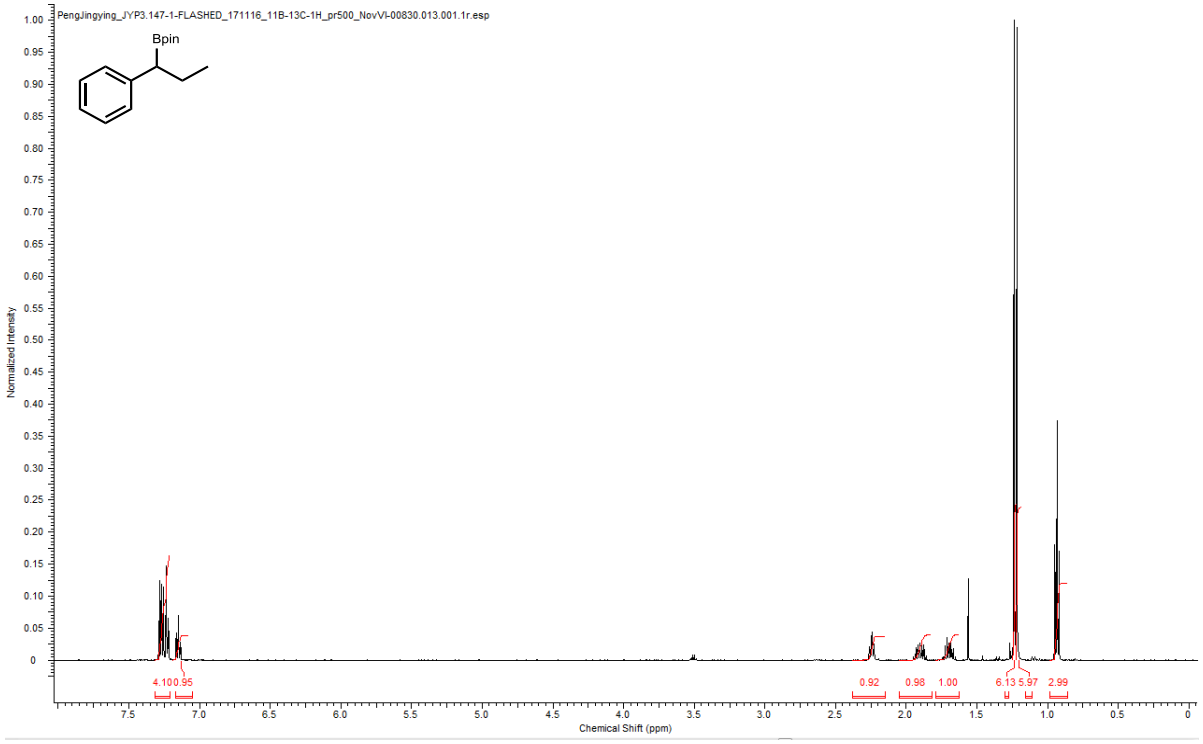
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-(4-(acetic acid methyl ester)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3t**)



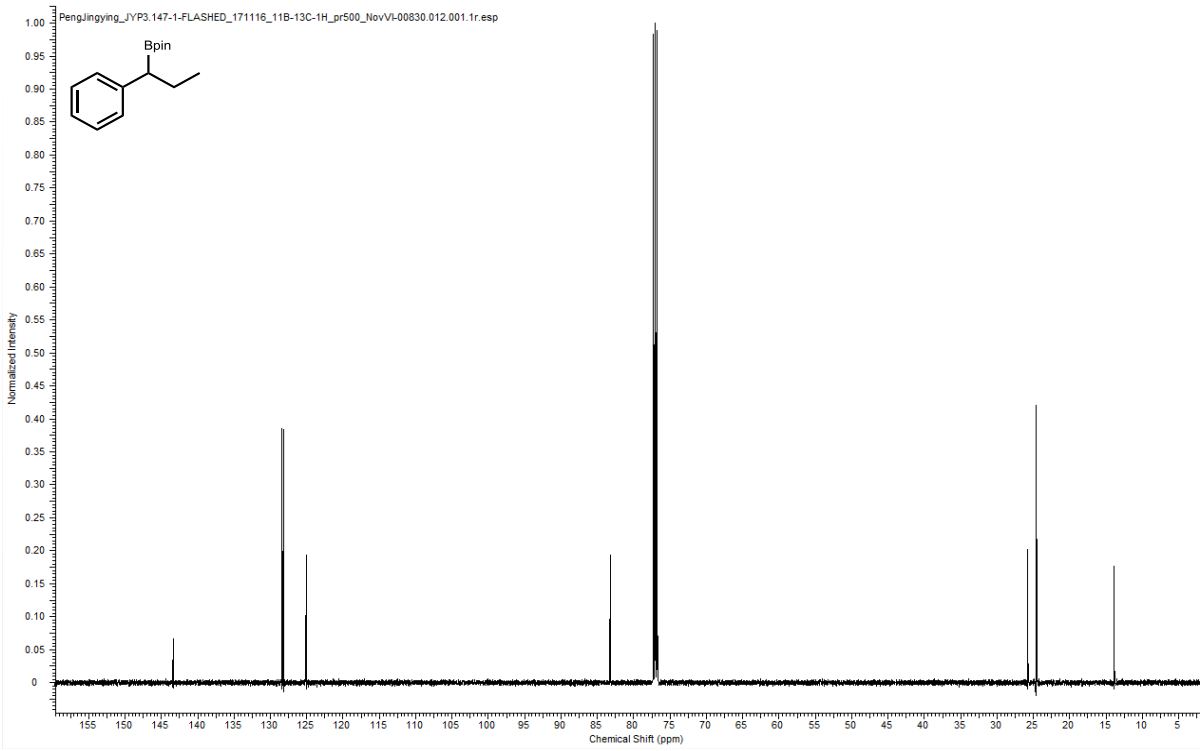
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-(4-(acetic acid methyl ester)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3t**)



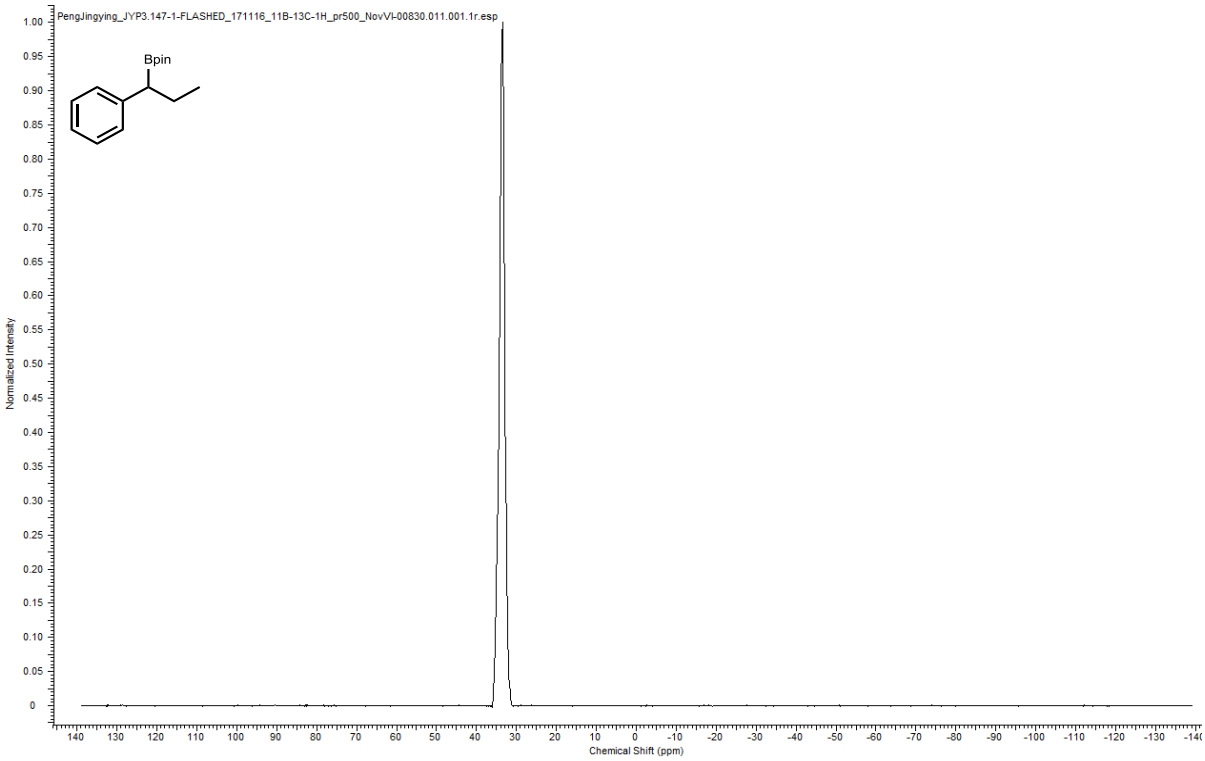
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-(4-(acetic acid methyl ester)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3t**)



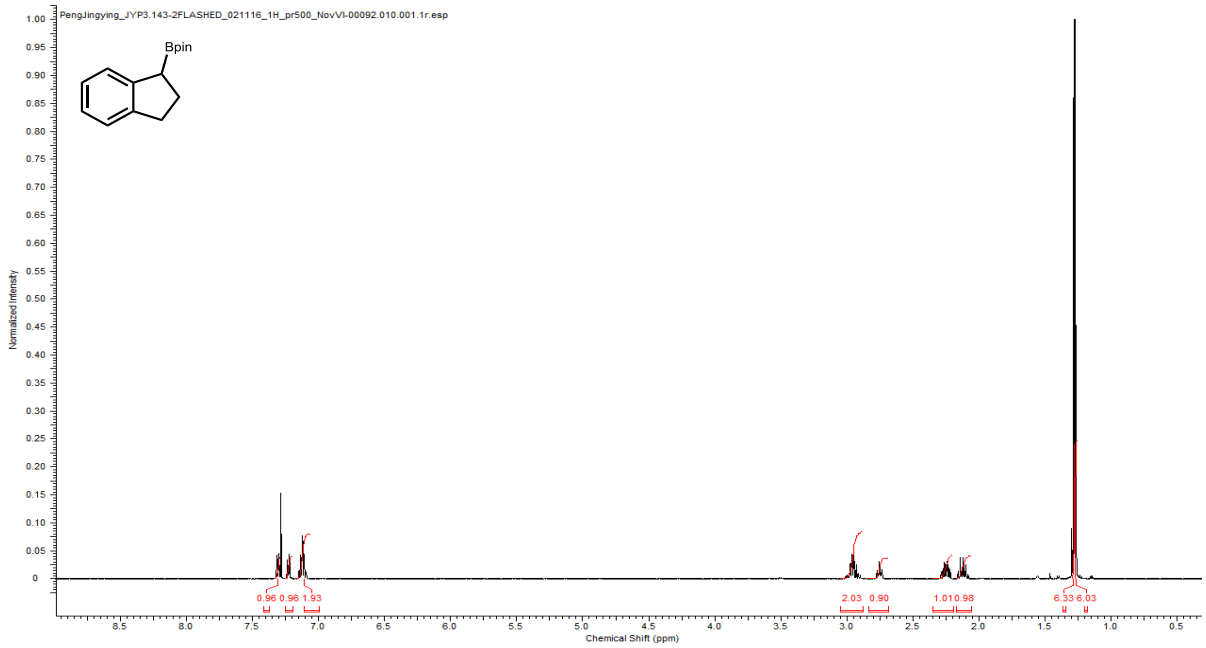
^{1}H NMR (500 MHz, $CDCl_3$) of 4,4,5,5-tetramethyl-2-(1-phenyl-propyl)-1,3,2-dioxaborolane (**3u**)



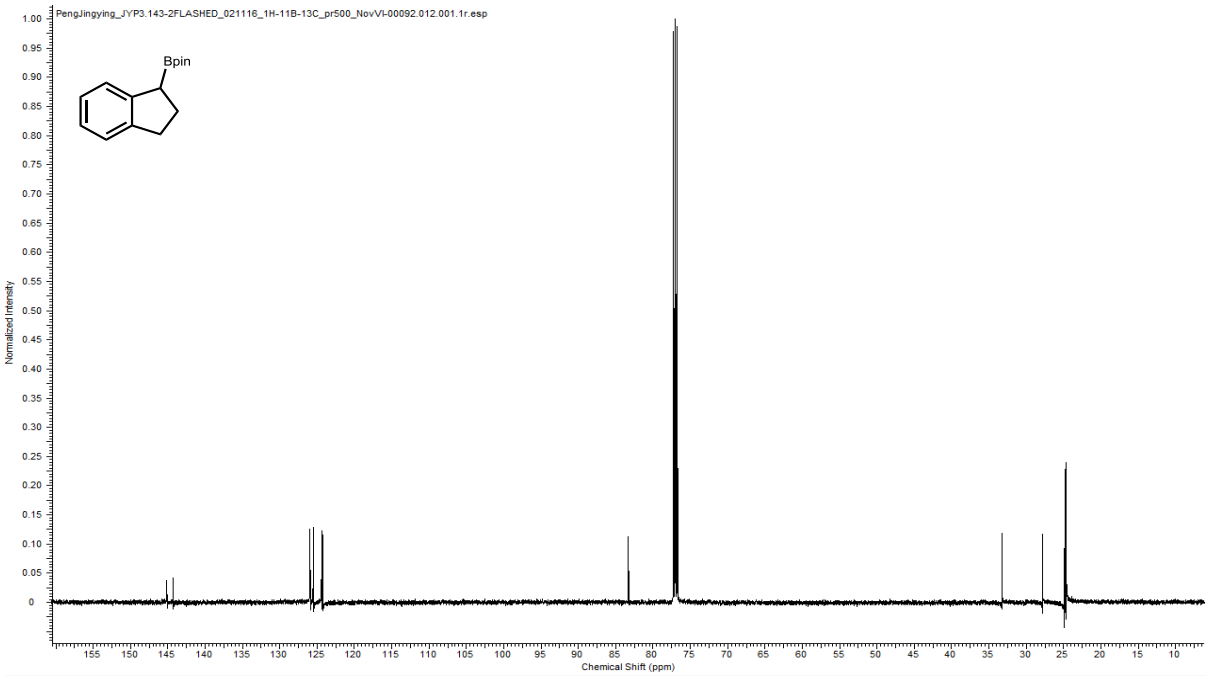
^{13}C NMR (125 MHz, $CDCl_3$) of 4,4,5,5-tetramethyl-2-(1-phenyl-propyl)-1,3,2-dioxaborolane (**3u**)



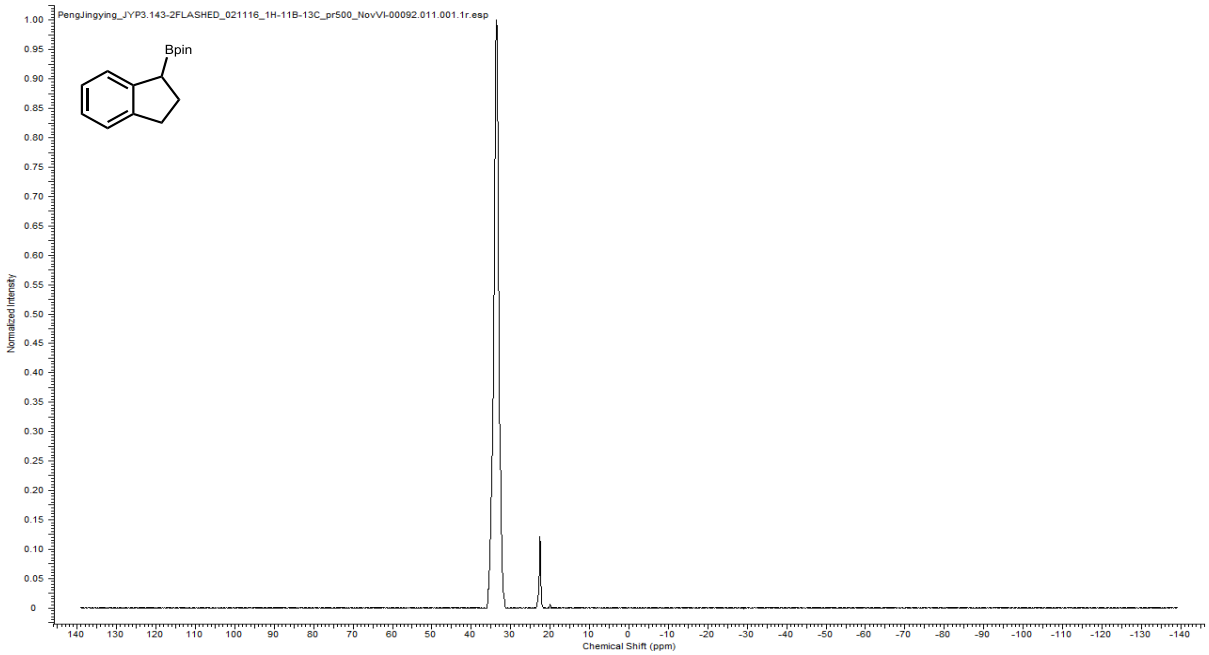
^{11}B NMR (160 MHz, $CDCl_3$) of 4,4,5,5-tetramethyl-2-(1-phenyl-propyl)-1,3,2-dioxaborolane (**3u**)



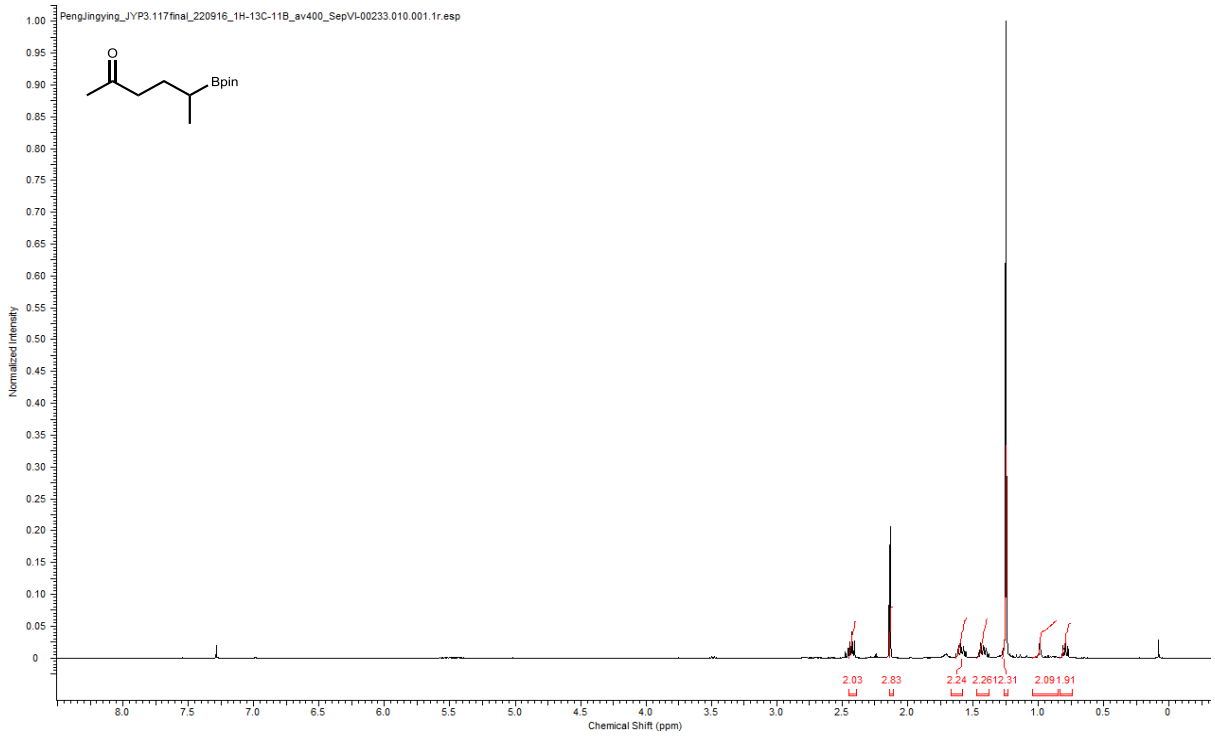
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(2,3-dihydro-1*H*-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3v**)



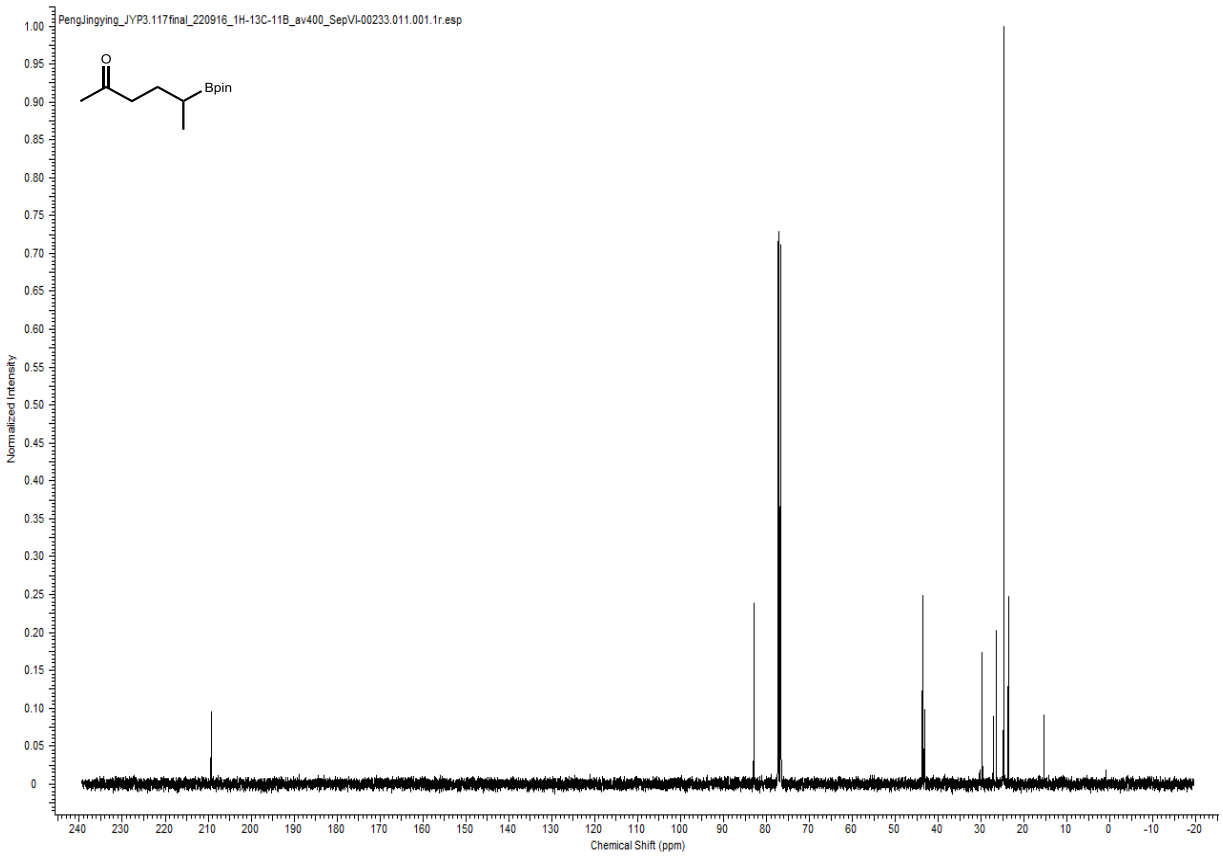
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(2,3-dihydro-1*H*-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3v**)



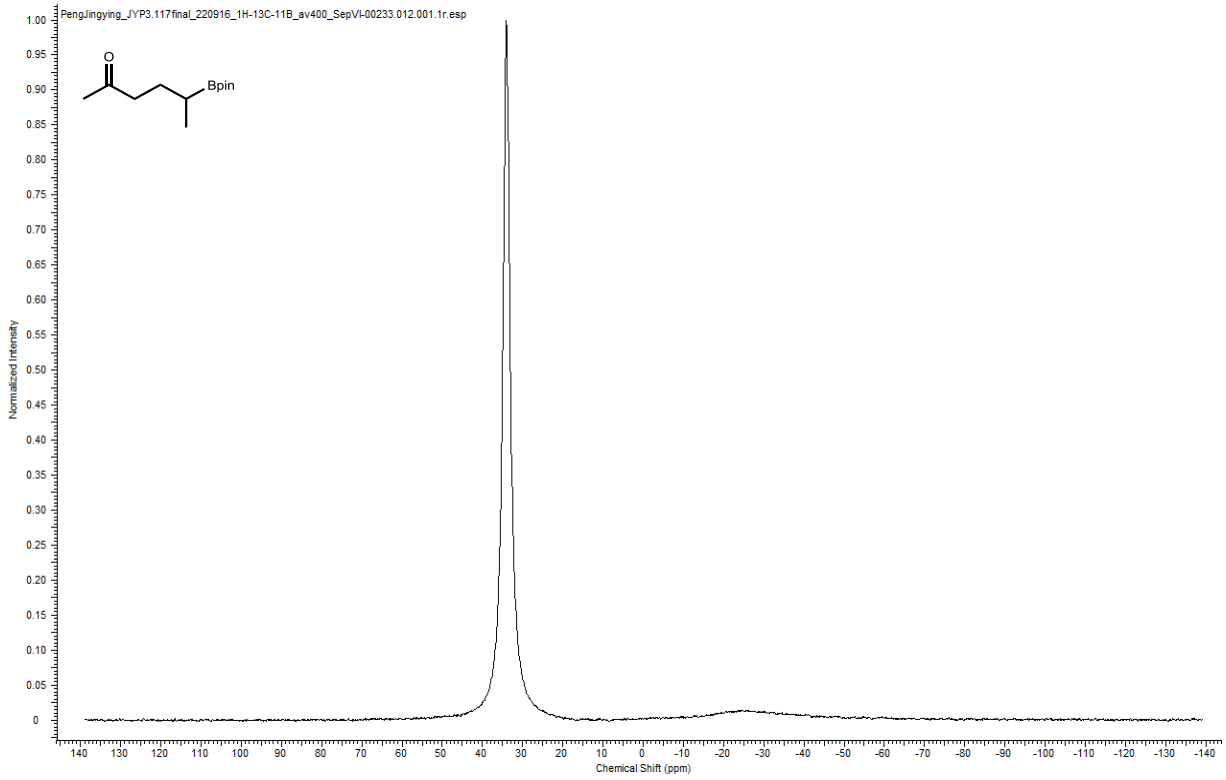
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(2,3-dihydro-1*H*-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3v**)



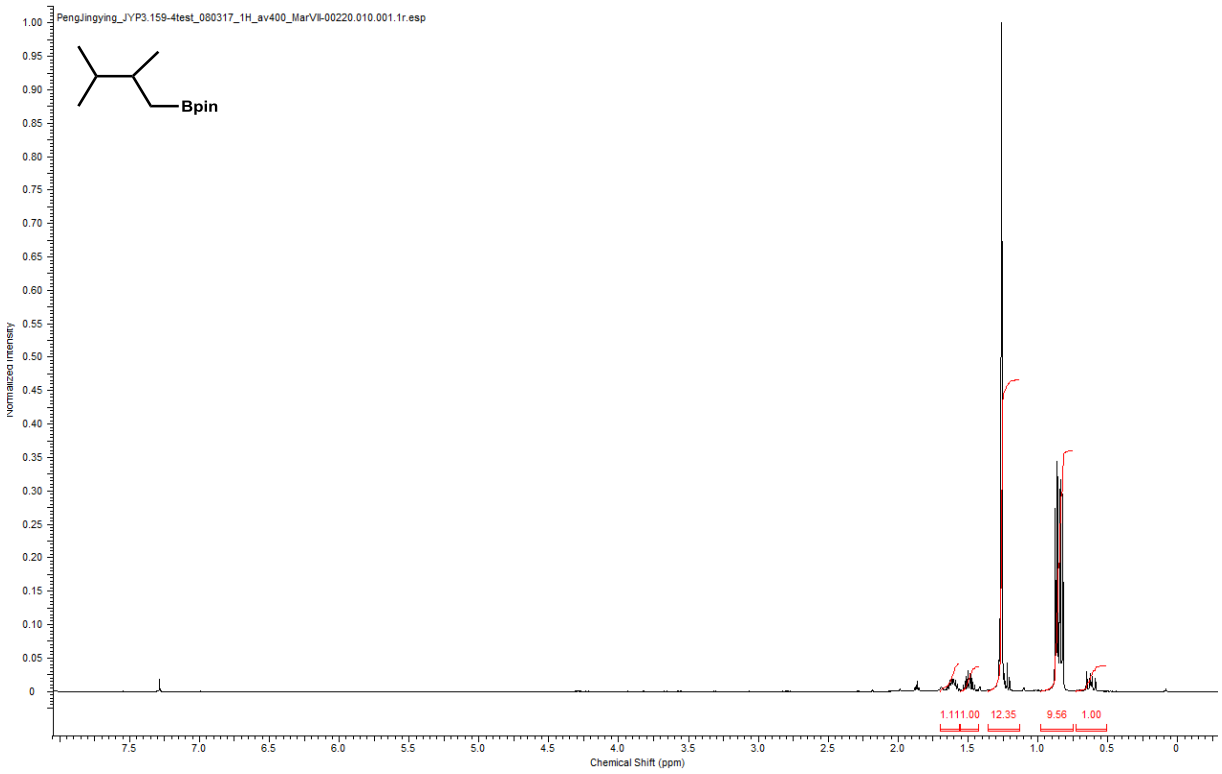
^{1}H NMR (500 MHz, $CDCl_3$) of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (**3w**)



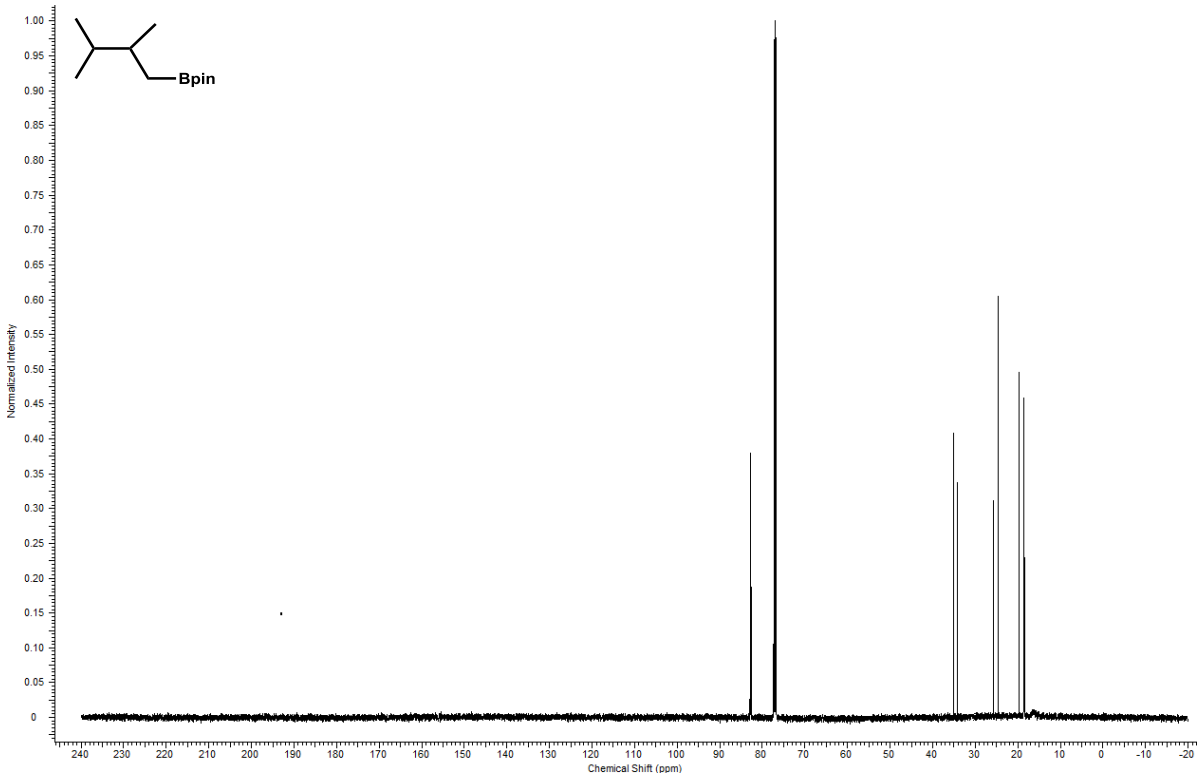
^{13}C NMR (125 MHz, $CDCl_3$) of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (**3w**)



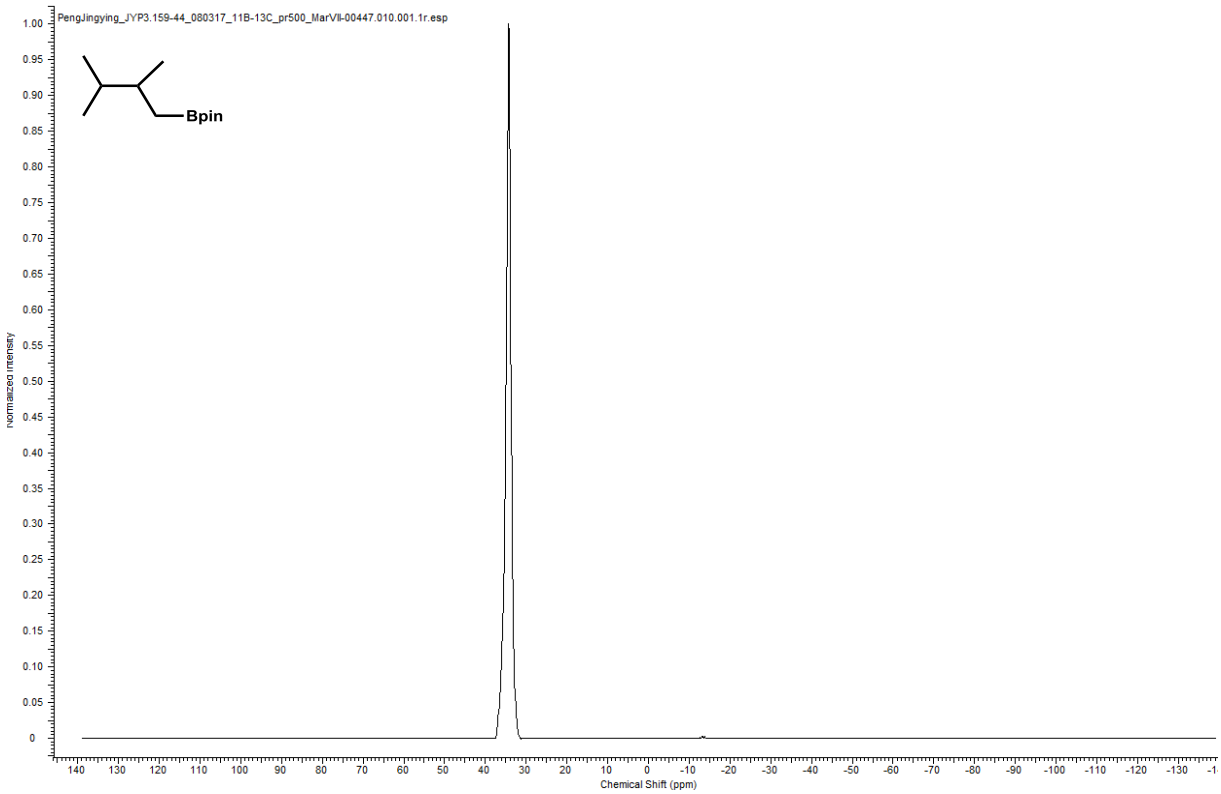
^{11}B NMR (160 MHz, $CDCl_3$) of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (**3w**)



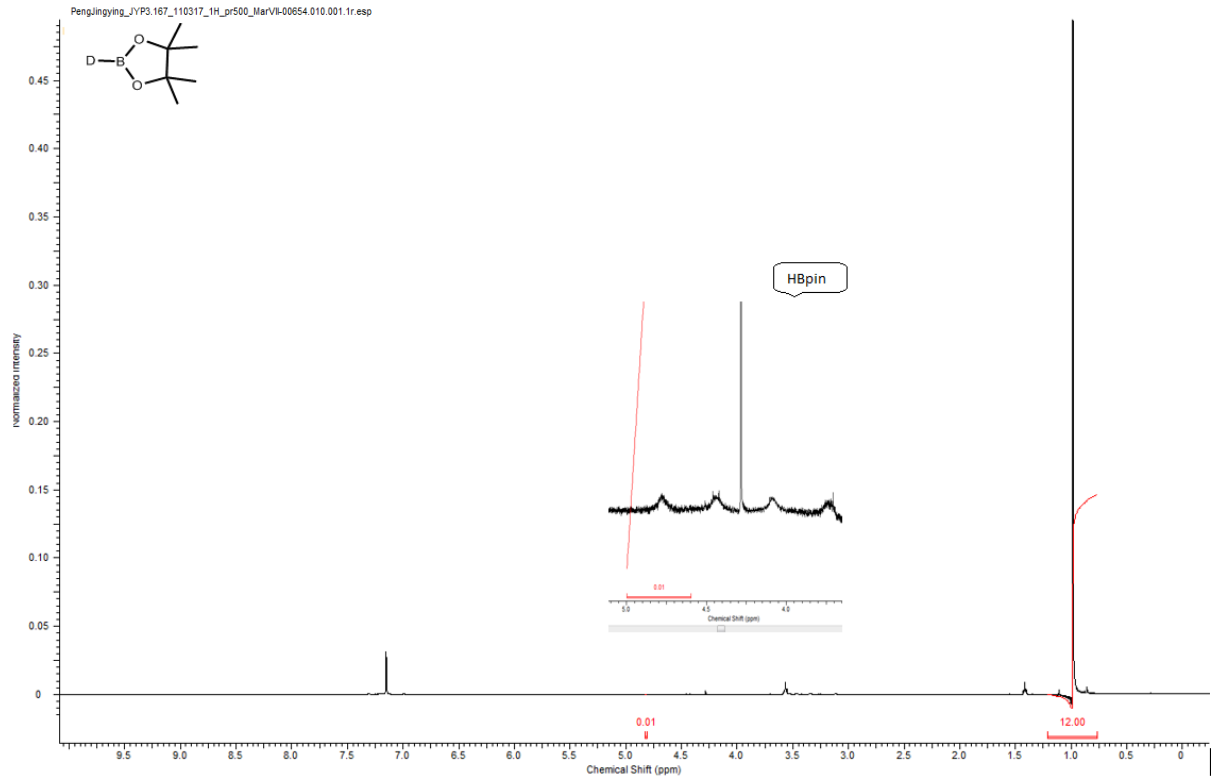
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(2,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3x**)



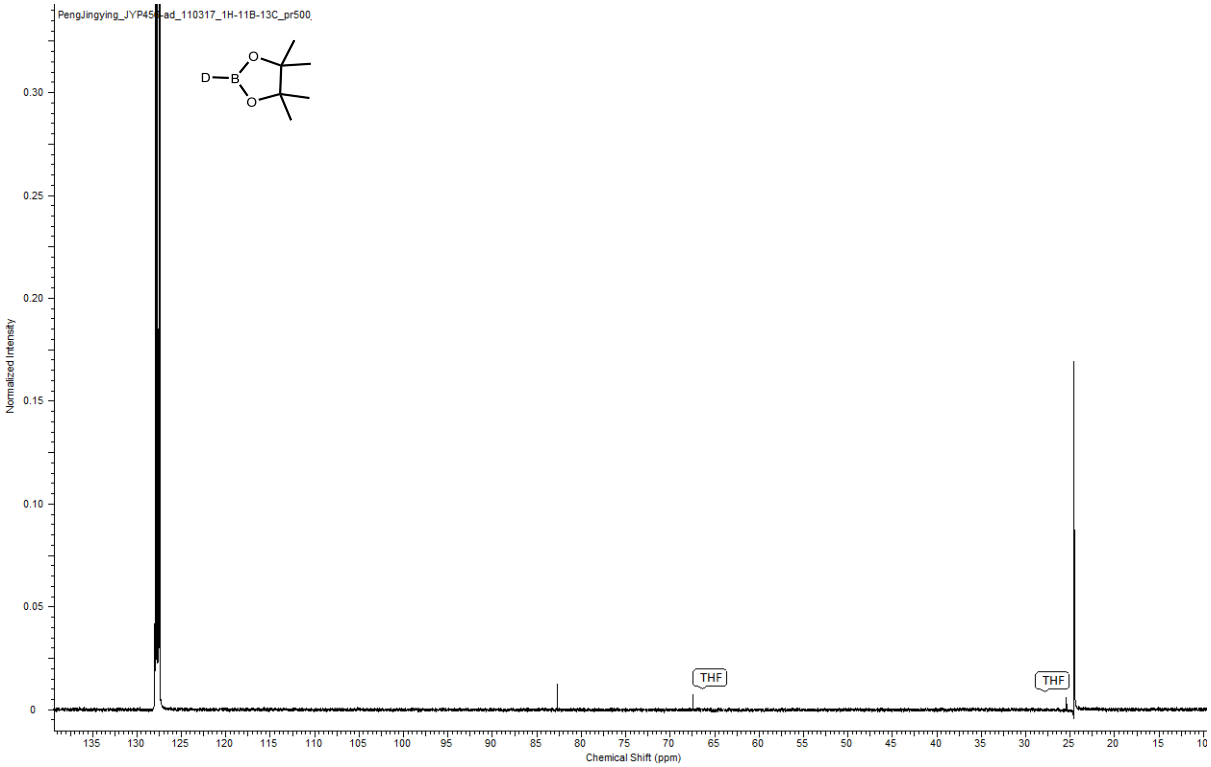
^{13}C NMR (125 MHz, CDCl3) of 2-(2,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3x**)



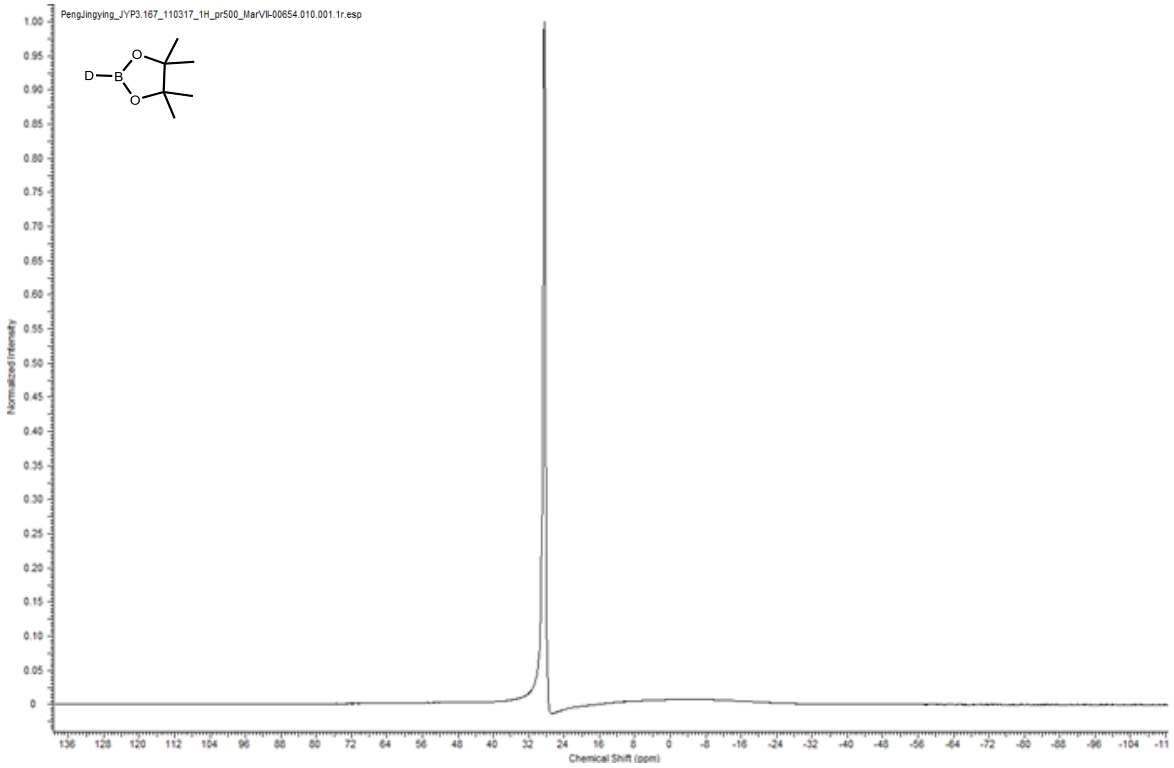
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(2,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3x**)



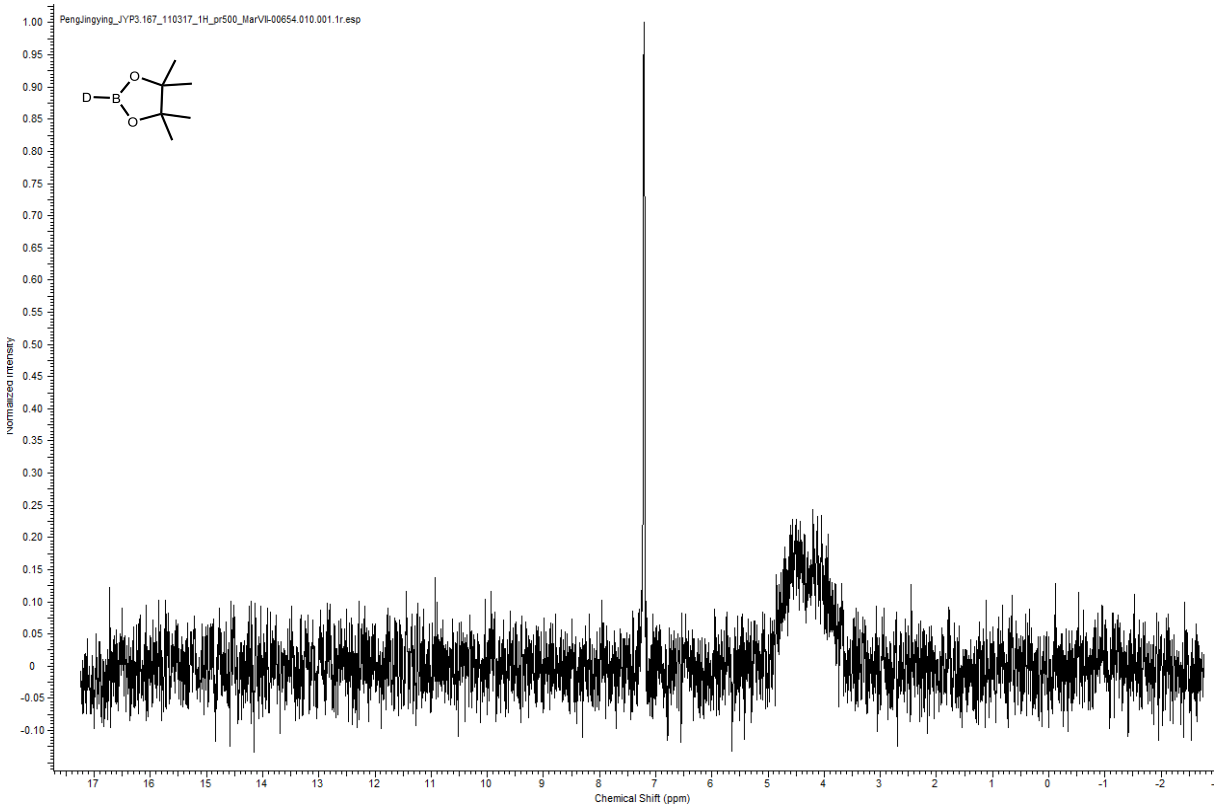
^{1}H NMR (500 MHz, $CDCl_3$) of d_1-pinacolborane



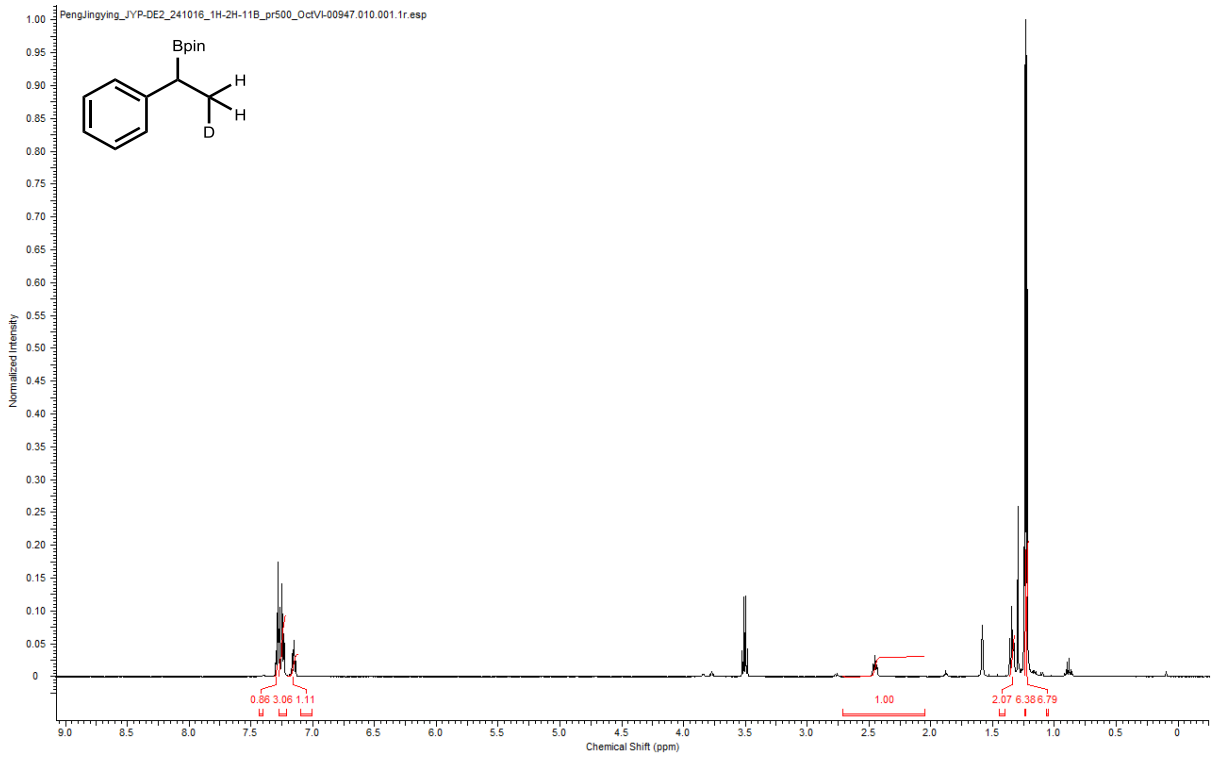
^{13}C NMR (125 MHz, CD_2Cl_2) of d_1-pinacolborane



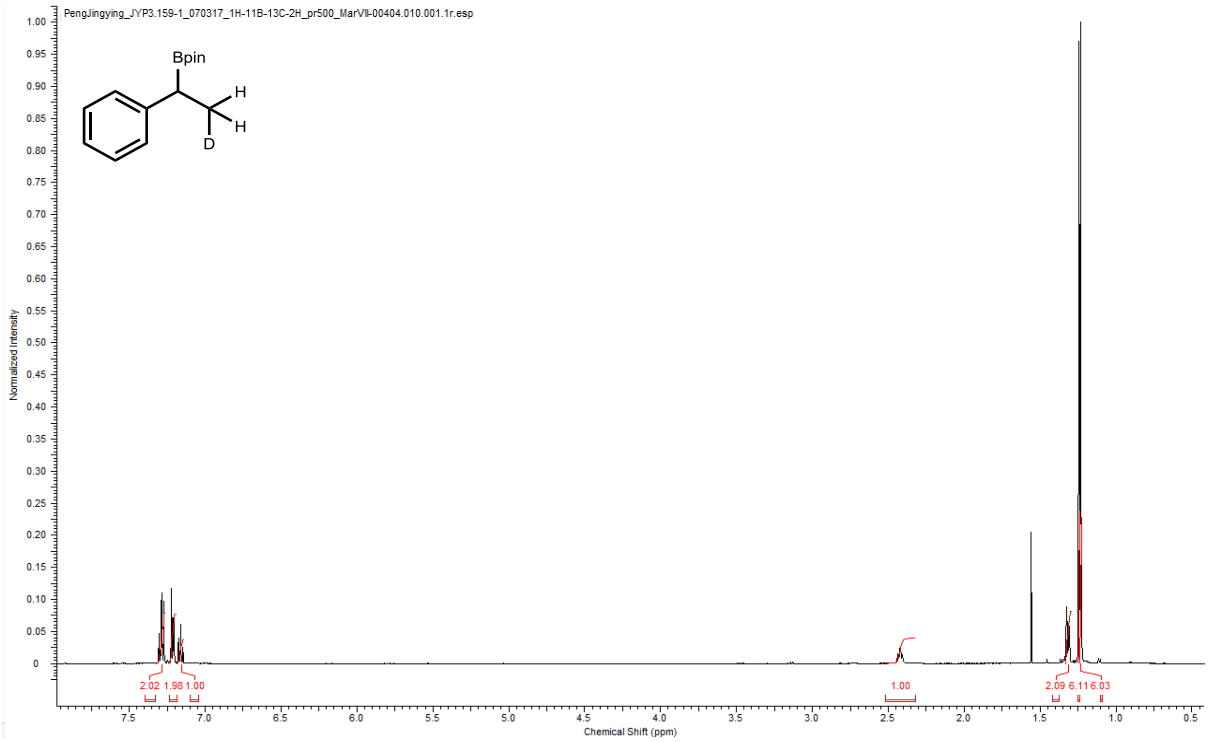
^{11}B NMR (160 MHz, $CDCl_3$) of d_1-pinacolborane



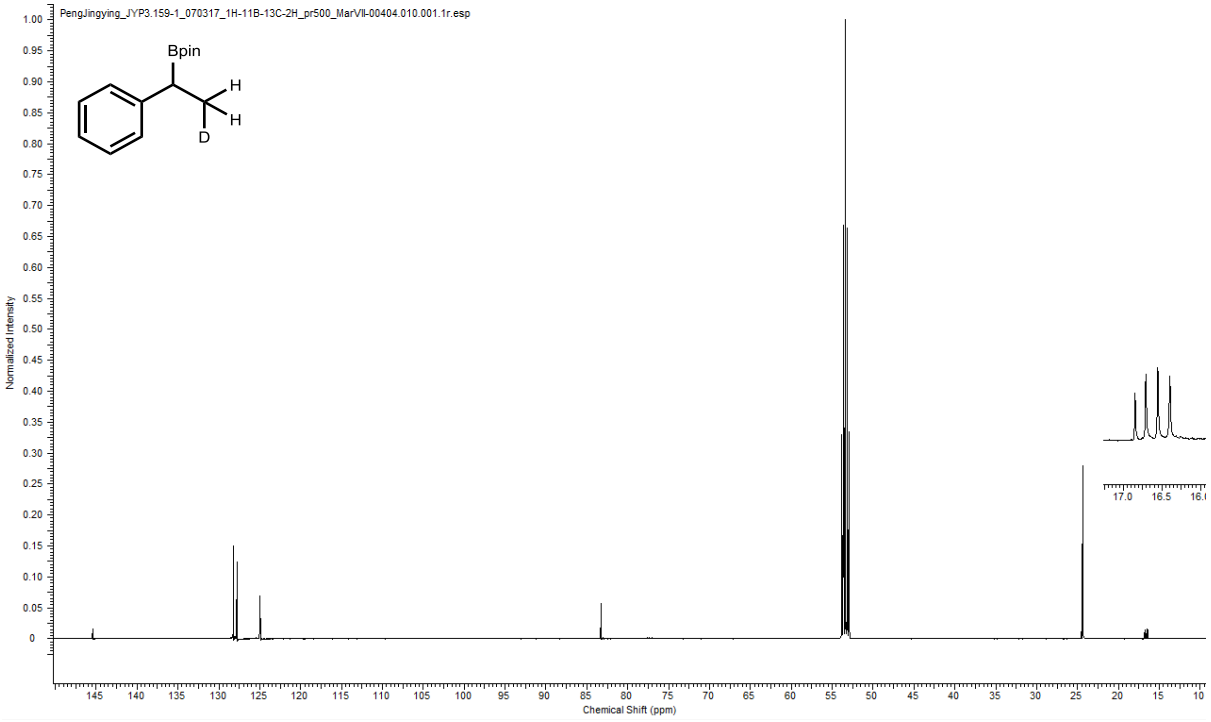
^{2}D NMR (77 MHz, $CHCl_3$) of d_1-pinacolborane



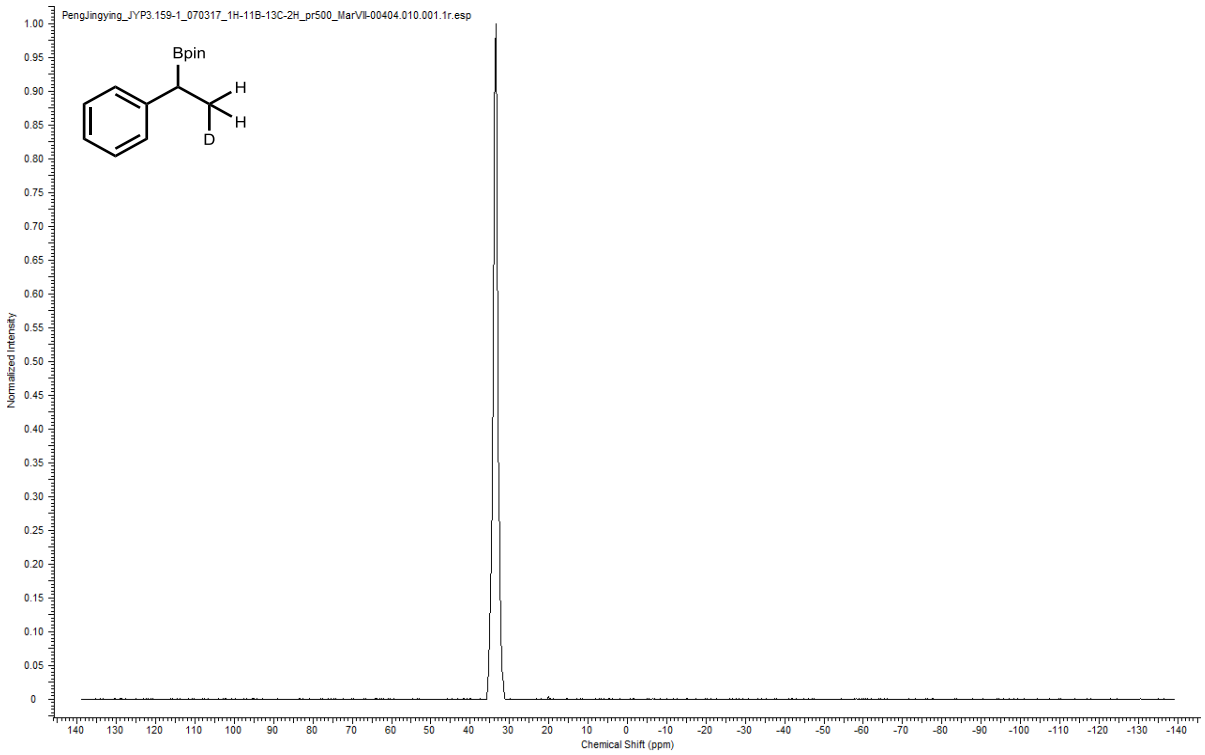
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-Phenyl-2-d_1-ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (d_1-**3a**) (crude)



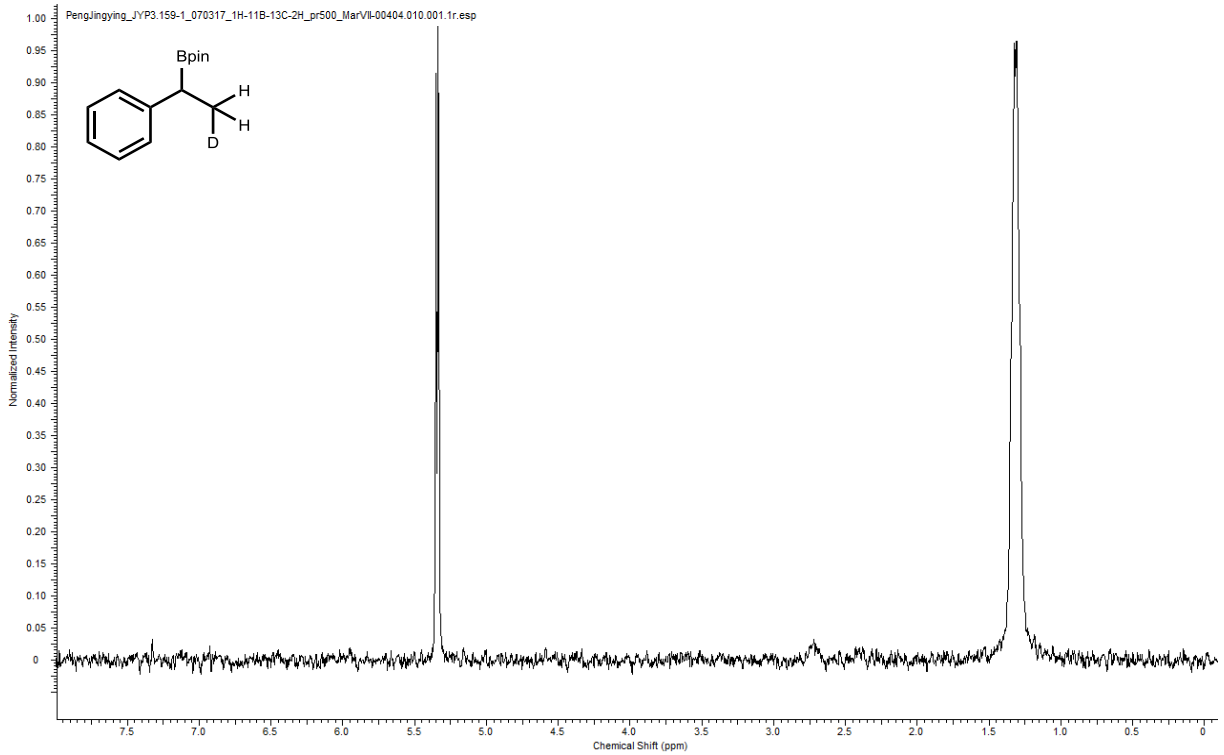
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-Phenyl-2-d_1-ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (d_1-**3a**)



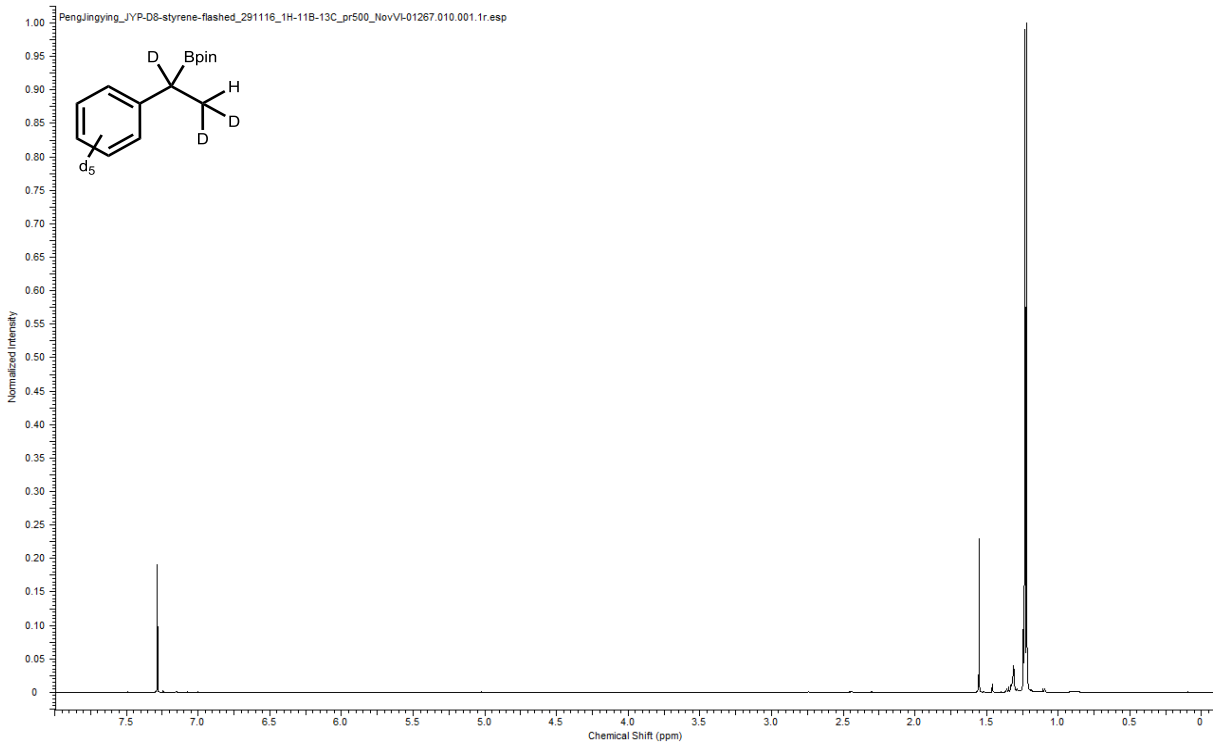
^{13}C NMR (125 MHz, CD_2Cl_2) of 2-(1-Phenyl-2-d_1-ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (d_1-**3a**)



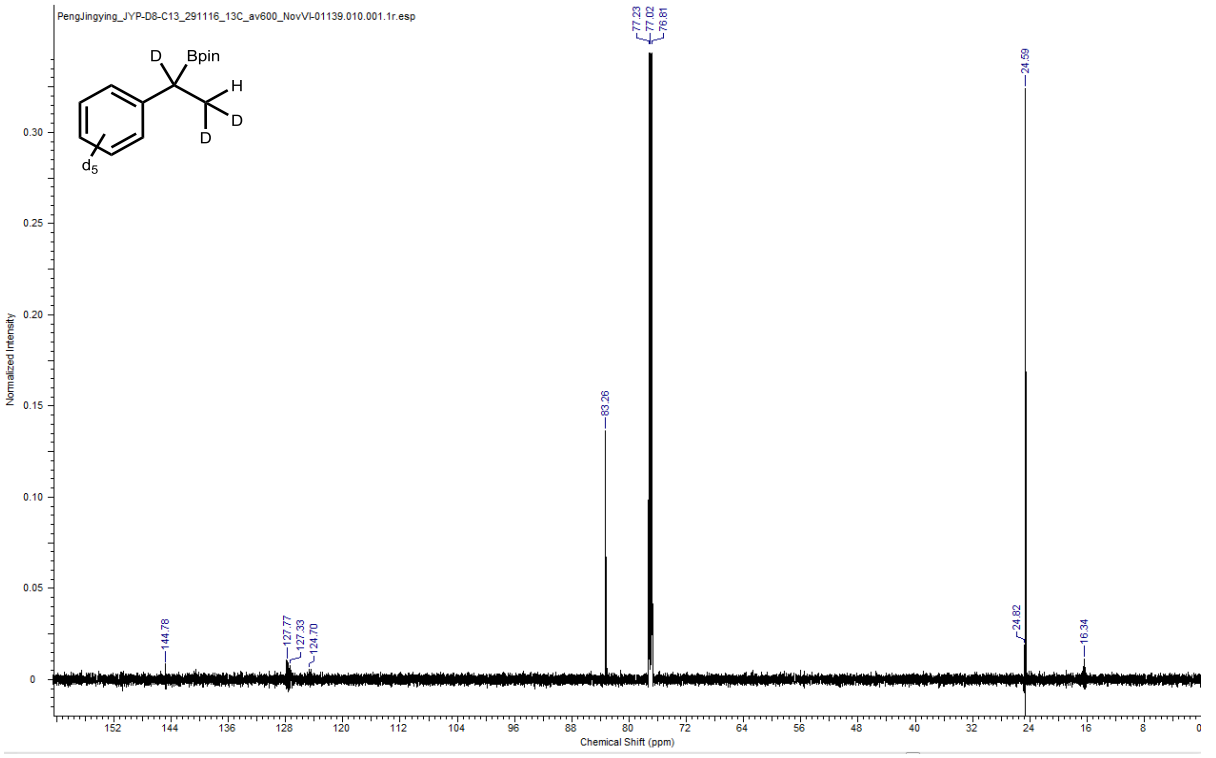
^{11}B NMR (160 MHz, $CDCl_3$) of 2-(1-Phenyl-2-d_1-ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (d_1-**3a**)



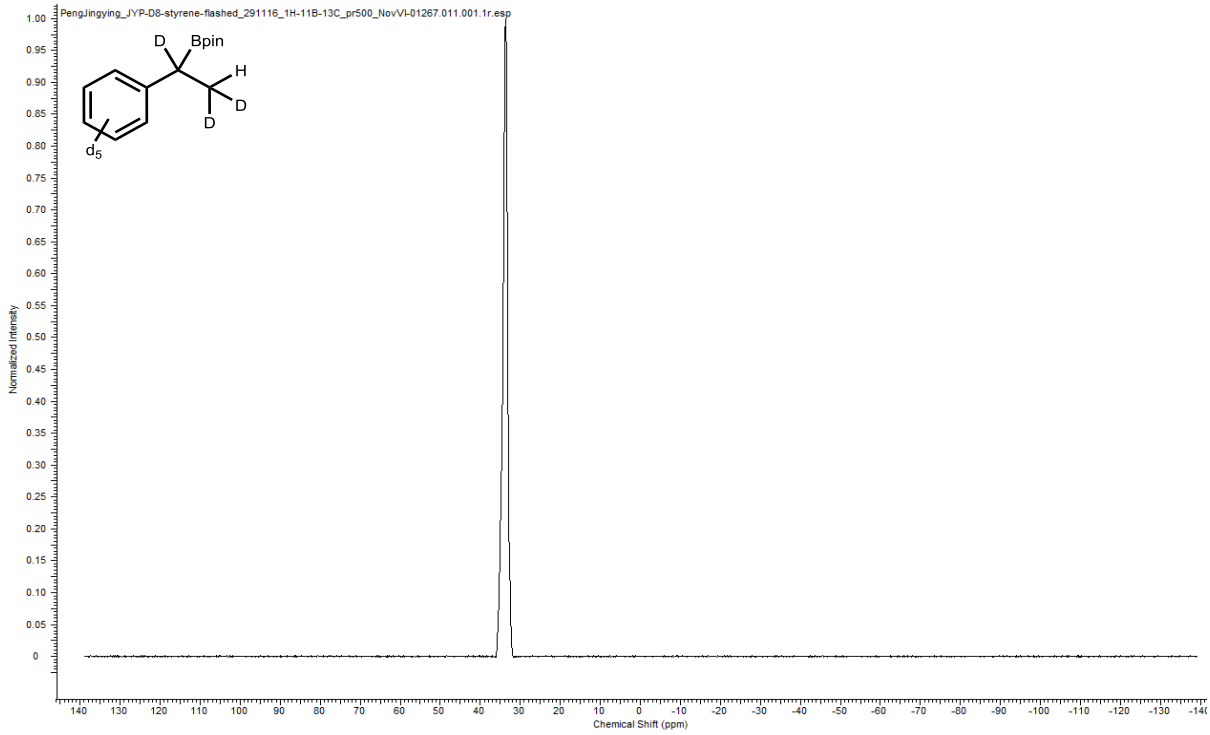
^{2}D NMR (77 MHz, CD_2Cl_2) of 2-(1-Phenyl-2-d_1-ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (d_1-**3a**)



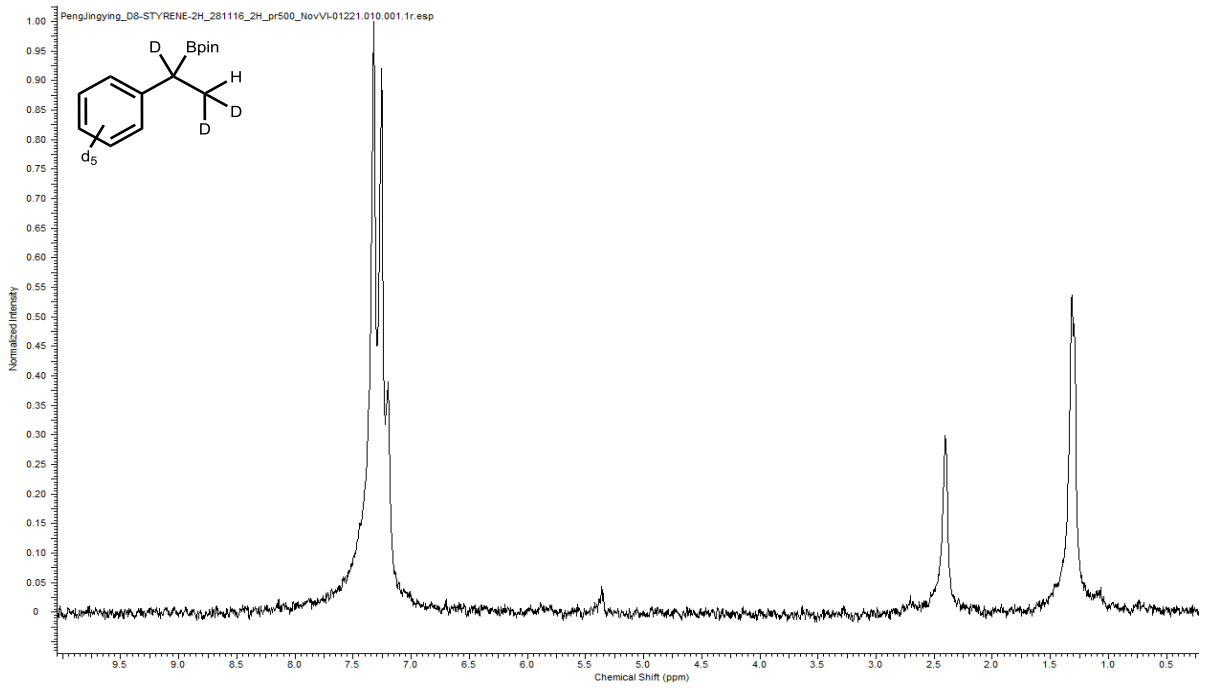
^{1}H NMR (500 MHz, $CDCl_3$) of 2-[1-(d_5-Phenyl)-1-d_1-2-d_2-ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (d_8-**3a**)



^{13}C NMR (125 MHz, $CDCl_3$) of 2-[1-(d_5-Phenyl)-1-d_1-2-d_2-ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (d_8-**3a**)



^{11}B NMR (160 MHz, $CDCl_3$) of 2-[1-(d_5-Phenyl)-1-d_1-2-d_2-ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (d_8-**3a**)



^{2}D NMR (77 MHz, $CHCl_3$) of 2-[1-(d_5-Phenyl)-1-d_1-2-d_2-ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (d_8-**3a**)