Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Efficient Rh-catalyzed C-H Borylation of Arene Derivatives under Photochemical Conditions

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Table of Contents

I. General Information

All the synthetic manipulations were carried out using standard schlenk tubes (1.2 mm thickness) technique in over dried Duran borosilicate glassware conducted in a nitrogen glove box. All the substrates, reagents and materials were purchased from Sigma Aldrich, Alfa Aesar and TCI Chemicals. Unless otherwise noted, all commercial reagents were used without further purification. Air and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk tubes are using 1.2 mm thickness. The catalyst *trans*-$Rh(PMe_3)_2(CO)Cl$ was prepared according to literature procedure.[1]

The portable Lumatec Superlite 400 (150 W, 100-240 V, 50-60 Hz) with highly flexible fiber optic cable of 5 mm diameter was used as light source throughout our study.[2] The power of light was measured using Laser point plus power and energy meter.[3] It should be noted that accuracy of such C-H borylation photocatalytic system; so stirring rate of 1000 rpm has been maintained. The product(s) were analyzed against authenticated sample and yield was determined by Gas Chromatographic technique using an Agilent 6890N network GC system with (60m×250µm×0.25µm) DB Wax column with respect to mesitylene as an internal standard after dilution of aliquot with acetone. Response factors of each analyte were determined by 'Multiple Point Internal Standard GC Quantitation Method' against authenticated samples with respect to mesitylene.

Air- and moisture-sensitive syntheses were performed under argon atmosphere. The products were characterized by ^1H NMR, ^{13}C NMR, HRMS spectroscopy. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 300 (300 MHz) or 400 (400 MHz) NMR spectrometers. The ^1H and ^{13}C NMR chemical shifts are reported relative to the center of solvent resonance [$CDCl_3$: 7.26 (^1H), 77.0 (^{13}C)] or [CD_2Cl_2: 5.32 (^1H), 54.0 (^{13}C)]. ^{31}P NMR was referenced to 85% H_3PO_4 at 0 ppm. ^{13}C-NMR spectra were acquired on a broad band decoupled mode. Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), ddd (double of double of doublet), dddd (doublet of doublet of doublet of doublet), q (quartert), m (multiplet) and. EI (Electron impact) mass spectra were recorded on an MAT 95XP spectrometer (70 eV, Thermo ELECTRON CORPORATION). ESI (electrospray ionization) high resolution mass spectra were recorded on an Agilent Technologies 6210 TOF LC/MS

using H_2O + 0.1% formic acid (10%) and methanol (90%) as eluent. GC analysis was performed on an Agilent 7890A chromatograph with a 29 m HP5 column. The products were isolated from the reaction mixture by solvent evaporation and further purified by column chromatography on silica gel.

II. General Experimental set up

Figure S1. The general experimental set up.

III. GC Table of conversion of phenylboronic esters (Table 1 Entry 1)

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                                                 Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\OCT-WAX1.M
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Last changed    : 3/17/2015 9:22:46 AM
                  (modified after loading)
Method Info     : 35/10-8-280/20

Additional Info : Peak(s) manually integrated
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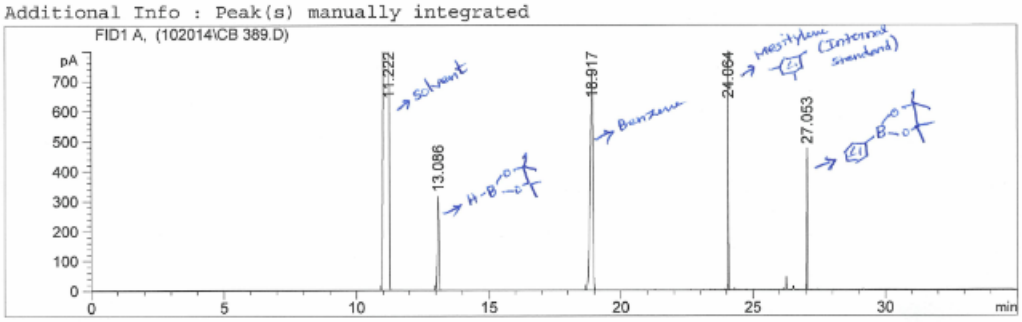


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======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  11.222 BB    0.1023 4.80727e4  5826.51660 84.96492
   2  13.086 BB    0.0637 1297.51428  314.61230  2.29326
   3  18.917 BB    0.0981 5178.38184  732.35791  9.15241
   4  24.064 BV    0.0153 1196.94580 1231.60083  2.11551
   5  27.053 BV    0.0274  833.92139  472.43069  1.47389

Totals :                  5.65794e4  8577.51834

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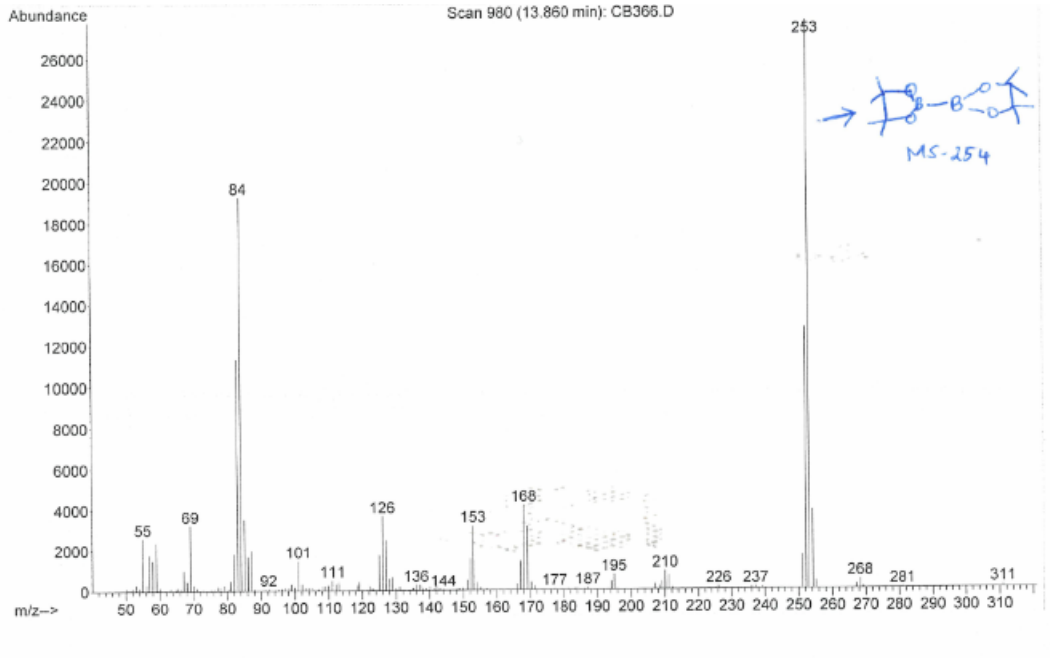
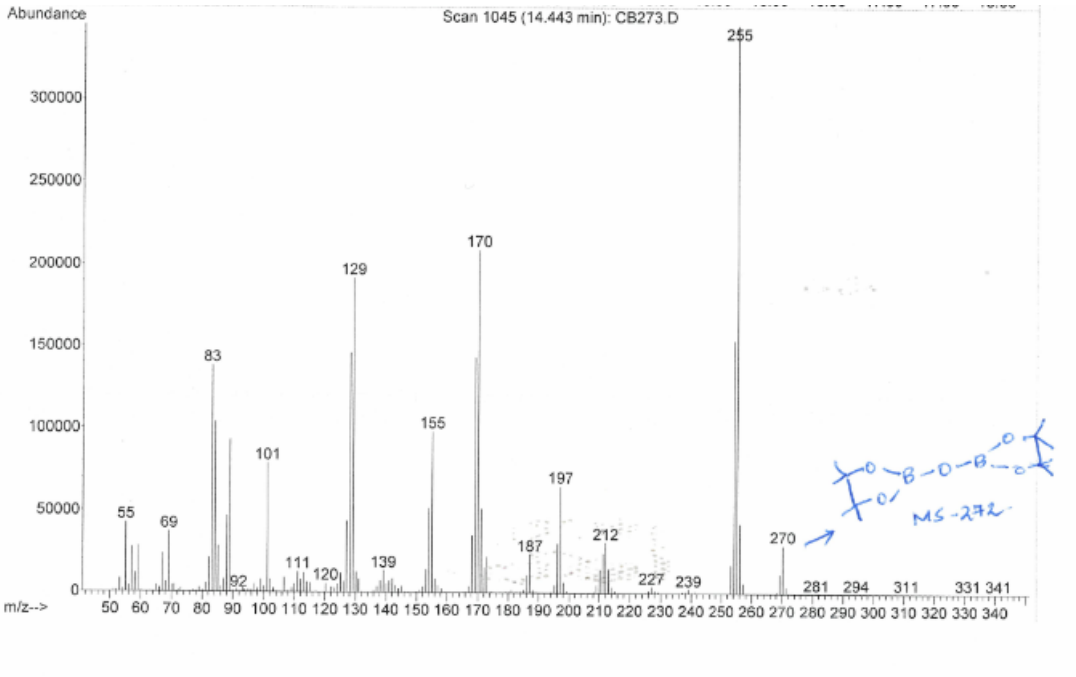
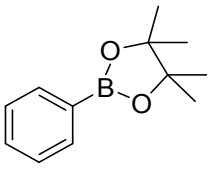
IV. GCMS of dehydrogenation of Pinacolborane (Table 1 Entry 13)





V. Experimental procedures and characterization of compounds

1b (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene.



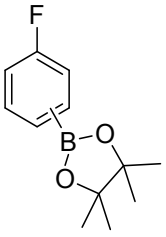
In an argon filled glove box, $[Rh(PMe_3)_2(CO)Cl]$ 0.5% (2.0 mg, 0.0062 mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalents of benzene (5.0 mmol, 0.45 mL). The reaction vessel is sealed and irradiated with light for 5h. After exposure to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (20:1). The product is obtained as a white solid in 83% yield based on HBPin.

^1H NMR (300MHz, $CDCl_3$) δ 7.83 (dd, J = 7.8, 1.4 Hz, 2H), 7.47 (dddd, J = 6.4, 6.4, 1.4, 1.4 Hz, 1H), 7.38 (ddd, J = 7.8, 6.4, 1.4 Hz, 2H), 1.36 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 134.86, 131.38, 127.83, 83.89, 24.99.

^{11}B NMR (96 MHz, $CDCl_3$) δ 31.01. ^1H and ^{13}C NMR data agree with previously reported data.[4]

2b (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)fluorobenzene



In an argon filled glove box, $[Rh(PMe_3)_2(CO)Cl]$ 0.5% (2.0 mg, 0.0062 mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalents of fluorobenzene (5.0 mmol, 0.67 mL). The reaction vessel is sealed and irradiated with light for 5h. After exposure

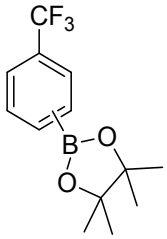
to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (20:1). The product is obtained as a white solid in 84% yield based on HBPin. The *ortho:meta:para* ratio was determined to be 0.1:0.5:0.4 by integration of the characteristic peaks in ^{1}H NMR.

^{1}H NMR (300 MHz, $CDCl_3$) δ (*ortho* isomer)7.85 – 7.77 (m, 1H), 7.46 – 7.41 (m, 1H), 7.18 – 7.14 (m, 1H),7.00 – 7.03 (m, 1H), 1.34 (s, 12H), (*meta* isomer)7.58 (d, J = 7.4 Hz, 1H), 7.49 (d, J = 9.5 Hz, 1H), 7.37 – 7.29 (m, 1H), 7.14 – 7.11 (m, 1H), 1.35 (s, 12H), (*para* isomer)7.82 – 7.77 (m, 2H), 7.06 – 7.02 (m, 2H), 1.37 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (*ortho* isomer)137.09 (d, J = 8.6 Hz), 133.39 (d, J = 8.8 Hz), 123.70 (d, J = 3.3 Hz), 114.94 (d, J = 20.2 Hz), 83.99, 24.93, (*meta* isomer) 162.60 (d, J = 246.3 Hz), 130.40 (d, J = 3.0 Hz), 129.58 (d, J = 7.1 Hz), 121.06 (d, J = 19.3Hz), 118.27 (d, J = 21.1 Hz), 84.19, 24.96, (*para* isomer) 167.30 (d, J = 250.9 Hz), 136.95 (d, J = 8.1 Hz), 115.35 (d, J = 24.0 Hz), 83.99, 24.93.

^{19}F NMR ($CDCl_3$, 282 MHz) δ (*ortho* isomer)-108.01 –-107.91 (m), (*meta* isomer)-102.27–-102.22 (m), (*para* isomer)-113.74–-113.81 (m). ^{11}B NMR (96 MHz, $CDCl_3$) δ 31.12. ^{1}H and ^{13}C NMR data of the para isomer agree with previously reported data.[13-15]

3b (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)(trifluoromethyl)benzene.



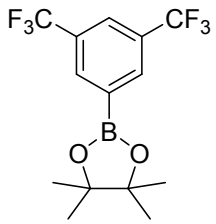
In an argon filled glove box, [$Rh(PMe_3)_2(CO)Cl$] 0.5% (2.0 mg, 0.0062 mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalents of (trifluoromethyl)benzene (5.0 mmol, 0.61 mL). The reaction vessel is sealed and irradiated with light for 5h. After exposure to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (20:1). The product is obtained as a white solid in 84% yield based on HBPin. The meta:para ratio was determined to be 0.6:0.4 by integration of the characteristic peaks in ^{1}H NMR.

^{1}H NMR (300 MHz, $CDCl_3$) δ (*meta* isomer) 8.07 (s, 1H), 7.98 (d, J = 7.4 Hz, 1H), 7.70 (d, J = 7.9 Hz, 1H), 7.47 (dd, J = 7.6, 7.6 Hz, 1H), 1.36 (s, 12H), (*para* isomer) 7.92 (d, J = 7.7 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 1.36 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (*meta* isomer) 138.13, 131.50 (q, J (CF) = 3.8 Hz), 129.94, 127.93 (q, J (CF) = 3.7 Hz), 124.35 (q, J (CF) = 272.4 Hz), 84.42, 24.99, (*para* isomer) 135.2, 130.15 (q, J (CF) = 32.1 Hz), 124.48 (q, J (CF) = 3.8 Hz), 124.19 (q, J (CF) = 272.9 Hz), 84.42, 24.99.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.23. ^{1}H and ^{13}C NMR data agree with previously reported data.[4]

4b 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)1,3-trifluoromethylbenzene

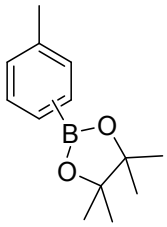


In an argon filled glove box, $[Rh(PMe_3)_2(CO)Cl]$ 0.5% (2.0 mg, 0.0062 mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalents of 1,3-bis (trifluoromethyl)benzene (5.0 mmol, 0.78 mL). The reaction vessel is sealed and irradiated with light for 5h. After exposure to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (20:1). The product is obtained as a white solid in 89% yield based on HBPin.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (s, 2H), 7.95 (s, 1H), 1.37 (s, 6H).^{13}C NMR (75 MHz, $CDCl_3$) δ 134.81 (d, J = 1.7 Hz), 131.04 (q, J = 33.2 Hz), 125.01 – 124.68 (m), 123.65 (q, J = 272.6 Hz), 85.00, 24.99.

^{19}F NMR ($CDCl_3$, 282 MHz) δ-62.48. ^{11}B NMR (96 MHz, $CDCl_3$) δ29.80. ^{1}H and ^{13}C NMR data of the para isomer agree with previously reported data.[16]

5b (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene.



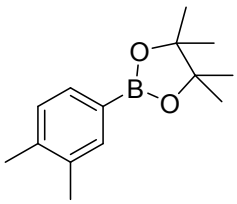
In an argon filled glove box, [Rh(PMe$_3$)$_2$(CO)Cl] 2.0% (8.0 mg, 0.025 mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalents of toluene (5.0 mmol, 0.53 mL). The reaction vessel is sealed and irradiated with light for 5h. After exposure to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (20:1). The product is obtained as a white solid in 73% yield based on HBPin. The *meta*:*para* ratio was determined to be 0.7:0.3 by integration of the characteristic peaks in ^{1}H NMR.

^{1}H NMR (300 MHz, $CDCl_3$) δ (*meta* isomer) 7.68 (s, 1H), 7.65-7.62 (m, 1H), 7.31-7.29 (m, 2H), 2.38 (s, 3H), 1.37 (s, 12H), (*para* isomer) 7.75 (d, J = 8.0, 1H), 7.21 (d, J = 8.1, 1H), 2.39 (s, 3H), 1.36 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (*meta* isomer) 137.22, 135.46, 132.16, 131.91, 127.81, 83.81, 24.97, 21.38, (*para* isomer) 141.49, 134.94, 128.63, 83.71, 24.97, 21.84.

^{11}B NMR (96MHz, $CDCl_3$) δ 31.06. ^{1}H and ^{13}C NMR data agree with previously reported data.[4]

6b 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-o-xylene.



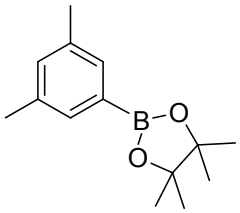
In an argon filled glove box, [Rh(PMe$_3$)$_2$(CO)Cl] 2.0% (8.0 mg, 0.025 mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalents of *o*-xylene (5.0 mmol, 0.6 mL). The reaction vessel is sealed and irradiated with light for 5h. After exposure to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (20:1). The product is obtained as a white solid in 80% yield based on HBPin.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.57 (d, J = 7.9, 1H), 7.17 (d, J = 7.8, 1H), 2.30 (s, 3H), 2.29 (s, 3H), 1.36 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.25, 136.05, 135.98, 132.53, 129.28, 83.70, 24.97, 20.14, 19.60.

^{11}B NMR (96MHz, $CDCl_3$) δ 30.60. ^{1}H and ^{13}C NMR data agree with previously reported data.[4]

7b 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-m-xylene.



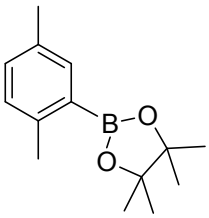
In an argon filled glove box, [Rh(PMe_3)$_2$(CO)Cl] 2.0% (8.0 mg, 0.025 mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalents of *m*-xylene (5.0 mmol, 0.62 mL). The reaction vessel is sealed and irradiated with light for 10h. After exposure to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (20:1). The product is obtained as a white solid in 73% yield based on HBPin.

^{1}H NMR (300 MHz, CD_2Cl_2) 7.38 (s, 1H), 7.11 (s, 1H), 2.32 (s, 3H), 1.33 (s, 7H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.67, 133.37, 132.87, 84.18, 25.25, 21.47.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.68.[4]

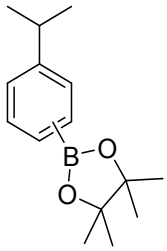
8b 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-p-xylene.



In an argon filled glove box, [Rh(PMe_3)$_2$(CO)Cl] 2.0% (8.0 mg, 0.025 mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalents of *p*-xylene (5.0 mmol,

0.62 mL). The reaction vessel is sealed and irradiated with light for 10h. After exposure to air the reaction mixture was stirred for 5 minutes. There was a no conversion of starting material.

9b (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cumene.



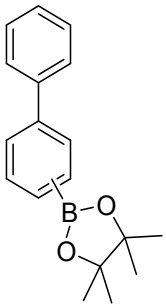
In an argon filled glove box, $[Rh(PMe_3)_2(CO)Cl]$ 2.0% (8.0 mg, 0.025 mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalents of cumene (5.0 mmol, 0.7 mL). The reaction vessel is sealed and irradiated with light for 10h. After exposure to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (20:1). The product is obtained as a white solid in 71% yield based on HBPin. The *meta*:*para* ratio was determined to be 0.7:0.3 by integration of the characteristic peaks in ^1H NMR.

^1H NMR (300 MHz, $CDCl_3$) δ (*meta* isomer) 7.60 (s, 1H), 7.5 (d, J = 7.2, 1H), 7.22 – 7.15 (m, 2H), 2.93 – 2.78 (m, 1H), 1.28 (s, 12H), 1.20 (d, J = 7.0, 6H), (*para* isomer) 7.69 (d, J = 8.1 Hz, 1H), 7.25 (dd, J = 8.4 Hz, 2H), 2.93 – 2.78 (m, 1H), 1.27 (s, 12H), 1.18 (d, J = 6.9 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (*meta* isomer) 148.14, 133.00, 132.49, 129.43, 127.89, 83.76, 34.25, 24.88, 24.14, (*par*a isomer) 152.39, 135.07, 128.28, 126.72, 126.00, 83.67, 34.45, 24.92, 23.96.

^{11}B NMR (96 MHz, $CDCl_3$) δ 31.06. ^1H and ^{13}C NMR data agree with previously reported data.[8]

10b (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl.



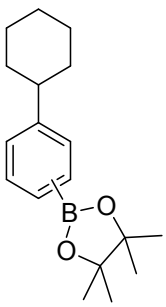
In an argon filled glove box, [Rh(PMe$_3$)$_2$(CO)Cl] 0.5% (2.0 mg, 0.0062 mmol), 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalents of biphenyl (5.0 mmol, 0.78 g) were dissolved in 1 mL of THF. The reaction vessel is sealed and irradiated with light for 12h. After exposure to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (20:1). The product is obtained as a white solid in 69% yield based on HBPin. The *meta*:*para* ratio was determined to be 0.7:0.3 by integration of the characteristic peaks in ^{1}H NMR.

^{1}H NMR (300 MHz, CD_2Cl_2) δ (*meta* isomer) 8.05 (s, 1H), 7.77 (ddd, J = 7.3, 1.2, 1.2 Hz, 1H), 7.72 (dd, J = 7.8, 1.2 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.51 – 7.42 (m, 3H), 7.41 – 7.32 (m, 1H), 1.37 (s, 12H), (*para* isomer) 7.86 (d, J = 8.3 Hz, 2H), 7.69 – 7.61 (m, 4H), 7.51 – 7.43 (m, 2H), 7.41 – 7.33 (m, 1H), 1.37 (s, 12H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ(*meta* and *para* isomer) 144.22, 141.59, 141.39, 140.95, 135.72, 134.11, 133.86, 130.40, 129.36, 129.29, 128.75, 128.18, 127.82, 127.65, 126.89, 84.45, 84.39, 25.28.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.87. ^{1}H and ^{13}C NMR data of the para isomer agree with previously reported data. [9]

11b (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenylcyclohexane.



In an argon filled glove box, $[Rh(PMe_3)_2(CO)Cl]$ 2.0% (8.0 mg, 0.025 mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalents of phenylcyclohexane (5.0 mmol, 0.85 mL). The reaction vessel is sealed and irradiated with light for 12h. After exposure to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (15:1). The product is obtained as a white solid in 71% yield based on HBPin. The *meta*:*para* ratio was determined to be 0.7:0.3 by integration of the characteristic peaks in ^1H NMR. The NMR signals are described for the mixture of *meta* and *para* isomers due to their complexity, highlighting the distinguishable peaks.

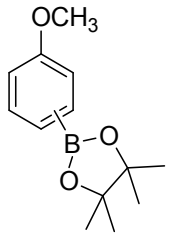
^1H NMR (300 MHz, CD_2Cl_2) δ (*meta* and *para* isomer) 7.67 (d, J = 8.0 Hz, 2H, *para* isomer), 7.58 (s, 1H, *meta* isomer), 7.54 – 7.57 (m, 1H, *meta* isomer), 7.24 – 7.19 (m, 2H, *meta* isomer), 7.14(d, J = 8.0 Hz, 2H, *para* isomer), 2.48 – 2.38 (m, 2H), 1.71 – 1.83 (m, 8H), 1.70 – 1.61 (m, 2H), 1.45 – 1.29 (m, 12H), 1.26 (s, 12H, *meta* isomer), 1.25 (s, 12H, *para* isomer), 1.23 – 1.09 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (*meta* and *para* isomer) 151.59, 147.38, 135.02, 133.44, 132.46, 129.88, 127.85, 126.45, 83.75, 83.68, 44.97, 44.74, 34.53, 34.37, 27.06, 26.97, 26.26, 24.98, 24.96.

^{11}B NMR (96 MHz, $CDCl_3$) δ 31.06.

HRMS (ESI): Calcd. for $C_{18}H_{28}BO_2$ $[M+H]^+$: 287.21802; Found: 287.21781.

12b (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)anisole.



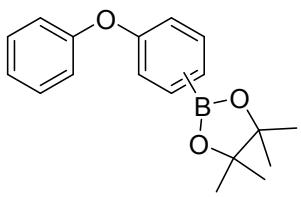
In an argon filled glove box, $[Rh(PMe_3)_2(CO)Cl]$ 2.0% (8.0 mg, 0.025 mmol) was dissolved in 1.0 equivalent of B_2Pin_2 (0.65 mmol, 165 mg) and 4.0 equivalents of anisole (5.0 mmol, 0.54 mL). The reaction vessel is sealed and irradiated with light for 8h. After exposure to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (20:1). The product is obtained as a colourless liquid with 52% yield based on HBPin.

The *meta*:*para* ratio was determined to be 0.6:0.4 by integration of the characteristic peaks in ^{1}H NMR.

^{1}H NMR (300 MHz, CD_2Cl_2) δ (*meta* isomer) 7.36-7.26 (m, 3H), 7.00 (ddd, J = 7.9, 2.8, 1.4 Hz, 1H), 3.82 (s, 3H), 1.34 (s, 12H), (*para* isomer) 7.70 (d, J = 8.7 Hz, 1H), 6.90 (d, J = 8.7 Hz, 1H), 3.82 (s, 6H), 1.32 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (*meta* isomer) 159.71, 129.45, 127.49, 119.41, 117.99, 84.39, 55.70, 25.24, (*para* isomer) 162.80, 136.91, 113.82, 84.09, 55.60, 25.24.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.44. ^{1}H and ^{13}C NMR data agree with previously reported data.[4]

13b (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)diphenylether



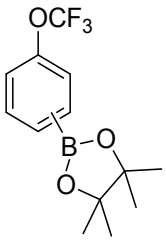
In an argon filled glove box, [Rh(PMe$_3$)$_2$(CO)Cl] 2.0% (8.0 mg, 0.025 mmol) was dissolved in 1.0 equivalent of B_2Pin_2 (0.65 mmol, 165 mg) and 3.0 equivalent of diphenyl ether (3.75 mmol, 0.64 g). The reaction vessel is sealed and irradiated with light for 10h. After exposure to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (20:1). The product is obtained as a colourless liquid with 63% yield based on HBPin. The *meta*:*para* ratio was determined to be 0.7:0.3 by integration of the characteristic peaks in ^{1}H NMR. The NMR signals are described for the mixture of *meta* and *para* isomers due to their complexity, highlighting the distinguishable peaks.

^{1}H NMR (300 MHz, CD_2Cl_2) δ (*meta* and *para* isomer)7.75 (d, J = 8.4 Hz, 2H, *para* isomer), 7.54 (d, J = 7.3Hz, 1H, *meta* isomer), 7.43 – 7.32 (m, 8H), 7.19 – 7.09 (m, 3H), 7.07 – 6.97 (m, 4H), 1.34 (s, 12H, *para* isomer), 1.33 (s, 12H, *meta* isomer).

^{13}C NMR (75 MHz, CD_2Cl_2) δ (*meta* and *para* isomer) 160.79, 158.09, 157.83, 157.26, 157.02, 137.06, 130.40, 130.31, 130.18, 129.86, 125.21, 124.33, 123.79, 123.65, 122.63, 120.08, 119.37, 119.22, 118.04, 84.52, 84.29, 25.22.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.44. ^{1}H and ^{13}C NMR data of the para isomer agree with previously reported data.[12]

14b 4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)(trifluoromethoxy)benzene.

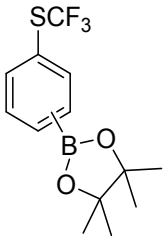


In an argon filled glove box, [Rh(PMe_3)$_2$(CO)Cl]] 0.5% (2.0 mg, 0.0062mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalent of (trifluoromethoxy)benzene (5.0 mmol, 0.67 mL). The reaction vessel is sealed and irradiated with light for 8h. After exposure to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (20:1). The product is obtained as a colourless liquid with 78% yield based on HBPin. The *meta*:*para* ratio was determined to be 0.8:0.2 by integration of the characteristic peaks in ^{1}H NMR.

^{1}H NMR (300 MHz, $CDCl_3$) δ (meta isomer) 7.64 (d, J = 7.2 Hz, 1H), 7.56 (s, 1H), 7.30 (dd, J = 8.1, 8.1 Hz, 1H), 7.20 (dd, J = 8.2, 2.5 Hz, 1H), 1.25 (s, 12H), (para isomer) 7.75 (d, J = 8.6 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 1.25 (s, 12H).

^{11}B NMR (96 MHz, $CDCl_3$) δ 31.37. HRMS (ESI): Calcd. for $C_{13}H_{16}BF_3O_3$ $[M+H]^+$: 287.11202; Found: 287.11781.

15b (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)(trifluoromethylsulfane)benzene.



In an argon filled glove box, [Rh(PMe_3)$_2$(CO)Cl]] 0.5% (2.0 mg, 0.0062mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalent of (trifluoromethylsulfane)benzene (5.0 mmol, 0.72 mL). The reaction vessel is sealed and irradiated with light for 8h. After exposure to air the reaction mixture was stirred for 5

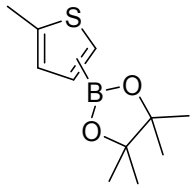
minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (20:1). The product is obtained as a colourless liquid with 75% yield based on HBPin. The *meta*:*para* ratio was determined to be 0.7:0.3 by integration of the characteristic peaks in ^{1}H NMR.

^{1}H NMR (300 MHz, $CDCl_3$) δ (*meta* isomer) 8.00 (s, 1H), 7.83 (ddd, J = 7.4, 1.2, 1.2 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.34 (dd, J = 7.7, 7.7 Hz, 1H), 1.27 (s, 12H), (*para* isomer) 7.77 (d, J = 8.2 Hz, 1H), 7.56 (d, J = 7.9 Hz, 1H), 1.27 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (*meta* isomer) 142.71, 139.09, 137.22, 129.06, 124.15, 84.38, 25.00, (*para* isomer) 135.7, 135.28, 127.62 84.38, 25.00.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.57. ^{1}H and ^{13}C NMR data agree with previously reported data.[4]

16b (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)(methyl)thiophene.



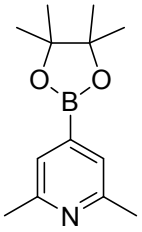
In an argon filled glove box, [$Rh(PMe_3)_2(CO)Cl$]] 0.5% (2.0 mg, 0.0062mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalent of 2-methylthiophene (5.0 mmol, 0.5 mL). The reaction vessel is sealed and irradiated with light for 8h. After exposure to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the product was purified by flash chromatography on SiO_2 using heptane:ethyl acetate (20:1). The product is obtained as a colourless liquid with 69% yield based on HBPin. The C3:C5 ratio was determined to be 0.5:0.5 by integration of the characteristic peaks in ^{1}H NMR.

^{1}H NMR (300 MHz, CD_2Cl_2) δ (2- tetramethyldioxaborolan 5-methyl isomer) 7.45 (d, J = 3.4 Hz, 1H), 6.84 (d, J = 3.4 Hz, 1H), 2.53 (s, 3H), 1.33 (s, 12H), (3- tetramethyldioxaborolan 2-methyl isomer) 7.21 (d, J = 5.1 Hz, 1H), 7.03 (d, J = 5.2 Hz, 1H), 2.69 (s, 3H), 1.32 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (2- tetramethyldioxaborolan 5-methyl isomer) 147.66, 137.77, 127.13, 84.01, 24.88, 15.52, (3- tetramethyldioxaborolan 2-methyl isomer) 133.21, 122.05, 83.32, 25.03, 15.77.

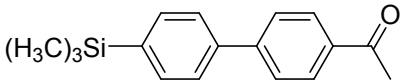
^{11}B NMR (96 MHz, $CDCl_3$) δ 28.98. ^{1}H and ^{13}C NMR data agree with previously reported data.[4]

17b 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-p-xylene.



In an argon filled glove box, [$Rh(PMe_3)_2(CO)Cl$]] 1.0% (4.0 mg, 0.0125 mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalent of of 2,6 lutidine (7.5 mmol, 0.9 mL). The reaction vessel is sealed and irradiated with light for 10h. After exposure to air the reaction mixture was stirred for 5 minutes. There was a no conversion of starting material.

18b 1-[4'-(Trimethylsilyl)biphenyl-4-yl]ethanone

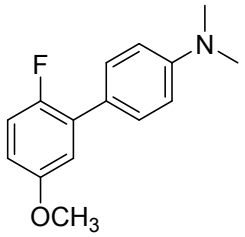


In an argon filled glove box, [$Rh(PMe_3)_2(CO)Cl$]] 0.5% (2.0 mg, 0.0062mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalent of phenyltrimethylsilane (5.0mmol, 0.86 mL). The reaction vessel is sealed and irradiated with light for 12h. After cooling, the catalyst $Pd(PPh_3)_4$ 5.0% (0.0625 mmol, 72 mg), 1.0 equivalent of 4-bromoacetophene (1.25 mmol, 249 mg) and 2.0 equivalent of sodium carbonate (2.5 mmol, 265 mg,) with respect to HBpin were added under argon atmosphere. Then, the reaction mixture was dissolved in dioxane/ethanol/water (5:4:1 ratio) and the reaction vessel was sealed and heated upto 110 ^{o}C in oil bath with stirring for 20 hours. Next, it was cooled to room temperature and filtered through a short plug of silica gel using heptane:Ethylacetate = 1:1 as eluants. After removing all the solvent under reduced pressure, the product was crystalised in ether:heptane and obtained as white crystals with 42% yield based on HBPin. The 1-tetramethyldioxaborolan-1-phenyl:1-tetramethyldioxaborolan-2-phenyl ratio was determined to be 0.9:0.1 by integration of the characteristic peaks in ^{1}H NMR.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.02 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.9 Hz, 2H), 7.63 – 7.65 (m, 4H), 2.61 (s, 3H), 0.31 (s, 9H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 197.91, 146.00, 141.23, 140.58, 136.56, 134.52, 129.35, 127.64, 126.96, 27.07, -0.95. ^{1}H and ^{13}C NMR data of the para isomer agree with previously reported data.[17]

19b 2'-Fluoro-5'-methoxy-N,N-dimethyl-[1,1'-biphenyl]-4-amine



In an argon filled glove box, $[Rh(PMe_3)_2(CO)Cl]$] 0.5% (2.0 mg, 0.0062mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) 6.0 equivalent of 4-fluoroanisole (7.5mmol, 0.85 mL). The reaction vessel is sealed and irradiated with light for 12h. After cooling, the catalyst $Pd(PPh_3)_4$ 5.0% (0.0625 mmol, 72 mg), 1.0 equivalent of 4-bromo-N,N-dimethylaniline (1.25 mmol, 250 mg) and 2.0 equivalent of sodium carbonate (2.5 mmol, 265 mg,) with respect to HBpin were added under argon atmosphere. Then, the reaction mixture was dissolved in dioxane/ethanol/water (5:4:1 ratio) and the reaction vessel was sealed and heated upto 110 ^{o}C in oil bath with stirring for 20 hours. Next, it was cooled to room temperature and filtered through a short plug of silica gel using diethylether as eluant. After removing all the solvent under reduced pressure, the product was the product was purified by flash chromatography on SiO_2 using pentane:diethylether (10:1) and obtained as yellowish liquid with 62% yield based on HBPin.

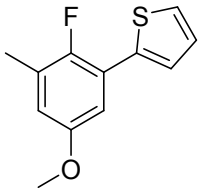
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.44 (dd,J = 9.0, 1.8 Hz, 1H), 7.04 (dd, J = 10.4, 8.9 Hz, 1H), 6.94 (dd, J = 6.5, 3.2 Hz, 1H), 6.79 (d, J = 9.0 Hz, 1H), 6.76 – 6.72 (m, 1H), 3.81 (s, 3H), 2.99 (s, 6H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ156.42 (d, J = 1.9 Hz), 156.35, 150.79, 132.06 (d, J = 230.2 Hz), 130.06 (d, J = 3.5 Hz), 123.80 (d, J = 1.2 Hz), 116.83 (d, J = 25.2 Hz), 115.36 (d, J = 3.8 Hz), 112.92 (d, J = 8.2 Hz), 112.66 , 56.25 , 40.76.

^{19}F NMR (CD_2Cl_2, 282 MHz) δ -129.52.

HRMS (ESI): Calcd. for $C_{15}H_{16}FNO$ $[M+H]^+$: 246.12887; Found: 246.12876.

20b 2-(5-Fluoro-2-methoxy-3-methylphenyl)thiophene



In an argon filled glove box, $[Rh(PMe_3)_2(CO)Cl]$] 1.0% (4.0 mg, 0.0125 mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) 4.0 equivalent of 4-fluoro-3-methylanisole (5.0 mmol, 0.65 mL). The reaction vessel is sealed and irradiated with light for 12h. After cooling, the catalyst $Pd(PPh_3)_4$ 5.0% (0.0625 mmol, 72 mg), 1.0 equivalent of 2-bromothiophene (1.25 mmol, 120 μL) and 2.0 equivalent of sodium carbonate (2.5 mmol, 265 mg,) with respect to HBpin were added under argon atmosphere. Then, the reaction mixture was dissolved in dioxane/ethanol/water (5:4:1 ratio) and the reaction vessel was sealed and heated upto 110 ^oC in oil bath with stirring for 20 hours. Next, it was cooled to room temperature and filtered through a short plug of silica gel using diethylether as eluant. After removing all the solvent under reduced pressure, the product was the product was purified by flash chromatography on SiO_2 using pentane:diethylether (10:1) and obtained as yellowish liquid with 63% yield based on HBPin.

^1H NMR (300 MHz, CD_2Cl_2) δ 7.47 (ddd, J = 3.6, 1.1, 1.1 Hz, 1H), 7.39 (dd, J = 5.2, 1.2 Hz, 1H), 7.12 (ddd, J = 5.0, 3.6, 1.1 Hz, 1H), 6.97 (dd, J = 5.7, 3.1 Hz, 1H), 6.68 (ddd, J = 5.8, 3.3, 0.8 Hz, 1H), 3.80 (s, 3H), 2.31 (d, J = 2.4 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 155.62 (d, J = 2.3 Hz), 152.51 (d, J = 240.9 Hz), 137.76 (d, J = 3.3 Hz), 127.89, 127.05 (d, J = 19.6 Hz), 126.66 (d, J = 6.1 Hz), 126.15 (d, J = 4.4 Hz), 122.35 (d, J = 15.3 Hz), 115.89 (d, J = 4.6 Hz), 111.01 (d, J = 2.9 Hz), 56.05, 15.21 (d, J = 4.7 Hz).

^{19}F NMR (CD_2Cl_2, 282 MHz) δ -128.63. HRMS (ESI):

Calcd. for $C_{12}H_{11}FOS$ $[M+H]^+$: 223.05874; Found: 223.05853.

Competitive C-H borylation experiments

In an argon filled glove box, $[Rh(PMe_3)_2(CO)Cl]$] 1.0% (4.0 mg, 0.0125 mmol) was dissolved in 1.0 equivalent of HBPin (1.25 mmol, 180 μL) and 4.0 equivalent of benzene (5.0

mmol, 0.45 mL) and 4.0 equivalent of 2,6 lutidine (5.0 mmol, 0.58 mL). The reaction vessel is sealed and irradiated with light for 16h. After exposure to air the reaction mixture was stirred for 5 minutes. The volatiles were then removed under reduced pressure and the only (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene was observed with 71% of yield of the product.

Photocatalytic C-H borylation of benzene with low amount of catalyst loading:

In an argon filled glove box, [$Rh(PMe_3)_2(CO)Cl$]] 0.1% (1.2 mg, 0.0038 mmol) was dissolved in 1.0 equivalent of HBPin (3.8 mmol, 550 μL) and 6.0 equivalent of benzene (22.8 mmol, 2.0 mL) . The reaction vessel is sealed and irradiated with light for 16h. After exposure to air the reaction mixture was stirred for 5 minutes. TON was then determined by GC with respect to mesitylene as an internal standard. Turnover numbers (TON) represented can be expressed as [mmol of product]/[mmol of catalyst] and TOF (turn over frequency) is expressed as (TON/Time in h). TONs reported in this study are averages of at least two runs.

Preparation of [Rh(Cl)(Me_2IMes)(COD)]

This [Rh(Cl)(Me_2IMes)(COD)] was prepared according to the procedure reported in the article.[18]

VI. References

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[2] See: http://www.forensicssource.com/ProductDetail.aspx?ProductName=1090964

[3] See: http://www.laserpoint.eu/product.php?f=2&p=18.

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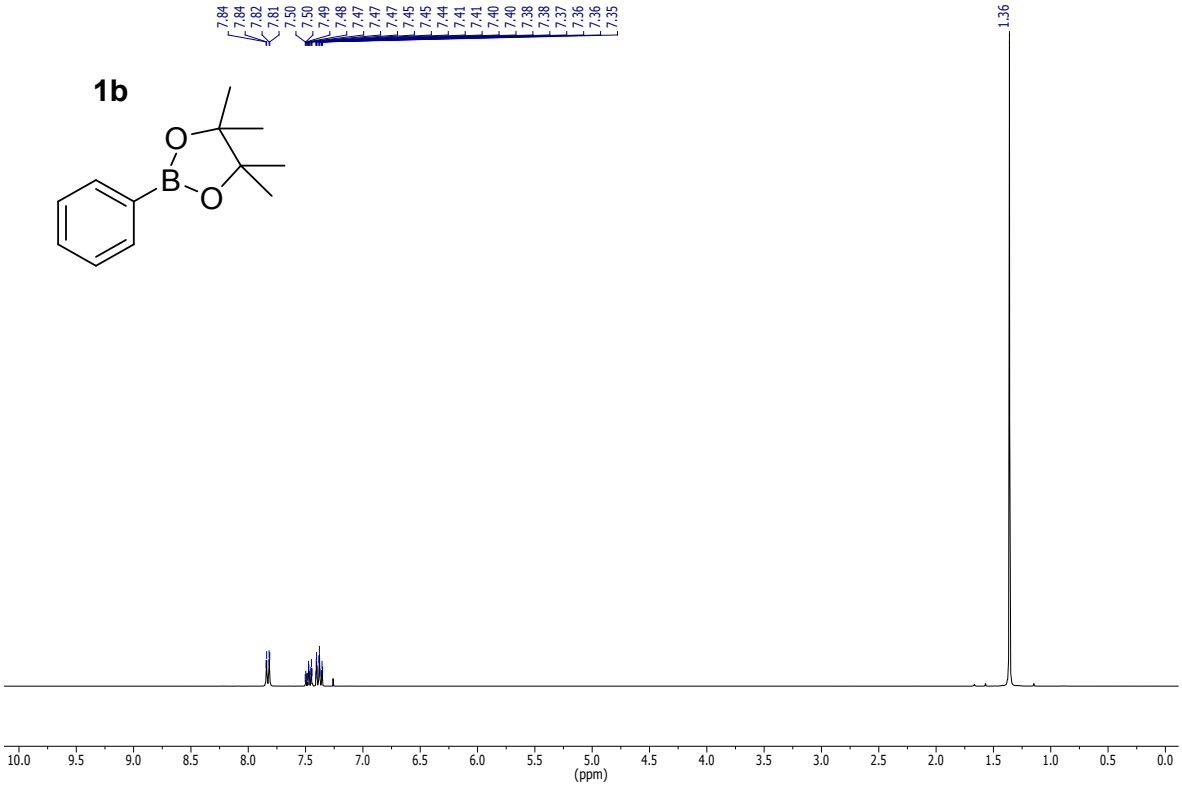
VII. NMR spectra of compounds

^{1}H NMR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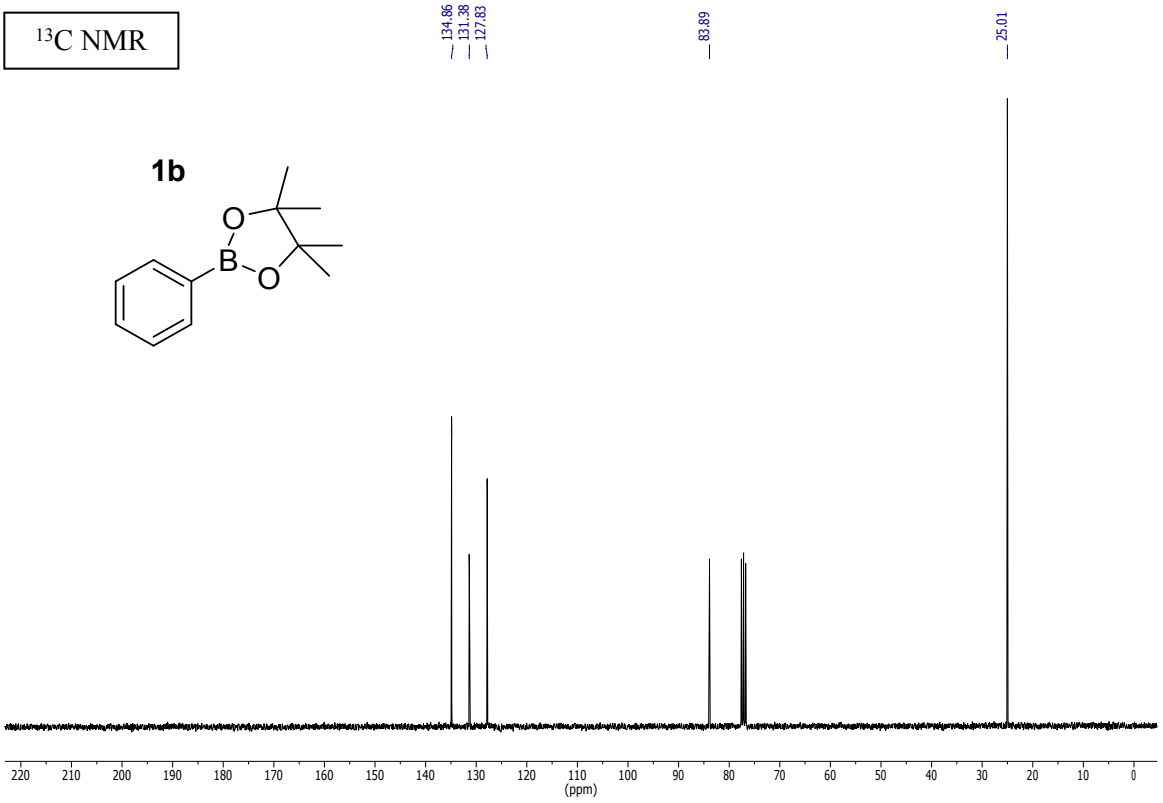
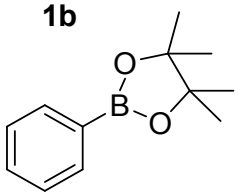
7.40
7.40
7.38
7.37
7.36
7.36
7.35
1.36
1b
O
B
O
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

^{13}C NMR


134.86
131.38
127.83
83.89
25.01
1b
O
B
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

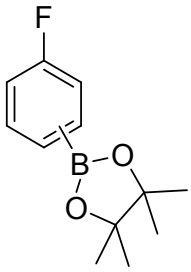
^{11}B NMR

1b

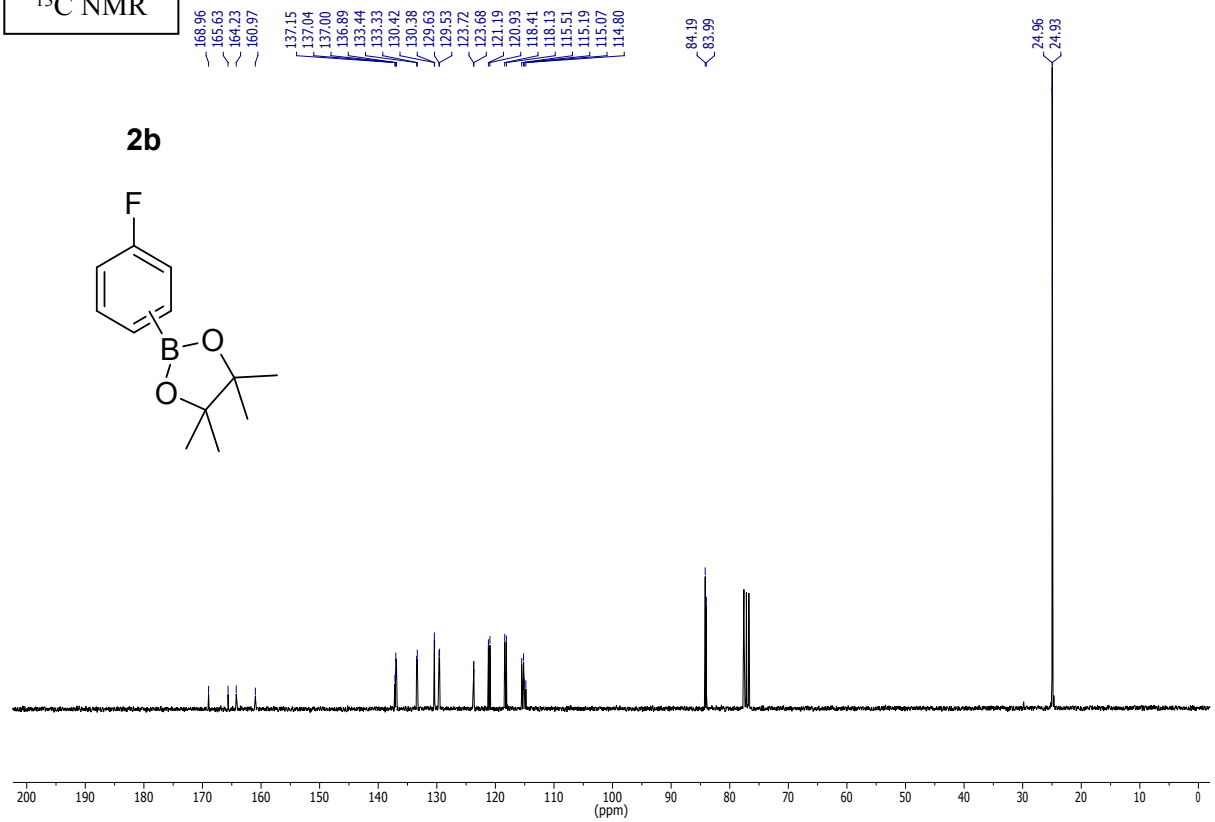


^{1}H NMR

2b

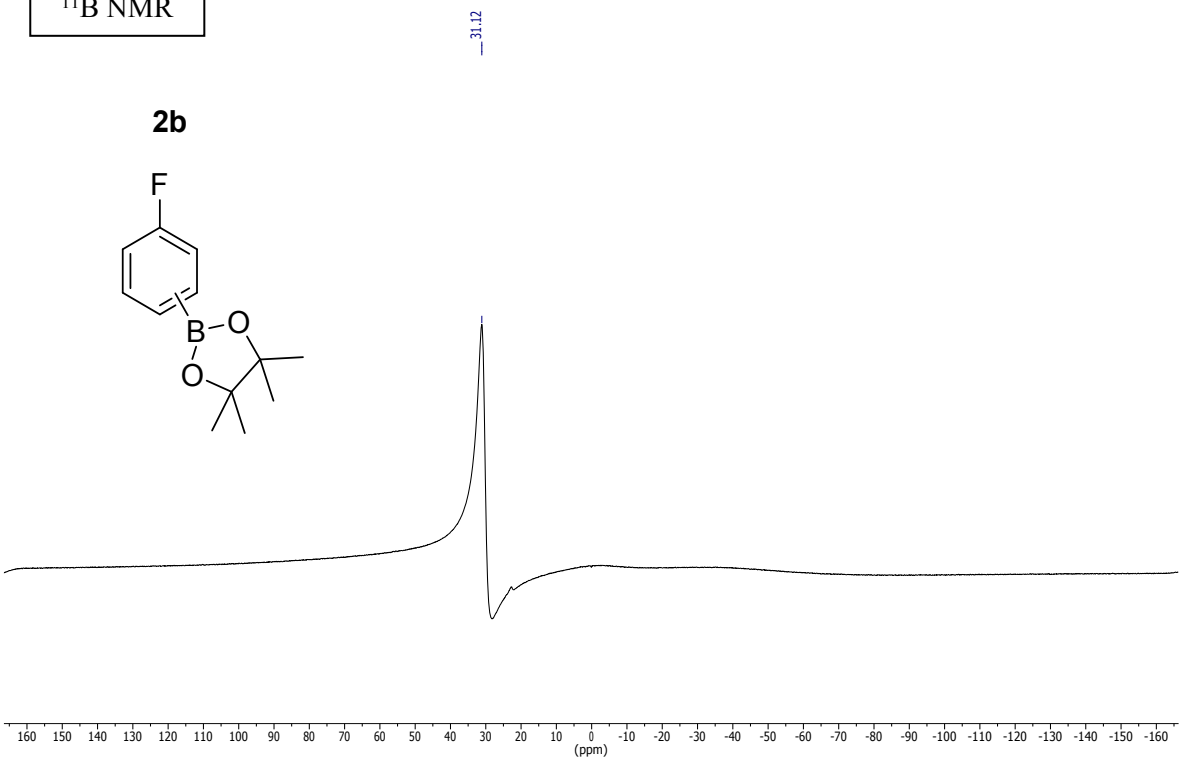


^{13}C NMR



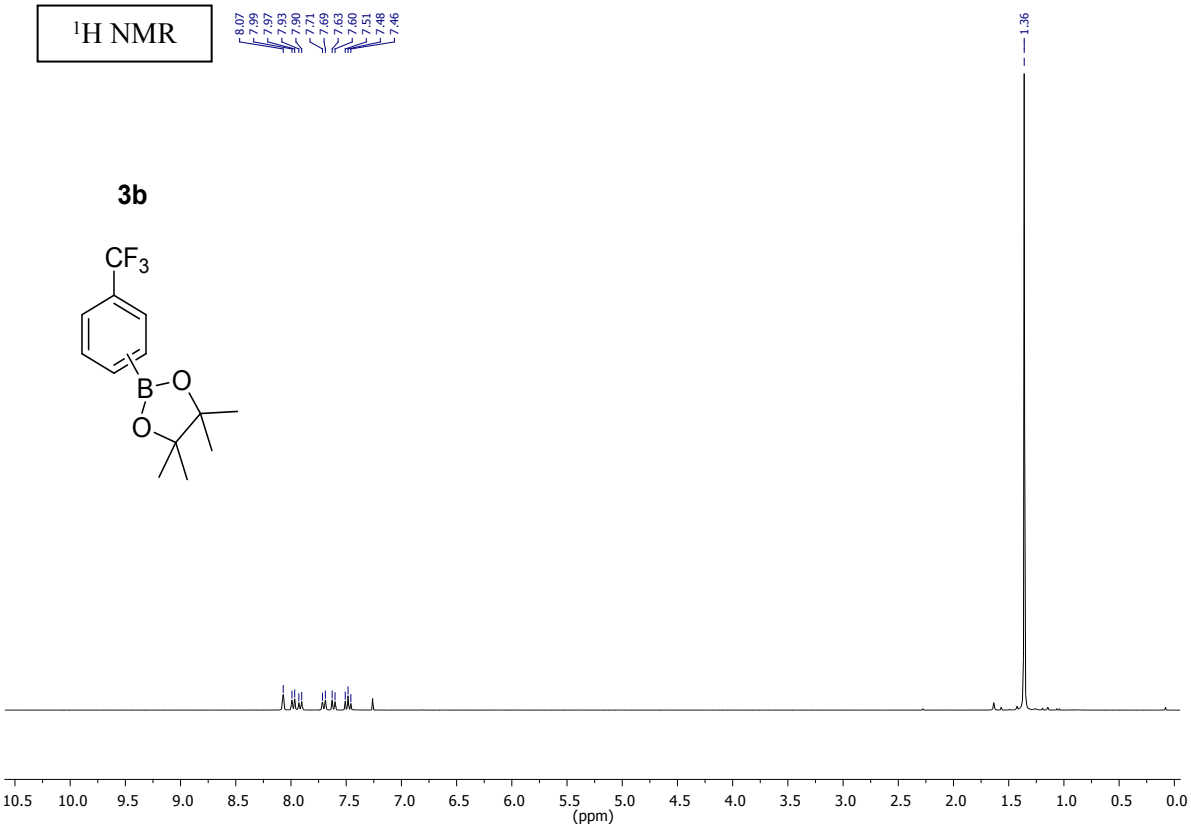
2b

^{11}B NMR

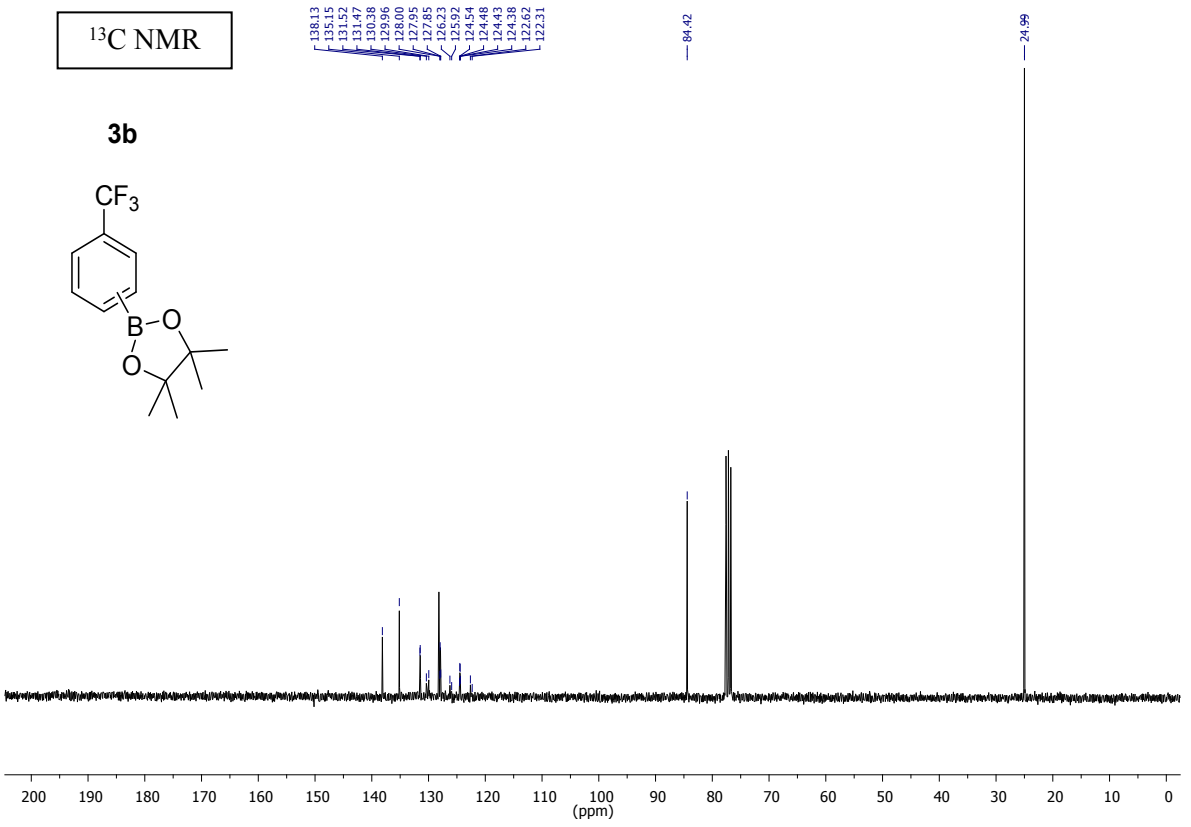


2b

^{1}H NMR

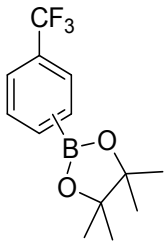


^{13}C NMR



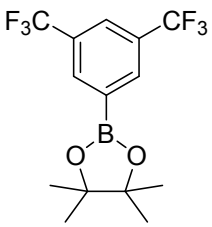
^{11}B NMR

3b

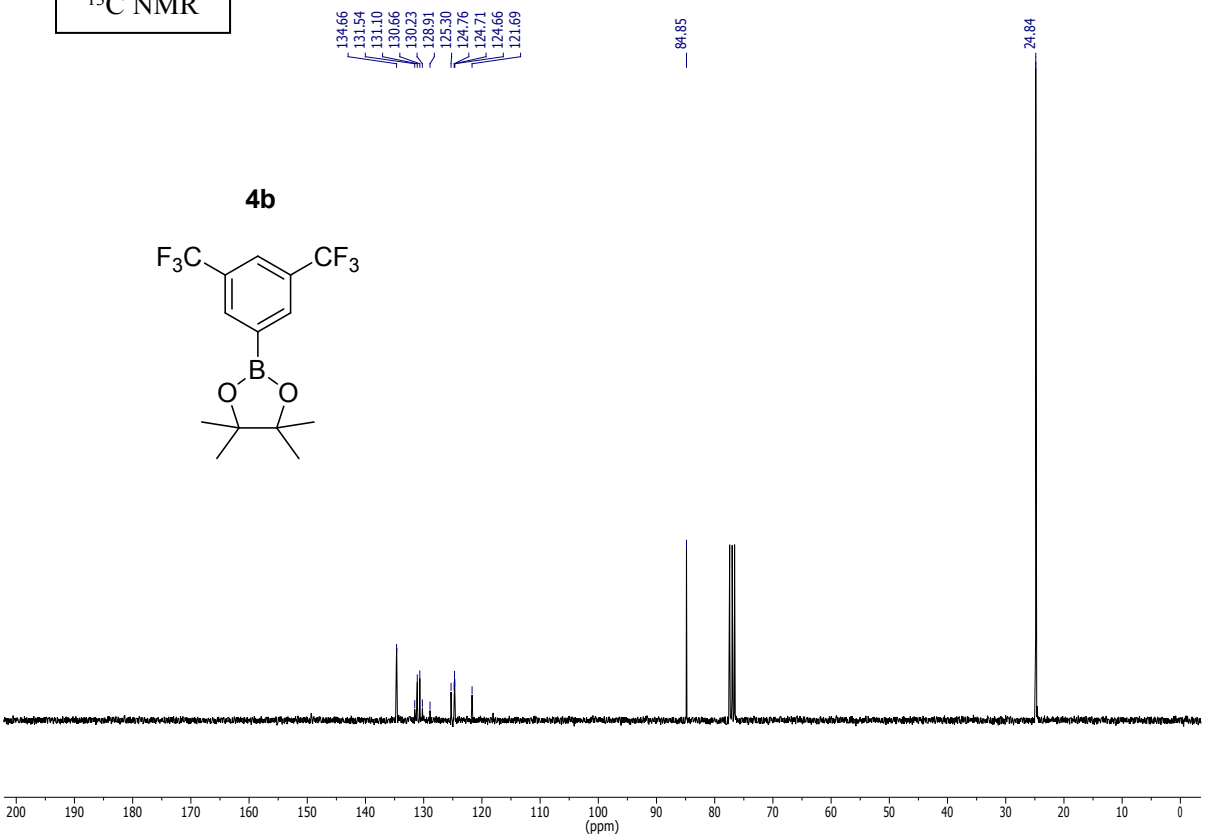


^{1}H NMR

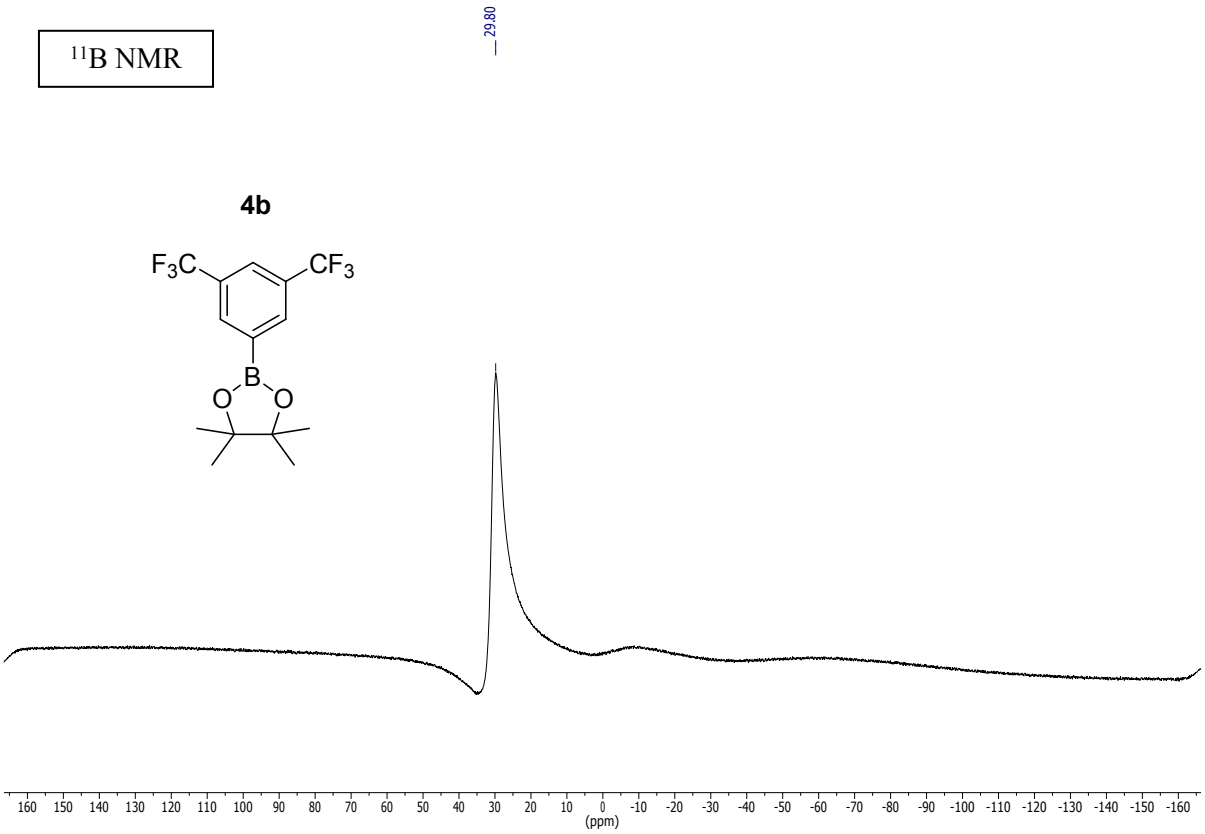
4b



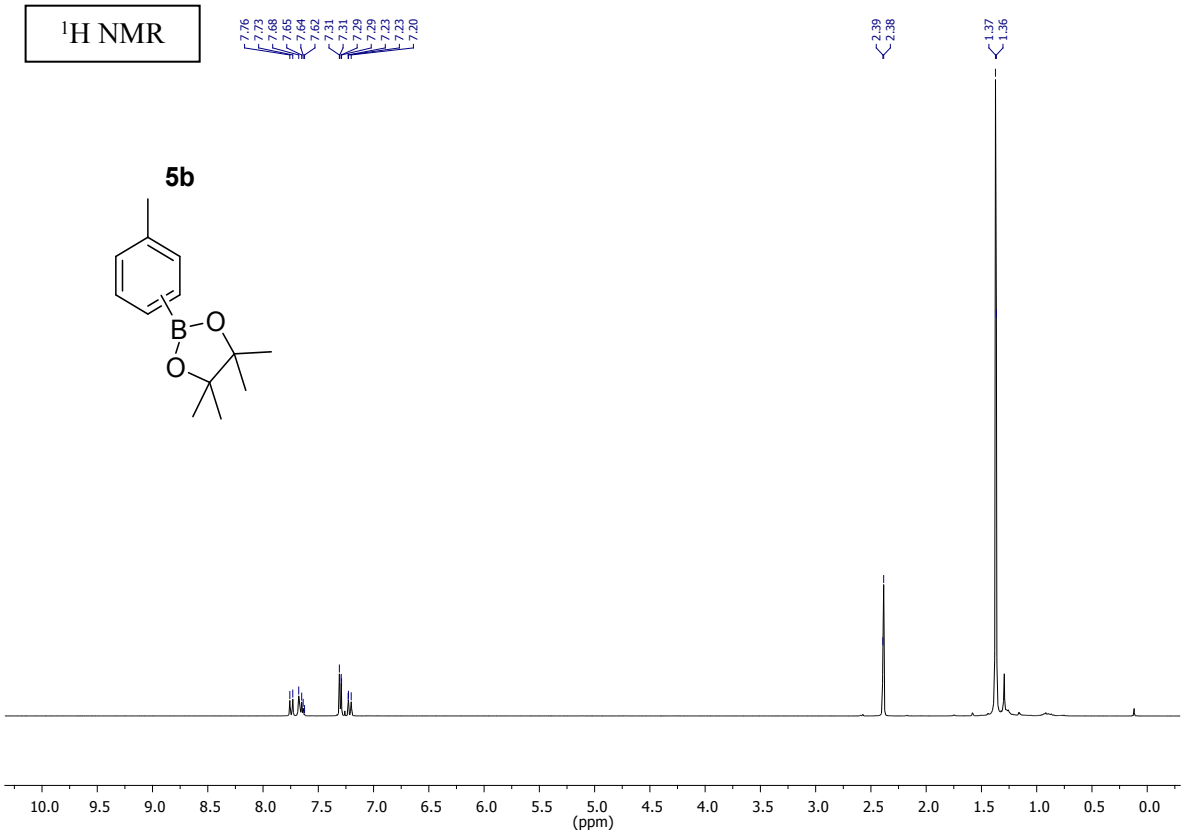
^{13}C NMR



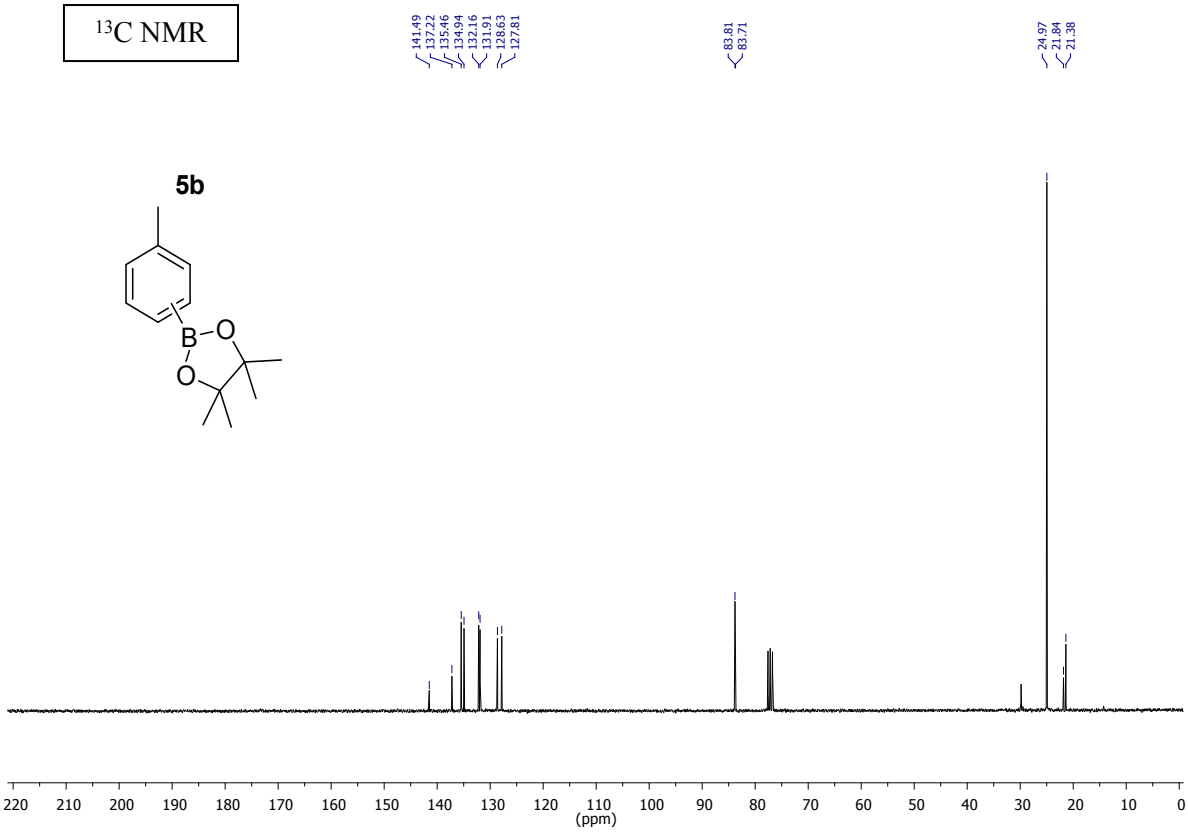
^{11}B NMR



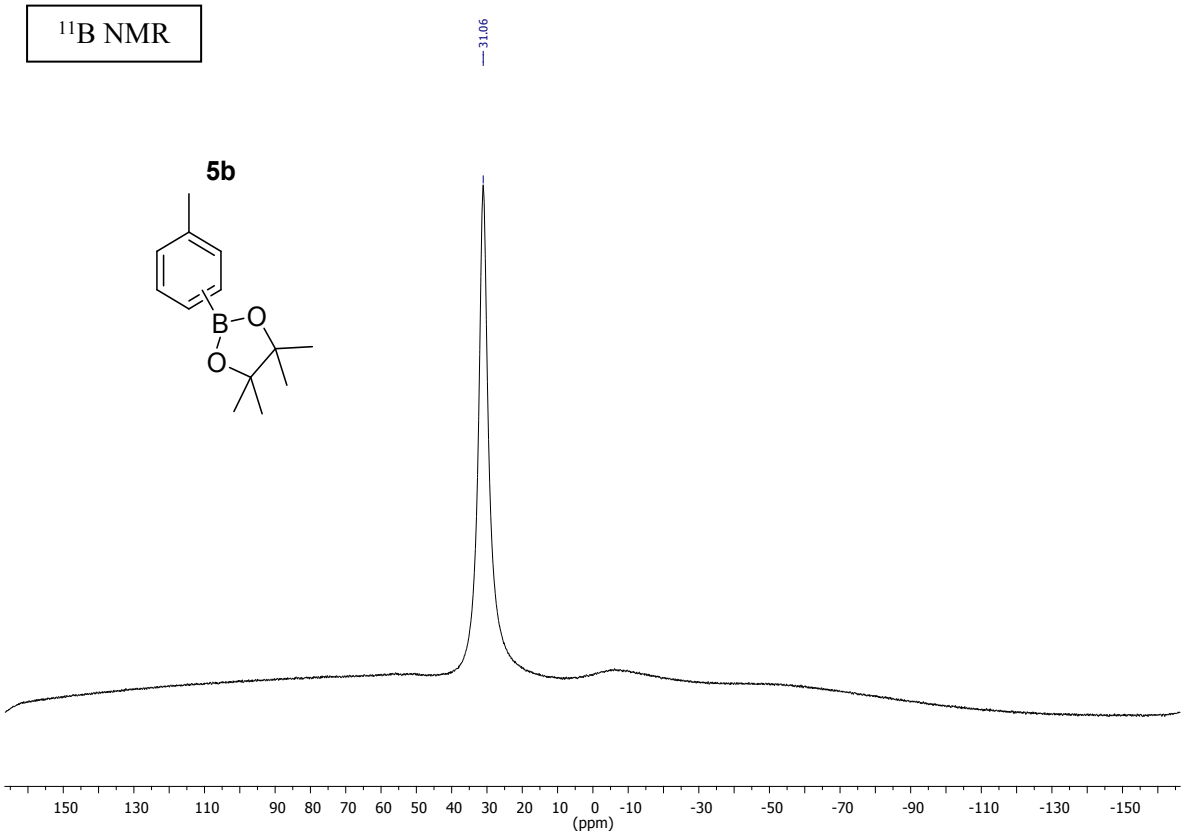
^{1}H NMR



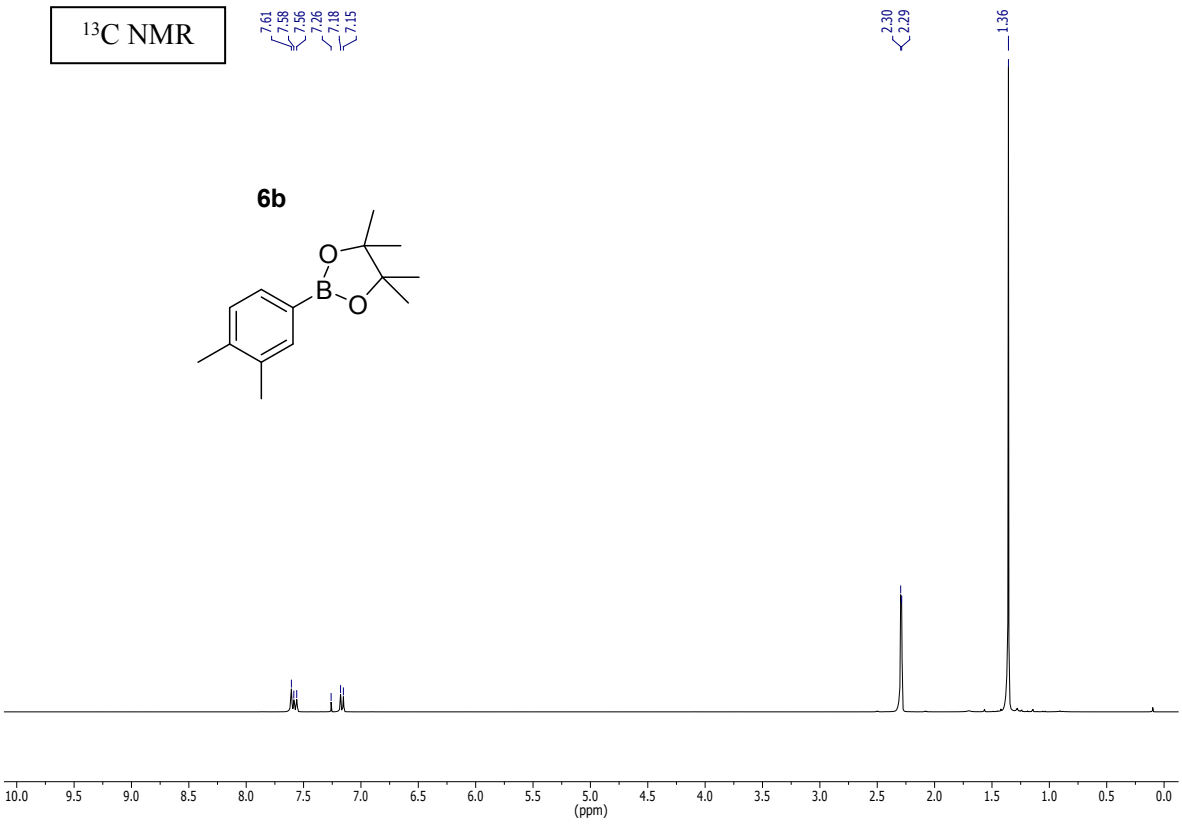
^{13}C NMR



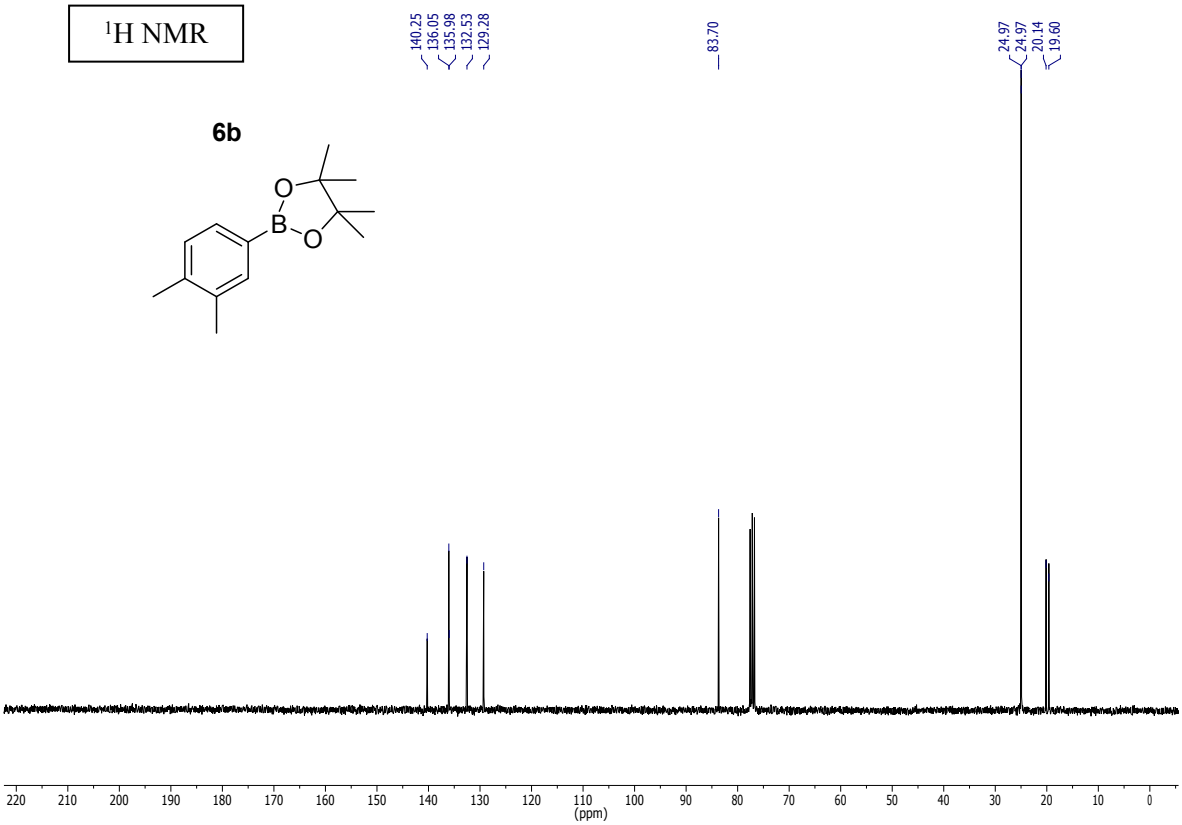
^{11}B NMR



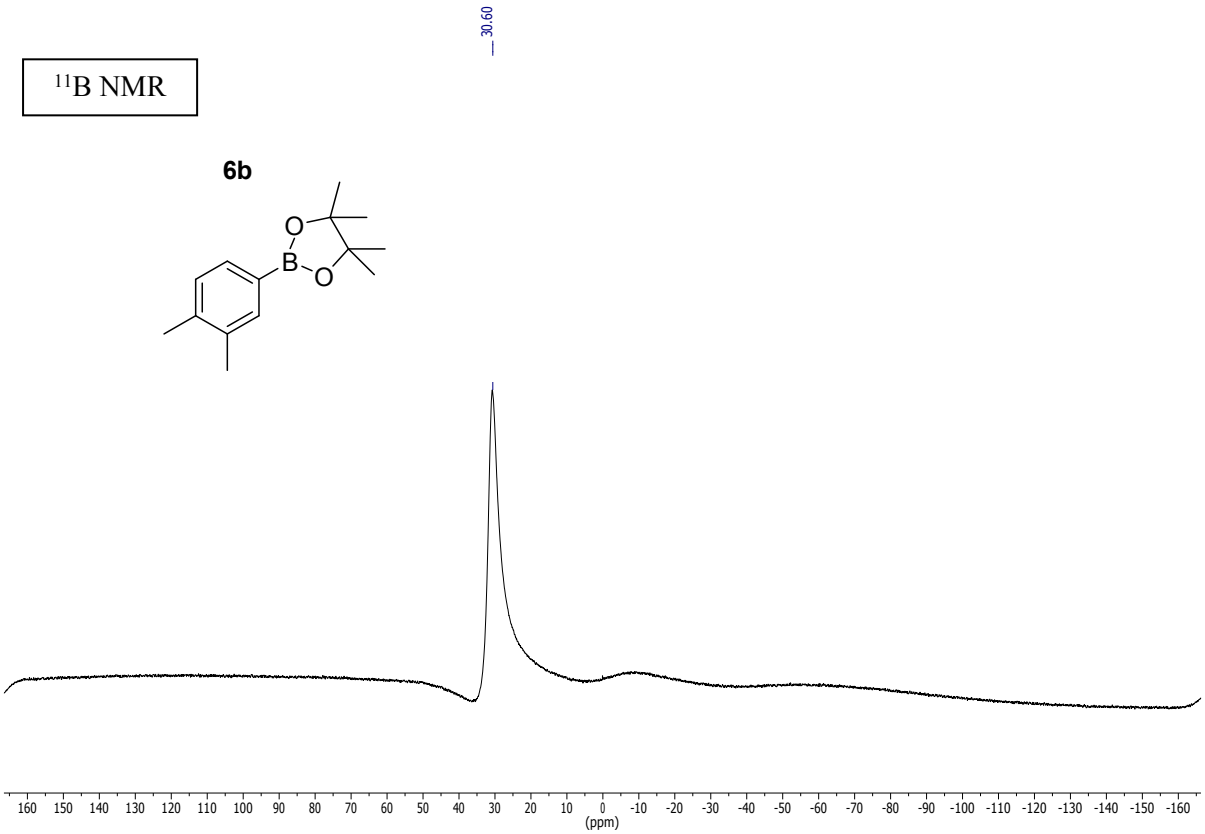
^{13}C NMR



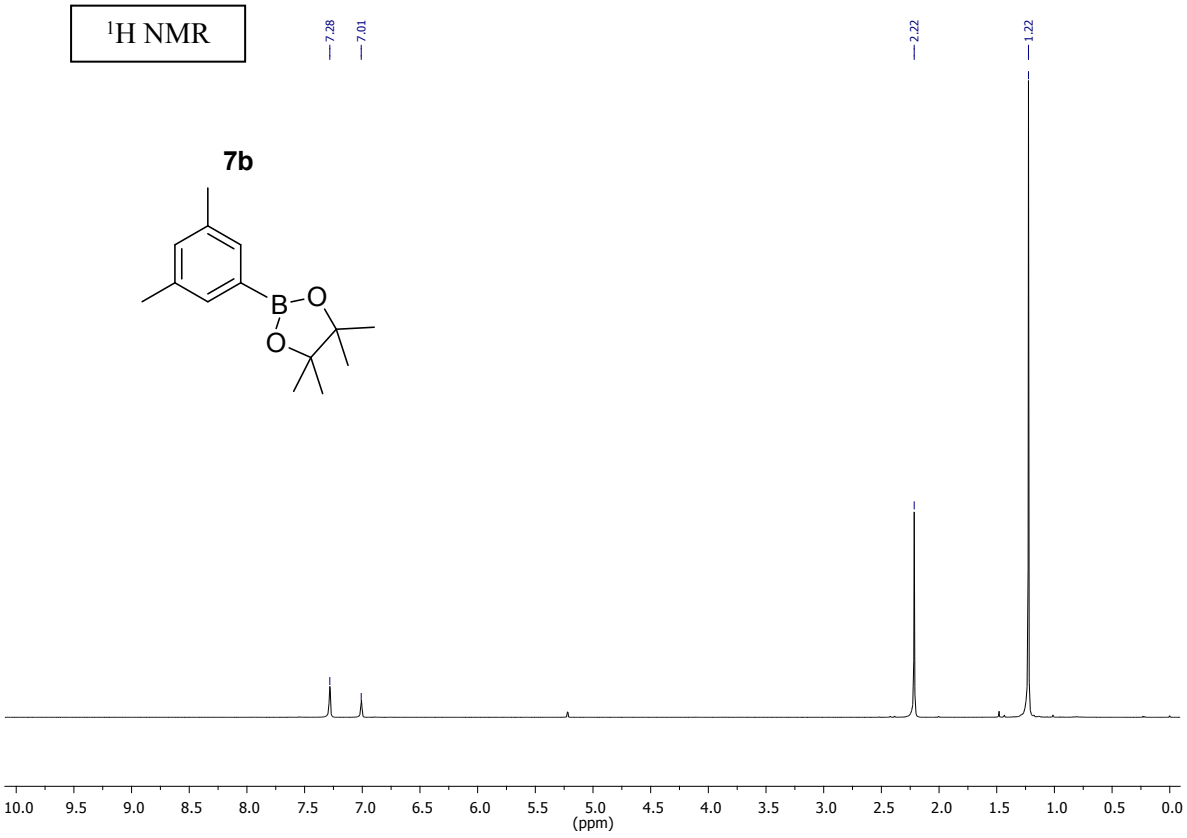
^{1}H NMR



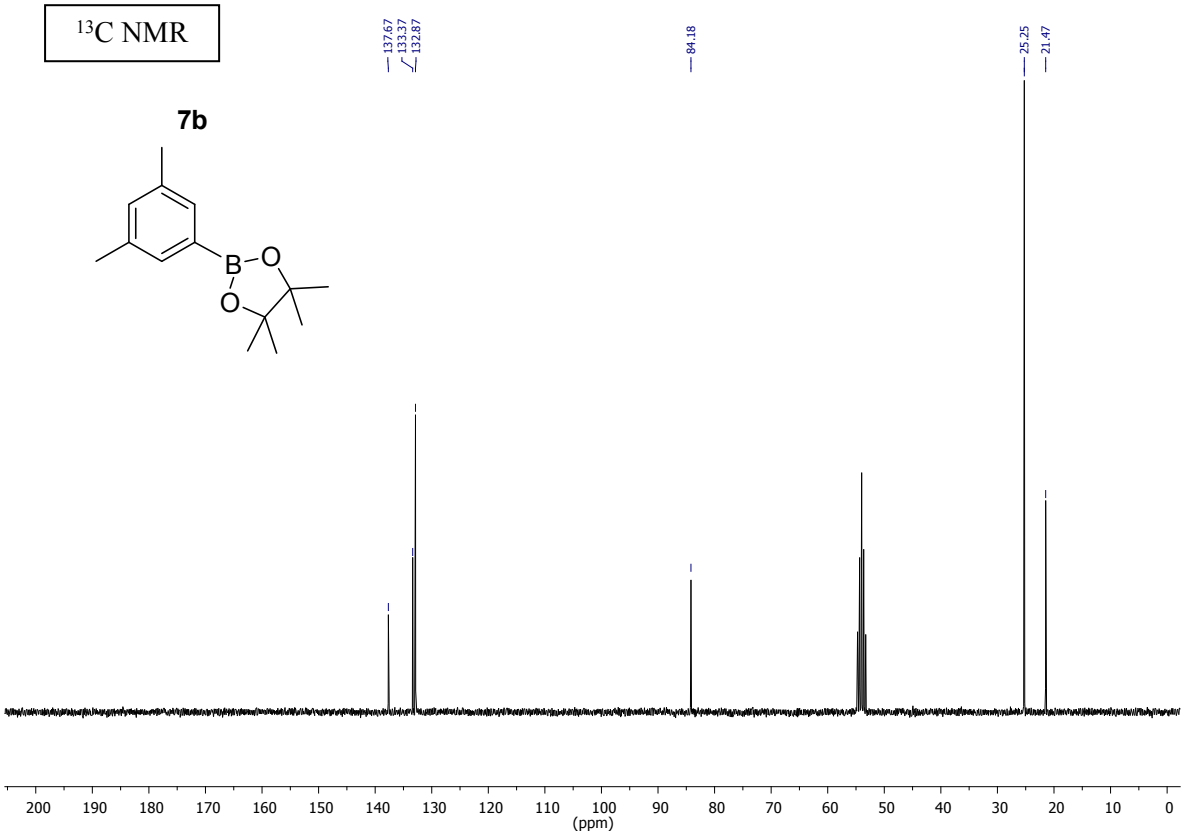
^{11}B NMR



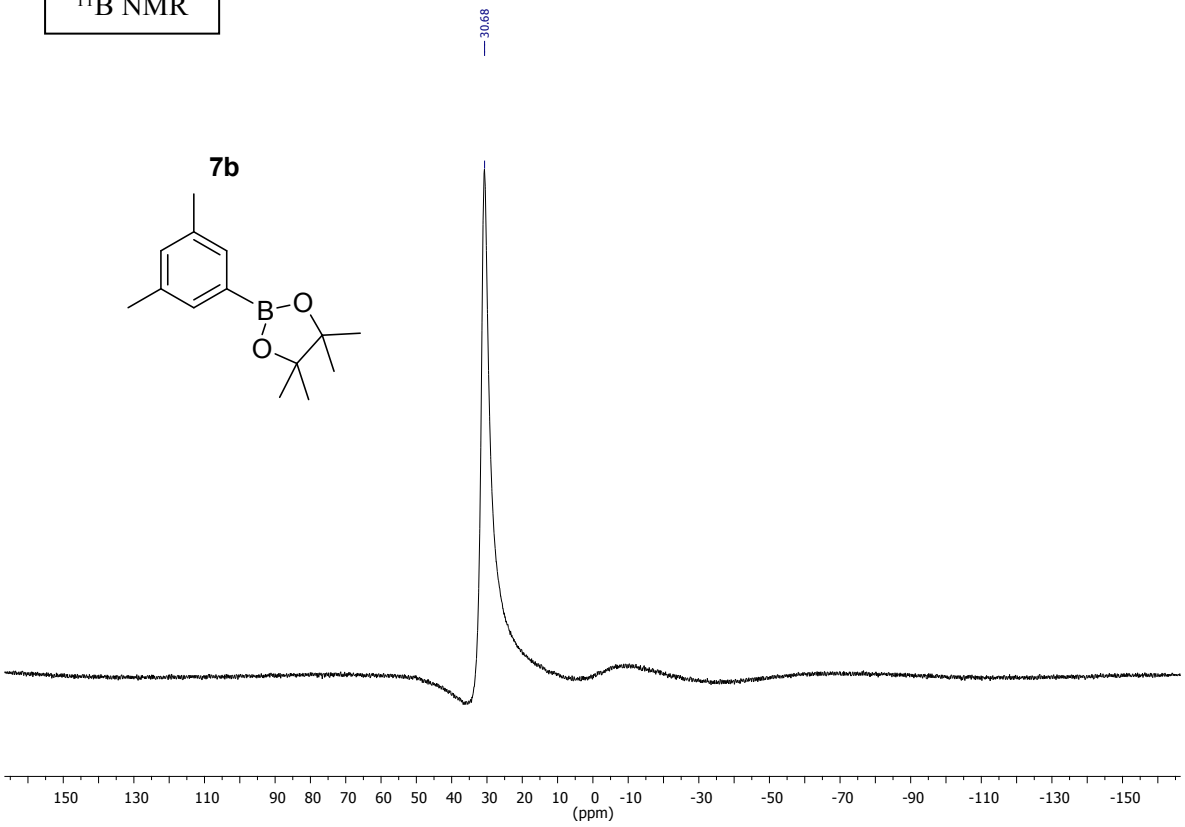
^{1}H NMR



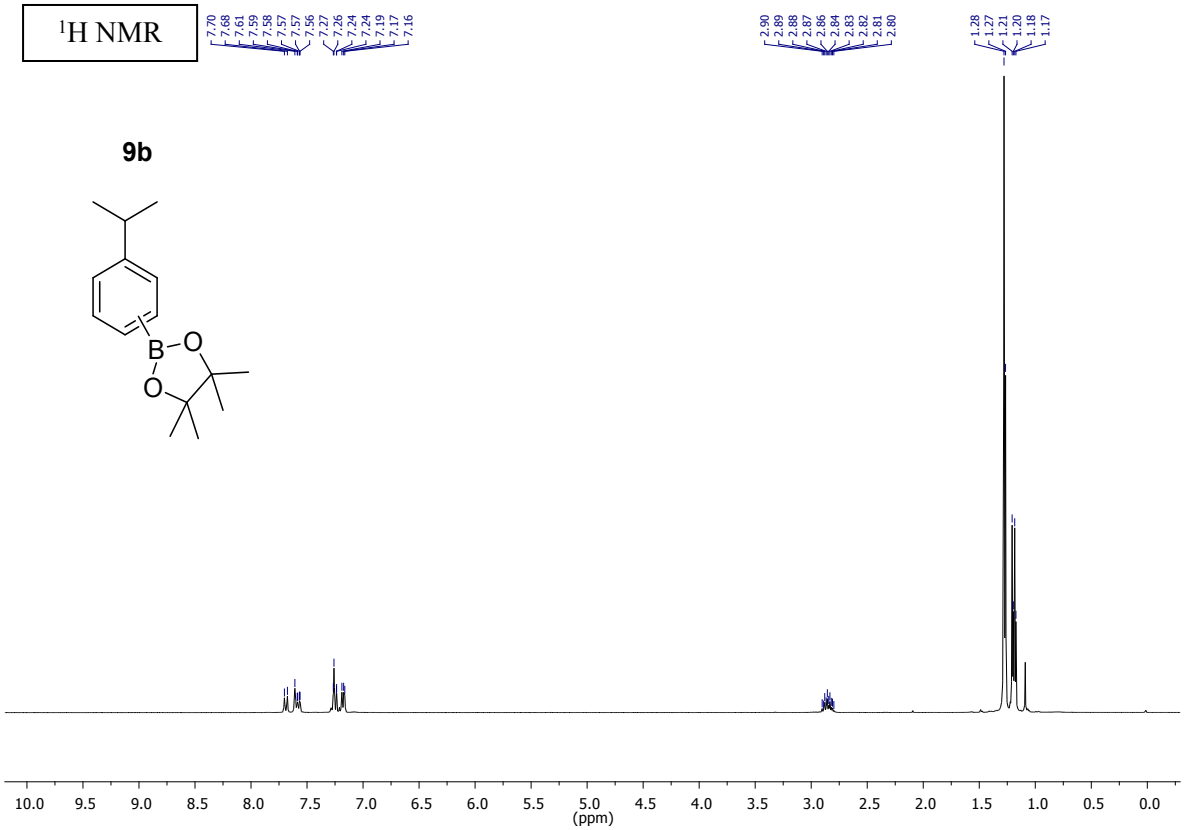
^{13}C NMR



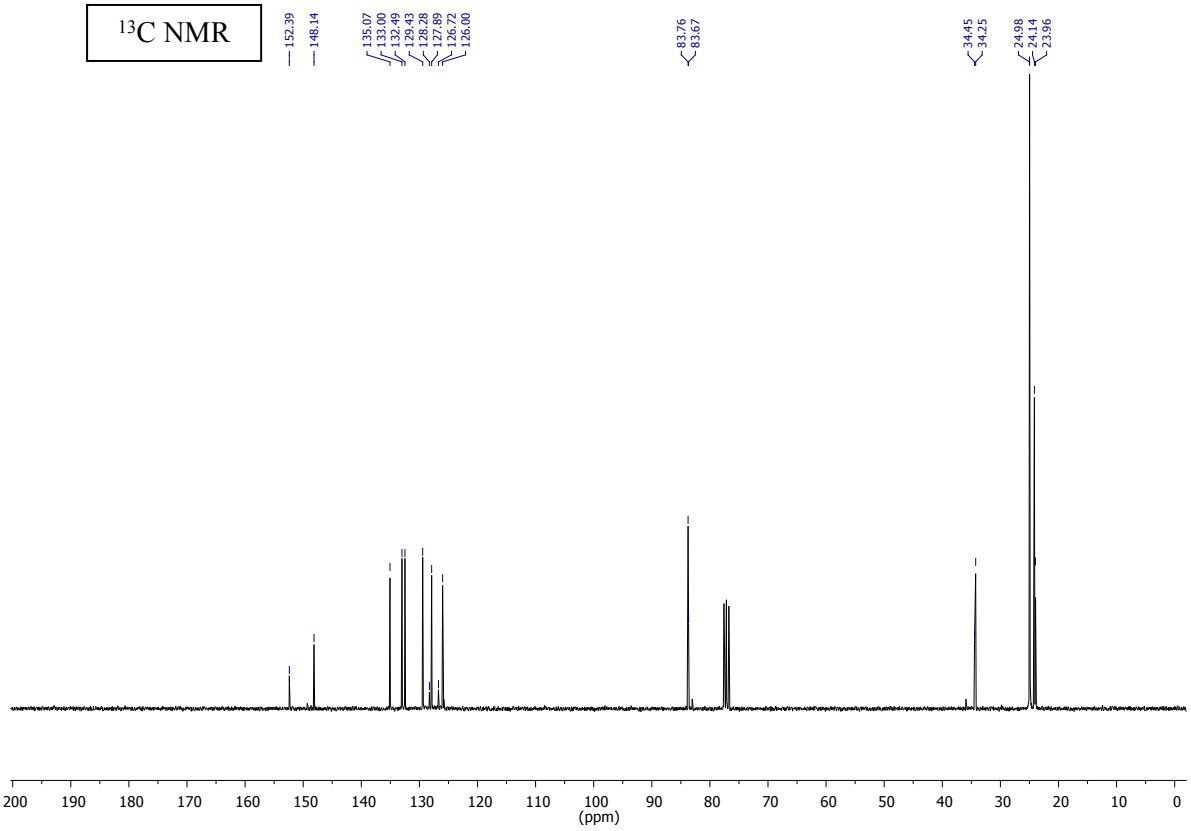
^{11}B NMR



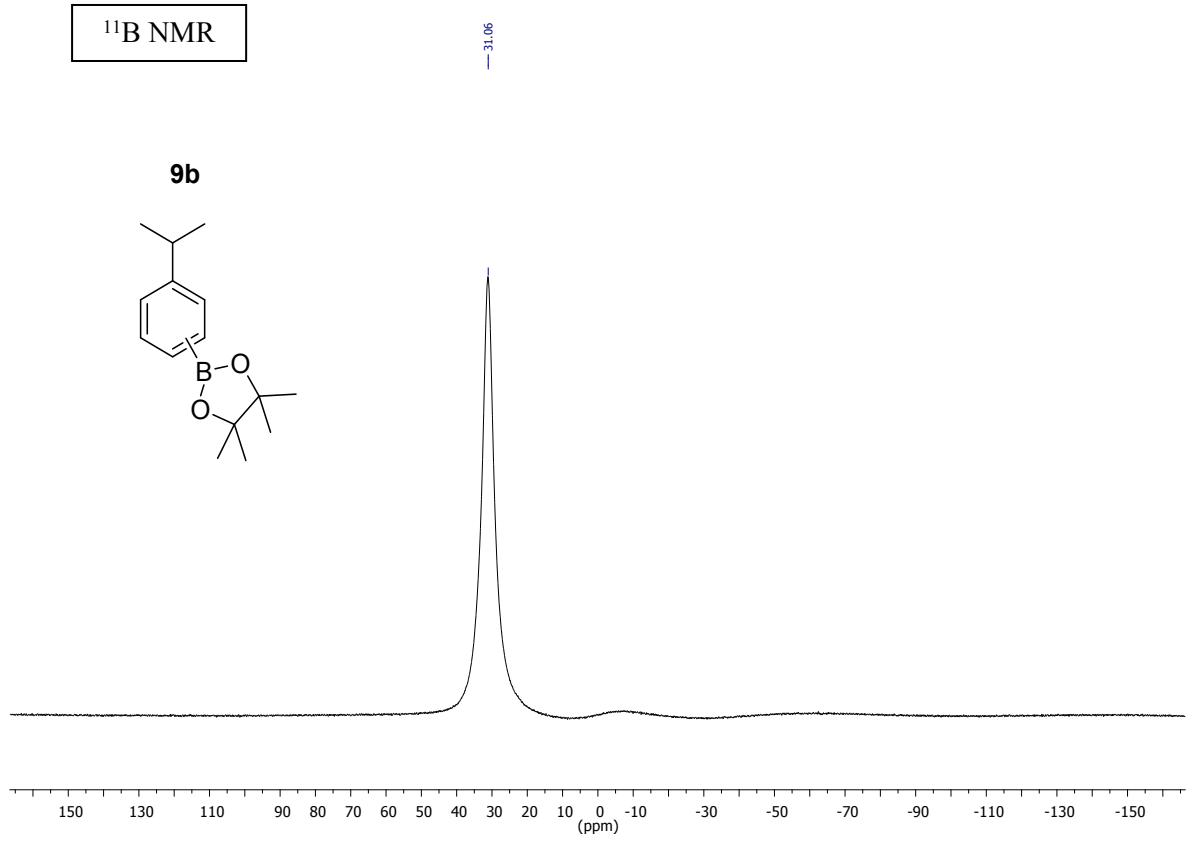
^{1}H NMR



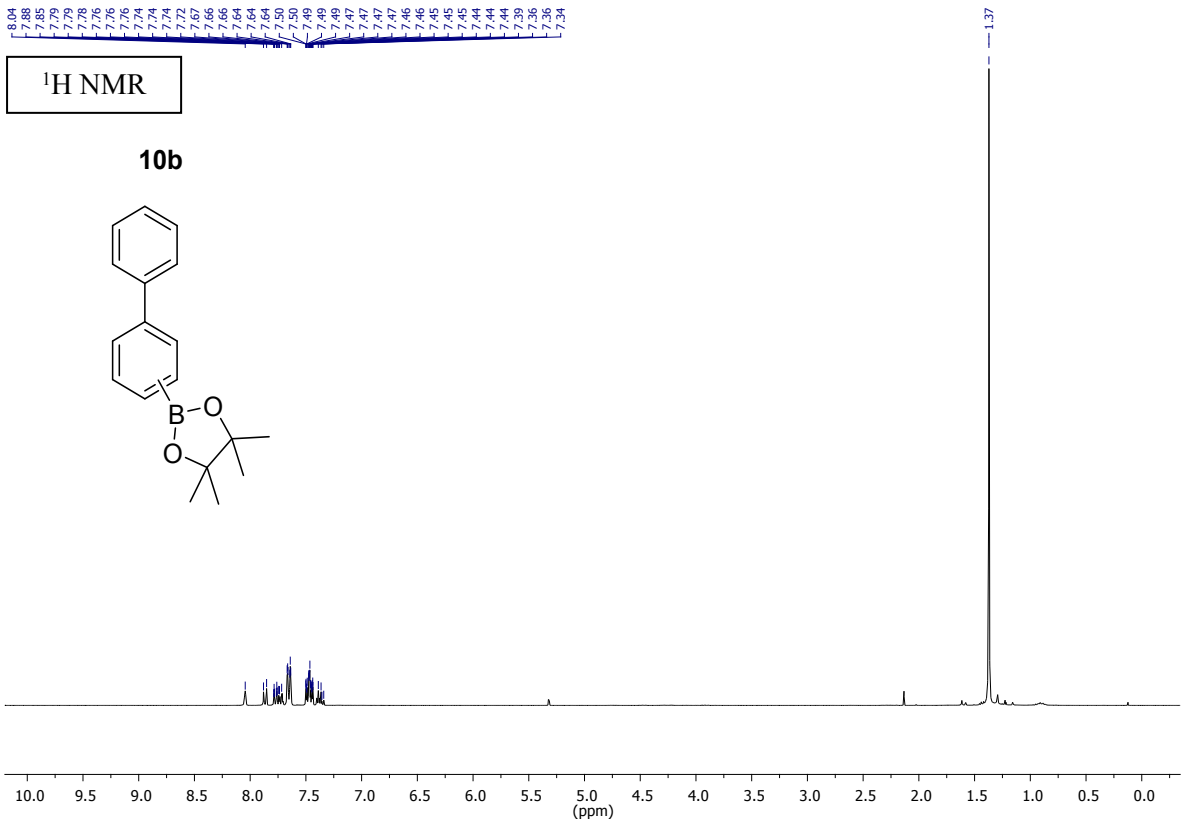
^{13}C NMR

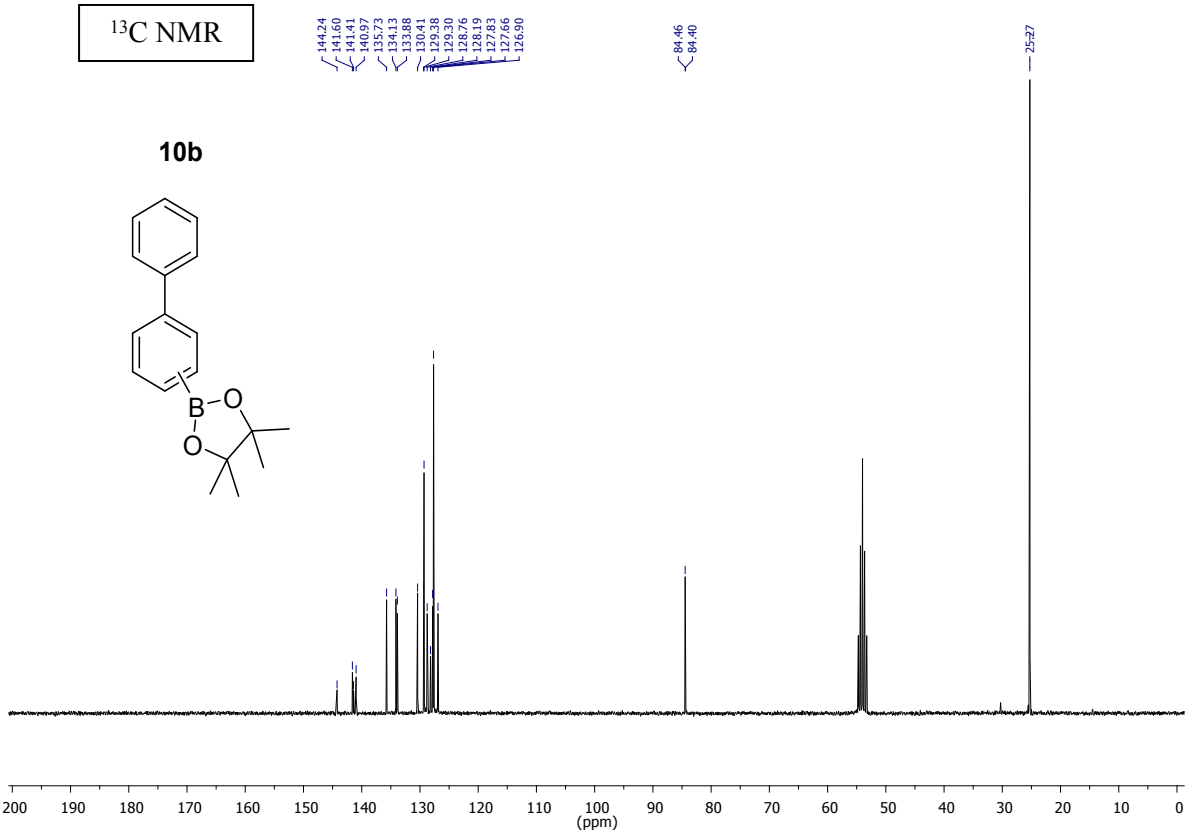


^{11}B NMR



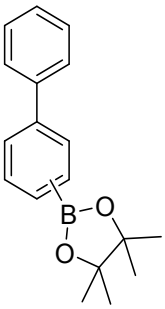
9b


8.04
7.88
7.85
7.79
7.79
7.78
7.76
7.76
7.76
7.74
7.74
7.74
7.72
7.67
7.66
7.66
7.64
7.64
7.64
7.50
7.50
7.49
7.49
7.49
7.47
7.47
7.47
7.47
7.47
7.46
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.44
7.39
7.36
7.36
7.34
1.37
[1]H NMR
10b
B
O
O
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


[13]C NMR
144.24
141.60
141.41
140.97
135.73
134.13
133.88
130.41
129.38
129.30
128.76
128.19
127.83
127.66
126.90
84.46
84.40
25.27
10b
B
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

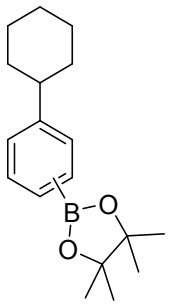
^{11}B NMR

10b

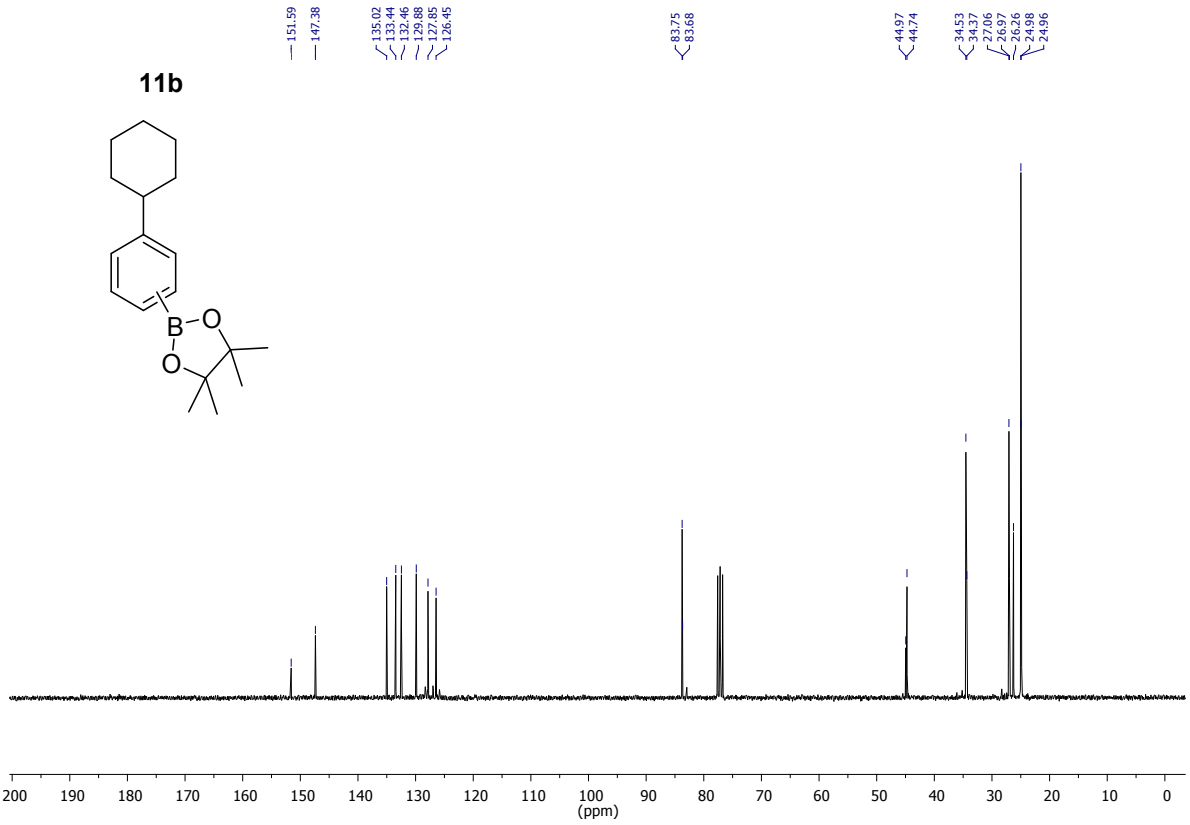


^{1}H NMR

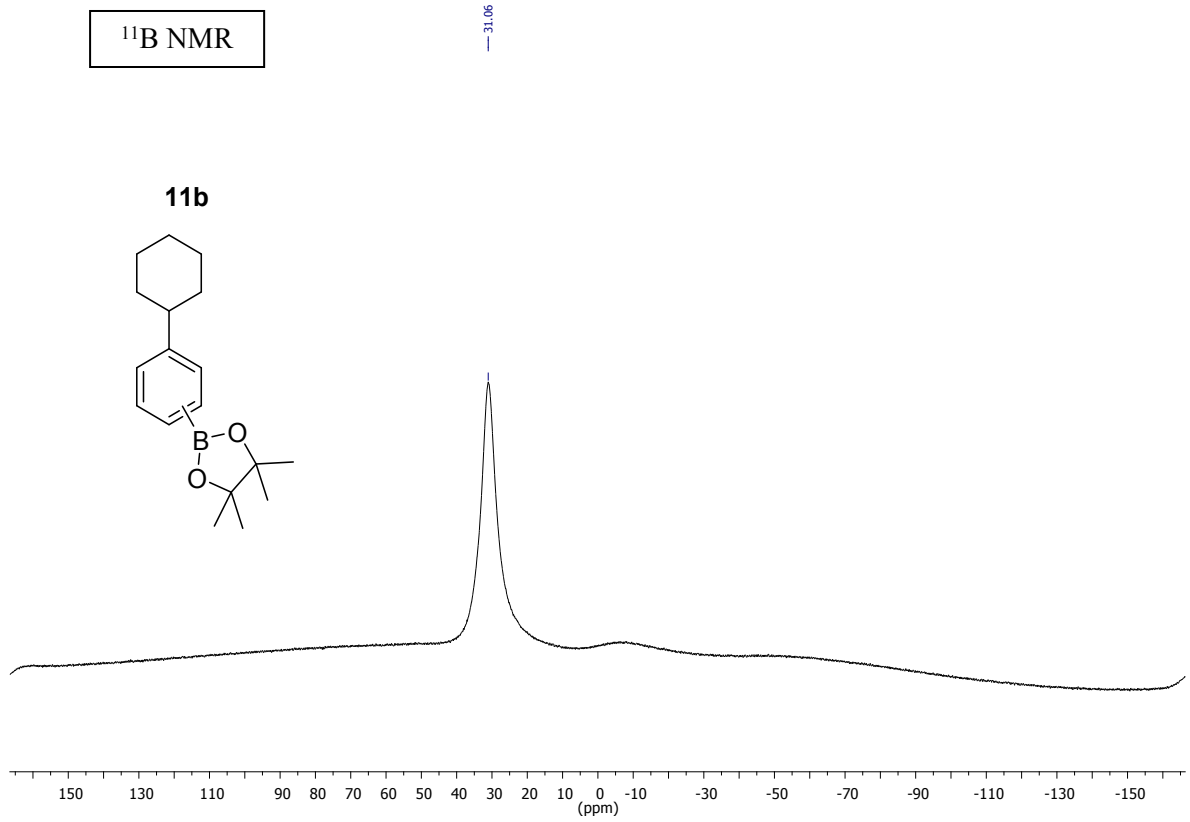
11b



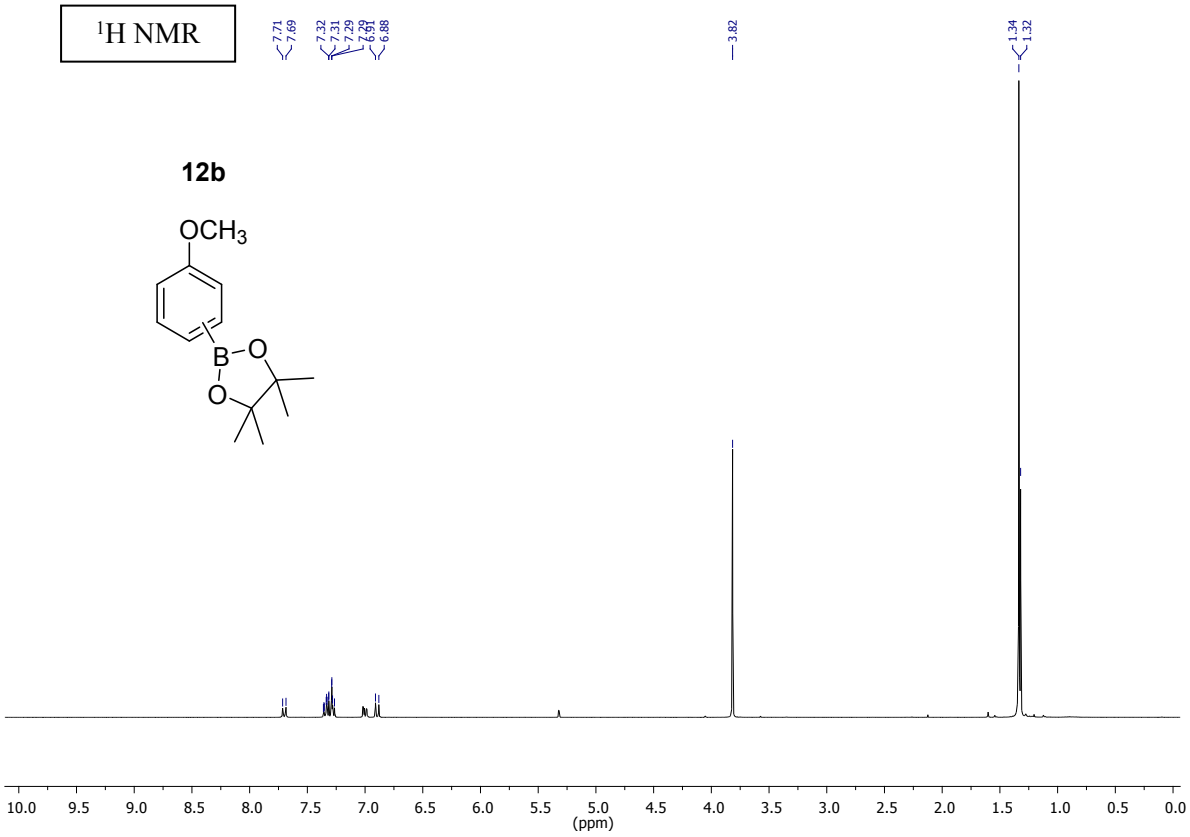
^{13}C NMR


151.59
147.38
135.02
133.44
132.46
129.88
127.85
126.45
83.75
83.68
44.97
44.74
34.53
34.37
27.06
26.97
26.26
24.98
24.96
11b
B
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

^{11}B NMR

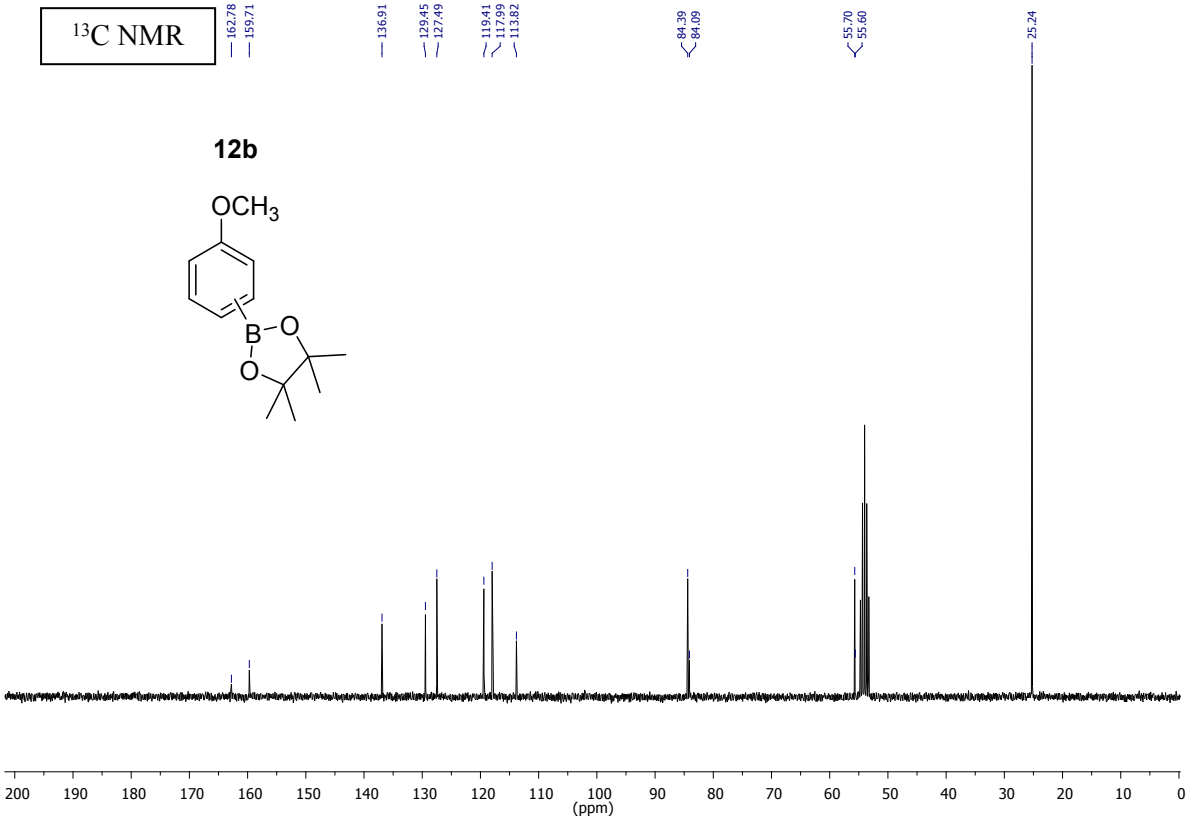

31.06
11b
B
O
O
150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150
(ppm)

^{1}H NMR



12b

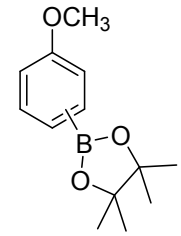
^{13}C NMR



12b

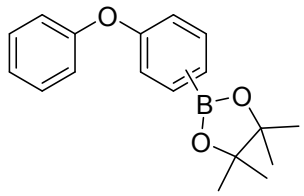
^{11}B NMR

12b



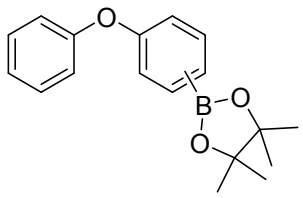
^{1}H NMR

13b



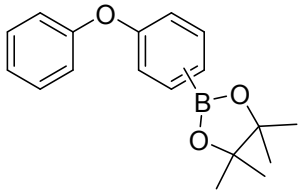
^{13}C NMR

13b

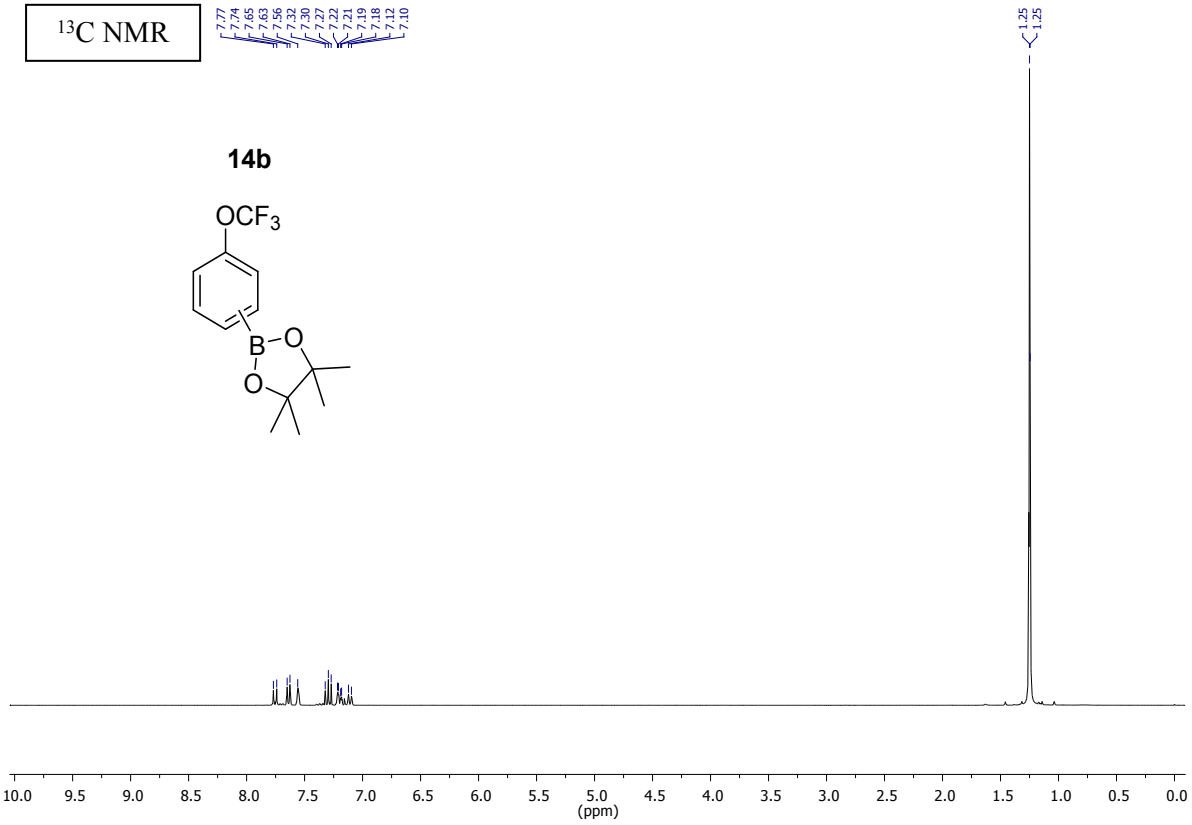


^{11}B NMR

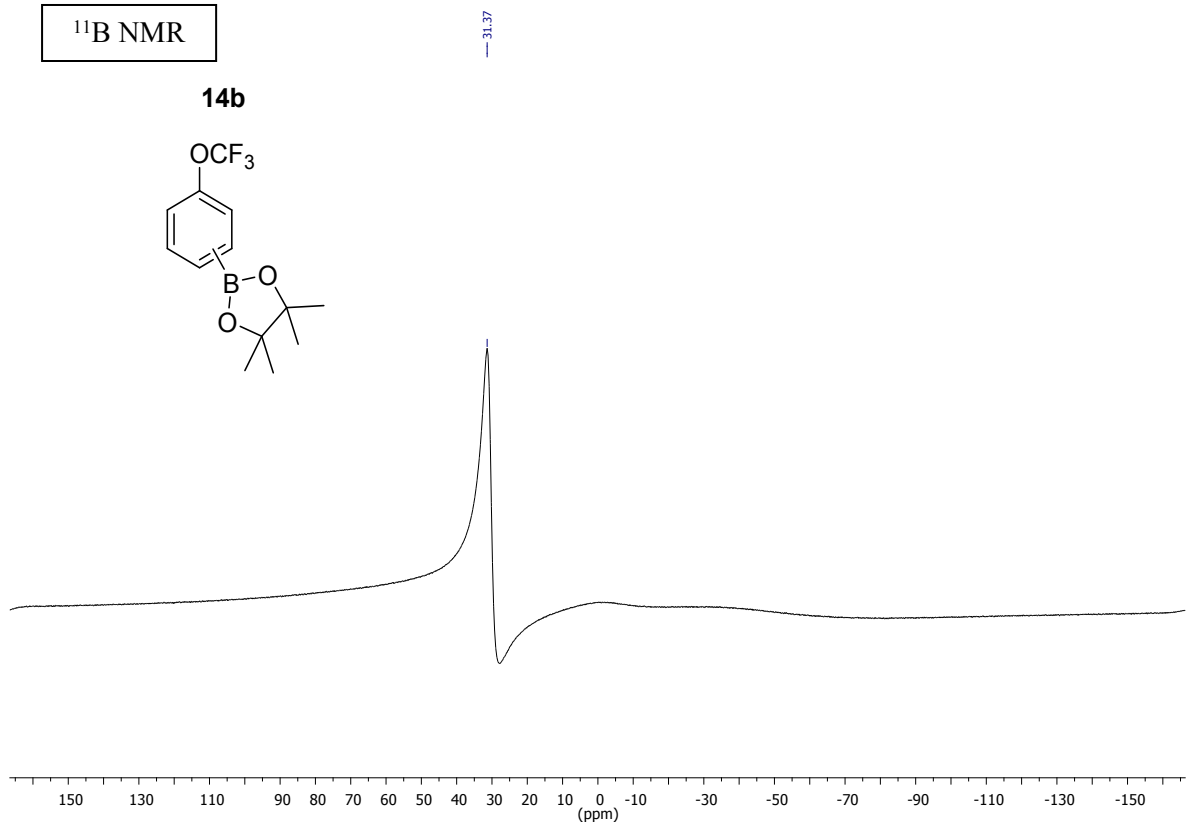
13b



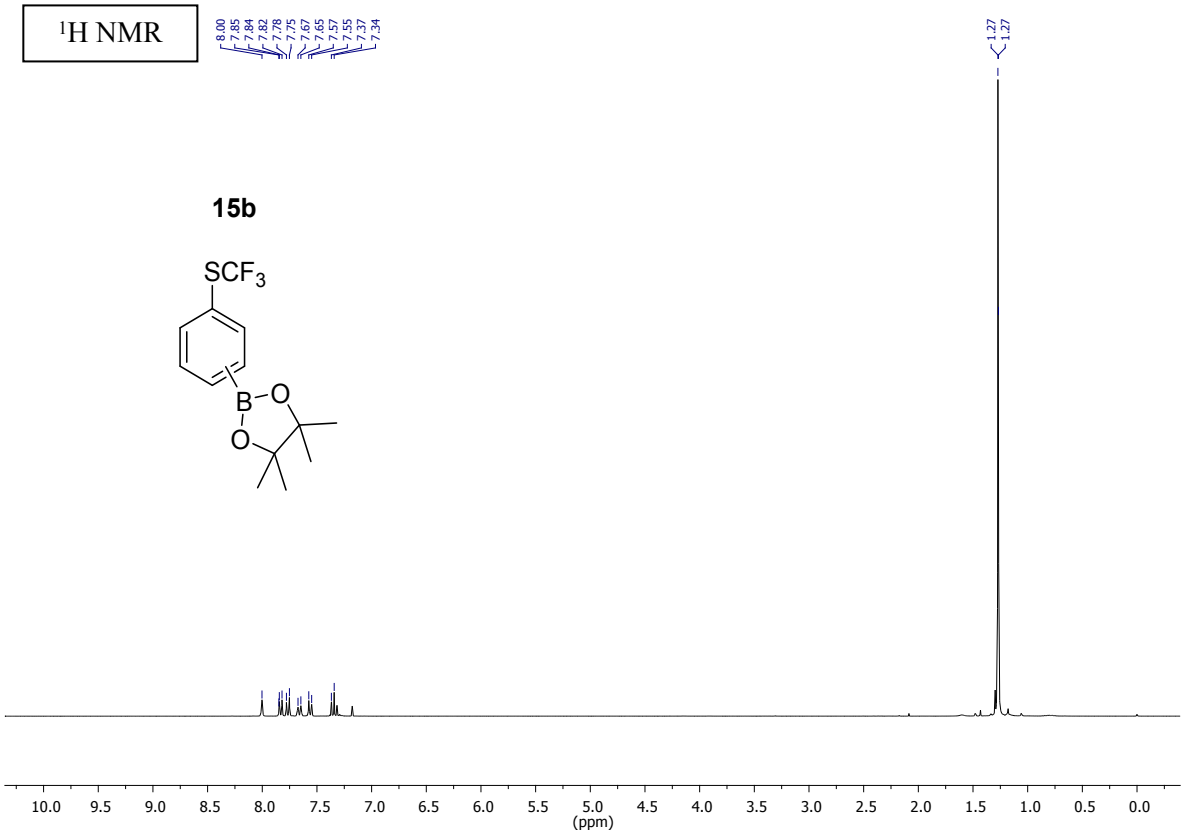
^{13}C NMR



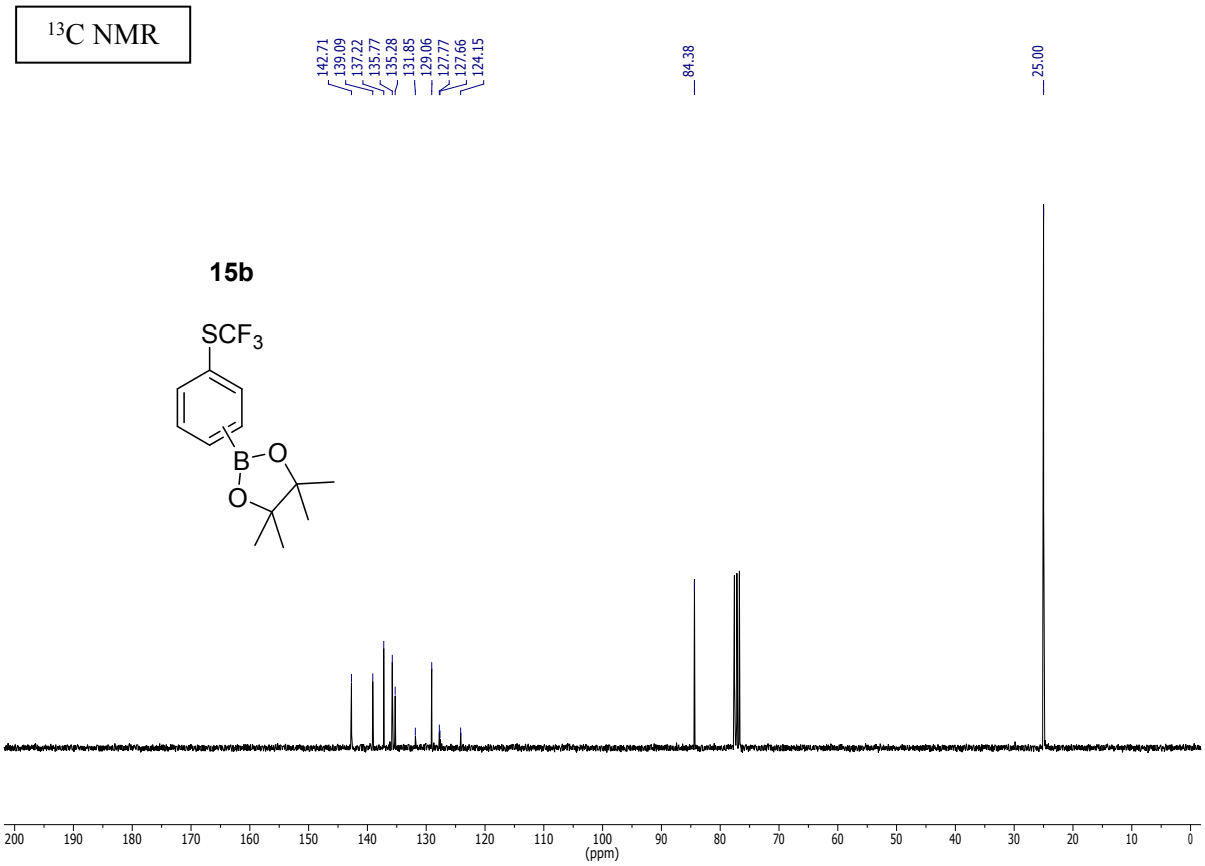
^{11}B NMR



^{1}H NMR

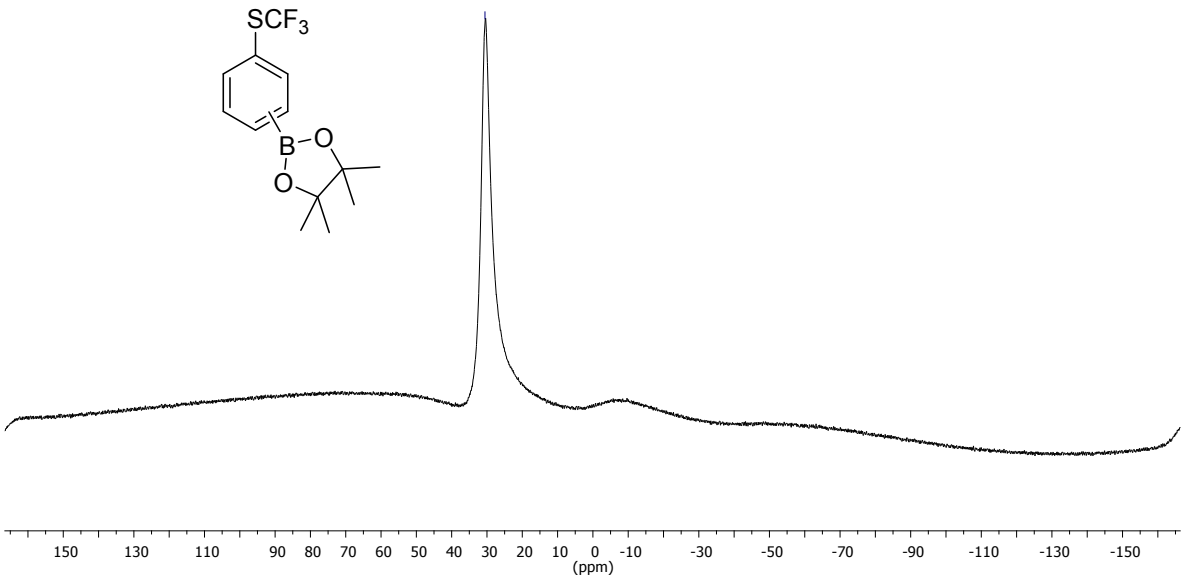


^{13}C NMR

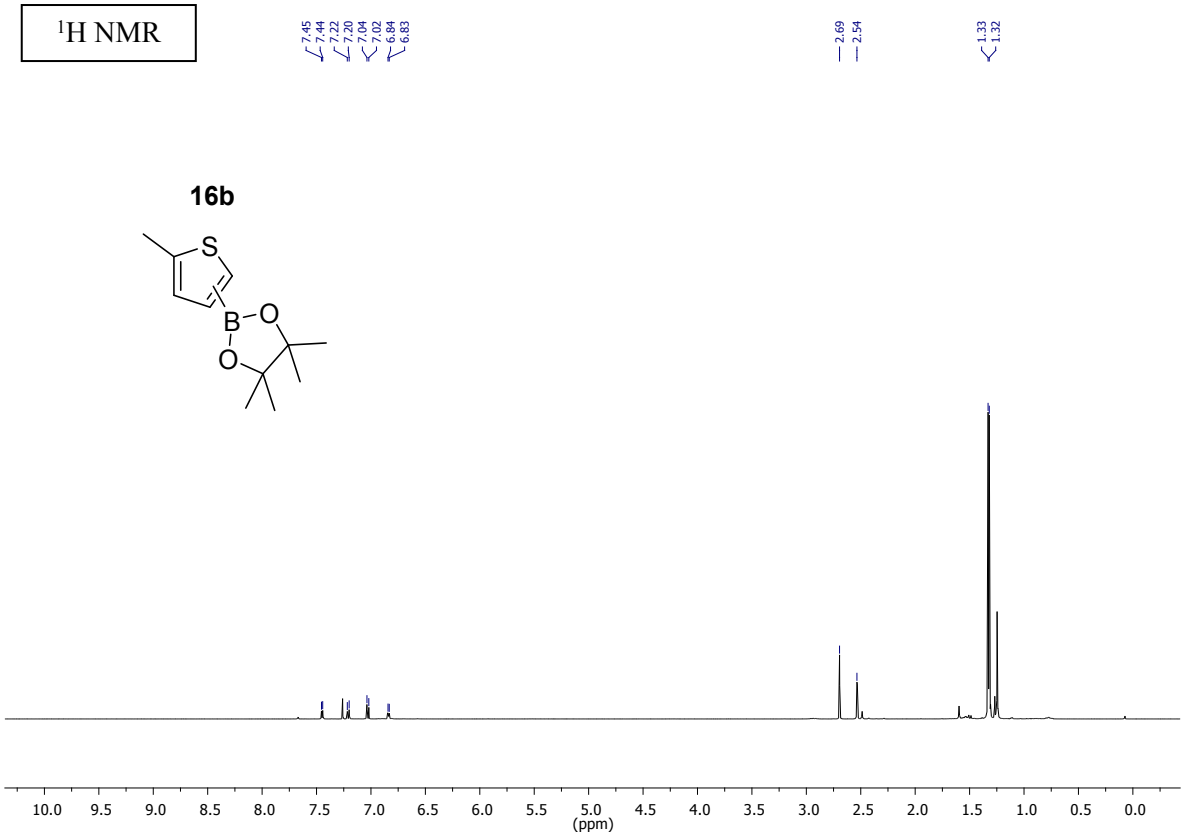


^{11}B NMR

15b

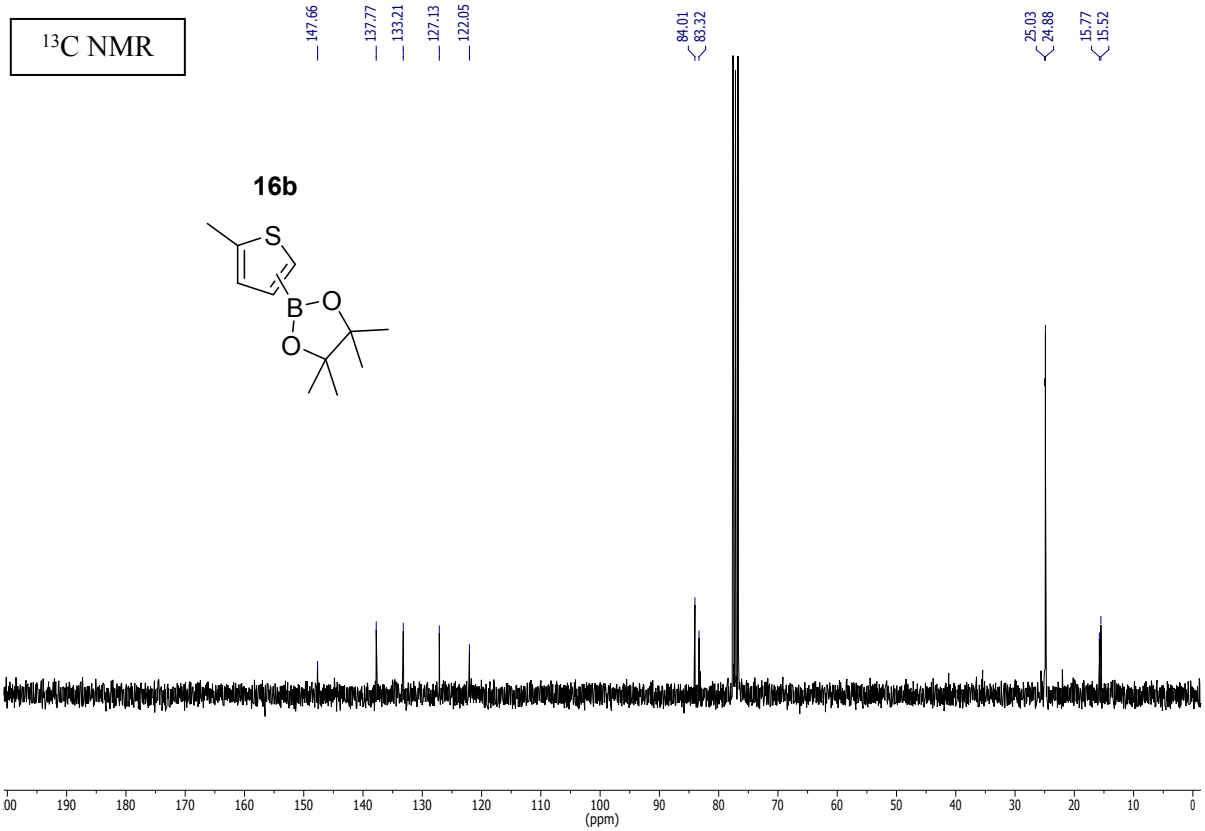


^{1}H NMR

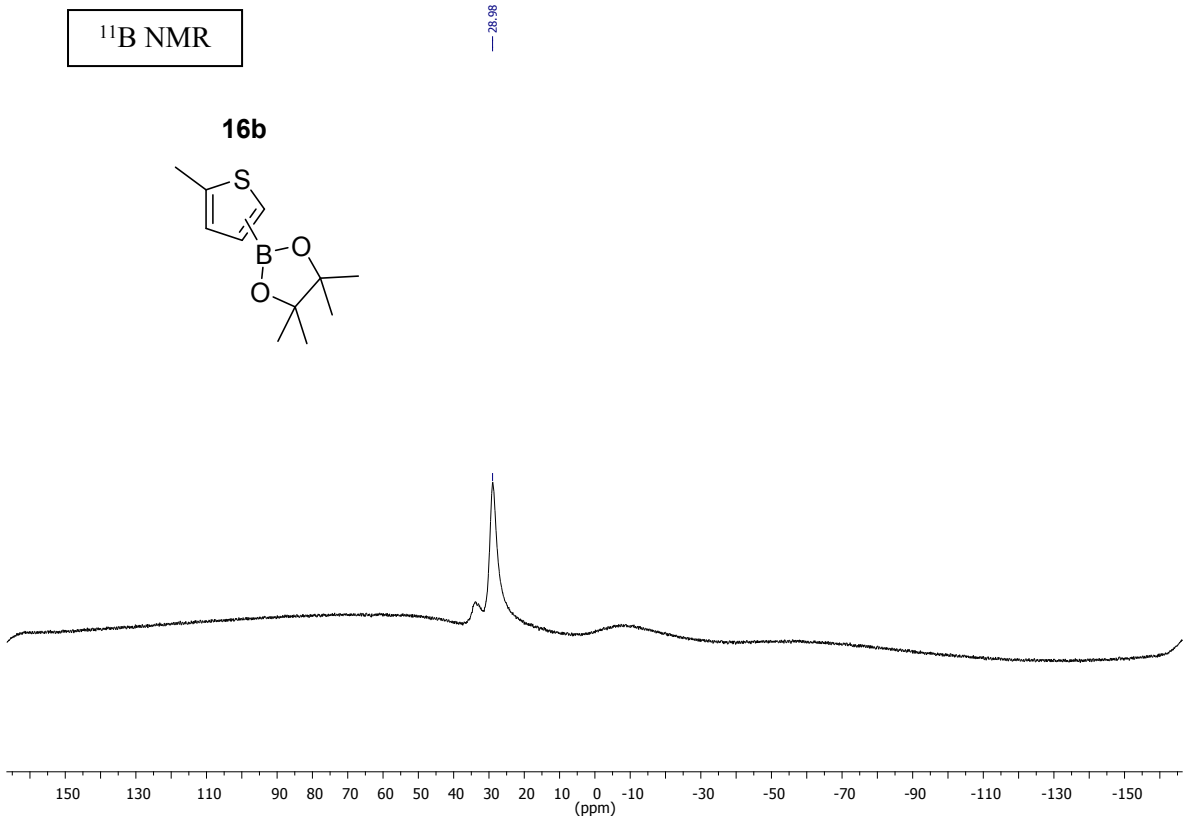


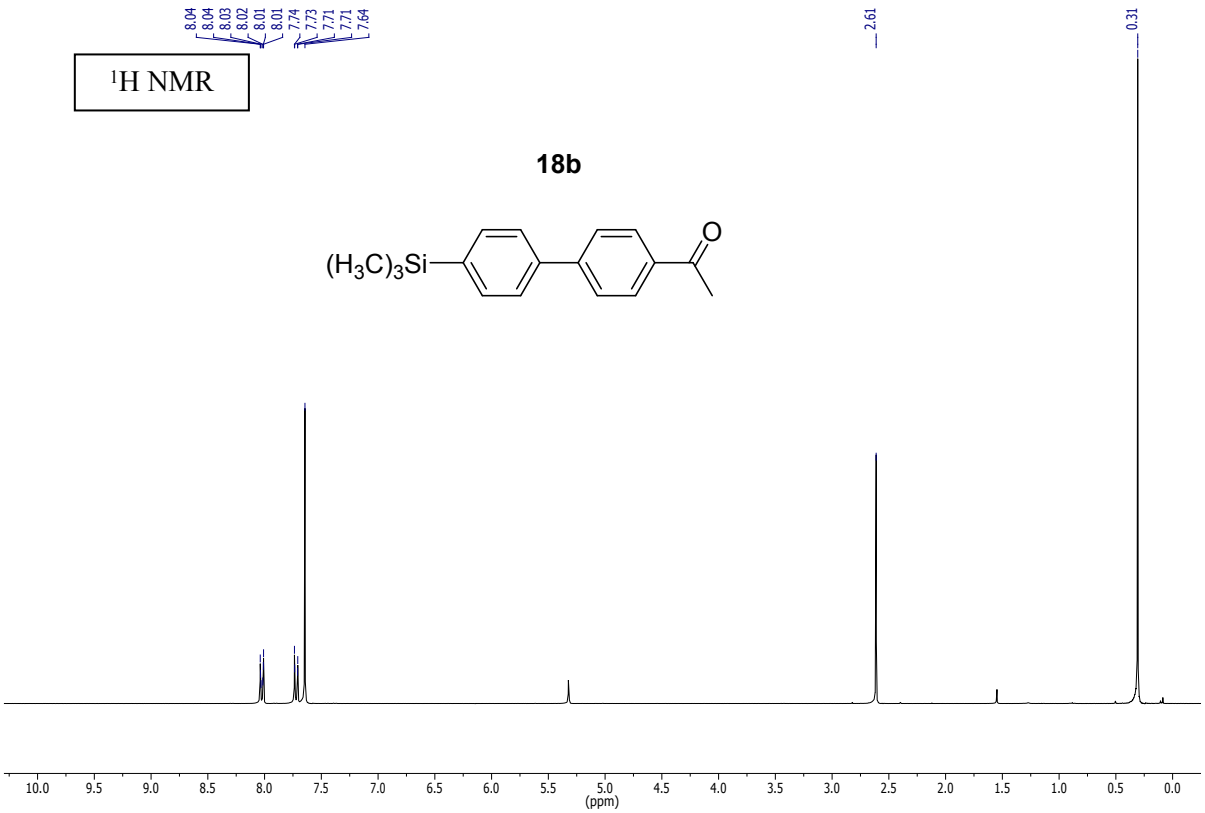
16b

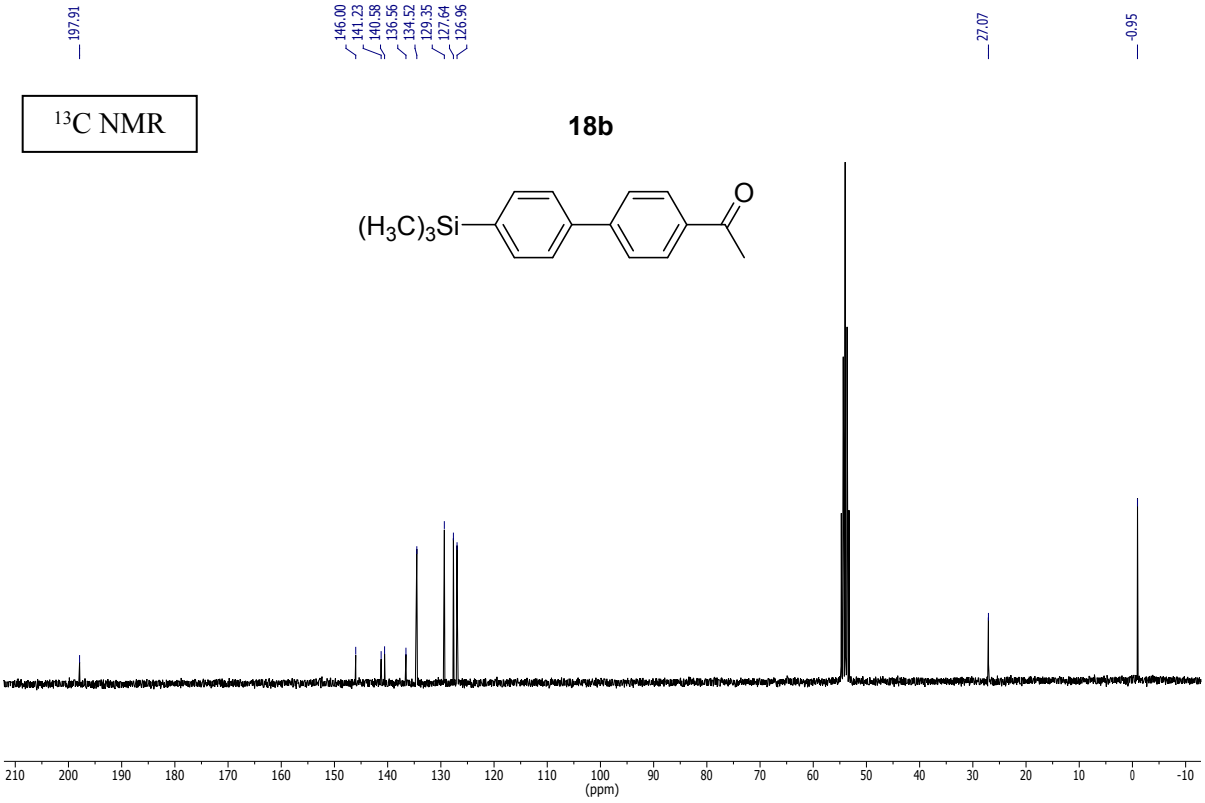
^{13}C NMR



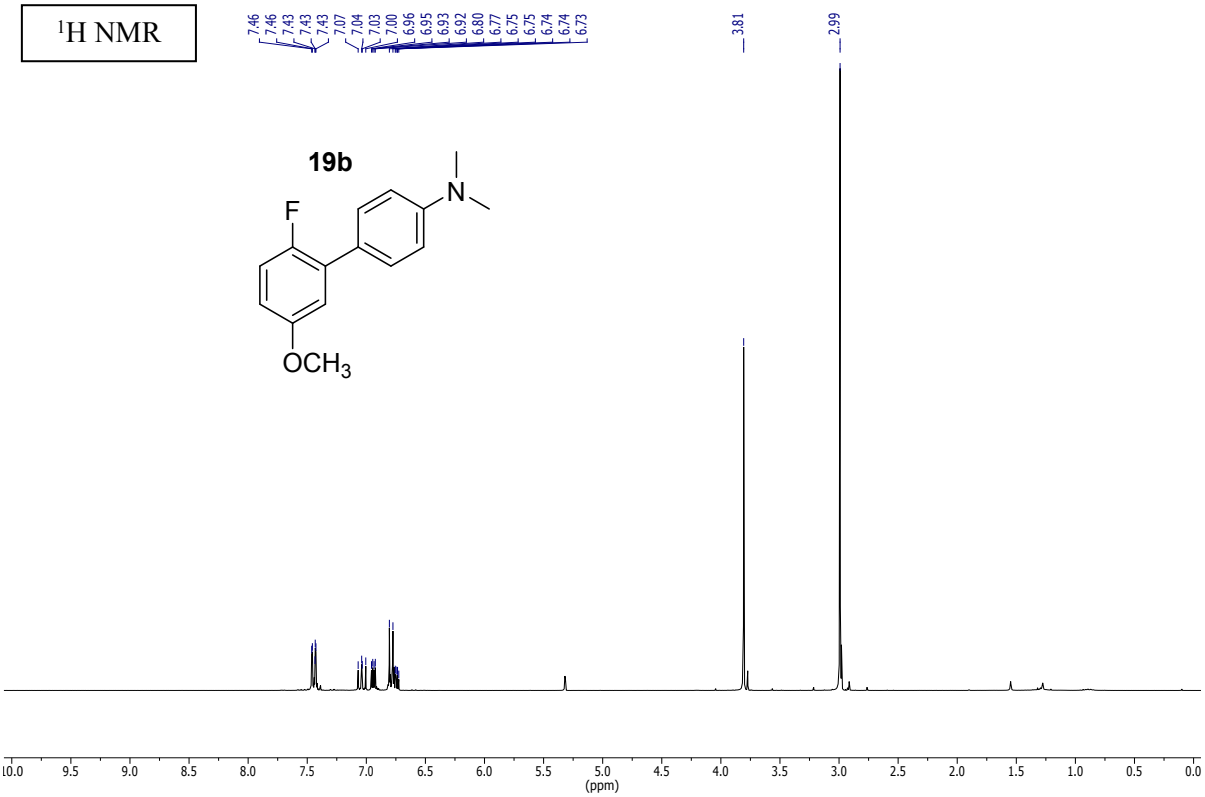
^{11}B NMR



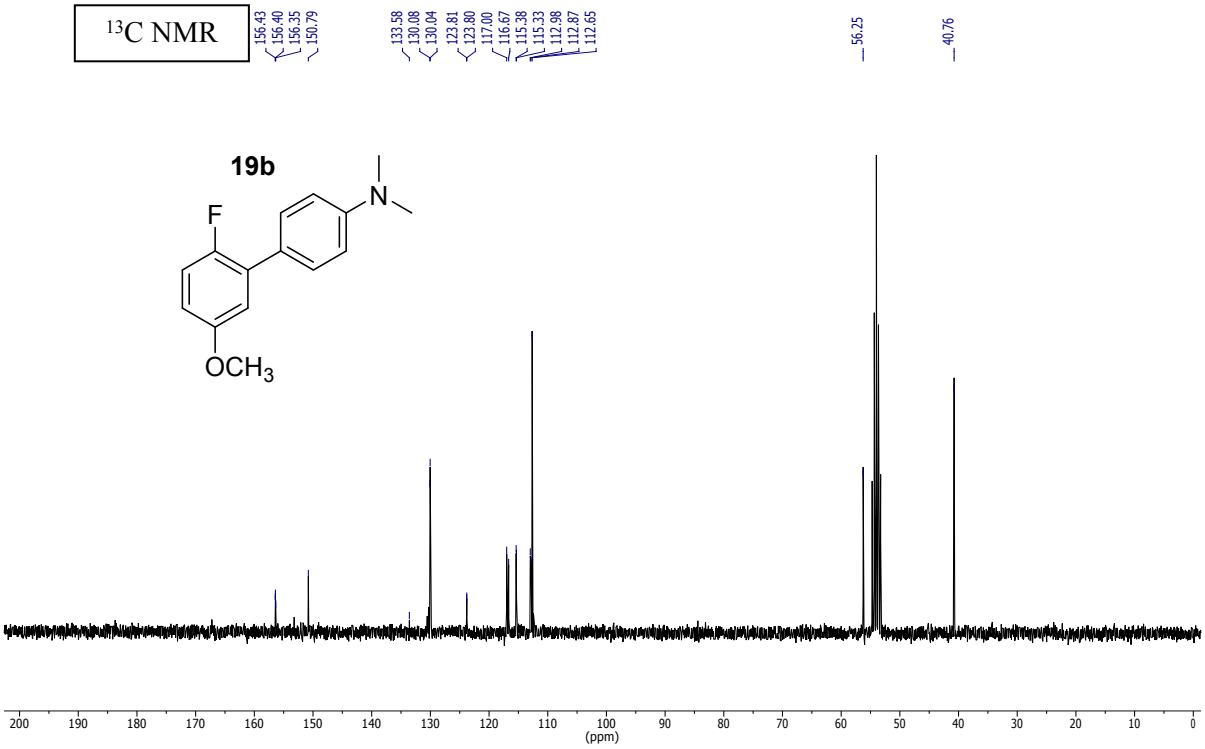

8.04
8.04
8.03
8.02
8.01
8.01
7.74
7.73
7.71
7.71
7.64
2.61
0.31
^{1}H NMR
18b
$(H_3C)_3Si$
O
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


197.91
146.00
141.23
140.58
136.56
134.52
129.35
127.64
126.96
27.07
-0.95
^{13}C NMR
18b
$(H_3C)_3Si$
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

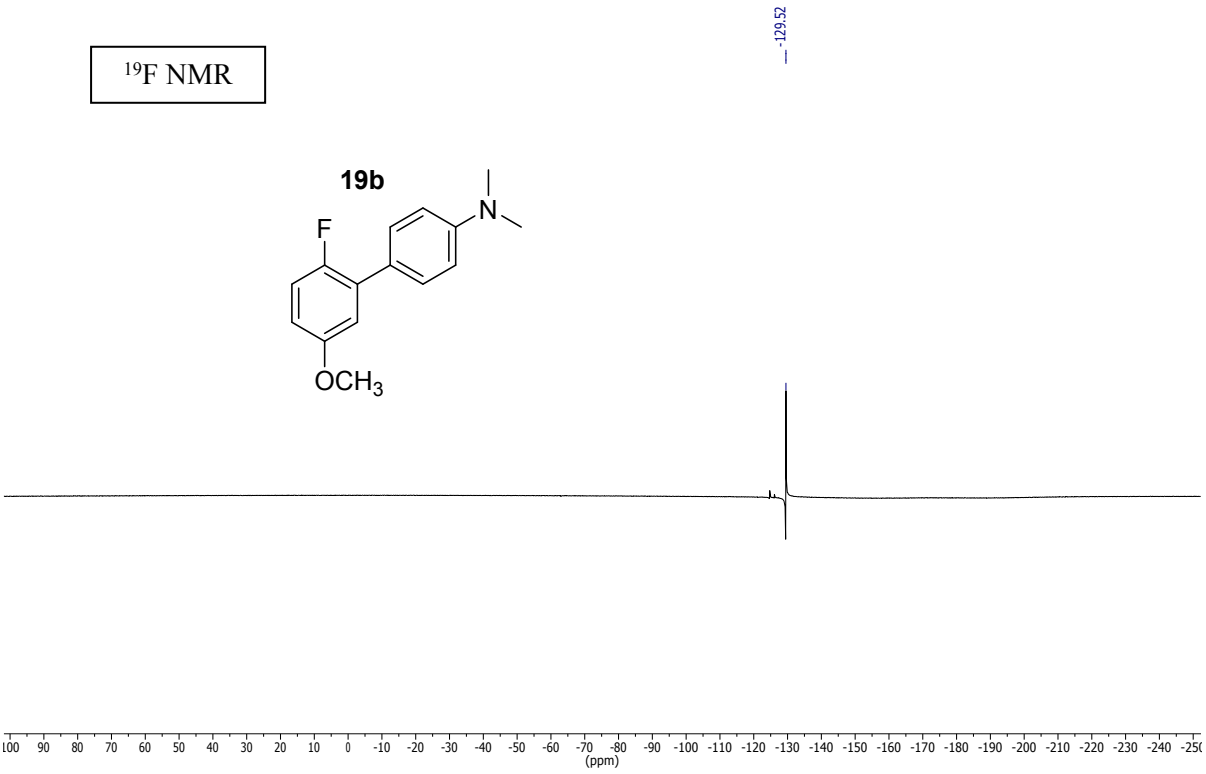
^{1}H NMR



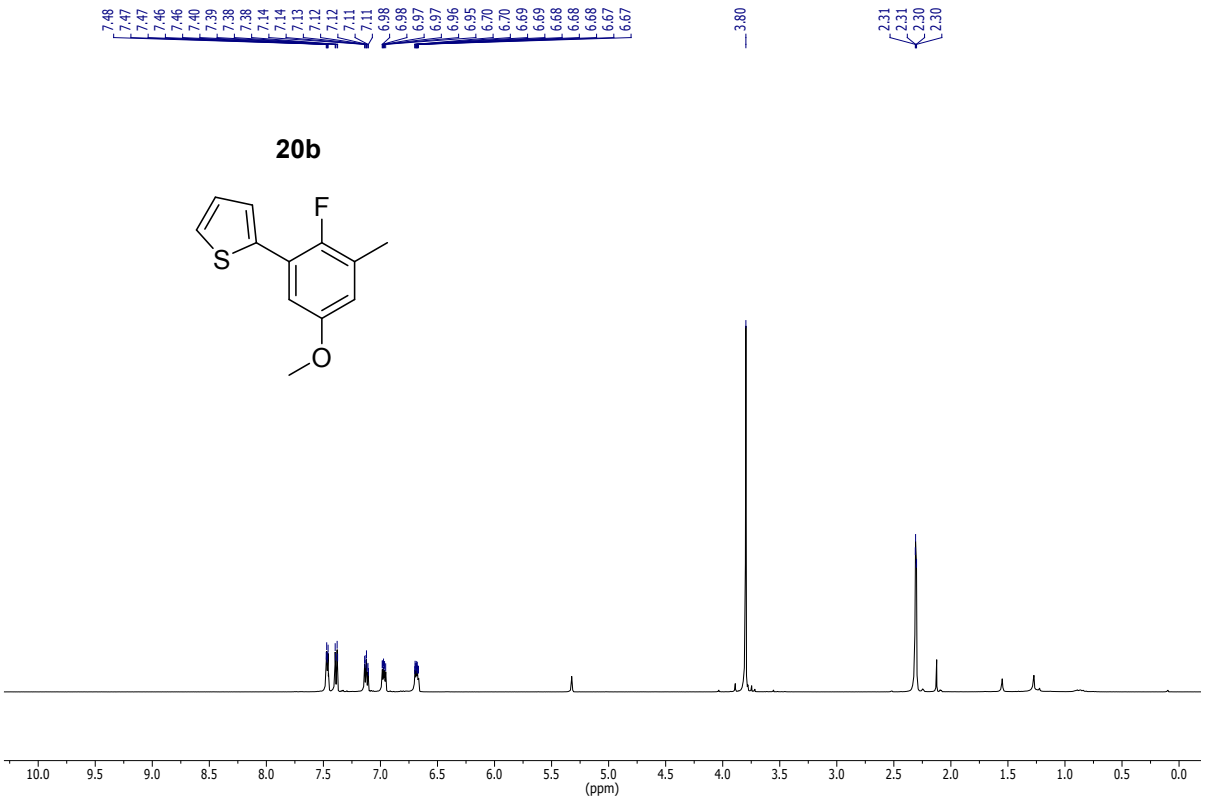
^{13}C NMR



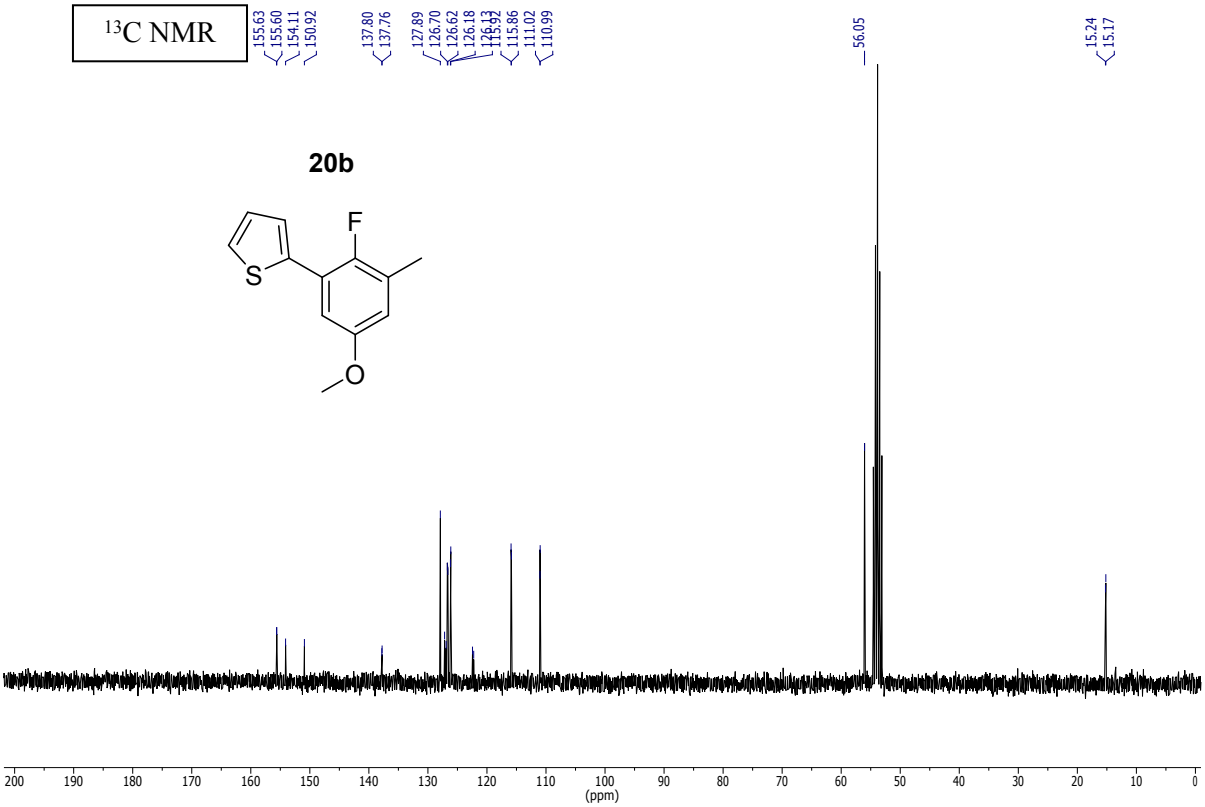
^{19}F NMR



^{1}H NMR

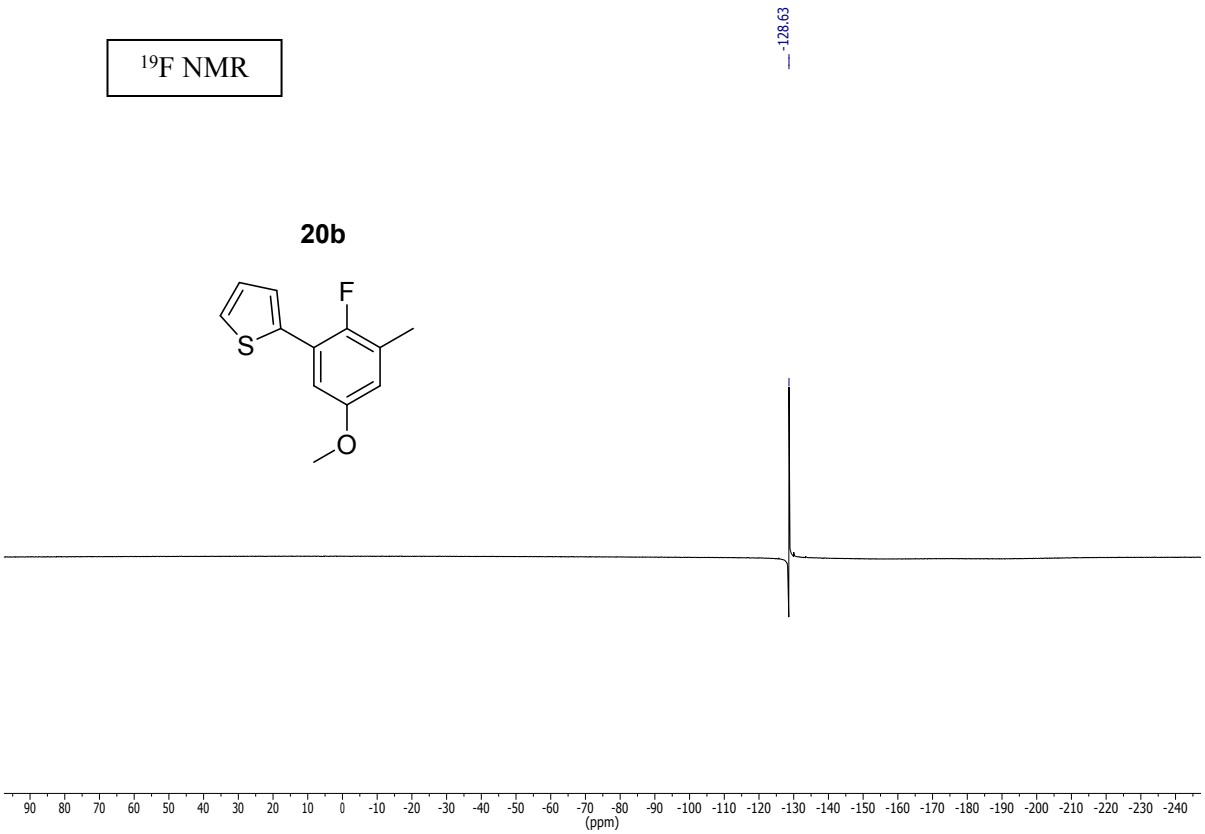


^{13}C NMR



20b

^{19}F NMR



20b