Supplementary Information

for

Benz-amidinato calcium iodide catalyzed aldehyde and ketone hydroboration with unprecedented functional group tolerance

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Contents:

1. **General consideration** : All reactions were operated under argon atmosphere using glovebox and Schlenk line. Dried solvents were used directly from M-Braun solvent purification system MB SPS-800. $CDCl_3$ was degassed by repeated freeze-thaw cycles and stored over activated 4 Å molecular sieves. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at room temperature using a Bruker Advance DPX 200 spectrophotometer. NMR chemical shifts were reported in ppm with repstect to tetramethylsilane. Chemicals were purchased from Sigma-Aldrich, Alfa-aesar, TCI chemicals and used without further purification. Compound **1** was prepared according to the literature procedure.[1]

2. **General Procedure for Catalytic Hydroboration of Aldehydes :**Aldehyde (0.25 mmol), pinacolborane (0.25mmol), LCaI(0.5-2 mol%) [benzene (1ml)] were charged in Schlenk tube inside glove box. The reaction mixture was allowed to run at room temperature. The progress of the reaction was monitored by ^1H NMR, which indicated the completion of the reaction by the disappearance of the aldehyde proton and appearance of a new CH_2 peak. Upon completion of reaction, the solvent was removed using high vacuum in Schlenk line and mesitylene (0.25mmol) as internal standard, was added while making the NMR in $CDCl_3$.

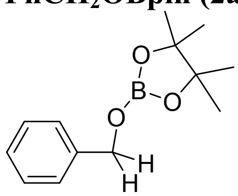
3. **Solvent Screening** : The reaction of benzaldehyde (0.25 mmol), pinacolborane(0.25mmol) was performed using different solvents as shown in table. The reaction conversion was found to be highest when we used benzene as reaction solvent.

Table S1.

Entry	Cat. (mol%)	Solvent	Time (min)	Conversion (%)
1	2	THF	40	94
2	2	Hexane	40	90
3	2	Xylene	40	96
4	2	Toluene	40	96
5	2	Benzene	40	>99

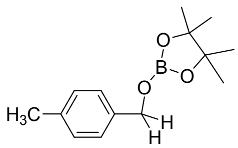
4. Spectroscopic data for aldehyde hydroboration products -

PhCH$_2$OBpin (2a): product from hydroboration of benzaldehyde.^{1}H NMR (CDCl$_3$, 200 MHz),



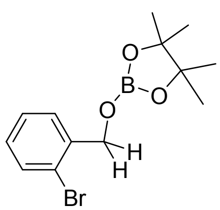
δ1.17 (s,12 H, Bpin-C*H*$_3$), 4.82 (s, 2H, pinBOC*H*$_2$), 7.24 (m, 5H, Ar-*H*); ^{13}C NMR (CDCl$_3$, 50.28 MHz), δ 24.68 (Bpin-*C*H$_3$), 66.77 (O*C*H$_2$Ph), 83.06 (Bpin-*C*), 126.82, 127.00, 128.37, 137.77, 139.31 (Ar-*C*)

4-CH$_3$PhCH$_2$OBpin (2b): product from hydroboration of 4-Methylbenzaldehyde.^{1}H NMR (CDCl$_3$,



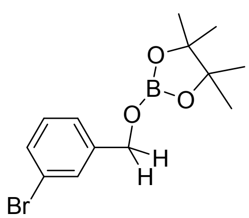
200 MHz), δ 1.17 (s,12 H, Bpin-C*H*$_3$), 2.25 (s, 3H, Ar-C*H*$_3$), 4.80 (s, 2H, pinBOC*H*$_2$), 7.07 (d,$^{3}J_{HH}$ = 7.7 Hz, 2H, Ar-*H*), 7.14 (d,$^{3}J_{HH}$ = 8.2 Hz, 2H, Ar-*H*); ^{13}C NMR (CDCl$_3$, 50.28 MHz), 21.26(Ph*C*H3), 24.67 (Bpin-*C*H$_3$), 66.66 (O*C*H$_2$Ph), 82.96 (Bpin-*C*), 126.98, 129.02, 129.93, 137.05, 137.75 (Ar-*C*).

2-BrPhCH$_2$OBpin (2c): product from hydroboration of 2-Bromobenzaldehyde.^{1}H NMR (CDCl$_3$,



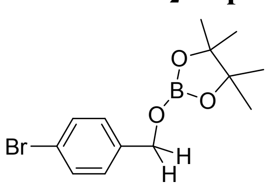
200 MHz), δ1.19 (s,12 H, Bpin-C*H*$_3$), 4.90 (s, 2H, pinBOC*H*$_2$), 7.03(d,$^{3}J_{HH}$ = 7.2 Hz, 1H, Ar-*H*), 7.27(m, 1H, Ar-*H*),7.40 (m, 1H, Ar-*H*), 7.44(dd, $^{3}J_{HH}$ = 7.1 Hz, 1H, Ar-*H*)^{13}C NMR (CDCl$_3$, 50.28 MHz) 24.66 (Bpin-*C*H$_3$), 66.37 (O*C*H$_2$Ph), 83.23 (Bpin-*C*), 126.97, 127.41, 127.88, 128.68, 132.32 (Ar-*C*).

3-BrPhCH$_2$OBpin (2d): product from hydroboration of 3-Bromobenzaldehyde.^{1}H NMR (CDCl$_3$,



200 MHz), δ1.17 (s,12 H, Bpin-C*H*$_3$), 4.80 (s, 2H, pinBOC*H*$_2$), 7.08(d, $^{3}J_{HH}$ = 7.6 Hz, 1H, Ar-*H*), 7.14(m, 1H, Ar-*H*),7.26 (m, 1H, Ar-*H*), 7.43(s, 1H, Ar-*H*) ^{13}C NMR (CDCl$_3$, 50.28 MHz) 24.67(Bpin-*C*H$_3$), 65.91 (O*C*H$_2$Ph), 83.23 (Bpin-*C*), 122.53, 125.22, 126.99, 128.40,130.50 (Ar-*C*).

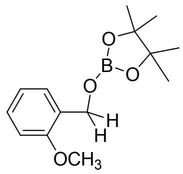
4-BrPhCH$_2$OBpin (2e): product from hydroboration of 4-Bromobenzaldehyde.^{1}H NMR (CDCl$_3$,



200 MHz), δ 1.17 (s,12 H, Bpin-C*H*$_3$), 4.78 (s, 2H, pinBOC*H*$_2$), 7.15 (d,$^{3}J_{HH}$ = 8.1 Hz, 2H, Ar-*H*), 7.34(d,$^{3}J_{HH}$ = 8.5 Hz, 2H, Ar-*H*),^{13}C NMR 23.86 (Bpin-

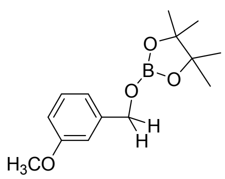
CH_3), 65.23 (OCH_2Ph), 82.37 (Bpin-*C*), 120.48, 126.18, 128.68, 130.64, 136.94 (Ar-*C*).

2-OCH_3PhCH_2OBpin (2f): product from hydroboration of 2-Methoxylbenzaldehyde.[1]H NMR



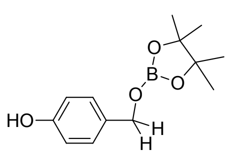
($CDCl_3$, 200 MHz), δ 1.18 (s,12 H, Bpin-CH_3), 3.70 (s, 3H, Ar-OCH_3), 4.90 (s, 2H, pinBOCH_2), 6.89 (m, 2H, Ar-*H*), 7.14 (m, 1H, Ar-*H*),7.34 (m, 1H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 50.28 MHz), 24.50 (Bpin-CH_3), 55.03 (PhOCH_3), 62.17 (OCH_2Ph), 82.72 (Bpin-*C*), 120.21, 127.22, 128.12, 137.58, 156.38 (Ar-*C*).

3-OCH_3PhCH_2OBpin (2g): product from hydroboration of 3-Methoxybenzaldehyde.[1]H NMR



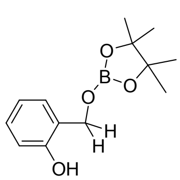
($CDCl_3$, 200 MHz), δ 1.18 (s,12 H, Bpin-CH_3), 3.70 (s, 3H, PhOCH_3), 4.82 (s, 2H, pinBOCH_2), 6.84 (d, 2H, Ar-*H*, J = 15.2 Hz), 7.11 (m, 2H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 50.28 MHz) 25.07 (Bpin-CH_3), 65.81 (OCH_2Ph), 83.48 (Bpin-*C*), 126.99, 129.06, 129.65, 131.81, 137.48(Ar-*C*),153.42(PhOCH_3).

4-$OHPhCH_2OBpin$ (2h): product from hydroboration of 4-Hydroxybenzaldehyde.[1]H NMR



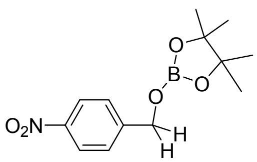
($CDCl_3$, 200 MHz), δ 1.18 (s,12 H, Bpin-CH_3), 4.75 (s, 2H, pinBOCH_2), 6.77 (d,$^3J_{HH}$ = 8.4 Hz, 2H, Ar-*H*), 7.07 (d, $^3J_{HH}$ = 8.5 Hz, 2H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 50.28 MHz) 24.49 (Bpin-CH_3), 66.54 (OCH_2Ph), 83.09 (Bpin-*C*), 119.32, 128.68, 130.91, 137.64, 155.35 (Ar-*C*).

2-$OHPhCH_2OBpin$ (2i): product from hydroboration of 2-Hydroxybenzaldehyde.[1]H NMR

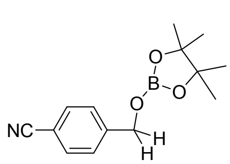


($CDCl_3$, 200 MHz), δ 1.18 (s,12 H, Bpin-CH_3), 4.88 (s, 2H, pinBOCH_2), 6.87 (d,$^3J_{HH}$ = 8.4 Hz, 2H, Ar-*H*), 7.07 (d, $^3J_{HH}$ = 8.5 Hz, 2H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 50.28 MHz) 25.07 (Bpin-CH_3), 72.54 (OCH_2Ph), 83.42 (Bpin-*C*), 121.48, 128.86, 131.83, 138.21, 144.14 (Ar-*C*).

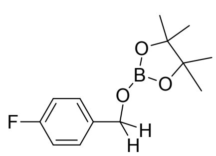
4-NO$_2$PhCH$_2$OBpin (2j): product from hydroboration of 4-Nitrobenzaldehyde.^{1}H NMR (CDCl$_3$, 200 MHz), δ1.19 (s,12 H, Bpin-CH_3), 4.93 (s, 2H, pinBOCH_2), 7.43(d, $^3J_{HH}$ = 8.6 Hz, 2H, Ar-H), 8.12(d,$^3J_{HH}$ = 8.9 Hz, 2H, Ar-H);^{13}C NMR (CDCl$_3$, 50.28 MHz) 24.63(Bpin-CH$_3$), 65.59 (OCH$_2$Ph), 83.43 (Bpin-C), 123.62, 126.93, 128.39, 130.49, 137.72(Ar-C).



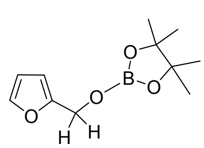
4-CNPhCH$_2$OBpin (2k): product from hydroboration of 4-Cyanobenzaldehyde.^{1}H NMR (CDCl$_3$, 200 MHz), δ 1.19 (s,12 H, Bpin-CH_3), 4.89 (s, 2H, pinBOCH_2), 7.37 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar-H), 7.51 (d,$^3J_{HH}$ = 8.4 Hz, 2H, Ar-H); ^{13}C NMR (CDCl$_3$, 50.28 MHz), 21.71 (Bpin-CH$_3$), 66.27 (OCH$_2$Ph), 83.85 (Bpin-C), 111.60 (PhCN), 119.38, 128.85, 132.68, 138.20, 145.12 (Ar-C).



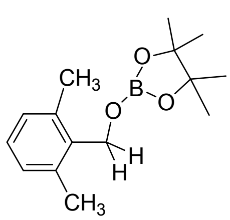
4-FPhCH$_2$OBpin (2l): product from hydroboration of 4-Fluorobenzaldehyde.^{1}H NMR (CDCl$_3$, 200 MHz), δ1.17 (s,12 H, Bpin-CH_3), 4.79 (s, 2H, pinBOCH_2), 6.92 (d,$^3J_{HH}$ = 8.9 Hz, 2H, Ar-H), 7.22 (d,$^3J_{HH}$ = 7.8 Hz, 2H, Ar-H); ^{13}C NMR (CDCl$_3$, 50.28 MHz) 24.62(Bpin-CH$_3$), 66.12 (OCH$_2$Ph),83.10 (Bpin-C), 126.96, 128.77, 132.19, 135.08, 137.75(Ar-C).



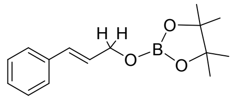
FurfuralOBpin (2m): product from hydroboration of Furfural.^{1}H NMR (CDCl$_3$, 200 MHz), δ 1.18 (s,12 H, Bpin-CH_3), 4.74 (s, 2H, pinBOCH_2), 6.22(s, 1H, Ar-H), 6.72 (s, 2H, Ar-H); ^{13}C NMR (CDCl$_3$, 50.28 MHz), 23.54 (Bpin-CH$_3$), 58.16 (OCH$_2$Ph), 82.02 (Bpin-C), 125.87, 136.64, 141.40, 151.42, (Ar-C).



2,6-MePhCH$_2$OBpin (2n): product from hydroboration of 2,6-Dimethylbenzaldehyde.^{1}H NMR (CDCl$_3$, 200 MHz), δ 1.17 (s,12 H, Bpin-CH_3), 2.34 (s, 6H, PhCH_3), 4.91(s, 2H, pinBOCH_2), 6.93(m, 3H, Ar-H); ^{13}C NMR (CDCl$_3$, 50.28 MHz), 19.42, 21.11(PhCH$_3$), 24.52 (Bpin-CH$_3$), 61.29 (OCH$_2$Ph), 82.71 (Bpin-C), 128.05, 134.94, 137.60 (Ar-C).

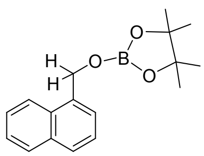


PhC$_3$H$_4$OBpin (2o): product from hydroboration of trans-Cinnamaldehyde.^{1}H NMR (CDCl$_3$, 200 MHz), δ 1.19 (s,12 H, Bpin-CH_3), 4.45 (d, 2H, ^{3}J=5.2 Hz,CH_2), 6.14-6.24 (m,

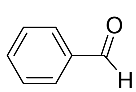
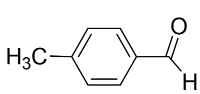
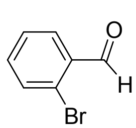


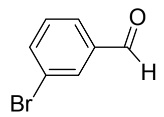
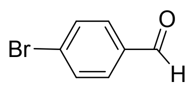
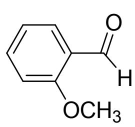
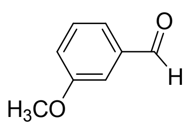
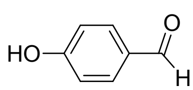
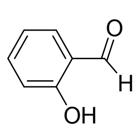
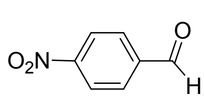
1H, CHC*H*), 6.50-6.58 (d, 1H, ^{3}J=15.7 Hz,ArC*H*), 7.22 (m, 5H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 50.28 MHz) 21.10(Bpin-*C*H_3), 65.18 (O*C*H_2Ph), 82.82 (Bpin-*C*), 126.35 (Ph*C*H*C*H), 127.41, 128.43, 130.55, 136.78, 137.59 (Ar-*C*).

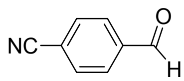
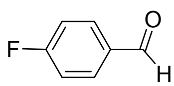
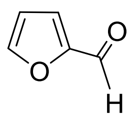
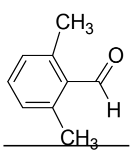
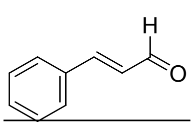
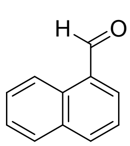
C_6H_5PhOBpin (2p): product from hydroboration of Napthaldehyde.^{1}H NMR ($CDCl_3$, 200 MHz), δ 1.19 (s,12 H, Bpin-C*H*$_3$), 5.32 (s, 2H, pinBOC*H*$_2$), 7.39 (m, 4H, Ar-*H*), 7.67 (m, 2H, Ar-*H*), 7.93 (m, 1H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 50.28 MHz) 25.20(Bpin-*C*H_3), 65.58(O*C*H_2Ph), 83.58 (Bpin-*C*), 124.03, 125.42, 125.91, 126.22, 126.66, 128.73, 129.11, 131.52, 134.13, 135.22, 138.26 (Ar-*C*).



5. Table S2 :TON and TOF table for aldehyde hydroboration.

Entry	Substrate	Time (min)	Catalyst Mol%	Yield (NMR)	TON	TOF[h^{-1}]
2a		40 min	0.5	83 %	166	249
2b		40 min	1	81 %	81	121.5
2c		40 min	2	96 %	48	72

2d		40 min	3	95 %	47.5	71.25
2e		40min	2	81 %	40.50	60.75
2f		40 min	2	83 %	41	62
2g		40 min	2	76%	38	57
2h		40 min	2	79 %	40	60
2i		40 min	2	71 %	35.5	53.25
2j		40 min	2	97 %	48.5	72.75

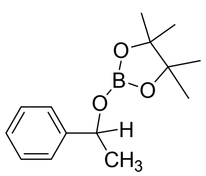
2k		40 min	2	80 %	40	60
2l		40 min	2	82%	41	62
2m		40 min	2	72 %	36	54
2n		40 min	1	95 %	94	142
2o		40 min	2	91 %	46	69
2p		40 min	2	83 %	42	63

6. **General Procedure for Catalytic Hydroboration of Ketone:**

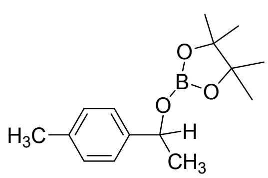
Ketone (0.25 mmol), pinacolborane (0.25mmol), LCaI (3mol%) [benzene (1ml)] were charged in Schlenk tube inside glove box. The reaction mixture was allowed to run at room temperature. The progress of the reaction was monitored by ^{1}H NMR, which indicated the completion of the reaction by the appearance of a new CH peak. Upon completion of reaction, the solvent was removed using high vacuum in Schlenk line and mesitylene as internal standard, (0.25mmol) was added while making the NMR in $CDCl_3$.

7. **Spectroscopic data for ketone hydroboration products:**

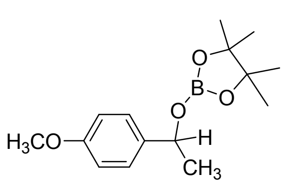
(Ph)(Me)CHOBpin (3a):product from hydroboration of acetophenone.^{1}H NMR ($CDCl_3$, 200 MHz), δ 1.13 (s,6 H, Bpin-CH_3), 1.16 (s, 6H, Ar-CH_3), 1.40 (d, $^{3}J_{HH}$ = 6.3 Hz, 3H, OCHCH_3), 5.18 (q, 1H, pinBOC*H*), 7.17 (m, 5H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 50.28 MHz), 21.10 (Bpin-*C*H_3), 72.51 (O*C*H_2Ph), 82.66 (Bpin-*C*), 125.25, 127.0, 128.11, 137.60, 144.49 (Ar-*C*).



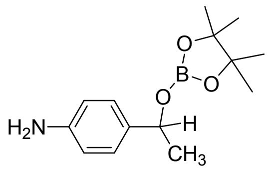
(4-CH$_3$Ph)(Me)CHOBpin (3b):product from hydroboration of 4-Methylacetophenone.^{1}H NMR ($CDCl_3$, 200 MHz), δ 1.13 (s,6 H, Bpin-CH_3), 1.16 (s, 6H, Ar-CH_3), 1.38 (d, $^{3}J_{HH}$ = 6.3 Hz, 3H, OCHCH_3), 2.24 (s, 3H, PhCH_3), 5.16 (q, 1H, pinBOC*H*), 7.01 (d,$^{3}J_{HH}$ = 7.4 Hz, 2H, Ar-*H*), 7.16 (d,$^{3}J_{HH}$ = 8.6 Hz, 2H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 50.28 MHz), 21.24(Ph*C*H3), 24.57 (Bpin-*C*H_3), 25.97 (OCH*C*H_3), 72.49 (O*C*H_2Ph), 83.14 (Bpin-*C*), 126.96, 128.39, 130.77, 137.75, 145.48 (Ar-*C*).



(4-OCH$_3$Ph)(Me)CHOBpin (3c):product from hydroboration of 4-Methoxyacetophenone.^{1}H NMR ($CDCl_3$, 200 MHz), δ 1.21 (s,6 H, Bpin-CH_3), 1.23 (s, 6H, Ar-CH_3), 1.46 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, OCHCH_3), 3.78 (s, 3H, PhOCH_3), 5.19 (q, 1H, pinBOC*H*), 6.87 (d,$^{3}J_{HH}$ = 8.1 Hz, 2H, Ar-*H*), 7.31(d, $^{3}J_{HH}$ = 8.9 Hz, 2H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 50.28 MHz),23.48 (Bpin-*C*H_3), 24.31 (OCH*C*H_3), 54.16 (PhO*C*H3), 71.20 (O*C*H_2Ph),81.63 (Bpin-*C*), 125.87, 129.58, 135.78, 136.65, 157.70(Ar-*C*).

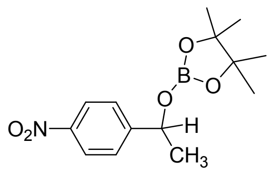


(4-NH_2Ph)(Me)CHOBpin (3d):product from hydroboration of 4-Aminoacetophenone.[1]H NMR



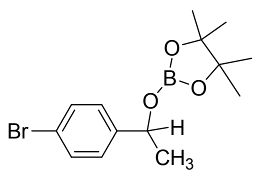
($CDCl_3$, 200 MHz), δ 1.68 (s, 12H, Bpin-CH_3),1.94 (d,$^3J_{HH}$ = 6.5 Hz, 3H, OCHCH_3), 4.09 (s, 2H, PhONH_2), 5.63 (q, 1H, pinBOC*H*), 7.11(d, $^3J_{HH}$ = 7.8 Hz, 2H, Ar-*H*), 7.61 (d,$^3J_{HH}$ = 8.7 Hz, 2H, Ar-*H*); [13]C NMR ($CDCl_3$, 50.28 MHz), 21.22 (OCH*C*H_3), 24.63 (Bpin-*C*H_3), 65.59 (O*C*H_2Ph),83.43(Bpin-*C*), 123.62, 126.93, 128.36, 137.72, 146.65(Ar-*C*).

(4-NO_2Ph)(Me)CHOBpin (3e):product from hydroboration of 4-Nitrolacetophenone.[1]H NMR



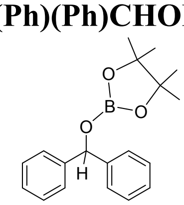
($CDCl_3$, 200 MHz), δ 1.71 (s,6 H, Bpin-CH_3), 1.73 (s, 6H, Ar-CH_3), 2.02(d, $^3J_{HH}$ = 6.4 Hz, 3H, OCHCH_3), 5.82 (q, 1H, pinBOC*H*), 7.96 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Ar-*H*), 8.16 (d,$^3J_{HH}$ = 8.0 Hz, 2H, Ar-*H*); [13]C NMR ($CDCl_3$, 50.28 MHz), 21.22(OCH*C*H_3), 24.57(Bpin-*C*H_3), 71.72 (O*C*H_2Ph), 83.18(Bpin-*C*), 126.93, 129.31, 131.59, 133.84, 137.72(Ar-*C*).

(4-BrPh)(Me)CHOBpin (3f):product from hydroboration of 4-Bromoacetophenone.[1]H NMR



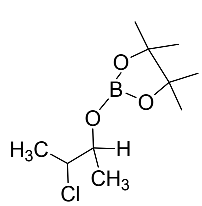
($CDCl_3$, 200 MHz), δ 1.12 (s,6 H, Bpin-CH_3), 1.15 (s, 6H, Ar-CH_3), 1.35 (d, $^3J_{HH}$ = 6.5 Hz ,3H, OCHCH_3), 5.12 (q, 1H, pinBOC*H*), 7.16 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-*H*), 7.26 (d,$^3J_{HH}$ = 8.6 Hz, 2H, Ar-*H*); [13]C NMR ($CDCl_3$, 50.28 MHz), 21.22(OCH*C*H_3), 23.80 (Bpin-*C*H_3), 68.91 (O*C*H_2Ph), 71.26 (Bpin-*C*), 120.14, 127.59, 130.55, 136.94, 142.87 (Ar-*C*).

(Ph)(Ph)CHOBpin (3g):product from hydroboration of Benzophenone.[1]H NMR ($CDCl_3$, 200



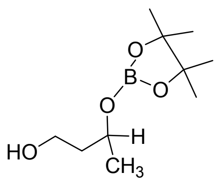
MHz), δ 1.11 (s, 12H, Bpin-CH_3), 6.12 (s, 1H, pinBOC*H*), 7.21 (m, 10H Ar-*H*); [13]C NMR ($CDCl_3$, 50.28 MHz), 20.46 (Bpin-*C*H_3), 82.25 (Bpin-*C*), 125.77, 126.18, 126.56, 127.51, 129.33, 136.94, 142.38, 143.17 (Ar-*C*).

(2-ClEt)(Me)CHOBpin (3h):product from hydroboration of 2-Chloroethylmethylketone.[1]H NMR



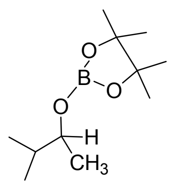
($CDCl_3$, 200 MHz), δ 1.18 (s,12 H, Bpin-CH_3), 1.40 (dd,$^3J_{HH}$ = 6.4 Hz, 3H, OCHCH_3), 4.19 (q, 1H, pinBOC*H*); [13]C NMR ($CDCl_3$, 50.28 MHz)18.61 (CCl*C*H_3), 20.03 (OCH*C*H_3), 21.75 (Bpin-*C*H_3), 61.24 (*C*ClCH_3), 74.36 (BpinO*C*CH_3), 83.47 (Bpin-*C*).

(3-OHEt)(Me)CHOBpin (3i):product from hydroboration of 3-Hydroxyoropylmethylketone.[1]H



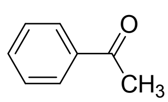
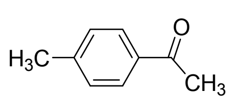
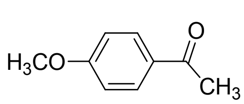
NMR ($CDCl_3$, 200 MHz), δ 1.17 (s,12H, Bpin-CH_3), 1.37 (m, 2H, $HOCH_2CH_2$),1.39 (dd, $^3J_{HH}$ = 6.4 Hz, 3H, OCHCH_3), 3.85 (q, 1H, pinBOC*H*), 4.16 (m, 2H); ^{13}C NMR ($CDCl_3$, 50.28 MHz), 20.16 (OCH*C*H_3), 23.54(Bpin-*C*H_3), 60.85 (OH*C*H_2), 66.92 ($OHCH_2CH_2$), 83.18 (Bpin-*C*).

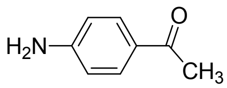
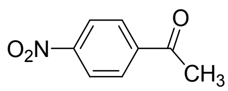
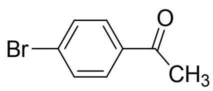
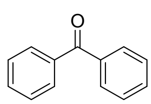
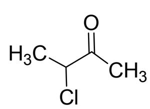
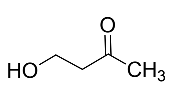
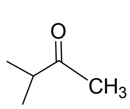
(^{i}Pr)(Me)CHOBpin (3j):product from hydroboration of Methyl isopropyl ketone.[1]H NMR ($CDCl_3$,



200 MHz), δ0.79 (d,$^3J_{HH}$= 2.79, 3H, Et*H*), 0.81(d,$^3J_{HH}$= 2.8Hz, 3H, Et*H*), 1.04 (d, $^3J_{HH}$= 6.09Hz, 3H, Me*H*), 1.16 (s,12 H, Bpin-CH_3), 1.56 (m,1H,Et*H*CH), 3.87 (q, 1H, pinBOC*H*); ^{13}C NMR ($CDCl_3$, 50.28 MHz),18.07 (Et*C*) , 21.12 (OCH*C*H_3), 24.47(Bpin-*C*H_3), 34.31 (Et*C*HCHOBpin), 82.32(Bpin-*C*).

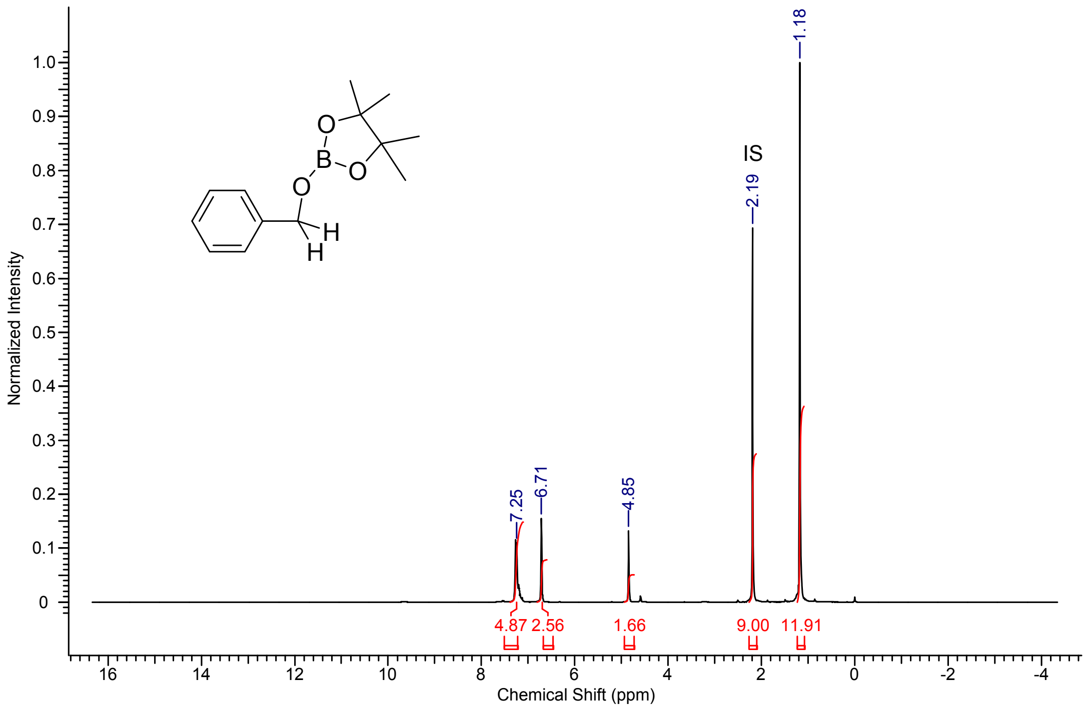
8. Table S3: TON and TOF table for ketone hydroboration:

Entry	Substrate	Time (h)	Catalyst mol%	Yield (NMR)	TON	TOF[h^{-1}]
3a		5 h	3	95 %	47	9.5
b		5 h	3	79 %	26	5.2
3c		5 h	3	78 %	26	5.2

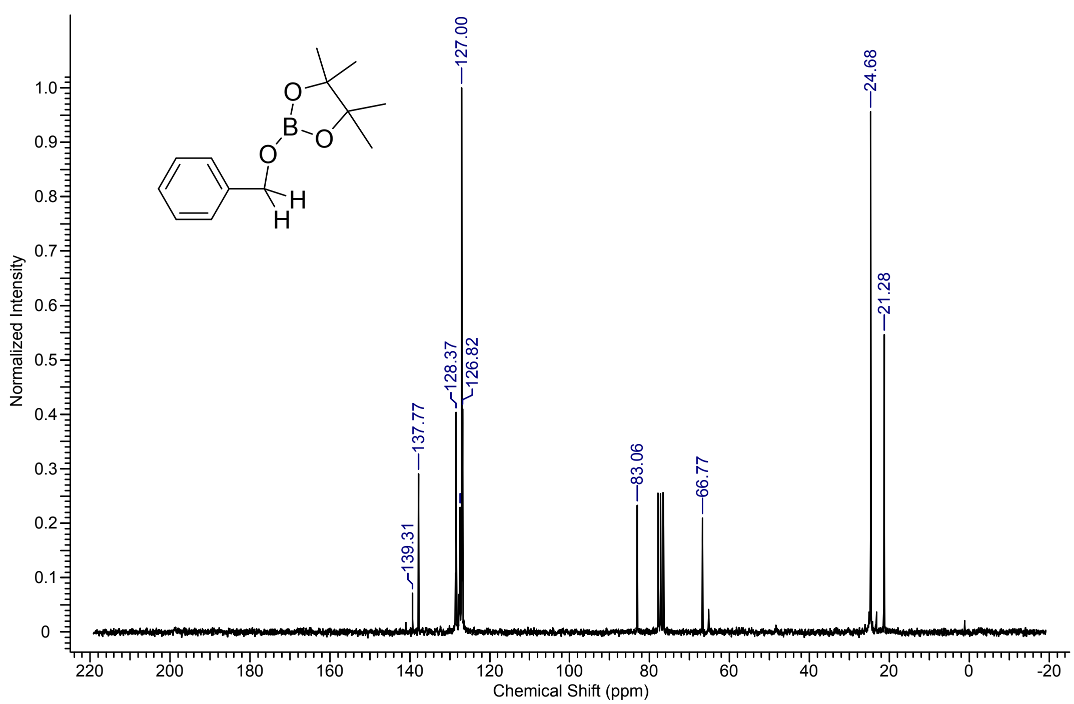
3d		5 h	3	80 %	40	8
3e		5 h	3	73 %	24	4.8
3f		5 h	3	83 %	27	5.5
3g		5 h	3	86 %	43	8.6
3h		5 h	3	75 %	23.6	4.73
3i		5 h	3	64 %	21.3	4.27
3j		5 h	3	72 %	23.3	4.67

9. NMR Spectra

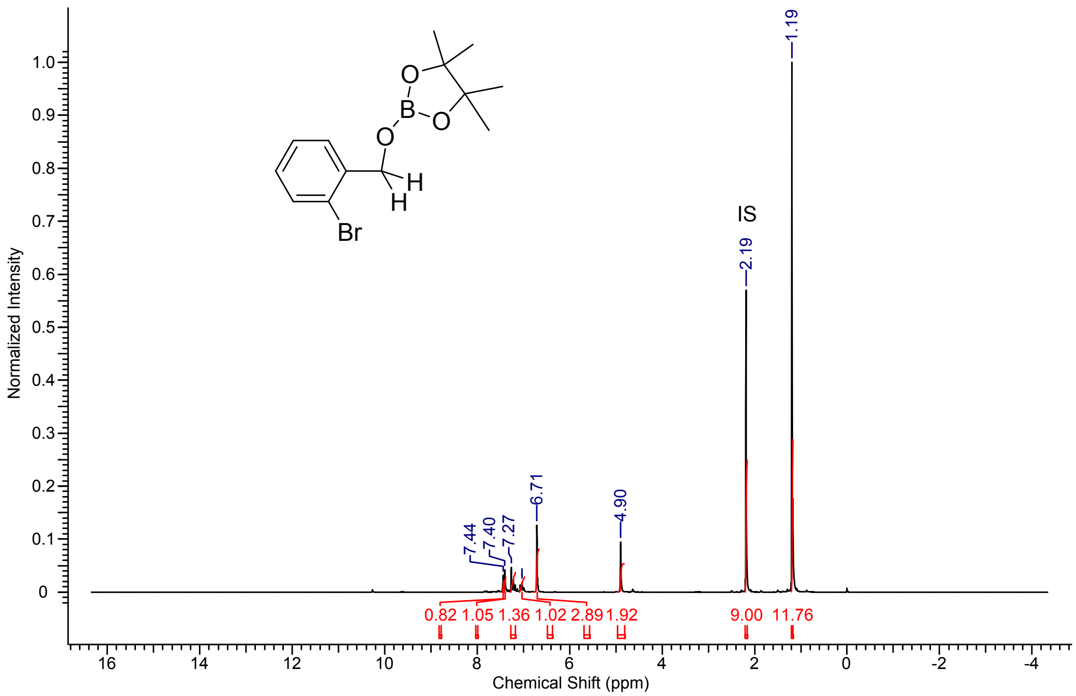
^1H NMR of $PhCH_2OBpin$ ($CDCl_3$, 200 MHz):



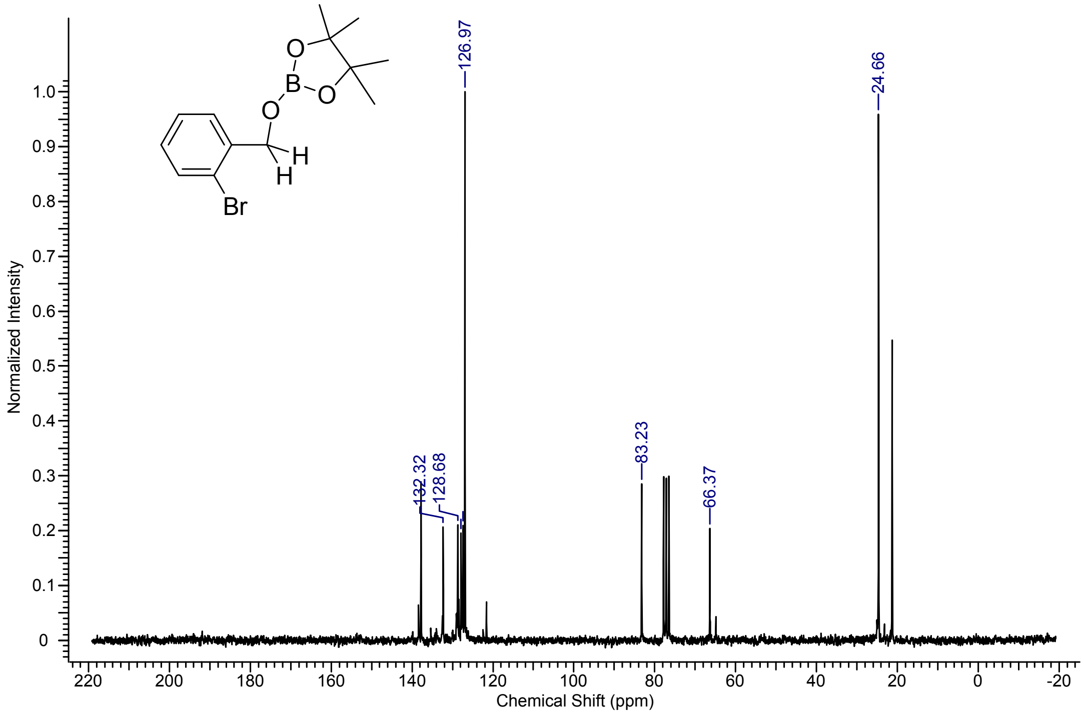
^{13}C NMR of $PhCH_2OBpin$ ($CDCl_3$, 50.28MHz):



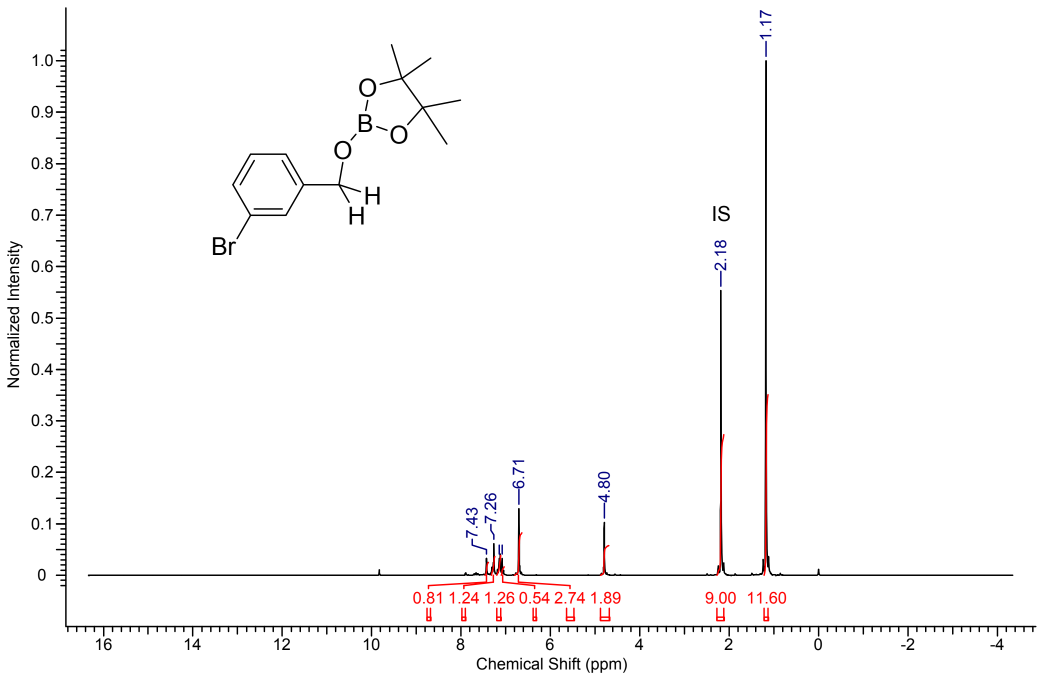
^{1}H NMR of 2-BrPhCH$_2$OBpin (CDCl$_3$, 200 MHz):



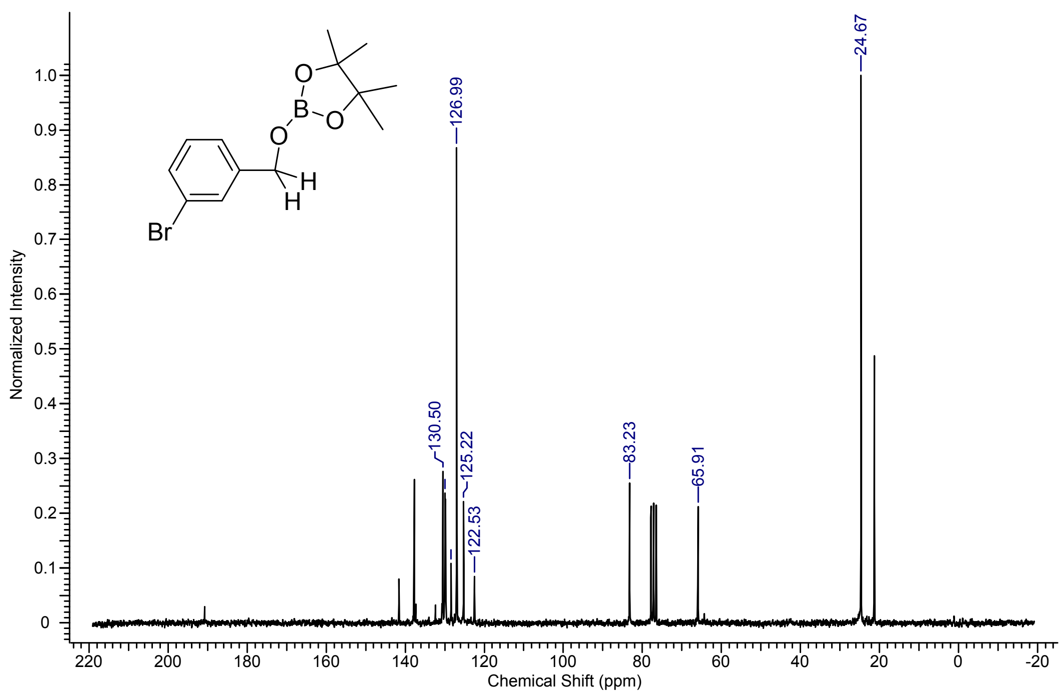
^{13}C NMRof2-BrPhCH$_2$OBpin(CDCl$_3$, 50.28 MHz)



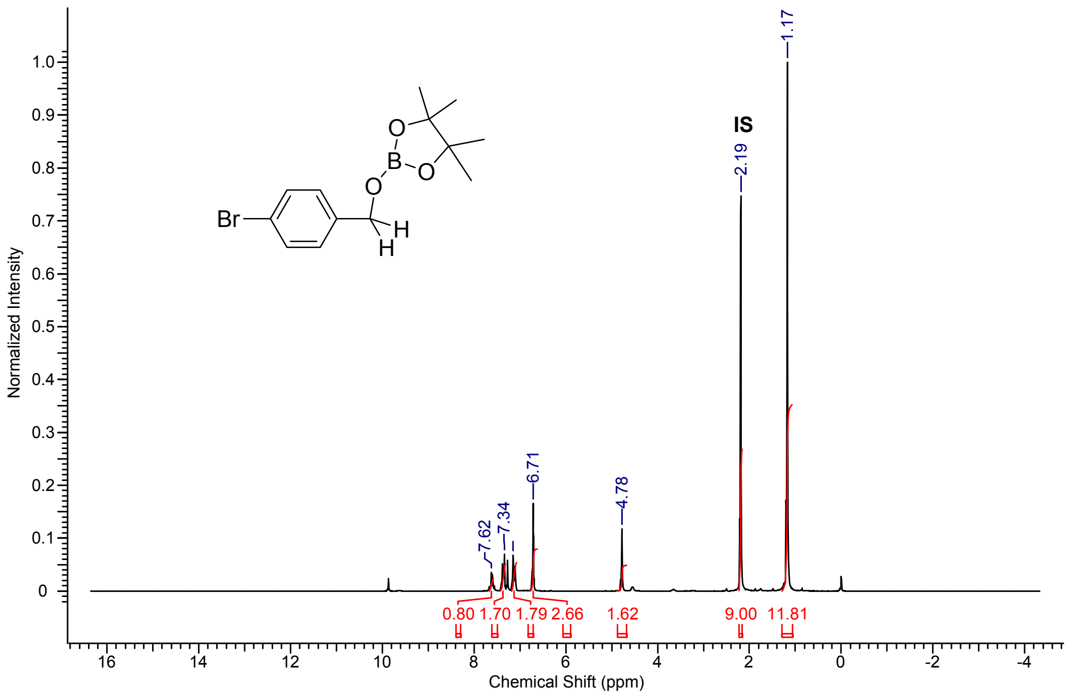
^{1}H NMR of 3-BrPhCH$_2$OBpin ($CDCl_3$, 200 MHz):



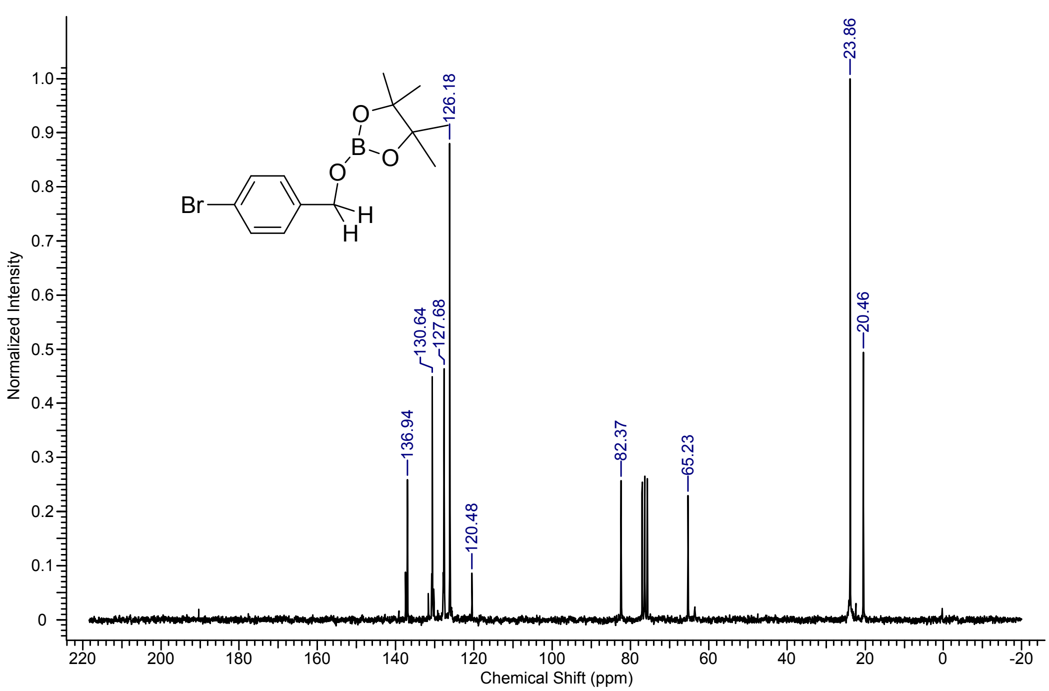
^{13}C NMRof3-BrPhCH$_2$OBpin($CDCl_3$, 50.28 MHz)



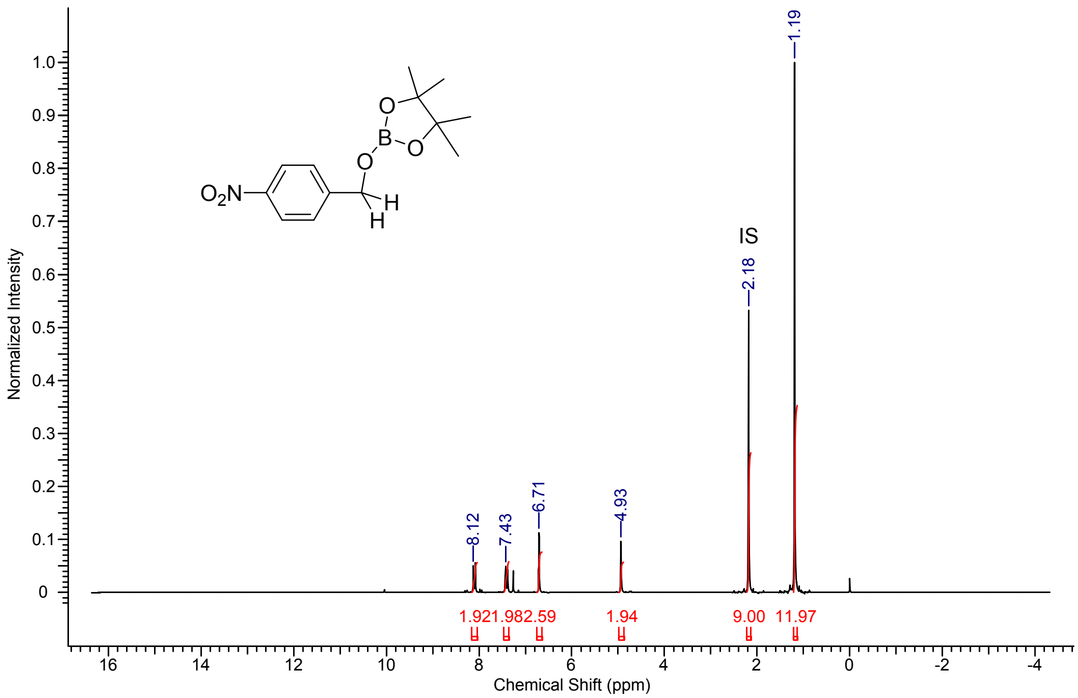
[1]H NMR of 4-BrPhCH_2OBpin ($CDCl_3$, 200 MHz):



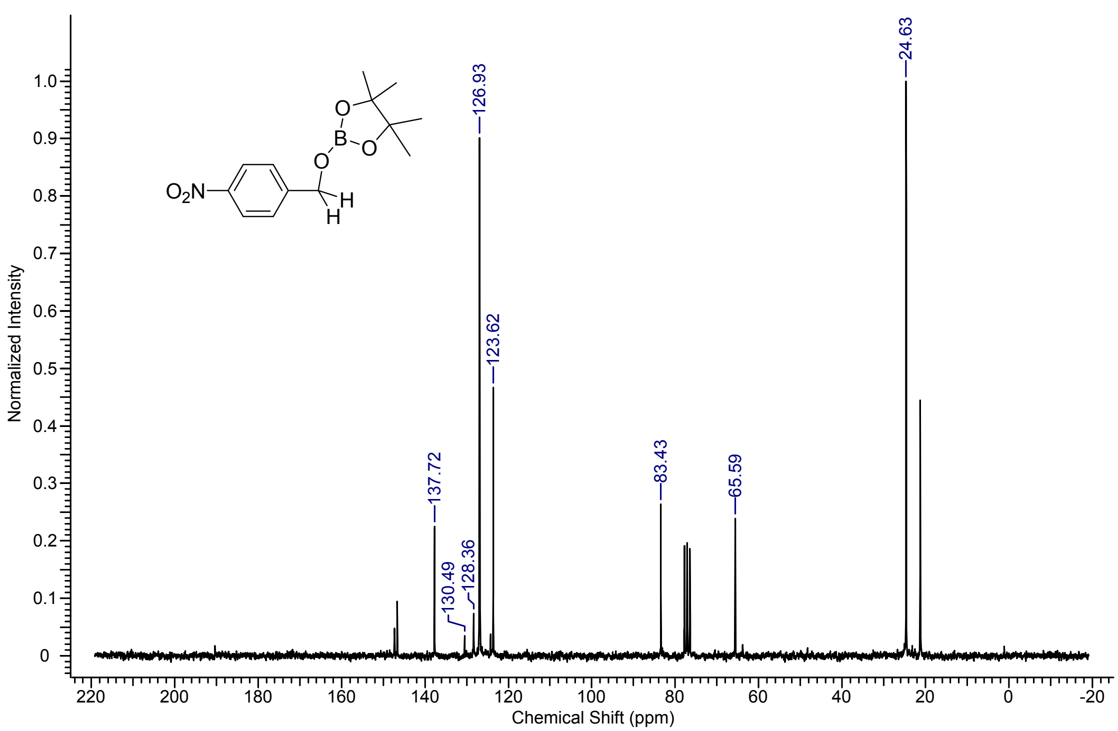
[13]C NMR of 4-BrPhCH_2OBpin ($CDCl_3$, 200 MHz):



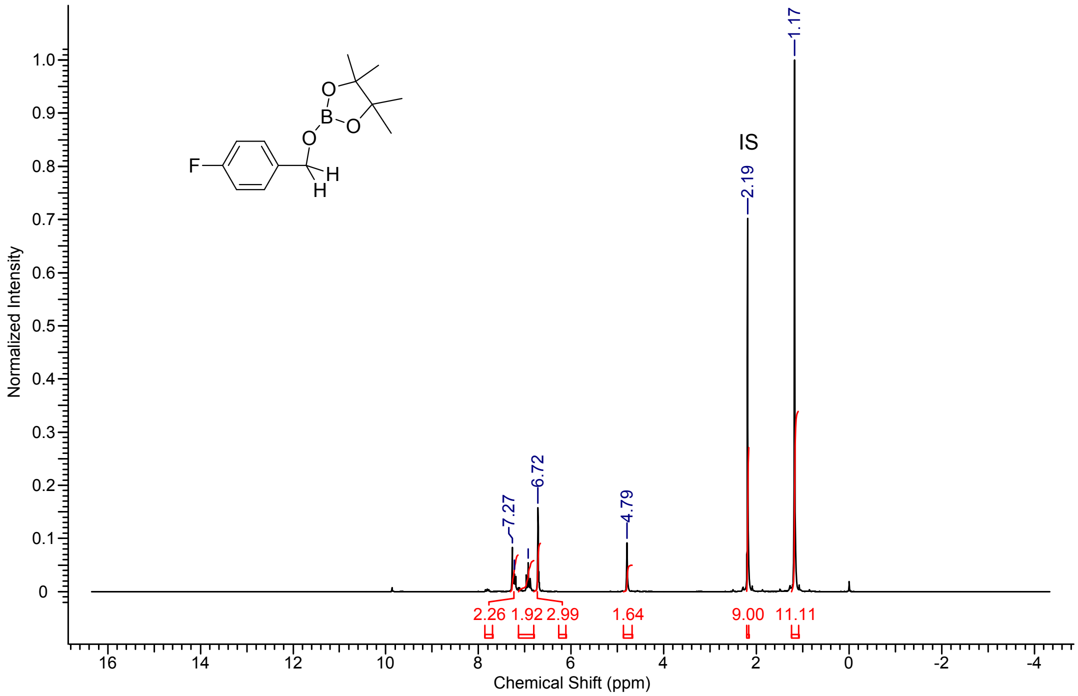
^{1}H NMR of 4-NO_2PhCH_2OBpin ($CDCl_3$, 200 MHz):



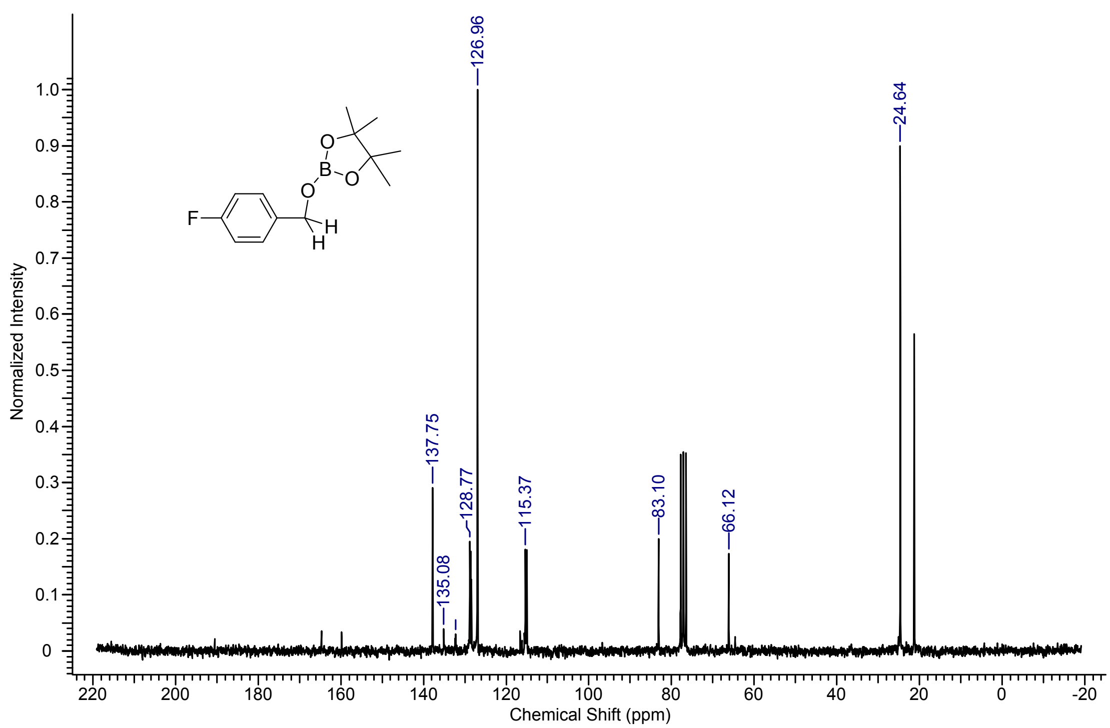
^{13}C NMR of 4-NO_2PhCH_2OBpin ($CDCl_3$, 200 MHz):



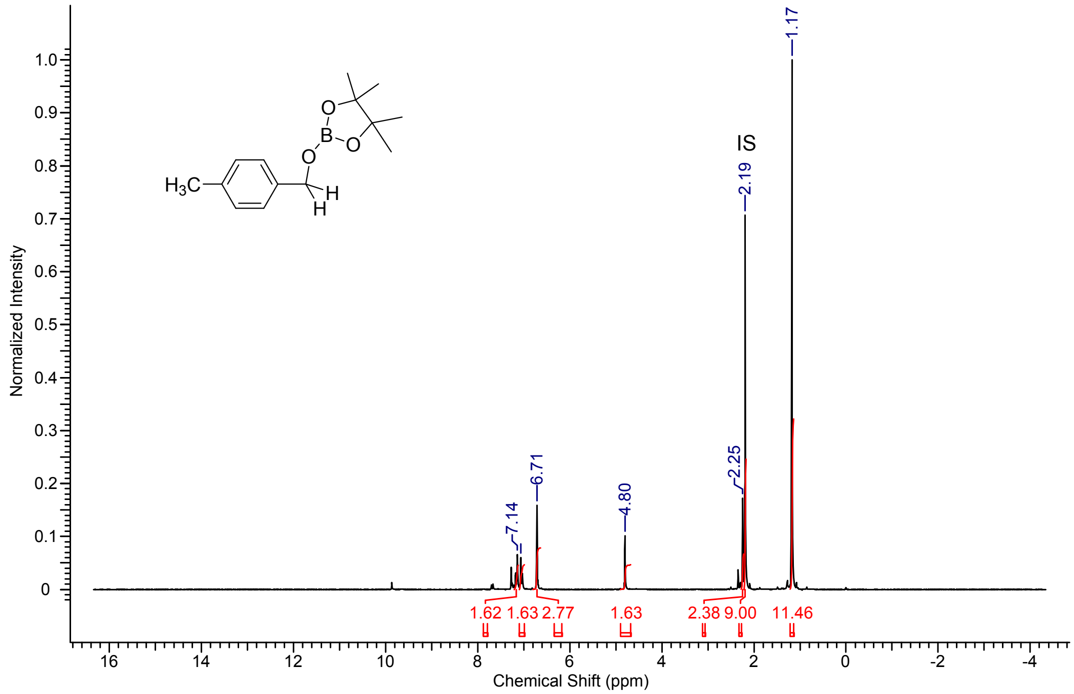
^{1}H NMR of 4-FPhCH$_2$OBpin (CDCl$_3$, 200 MHz):



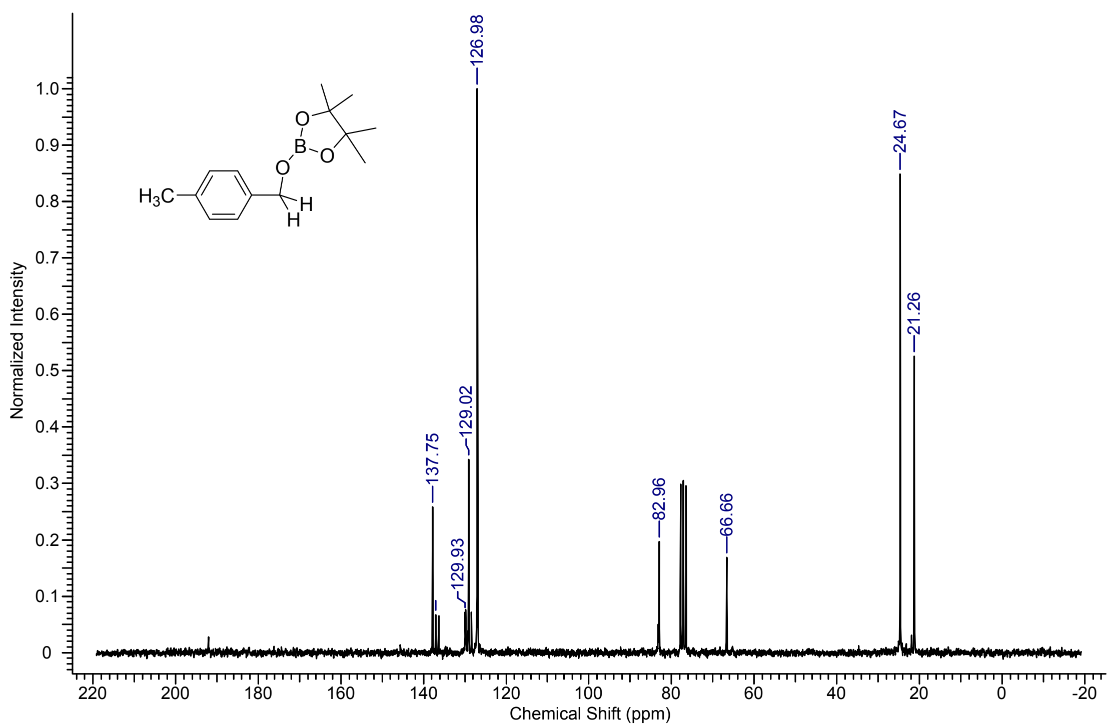
^{13}C NMRof4-FPhCH$_2$OBpin(CDCl$_3$, 50.28 MHz):



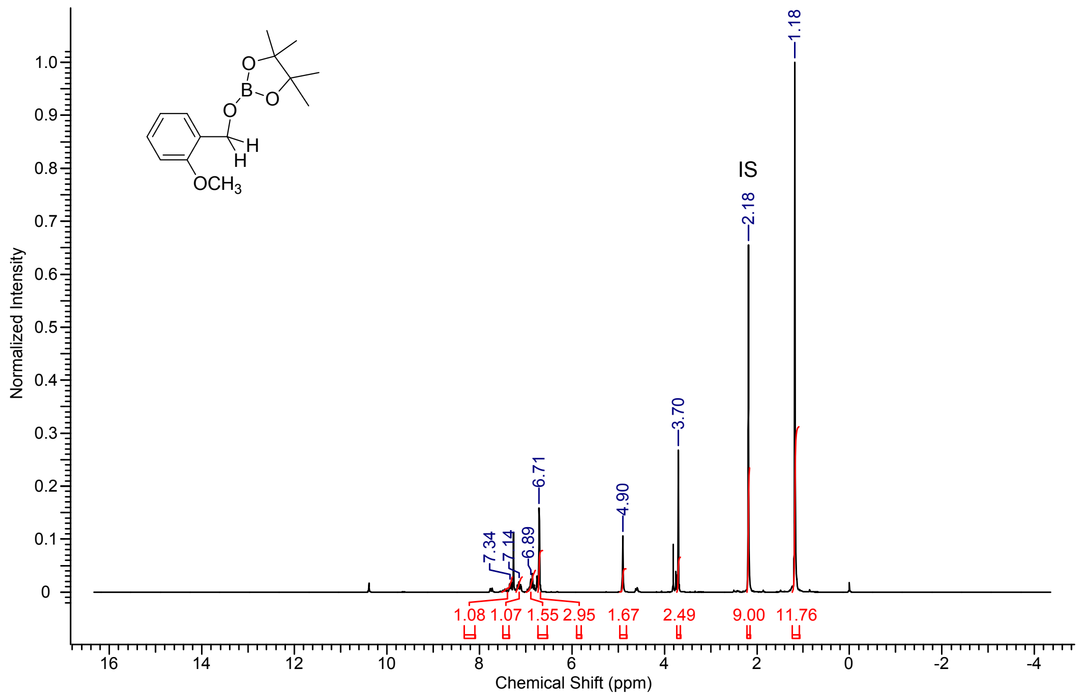
^{1}H NMR of 4-CH_3PhCH_2OBpin ($CDCl_3$, 200 MHz):



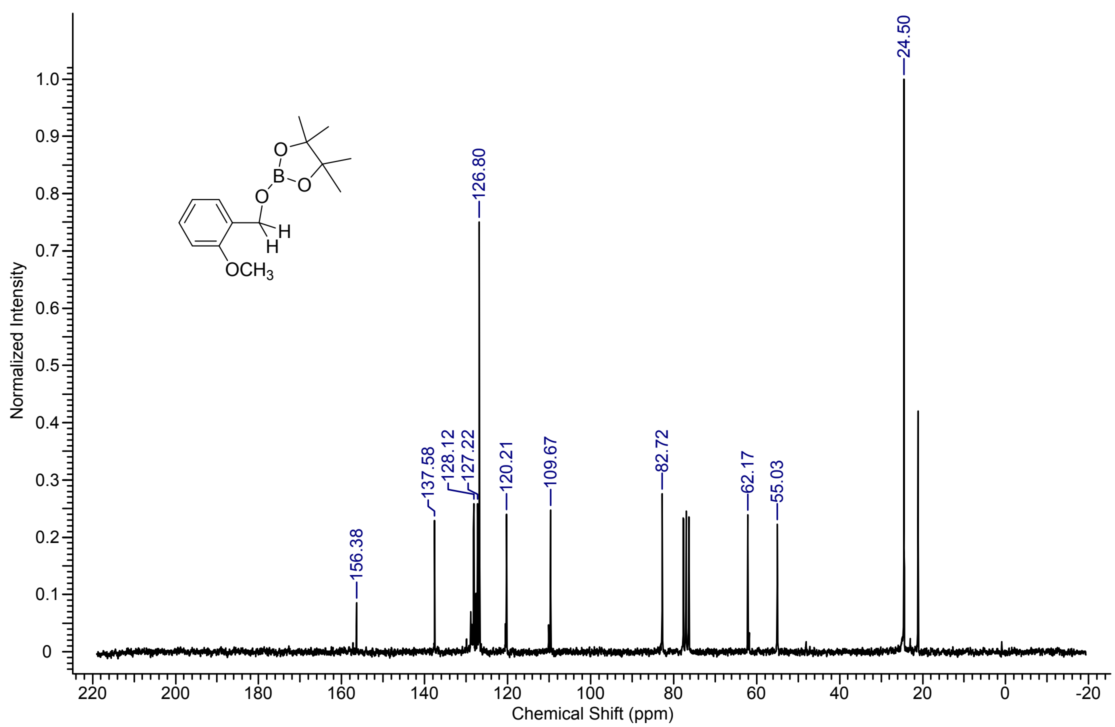
^{13}C NMRof4-CH_3PhCH_2OBpin($CDCl_3$, 50.28 MHz):



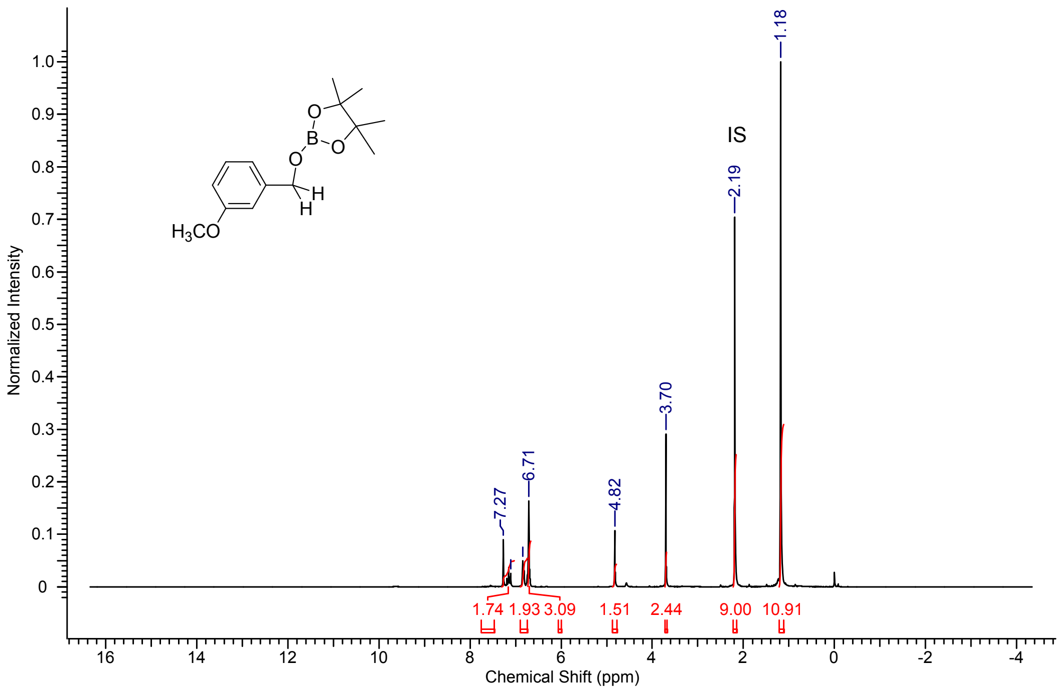
^{1}H NMR of 2-OCH_3PhCH_2OBpin ($CDCl_3$, 200 MHz):



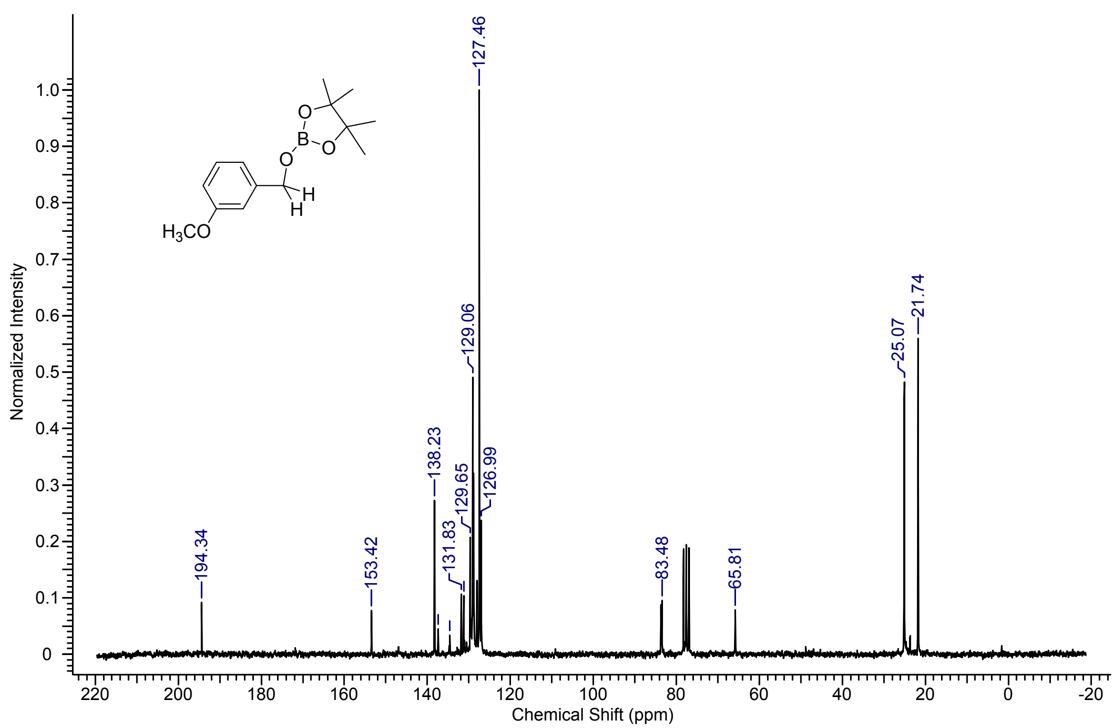
^{13}C NMRof2-OCH_3PhCH_2OBpin($CDCl_3$, 50.28 MHz):



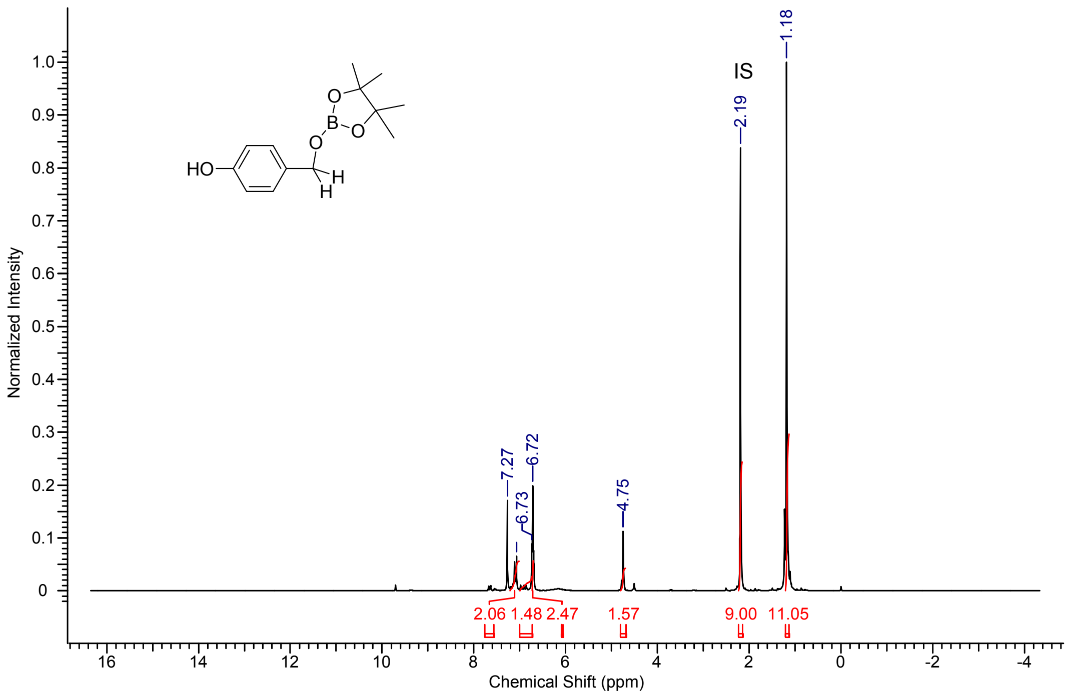
[1]H NMR of 3-OCH_3PhCH_2OBpin ($CDCl_3$, 200 MHz):



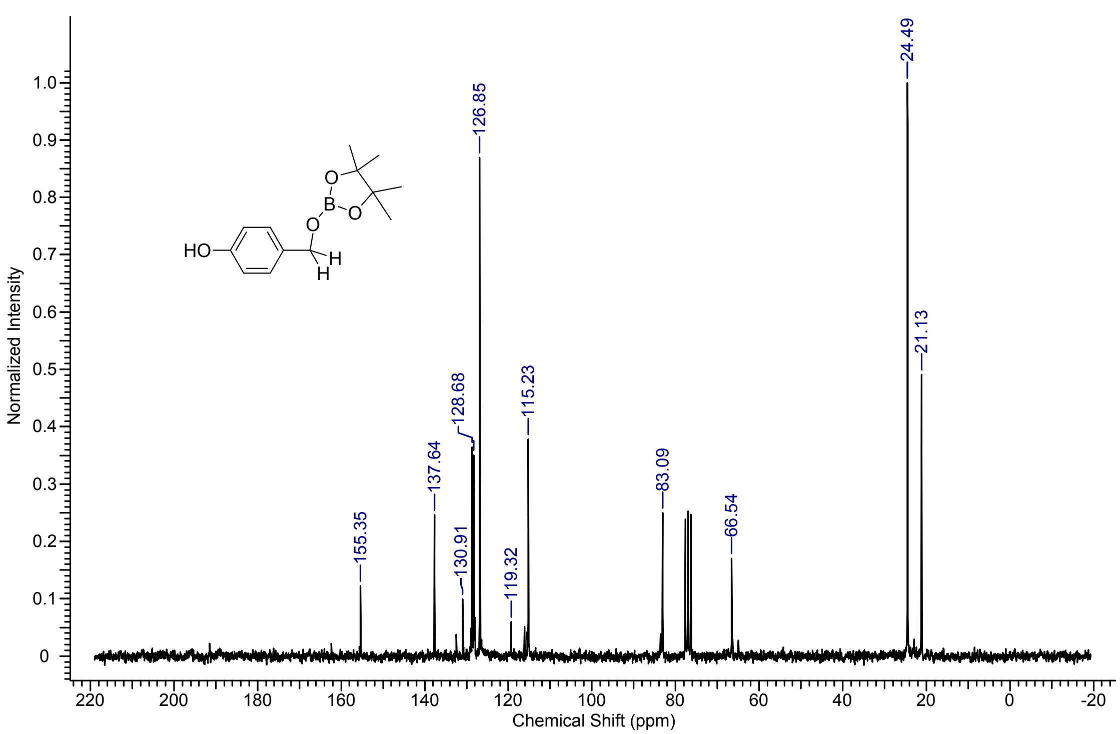
[13]C NMRof3-OCH_3PhCH_2OBpin($CDCl_3$, 50.28 MHz):



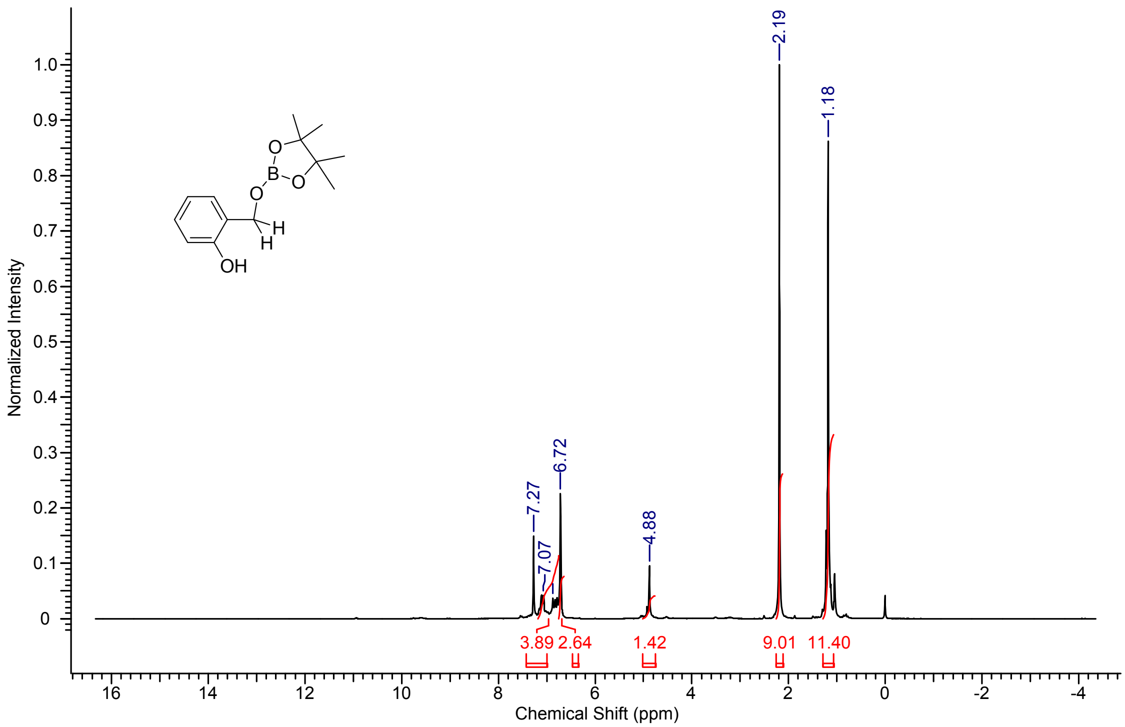
^{1}H NMR of 4-OHPhCH$_2$OBpin ($CDCl_3$, 200 MHz):



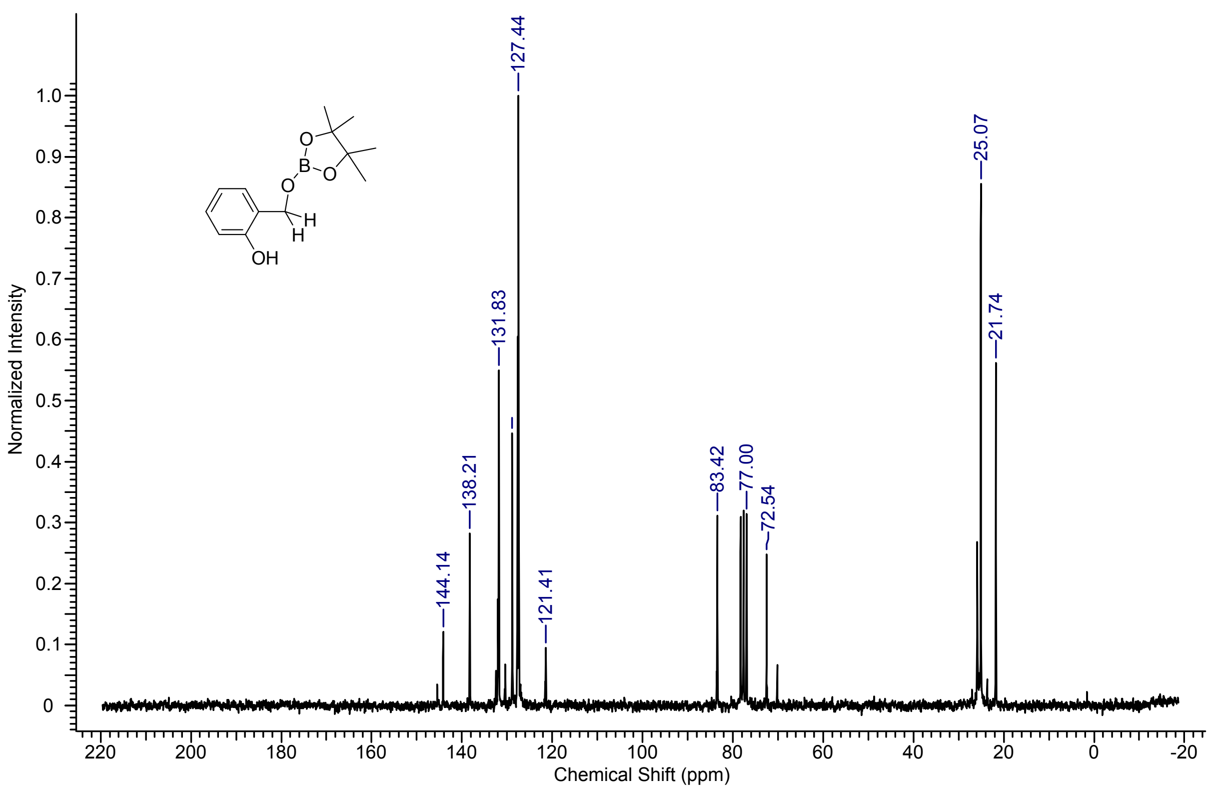
^{13}C NMRof4-OHPhCH$_2$OBpin($CDCl_3$, 50.28 MHz):



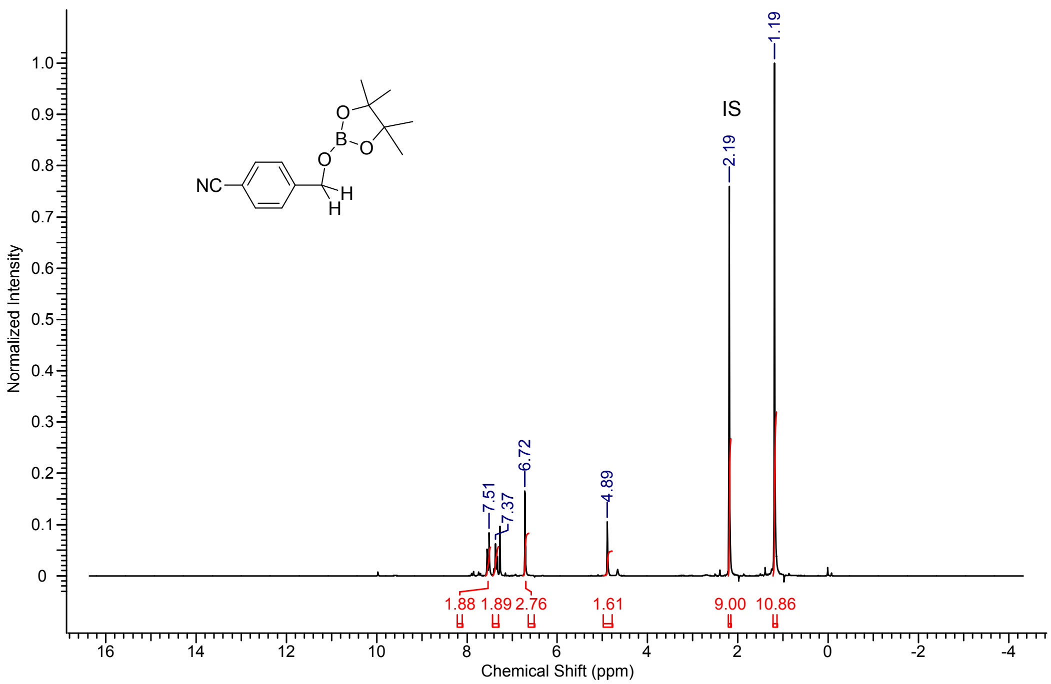
^{1}H NMR of 2-OHPhCH$_2$OBpin (CDCl$_3$, 200 MHz):



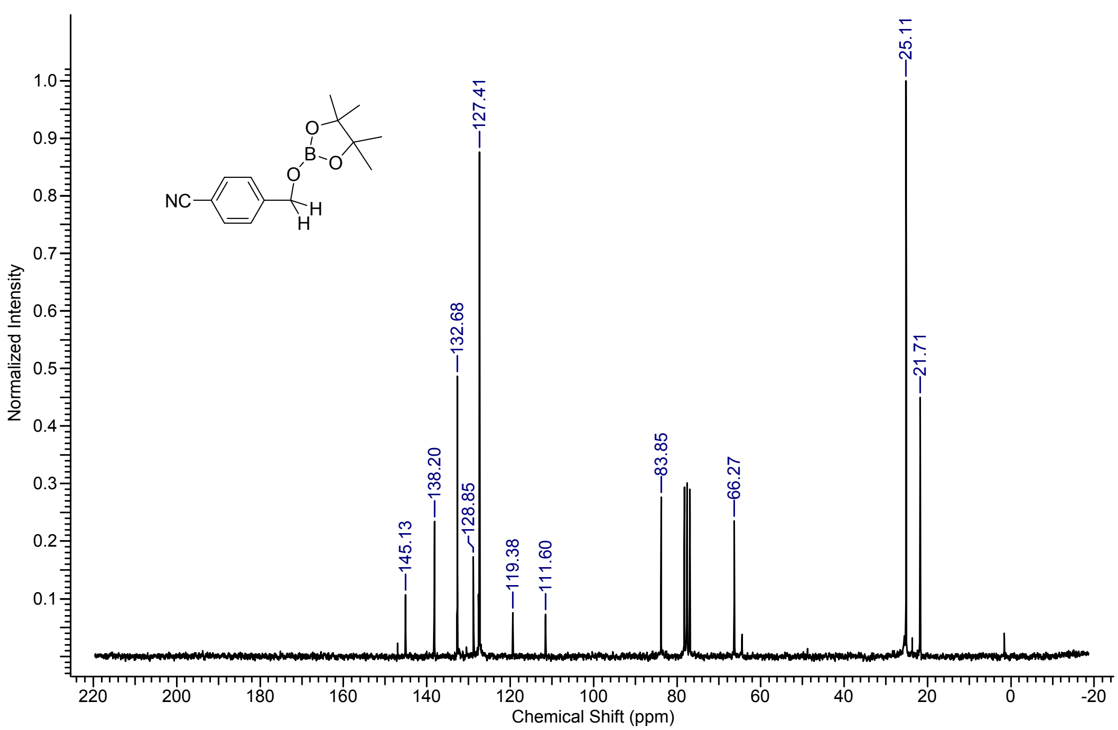
^{13}C NMR of 2-OHPhCH$_2$OBpin(CDCl$_3$, 50.28 MHz):



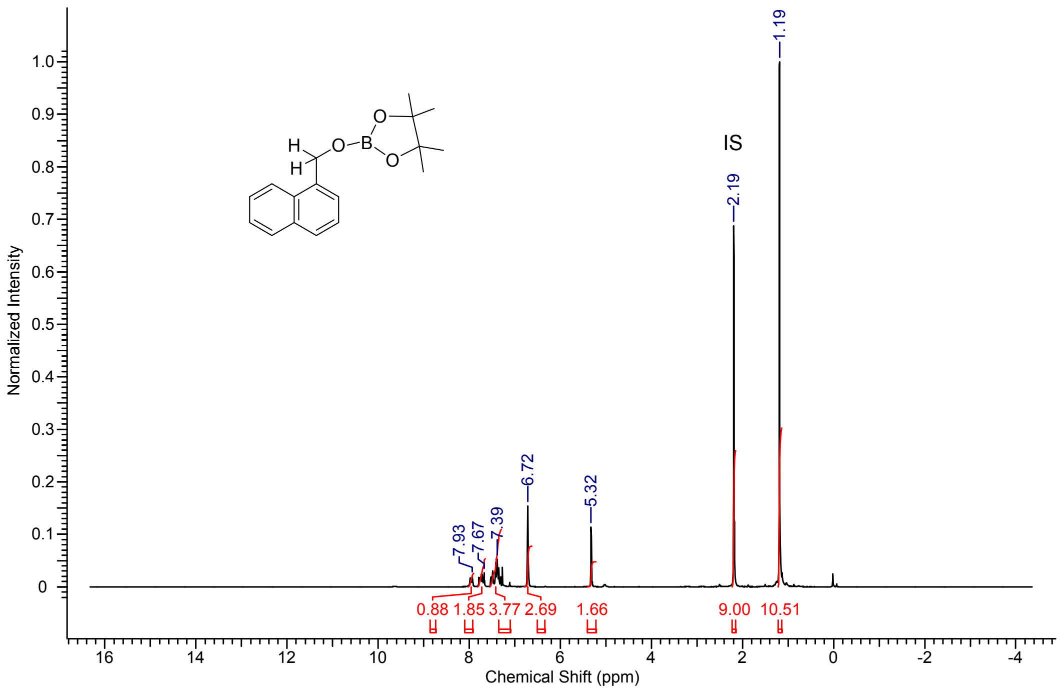
[1]H NMR of 4-CNPhCH$_2$OBpin (CDCl$_3$, 200 MHz):



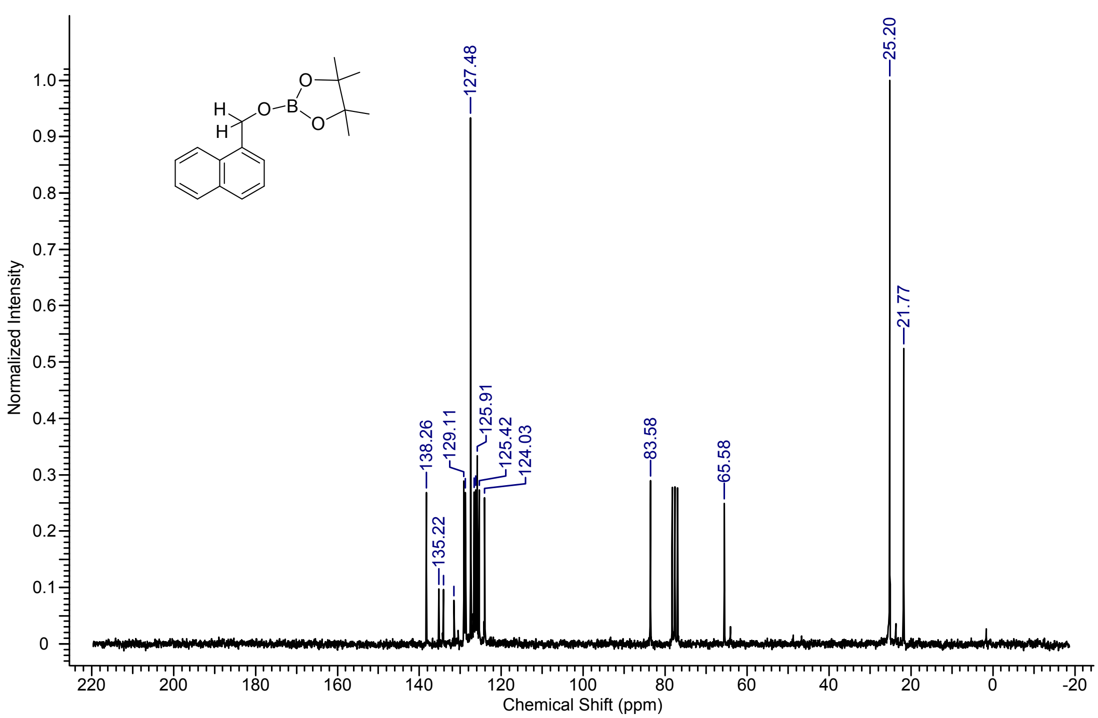
[13]C NMR of 4-CNPhCH$_2$OBpin (CDCl$_3$, 50.28 MHz):



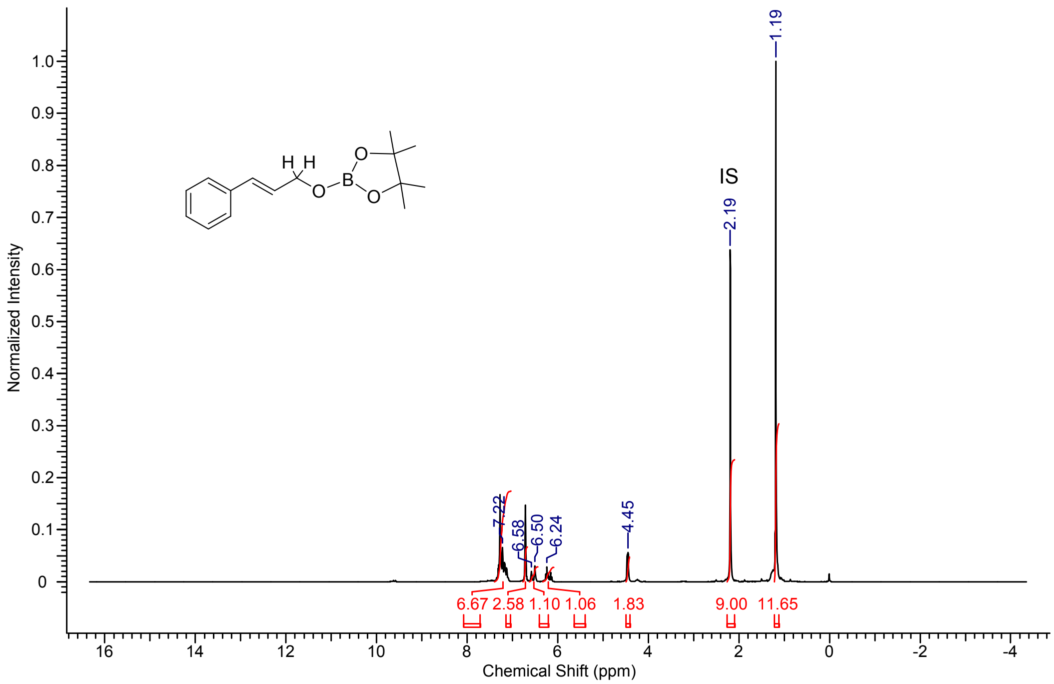
^{1}H NMR of $C_6H_5PhCH_2OBpin$ ($CDCl_3$, 200 MHz):



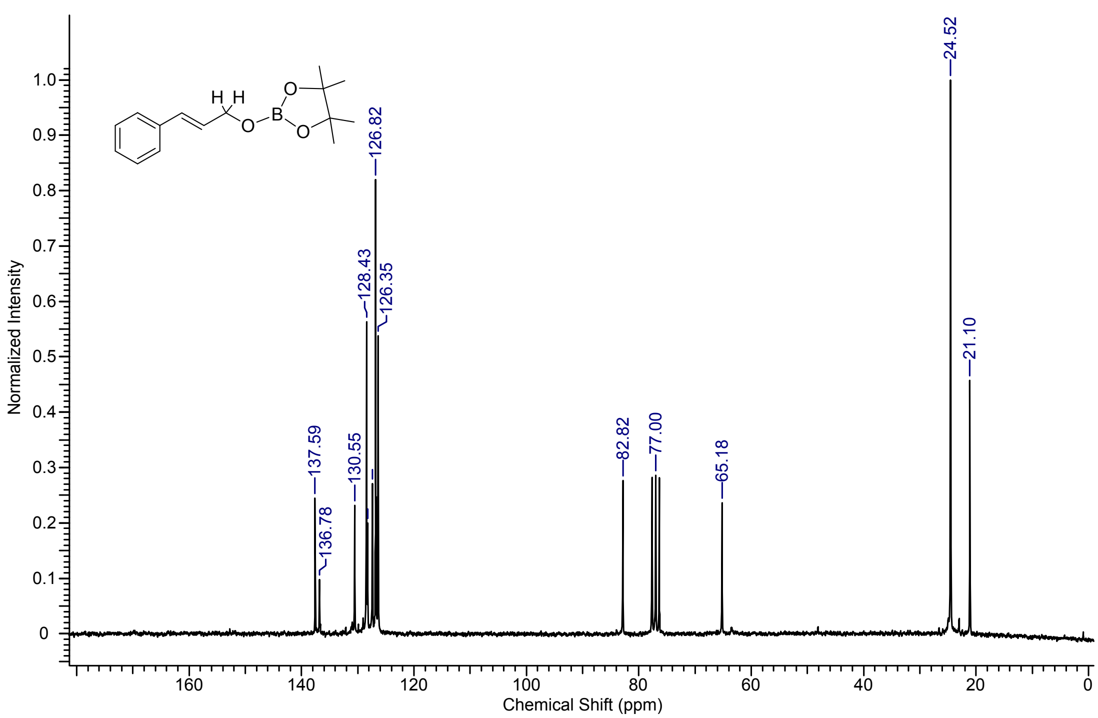
^{13}C NMR of $C_6H_5PhCH_2OBpin$ ($CDCl_3$, 50.28 MHz):



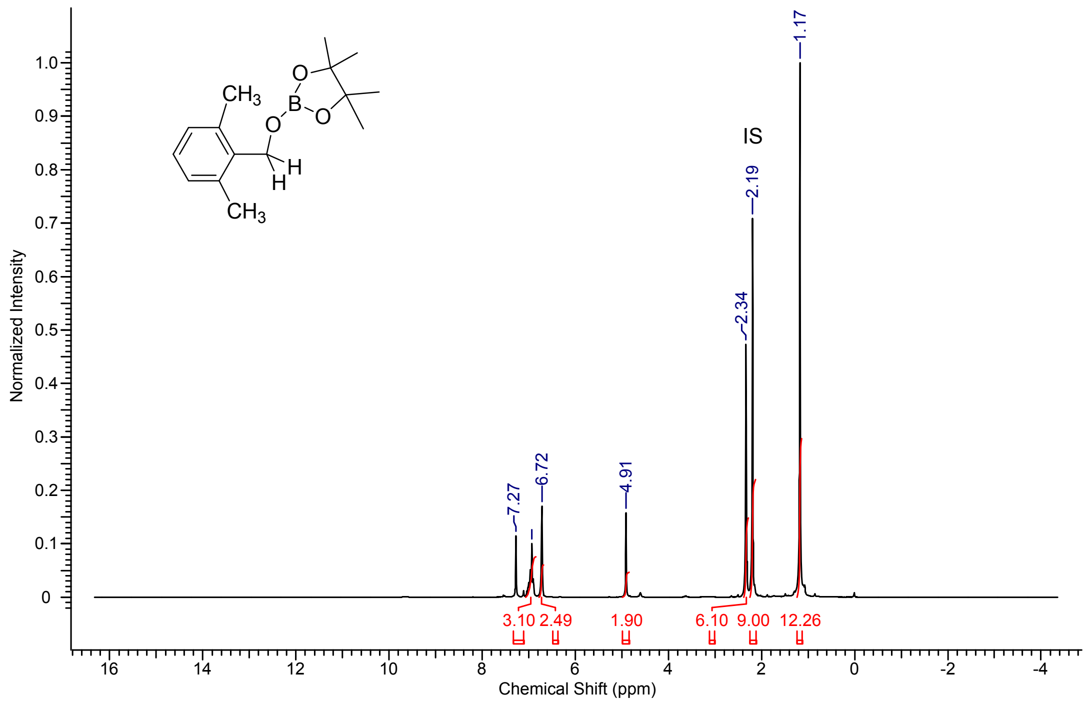
^{1}H NMR of PhC_3H_4OBpin ($CDCl_3$, 200 MHz):



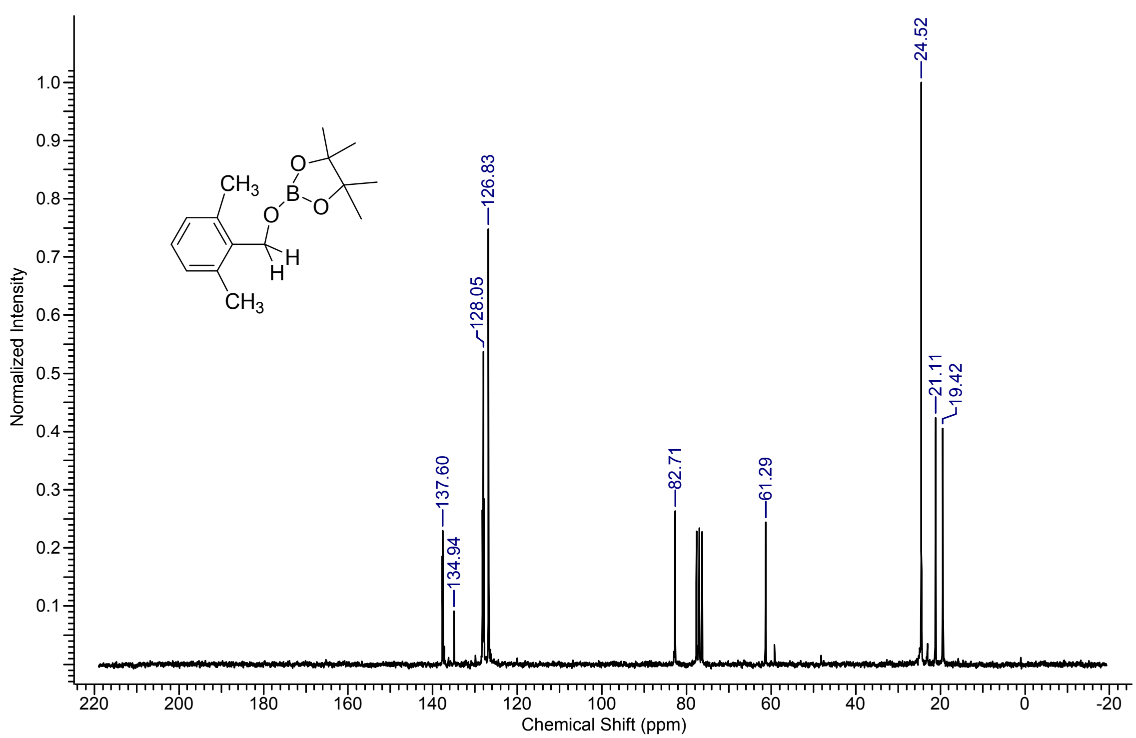
^{13}C NMR of PhC_3H_4OBpin ($CDCl_3$, 50.28 MHz):



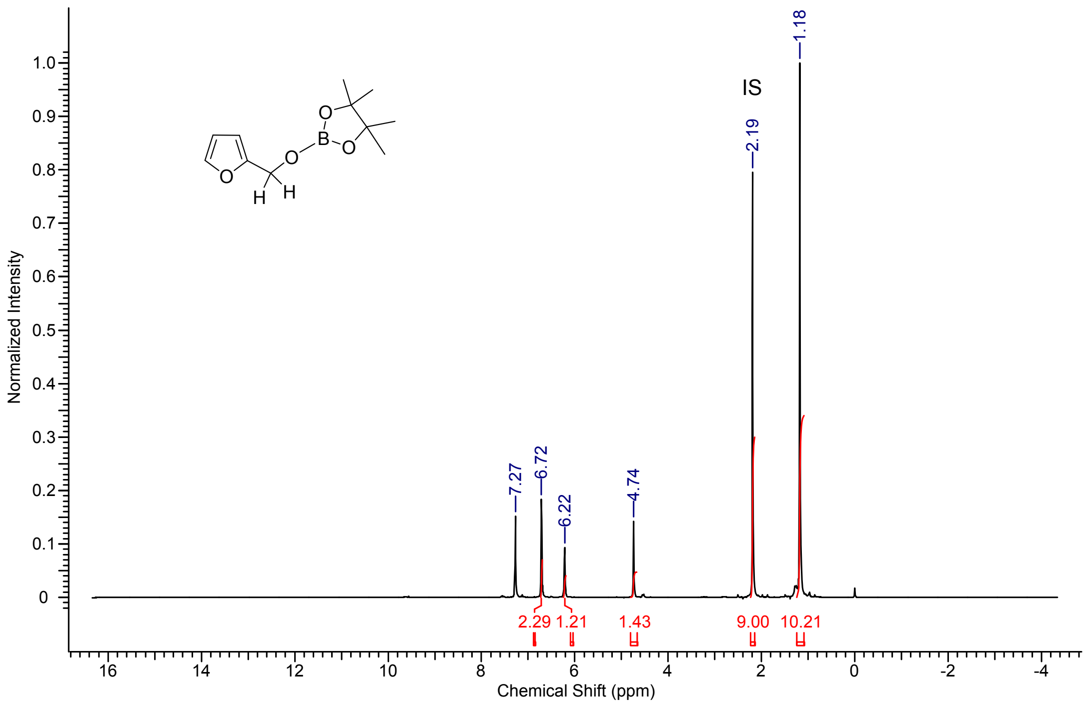
^{1}H NMR of 2,6-MePhCH$_2$OBpin (CDCl$_3$, 200 MHz):



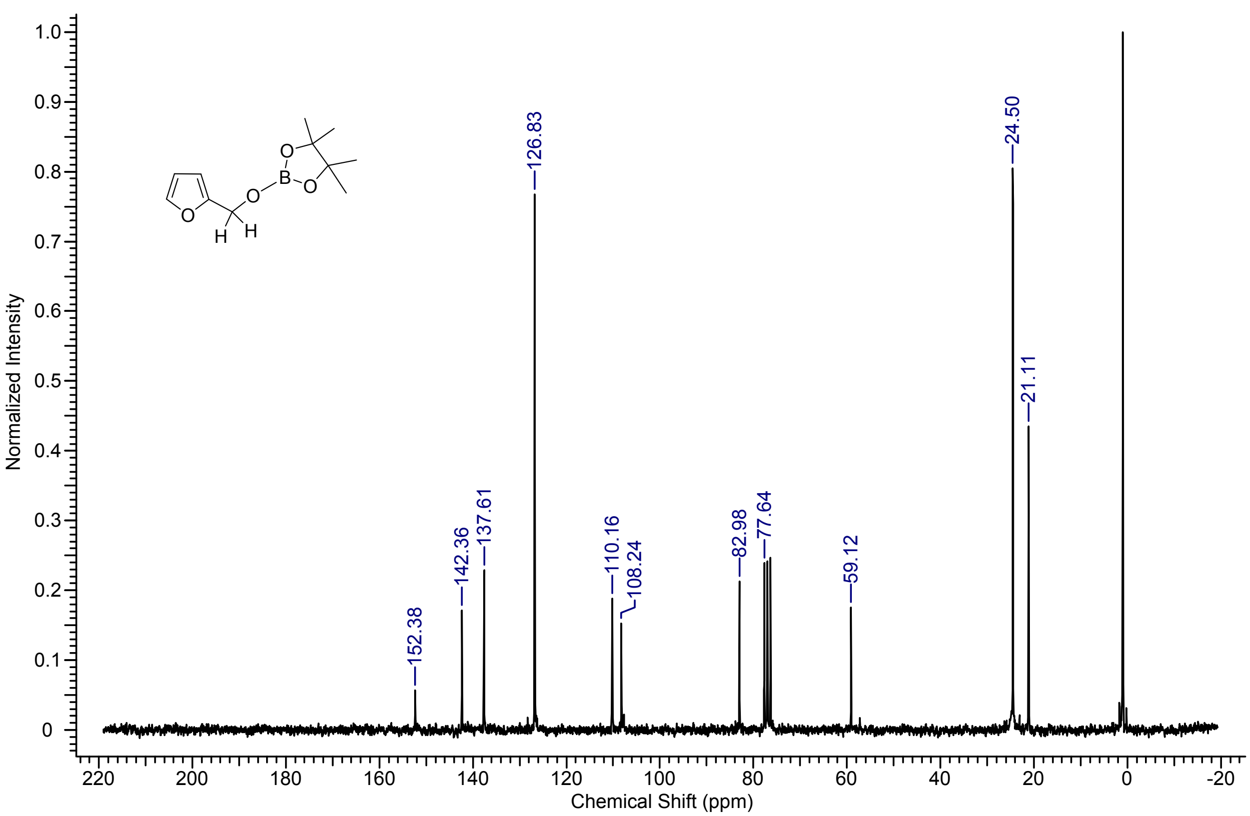
^{13}C NMR of 2,6-MePhCH$_2$OBpin (CDCl$_3$, 50.28 MHz):



^{1}H NMR of FurfuralOBpin ($CDCl_3$, 200 MHz):

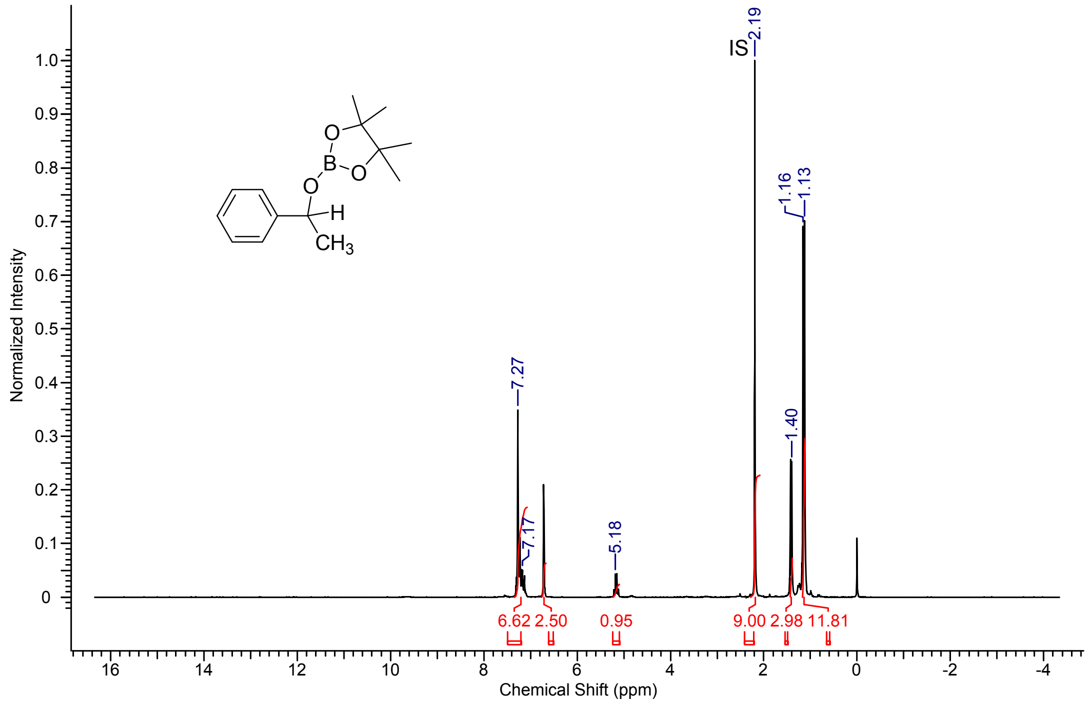


^{13}C NMRofFurfuralOBpin($CDCl_3$, 50.28 MHz):

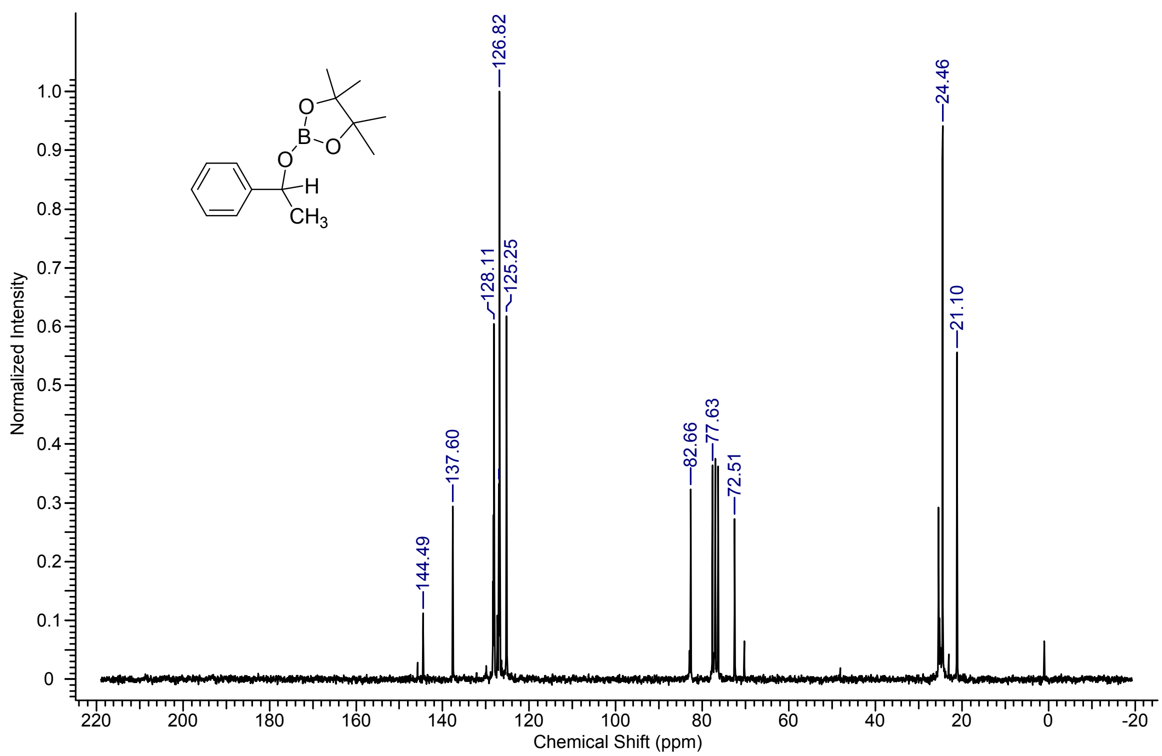


Ketone

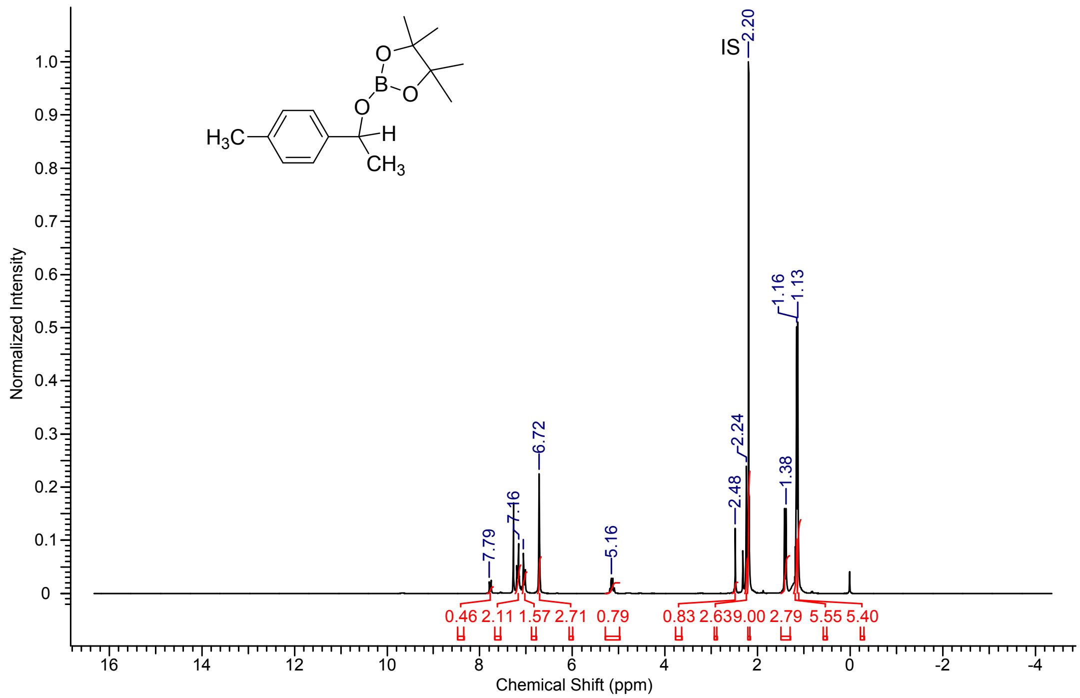
[1]H NMR of (Ph)CHOBpin ($CDCl_3$, 200 MHz):



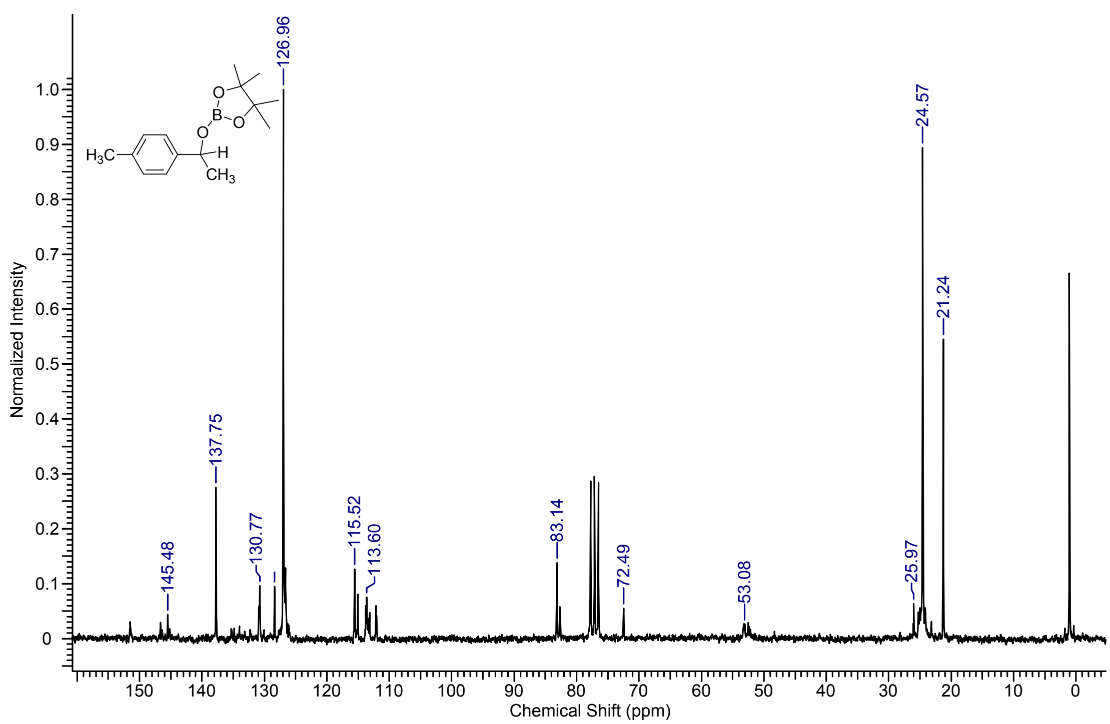
[13]C NMR of (Ph)(CHOBpin ($CDCl_3$, 50.28 MHz):



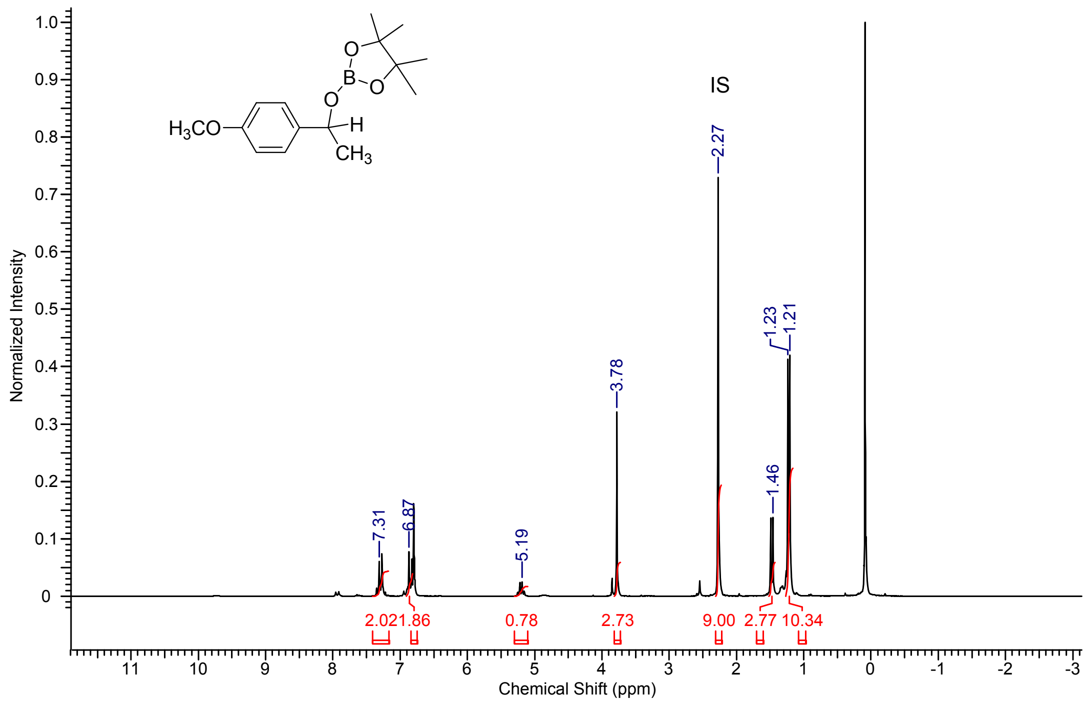
^{1}H NMR of (4-CH_3Ph)(Me)CHOBpin ($CDCl_3$, 200 MHz):



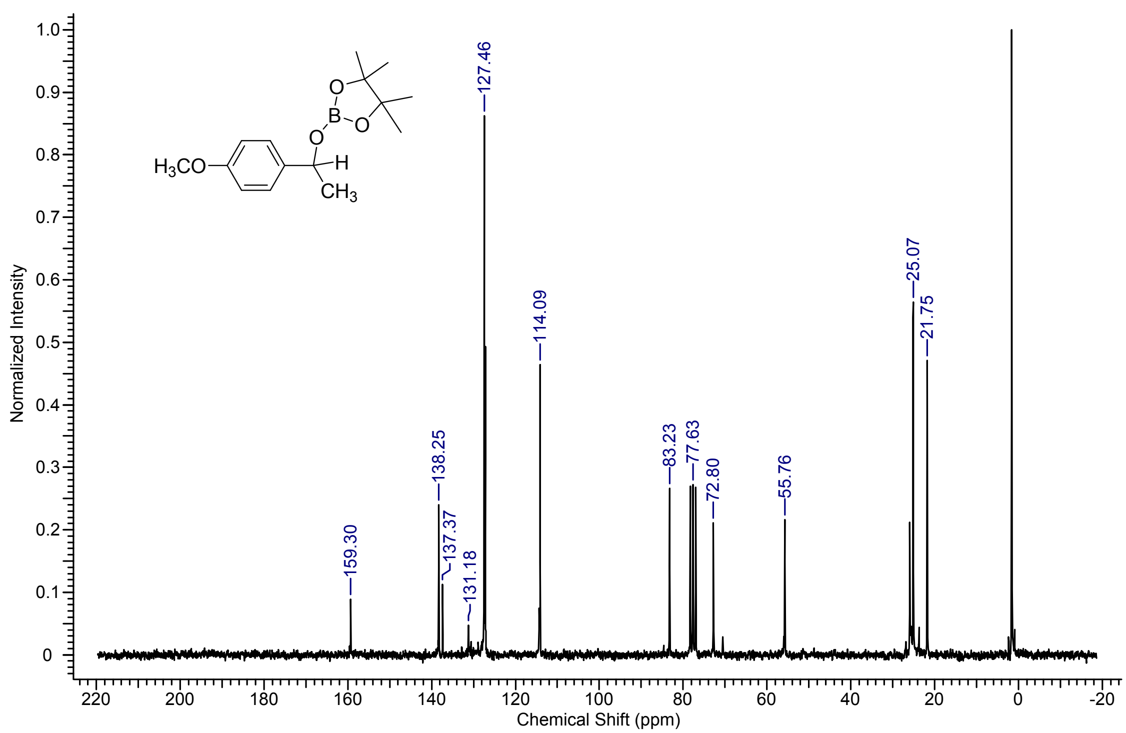
^{13}C NMR of (4-CH_3Ph)(Me)CHOBpin ($CDCl_3$, 50.28 MHz):



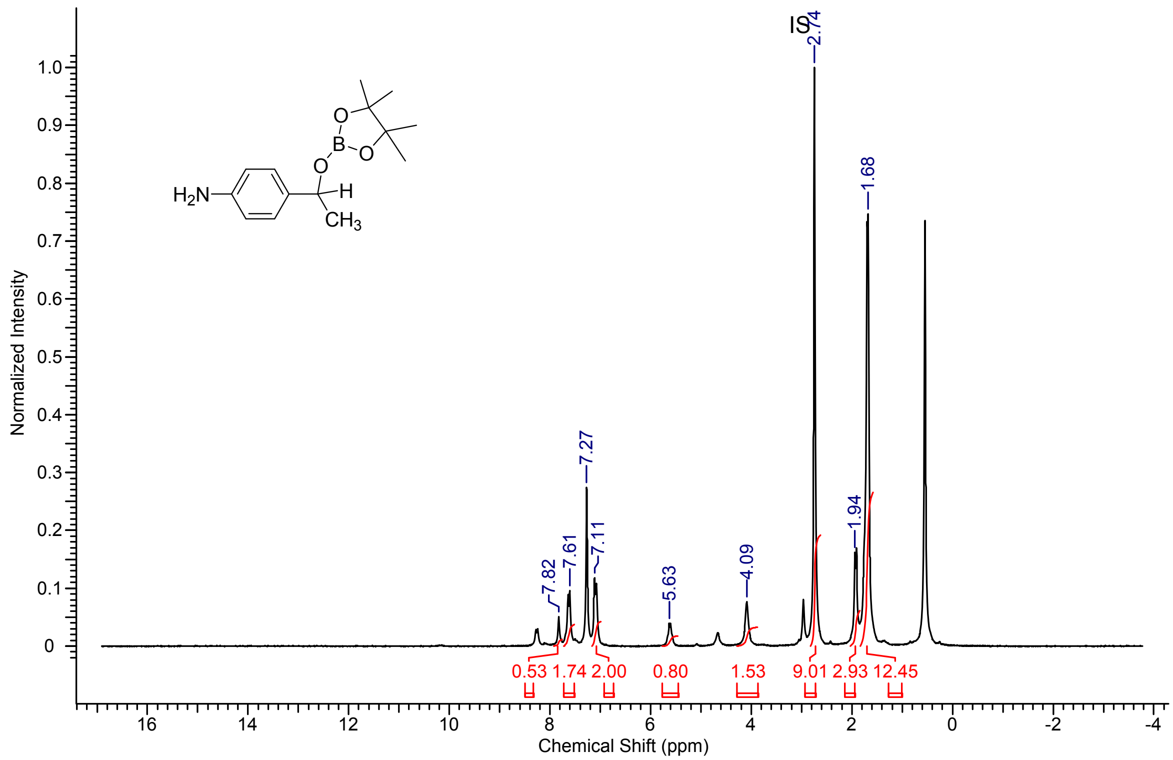
[1]H NMR of (4-OCH$_3$Ph)(Me)CHOBpin (CDCl$_3$, 200 MHz):



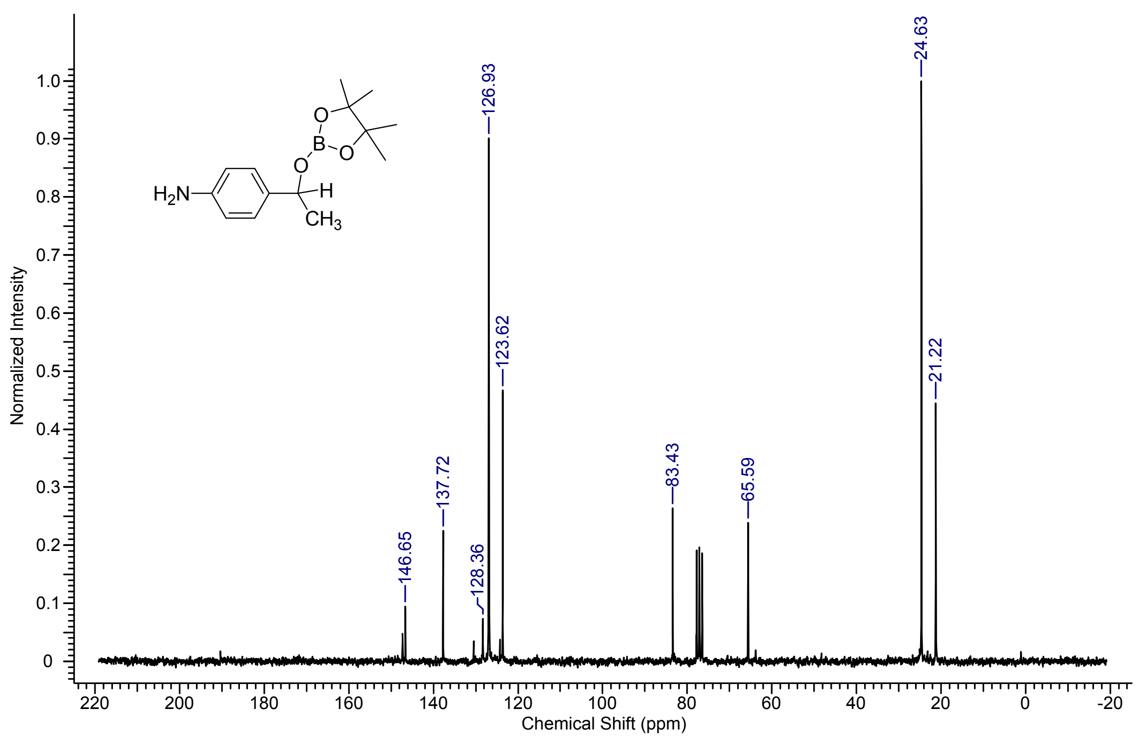
[13]C NMR of (4-OCH$_3$Ph)(Me)CHOBpin (CDCl$_3$, 50.28 MHz)



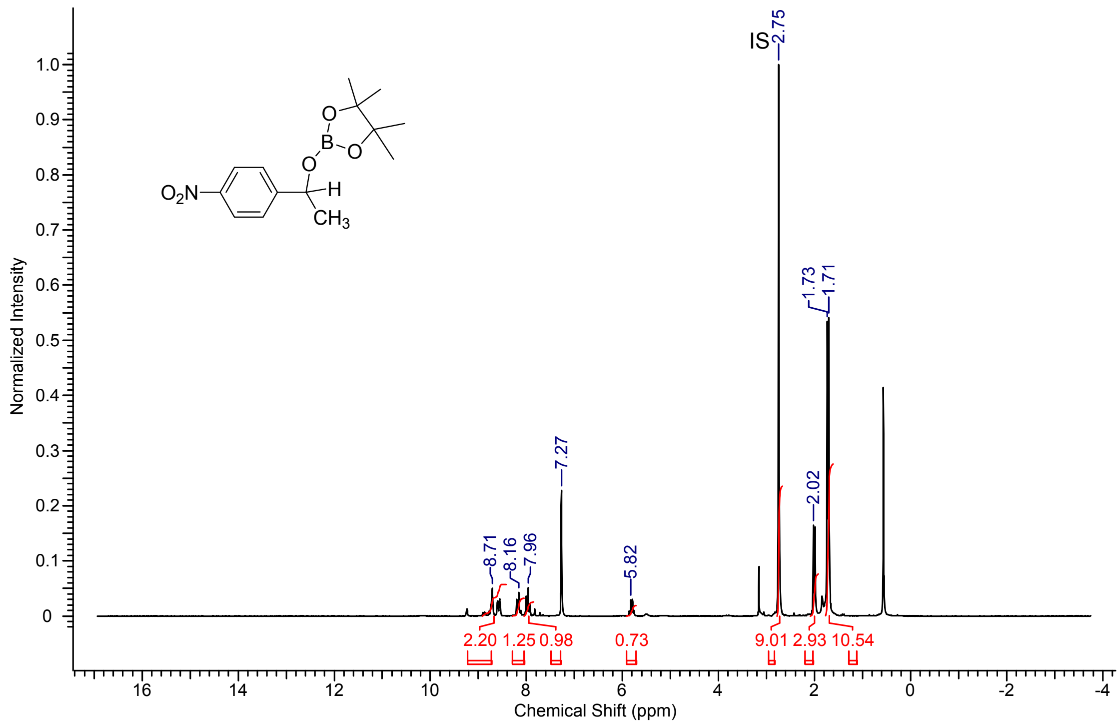
^{1}H NMR of (4-NH_2Ph)(Me)CHOBpin ($CDCl_3$, 200 MHz):



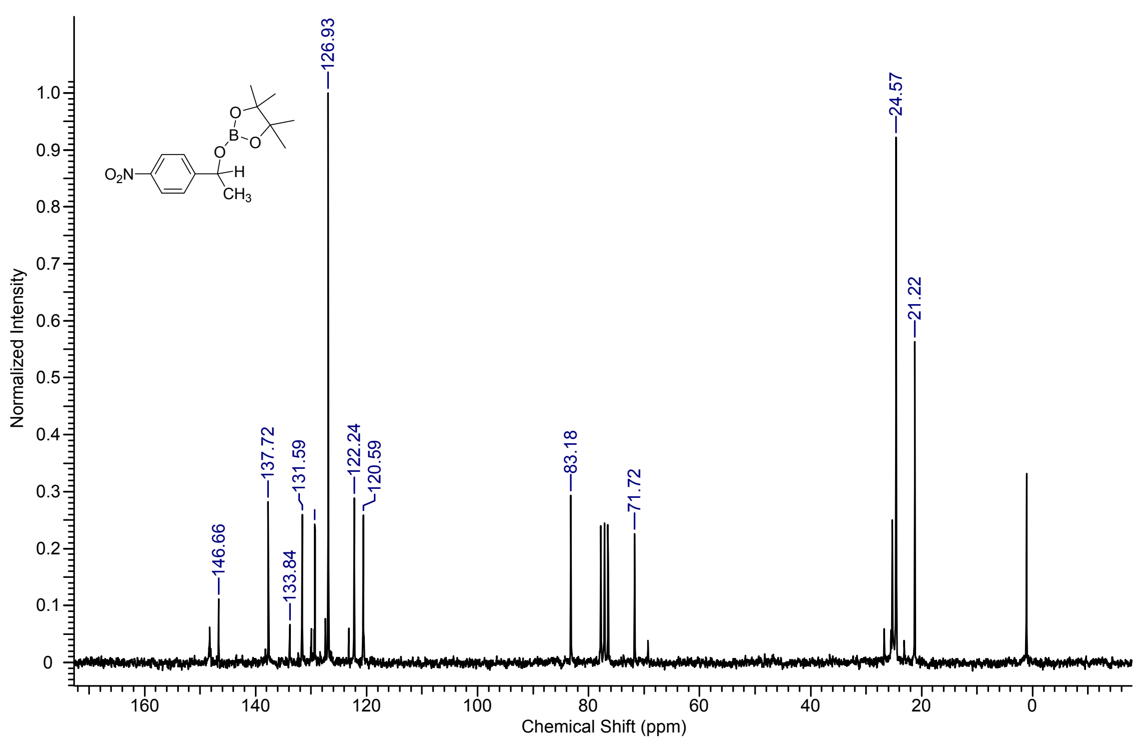
^{13}C NMR of (4-NH_2Ph)(Me)CHOBpin ($CDCl_3$, 50.28 MHz):



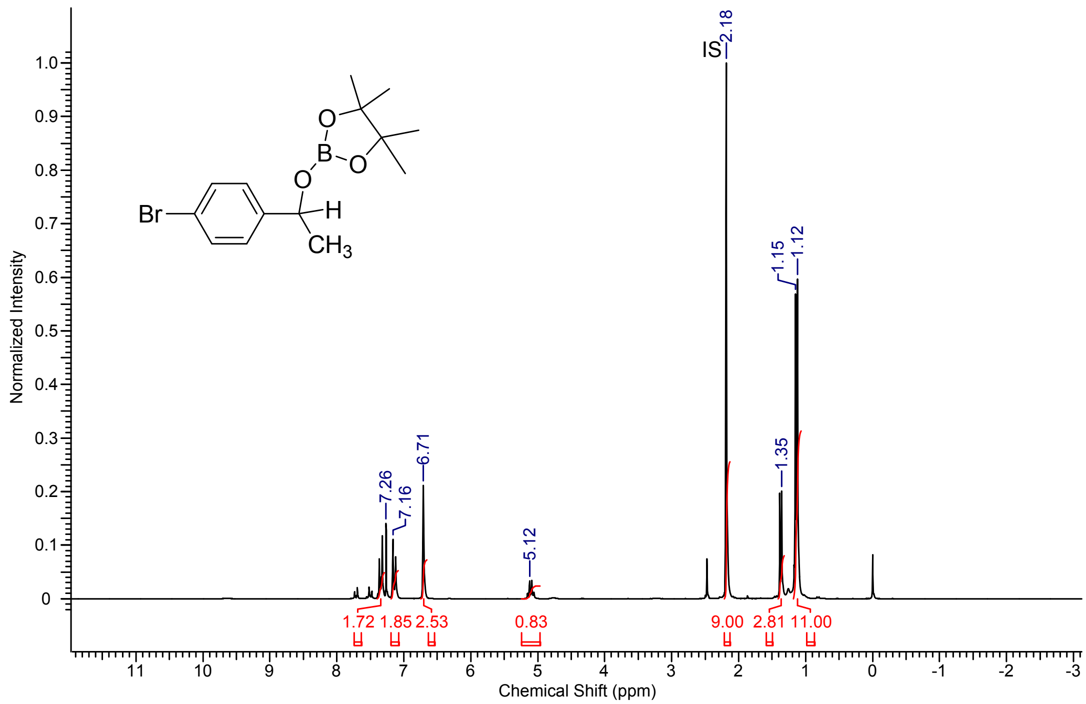
^{1}H NMR of (4-NO_2Ph)(Me)CHOBpin ($CDCl_3$, 200 MHz):



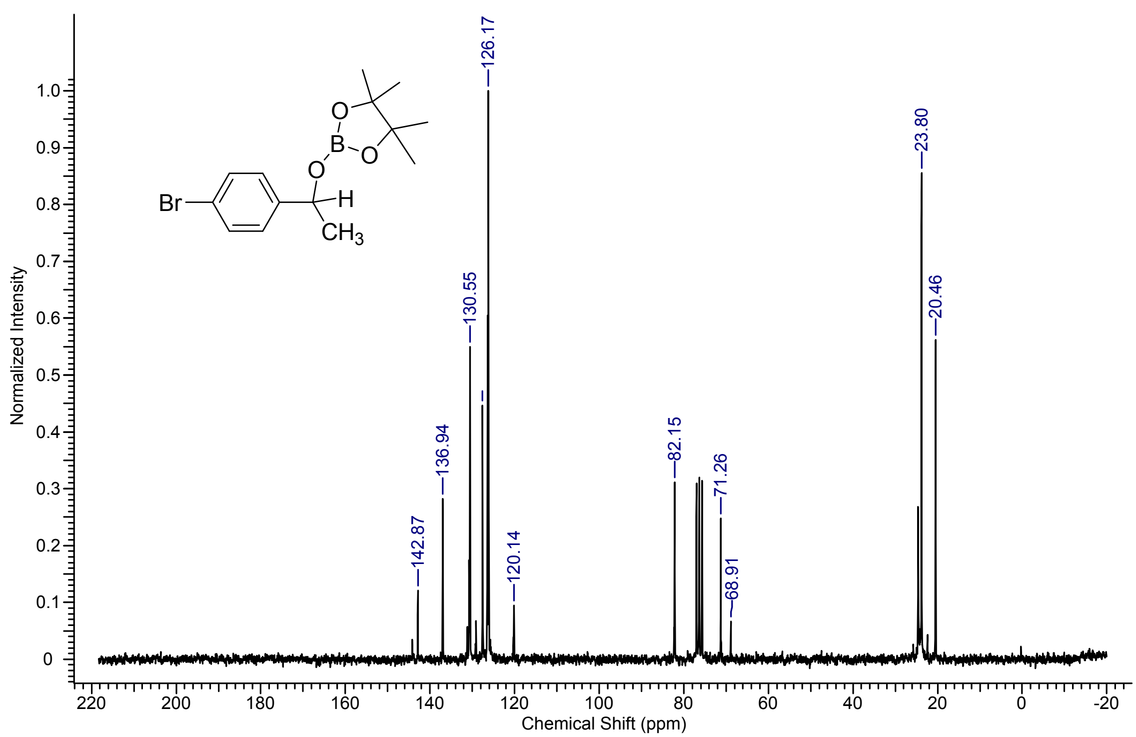
^{13}C NMR of (4-NO_2Ph)(Me)CHOBpin ($CDCl_3$, 50.28 MHz):



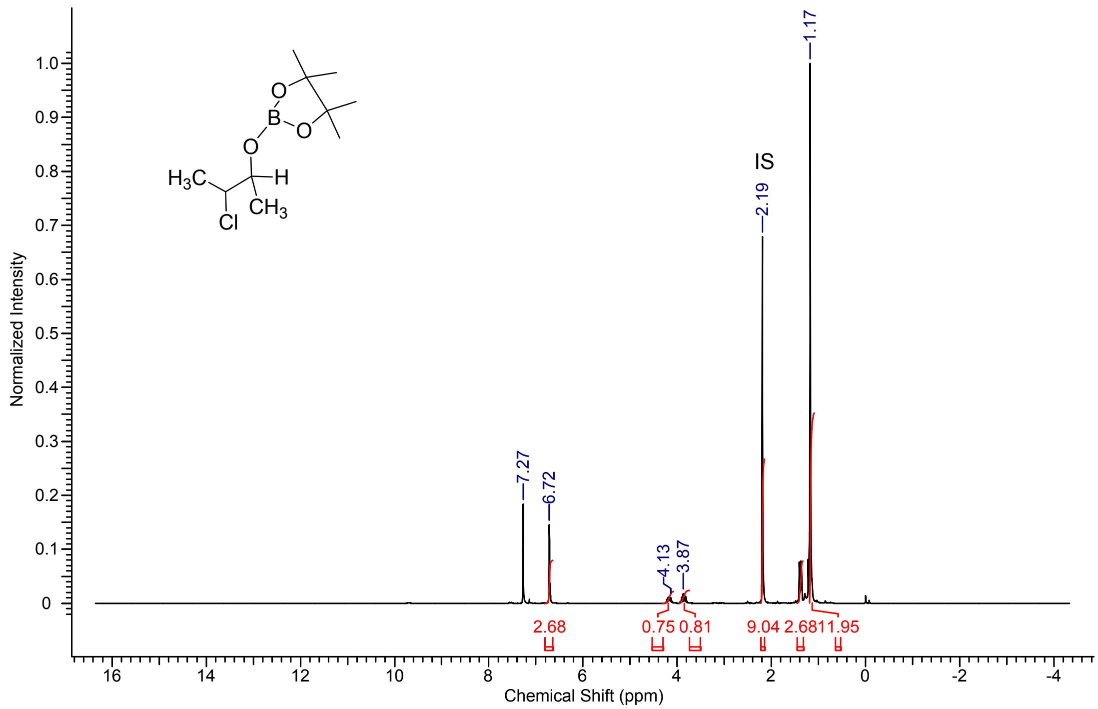
^{1}H NMR of (4-BrPh)(Me)CHOBpin ($CDCl_3$, 200 MHz):



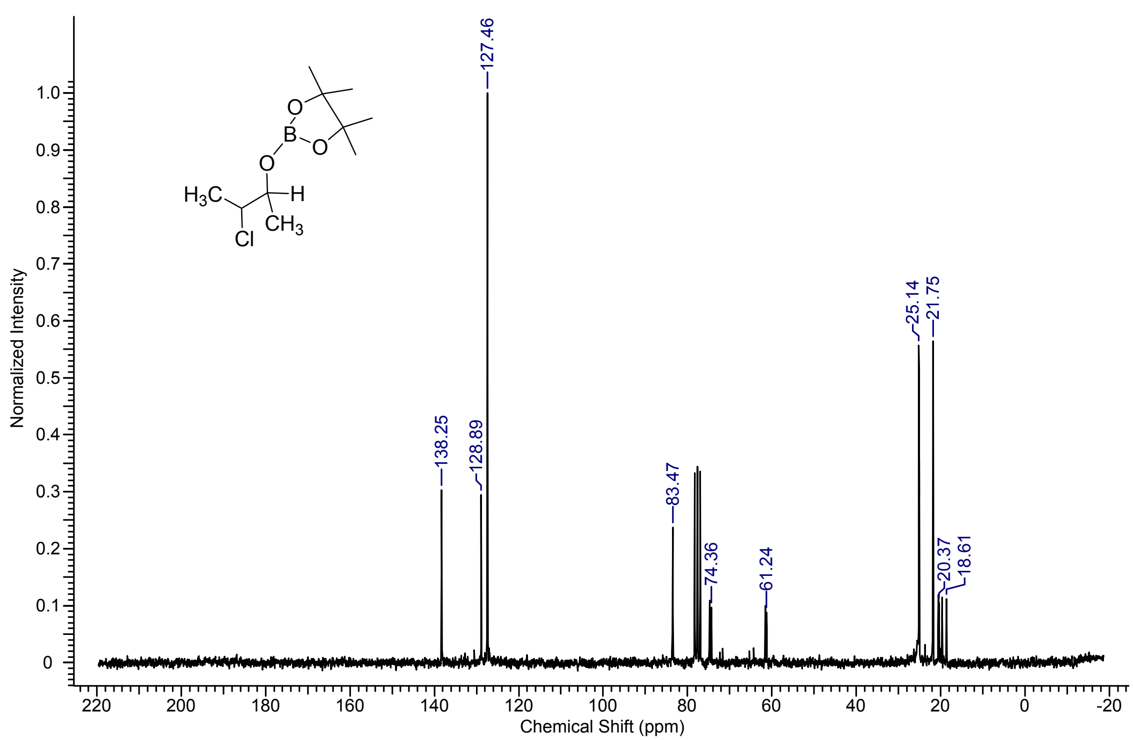
^{13}C NMR of (4-BrPh)(Me)CHOBpin ($CDCl_3$, 50.28 MHz):



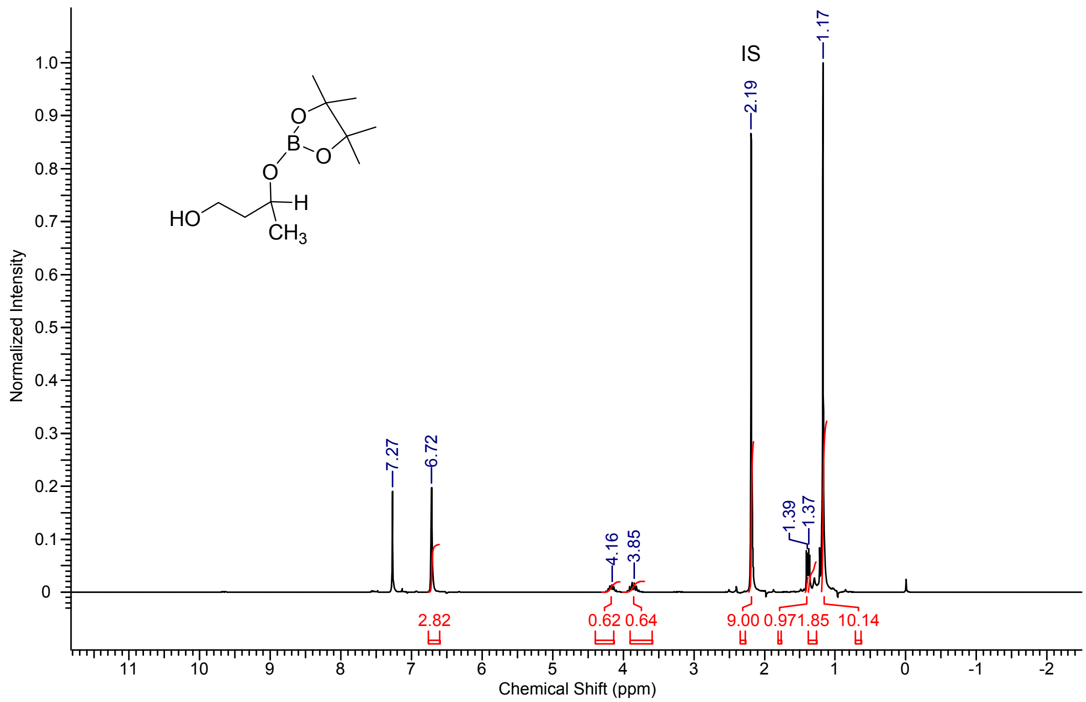
[1]H NMR of(2-ClEt)(Me)CHOBpin($CDCl_3$, 200 MHz):



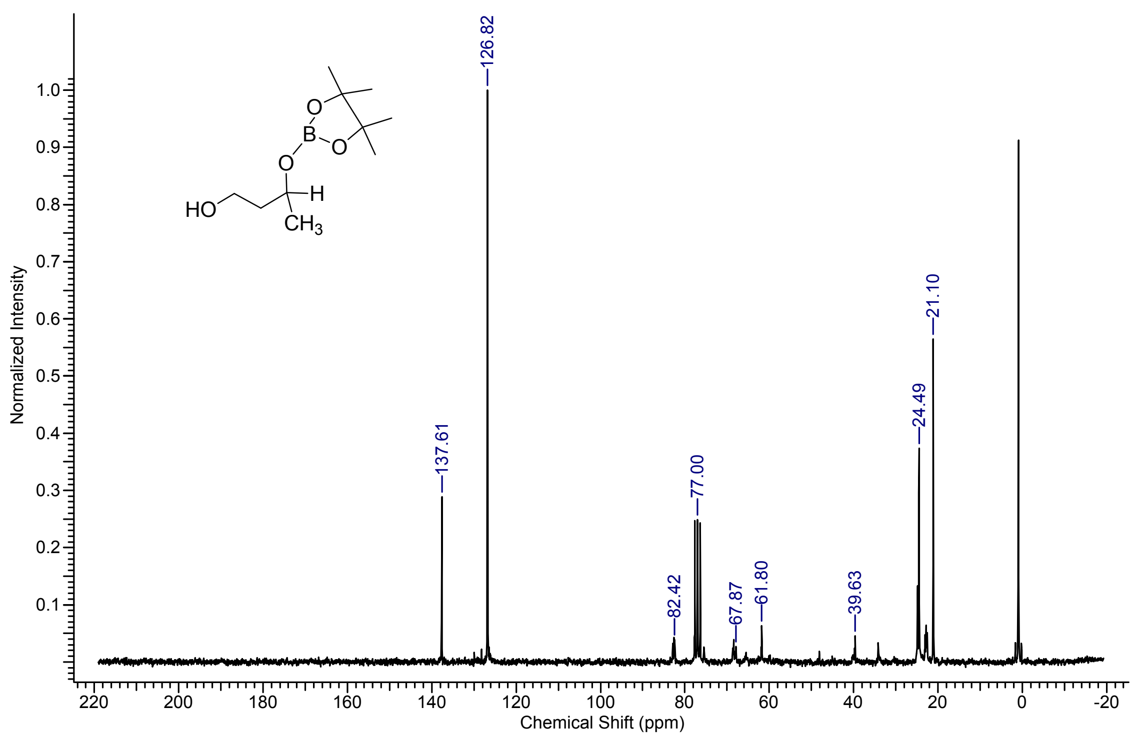
[13]C NMR of(2-ClEt)(Me)CHOBpin($CDCl_3$, 50.28 MHz):



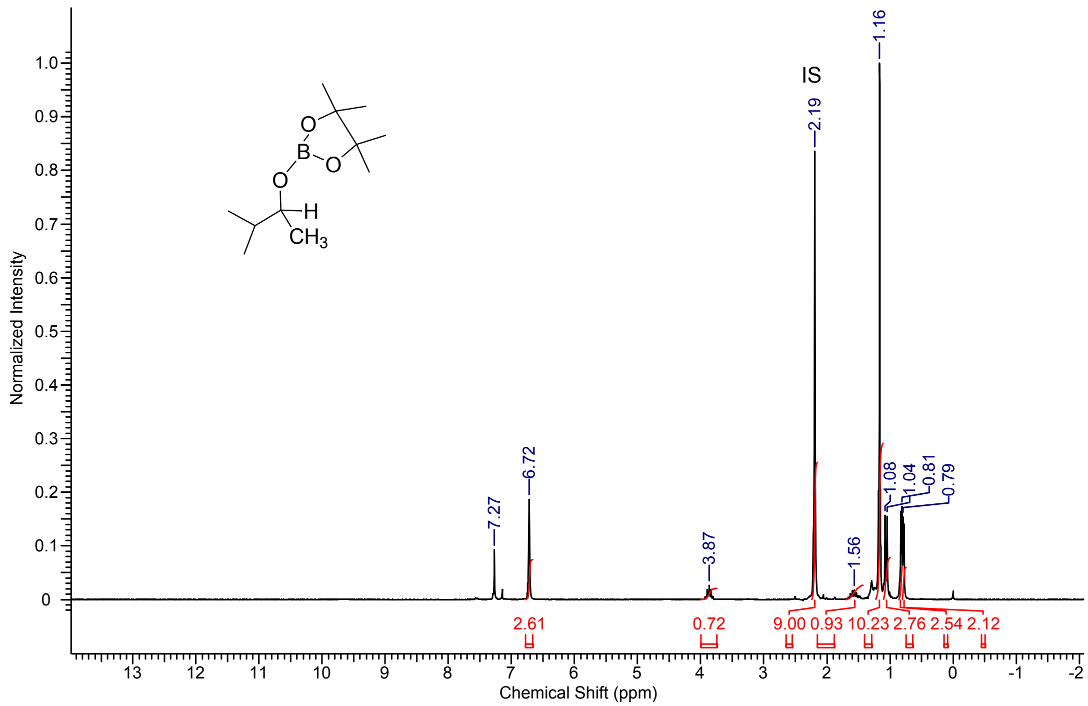
[1]H NMR of (4-OHEt)(Me)CHOBpin($CDCl_3$, 200 MHz):



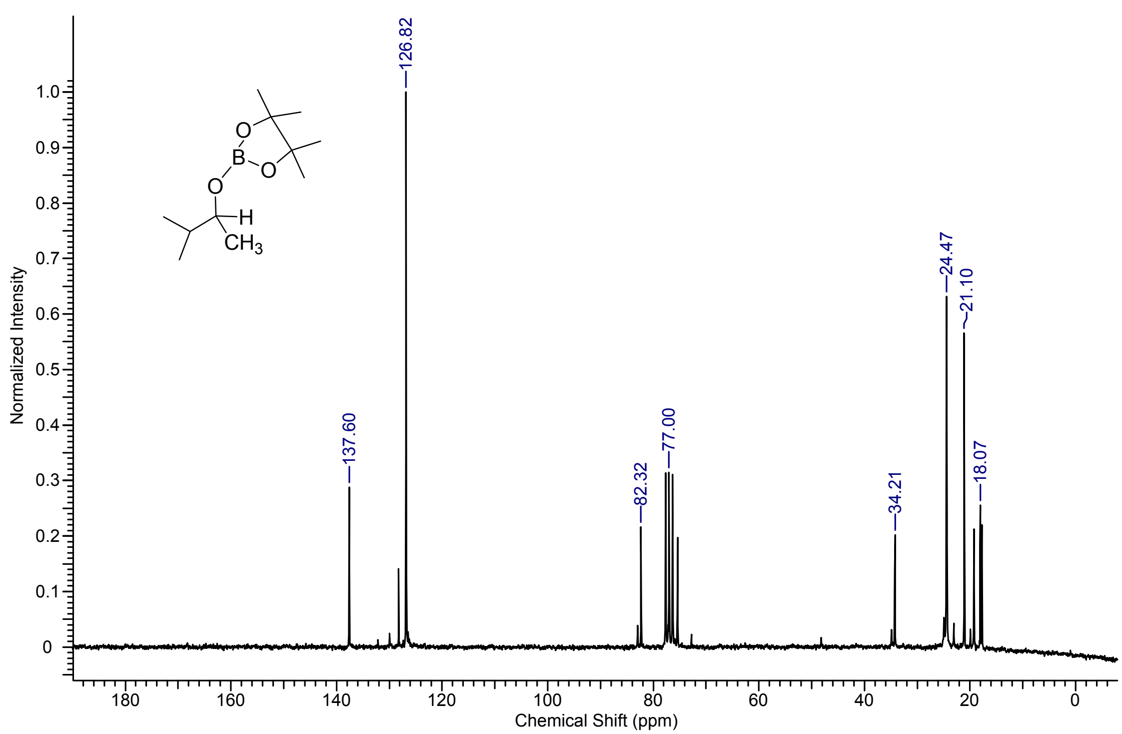
[13] C NMR of (4-OHEt)(Me)CHOBpin($CDCl_3$, 50.28 MHz):



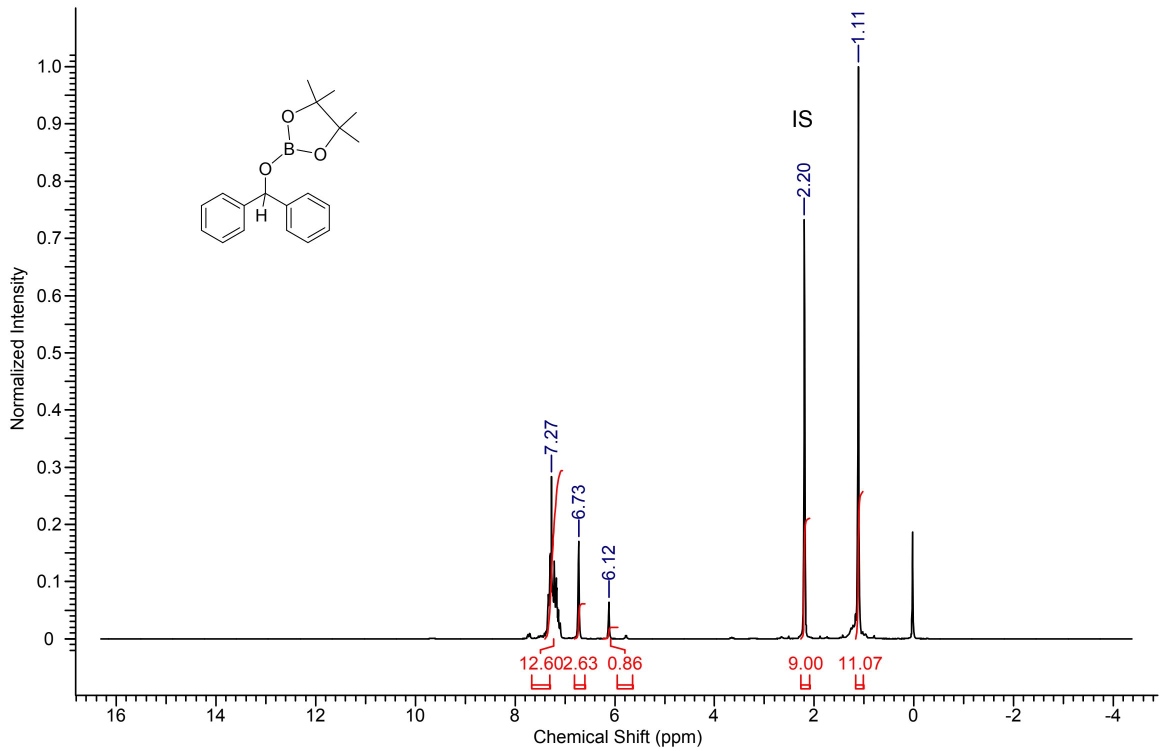
^{1}H NMR of(Et)(Me)CHOBpin($CDCl_3$, 200 MHz):



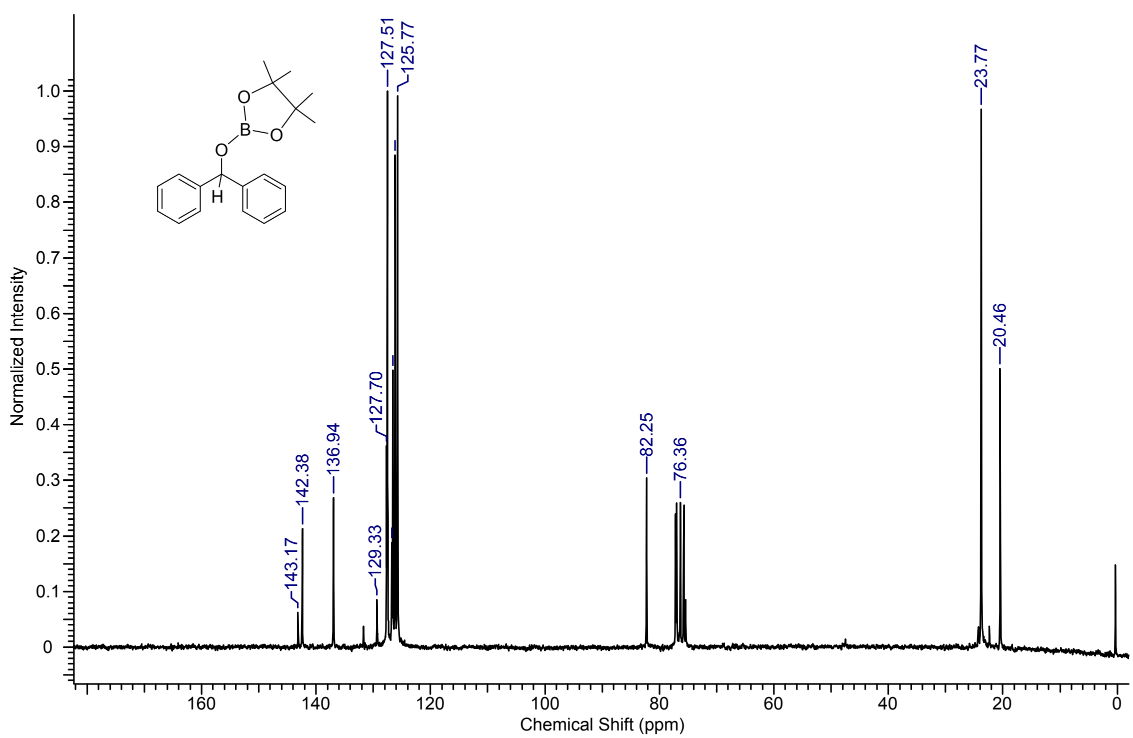
^{13} C NMR of(Et)(Me)CHOBpin ($CDCl_3$, 50.28 MHz):



^{1}H NMR of(Ph)(Ph)CHOBpin($CDCl_3$, 200 MHz):



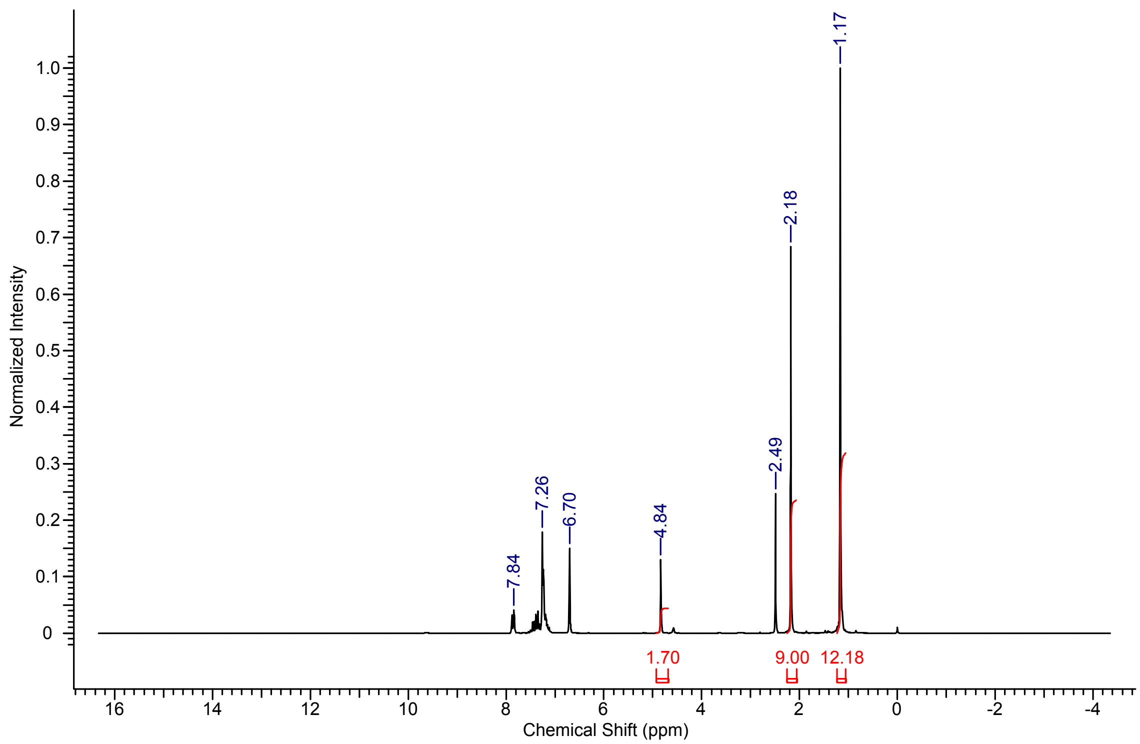
^{13}C NMR of(Ph)(Ph)CHOBpin ($CDCl_3$, 50.28 MHz):



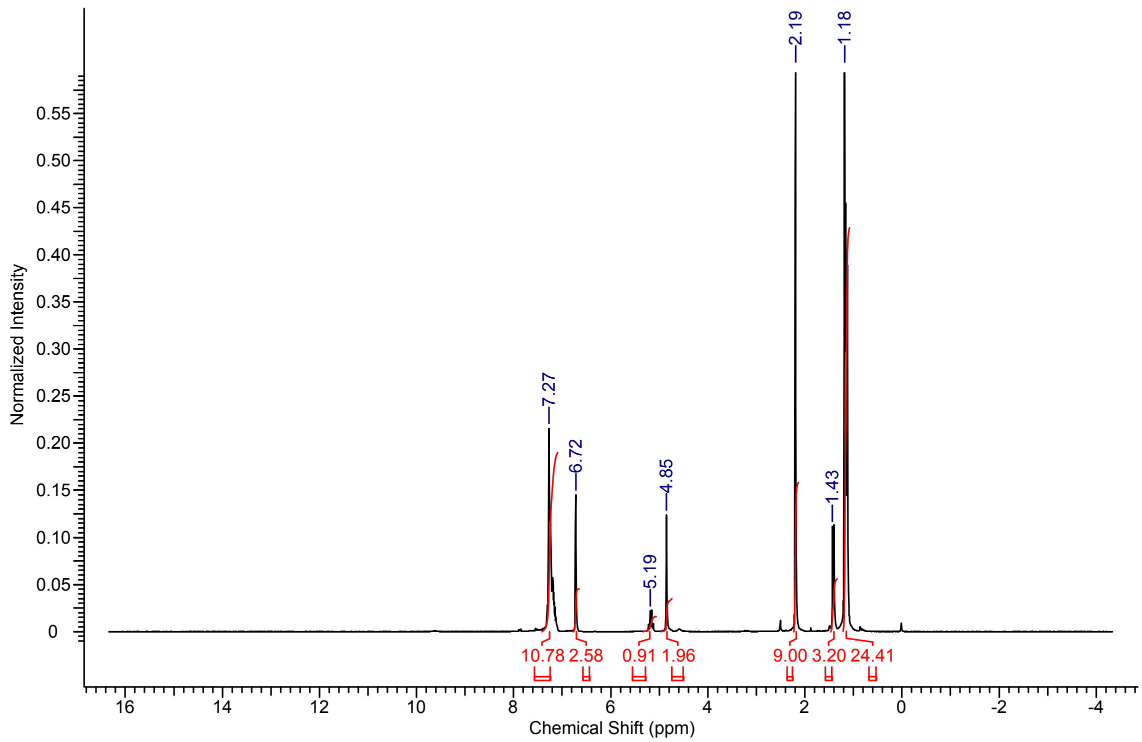
10. Chemoselective hydroboration of aldehydes versus ketones:

1 Equivalent of benzaldehyde and 1 equivalent of acetophenone were charged in Schlenk tube with catalyst and 1 equivalent of HBPin, it led to almost quantitative hydroboration of benzaldehyde and complete recycle of acetophenone. Subsequent addition of a second equivalent of HBpin afforded both hydroborated products in more than 90% yield.

A. 1 Eq. PhCHO + 1 Eq. PhCOCH3 + 1 Eq. HBPin + Catalyst



B. **1 Eq. PhCHO + 1 Eq. PhCOCH3 + 2 Eq. HBPin + Catalyst**



11. References

1. S. Yadav, V.S. V. S. N. Swamy, R. Gonnade and S. S. Sen, *ChemistrySelect,* 2016, **1**, 1066-1071.