# Copper-catalyzed B–H bond insertion reaction of triboranes ($L \cdot B_3H_7$) with diazo compounds

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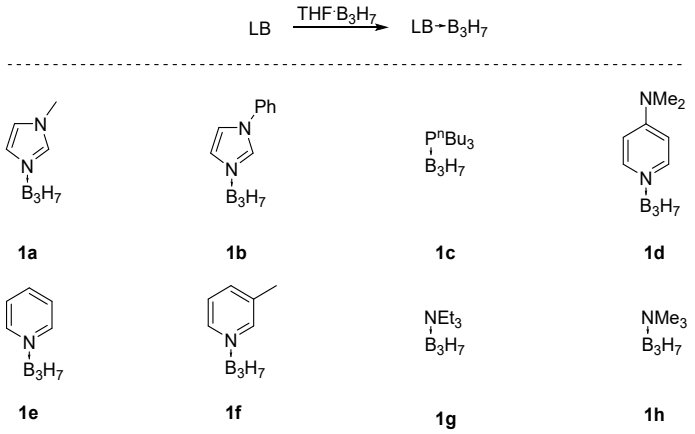
# General information

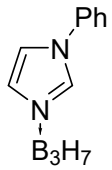
$^{1}H$ NMR spectra were recorded on a Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet; t = triplet; q = quartet; sept = septet; m = multiplet; br = broad), coupling constants (Hz), and integration. $^{13}C$ $\{^{1}H\}$ NMR data were collected on a Bruker Avance III HD 150 or Avance 100 MHz spectrometer. $^{11}B$ NMR data were collected on a Bruker Avance III HD 193 or Avance 128 MHz spectrometer. $^{10}B$ NMR data were collected on a Bruker Avance III HD 64 MHz spectrometer. $^{31}P$ NMR data were collected on a Bruker Avance III HD 243 MHz spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane, with the solvent resonance as an internal standard. HRMS was recorded on an ABI/Sciex QStar Mass Spectrometer (ESI). Single-crystal X-ray crystallography data were obtained on the Supernova Atlas S2 CCD detector. DCM was purchased with extra dry solvents. Other solvents used for work-up and purification were purchased in technical grade and distilled using a rotary evaporator before use. $NaBAr_F$ (Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate). TEMPO (2,2,6,6-Tetramethyl-1-piperinedinyloxy).

## Synthesis adducts of $B_3H_7$ (1a-1h)




**1a-1h** were prepared according to literature precedent.[1] Among these substrates, **1b**, **1c** and **1d** were new compounds and their characterization data were listed as follows.

The corresponding Lewis base (10 mmol) was dissolved in 30 mL THF in a Schlenk flask, and the flask was evacuated and backfilled with $N_2$ three times. Then, a THF·$B_3H_7$ solution (0.8M, 15 mL, 12 mmol) was slowly added. The reaction mixture was stirred for 5 h at room temperature. After imidazole was consumed (detected by TLC), the solution was concentrated in vacuo. The residue was purified by column chromatography to afford the corresponding products.



**1b**

1.510 g, 82% yield

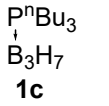
**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.60 – 7.50 (m, 3H), 7.42 – 7.37 (m, 2H), 7.33 (s, 1H), 7.23 (t, *J* = 1.8 Hz, 1H), 1.88 (br, 7H).

**$^1$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.60 – 7.50 (m, 3H), 7.42 – 7.37 (m, 2H), 7.33 (s, 1H), 7.23 (t, *J* = 1.8 Hz, 1H), 1.88 (s, 7H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ -10.30, -28.59.

**$^{13}$C{$^1$H} NMR** (151 MHz, Chloroform-*d*) δ 135.6, 135.2, 130.6, 129. 9, 128.1, 122.2, 119.3.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_9H_{15}B_3N_2Na$ 207.1407; found 207.1414.



**1c**

1.938 g, 80% yield

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 1.69 – 1.58 (m, 6H), 1.51 – 1.32 (m, 12H), 1.05 – 0.61 (m, 16H).

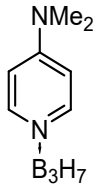
**$^1$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 1.69 – 1.58 (m, 6H), 1.51 – 1.32 (m, 12H), 0.93 (t, *J* = 7.2 Hz, 9H), 0.82 (s, 7H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ -16.65, -47.56, -47.95.

**$^{13}$C{$^1$H} NMR** (151 MHz, Chloroform-*d*) δ 24.5, 24.5, 24.4, 24.3, 21.2, 20.9, 13.6.

**$^{31}$P NMR** (243 MHz, Chloroform-*d*) δ 13.30 (dd, *J* = 199.0, 92.8 Hz).

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{34}B_3NaP$ 265.2570; found 265.2579.



**1d**

1.216 g, 75% yield

**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 6.6 Hz, 2H), 6.47 (d, *J* = 6.6 Hz, 2H), 3.09 (s, 6H), 1.78 (br, 7H).

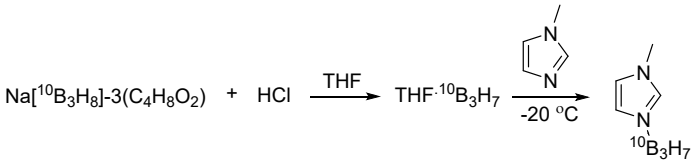
**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 6.6 Hz, 2H), 6.47 (d, *J* = 6.6 Hz, 2H), 3.09 (s, 6H), 1.78 (s, 7H).

**$^{11}$B NMR** (128 MHz, Chloroform-*d*) δ -10.84, -23.84.

**$^{13}$C{$^{1}$H} NMR** (101 MHz, Chloroform-*d*) δ 155.3, 146.1, 106.3, 39.7.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_7H_{17}B_3N_2Na$ 185.1563; found 185.1569.

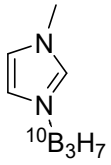
**Synthesis of 1a-$^{10}$B**



**1a-$^{10}$B**

The $Na[^{10}B_3H_8]\cdot 3(C_4H_8O_2)$ were prepared according to literature precedent.[2]

$Na[^{10}B_3H_8]\cdot 3(C_4H_8O_2)$ (1.63g, 5 mmol) was added to a 50 mL Schlenk flask. The flask was connected with a Schlenk line, and 20 mL of THF was injected. A solution of 1.0 M HCl in THF (5 mL, 5 mmol) was added dropwise to the flask at room temperature, and the mixture was stirred for 0.5 h. Then, the reaction mixture was filtered, and the filtrate is the THF solution of $THF\cdot{}^{10}B_3H_7$. Next, at -20 °C, 5 mmol of 1-methylimidazole was added to the filtrate. After stirring for 5 min, THF was removed from the reaction mixture under dynamic vacuum, leavinge an oily product. Separation of the mixture by flash chromatography (PE/DCM = 3:1, v/v) yielded a colorless oil **1a-$^{10}$B** (422.1 mg, 71% yield).



**1a-$^{10}$B**

422.1 mg, 71% yield

**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.13 (s, 1H), 6.86 (s, 1H), 3.76 (s, 3H), 1.76 (br, 7H).

**$^{1}$H{$^{10}$B} NMR** (600 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.13 (s, 1H), 6.86 (s, 1H), 3.76 (s, 3H), 1.76 (s, 7H).

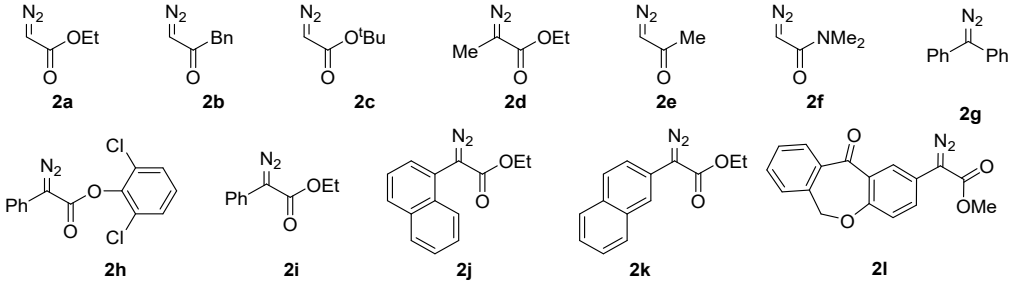
**$^{10}$B NMR** (64 MHz, Chloroform-*d*) δ -10.98, -28.68.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 137.0, 127.4, 120.9, 35.3.

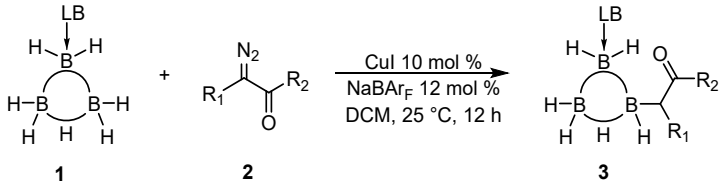
**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_4H_{13}{}^{10}B_3N_2Na$ 142.1359; found 142.1353.

## Synthesis of carbene precursors (2a-2l)

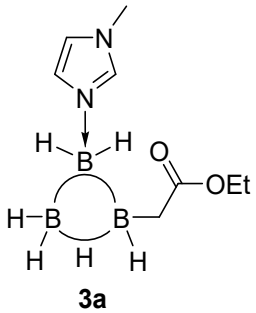
α-Diazo compounds (**2a**-**2l**) were purchased from commercial sources or prepared according to literature precedent.[3]




## Typical Procedure for Cu-Catalyzed B–H Bond Insertion Reactions of α-Diazo Compounds




In a Schlenk tube (25 mL), LB·$B_3H_7$ **1** (0.1 mmol), $Cu(MeCN)_4PF_6$ (3.7 mg, 10 mol %) and $NaBAr_F$ (10.6 mg, 12 mol %) were charged. Then DCM (2.0 mL) and α-diazo compounds **2** (0.2 mmol) were added, and the reaction vessel was evacuated and backfilled with $N_2$ three times. The reaction mixture was stirred at 25 °C for 12 h (**3m** and **3n** were stirred for 24 h) until the diazo compound disappeared. The residue was purified by flash column chromatography to afford the corresponding B–H bond insertion products **3**.




16.7 mg, 80% yield

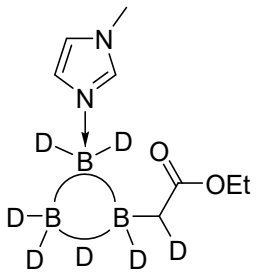
**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.13 (t, *J* = 1.8 Hz, 1H), 6.85 (t, *J* = 1.8 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 1.97 (br, 6H), 1.78 (s, 2H), 1.24 (t, *J* = 7.2 Hz, 3H).

**$^1$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.13 (t, *J* = 1.8 Hz, 1H), 6.85 (t, *J* = 1.8 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 1.97 (s, 6H), 1.78 (s, 2H), 1.24 (t, *J* = 7.2 Hz, 3H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ 0.95, -8.31, -26.87.

**$^{13}$C{$^1$H} NMR** (151 MHz, Chloroform-*d*) δ 178.0, 137.1, 127.6, 120.8, 59.4, 35.3, 28.2, 14.6.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_8H_{19}B_3N_2NaO_2$ 231.1618; found 231.1610.



**3a-D**, 80%D

16.3 mg, 76% yield from

**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.13 (d, *J* = 1.8 Hz, 1H), 6.85 (t, *J* = 1.8 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 2.09 – 1.89 (m, 1.2H), 1.80 – 1.73 (m, 1.2H), 1.24 (t, *J* = 7.2 Hz, 3H).

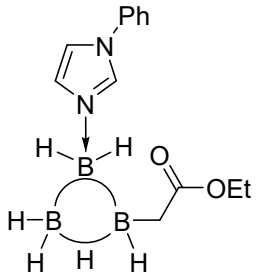
**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.13 (s, 1H), 6.84 (t, *J* = 1.8 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 1.99 (s, 1.2H), 1.80 – 1.73 (m, 1.2H), 1.24 (t, *J* = 7.2 Hz, 3H).

**$^{2}$D NMR** (92 MHz, Dichloromethane) δ 1.86, 1.65.

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ 0.92, -8.32, -27.15.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 178.1, 137.2, 127.6, 120.7, 59.4, 35.3, 14.7.

**HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_8H_{13}D_7B_3N_2O_2$ 216.2238; found 216.2232.



**3b**

20.5 mg, 76% yield

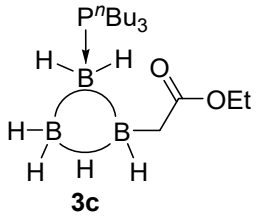
**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 7.60 – 7.54 (m, 2H), 7.54 – 7.50 (m, 1H), 7.43 – 7.37 (m, 2H), 7.30 (t, *J* = 1.6 Hz, 1H), 7.23 (t, *J* = 1.8 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.06 (br, 6H), 1.83 (s, 2H), 1.25 (t, *J* = 7.2 Hz, 3H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 7.60 – 7.54 (m, 2H), 7.54 – 7.50 (m, 1H), 7.43 – 7.37 (m, 2H), 7.30 (t, *J* = 1.6 Hz, 1H), 7.23 (t, *J* = 1.8 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.07 (s, 6H), 1.83 (s, 2H), 1.25 (t, *J* = 7.2 Hz, 3H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ 1.34, -8.04, -26.62.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 177.9, 135.5, 135.3, 130.6, 129.9, 128.1, 122.2, 119.2, 59.5, 28.2, 14.65, 1.15.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{21}B_3N_2NaO_2$ 293.1774; found 293.1783.



**3c**

25.9 mg, 79% yield

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 4.08 (q, *J* = 7.2 Hz, 2H), 1.75 (s, 2H), 1.69 – 1.60 (m, 6H), 1.47 – 1.36 (m, 12H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.07 – 0.79 (m, 15H).

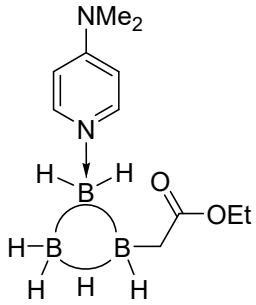
**$^1$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 4.08 (q, *J* = 7.2 Hz, 2H), 1.75 (s, 2H), 1.69 – 1.60 (m, 6H), 1.47 – 1.36 (m, 12H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.07 – 0.79 (m, 15H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ -2.45, -16.76, -44.77.

**$^{13}$C{$^1$H} NMR** (151 MHz, Chloroform-*d*) δ 177.5, 59.5, 24.5, 24.5, 24.4, 21.2, 20.9, 14.6, 13.7.

**$^{31}$P NMR** (243 MHz, Chloroform-*d*) δ 13.46 – 10.33 (m).

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{40}B_3NaO_2P$ 351.2937; found 351.2929.




**3d**

18.6 mg, 75% yield

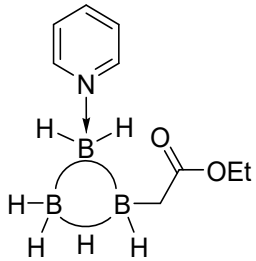
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.2 Hz, 2H), 6.47 (d, *J* = 7.2 Hz, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.10 (s, 6H), 2.04 (br, 6H), 1.81 (s, 2H), 1.24 (t, *J* = 7.2 Hz, 3H).

**$^1$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.2 Hz, 2H), 6.47 (d, *J* = 7.2 Hz, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.10 (s, 6H), 2.04 (s, 6H), 1.81 (s, 2H), 1.24 (t, *J* = 7.2 Hz, 3H).

**$^{11}$B NMR** (128 MHz, Chloroform-*d*) δ 1.30, -7.66, -22.10.

**$^{13}$C{$^1$H} NMR** (101 MHz, Chloroform-*d*) δ 178.0, 155.3, 146.6, 106.3, 59.4, 39.7, 14.7.

**HRMS** (ESI-TOF) m/z: $[M+K]^+$ calcd for $C_{11}H_{23}B_3KN_2O_2$ 287.1670; found 287.1667.




**3e**

14.6 mg, 71% yield

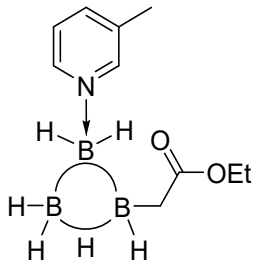
**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 5.4 Hz, 2H), 8.04 – 7.96 (m, 1H), 7.58 – 7.50 (m, 2H), 4.15 – 4.01 (m, 2H), 2.20 (br, 6H), 1.86 (s, 2H), 1.24 (t, *J* = 7.2 Hz, 3H).

**$^1$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 5.4 Hz, 2H), 8.04 – 7.96 (m, 1H), 7.58 – 7.48 (m, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.20 (s, 6H), 1.86 (s, 2H), 1.24 (t, *J* = 7.2 Hz, 3H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ 2.41, -5.90, -20.68.

**$^{13}$C{$^1$H} NMR**(151 MHz, Chloroform-*d*) δ 177.6, 147.8, 140.8, 125.5, 59.5, 28.2, 14.6.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_9H_{18}B_3NNaO_2$ 228.1509; found 228.1514.



**3f**

15.1 mg, 69% yield

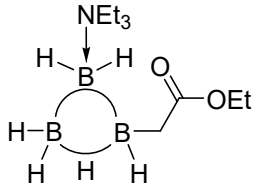
**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 8.50 – 8.34 (m, 2H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.42 (dd, *J* = 7.8, 6.0 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.19 (br, 6H), 1.86 (s, 2H), 1.25 (t, *J* = 7.2 Hz, 3H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 8.50 – 8.34 (m, 2H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.42 (dd, *J* = 7.8, 6.0 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.18 (s, 6H), 1.86 (s, 2H), 1.25 (t, *J* = 7.2 Hz, 3H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ 2.15, -6.22, -20.85.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 177.7, 147.7, 145.1, 141.3, 136.1, 124.9, 59.5, 28.3,18.7, 14.7.

**HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_{21}B_3NO_2$ 220.1846; found 220.1852.



**3g**

16.4 mg, 72% yield

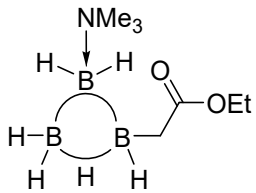
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 4.07 (q, *J* = 7.2 Hz, 2H), 2.96 – 2.79 (m, 6H), 1.60 (br, 2H), 1.45 – 1.15 (m, 18H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 4.07 (q, *J* = 7.2 Hz, 2H), 2.96 – 2.79 (m, 6H), 1.58 (s, 2H), 1.33 (s, 6H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 9H).

**$^{11}$B NMR** (128 MHz, Chloroform-*d*) δ -3.98, -20.98.

**$^{13}$C{$^{1}$H} NMR** (101 MHz, Chloroform-*d*) δ 177.7, 59.4, 52.6, 14.6, 8.7.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{28}B_3NNaO_2$ 250.2291; found 250.2284.



**3h**

6.9 mg, 37% yield

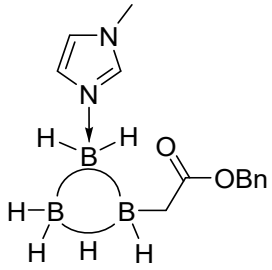
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 4.07 (q, *J* = 7.2 Hz, 2H), 2.66 (s, 9H), 1.65 (s, 2H), 1.58 (br, 6H), 1.23 (d, *J* = 7.2 Hz, 3H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 4.07 (q, *J* = 7.2 Hz, 2H), 2.66 (s, 9H), 1.65 (s, 2H), 1.58 (s, 6H), 1.23 (d, *J* = 7.2 Hz, 3H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ -5.22, -15.31, -17.09.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 177.6, 59.3, 54.6, 14.5.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_7H_{22}B_3NNaO_2$ 208.1822; found 208.1830.



**3i**

23.2 mg, 86% yield

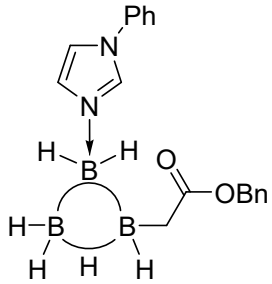
**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 1.2 Hz, 1H), 6.82 (t, *J* = 1.2 Hz, 1H), 5.09 (s, 2H), 3.72 (s, 3H), 2.00 (br, 6H), 1.86 (s, 2H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.09 (s, 1H), 6.82 (s, 1H), 5.09 (s, 2H), 3.72 (s, 3H), 1.99 (s, 6H), 1.86 (s, 2H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ 0.75, -7.97, -26.82.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 177.8, 137.4, 137.1, 128.5, 128.2, 127.7, 127.6, 120.7, 65.4, 35.2, 28.1.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{21}B_3N_2NaO_2$ 293.1774; found 293.1769.



**3j**

26.9 mg, 81% yield

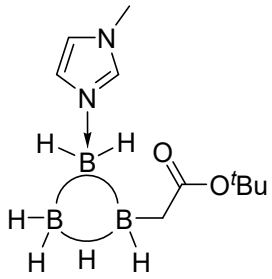
**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.61 – 7.49 (m, 3H), 7.42 – 7.35 (m, 4H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 1.8 Hz, 1H), 5.10 (s, 2H), 2.09 (br, 6H), 1.91 (s, 2H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.61 – 7.49 (m, 3H), 7.42 – 7.35 (m, 4H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 1.8 Hz, 1H), 5.10 (s, 2H), 2.8 (s, 6H), 1.90 (s, 2H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ 0.73, -8.37, -27.63.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 177.7, 137.4, 135.5, 135.3, 130.6, 129.8, 128.4, 128.1, 128.0, 127.7, 122.2, 119.2, 65.4, 27.8.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{23}B_3N_2NaO_2$ 355.1931; found 355.1940.



**3k**

11.3 mg, 48% yield

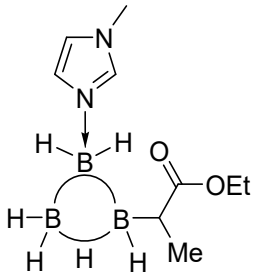
**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.14 (s, 1H), 6.84 (s, 1H), 3.76 (s, 3H), 2.00 (br, 6H), 1.69 (s, 2H), 1.44 (s, 9H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.14 (s, 1H), 6.84 (s, 1H), 3.76 (s, 3H), 1.97 (s, 6H), 1.69 (s, 2H), 1.44 (s, 9H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ 1.81, -9.06, -26.90.

**$^{13}$C{$^{1}$H} NMR** (101 MHz, Chloroform-*d*) δ 177.5, 137.2, 127.7, 120.7, 78.4, 35.3, 28.5.

**HRMS** (ESI-TOF) m/z: $[M+K]^+$ calcd for $C_{10}H_{23}B_3KN_2O_2$ 275.1670; found 275.1680.



**3l**

16.6 mg, 75% yield

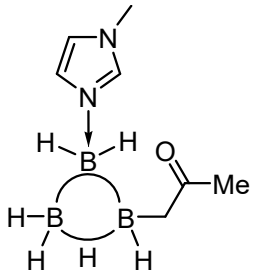
**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.12 (s, 1H), 6.84 (s, 1H), 4.14 – 4.03 (m, 2H), 3.76 (s, 3H), 2.08 – 1.82 (m, 7H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.12 (d, *J* = 6.6 Hz, 3H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.12 (s, 1H), 6.84 (s, 1H), 4.14 – 4.03 (m, 2H), 3.76 (s, 3H), 2.01 – 1.97 (m, 1H), 1.94 – 1.84 (s, 6H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.12 (d, *J* = 6.6 Hz, 3H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ 3.15, -10.46, -26.82.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 180.7, 137.1, 127.6, 120.7, 59.3, 35.3, 32.0, 16.4, 14.7.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_9H_{21}B_3N_2NaO_2$ 245.1774; found 245.1771.



**3m**

9.1 mg, 51% yield

**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.14 (s, 1H), 6.86 (s, 1H), 3.77 (s, 3H), 2.12 (s, 3H), 2.08 – 1.73 (m, 8H).

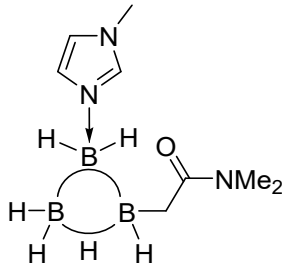
**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.14 (s, 1H), 6.85 (s, 1H), 3.77 (s, 3H), 2.12 (s,

3H), 2.04 (s, 2H), 1.96 (s, 6H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ 0.74, -8.35, -26.99.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 214.8, 137.2, 127.7, 120.8, 35.3, 30.5.

**HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_7H_{18}B_3N_2O$ 179.1693; found 179.1697.



**3n**

9.5 mg, 46% yield

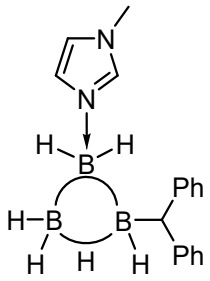
**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.13 (t, *J* = 1.8 Hz, 1H), 6.85 (t, *J* = 1.8 Hz, 1H), 3.75 (s, 3H), 3.02 (s, 3H), 2.92 (s, 3H), 2.02 – 1.80 (m, 8H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.13 (s, 1H), 6.84 (t, *J* = 1.8 Hz, 1H), 3.75 (s, 3H), 3.02 (s, 3H), 2.92 (s, 3H), 1.94 (s, 6H), 1.86 (s, 2H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ 1.67, -9.57, -26.64.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 178.3, 137.6, 127.6, 120.7, 38.4, 35.5, 35.3, 27.9.

**HRMS** (ESI-TOF) m/z: $[2M+Na]^+$ calcd for $C_{16}H_{40}B_6N_6NaO_2$ 437.3663; found 437.3668.



**3o**

12.4 mg, 43% yield

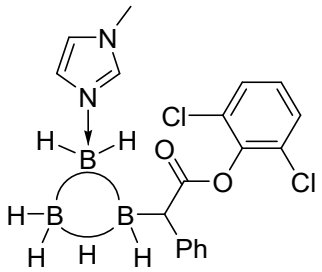
**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 7.57 (s, 1H), 7.43 – 7.36 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.16 (m, 4H), 7.11 – 6.99 (m, 3H), 6.76 (s, 1H), 3.65 (s, 3H), 3.19 (s, 1H), 2.03 (br, 6H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 7.57 (s, 1H), 7.43 – 7.36 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.16 (m, 4H), 7.11 – 6.99 (m, 3H), 6.76 (s, 1H), 3.65 (s, 3H), 3.19 (s, 1H), 2.03 (s, 6H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ 7.18, -12.33, -27.06.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 149.6, 149.4, 137.0, 129.4, 128.3, 127.9, 127.4, 124.4, 120.4, 35.0.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{23}B_3N_2Na$ 311.2033; found 311.2042.



**3p**

28.1 mg, 70% yield

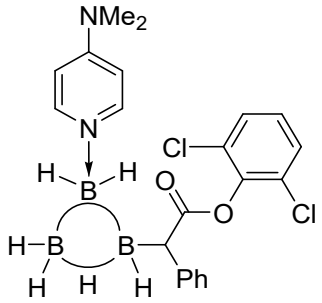
**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 7.77 (s, 0.5H), 7.53 (s, 0.5H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.28 – 7.14 (m, 5H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.73 (s, 1H), 3.62 (s, 3H), 3.35 (s, 1H), 2.10 (br, 6H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 7.77 (s, 0.5H), 7.53 (s, 0.5H), δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.24 – 7.16 (m, 5H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.72 (s, 1H), 3.62 (s, 3H), 3.35 (s, 1H), 2.10 (s, 6H).

**$^{11}$B NMR** (128 MHz, Chloroform-*d*) δ -1.05, -27.75.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 174.0, 145.0, 142.6, 137.1, 129.6, 129.5, 128.5, 127.9, 127.4, 126.6, 125.4, 120.8, 47.1, 35.2.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{21}B_3Cl_2N_2NaO_2$ 423.1151; found 423.1161.



**3q**

29.9 mg, 68% yield

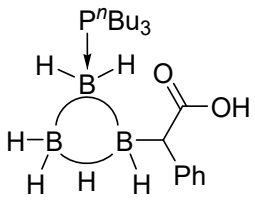
**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.80 (s, 1H), 7.49 (s, 2H), 7.31 – 7.26 (m, 4H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 8.4 Hz, 1H), 6.43 (s, 2H), 3.45 (s, 1H), 3.09 (s, 6H), 2.23 (br, 6H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.81 (s, 1H), 7.49 (d, *J* = 6.0 Hz, 2H), 7.31 – 7.26 (m, 4H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 8.4 Hz, 1H), 6.44 (s, 2H), 3.45 (s, 1H), 3.09 (s, 6H), 2.23 (s, 6H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ -0.90, -8.22, -22.40.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 174.0, 155.3, 146.5, 146.4, 145.1, 129.7, 129.5, 128.5, 127.9, 126.5, 125.3, 106.3, 47.4, 39.7.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{25}B_3Cl_2N_2NaO_2$ 463.1464; found 463.1474.



**3r**

26.7 mg, 71% yield

**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 11.10 (br, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.23 (q, *J* = 7.8 Hz, 2H), 7.15 – 7.07 (m, 1H), 3.04 (s, 1H), 1.67 – 1.56 (m, 3H), 1.51 – 1.34 (m, 9H), 1.32 – 1.26 (m, 3H), 1.26 – 1.20 (m, 3H), 1.15 – 0.73 (m, 15H).

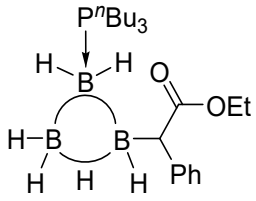
**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 10.94 (br, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.23 (q, *J* = 7.8 Hz, 2H), 7.11 (q, *J* = 7.8 Hz, 1H), 3.04 (s, 1H), 1.67 – 1.56 (m, 3H), 1.52 – 1.34 (m, 9H), 1.32 – 1.26 (m, 3H), 1.26 – 1.20 (m, 3H), 1.16 – 0.96 (m, 6H), 0.94 – 0.83 (m, 9H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ -3.85, -6.10, -15.31, -45.74.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 182.9, 182.6, 143.2, 142.9, 129.2, 128.7, 128.0, 127.8, 125.3, 125.2, 47.9, 24.4, 24.4, 24.3, 24.3, 24.2, 24.2, 21.0, 20.9, 20.7, 20.6, 13.6, 13.6.

**$^{31}$P NMR** (243 MHz, Chloroform-*d*) δ 13.33 – 7.62 (m).

**HRMS** (ESI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{40}B_3O_2P$ 376.3040; found 376.3030.




**3s**

28.3 mg, 70% yield

**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.24 (q, *J* = 7.2 Hz, 2H), 7.11 (q, *J* = 7.2 Hz, 1H), 4.16 – 4.04 (m, 2H), 3.10 (s, 0.5H), 3.01 (s, 0.5H), 1.65 – 1.58 (m, 3H), 1.51 – 1.44 (m, 3H), 1.43 – 1.35 (m, 6H), 1.33 – 1.28 (m, 3H), 1.27 – 1.21 (m, 6H), 1.15 – 0.81 (m, 15H).

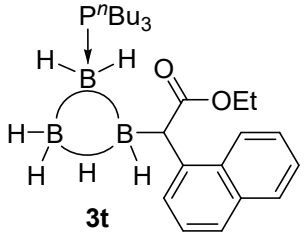
**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.24 (q, *J* = 7.2 Hz, 2H), 7.11 (q, *J* = 7.2 Hz, 1H), 4.16 – 4.03 (m, 2H), 3.10 (s, 0.5H), 3.02 (s, 0.5H), 1.66 – 1.57 (m, 3H), 1.51 – 1.44 (m, 3H), 1.43 – 1.35 (m, 6H), 1.33 – 1.29 (m, 3H), 1.27 – 1.20 (m, 6H), 1.10 – 0.96 (m, 6H), 0.93 (t, *J* = 7.2 Hz, 4.5H), 0.88 (t, *J* = 7.2 Hz, 4.5H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ -1.30, -3.85, -13.39, -16.08, -45.66.

**$^{13}$C{$^{1}$H} NMR** (101 MHz, Chloroform-*d*) δ 177.3, 177.0, 143.7, 143.2, 129.1, 128.4, 128.0, 127.8, 125.2, 125.1, 59.9, 59.7, 48.0, 24.5, 24.4, 24.4, 24.3, 24.3, 24.3, 24.2, 21.1, 20.9, 20.7, 20.5, 14.6, 14.5, 13.7, 13.6.

**$^{31}$P NMR** (243 MHz, Chloroform-*d*) δ 12.04 – 9.78 (m).

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{22}H_{44}B_3NaO_2P$ 427.3250; found 427.3258.




**3t**

27.7 mg, 61% yield

**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.4 Hz, 0.5H), 8.17 (d, *J* = 8.4 Hz, 0.5H), 7.99 (d, *J* = 7.2 Hz, 0.5H), 7.89 – 7.85 (m, 0.5H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.37 (m, 3H), 4.15 – 4.05 (m, 2H), 3.94 (s, 0.5H), 3.89 (s, 0.5H), 1.62 – 1.59 (m, 3H), 1.49 – 1.34 (m, 9H),

1.28 – 1.05 (m, 15H), 0.92 (t, *J* = 7.2 Hz, 4.5H), 0.84 (t, *J* = 7.2 Hz, 4.5H).

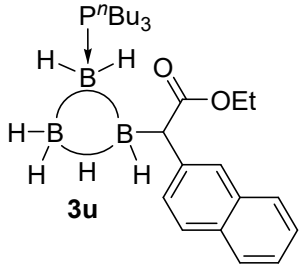
**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.4 Hz, 0.5H), 8.17 (d, *J* = 8.4 Hz, 0.5H), 7.98 (d, *J* = 7.2 Hz, 0.5H), 7.89 – 7.85 (m, 0.5H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.36 (m, 3H), 4.14 – 4.04 (m, 2H), 3.94 (s, 0.5H), 3.89 (s, 0.5H), 1.62 – 1.59 (m, 3H), 1.49 – 1.35 (m, 9H), 1.27 – 1.18 (m, 9H), 1.17 – 1.10 (m, 6H), 0.93 (t, *J* = 7.2 Hz, 4.5H), 0.84 (t, *J* = 7.2 Hz, 4.5H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ -1.86, -3.76, -14.66, -16.33, -45.92.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 177.2, 177.1, 134.1, 134.0, 132.4, 131.9, 128.7, 128.7, 127.0, 126.1, 125.8, 125.7, 125.6, 125.4, 125.3, 125.0, 125.0, 124.3, 60.0, 59.8, 24.5, 24.4, 24.4, 24.3, 24.3, 24.2, 21.0, 20.9, 20.8, 20.6, 14.6, 14.5, 13.7, 13.6.

**$^{31}$P NMR** (243 MHz, Chloroform-*d*) δ 11.47 – 9.50 (m).

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{26}H_{46}B_3NaO_2P$ 477.3407; found 477.3411.




**3u**

26.8 mg, 59% yield

**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 0.44H), 7.83 – 7.69 (m, 3.56H), 7.68 – 7.59 (m, 1H), 7.45 – 7.31 (m, 2H), 4.20 – 4.05 (m, 2H), 3.28 (s, 0.44H), 3.17 (s, 0.56H), 1.65 – 1.52 (m, 3H), 1.50 – 1.32 (m, 9H), 1.29 – 1.24 (m, 4H), 1.23 – 0.98 (m, 11H), 0.92 (t, *J* = 7.2 Hz, 4H), 0.78 (t, *J* = 7.2 Hz, 5H).

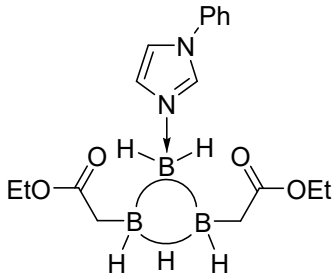
**$^{1}$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 0.44H), 7.83 – 7.69 (m, 3.56H), 7.68 – 7.59 (m, 1H), 7.45 – 7.31 (m, 2H), 4.20 – 4.05 (m, 2H), 3.28 (s, 0.44H), 3.17 (s, 0.56H), 1.65 – 1.52 (m, 3H), 1.50 – 1.32 (m, 9H), 1.29 – 1.24 (m, 4H), 1.23 – 1.17 (m, 5H), 1.15 – 0.96 (m, 6H), 0.92 (t, *J* = 7.2 Hz, 4H), 0.78 (t, *J* = 7.2 Hz, 5H).

**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ -2.04, -4.82, -13.30, -16.21, -46.09.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 177.3, 176.9, 141.4, 140.9, 133.8, 133.7, 131.9, 131.9, 128.6, 128.0, 127.8, 127.8, 127.6, 127.3, 127.1, 126.8, 126.0, 125.5, 125.4, 124.7, 124.7, 60.0, 59.8, 24.4, 24.4, 24.3, 24.3, 24.2, 24.2, 24.2, 21.0, 20.8, 20.8, 20.6, 14.6, 14.5, 13.7, 13.5.

**$^{31}$P NMR** (243 MHz, Chloroform-*d*) δ 12.23 – 9.29 (m).

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{26}H_{46}B_3NaO_2P$ 477.3407; found 477.3414.




**3v**

18.2 mg, 51% yield

**$^{1}$H NMR** (600 MHz, Methylene Chloride-$d_2$) δ 8.50(s, 34H), δ 8.25 (s, 0.66H), 7.62 – 7.55 (m, 2H), 7.54 – 7.50 (m, 1H), 7.49 – 7.40 (m, 2H), 7.36 – 7.24 (m, 2H), 4.08 – 3.97 (m, 4H), 2.25 (br, 5H), 1.78 (q, *J*

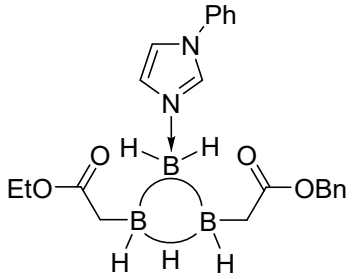
= 12.0 Hz, 4H), 1.24 – 1.19 (m, 6H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Methylene Chloride-$d_2$) δ 8.50(s, 34H), δ 8.25 (s, 0.66H), 7.52 – 7.41 (m, 3H), 7.40 – 7.31 (m, 2H), 7.27 – 7.15 (m, 2H), 4.01 – 3.87 (m, 4H), 2.15 (s, 5H), 1.78 (q, $J$ = 12.0 Hz, 4H), 1.24 – 1.19 (m, 6H).

**$^{11}$B NMR** (193 MHz, Methylene Chloride-$d_2$) δ 10.34, 2.06, -13.25, -24.52.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Methylene Chloride-$d_2$) δ 177.7, 176.2, 137.4, 136.1, 136.0, 130.9, 130.2, 130.1, 128.9, 122.6, 120.0, 59.9, 59.9, 14.8, 14.8.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{27}B_3N_2NaO_4$ 379.2142; found 379.2149.




**3w**

23.4 mg, 56% yield

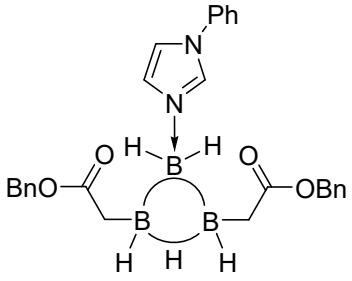
**$^{1}$H NMR** (600 MHz, Methylene Chloride-$d_2$) δ 8.40 (s, 0.36H), 8.14 (s, 0.64H), 7.64 – 7.48 (m, 3H), 7.47 – 7.39 (m, 2H), 7.39 – 7.24 (m, 7H), 5.04 (d, $J$ = 35.9 Hz, 2H), 4.07 – 3.96 (m, 2H), 2.25 (br, 5H), 1.93 – 1.72 (m, 4H), 1.23 – 1.15 (m, 3H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Methylene Chloride-$d_2$) δ 8.40 (s, 0.36H), 8.14 (s, 0.64H), 7.64 – 7.48 (m, 3H), 7.47 – 7.39 (m, 2H), 7.39 – 7.24 (m, 7H), 5.04 (d, $J$ = 35.9 Hz, 2H), 4.07 – 3.96 (m, 2H), 2.25 (s, 5H), 1.93 – 1.72 (m, 4H), 1.23 – 1.15 (m, 3H).

**$^{11}$B NMR** (193 MHz, Methylene Chloride-$d_2$) δ 0.56, -23.11.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Methylene Chloride-$d_2$) δ 177.7, 177.5, 137.7, 136.0, 130.9, 130.2, 128.9, 128.7, 128. 5, 128.3, 128.2, 122.7, 120.0, 66.0, 65.7, 59.9, 59.9, 14.8, 14.8.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{22}H_{29}B_3N_2NaO_4$ 441.2299; found 441.2296.




**3x**

25.4 mg, 53% yield

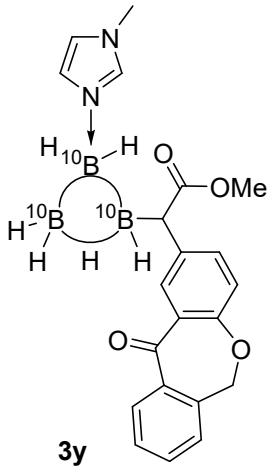
**$^{1}$H NMR** (600 MHz, Methylene Chloride-$d_2$) δ 8.30 (s, 0.33H), 8.06 (s, 0.67H), 7.62 – 7.50 (m, 3H), 7.48 – 7.00 (m, 14H), 5.12 – 4.94 (m, 4H), 2.56 – 2.06 (m, 5H), 1.95 – 1.75 (m, 4H).

**$^{1}$H{$^{11}$B} NMR** (600 MHz, Methylene Chloride-$d_2$) δ 8.30 (s, 0.33H), 8.06 (s, 0.67H), 7.62 – 7.50 (m, 3H), 7.48 – 7.00 (m, 14H), 5.12 – 4.94 (m, 4H), 2.26 (s, 5H), 1.95 – 1.75 (m, 4H).

**$^{11}$B NMR** (193 MHz, Methylene Chloride-$d_2$) δ 2.04, -24.89.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 177. 4, 176.0, 138.0, 137.6, 137.2, 136.0, 130.9, 130.8, 130.2, 130.1, 128.9, 128.7, 128.7, 128.4, 128.3, 128.2, 122.7, 120.1, 120.0, 66.0, 65.7.

**HRMS** (ESI-TOF) m/z: $[M+MeOH+H]^+$ calcd for $C_{28}H_{36}B_3N_2O_5$ 513.2898; found 513.2897.



**3y**

24.7mg, 62% yield

**$^{1}$H NMR** (600 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.90 – 7.59 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 6.6 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.11 – 7.05 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.82 (s, 1H), 5.16 (s, 2H), 3.76 – 3.70 (m, 3H), 3.65 – 3.60 (m, 3H), 3.24 (s, 1H), 2.02 (br, 6H).

**$^{1}$H{$^{10}$B} NMR** (600 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.90 – 7.59 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 6.6 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.11 – 7.05 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.82 (s, 1H), 5.16 (s, 2H), 3.76 – 3.70 (m, 3H), 3.65 – 3.60 (m, 3H), 3.24 (s, 1H), 2.06 – 1.96 (m, 6H).

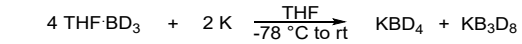
**$^{10}$B NMR** (64 MHz, Chloroform-*d*) δ 0.37, -7.69, -27.28.

**$^{13}$C{$^{1}$H} NMR** (151 MHz, Chloroform-*d*) δ 159.3, 137.2, 133.4, 132.8, 132.6, 129.6, 129.2, 127.8, 127.5, 124.9, 120.8, 120.1, 73.7, 51.4, 37.8, 35.3.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{25}{}^{10}B_3N_2NaO_4$ 422.2095; found 422.2089.

## Control Experiments

### Synthesis of $KB_3D_8$



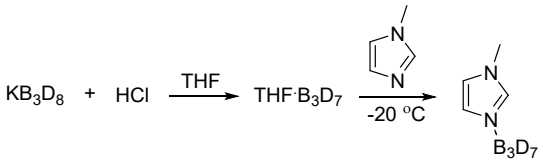

$KB_3D_8$ were prepared according to literature precedent.[4]

Potassium (585 mg, 15 mmol) was cut into a small piece($3 \times 3 \times 3$ mm$^3$) in a glovebox and added to a 100 mL Schlenk flask. The flask was connected with a Schlenk line into which $THF{\cdot}BD_3$ (0.3M, 100 mL, 30 mmol) was condensed at -78 °C. The reaction mixture was stirred at room temperature until potassium was completely consumed and a large amount of $KBD_4$ white precipitate formed (about 24 h). The $KBD_4$ precipitate was filtered out. Removal of THF from the filtrate yielded a sticky solid, to which 30 mL of toluene was added, producing a white precipitate. Part of the solvent was removed under dynamic vacuum. The precipitate was filtered, washed with toluene ($3 \times 30$ mL), and then dried under dynamic vacuum to yield $KB_3D_8$ as a white powder (842 mg, 85% yield).

**$^2$D NMR** (92 MHz, Tetrahydrofuran): δ 0.39.

**$^{11}$B NMR** (193 MHz, Tetrahydrofuran): δ -30.5.

### Synthesis of 1a-D




**1a-D**, 80% D

The prepared $KB_3D_8$ (0.44 g, 5 mmol) was added to a 50 mL Schlenk flask. The flask was connected with a Schlenk line, and 20 mL of THF was injected. A solution of 1.0 M HCl in THF (5 mL, 5 mmol) was added dropwise to the flask at room temperature, and the mixture was stirred for 0.5 h. Then, the reaction mixture was filtered, and the filtrate was the THF solution of $THF{\cdot}B_3H_7$. Next, at -20 °C, 5 mmol of 1-methylimidazole was added to the filtrate. After stirring for 5 min, THF was removed from the reaction mixture under dynamic vacuum, leaving an oily product. Separation of the mixture by flash chromatography (PE/DCM = 3:1, v/v) yielded a colorless oil **1a-D** (483.3 mg, 75% yield).

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.14 (t, $J$ = 1.6 Hz, 1H), 6.85 (t, $J$ = 1.7 Hz, 1H), 3.76 (s, 3H), 1.77 (br, 1.4H).

**$^1$H{$^{11}$B} NMR** (600 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.14 (s, 1H), 6.85 (t, $J$ = 1.8 Hz, 1H), 3.76 (s, 3H), 1.77 (s, 1.4H).

**$^2$D NMR** (92 MHz, Dichloromethane) δ 1.63.

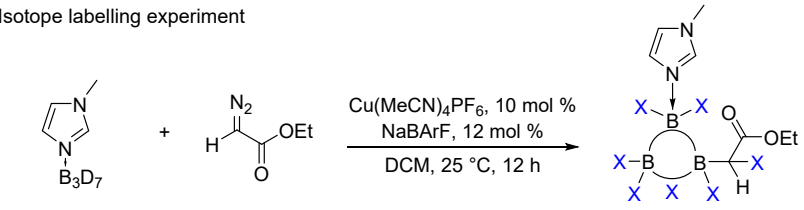
**$^{11}$B NMR** (193 MHz, Chloroform-*d*) δ -10.76, -29.05.

**$^{13}$C{$^1$H} NMR** (151 MHz, Chloroform-*d*) δ 137.0, 127.5, 120.8, 35.3.

**HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_4H_6D_7B_3N_2Na$ 152.1689; found 152.1680.

## KIE experiments with diazo compound as the substrate

(a) Isotope labelling experiment

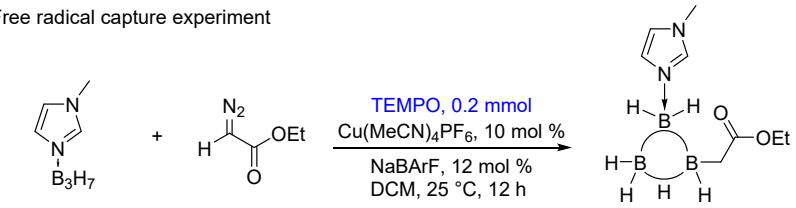



**1a-D,** 80% D
0.1 mmol

**2a**
0.2 mmol

**3a-D,** 76% yield
X = H or D, 80% D

(b) Free radical capture experiment

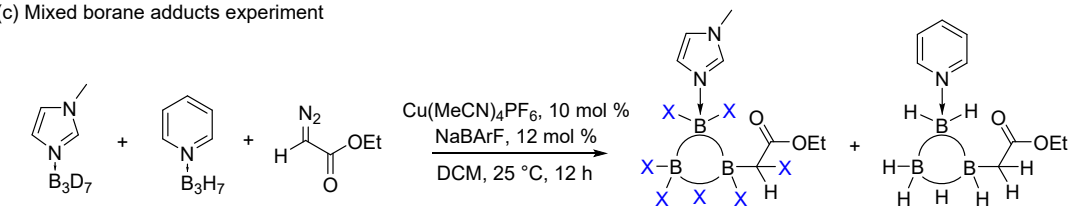



**1a**
0.1 mmol

**2a**
0.2 mmol

**3a,** 75% yield

(c) Mixed borane adducts experiment




**1a-D,** 80% D
0.2 mmol

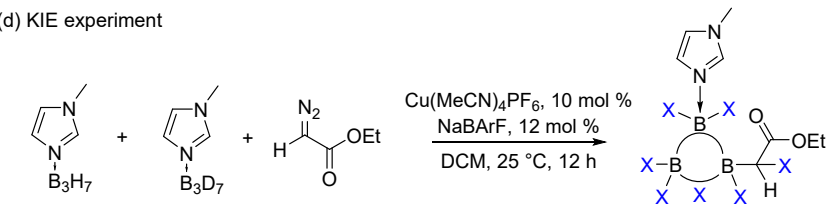
**1e,** 0% D
0.2 mmol

**2a**
0.1 mmol

**3a-D,** 49% yield
X = H or D, 80% D

**3e,** 27% yield
0% D

(d) KIE experiment




**1a**
0.2 mmol

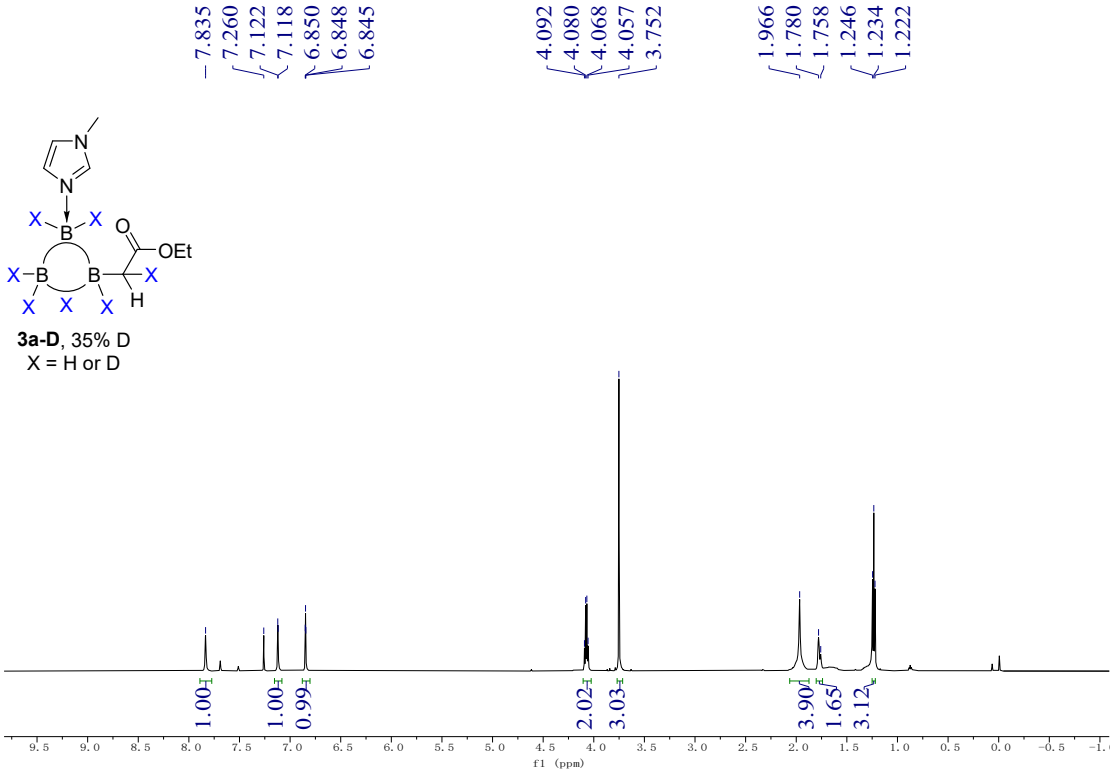
**1a-D,** 80% D
0.2 mmol

**2a**
0.1 mmol

**3a-D,** 82% yield
X = H or D, 35% D
$k_H/k_D$ = 1.24

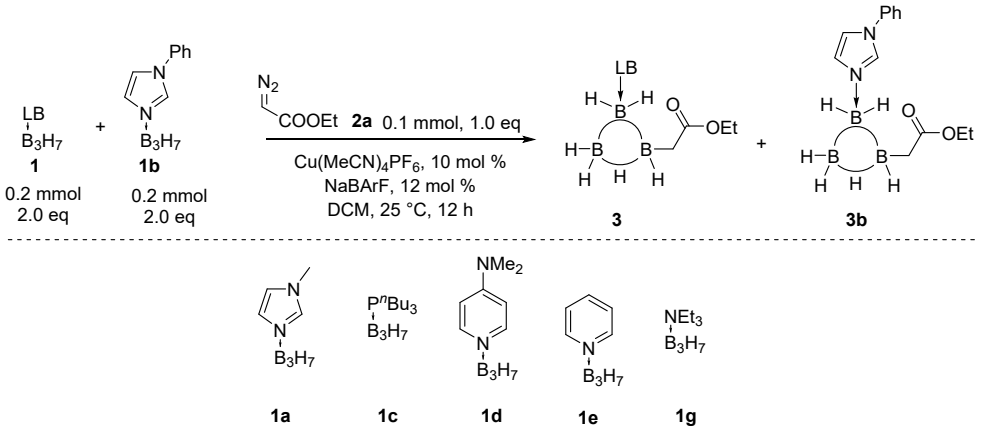
**KIE experiment**: In a Schlenk tube (25 mL), **1a** (0.2 mmol), **1a-D** (0.2 mmol), $Cu(MeCN)_4PF_6$ (3.7 mg, 10 mol %) and $NaBAr_F$ (10.6 mg, 12 mol %) were charged. Then DCM (2.0 mL), and ethyl diazoacetate **2a** (0.2 mmol) were added, and the reaction vessel was evacuated and backfilled with $N_2$ three times. The reaction mixture was stirred at 25 °C for 12 h until the diazo compound disappeared. The residue was purified by flash column chromatography to afford the corresponding B–H bond insertion products **3a-D**, 35% D (17.5 mg, 82% yield). After purification by chromatography, the deuterated ratio of **3a-D** was determined by $^1H\{^{11}B\}$ NMR according to integration of residual boryl H and benzyl H.

**$^{1}H\{^{11}B\}$ NMR of 3a-D from KIE experiment**



**Competitive B−H Insertion Experiments with Two Ligated $B_3H_7$.**

**Table S1.**

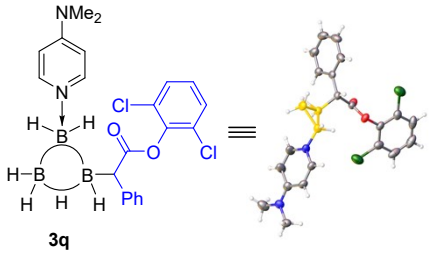



| Entry | LB-$B_3H_7$ | Products | Ratio[a] ($k_3$ / $k_{3b}$) |
|---|---|---|---|
| 1 | **1a** | **3a**/**3b** | 1.75 / 1 |
| 2 | **1d** | **3d**/**3b** | 1.60 / 1 |
| 3 | **1c** | **3c**/**3b** | 0.76 / 1 |
| 4 | **1g** | **3g**/**3b** | 0.64 / 1 |
| 5 | **1e** | **3e**/**3b** | 0.56 / 1 |

[a]Determined by integration of the $^1H$ or $^{11}B$ NMR spectrum of the reaction mixture.

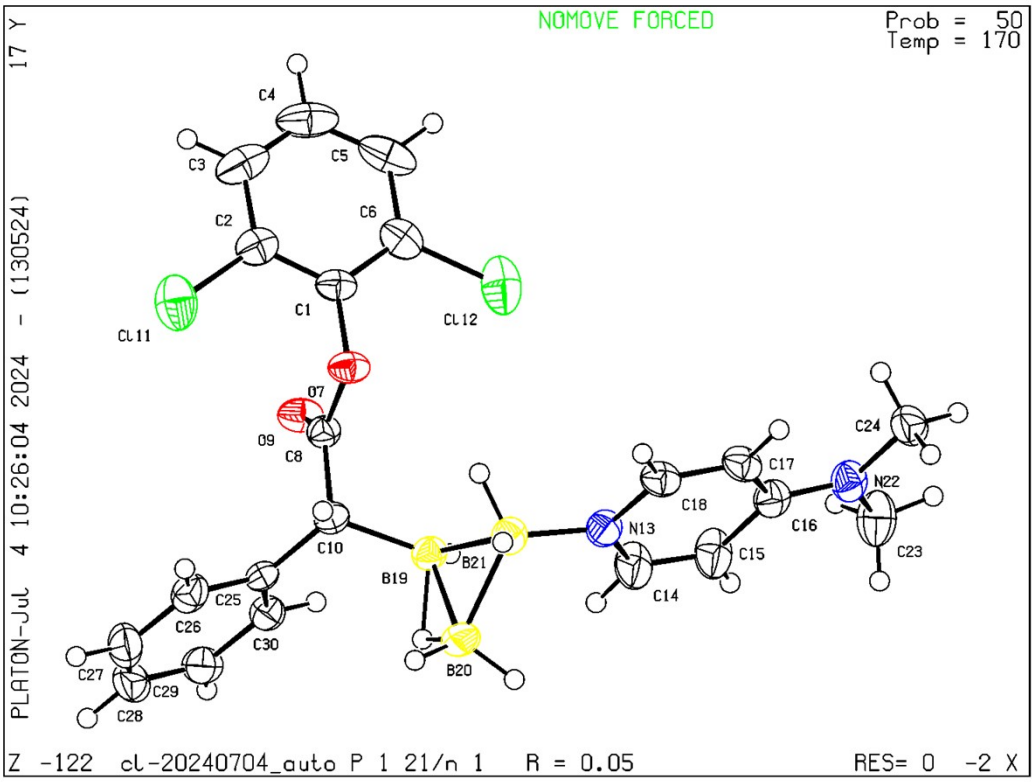
# X-ray data of 3q

**Figure S1.** X-Ray crystal structure of **3q** (The crystal was obtained by slow evaporation of **3q** in a mixture of Pet/EtOAc). (CCDC: 2487579) (Ellipsoid set at 50% probability level)




**3q**

| Identification code | **3q** |
|---|---|
| Empirical formula | $C_{21}H_{25}B_3Cl_2N_2O_2$ |
| Formula weight | 440.76 |
| Temperature/K | 170.00(10) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 9.7778(2) |
| b/Å | 11.3784(2) |
| c/Å | 20.6155(3) |
| α/° | 90 |
| β/° | 96.410(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 2279.25(7) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.284 |
| μ/mm$^{-1}$ | 2.714 |
| F(000) | 920.0 |
| Crystal size/mm$^3$ | 0.02 × 0.01 × 0.01 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.632 to 142.672 |
| Index ranges | $-11 \le h \le 12$, $-13 \le k \le 11$, $-18 \le l \le 25$ |
| Reflections collected | 10599 |
| Independent reflections | 4349 [$R_{int}$ = 0.0254, $R_{sigma}$ = 0.0293] |
| Data/restraints/parameters | 4349/0/293 |
| Goodness-of-fit on $F^2$ | 1.050 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0485, $wR_2$ = 0.1249 |
| Final R indexes [all data] | $R_1$ = 0.0546, $wR_2$ = 0.1302 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.67/-0.56 |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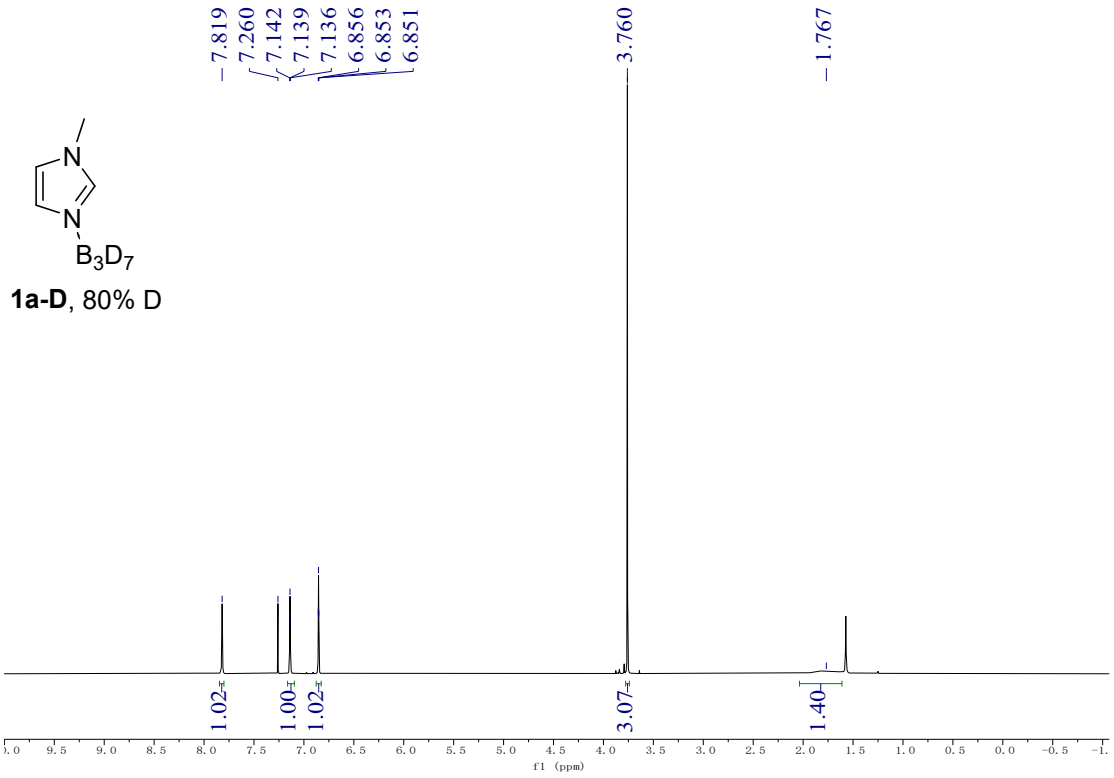
Temp = 170
17 Y
PLATON-Jul 4 10:26:04 2024 - (130524)
C4
C3
C5
C2
C6
C1
CL11
CL12
O7
O9
C8
C10
B19
B21
B20
C25
C26
C30
C27
C29
C28
N13
C18
C17
C24
N22
C16
C15
C23
C14
Z -122 cl-20240704_auto P 1 21/n 1 R = 0.05
RES= 0 -2 X

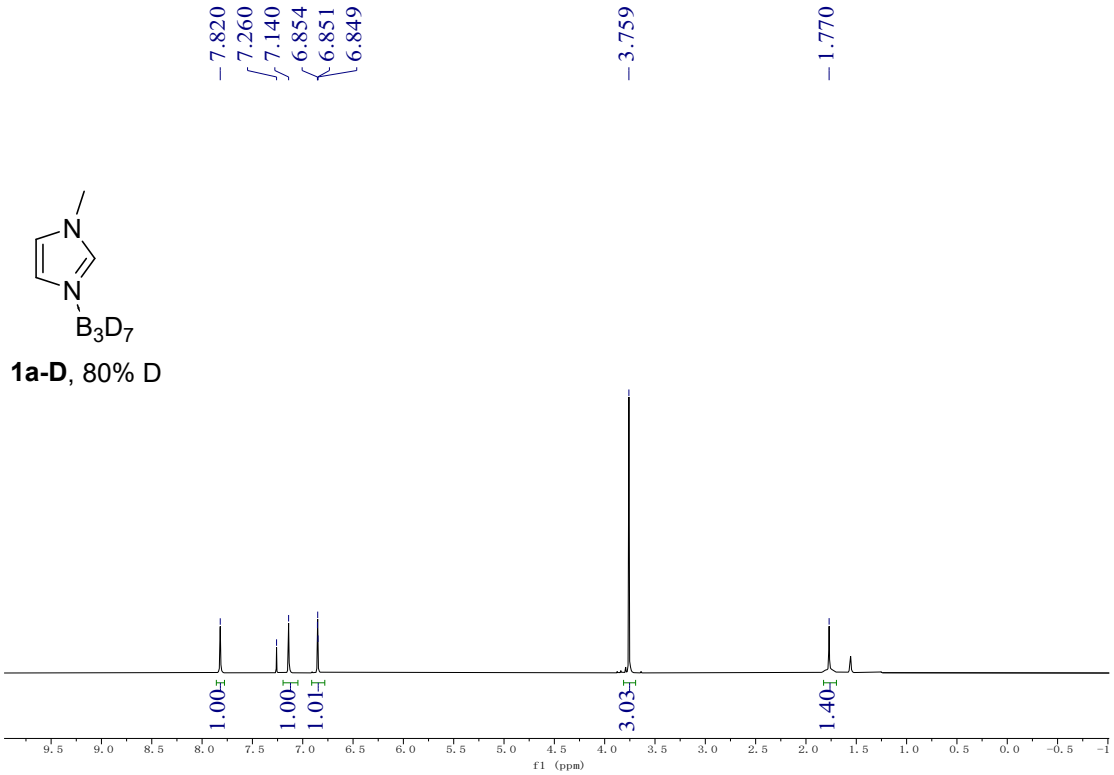
# NMR spectra

**$^{1}$H NMR of 1a-D**



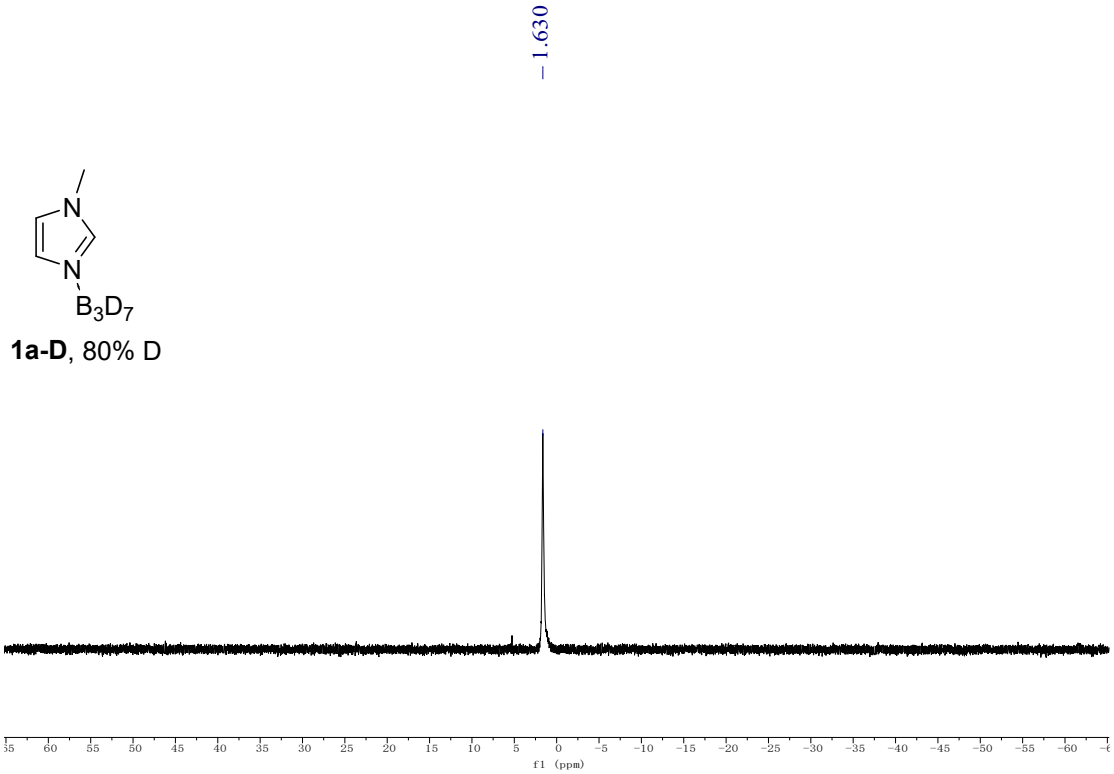

**1a-D**, 80% D

**$^{1}$H{$^{11}$B} NMR of 1a-D**



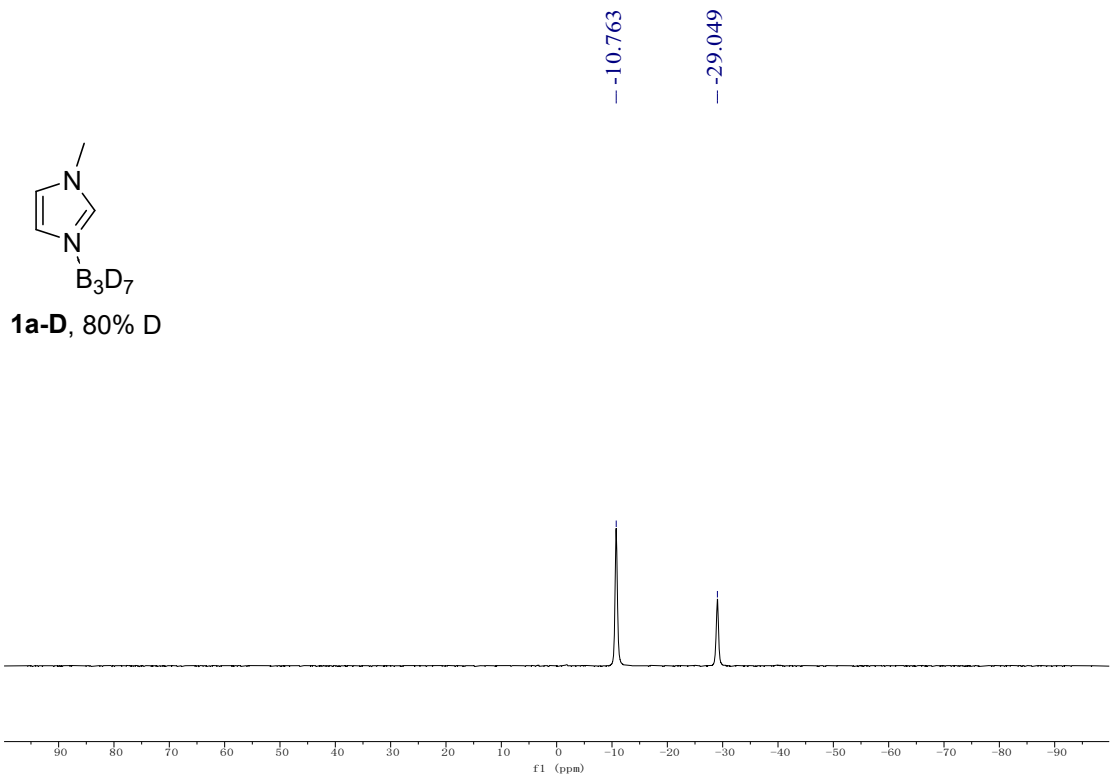

**1a-D**, 80% D

**$^{2}$D NMR of 1a-D**



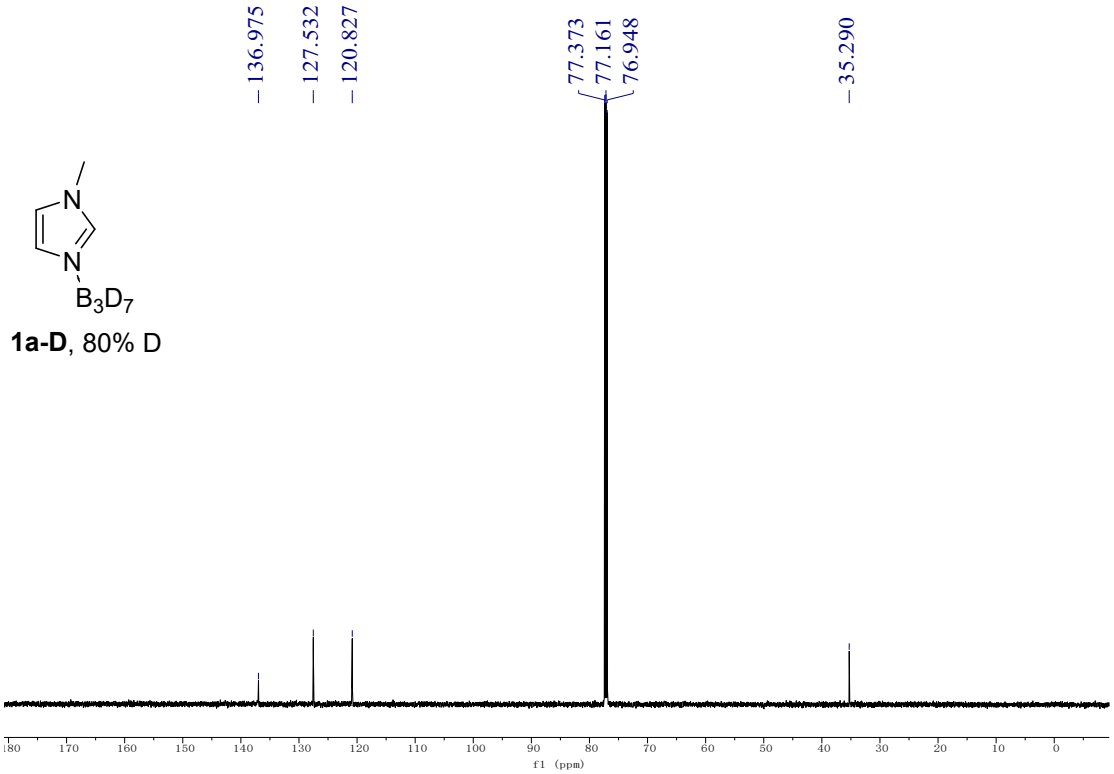

**1a-D**, 80% D

**$^{11}$B NMR of 1a-D**



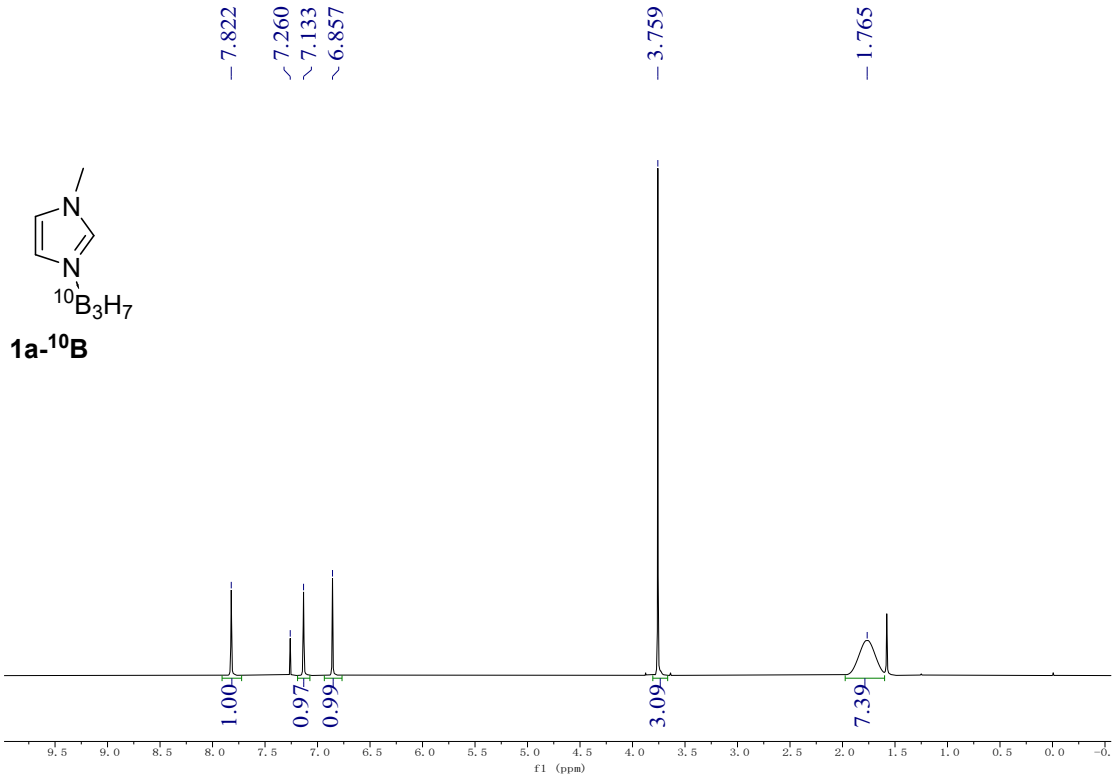

**1a-D**, 80% D

**$^{13}C\{^{1}H\}$ NMR of 1a-D**



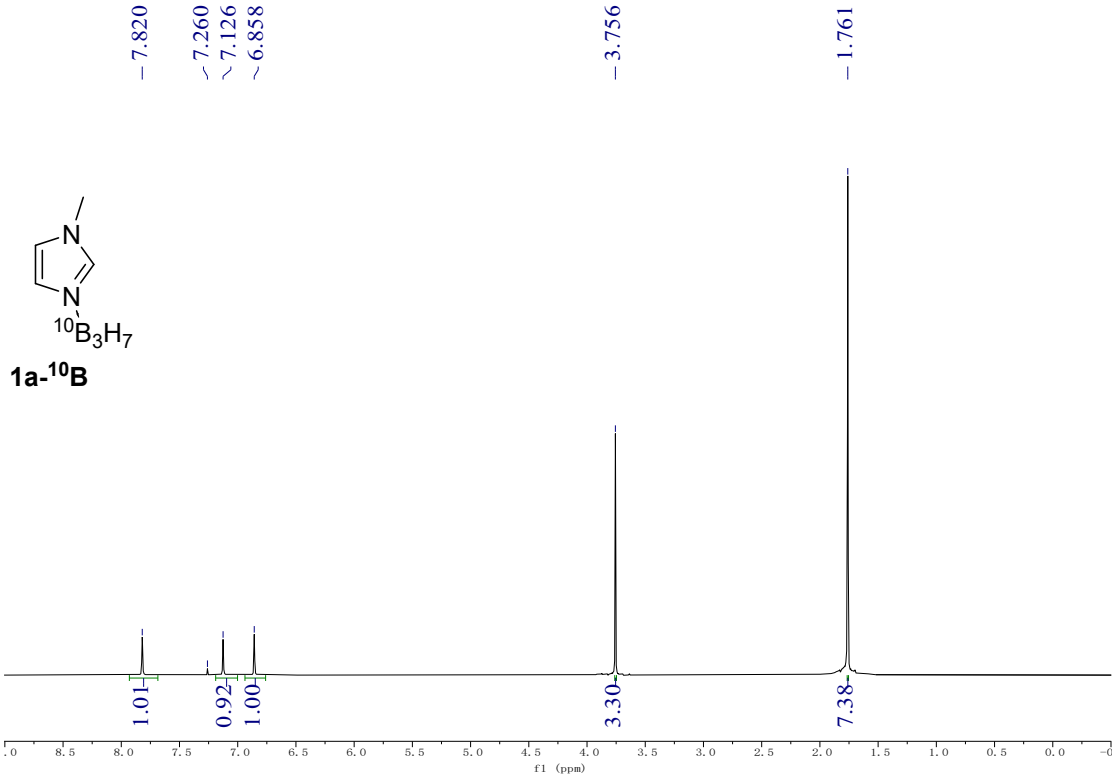

**1a-D**, 80% D

**$^{1}H$ NMR of 1a-$^{10}B$**



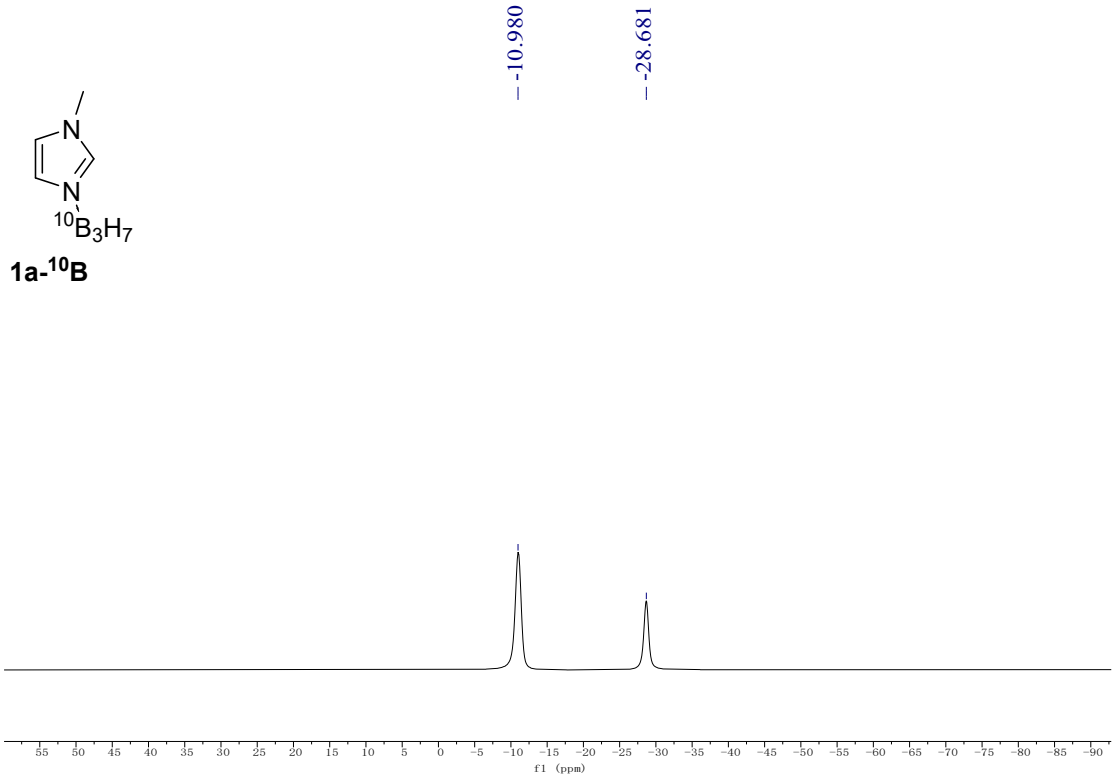

**1a-$^{10}B$**

**$^{1}H\{^{10}B\}$ NMR of 1a-$^{10}B$**



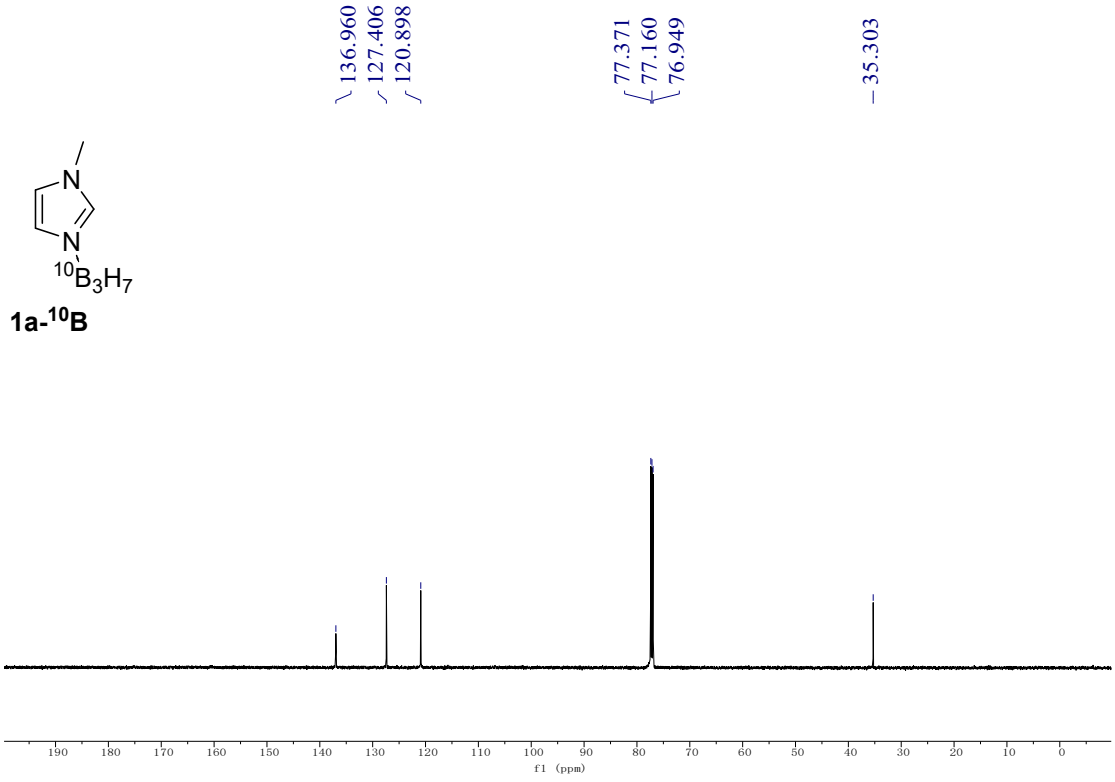

**1a-$^{10}B$**

**$^{10}B$ NMR of 1a-$^{10}B$**



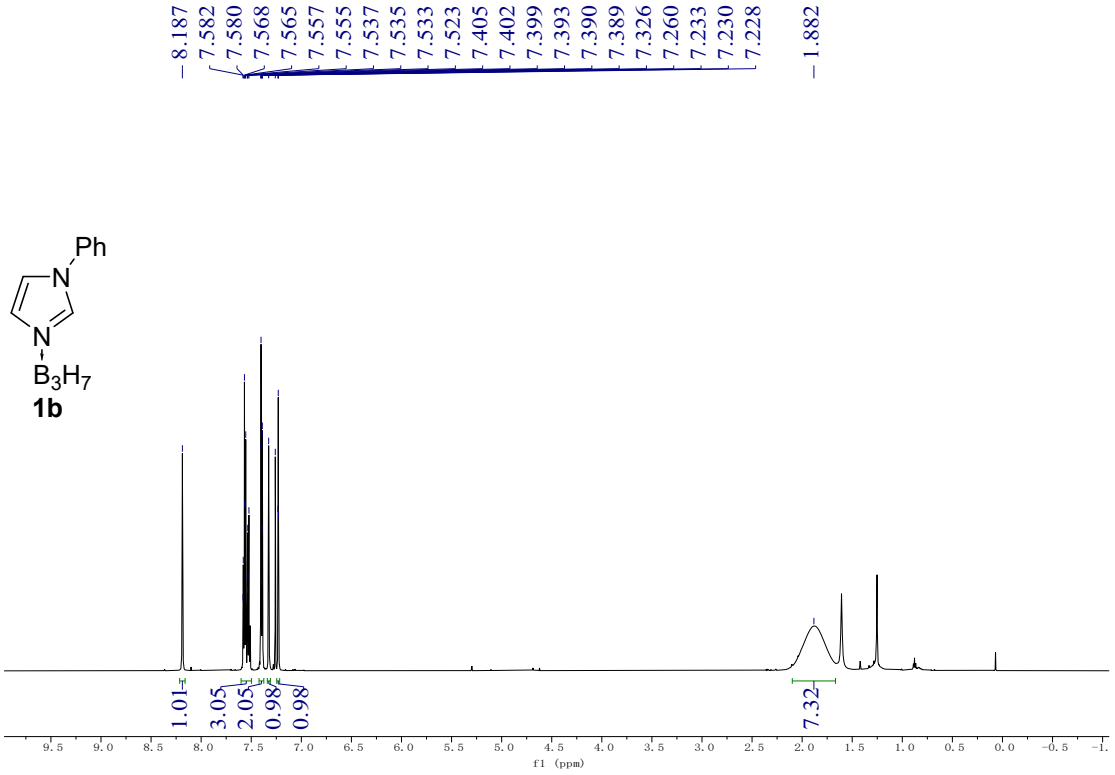

**1a-$^{10}B$**

**$^{13}C\{^{1}H\}$ NMR of 1a-$^{10}B$**



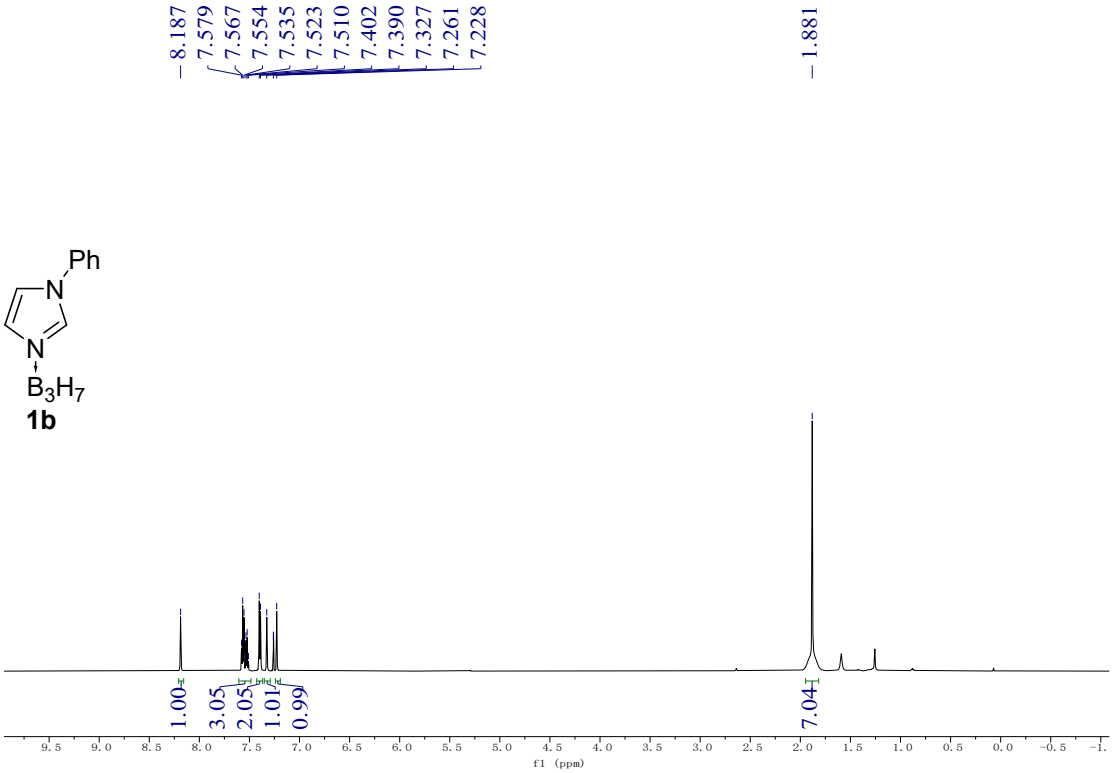

**1a-$^{10}B$**

**$^{1}H$ NMR of 1b**




**1b**

**$^{1}H\{^{11}B\}$ NMR of 1b**

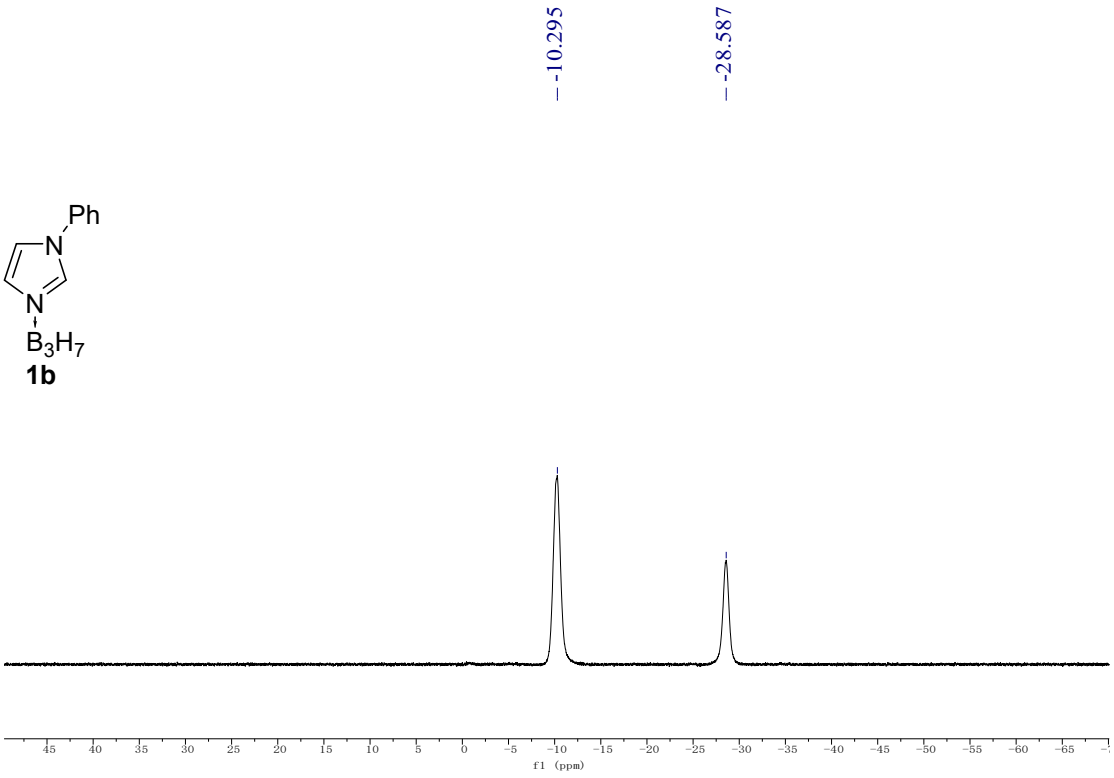






**1b**

**$^{11}B$ NMR of 1b**

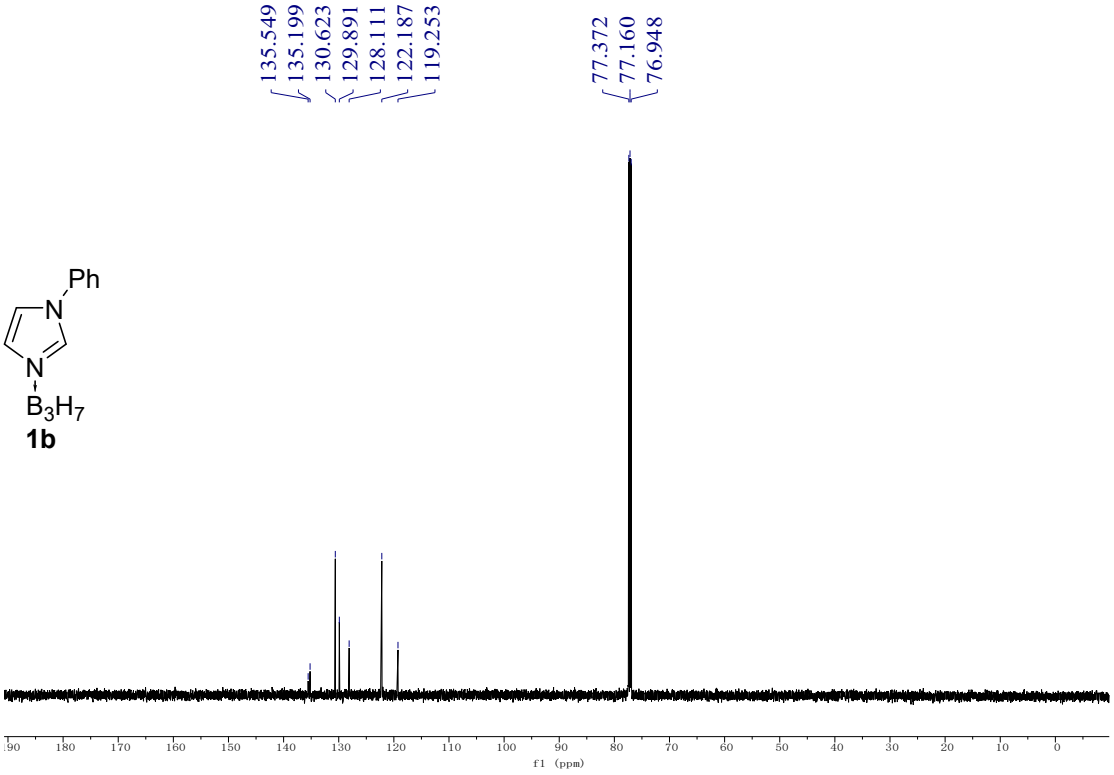




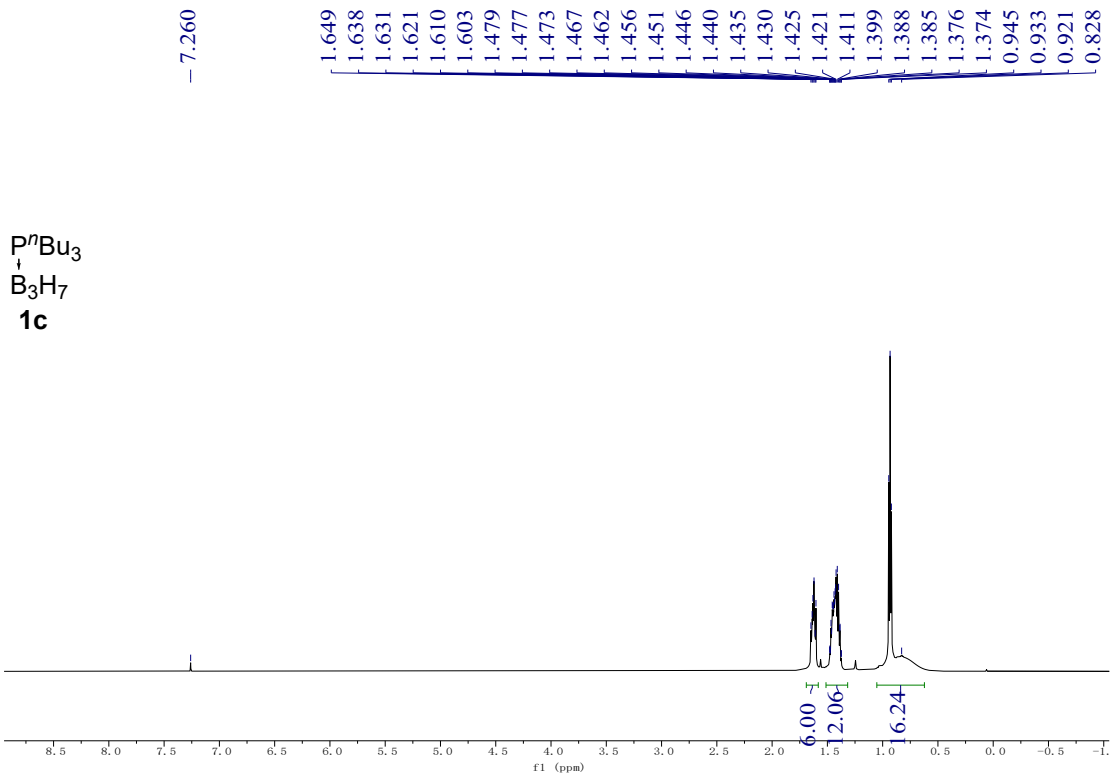


**1b**

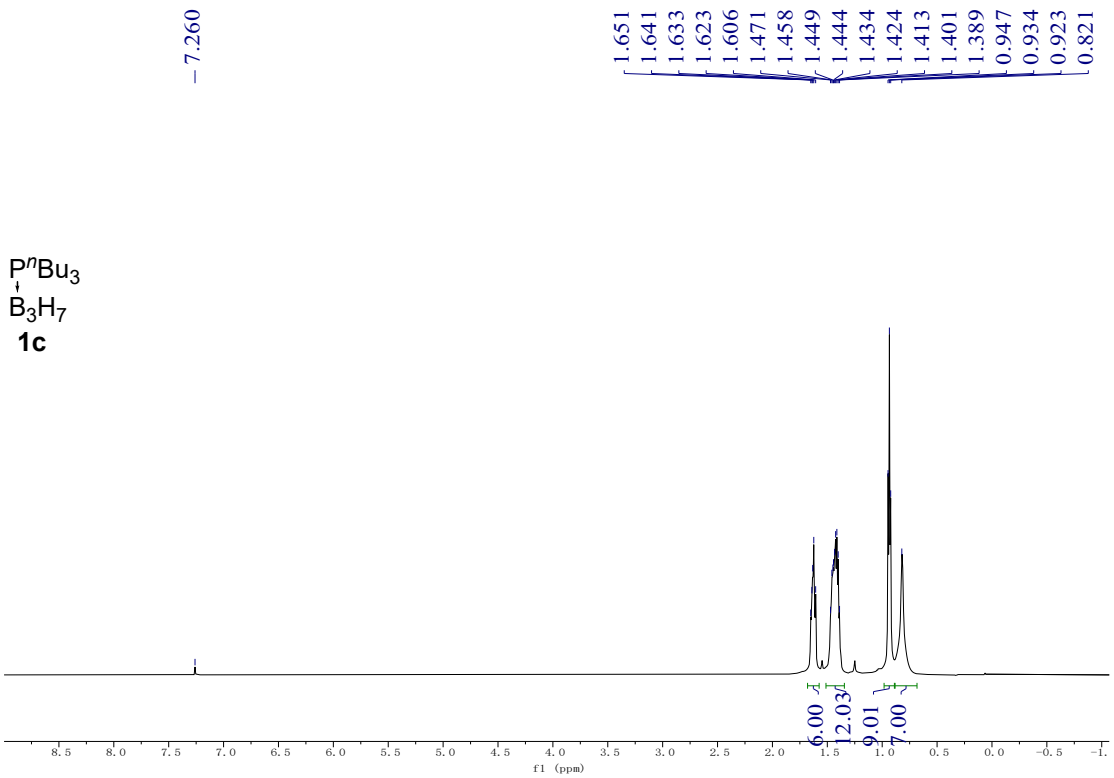
**$^{13}C\{^{1}H\}$ NMR of 1b**



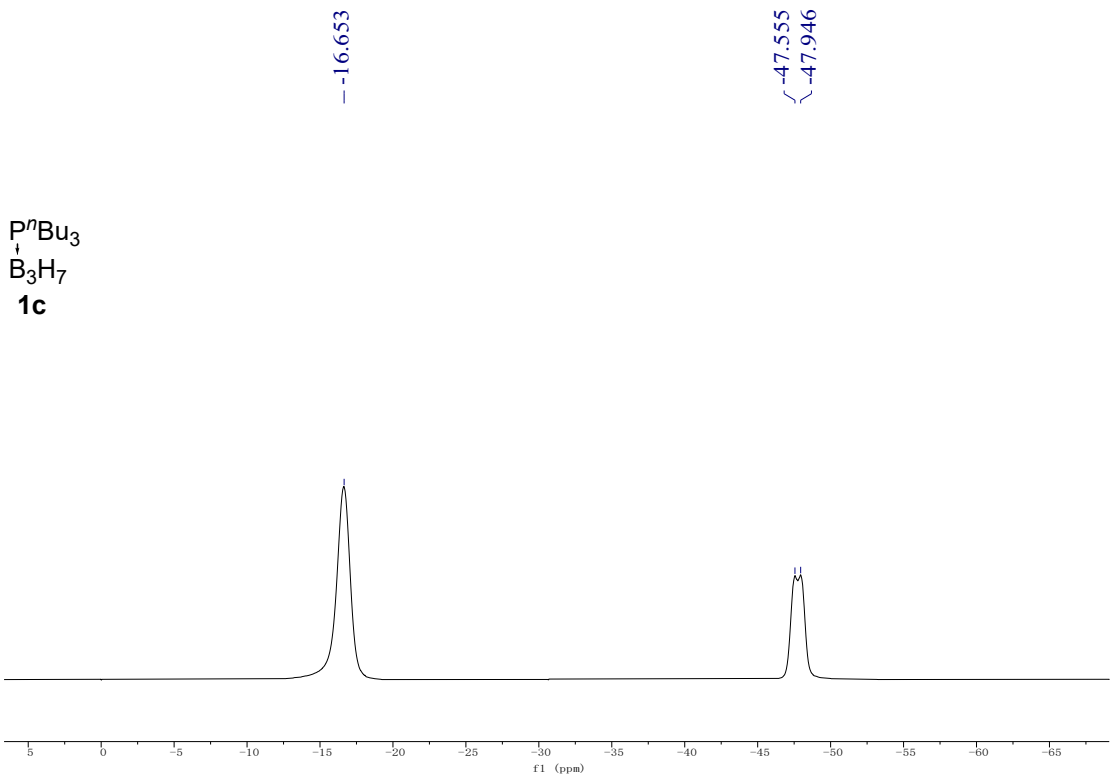

**$^{1}H$ NMR of 1c**



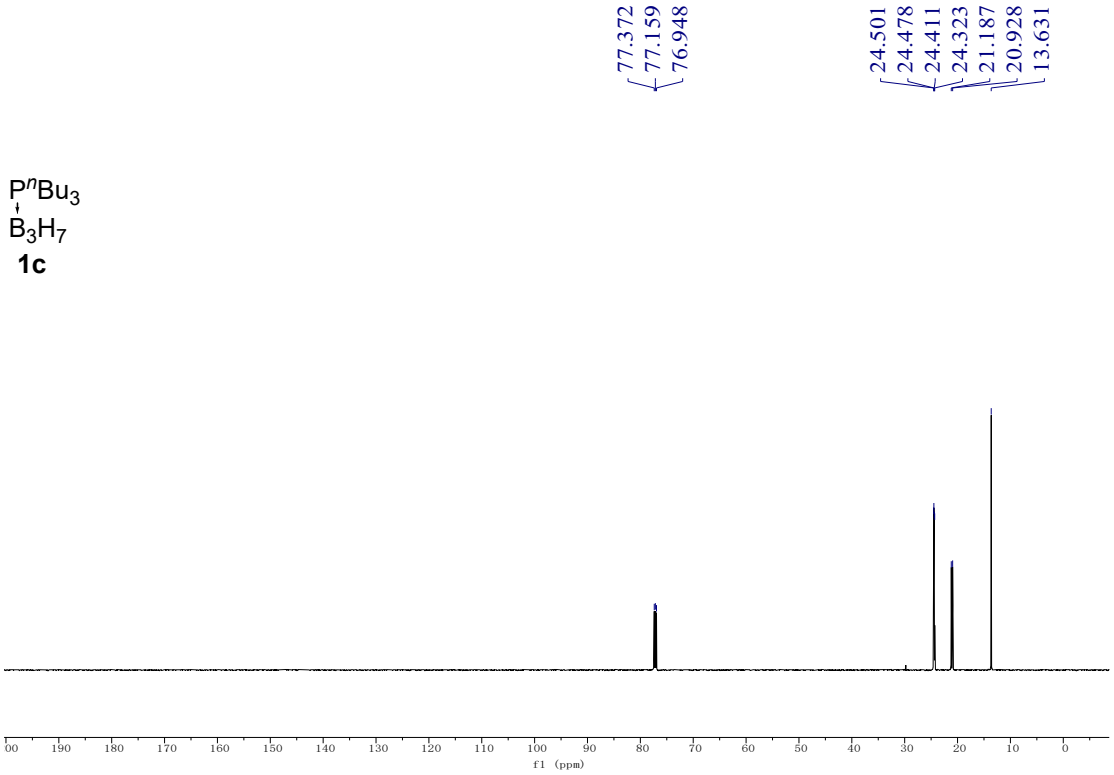
**$^{1}H\{^{11}B\}$ NMR of 1c**



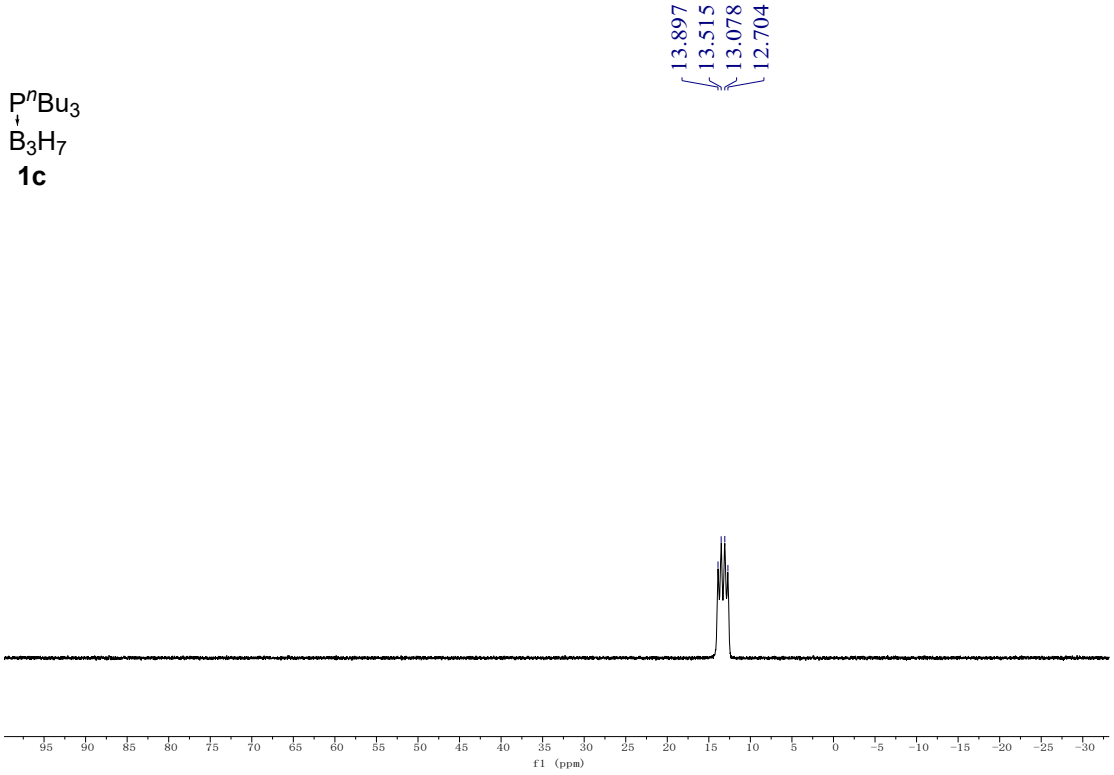

**$^{11}B$ NMR of 1c**



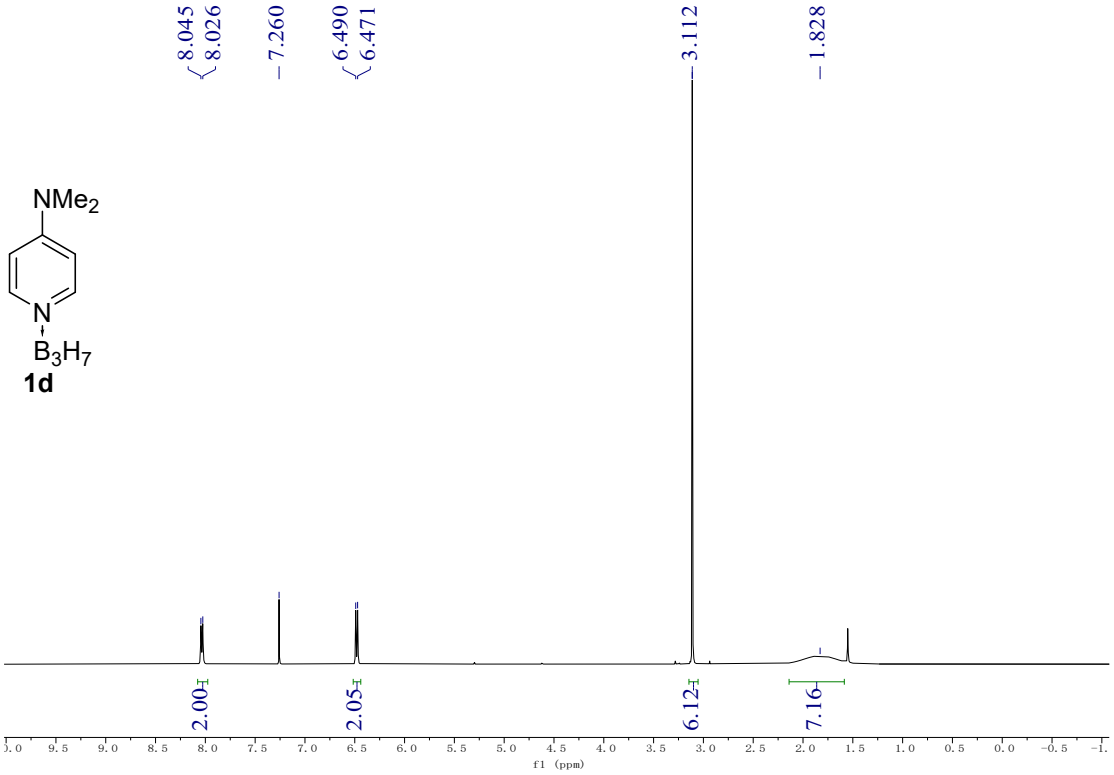
**$^{13}C\{^{1}H\}$ NMR of 1c**



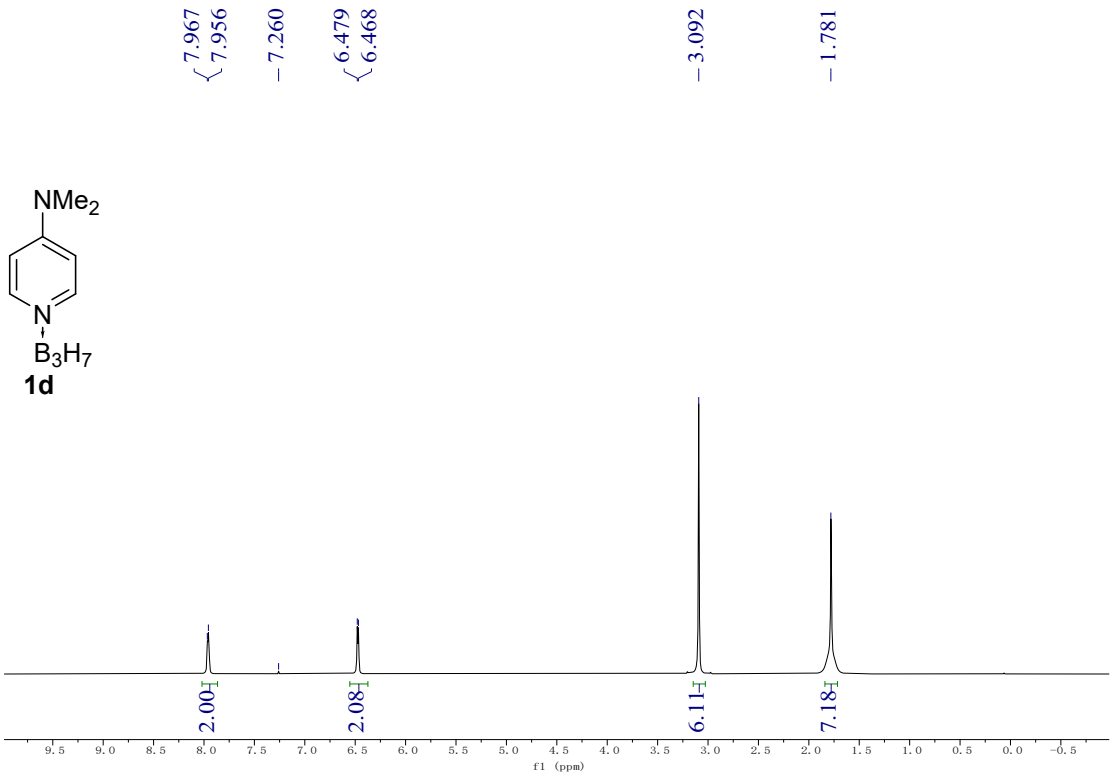

**$^{31}P$ NMR of 1c**



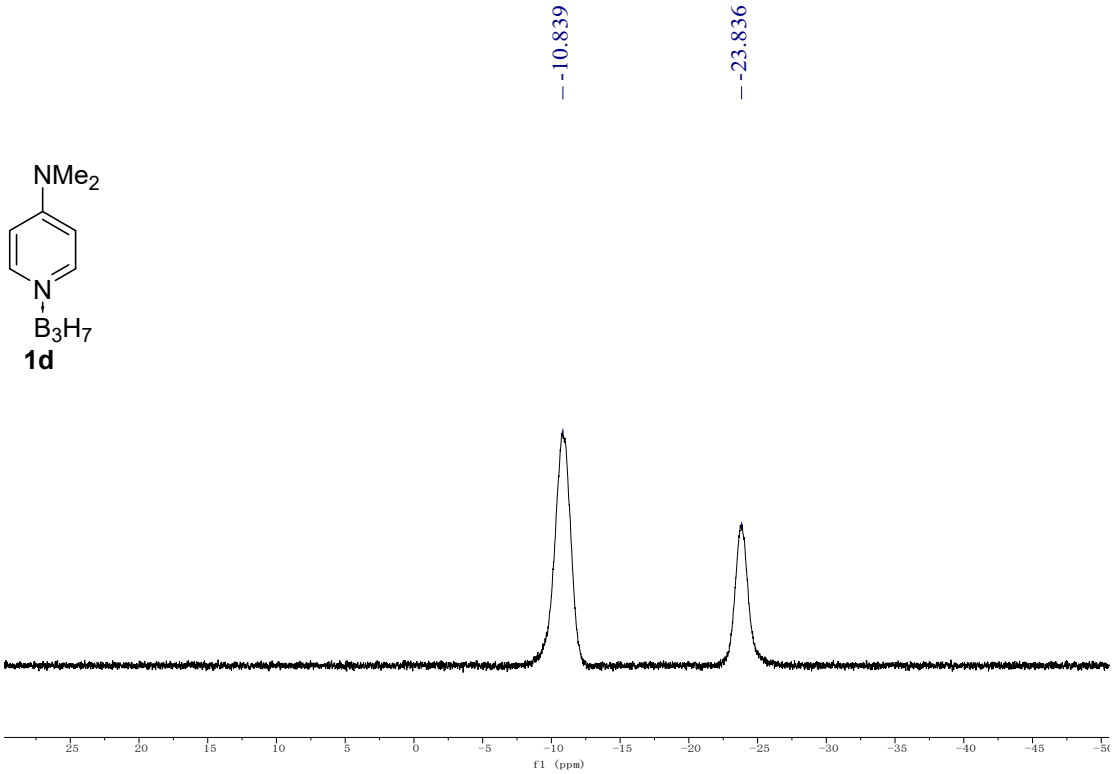
**$^{1}$H NMR of 1d**



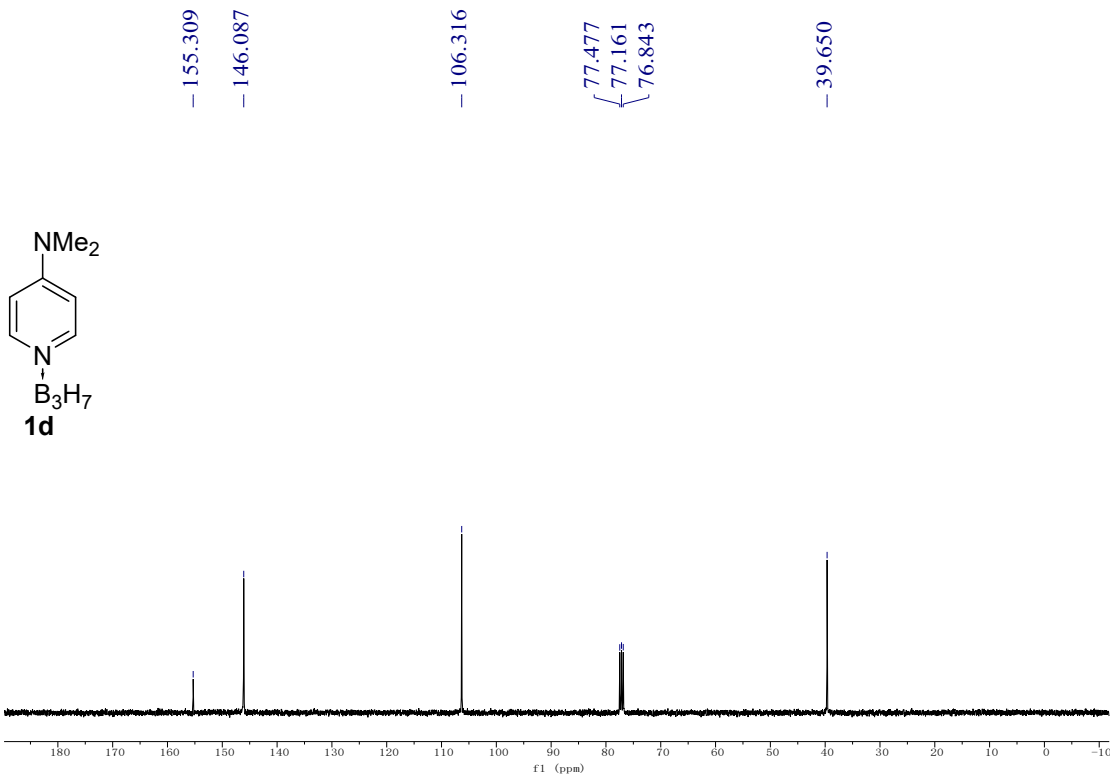

**$^{1}$H{$^{11}$B} NMR of 1d**



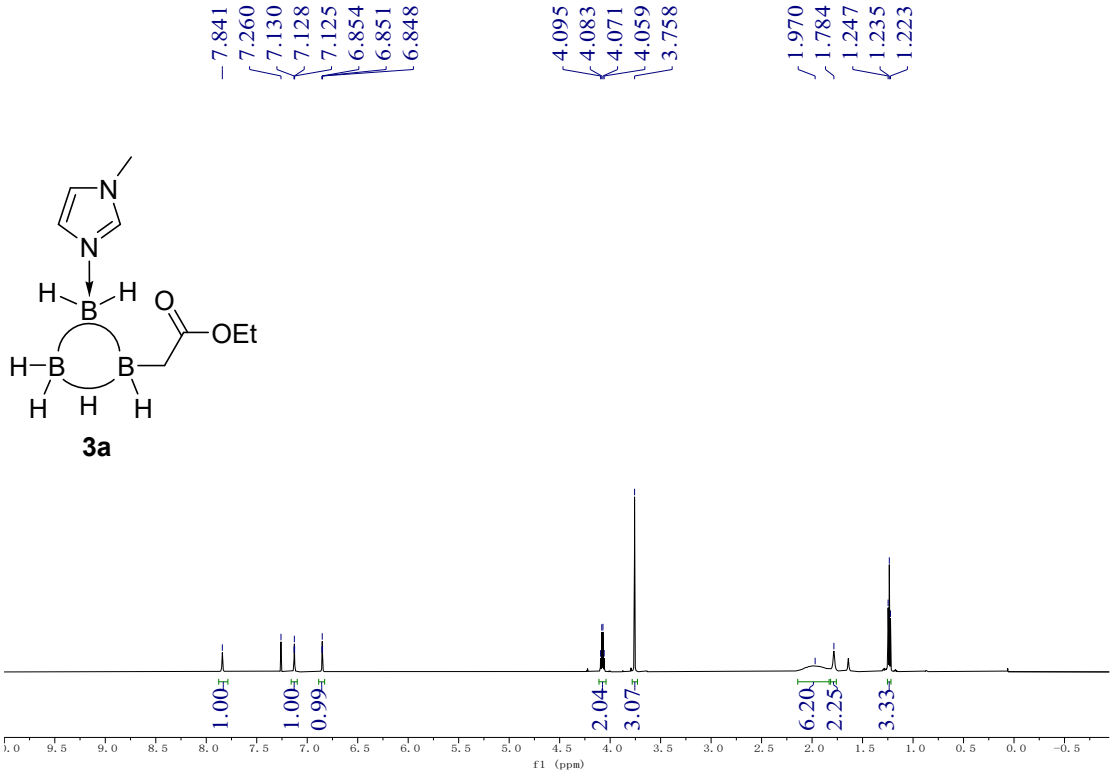
**$^{11}$B NMR of 1d**




**$^{13}$C{$^{1}$H} NMR of 1d**

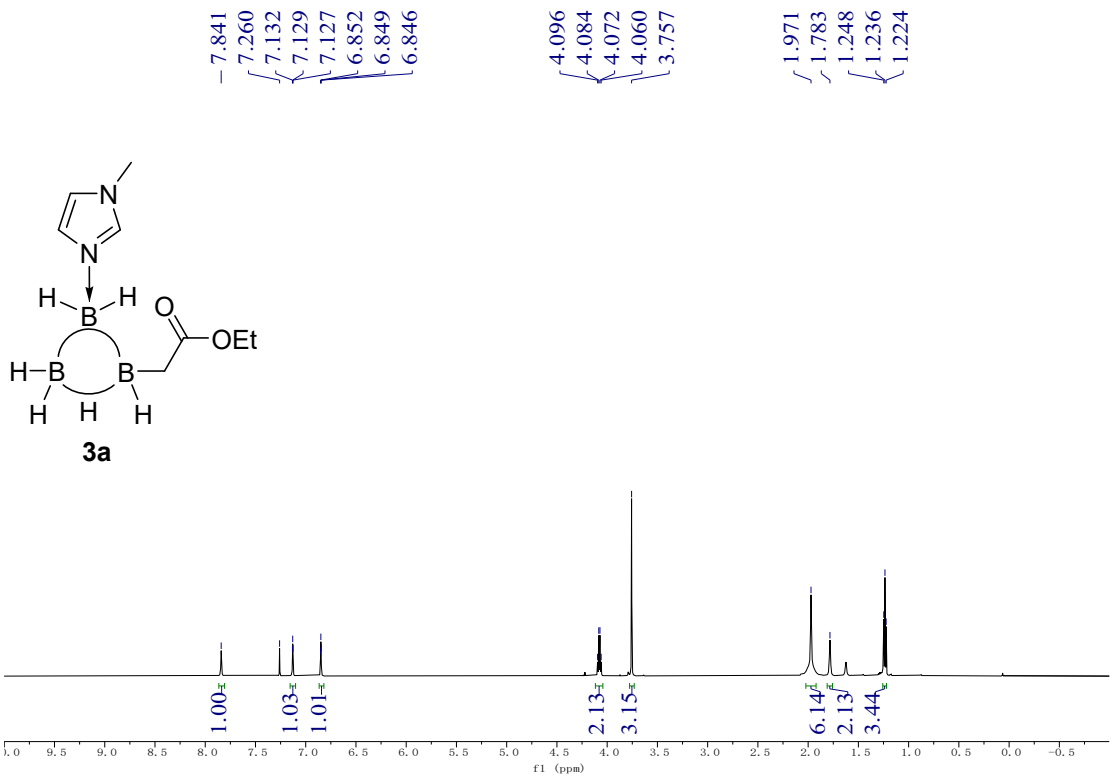


**$^{1}$H NMR of 3a**



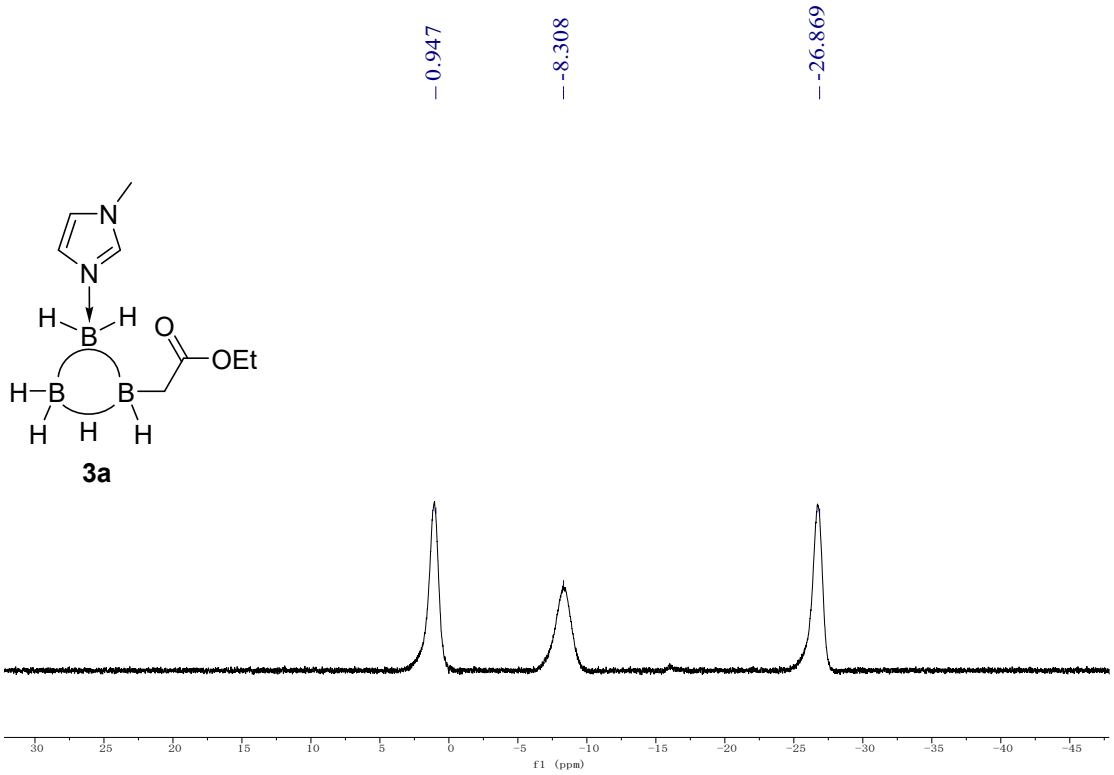

**3a**

**$^{1}$H{$^{11}$B} NMR of 3a**

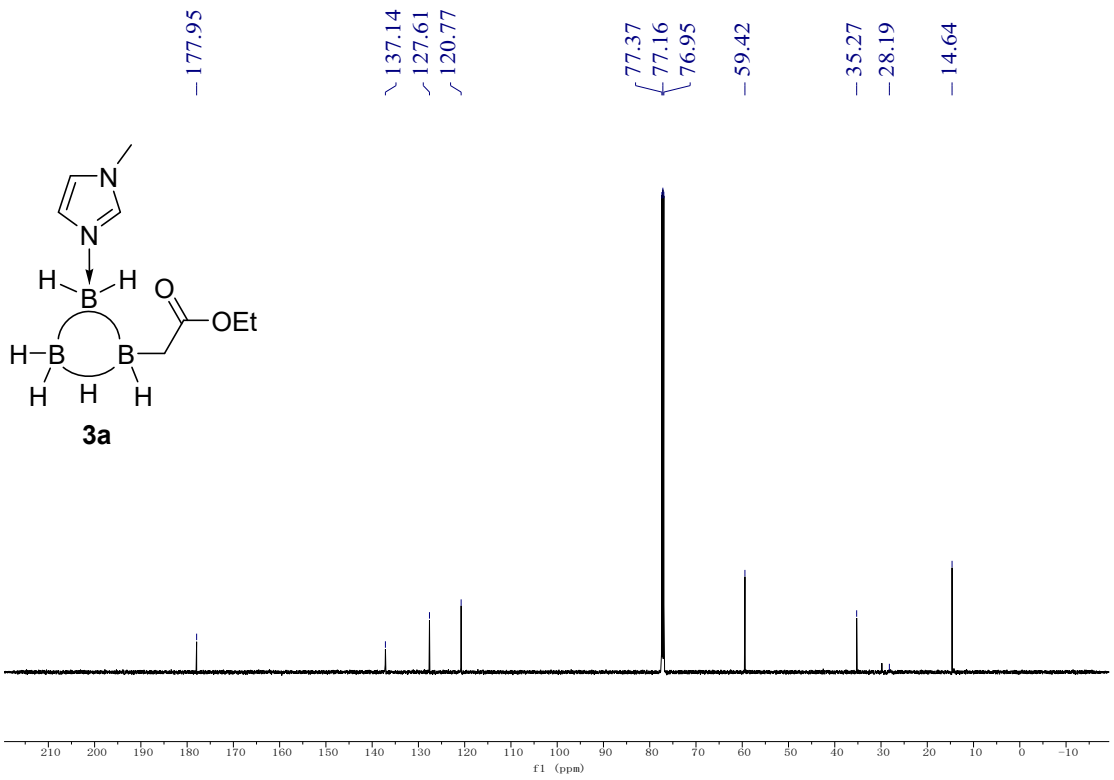



**3a**

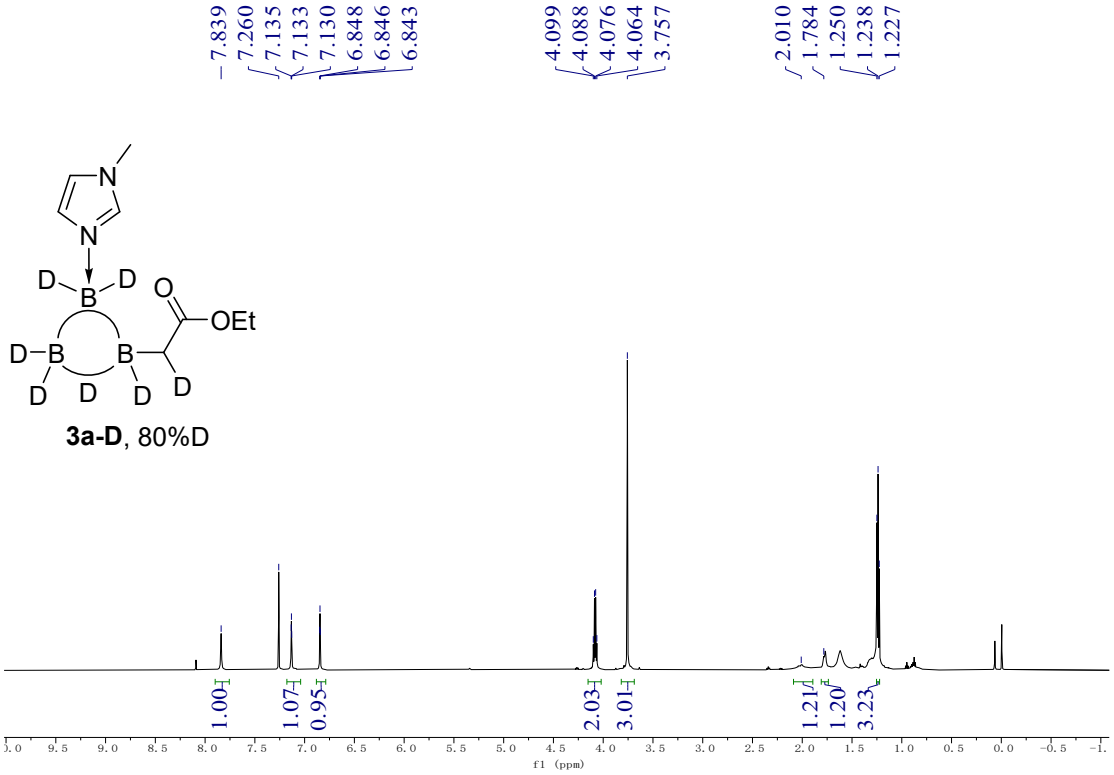
**$^{11}$B NMR of 3a**



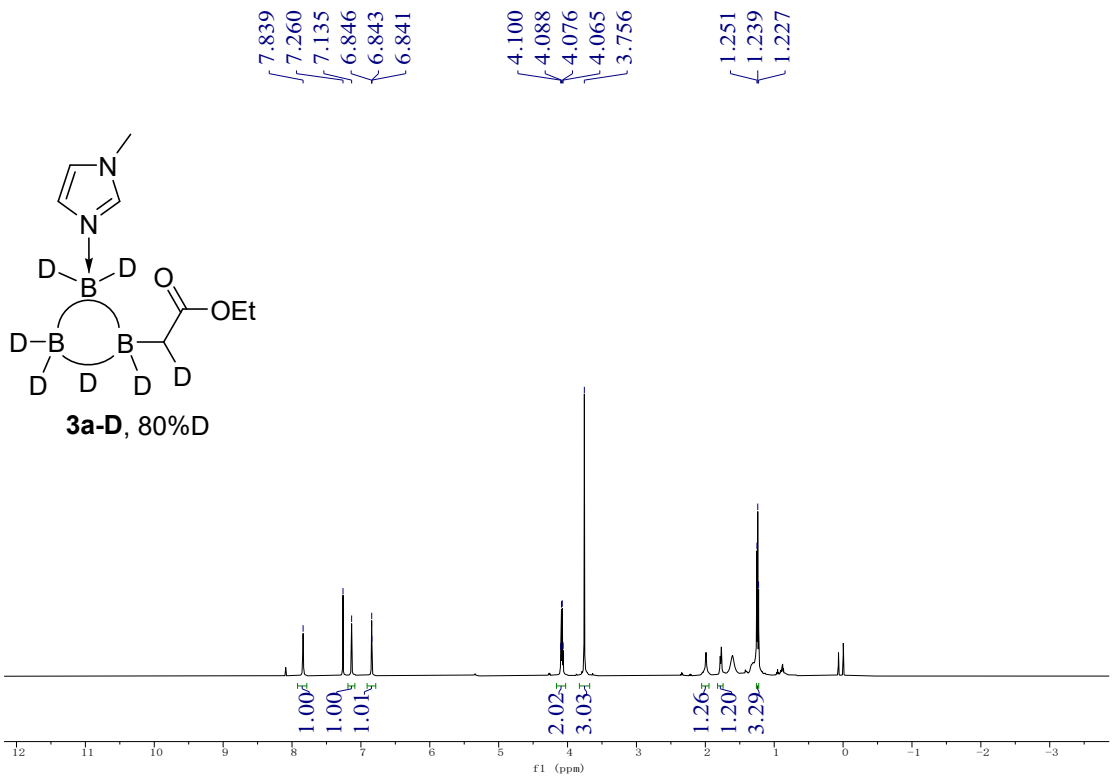

**$^{13}$C{$^{1}$H} NMR of 3a**



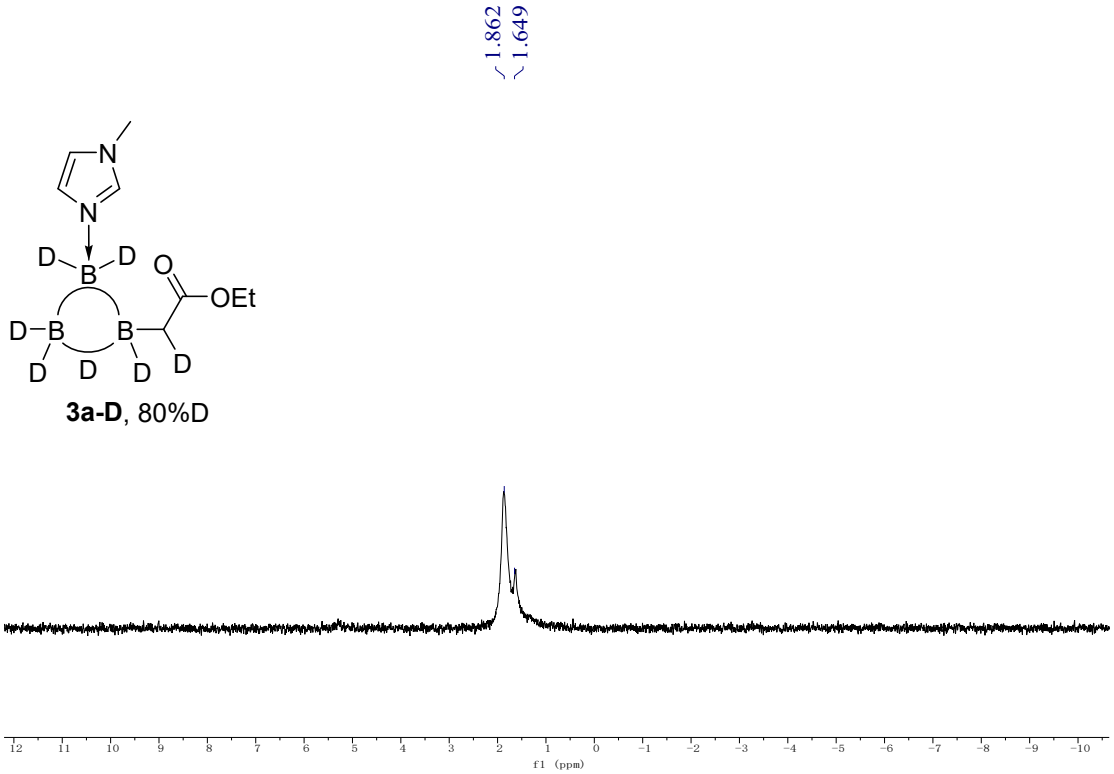
**$^{1}$H NMR of 3a-D**




**$^{1}$H{$^{11}$B} NMR of 3a-D**

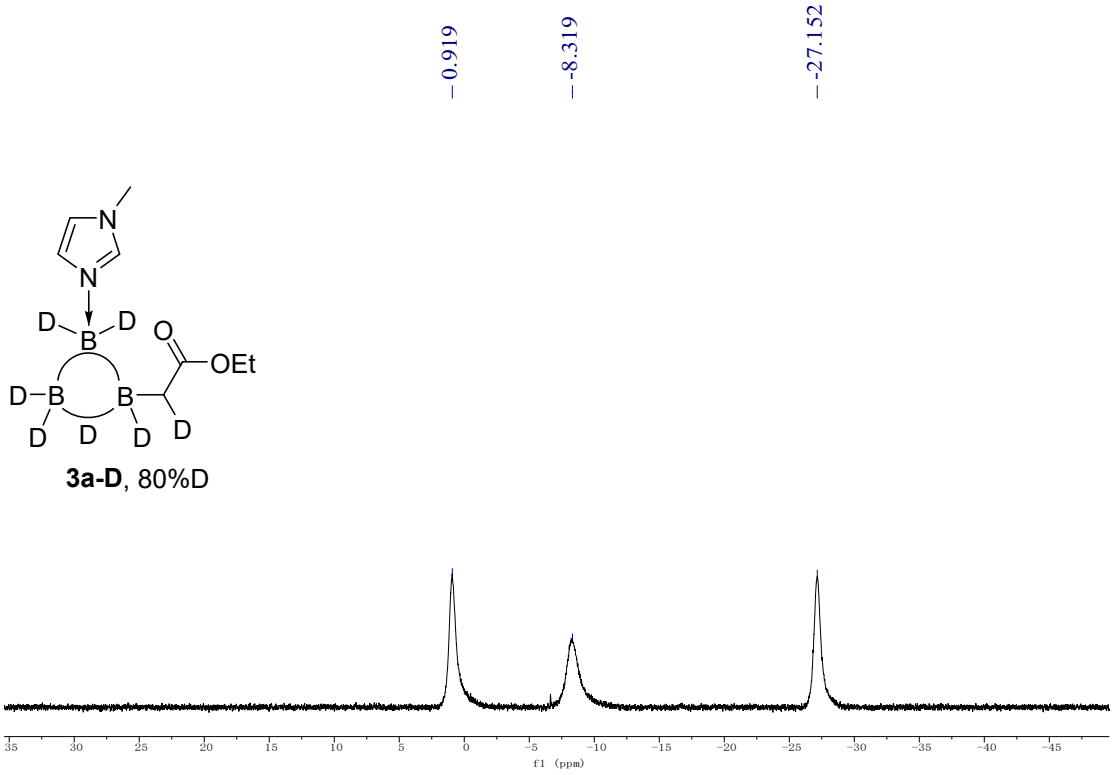


**$^{2}$D NMR of 3a-D**



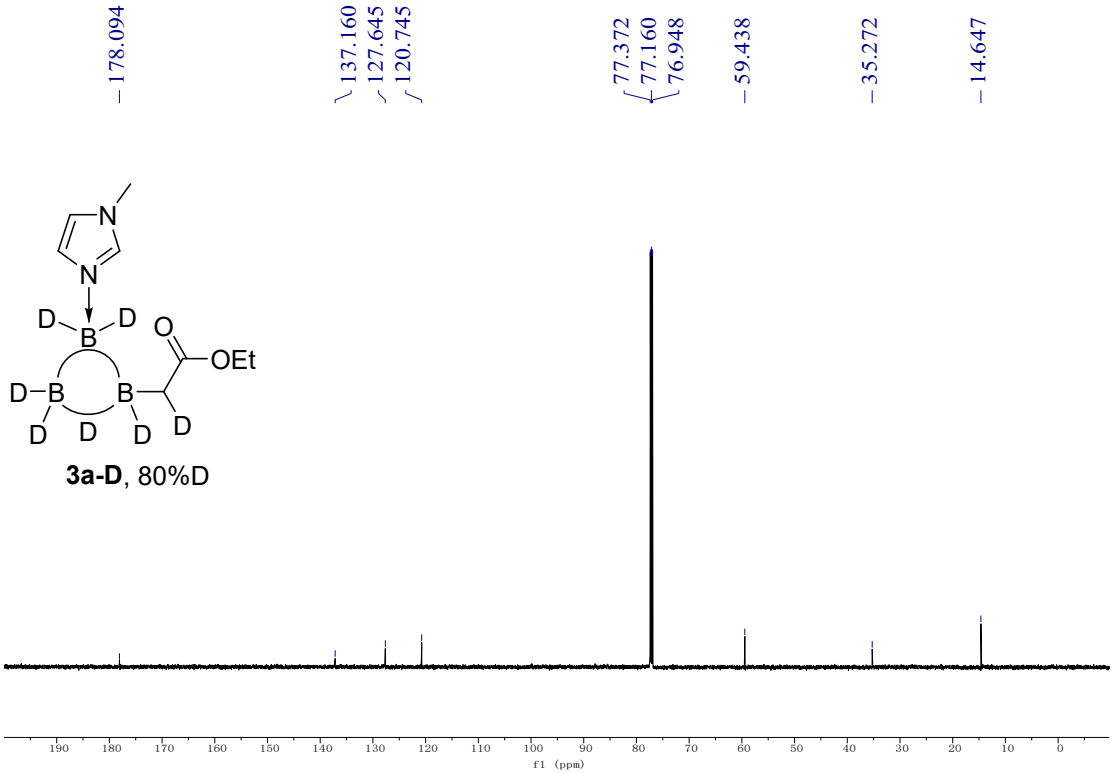

**3a-D**, 80%D

**$^{11}$B NMR of 3a-D**



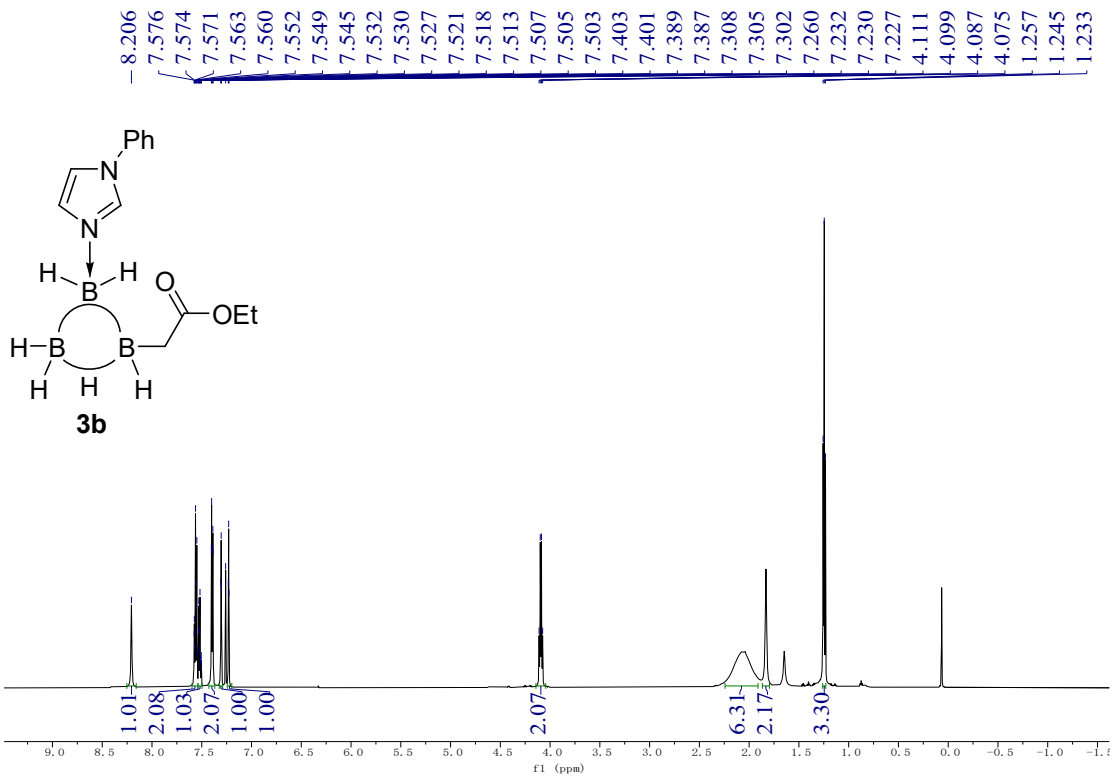

**3a-D**, 80%D

**$^{13}C\{^{1}H\}$ NMR of 3a-D**



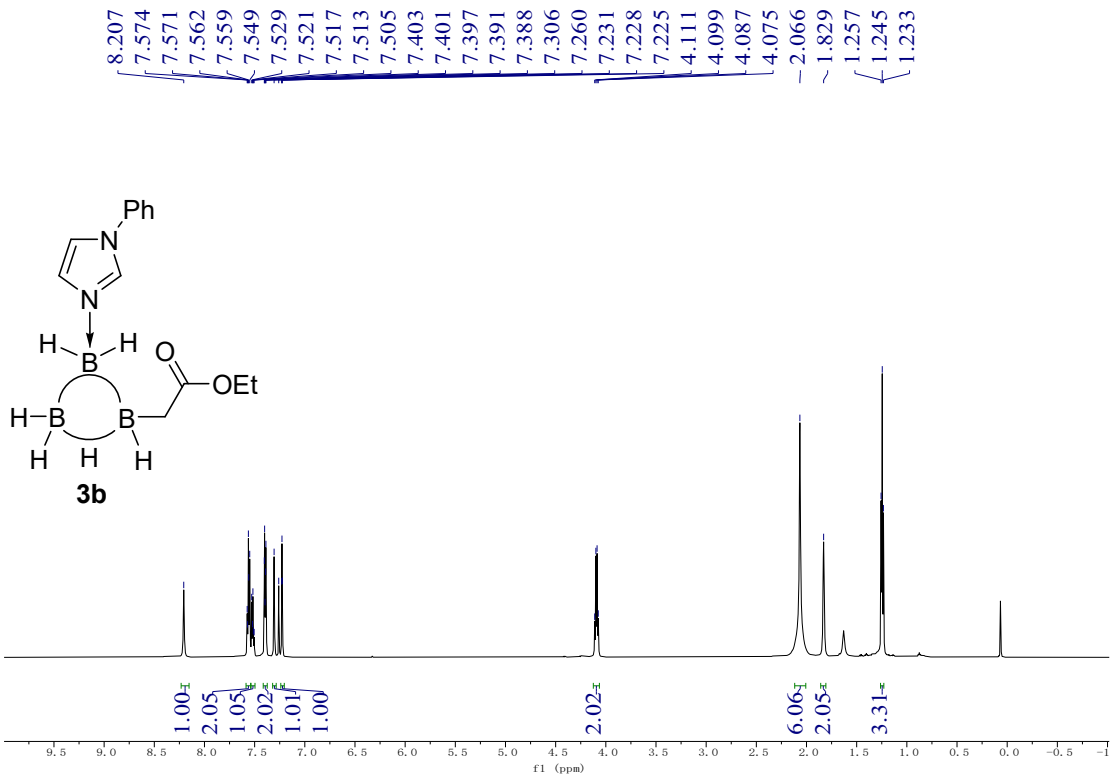

**3a-D**, 80%D

**$^{1}H$ NMR of 3b**

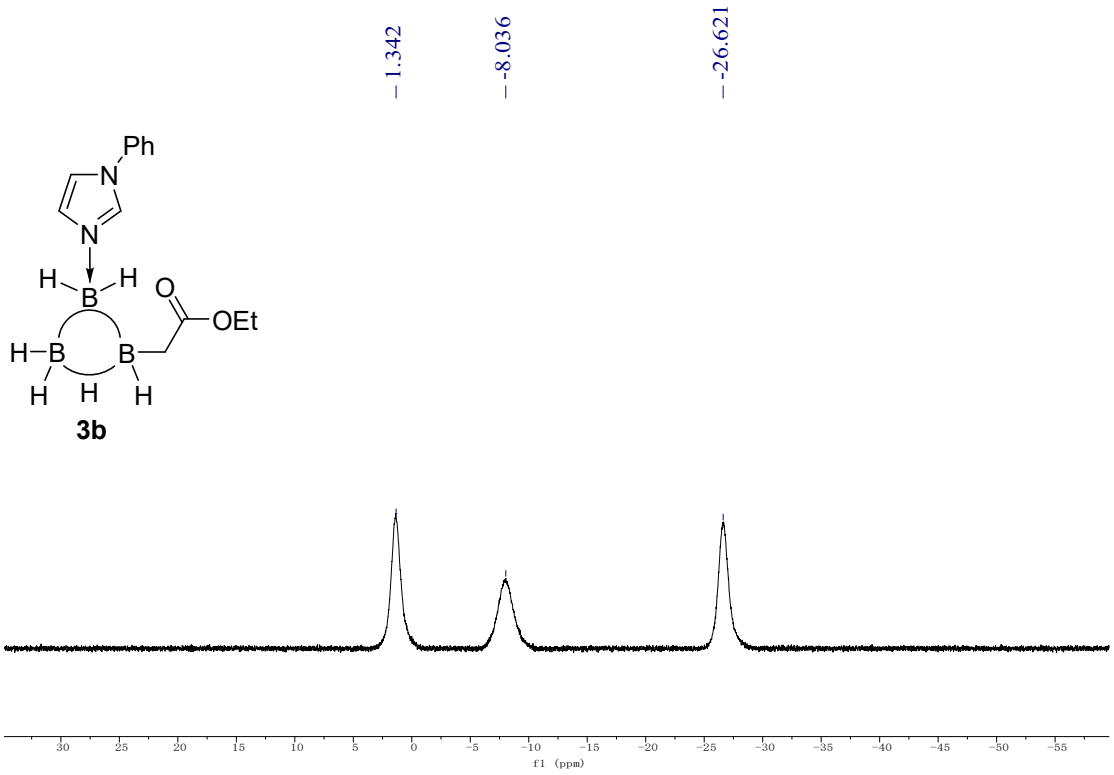



**3b**

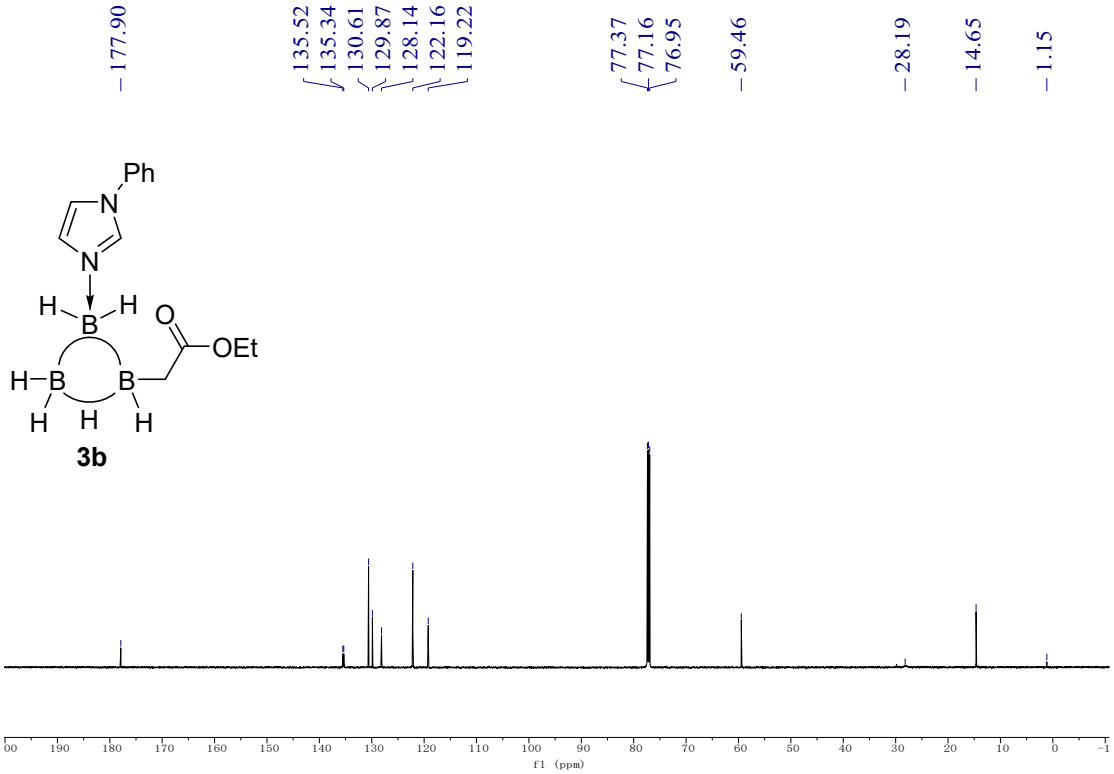
**$^{1}H\{^{11}B\}$ NMR of 3b**



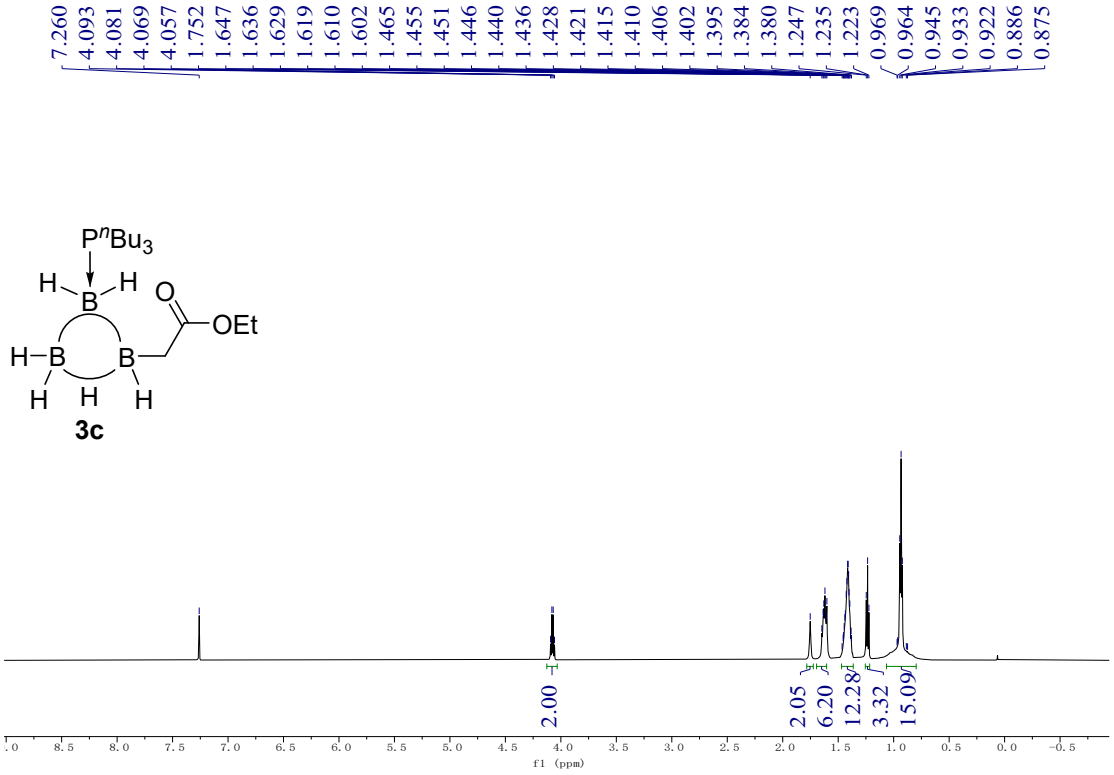

**$^{11}B$ NMR of 3b**



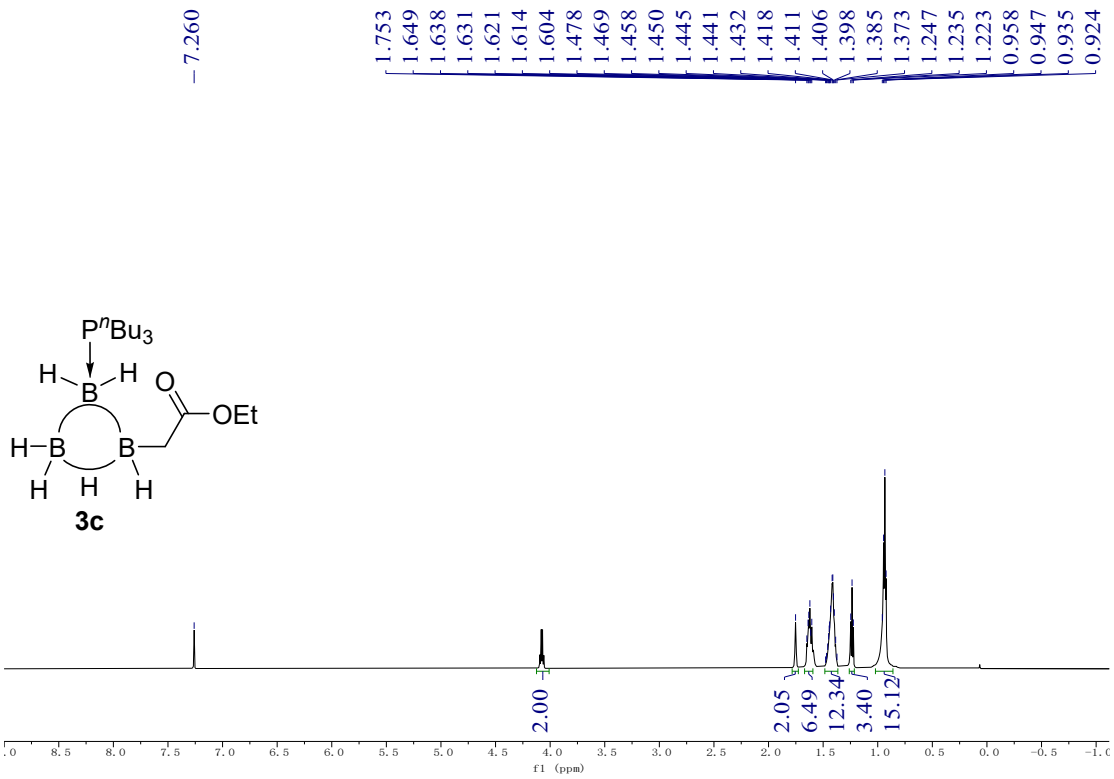
**$^{13}C\{^{1}H\}$ NMR of 3b**



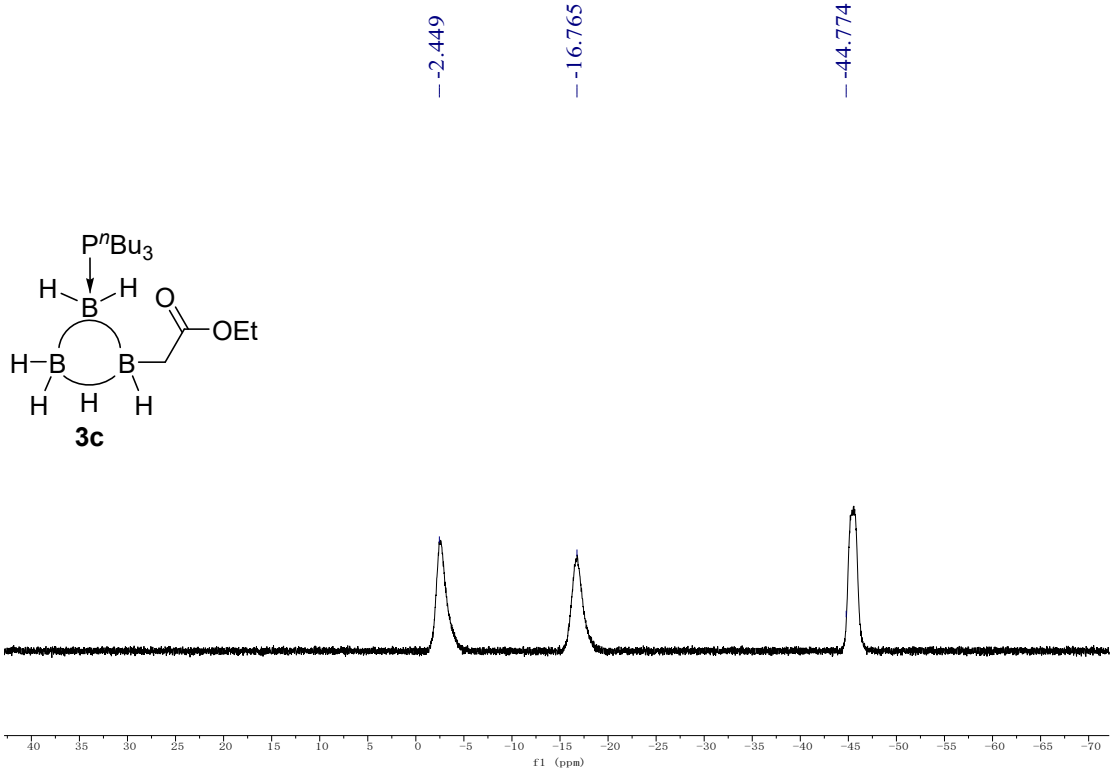

**$^{1}H$ NMR of 3c**



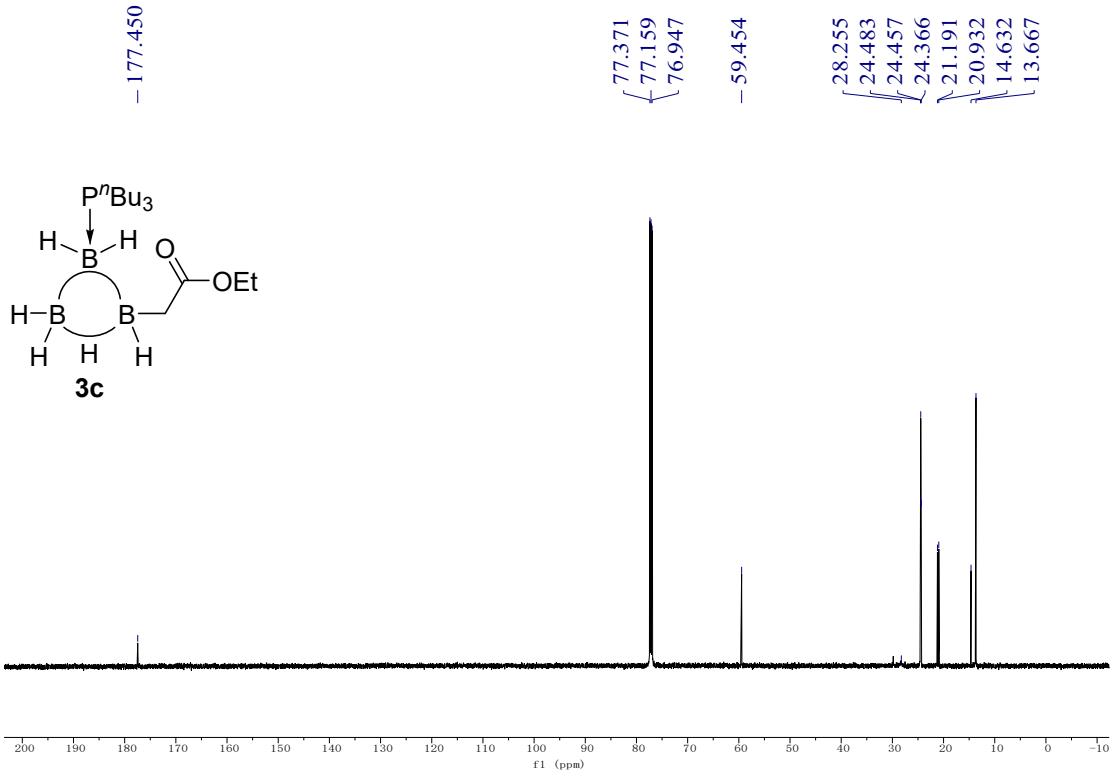
**$^{1}H\{^{11}B\}$ NMR of 3c**



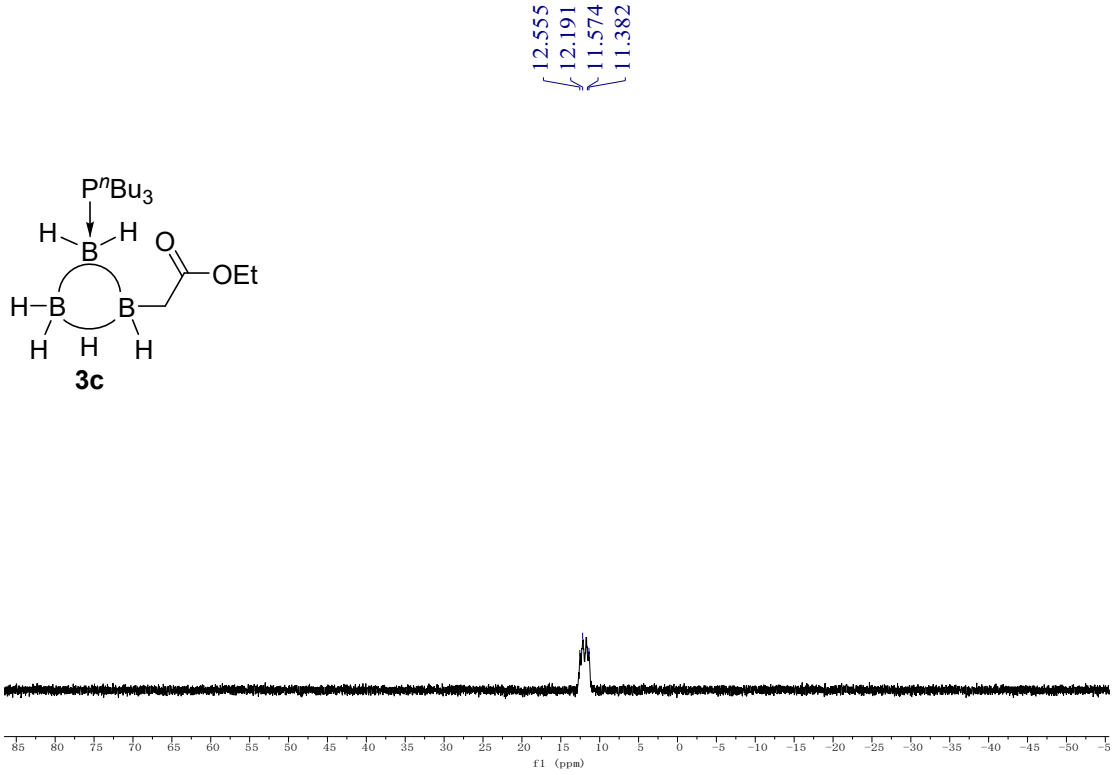

**$^{11}B$ NMR of 3c**



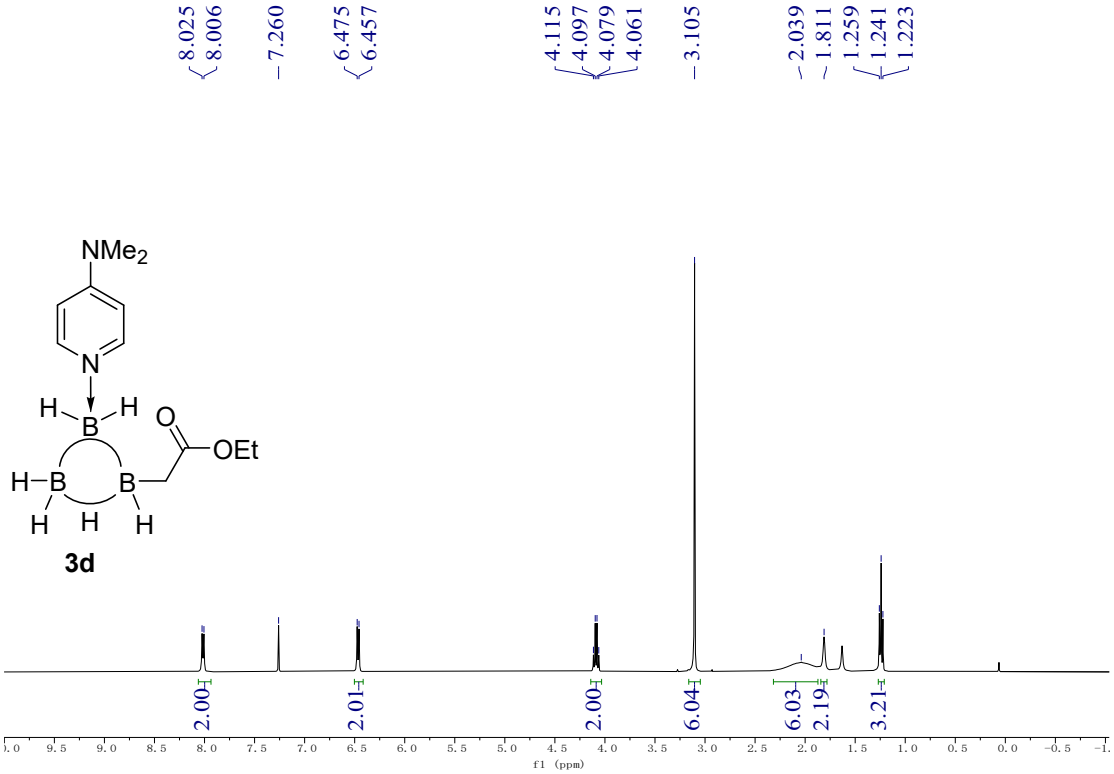
**$^{13}C\{^{1}H\}$ NMR of 3c**



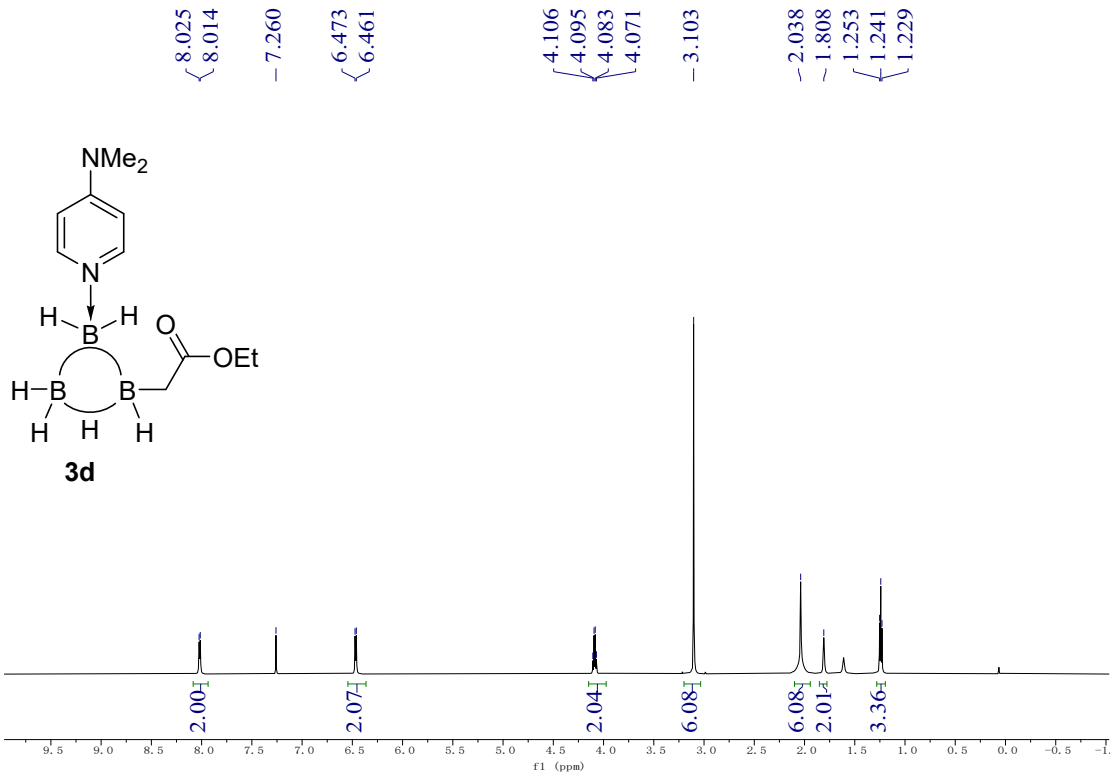

**$^{31}P$ NMR of 3c**



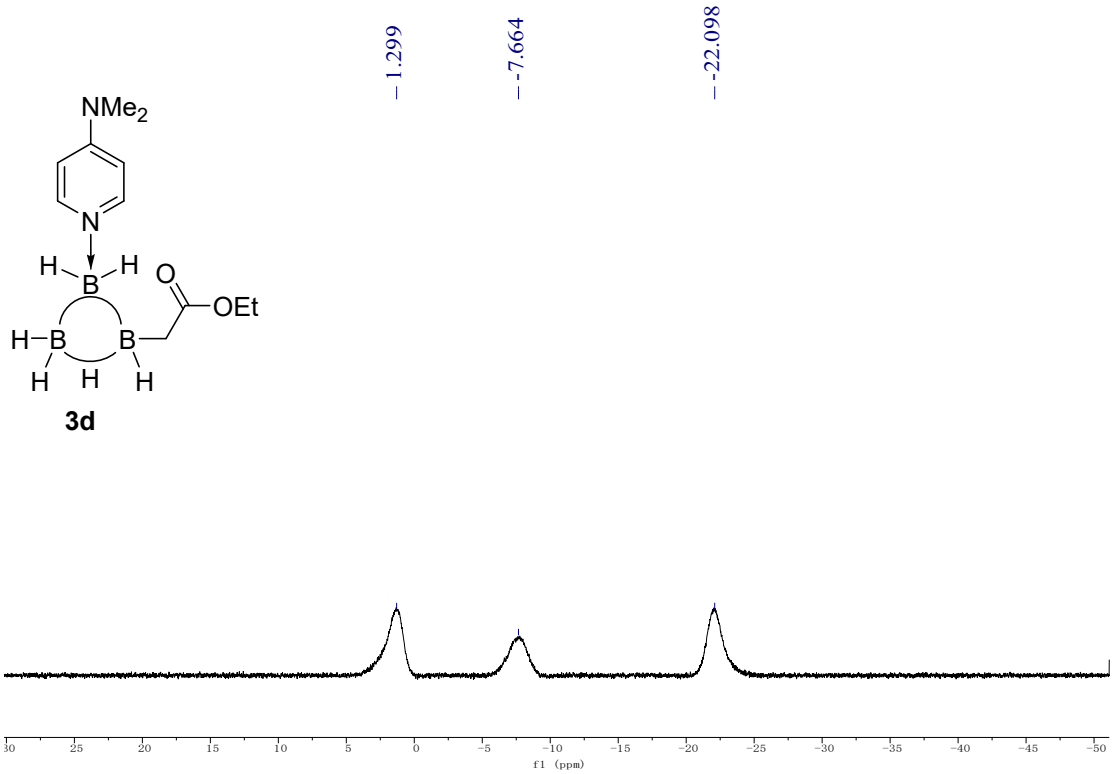
**$^{1}$H NMR of 3d**



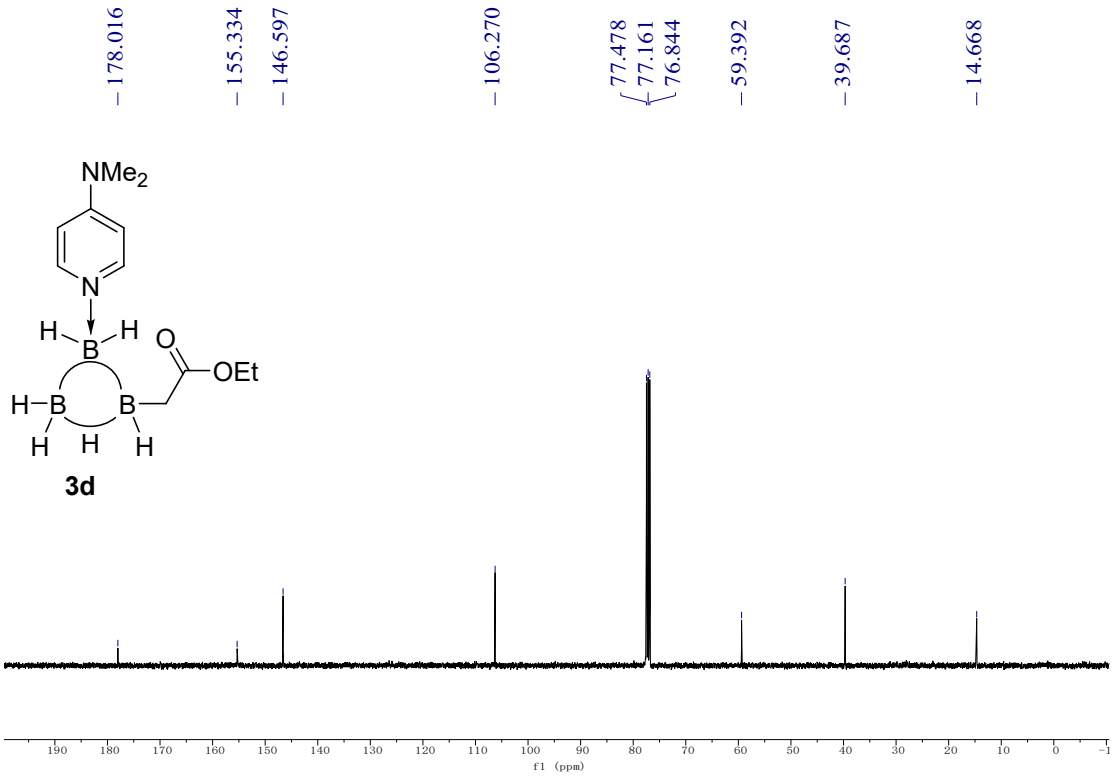

**$^{1}$H{$^{11}$B} NMR of 3d**



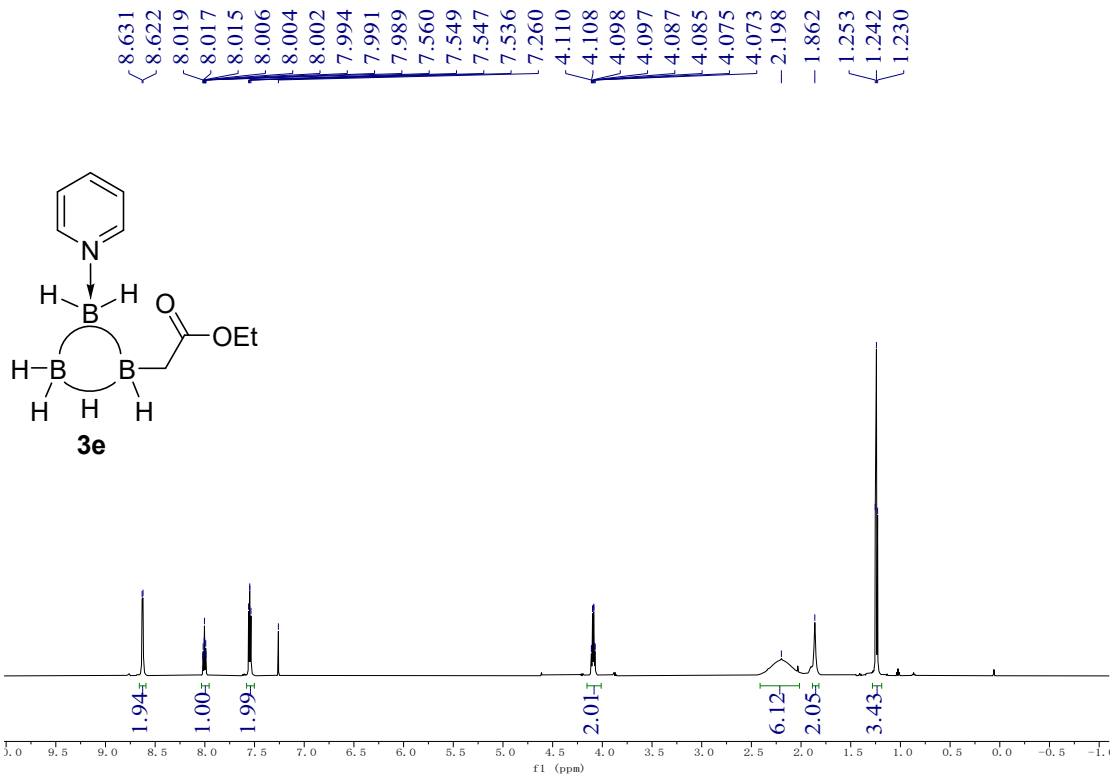
**$^{11}$B NMR of 3d**



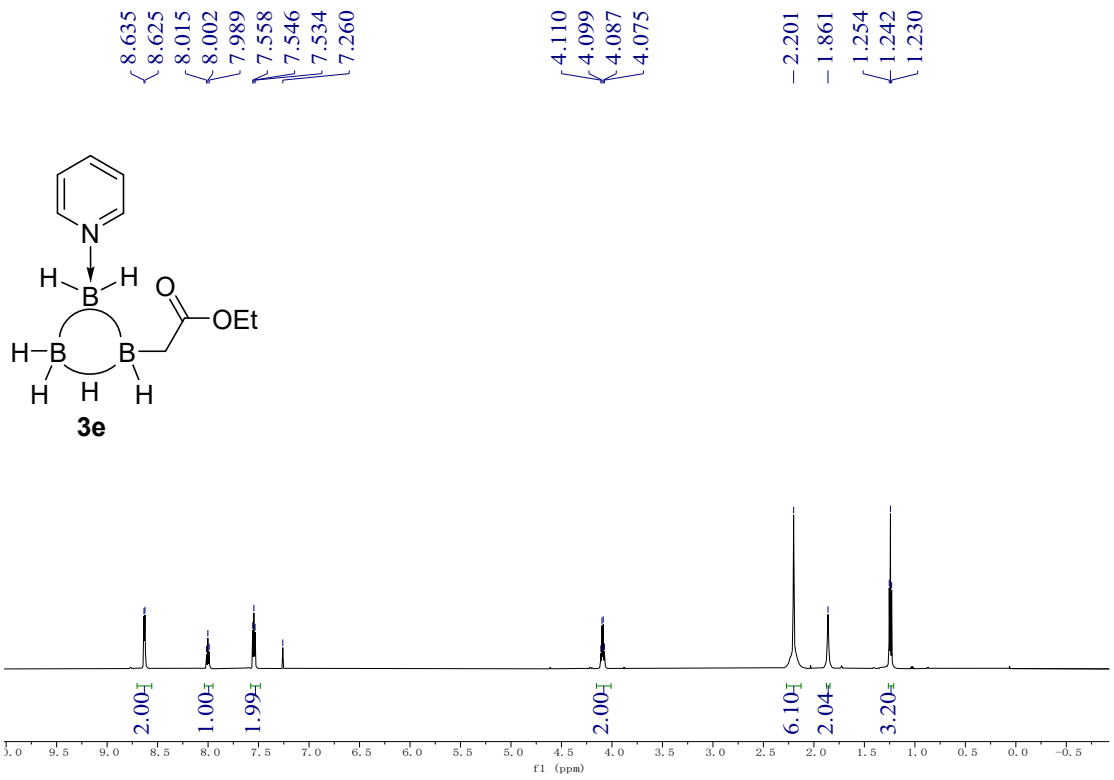

**$^{13}$C{$^{1}$H} NMR of 3d**



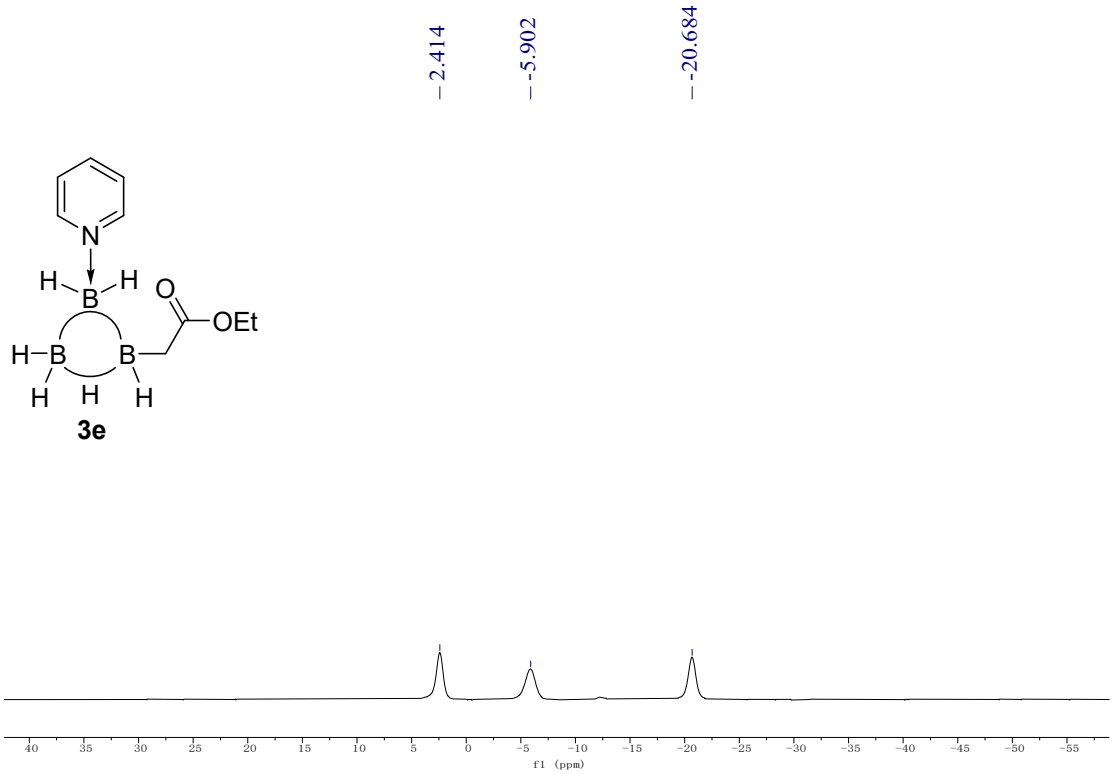
**$^{1}$H NMR of 3e**



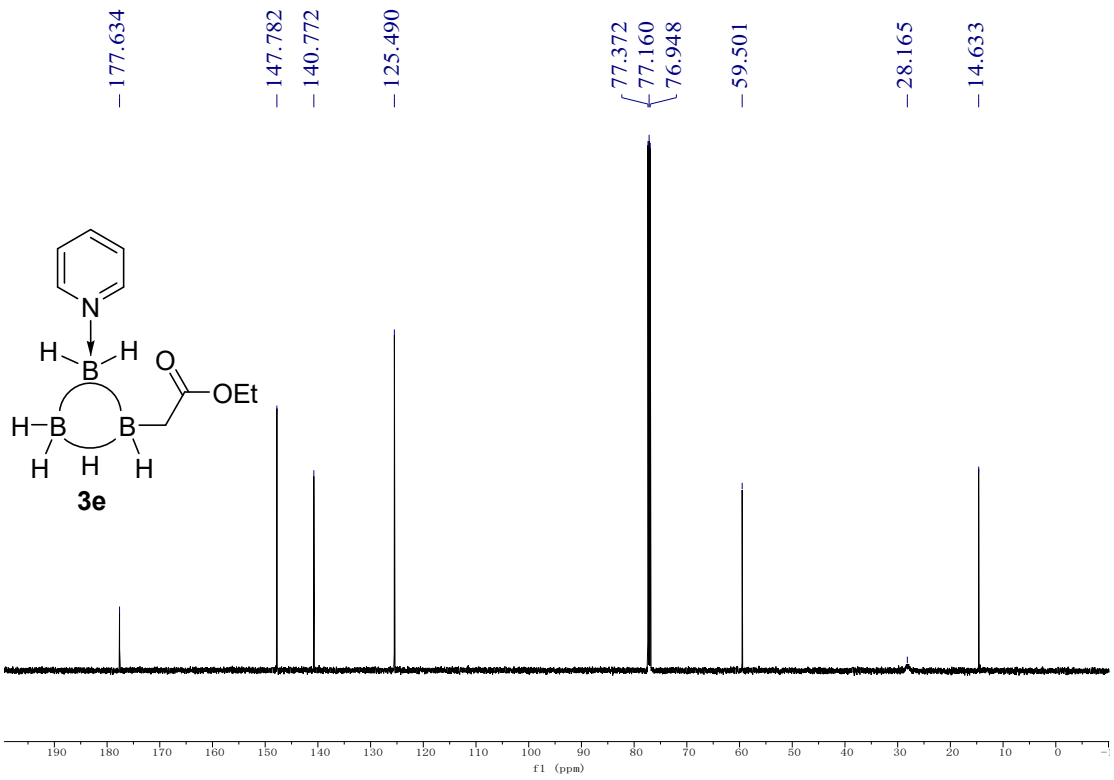

**$^{1}$H{$^{11}$B} NMR of 3e**



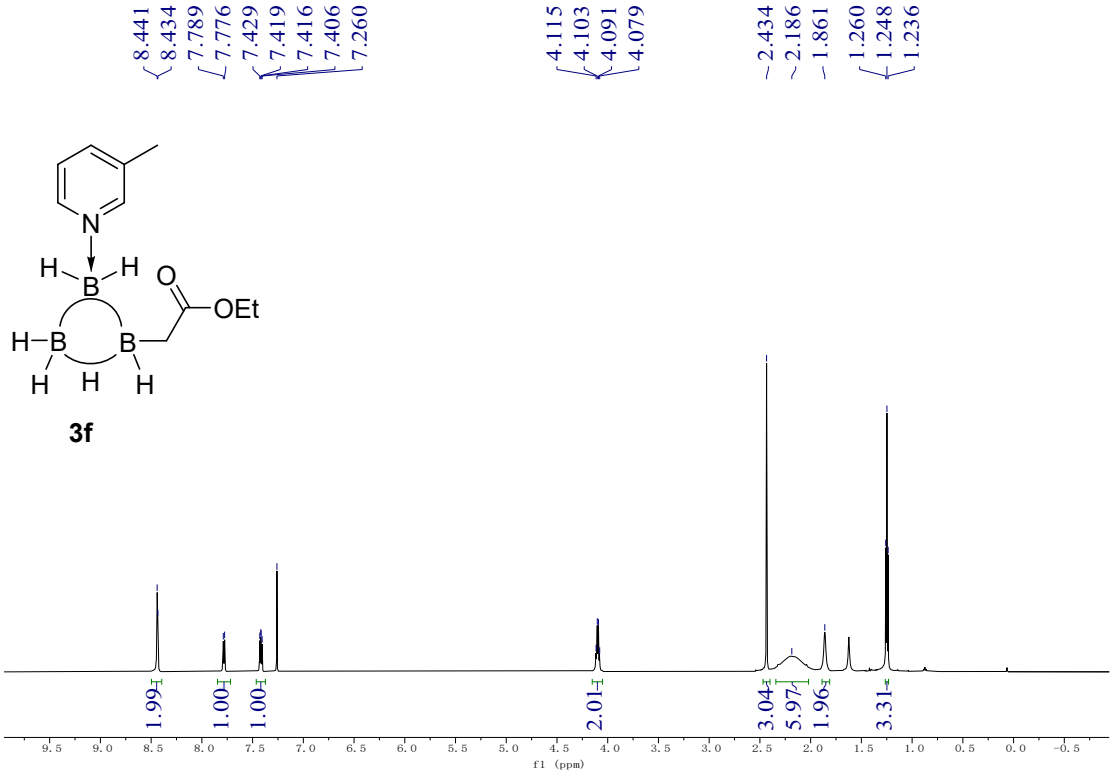
**$^{11}$B NMR of 3e**



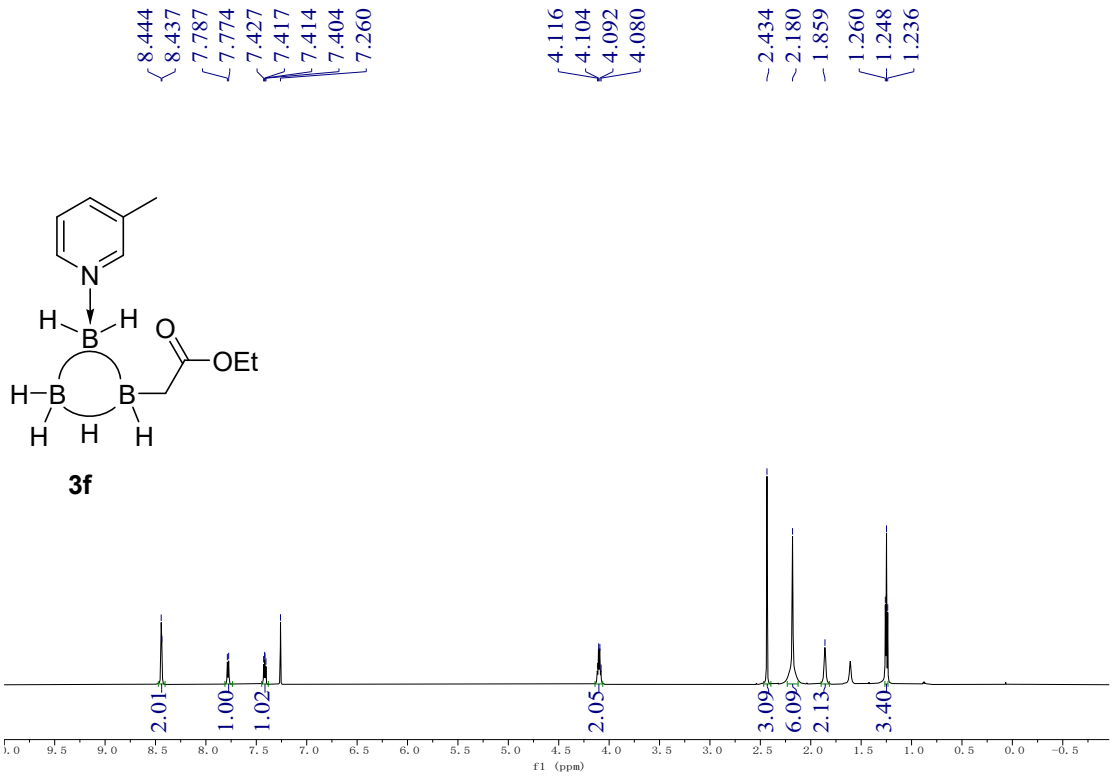

**$^{13}$C{$^{1}$H} NMR of 3e**



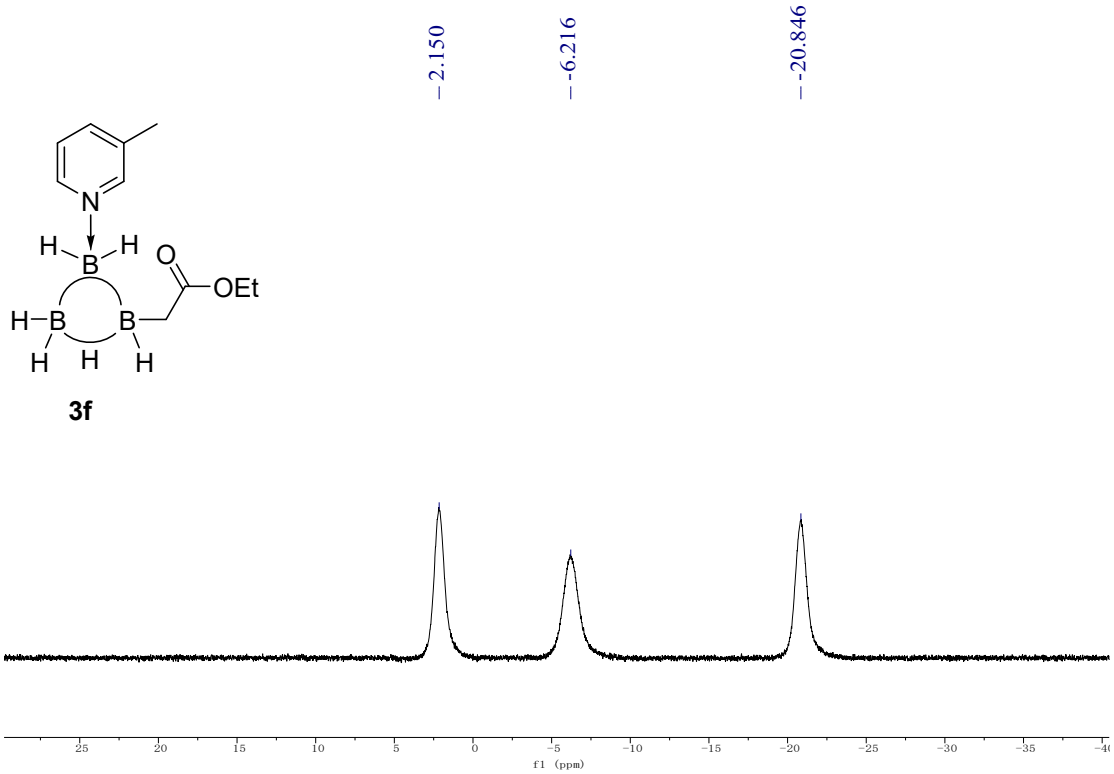
**$^{1}$H NMR of 3f**




**$^{1}$H{$^{11}$B} NMR of 3f**

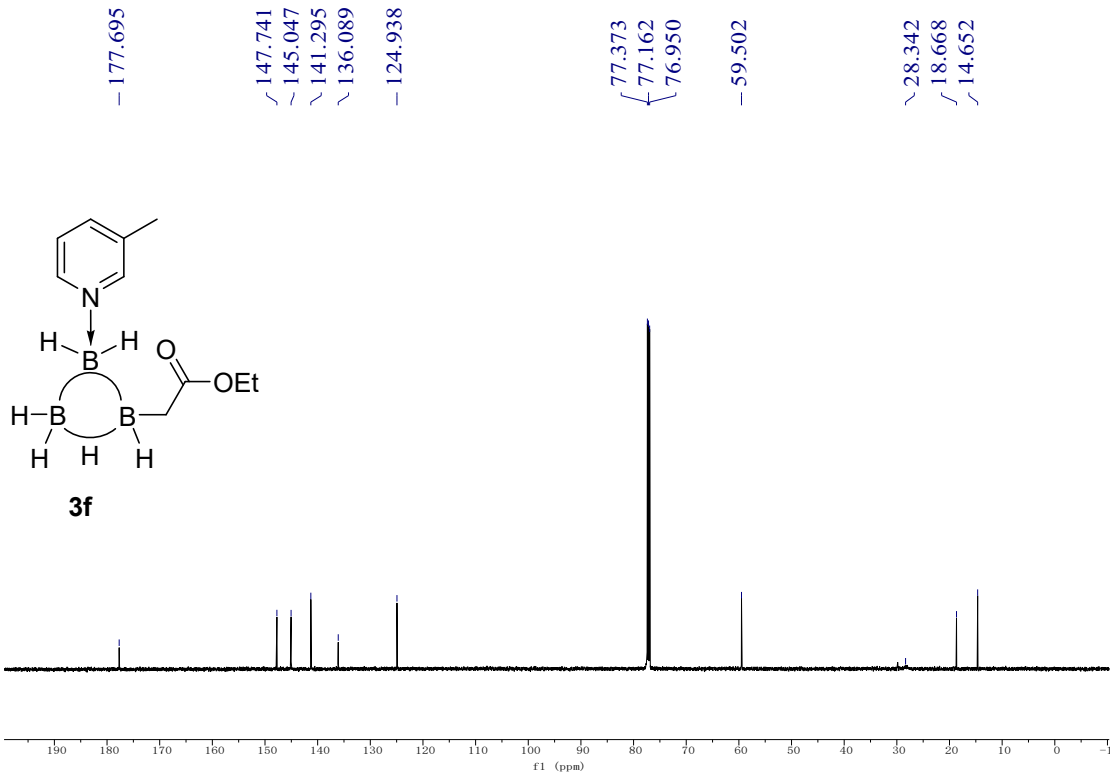


**$^{11}$B NMR of 3f**



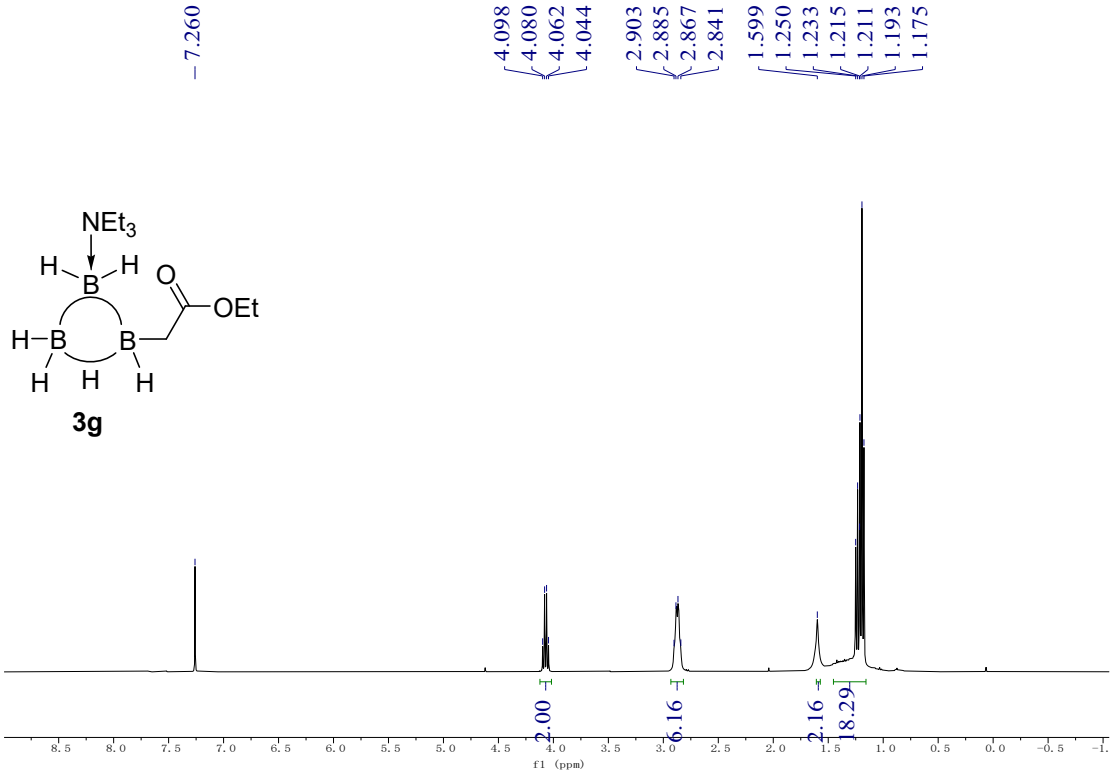

**3f**

**$^{13}$C{$^{1}$H} NMR of 3f**

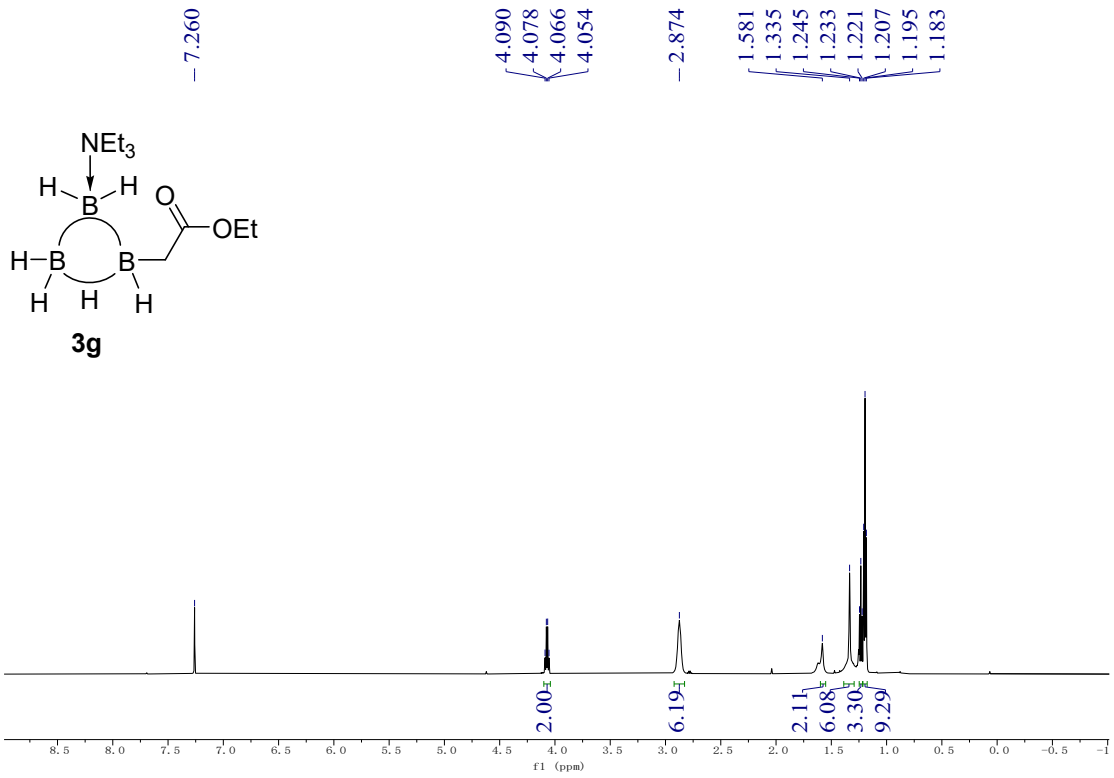



**3f**

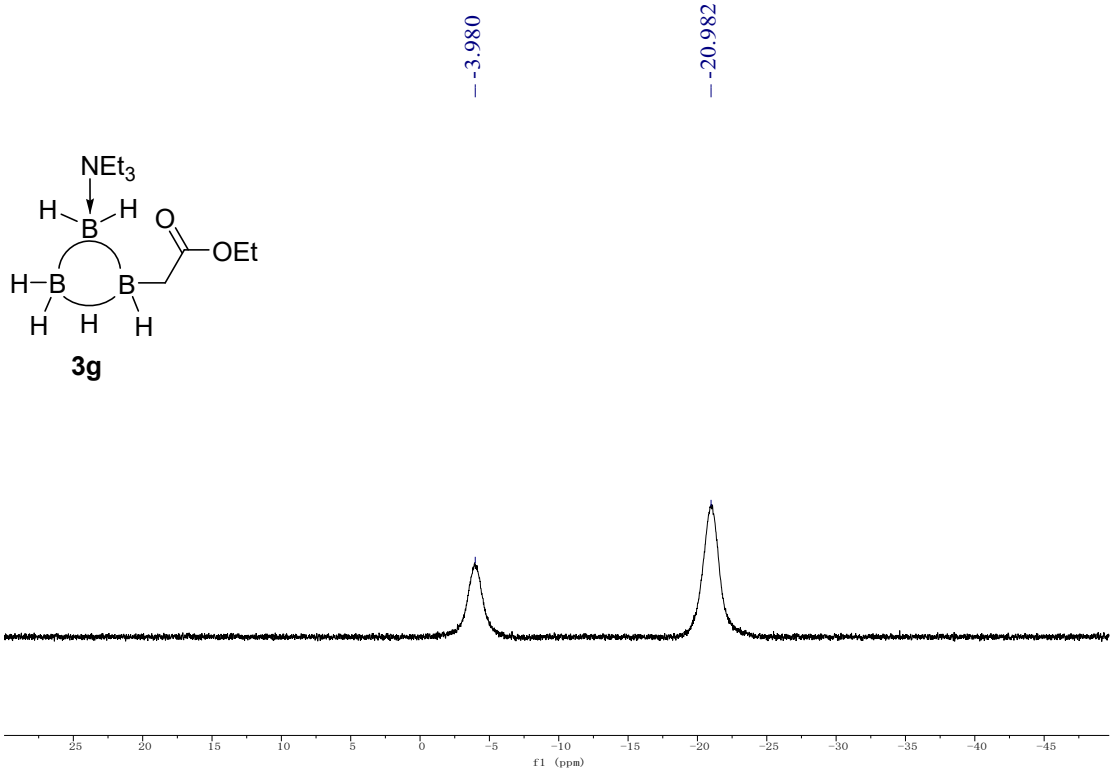
**$^{1}$H NMR of 3g**



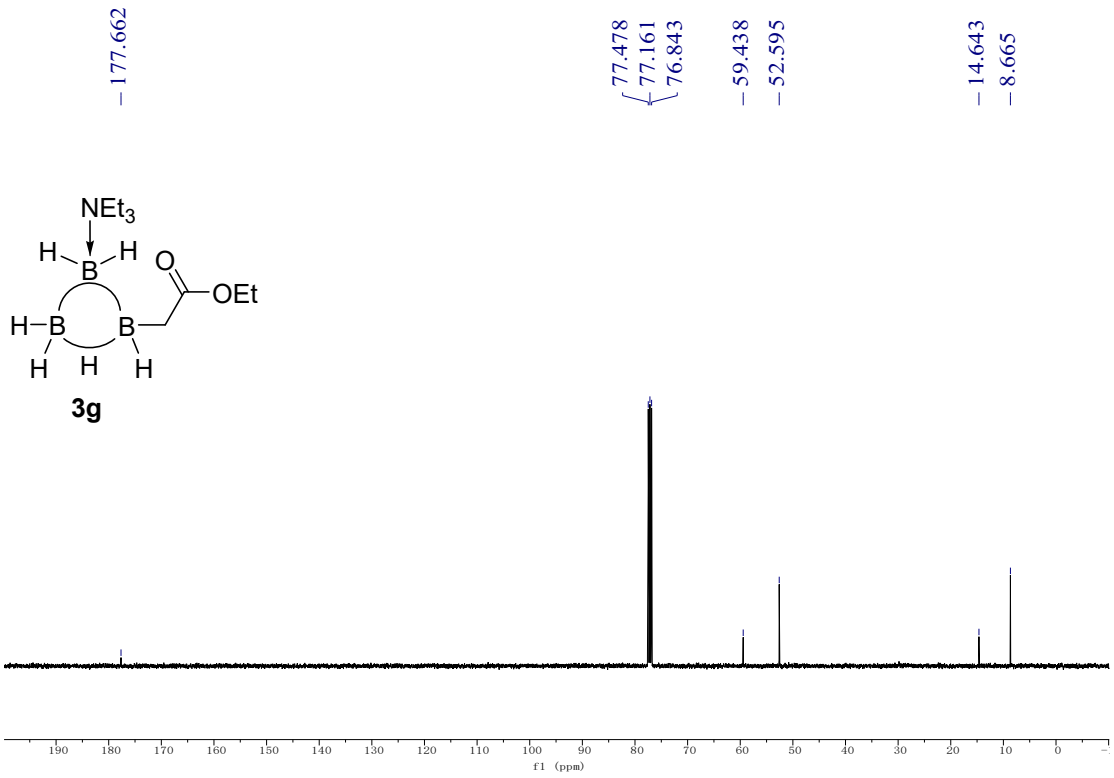

**$^{1}$H{$^{11}$B} NMR of 3g**



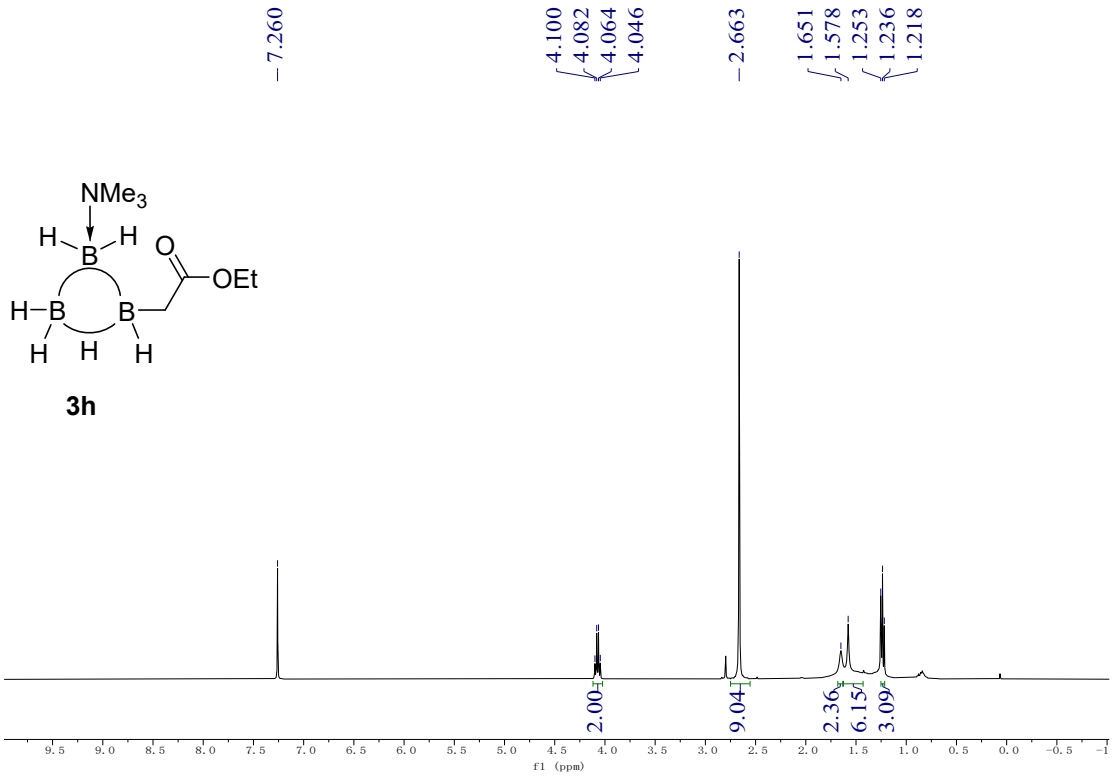
**$^{11}$B NMR of 3g**




**$^{13}$C{$^{1}$H} NMR of 3g**

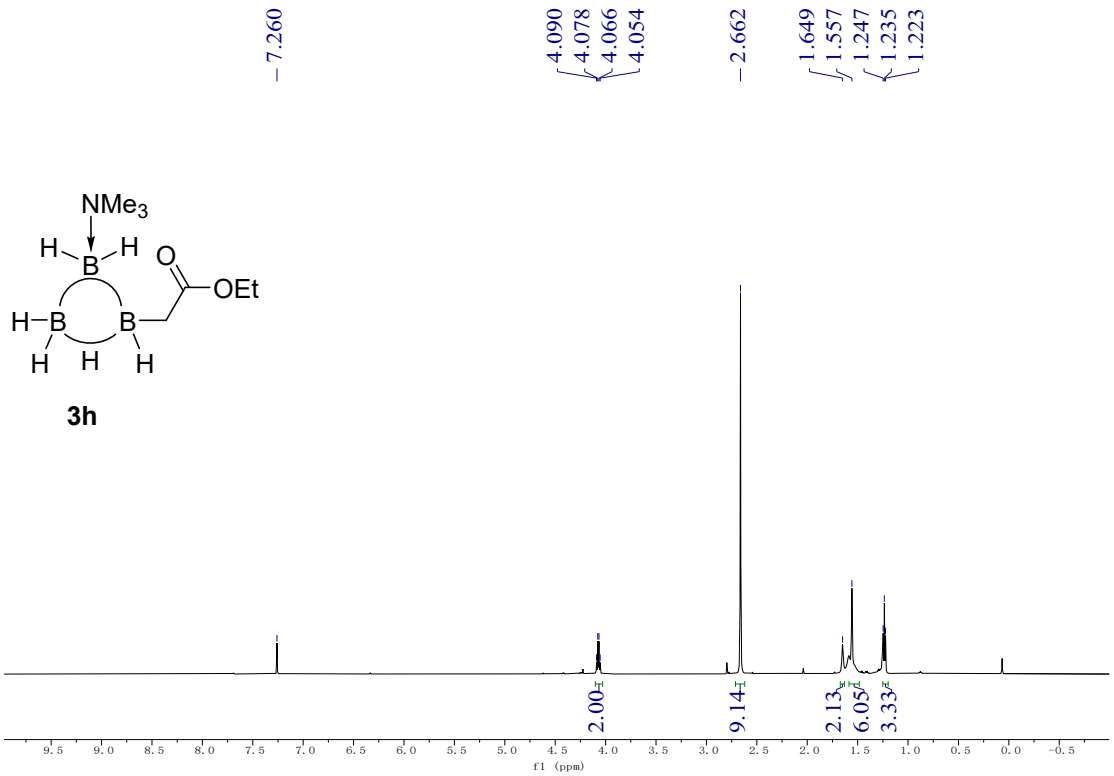


**$^{1}$H NMR of 3h**



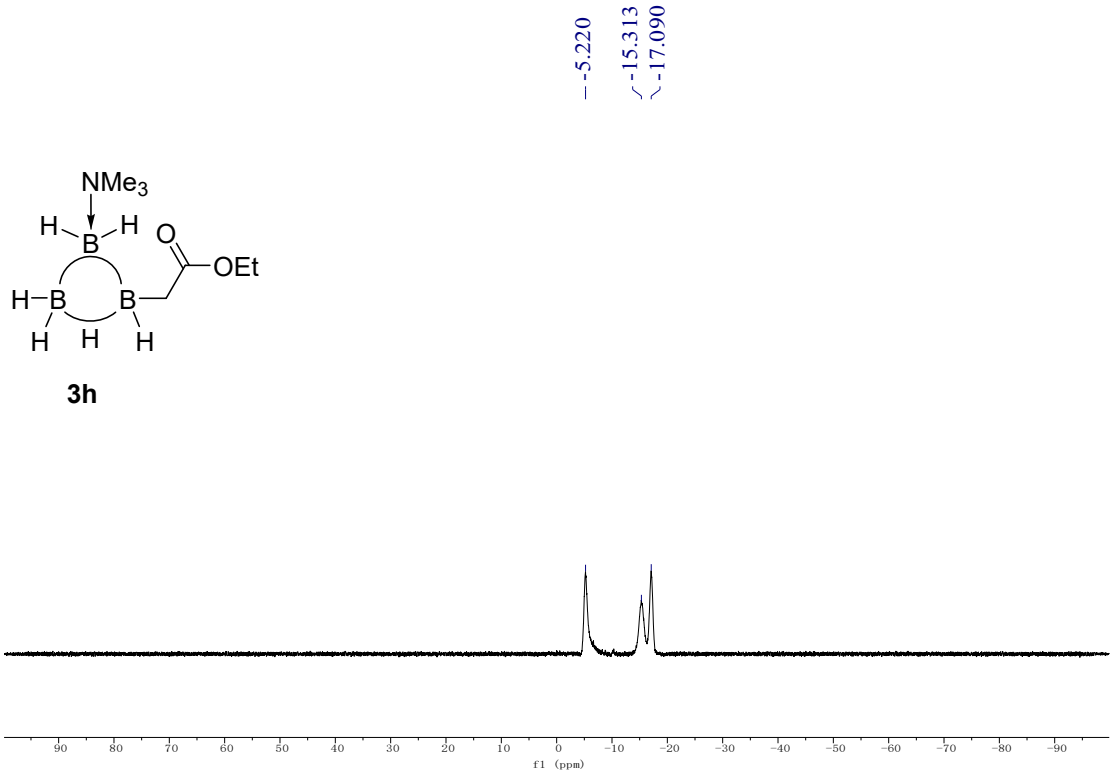

**3h**

**$^{1}$H{$^{11}$B} NMR of 3h**

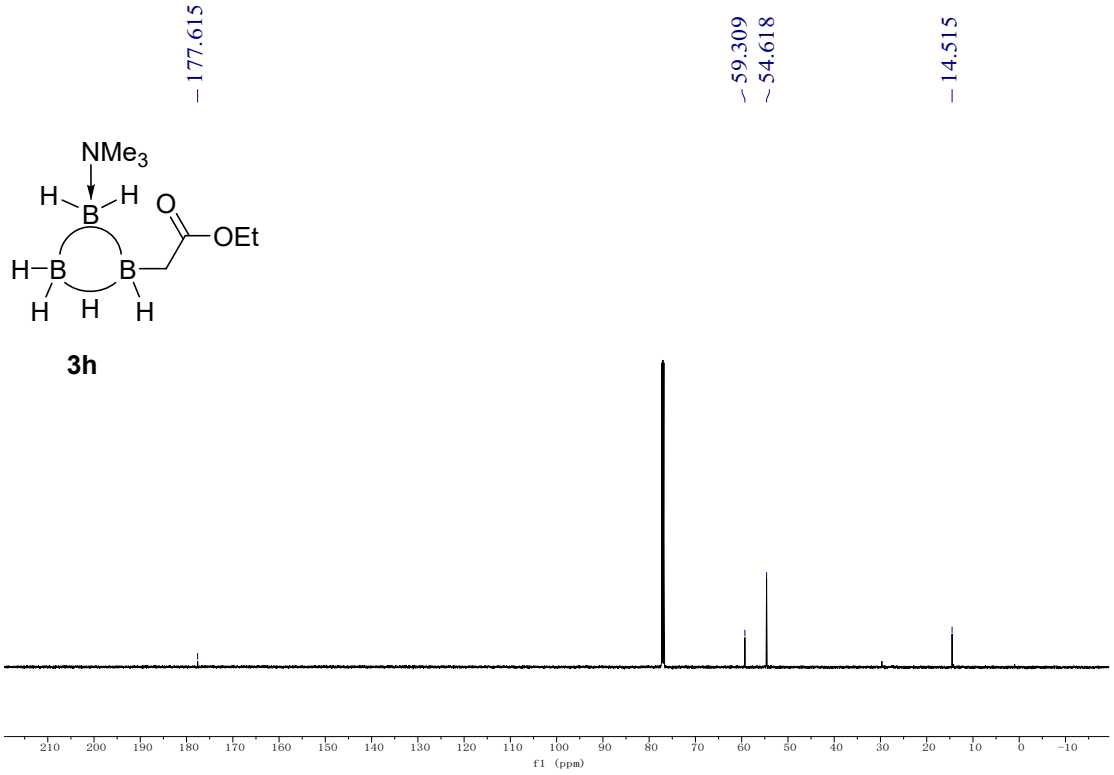



**3h**

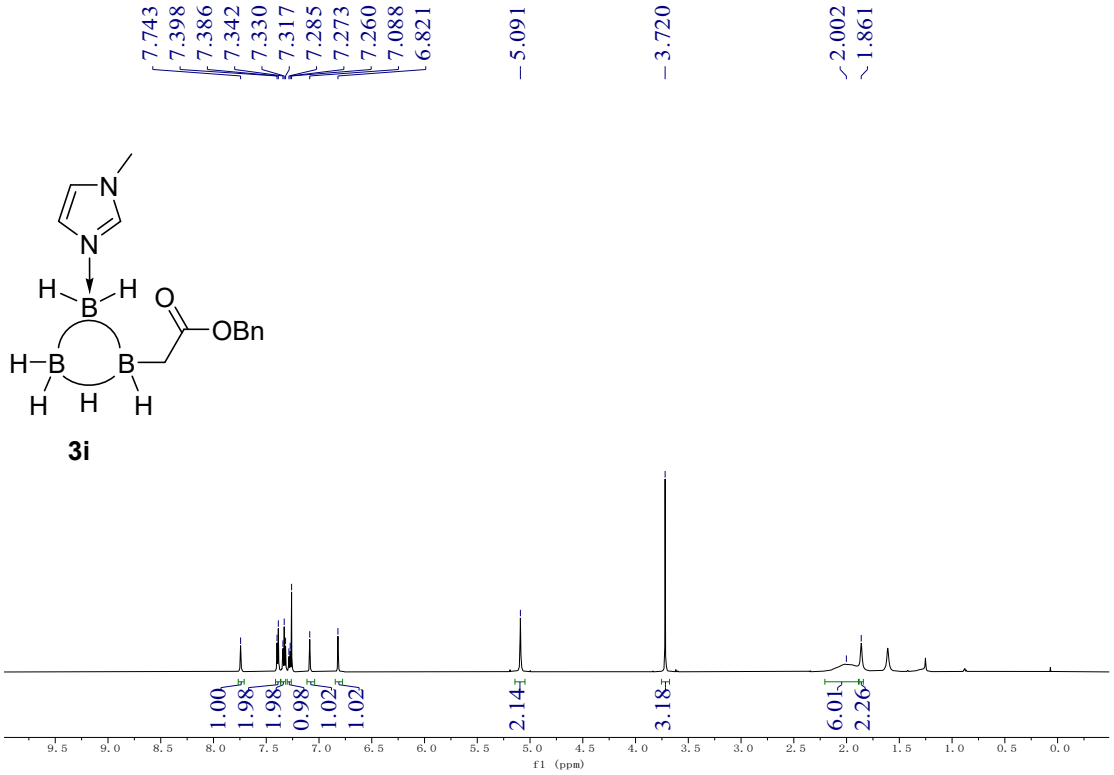
**$^{11}$B NMR of 3h**




**$^{13}$C{$^{1}$H} NMR of 3h**

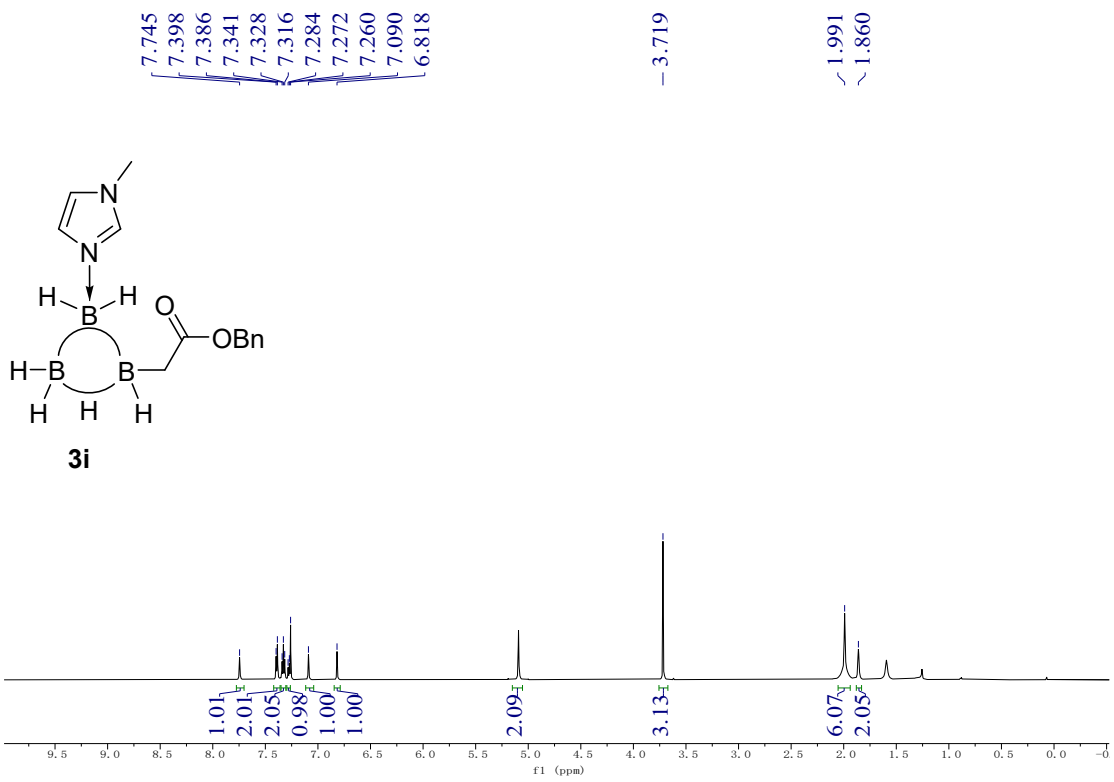


**$^{1}$H NMR of 3i**



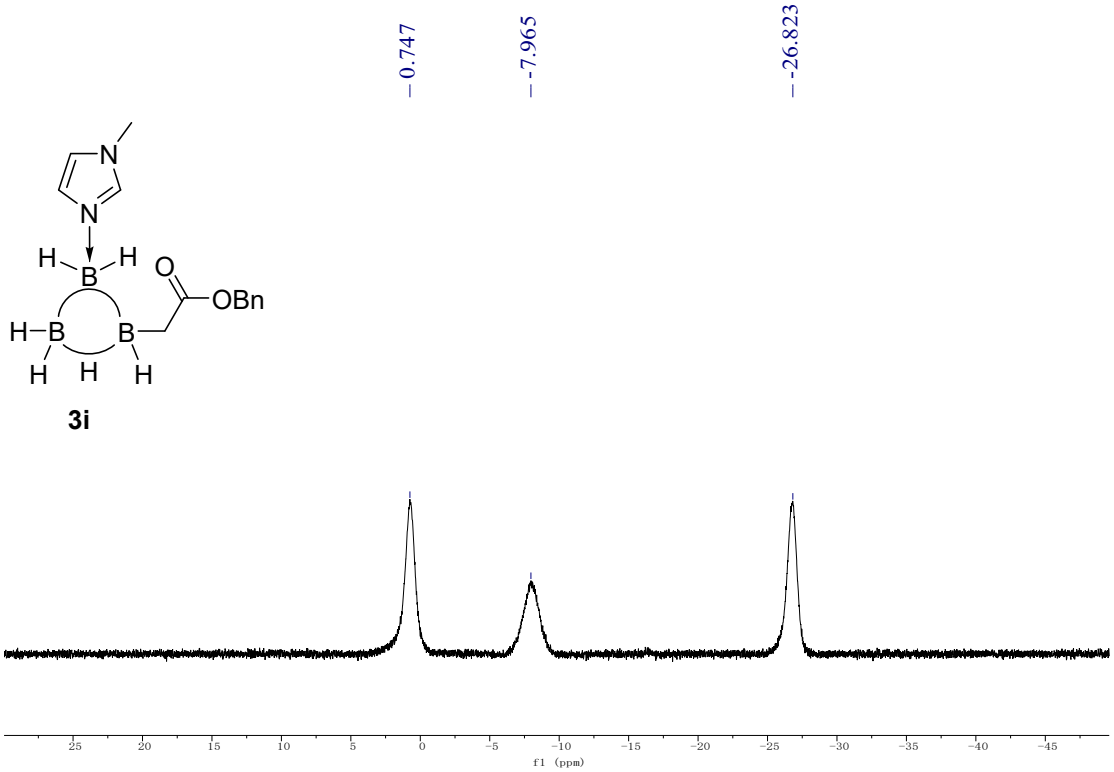

**3i**

**$^{1}$H{$^{11}$B} NMR of 3i**

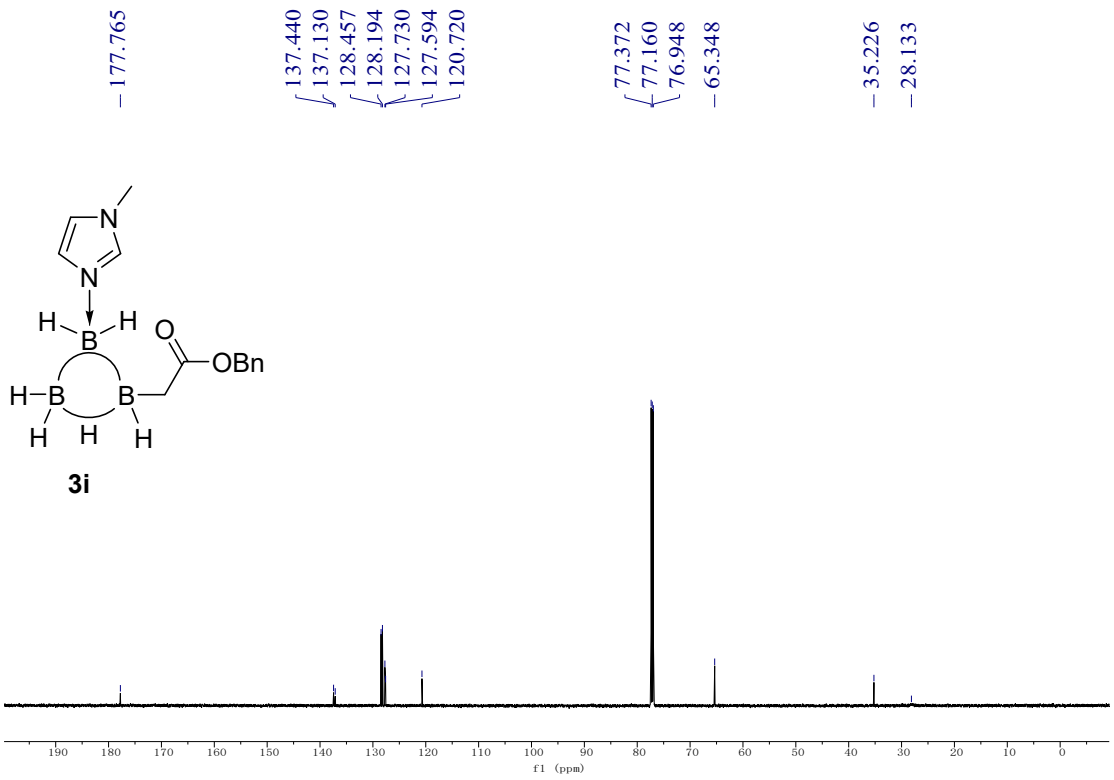



**3i**

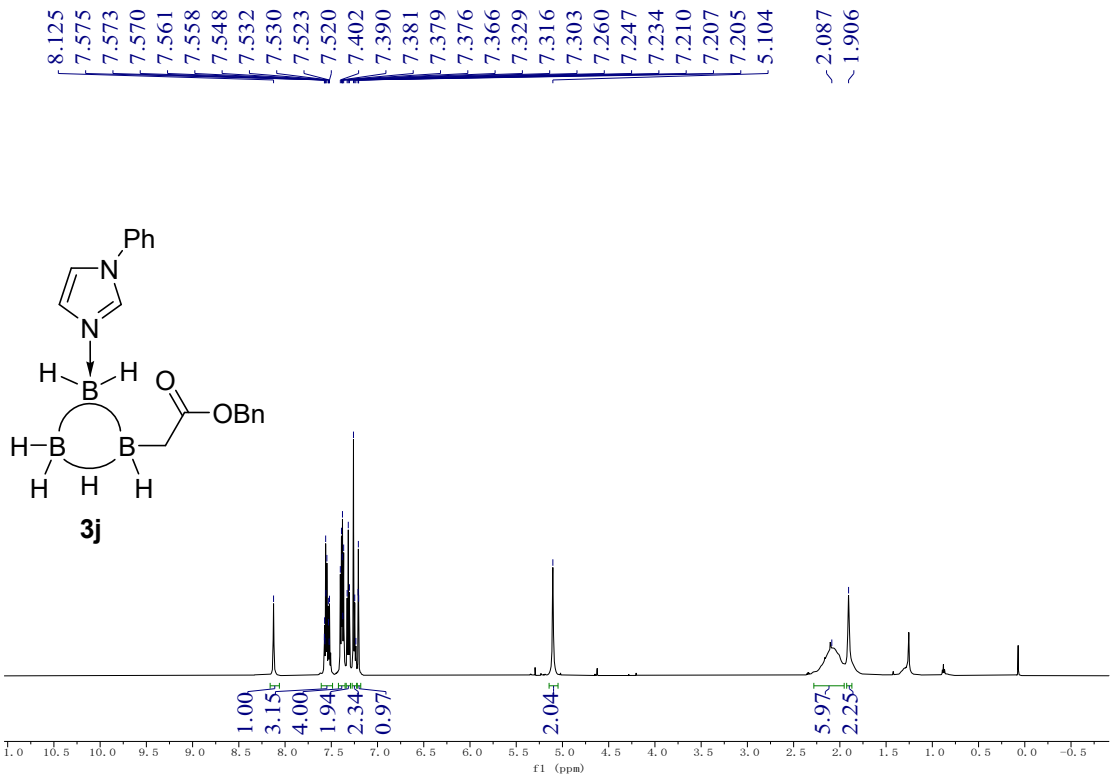
**$^{11}$B NMR of 3i**



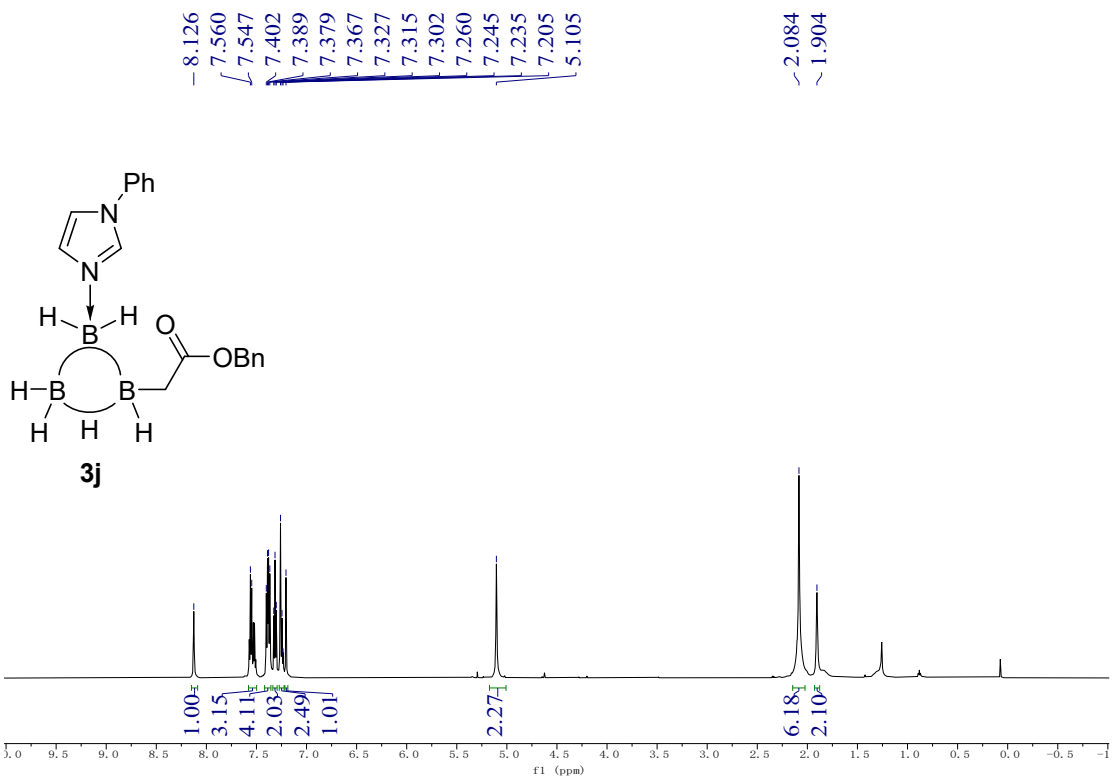

**$^{13}$C{$^{1}$H} NMR of 3i**



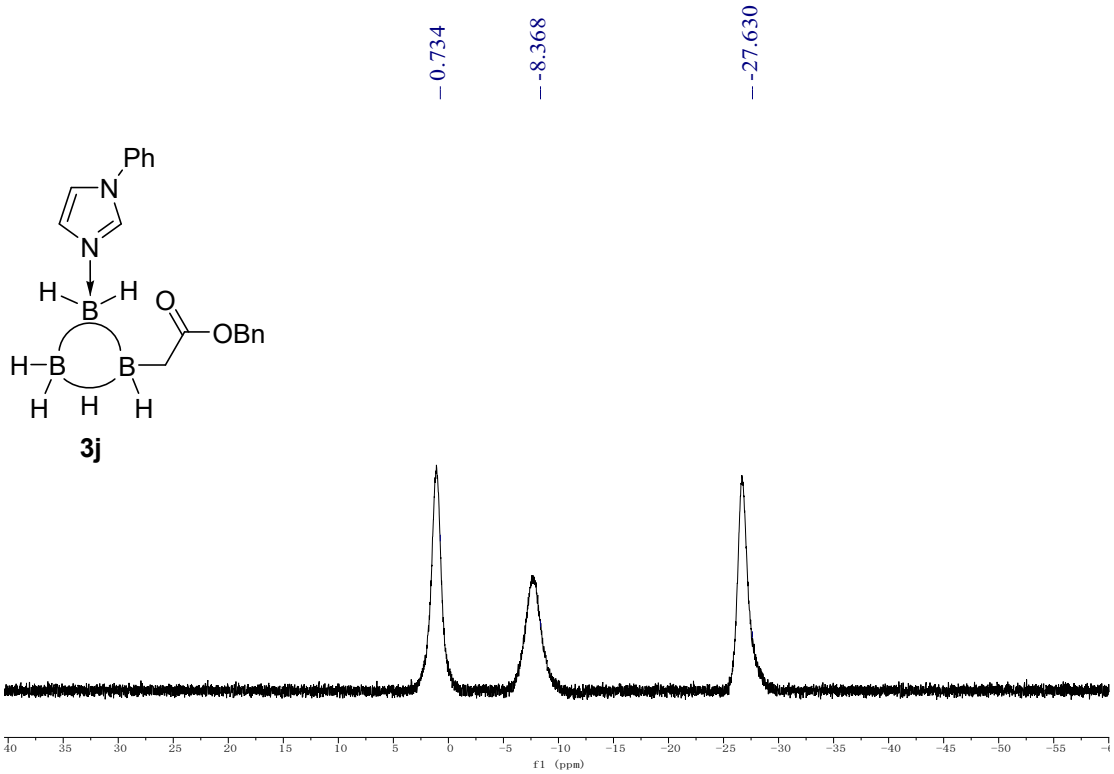
**$^{1}$H NMR of 3j**



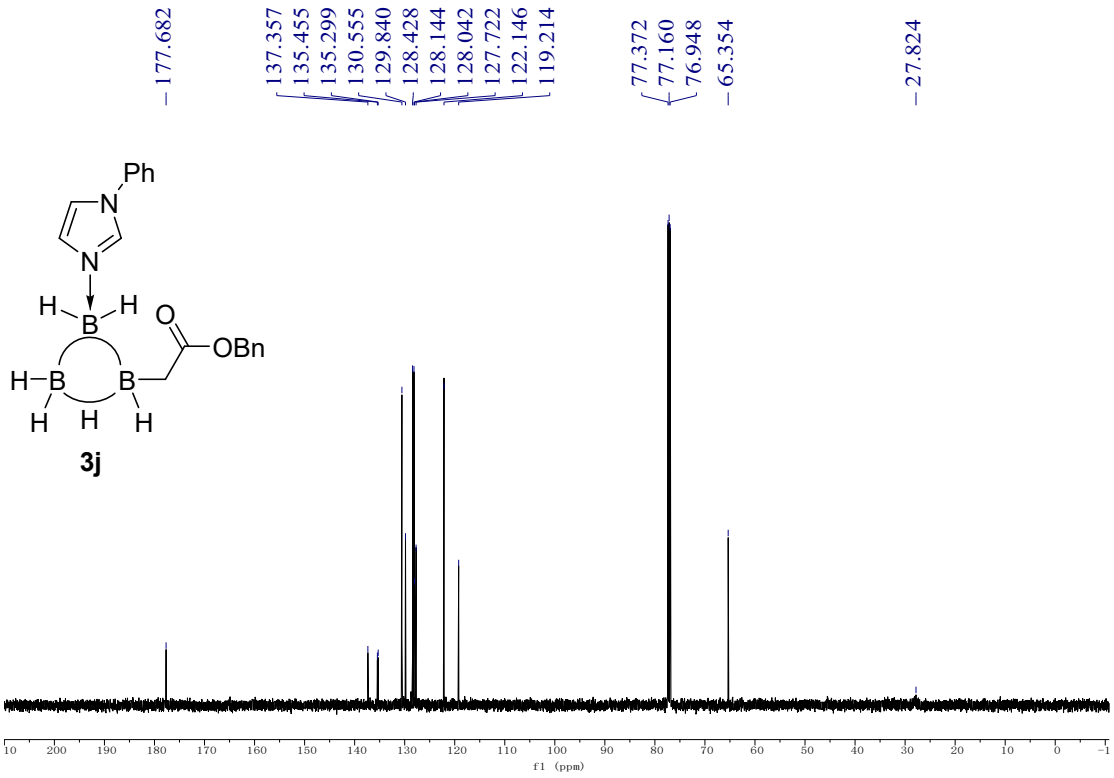

**$^{1}$H{$^{11}$B} NMR of 3j**



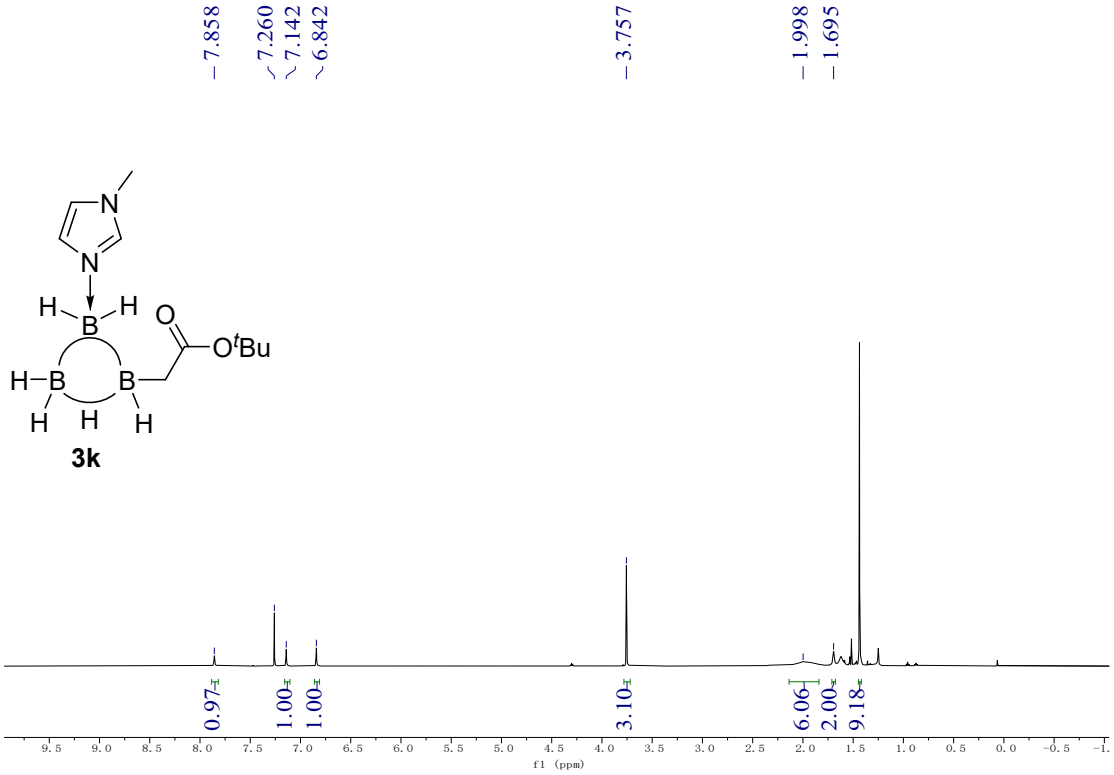
**$^{11}$B NMR of 3j**



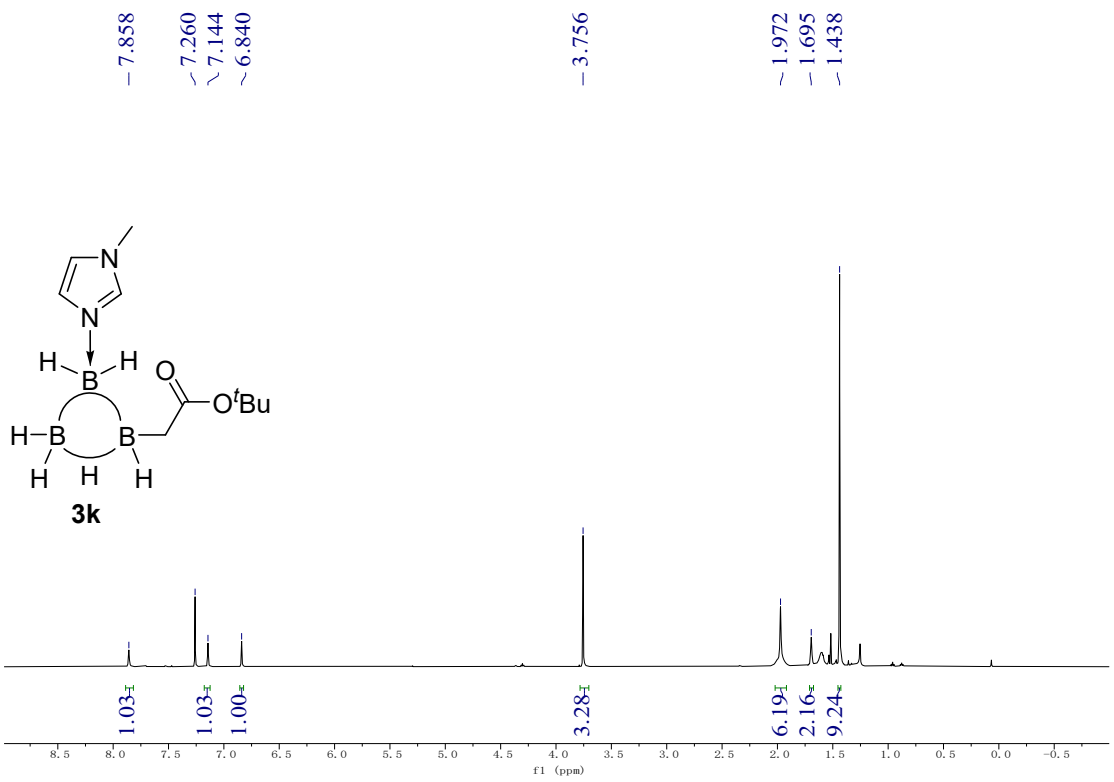

**$^{13}$C{$^{1}$H} NMR of 3j**



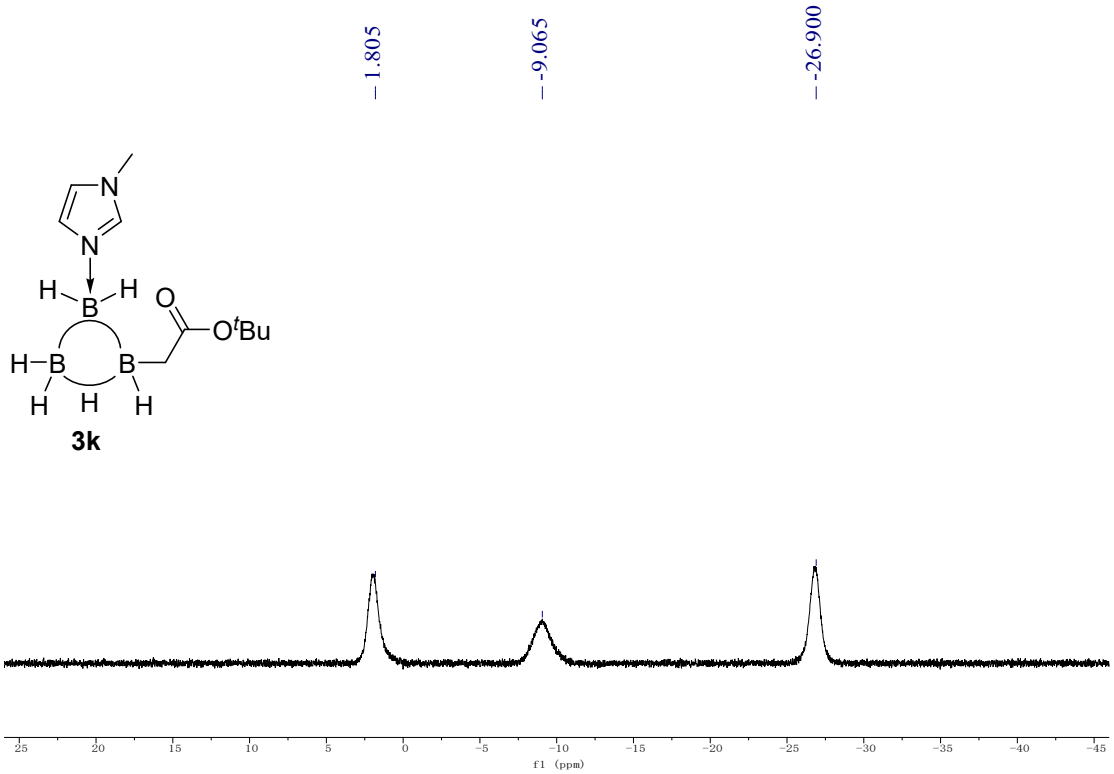
**$^{1}$H NMR of 3k**



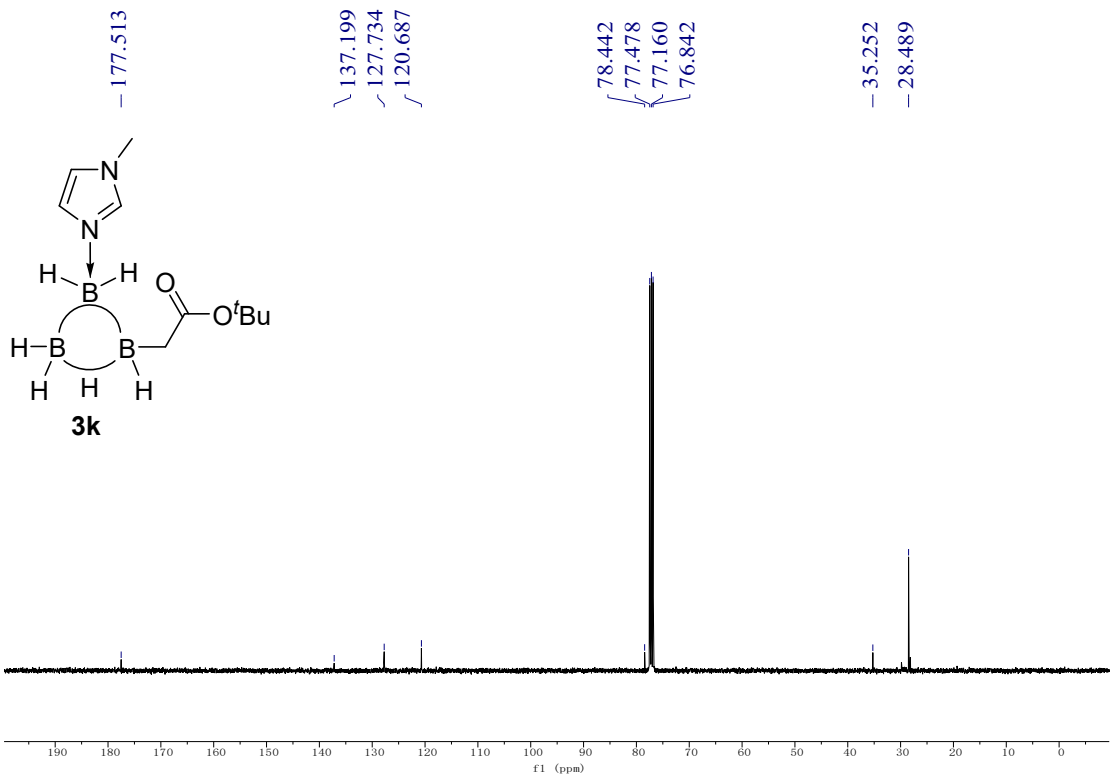

**$^{1}$H{$^{11}$B} NMR of 3k**



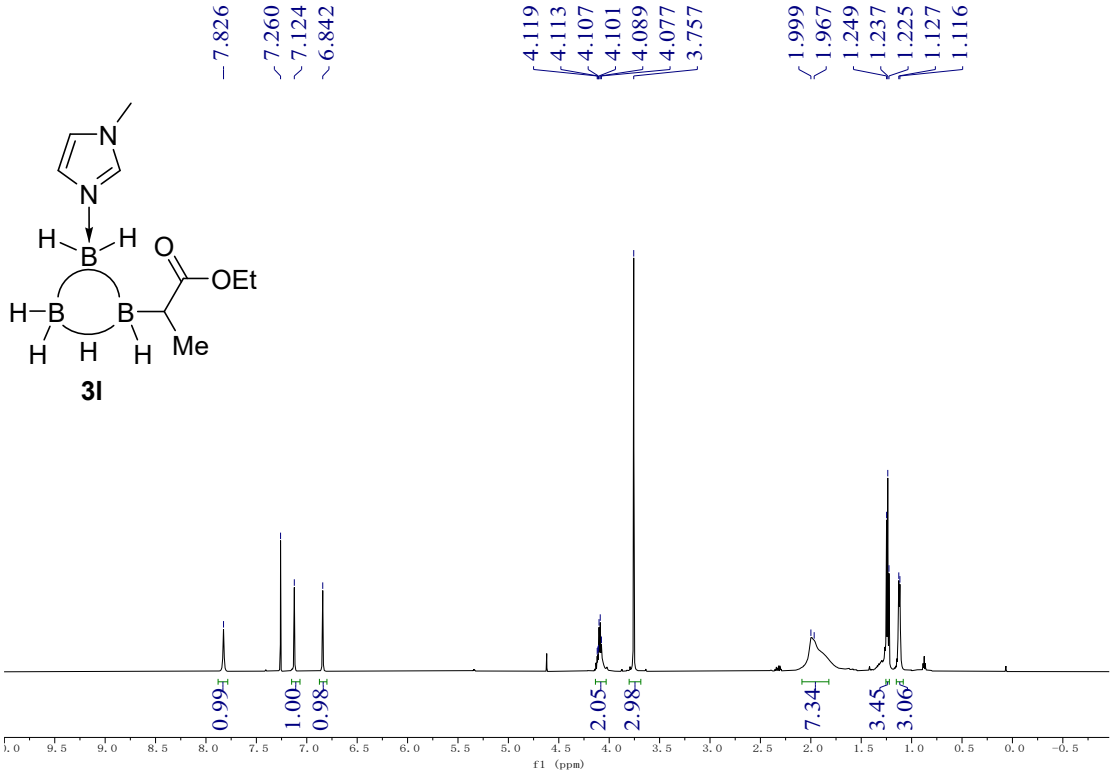
**$^{11}$B NMR of 3k**




**$^{13}$C{$^{1}$H} NMR of 3k**

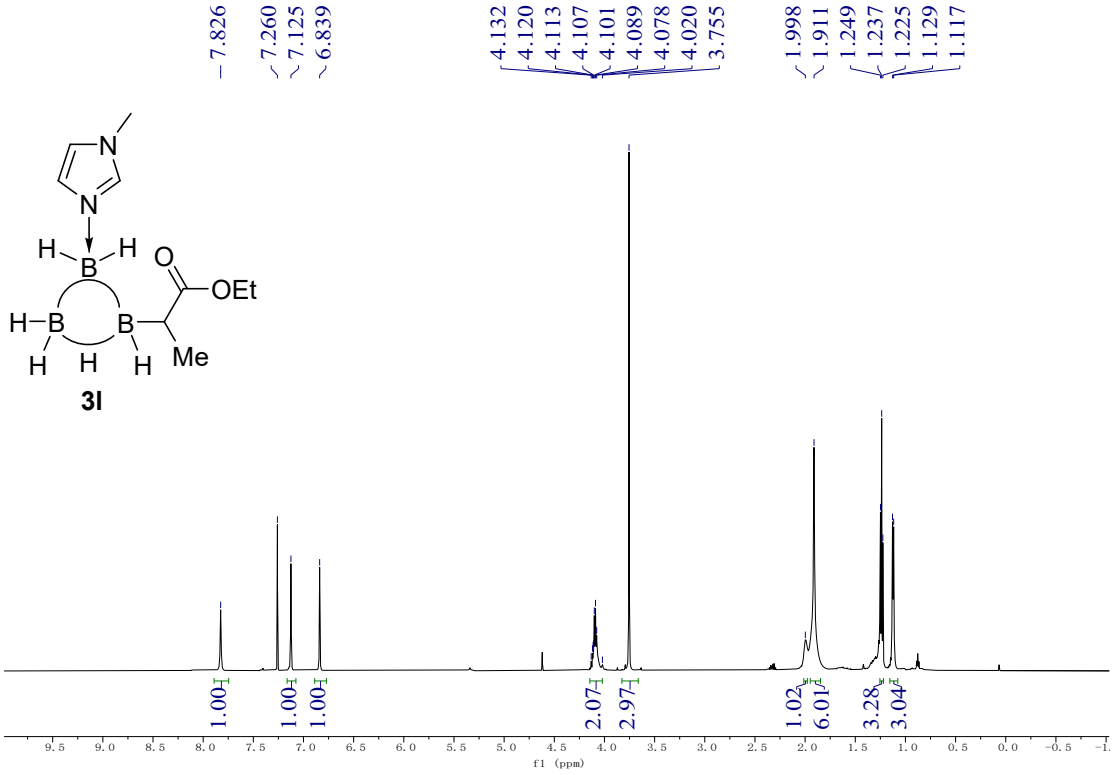


**$^{1}$H NMR of 3l**



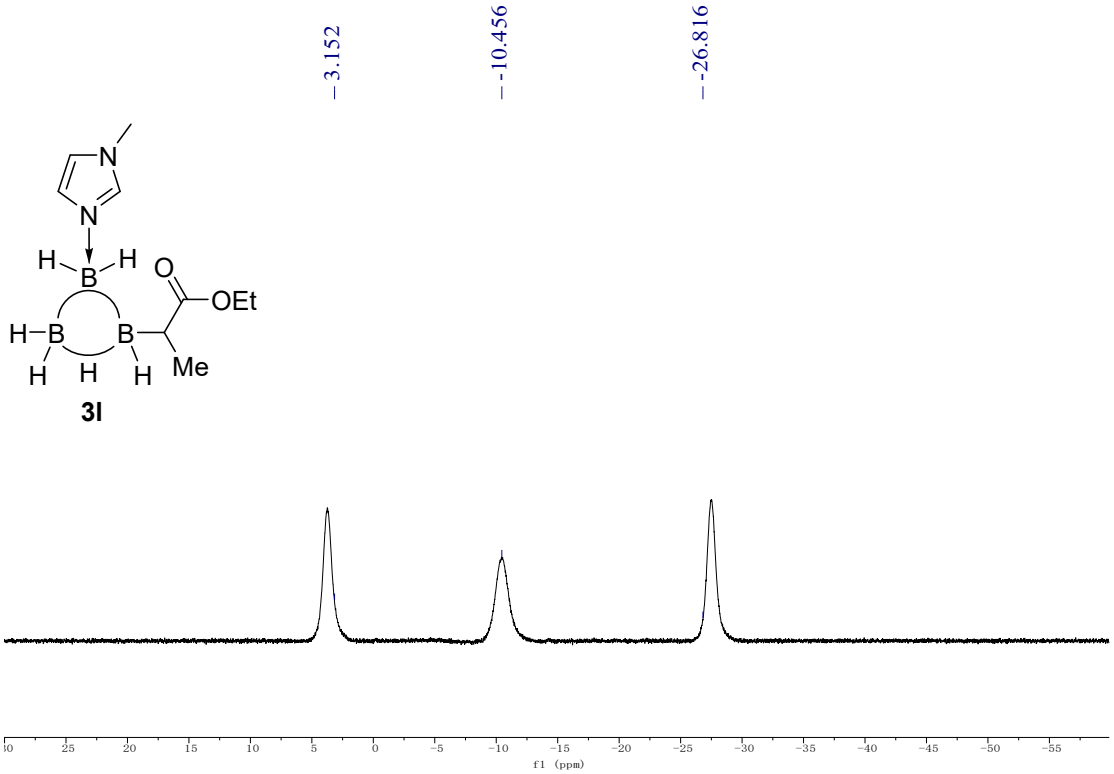

**3l**

**$^{1}$H{$^{11}$B} NMR of 3l**

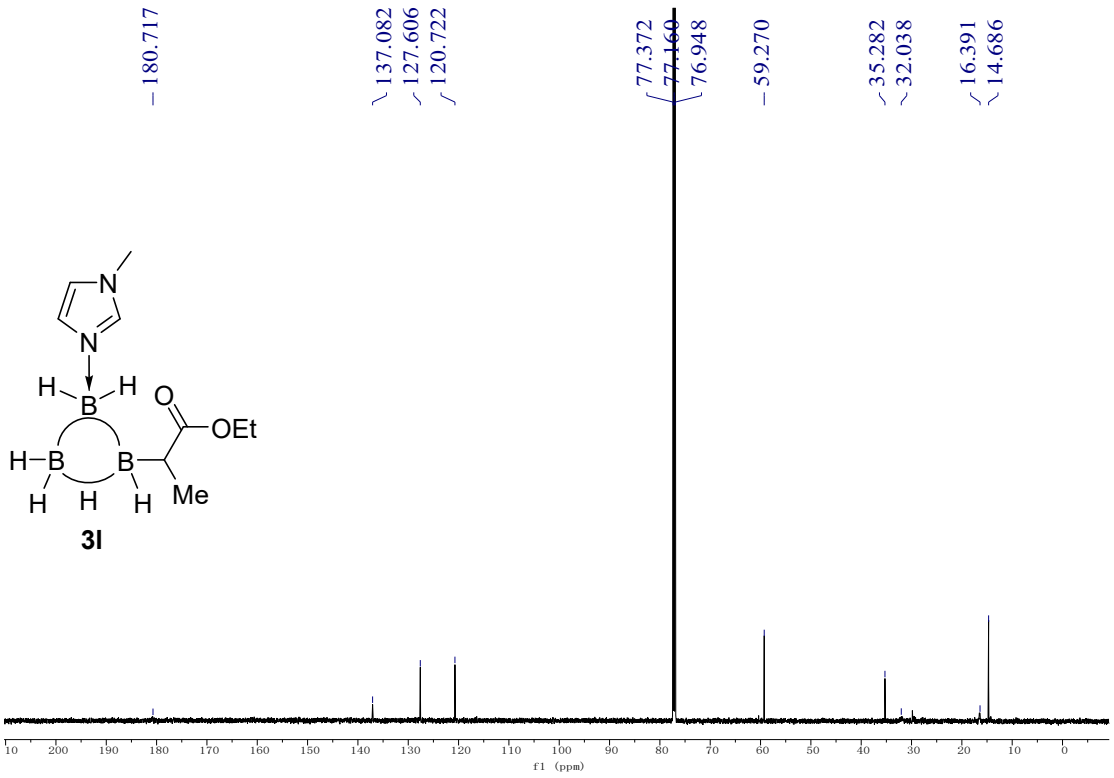



**3l**

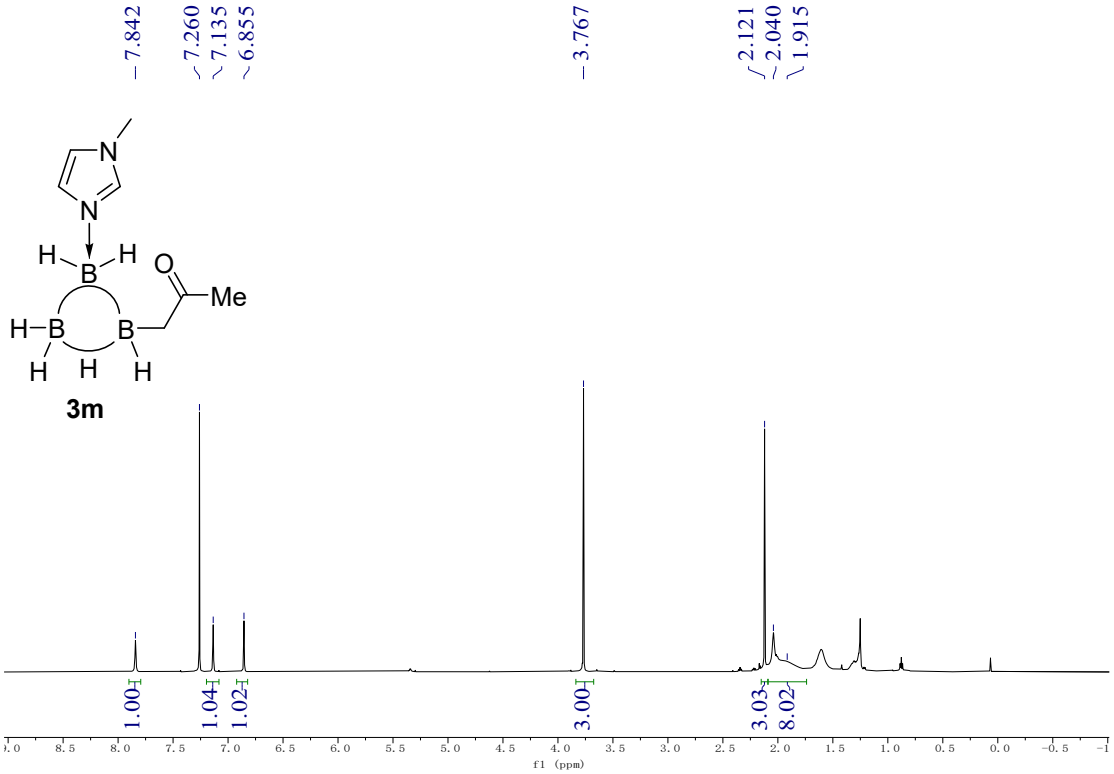
**$^{11}$B NMR of 3l**




**$^{13}$C{$^{1}$H} NMR of 3l**

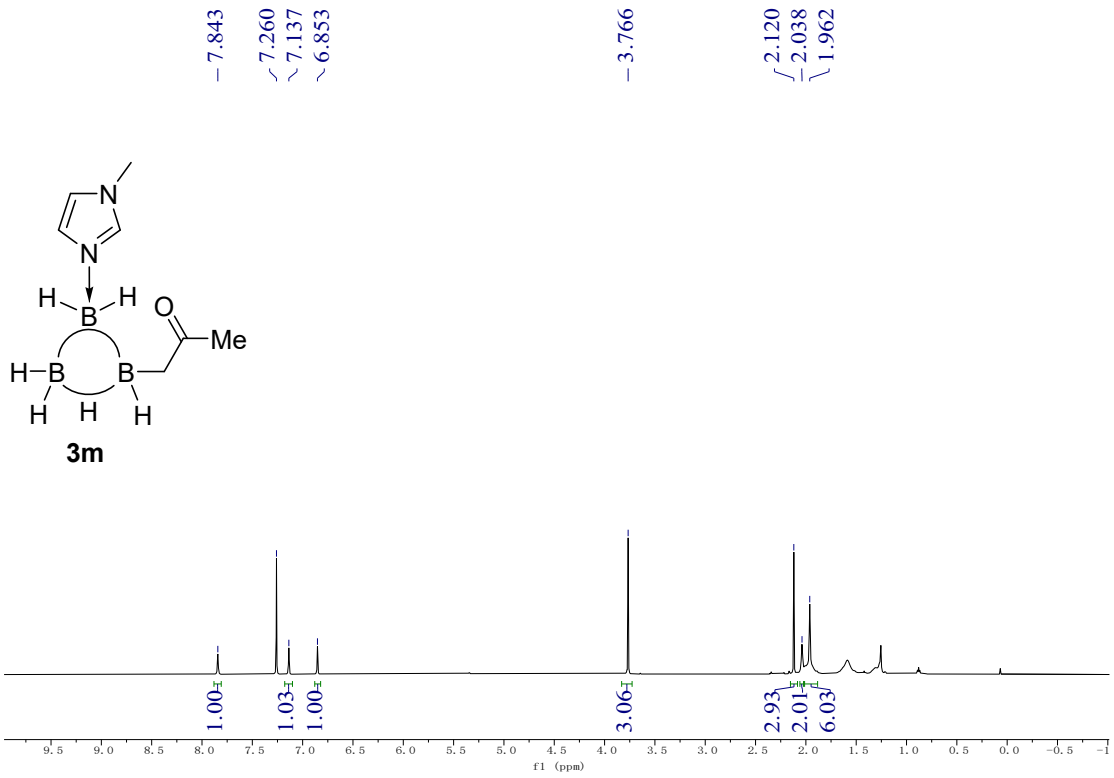


**$^{1}$H NMR of 3m**



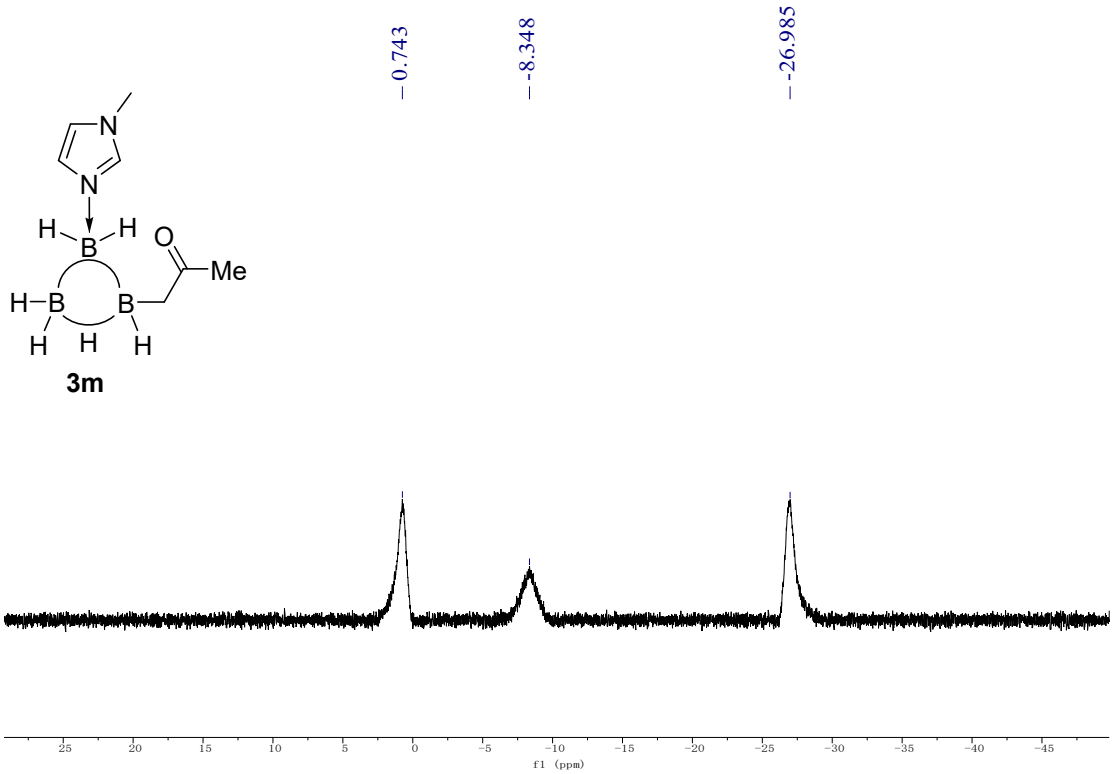

3m

**$^{1}$H{$^{11}$B} NMR of 3m**

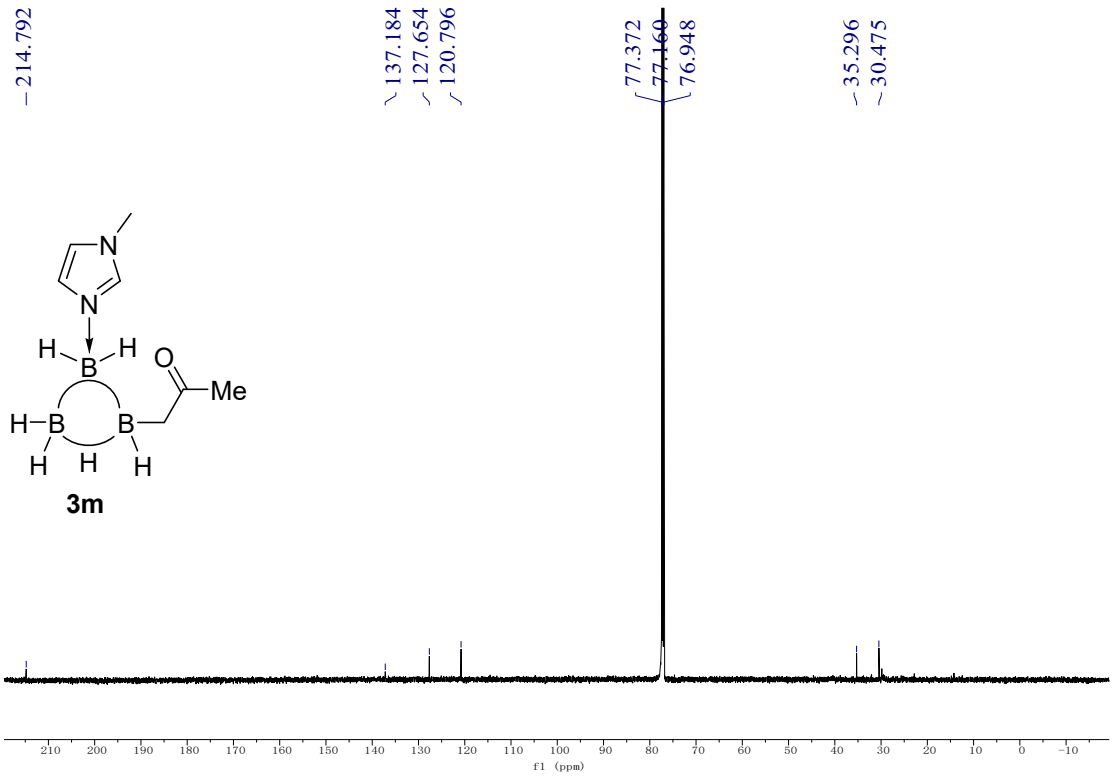



3m

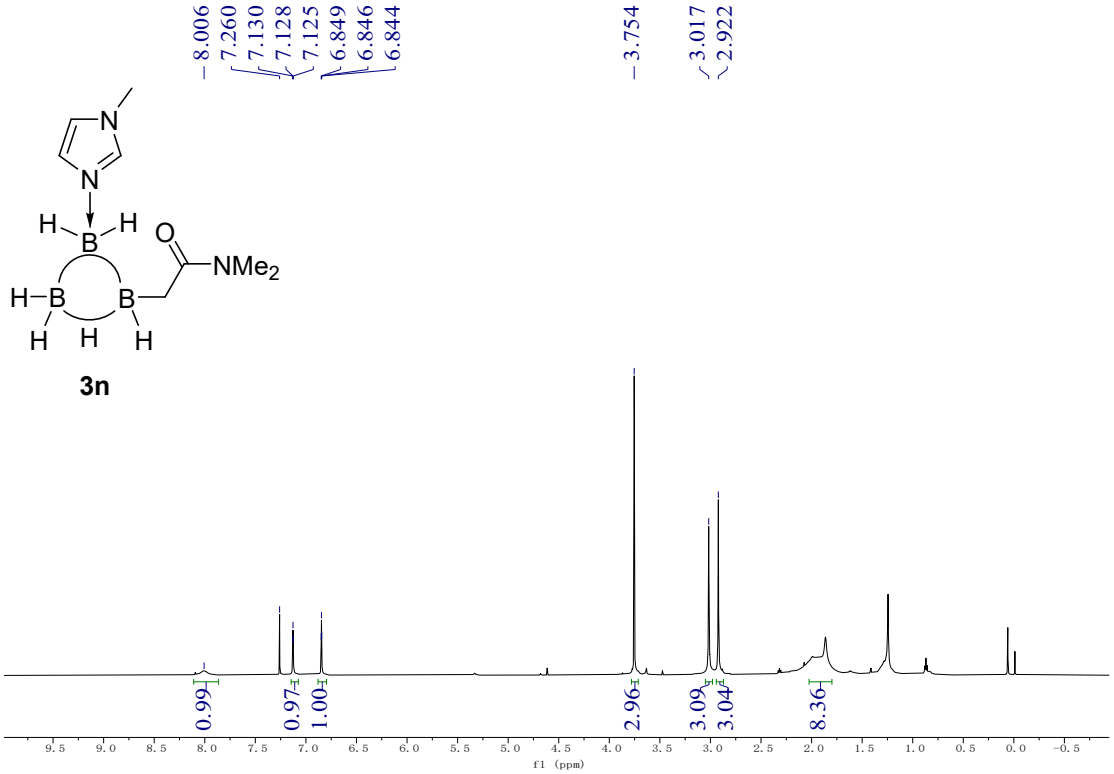
**$^{11}$B NMR of 3m**




**$^{13}$C{$^{1}$H} NMR of 3m**

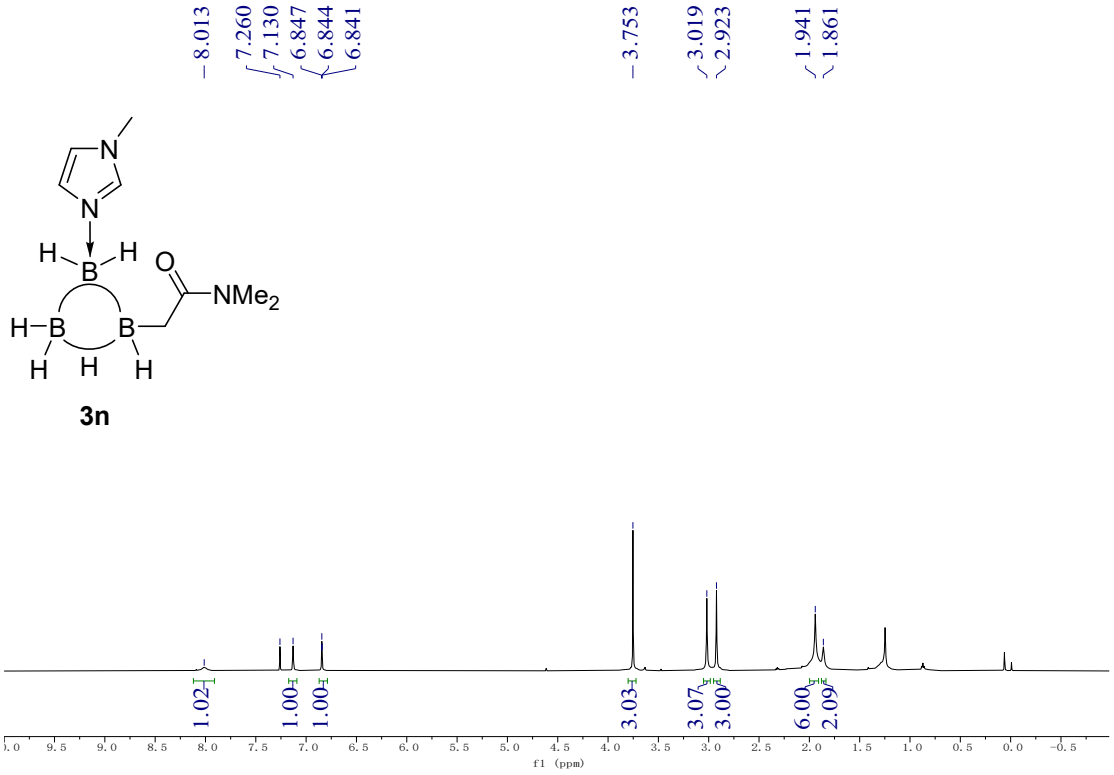


**$^{1}$H NMR of 3n**



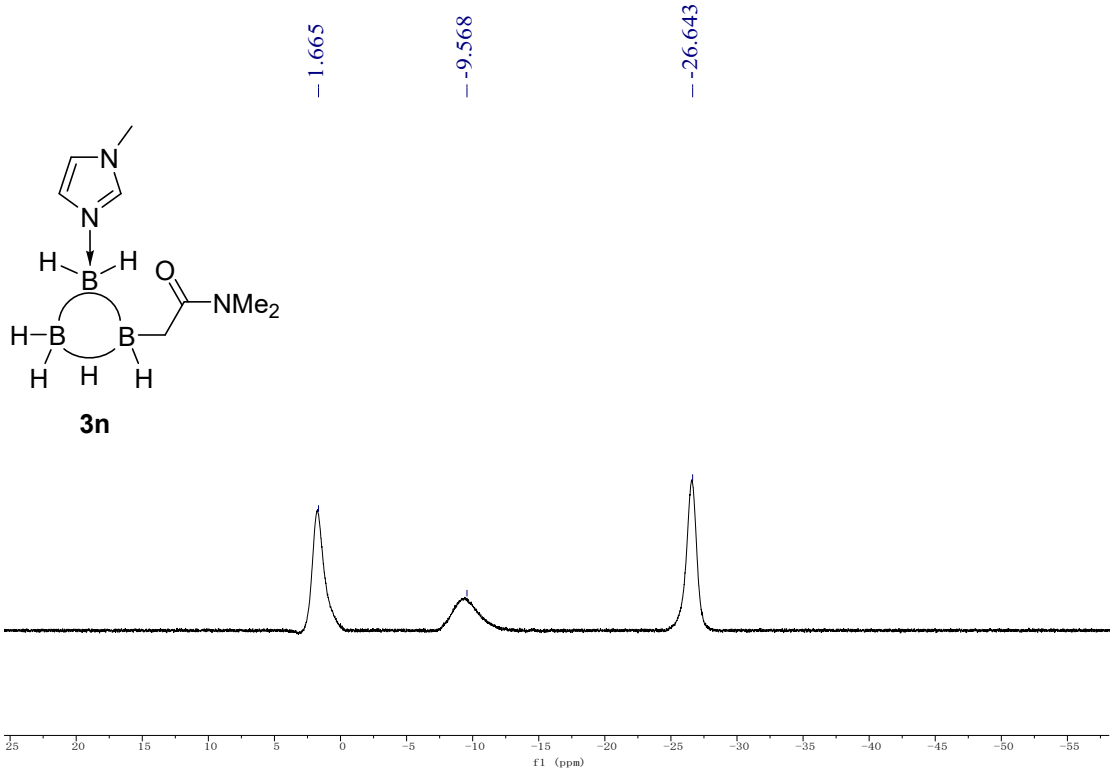

**3n**

**$^{1}$H{$^{11}$B} NMR of 3n**

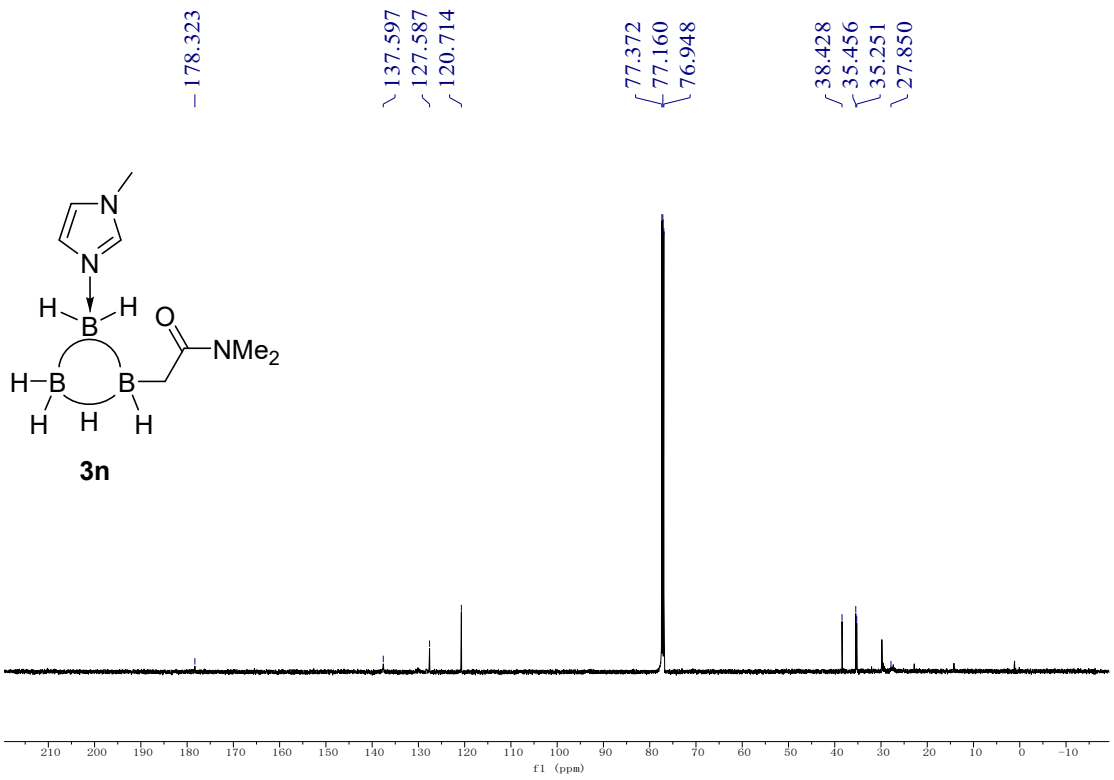



**3n**

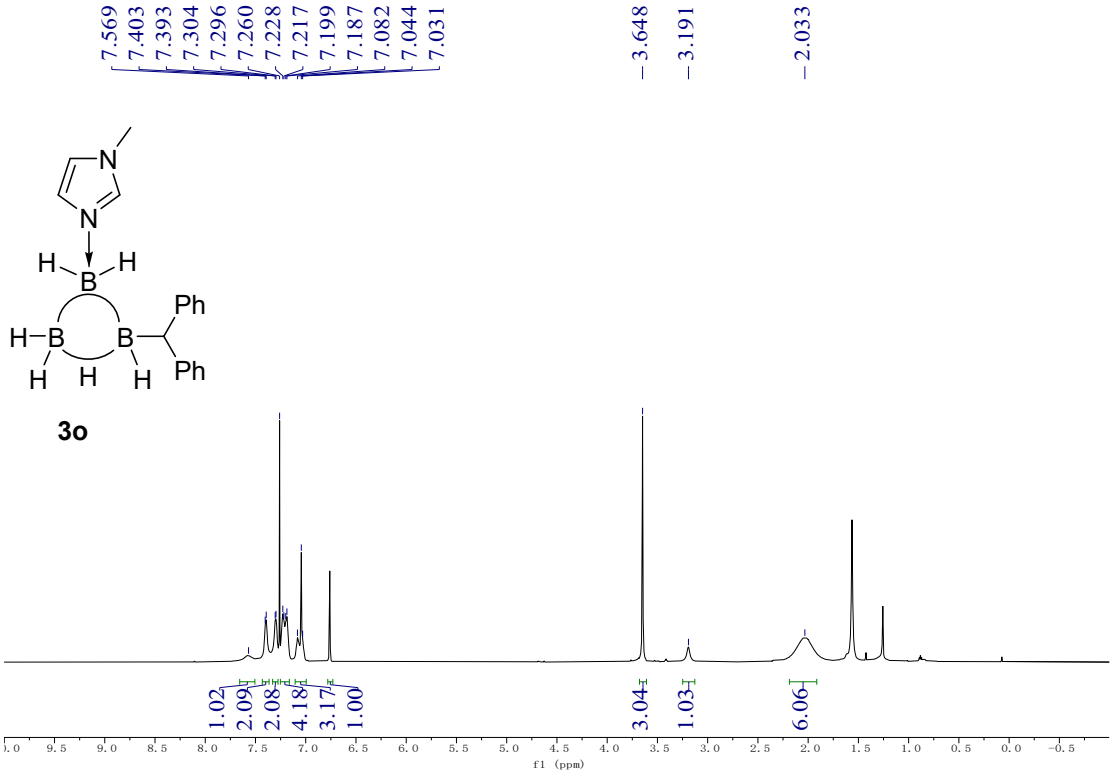
**$^{11}$B NMR of 3n**



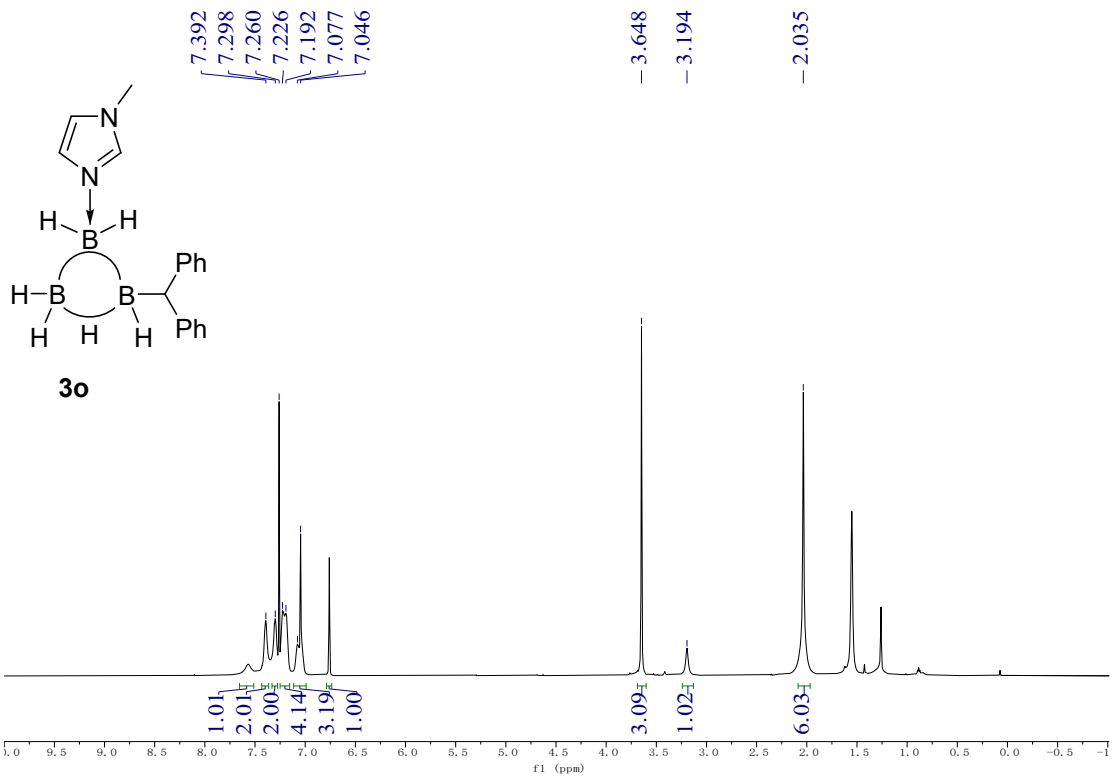

**$^{13}$C{$^{1}$H} NMR of 3n**



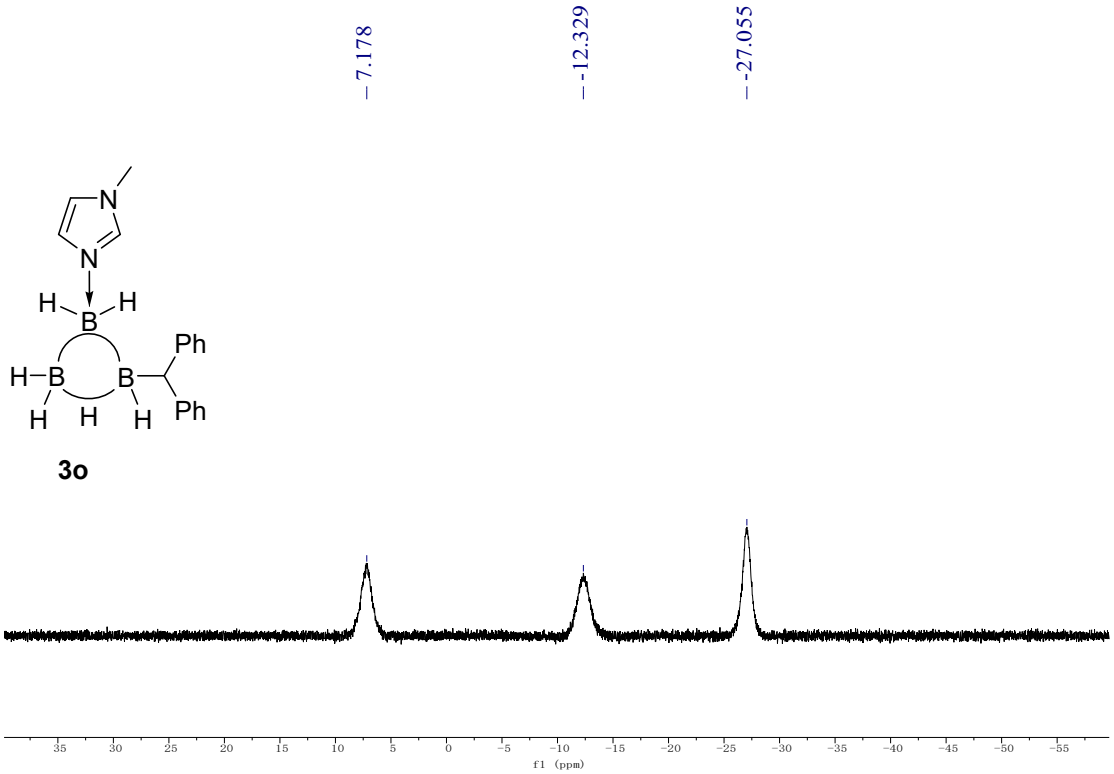
**$^{1}$H NMR of 3o**



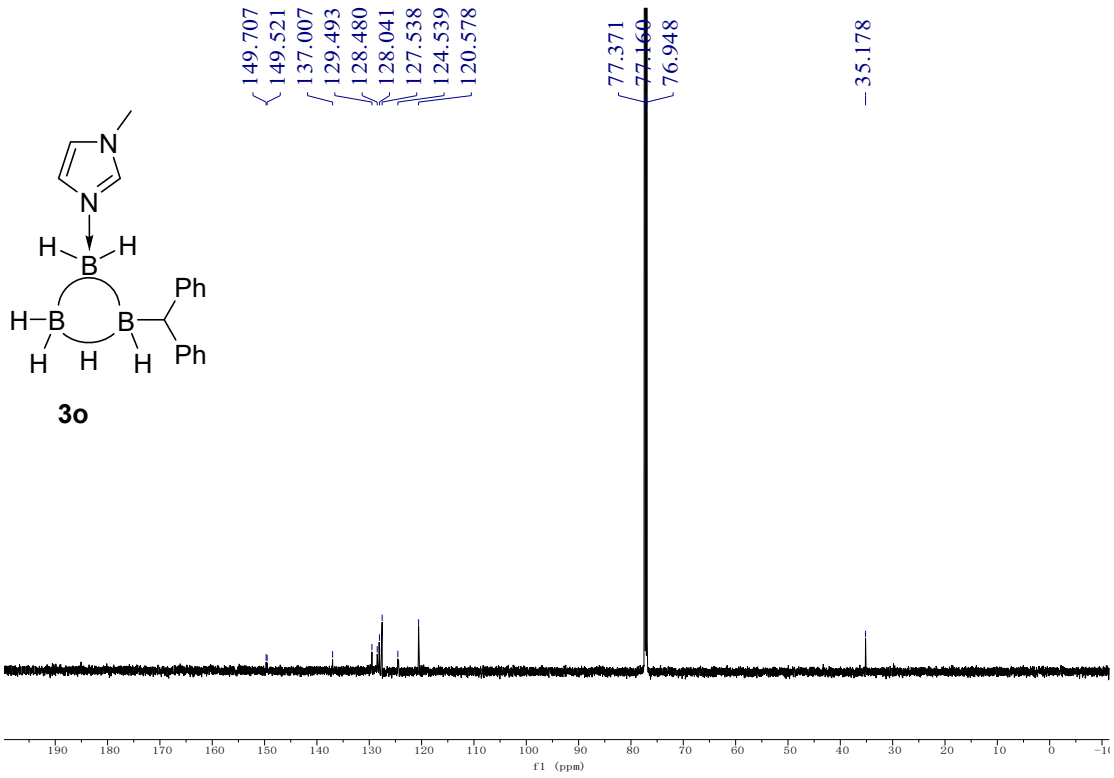

**$^{1}$H{$^{11}$B} NMR of 3o**



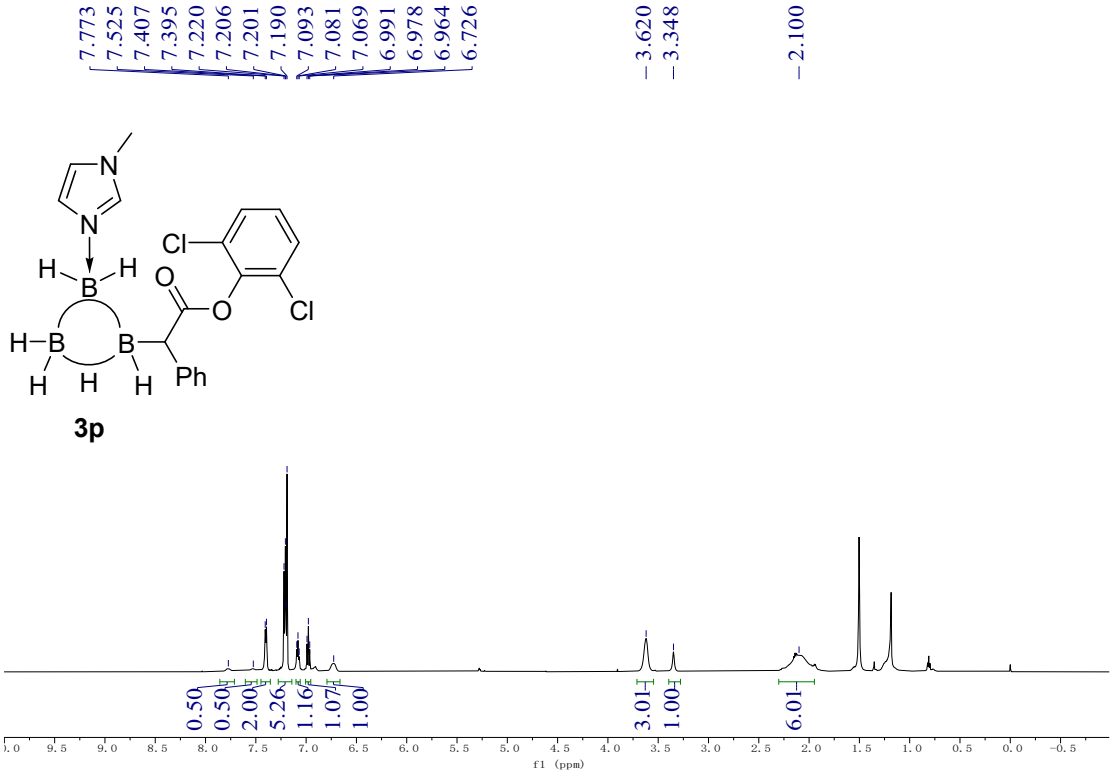
**$^{11}$B NMR of 3o**




**$^{13}$C{$^{1}$H} NMR of 3o**

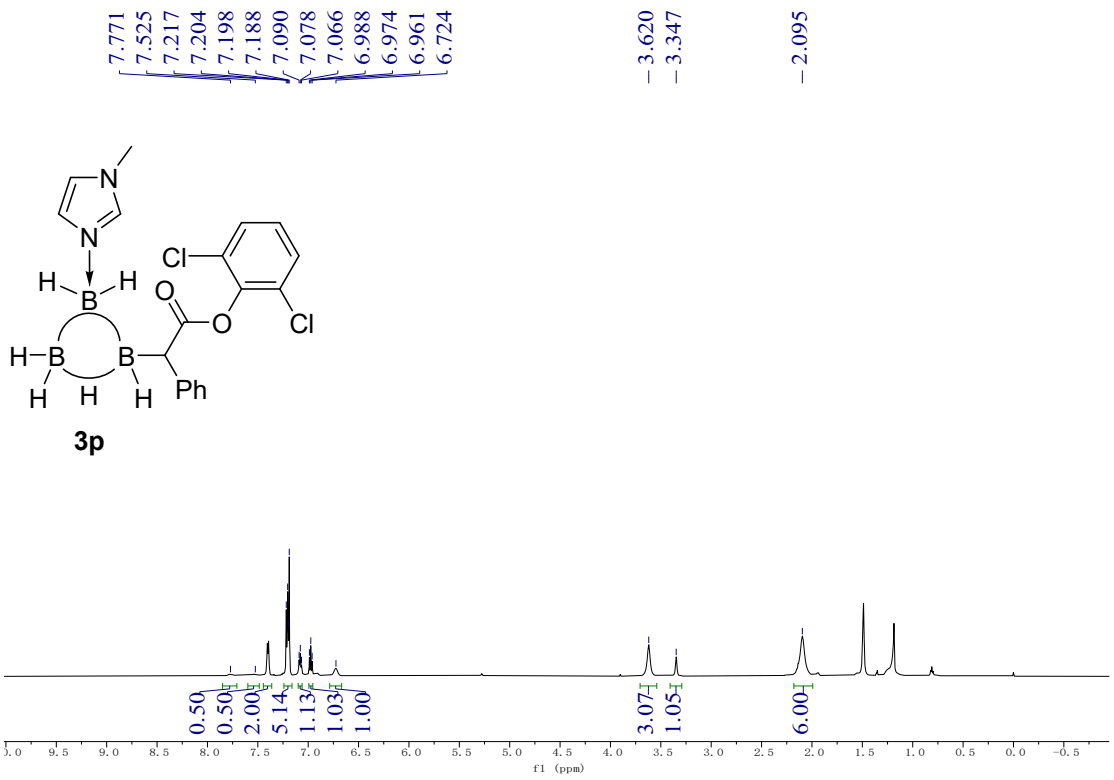


**$^{1}$H NMR of 3p**



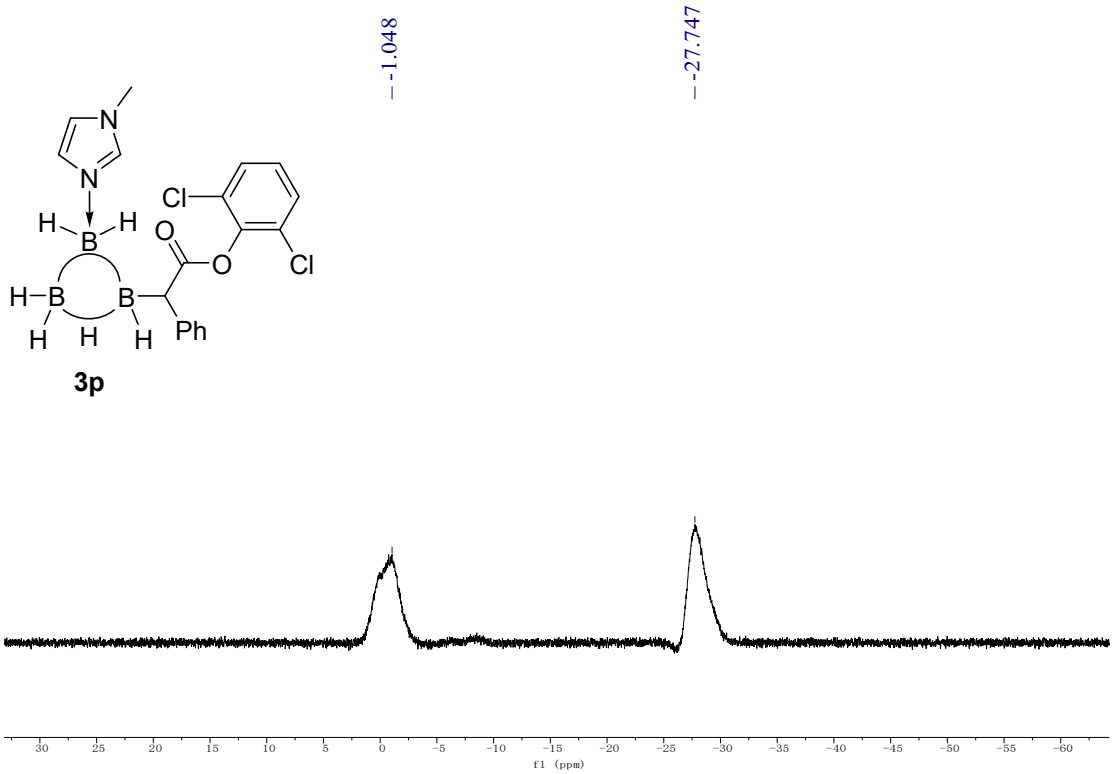

**3p**

**$^{1}$H{$^{11}$B} NMR of 3p**

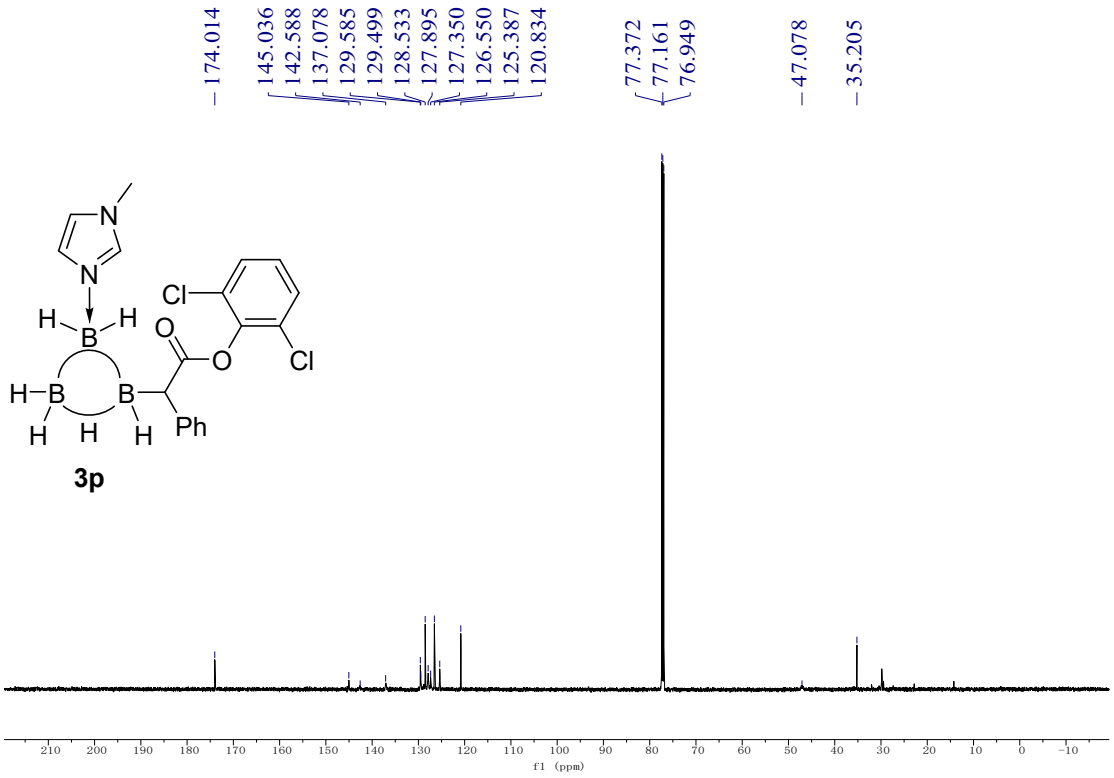



**3p**

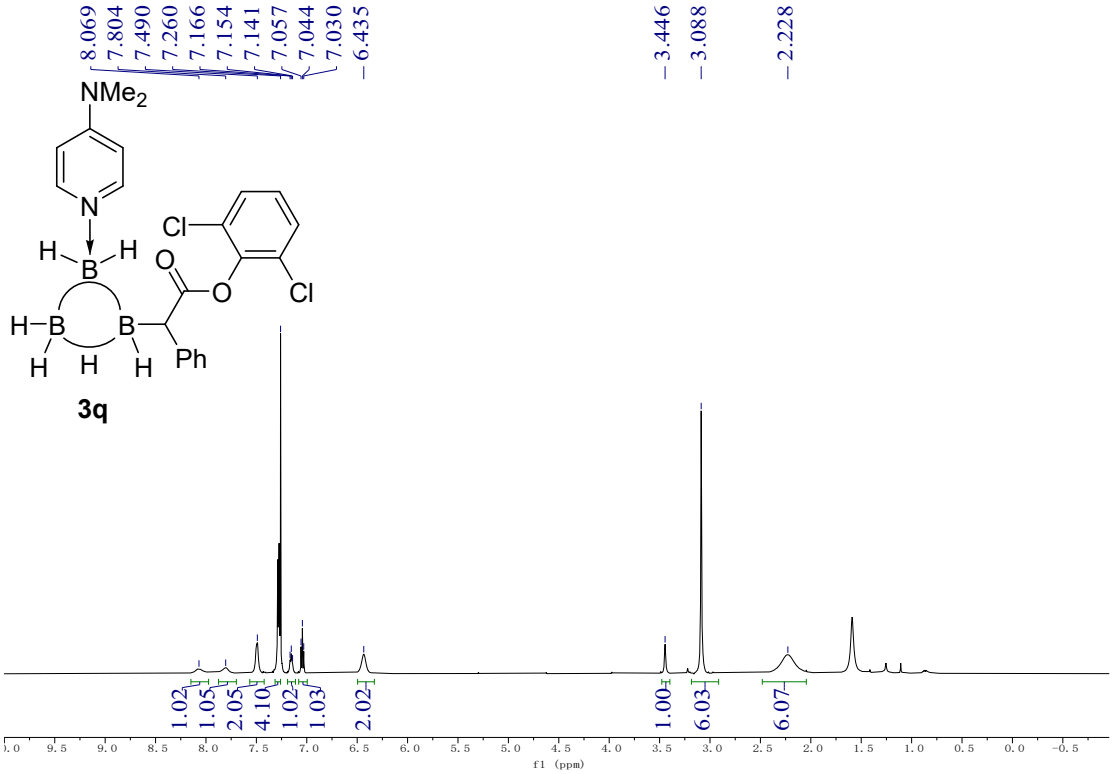
**$^{11}$B NMR of 3p**



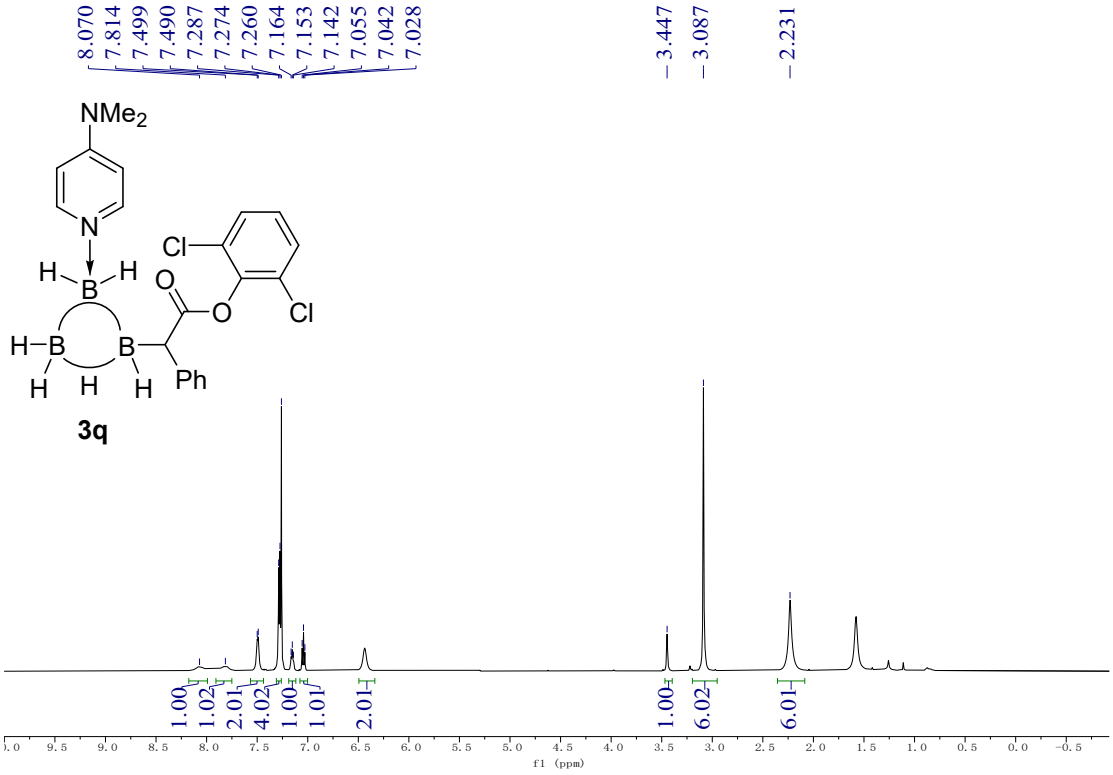

**$^{13}$C{$^{1}$H} NMR of 3p**



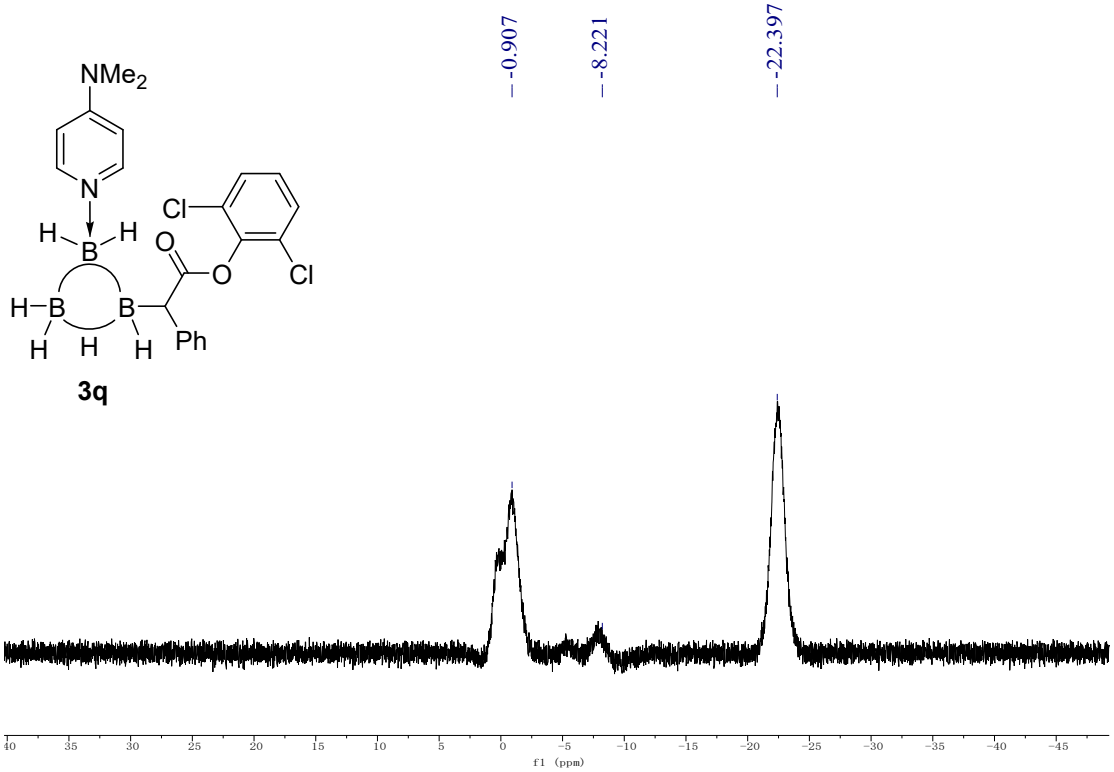
**$^{1}$H NMR of 3q**



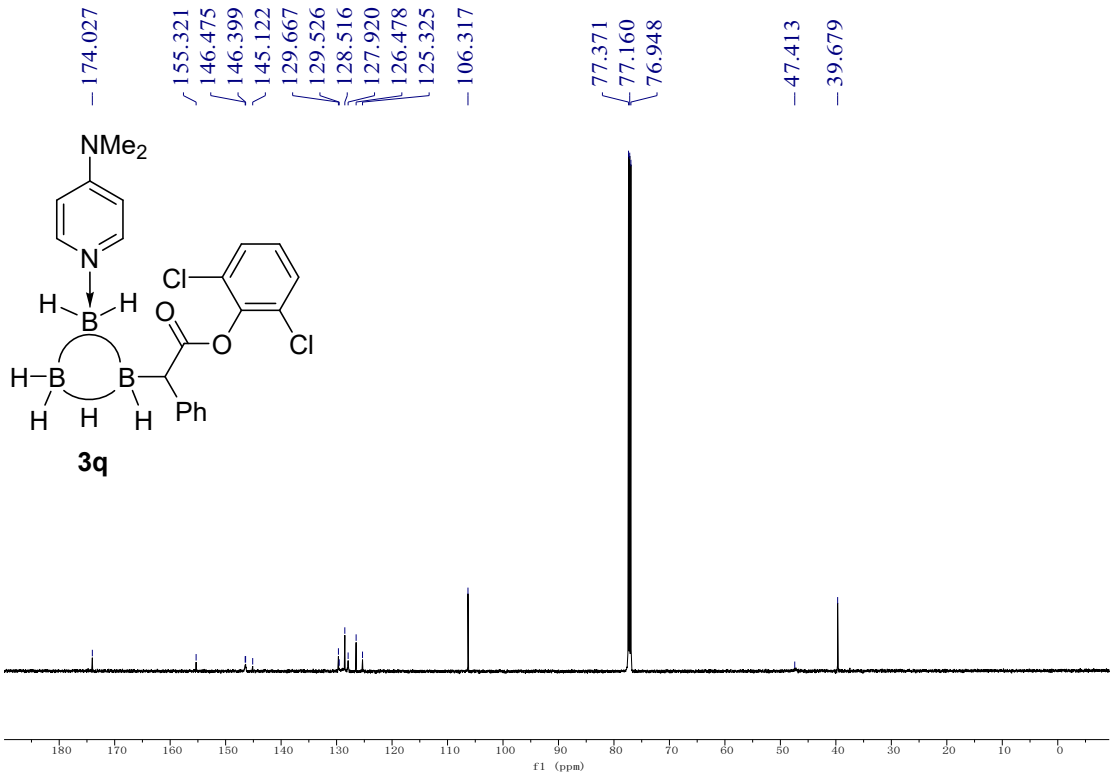

**$^{1}$H{$^{11}$B} NMR of 3q**



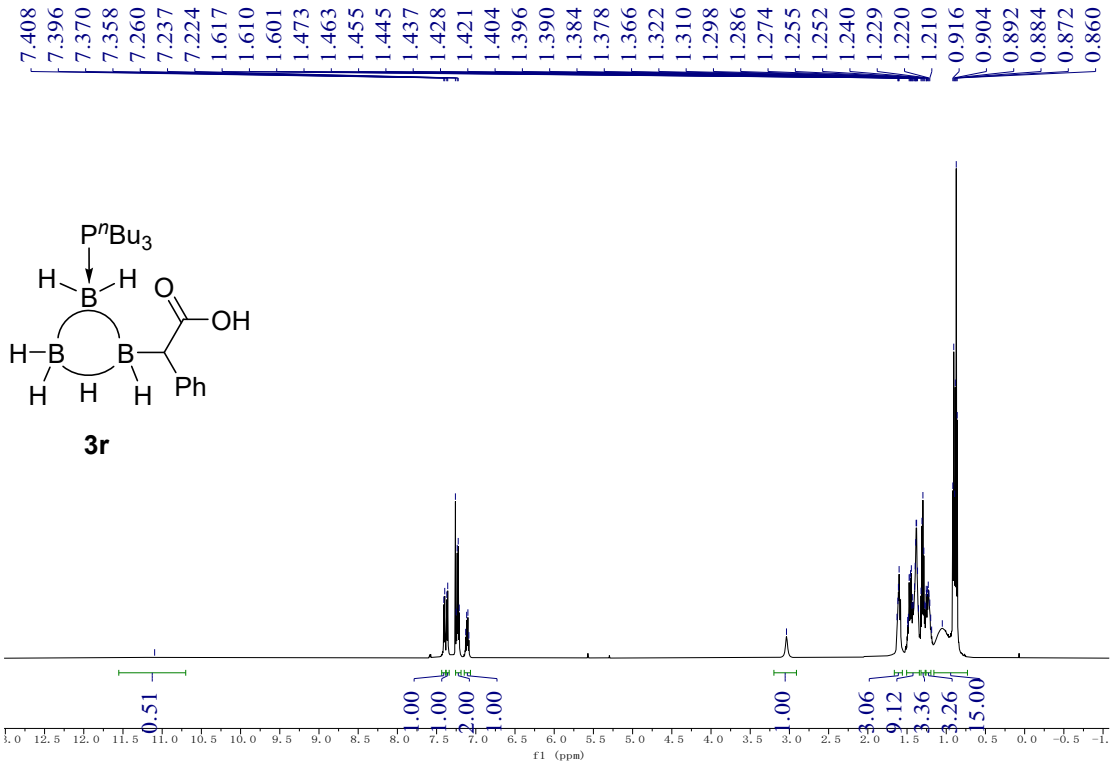
**$^{11}$B NMR of 3q**



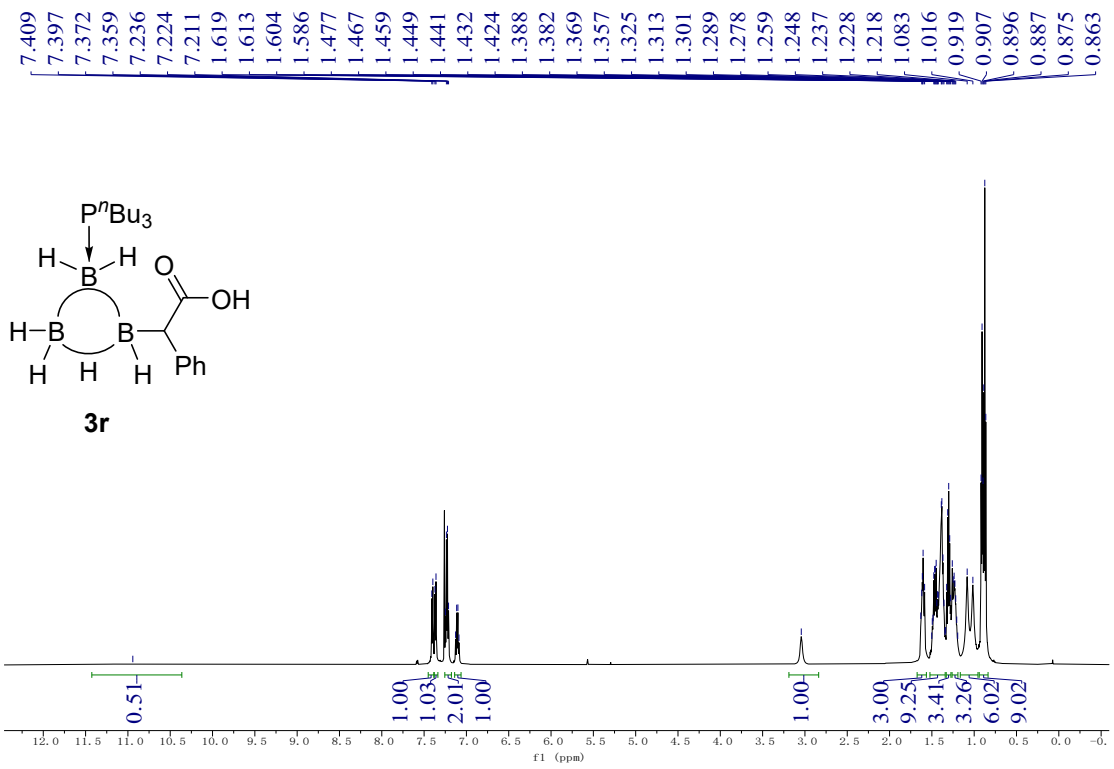

**$^{13}$C{$^{1}$H} NMR of 3q**



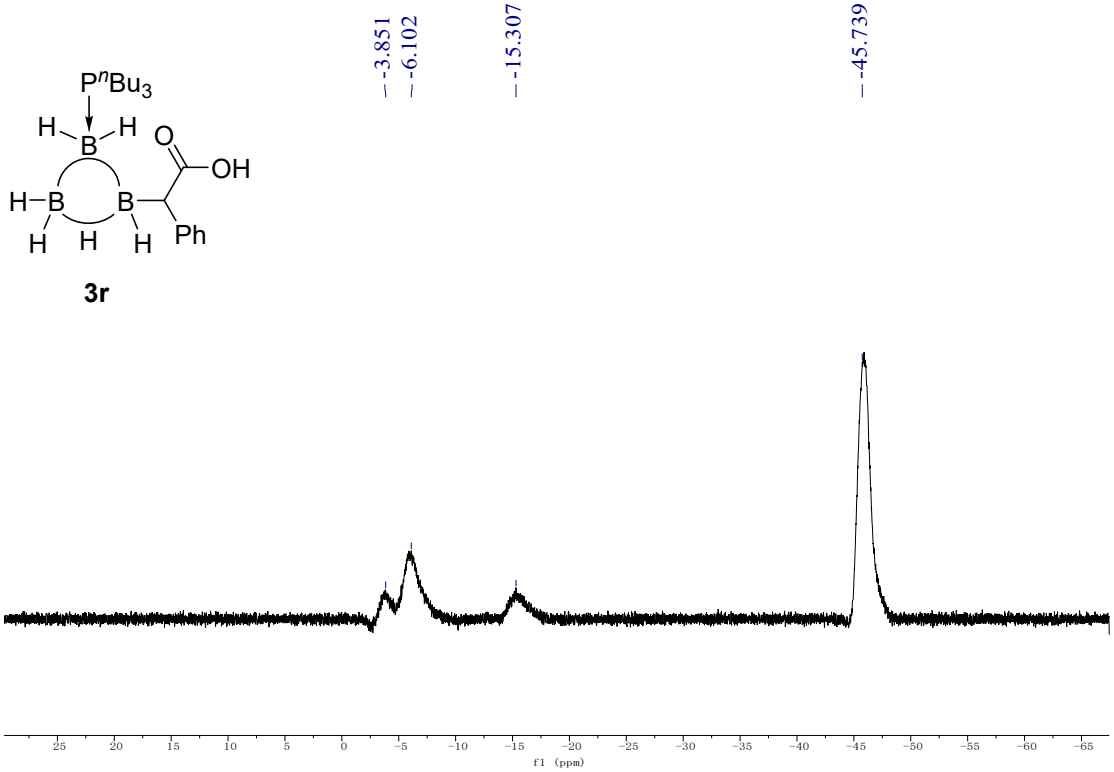
**$^{1}$H NMR of 3r**




**$^{1}$H{$^{11}$B} NMR of 3r**

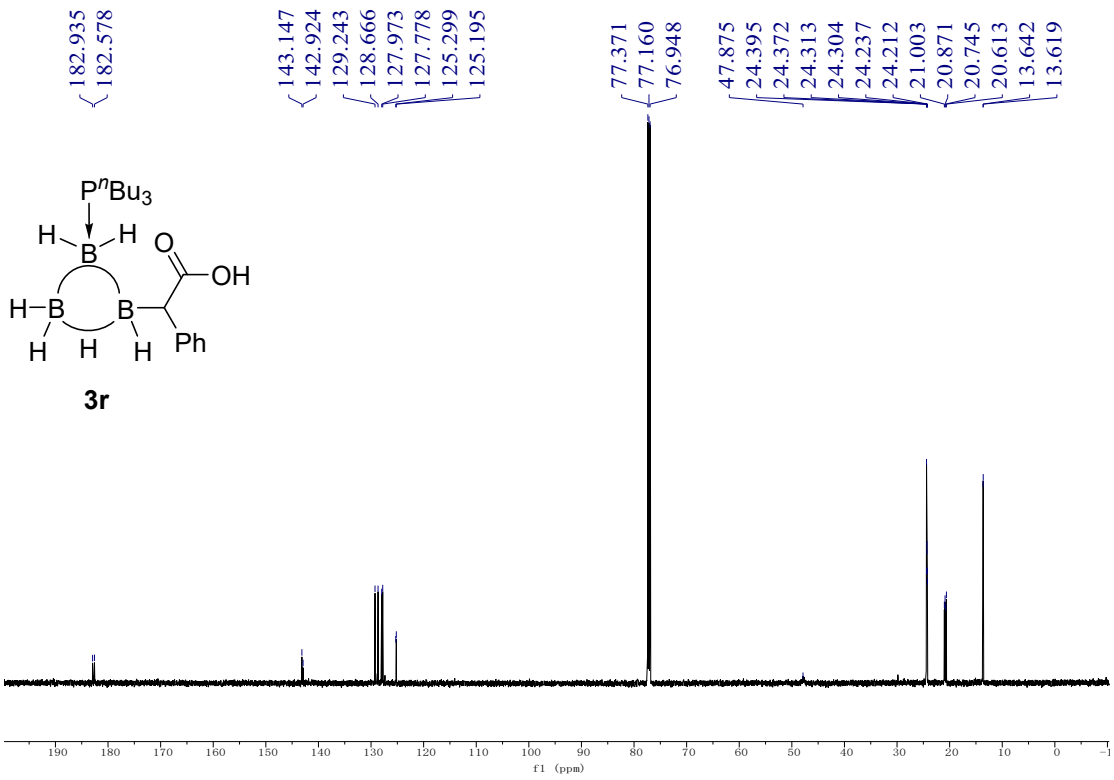


**$^{11}$B NMR of 3r**



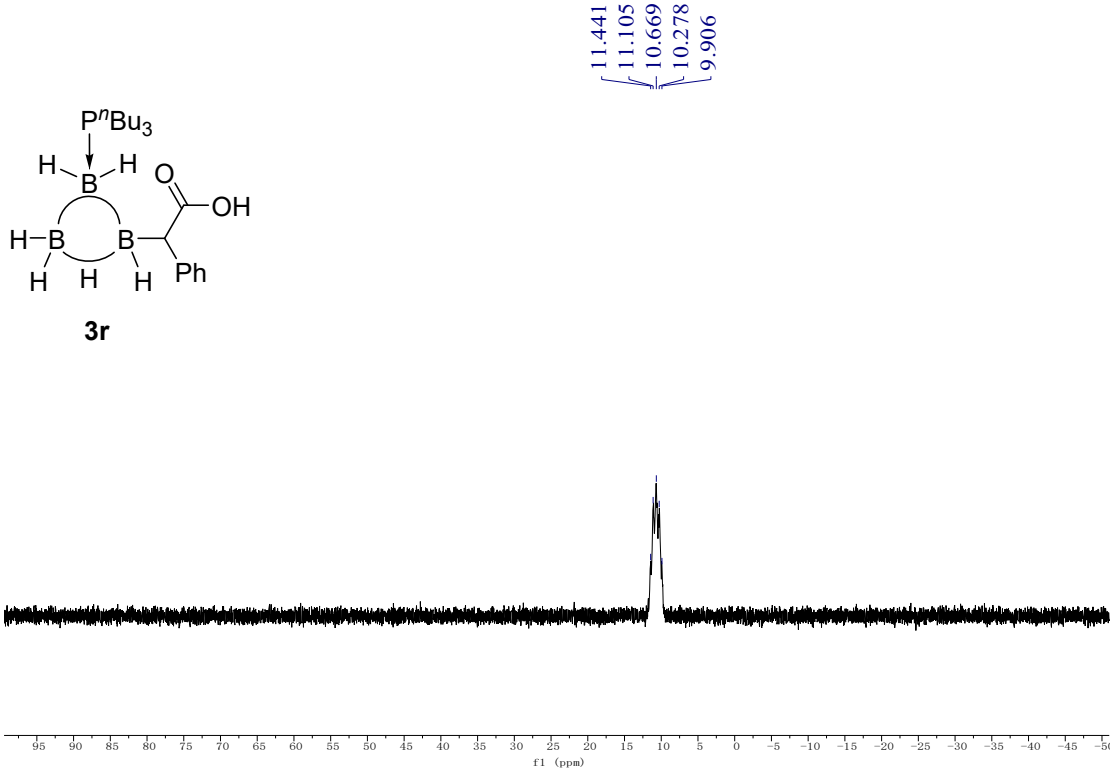

**3r**

**$^{13}$C{$^{1}$H} NMR of 3r**



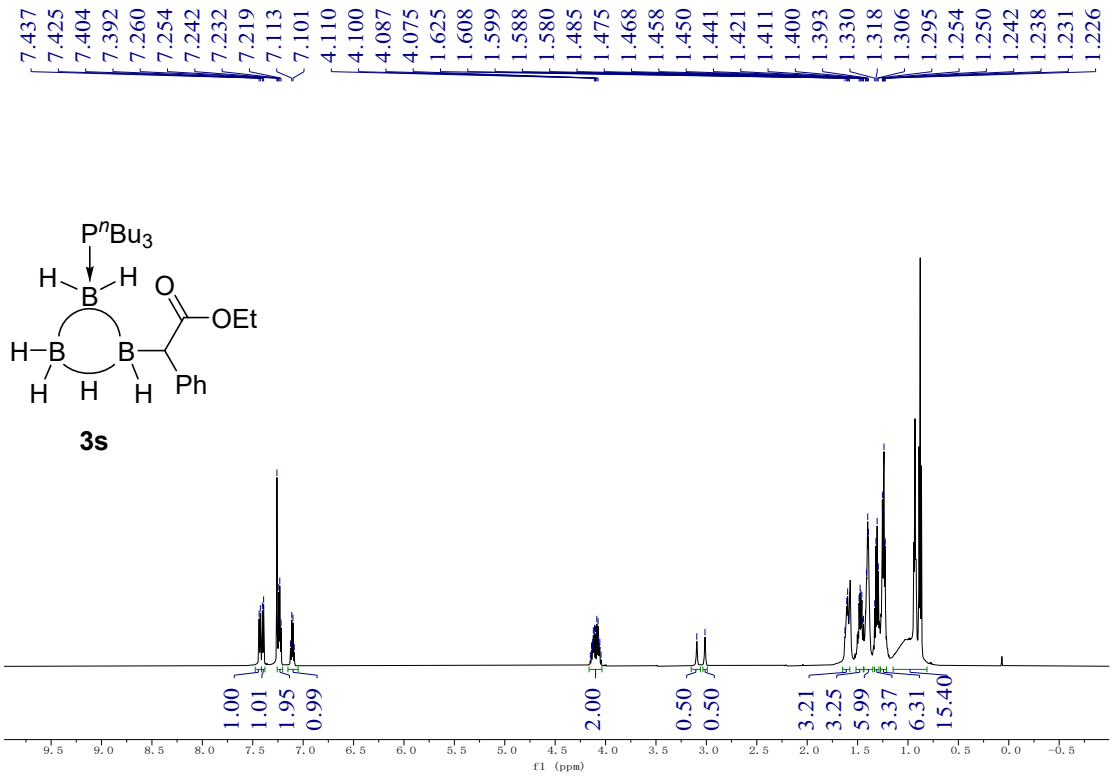

**3r**

**$^{31}$P NMR of 3r**



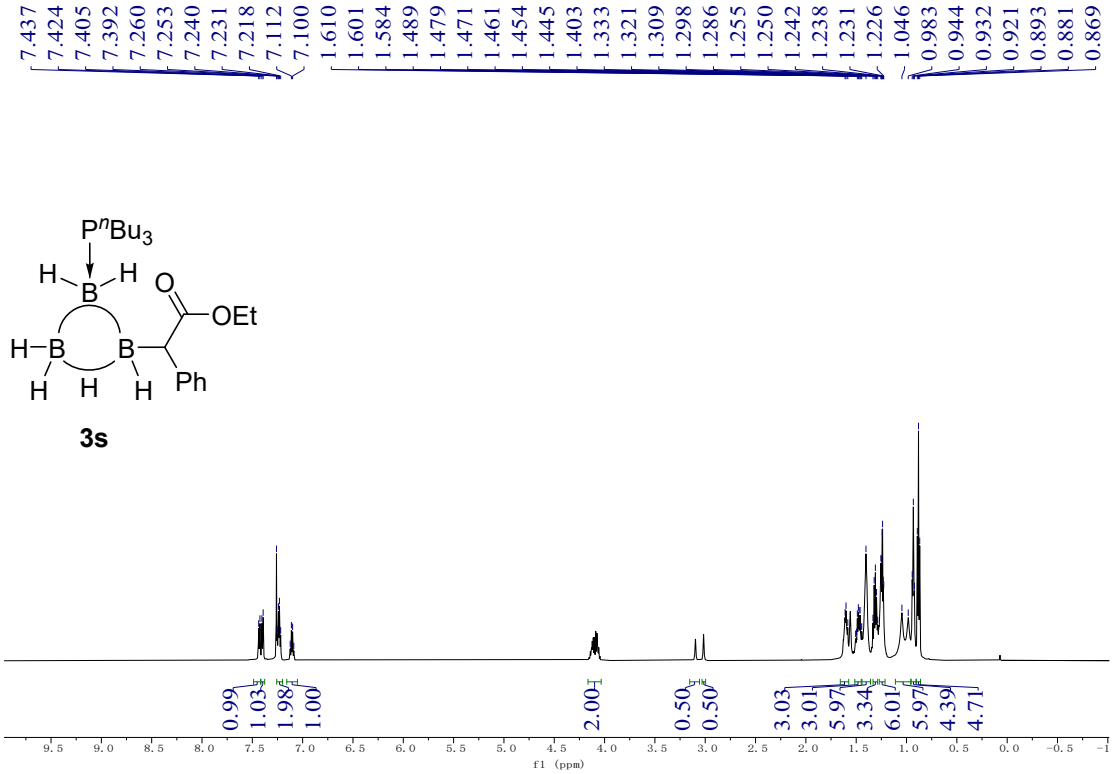

**3r**

**$^{1}$H NMR of 3s**

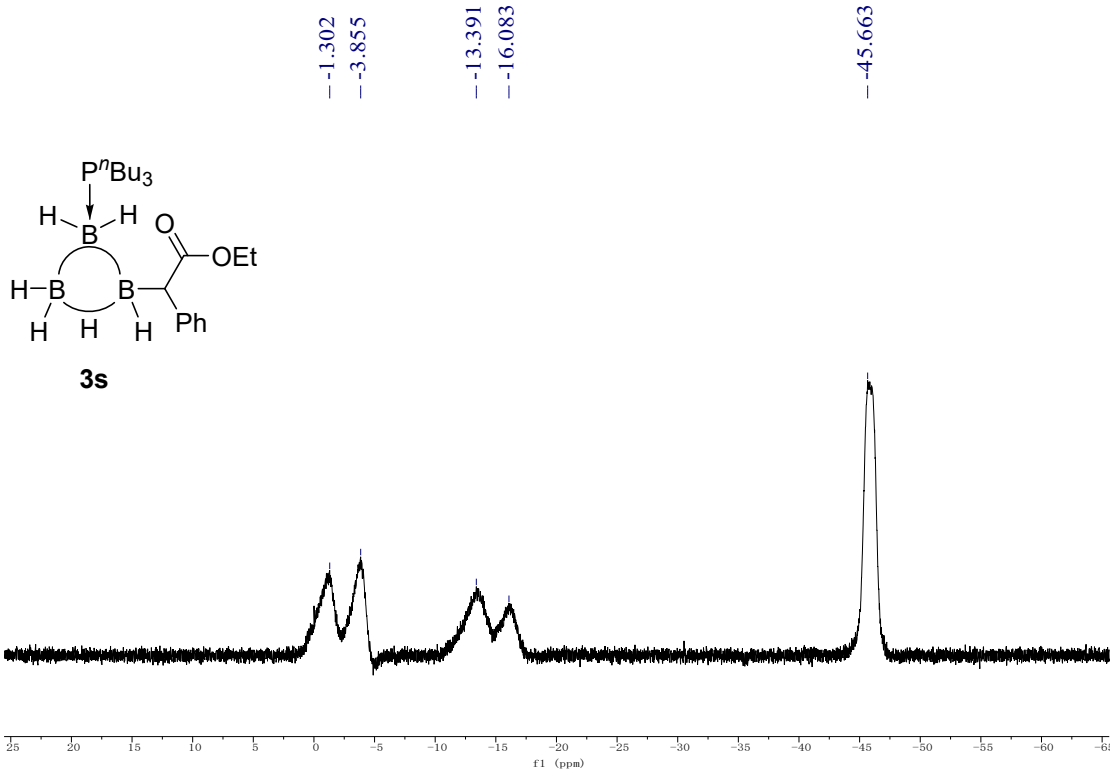



**3s**

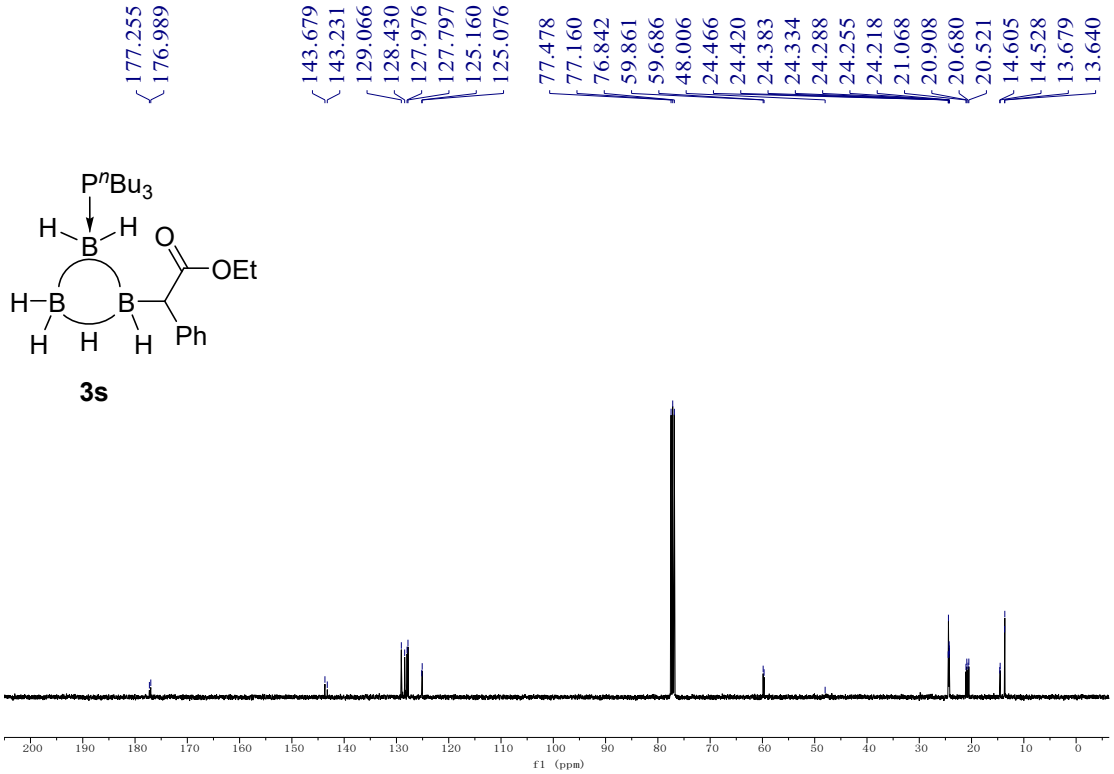
**$^{1}H\{^{11}B\}$ NMR of 3s**




**$^{11}B$ NMR of 3s**

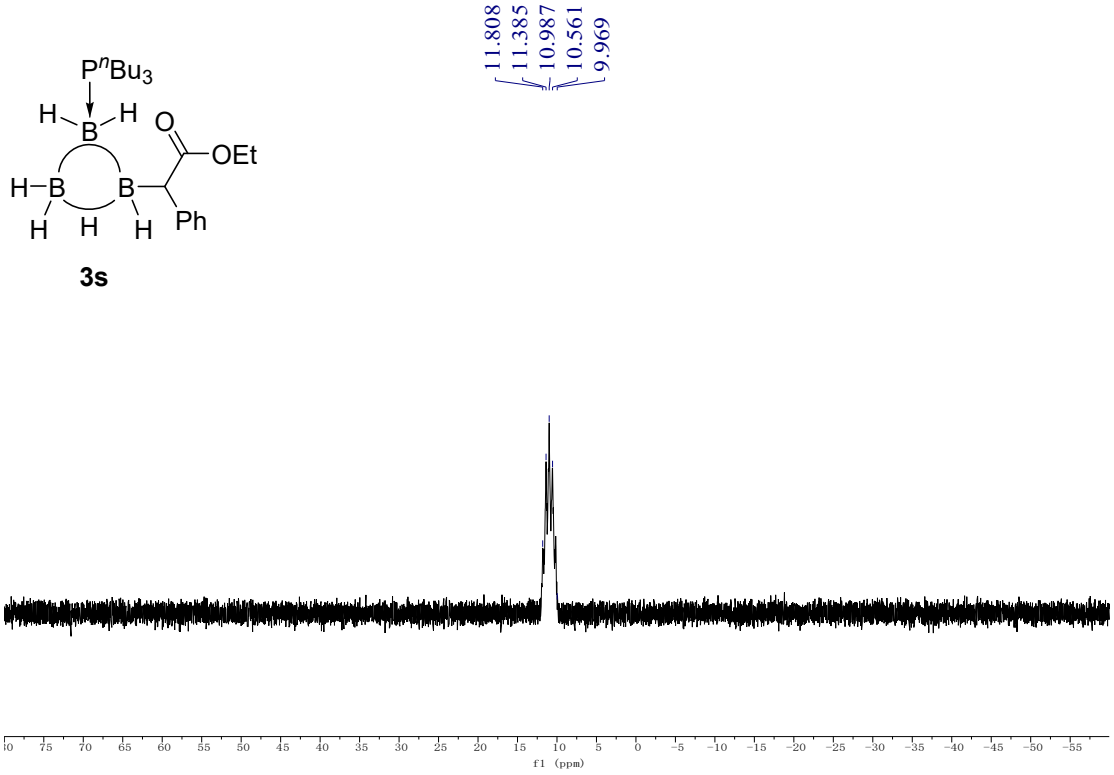


**$^{13}C\{^{1}H\}$ NMR of 3s**



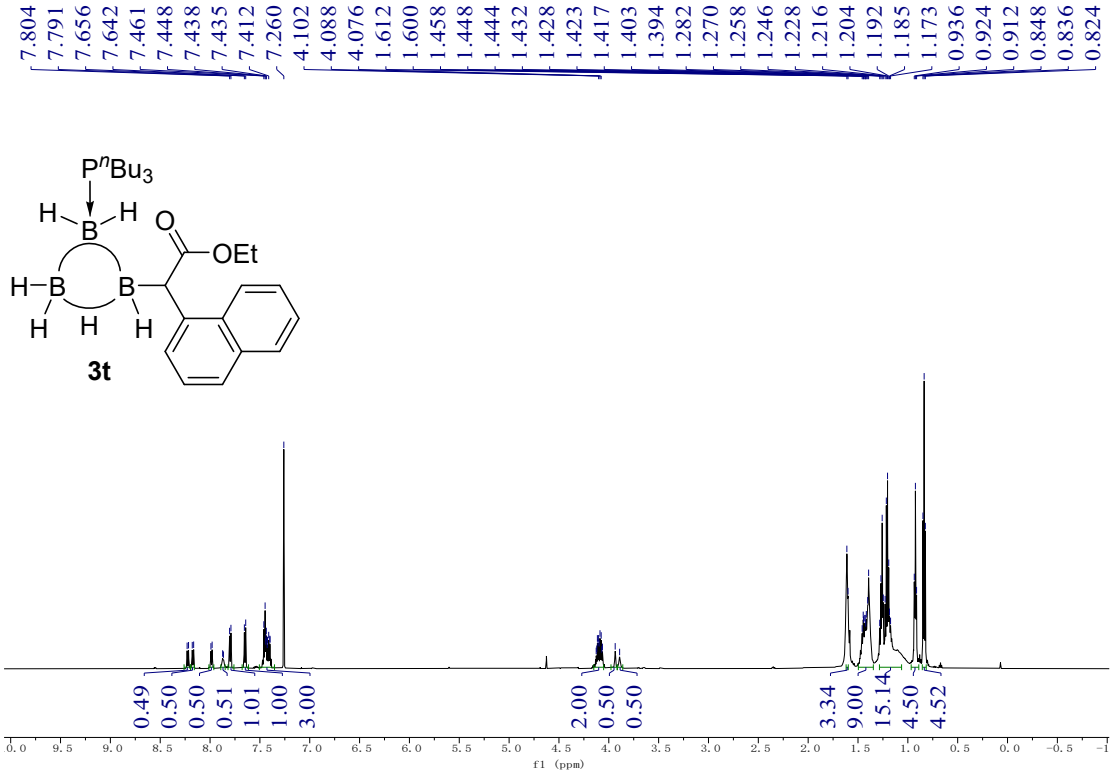

**3s**

**$^{31}P$ NMR of 3s**

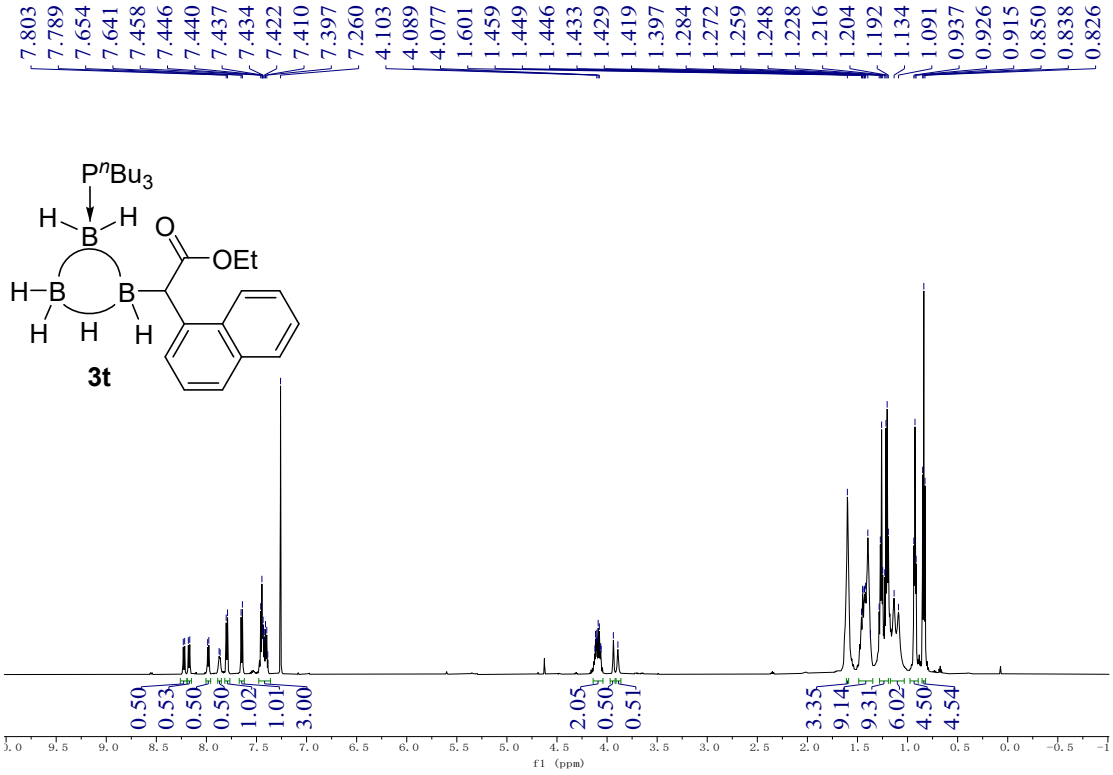



**3s**

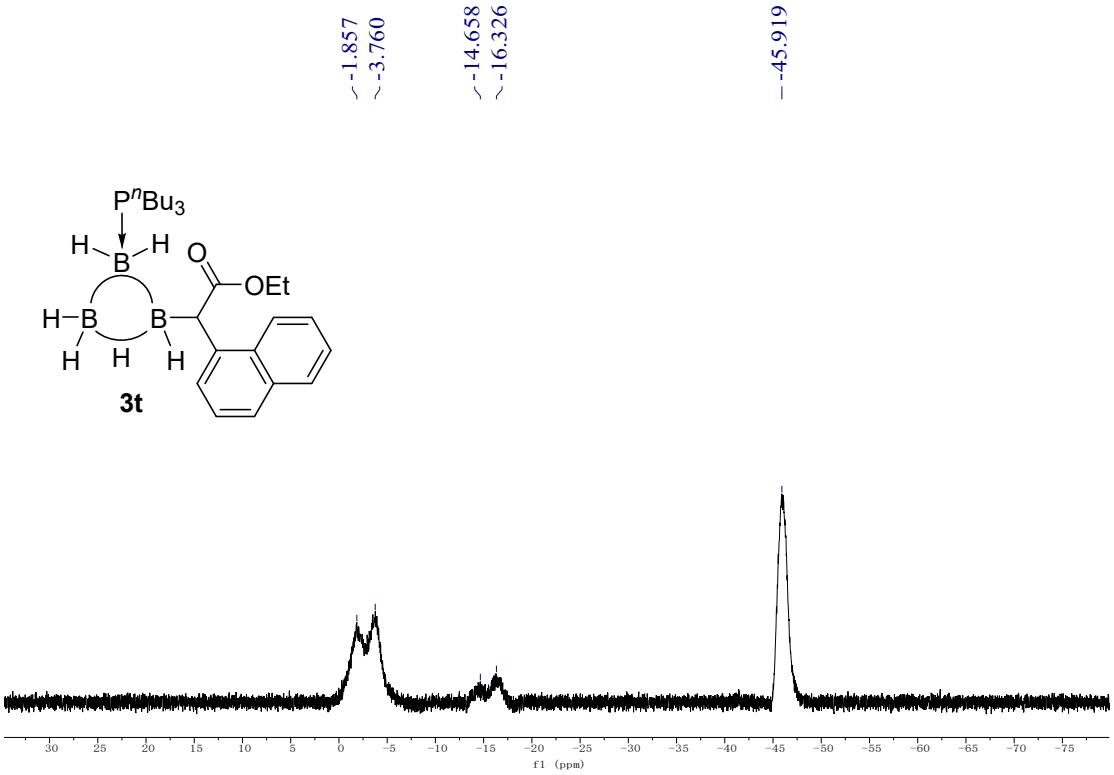
**$^{1}$H NMR of 3t**



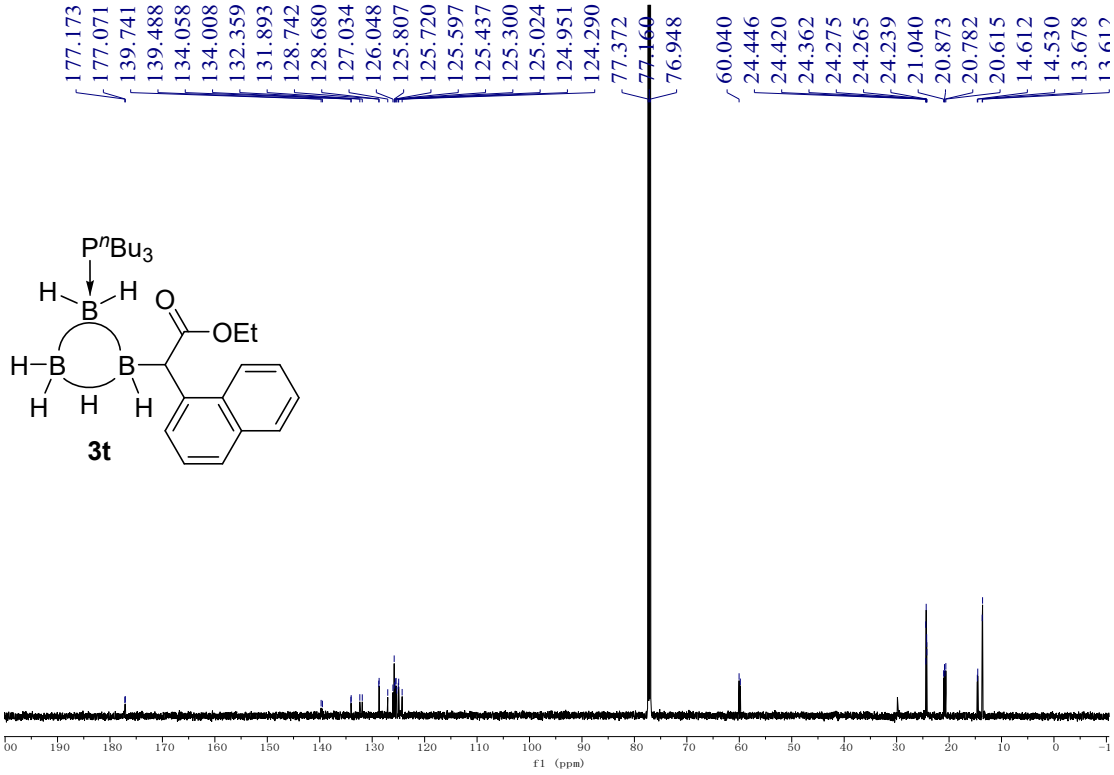

**$^{1}$H{$^{11}$B} NMR of 3t**



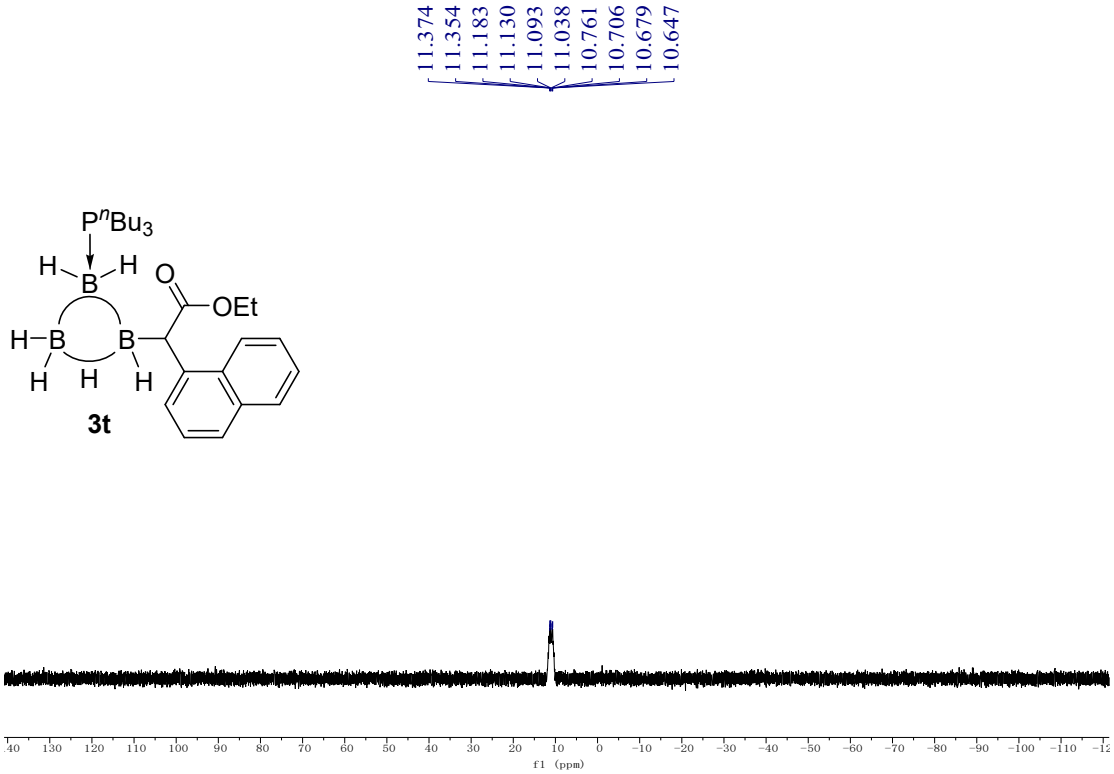
**$^{11}$B NMR of 3t**



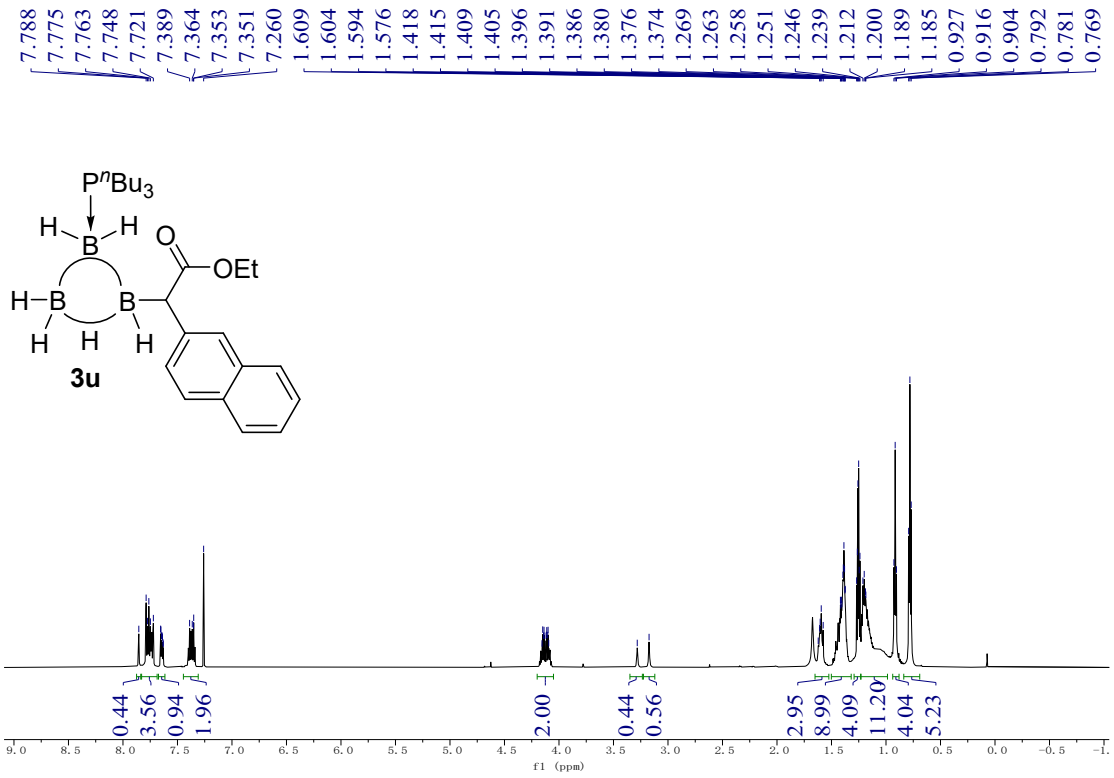

**$^{13}$C{$^1$H} NMR of 3t**



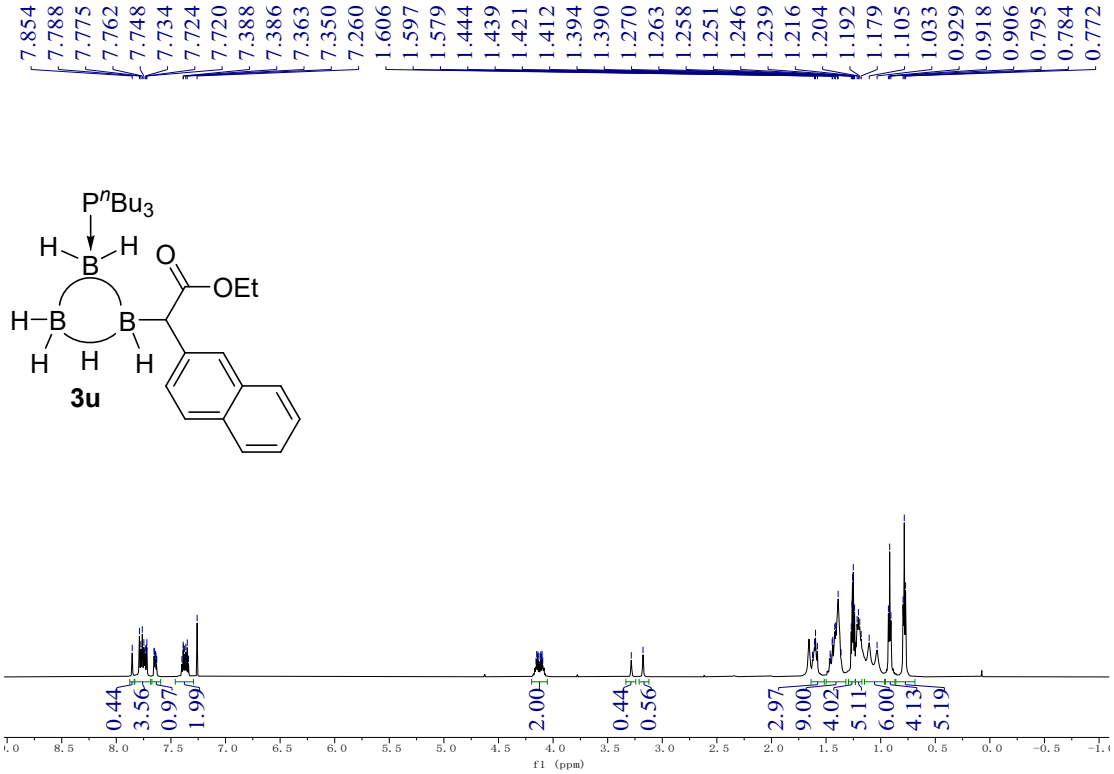
**$^{31}$P NMR of 3t**



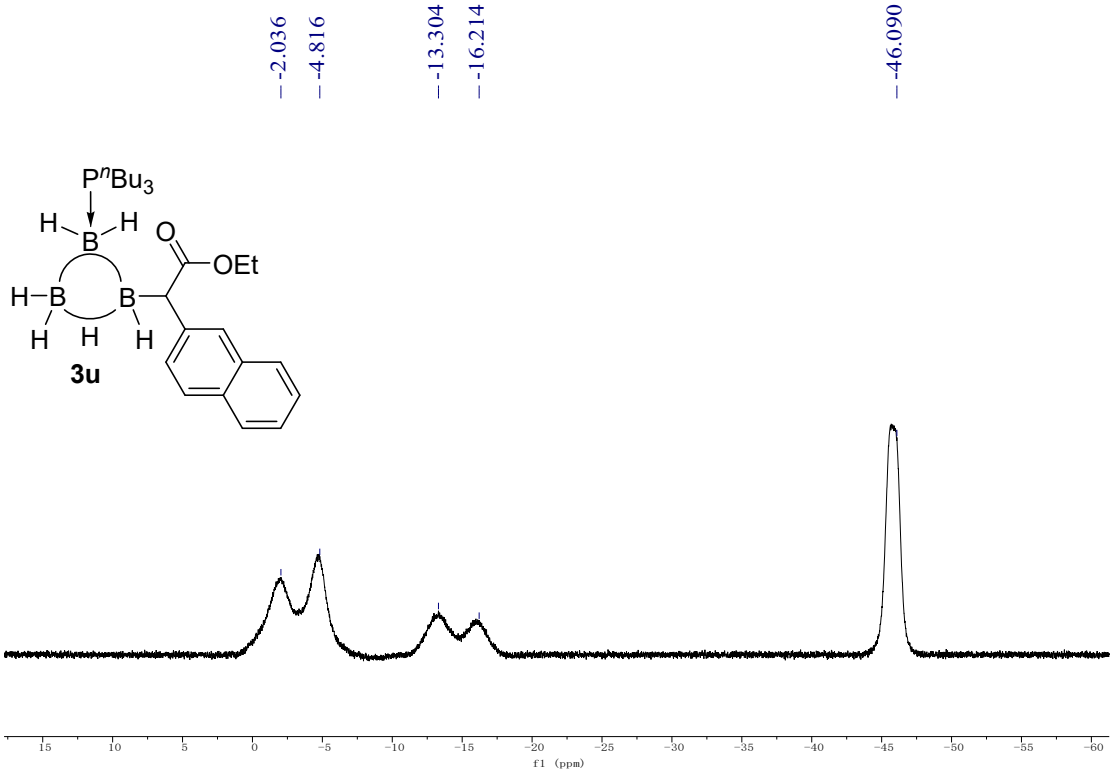

**$^{1}$H NMR of 3u**



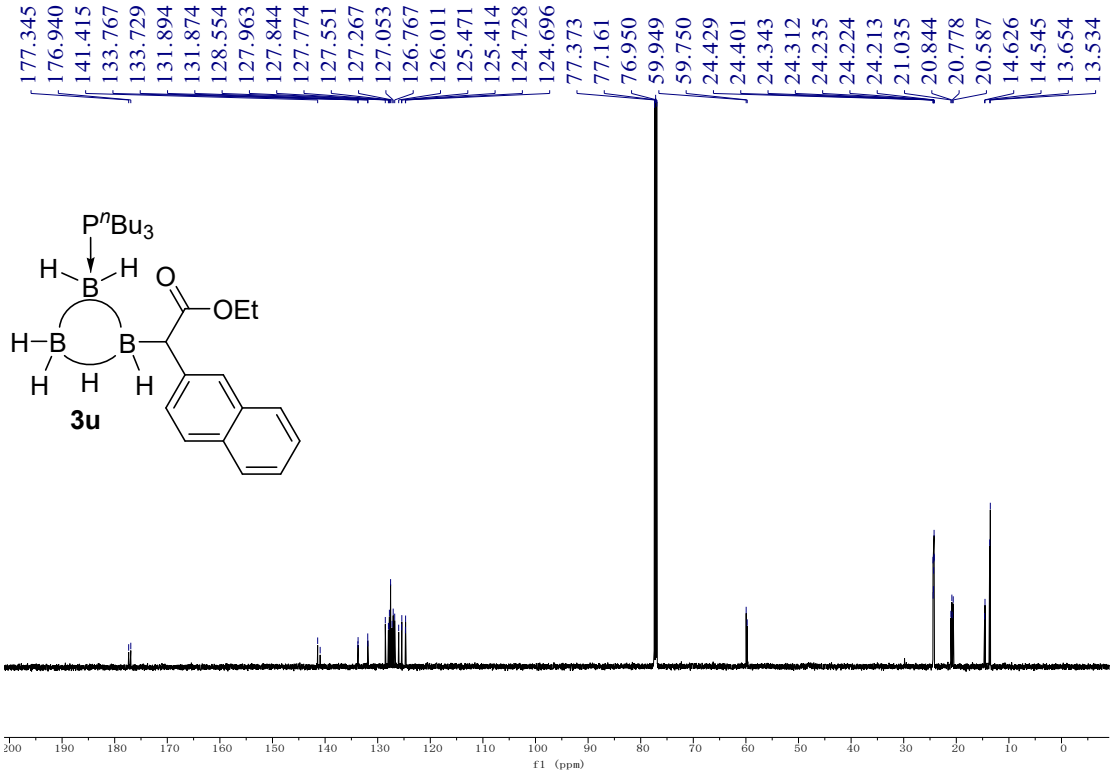
**$^{1}H\{^{11}B\}$ NMR of 3u**



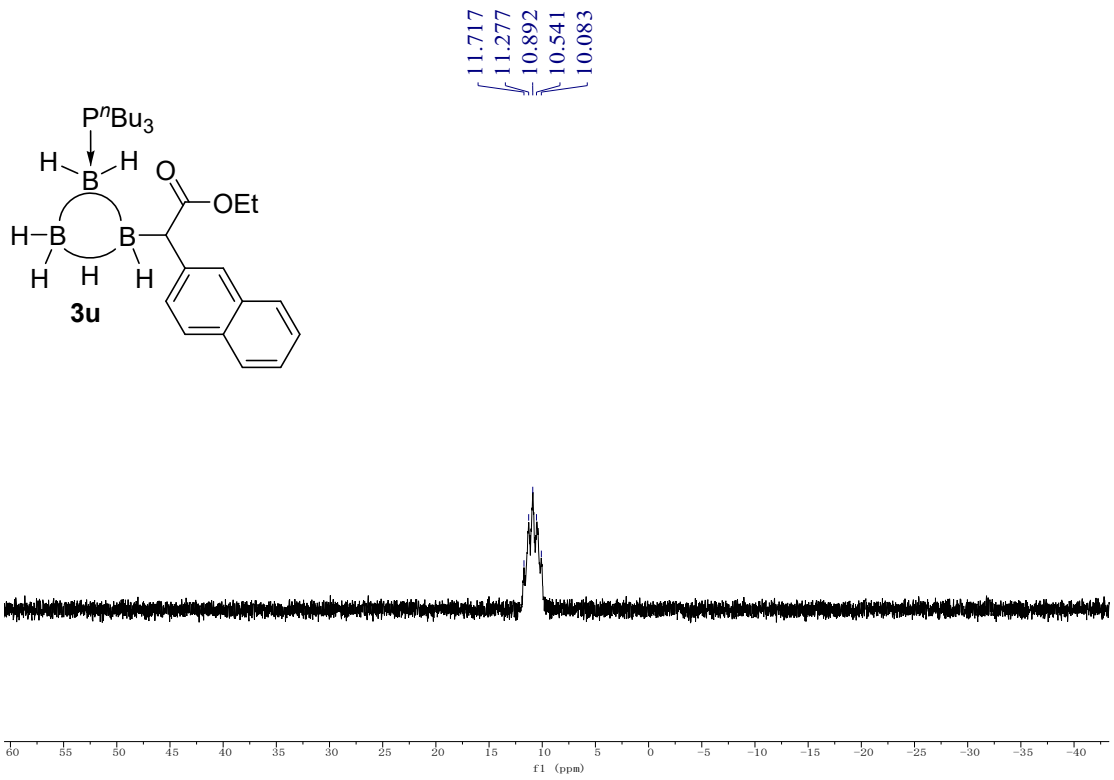

**$^{11}B$ NMR of 3u**



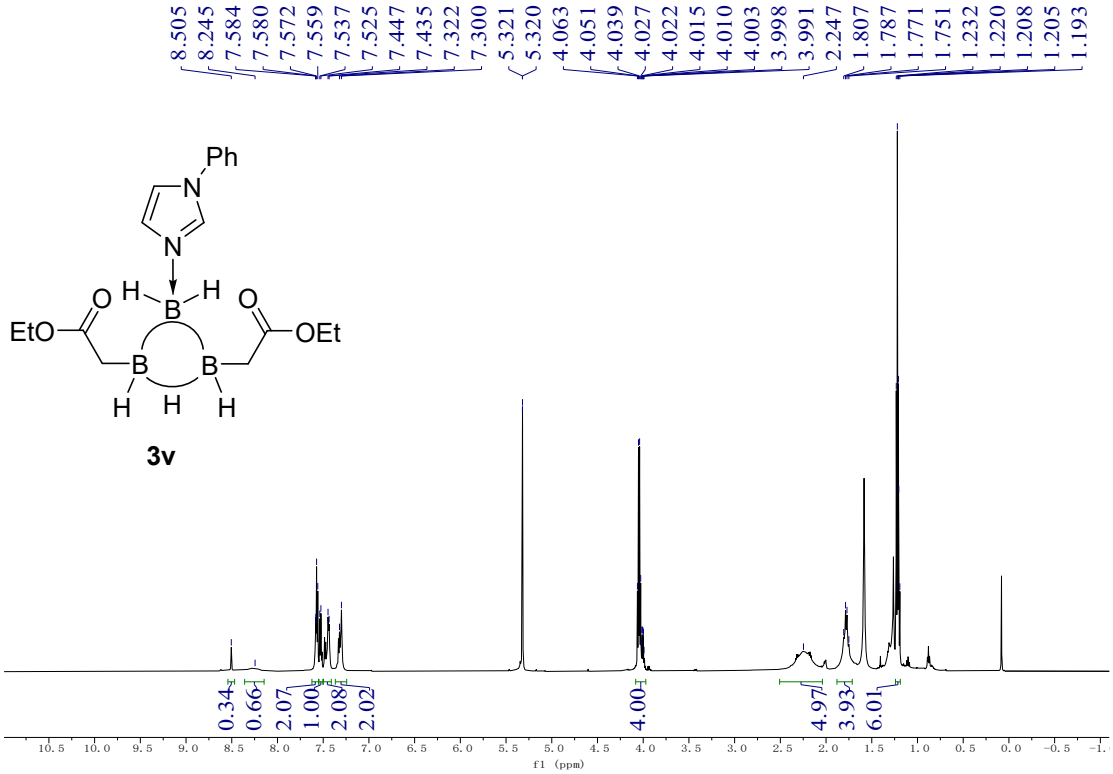
**$^{13}C\{^{1}H\}$ NMR of 3u**



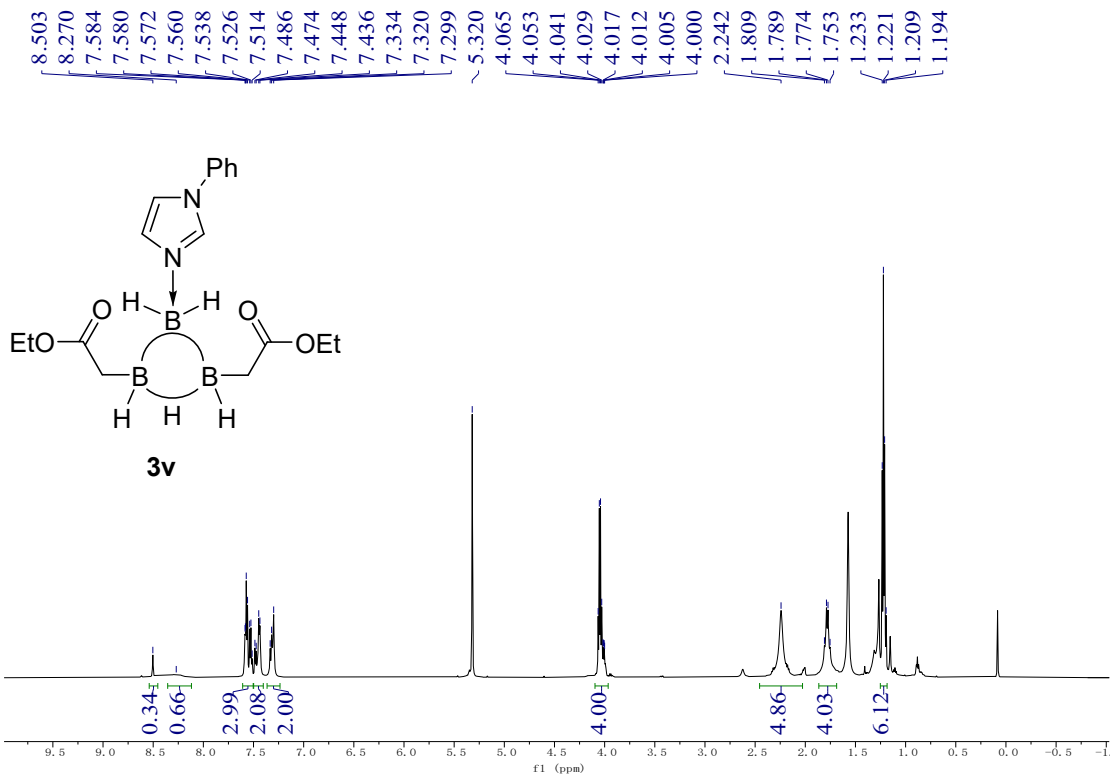

**$^{31}P$ NMR of 3u**



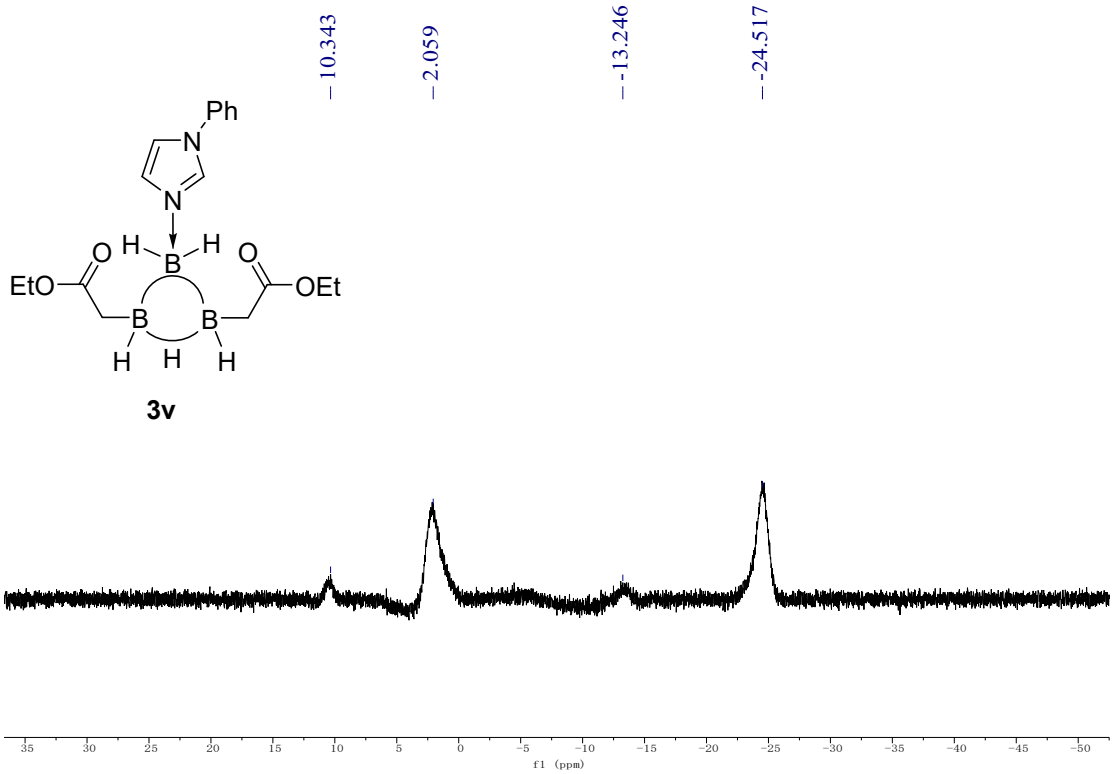
**$^{1}$H NMR of 3v**




**$^{1}$H{$^{11}$B} NMR of 3v**

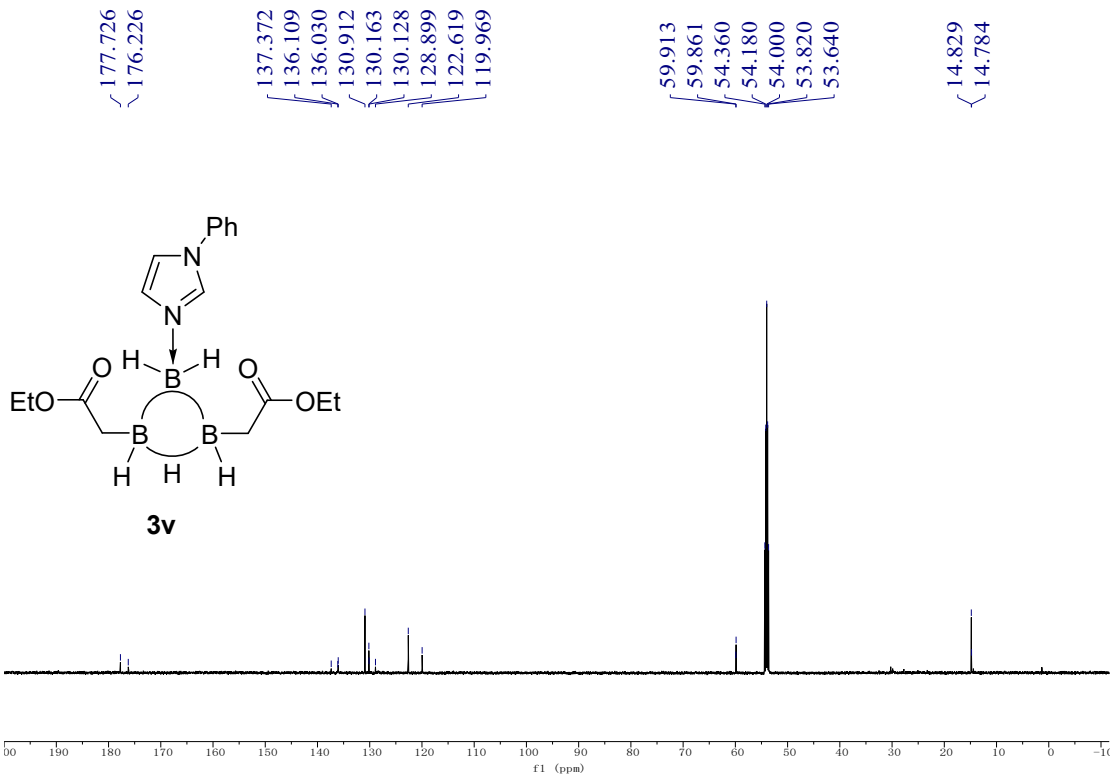


**$^{11}$B NMR of 3v**



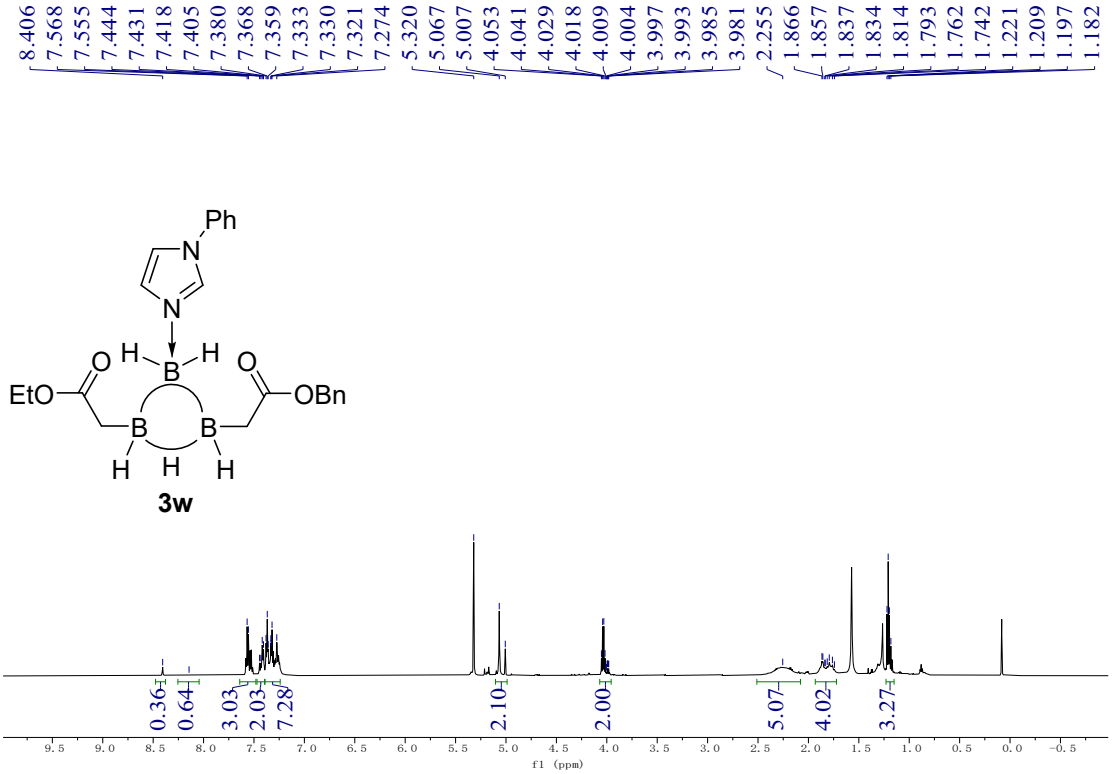

**3v**

**$^{13}$C{$^{1}$H} NMR of 3v**

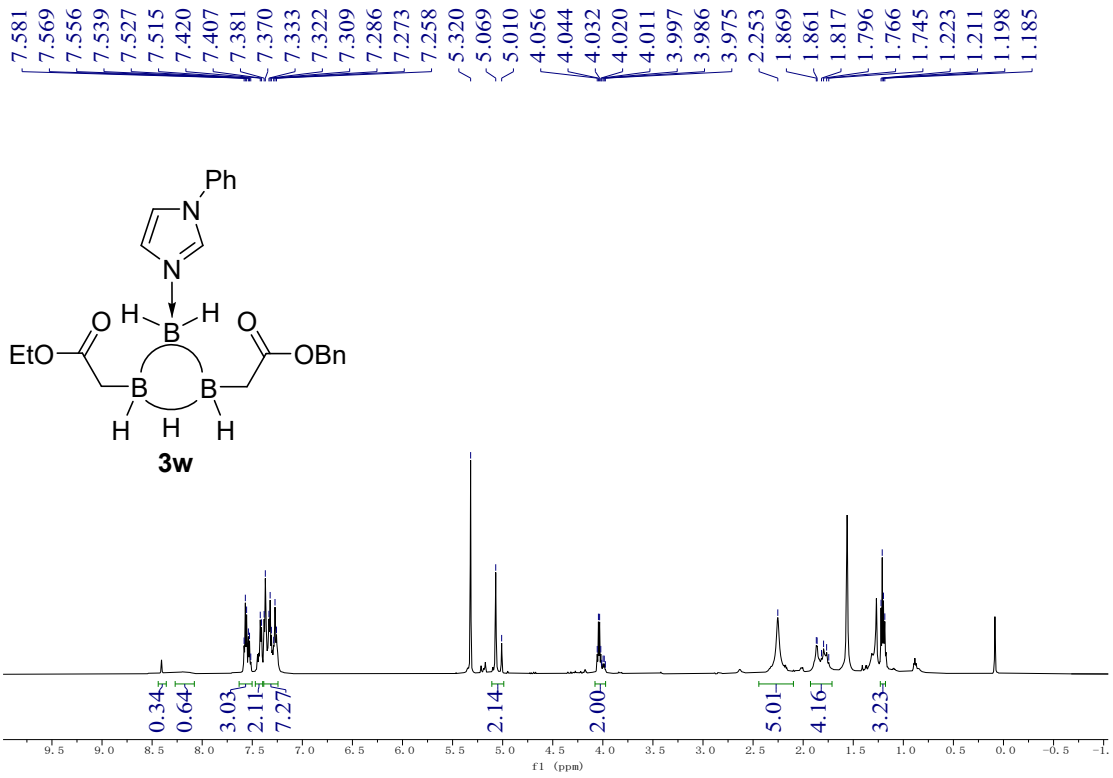



**3v**

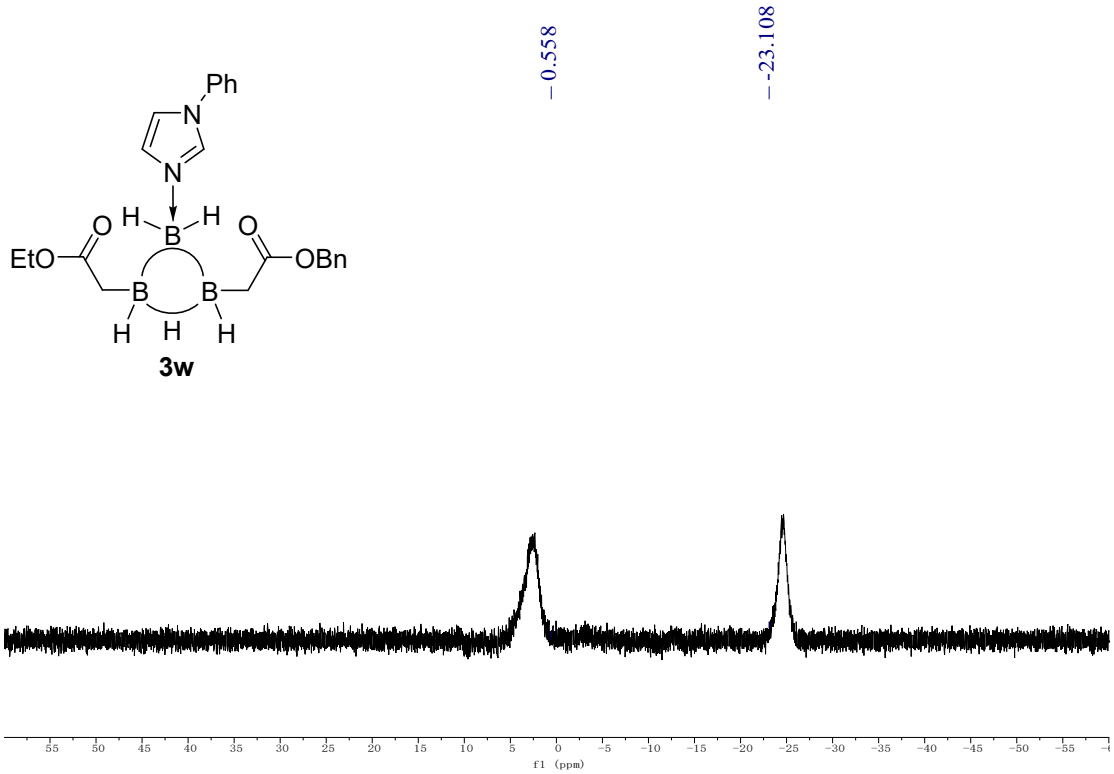
**$^{1}$H NMR of 3w**



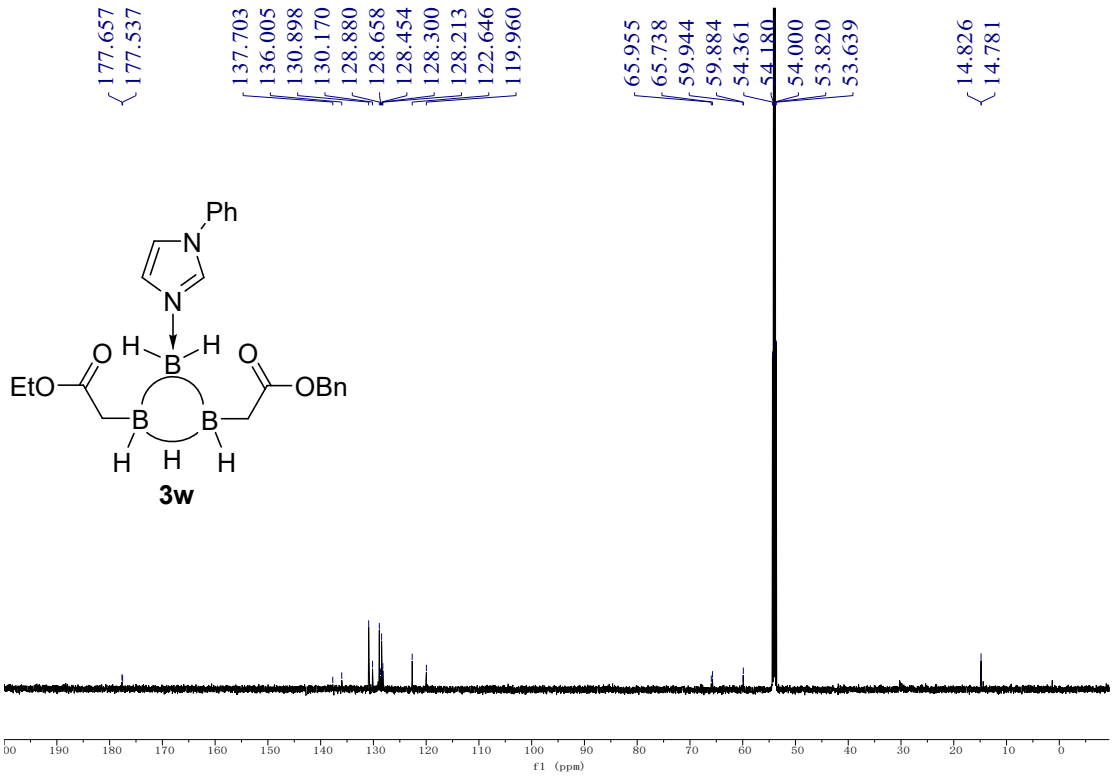

**$^{1}$H{$^{11}$B} NMR of 3w**



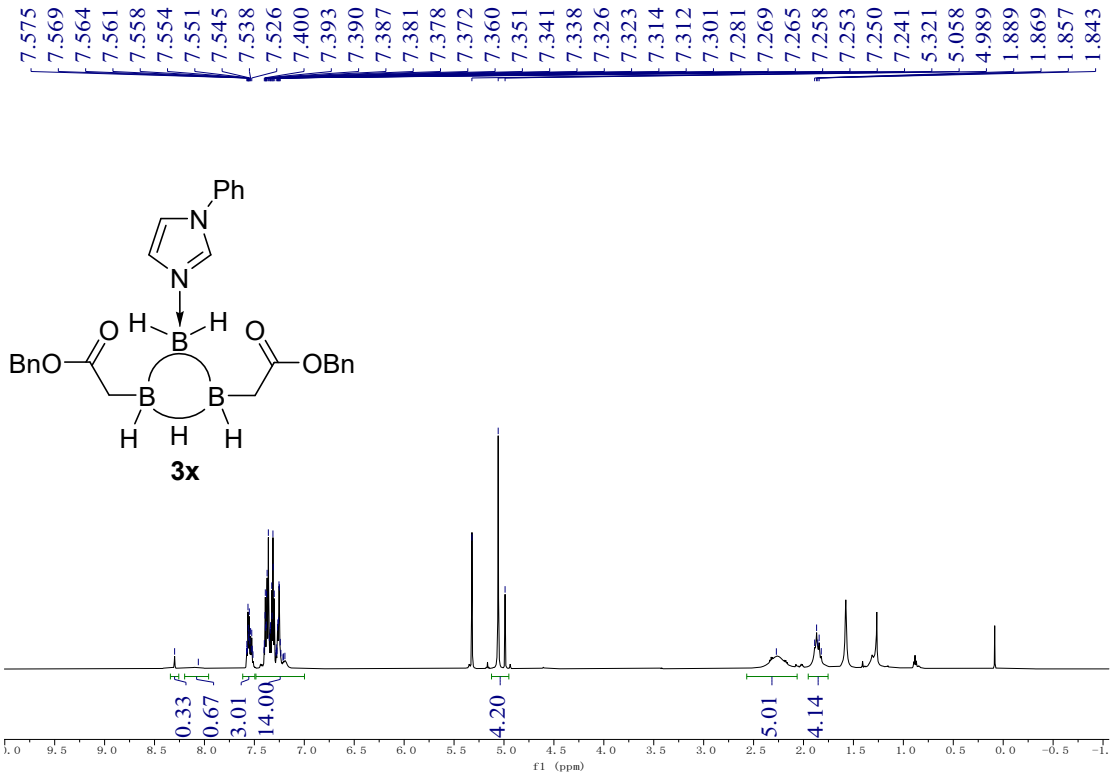
**$^{11}$B NMR of 3w**



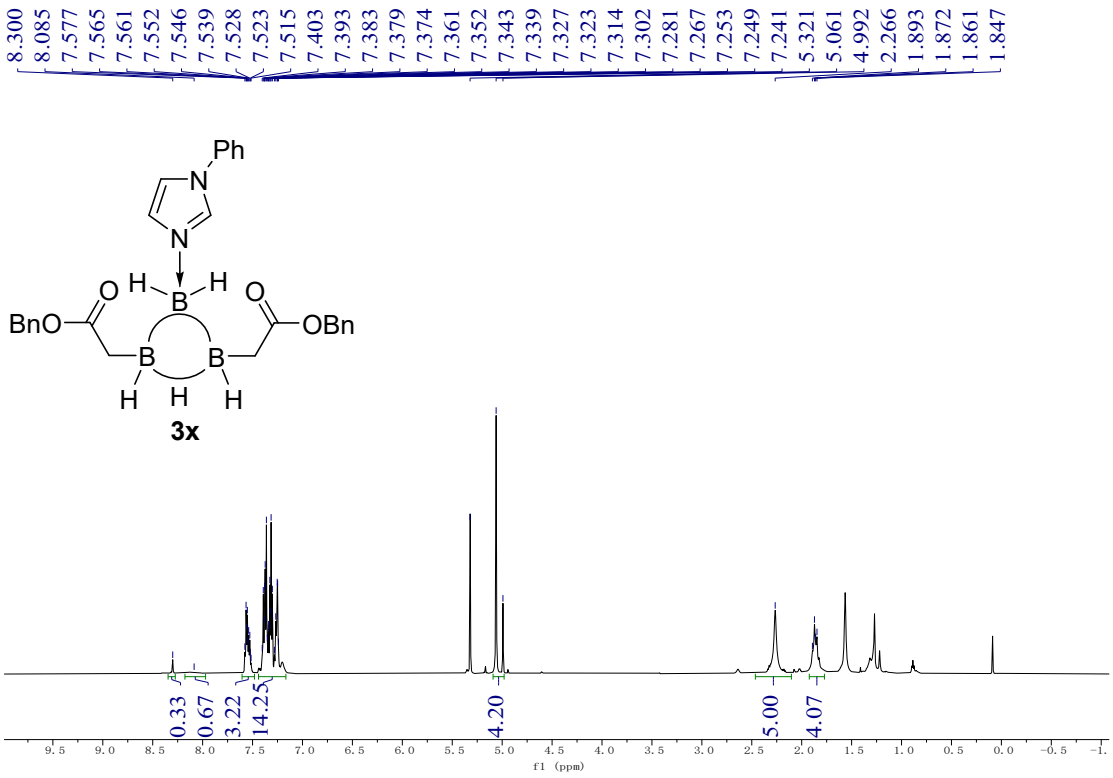

**$^{13}$C{$^{1}$H} NMR of 3w**



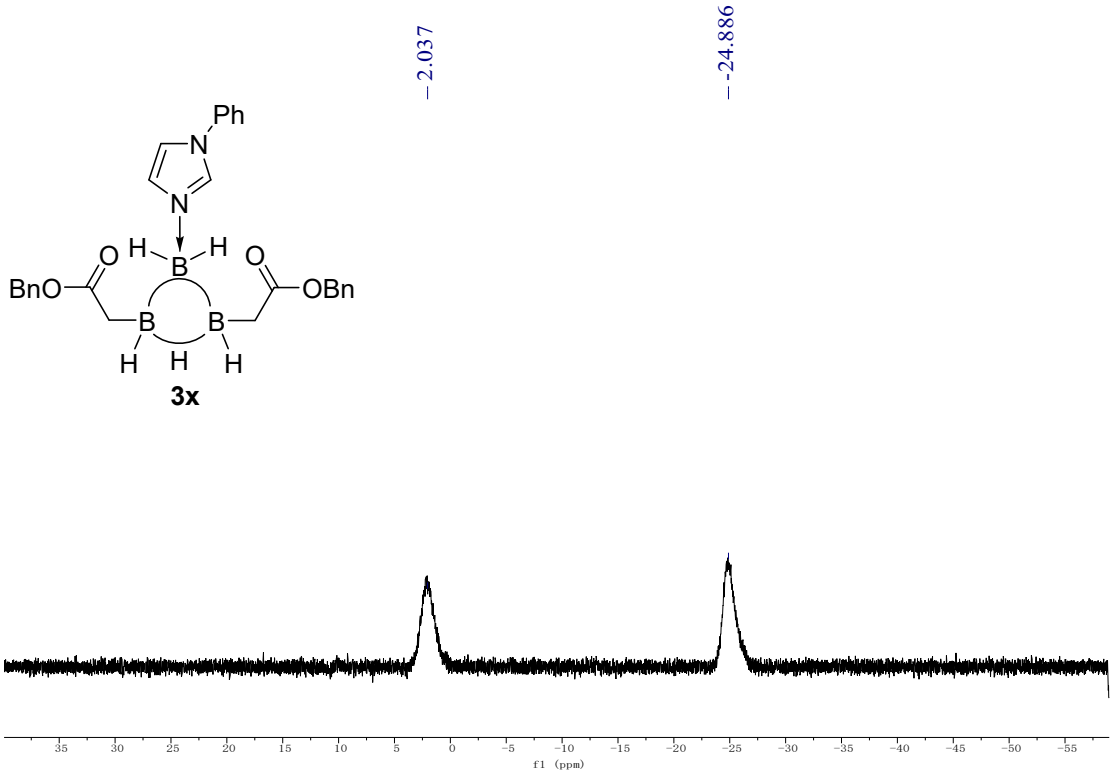
**$^{1}$H NMR of 3x**



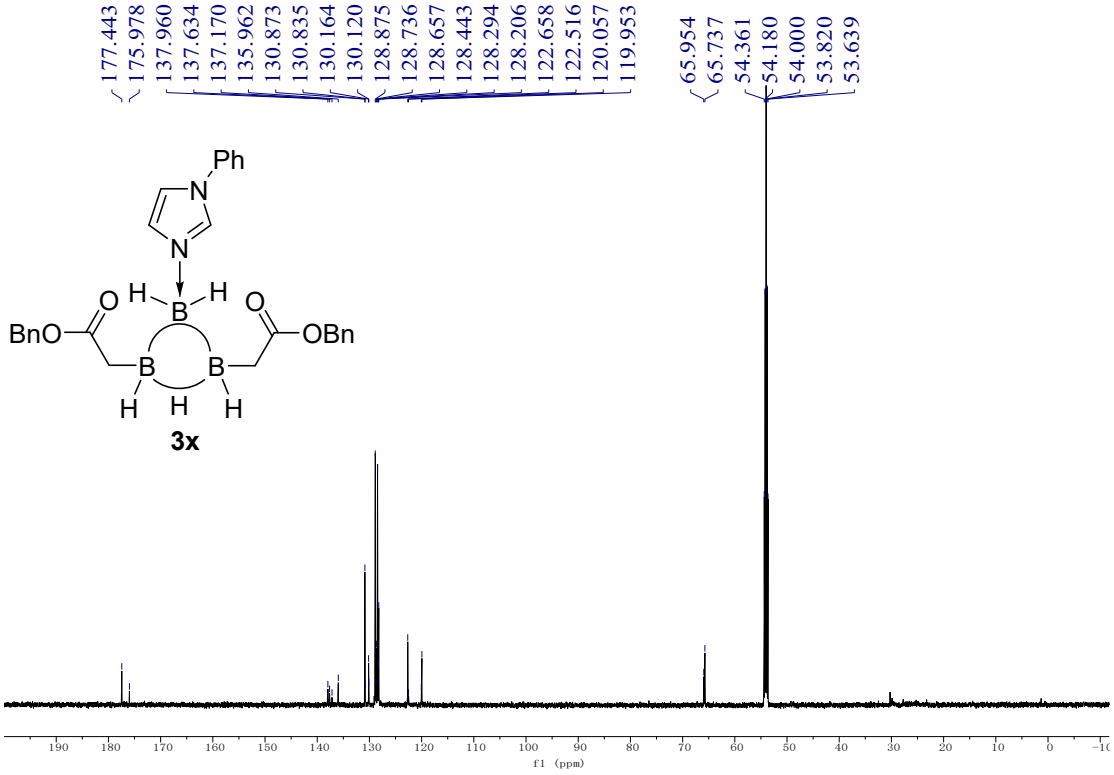

**$^{1}$H{$^{11}$B} NMR of 3x**



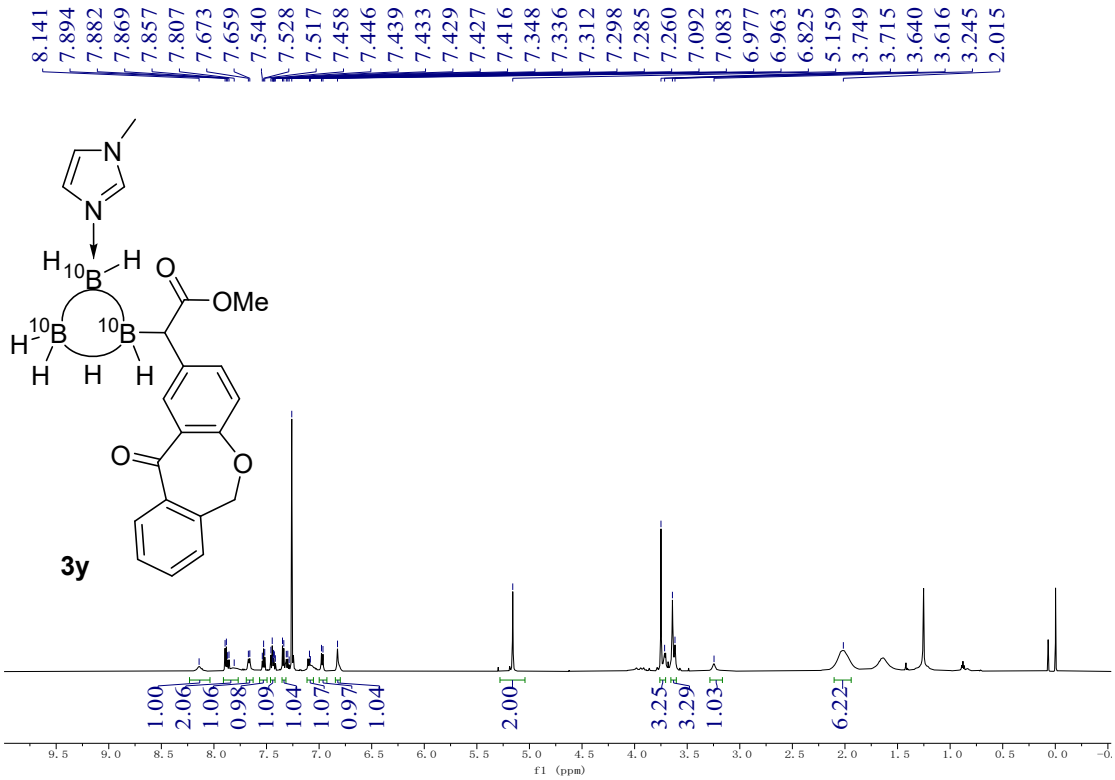
**$^{11}$B NMR of 3x**



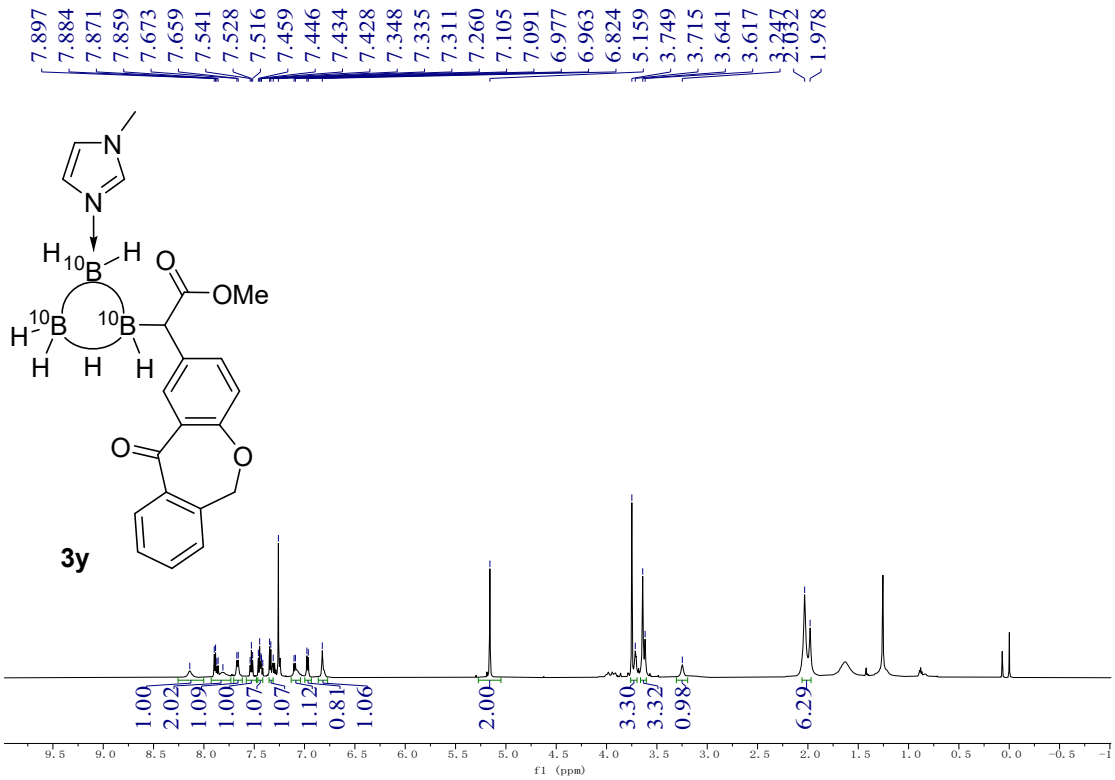

**$^{13}$C{$^{1}$H} NMR of 3x**



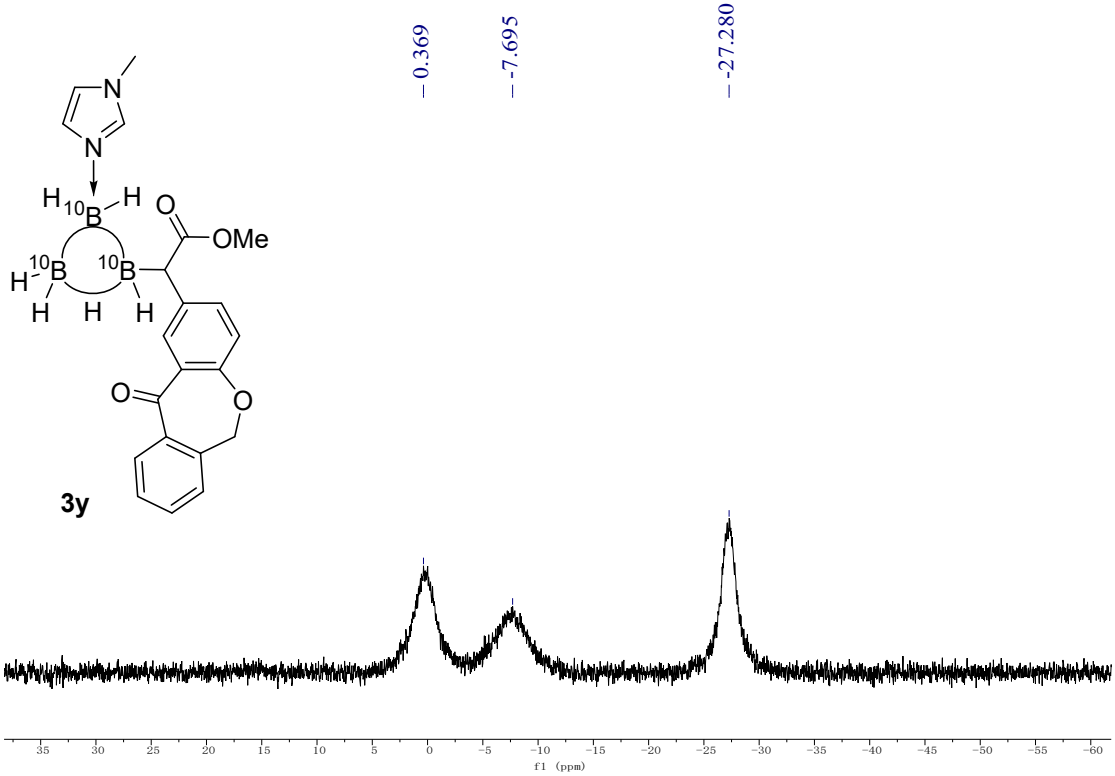
**$^{1}$H NMR of 3y**



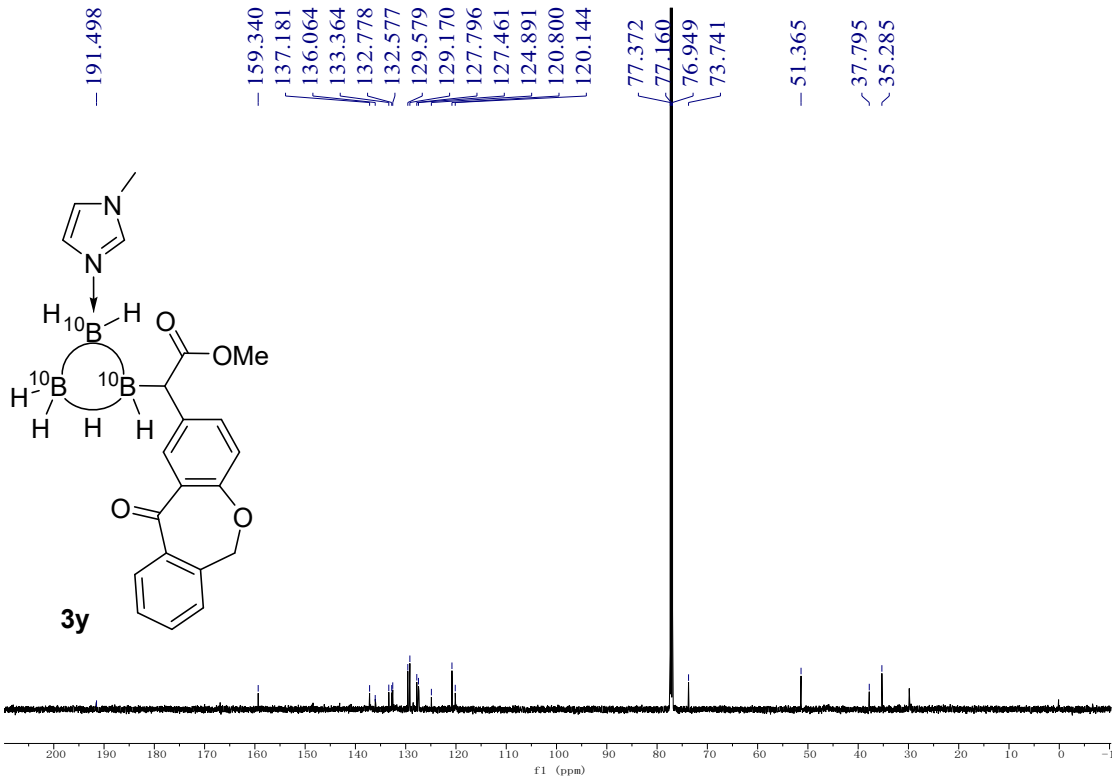

**$^{1}$H{$^{10}$B} NMR of 3y**



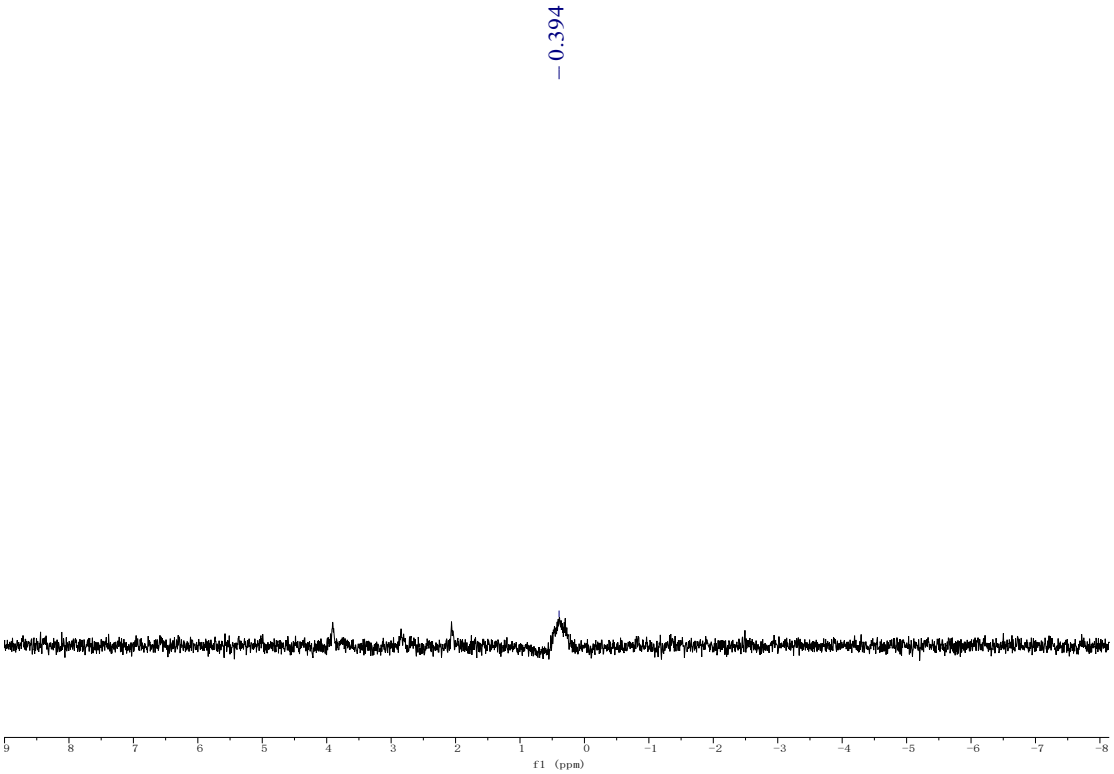
**$^{10}$B NMR of 3y**



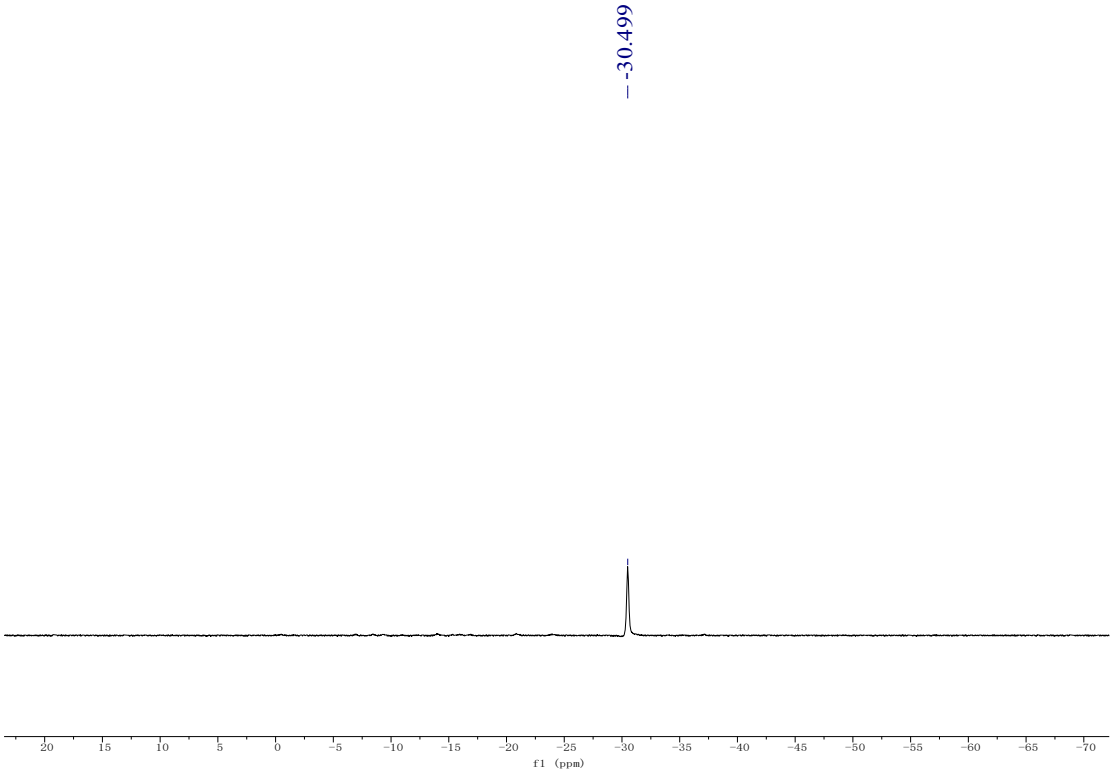

**$^{13}$C{$^{1}$H} NMR of 3y**



**$^{2}$D NMR of $KB_3D_8$**




**$^{11}$B NMR of $KB_3D_8$**



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