

## Supporting Information for

# Selective Multifunctionalization of *N*-Heterocyclic Carbene Boranes via the Intermediacy of Boron-Centered Radical

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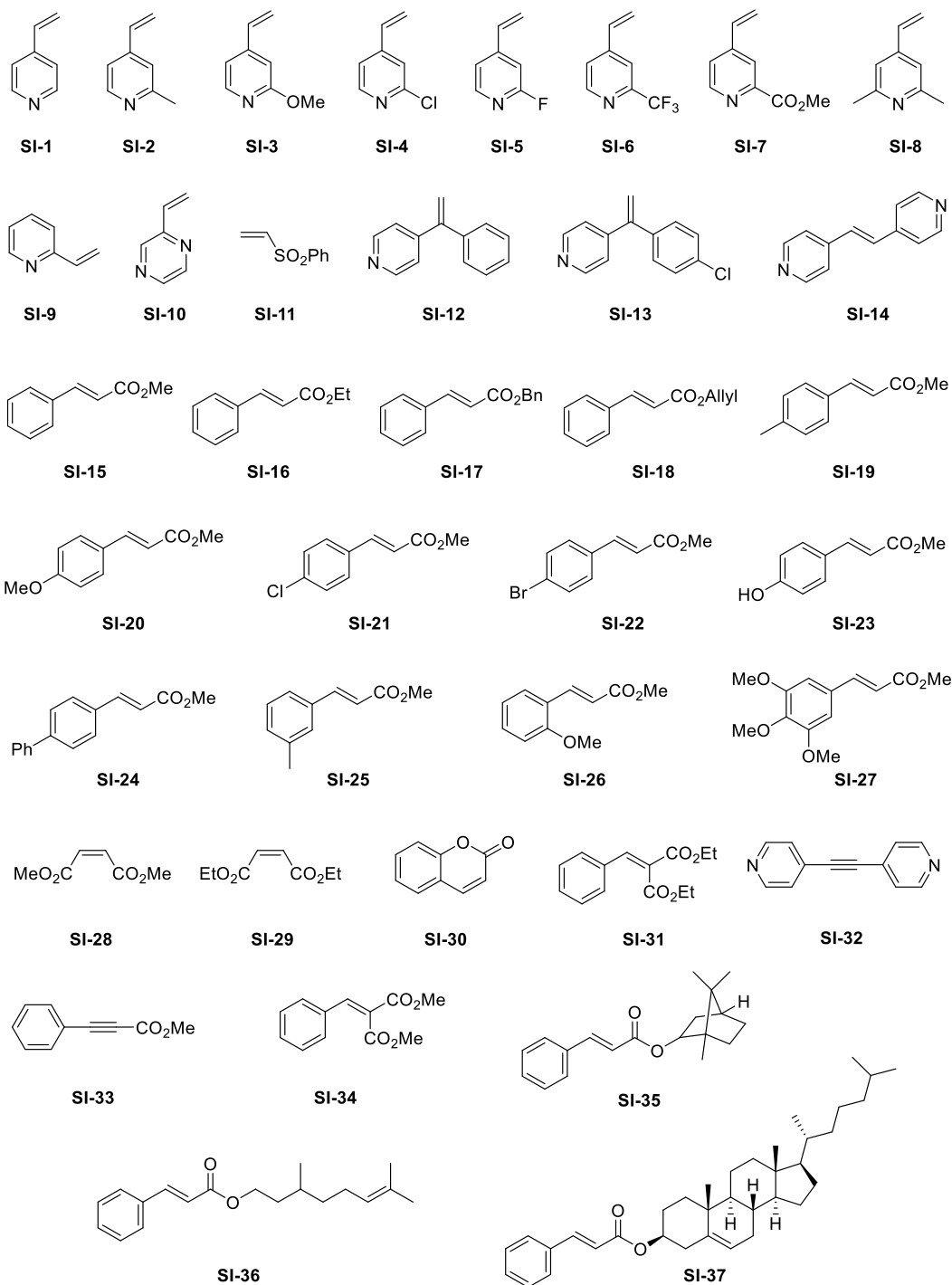
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## 1. Materials and Methods

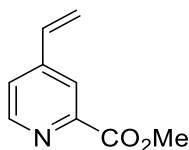
Reactions were performed by using flame-dried glassware in a glove box, unless otherwise indicated. Organic solvents were dried and distilled by standard methods prior to use, extra dry DMA was purchased from Energy<sup>®</sup>. Analytical TLC were performed on Yantai Chemical Industry Research Institute silica gel 60 F254 plates. Flash column chromatography was performed on Qingdao-Haiyang<sup>®</sup> silica gel (200–300 mesh) or Macklin<sup>®</sup> neutral aluminum oxide (200–300 mesh). <sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B and <sup>19</sup>F NMR spectra were recorded on Bruker 400 or JEOL 600 spectrometer at 400/600, 100/150, 128/192 and 376/564 MHz, respectively. Peaks recorded are relative to the internal standards: TMS ( $\delta = 0.00$ ) for <sup>1</sup>H NMR and CDCl<sub>3</sub> ( $\delta = 77.00$ ) for <sup>13</sup>C NMR spectra, and to external BF<sub>3</sub>·OEt<sub>2</sub> ( $\delta = 0.00$ ) for <sup>11</sup>B NMR spectra. For the <sup>1</sup>H & <sup>13</sup>C NMR spectral data, the protons and carbons on boron are not listed due to quadrupole broadening and spin-spin coupling with boron. High resolution mass spectra (HRMS) were obtained on a Waters Xevo G2-XS ToF mass spectrometer. Kessil PR160-390 (370-420 nm) LED was used. Commercially available reagents were used without further purification.

## 2. Preparation of Starting Materials

NHC-boranes used in this research were prepared according to the literature method.<sup>1</sup> Electron-deficient vinylpyridines **SI-2**~**SI-8** were prepared according to the reported procedure.<sup>2</sup> **SI-12**~**SI-13**,<sup>3</sup> **SI-24**~**SI-26**,<sup>4</sup> **SI-34**,<sup>5</sup> **SI-35**,<sup>6</sup> **SI-36**~**SI-37**<sup>7</sup> were known compounds and prepared according to the literature procedures. Substrates **SI-1**, **SI-9**~**SI-11**, **SI-14**~**SI-23**, **SI-27**~**SI-33** were purchased and used directly without additional purification.

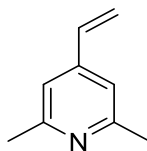


### Methyl 4-vinylpicolinate (SI-7)



Following the reported procedure,<sup>2</sup> **SI-7** was obtained as a colorless oil (132 mg, 54%) from the reaction of methyl 4-bromopyridine-2-carboxylate (324 mg, 1.5 mmol) and DVDS (350  $\mu$ L, 1.5 mmol). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.67 (d,  $J$  = 5.0 Hz, 1H), 8.13 (s, 1H), 7.42 (dd,  $J$  = 5.0 Hz, 1.6 Hz, 1H), 6.71 (dd,  $J$  = 17.6 Hz, 10.9 Hz, 1H), 6.06 (d,  $J$  = 17.6 Hz, 1H), 5.57 (d,  $J$  = 10.9 Hz, 1H), 4.01 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  165.7, 150.1, 148.3, 146.1, 133.9, 123.8, 122.1, 120.0, 52.9; HRMS (ESI):  $m/z$  calcd for C<sub>9</sub>H<sub>9</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup> 186.0531, found 186.0521.

### 2,6-Dimethyl-4-vinylpyridine (SI-8)

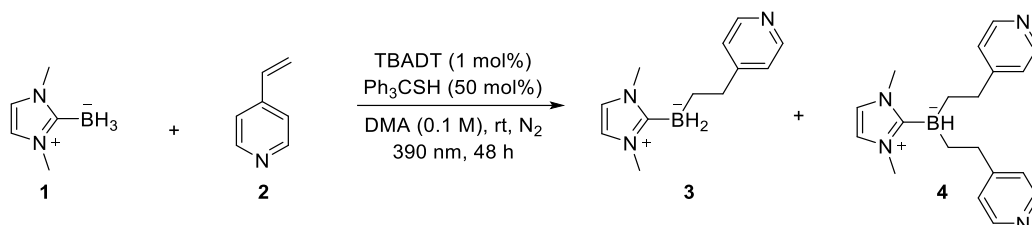


Following the reported procedure,<sup>2</sup> **SI-8** was obtained as a colorless oil (146 mg, 73%) from the reaction of 4-bromo-2,6-dimethylpyridine (279 mg, 1.5 mmol) and DVDS (350  $\mu$ L, 1.5 mmol). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  6.92 (s, 2H), 6.59–6.54 (m, 1H), 5.89 (d,  $J$  = 17.6 Hz, 1H), 5.39 (d,  $J$  = 10.9 Hz, 1H), 2.49 (s, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  157.9, 145.2, 135.0, 117.8, 117.3, 24.2; HRMS (ESI):  $m/z$  calcd for C<sub>9</sub>H<sub>12</sub>N [M+H]<sup>+</sup> 134.0970, found 134.0967.



### 3. Complementary Reaction Optimization

**Table S1.** Optimization of the reaction conditions.<sup>a</sup>



entry	Variation from the standard conditions A	Yield [%] ( <b>3/4</b> ) <sup>b</sup>
1	none	0/61
2	DMF instead of DMA	27/34
3	MeCN instead of DMA	20/28
4	20 mol% of Ph <sub>3</sub> CSH	18/27
5	without Ph <sub>3</sub> CSH	NR
6	without TBADT	0/trace
7	without N <sub>2</sub>	ND
8	no light irradiation	NR
9	Wang's reaction conditions <sup>c</sup>	NR
10	An's reaction conditions <sup>d</sup>	trace/0
11	Dai's reaction conditions <sup>e</sup>	11/48
12	Zhu's reaction conditions <sup>f</sup>	trace/0
13	standard conditions B <sup>g</sup> instead of A	52/trace
Variation from the standard conditions B		
14	1 eq <b>1</b> was used	42/trace <sup>h</sup>
15	2 eq <b>1</b> was used	45/trace

<sup>a</sup>Standard conditions A: **1** (0.1 mmol), **2** (0.3 mmol), TBADT (1 mol%), Ph<sub>3</sub>CSH (50 mmol%), DMA (1 mL), N<sub>2</sub>, rt, 390 nm, 48 h.

<sup>b</sup>The resultant mixture was first subjected to <sup>11</sup>B NMR analysis, then flash column chromatography was carried out to give the isolated yields of the corresponding products.

<sup>c</sup>Wang's reaction conditions: AIBN (20 mol%), PhSH (20 mol%), MeCN (1 mL), 80 °C, 24 h.<sup>8</sup>

<sup>d</sup>An's reaction conditions: PhSSPh (10 mol%), MeCN (1 mL), blue LEDs, 24 h, rt.<sup>9</sup>

<sup>e</sup>Dai's reaction conditions: 4-DPAIPN (10 mol%), MeCN (1 mL), blue LEDs, 48 h, rt.<sup>10</sup>

<sup>f</sup>Zhu's reaction conditions: Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (1 mol%), <sup>t</sup>BuSH (20 mol%), NaH (20 mol%), MeCN (1 mL), 12 W CFL bulb, 48 h, rt.<sup>11</sup>

<sup>g</sup>Standard conditions B: **1** (0.15 mmol), **2** (0.1 mmol), TBADT (1 mol%), Ph<sub>3</sub>CSH (20 mol%), DMA (1 mL), N<sub>2</sub>, rt, 390 nm, 48 h.

<sup>h</sup>About 40% of **1** remained unreacted.

## 4. Analytical Data of the Products

### General Procedure A

In a glovebox, a 10 mL seal tube equipped with a magnetic stir bar was added NHC borane (11.0 mg, 0.1 mmol), 4-vinylpyridine (32  $\mu$ L, 0.3 mmol), TBADT (3.3 mg, 0.001 mmol), Ph<sub>3</sub>CSH (13.8 mg, 0.05 mmol) and extra dry DMA (1 mL). The resulting mixture was then taken out of the glove box and stirred under irradiation of 390 nm LED (75 W) for 48 h at room temperature. The reaction was first subjected to <sup>11</sup>B NMR analysis, then quenched with water, and extracted with ethyl acetate. The combined organic layer was washed with water and brine, dried over MgSO<sub>4</sub>, filtered, and concentrated. The crude residue was purified by flash column chromatography to give the desired di-substituted product **4** (19.6 mg, 61%).

### General Procedure B

In a glovebox, a 10 mL seal tube equipped with a magnetic stir bar was added NHC borane (16.5 mg, 0.15 mmol), 4-vinylpyridine (11  $\mu$ L, 0.1 mmol), TBADT (3.3 mg, 0.001 mmol), Ph<sub>3</sub>CSH (5.5 mg, 0.02 mmol) and extra dry DMA (1 mL). The resulting mixture was then taken out of the glove box and stirred under irradiation of 390 nm LED (75 W) for 48 h at room temperature. The reaction was first subjected to <sup>11</sup>B NMR analysis, then quenched with water, and extracted with ethyl acetate. The combined organic layer was washed with water and brine, dried over MgSO<sub>4</sub>, filtered, and concentrated. The crude residue was purified by flash column chromatography to give the desired mono-substituted product **3** (11.0 mg, 52%).

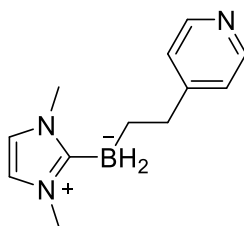
### General Procedure C

In a glovebox, a 10 mL seal tube equipped with a magnetic stir bar was added mono/di-substituted NHC borane (0.1 mmol), electron-deficient alkene (0.2 mmol), TBADT (3.3 mg, 0.001 mmol), Ph<sub>3</sub>CSH (13.8 mg, 0.05 mmol) and extra dry DMA (1 mL). The resulting mixture was then taken out of the glove box and stirred under irradiation of 390 nm LED (75 W) for 48 h at room temperature. The reaction was first subjected to <sup>11</sup>B NMR analysis, then quenched with water, and extracted with ethyl acetate. The combined organic layer was washed with water and brine, dried over MgSO<sub>4</sub>, filtered, and concentrated. The crude residue was purified by flash column chromatography to give the desired

di/tri-substituted product.

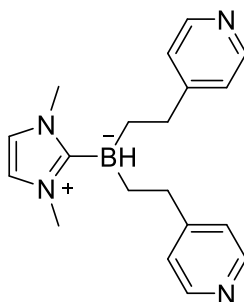
**Note:** Most of the products were purified by flash column chromatography using 200–300 mesh silica gel basified with triethylamine. In some examples (such as **18–19**, **45**, **49–50**, **55**), 200–300 mesh neutral aluminum oxide was used for purification.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(pyridin-4-yl)ethyl)dihydroborate (3)**



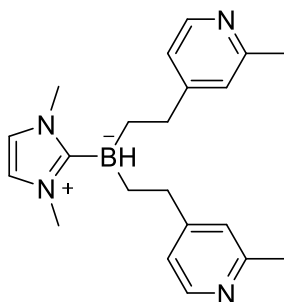
Following the **General Procedure B**, **3** was obtained as a colorless oil (11.0 mg, 52%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.38 (d, *J* = 5.9 Hz, 2H), 7.13 (d, *J* = 5.8 Hz, 2H), 6.79 (s, 2H), 3.76 (s, 6H), 2.55 (t, *J* = 8.2 Hz, 2H), 0.72 (br s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 157.5, 148.7, 123.7, 120.1, 38.1, 35.9; <sup>11</sup>B NMR (192 MHz, CDCl<sub>3</sub>) δ -28.2 (t, *J* = 84.5 Hz); HRMS (ESI): *m/z* calcd for C<sub>12</sub>H<sub>19</sub>BN<sub>3</sub> [M+H]<sup>+</sup> 216.1672, found 216.1673.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(2-(pyridin-4-yl)ethyl)hydroborate (4)**



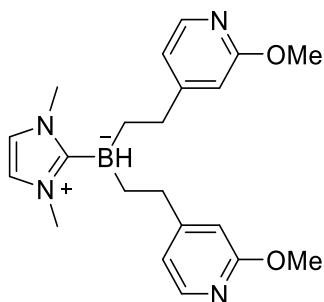
Following the **General Procedure A**, **4** was afforded as a white solid (19.6 mg, 61%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.39–8.37 (m, 4H), 7.11 (d, *J* = 6.0 Hz, 4H), 6.74 (s, 2H), 3.71 (s, 6H), 2.65–2.57 (m, 2H), 2.34–2.26 (m, 2H), 0.93–0.84 (m, 2H), 0.78–0.69 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 158.2, 148.2, 123.8, 120.7, 37.0, 36.3; <sup>11</sup>B NMR (192 MHz, CDCl<sub>3</sub>) δ -19.8 (d, *J* = 81.8 Hz); HRMS (ESI): *m/z* calcd for C<sub>19</sub>H<sub>26</sub>BN<sub>4</sub> [M+H]<sup>+</sup> 321.2251, found 321.2250.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(2-(2-methylpyridin-4-yl)ethyl)hydroborate (5)**



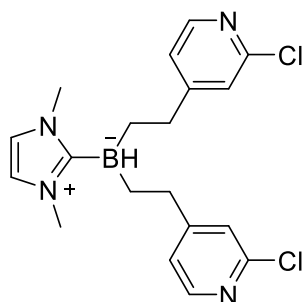
Following the **General Procedure A**, **5** was afforded as a colorless oil (19.5 mg, 56%) by using 4 equiv of vinylpyridine.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (d,  $J = 5.3$  Hz, 2H), 6.97 (s, 2H), 6.92 (d,  $J = 5.2$  Hz, 2H), 6.74 (s, 2H), 3.71 (s, 6H), 2.60–2.54 (m, 2H), 2.51 (s, 6H), 2.28–2.22 (m, 2H), 0.88–0.82 (m, 2H), 0.74–0.68 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  158.5, 156.9, 147.4, 123.3, 121.0, 120.6, 36.9, 36.2, 23.7;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.7 (d,  $J = 79.0$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{21}\text{H}_{30}\text{BN}_4$   $[\text{M}+\text{H}]^+$  349.2564, found 349.2567.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(2-(2-methoxypyridin-4-yl)ethyl)hydroborate (6)**



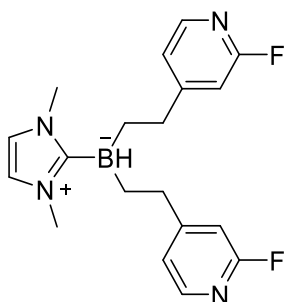
Following the **General Procedure A**, **6** was afforded as a colorless oil (20.5 mg, 54%) by using 4 equiv of vinylpyridine.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 5.3$  Hz, 2H), 6.70 (s, 2H), 6.68 (d,  $J = 5.3$  Hz, 2H), 6.49 (s, 2H), 3.88 (s, 6H), 3.71 (s, 6H), 2.57–2.50 (m, 2H), 2.25–2.18 (m, 2H), 0.89–0.82 (m, 2H), 0.75–0.67 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  164.3, 160.1, 145.8, 120.6, 117.6, 109.4, 53.2, 36.8, 36.2;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.7 (d,  $J = 82.2$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{21}\text{H}_{29}\text{BN}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$  403.2281, found 403.2283.

**Bis(2-(2-chloropyridin-4-yl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)hydroborate (7)**



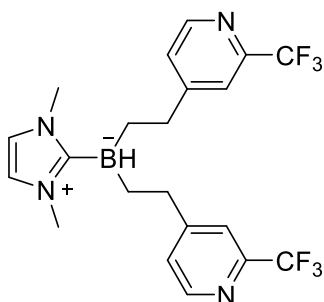
Following the **General Procedure A**, **7** was afforded as a colorless oil (20.6 mg, 53%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (d,  $J = 5.0$  Hz, 2H), 7.06 (s, 2H), 6.98 (d,  $J = 5.0$  Hz, 2H), 6.74 (s, 2H), 3.71 (s, 6H), 2.61–2.55 (m, 2H), 2.30–2.24 (m, 2H), 0.87–0.82 (m, 2H), 0.74–0.67 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  160.5, 151.0, 148.8, 123.6, 122.5, 120.8, 36.6, 36.2;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.9 (d,  $J = 82.6$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{19}\text{H}_{24}\text{BCl}_2\text{N}_4$   $[\text{M}+\text{H}]^+$  389.1471, found 389.1467.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(2-(2-fluoropyridin-4-yl)ethyl)hydroborate (8)**



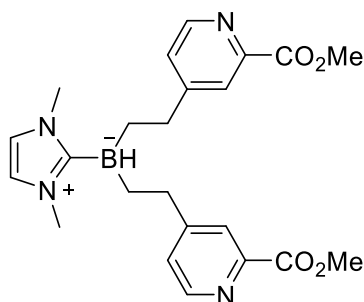
Following the **General Procedure A**, **8** was afforded as a colorless oil (22.1 mg, 62%) by using 4 equiv of vinylpyridine.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 5.2$  Hz, 2H), 6.95–6.91 (m, 2H), 6.75 (s, 2H), 6.66 (s, 2H), 3.72 (s, 6H), 2.64–2.55 (m, 2H), 2.35–2.25 (m, 2H), 0.89–0.81 (m, 2H), 0.76–0.66 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  164.0 (d,  $J = 225.1$  Hz), 163.2 (d,  $J = 4.3$  Hz), 146.4 (d,  $J = 15.3$  Hz), 121.4 (d,  $J = 3.3$  Hz), 120.8, 108.2 (d,  $J = 36.0$  Hz), 36.8 (d,  $J = 2.2$  Hz), 36.2;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.9 (d,  $J = 81.1$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.5 (s, 1F); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{19}\text{H}_{23}\text{BF}_2\text{N}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  379.1882, found 379.1884.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(2-(2-(trifluoromethyl)pyridin-4-yl)ethyl)hydroborate (9)**



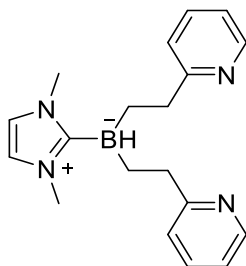
Following the **General Procedure A**, **9** was afforded as a colorless oil (22.8 mg, 50%) by using 4 equiv of vinylpyridine.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (d,  $J = 5.0$  Hz, 2H), 7.41 (s, 2H), 7.25 (d,  $J = 4.9$  Hz, 2H), 6.72 (s, 2H), 3.70 (s, 6H), 2.70–2.64 (m, 2H), 2.41–2.35 (m, 2H), 0.91–0.85 (m, 2H), 0.78–0.70 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 149.2, 147.5 (q,  $J = 33.7$  Hz), 126.1, 121.9 (q,  $J = 274.2$  Hz), 120.8, 120.2 (d,  $J = 2.4$  Hz), 36.9, 36.2;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.9 (d,  $J = 81.6$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -67.7 (s, 1F); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{21}\text{H}_{23}\text{BF}_6\text{N}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  479.1818, found 479.1819.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(2-(2-(methoxycarbonyl)pyridin-4-yl)ethyl)hydroborate (10)**



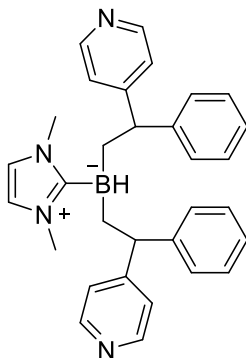
Following the **General Procedure A**, **10** was afforded as a colorless oil (25.3 mg, 58%) by using 4 equiv of vinylpyridine.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (d,  $J = 4.9$  Hz, 2H), 7.85 (s, 2H), 7.23 (d,  $J = 4.9$  Hz, 2H), 6.67 (s, 2H), 3.95 (s, 6H), 3.68 (s, 6H), 2.68–2.62 (m, 2H), 2.37–2.31 (m, 2H), 0.90–0.84 (m, 2H), 0.77–0.70 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 158.3, 149.1, 147.1, 126.8, 125.0, 120.7, 52.6, 36.8, 36.2;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.9 (d,  $J = 79.1$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{29}\text{BN}_4\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  459.2180, found 459.2187.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(2-(pyridin-2-yl)ethyl)hydroborate (11)**



Following the **General Procedure A**, **11** was afforded as a colorless oil (10.9 mg, 34%) by using 4 equiv of vinylpyridine.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46–8.43 (m, 2H), 7.67 (td,  $J = 7.7$  Hz, 1.7 Hz, 2H), 7.32 (d,  $J = 7.9$  Hz, 2H), 7.13–7.10 (m, 2H), 6.74 (s, 2H), 3.79 (s, 6H), 2.84–2.77 (m, 2H), 2.60–2.54 (m, 2H), 0.97–0.88 (m, 4H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 146.5, 137.8, 123.0, 120.7, 120.4, 38.9, 36.4;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.4 (d,  $J = 88.5$  Hz); HRMS (ESI):  $m/z$  calcd  $\text{C}_{19}\text{H}_{25}\text{BN}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  343.2070, found 343.2074.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(2-phenyl-2-(pyridin-4-yl)ethyl)hydroborate (12)**



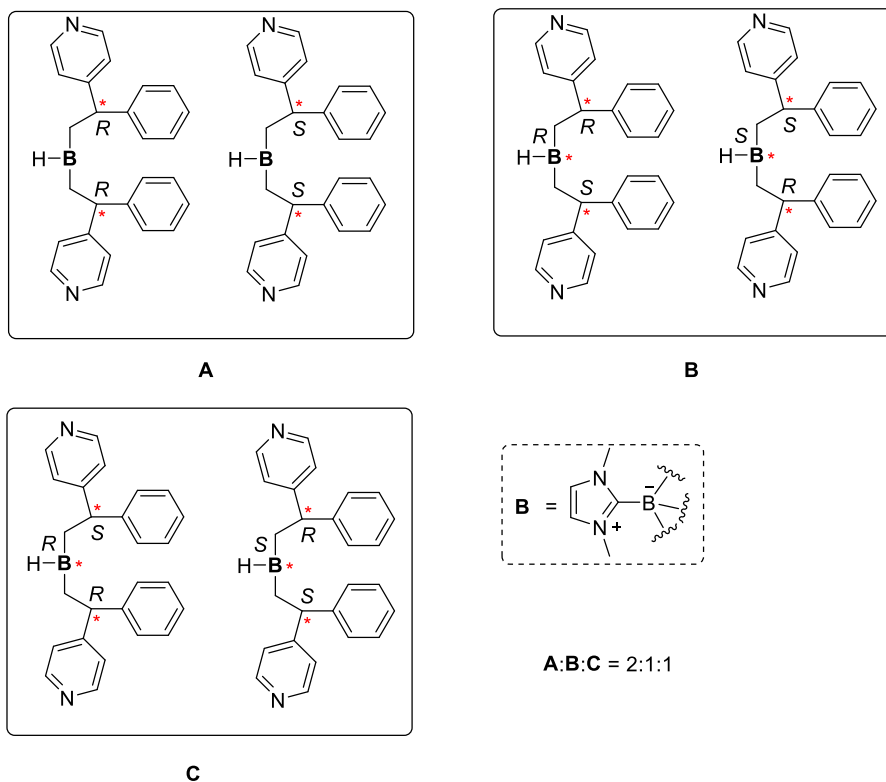
Following the **General Procedure A**, **12** was afforded as colorless oil in the form of one pair of diastereomers (8.5 mg, 18%) and two pairs of diastereomers (18.9 mg, 40%).

One pair of diastereomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (d,  $J = 4.7$  Hz, 4H), 7.23–7.15 (m, 8H), 7.13–7.09 (m, 2H), 6.98 (d,  $J = 5.6$  Hz, 4H), 6.46 (s, 2H), 3.65 (t,  $J = 7.6$  Hz, 2H), 3.28 (br s, 6H), 2.08–1.94 (m, 4H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 148.8, 147.5, 128.1, 127.7, 125.6, 123.1, 120.3, 53.1, 35.7;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -21.8 (d,  $J = 83.2$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{31}\text{H}_{34}\text{BN}_4$   $[\text{M}+\text{H}]^+$  473.2877, found 473.2886.

Two pairs of diastereomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.37 (d,  $J = 5.5$  Hz, 2H), 8.24 (d,  $J = 5.2$  Hz, 2H), 7.22–7.19 (m, 2H), 7.17–7.14 (m, 2H), 7.12–7.08 (m, 3H), 7.06–7.03 (m, 2H), 7.01–6.96 (m, 5H), 6.40 (s, 2H), 3.67–3.62 (m, 2H), 3.26 (br s, 6H), 1.91 (br s, 4H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )



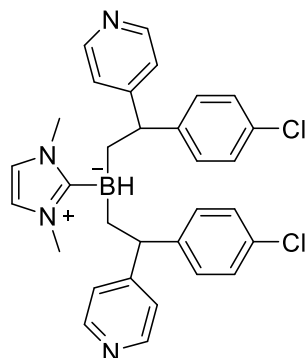
$\delta$  158.63/158.14, 149.04/148.83, 147.46/146.78, 128.09/127.86, 127.71/127.46, 125.63/125.41, 123.24/123.06, 120.24, 53.23/53.10, 35.69;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -21.5 (d,  $J = 81.4$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{31}\text{H}_{34}\text{BN}_4$   $[\text{M}+\text{H}]^+$  473.2877, found 473.2885.



**Scheme S1.** Three pairs of diastereomers **A**, **B**, **C** in the product **12**

**Note:** The hydroboration constructed two chiral carbon centers (highlighted in red). When their stereo-configurations were different, a chiral boron center was formed. In this way, three pairs of diastereomers **A**, **B**, **C** were produced with a ratio of 2:1:1 as shown in Scheme S1. The following cases such as **13–14**, **20–37**, had the same situation as **12**.

**Bis(2-(4-chlorophenyl)-2-(pyridin-4-yl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)hydroborate (13)**

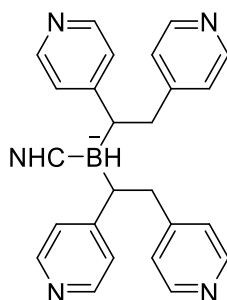


Following the **General Procedure A**, **13** was afforded as colorless oil in the form of one pair of diastereomers (11.9 mg, 22%) and two pairs of diastereomers (16.7 mg, 31%).

One pair of diastereomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (d,  $J = 3.9$  Hz, 4H), 7.20–7.16 (m, 4H), 7.10–7.06 (m, 4H), 6.93 (d,  $J = 5.9$  Hz, 4H), 6.49 (s, 2H), 3.59 (t,  $J = 7.7$  Hz, 2H), 3.30 (br s, 6H), 2.08–1.84 (m, 4H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  157.7, 148.8, 145.8, 131.3, 129.1, 128.2, 122.9, 120.5, 52.3, 35.8;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -21.9 (d,  $J = 82.6$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{31}\text{H}_{32}\text{BCl}_2\text{N}_4$   $[\text{M}+\text{H}]^+$  541.2097, found 541.2103.

Two pairs of diastereomers:  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (d,  $J = 6.1$  Hz, 2H), 8.27 (d,  $J = 5.9$  Hz, 2H), 7.19–7.17 (m, 2H), 7.09–7.05 (m, 4H), 7.04–7.02 (m, 2H), 6.95–6.92 (m, 4H), 6.47 (s, 2H), 3.66–3.57 (m, 4H), 3.35–3.22 (m, 6H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  157.99/157.65, 149.20/148.98, 145.80/145.29, 131.35/131.06, 129.10/128.84, 128.18/127.90, 123.09/122.92, 120.38, 52.42/52.37, 35.78;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -21.6 (d,  $J = 78.3$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{31}\text{H}_{32}\text{BCl}_2\text{N}_4$   $[\text{M}+\text{H}]^+$  541.2097, found 541.2101.

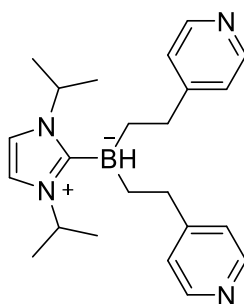
**Bis(1,2-di(pyridin-4-yl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)hydroborate (14)**



Following the **General Procedure A**, **14** was afforded as a colorless oil (21.3 mg, 45%) including

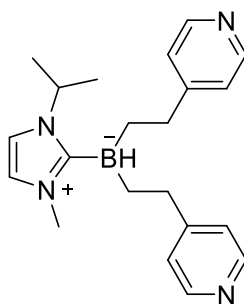
three pairs of diastereomers.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51–8.48 (m, 1H), 8.38–8.32 (m, 3H), 8.30–8.28 (m, 1H), 8.23–8.20 (m, 1H), 8.15–8.09 (m, 2H), 7.08–7.05 (m, 1H), 6.95–6.89 (m, 2H), 6.80–6.78 (m, 1H), 6.73–6.61 (m, 4H), 6.58–6.41 (m, 2H), 3.63–3.46 (m, 6H), 3.03–2.86 (m, 3H), 2.64–2.49 (m, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  160.74/160.53, 152.34/152.26/151.85, 149.84/149.26/149.24, 148.93/148.71/148.54/148.42, 124.02/123.90/123.79/123.66, 123.18/123.08/122.74, 121.73/121.44/120.97/120.66, 43.01/42.70/40.88, 36.92/36.80/36.38/35.90/35.65;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -13.8 (d,  $J = 81.1$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{29}\text{H}_{32}\text{BN}_6$   $[\text{M}+\text{H}]^+$  475.2782, found 475.2787.

**(1,3-Diisopropyl-1H-imidazol-3-ium-2-yl)bis(2-(pyridin-4-yl)ethyl)hydroborate (15)**



Following the **General Procedure A**, **15** was afforded as a colorless oil (19.6 mg, 52%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (d,  $J = 4.4$  Hz, 4H), 7.08 (d,  $J = 4.4$  Hz, 4H), 6.98 (s, 2H), 5.23 (br s, 2H), 2.62–2.54 (m, 2H), 2.25–2.18 (m, 2H), 1.39 (d,  $J = 6.6$  Hz, 12H), 0.88–0.83 (m, 2H), 0.70–0.63 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  157.5, 149.0, 123.6, 115.8, 48.9, 37.4, 23.5;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.2 (d,  $J = 82.4$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{34}\text{BN}_4$   $[\text{M}+\text{H}]^+$  377.2877, found 377.2874.

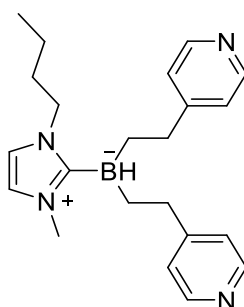
**(1-Isopropyl-3-methyl-1H-imidazol-3-ium-2-yl)bis(2-(pyridin-4-yl)ethyl)hydroborate (16)**



Following the **General Procedure A**, **16** was afforded as a colorless oil (16.0 mg, 46%).  $^1\text{H}$  NMR

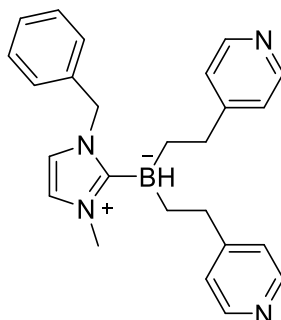
(600 MHz, CDCl<sub>3</sub>)  $\delta$  8.38 (d,  $J$  = 4.9 Hz, 4H), 7.08 (d,  $J$  = 5.3 Hz, 4H), 6.93 (d,  $J$  = 1.9 Hz, 1H), 6.82 (d,  $J$  = 1.7 Hz, 1H), 5.23–5.14 (m, 1H), 3.74 (s, 3H), 2.62–2.55 (m, 2H), 2.29–2.22 (m, 2H), 1.40 (s, 3H), 1.39 (s, 3H), 0.90–0.85 (m, 2H), 0.74–0.67 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  157.3, 149.0, 123.6, 121.4, 115.0, 49.1, 37.1, 36.3, 23.4; <sup>11</sup>B NMR (192 MHz, CDCl<sub>3</sub>)  $\delta$  -19.5 (d,  $J$  = 81.1 Hz); HRMS (ESI):  $m/z$  calcd for C<sub>21</sub>H<sub>30</sub>BN<sub>4</sub> [M+H]<sup>+</sup> 349.2564, found 349.2574.

**(1-Butyl-3-methyl-1H-imidazol-3-ium-2-yl)bis(2-(pyridin-4-yl)ethyl)hydroborate (17)**



Following the **General Procedure A**, **17** was afforded as a colorless oil (15.9 mg, 44%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.38 (d,  $J$  = 5.9 Hz, 4H), 7.09 (d,  $J$  = 5.8 Hz, 4H), 6.81 (d,  $J$  = 1.8 Hz, 1H), 6.76 (d,  $J$  = 1.7 Hz, 1H), 4.10 (t,  $J$  = 7.7 Hz, 2H), 3.72 (s, 3H), 2.65–2.56 (m, 2H), 2.32–2.23 (m, 2H), 1.77–1.68 (m, 2H), 1.40–1.32 (m, 2H), 0.96 (t,  $J$  = 7.4 Hz, 3H), 0.91–0.85 (m, 2H), 0.75–0.65 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  157.7, 148.6, 123.7, 120.8, 119.2, 48.4, 37.0, 36.2, 33.0, 19.7, 13.7; <sup>11</sup>B NMR (192 MHz, CDCl<sub>3</sub>)  $\delta$  -19.7 (d,  $J$  = 78.9 Hz); HRMS (ESI):  $m/z$  calcd for C<sub>22</sub>H<sub>32</sub>BN<sub>4</sub> [M+H]<sup>+</sup> 363.2720, found 363.2719.

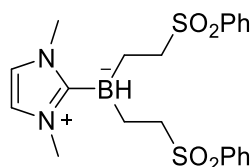
**(1-Benzyl-3-methyl-1H-imidazol-3-ium-2-yl)bis(2-(pyridin-4-yl)ethyl)hydroborate (18)**



Following the **General Procedure A**, **18** was afforded as a colorless oil (13.5 mg, 34%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.39–8.37 (m, 4H), 7.38–7.33 (m, 3H), 7.19–7.16 (m, 2H), 7.06 (d,  $J$  = 5.7 Hz, 4H), 6.78 (d,  $J$  = 1.8 Hz, 1H), 6.72 (d,  $J$  = 1.9 Hz, 1H), 5.35 (s, 2H), 3.77 (s, 3H), 2.63–2.57 (m, 2H),

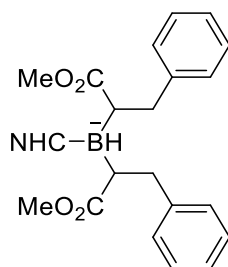
2.33–2.27 (m, 2H), 0.92–0.87 (m, 2H), 0.77–0.70 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  157.8, 148.5, 136.0, 129.0, 128.3, 127.7, 123.8, 121.2, 119.6, 52.0, 37.0, 36.3;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.5 (d,  $J = 85.1$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{25}\text{H}_{30}\text{BN}_4$   $[\text{M}+\text{H}]^+$  397.2564, found 397.2568.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(2-(phenylsulfonyl)ethyl)hydroborate (19)**



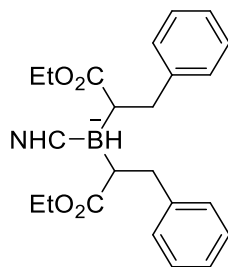
Following the **General Procedure A**, **19** was afforded as a colorless oil (31.2 mg, 70%) by using 2.6 equiv of phenyl vinyl sulfone.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85–7.82 (m, 4H), 7.61–7.58 (m, 2H), 7.53–7.50 (m, 4H), 6.79 (s, 2H), 3.64 (s, 6H), 2.97 (td,  $J = 13.7$  Hz, 4.6 Hz, 2H), 2.62 (td,  $J = 13.8$  Hz, 3.6 Hz, 2H), 0.77–0.69 (m, 2H), 0.68–0.61 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  139.5, 133.0, 128.8, 128.0, 121.3, 58.8, 36.3;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.8 (d,  $J = 84.5$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{21}\text{H}_{27}\text{BN}_2\text{NaO}_4\text{S}_2$   $[\text{M}+\text{Na}]^+$  469.1403, found 469.1406.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(1-methoxy-1-oxo-3-phenylpropan-2-yl)hydroborate (20)**



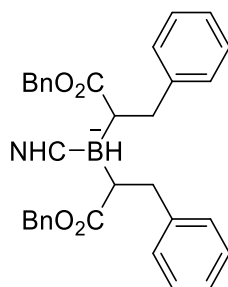
Following the **General Procedure A**, **20** was afforded as a colorless oil (31.7 mg, 73%) including three pairs of diastereomers.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22–7.20 (m, 4H), 7.18–7.14 (m, 2H), 7.12–7.04 (m, 4H), 6.83–6.74 (m, 2H), 3.85–3.73 (m, 6H), 3.54 (d,  $J = 15.7$  Hz, 3H), 3.29 (s, 2H), 3.08 (s, 1H), 3.04–2.99 (m, 1H), 2.98–2.93 (m, 1H), 2.89–2.71 (m, 1H), 2.58–2.33 (m, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  180.86/180.75/180.65, 144.41/143.91/143.52, 128.34/128.29/128.21/128.12, 128.01/127.99/127.97, 125.27/125.22/125.11, 121.38/121.28, 50.63/50.51/50.14/49.97, 38.81/38.60/38.52, 37.66/37.15/37.02;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.1–-17.0 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{25}\text{H}_{31}\text{BN}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  457.2275, found 457.2279.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(1-ethoxy-1-oxo-3-phenylpropan-2-yl)hydroborate**  
**(21)**



Following the **General Procedure A**, **21** was afforded as a colorless oil (34.7 mg, 75%) including three pairs of diastereomers.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23–7.14 (m, 7H), 7.11–7.06 (m, 3H), 6.82–6.74 (m, 2H), 4.07–3.99 (m, 1H), 3.95–3.90 (m, 1H), 3.89–3.73 (m, 6H), 3.72–3.69 (m, 1H), 3.60–3.48 (m, 1H), 3.06–2.92 (m, 3H), 2.81–2.36 (m, 3H), 1.09 (t,  $J = 7.1$  Hz, 2H), 0.92 (t,  $J = 7.1$  Hz, 2H), 0.84 (t,  $J = 7.1$  Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  180.63/180.50/180.37, 144.66/144.48/143.98/143.70, 128.44/128.40/128.28/128.22, 127.94/127.90, 125.24/125.20/125.17/125.04, 121.26, 59.07/58.93/58.54/58.38, 38.65/38.40, 37.62/37.44/37.31/37.10, 14.43/14.33/14.24/14.14;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.1–-17.1 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{27}\text{H}_{35}\text{BN}_2\text{NaO}_4$  [ $\text{M}+\text{Na}$ ] $^+$  485.2588, found 485.2590.

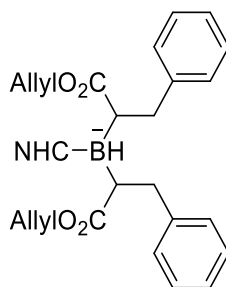
**Bis(1-(benzyloxy)-1-oxo-3-phenylpropan-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)hydroborate (22)**



Following the **General Procedure A**, **22** was afforded as a colorless oil (33.4 mg, 57%) including three pairs of diastereomers.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24–7.22 (m, 6H), 7.21–7.18 (m, 6H), 7.14–7.11 (m, 3H), 7.08–7.02 (m, 5H), 6.60–6.49 (m, 2H), 5.09–4.85 (m, 1H), 4.77–4.49 (m, 3H), 3.74–3.48 (m, 6H), 3.07–2.97 (m, 3H), 2.90–2.79 (m, 1H), 2.56–2.38 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  180.21/180.14/180.00, 144.42/144.25/143.50, 136.96/136.82, 128.43/128.29, 128.24/128.20/128.18, 127.98/127.95, 127.60/127.45, 125.28/125.19/125.13, 121.12/120.99,

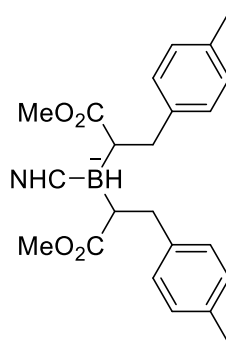
64.97/64.66/64.51, 38.76/38.70/38.18, 37.14/37.07;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -15.9--16.7 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{37}\text{H}_{39}\text{BN}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  609.2901, found 609.2903.

**Bis(1-(allyloxy)-1-oxo-3-phenylpropan-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)hydroborate (23)**



Following the **General Procedure A**, **23** was afforded as a colorless oil (28.2 mg, 58%) including three pairs of diastereomers.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23–7.14 (m, 7H), 7.12–7.06 (m, 3H), 6.82–6.72 (m, 2H), 5.82–5.46 (m, 2H), 5.13–4.99 (m, 4H), 4.54–4.34 (m, 1H), 4.23–4.03 (m, 2H), 3.93–3.87 (m, 1H), 3.86–3.68 (m, 6H), 3.08–2.94 (m, 3H), 2.82–2.38 (m, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  180.02/179.88, 144.46/144.31/143.53, 133.13/133.06/133.04, 128.47/128.43/128.23, 127.99/127.94, 125.30/125.24/125.12, 121.28, 117.36/117.19, 64.12/63.83/63.76, 38.78/38.65/38.39, 37.49/37.39/37.06;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.1--16.9 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{29}\text{H}_{35}\text{BN}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  509.2588, found 509.2594.

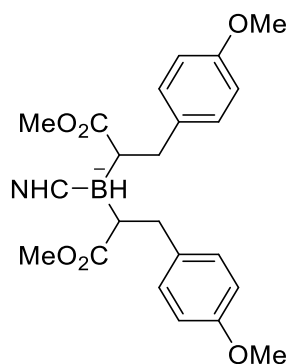
**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(1-methoxy-1-oxo-3-(p-tolyl)propan-2-yl)hydroborate (24)**



Following the **General Procedure A**, **24** was afforded as a colorless oil (37.9 mg, 82%) including three pairs of diastereomers.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.11–7.00 (m, 5H), 6.99–6.94 (m, 3H),

6.82–6.75 (m, 2H), 3.85–3.74 (m, 6H), 3.54 (d,  $J = 7.2$  Hz, 2H), 3.28 (s, 2H), 3.09 (s, 2H), 3.04–2.81 (m, 3H), 2.70–2.40 (m, 3H), 2.28–2.25 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  180.95/180.82/180.74, 141.51/141.36/140.86/140.48, 134.56/134.48/134.36, 128.72/128.68, 128.17/128.13/128.04/127.95, 121.24, 50.64/50.51/50.15/49.99, 38.33/38.08/38.04, 37.18/37.06, 20.97/20.93/20.92;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.2--16.8 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{27}\text{H}_{35}\text{BN}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  485.2588, found 485.2591.

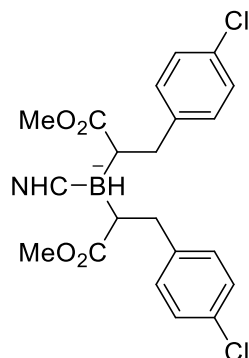
**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(1-methoxy-3-(4-methoxyphenyl)-1-oxopropan-2-yl)hydroborate (25)**



Following the **General Procedure A**, **25** was afforded as a colorless oil (41.0 mg, 83%) including three pairs of diastereomers.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13–7.10 (m, 2H), 7.02–6.96 (m, 2H), 6.82–6.70 (m, 6H), 3.87–3.77 (m, 6H), 3.76–3.73 (m, 6H), 3.55–3.08 (m, 6H), 2.98–2.88 (m, 2H), 2.83–2.63 (m, 1H), 2.47–2.35 (m, 2H), 2.31–2.61 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  180.94/180.80/180.74, 157.30/157.22, 136.81/136.63/136.12/135.72, 129.18/129.12/129.05/128.97, 121.34/121.24, 113.42/113.39, 55.15/55.12, 50.59/50.48/50.12/49.96, 37.89/37.63/37.41, 37.12/37.01/36.70;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.3--16.8 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{27}\text{H}_{35}\text{BN}_2\text{NaO}_6$   $[\text{M}+\text{Na}]^+$  517.2486, found 517.2492.

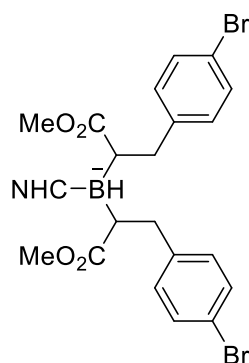


**Bis(3-(4-chlorophenyl)-1-methoxy-1-oxopropan-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)hydroborate (26)**



Following the **General Procedure A**, **26** was afforded as a colorless oil (32.1 mg, 64%) including three pairs of diastereomers.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19–7.16 (m, 2H), 7.15–7.11 (m, 4H), 7.03–6.96 (m, 2H), 6.87–6.78 (m, 2H), 3.90–3.72 (m, 6H), 3.54–3.39 (m, 3H), 3.28–3.08 (m, 3H), 2.96–2.87 (m, 2H), 2.82–2.63 (m, 1H), 2.53–2.25 (m, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  180.53/180.36, 142.95/142.77/142.31/141.91, 130.97/130.90/130.78, 130.08/130.01, 129.72/129.65/129.58/129.50, 128.12/128.10/128.06, 121.40, 50.69/50.60/50.24/50.08, 38.17/38.02/37.83, 37.05/36.93;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.2–-17.2 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{25}\text{H}_{29}\text{BCl}_2\text{N}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  525.1495, found 525.1498.

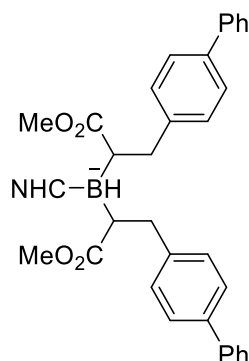
**Bis(3-(4-bromophenyl)-1-methoxy-1-oxopropan-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)hydroborate (27)**



Following the **General Procedure A**, **27** was afforded as a colorless oil (40.1 mg, 68%) including three pairs of diastereomers.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35–7.32 (m, 2H), 7.31–7.26 (m, 2H), 7.09–7.05 (m, 2H), 6.99–6.91 (m, 2H), 6.88–6.78 (m, 2H), 3.85–3.72 (m, 6H), 3.54 (s, 1H), 3.52 (s, 2H), 3.29 (s, 2H), 3.08 (s, 1H), 3.01–2.79 (m, 3H), 2.65–2.48 (m, 1H), 2.45–2.33 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  180.52/180.34, 143.28/142.82, 131.05/131.03, 130.17/130.09/130.01/129.92,

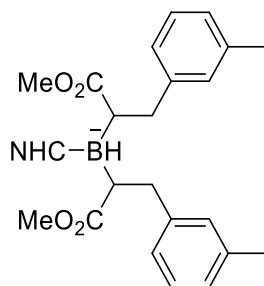
121.52/121.41, 119.05/118.99, 50.71/50.62/50.26/50.10, 38.22/38.08/37.87, 37.48/37.17/37.06/36.98;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.2--17.2 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{25}\text{H}_{29}\text{BBr}_2\text{N}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  613.0485, found 613.0493.

**Bis(3-([1,1'-biphenyl]-4-yl)-1-methoxy-1-oxopropan-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)hydroborate (28)**



Following the **General Procedure A**, **28** was afforded as a colorless oil (38.1 mg, 65%) including three pairs of diastereomers.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59–7.52 (m, 5H), 7.48–7.44 (m, 2H), 7.43–7.39 (m, 6H), 7.32–7.27 (m, 4H), 7.18–7.12 (m, 1H), 6.85–6.74 (m, 2H), 3.88–3.75 (m, 6H), 3.62–3.56 (m, 3H), 3.32 (s, 2H), 3.11 (s, 1H), 3.07–2.93 (m, 3H), 2.58–2.44 (m, 2H), 2.43–2.25 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  180.88/180.74/180.67, 143.80/143.61, 143.09/142.68, 141.38/141.33/141.19, 138.11/137.98, 128.77/128.70//128.68, 128.64/128.61/128.55, 126.92/126.87/126.84, 126.81/126.75/126.72, 121.44/121.33, 50.75/50.62/50.24/50.06, 38.48/38.27/38.17, 37.31/37.21/37.09;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.0--16.7 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{37}\text{H}_{39}\text{BN}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  609.2901, found 609.2903.

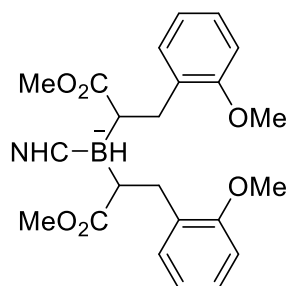
**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(1-methoxy-1-oxo-3-(m-tolyl)propan-2-yl)hydroborate (29)**



Following the **General Procedure A**, **29** was afforded as a colorless oil (28.2 mg, 61%) including

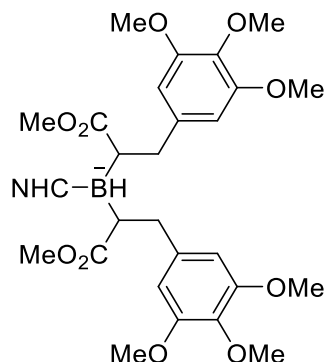
three pairs of diastereomers.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13–7.05 (m, 2H), 7.04–6.99 (m, 2H), 6.94–6.85 (m, 4H), 6.83–6.72 (m, 2H), 3.84–3.72 (m, 6H), 3.56 (d,  $J = 14.9$  Hz, 3H), 3.29 (s, 2H), 3.09 (s, 1H), 3.04–2.84 (m, 3H), 2.70–2.52 (m, 1H), 2.50–2.38 (m, 2H), 2.30–2.25 (m, 6H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  180.96/180.92/180.84/180.70, 144.53/144.37/143.84/143.42, 137.37/137.34/137.30, 129.21/129.18/129.06/128.92, 127.89/127.87//127.84, 126.05/126.03/125.98/125.88, 125.29/125.25/125.18/125.13, 121.35/121.24/121.05, 50.63/50.48/50.12/49.95, 38.72/38.45, 37.59/37.41/37.16/37.01, 21.41/21.36;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.3--16.8 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{27}\text{H}_{35}\text{BN}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  485.2588, found 485.2596.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(1-methoxy-3-(2-methoxyphenyl)-1-oxopropan-2-yl)hydroborate (30)**



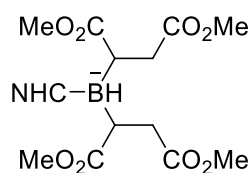
Following the **General Procedure A**, **30** was afforded as a colorless oil (38.0 mg, 77%) including three pairs of diastereomers.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21–7.18 (m, 1H), 7.13–7.05 (m, 3H), 6.86–6.78 (m, 4H), 6.77–6.72 (m, 2H), 3.95–3.84 (m, 4H), 3.80–3.69 (m, 8H), 3.48–3.43 (m, 3H), 3.25–3.10 (m, 3H), 3.00–2.70 (m, 3H), 2.65–2.43 (m, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  181.32/181.23/181.06/180.99, 157.50/157.09, 132.88/132.75/131.88/131.83, 130.02/129.83/129.75/129.27, 126.42/126.35//126.24/126.06, 121.04, 120.17/120.14/120.01/119.96, 109.87/109.79/109.76/109.72, 55.00/54.85, 50.33/50.30/50.00/49.92, 37.24/36.86, 33.17/32.56/32.45/32.22;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.0--16.6 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{27}\text{H}_{35}\text{BN}_2\text{NaO}_6$   $[\text{M}+\text{Na}]^+$  517.2486, found 517.2488.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(1-methoxy-1-oxo-3-(3,4,5-trimethoxyphenyl)propan-2-yl)hydroborate (31)**



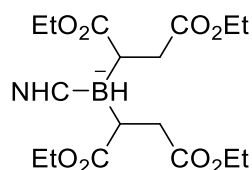
Following the **General Procedure A**, **31** was afforded as a colorless oil (31.9 mg, 52%) including three pairs of diastereomers.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  6.88–6.76 (m, 2H), 6.46–6.29 (m, 4H), 3.83–3.77 (m, 24H), 3.63 (s, 2H), 3.34 (s, 2H), 3.12 (s, 2H), 3.02–2.83 (m, 3H), 2.70–2.52 (m, 1H), 2.50–2.32 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  180.88/180.72/180.67, 152.78/152.75/152.72, 140.54/140.27/139.27, 135.71/135.56, 121.51/121.34, 105.18/105.09/105.00, 60.76/60.74, 55.94/55.92/55.85, 50.69/50.24/50.07, 39.34/38.99, 37.98/37.48/37.22/37.07;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.1--17.0 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{31}\text{H}_{43}\text{BN}_2\text{NaO}_{10}$   $[\text{M}+\text{Na}]^+$  637.2908, found 637.2907.

**Bis(1,4-dimethoxy-1,4-dioxobutan-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)hydroborate (32)**



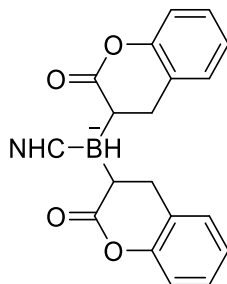
Following the **General Procedure A**, **32** was afforded as a colorless oil (29.9 mg, 75%) including three pairs of diastereomers.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  6.83 (s, 2H), 3.63 (s, 3H), 3.612 (s, 3H), 3.607 (s, 3H), 3.54 (s, 3H), 3.37 (s, 3H), 3.21 (s, 3H), 2.80–2.70 (m, 2H), 2.67–2.61 (m, 1H), 2.55–2.50 (m, 1H), 2.35–2.28 (m, 1H), 1.95–1.90 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  180.66/180.50/180.25, 175.35/175.12/174.60, 121.53/121.46, 51.37/51.26, 50.79/50.57/50.43, 37.07/36.97/36.80/36.57;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -17.4 (d,  $J = 93.9$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{27}\text{BN}_2\text{NaO}_8$   $[\text{M}+\text{Na}]^+$  421.1758, found 421.1759.

**Bis(1,4-diethoxy-1,4-dioxobutan-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)hydroborate (33)**



Following the **General Procedure A**, **33** was afforded as a colorless oil (30.4 mg, 67%) including three pairs of diastereomers.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  6.82 (s, 2H), 4.11–3.97 (m, 6H), 3.90–3.68 (m, 7H), 3.63–3.56 (m, 1H), 2.78–2.56 (m, 2H), 2.54–2.32 (m, 3H), 1.96–1.89 (m, 1H), 1.25–1.16 (m, 9H), 1.02–0.91 (m, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  180.37/180.21/180.01, 174.97/174.72/174.26, 121.36, 60.05/59.96/59.81, 59.38/58.85/58.73, 37.22/37.18/37.08/36.82, 14.28/14.21/14.14/14.12;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -17.5 (d,  $J = 92.5$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{21}\text{H}_{35}\text{BN}_2\text{NaO}_8$   $[\text{M}+\text{Na}]^+$  477.2384, found 477.2386.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(2-oxochroman-3-yl)hydroborate (34)**



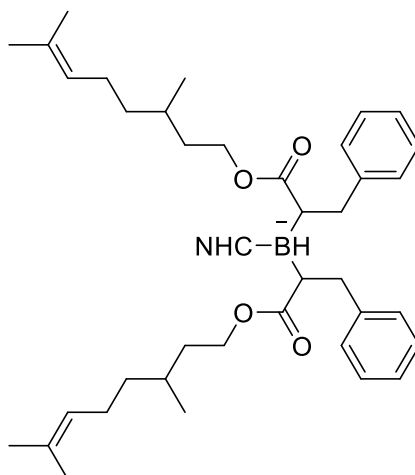
Following the **General Procedure A**, **34** was afforded as colorless oil in the form of one pair of diastereomers (12.0 mg, 30%) and two pairs of diastereomers (12.1 mg, 30%).

One pair of diastereomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.07–7.00 (m, 4H), 6.96–6.92 (m, 2H), 6.76 (d,  $J = 8.1$  Hz, 2H), 6.61 (d,  $J = 1.6$  Hz, 1H), 6.43 (d,  $J = 1.7$  Hz, 1H), 3.91 (s, 3H), 3.31–3.22 (m, 2H), 3.05 (s, 3H), 2.82–2.76 (m, 2H), 2.61 (br s, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  176.7, 152.2, 128.0, 127.0, 123.9, 123.4, 121.8, 121.5, 115.2, 37.5, 36.7, 29.3;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.8 (d,  $J = 93.6$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{23}\text{BN}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  425.1649, found 425.1655.

Two pairs of diastereomers:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.07 (d,  $J = 8.2$  Hz, 2H), 7.01–6.97 (m, 1H), 6.94–6.89 (m, 2H), 6.83–6.79 (m, 2H), 6.69–6.65 (m, 1H), 6.60 (d,  $J = 1.6$  Hz, 1H), 6.52 (d,  $J = 7.4$  Hz, 1H), 3.89 (s, 3H), 3.19–3.08 (m, 2H), 2.99–2.88 (m, 2H), 2.64 (s, 3H), 2.17–2.04 (m, 1H), 1.86–1.79 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  177.08/176.93, 152.90/152.21, 128.76/127.38, 126.68/126.58, 124.66, 123.49/123.45, 122.88, 121.73/121.26, 115.86/114.66, 36.71/36.12,

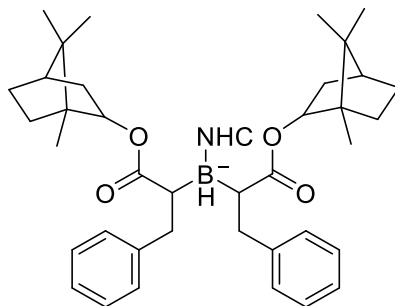
29.31/28.94;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -20.9 (d,  $J = 95.9$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{23}\text{BN}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  425.1649, found 425.1650.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(1-((3,7-dimethyloct-6-en-1-yl)oxy)-1-oxo-3-phenylpropan-2-yl)hydroborate (35)**



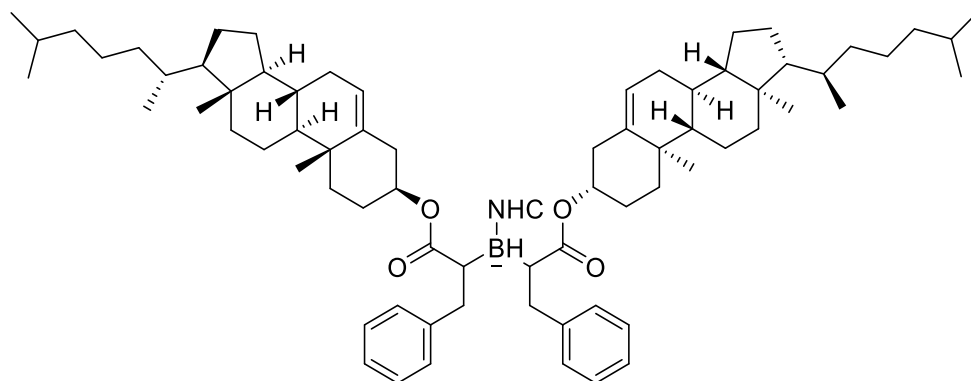
Following the **General Procedure A**, **35** was afforded as a colorless oil (38.2 mg, 56%) including three pairs of diastereomers.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31–7.24 (m, 1H), 7.23–7.15 (m, 6H), 7.14–7.04 (m, 3H), 6.84–6.70 (m, 2H), 5.11–4.99 (m, 2H), 4.09–3.98 (m, 1H), 3.93–3.70 (m, 6H), 3.66–3.55 (m, 1H), 3.45–3.29 (m, 1H), 3.17–3.04 (m, 1H), 3.02–2.78 (m, 4H), 2.54–2.38 (m, 2H), 2.03–2.01 (m, 1H), 1.96–1.83 (m, 4H), 1.70–1.67 (m, 6H), 1.60–1.58 (m, 6H), 1.35–1.16 (m, 6H), 1.13–1.00 (m, 3H), 0.86–0.73 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  180.6, 144.4, 131.2, 128.72/128.36/128.17/127.93, 126.9/126.4, 125.16/124.79/124.60, 121.2, 61.8/61.2, 38.68/38.38, 37.33/37.01, 35.64/35.26, 29.3, 25.7/25.3, 19.2, 17.6;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  -15.2–-16.1 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{43}\text{H}_{64}\text{BN}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  683.4959, found 683.4961.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(1-oxo-3-phenyl-1-(((1R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)propan-2-yl)(1-oxo-3-phenyl-1-(((1S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)propan-2-yl)hydroborate (36)**



Following the **General Procedure A**, **36** was afforded as a colorless oil (37.3 mg, 55%) including three pairs of diastereomers.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25–7.13 (m, 8H), 7.11–7.06 (m, 2H), 6.82–6.78 (m, 2H), 4.73–4.18 (m, 2H), 4.02–3.73 (m, 6H), 3.16–3.05 (m, 1H), 3.03–2.94 (m, 2H), 2.61–2.52 (m, 2H), 2.16–1.84 (m, 4H), 1.79–1.73 (m, 1H), 1.60–1.56 (m, 1H), 1.52–1.45 (m, 2H), 1.27–1.21 (m, 1H), 1.17–0.86 (m, 5H), 0.81–0.73 (m, 12H), 0.66–0.54 (m, 4H), 0.49–0.48 (m, 2H), 0.35–0.15 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  180.97/180.87/180.81/180.66, 144.52/144.22/144.17/143.68, 128.43/128.36/128.20, 128.00/127.89/127.85/127.82, 125.26/125.16/125.08/124.95, 121.55/121.25/121.18, 78.58/78.39/78.15/77.65/77.62, 48.72/48.57/48.49/48.14, 47.62/47.55/47.52/47.48/47.45, 44.88/44.78/44.72/44.68, 39.58/38.96/38.71/38.42, 37.95/37.50/37.30/36.92, 36.29/36.16/36.11, 27.91/27.89/27.83, 27.26/27.20/27.15/27.09/27.02, 19.68/19.63/18.83/18.77/18.74, 13.42/13.31/13.26/13.04;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.1–-17.2 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{43}\text{H}_{59}\text{BN}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  701.4466, found 701.4474.

**Bis(1-(((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)-1-oxo-3-phenylpropan-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)hydroborate (37)**



Following the **General Procedure A**, **37** was afforded as colorless oil in the form of isomers A (19.4 mg, 17%) and isomers B (24.0 mg, 21%).

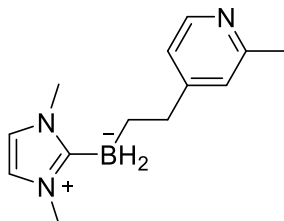
Isomers A:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25–7.19 (m, 8H), 7.12–7.08 (m, 2H), 6.84–6.80 (m, 2H), 5.25–5.19 (m, 2H), 4.26–4.16 (m, 2H), 3.90–3.76 (m, 6H), 3.07–2.91 (m, 4H), 2.51–2.43 (m, 2H), 2.01–1.88 (m, 8H), 1.86–1.68 (m, 6H), 1.53–1.47 (m, 4H), 1.44–1.40 (m, 5H), 1.38–1.37 (m, 2H), 1.34–1.31 (m, 5H), 1.28–1.21 (m, 5H), 1.13–1.04 (m, 12H), 1.02–0.96 (m, 7H), 0.93–0.89 (m, 12H), 0.87–0.85 (m, 12H), 0.65 (br s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.9, 144.4, 140.06/139.97, 128.50/128.48, 127.9, 125.1, 122.1, 121.29/121.17, 71.9, 56.6, 56.1, 50.0, 42.2, 39.7, 39.5, 38.21/38.05, 37.6, 36.9, 36.53/36.50, 36.1, 35.8, 31.8, 28.2, 28.0, 27.78/27.62, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  -15.2--15.8 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{77}\text{H}_{115}\text{BN}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  1165.8848, found 1165.8854.

Isomers B:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24–7.15 (m, 6H), 7.12–7.06 (m, 4H), 6.82–6.76 (m, 2H), 5.26–5.15 (m, 2H), 4.47–4.38 (m, 1H), 4.14–4.03 (m, 1H), 3.97–3.69 (m, 6H), 3.06–2.96 (m, 2H), 2.92–2.85 (m, 1H), 2.51–2.39 (m, 3H), 2.08–1.86 (m, 8H), 1.84–1.68 (m, 6H), 1.55–1.47 (m, 5H), 1.46–1.39 (m, 7H), 1.36–1.29 (m, 8H), 1.26–1.19 (m, 3H), 1.15–1.05 (m, 13H), 1.00–0.96 (m, 4H), 0.94–0.93 (br s, 3H), 0.91–0.88 (m, 9H), 0.87–0.84 (m, 12H), 0.65 (br s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.9, 143.8, 140.27/140.19, 128.50/128.26, 127.93/127.82, 125.24/124.99, 122.1, 121.1, 72.5/71.7, 56.64/56.59, 56.1, 49.9, 42.25/42.23, 39.7, 39.5, 38.36/38.17, 37.35/36.91, 36.53/36.49/36.46, 36.1, 36.1, 35.8, 31.8, 28.2, 28.0, 27.7, 24.2, 23.8, 22.8, 22.5, 20.9, 19.3, 18.7, 11.8;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  -15.7--16.4 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{77}\text{H}_{115}\text{BN}_2\text{NaO}_4$



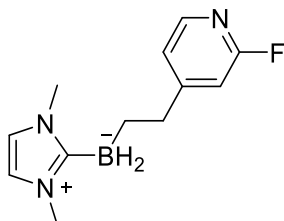
$[M+Na]^+$  1165.8848, found 1165.8848.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(2-methylpyridin-4-yl)ethyl)dihydroborate (38)**



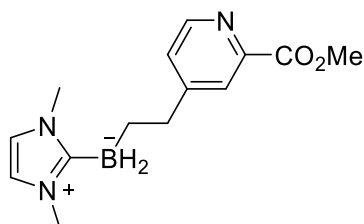
Following the **General Procedure B**, **38** was afforded as a colorless oil (8.9 mg, 39%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (d,  $J = 5.2$  Hz, 1H), 6.99 (s, 1H), 6.93 (d,  $J = 5.2$  Hz, 1H), 6.78 (s, 2H), 3.76 (s, 6H), 2.54–2.50 (m, 2H), 2.49 (s, 3H), 0.71 (br s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.3, 148.2, 123.1, 120.8, 120.0, 38.0, 35.9, 24.2, one carbon signal missing due to signal overlapping;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  -27.2 (t,  $J = 84.2$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{21}\text{BN}_3$   $[M+H]^+$  230.1829, found 230.1830.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(2-fluoropyridin-4-yl)ethyl)dihydroborate (39)**



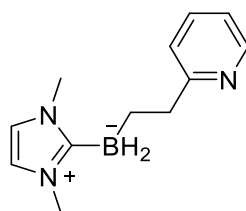
Following the **General Procedure B**, **39** was afforded as a colorless oil (8.2 mg, 35%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 5.2$  Hz, 1H), 6.99 (d,  $J = 4.8$  Hz, 1H), 6.80 (s, 2H), 6.73 (s, 1H), 3.77 (s, 6H), 2.58 (t,  $J = 8.2$  Hz, 2H), 0.70 (br s, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  164.9, 163.4 (d,  $J = 22.6$  Hz), 146.4 (d,  $J = 15.3$  Hz), 121.5 (d,  $J = 3.4$  Hz), 120.1, 108.3 (d,  $J = 36.1$  Hz), 38.0 (d,  $J = 2.5$  Hz), 35.9;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  -29.0 (t,  $J = 85.1$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.8 (s, 1F); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_{18}\text{BFN}_3$   $[M+H]^+$  234.1578, found 234.1582.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(2-(methoxycarbonyl)pyridin-4-yl)ethyl)dihydroborate (40)**



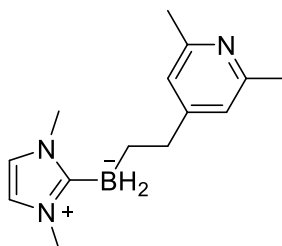
Following the **General Procedure B**, **40** was afforded as a colorless oil (9.8 mg, 36%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.52 (d, *J* = 4.9 Hz, 1H), 7.96 (s, 1H), 7.33–7.29 (m, 1H), 6.78 (s, 2H), 3.98 (s, 3H), 3.76 (s, 6H), 2.63 (t, *J* = 8.1 Hz, 2H), 0.74 (br s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 166.4, 158.5, 149.2, 147.2, 127.0, 125.2, 120.1, 52.7, 38.0, 35.9; <sup>11</sup>B NMR (192 MHz, CDCl<sub>3</sub>) δ -28.3 (t, *J* = 83.9 Hz); HRMS (ESI): *m/z* calcd for C<sub>14</sub>H<sub>21</sub>BN<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 274.1727, found 274.1733.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(pyridin-2-yl)ethyl)dihydroborate (41)**



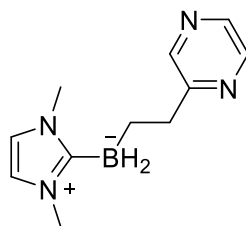
Following the **General Procedure B**, **41** was afforded as a colorless oil (8.2 mg, 38%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.43 (d, *J* = 4.2 Hz, 1H), 7.57 (td, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.05–7.00 (m, 1H), 6.77 (s, 2H), 3.78 (s, 6H), 2.74–2.68 (m, 2H), 0.85 (br s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 167.1, 148.0, 136.4, 122.4, 120.0, 40.9, 35.9, one carbon signal missing due to signal overlapping; <sup>11</sup>B NMR (192 MHz, CDCl<sub>3</sub>) δ -28.1 (t, *J* = 83.0 Hz); HRMS (ESI): *m/z* calcd for C<sub>12</sub>H<sub>17</sub>BN<sub>3</sub> [M-H]<sup>+</sup> 214.1516, found 214.1515.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(2,6-dimethylpyridin-4-yl)ethyl)dihydroborate (42)**



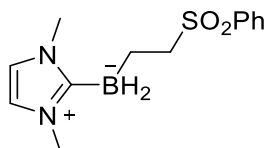
Following the **General Procedure A**, **42** was afforded as a colorless oil (11.7 mg, 48%) by using 4 equiv of vinylpyridine.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  6.79 (s, 2H), 6.77 (s, 2H), 3.76 (s, 6H), 2.45 (s, 6H), 1.84 (br s, 2H), 0.69 (br s, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 120.2, 120.0, 38.0, 35.9, 24.2;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -28.1 (t,  $J = 84.0$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{14}\text{H}_{23}\text{BN}_3$   $[\text{M}+\text{H}]^+$  244.1985, found 244.1989.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(pyrazin-2-yl)ethyl)dihydroborate (43)**



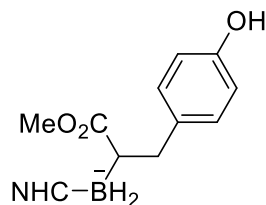
Following the **General Procedure B**, **43** was afforded as a colorless oil (2.8 mg, 13%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.50 (s, 1H), 8.39–8.37 (m, 1H), 8.28 (d,  $J = 2.5$  Hz, 1H), 6.78 (s, 2H), 3.78 (s, 6H), 2.75 (t,  $J = 8.2$  Hz, 2H), 0.82 (br s, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7, 144.7, 143.4, 140.9, 120.1, 38.5, 35.9;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -28.2 (t,  $J = 84.0$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{11}\text{H}_{16}\text{BN}_4$   $[\text{M}-\text{H}]^+$  215.1468, found 215.1469.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(phenylsulfonyl)ethyl)dihydroborate (44)**



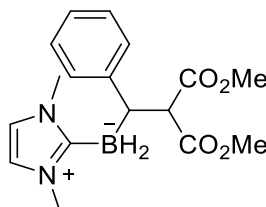
Following the **General Procedure A**, **44** was afforded as a colorless oil (14.7 mg, 53%) by using 1.2 equiv of phenyl vinyl sulfone.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 7.6$  Hz, 2H), 7.61–7.57 (m, 1H), 7.53–7.50 (m, 2H), 6.80 (s, 2H), 3.71 (s, 6H), 3.08–3.04 (m, 2H), 0.69 (br s, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 132.8, 128.8, 128.1, 120.4, 60.2, 35.9;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -28.9 (t,  $J = 85.5$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{19}\text{BN}_2\text{NaO}_2\text{S}$   $[\text{M}+\text{Na}]^+$  301.1158, found 301.1161.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(3-(4-hydroxyphenyl)-1-methoxy-1-oxopropan-2-yl)dihydroborate (45)**



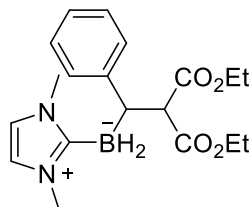
Following the **General Procedure A**, **45** was afforded as a colorless oil (15.6 mg, 54%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.01 (d,  $J = 7.5$  Hz, 2H), 6.80 (s, 2H), 6.61 (d,  $J = 7.4$  Hz, 2H), 5.65 (br s, 1H), 3.73 (s, 6H), 3.41 (s, 3H), 3.05–2.93 (m, 1H), 2.66–2.57 (m, 1H), 2.19 (br s, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  182.6, 153.4, 136.5, 129.3, 120.4, 114.8, 50.5, 38.1, 36.0;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -26.0 (t,  $J = 91.2$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{21}\text{BN}_2\text{NaO}_3$   $[\text{M}+\text{Na}]^+$  311.1543, found 311.1542.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(3-methoxy-2-(methoxycarbonyl)-3-oxo-1-phenylpropyl)dihydroborate (46)**



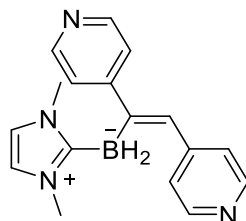
Following the **General Procedure A**, **46** was afforded as a colorless oil (23.1 mg, 70%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.02 (t,  $J = 7.6$  Hz, 2H), 6.91 (t,  $J = 7.3$  Hz, 1H), 6.82 (d,  $J = 7.5$  Hz, 2H), 6.68 (s, 2H), 4.00 (d,  $J = 12.3$  Hz, 1H), 3.79 (s, 3H), 3.42 (s, 3H), 3.33 (s, 6H), 2.66–2.60 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 170.9, 149.6, 127.6, 126.7, 123.4, 120.1, 58.2, 52.0, 51.8, 35.4;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -25.0 (t,  $J = 87.8$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{23}\text{BN}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  353.1649, found 353.1651.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(3-ethoxy-2-(ethoxycarbonyl)-3-oxo-1-phenylpropyl)dihydroborate (47)**



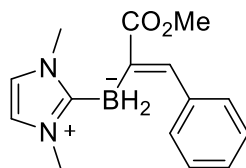
Following the **General Procedure A**, **47** was afforded as a colorless oil (22.2 mg, 62%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.01 (t,  $J = 7.4$  Hz, 2H), 6.90 (t,  $J = 7.2$  Hz, 1H), 6.84 (d,  $J = 7.4$  Hz, 2H), 6.68 (s, 2H), 4.29–4.21 (m, 2H), 3.95 (d,  $J = 12.3$  Hz, 1H), 3.92–3.84 (m, 2H), 3.34 (s, 6H), 2.65–2.60 (m, 1H), 1.33 (t,  $J = 7.1$  Hz, 3H), 0.89 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 170.5, 149.8, 127.5, 127.0, 123.3, 120.1, 60.7, 60.4, 58.5, 35.4, 14.2, 13.8;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -24.0 (t,  $J = 87.9$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{19}\text{H}_{27}\text{BN}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$  381.1962, found 381.1976.

**(E)-(1,2-Di(pyridin-4-yl)vinyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (48)**



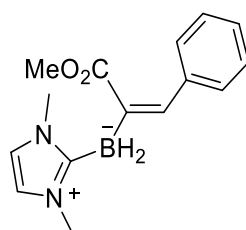
Following the **General Procedure A**, **48** was afforded as a colorless oil (6.4 mg, 22%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.47 (d,  $J = 6.0$  Hz, 2H), 8.40 (d,  $J = 5.9$  Hz, 2H), 7.42 (d,  $J = 6.0$  Hz, 2H), 7.18–7.15 (m, 2H), 6.70 (br s, 1H), 6.62 (s, 2H), 3.55 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.8, 148.3, 131.5, 123.9, 121.6, 120.4, 35.8;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  -27.6 (t,  $J = 88.2$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{20}\text{BN}_4$   $[\text{M}+\text{H}]^+$  291.1781, found 291.1789.

**(E)-(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(3-methoxy-3-oxo-1-phenylprop-1-en-2-yl)dihydroborate (49)**



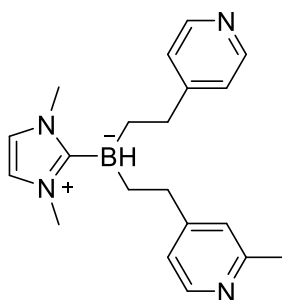
Following the **General Procedure A**, **49** (12.7 mg, 47%) and **50** (7.0 mg, 26%) were afforded as colorless oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (s, 1H), 7.61 (d,  $J = 7.5$  Hz, 2H), 7.30 (t,  $J = 7.6$  Hz, 2H), 7.19 (t,  $J = 7.4$  Hz, 1H), 6.72 (s, 2H), 3.65 (s, 6H), 3.59 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  175.5, 142.1, 139.5, 130.1, 127.3, 126.7, 120.0, 51.3, 35.9;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -30.1 (t,  $J = 87.1$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{19}\text{BN}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$  293.1437, found 293.1436.

**(Z)-(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)borate (50)**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23–7.18 (m, 4H), 7.14–7.10 (m, 1H), 6.86 (s, 2H), 6.36–6.30 (br s, 1H), 3.80 (s, 6H), 3.60 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  177.6, 138.9, 132.0, 128.1, 127.2, 126.2, 120.5, 51.1, 36.1;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -26.2 (t,  $J = 89.1$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{19}\text{BN}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$  293.1437, found 293.1439.

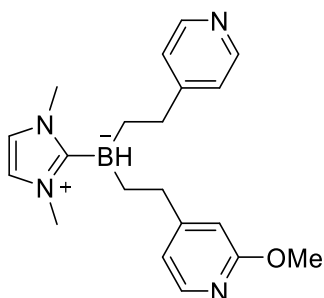
**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(2-methylpyridin-4-yl)ethyl)(2-(pyridin-4-yl)ethyl)borate (51)**



Following the **General Procedure C**, **51** was afforded as a colorless oil (16.7 mg, 50%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.37 (d,  $J = 5.6$  Hz, 2H), 8.26 (d,  $J = 5.1$  Hz, 1H), 7.05 (d,  $J = 5.7$  Hz, 2H), 6.92

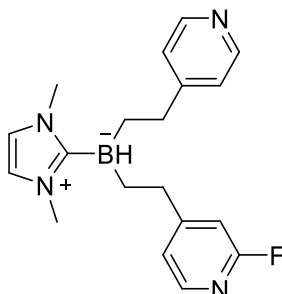
(s, 1H), 6.86 (d,  $J = 5.0$  Hz, 1H), 6.72 (s, 2H), 3.71 (s, 6H), 2.62–2.54 (m, 2H), 2.47 (s, 3H), 2.31–2.21 (m, 2H), 0.91–0.85 (m, 2H), 0.77–0.70 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  157.45, 157.36, 157.1, 149.0, 148.4, 123.6, 123.0, 120.74, 120.61, 36.88, 36.85, 36.3, 24.2;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.7 (d,  $J = 80.4$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_{28}\text{BN}_4$   $[\text{M}+\text{H}]^+$  335.2407, found 335.2417.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(2-methoxypyridin-4-yl)ethyl)(2-(pyridin-4-yl)ethyl)hydroborate (52)**



Following the **General Procedure C**, **52** was afforded as a colorless oil (18.2 mg, 52%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (d,  $J = 5.9$  Hz, 2H), 7.95 (d,  $J = 5.2$  Hz, 1H), 7.06 (d,  $J = 5.7$  Hz, 2H), 6.72 (s, 2H), 6.68 (d,  $J = 5.5$  Hz, 1H), 6.50 (s, 1H), 3.89 (s, 3H), 3.71 (s, 6H), 2.63–2.50 (m, 2H), 2.32–2.18 (m, 2H), 0.93–0.84 (m, 2H), 0.77–0.68 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.3, 160.0, 157.3, 148.9, 145.8, 123.6, 120.6, 117.5, 109.4, 53.1, 36.89, 36.79, 36.3;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  -18.7 (d,  $J = 82.4$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_{28}\text{BN}_4\text{O}$   $[\text{M}+\text{H}]^+$  351.2356, found 351.2357.

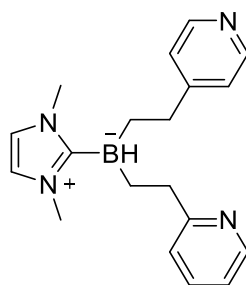
**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(2-fluoropyridin-4-yl)ethyl)(2-(pyridin-4-yl)ethyl)hydroborate (53)**



Following the **General Procedure C**, **53** was afforded as a colorless oil (13.5 mg, 40%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (br s, 2H), 7.98 (d,  $J = 5.2$  Hz, 1H), 7.06 (d,  $J = 5.9$  Hz, 2H), 6.94 (d,  $J = 5.0$  Hz, 1H), 6.74 (s, 2H), 6.67 (s, 1H), 3.72 (s, 6H), 2.65–2.56 (m, 2H), 2.35–2.25 (m, 2H), 0.90–0.84

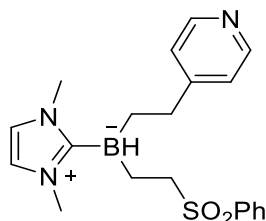
(m, 2H), 0.77–0.70 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  164.8, 163.3 (d,  $J = 16.2$  Hz), 157.1, 149.0, 146.5 (d,  $J = 15.4$  Hz), 123.6, 121.4 (d,  $J = 3.4$  Hz), 120.7, 108.2 (d,  $J = 36.0$  Hz), 36.8, 36.3, one carbon signal missing due to signal overlapping;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.8 (d,  $J = 81.1$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.5 (s, 1F); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{19}\text{H}_{25}\text{BFN}_4$   $[\text{M}+\text{H}]^+$  339.2156, found 339.2158.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(pyridin-2-yl)ethyl)(2-(pyridin-4-yl)ethyl)hydroborate (54)**



Following the **General Procedure C**, **54** was afforded as a colorless oil (14.7 mg, 46%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (d,  $J = 4.4$  Hz, 1H), 8.36 (d,  $J = 5.5$  Hz, 2H), 7.54 (t,  $J = 7.6$  Hz, 1H), 7.20 (d,  $J = 7.9$  Hz, 1H), 7.06 (d,  $J = 5.4$  Hz, 2H), 7.00 (t,  $J = 6.2$  Hz, 1H), 6.71 (s, 2H), 3.74 (s, 6H), 2.79–2.71 (m, 1H), 2.66–2.58 (m, 1H), 2.50–2.41 (m, 1H), 2.35–2.26 (m, 1H), 0.96–0.84 (m, 3H), 0.81–0.73 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 157.2, 149.0, 148.5, 135.9, 123.6, 122.0, 120.6, 119.9, 40.0, 37.0, 36.3;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  -18.5 (d,  $J = 85.6$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{19}\text{H}_{25}\text{BN}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  343.2070, found 343.2072.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(phenylsulfonyl)ethyl)(2-(pyridin-4-yl)ethyl)hydroborate (55)**

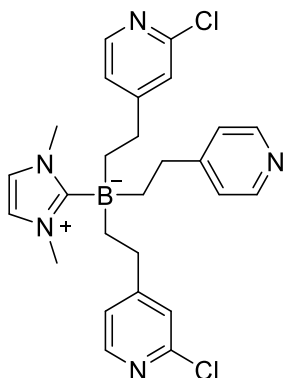


Following the **General Procedure C**, **55** was afforded as a colorless oil (22.6 mg, 59%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.35 (s, 2H), 7.91–7.87 (m, 2H), 7.62–7.59 (m, 1H), 7.55–7.51 (m, 2H), 7.00 (d,  $J = 4.8$  Hz, 2H), 6.76 (s, 2H), 3.68 (s, 6H), 3.14–3.08 (m, 1H), 2.76–2.69 (m, 1H), 2.50–2.44 (m, 1H),



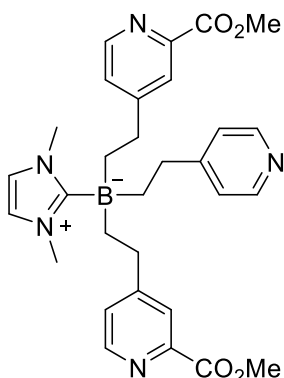
2.24–2.17 (m, 1H), 0.83–0.74 (m, 3H), 0.71–0.64 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  156.8, 148.8, 139.8, 132.9, 128.8, 128.1, 123.6, 121.0, 59.3, 36.48, 36.33;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.4 (d,  $J = 83.1$  Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_{27}\text{BN}_3\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$  384.1917, found 384.1915.

**Bis(2-(2-chloropyridin-4-yl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-(pyridin-4-yl)ethyl)borate (56)**



Following the **General Procedure C**, **56** was afforded as a colorless oil (19.2 mg, 39%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (d,  $J = 5.7$  Hz, 2H), 8.19 (d,  $J = 5.0$  Hz, 2H), 7.10 (s, 2H), 7.08 (d,  $J = 5.6$  Hz, 2H), 7.01 (d,  $J = 4.9$  Hz, 2H), 6.67 (s, 2H), 3.78 (s, 6H), 2.39–2.34 (m, 6H), 0.94–0.90 (m, 6H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  160.4, 156.8, 151.2, 149.3, 149.0, 123.56, 123.49, 122.43, 122.32, 38.1, 33.29, 33.18;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -15.3 (s, 1B); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{26}\text{H}_{30}\text{BCl}_2\text{N}_5\text{Na}$   $[\text{M}+\text{Na}]^+$  516.1869, found 516.1860.

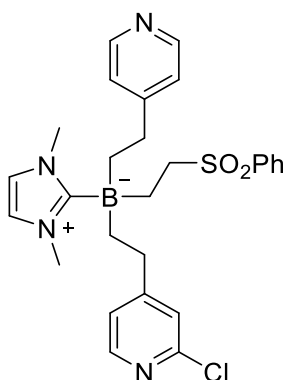
**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(2-(2-(methoxycarbonyl)pyridin-4-yl)ethyl)(2-(pyridin-4-yl)ethyl)borate (57)**



Following the **General Procedure C**, **57** was afforded as a colorless oil (11.9 mg, 22%).  $^1\text{H}$  NMR

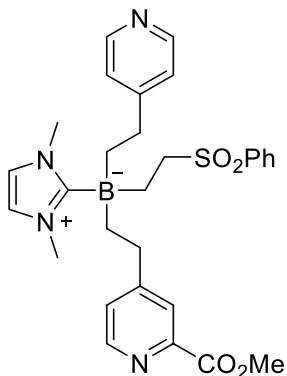
(600 MHz, CDCl<sub>3</sub>)  $\delta$  8.54 (d,  $J$  = 4.9 Hz, 2H), 8.42 (d,  $J$  = 5.3 Hz, 2H), 7.91 (s, 2H), 7.29–7.27 (m, 2H), 7.10 (d,  $J$  = 5.7 Hz, 2H), 6.62 (s, 2H), 4.00 (s, 6H), 3.76 (s, 6H), 2.50–2.45 (m, 4H), 2.40–2.36 (m, 2H), 0.99–0.94 (m, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  166.3, 158.3, 156.9, 149.36, 149.23, 147.4, 126.8, 124.9, 123.5, 122.2, 52.8, 38.1, 33.41, 33.30; <sup>11</sup>B NMR (192 MHz, CDCl<sub>3</sub>)  $\delta$  -15.2 (s, 1B); HRMS (ESI):  $m/z$  calcd for C<sub>30</sub>H<sub>37</sub>BN<sub>5</sub>O<sub>4</sub> [M+H]<sup>+</sup> 542.2939, found 542.2947.

**(2-(2-Chloropyridin-4-yl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-(phenylsulfonyl)ethyl)(2-(pyridin-4-yl)ethyl)borate (58)**



Following the **General Procedure C**, **58** was afforded as a colorless oil (19.8 mg, 38%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.38 (d,  $J$  = 4.6 Hz, 2H), 8.15 (d,  $J$  = 5.0 Hz, 1H), 7.93 (d,  $J$  = 7.3 Hz, 2H), 7.64 (t,  $J$  = 7.4 Hz, 1H), 7.57 (t,  $J$  = 7.6 Hz, 2H), 6.98–6.95 (m, 3H), 6.89 (d,  $J$  = 5.1 Hz, 1H), 6.69 (s, 2H), 3.74 (s, 6H), 2.84–2.80 (m, 2H), 2.27–2.20 (m, 2H), 2.15–2.10 (m, 2H), 0.97–0.93 (m, 2H), 0.79–0.74 (m, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  159.8, 156.4, 151.2, 149.05, 149.03, 139.5, 133.2, 129.0, 128.2, 123.46, 123.43, 122.6, 122.3, 56.5, 38.2, 32.93, 32.78; <sup>11</sup>B NMR (192 MHz, CDCl<sub>3</sub>)  $\delta$  -15.5 (s, 1B); HRMS (ESI):  $m/z$  calcd for C<sub>27</sub>H<sub>33</sub>BClN<sub>4</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 523.2106, found 523.2109.

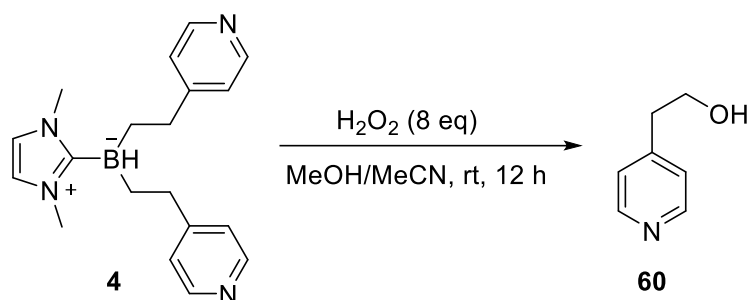
**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(2-(methoxycarbonyl)pyridin-4-yl)ethyl)(2-(phenylsulfonyl)ethyl)(2-(pyridin-4-yl)ethyl)borate (59)**



Following the **General Procedure C**, **59** was afforded as a colorless oil (24.6 mg, 45%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51 (d,  $J = 4.9$  Hz, 1H), 8.38 (s, 1H), 7.93 (d,  $J = 7.7$  Hz, 2H), 7.79 (s, 1H), 7.63 (t,  $J = 7.4$  Hz, 1H), 7.57 (t,  $J = 7.6$  Hz, 2H), 7.17–7.14 (m, 2H), 6.98 (s, 2H), 6.66 (s, 2H), 4.00 (s, 3H), 3.73 (s, 6H), 2.88–2.79 (m, 2H), 2.36–2.30 (m, 1H), 2.28–2.19 (m, 2H), 2.15–2.10 (m, 1H), 0.98–0.94 (m, 2H), 0.83–0.77 (m, 4H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 157.7, 156.6, 149.4, 149.0, 147.4, 139.5, 133.2, 129.0, 128.2, 126.7, 124.8, 123.5, 122.5, 56.5, 52.8, 38.2, 33.00, 32.95;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CDCl}_3$ )  $\delta$  -15.3 (s, 1B); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{29}\text{H}_{35}\text{BN}_4\text{NaO}_4\text{S}$   $[\text{M}+\text{Na}]^+$  569.2370, found 569.2371.

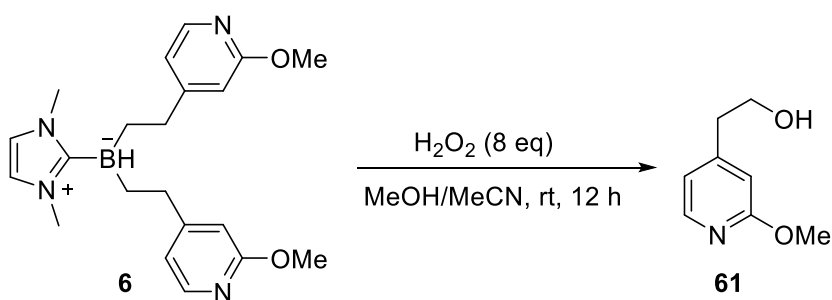
## 5. Transformations of the Products

### 2-(Pyridin-4-yl)ethan-1-ol (**60**)



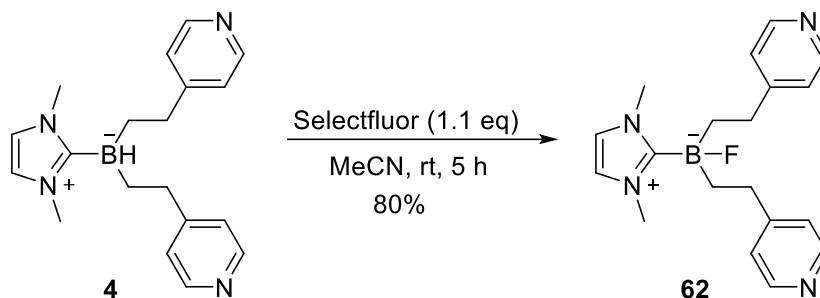
To a solution of **4** (12.8 mg, 0.04 mmol) in MeOH/MeCN (v/v = 1:1, 2 mL) was added H<sub>2</sub>O<sub>2</sub> (30% aq, 37  $\mu$ L) at room temperature. The reaction mixture was stirred for 12 h and then quenched with saturated NH<sub>4</sub>Cl (aq). The reaction mixture was extracted three times with ethyl acetate. The combined organic layer was washed with water and brine, dried over MgSO<sub>4</sub>, filtered, and concentrated. The crude residue was purified by flash column chromatography to give **60** as a colorless oil (8.4 mg, 170% based on boron moiety). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.52 (d, *J* = 5.8 Hz, 2H), 7.18 (d, *J* = 5.8 Hz, 2H), 4.98 (s, 1H), 3.92 (t, *J* = 6.4 Hz, 2H), 2.88 (t, *J* = 6.4 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  149.5, 148.4, 124.5, 62.4, 38.4; HRMS (ESI): *m/z* calcd for C<sub>7</sub>H<sub>10</sub>NO [M+H]<sup>+</sup> 124.0762, found 124.0757. The characterization data matched that reported in the literature.<sup>12</sup>

### 2-(2-Methoxypyridin-4-yl)ethan-1-ol (**61**)



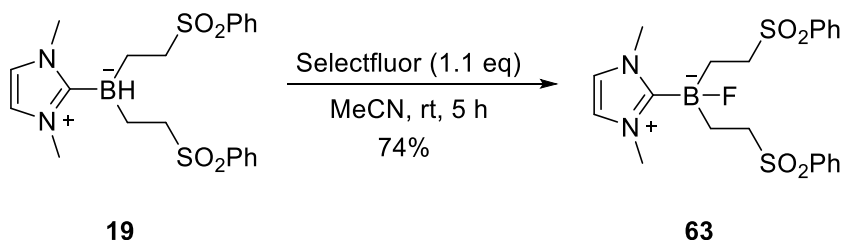
**61** was obtained from **6** (15.2 mg, 0.04 mmol) using the same experimental procedure as that for **60**. Colorless oil, 10.7 mg, 174% based on boron moiety. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 (d, *J* = 5.2 Hz, 1H), 6.76 (d, *J* = 5.2 Hz, 1H), 6.62 (s, 1H), 3.92 (s, 3H), 3.88 (t, *J* = 6.4 Hz, 2H), 2.82 (t, *J* = 6.4 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  164.5, 150.6, 146.8, 117.8, 111.0, 62.5, 53.4, 38.3; HRMS (ESI): *m/z* calcd for C<sub>8</sub>H<sub>12</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 154.0868, found 154.0864. The characterization data matched that reported in the literature.<sup>13</sup>

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)fluorobis(2-(pyridin-4-yl)ethyl)borate (62)**



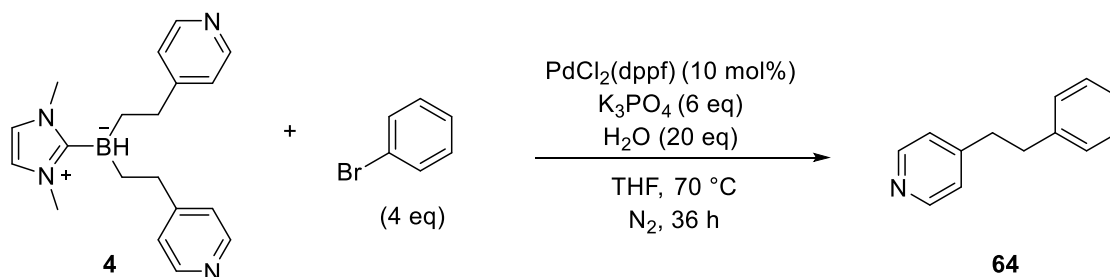
To a solution of **4** (25.6 mg, 0.08 mmol) in MeCN (1 mL) was added Selectfluor (31.9 mg, 0.09 mmol) at room temperature. The reaction mixture was stirred at room temperature for 5 h and then evaporated. The crude residue was purified by flash column chromatography to give **62** as a colorless oil (21.6 mg, 80%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.38 (d, *J* = 5.8 Hz, 4H), 7.06 (d, *J* = 5.8 Hz, 4H), 6.73 (s, 2H), 3.79 (s, 6H), 2.70–2.65 (m, 2H), 2.33–2.27 (m, 2H), 0.96–0.88 (m, 2H), 0.84–0.75 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 156.6, 149.1, 123.6, 121.7, 36.8 (d, *J* = 8.9 Hz), 32.1; <sup>11</sup>B NMR (192 MHz, CDCl<sub>3</sub>) δ -2.5 (s); <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -150.78–-150.84 (m, 1F); HRMS (ESI): *m/z* calcd for C<sub>19</sub>H<sub>25</sub>BFN<sub>4</sub> [M+H]<sup>+</sup> 339.2156, found 339.2157.

**(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)fluorobis(2-(phenylsulfonyl)ethyl)borate (63)**

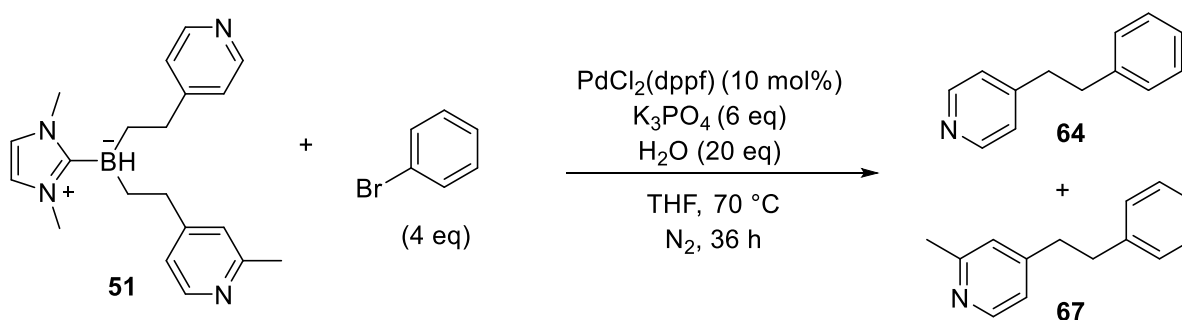


**63** was obtained from **19** (35.7 mg, 0.08 mmol) using the same experimental procedure as that for **62**. Colorless oil, 27.5 mg, 74%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88–7.82 (m, 4H), 7.63–7.59 (m, 2H), 7.56–7.50 (m, 4H), 6.83 (s, 2H), 3.74 (s, 6H), 3.11–3.03 (m, 2H), 2.69–2.60 (m, 2H), 0.92–0.79 (m, 2H), 0.78–0.66 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 139.3, 133.1, 129.0, 128.0, 122.4, 55.0, 37.0 (d, *J* = 8.6 Hz); <sup>11</sup>B NMR (192 MHz, CDCl<sub>3</sub>) δ -1.8 (s); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -151.89– -151.95 (m, 1F); HRMS (ESI): *m/z* calcd for C<sub>21</sub>H<sub>26</sub>BFN<sub>2</sub>NaO<sub>4</sub>S<sub>2</sub> [M+Na]<sup>+</sup> 487.1309, found 487.1309.

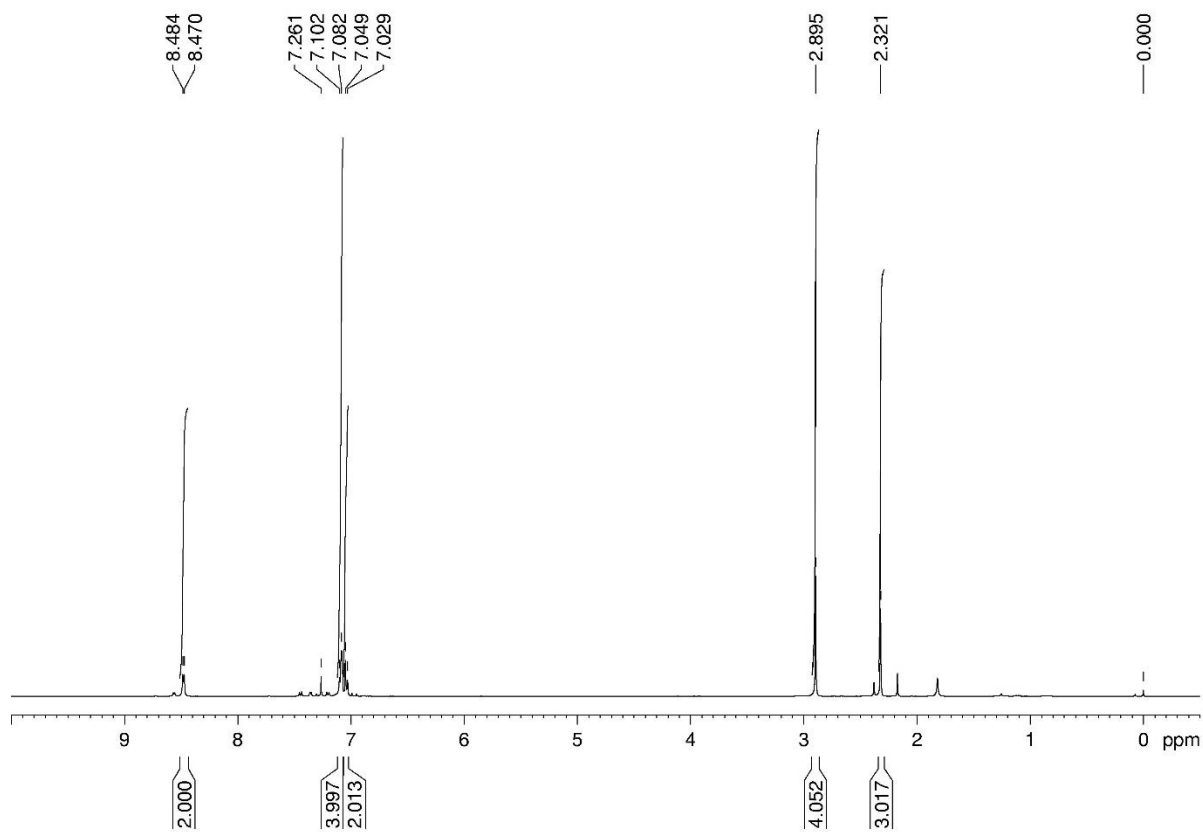
#### 4-Phenethylpyridine (**64**)



A 10 mL Schlenk tube protected under nitrogen was charged with **4** (17.0 mg, 0.053 mmol), bromobenzene (23  $\mu$ L, 0.21 mmol), PdCl<sub>2</sub>(dppf) (3.8 mg, 10 mol%), K<sub>3</sub>PO<sub>4</sub> (67.9 mg, 0.32 mmol), dry THF (1 mL) and H<sub>2</sub>O (19  $\mu$ L, 20 eq.). The mixture was stirred at 70 °C for 36 h, then diluted with ethyl acetate, and filtered on silica gel. The solvent was concentrated and purified by column chromatography on silica gel to afford **64** as a colorless oil (13.2 mg, 136% based on boron moiety). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.48 (br s, 2H), 7.31–7.26 (m, 2H), 7.23–7.18 (m, 1H), 7.16–7.12 (m, 2H), 7.08 (d,  $J$  = 5.6 Hz, 2H), 2.93 (s, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.6, 149.5, 140.6, 128.43, 128.36, 126.2, 124.0, 37.0, 36.5. The characterization data matched that reported in the literature.<sup>14</sup>

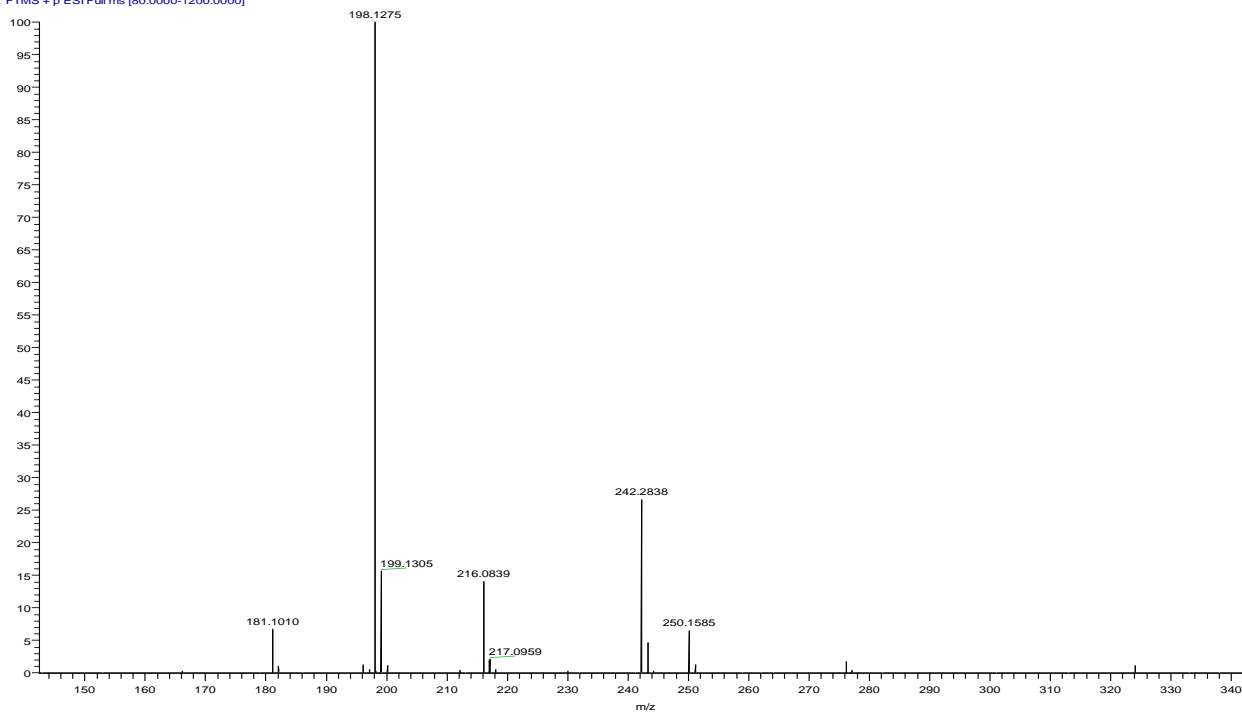


Di-substituted borane **51** was used as the feedstock for Suzuki-type coupling reaction with bromobenzene using the same experimental procedure as above. Products **64** and **67** were detected with a ratio of 1/1 by GC-MS analysis in 112% yield based on boron. **67** was also observed by its crude <sup>1</sup>H NMR and HRMS (ESI):  $m/z$  calcd for C<sub>14</sub>H<sub>16</sub>N [M+H]<sup>+</sup> 198.1283, found 198.1275.



**Figure S1.** Crude  $^1\text{H}$  NMR spectrum of **67**

Lifengxing-57 #14 RT: 0.10 AV: 1 NL: 5.31E9  
T: FTMS + p ESI Full ms [80.0000-1200.0000]



**Figure S2.** HRMS data of **67**

## 6. Preliminary Mechanistic Study

### Radical capture experiment

The radical capture TEMPO could totally inhibit the formation of di-substituted product **4**, and HRMS analysis of the crude reaction mixture obviously showed the peak assigned to the radical adduct **65**, indicating the involvement of boryl radicals in the reaction pathway.

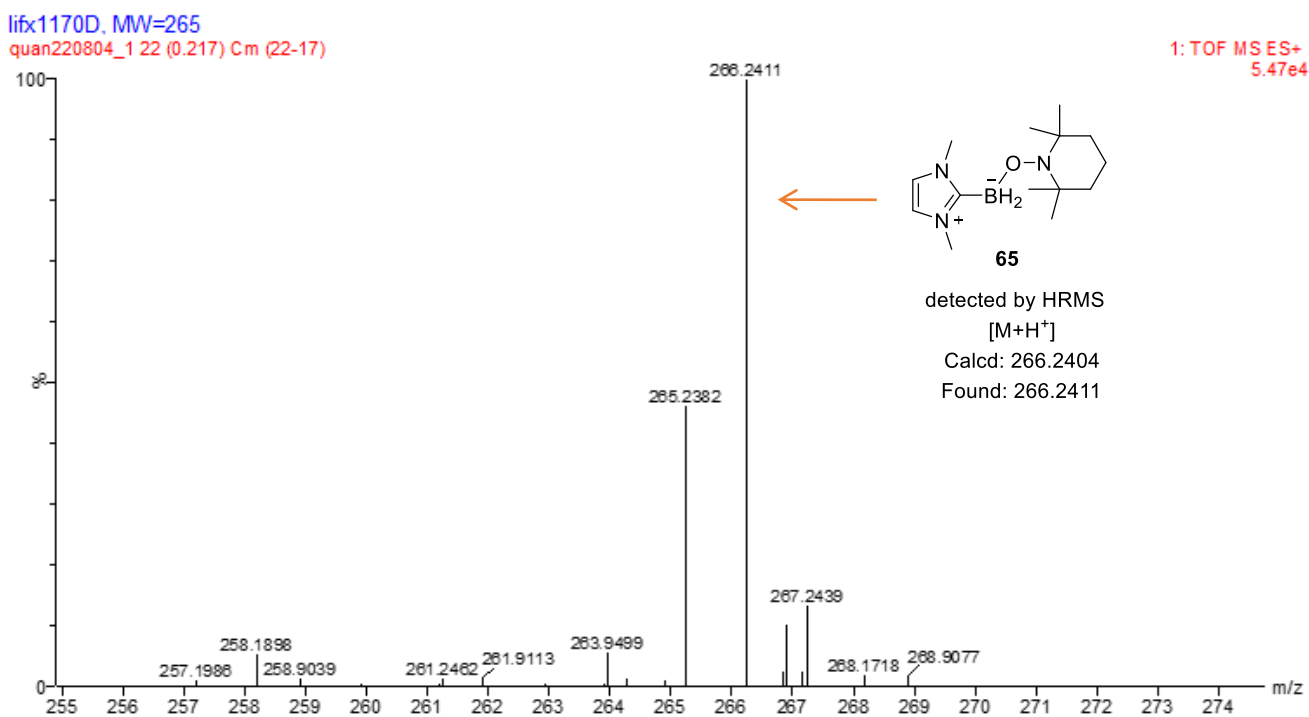
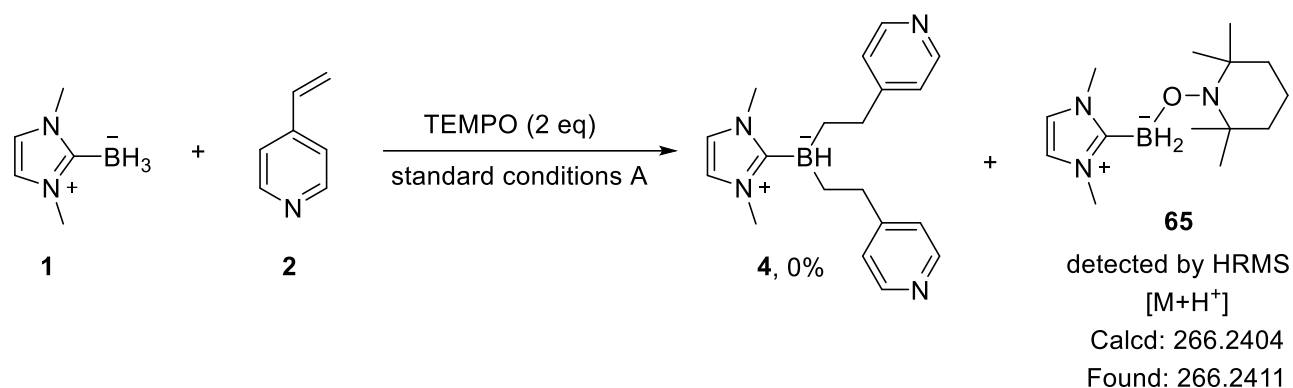


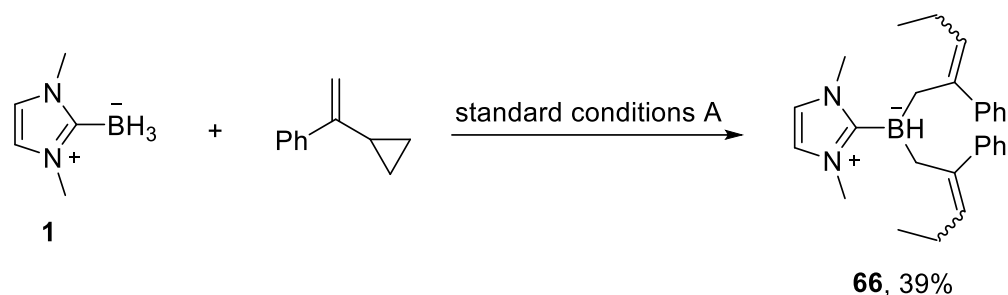
Figure S3. HRMS data of the reaction mixture

### Radical clock experiment

The use of radical clock substrate (1-cyclopropylvinyl)benzene only afforded the ring-opened products **66** in 39% yield, further implying that a radical pathway was involved in this transformation.



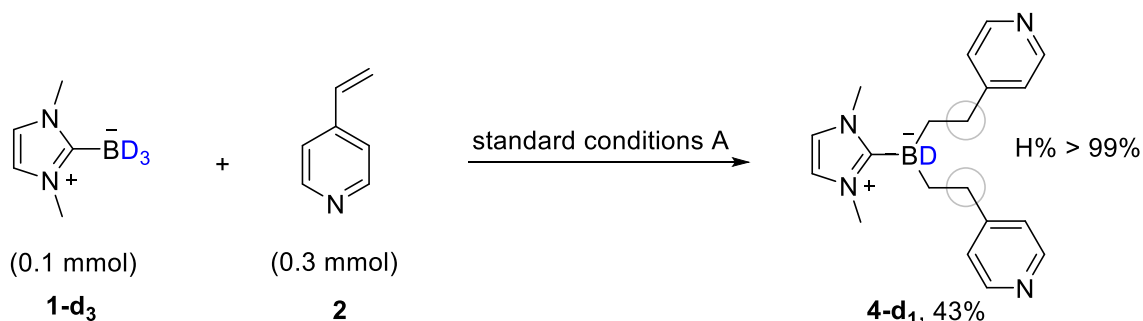
### (1,3-Dimethyl-1H-imidazol-3-ium-2-yl)bis(2-phenylpent-2-en-1-yl)hydroborate (**66**)

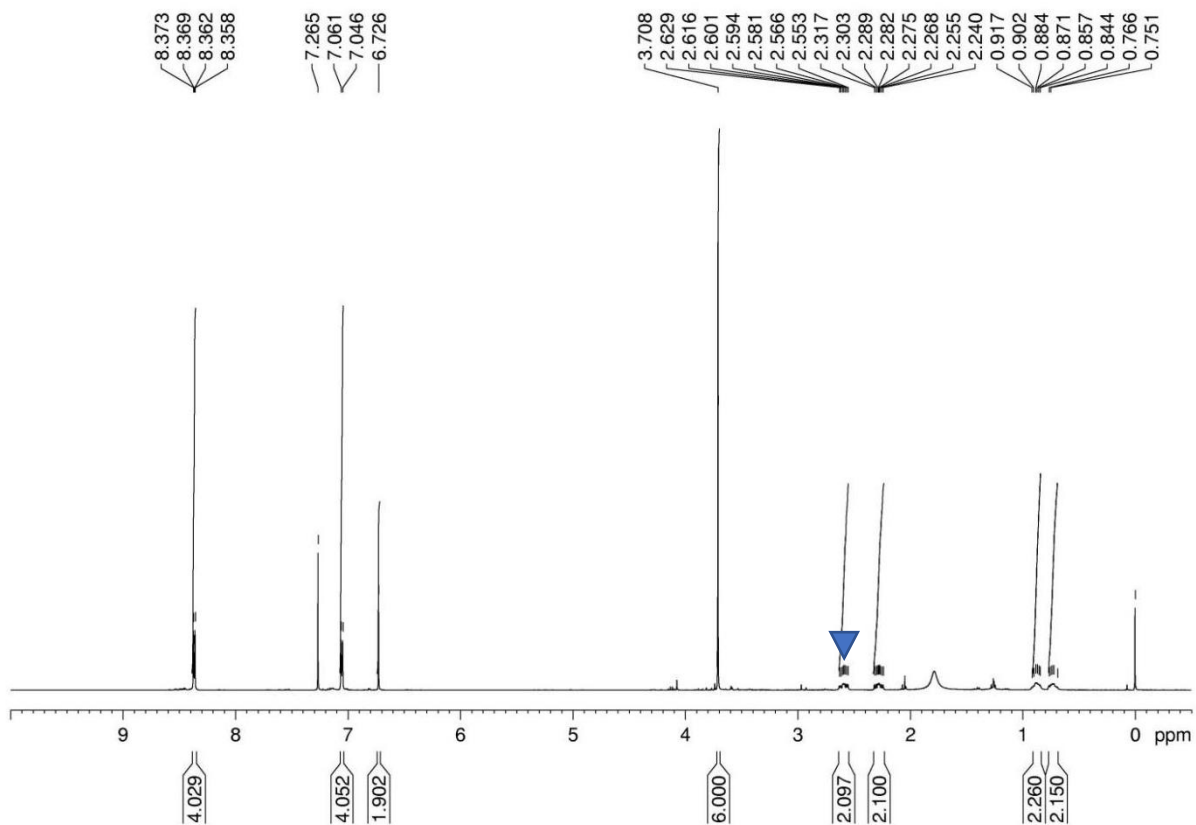


The presence of new vinyl protons and their splitting patterns in the  $^1\text{H}$  NMR spectrum showed that a mixture of isomers was obtained after flash column chromatography, confirming the formation of ring opening products **66**. The characterization data were given for the mixture of isomers. Colorless oil, 15.5 mg, 39%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34–7.27 (m, 1H), 7.12–7.05 (m, 5H), 7.04–6.95 (m, 3H), 6.88–6.81 (m, 2H), 6.37–6.29 (m, 1H), 5.16–5.00 (m, 2H), 3.30–3.15 (m, 6H), 2.36–1.86 (m, 6H), 1.82–1.74 (m, 2H), 1.00–0.93 (m, 3H), 0.82–0.75 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  128.05/127.99, 127.23/127.17, 127.0, 126.32/126.15, 125.0, 124.2, 119.8, 35.8, 22.23/21.82/21.78, 15.3/14.7;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  -19.0–-20.4 (m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{27}\text{H}_{35}\text{BKN}_2$   $[\text{M}+\text{K}]^+$  437.2530, found 437.2530.

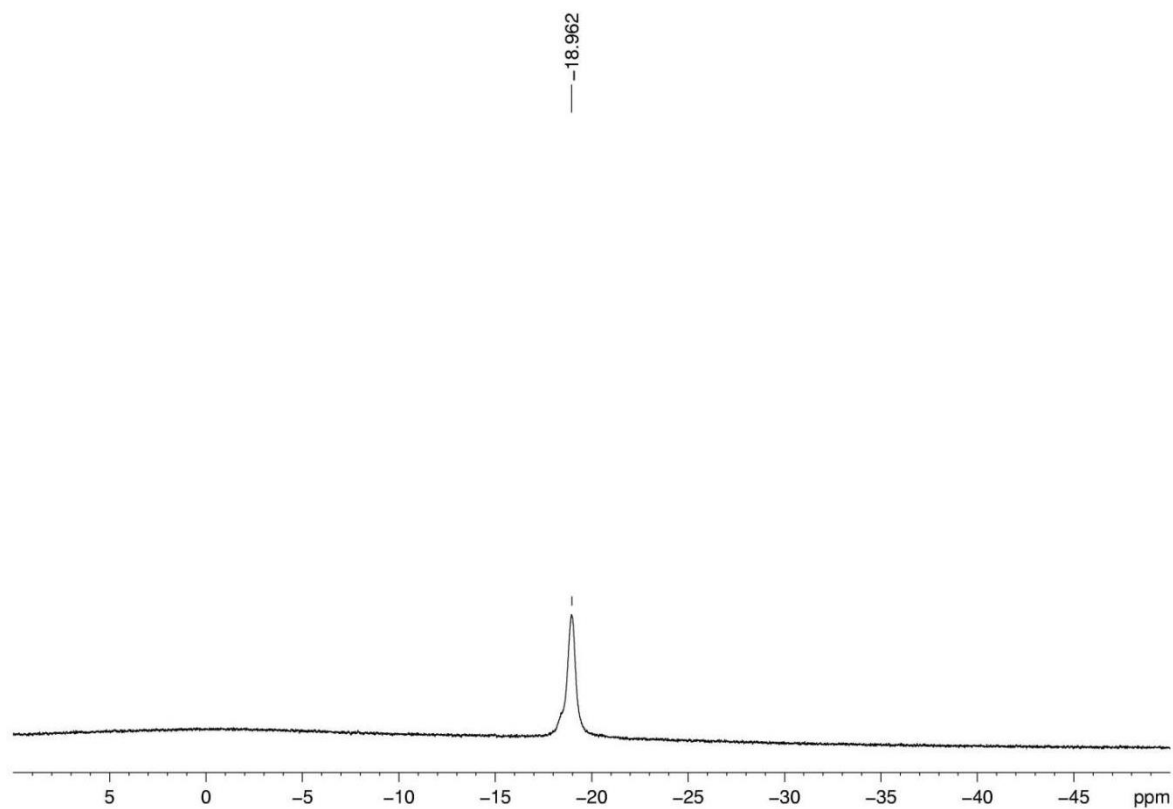
### Deuterium labeling experiment

Deuterated NHC-borane **1-d<sub>3</sub>** was used to conduct the disubstitution reaction under the standard conditions A. The desired di-substituted product **4-d<sub>1</sub>** was obtained in 43% yield after flash column chromatography, without deuteration at the  $\beta$ -position of boron atom as shown by  $^1\text{H}$  NMR.





**Figure S4.**  $^1\text{H}$  NMR spectrum of **4-d<sub>1</sub>**



**Figure S5.**  $^{11}\text{B}$  NMR spectrum of **4-d<sub>1</sub>**

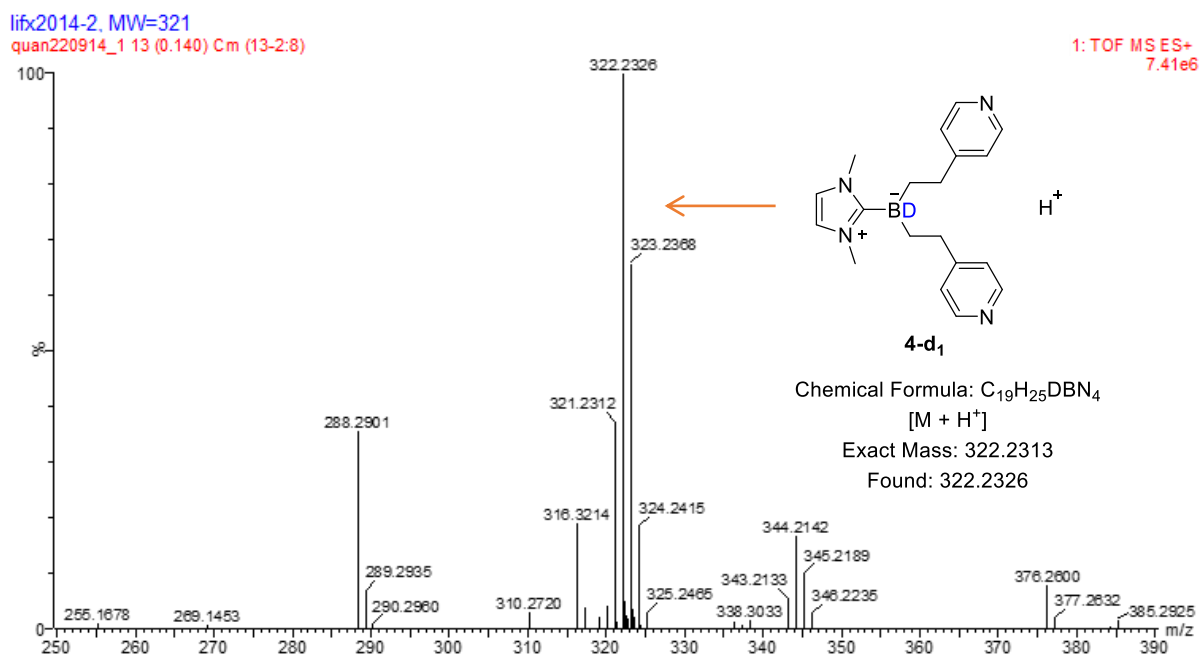
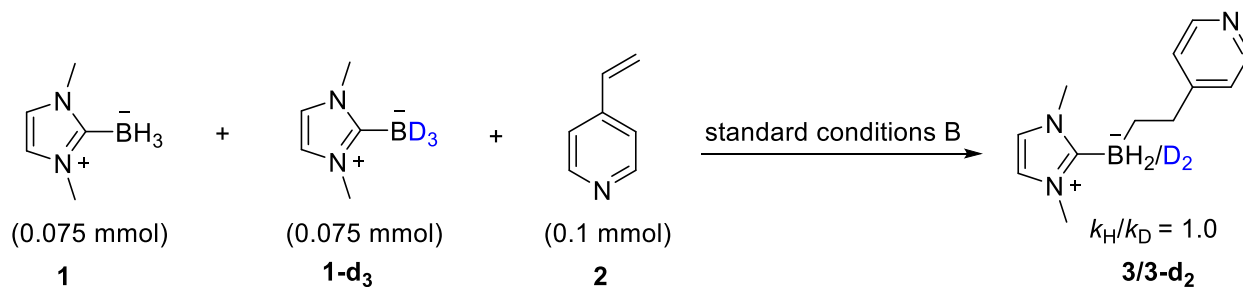
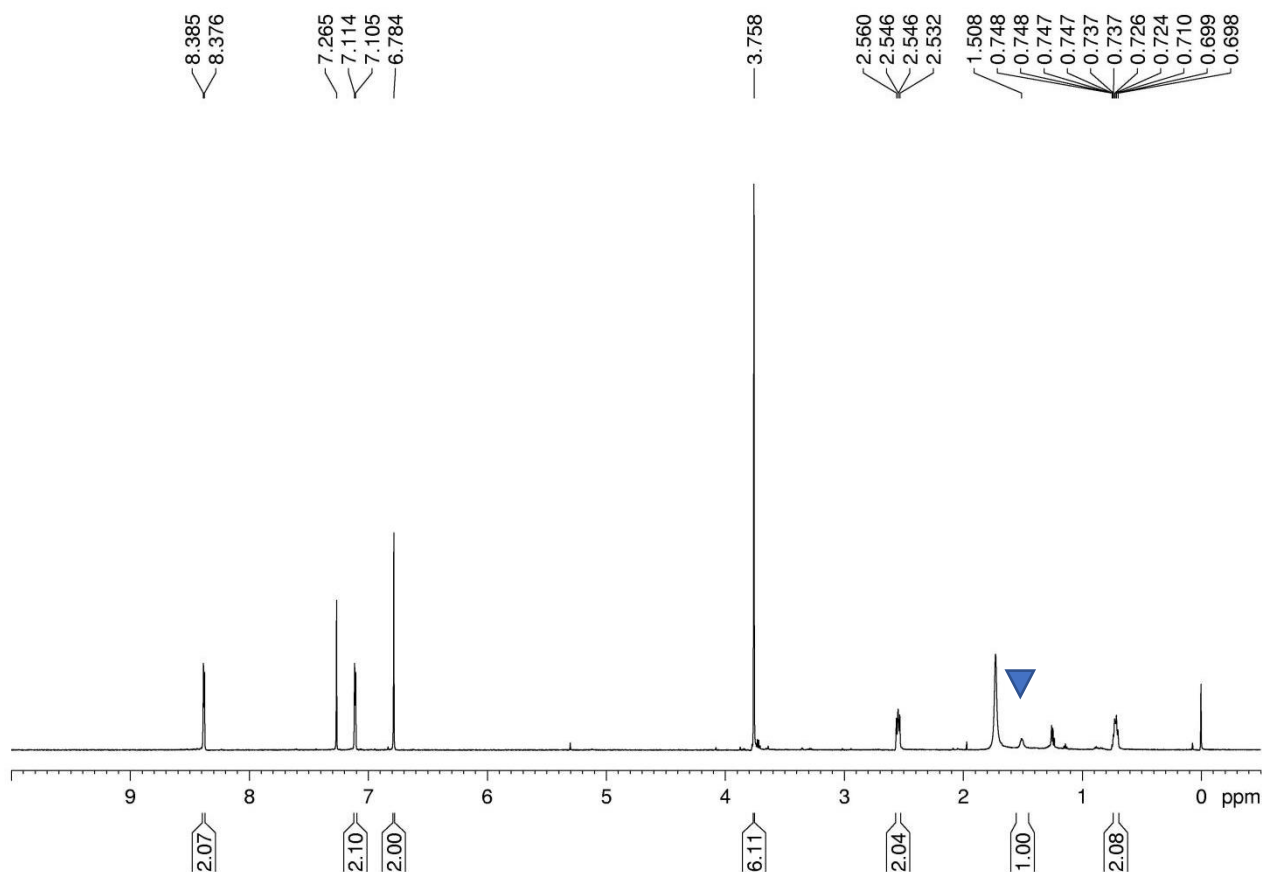


Figure S6. HRMS data of 4-d<sub>1</sub>

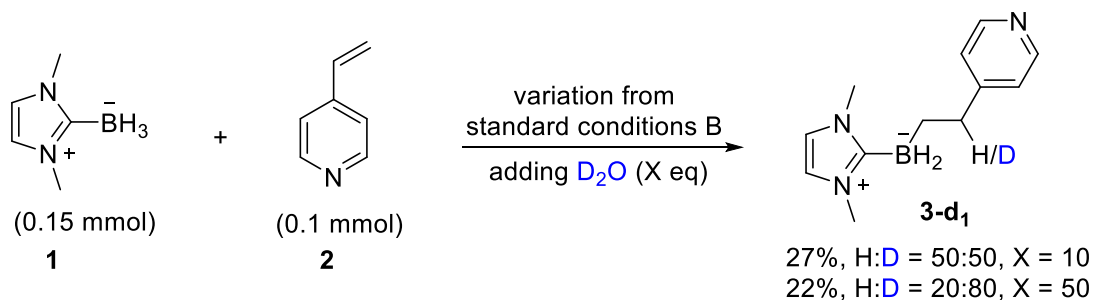
### KIE determination

In a glovebox, a 10 mL seal tube equipped with a magnetic stir bar was added NHC-BH<sub>3</sub> (8.2 mg, 0.075 mmol), NHC-BD<sub>3</sub> (8.2 mg, 0.075 mmol), 4-vinylpyridine (10.5 mg, 0.1 mmol), TBADT (3.3 mg, 0.001 mmol), Ph<sub>3</sub>CSH (5.5 mg, 0.02 mmol) and extra dry DMA (1 mL). The resulting mixture was then taken out of the glove box and stirred under irradiation of 390 nm LED (75 W) for 2 h at room temperature. The reaction was quenched with water and extracted with ethyl acetate. The combined organic layer was washed with water and brine, dried over MgSO<sub>4</sub>, filtered, and concentrated. The crude residue was purified by flash column chromatography to give a 1.1 mg mixture of **3** and **3-d<sub>2</sub>** with a ratio of 1:1 (determined by <sup>11</sup>B-decoupled <sup>1</sup>H NMR) in 5% yield.

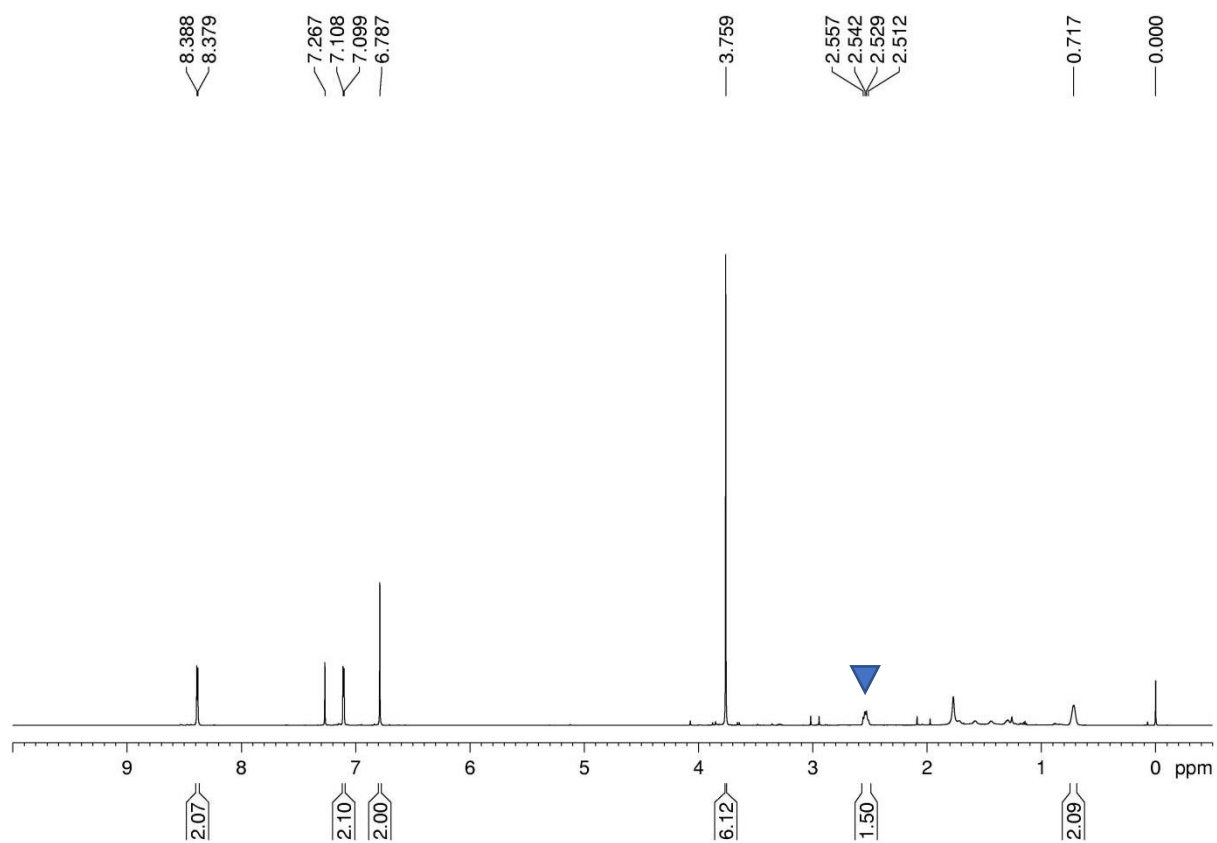




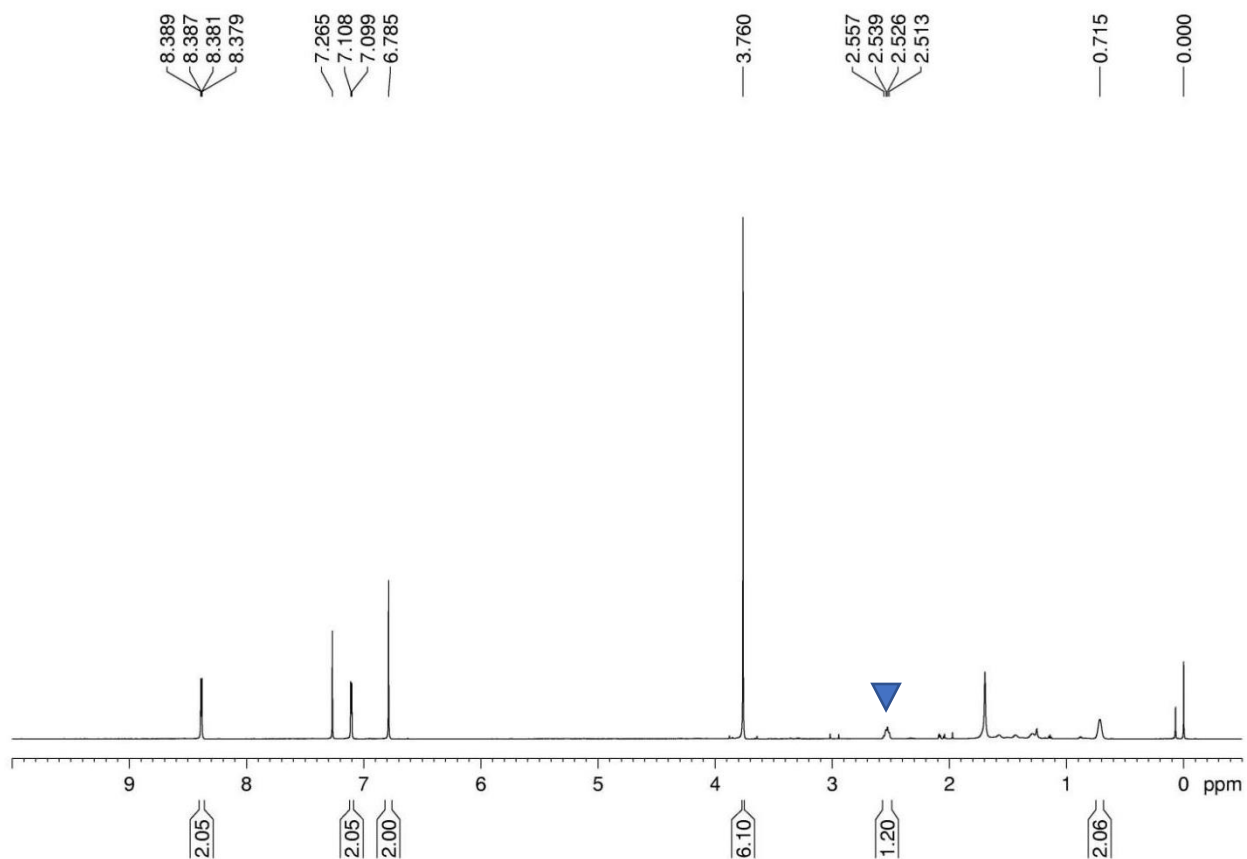
**Figure S7.**  $^{11}\text{B}$ -decoupled  $^1\text{H}$  NMR spectrum of a mixture of **3/3-d<sub>2</sub>**



The designed reactions were set up by adding 10 or 50 equiv. of  $\text{D}_2\text{O}$  to the reaction mixture under the standard conditions B. The mono-substituted product **3-d<sub>1</sub>** was analyzed by  $^1\text{H}$  NMR, indicating 50% and 80% deuteration of one of the  $\beta$ -hydrogens, respectively.



**Figure S8.**  $^1\text{H}$  NMR spectrum of **3-d<sub>1</sub>** when adding 10 equiv. of  $\text{D}_2\text{O}$



**Figure S9.**  $^1\text{H}$  NMR spectrum of **3-d<sub>1</sub>** when adding 50 equiv. of  $\text{D}_2\text{O}$

lfx2062B-2, MW=216  
quan221025\_1 12 (0.131) Cm (12-1:8)

1: TOF MSES+  
6.99e6

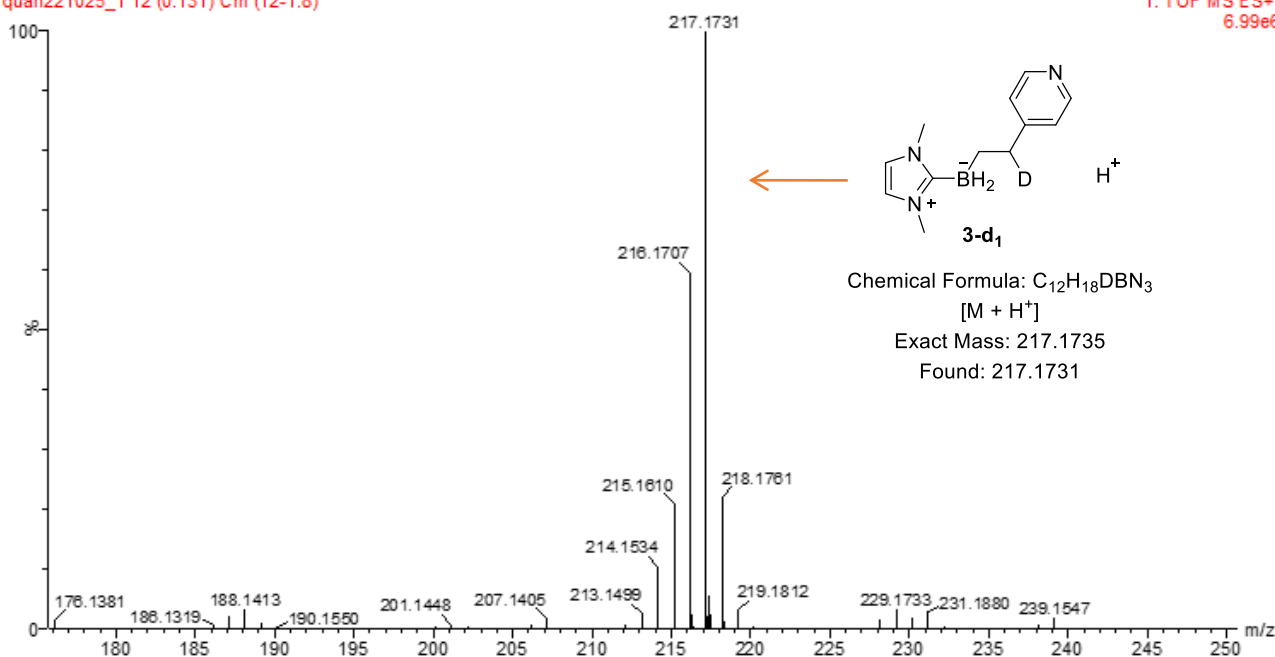
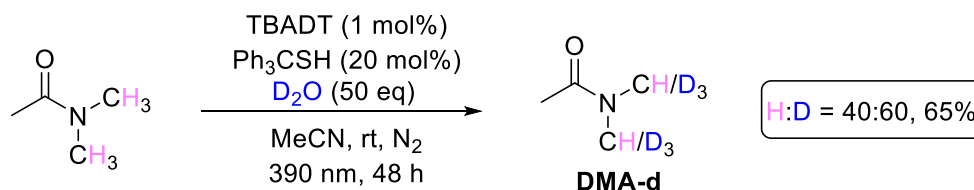
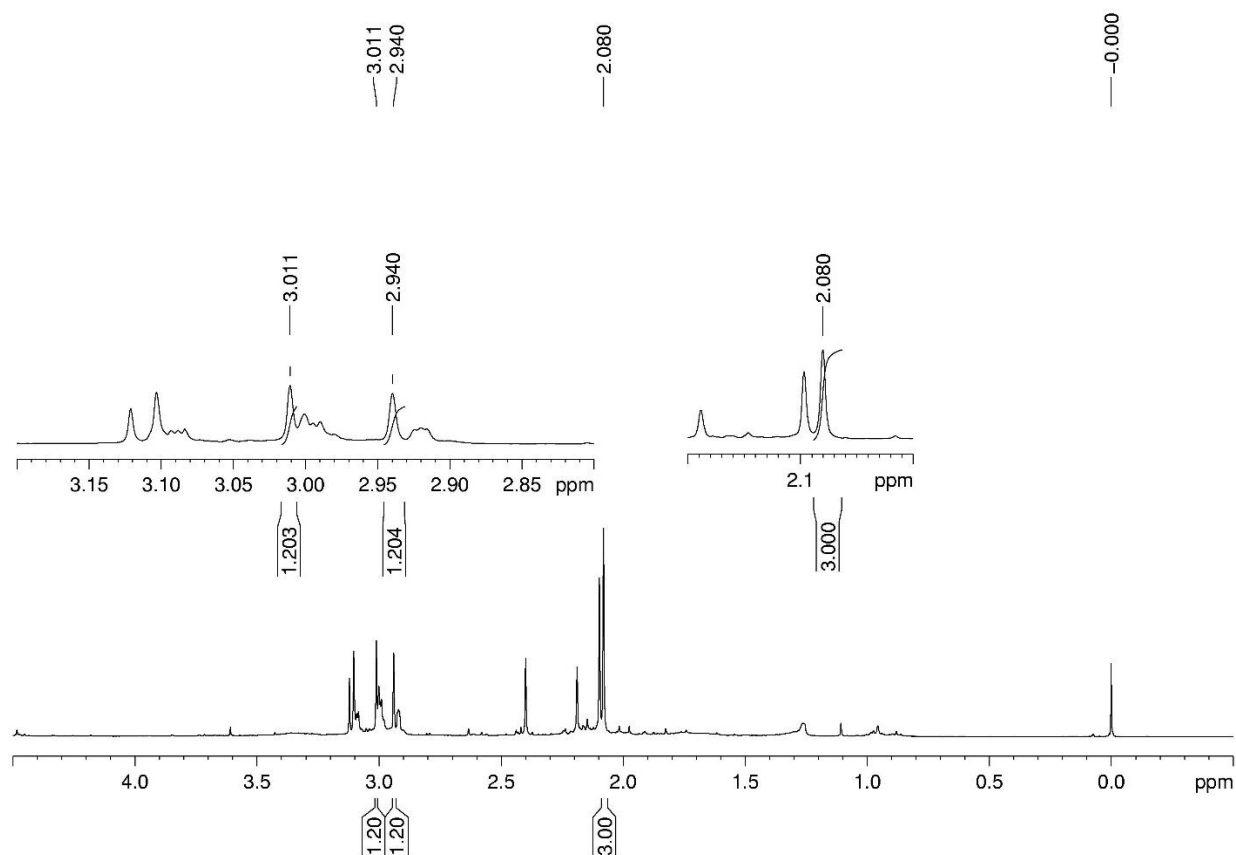


Figure S10. HRMS data of **3-d<sub>1</sub>**

In a glovebox, a 10 mL seal tube equipped with a magnetic stir bar was added extra dry DMA (8.7 mg, 0.1 mmol), TBADT (3.3 mg, 0.001 mmol), Ph<sub>3</sub>CSH (5.5 mg, 0.02 mmol), 50 equiv. of D<sub>2</sub>O and extra dry MeCN (1 mL). The reaction was then taken out of the glove box and stirred under irradiation of 390 nm LED (75 W) for 48 h at room temperature. The resulting reaction mixture was concentrated and analyzed by crude <sup>1</sup>H NMR, indicating 60% deuteration of two methyl groups bonded with nitrogen in DMA, evidencing the H/D exchange between DMA and D-thiol, originating from the H/D exchange between thiol and D<sub>2</sub>O.

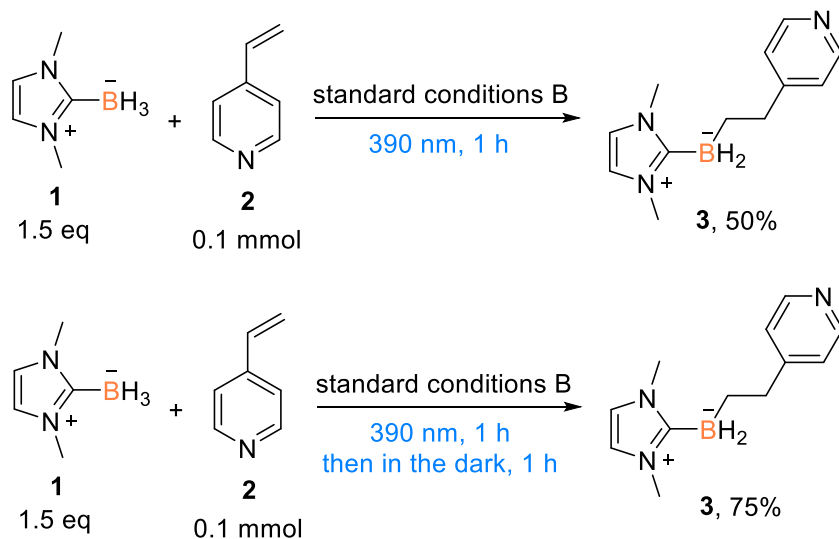




**Figure S11.** Crude  $^1\text{H}$  NMR spectrum of DMA-d

### Light on/off experiments

Light on/off experiments of monosubstitution reaction were set up parallel on a 0.1 mmol scale according to the standard conditions B. After being irradiated for 1 h, one light-on reaction stopped, and another reaction continued stirring for 1 h in the dark. Both of their yields were analyzed in the identical way (determined by  $^1\text{H}$  NMR using  $\text{CH}_2\text{Br}_2$  as the internal standard). The results suggested the continuation of coupling reaction in the dark, supporting the HAT reaction between thiyl radical and borane as well as the involvement of a radical chain pathway.

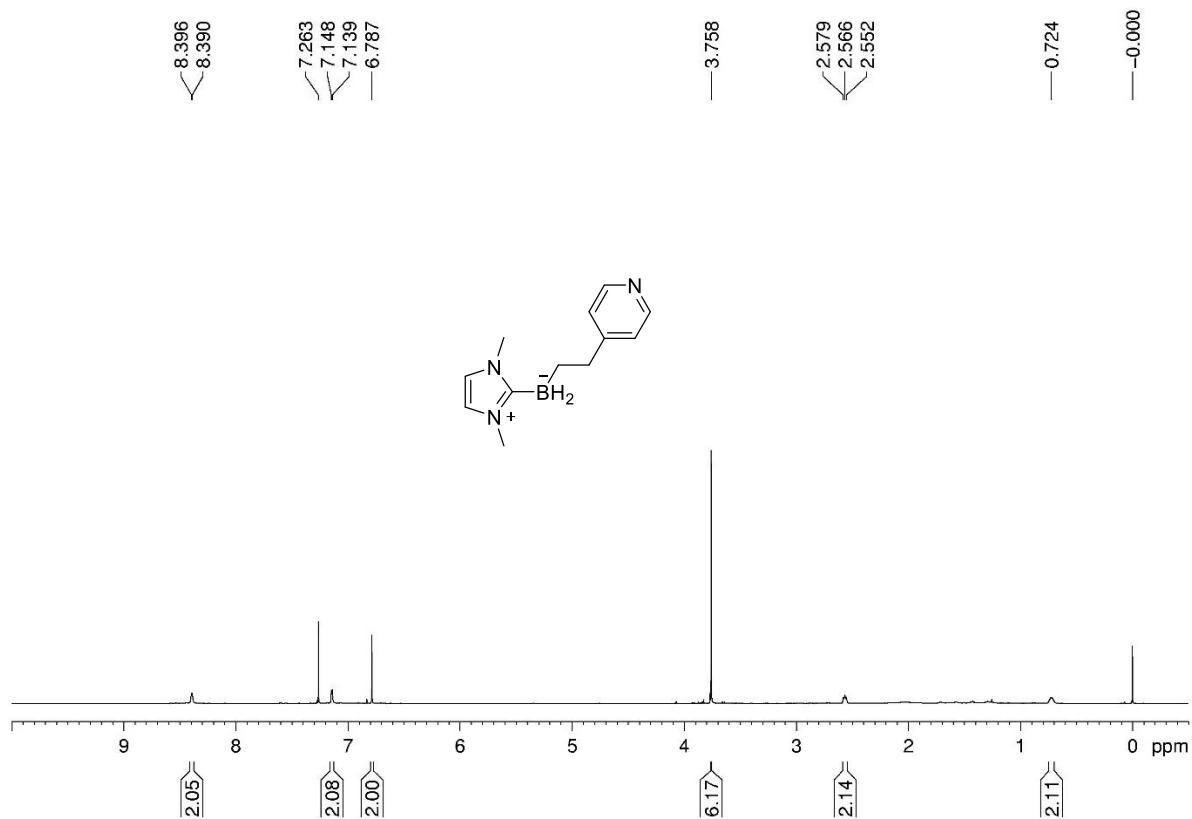


**Scheme S2.** Light on/off experiments

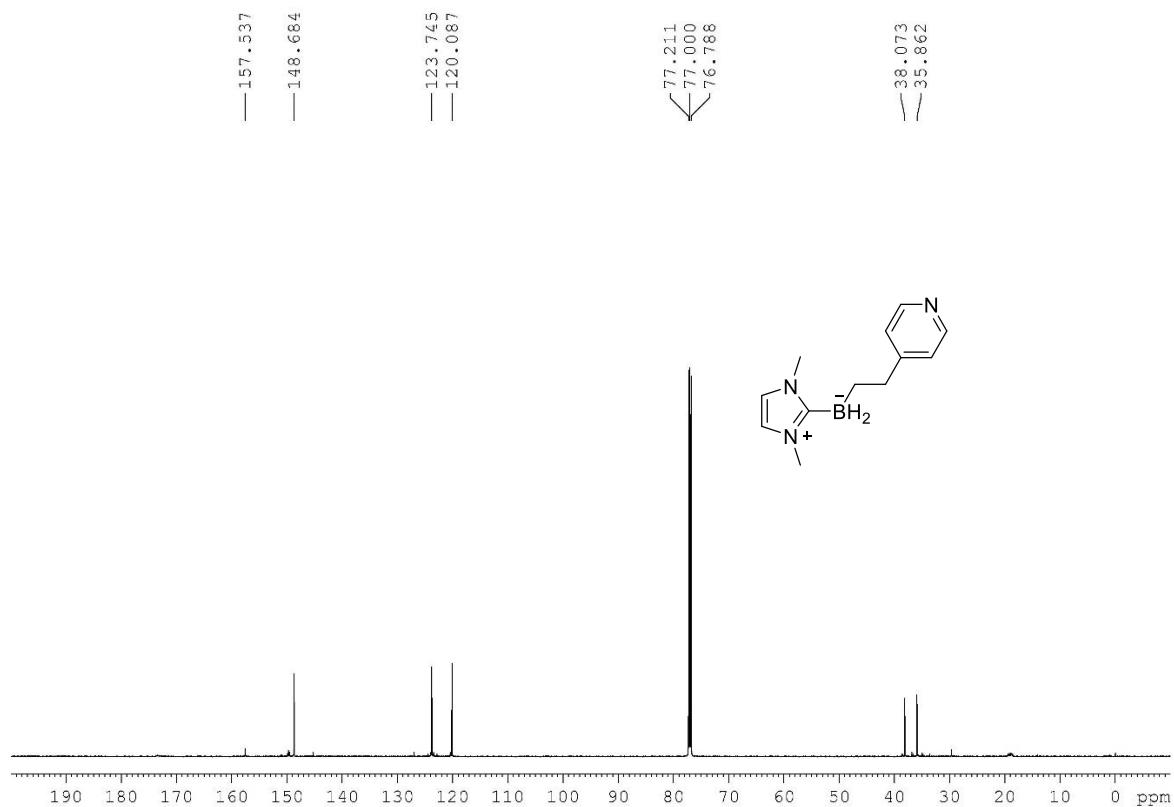


## 7. NMR Spectra

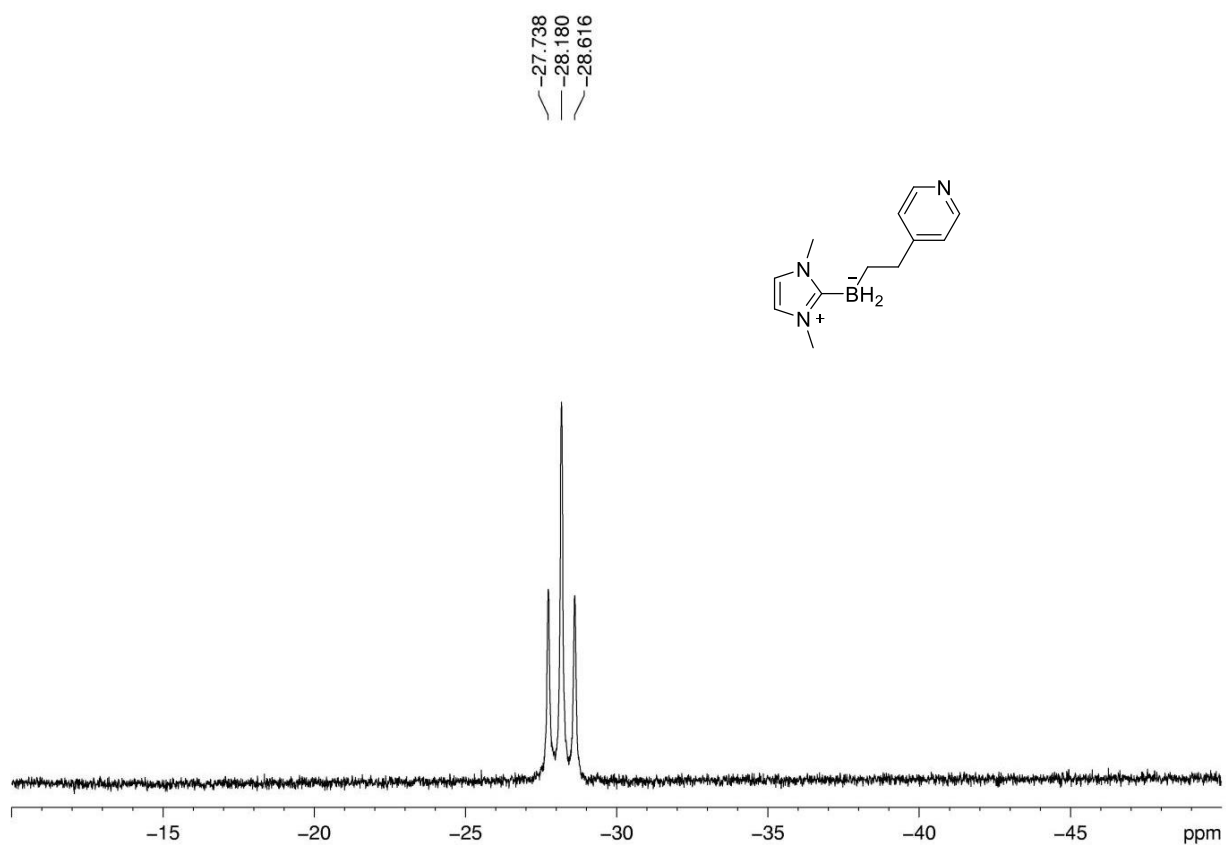
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **3**



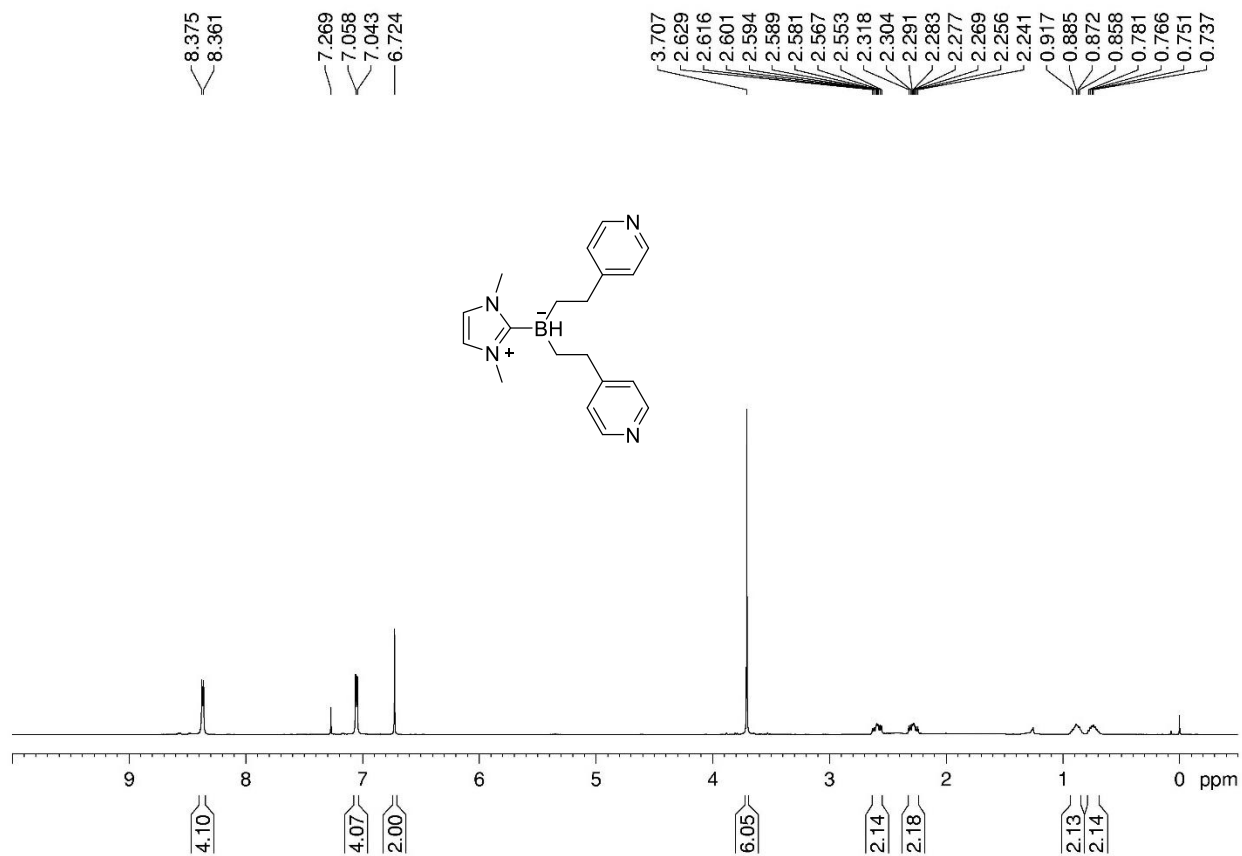
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **3**



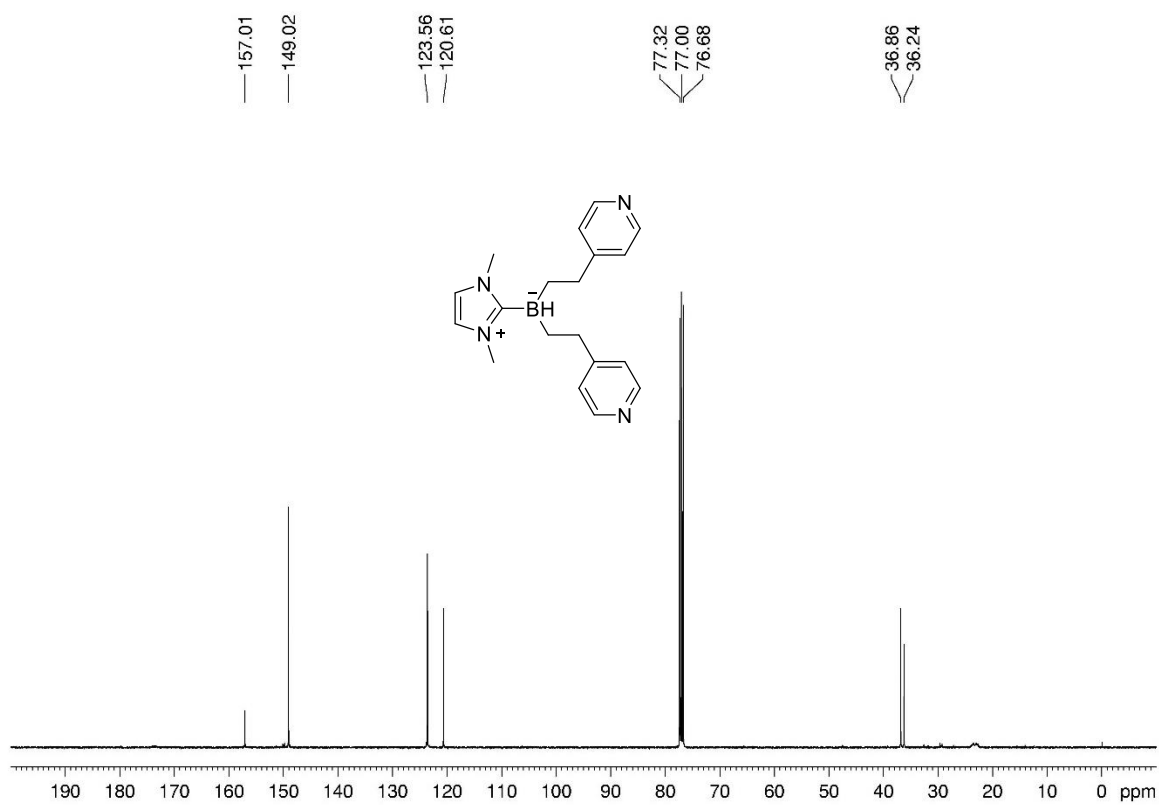
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **3**



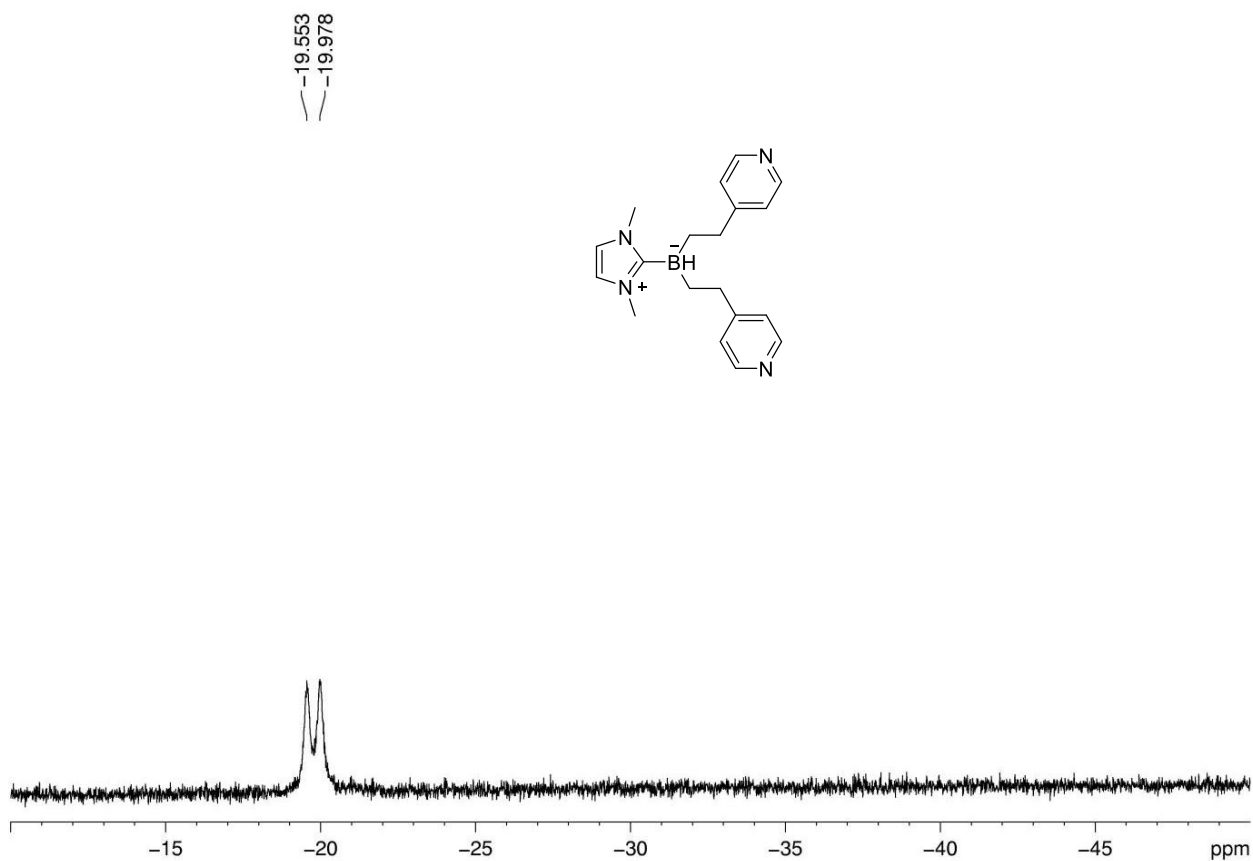
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **4**



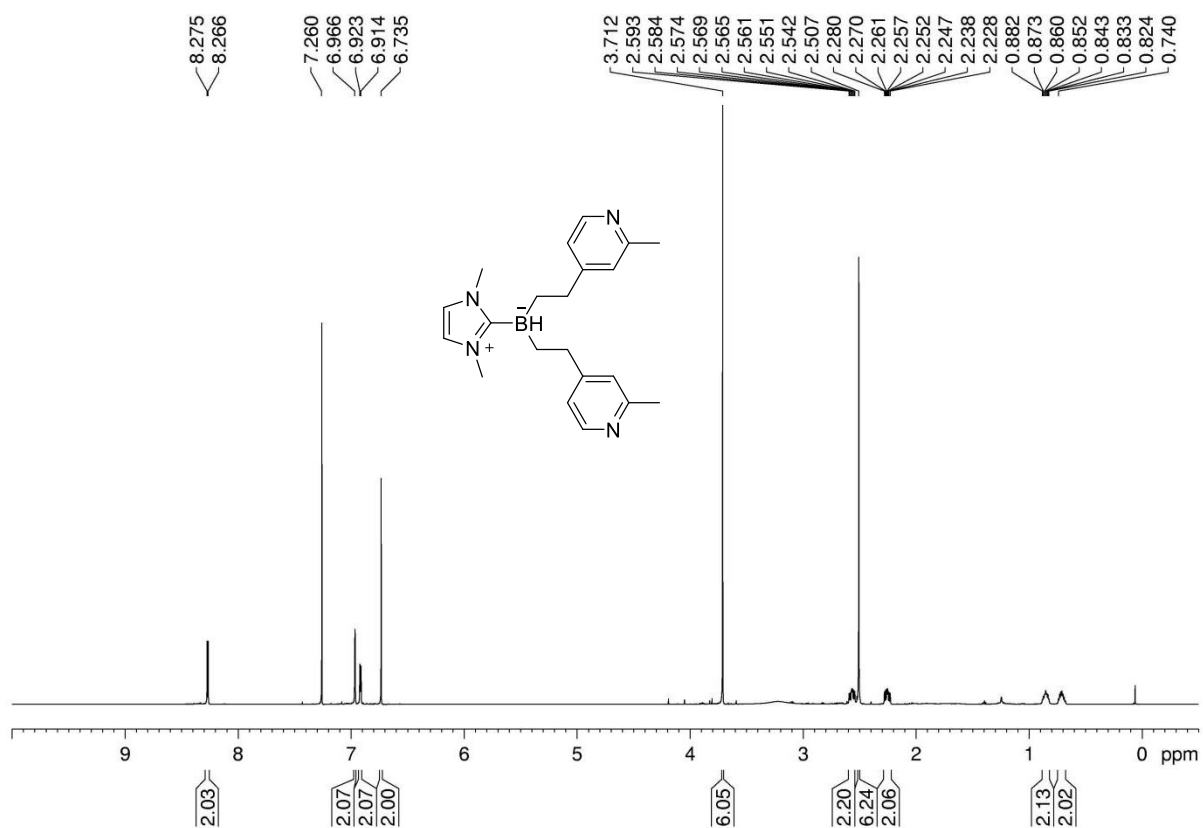
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **4**



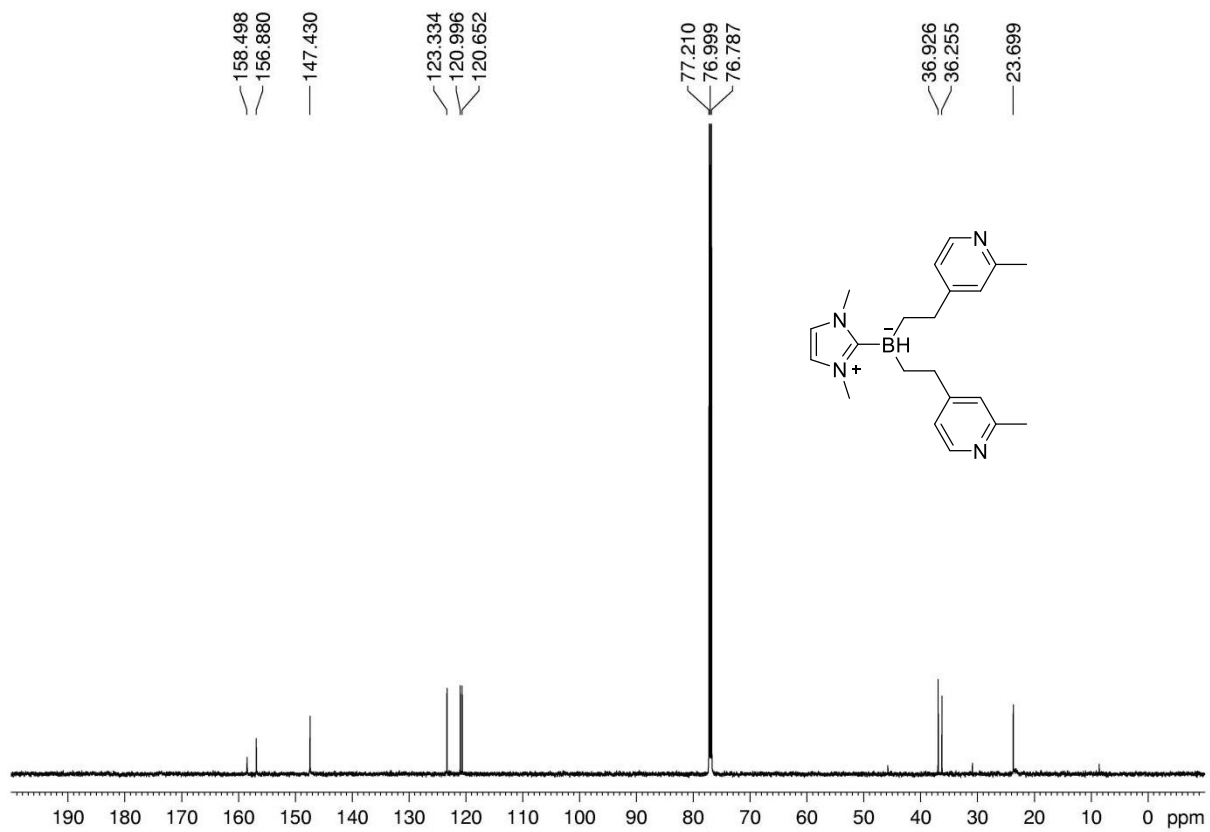
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **4**



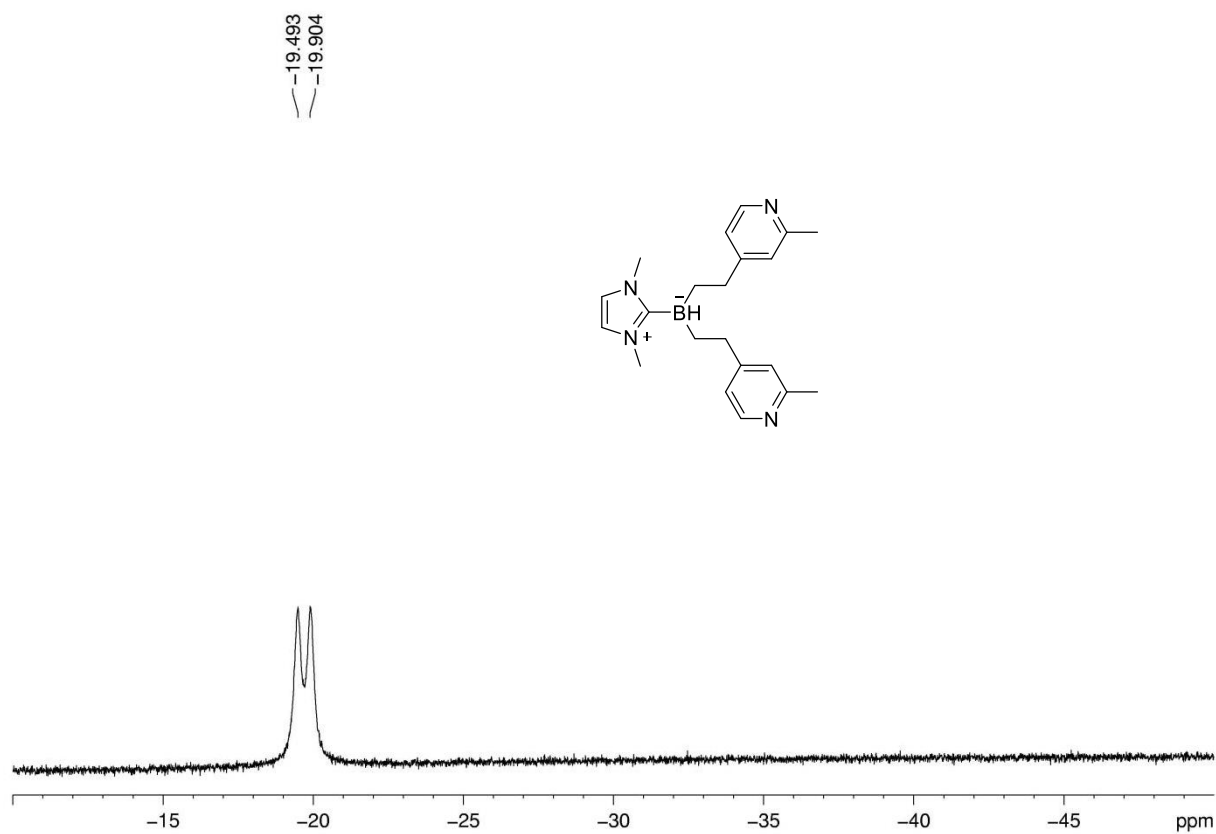
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **5**



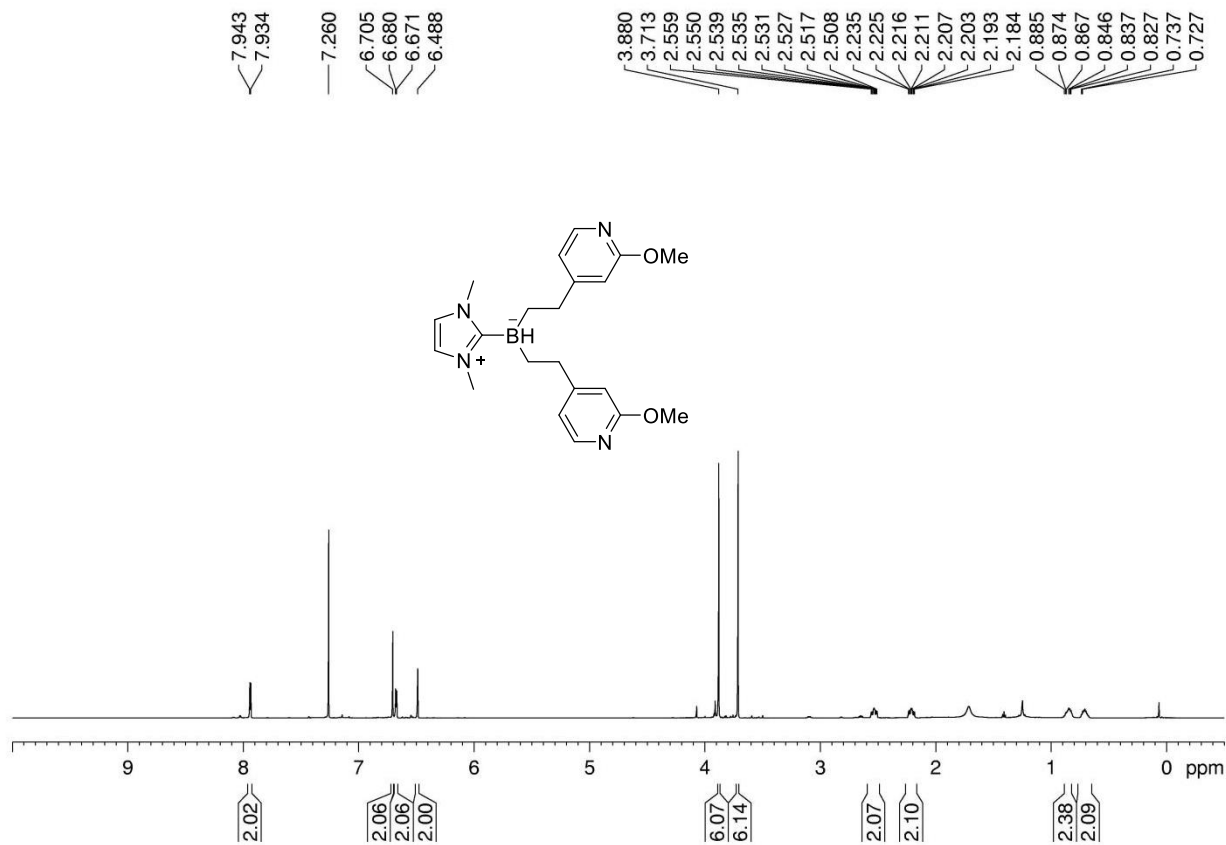
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **5**



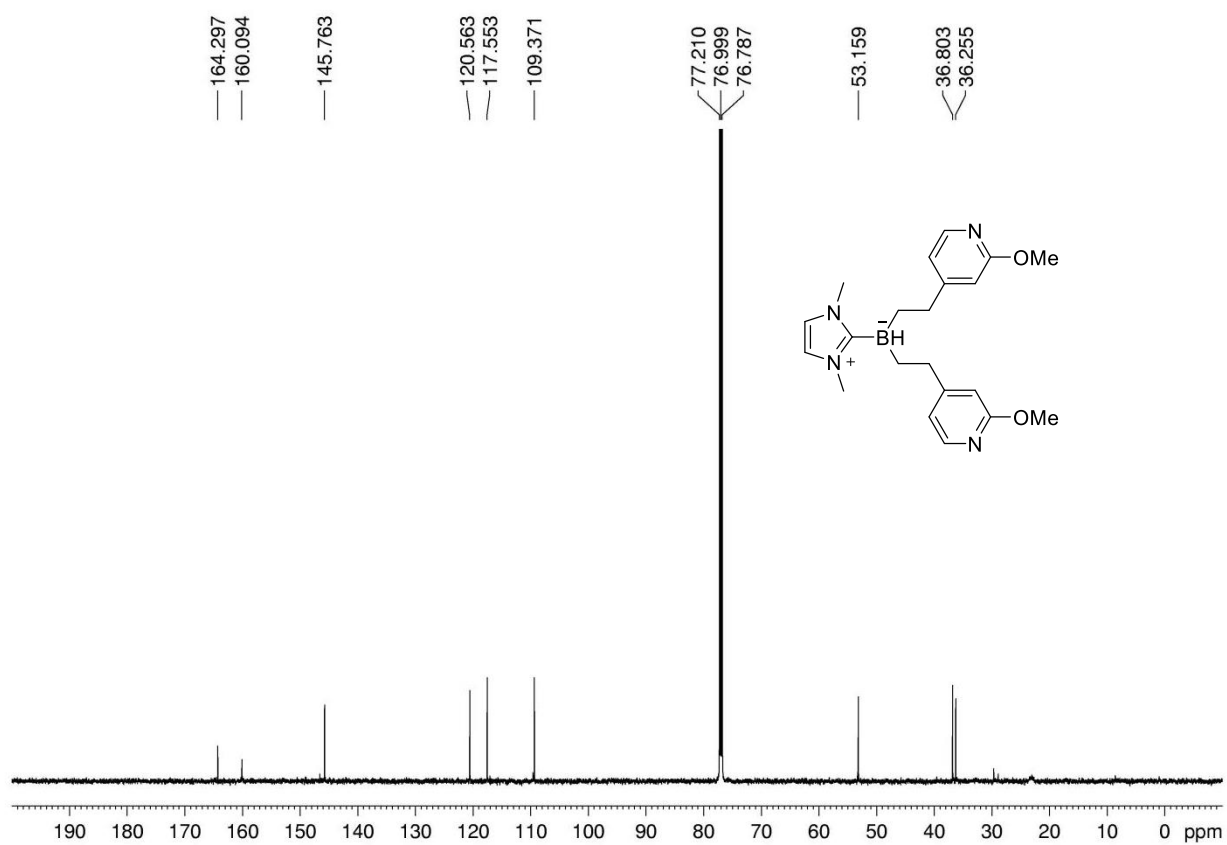
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **5**



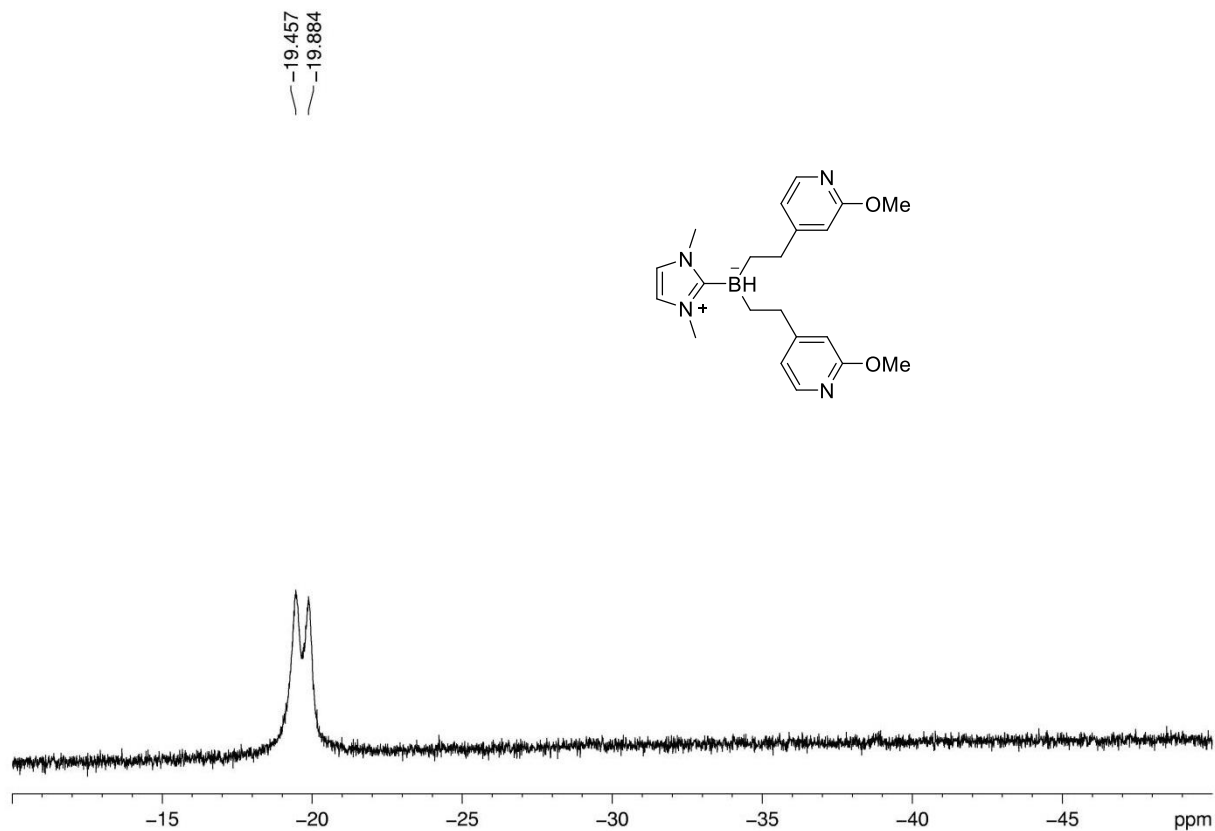
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **6**



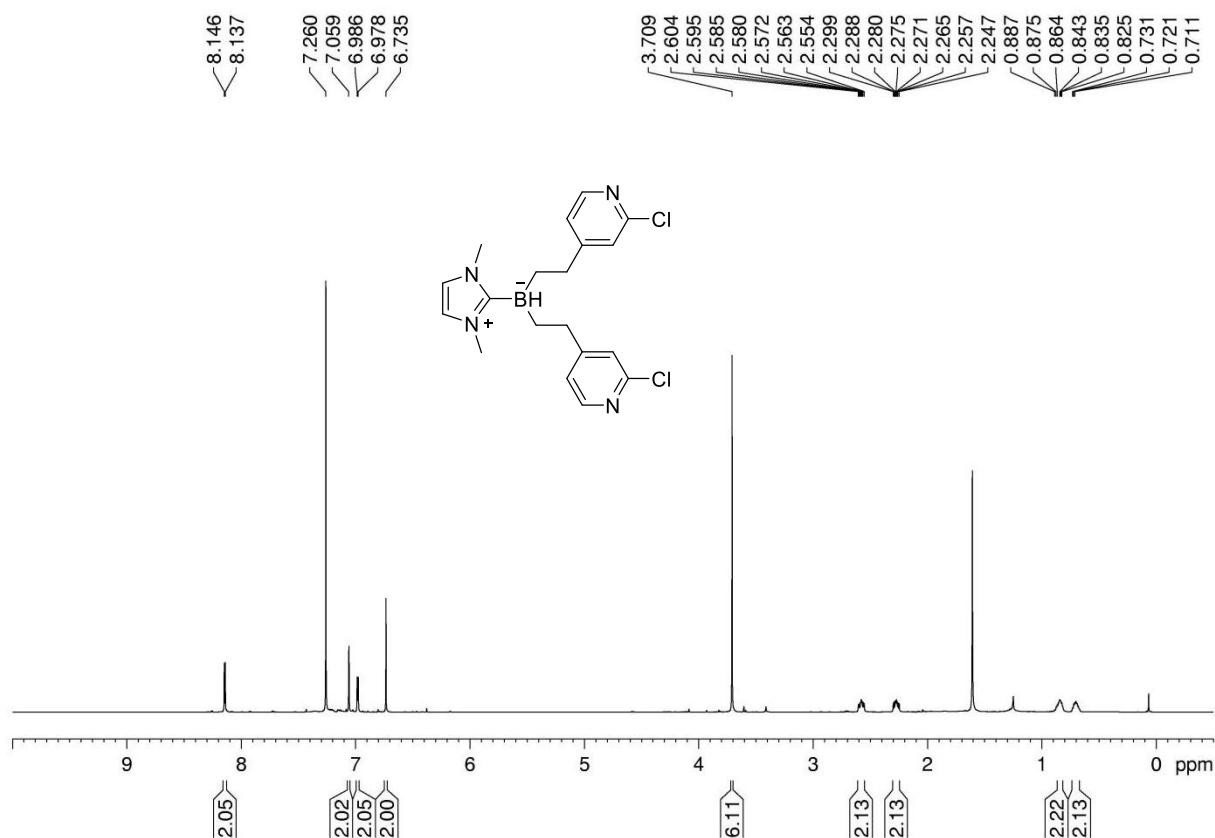
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **6**



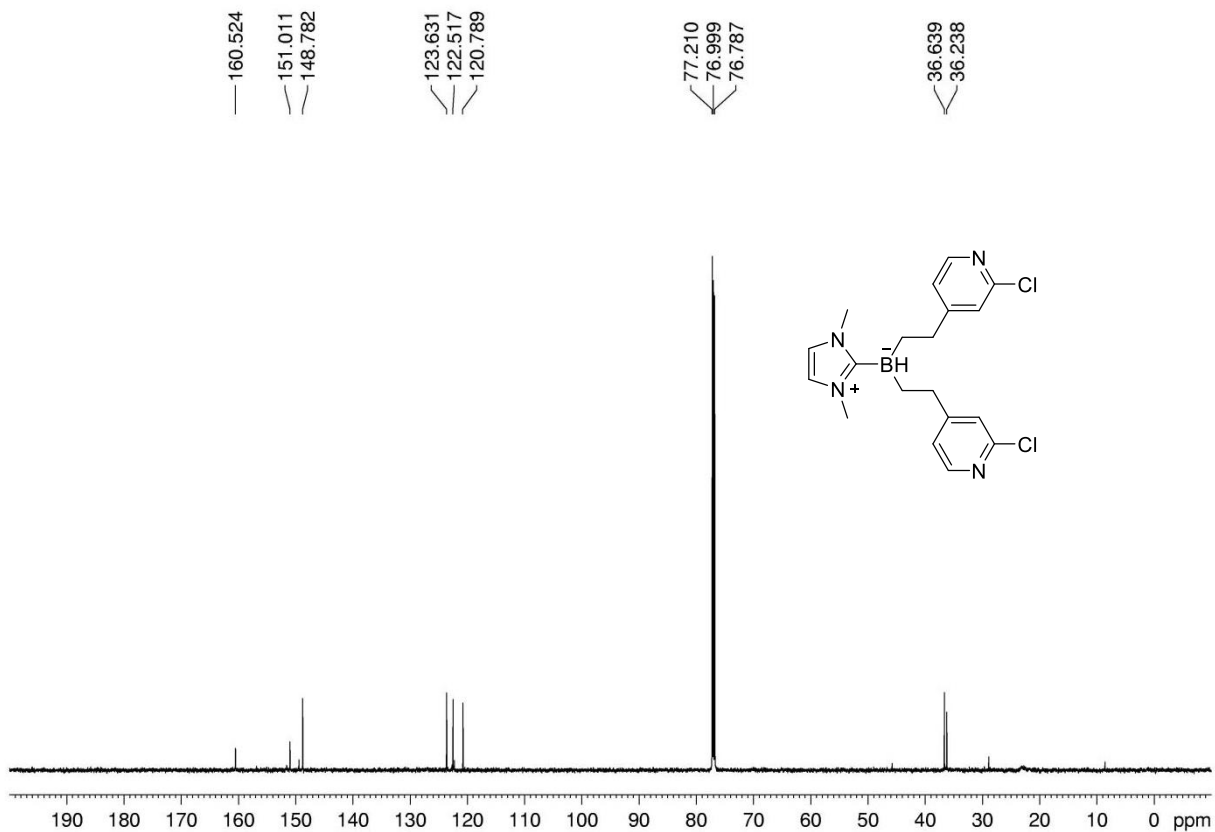
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **6**



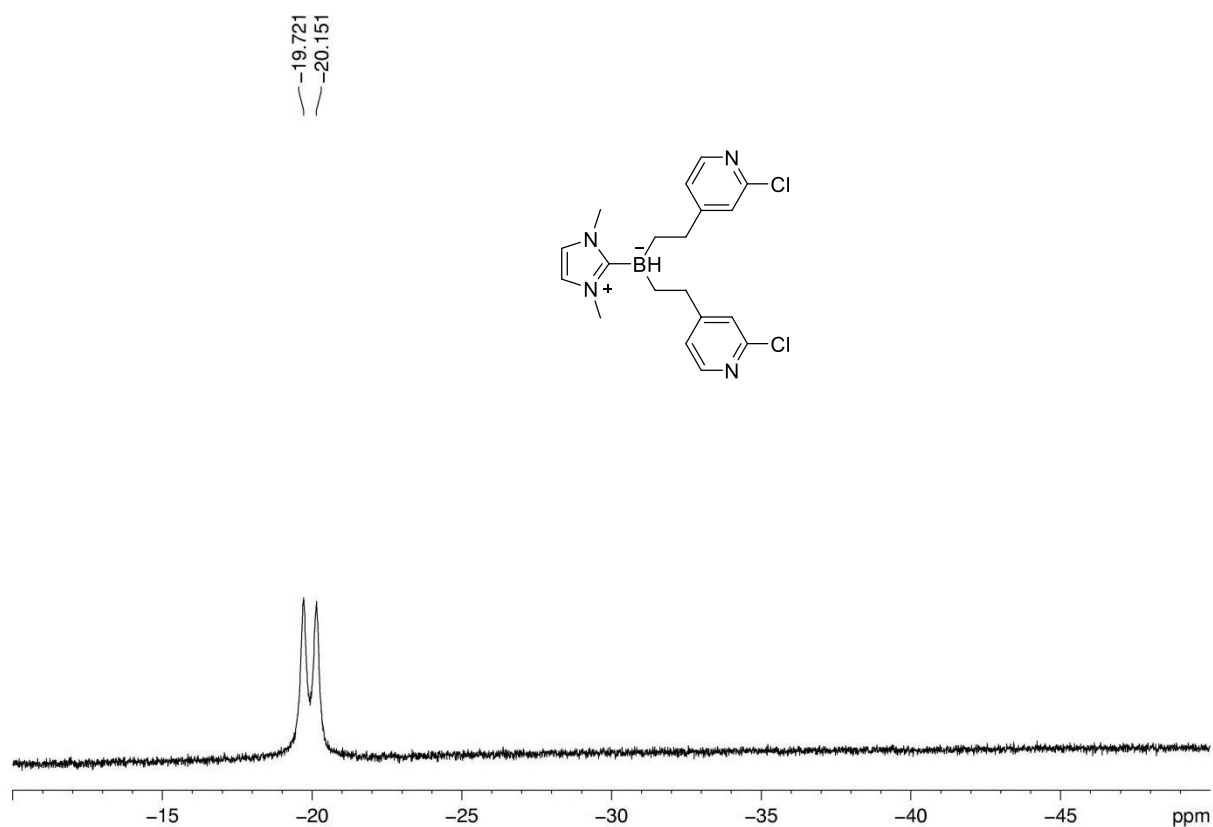
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **7**



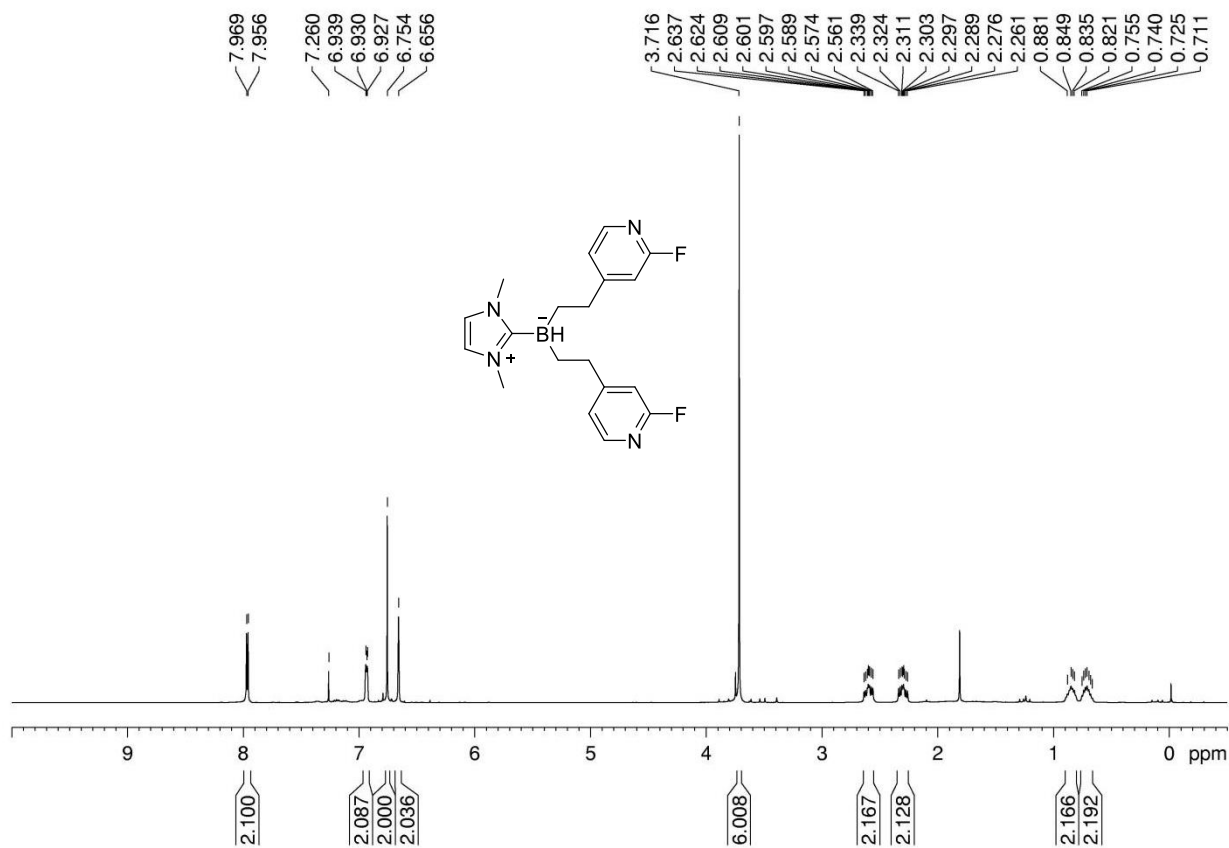
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **7**



$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **7**

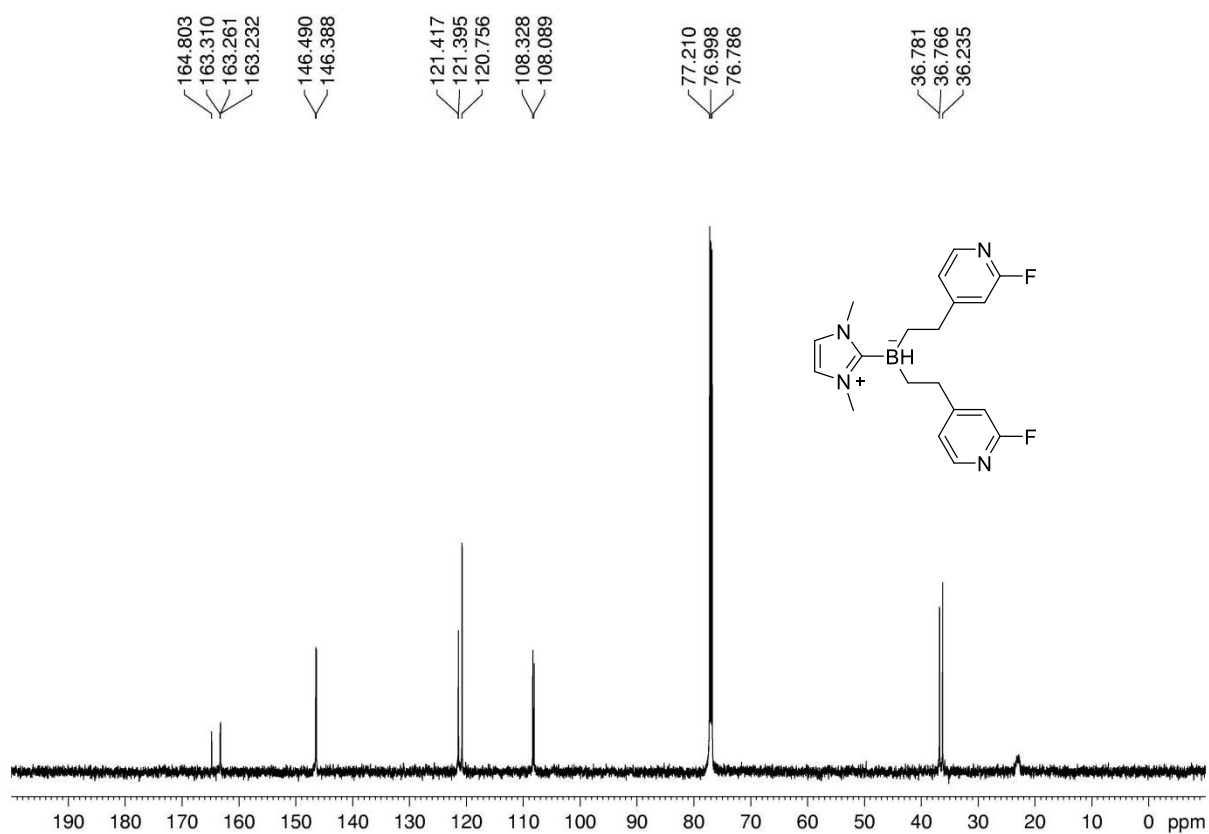


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **8**

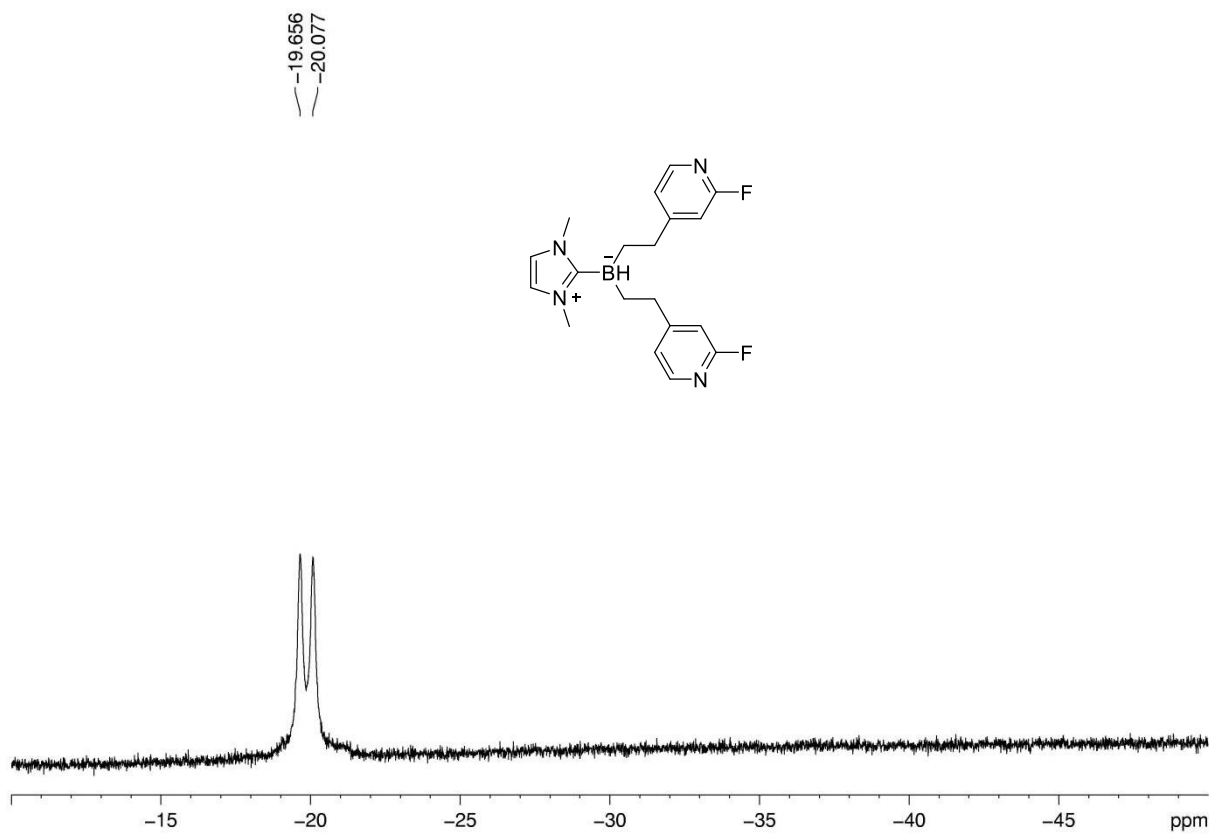




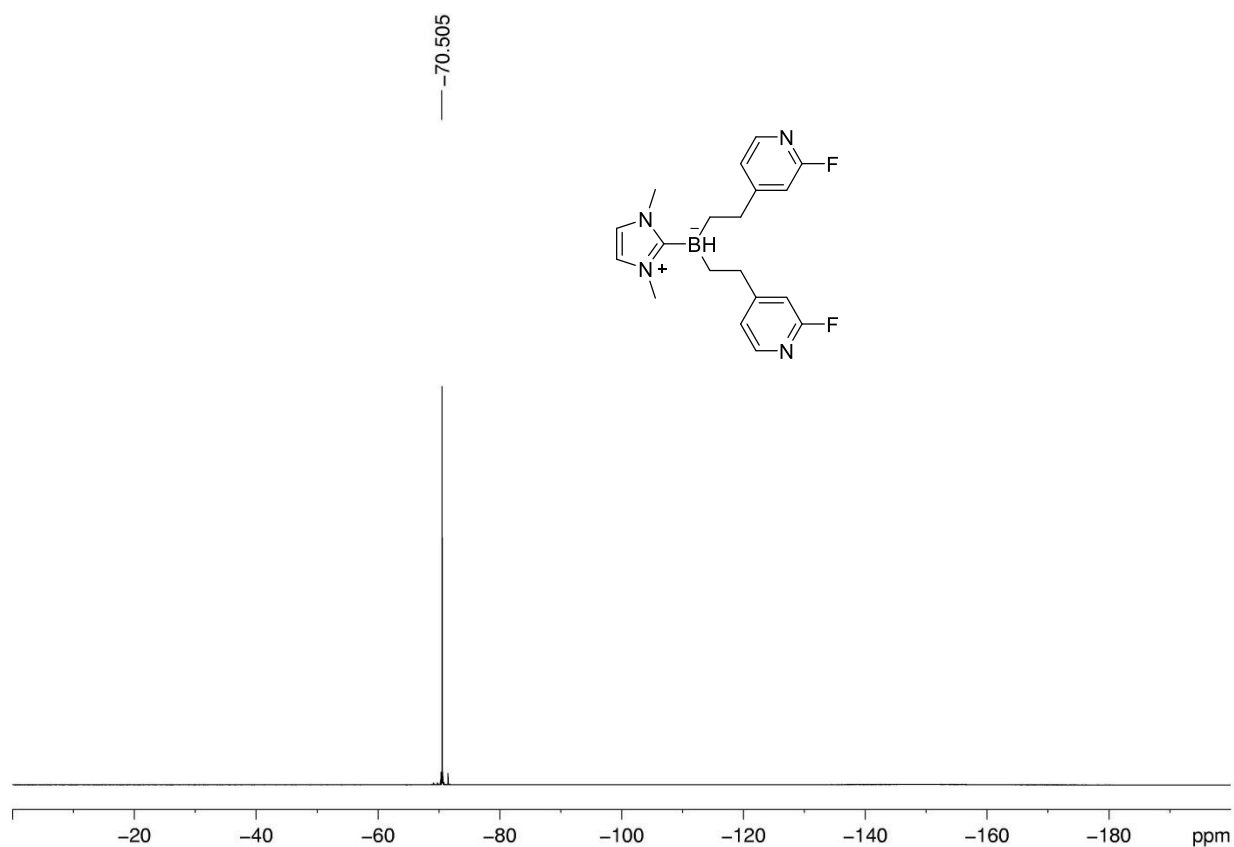
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **8**



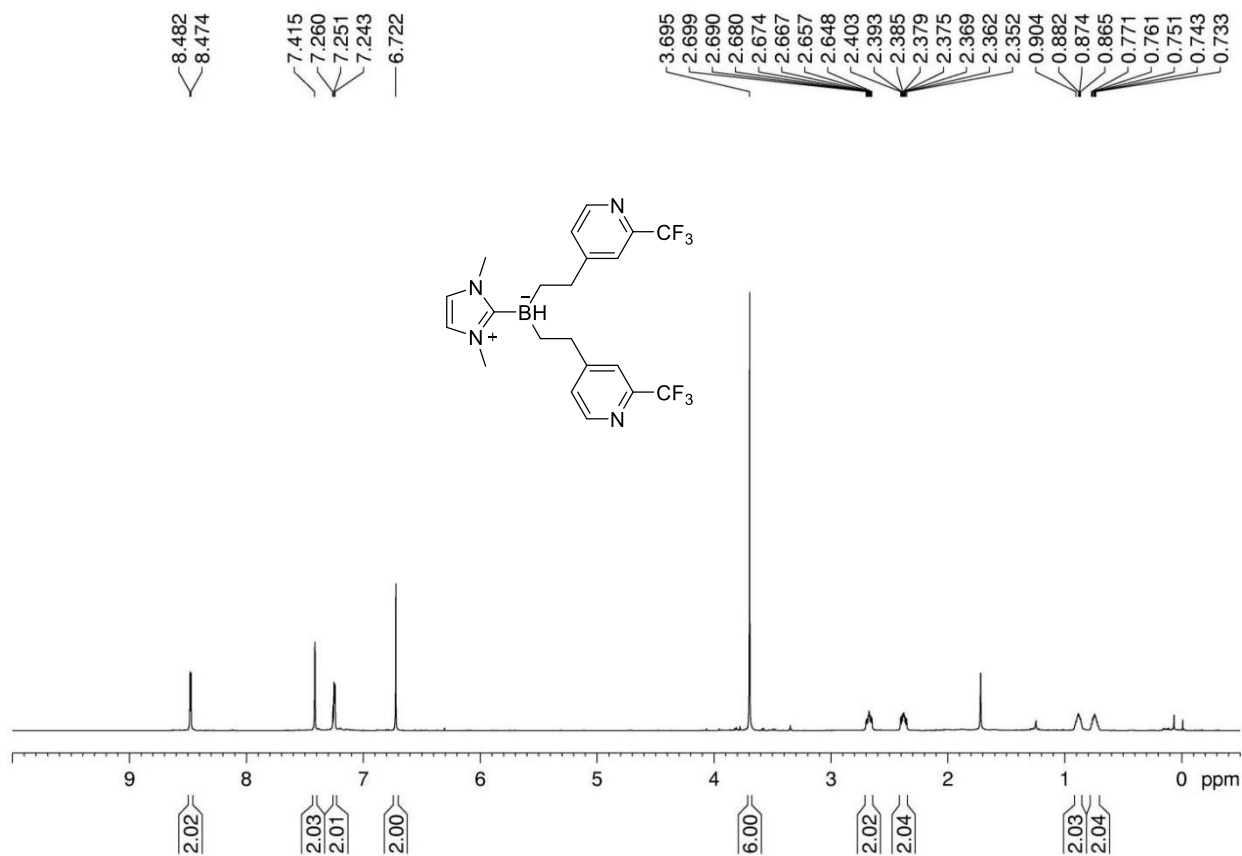
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **8**



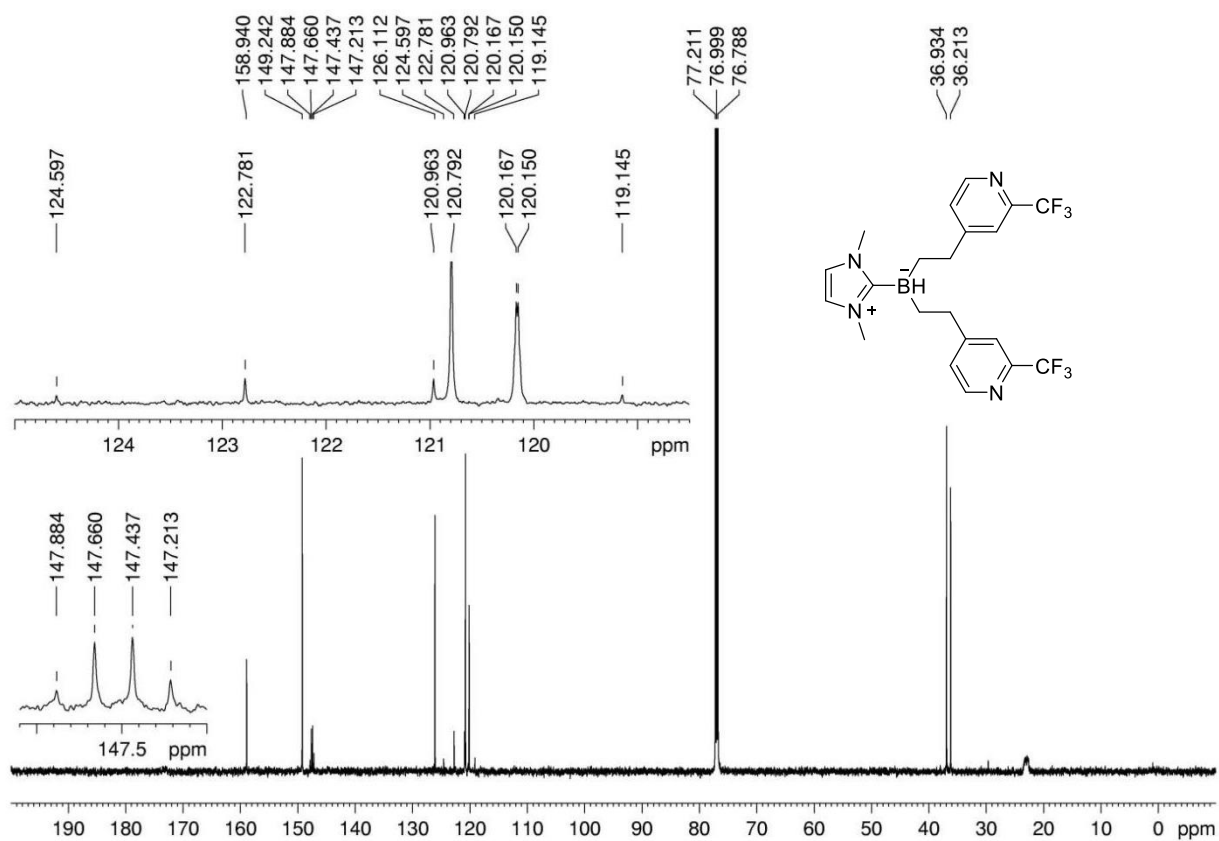
$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 564 MHz) spectrum of **8**



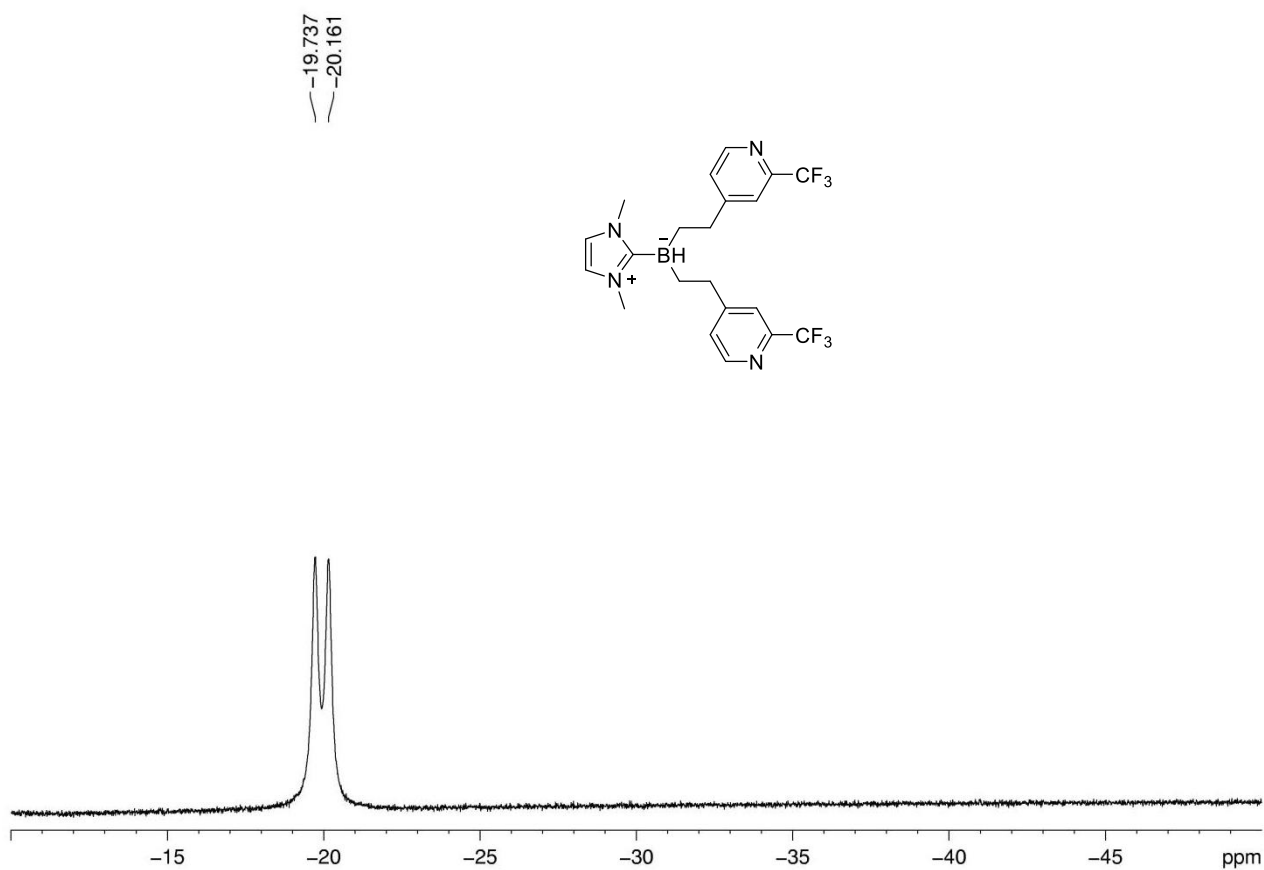
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **9**



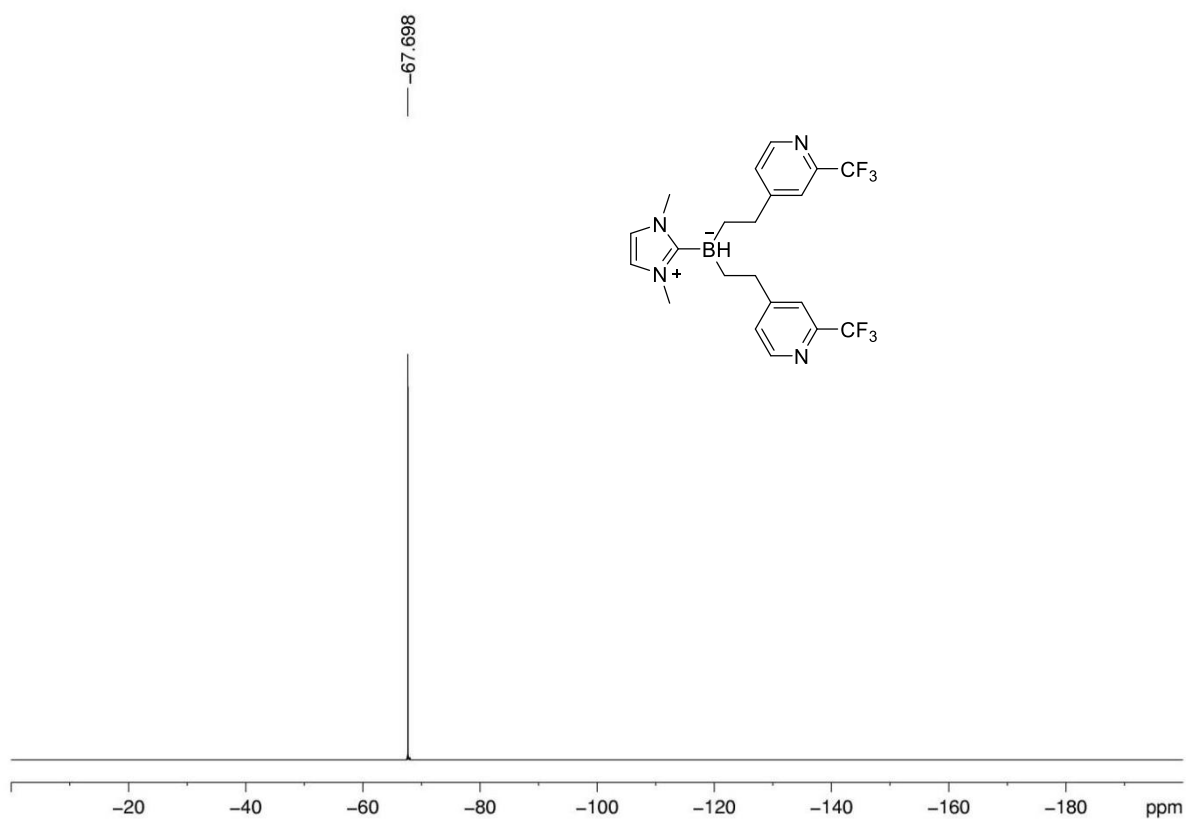
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **9**



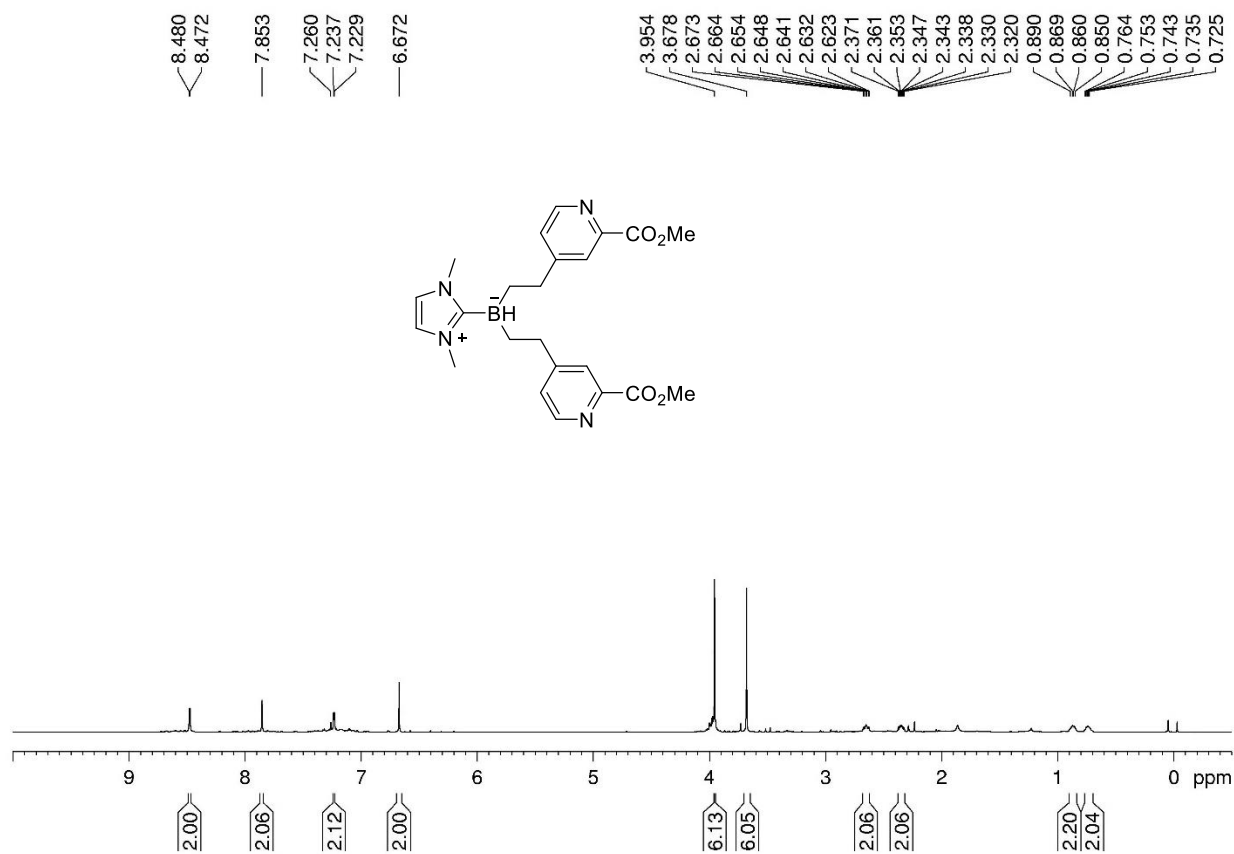
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **9**



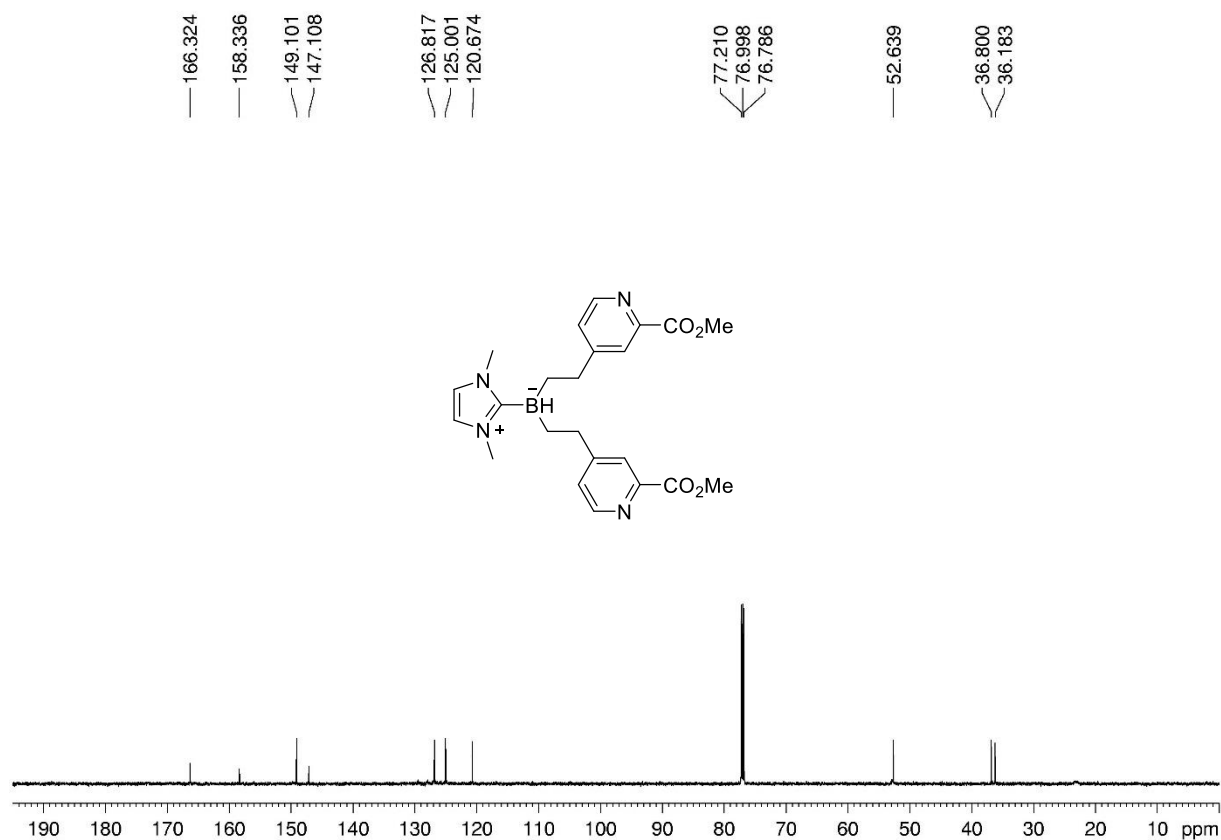
$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 564 MHz) spectrum of **9**



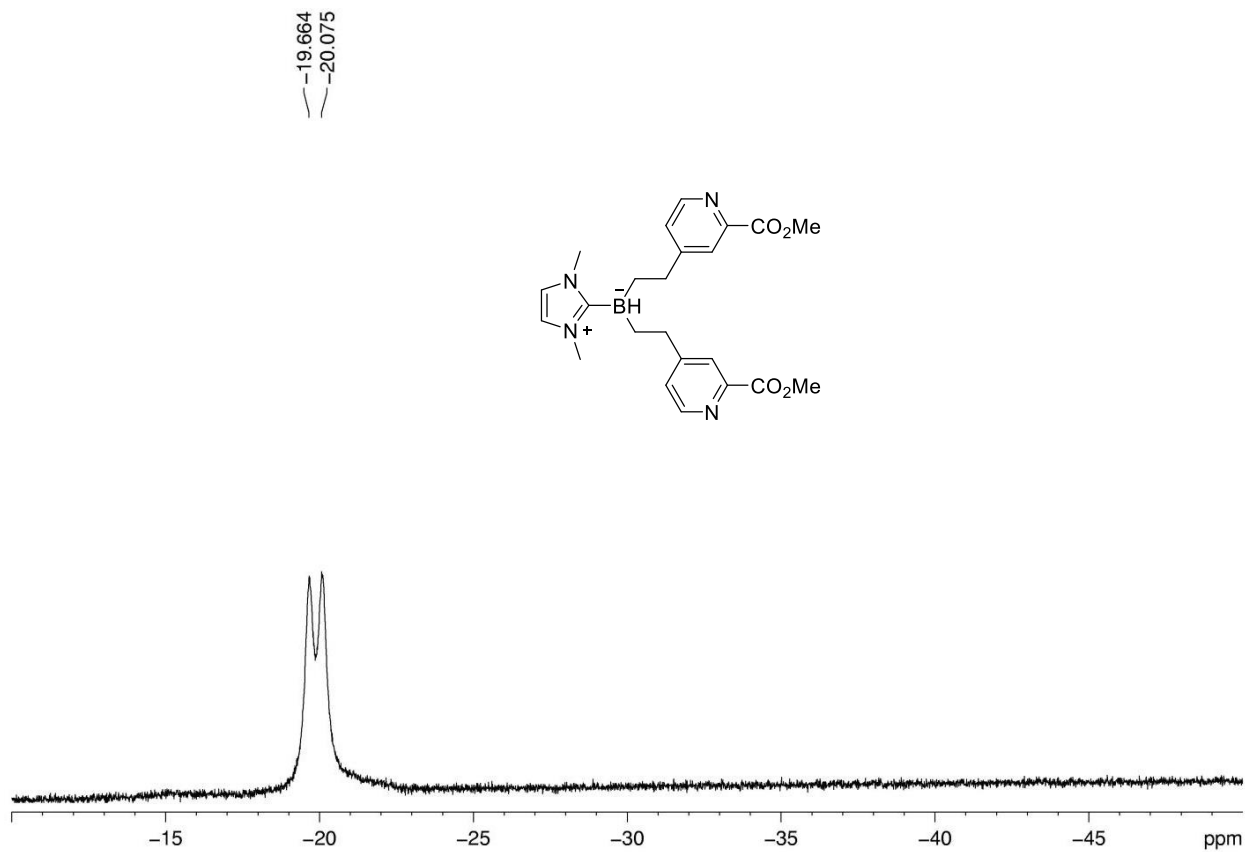
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **10**



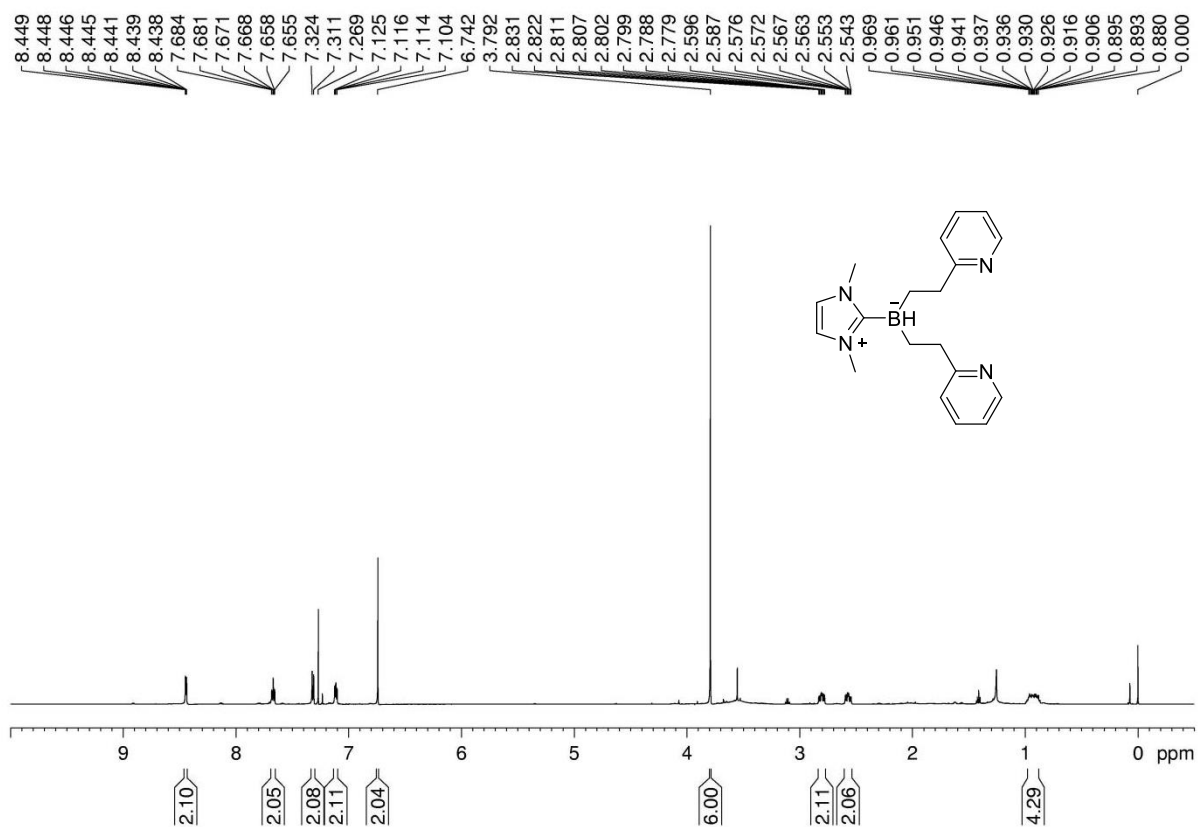
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **10**



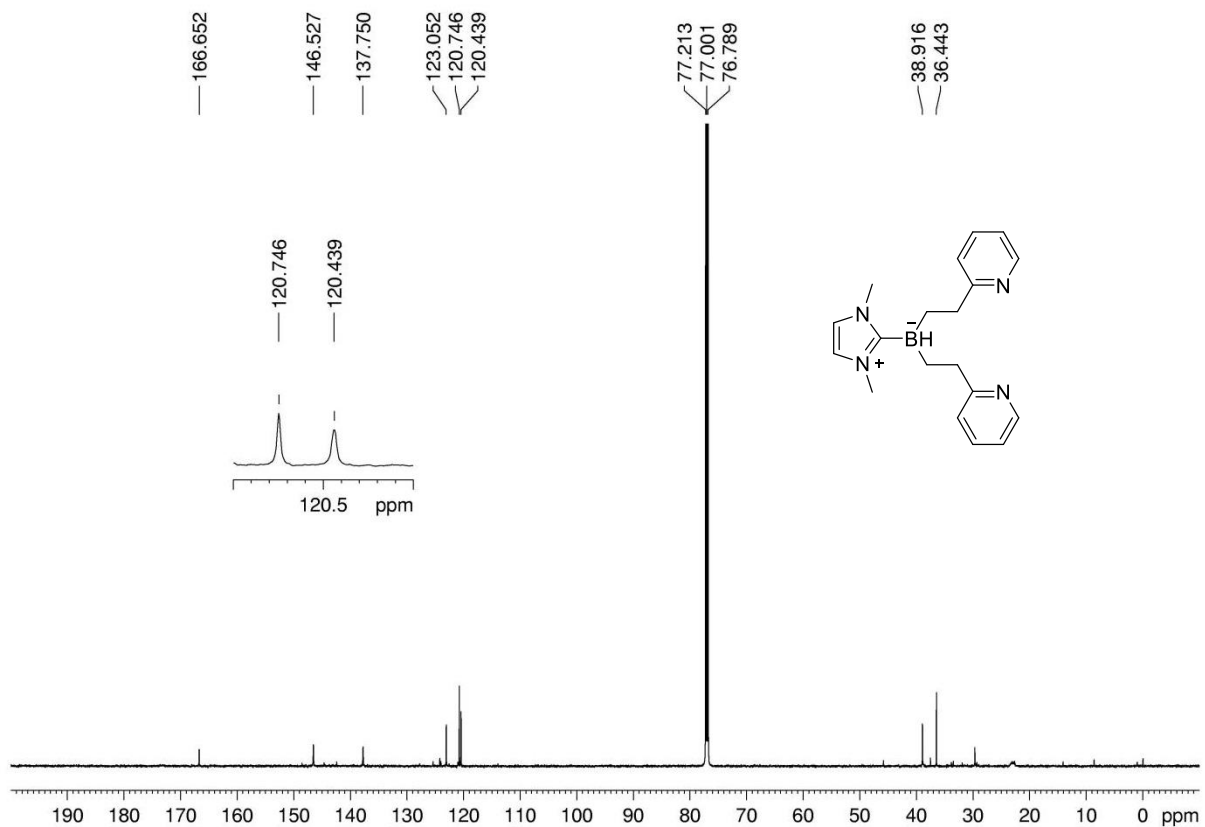
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **10**



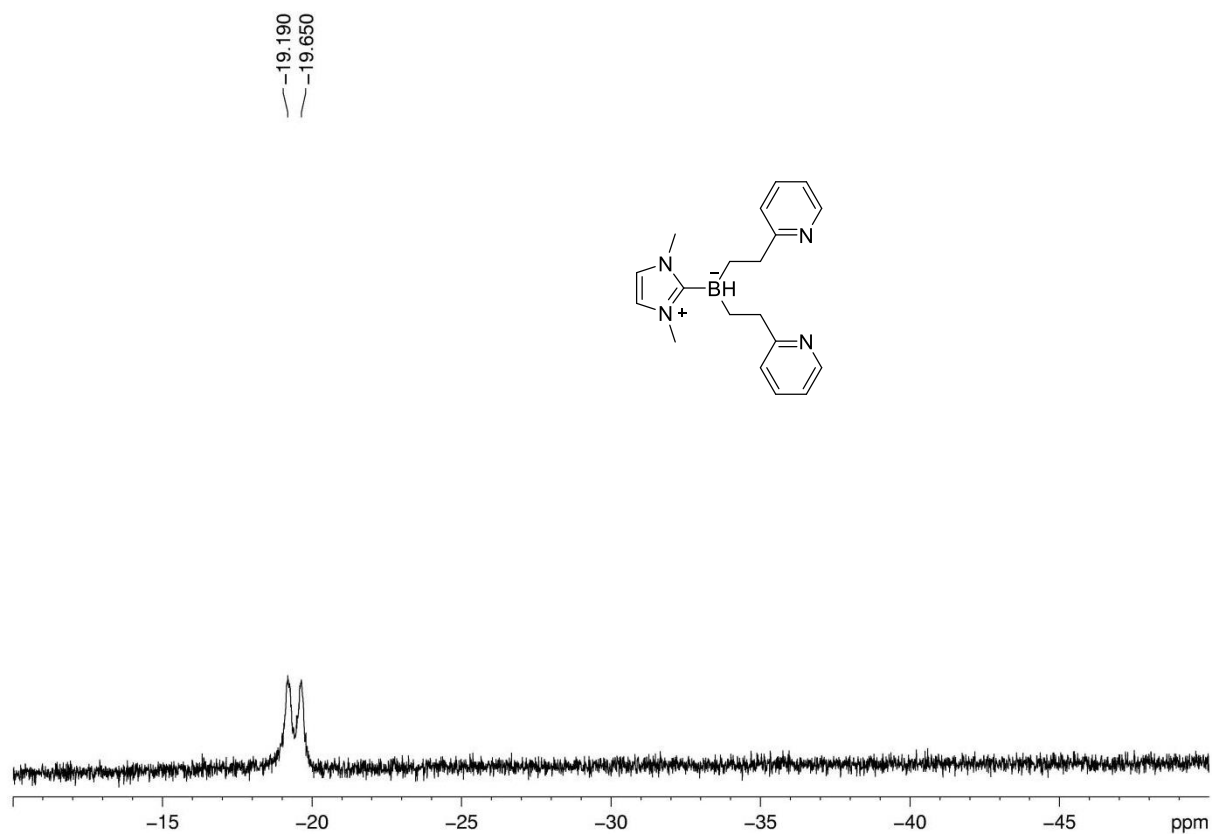
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) spectrum of **11**



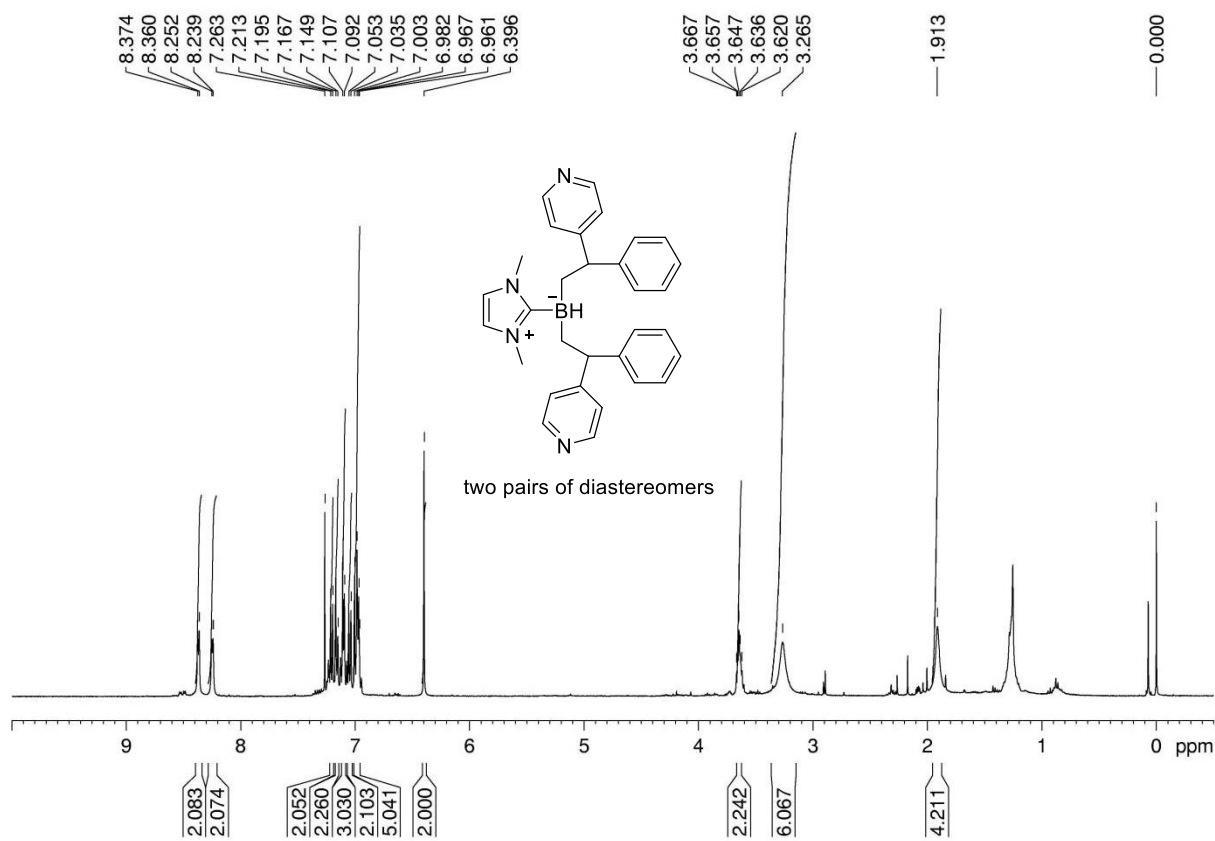
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) spectrum of **11**



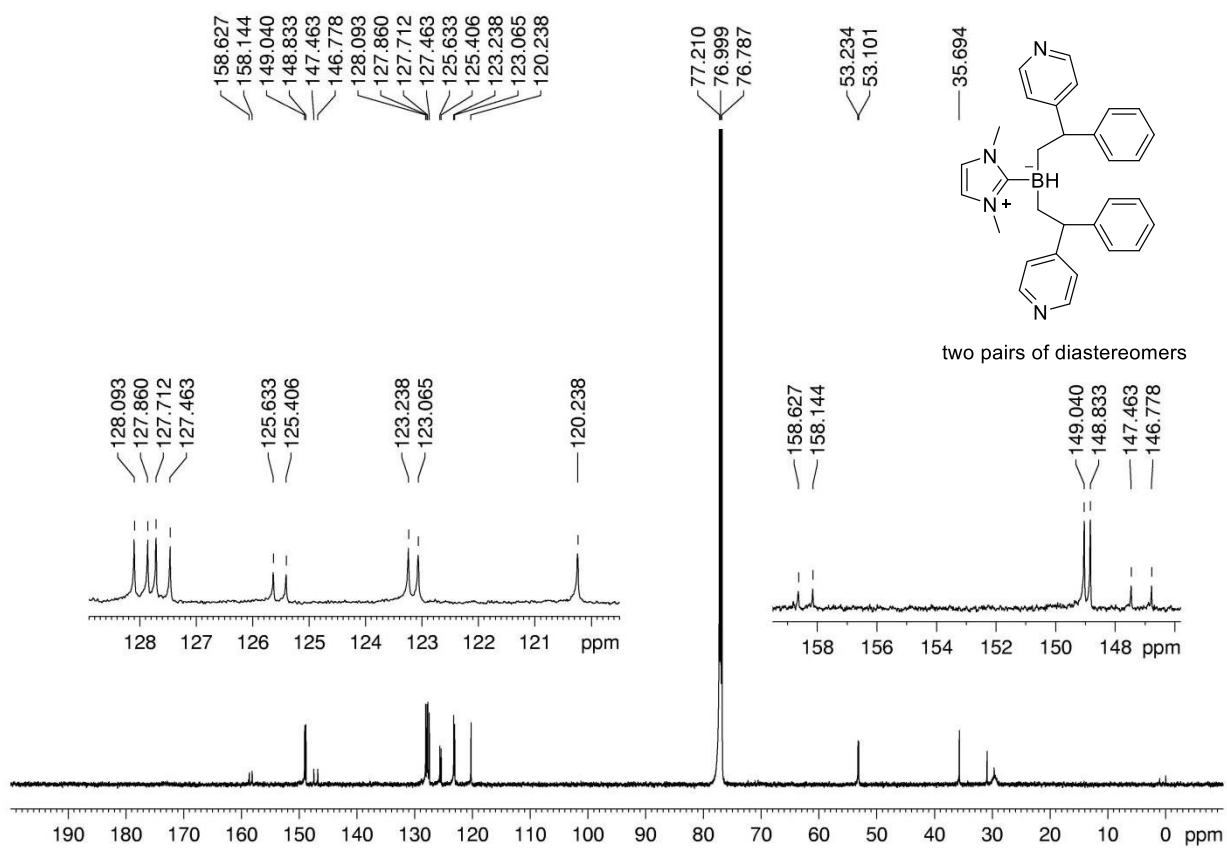
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **11**



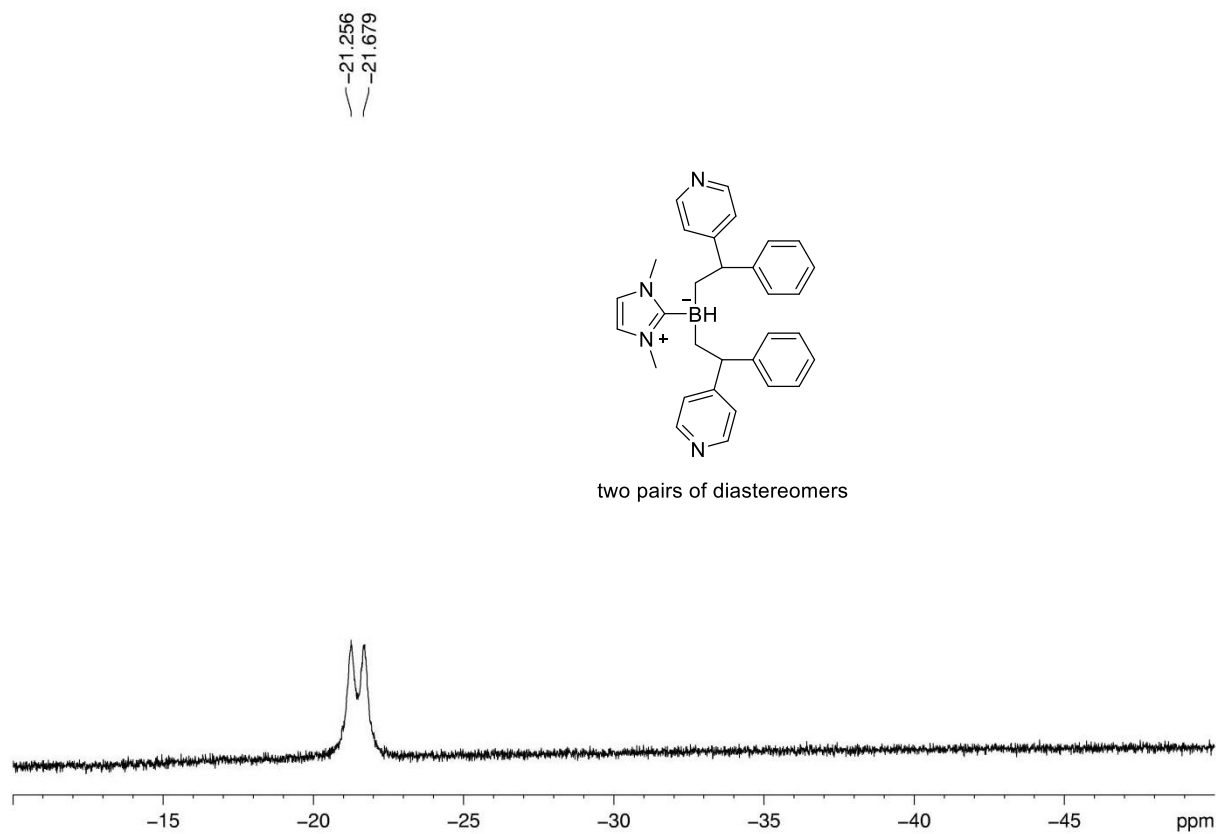
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **12**



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **12**

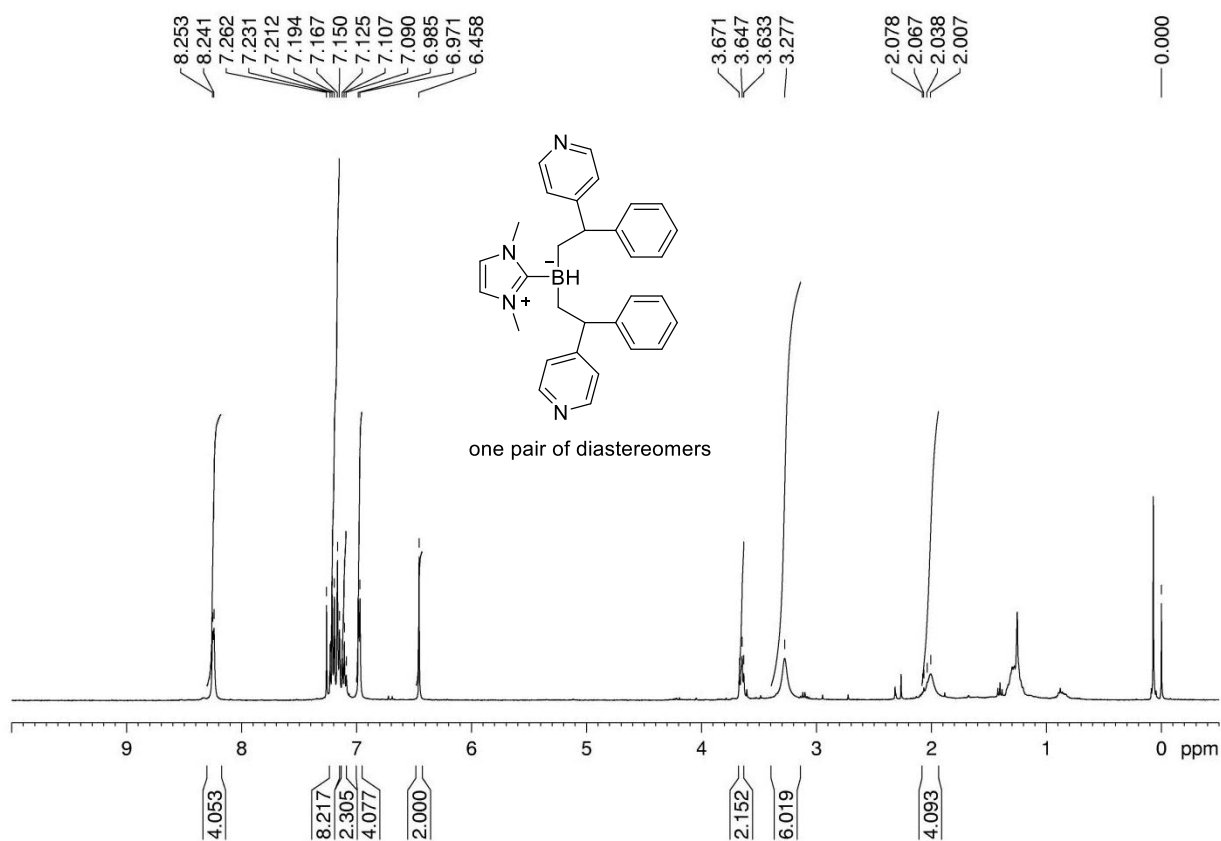


$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **12**

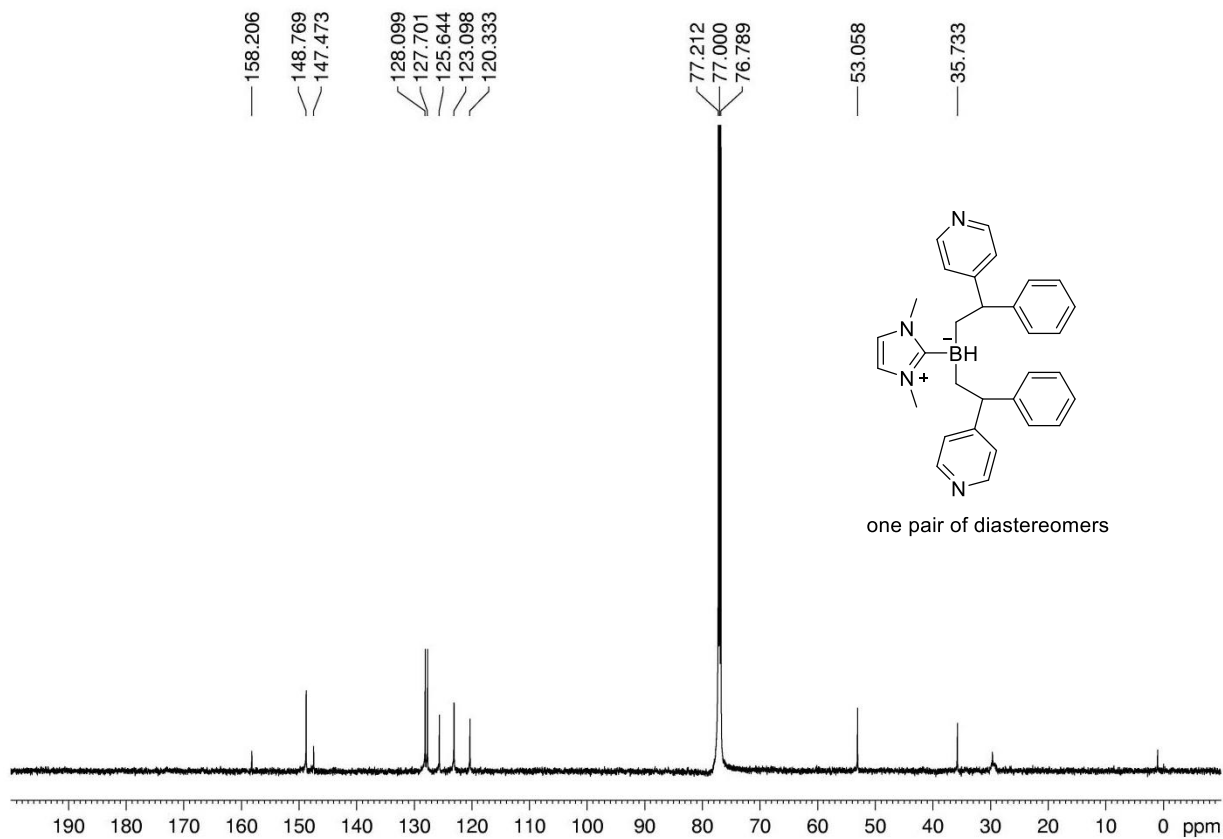




$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **12**

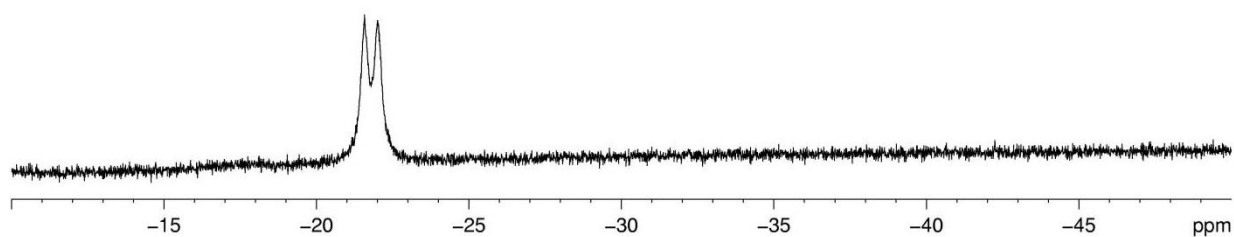
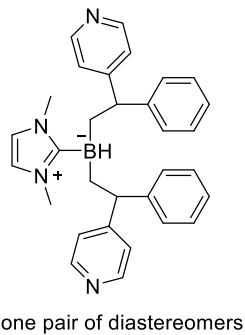


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **12**



$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **12**

-21.580  
-22.012

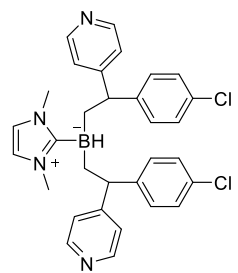


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **13**

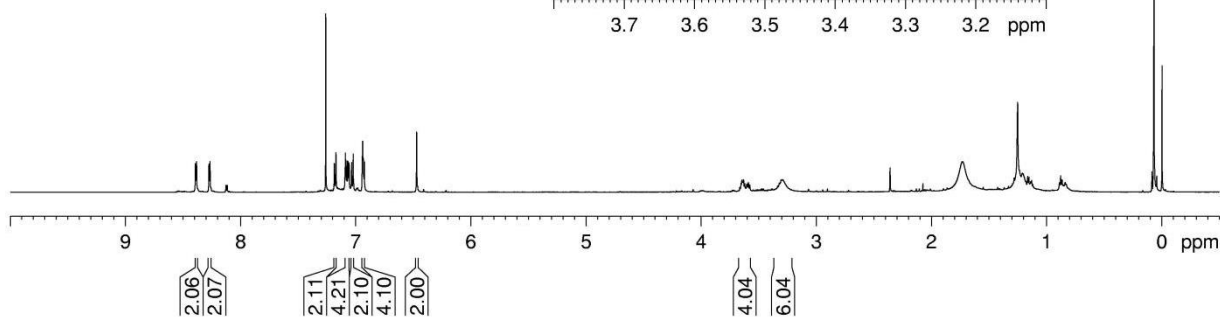
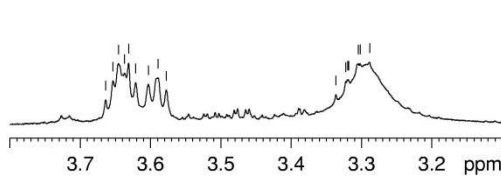
8.390  
8.380  
8.272  
8.262  
7.260  
7.186  
7.172  
7.090  
7.083  
7.076  
7.068  
7.058  
7.036  
7.022  
6.943  
6.939  
6.936  
6.934  
6.925  
6.471

3.664  
3.653  
3.646  
3.637  
3.631  
3.621  
3.603  
3.589  
3.578  
3.336  
3.322  
3.320  
3.318  
3.305  
3.302  
3.288

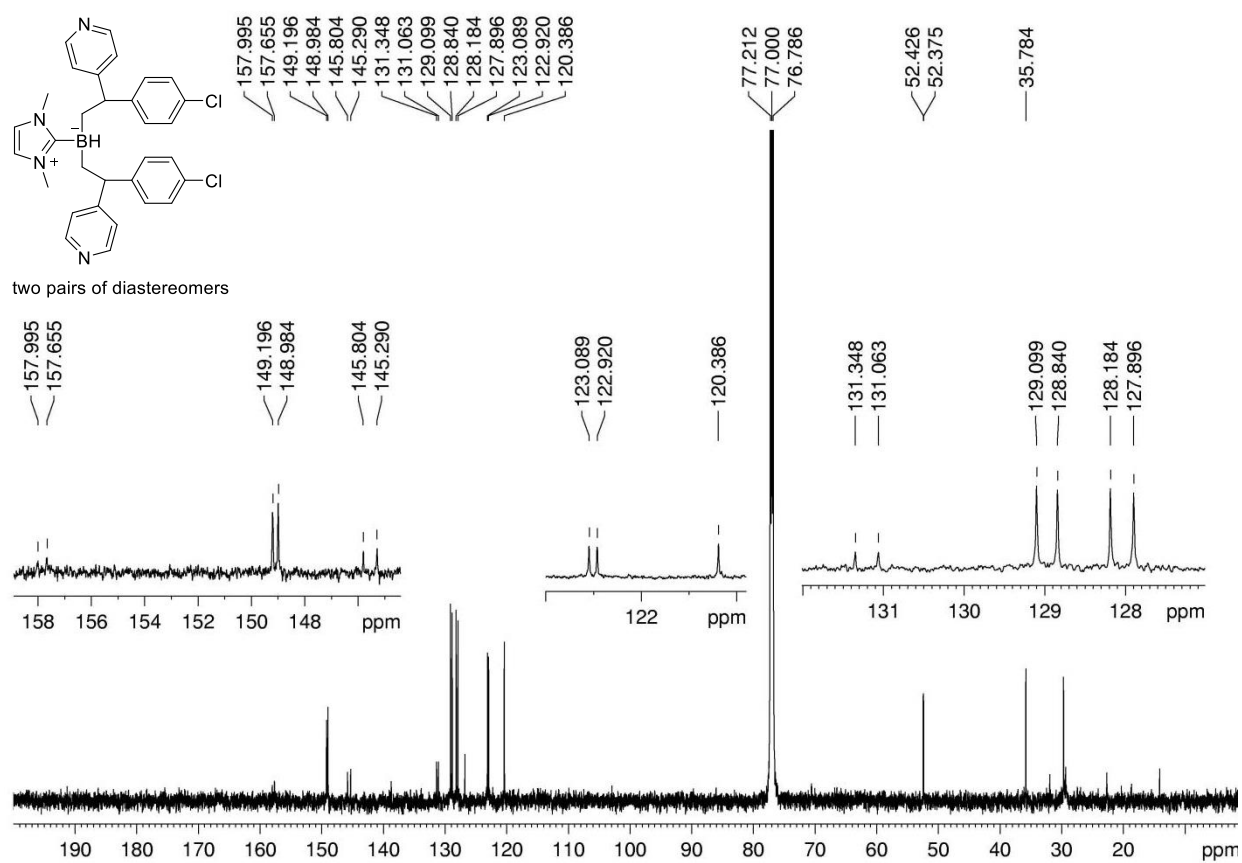
0.003



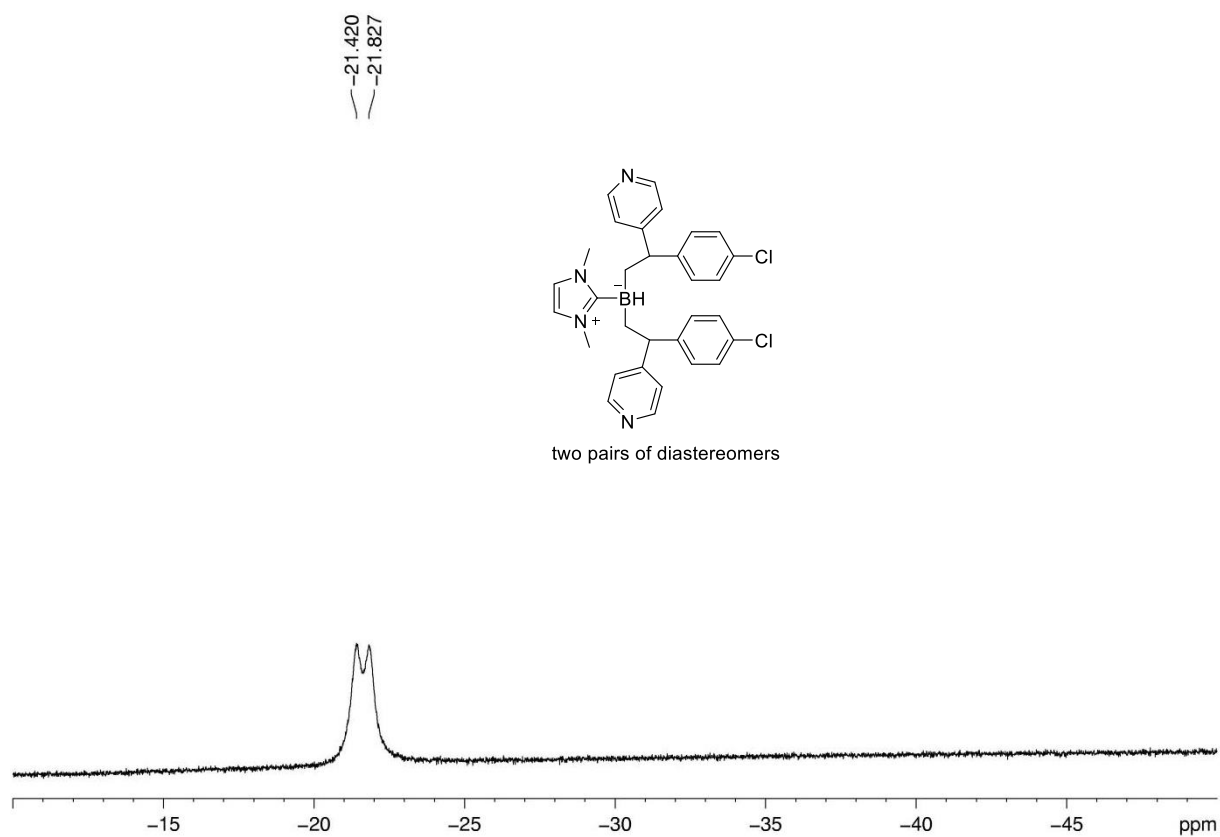
3.664  
3.653  
3.646  
3.637  
3.631  
3.621  
3.603  
3.589  
3.578  
3.336  
3.322  
3.320  
3.318  
3.305  
3.302  
3.288



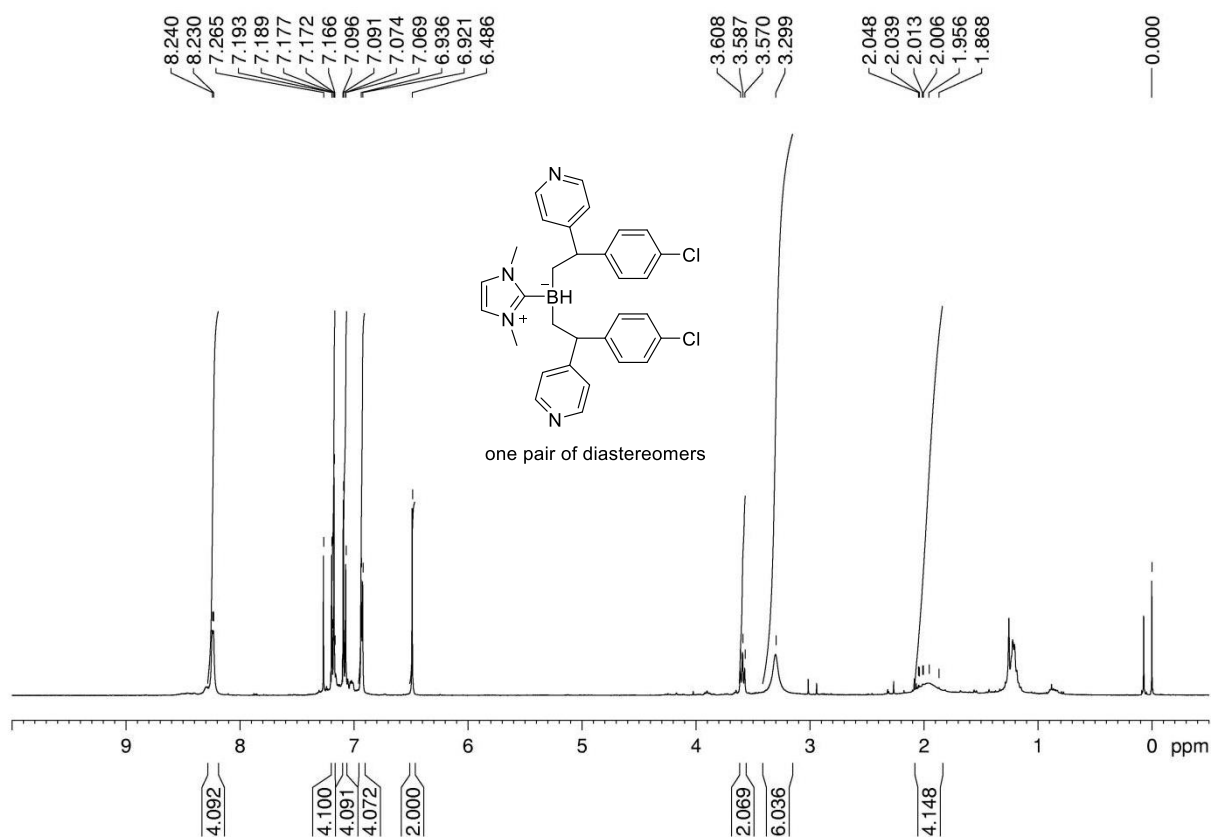
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **13**



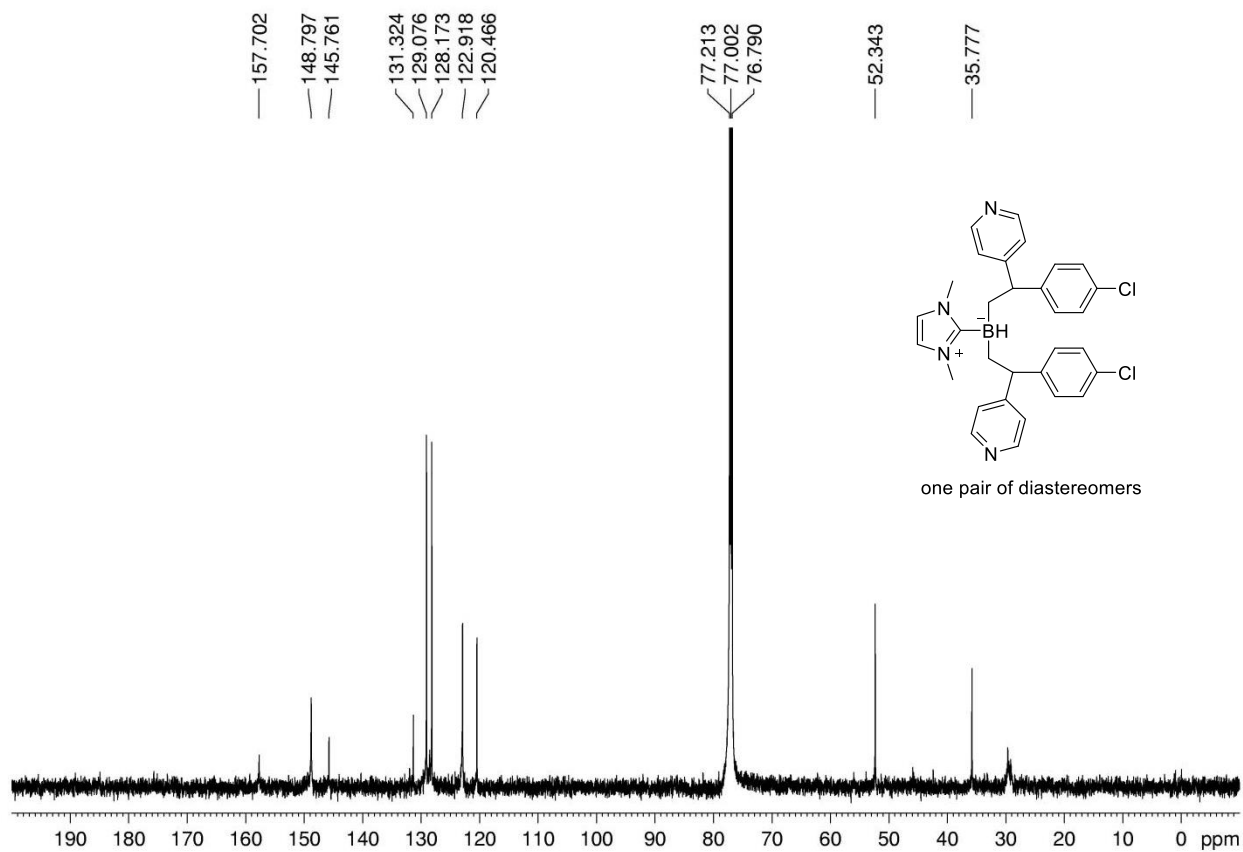
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **13**



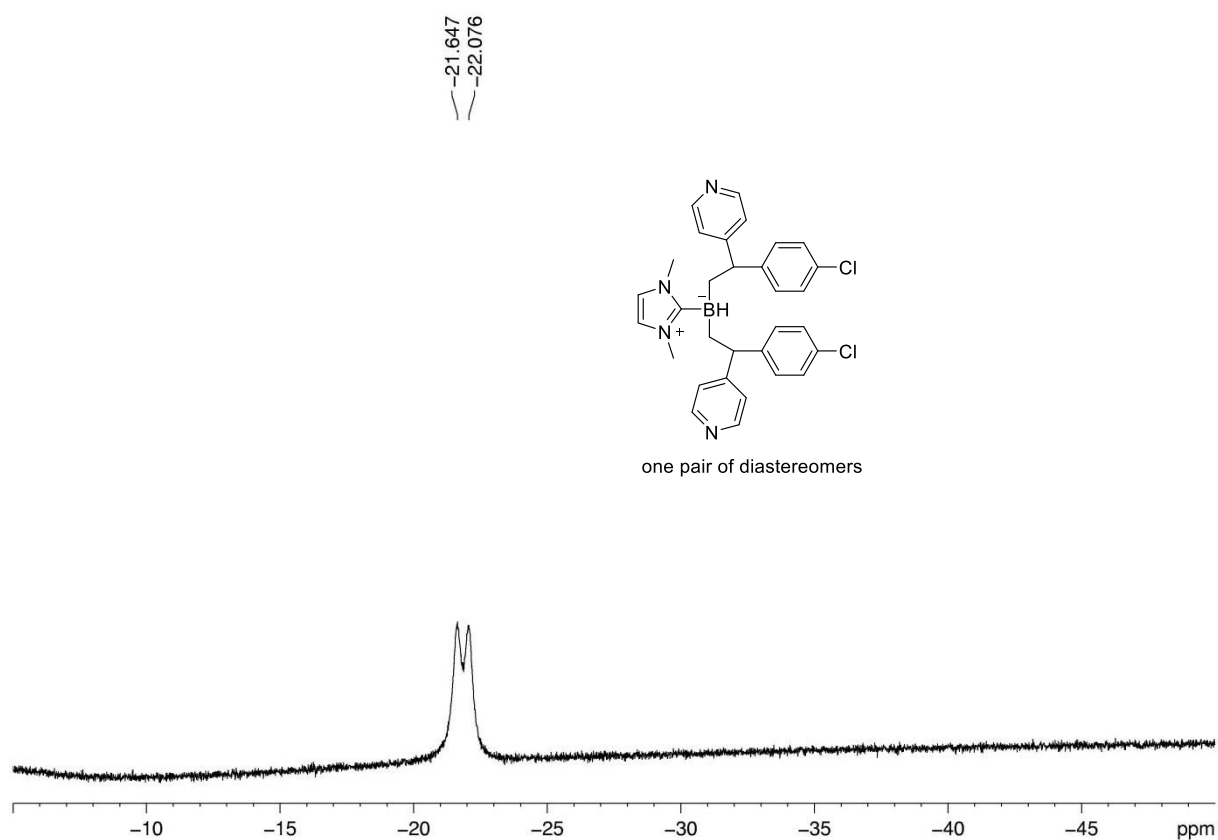
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **13**



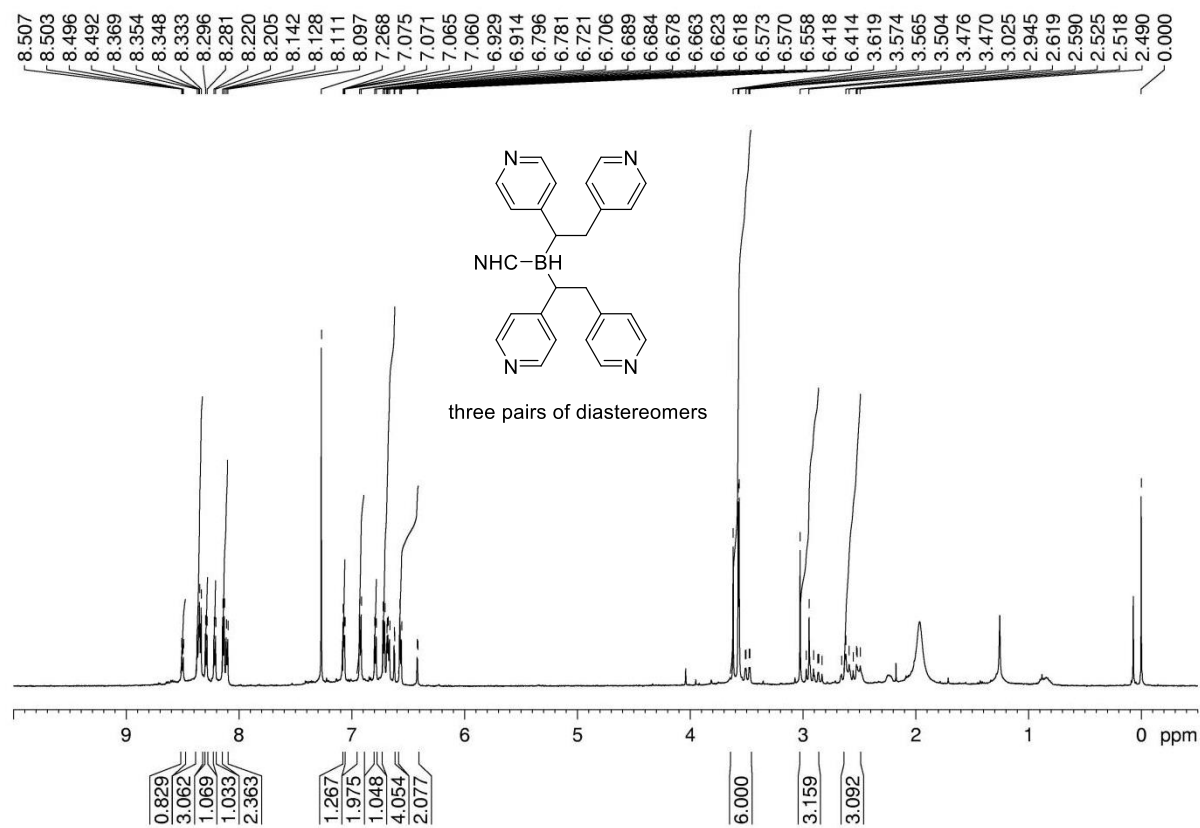
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **13**



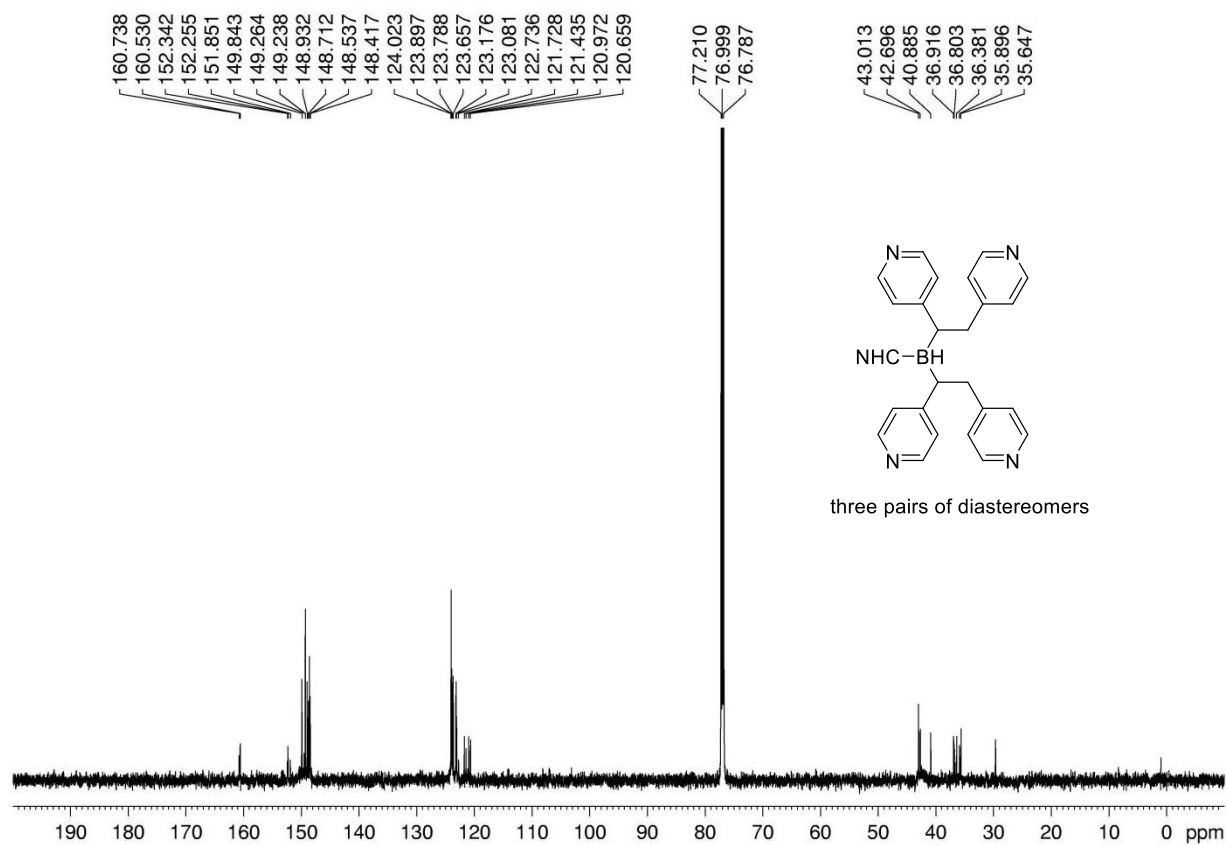
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **13**



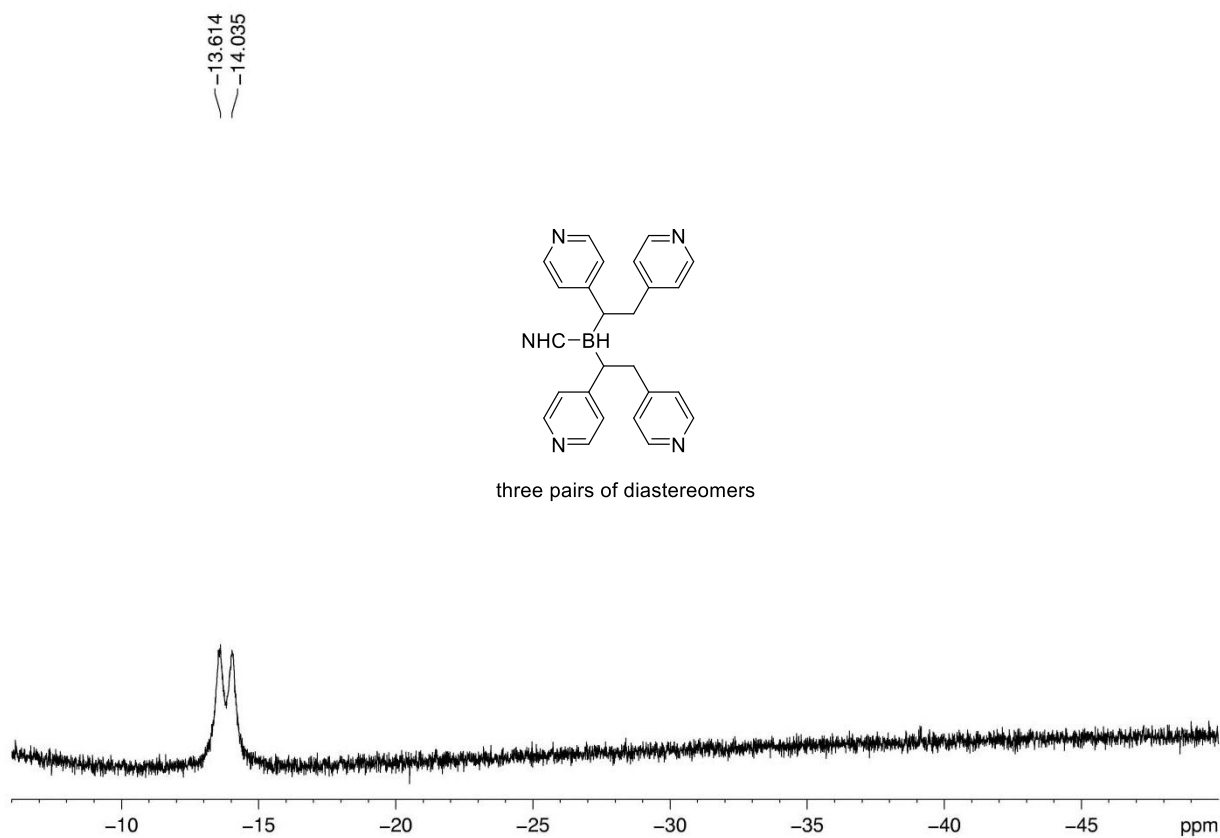
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **14**



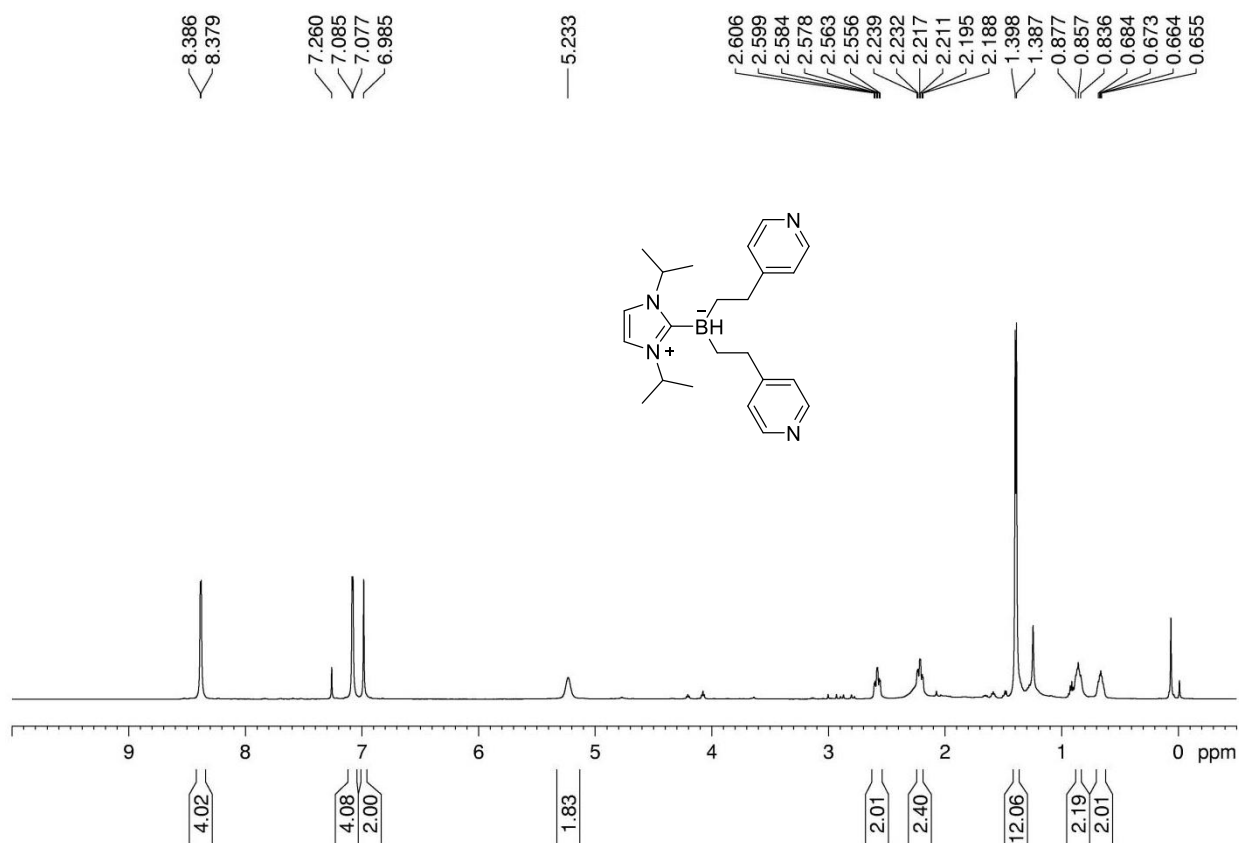
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **14**



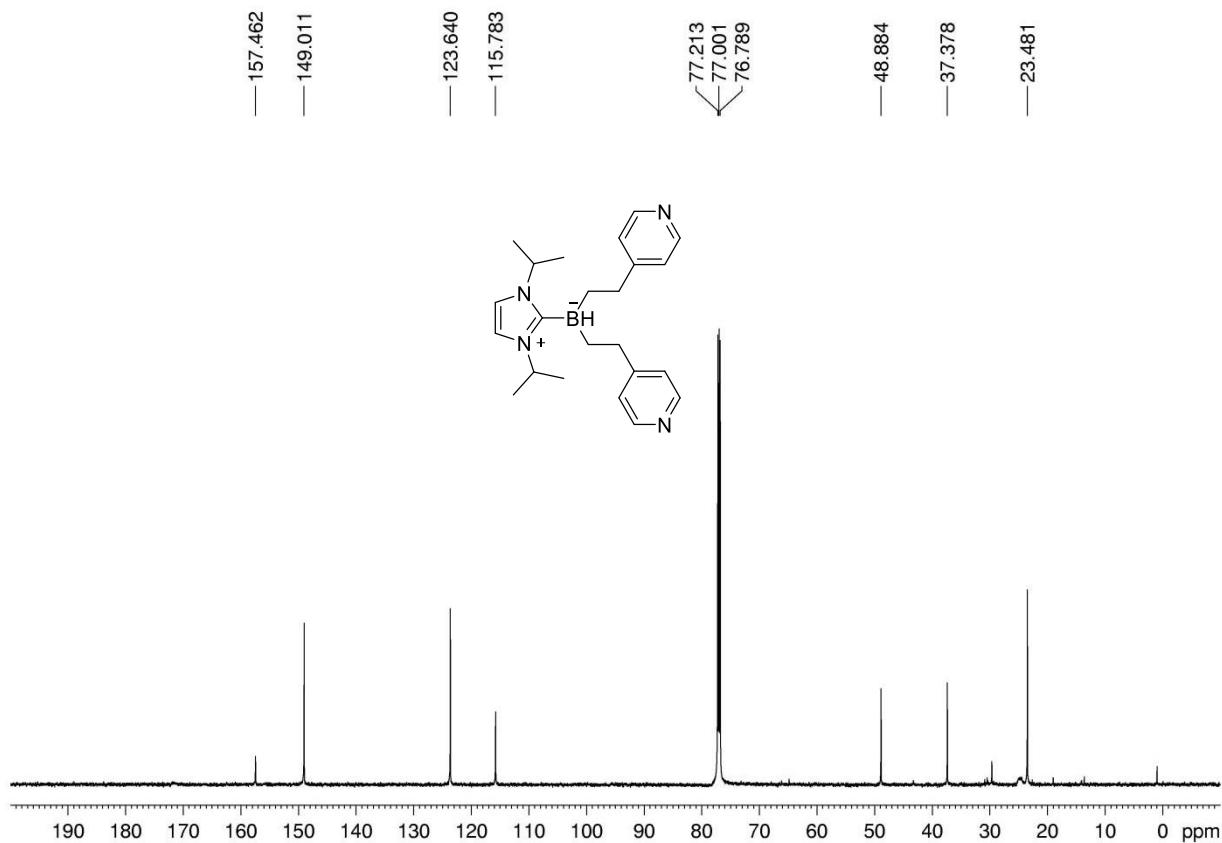
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **14**



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **15**

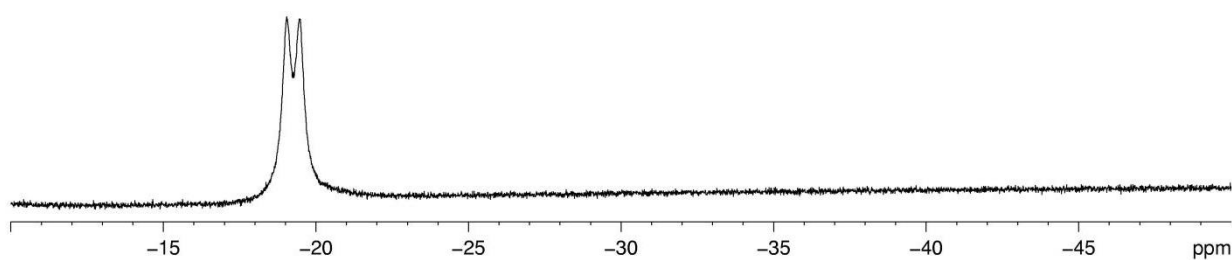
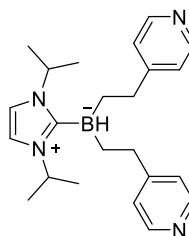


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **15**



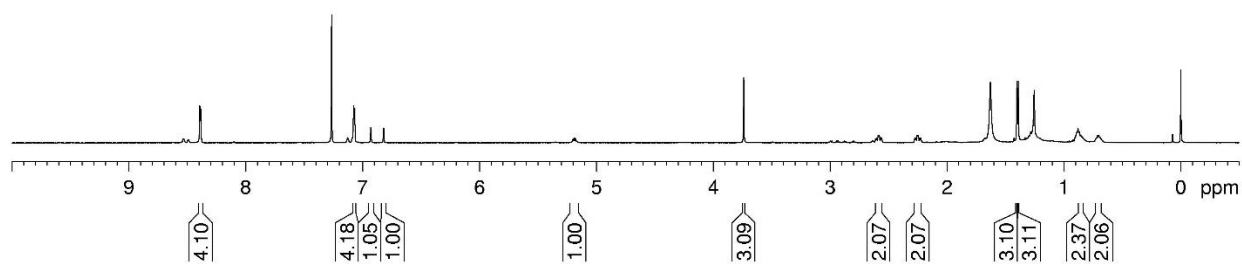
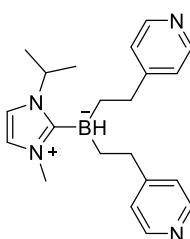
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **15**

-19.044  
-19.471



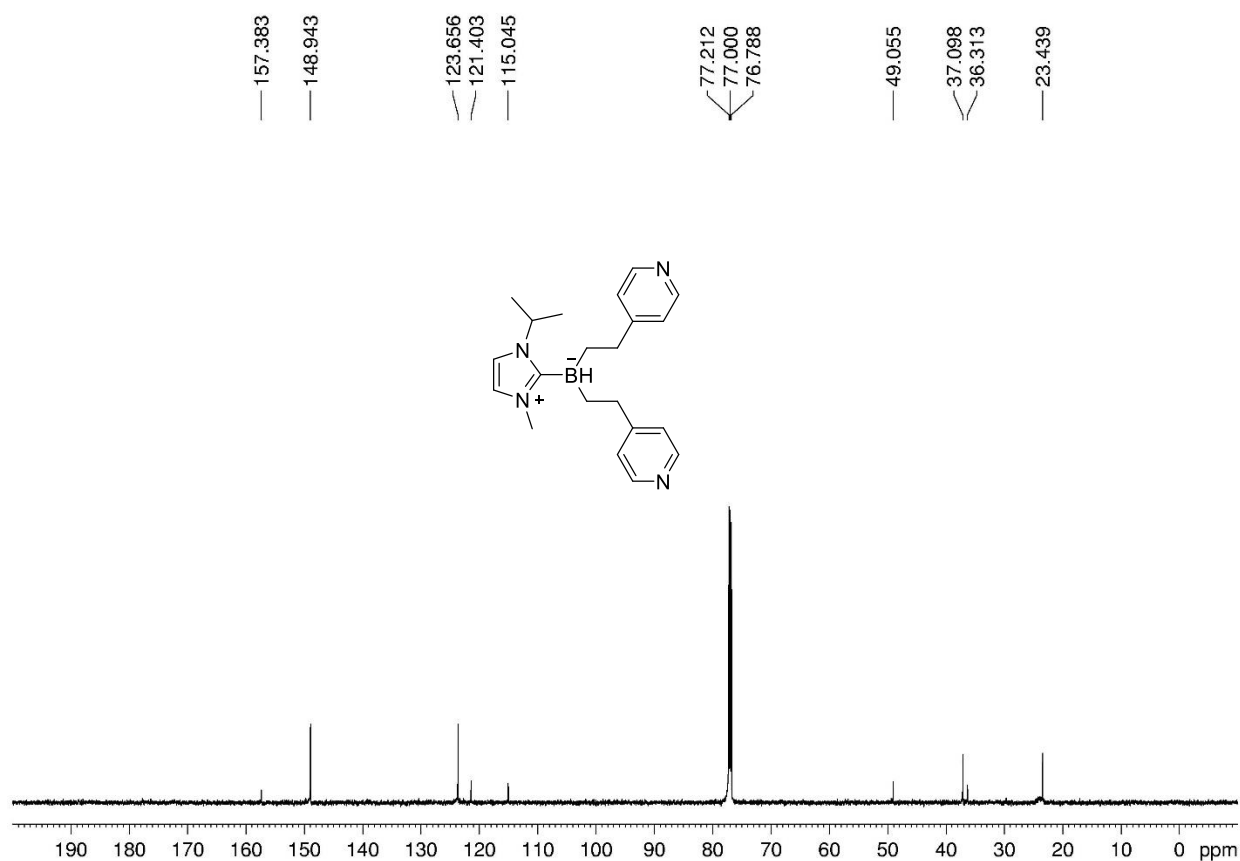
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **16**

8.391  
8.382  
7.263  
7.075  
7.066  
6.928  
6.821  
5.189  
5.188  
3.739  
2.590  
2.589  
2.588  
2.588  
2.587  
2.585  
2.582  
2.581  
2.580  
2.579  
2.567  
2.559  
2.268  
2.267  
2.255  
2.254  
2.252  
2.251  
2.251  
2.247  
2.247  
2.245  
2.233  
2.225  
1.402  
1.391  
0.891  
0.891  
0.890  
0.889  
0.880  
0.869  
0.868  
0.856  
-0.723  
-0.722  
-0.712  
-0.712  
-0.701  
-0.701  
-0.692  
-0.691  
-0.000

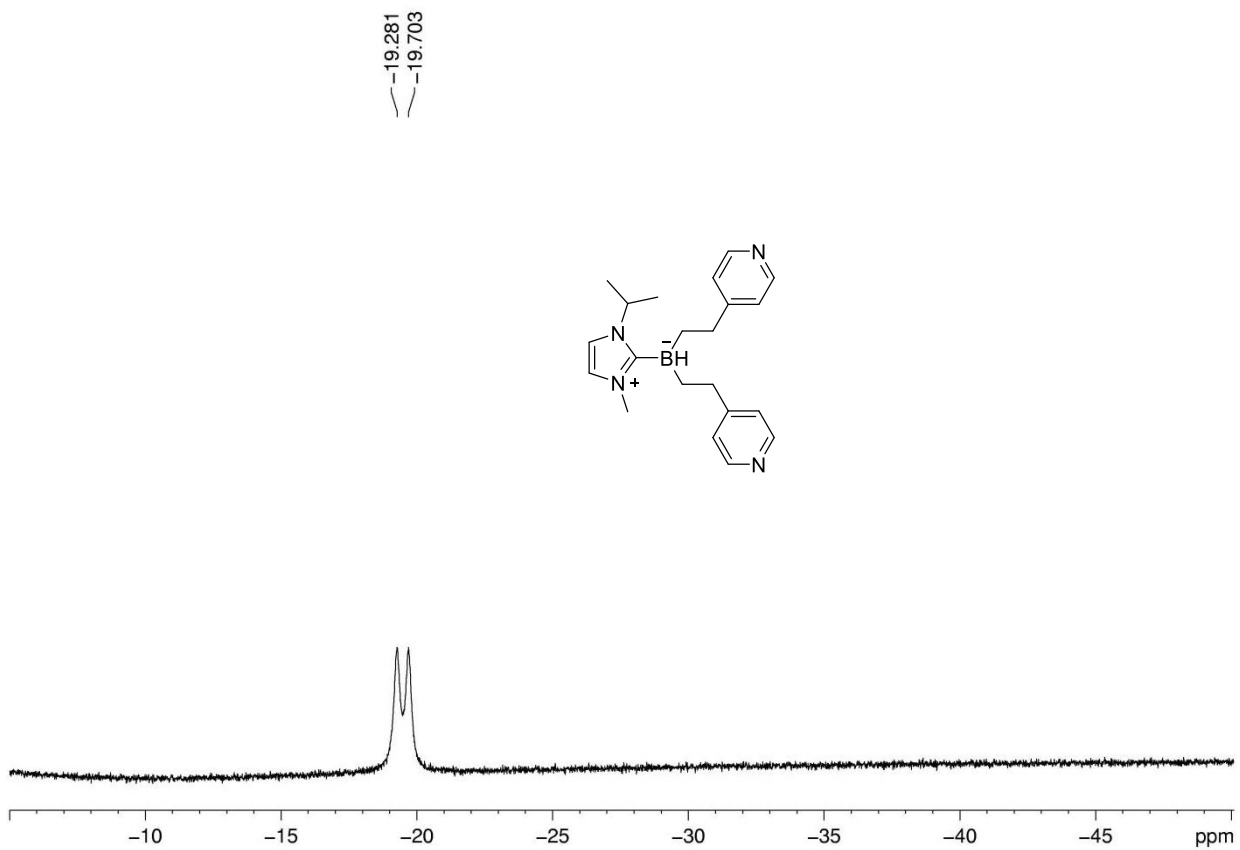




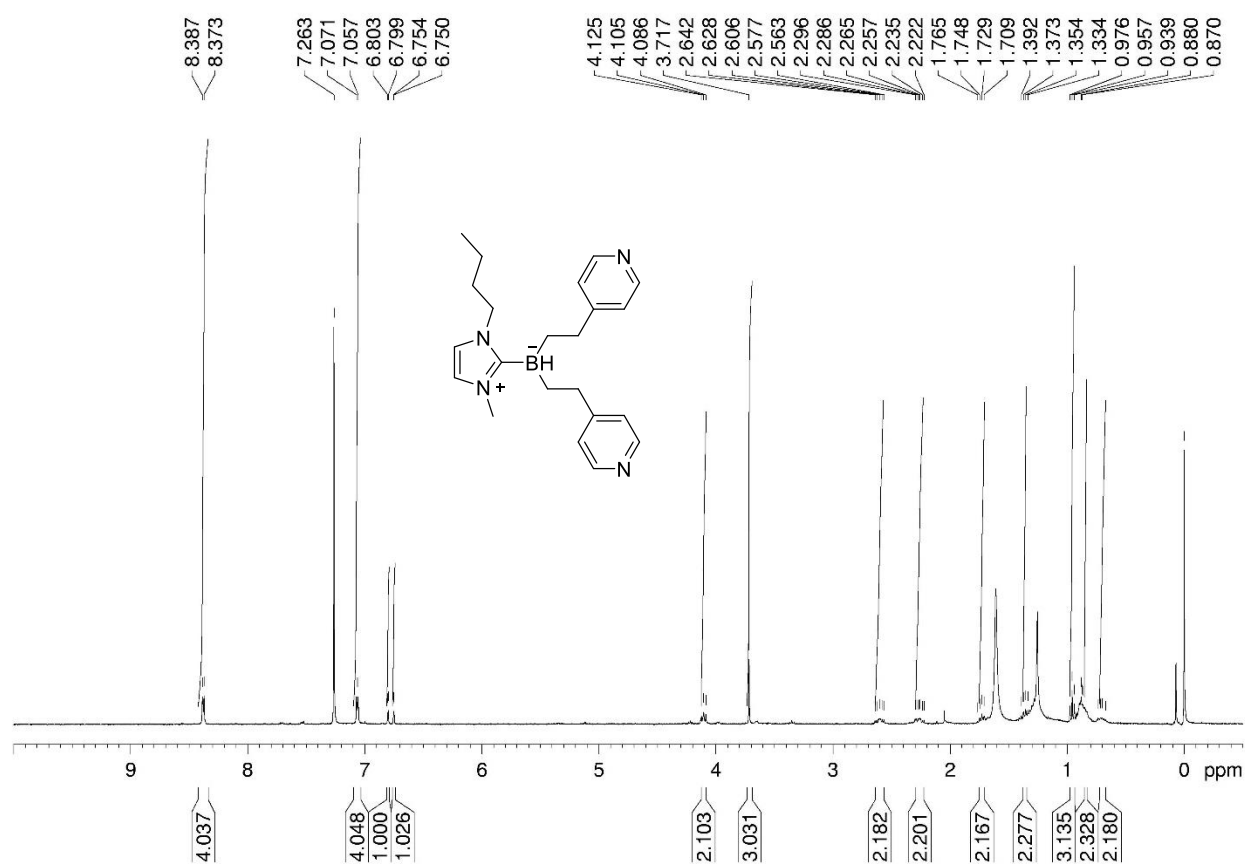
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **16**



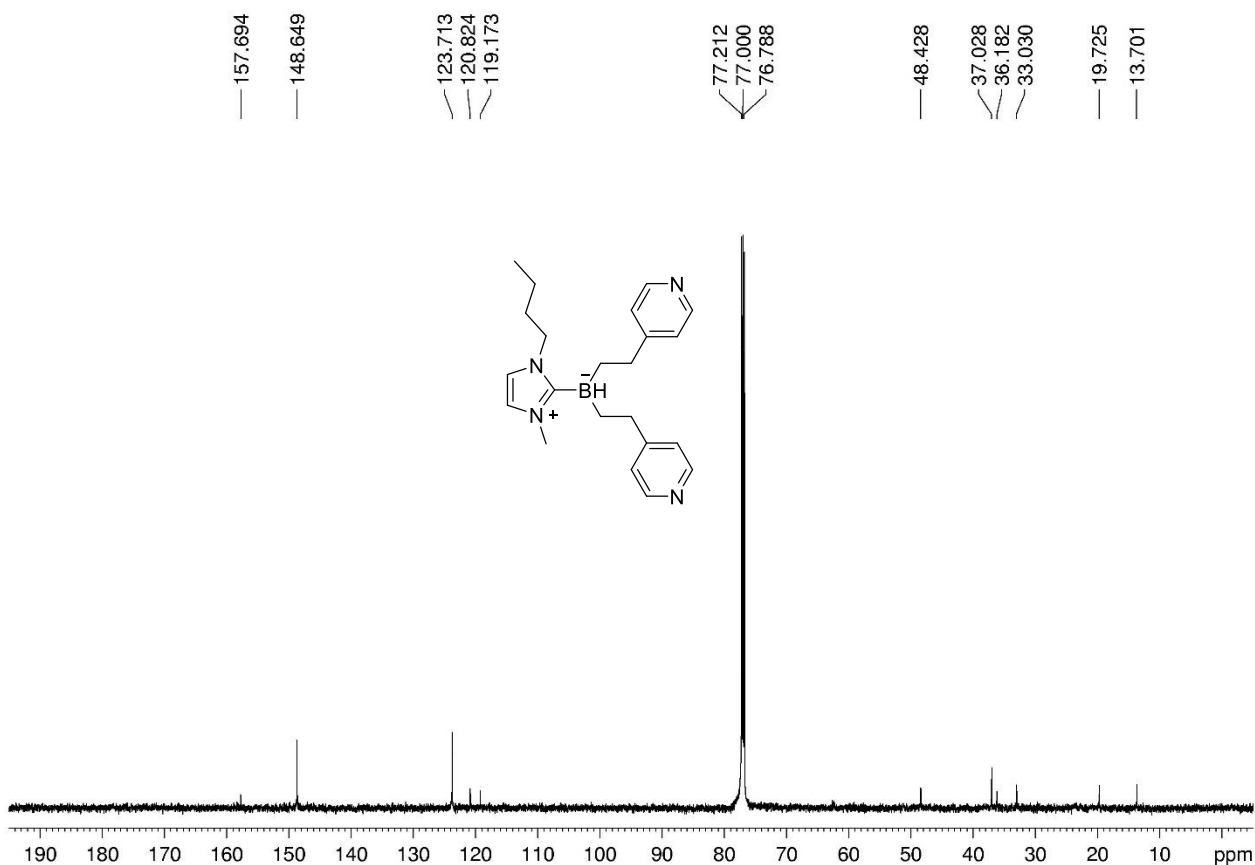
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **16**



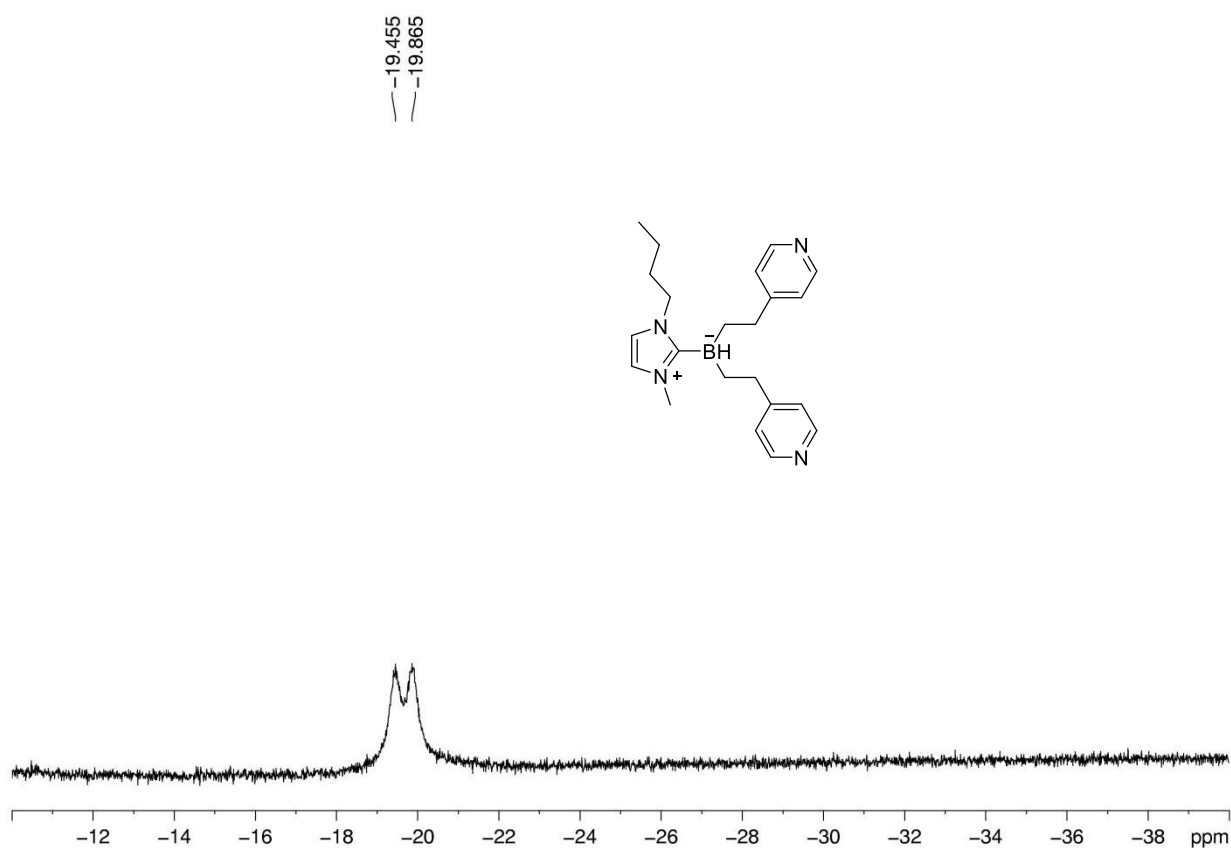
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **17**



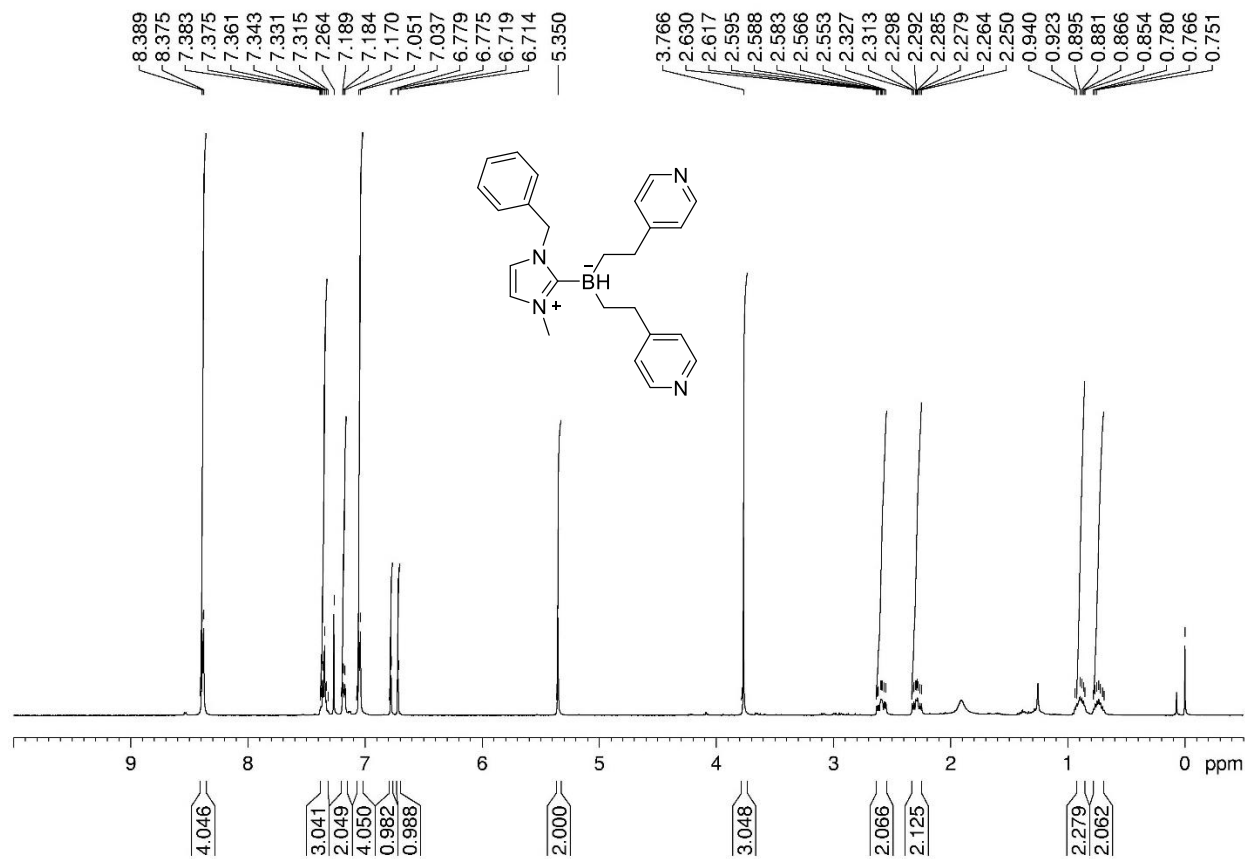
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **17**



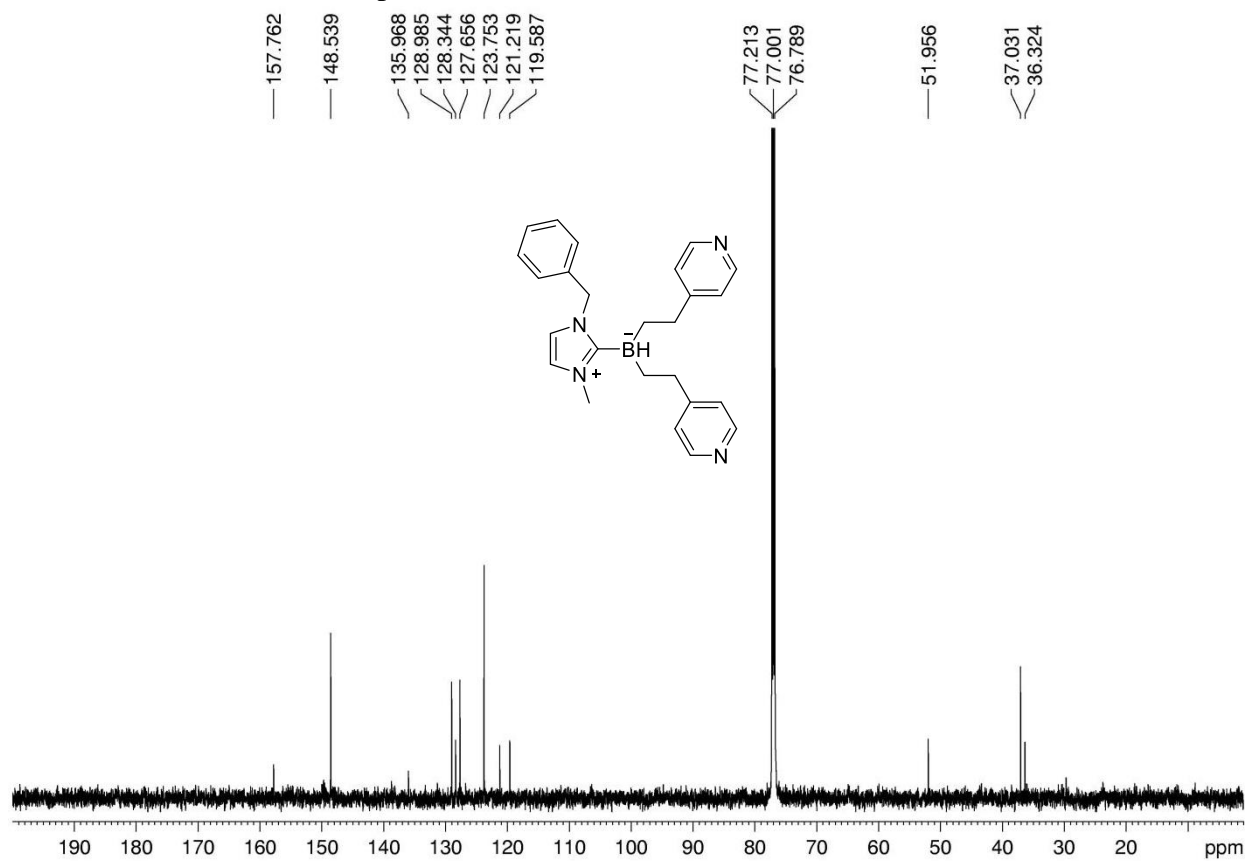
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **17**



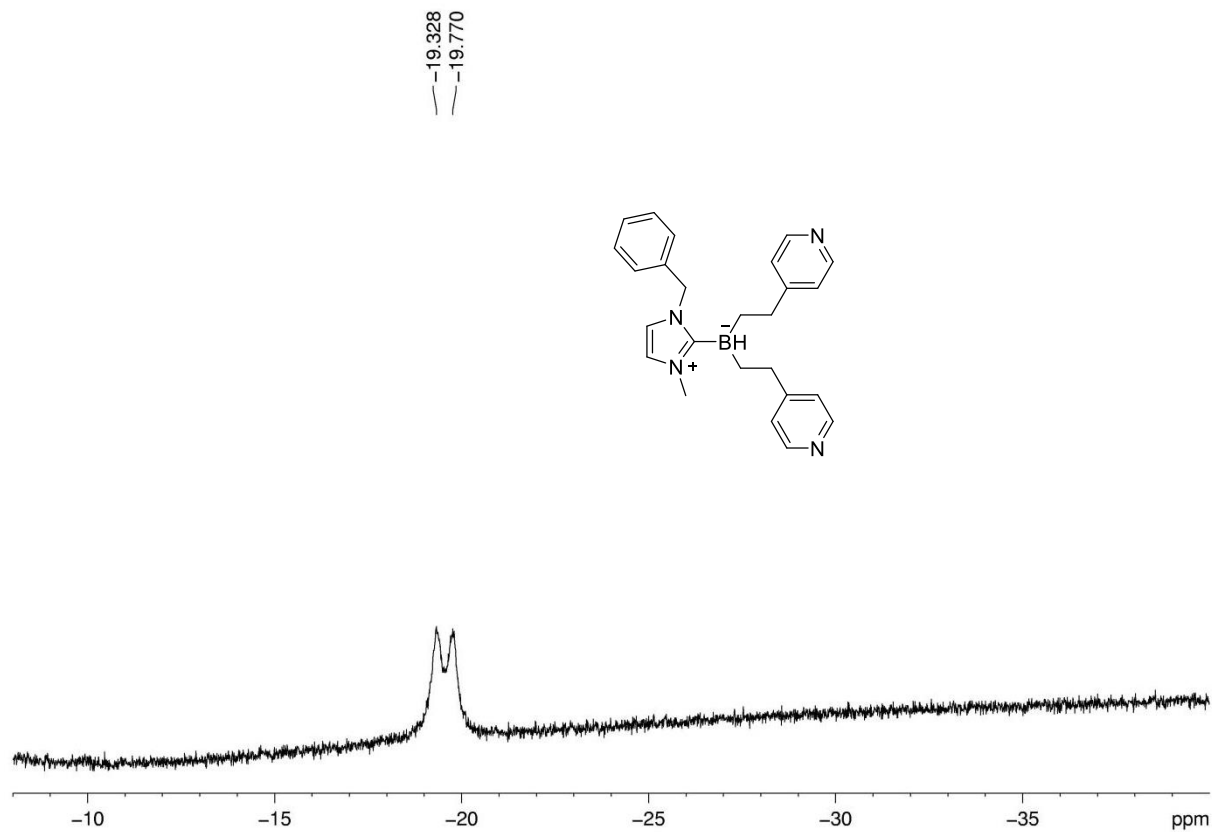
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **18**



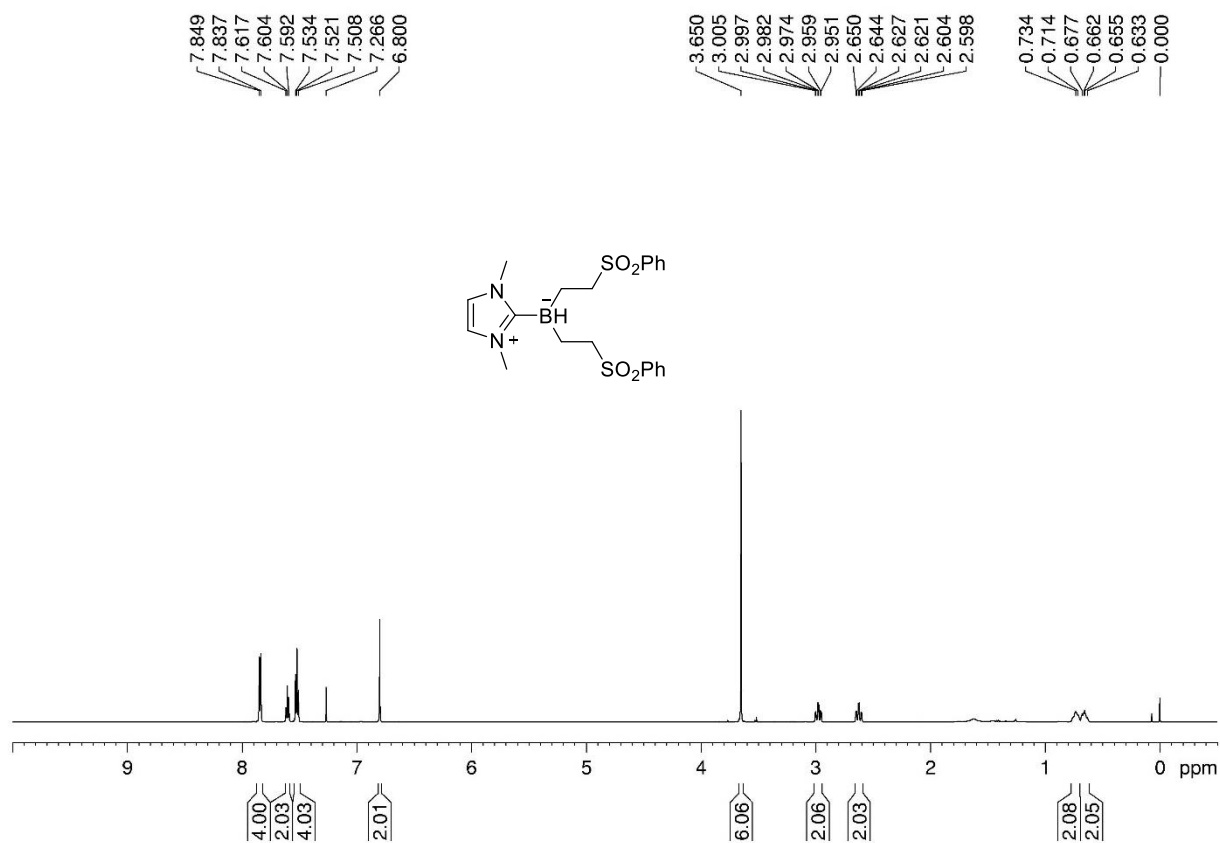
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **18**



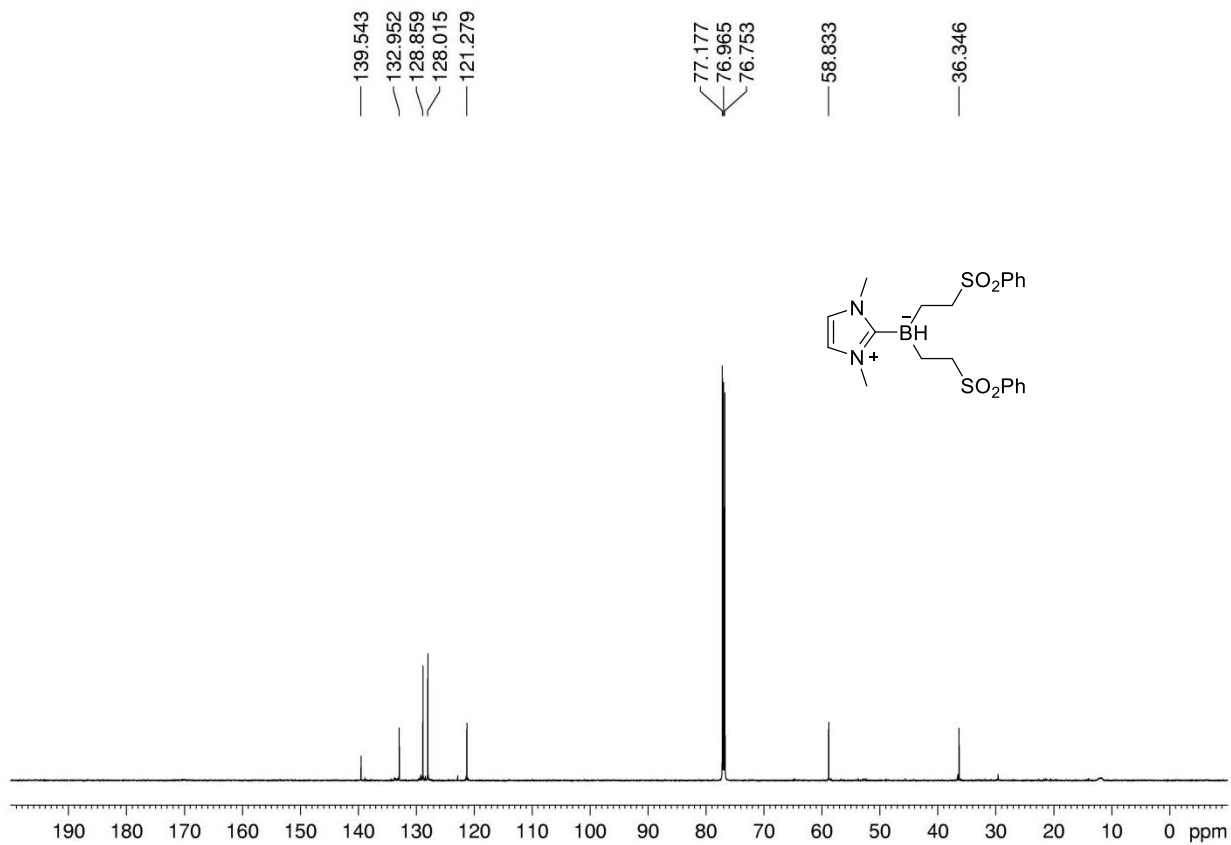
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **18**



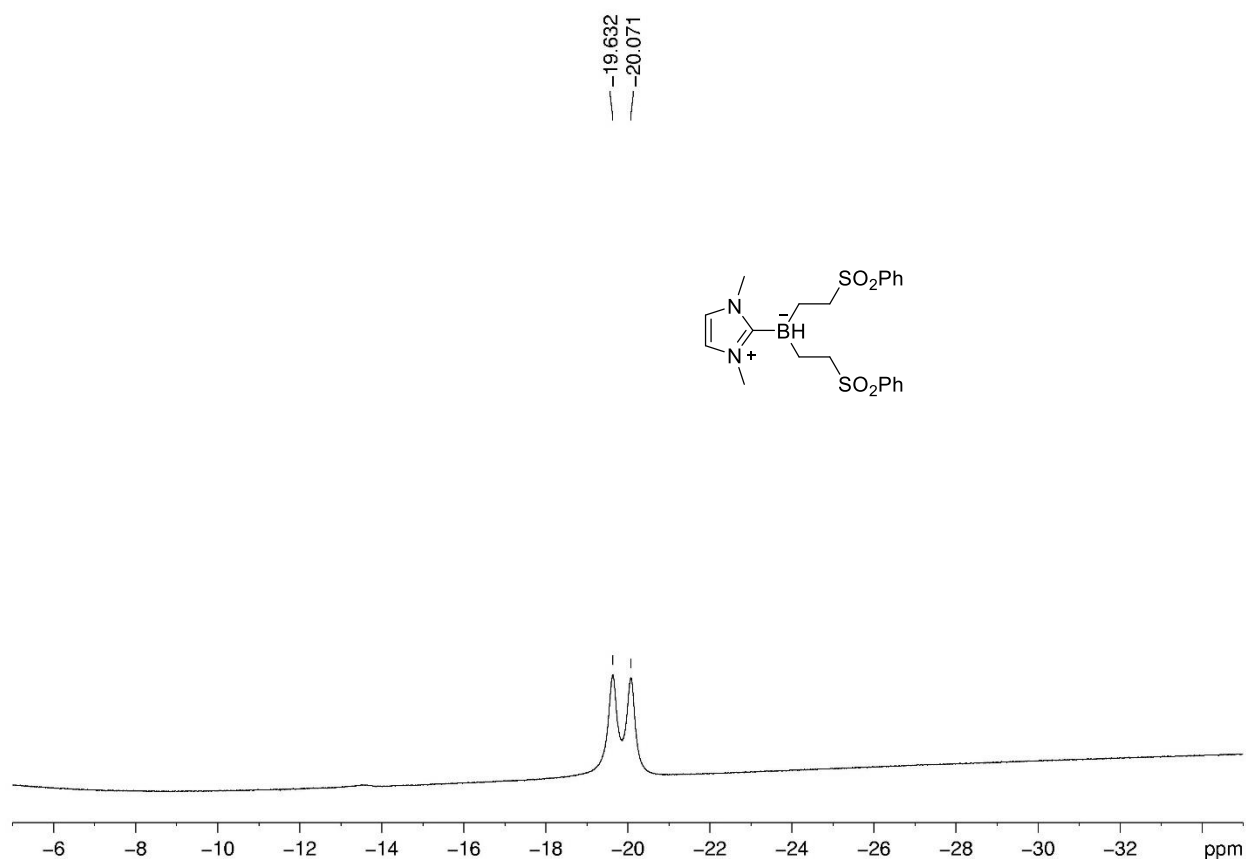
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **19**



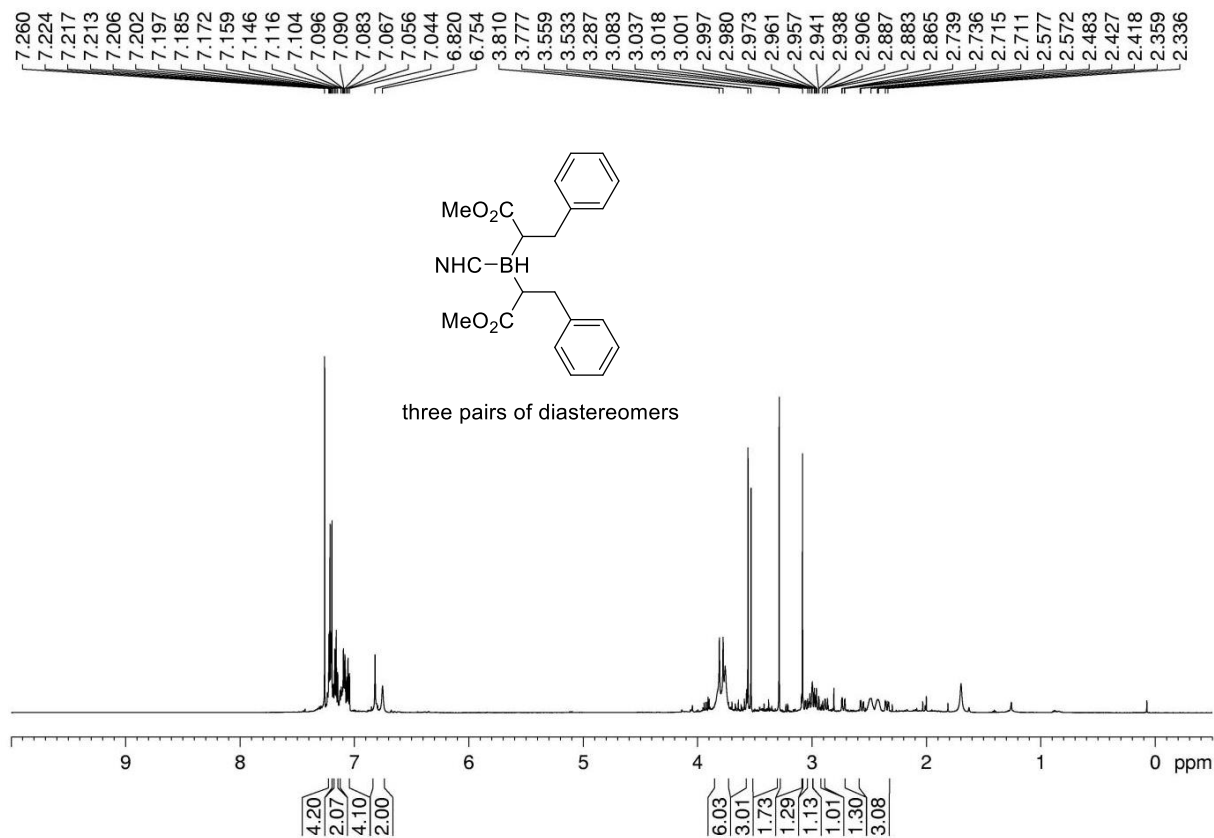
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **19**



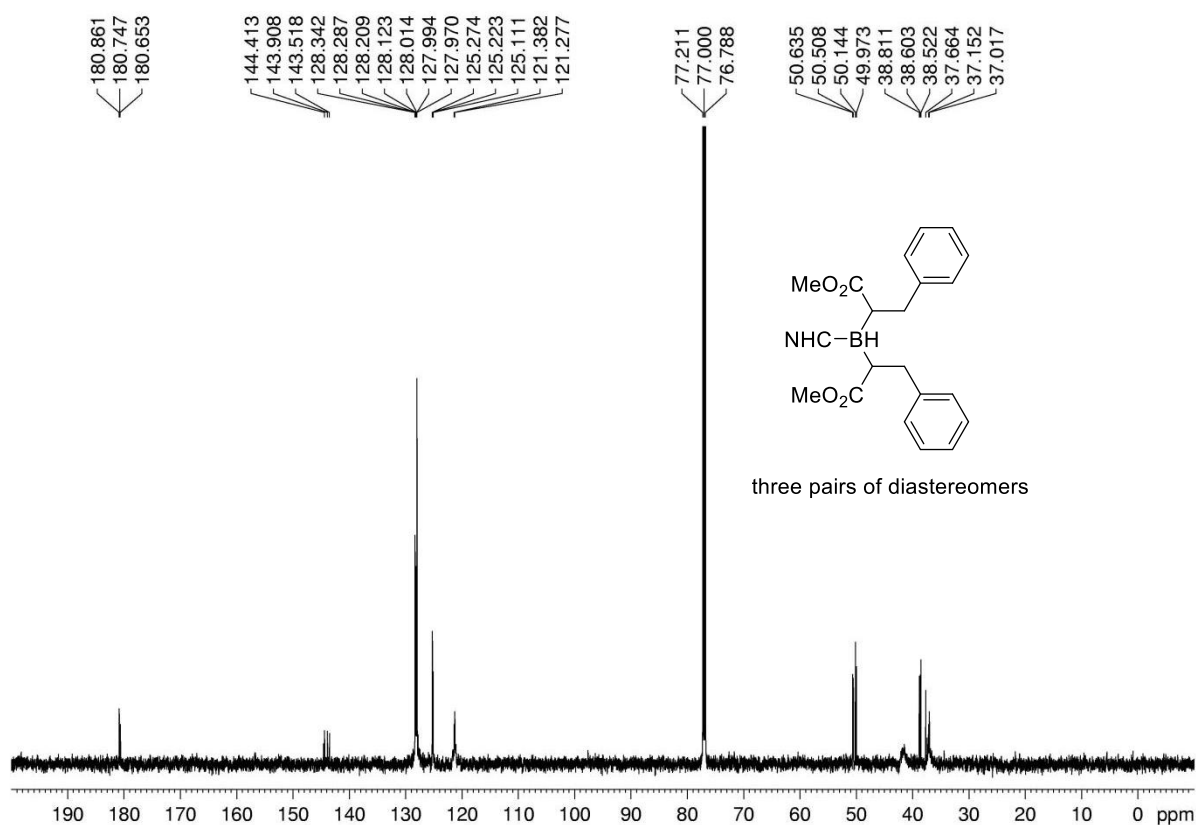
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **19**



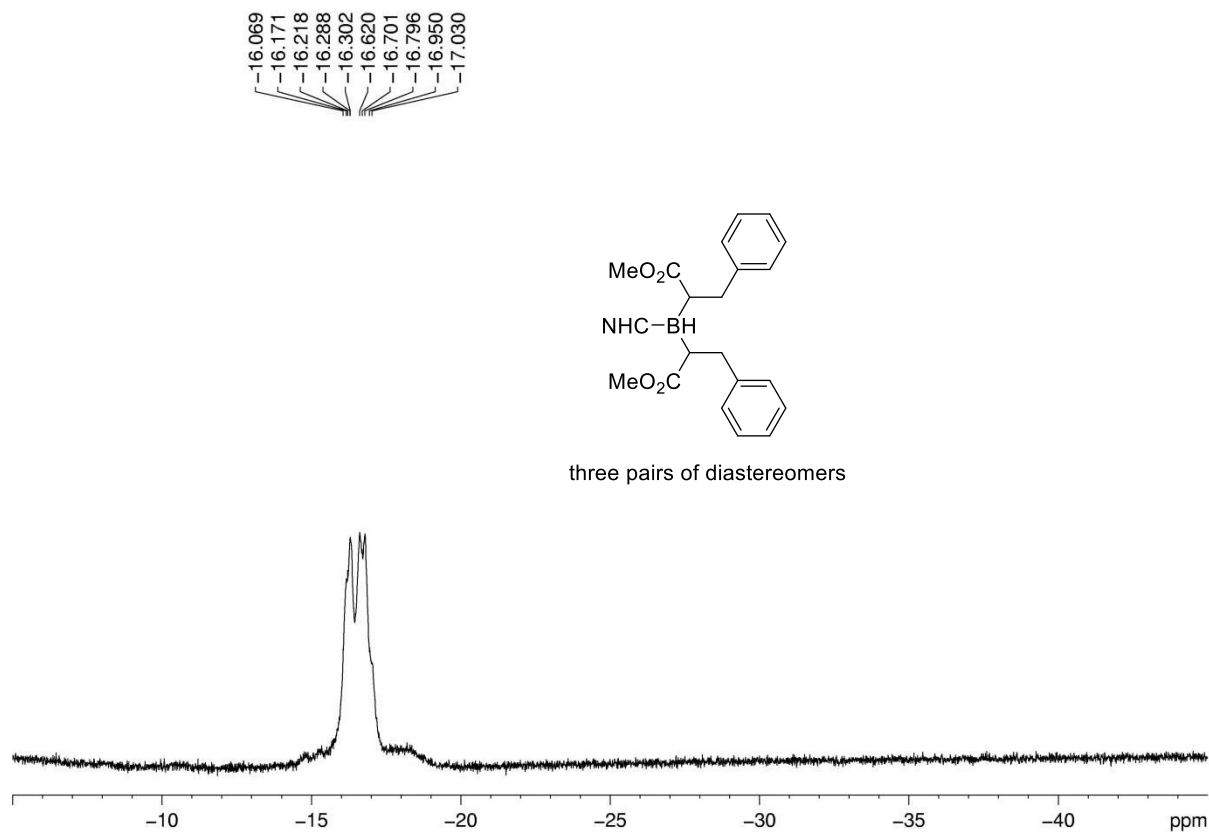
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **20**



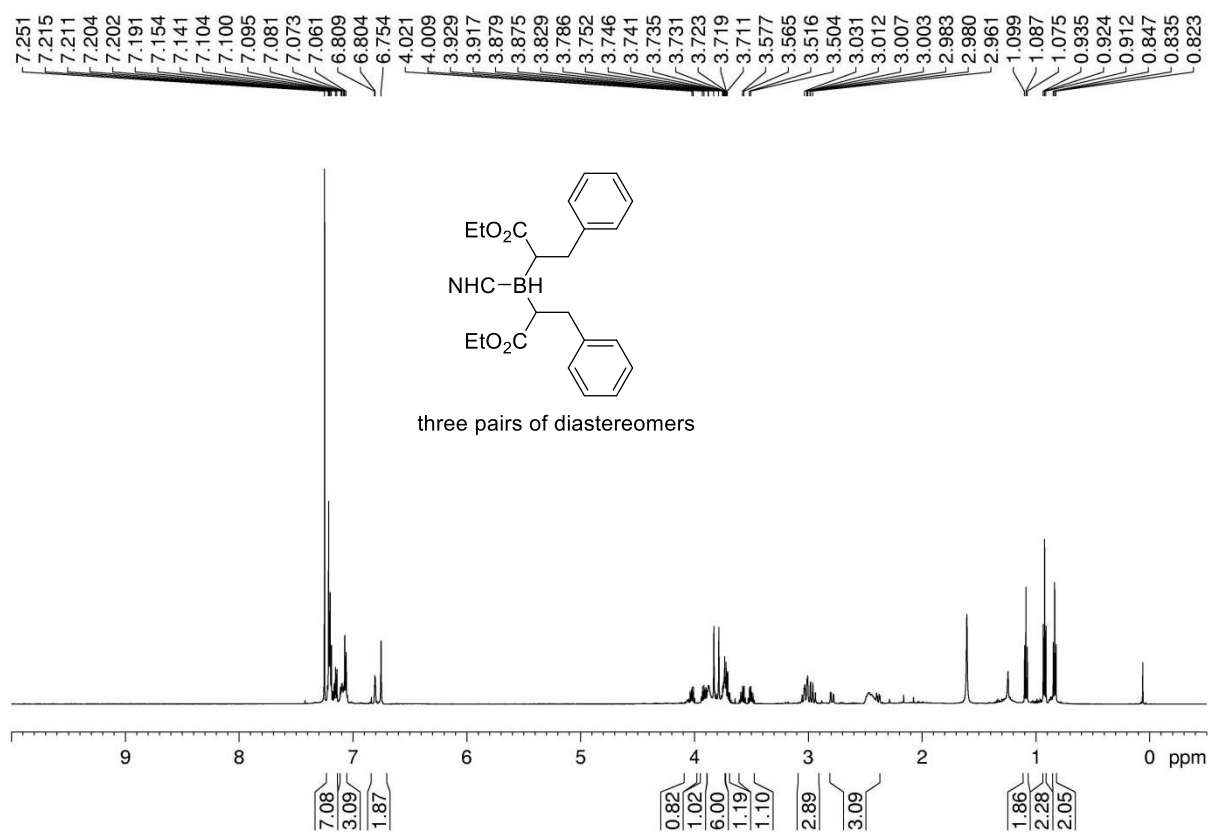
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) spectrum of **20**



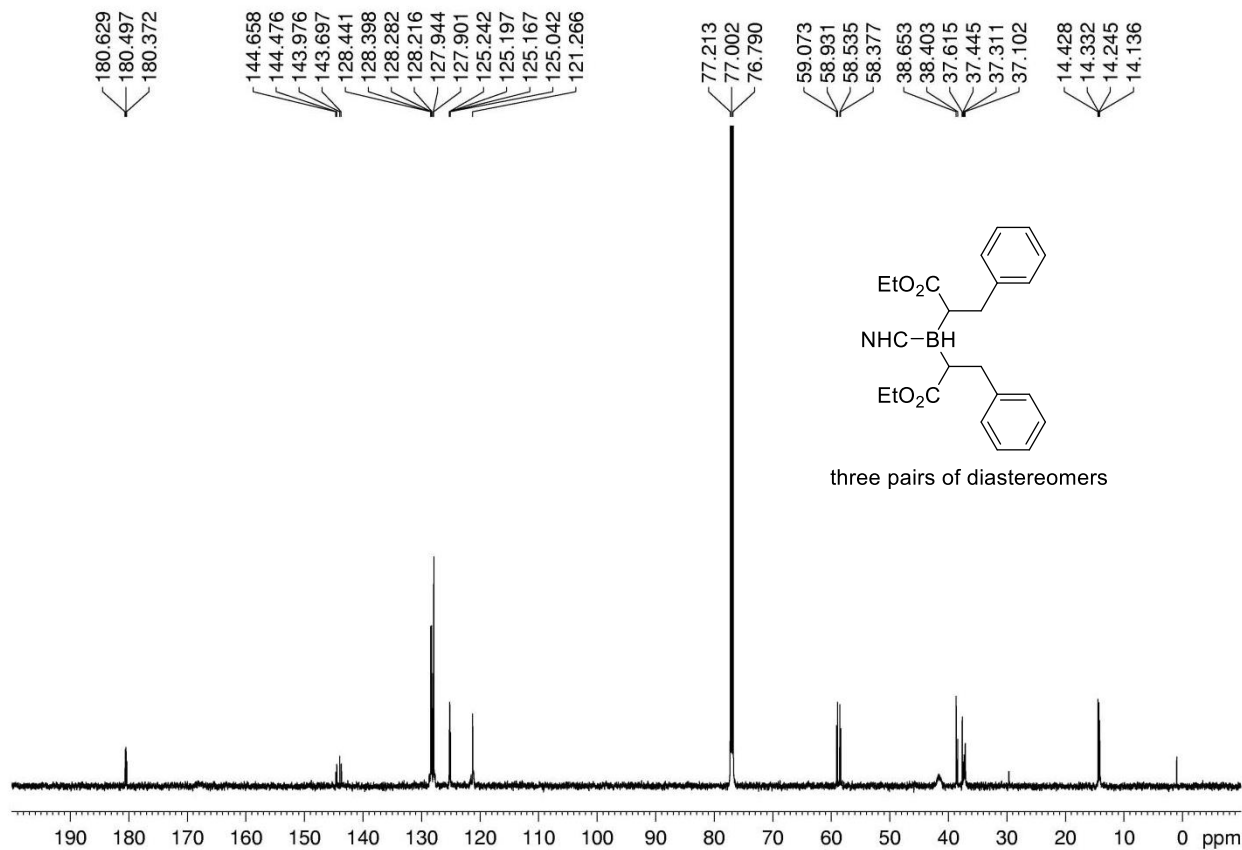
<sup>11</sup>B NMR (CDCl<sub>3</sub>, 192 MHz) spectrum of **20**



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) spectrum of **21**

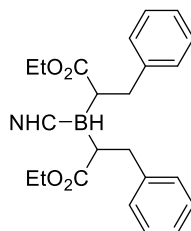
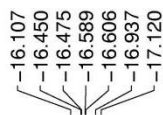


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) spectrum of **21**

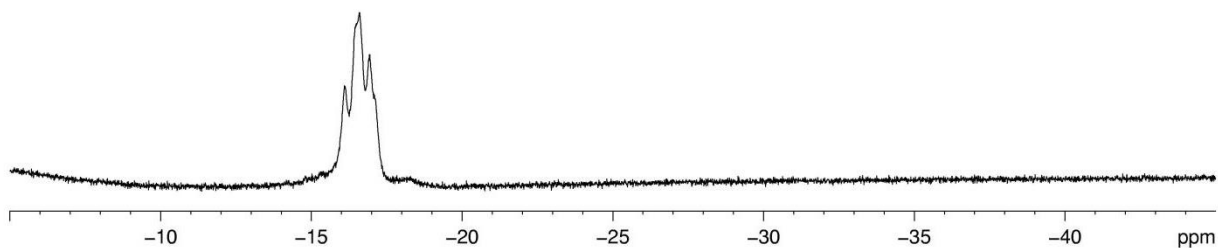




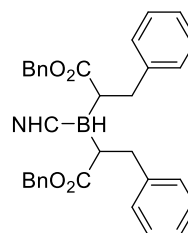
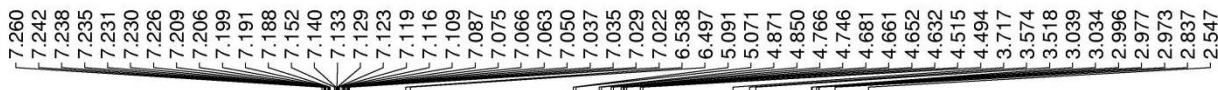
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **21**



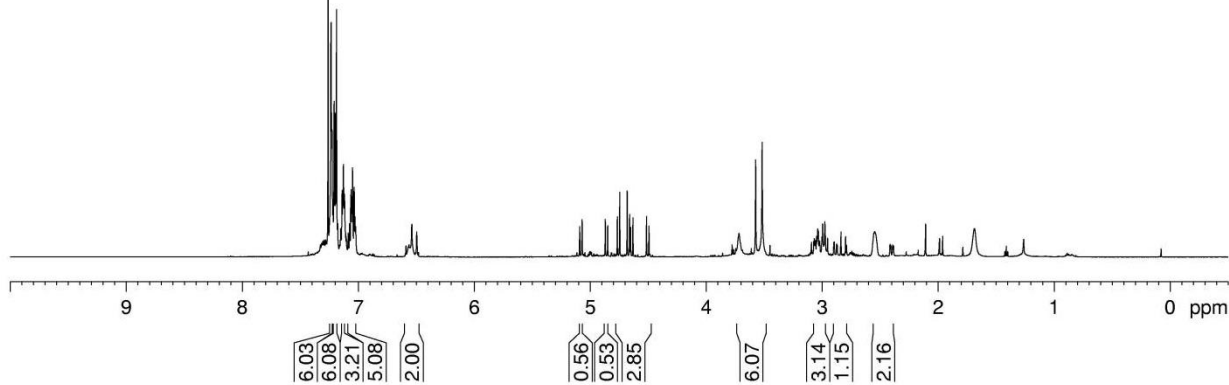
three pairs of diastereomers



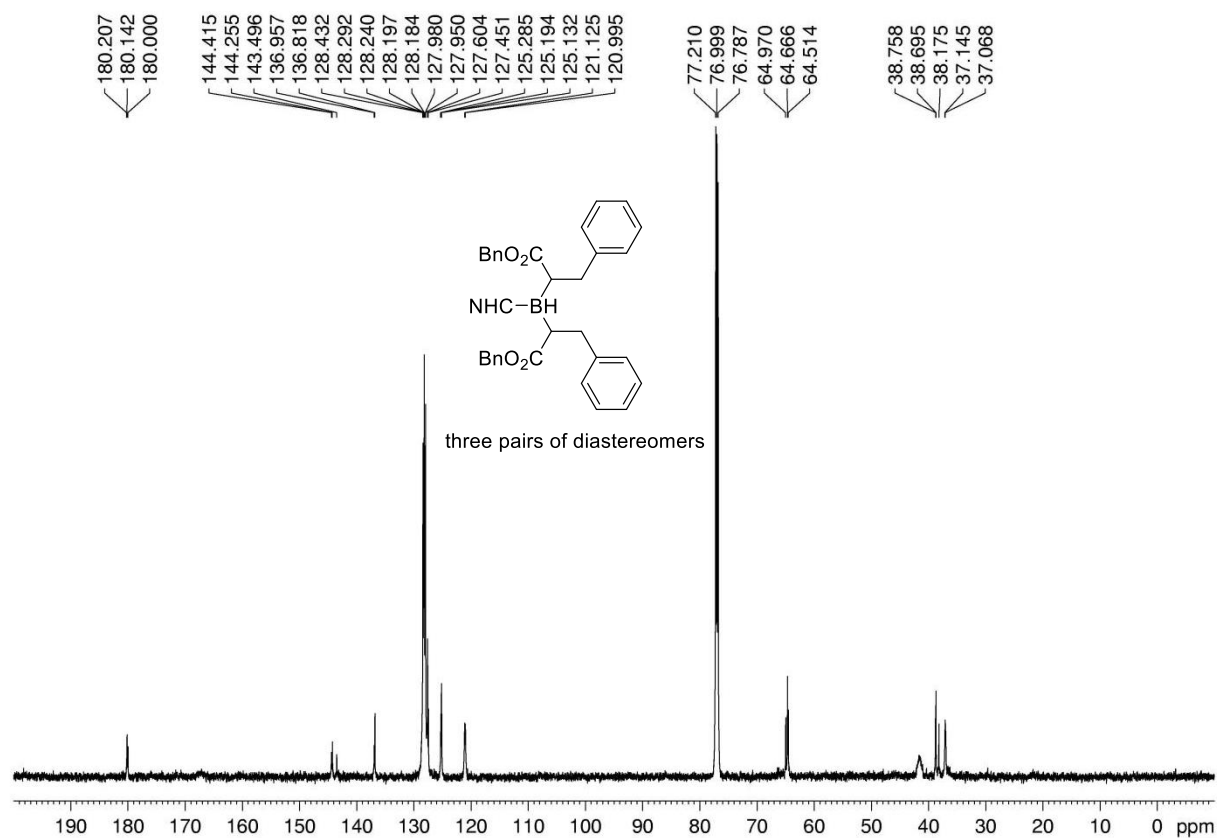
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **22**



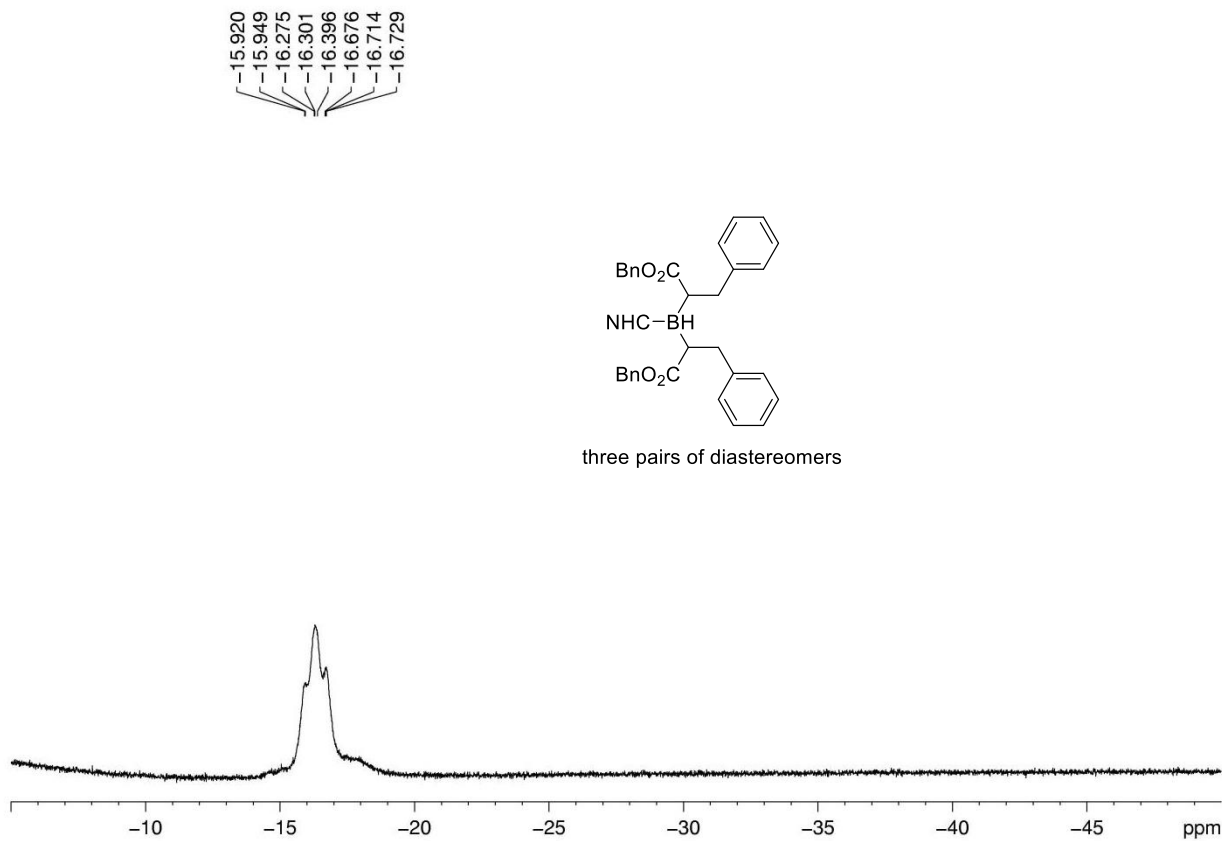
three pairs of diastereomers



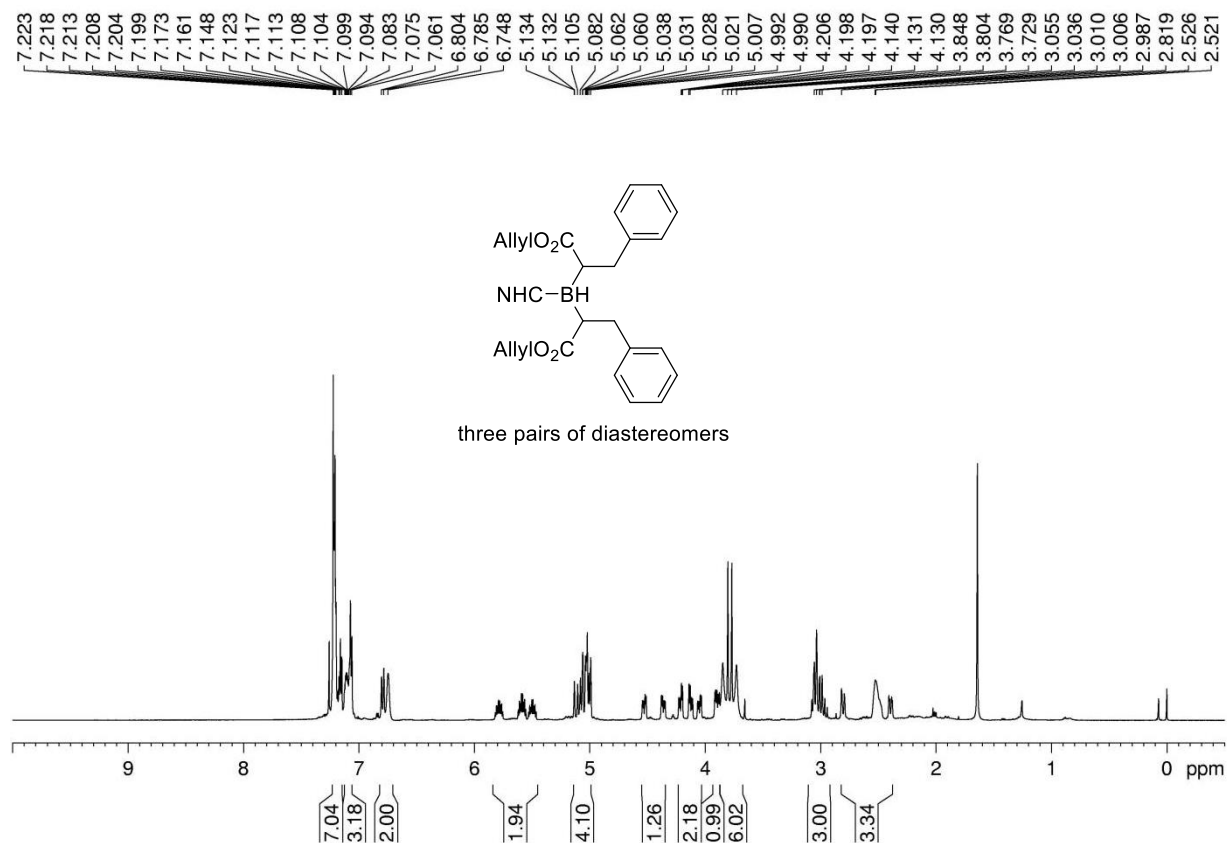
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **22**



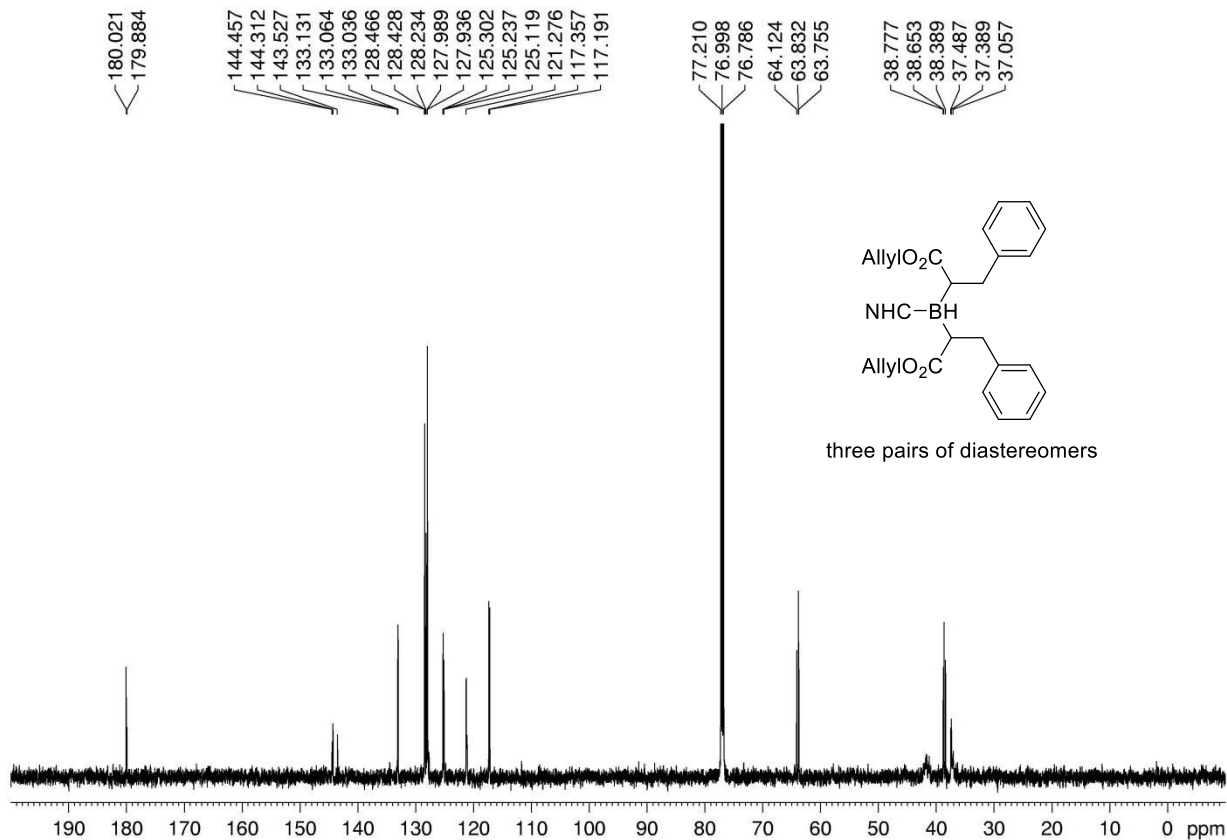
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **22**



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **23**

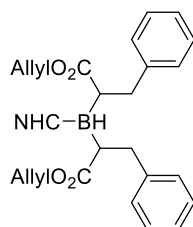


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **23**

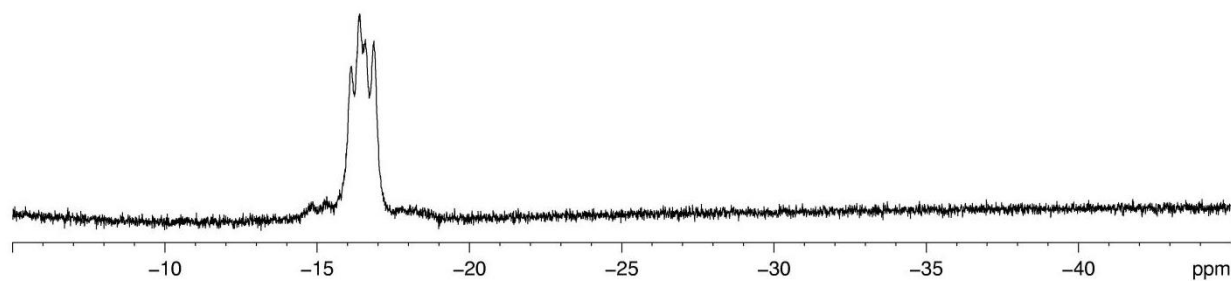


$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **23**

16.128  
16.370  
16.395  
16.586  
16.840  
16.863

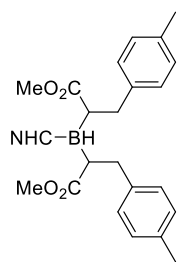


three pairs of diastereomers

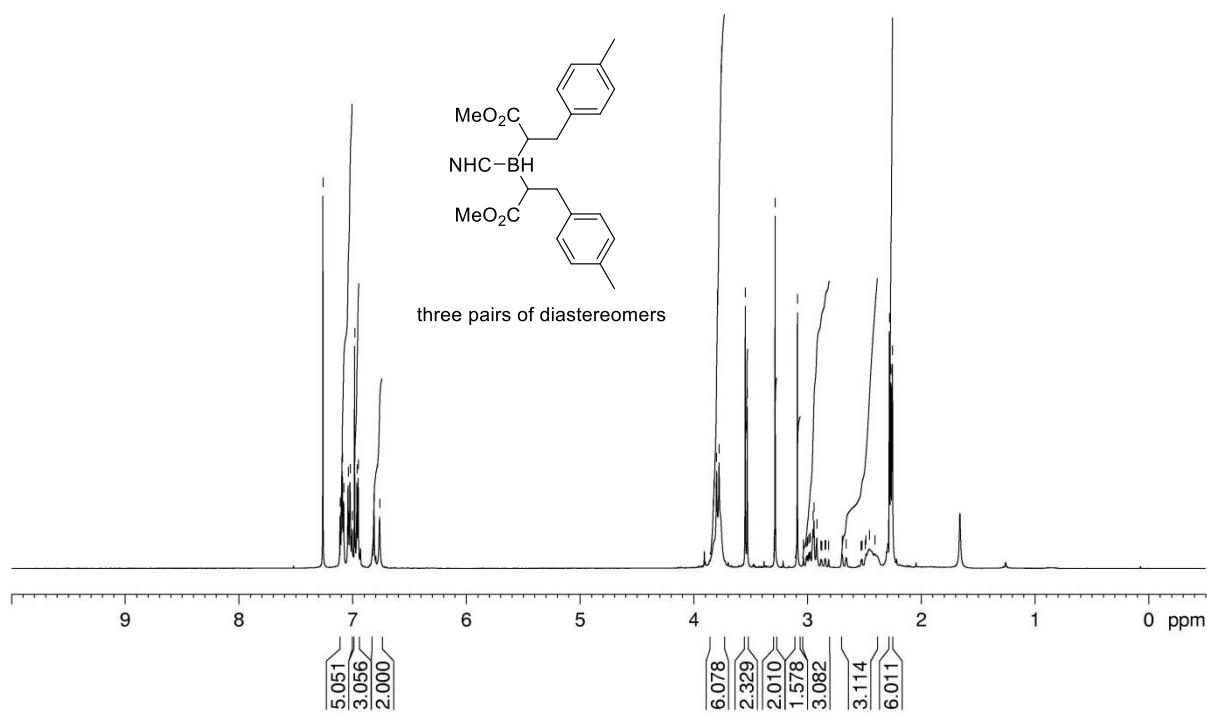


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **24**

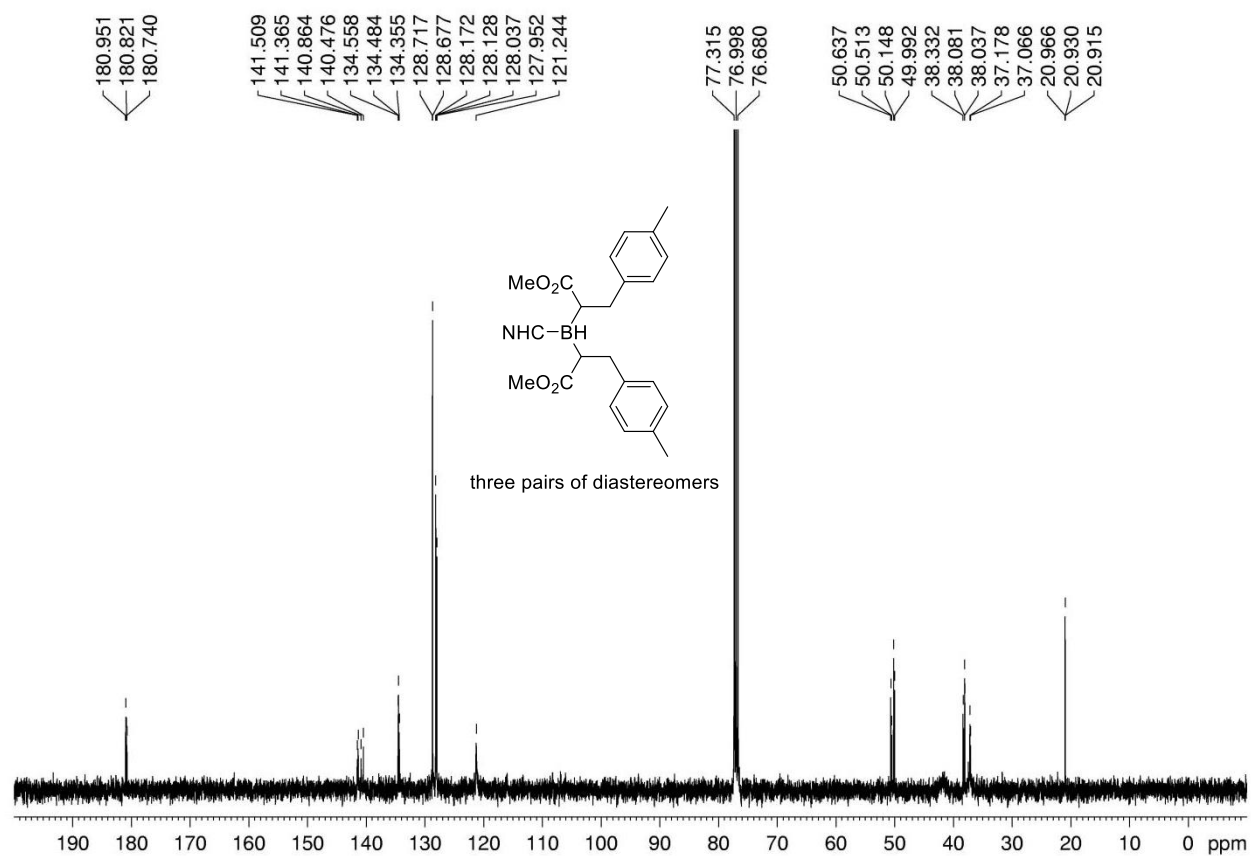
7.260  
7.109  
7.089  
7.078  
7.039  
7.023  
7.004  
6.982  
6.961  
6.950  
6.811  
6.762  
3.801  
3.779  
3.549  
3.531  
3.286  
3.090  
3.037  
3.011  
3.002  
2.990  
2.977  
2.954  
2.945  
2.919  
2.883  
2.876  
2.849  
2.842  
2.815  
2.695  
2.662  
2.530  
2.522  
2.495  
2.487  
2.458  
2.409  
2.281  
2.269  
2.258  
2.254



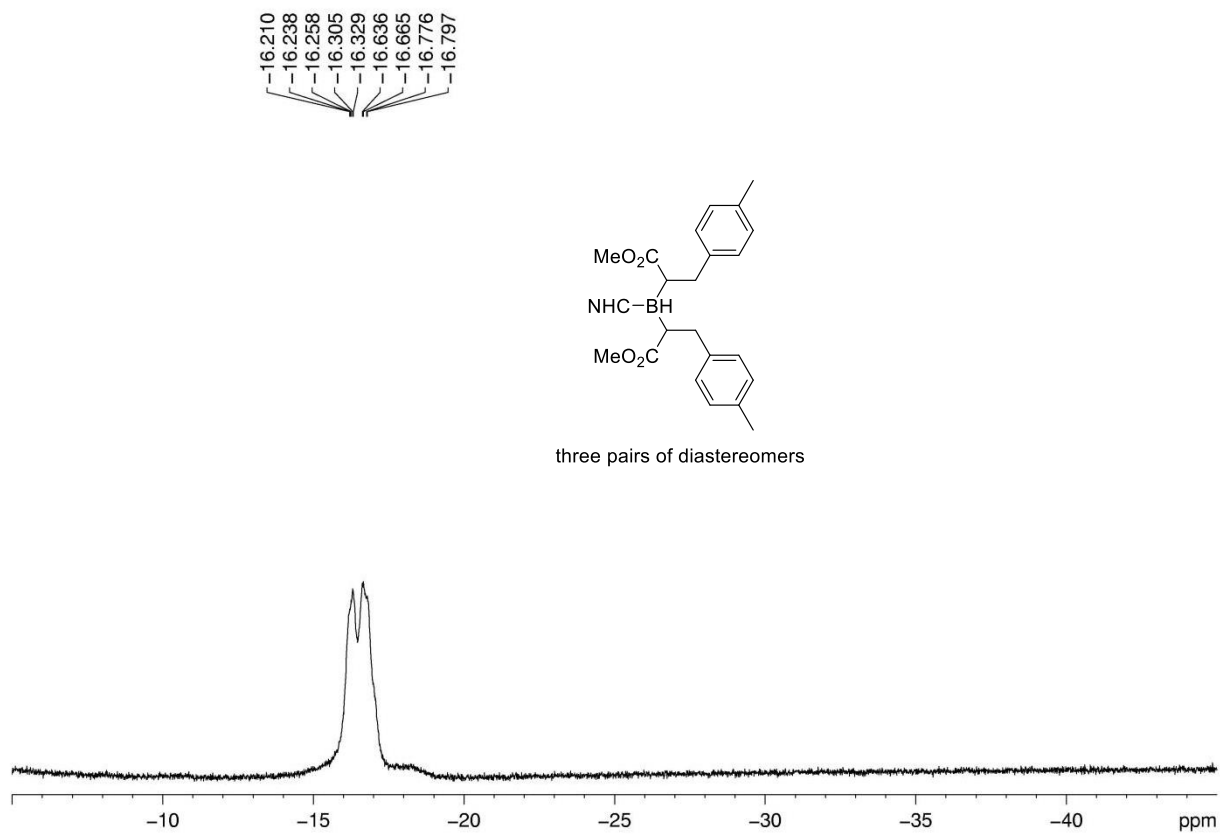
three pairs of diastereomers



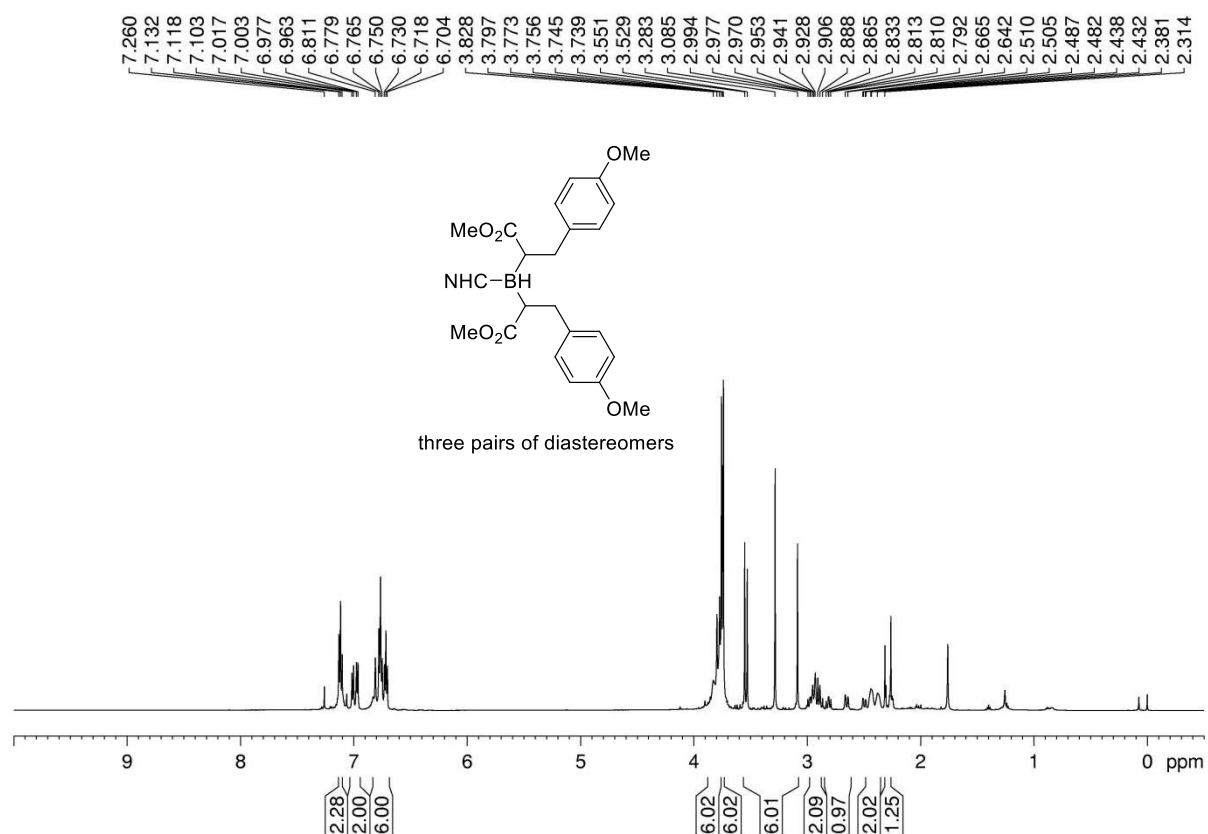
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) spectrum of **24**



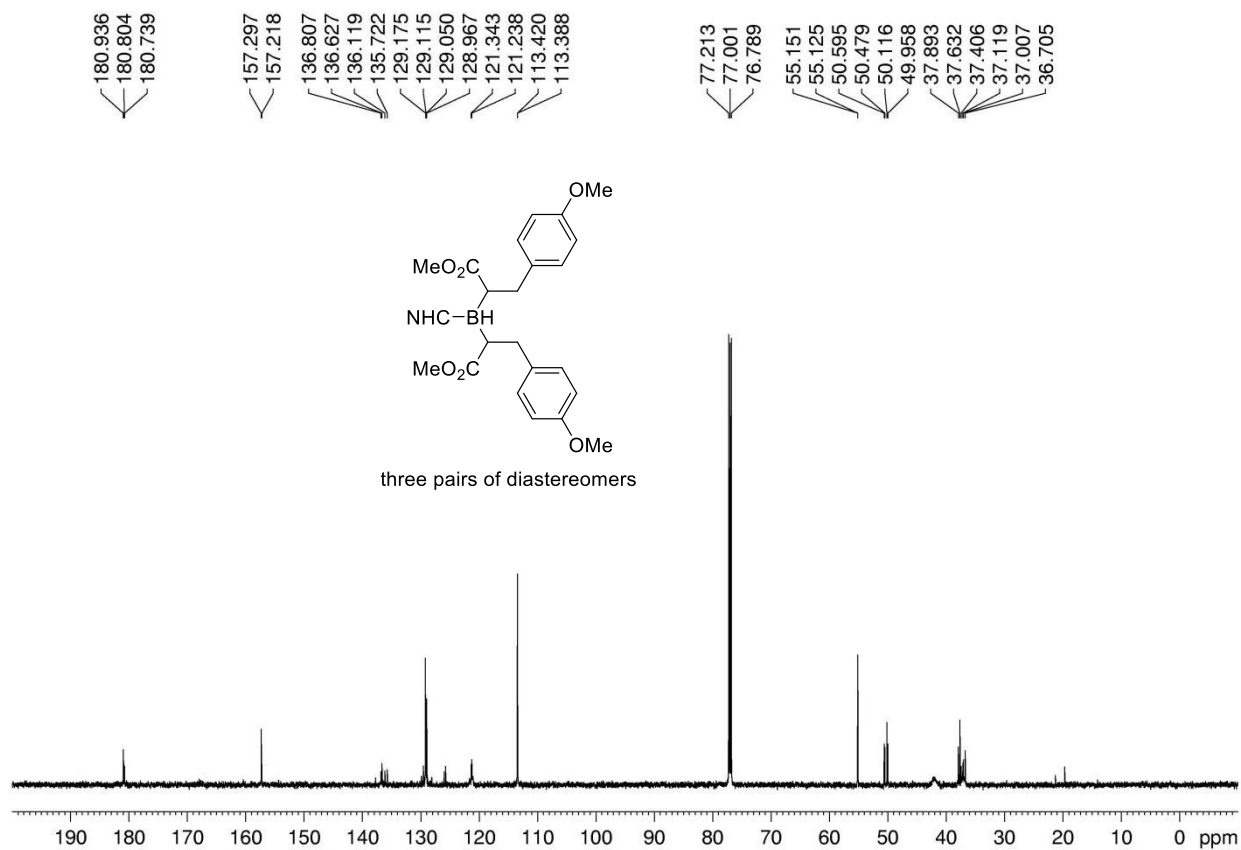
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **24**



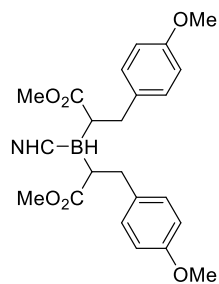
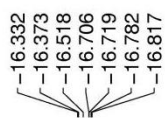
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) spectrum of **25**



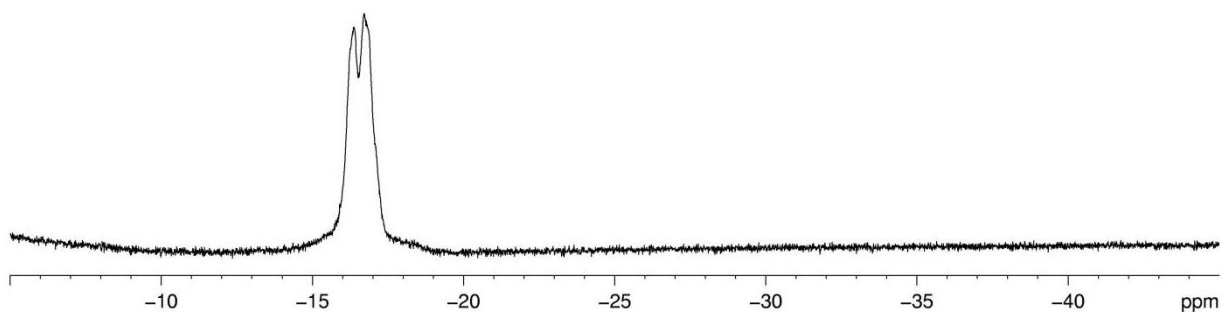
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) spectrum of **25**



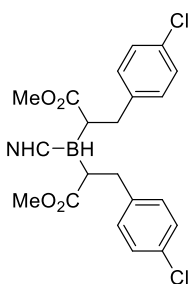
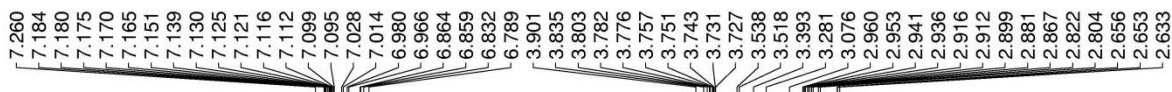
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **25**



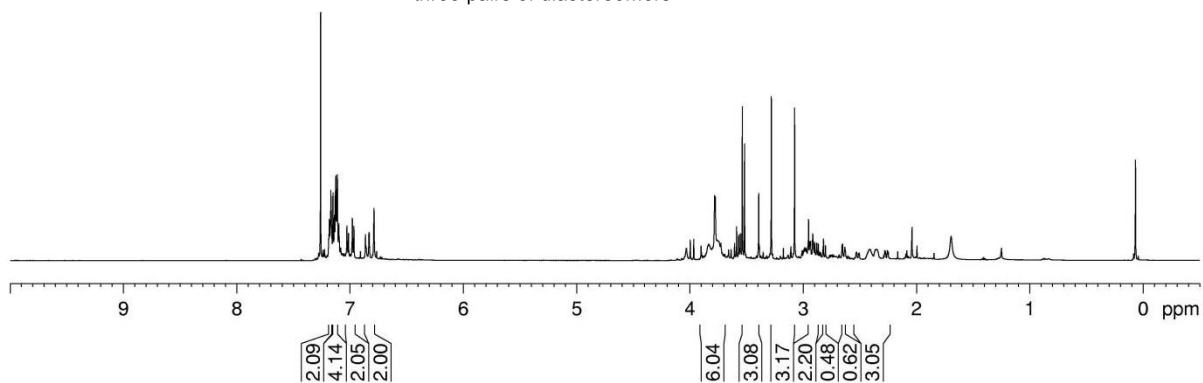
three pairs of diastereomers



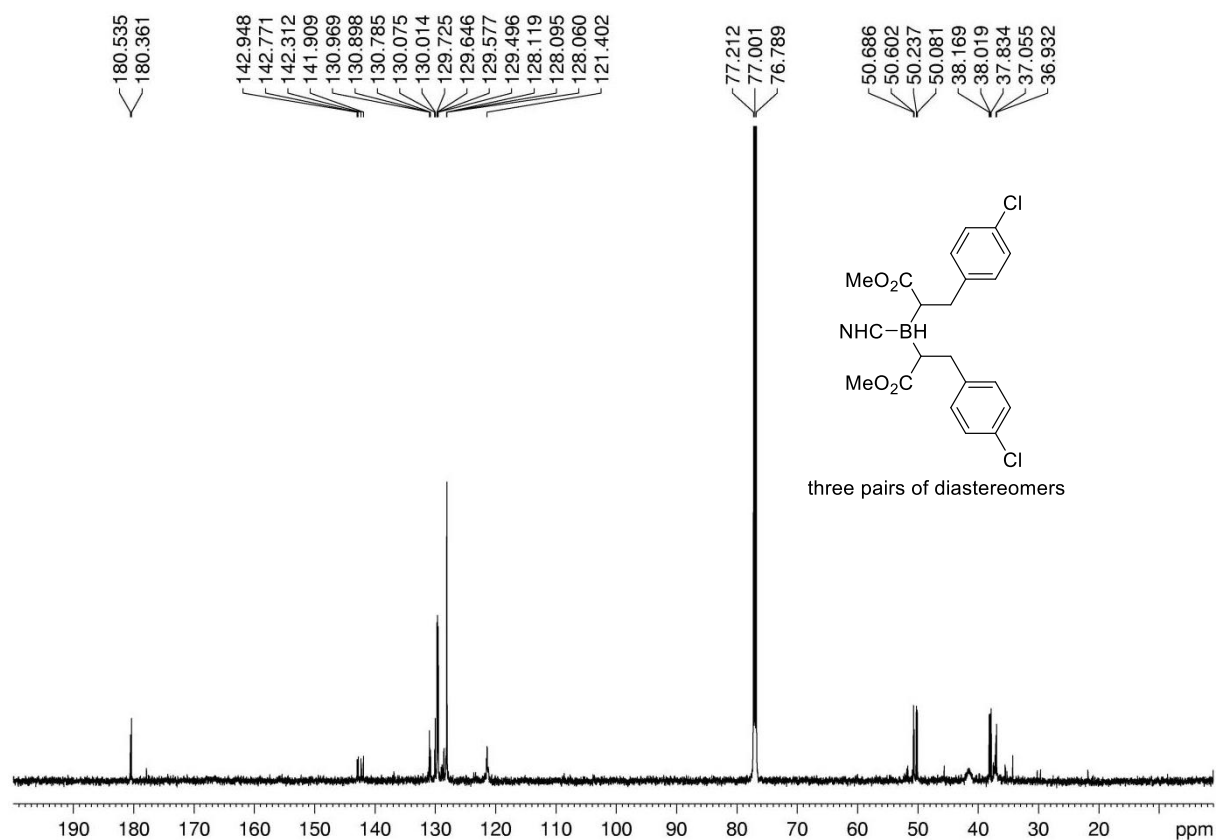
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **26**



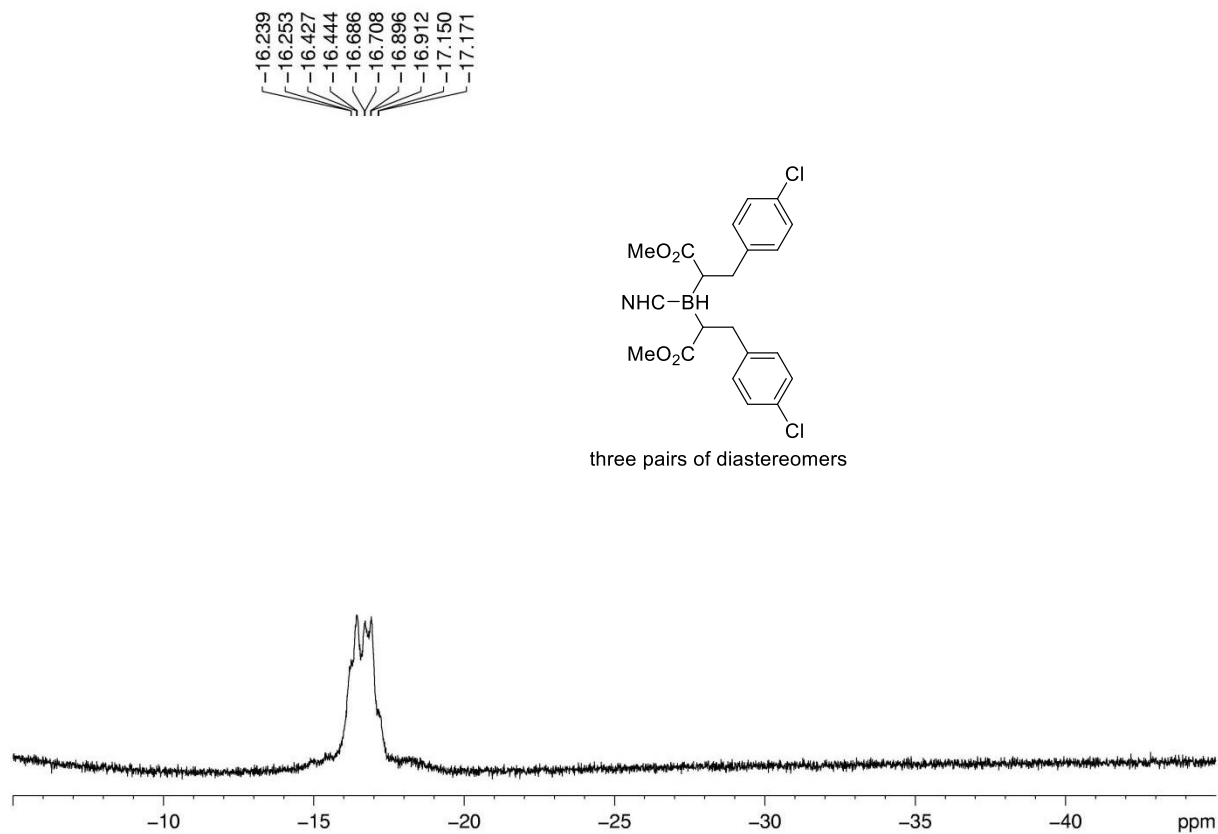
three pairs of diastereomers



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **26**

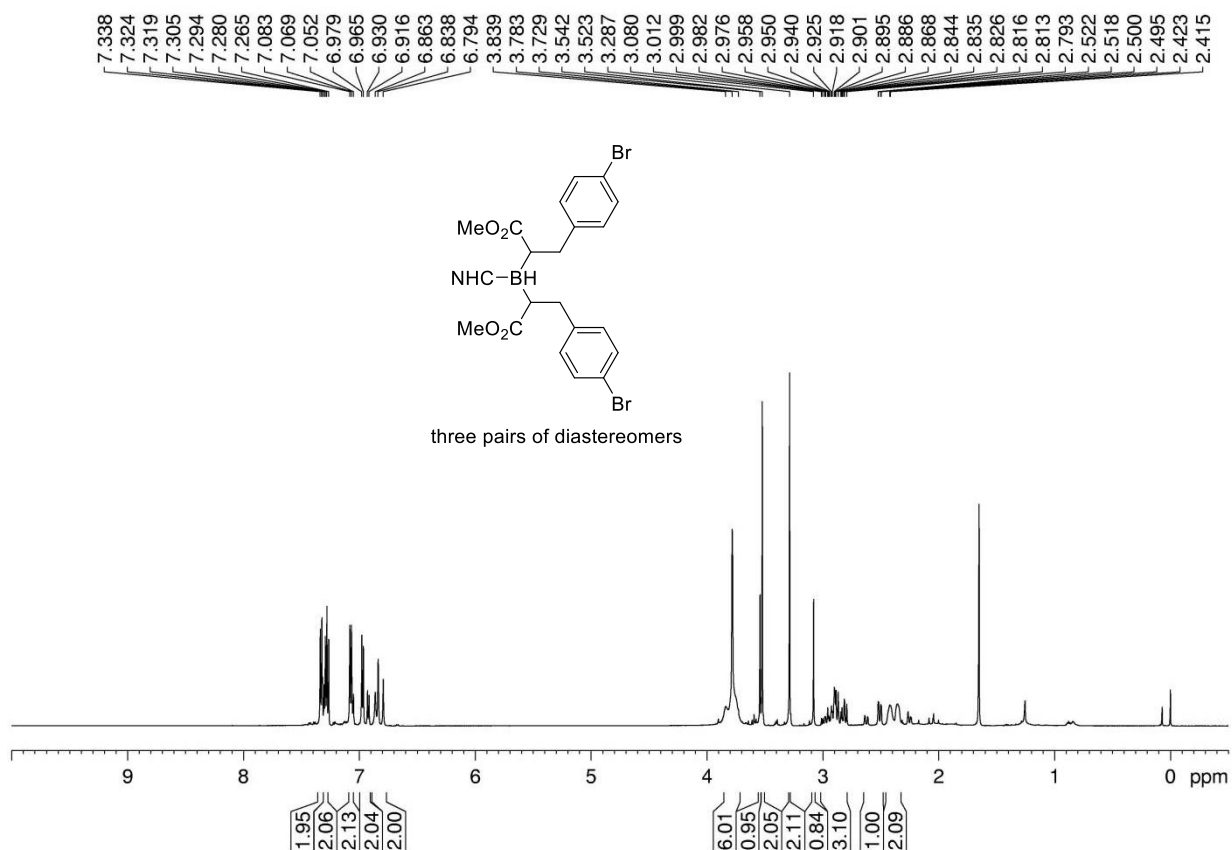


$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **26**

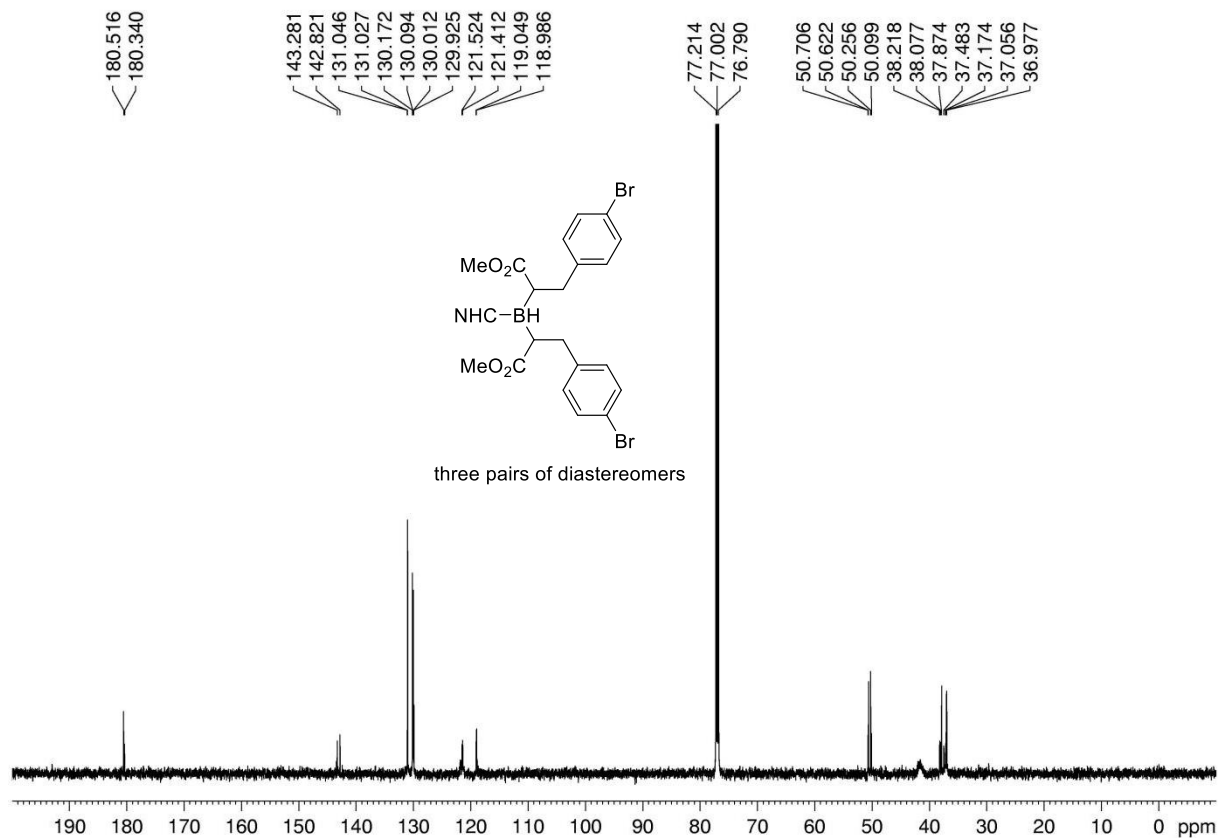




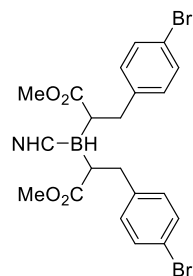
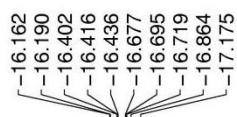
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) spectrum of **27**



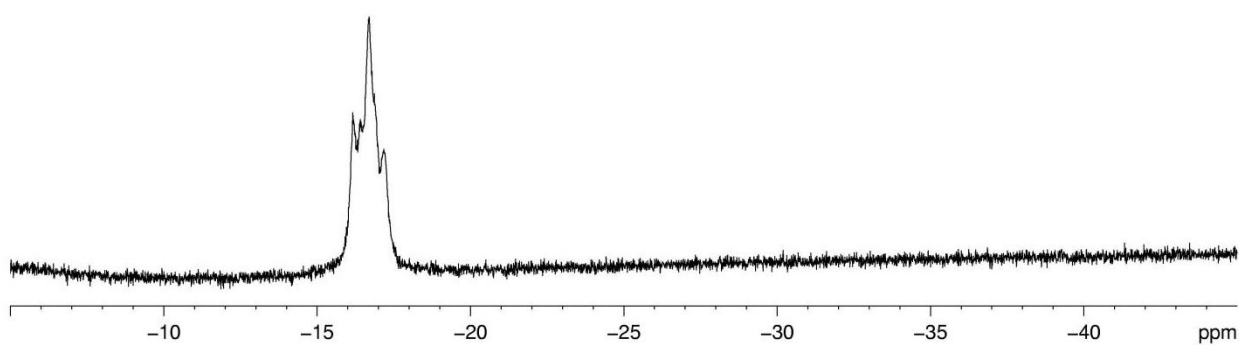
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) spectrum of **27**



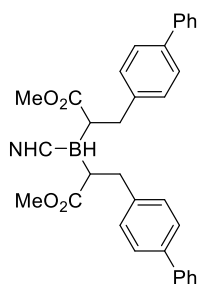
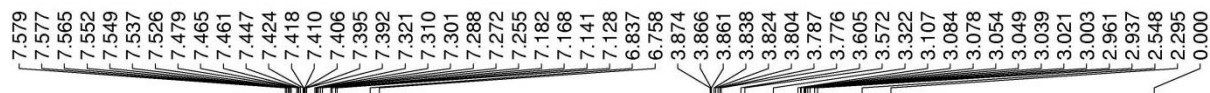
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **27**



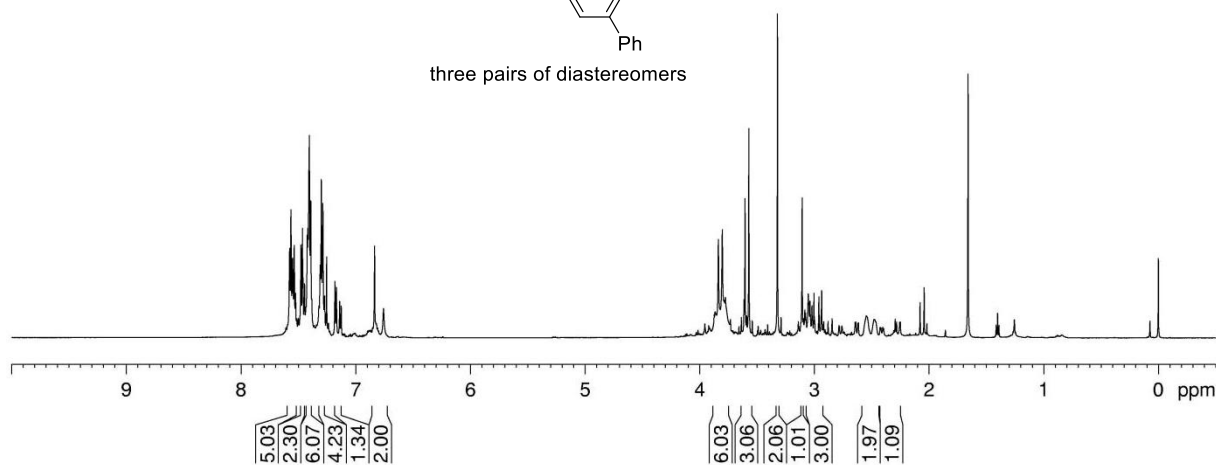
three pairs of diastereomers



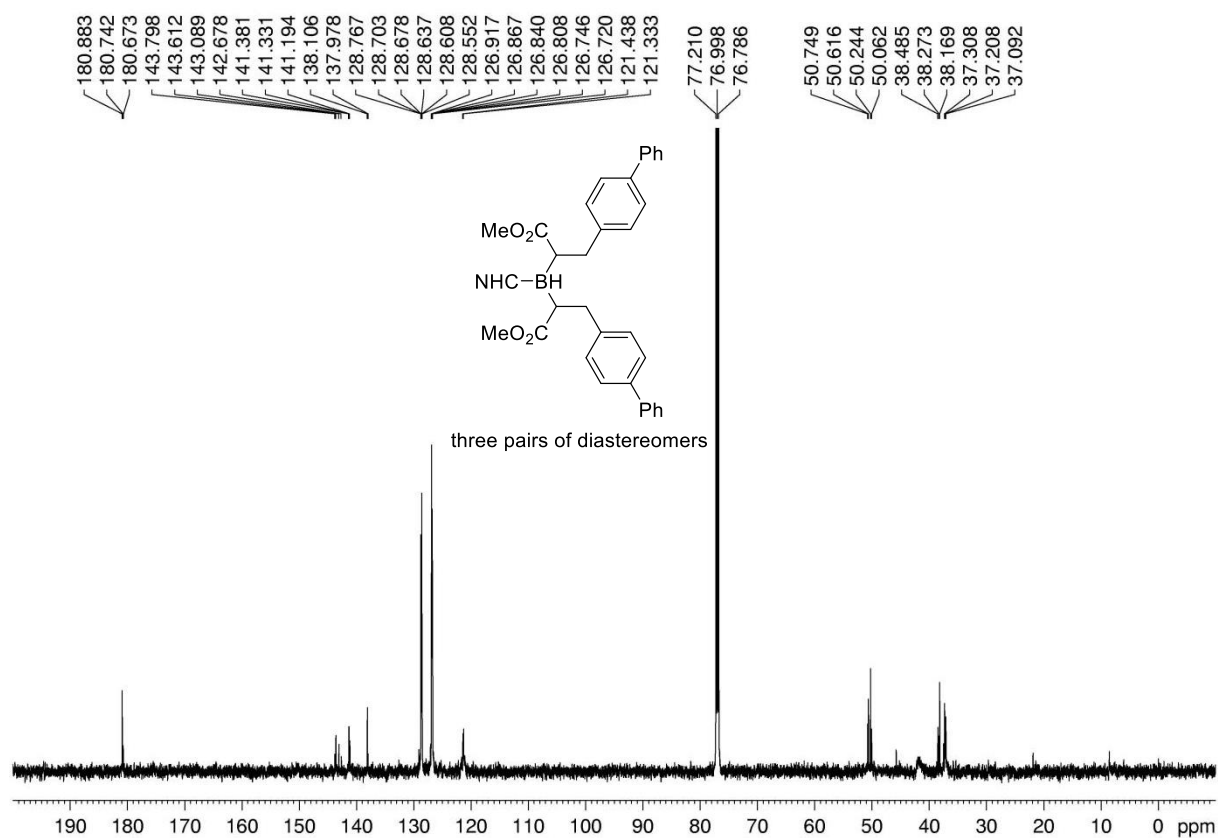
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **28**



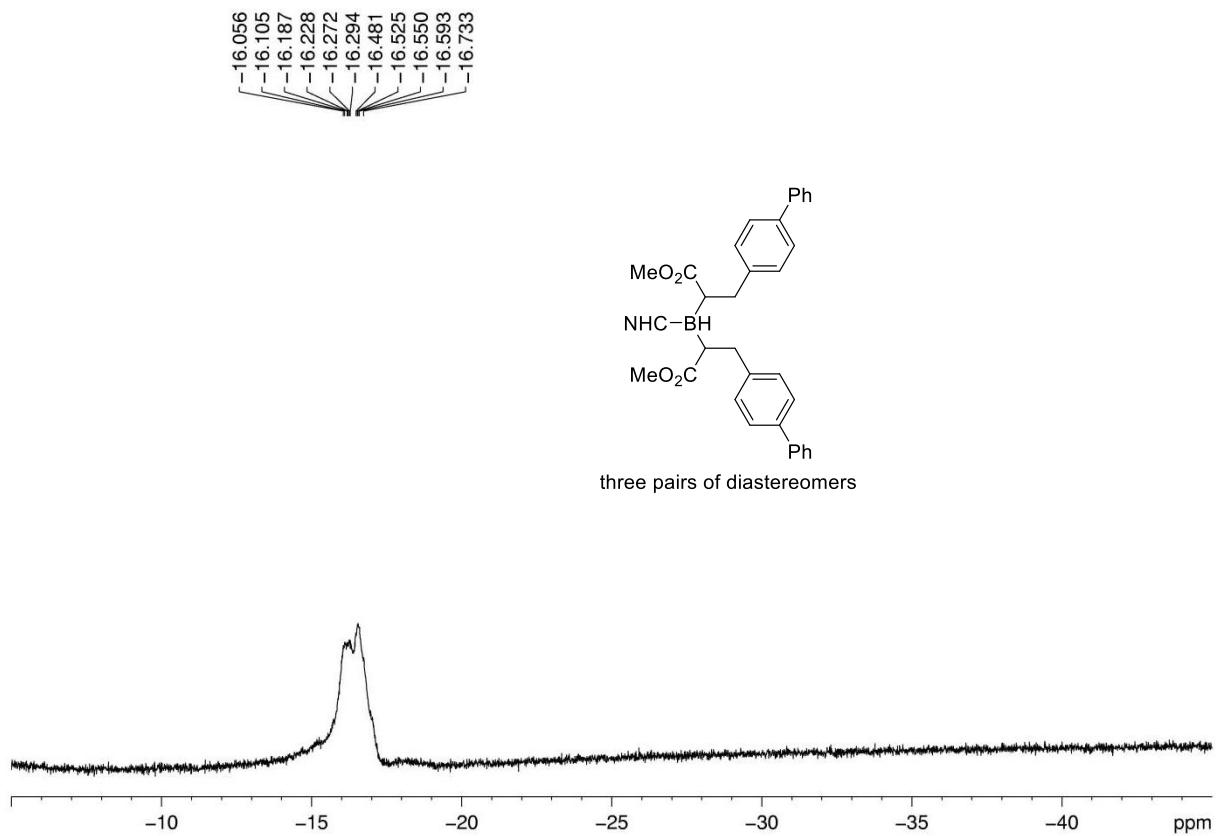
three pairs of diastereomers



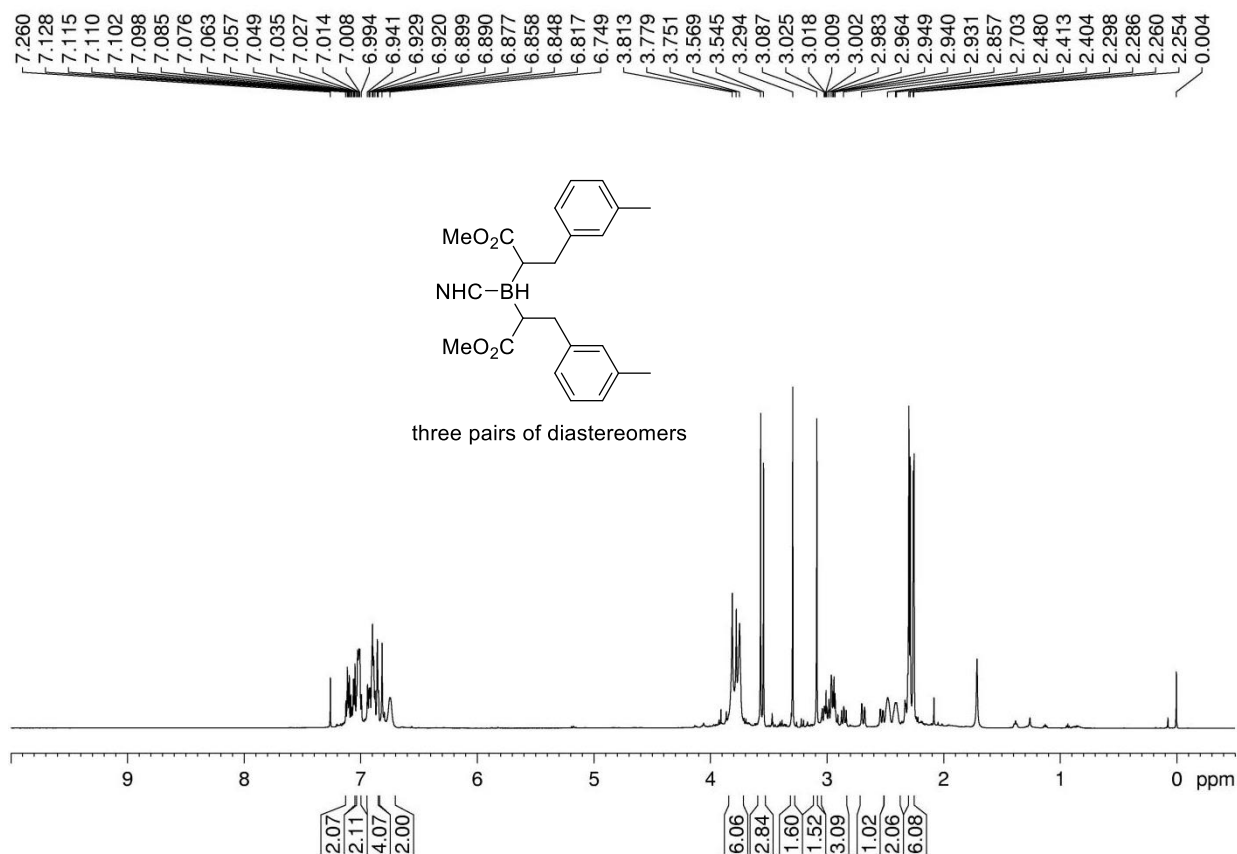
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **28**



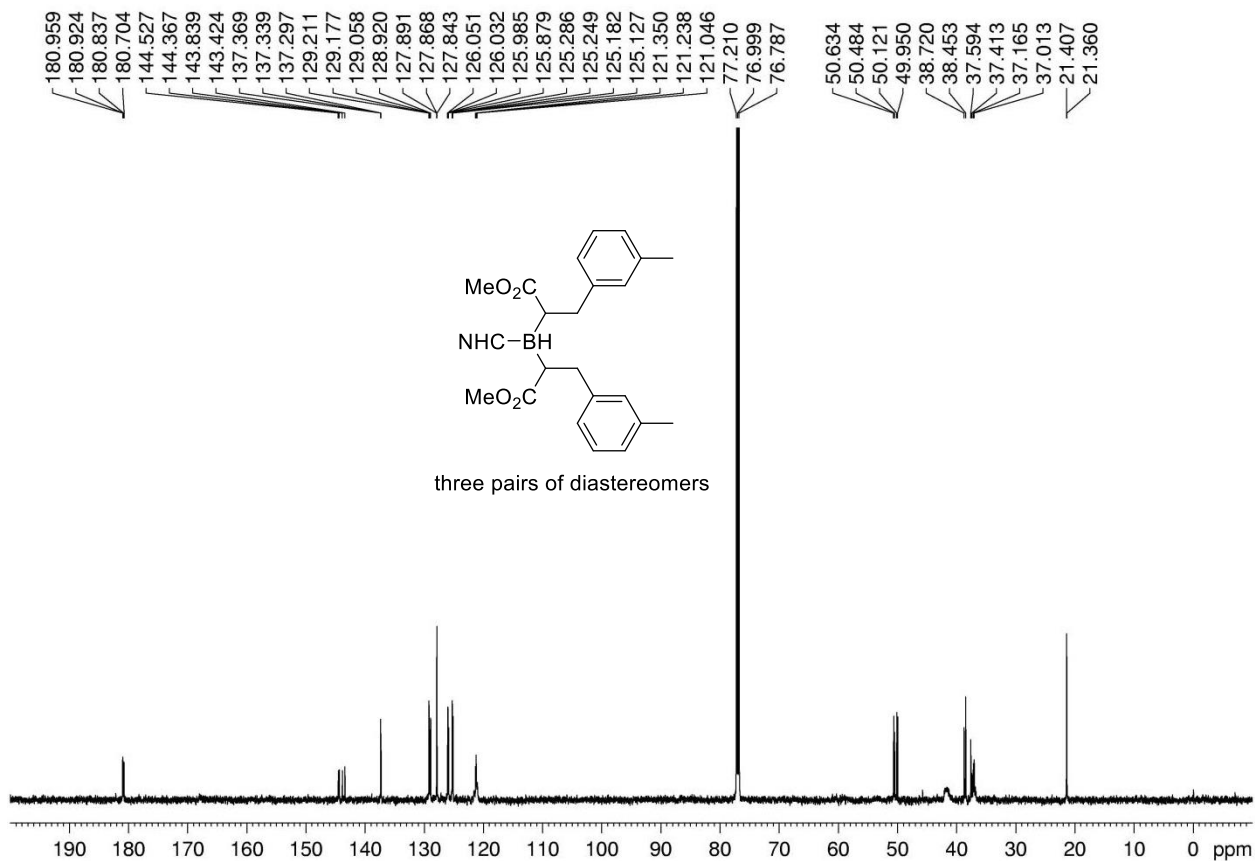
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **28**



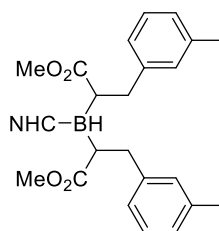
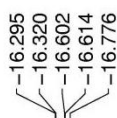
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **29**



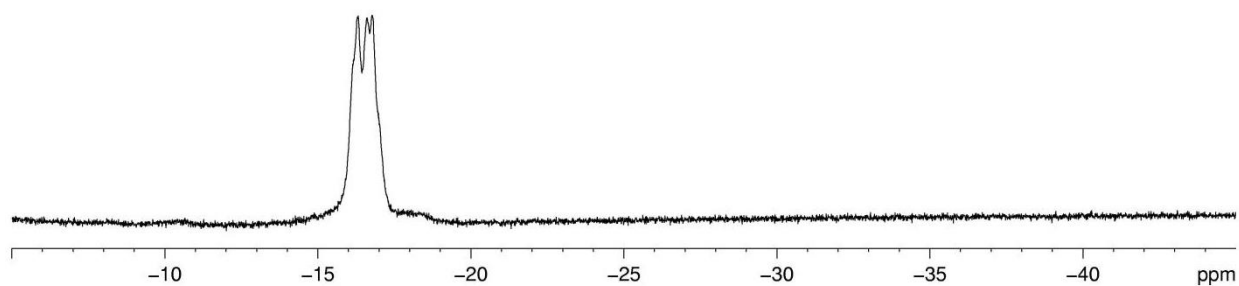
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **29**



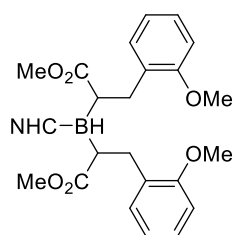
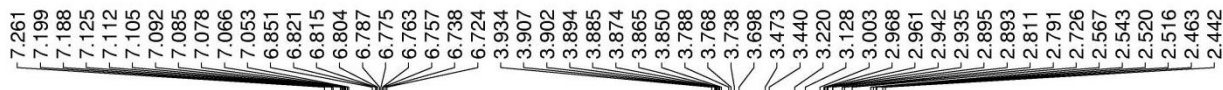
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **29**



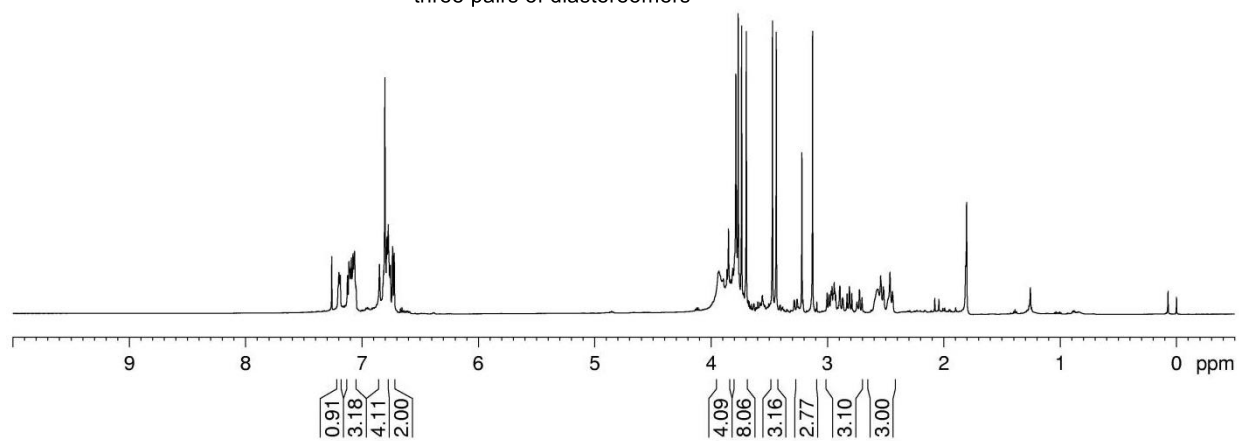
three pairs of diastereomers



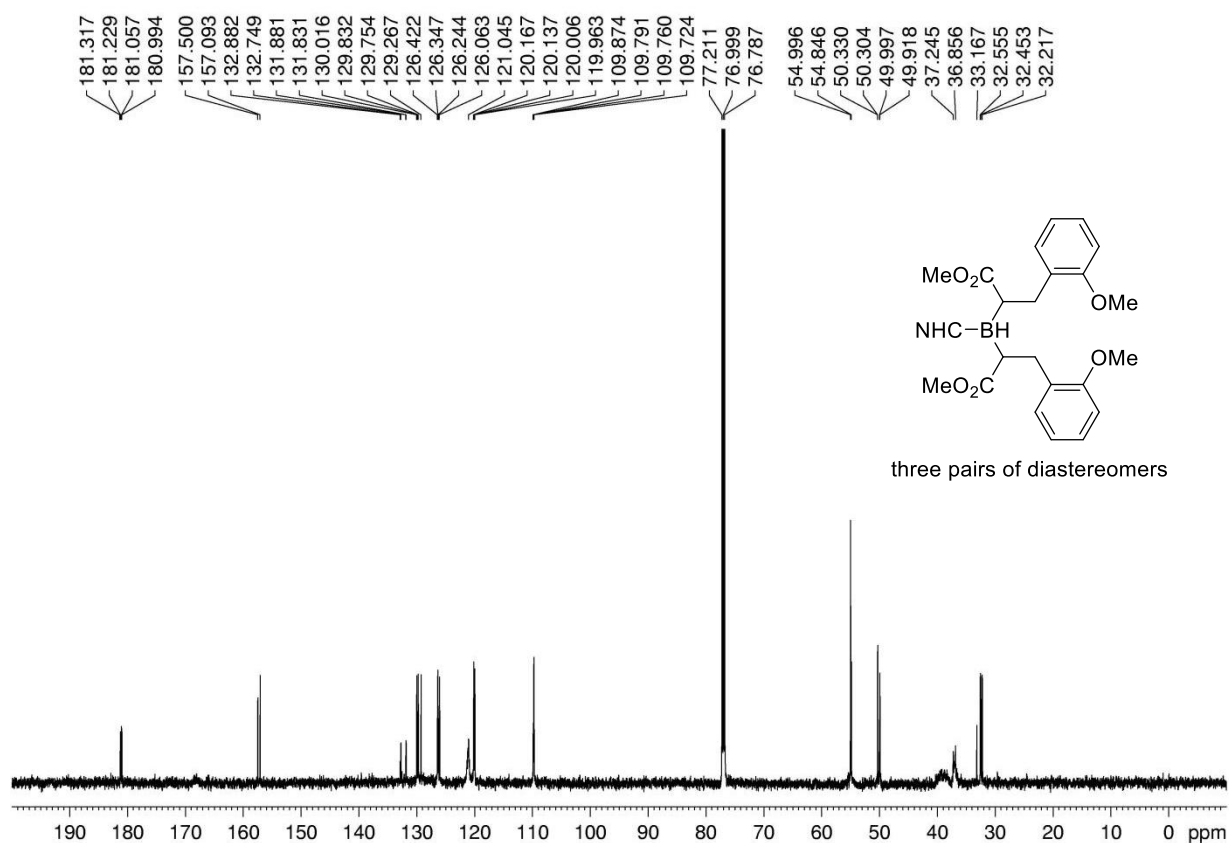
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **30**



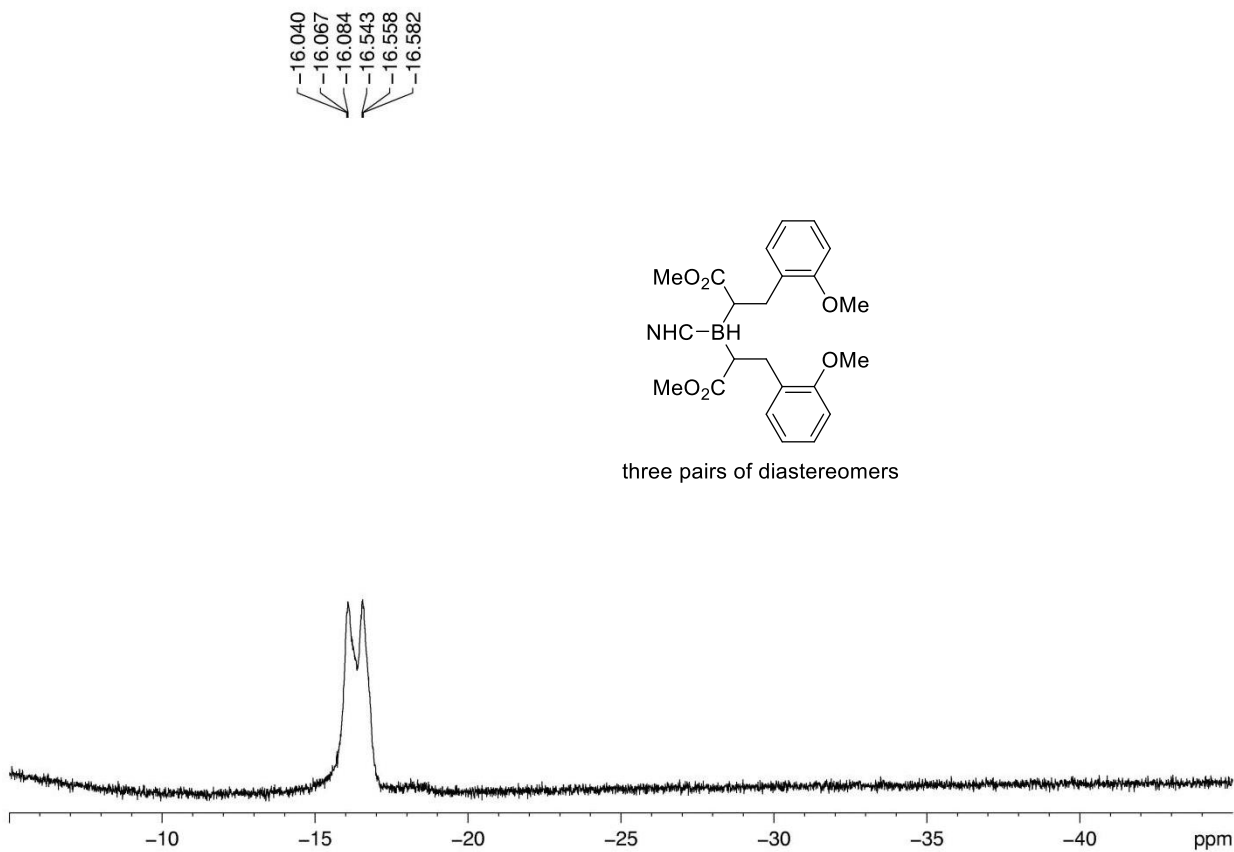
three pairs of diastereomers



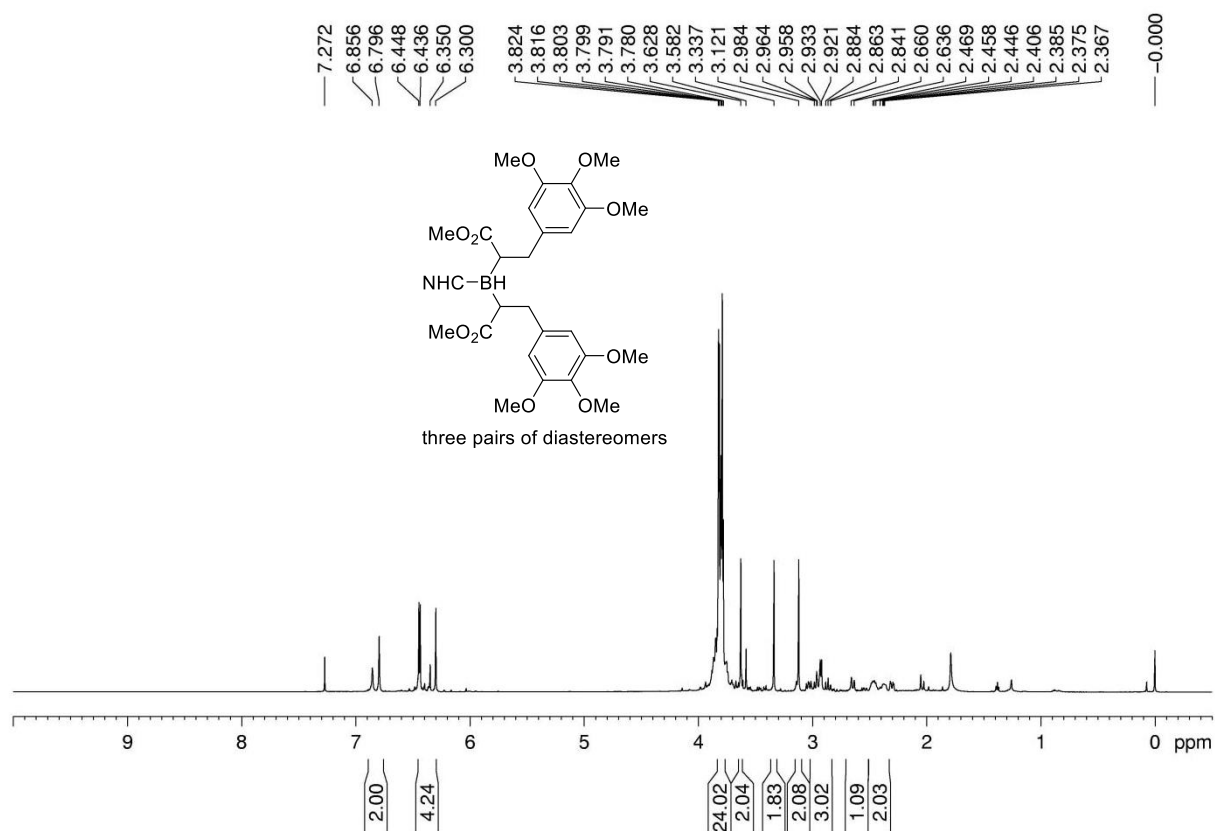
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **30**



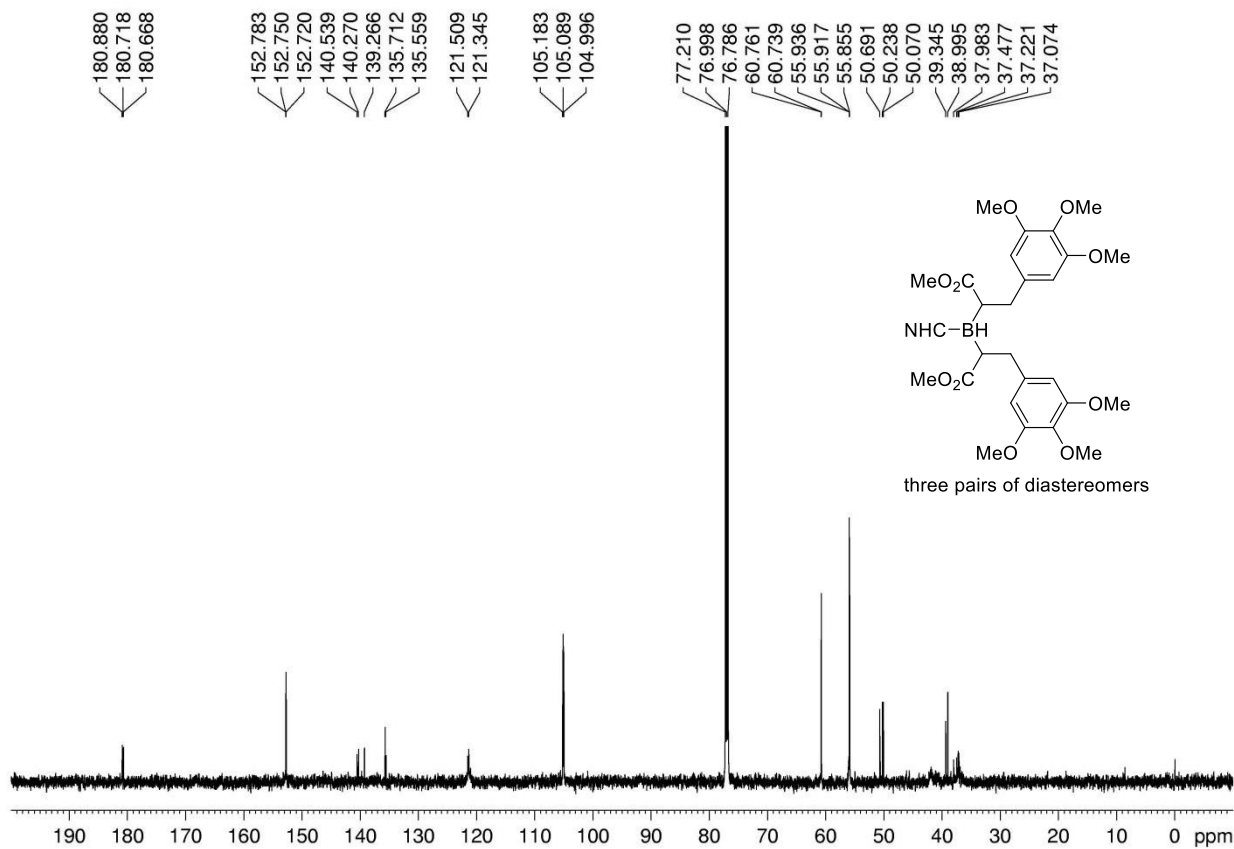
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **30**



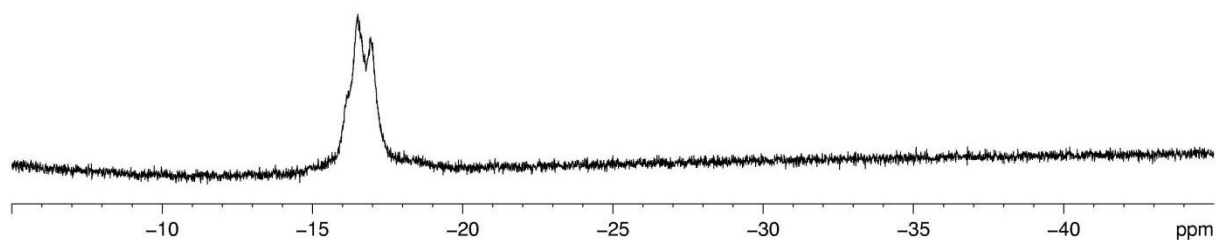
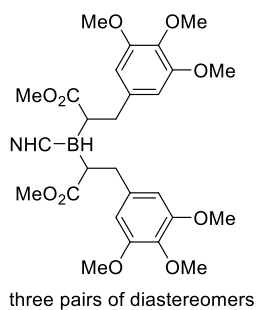
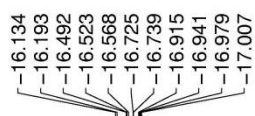
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) spectrum of **31**



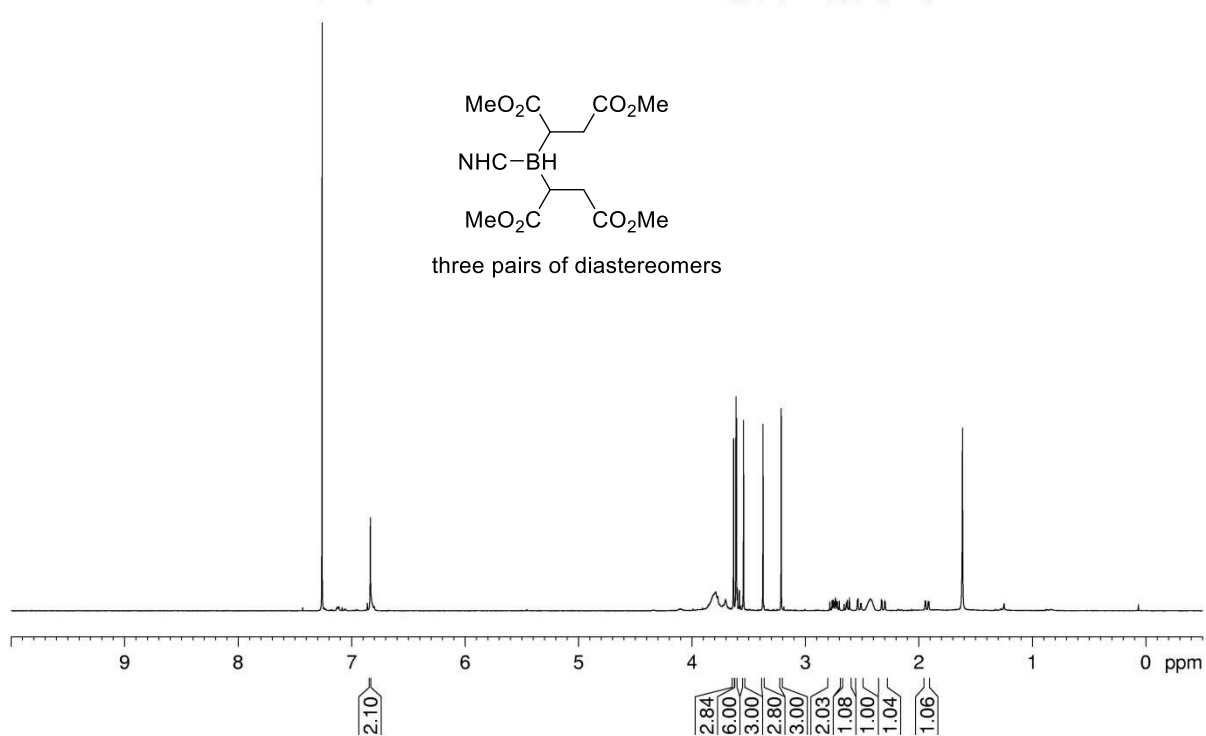
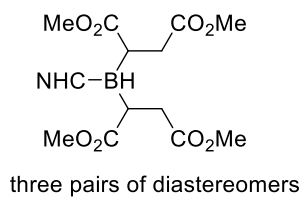
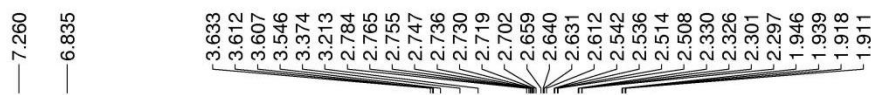
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) spectrum of **31**



$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **31**

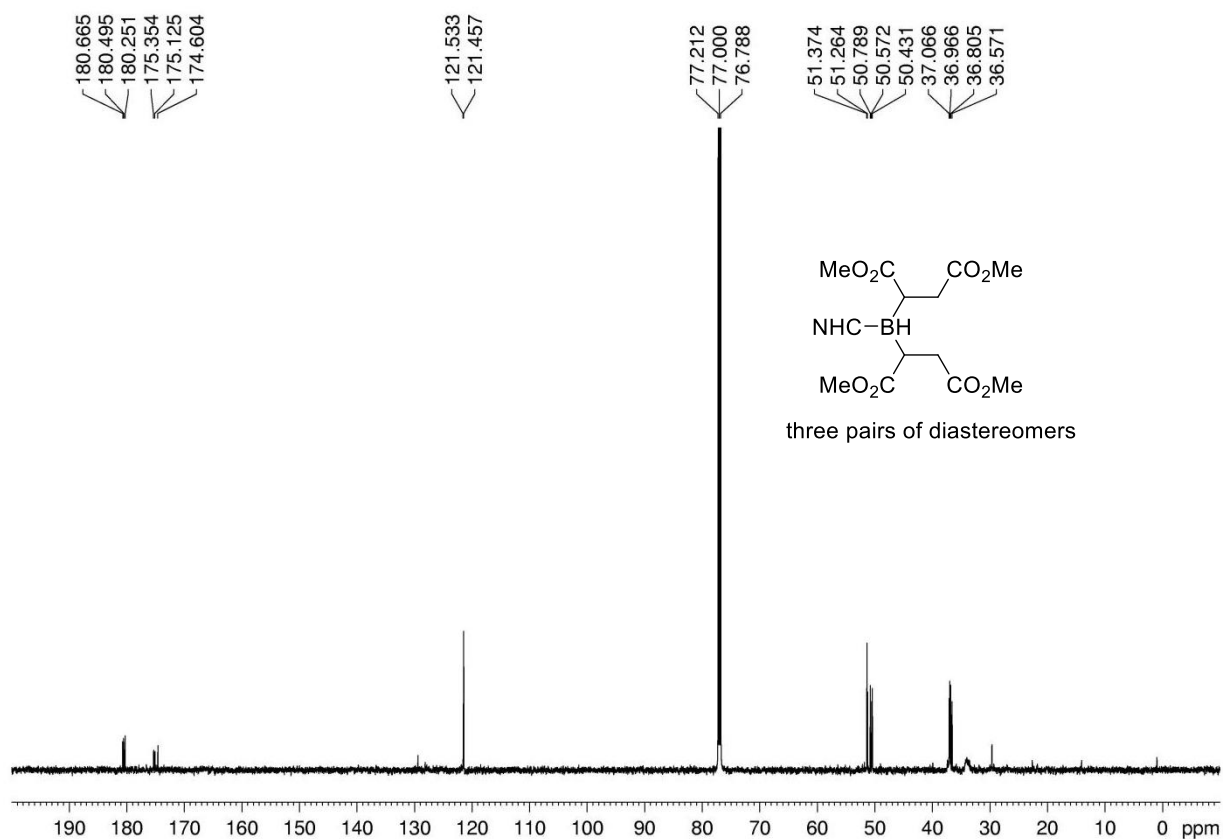


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **32**

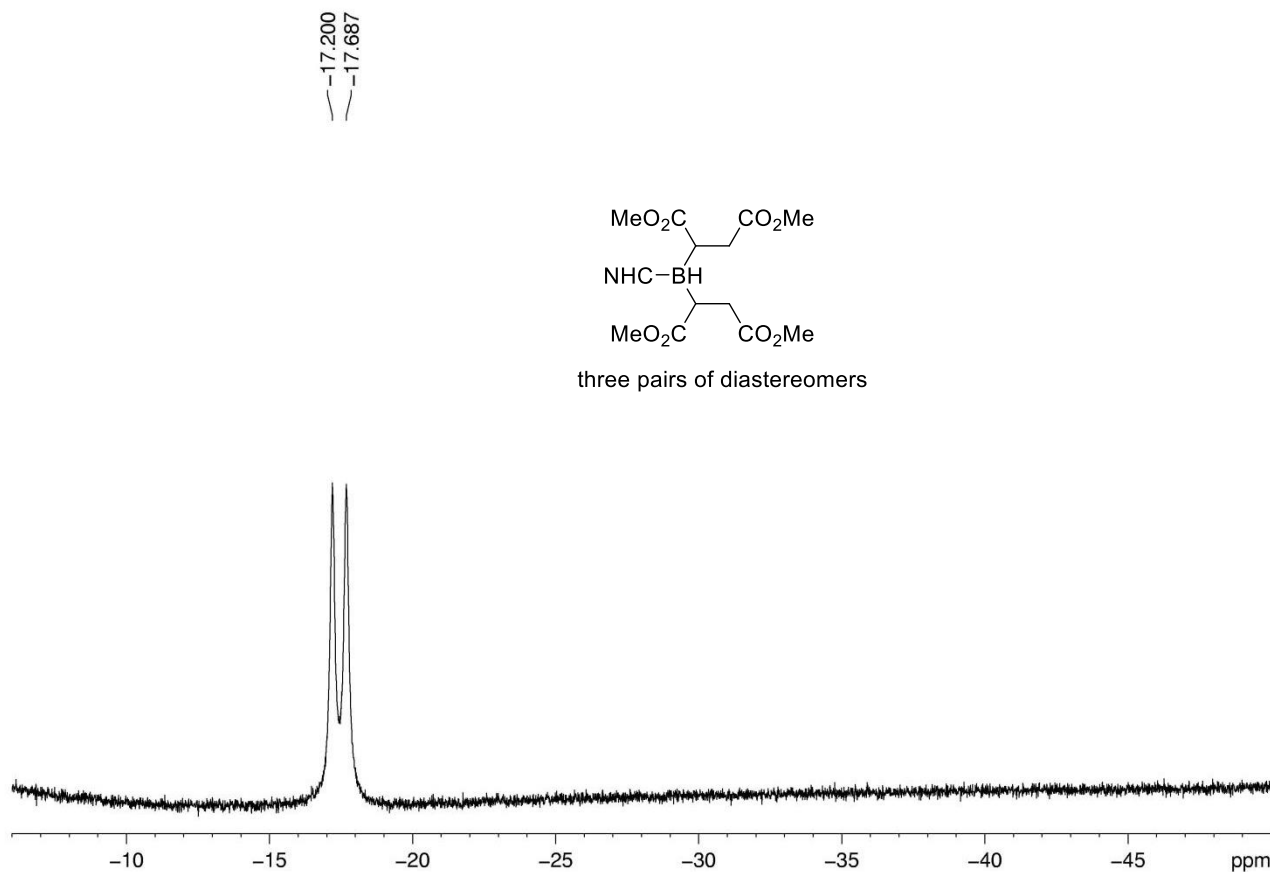




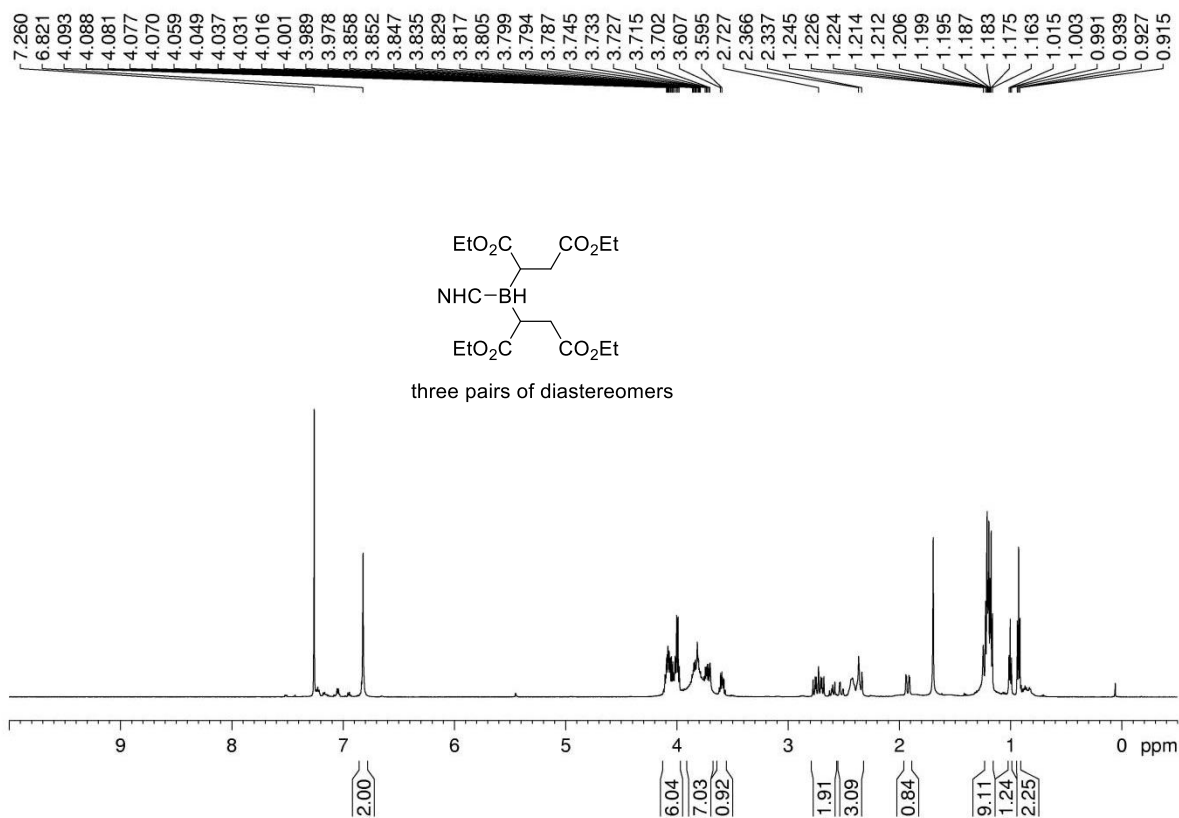
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **32**



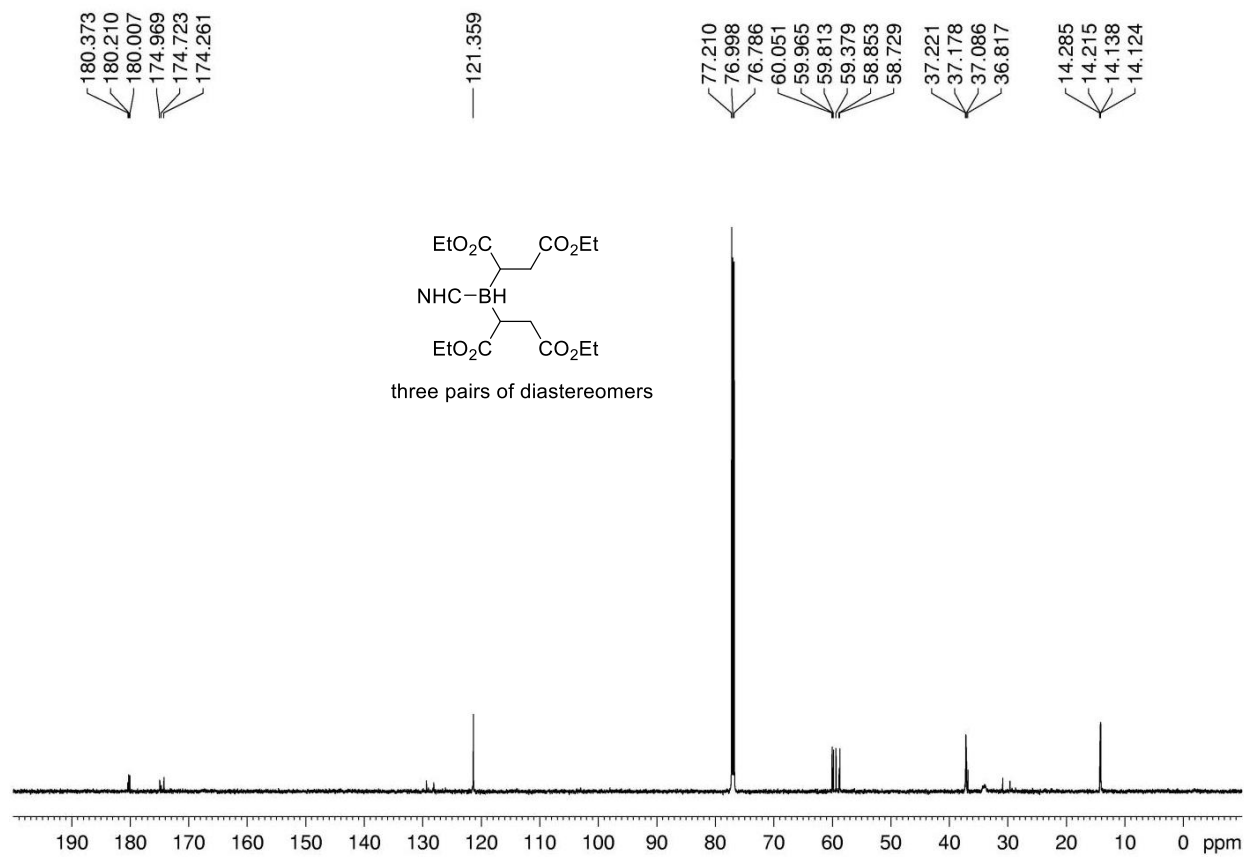
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **32**



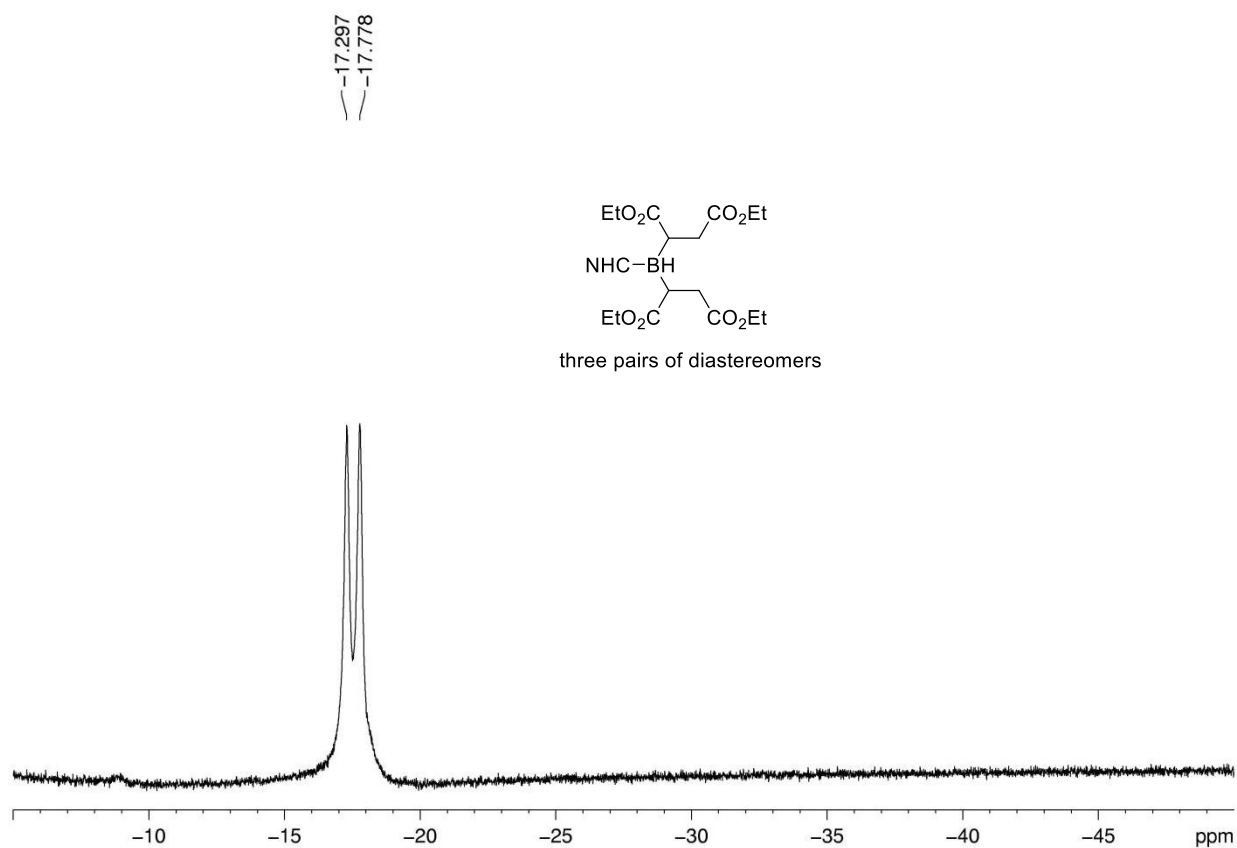
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) spectrum of **33**



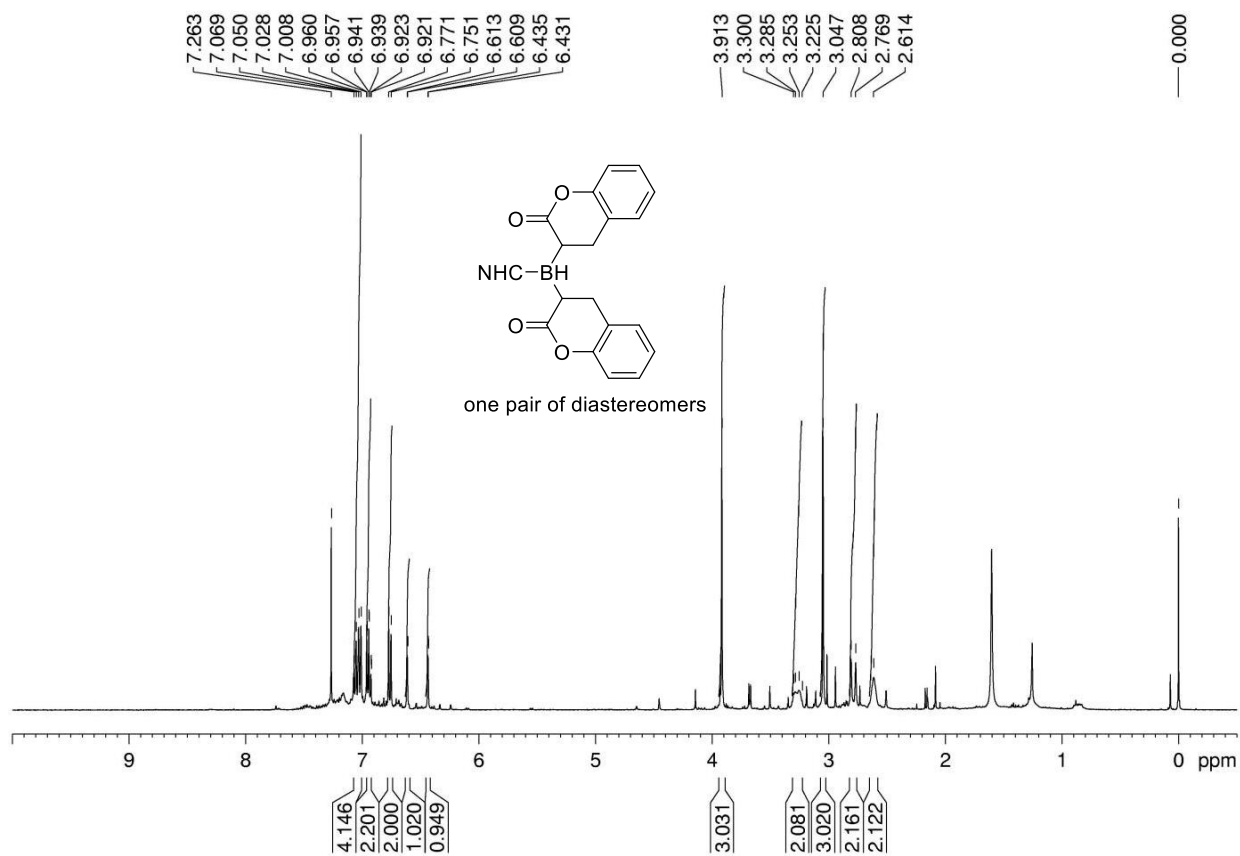
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) spectrum of **33**



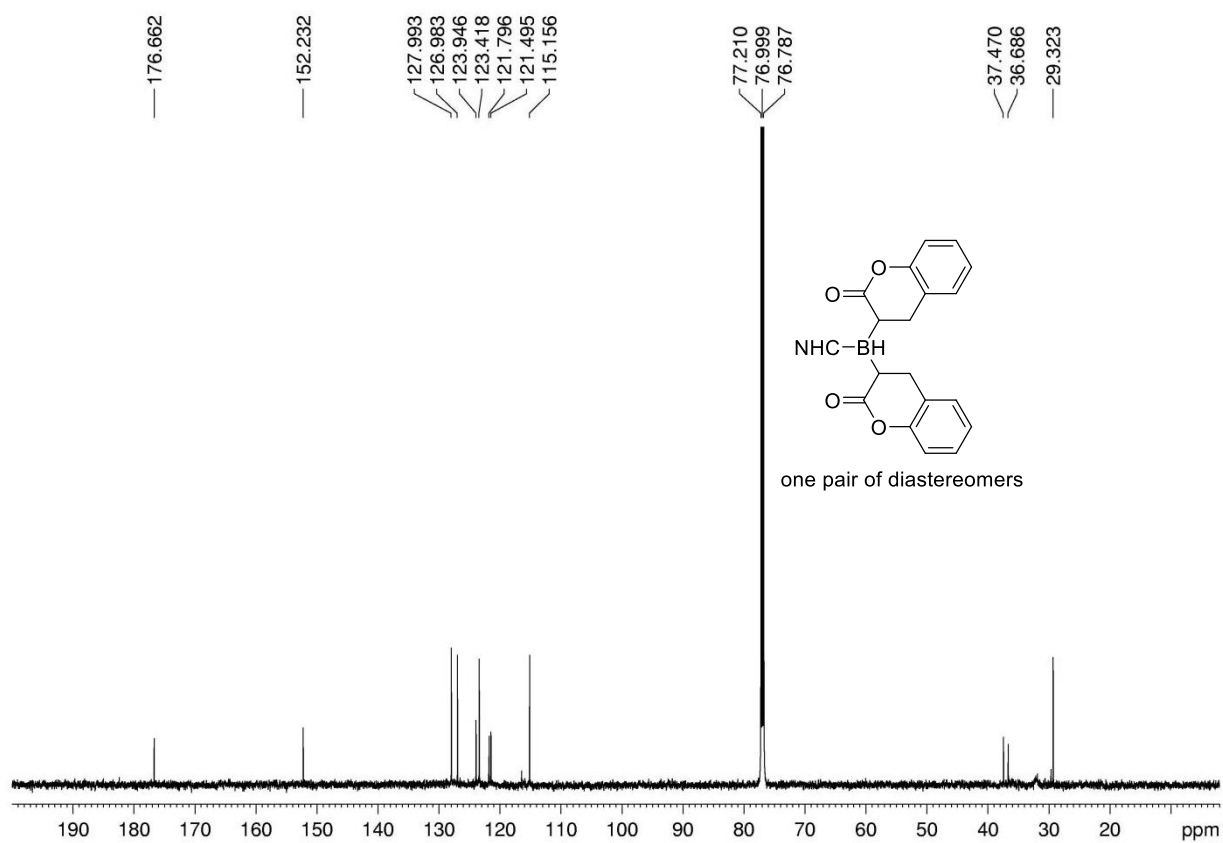
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **33**



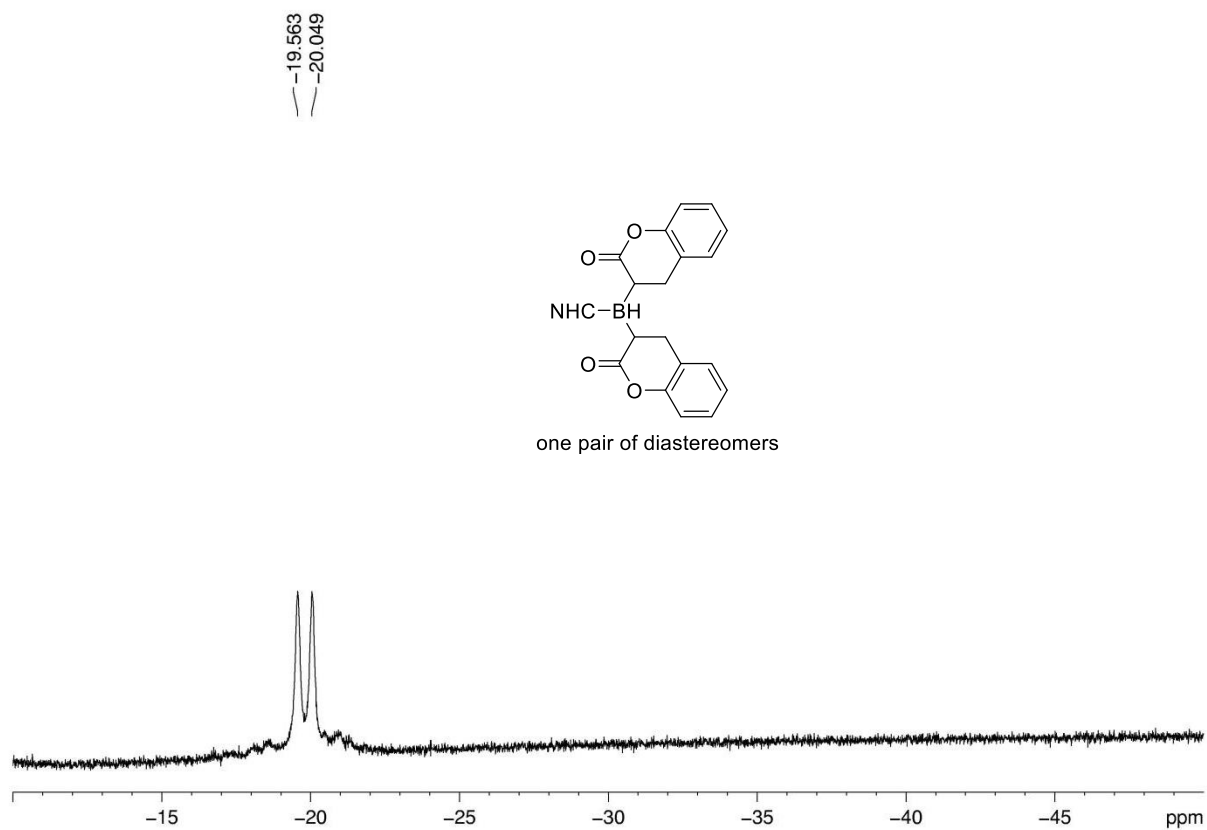
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **34**



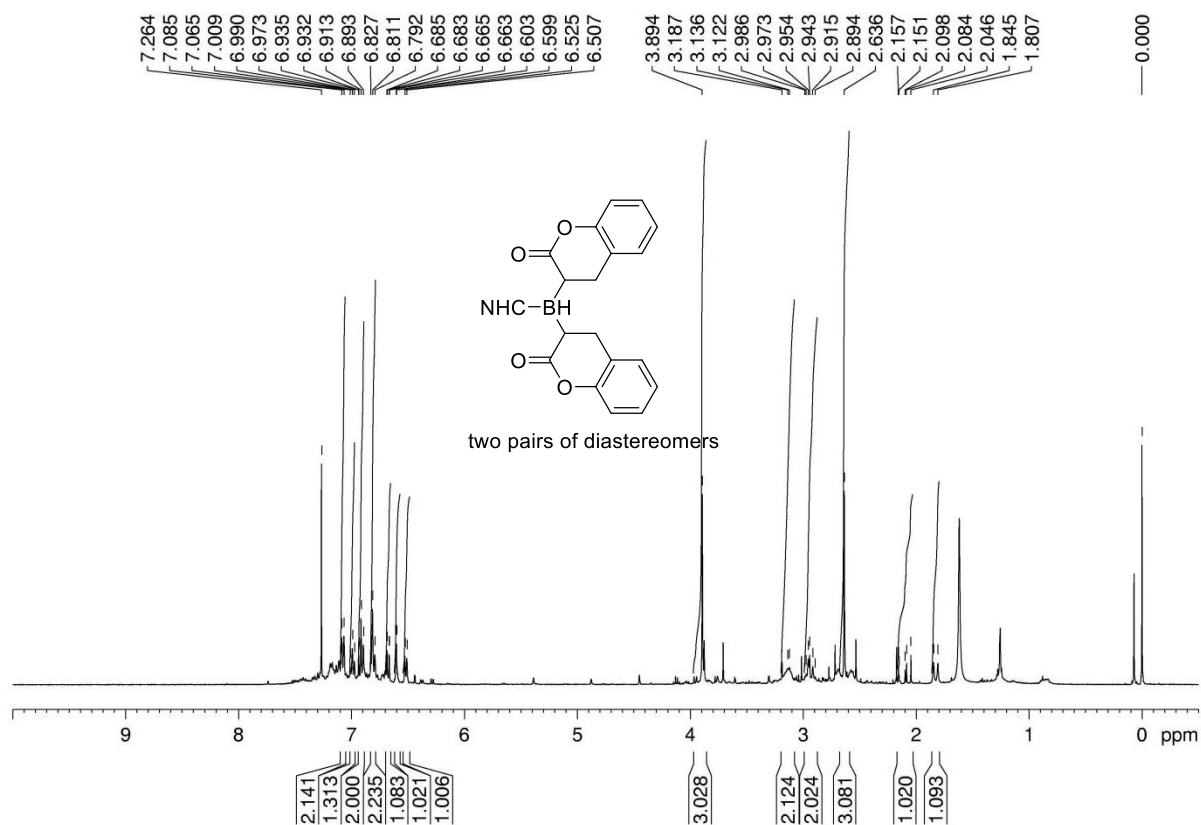
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **34**



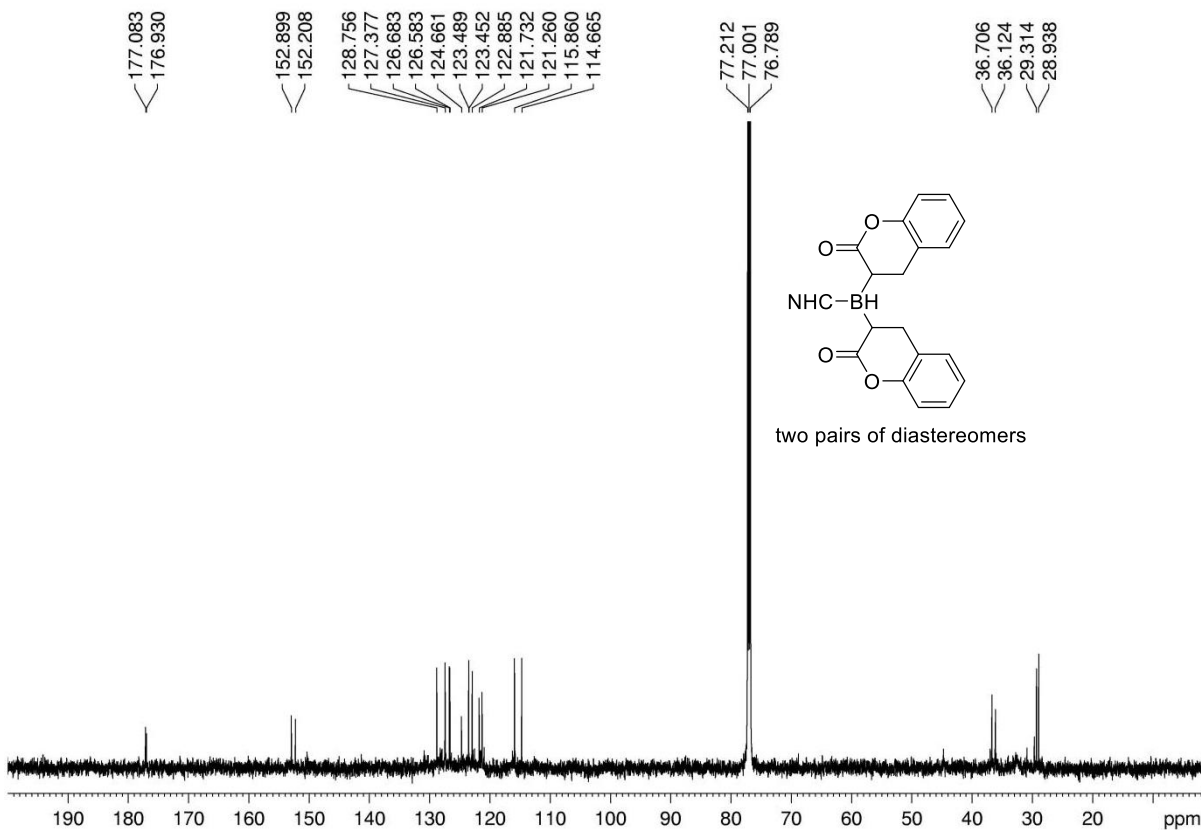
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **34**



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **34**

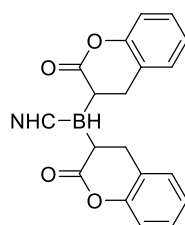


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **34**

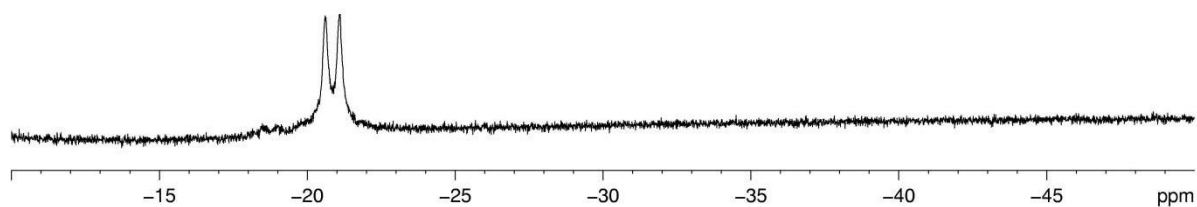


$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **34**

-20.610  
-21.108

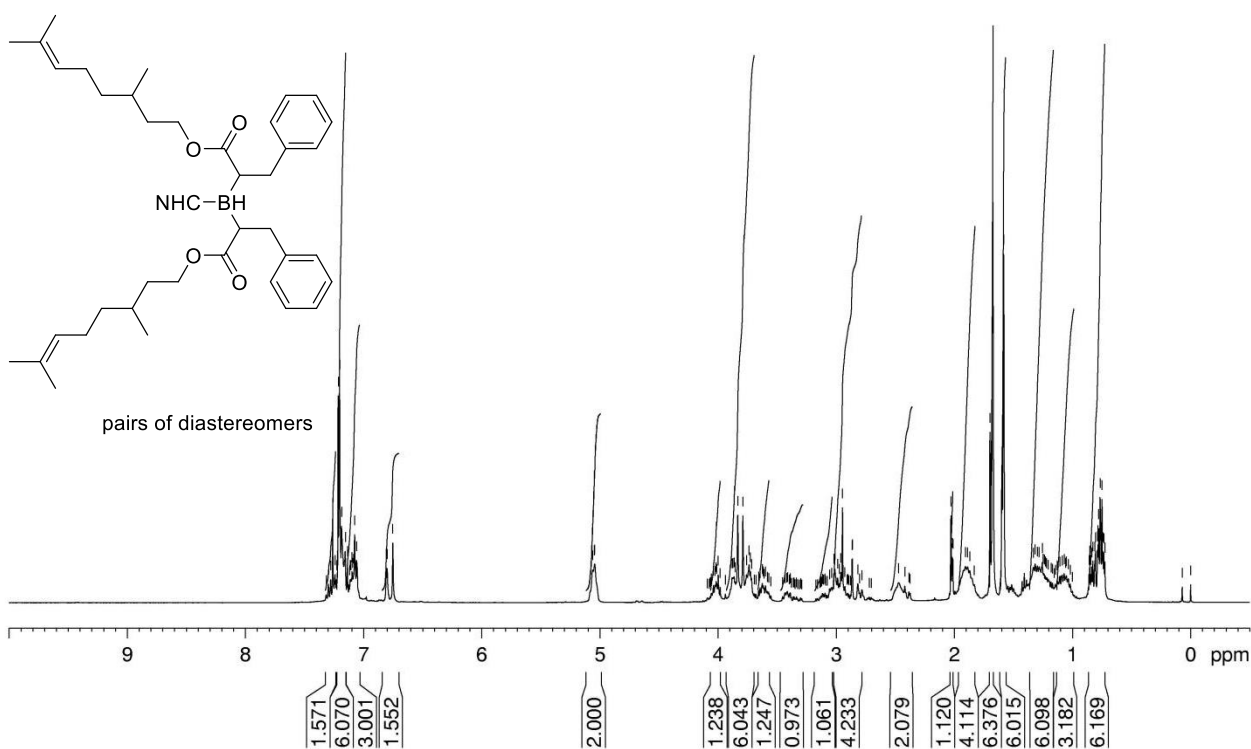


two pairs of diastereomers

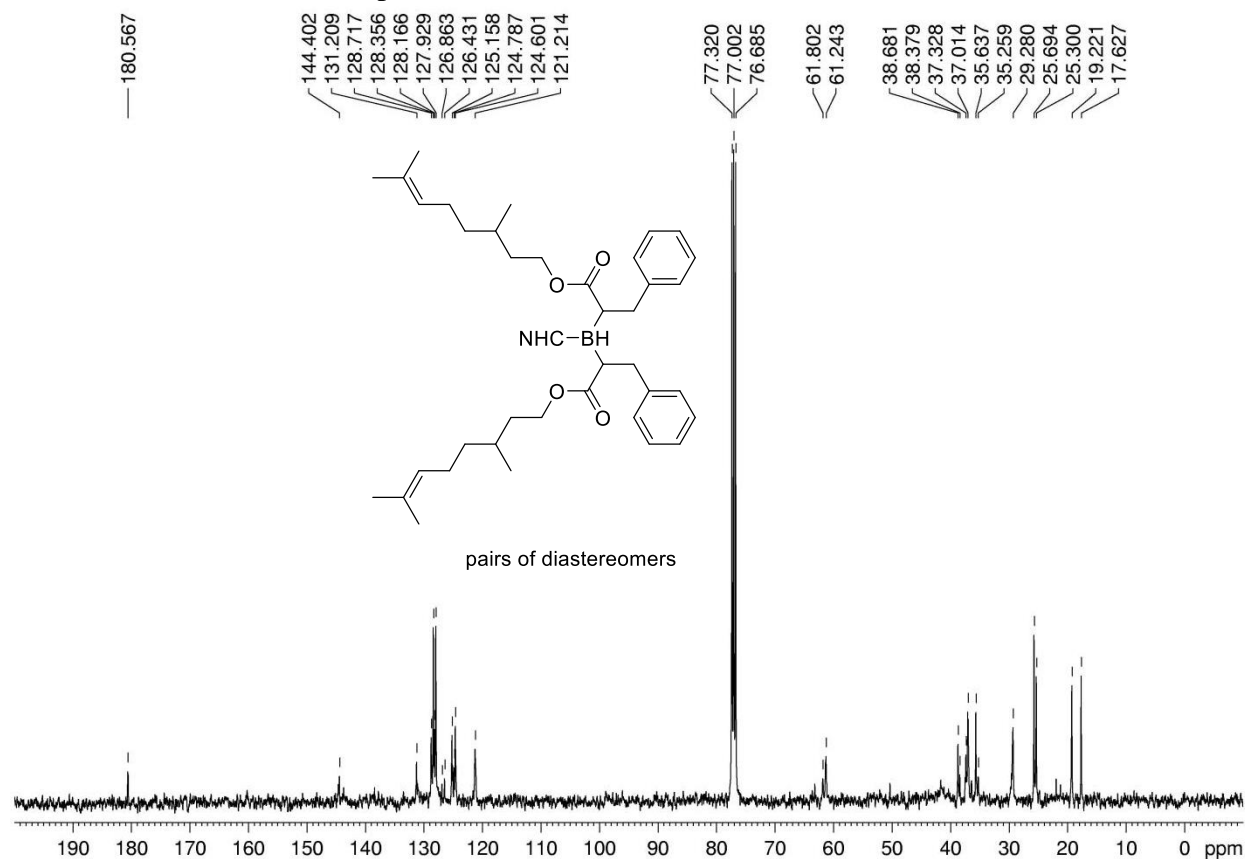


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **35**

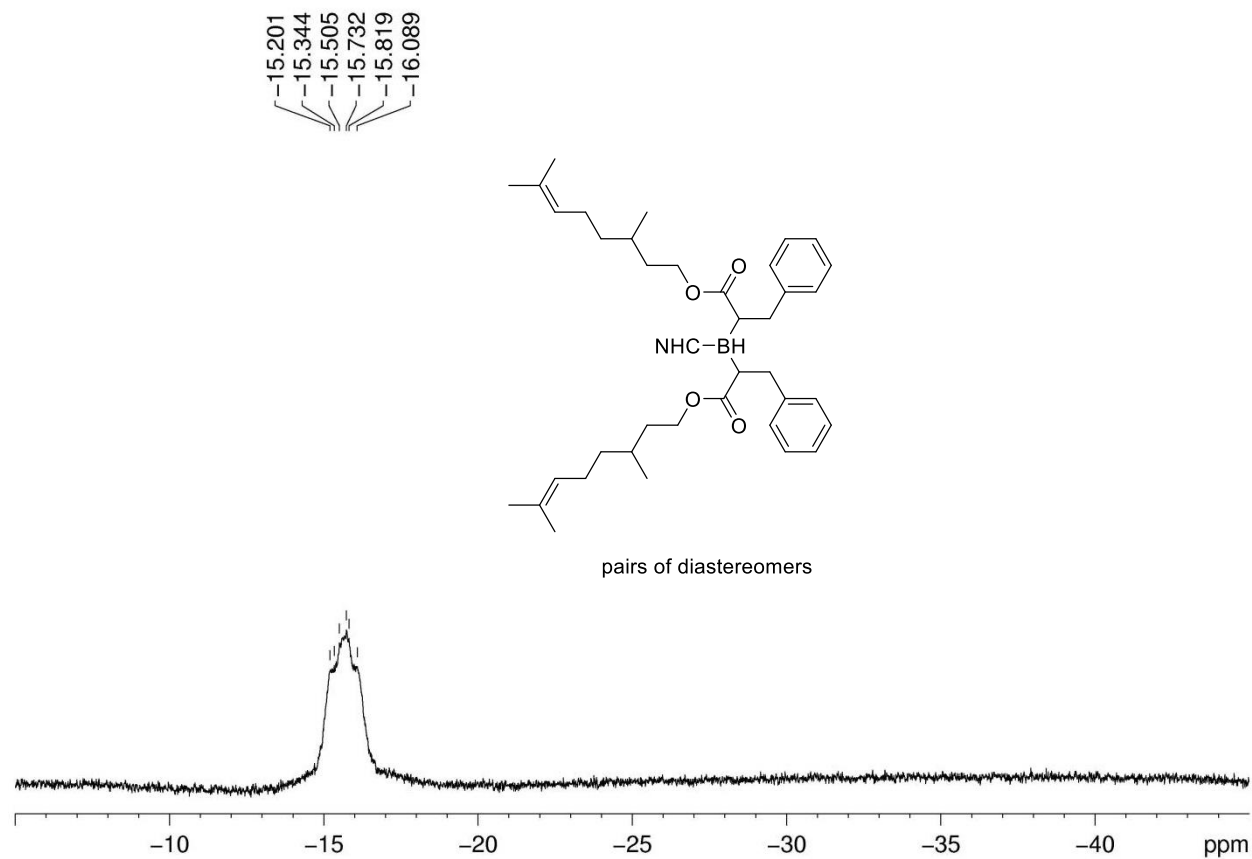
7.260  
7.214  
7.202  
7.185  
7.154  
7.136  
7.099  
7.076  
7.060  
6.808  
6.801  
6.754  
5.061  
5.047  
5.044  
3.834  
3.790  
3.738  
3.726  
3.011  
2.961  
2.947  
2.867  
2.863  
2.029  
2.019  
2.013  
2.013  
1.906  
1.889  
1.870  
1.699  
1.675  
1.597  
1.583  
1.331  
1.317  
1.297  
1.283  
1.256  
1.248  
0.854  
0.838  
0.827  
0.811  
0.806  
0.789  
0.785  
0.779  
0.767  
0.750  
0.742  
0.734  
0.726



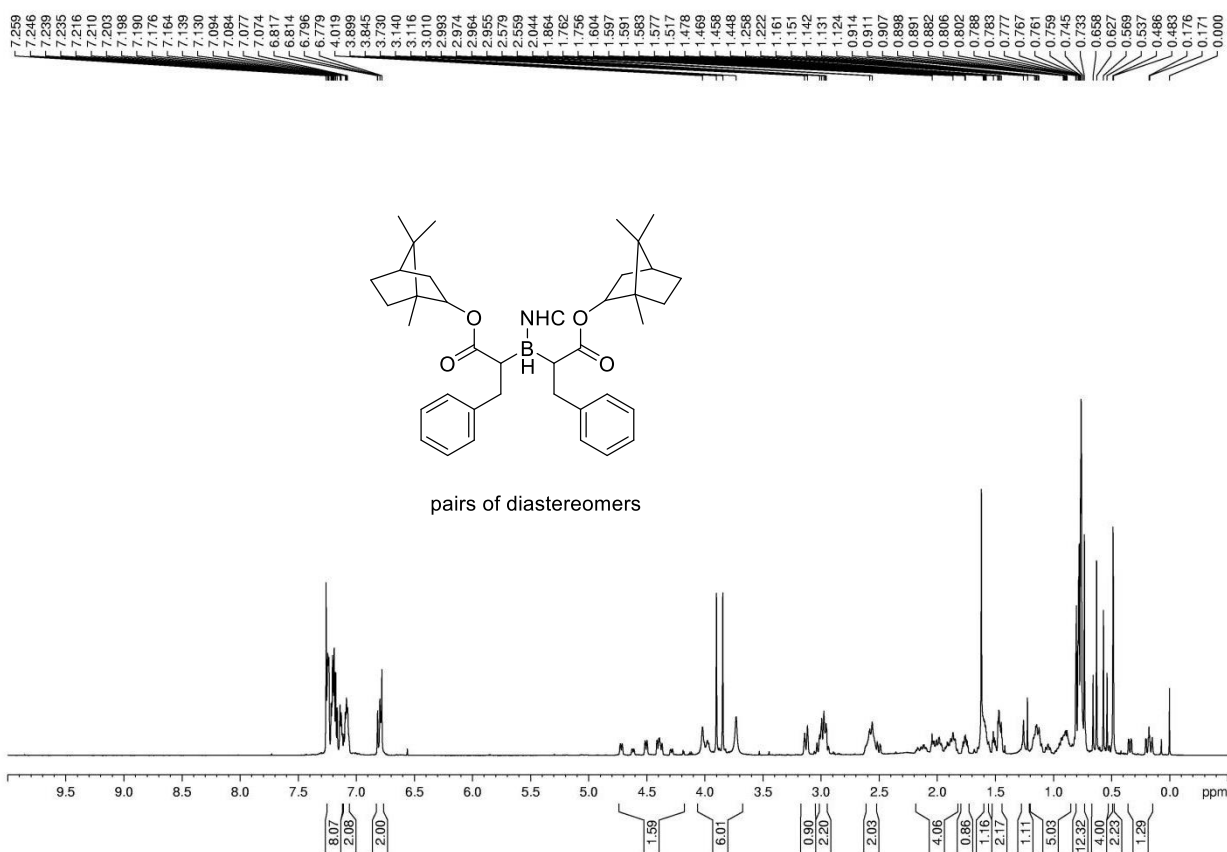
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) spectrum of **35**



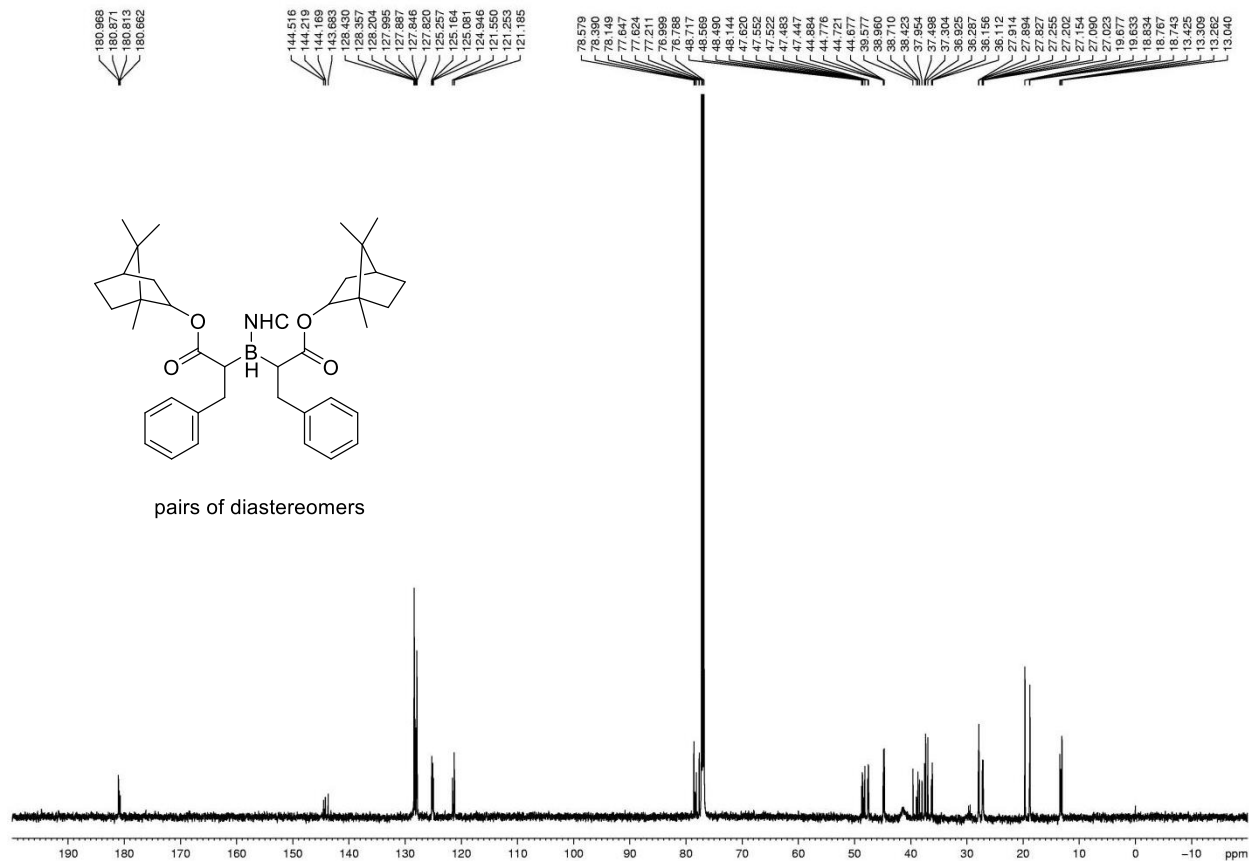
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz) spectrum of **35**



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **36**



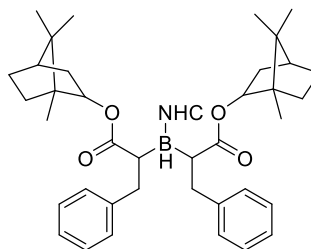
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **36**



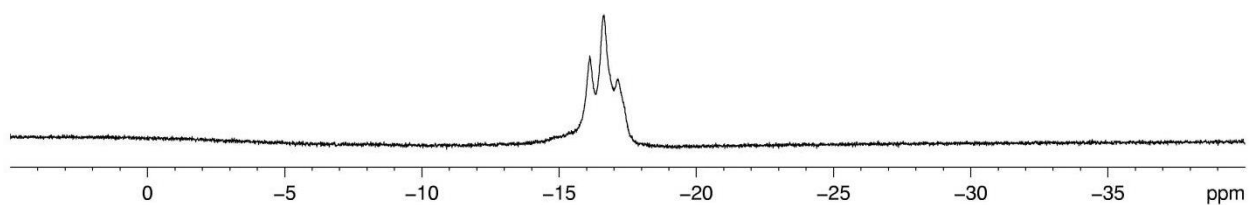


$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **36**

-16.131  
-16.617  
-16.644  
-17.125  
-17.161

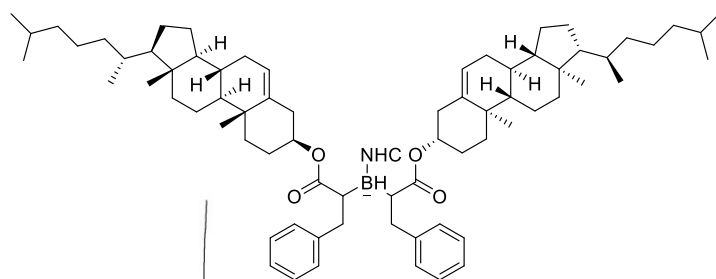


pairs of diastereomers

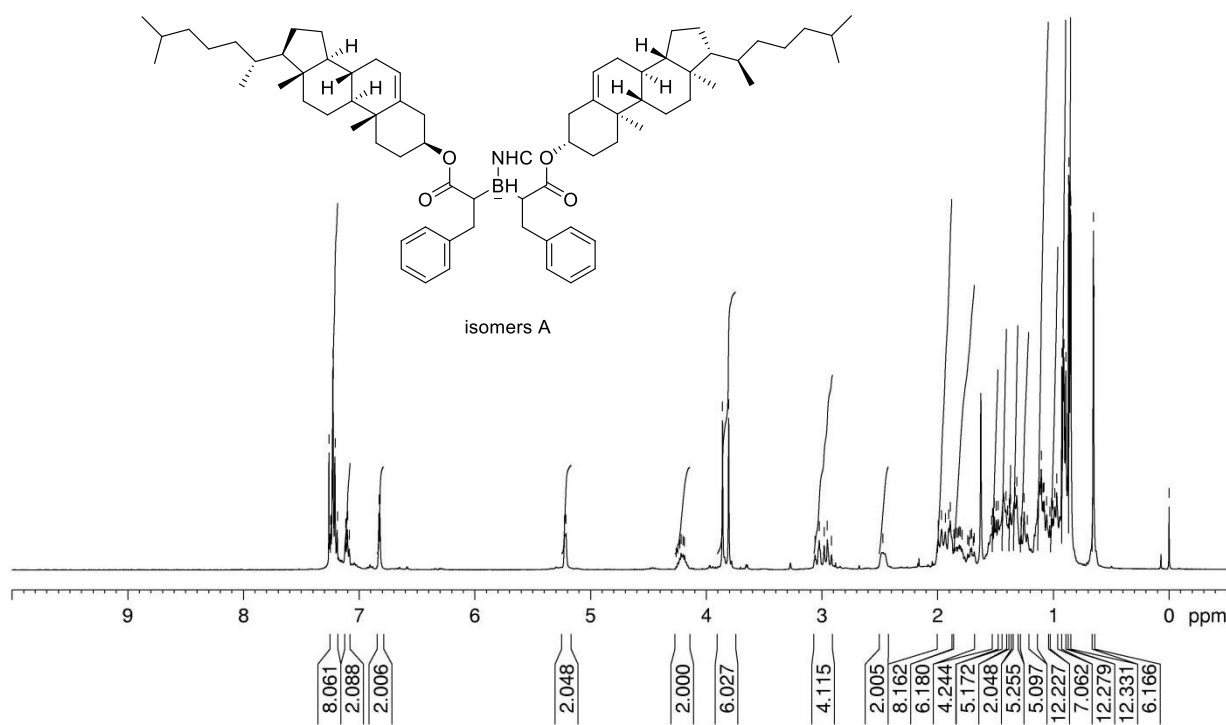


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **37**

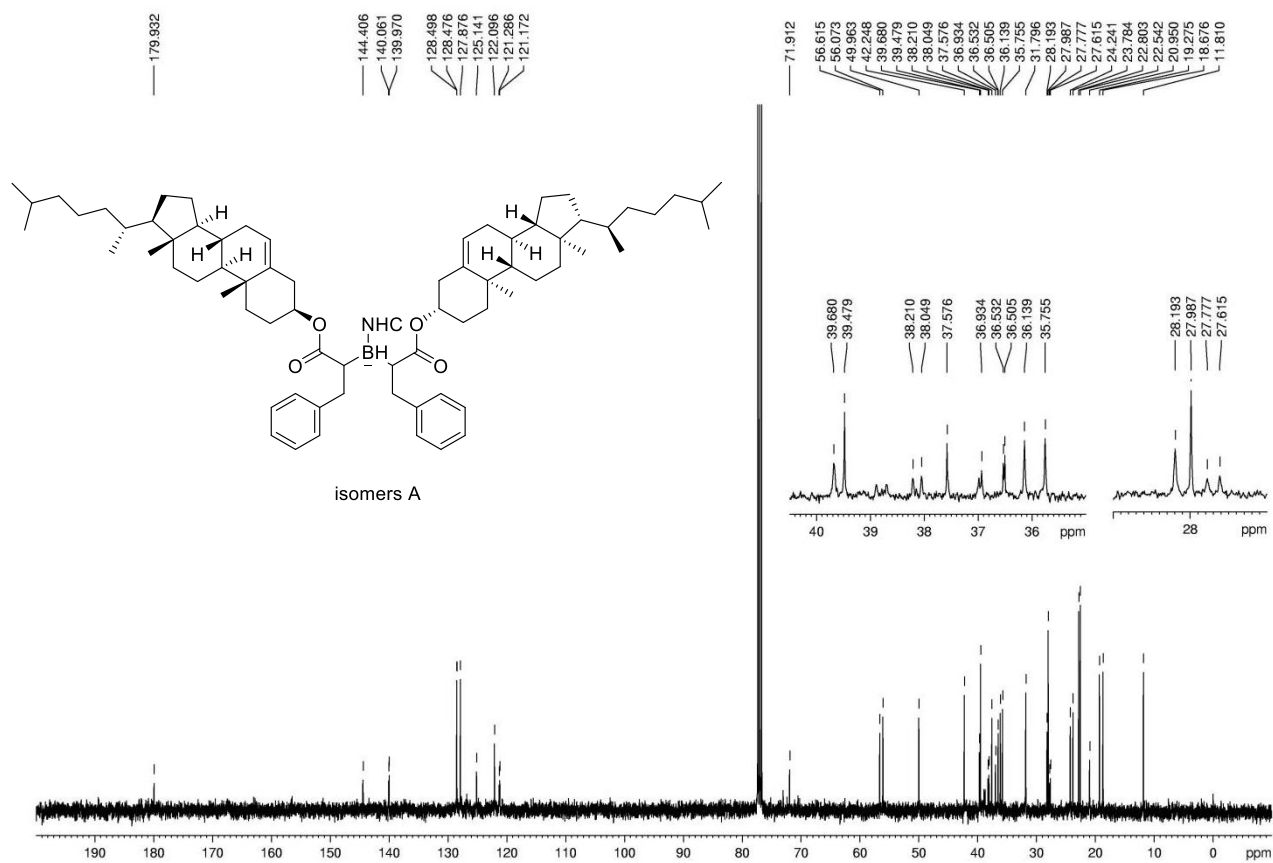
7.260  
7.247  
7.226  
7.208  
7.188  
7.117  
7.100  
6.827  
6.819  
5.225  
5.214  
3.860  
3.807  
1.967  
1.934  
1.905  
1.892  
1.535  
1.527  
1.510  
1.494  
1.477  
1.431  
1.410  
1.396  
1.381  
1.370  
1.337  
1.329  
1.317  
1.279  
1.253  
1.226  
1.123  
1.105  
1.091  
1.080  
1.057  
1.032  
1.016  
1.006  
0.989  
0.971  
0.927  
0.916  
0.908  
0.892  
0.869  
0.865  
0.853  
0.849  
0.654  
-0.000



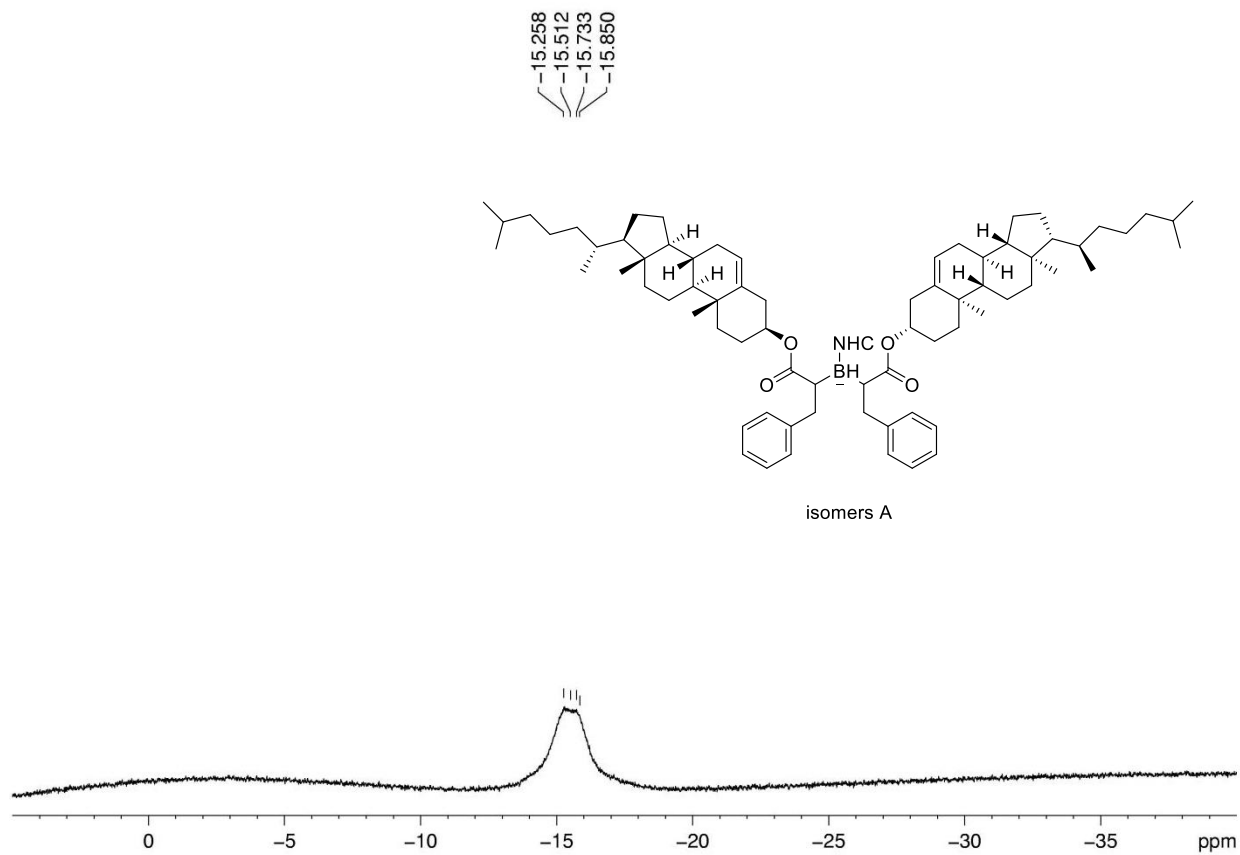
isomers A



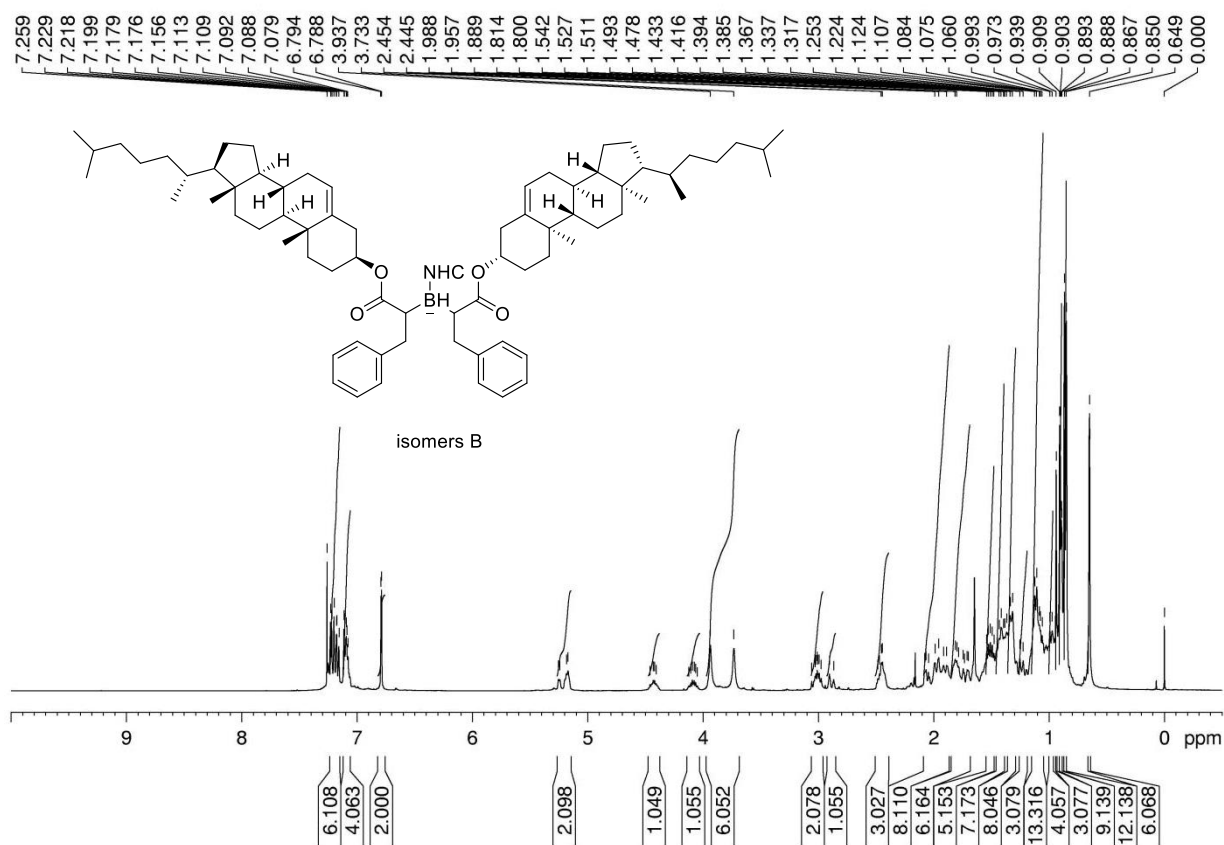
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) spectrum of **37**



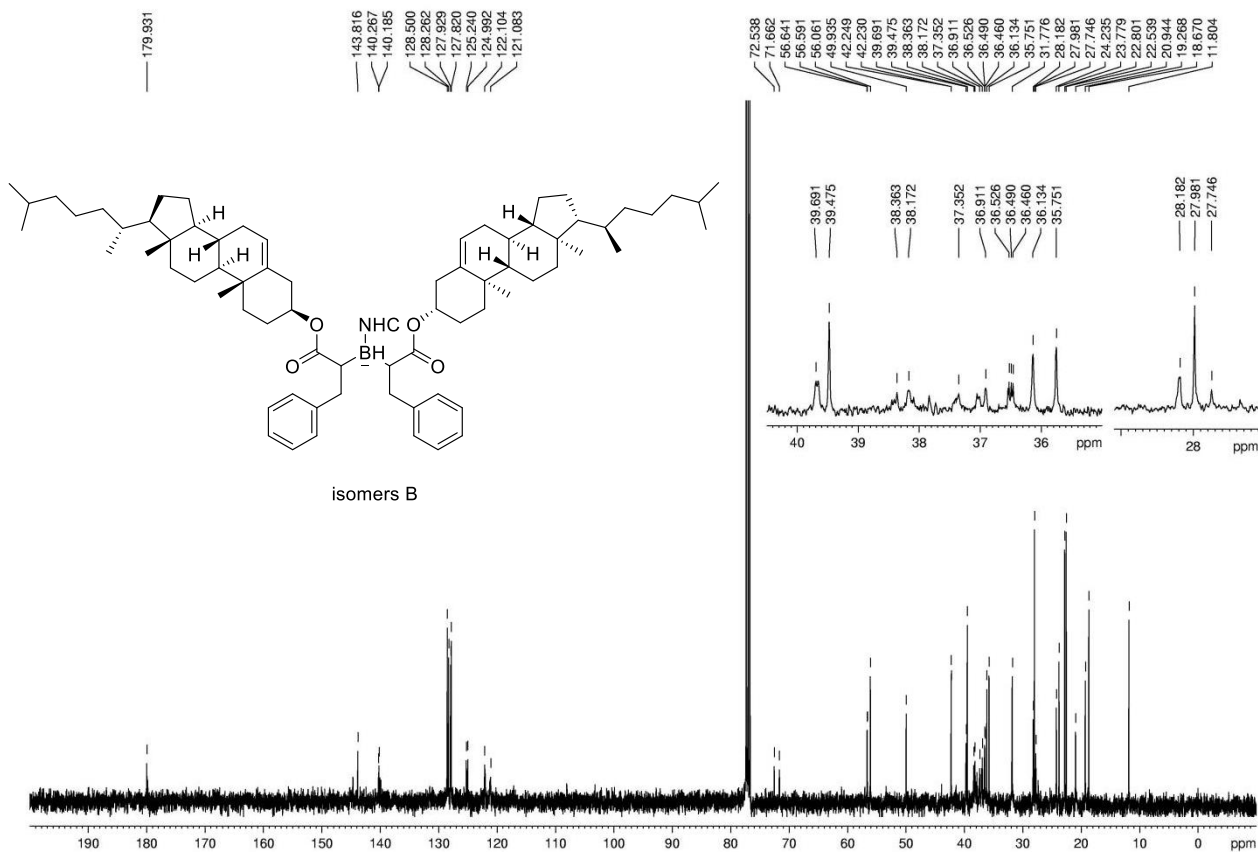
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz) spectrum of **37**



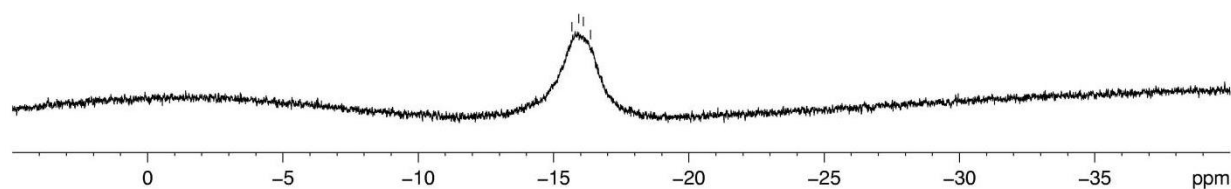
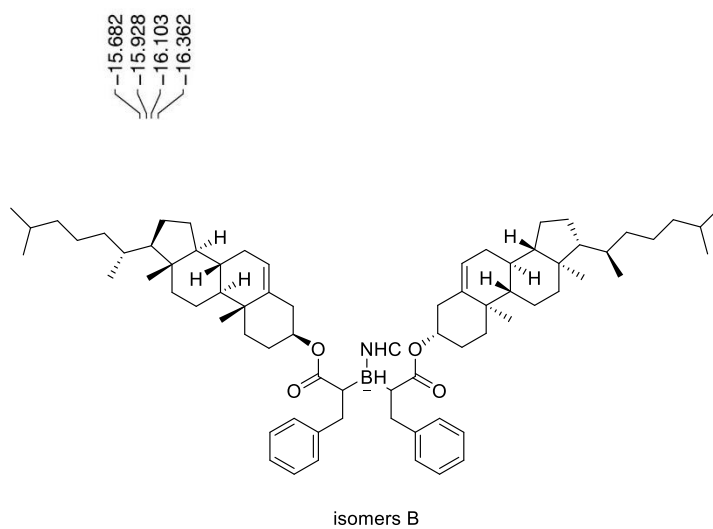
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **37**



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) spectrum of **37**

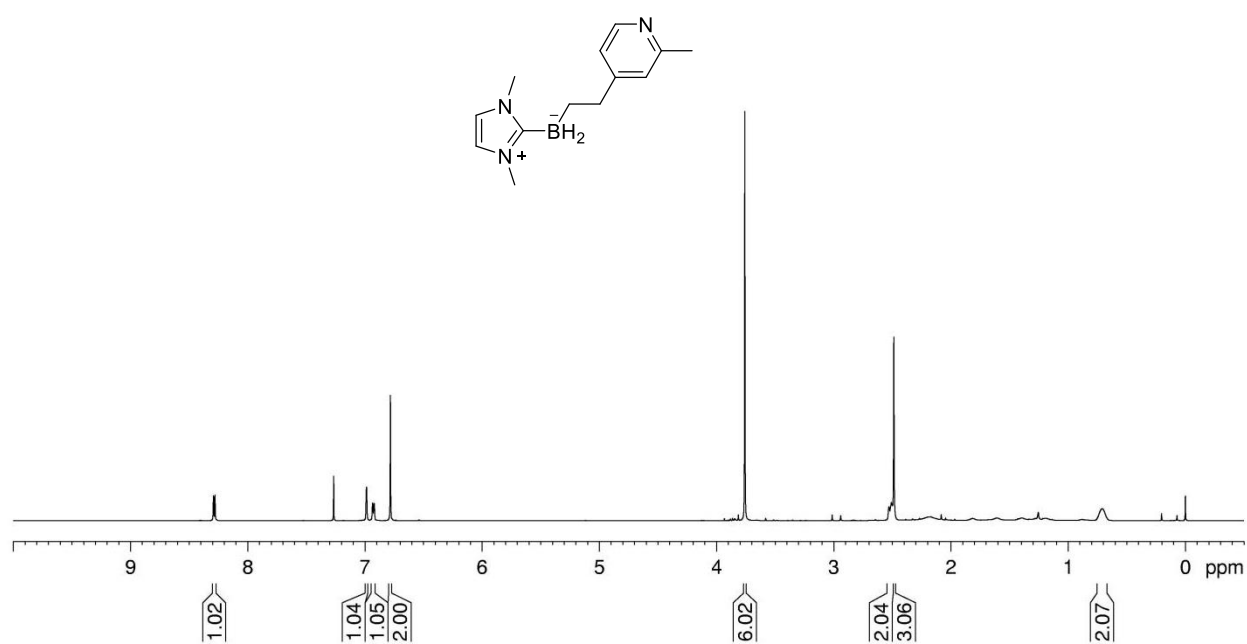


$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz) spectrum of **37**

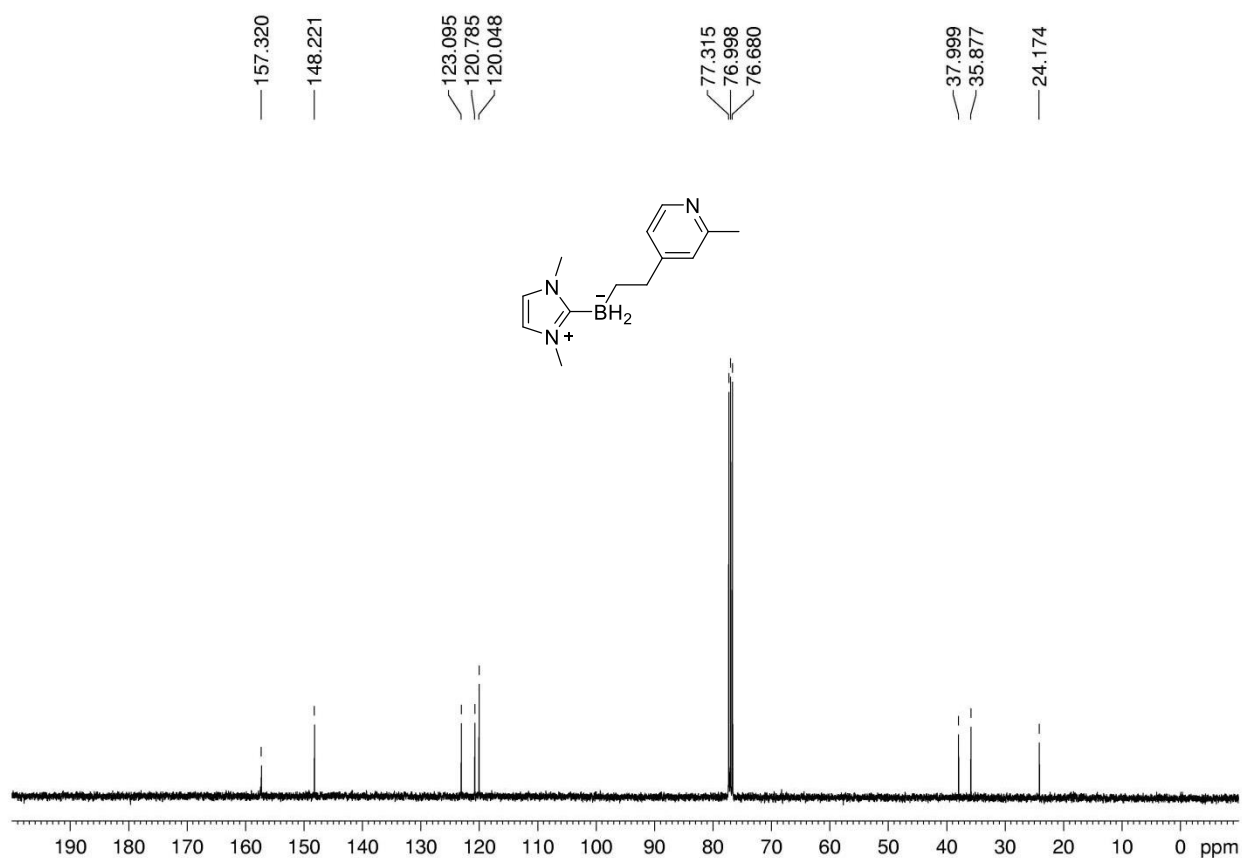


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **38**

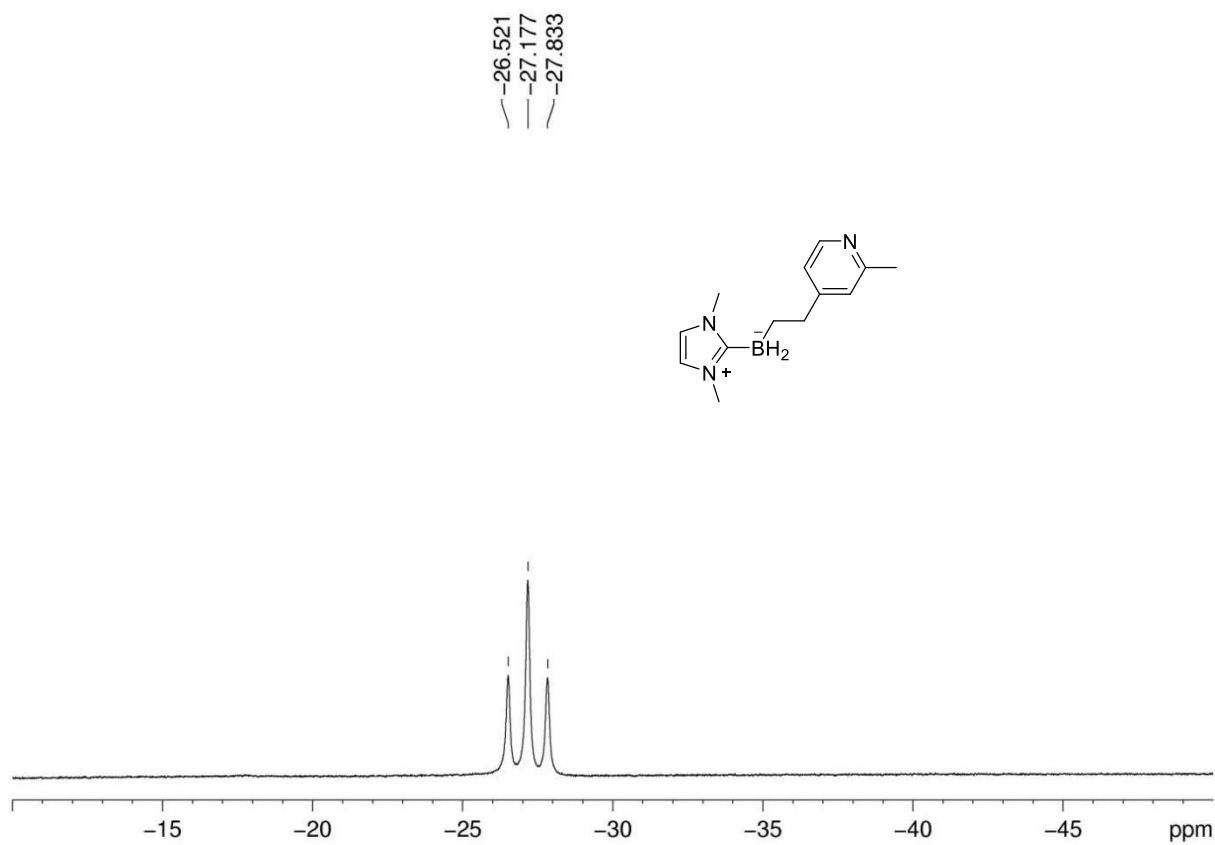
8.293  
8.281  
7.268  
6.987  
6.936  
6.923  
6.784  
3.759  
2.529  
2.508  
2.488  
0.710  
0.000



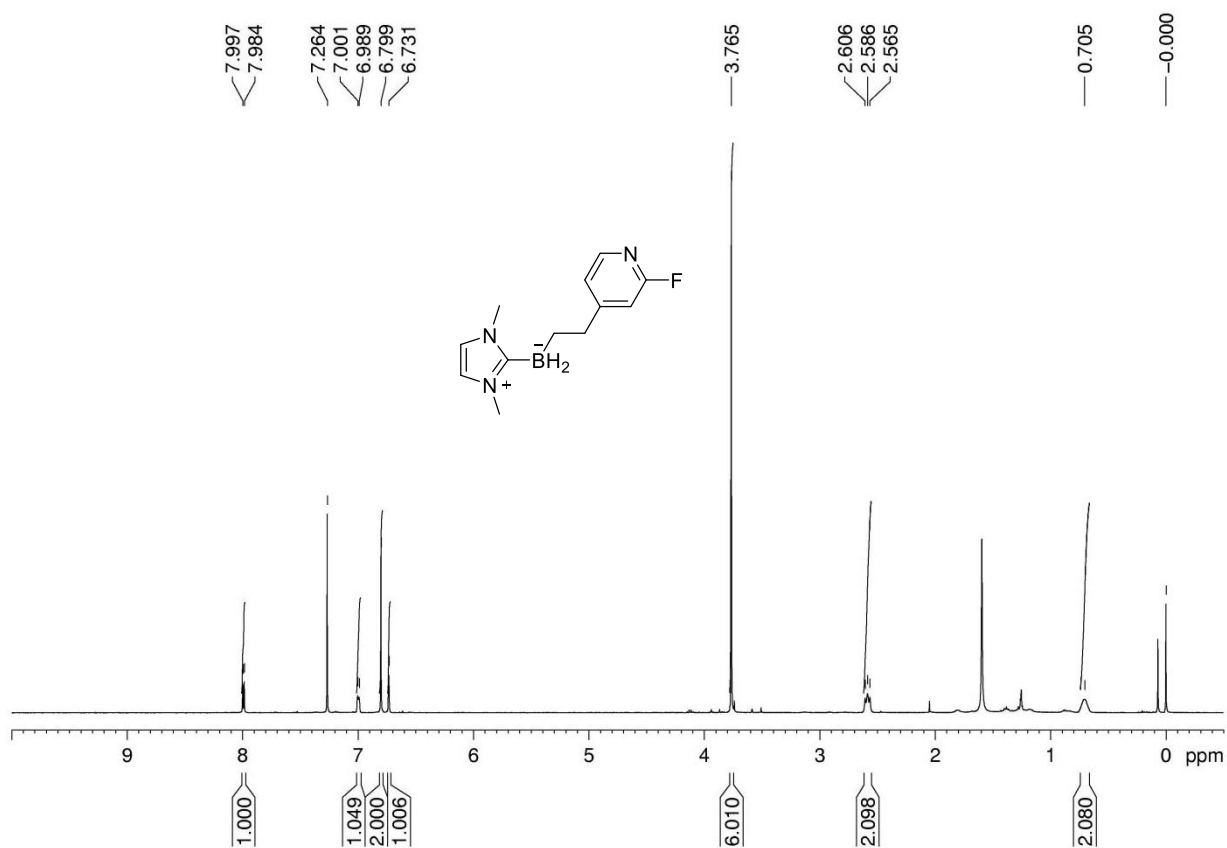
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) spectrum of **38**



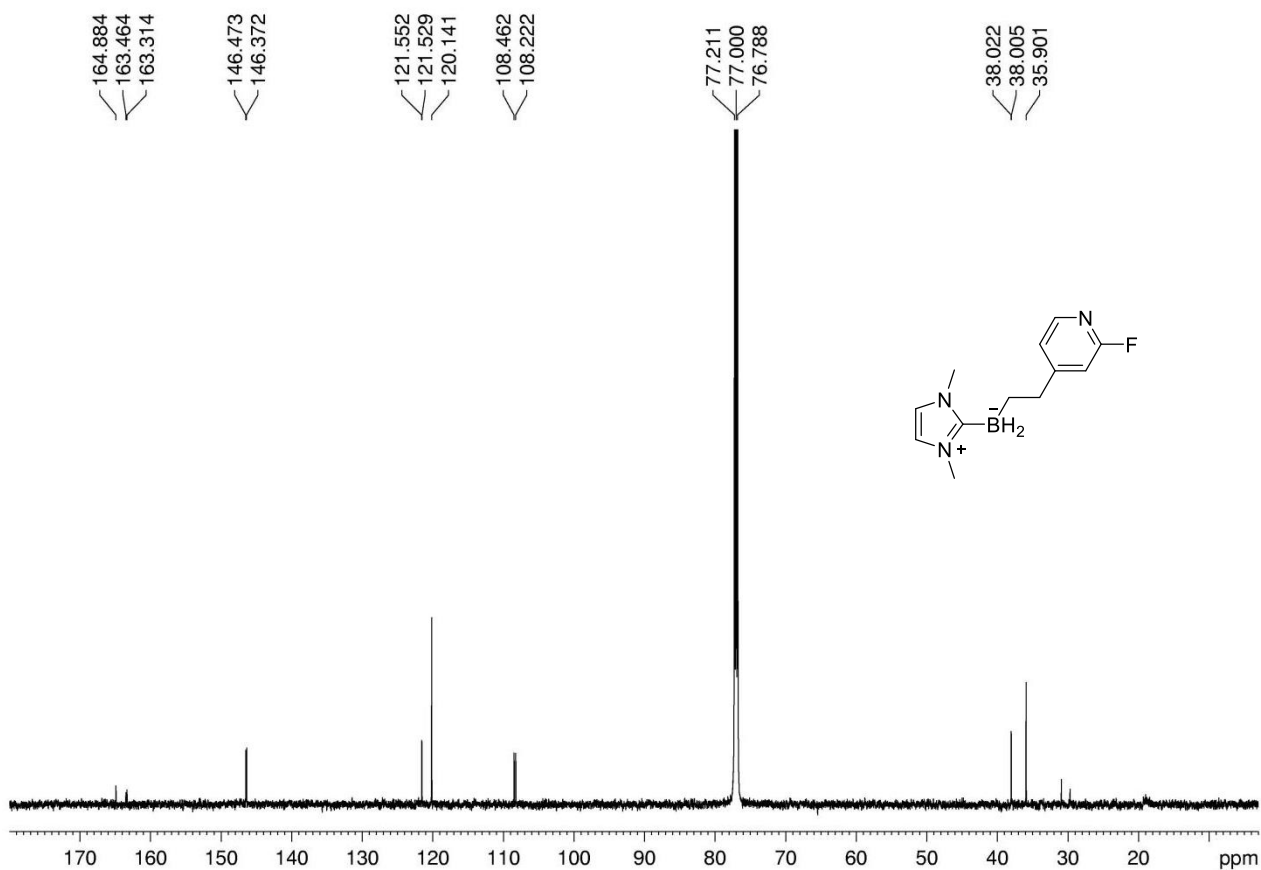
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz) spectrum of **38**



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **39**

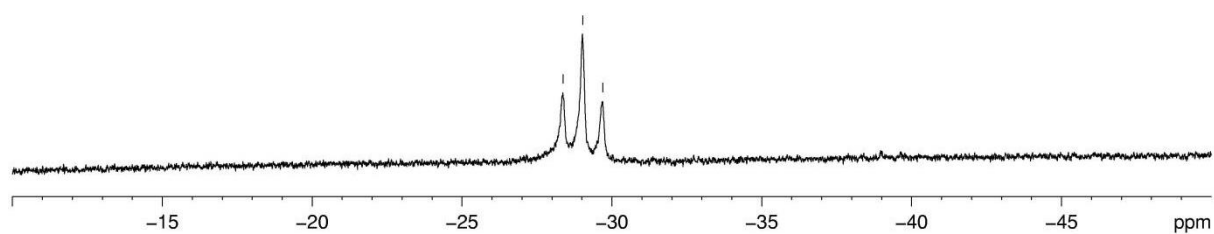
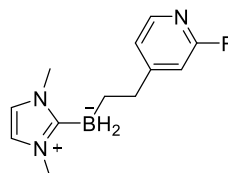


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **39**



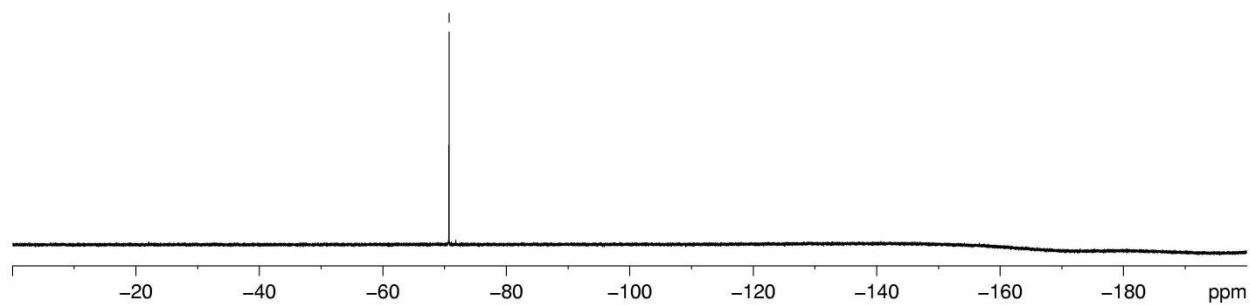
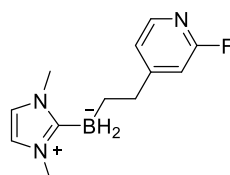
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz) spectrum of **39**

-28.371  
-29.025  
-29.697

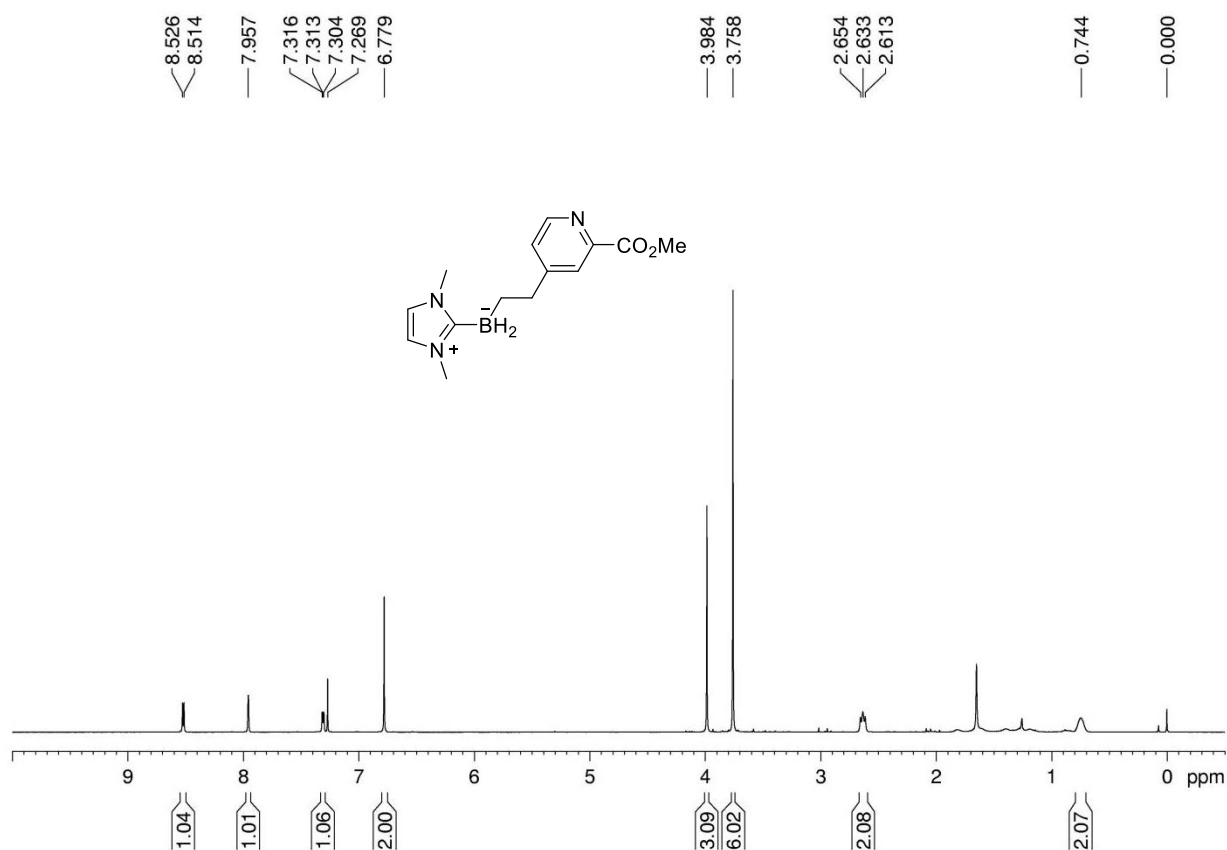


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz) spectrum of **39**

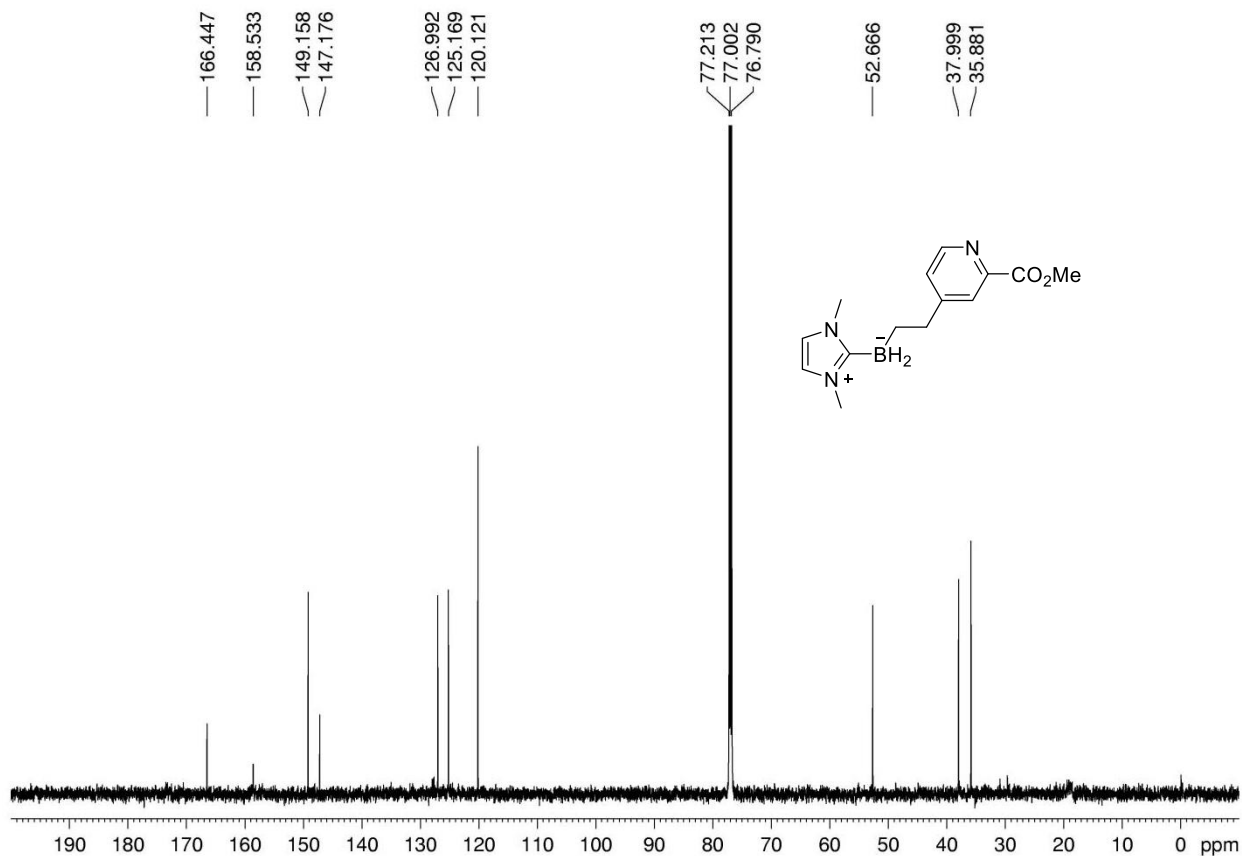
-70.759



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **40**

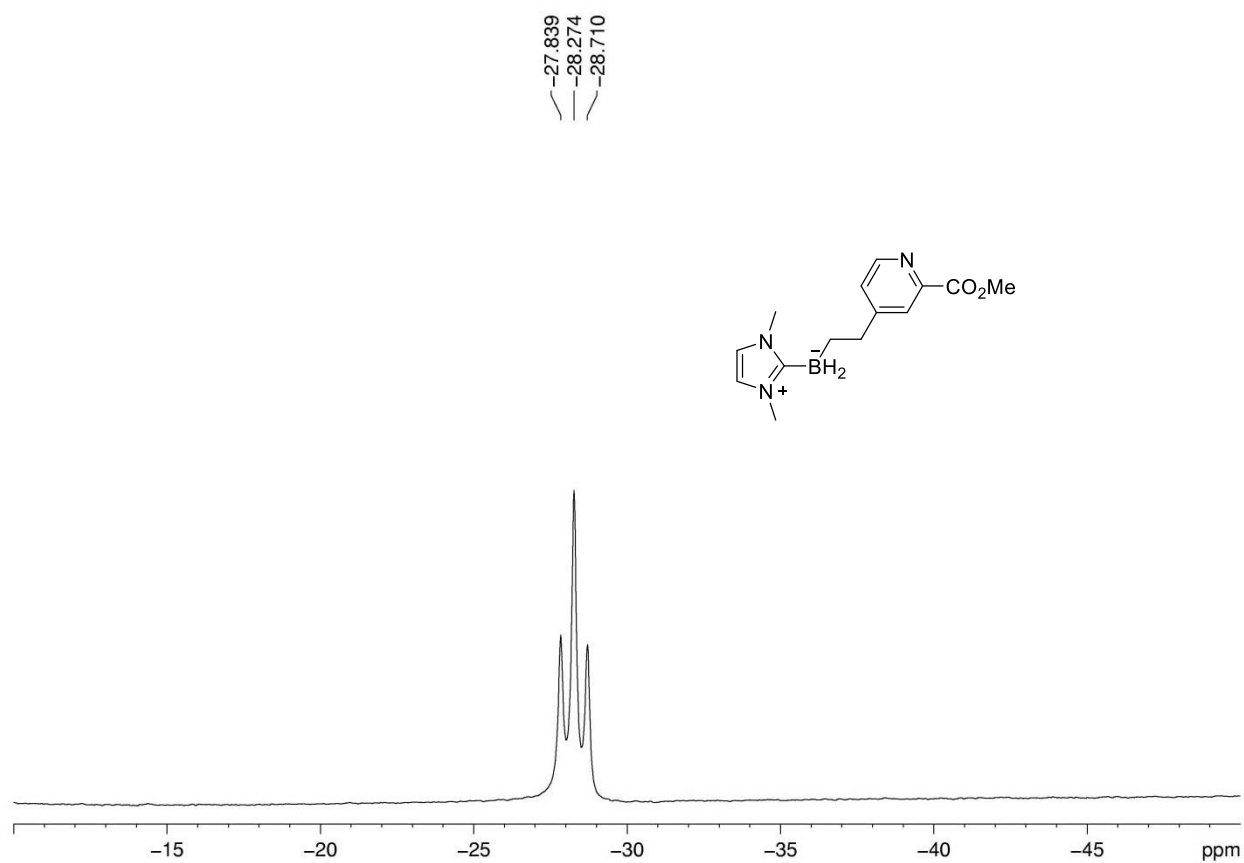


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **40**

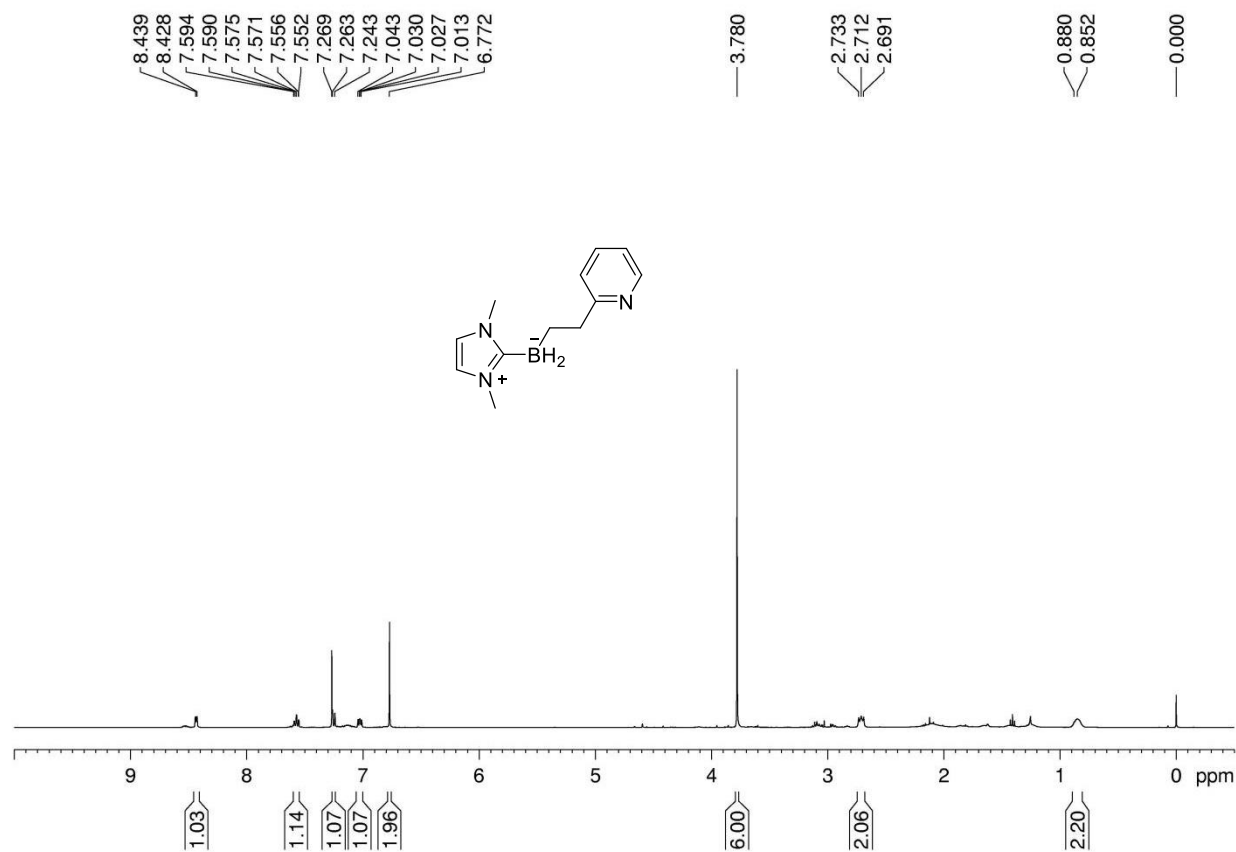




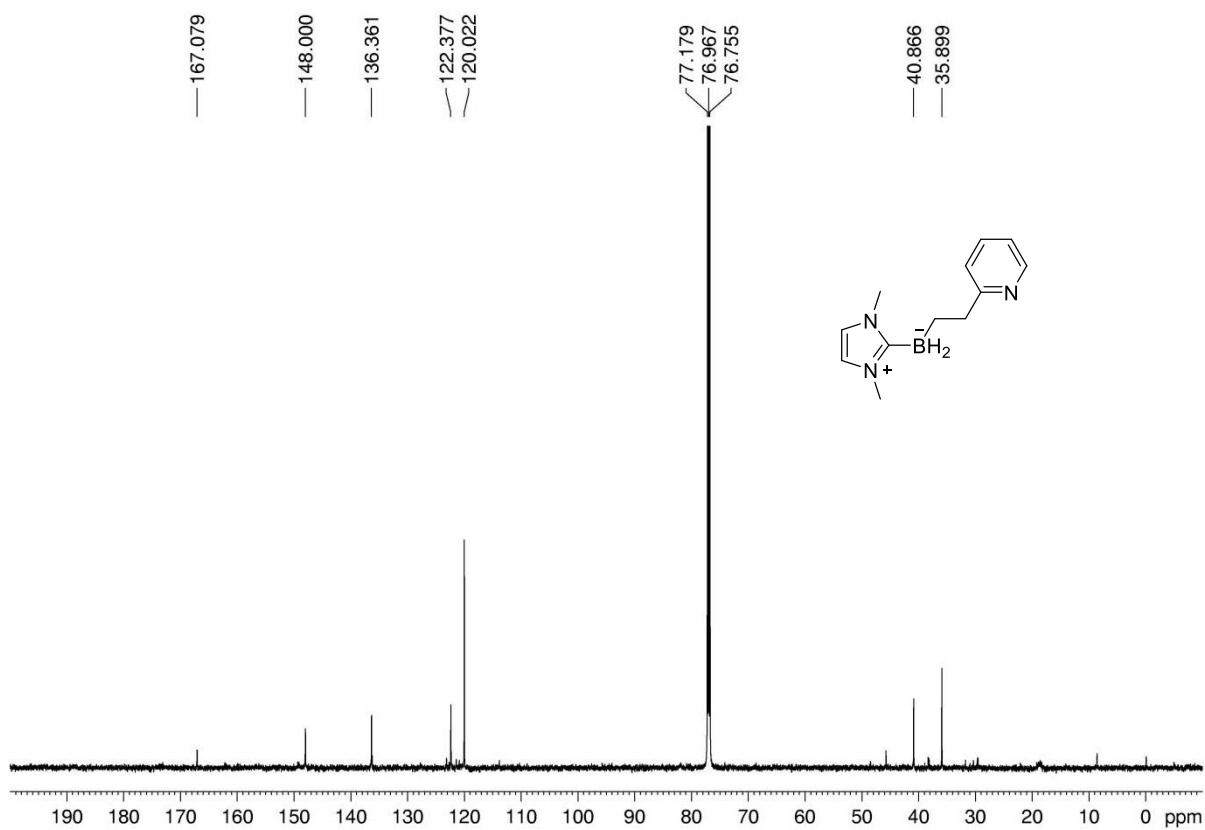
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **40**



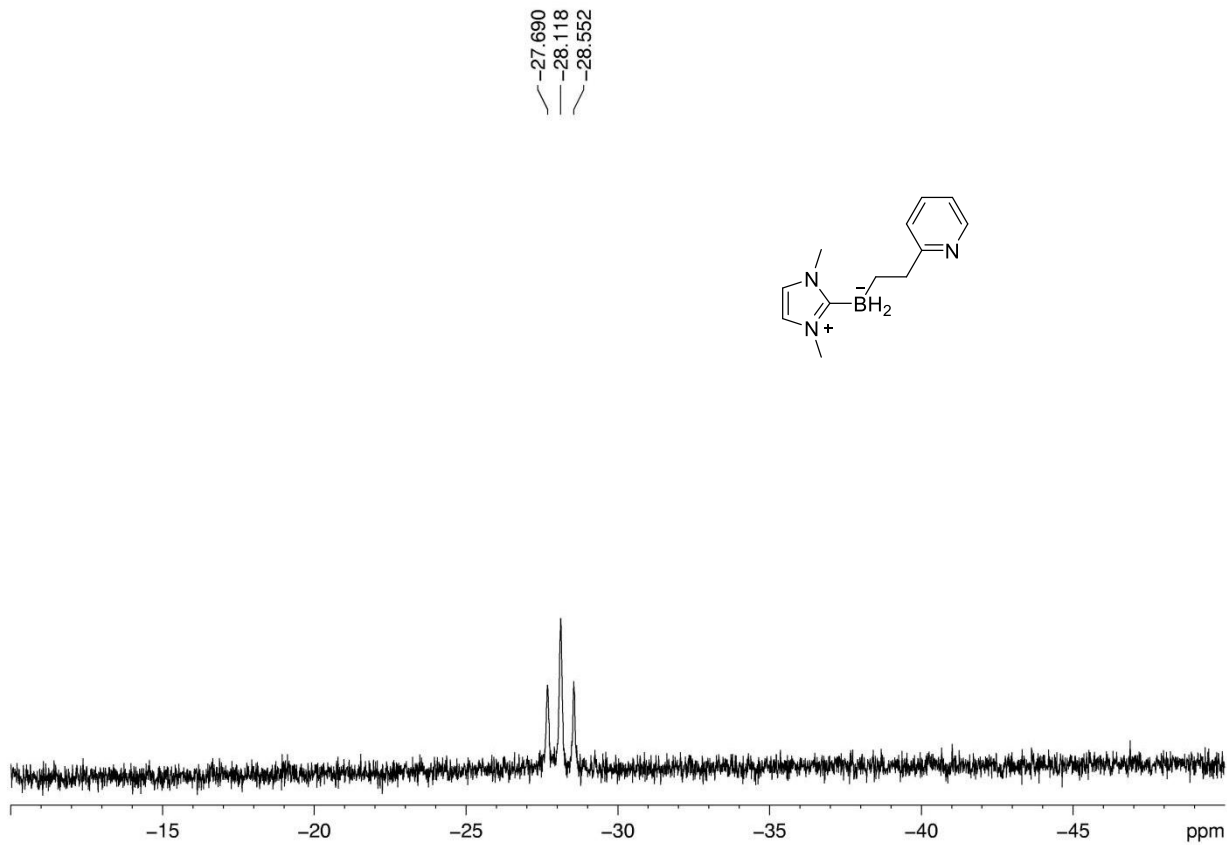
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **41**



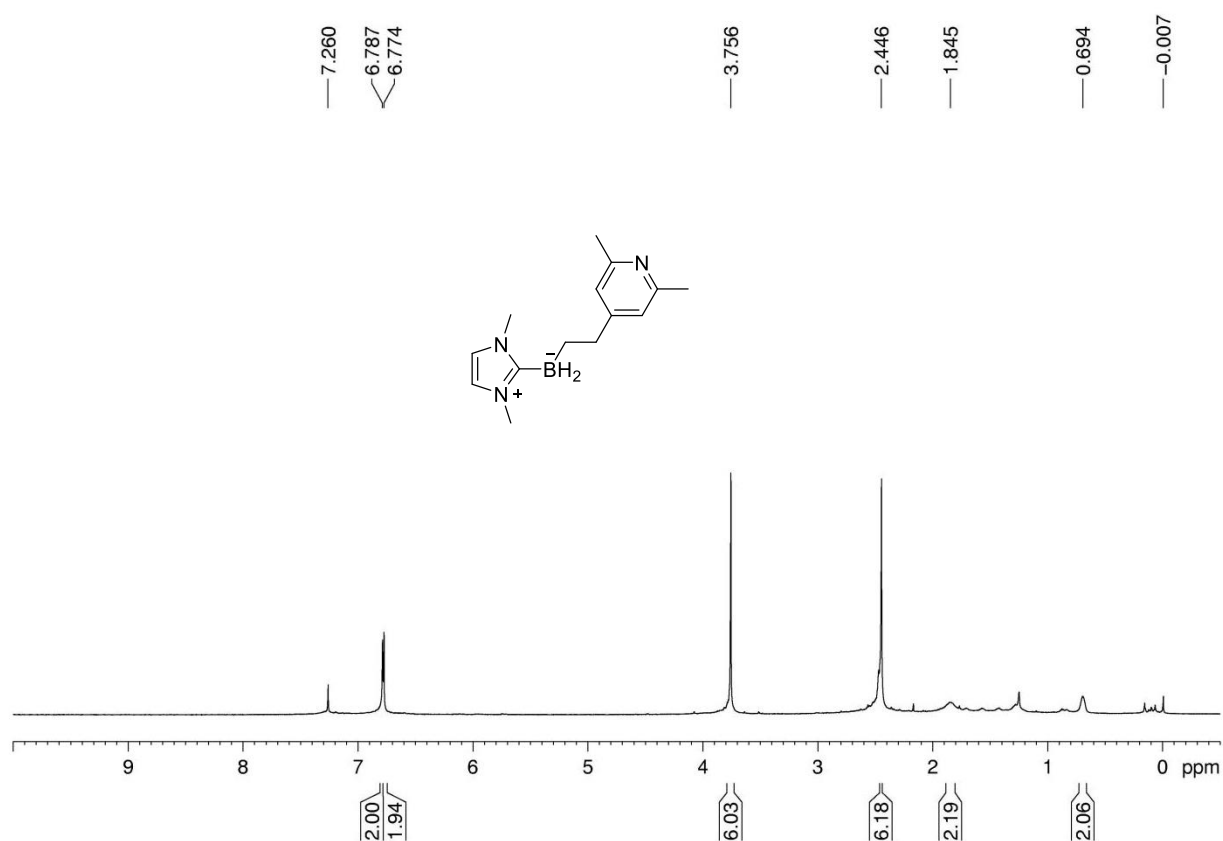
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **41**



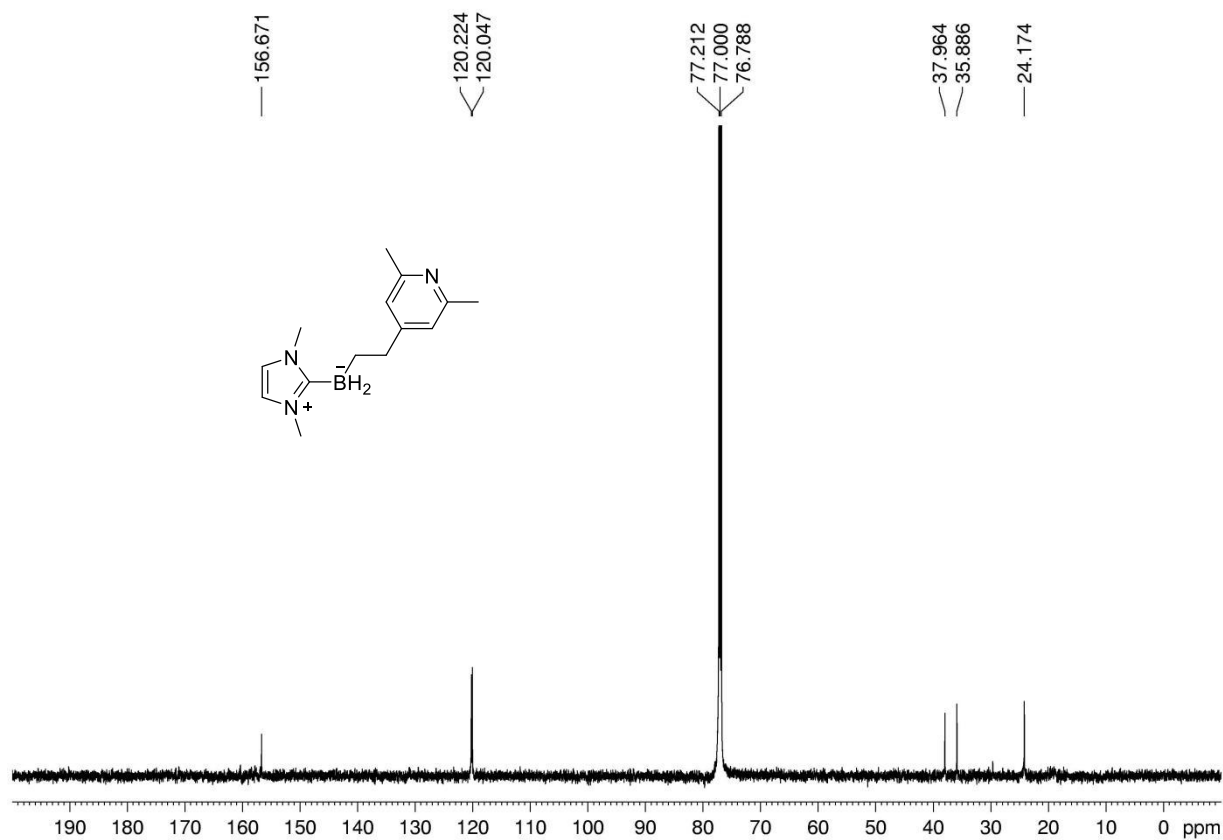
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **41**



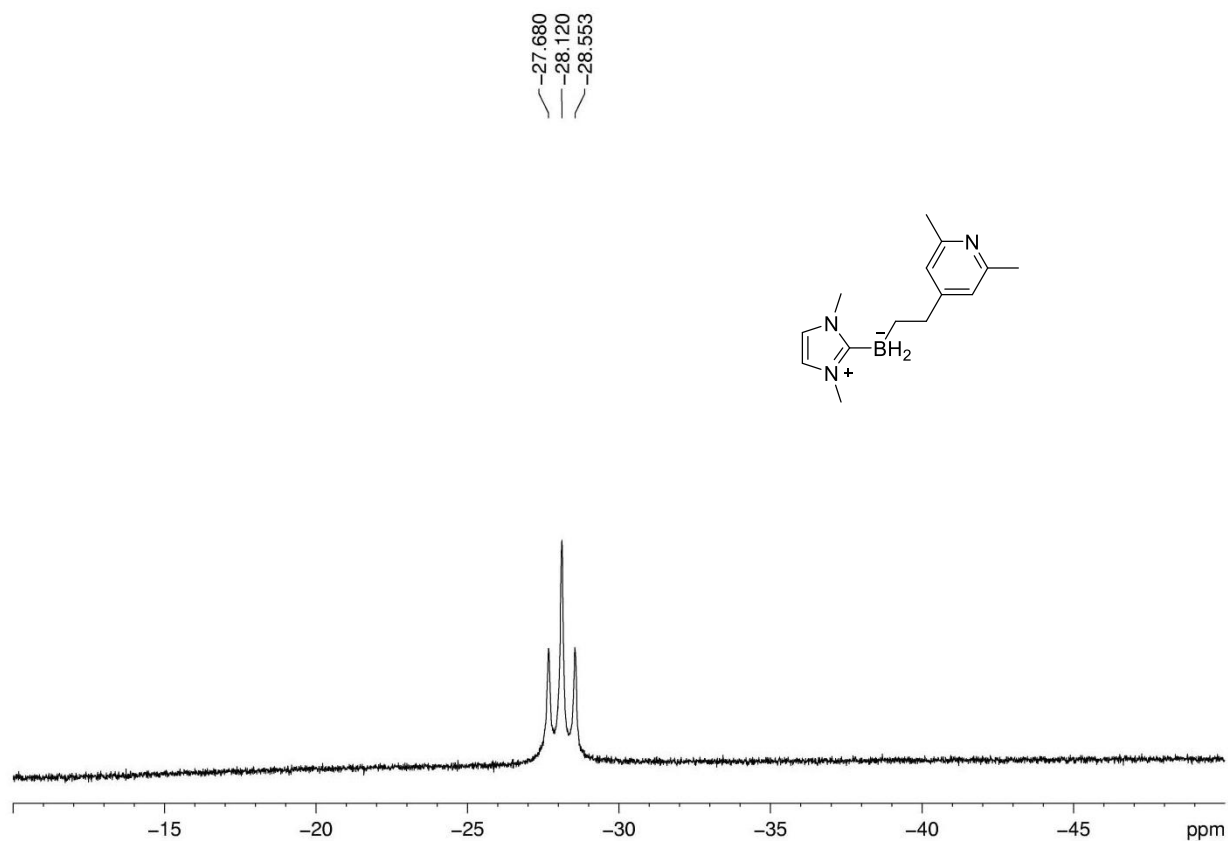
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **42**



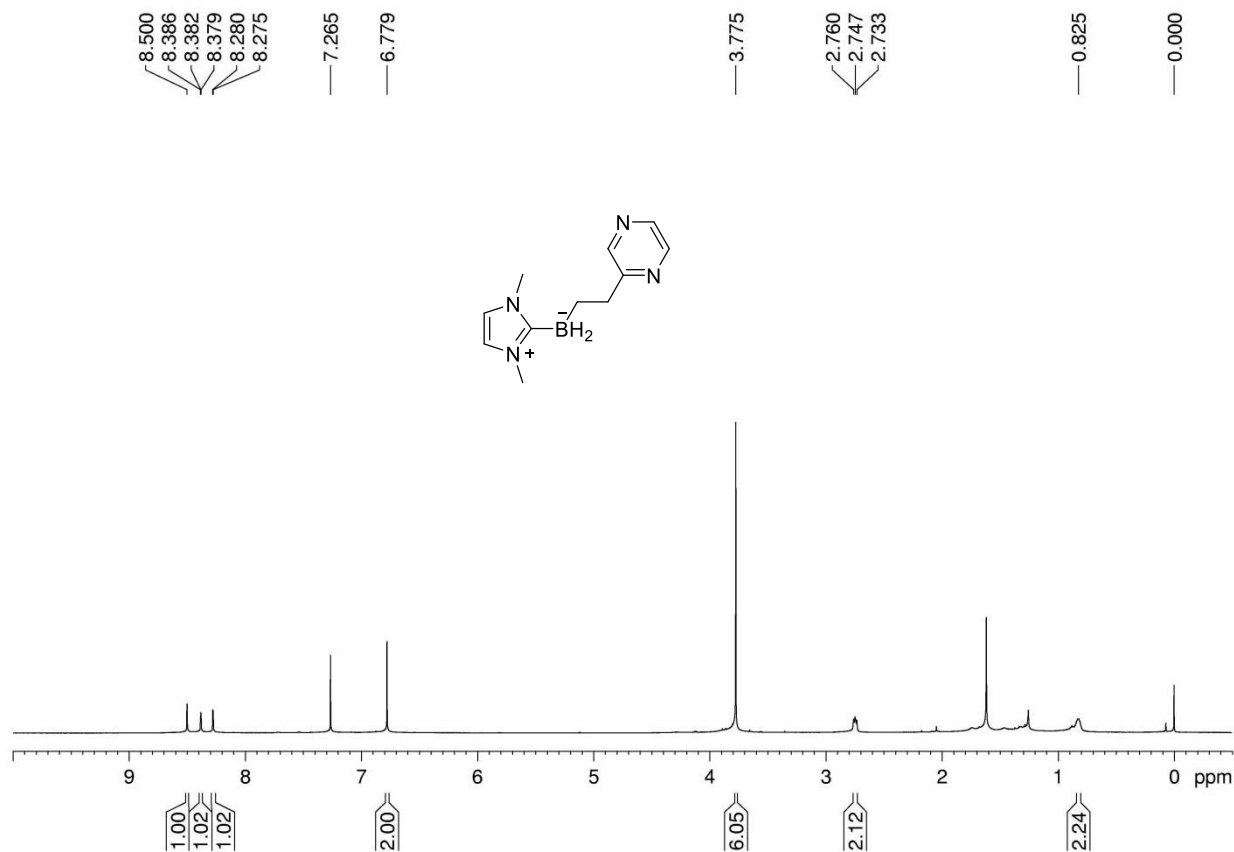
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **42**



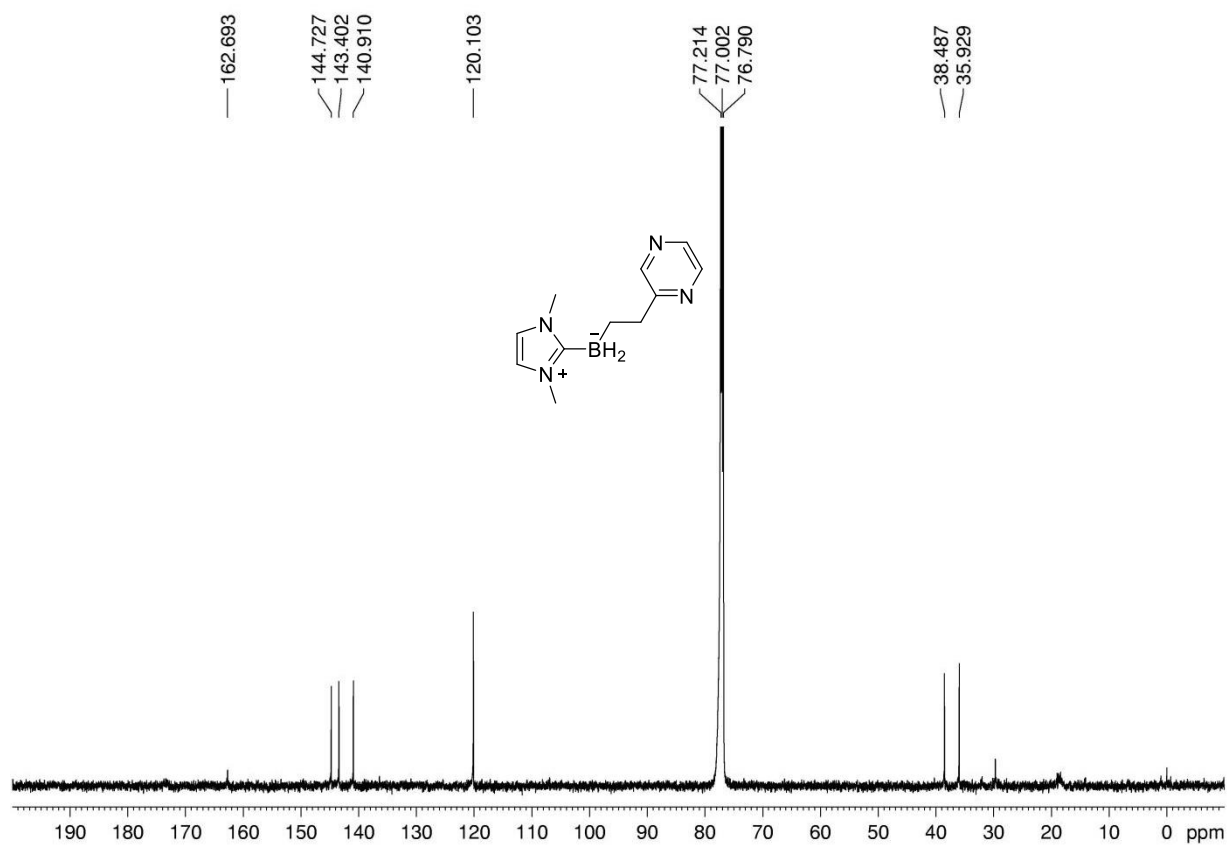
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **42**



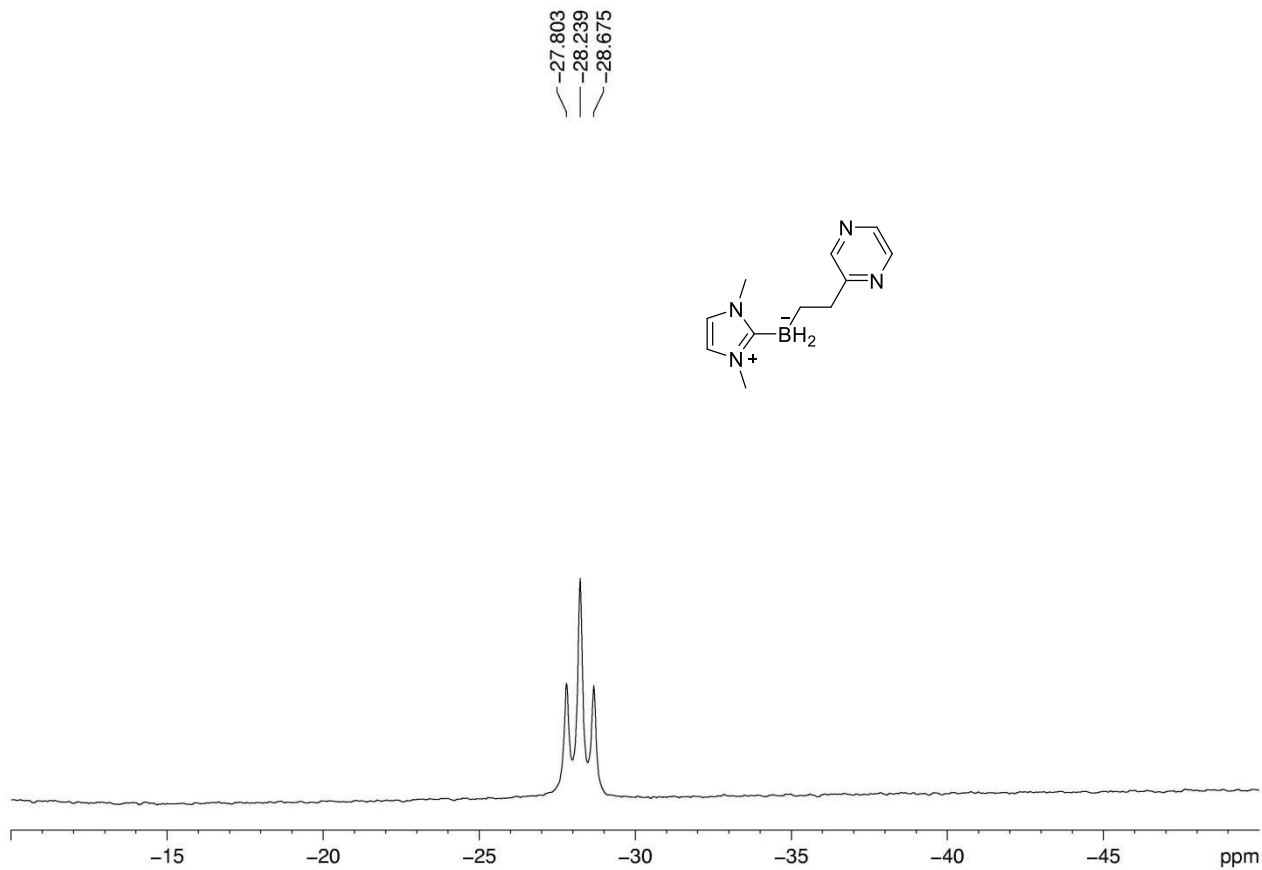
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **43**



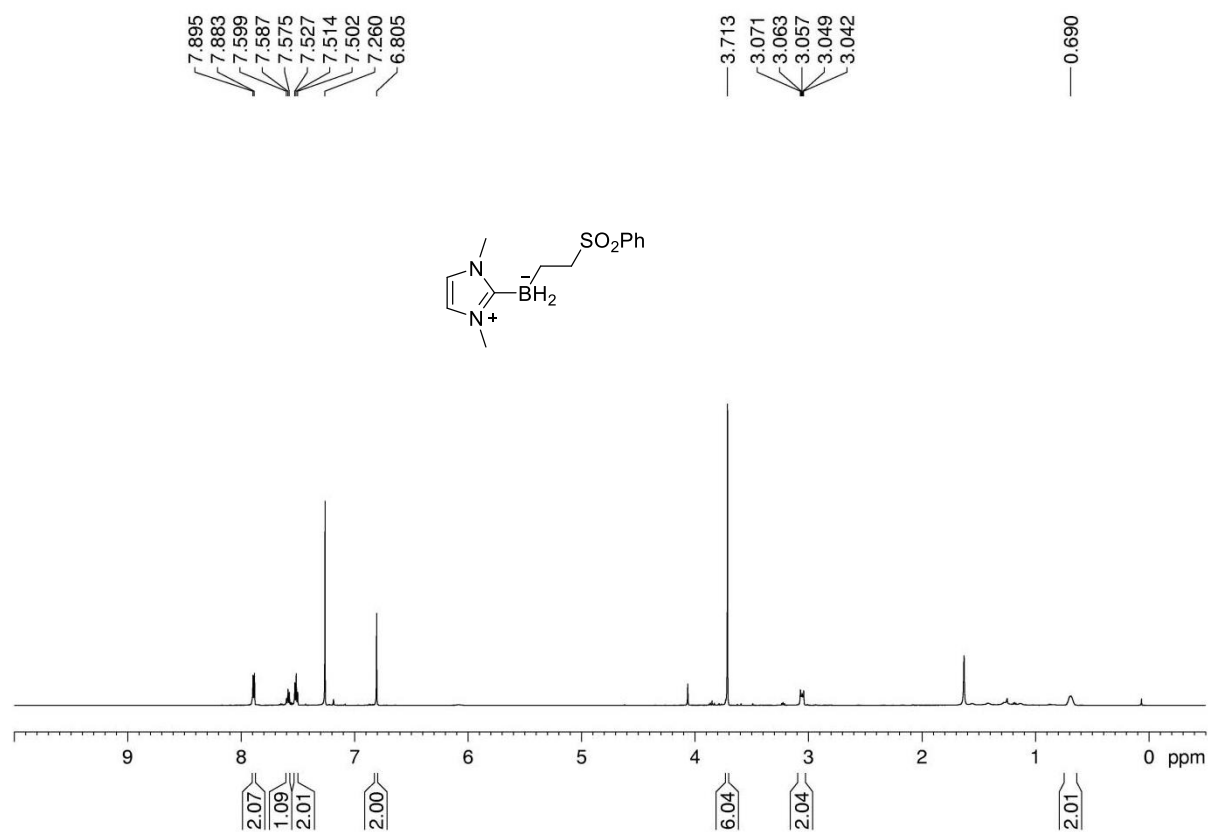
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **43**



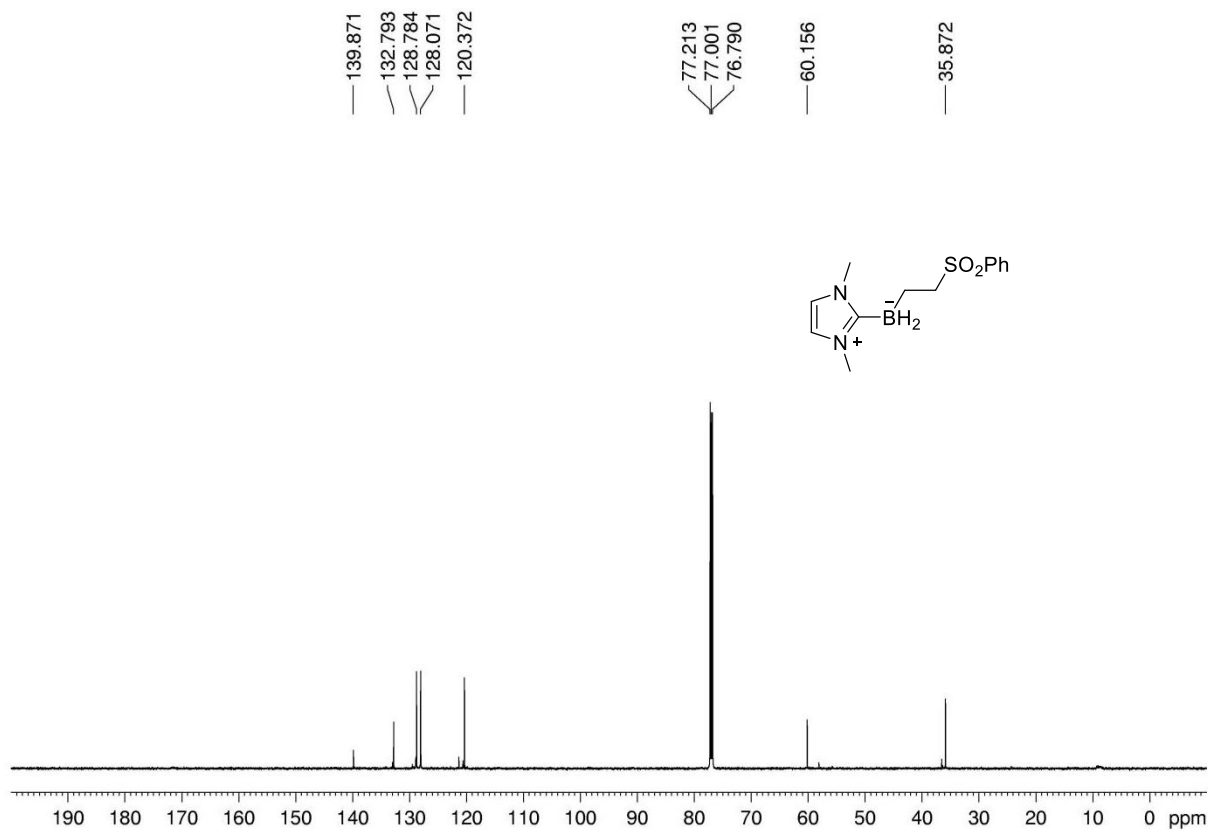
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **43**



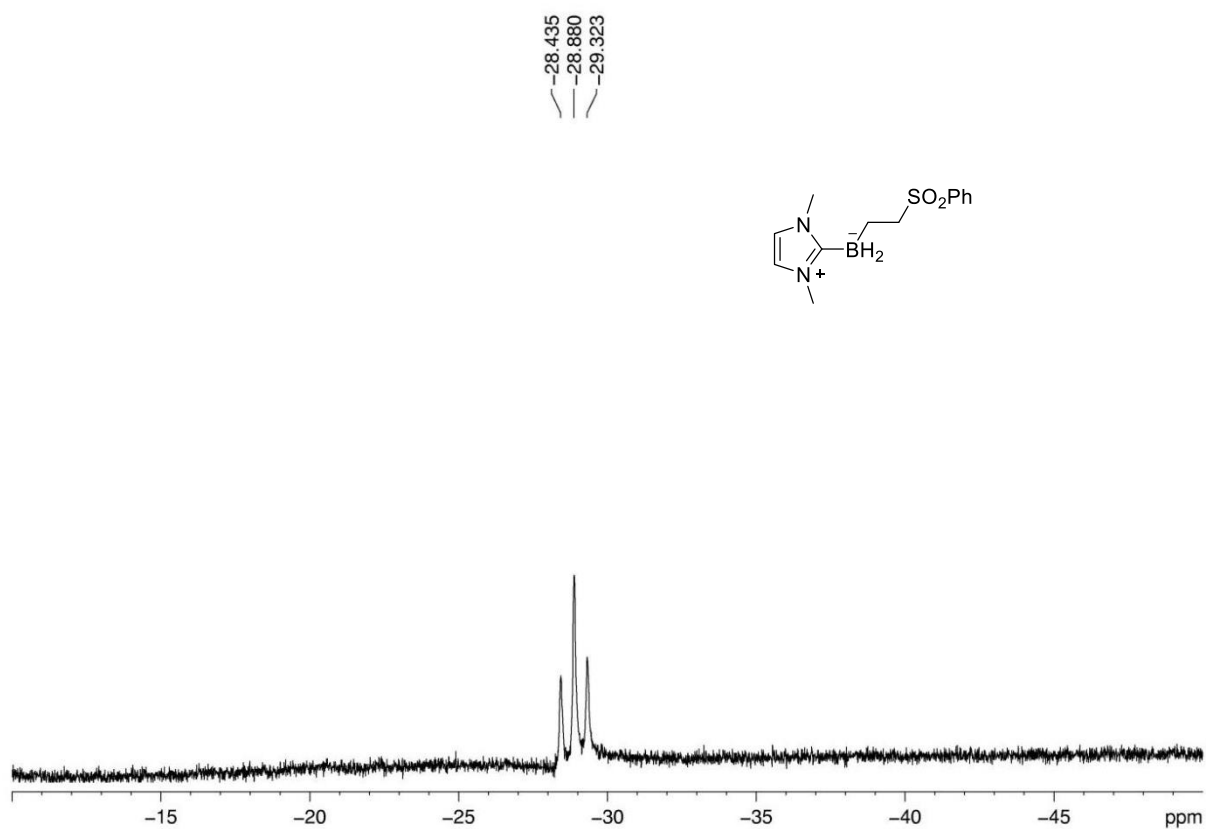
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **44**



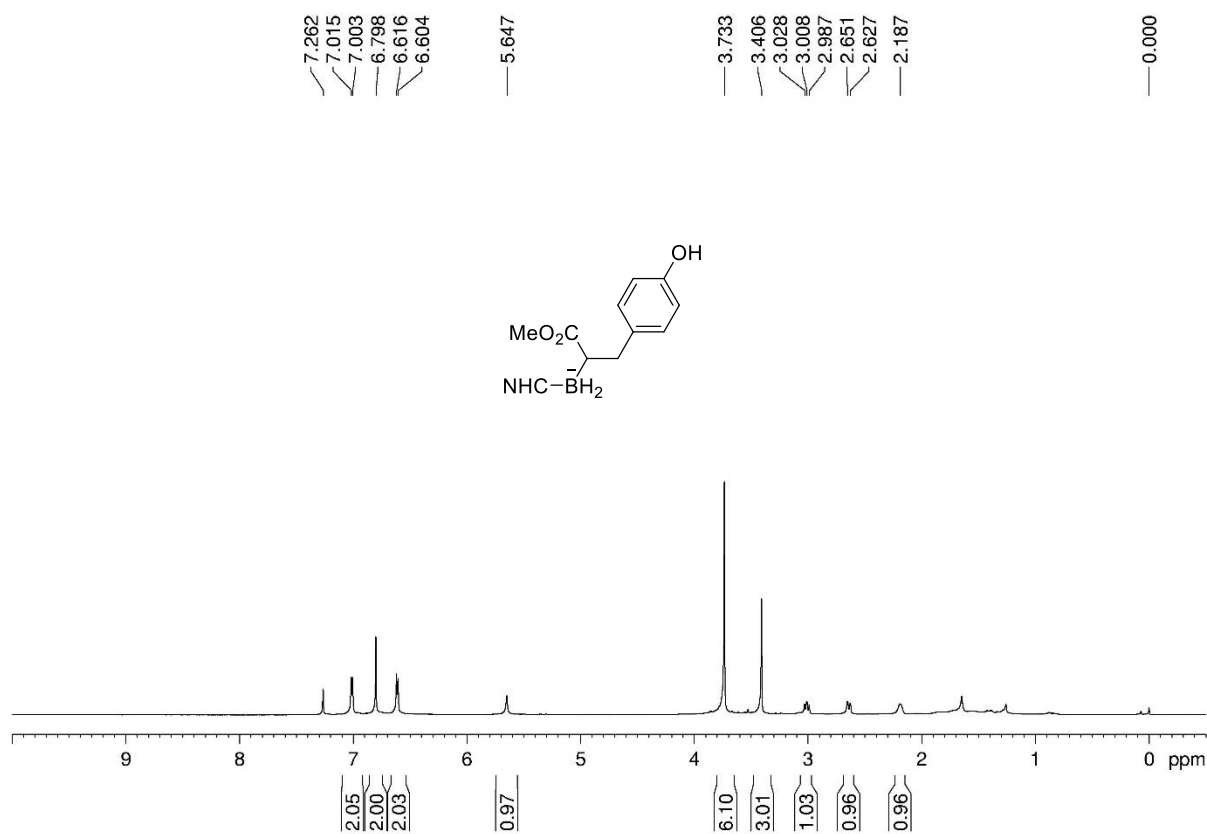
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **44**



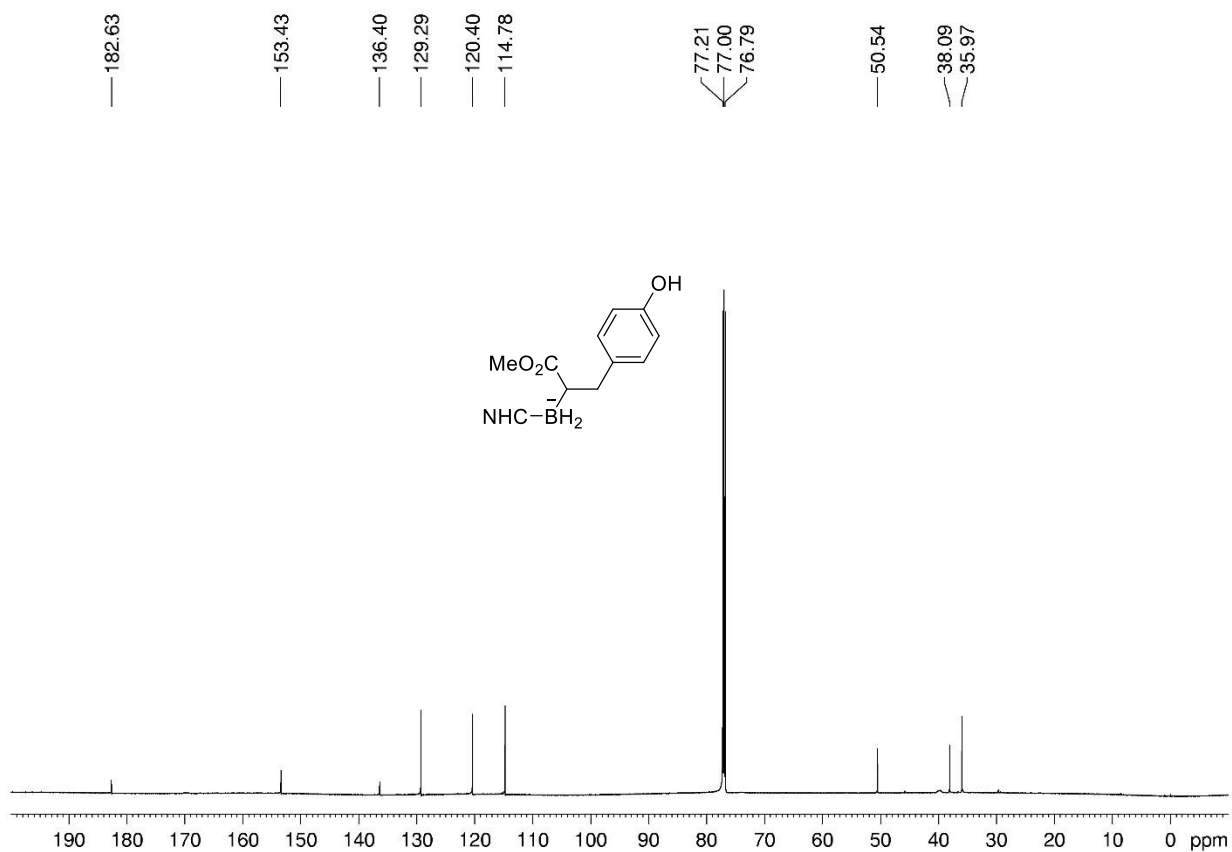
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **44**



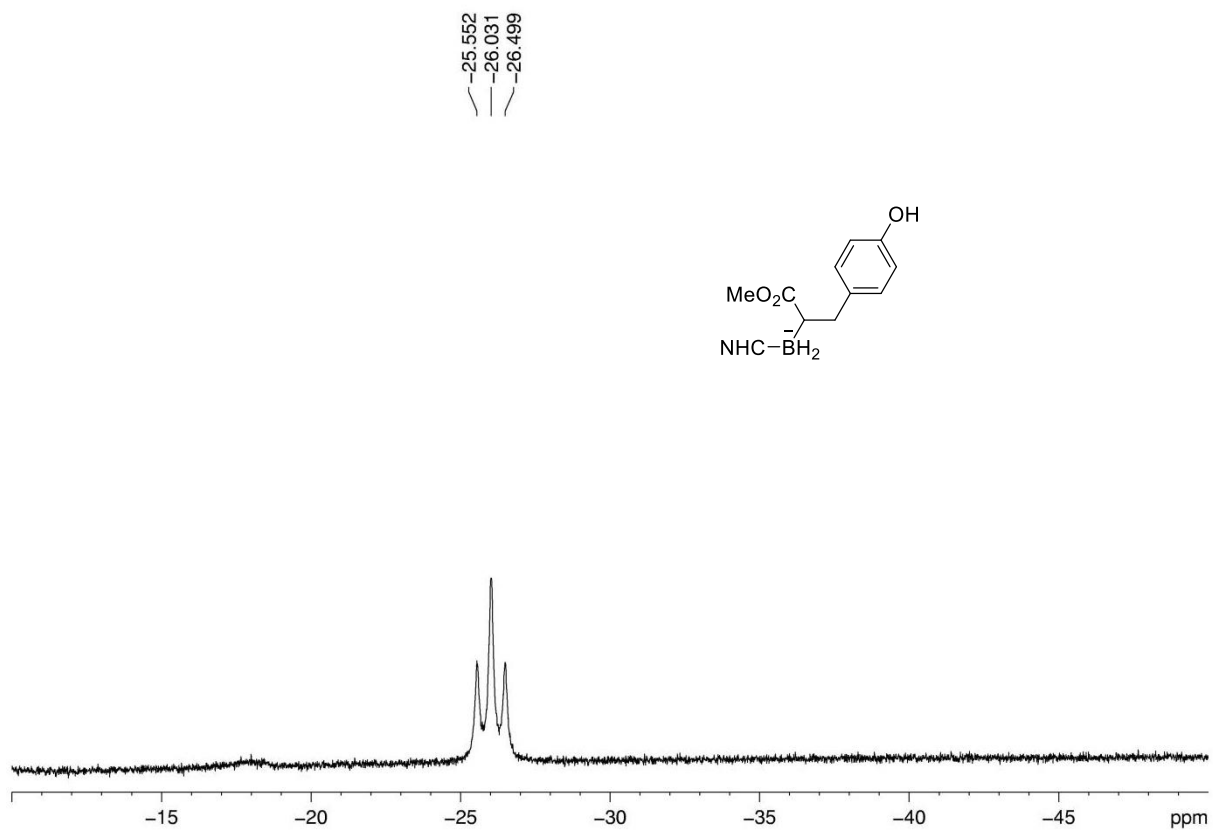
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **45**



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **45**

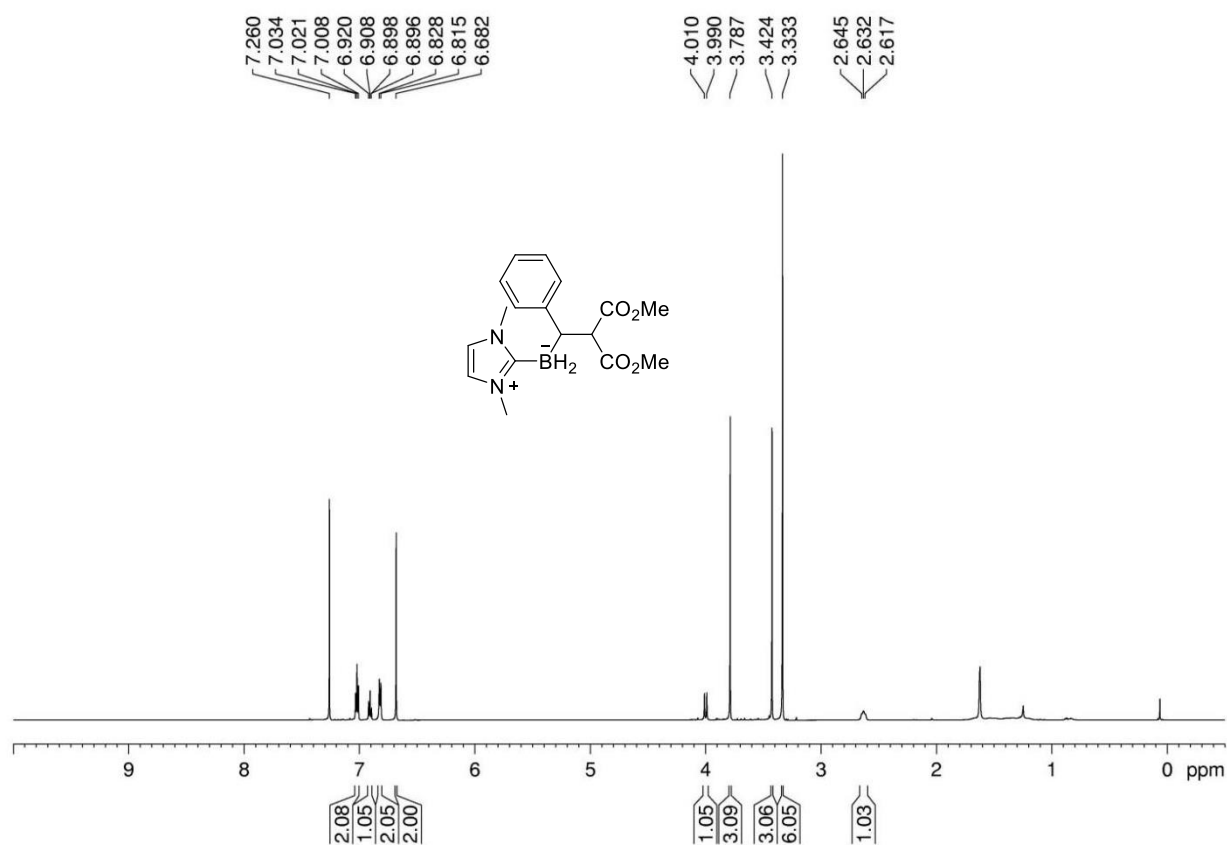


$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **45**

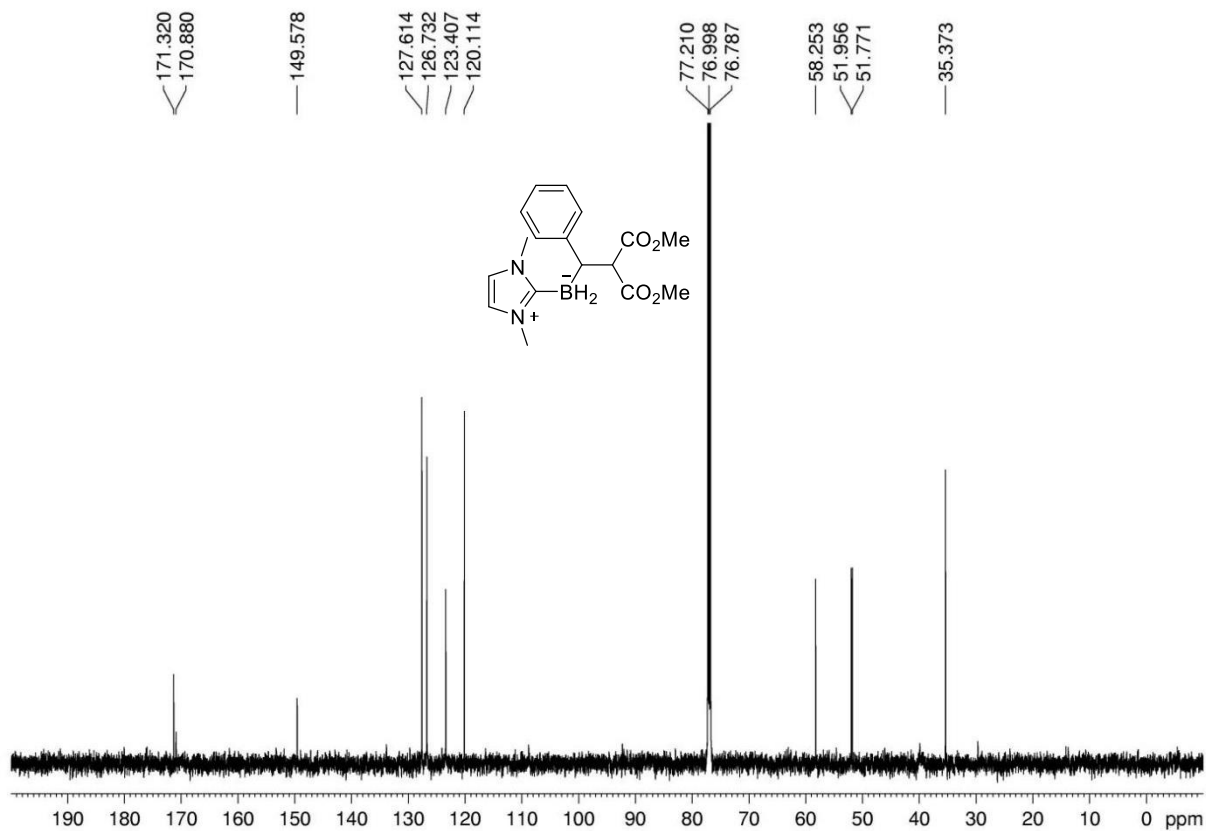




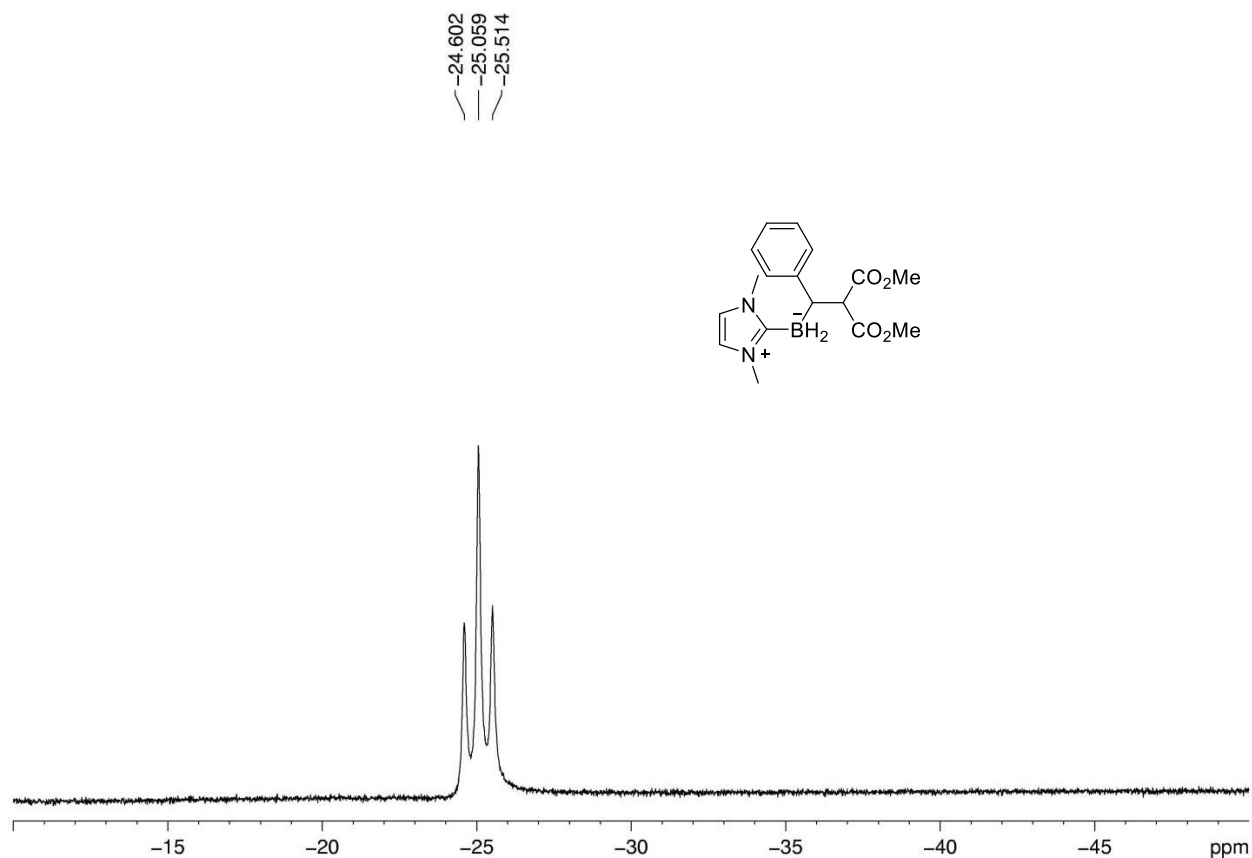
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **46**



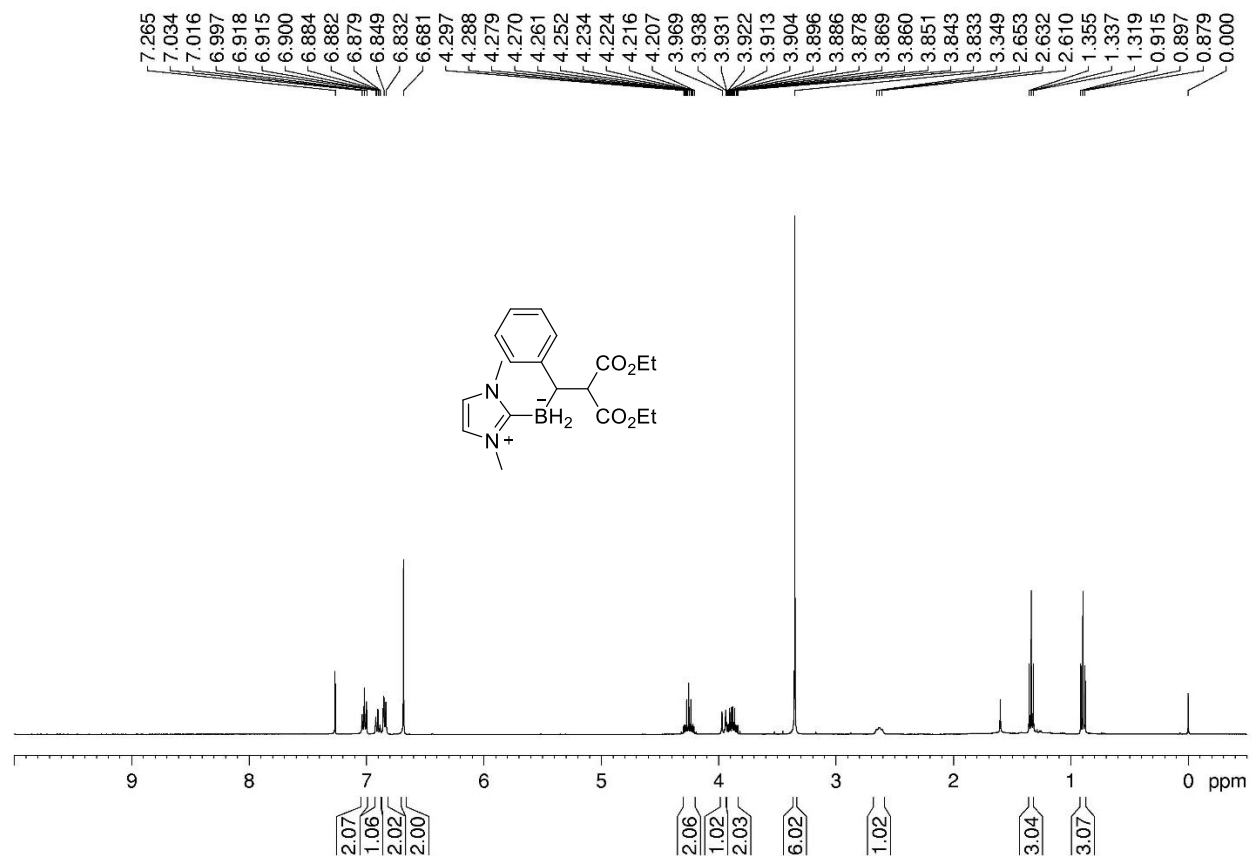
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **46**



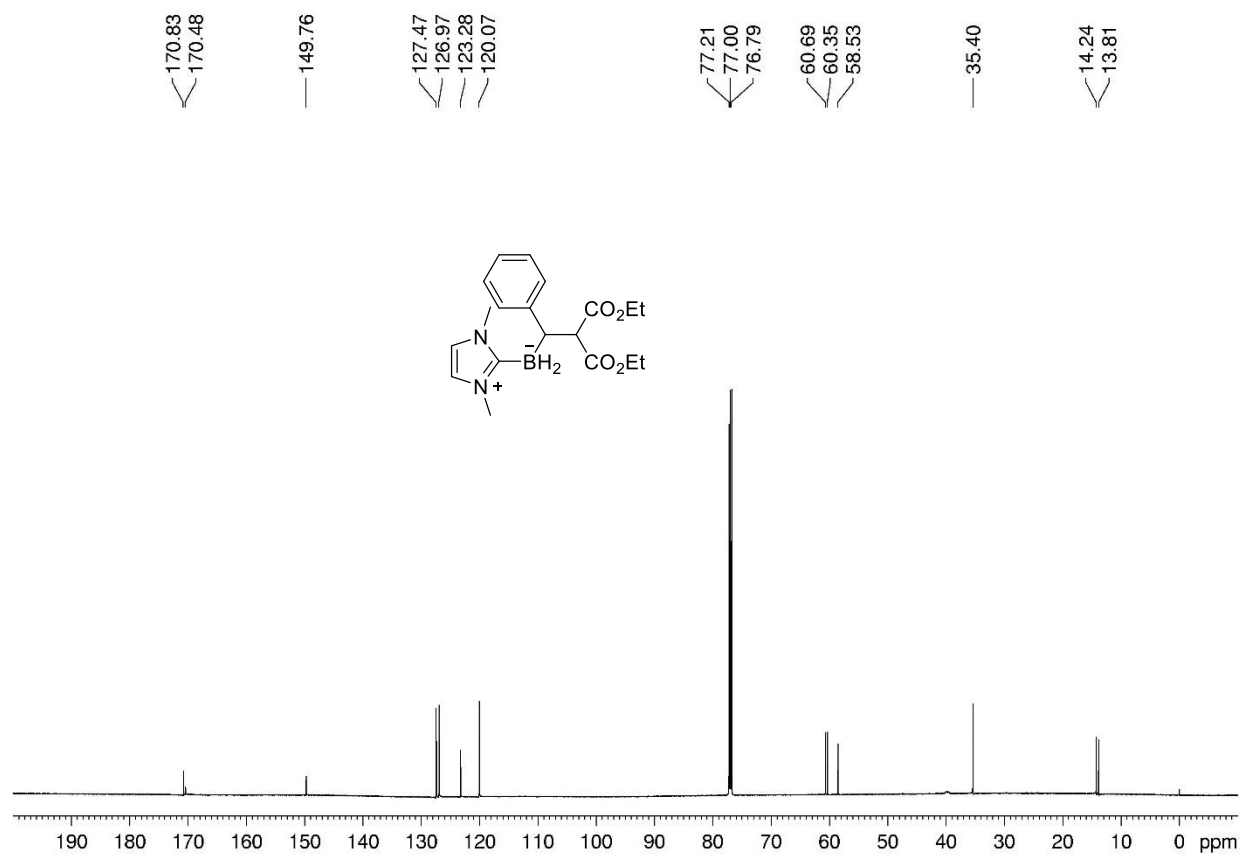
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **46**



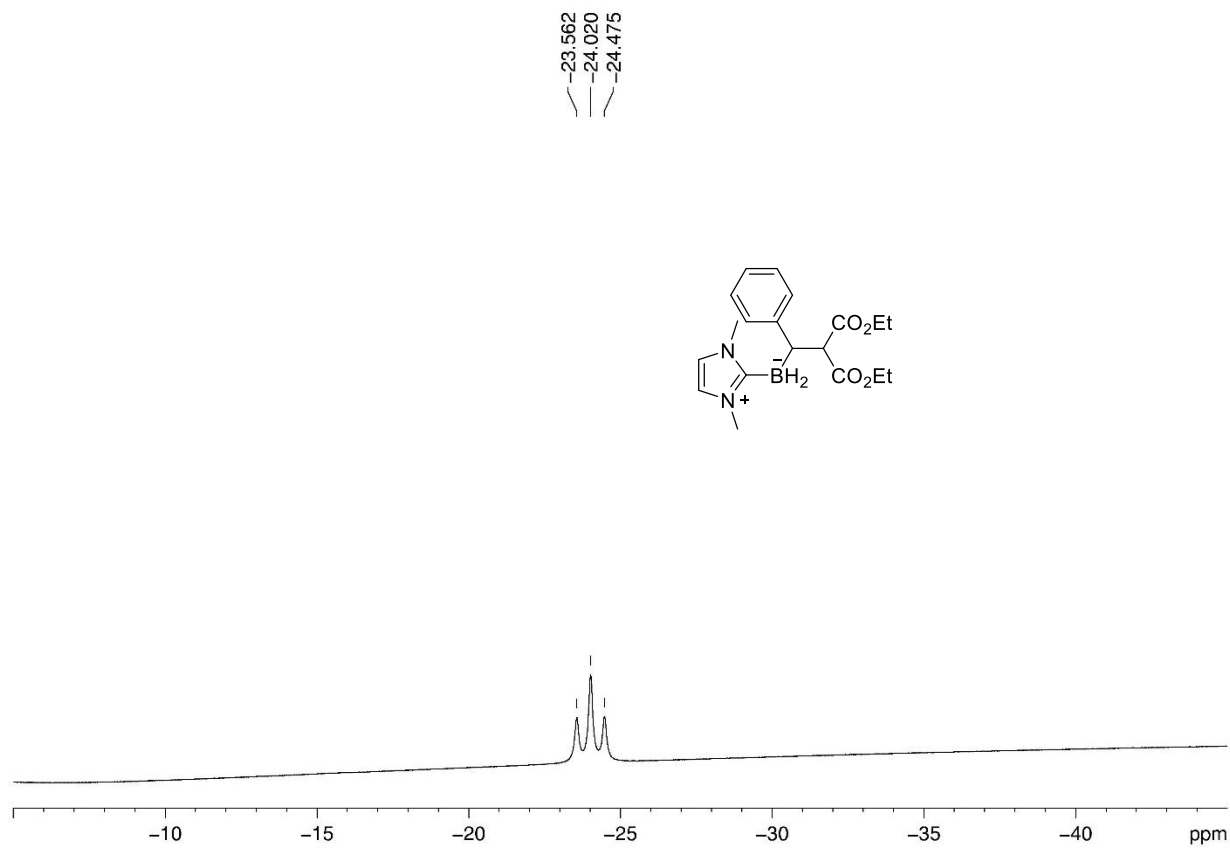
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **47**



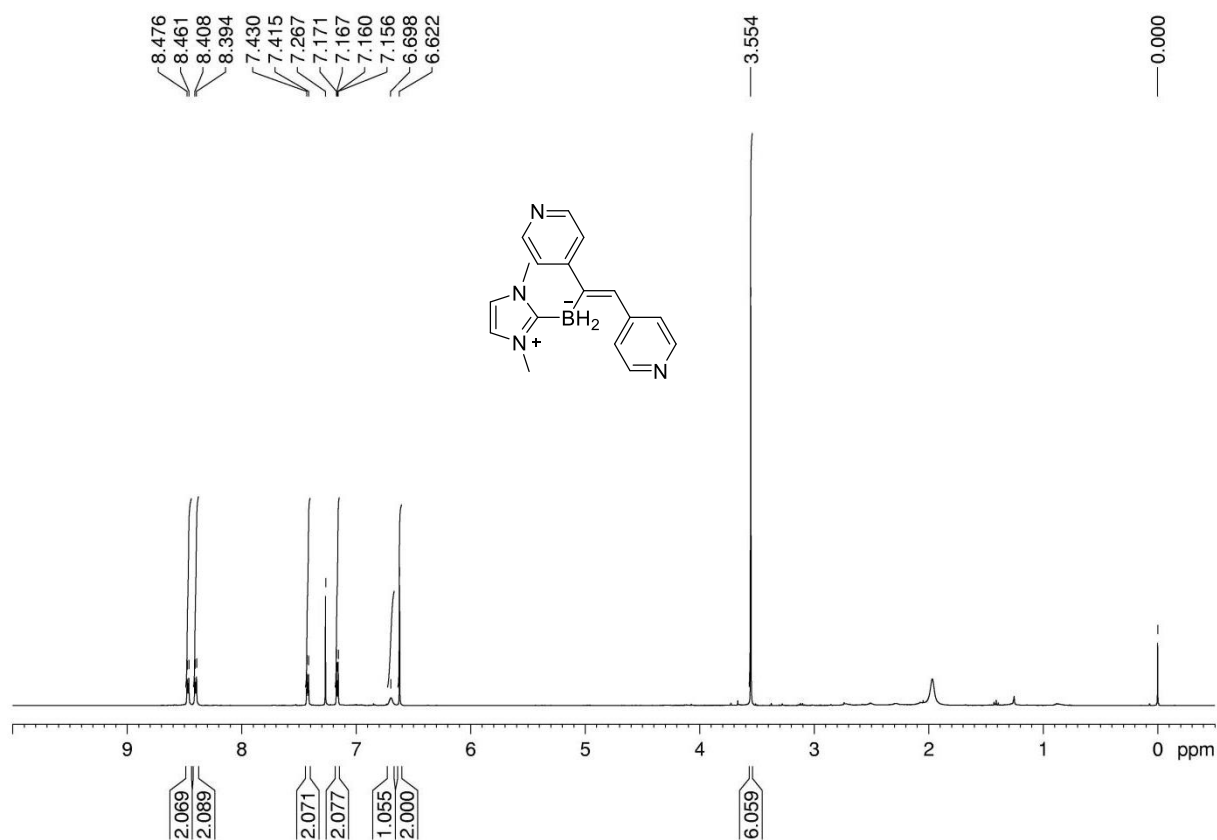
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **47**



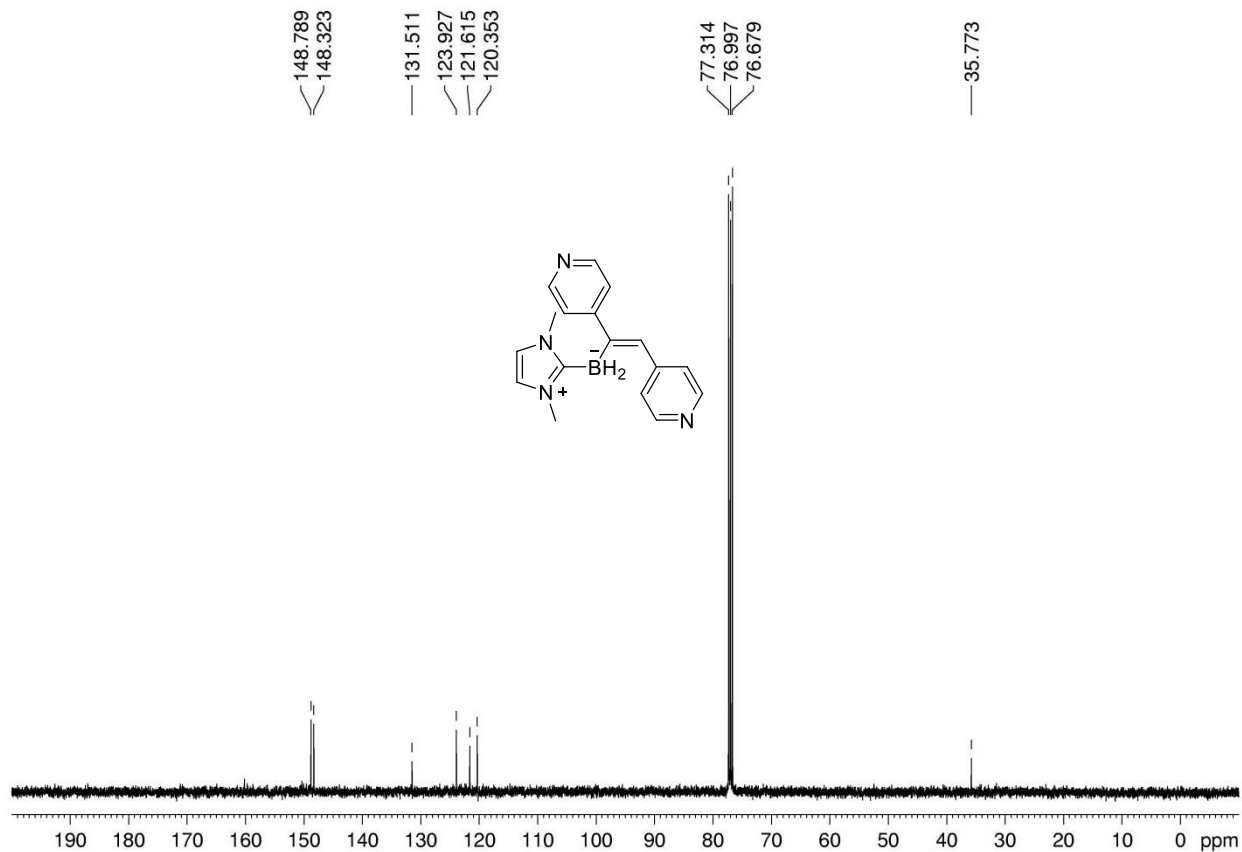
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **47**



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **48**

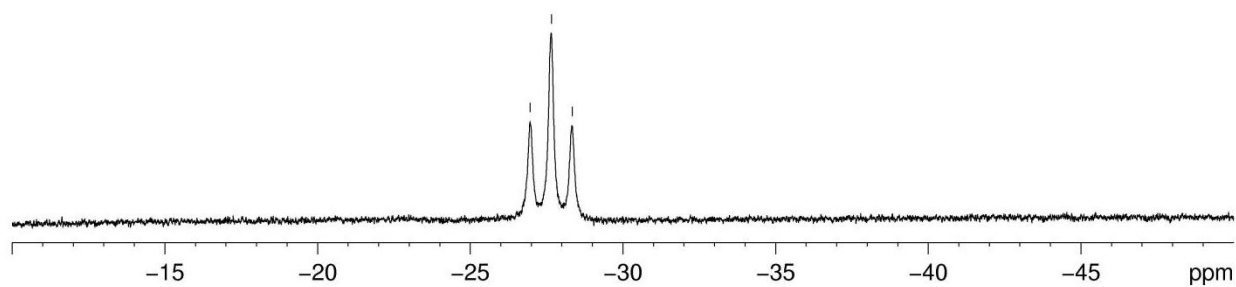
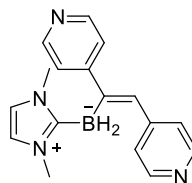


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) spectrum of **48**



$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz) spectrum of **48**

-26.962  
-27.657  
-28.336

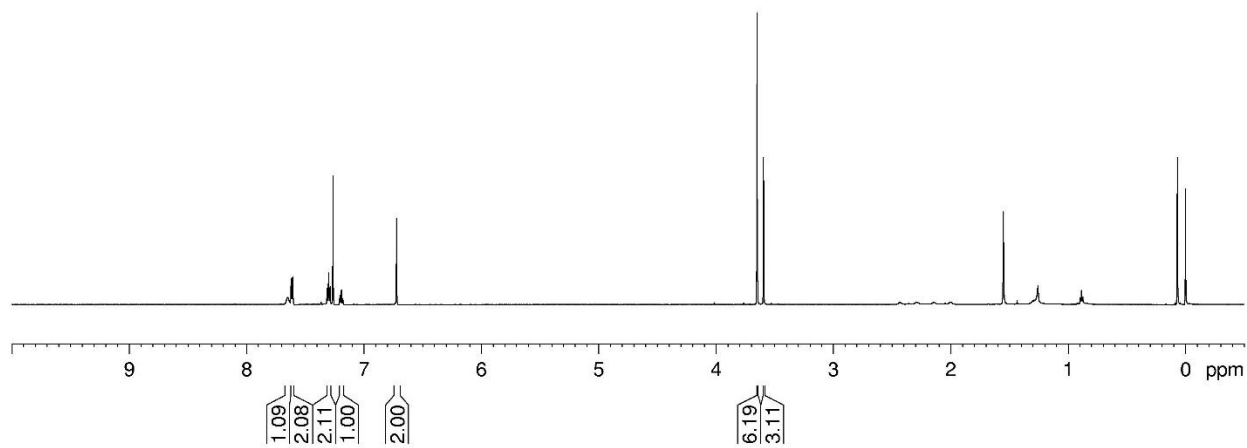
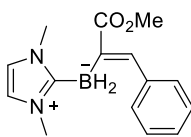


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **49**

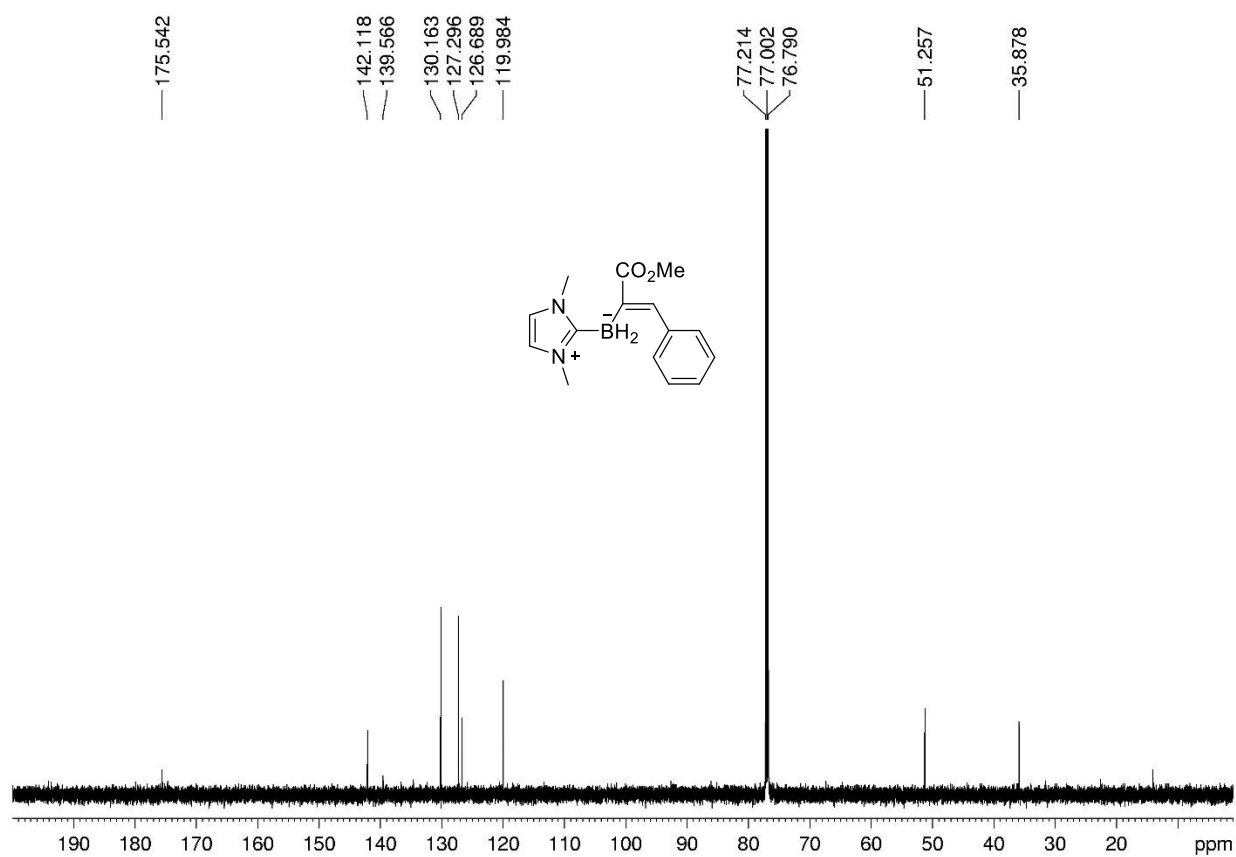
7.646  
7.617  
7.604  
7.311  
7.299  
7.286  
7.261  
7.202  
7.190  
7.178  
6.720

3.648  
3.593

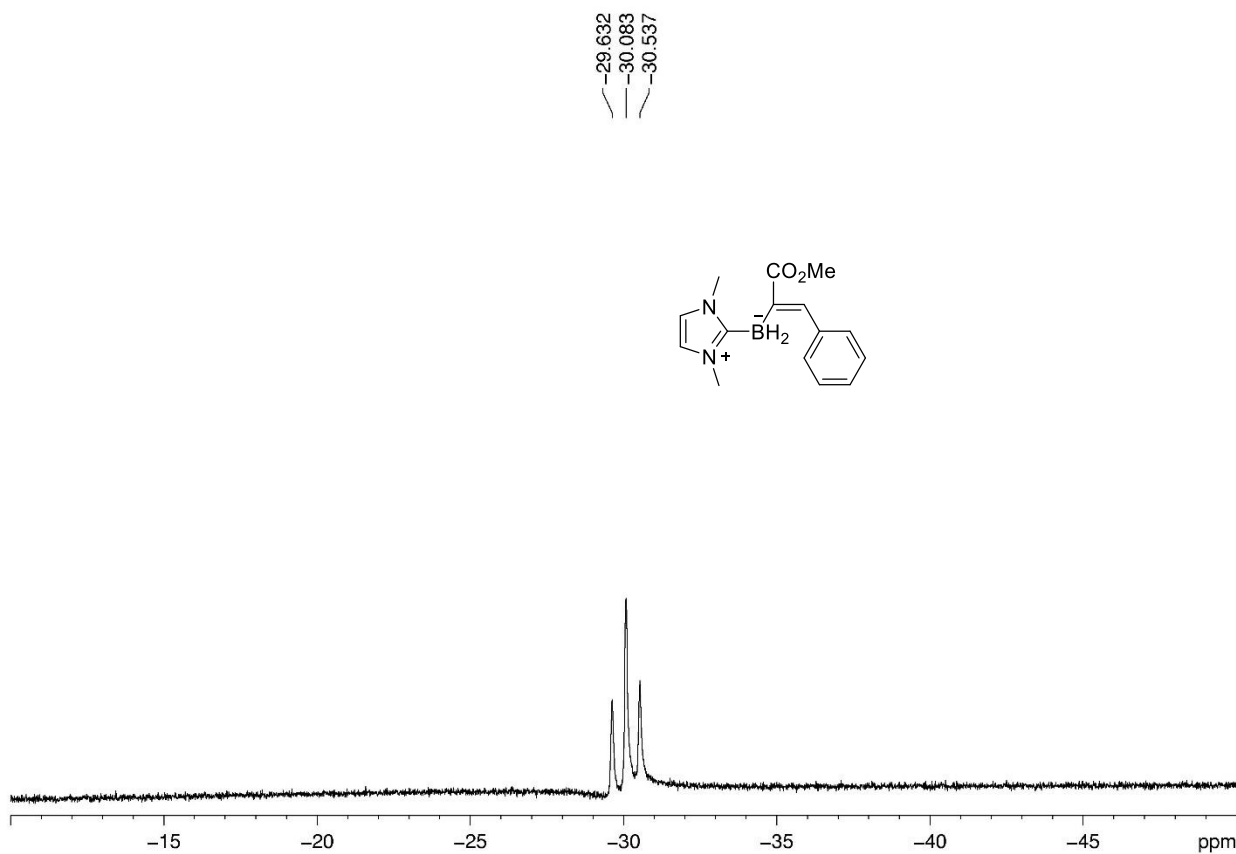
0.000



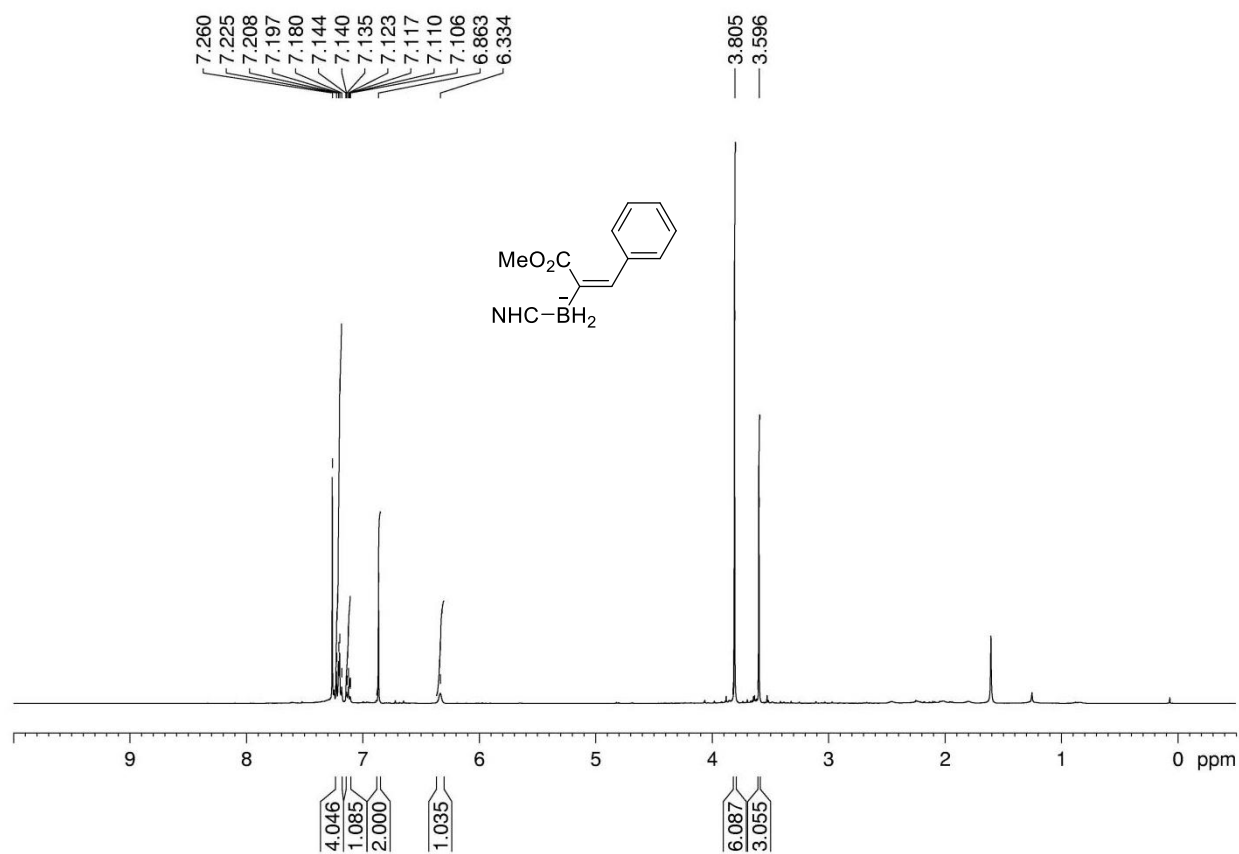
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **49**



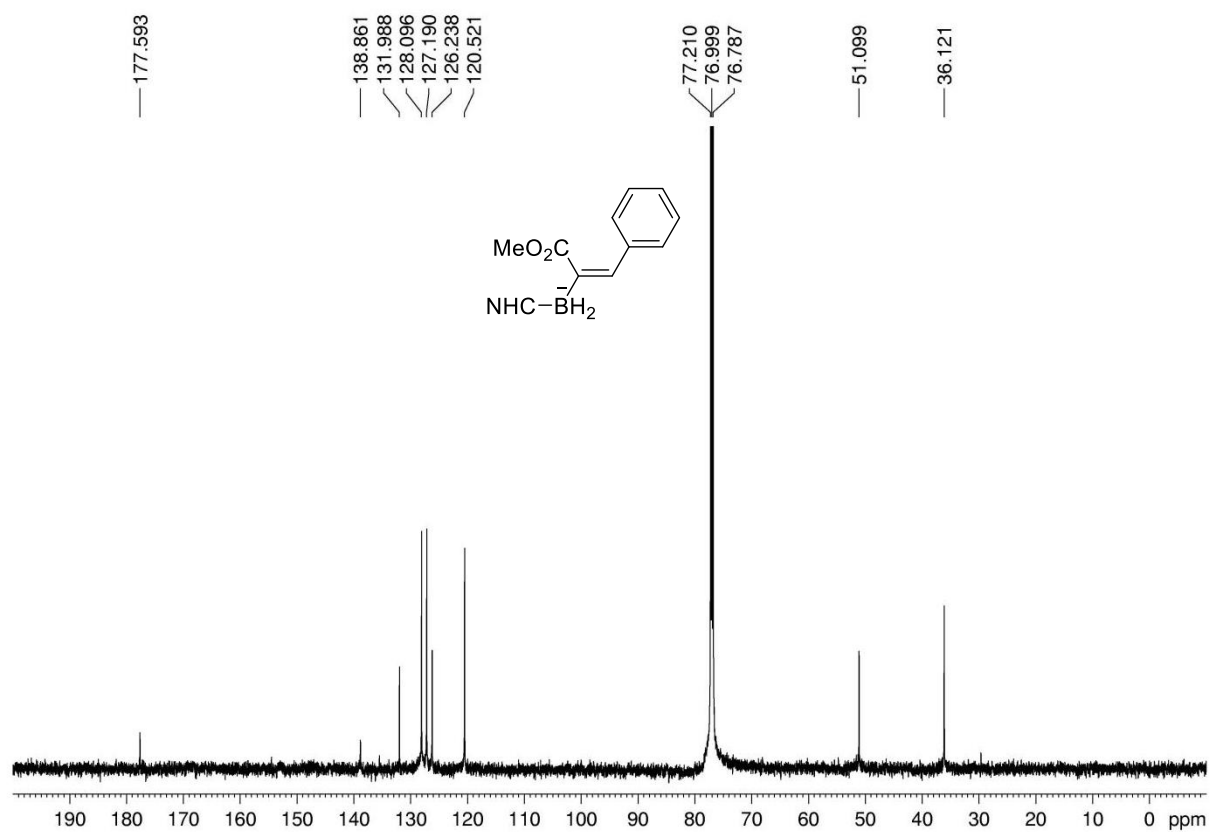
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **49**



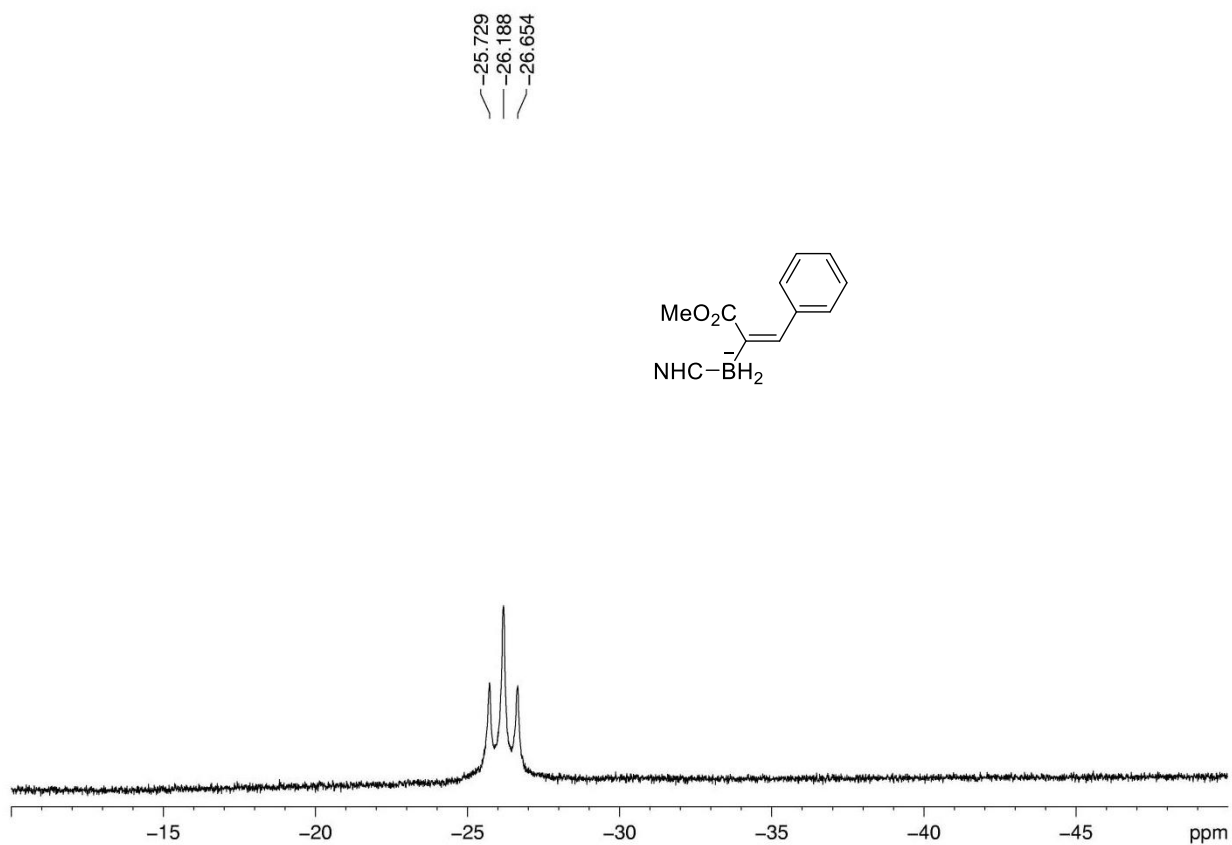
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **50**



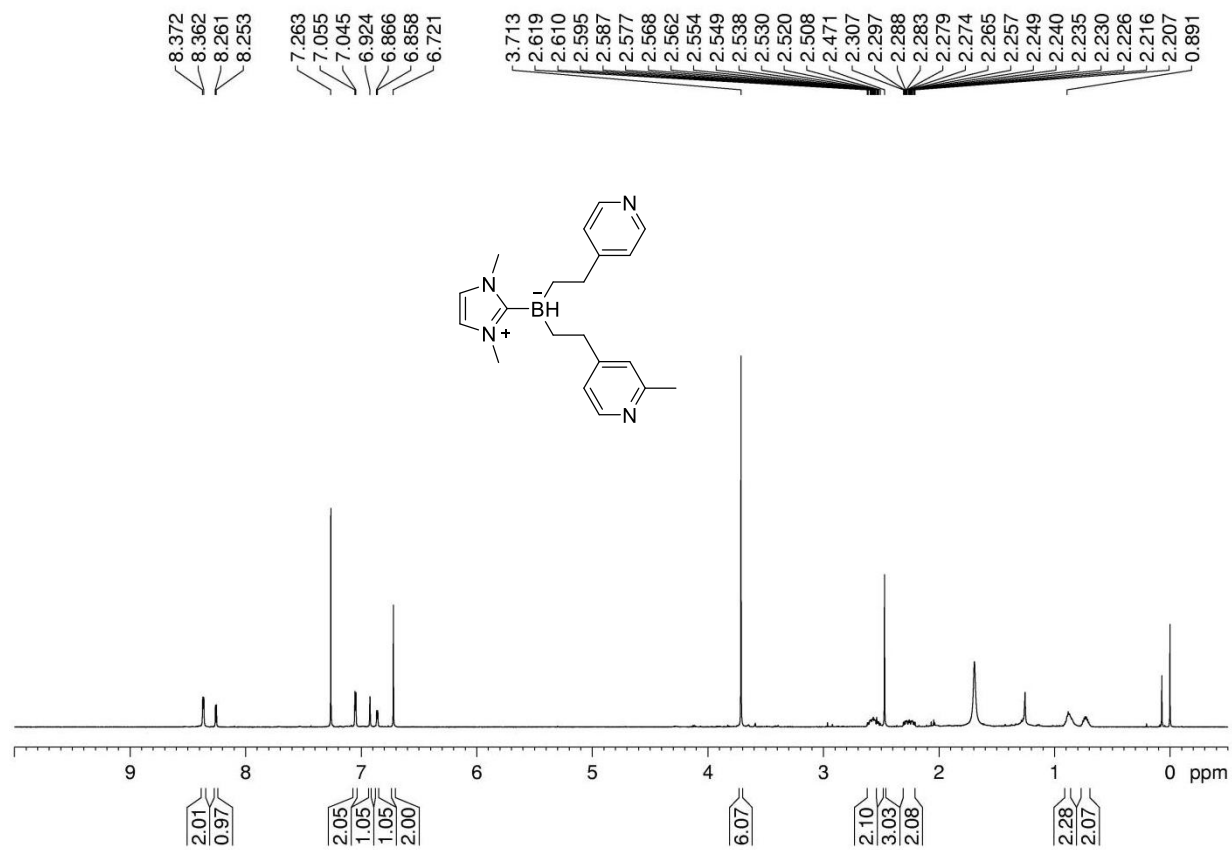
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **50**



$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **50**

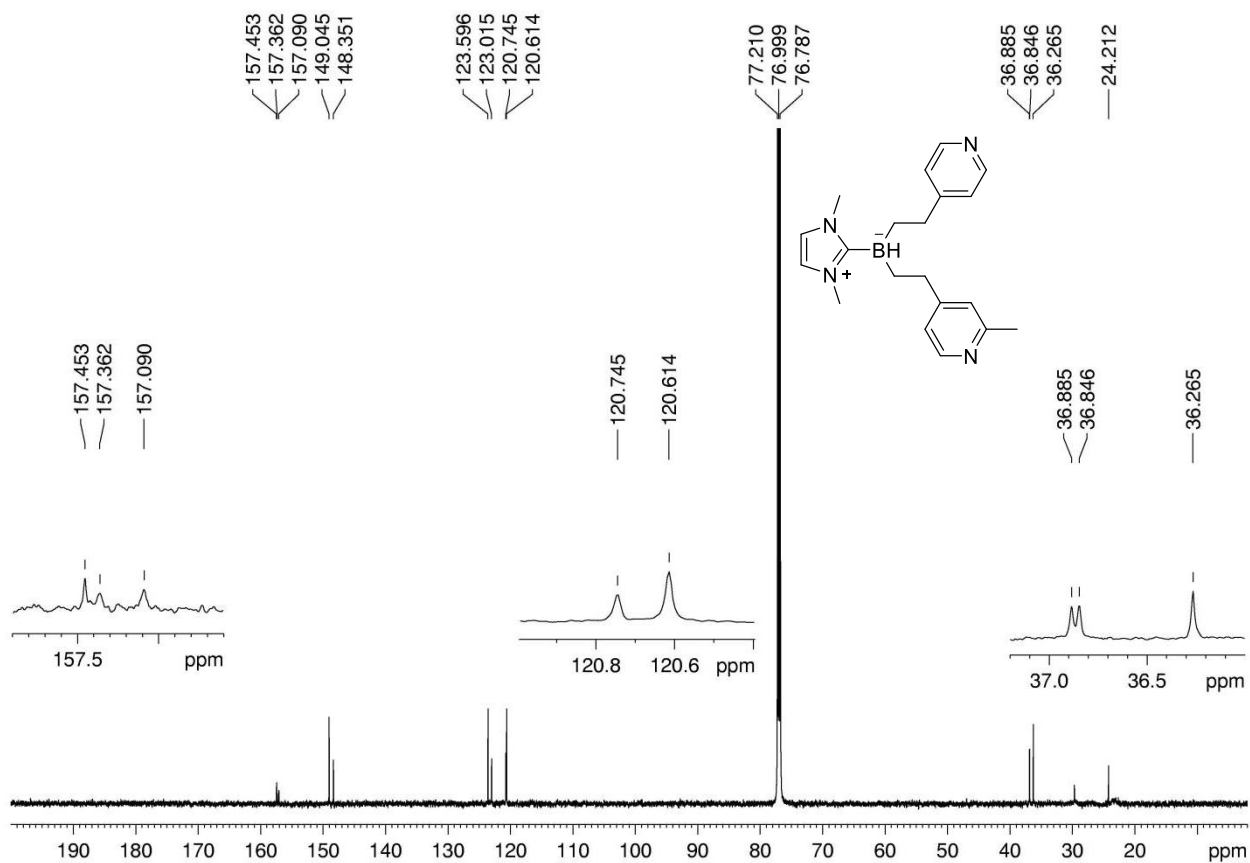


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **51**

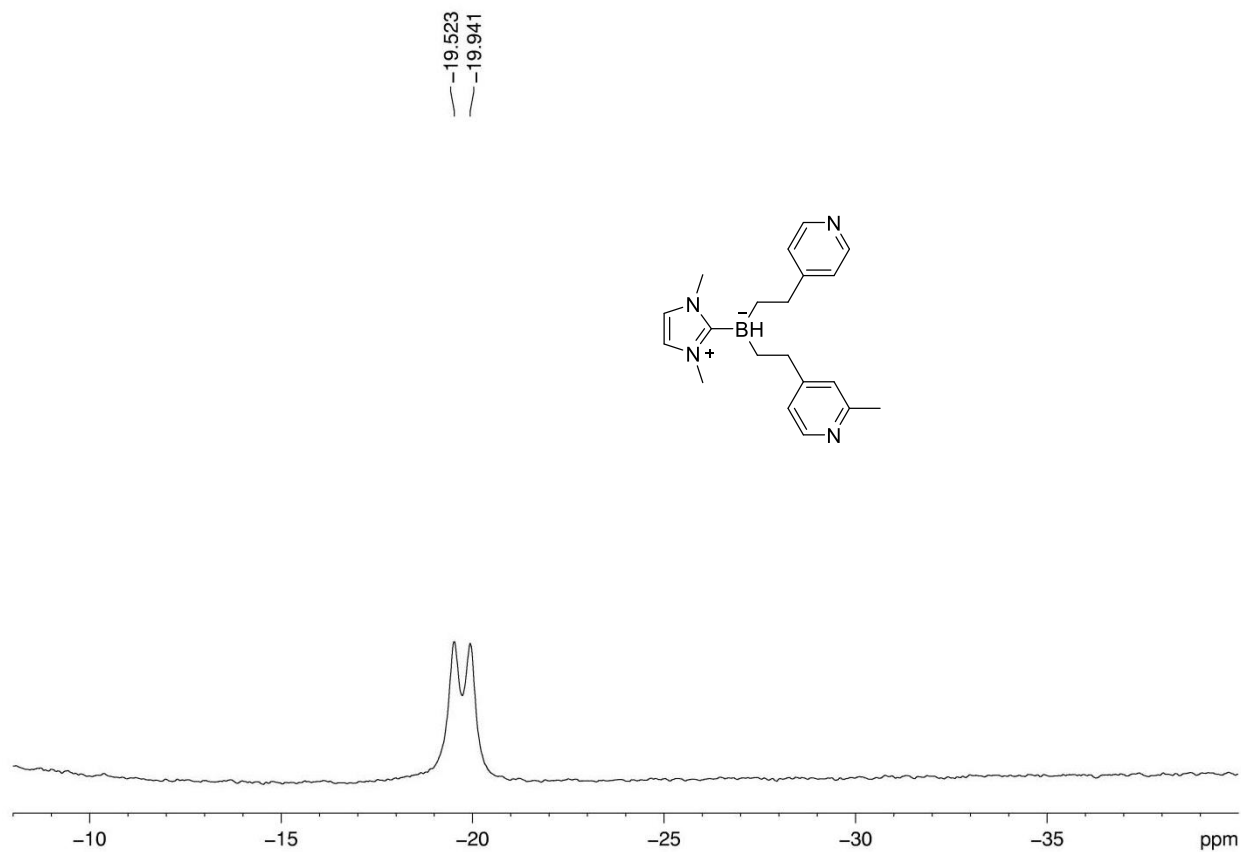




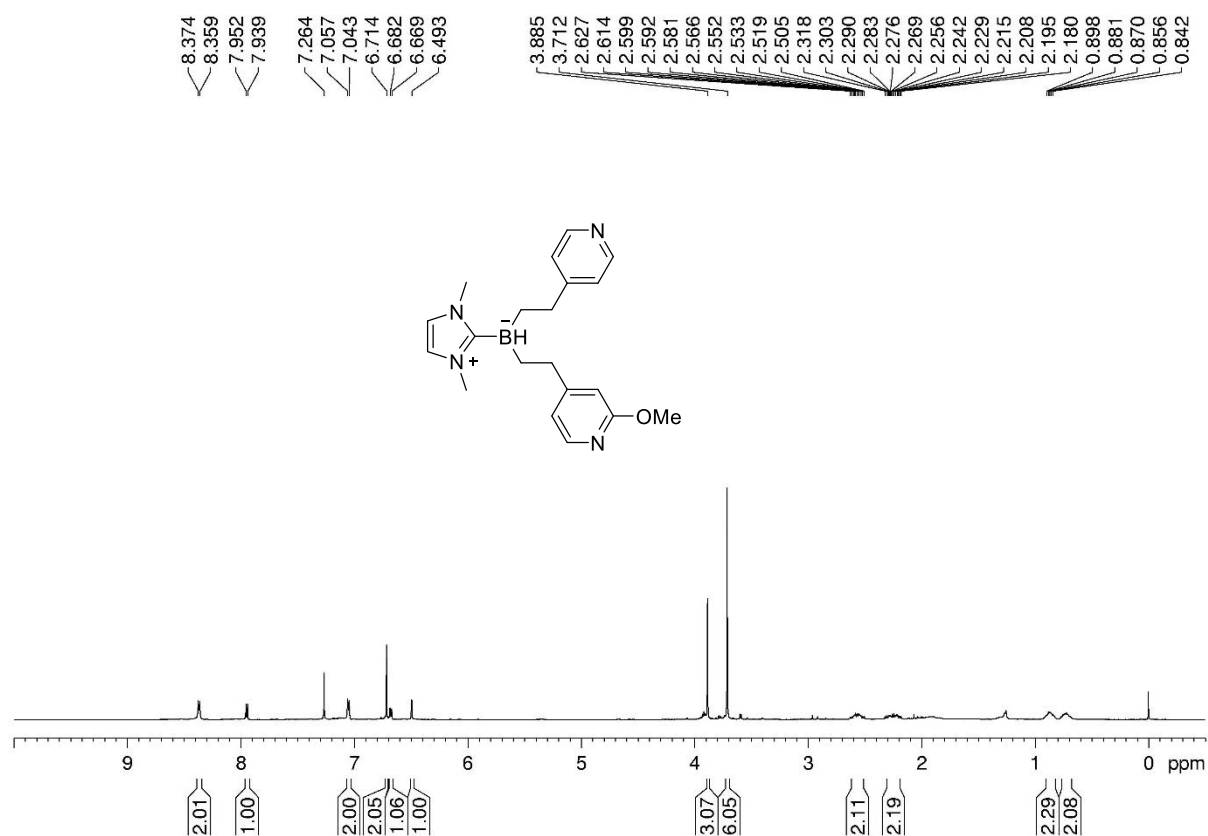
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **51**



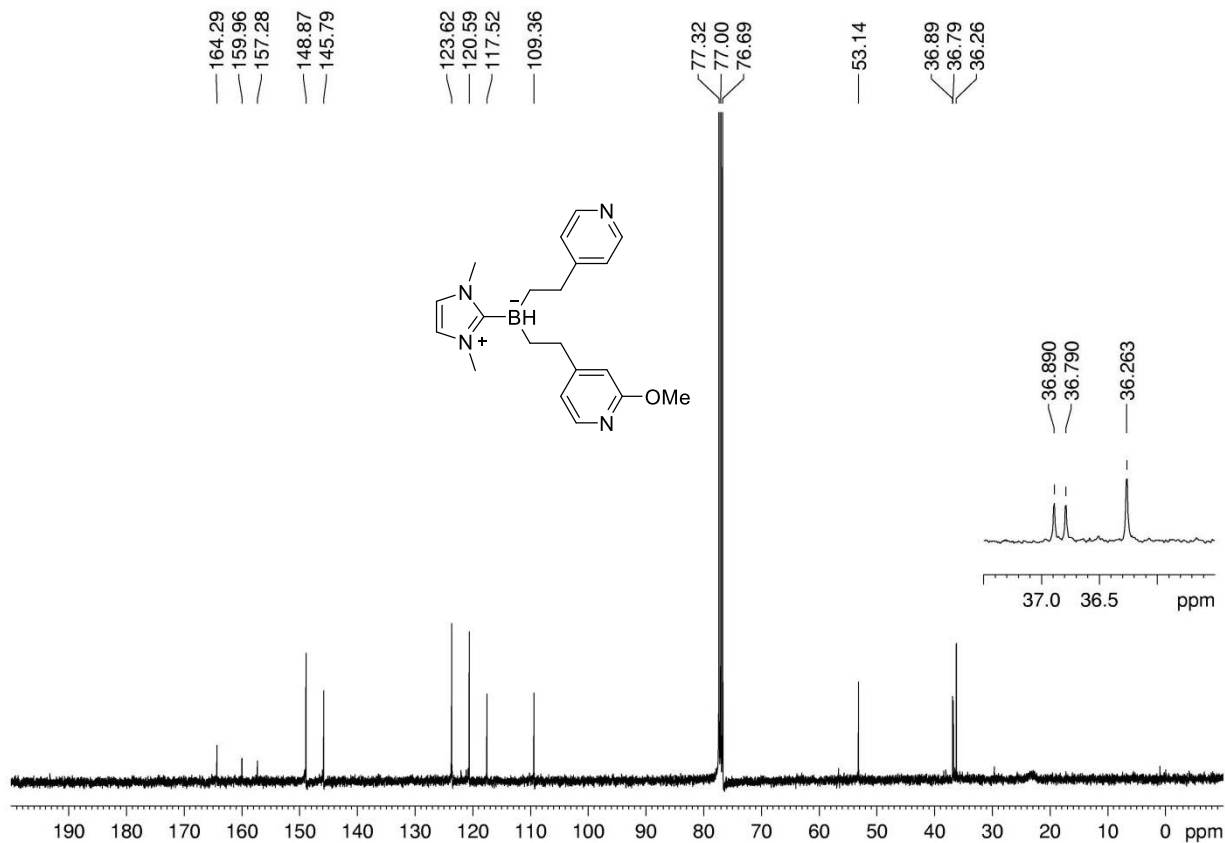
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **51**



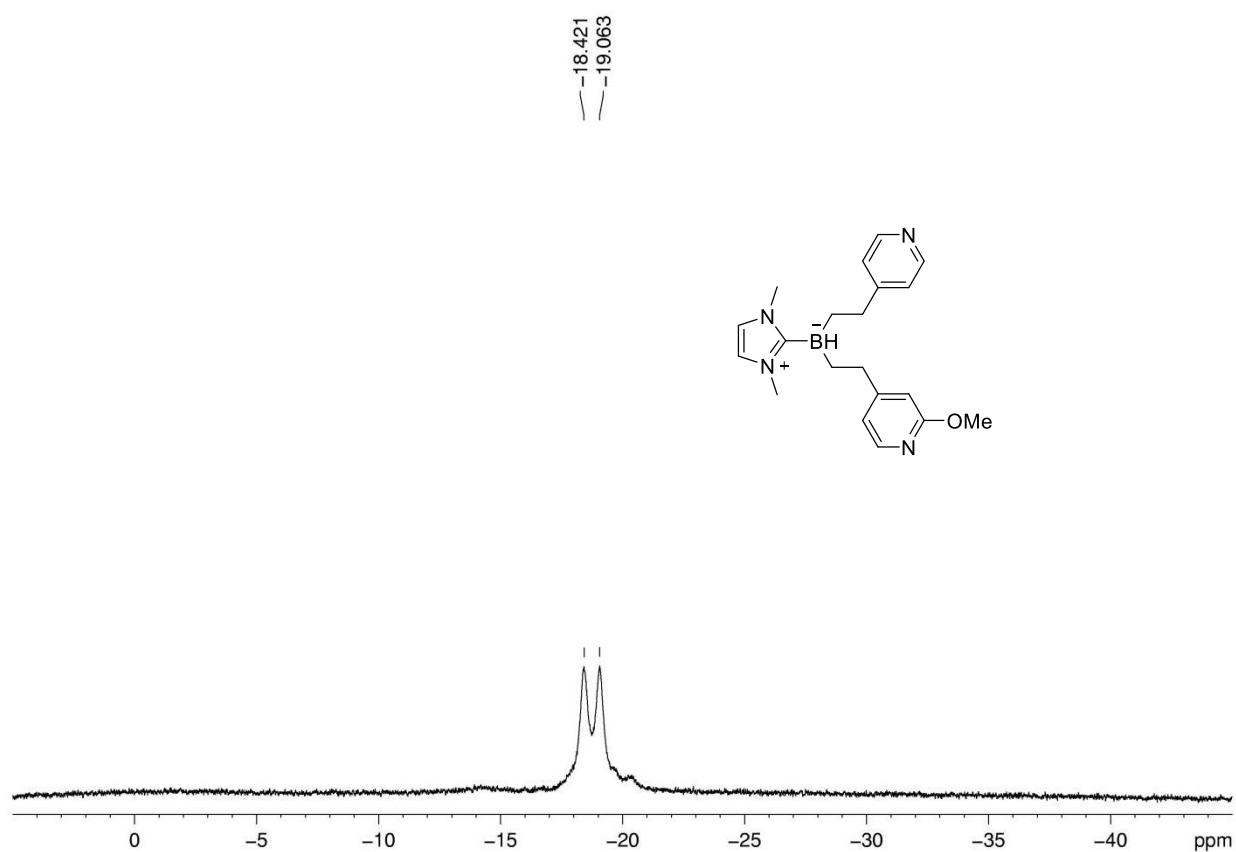
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **52**



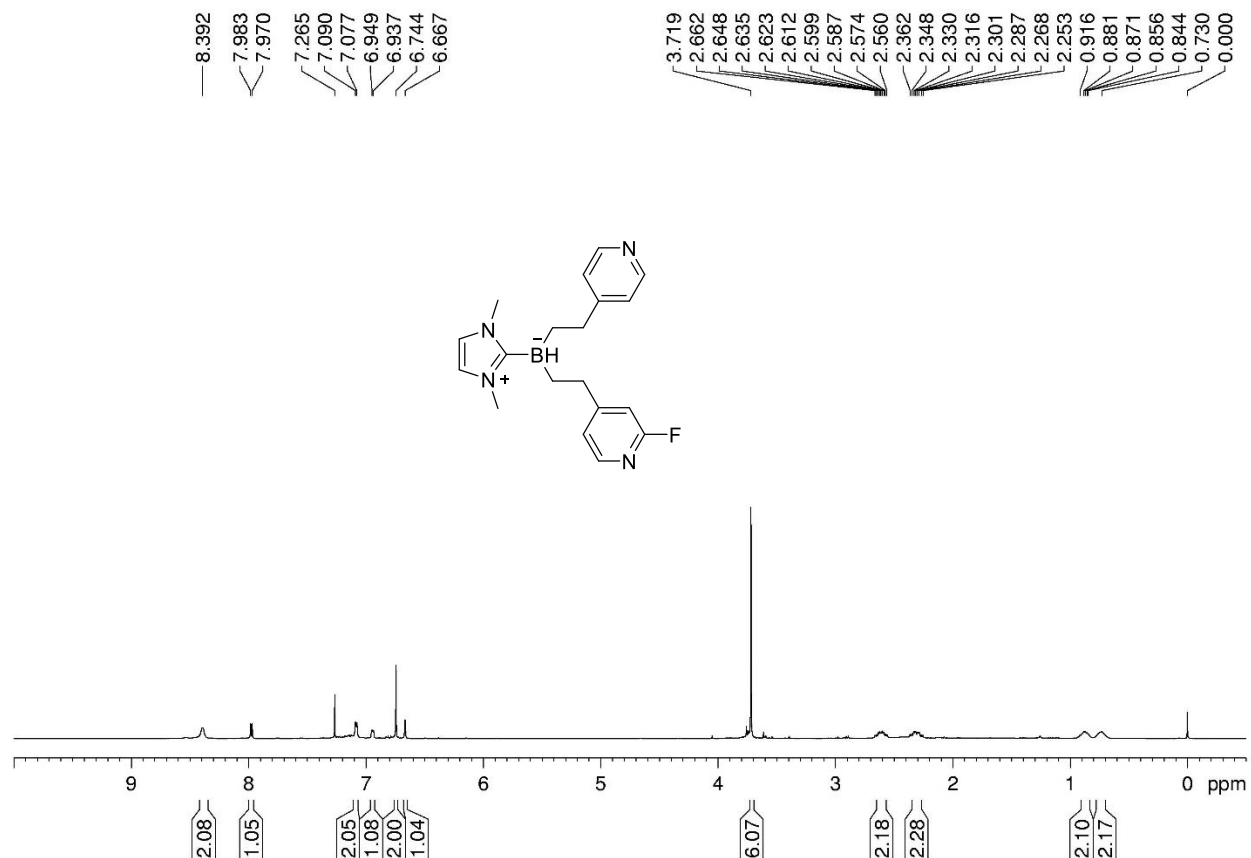
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) spectrum of **52**



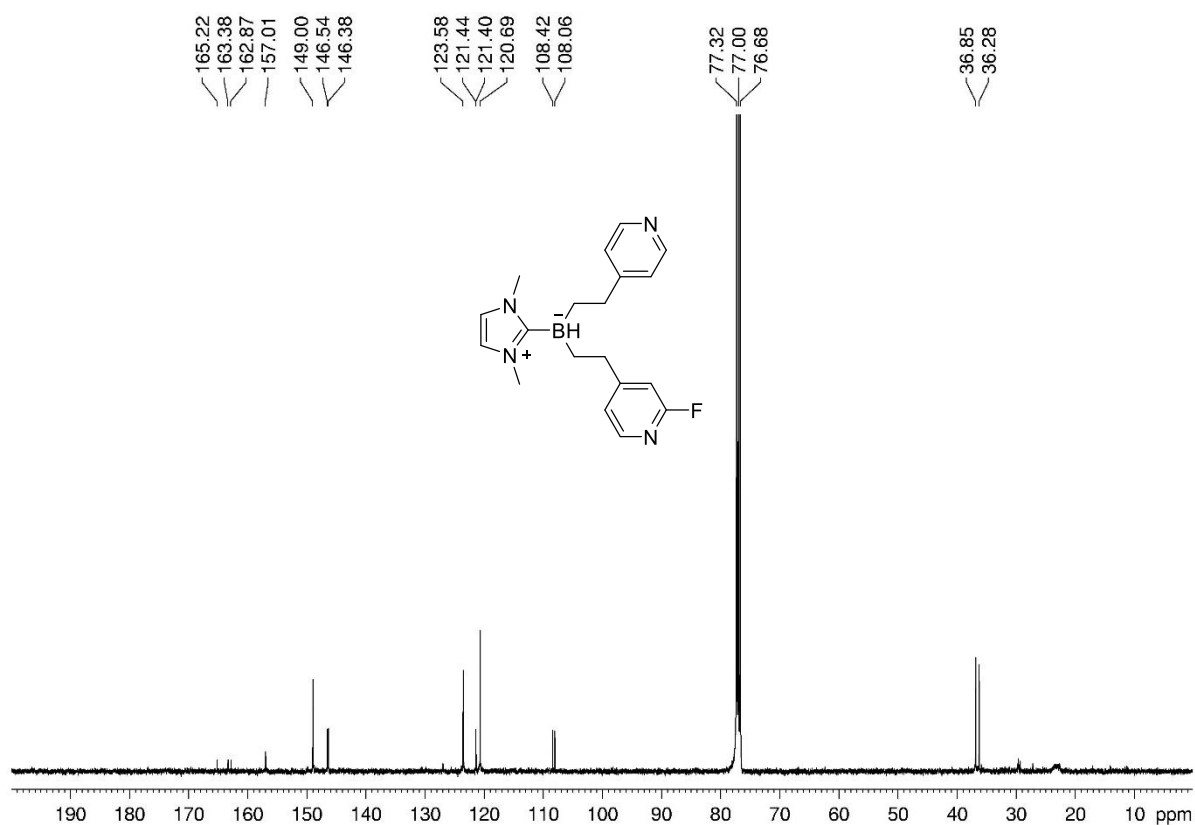
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz) spectrum of **52**



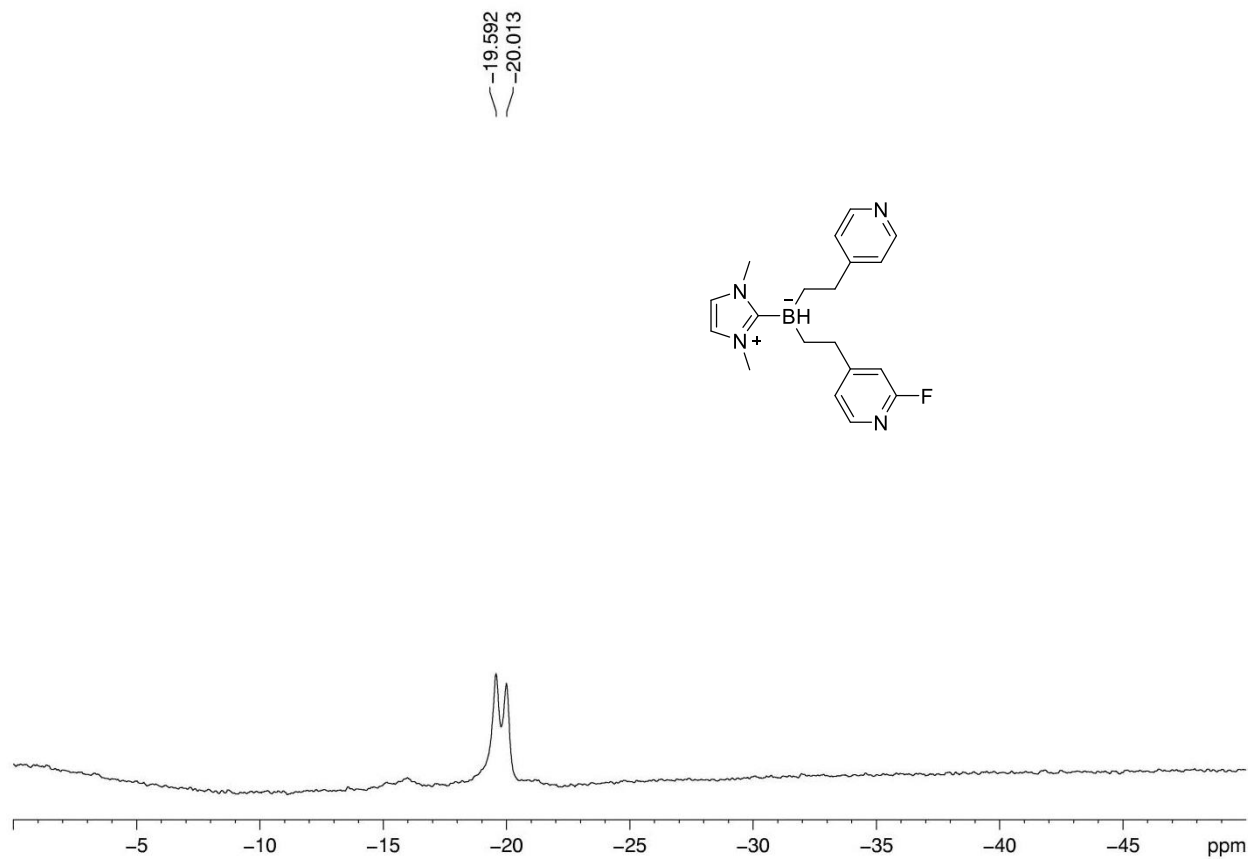
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **53**



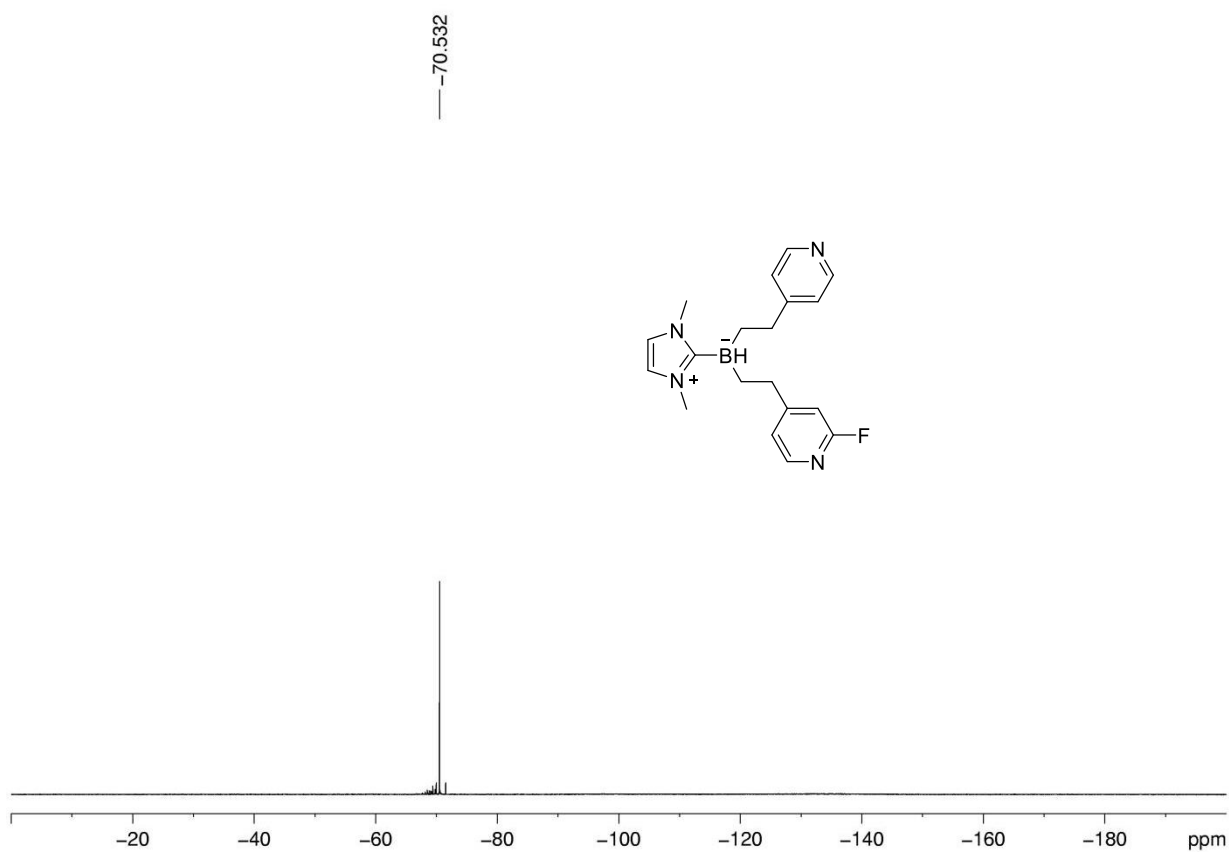
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **53**



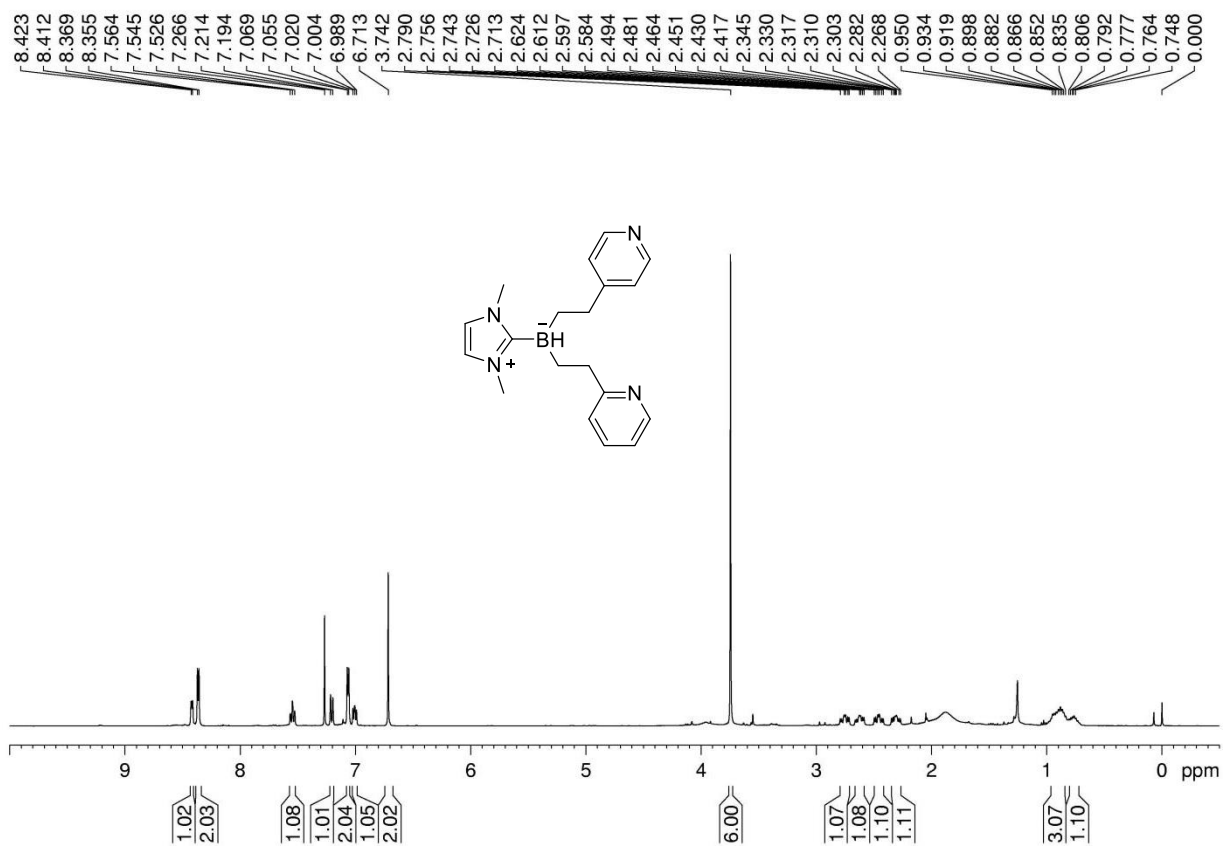
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **53**



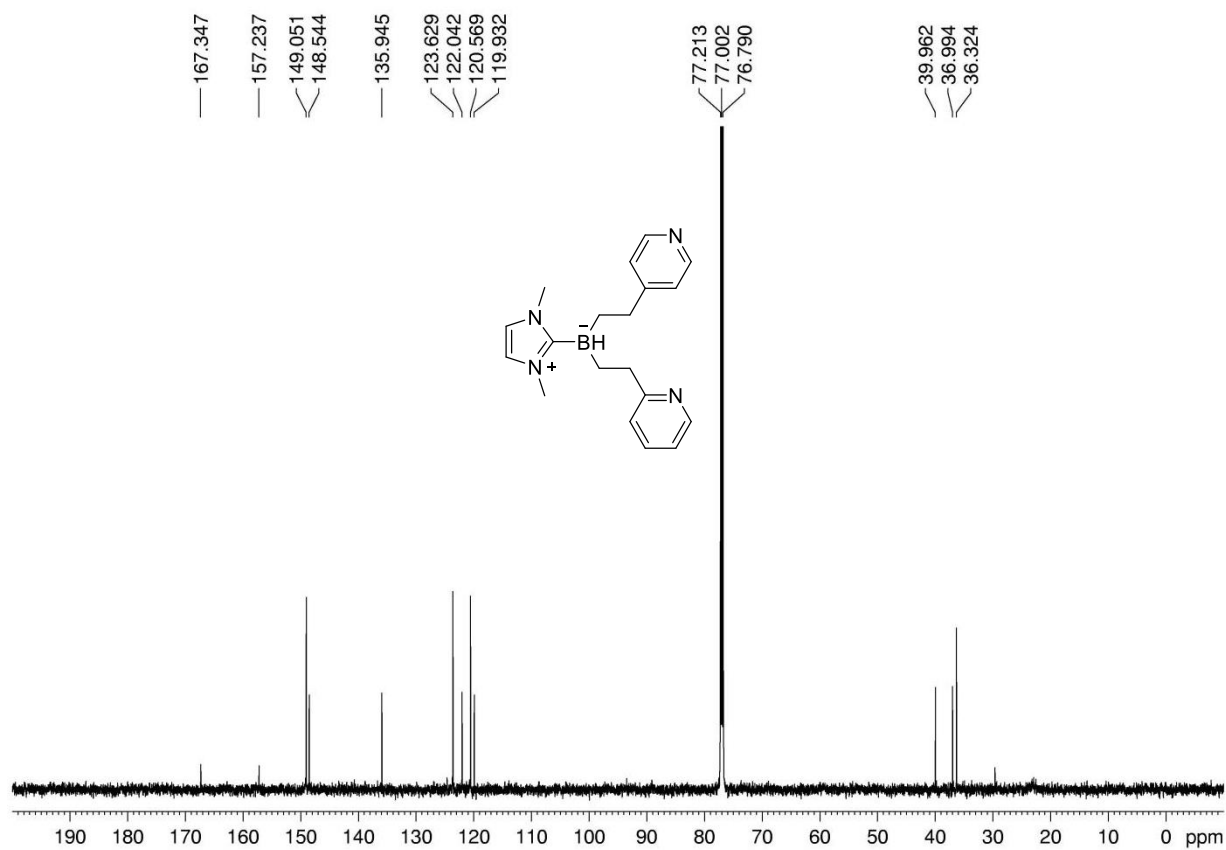
$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 564 MHz) spectrum of **53**



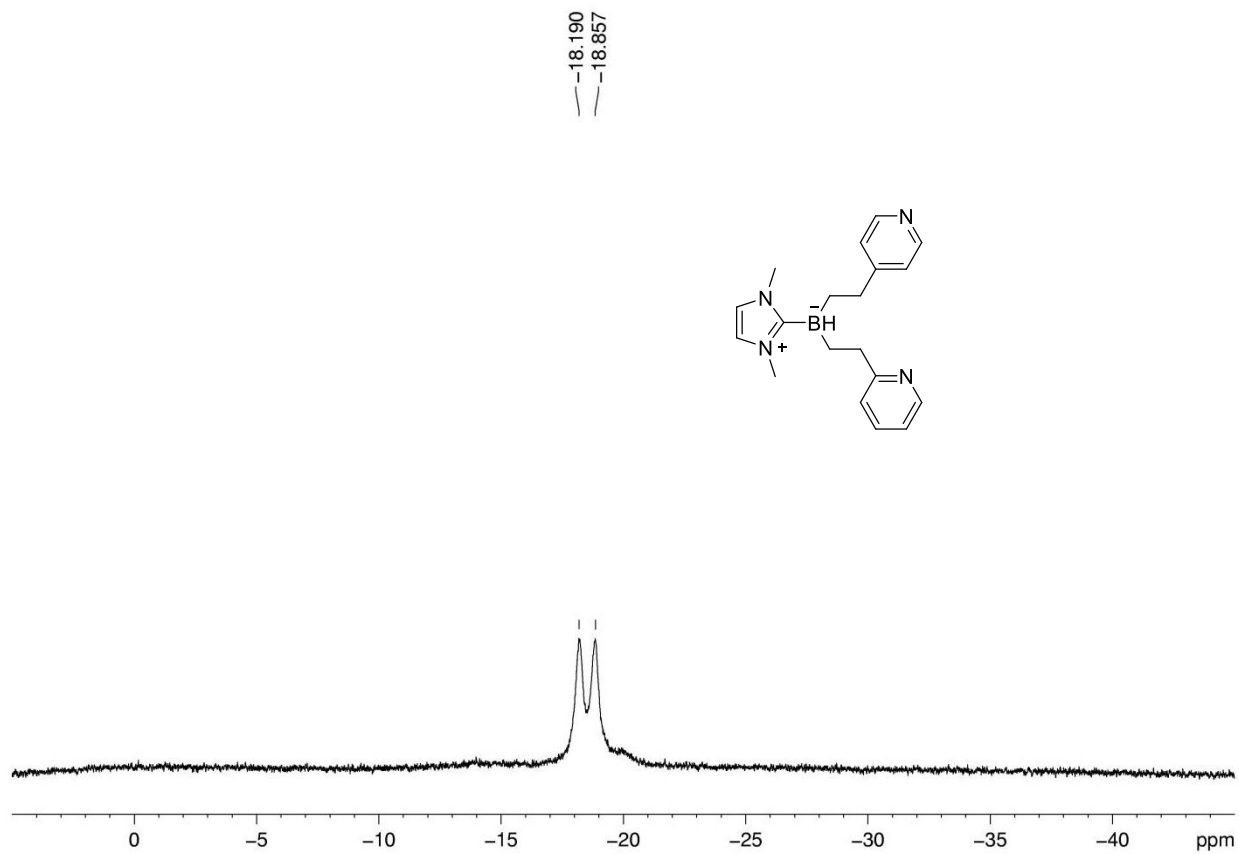
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **54**



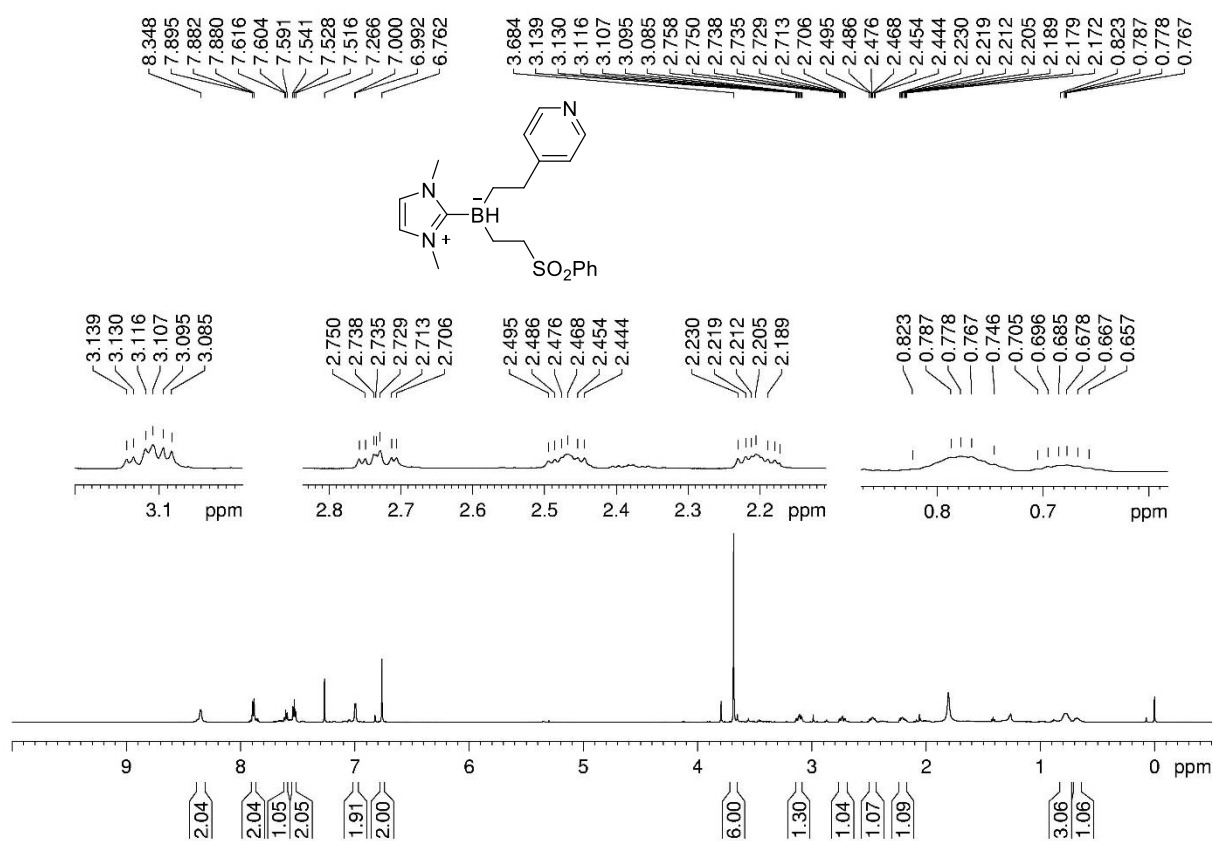
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **54**



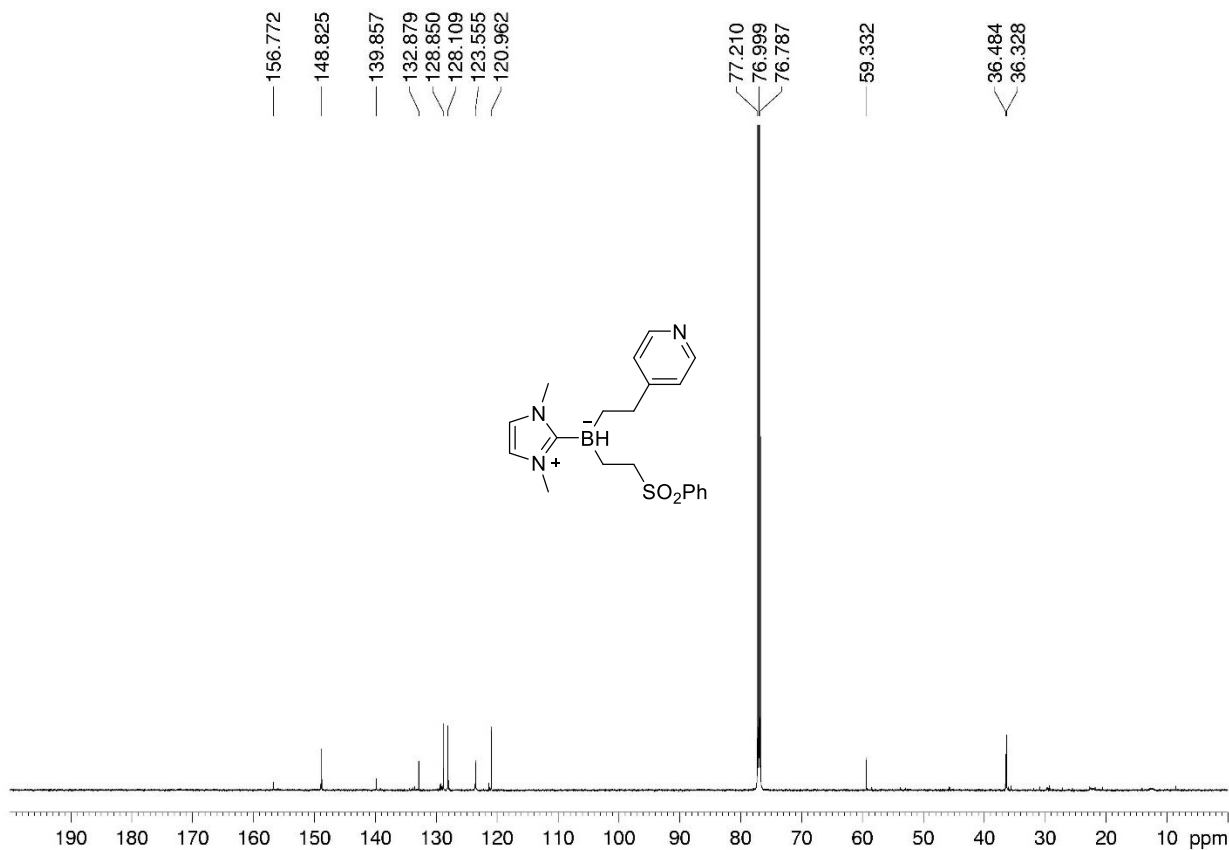
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz) spectrum of **54**



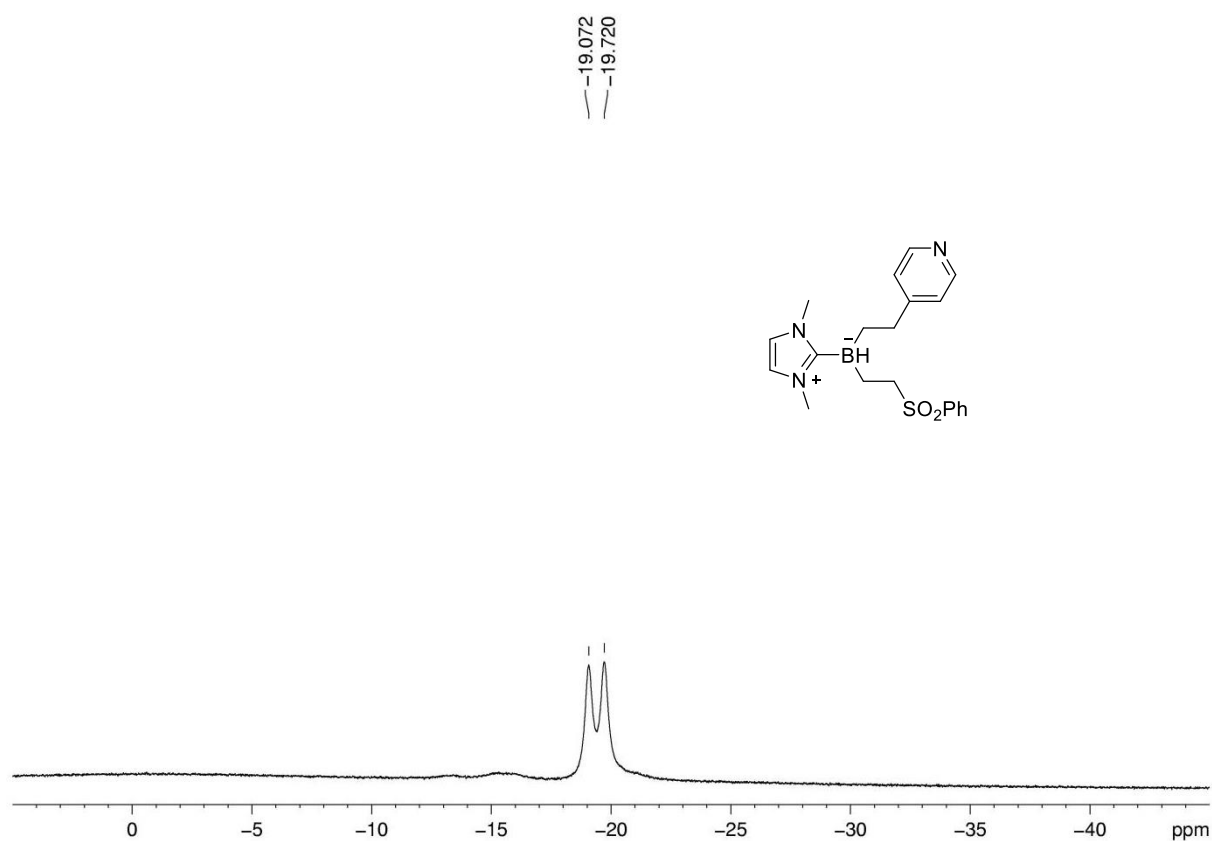
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) spectrum of **55**



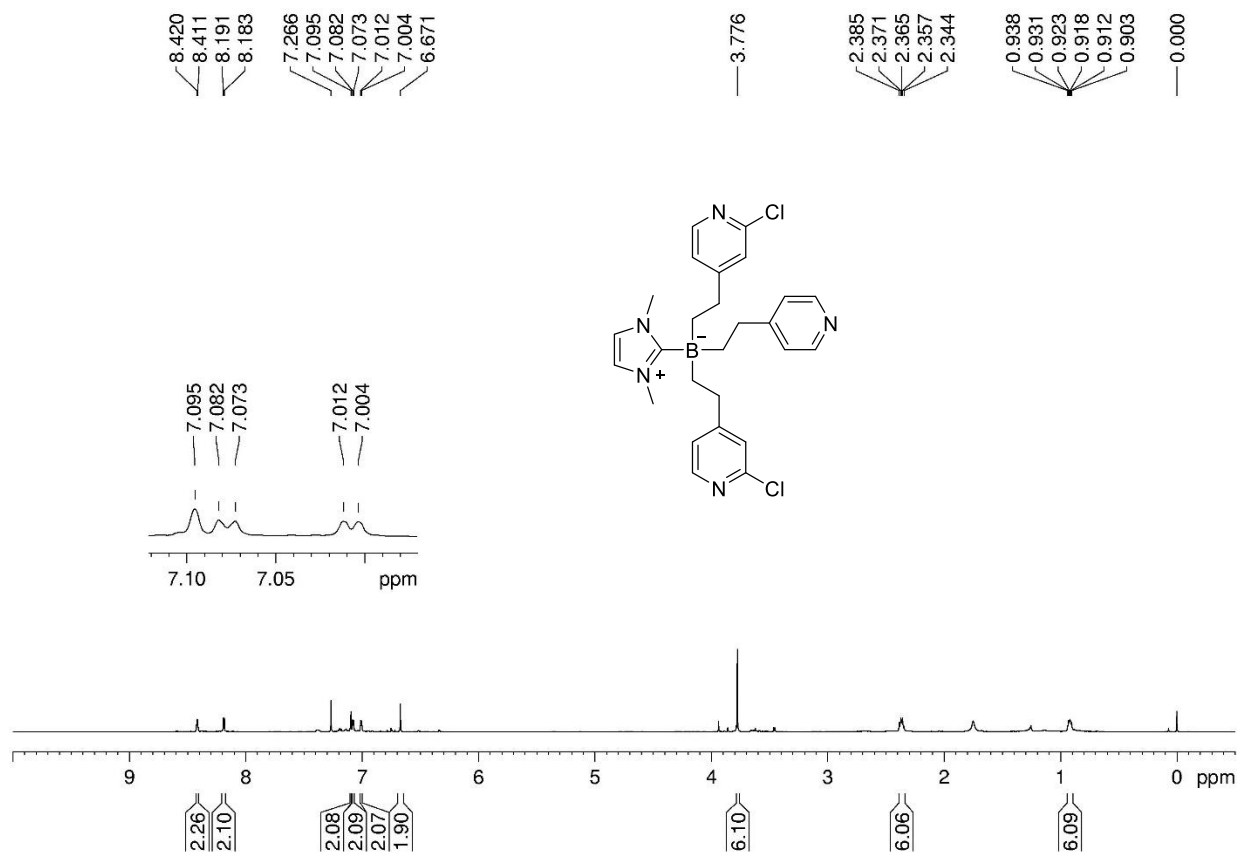
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) spectrum of **55**



$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz) spectrum of **55**

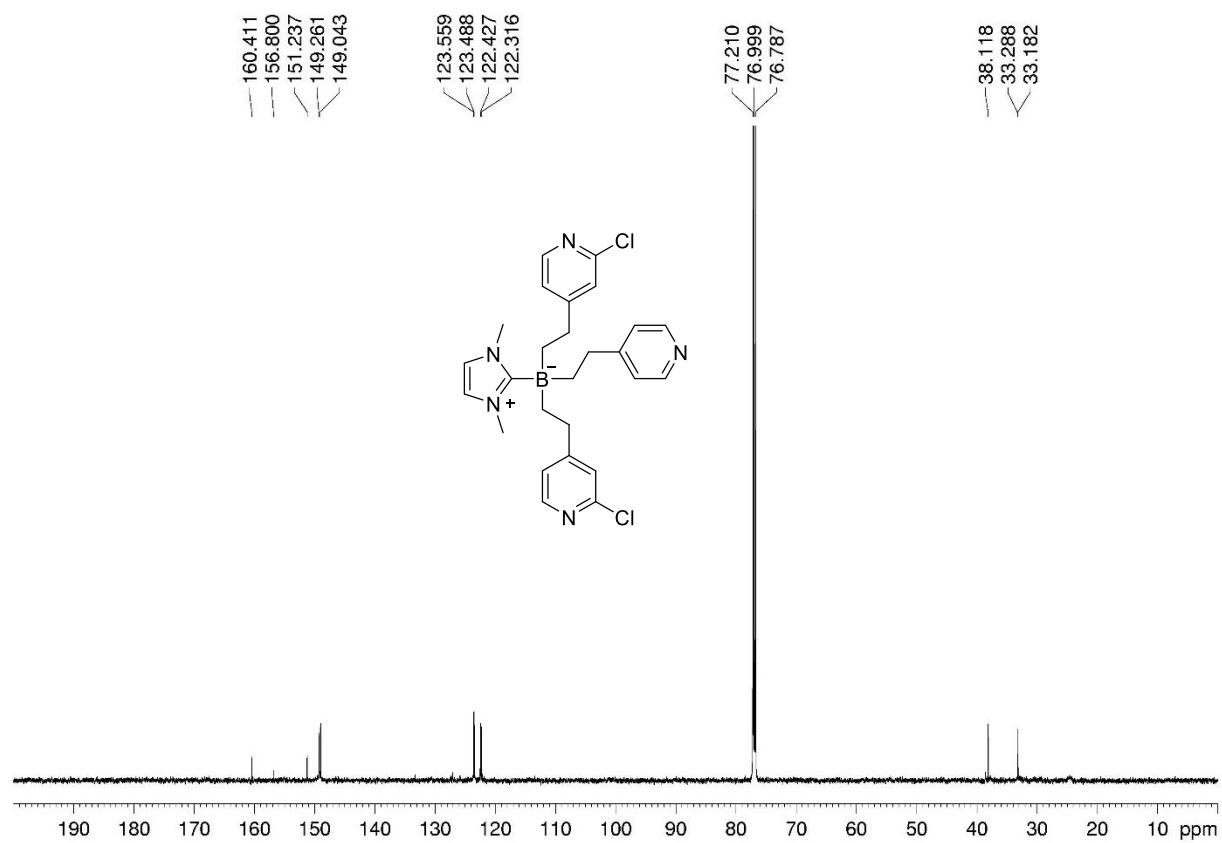


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **56**

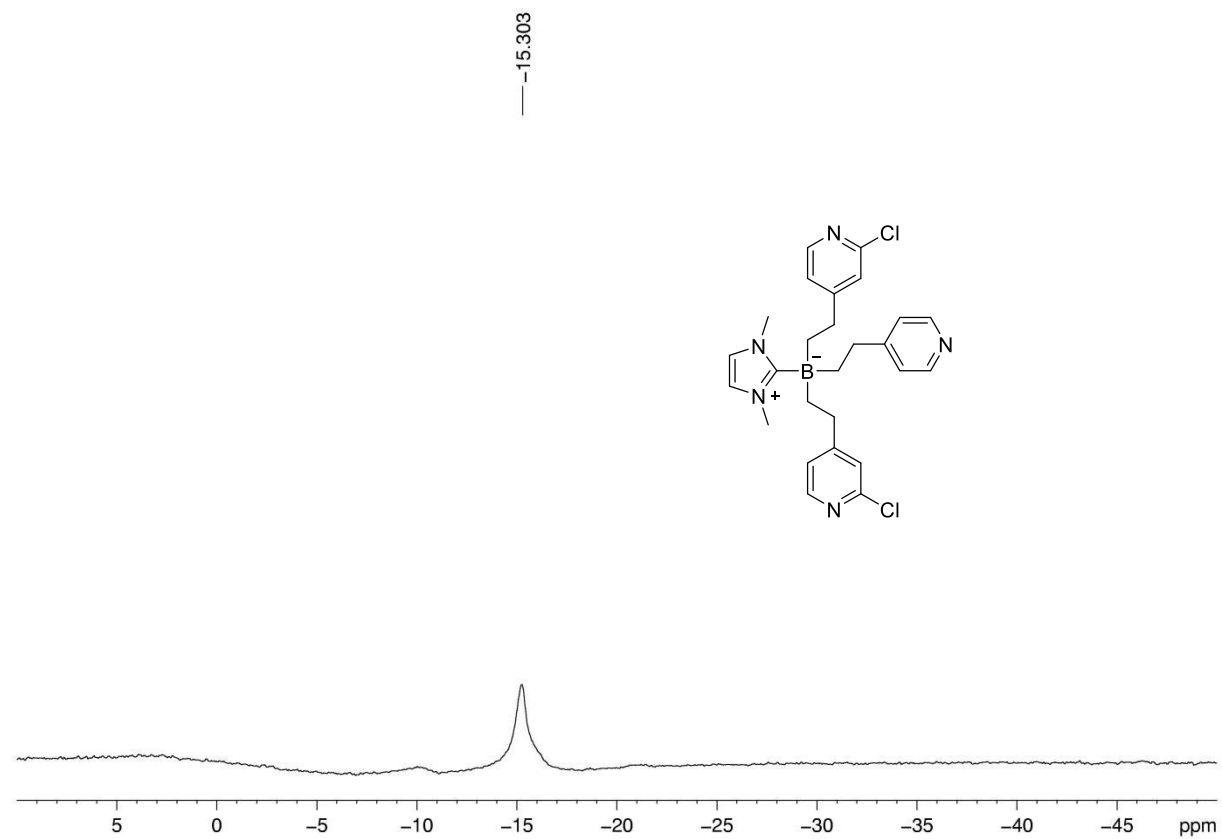




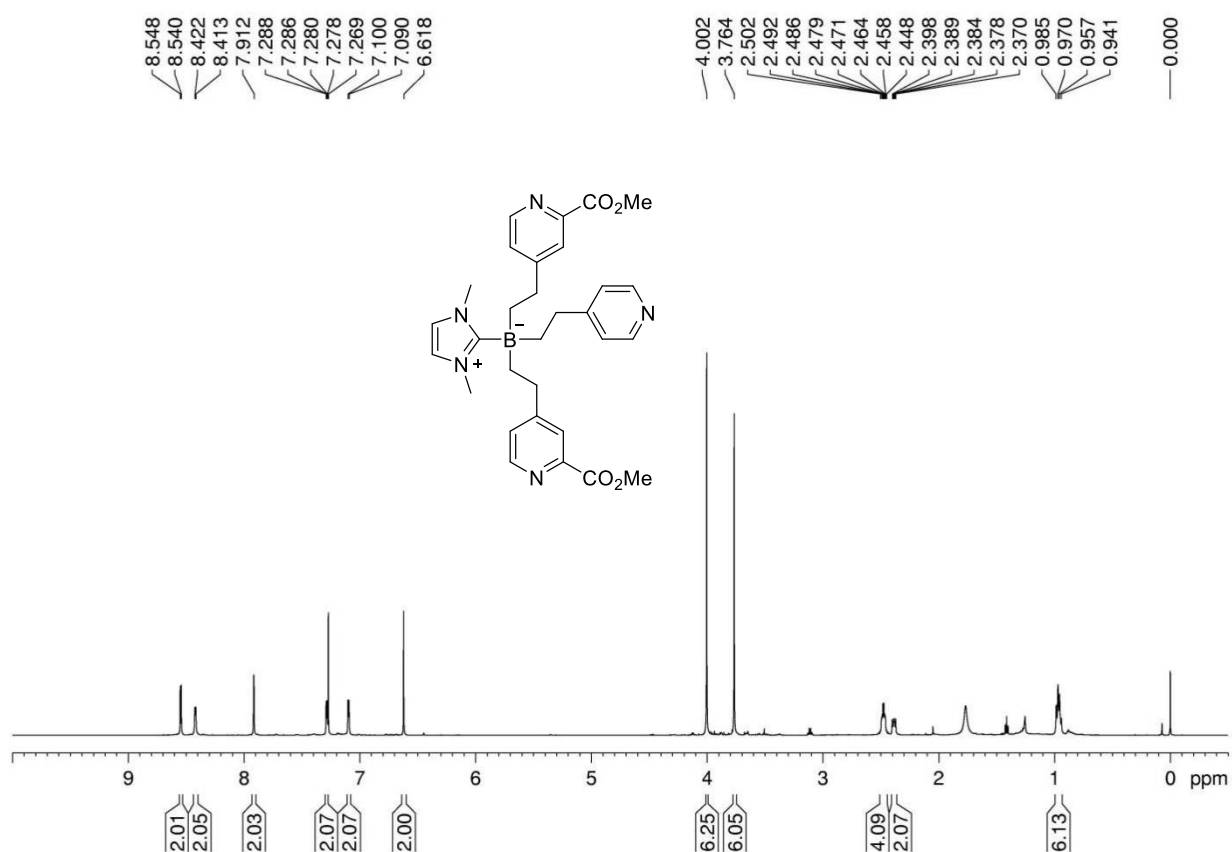
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **56**



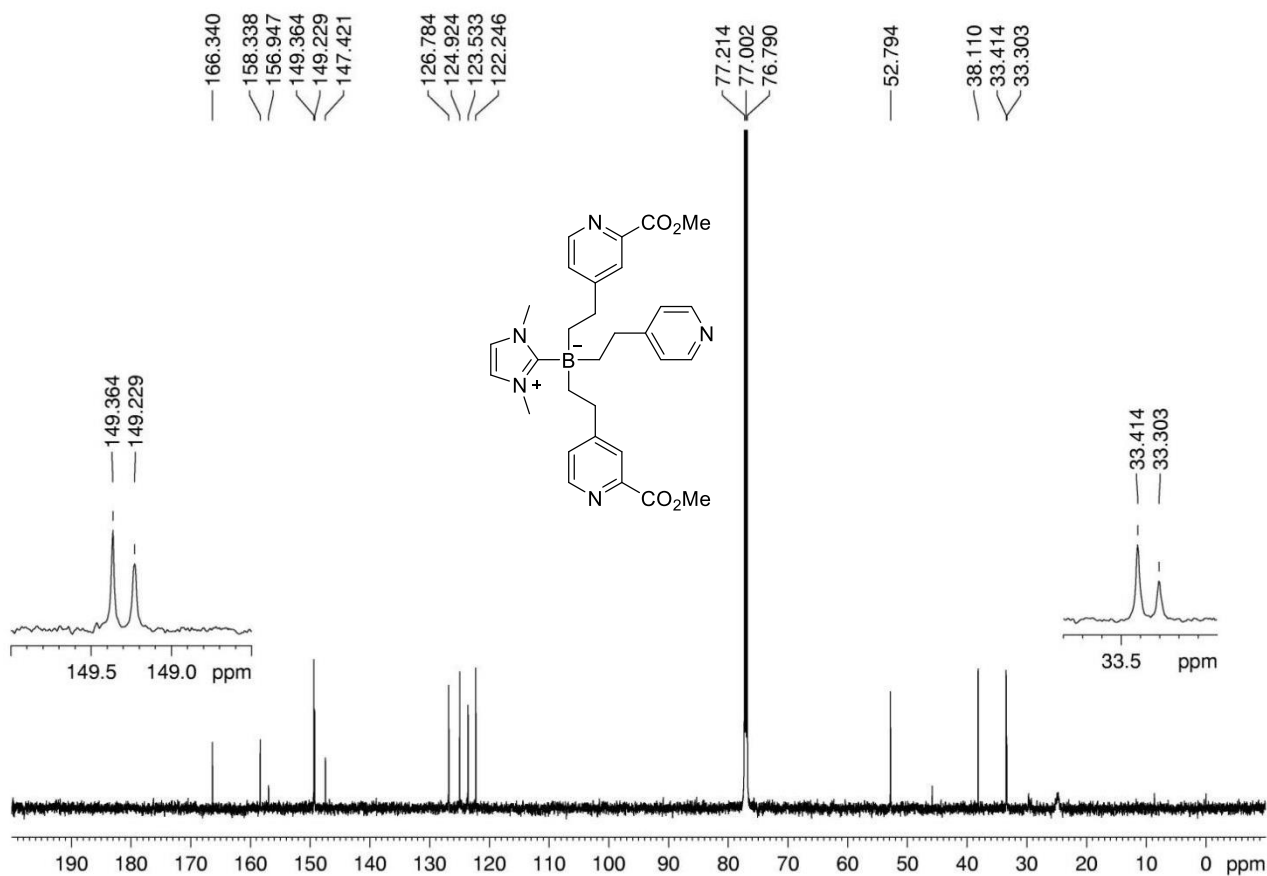
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **56**



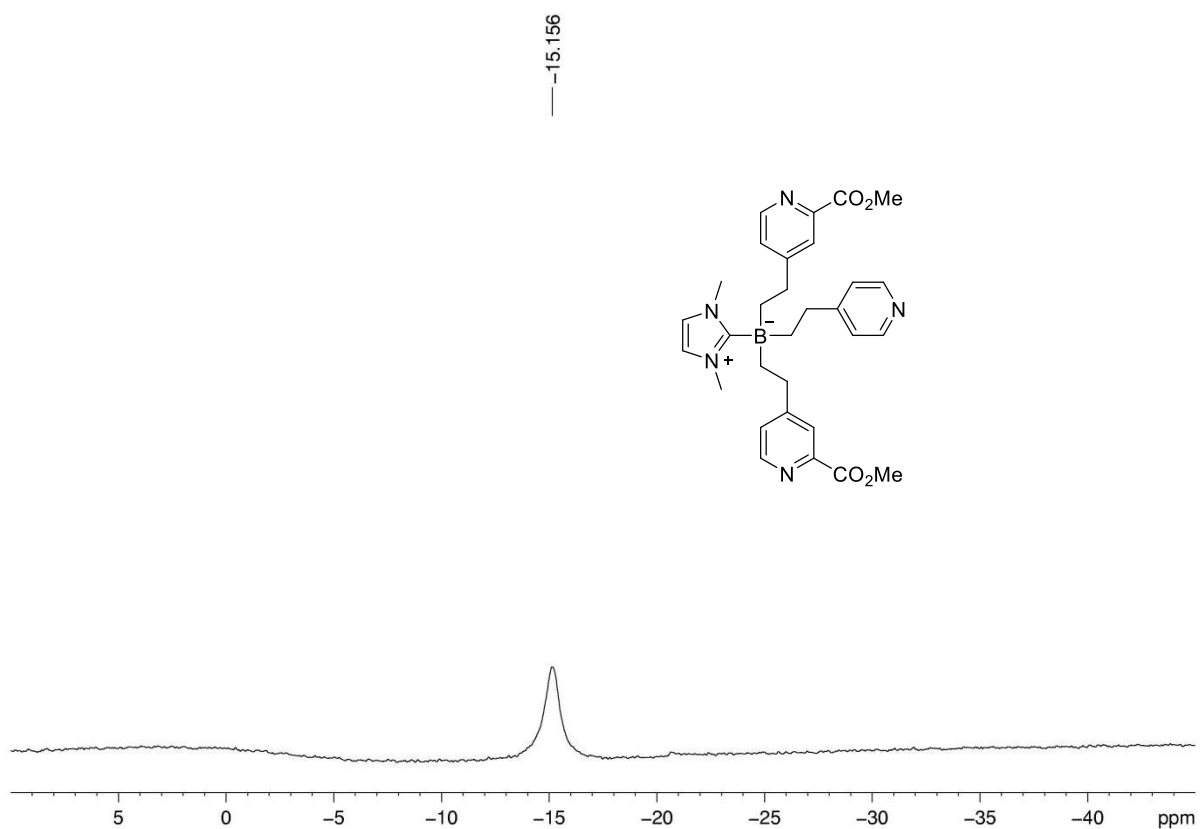
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **57**



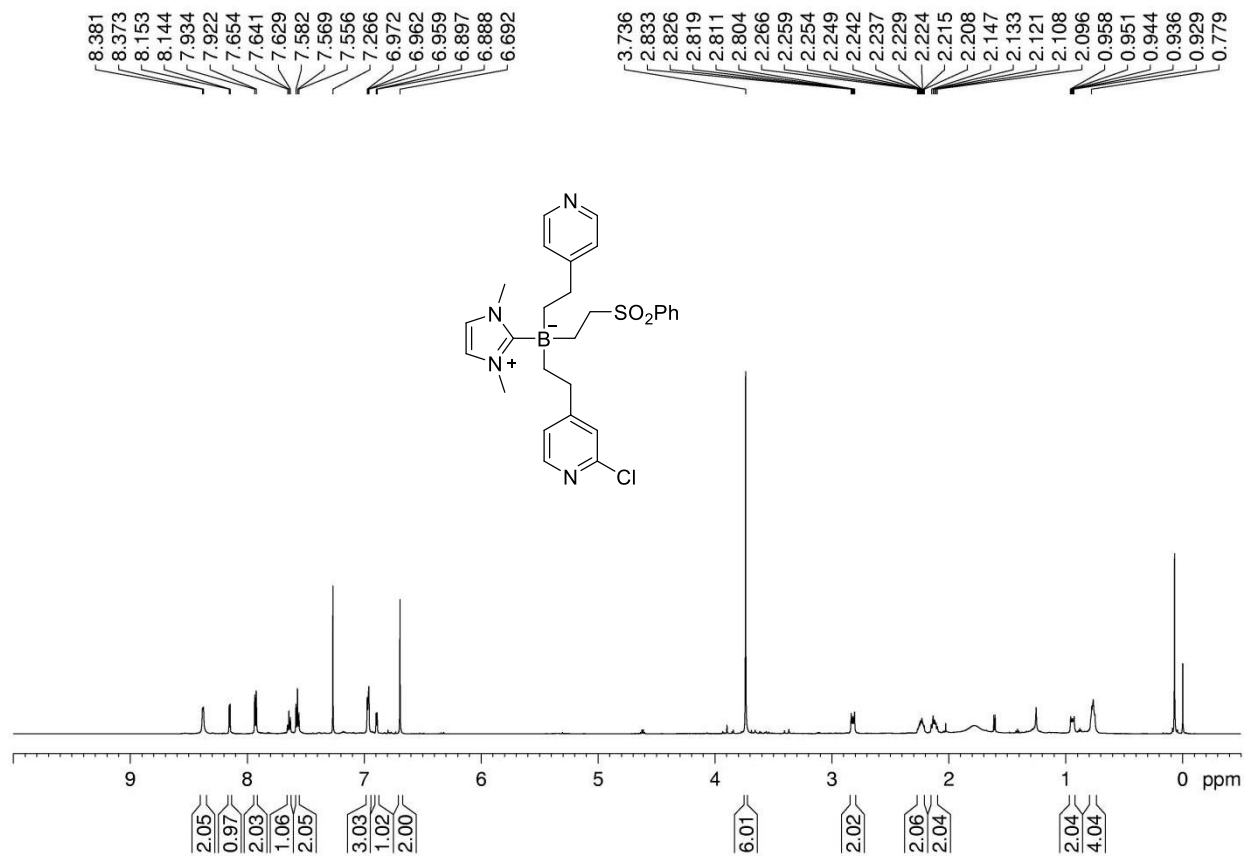
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **57**



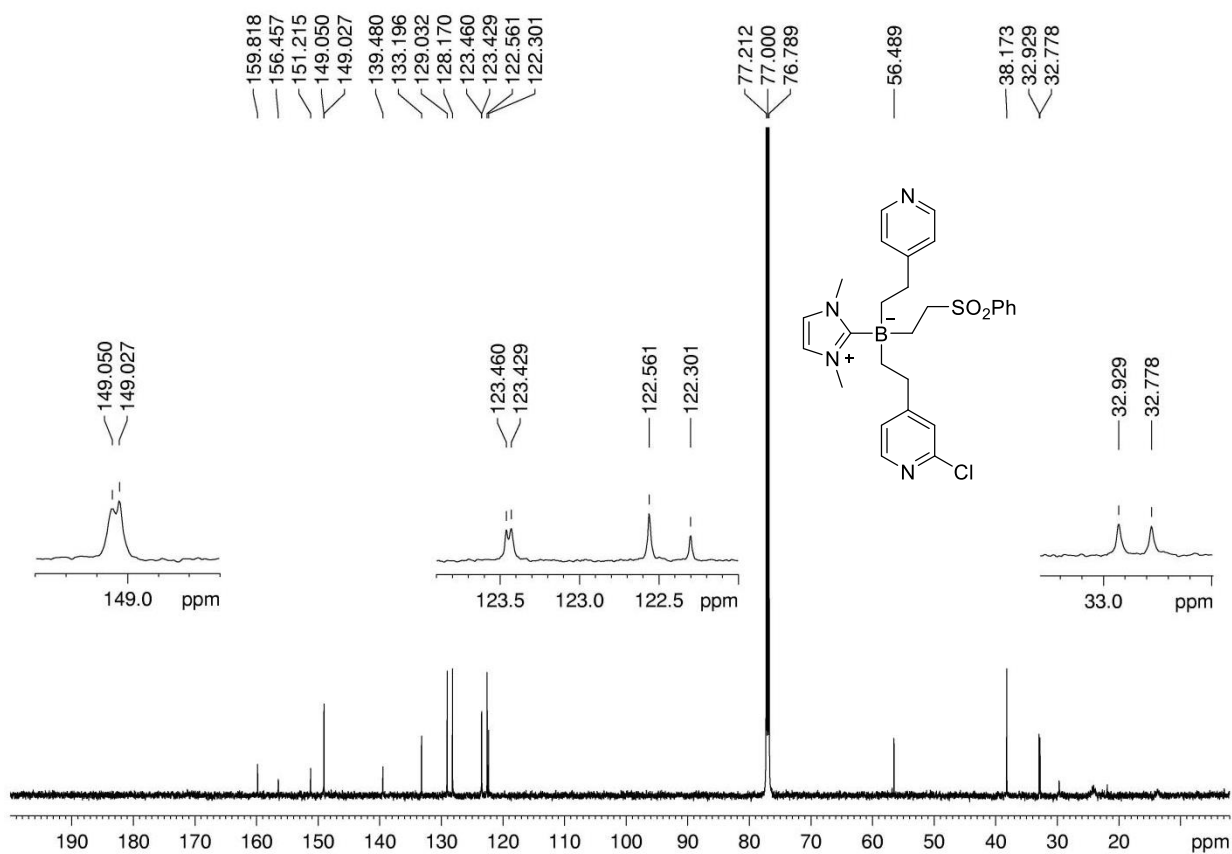
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **57**



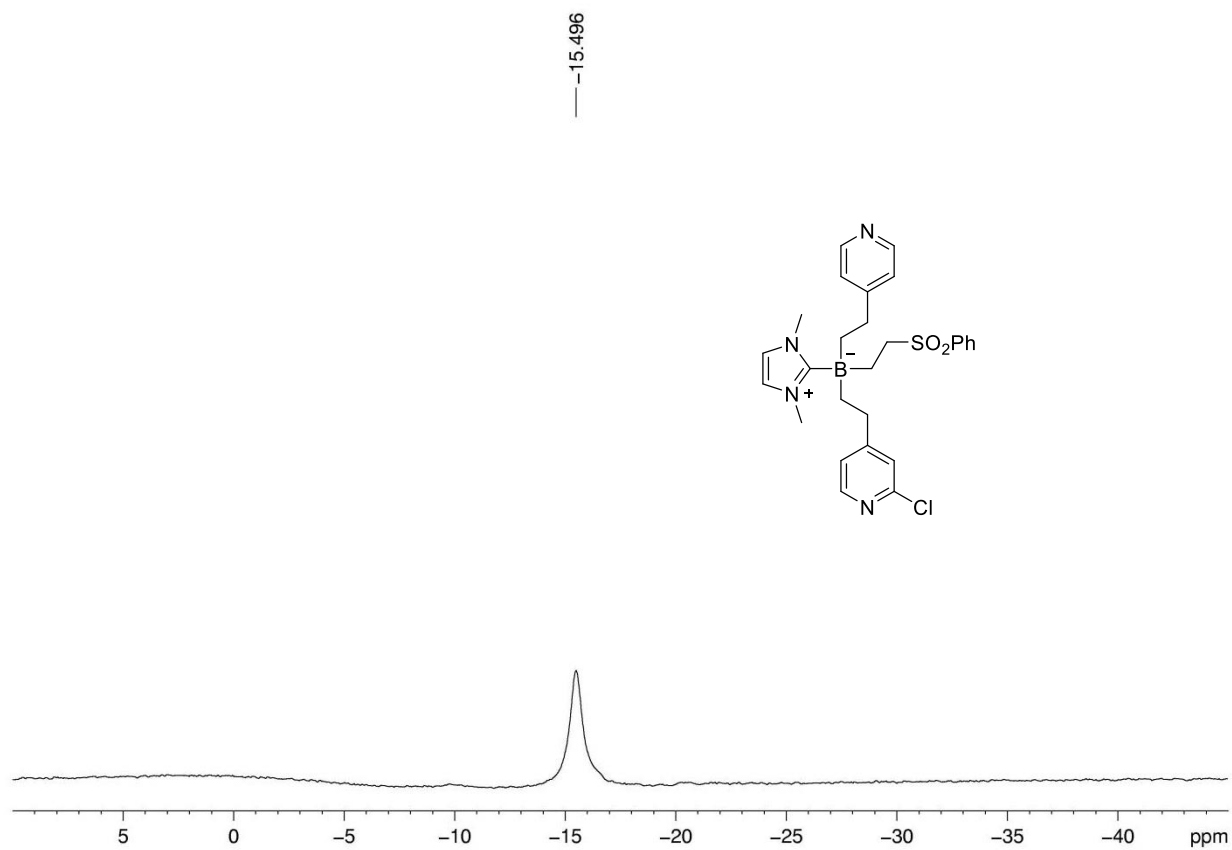
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **58**



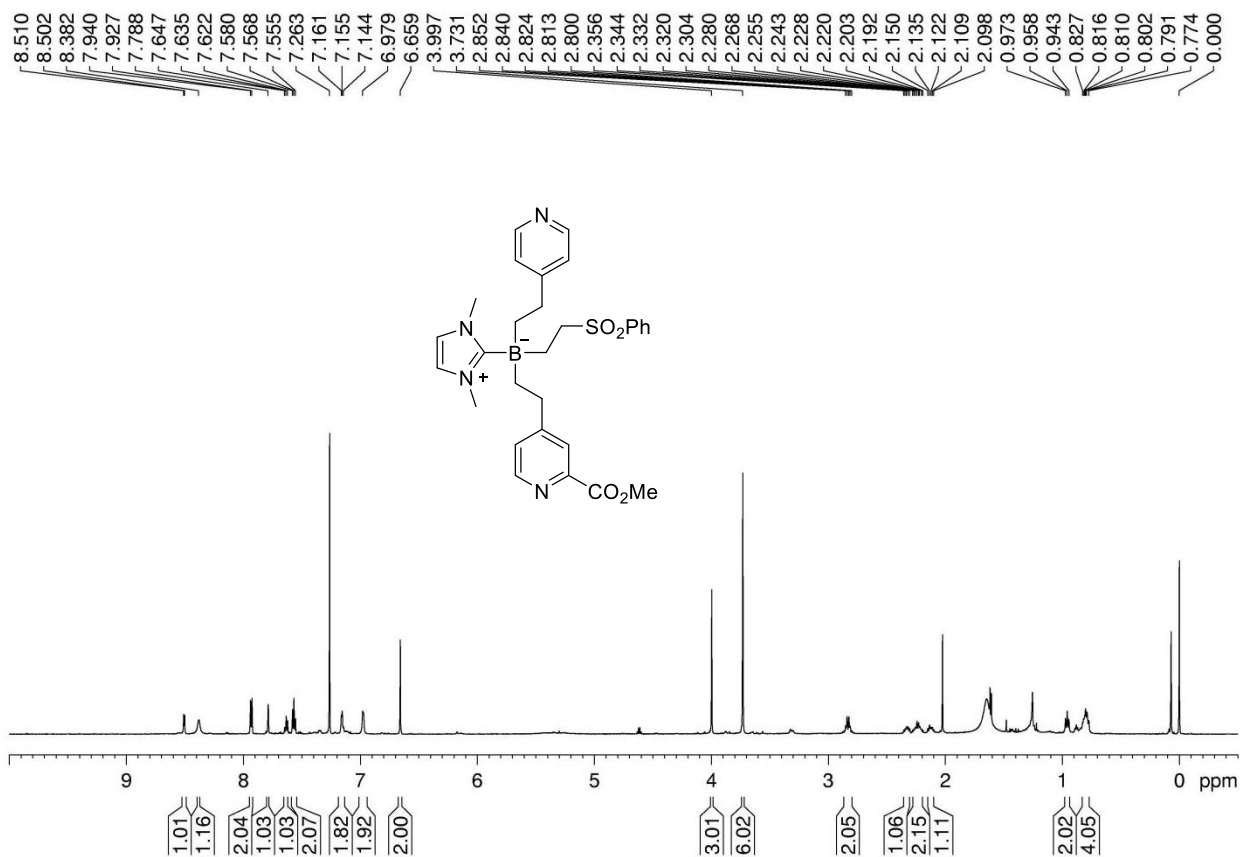
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **58**



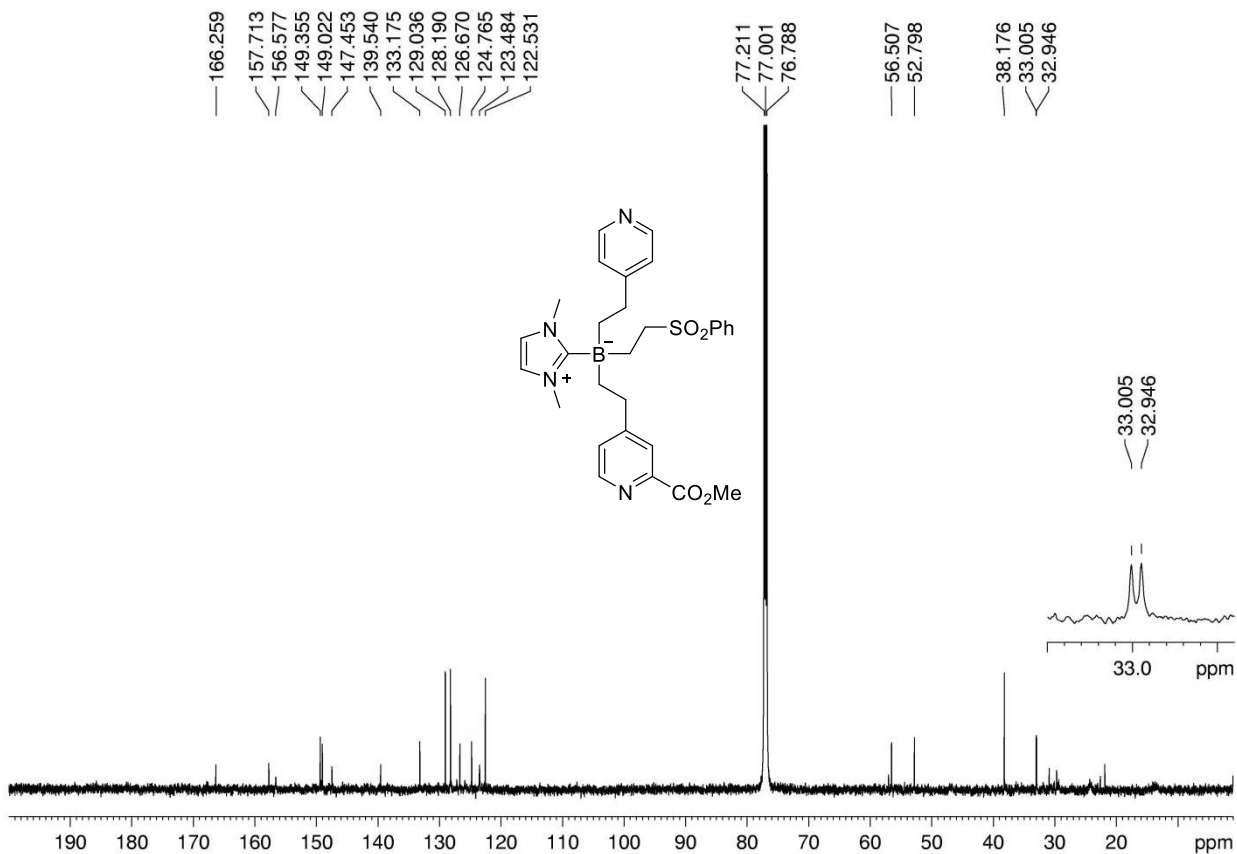
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **58**



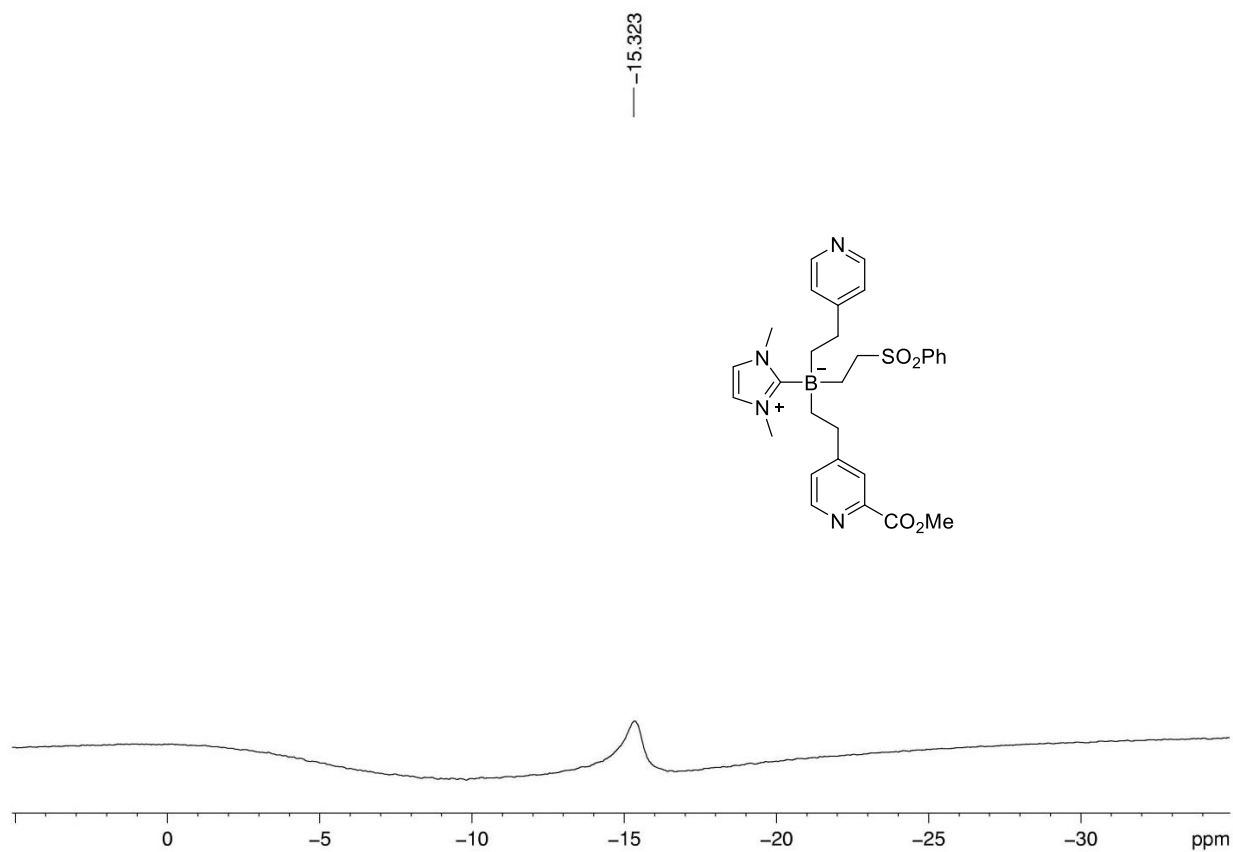
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) spectrum of **59**



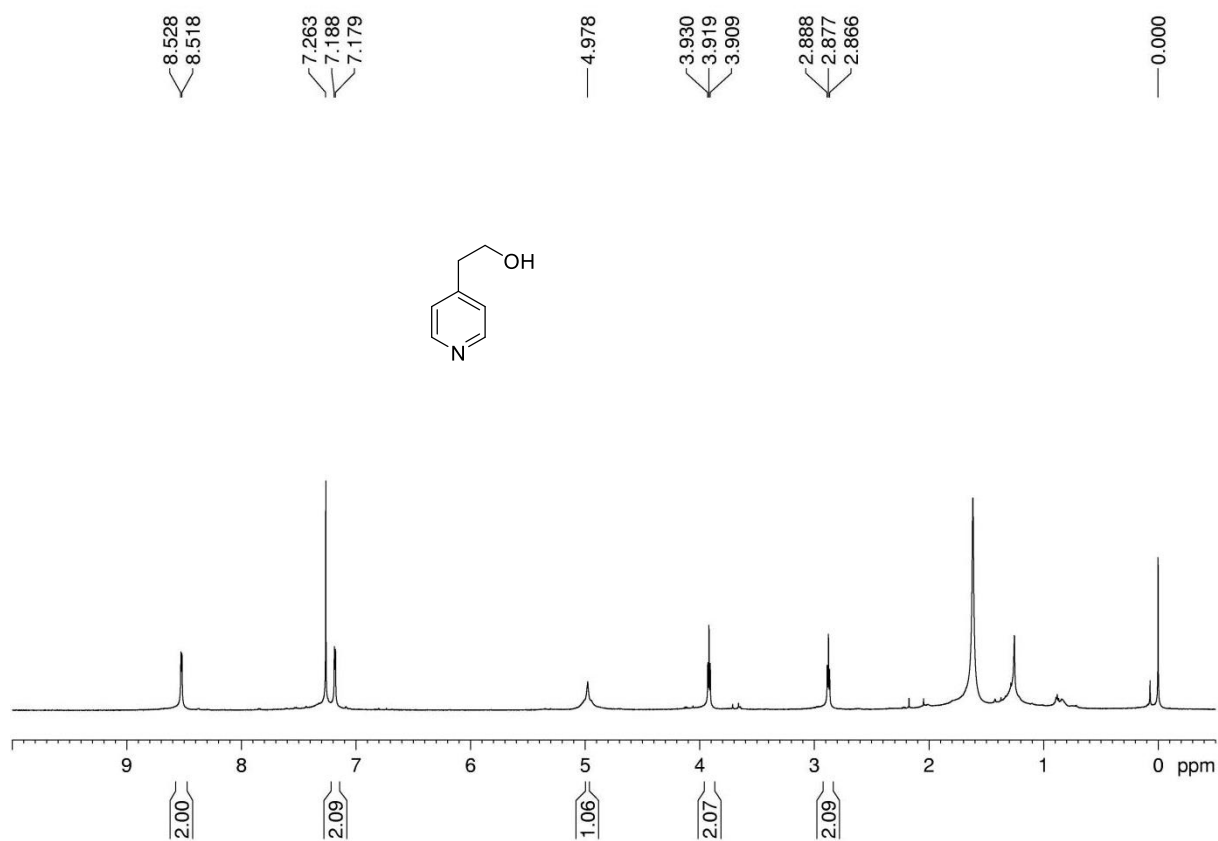
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) spectrum of **59**



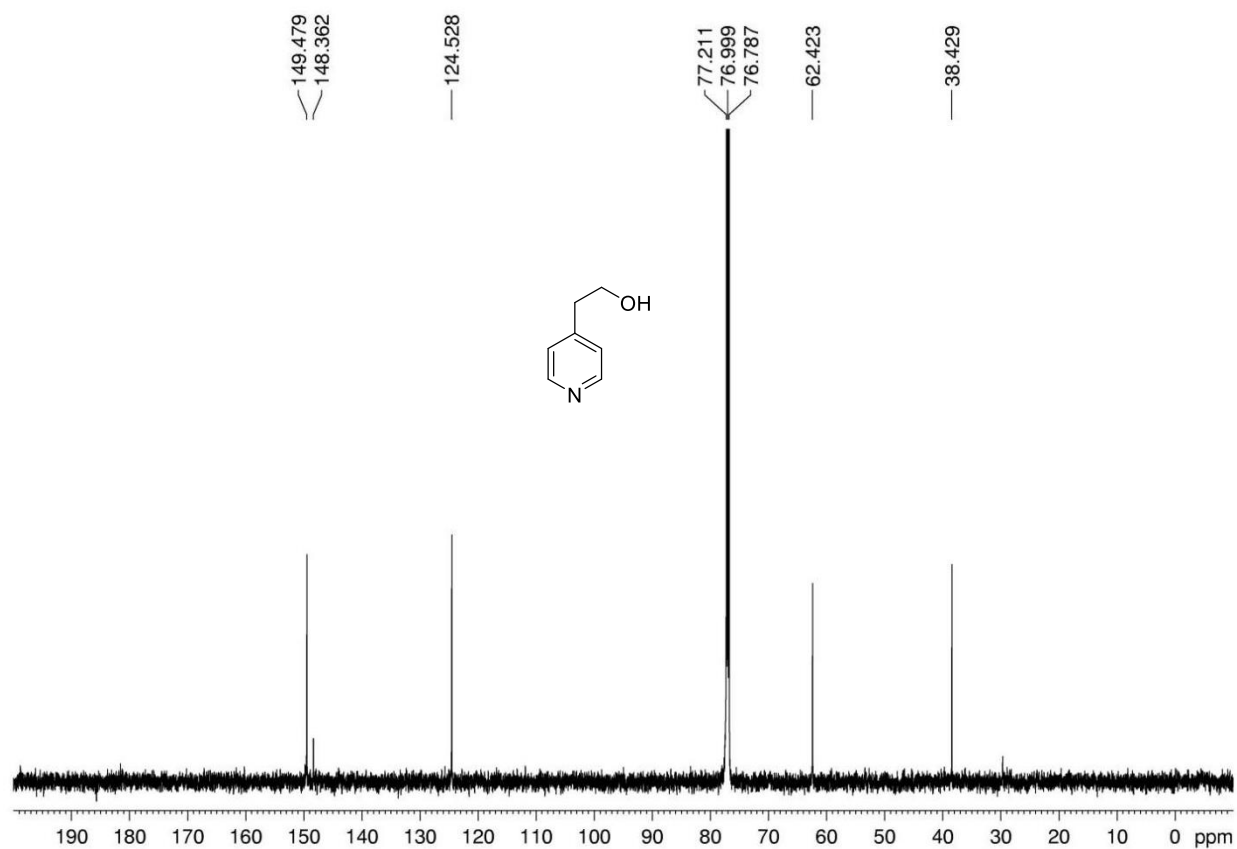
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **59**



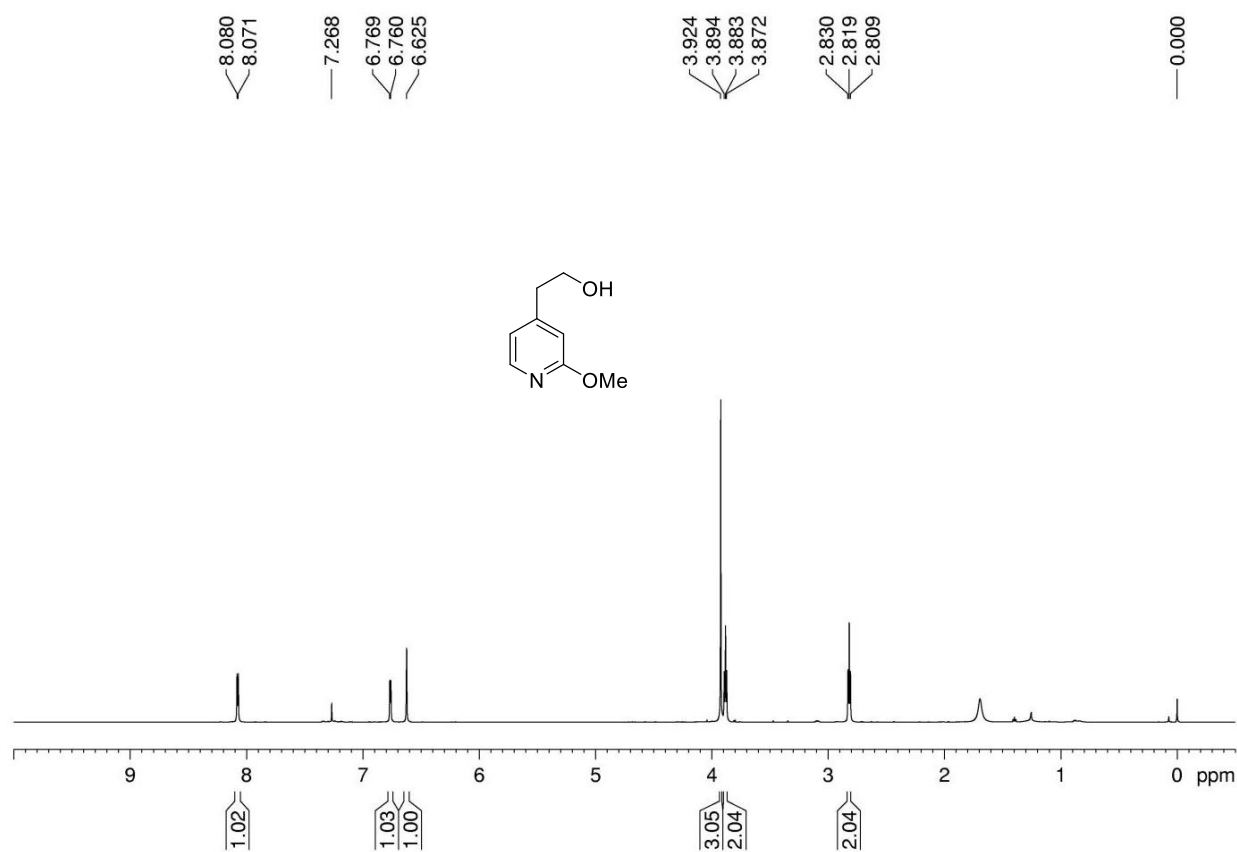
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **60**



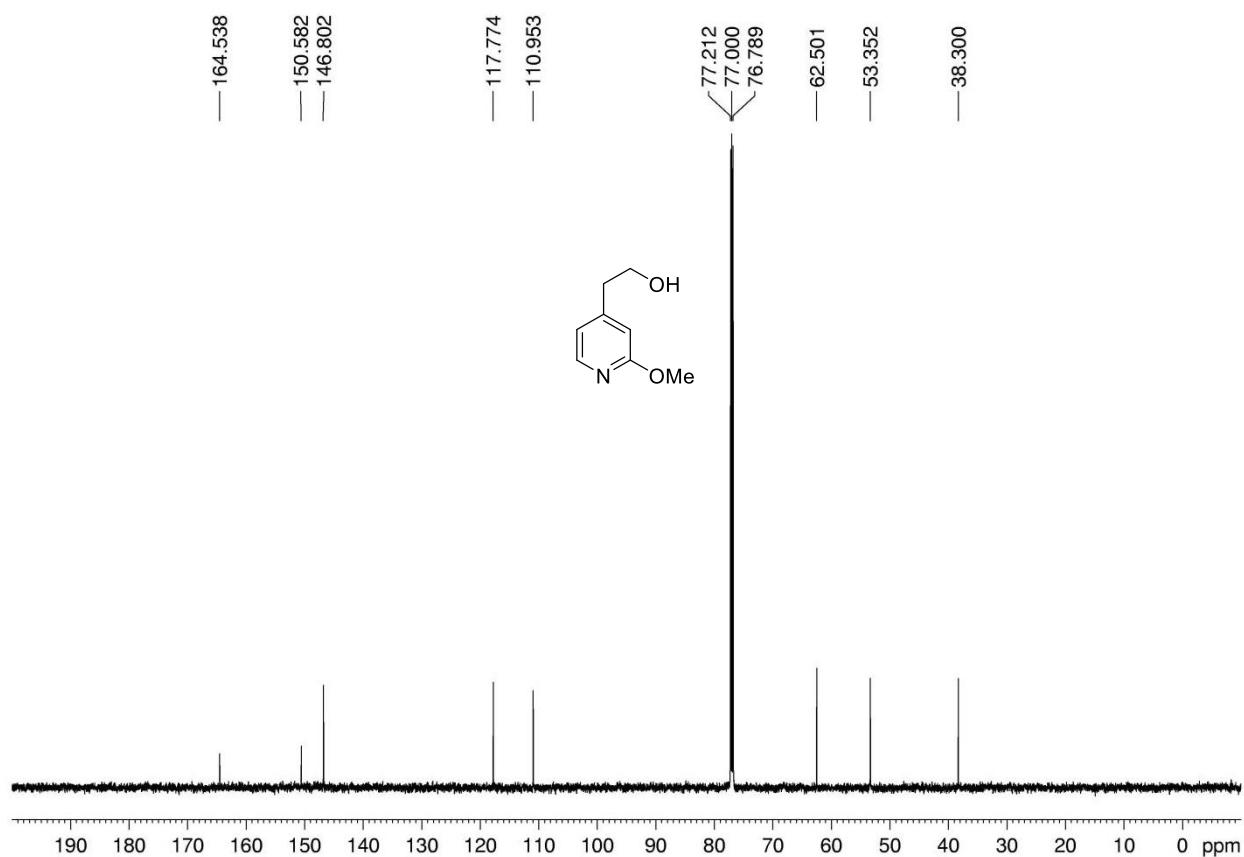
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **60**



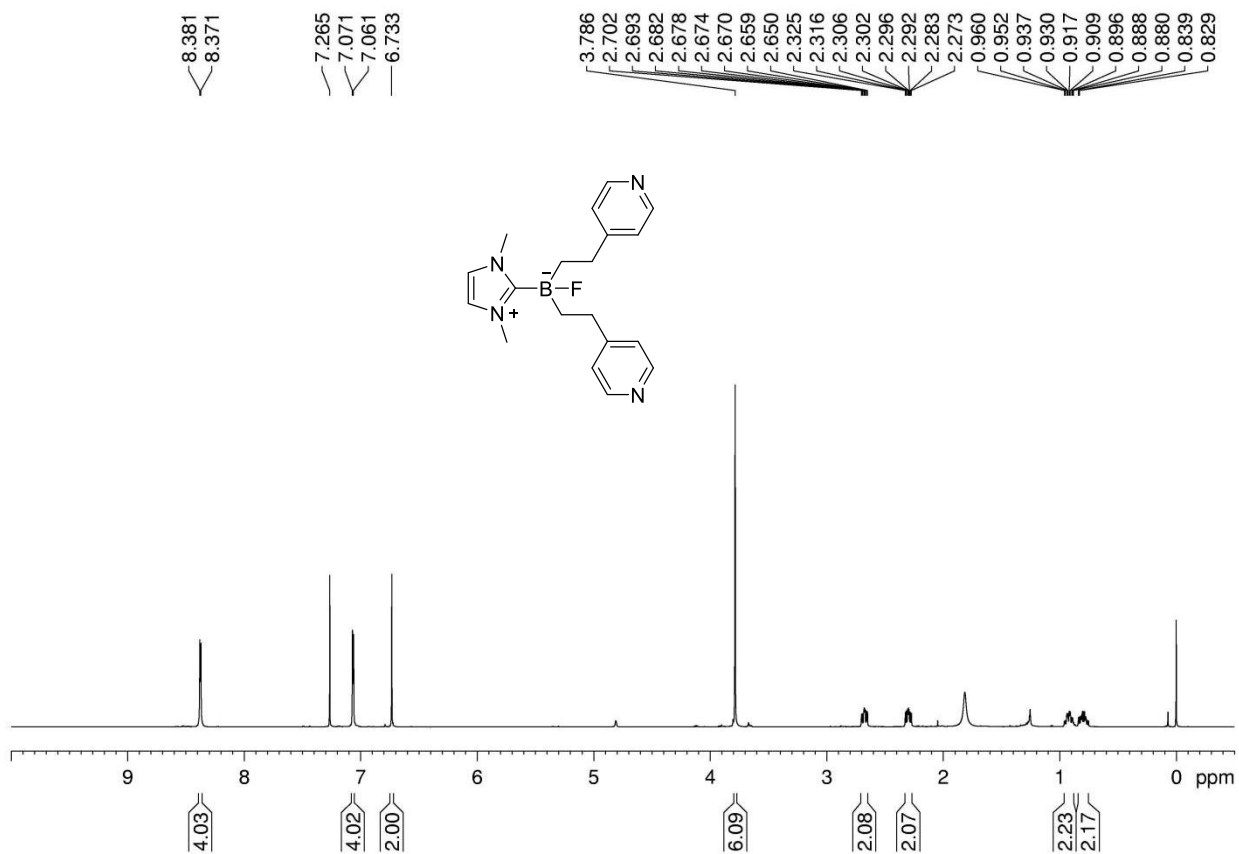
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **61**



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **61**

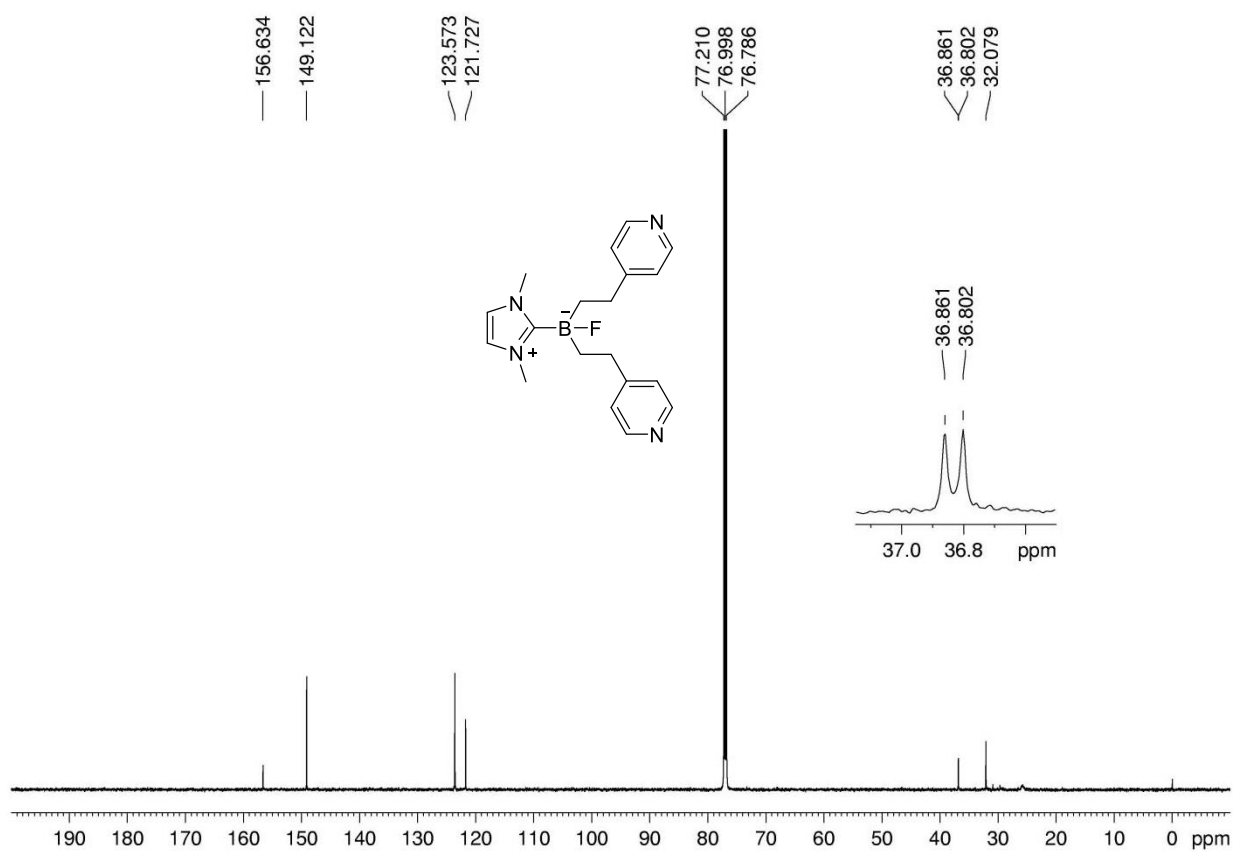


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **62**

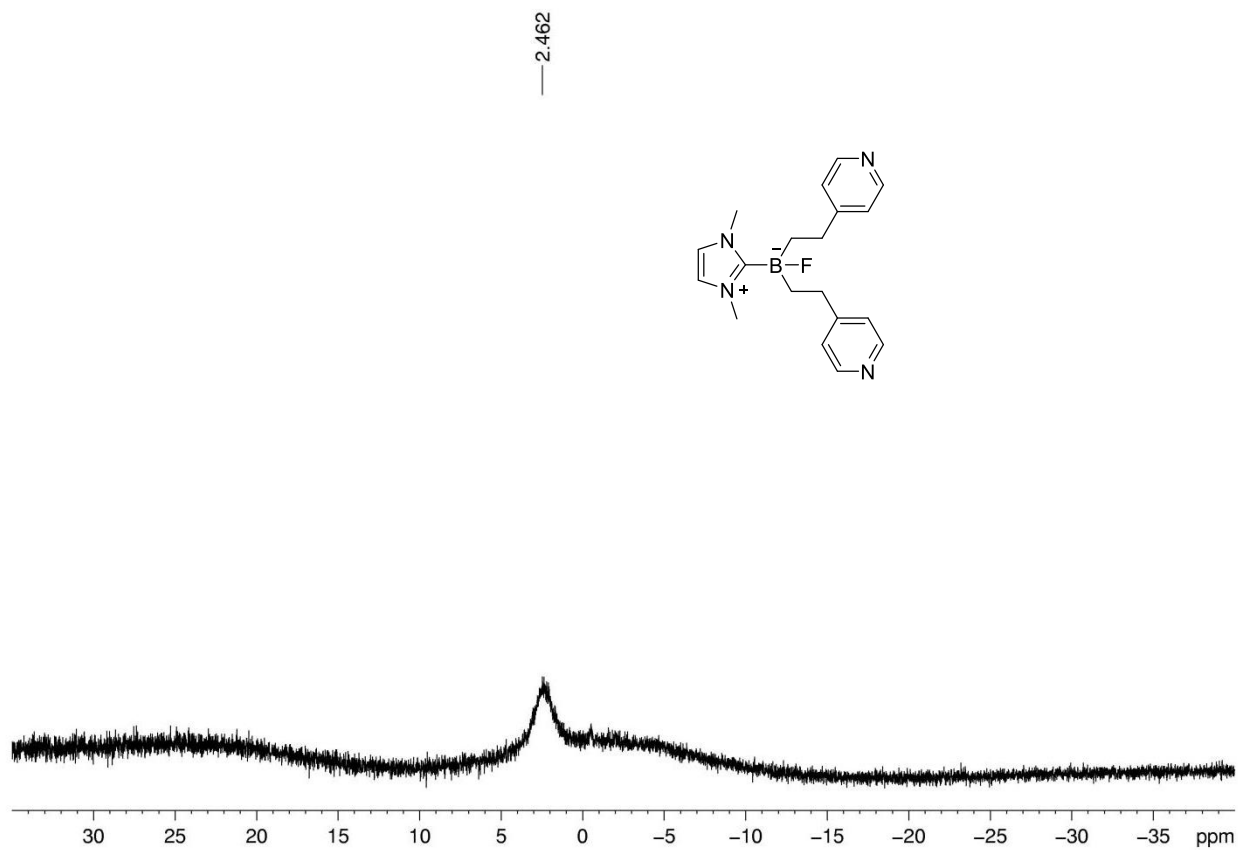




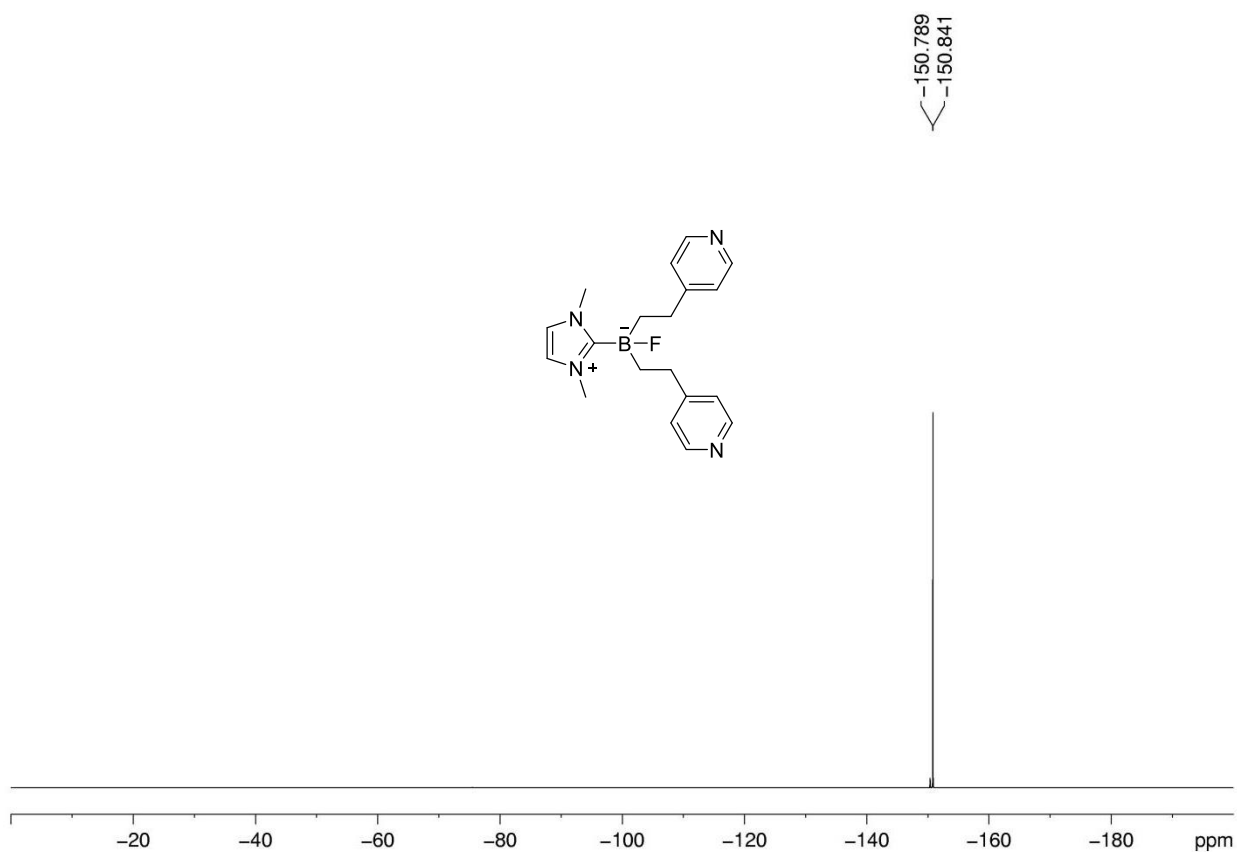
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **62**



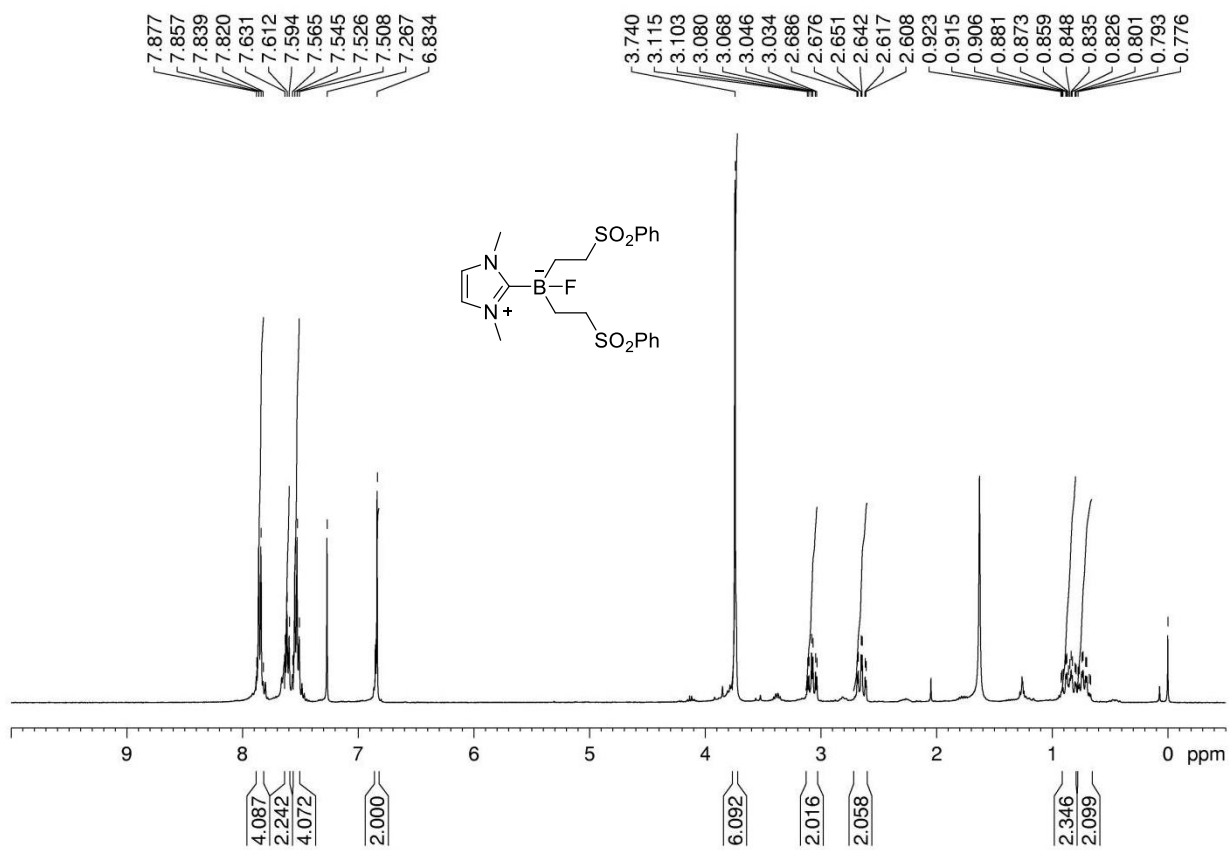
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **62**



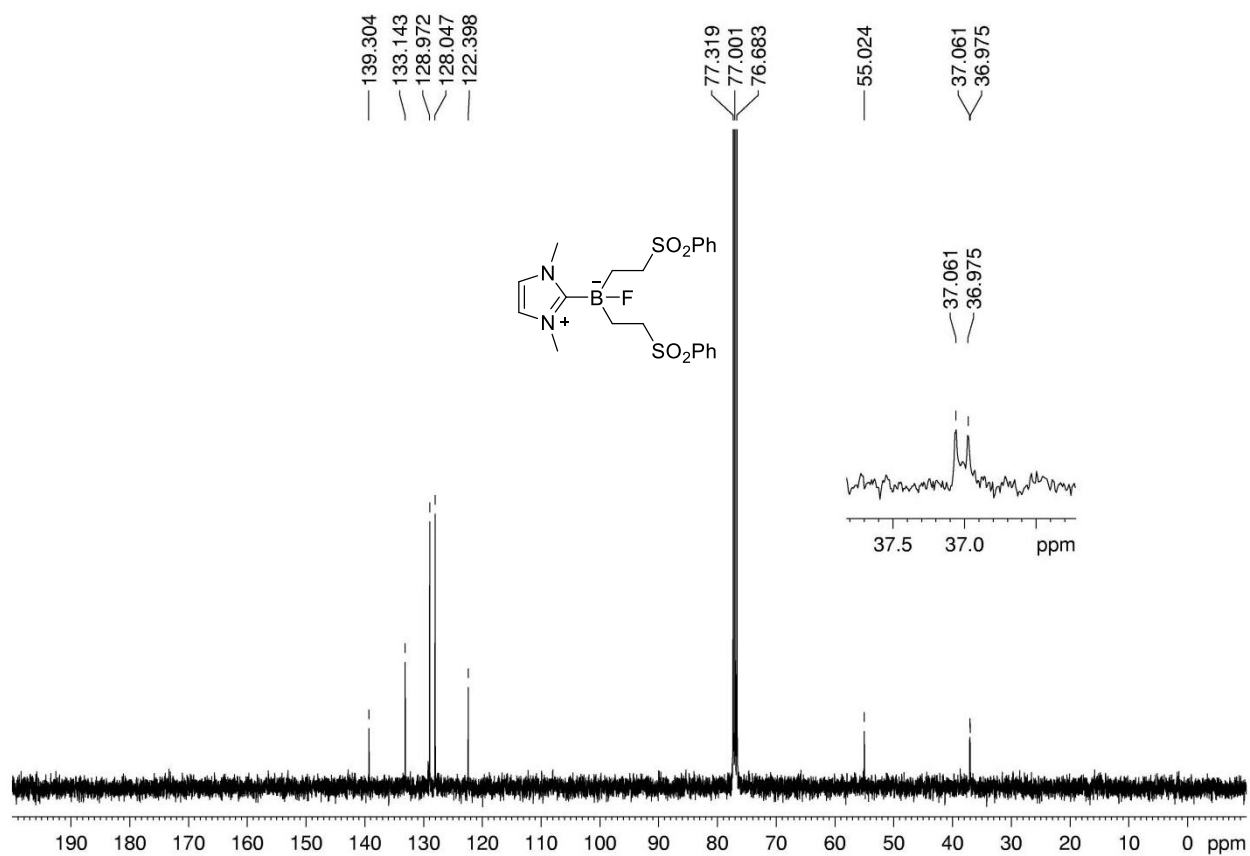
$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 564 MHz) spectrum of **62**



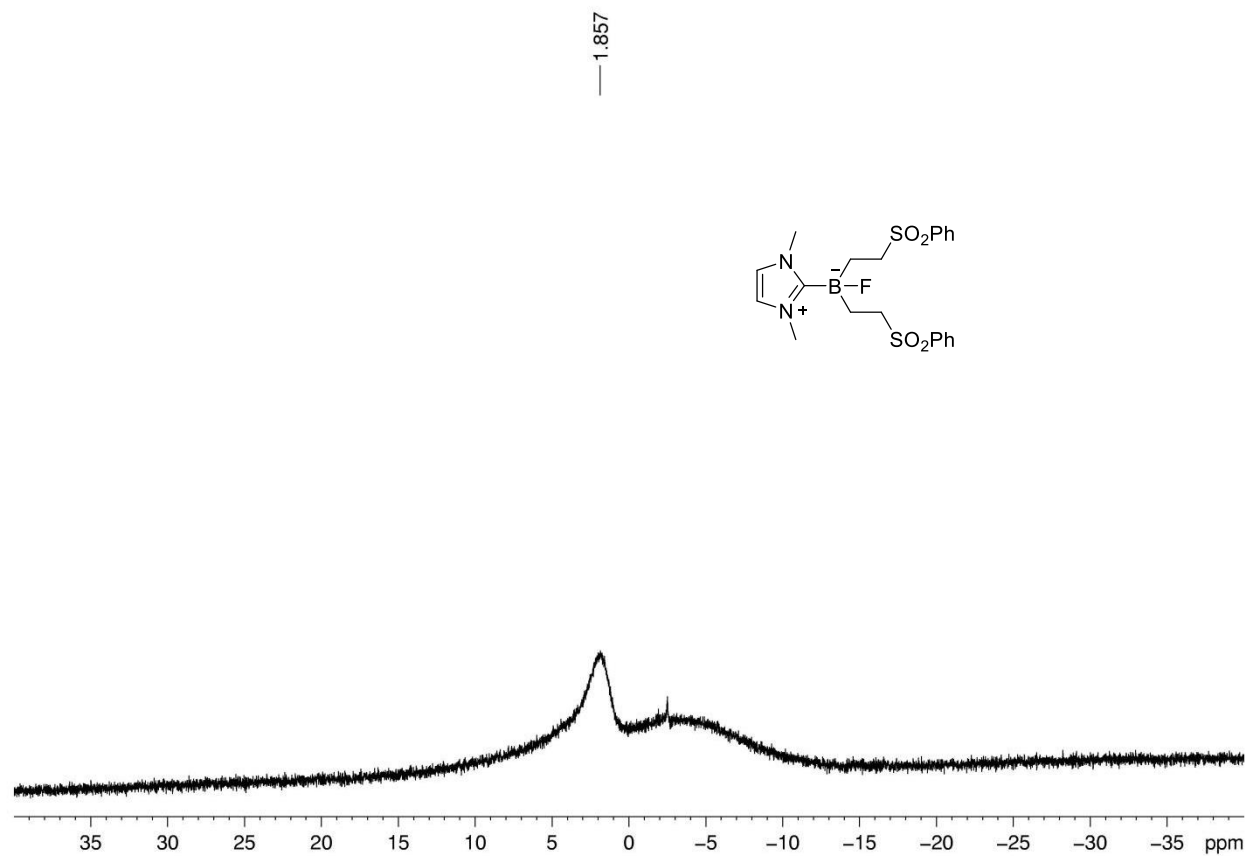
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **63**



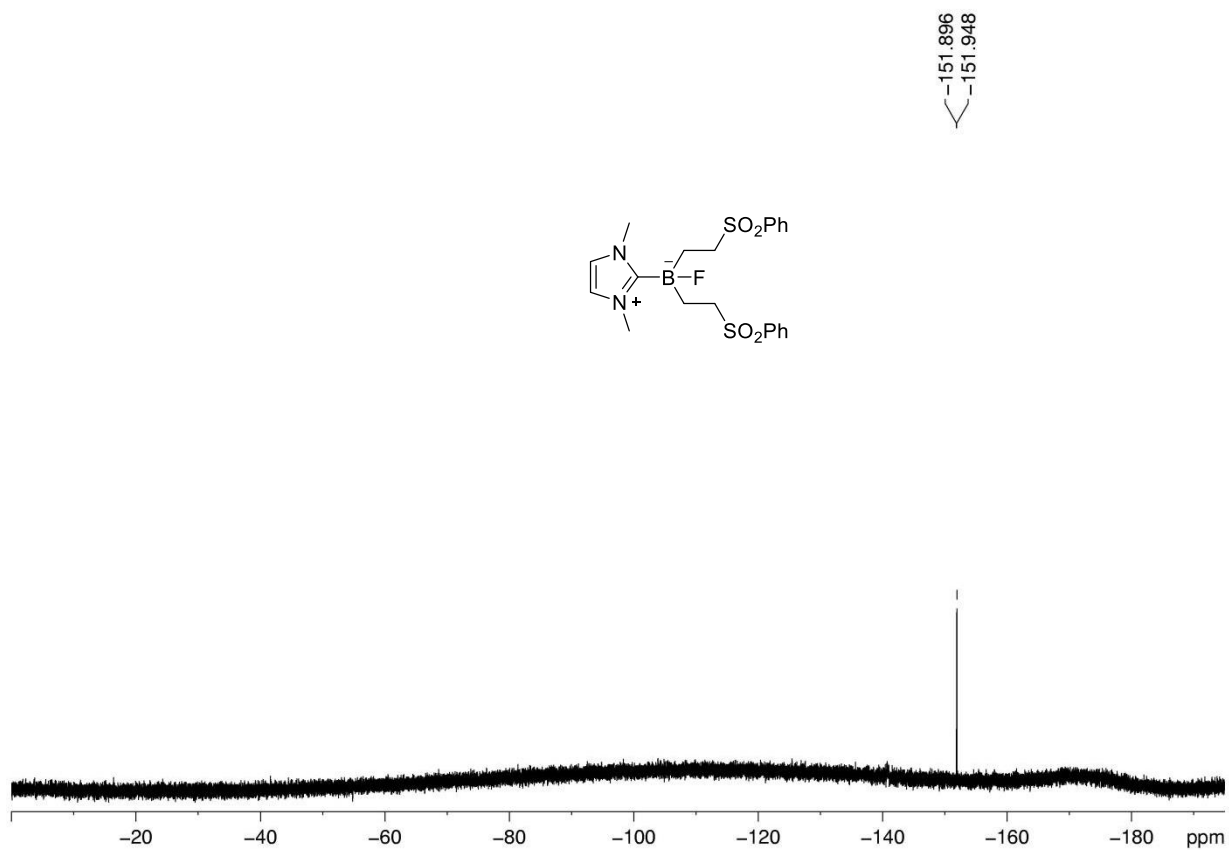
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) spectrum of **63**



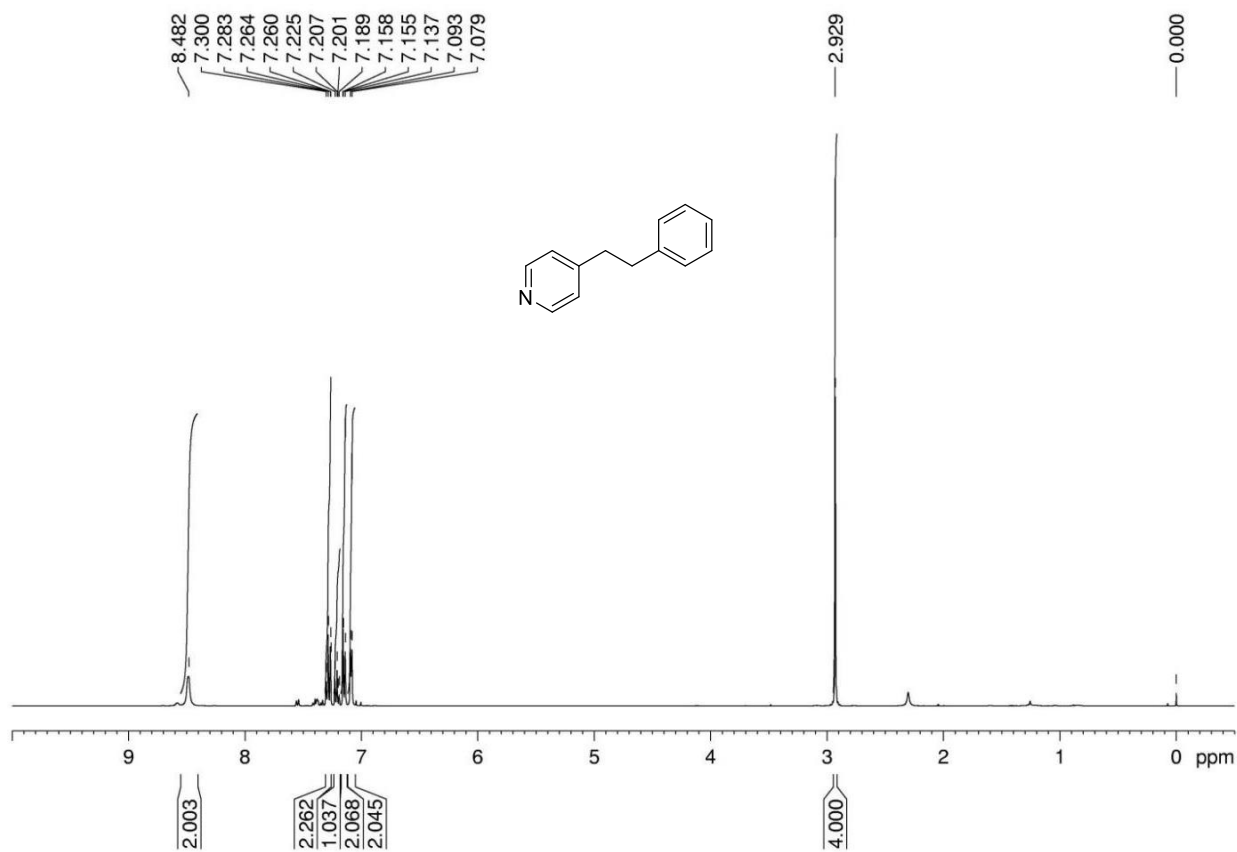
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **63**



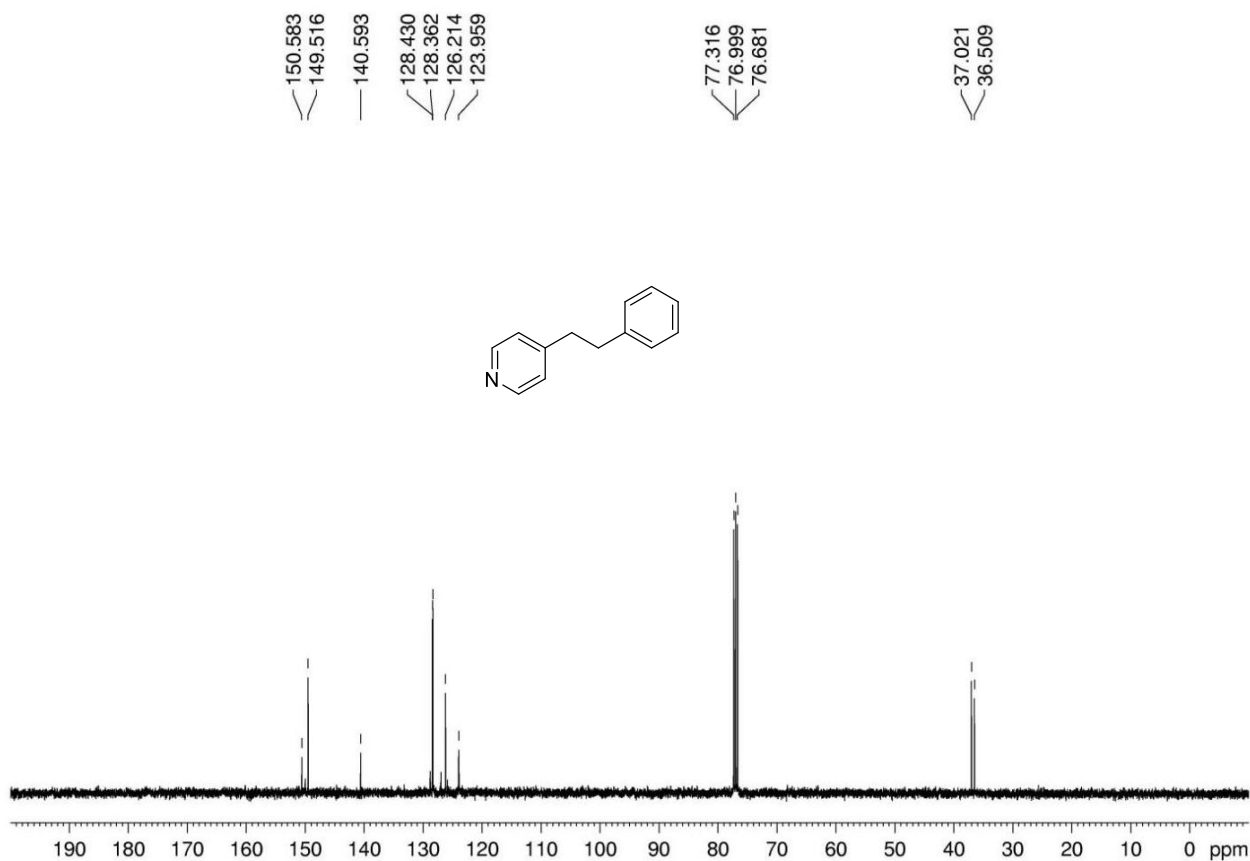
$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz) spectrum of **63**



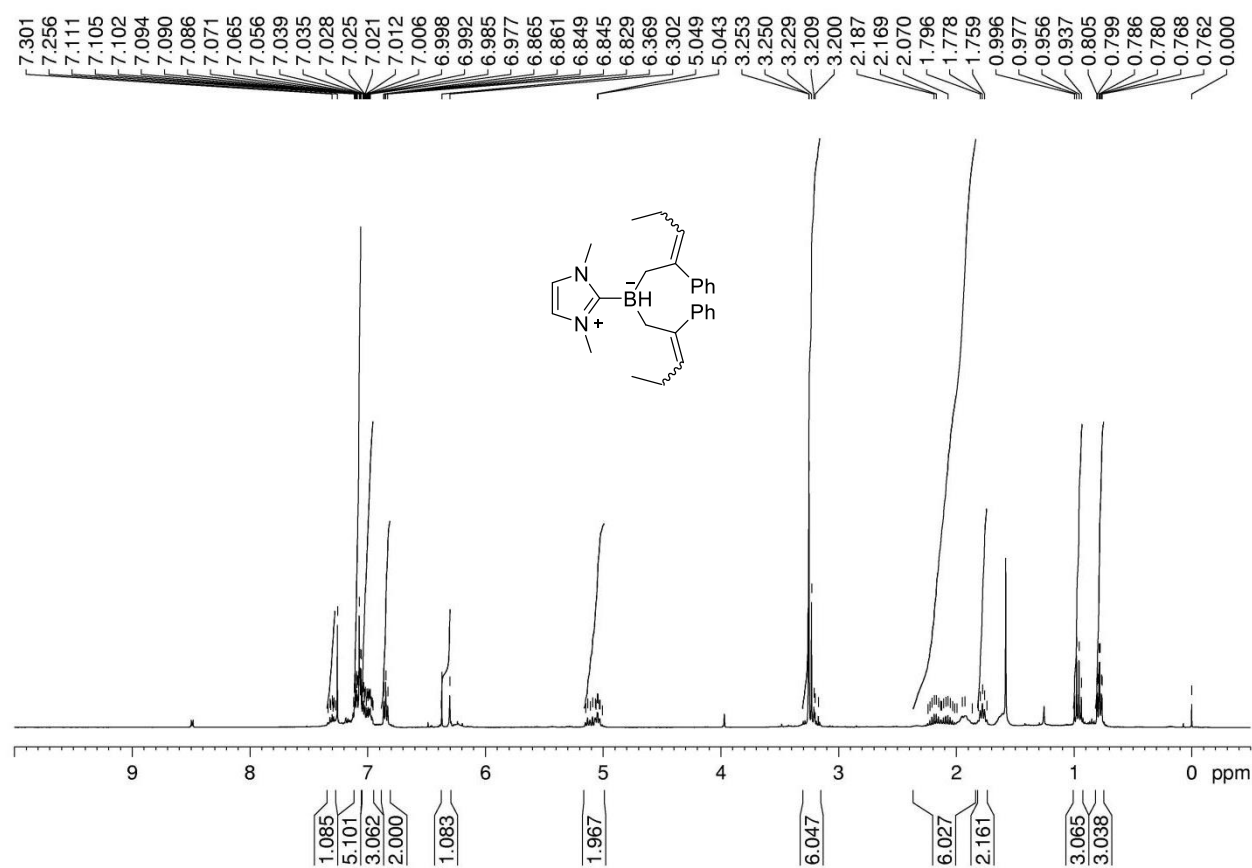
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **64**



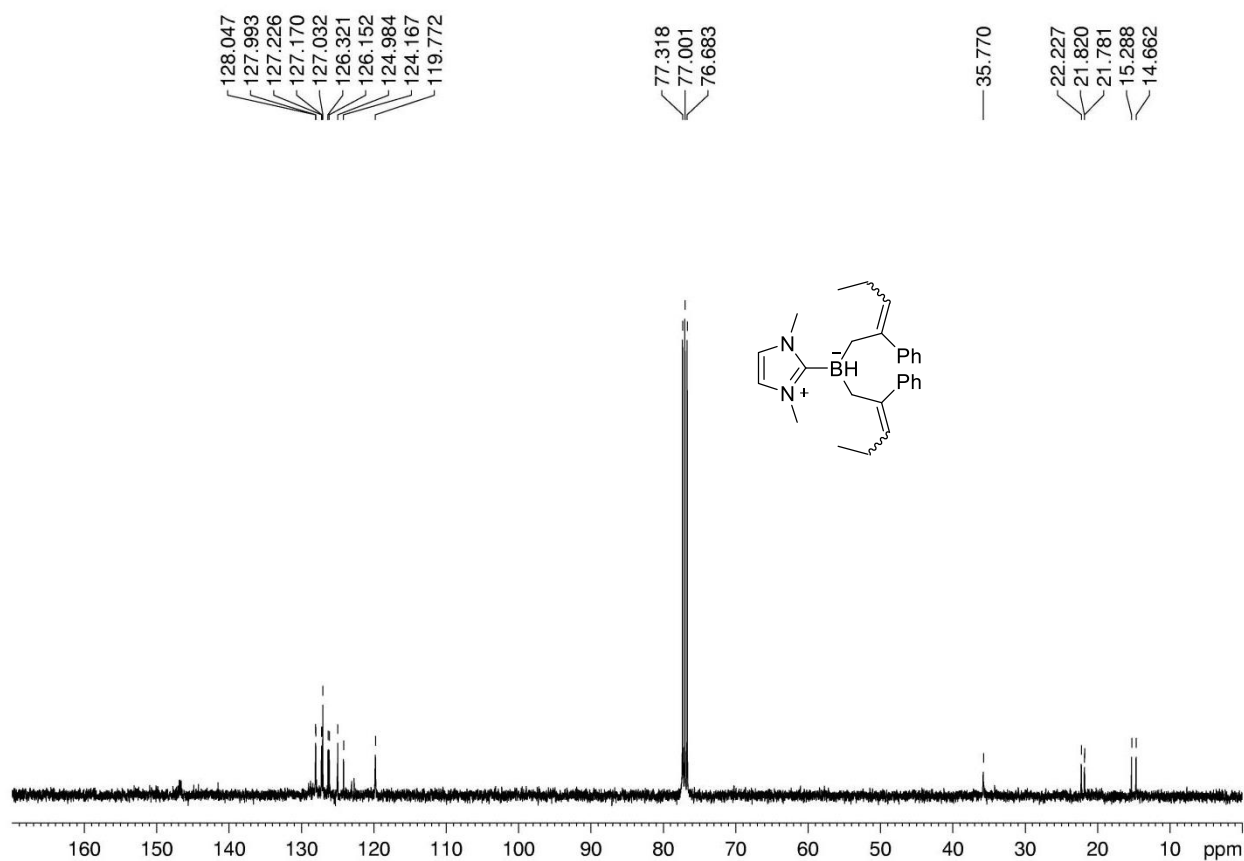
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) spectrum of **64**



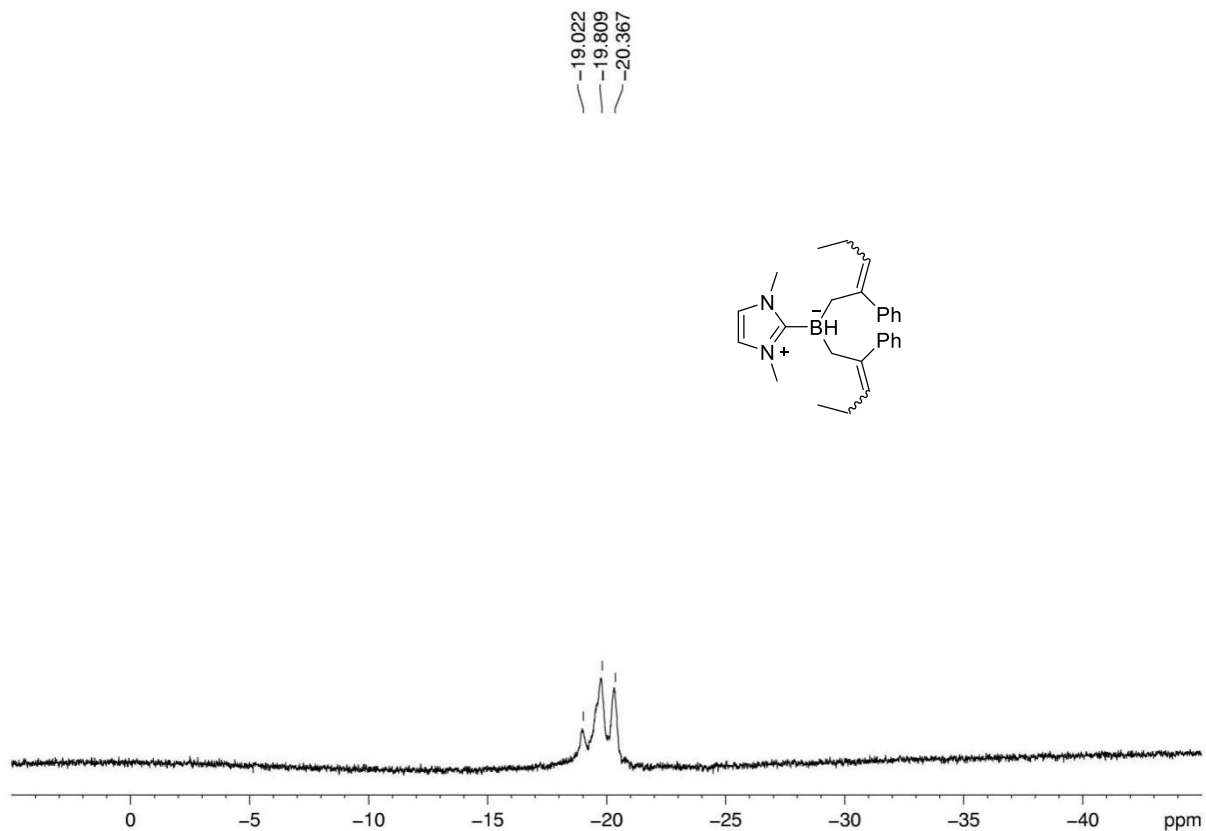
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of **66**



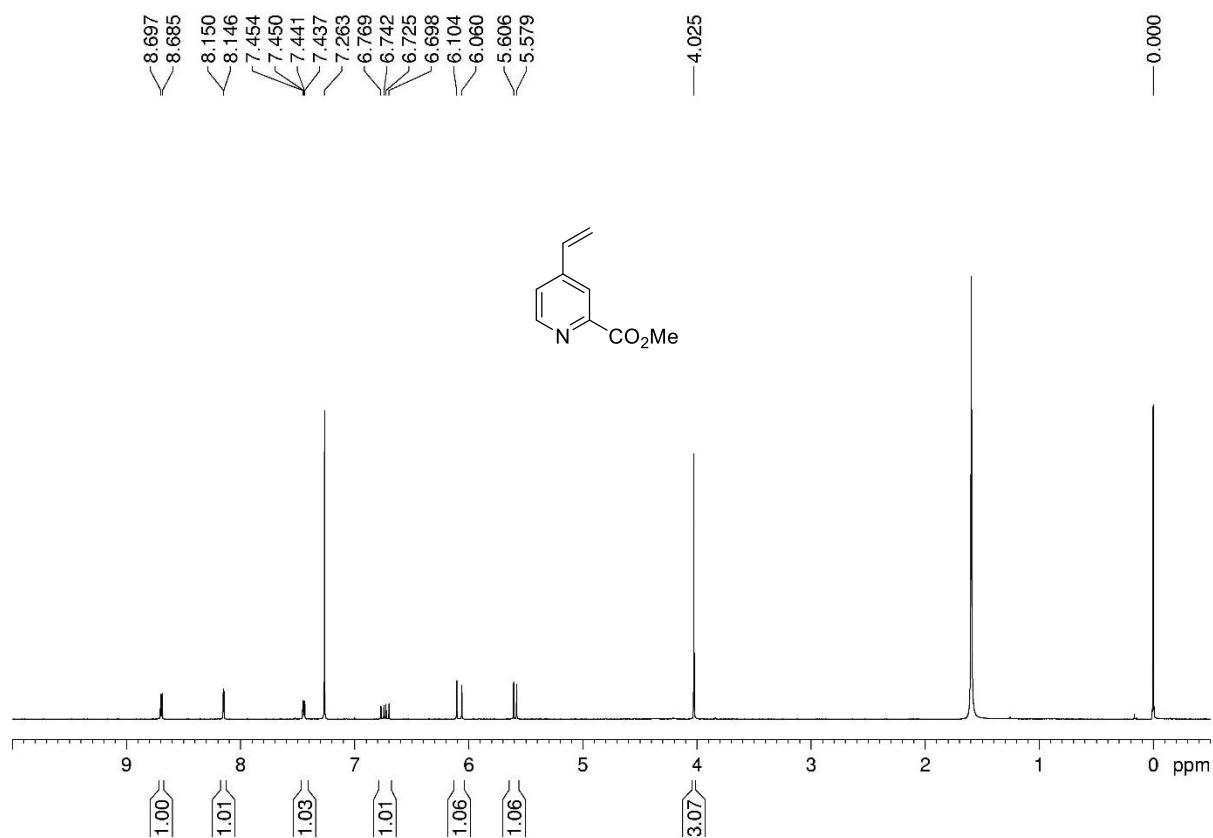
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of **66**



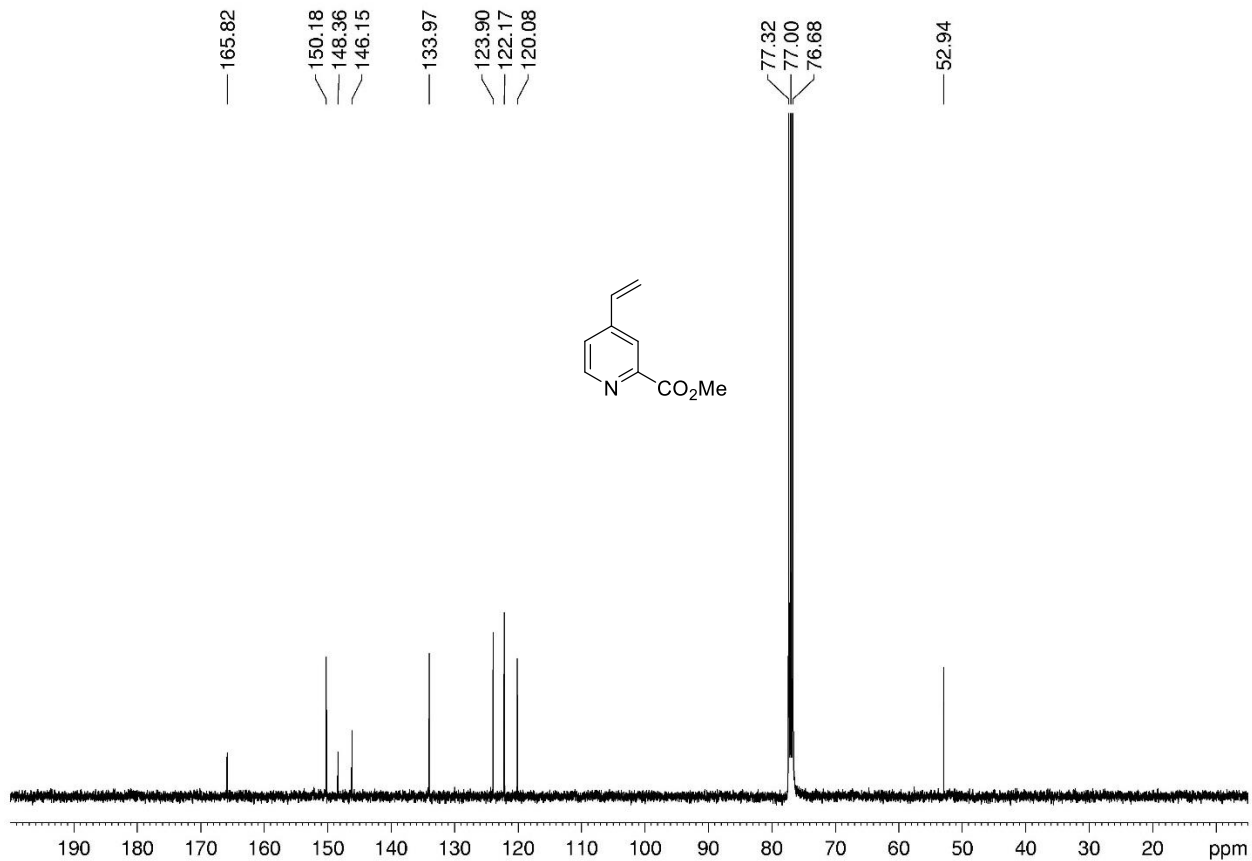
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of **66**



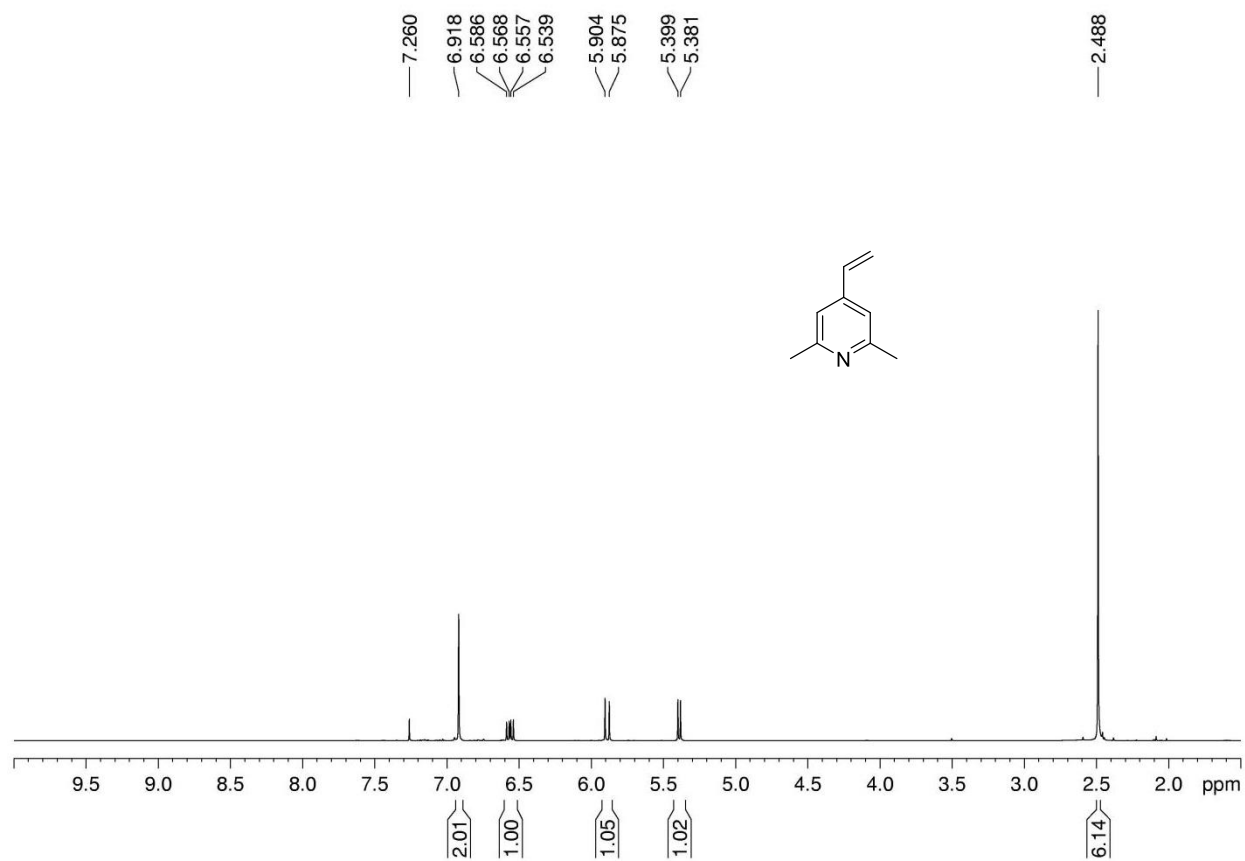
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz) spectrum of SI-7



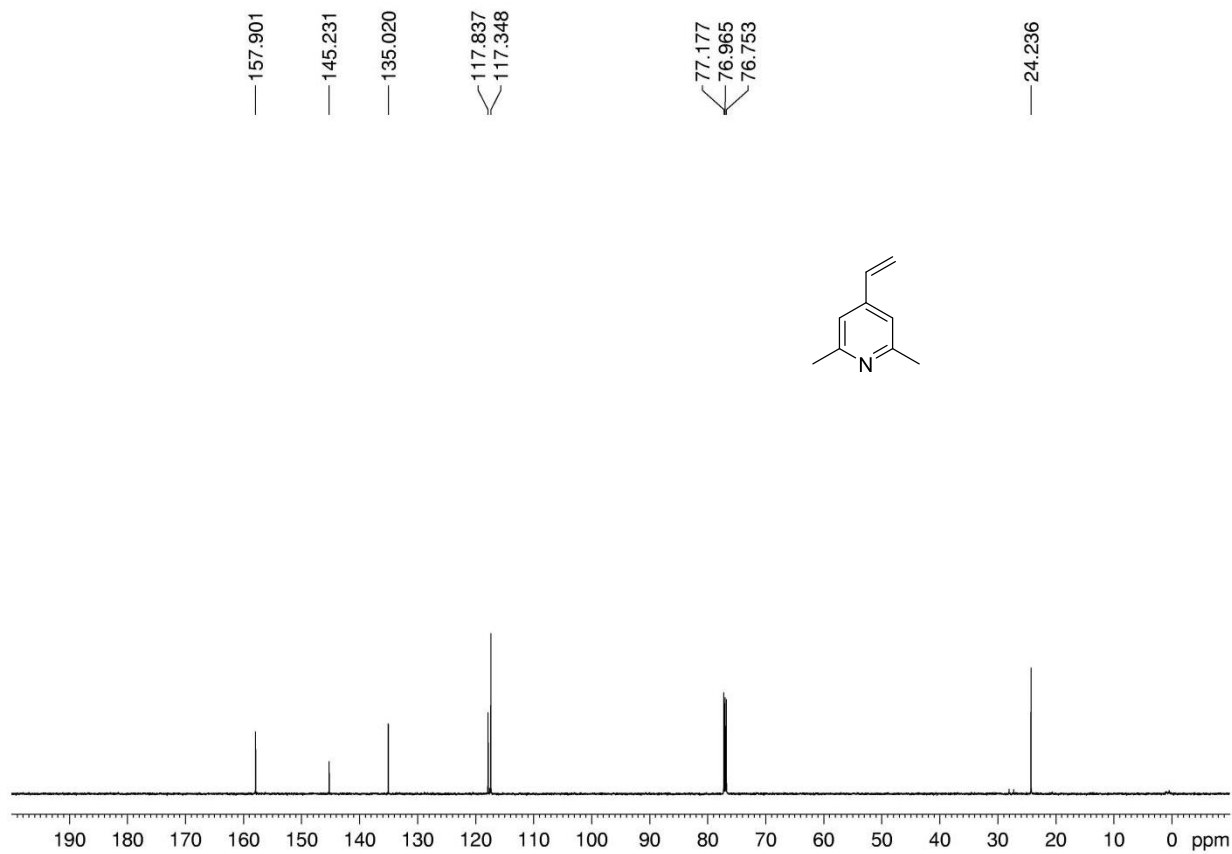
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz) spectrum of SI-7



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) spectrum of **SI-8**

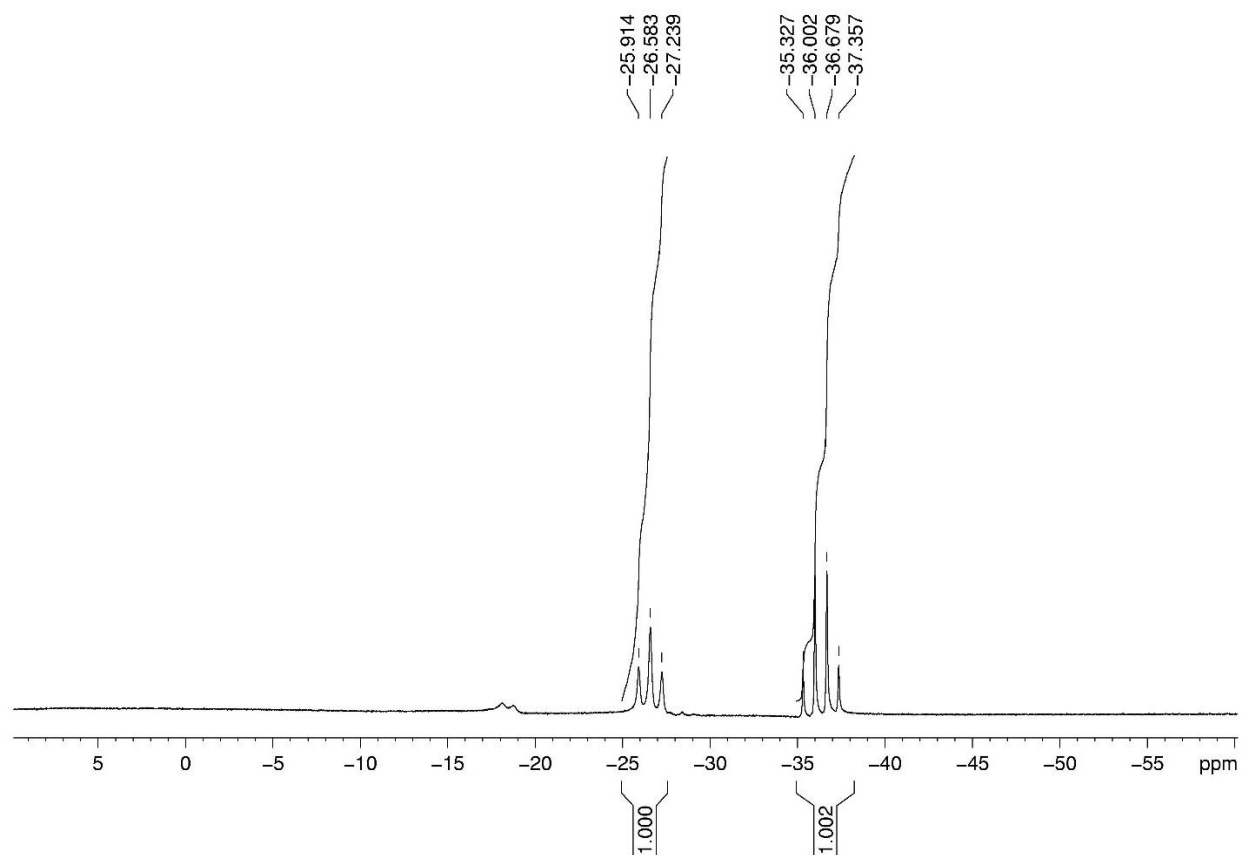


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) spectrum of **SI-8**

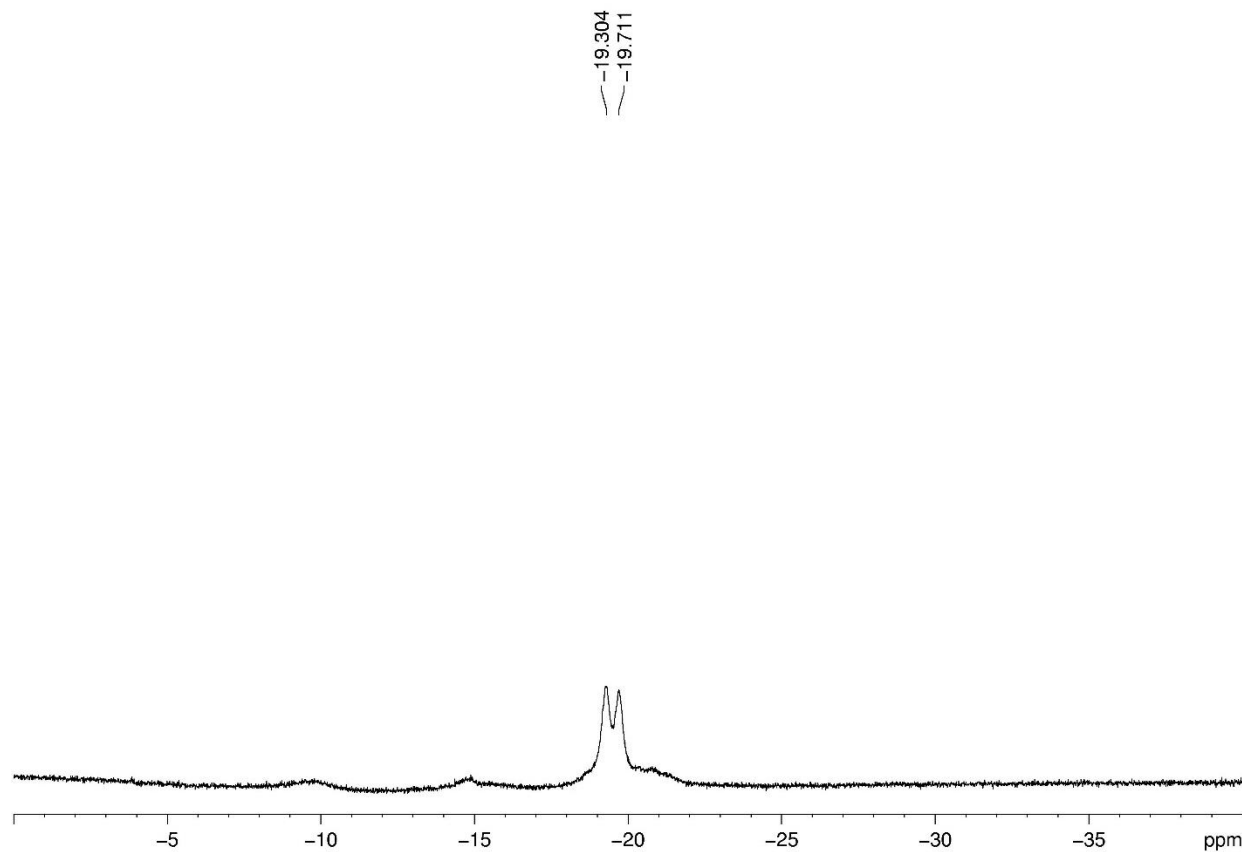




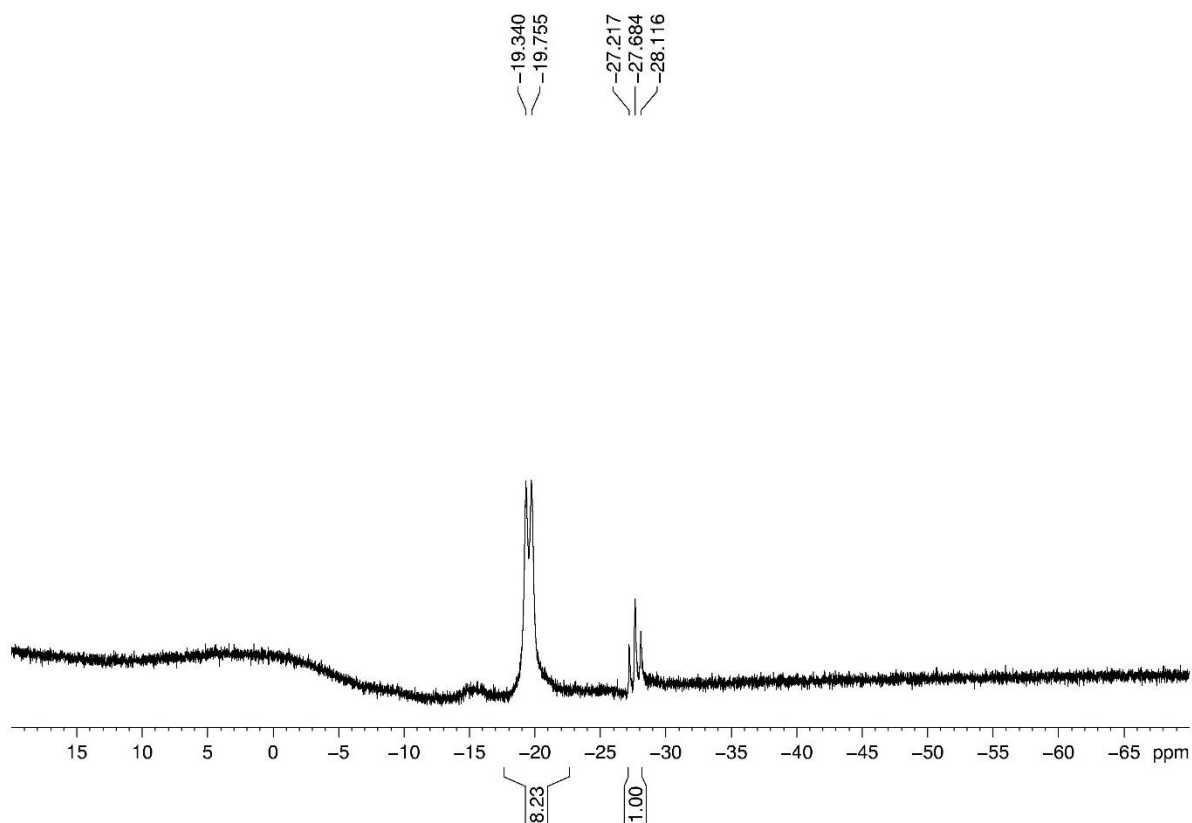
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **3**



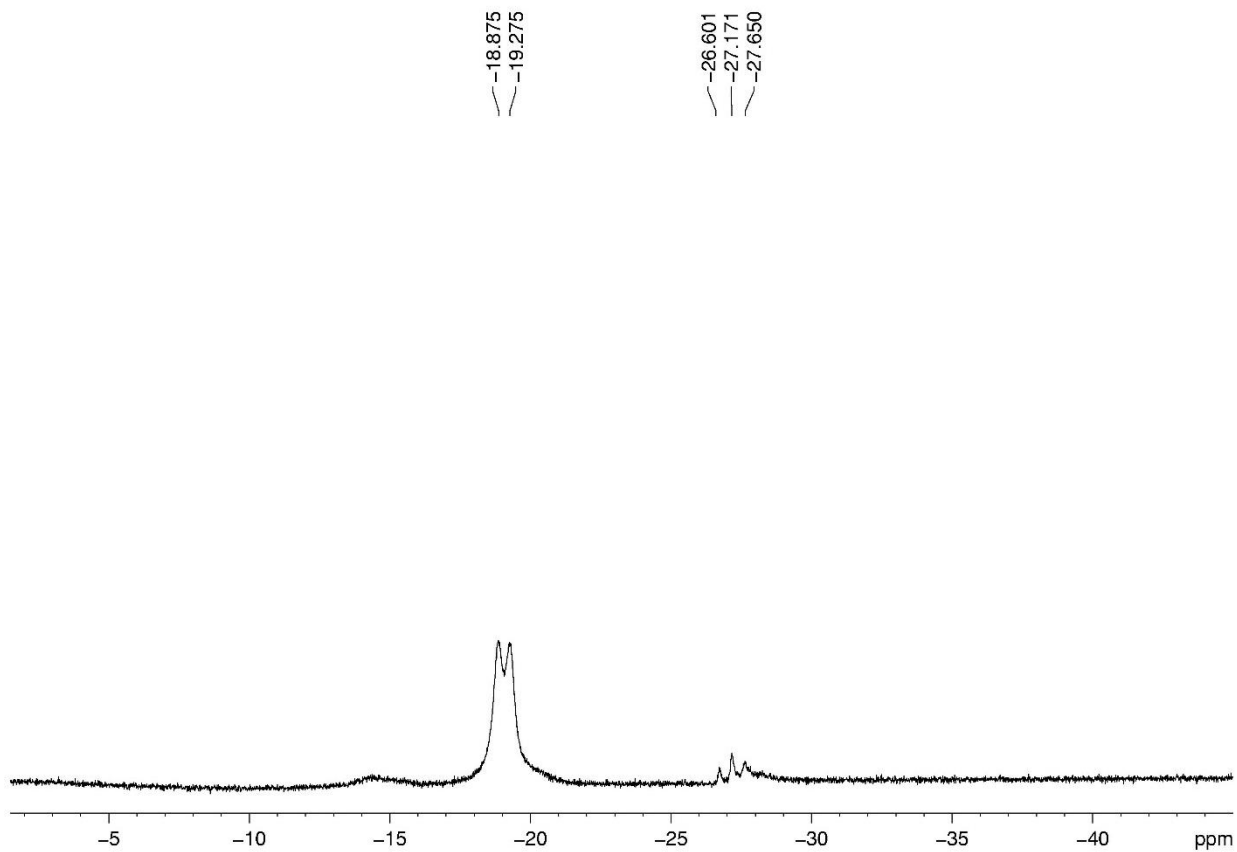
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **4**



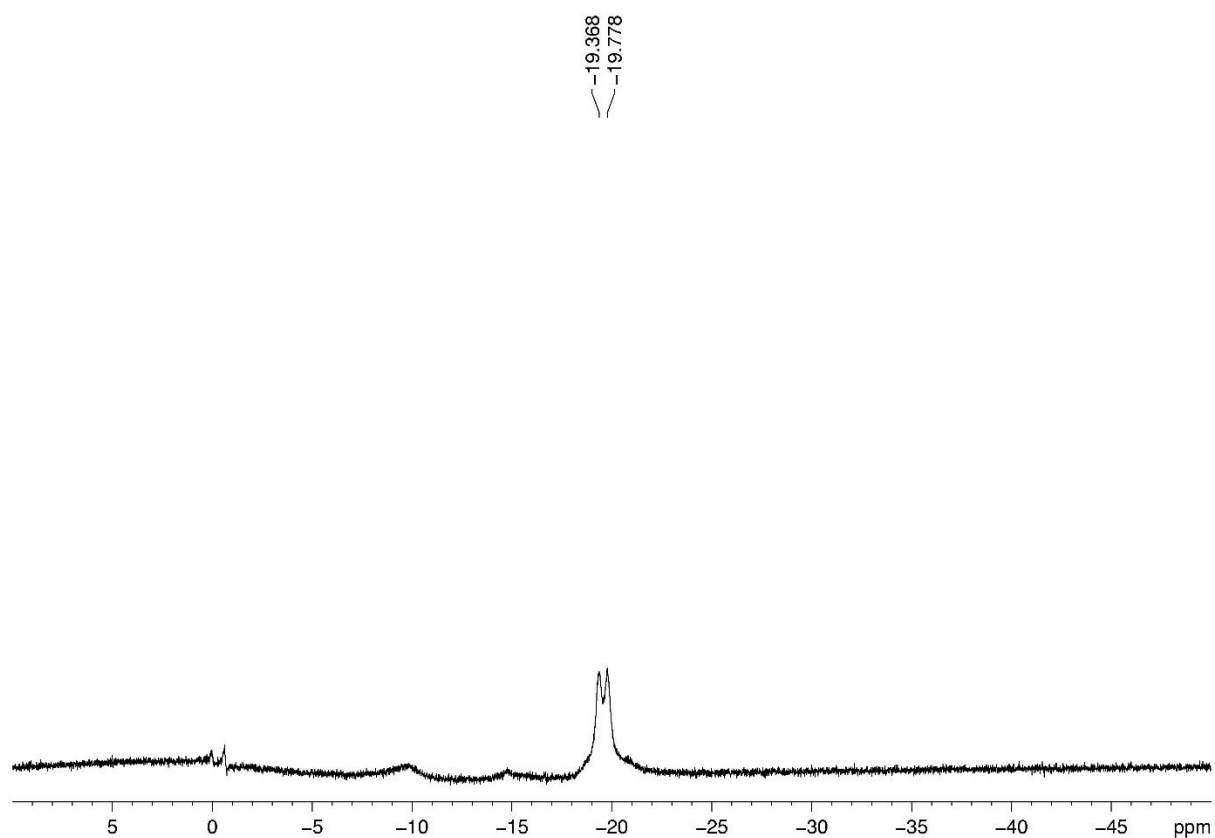
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **5**



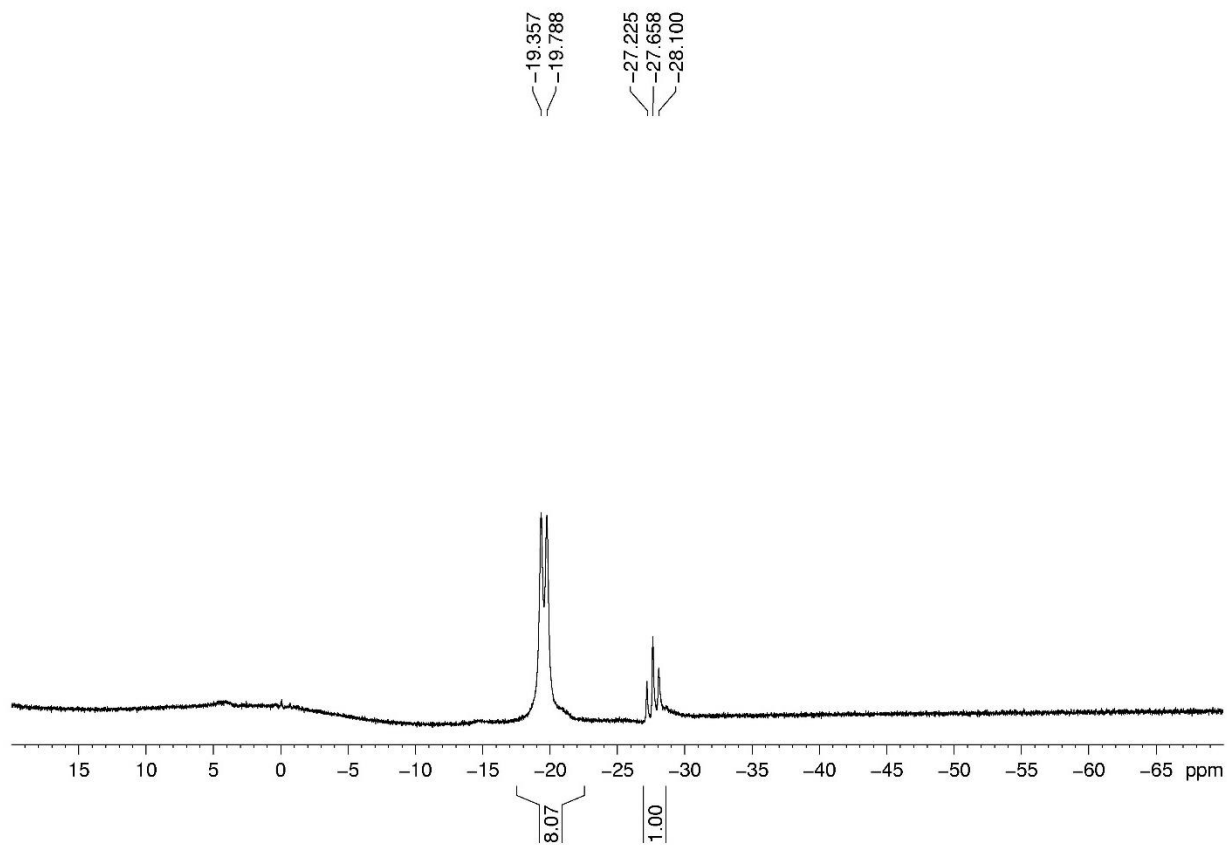
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **6**



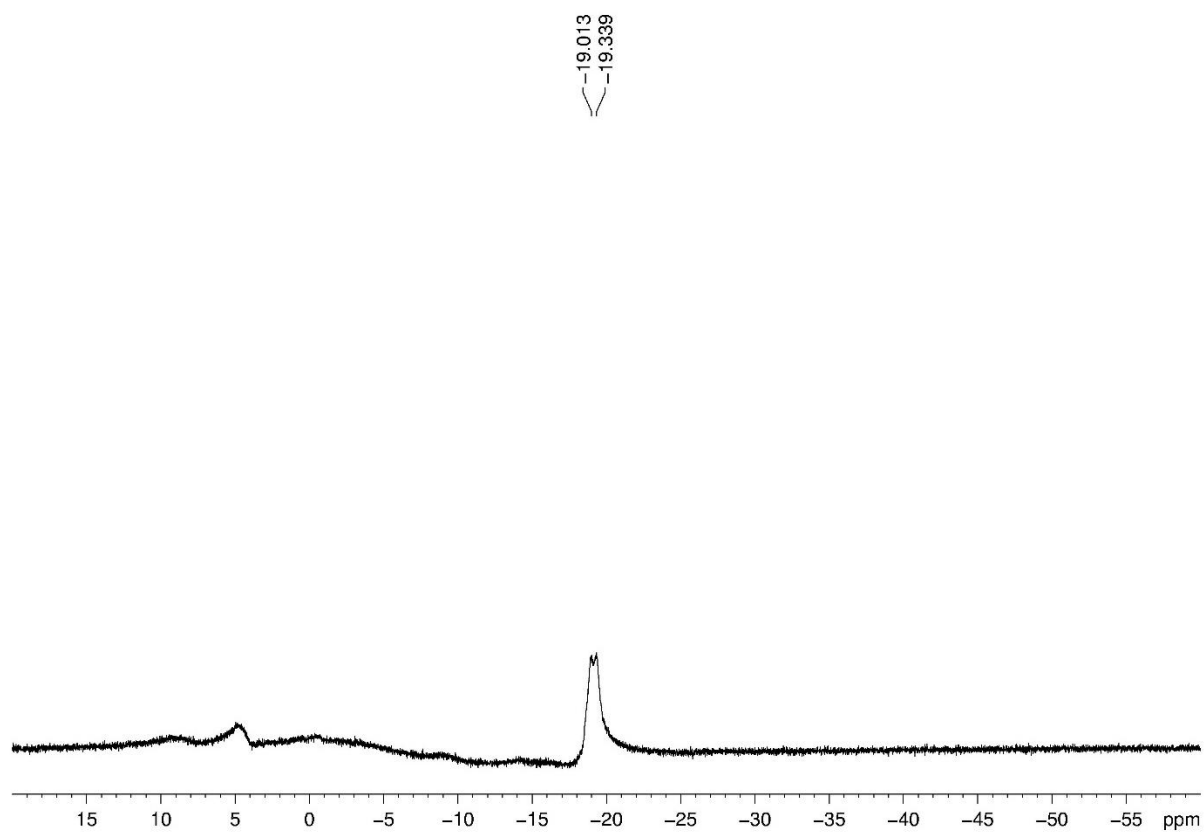
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **7**



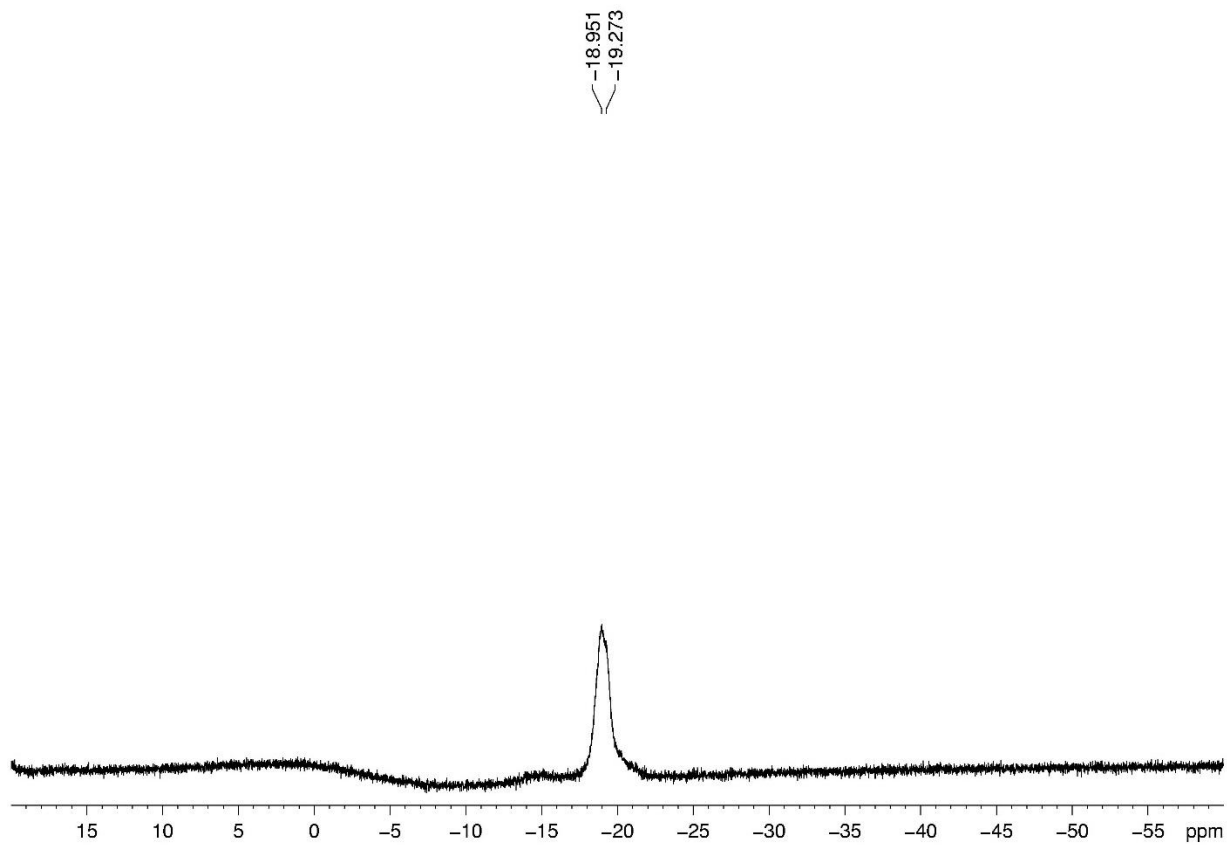
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **8**



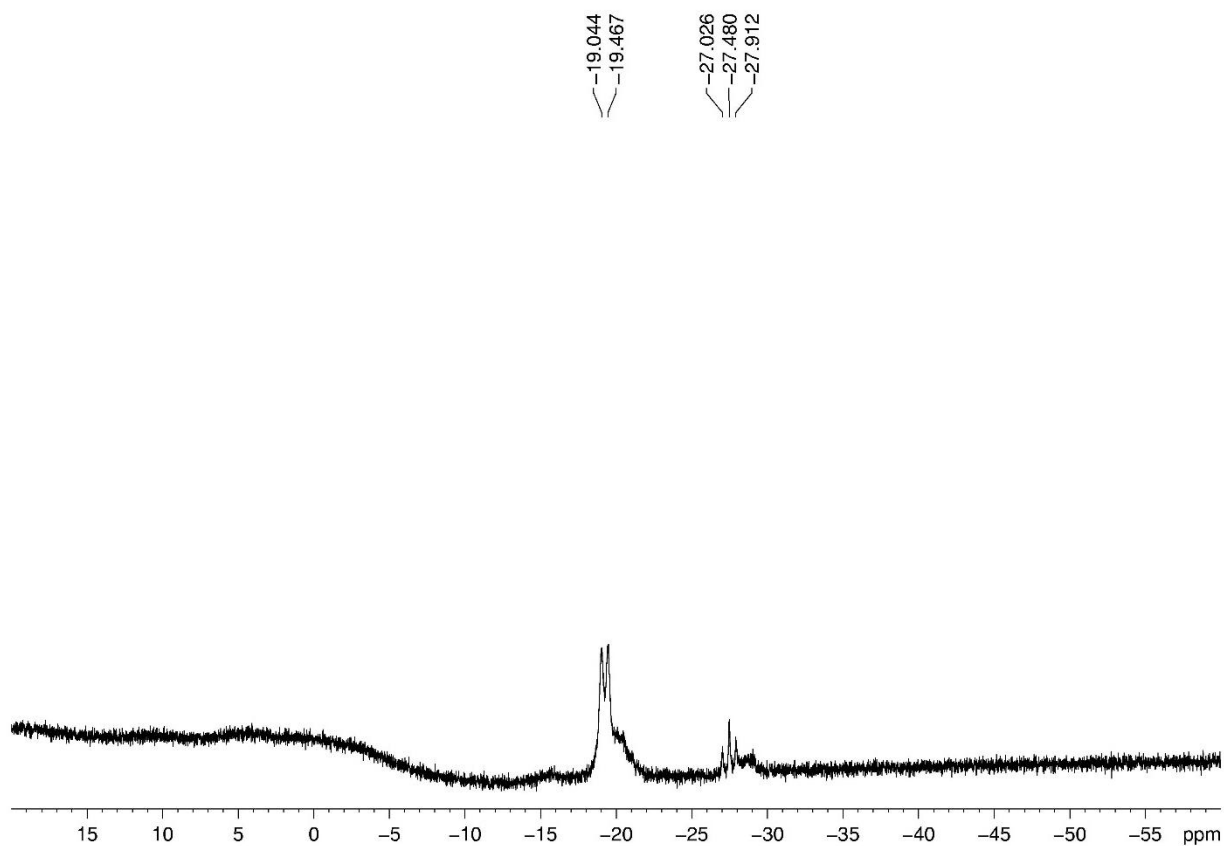
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **9**



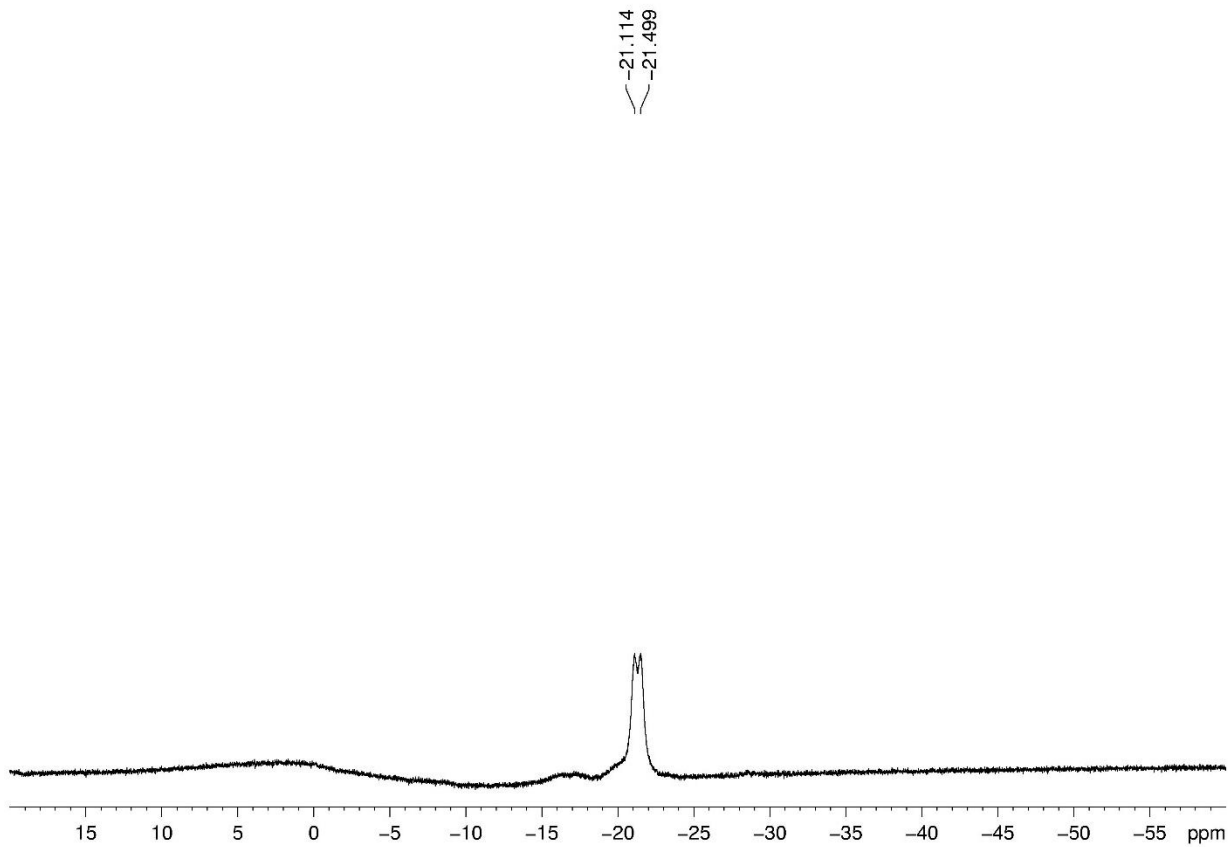
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **10**



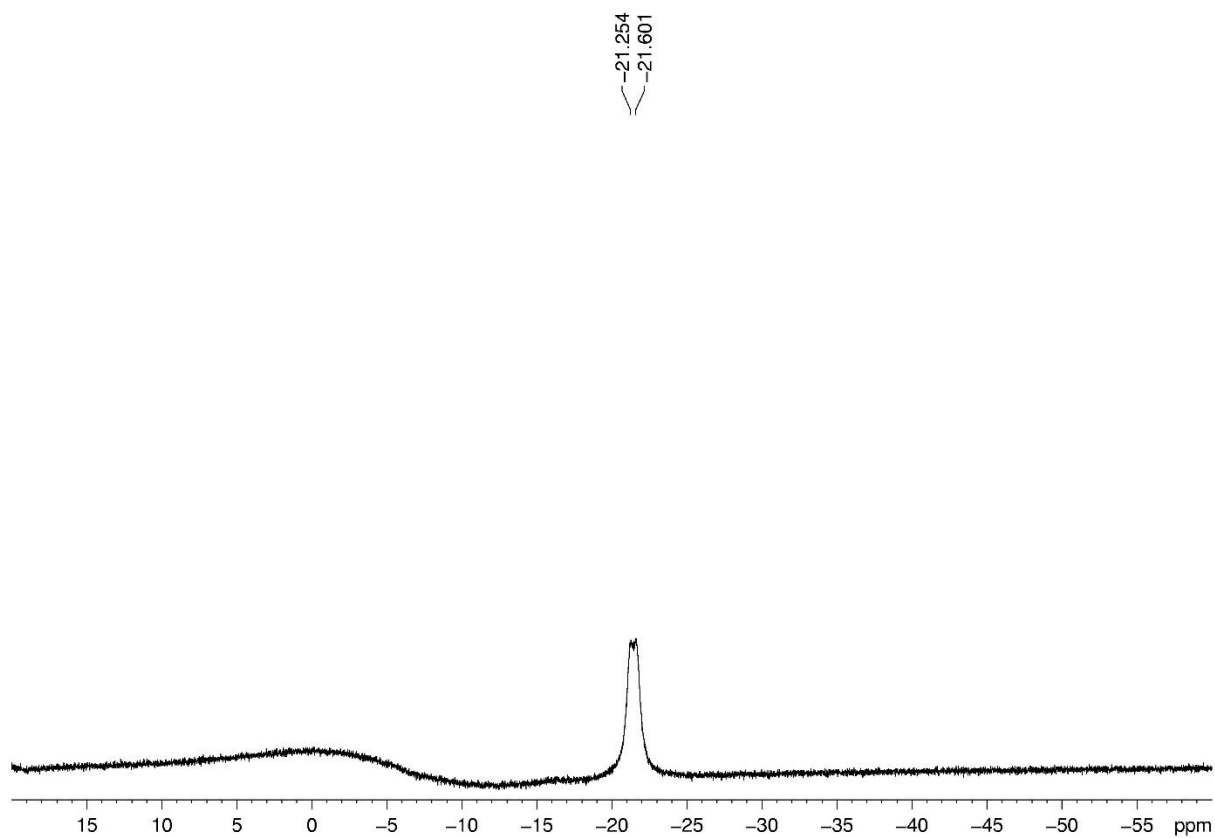
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **11**



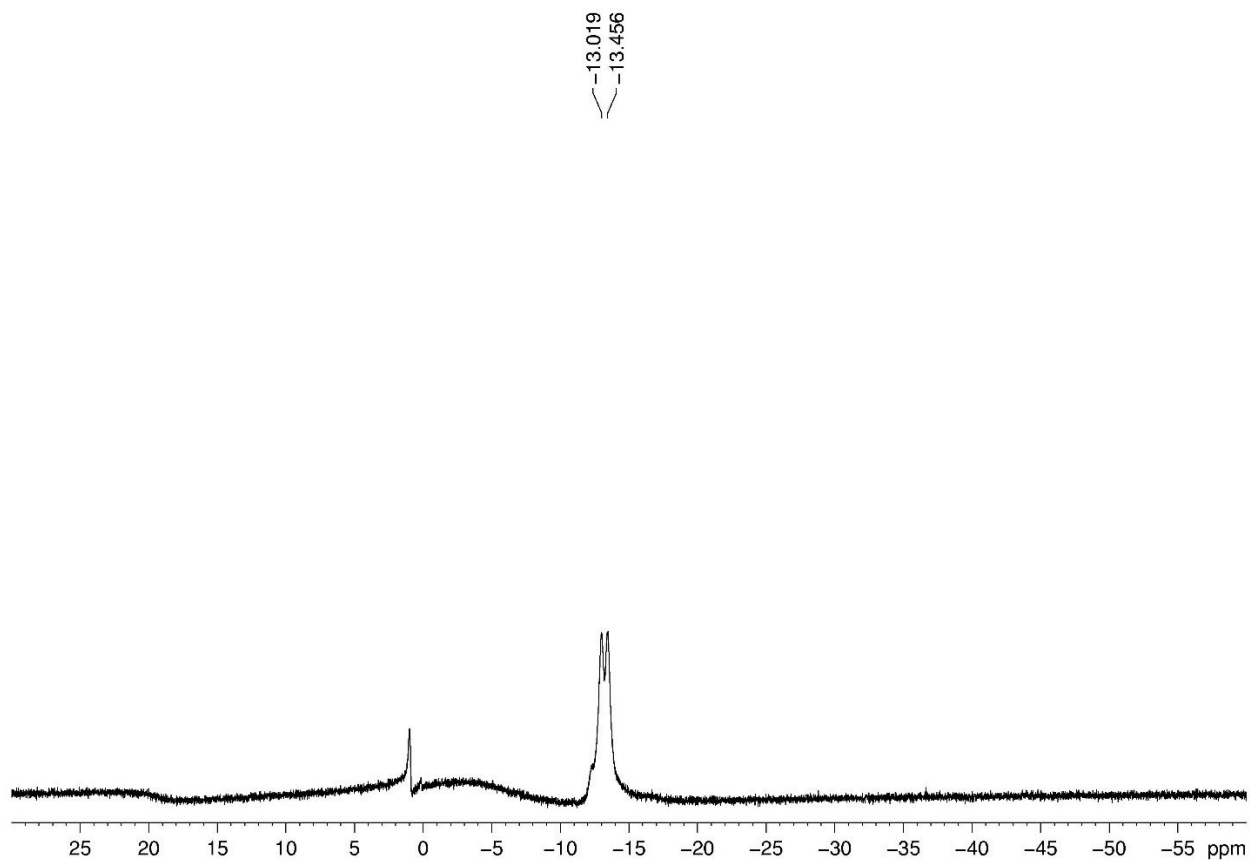
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **12**



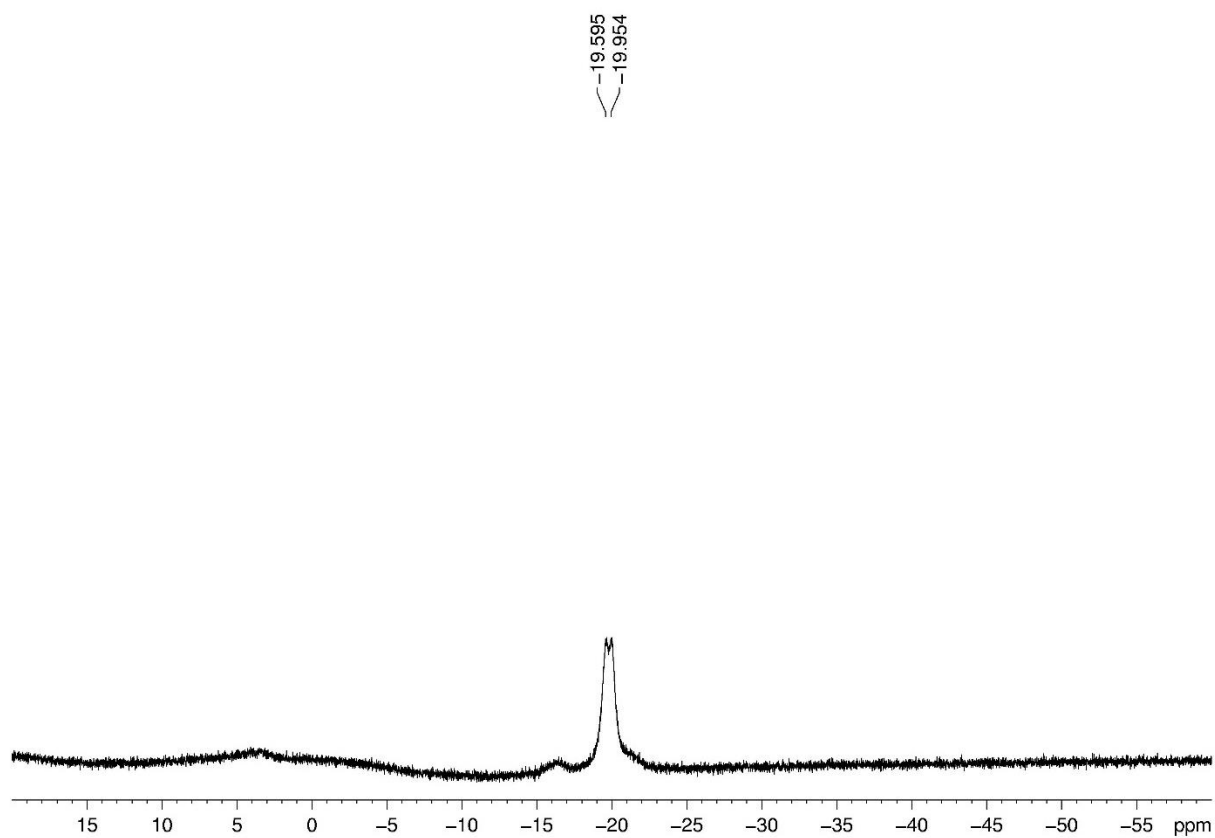
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **13**



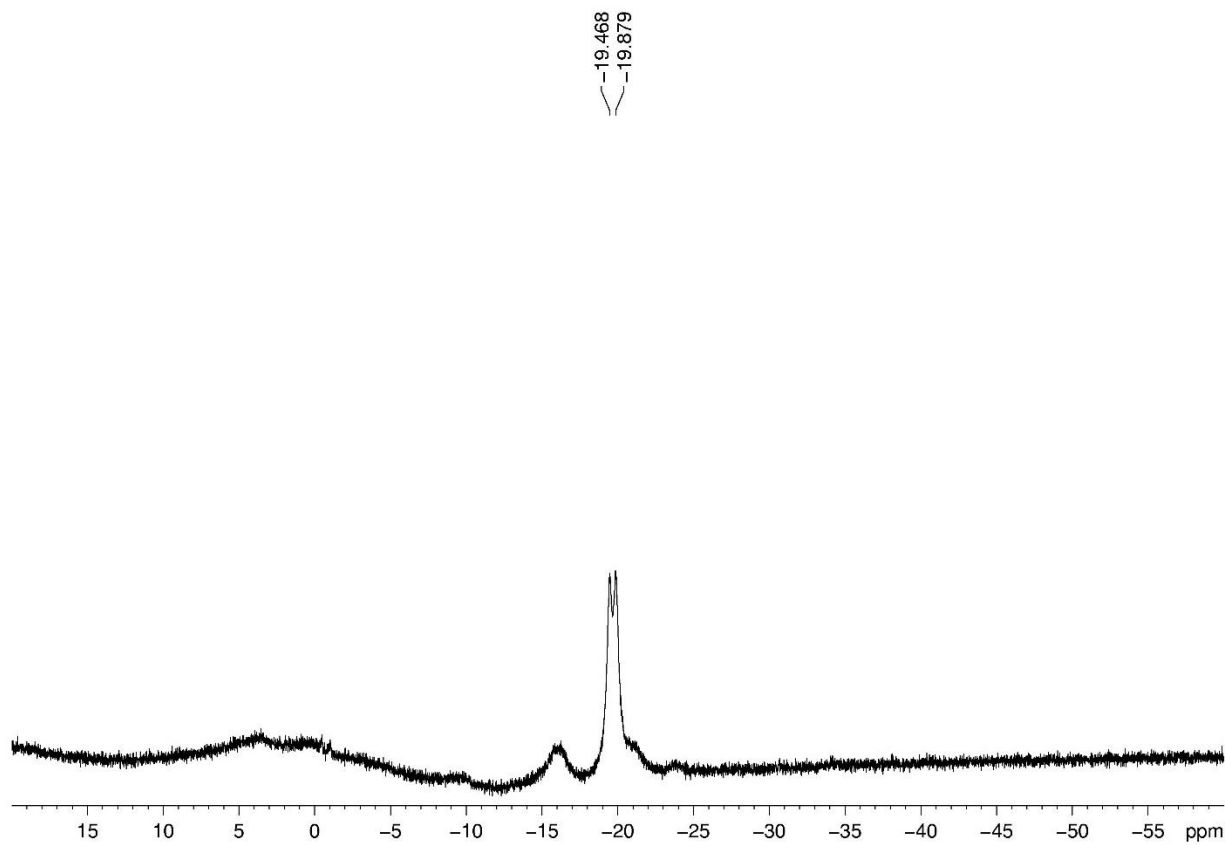
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **14**



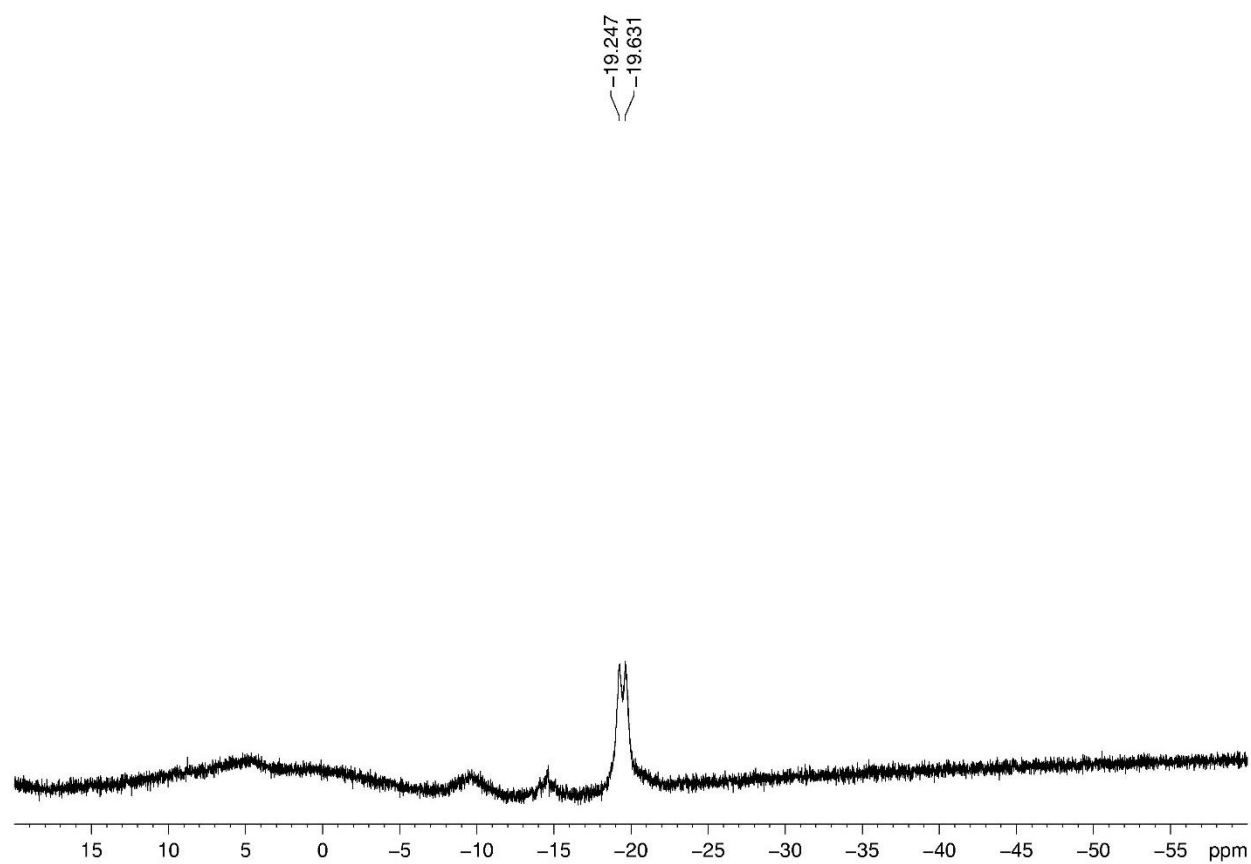
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **15**



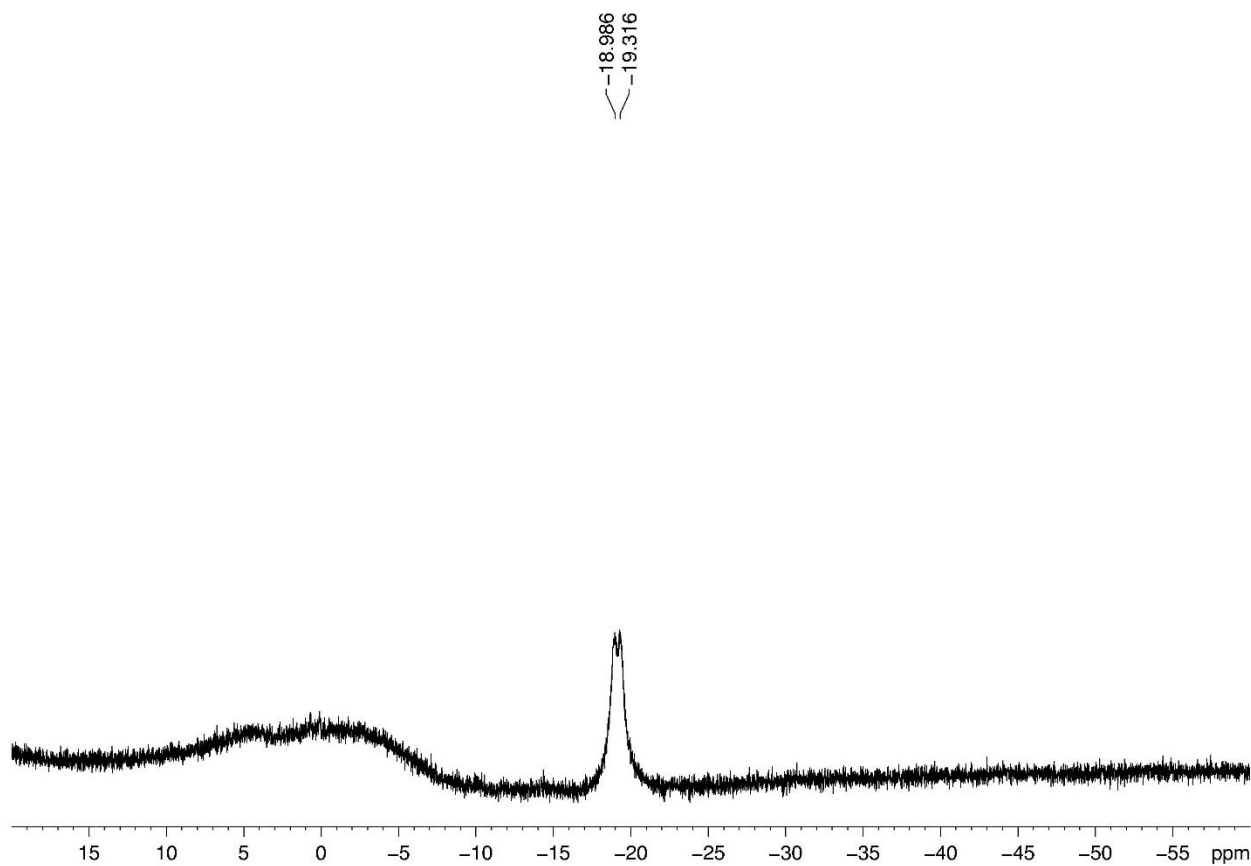
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **16**



$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **17**

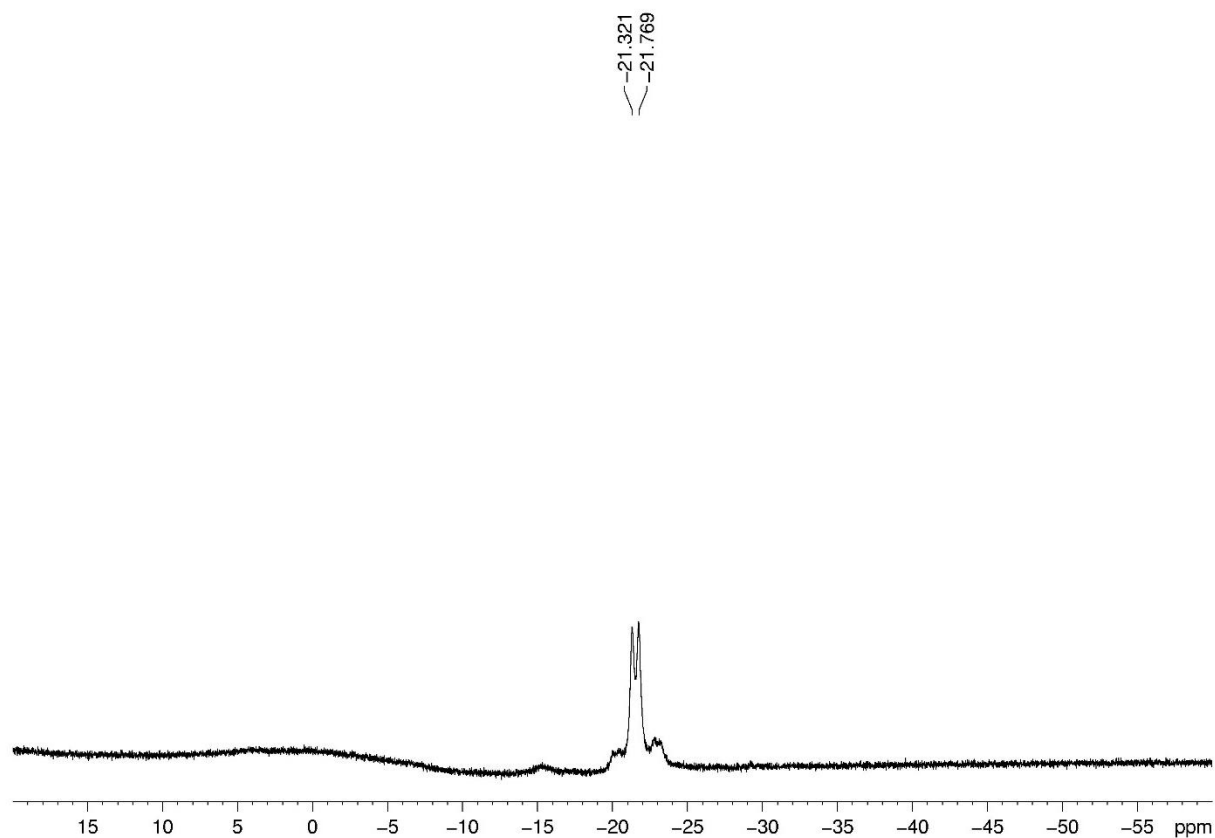


$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **18**

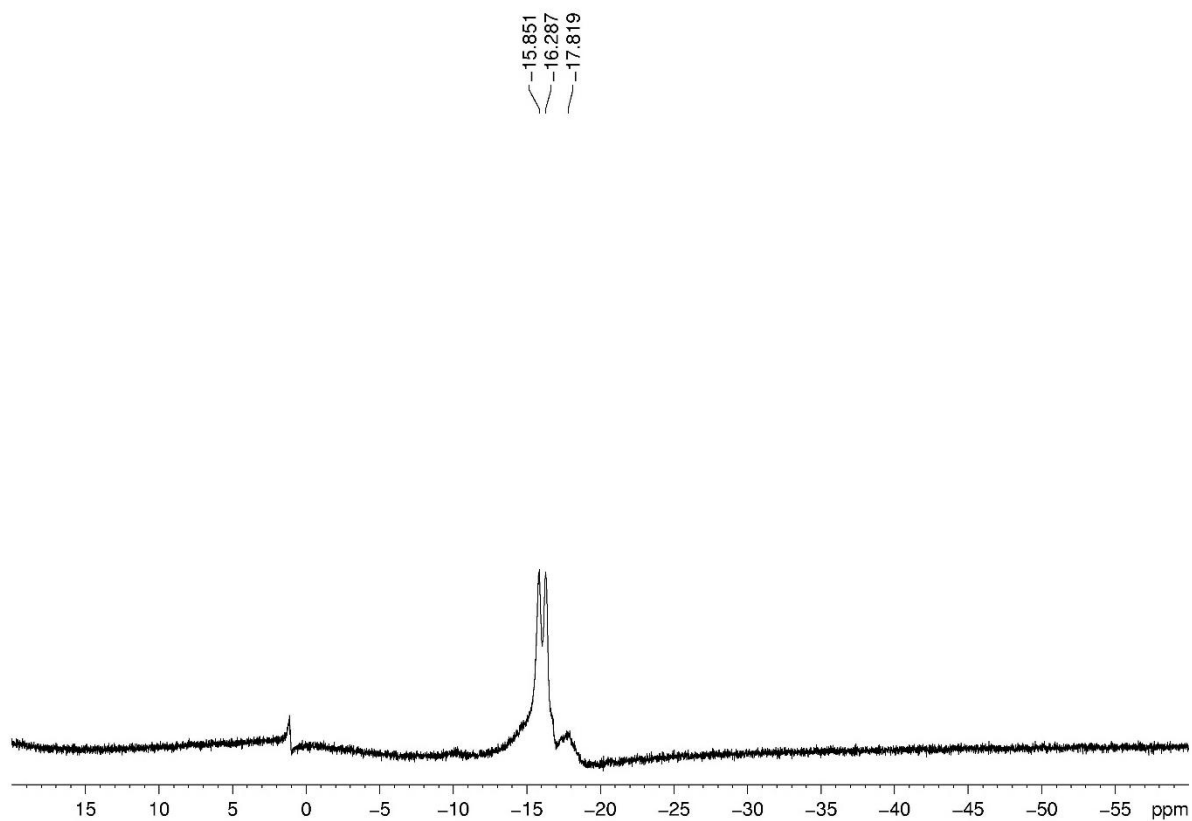




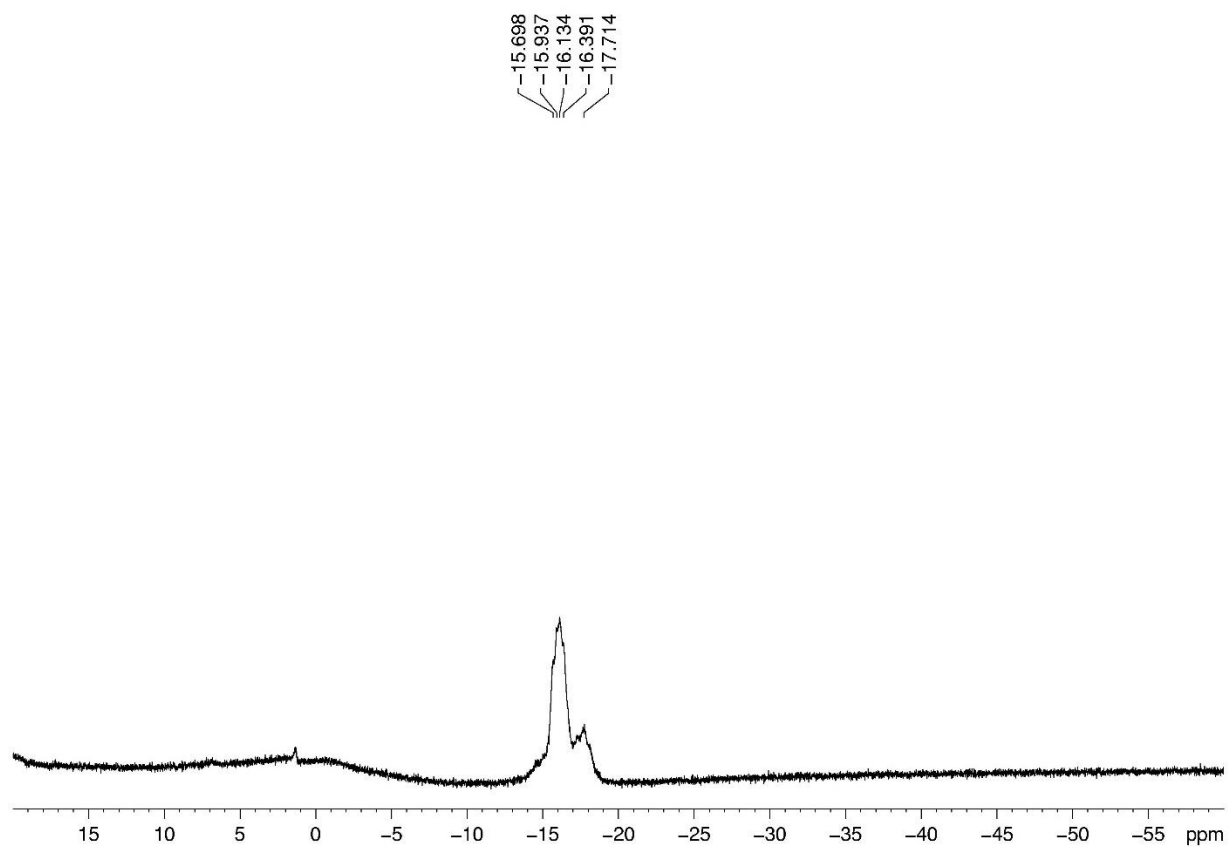
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **19**



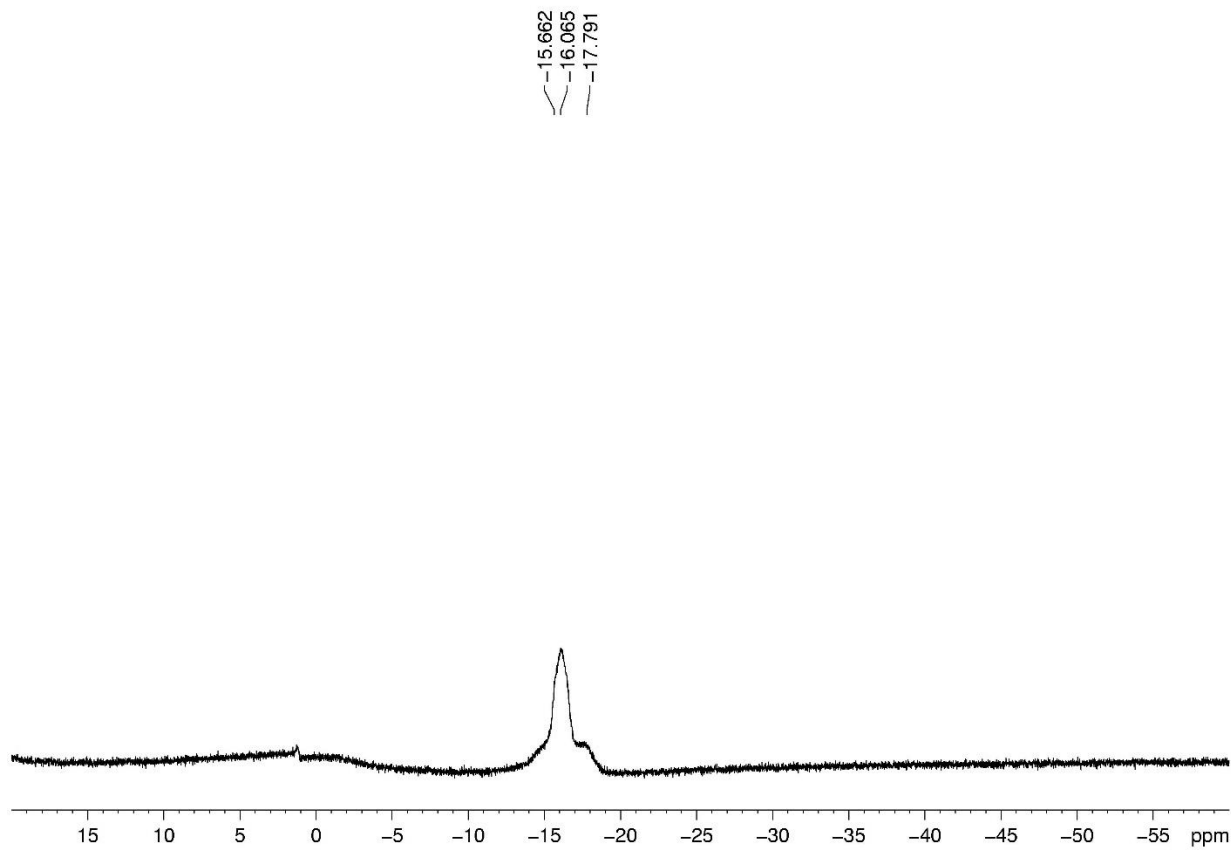
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **20**



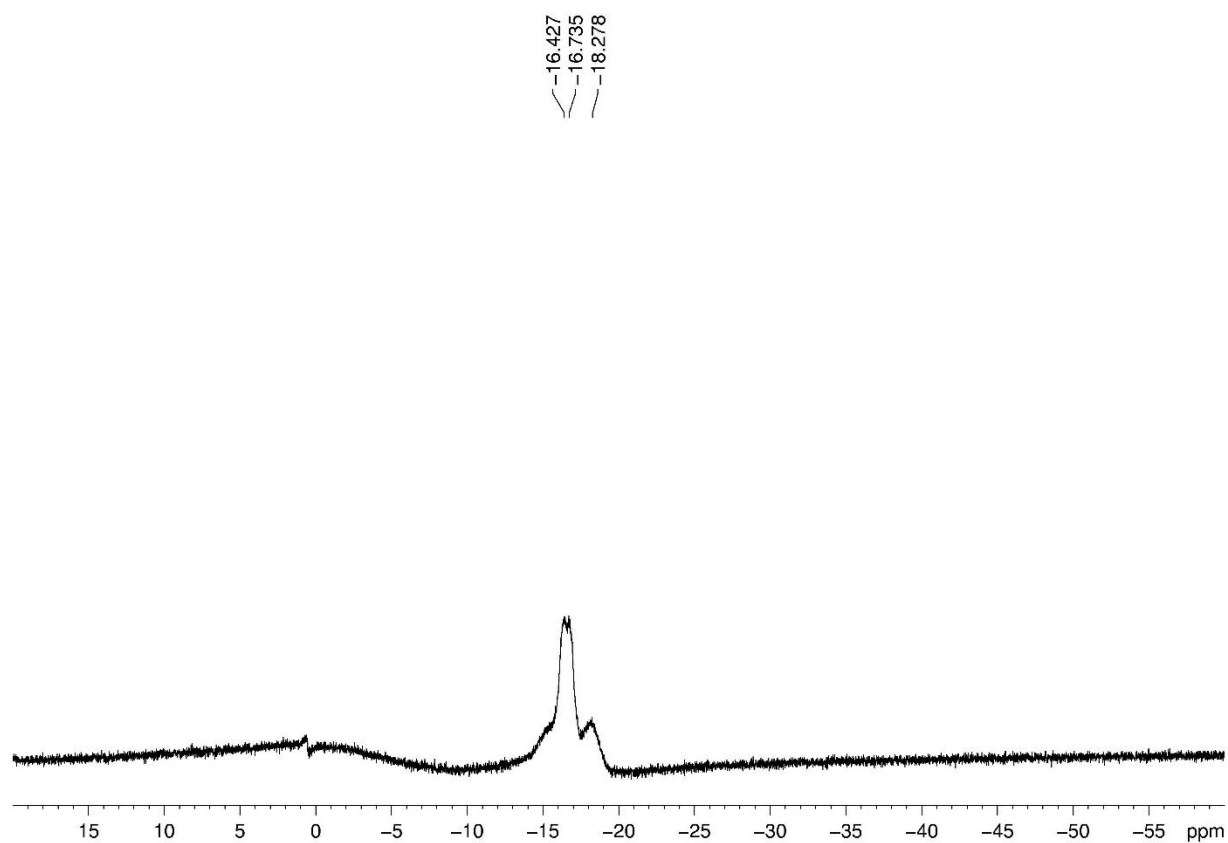
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **21**



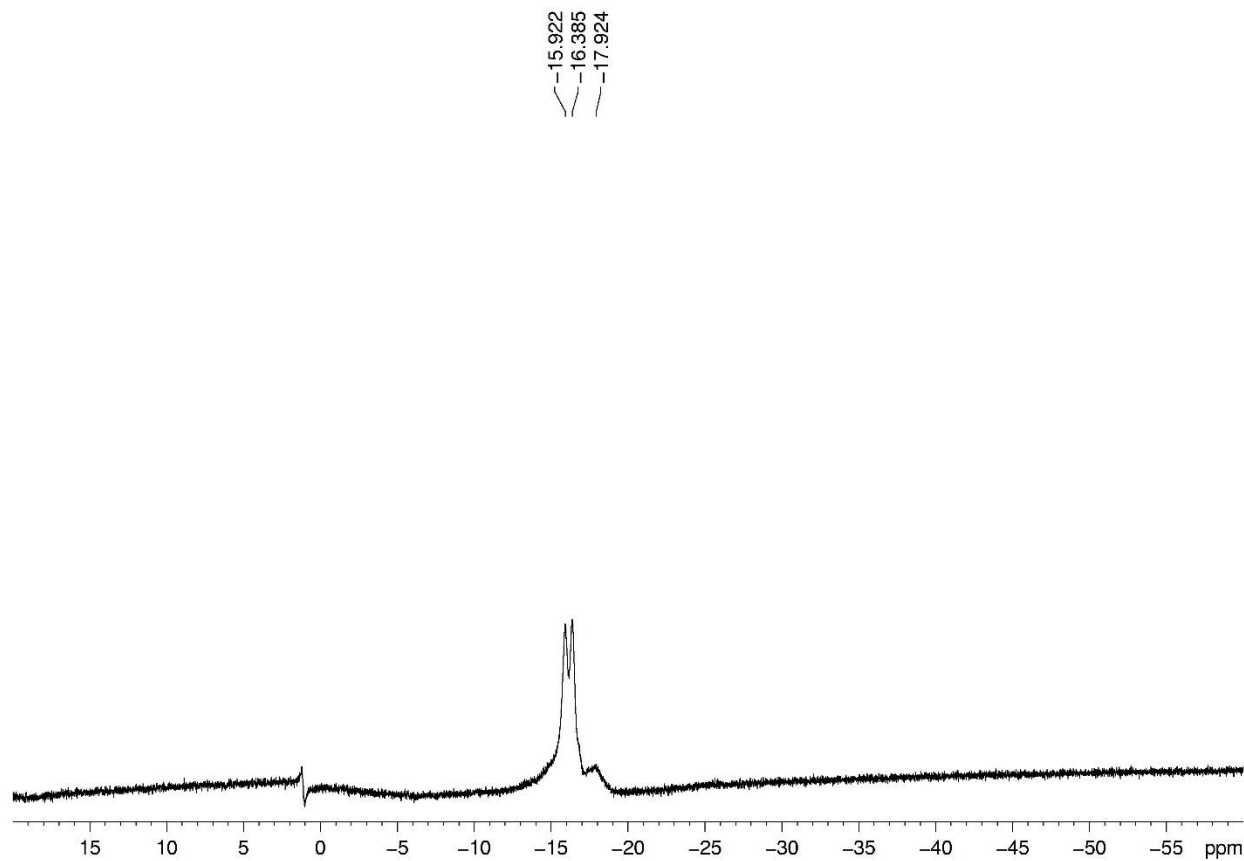
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **22**



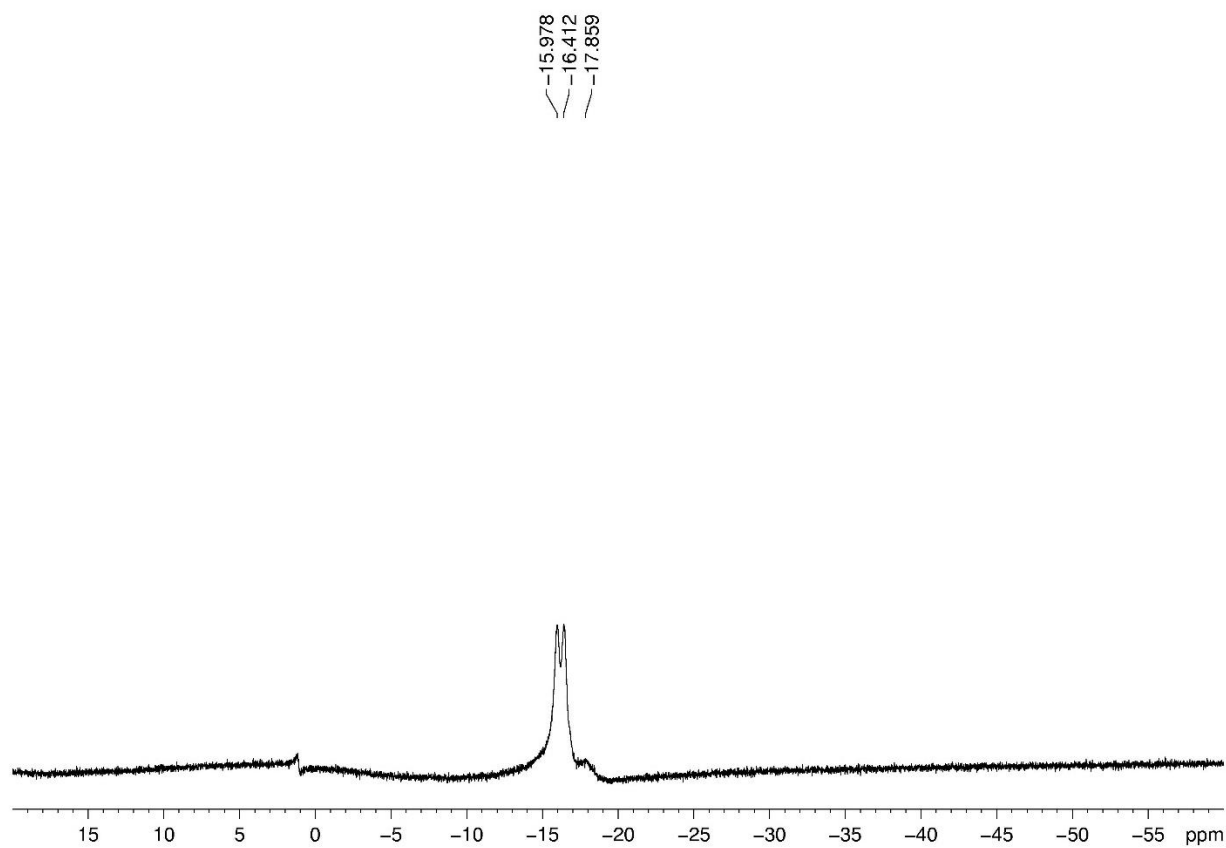
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **23**



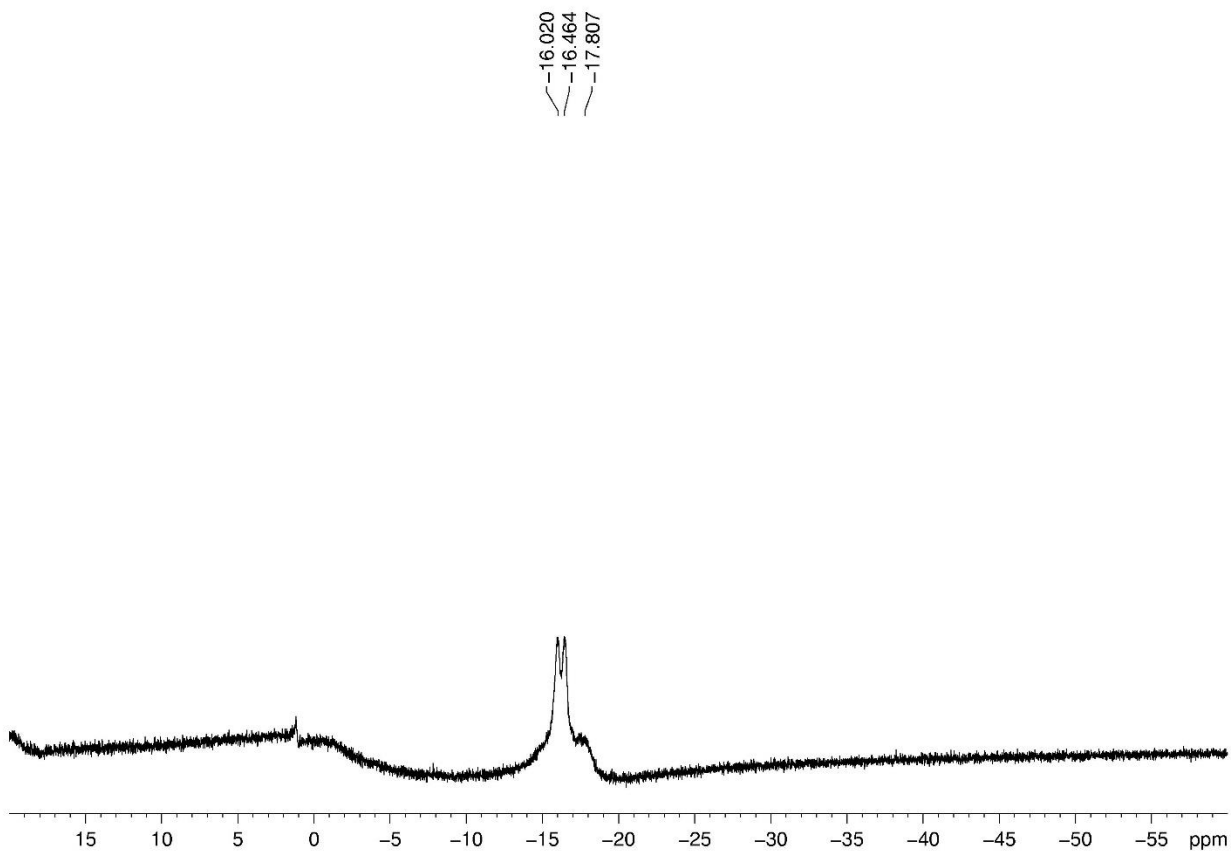
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **24**



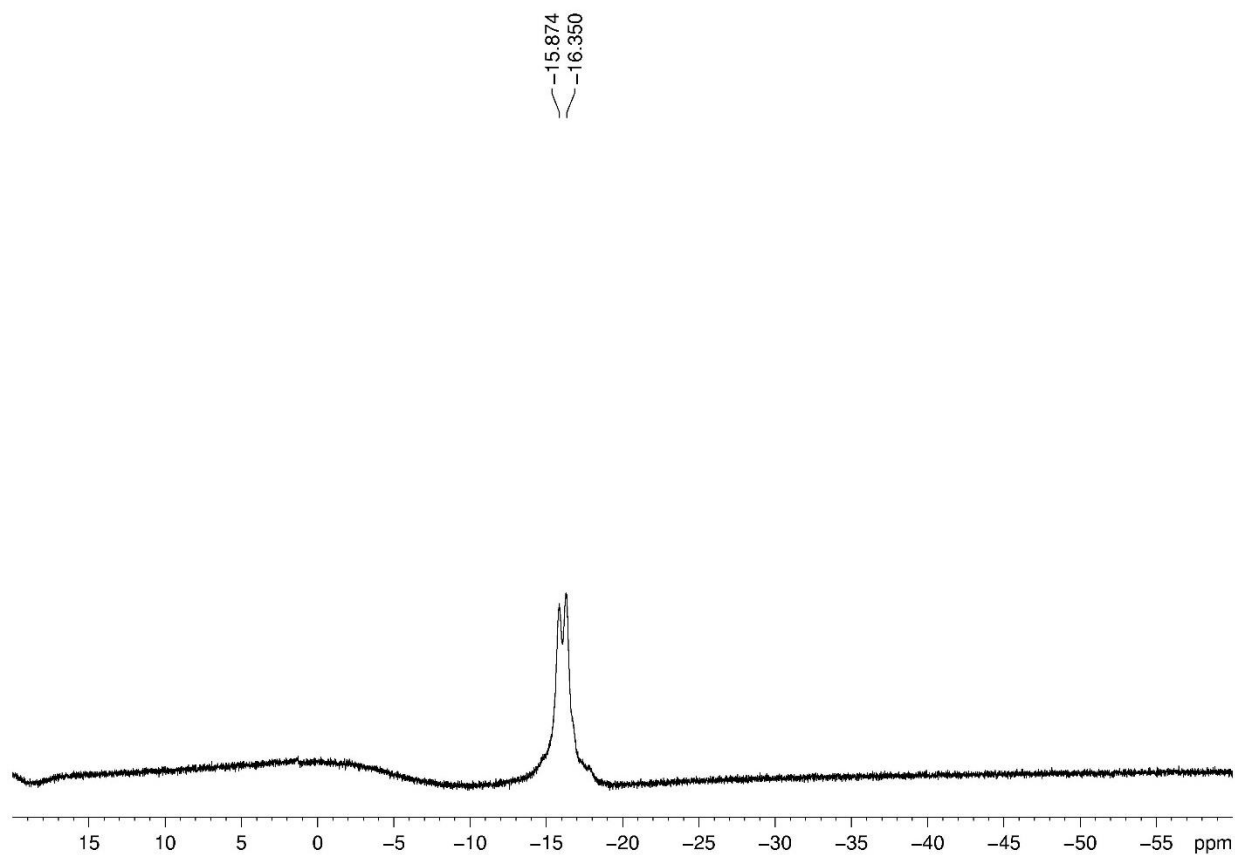
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **25**



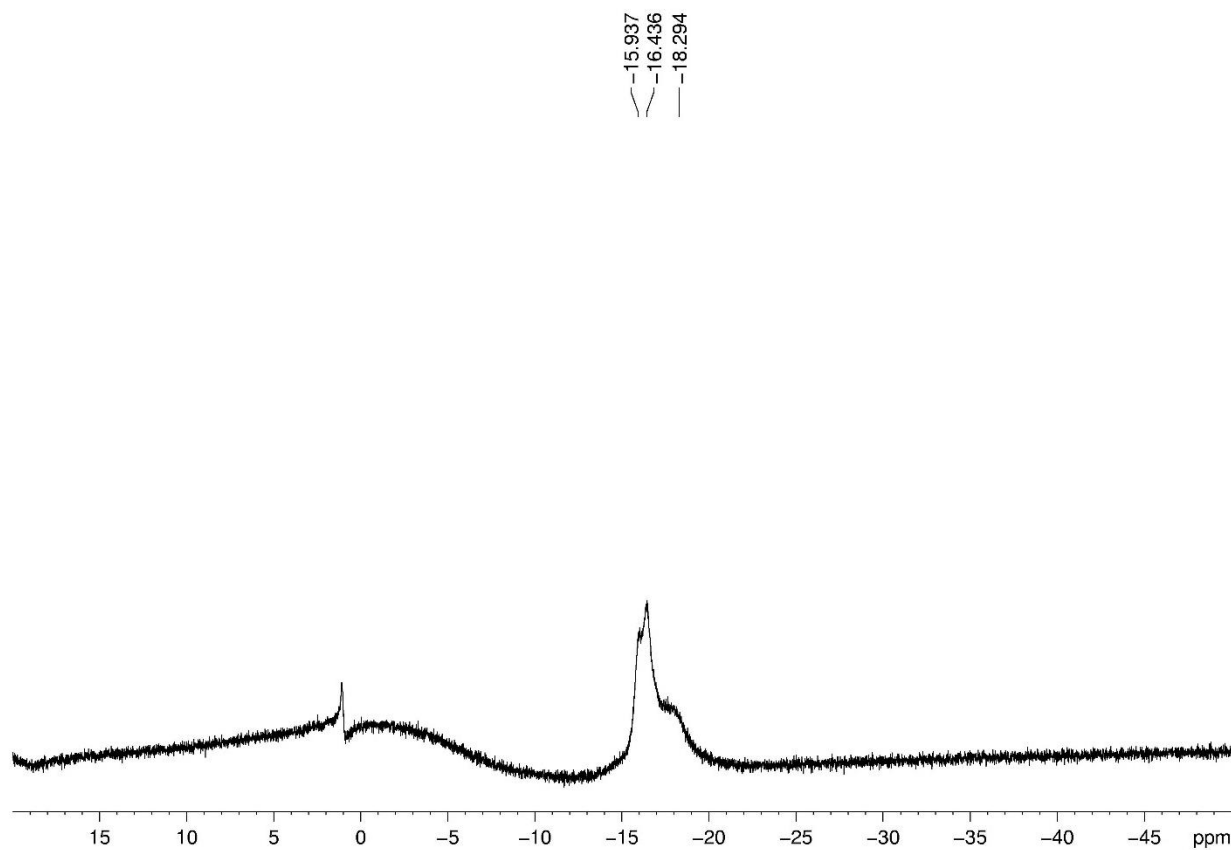
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **26**



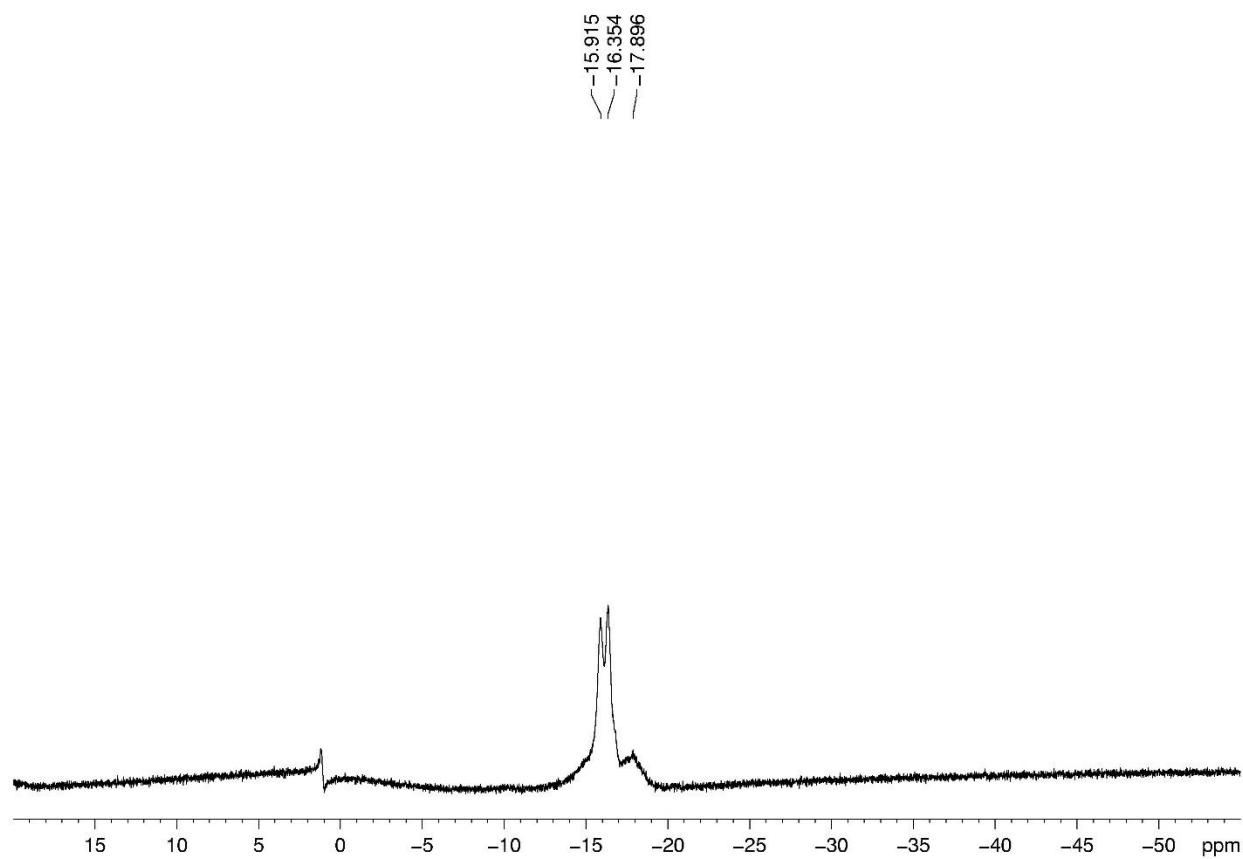
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **27**



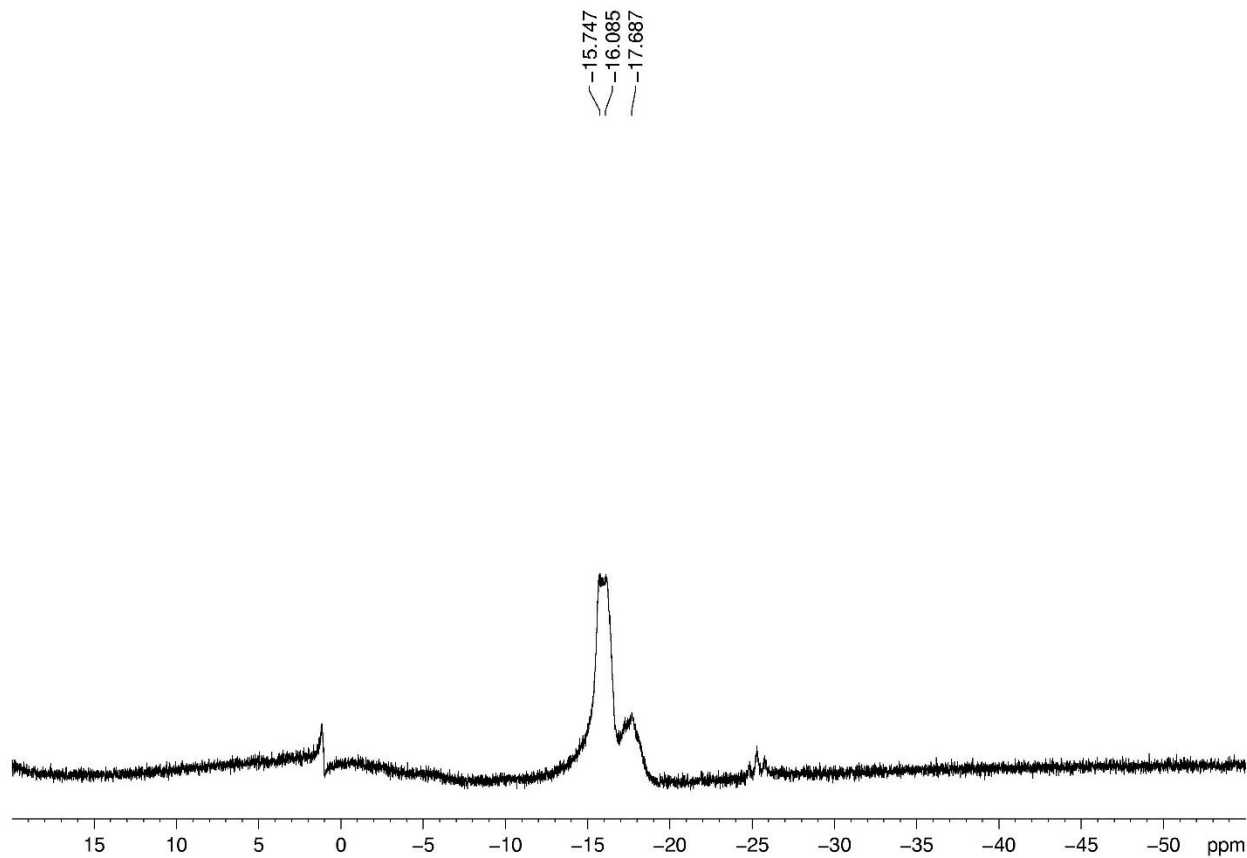
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **28**



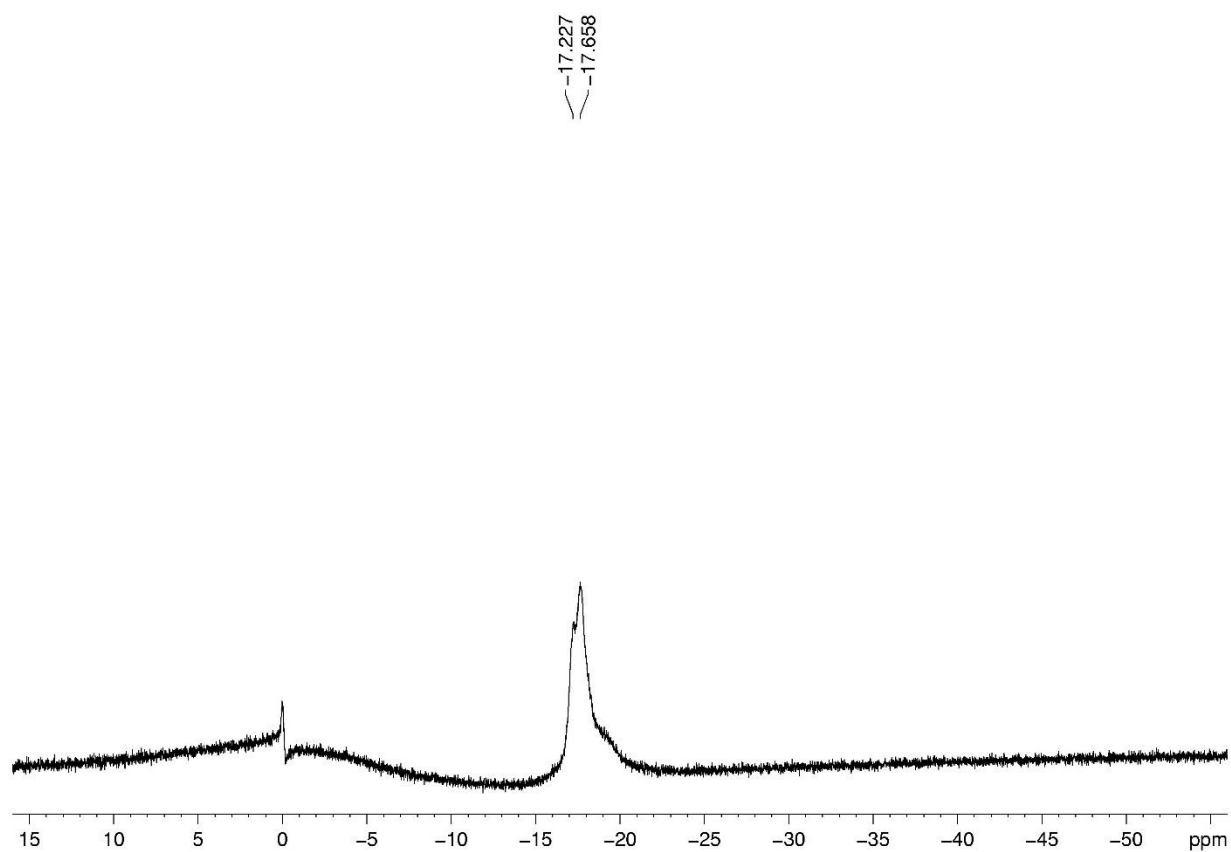
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **29**



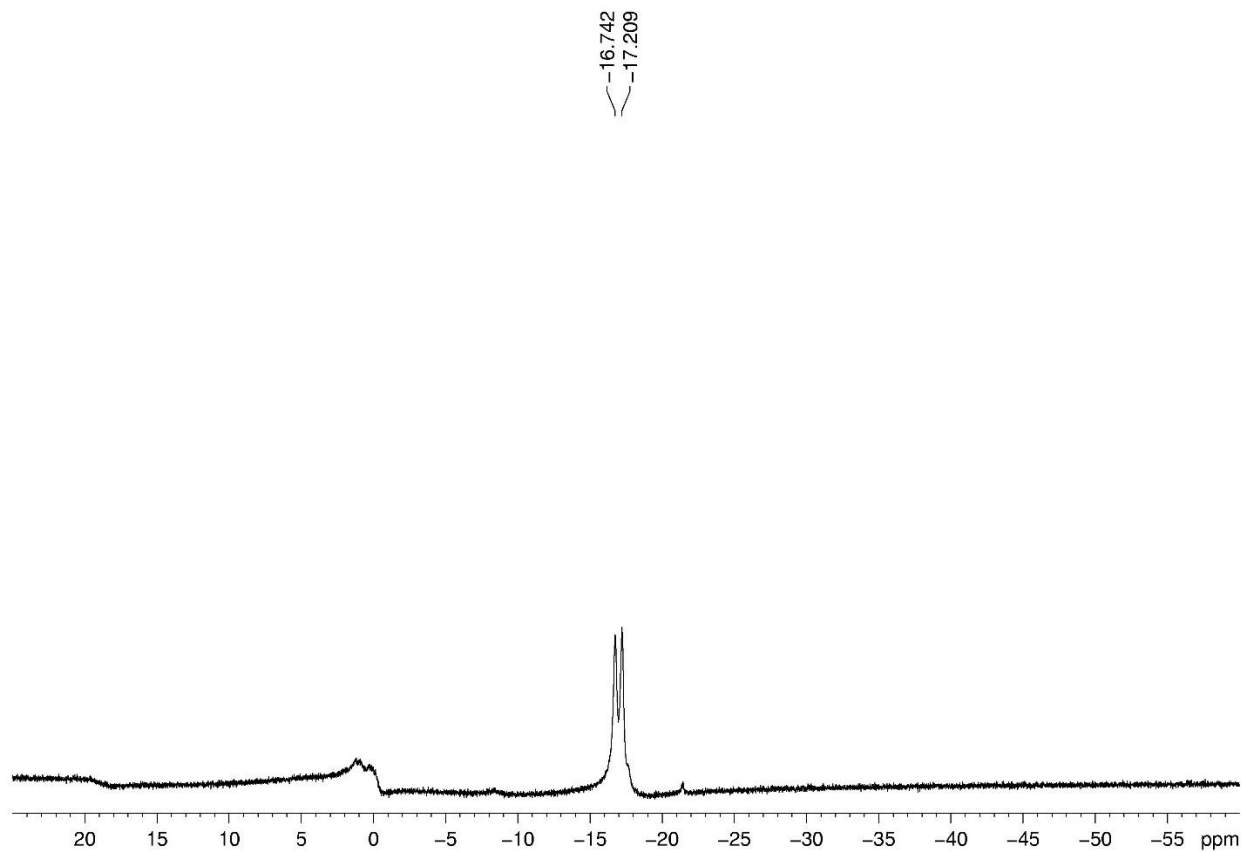
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **30**



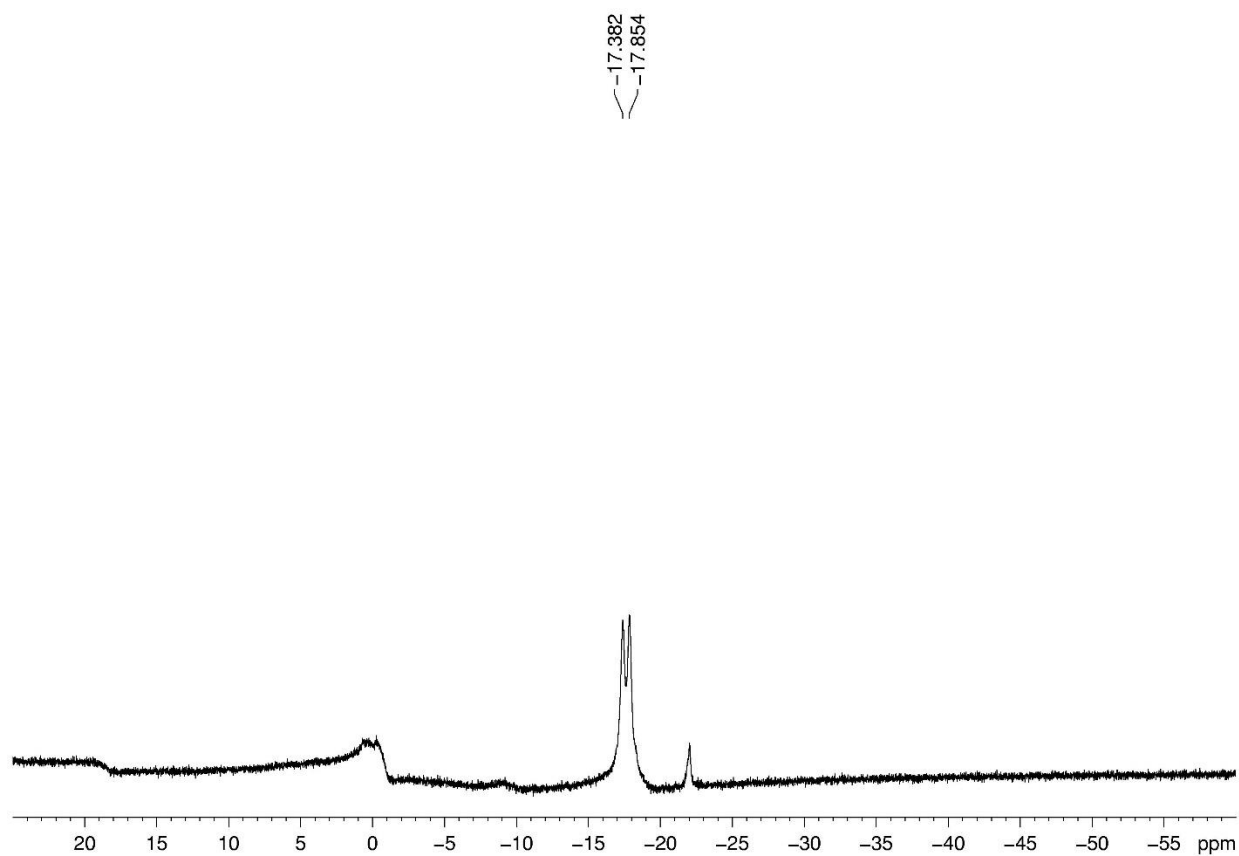
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **31**



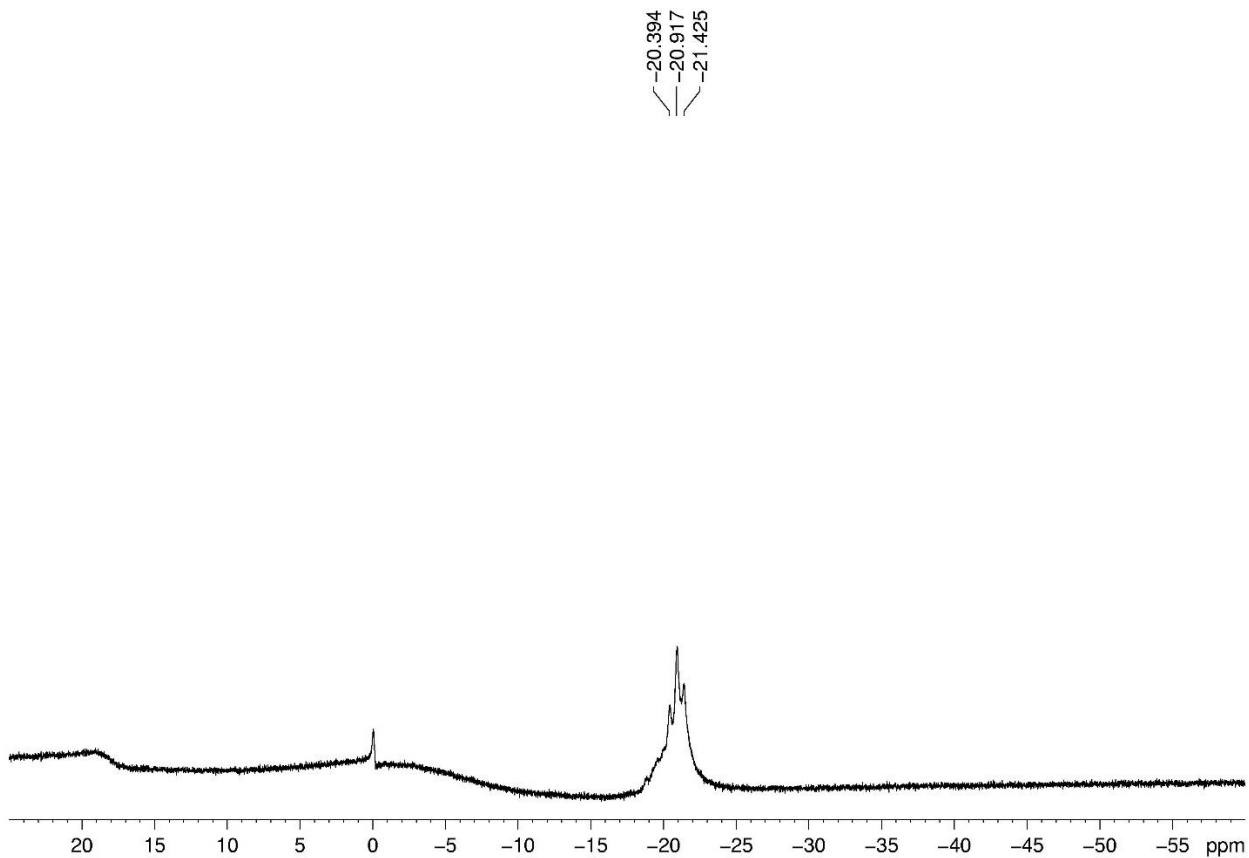
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **32**



$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **33**

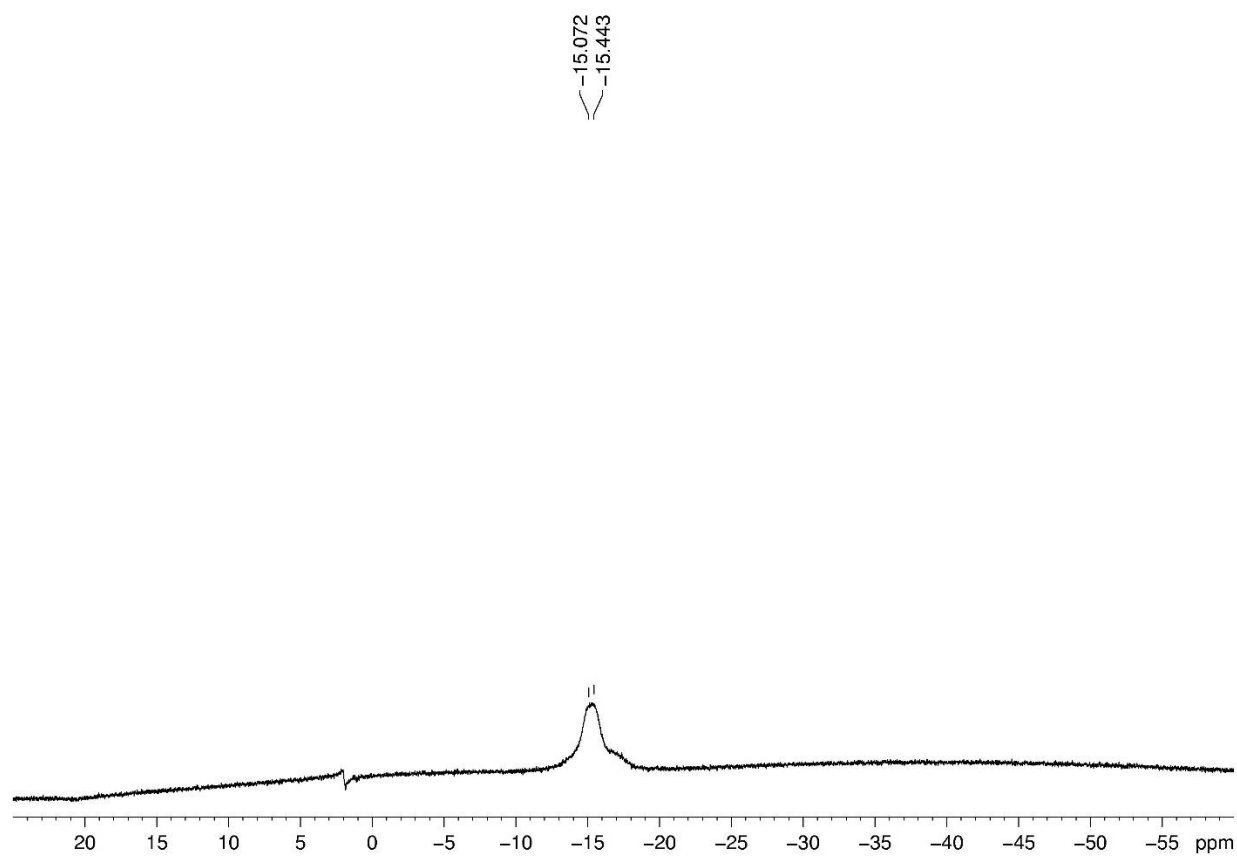


$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **34**

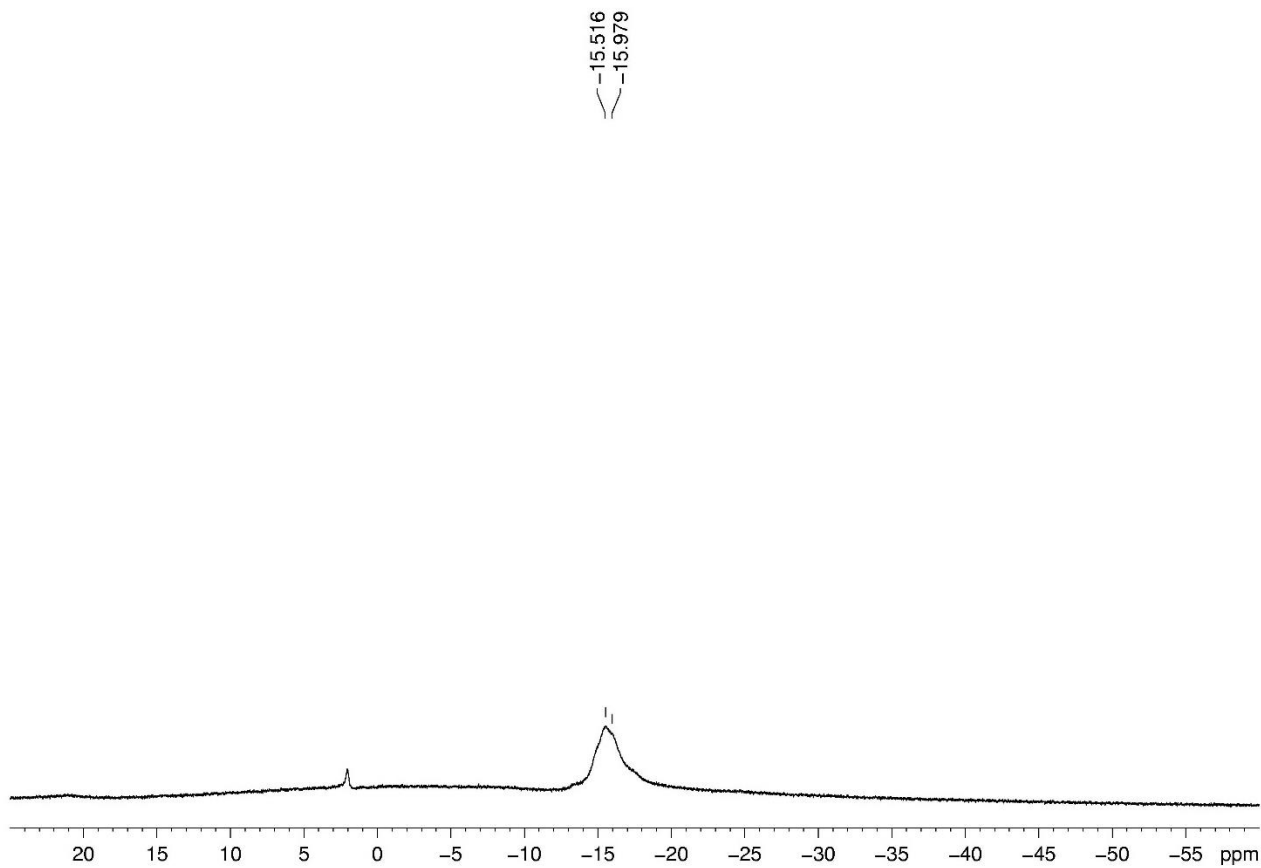




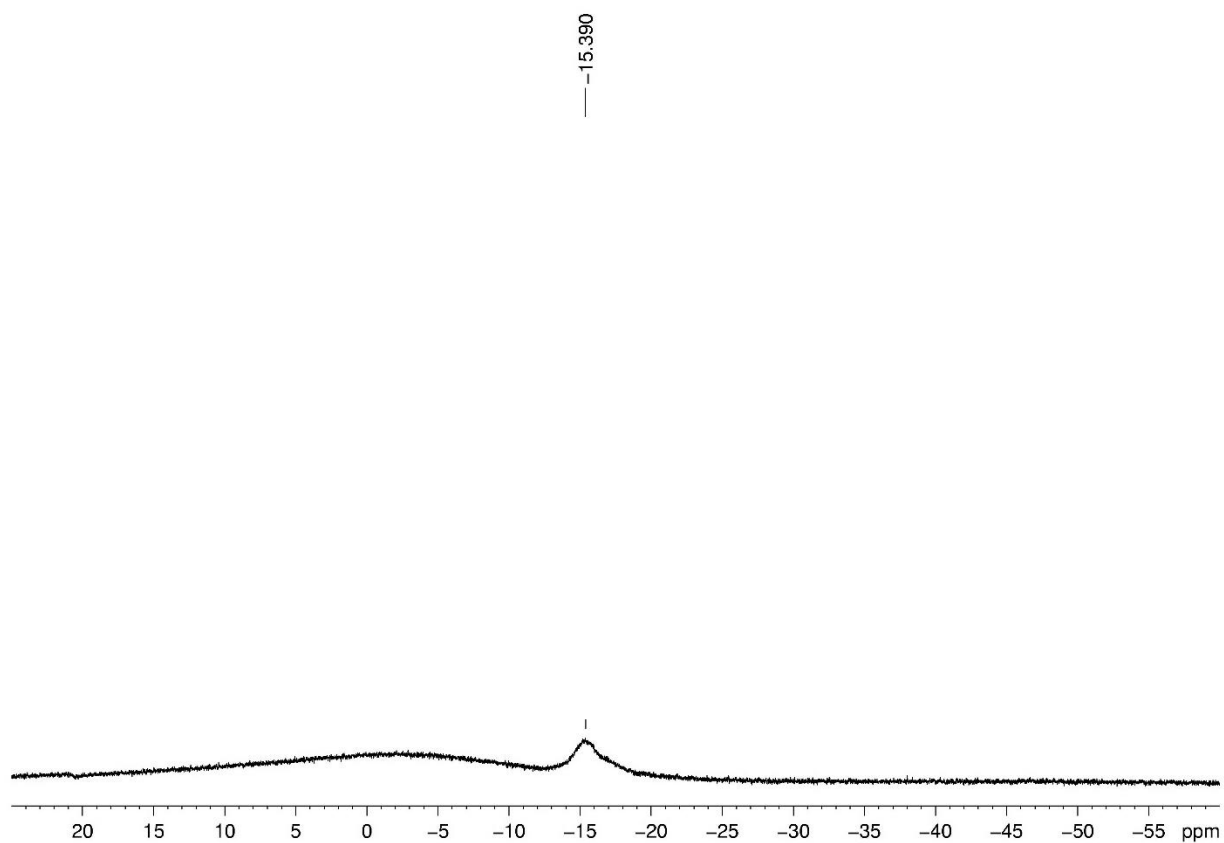
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **35**



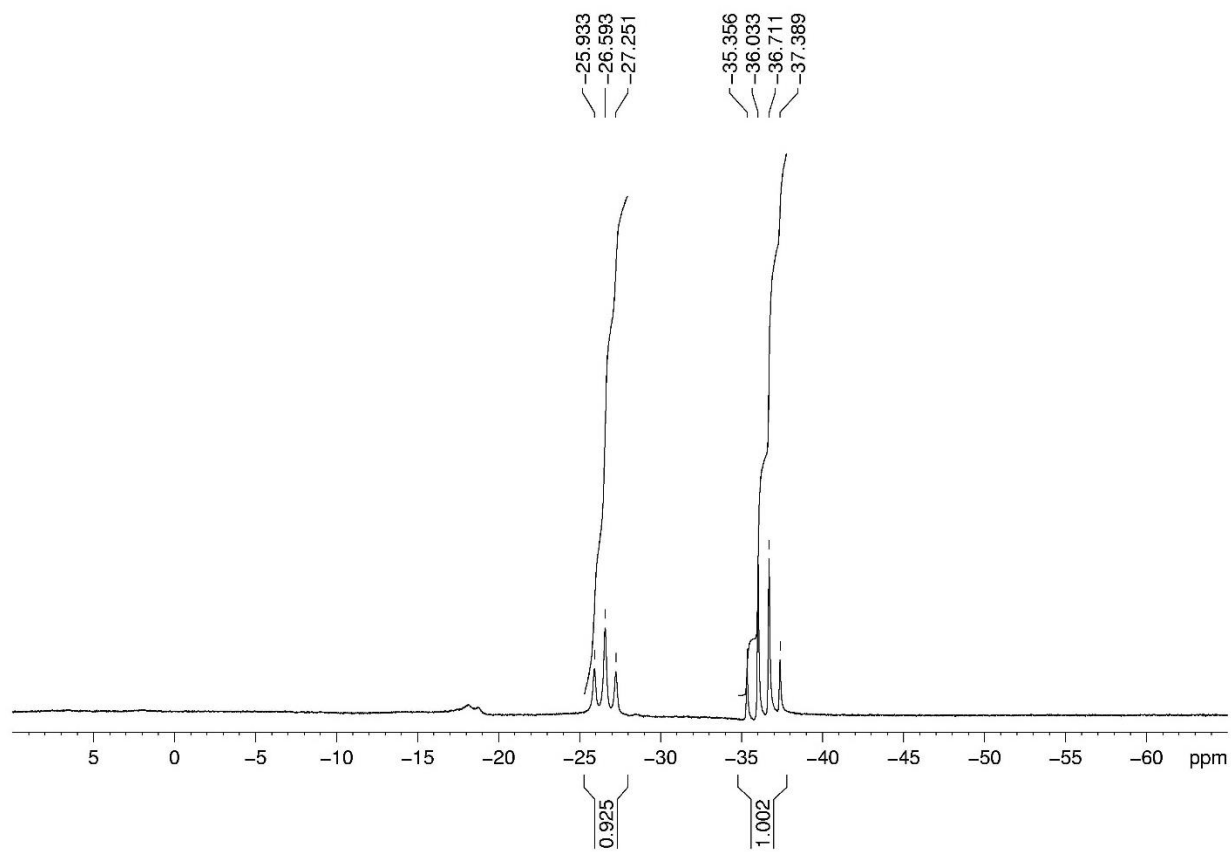
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **36**



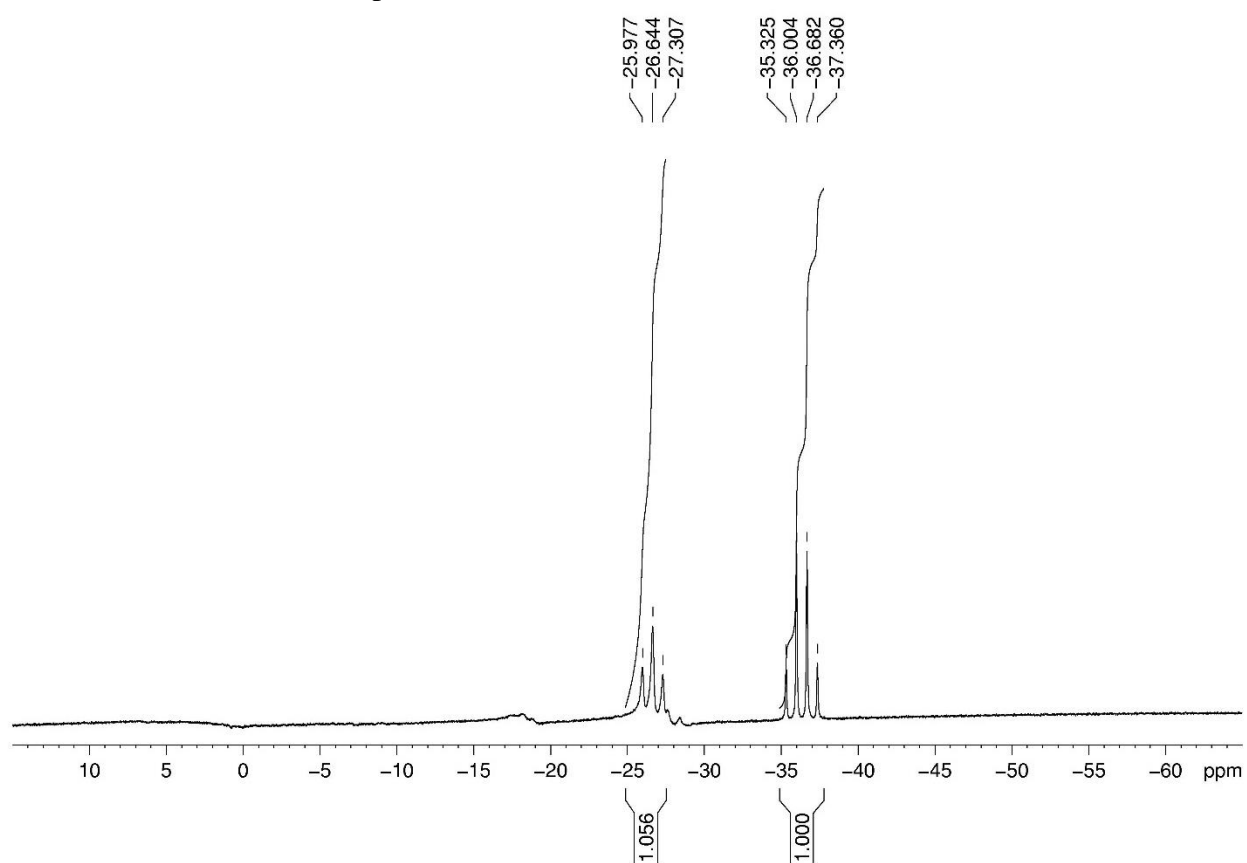
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **37**



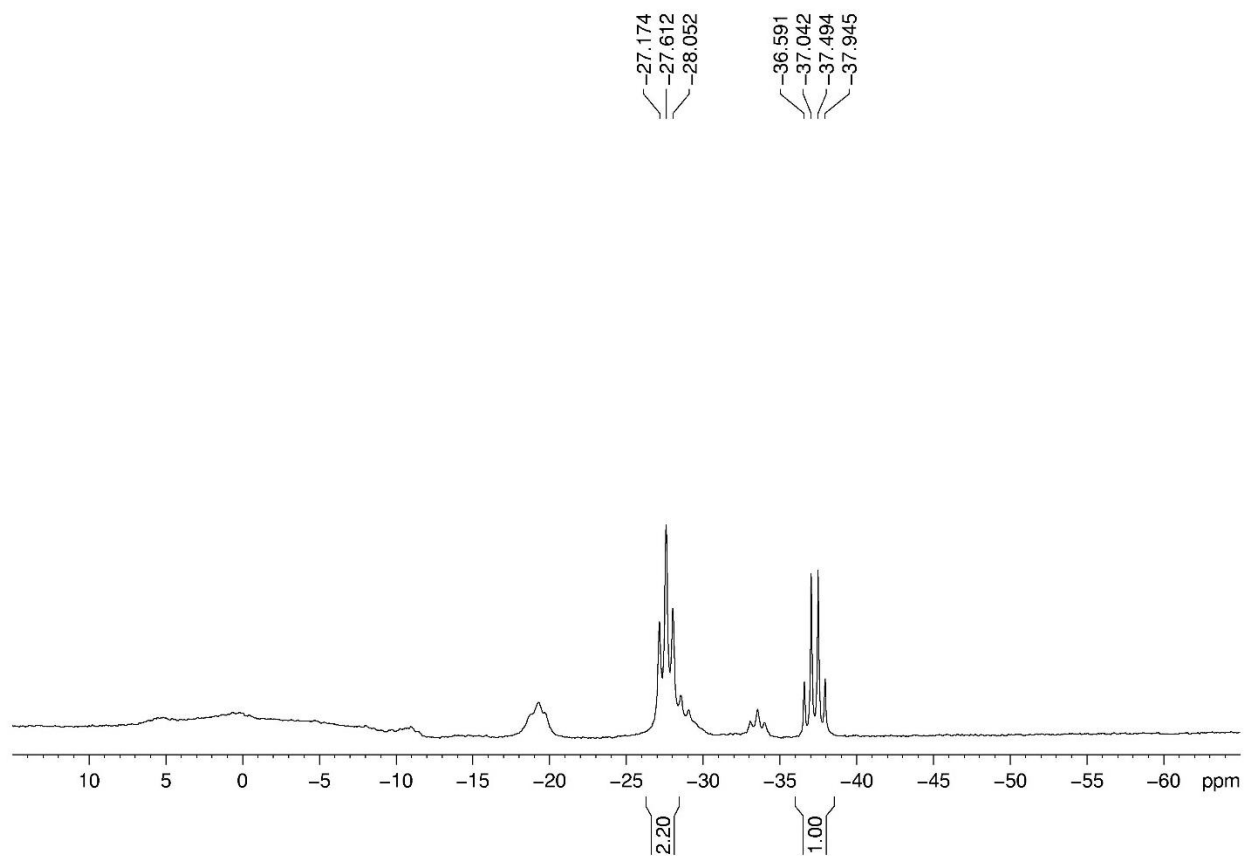
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **38**



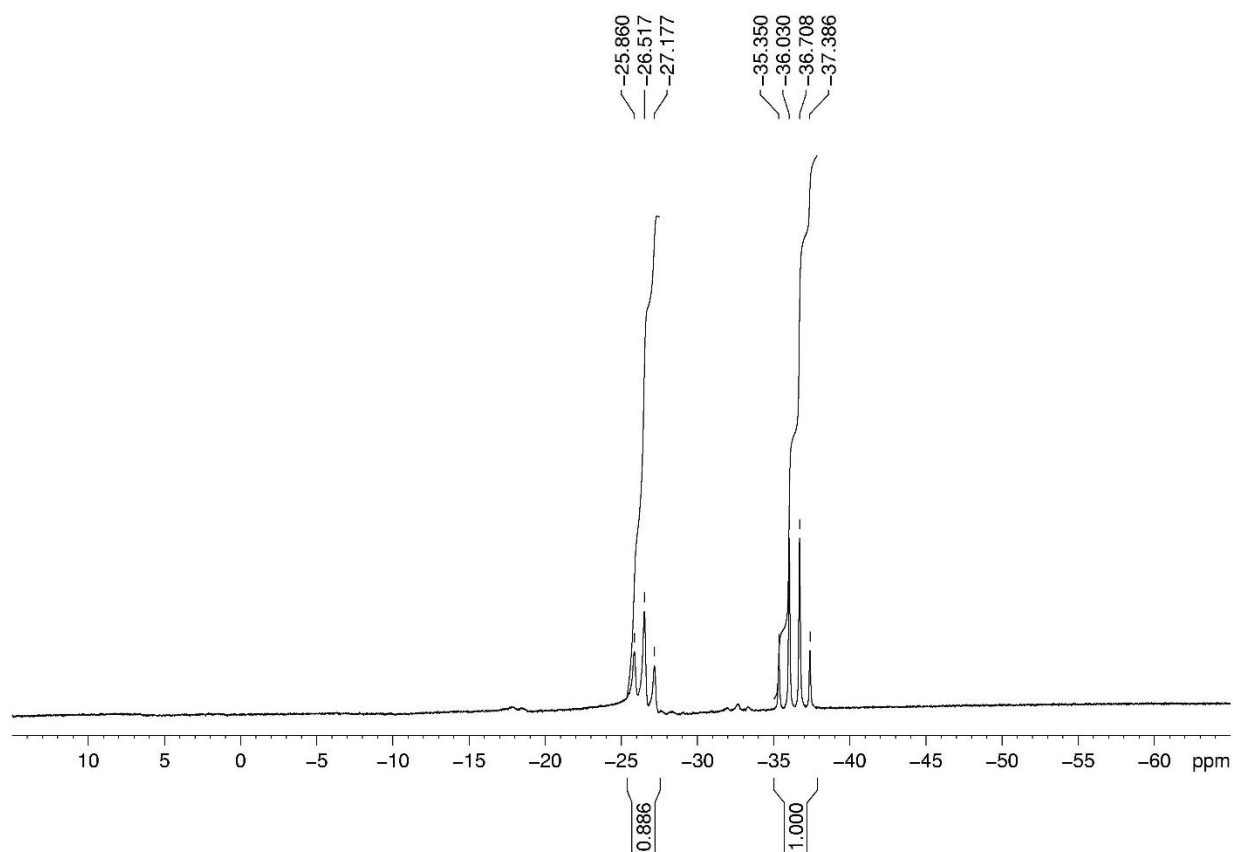
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **39**



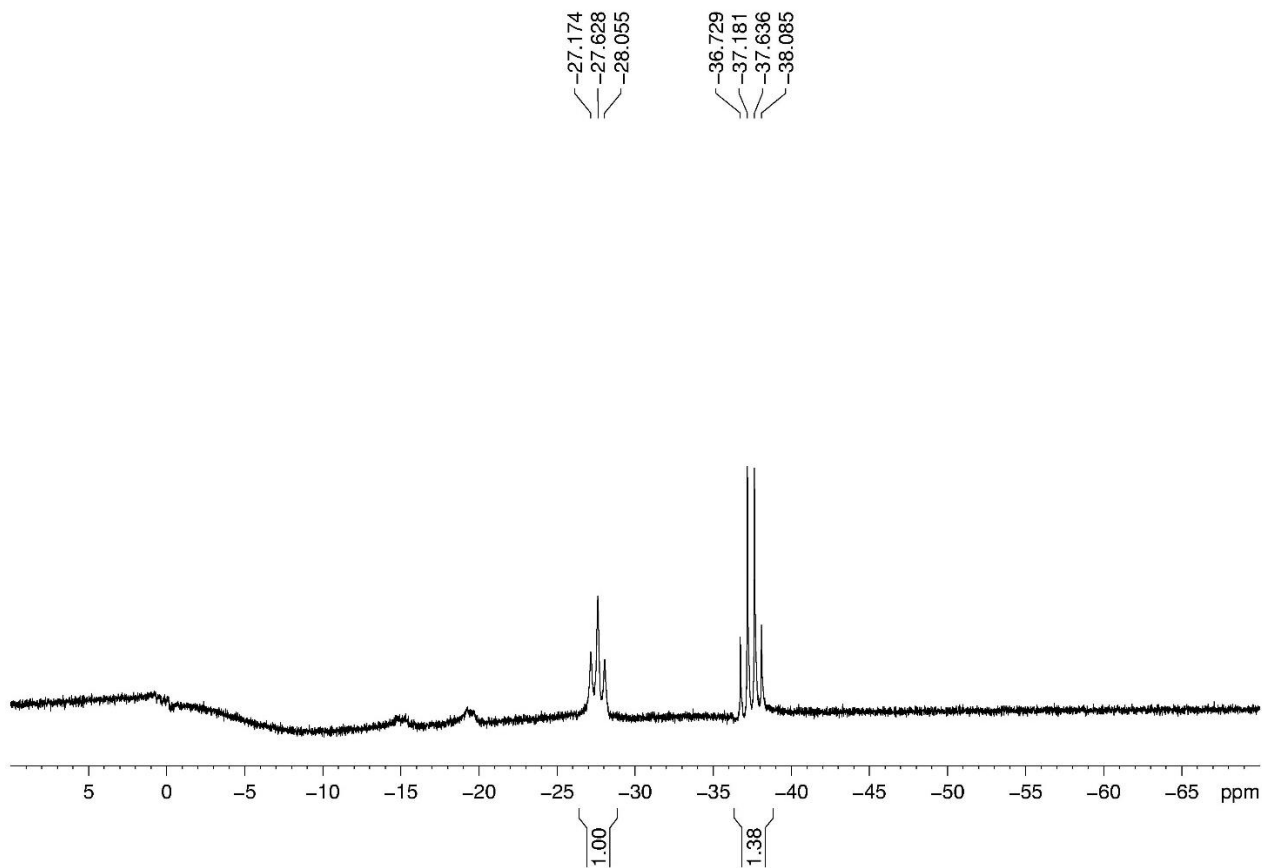
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **40**



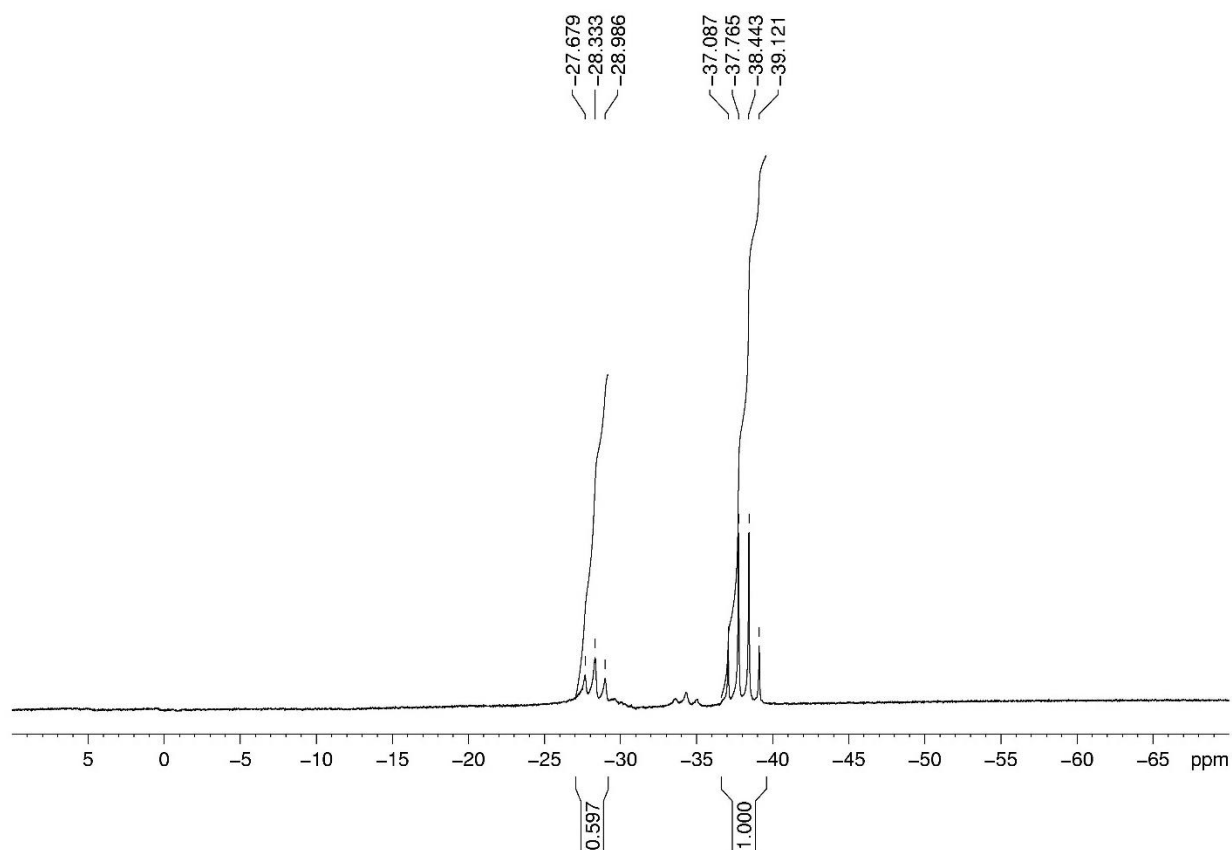
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **41**



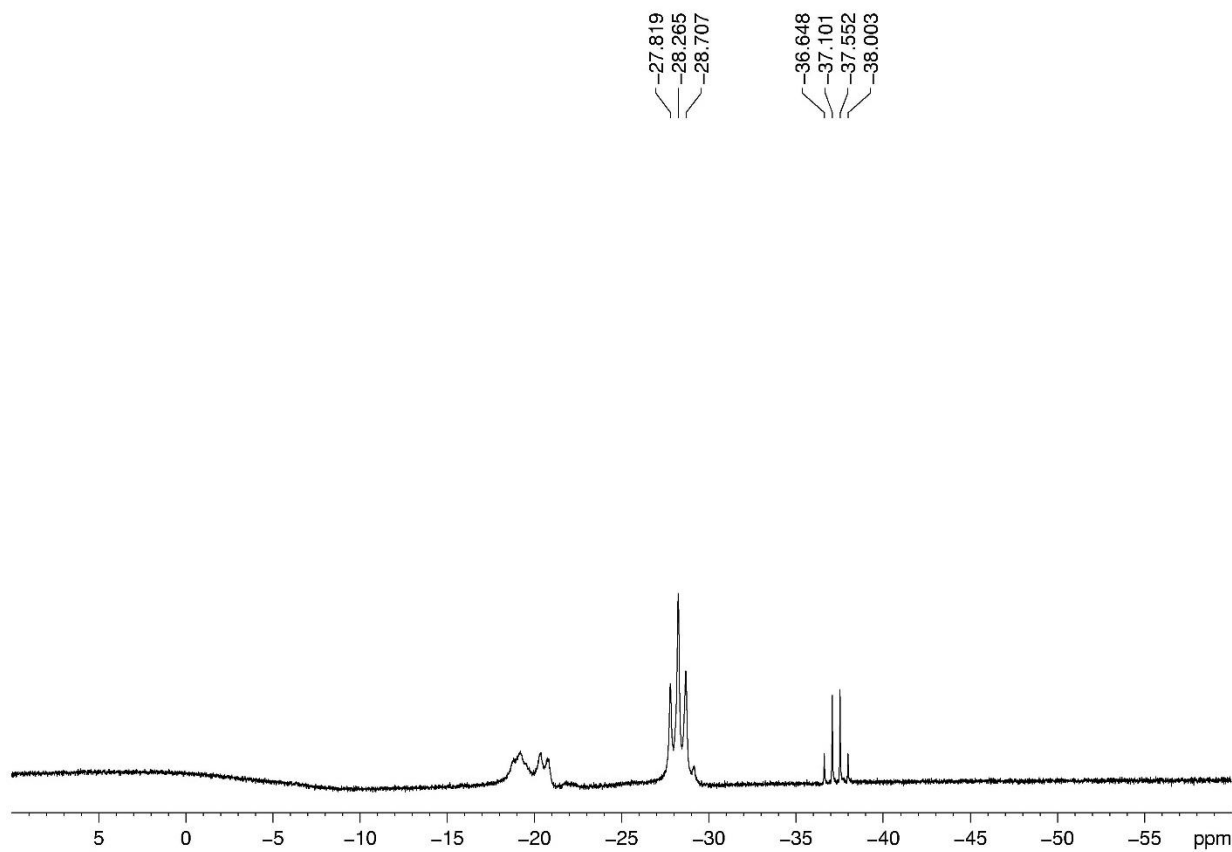
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **42**



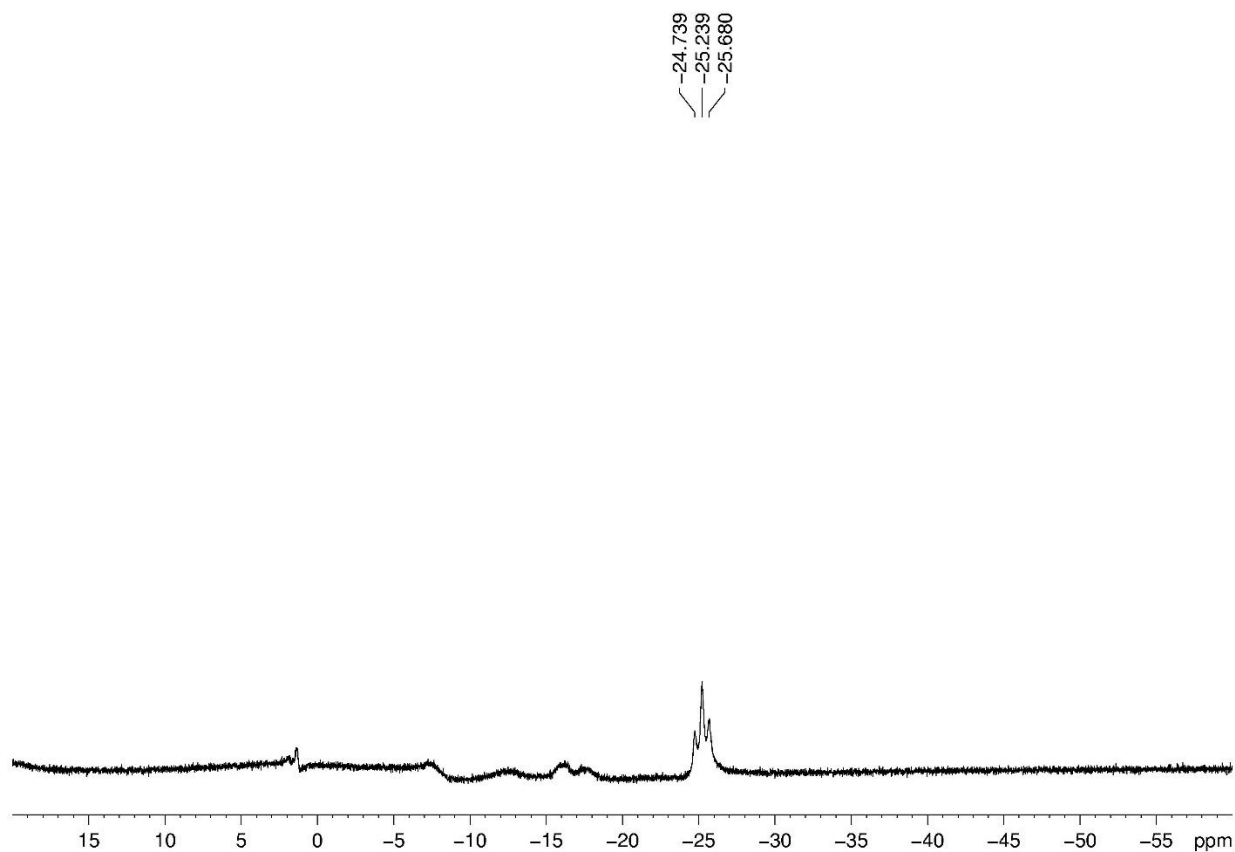
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **43**



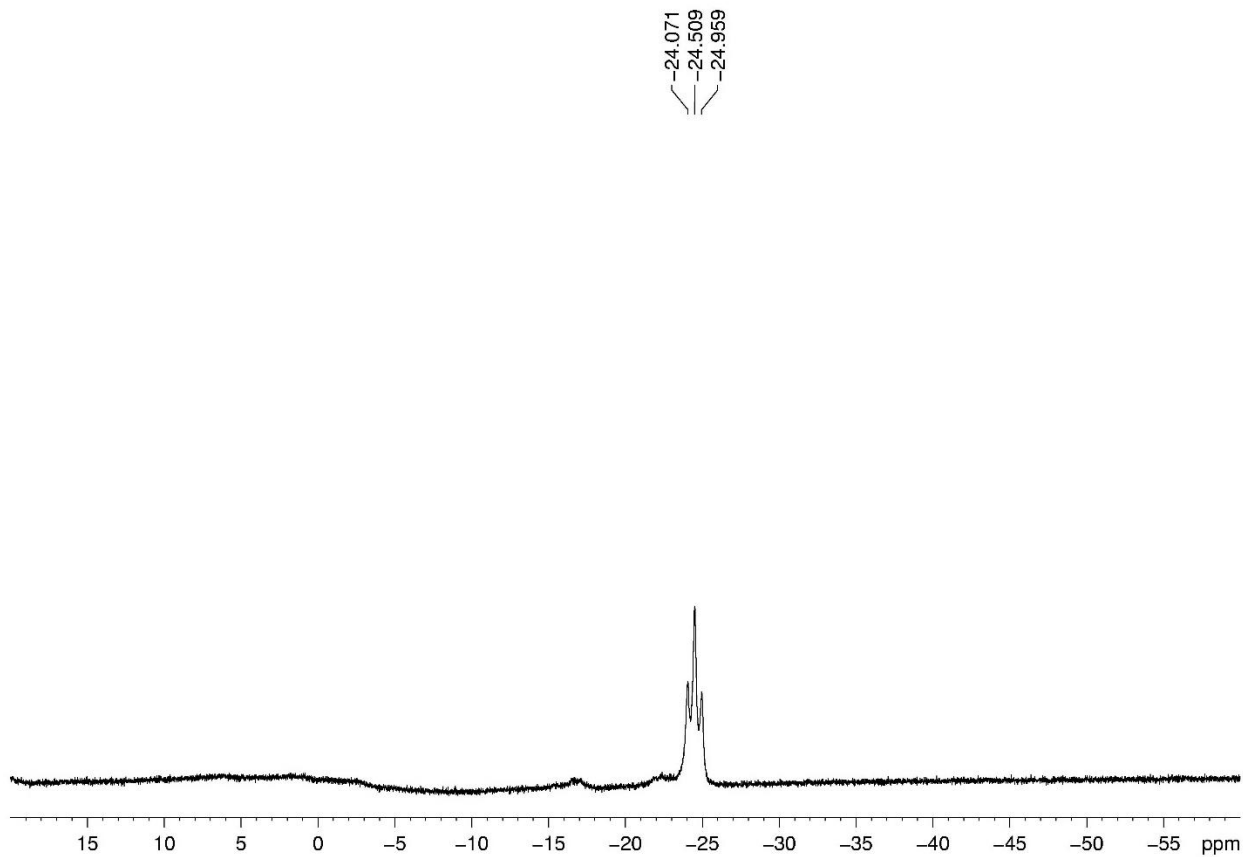
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **44**



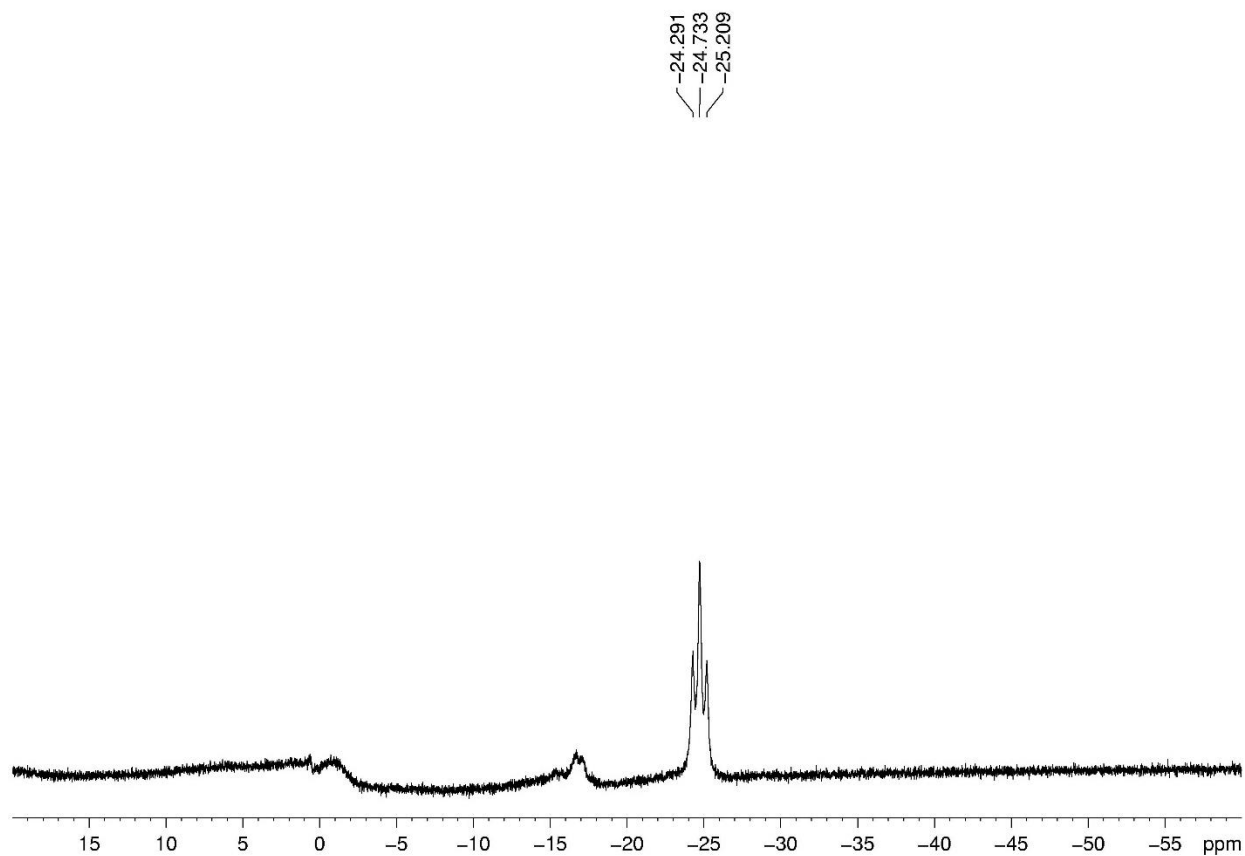
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **45**



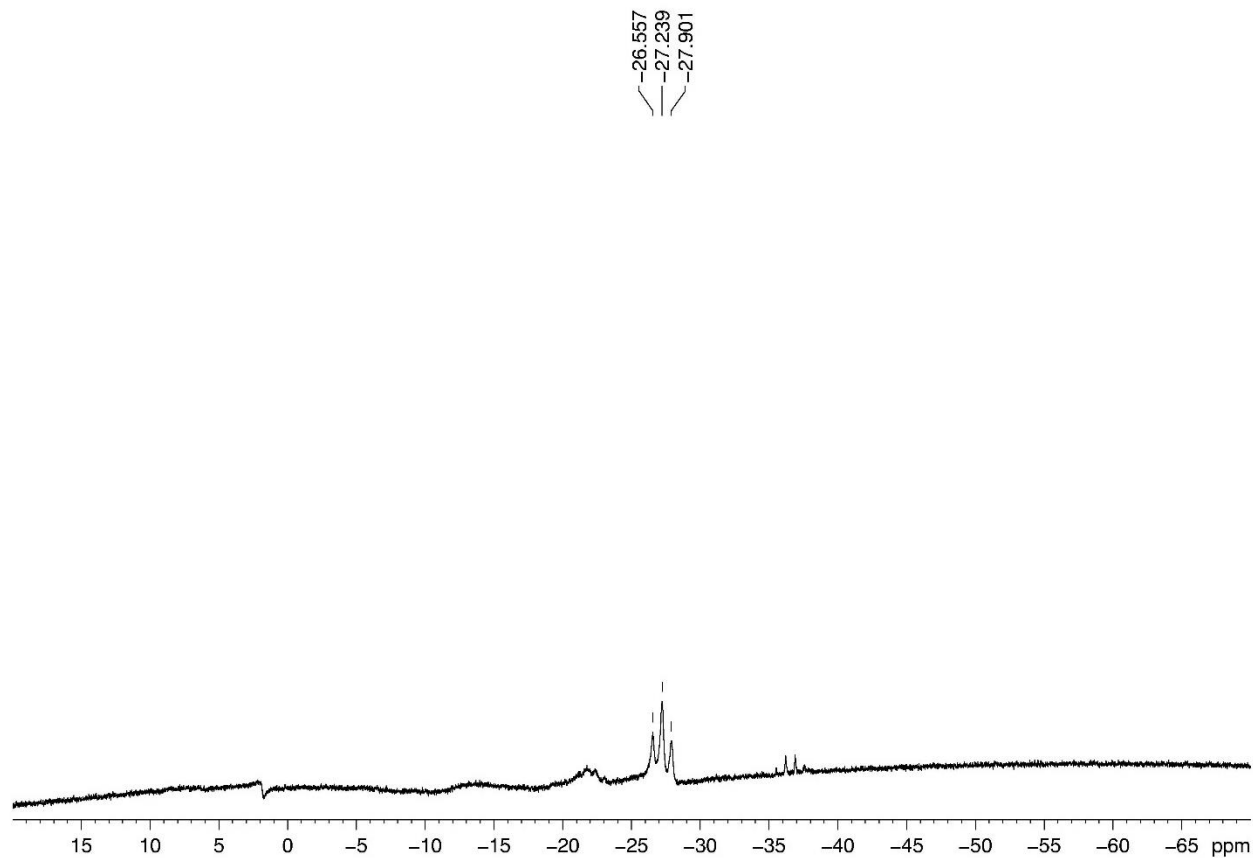
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **46**



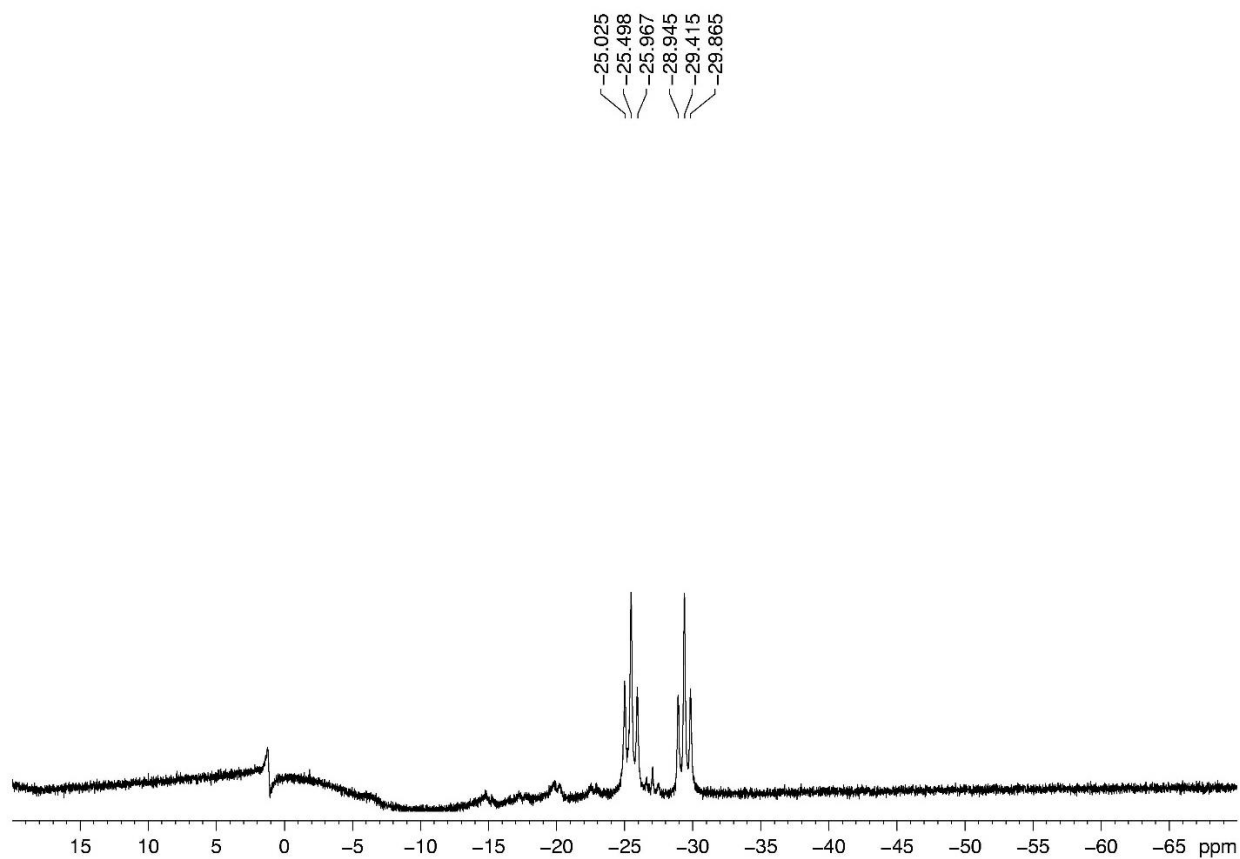
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **47**



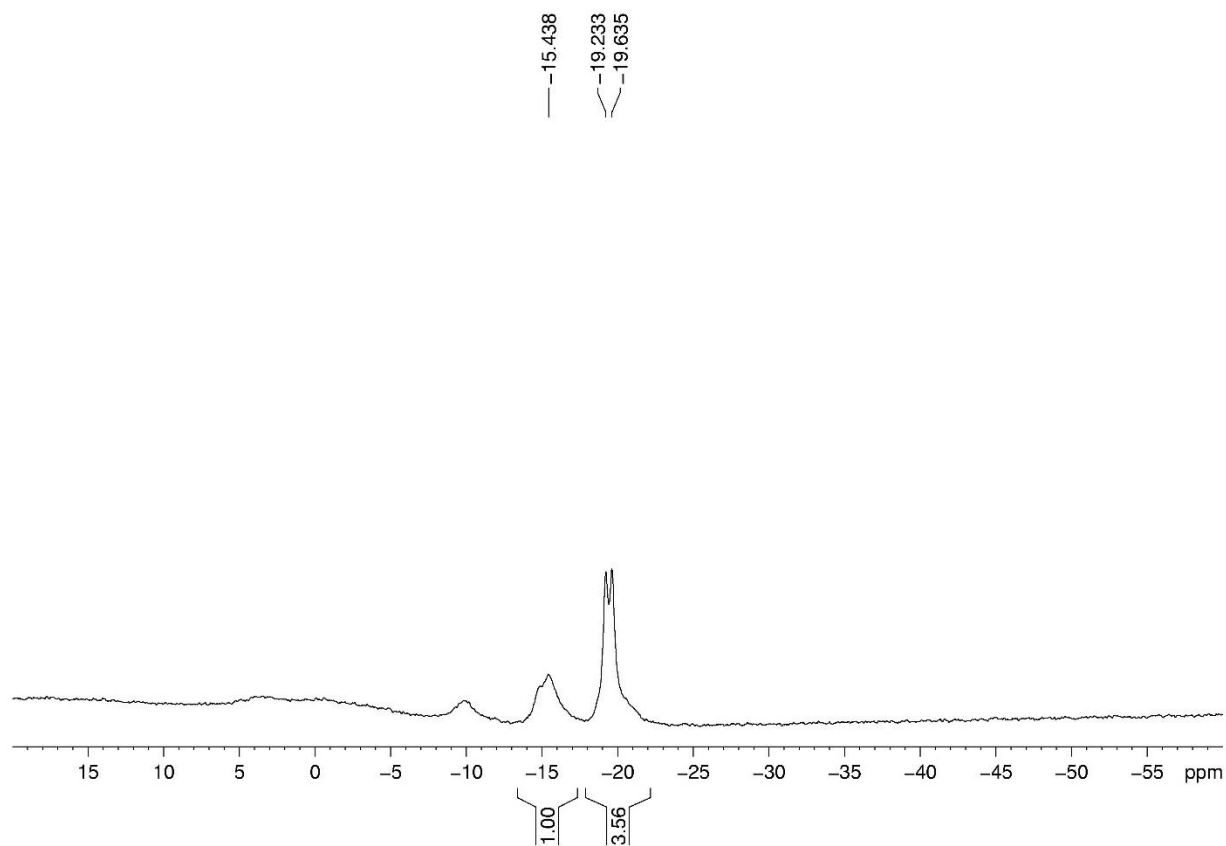
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **48**



$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **49** and **50**

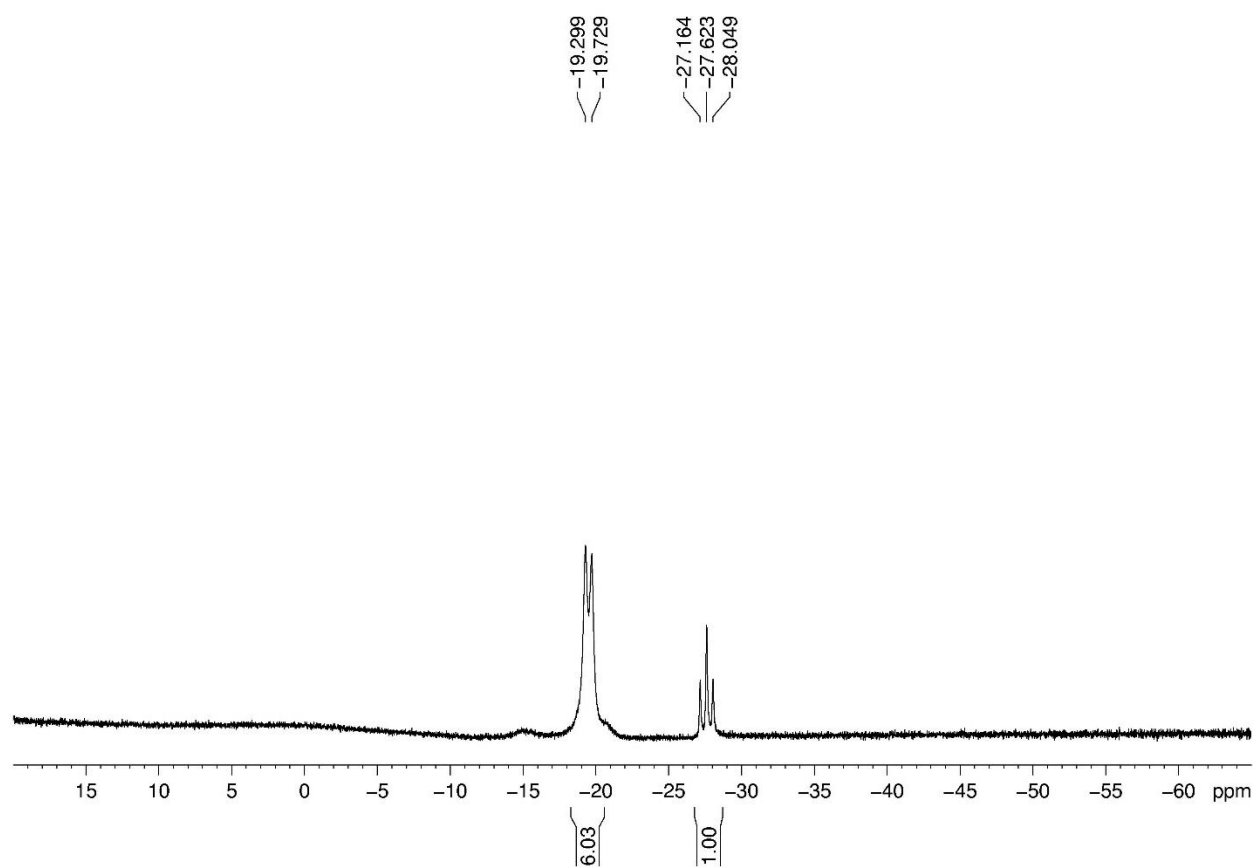


$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **51**

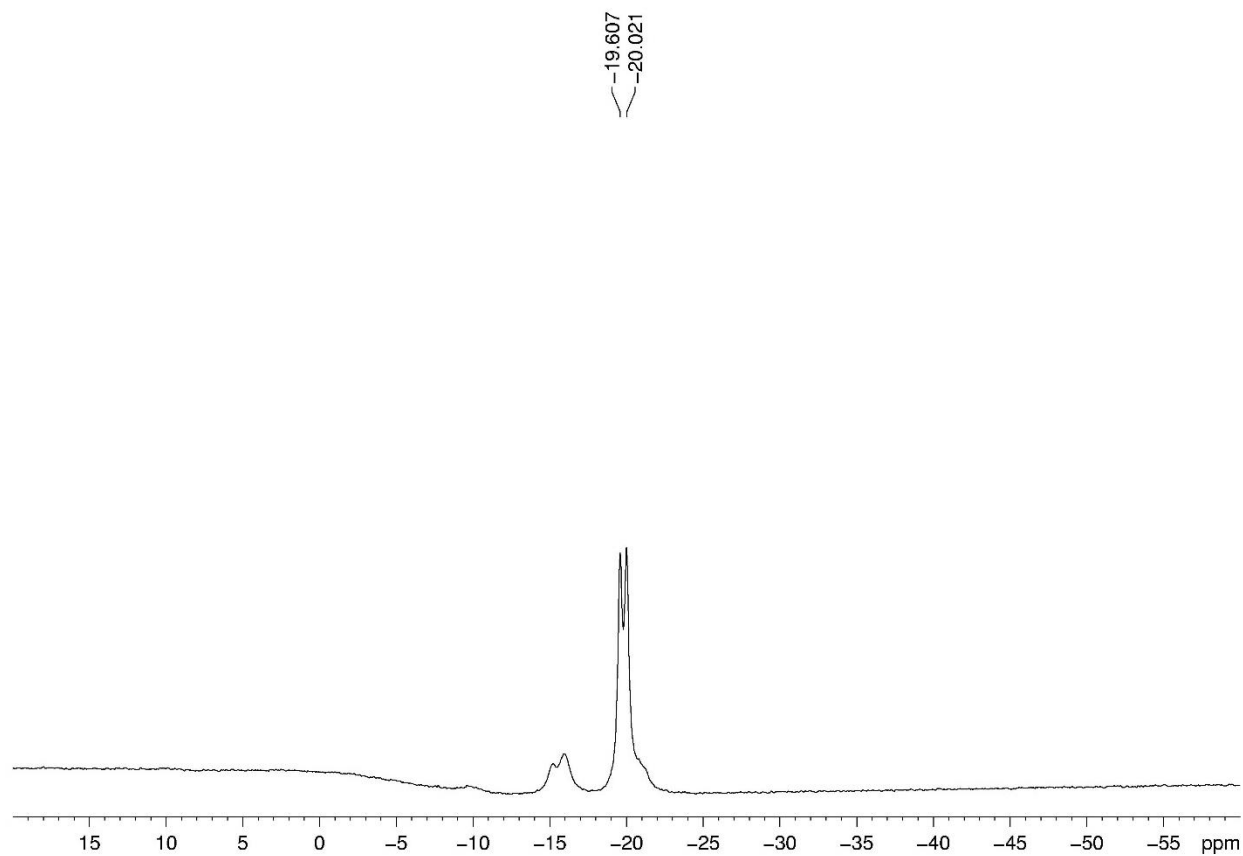




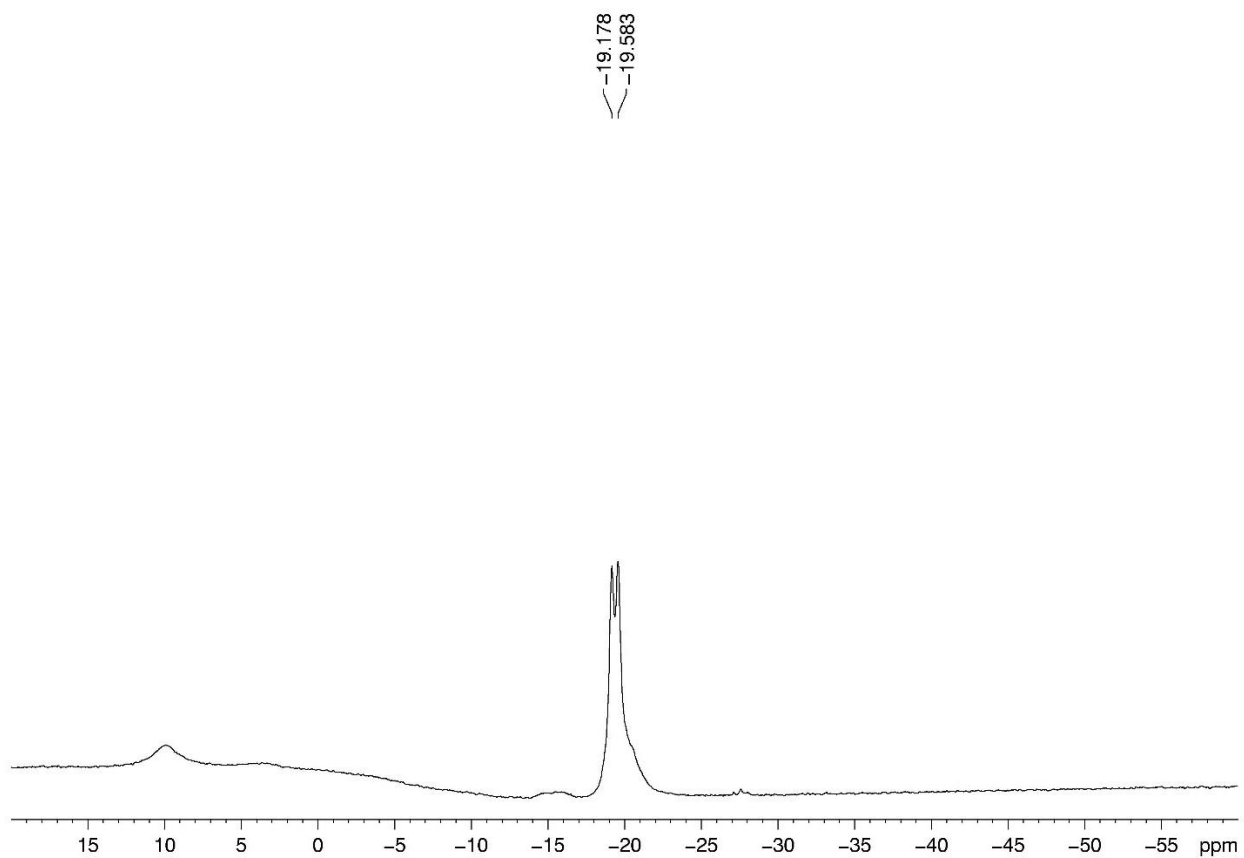
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **52**



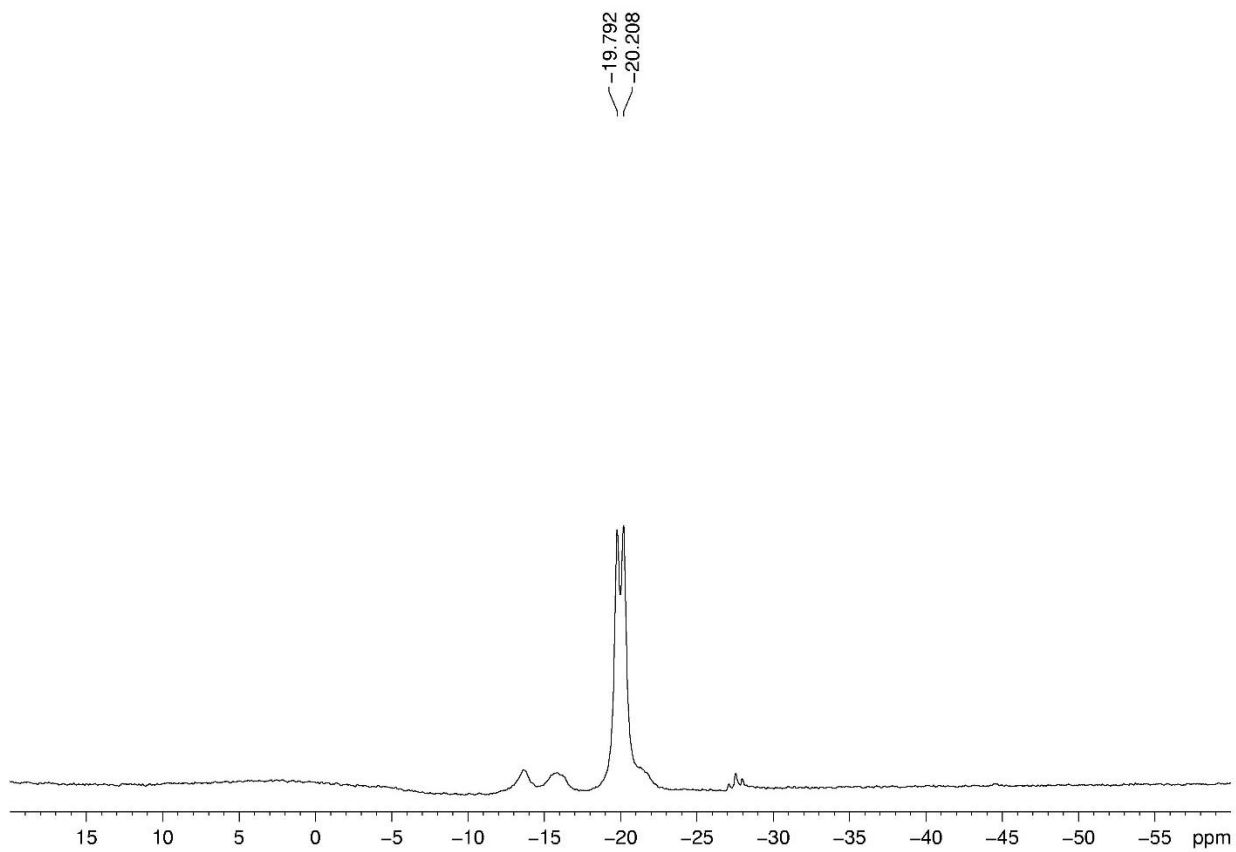
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **53**



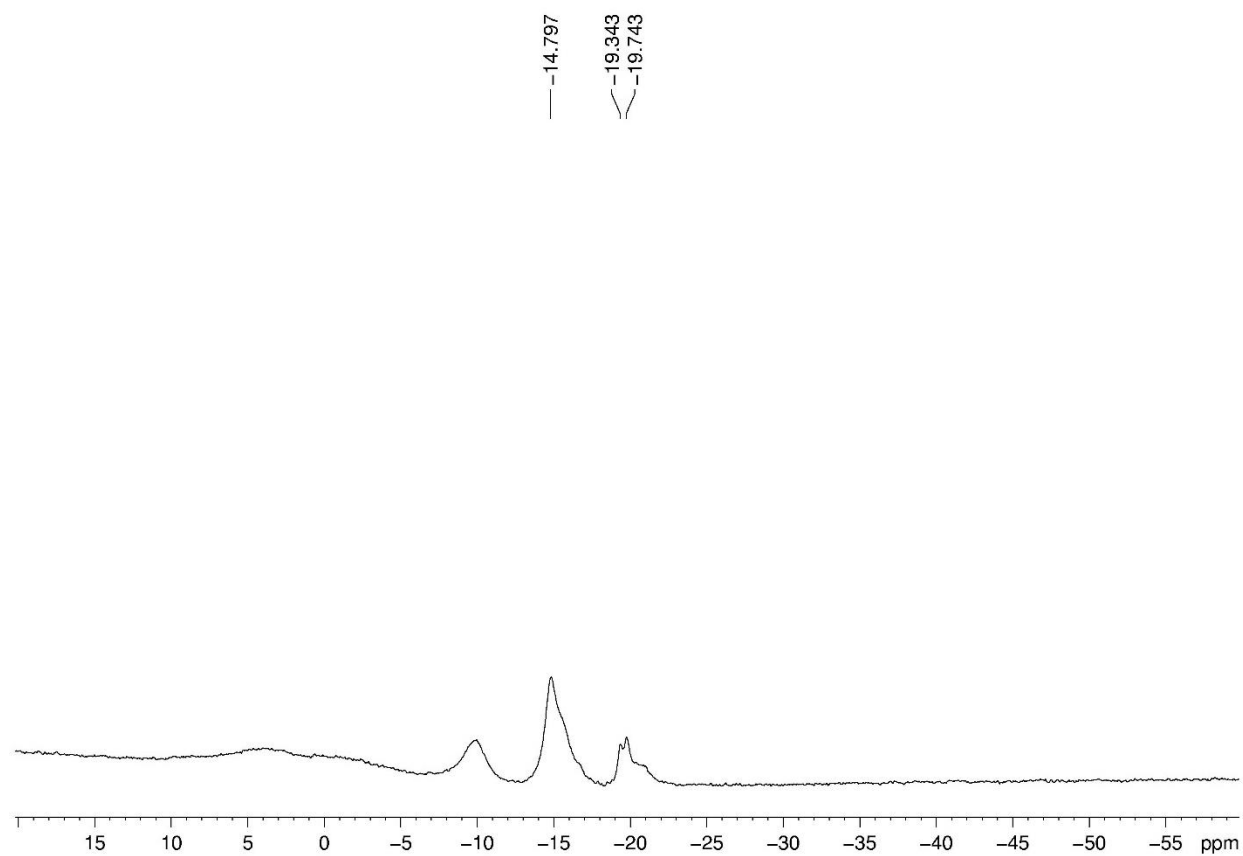
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **54**



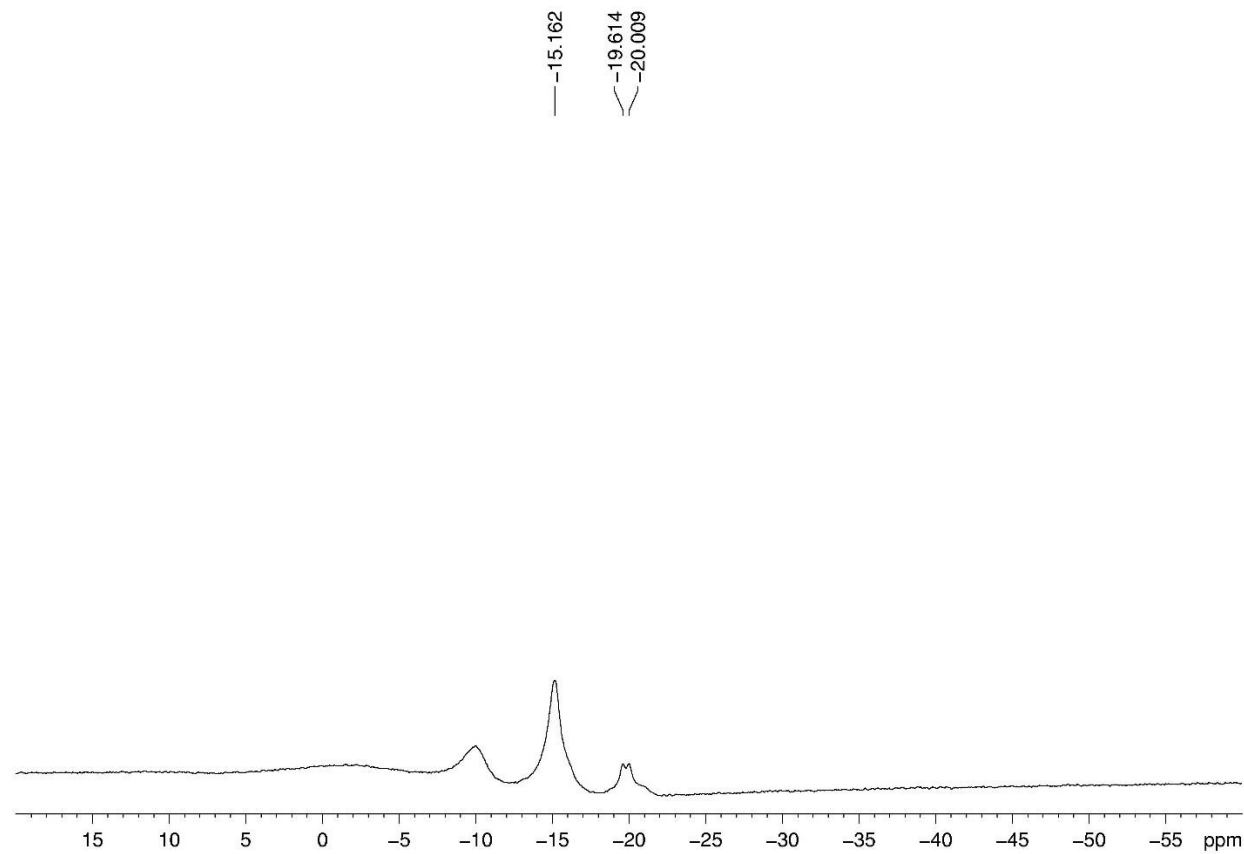
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **55**



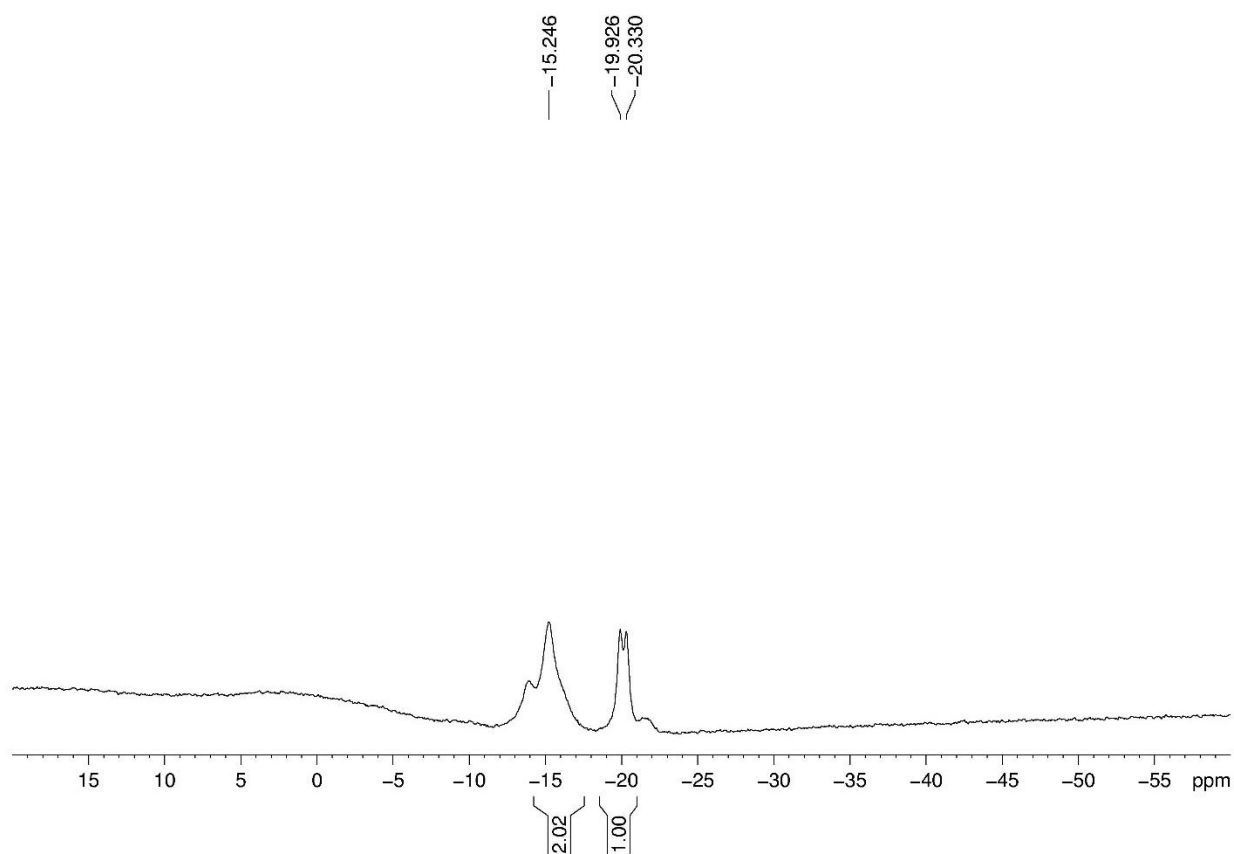
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **56**



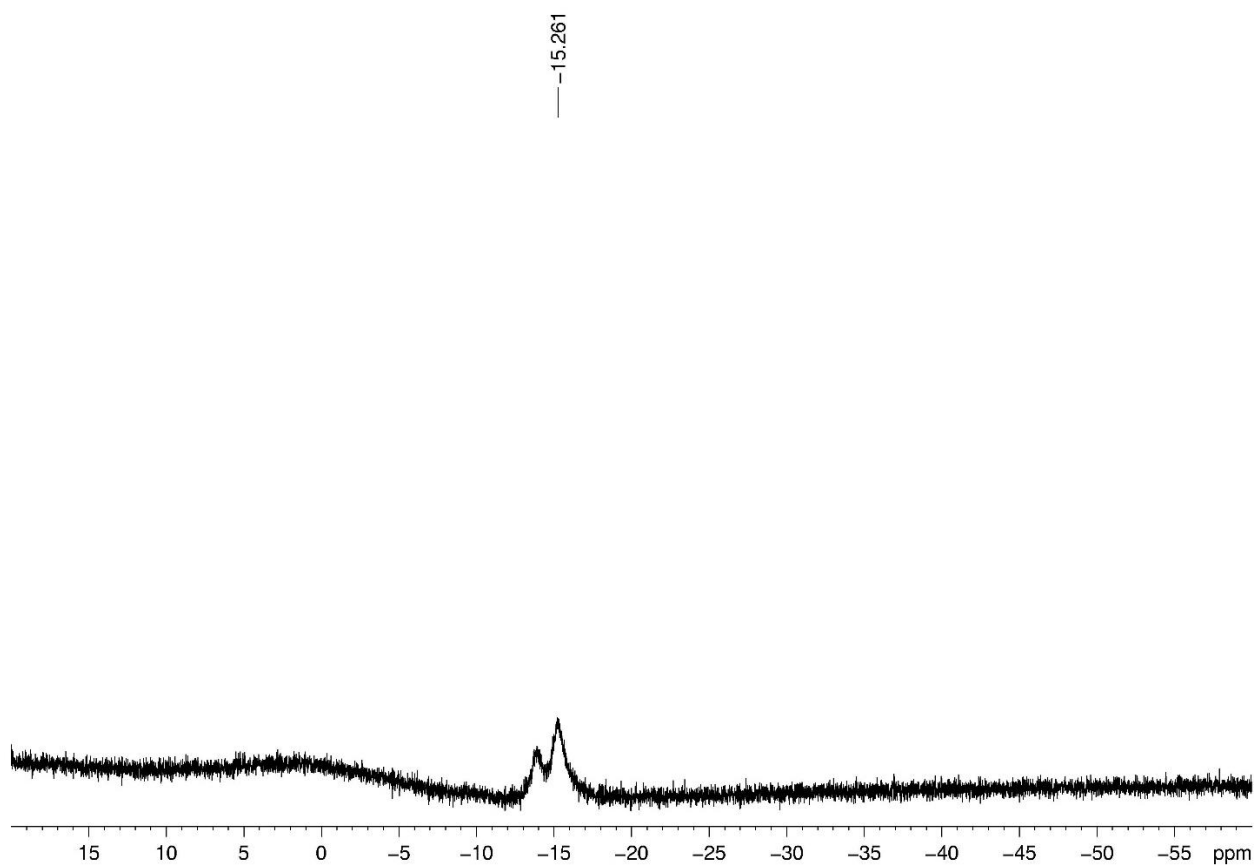
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **57**



$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **58**



$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 192 MHz) spectrum of the crude reaction mixture for **59**



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