Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Photoinduced Successive Oxidative Ring-Opening and Borylation of Indolizines with NHC-Boranes

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1. General considerations

Unless otherwise noted, commercial reagents were purchased from Adamas, Alfa Aesar, TCI, or Maclin and used without further purification. All reactions were carried out using oven-dried glassware and all catalytic reactions proceeded without special care. Column chromatography was performed on 200-300 mesh silica gel (Huanghai, China).

^{1}H, ^{19}F and $^{13}C\{^{1}H\}$ NMR spectra were recorded on an Bruker Ascend 400MHz spectrometer and Bruker Ultrashield 300MHz at ambient temperature. ^{1}H NMR spectra are referred to the TMS signal (δ = 0 ppm) and ^{13}C NMR spectra are referred to the residual solvent signal (δ = 77.16 ppm). Data for ^{1}H NMR are reported as follows: chemical shifts (δ ppm), multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), integration.

Photochemical reaction experiments were carried out on a PL-SX100A Model Multi-channel photochemical reaction instrument (the light source is 20 W blue LED, the working current is 0.5-1.7 A, the input power is 120 W, the temperature is controlled by circulating water cooling, and the stirring speed is 0-1500 r/min). The material of the irradiation vessel is borosilicate glass and it is 3 cm away from the light source. The data of HRMS was carried out on a waters G2-XS high-resolution mass spectrometer (HR-ESI-MS) or Agilent 7250 GC/QTOF.

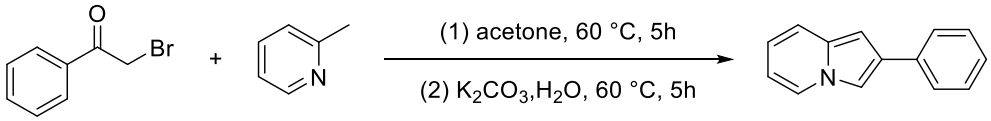
Note: In the ^{13}C NMR spectral data, the carbons connected to boron are not listed due to quadrupole broadening and spin–spin coupling with boron.

2. Experimental procedures and characterization data

2.1 Experimental procedures

Synthesis of compounds 1 according to the following procedure[1-2]:

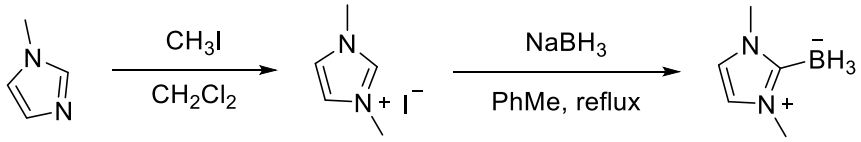
As exemplified for **1a**:



A solution of 2-picoline (0.93 g, 10 mmol, 1.0 equiv.) and 2 bromoacetophenone (1.99 g, 10 mmol, 1.0 equiv.) in acetone (50 mL) were added to a 100 mL round bottom flask and heated with a heating mantle at 60 °C for 5 hours. The precipitate obtained by filtration separation was redissolved in 20 mL of hot water (60 °C). Then, K_2CO_3 (1.38 g, 10 mmol, 1.0 equiv.) was added and heated at 60 °C for 5 hours. After filtration and drying in vacuo, a white solid compound was obtained in 50% overall yield (0.965 g, 5 mmol) without further purification.

Synthesis of NHC-BH_3 compounds 2 according to the following procedure[3]:

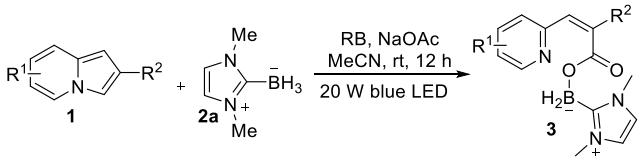
As exemplified for **2a**:



To a mixture of 1-methylimidazole (50 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) was added methyl iodide (60 mmol, 1.2 equiv.) dropwise over 15 min at 0 °C. The mixture was allowed to stir for 2 h at room temperature. The crude product was then obtained after removing the solvent, and directly used for next step without further purification. To a mixture of imidazolium salt (40 mmol, 1.0 equiv) in toluene (40 mL) was added sodium borohydride (48 mmol, 1.2 equiv). The flask was fitted with a cold water condenser and placed in an oil bath at 125-130 °C for 24 h. The hot reaction solvent was cautiously decanted from the insoluble mixture, and the remaining residue was extracted with hot toluene (20 mL × 2 times). The organic extracts were combined, concentrated, and further recrystallized over water to give the pure product as a fine white crystal (3.7 g).

Synthesis of products 3 and 4 according to the following procedure:

As exemplified for **3a**:



1 2a 3

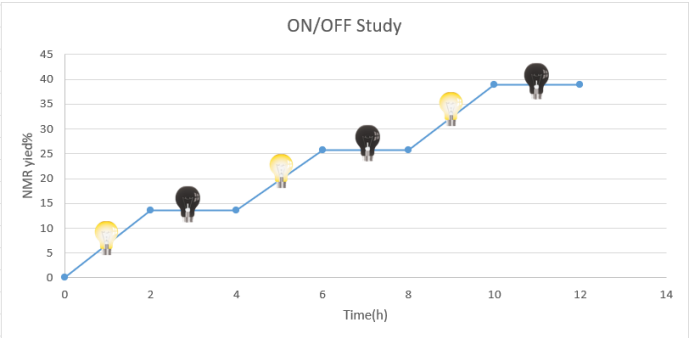
A 25 mL sealed tube was charged with a stirring bar, and added 2-phenylindolizine (**1a**, 38.6 mg, 0.2 mmol), NHC-borane (**2a**, 44 mg, 0.4 mmol), NaOAc(32.8mg, 0.4 mmol), rose bengal (10 mg, 0.01mmol), and MeCN (2.0 mL). The reaction was irradiated with a 20W blue LED at room temperature stirring for 12 h and monitored by TLC. The reaction mixture was then diluted with EtOAc and water, extracted with EtOAc. The organic layers were washed with brine and dried over $MgSO_4$, evaporated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 1 : 1) to give **3a** in 72% yield (47.9 mg).

Scale-up reaction for 3a:

A 50 mL round bottom flask was charged with a stirring bar, and added 2-phenylindolizine (**1a**, 193mg, 1 mmol), NHC-borane (**2a**, 220 mg, 2 mmol), NaOAc (164 mg, 2 mmol), rose bengal (50 mg, 0.05 mmol), and MeCN (10.0 mL). The reaction was irradiated with a 20W blue LED at room temperature stirring for 12 h and monitored by TLC. The reaction mixture was then diluted with EtOAc and water, extracted with EtOAc. The organic layers were washed with brine and dried over $MgSO_4$, evaporated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 1 : 1) to give **3a** in 70% yield (222.6 mg).

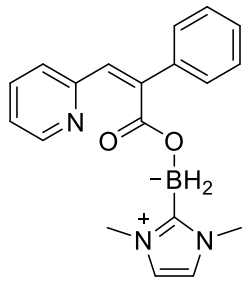
On/Off experiment

Standard reactions were set up parallel on a 0.20 mmol scale. After being irradiated for 2 h, an aliquot (150 μL) from the reaction mixture was transferred into a nuclear magnetic tube charged with 0.5 mL of $CDCl_3$. The yield of product **3a** was determined by ^1H NMR. Then the reaction mixture was stirred for 2 h with light-off. All of the following yields were analyzed in the identical way after a 2 h light on or off.



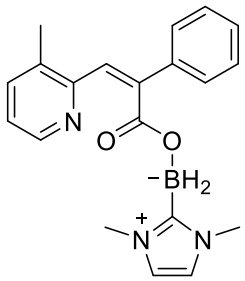
2.2 Characterization data

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((2-phenyl-3-(pyridin-2-yl)acryloyl)oxy)dihydroborate (3a)



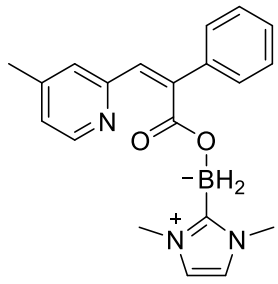
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3a**. Brown liquid (47.9 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 3.9 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 3H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.07 – 7.03 (m, 1H), 6.87 (s, 1H), 6.85 (s, 2H), 3.74 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 155.0, 149.1, 141.9, 137.2, 136.2, 128.6, 128.3, 126.5, 125.2, 123.1, 121.8, 120.8, 36.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ -13.51. IR (KBr): 3416, 3125, 2954, 1672, 1382, 1113, 778, cm−1. HR-ESI-MS (m/z): calcd for $C_{19}H_{21}BN_3O_2$ $[M + H]^+$: 334.1722, found: 334.1728.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((3-(3-methylpyridin-2-yl)-2-phenylacryloyl)oxy)dihydroborate (3b)



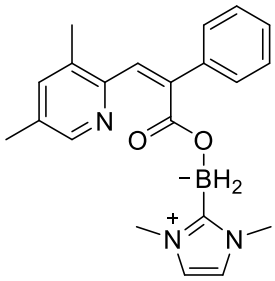
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3b**. Brown liquid (48.6 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 3.1 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.41– 7.25 (m, 4H), 6.99 – 6.93 (m, 1H), 6.92 (s, 1H), 6.86 (s, 2H), 3.79 (s, 6H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 153.2, 146.2, 142.4, 137.9, 137.5, 131.4, 128.4, 128.1, 126.8, 122.2, 121.7, 120.6, 36.1, 19.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ -15.51 (t, *J* = 134.7 Hz). IR (KBr): 3416, 3121, 2925, 1671, 1377, 1113, 764, cm−1. HR-ESI-MS (m/z): calcd for $C_{20}H_{23}BN_3O_2$ $[M + H]^+$: 348.1877, found: 348.1865.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl) (3-(4-methylpyridin-2-yl)-2-phenylacryloyl)oxy)dihydroborate (3c)



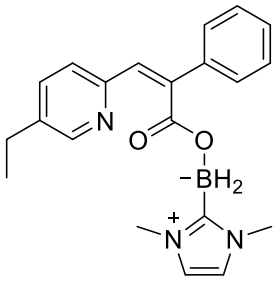
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3c**. Red brown liquid (50.6 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 5.0 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.37 – 7.27 (m, 5H), 6.90 (d, *J* = 4.5 Hz, 1H), 6.85 (s, 2H), 3.75 (s, 6H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 154.7, 148.7, 147.1, 141.5, 137.3, 128.5, 128.1, 126.4, 125.3, 124.0, 122.8, 120.8, 36., 21.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ -17.23. IR (KBr): 3416, 3163, 2956, 1671, 1301, 1113, 699, cm−1. HR-ESI-MS (m/z): calcd for $C_{20}H_{23}BN_3O_2$ $[M + H]^+$: 348.1877, found: 348.1891.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((3-(3,5-dimethylpyridin-2-yl)-2-phenylacryloyl)oxy)dihydrobor ate (3d)



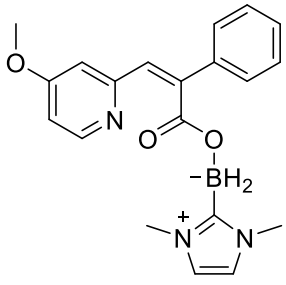
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3d**. Brown liquid (49.1 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.1 Hz, 1H), 7.55 (d, *J* = 7.0 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.19 (s, 1H), 6.89 (s, 1H), 6.85 (s, 2H), 3.77 (s, 6H), 2.33 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 150.5, 146.7, 141.6, 138.1, 138.0, 131.1, 130.9, 128.4, 127.9, 126.8, 122.4, 120.6, 36.1, 18.8, 18.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ -14.84. IR (KBr): 3409, 3158, 2958, 1694, 1401, 1082, 771, cm−1. HR-ESI-MS (m/z): calcd for $C_{21}H_{25}BN_3O_2$ [M + H]$^+$: 362.2034, found: 362.2025.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((3-(3,5-dimethylpyridin-2-yl)-2-phenylacryloyl)oxy)dihydrobor ate (3e)



Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3e**. Brown liquid (46.2 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.53 (d, *J* = 7.3 Hz, 2H), 7.39 (s, 2H), 7.36 – 7.27 (m, 3H), 6.87 (s, 1H), 6.85 (s, 2H), 3.74 (s, 6H), 2.61 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 152.4, 148.8, 140.8, 137.4, 137.2, 135.5, 128.5, 128.1, 126.3, 125.2, 122.6, 120.8, 36.0, 25.9, 15.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ -13.76. IR (KBr): 3393, 3117, 2965, 1671, 1380, 1112, 759, cm−1. HR-ESI-MS (m/z): calcd for $C_{21}H_{25}BN_3O_2$ [M + H]$^+$: 362.2034, found: 362.2041.

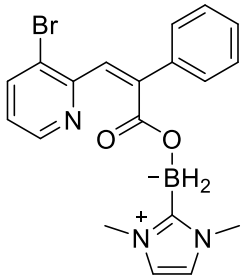
(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((3-(4-methoxypyridin-2-yl)-2-phenylacryloyl)oxy)dihydroborat -e (3f)



Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3f**. Yellow brown liquid (42.8 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 5.7 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.37 – 7.26 (m, 3H), 7.11 (d, J = 2.4 Hz, 1H), 6.86 (s, 1H), 6.85 (s, 2H), 6.65 – 6.61 (m, 1H), 3.87 (s, 3H), 3.74 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 165.9, 156.6, 150.1, 141.9, 137.1, 128.5, 128.3, 126.5, 125.4, 120.9, 109.00, 108.1, 55.3, 36.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ -13.89. IR (KBr): 3323,

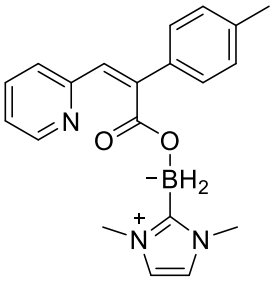
3158, 2960, 1581, 1428, 1179, 777, cm−1. HR-ESI-MS (m/z): calcd for $C_{20}H_{23}BN_3O_3$ [M + H]$^+$: 364.1827, found: 364.1823.

3-(3-Bromopyridin-2-yl)-2-phenylacryloyl)oxy)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3g)



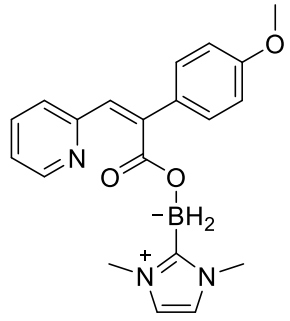
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3g**. Brown liquid (46.0 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 3.1 Hz, 1H), 7.78 (d, *J* = 6.5 Hz, 1H), 7.59 (d, *J* = 6.4 Hz, 2H), 7.37 – 7.29 (m, 3H), 7.20 (s, 1H), 6.92 (dd, *J* = 8.1, 4.6 Hz, 1H), 6.86 (s, 2H), 3.79 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 152.6, 147.1, 144.2, 140.2, 137.2, 128.5, 127.4, 126.9, 122.8, 121.8, 121.1, 120.7, 36.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ -14.72. IR (KBr): 3431, 3143, 2957, 1661, 1430, 1103, 781, cm−1. HR-ESI-MS (m/z): calcd for $C_{19}H_{20}BBrN_3O_2$ [M + H]$^+$: 412.0827, found: 412.0837.

1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((3-(pyridin-2-yl)-2-(p-tolyl)acryloyl)oxy)dihydroborate (3h)



Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3h**. Brown liquid (49.3 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 4.9 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.46 – 7.41 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.07 – 7.02 (m, 1H), 6.91 – 6.82 (m, 3H), 3.74 (s, 6H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 155.1, 149.0, 141.7, 138.2, 136.1, 134.2, 129.2, 126.3, 124.1, 122.9, 121.5, 120.8, 36.1, 21.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ -14.37. IR (KBr): 3416, 3121, 2925, 1671, 1301, 1180, 764, cm−1. HR-ESI-MS (m/z): calcd for $C_{20}H_{23}BN_3O_2$ [M + H]$^+$: 348.1877, found: 348.1887.

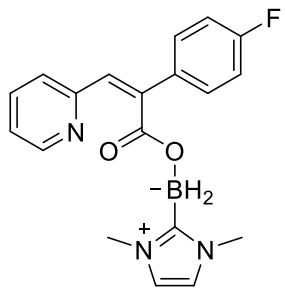
1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((2-(4-methoxyphenyl)-3-(pyridin-2-yl)acryloyl)oxy)dihydroborate (3i)



Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3i**. Brown liquid (45.7 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 3.1 Hz, 1H), 7.58 – 7.43 (m, 4H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.03 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.87 (d, *J* = 5.9 Hz, 3H), 6.79 (s, 1H), 3.80 (s, 3H), 3.73 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 159.8, 155.1, 148.9, 141.3, 136.1, 129.6, 127.7,

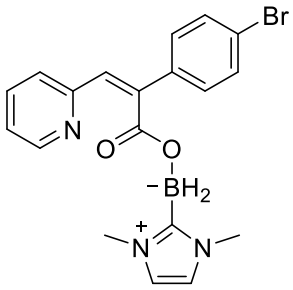
123.1, 122.8, 121.4, 120.8, 113.9, 55.3, 36.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ -13.65. IR (KBr): 3223, 3158, 2960, 1581, 1317, 1179, 777, cm−1. HR-ESI-MS (m/z): calcd for $C_{20}H_{23}BN_3O_3$ [M + H]$^+$: 364.1827, found: 364.1838.

1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((2-(4-fluorophenyl)-3-(pyridin-2-yl)acryloyl)oxy)dihydroborate (3j)



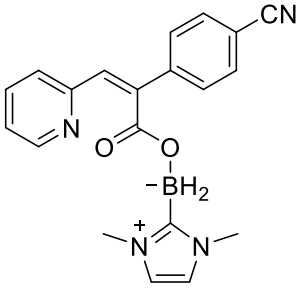
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3j**. Brown liquid (47.1 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 3.2 Hz, 1H), 7.61 – 7.50 (m, 3H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.09 – 6.98 (m, 3H), 6.87 (s, 2H), 6.80 (s, 1H), 3.75 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 164.0, 161.5, 154.7, 149.0, 140.7, 136.1, 133.3 (d, *J* = 3.3 Hz), 128.2 (d, *J* = 8.2 Hz), 124.9, 123.0, 121.7, 120.7, 115.4 (d, *J* = 21.6 Hz), 36.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ -14.55. IR (KBr): 3400, 3159, 2927, 1579, 1320, 1171, 777, cm−1. HR-ESI-MS (m/z): calcd for $C_{19}H_{20}BFN_3O_2$ [M + H]$^+$: 352.1627, found: 352.1638.

2-(4-Bromophenyl)-3-(pyridin-2-yl)acryloyl)oxy)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3k)



Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3k**. Brown liquid (57.5 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 4.8 Hz, 1H), 7.57 (d, *J* = 1.9 Hz, 1H), 7.48 – 7.39 (m, 5H), 7.08 (d, *J* = 4.0 Hz, 1H), 6.87 (s, 2H), 6.85 (s, 1H), 3.74 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 154.5, 149.0, 140.6, 136.2, 136.1, 131.6, 128.0, 125.4, 123.2, 122.3, 121.9, 120.8, 36.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ -15.18. IR (KBr): 3431, 3143, 2925, 1661, 1315, 1179, 781, cm−1. HR-ESI-MS (m/z): calcd for $C_{19}H_{20}BBrN_3O_2$ [M + H]$^+$: 412.0826, found: 412.0837.

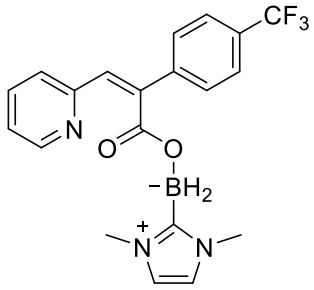
2-(4-Cyanophenyl)-3-(pyridin-2-yl)acryloyl)oxy)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3l)



Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3l**. Red brown liquid (56.2 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J*

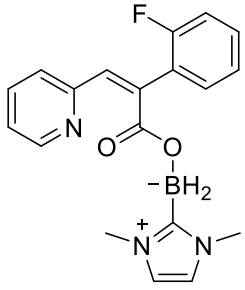
= 3.4 Hz, 1H), 7.71 – 7.56 (m, 5H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.14 – 7.08 (m, 1H), 6.93 (s, 1H), 6.90 (s, 2H), 3.76 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 154.0, 149.1, 141.7, 140.0, 136.2, 132.3, 127.6, 127.0, 123.6, 122.3, 120.8, 118.8, 111.4, 36.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ -14.33. IR (KBr): 3368, 3161, 2227, 1580, 1398, 1176, 923, 776, cm−1. HR-ESI-MS (m/z): calcd for $C_{20}H_{19}BN_4NaO_2$ [M + Na]$^+$: 381.1493, found: 381.1495.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((3-(pyridin-2-yl)-2-(4-(trifluoromethyl)phenyl)acryloyl)oxy)dih-ydroborate (3m)



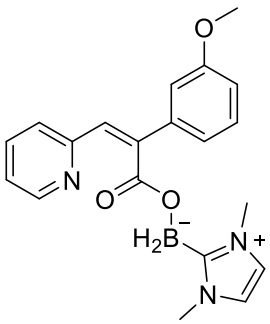
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3m**. Yellow brown liquid (60.1 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 3.3 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.54 (m, 3H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.14 – 7.05 (m, 1H), 6.92 (s, 1H), 6.88 (s, 2H), 3.74 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 154.2, 149.0, 140.7, 140.4, 136.2, 129.9 (q, *J* = 32.4 Hz), 126.9, 126.7, 125.4 (q, *J* = 3.9 Hz), 123.4, 122.1, 120.8, 36.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ -13.99. IR (KBr): 3338, 3161, 2862, 1582, 1326, 1198, 777, cm−1. HR-ESI-MS (m/z): calcd for $C_{20}H_{19}BF_3N_3NaO_2$ [M + Na]$^+$: 424.1415, found: 424.1410.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((2-(2-fluorophenyl)-3-(pyridin-2-yl)acryloyl)oxy)dihydroborate (3n)



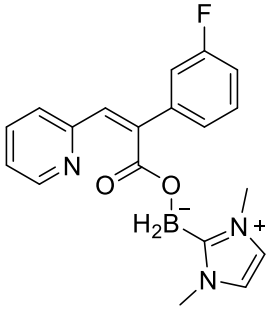
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3n**. Brown liquid (51.2 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.9 Hz, 1H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.50 (d, *J* = 6.5 Hz, 2H), 7.15 – 7.08 (m, 2H), 7.07 – 6.96 (m, 3H), 6.85 (s, 2H), 3.76 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 154.8, 148.9, 136.3, 136.0, 130.7 (d, *J* = 5.3 Hz), 130.2 (d, *J* = 3.4 Hz), 129.6 (d, *J* = 8.6 Hz), 124.2 (d, *J* = 3.5 Hz), 123.6, 122.0, 120.6, 115.9, 115.7, 36.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ -13.19. IR (KBr): 3400, 3111, 2857, 1579, 1427, 1171, 777, cm−1. HR-ESI-MS (m/z): calcd for $C_{19}H_{20}BFN_3O_2$ [M + H]$^+$: 352.1627, found: 352.1618.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((2-(3-methoxyphenyl)-3-(pyridin-2-yl)acryloyl)oxy)dihydrobor-ate (3o)



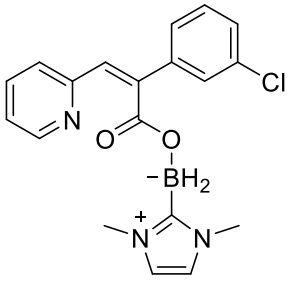
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3o**. Brown liquid (47.2 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 4.8 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.17 – 7.03 (m, 4H), 6.90 – 6.83 (m, 4H), 3.81 (s, 3H), 3.77 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 159.6, 154.8, 149.0, 141.7, 136.1, 129.4, 125.3, 123.0, 121.7, 120.7, 120.7, 119.1, 114.2, 111.6, 55.3, 36.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ -13.81 (d, *J* = 79.0 Hz). IR (KBr): 3223, 3111, 2960, 1581, 1248, 1179, 777, cm−1. HR-ESI-MS (m/z): calcd for $C_{20}H_{23}BN_3O_3$ [M + H]$^+$: 364.1827, found: 364.1839.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((2-(3-fluorophenyl)-3-(pyridin-2-yl)acryloyl)oxy)dihydroborate (3p)



Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3p**. Brown liquid (46.3 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 5.4 Hz, 1H), 7.63 – 7.53 (m, 1H), 7.43 (d, *J* = 6.9 Hz, 1H), 7.39 – 7.30 (m, 2H), 7.22 (d, *J* = 10.5 Hz, 1H), 7.13 – 7.05 (m, 1H), 7.02 – 6.94 (m, 1H), 6.88 (s, 2H), 6.87 (s, 1H), 3.77 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 164.0, 161.6, 154.4, 149.1, 140.5 (d, *J* = 2.7 Hz), 139.4 (d, *J* = 7.8 Hz), 136.2, 129.9 (d, *J* = 8.4 Hz), 125.9, 123.2, 122.1(d, *J* = 2.8 Hz), 121.9, 120.8, 115.1, 114.9, 113.4, 113.1, 36.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ -14.10. IR (KBr): 3400, 3159, 2857, 1579, 1395, 1171, 777, cm−1. HR-ESI-MS (m/z): calcd for $C_{19}H_{20}BFN_3O_2$ [M + H]$^+$: 352.1627, found: 352.1632.

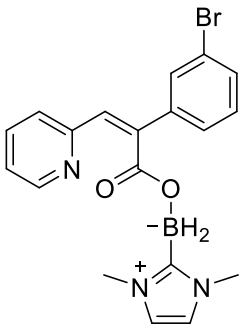
((2-(3-chlorophenyl)-3-(pyridin-2-yl)acryloyl)oxy)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (3q)



Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3q**. Yellow brown liquid (52.1mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 3.9 Hz, 1H), 7.67 – 7.53 (m, 1H), 7.51 – 7.40 (m, 3H), 7.27 (d, *J* = 2.8 Hz, 2H), 7.12 – 7.06 (m, 1H), 6.89 (s, 2H), 6.86 (s, 1H), 3.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 154.4, 149.1, 140.3, 139.0, 136.2, 134.3, 129.7, 128.1, 126.4, 126.1, 124.6, 123.2, 122.0, 120.8, 36.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ -15.02. IR (KBr): 3413, 3050,

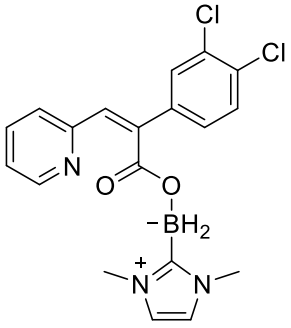
2925, 1661, 1381, 1179, 781, cm−1. HR-ESI-MS (m/z): calcd for $C_{19}H_{19}BClN_3NaO_2$ [M + H]$^+$: 390.1151, found: 390.1168.

((2-(3-Bromophenyl)-3-(pyridin-2-yl)acryloyl)oxy)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3r)



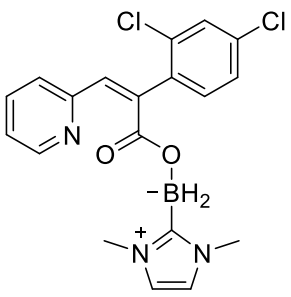
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3r**. Yellow brown liquid (60.0mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 4.1 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.13 – 7.02 (m, 1H), 6.88 (s, 2H), 6.85 (s, 1H), 3.77 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 154.3, 149.1, 140.2, 139.4, 136.2, 131.0, 130.0, 129.3, 126.2, 125.0, 123.2, 122.5, 122.0, 120.8, 36.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ -13.83. IR (KBr): 3431, 3143, 2957, 1661, 1381, 1103, 781, cm−1. HR-ESI-MS (m/z): calcd for $C_{19}H_{20}BBrN_3O_2$ [M + H]$^+$: 412.0826, found: 412.0825.

((2-(3,4-Dichlorophenyl)-3-(pyridin-2-yl)acryloyl)oxy)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydrobo-rate (3s)



Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3s**. Brown liquid (56.1mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 5.0 Hz, 1H), 7.66 – 7.51 (m, 2H), 7.47 – 7.35 (m, 3H), 7.16 – 7.03 (m, 1H), 6.89 (s, 2H), 6.84 (s, 1H), 3.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 154.1, 149.1, 139.3, 137.3, 136.2, 132.5, 132.0, 130.4, 128.2, 126.4, 125.7, 123.3, 122.1, 120.8, 36.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ -14.39. IR (KBr): 3119, 2956, 1672, 1473, 1112, 743, cm−1. HR-ESI-MS (m/z): calcd for $C_{19}H_{19}BCl_2N_3O_2$ [M + H]$^+$: 402.0942, found: 402.0942.

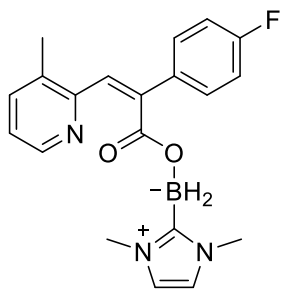
((2-(2,4-Dichlorophenyl)-3-(pyridin-2-yl)acryloyl)oxy)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydrobo-rate (3t)



Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3t**. Brown liquid (57.7mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.47 (m, 1H), 7.67 – 7.54 (m, 2H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.36 (d, *J* = 2.1 Hz, 1H), 7.24

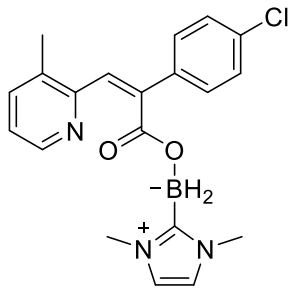
(dd, *J* = 8.3, 2.2 Hz, 1H), 7.18 – 7.10 (m, 1H), 6.82 (s, 2H), 6.79 (s, 1H), 3.71 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 154.4, 148.9, 138.1, 137.2, 135.8, 134.2, 134.0, 133.7, 132.0, 129.3, 127.1, 124.0, 122.3, 120.7, 36.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ -13.92. IR (KBr): 3162, 2926, 1672, 1368, 1112, 776, cm−1. HR-ESI-MS (m/z): calcd for $C_{19}H_{19}BCl_2N_3O_2$ $[M + H]^+$: 402.0942, found: 402.0941.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((2-(4-fluorophenyl)-3-(3-methylpyridin-2-yl)acryloyl)oxy)dihyd -roborate (3u)



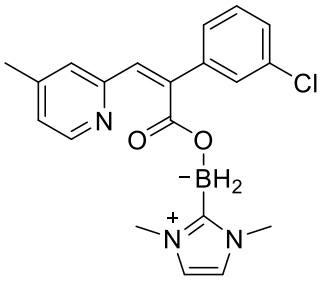
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3u**. Brown liquid (45.2mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 3.1 Hz, 1H), 7.61 – 7.50 (m, 2H), 7.38 (d, *J* = 6.7 Hz, 1H), 7.03 (t, *J* = 8.7 Hz, 2H), 6.95 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.87 (s, 2H), 6.86 (s, 1H), 3.77 (s, 6H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 163.9, 161.5, 153.0, 146.1, 141.3, 137.5, 134.1 (d, *J* = 3.2 Hz), 131.4, 128.5 (d, *J* = 8.1 Hz), 122.1 (d, *J* = 1.7 Hz), 121.7, 120.6, 115.4, 115.2, 36.0, 18.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ -15.27. IR (KBr): 3382, 3161, 2927, 1576, 1397, 1167, 778, cm−1. HR-ESI-MS (m/z): calcd for $C_{20}H_{22}BFN_3O_2$ $[M + H]^+$: 366.1784, found: 366.1779.

((2-(4-Chlorophenyl)-3-(3-methylpyridin-2-yl)acryloyl)oxy)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihy droborate (3v)



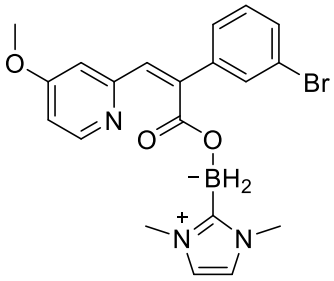
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3v**. Red brown liquid (48.7mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 4.0 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.00 – 6.92 (m, 1H), 6.90 (s, 1H), 6.87 (s, 2H), 3.78 (s, 6H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 152.9, 146.1, 141.2, 137.5, 136.4, 133.9, 131.5, 128.5, 128.1, 122.6, 121.9, 120.6, 36., 18.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ -15.46. IR (KBr): 3400, 3120, 2956, 1671, 1376, 1113, 831, cm−1. HR-ESI-MS (m/z): calcd for $C_{20}H_{21}BClN_3NaO_2$ $[M + Na]^+$: 404.1308, found: 404.1303.

((2-(3-Chlorophenyl)-3-(4-methylpyridin-2-yl)acryloyl)oxy)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihy droborate (3w)



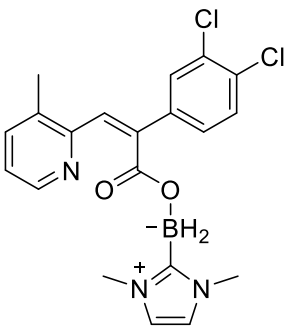
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3w**. Brown solid (52.5mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 5.0 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.36 – 7.25 (m, 3H), 6.91 (d, *J* = 5.1 Hz, 1H), 6.87 (s, 2H), 6.83 (s, 1H), 3.75 (s, 6H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 154.1, 148.8, 147.2, 140.0, 139.1, 134.2, 129.7, 128.0, 126.4, 126.3, 124.5, 124.2, 123.1, 120.8, 36.0, 21.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ -13.72. IR (KBr): 3400, 3120, 2926, 1671, 1299, 1113, 800, cm−1. HR-ESI-MS (m/z): calcd for $C_{20}H_{22}BClN_3O_2$ $[M + H]^+$: 382.1488, found: 382.1492.

((2-(3-Bromophenyl)-3-(4-methoxypyridin-2-yl)acryloyl)oxy)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dih -ydroborate (3x)



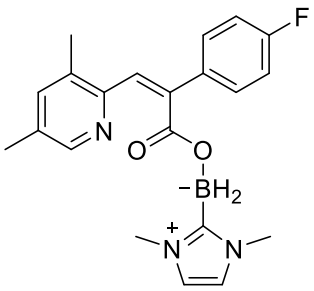
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3x**. Brown liquid (52.0mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 5.7 Hz, 1H), 7.57 (d, *J* = 1.9 Hz, 1H), 7.50 (d, *J* = 7.0 Hz, 1H), 7.41 (d, *J* = 6.9 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.10 (d, *J* = 2.3 Hz, 1H), 6.88 (s, 2H), 6.84 (s, 1H), 6.65 (d, *J* = 3.4 Hz, 1H), 3.87 (s, 3H), 3.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 165.9, 156.0, 150.1, 140.3, 139.2, 131.0, 130.0, 129.3, 126.5, 125.0, 122.5, 120.8, 109.2, 108.3, 55.2, 36.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ -14.43. IR (KBr): 3423, 3124, 2956, 1671, 1309, 1112, 786, cm−1. HR-ESI-MS (m/z): calcd for $C_{20}H_{22}BBrN_3O_3$ $[M + H]^+$: 442.0932, found: 442.0940.

((2-(3,4-Dichlorophenyl)-3-(3-methylpyridin-2-yl)acryloyl)oxy)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)di hydroborate (3y)



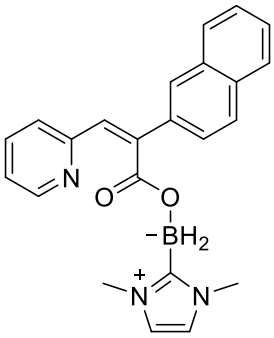
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3y**. Brown liquid (52.3mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 4.6 Hz, 1H), 7.61 (d, *J* = 2.1 Hz, 1H), 7.47 – 7.35 (m, 3H), 7.02 – 6.95 (m, 1H), 6.91 (s, 1H), 6.89 (s, 2H), 3.79 (s, 6H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 152.5, 146.2, 140.0, 138.1, 137.6, 132.4, 131.8, 131.7, 130.3, 128.5, 126.2, 123.7, 122.1, 120.7, 36.1, 18.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ -14.38. IR (KBr): 3400, 3163, 2956, 1671, 1376, 1113, 775, cm−1. HR-ESI-MS (m/z): calcd for $C_{20}H_{21}BCl_2N_3O_2$ $[M + H]^+$: 416.1098, found: 416.1113.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((3-(3,5-dimethylpyridin-2-yl)-2-(4-fluorophenyl)acryloyl)oxy)dihydroborate (3z)



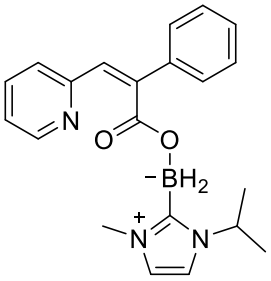
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3z**. Brown liquid (50.8mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 2.1 Hz, 1H), 7.58 – 7.46 (m, 2H), 7.22 – 7.16 (m, 1H), 7.02 (t, *J* = 8.6 Hz, 2H), 6.87 (s, 2H), 6.83 (s, 1H), 3.78 (s, 6H), 2.33 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 163.8, 161.4, 150.3, 146.6, 140.4, 138.1, 134.2 (d, *J* = 3.4 Hz), 131.2, 130.8, 128.4 (d, *J* = 8.1 Hz), 122.3, 120.6, 115.4, 115.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ -15.09. IR (KBr): 3388, 3165, 2926, 1671, 1380, 1231, 841, cm−1. HR-ESI-MS (m/z): calcd for $C_{21}H_{24}BFN_3O_2$ [M + H]$^+$: 380.1940, found: 380.1938.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((2-(naphthalen-2-yl)-3-(pyridin-2-yl)acryloyl)oxy)dihydroborat-e (3aa)



Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **3aa**. Brown liquid (53.6mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.0 Hz, 1H), 7.94 – 7.90 (m, 1H), 7.84 – 7.76 (m, 3H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.60 (t, *J* = 8.6 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.13 – 7.04 (m, 1H), 7.03 (s, 1H), 6.86 (s, 2H), 3.75 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 154.89, 149.1, 141.6, 136.2, 134.3, 133.3, 133.1, 128.4, 128.1, 127.5, 126.3 – 126.0 (m), 125.4, 123.9, 123.1, 121.7, 120.7, 36.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ -14.20. IR (KBr): 3417, 3160, 2923, 1581, 1381, 1175, 756, cm−1. HR-ESI-MS (m/z): calcd for $C_{23}H_{23}BN_3O_2$ [M + H]$^+$: 384.1878, found: 384.1870.

(1-Isopropyl-3-methyl-1*H*-imidazol-3-ium-2-yl)((2-phenyl-3-(pyridin-2-yl)acryloyl)oxy)dihydroborate (4a)

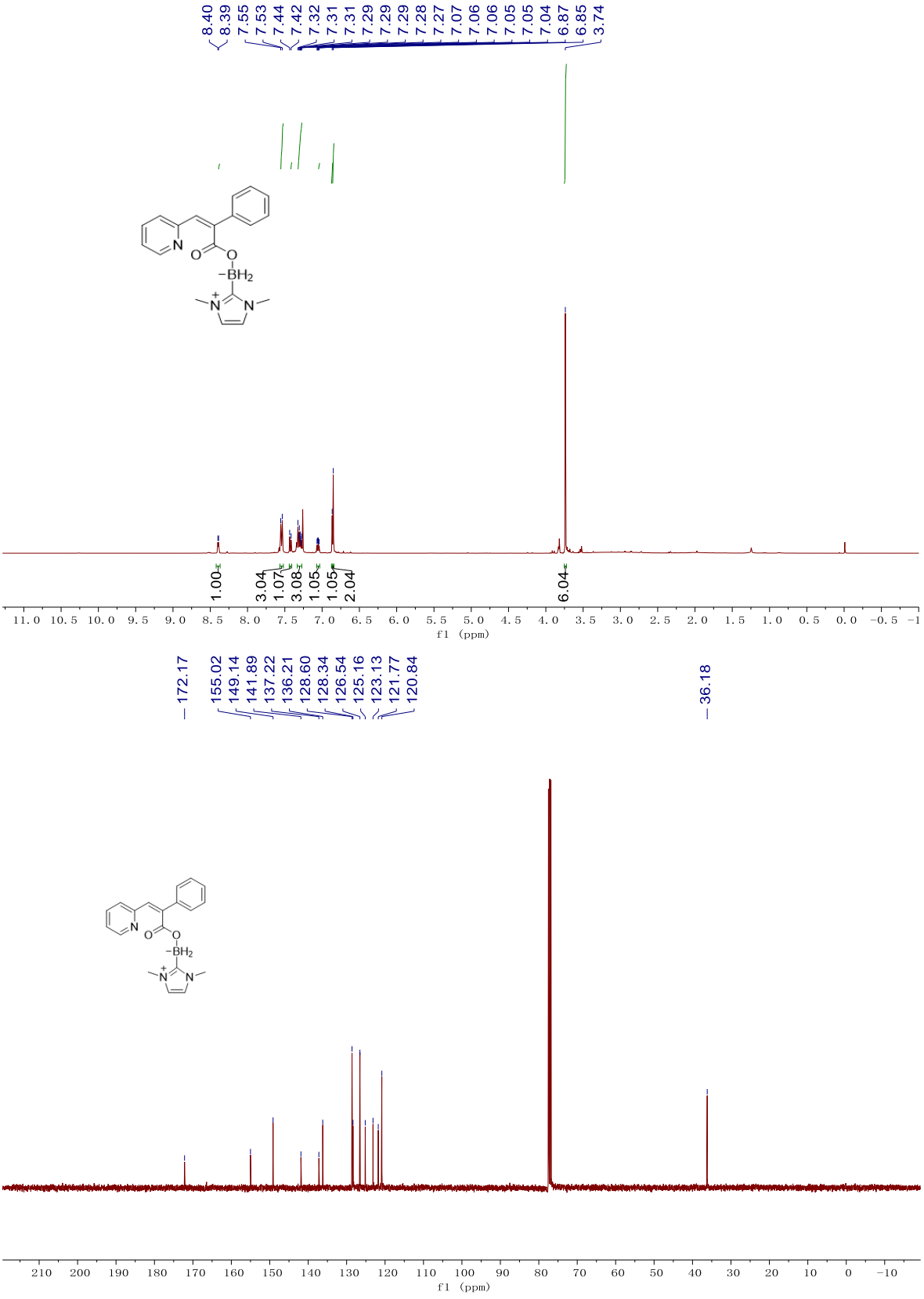


Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford **4a**. Brown liquid (52.7mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 5.6 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 3H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.37 – 7.27 (m, 3H), 7.11 – 7.03 (m, 1H), 6.96 (d, *J* = 1.9 Hz, 1H), 6.89 (s, 1H), 6.87 (s, 1H), 5.22 – 5.06 (m,

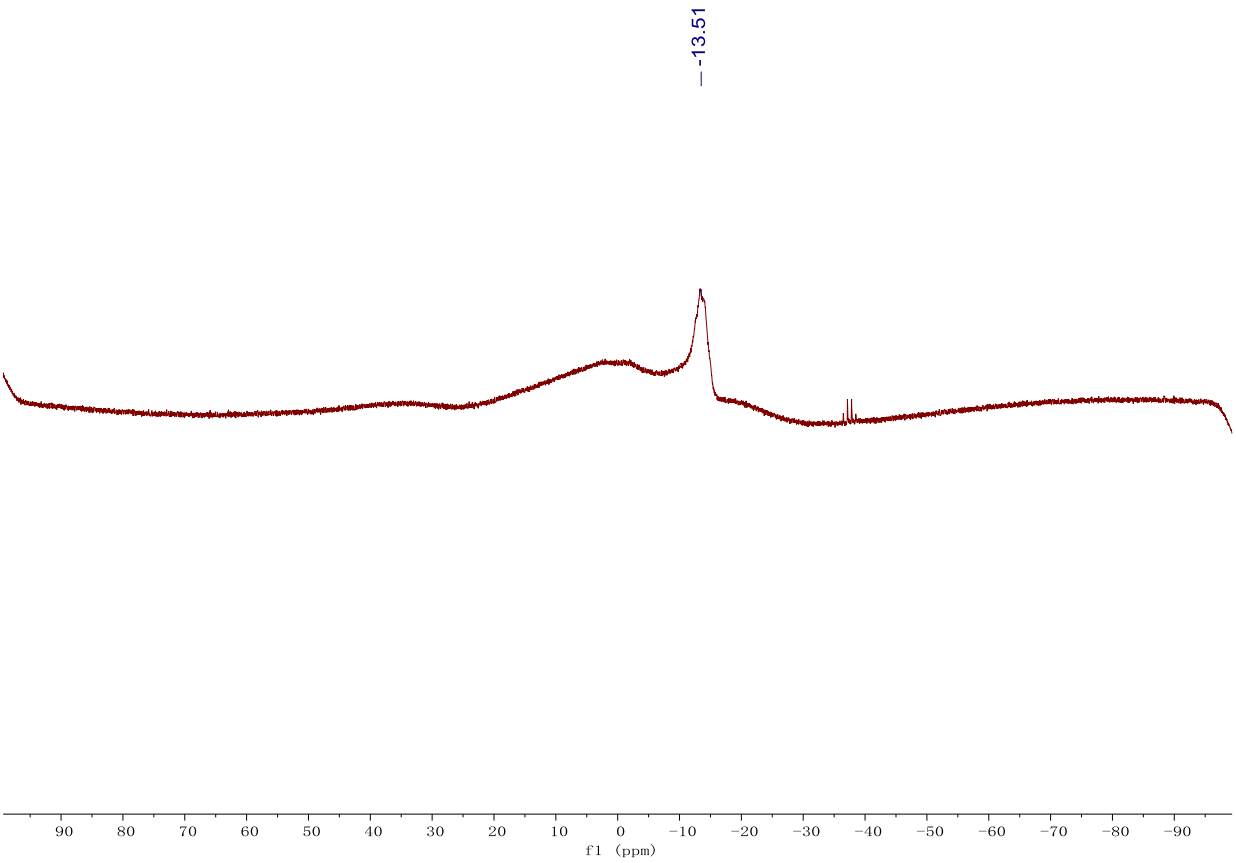
1H), 3.72 (s, 3H), 1.29 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 154.8, 149.1, 141.8, 137.0, 136.1, 128.4, 128.2, 126.4, 125.2, 122.8, 121.7, 121.3, 115.4, 50.0, 35.9, 23.02. ^{11}B NMR (128 MHz, $CDCl_3$) δ -15.17. IR (KBr): 3457, 2925, 1672, 1378, 1109, 778, cm−1. HR-ESI-MS (m/z): calcd for $C_{21}H_{25}BN_3O_2$ [M + H]$^+$: 362.2034, found: 362.2030.

3. NMR spectra for new compounds

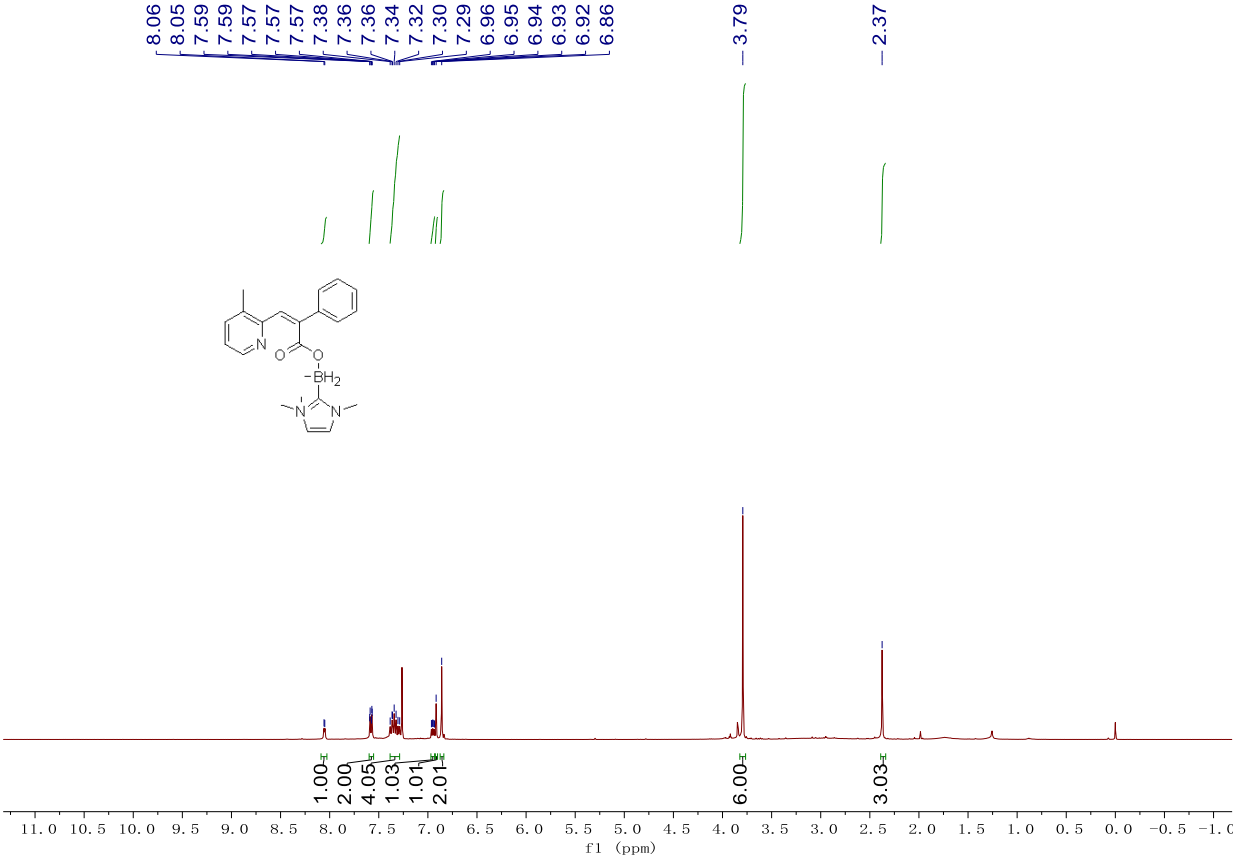
^{1}H NMR and ^{13}C NMR spectrum of compound **3a**

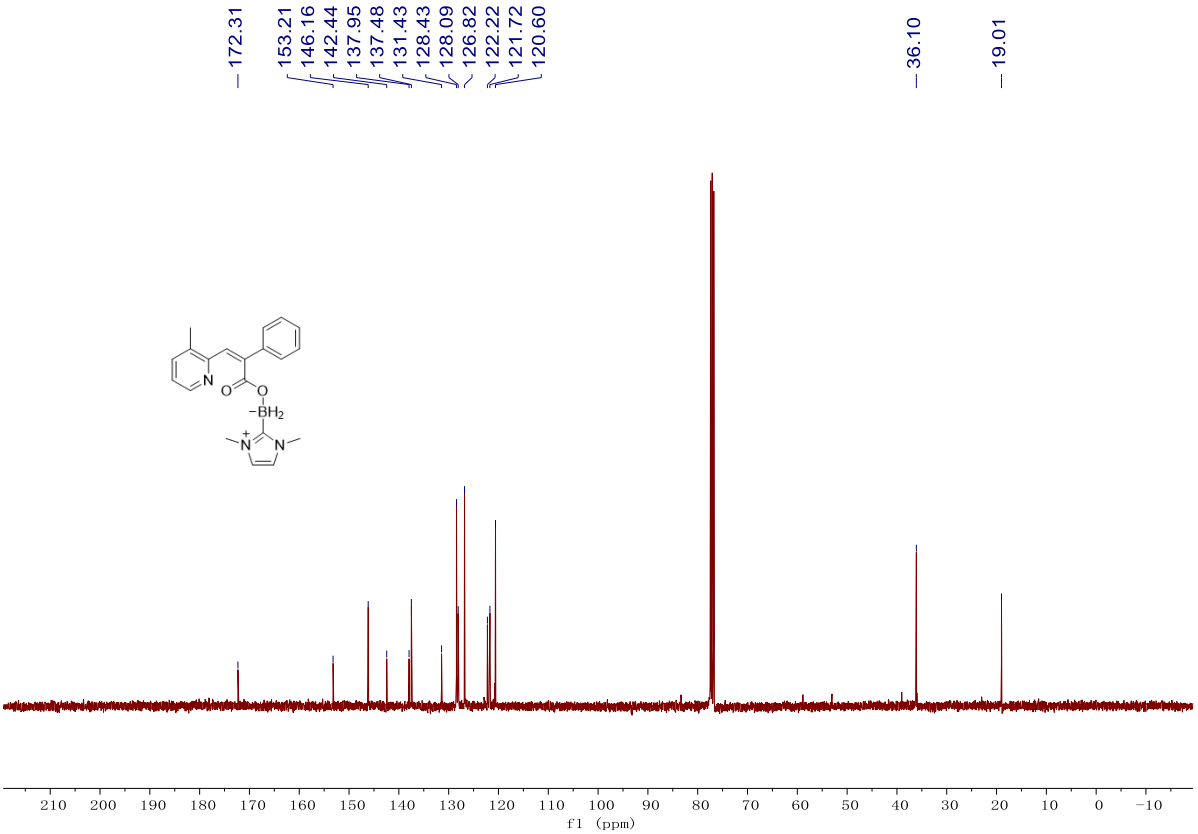


^{11}B NMR spectrum of compound **3a**

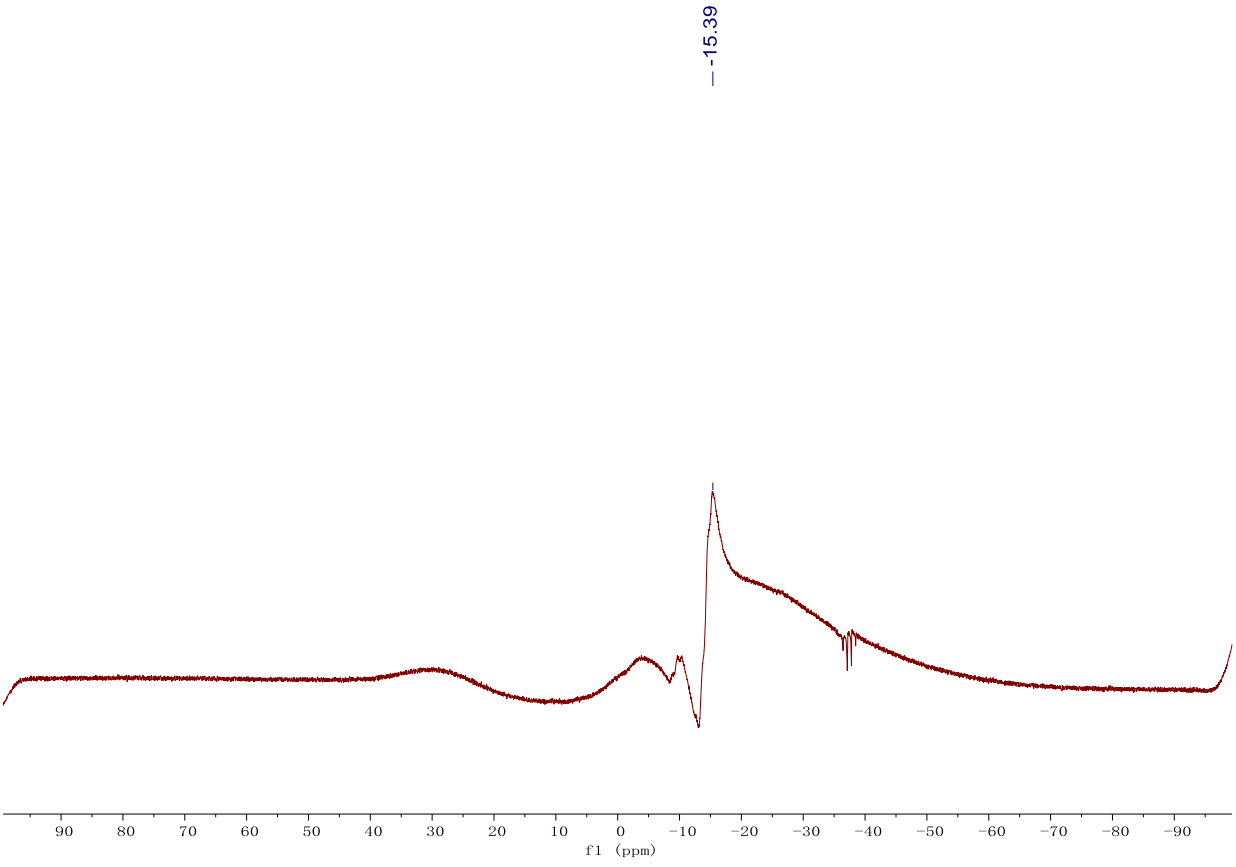


^{1}H NMR and ^{13}C NMR spectrum of compound **3b**

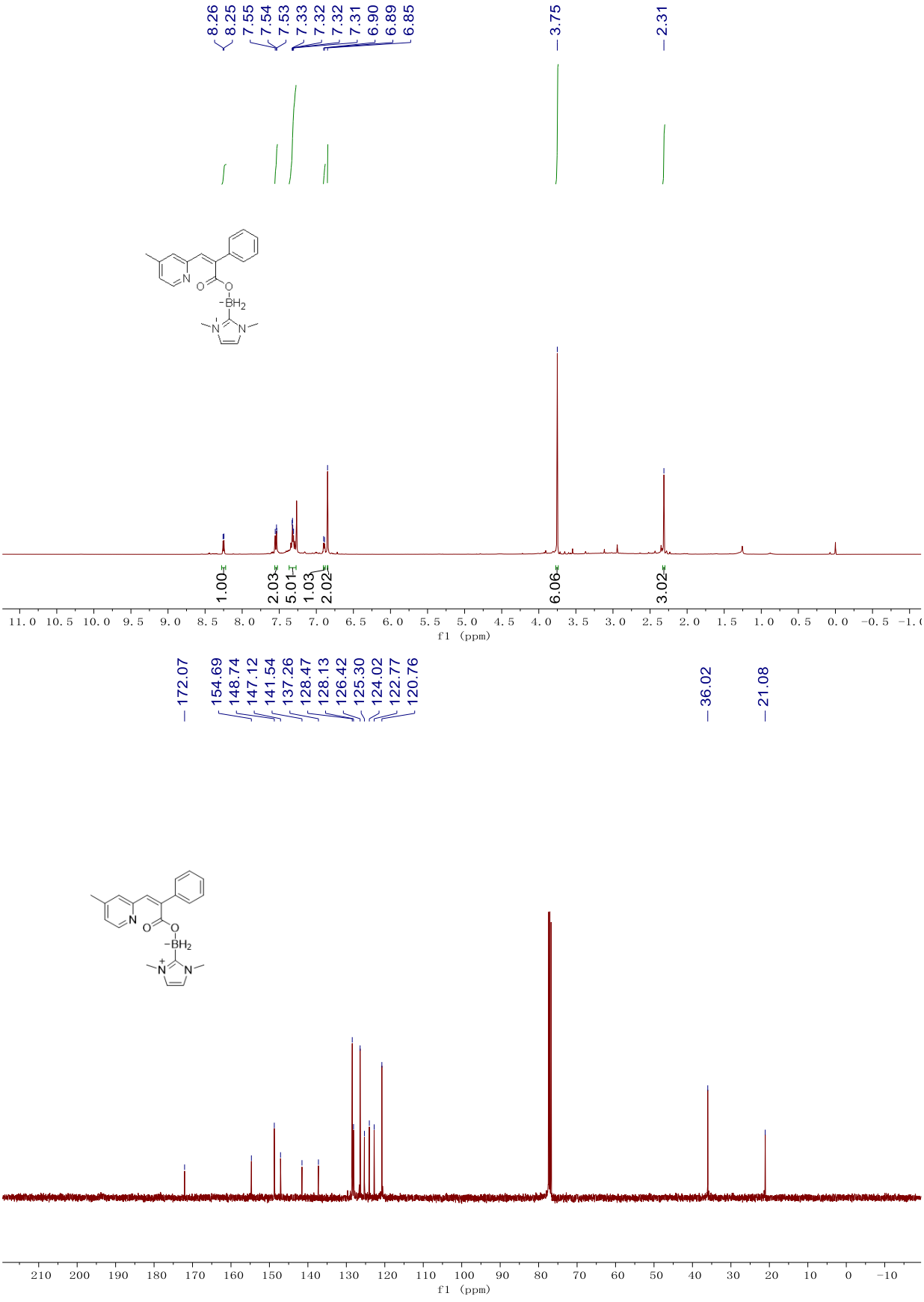




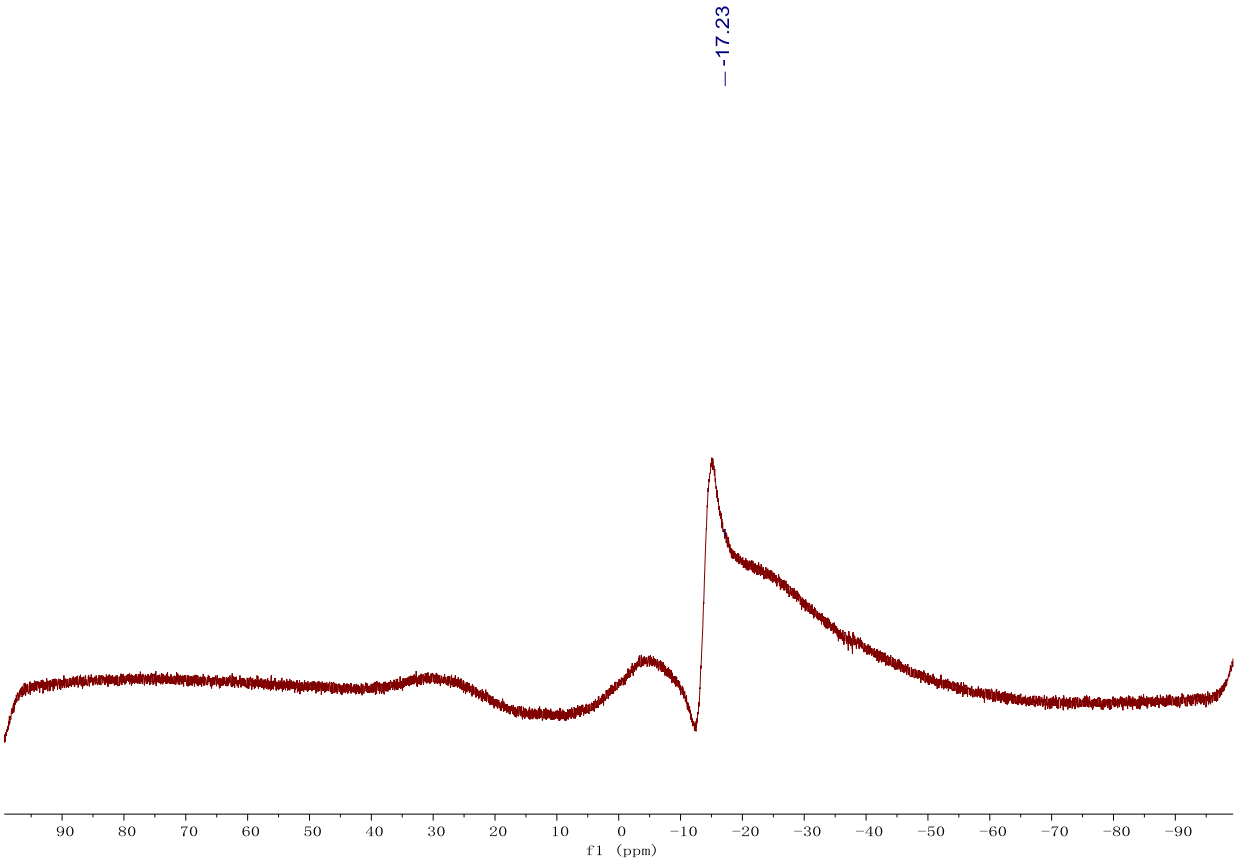
^{11}B NMR spectrum of compound **3b**



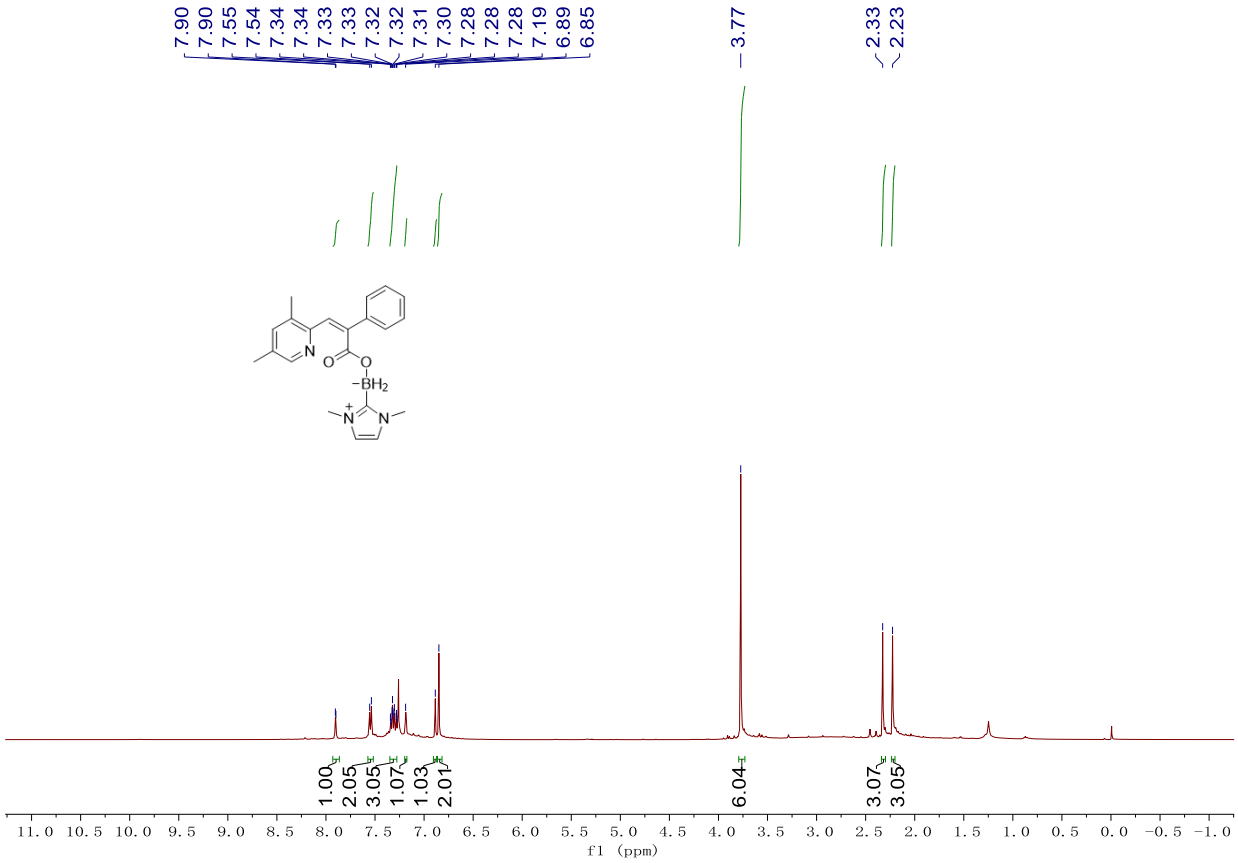
^{1}H NMR and ^{13}C NMR spectrum of compound **3c**

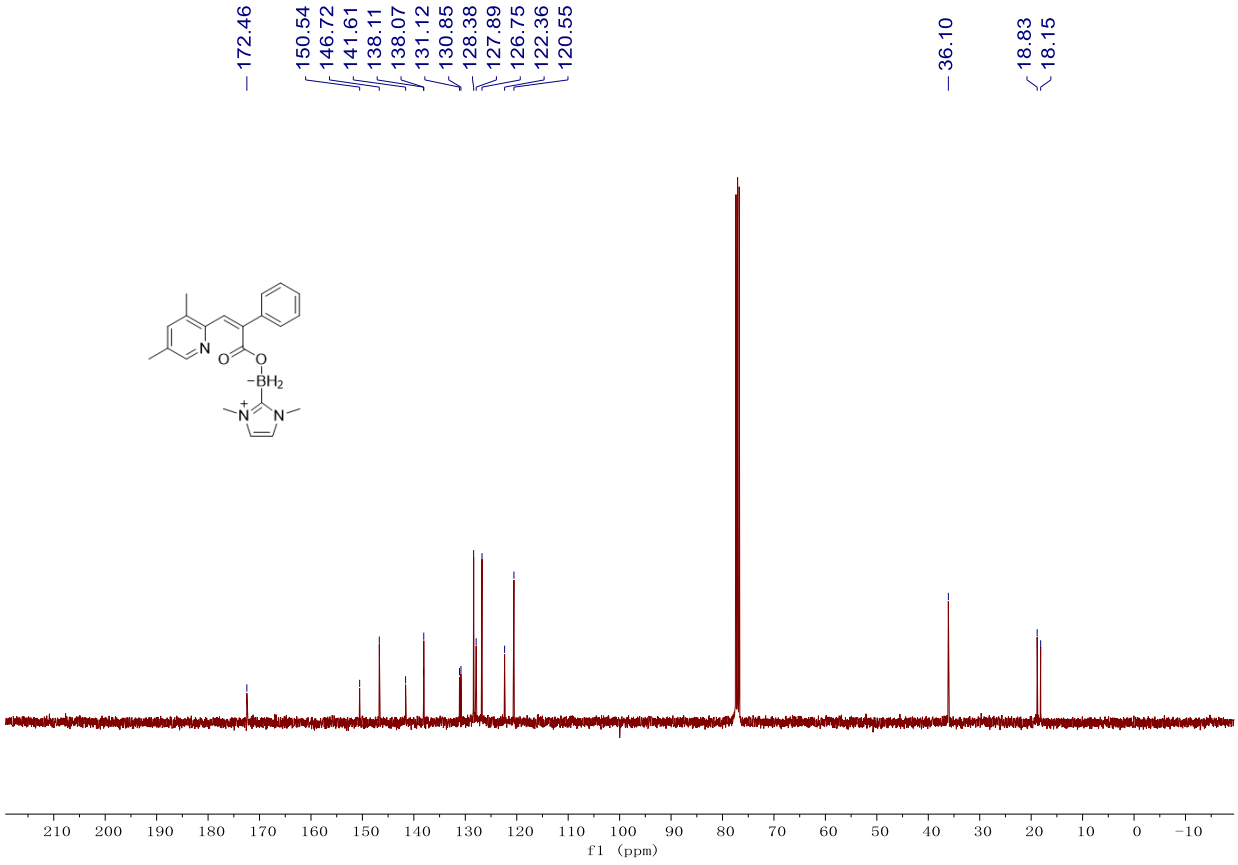


^{11}B NMR spectrum of compound **3c**

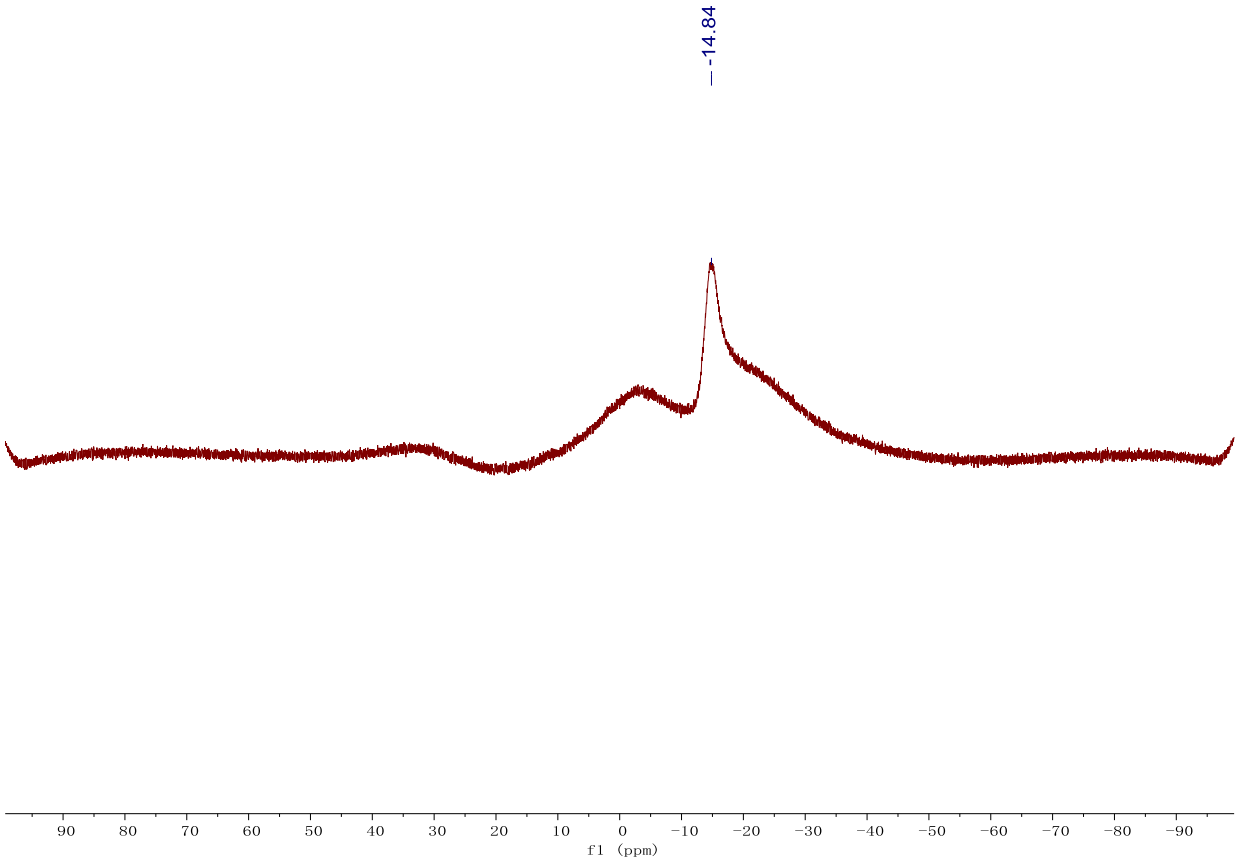


^{1}H NMR and ^{13}C NMR spectrum of compound **3d**

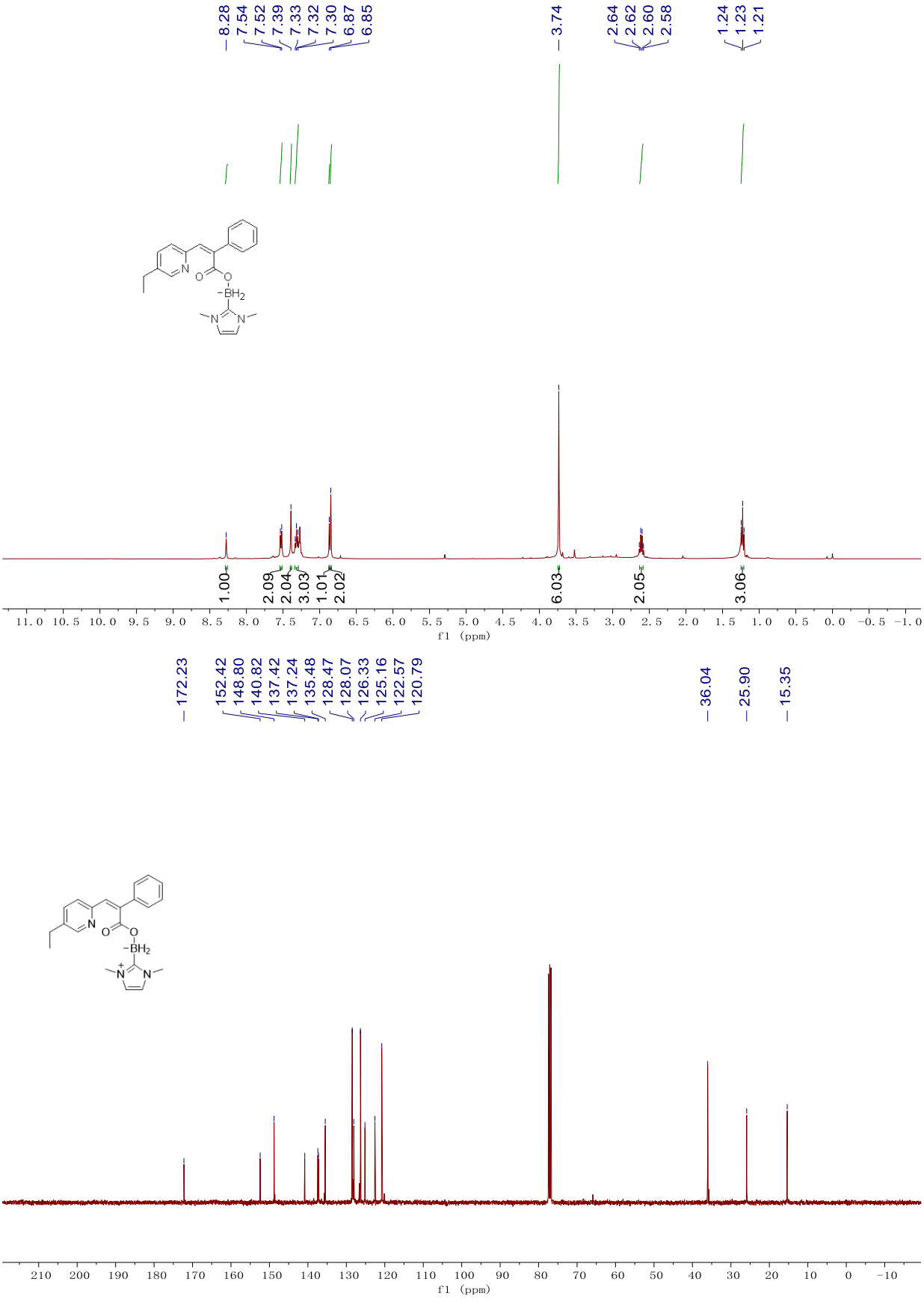




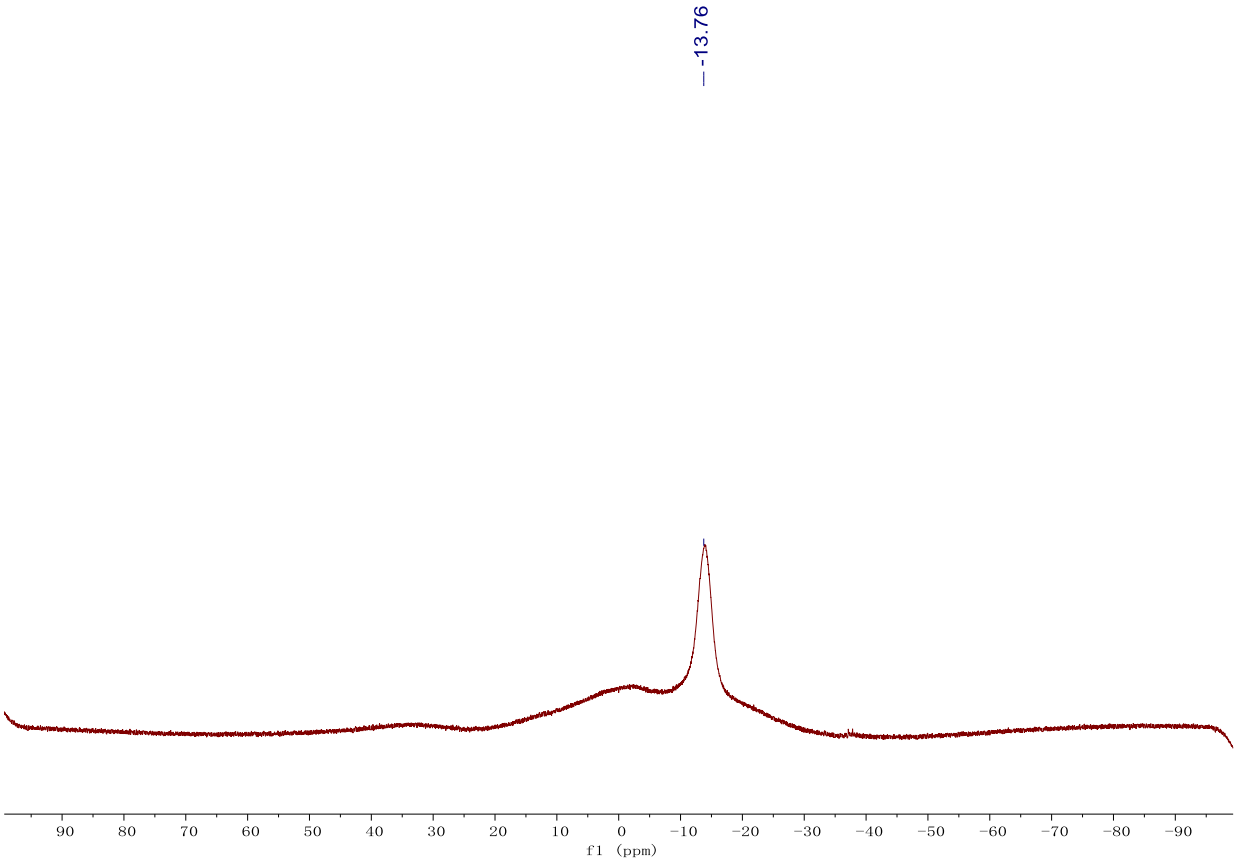
^{11}B NMR spectrum of compound **3d**



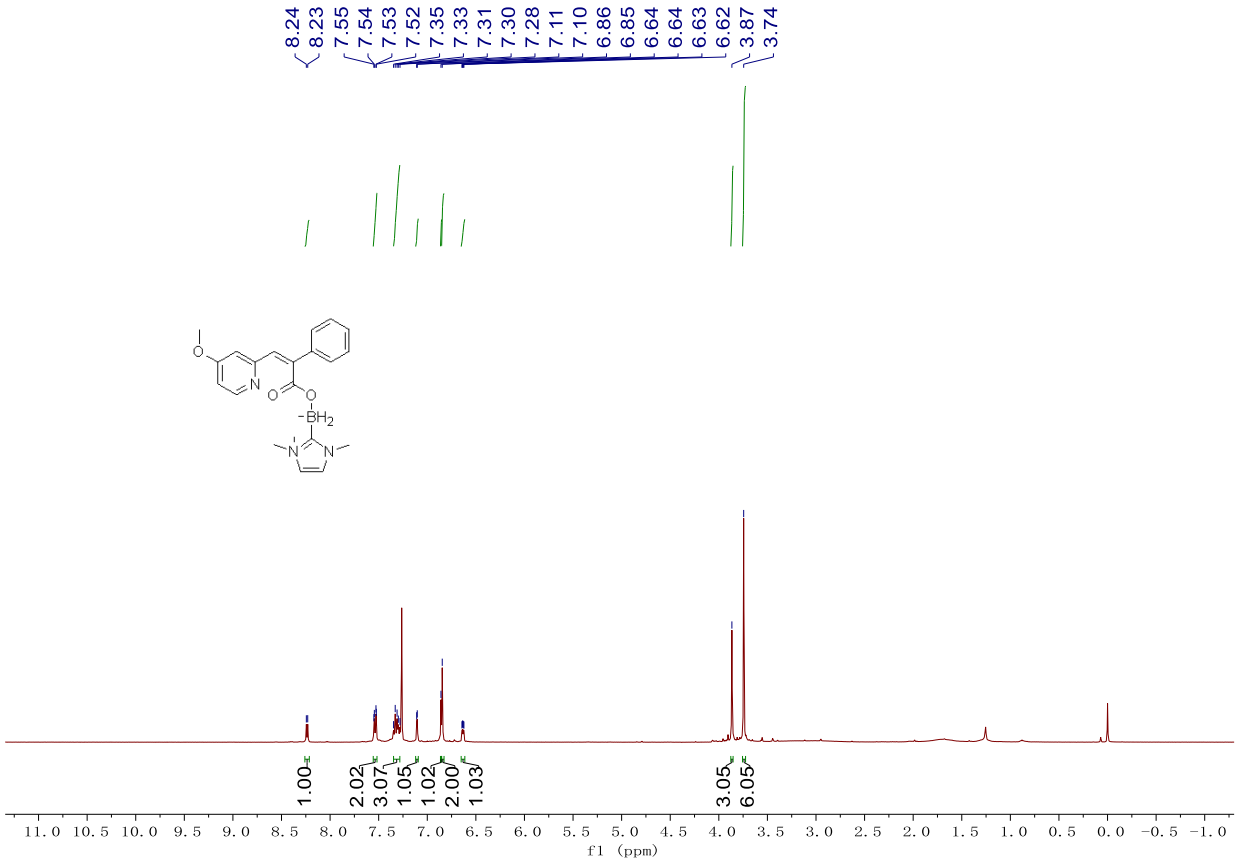
^{1}H NMR and ^{13}C NMR spectrum of compound **3e**

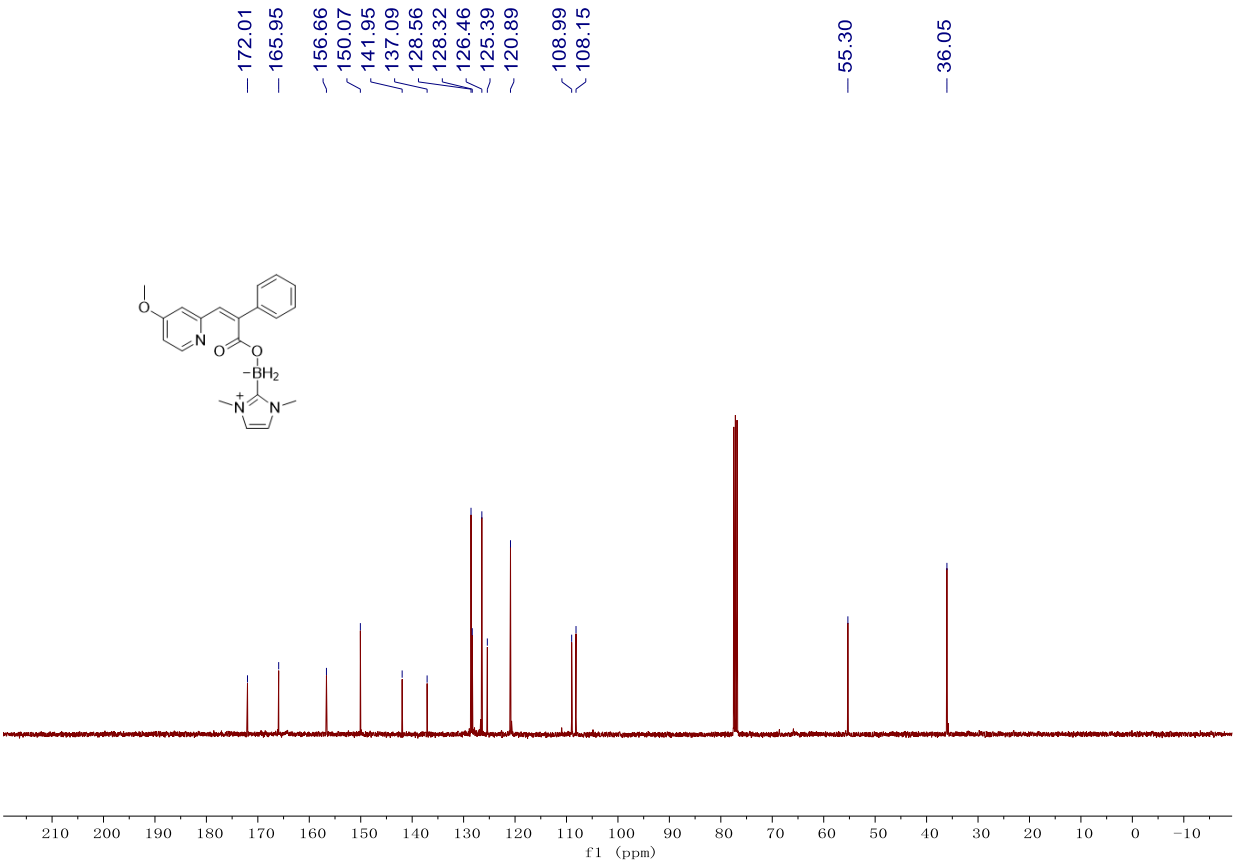


^{11}B NMR spectrum of compound **3e**

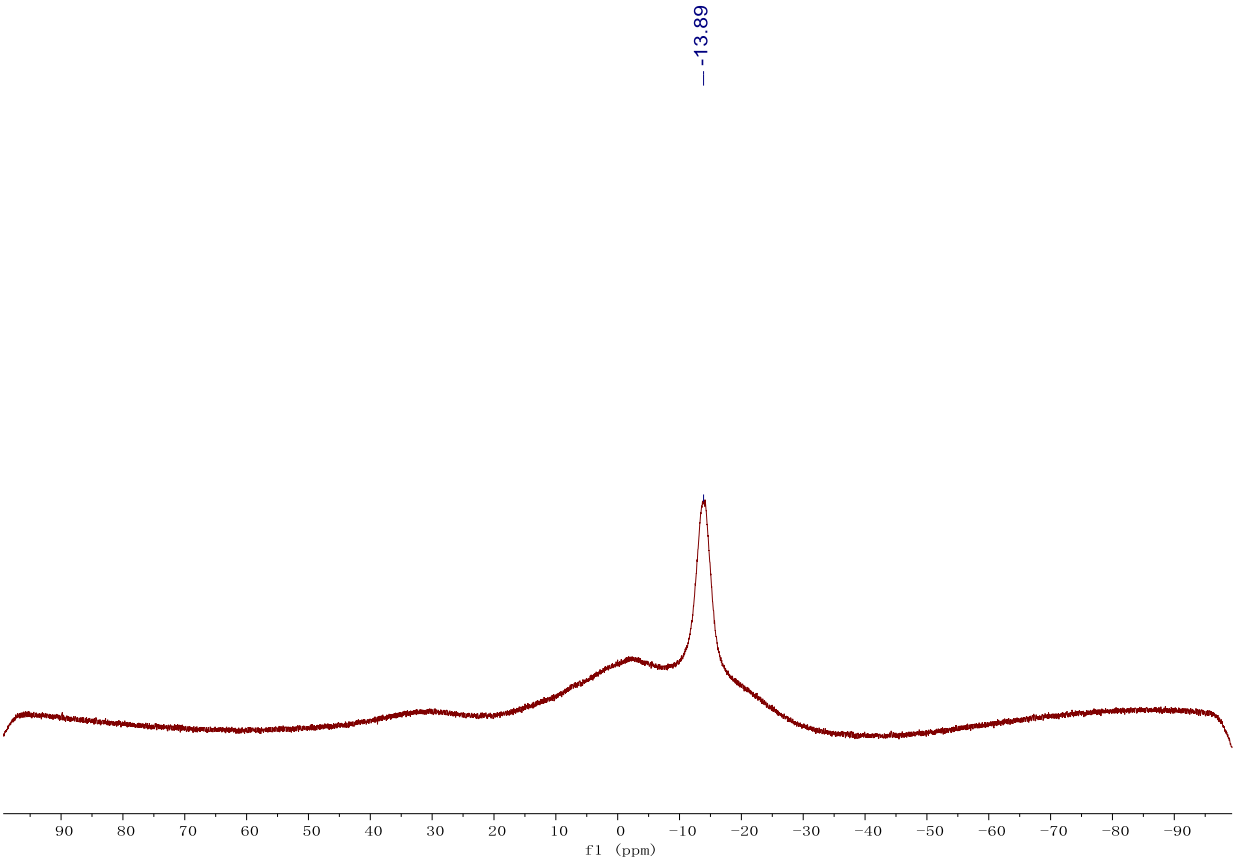


^{1}H NMR and ^{13}C NMR spectrum of compound **3f**

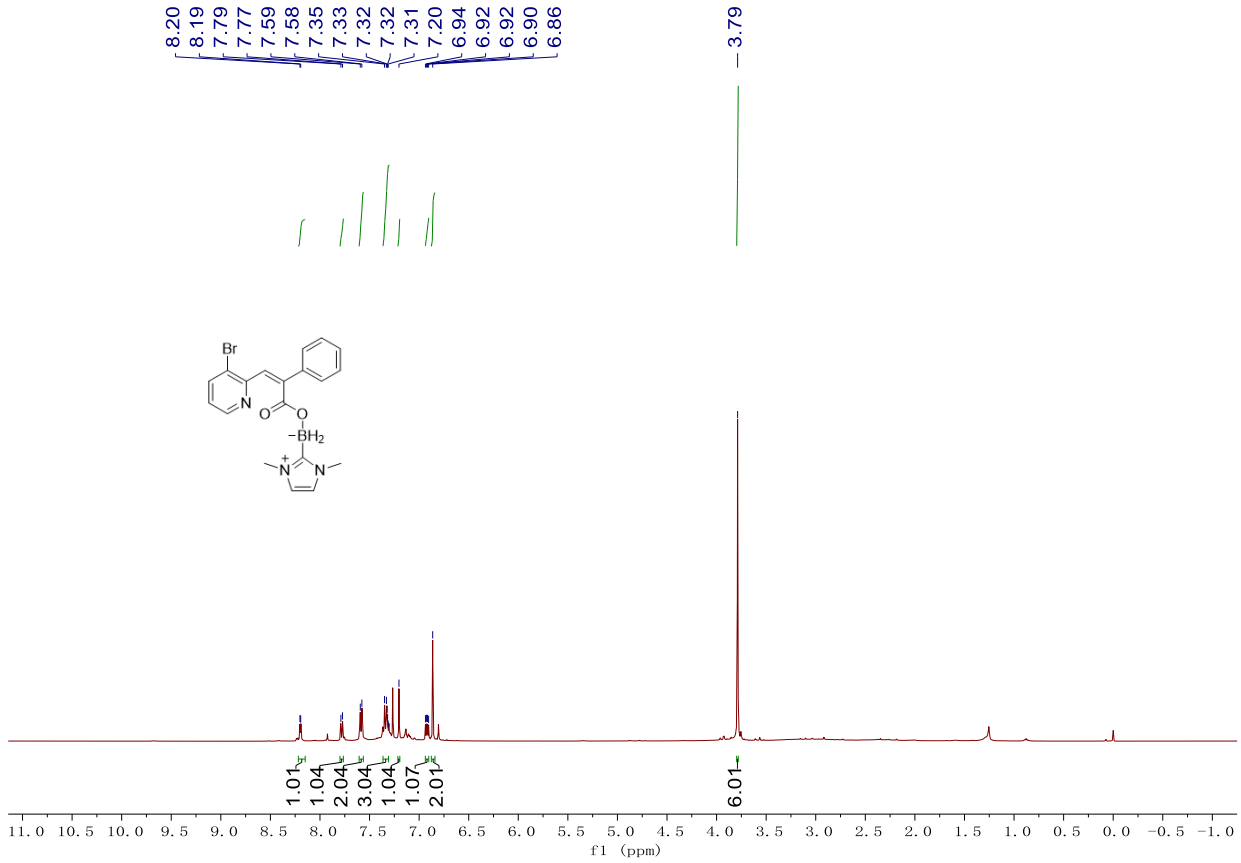


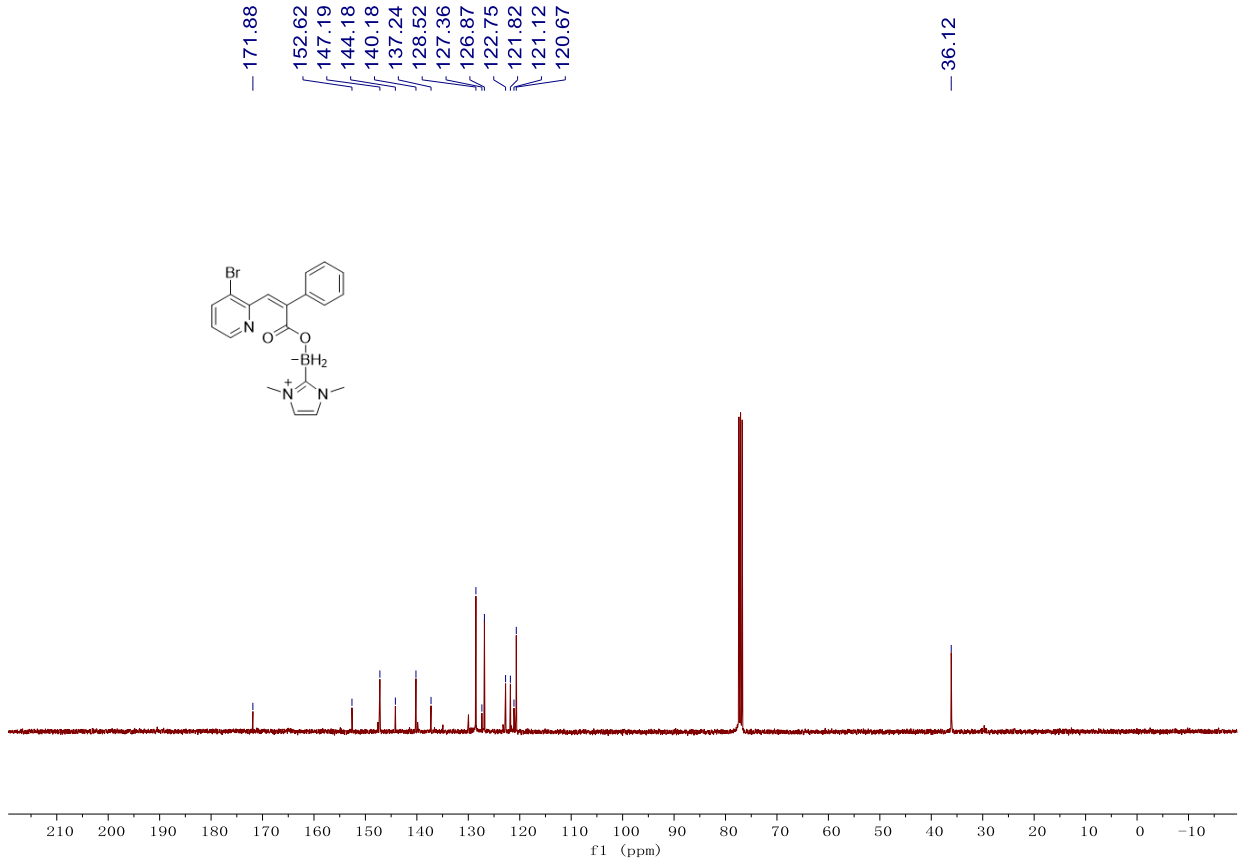


^{11}B NMR spectrum of compound **3f**

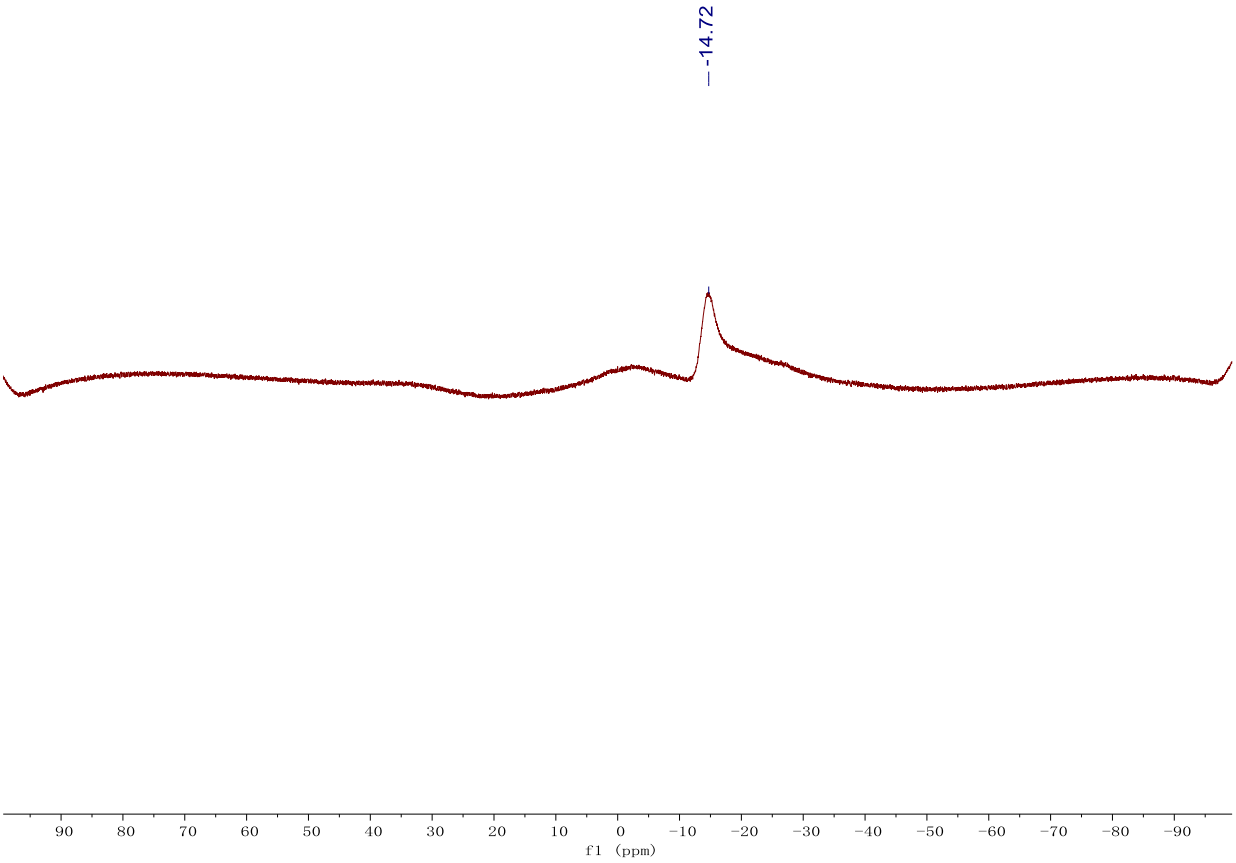


^{1}H NMR and ^{13}C NMR spectrum of compound **3g**

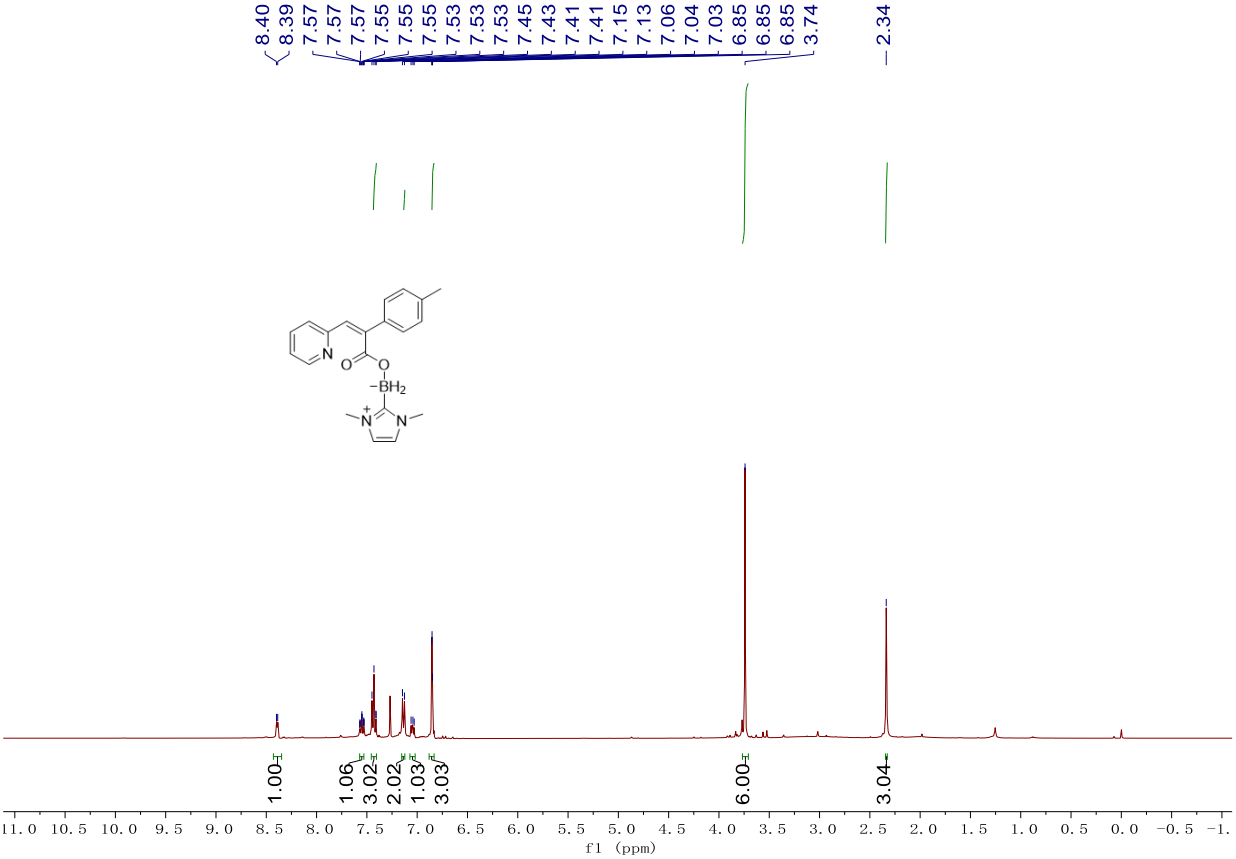


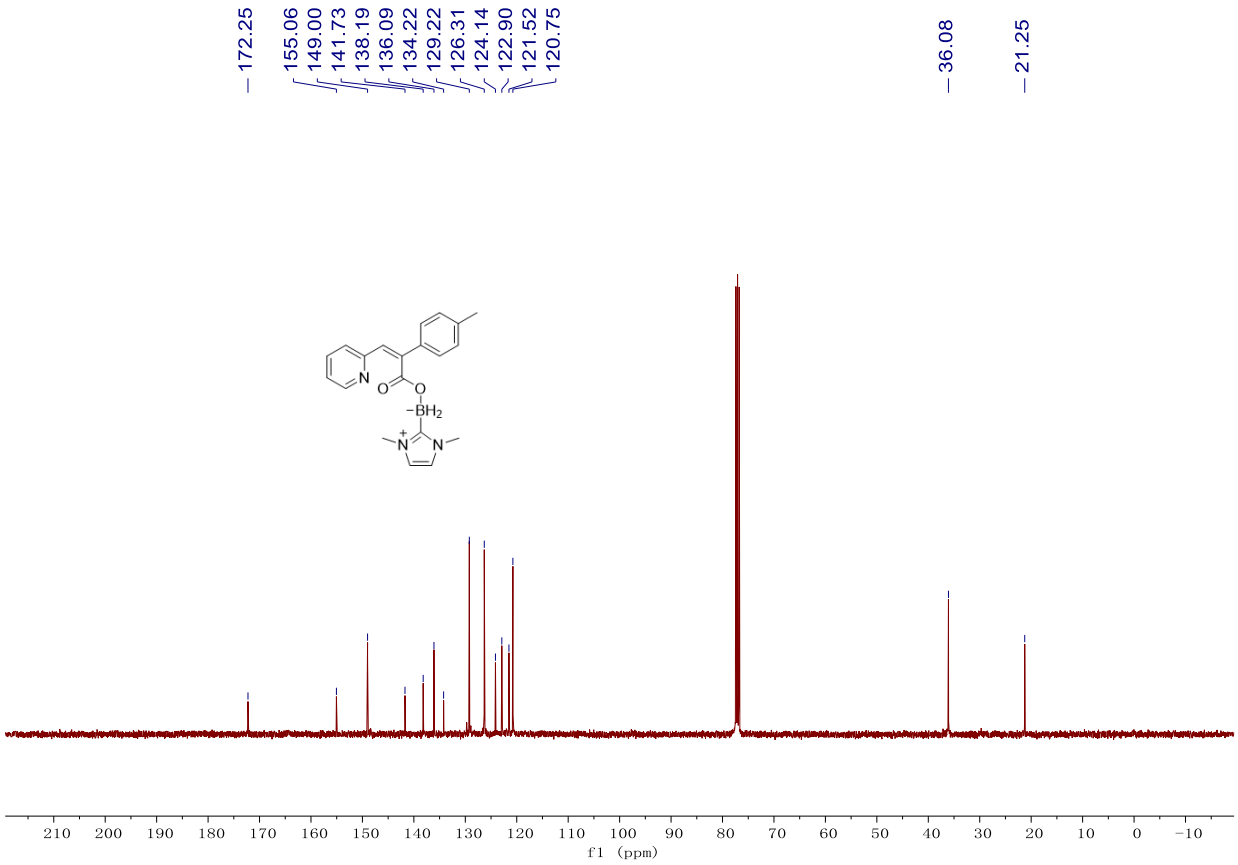


^{11}B NMR spectrum of compound **3g**

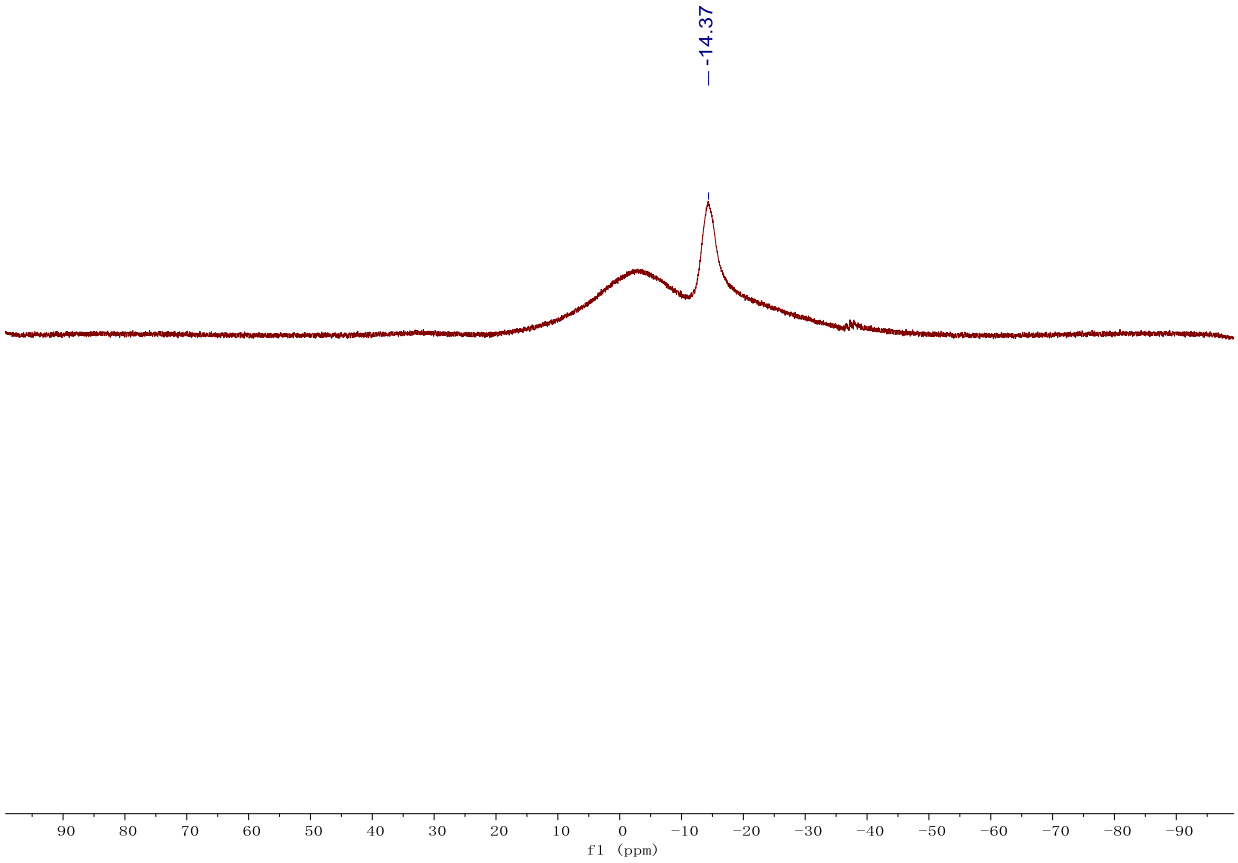


^{1}H NMR and ^{13}C NMR spectrum of compound **3h**

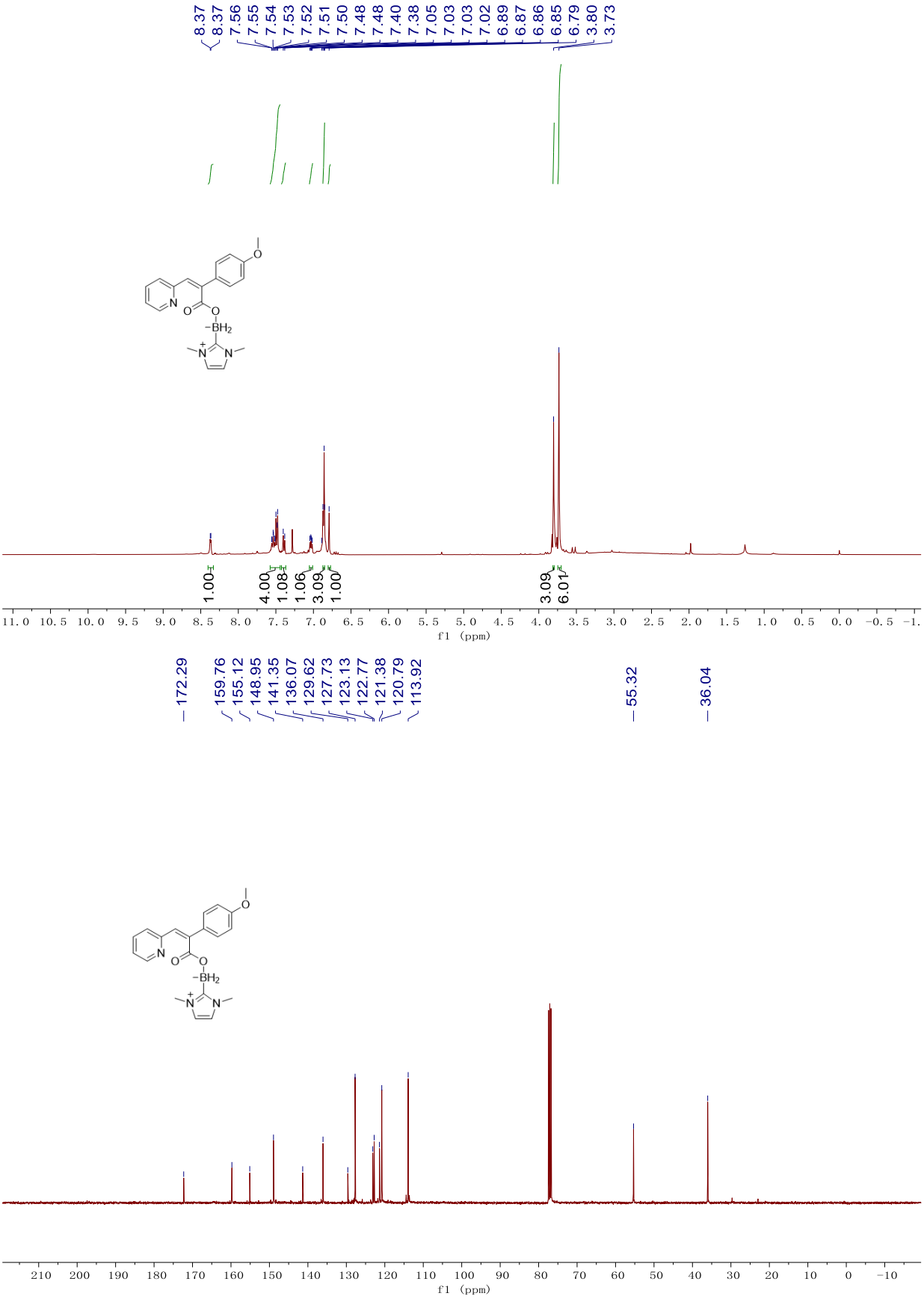




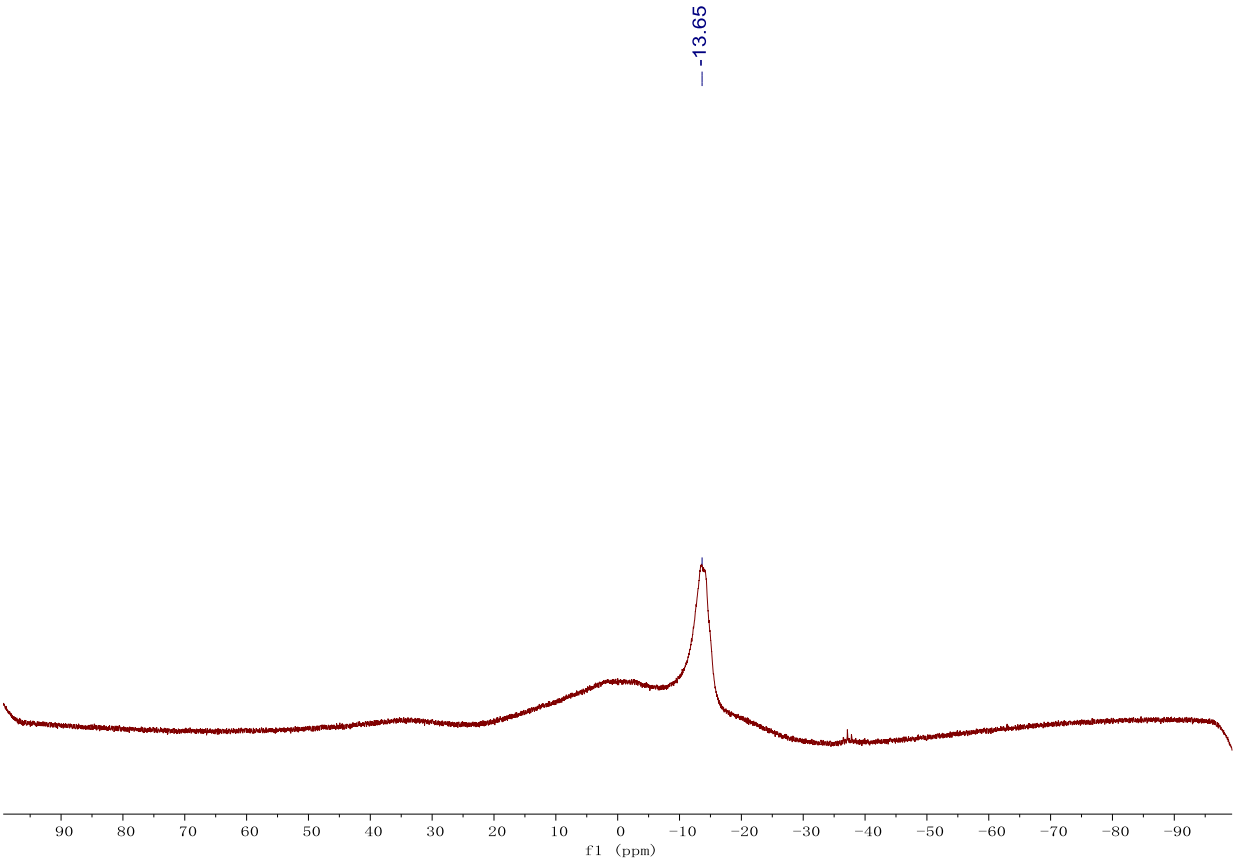
^{11}B NMR spectrum of compound **3h**



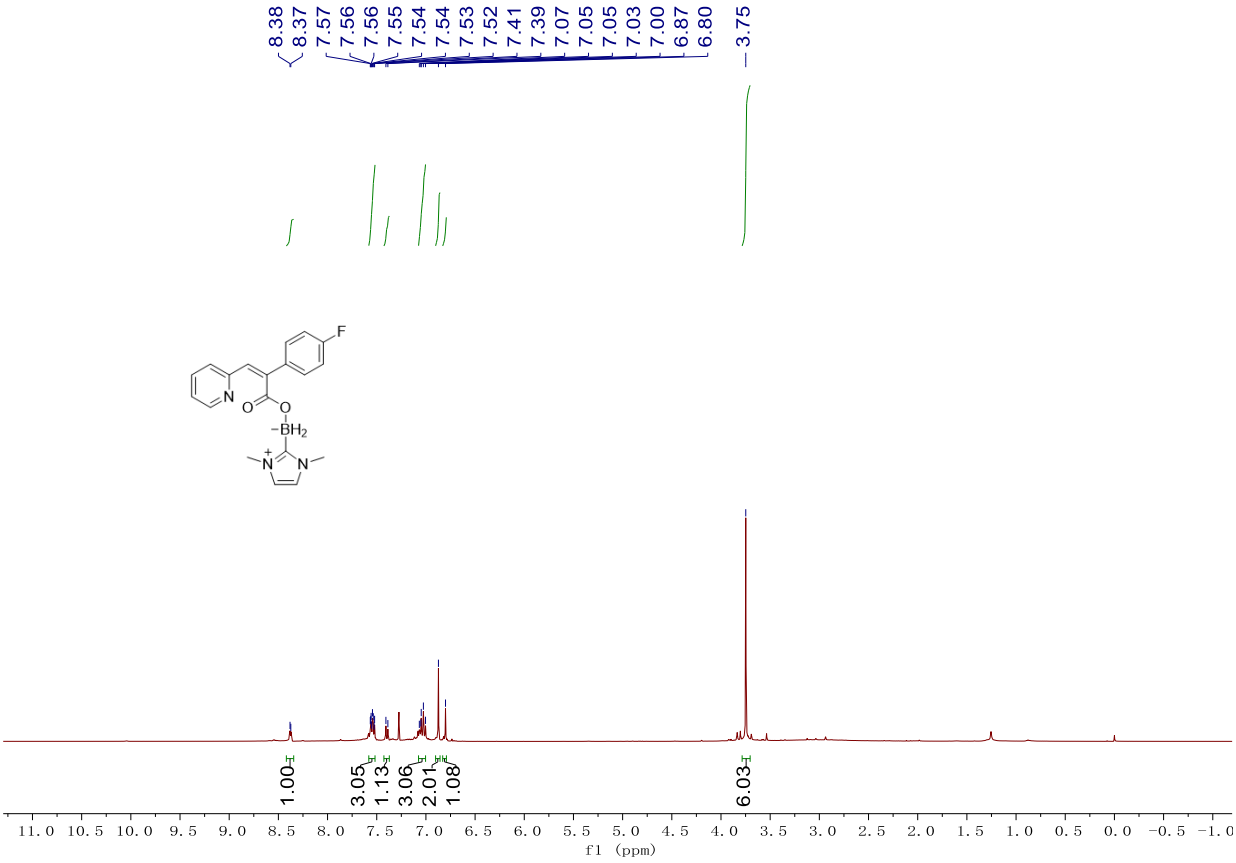
^{1}H NMR and ^{13}C NMR spectrum of compound **3i**

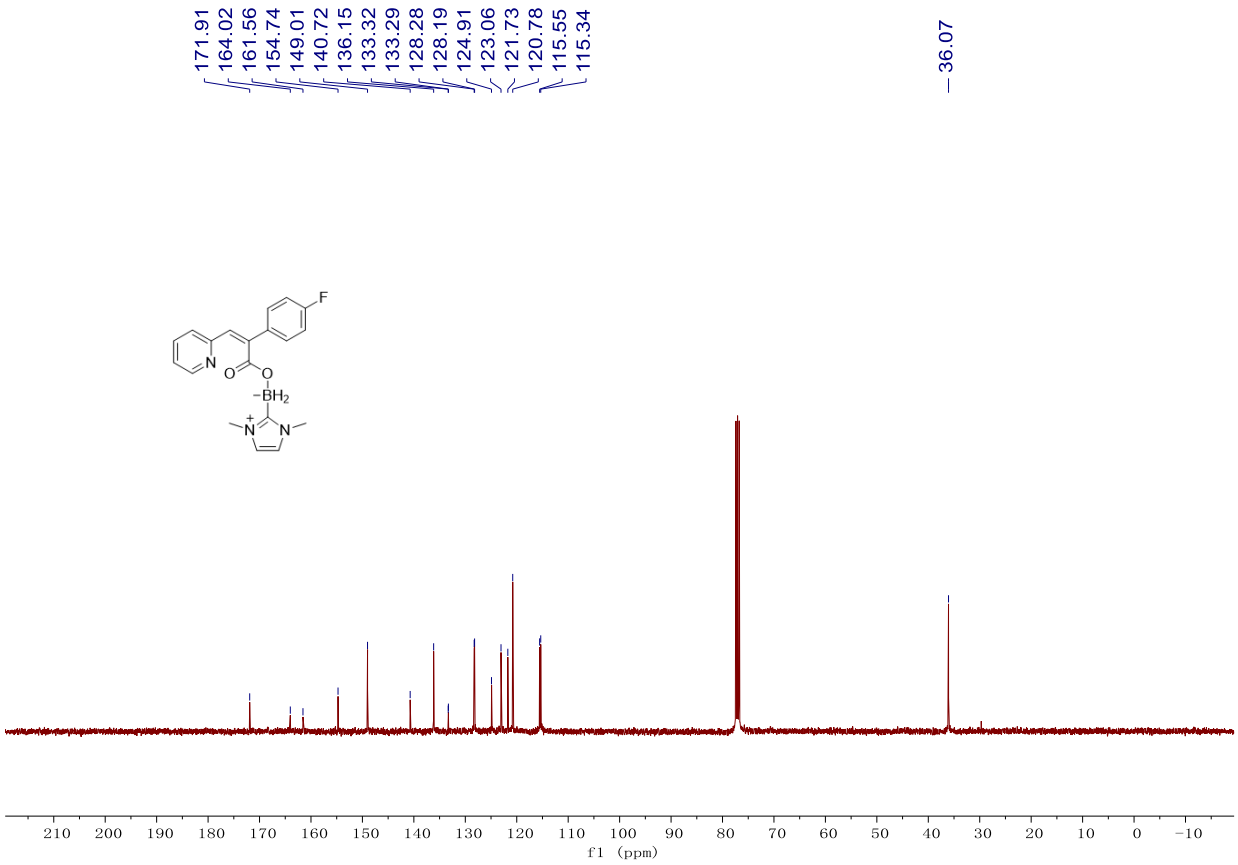


^{11}B NMR spectrum of compound **3i**

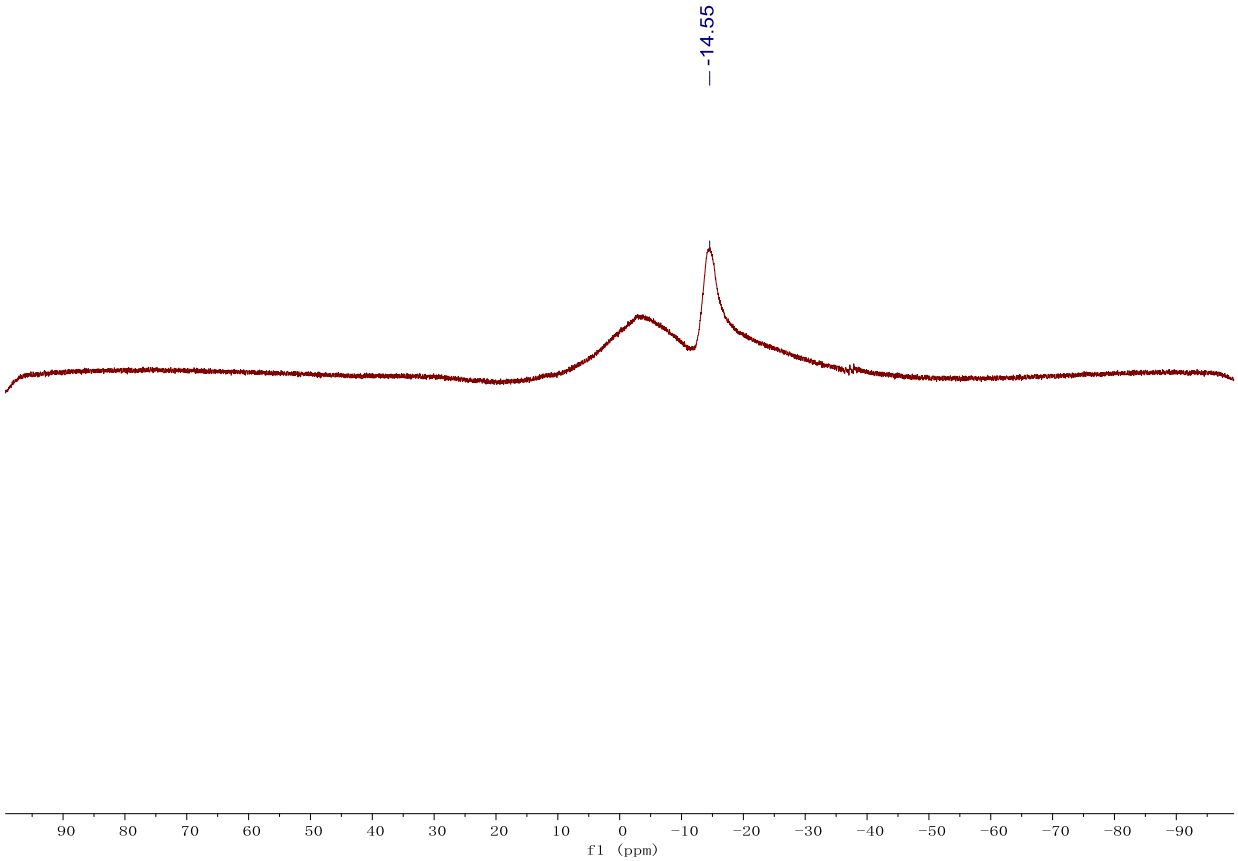


^{1}H NMR and ^{13}C NMR spectrum of compound **3j**

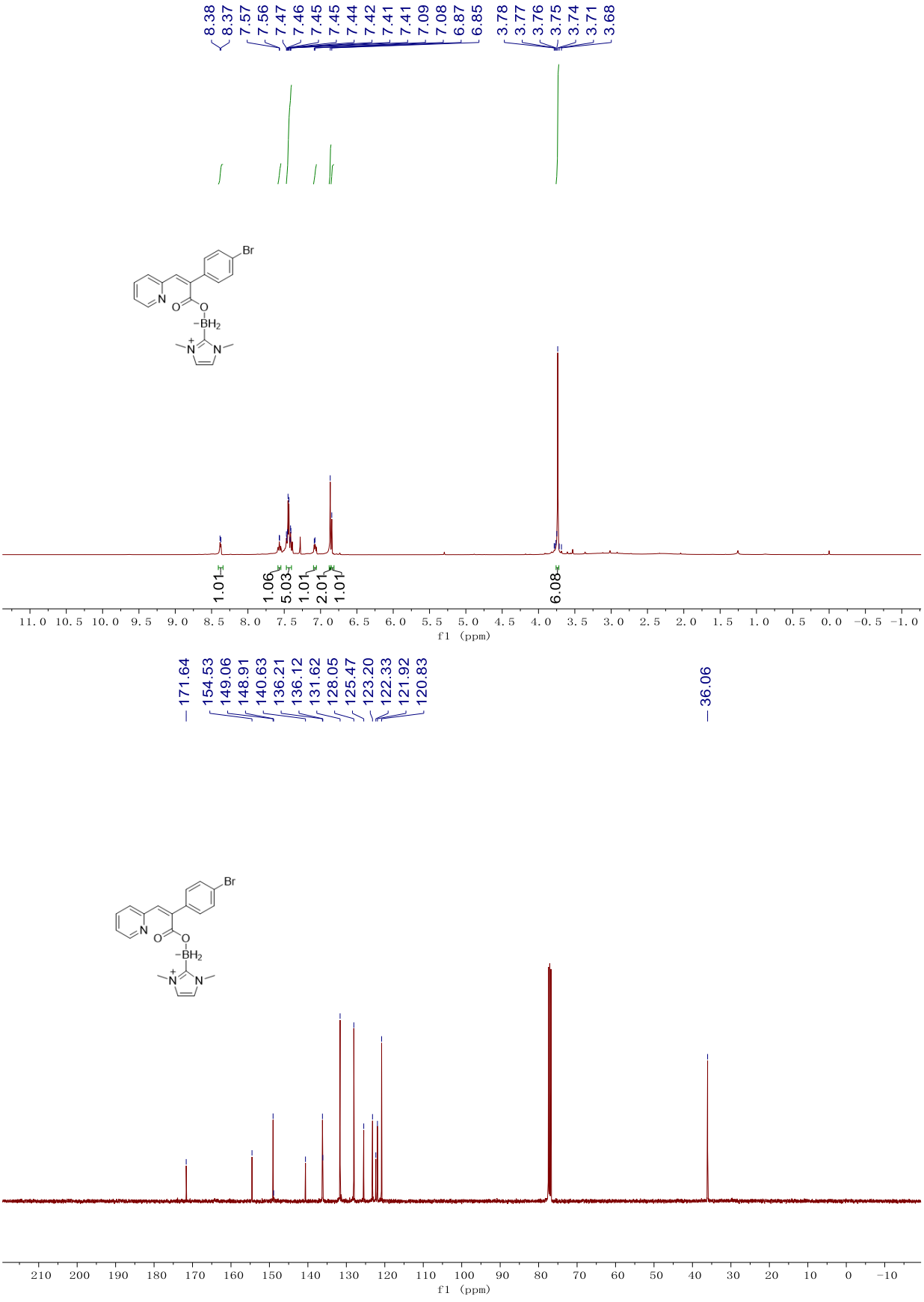




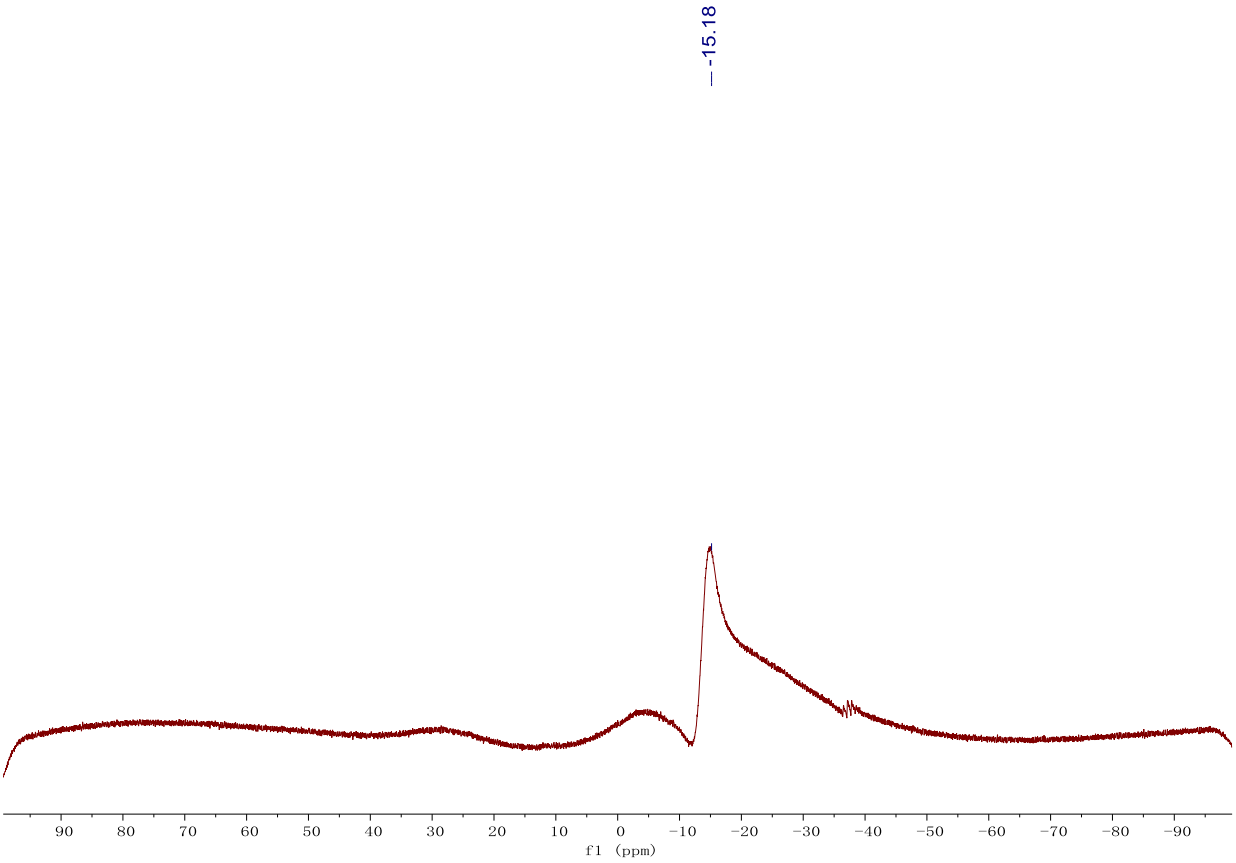
^{11}B NMR spectrum of compound **3j**



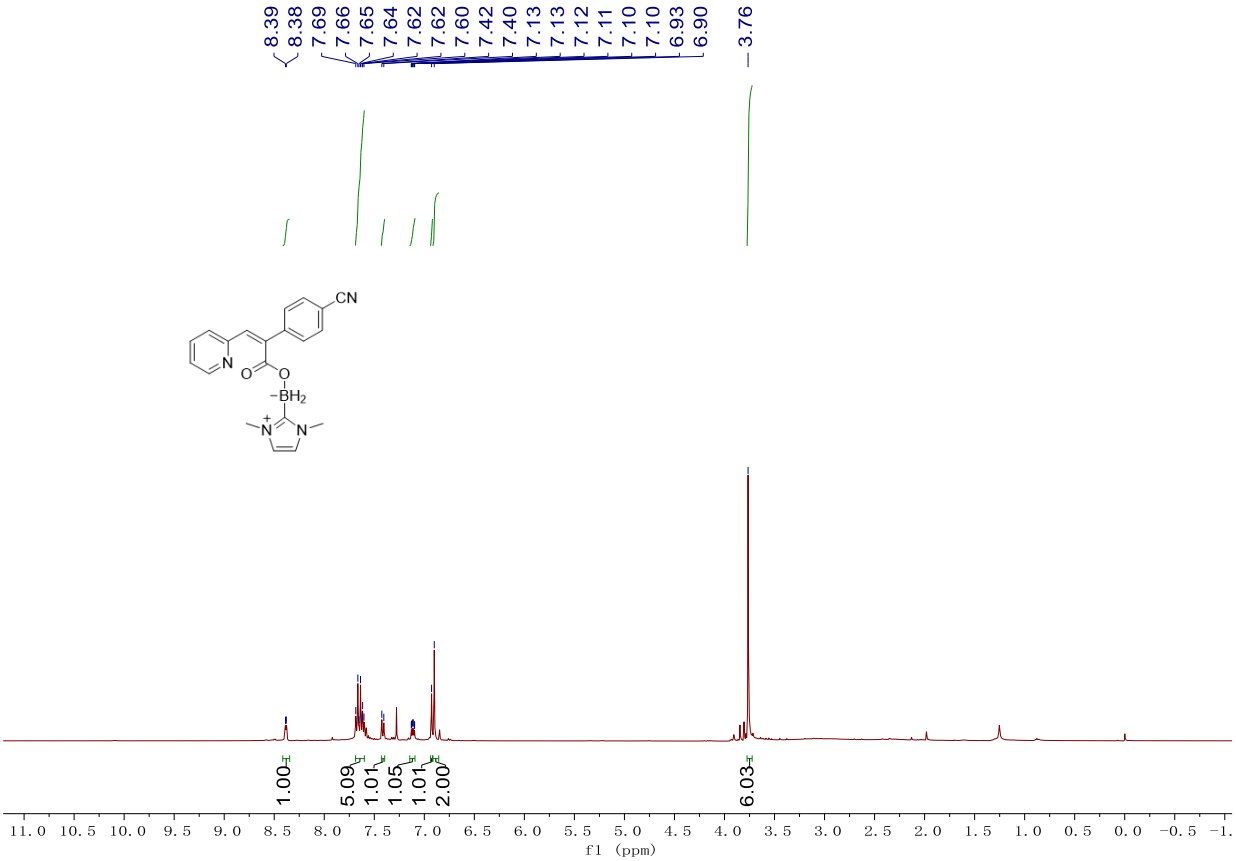
^{1}H NMR and ^{13}C NMR spectrum of compound **3k**

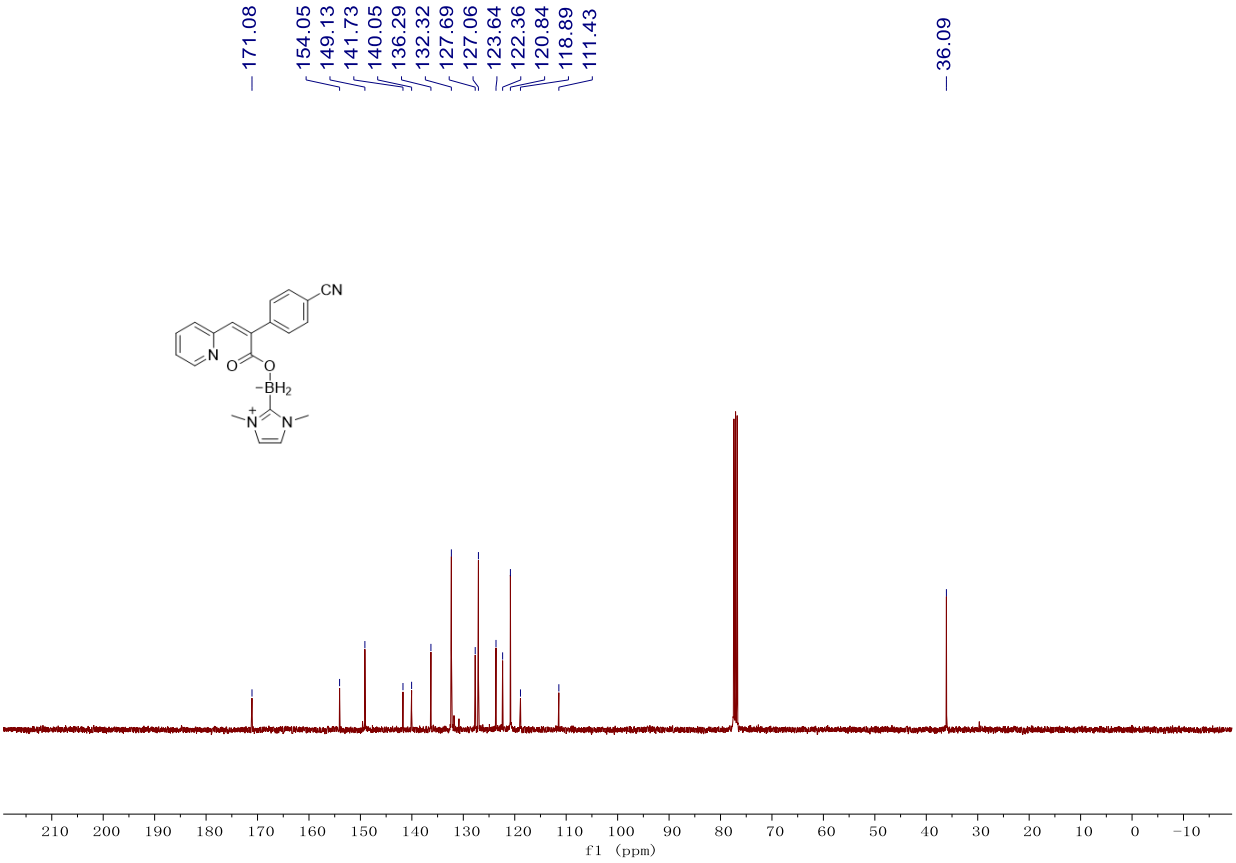


^{11}B NMR spectrum of compound **3k**

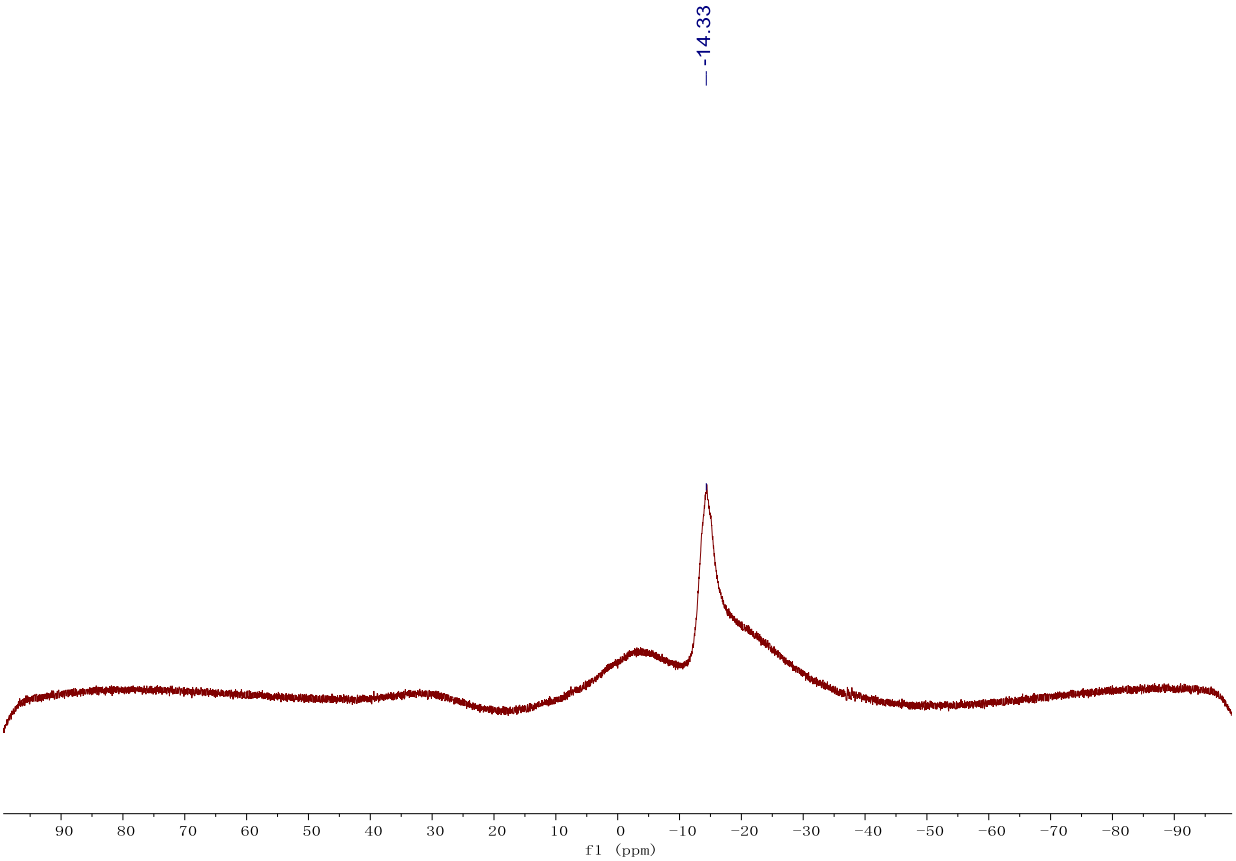


^{1}H NMR and ^{13}C NMR spectrum of compound **3l**

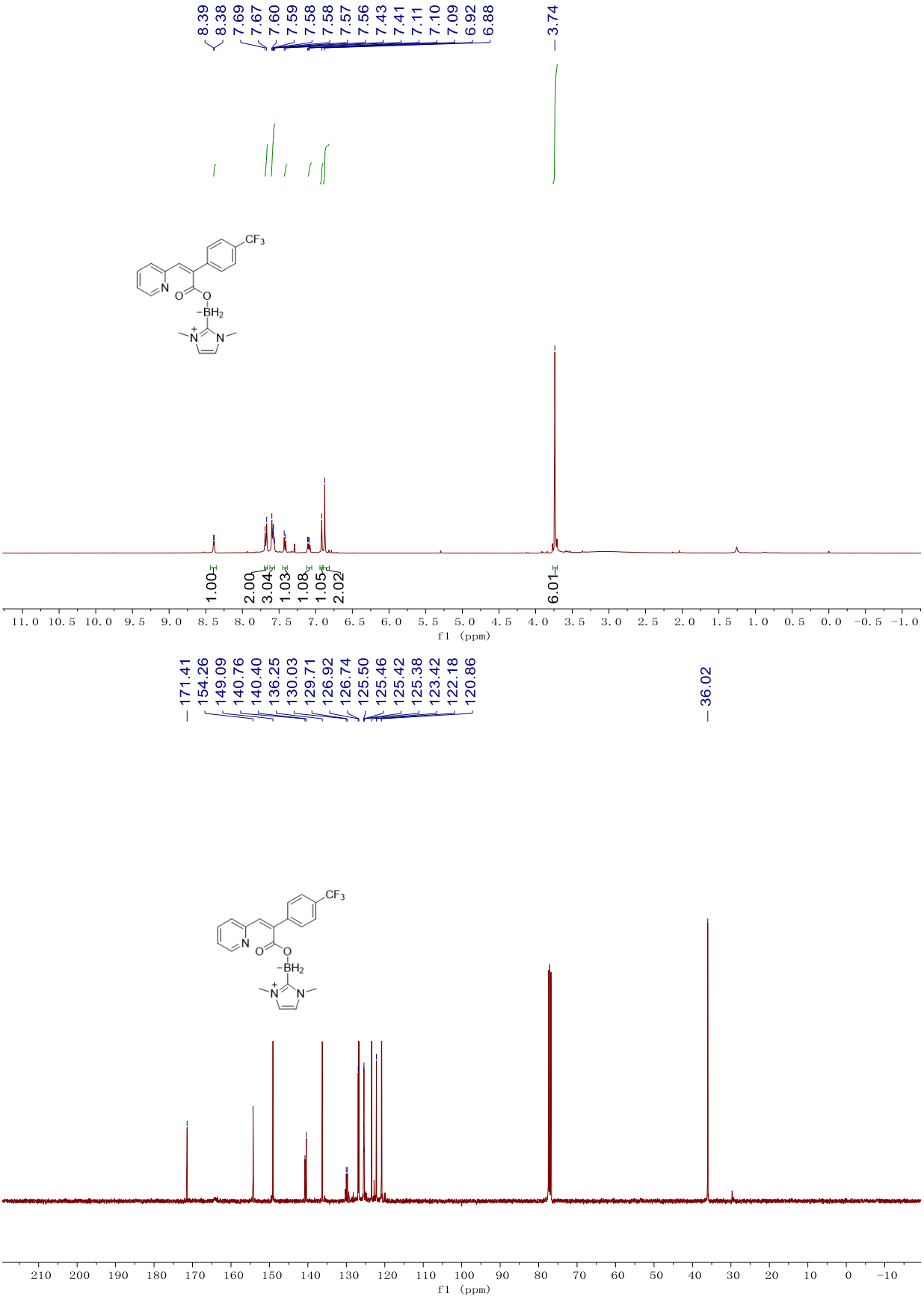




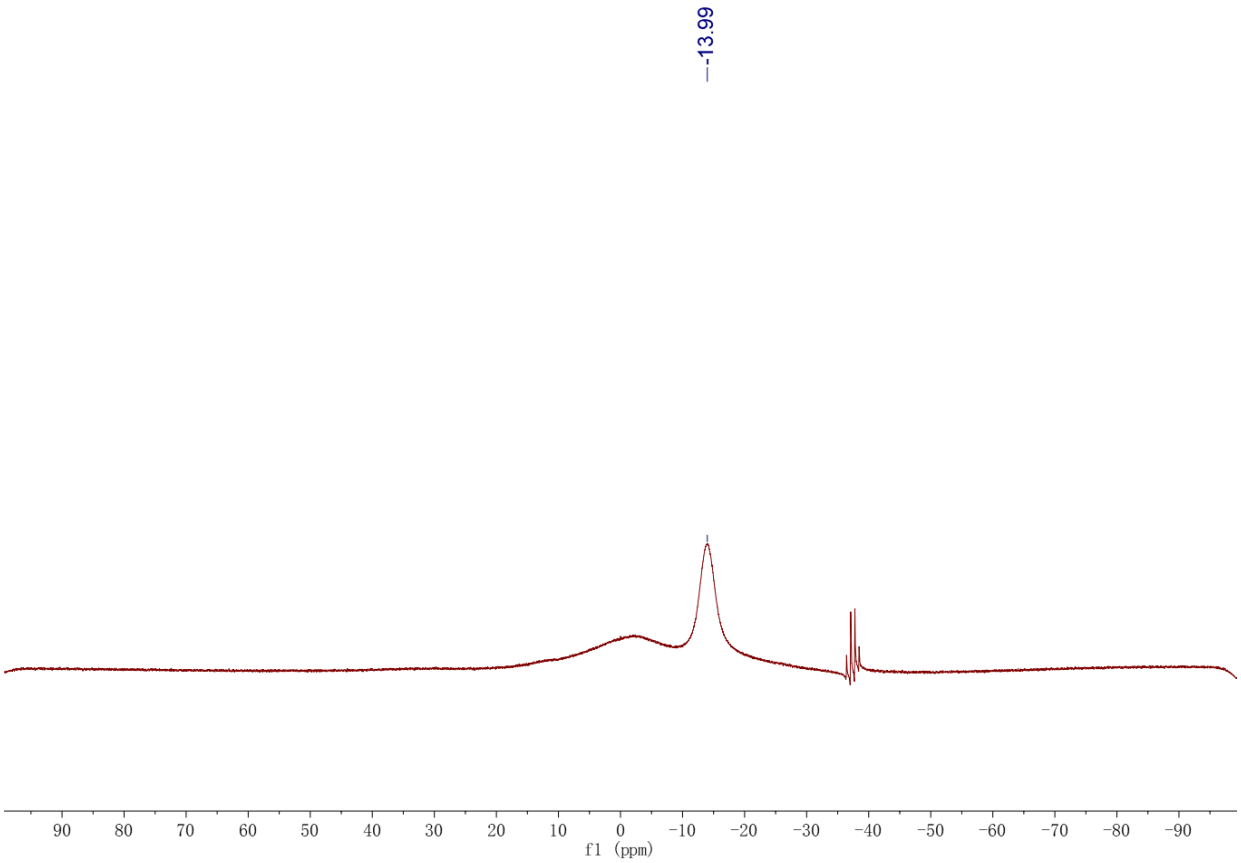
^{11}B NMR spectrum of compound **3l**



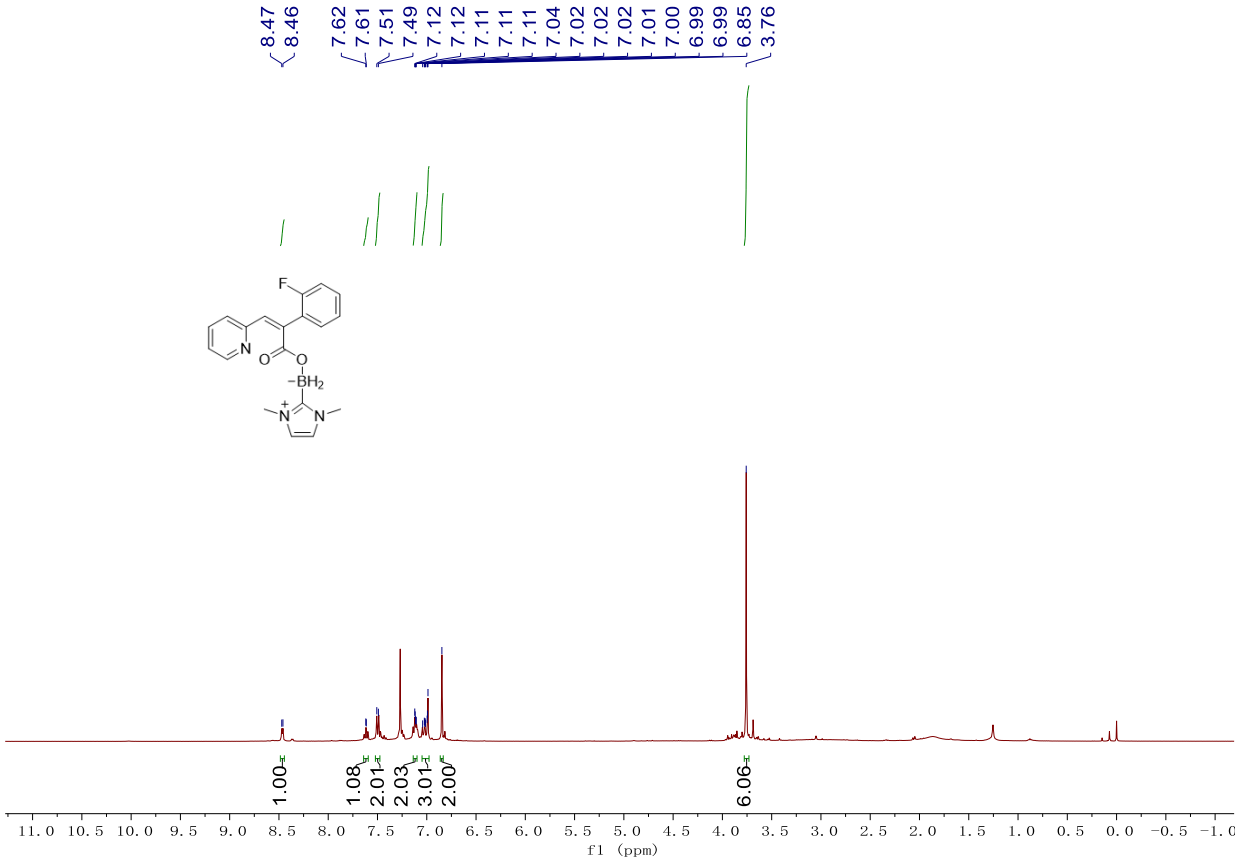
^{1}H NMR and ^{13}C NMR spectrum of compound **3m**

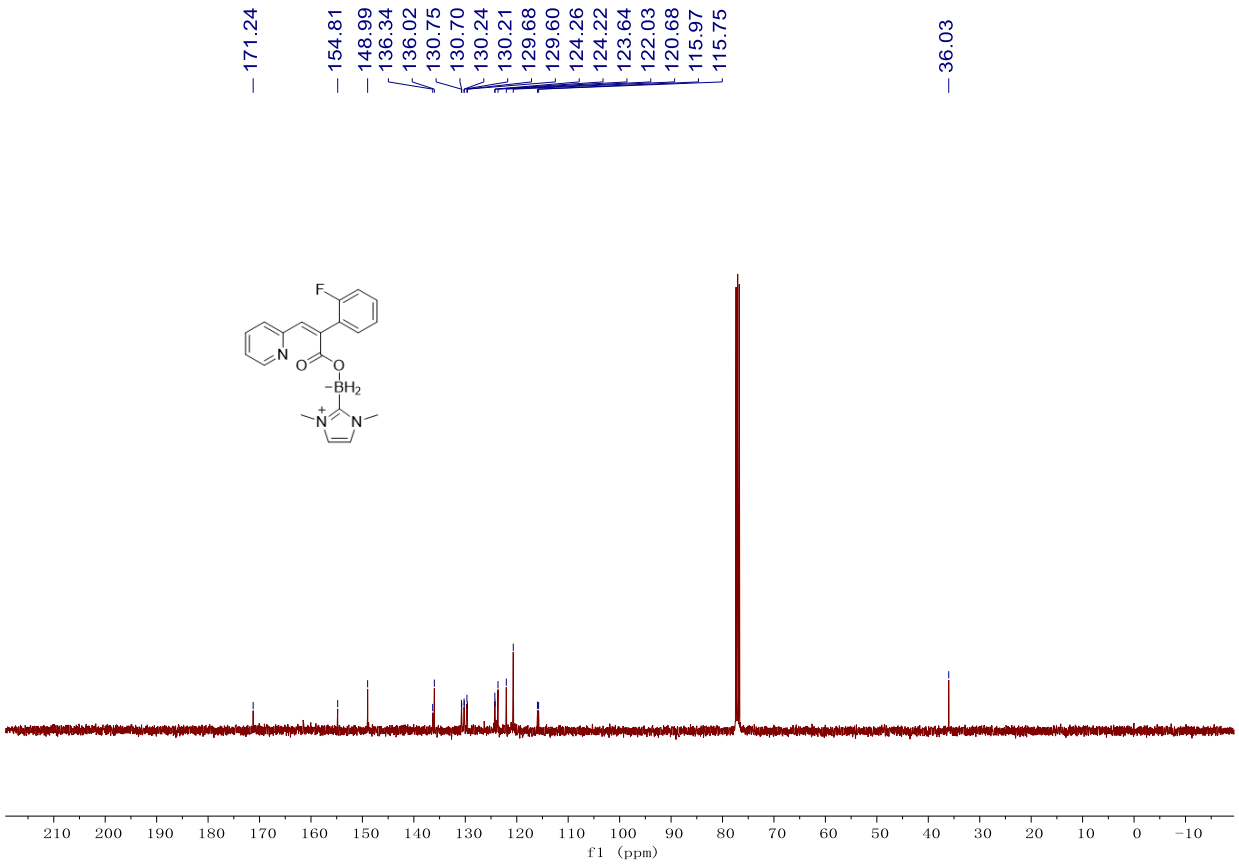


^{11}B NMR spectrum of compound **3m**

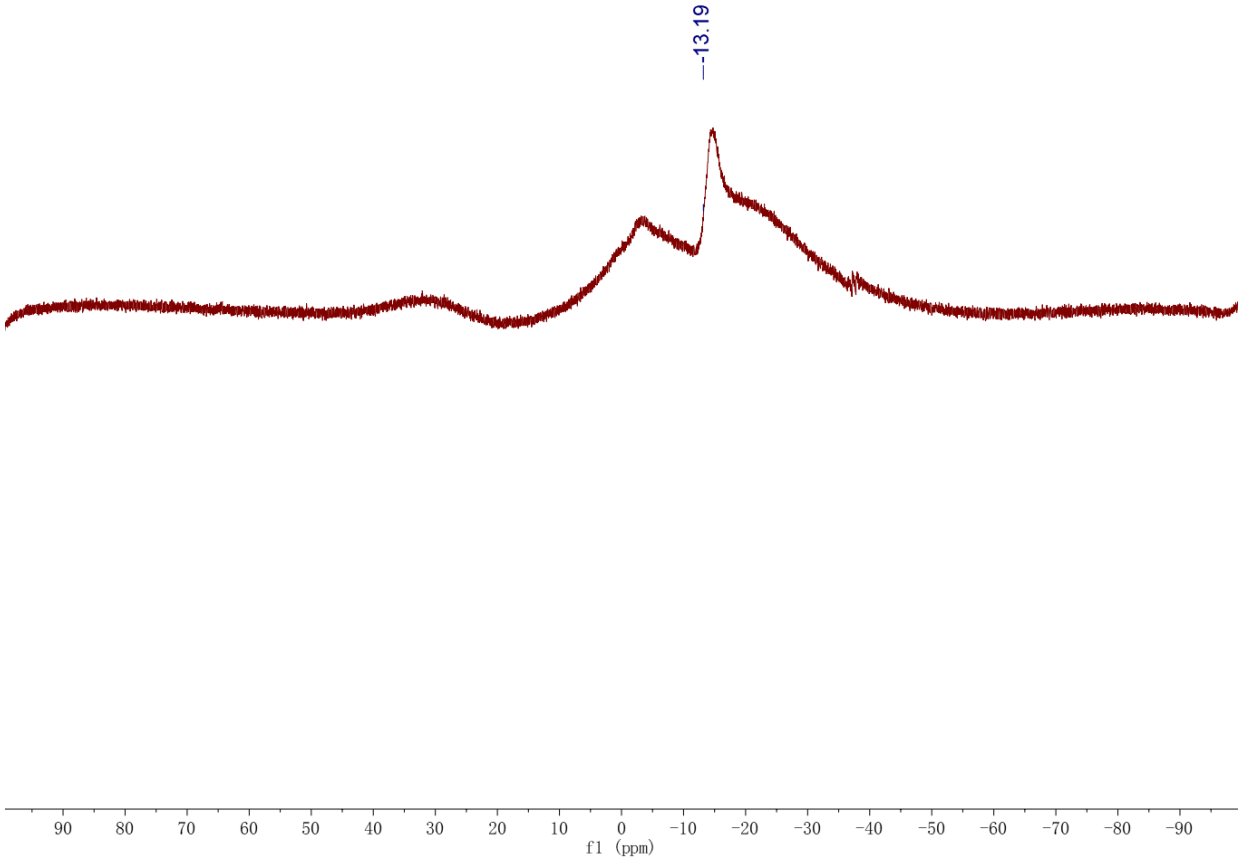


^{1}H NMR and ^{13}C NMR spectrum of compound **3n**

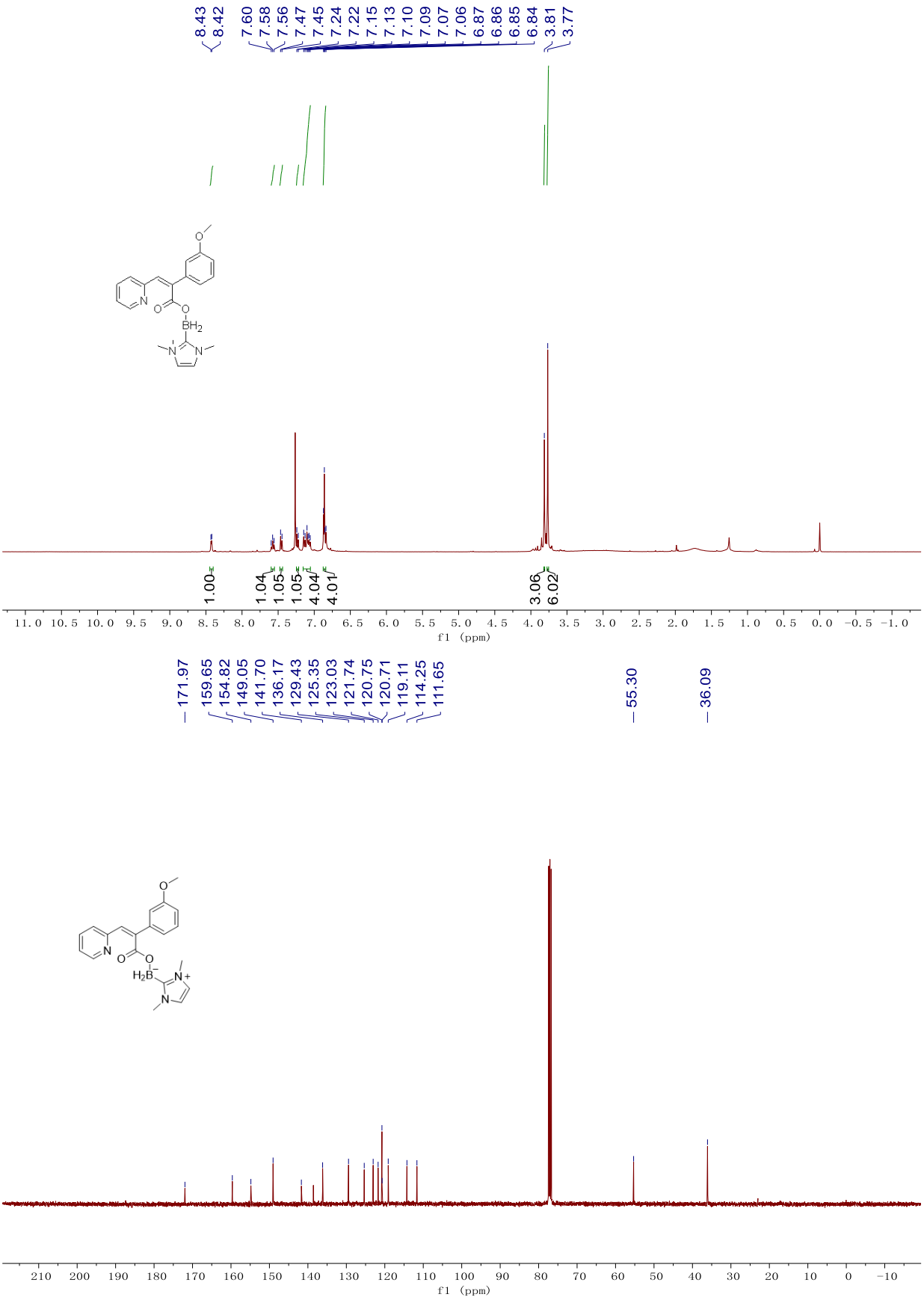




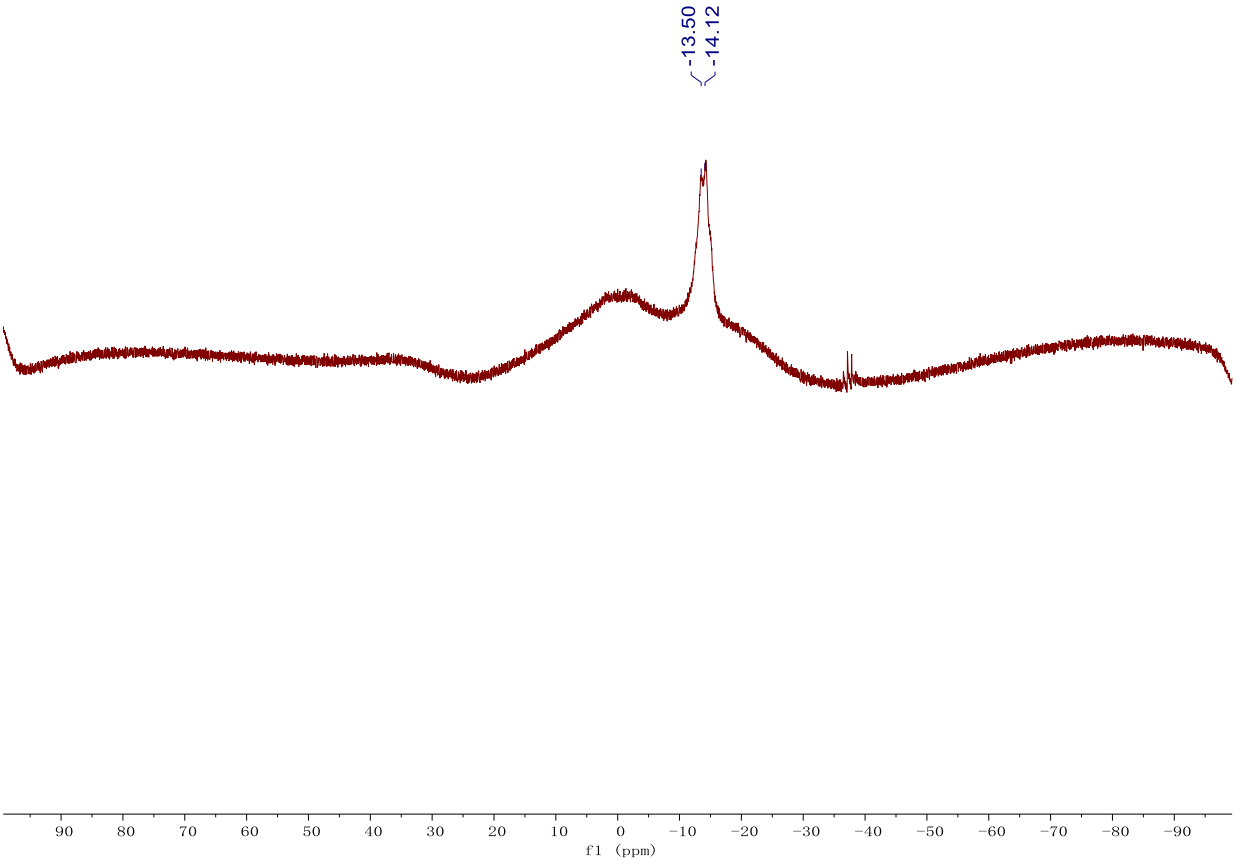
^{11}B NMR spectrum of compound **3n**



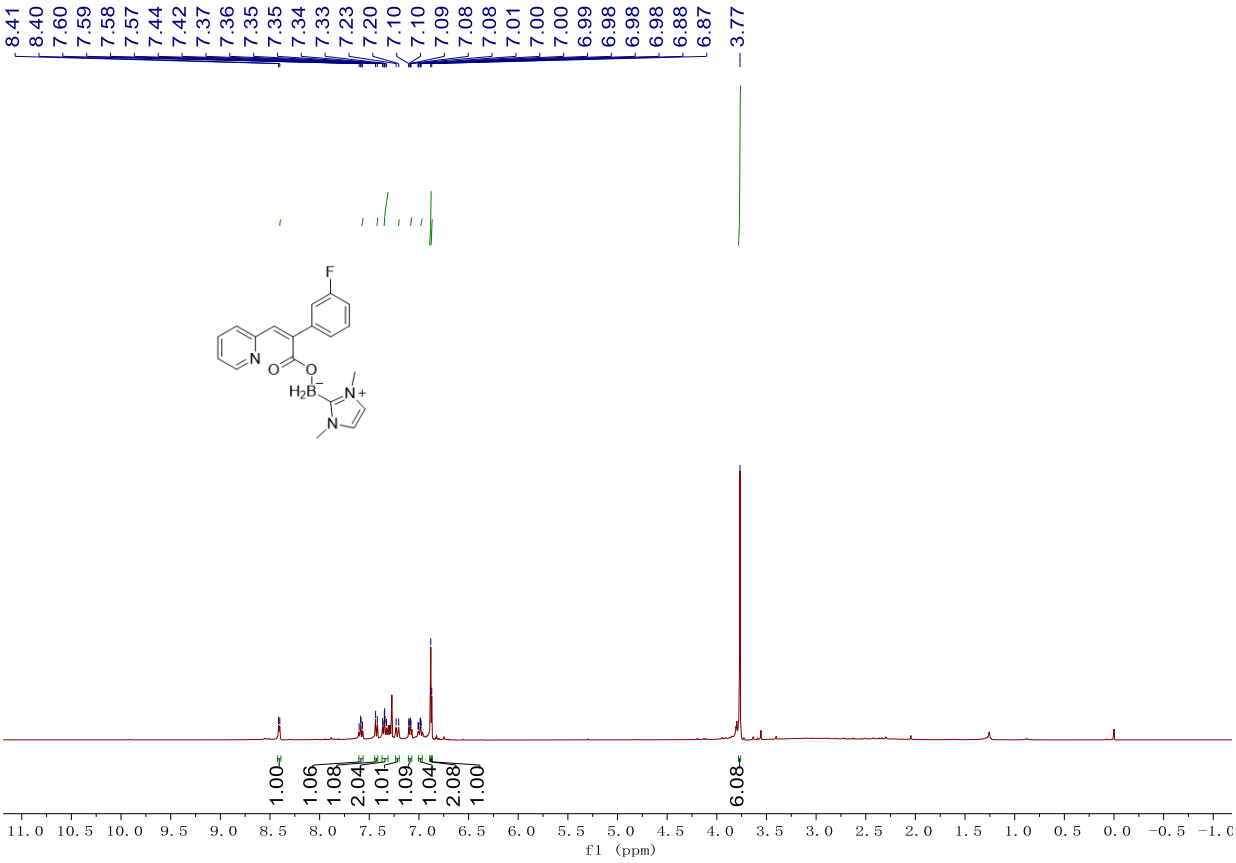
^{1}H NMR and ^{13}C NMR spectrum of compound **3o**

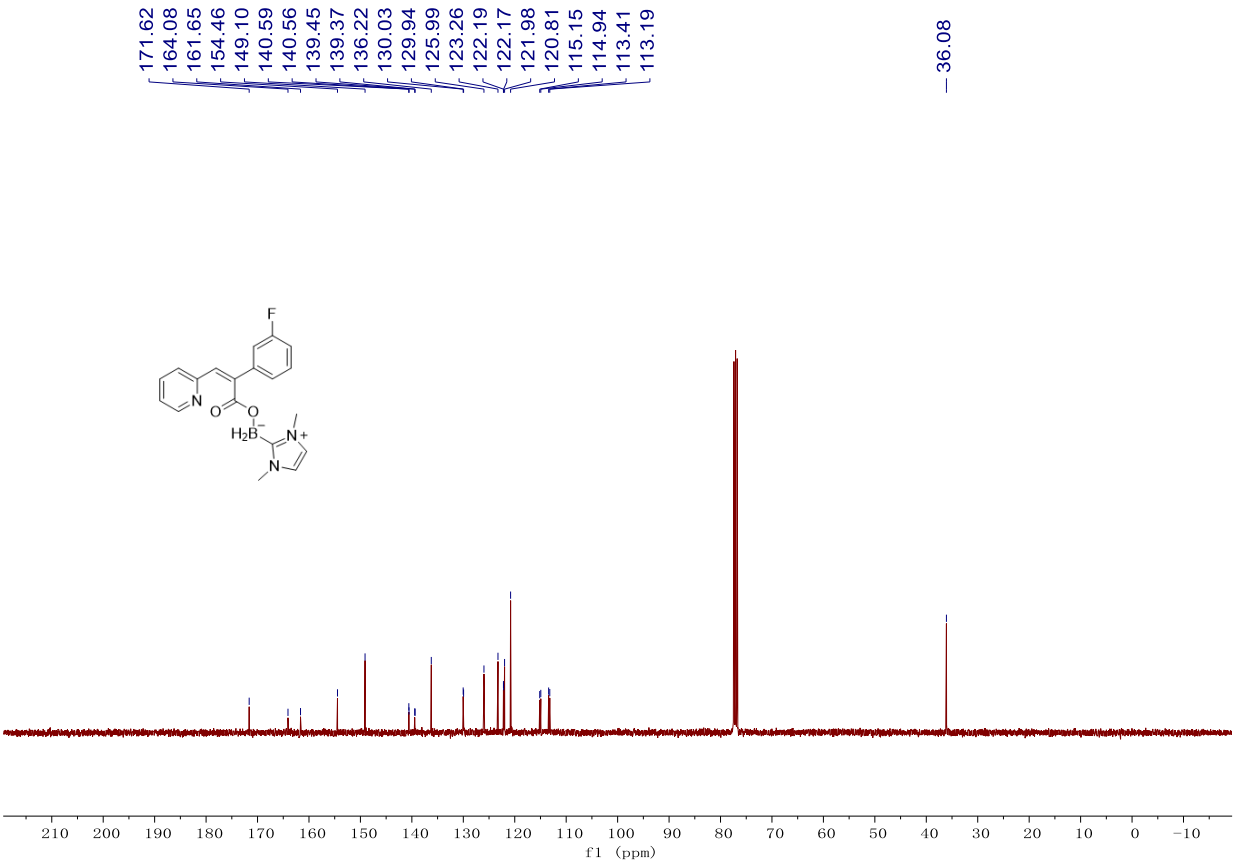


^{11}B NMR spectrum of compound **3o**

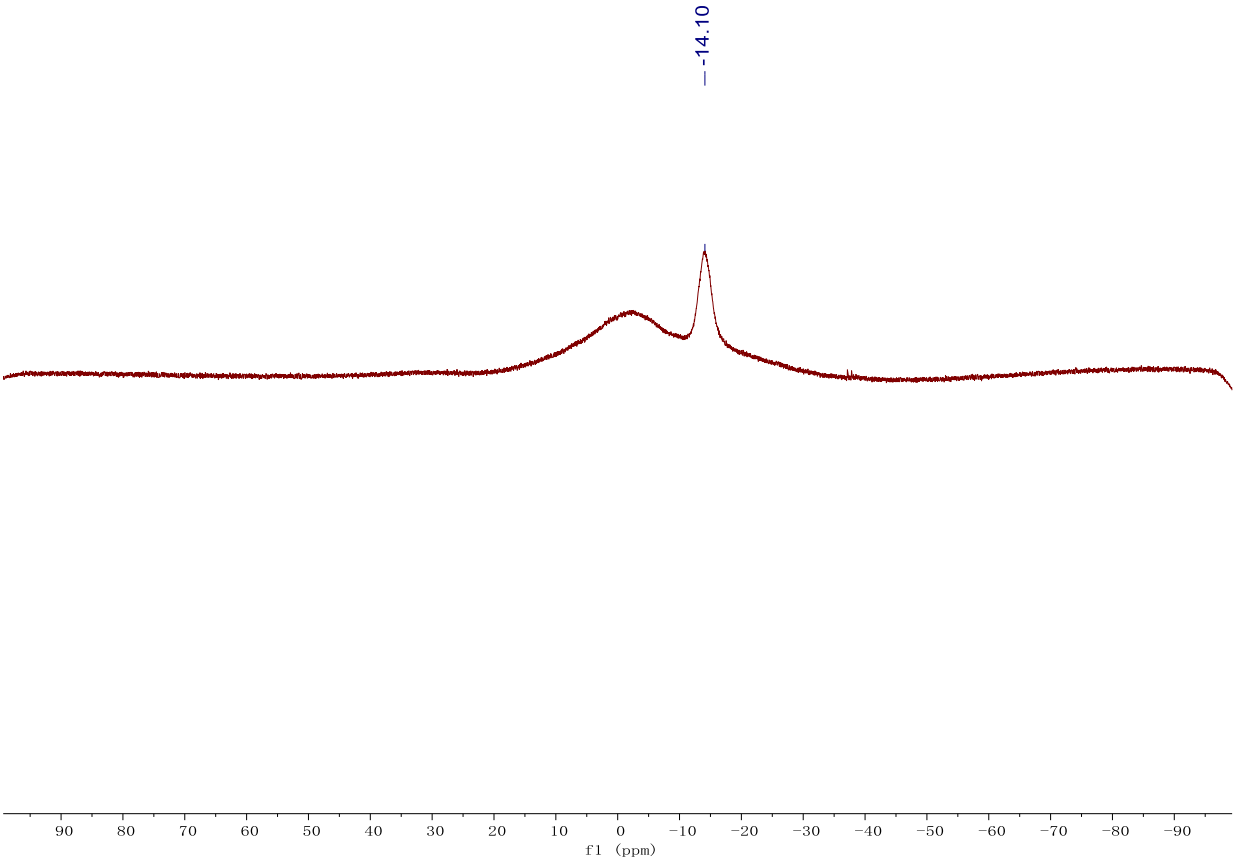


^{1}H NMR and ^{13}C NMR spectrum of compound **3p**

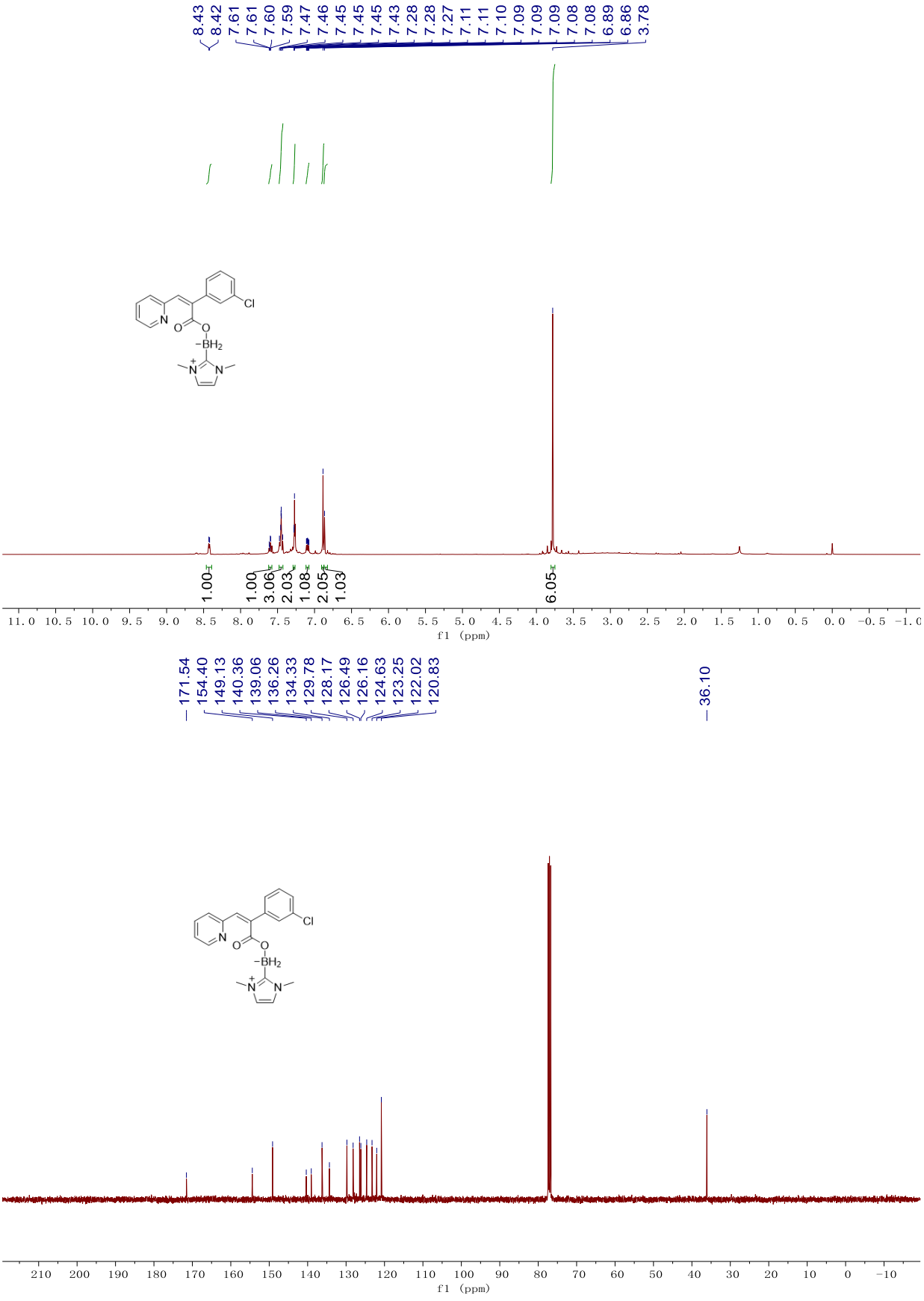




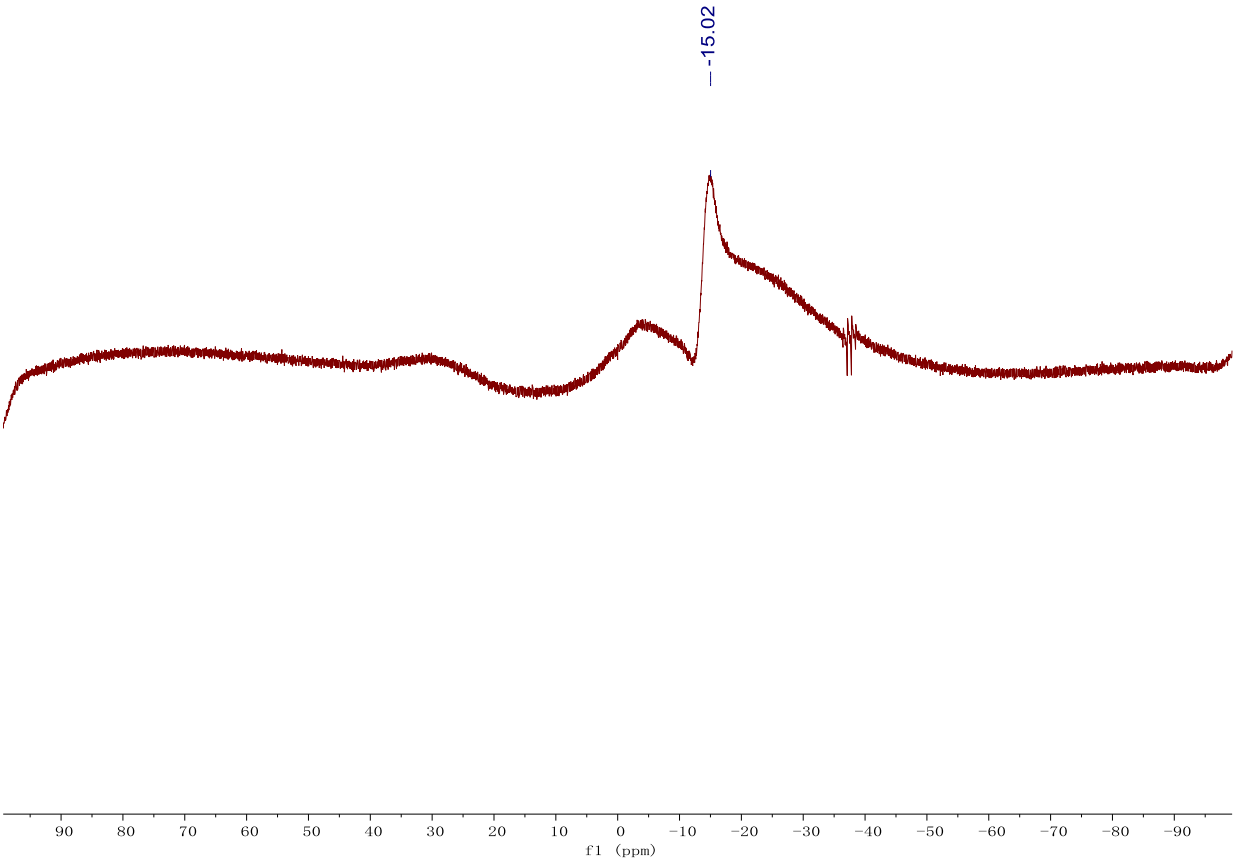
^{11}B NMR spectrum of compound **3p**



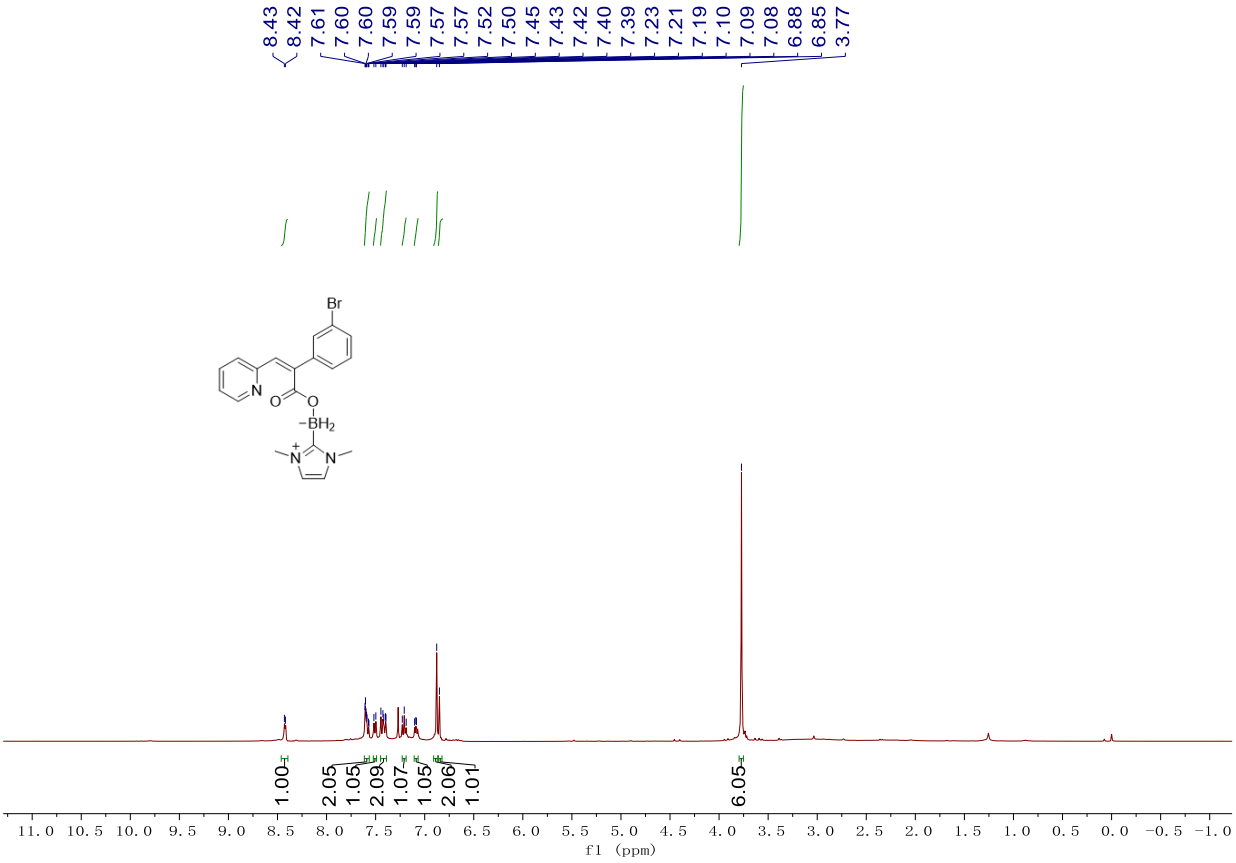
^{1}H NMR and ^{13}C NMR spectrum of compound **3q**

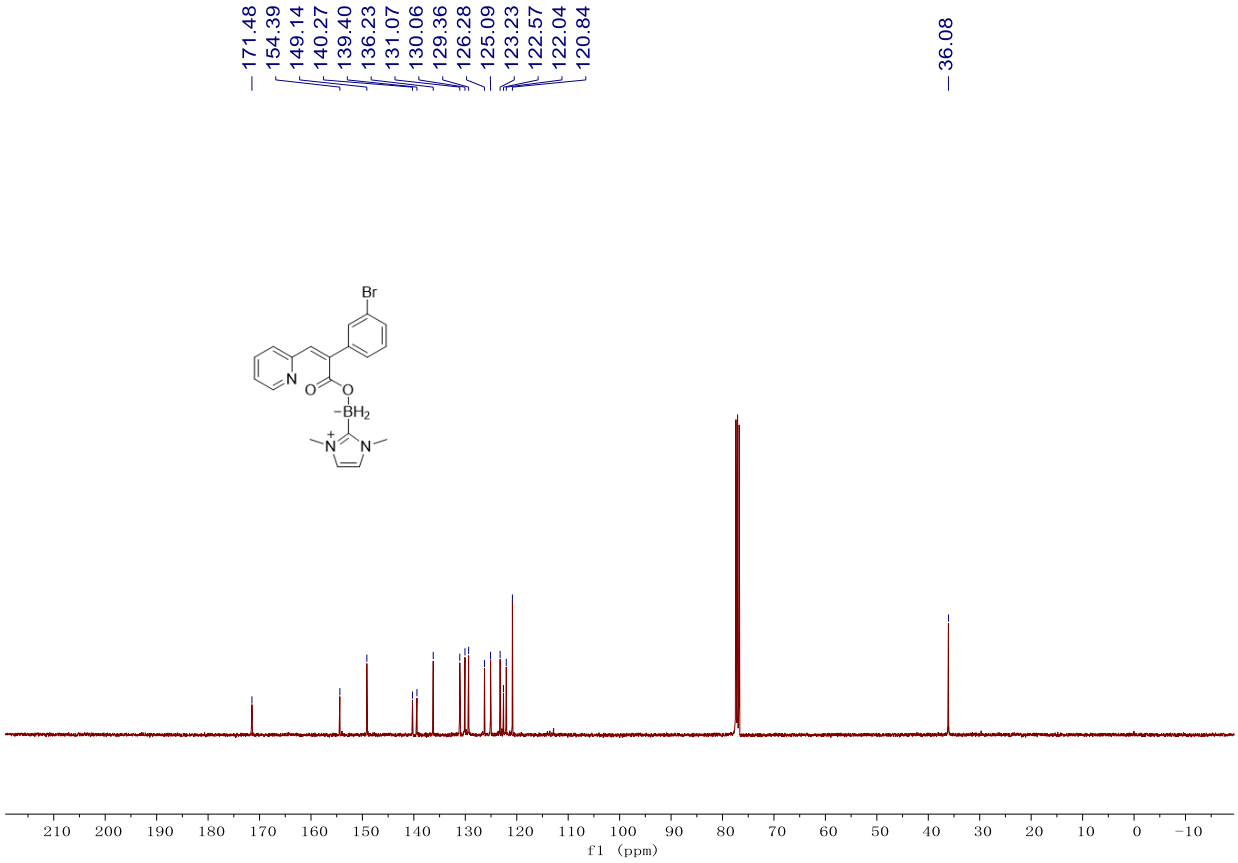


^{11}B NMR spectrum of compound **3q**

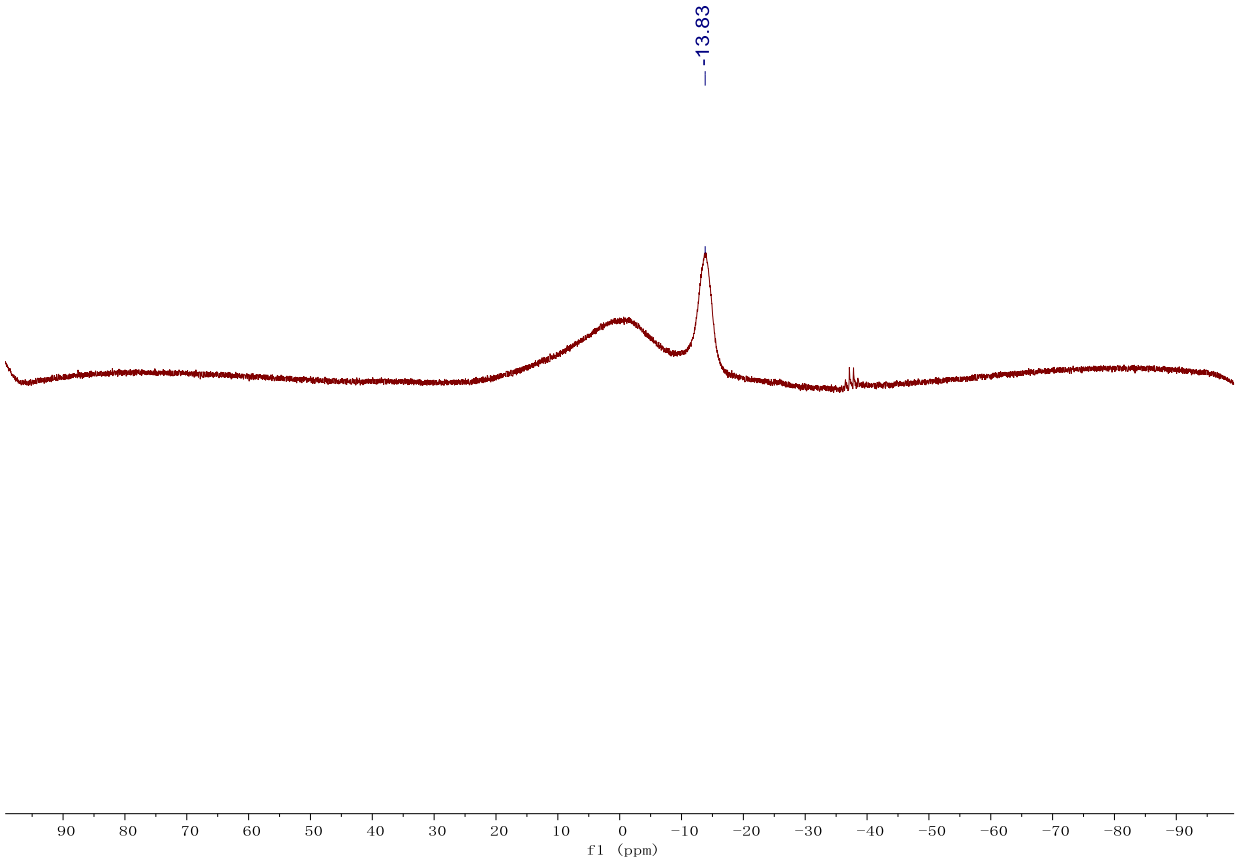


^{1}H NMR and ^{13}C NMR spectrum of compound **3r**

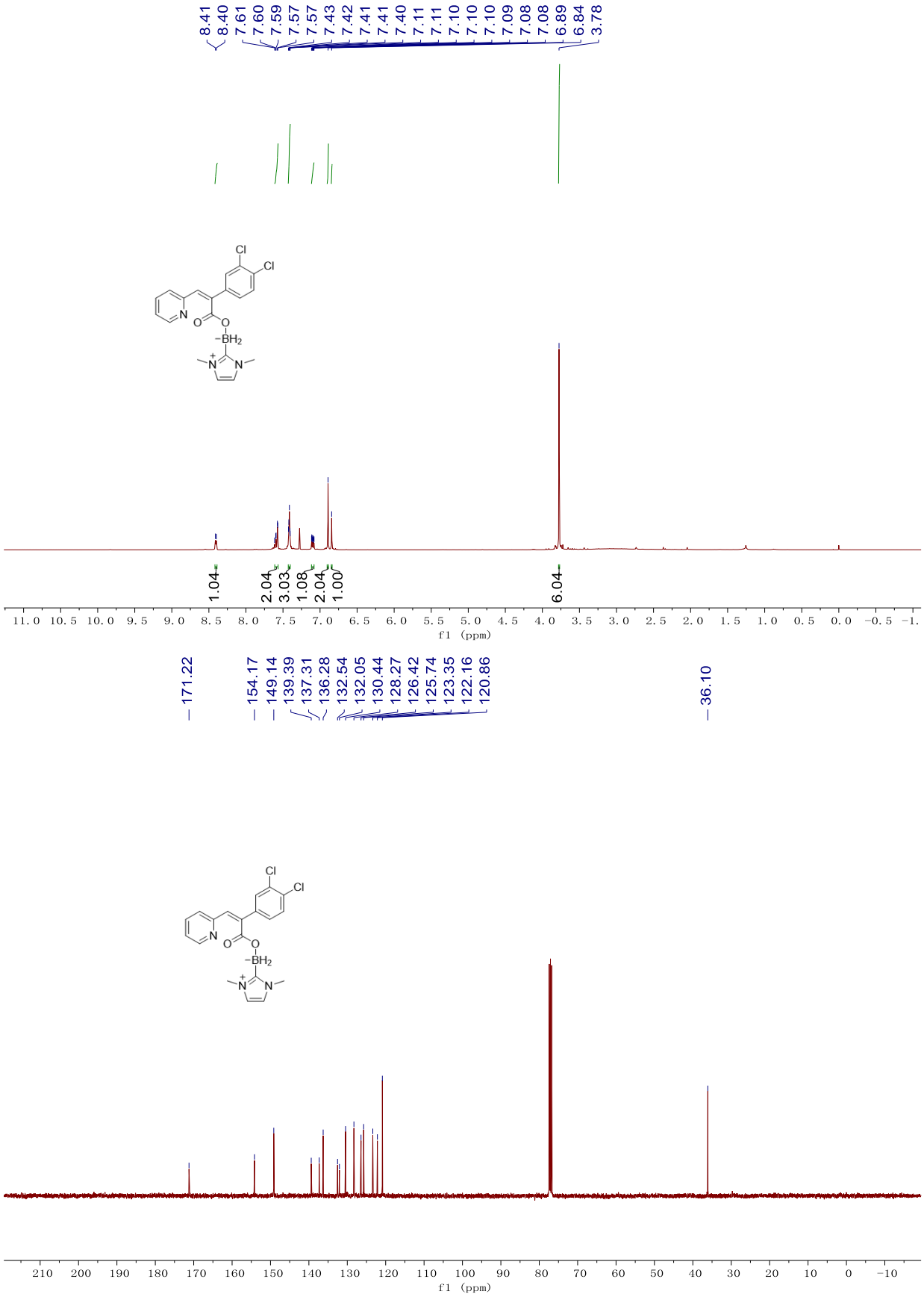




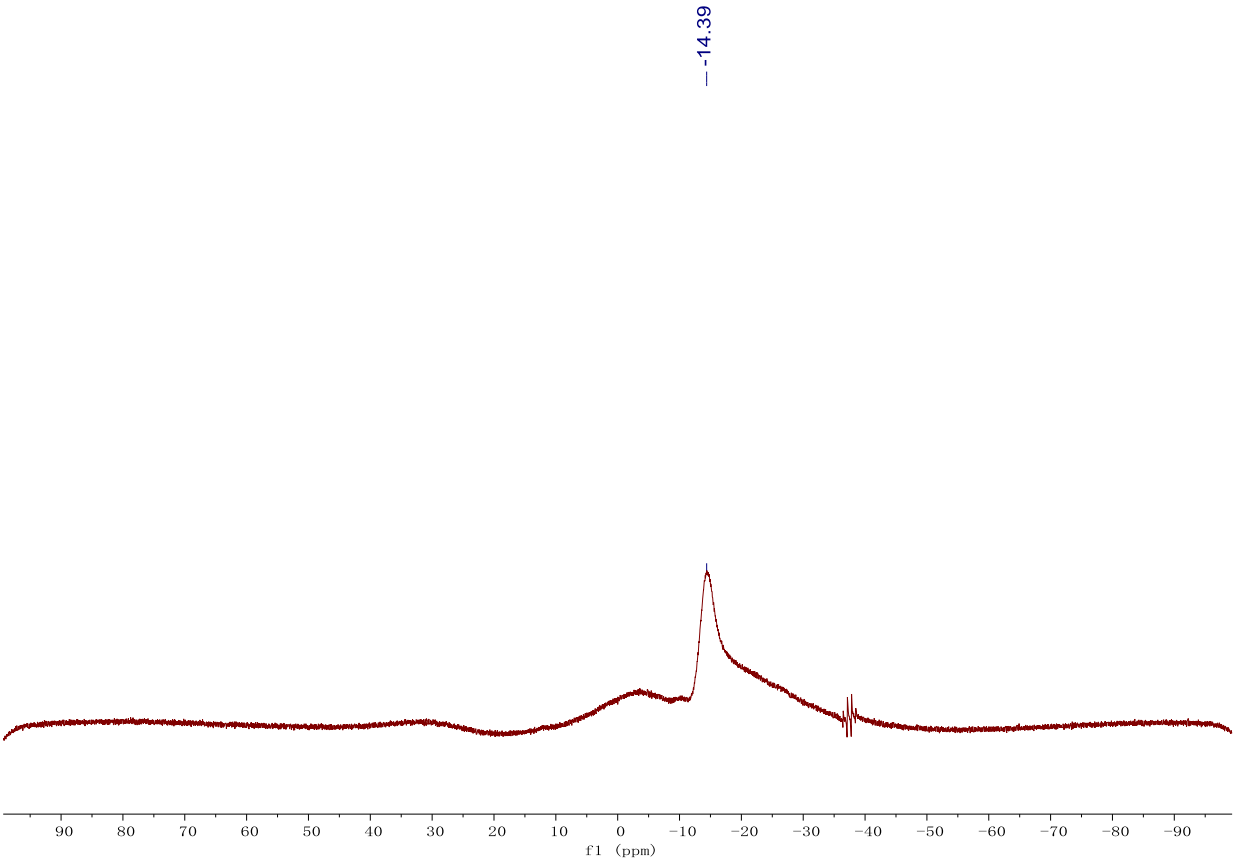
^{11}B NMR spectrum of compound **3r**



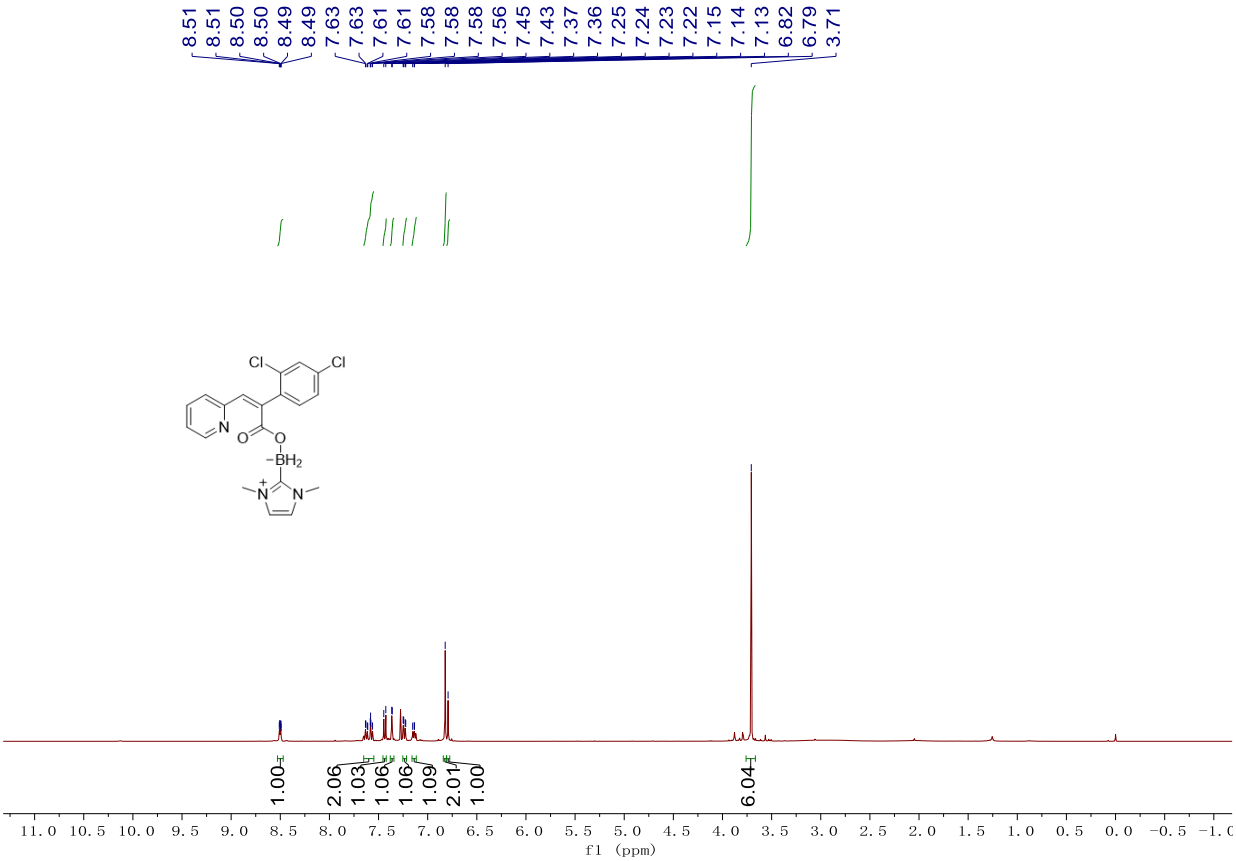
^{1}H NMR and ^{13}C NMR spectrum of compound **3s**

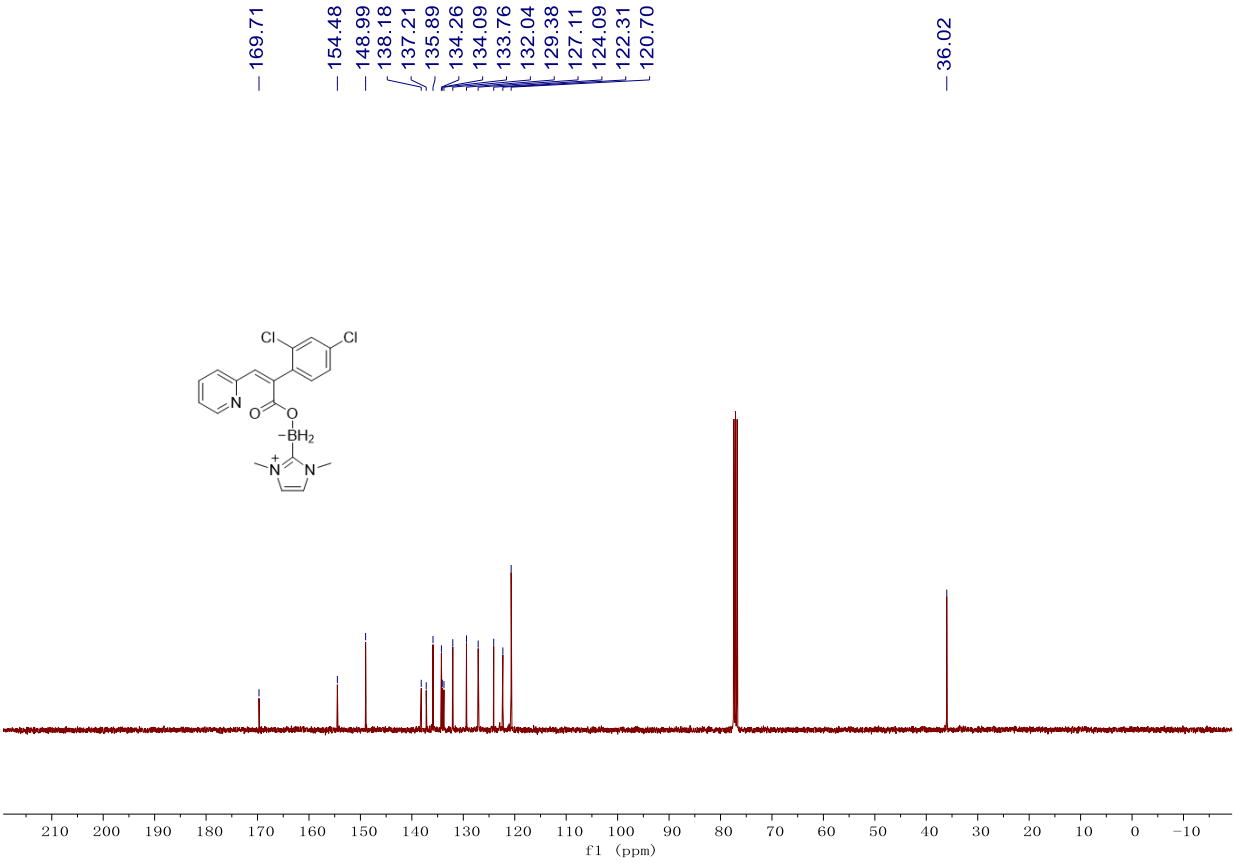


^{11}B NMR spectrum of compound **3s**

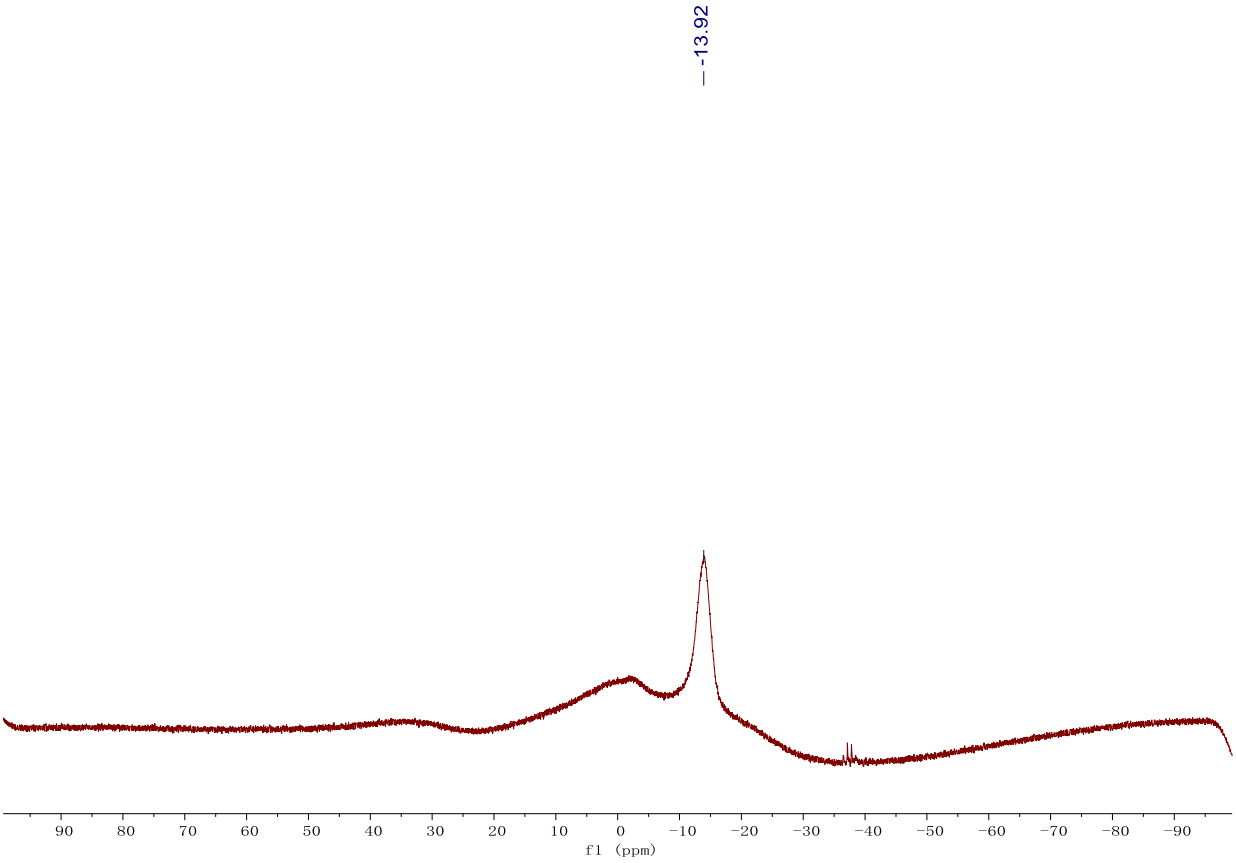


^{1}H NMR and ^{13}C NMR spectrum of compound **3t**

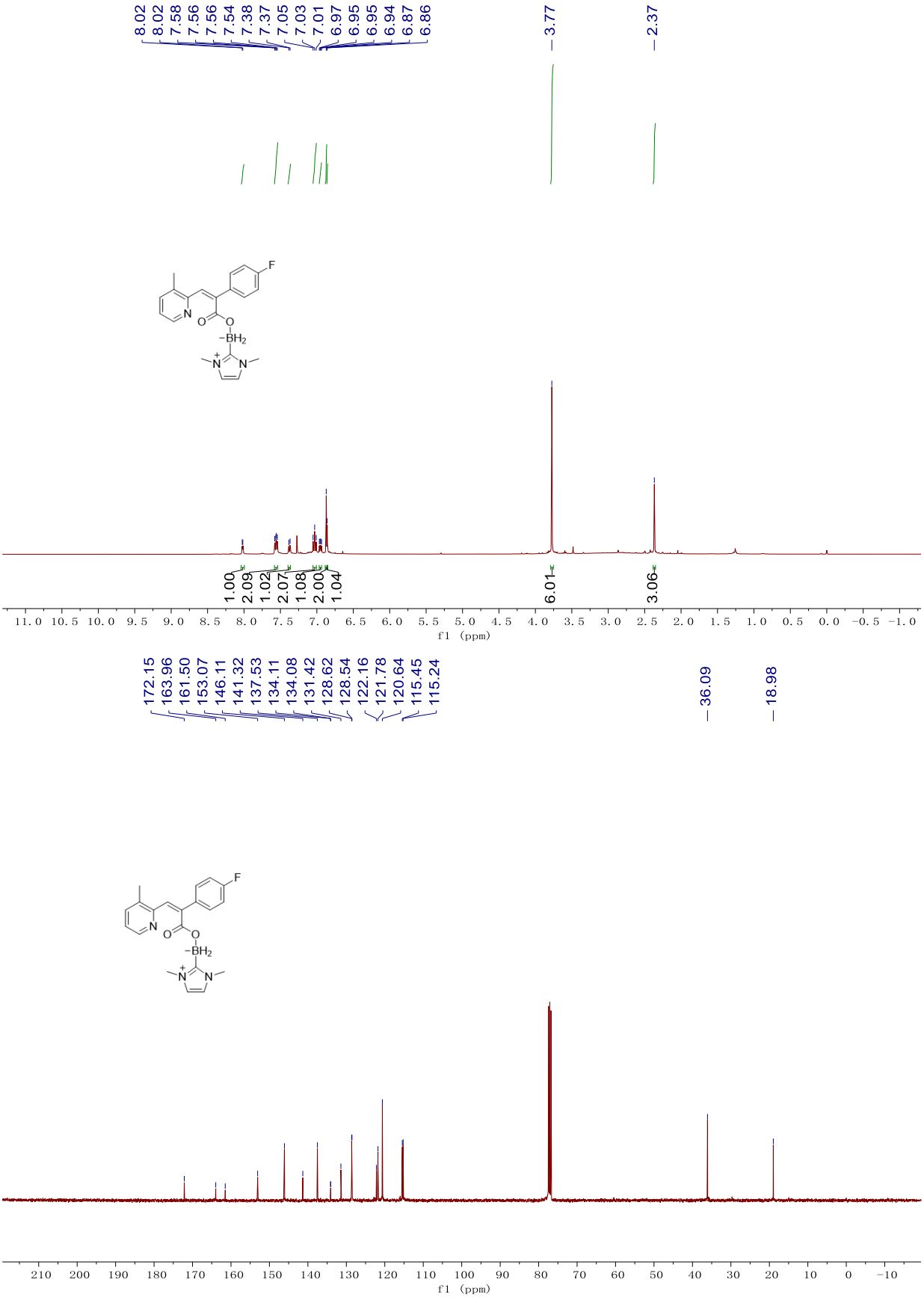




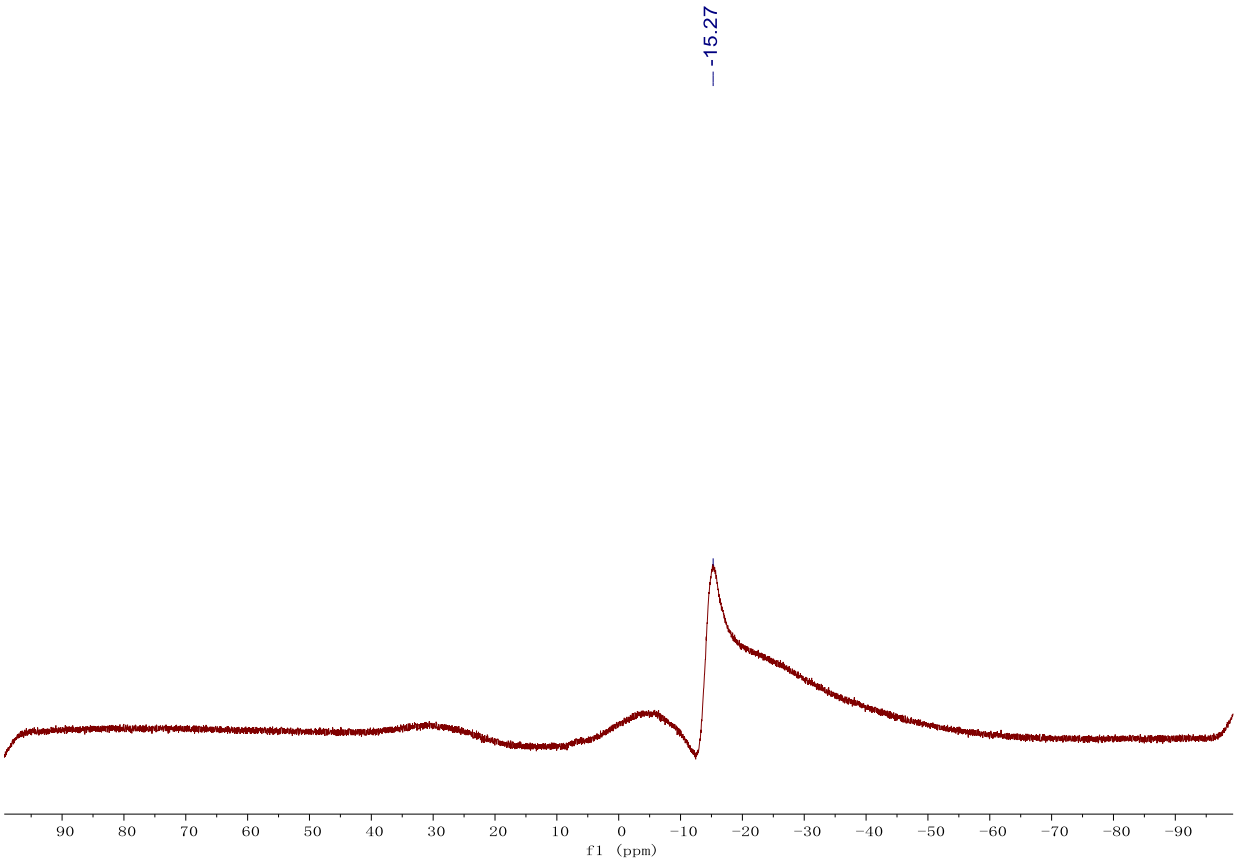
^{11}B NMR spectrum of compound **3t**



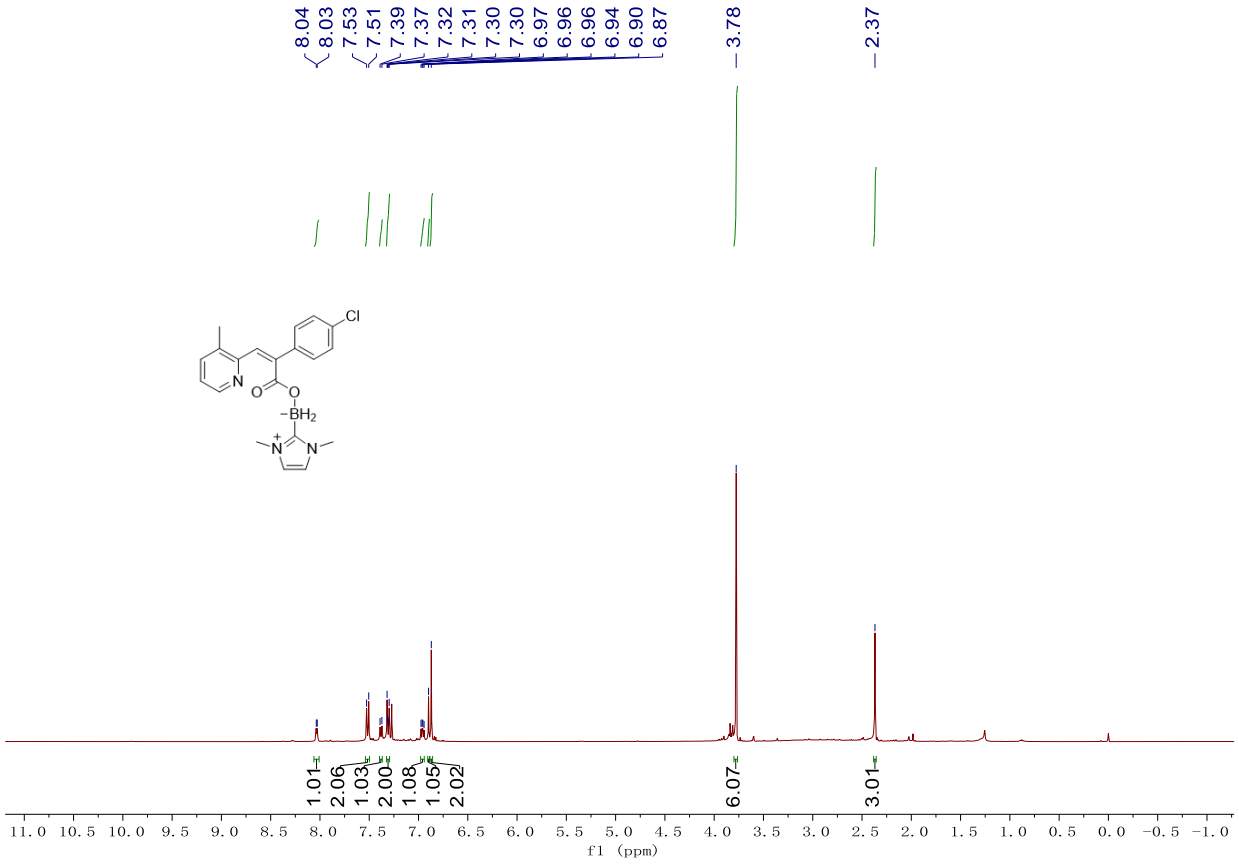
^{1}H NMR and ^{13}C NMR spectrum of compound **3u**

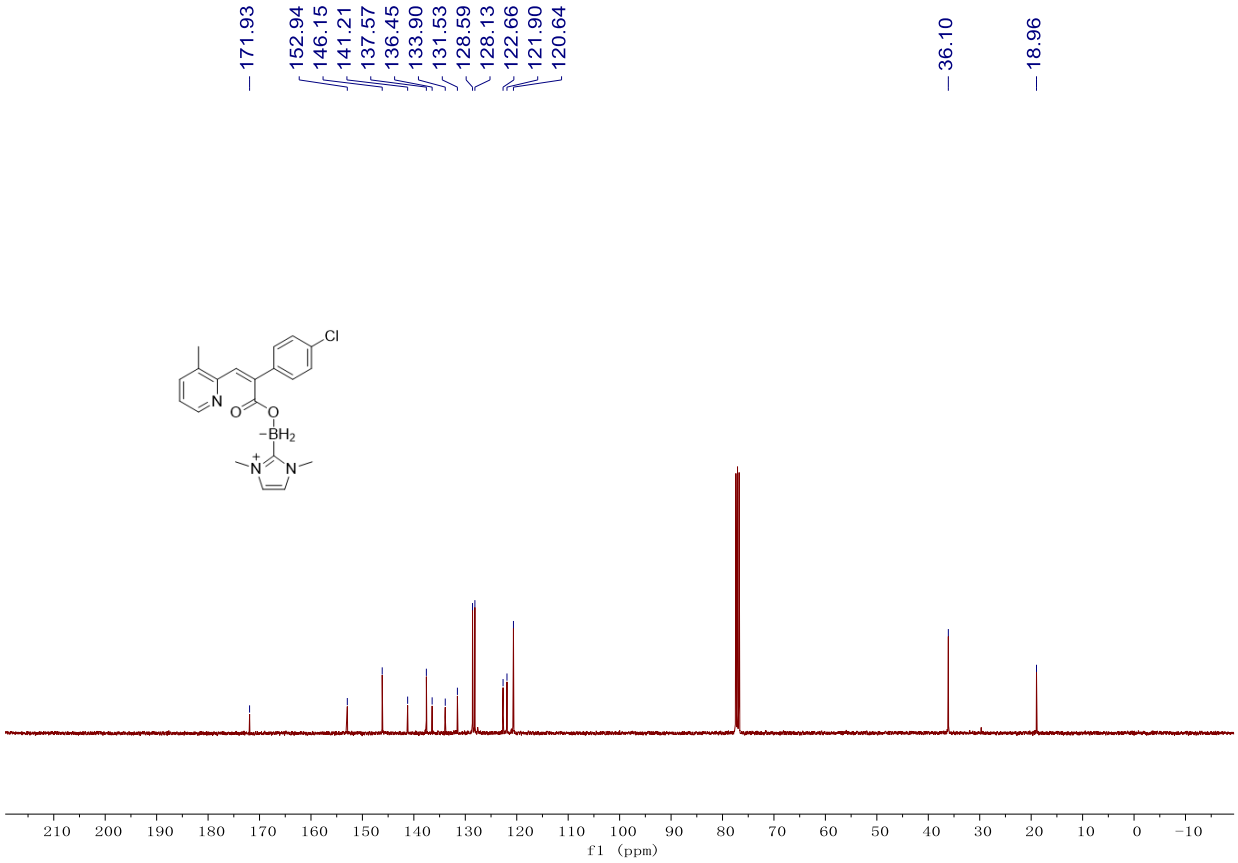


^{11}B NMR spectrum of compound **3u**

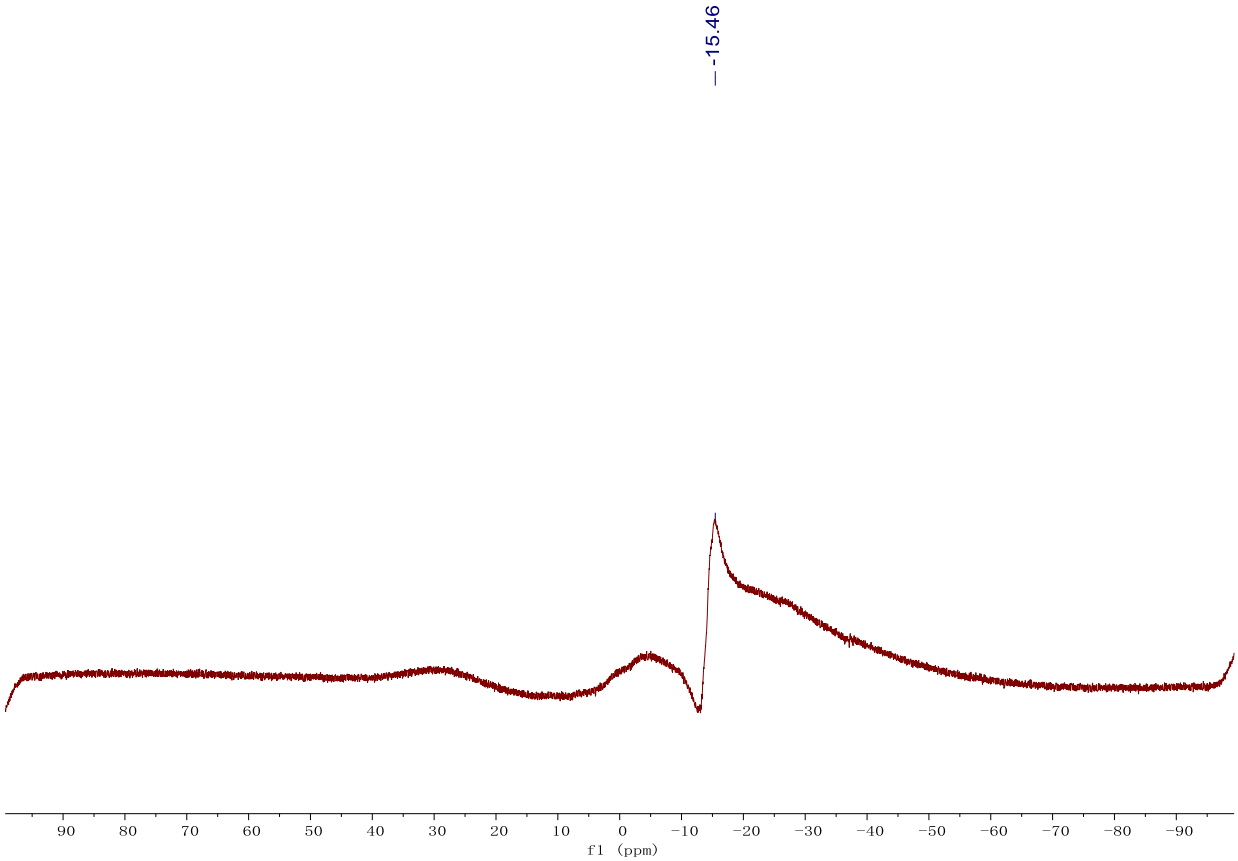


^{1}H NMR and ^{13}C NMR spectrum of compound **3v**

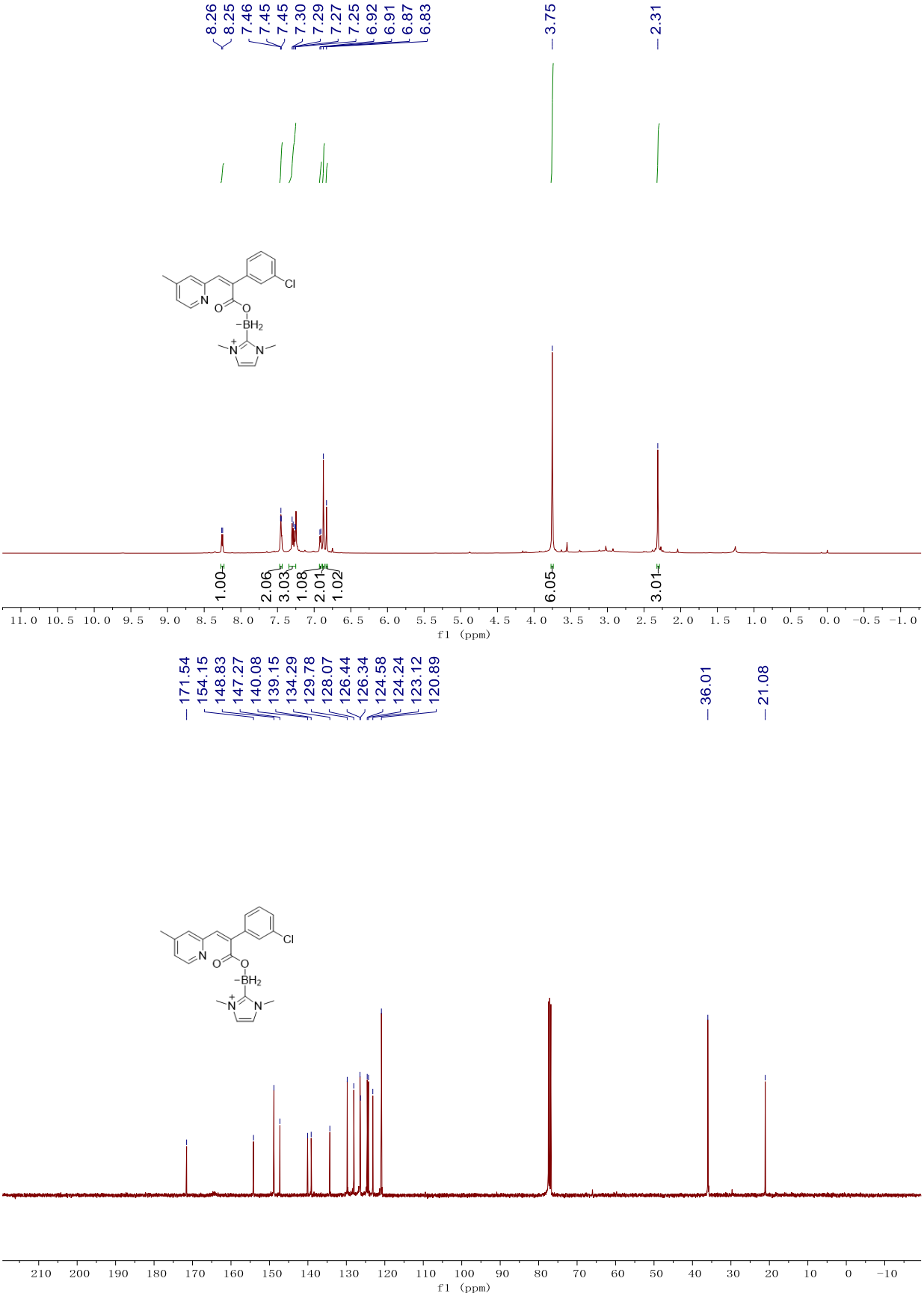




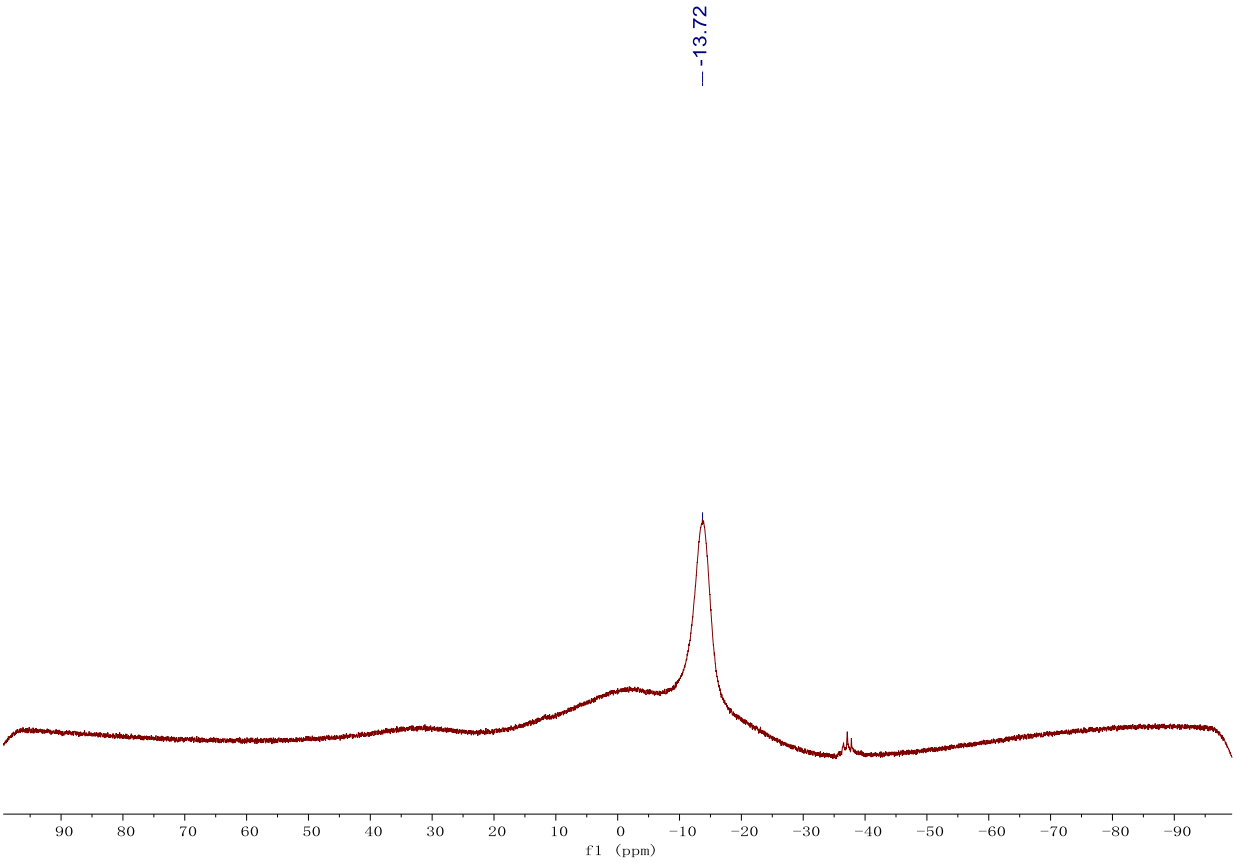
^{11}B NMR spectrum of compound **3v**



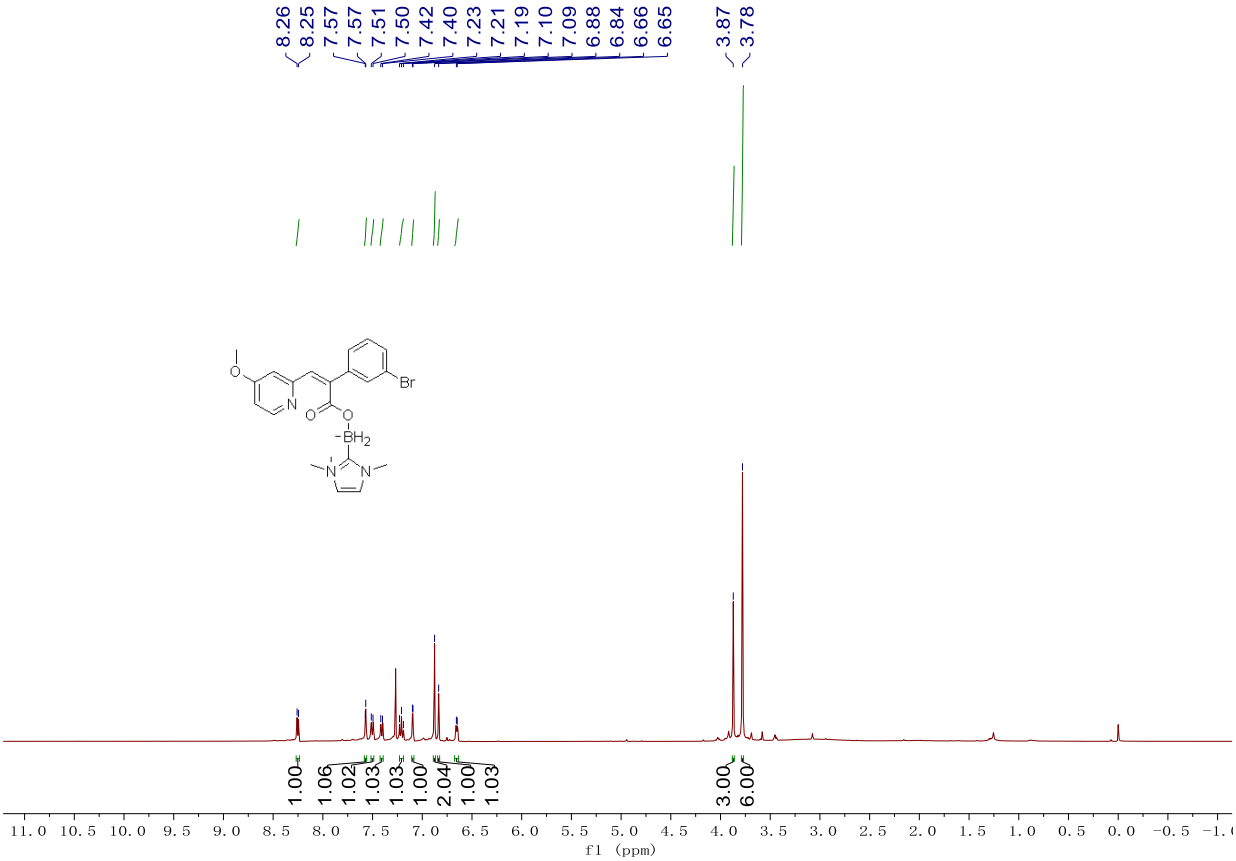
^{1}H NMR and ^{13}C NMR spectrum of compound **3w**

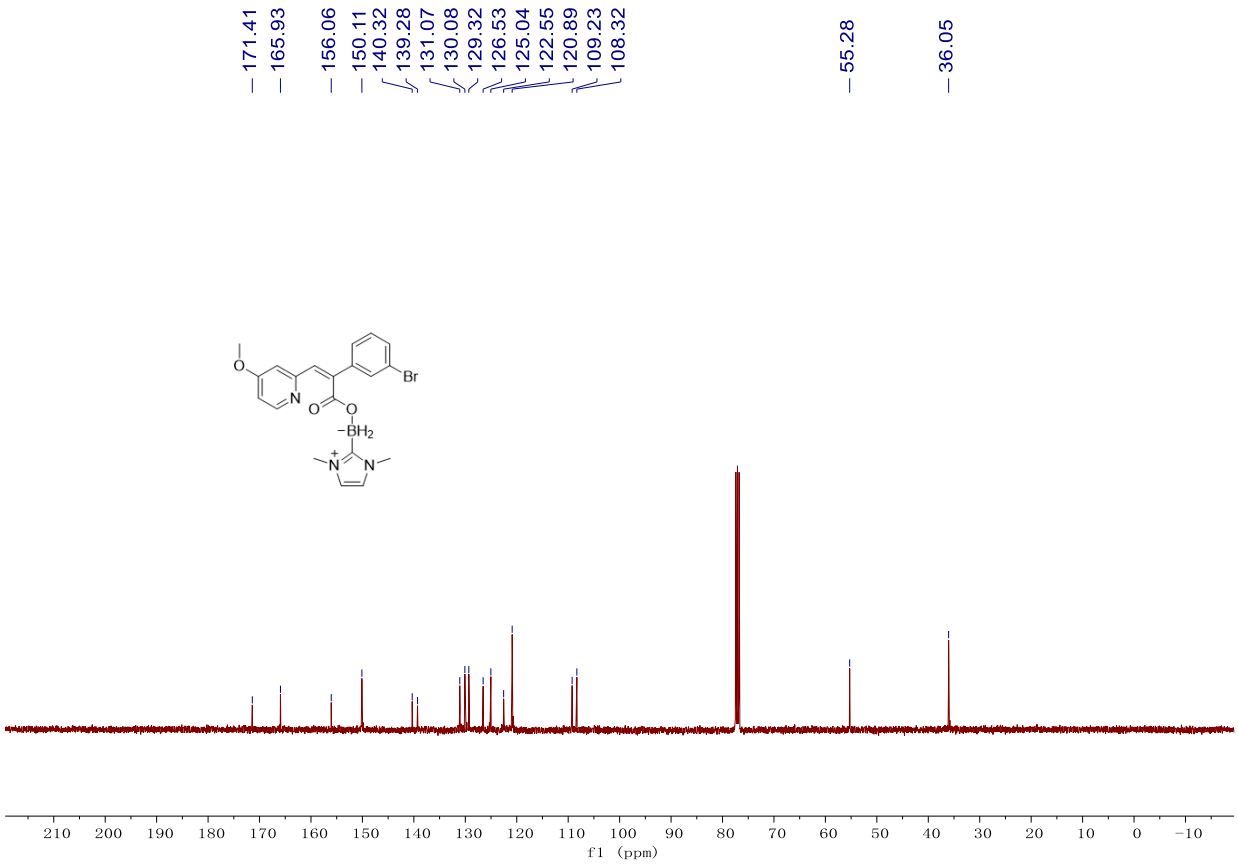


^{11}B NMR spectrum of compound **3w**

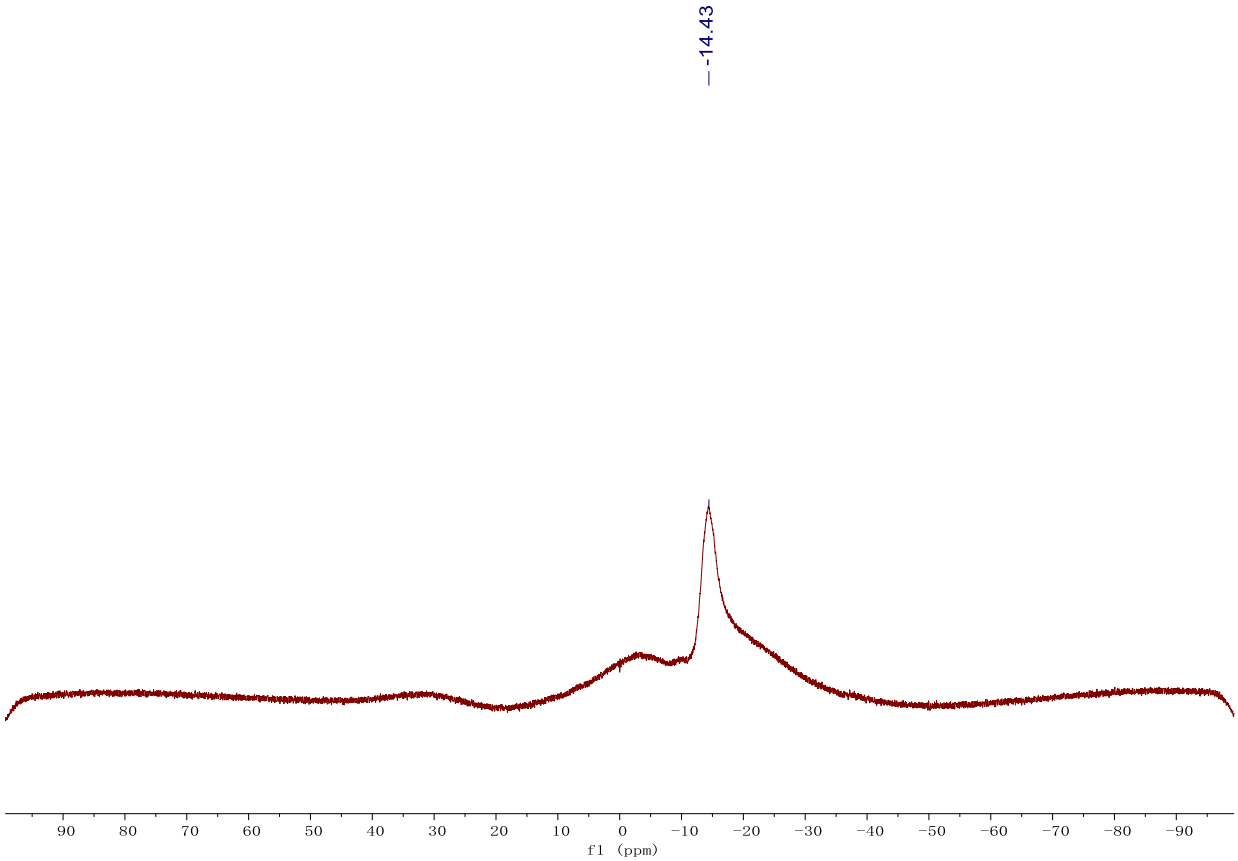


^{1}H NMR and ^{13}C NMR spectrum of compound **3x**

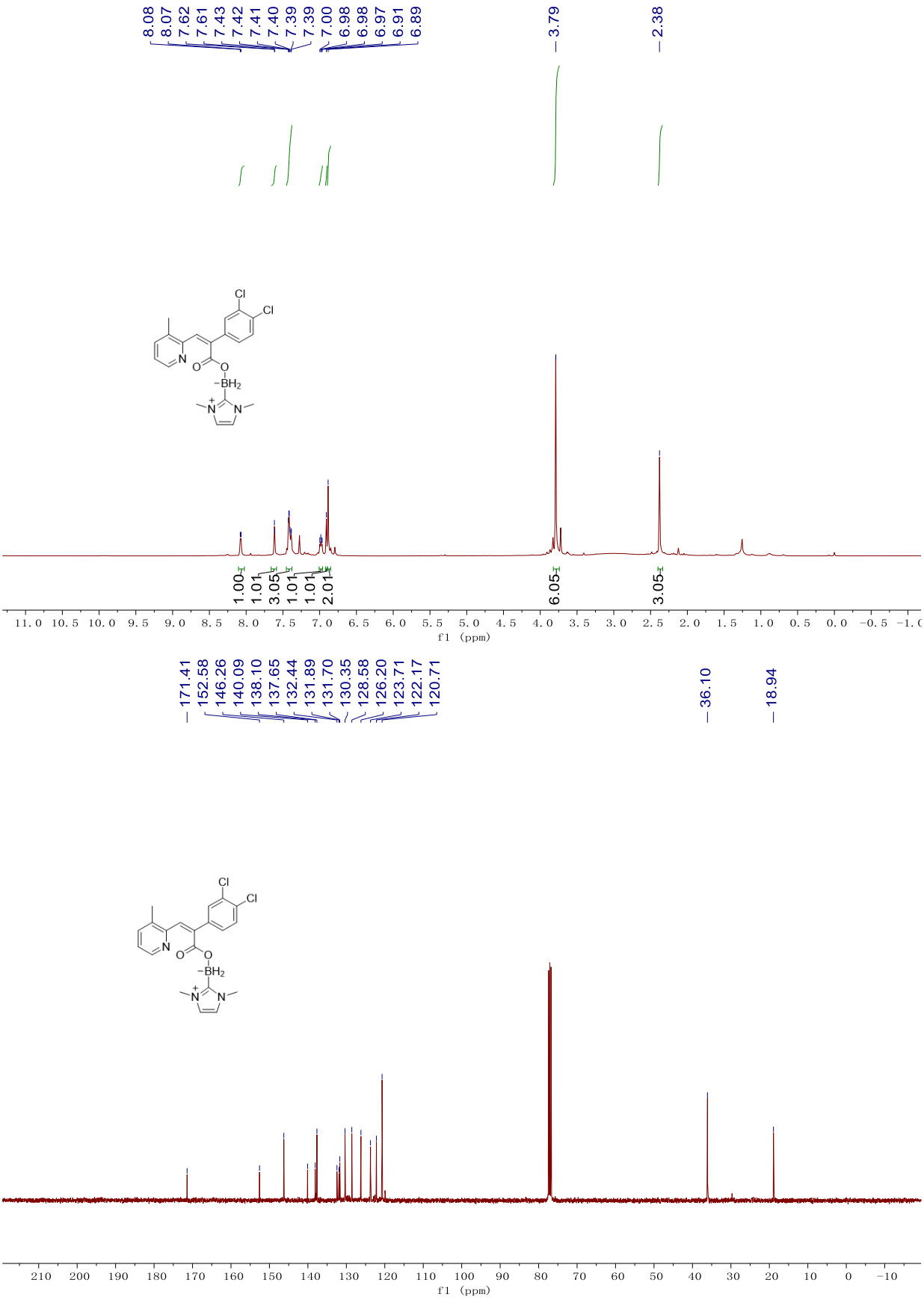




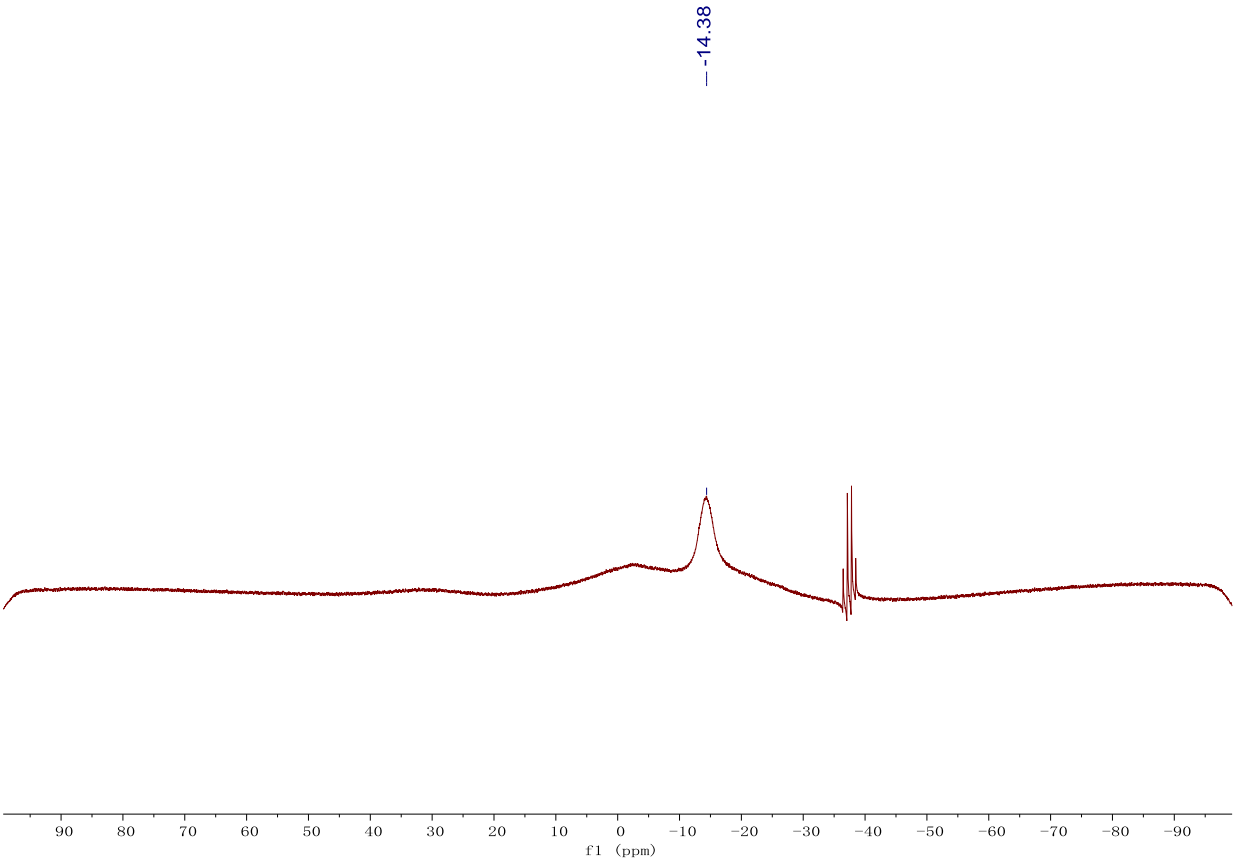
^{11}B NMR spectrum of compound **3x**



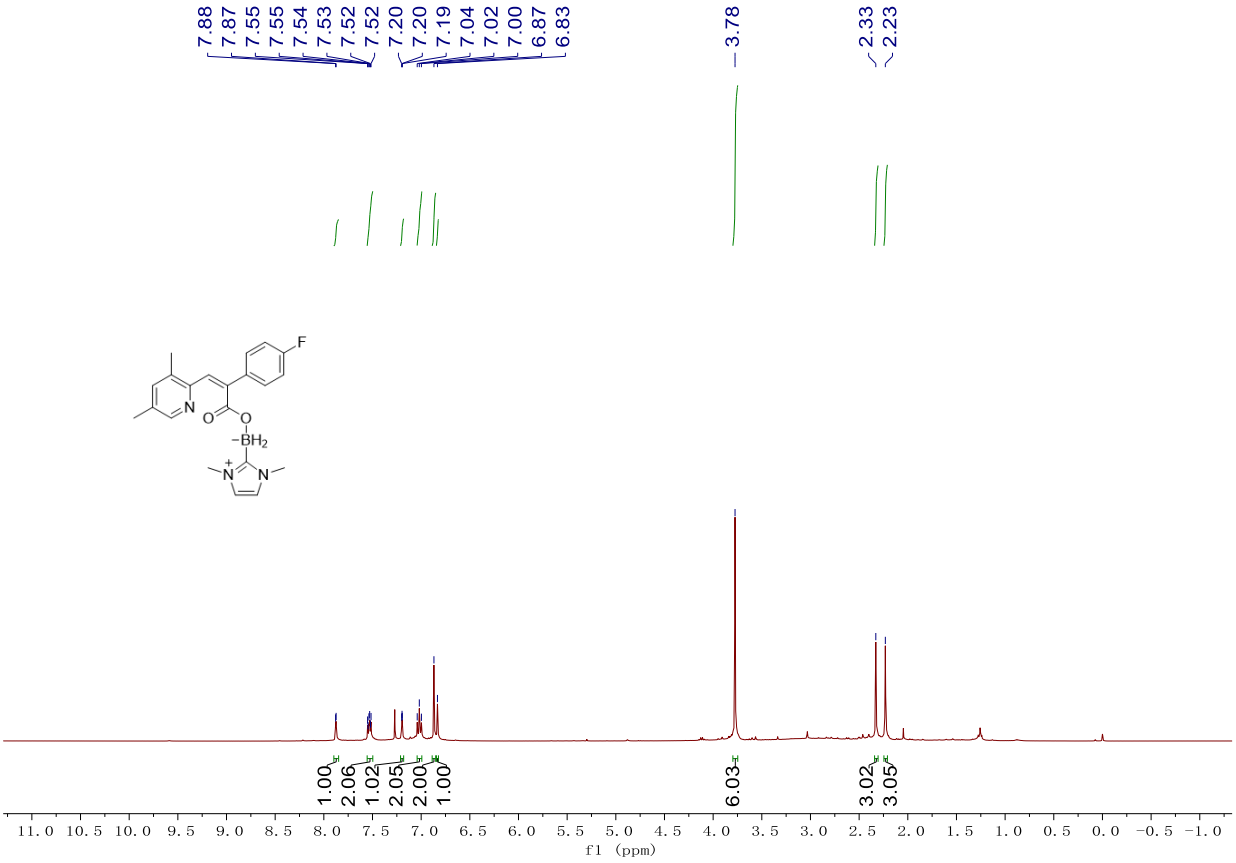
^{1}H NMR and ^{13}C NMR spectrum of compound **3y**

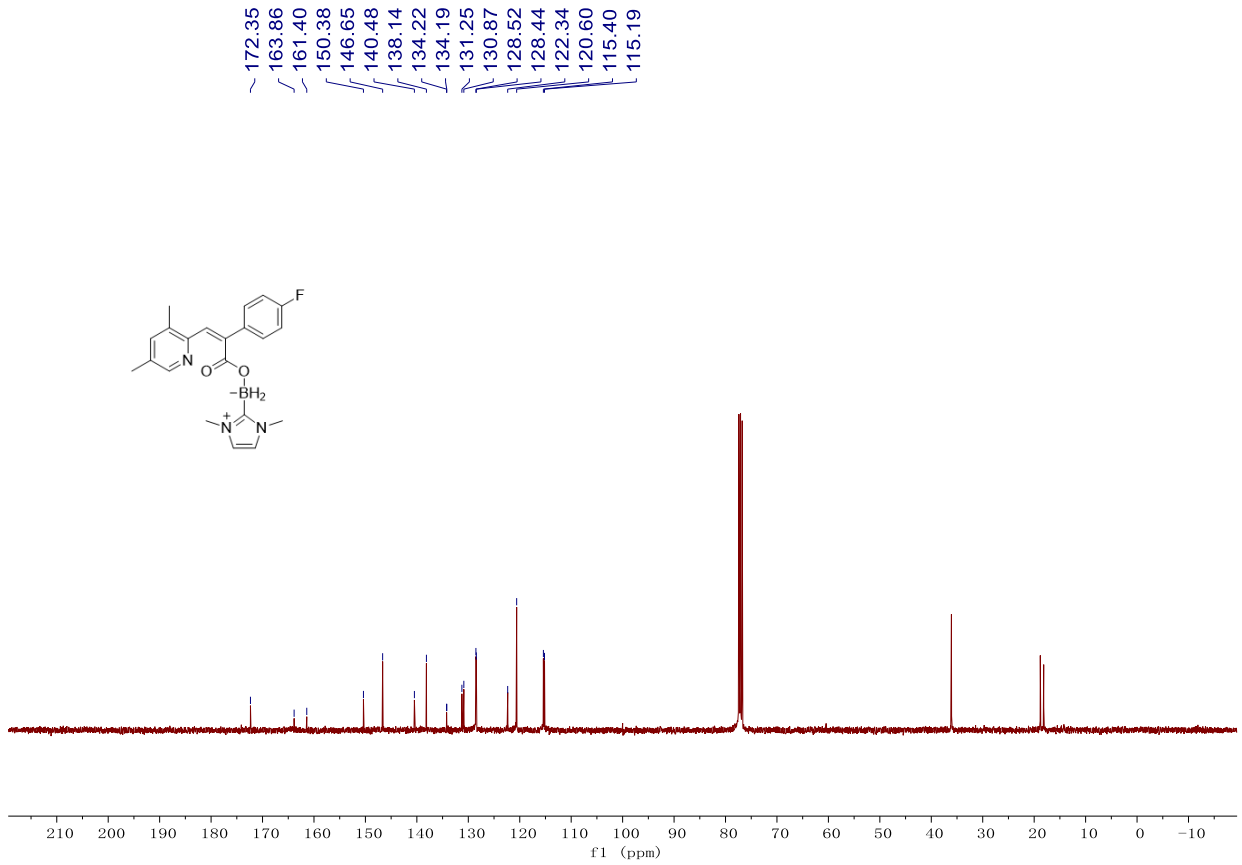


^{11}B NMR spectrum of compound **3y**

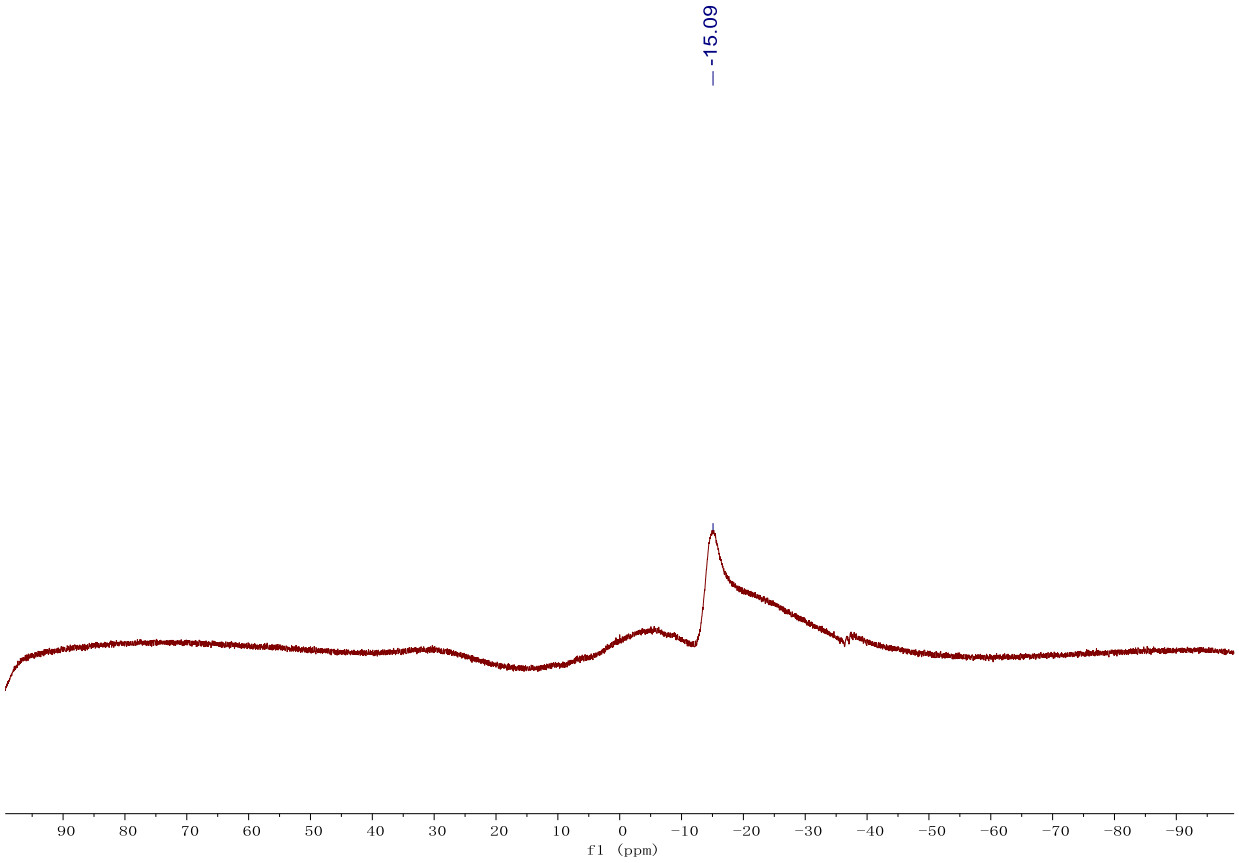


^{1}H NMR and ^{13}C NMR spectrum of compound **3z**

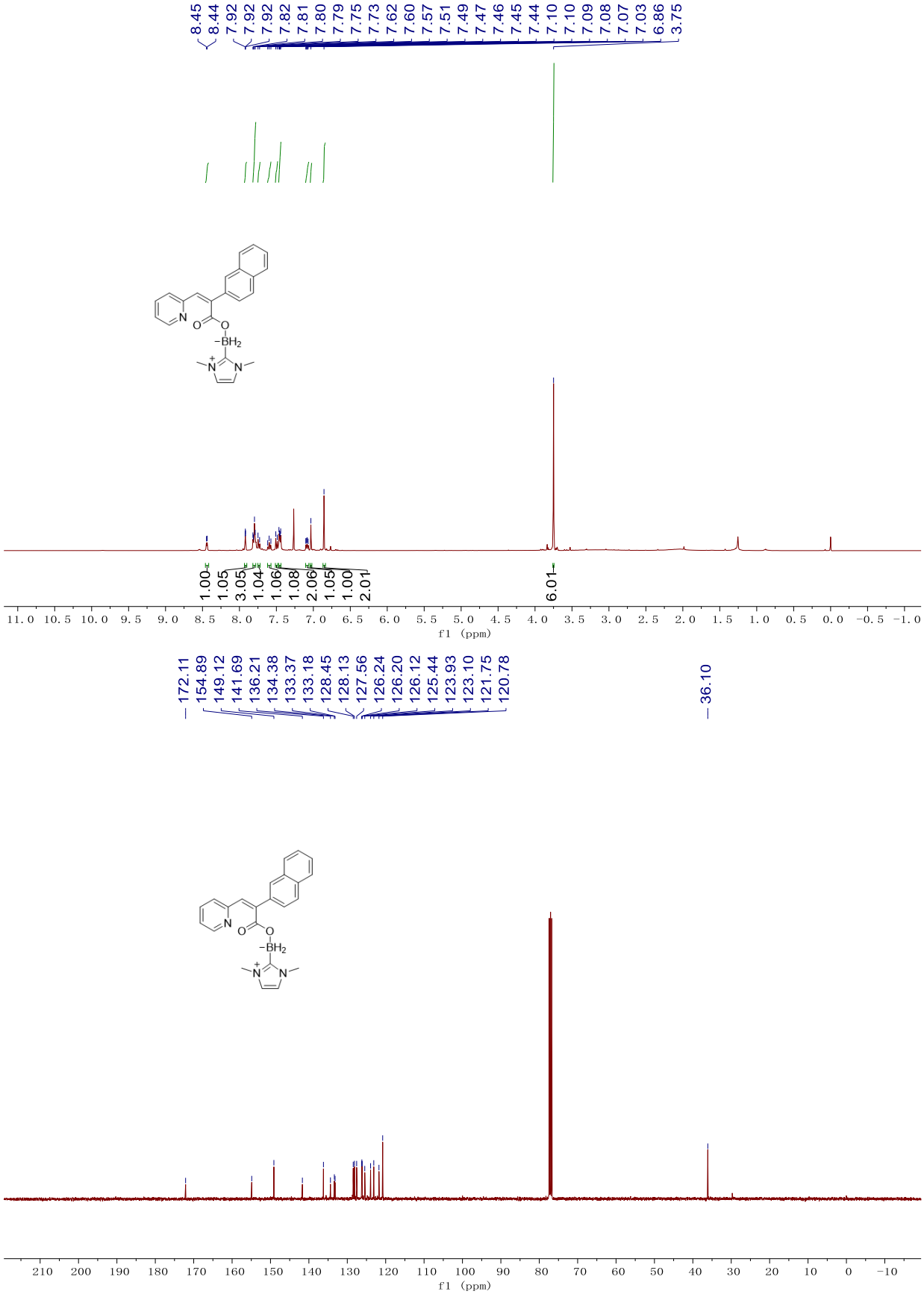




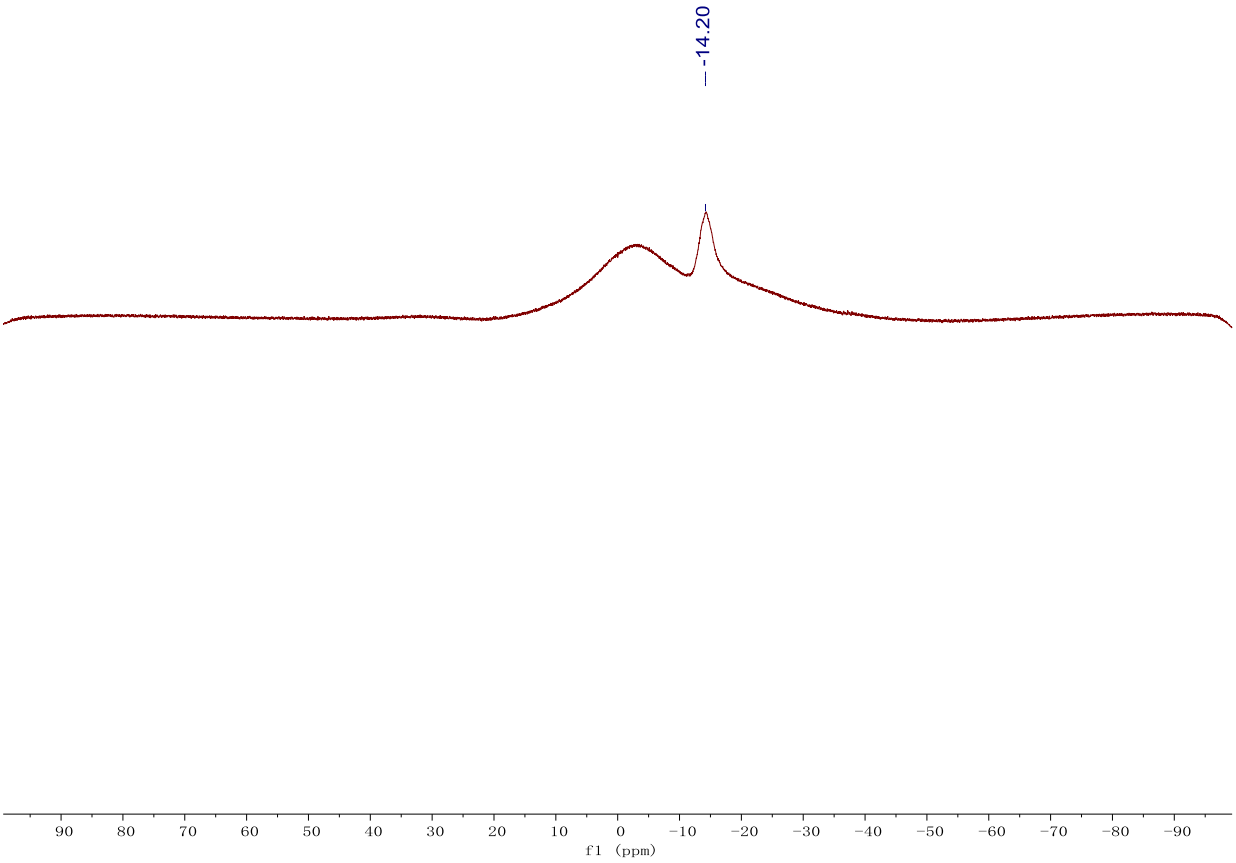
^{11}B NMR spectrum of compound **3z**



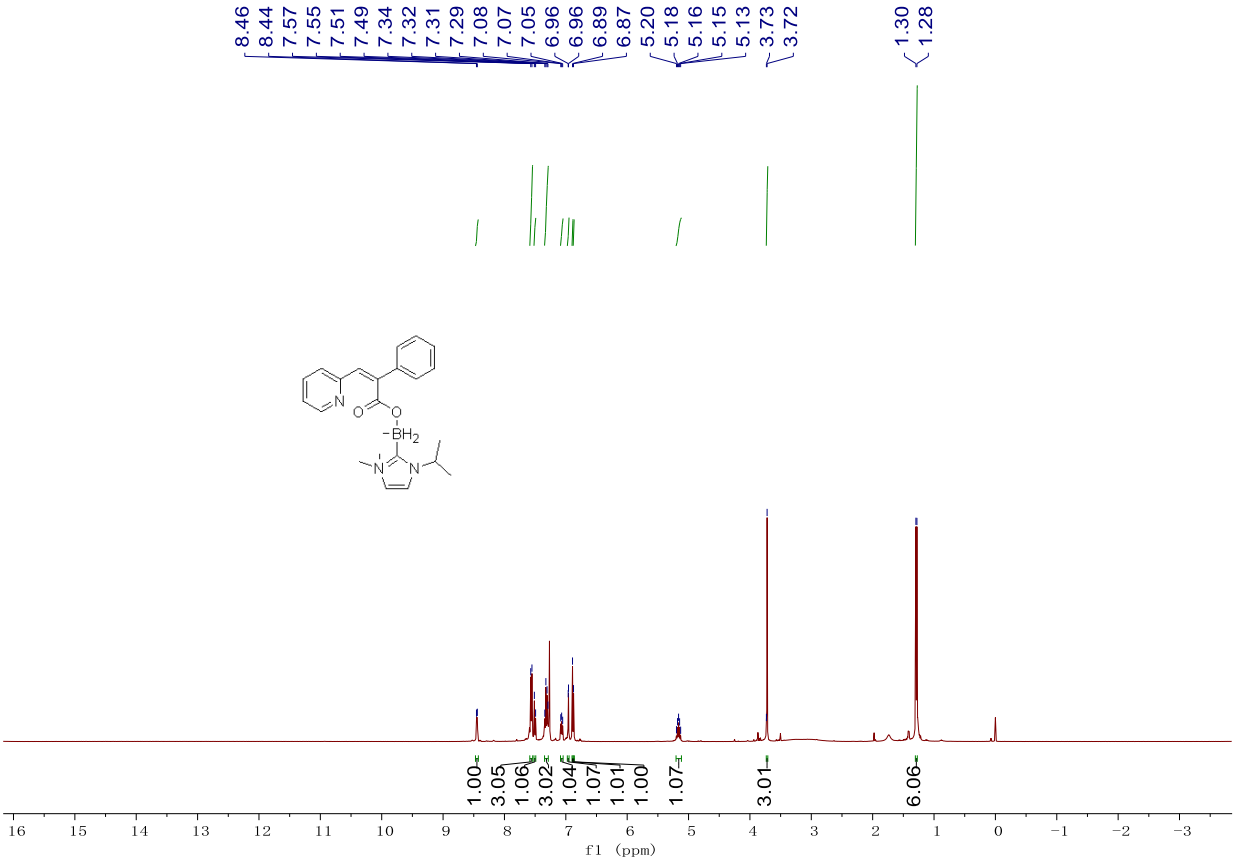
^{1}H NMR and ^{13}C NMR spectrum of compound **3aa**

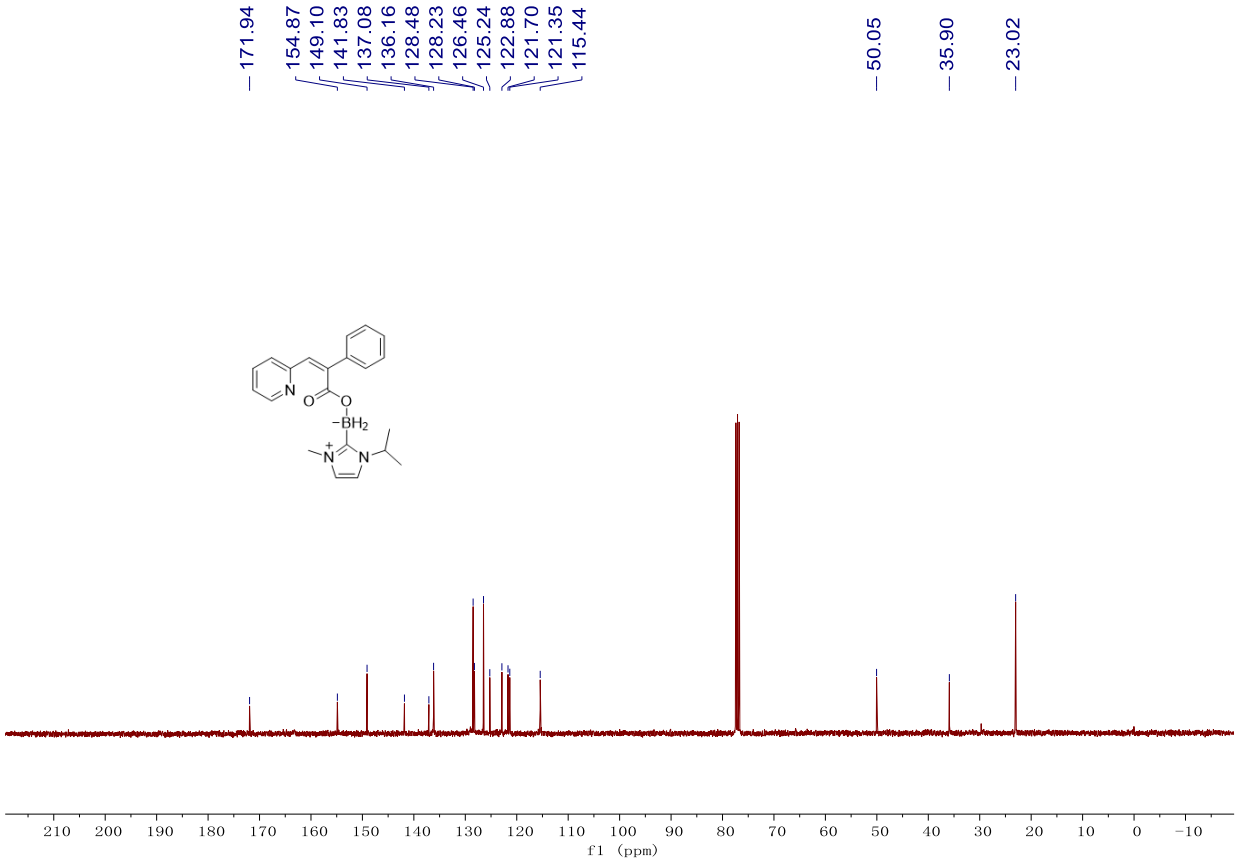


^{11}B NMR spectrum of compound **3aa**

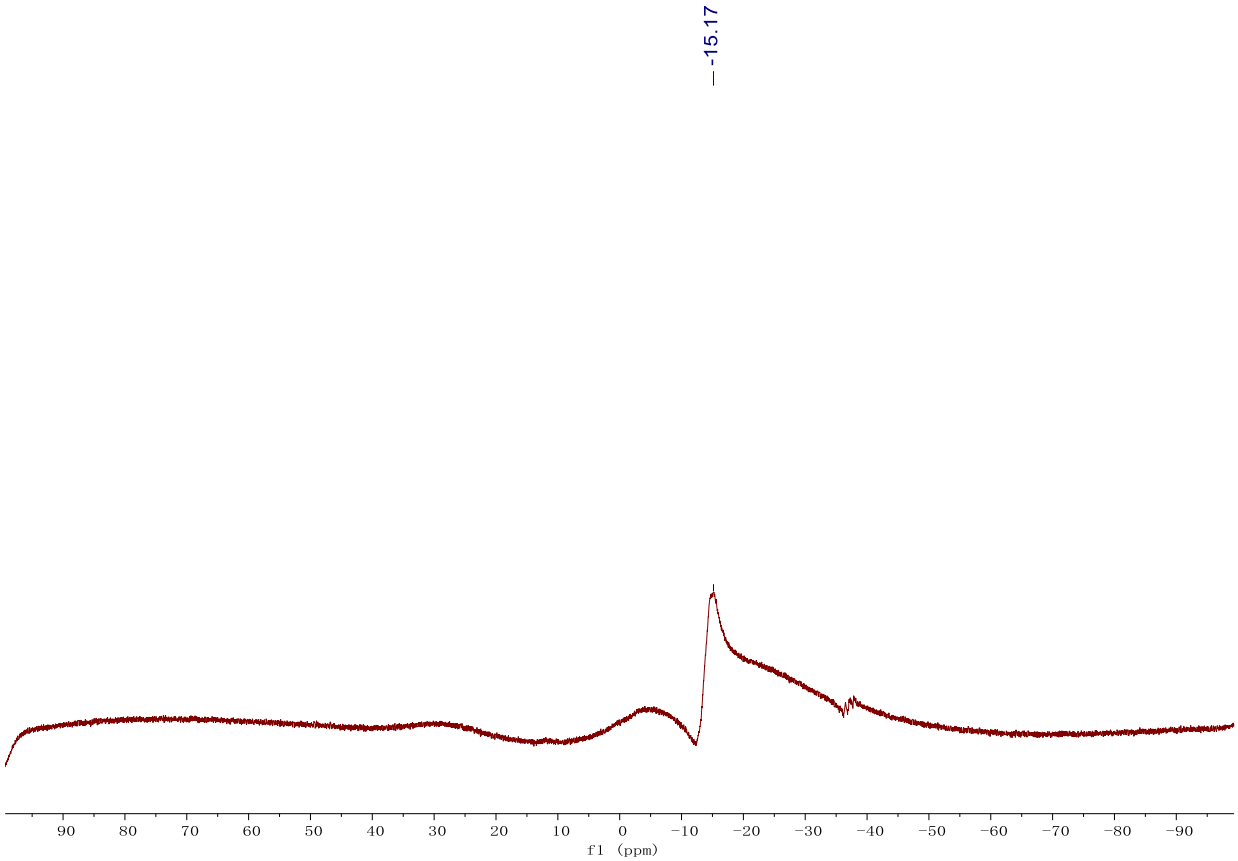


^{1}H NMR and ^{13}C NMR spectrum of compound **4a**



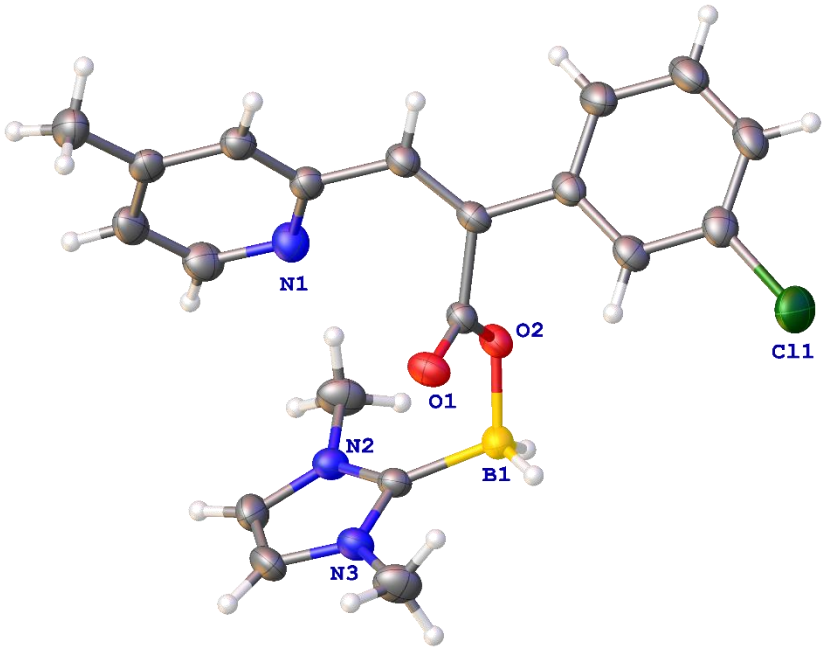


^{11}B NMR spectrum of compound **4a**



4. X-ray crystallographic data

Figure S1 X-ray single crystal structure of **3w**



Single crystals of **3w** were grown by slow evaporation of its DCM/PE solution. Single-crystal X-ray diffraction data were collected with a 'multiwire proportional' diffractometer. The crystal was kept at 149.99 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Least Squares minimization. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2116778).

Table S1 Crystal data and structure refinement for **3w**

Identification code	2-477
Empirical formula	$C_{20}H_{21}BClN_3O_2$
Formula weight	381.66
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	Cc
a/Å	13.0381(3)
b/Å	20.5925(7)
c/Å	7.15692(19)
α/°	90
β/°	91.598(3)
γ/°	90
Volume/Å^3	1920.80(10)
Z	4
ρ_{calc}g/cm^3	1.320
μ/mm^{-1}	1.920

F(000)	800.0
Crystal size/mm^3	0.14 × 0.11 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.028 to 147.396
Index ranges	-14 ≤ h ≤ 16, -25 ≤ k ≤ 20, -6 ≤ l ≤ 8
Reflections collected	3641
Independent reflections	2528 [R_{int} = 0.0275, R_{sigma} = 0.0389]
Data/restraints/parameters	2528/2/248
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0346, wR_2 = 0.0857
Final R indexes [all data]	R_1 = 0.0361, wR_2 = 0.0880
Largest diff. peak/hole / e Å-3	0.17/-0.20
Flack parameter	0.02(2)

Table S2 Bond Lengths for **3w**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C12	1.744(3)	C9	C20	1.399(4)
O1	C8	1.216(3)	N2	C18	1.456(4)
O2	C8	1.309(3)	N3	C14	1.352(3)
O2	B1	1.526(4)	N3	C16	1.379(4)
N1	C1	1.351(4)	N3	C17	1.457(4)
N1	C5	1.335(4)	C1	C2	1.381(4)
N2	C14	1.343(3)	C1	C6	1.476(3)
N2	C15	1.374(4)	C2	C3	1.397(4)
C3	C4	1.377(5)	C10	C11	1.386(5)
C3	C19	1.495(4)	C11	C12	1.381(4)
C4	C5	1.389(5)	C12	C13	1.389(4)
C6	C7	1.339(4)	C13	C20	1.398(4)
C7	C8	1.514(4)	C14	B1	1.622(4)
C7	C20	1.482(3)	C15	C16	1.343(5)
C9	C10	1.398(4)			

Table S3 Bond Angles for **3w**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C8	O2	B1	118.5(2)	C20	C7	C8	114.7(2)
C5	N1	C1	116.2(3)	O1	C8	O2	125.6(2)
C14	N2	C15	111.0(2)	O1	C8	C7	120.9(2)
C14	N2	C18	124.4(2)	O2	C8	C7	113.3(2)
C15	N2	C18	124.5(3)	C10	C9	C20	120.0(3)
C14	N3	C16	110.2(2)	C11	C10	C9	120.9(3)

C14	N3	C17	125.9(2)	C12	C11	C10	118.4(3)
C16	N3	C17	123.9(2)	C11	C12	Cl1	120.1(2)
N1	C1	C2	123.0(3)	C11	C12	C13	122.2(3)
N1	C1	C6	117.2(3)	C13	C12	Cl1	117.7(2)
C2	C1	C6	119.7(3)	C12	C13	C20	119.4(3)
C1	C2	C3	120.2(3)	N2	C14	N3	105.2(2)
C2	C3	C19	122.3(3)	N2	C14	B1	126.1(2)
C4	C3	C2	116.6(3)	N3	C14	B1	128.7(2)
C4	C3	C19	121.2(3)	C16	C15	N2	106.6(3)
C3	C4	C5	119.9(3)	C15	C16	N3	107.1(2)
N1	C5	C4	123.9(3)	C9	C20	C7	121.6(2)
C7	C6	C1	125.3(2)	C13	C20	C7	119.3(2)
C6	C7	C8	122.5(2)	C13	C20	C9	119.1(2)
C6	C7	C20	122.4(2)	O2	B1	C14	110.2(2)

5. References

1. H. Cao, H. Zhan, Y. Lin, X. Lin, Z. Du, H. Jiang, *Org. Lett.* **2012**, 14, 1688–1691.
2. H. Zhan, L. Zhao, N. Li, L. Chen, J. Liu, J. Liao, H. Cao, *RSC Adv.* **2014**, 4, 32013–32016.
3. S. Gardner, T. Kawamoto, Dennis P. Curran, *J. Org. Chem.* **2015**, 80, 9794−9797