Supporting Information

Photoinduced, Catalyst-Free Borylation of Alkenyl Triflates with Lewis Base Complexes of Boranes

Zhi-Peng Ye,‡[a] Si-Jia Yang,‡[a] Zhi-Lin, Liu,[a] Jie, Gao,[a] Jian-Ping, Guan,[a] Hong-Bin, Chen,[b] Peng-Ju, Xia,[c] Kai, Chen,[a] Hao-Yue, Xiang,*[a,d] Hua, Yang.*[a]

[a]College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P. R. China.

[b]Jiangxi Time Chemical Company, Ltd., Fuzhou 344800, P. R. China.

[c]School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Guilin 541004, P. R. China.

[d]School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007 Henan, P. R. China.

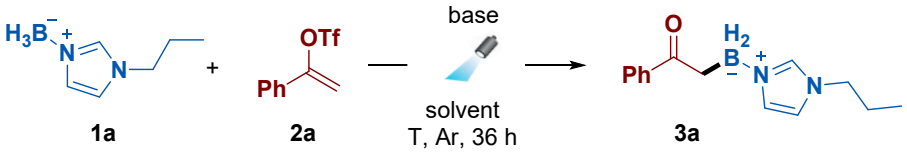
E-mail: hyangchem@csu.edu.cn, xianghaoyue@csu.edu.cn

Contents

1. General Experimental Methods.

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet, *br* = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. ^{19}F NMR data were collected at 376 MHz with complete proton decoupling. UV–Vis spectra were recorded using a shimadzu UV-2600. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES+ mass spectrometer and acetonitrile was used to dissolve the sample. Emission intensities were recorded using Perkin-Elemer LS 55 Fluorescence Spectrometer. Column chromatography was carried out on alkaline silica gel (200-300 mesh).

2. Detailed optimization of reaction conditions[a]



1a 2a 3a

entry	solvent	T（°C）	Base（mmol）	yield (%)
1	DCM	30	DIPEA(0.05)	trace
2	DCM	30	DIPEA(0.2)	trace
3	DCM	30	DIPEA(0.6)	38
4	DCM	30	DIPEA(1.5)	10
6	MeCN	30	DIPEA(0.6)	trace
7	THF	30	DIPEA(0.6)	26
8	DCE	30	DIPEA(0.6)	31
9	Pentane	30	DIPEA(0.6)	37
10	EA	30	DIPEA(0.6)	10
11	1,4-dioxane	30	DIPEA(0.6)	33
12	PhMe	30	DIPEA(0.6)	30
14	DCM	10	DIPEA(0.6)	42
15	DCM	0	DIPEA(0.6)	45

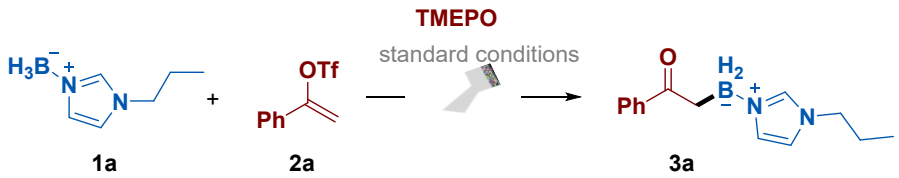
16	DCM	-10	DIPEA(0.6)	56
17	DCM	-30	DIPEA(0.6)	43
18	DCM	-10	DIPEA (0.9)	65
19	DCM	-10	DIPEA (1.2)	55
20	DCM	-10	K_2HPO_4 (0.9)	trace
21	DCM	-10	TMEDA (0.9)	trace
22	DCM	-10	-	trace
23[b]	DCM	-10	DIPEA(0.9)	trace
24[c]	DCM	-10	DIPEA(0.9)	15

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (1.2 mmol, 6.0 equiv.), solvent (2.0 mL), base, 30 W 450 nm blue LEDs, Ar, 36 h. [b]no Ar or light, [c]405 nm.

3. Mechanistic Studies.

3.1 Trapping Experiment

In order to ensure whether the putative radical was trapped by TEMPO, ESI-MS analysis of the crude reaction mixture was performed. The resulting mass spectrum clearly shows peaks corresponding to the adduct products between TEMPO radical and possible radical intermediates: **TEMPO** + **boron** radical: $C_{15}H_{31}BN_3O^+$ [M+H$^+$] calcd 280.2555, found 280.2560, **TEMPO** + **CF_3** radical: $C_{10}H_{18}F_3NNaO^+$ [M+H$^+$] calcd 248.1233, found 248.1246 (**Figure S1**).



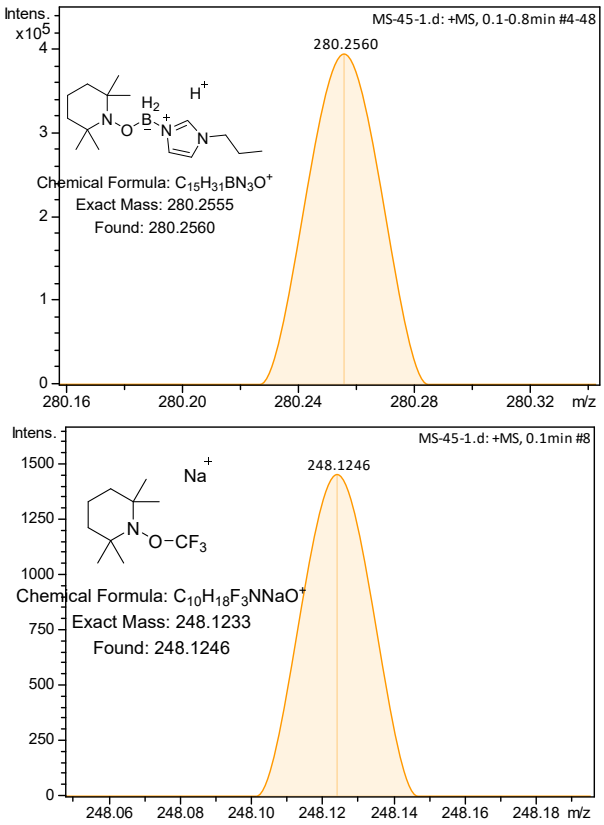


Figure S1. Crude ESI-MS of the TEMPO trapping experiments described above

3.2 UV–Vis spectrum

The UV–Vis spectra of **2a**, feature a maximum absorption (λ_{max}) at 247nm (**Figure S2**).

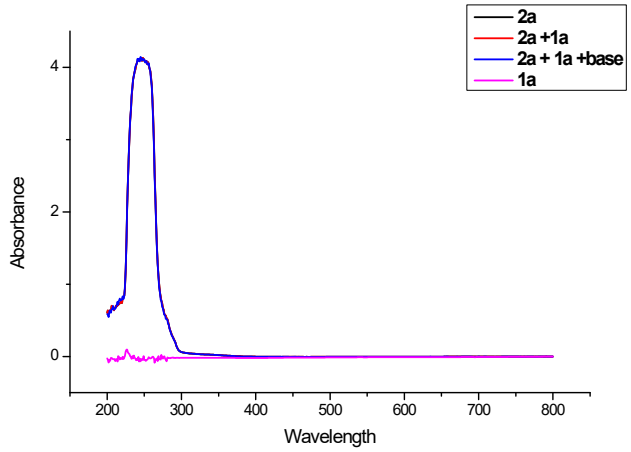


Figure S2. Absorbance of 1×10^{-4} M solution of **1a, 2a, base** in DCM

3.3 Emission Quenching Experiments (Stern–Volmer Studies)

All fluorescence measurements were recorded using a Hitachi FL-7000 Fluorometer. Quenching studies were conducted in DCM. All **2a** solutions (concentration of 100 μM) were excited at 340 nm and the emission intensity was collected at 405 nm. Measurements using corresponding quencher **1a and 1a+base** was taken in triplicate at different concentrations (Figure S3).

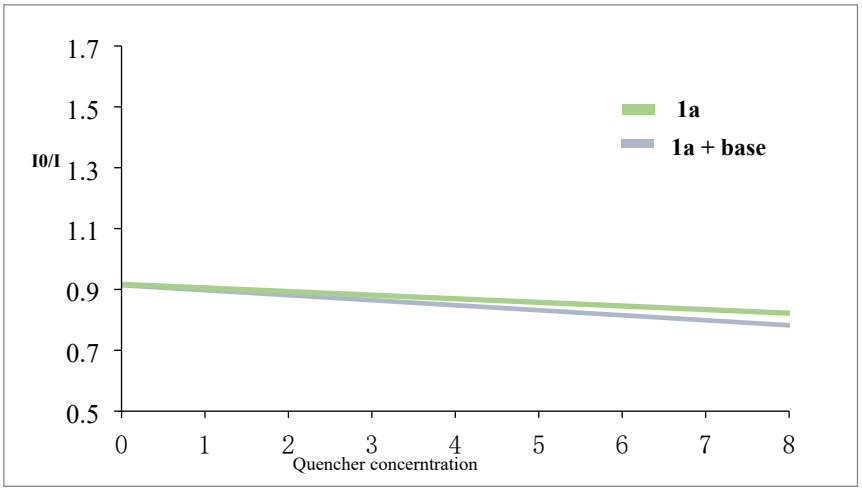
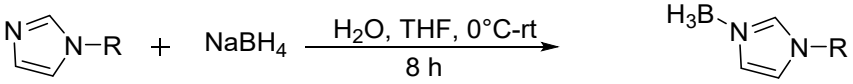


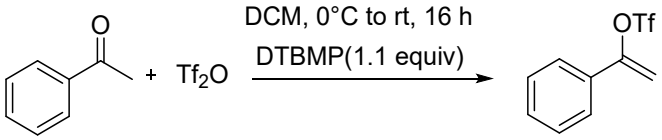
Figure S3. The Stern-Volmer plot for quenching the fluorescence of **2a** using the quencher **1a** and **1a+base**

4. General Preparation Process

4.1 General procedure for the synthesis of compounds 1 and 2

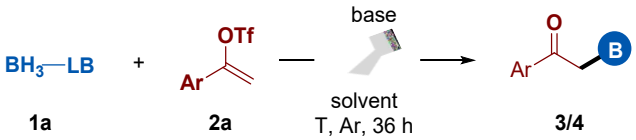


General procedure for the preparation of 1： To a solution of imidazole (10 mmol, 1.0 equiv) in THF (1.0 M) , was added sodium borohydride (15 mmol, 1.5 equiv.) and $NaHCO_3$ (3.0 equiv). Subsequently, H_2O (3.0 equiv.) was added to reaction mixtures. The reaction process was monitored by TCL until the reaction was completed. Thereafter, the reaction mixtures were filtered through sodium sulfate and celite, and then collected filtrate was dried over anhydrous sodium sulfate. The solvent was removed *in vacuo*, and then the residue was purified by column chromatography using PE/EA.[1]



General procedure for the preparation of 2： A solution of acetophenone (15 mmol) in dichloromethane (45 mL) was cooled to 0 °C. Then Na_2CO_3 (19.5 mmol) and trifluoromethanesulfonic anhydride (18 mmol) were successively added. The obtained mixture was slowly warmed to room temperature and the reaction process was monitored by TCL. Thereafter, the mixture was quenched via added water (30 mL). the organic layer was washed by brine solution (30 mL ×3). Collect the organic phase to dry over anhydrous Na_2SO_4, which was removed under reduced pressure and then the residue was purified by column chromatography using PE/EA.[2]

4.2 General procedure for the synthesis of compounds 3 and 4



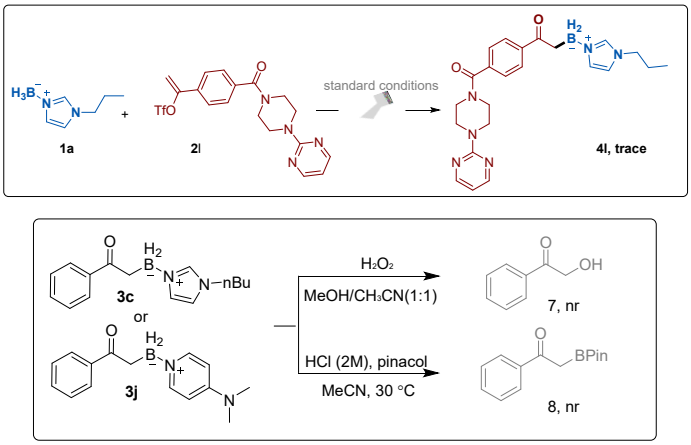
1 (2.0 mmol, 24.8 mg), **2** (1.2 mmol, 302.4 mg), DIPEA (0.9 mmol, 116.3 mg) and CH_2Cl_2 (2.0 mL) were added to a 15 mL seal tube equipped with a stirring bar. The seal tube was evacuated and backfilled with Ar three times. The tube was screw-capped and stirred at -10 °C under irradiation of 30 W blue LEDs (distance app. 5 cm) for 36 h. Thereafter, the solvent was removed under reduced pressure and then the residue was further purified by flash chromatography using alkaline silica gel (EtOAc/PE = 1:6 to 1:3) to afford the desired products **3** and **4**.

4.3 Scale-up reaction

1a (2.00 mmol, 248 mg), **2a** (12.00 mmol, 3024 mg), DIPEA (9.00 mmol, 1163 mg) and CH_2Cl_2 (20.0 mL) were added to a 120 mL seal tube equipped with a stirring bar. The seal tube was evacuated and backfilled with Ar three times. The tube was screw-capped and stirred at -10

°C under irradiation of 30 W blue LEDs (distance app. 5 cm) for 36 h. Thereafter, the solvent was removed under reduced pressure and then the residue was further purified by flash chromatography using alkaline silica gel (EtOAc/PE = 1:6 to 1:3) to afford the desired product **3a** in 48% yield (232.3 mg).

4.4 Unsuccessful attempt



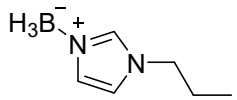
5. References

[1] (a) P. V. Ramachandran, H. *J*. Hamanna and R. Lina. Activation of sodium borohydride *via* carbonyl reduction for the synthesis of amine- and phosphine-boranes. *Dalton Trans.,* 2021, **50**, 16770-16774. (b) P. V. Ramachandran, A. S. Kulkarni, Y. Zhao and J.-.G. Mei. Amine-boranes bearing borane-incompatiblefunctionalities: application to selective amineprotection and surface functionalization, *Chem. Commun*., 2016, **52**, 11885-11888.

[2] (a) W, Dai, S, J. Geib, and D, P. Curran, Facile Synthesis of *α*-*N*-Heterocyclic Carbene-Boryl Ketones from N-Heterocyclic Carbene-Boranes and Alkenyl Triflates, *J. Am. Chem. Soc.* 2019*,* **141**, 12355-12361. (b) X,-L. Su, H.-G. Huang and Y.-F. Yuan, Radical Desulfur-Fragmentation and Reconstruction of Enol Triflates: Facile Access to *α*-Trifluoromethyl Ketones, *Angew. Chem. Int. Ed.* 2017, **56**, 1338-1341.

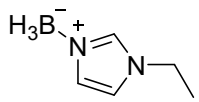
6. Characterization Data of Compound

6.1. Characterization data of starting materials 1a-1e, 1g-1i, 1k.



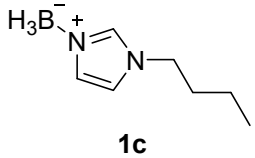
1a

***1-propylimidazoloborane* (1a).** Colorless oil (yield 80%), the product was purified by flash column chromatography (PE/EtOAc = 5:1 to 3:1) to afford the desired product; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3132, 2966, 2302, 1541, 1168, 1126, 830, 747, 640 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (s, 1H), 7.013 (d, *J* = 8.8 Hz, 2H), 3.99 (t, *J* = 7.2 Hz, 2H), 2.62 - 1.98 (m, 3H), 1.88 - 1.78 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); **^{11}B NMR** (128 MHz, $CDCl_3$) δ -19.41 (q, *J* = 99.0 Hz); **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 136.1, 127.7, 119.8, 50.1, 23.9, 10.9; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_6H_{13}BN_2Na^+$ 147.1064; Found 147.1075.



1b

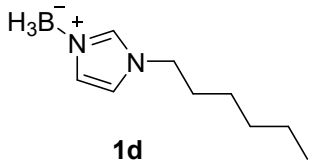
***1-ethylimidazoleborane* (1b).** Colorless oil (yield 70%), the product was purified by flash column chromatography (PE/EtOAc = 5:1 to 3:1) to afford the desired product; R_f = 0.4 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3133, 2301, 1541, 1169, 1123, 829, 745, 640 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (s, 1H), 7.07 (s, 1H), 6.94 (t, *J* = 1.6 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 2.60 - 1.88 (m, 3H), 1.50 (t, *J* = 7.2 Hz, 3H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -19.44 (q, *J* = 95.0 Hz); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 135.7, 127.8, 119.4, 43.4, 15.7; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_5H_{11}BN_2Na^+$ 133.0907; Found 133.0917.



1c

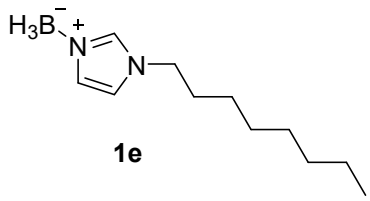
***1-butylimidazoliumborane* (1c).** White solid (yield 85%), the product was purified by flash column chromatography (PE/EtOAc = 5:1 to 3:1) to afford the desired product; **m.p.** 37 - 39 °C; R_f = 0.5 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3130, 2953, 2260, 1543, 1179, 1117, 854, 758, 646 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (s, 1H), 7.06 (t, *J* = 1.6 Hz, 1H), 6.90 (t, *J* = 1.6 Hz, 1H), 3.97 (t, *J* = 7.2 Hz, 2H), 1.83 - 1.75 (m, 2H), 2.72 - 2.0 (m, 3H), 1.40 - 1.30 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -19.44 (q, *J* = 95.5 Hz); **^{13}C{^{1}H}**

NMR (100 MHz, $CDCl_3$) δ 136.1, 127.7, 119.7, 48.3, 32.4, 19.5, 13.4; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_7H_{15}BN_2Na^+$ 161.1221; Found 161.1230.



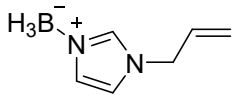
1d

1-Hexylimidazolium borane **(1d).** Colorless oil (yield 70%), the product was purified by flash column chromatography (PE/EtOAc = 5:1 to 3:1) to afford the desired product; R_f = 0.4 (pentane/EtOAc = 1/1); **IR (neat)** *v* 2929, 2303, 1541, 1167, 1124, 823, 745, 640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.05 (t, *J* = 1.6 Hz, 1H), 6.92 (t, *J* = 1.6 Hz, 1H), 3.97 (t, *J* = 7.2 Hz, 2H), 2.72 - 1.94 (m, 3H), 1.83 - 1.76 (m, 2H), 1.33 - 1.26 (m, 6H), 0.92 - 0.86 (m, 3H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -19.45 (q, *J* = 98.2 Hz); **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 136.1, 127.6, 119.8, 48.6, 31.1, 30.4, 26.0, 22.3, 13.9; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_9H_{19}BN_2Na^+$ 189.1534; Found 189.1526.



1e

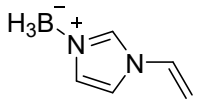
1-Octylimidazolium borane **(1e).** Colorless oil (yield 84%), the product was purified by flash column chromatography (PE/EtOAc = 5:1 to 3:1) to afford the desired product; R_f = 0.4 (pentane/EtOAc = 1/1); **IR (neat)** *v* 2925, 2855, 2302, 2258, 1732, 1542, 1243, 1168, 1124, 1045, 823, 745 cm^{-1}; 1H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.02 (t, *J* = 1.2 Hz, 1H), 6.96 (t, *J* = 1.2 Hz, 1H), 3.99 (t, *J* = 7.2 Hz, 2H), 2.58 - 1.99 (m, 3H), 1.83 - 1.76 (m, 2H), 1.35 - 1.23 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -19.48 (q, *J* = 95.2 Hz); **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 136.1, 127.4, 119.9, 48.5, 31.6, 30.5, 28.9, 28.8, 26.2, 22.5, 14.0; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for C11H23BN2Na$^+$ 217.1847; Found 217.1828.



1g

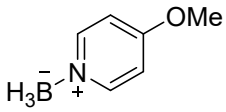
1-allylimidazoloborane **(1g).** Colorless oil (yield 83%), the product was purified by flash column chromatography (PE/EtOAc = 5:1 to 3:1) to afford the desired product; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3132, 2302, 1538, 1168, 1114, 939, 828, 744, 639 cm^{-1}; **^1H NMR (400 MHz, $CDCl_3$)** δ 7.78 (s, 1H), 7.08 (t, *J* = 1.6 Hz, 1H), 6.92 (t, *J* = 1.6 Hz, 1H), 5.99 - 5.90 (m, 1H), 5.40 (d, *J* = 10.8 Hz,

1H), 5.31 (d, *J* = 17.2 Hz, 1H), 4.59 (d, *J* = 6.0 Hz, 2H), 2.50 - 1.85 (m, 3H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -19.37 (q, *J* = 95.3 Hz); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 136.2, 130.7, 127.9, 120.9, 119.9, 50.8; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_6H_{11}BN_2Na^+$ 145.0907; Found 145.0918.



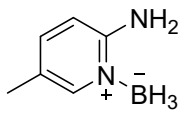
1h

***1-vinylimidazoloborane* (1h).** Colorless solid (yield 77%), the product was purified by flash column chromatography (PE/EtOAc = 5:1 to 3:1) to afford the desired product; **m.p.** 84 - 86 °C; R_f = 0.5 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3130, 2305, 1554, 1527, 1172, 1126, 898, 839, 751, 632 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (s, 1H), 7.17 - 7.15 (m, 2H), 6.87 (dd, *J* = 15.6, 8.8 Hz, 1H), 5.48 (dd, *J* = 15.6, 2.4 Hz, 1H), 5.19 (dd, *J* = 8.4, 2.4 Hz, 1H), 2.60 - 1.83 (m, 3H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -19.20 (q, *J* = 96.3 Hz); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 134.9, 128.6, 128.4, 116.9, 106.2; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_5H_9BN_2Na^+$ 131.0751; Found 131.0748.



1i

***4-Methoxypyridine borane* (1i).** White solid (yield 77%), the product was purified by flash column chromatography (PE/EtOAc = 5:1 to 3:1) to afford the desired product; **m.p.** 90 - 92 °C; R_f = 0.4 (pentane/EtOAc = 1/1); **IR (neat)** *v* 2360, 1626, 1510, 1298, 1163, 1096, 1010, 822 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.40 (d, *J* = 6.8 Hz, 2H), 6.93 - 6.91 (m, 2H), 3.95 (s, 3H), 2.91 - 2.07 (m, 3H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -12.90 (q, *J* = 97.3 Hz); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.3, 149.0, 110.9, 56.2; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_6H_{10}BNNaO^+$ 146.0748; Found 146.0726.

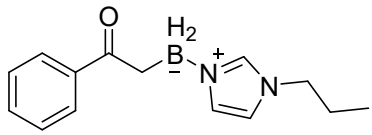


1k

***2-amino-4-methylpyridine borane* (1k).** White solid (yield 81%), the product was purified by flash column chromatography (PE/EtOAc = 5:1 to 3:1) to afford the desired product; **m.p.** 104 - 106 °C; R_f = 0.4 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3436, 3337, 2313, 1648, 1613, 1517, 1168, 1152, 888, 823 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (s, 1H), 7.38 (d, *J* = 9.2 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 5.47 (s, 2H), 2.56 - 1.76 (m, 6H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -17.36 (q, *J* = 96.0 Hz); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 153.6, 144.4, 141.4, 122.3, 111.3, 17.2; **HRMS (ESI-TOF)** m/z:

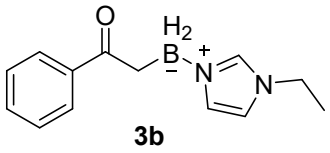
[M+Na+CH_3CN]$^+$ Calcd for $C_6H_{11}BKN_2^+$ 186.1173; Found 186.1152.

6.2. Characterization data of products 3 and 4.



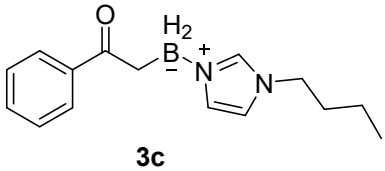
3a

***(2-phenyl-2-oxoethyl)(1-propyl-1H-imidazole)-dihydroborate* (3a).** Yellow oil (31.5 mg, 65%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.7 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3133, 2966, 2353, 1446, 1276, 1128, 1014, 695, 663 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 - 7.98 (m, 2H), 7.72 (t, *J* = 2.4 Hz, 1H), 7.46 - 7.42 (m, 1H), 7.40 - 7.39 (m, 2H), 7.04 (t, *J* = 1.6 Hz, 1H), 6.85 (t, *J* = 1.6 Hz, 1H), 3.87 (t, *J* = 7.2 Hz, 2H), 2.56 - 2.53 (m, 2H), 1.84 – 1.75 (m, *J* = 7.2 Hz, 2H), 0.92 (t, *J* = 7.6 Hz, 3H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -12.08 (t, *J* = 101.9 Hz); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 207.7, 138.3, 135.9, 131.5, 128.4, 127.9, 126.2, 119.6, 50.2, 37.5, 23.8, 10.9; **HRMS (ESI-TOF)** m/z: [M+Na]$^+$ Calcd for $C_{14}H_{19}BN_2NaO^+$ 265.1483; Found 265.1479.



3b

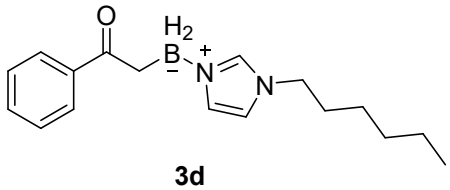
***(2-phenyl-2-oxoethyl)(1-ethyl-1H-imidazole)-dihydroborate* (3b).** Colorless oil (18.2 mg, 40%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.5 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3135, 2922, 2331, 1644, 1446, 1276, 1126, 825, 665 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 - 8.00 (m, 2H), 7.78 (s, 1H), 7.48 - 7.43 (m, 1H), 7.42 - 7.36 (t, *J* = 8.0 Hz, 2H), 7.06 (s, 1H), 6.89 (t, *J* = 1.6 Hz, 1H), 3.99 (q, *J* = 7.2 Hz, 2H), 2.56 (s, 2H), 1.47 (t, *J* = 7.2 Hz, 3H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -12.13 (t, *J* = 100.9 Hz); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 207.9, 138.3, 135.4, 131.4, 128.5, 127.9, 126.9, 119.1, 43.5, 37.6, 15.6; **HRMS (ESI-TOF)** m/z: [M+Na]$^+$ Calcd for $C_{13}H_{17}BN_2NaO^+$ 251.1326; Found 251.1330.



3c

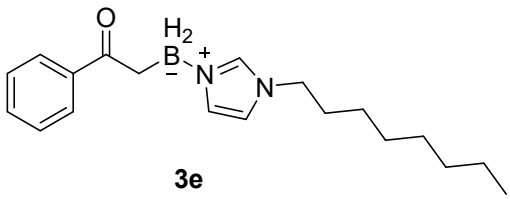
***(2-phenyl-2-oxoethyl)(1-butyl-1H-imidazole)-dihydroborate* (3c)**. Colorless oil (23.6 mg, 46%), the product was purified by flash column chromatography

(PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3134, 2930, 2332, 1644, 1275, 1126, 1091, 753, 661 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.75 (s, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.06 (s, 1H), 6.86 (s, 1H), 3.92 (t, *J* = 7.3 Hz, 2H), 2.56 (s, 2H), 1.80 - 1.73 (m, 2H), 1.38 - 1.29 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -12.52 (d, *J* = 97.9 Hz); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 207.8, 138.3, 135.8, 131.4, 128.5, 127.9, 126.8, 119.5, 48.4, 37.6, 32.3, 19.5, 13.4; **HRMS (ESI-TOF)** m/z: $[M+K]^+$ Calcd for $C_{15}H_{21}BKN_2O^+$ 295.1379; Found 295.1385.



3d

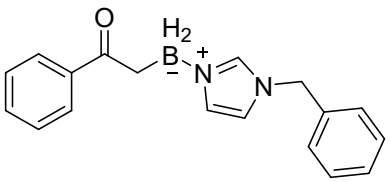
(2-phenyl-2-oxoethyl)ethyl)(1-hexyl-1H-imidazole)-dihydroborate **(3d).** Colorless oil (25.6 mg, 45%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.5 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3133, 2929, 2350, 1636, 1446, 1277, 1084, 985, 755, 694 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.73 (s, 1H), 7.45 (t, *J* = 7.1 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.04 (s, 1H), 6.86 (s, 1H), 3.89 (t, *J* = 7.2 Hz, 2H), 2.55 (s, 2H), 1.78 - 1.72 (m, *J* = 7.2 Hz, 2H), 1.29 – 1.26 (s, 6H), 0.89 (t, *J* = 7.2 Hz, 3H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -12.14 (t, *J* = 93.4 Hz); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 207.7, 138.4, 135.8, 131.4, 128.5, 127.9, 126.7, 119.6, 48.6, 37.5, 31.1, 30.4, 26.0, 22.4, 13.9; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{17}H_{25}BN_2NaO^+$ 307.1952; Found 307.1967.



3e

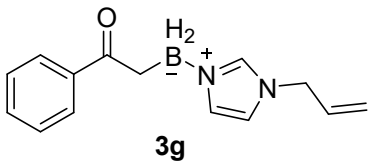
(2-phenyl-2-oxoethyl)ethyl)(1-octyl-1H-imidazole)-dihydroborate **(3e).** Colorless oil (26.9 mg, 43%), the product was purified by flash column chromatography (PE/EtOAc = 4:1 to 3:1) to afford the desired product; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** v 3133, 2925, 2327, 1647, 1541, 1446, 1274, 1092, 907, 756 cm^{-1}; **^{1}H NMR (400 MHz, CD_3CN)** δ 7.90 - 7.88 (m, 2H), 7.81 (s, 1H), 7.48 - 7.44 (m, 1H), 7.40 - 7.36 (m, 2H), 7.06 (t, *J* = 1.6 Hz, 1H), 7.00 (t, *J* = 1.6 Hz, 1H), 3.92 (t, *J* = 7.2 Hz, 2H), 2.42 (t, *J* = 4.8 Hz, 2H), 1.74 - 1.67 (m, 2H), 1.32 - 1.22 (m, 10H), 0.876 (t, *J* = 6.8 Hz, 3H); **^{11}B NMR (128 MHz, CD_3CN)** δ -12.10 (t, *J* = 100.4 Hz); **^{13}C{^{1}H} NMR (100**

MHz, CD_3CN) δ 206.4, 139.4, 137.1, 131.8, 128.6, 128.5, 126.3, 121.1, 48.7, 37.8, 32.1, 30.6, 29.4, 29.2, 26.4, 23.0, 14.0; **HRMS (ESI-TOF)** m/z: [M+Na]+ Calcd for $C_{19}H_{29}BN_2NaO^+$ 335.2265; Found 335.2275.



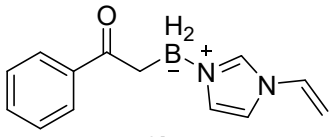
3f

***(2-phenyl-2-oxoethyl)(1-benzyl-1H-imidazole)-dihydroborate* (3f).** Colorless oil (27.3 mg, 47%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3133, 2332, 1643, 1539, 1446, 1276, 1077, 915, 693 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 - 7.99 (m, 2H), 7.78 (s, 1H), 7.47 - 7.43 (m, 1H), 7.42 - 7.36 (m, 5H), 7.20 - 7.17 (m, 2H), 7.07 (t, *J* = 1.6 Hz, 1H), 6.84 (t, *J* = 1.6 Hz, 1H), 5.07 (s, 2H), 2.56 (t, *J* = 4.8 Hz, 2H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -12.45 (t, *J* = 109.5 Hz); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 207.7, 138.3, 136.2, 133.6, 131.5, 129.4, 129.2, 128.5, 128.0, 127.9, 127.1, 119.9, 52.3, 37.7; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{18}H_{19}BN_2NaO^+$ 313.1483; Found 313.1501.



3g

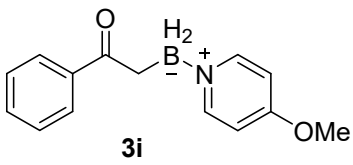
***(2-phenyl-2-oxoethyl)(1-allyl-1H-imidazole)-dihydroborate* (3g).** Colorless oil (13.4 mg, 28%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.7 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3134, 2926, 2330, 1644, 1541, 1275, 1091, 1030, 755, 695, 638 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.77 (s, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.07 (s, 1H), 6.87 (s, 1H), 5.95 - 5.85 (m, 1H), 5.39 (d, *J* = 10.2 Hz, 1H), 5.34 (d, *J* = 16.9 Hz, 1H), 4.53 (d, *J* = 6.0 Hz, 2H), 2.56 (s, 2H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -12.22 (t, *J* = 83.2 Hz); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 207.8, 138.3, 136.0, 131.5, 130.5, 128.5, 128.0, 126.9, 121.0, 119.7, 50.8, 37.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{17}BN_2NaO$ 263.1326; Found 263.1347.



3h

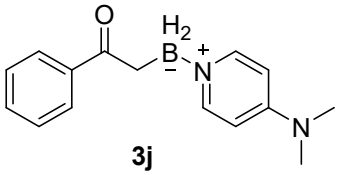
***(2-phenyl-2-oxoethyl)ethyl)(1-vinyl-1H-imidazole)-dihydroborate* (3h).** Colorless oil (20.8 mg, 46%), the product

was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.7 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3131, 2922, 2332, 1645, 1527, 1276, 1126, 1089, 756, 694 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 - 8.00 (m, 3H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.83 (dd, *J* = 15.6, 8.6 Hz, 1H), 5.45 (dd, *J* = 15.6, 2.4Hz, 1H), 5.16 (dd, *J* = 8.8, 2.4 Hz, 1H), 2.57 (t, *J* = 4.8 Hz, 2H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -11.96 (t, *J* = 103.5 Hz); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 207.9, 138.2, 134.8, 131.6, 128.5, 128.0, 127.6, 116.6, 106.3, 37.1; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{13}H_{15}BN_2NaO^+$ 249.1170; Found 249.1148.



3i

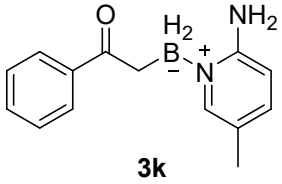
(2-phenyl-2-oxoethyl)(2-methoxypyridin)-dihydroborate **(3i).** Colorless oil (18.3 mg, 38%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** *v* 2922, 2848, 2368, 1627, 1513, 1304, 1078, 834, 694 cm^{-1}; **^{1}H NMR (400 MHz, CD_3CN)** δ 8.22 (d, *J* = 6.8 Hz, 2H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 3.93 (s, 3H), 2.48 (t, *J* = 8.0 Hz, 2H); **^{11}B NMR (128 MHz, CD_3CN)** δ -6.32 (t, *J* = 101.7 Hz); **^{13}C{^{1}H} NMR (100 MHz, CD_3CN)** δ 205.9, 168.8, 149.1, 139.2, 132.0, 128.6, 111.9, 57.1, 38.4; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{14}H_{16}BNNaO_2^+$ 264.1166; Found 264.1155.



3j

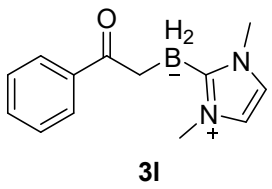
(2-phenyl-2-oxoethyl)(4-N,N-dimethylpyridin)-dihydroborate **(3j).** White solid (23.4 mg, 46%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; **m.p.** 90 - 92 °C; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** *v* 2921, 2346, 1634, 1272, 1143, 1092, 810, 773, 699 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 7.2 Hz, 2H), 7.46 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.39 (t, *J* = 6.8, 2H), 6.47 (d, *J* = 7.6 Hz, 2H), 3.08 (s, 6H), 2.57 (t, *J* = 4.8 Hz, 2H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -7.06 (t, *J* = 84.8 Hz); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 207.3, 155.0, 146.3, 138.4, 131.4, 128.6, 128.0, 106.4, 39.5, 38.7; **HRMS (ESI-TOF)** m/z: $[2M+H]^+$

Calcd for $C_{30}H_{39}B_2N_4O_2^+$ 509.3254; Found 509.3268.



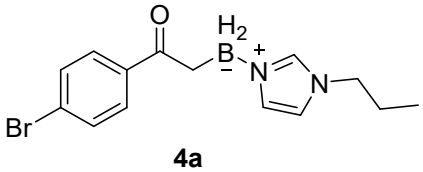
3k

***(2-phenyl-2-oxoethyl)(2-amino-5-methylpyridin)-dihydroborate* (3k).** White solid (19.2 mg, 40%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; **m.p.** 106 - 108 °C; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3412, 3157, 2922, 2390, 1647, 1519, 1280, 1147 , 825, 687 cm^{-1}; **^{1}H NMR (400 MHz, CD_3CN)** δ 7.91 - 7.88 (m, 2H), 7.55 (s, 1H), 7.50 (tt, *J* = 5.6, 1.6 Hz, 1H), 7.44 - 7.39 (m, 3H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.01 (s, 2H), 2.46 (t, *J* = 5.2 Hz, 2H), 2.07 (s, 3H); **^{11}B NMR** (128 MHz, CD_3CN) δ -10.44 (t, *J* = 99.6 Hz); **^{13}C{^{1}H} NMR (100 MHz, CD_3CN)** δ 206.4, 154.6, 143.7, 142.4, 139.2, 132.0, 128.6, 128.5, 122.3, 112.6, 34.6, 16.7; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{14}H_{17}BN_2NaO^+$ 263.1326; Found 263.1348.



3l

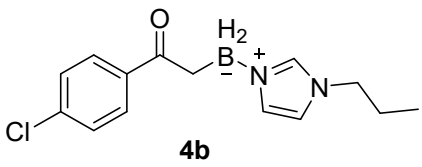
***(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-oxo-2-phenylethyl)-dihydroborate* (3l).** White solid (39.7 mg, 87%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.6 (pentane/EtOAc = 1/1); **^{1}H NMR (400 MHz, CD_3CN)** δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 6.92 (s, 2H), 3.56 (s, 6H), 2.32 (s, 2H).[2a]



4a

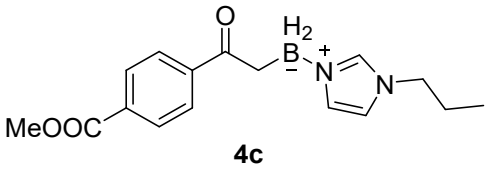
***(2-(4-bromophenyl)-2-oxoethyl)(1-propyl-1H-imidazole)-dihydroborate* (4a).** White solid (33.3 mg, 52%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; **m.p.** 99 - 101 °C; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3390, 3189, 3120, 2917, 2849, 2359, 2328, 1643, 1277, 1134, 1085, 846, 654 cm^{-1}; **^{1}H NMR (400 MHz, CD_3CN)** δ 7.80 - 7.70 (m, 3H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.07 (t, *J* = 1.6 Hz, 1H), 7.00 (t, *J* = 2.0 Hz, 1H), 3.91 (t, *J* = 7.2 Hz, 2H), 2.39 (t, *J* = 4.8 Hz, 2H), 1.79 - 1.70 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H); **^{11}B NMR (128 MHz, CD_3CN)** δ -12.17 (t, *J* = 99.9 Hz); **^{13}C{^{1}H} NMR (100 MHz, CD_3CN)** δ 205.2,

138.3, 137.2, 131.6, 130.6, 126.3, 126.0, 121.2, 50.2, 37.9, 24.0, 10.5; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{14}H_{18}BBrN_2NaO^+$ 343.0588; Found 343.0614.



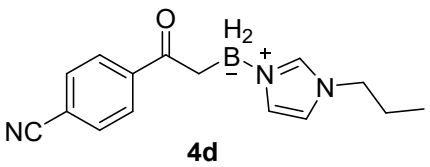
4b

(2-(4-Chlorophenylphenyl)-2-oxoethyl)(1-propyl-1H-imidazole)-dihydroborate **(4b)**. Colorless oil (35.3 mg, 64%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3133, 2966, 2352, 1646, 1272, 1087, 1011, 821, 744, 658 cm^{-1}; **^{1}H NMR (400 MHz, CD_3CN)** δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.81 (s, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.08 (t, *J* = 1.6 Hz, 1H), 7.00 (t, *J* = 1.6 Hz, 1H), 3.91 (t, *J* = 7.2 Hz, 2H), 2.41 (d, *J* = 5.2 Hz, 2H), 1.79 - 7.70 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H); **^{11}B NMR (128 MHz, CD_3CN)** δ -12.17 (t, *J* = 100.1 Hz); **^{13}C{^{1}H} NMR (100 MHz, CD_3CN)** δ 205.1, 137.9, 137.4, 137.2, 130.4, 128.6, 126.3, 121.1, 50.2, 38.0, 24.0, 10.5; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{14}H_{18}BClN_2NaO^+$ 299.1093; Found 299.1105.



4c

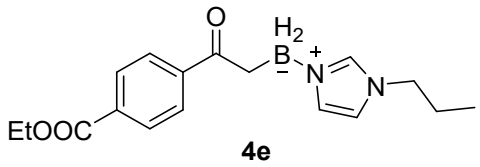
(2-(4-(methoxycarbonyl)phenyl)-2-oxoethyl)(1-propyl-1H-imidazole)-dihydroborate **(4c)**. Yellow oil (8.4 mg, 14%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.7 (pentane/EtOAc = 1/1); IR (neat) *v* 3342, 2958, 1719, 1677, 1435, 1278, 1111, 1014, 768, 697 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (s, 4H), 7.73 (t, *J* = 1.6 Hz, 1H), 7.06 (t, *J* = 1.6 Hz, 1H), 6.89 (t, *J* = 1.6 Hz, 1H), 3.93 (s, 3H), 3.91 (t, *J* = 7.2 Hz, 2H), 2.58 (t, *J* = 4.0 Hz, 2H), 1.87 - 1.78 (m, 2H), 0.95 (t, *J* = 7.6 Hz, 3H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -12.28 (t, *J* = 106.0 Hz); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 206.9, 166.8, 141.9, 135.8, 132.3, 129.3, 128.4, 126.8, 119.6, 52.2, 50.3, 37.7, 23.8, 10.9; **HRMS (ESI-TOF)** m/z: $[2M+H]^+$ Calcd for $C_{32}H_{43}B_2N_4O_6^+$ 601.3363; Found 601.3381.



4d

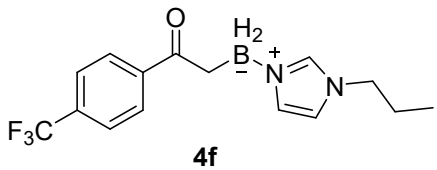
(2-(4-Cyanophenylphenyl)-2-oxoethyl)(1-propyl-1H-imidazole)-dihydroborate **(4d).** Green solid (11.2 mg,

21%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; **m.p.** 49 - 51 °C; R_f = 0.7 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3139, 2966, 2339, 2229, 1654, 1270, 1130, 1080, 825, 757, 659 cm^{-1}; **^{1}H NMR (400 MHz, CD_3CN)** δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.80 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.09 (t, *J* = 1.6 Hz, 1H), 7.00 (t, *J* = 1.6 Hz, 1H), 3.92 (t, *J* = 7.2 Hz, 2H), 2.45 (t, *J* = 4.8 Hz, 2H), 1.80 - 1.71 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H); **^{11}B NMR (128 MHz, CD_3CN)** δ -12.36 (t, *J* = 101.4 Hz); **^{13}C{^{1}H} NMR (100 MHz, CD_3CN)** δ 204.9, 142.6, 137.2, 132.6, 129.1, 126.2, 121.2, 119.0, 114.7, 50.2, 38.1, 24.0, 10.5; **HRMS (ESI-TOF)** m/z: $[M+H+CH_3CN]^+$ Calcd for $C_{17}H_{22}BN_4O^+$ 309.1881; Found 309.1890.



4e

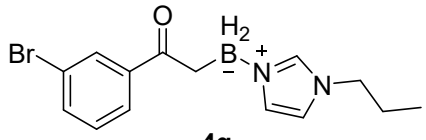
(2-(4-(ethoxycarbonyl)-2-oxoethyl)ethyl)dihydroborate)(1-propyl-1H-imidazole)-dihydroborate **(4e)**. Yellow oil (20.1 mg, 32%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.7 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3134, 2966, 2351, 1712, 1650, 1269, 1100, 1016, 764, 707 cm^{-1}; **^{1}H NMR (400 MHz, CD_3CN)** δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.83 (s, 1H), 7.10 (s, 1H), 7.03 (s, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.93 (t, *J* = 7.2 Hz, 2H), 2.48 (s, 2H), 7.81 - 1.72 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H); **^{11}B NMR (128 MHz, CD_3CN)** δ -12.24 (t, *J* = 93.3 Hz); **^{13}C{^{1}H} NMR (100 MHz, CD_3CN)** δ 205.8, 166.4, 142.9, 137.2, 133.2, 129.5, 128.6, 126.3, 121.2, 61.6, 50.2, 38.2, 24.0, 14.6, 10.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{23}BN_2NaO_3^+$ 337.1694; Found 337.1671.



4f

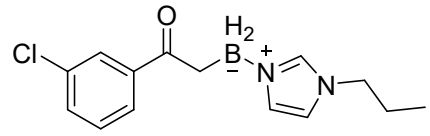
(2-(4-(trifluoromethyl)phenyl)-2-oxoethyl)(1-propyl-1H-imidazole)-dihydroborate **(4f).** Colorless oil (23.6 mg, 38%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3134, 2933, 2357, 1652, 1323, 1120, 1064, 1015, 830, 740, 663 cm^{-1}; **^{1}H NMR (400 MHz, CD_3CN)** δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.80 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.09 (t, *J* = 1.6 Hz, 1H), 7.00 (t, *J* = 1.6 Hz, 1H), 3.92 (t, *J* = 7.2 Hz, 2H), 2.45 (t, *J* = 5.2 Hz, 2H), 1.80 - 1.71 (m, 2H), 0.86 (t, *J* = 7.6 Hz, 3H); **^{11}B NMR (128 MHz,**

$CDCl_3$) δ -12.31 (t, J = 101.0 Hz); **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 206.4, 141.0, 135.8, 132.8 (q, $^2J_{C-F}$ = 32.2 Hz), 128.8, 126.8, 125.0 (q, $^3J_{C-F}$ = 3.7 Hz), 124.0 (q, $^1J_{C-F}$ = 272.4 Hz), 119.7, 50.3, 37.9, 23.8, 10.9; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{15}H_{18}BF_3N_2NaO^+$ 333.1356; Found 333.1384.



4g

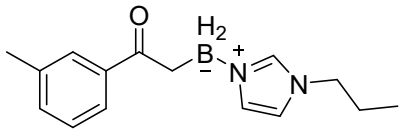
***(2-(4-(bromo)phenyl)-2-oxoethyl)(1-propyl-1H-imidazole)-dihydroborate* (4g).** White oil (30.1 mg, 47%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3135, 2963, 2352, 1650, 1280, 1257, 1127, 1080, 778, 742, 659 cm^{-1}; **^1H NMR (400 MHz, $CDCl_3$)** δ 8.11 (t, J = 1.8 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.72 (s, 1H), 7.59 - 7.56 (m, 1H), 7.29 – 7.26 (m, 1H), 7.06 (s, 1H), 6.89 (t, J = 1.5 Hz, 1H), 3.91 (t, J = 7.2 Hz, 2H), 2.52 (t, J = 4.7 Hz, 2H), 1.88 – 1.79 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -12.27 (d, J = 103.6 Hz); **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 206.0, 140.1, 135.8, 134.3, 131.4, 129.6, 127.3, 126.8, 122.4, 119.7, 50.3, 37.7, 23.8, 10.9; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{18}BBrN_2NaO^+$ 343.0588; Found 343.0591.



4h

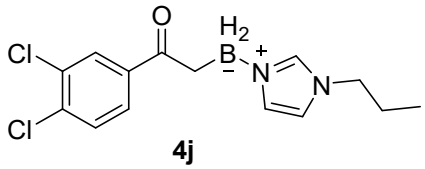
***(2-(3-(chlorophenyl)phenyl)-2-oxoethyl)(1-propyl-1H-imidazole)-dihydroborate* (4h).** Yellow oil (20.4 mg, 37%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3134, 2965, 2353, 1650, 1280, 1258, 1128, 1092, 783, 744, 668 cm^{-1}; **^1H NMR (400 MHz, $CDCl_3$)** δ 7.95 (t, J = 1.6 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.73 (s, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.06 (s, 1H), 6.89 (s, 1H), 3.91 (t, J = 7.2 Hz, 2H), 2.52 (d, J = 4.8 Hz, 2H), 1.88 - 1.79 (m, 2H), 0.96 (d, J = 7.2 Hz, 3H); **^{11}B NMR (128 MHz, $CDCl_3$)** δ -12.25 (d, J = 109.4 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 206.1, 140.0, 135.8, 134.2, 131.3, 129.3, 128.5, 126.8, 119.6, 50.3, 37.7, 23.8, 10.9; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{14}H_{18}BClN_2NaO^+$ 299.1093; Found 299.1118.

(2-(3-(methyl)phenyl)-2-oxoethyl)(1-propyl-1H-



4i

imidazole)-dihydroborate **(4i).** White oil (16.0 mg, 31%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3130.5, 2964.8, 2326.5, 1644.2, 1280.6, 1125.7, 1091.5, 787.3, 745.2, 703.8, 655.2 cm^{-1}; **^{1}H NMR (400 MHz, CD_3CN)** δ 7.79 (s, 1H), 7.68 – 7.66 (m, 2H), 7.30 – 7.24 (m, 2H), 7.07 (t, *J* = 1.6 Hz, 1H), 7.00 (t, *J* = 1.6 Hz, 1H), 3.90 (t, *J* = 7.2 Hz, 2H), 2.34 (t, *J* = 4.8 Hz, 2H), 2.35 (s, 3H), 1.79 – 1.70 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H). **^{11}B NMR (128 MHz, CD_3CN)** δ -12.13 (t, *J* = 99.9 Hz). **^{13}C NMR (100 MHz, CD_3CN)** 206.7, 139.6, 138.2, 137.2, 132.5, 129.12, 128.5, 126.4, 125.9, 121.1, 50.2, 37.6, 24.0, 21.0, 10.6. HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{15}H_{21}BKN_2O^+$ 295.1379; found:295.1402.



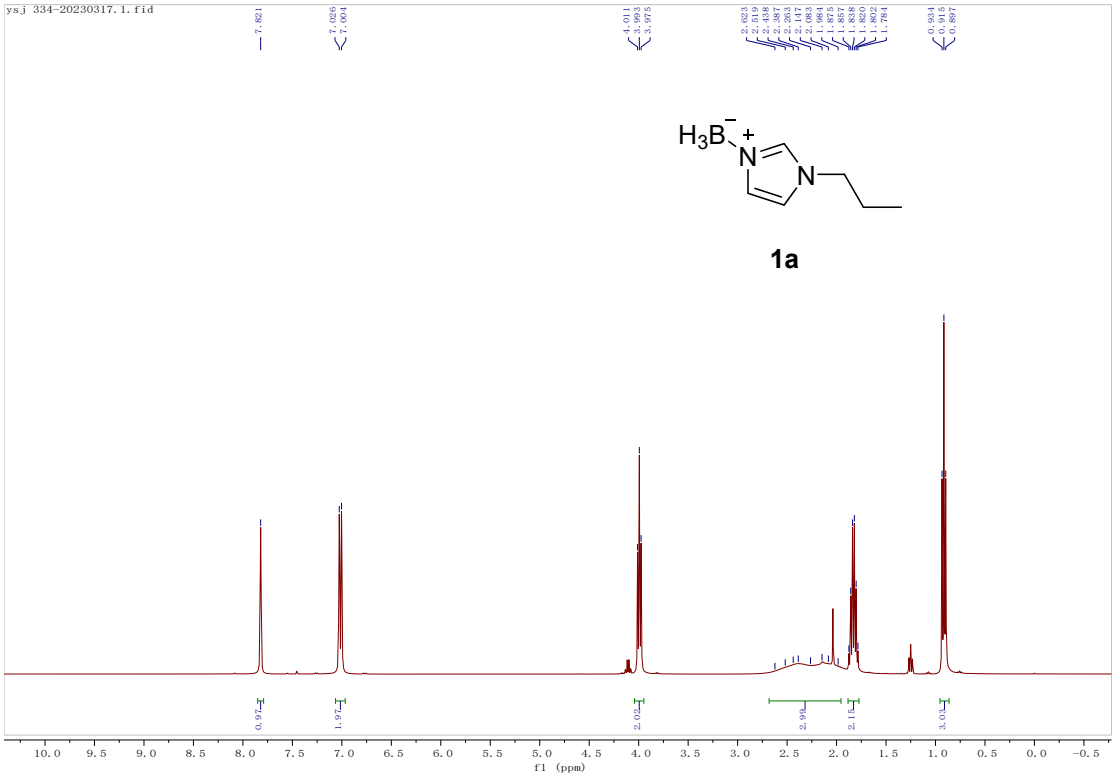
4j

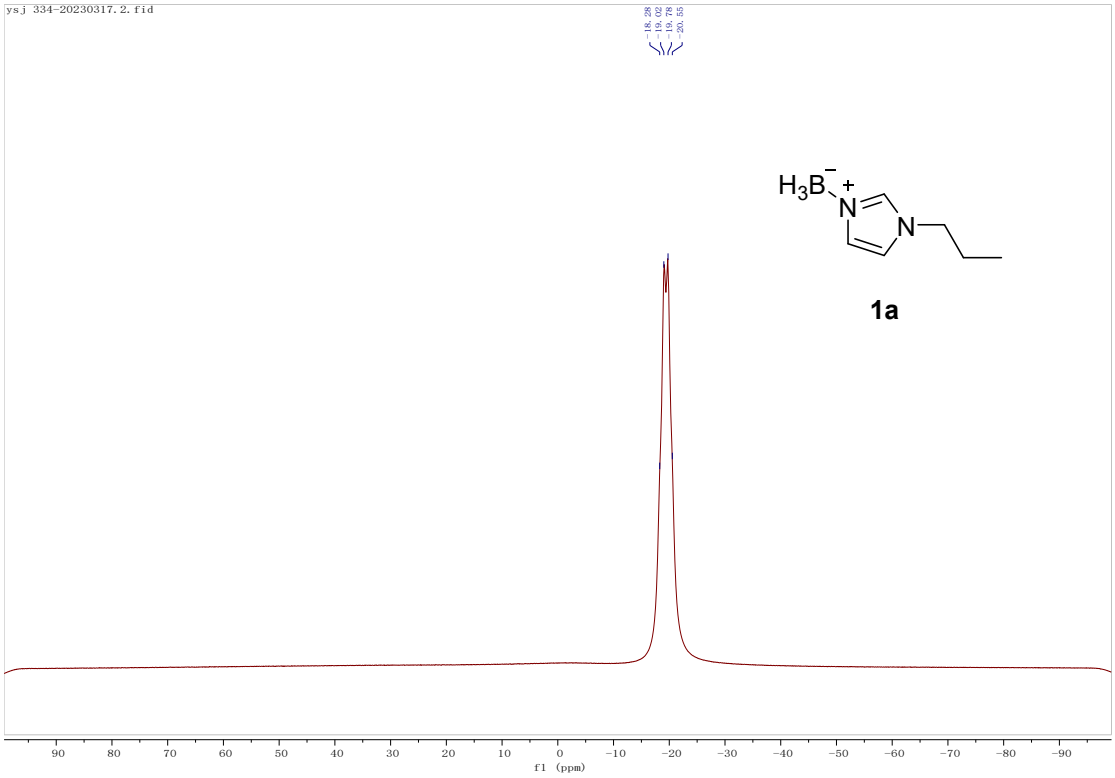
(2-(3,4-dichlorophenylphenyl)-2-oxoethyl)(1-propyl-1H-imidazole)-dihydroborate **(4j).** White solid (31.6 mg, 51%), the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 2:1) to afford the desired product; **m.p.** 49 - 51 °C; R_f = 0.6 (pentane/EtOAc = 1/1); **IR (neat)** *v* 3122, 2971, 2920, 2360, 2329, 1642, 1281, 1133, 1085, 1029, 980, 801, 766, 679, 655 cm^{-1}; **^{1}H NMR (400 MHz, CD_3CN)** δ 7.955 (d, *J* = 2.0 Hz, 1H), 7.80 (s, 1H), 7.77 (dd, *J* = 8.4, 2.0 Hz, 1H) 7.536 (d, *J* = 8.0 Hz, 1H), 7.09 (s, 1H), 7.01 (s, 1H), 3.91 (t, *J* = 7.1 Hz, 2H), 2.40 (s, 2H), 1.77 - 1.72 (m, 2H), 0.85 (t, *J* = 7.6 Hz, 3H); **^{11}B NMR (128 MHz, CD_3CN)** δ -12.23 (t, *J* = 94.4 Hz); **^{13}C{^{1}H} NMR (100 MHz, CD_3CN)** δ 203.8, 139.3, 137.2, 135.3, 132.2, 130.8, 130.5, 128.4, 126.2, 121.2, 50.2, 37.8, 24.0, 10.5; HRMS (ESI-TOF) m/z: $[2M+Na]^+$ Calcd for $C_{28}H_{34}B_2Cl_4N_4NaO_2^+$ 643.1514; Found 643.1503.

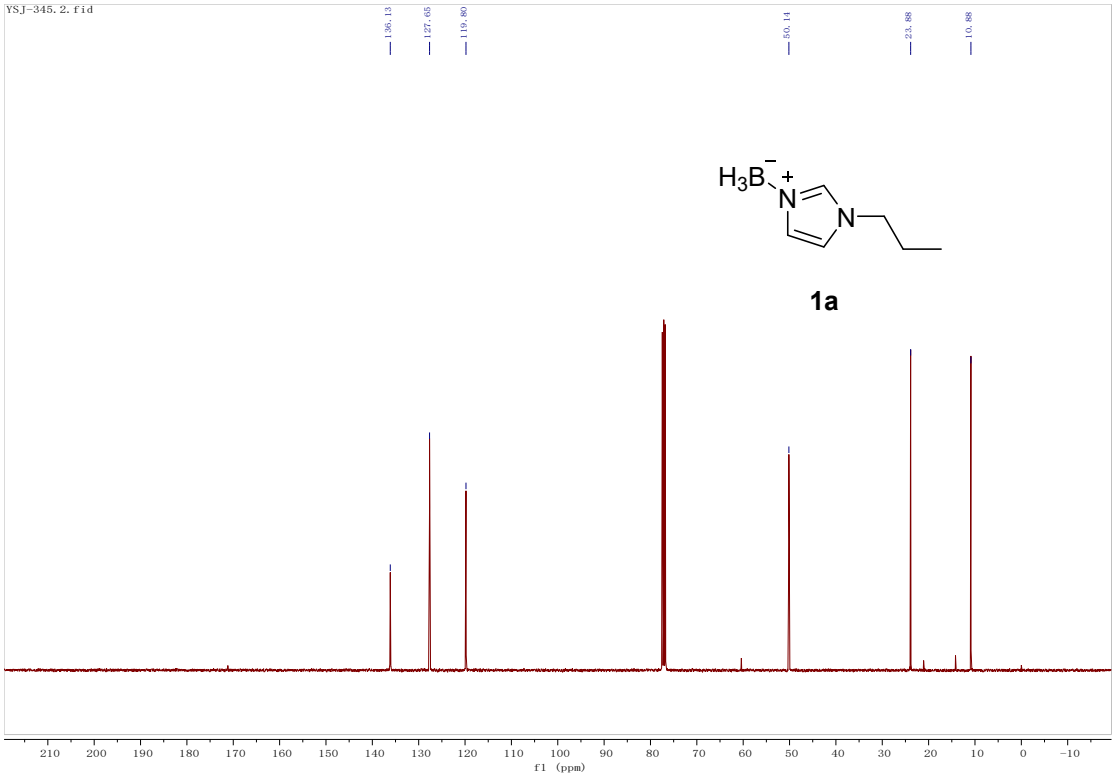
7. Copies of NMR Spectra

7.1. Starting materials 1a-1e, 1g-1i, 1k.

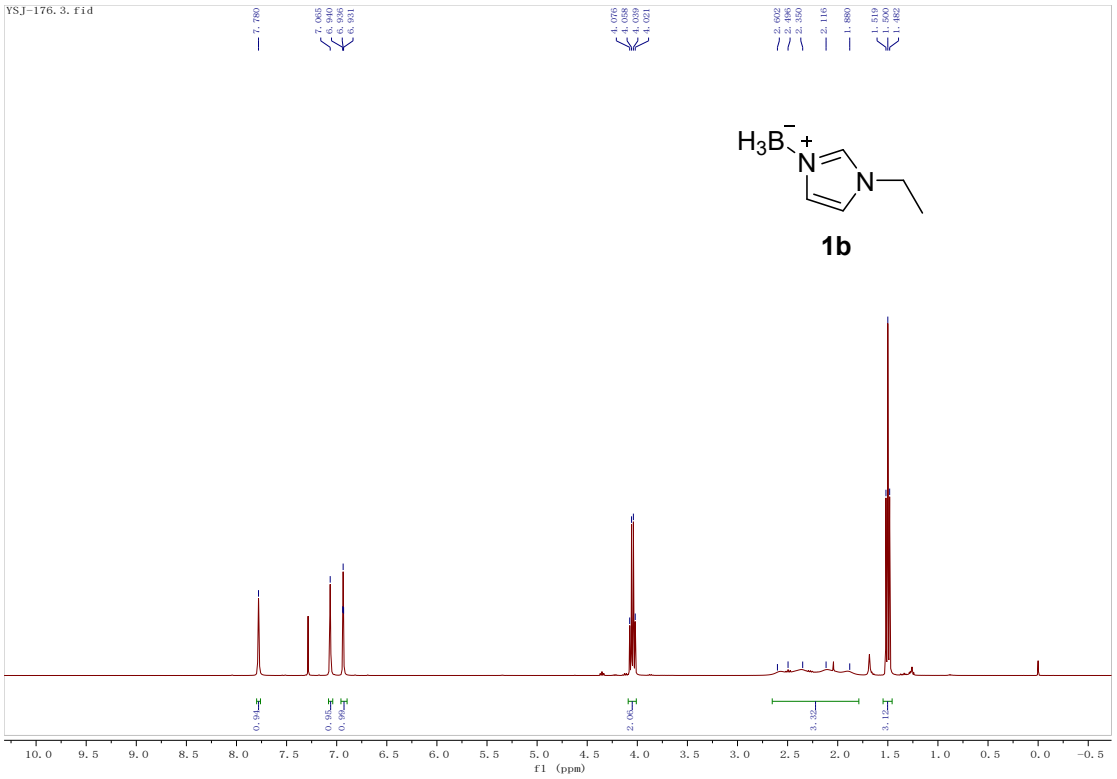
Material 1a: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

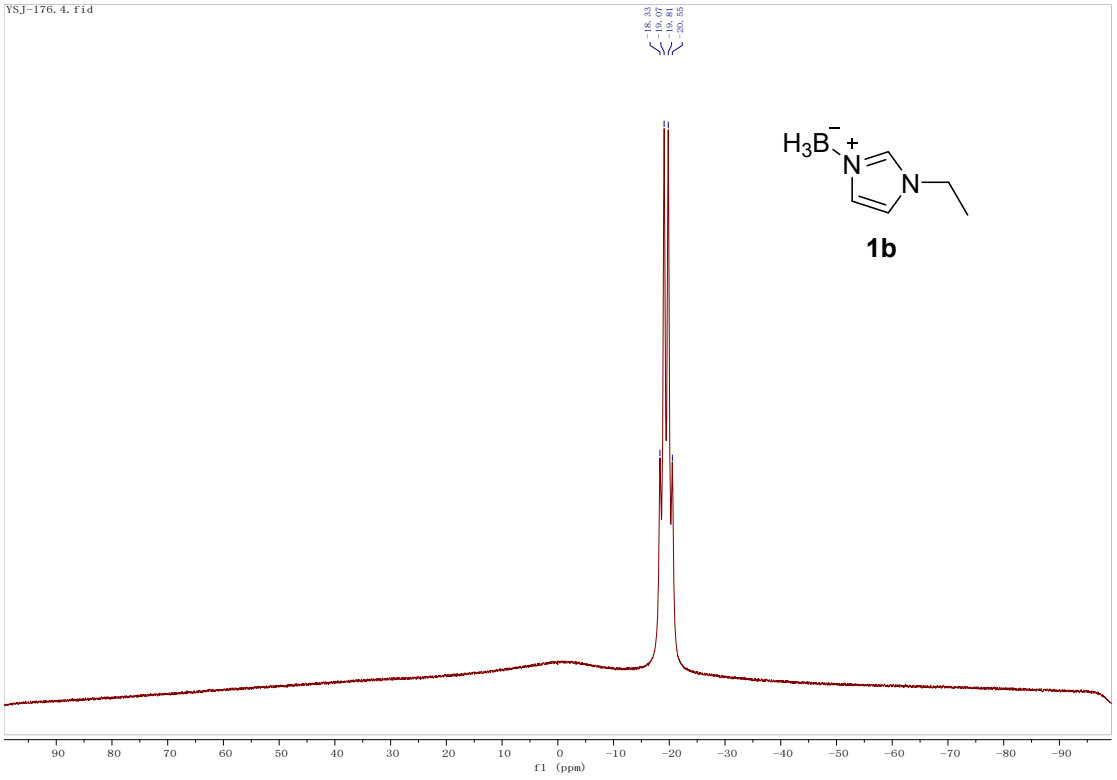


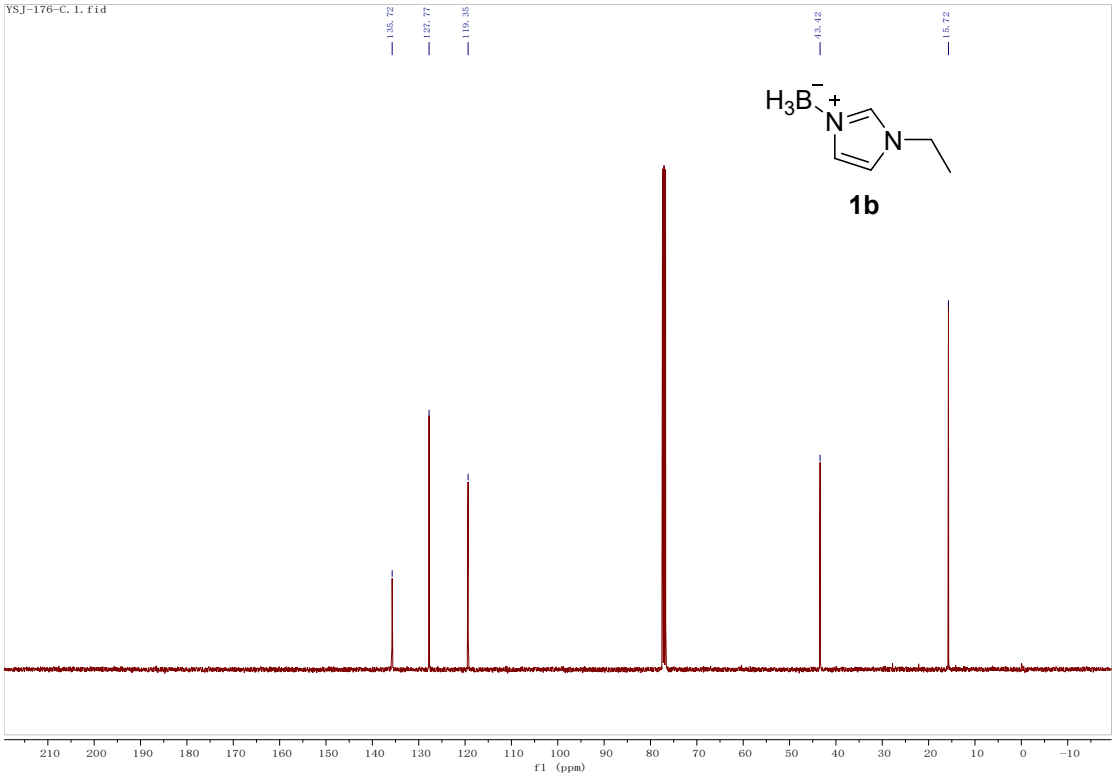

ysj 334-20230317.2.fid
-18.28
-19.22
-19.78
-20.55
H_3B^-
N
N
1a
f1 (ppm)


YSJ-345.2.fid
136.13
127.65
119.80
50.14
23.88
10.88
H_3B^-
N
N
1a
f1 (ppm)

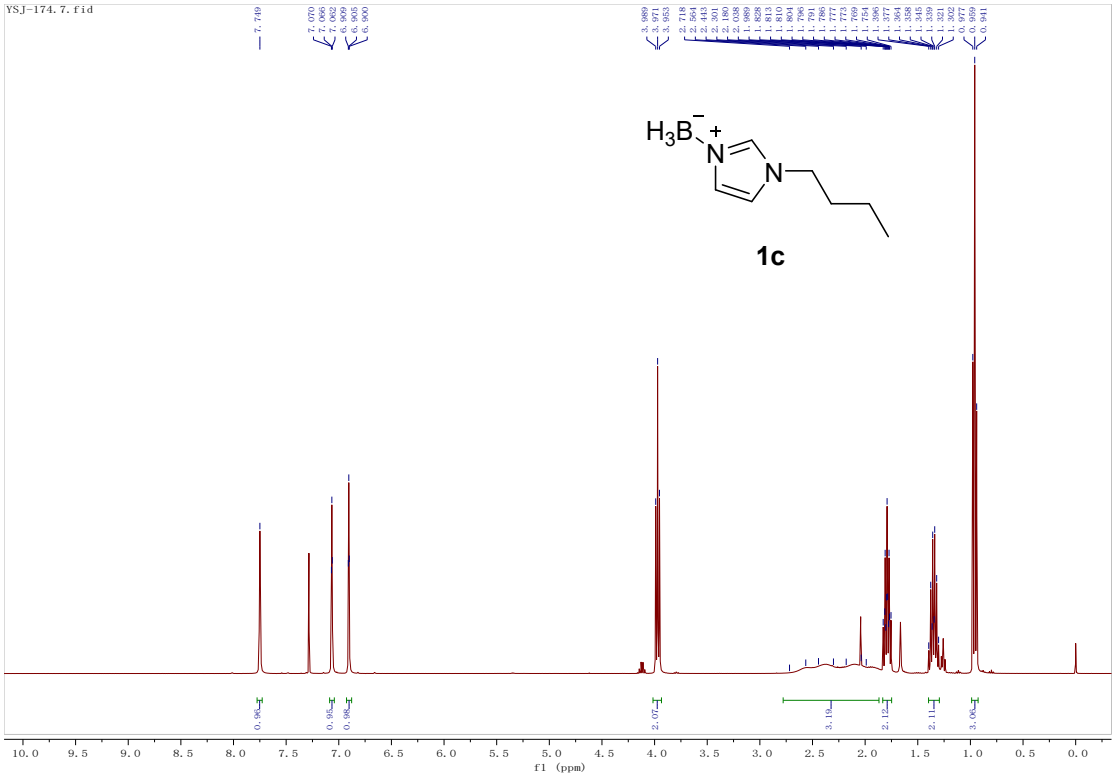
Material 1b: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

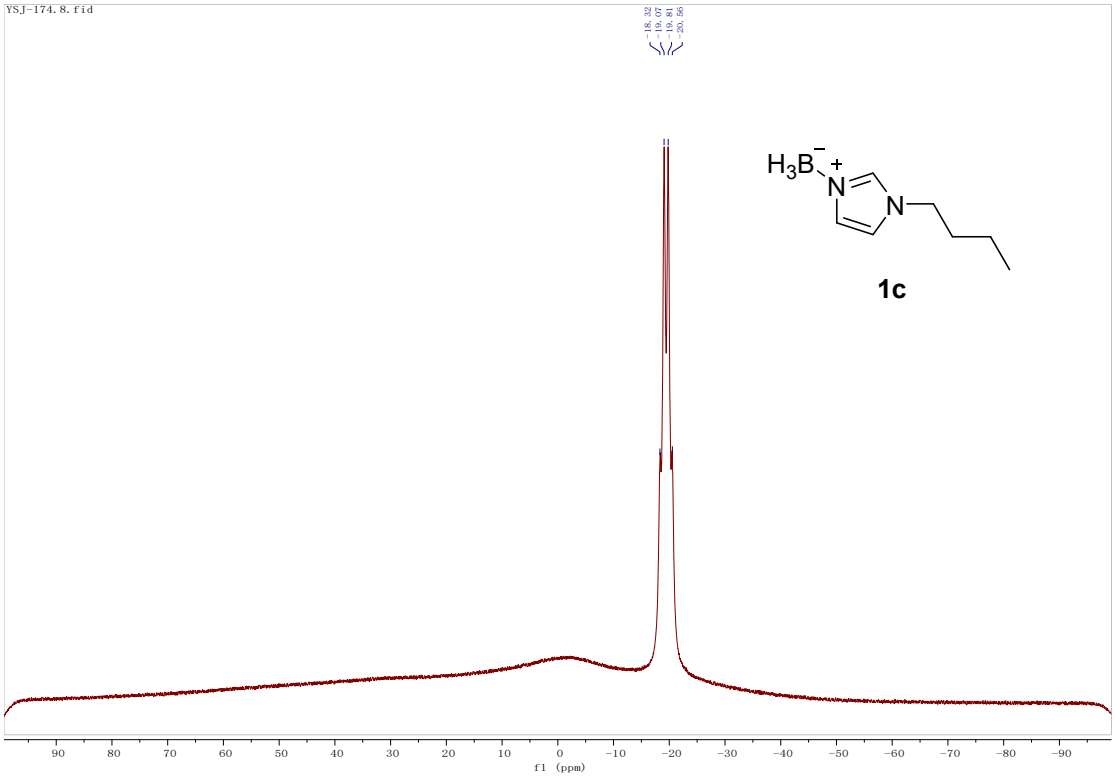


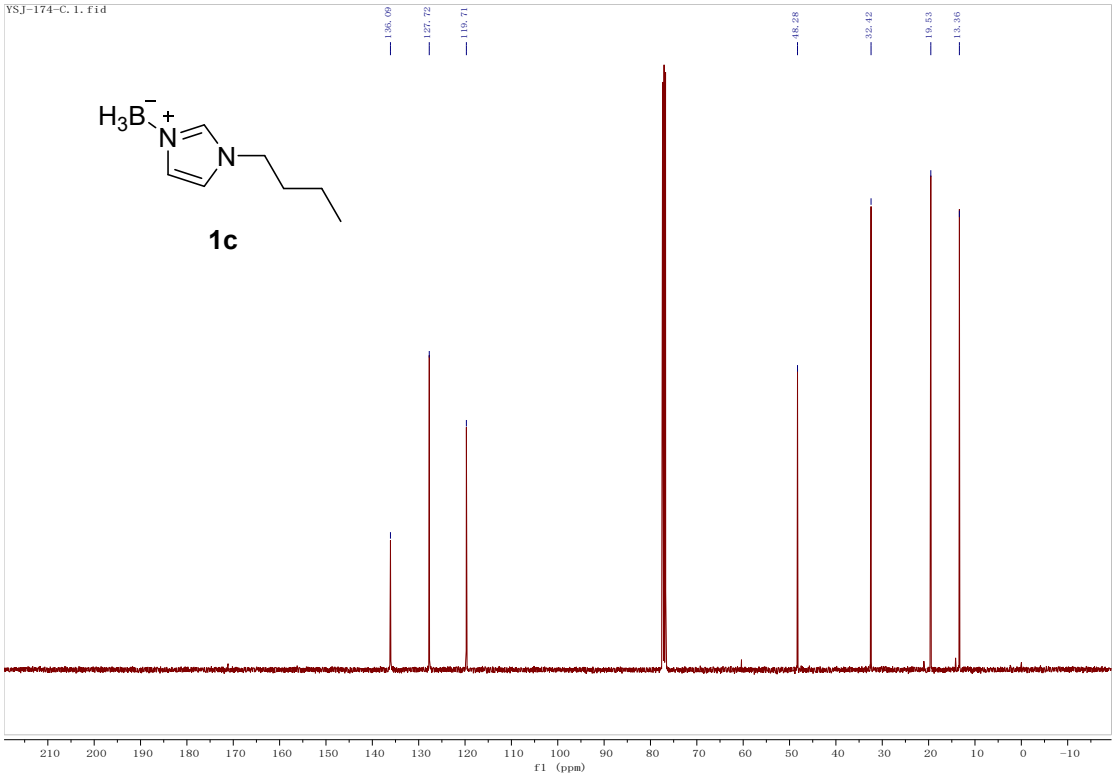



YSJ-176-C.1.fid
135.72
127.77
119.35
43.42
15.72
H_3B^-
N
+
N
1b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

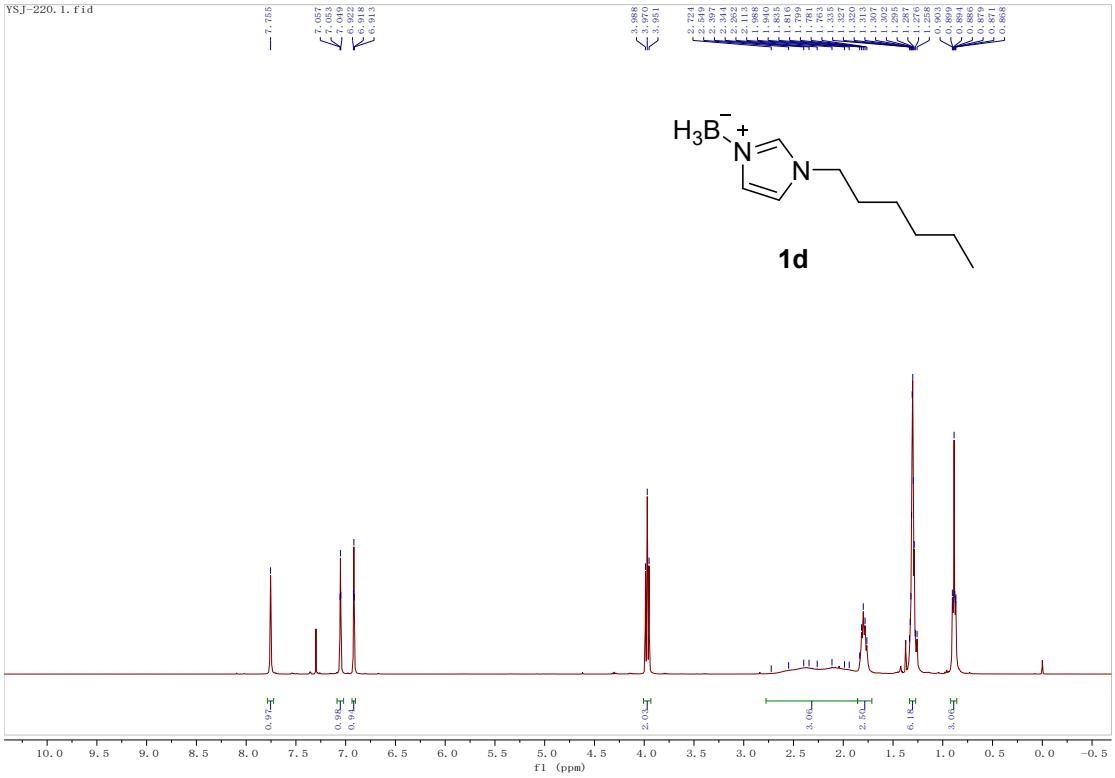
Material 1c: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

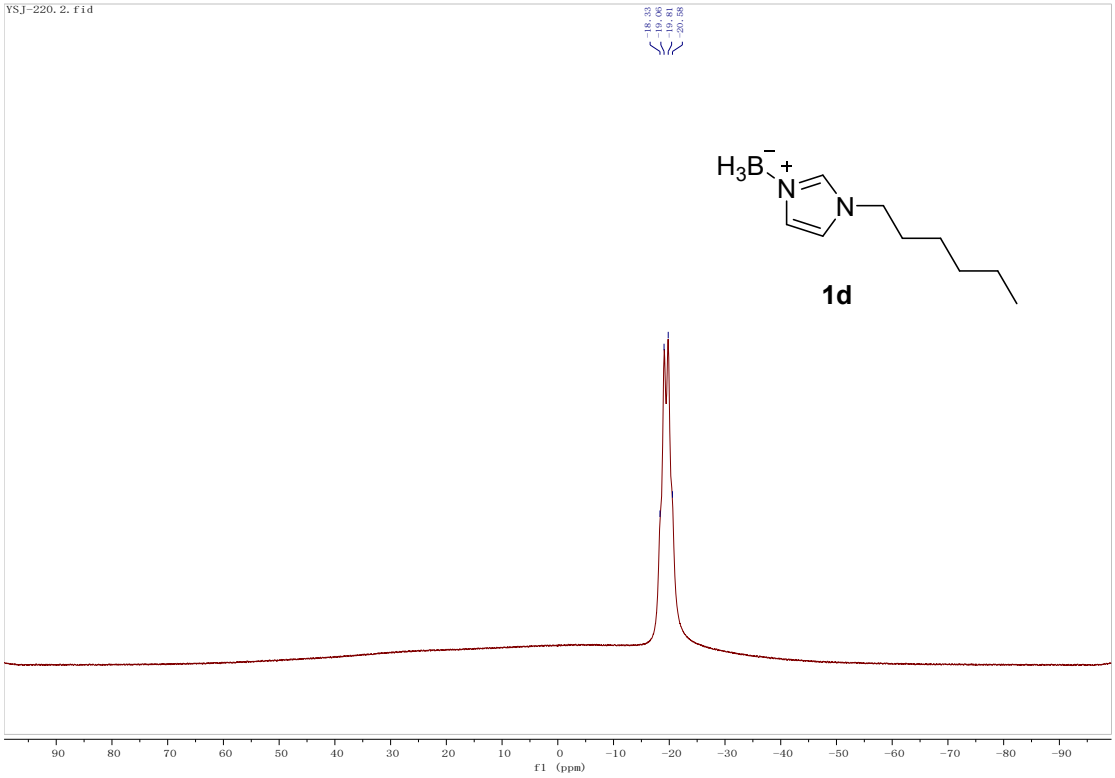


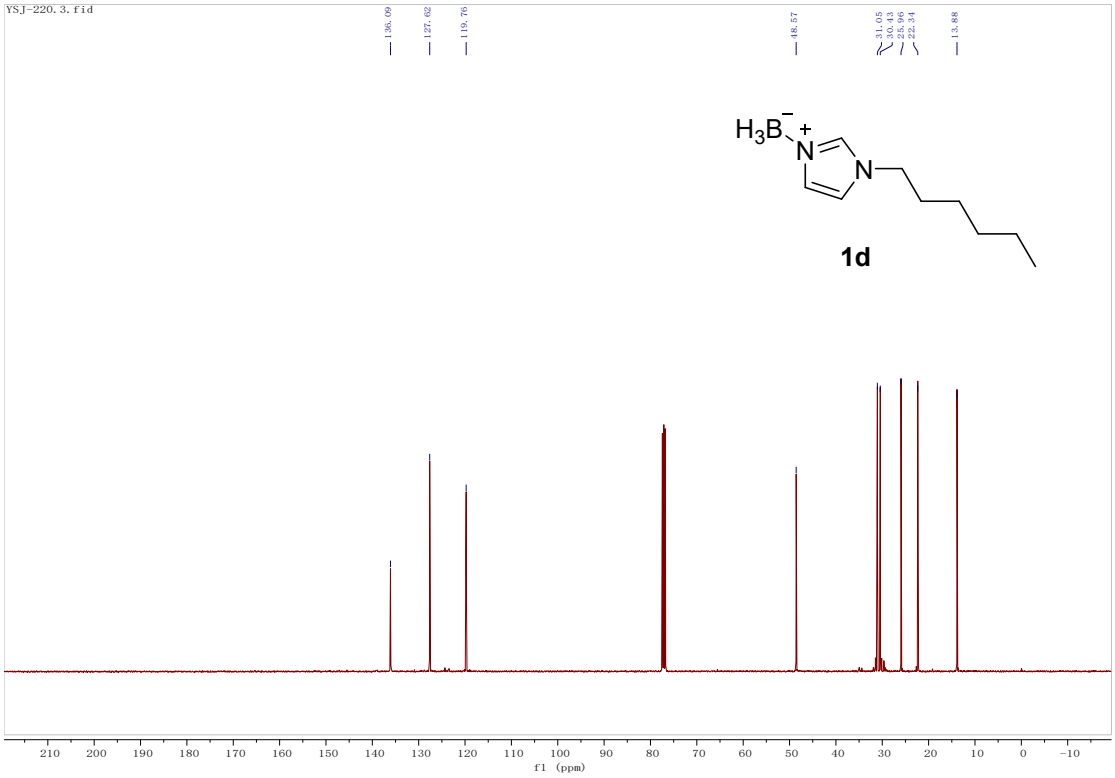



YSJ-174-C.1.fid
136.09
127.72
119.71
48.28
32.42
19.53
13.36
1c
f1 (ppm)

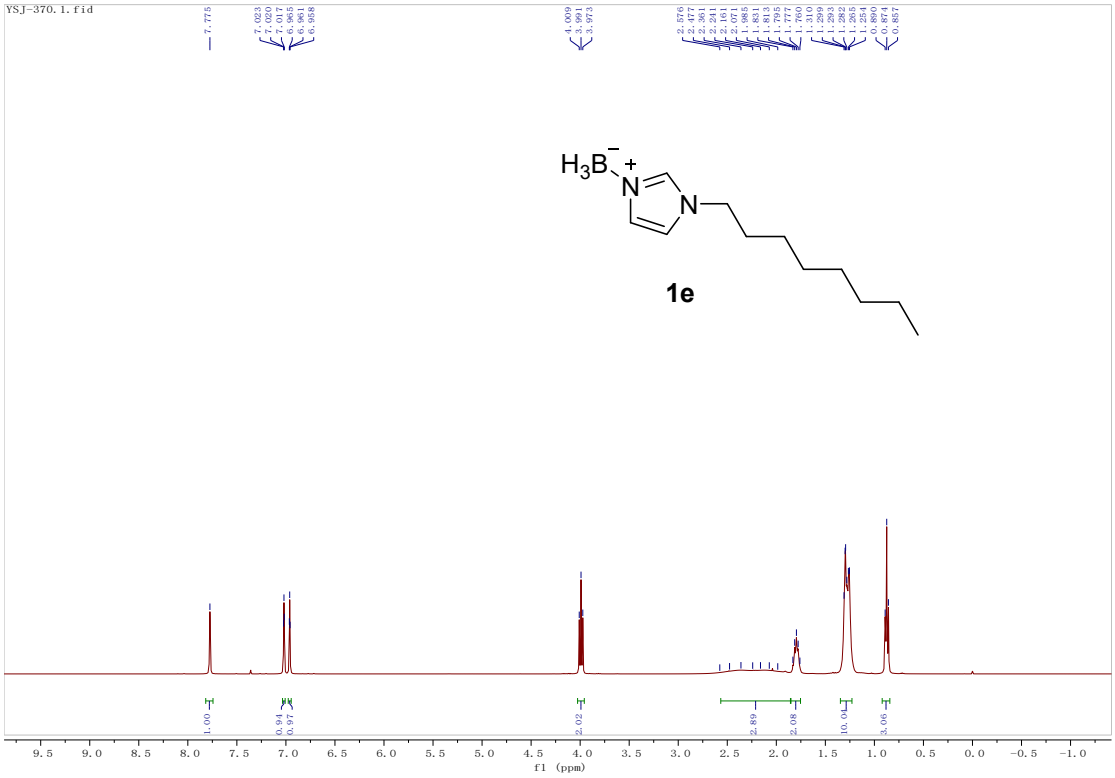
Material 1d: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

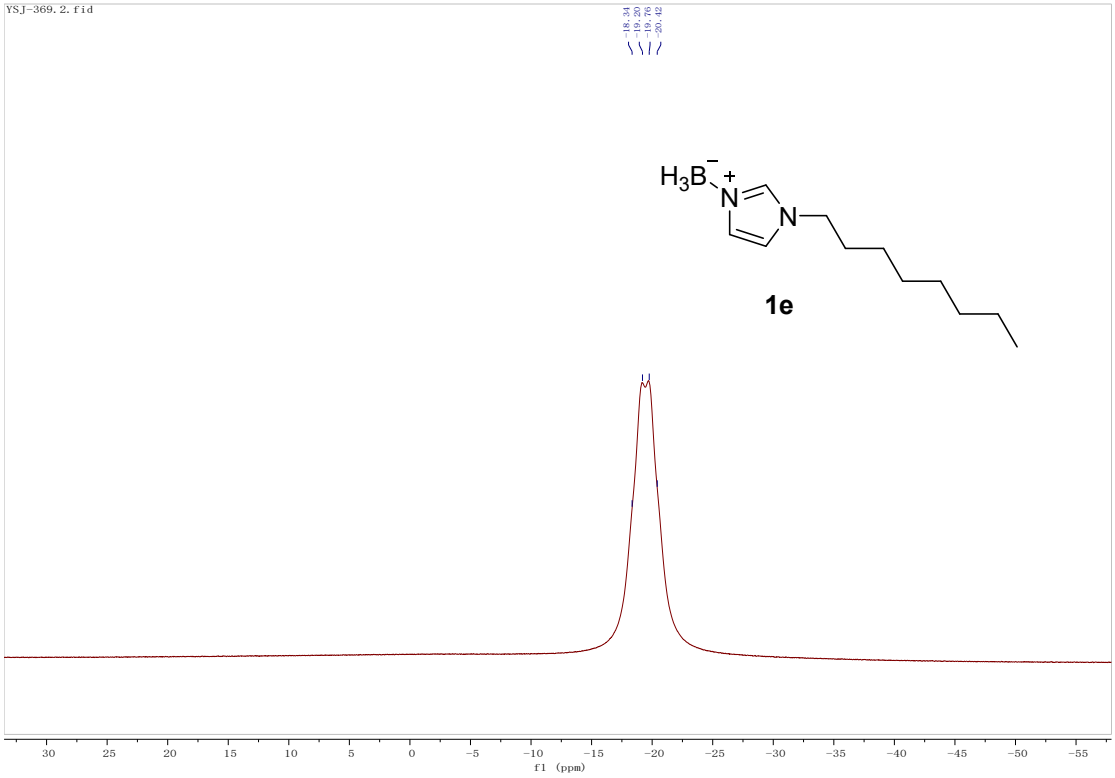


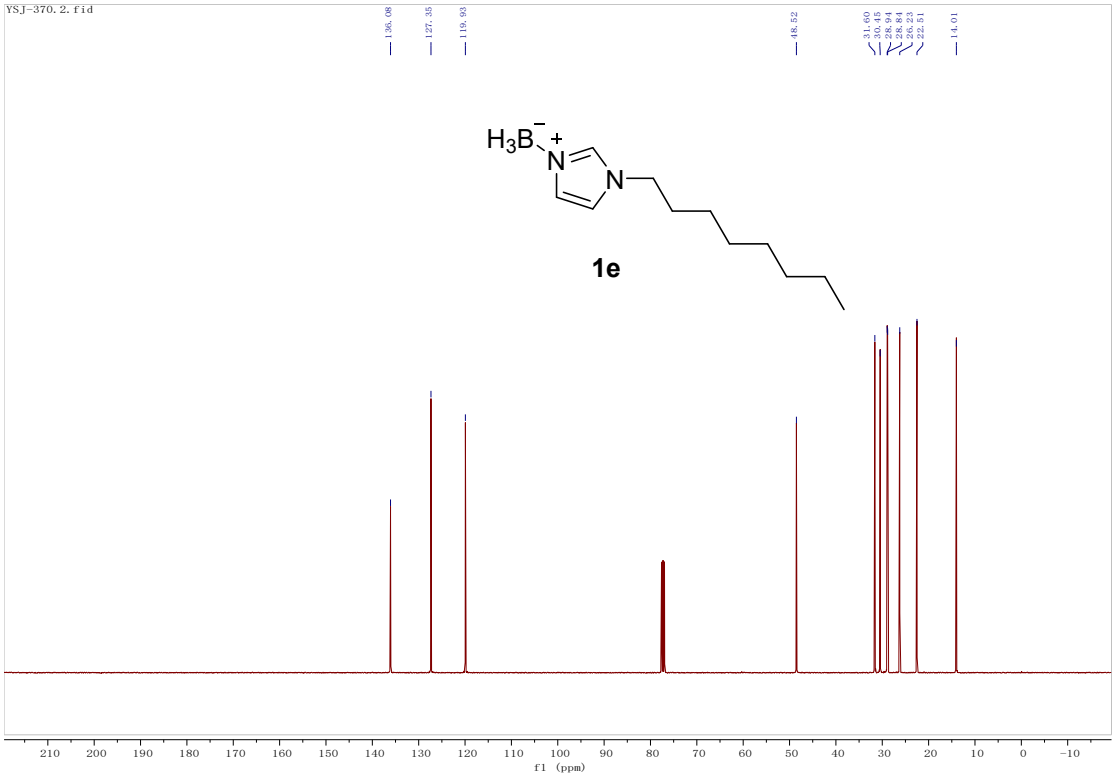



YSJ-220.3.fid
136.09
127.62
119.76
48.57
31.05
30.43
25.96
22.34
13.88
H_3B
N
N
1d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

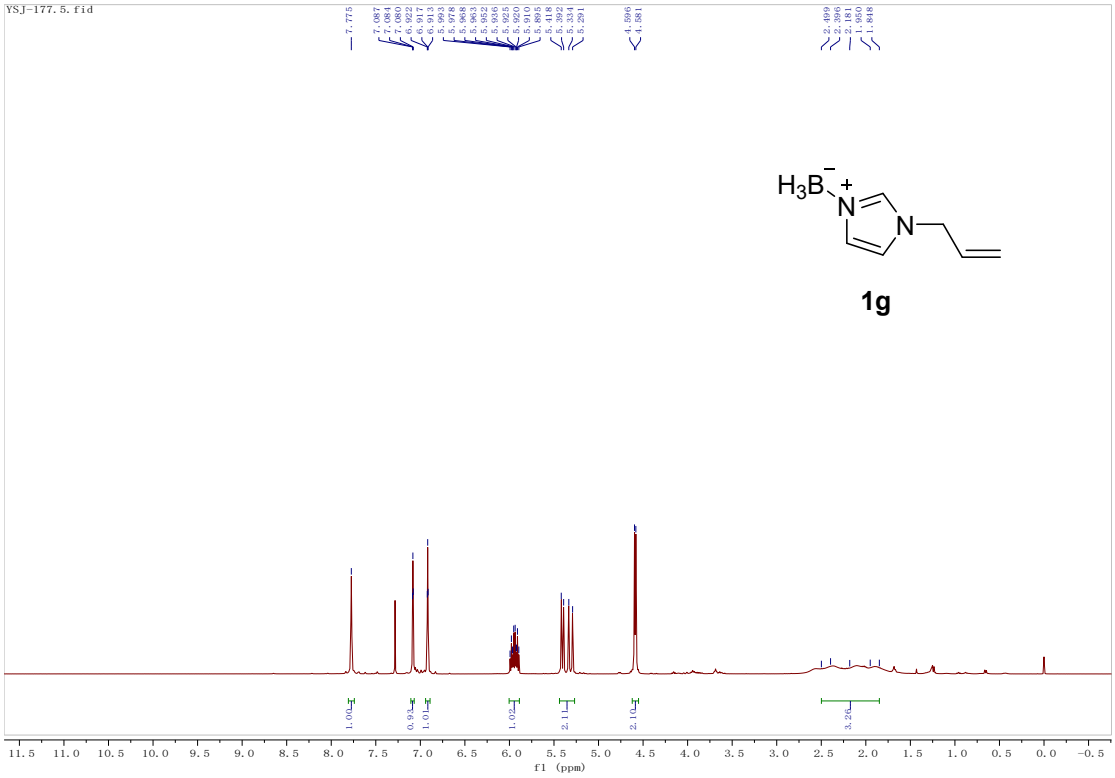
Material 1e: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

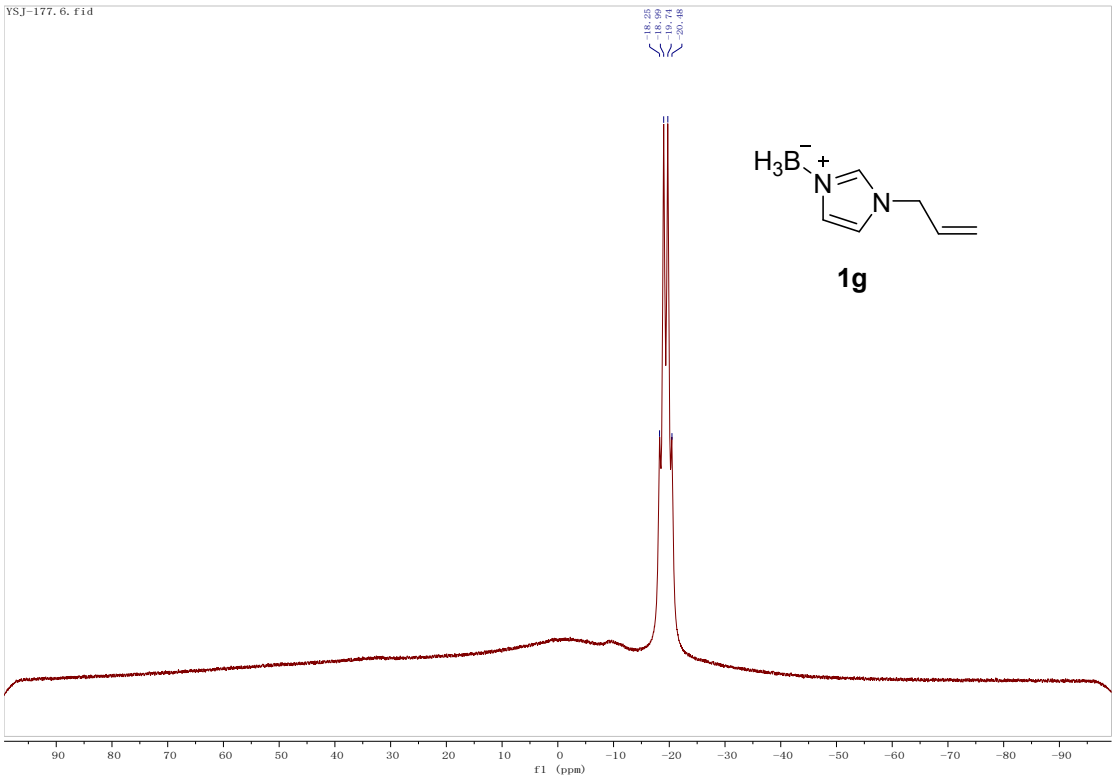


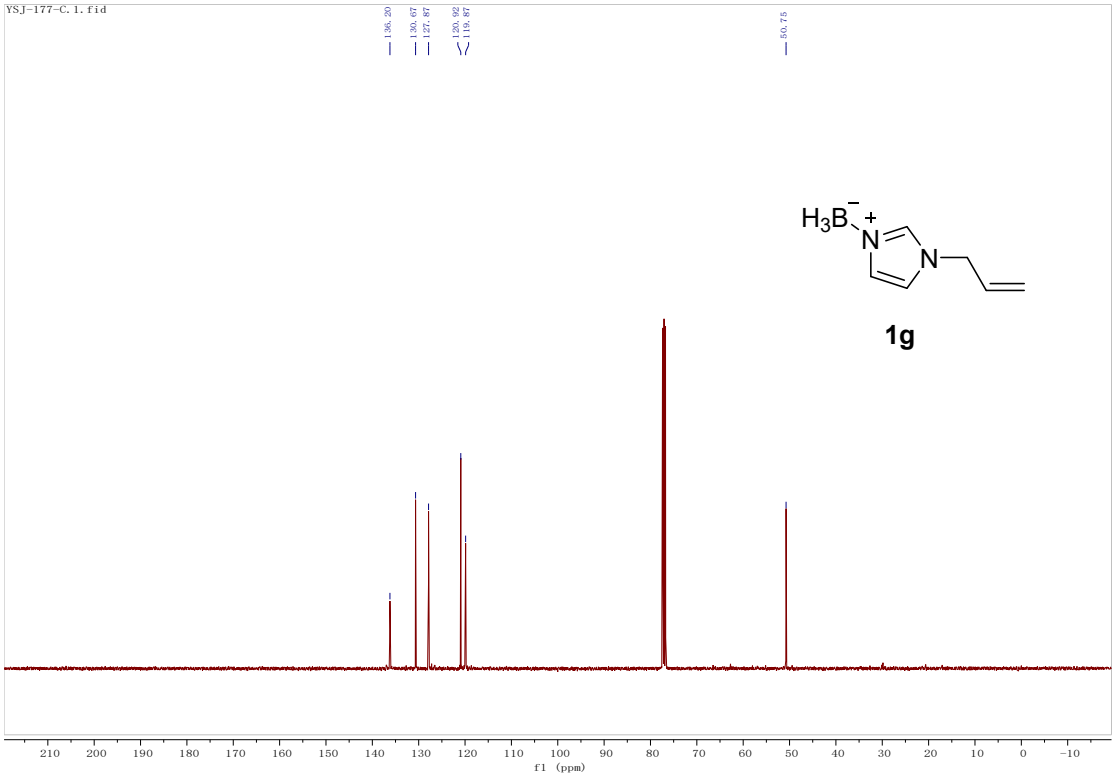



YSJ-370.2.fid
136.08
127.35
119.93
48.52
31.60
30.45
28.94
28.64
25.23
22.51
14.01
H_3B^-
N
N
1e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

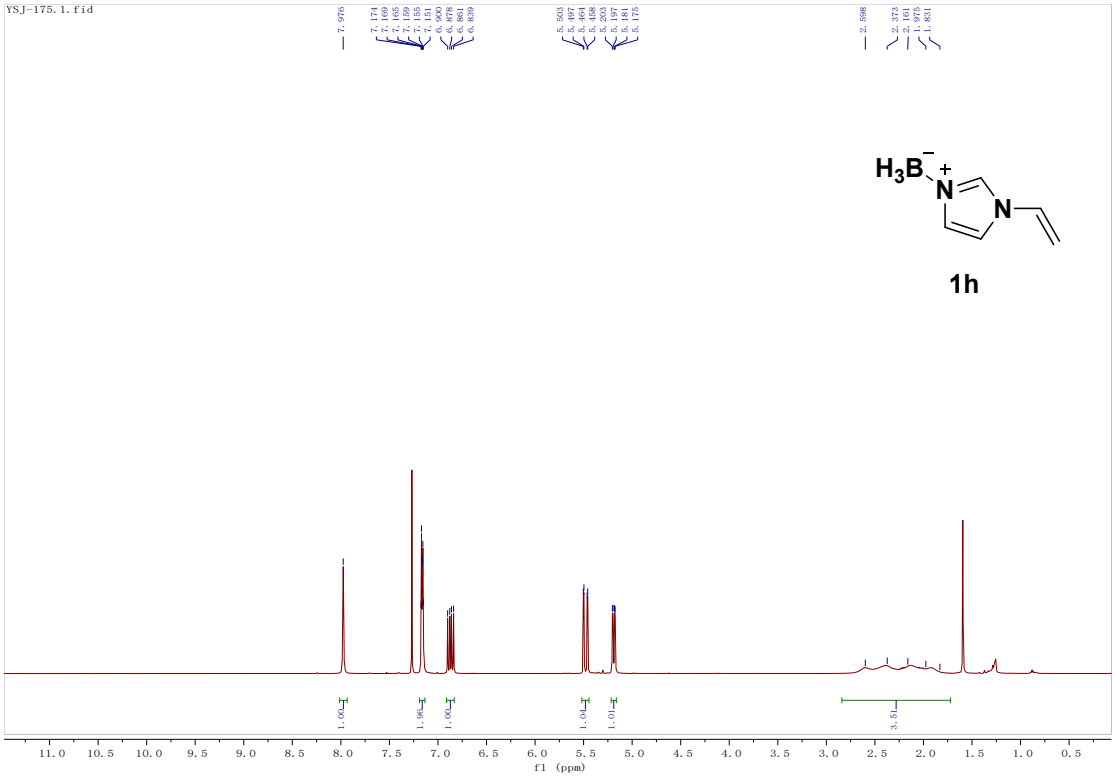
Material 1g: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

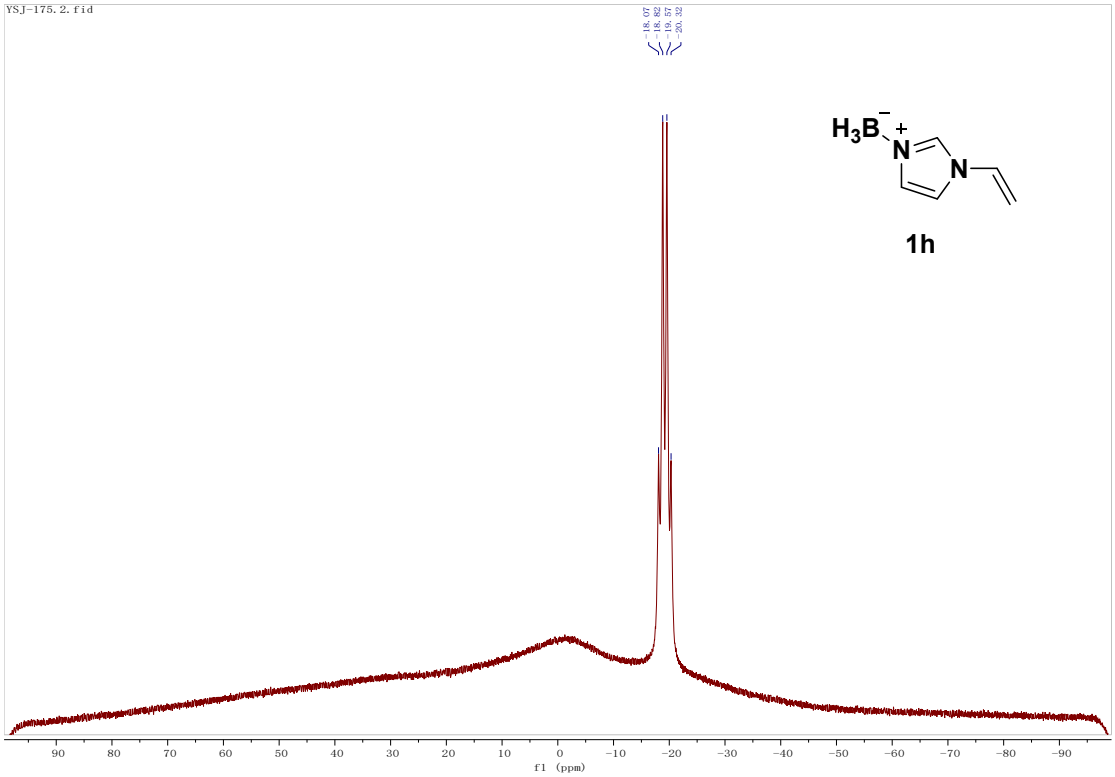


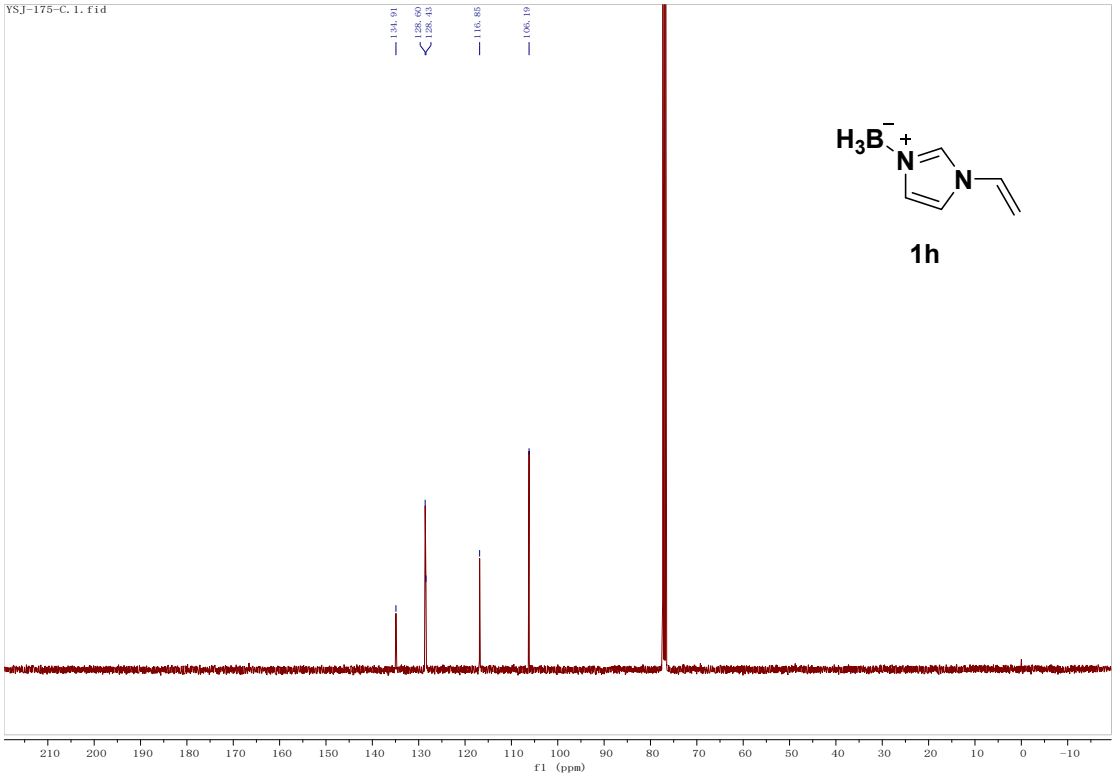



YSJ-177-C.1.fid
136.20
130.67
127.87
120.92
115.87
50.75
H3B
N
N
1g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

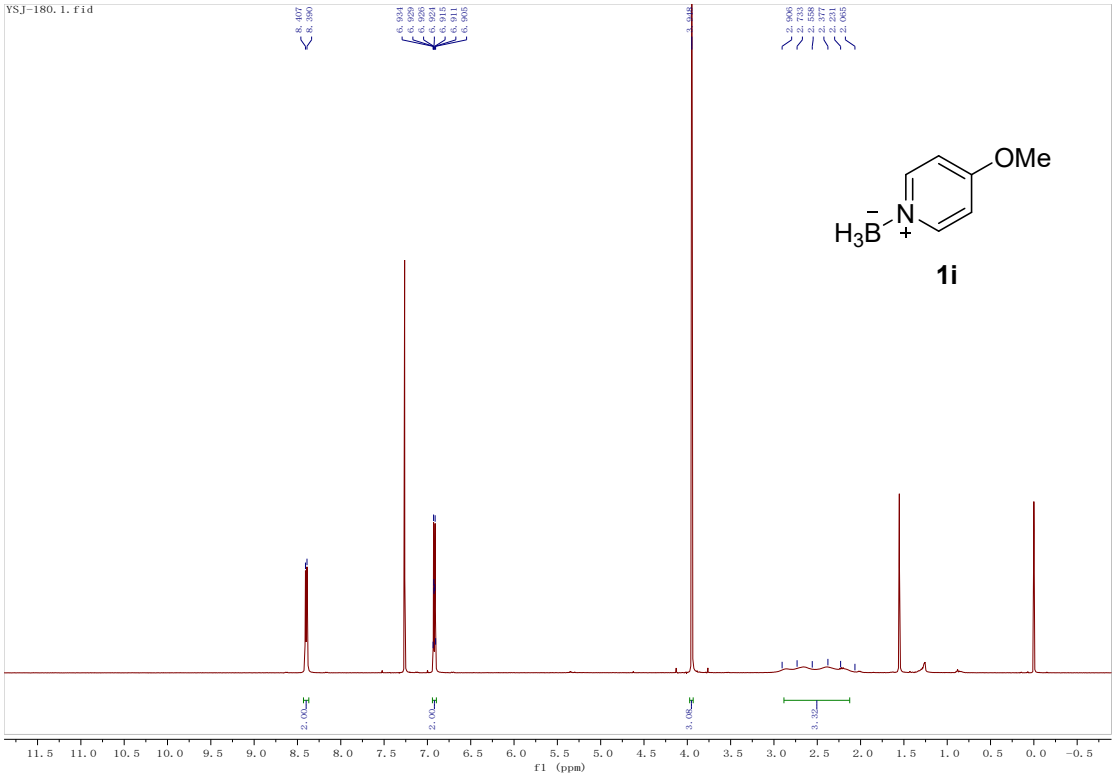
Material 1h: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

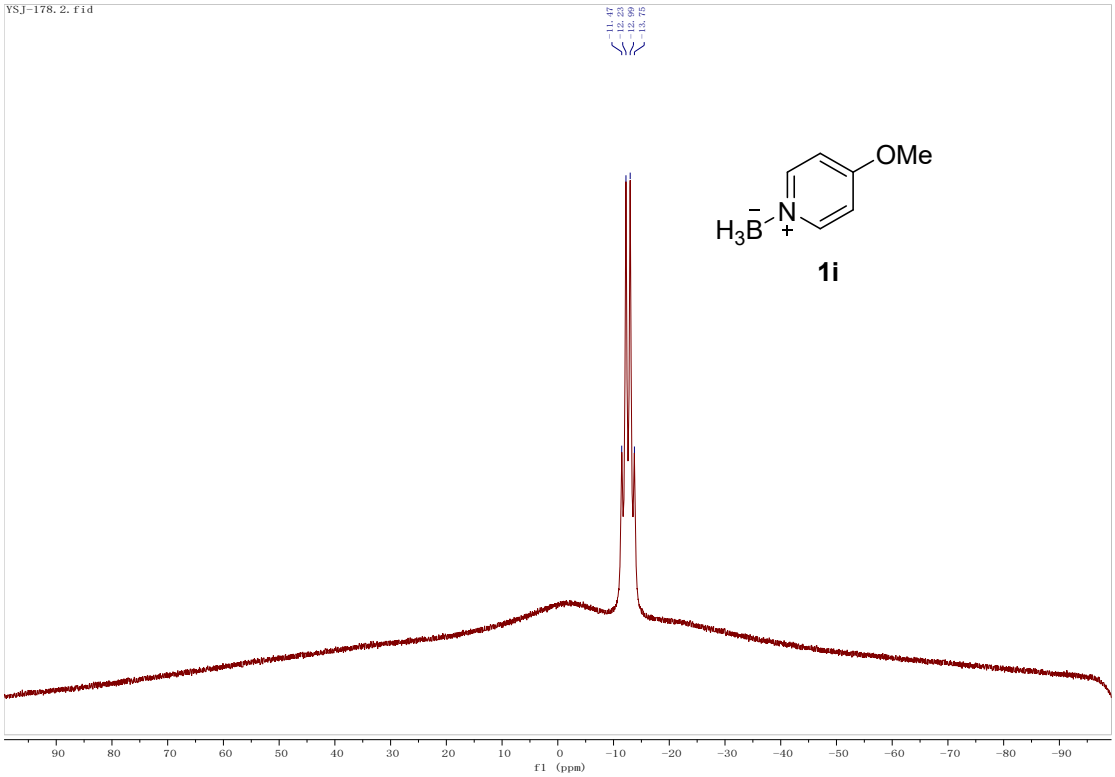


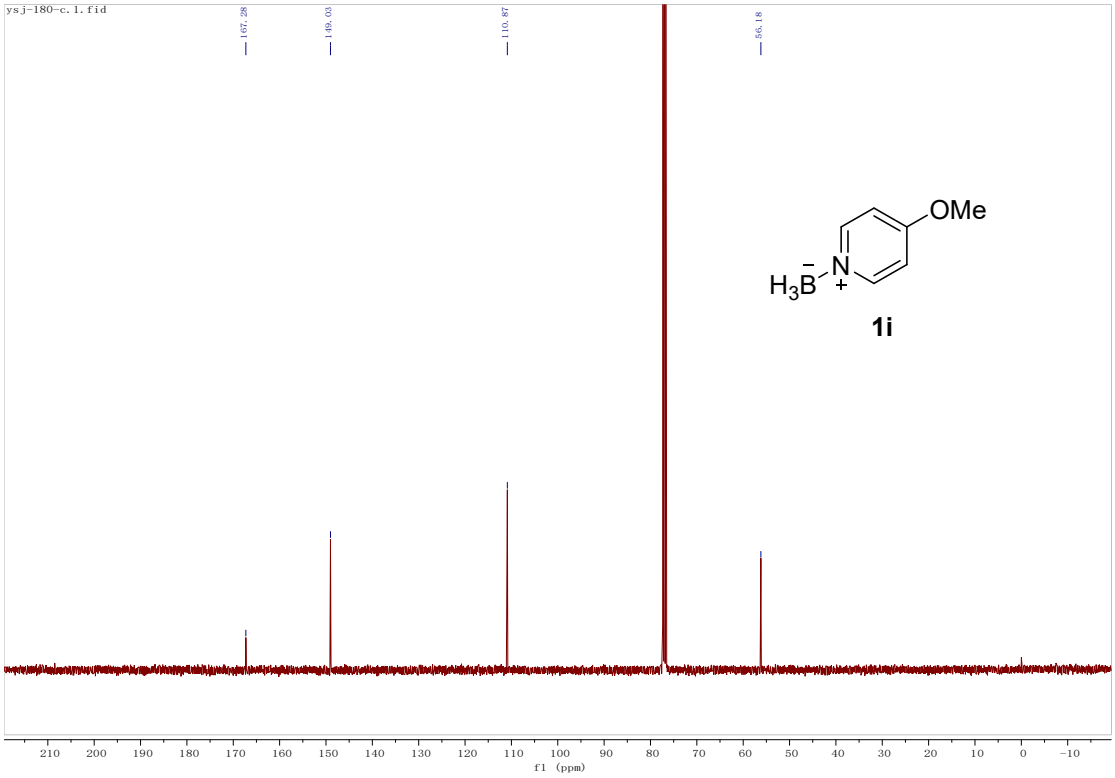



YSJ-175-C.1.fid
134.91
128.60
128.43
116.85
106.19
1h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Material 1i: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

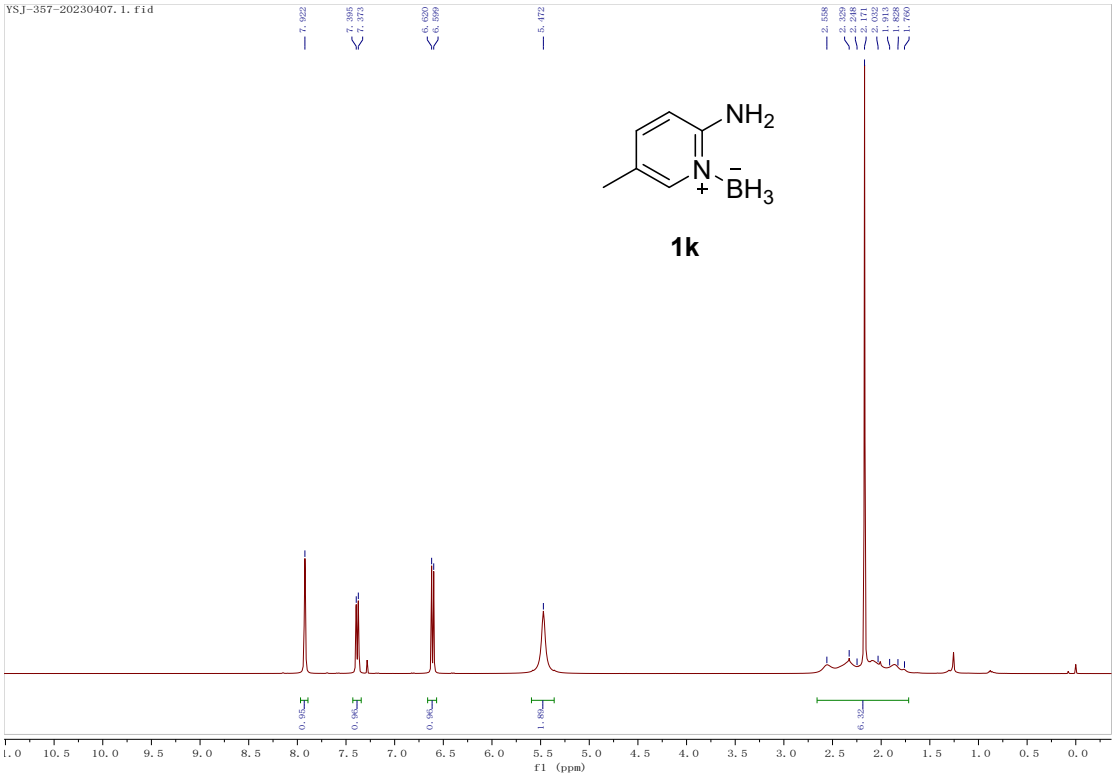


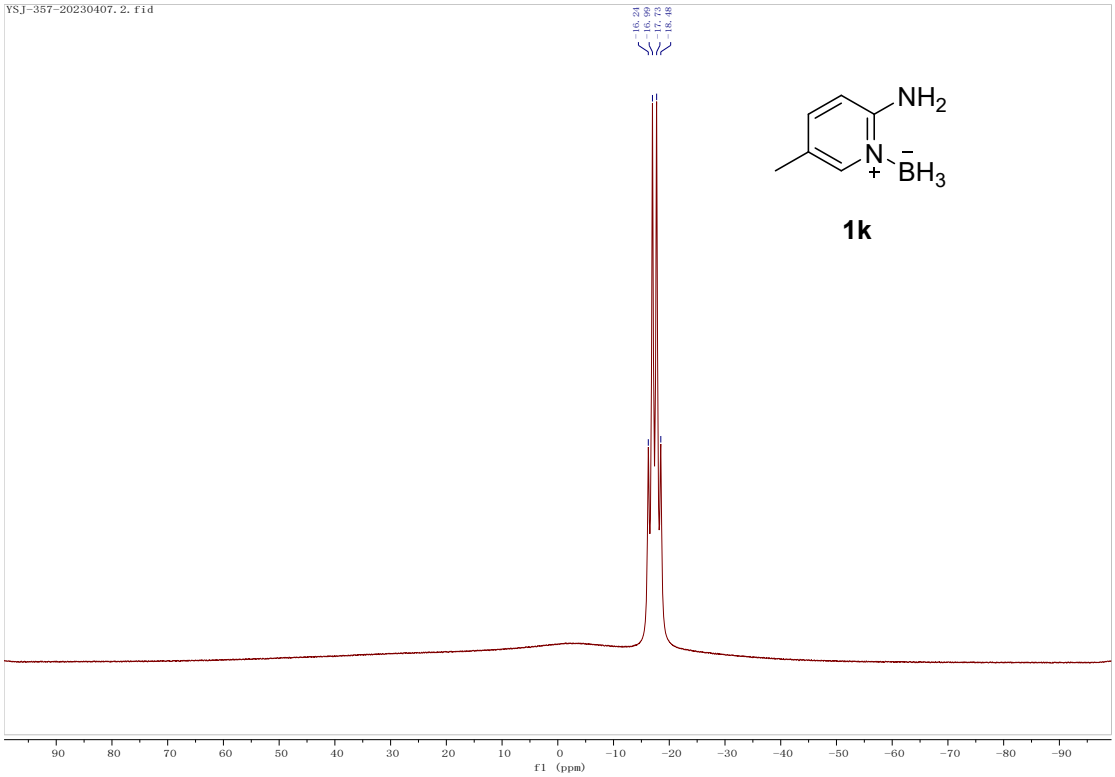


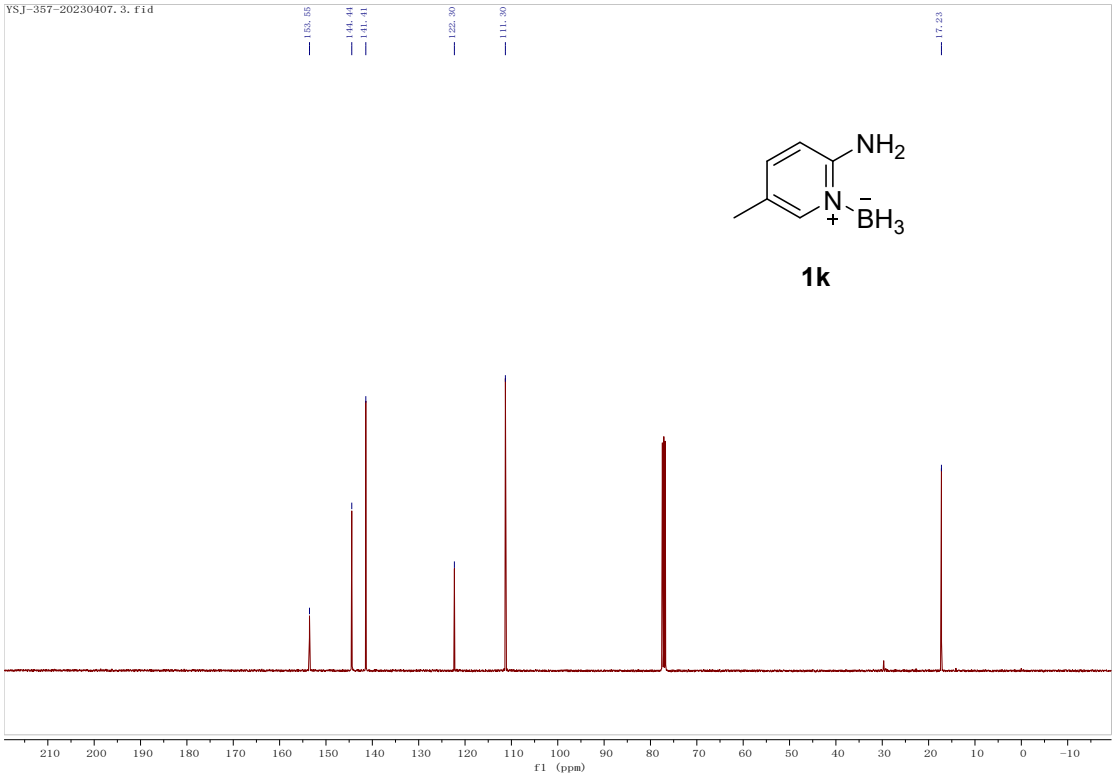

ysj-180-c.1.fid
167.28
149.03
110.87
56.18
OMe
N
H3B
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1i

Material 1k: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

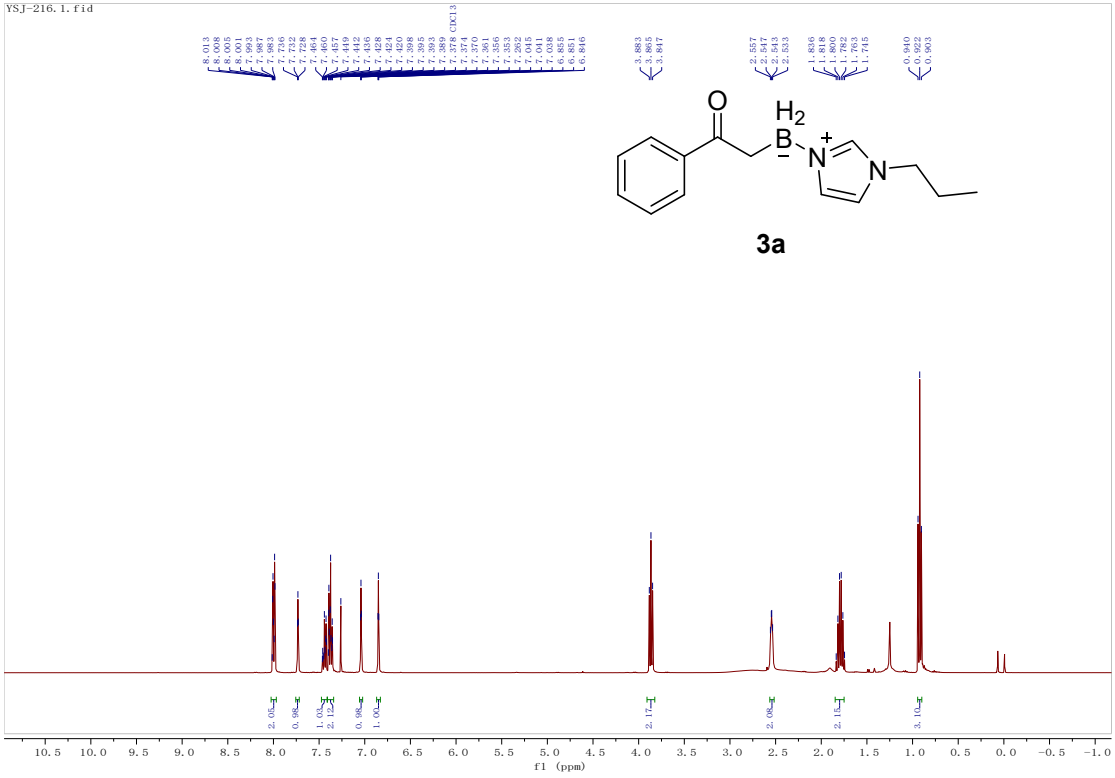


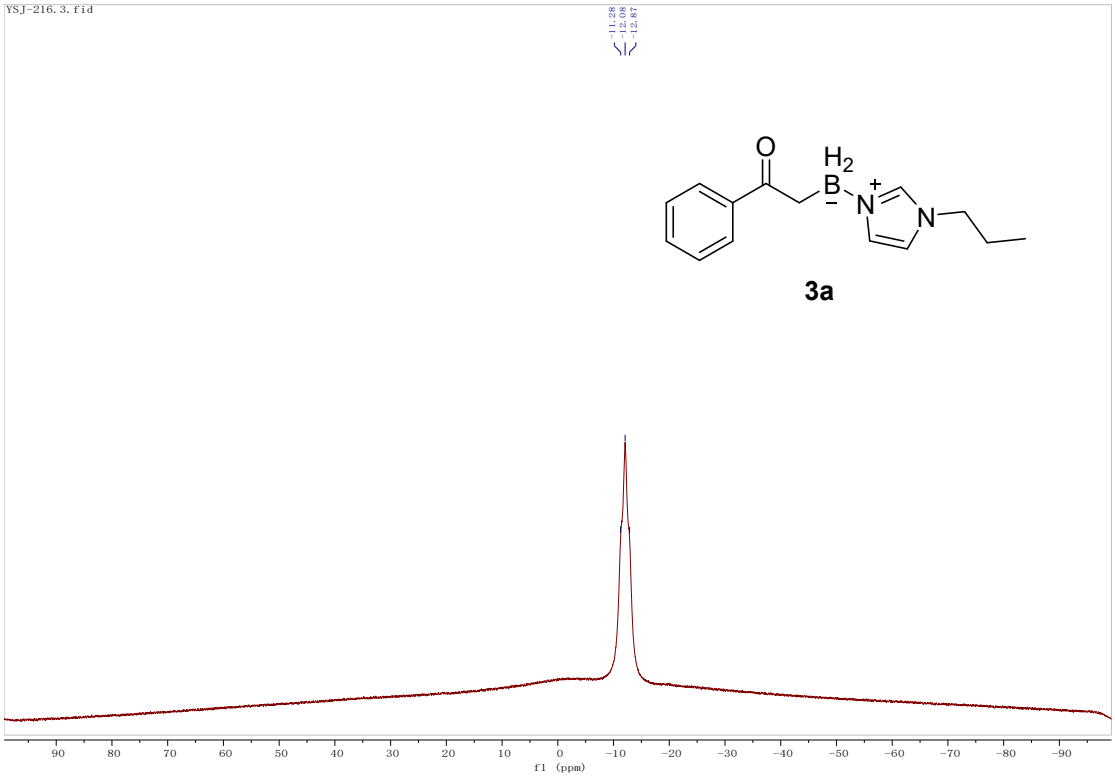


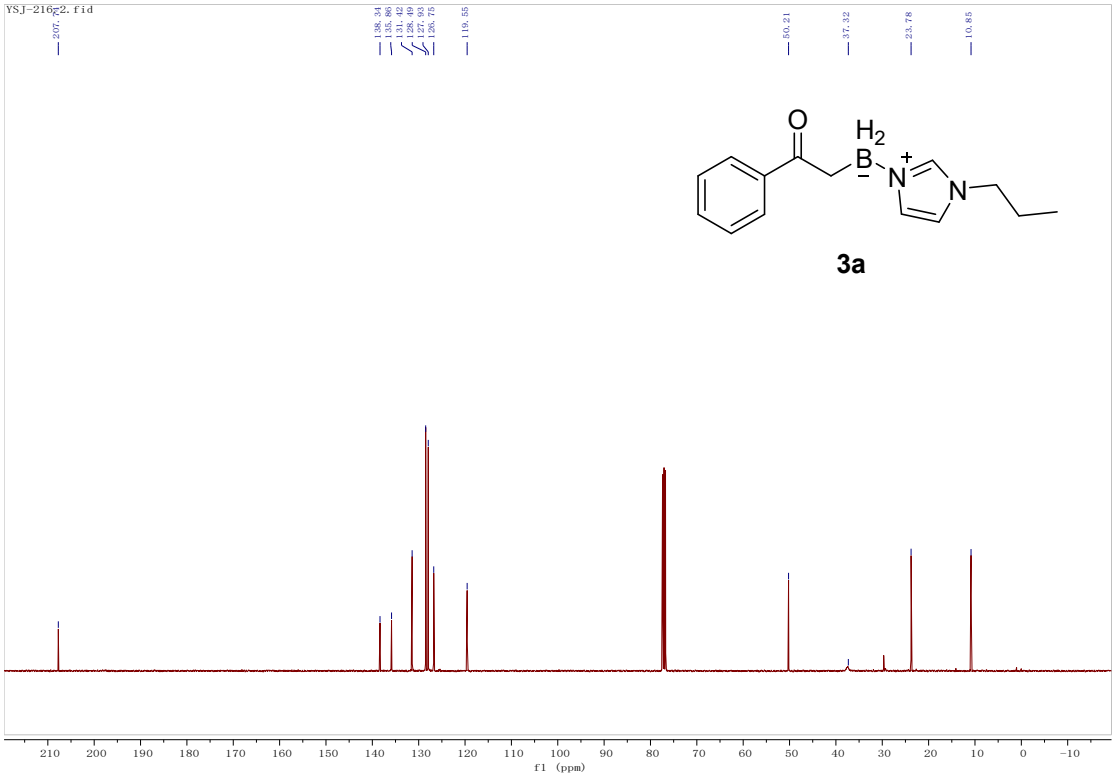

YSJ-357-20230407.3.fid
153.55
144.44
141.41
122.30
111.30
17.23
NH2
N
BH3
1k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

7.2 Products 3 and 4

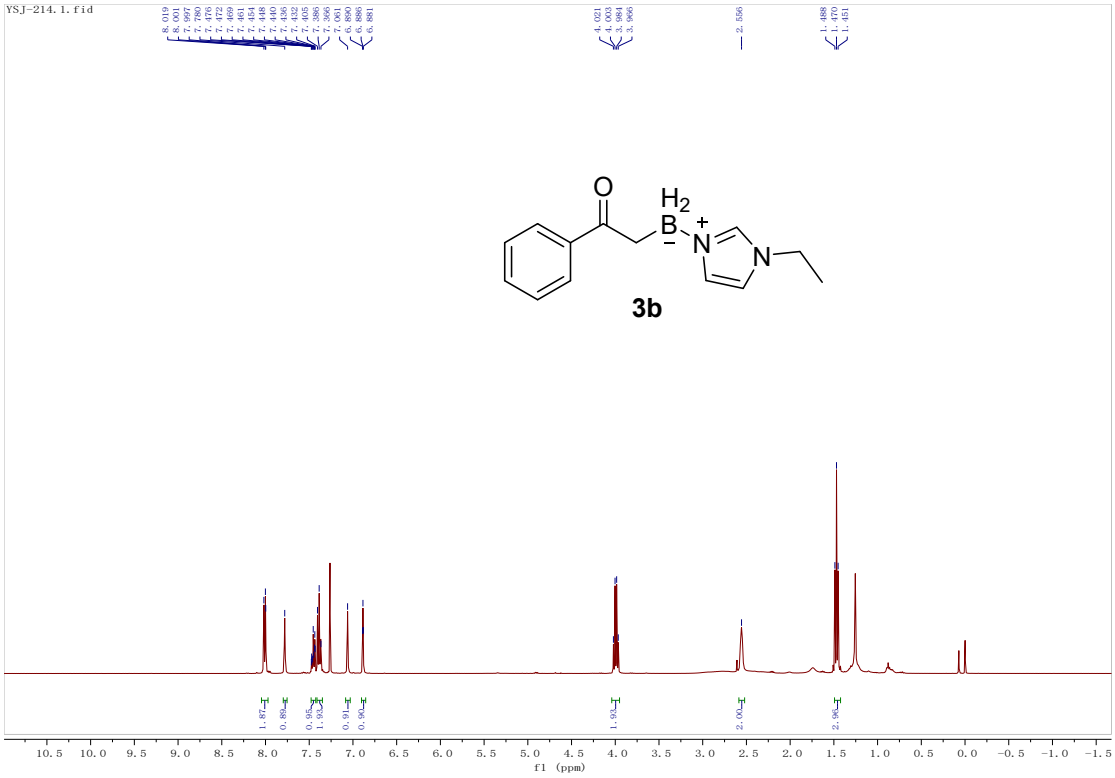
Product 3a: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

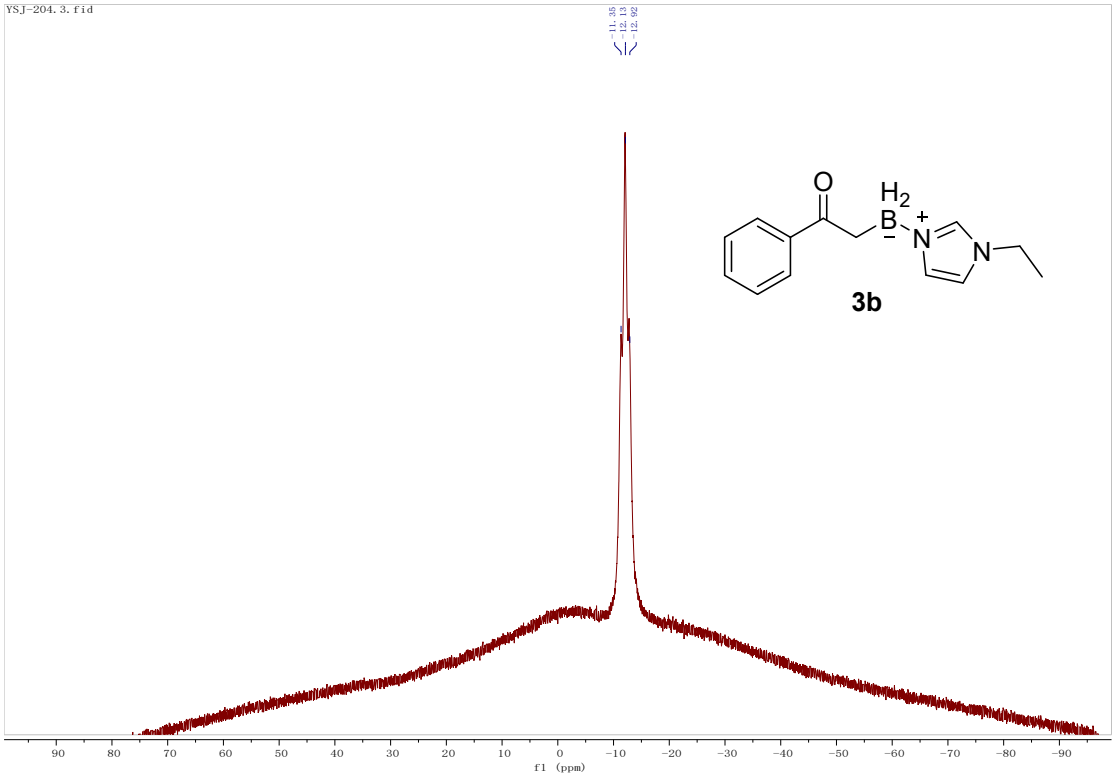


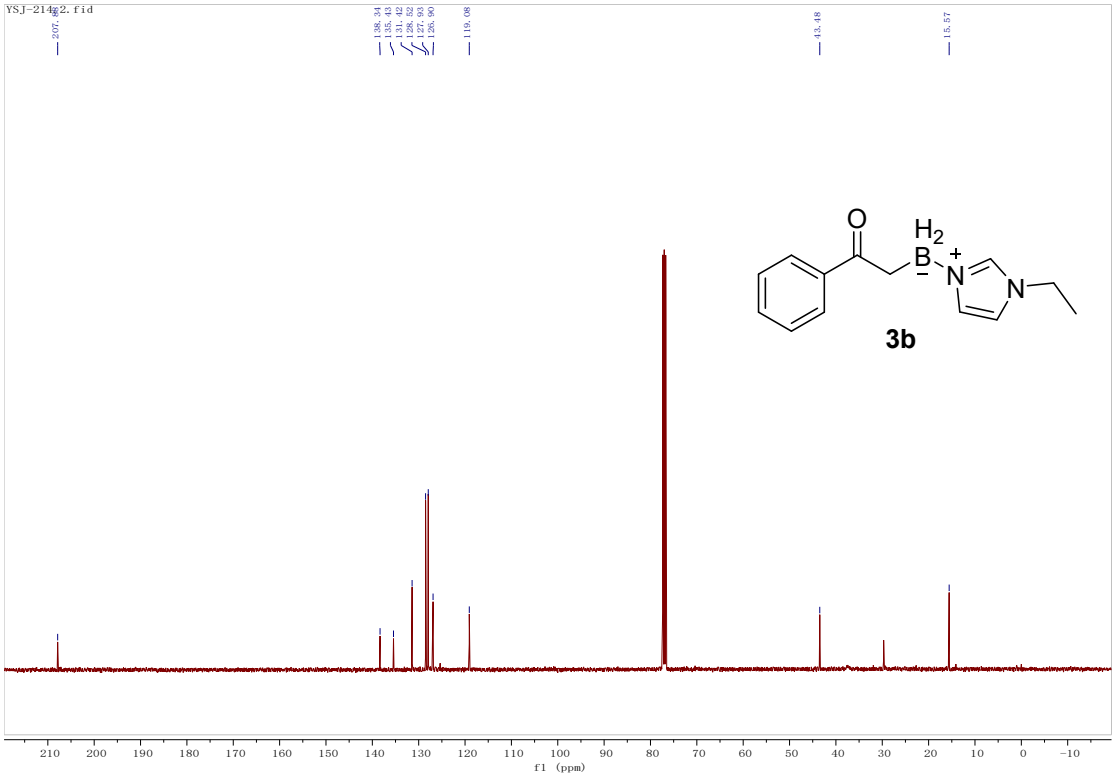



YSJ-216-2.fid
207.72
138.34
135.86
131.42
128.49
127.95
126.75
119.55
50.21
37.32
23.78
10.85
O
H2
B
N
N
3a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

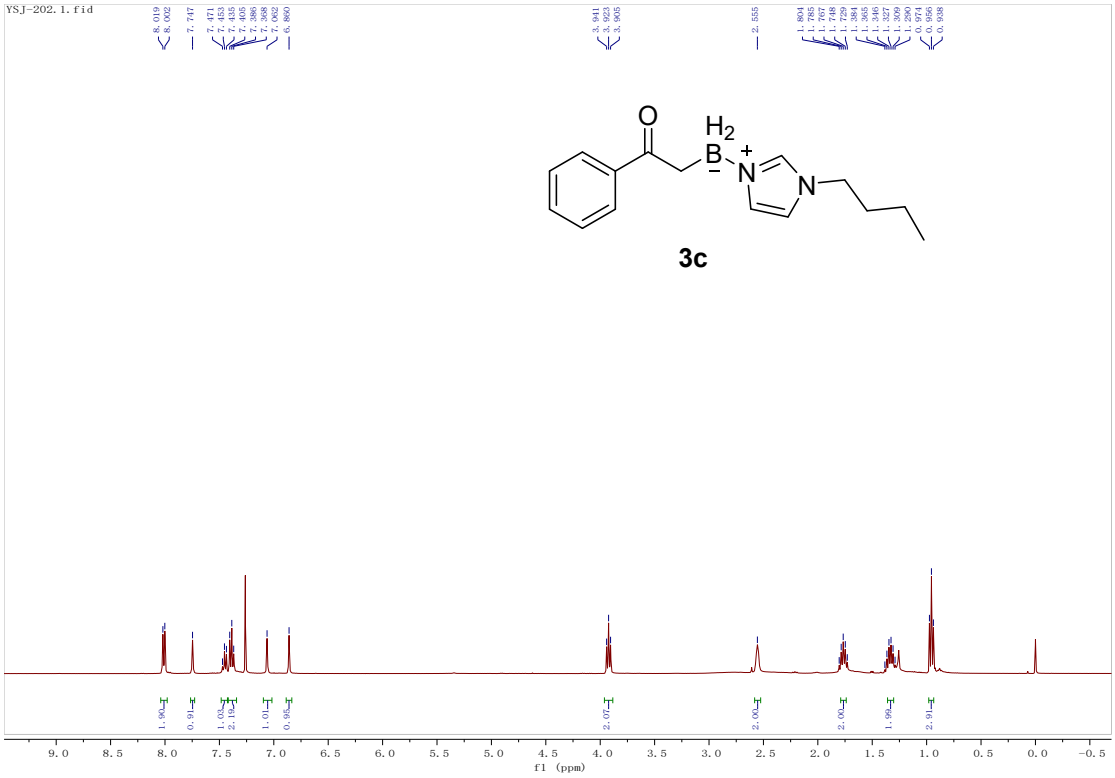
Product 3b: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

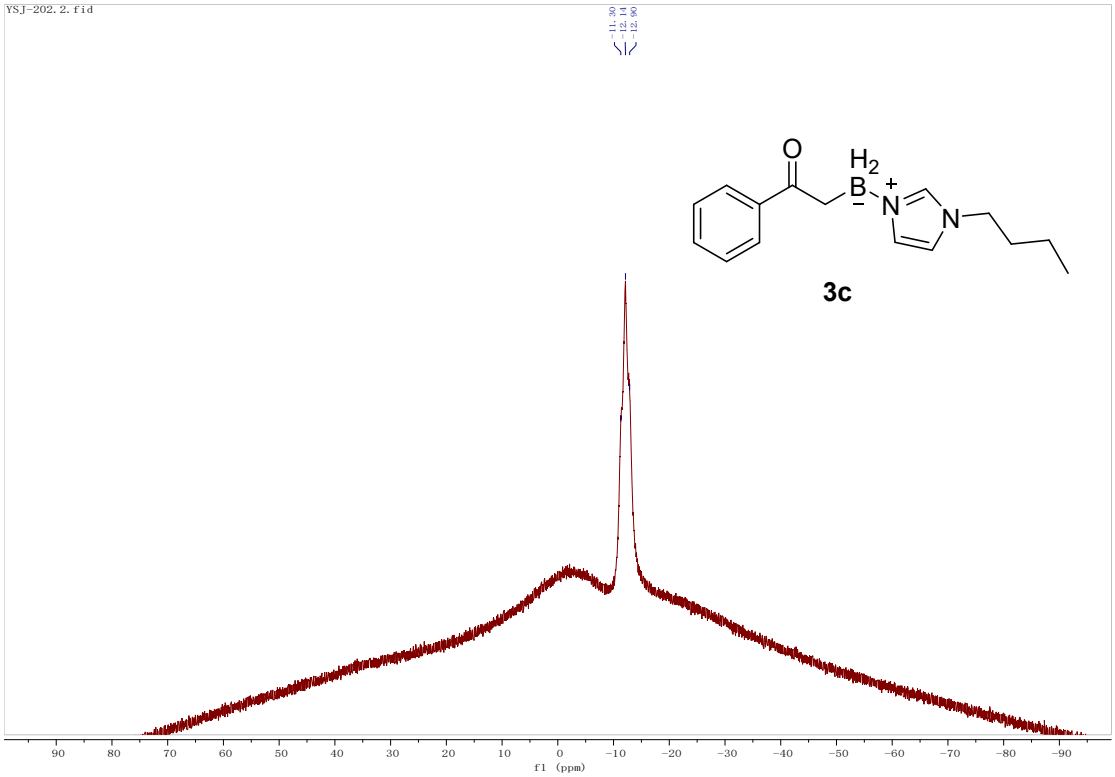


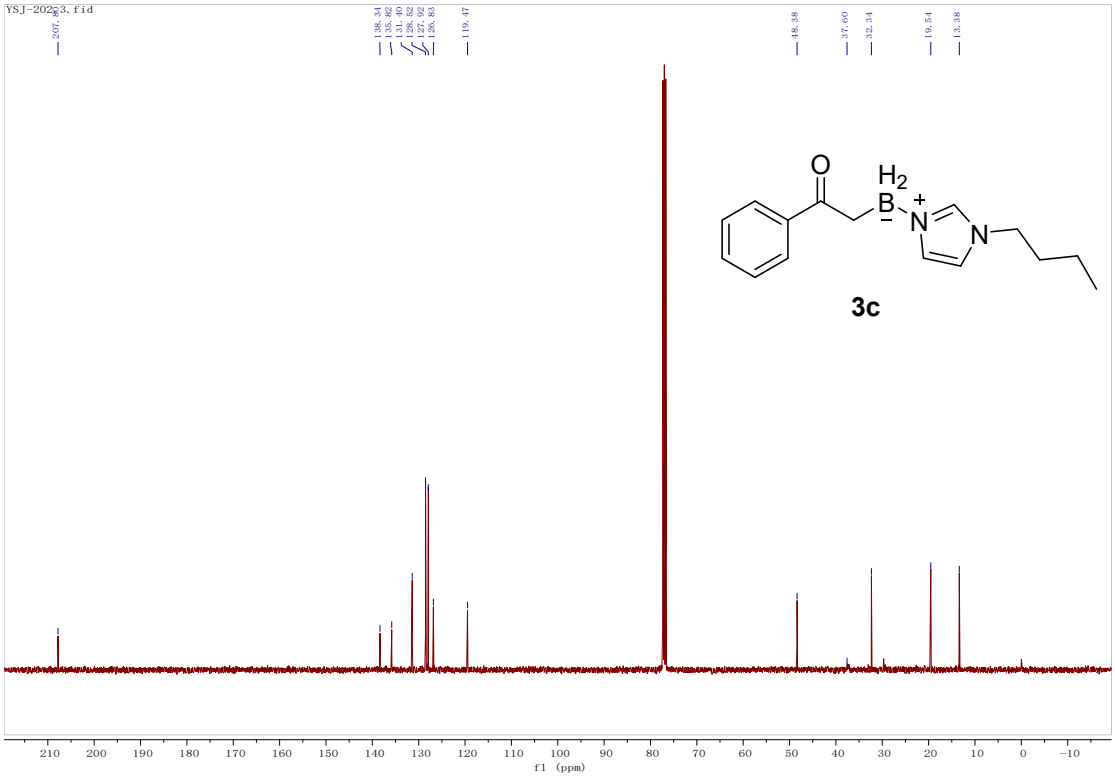



YSJ-214g2.fid
207.48
138.34
135.43
131.42
128.82
127.95
126.90
119.08
43.48
15.57
O
H2
B
N
N
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

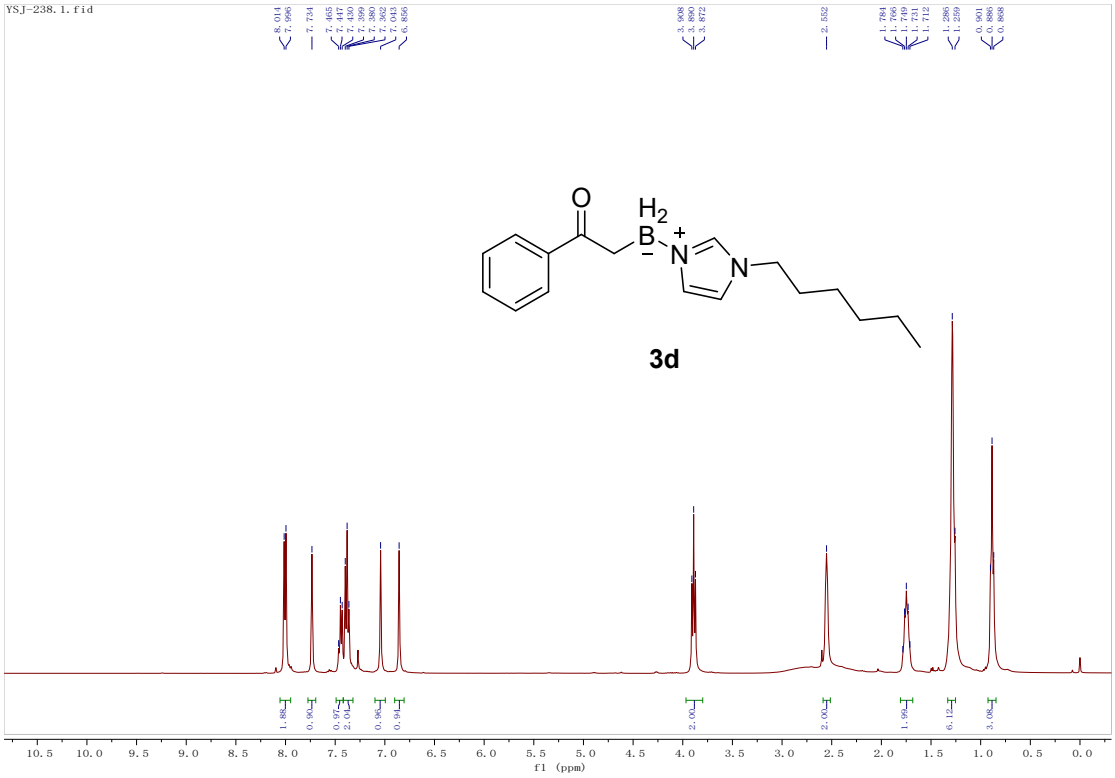
Product 3c: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

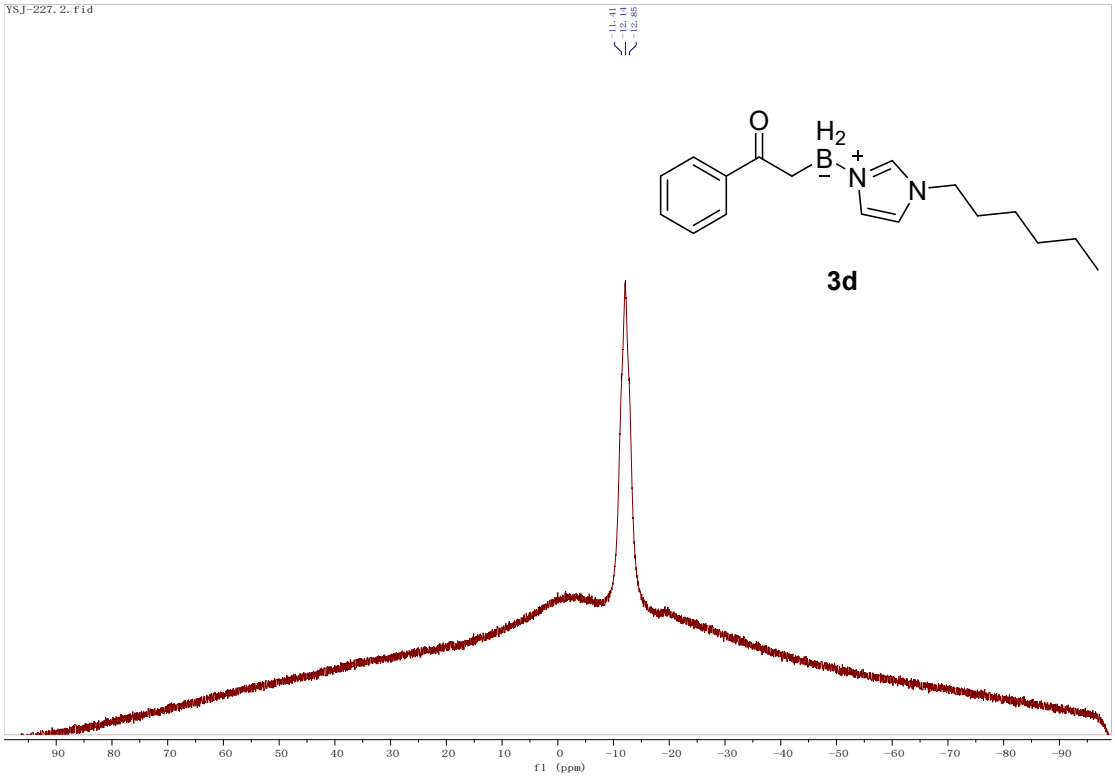


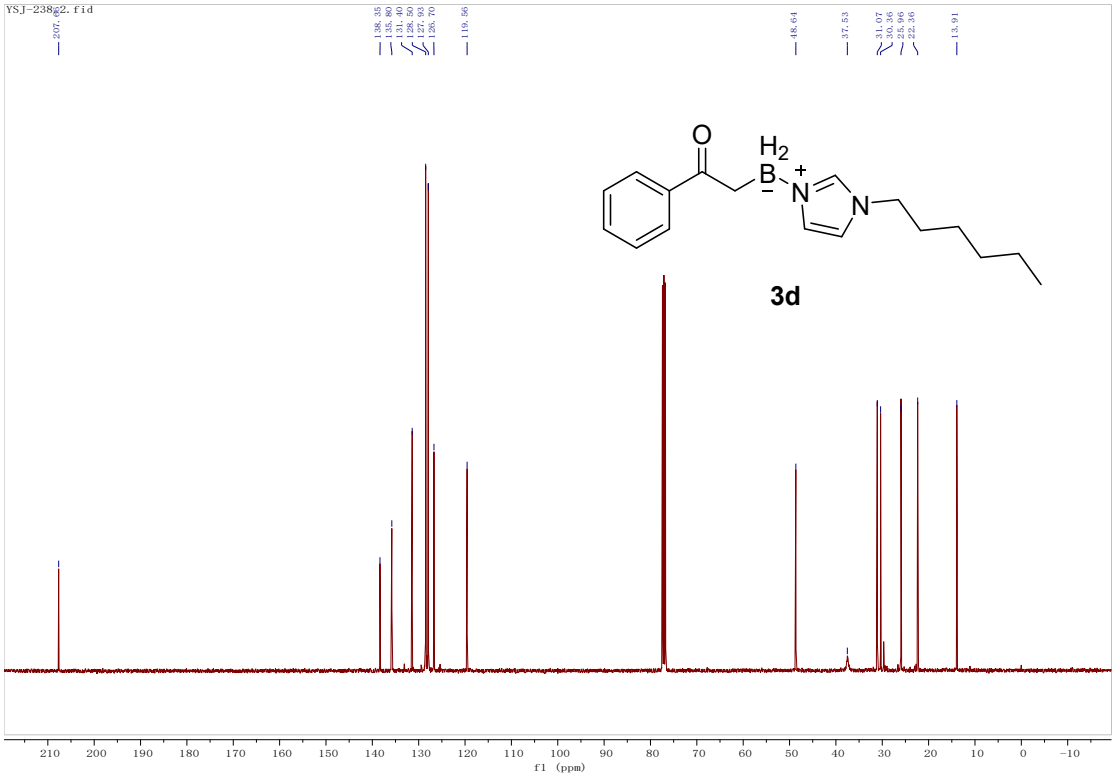



YSJ-20253.fid
207.84
138.34
135.82
131.40
128.52
127.99
126.83
119.47
48.38
37.60
32.34
19.54
13.38
O
H2
B
N
N
3c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

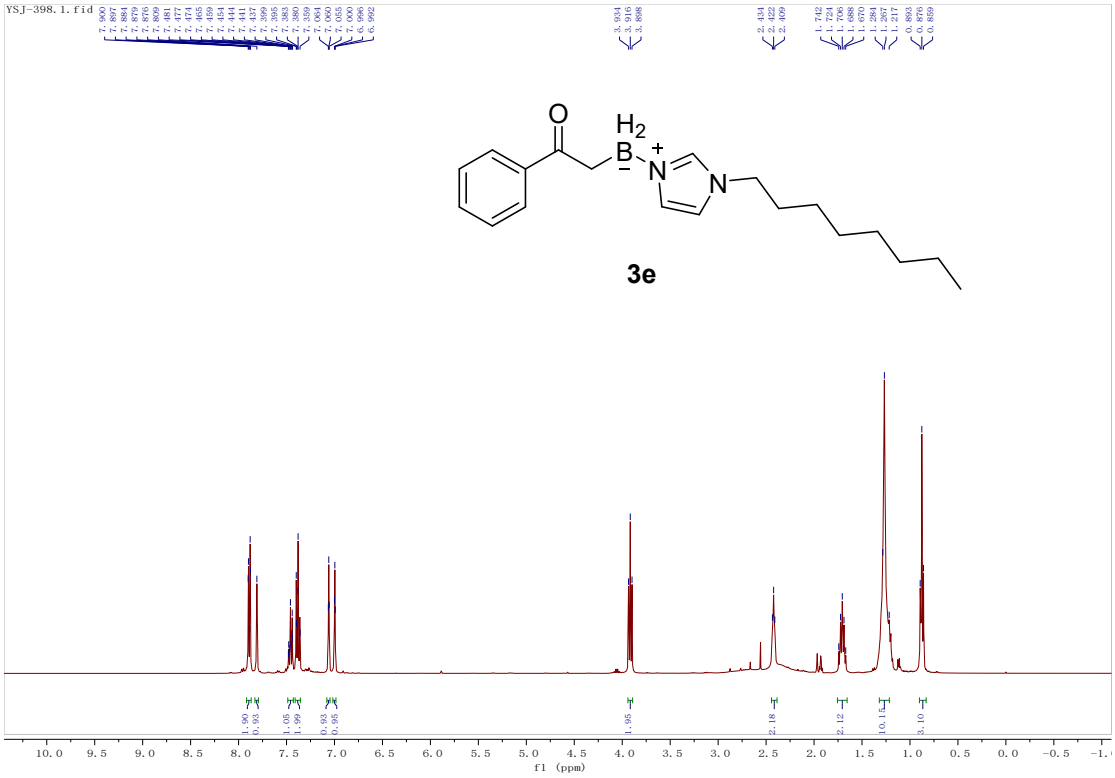
Product 3d: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

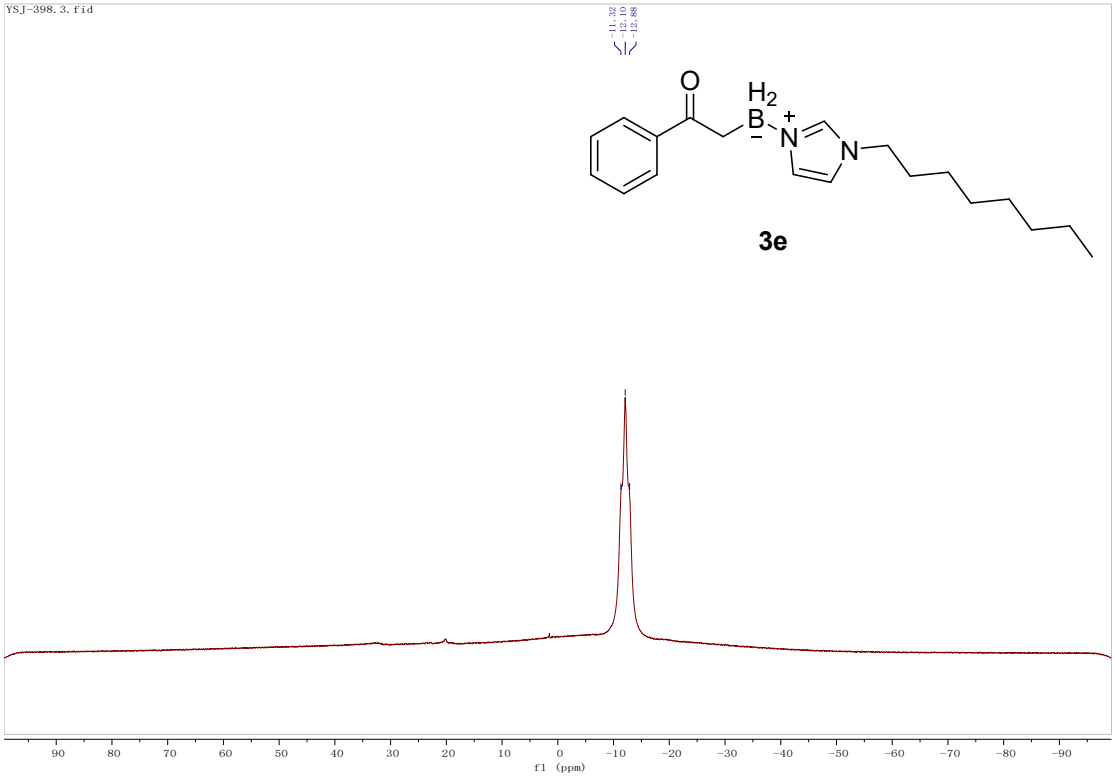


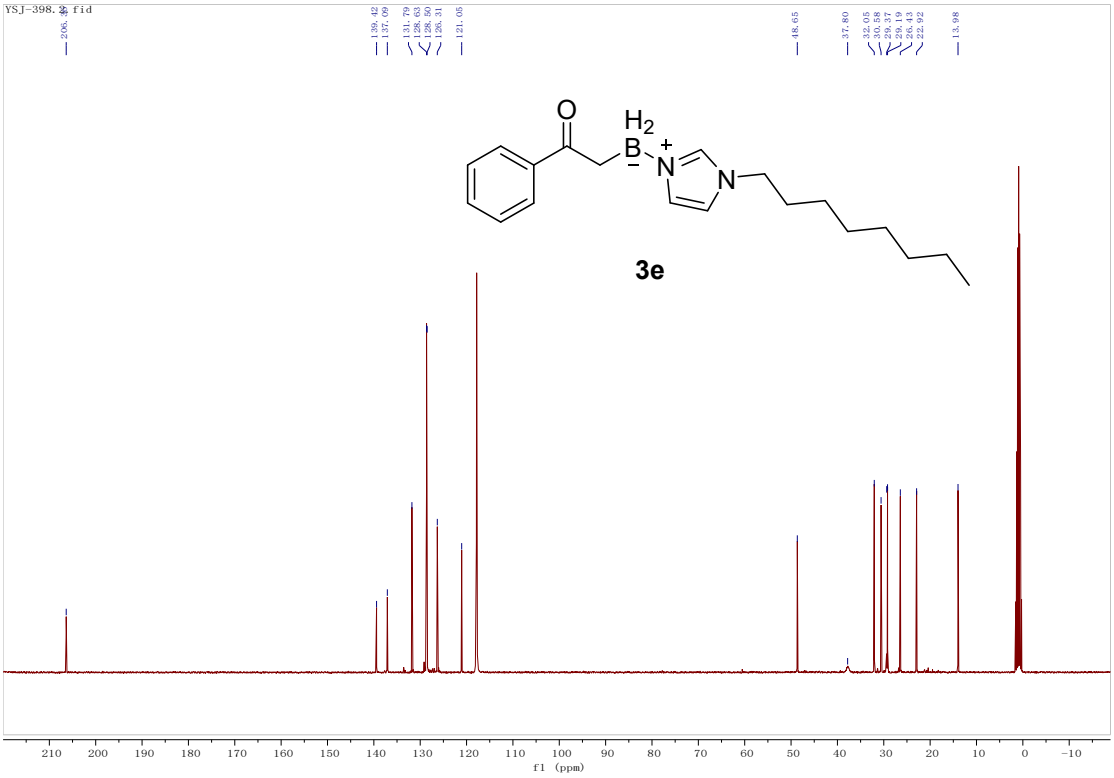



YSJ-238g2.fid
207.62
138.35
135.80
131.40
128.89
127.95
126.70
119.86
48.64
37.53
31.07
30.36
25.96
22.36
13.91
O
H2
B
N
N
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

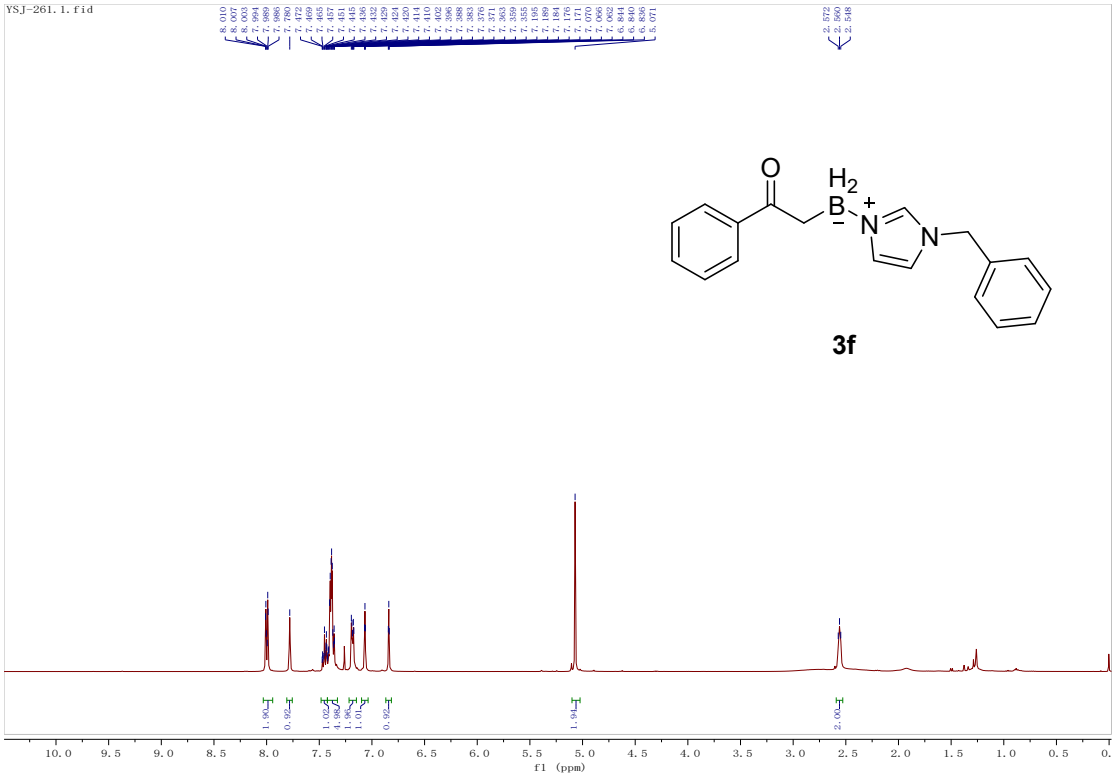
Product 3e: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

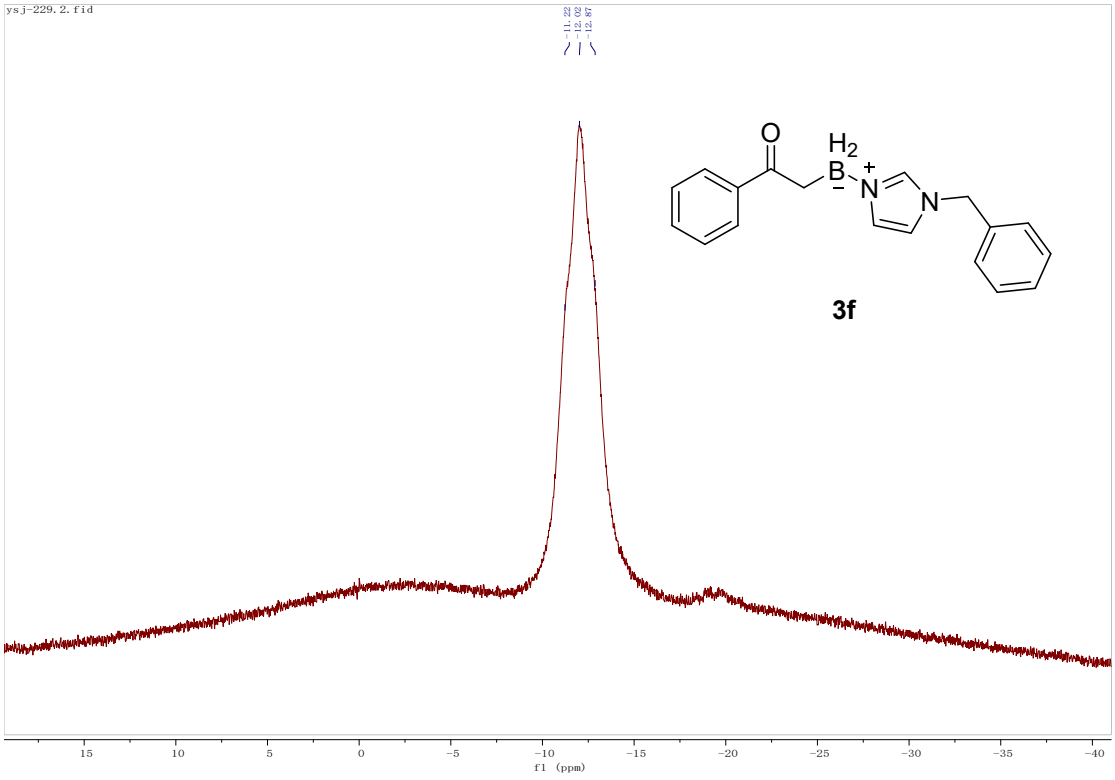


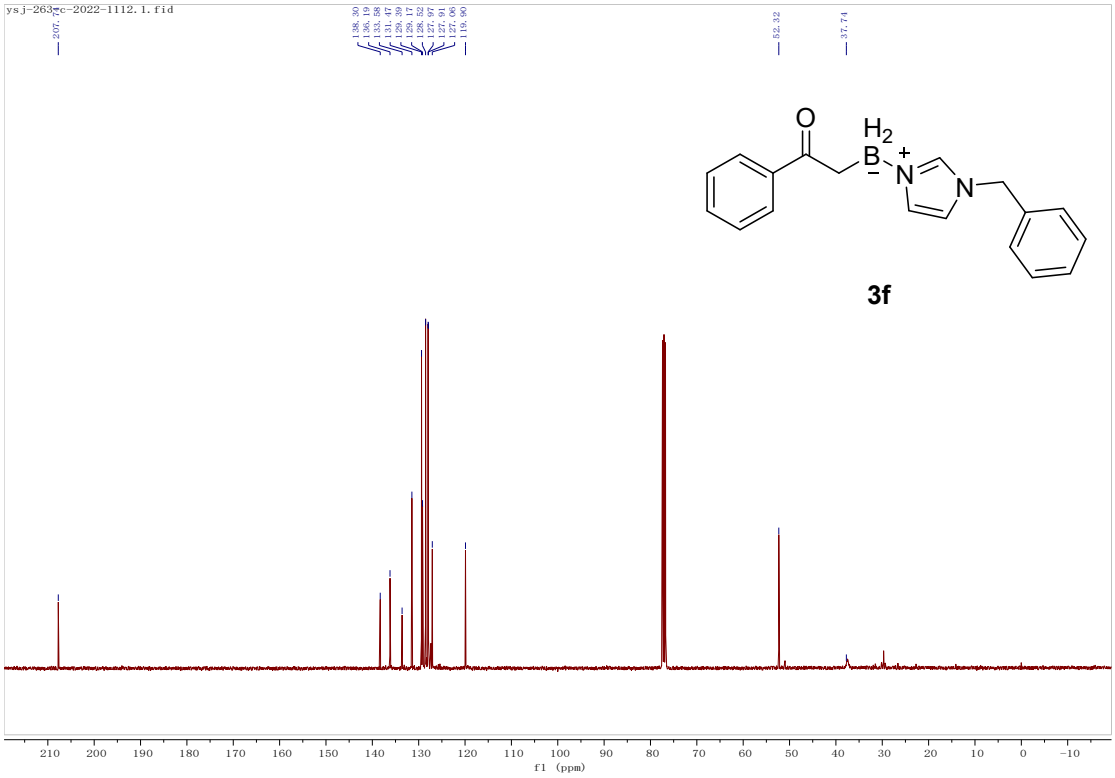



YSJ-398.10.fid
206.38
139.42
137.09
131.79
128.63
128.50
126.31
121.05
48.65
37.80
32.05
30.58
29.37
29.19
26.45
22.92
13.98
O
H2
B
N
N
3e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

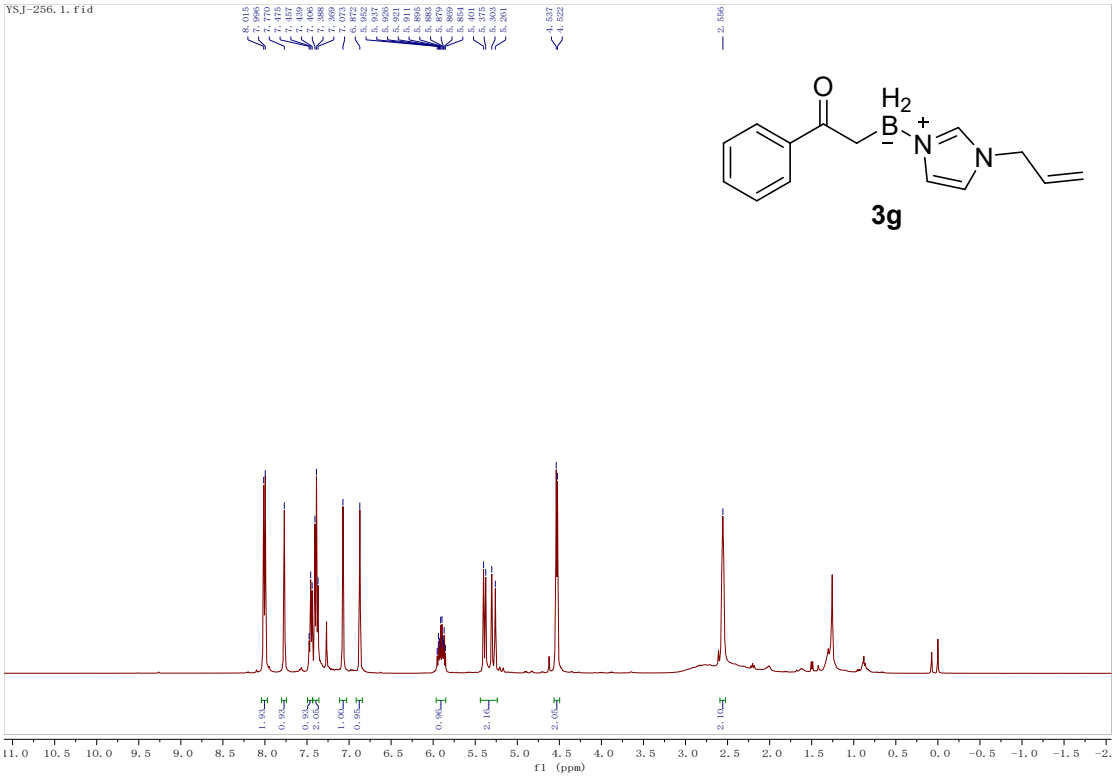
Product 3f: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

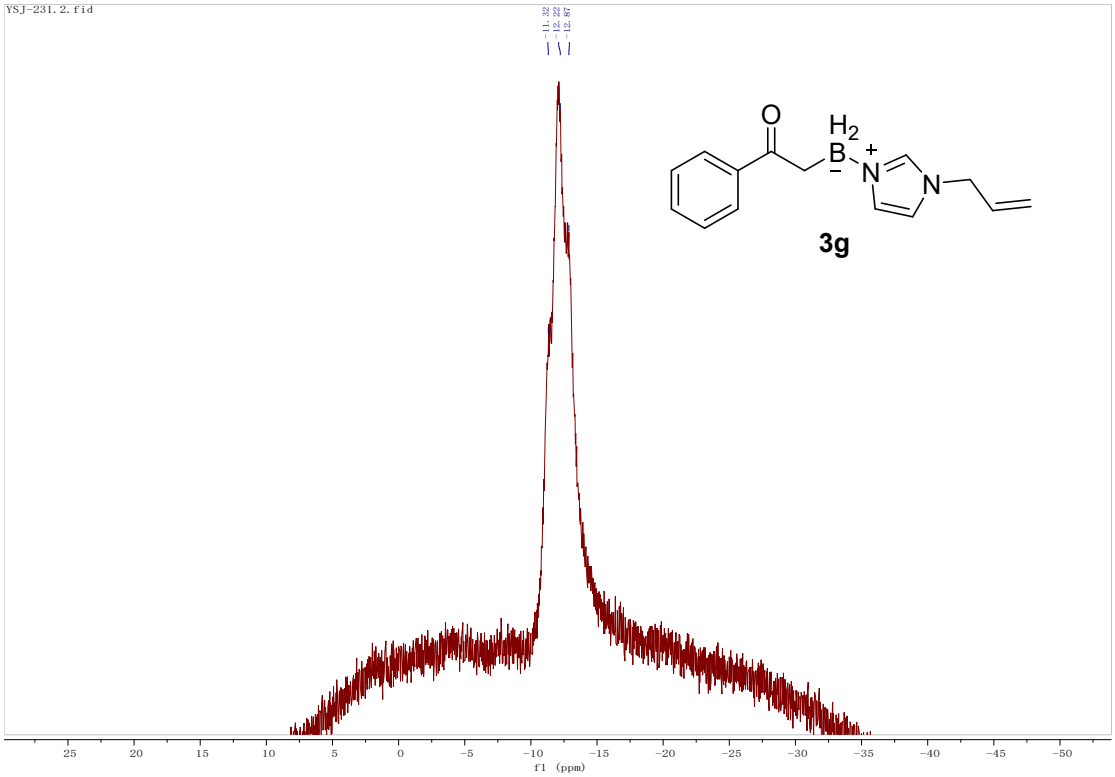


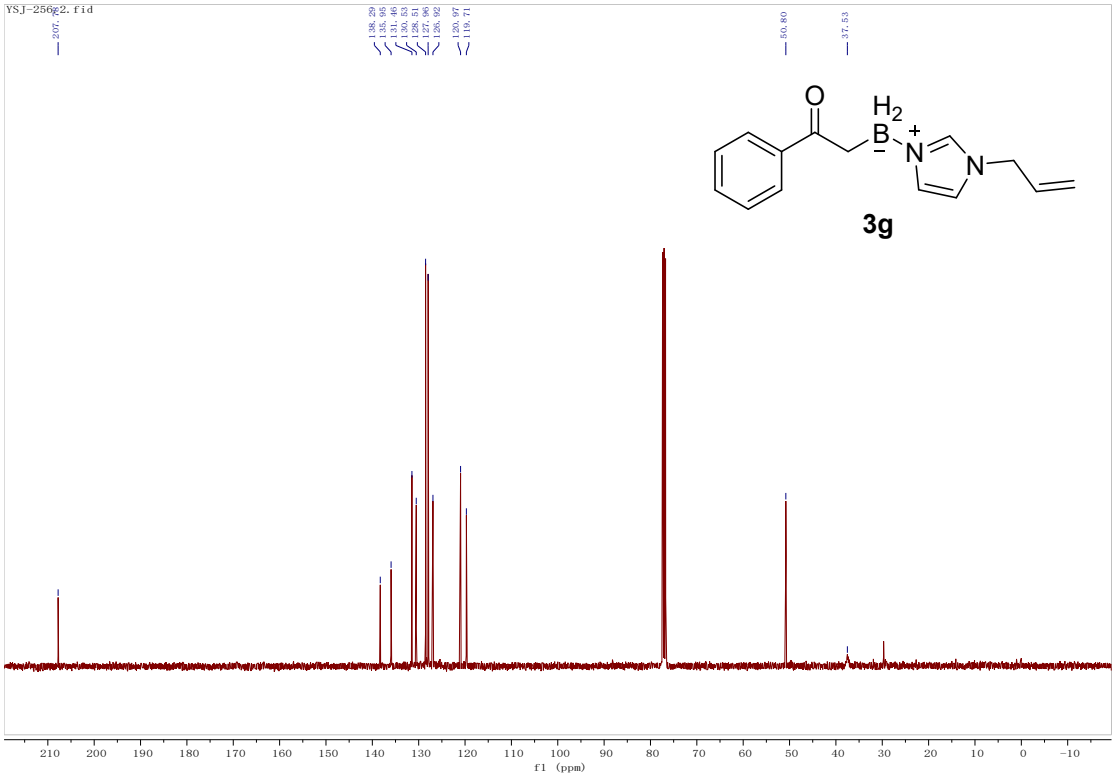



ysj-263-c-2022-1112.1.fid
207.74
138.30
133.19
130.58
131.47
129.39
128.17
127.82
127.97
127.91
127.06
119.80
82.32
37.74
O
H2
B
N
N
3f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

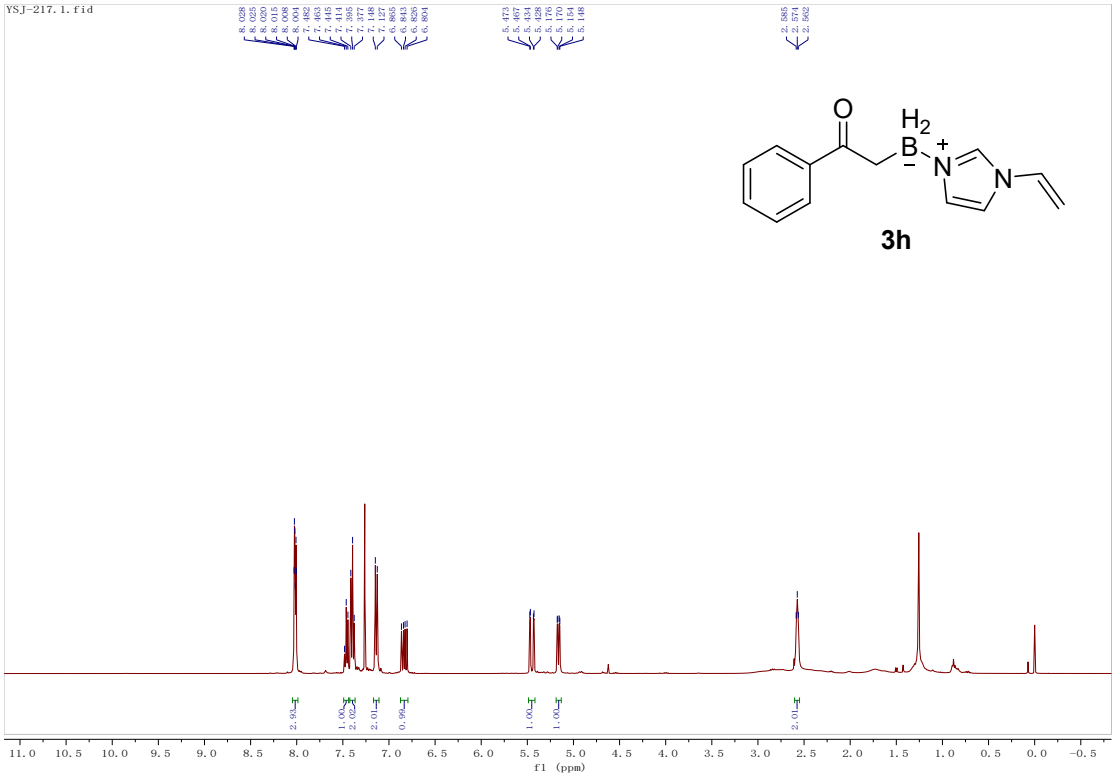
Product 3g: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

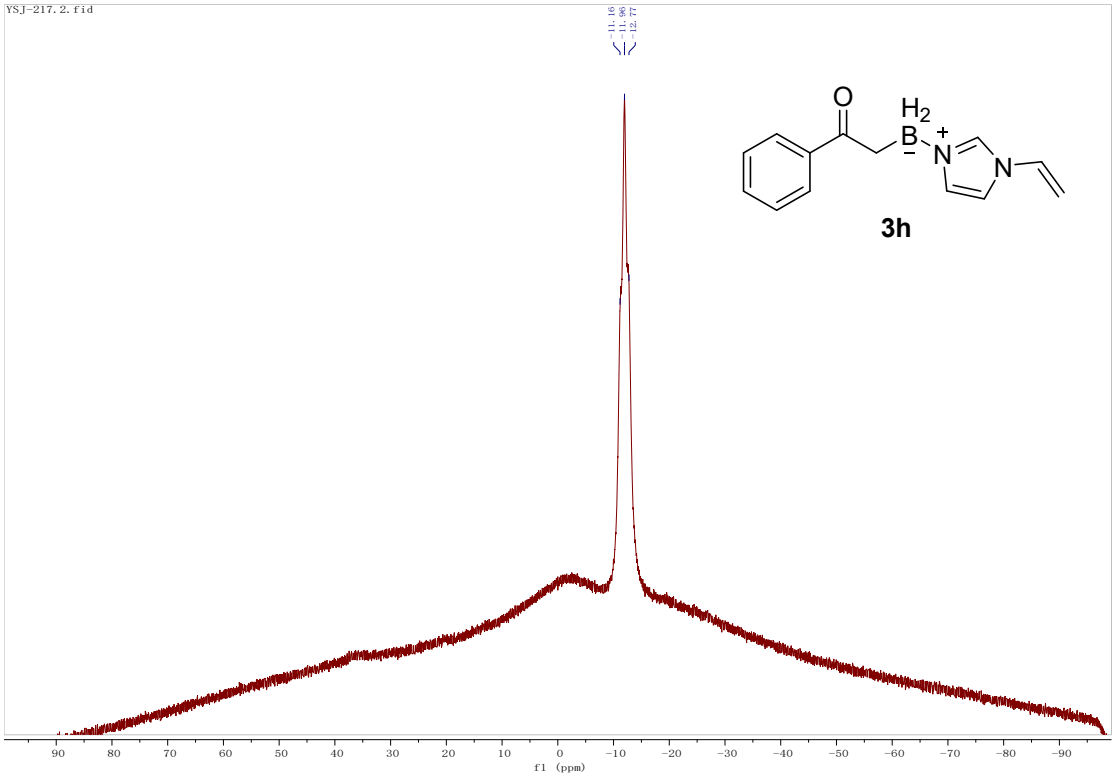


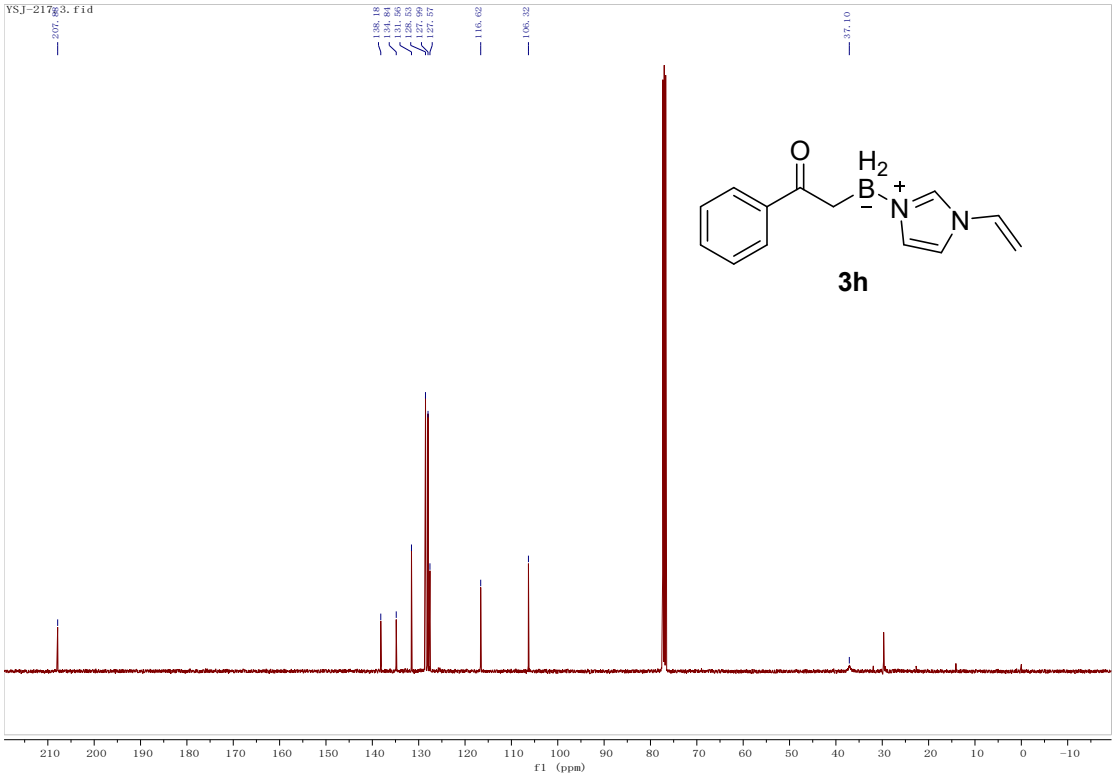



YSJ-256g2.fid
207.78
138.29
135.95
131.46
130.53
128.51
127.96
126.92
120.97
119.71
50.80
37.53
O
H2
B
N
N
3g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

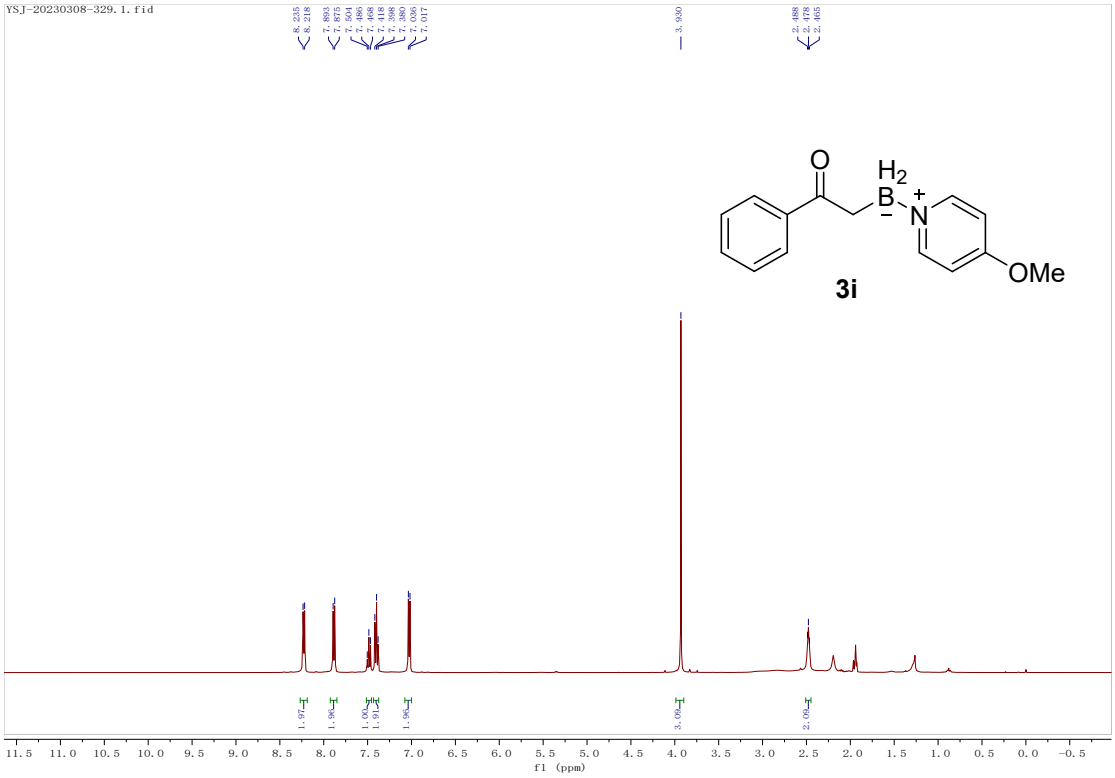
Product 3h: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

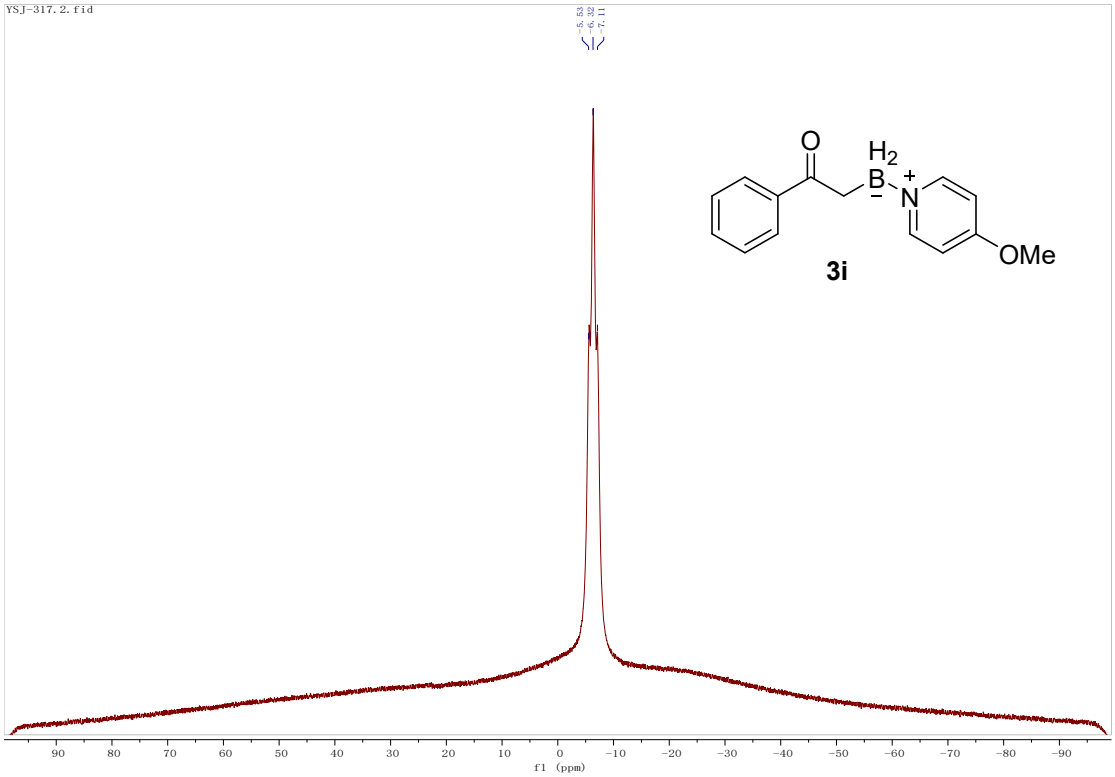


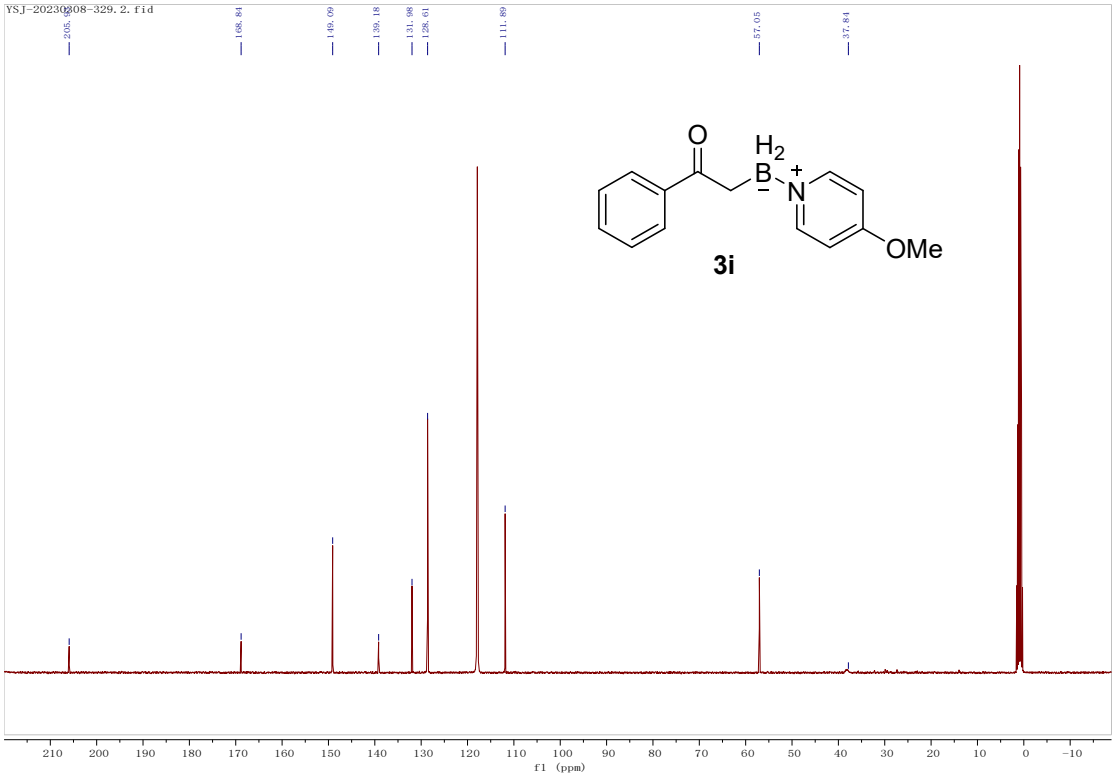



YSJ-217-3.fid
207.88
138.18
134.84
131.56
128.83
127.59
127.57
116.62
106.32
37.10
O
H2
B
N
N
3h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

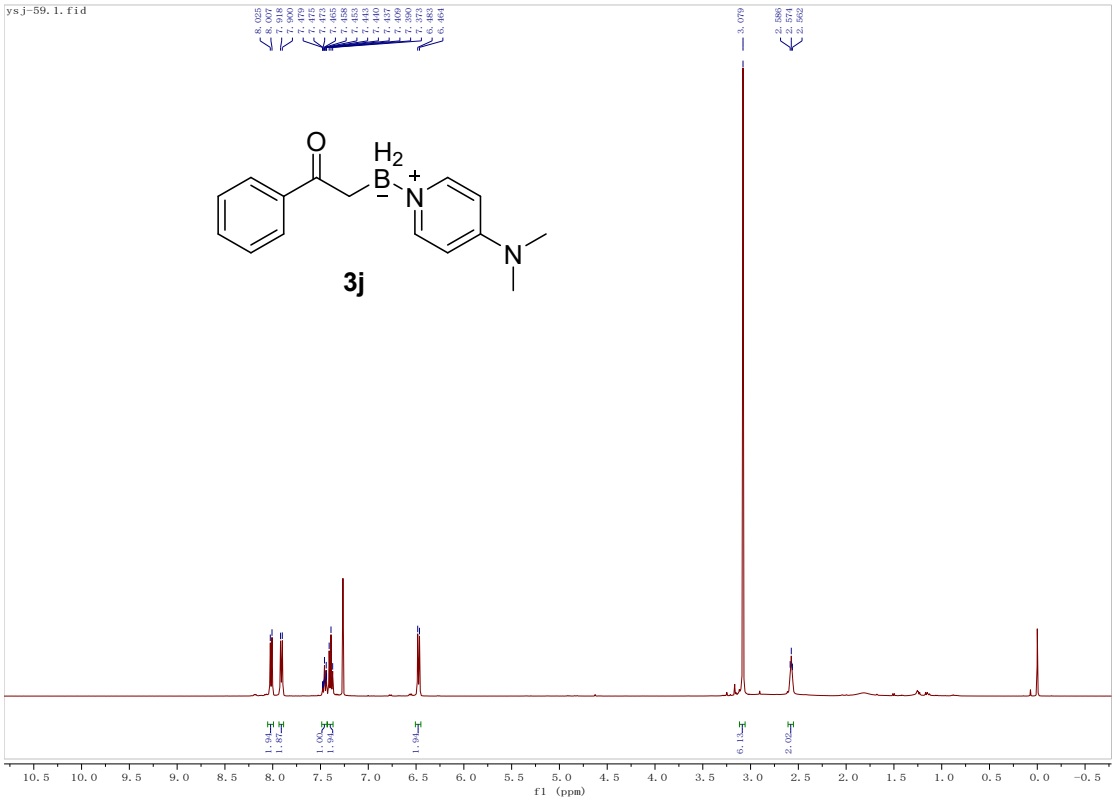
Product 3i: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

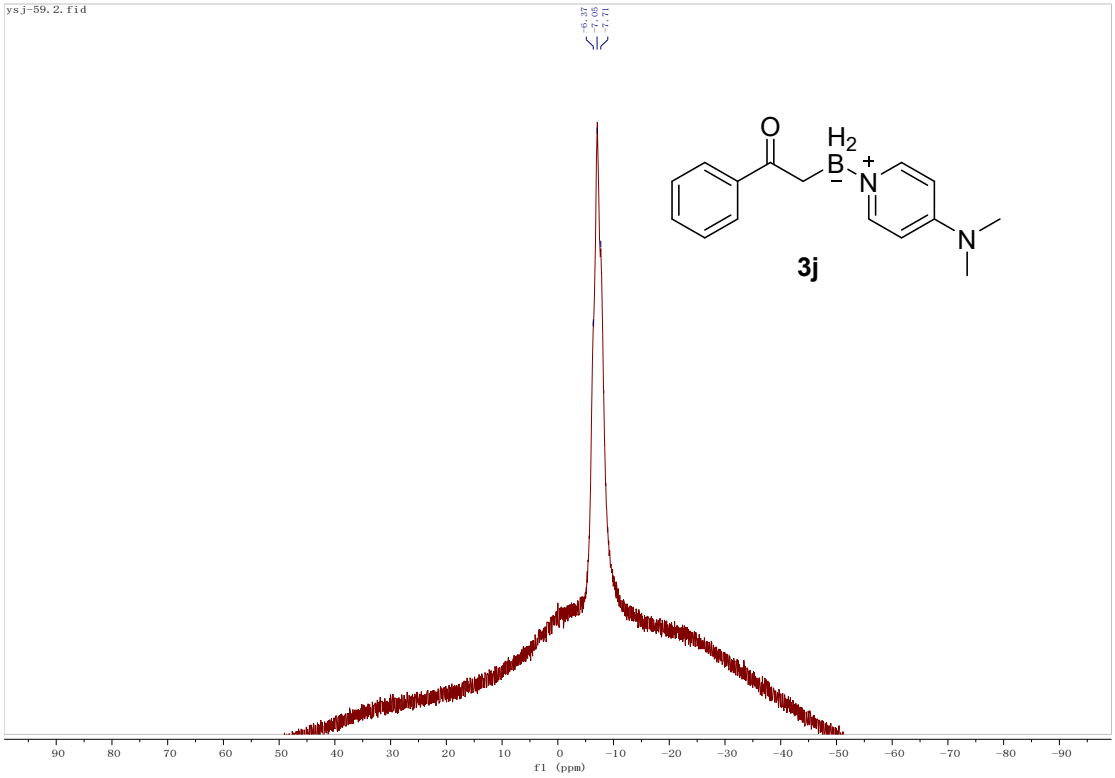


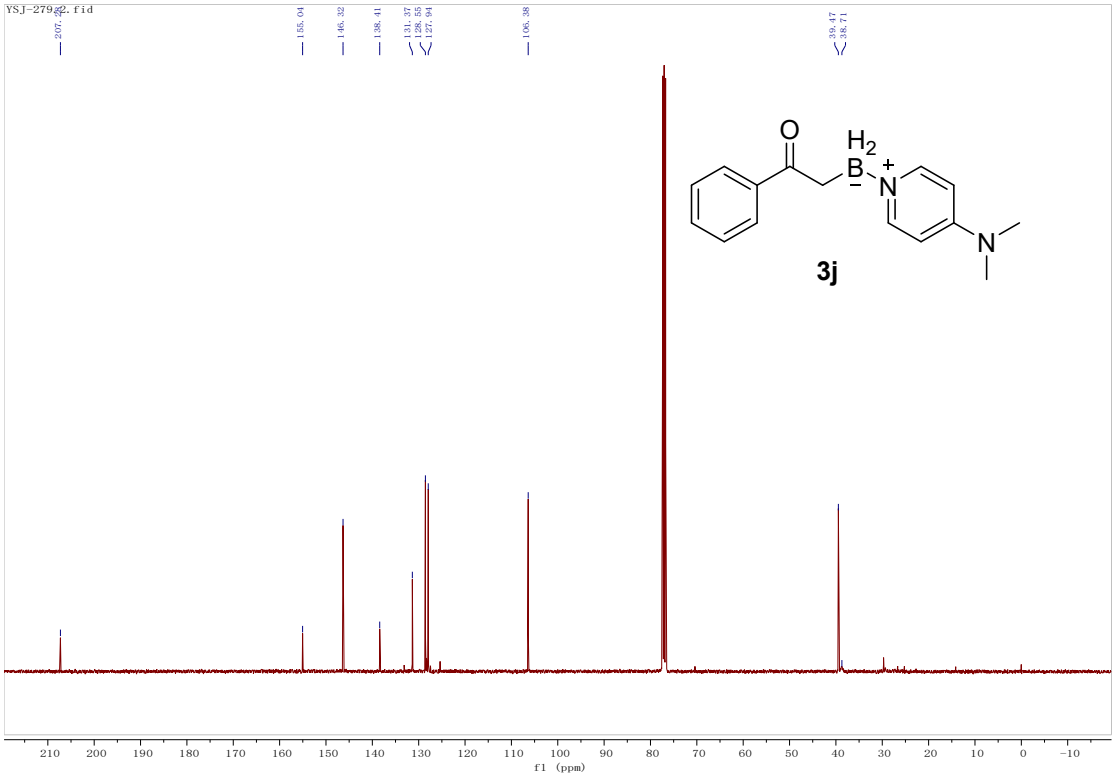



YSJ-20230308-329.2.fid
205.42
168.84
149.09
139.18
131.98
128.61
111.89
57.05
37.84
O
H2
B
N
OMe
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

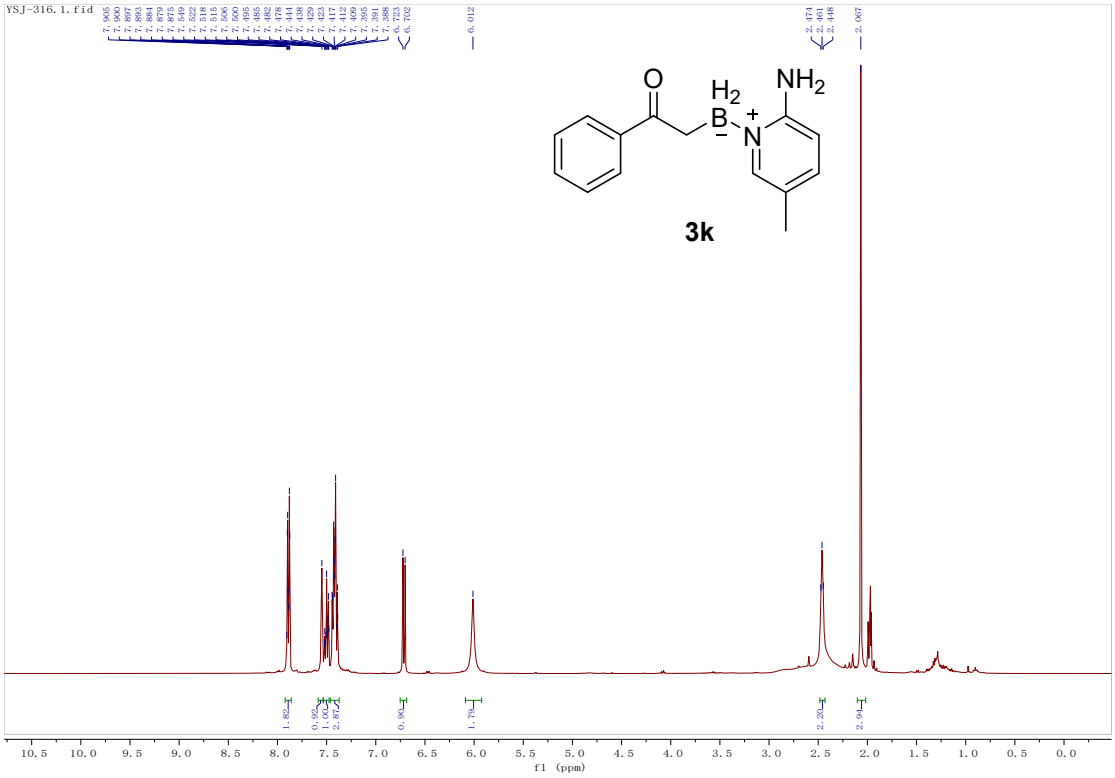
Product 3j: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

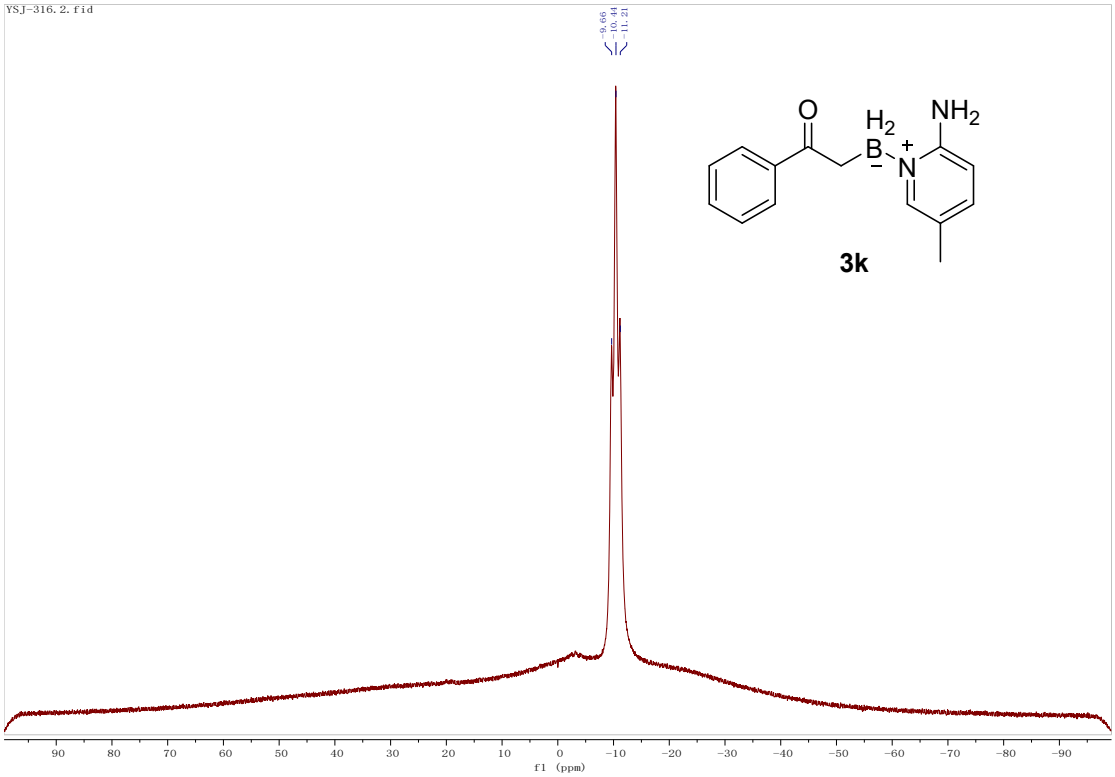


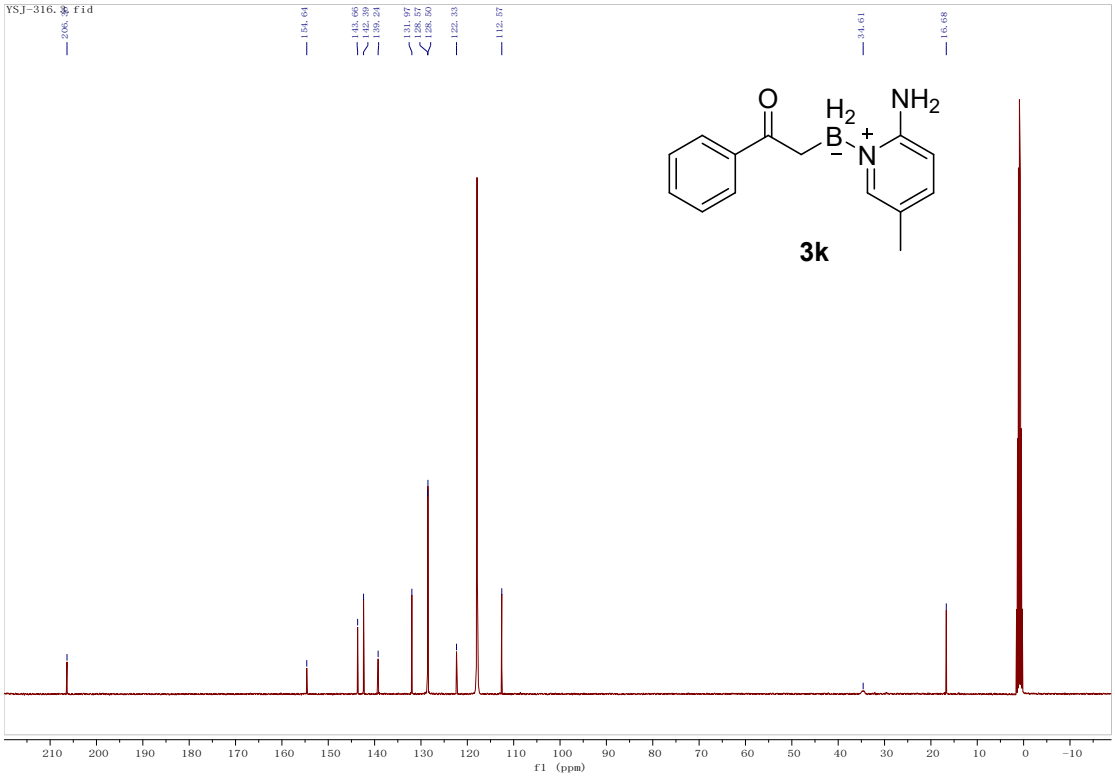



YSJ-2792.fid
207.72
155.04
146.32
138.41
131.37
128.55
127.94
106.38
39.47
38.71
O
H2
B
N
N
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

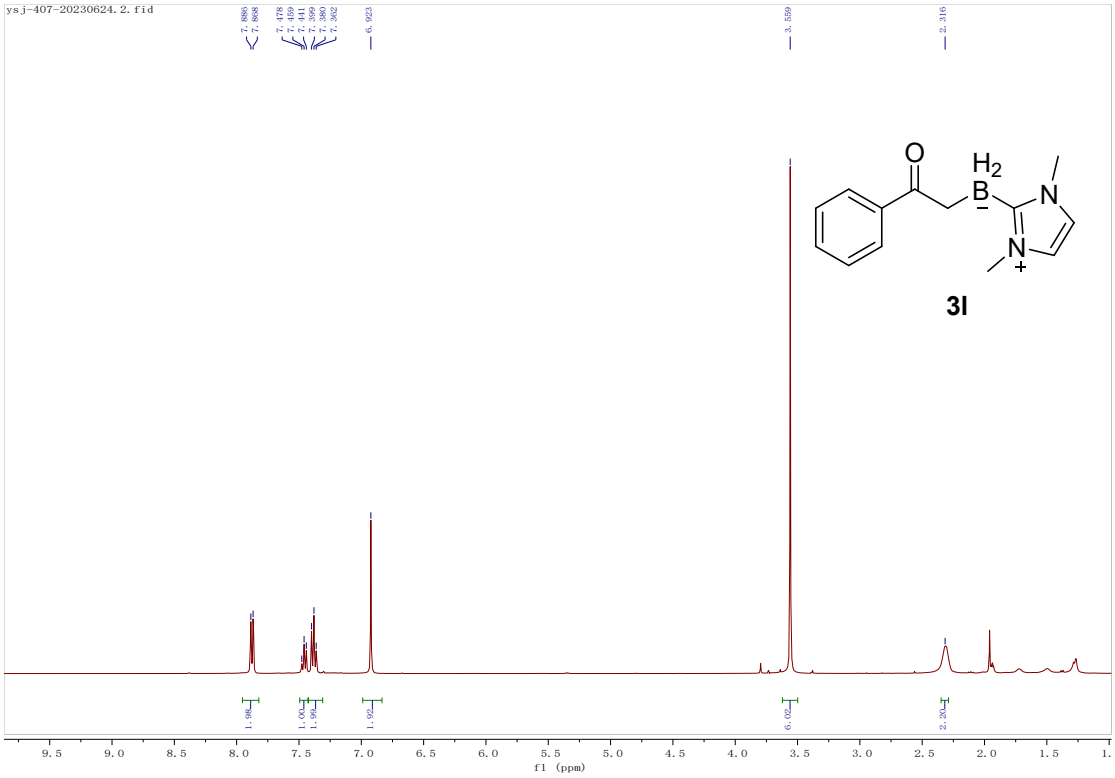
Product 3k: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.



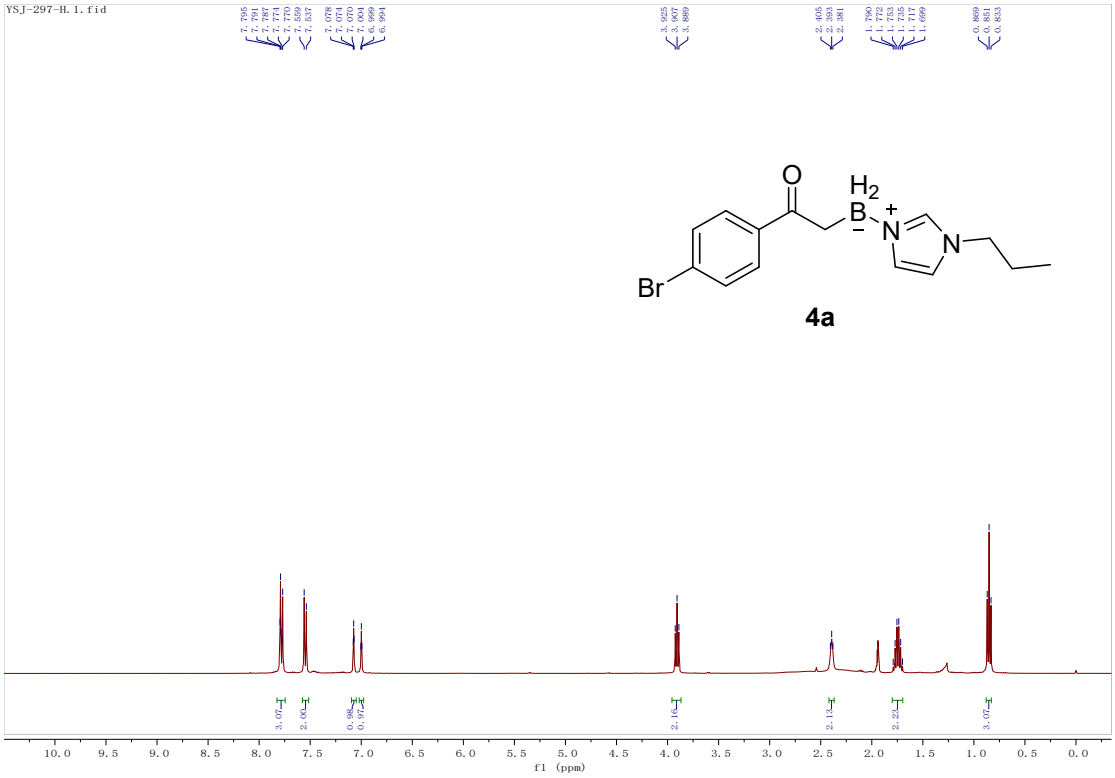


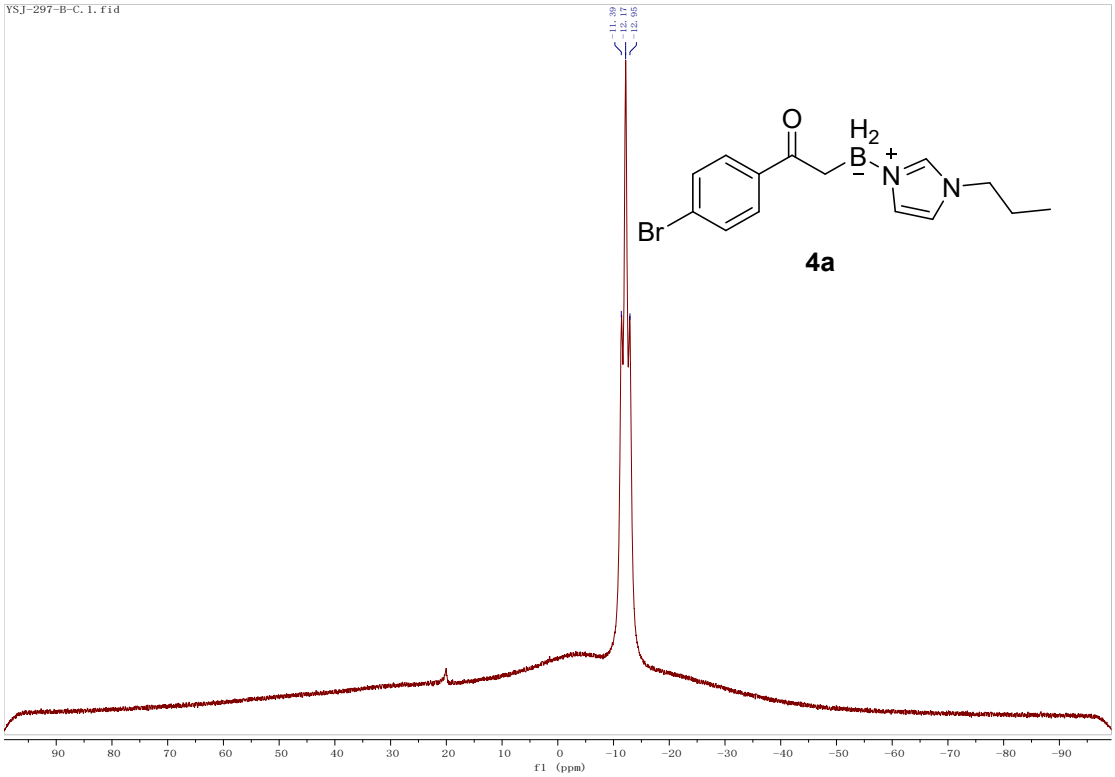

YSJ-316.10.fid
206.38
154.64
143.66
142.39
138.24
131.97
128.57
128.80
122.33
112.57
34.61
16.68
O
H2
B
N
NH2
3k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

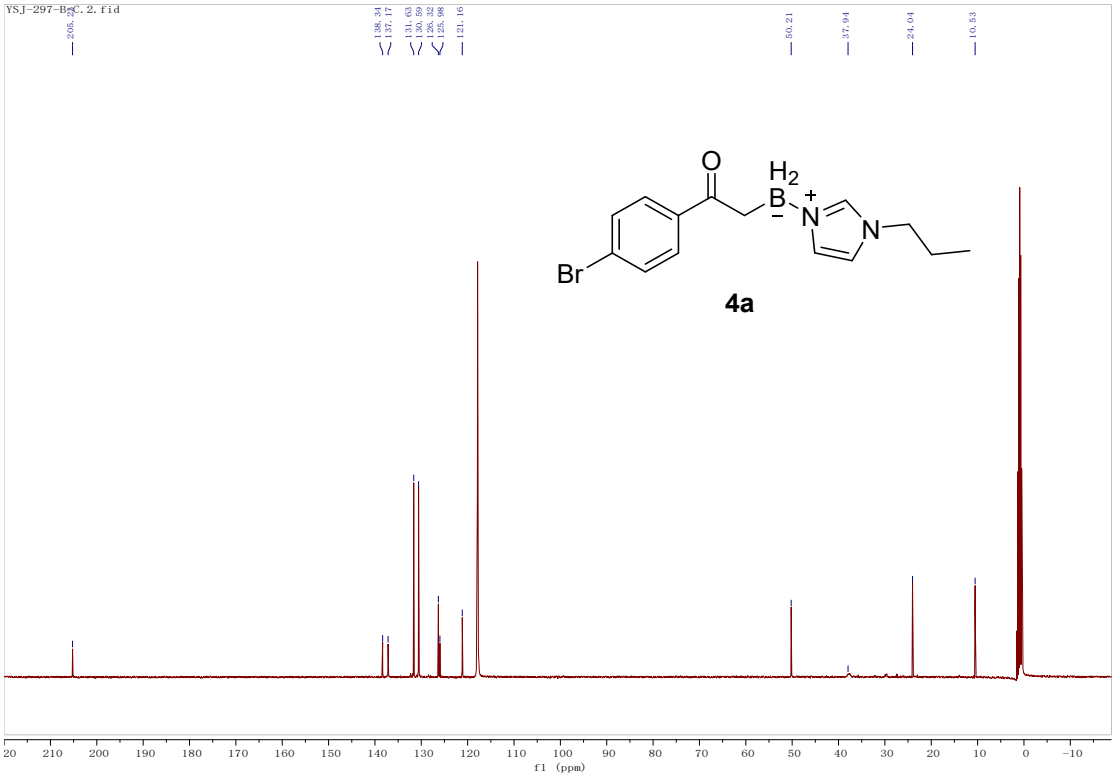
Product 3l: ^{1}H NMR



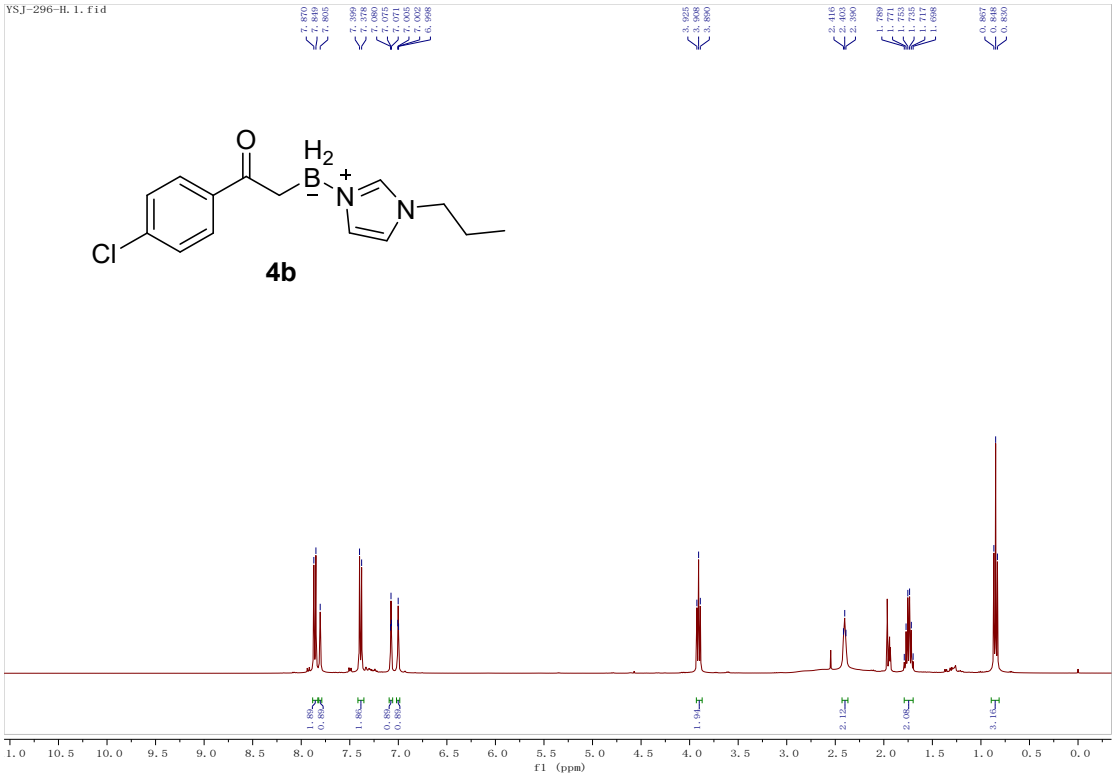
Product 4a: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

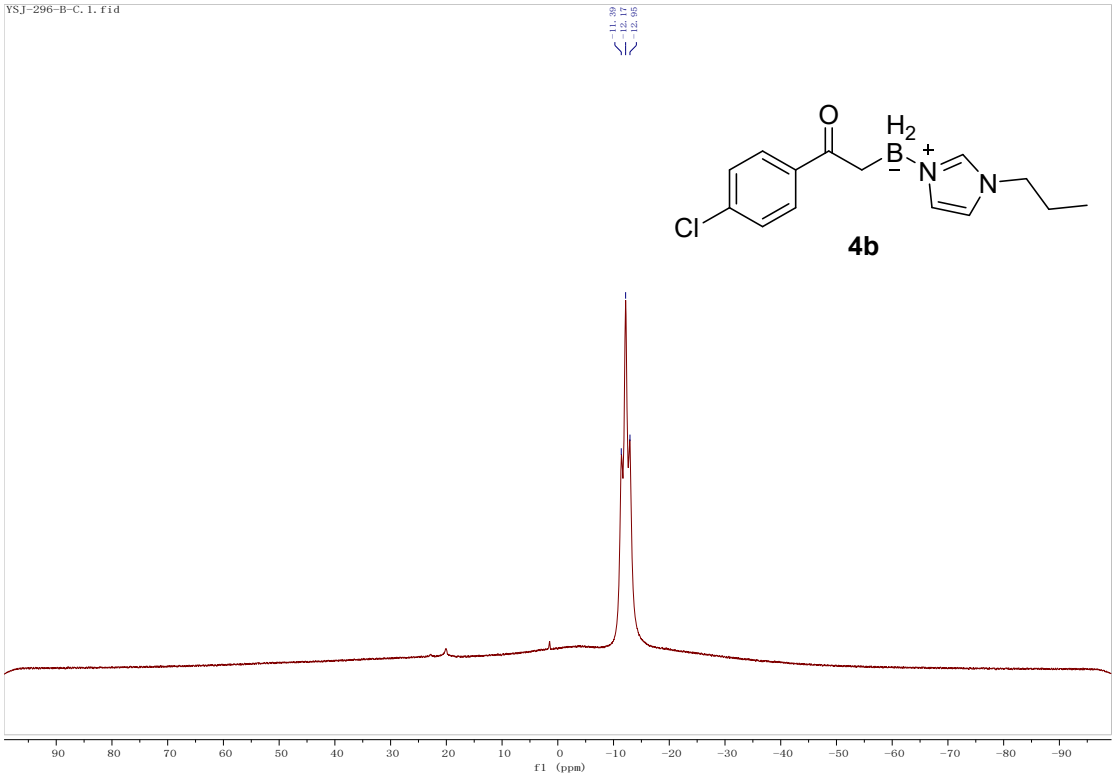


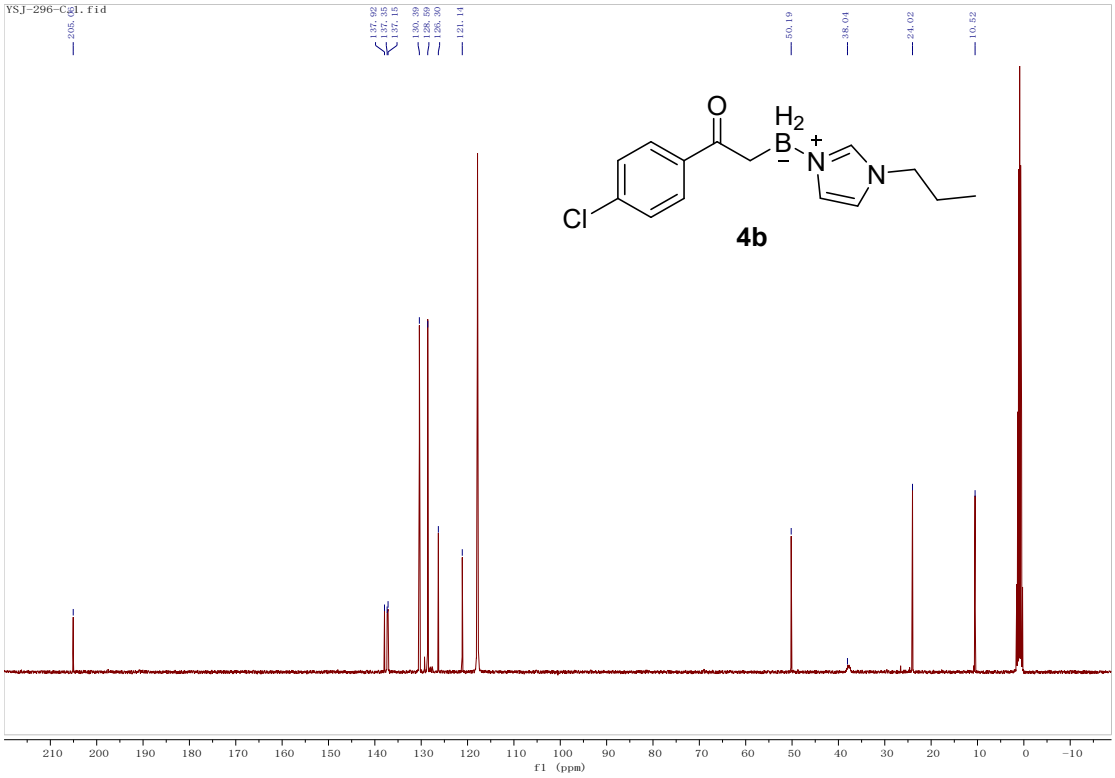



YSJ-297-BrC.2.fid
200.52
138.34
137.17
131.63
130.59
126.32
125.98
121.16
50.21
37.94
24.04
10.53
O
H2
B
N
N
Br
4a
f1 (ppm)

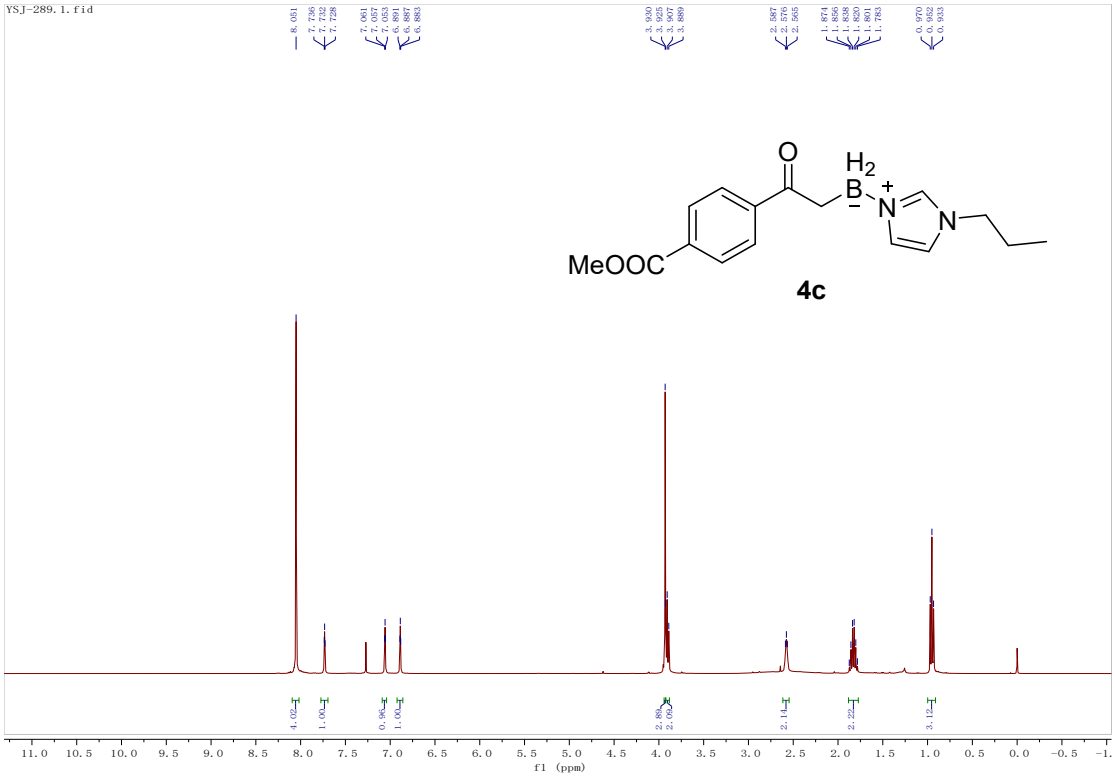
Product 4b: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

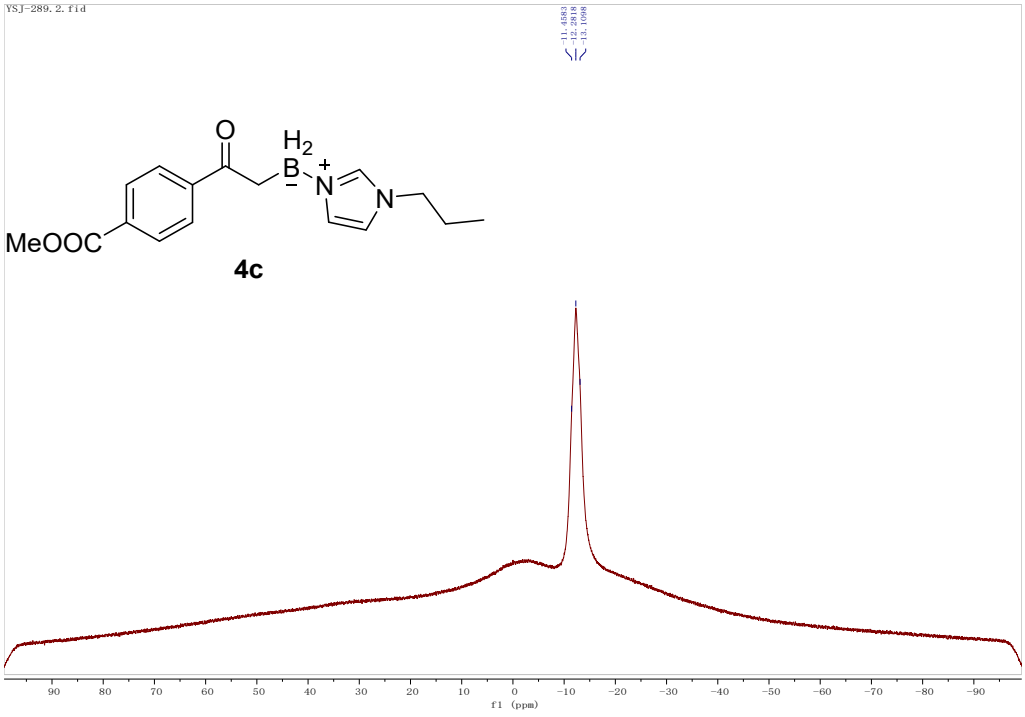


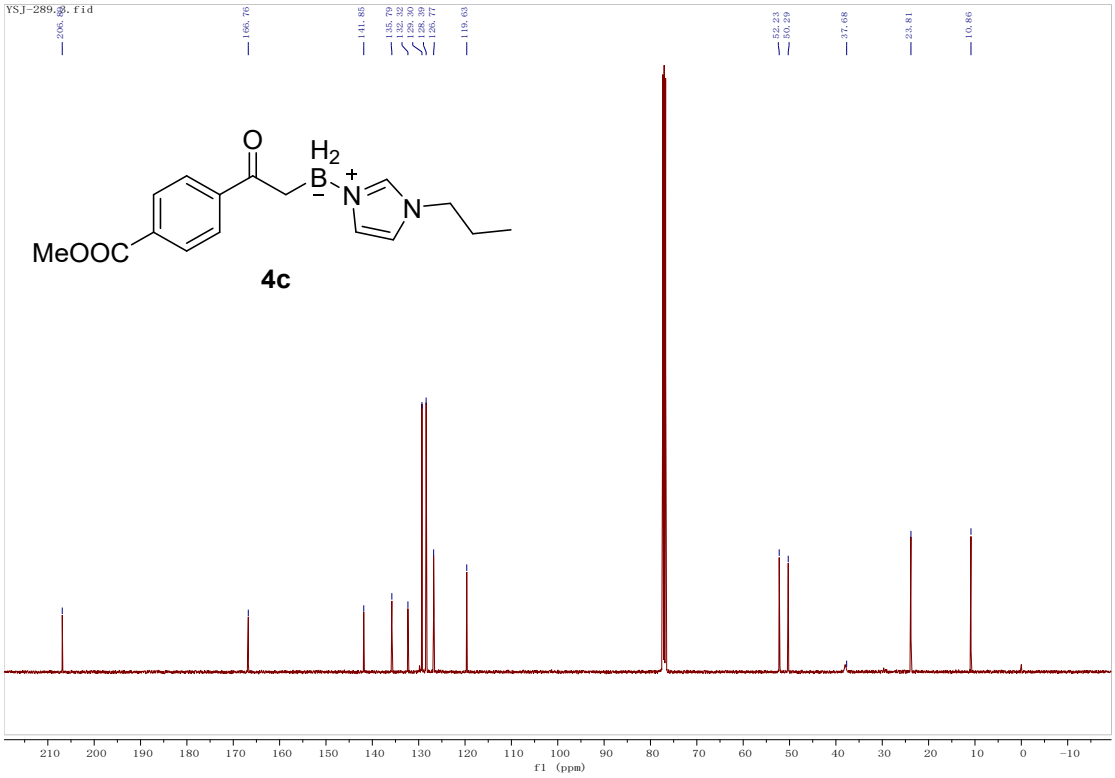



YSJ-296-C.1.fid
205.61
137.92
137.35
137.15
130.39
128.59
126.30
121.14
50.19
38.04
24.02
10.52
O
H2
B
N
N
Cl
4b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

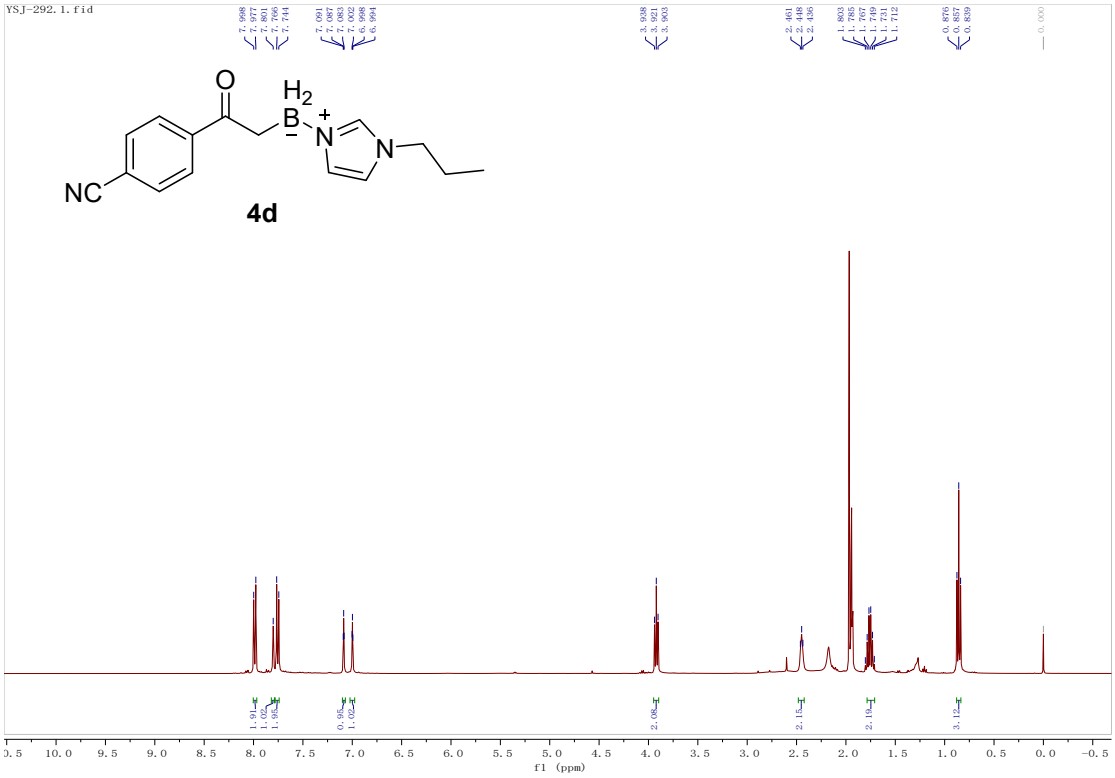
Product 4c: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

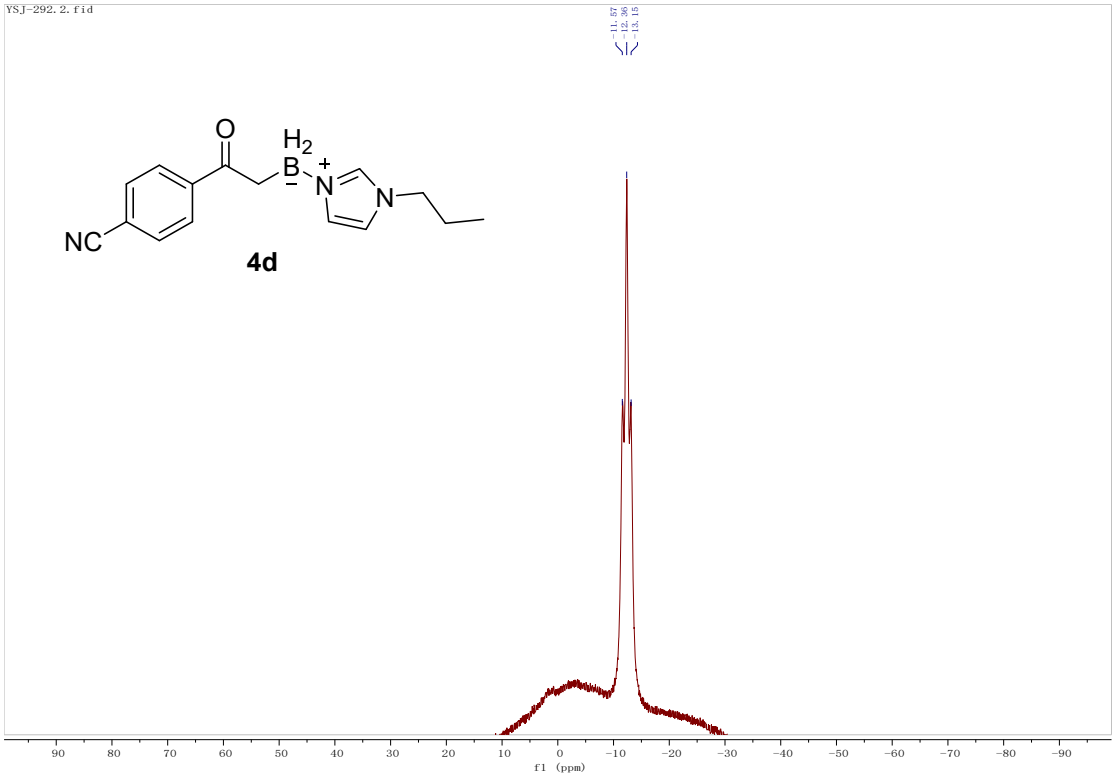


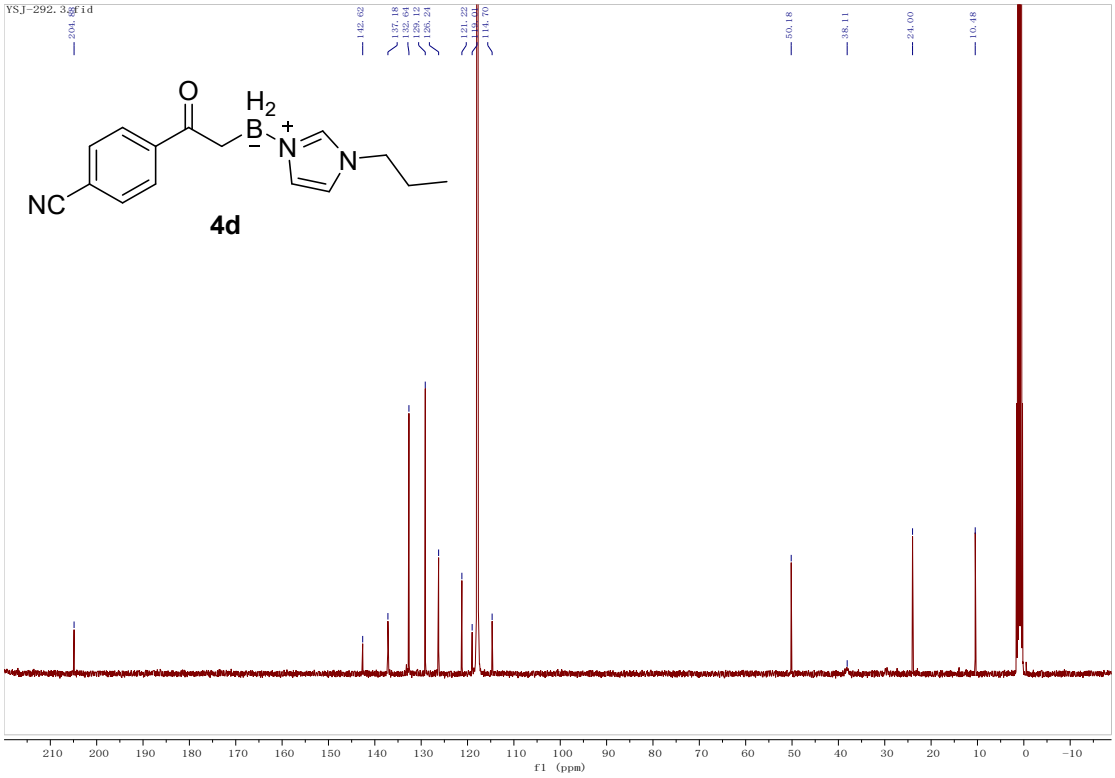



YSJ-289.3.fid
206.82
166.76
141.85
135.79
132.32
129.30
128.89
126.77
119.63
52.23
50.29
37.68
23.81
10.86
O
H2
B
N
N
MeOOC
4c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

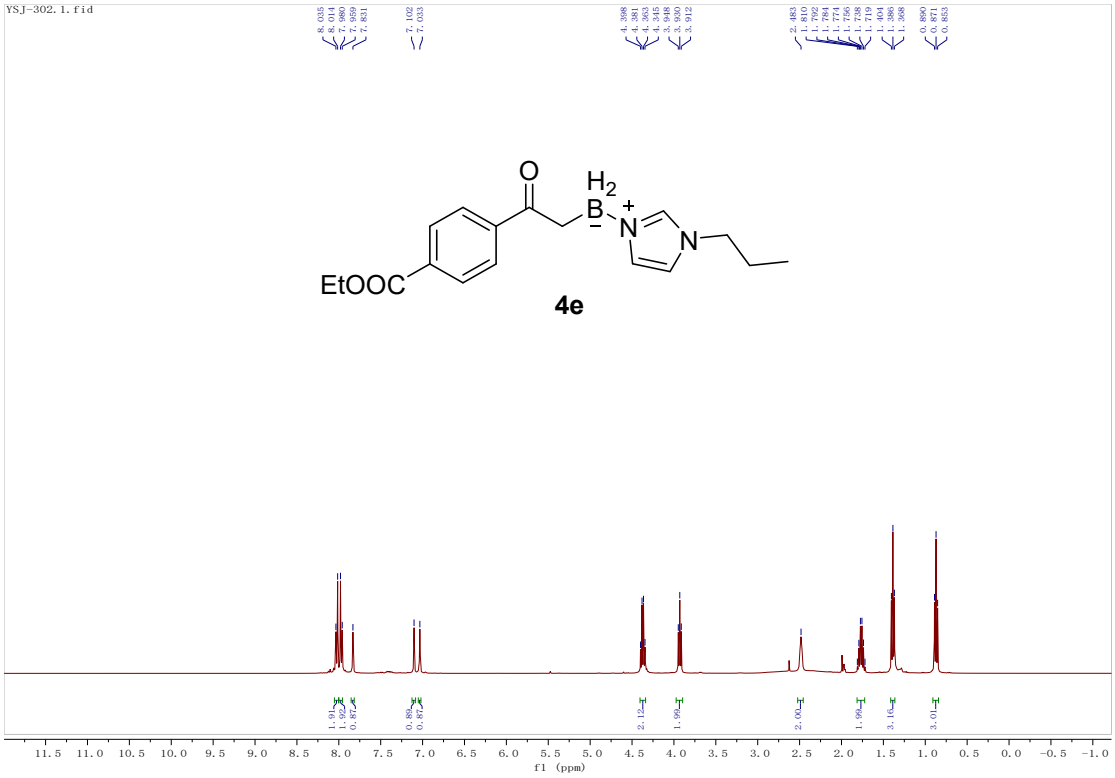
Product 4d: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

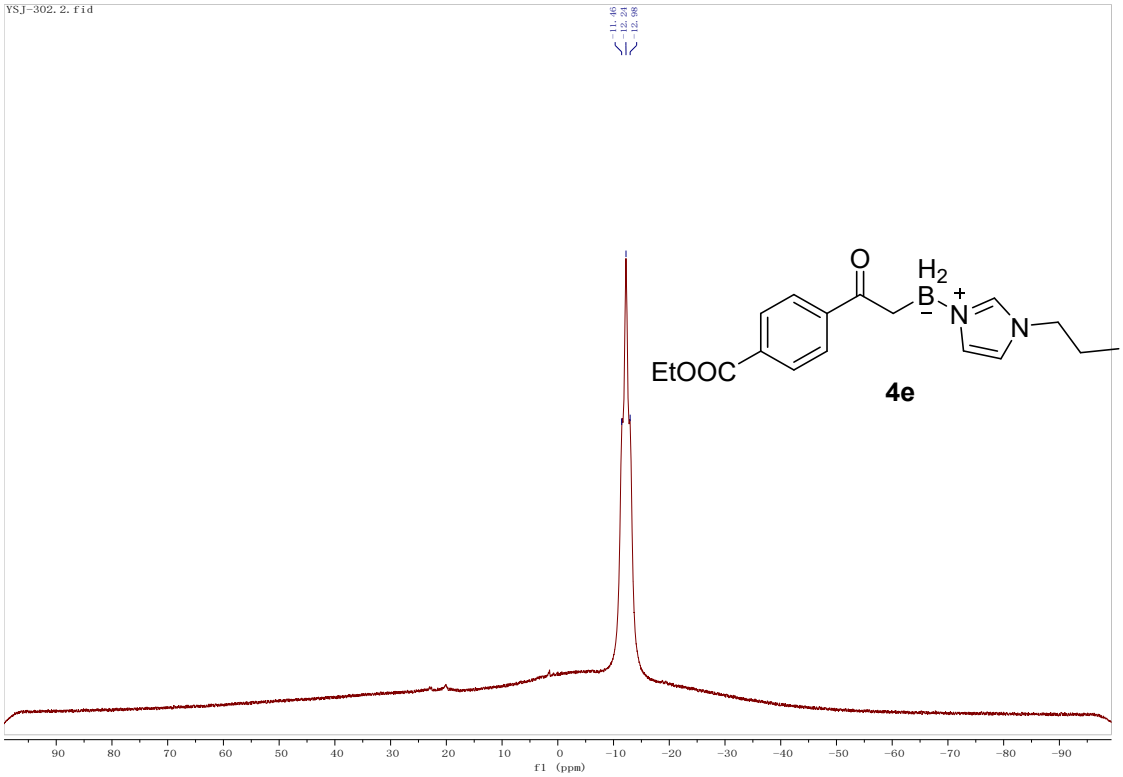


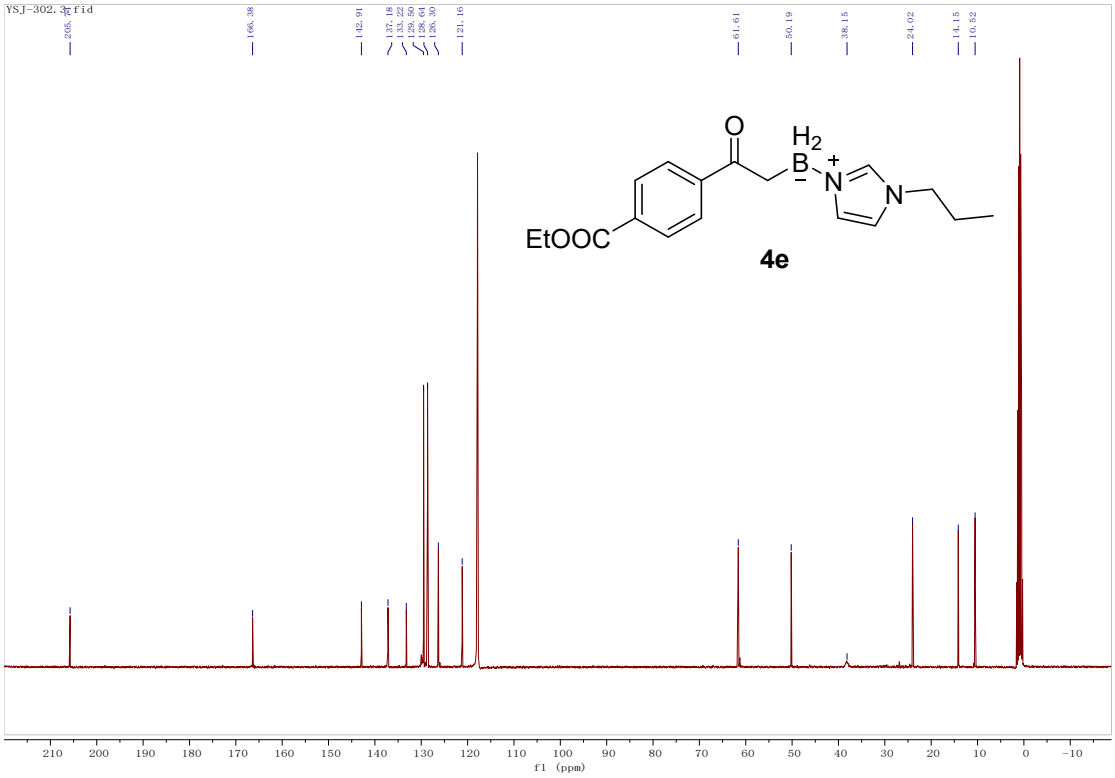



YSJ-292.3.fid
204.82
142.62
137.18
132.64
129.12
126.24
121.22
119.01
114.70
50.18
38.11
24.00
10.48
O
H2
B
N
N
NC
4d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

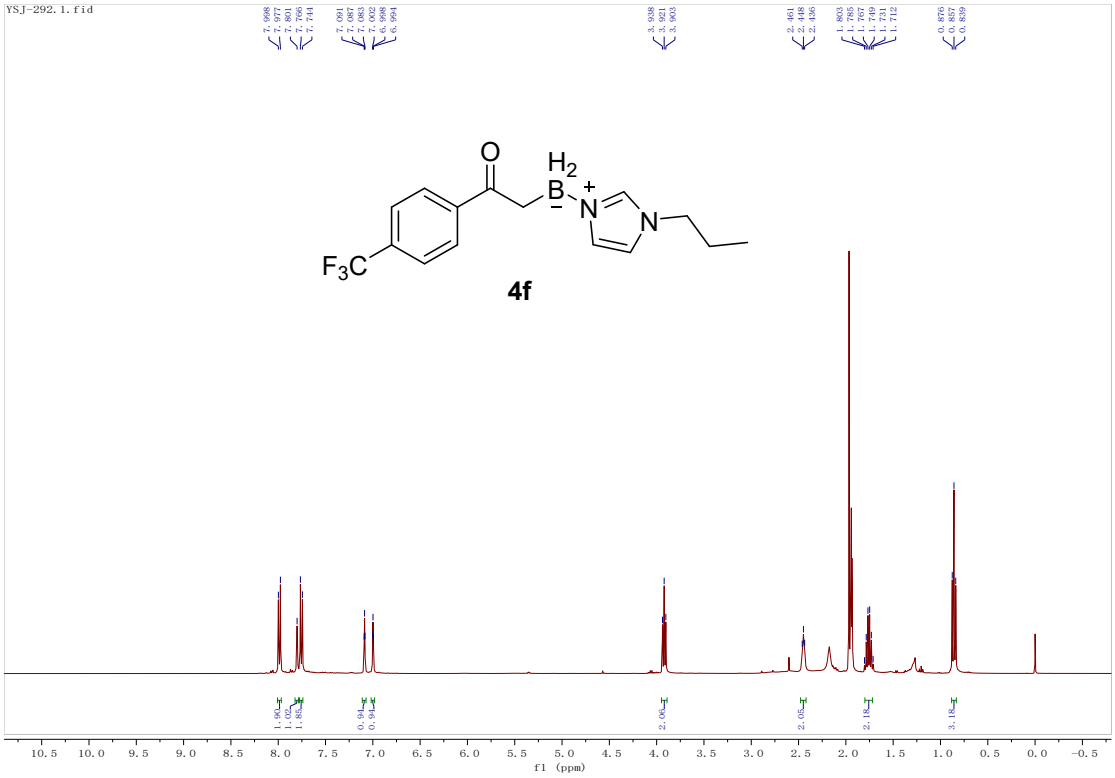
Product 4e: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

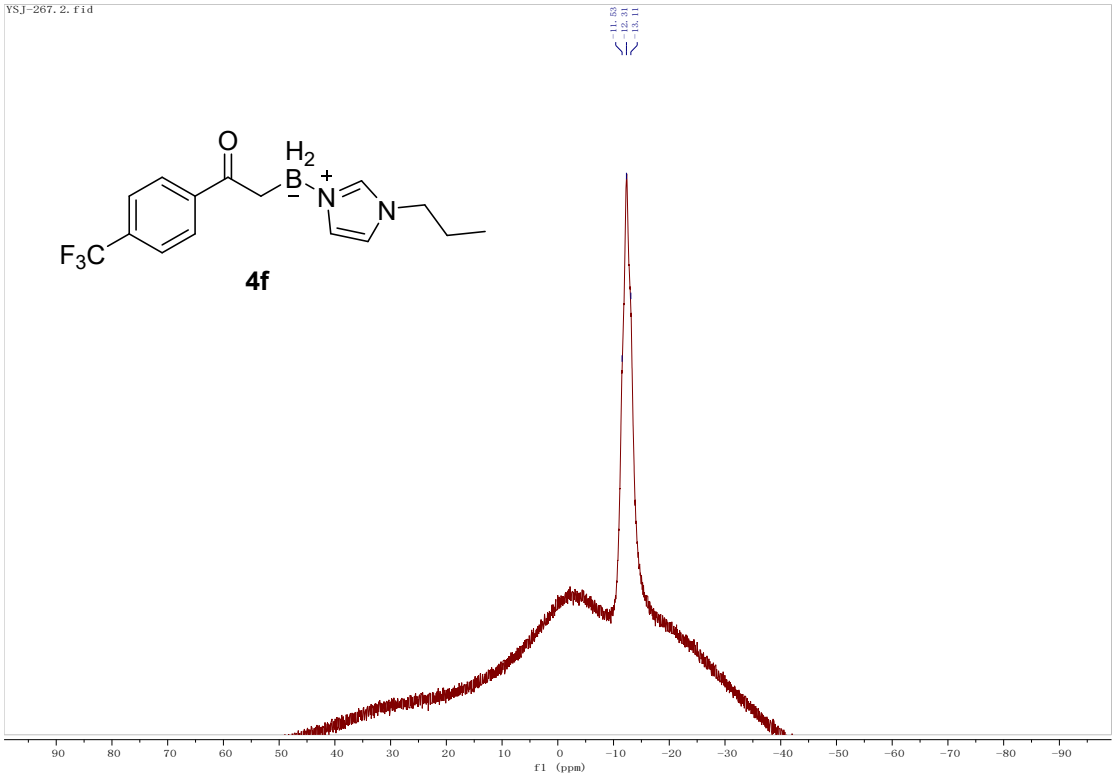


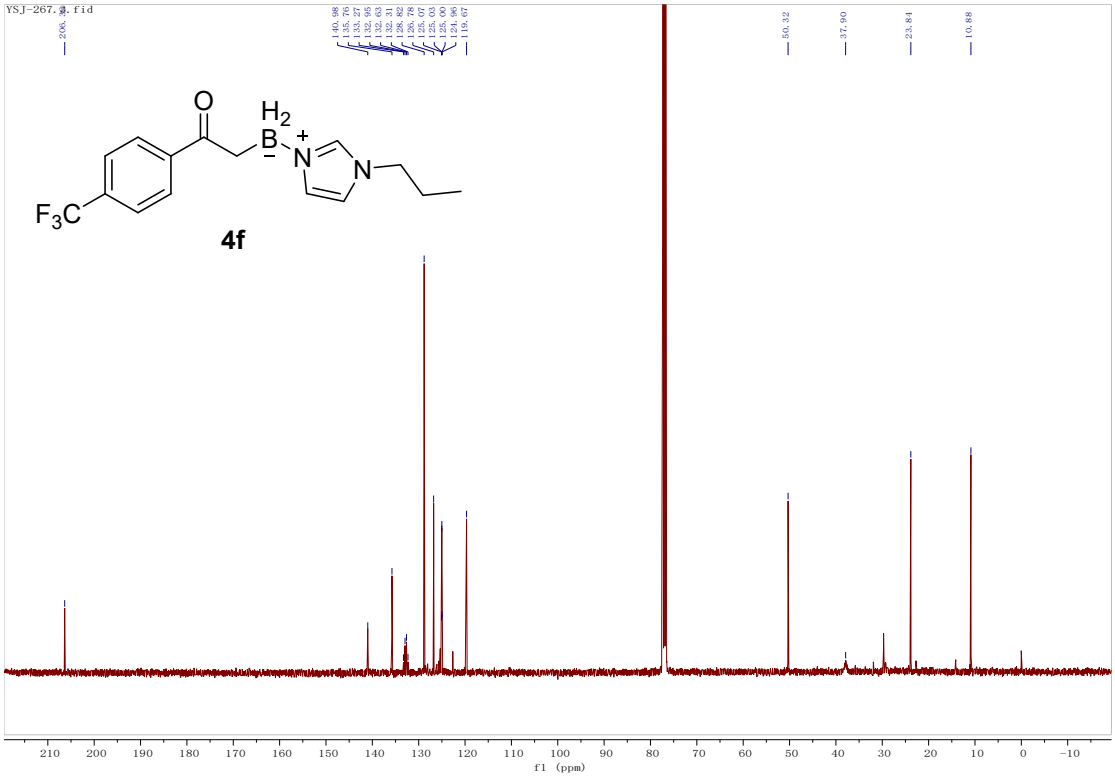



YSJ-302.3.1.fid
205.74
166.38
142.91
137.18
133.22
129.50
128.64
126.50
121.16
61.61
50.19
38.15
24.02
14.15
10.52
O
H2
B
N
N
EtOOC
4e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

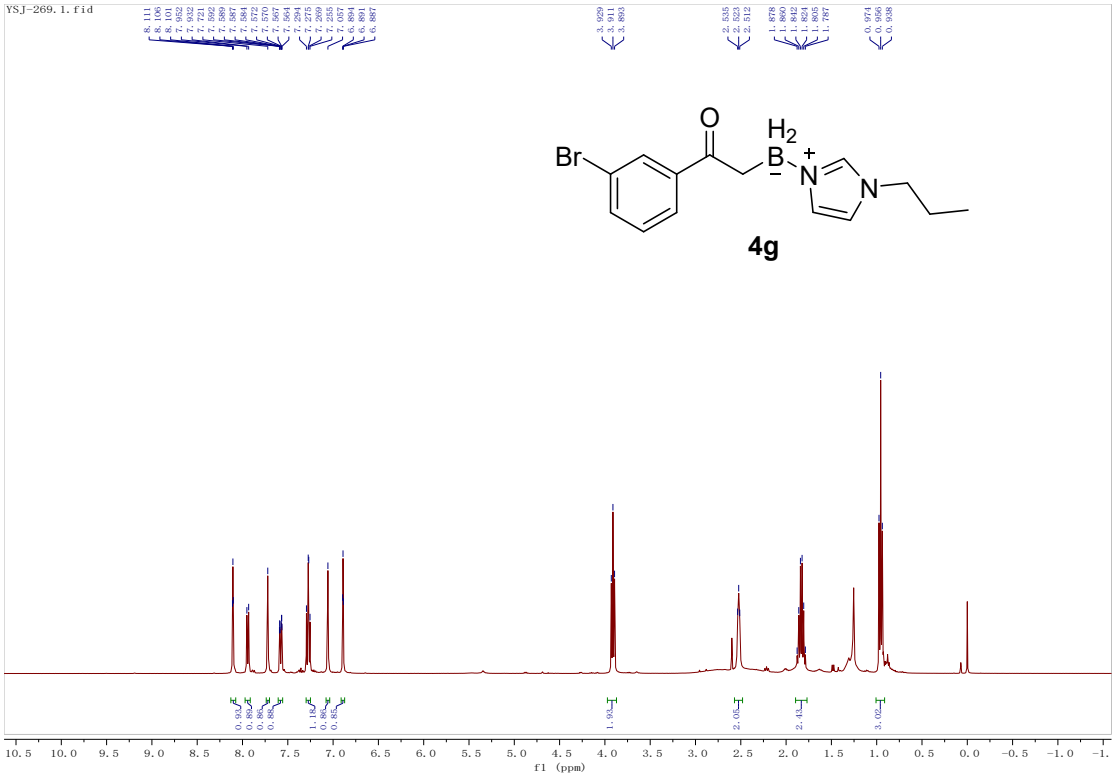
Product 4f: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

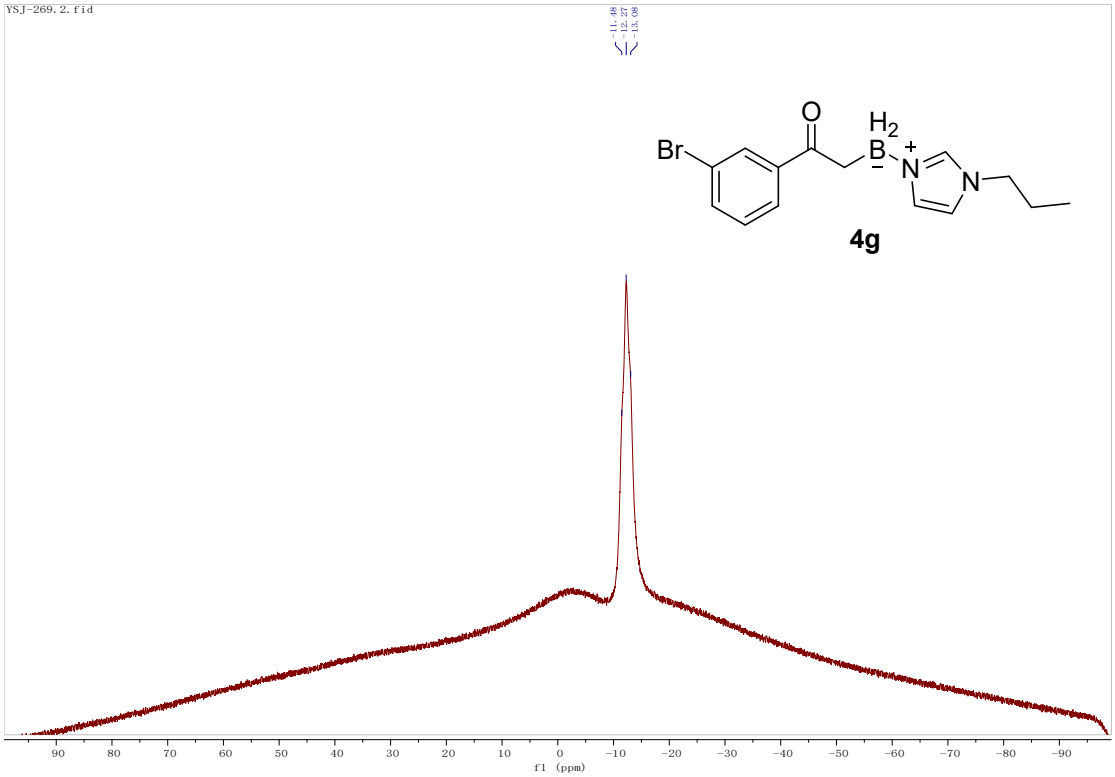


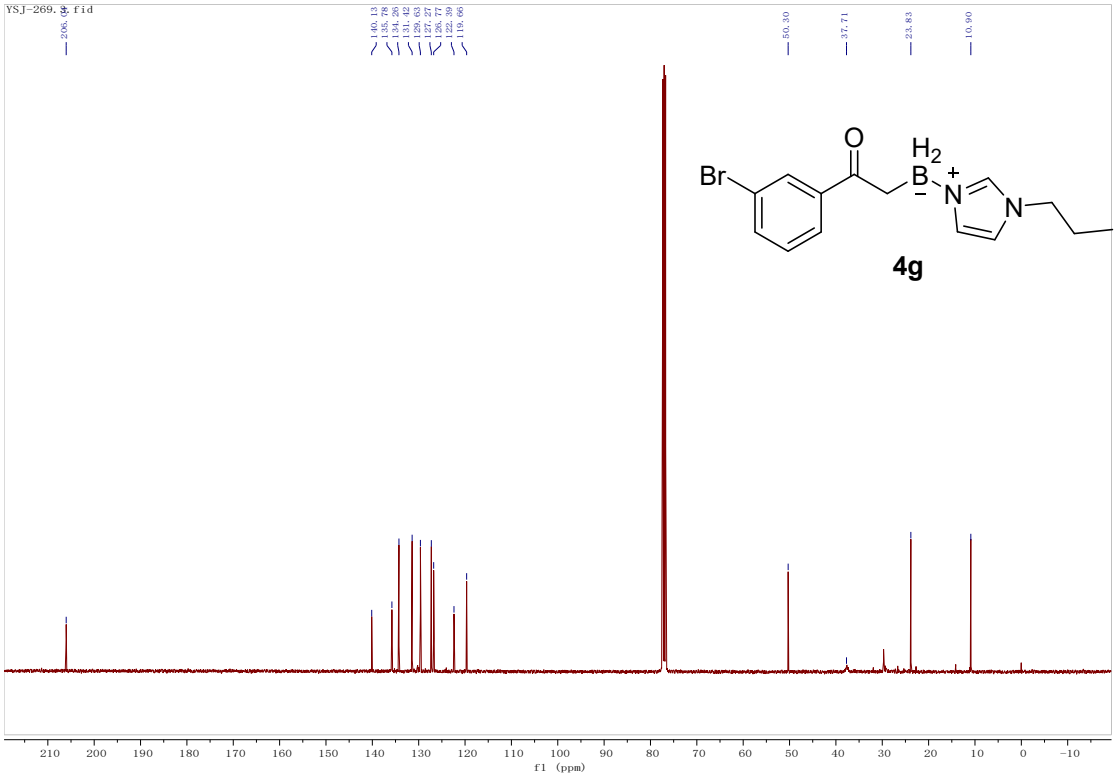



YSJ-267.3.fid
206.3
140.98
135.76
133.27
132.95
132.63
132.31
126.82
126.78
125.67
125.03
125.00
124.96
118.67
50.32
37.90
23.84
10.88
O
H2
B
N
N
F3C
4f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

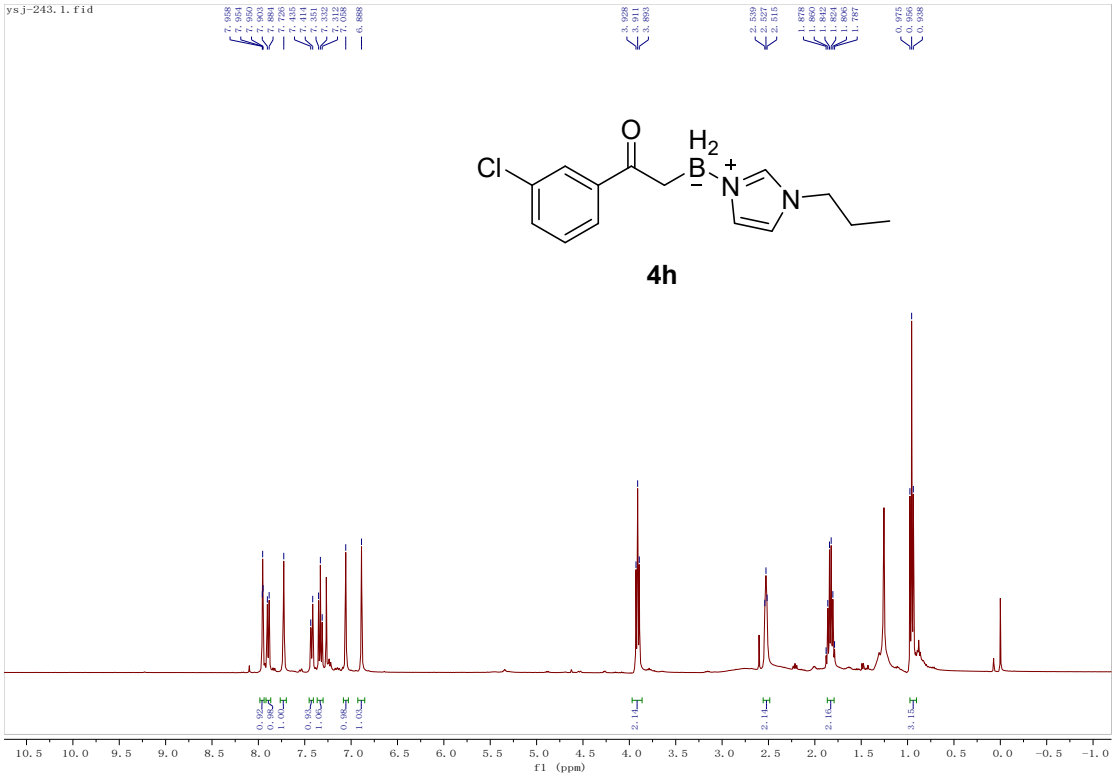
Product 4g: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

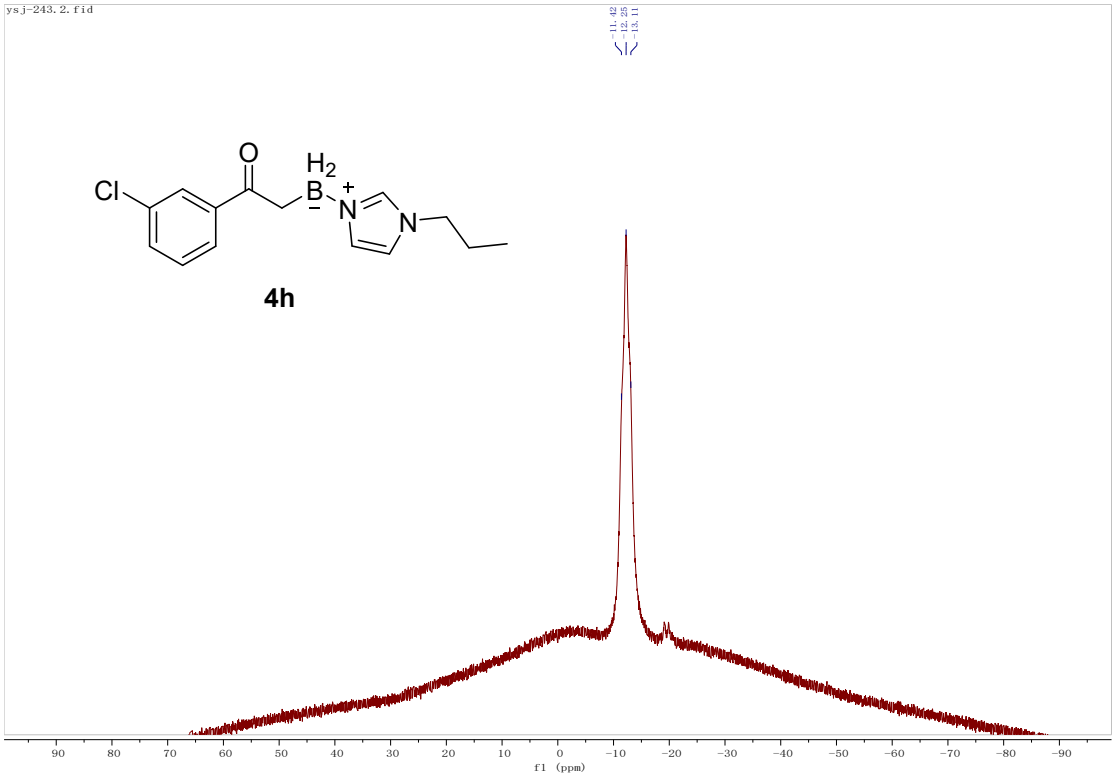


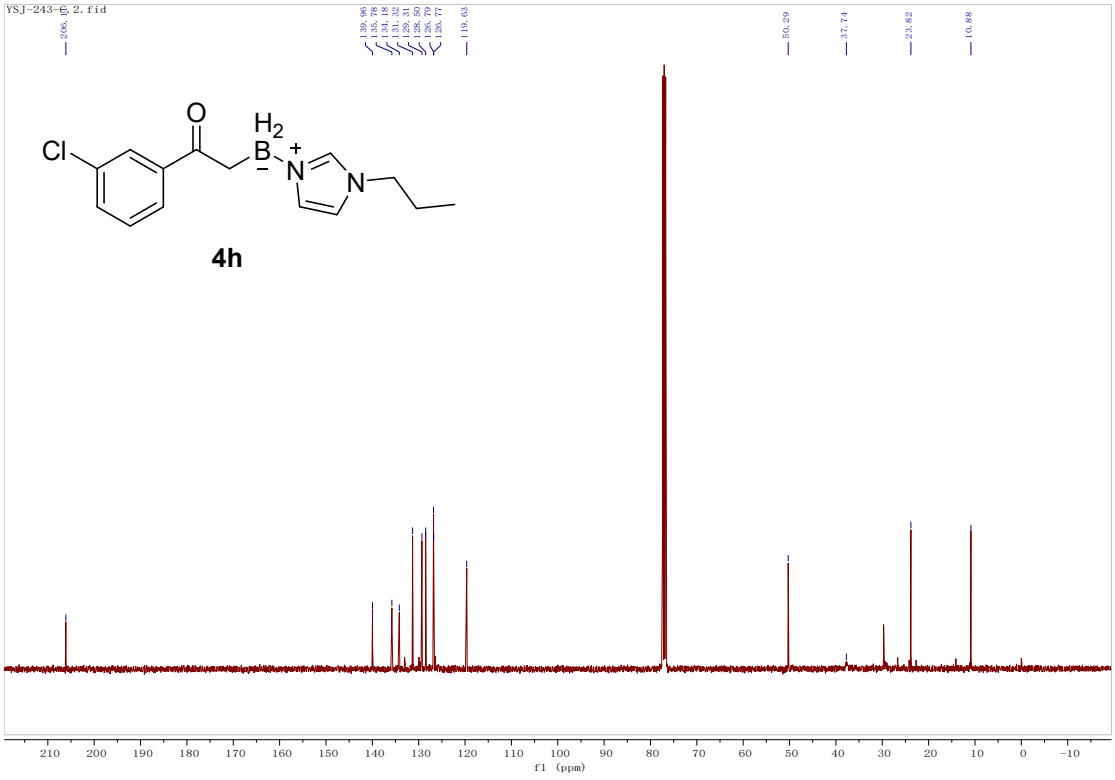



YSJ-269.4.fid
206.04
140.13
135.78
134.28
131.42
129.63
127.27
126.77
122.98
119.66
50.30
37.71
23.83
10.90
O
H2
B
N
N
Br
4g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

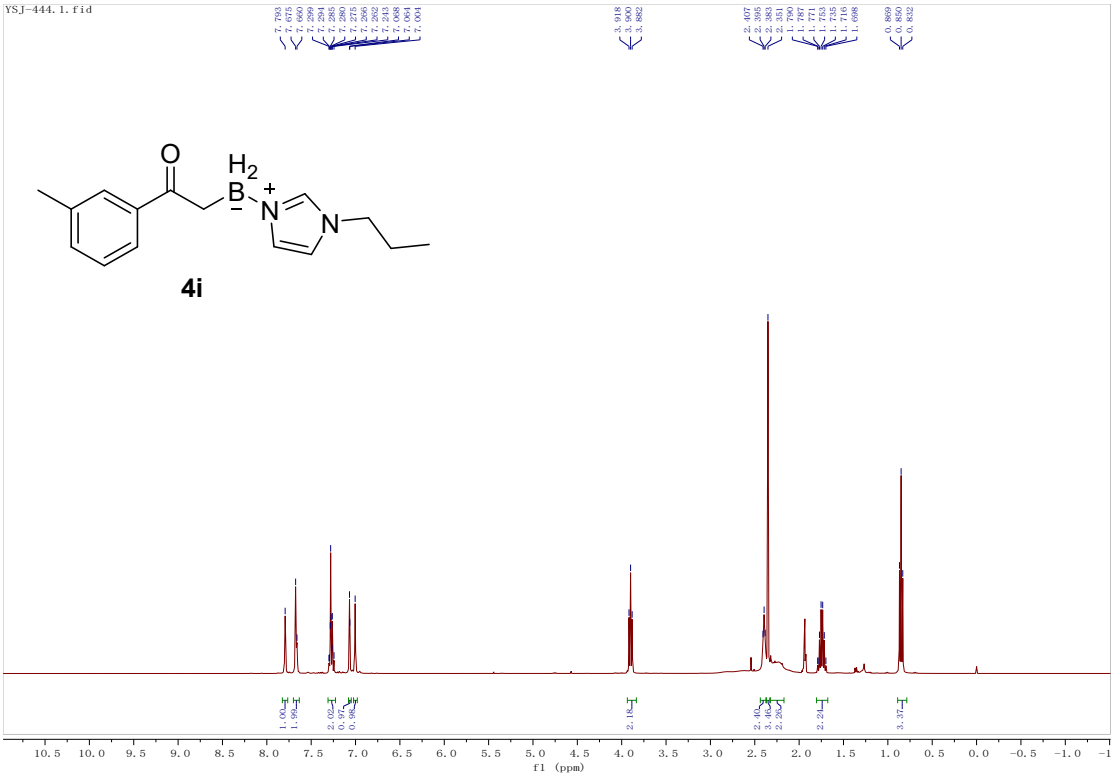
Product 4h: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

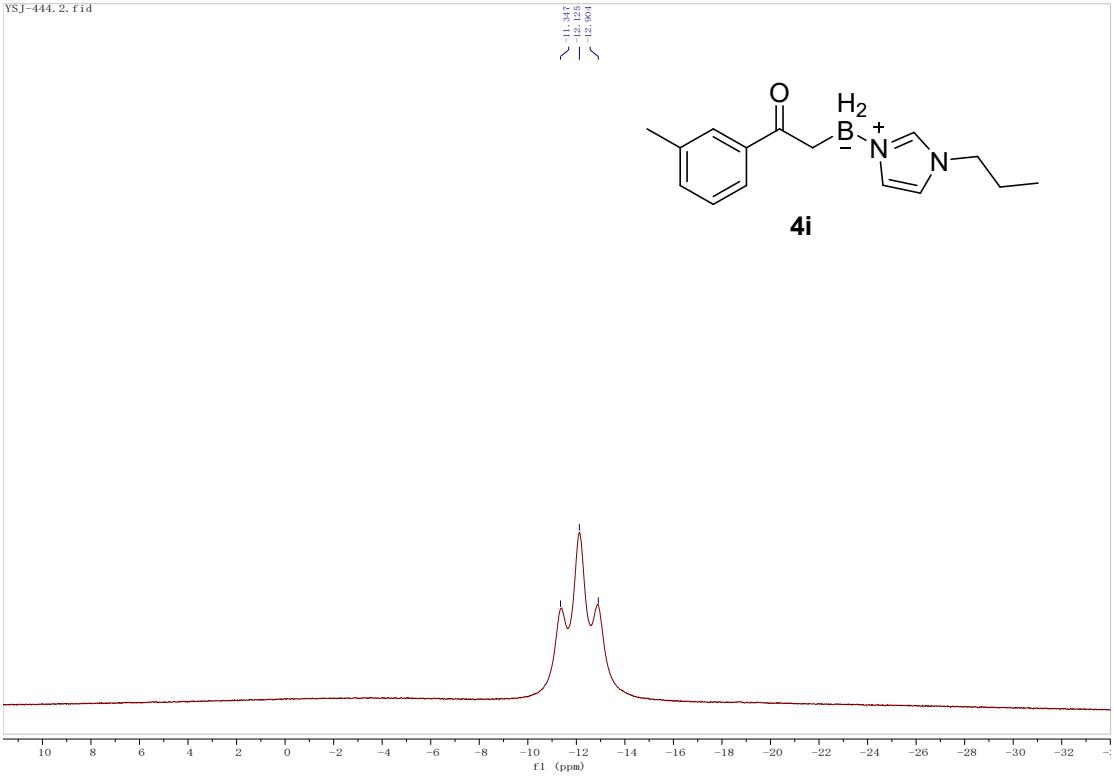


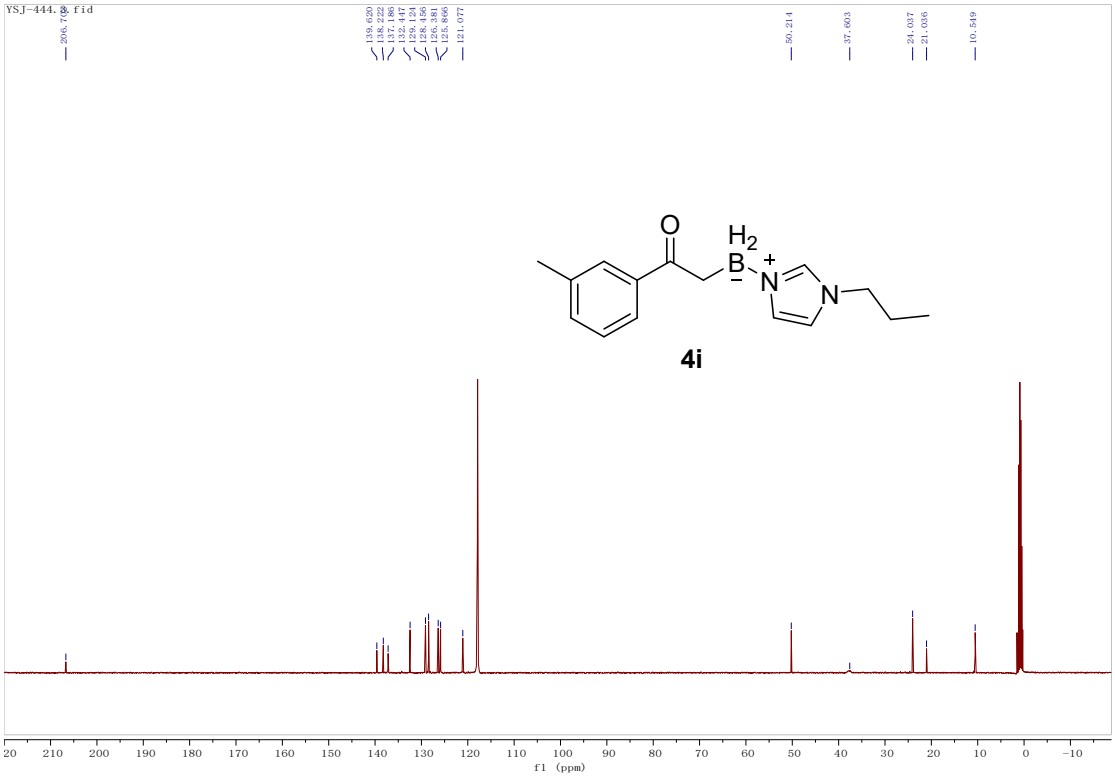



YSJ-243-C 2.fid
206.10
139.98
135.78
134.18
131.32
129.71
128.50
126.79
126.77
119.63
50.29
37.74
23.82
10.88
O
H2
B
N
N
Cl
4h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

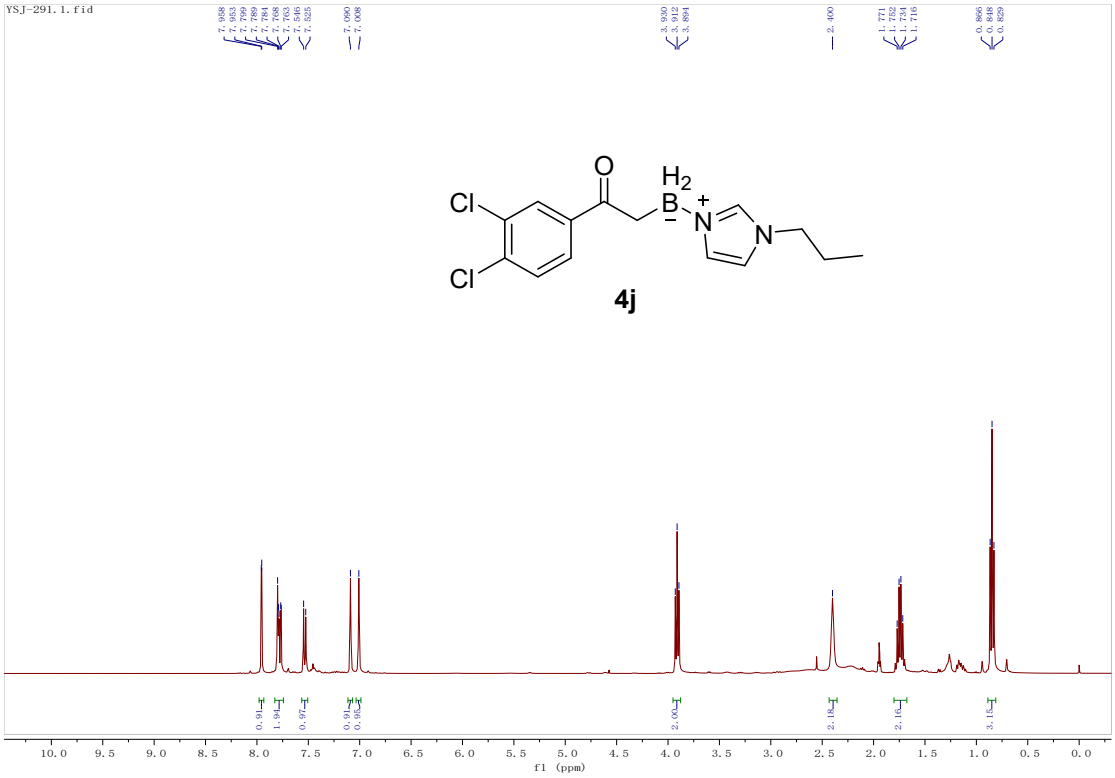
Product 4i: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.

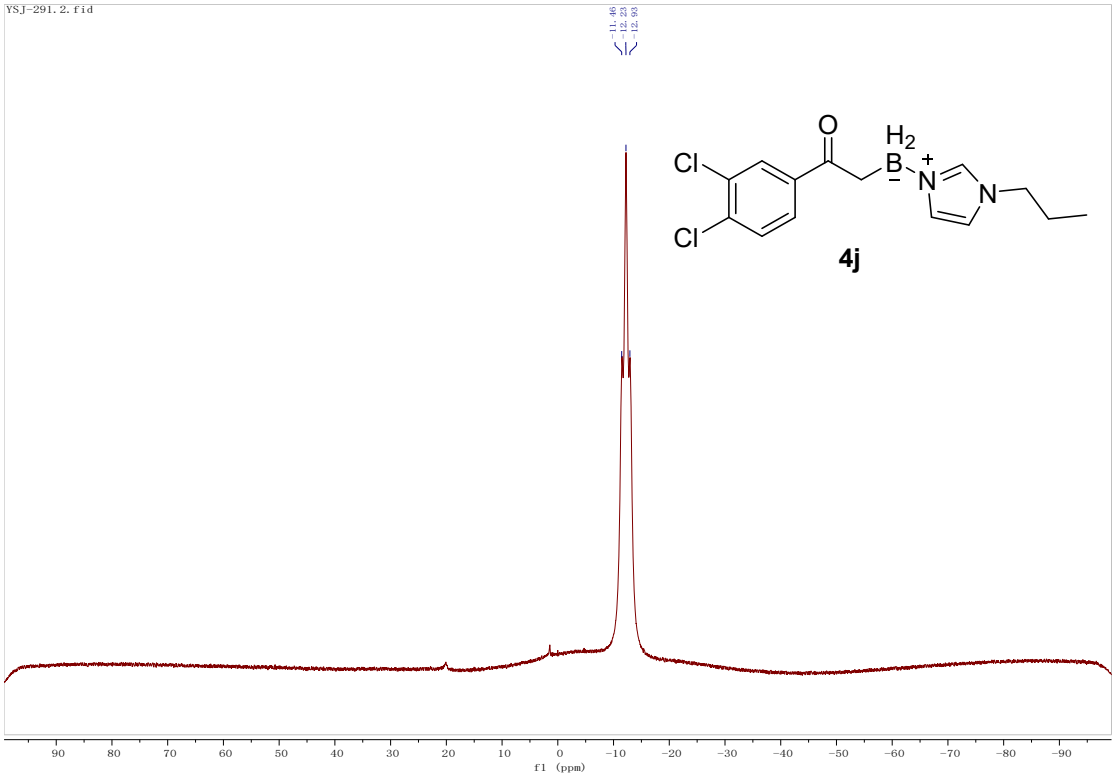


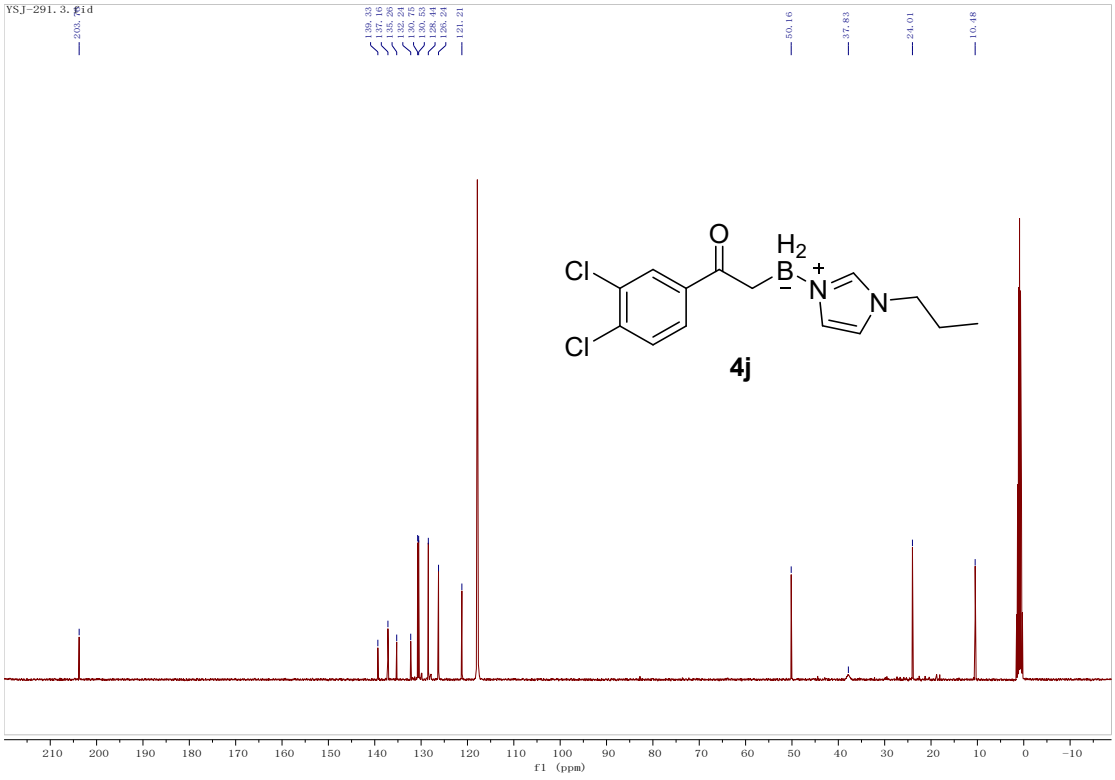



YSJ-444.10.fid
206.709
139.620
138.222
137.186
132.447
129.124
128.495
126.381
125.866
121.077
50.214
37.603
24.037
21.036
10.549
O
H2
B
N
N
4i
f1 (ppm)

Product 4j: ^{1}H NMR ^{11}B NMR and ^{13}C NMR.






YSJ-291.3.fid
203.71
139.53
137.16
135.26
132.24
130.75
128.63
128.44
126.24
121.21
50.16
37.83
24.01
10.48
Cl
Cl
O
B
H2
N
N
4j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)