Supplementary Information (SI) for Chemical Science.

Nickel Catalyzed Diastereoselective Hydroboration of Acrylates with a Vinylborane Reagent

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1. General Information

Staring materials and reagents were purchased from commercial sources and used without further purification. Organic solvents were dried and distilled by standard methods prior to use. Analytical TLC analyses were performed on Yantai Chemical Industry Research Institute silica gel 60 F254 plates. Flash column chromatography was performed on Qingdao-Haiyang® silica gel (200-300 mesh) or Macklin neutral aluminum oxide (200-300 mesh). Nickel-catalyzed hydroboration reactions were performed under a N_2 atmosphere in a glove box using flame-dried glassware with a stirring bar and anhydrous solvent unless otherwise indicated. $NiCl_2$ and $Ni(COD)_2$ were purchased from Energy. Reaction temperatures were reported as the temperatures of the bather surrounding the flasks or vials. ^1H ,^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on a Bruker 400 or JEOL 600 spectrometer at 400/600, 101/151, 128/193, and 376/565 MHZ, respectively. Peaks recorded are relative to the internal standards: $CDCl_3$ (δ = 7.26) for ^1H NMR and $CDCl_3$ (δ = 77.16) for ^{13}C spectra, All the ^{11}B chemical shifts were referenced to external $BF_3{\cdot}OEt_2$ (δ = 0.00). All the ^{19}F chemical shifts were not referenced. Data for ^1H NMR and ^{13}C NMR spectra were reported as follows: chemical shift (ppm, referenced to protium; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad, coupling constant (Hz), and integration). For the ^1H & ^{13}C NMR spectral data, the hydrogens and carbons bonded with boron are not listed due to quadrupole broadening and spin-spin coupling with boron. The dr values of related products were measured via ^1H NMR. High resolution mass spectra (HRMS) were obtained on a Waters Xevo G2-XS Tof mass spectrometer.

2. Reagents and Substrates

2.1. Olefin Substrate Preparation

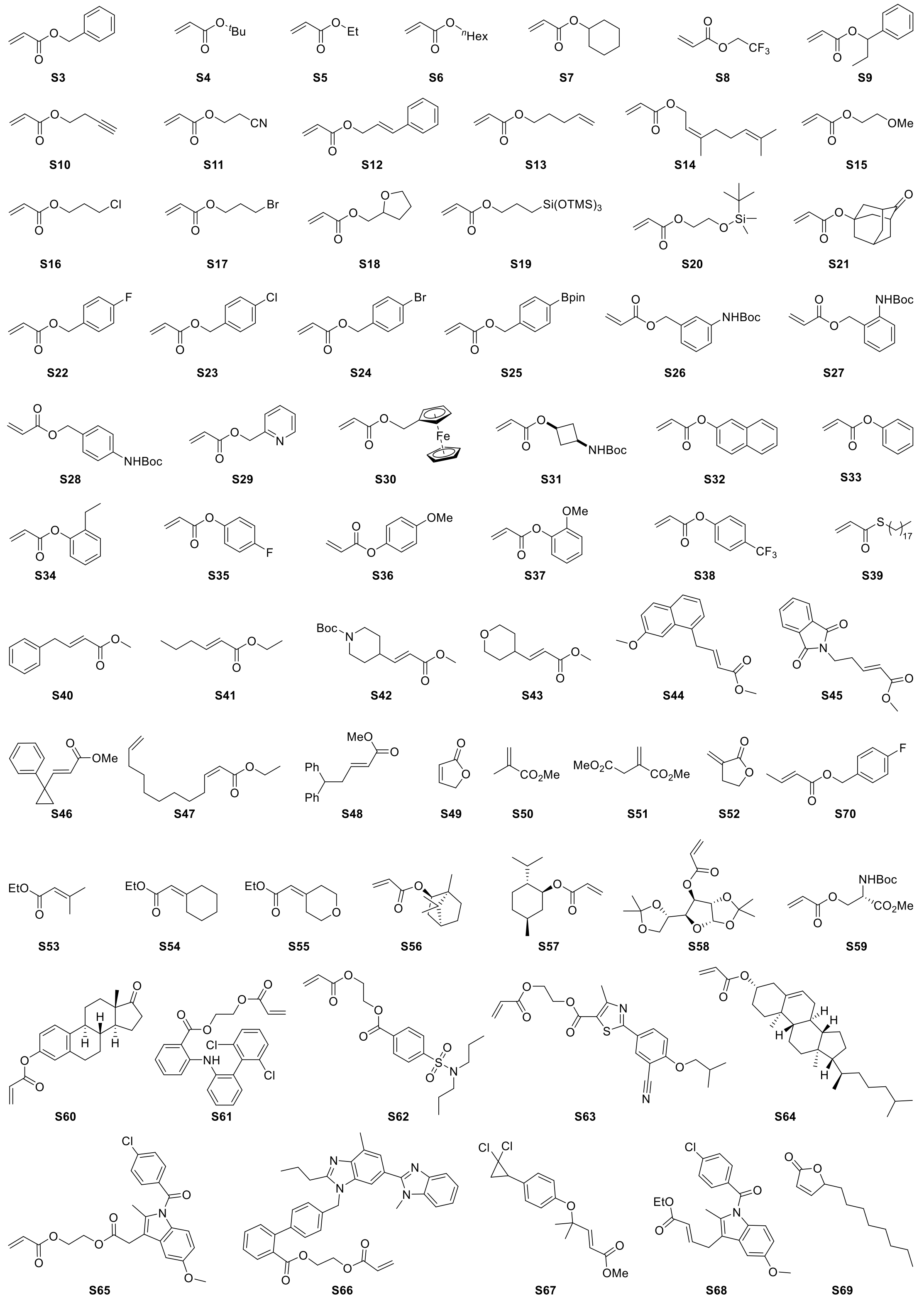
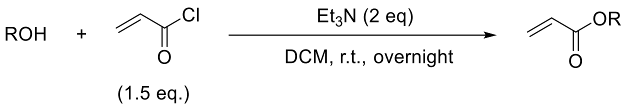


Fig. S1. List of substrates used in this work.

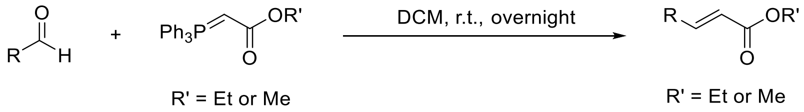
S3-8, **S11**, **S15**, **S18-19**, **S33**, **S41**, **S49-55**, **S69** are commercially available and used without purification when received. **S9-14**, **S16-17**, **S30-S32**, **S34-39**, **S56-60** and **S64** are synthesized according to procedure A, and their NMR spectra correspond to the reported data.[1-16] **S40**, **S42-48**, **S67-68 and S70** are synthesized according to procedure B, and their NMR spectra correspond to the reported data.[17-21] **S61-63** and **S65-66** are synthesized according to procedure C, and their spectra correspond to the reported data.[22]

Procedure A



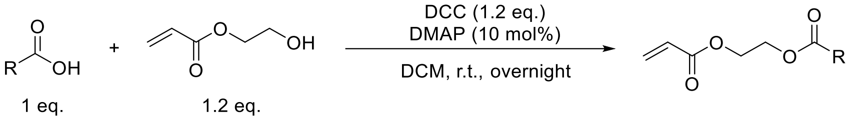
In a 100 mL round-bottom flask, ROH (5 mmol, 1.0 eq.) was dissolved in 20 mL DCM, followed by the addition of TEA (10 mmol, 2 eq.). After that, acryloyl chloride (7.5 mmol, 1.5 eq.) was added under 0 °C. The resulting mixture was stirred overnight. When the reaction was completed, water was added. The aqueous phase was extracted by DCM three times. The organic phase was combined and evacuated under reduced pressure. The residue was subjected to column chromatography (SiO_2) to give the pure products.

Procedure B

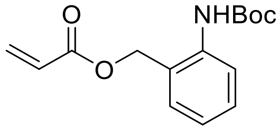


In a 100 mL round-bottom flask, methyl (or ethyl) (triphenylphosphoranylidene)acetate (6 mmol, 1.2 eq.) was dissolved in 20 mL anhydrous DCM, followed by the addition of a ROH (5 mmol) solution in anhydrous DCM. Then the mixture was stirred overnight. When the reaction was completed, water was added. The aqueous phase was extracted by DCM three times. The organic phase was combined and evacuated under reduced pressure. The residue was subjected to column chromatography (SiO_2) to give the pure products.

Procedure C

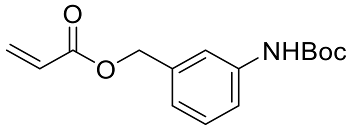


In a 100 mL round bottom flask, acid (10 mmol) and 2-hydroxyethyl acrylate (12 mmol, 1.2 eq.) were dissolved in anhydrous DCM. Then, DMAP (1 mmol, 10 mol%) and DCC (10 mmol, 1 eq.) were added to the solution. The resulting mixture was stirred at room temperature for 22 h. After that, the reaction was quenched with water, and the aqueous phase was extracted with DCM three times. The combined organic phase was then dried with anhydrous Na_2SO_4 and evacuated under reduced pressure. The residue was subjected to column chromatography (SiO_2) to give the pure products.



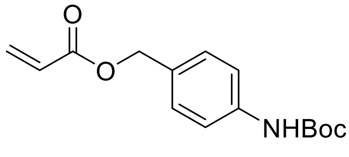
S27, colorless oil, 83%. Procedure A.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.41 (s, 1H), 7.37 – 7.32 (m, 2H), 7.0810 – 7.06 (m 1H), 6.45 (dd, *J* = 17.3, 1.3 Hz, 1H), 6.15 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.88 (dd, *J* = 10.5, 1.3 Hz, 1H), 5.20 (s, 2H), 1.53 (s, 9H).



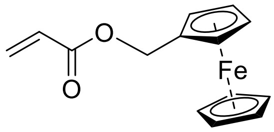
S26, colorless oil, 78%. Procedure A.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 (s, 1H), 7.31 – 7.25 (m, 2H), 7.07 – 7.00 (m, 1H), 6.47 (s, 1H), 6.44 (dd, *J* = 17.4, 1.4 Hz, 1H), 6.15 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.85 (d, *J* = 1.4 Hz, 1H), 5.15 (s, 2H), 1.51 (s, 9H).



S28, colorless oil, 76%. Procedure A.

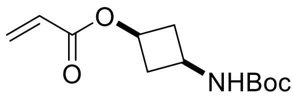
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.48 (s, 1H), 6.41 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.13 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.82 (dd, *J* = 10.4, 1.5 Hz, 1H), 5.12 (s, 2H), 1.51 (s, 9H).



S30, orange solid, 89%. Procedure A.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.40 (dd, *J* = 17.3, 1.4 Hz, 1H), 6.10 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.80 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.97 (s, 2H), 4.28 (t, *J* = 1.8 Hz, 2H), 4.18 (t, *J* = 1.9 Hz, 2H), 4.16 (s, 5H).

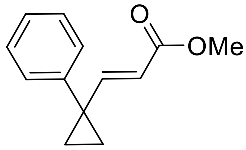
^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.14, 130.90, 128.58, 81.34, 69.69, 68.91, 68.67, 63.01, 0.08.



S31, colorless oil, 95%. Procedure A

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.37 (d, *J* = 17.3 Hz, 1H), 6.07 (dd, *J* = 17.4, 10.5 Hz, 1H), 5.81 (d, *J* = 10.4 Hz, 1H), 4.82 – 4.63 (m, 2H), 3.83 (t, *J* = 8.4 Hz, 1H), 2.86 (d, *J* = 9.3 Hz, 2H), 1.99 – 1.90 (m, 2H), 1.42 (s, 9H).

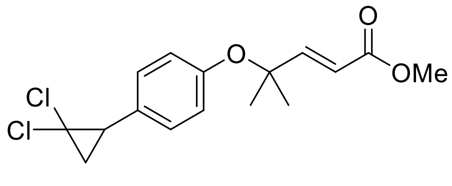
^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.59, 154.92, 131.08, 128.32, 79.66, 62.74, 39.07, 38.47, 28.45.



S46, colorless oil, 89%. Procedure B.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.25 (m, 5H), 6.73 (d, *J* = 15.5 Hz, 1H), 5.32 (d, *J* = 15.5 Hz, 1H), 3.69 (s, 3H), 1.40 – 1.18 (m, 4H).

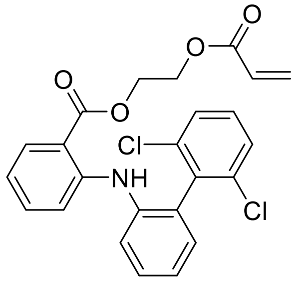
^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.41, 157.31, 141.02, 130.34, 128.60, 127.26, 118.53, 51.36, 29.19, 16.41.



S67, colorless oil, 49%. Procedure B.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.17 (d, *J* = 16.0 Hz, 1H), 7.12 – 7.05 (m, 2H), 6.91 – 6.85 (m, 2H), 5.96 (d, *J* = 16.0 Hz, 1H), 3.75 (s, 3H), 2.82 (dd, *J* = 10.8, 8.3 Hz, 1H), 1.93 (dd, *J* = 10.7, 7.3 Hz, 1H), 1.77 (t, *J* = 7.9 Hz, 1H), 1.46 (s, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.87, 154.81, 153.22, 129.52, 128.80, 121.17, 119.54, 78.54, 60.85, 51.76, 34.88, 26.94, 26.90, 25.87.

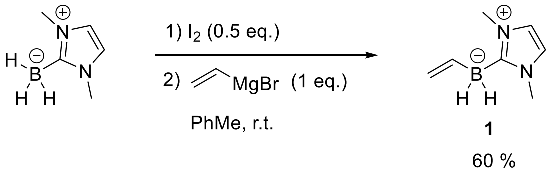


S61, colorless oil, 40%. Procedure C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.1 Hz, 2H), 7.22 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.11 (td, *J* = 7.7, 1.6 Hz, 1H), 7.00 – 6.91 (m, 2H), 6.85 (s, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 6.37 (dd, *J* = 17.4, 1.4 Hz, 1H), 6.08 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.81 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.43 – 4.31 (m, 4H), 3.83 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.27, 165.96, 142.81, 137.88, 131.57, 130.98, 129.59, 128.97, 128.17, 127.94, 124.19, 124.15, 122.17, 118.44, 62.96, 62.17, 38.47, 0.08.

2.2 Synthesis of the vinylborane reagent



To a flame-dried round-bottom flask was added NHC-borane (30 mmol, 1 eq.). Then the flask was evacuated and re-filled with N_2 three times. A solution of I_2 (15 mmol, 0.5 eq.) in dry toluene was then added dropwise at room temperature. After stirring for 1 hour, the solution was cooled to -78 °C, to which was added vinylmagnesium bromide (30 mmol, 1M in THF, 1.0 eq.) dropwise. The reaction was then quenched with water after TLC monitoring. The aqueous phase was extracted with EtOAc three times. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Purification by column chromatography (SiO_2 or Al_2O_3) gave the pure product as a colorless oil with 60% isolation yield.

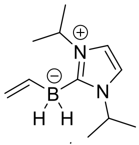
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.83 (s, 2H), 6.31 (t, *J* = 16.2 Hz, 1H), 5.21 (s, 1H), 4.78 (d, *J* = 19.1 Hz, 1H), 3.77 (s, 6H), 2.18 – 1.68 (m, 2H) (BH_2).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -27.94 (t, *J* = 84.3, 1B)

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -27.94 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ170.93 (br, 1C), 150.46 (q, *J* = 52.8, 1C) 120.30, 118.54, 35.93.

HRMS(ESI) m/z (M-H$^+$) calculated for $C_{20}H_{29}BN$ - H$^+$ 135.1099, found 135.1093.



1-I^{i}Pr

1-I^{i}Pr, white solid, 32%

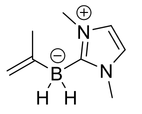
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.96 (s, 2H), 6.39 – 6.29 (m, 1H), 5.21 – 5.10 (m, 3H), 4.72 (d, *J* = 19.4 Hz, 1H), 1.39 (d, *J* = 6.8 Hz, 12H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -27.85 (d, *J* = 84.1 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -27.85 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 117.56, 114.69, 48.57, 22.53.

HRMS(ESI) m/z (M+H$^+$) calculated for $C_{17}H_{23}BN_2O_2$+H$^+$ 193.1871, found 193.1865.



1-Me

1-Me, colorless oil, 37%

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.84 (s, 2H), 4.86 (s, 1H), 4.18 (s, 1H), 3.77 (s, 6H), 1.80 (s, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -26.74 (d, *J* = 84.2 Hz, 1B).

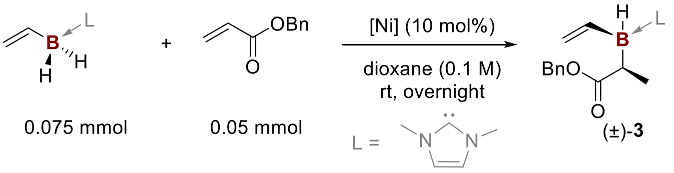
^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -26.74 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 120.23, 112.07, 36.02, 28.22.

HRMS(ESI) m/z (M+H$^+$) calculated for $C_{17}H_{23}BN_2O_2$+H$^+$ 151.1401, found 151.1397.

3. Reaction Optimization

Table S1a. Optimization of different nickel catalysts

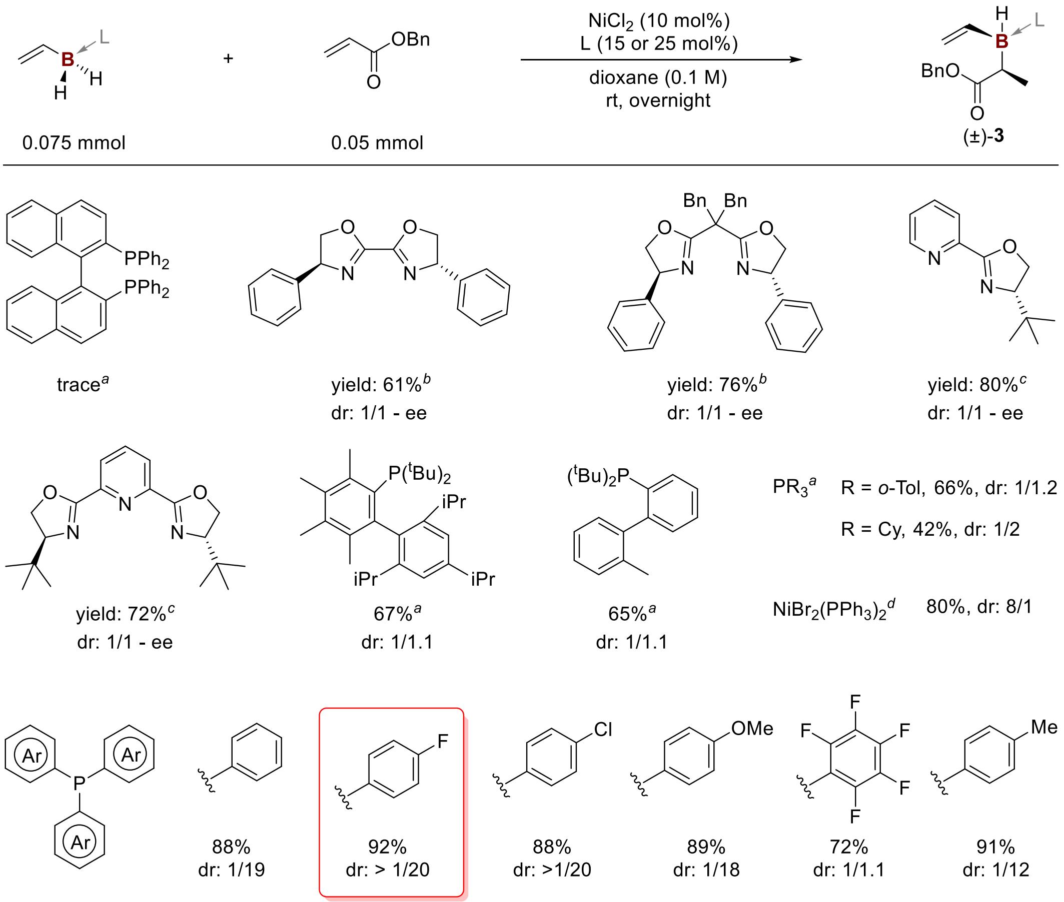


Entry	[Ni]	yield (%)	d.r.
1	$NiBr_2$(DME)	60	1/1.4
2	$NiCl_2$(DME)	69	1/1
3	$NiCl_2$	75	1.1/1
4	$Ni(COD)_2$	56	1/2.3
5	$Ni(acac)_2$	46	1.3/1
6	$Ni(OTf)_2$	63	1.4/1
7	-	N.R.	-

^{1}H NMR yields with 1,3,5-trimethoxybenzene as an internal
The diastereomeric ratio is determined by ^{1}H NMR

Note: Both Ni(II) and Ni(0) catalysts tested were effective in catalyzing the hydroboration, resulting in **3** with moderate to good yields. However, the ligands bonded with nickel center affected the dr values. Without a nickel catalyst, no reaction was observed.

Table S1b. Optimization of ligands



^{a} NiCl$_2$ (5 mol%), Ligand (6 mol% or 12.5 mol%), dioxane (0.1 M), rt, 18 h

^{b} NiBr$_2$(DME) (10 mol%), ligand (15 mol%), THF (0.1 M), rt, 18 h

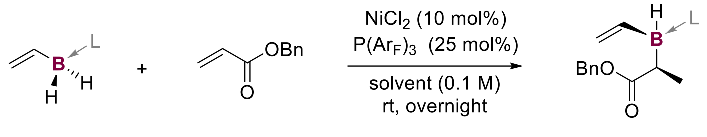
^{c} NiBr$_2$(DME) (10 mol%), ligand (15 mol%), dioxane (0.1 M), rt, 18 h

^{d} NiBr$_2$(PPh$_3$)$_2$ (10 mol%), dioxane (0.1 M), rt, 18 h

^{1}H NMR yield with 1,3,5-trimethoxybenzene as an internal. The diastereomeric ratio is determined by ^{1}H NMR

Note: Multidentate ligands were not effective in improving the drs for **3**, meanwhile some mono-phosphine ligands provided excellent drs of up to > 20:1. This experimental finding is consistent with the proposed reaction mechanism (Fig. 2f), wherein the key transition state, determining the product configuration, only has one vacancy for σ-coordination.

Table S1c. Optimization of solvents



0.075 mmol 0.05 mmol (±)-**3**

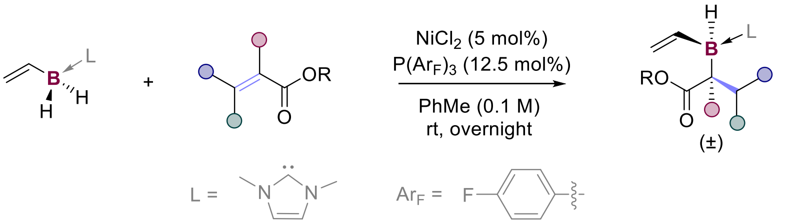
entry	solvent	yield (%)	d.r.
1	dioxane	>95%	>20/1
2	THF	89%	>20/1
3	PhMe	>95%	>20/1
4	MeCN	37%	11/1
5	DMA	87%	14/1
7[a]	PhMe	84%	>20/1
8[b]	PhMe	97%	>20/1

[a] **1** (0.05 mmol), Benzyl acrylate (0.06 mmol)
[b] **1** (0.12 mmol), Benzyl acrylate (0.10 mmol), isolated yield
^{1}H NMR yield with 1,3,5-trimethoxybenzene as an internal, The diastereomeric ratio is determined by ^{1}H NMR

Note: Less polar toluene as the solvent provided the highest yield with an excellent dr of > 20:1.

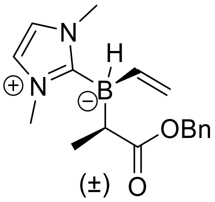
4. Analytical Data of Products

4.1 General procedure for nickel-catalyzed diastereoselective hydroboration



Under an atmosphere of dry N$_2$, NiCl$_2$ (0.005 mmol, 5 mol%) and (*p*-F-Ph)$_3$P (0.0125 mmol, 12.5 mol%) were mixed in a 10 mL Schlenk tube with a stirring bar. Toluene (0.5 mL) was then added. The mixture was stirred for at least 45 min at room temperature. After that, a sequence of alkene (0.1 mmol, 1.0 eq.), toluene (0.5 mL), and borane (0.12 mmol, 1.2 eq.) was added to the reaction mixture. The tube was then tightly sealed and stirred at room temperature for 16 hours. After the reaction, the mixture was quenched under air, and the solvents were evacuated *in vacuo*. The obtained crude mixture was analyzed by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard and then subjected to flash column chromatography on neutral aluminum oxide (200 – 300 mesh) to give the corresponding products.

4.2 Analytical data of products.



3, major configuration, colorless oil, 97%, d.r. > 20/1.

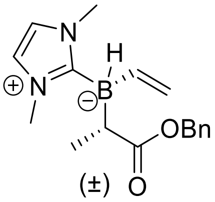
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 – 7.24 (m, 3H), 7.16 – 7.14 (m, 2H), 6.57 (s, 2H), 6.32 – 6.36 (m, 1H), 5.29 (br, 1H), 4.88 (d, *J* = 21.2 Hz, 1H), 4.79 – 4.67 (m, 2H), 3.62 (s, 6H), 2.03 (s, 1H), 1.22 (d, *J* = 6.1 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.92 (d, *J* = 88.0 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.92 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.63, 137.40, 128.39, 128.30, 127.69, 120.66, 119.40, 64.67, 36.61, 16.39.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{17}H_{23}BN_2O_2$+Na$^+$ 321.1745, found 321.1754.



Minor configuration, colorless oil

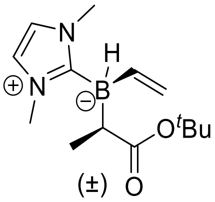
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36-7.30 (m, 4H), 7.28-7.25 (m, 1H), 6.76 (s, 2H), 6.41 – 6.35 (m, 1H), 5.31 (br, 1H), 5.07 – 5.02 (m, 2H), 4.98 (d, *J* = 19.2 Hz, 1H), 3.69 (s, 6H), 2.08 (sbr, 1H), 0.97 (d, *J* = 6.8 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.97 (d, *J* = 87.6 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.92 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.54, 137.67, 128.34, 128.13, 127.57, 121.01, 119.76, 64.86, 36.75, 16.09.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{17}H_{23}BN_2O_2$+Na$^+$ 321.1745, found 321.1754.



4, White crystal, 75%, d.r. > 20/1.

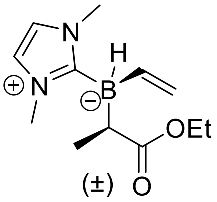
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.83 (s, 2H), 6.31 (m, 1H), 5.30 (s, 1H), 4.87 (d, *J* = 19.6 Hz, 1H), 3.79 (s, 6H), 1.91 (s, 1H), 1.16 (d, *J* = 6.5 Hz, 3H), 1.13 (s, 9H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.94 (d, *J* = 87.8 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.94 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.57, 120.79, 118.99, 76.62, 36.77, 28.08, 16.43.

HRMS(ESI) m/z (M+Na^{++}) calculated for $C_{14}H_{25}BN_2O_2$+Na$^+$ 287.1901, found 287.1910.



5, colorless oil, 81%, d.r. > 20/1.

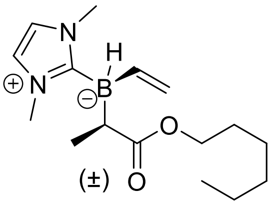
^{1}H NMR (400 MHz, Chloroform-d) δ 6.81 (s, 2H), 6.38 – 6.29 (m, 1H), 5.33 (br, 1H), 4.94 (d, *J* = 19.4 Hz, 1H), 3.81 – 3.73 (m, 1H), 3.78 (s, 6H), 3.70 – 3.62 (m, 1H), 1.98 (s, 1H), 1.19 (d, *J* = 5.3 Hz, 3H), 0.93 (t, *J* = 7.1 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-d) δ -18.72 (d, *J* = 88.0 Hz, 1B).

^{11}B {1H} NMR (193 MHz, Chloroform-d) δ -18.72 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-d) δ 182.87, 120.73, 119.37, 58.28, 36.68, 16.22, 14.28.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{12}H_{21}BN_2O_2$+Na$^+$ 259.1588, found 259.1599.



6, colorless oil, 98%, d.r. > 20/1.

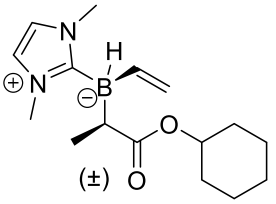
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.79 (s, 2H), 6.35 – 6.29 (m, 1H), 5.31 (br, 1H), 4.93 (d, *J* = 19.4 Hz, 1H), 3.76 (s, 6H), 3.75 – 3.70 (m, 1H), 3.56 – 3.51 (m, 1H), 1.98 – 1.96 (m, 1H), 1.35 – 1.22 (m, 4H), 1.20 – 1.18 (m, 7H), 0.86 (t, *J* = 7.2 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.91 (d, *J* = 88.1 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.91 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 183.02, 120.80, 119.43, 62.86, 36.75, 31.60, 28.87, 25.72, 22.62, 16.31, 14.08.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{16}H_{29}BN_2O_2+Na^+$ 315.2214, found 315.2226.



7, colorless oil, 98%, d.r. > 20/1.

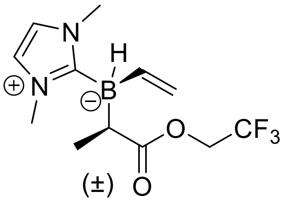
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.78 (s, 2H), 6.32 – 6.26 (m, 1H), 5.30 (br, 1H), 4.87 (d, *J* = 19.6 Hz, 1H), 4.39 – 4.35 (m, 1H), 3.75 (s, 6H), 1.96 – 1.64 (m, 1H), 1.70 – 1.66 (m, 1H), 1.65 – 1.59 (m, 1H), 1.55 – 1.49 (m, 1H), 1.47 – 1.44 (m, 1H), 1.39 – 1.33 (m, 1H), 1.26 – 1.06 (m, 7H), 0.79 – 0.73 (m, 1H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.92 (d, *J* = 87.9 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.92 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.43, 120.81, 119.15, 69.99, 36.78, 32.15, 31.79, 25.59, 24.08, 24.05, 16.45.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{16}H_{29}BN_2O_2$+Na$^+$ 313.2058, found 313.2069.



8, colorless oil, 78%, d.r. = 16/1.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.79 (s, 2H), 6.32 – 6.26 (m, 1H), 5.31 (br, 1H), 4.89 (d, *J* = 19.7 Hz, 1H), 4.13 – 4.03 (m, 2H), 3.76 (s, 6H), 2.12 – 2.07 (m, 1H), 1.23 (d, *J* = 6.1 Hz, 3H).

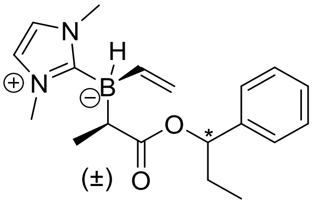
^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.84 (d, *J* = 88.8 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.84 (s, 1B).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -73.47 (t, *J* = 8.8 Hz) (minor configuration), -74.04 (t, *J* = 9.0 Hz) (major configuration).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 181.00, 123.56 (q, *J* = 277.8 Hz, 1C), 121.03, 119.67, 59.34 (q, *J* = 35.5 Hz, 1C), 36.64, 16.25.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{12}H_{18}BF_3N_2O_2$+Na$^+$ 313.1306, found 313.1313.



9, colorless oil, 93%, d.r. > 20/1.

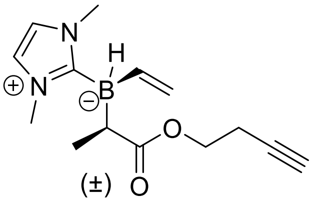
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.26 (m, 1H), 7.25 – 7.21 (m, 3H), 7.09 – 7.11 (m, 1H), 6.72 (s, 1H), 6.39 (s, 1H), 6.35 – 6.21 (m, 1H), 5.44 (t, *J* = 6.8 Hz, 0.5H), 5.35 (t, *J* = 6.9 Hz, 0.5H), 5.29 (br, 1H), 4.90 – 4.80 (m, 1H), 3.58 (s, 3H), 3.57 (s, 3H), 2.07 – 2.01 (m, 1H), 1.85 – 1.78 (m, 0.5H), 1.67 – 1.60 (m, 1H), 1.53 – 1.46 (m, 1H), 1.23 (d, *J* = 6.2 Hz, 3H), 0.76 (t, *J* = 7.4 Hz, 1.5H), 0.72 (t, *J* = 7.4 Hz, 1.5H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -18.03 (d, *J* = 88.4 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -18.03 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.36/181.88, 141.71/141.38, 128.17/128.09, 127.38/127.33, 127.22/126.91, 120.77/120.45, 119.24/119.19, 75.34/74.83, 36.54, 29.30, 16.59/16.29, 10.01/9.84.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{19}H_{27}BN_2O_2$+Na$^+$ 349.2058, found 349.2071.



10, colorless oil, 50%, d.r. > 20/1.

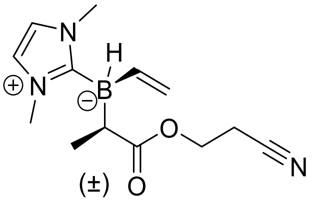
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.81 (s, 2H), 6.34 – 6.28 (m, 1H), 5.32 (br, 1H), 4.93 (d, *J* = 19.5 Hz, 1H), 3.91 – 3.83 (m, 1H), 3.78 (s, 6H), 3.73 – 3.66 (m, 1H), 2.24 – 2.19 (m, 1H), 2.15 – 2.09 (m, 1H), 2.05 – 1.99 (m, 1H), 1.93 (t, *J* = 2.7 Hz, 1H), 1.20 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.89 (d, *J* = 88.7 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.89 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.52, 120.89, 119.57, 80.92, 69.45, 60.48, 36.81, 19.13, 16.26.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{14}H_{21}BN_2O_2$+Na$^+$ 283.1588, found 283.1599.



11, colorless oil, 88%, d.r. = 15/1.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.84 (s, 2H), 6.33 – 6.26 (m, 1H), 5.32 (br, 1H), 4.93

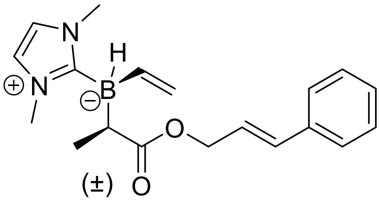
(d, *J* = 19.3 Hz, 1H), 4.02 – 3.99 (m, 1H), 3.79 (s, 6H), 3.72 – 3.68 (m, 1H), 2.48 – 2.43 (m, 1H), 2.34 – 2.29 (s, 1H), 2.04 – 2.02 (m, 1H), 1.19 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.85 (d, *J* = 89.0 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.85 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.22, 121.10, 119.82, 117.58, 57.19, 36.85, 36.82, 18.23, 16.21.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{13}H_{20}BN_3O_2$+Na$^+$ 284.1541, found 284.1550.



12, colorless oil, 76%, d.r. > 20/1.

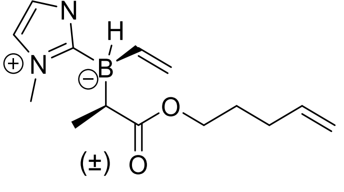
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 – 7.31 (m, 4H), 7.27 – 7.25 (m, 1H), 6.64 (s, 2H), 6.46 – 6.43 (m, 1H), 6.35 – 6.29 (m, 1H), 5.96 (dt, *J* = 15.8, 6.6 Hz, 1H), 5.32 (br, 1H), 4.92 (d, *J* = 19.1 Hz, 1H), 4.40 – 4.31 (m, 2H), 3.71 (s, 6H), 2.04 – 2.04 (m, 1H), 1.23 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.84 (d, *J* = 88.4 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.84 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.55, 136.66, 133.15, 128.71, 127.99, 126.51, 124.71, 120.79, 119.48, 63.36, 36.74, 16.35.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{19}H_{25}BN_2O_2$+Na$^+$ 347.1901, found 347.1912.



13, colorless oil, 88%, d.r. > 20/1.

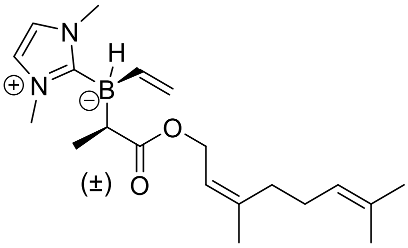
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.80 (s, 2H), 6.36 – 6.30 (m, 1H), 5.78 – 5.71 (m, 1H), 5.32 (br, 1H), 5.00 – 4.96 (m, 1H), 4.96 – 4.90 (m, 2H), 3.77 (s, 6H), 3.75 – 3.78 (m, 1H), 3.61 – 3.57 (m, 1H), 2.01 – 1.96 (m, 3H), 1.48 – 1.36 (m, 2H), 1.20 (d, *J* = 6.5 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.91 (d, *J* = 88.3 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.91 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.93, 137.94, 120.83, 119.48, 114.95, 62.15, 36.75, 30.18, 28.16, 16.29.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{15}H_{25}BN_2O_2$+Na^{+} 299.1901, found 299.1910.



14, colorless oil, 93%, d.r. > 20/1.

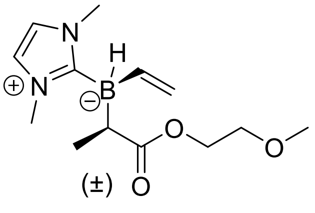
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.77 (s, 2H), 6.34 – 6.28 (m, 1H), 5.31 (br, 1H), 5.05 – 5.02 (m, 1H), 4.96 – 4.88 (m, 2H), 4.23 – 4.11 (m, 2H), 3.75 (s, 6H), 2.03 – 1.94 (m, 5H), 1.67 (s, 3H), 1.65 (s, 3H), 1.57 (s, 3H), 1.19 (d, *J* = 6.5 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.91 (d, *J* = 88.2 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.91 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.84, 140.23, 132.09, 123.78, 120.77, 120.56, 119.39, 59.32, 36.74, 32.19, 26.77, 25.77, 23.65, 17.74, 16.39.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{20}H_{33}BN_2O_2$+Na^{+} 367.2527, found 367.2537.



15, colorless oil, 98%, d.r. > 20/1.

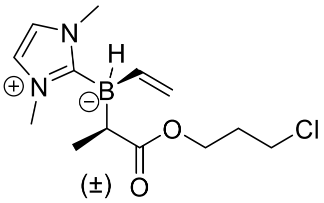
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.77 (s, 2H), 6.33 – 6.27 (m, 1H), 5.30 (br, 1H), 4.92 (d, *J* = 19.4 Hz, 1H), 3.91 – 3.88 (m, 1H), 3.75 (s, 6H), 3.64 – 3.59 (m, 1H), 3.35 – 3.31 (m, 1H), 3.27 (s, 3H), 3.26 – 3.23 (m, 1H), 2.04 – 1.98 (m, 1H), 1.18 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.89 (d, *J* = 88.4 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.89 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.83, 120.83, 119.41, 70.95, 61.75, 58.82, 36.74, 16.38.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{13}H_{23}BN_2O_3$+Na$^+$ 289.1694, found 289.1711.



16, colorless oil, 93%, d.r. > 20/1.

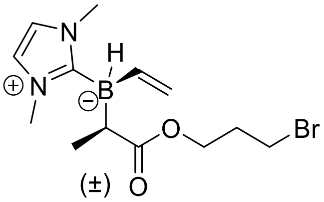
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.83 (s, 2H), 6.36 – 6.30 (m, 1H), 5.33 (br, 1H), 4.94 (d, *J* = 18.1 Hz, 1H), 3.96 – 3.90 (m 1H), 3.78 (s, 6H), 3.76 – 3.70 (m, 1H), 3.54 – 3.42 (m, 2H), 1.98 – 2.00 (m, 1H), 1.90 – 1.77 (m, 2H), 1.19 (d, *J* = 6.5 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.90 (d, *J* = 88.6 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.90 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.72, 120.96, 119.64, 59.34, 41.67, 36.77, 32.09, 16.24.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{13}H_{22}BClN_2O_2$+Na$^+$ 307.1355, found 307.1364.



17, colorless oil, 80%, d.r.= 16/1.

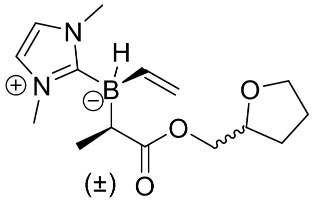
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.82 (s, 2H), 6.36 – 6.26 (m, 1H), 5.31 (br, 1H), 4.92 (d, *J* = 19.5 Hz, 1H), 3.94 – 3.87 (m, 1H), 3.77 (s, 6H), 3.74 – 3.68 (m, 1H), 3.36 – 3.27 (m, 2H), 2.02 – 1.96 (m, 1H), 1.96 – 1.79 (m, 2H), 1.17 (d, *J* = 6.5 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.90 (d, *J* = 88.2 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.90 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.69, 120.99, 119.66, 60.39, 36.82, 32.33, 30.11, 16.27.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{13}H_{22}BBrN_2O_2$+Na^{+} 351.0850, found 351.0858.



18, colorless oil, 86%, d.r. > 20/1.

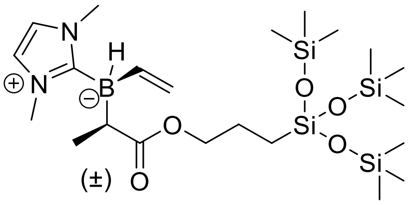
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.79 (s, 1H), 6.77 (s, 1H), 6.35 – 6.27 (m, 1H), 5.31 (br, 1H), 4.99 – 4.86 (m, 1H), 3.86 – 3.67 (m, 4H), 3.76 (d, *J* = 2.0 Hz, 6H), 3.56 – 3.52 (m, 0.5H), 3.40 – 3.34 (m, 0.5H), 2.05 – 1.96 (m, 1H), 1.89 – 1.79 (m, 3H), 1.51 – 1.44 (m, 1H), 1.19 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.87 (d, *J* = 88.6 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.87 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.81/182.78, 120.85, 119.40, 76.92, 68.27/68.18, 65.22/64.95, 36.75, 28.21/28.03, 25.71/25.63, 16.41.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{15}H_{25}BN_2O_3$+Na^{+} 315.1850, found 315.1864.



19, colorless oil, 79%, d.r. > 20/1.

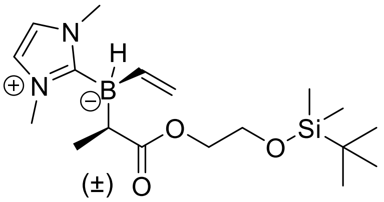
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.77 (s, 2H), 6.36 – 6.27 (m, 1H), 5.31 (br, 1H), 4.96 – 4.90 (m, 1H), 3.75 (s, 6H), 3.73 – 3.68 (m, 1H), 3.48 – 3.42 (m, 1H), 1.98 – 1.96 (m, 1H), 1.37 – 1.32 (m, 2H), 1.18 (d, *J* = 6.5 Hz, 3H), 0.38 – 0.23 (m, 2H), 0.08 (s, 27H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.94 (d, *J* = 88.1 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.94 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.95, 120.78, 119.44, 65.18, 36.74, 22.90, 16.35, 10.62, 1.83.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{22}H_{49}BN_2O_5Si_4$+Na$^+$ 567.2704, found 567.2713.



20, colorless oil, 94%, d.r. > 20/1.

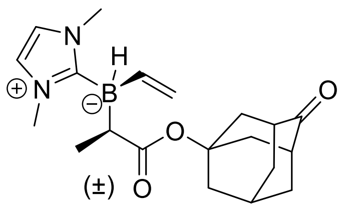
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.77 (s, 2H), 6.35 – 6.27 (m, 1H), 5.31 (br, 1H), 4.93 (d, *J* = 18.1 Hz, 1H), 3.89 – 3.83 (m, 1H), 3.75 (s, 6H), 3.59 – 3.42 (m, 3H), 2.00 – 1.93 (m, 1H), 1.18 (d, *J* = 6.4 Hz, 3H), 0.86 (s, 9H), 0.02 (s, 6H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.89 (d, *J* = 88.3 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.89 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.75, 120.82, 119.50, 63.93, 61.66, 36.76, 25.97, 18.43, 16.36, -5.19.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{18}H_{35}BN_2O_3Si$+Na$^+$ 389.2402, found 389.2410.



21, white crystal, 76%, d.r. = 20/1.

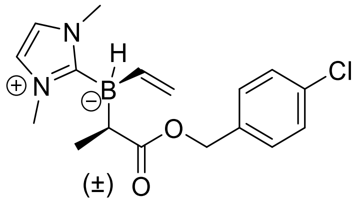
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.82 (s, 2H), 6.29 – 6.22 (m, 1H), 5.27 (br, 1H), 4.86 – 4.82 (m, 1H), 3.75 (s, 6H), 2.51 – 2.47 (m, 2H), 2.23 – 2.16 (m, 2H), 2.11 – 2.04 (m, 3H), 1.93 – 1.80 (m, 6H), 1.12 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.89 (d, *J* = 88.5 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.89 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 216.44, 182.32, 120.87, 119.31, 74.34, 47.11, 47.07, 41.88, 41.22, 39.78, 38.27, 38.24, 36.81, 29.70, 16.30.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{20}H_{29}BN_2O_3$+Na$^+$ 379.2163, found 379.2172.



22, colorless oil, 91%, d.r. > 20/1.

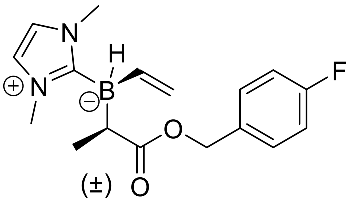
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 – 7.22 (m, 2H), 7.11 – 7.08 (m, 2H), 6.61 (s, 2H), 6.31 – 6.35 (m, 1H), 5.28 (br, 1H), 4.90 – 4.84 (m, 1H), 4.76 – 4.65 (m, 2H), 3.63 (s, 6H), 2.03 – 2.01 (m, 1H), 1.21 (d, *J* = 6.3 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.92 (d, *J* = 88.3 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.92 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.48, 136.00, 133.48, 129.75, 128.44, 120.68, 119.51, 63.80, 36.64, 16.33.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{17}H_{22}BClN_2O_2$+Na$^+$ 355.1355, found 355.1375.



23, colorless oil, 94%, d.r. > 20/1.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.17 – 7.11 (m, 2H), 6.98 – 6.92 (m, 2H), 6.60 (s, 2H), 6.31 – 6.25 (m, 1H), 5.28 (br, 1H), 4.87 (d, *J* = 18.7 Hz, 1H), 4.76 – 4.64 (m, 2H), 3.62 (s, 6H), 2.02 (s, 1H), 1.21 (d, *J* = 6.4 Hz, 3H).

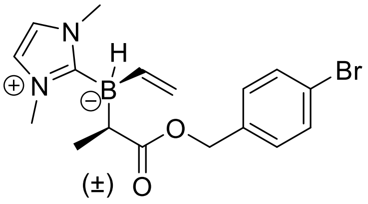
^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.93 (d, *J* = 88.0 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.93 (s, 1B).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.51 (s) (major configuration), -115.00 (s) (minor configuration).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.56, 162.34 (d, *J* = 246.1 Hz, 1C), 133.33 (d, *J* = 3.2 Hz), 130.22 (d, *J* = 8.0 Hz), 120.67, 119.48, 115.11 (d, *J* = 21.2 Hz), 63.89, 36.63, 16.33.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{17}H_{22}BFN_2O_2$+Na$^+$ 339.1651, found 339.1660.



24, colorless oil, 92%, d.r. > 20/1.

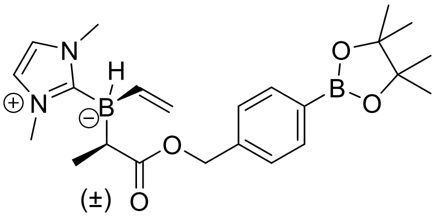
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 – 7.30 (m, 2H), 7.12 – 6.95 (m, 2H), 6.61 (s, 2H), 6.31 – 6.24 (m, 1H), 5.28 (br, 1H), 4.87 (d, *J* = 20.9 Hz, 1H), 4.76 – 4.58 (m, 2H), 3.62 (s, 6H), 2.05 – 1.99 (m, 1H), 1.21 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.92 (d, *J* = 88.6 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.92 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.47, 136.51, 131.41, 130.08, 121.59, 120.69, 119.51, 63.82, 36.64, 16.34.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{17}H_{22}BBrN_2O_2$+Na$^+$ 399.0850, found 399.0867.



25, colorless oil, 33%, d.r. > 20/1.

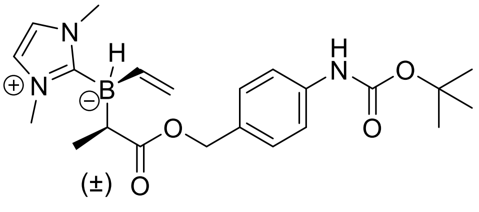
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 6.57 (s, 2H), 6.34 – 6.25 (m, 1H), 5.29 (br, 1H), 4.89 (dd, *J* = 19.1, 4.4 Hz, 1H), 4.80 (d, *J* = 12.6 Hz, 1H), 4.65 (d, *J* = 12.6 Hz, 1H), 3.63 (s, 6H), 2.08 – 2.01 (m, 1H), 1.34 (s, 12H), 1.23 (d, *J* = 6.5 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ 29.83 (s,1B), -18.02 (d, *J* = 87.6 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ 29.83 (s,1B), -18.02 (s,1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.69, 140.43, 134.81, 127.48, 120.74, 119.50, 83.99, 64.69, 36.69, 24.99, 16.43.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{23}H_{34}B_2N_2O_4$+Na$^+$ 447.2597, found 447.2608.



26, colorless oil, 62%, d.r. > 20/1.

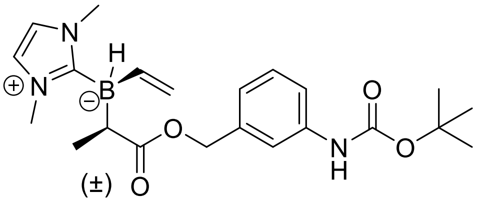
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 – 7.23 (m, 2H), 7.08 – 7.00 (m, 2H), 6.58 (s, 2H), 6.30 – 6.24 (m, 1H), 5.34 – 5.23 (m, 1H), 4.82 – 4.87 (m, 1H), 4.66 (q, *J* = 12.1 Hz, 2H), 3.59 (s, 6H), 2.00 (s, 1H), 1.50 (s, 9H), 1.20 (d, *J* = 6.3 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.94 (d, *J* = 88.4 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.94 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.74, 152.89, 137.96, 132.03, 129.43, 120.74, 119.33, 118.50, 80.70, 64.30, 36.58, 28.43, 16.41.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{22}H_{32}BN_3O_4+Na^+$ 436.2378, found 436.2385.



27, colorless oil, 76%, d.r. > 20/1.

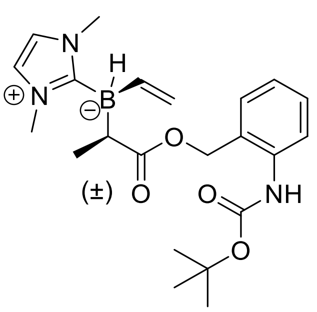
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 – 7.14 (m, 3H), 6.83 (d, *J* = 7.1 Hz, 1H), 6.62 (s, 2H), 6.58 (s, 1H), 6.34 – 6.25 (m, 1H), 5.29 (br, 1H), 4.89 (dd, *J* = 19.4, 4.6 Hz, 1H), 4.73 (d, *J* = 12.2 Hz, 1H), 4.58 (d, *J* = 12.2 Hz, 1H), 3.64 (s, 6H), 2.08 – 1.98 (m, 1H), 1.52 (s, 9H), 1.23 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.91 (d, *J* = 87.9 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.91 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.72, 152.89, 138.47, 138.20, 128.91, 119.42, 118.73, 118.13, 80.71, 64.68, 36.64, 28.45, 16.43.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{22}H_{32}BN_3O_4+Na^+$ 436.2378, found 436.2389.



28, colorless oil, 78%, d.r. = 9/1.

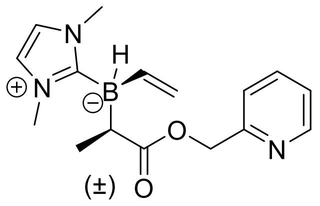
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.08 – 7.05 (m, 1H), 6.95 – 6.91 (m, 1H), 6.43 (s, 2H), 6.27 – 6.20 (m, 1H), 5.33 – 5.20 (m, 1H), 4.91 – 4..89 (m, 1H), 4.87 – 4.81 (m, 1H), 4.73 – 4.69 (m, 1H), 3.48 (s, 6H), 2.04 – 1.98 (m, 1H), 1.52 (s, 9H), 1.22 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.95 (d, *J* = 88.4 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.95 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 183.23, 153.38, 137.92, 131.38, 129.27, 122.78, 120.99, 120.65, 119.49, 80.25, 62.05, 36.35, 28.51, 16.41.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{22}H_{32}BN_3O_4$+Na$^+$ 436.2378, found 436.2388.



29, yellow oil, 89%, d.r. > 20/1.

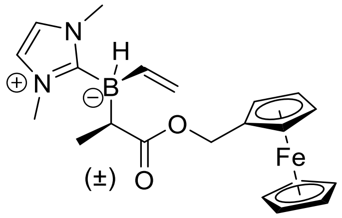
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.55 – 8.47 (m, 1H), 7.67 – 7.62 (m, 1H), 7.28 – 7.27 (m, 1H), 7.18 – 7.15 (m, 1H), 6.68 (s, 2H), 6.38 – 6.30 (m, 1H), 5.33 (br, 1H), 4.98 (d, *J* = 13.6 Hz, 1H), 4.97 – 4.91 (m, 1H), 4.69 (d, *J* = 13.6 Hz, 1H), 3.72 (s, 6H), 2.14 – 2.07 (m, 1H), 1.27 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.83 (d, *J* = 88.2 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.83 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.29, 157.43, 149.07, 136.58, 122.43, 121.73, 120.81, 119.62, 65.60, 36.70, 16.31.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{16}H_{22}BN_3O_2$+Na$^+$ 322.1697, found 322.1713.



30, yellow oil, 94%, d.r. > 20/1.

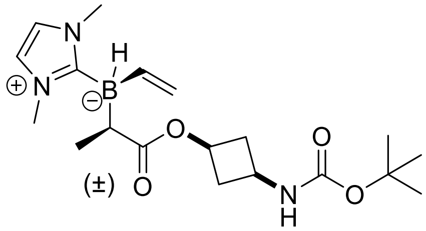
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.63 (s, 2H), 6.32 – 6.23 (m, 1H), 5.28 (br, 1H), 4.92 – 4.83 (m, 1H), 4.60 – 4.47 (m, 2H), 4.18 – 3.98 (m, 9H), 3.62 (s, 6H), 2.00 – 1.91 (m, 1H), 1.20 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.98 (d, *J* = 88.4 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.98 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.62, 120.77, 119.23, 82.62, 69.94, 69.72, 68.54, 68.33, 68.27, 60.87, 36.69, 16.46.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{21}H_{27}BFeN_2O_2$+Na$^+$ 429.1407, found 429.1423.



31, colorless oil, 99%, d.r. > 20/1.

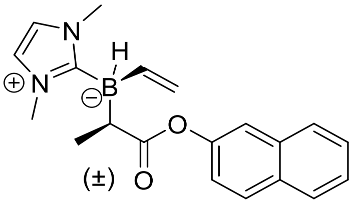
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.79 (s, 2H), 6.31 – 6.24 (m, 1H), 5.33 – 5.25 (m, 1H), 4.94 – 4.86 (m, 1H), 4.57 (s, 1H), 4.28 (p, *J* = 7.4 Hz, 1H), 3.73 (s, 6H), 3.69 – 3.49 (m, 1H), 2.69 – 2.60 (m, 1H), 2.53 – 2.45 (m, 1H), 1.95 – 1.89 (m, 1H), 1.73 – 1.52 (m, 1H), 1.39 (s, 9H), 1.14 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.93 (d, *J* = 88.5 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.93 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.25, 154.93, 120.87, 119.56, 60.34, 39.17, 39.07, 36.76, 28.45, 16.14.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{14}H_{25}BN_2O_2$+Na$^+$ 287.2901, found 287.2910.



32, colorless oil, 91%, d.r. = 11/1.

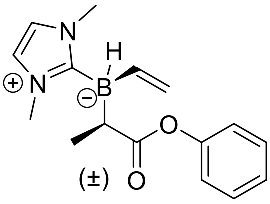
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 – 7.76 (m, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.68 (d, *J* = 1.1 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.12 (d, *J* = 2.2 Hz, 1H), 6.85 – 6.81 (m, 3H), 6.45 – 6.37 (m, 1H), 5.40 (br, 1H), 5.05 – 4.98 (m, 1H), 3.83 (s, 6H), 2.32 – 2.28 (m, 1H), 1.37 (d, *J* = 6.3 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.66 (d, *J* = 88.7 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.66 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 181.20, 149.34, 133.92, 130.98, 128.91, 127.73, 127.44, 126.28, 125.17, 121.70, 121.12, 119.83, 118.05, 36.89, 16.46.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{20}H_{23}BN_2O_2$+Na$^+$ 357.1745, found 357.1748.



33, colorless oil, 98%, d.r. = 11/1.

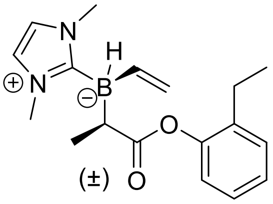
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 – 7.20 (m, 2H), 7.08 – 7.04 (m, 1H), 6.82 (s, 2H), 6.65 – 6.62 (m, 2H), 6.39 – 6.33 (m, 1H), 5.36 (br, 1H), 4.97 (d, *J* = 19.4 Hz, 1H), 3.81 (s, 6H), 2.24 – 2.20 (m, 1H), 1.31 (d, *J* = 6.3 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.73 (d, *J* = 88.7 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.73 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 181.06, 151.61, 129.11, 124.67, 121.60, 121.09, 119.73, 36.87, 16.44.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{16}H_{21}BN_2O_2$+Na$^+$ 307.1588, found 307.1599.



34, colorless oil, 80%, d.r. = 11/1.

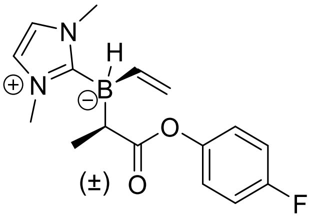
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.20 – 7.14 (m, 1H), 7.07 – 7.04 (m, 2H), 6.82 (s, 2H), 6.42 – 6.33 (m, 2H), 5.36 (br, 1H), 5.05 – 4.90 (m, 1H), 3.84 (s, 6H), 2.52 – 2.39 (m, 2H), 2.30 – 2.24 (m, 1H), 1.36 (d, *J* = 6.4 Hz, 3H), 1.14 (t, *J* = 7.6 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.79 (d, *J* = 88.5 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.79 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 181.04, 149.69, 136.32, 129.17, 126.43, 125.12, 121.92, 121.10, 119.55, 36.87, 23.19, 16.63, 14.33.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{18}H_{25}BN_2O_2$+Na$^+$ 335.1901, found 335.1917.



35, colorless oil, 98%, d.r. = 10/1.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.93 – 6.87 (m, 2H), 6.83 (s, 2H), 6.65 – 6.53 (m, 2H), 6.38 – 6.31 (m, 1H), 5.35 (br, 1H), 4.96 (d, *J* = 19.2 Hz, 1H), 3.80 (s, 6H), 2.24 – 2.19 (m, 1H), 1.29 (d, *J* = 6.2 Hz, 3H).

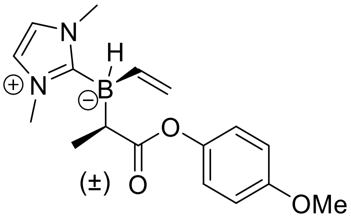
^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.74 (d, *J* = 89.4 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.74 (s, 1B).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -118.76 (s) (major configuration), -118.98 (s) (minor configuration).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 181.07, 159.59 (d, *J* = 242.7 Hz, 1C), 147.47 (d, *J* = 2.8 Hz, 2C), 122.83 (d, *J* = 8.4 Hz, 2C), 121.10, 119.86, 115.66 (d, *J* = 23.1 Hz, 2C), 36.86, 16.34.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{16}H_{20}BFN_2O_2$+Na^{+} 325.1494, found 325.1504.



36, colorless oil, 99%, d.r. = 12/1.

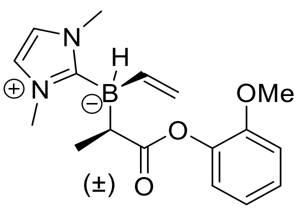
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.83 (s, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.55 (d, *J* = 8.9 Hz, 2H), 6.41 – 6.33 (m, 1H), 5.36 (br, 1H), 5.03 – 4.92 (m, 1H), 3.81 (s, 6H), 3.74 (s, 3H), 2.24 – 2.19 (m, 1H), 1.31 (d, *J* = 6.3 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.75 (d, *J* = 88.7 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.75 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 181.42, 156.47, 145.11, 122.30, 121.07, 119.69, 114.23, 55.63, 36.86, 16.47.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{17}H_{23}BN_2O_3$+Na^{+} 337.1694, found 337.1703.



37, colorless oil, 33%, d.r. = 13/1.

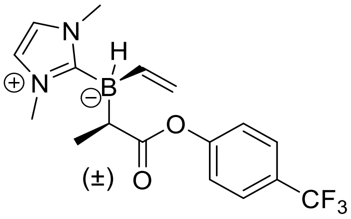
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.10 – 7.04 (m, 1H), 6.88 – 6.86 (m, 1H), 6.83 (s, 2H), 6.81 – 6.78 (m, 1H), 6.50 – 6.25 (m, 2H), 5.36 (br, 1H), 4.97 (d, *J* = 19.4 Hz, 1H), 3.83 (s, 6H), 3.75 (s, 3H), 2.29 (s, 1H), 1.35 (d, *J* = 6.3 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.78 (d, *J* = 88.7 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.78 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 180.70, 151.81, 140.85, 125.81, 122.67, 120.98, 120.58, 119.52, 112.63, 56.03, 36.88, 16.69.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{17}H_{23}BN_2O_3+Na^+$ 337.1694, found 337.1711.



38, colorless oil, 80%, d.r. = 12/1.

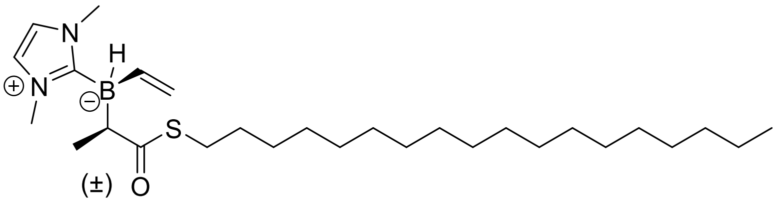
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.7 Hz, 2H), 6.84 (s, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.39 – 6.33 (m, 1H), 5.37 (br, 1H), 5.03 – 4.93 (m, 1H), 3.81 (s, 6H), 2.26 – 2.23 (m, 1H), 1.32 (d, *J* = 6.3 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.69 (d, *J* = 88.8 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.69 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 180.46, 154.32, 127.00 (q, *J* = 33.2 Hz, 1C), 126.46 (q, *J* = 4.3 Hz, 2C), 124.13 (q, *J* = 273.3 Hz, 1c), 121.91, 121.14, 120.03, 36.86, 16.22

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{17}H_{20}BF_3N_2O_2+Na^+$ 375.1462, found 375.1465.



39, colorless oil, 56%, d.r. > 20/1.

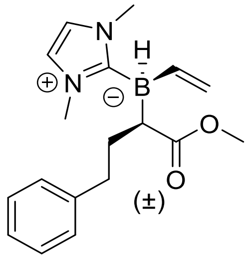
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.82 (s, 2H), 6.35 – 6.24 (m, 1H), 5.42 – 5.25 (m, 1H), 5.16 – 5.04 (m, 1H), 3.84 (s, 6H), 2.40 – 2.19 (m, 2H), 1.53 – 1.42 (m, 2H), 1.34 – 1.18 (m, 33H), 0.86 (t, *J* = 6.8 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.65 (d, *J* = 99.2 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.65 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 121.16, 120.26, 36.80, 32.97, 32.03, 31.39, 29.82, 29.77, 29.60, 29.59, 29.47, 22.80, 14.24.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{28}H_{53}BN_2OS$+Na$^+$ 499.3864, found 499.3871.



40, colorless oil, 95%, d.r. > 20/1.

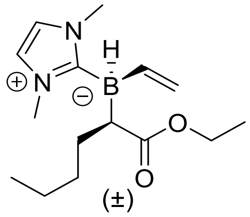
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 – 7.22 (m, 2H), 7.21 – 7.18 (m, 2H), 7.15 – 7.11 (m, 1H), 6.78 (s, 2H), 6.33 – 6.25 (m, 1H), 5.31 (br, 1H), 4.95 (dd, *J* = 19.6, 4.5 Hz, 1H), 3.74 (s, 6H), 3.25 (s, 3H), 2.71 – 2.65 (m, 1H), 2.53 – 2.48 (m, 1H), 2.14 – 2.07 (m, 1H), 2.02 – 1.96 (m, 1H), 1.92 – 1.86 (m, 1H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -18.51 (d, *J* = 88.4 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -18.51 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.02, 143.69, 128.72, 128.08, 125.27, 120.88, 119.75, 50.15, 37.24, 36.74, 34.10.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{18}H_{25}BN_2O_2$+Na$^+$ 355.1901, found 355.1912.



41, colorless oil, 98%, d.r. > 20/1.

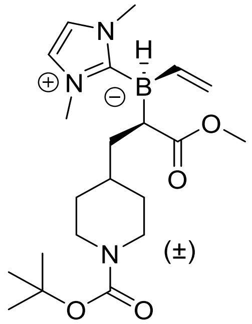
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.78 (s, 2H), 6.34 – 6.27 (m, 1H), 5.32 (br, 1H), 5.01 – 4.92 (m, 1H), 3.77 (s, 6H), 3.76 – 3.71 (m, 1H), 3.66 – 3.59 (m, 1H), 1.93 – 1.87 (m, 1H), 1.81 – 1.72 (m, 1H), 1.61 – 1.55 (m, 1H), 1.35 – 1.27 (m, 3H), 1.23 – 1.16 (m, 1H), 0.93 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -19.55 (d, *J* = 88.1 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -19.55 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.16, 120.85, 119.46, 58.28, 36.84, 33.46, 32.13, 23.11, 14.45, 14.33.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{15}H_{27}BN_{2}O_{2}$+Na^{+} 301.2058, found 301.2078.-



42, colorless oil, 91%, d.r. > 20/1.

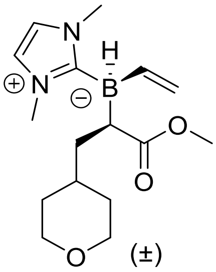
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.81 (s, 2H), 6.31 – 6.20 (m, 1H), 5.40 – 5.28 (m, 1H), 5.00 (dd, *J* = 19.2, 4.5 Hz, 1H), 4.02 (s, 2H), 3.77 (s, 6H), 3.21 (s, 3H), 2.73 – 2.54 (m, 2H), 2.10 – 2.01 (m, 1H), 1.87 – 1.81 (m, 1H), 1.74 (d, *J* = 13.1 Hz, 1H), 1.63 – 1.54 (m, 1H), 1.50 – 1.40 (m, 10H), 1.40 – 1.29 (m, 1H), 1.16 – 0.96 (m, 2H)...

^{11}B NMR (128 MHz, Chloroform-*d*) δ -18.82 (d, *J* = 89.1 Hz, 1B).

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -18.82 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.24, 155.03, 120.92, 119.84, 79.03, 50.18, 38.98, 37.00, 36.74, 28.57.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{21}H_{36}BN_2O_3$+Na^{+} 428.2691, found 428.2704.



43, colorless oil, 99%, d.r. > 20/1.

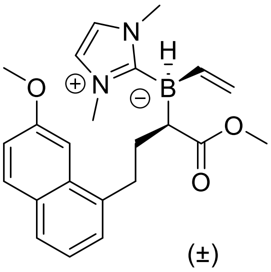
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.79 (s, 2H), 6.29 – 6.21 (m, 1H), 5.38 – 5.29 (m, 1H), 4.99 (dd, *J* = 19.4, 4.4 Hz, 1H), 3.93 – 3.86 (m, 2H), 3.77 – 3.75 (m, 6H), 3.35 – 3.29 (m, 2H), 3.20 (s, 3H), 2.09 – 2.02 (m, 1H), 1.87 – 1.80 (m, 1H), 1.69 – 1.64 (m, 1H), 1.54 – 1.49 (m, 1H), 1.49 – 1.39 (m, 2H), 1.30 – 1.16 (m, 2H).

^{11}B NMR (128 MHz, Chloroform-*d*) δ -18.65 (d, *J* = 88.7 Hz, 1B).

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -18.65 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.27, 120.93, 119.82, 68.42, 68.39, 50.15, 39.45, 36.77, 36.05, 33.93, 32.96.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{16}H_{27}BN_2O_3$+Na^{+} 329.2007, found 329.2027.



44, colorless oil, 89%, d.r. > 20/1.

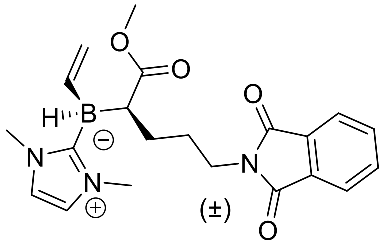
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.9 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 2.5 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.25 – 7.20 (m, 1H), 7.11 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.73 (s, 2H), 6.34 – 6.23 (m, 1H), 5.36 – 5.22 (m, 1H), 5.03 – 4.93 (m, 1H), 3.98 (s, 3H), 3.73 (s, 6H), 3.27 (s, 3H), 3.16 – 3.05 (m, 1H), 2.94 – 2.84 (m, 1H), 2.33 – 2.22 (m, 1H), 2.15 – 2.07 (m, 1H), 2.05 – 1.96 (m, 1H).

^{11}B NMR (128 MHz, Chloroform-*d*) δ -18.85 (d, *J* = 88.6 Hz, 1B).

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -18.85 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.03, 157.49, 138.59, 133.36, 129.96, 129.30, 126.45, 125.84, 123.31, 120.88, 119.76, 117.97, 103.17, 55.53, 50.20, 36.75, 34.98, 33.12.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{23}H_{29}BN_2O_3$+Na$^+$ 415.2163, found 415.2168.



45, colorless oil, 93%, d.r. > 20/1.

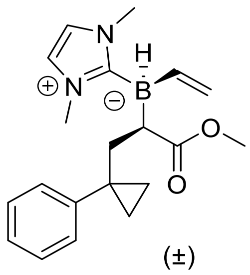
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 – 7.73 (m, 2H), 7.68 – 7.63 (m, 2H), 6.78 (s, 2H), 6.29 – 6.22 (m, 1H), 5.32 – 5.20 (m, 1H), 4.99 – 4.91 (m, 1H), 3.74 (s, 6H), 3.70 – 3.59 (m, 2H), 3.21 (s, 3H), 2.01 – 1.91 (m, 1H), 1.86 – 1.67 (m, 2H), 1.65 – 1.51 (m, 2H).

^{11}B NMR (128 MHz, Chloroform-*d*) δ -18.74 (d, *J* = 88.4 Hz, 1B).

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -18.74 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 181.80, 168.52, 133.75, 132.43, 123.09, 120.92, 119.91, 50.17, 38.39, 36.76, 29.52, 29.21.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{21}H_{26}BN_3O_4$+Na$^+$ 418.1909, found 418.1915.



46, colorless oil, 92%, d.r. > 20/1.

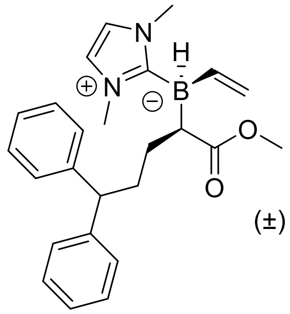
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 – 7.31 (m, 2H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.12 – 7.08 (m, 1H), 6.72 (s, 2H), 6.19 – 6.10 (m, 1H), 5.32 – 5.22 (m, 1H), 4.90 – 4.81 (m, 1H), 3.67 (s, 6H), 3.01 (s, 3H), 2.09 (dd, *J* = 14.3, 10.8 Hz, 1H), 2.02 – 1.96 (m, 1H), 1.94 (d, *J* = 14.4 Hz, 1H), 0.81 – 0.77 (m, 1H), 0.73 – 0.61 (m, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -18.68 (d, *J* = 88.0 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -18.68 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.01, 146.31, 129.93, 127.70, 125.52, 120.81, 119.86, 49.86, 42.51, 36.67, 27.75, 12.68, 12.45.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{20}H_{27}BN_2O_2$+Na$^+$ 361.2058, found 361.2073.



47, colorless oil, 99%, d.r. > 20/1.

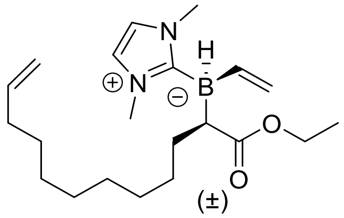
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.21 (m, 8H), 7.15 – 7.08 (m, 2H), 6.76 – 6.65 (m, 2H), 6.25 – 6.14 (m, 1H), 5.34 – 5.17 (m, 1H), 4.88 (dd, *J* = 19.3, 4.5 Hz, 1H), 3.91 (t, *J* = 7.7 Hz, 1H), 3.69 (s, 6H), 3.23 (s, 3H), 2.17 – 2.05 (m, 1H), 1.99 – 1.90 (m, 2H), 1.86 – 1.74 (m, 1H), 1.63 – 1.52 (m, 1H).

^{11}B NMR (128 MHz, Chloroform-*d*) δ -19.62 (d, *J* = 88.8 Hz, 1B).

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -19.62 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.07, 146.13, 145.51, 128.29, 128.16, 128.00, 125.81, 125.77, 120.83, 119.50, 51.82, 50.13, 37.00, 36.69, 30.64.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{25}H_{31}BN_2O_2$+Na$^+$ 425.2371, found 425.2379.



48, colorless oil, 94%, d.r. > 20/1.

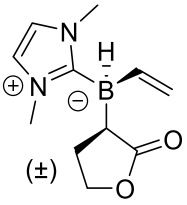
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.78 (s, 2H), 6.33 – 6.25 (m, 1H), 5.83 – 5.76 (m, 1H), 5.38 – 5.22 (m, 1H), 4.99 – 4.92 (m, 2H), 4.92 – 4.88 (m, 1H), 3.76 (s, 6H), 3.75 – 3.70 (m, 1H), 3.65 – 3.58 (m, 1H), 2.03 – 1.99 (m, 2H), 1.92 – 1.86 (m, 1H), 1.76 – 1.71 (m, 1H), 1.59 – 1.52 (m, 1H), 1.36 – 1.19 (m, 12H), 0.92 (t, *J* = 7.1 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -18.53 (d, *J* = 88.9 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -18.53 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.10, 139.46, 120.83, 119.42, 114.10, 58.24, 36.80, 33.94, 32.41, 31.13, 30.03, 29.76, 29.65, 29.28, 29.08, 14.43.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{21}H_{37}BN_2O_2$+Na$^+$ 383.2840, found 383.2851.



49, colorless oil, 79%, d.r. > 20/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.80 (s, 2H), 6.33 – 6.20 (m, 1H), 5.36 (s, 1H), 4.99 (d,

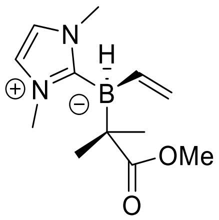
J = 19.4 Hz, 1H), 4.44 – 4.36 (m, 1H), 4.29 – 4.22 (m, 1H), 3.77 (s, 6H), 2.47 – 2.30 (m, 1H), 2.15 – 2.07 (m, 1H), 2.05 – 1.97 (m, 1H).

^{11}B NMR (128 MHz, Chloroform-*d*) δ -21.54 (d, J = 85.7 Hz, 1B).

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -18.53 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.35, 121.07, 120.01, 67.75, 36.68, 29.08.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{11}H_{17}BN_2O_2$+Na$^+$ 243.1275, found 243.1281.



50, colorless oil, 74%. Using Ni(COD)$_2$ (10 mol%) and (*p*-F-Ph)$_3$P (25 mol%).

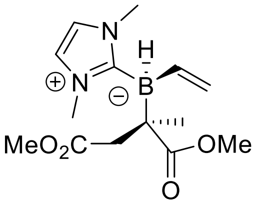
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.81 (s, 2H), 6.54 – 6.46 (m, 1H), 5.34 (br, 1H), 4.96 (d, J = 19.5 Hz, 1H), 3.74 (s, 6H), 3.50 (s, 3H), 1.17 (s, 3H), 1.07 (s, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -15.66 (d, J = 88.3 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -15.66 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.57, 121.30, 120.88, 50.62, 37.47, 26.37, 25.49.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{12}H_{21}BN_2O_2$+Na$^+$ 259.1588, found 259.1606.



51, colorless oil, 41%, d.r. = 1/1. Using Ni(COD)$_2$ (10 mol%) and (*p*-F-Ph)$_3$P (25 mol%).

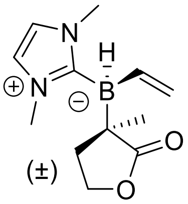
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.82 (s, 2H), 6.54 – 6.34 (m, 1H), 5.34 (br, 1H), 5.06 – 4.90 (m, 1H), 3.82 – 3.68 (m, 6H), 3.59 (d, J = 6.3 Hz, 3H), 3.55 (s, 1.5H), 3.49 (s, 1.5H), 3.15 (d, J = 16.7 Hz, 0.5H), 2.86 (d, J = 16.8 Hz, 0.5H), 2.37 – 2.25 (m, 1H), 1.25 (s, 1.5H), 1.08 (s, 1.5H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -16.00 (d, *J* = 89.7 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -16.00 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.67/182.47, 174.79/174.52, 122.14/121.73, 121.54, 51.09/50.72, 43.88/43.57, 37.41, 22.82, 21.28.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{14}H_{23}BN_2O_4$+Na$^+$ 317.1643, found 317.1650.



52, colorless oil, 48%, d.r. > 20/1. Using Ni(COD)$_2$ (10 mol%) and (*p*-F-Ph)$_3$P (25 mol%).

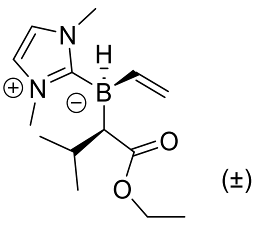
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.81 (s, 2H), 6.42 – 6.35 (m, 1H), 5.45 (br, 1H), 5.13 (d, *J* = 19.3 Hz, 1H), 4.39 – 3.33 (m, 1H), 4.21 – 4.19 (m, 1H), 3.77 (s, 6H), 2.38 – 2.33 (m, 1H), 1.93 – 1.86 (m, 1H), 1.18 (s, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -20.34 (d, *J* = 86.1 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -20.34 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.15, 122.66, 121.53, 65.73, 37.59, 37.46, 21.99.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{12}H_{19}BN_2O_2$+Na$^+$ 257.1432, found 257.1447.



53, colorless oil, 47%, d.r. = 13/1. Using Ni(COD)$_2$ (10 mol%) and (*p*-F-Ph)$_3$P (25 mol%).

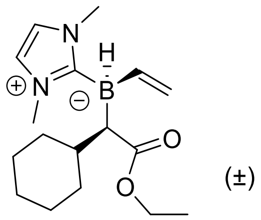
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.76 (s, 2H), 6.40 – 6.32 (m, 1H), 5.29 (br, 1H), 4.96 (d, *J* = 19.3 Hz, 1H), 3.76 (s, 6H), 3.70 – 3.63 (m, 1H), 3.57 – 3.50 (m, 1H), 2.04 – 1.96 (m, 1H), 1.79 – 1.75 (m, 1H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.99 – 0.95 (m, 6H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -19.47 (d, *J* = 89.1 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -19.47 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.56, 120.77, 119.30, 58.19, 37.03, 32.35, 23.04, 22.94, 14.50.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{14}H_{25}BN_2O_2$+Na$^+$ 287.1901, found 287.1911.



54, colorless oil, 80%, d.r. = 16/1. Using Ni(COD)$_2$ (10 mol%) and (*p*-F-Ph)$_3$P (25 mol%).

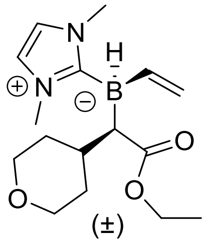
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.75 (s, 2H), 6.39 – 6.31 (m, 1H), 5.31 – 5.23 (m, 1H), 4.98 – 4.90 (m, 1H), 3.75 (s, 6H), 3.70 – 3.62 (m, 1H), 3.54 – 5.47 (m, 1H), 2.05 – 1.98 (m, 1H), 1.83 – 1.75 (m, 2H), 1.71 – 1.58 (m, 4H), 1.33 – 0.98 (m, 5H), 0.95 (t, *J* = 7.1 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -19.71 (d, *J* = 88.6 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -19.71 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.54, 120.75, 119.17, 58.18, 42.51, 37.04, 33.77, 33.32, 27.40, 27.22, 27.10, 14.51.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{17}H_{29}BN_2O_2$+Na$^+$ 327.2214, found 327.2223.



55, colorless oil, 84%, d.r. = 18/1. Using Ni(COD)$_2$ (10 mol%) and (*p*-F-Ph)$_3$P (25 mol%).

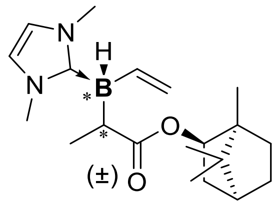
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.75 (s, 2H), 6.34 – 6.27 (m, 1H), 5.27 (br, 1H), 5.03 – 4.91 (m, 1H), 3.96 – 3.91 (m, 1H), 3.90 – 3.86 (m, 1H), 3.74 (s, 6H), 3.68 – 3.62 (m, 1H), 3.50 – 3.44 (m, 1H), 3.39 – 3.33 (m, 2H), 1.96 – 1.86 (m, 2H), 1.84 – 1.79 (m, 1H), 1.66 – 1.61 (m, 1H), 1.44 – 1.36 (m, 1H), 1.36 – 1.27 (m, 1H), 0.93 (t, *J* = 7.1 Hz, 3H)..

^{11}B NMR (193 MHz, Chloroform-*d*) δ -19.69 (d, *J* = 88.3 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -19.69 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.88, 120.84, 119.69, 69.10, 68.86, 58.37, 39.87, 37.03, 33.78, 33.37, 14.46.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{16}H_{27}BN_2O_3$+Na$^+$ 329.2007, found 329.2063.



56, colorless oil, 96%, d.r. > 20/1.

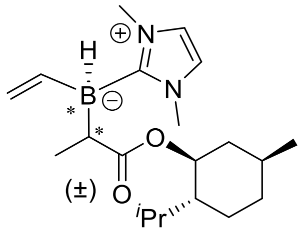
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.80 (s, 1H), 6.78 (s, 1H), 6.36 – 6.28 (m, 1H), 5.29 (br, 1H), 4.90 – 4.82 (m, 1H), 4.65 – 4.57 (m, 1H), 3.78 (s, 6H), 2.22 – 2.17 (m, 0.5H), 2.16 – 2.09 (m, 0.5H), 2.04 – 1.96 (m, 1H), 1.90 – 1.85 (m, 0.5H), 1.73 (s, 1H), 1.76 – 1.70 (m, 0.5H), 1.70 – 1.59 (m, 1H), 1.59 – 1.49 (m, 1H), 1.20 (d, *J* = 5.9 Hz, 3H), 1.18 – 1.13 (m, 1H), 0.96 – 0.89 (m, 1H), 0.83 – 0.79 (m, 6H), 0.73 (s, 1.5H), 0.73 – 0.70 (m, 1H), 0.63 (s, 1.5H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.96 (d, *J* = 87.7 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.96 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.42/ 183.28, 120.95--, 119.28/119.17, 77.74/77.25, 48.67/48.62, 47.72/47.69, 45.03/44.91, 37.23/36.87, 36.84/36.81, 28.25/28.21, 27.23/27.21, 19.83, 18.94/18.92, 16.70/16.51, 13.56/13.50.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{20}H_{33}BN_2O_2$+Na$^+$ 367.2527, found 367.2541.



57, colorless oil, 89%, d.r. = 10/1.

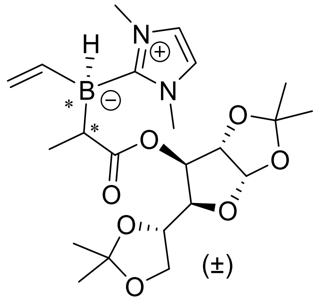
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.81 (s, 2H), 6.38 – 6.26(m, 1H), 5.29 (br, 1H), 4.89 – 4.81 (m, 1H), 4.49 – 4.33 (m, 1H), 3.81/3.79 (s, 6H), 2.05 – 1.99 (m, 1H), 1.68 – 1.57 (m, 3H), 1.51 – 1.25 (m, 2H), 1.23 – 1.18 (m, 3H), 1.08 – 0.75 (m, 10H), 0.73 – 0.64 (m, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.96 (d, *J* = 87.8 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.96 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.56/182.46, 120.88/120.81, 119.00/118.96, 71.82/71.28, 47.49/47.15, 41.35/41.07, 36.88/36.79, 34.51/34.47, 31.35/31.09, 26.40/25.67/, 23.71/23.18, 22.31/22.25, 21.25/20.98, 16.71/16.52, 16.03.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{21}H_{39}BN_2O_3$+Na$^+$ 369.2684, found 369.2699.



58, white solid, 94%, d.r. = 13/1.

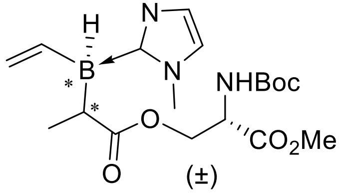
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.83/6.81 (s, 2H), 6.37 – 6.24 (m, 1H), 5.80 (d, *J* = 3.6 Hz)/5.60 (d, *J* = 3.6 Hz) (1H), 5.34 – 5.22 (m, 1H), 5.00 – 4.93 (m, 1H), 4.91 – 4.83 (m, 1H), 4.26 – 3.93 (m, 5H), 3.78 – 3.75 (m, 6H), 2.05 – 1.97 (m, 1H), 1.46 (d, *J* = 9.5 Hz, 3H), 1.37 (d, *J* = 3.1 Hz, 3H), 1.31 (d, *J* = 2.4 Hz, 3H), 1.24 (s, 2H), 1.22 (s, 1H), 1.15 (dd, *J* = 11.6, 6.5 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.93 (d, *J* = 88.4 Hz, 1B)

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.93 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.45/181.26, 121.09/120.98, 119.88/119.74, 111.98/111.94, 109.07/109.03, 105.07/104.99, 83.74/83.57, 80.08/79.97, 74.87/74.52, 72.76/72.50, 67.15/66.90, 36.90/36.84, 26.90/26.85, 26.77, 26.31/26.25, 25.46/25.44, 16.39/15.94.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{22}H_{35}BN_2O_7$+Na^{+} 473.2430, found 473.2440.



59, colorless oil, 94%, d.r. > 20/1.

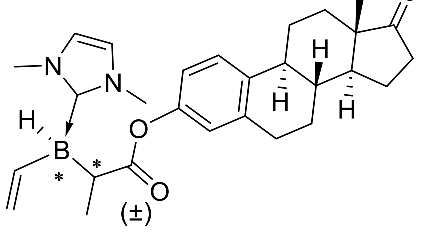
^{1}H NMR (600 MHz, Chloroform-*d*) 6.83 (d, *J* = 22.4 Hz, 2H), 6.34 – 6.24 (m, 1H), 5.31 (br, 1H), 5.22 – 4.78 (m, 2H), 4.35 – 4.24 (m, 1H), 4.13 – 4.01 (m, 1H), 3.96 – 3.84 (m, 1H), 3.74 (s, 6H), 3.72 (s, 3H), 2.02 – 1.93 (m, 1H), 1.45 (d, *J* = 8.5 Hz, 9H), 1.15 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.93 (d, *J* = 88.7 Hz, 1B)

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.93 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.42, 170.81/170.73, 155.34/155.23, 121.13/121.07, 119.77, 80.25/80.22, 63.34/62.78, 53.49/53.16, 52.67/52.60, 36.77, 28.50/28.46, 16.21/16.11.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{19}H_{32}BN_3O_6$+Na^{+} 432.2276, found 432.2288.



60, white solid, 94%, d.r. = 13/1.

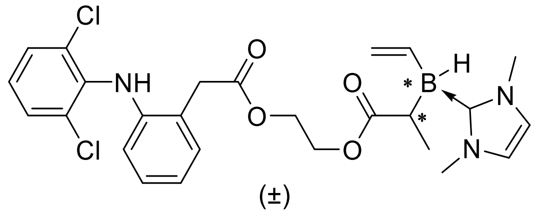
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 8.5 Hz, 1H), 6.85 (s, 2H), 6.57 – 6.22 (m, 3H), 5.43 – 5.31 (m, 1H), 5.03 – 4.92 (m, 1H), 3.82 (s, 6H), 2.89 – 2.77 (m, 2H), 2.49 (dd, *J* = 18.9, 8.7 Hz, 1H), 2.38 – 2.31 (m, 1H), 2.26 – 1.89 (m, 7H), 1.65 – 1.37 (m, 6H), 1.31 (d, *J* = 6.4 Hz, 3H), 0.88 (s, 3H).

^{11}B NMR (128 MHz, Chloroform-*d*) δ -18.44 (d, *J* = 88.6 Hz)

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -18.44 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.39, 149.41/149.39, 137.51, 136.17, 126.07, 121.87, 121.07, 119.67, 118.79/118.76, 50.48, 48.03, 44.17, 38.13, 36.88, 35.95, 31.67/31.63, 29.49/29.47, 26.46/25.82, 22.74, 21.66, 16.49, 14.22, 13.91.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{28}H_{37}BN_2O_3$+Na$^+$ 483.2789, found 483.2800.



61, colorless oil, 94%, d.r. = 20/1.

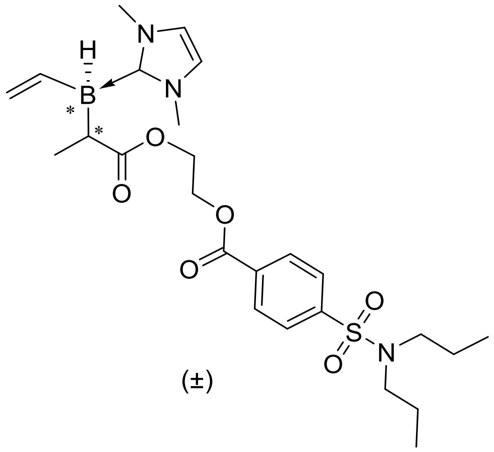
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.23 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.14 (td, *J* = 7.7, 1.6 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.97 (td, *J* = 7.4, 1.2 Hz, 1H), 6.88 (s, 1H), 6.70 (s, 2H), 6.56 (d, *J* = 7.9 Hz, 1H), 6.32 – 6.25 (m, 1H), 5.31 (br, 1H), 4.91 (dd, *J* = 19.5, 4.5 Hz, 1H), 4.03 – 3.91 (m, 3H), 3.84 – 3.78 (m, 3H), 3.68 (s, 6H), 1.99 – 1.94 (m, 1H), 1.19 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.91 (d, *J* = 88.6 Hz).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.91 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.47, 172.29, 142.89, 137.81, 131.02, 129.68, 129.04, 128.28, 124.35, 124.16, 122.17, 120.89, 119.63, 118.40, 63.67, 60.07, 38.64, 36.68, 16.25.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{26}H_{30}BCl_2N_3O_4$+Na$^+$ 552.1598, found 552.1603.



62, colorless oil, 94%, d.r. = 18/1.

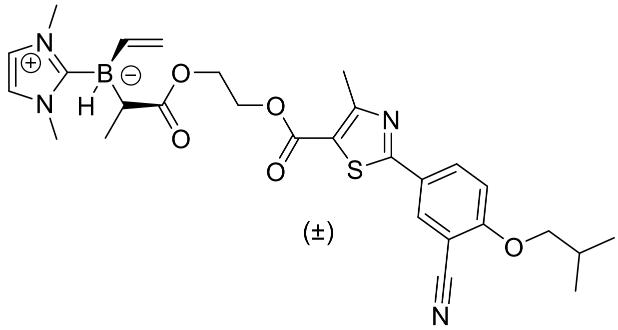
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 2H), 6.75 (s, 2H), 6.34 – 6.24 (m, 1H), 5.35 – 5.23 (m, 1H), 4.96 – 4.84 (m, 1H), 4.28 – 4.16 (m, 2H), 4.16 – 4.07 (m, 1H), 3.98 – 3.88 (m, 1H), 3.72 (s, 6H), 3.14 – 3.06 (m, 4H), 2.05 – 1.96 (m, 1H), 1.59 – 1.47 (m, 4H), 1.17 (d, *J* = 6.4 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 6H).

^{11}B NMR (128 MHz, Chloroform-*d*) δ -17.91 (d, *J* = 88.0 Hz).

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -17.91 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.47, 165.10, 144.56, 133.28, 130.36, 127.13, 120.93, 119.73, 63.85, 60.14, 49.99, 36.74, 21.99, 16.21, 11.23.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{25}H_{38}BN_3O_6S$+Na$^+$ 542.2467, found 542.2479.



63, colorless oil, 87%, d.r. = 19/1.

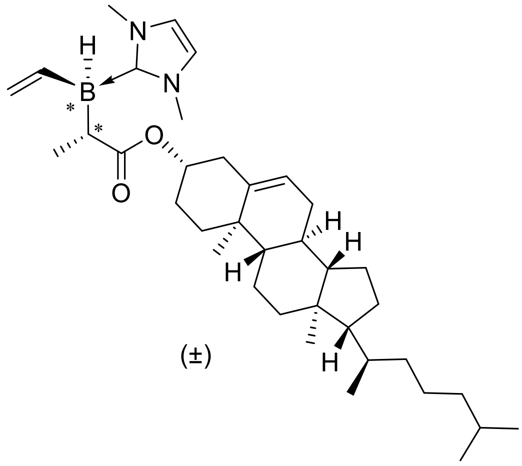
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 2.3 Hz, 1H), 8.05 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 1H), 6.78 (s, 2H), 6.32 – 6.24 (m, 1H), 5.36 – 5.22 (m, 1H), 4.90 (dd, *J* = 19.6, 4.5 Hz, 1H), 4.21 – 4.15 (m, 1H), 4.13 – 4.02 (m, 2H), 3.92 – 3.85 (m, 3H), 3.74 (s, 6H), 2.72 (s, 3H), 2.20 – 2.15 (m, 1H), 2.03 – 1.97 (m, 1H), 1.17 (d, *J* = 6.3 Hz, 3H), 1.06 (d, *J* = 6.9 Hz, 6H).

^{11}B NMR (128 MHz, Chloroform-*d*) δ -17.89 (d, *J* = 88.4 Hz).

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -17.89 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.45, 167.66, 162.68, 161.84, 161.65, 132.72, 132.18, 125.96, 121.43, 120.95, 119.73, 115.46, 112.78, 103.09, 75.81, 63.51, 60.14, 36.78, 28.23, 19.13, 17.64, 16.23.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{28}H_{35}BN_4O_5S+Na^{+}$ 573.2313, found 573.2324.



64, colorless oil, 94%, d.r. > 20/1.

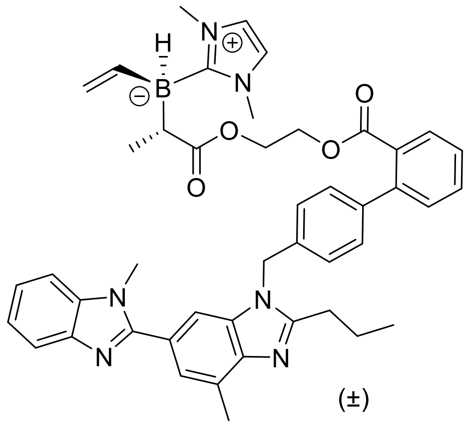
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.81 (d, *J* = 5.2 Hz, 2H), 6.35 – 6.26 (m, 1H), 5.35 – 5.19 (m, 2H), 4.88 (dd, *J* = 19.3, 4.5 Hz, 1H), 4.26 – 4.17 (m, 1H), 3.77 (d, *J* = 2.6 Hz, 6H), 2.18 – 1.65 (m, 8H), 1.57 – 1.21 (m, 11H), 1.18 (d, *J* = 6.4 Hz, 3H), 1.15 – 0.94 (m, 9H), 0.92 – 0.88 (m, 6H), 0.85 (dd, *J* = 6.7, 2.7 Hz, 6H), 0.65 (s, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.89 (d, *J* = 88.5 Hz).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.89 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.79, 140.78/140.63, 122.63/122.55, 121.28/121.26, 119.67, 71.93/71.89, 57.23/57.21, 56.68, 50.56, 42.85, 40.30/40.26, 40.07, 39.01, 38.63, 37.58/37.56, 37.28, 37.14/37.10, 36.73, 36.34, 32.41, 28.77, 28.56, 28.59/28.13, 24.83, 24.38, 23.37, 23.11, 21.56/21.54, 19.86, 19.26, 16.86/16.85, 12.40.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{37}H_{61}BN_2O_2$+Na$^+$ 599.4718, found 599.4727.



65, colorless oil, 55%, d.r. > 20/1.

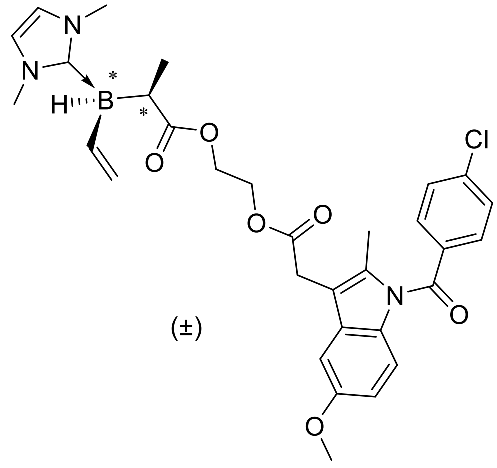
^{1}H NMR (600 MHz, Chloroform-*d*) 7.82 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.79 – 7.77 (m, 1H), 7.54 (d, *J* = 1.5 Hz, 1H), 7.52 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.45 (s, 1H), 7.44 – 7.40 (m, 1H), 7.39 – 7.36 (m, 1H), 7.31 – 7.27 (m, 3H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.61 (s, 2H), 6.31 – 6.23 (m, 1H), 5.51 – 5.44 (m, 2H), 5.32 – 5.25 (m, 1H), 4.89 (dd, *J* = 19.4, 4.5 Hz, 1H), 3.94 – 3.85 (m, 2H), 3.82 (s, 3H), 3.66 – 3.59 (m, 7H), 3.54 – 3.47 (m, 1H), 2.96 – 2.93 (m, 2H), 2.77 (s, 3H), 1.97 – 1.92 (m, 1H), 1.91 – 1.85 (m, 2H), 1.18 (d, *J* = 6.4 Hz, 3H), 1.06 (t, *J* = 7.3 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -17.99 (d, *J* = 88.4 Hz).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -17.99 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.28, 167.78, 156.61, 154.76, 143.20, 142.80, 142.00, 141.00, 136.65, 135.06, 131.63, 130.83, 130.35, 129.99, 129.49, 129.01, 127.44, 125.87, 123.95, 123.83, 122.54, 122.32, 120.74, 119.54, 119.43, 109.66, 109.00, 69.53, 62.73, 60.18, 53.90, 47.04, 36.52, 31.87, 29.81, 29.30, 21.89, 16.89, 16.20, 14.10.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{45}H_{49}BN_6O_4$+Na$^+$ 771.3800, found 771.3810.



66, yellow oil, 82%, d.r. > 20/1.

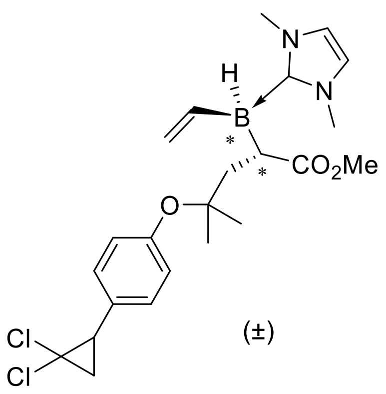
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 2.5 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.74 (s, 2H), 6.67 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.34 – 6.22 (m, 1H), 5.39 – 5.25 (m, 1H), 4.96 – 4.86 (mz, 1H), 4.01 – 3.90 (m, 3H), 3.83 (s, 3H), 3.79 – 3.71 (m, 1H), 3.67 (s, 6H), 3.65 (s, 2H), 2.37 (s, 3H), 1.97 – 1.87 (m, 1H), 1.15 (d, *J* = 6.4 Hz, 3H).

^{11}B NMR (128 MHz, Chloroform-*d*) δ -17.98 (d, *J* = 87.9 Hz).

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -17.98 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.41, 170.72, 168.39, 156.17, 139.43, 136.13, 133.91, 131.27, 130.89, 130.67, 129.26, 120.89, 119.68, 115.03, 112.40, 111.63, 101.54, 63.11, 60.21, 55.83, 36.63, 30.32, 16.21, 13.45.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{31}H_{35}BClN_3O_6$+Na$^+$ 614.2200, found 614.2209.



67, colorless oil, 20%, d.r. = 12/1.

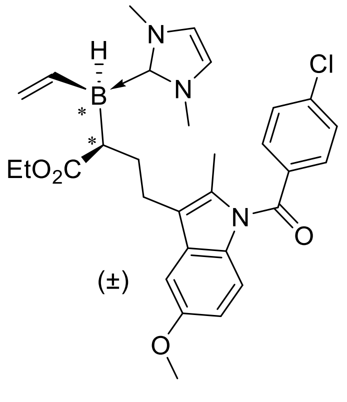
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.07 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.78 (s, 2H), 6.29 – 6.20 (m, 1H), 5.34 (d, *J* = 12.7 Hz, 1H), 5.04 (dd, *J* = 19.2, 4.5 Hz, 1H), 3.77 (s, 6H), 3.16 (d, *J* = 1.0 Hz, 3H), 2.85 – 2.80 (m, 1H), 2.35 – 2.29 (m, 1H), 2.26 – 2.21 (m, 1H), 2.03 – 1.96 (m, 1H), 1.93 – 1.88 (m, 1H), 1.79 – 1.75 (m, 1H), 1.24 (d, *J* = 3.4 Hz, 6H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -18.44 (d, *J* = 91.4 Hz).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -18.44 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.62, 155.93, 129.25, 128.40, 123.31, 123.29, 120.95, 120.32, 82.16, 61.18, 50.21, 44.59, 44.55, 36.85, 35.18, 26.76, 25.96.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{23}H_{31}BCl_2N_2O_3$+Na$^+$ 487.1697, found 487.1708.



68, yellow oil, 87%, d.r. > 20/1.

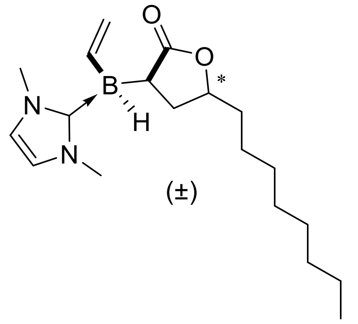
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.07 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.78 (s, 2H), 6.29 – 6.20 (m, 1H), 7.65 – 7.60 (m, 2H), 7.46 – 7.43 (m, 2H), 7.04 (d, *J* = 2.6 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 1H), 6.78 (s, 6H), 6.64 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.30 – 6.21 (m, 1H), 5.33 – 5.25 (m, 1H), 4.94 (dd, *J* = 19.0, 4.4 Hz, 1H), 3.85 (s, 3H), 3.79 – 3.72 (m, 7H), 3.67 – 3.60 (m, 1H), 2.72 – 2.65 (m, 1H), 2.61 – 2.55 (m, 1H), 2.27 (s, 3H), 2.15 – 2.06 (m, 1H), 2.06 – 2.00 (m, 1H), 1.94 – 1.86 (m, 1H), 0.94 (t, *J* = 7.1 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -18.59 (d, *J* = 88.9 Hz).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -18.59 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 181.62, 168.45, 155.99, 138.73, 134.79, 133.57, 131.91, 131.19, 131.14, 129.05, 121.35, 120.89, 119.62, 114.91, 111.14, 101.98, 58.42, 55.84, 36.78, 32.04, 25.16, 14.42, 13.49.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{30}H_{35}BClN_3O_4$+Na$^+$ 570.2301, found 570.2311.



69, colorless oil, 74%, d.r. = 5/1.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.79 (d, *J* = 4.1 Hz, 2H), 6.29 – 6.20 (m, 1H), 5.41 – 5.30 (m, 1H), 5.10 – 4.87 (m, 1H), 4.64 – 4.55 (m, 1H), 3.75 (d, *J* = 10.4 Hz, 6H), 2.23 – 2.18 (m, 1H), 2.07 (t, *J* = 8.8 Hz, 1H), 1.93 (q, *J* = 10.0 Hz, 1H), 1.87 – 1.23 (m, 15H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -18.90 (d, *J* = 85.0 Hz, minor configuration), -20.54 (d, *J* = 85.9 Hz, major configuration).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -18.90 (s, minor configuration), -20.54 (s, major configuration).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 186.76, 121.03/120.88, 119.95/119.49, 80.36/79.72, 36.99/36.65, 36.60/36.20, 35.69/34.97, 31.95, 29.65, 29.60, 29.29, 25.78/25.64, 22.73, 14.17.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{19}H_{33}BN_2O_2$+Na$^+$ 355.2527, found 355.2537.

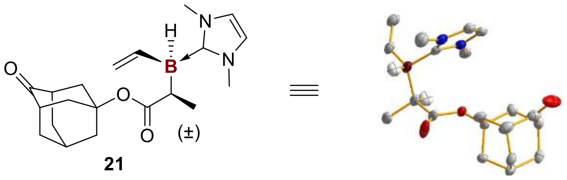
4.3 X-ray crystal structures of 4 (CCDC 2381592) and 21 (CCDC 2381593)

4

Table S2. Crystal data and structure refinement for 4

Identification code	ghuaf1CuLT_auto
Empirical formula	$C_{14}H_{25}BN_2O_2$
Formula weight	264.17
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.70607(10)
b/Å	14.11052(14)
c/Å	11.39150(12)
α/°	90
β/°	93.1395(9)
γ/°	90
Volume/Å^3	1557.81(3)
Z	4
ρ_{calc}g/cm^3	1.126
μ/mm^{-1}	0.583
F(000)	576.0
Crystal size/mm^3	0.25 × 0.22 × 0.2
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.988 to 148.966
Index ranges	$-12 \le h \le 11$, $-12 \le k \le 17$, $-14 \le l \le 13$
Reflections collected	9190
Independent reflections	3124 [R_{int} = 0.0151, R_{sigma} = 0.0147]

Data/restraints/parameters	3124/0/179
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	$R_1 = 0.0345$, $wR_2 = 0.0900$
Final R indexes [all data]	$R_1 = 0.0365$, $wR_2 = 0.0920$
Largest diff. peak/hole / e Å^{-3}	0.30/-0.23



21

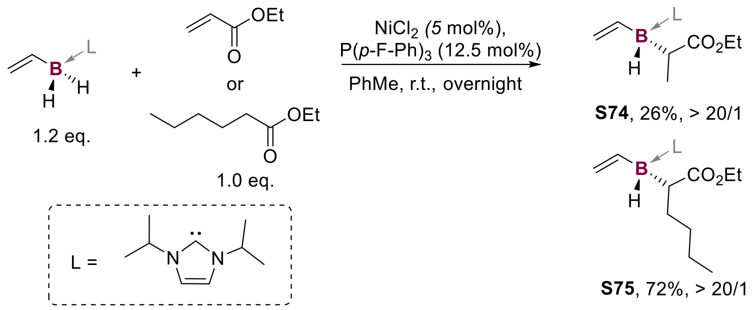
Table S3. Crystal data and structure refinement for 21

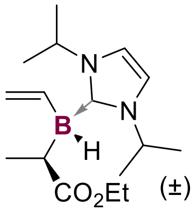
Identification code	ghuaf2CuLT
Empirical formula	$C_{20}H_{29}BN_2O_3$
Formula weight	356.26
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.3051(3)
b/Å	13.6933(5)
c/Å	13.8874(3)
α/°	90
β/°	103.092(3)
γ/°	90
Volume/Å^3	1908.73(10)
Z	4
ρ_{calc}g/cm^3	1.240
μ/mm^{-1}	0.653
F(000)	768.0
Crystal size/mm^3	0.3 × 0.25 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.81 to 148.948
Index ranges	$-8 \leq h \leq 12$, $-16 \leq k \leq 15$, $-17 \leq l \leq 14$
Reflections collected	6720
Independent reflections	3743 [$R_{int} = 0.0291$, $R_{sigma} = 0.0343$]
Data/restraints/parameters	3743/490/338
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	$R_1 = 0.0599$, $wR_2 = 0.1487$

Final R indexes [all data] $R_1 = 0.0739$, $wR_2 = 0.1605$

Largest diff. peak/hole / e Å^{-3} 0.51/-0.41

4.4 Reaction with I^{i}Pr coordinated boranes





S74, colorless oil, 26%, d.r. > 20/1.

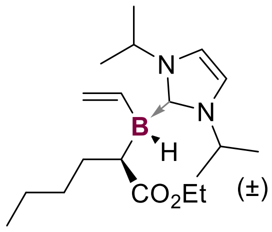
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.98 (s, 2H), 6.43 – 6.31 (m, 1H), 5.32 (s, 1H), 5.12 (p, *J* = 6.8 Hz, 2H), 4.94 (d, *J* = 18.2 Hz, 1H), 3.87 – 3.60 (m, 2H), 1.97 – 1.87 (m, 1H), 1.41 (dd, *J* = 21.1, 6.7 Hz, 12H), 1.22 (d, J = 6.4 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H).

^{11}B NMR (128 MHz, Chloroform-*d*) δ -18.54 (d, *J* = 88.9 Hz).

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -18.18 (s, 1B).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.82, 119.48, 115.67, 58.14, 49.39, 23.49, 22.81, 16.07, 14.24.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{16}H_{29}BN_2O_2$+Na$^+$ 315.2214, found 315.2206.



S75, colorless oil, 72%, d.r. > 20/1.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.93 (s, 2H), 6.34 – 6.27 (m, 1H), 5.32 – 5.24 (m, 1H), 5.13 – 5.05 (m, 2H), 4.94 (dd, J = 19.2, 4.6 Hz, 1H), 3.68 (ddq, *J* = 67.7, 10.9, 7.2 Hz, 2H), 1.85 – 1.76 (m, 1H), 1.76 – 1.70 (m, 1H), 1.63 – 1.53 (m, 1H), 1.39 (d, *J* = 6.8 Hz, 6H), 1.34 (d, *J* = 6.7 Hz, 6H), 1.32 – 1.24 (m, 3H), 1.21 – 1.14 (m, 1H), 0.89 – 0.84 (m, 6H).

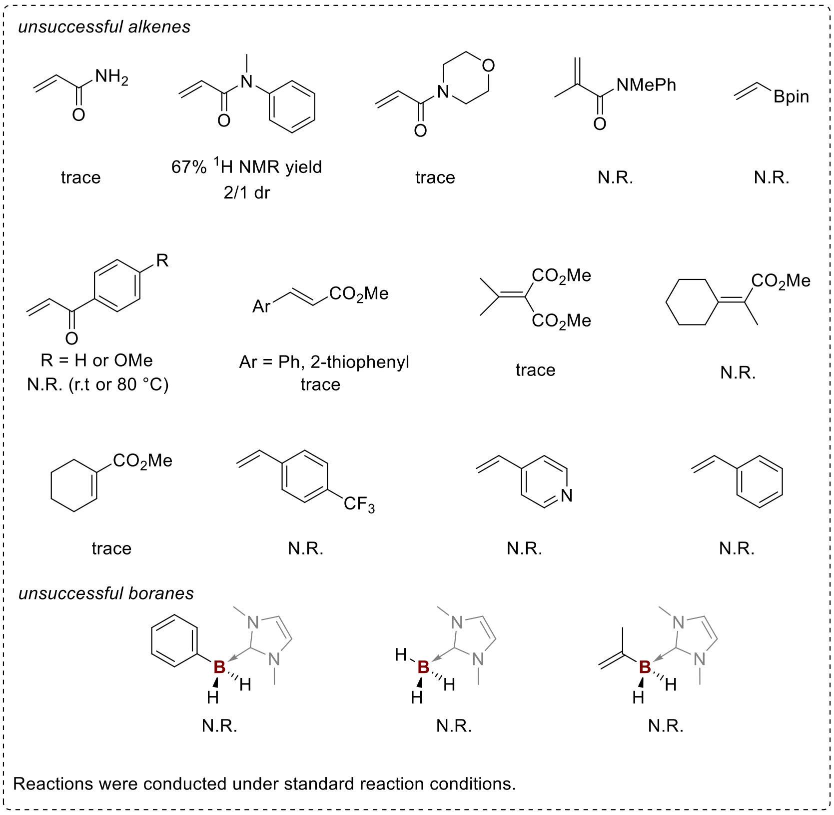
^{11}B NMR (128 MHz, Chloroform-*d*) δ -18.43 (d, *J* = 88.1 Hz).

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -18.43 (s, 1B)

^{13}C NMR (151 MHz, Chloroform-*d*) δ182.00, 119.59, 115.78, 58.08, 49.48, 33.39, 31.80, 23.60, 23.22, 23.14, 22.89, 14.38, 14.31.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{19}H_{35}BN_2O_2$+Na$^+$ 357.2684, found 357.2672.

4.5 Unsuccessful substrates



5. Downstream Transformations

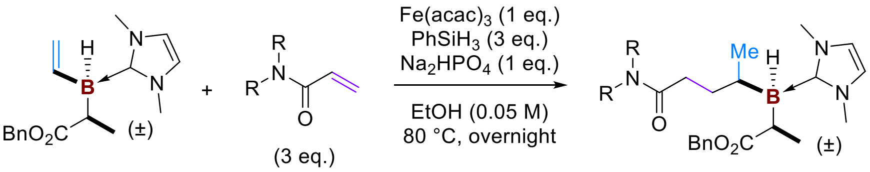
5.1 Gram scale reaction of 3

Under the dry N_2 atmosphere, $NiCl_2$ (26 mg, 0.2 mmol, 5 mol%) and (*p*-F-Ph)$_3$P (158 mg, 0.5 mmol, 12.5 mol%) were mixed in a 100 mL round-bottom flask. PhMe (40 mL) was then added. After stirring for 1 hour, benzyl acrylate (650 mg, 4 mmol, 1 eq.) and borane **1** (650 mg, 4.8 mmol, 1.2 eq.) were sequentially added. The resulting mixture was stirred at room temperature for 18 hours, and monitored by ^{11}B NMR. After completion, the reaction was quenched by air, and the solvent was evacuated under reduced pressure. The residue was purified by column chromatography (neutral Al_2O_3) to give **3** (1.16 g, 97% yield, > 20/1 dr).

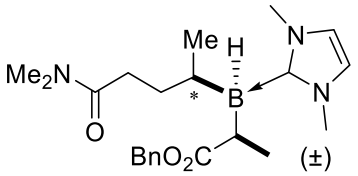
Fig. S2. Gram scale synthesis, from left to right: after reaction set-up, after reaction completion, quenched under air, and isolated **3** (1.16 g, 97% yield, > 20/1 dr)

5.2 Fe-mediated C=C modifications

5.2.1 Reaction with acrylamides



Under the dry N_2 atmosphere, **3** (0.1 mmol, 1.0 eq.) was dissolved in anhydrous EtOH (2 mL, 0.05 M), followed by the sequential addition of Na_2HPO_4 (0.1 mmol, 1.0 eq.), Fe(acac)$_3$ (0.1 mmol, 1.0 eq.), acrylamides (0.3 mmol, 3.0 eq.), and $PhSiH_3$ (0.3 mmol, 3.0 eq.). Bubbles were observed after adding silanes. The tube was then tightly sealed and heated at 80 °C with stirring overnight. After the reaction, the solvents were evacuated under reduced pressure, and the residue was subjected to column chromatography (triethylamine-activated SiO_2) to give the products.



72, colorless oil, 94%, d.r. = 2/1.

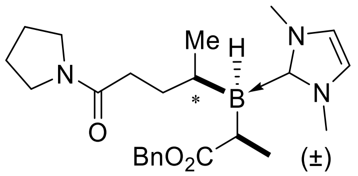
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 – 7.20 (m, 5H), 6.70 – 6.61 (m, 2H), 4.88 – 4.76 (m, 2H), 3.71 – 3.56 (m, 6H), 2.97 (s, 3H), 2.90 (s, 1H), 2.87 (s, 2H), 2.55 – 2.31 (m, 1H), 2.25 – 2.07 (m, 2H), 1.33 – 1.15 (m, 2H), 1.12 (d, *J* = 6.7 Hz, 3H), 1.07 – 0.97 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 2H), 0.60 (d, *J* = 7.0 Hz, 1H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -15.59 (d, *J* = 93.6 Hz), -16.08 (d, *J* = 94.2 Hz).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -15.59 (s, minor configuration), -16.08 (s, major configuration).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 183.31/183.28, 175.39/175.14, 137.44, 128.42/128.25, 128.32, 127.69/127.67, 120.97, 64.66, 37.60 /37.51, 35.34, 33.83, 33.20, 32.80, 20.08/19.32, 17.82/17.25.

HRMS(ESI) m/z ($M+Na^+$) calculated for $C_{22}H_{34}BN_3O_3+Na^+$ 422.2585, found 448.2601.



73, colorless oil, 86%, d.r. = 2/1.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 6.66 – 6.57 (m, 2H), 4.83 – 4.74 (m, 2H), 3.62 (s, 7H), 3.43 – 3.34 (m, 5H), 2.43 – 2.27 (m, 1H), 2.19 –

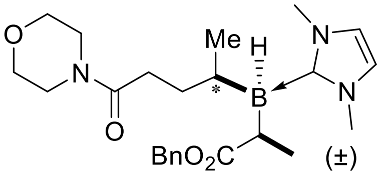
2.07 (m, 2H), 1.90 – 1.85 (m, 2H), 1.80 – 1.75 (m, 2H), 1.33 – 1.24 (m, 1H), 1.10 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 2H), 0.58 (d, *J* = 7.0 Hz, 1H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -14.59 (*J* = 97.6 Hz,), -15.09 (*J* = 97.4 Hz,).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -14.59 (s, major configuration), -15.09 (s, configuration),

^{13}C NMR (151 MHz, Chloroform-d) δ 183.36/183.32, 174.02/173.71, 137.50, 128.44/128.26, 128.35, 127.70/127.68, 120.99, 64.68, 46.76, 45.58, 35.27/34.17, 33.62/32.96, 29.81, 26.31/26.26, 24.58/24.55, 20.17/19.39, 17.88/17.28.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{24}H_{36}BN_3O_3$+Na^{+} 448.2747, found 448.2755.



74, colorless oil, 86%, d.r. =2/1.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.23 (m, 5H), 6.70 – 6.60 (m, 2H), 4.87 – 4.75 (m, 2H), 3.71 – 3.53 (m, 14H), 3.45 –3.38 (m, 2H), 2.52 – 2.36 (m, 1H), 2.26 – 2.07 (m, 2H), 1.32 – 1.27 (m, 1H), 1.11 (dd, *J* = 9.2, 6.6 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 2H), 0.57 (d, *J* = 7.0 Hz, 1H).

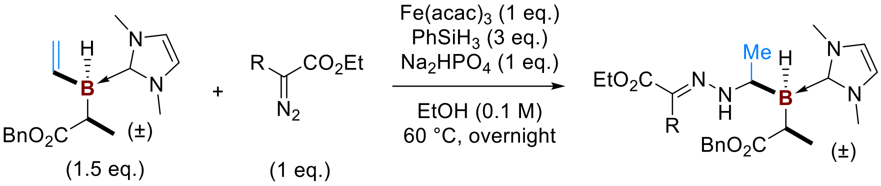
^{11}B NMR (193 MHz, Chloroform-*d*) δ -14.70 (d, *J* = 88.8 Hz). -15.16 (d, *J* = 92.0 Hz).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -14.70 (s, major configuration), -15.16 (s, configuration),

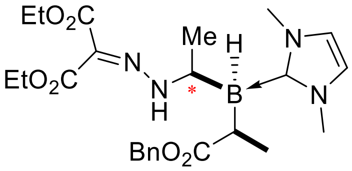
^{13}C NMR (151 MHz, Chloroform-d) δ 183.36/183.32, 174.02/173.71, 137.50, 128.44/128.26, 128.35, 127.70/127.68, 120.99, 64.68, 46.76, 45.58, 35.27/34.17, 33.62/32.96, 29.81, 26.31/26.26, 24.58/24.55, 20.17/19.39, 17.88/17.28.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{24}H_{36}BN_3O_4$+Na^{+} 464.2691, found 464.2701.

5.2.2 Reaction with diazo compounds



Under a dry N_2 atmosphere, $Fe(acac)_3$ (1 mmol, 1.0 eq.) was dissolved in EtOH (0.1 M) in an oven-dried 10 mL tube. Then, **3** (1.5 mmol, 1.5 eq.), diazo compound (1 mmol, 1.0 eq.), and $PhSiH_3$ (3.0 mmol, 3.0 eq.) were added sequentially. The tube was sealed tightly, and the mixture was stirred at 60 °C overnight. After the reaction, the solvents were evacuated under reduced pressure, and the residue was subjected column chromatography (triethylamine activated SiO_2) to give the products.



70, colorless oil, 35%, d.r. = 3/2.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 3H), 7.26 – 7.21 (m, 2H), 6.64 – 6.51 (m, 2H), 4.91 – 4.76 (m, 2H), 4.26 – 4.12 (m, 4H), 3.64 – 3.53 (m, 7H), 2.13 – 2.05 (m, 1H), 1.36 – 1.32 (m, 3H), 1.28 (q, *J* = 7.3 Hz, 6H), 1.16 (d, *J* = 6.6 Hz, 3H);

7.32 – 7.26 (m, 3H), 7.25 – 7.14 (m, 2H), 6.63 (s, 2H), 4.83 – 4.70 (m, 2H), 4.29 – 4.24 (m, 4H), 3.60 (s, 6H), 3.47 (q, *J* = 6.9 Hz, 1H), 2.08 (t, *J* = 6.5 Hz, 1H), 1.33 (dt, *J* = 19.9, 7.1 Hz, 6H), 1.08 (d, *J* = 6.6 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 3H).

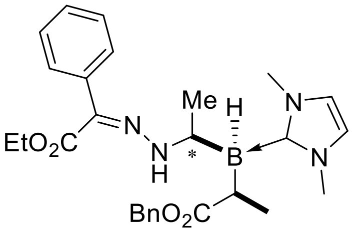
^{11}B NMR (193 MHz, Chloroform-*d*) δ –15.95 (d, *J* = 90.7 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -15.95 (s, 1B)

^{13}C NMR (151 MHz, Chloroform-d) δ 182.29, 164.96, 164.52, 137.10, 128.42, 128.37, 127.84, 121.17, 112.25, 64.96, 59.89, 59.82, 20.65, 17.42, 14.59, 14.32;

δ 182.11, 164.96, 137.27, 128.61, 128.41, 127.87, 121.18, 113.77, 64.89, 60.16, 60.04, 36.87, 29.84, 21.72, 17.10, 14.64, 14.45.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{24}H_{35}BN_4O_6$+Na$^+$ 509.2452, found 509.2551.



71, colorless oil, 36 %, d.r. =1/1.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 – 7.53 (m, 1H), 7.38 – 7.26 (m, 5H), 7.26 – 7.14 (m, 3H), 6.92 – 6.88 (m, 1H), 6.66 – 6.59 (m, 2H), 4.95 – 4.65 (m, 2H), 4.27 – 4.11 (m, 2H), 3.67 – 3.61 (m, 6H), 3.45 – 3.38 (m, 1H), 2.19 – 2.11 (m, 0.5H), 2.02 – 1.96 (m, 0.5H), 1.31 (t, *J* = 7.1 Hz, 1.5H), 1.25 (t, *J* = 7.1 Hz, 1.5H). 1.20 (dd, *J* = 9.7, 6.7 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 1.5H), 0.89 (d, *J* = 6.9 Hz, 1.5H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ -15.98 (d, *J* = 100.8). -16.52 (d, *J* = 100.8).

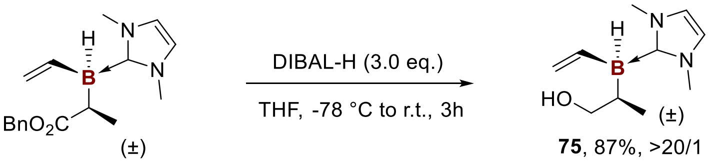
^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -15.98, -16.52.

^{13}C NMR (151 MHz, Chloroform-d) δ 182.52, 165.17/164.08, 138.83, 137.34/137.16, 131.76, 129.48/128.99, 128.47/128.45, 128.40/128.37, 128.27/127.70, 127.88/127.78, 125.70, 121.08, 64.97/64.83, 60.24/59.61, 37.03, 22.44/22.41, 17.70/17.26, 14.70/14.55.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{27}H_{35}BN_4O_4$+Na$^+$ 513.2643, found 513.2650.

5.3 Ester reduction

5.3.1 Reduction of 3



75, 87%, >20/1

To a solution of **3** (29.8 mg, 0.1 mmol, 1.0 eq.) in anhydrous THF (1 mL), DIBAL-H (0.3 mmol, 1.5 M in toluene, 3.0 eq.) was added dropwise at -78°C. After stirring at this temperature for 30 min, the mixture was warmed to room temperature and stirred for another 2.5 hours. After completion, water was added to quench the reaction. The aqueous phase was extracted by ethyl acetate three times. The organic phase was combined and dried with anhydrous Na_2SO_4. After being evacuated under reduced pressure, the residue was subjected to column chromatography (triethylamine-activated SiO_2) to give **75** as a colorless oil. (87%, > 20/1 d.r.) Fresh DIBAL-H is essential to repeat this reaction.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.80 (s, 2H), 6.46 – 6.38 (m, 1H), 5.30 (s, 1H), 4.88 (d, *J* = 19.4 Hz, 1H), 3.76 (s, 6H), 3.32 – 3.24 (m, 2H), 1.64 (s, 1H), 0.99 (s, 3H).

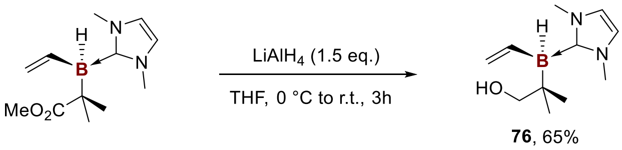
^{11}B NMR (193 MHz, Chloroform-*d*) δ –19.76 (d, *J* = 81.9 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -19.76 (s, 1B)

^{13}C NMR (151 MHz, Chloroform-d) δ 120.87, 119.36, 71.20, 36.74, 17.16.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{10}H_{19}BN_2O+Na^+$ 217.1483, found 217.1495.

5.3.2 Reduction of 50



To a suspension of $LiAlH_4$ (6 mg, 0.15 mmol, 1.5 eq.) in anhydrous THF (1 mL), solution of **50** (23.6 mg, 0.1 mmol, 1.0 eq.) in anhydrous THF (1 mL) was added at 0 °C dropwise. The reaction was stirred at room temperature for 3 hours. After the start materials were all consumed, water was added to quench the reaction. The aqueous phase was extracted by ethyl acetate three times. The organic phase was combined and dried with anhydrous Na_2SO_4. After being evacuated under reduced pressure, the residue was subjected to column chromatography (triethylamine-activated SiO_2) to give **76** as a colorless oil. (13.3 mg, 65%)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.83 (s, 2H), 6.56 – 6.48 (m, 1H), 5.35 (s, 1H), 5.08 (d, *J* = 19.2 Hz, 1H), 3.81 (s, 6H), 3.39 (d, *J* = 9.7 Hz, 1H), 3.18 – 3.08 (m, 1H), 2.12 (s, 1H), 0.79 (s, 3H), 0.70 (s, 3H).

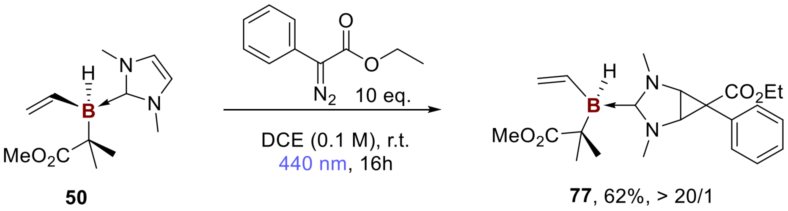
^{11}B NMR (193 MHz, Chloroform-*d*) δ –18.74 (d, *J* = 80.4 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -18.73 (s, 1B)

^{13}C NMR (151 MHz, Chloroform-d) δ 120.60, 120.41, 74.73, 36.78, 25.96, 24.82.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{11}H_{21}BN_2O+Na^{+}$ 231.1639, found 231.1635.

5.4 Reaction of 50 with carbene



50 (23.6 mg, 0.1 mmol, 1 eq.) and ethyl 2-diazo-2-phenylacetate (158 mg, 1 mmol, 10 eq.) were added to a 10 mL Schlenk tube. The tube was evacuated and refilled with N_2 three times. Then, anhydrous DCE (1 mL) was added before the tube was sealed tight. The reaction tube was placed 3 cm from a blue LED Kessil lamp (440 nm) at 40W with cooling fans and a water bath for 16 hours. After the reaction, the mixture was quenched under air, and the solvents were evacuated *in vacuo*. The residue was then subjected to flash column chromatography on neutral aluminum oxide (200 – 300 mesh) to give **77** as a colorless oil. (24.8 mg, 87%, > 20/1 d.r.)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 – 7.31 (m, 3H), 7.06 – 7.04 (m, 2H), 5.93 – 5.84 (m, 1H), 4.93 – 4.73 (m, 1H), 4.32 (dd, *J* = 40.7, 6.8 Hz, 2H), 4.14 – 4.05 (m, 2H), 3.87 – 3.64 (m, 1H), 3.51 (s, 3H), 3.39 (s, 3H), 3.18 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.99 (s, 3H), 0.94 – 0.84 (m, 3H).

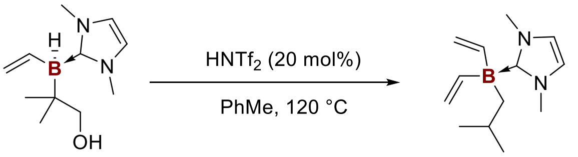
^{11}B NMR (193 MHz, Chloroform-*d*) δ –16.82 (d, *J* = 89.5 Hz, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -16.80 (s, 1B)

^{13}C NMR (151 MHz, Chloroform-d) δ 184.02, 171.72, 131.89, 129.05, 128.87, 127.58, 121.04, 62.00, 55.34, 54.95, 50.58, 37.82, 37.32, 27.72, 25.88, 25.58, 14.18.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{22}H_{31}BN_2O$+Na^{+} 421.2269, found 421.2278.

5.5 *1,2*-Boryl migration



76

78, 32%

Under a dry N_2 atmosphere, **76** (20.8 mg, 0.1 mmol, 1.0 eq.) was dissolved in anhydrous PhMe (0.1 M) in an oven-dried 10 mL Schlenk tube. Then, $HNTf_2$ (0.02 mmol, 20 mol%) was added before the tube was sealed tightly. The mixture was stirred at 110 °C overnight. After the reaction, the solvents were evacuated under reduced pressure, and the residue was subjected to column chromatography (neutral Al_2O_3) to give **78** as a colorless oil. (7.0 mg, 32%)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.73 (s, 2H), 6.49 – 6.41 (m, 2H), 5.28 (d, – = 12.5 Hz, 2H), 4.97 – 4.89 (m, 2H), 3.78 (s, 6H), 1.55 – 1.51 (m, 1H), 0.65 (d, *J* = 6.5 Hz, 6H), 0.61 (d, *J* = 6.2 Hz, 2H).

^{11}B NMR (193 MHz, Chloroform-*d*) δ –16.47 (s, 1B).

^{11}B {^{1}H} NMR (193 MHz, Chloroform-*d*) δ -16.47 (s, 1B)

^{13}C NMR (151 MHz, Chloroform-d) δ 121.40, 116.24, 38.04, 27.02, 26.45.

HRMS(ESI) m/z (M+Na^{+}) calculated for $C_{13}H_{23}BN_2$+Na^{+} 241.1847, found 241.1847.

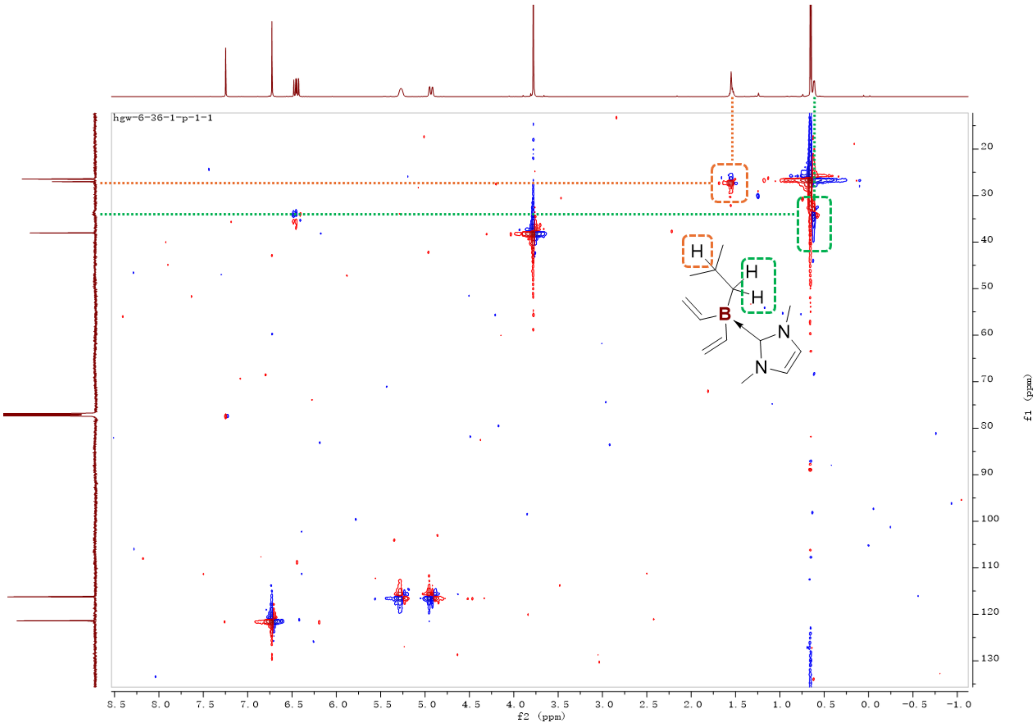


Fig. S3. ^{13}C-^{1}H HSQC spectrum of **78**

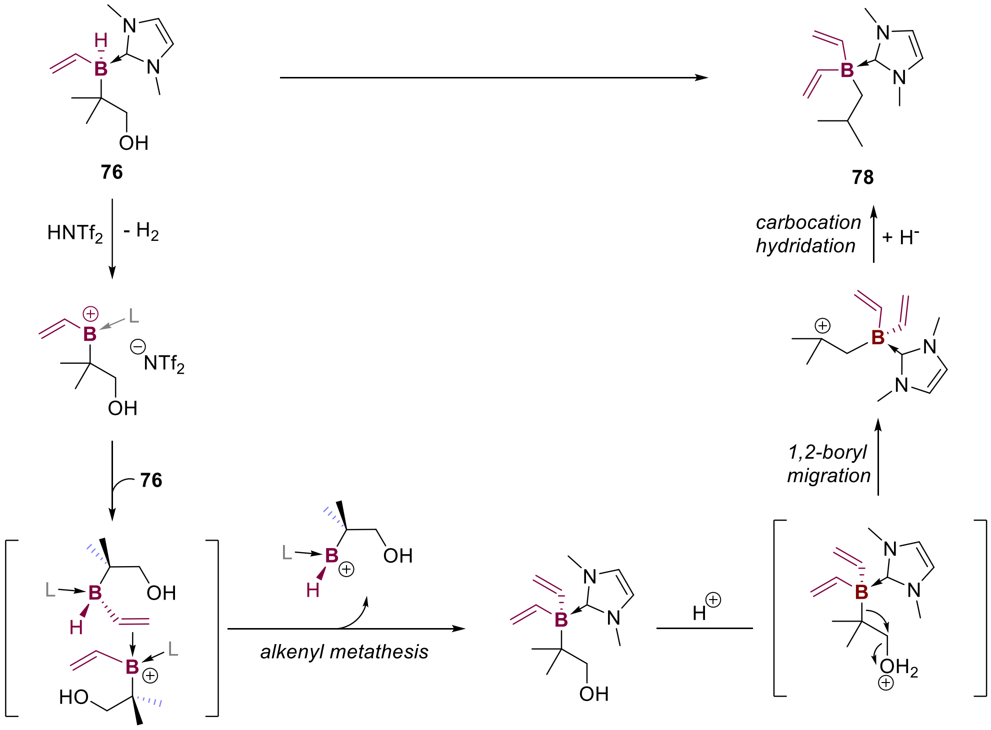
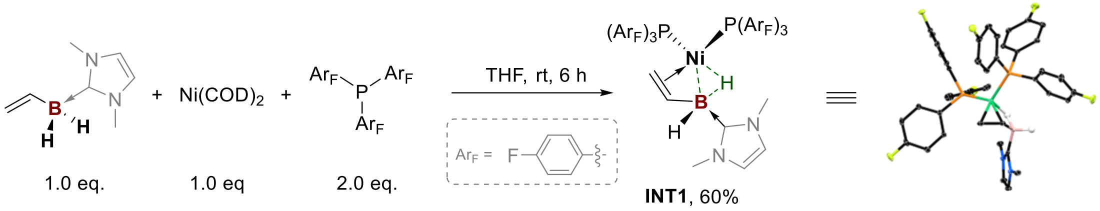


Fig. S4. Proposed mechanism of 1,2-boryl migration

6. Mechanistic Investigations

6.1. Synthesis of INT1



In a N_2-filled glove box, $Ni(COD)_2$ (27.5 mg, 0.1 mmol) and P(*p*-F-Ph)$_3$ (63.2 mg, 0.2 mmol, 2.0 eq.) were mixed in a 20 mL flamed-dried vial with a stirring bar. Anhydrous THF (4 mL) was then added. After being stirred for 45 min, to the mixture was added a solution of borane (13.6 mg, 0.1 mmol, 1.0 eq.) in anhydrous THF (1 mL). The resulting mixture was then stirred at room temperature for 6 hours. After the reaction, the THF solvent was evacuated under reduced pressure, and anhydrous hexane (4 mL) was added to the tube. After stirring for 30 minutes, yellow solids were precipitated, which were collected through filtration and washed with hexane (2*3 mL). The single crystal of **INT1** was obtained by slowly evacuating the solvent of a benzene solution of yellow to orange solids in the glove box (49 mg, 60%).

Fig. S5. Picture of **INT1** (49 mg)

^{1}H NMR (600 MHz, Benzene-*d*) δ 7.39 – 7.31 (m, 6H), 7.27 – 7.18 (m, 6H), 6.75 – 6.63 (m, 12H), 5.43 (s, 2H), 4.10 – 4.01 (m, 1H), 3.74 (d, *J* = 9.9 Hz, 1H), 2.99 (s, 6H), 2.85 (t, *J* = 13.3 Hz, 1H), 0.81 – 0.42 (br, 1H, B*H*), -0.63 – -1.12 (br, 1H, B*H*).

^{11}B NMR (193 MHz, Benzene -*d6*) δ -29.29 (brs, 1B)

^{11}B {^{1}H} NMR (193 MHz, Benzene -d6) δ -29.29 (s, 1B).

^{13}C NMR (151 MHz, Benzene-*d6*) δ 163.89 (d, *J* = 13.3 Hz), 162.25 (d, *J* = 12.9 Hz), 136.25 (d, *J* = 23.8 Hz), 135.70 (d, *J* = 7.8 Hz), 135.60 (d, *J* = 7.4 Hz), 135.19 (d, *J* = 7.8 Hz), 135.09 (d, *J* = 7.5 Hz), 119.77, 114.78 (d, *J* = 8.7 Hz), 114.64 (d, *J* = 8.8 Hz), 65.48, 35.96,

^{19}F NMR (151 MHz, Benzene-*d6*) δ -113.44, -114.02**.**

^{31}P NMR (243 MHz, Benzene-*d6*) δ 42.84 (d, *J* = 72.3 Hz), 13.80 (d, *J* = 72.1 Hz)

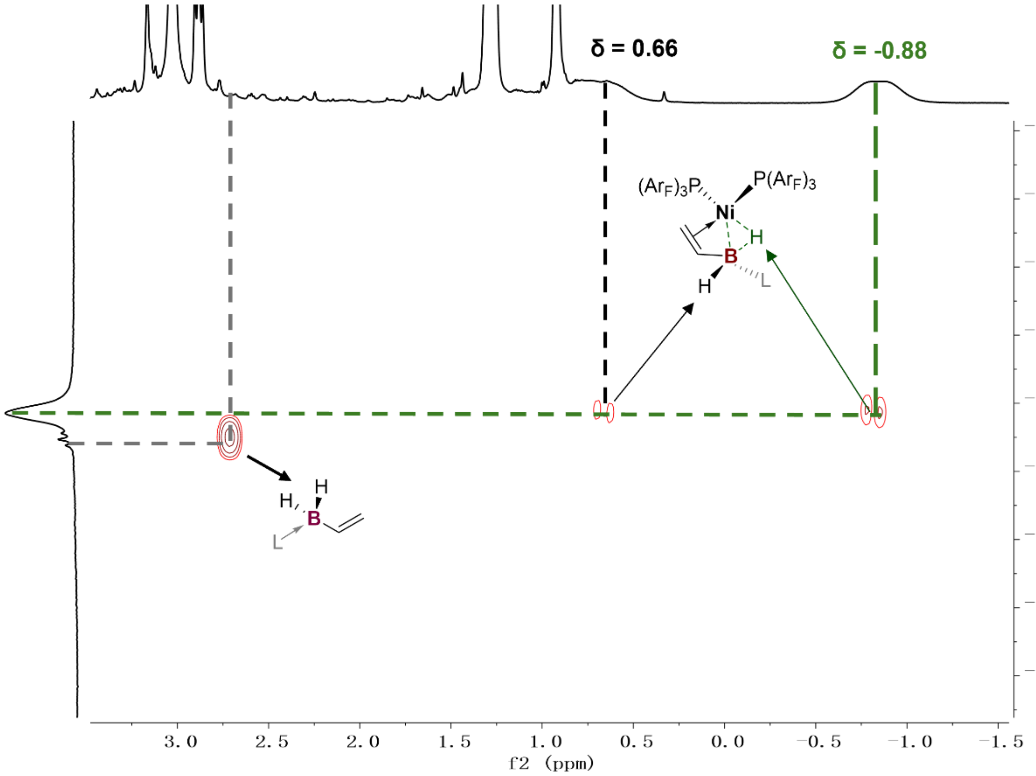
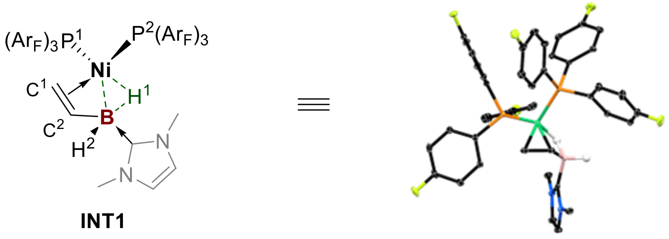


Fig. S6. ^{11}B-^{1}H HMQC spectrum of **INT1**, broad peaks at 0.66 and -0.88 ppm were assigned to two B-Hs; a small portion of feedstock **1** was also observed.

X-ray crystal structure of INT1



INT1

Key bond lengths (Å)

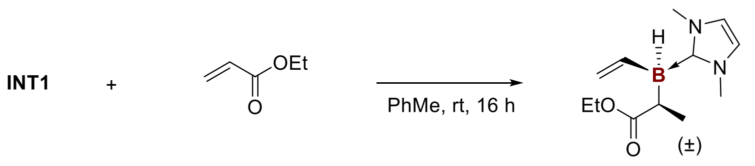
	Ni-C¹	Ni-C²	Ni-B	Ni-H¹
Bond Lengths (Å)	2.1204(18)	2.0023(18)	2.2841(19)	1.65(2)
	B-H¹	B-H²	Ni-P¹	Ni-P²
Bond Lengths (Å)	1.30(2)	1.12(2)	2.1340(5)	2.1763(5)

Table S4. Crystal data and structure refinement for INT1 (CCDC 2381595).

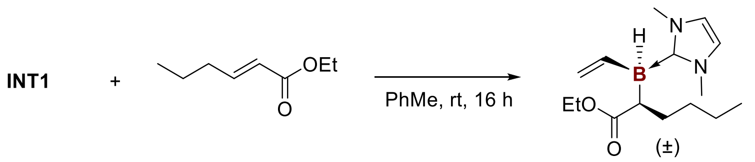
Identification code	GHUAF4_Cu100k_auto
Empirical formula	$C_{46}H_{43.75}BF_6N_2NiP_2$
Formula weight	870.04
Temperature/K	99.98(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.01864(11)
b/Å	11.91416(9)
c/Å	28.8690(2)
α/°	90
β/°	92.2828(8)
γ/°	90
Volume/Å^3	4130.53(6)
Z	4
ρ_{calc}g/cm^3	1.399
μ/mm^{-1}	1.943
F(000)	1803
Crystal size/mm^3	0.15 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.362 to 145.982
Index ranges	$-14 \leq h \leq 14$, $-9 \leq k \leq 14$, $-35 \leq l \leq 34$
Reflections collected	12865
Independent reflections	7963 [R_{int} = 0.0136, R_{sigma} = 0.0237]
Data/restraints/parameters	7963/70/600
Goodness-of-fit on F^2	1.026

Final R indexes [I>=2σ (I)]	$R_1 = 0.0349$, $wR_2 = 0.0903$
Final R indexes [all data]	$R_1 = 0.0411$, $wR_2 = 0.0947$
Largest diff. peak/hole / e Å^{-3}	0.77/-0.53

6.2. Hydroboration using INT1 as a substrate



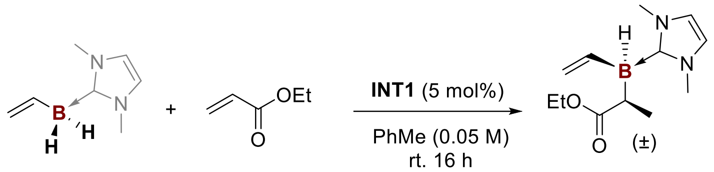
4, 28%, dr = 18/1



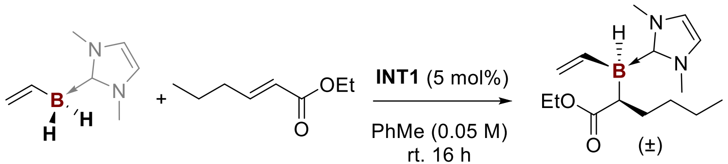
41, 21%, dr > 20/1

In a N_2-filled glove box, **INT1** (42 mg, 0.05 mmol, 1.0 eq.) was dissolved in anhydrous toluene (1 mL) in a flamed-dried 4 mL vial with a stirring bar. Ethyl acrylate (5 mg, 0.05 mmol, 1.0 eq.) or ethyl *trans*-2-hexenoate (7.1mg, 0.05 mmol, 1.0 eq.) was then added to the solution. The vial was then sealed tightly and stirred at room temperature for 16 hours. After completion, the solvent was evacuated under reduced pressure, and the residue was subjected to flash column chromatography on neutral aluminum oxide (200 – 300 mesh) to give **4** (28%, dr = 18/1) or **41** (21%, dr > 20/1).

6.3. Hydroboration using INT1 as a catalyst



4, 85%, dr = 7/1



41, 88%, dr = 16/1

In a N_2-filled glove box, **INT1** (2.1 mg, 0.0025 mmol, 5 mol%) was dissolved in anhydrous toluene (x mL) in a flamed-dried 4 mL vial with a stirring bar. Ethyl acrylate (x mg, 0.05 mmol, 1.0 eq.) or ethyl *trans*-2-hexenoate (7.1 mg, 0.05 mmol, 1.0 eq.) was then added to the solution, followed by the addition of **1** (8.4 mg, 0.06 mmol, 1.2 eq.). The vial was sealed tightly and stirred at room temperature for 16 hours. After completion, the solvent was evacuated under reduced pressure, and the residue was subjected to flash column chromatography on neutral aluminum oxide (200 – 300 mesh) to give **4** (85%, dr = 7/1) or **41** (88%, dr > 18/1)

6.4. Deuterium labelling experiments

6.4.1. Synthesis of 1-*D2*

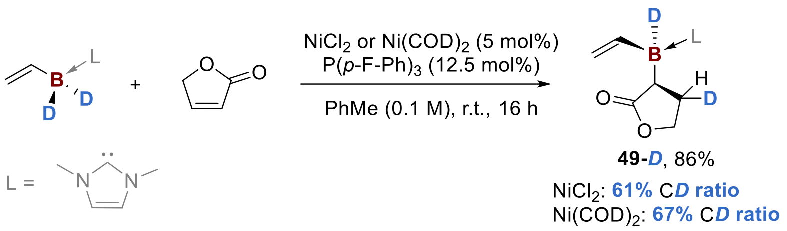
1-*D2* was synthesized using the same procedure for synthesizing **1** using NHC-BD_3 as the starting material. Purification by column chromatography (triethylamine activated SiO_2) gave the pure product as a colorless oil with 33% isolation yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.83 (s, 2H), 6.33 – 6.25 (m, 1H), 5.29 – 5.13 (br, 1H), 4.79 (d, *J* = 18.7 Hz, 1H), 3.77 (s, 6H).

^{11}B NMR (193 MHz, Benzene -*d6*) δ -28.26 (brs, 1B)

^{11}B {^{1}H} NMR (193 MHz, Benzene -d6) δ -28.26 (brs, 1B).

6.4.2. Hydroboration with 1-*D2*



49-*D*, 86%

NiCl$_2$: **61% C*D* ratio**

Ni(COD)$_2$: **67% C*D* ratio**

Under a dry N_2 atmosphere, $NiCl_2$ (0.6 mg, 5 mol%) or Ni(COD)$_2$ (1.3 mg, 5 mol%) and (*p*-F-Ph)$_3$P (4 mg, 12.5 mol%) were dissolved in toluene (0.5 mL) a 10 mL Schlenk tube with a stirring bar. The mixture was stirred for at least 45 min at room temperature. After that, 2(5H)-furanone (8.4 mg, 0.1 mmol, 1.0 equiv.), toluene (0.5 mL), and **1-*D2*** (13.8 mg, 0.1 mmol, 1.0 eq.) were sequentially added to the reaction mixture. The tube was tightly sealed and stirred at room temperature for 16 hours. After the reaction, the mixture was evacuated *in vacuo* and then subjected to flash column chromatography on neutral aluminum oxide (200 – 300 mesh) to give **49-*D*** with one hydrogen of β-CH_2 referred to boron was deuterated.

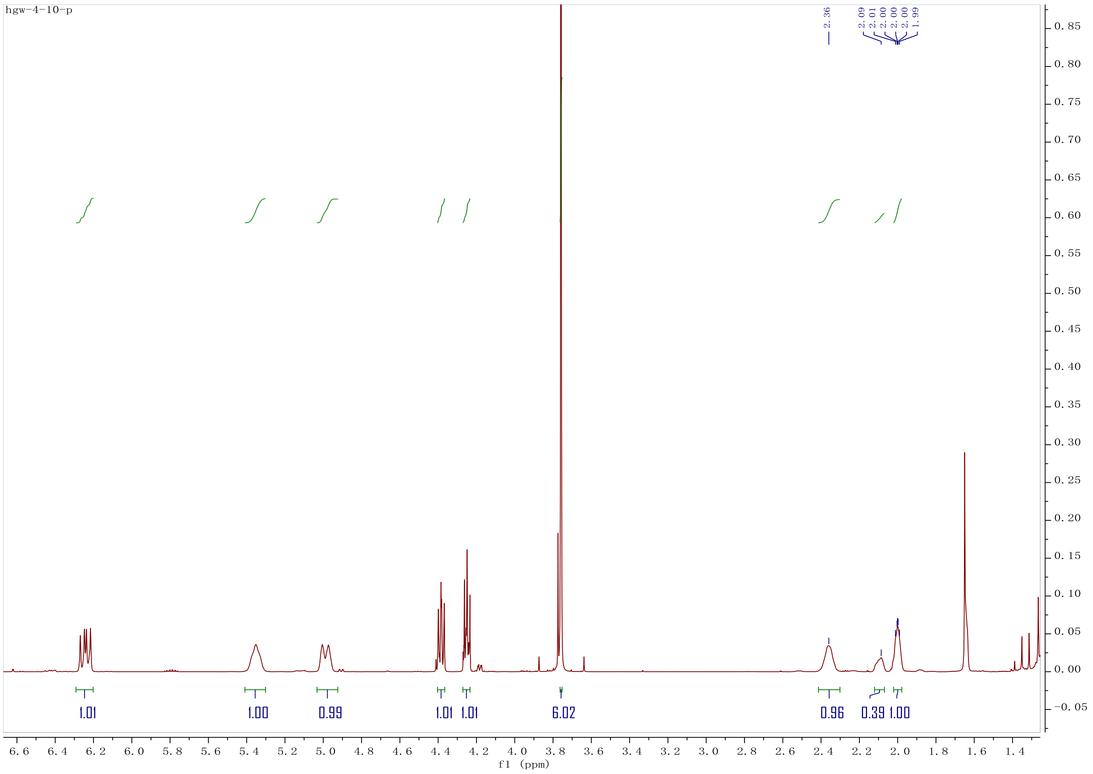


Fig. S7. ^{1}H NMR spectrum of **49-*D*** using $NiCl_2$ as a catalyst.

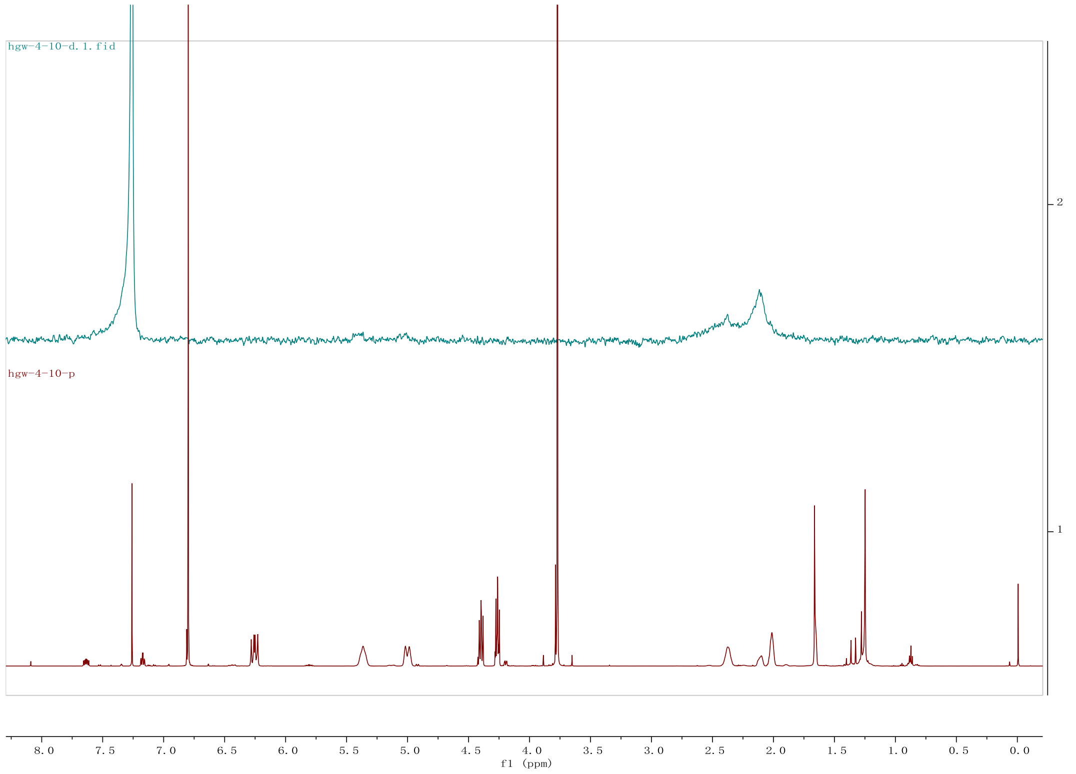


Fig. S8. Comparison between ^{1}H NMR and ^{2}H NMR spectra of **49-D** using $NiCl_2$ as a catalyst.

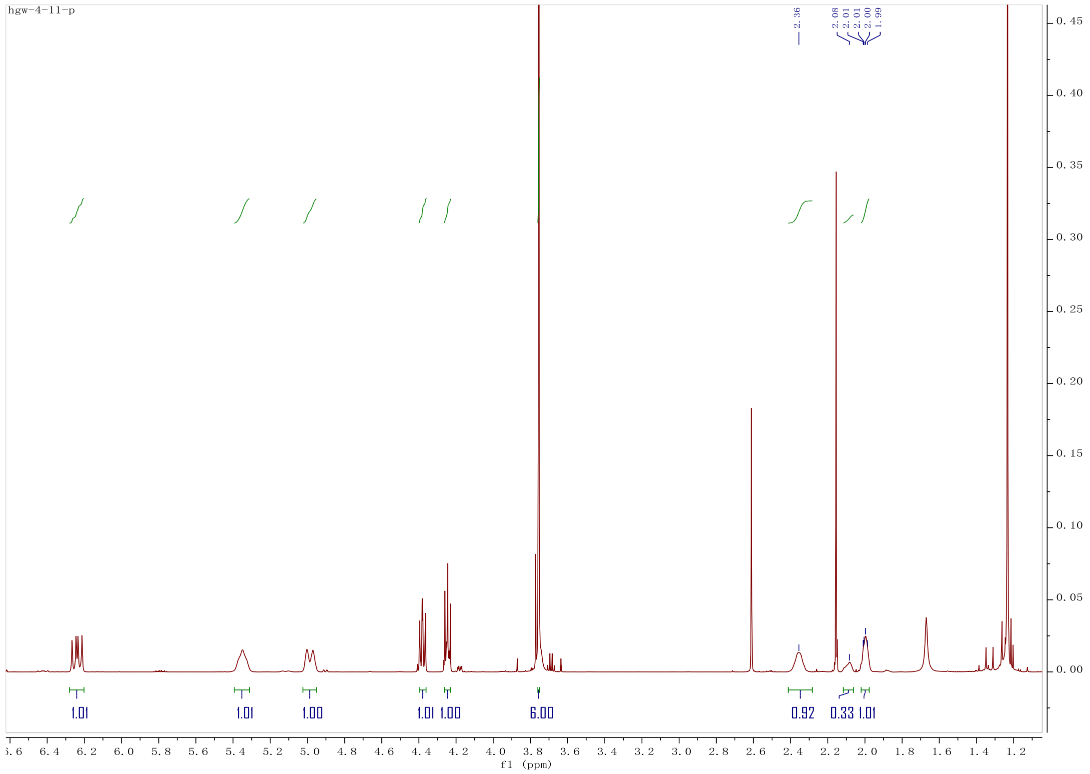


Fig. S9. ^{1}H NMR spectrum of **49-*D*** using $Ni(COD)_2$ as a catalyst.

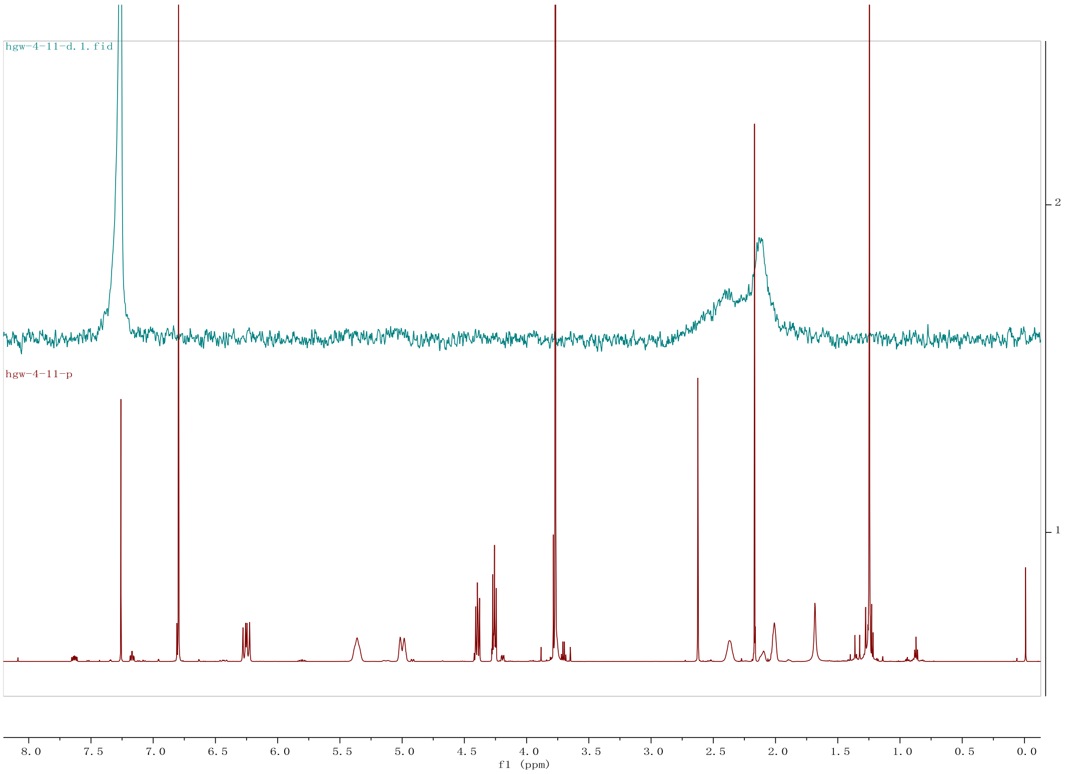
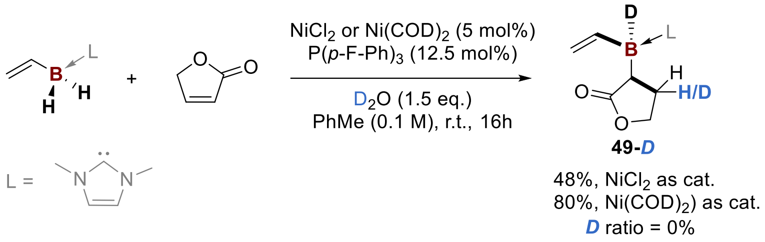


Fig. S10. Comparison between ^{1}H NMR and ^{2}H NMR spectra of **49-D** using Ni(COD)$_2$ as a catalyst.

6.4.3. Hydroboration with D$_2$O as an additive.



Under a dry N$_2$ atmosphere, NiCl$_2$ (0.6 mg, 5 mol%) or Ni(COD)$_2$ (1.3 mg, 5 mol%) and (*p*-F-Ph)$_3$P (4 mg, 12.5 mol%) were dissolved in toluene (0.5 mL) a 10 mL Schlenk tube with a stirring bar. The mixture was stirred for at least 45 min at room temperature. After that, 2(5H)-Furanone (8.4 mg, 0.1 mmol, 1.0 equiv.), toluene (0.5 mL), **1** (6.8 mg, 0.1 mmol, 1.0 eq.) and D$_2$O (3 mg, 0.15 mmol, 1.5 eq.) were sequentially added to the reaction mixture. The tube was tightly sealed and stirred at room temperature for 16 hours. After the reaction, the mixture was evacuated *in vacuo* and then subjected to flash column chromatography on neutral aluminum oxide (200 – 300 mesh) to give **49**-*D*. No deuteration of B-H or C-H was observed.

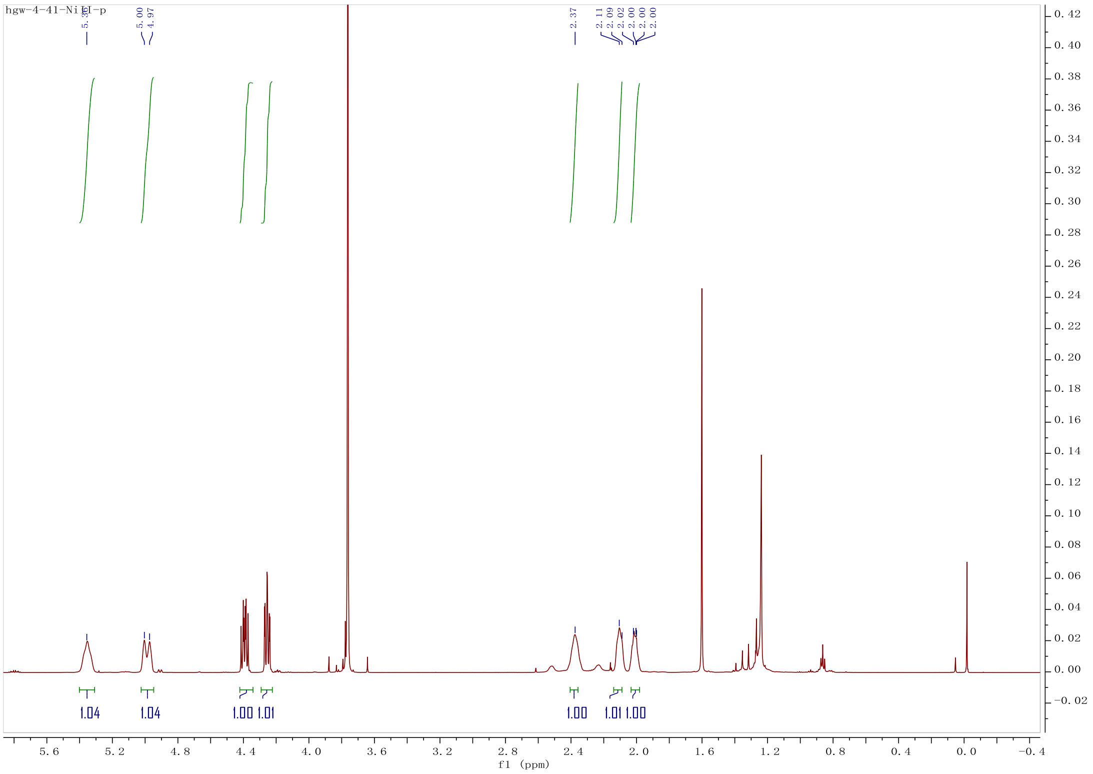


Fig. S11. ^{1}H NMR spectrum of **49** with D2O as the additive using NiCl$_2$ as a catalyst.

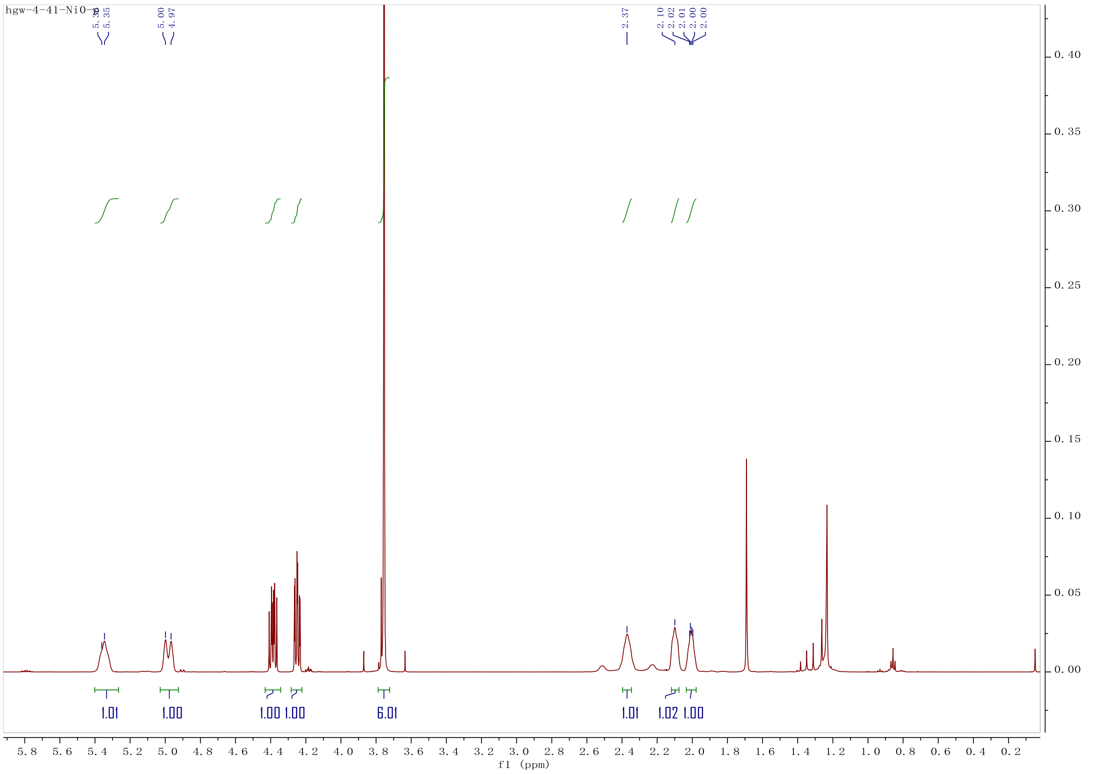
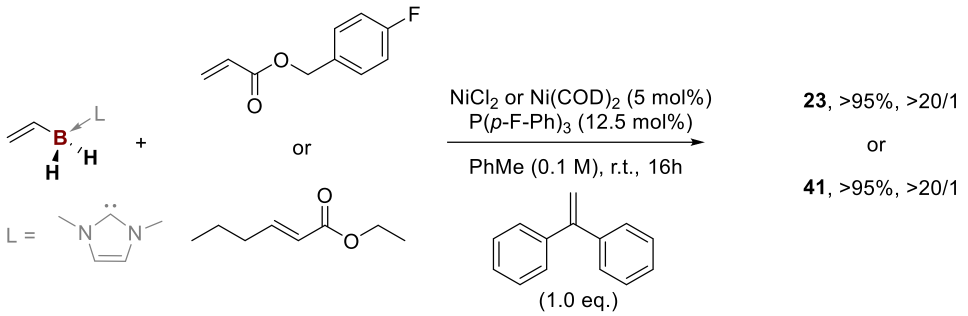


Fig. S12. ^{1}H NMR spectrum of **49** with D2O as the additive using Ni(COD)$_2$ as a catalyst.

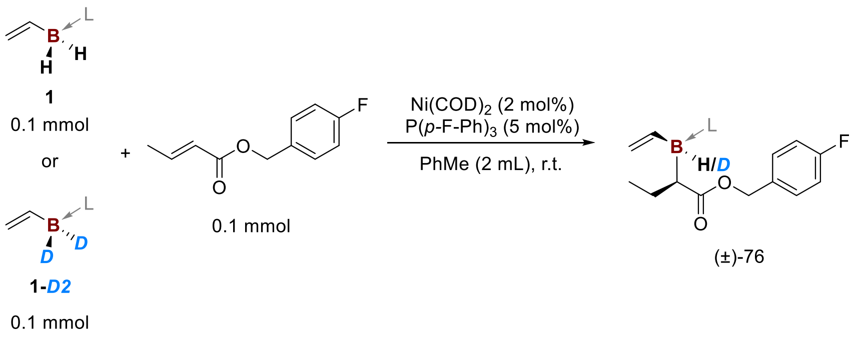
6.5. Radical capture experiment.



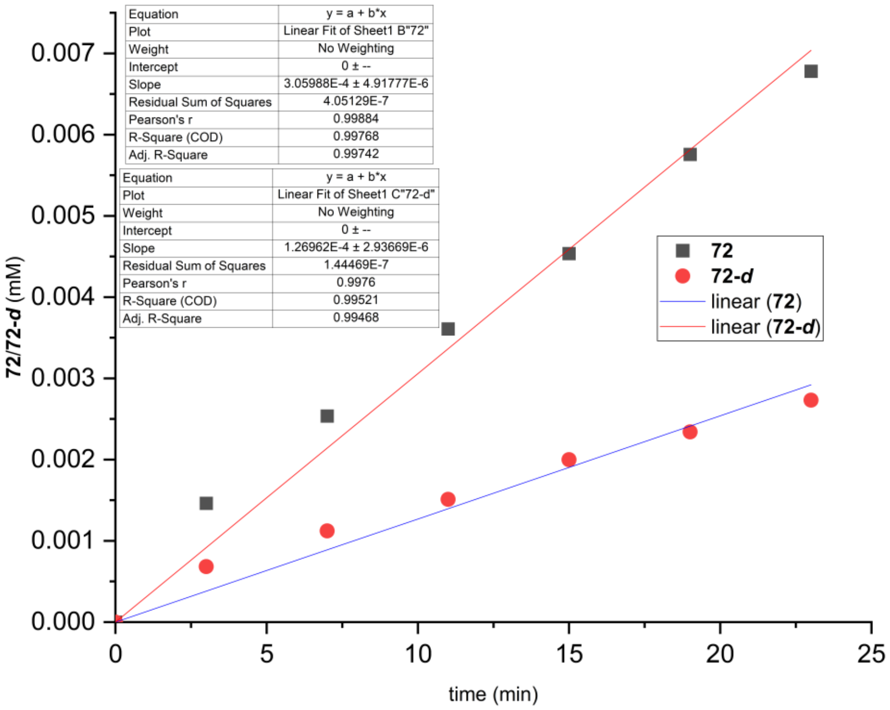
Under a dry N_2 atmosphere, $NiCl_2$ (0.6 mg, 5 mol%) or $Ni(COD)_2$ (1.3 mg, 5 mol%) and (*p*-F-Ph)$_3$P (4 mg, 12.5 mol%) were dissolved in toluene (0.5 mL) a 10 mL Schlenk tube with a stirring bar. The mixture was stirred for at least 45 min at room temperature. After that, 4-fluorobenzyl acrylate (18 mg, 0.1 mmol, 1.0 equiv.) or ethyl *trans*-2-hexenoate (14.2 mg, 0.1 mmol, 1.0 equiv.), toluene (0.5 mL), **1** (16.3 mg, 0.12 mmol, 1.2 eq.) and 1,1'-diphenylethene (18 mg, 0.1 mmol, 1 eq.) were sequentially added to the reaction mixture. The tube was tightly sealed and stirred at room temperature for 16 hours. After the reaction, the solvent was evacuated in vacuo, and the residue was subjected to ^{1}H NMR analyses to identify the yields and drs using 1,3,5-trimethoxybenzene as an internal standard. The experimental results indicated that the presence of a radical capture did not affect the hydroboration, negating the involvement of a radical pathway.

6.6. KIE experiments

6.6.1 Parallel experiments



The parallel experiments were performed using **1** or **1-*D2*** to react with 4-fluorobenzyl (E)-but-2-enoate. In a N_2-filled glove box, $Ni(COD)_2$ (27.5 mg, 0.01 mmol) and (*p*-F-Ph)$_3$P (80 mg, 0.025 mmol) were added to an oven-dried vial. Then, 2 mL anhydrous toluene was added through micro-syringe. This nickel-complex solution was stirred for at least 30 min before use. In another oven-dried 10 mL Schlenk tube, 2 mL anhydrous toluene was added through micro-syringe, followed by adding the prepared [*Ni*] solution (40 μL), 1-fluornaphthalene (internal standard, 10 μL, 1 M in toluene), 4-fluorobenzyl (E)-but-2-enoate (19.4 mg, 0.11 mmol, 1 eq.) and **1** (13.6 mg, 0.1 mmol) or **1-*D2*** (13.8 mg, 0.1 mmol) in sequence before the tube was taken out of the glove box. Aliquots of the reaction mixture were taken via syringe (100 μL) at 3, 7, 11, 15, 19, and 23 min, and immediately placed in acetone (0.5 mL) under air. The yield of the product was detected by ^{19}F NMR. The initial reaction rate was determined through plotting the yield against reaction time. Subsequently, parallel KIE was calculated by comparing the initial rates **(k_H/k_D = 2.41)**.

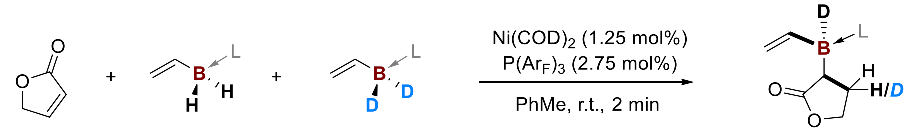


Equation	y = a + b*x
Plot	Linear Fit of Sheet1 B"72"
Weight	No Weighting
Intercept	0 ± --
Slope	3.05988E-4 ± 4.91777E-6
Residual Sum of Squares	4.05129E-7
Pearson's r	0.99884
R-Square (COD)	0.99768
Adj. R-Square	0.99742

Equation	y = a + b*x
Plot	Linear Fit of Sheet1 C"72-d"
Weight	No Weighting
Intercept	0 ± --
Slope	1.26962E-4 ± 2.93669E-6
Residual Sum of Squares	1.44469E-7
Pearson's r	0.9976
R-Square (COD)	0.99521
Adj. R-Square	0.99468

Fig. S13. Determination of the kinetic isotope effect.

6.6.2. Competitive experiments



0.1 mmol

1, 0.05 mmol

1-*D2*, 0.05 mmol

49(***D***), 15%, ***H*/*D*** = 81/19

k_H/k_D = 2.53

In a N_2-filled glove box, $Ni(COD)_2$ (1.3 mg, 0.005 mmol) and $(p\text{-F-Ph})_3P$ (8 mg, 0.0125 mmol) were dissolved in toluene (2 mL) in a 20 mL flamed-dried vial with a stirring bar. The mixture was stirred for 45 min. Then, 0.1 mL of the catalyst solution was added to a 4 mL flamed-dried vial with a stirring bar. To the vial was sequentially added 2(5H)-furanone (8.4 mg, 0.1 mmol), toluene (1 mL), **1** (6.8 mg, 0.05 mmol, 0.5 eq.), and **1-*D2*** (6.9 mg, 0.05 mmol, 0.5 eq.). The reaction was then stirred for 2 min, followed by being exposed in air for quenching. The crude mixture was dried under vacuum and subjected to ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

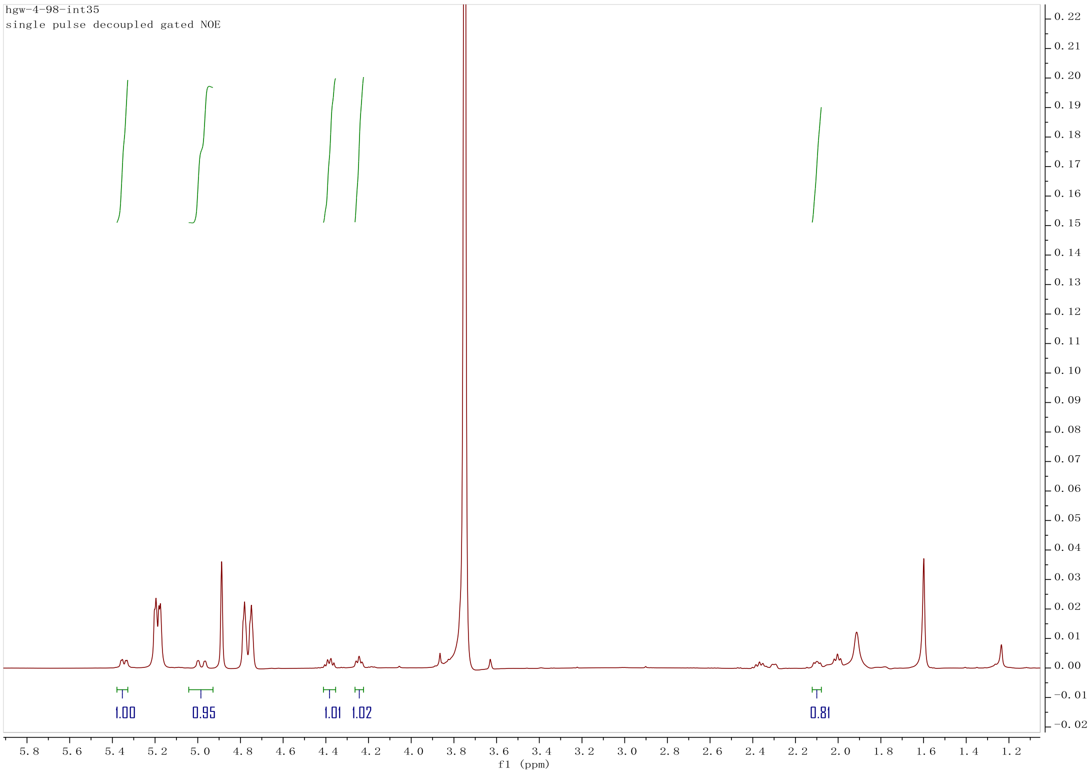


Fig. S14. $^1H\{^{11}B\}$ NMR spectrum of the competitive reaction mixture. The H/D ratio of generated **49** was measured as 81/19, leading to a corresponding k_H/k_D ratio of 2.53.

6.7 Comparison between this nickel catalysis and boryl radical-mediated hydroboration

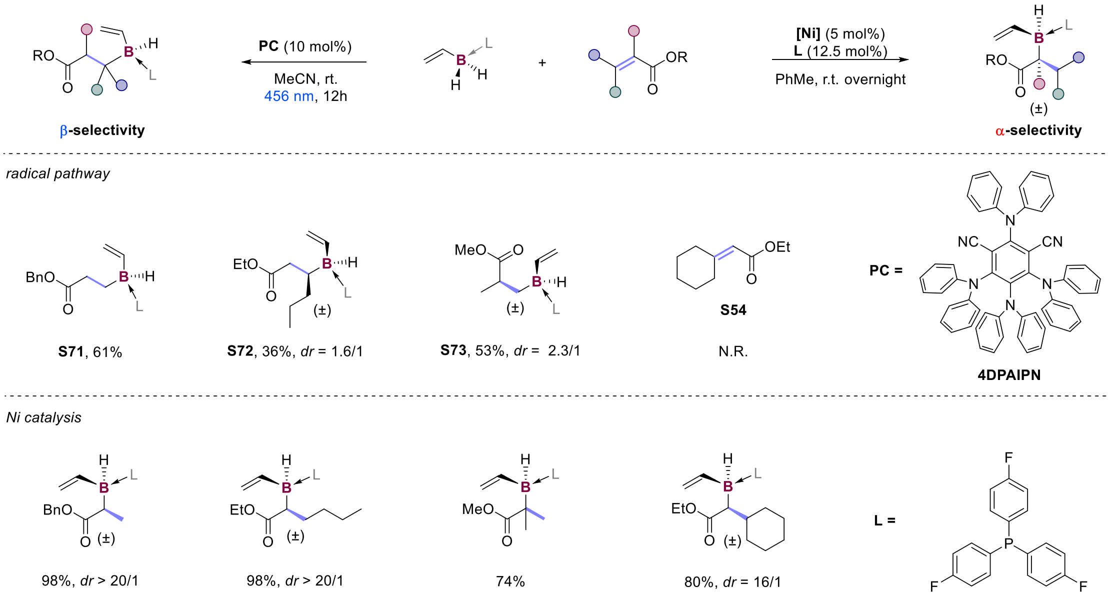
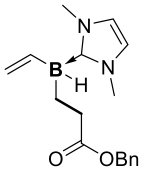


Fig. S14. Representative comparison between Ni-catalysis and boryl radical method.

Under an atmosphere of N_2, 4DPAIPN (8.0 mg, 0.01 mmol, 10 mol%), **1** (0.11 mmol, 1.1 eq.), and alkene (0.1 mmol, 1.0 eq.) were added in a 10 mL Schlenk tube with a stirring bar. Anhydrous MeCN (1 mL) was then added before the tube was tightly sealed. The reaction tube was placed 3 cm from a blue LED Kessil lamp (456 nm) at 40W with cooling fans and a water bath for 12h. After completion, the mixture was quenched under air, and the solvents were evacuated *in vacuo*. The residue was then subjected to flash column chromatography on neutral aluminum oxide (200 – 300 mesh) to give the corresponding products. All yields in this section are isolated yields.

NOTE: The comparison highlights the distinct regioselectivity between our developed Ni-catalysis and the traditional boryl radical-mediated hydroboration. Moreover, the Ni-catalysis protocol is distinguished by its remarkable diastereoselectivity control.



S71, colorless oil, 61%

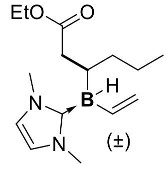
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 5H), 6.76 (s, 2H), 6.37 – 6.26 (m, 1H), 5.34 – 5.22 (m, 1H), 5.02 (s, 2H), 4.95 (d, *J* = 19.4 Hz, 1H), 3.73 (s, 6H), 2.41 – 2.31 (m, 1H), 2.14 – 2.06 (m, 1H), 1.04 – 0.90 (m, 1H), 0.86 – 0.74 (m, 1H).

^{11}B NMR (128 MHz, Chloroform-*d*) δ -20.52 (d, *J* = 82.1 Hz, 1B).

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -20.51 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 128.56, 128.13, 127.99, 120.78, 120.32, 118.67, 118.16, 65.63, 36.56, 35.70.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{17}H_{23}BN_2O_2$+Na$^+$ 321.1745, found 321.1748.



S72, colorless oil, 36%, d.r. = 1.6/1

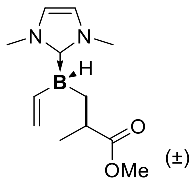
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.79/6.77 (s/s, 2H), 6.45 – 6.29 (m, 1H), 5.28 – 5.22 (m, 1H), 4.93 – 4.76 (m, 1H), 4.10 – 4.04/3.90 – 3.80 (m/m, 2H), 3.79 – 3.77 (m, 6H), 2.21 – 2.11 (m, 1H), 2.44 (dd, *J* = 15.0, 5.1 Hz, 0.4H).1.84 (dd, *J* = 14.2, 7.0 Hz, 0.6H), 1.54 – 1.41 (m, 1H), 1.31 – 1.08 (m, 6H), 1.05 – 0.96 (m, 1H), 0.79 (dt, *J* = 91.1, 7.1 Hz, 3H).

^{11}B NMR (128 MHz, Chloroform-*d*) δ -18.17 (d, J = 83.2 Hz, 1B)..

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -18.17 (s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.47/176.70, 120.72, 119.28/118.77, 59.49, 41.03/ 40.39, 38.65/37.84, 36.78/36.69, 21.60/21.22, 15.07/14.92, 14.45/14.35.

HRMS(ESI) m/z (M+Na$^+$) calculated for $C_{15}H_{27}BN_2O_2$+Na$^+$ 301.2051, found 301.2059.



S72, colorless oil, 53%, d.r. = 2.3/1

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.77/6.76 (s/s, 2H), 6.31 – 6.23 (m, 1H), 5.29 – 5.18 (m, 1H), 4.92 – 4.85 (m, 1H), 3.75 – 3.73 (m, 6H), 3.55 (s, 2.2H), 3.41 (s, 0.8H), 2.32 –2.25 (m, 1H), 1.12 – 0.83 (m, 4H), 0.80 – 0.74 (m, 0.3H), 0.63 – 0.55 (m, 0.7H).

^{11}B NMR (128 MHz, Chloroform-*d*) δ -21.74 (d, *J* = 78.4 Hz, 1B)..

^{11}B {^{1}H} NMR (128 MHz, Chloroform-*d*) δ -21.55/-21.94 (s/s, 1B).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 180.55, 120.73/120.69, 117.85/117.49, 51.11/50.99, 41.17/40.19, 36.51/36.45, 20.73/19.22.

HRMS(ESI) m/z (M-H$^+$) calculated for $C_{12}H_{21}BN_2O_2$ -H$^+$ 235.1618, found 235.1619.

6.8 DFT calculation

All computations were carried out using Gaussian 16 software,[23] and the structures were visualized using GaussView 6 software. More concretely, the structures were optimized under M06[24] / def2-TZVP[25] (Cu, P), 6-31G(d,p) (rest) PCM (toluene) level, while single point energies were obtained under M06 / def2-TZVP SMD (toluene) level. IRC calculations were performed to ensure the transition states related to intermediates. The Cartesian coordinates of all the calculated intermediates and transition states are given in a separate .xyz file.

Fig. S15a depicted the optimized structure of **INT1** together with selected calculated and experimental bond lengths. Fig. S15b shows the energy profiles, considering the four diastereomers. Fig. S15c shows the four diastereomeric **TS1** structures, originating from the three chiral [B, Ni, and C (bonded with the ester group)] centers.

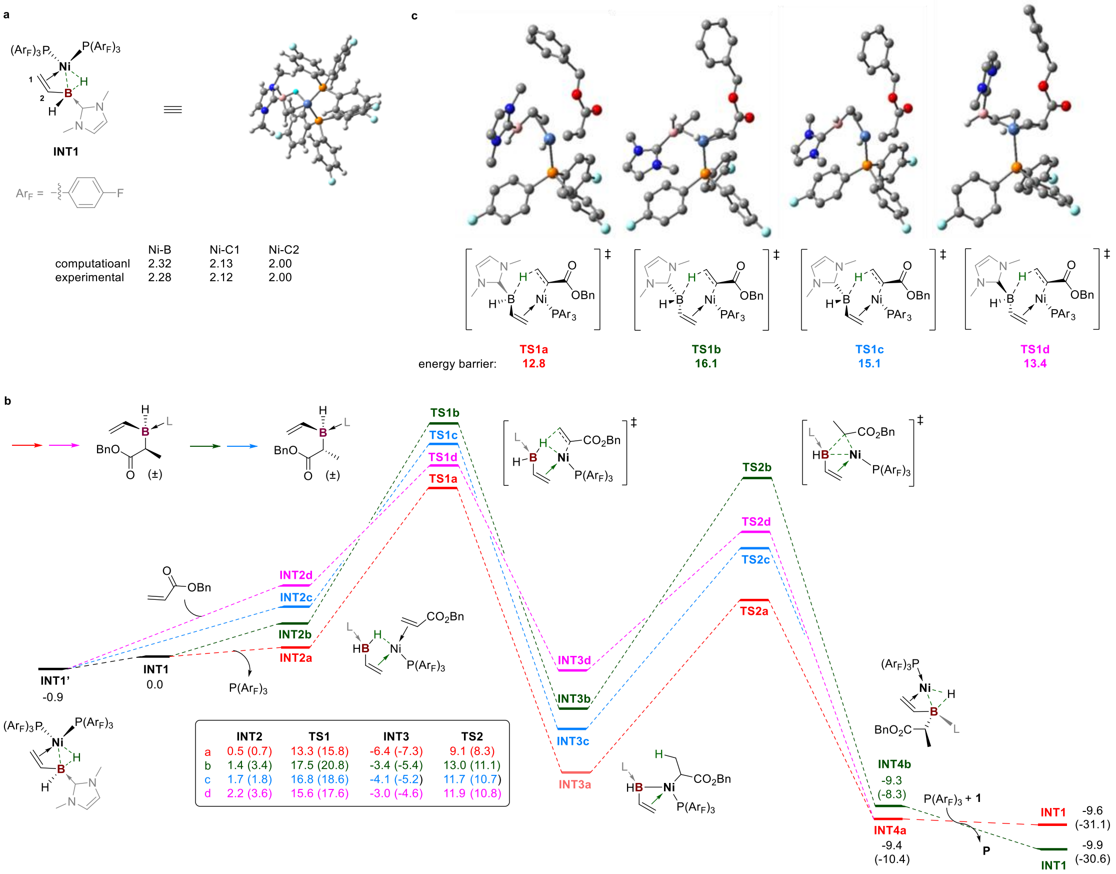
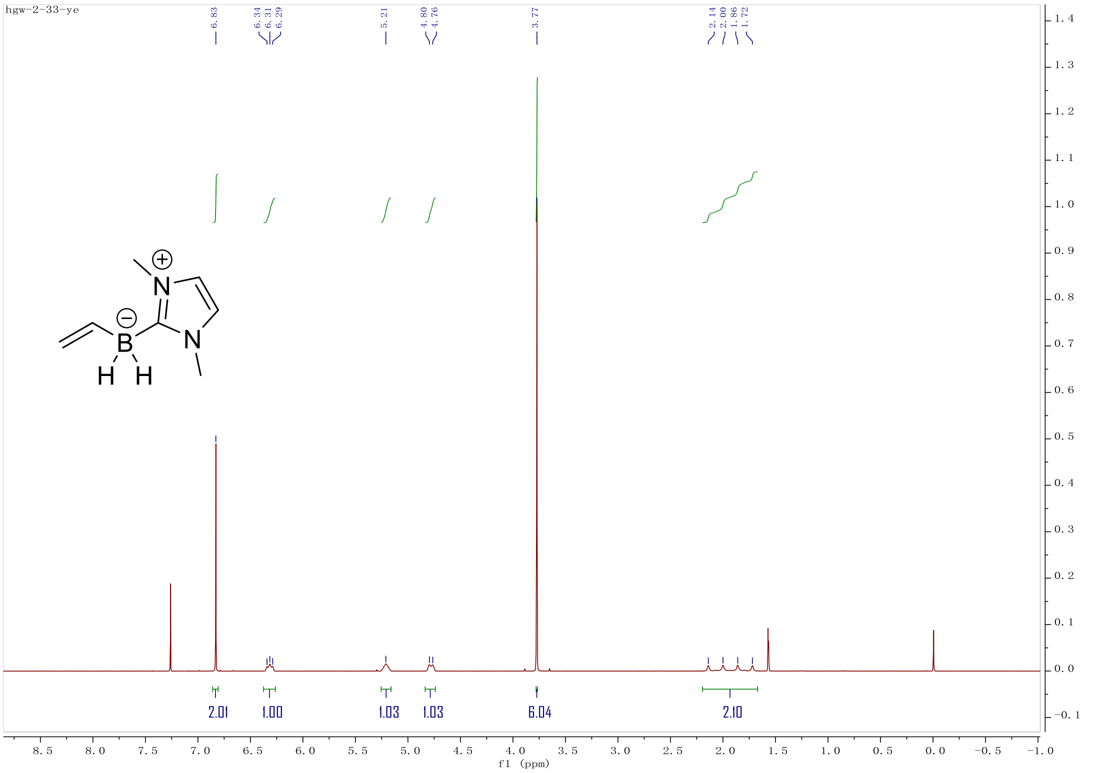


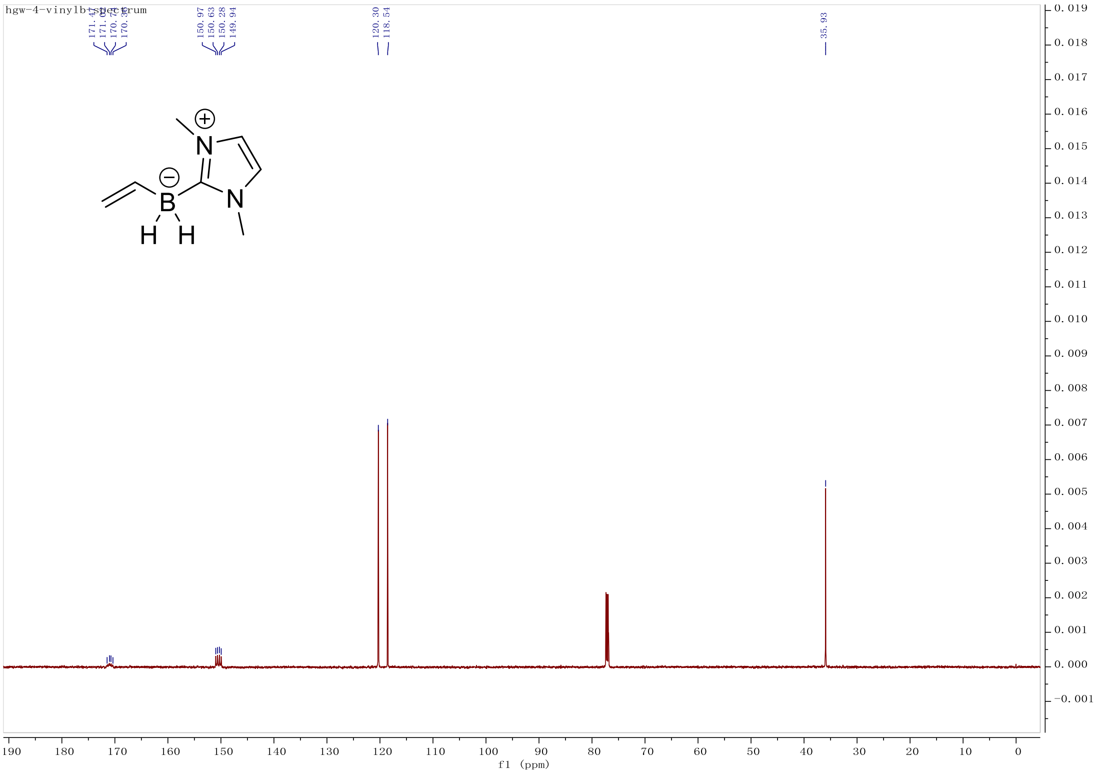
Fig. S15. (**a**) The optimized structure of **INT1** together with selected, calculated and experimental bond lengths. (**b**) Energy profiles, considering the four diastereomers. (**c**) Optimized structures of four diastereomeric **TS1** transition states. H atoms except B*H* were omitted for clarity.

7. NMR Spectra

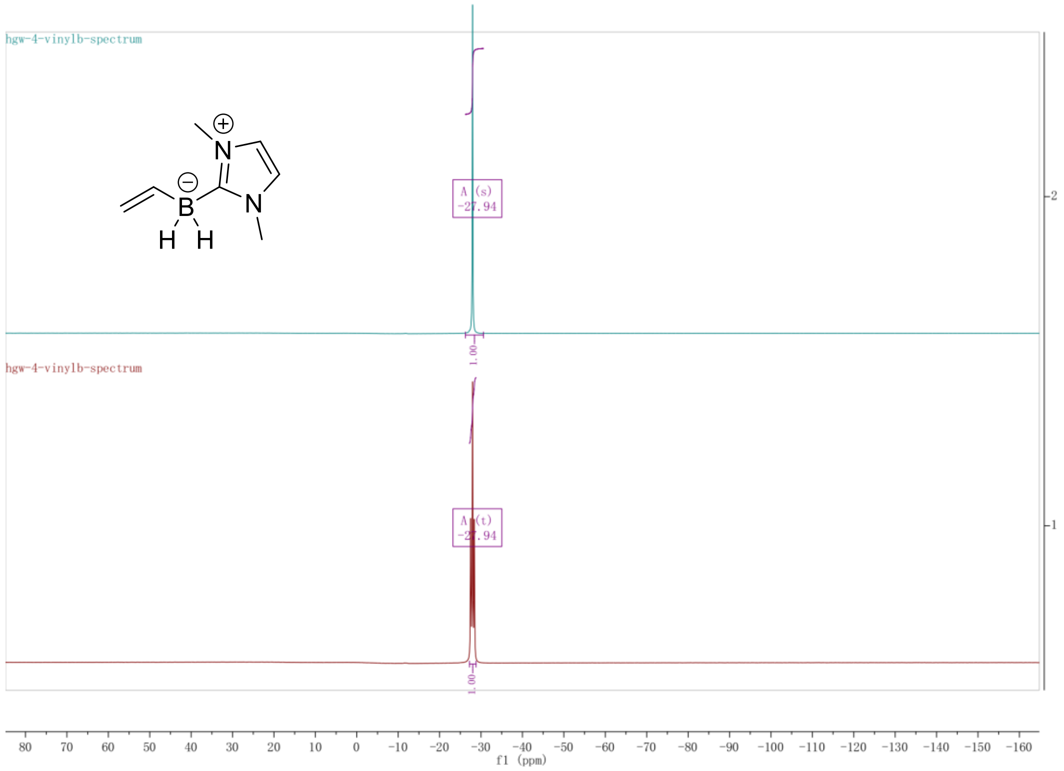
^{1}H NMR of 1



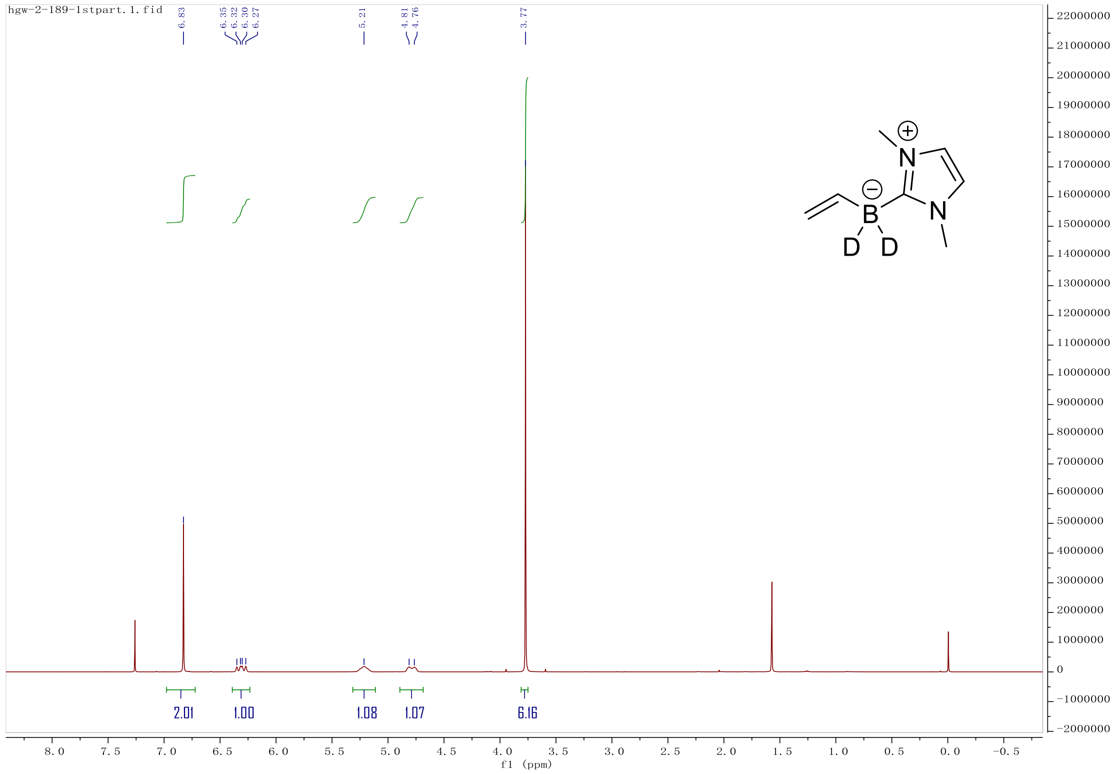
^{13}C NMR of 1



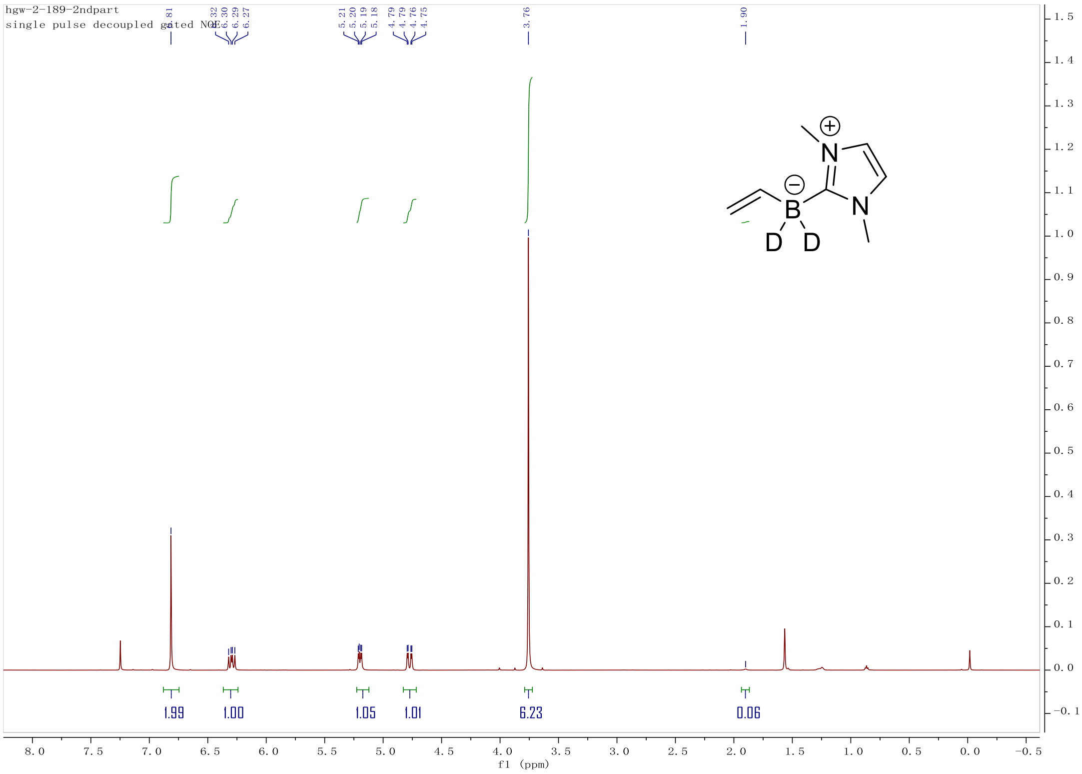
^{11}B NMR and ^{11}B {^1H} NMR of 1



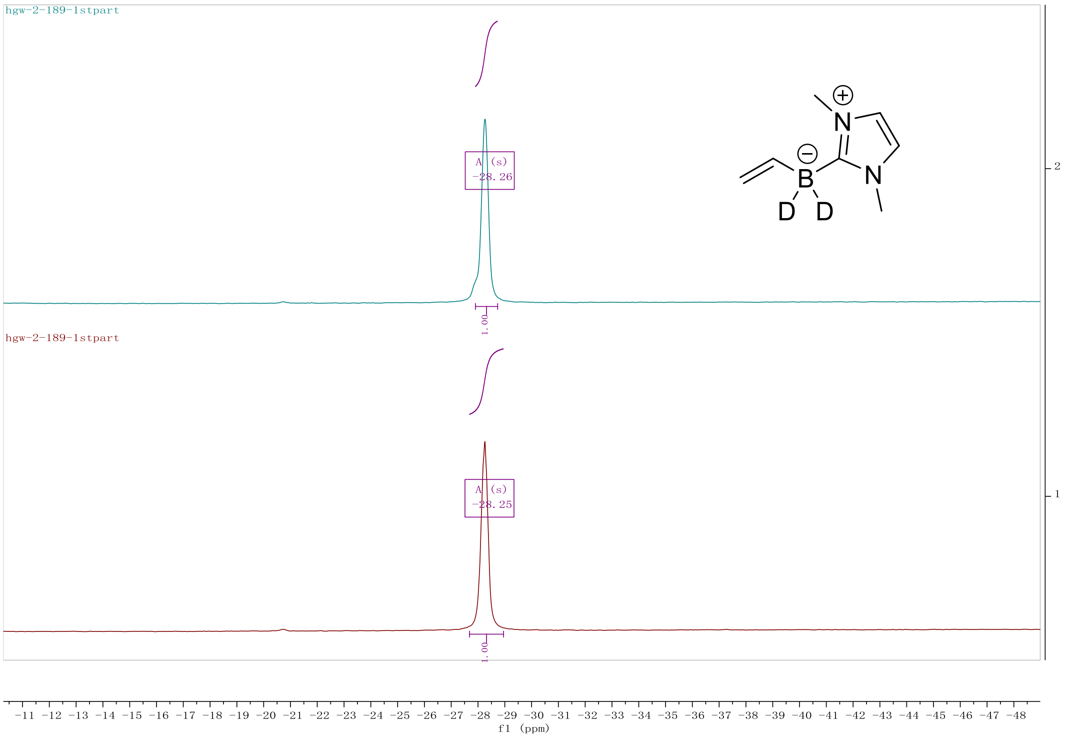
^1H NMR of 1-*D2*



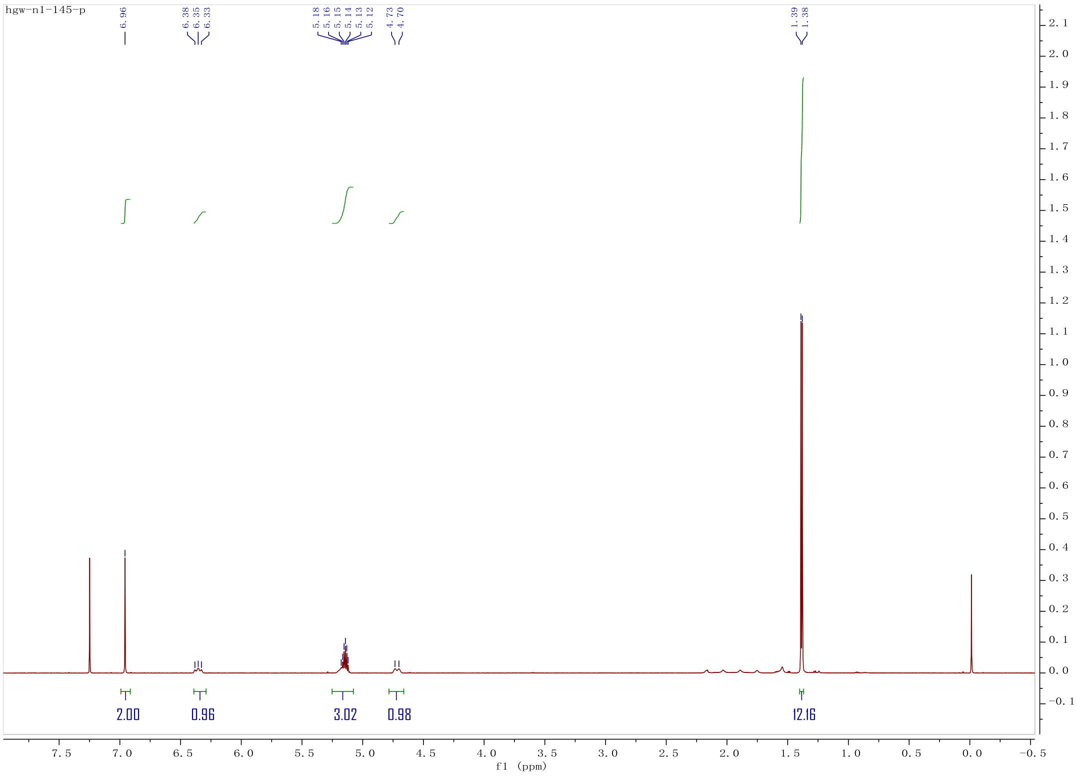
^{1}H{^{1}B } NMR of 1-*D2*



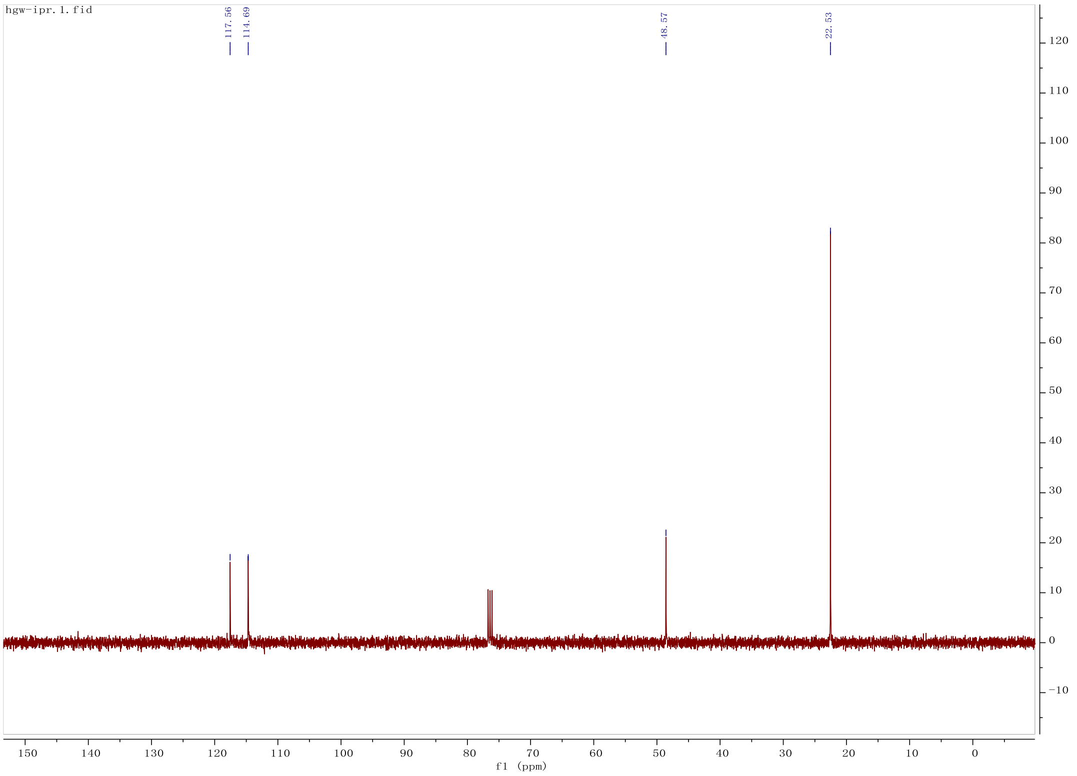
^{11}B NMR and ^{11}B {^{1}H} NMR of 1-*D2*



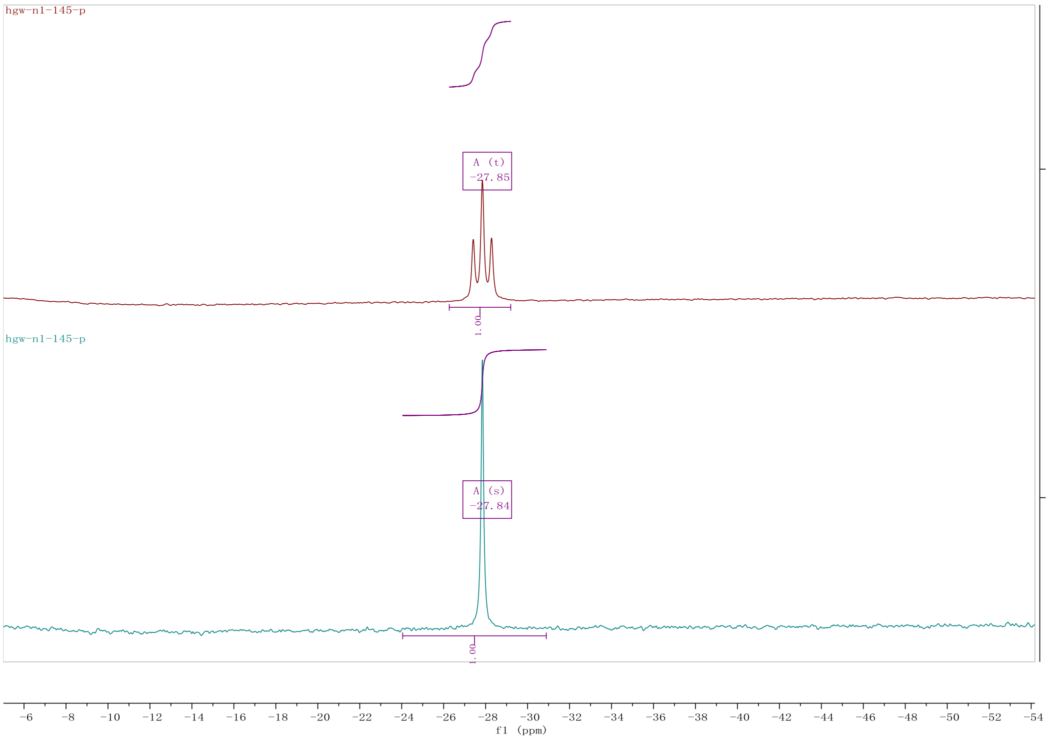
^{1}H NMR of 1-I^{i}Pr



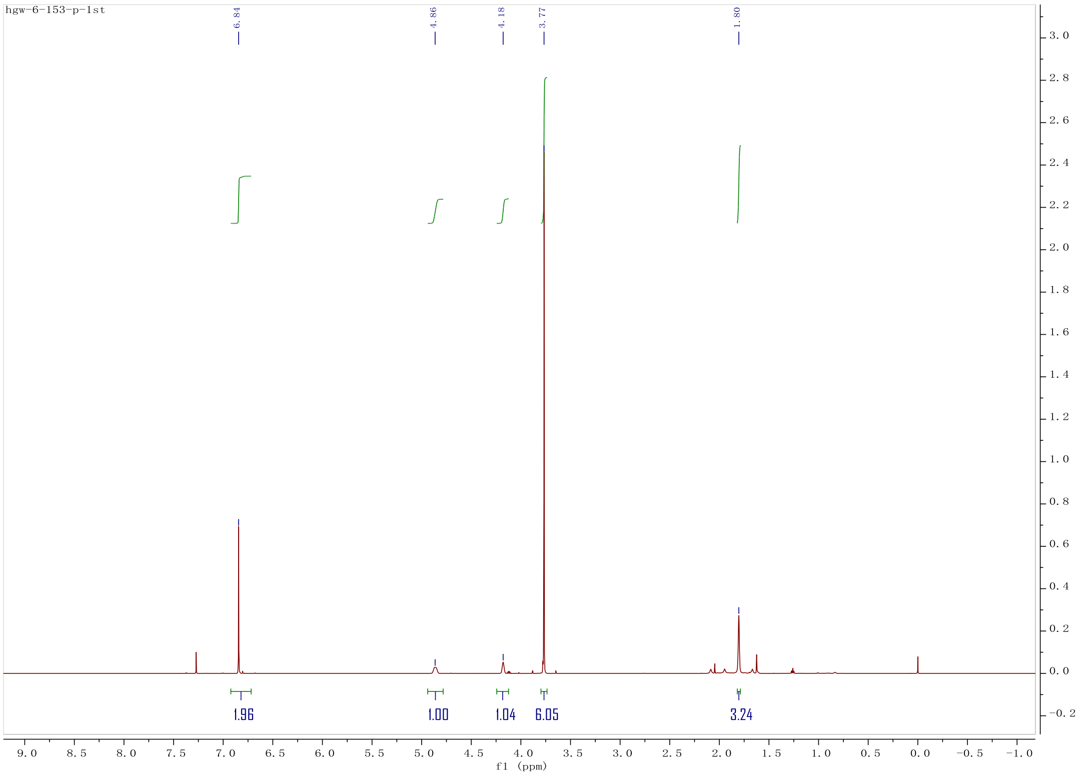
^{13}C NMR of 1-I^{i}Pr



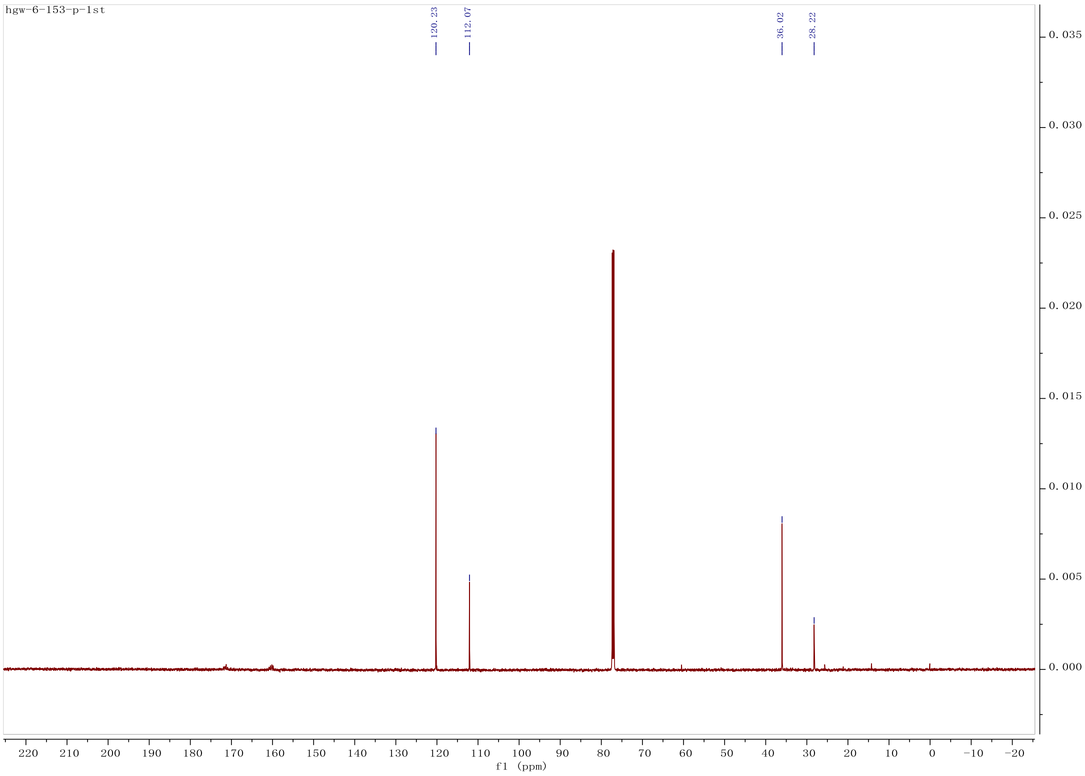
^{11}B NMR and ^{11}B {^{1}H} NMR of 1-I^{i}Pr



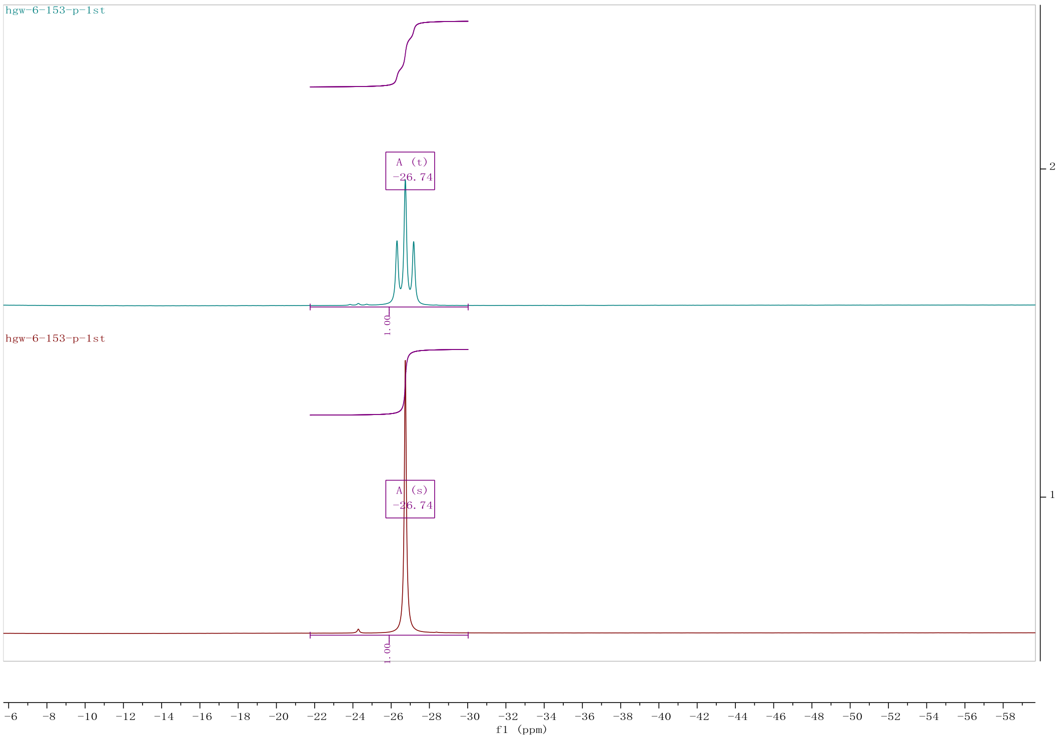
^{1}H NMR of 1-Me



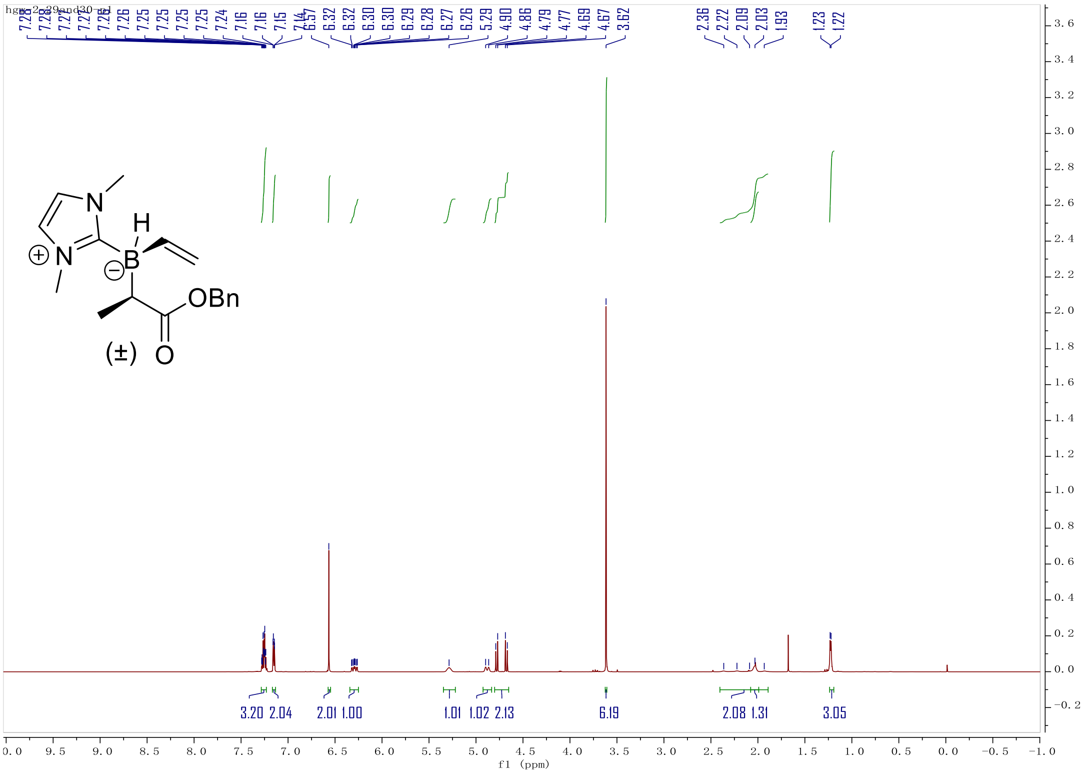
^{13}C NMR of 1-Me



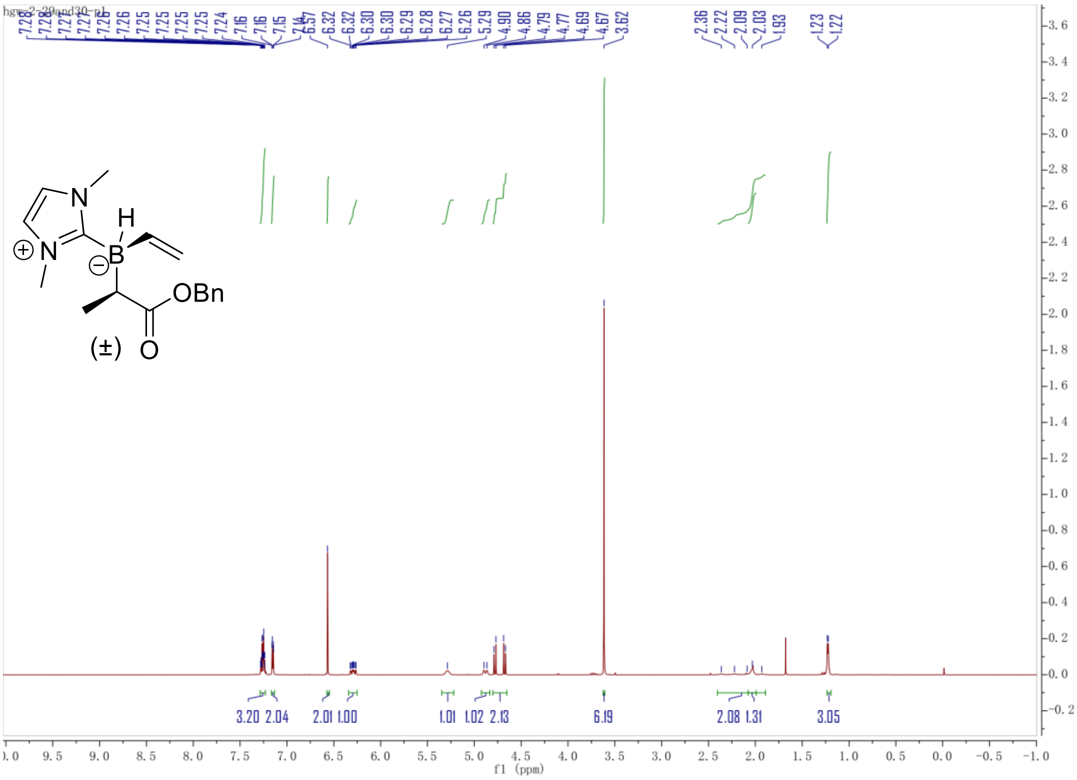
^{11}B NMR and ^{11}B {^{1}H} NMR of 1-Me



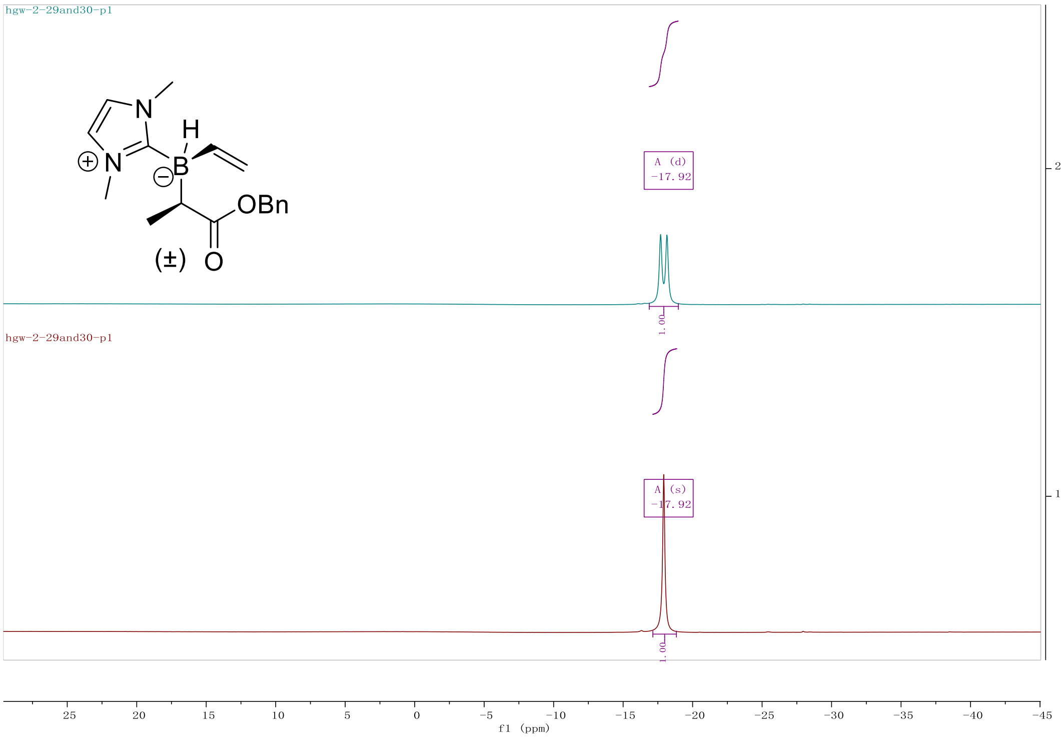
^{1}H NMR of 3



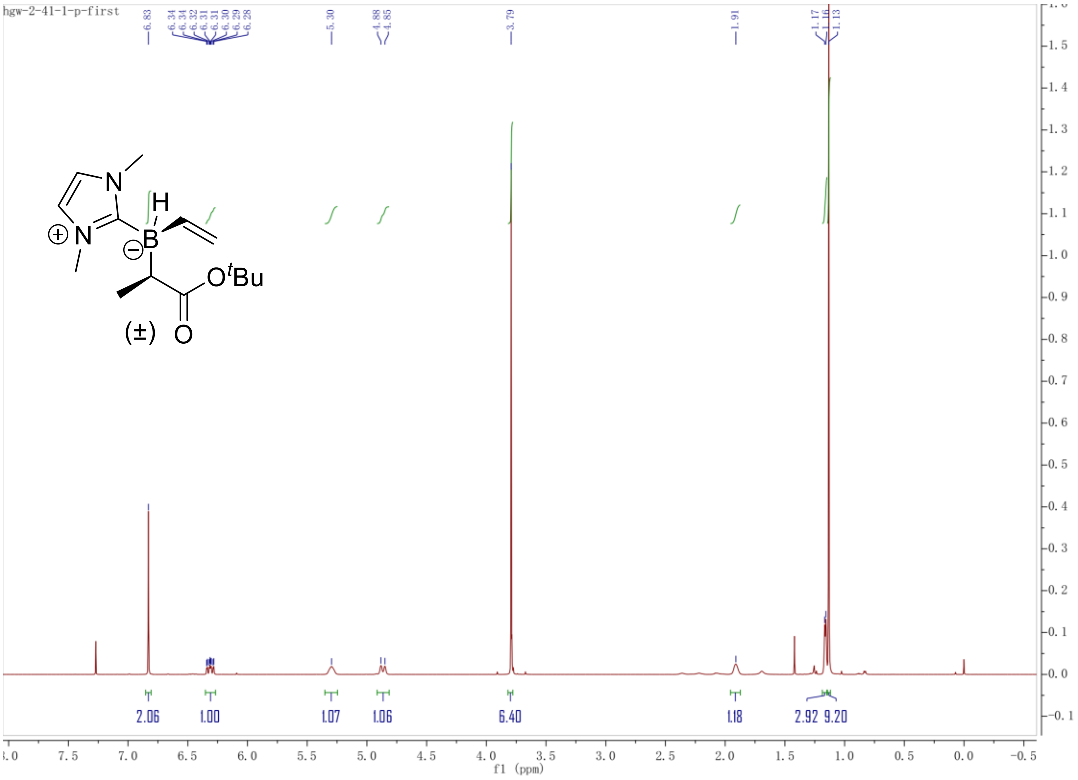
^{13}C NMR of 3



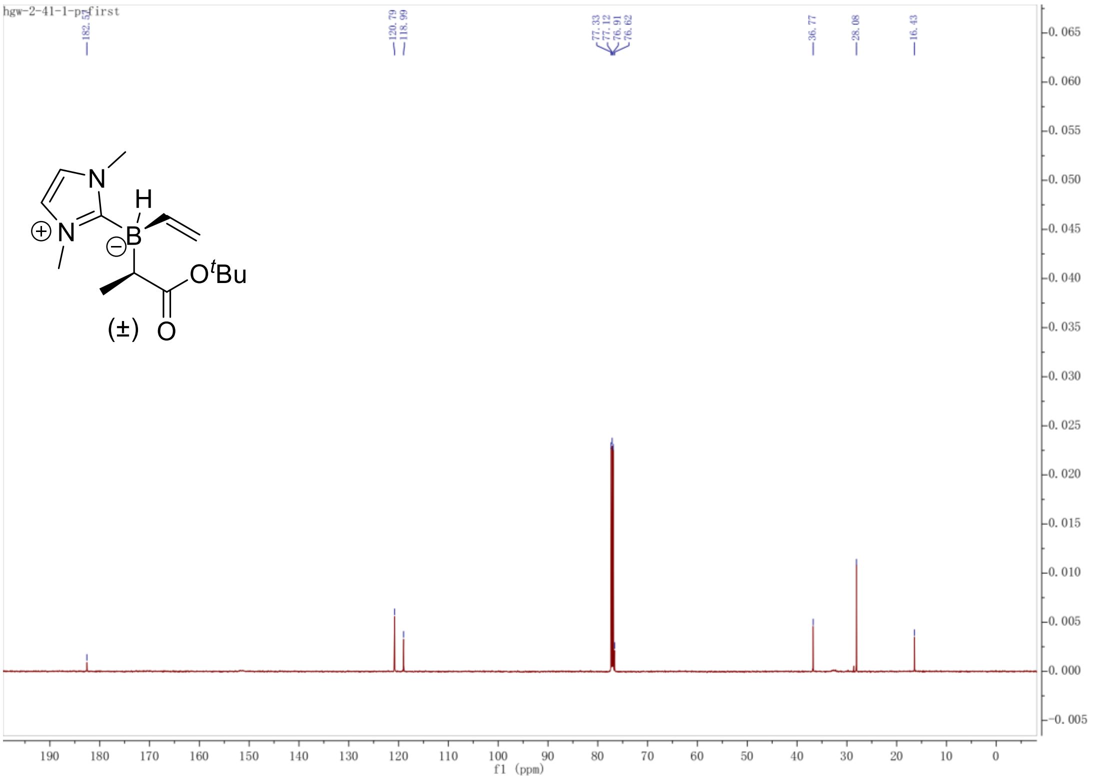
^{11}B NMR and ^{11}B {^{1}H} NMR of 3



^{1}H NMR of 4

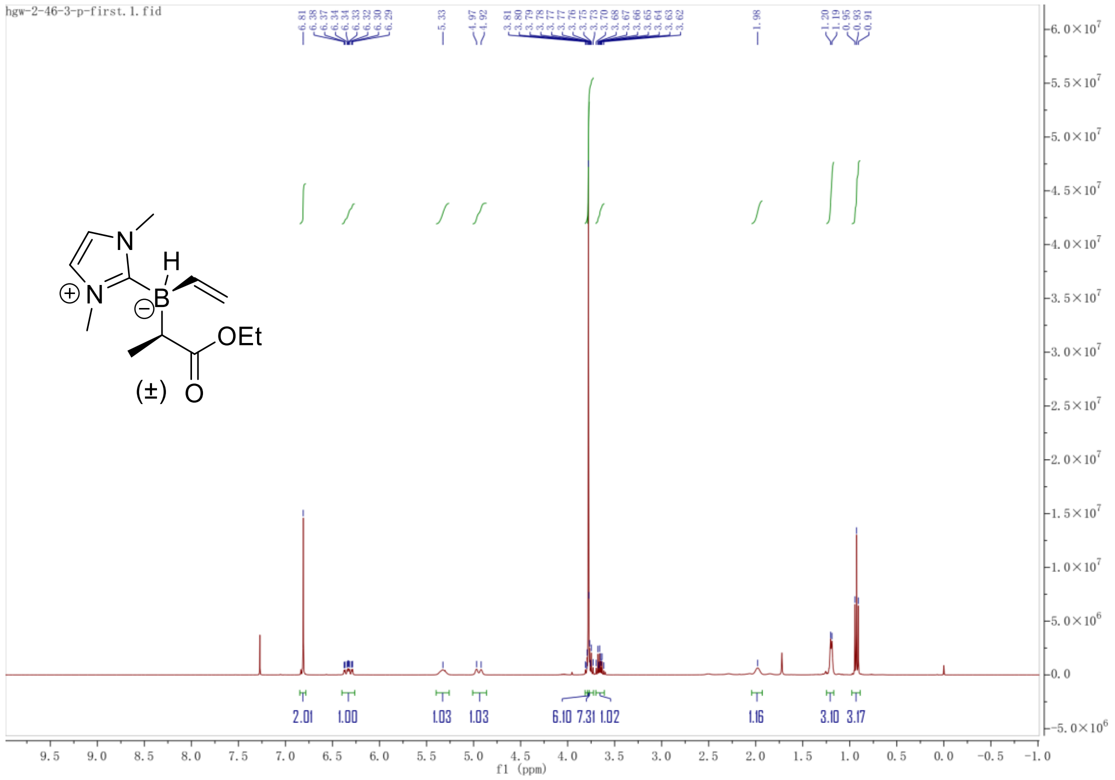


^{13}C NMR of 4

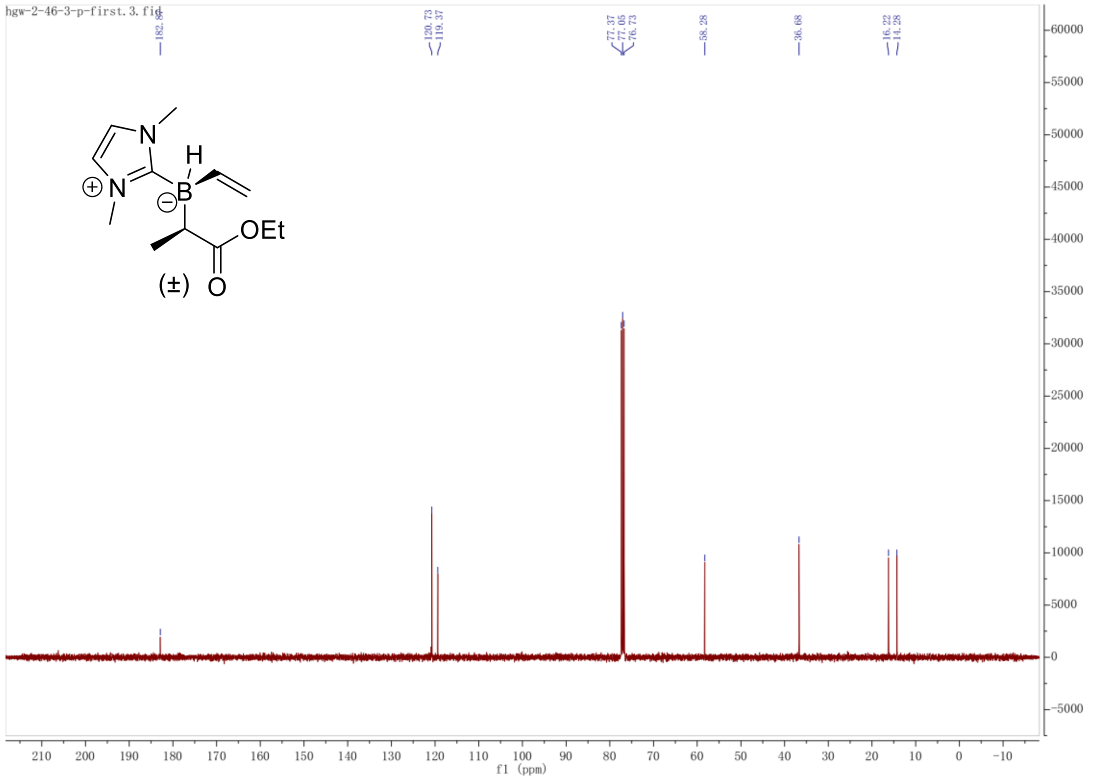


^{11}B NMR and ^{11}B {^{1}H} NMR of 4

^{1}H NMR of 5

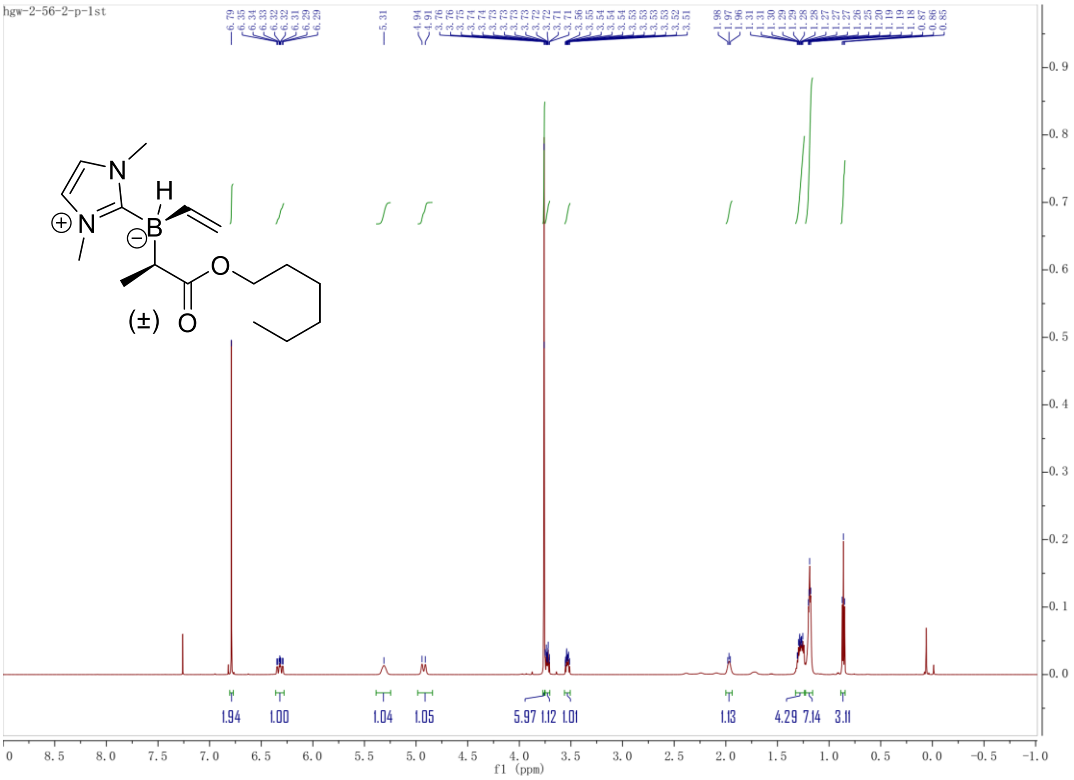


^{13}C NMR of 5

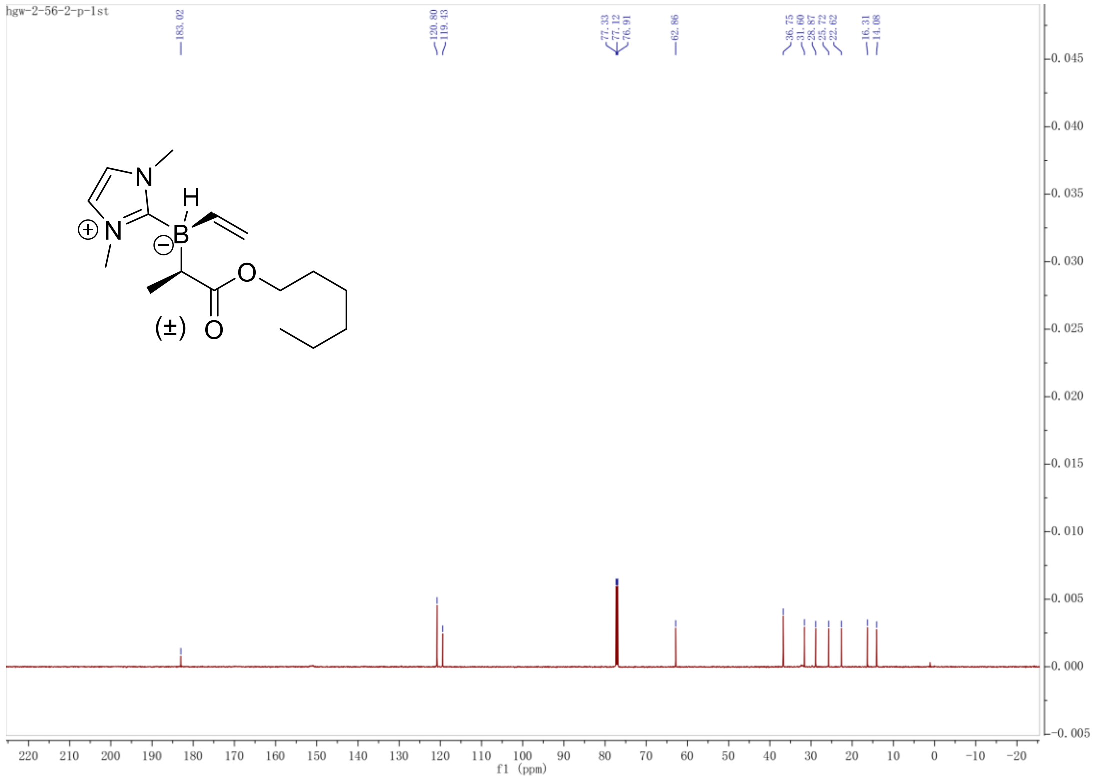


^{11}B NMR and ^{11}B {^{1}H} NMR of 5

^{1}H NMR of 6

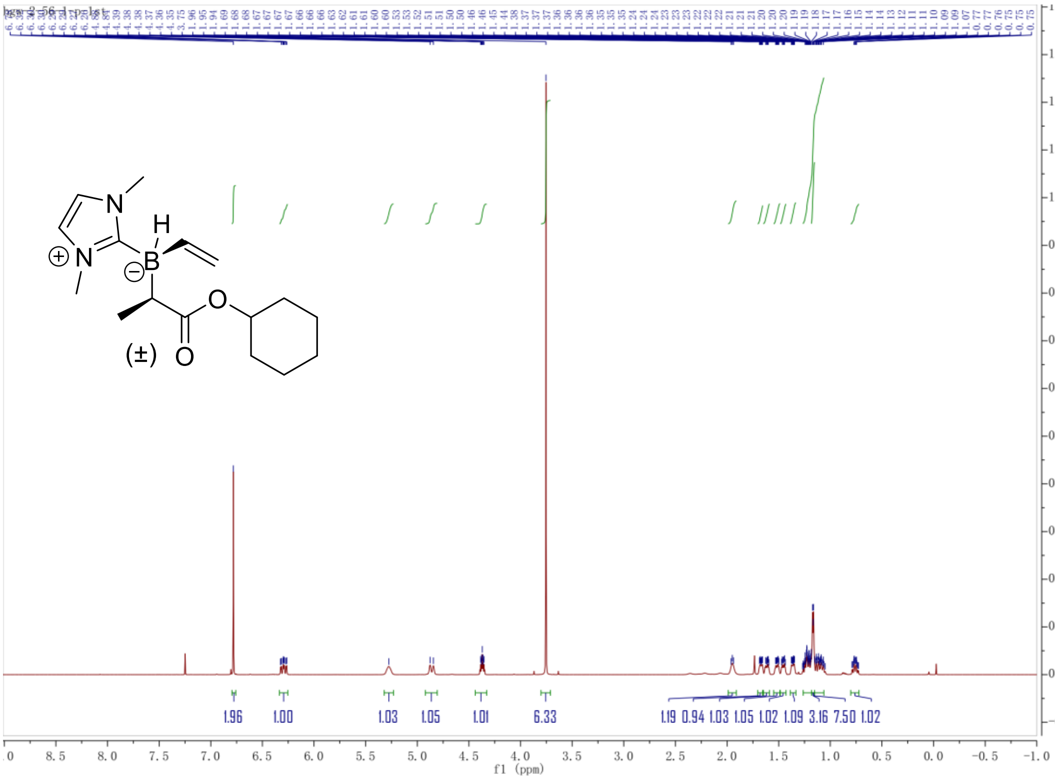


^{13}C NMR of 6

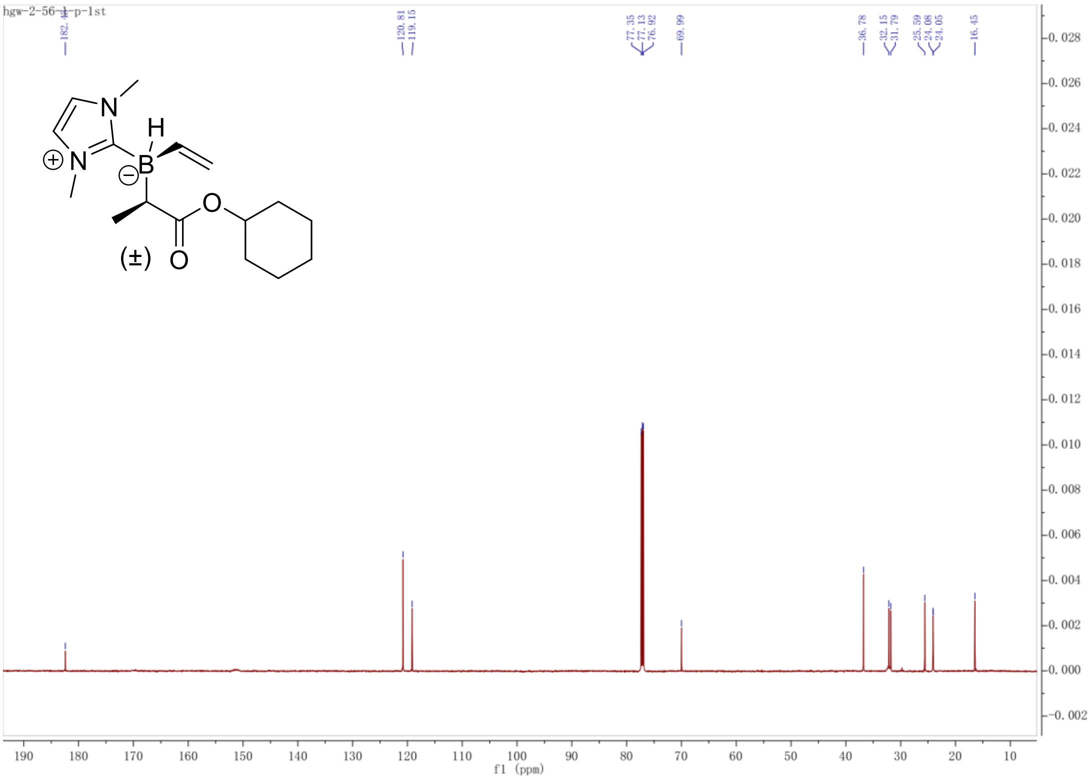


^{11}B NMR and ^{11}B {^{1}H} NMR of 6

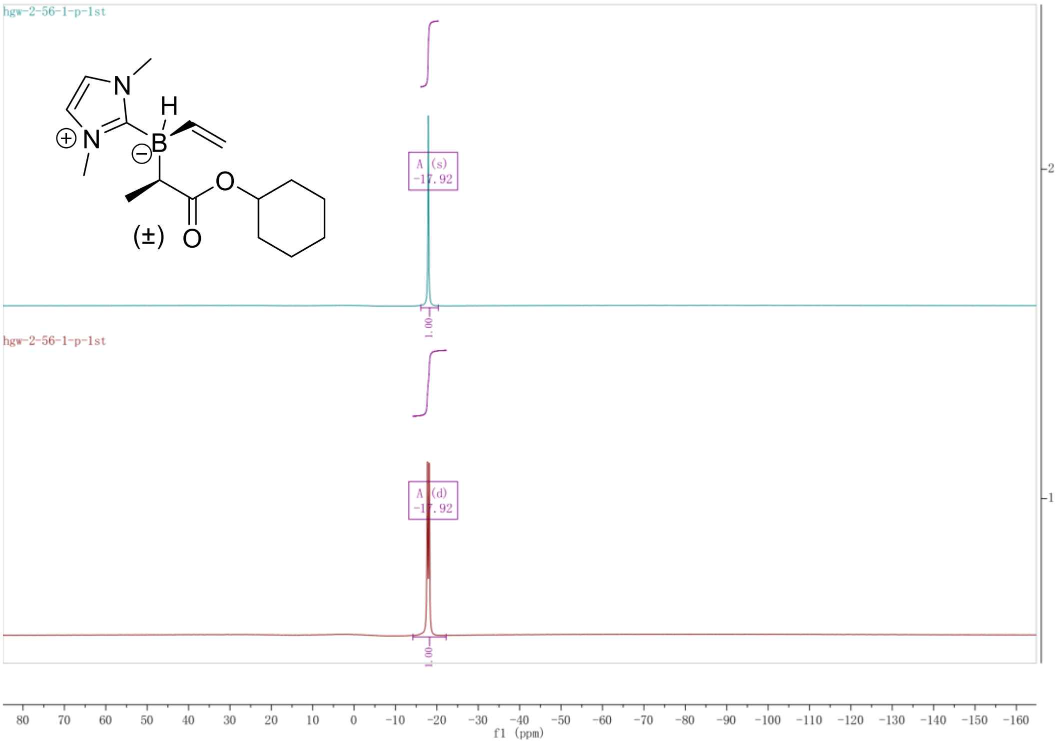
^{1}H NMR of 7



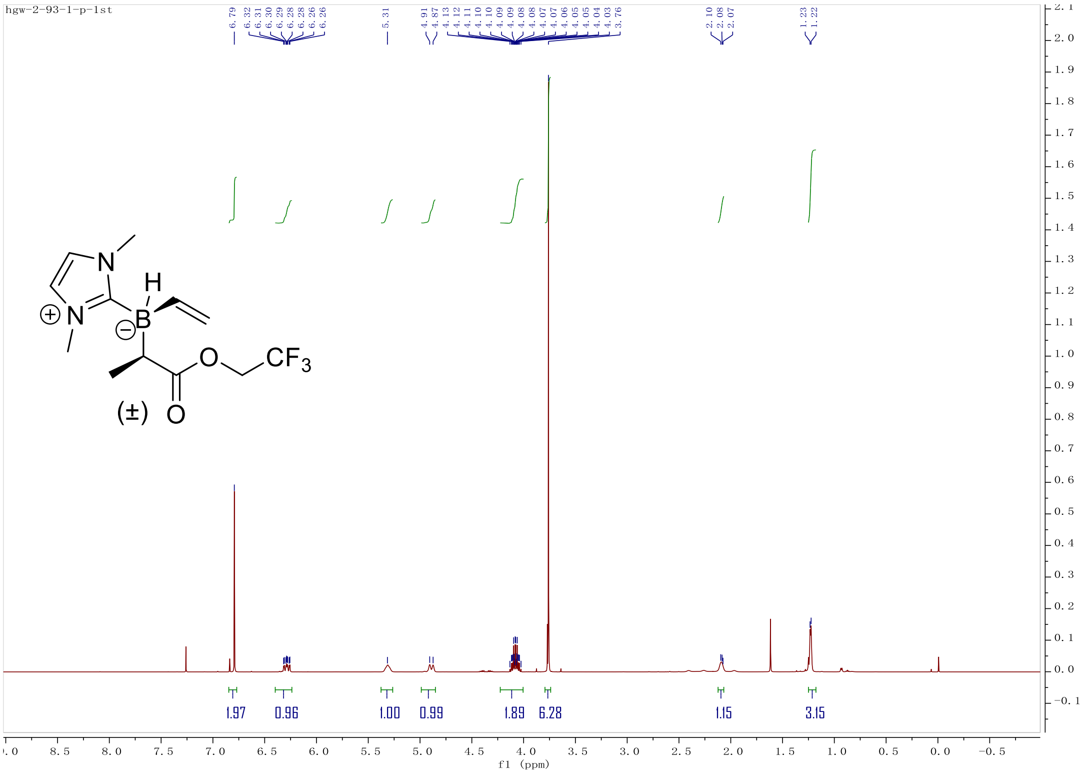
^{13}C NMR of 7



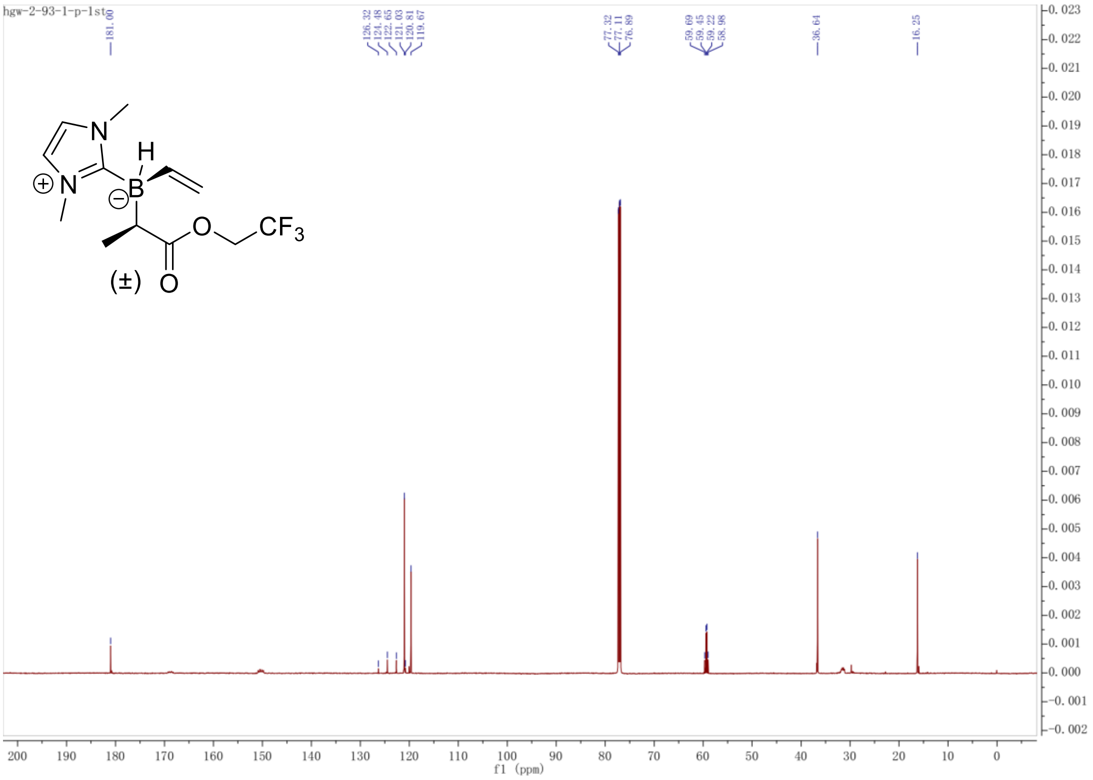
^{11}B NMR and ^{11}B {^{1}H} NMR of 7



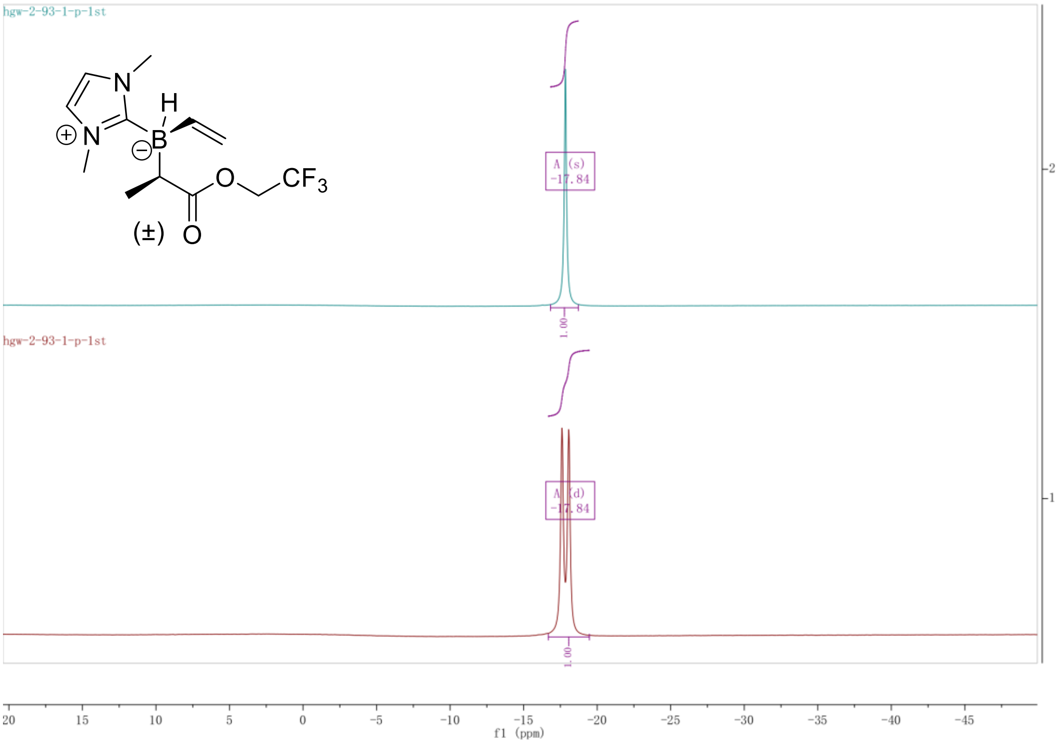
^{1}H NMR of 8



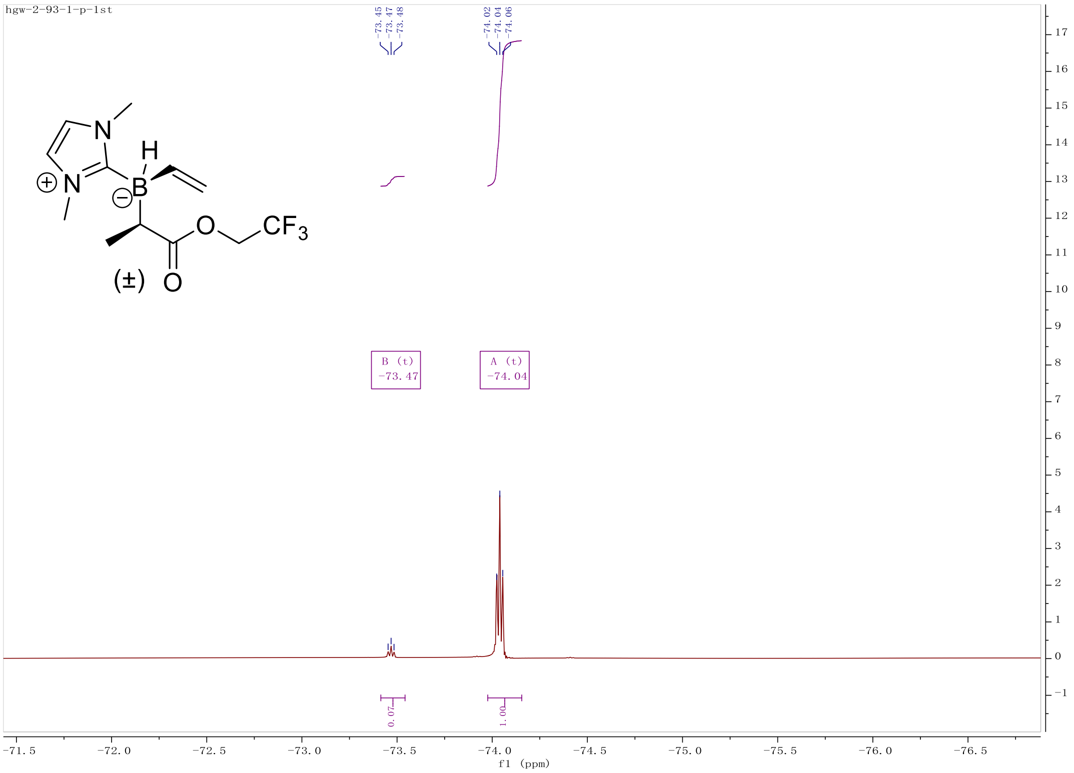
^{13}C NMR of 8



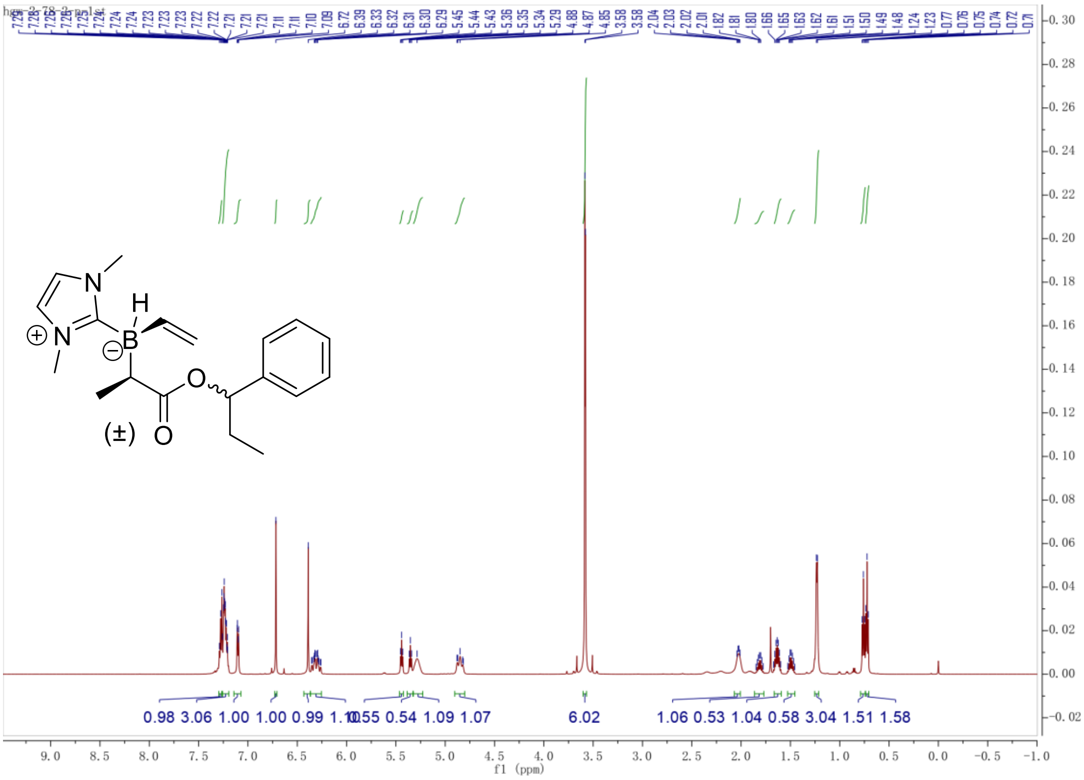
^{11}B NMR and ^{11}B {^{1}H} NMR of 8



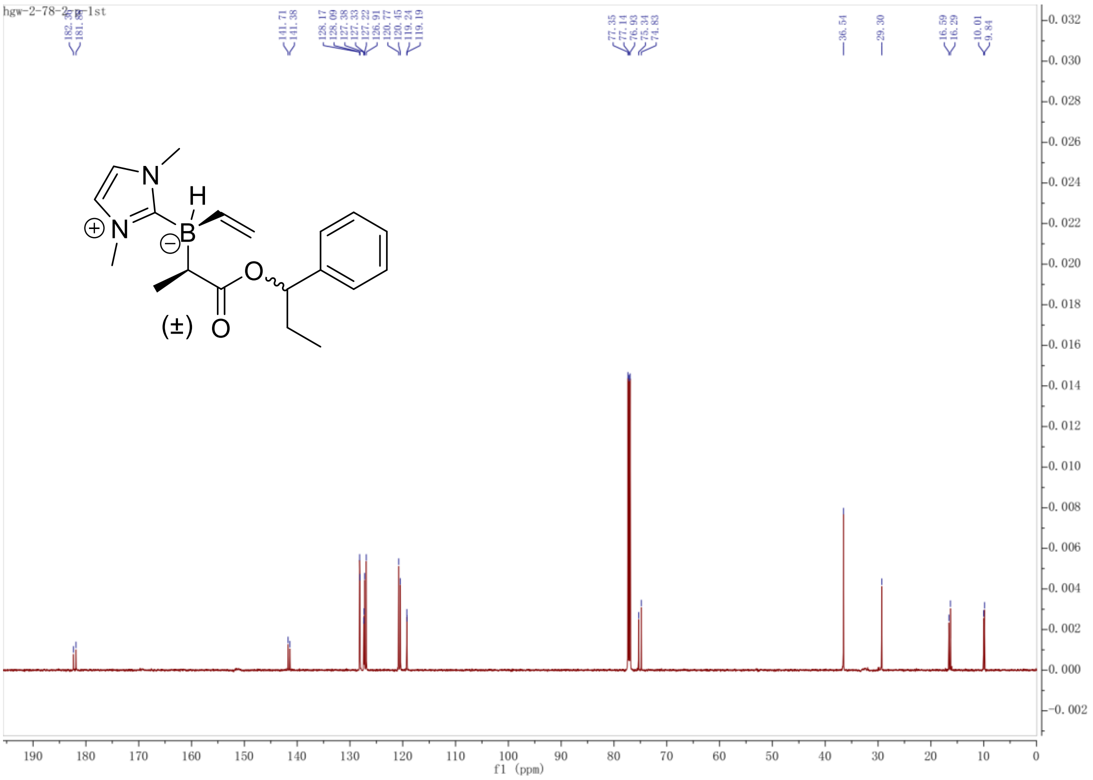
^{19}F NMR of 8



^{1}H NMR of 9

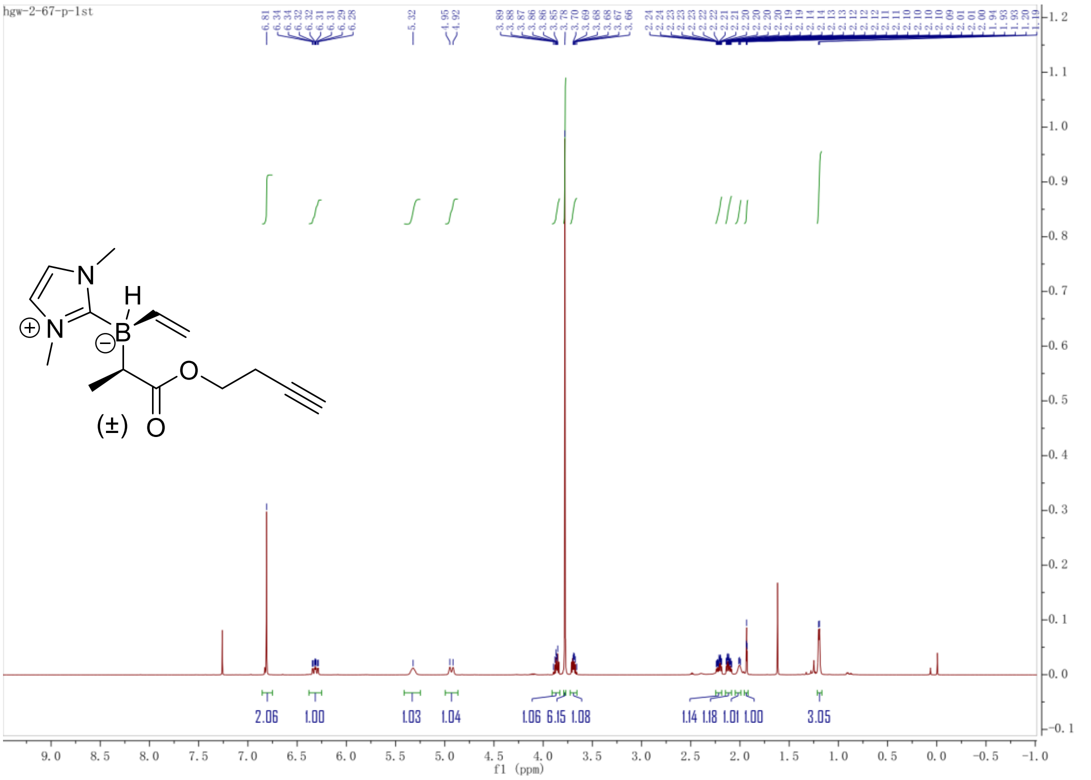


^{13}C NMR of 9

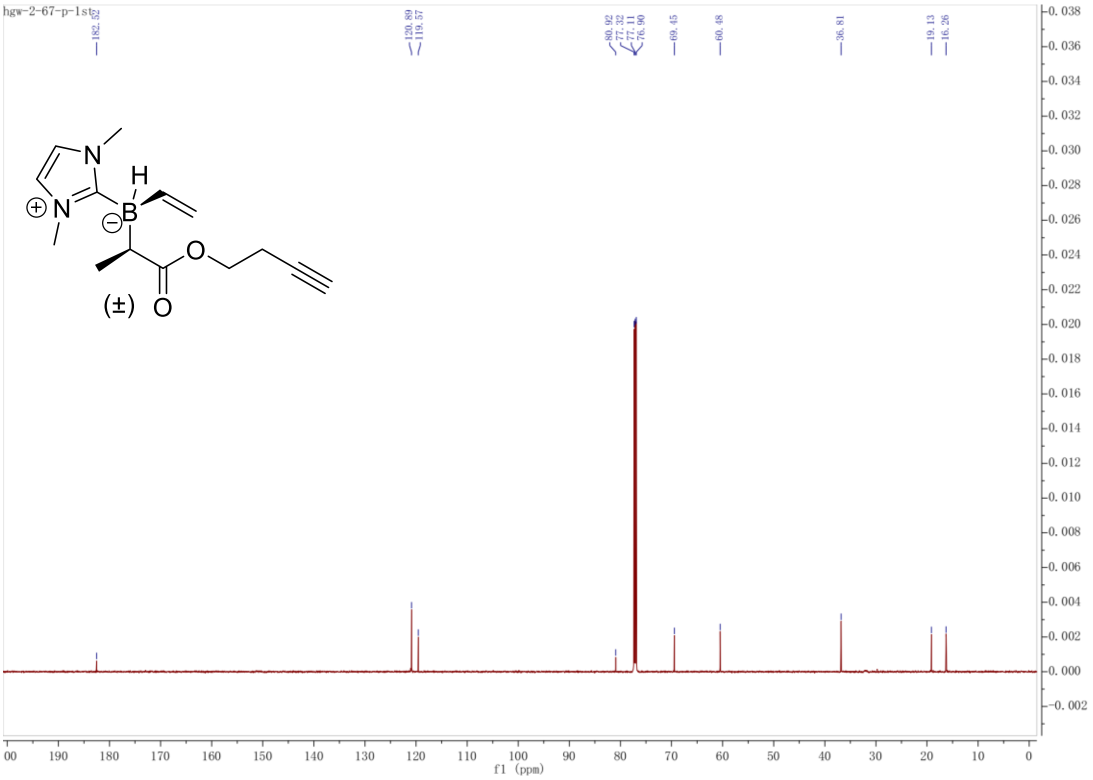


^{11}B NMR and ^{11}B {^{1}H} NMR of 9

^{1}H NMR of 10

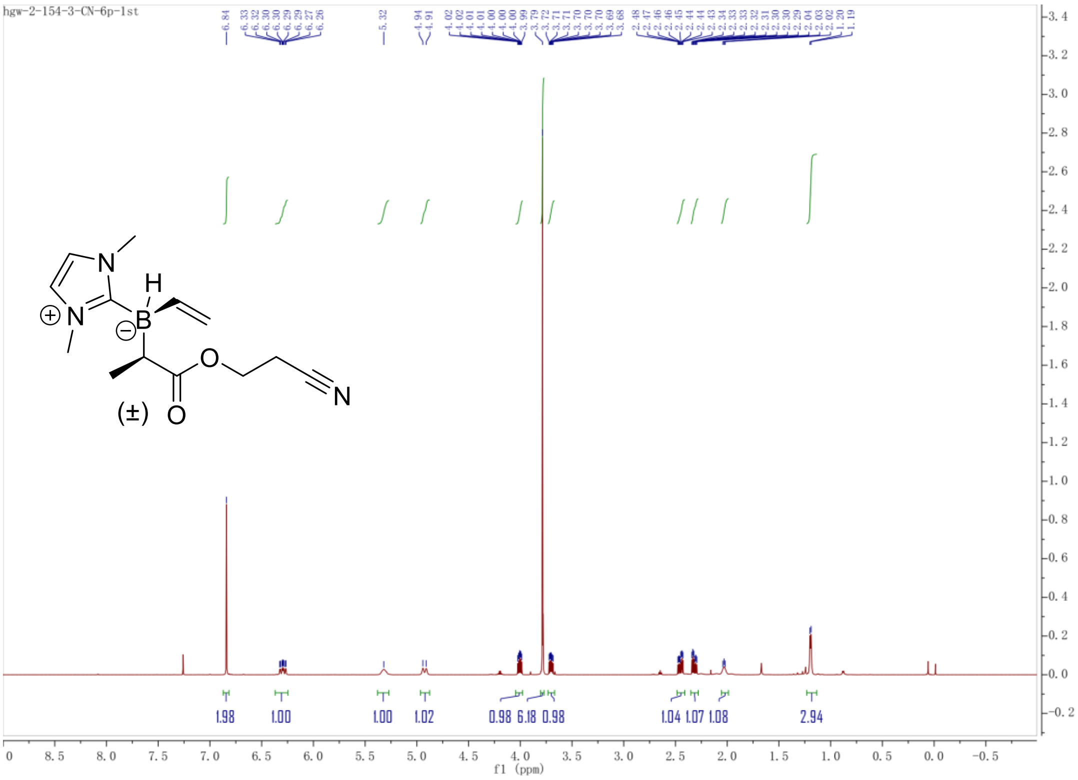


^{13}C NMR of 10

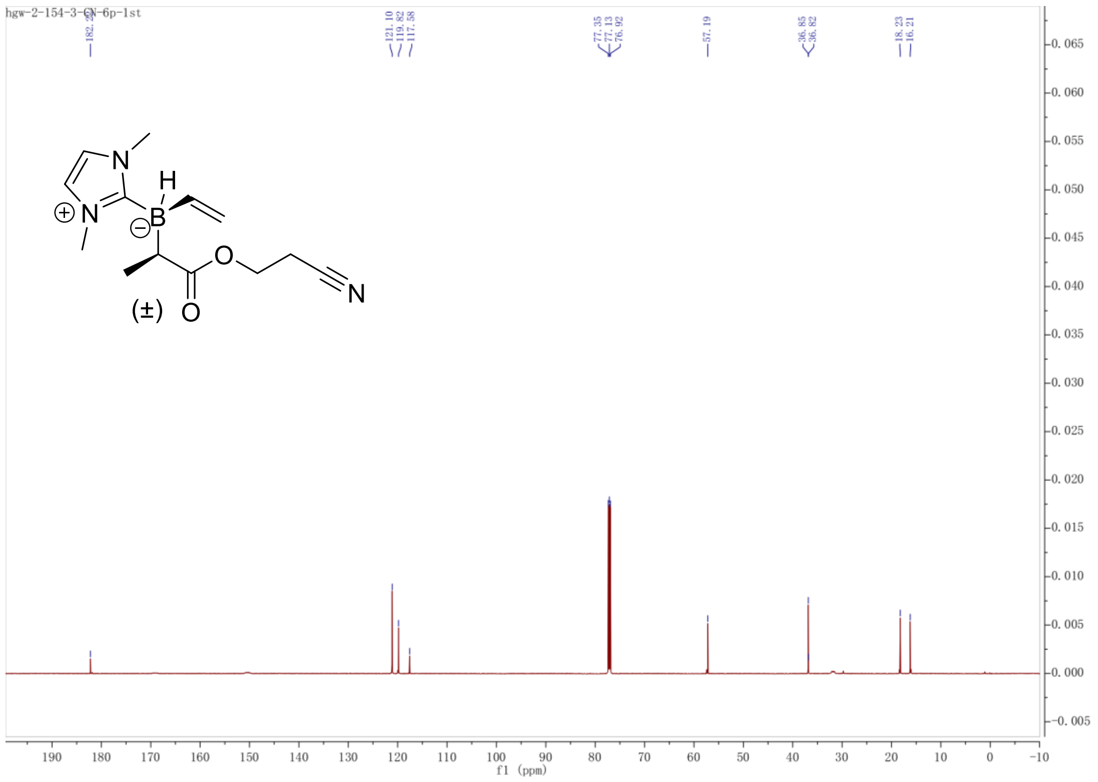


^{11}B NMR and ^{11}B {^{1}H} NMR of 10

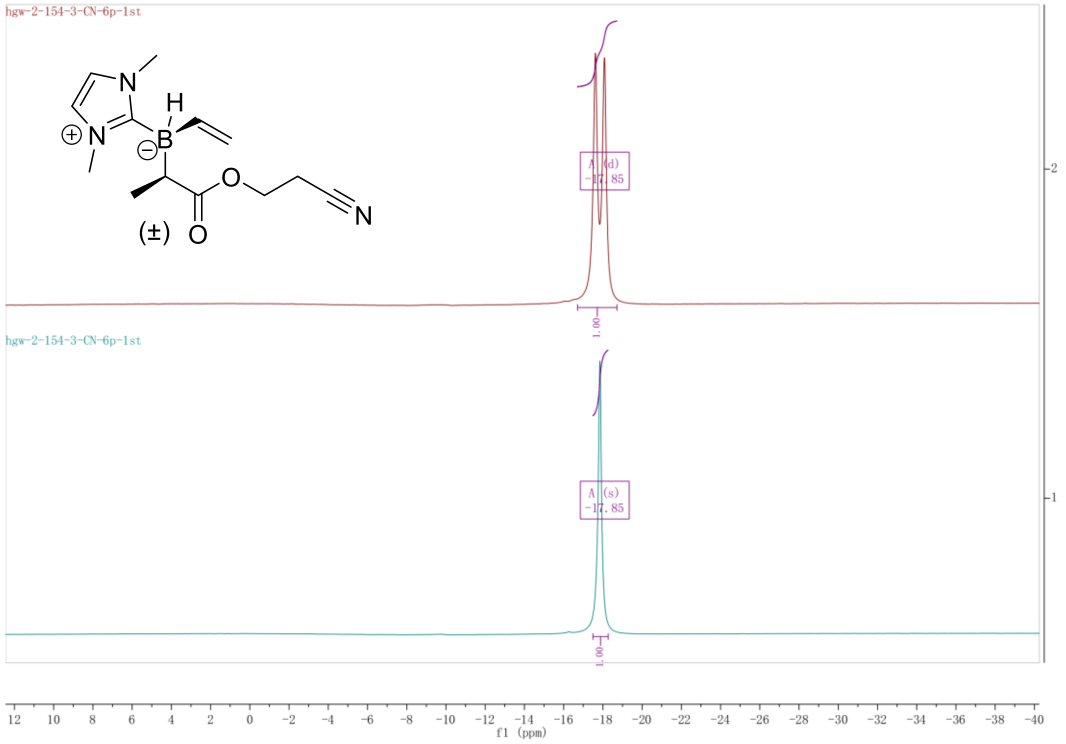
^{1}H NMR of 11



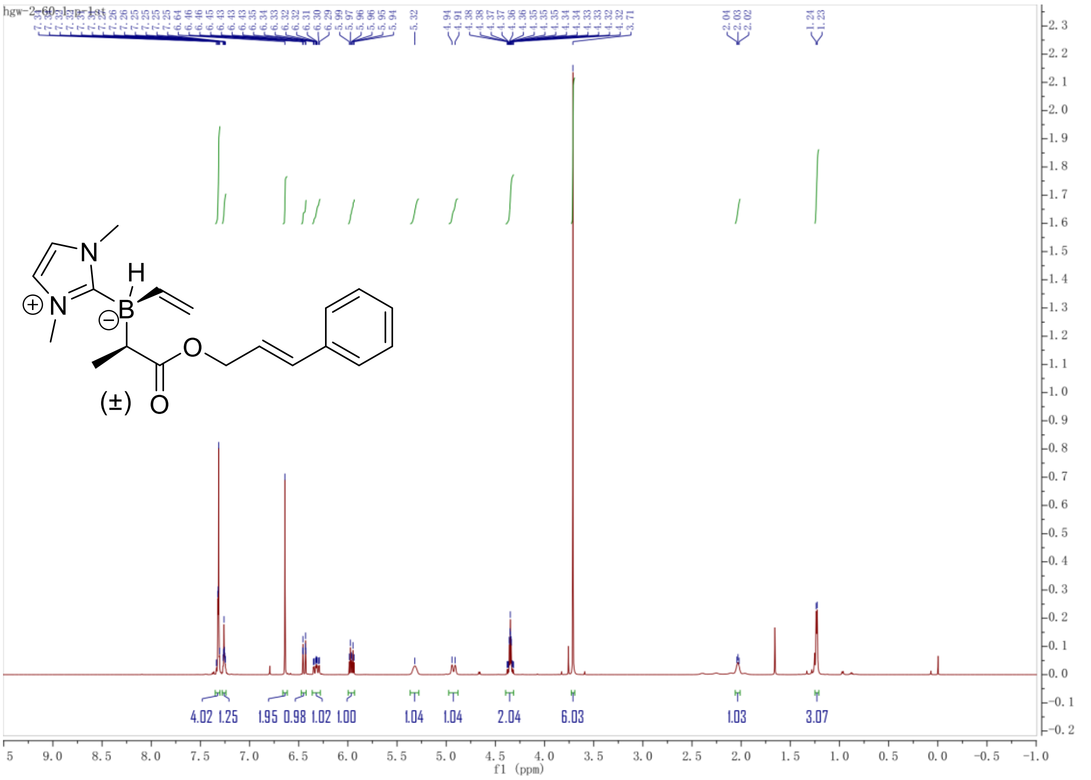
^{13}C NMR of 11



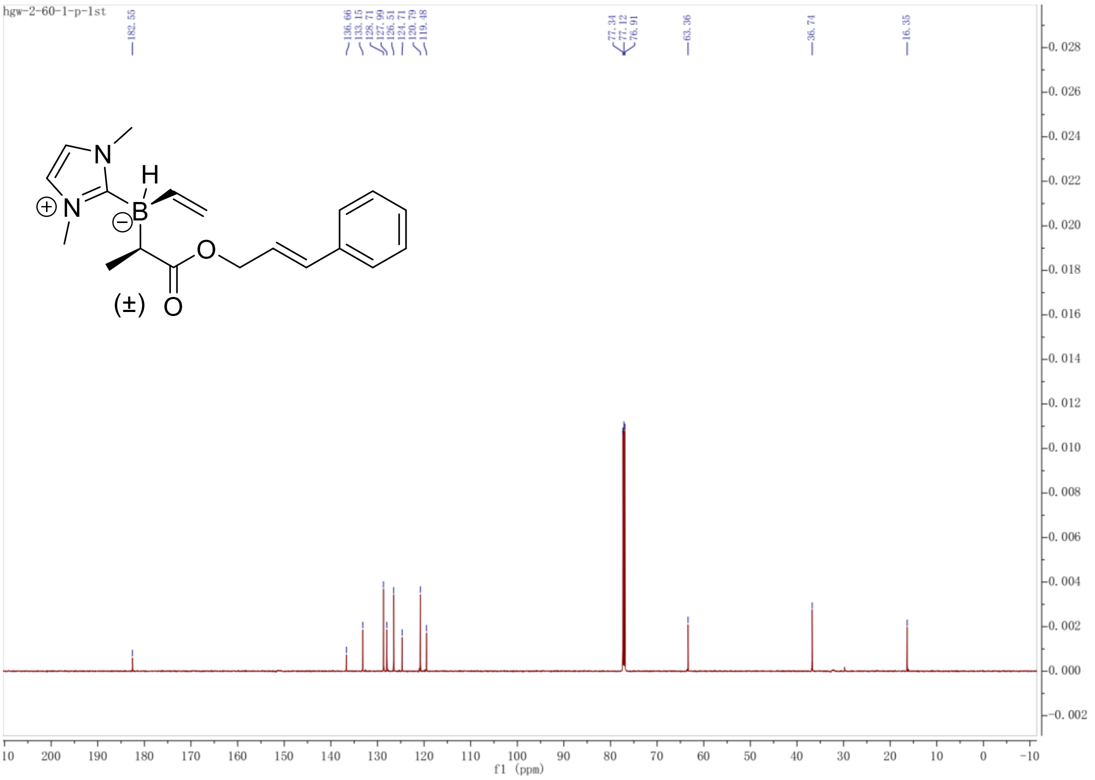
^{11}B NMR and ^{11}B {^{1}H} NMR of 11



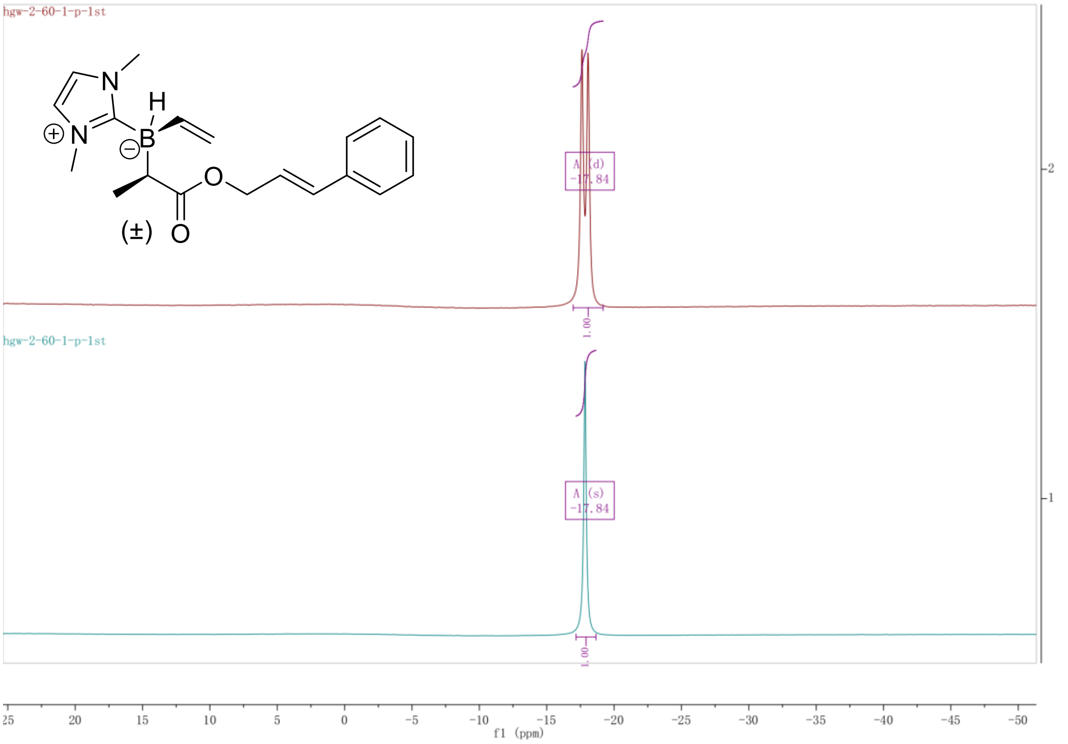
^{1}H NMR of 12



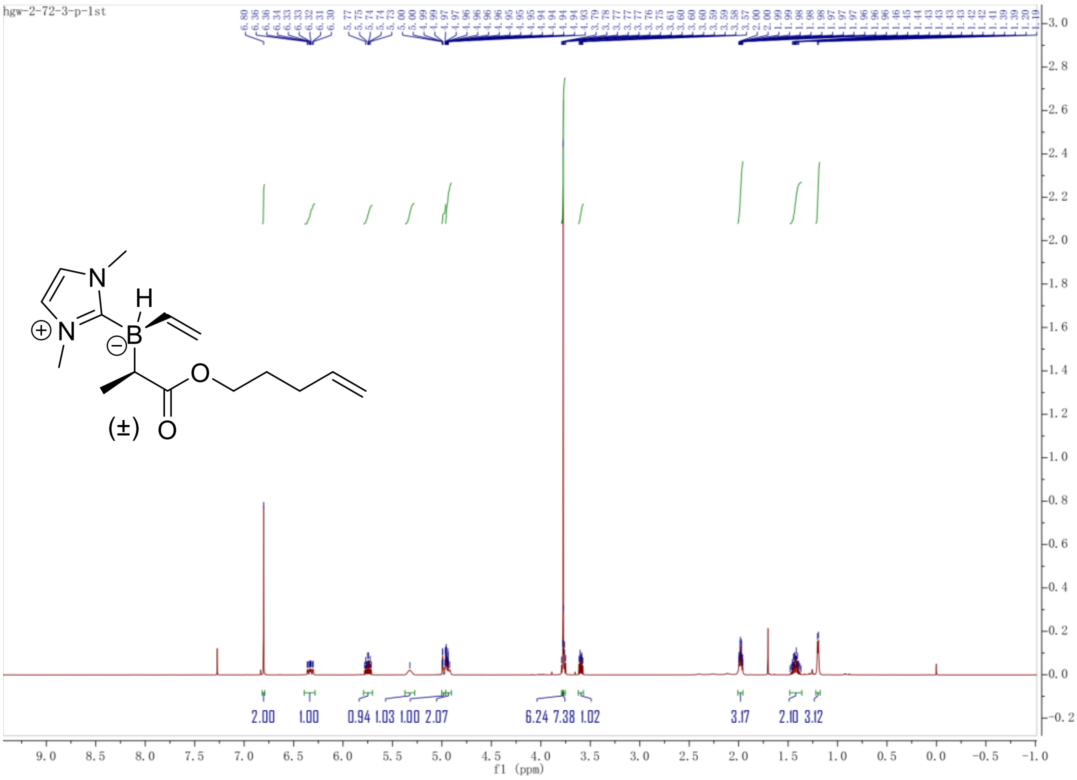
^{13}C NMR of 12



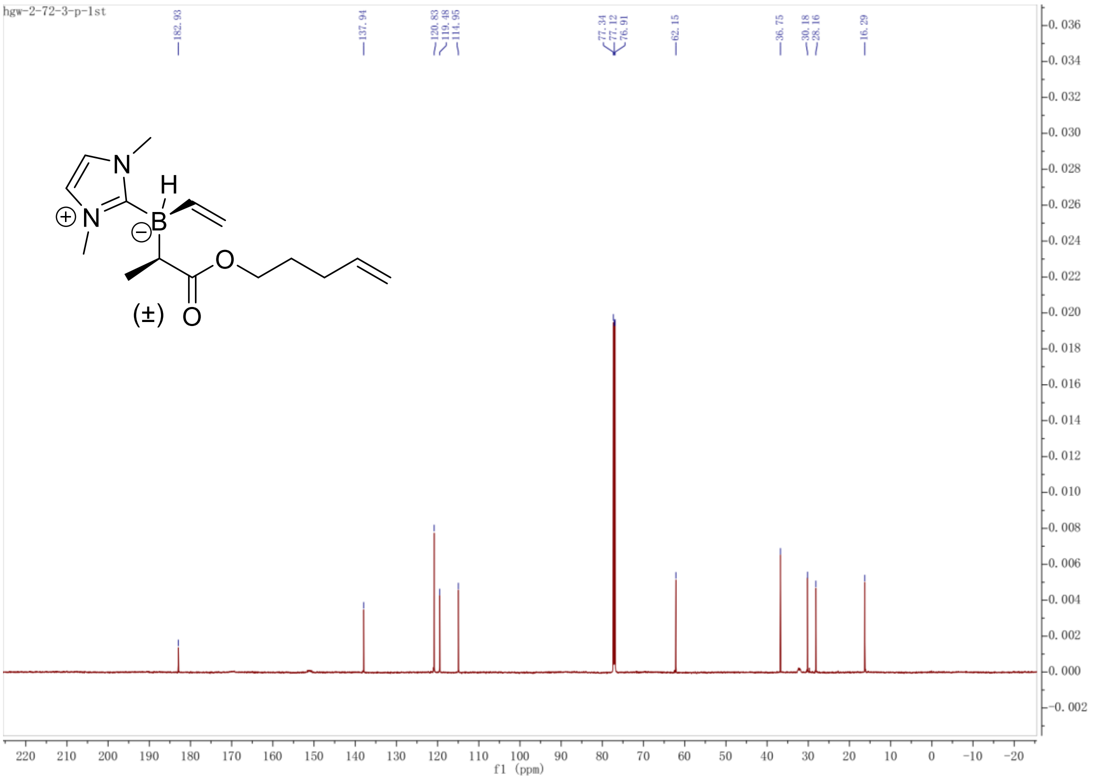
^{11}B NMR and ^{11}B {^{1}H} NMR of 12



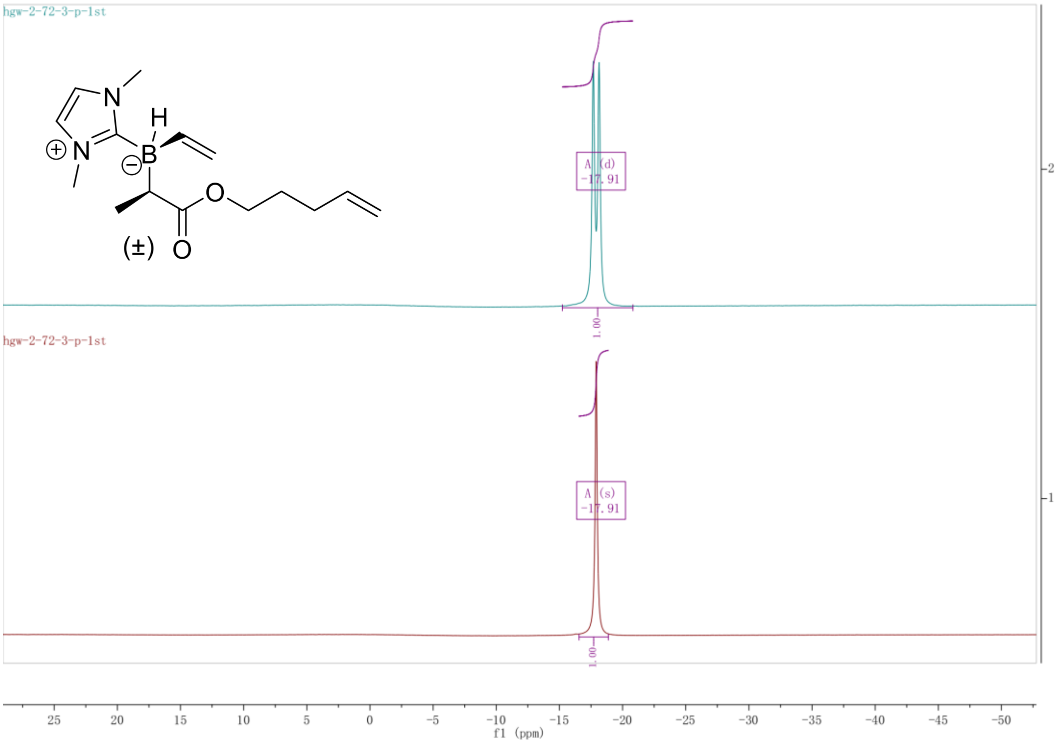
^{1}H NMR of 13



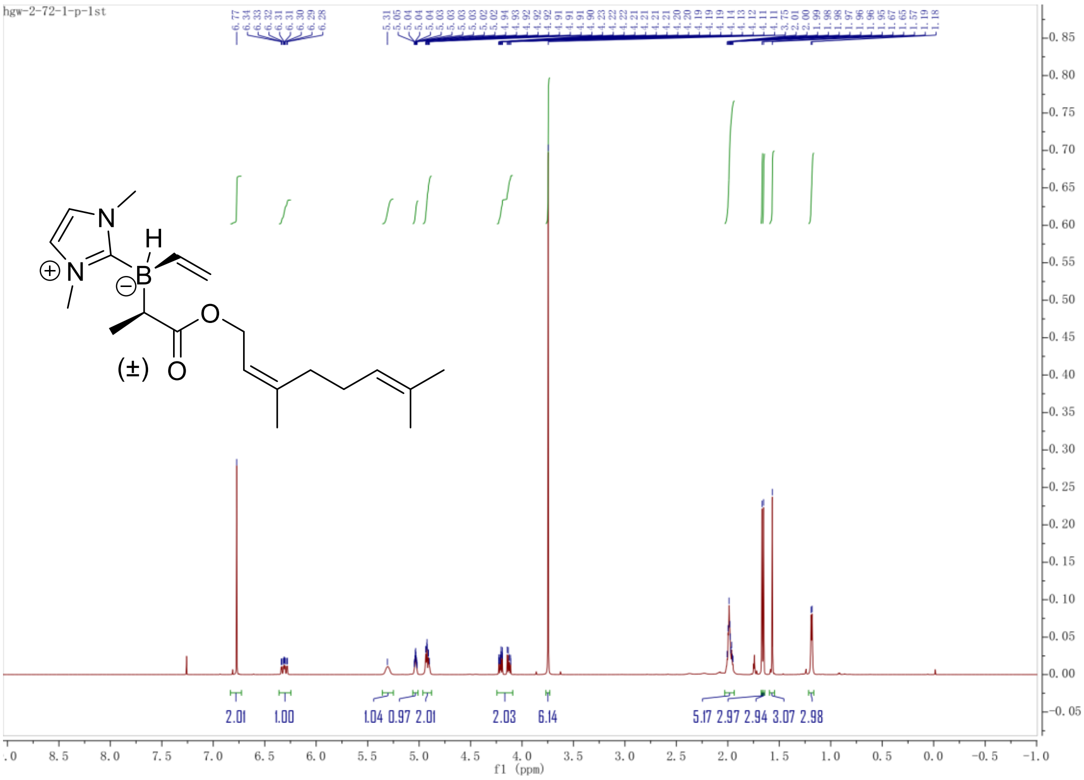
^{13}C NMR of 13



^{11}B NMR and ^{11}B {^{1}H} NMR of 13

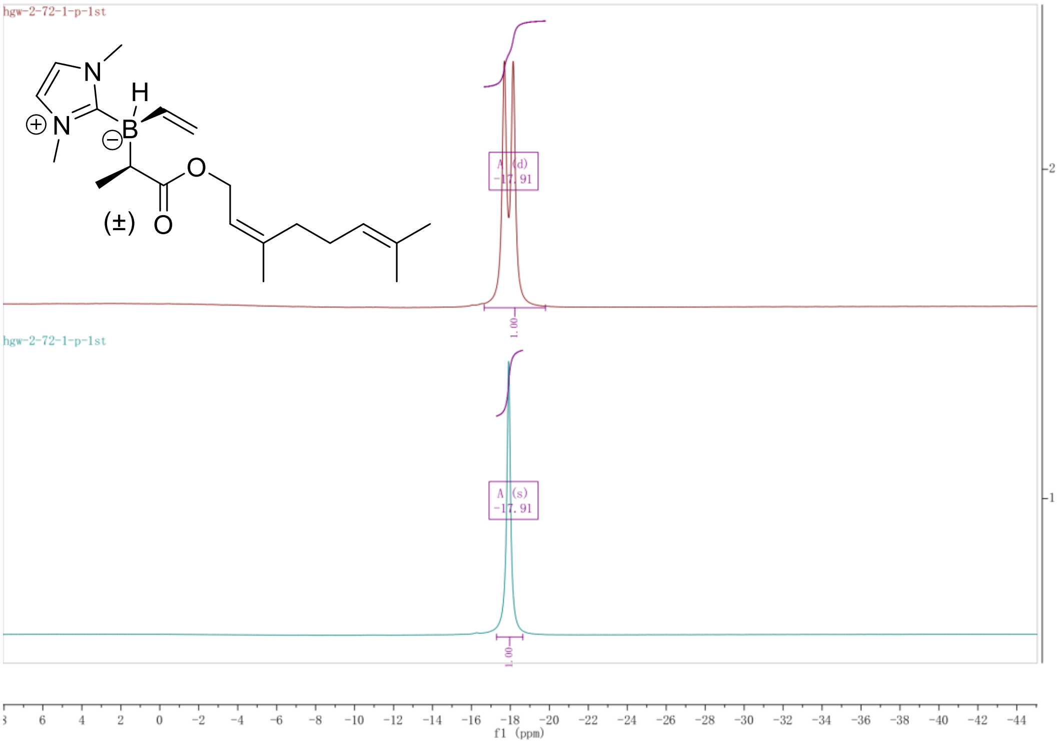


^{1}H NMR of 14



^{13}C NMR of 14

^{11}B NMR and ^{11}B {^{1}H} NMR of 14



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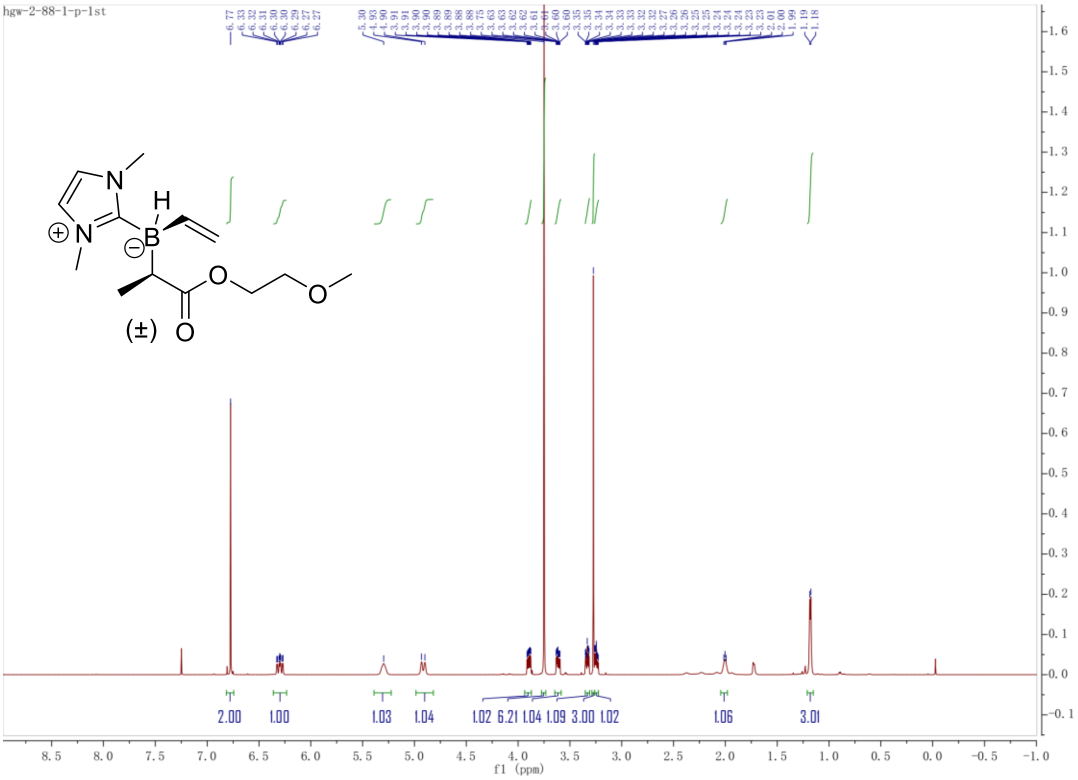

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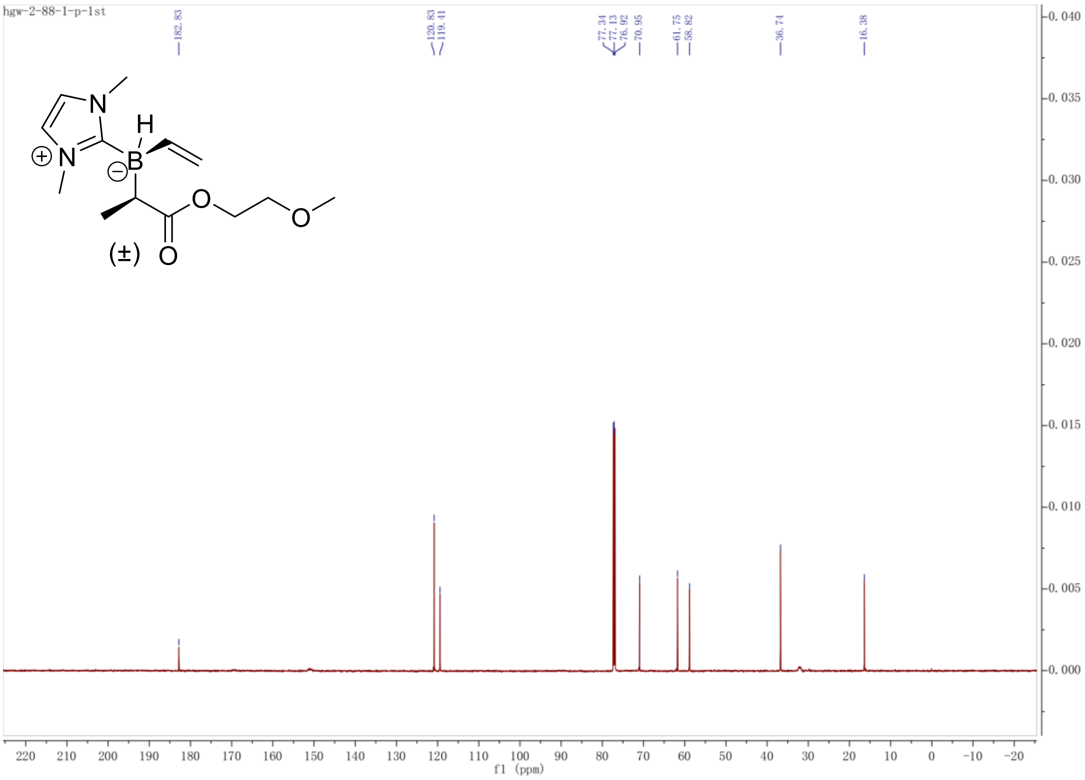
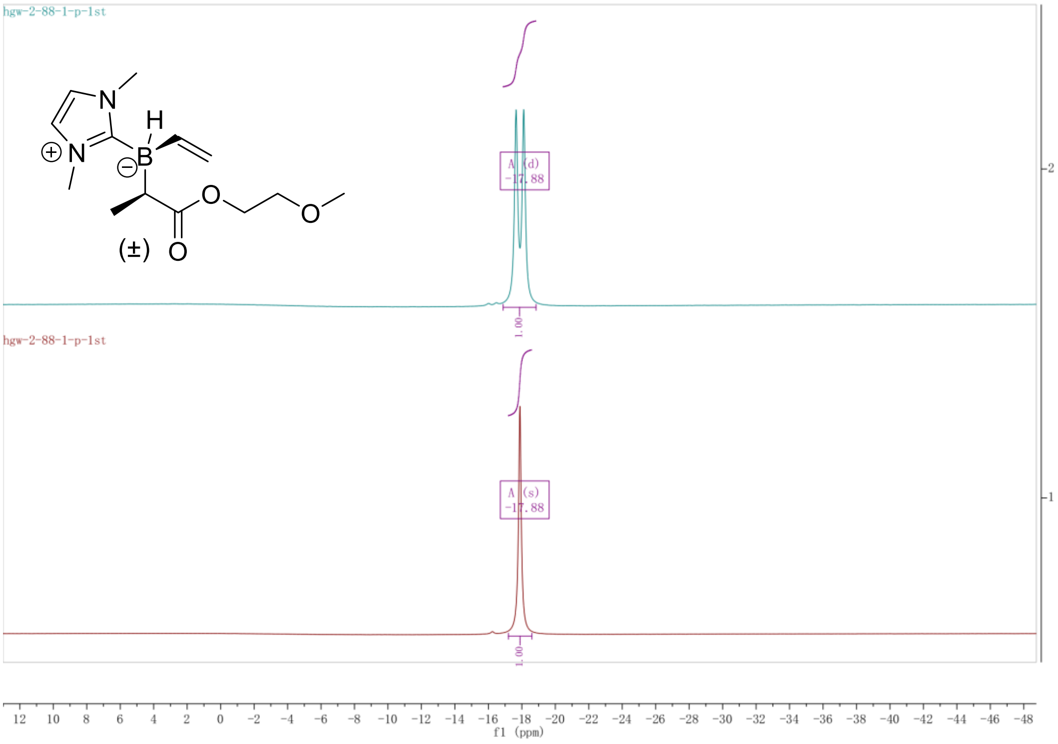


^{11}B NMR and ^{11}B {^{1}H} NMR of 15



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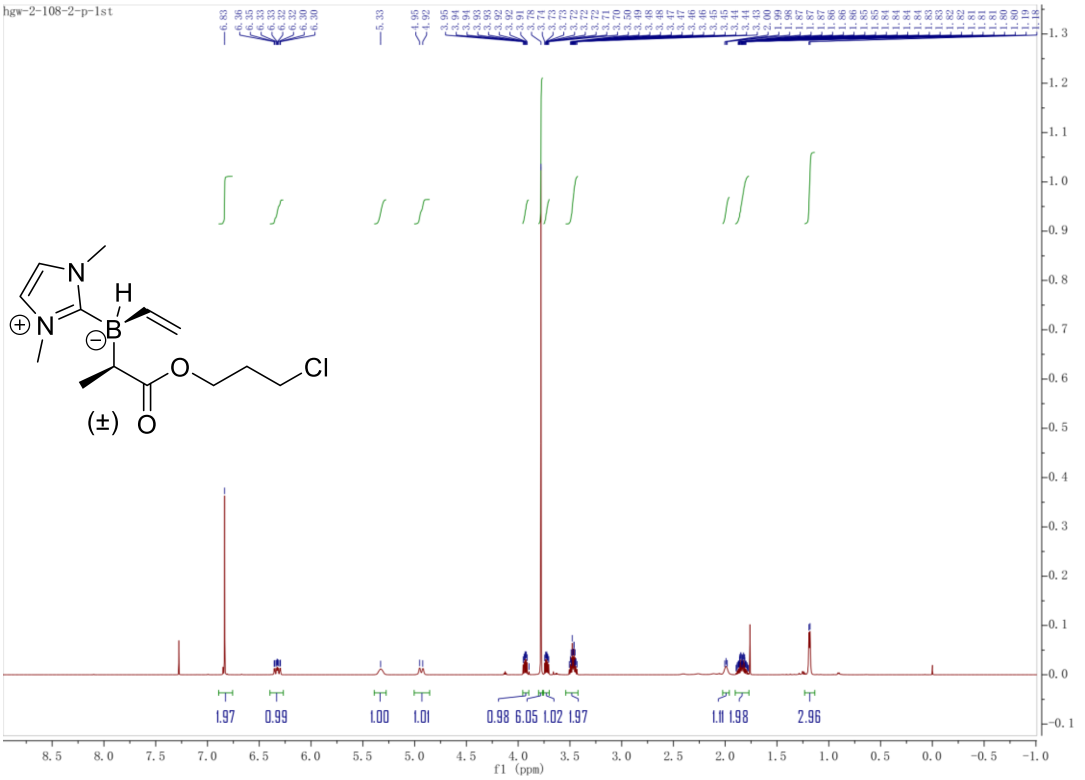

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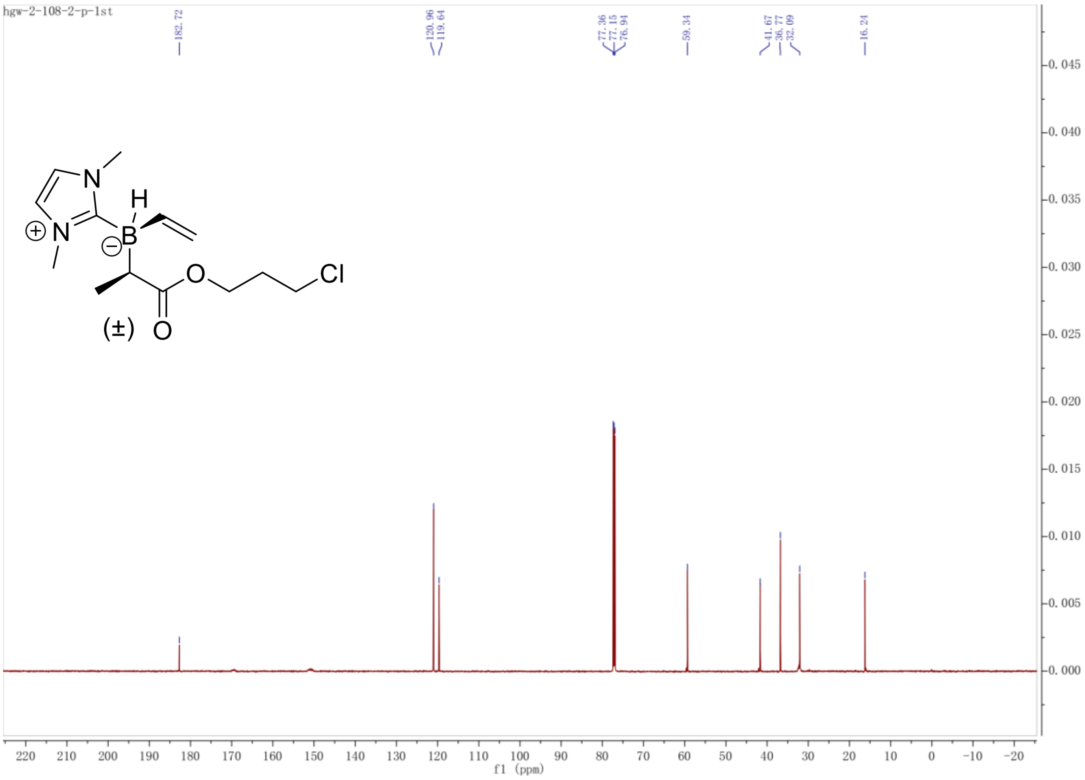
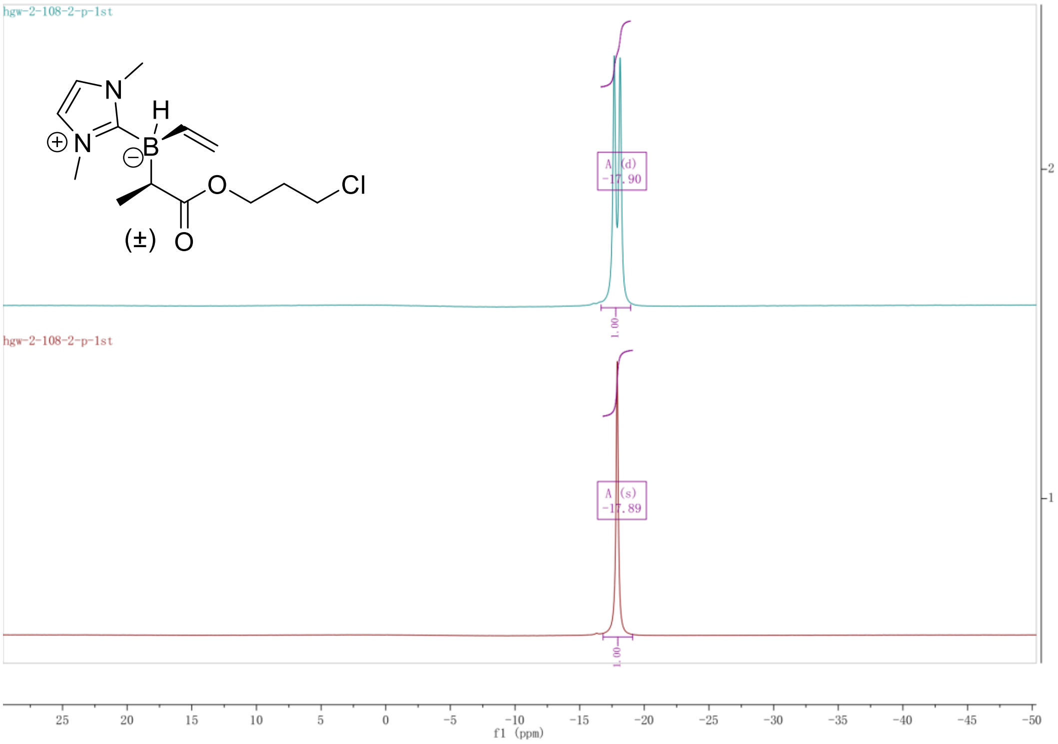
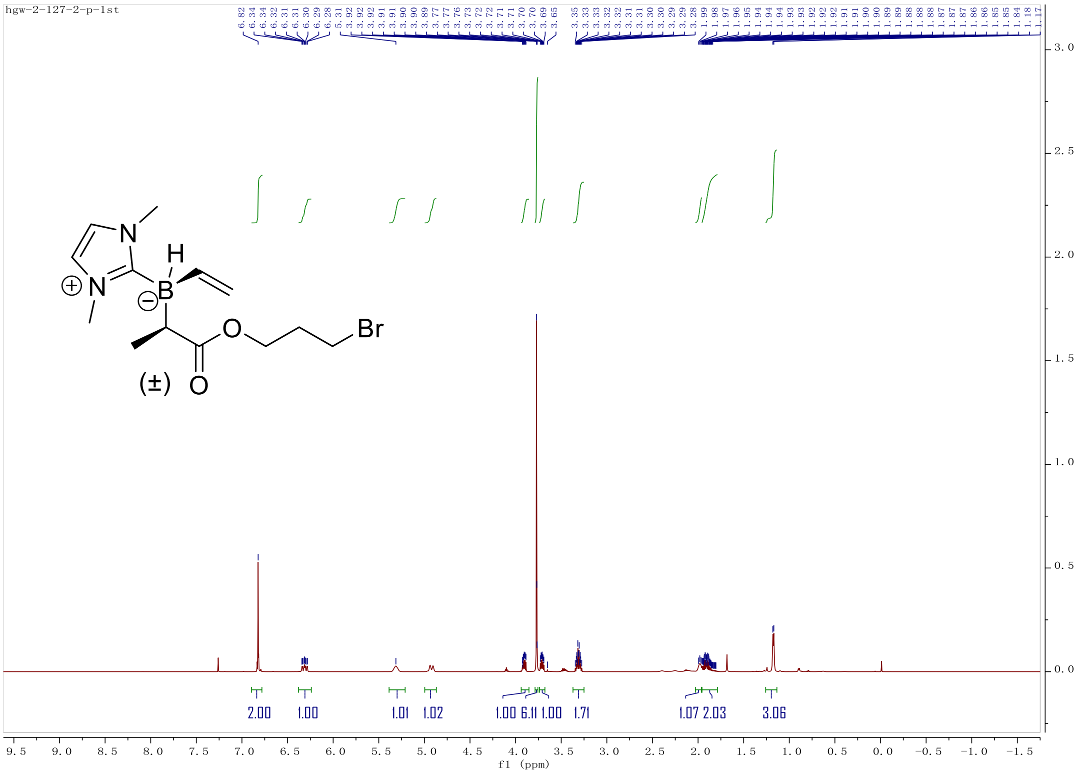


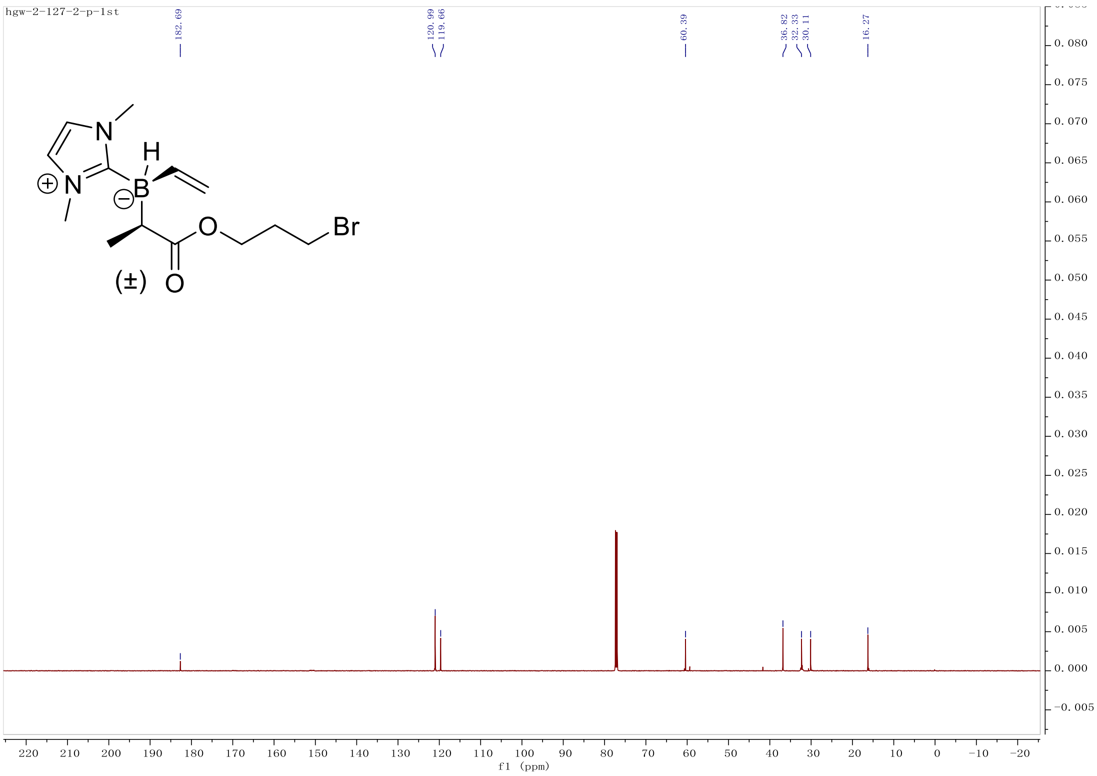
^{11}B NMR and ^{11}B {^1H} NMR of 16



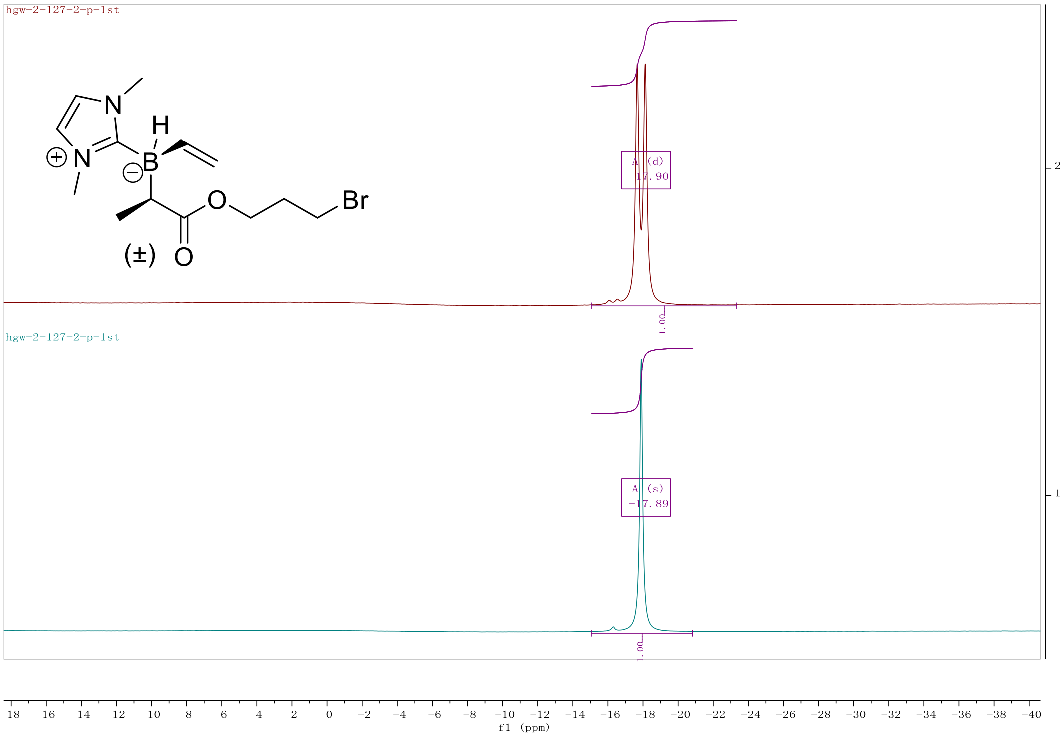
^1H NMR of 17



^{13}C NMR of 17



^{11}B NMR and ^{11}B {^{1}H} NMR of 17



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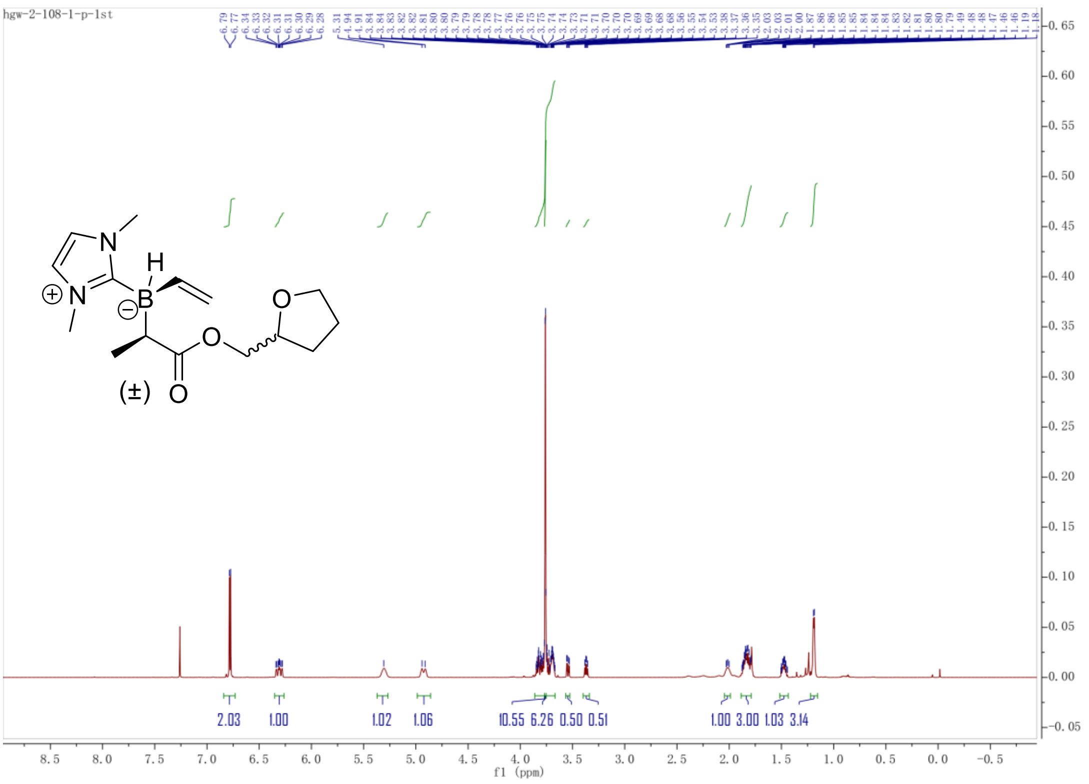
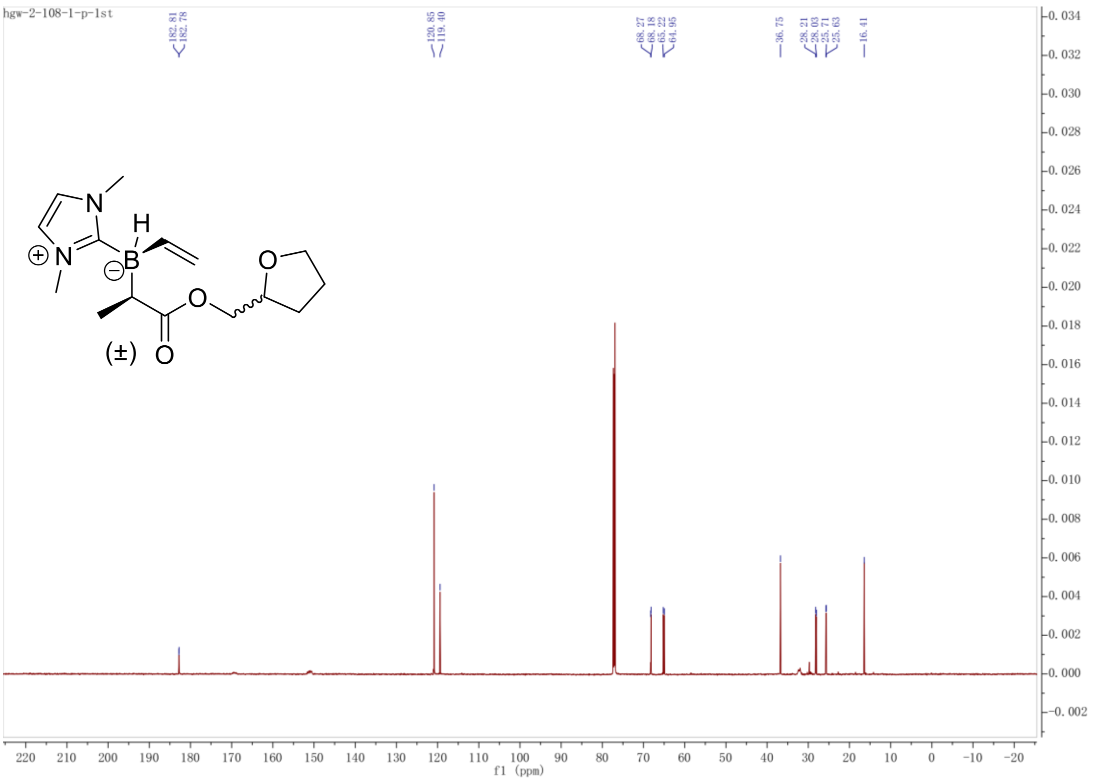
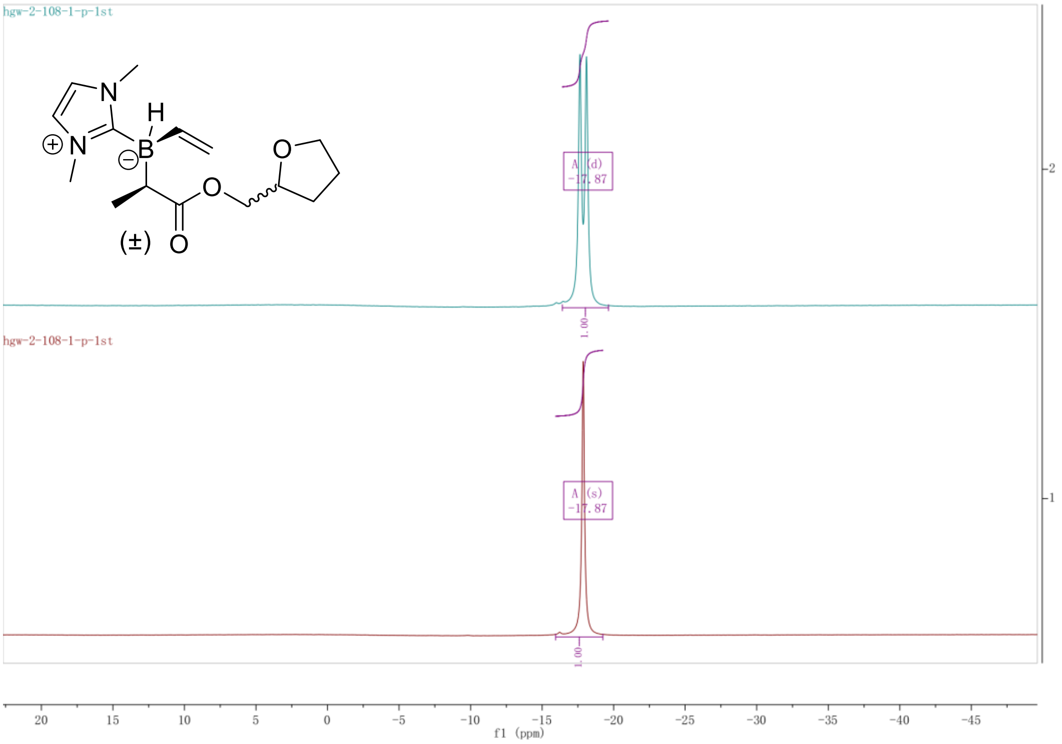


^{13}C NMR of 18



^{11}B NMR and ^{11}B {^{1}H} NMR of 18



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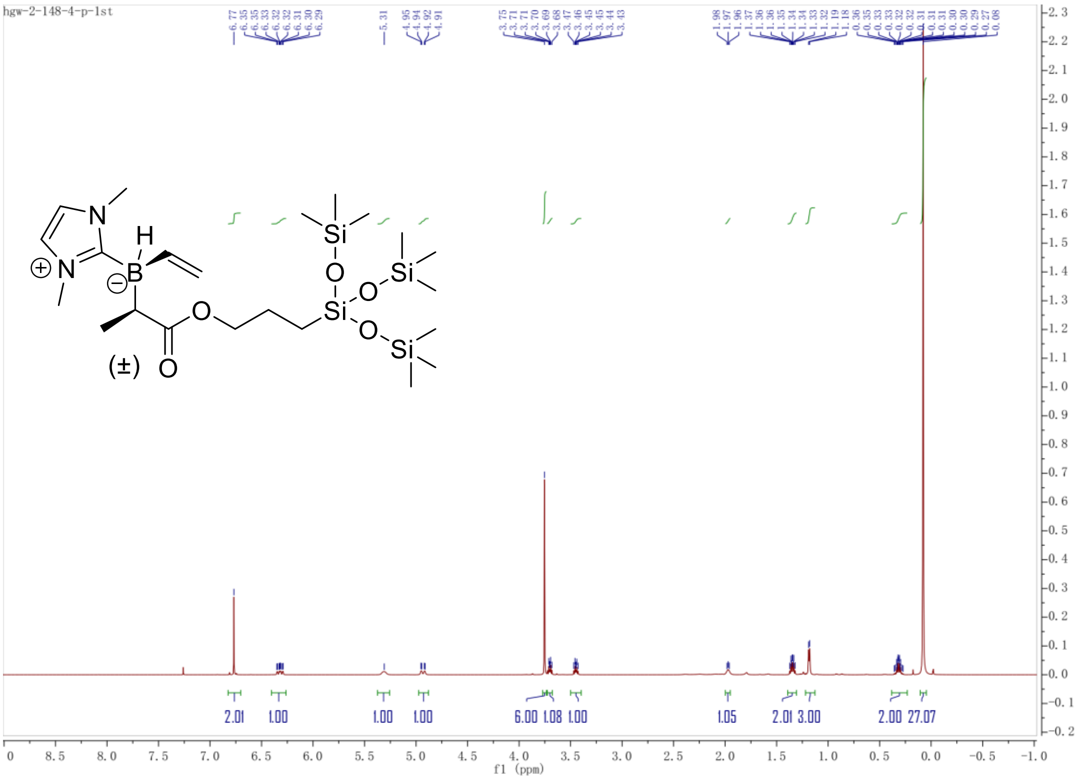

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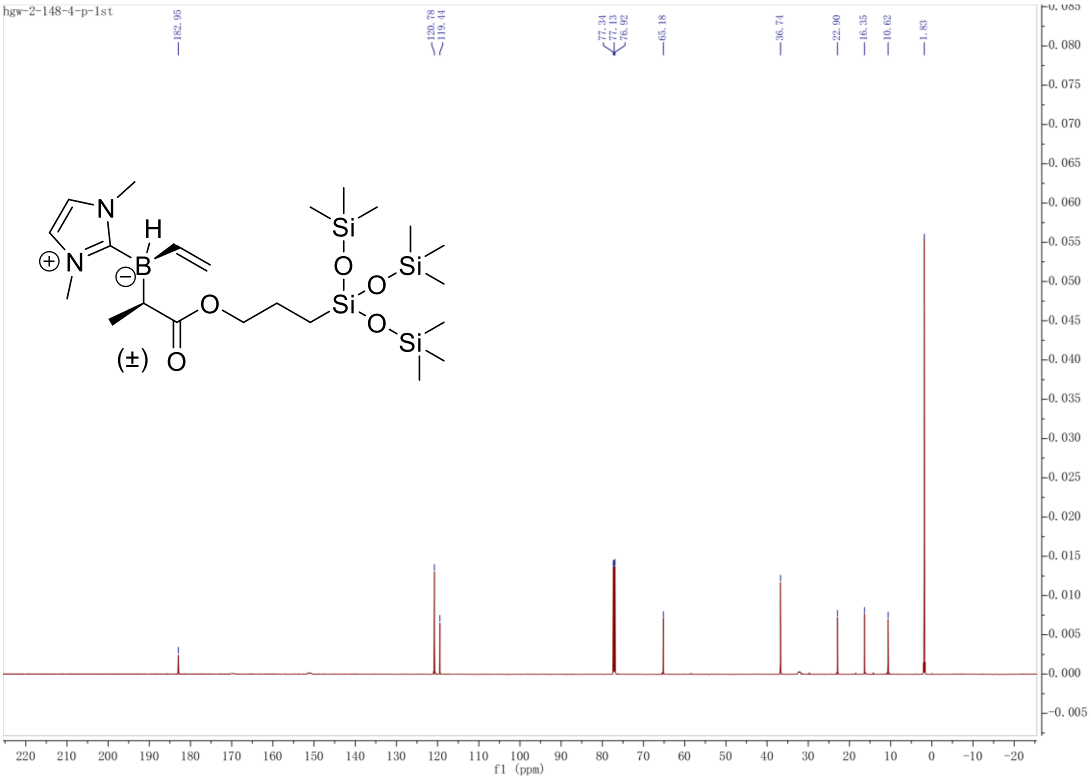
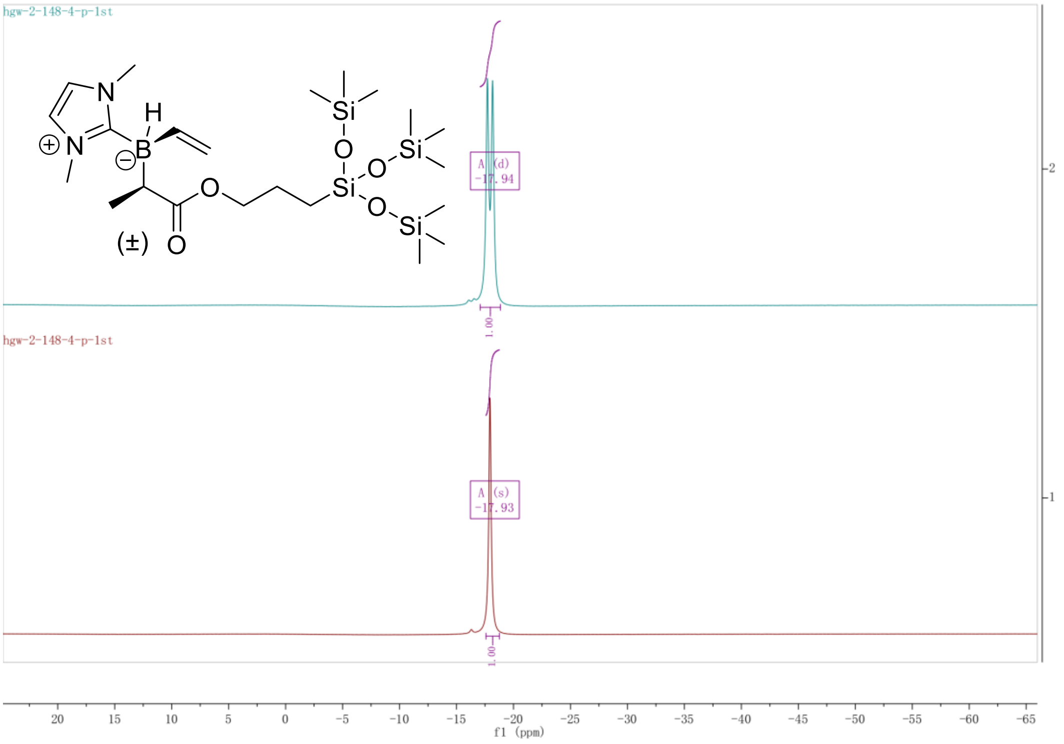


^{11}B NMR and ^{11}B {^{1}H} NMR of 19



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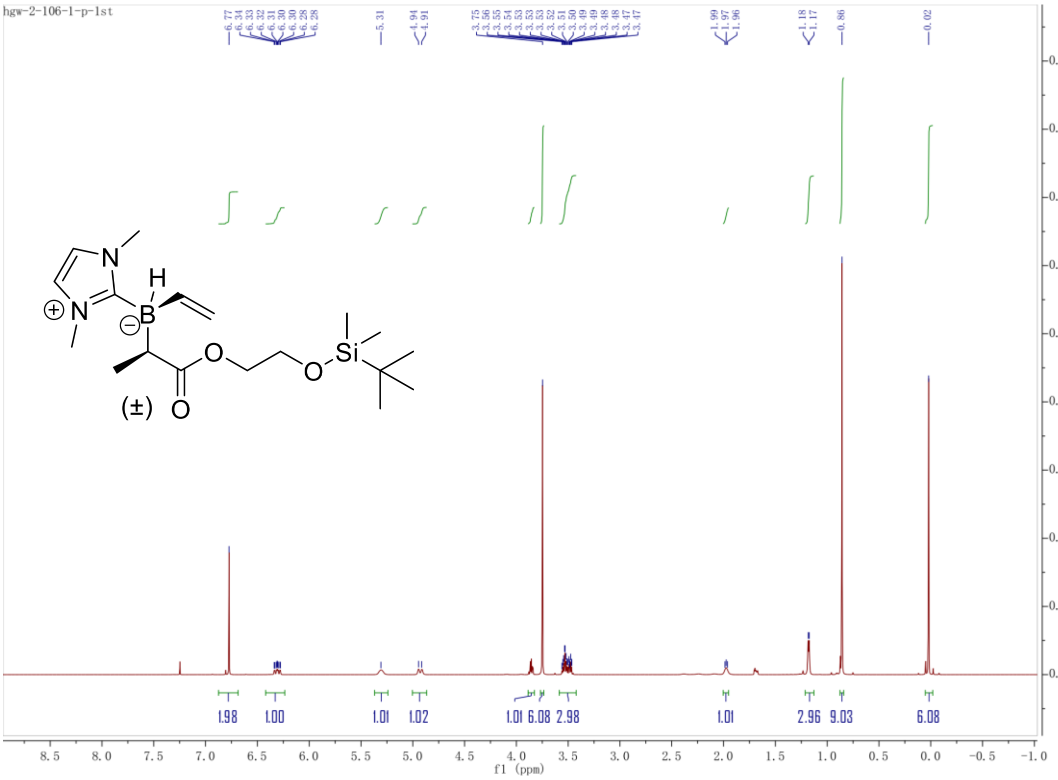

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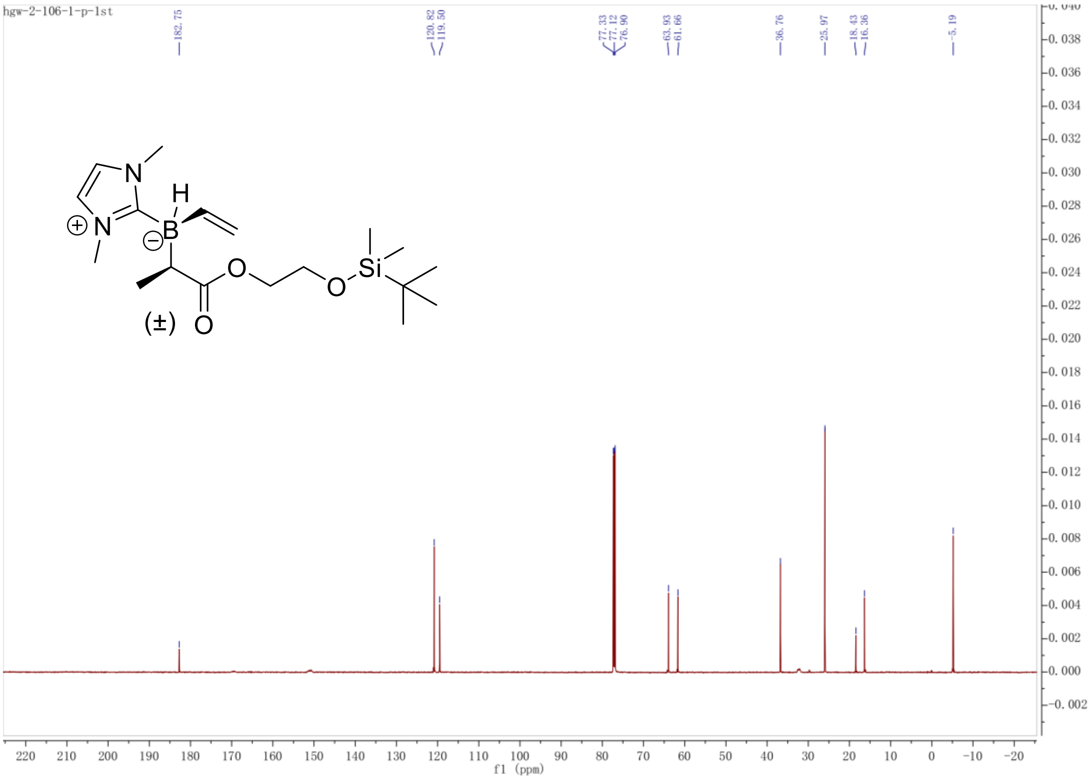

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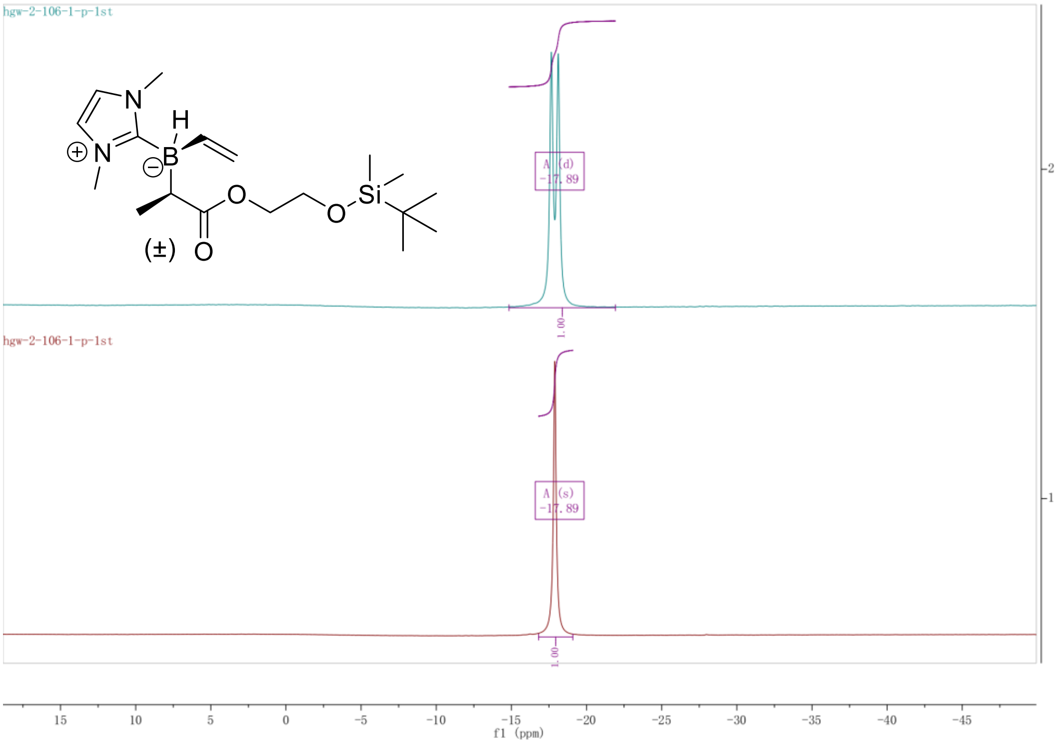

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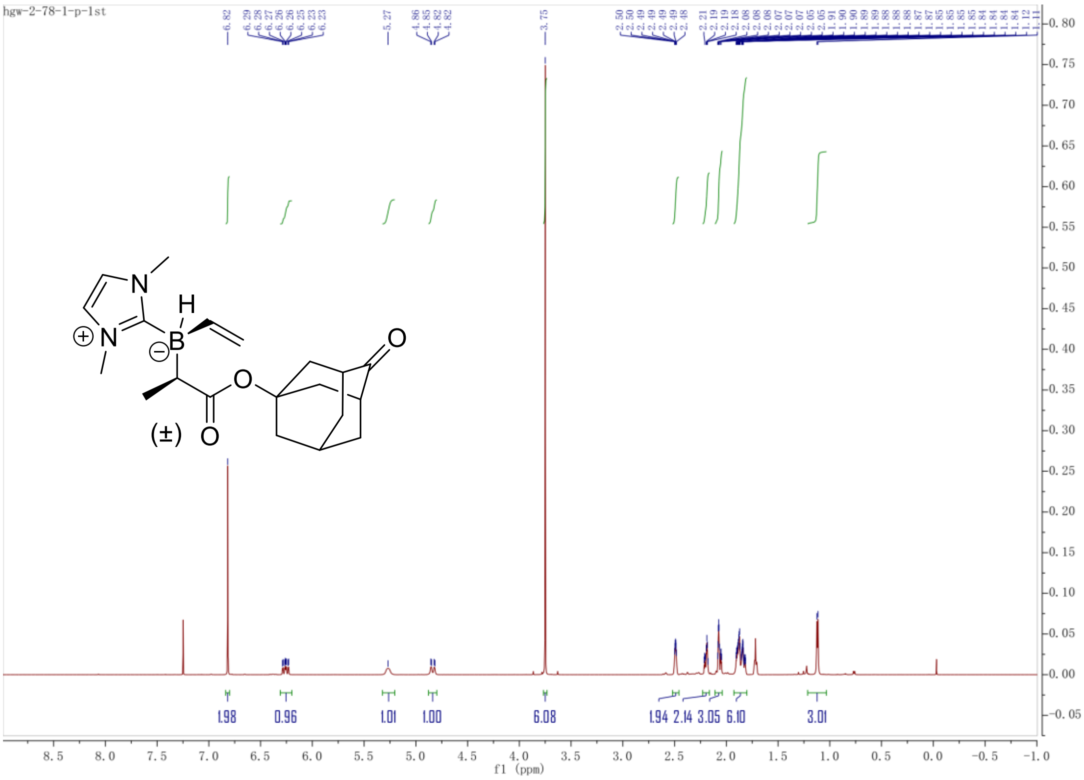

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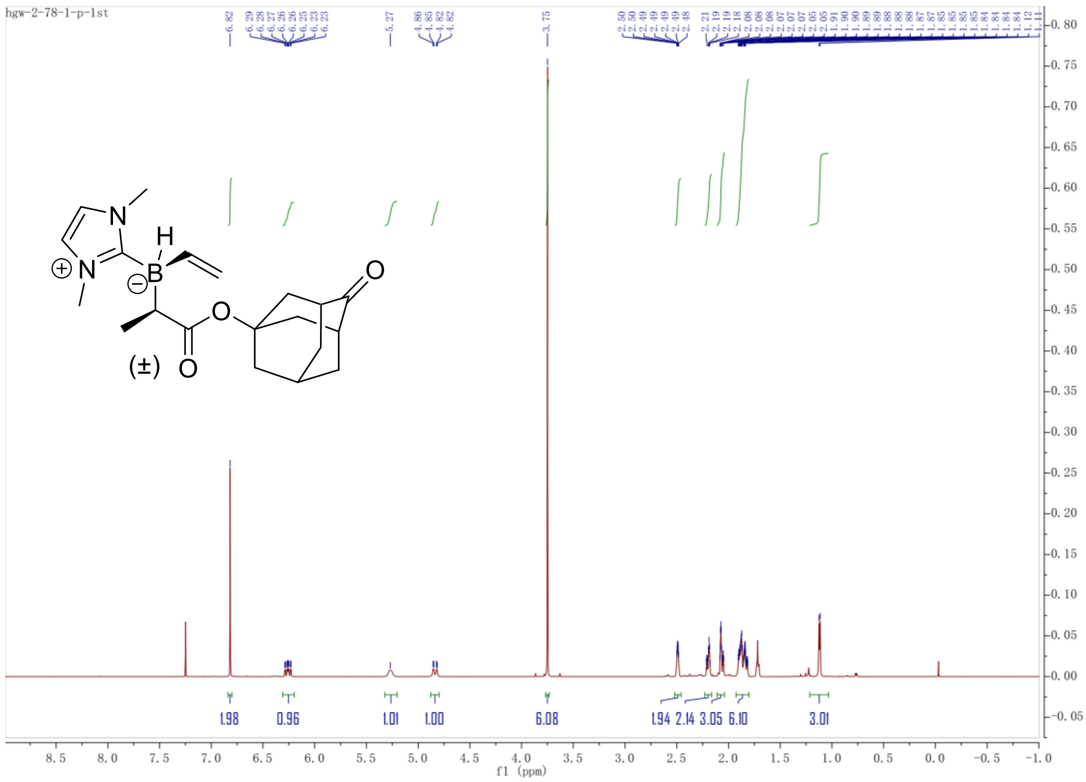
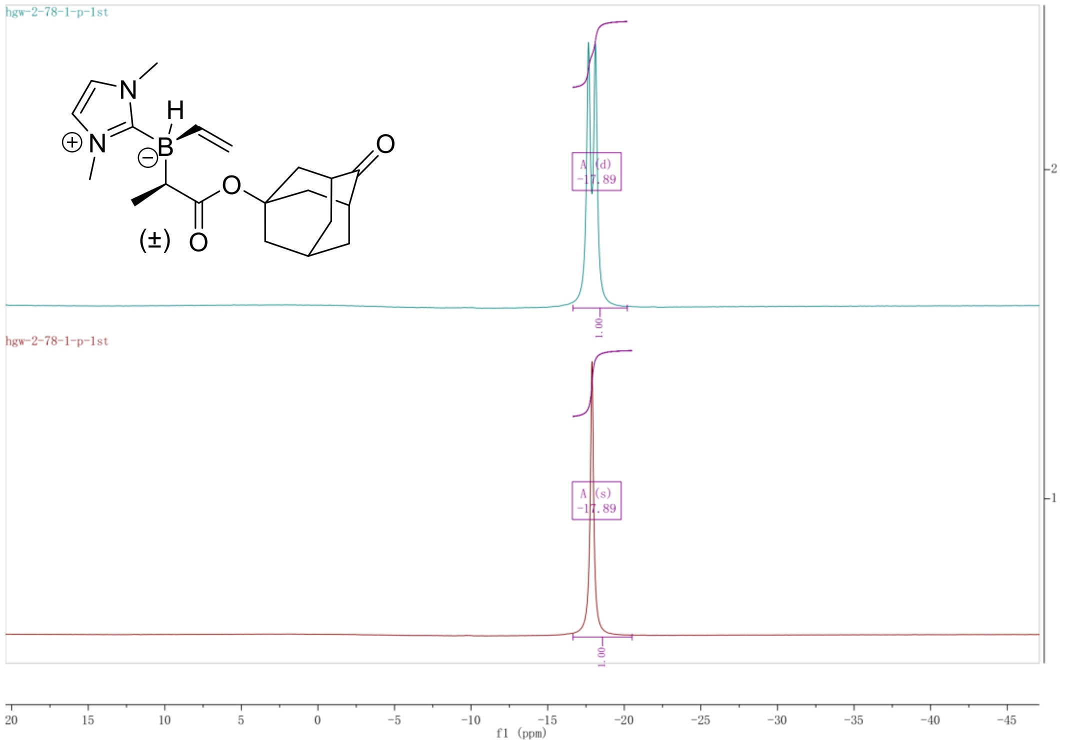


^{11}B NMR and ^{11}B {^{1}H} NMR of 21



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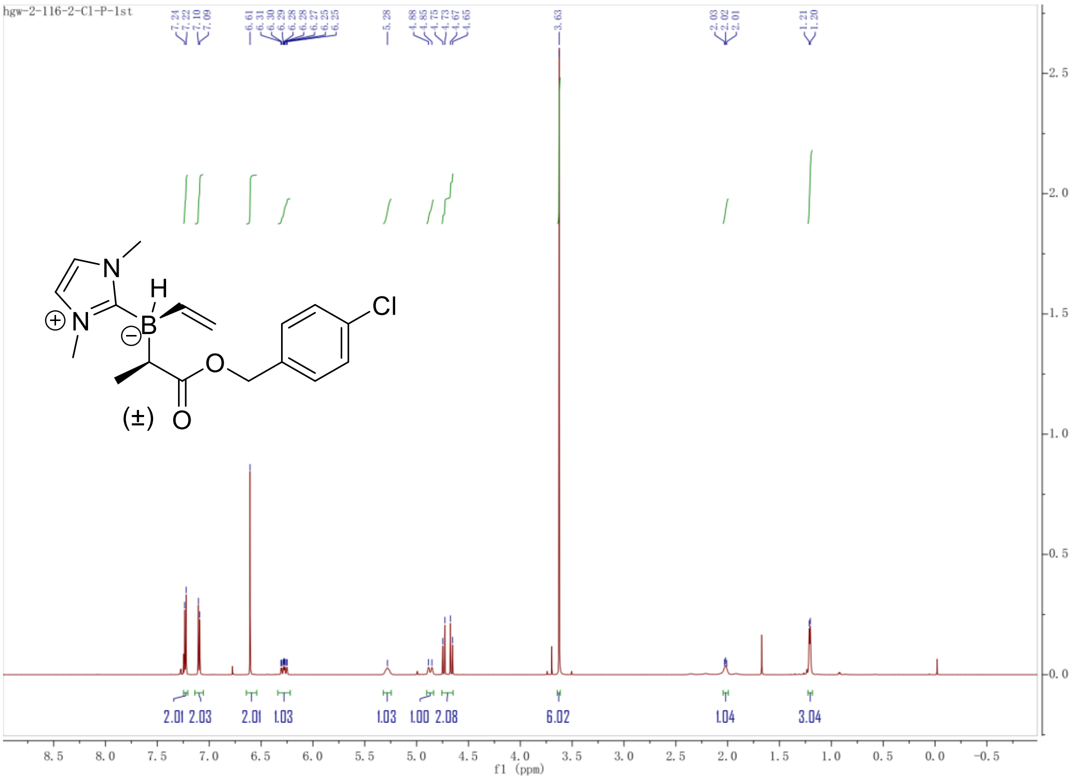

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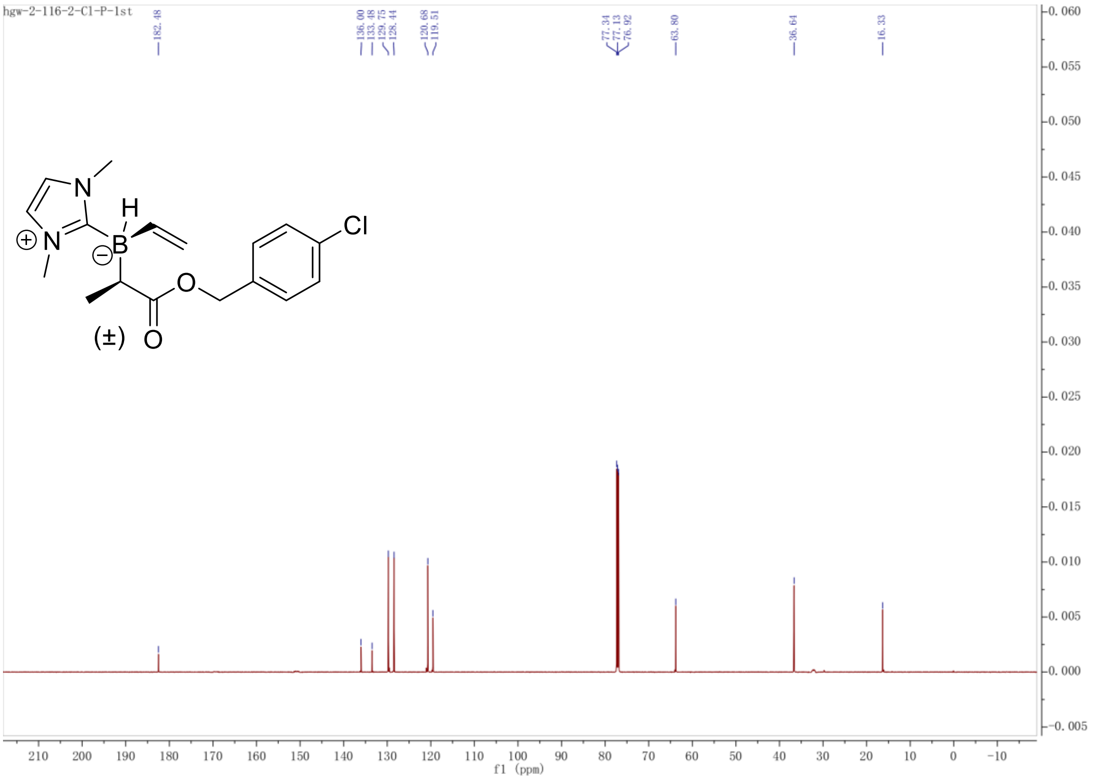
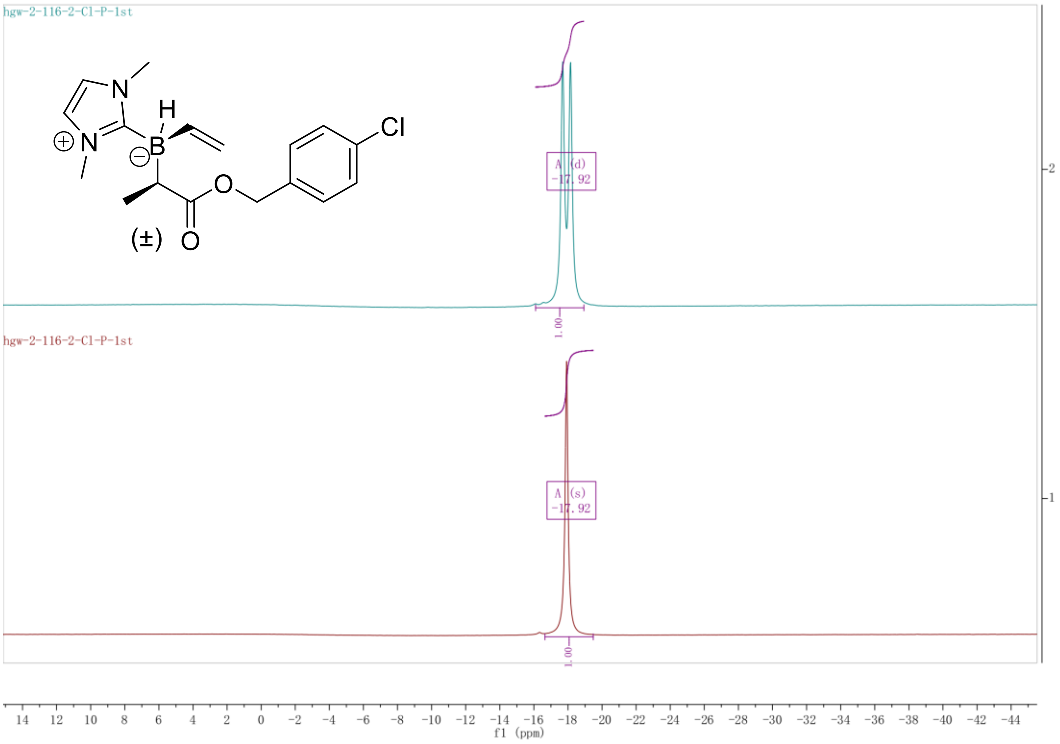


^{11}B NMR and ^{11}B {^{1}H} NMR of 22



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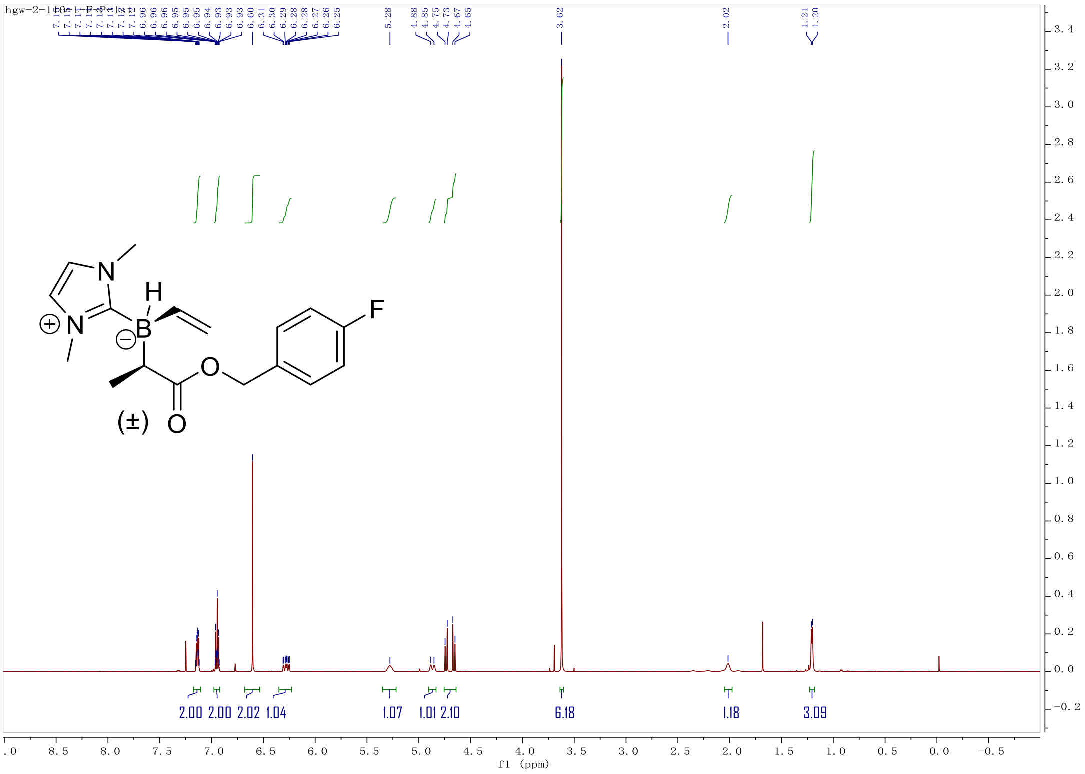

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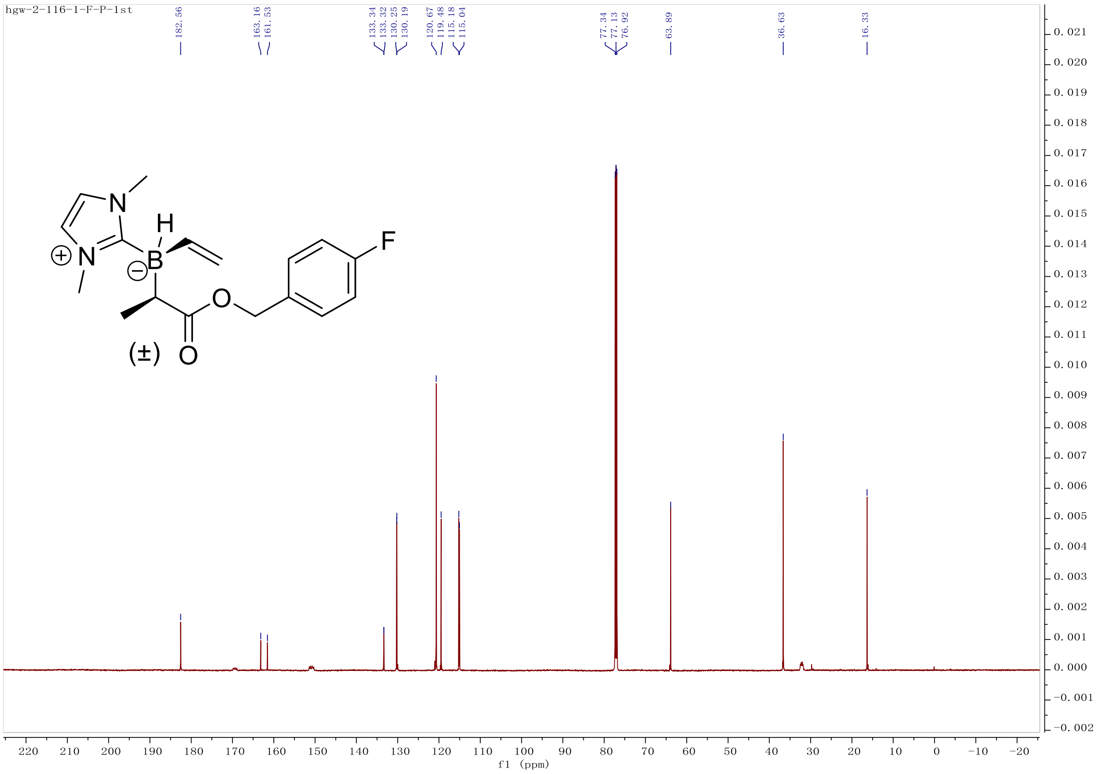
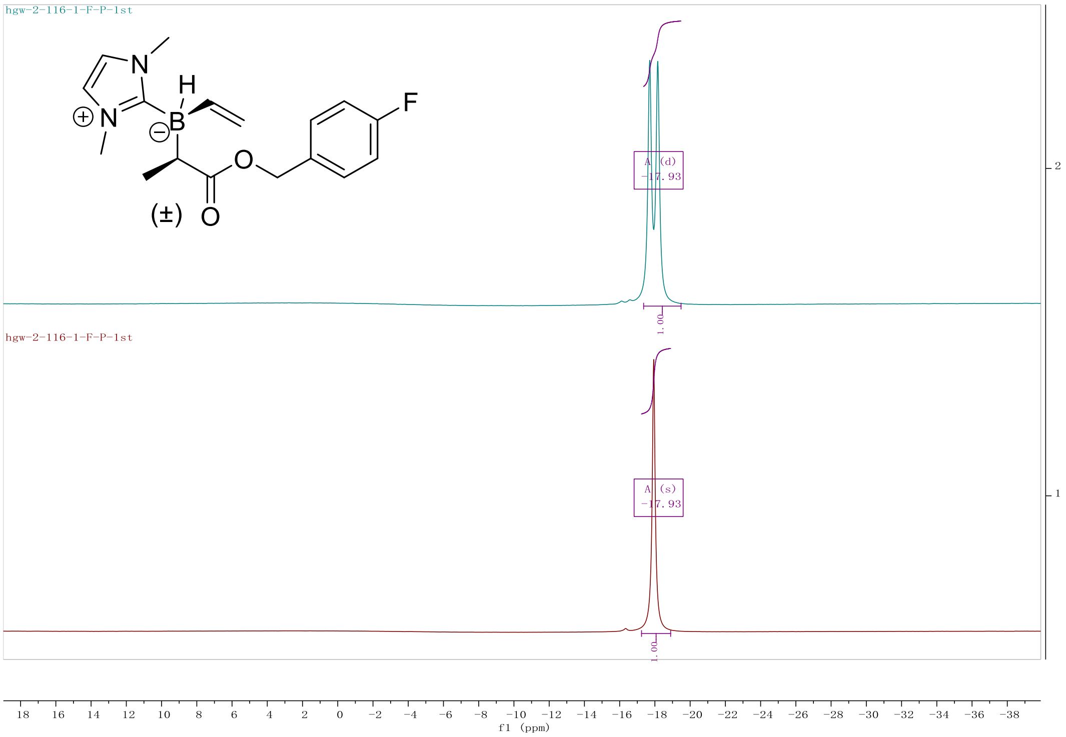
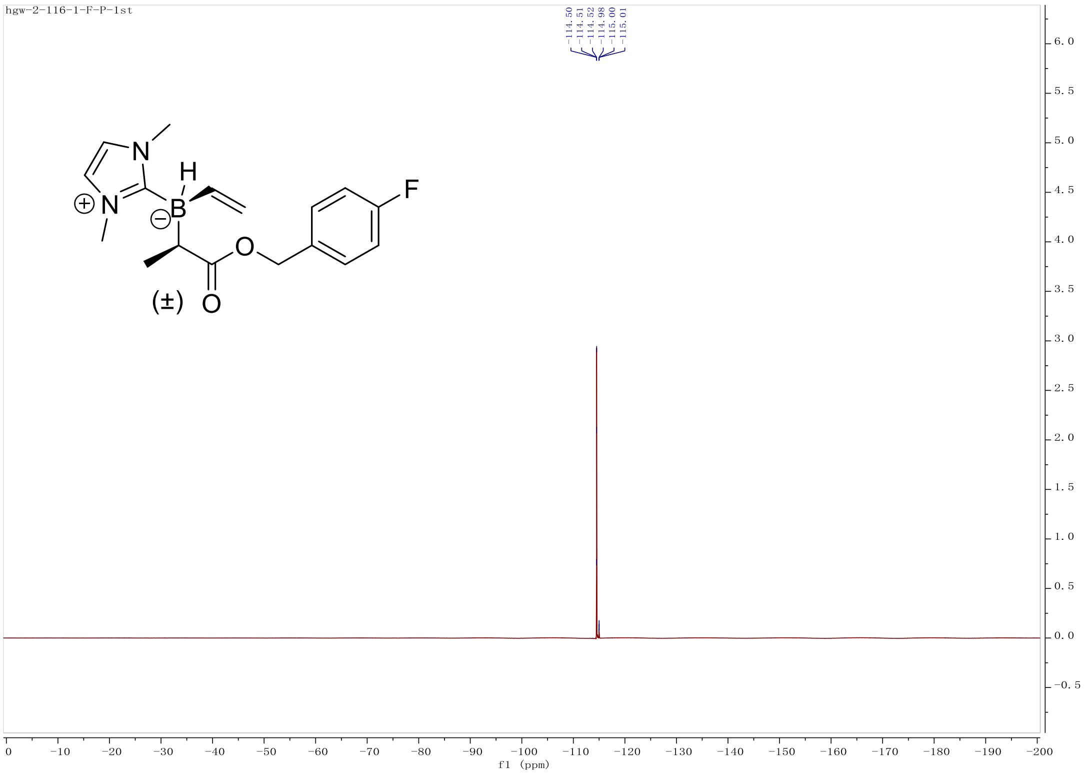


^{11}B NMR and ^{11}B {^{1}H} NMR of 23



^{19}F NMR of 23



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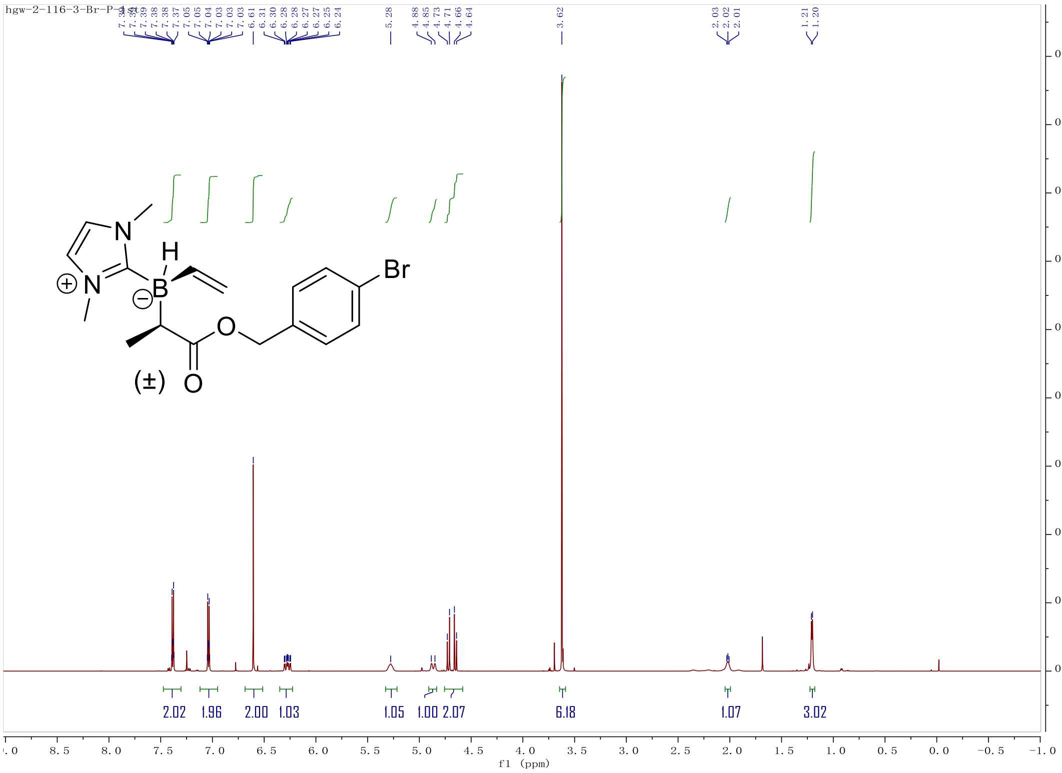
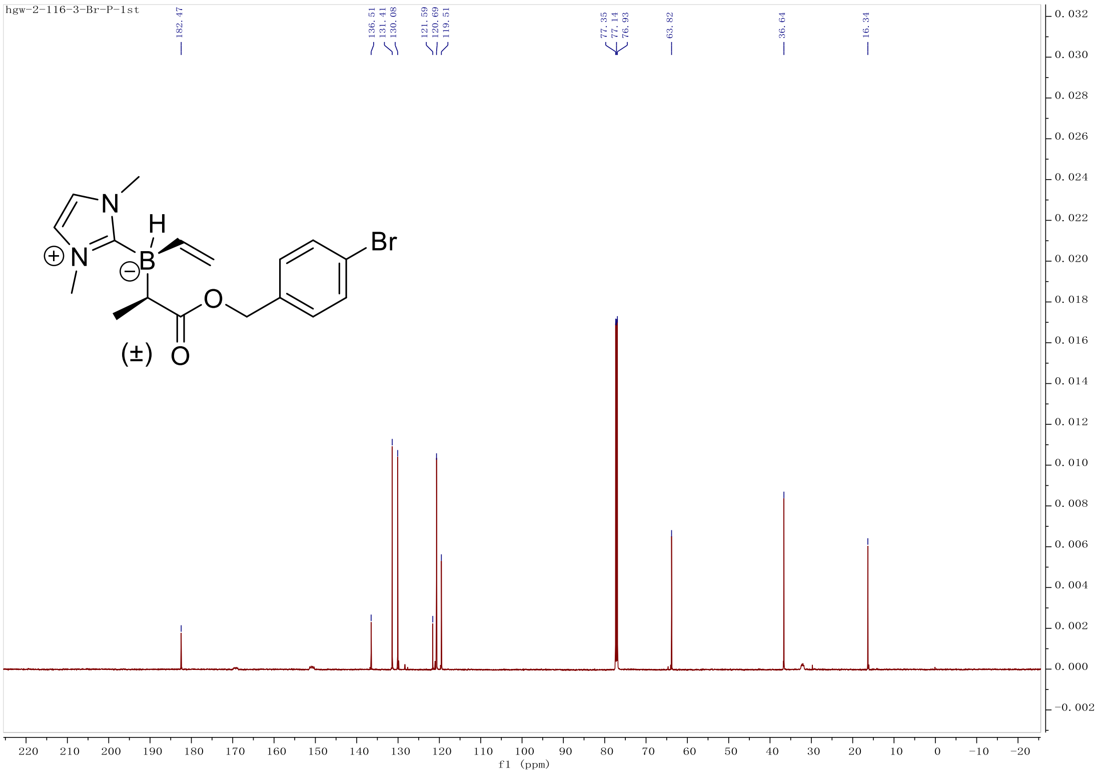
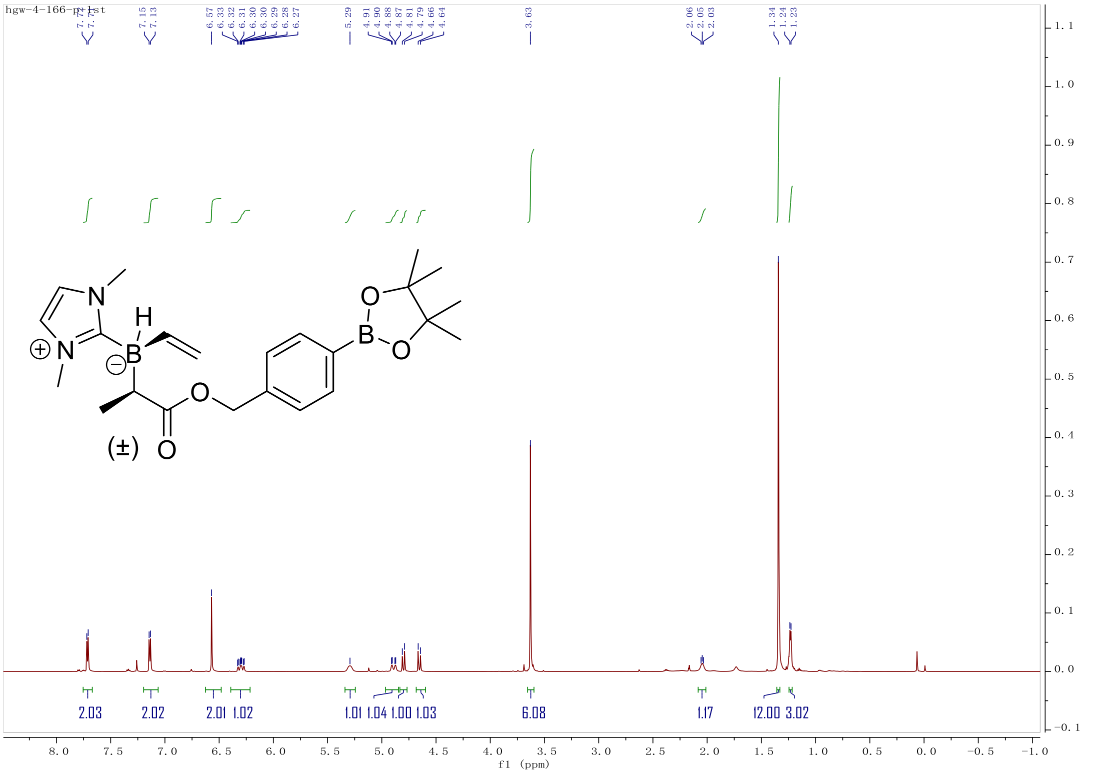


^{13}C NMR of 24



^{11}B NMR and ^{11}B {^{1}H} NMR of 24

^{1}H NMR of 25



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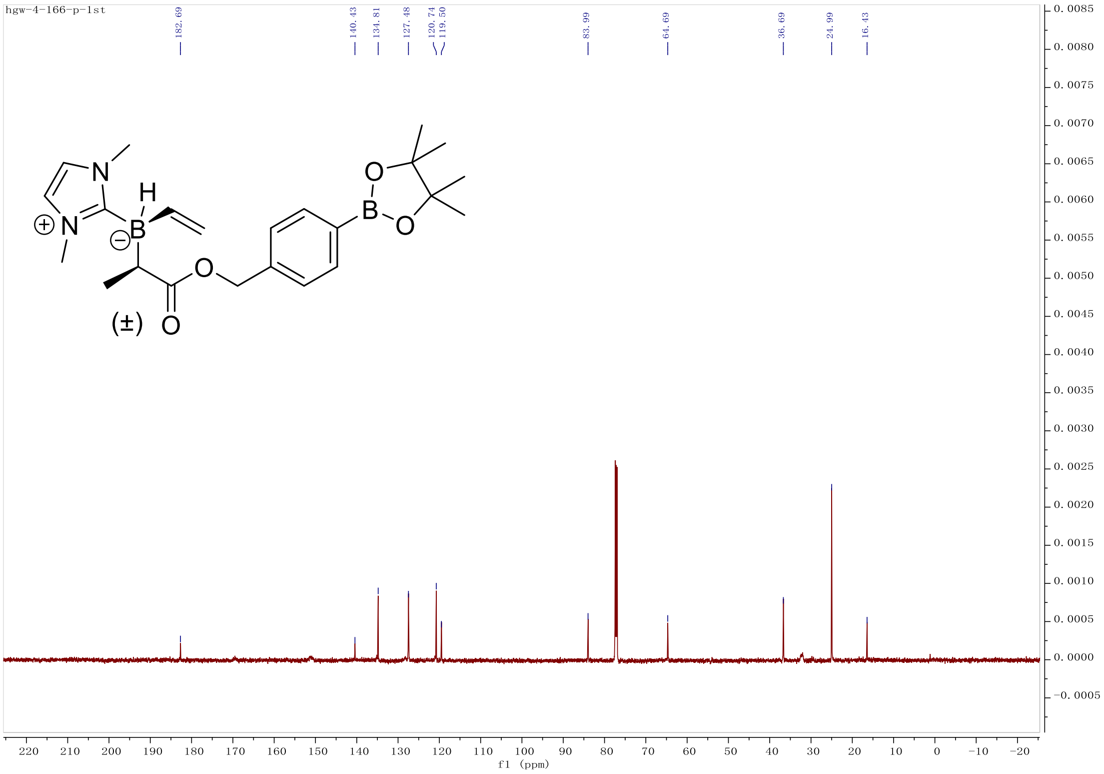
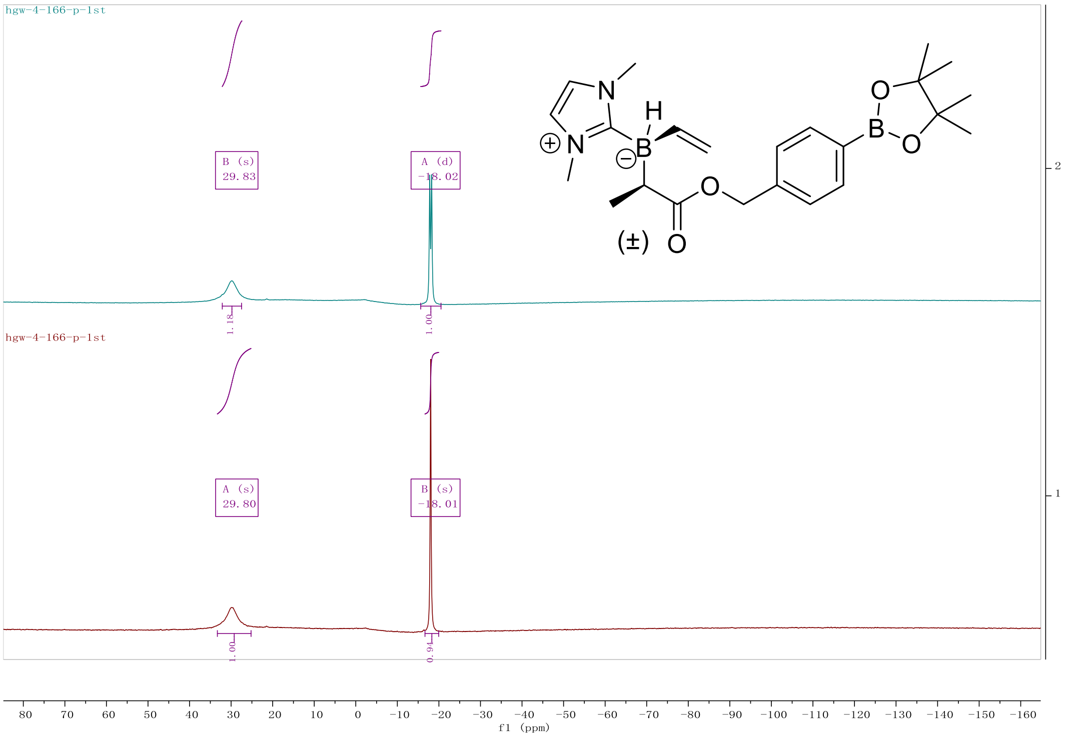
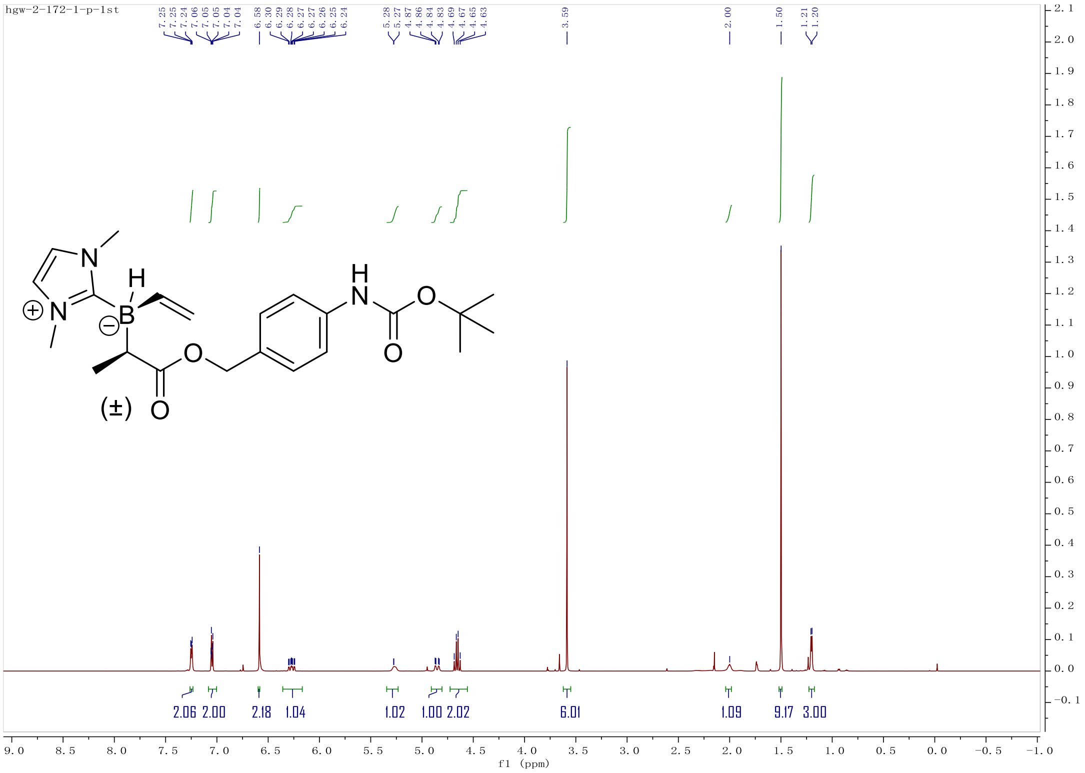


^{11}B NMR and ^{11}B {^{1}H} NMR of 25



^{1}H NMR of 26



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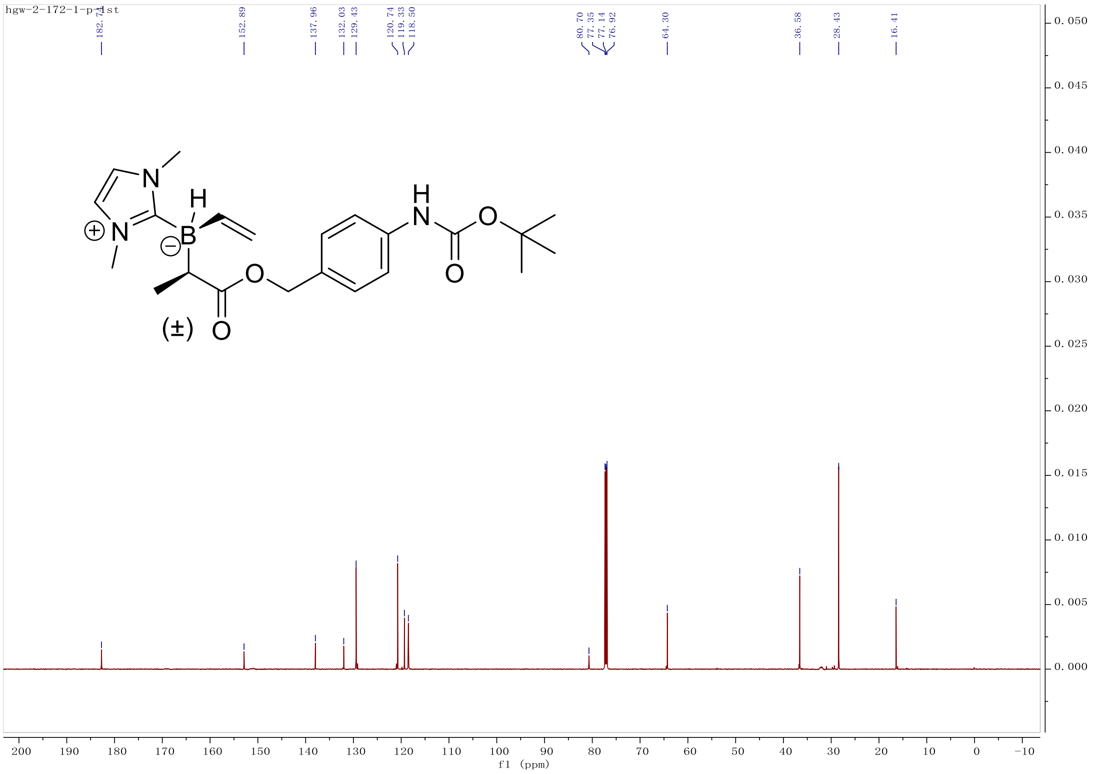
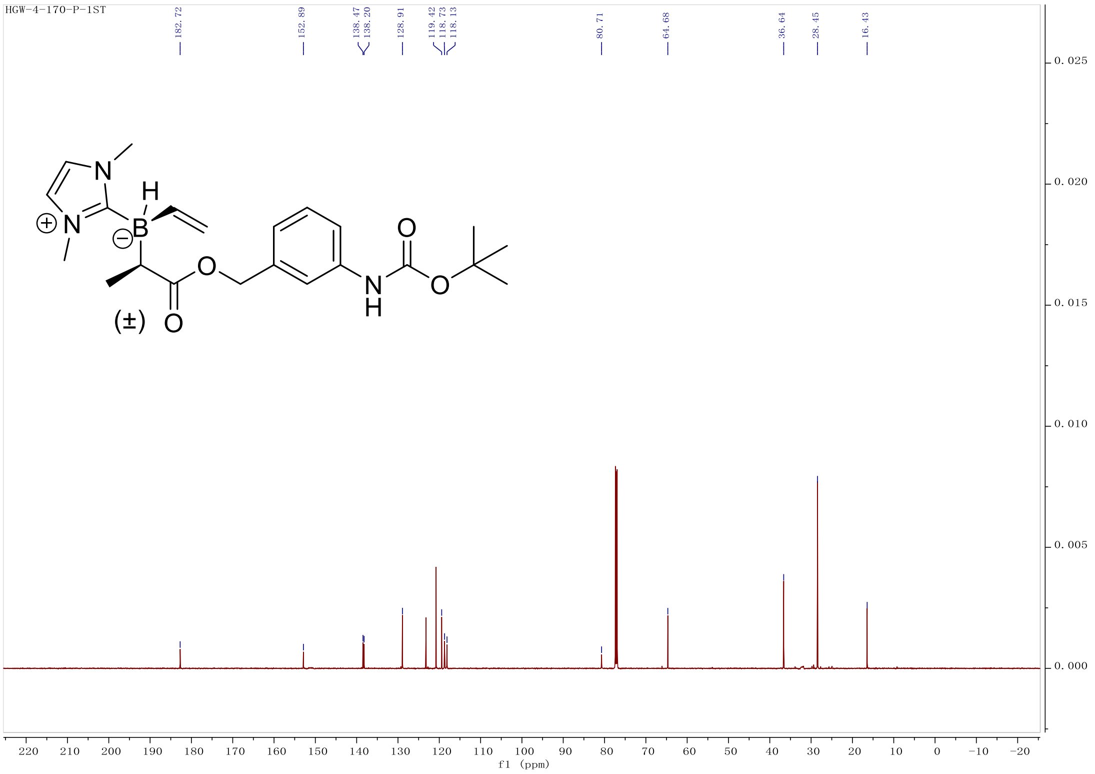


^{11}B NMR and ^{11}B {^{1}H} NMR of 26

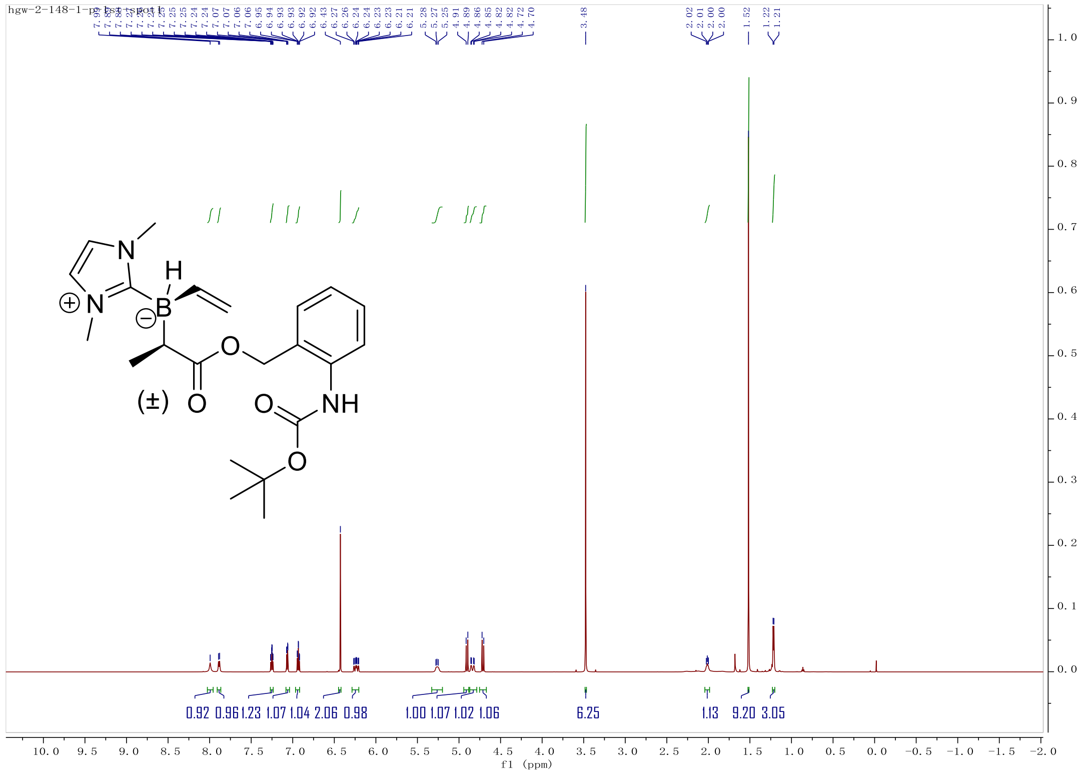
^{1}H NMR of 27

^{13}C NMR of 27

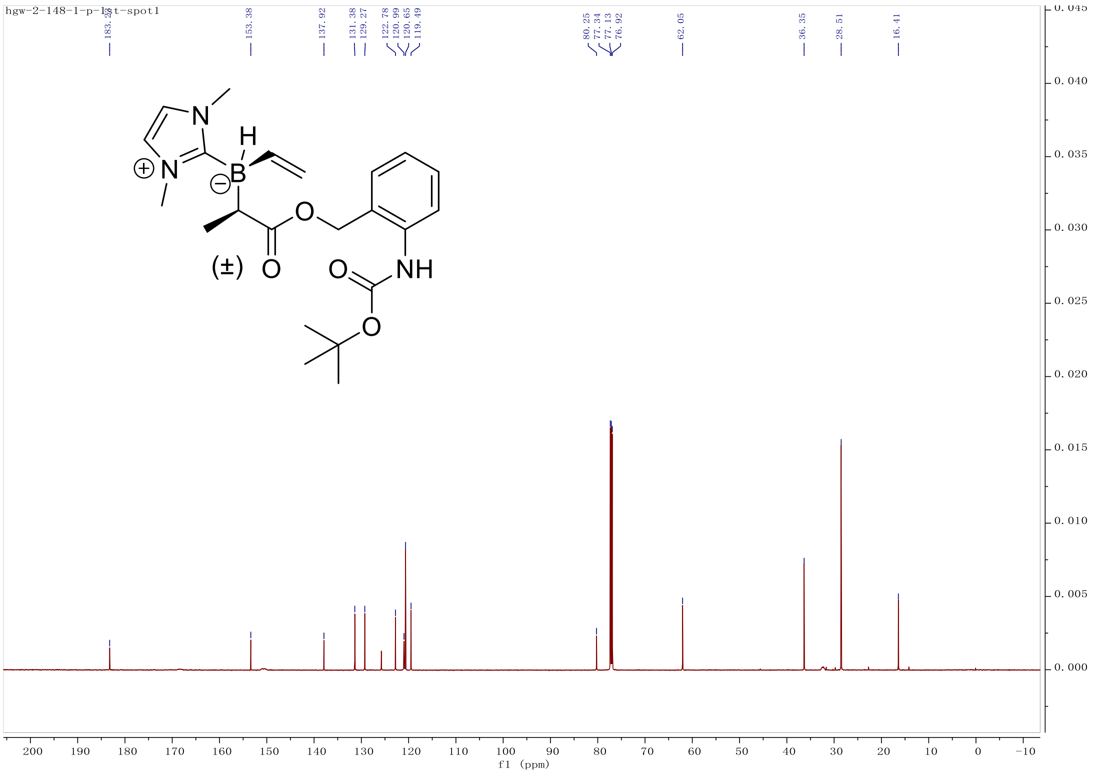


^{11}B NMR and ^{11}B {^{1}H} NMR of 27

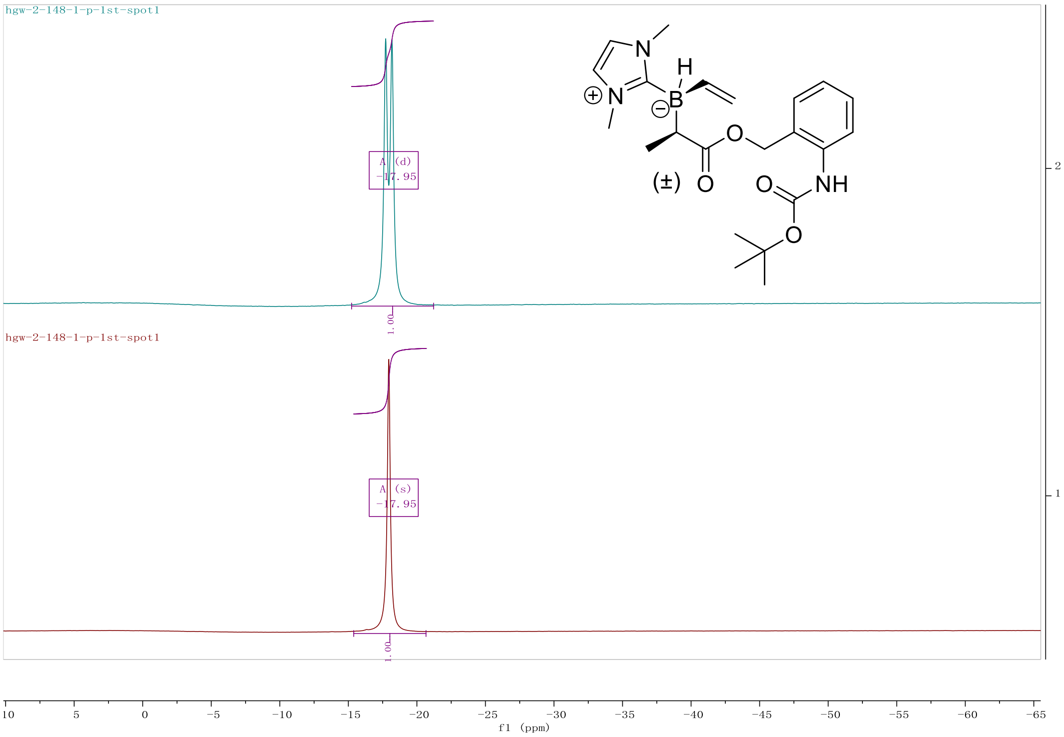
^{1}H NMR of 28



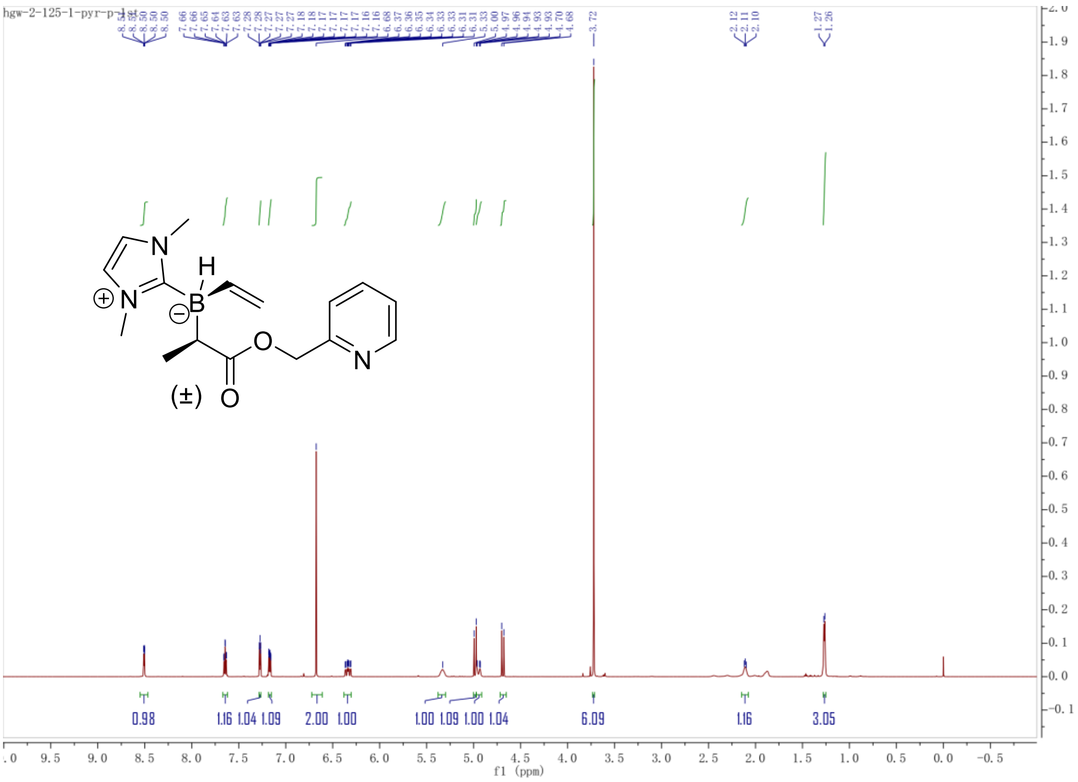
^{13}C NMR of 28



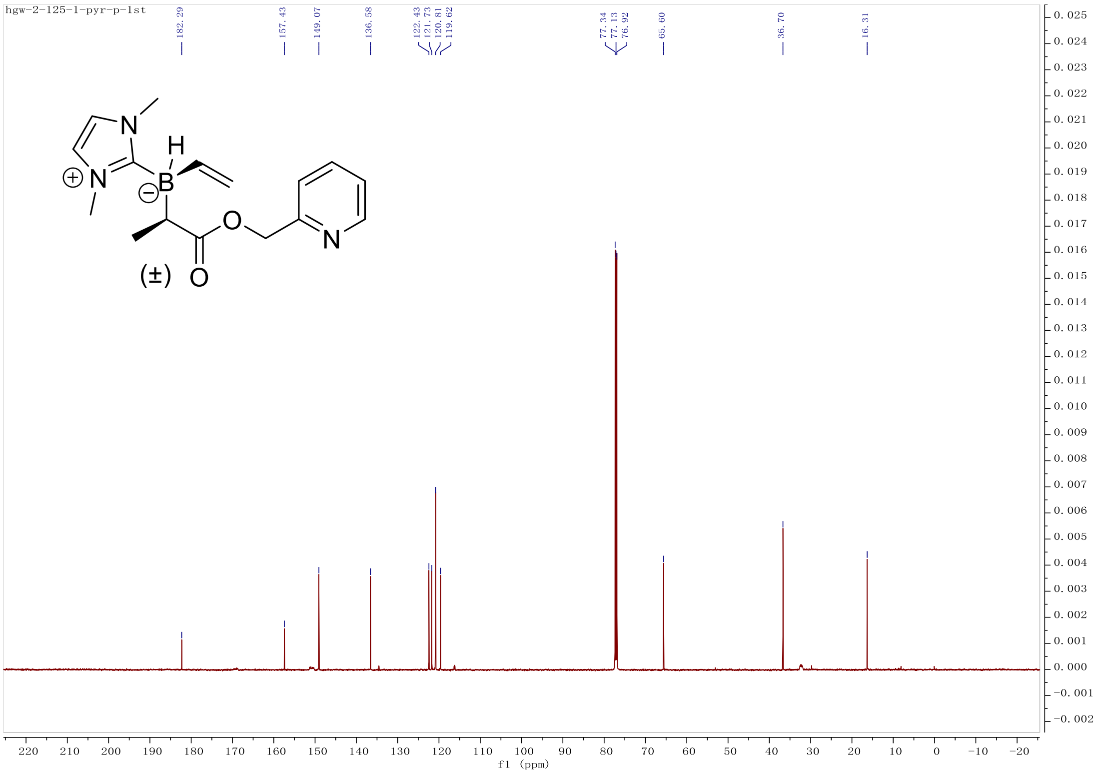
^{11}B NMR and ^{11}B {^{1}H} NMR of 28



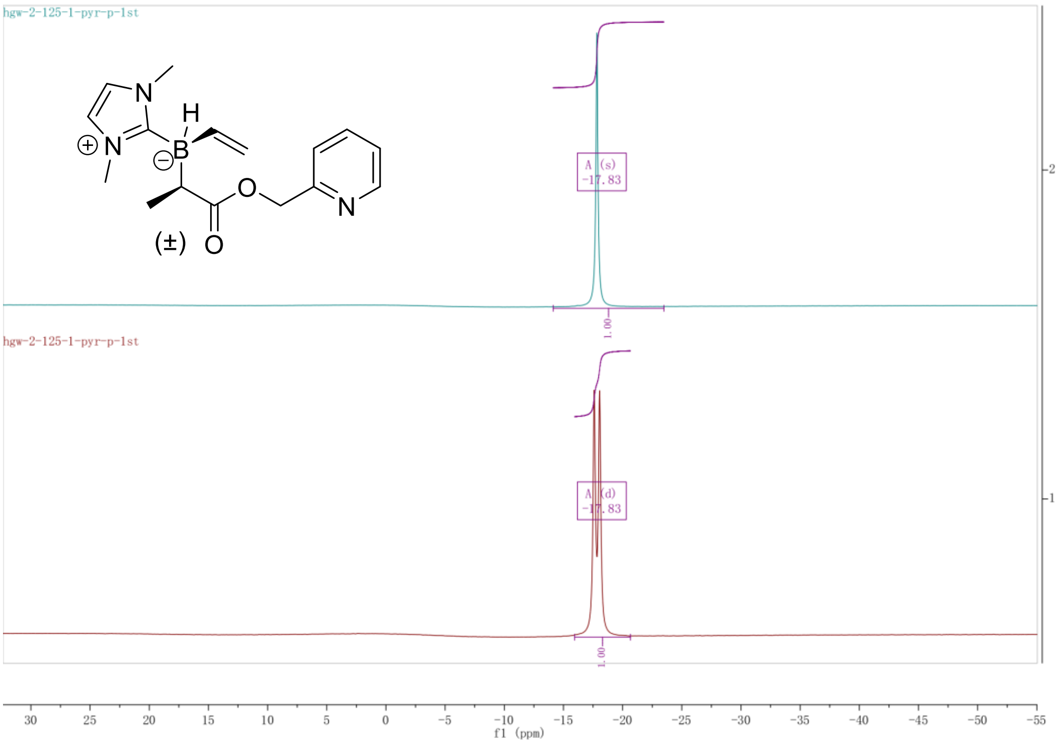
^{1}H NMR of 29



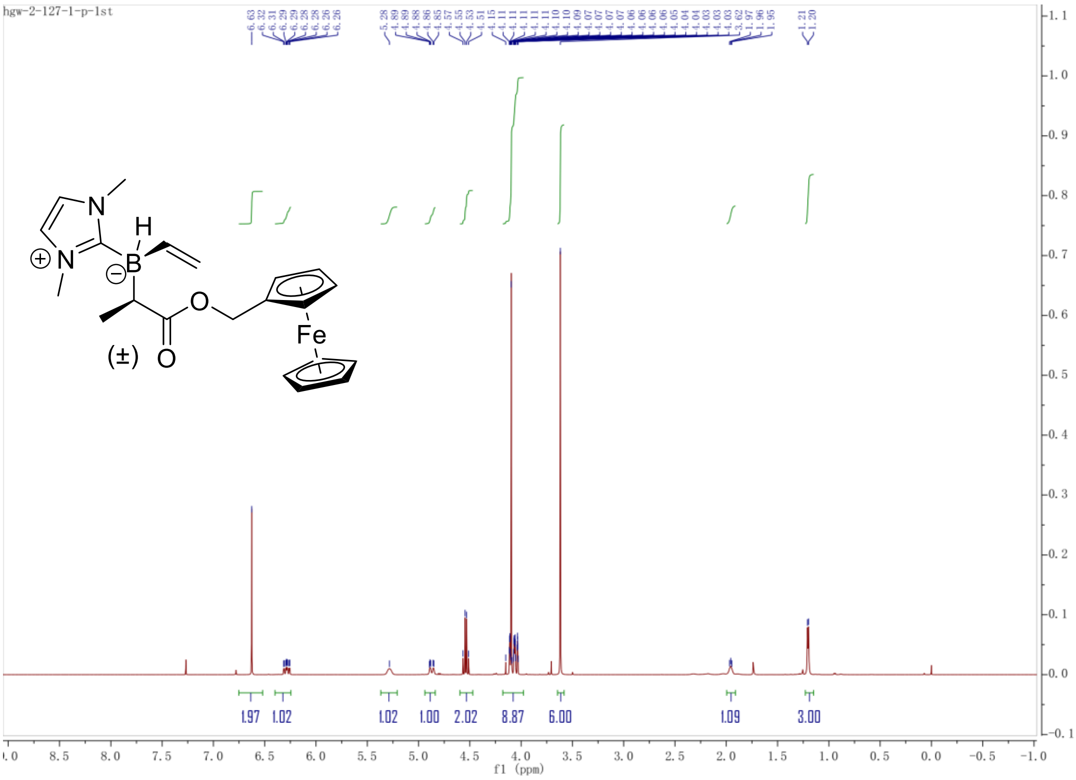
^{13}C NMR of 29



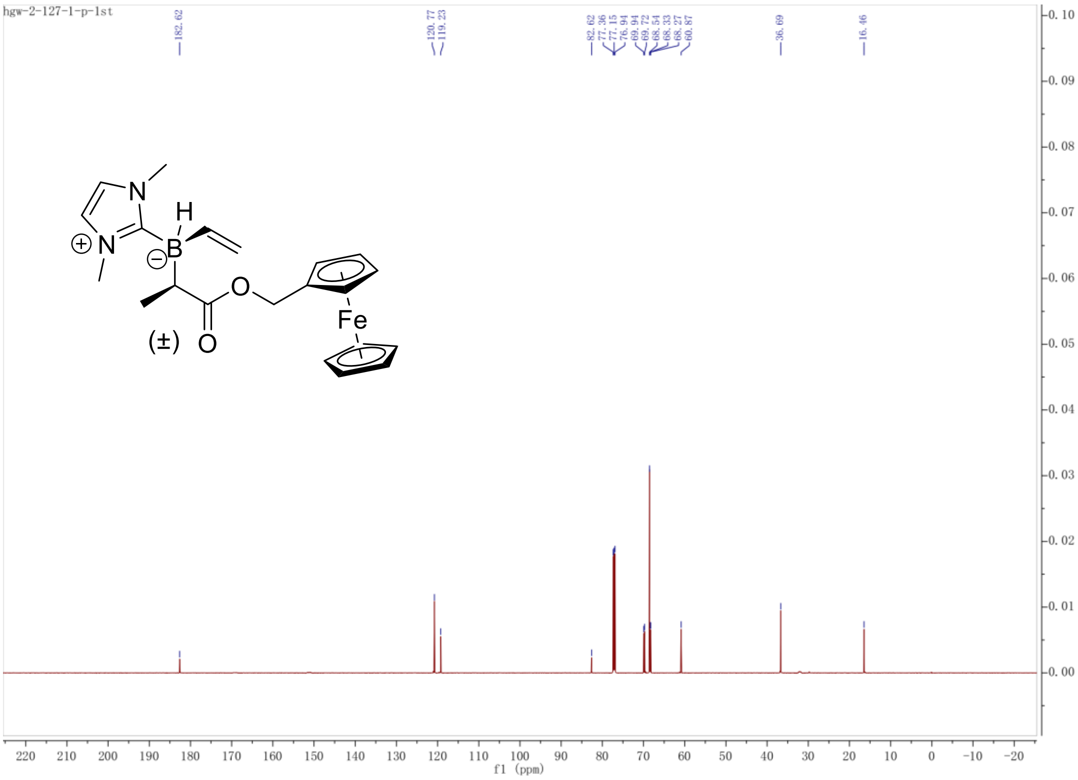
^{11}B NMR and ^{11}B {^{1}H} NMR of 29



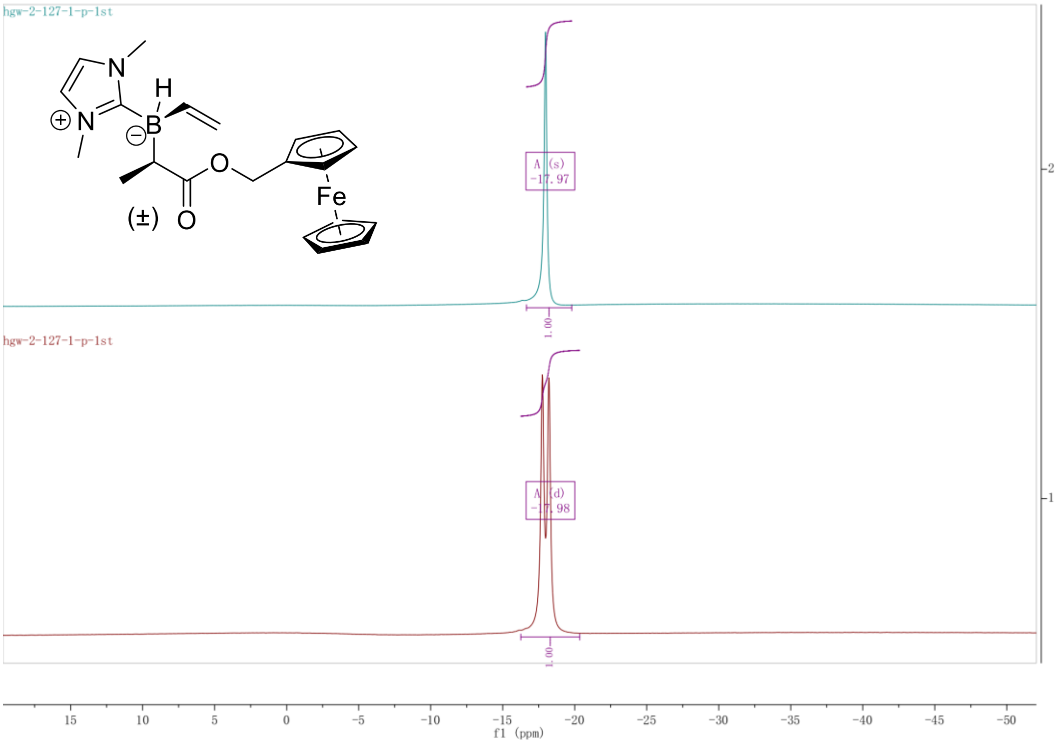
^{1}H NMR of 30



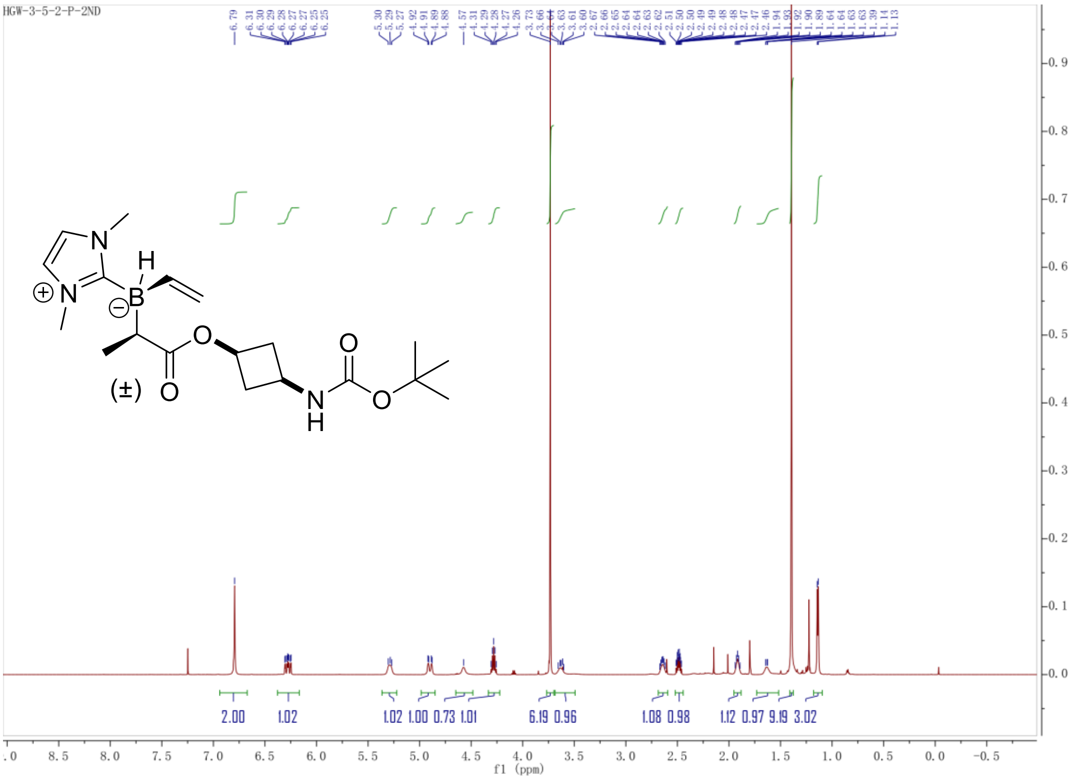
^{13}C NMR of 30



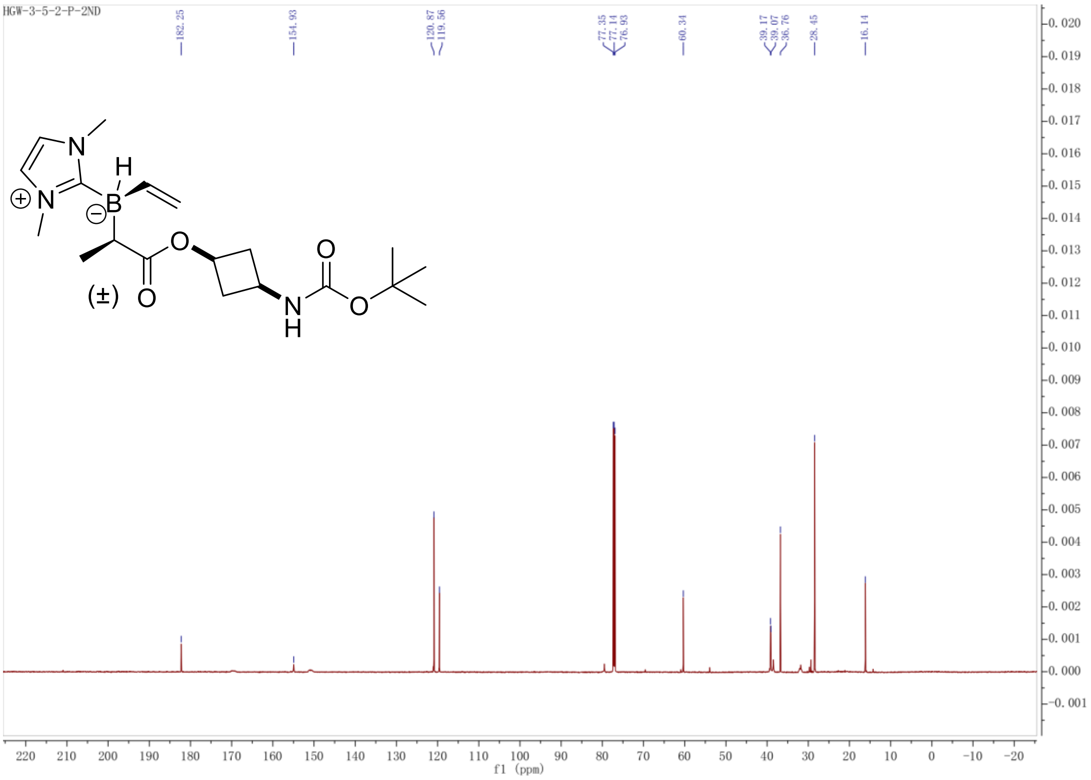
^{11}B NMR and ^{11}B {^{1}H} NMR of 30



^{1}H NMR of 31

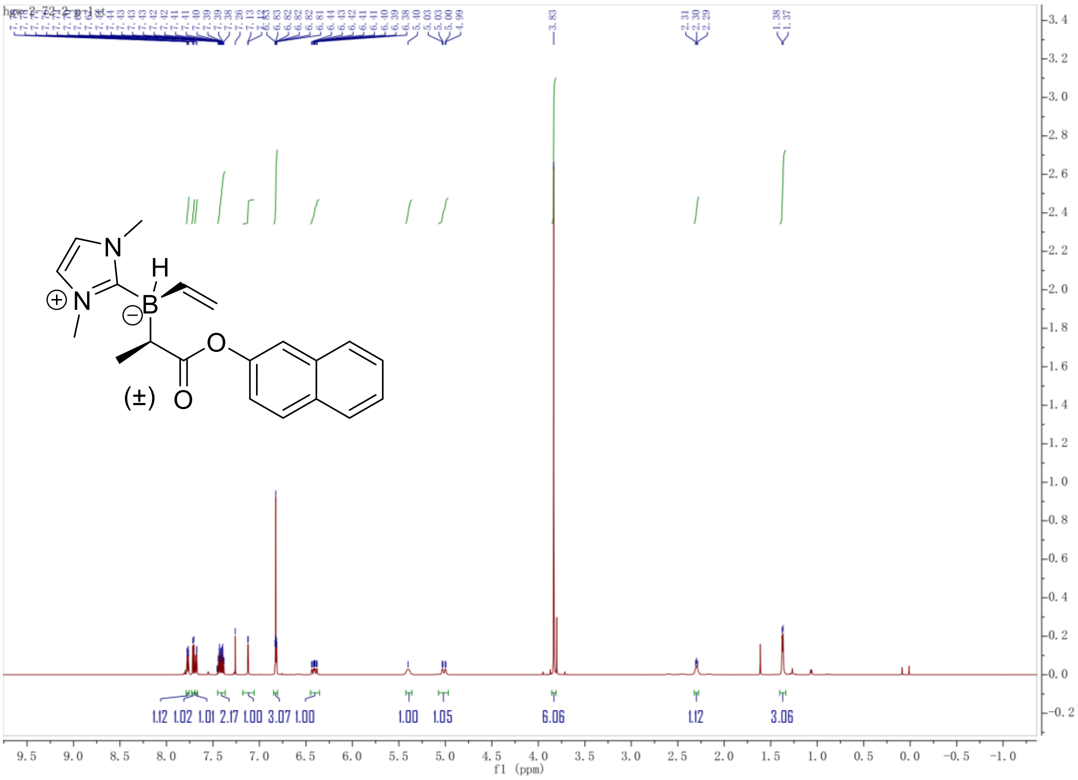


^{13}C NMR of 31

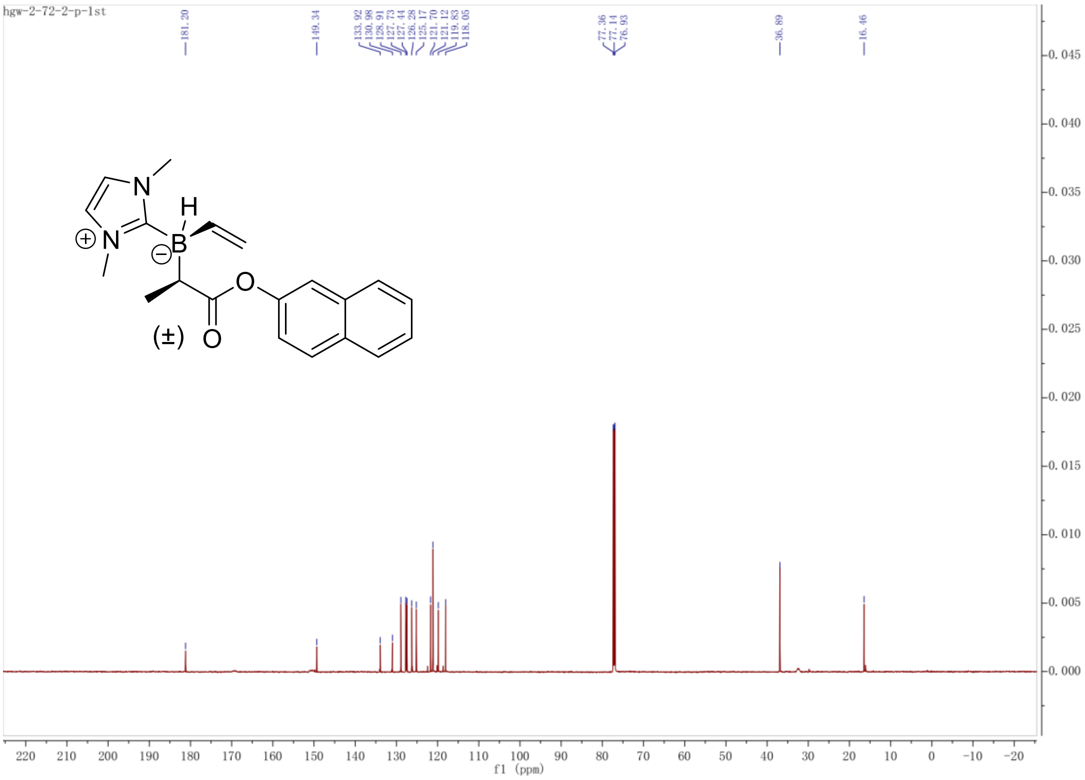


^{11}B NMR and ^{11}B {^{1}H} NMR of 31

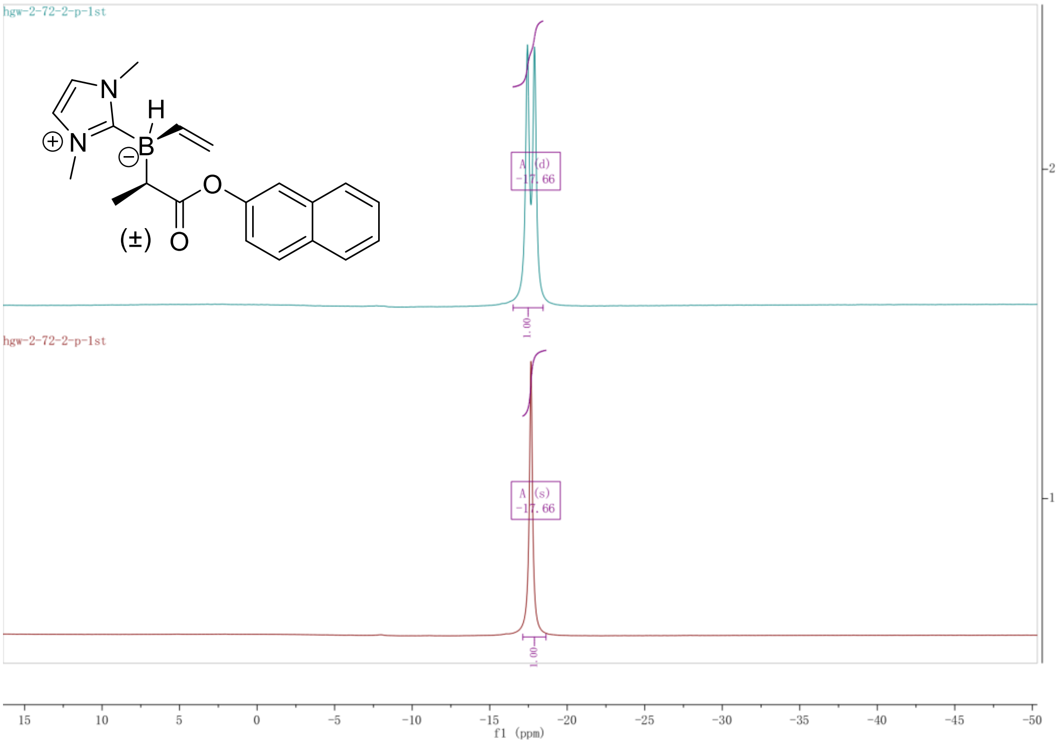
^{1}H NMR of 32



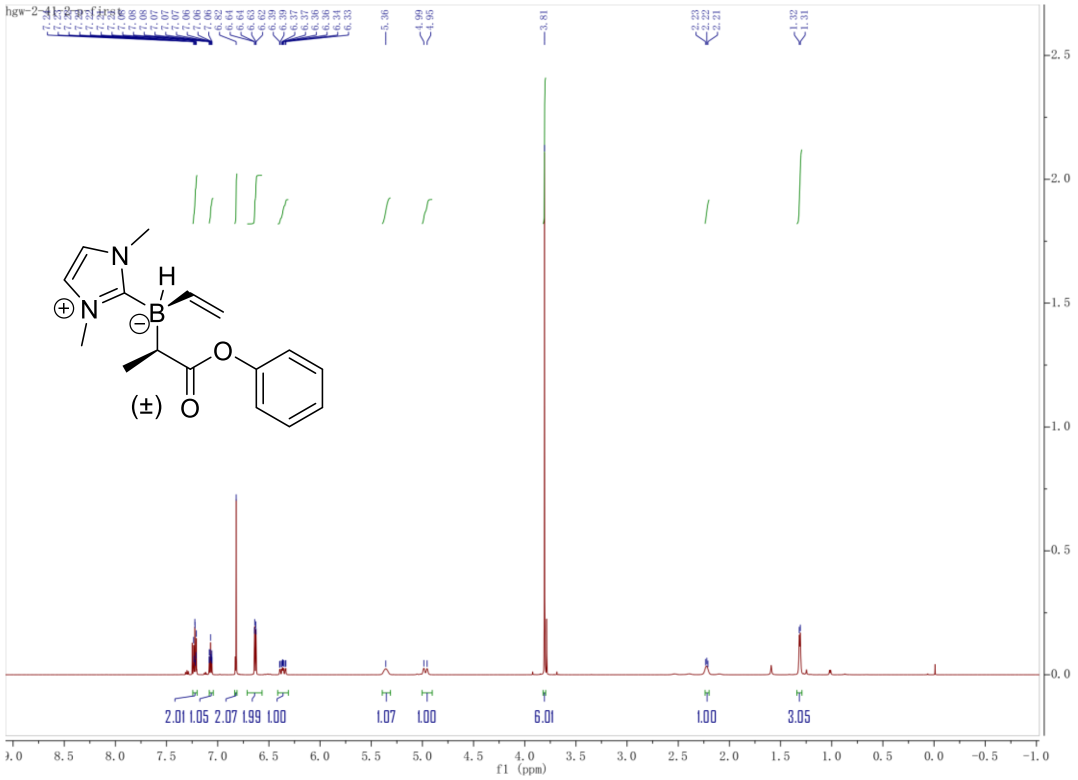
^{13}C NMR of 32



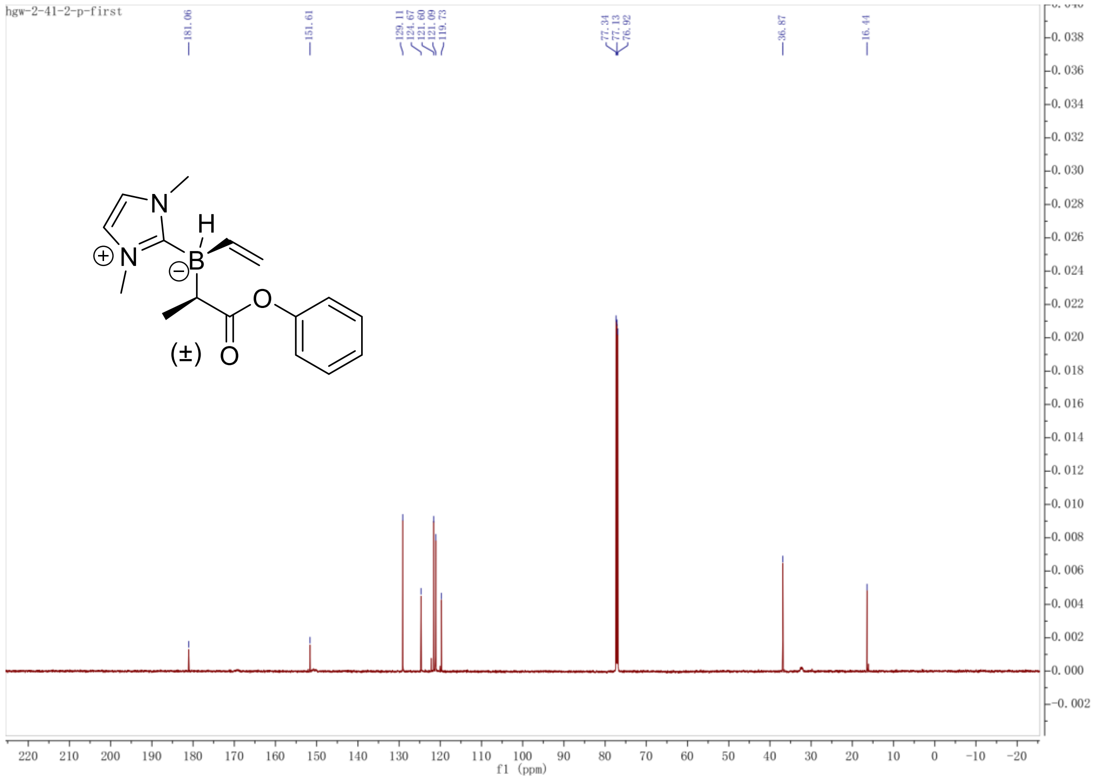
^{11}B NMR and ^{11}B {^{1}H} NMR of 32



^{1}H NMR of 33

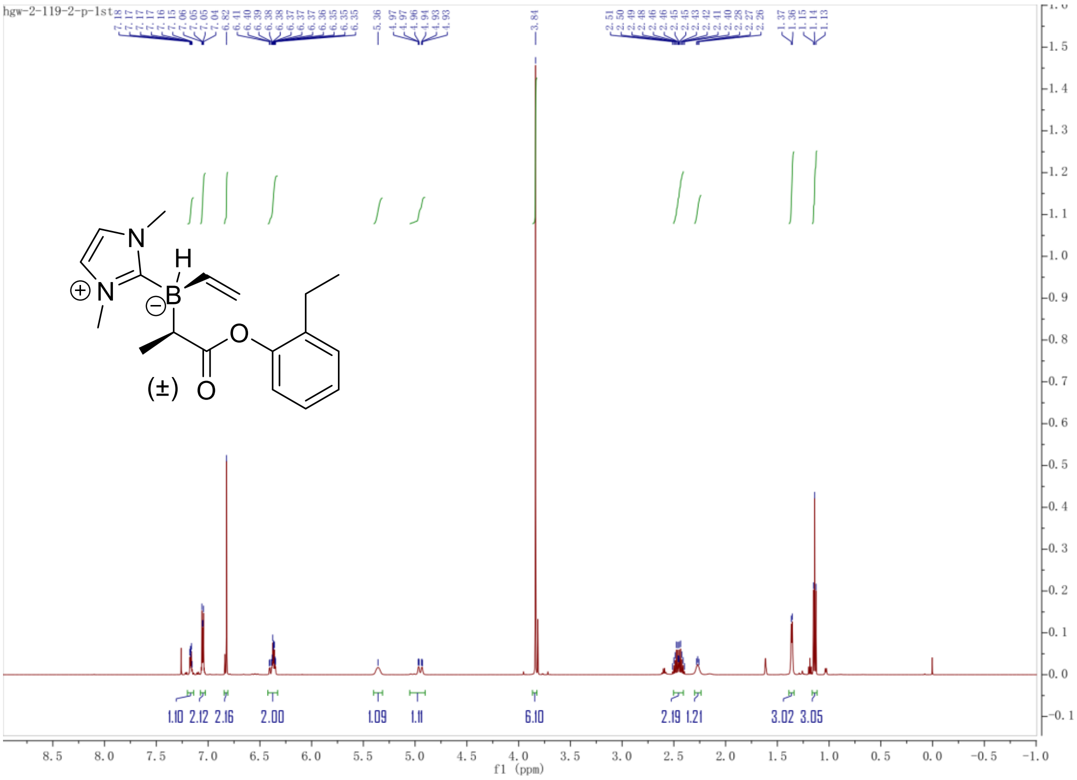


^{13}C NMR of 33

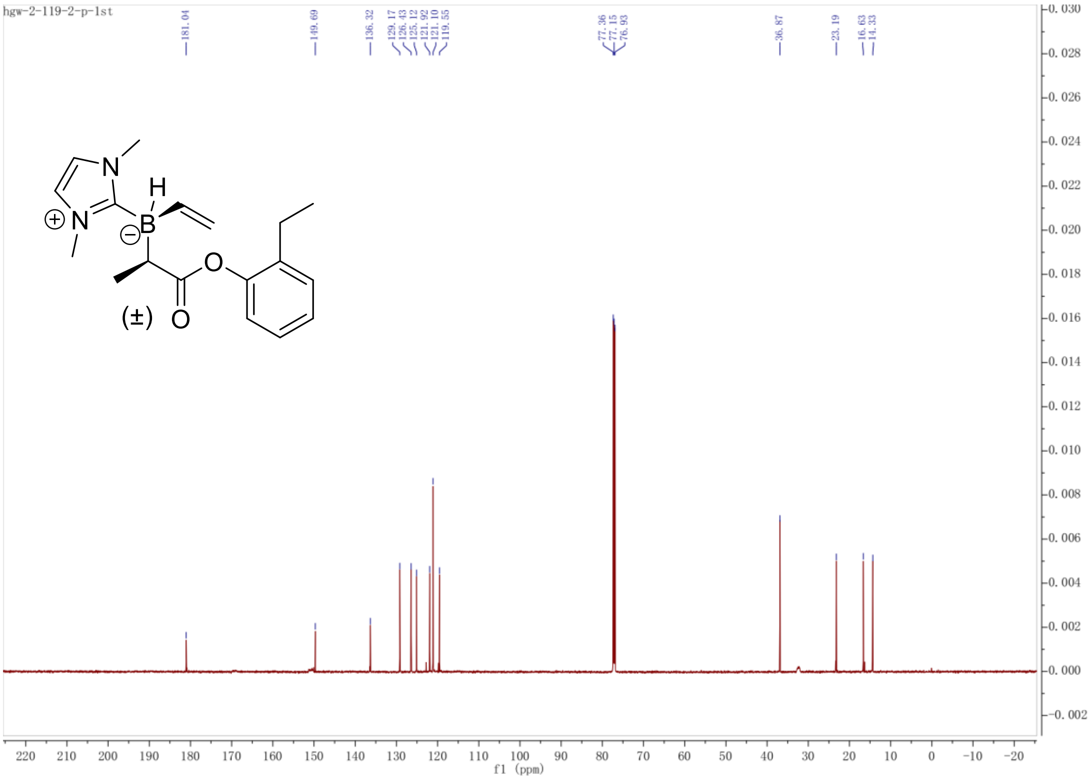


^{11}B NMR and ^{11}B {^{1}H} NMR of 33

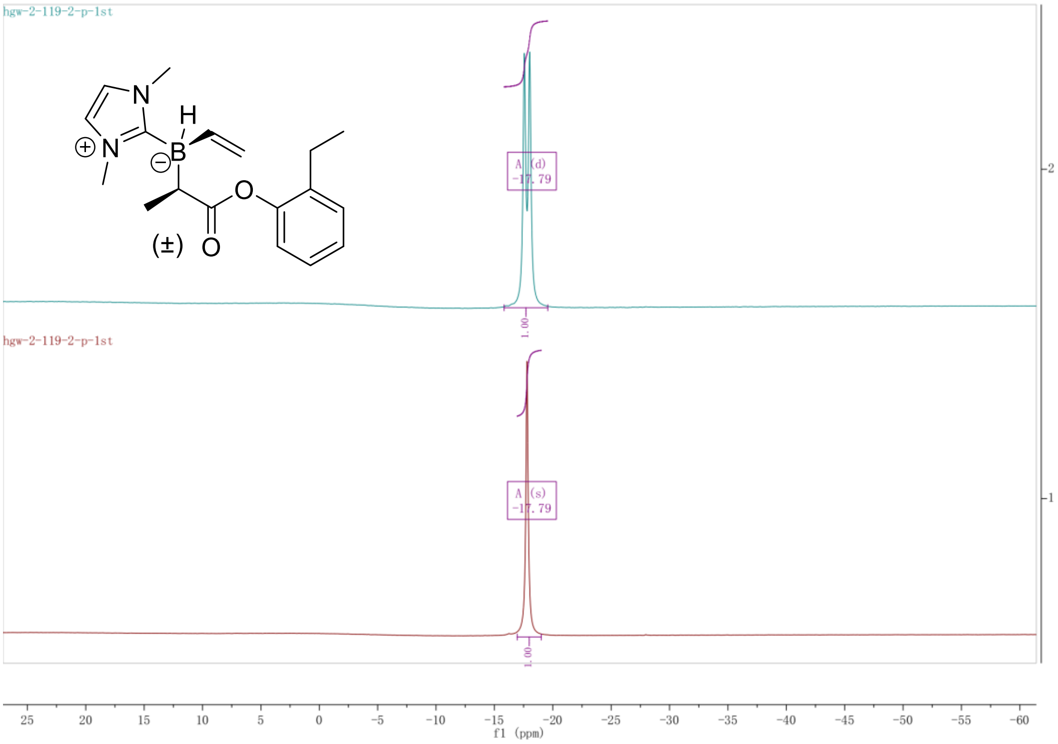
^{1}H NMR of 34



^{13}C NMR of 34



^{11}B NMR and ^{11}B {^{1}H} NMR of 34



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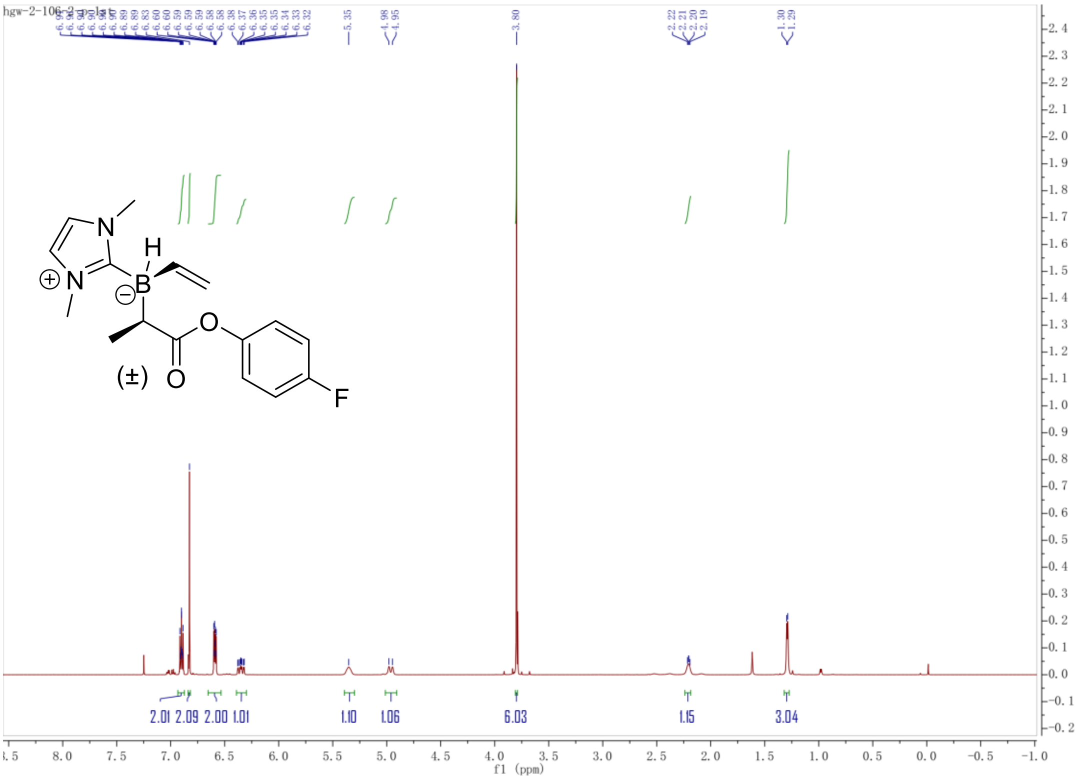
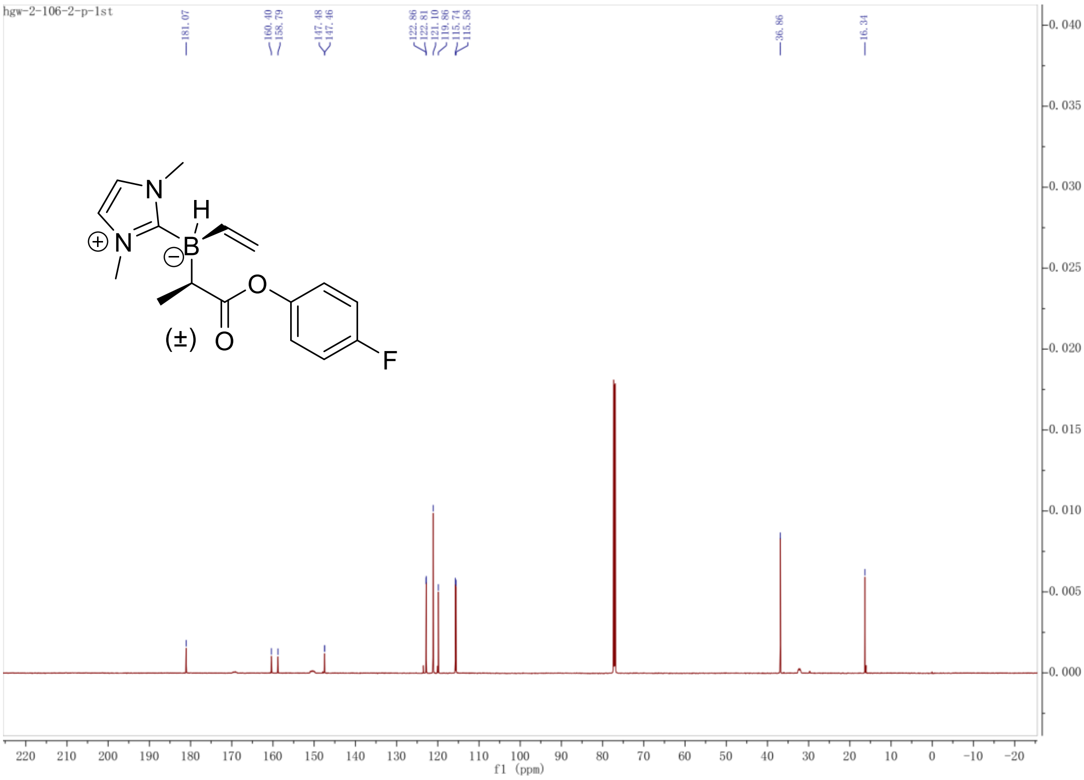
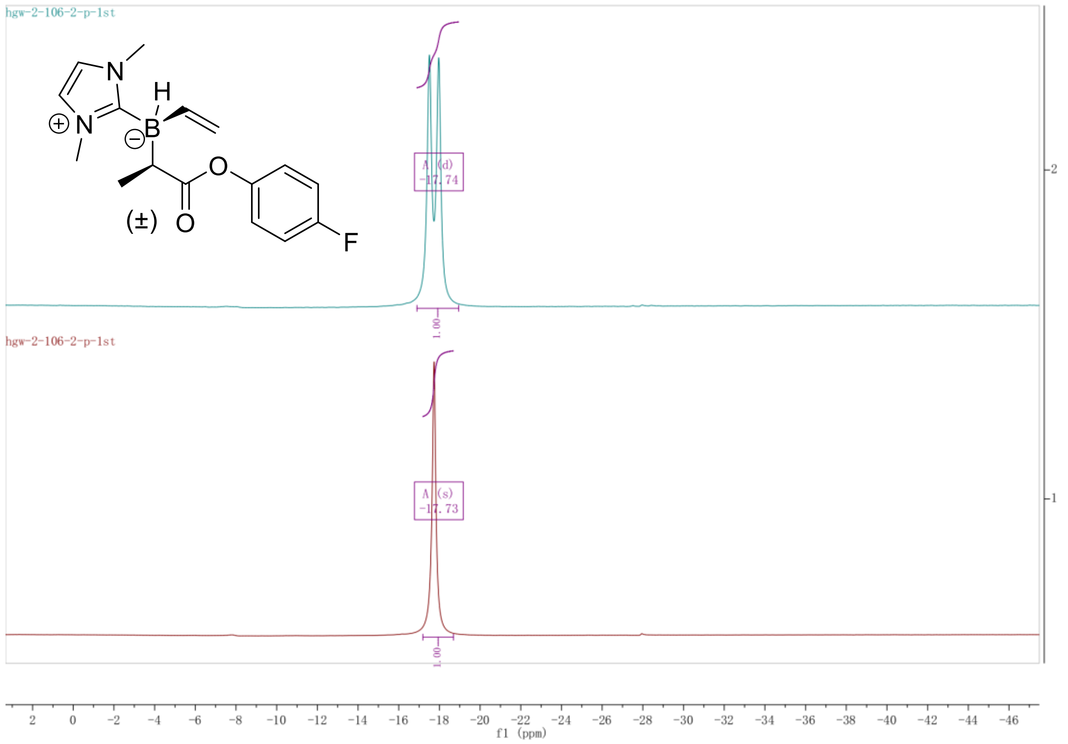


^{13}C NMR of 35



^{11}B NMR and ^{11}B {^{1}H} NMR of 35



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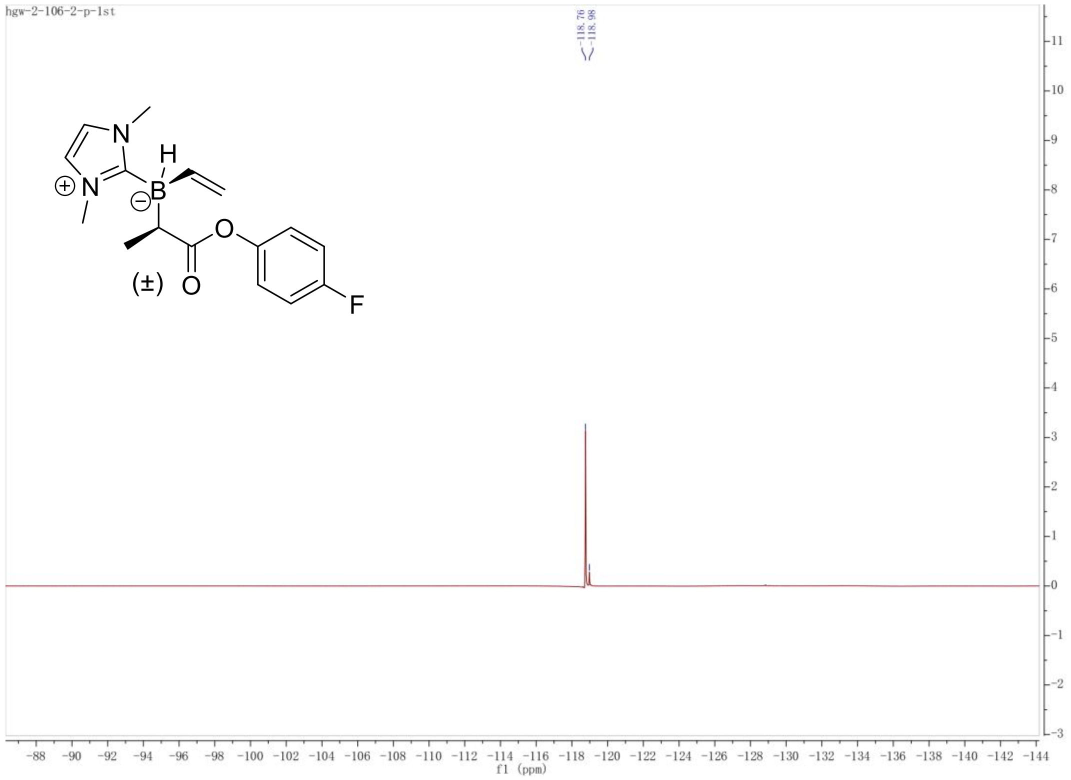
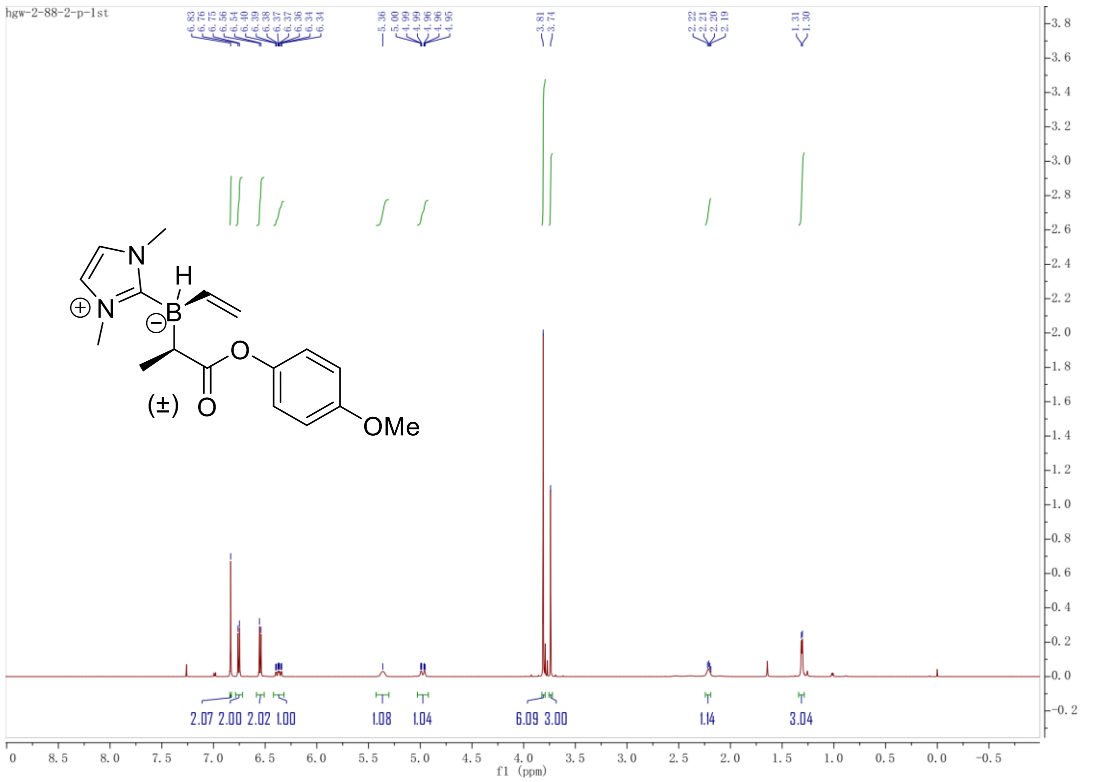
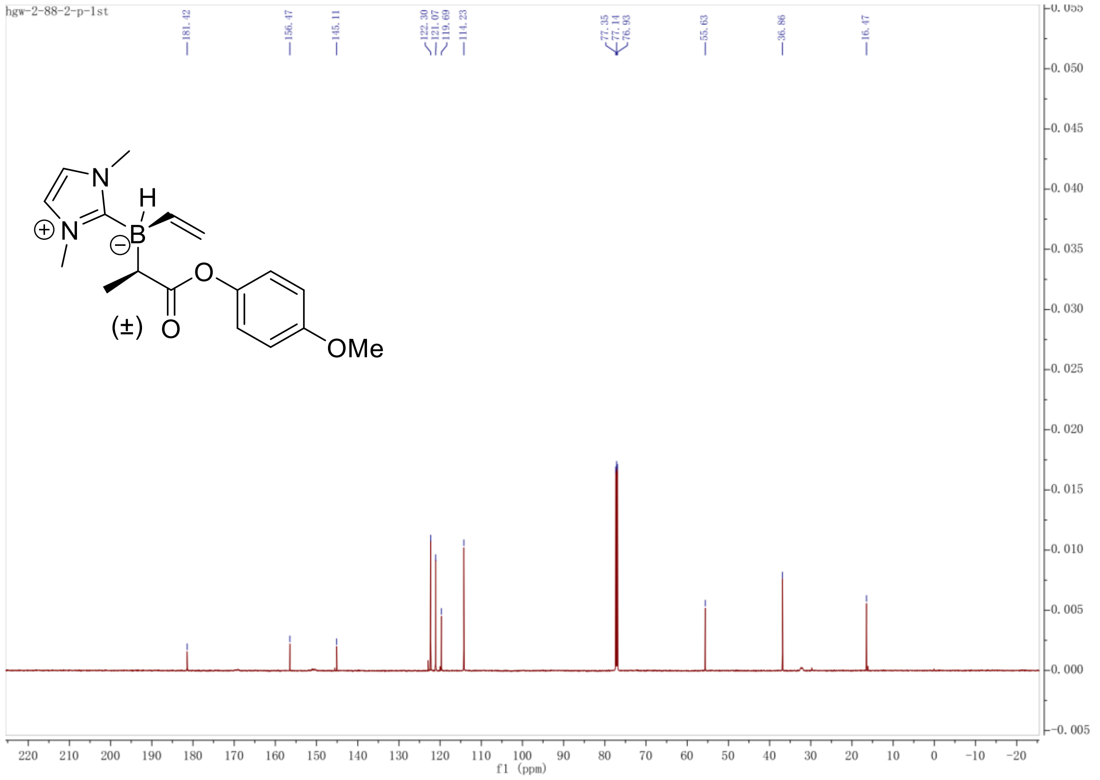


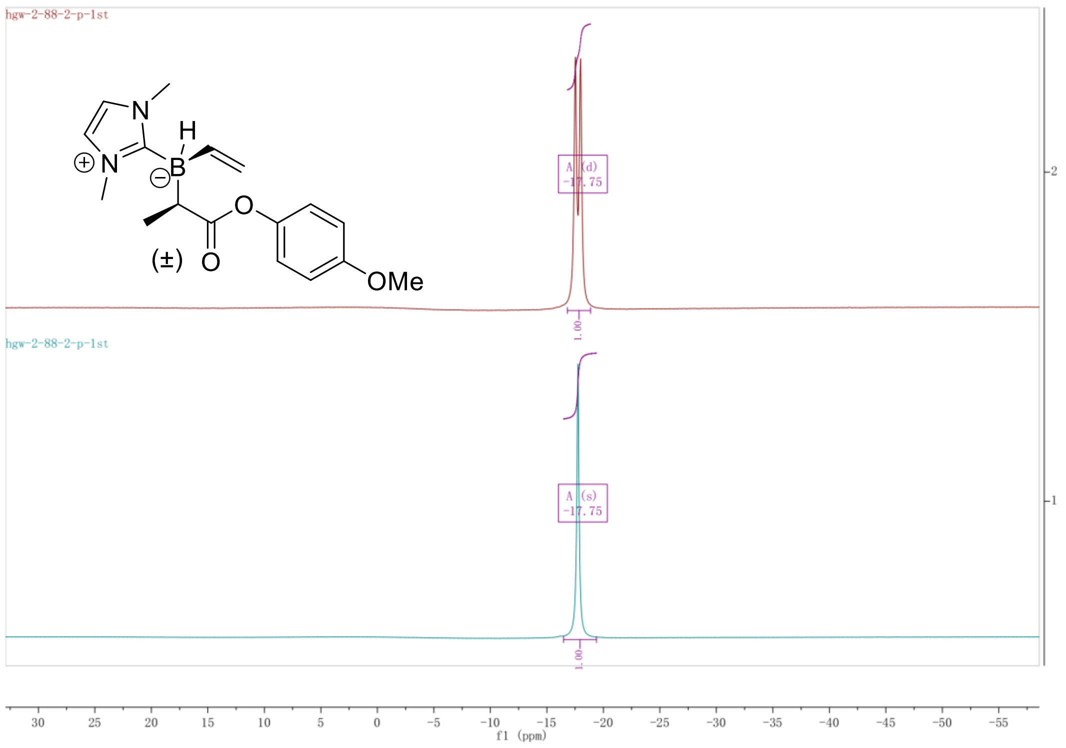
^{1}H NMR of 36



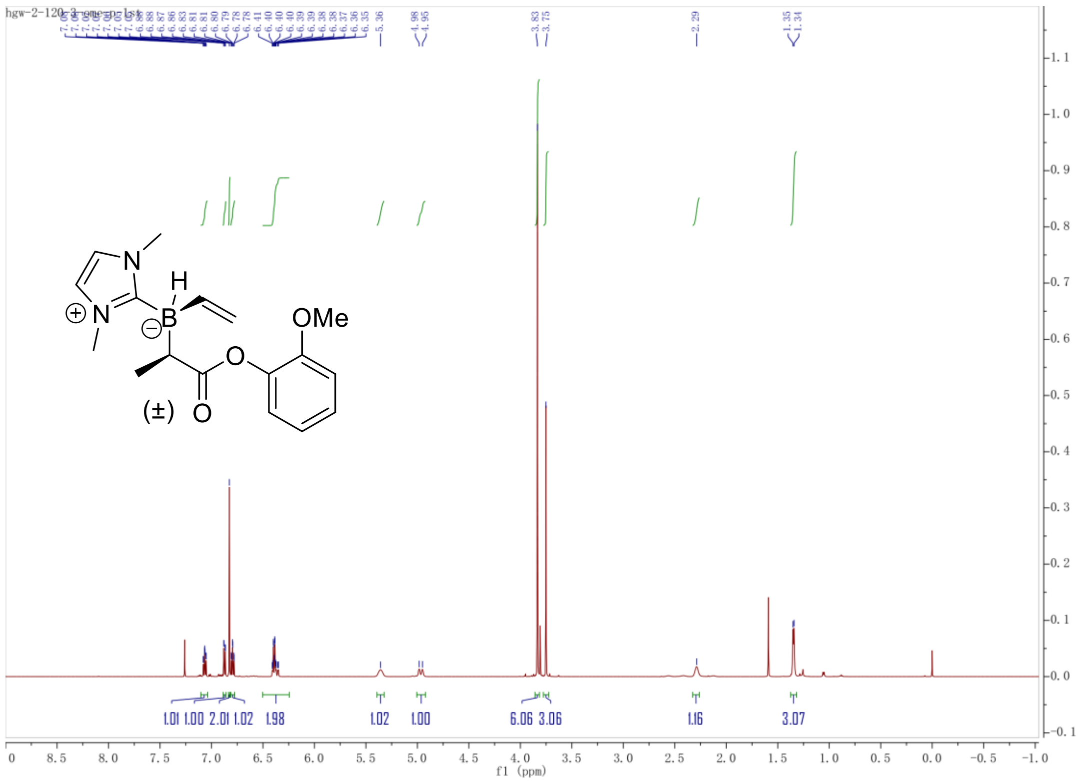
^{13}C NMR of 36



^{11}B NMR and ^{11}B {^{1}H} NMR of 36



^{1}H NMR of 37



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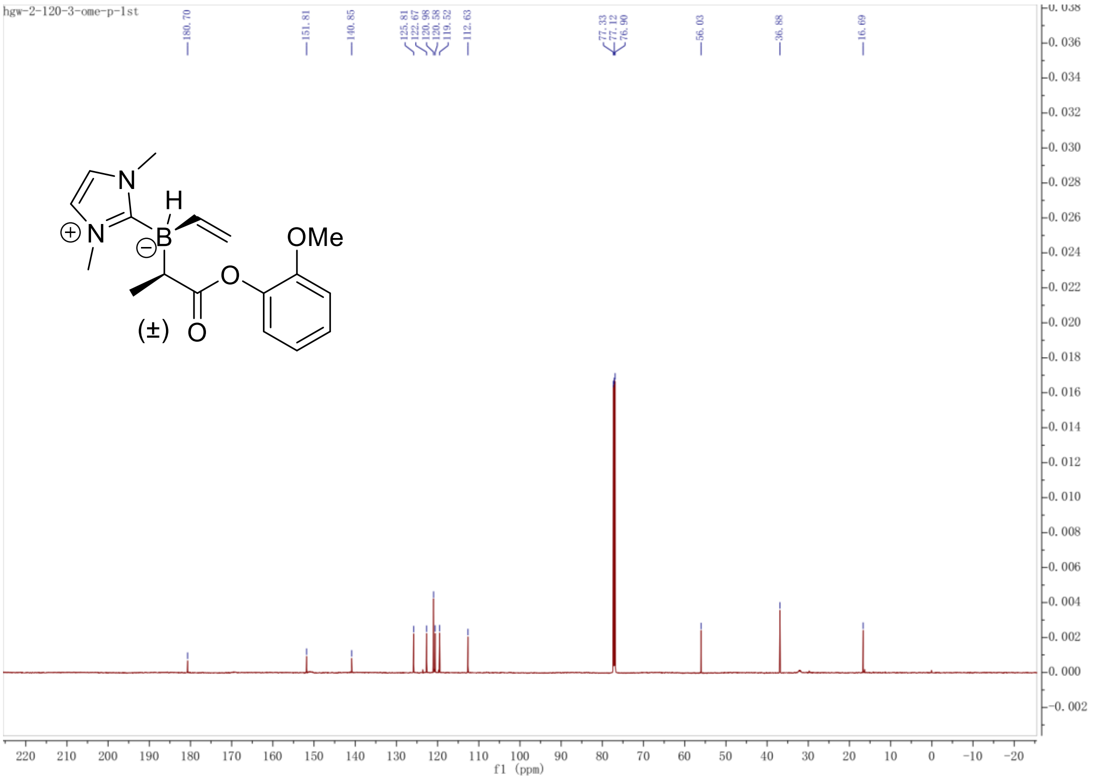
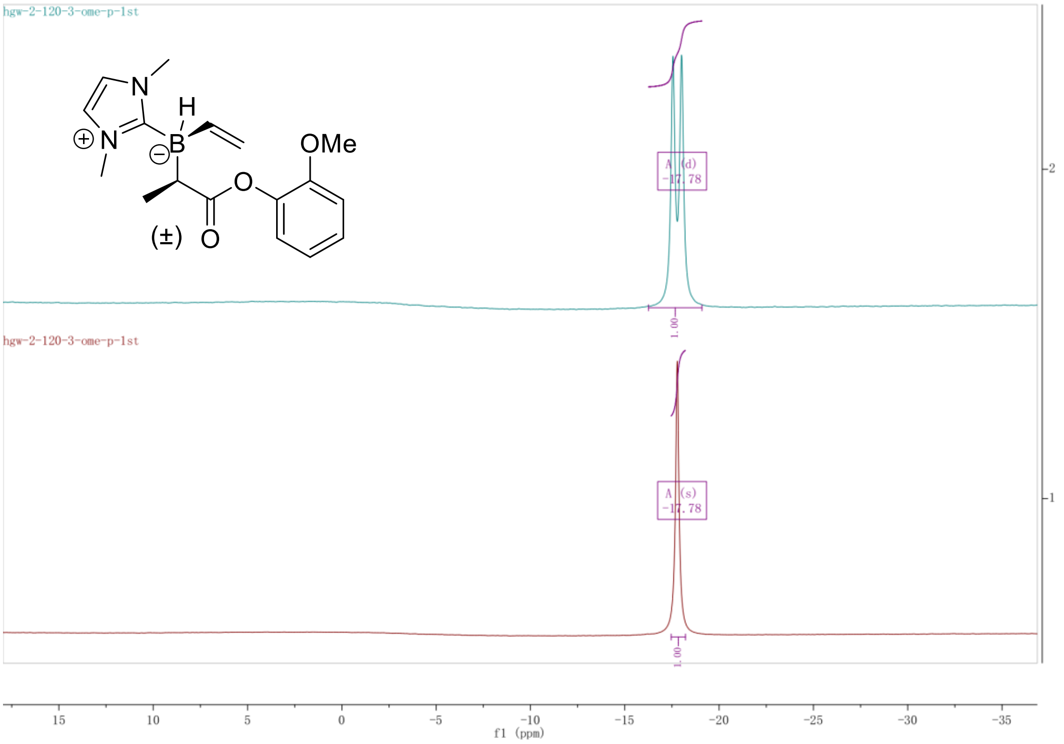
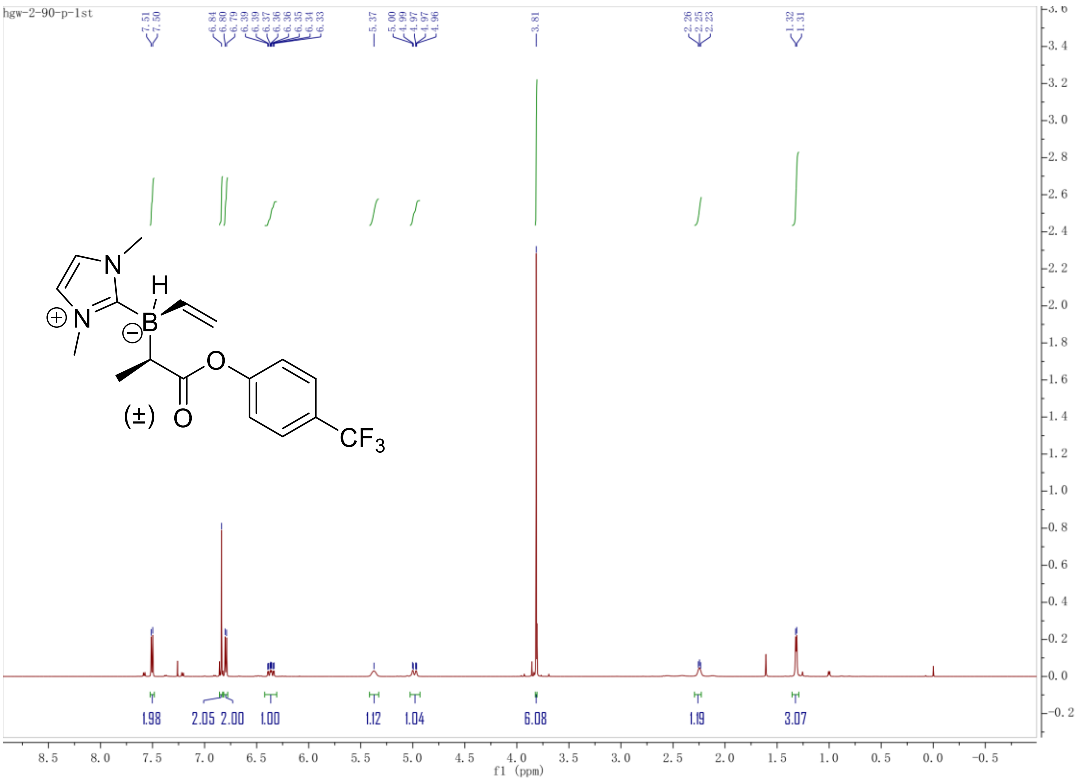


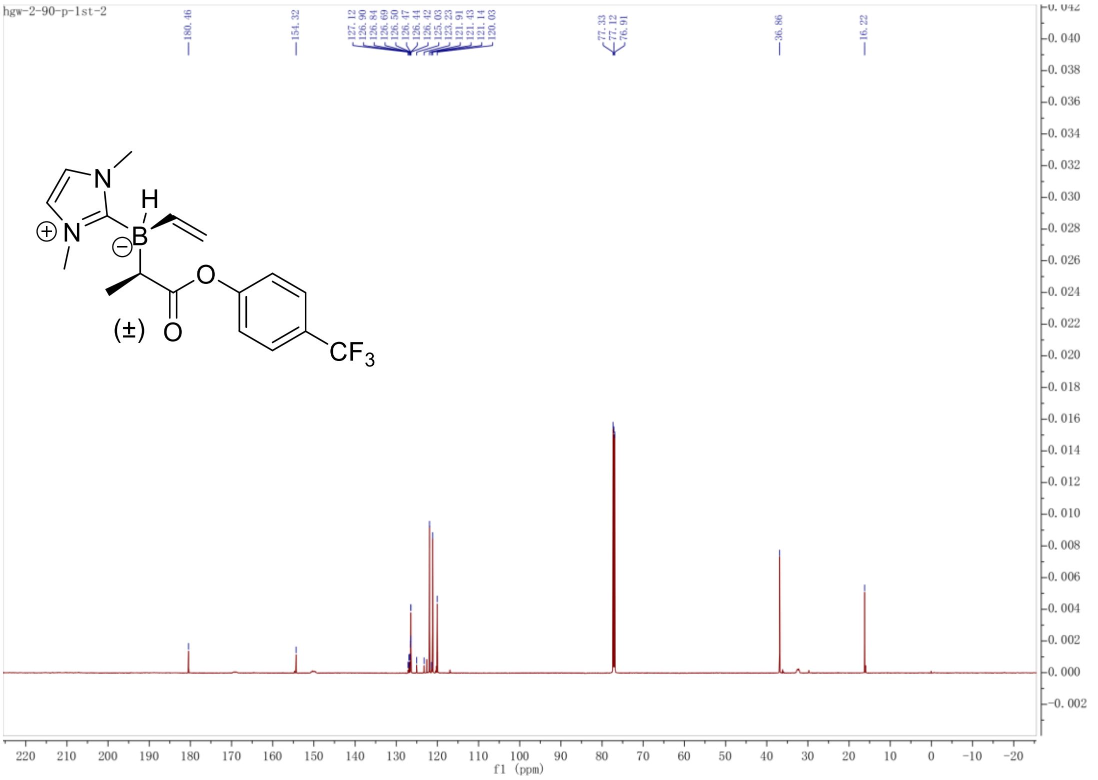
^{11}B NMR and ^{11}B {^{1}H} NMR of 37



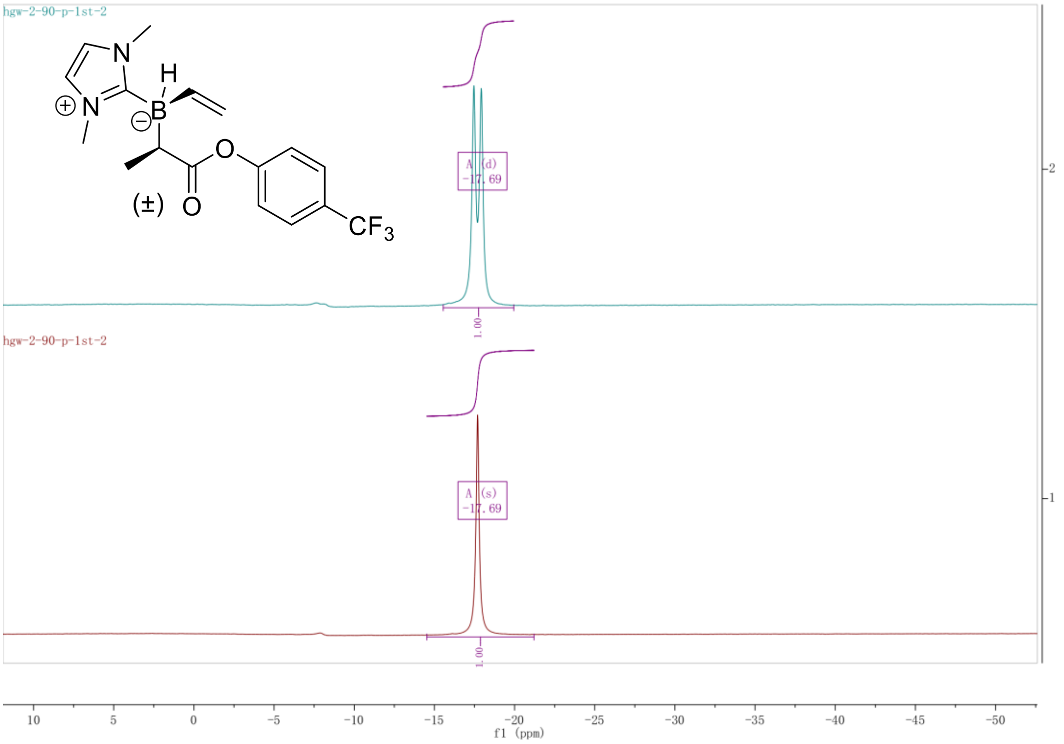
^{1}H NMR of 38



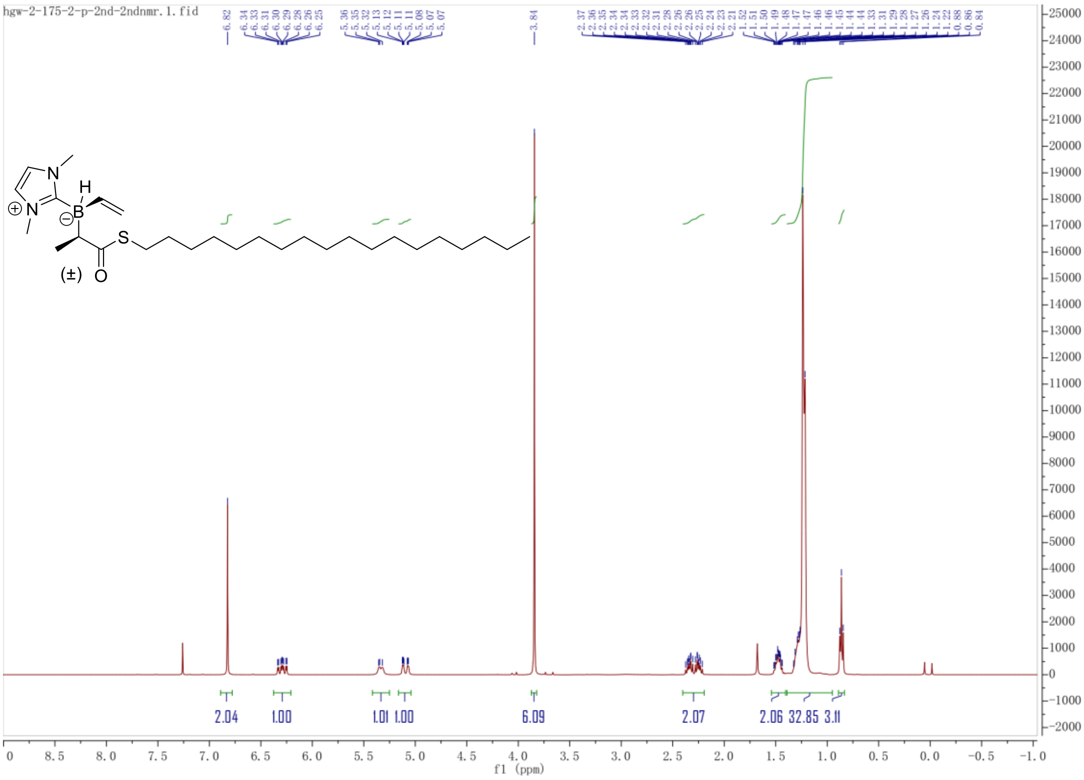
^{13}C NMR of 38



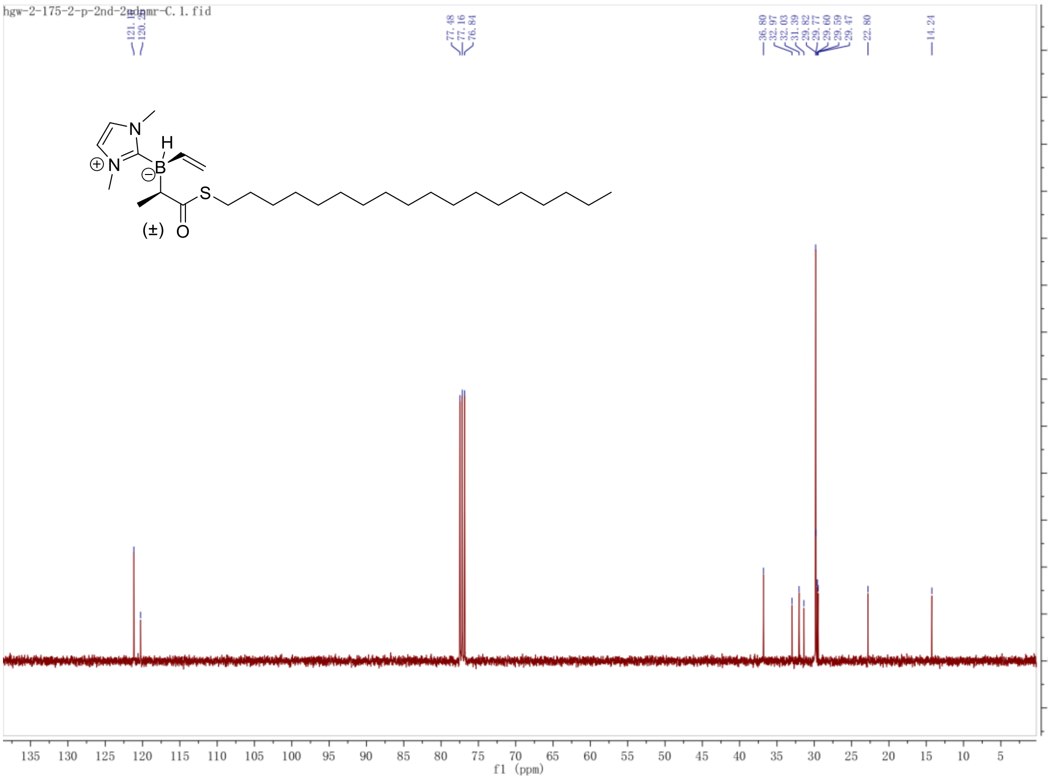
^{11}B NMR and ^{11}B {^{1}H} NMR of 38



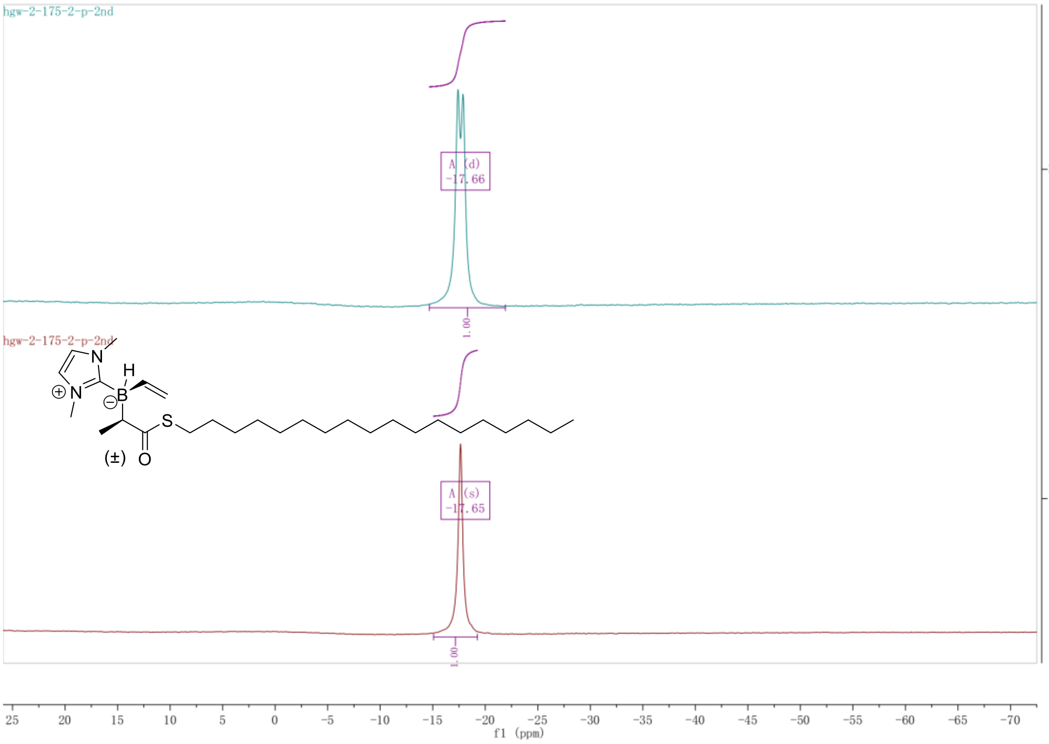
^{1}H NMR of 39



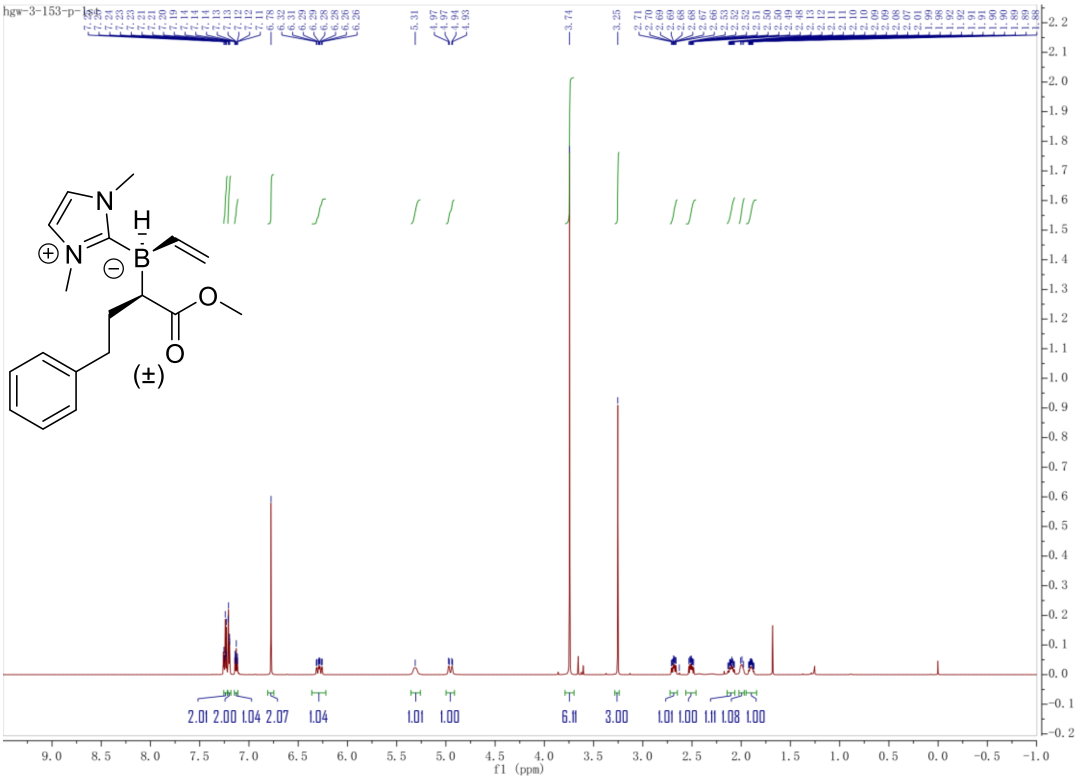
^{13}C NMR of 39



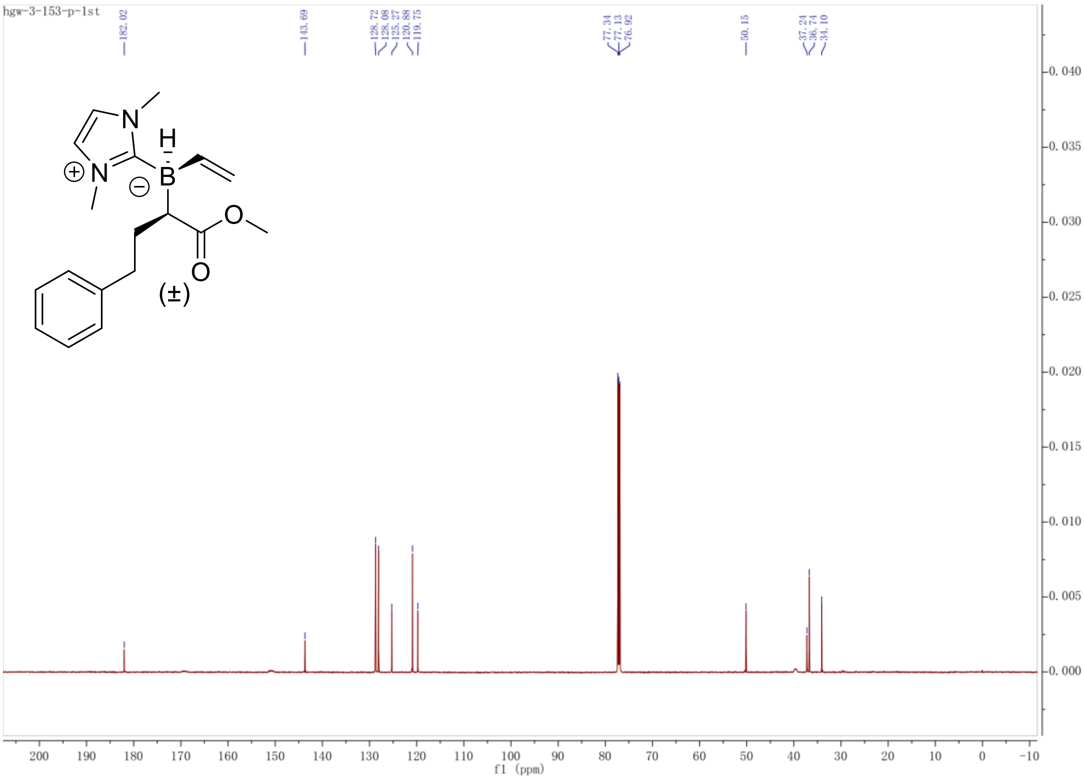
^{11}B NMR and ^{11}B {^{1}H} NMR of 39



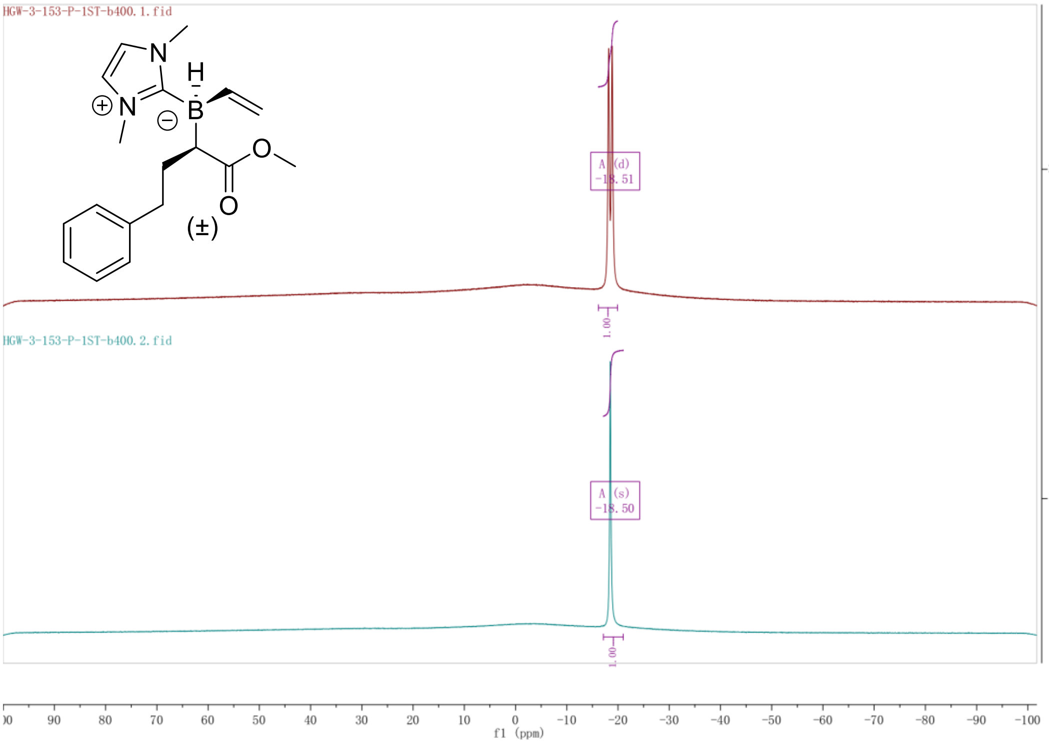
^{1}H NMR of 40



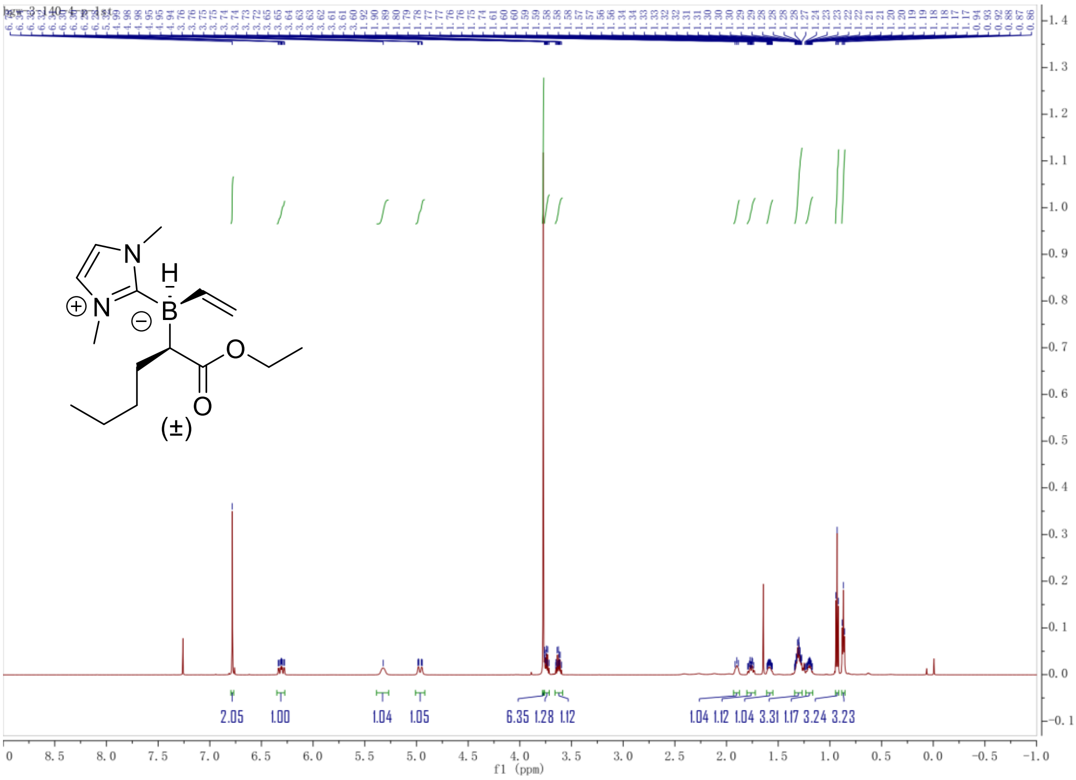
^{13}C NMR of 40



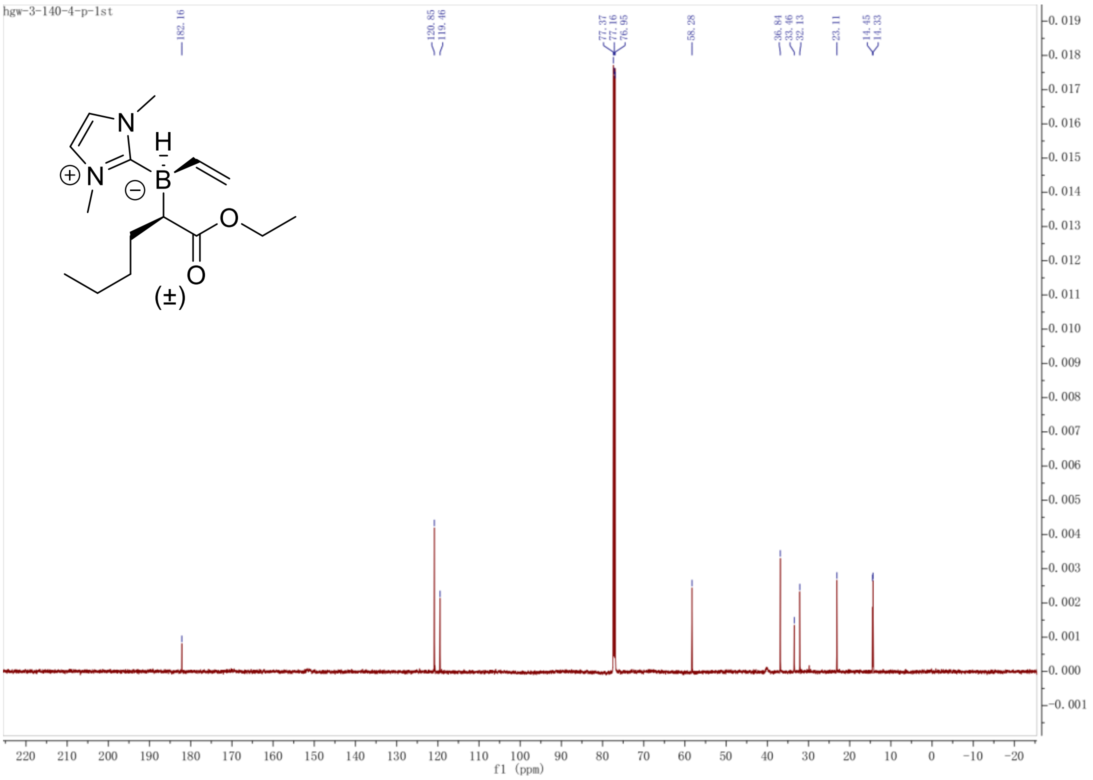
^{11}B NMR and ^{11}B {^{1}H} NMR of 40



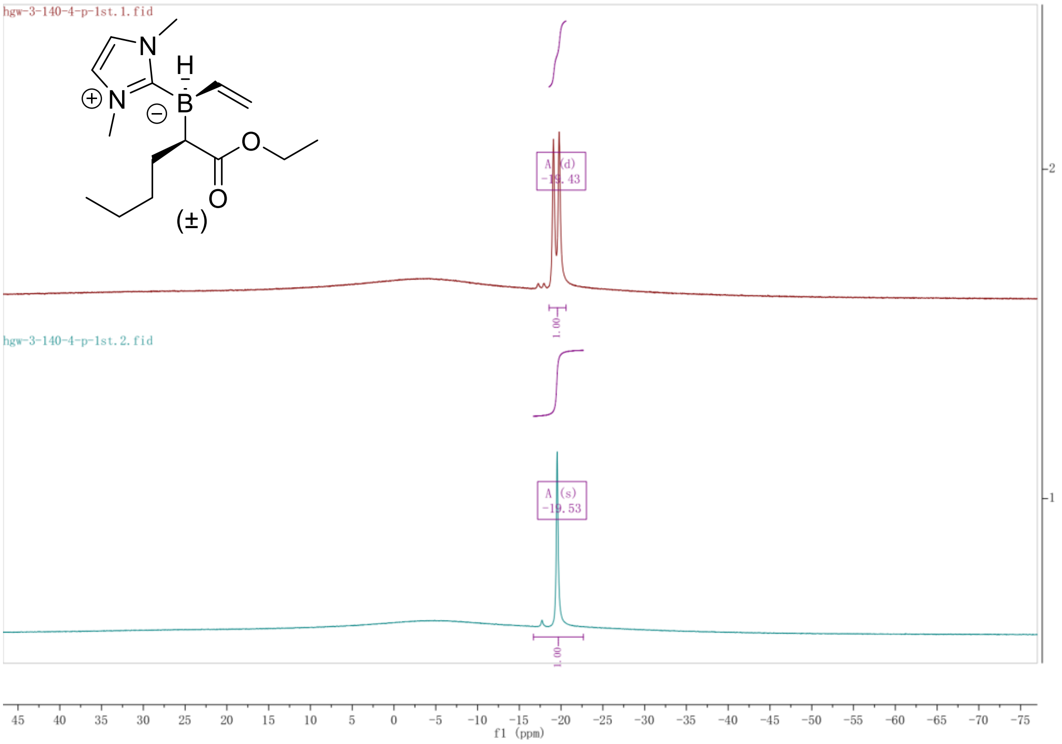
^{1}H NMR of 41



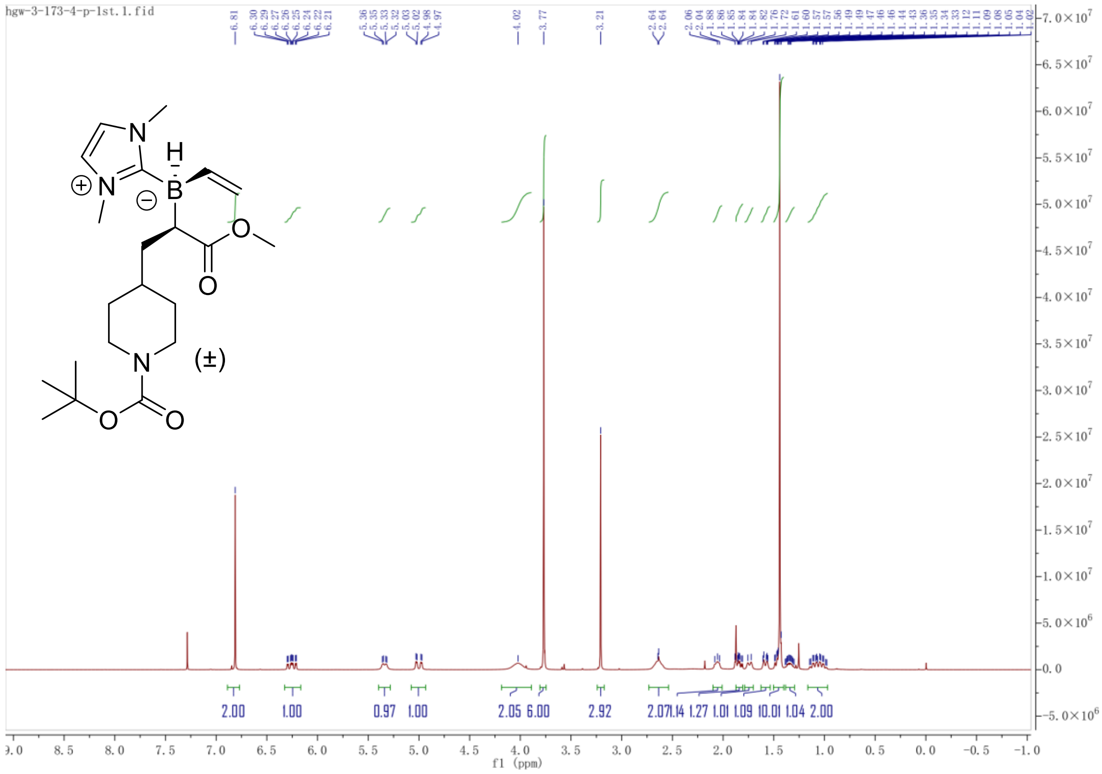
^{13}C NMR of 41



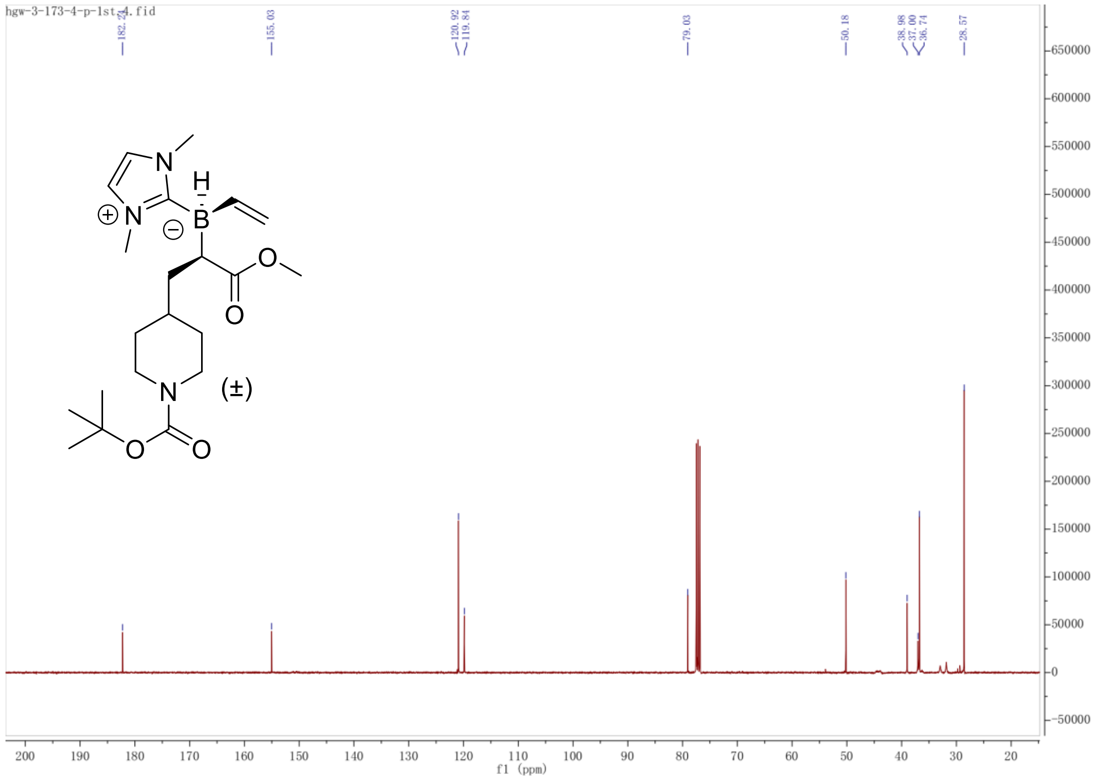
^{11}B NMR and ^{11}B {^{1}H} NMR of 41



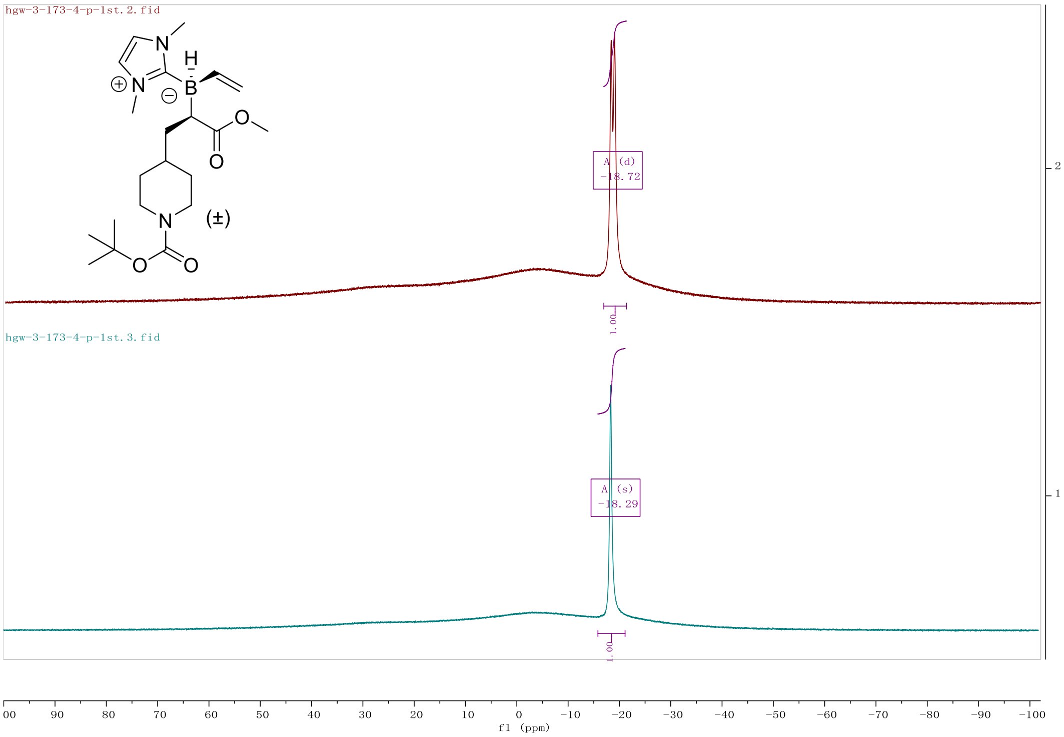
^{1}H NMR of 42



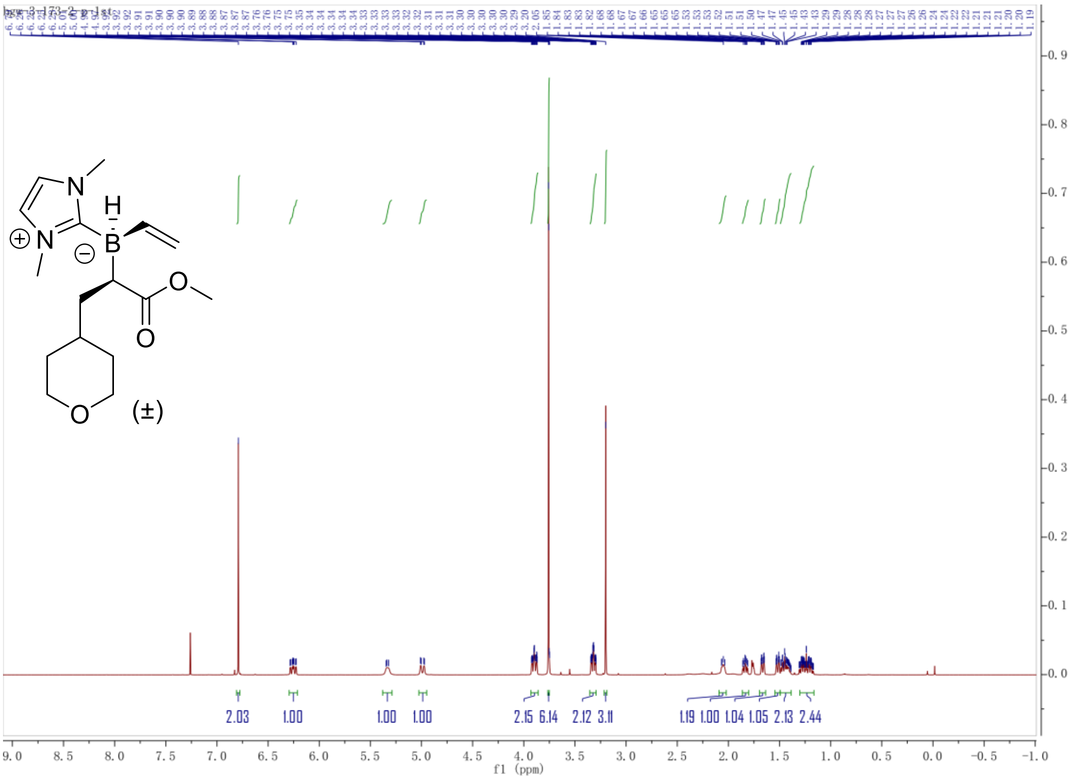
^{13}C NMR of 42



^{11}B NMR and ^{11}B {^{1}H} NMR of 42



^{1}H NMR of 43



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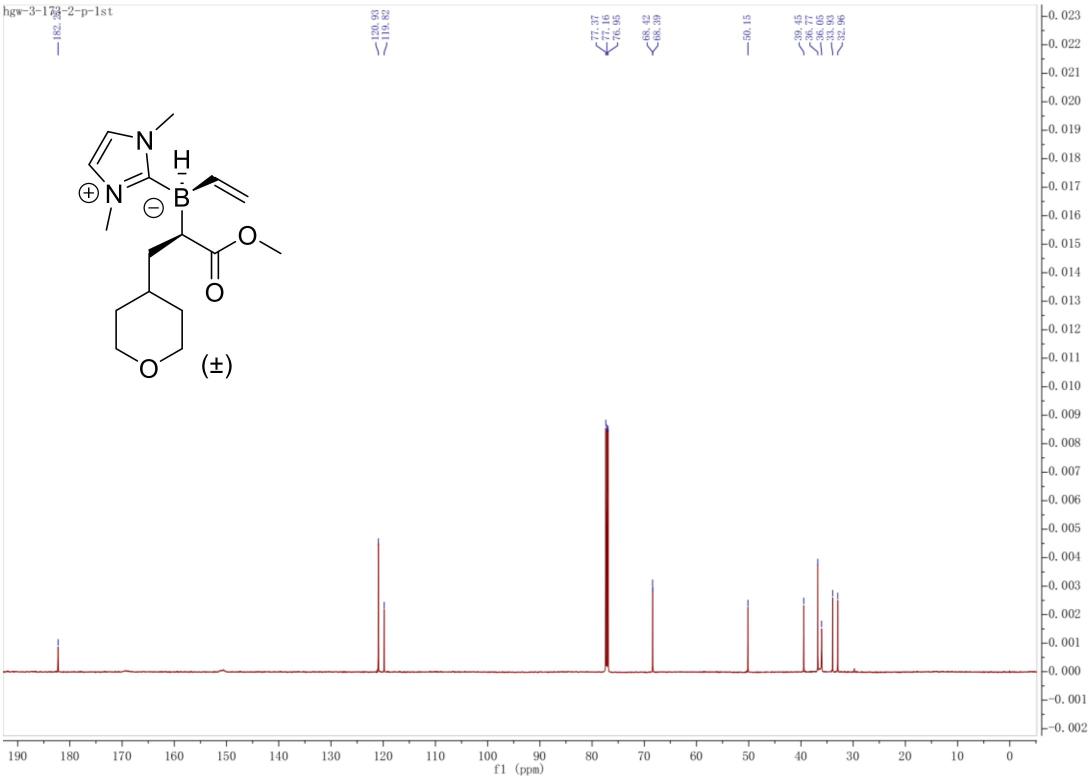
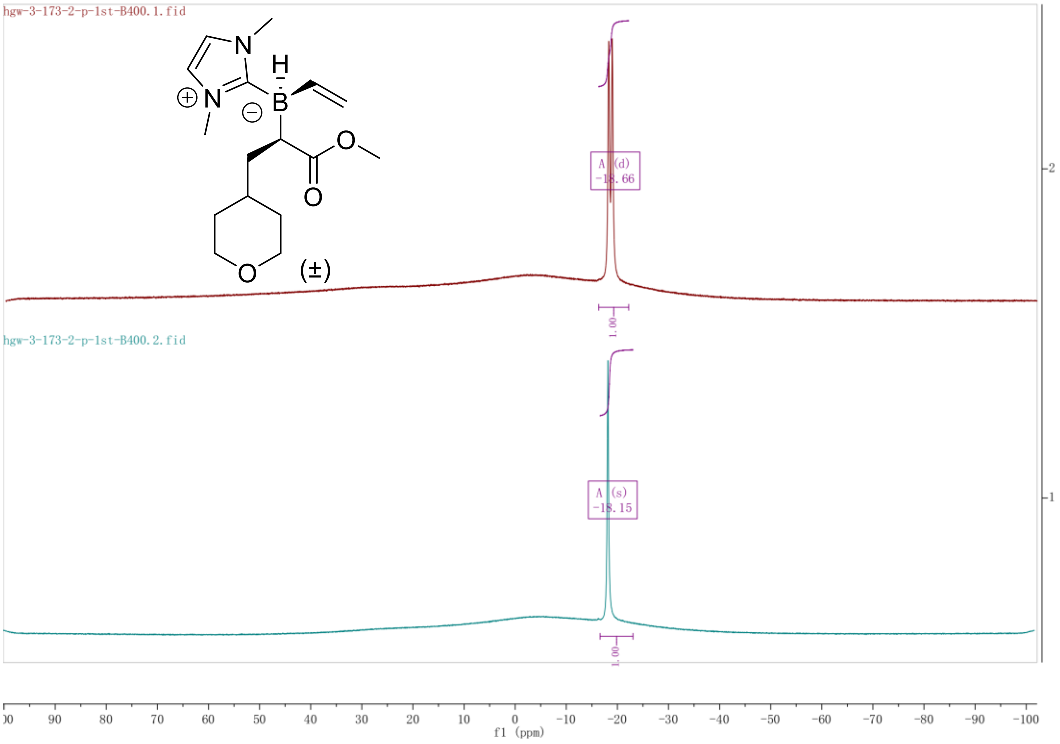


^{11}B NMR and ^{11}B {^{1}H} NMR of 43



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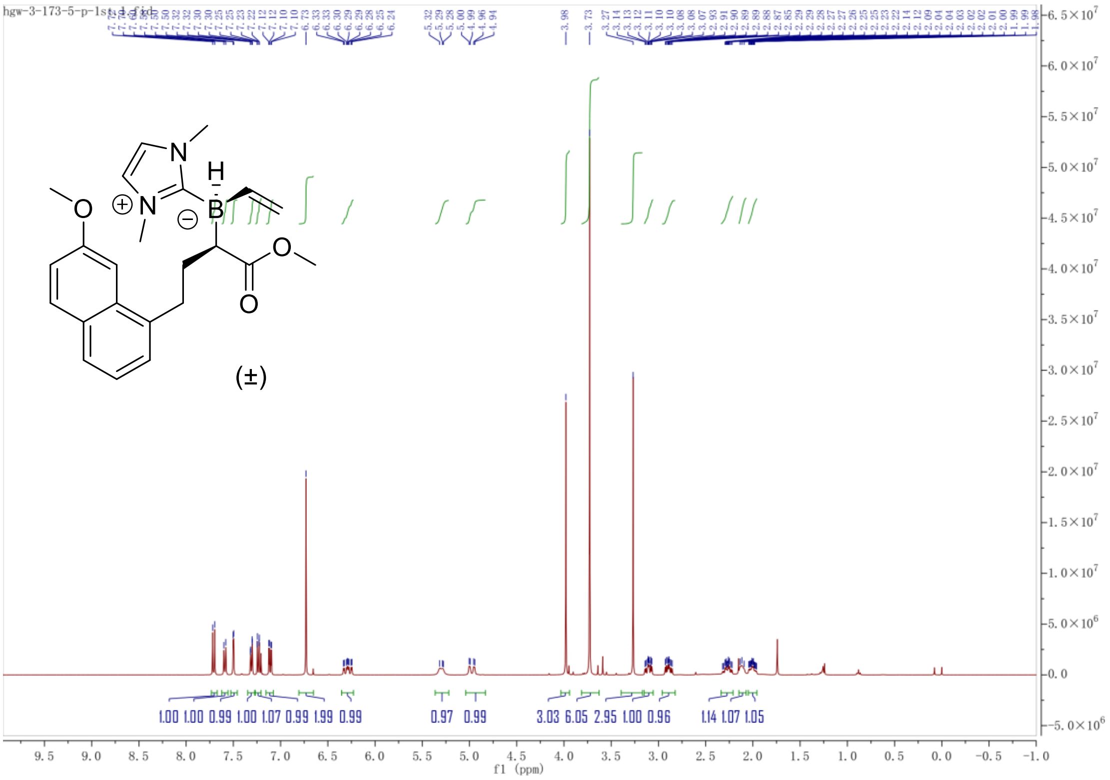
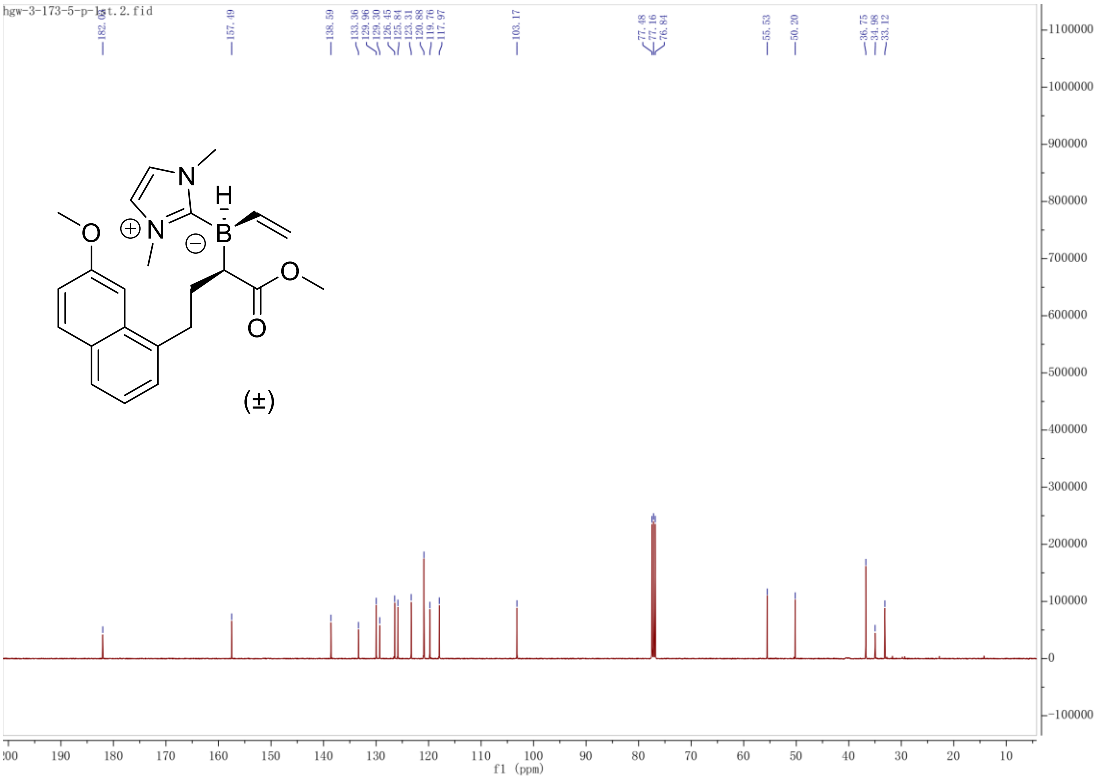
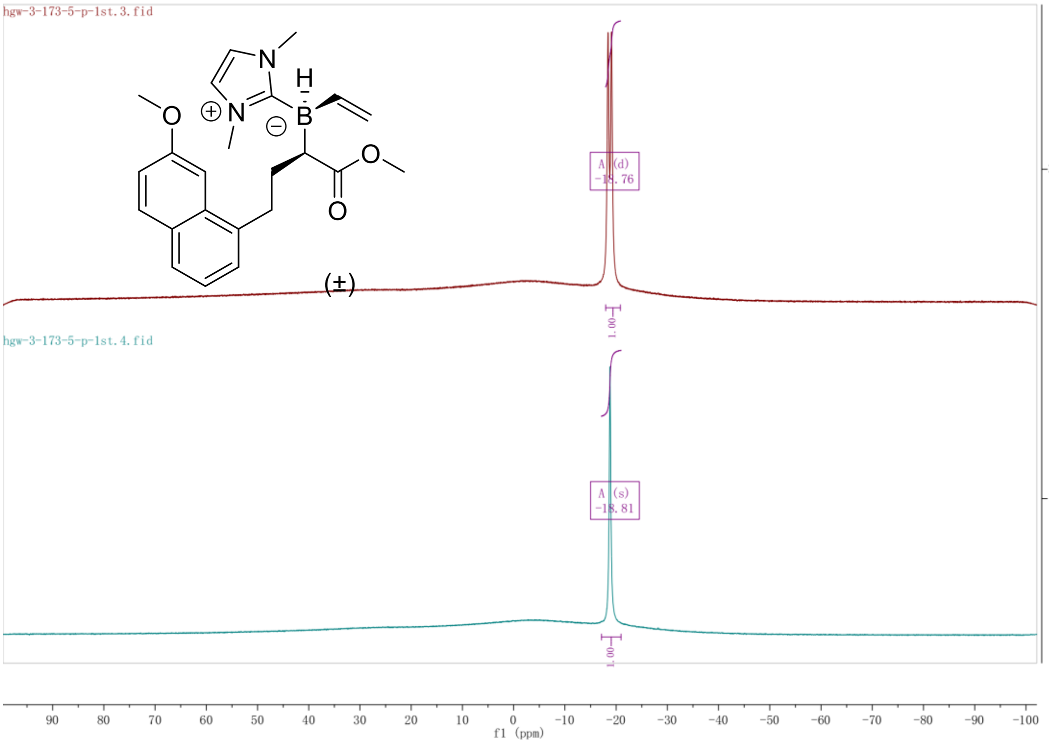


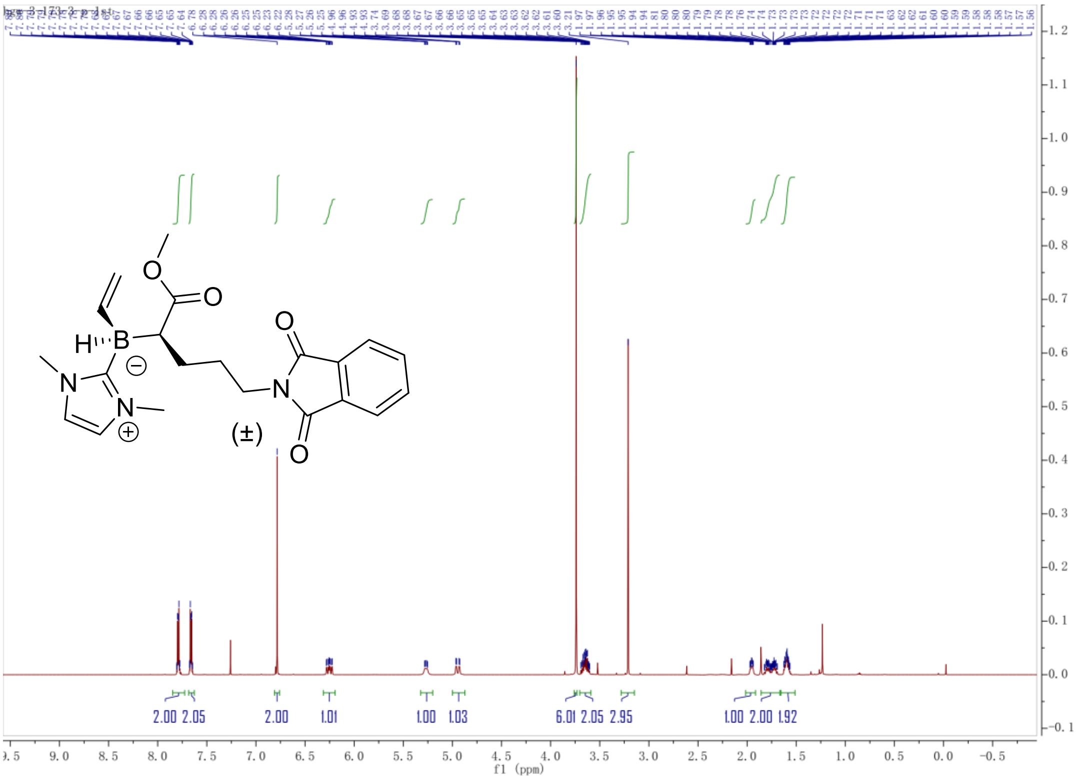
^{13}C NMR of 44



^{11}B NMR and ^{11}B {^{1}H} NMR of 44



^{1}H NMR of 45



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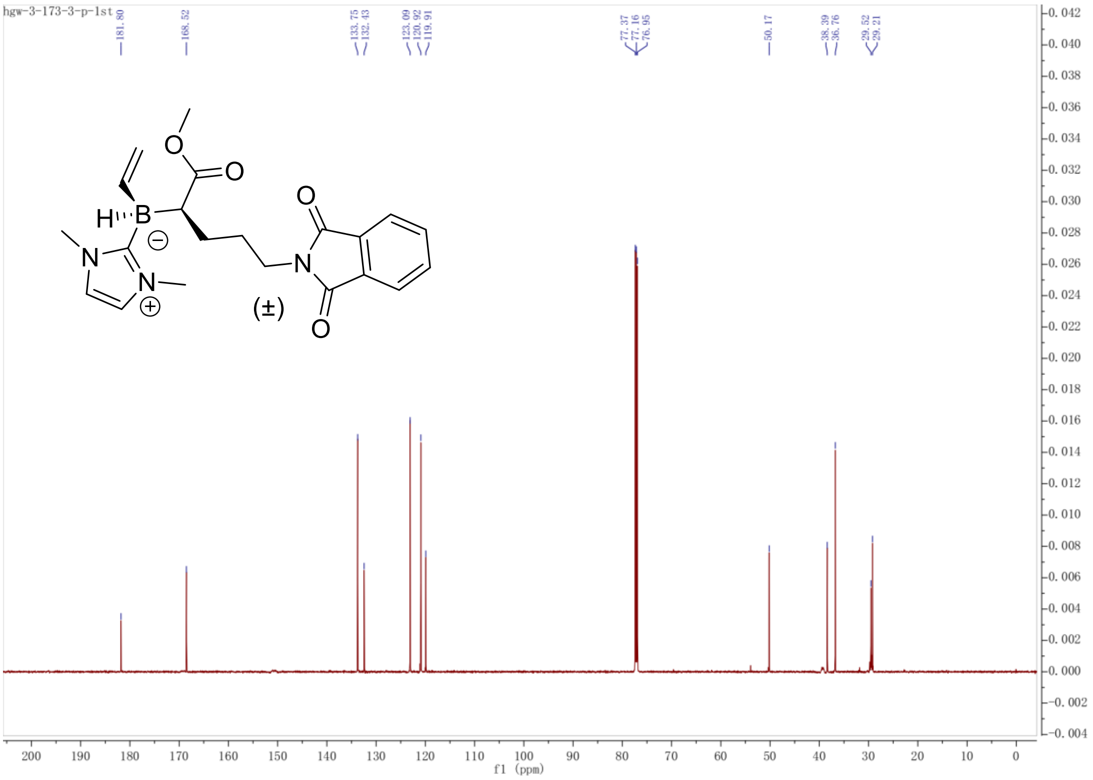
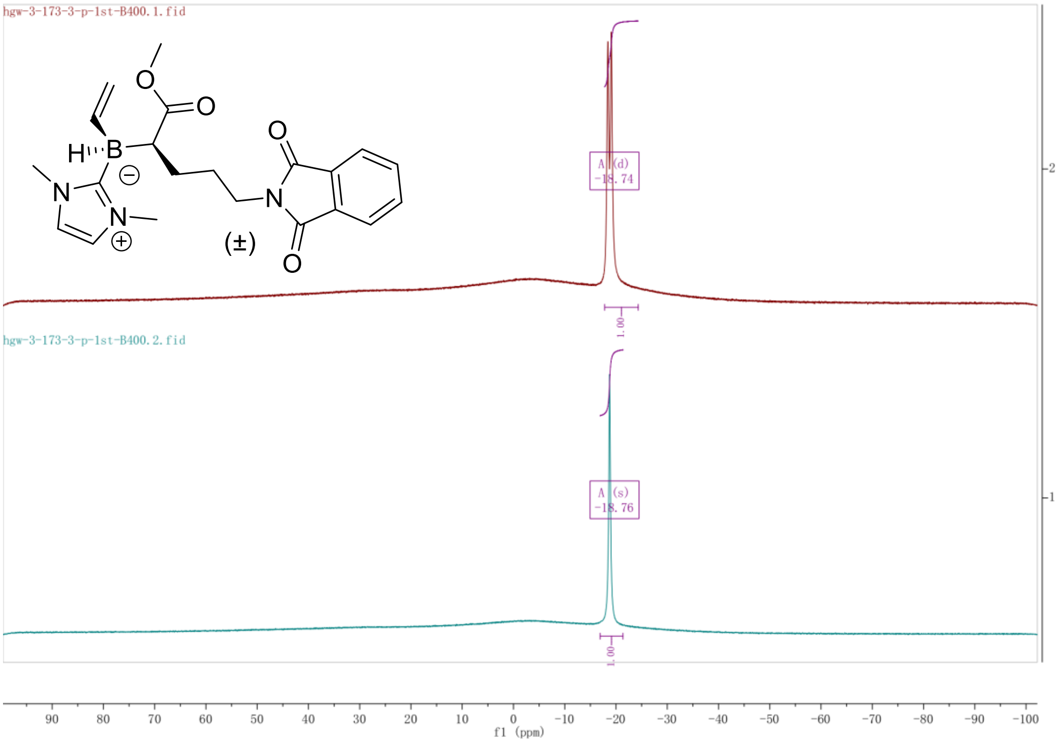


^{11}B NMR and ^{11}B {^{1}H} NMR of 45



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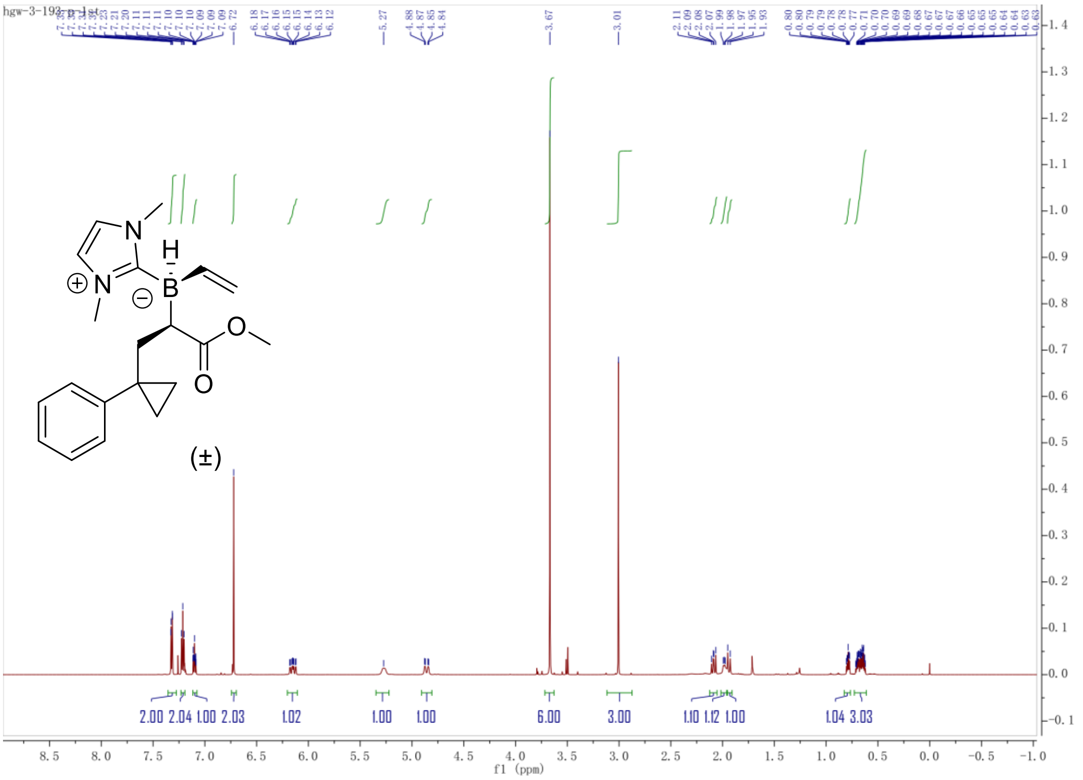
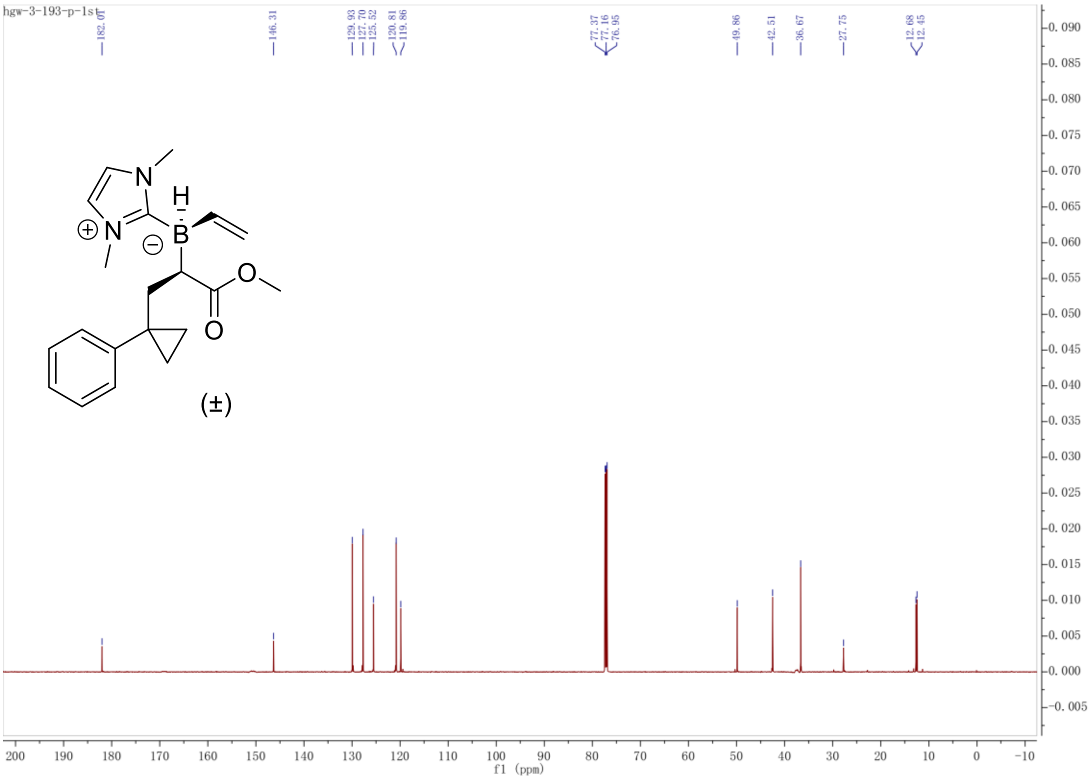
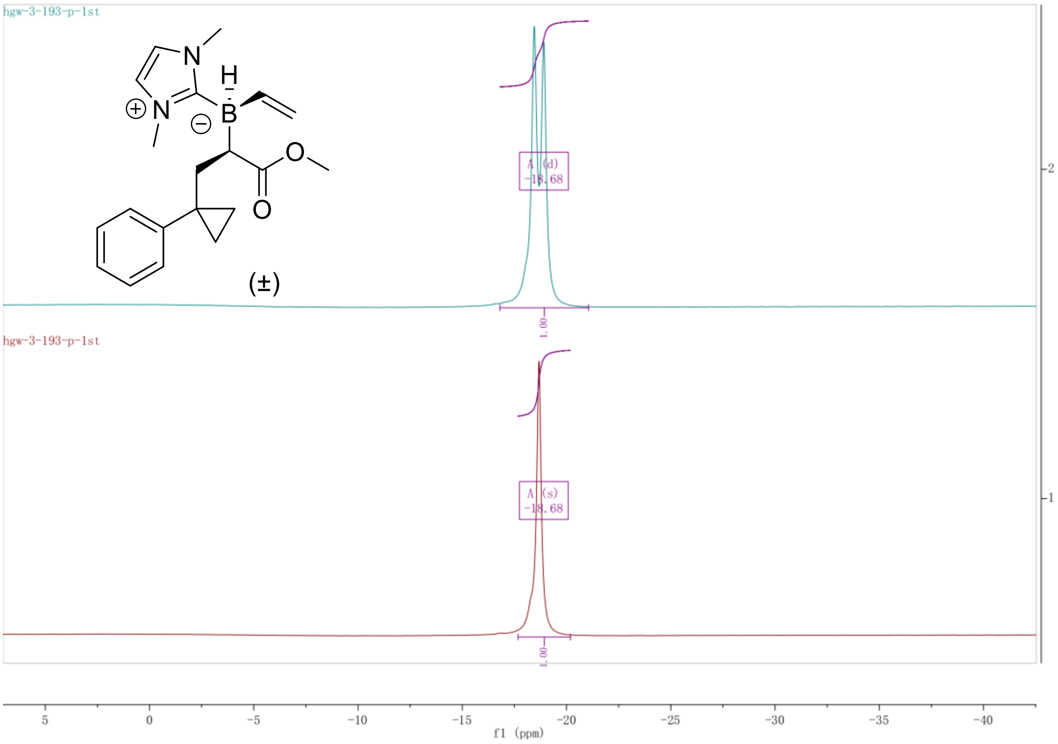


^{13}C NMR of 46



^{11}B NMR and ^{11}B {^{1}H} NMR of 46



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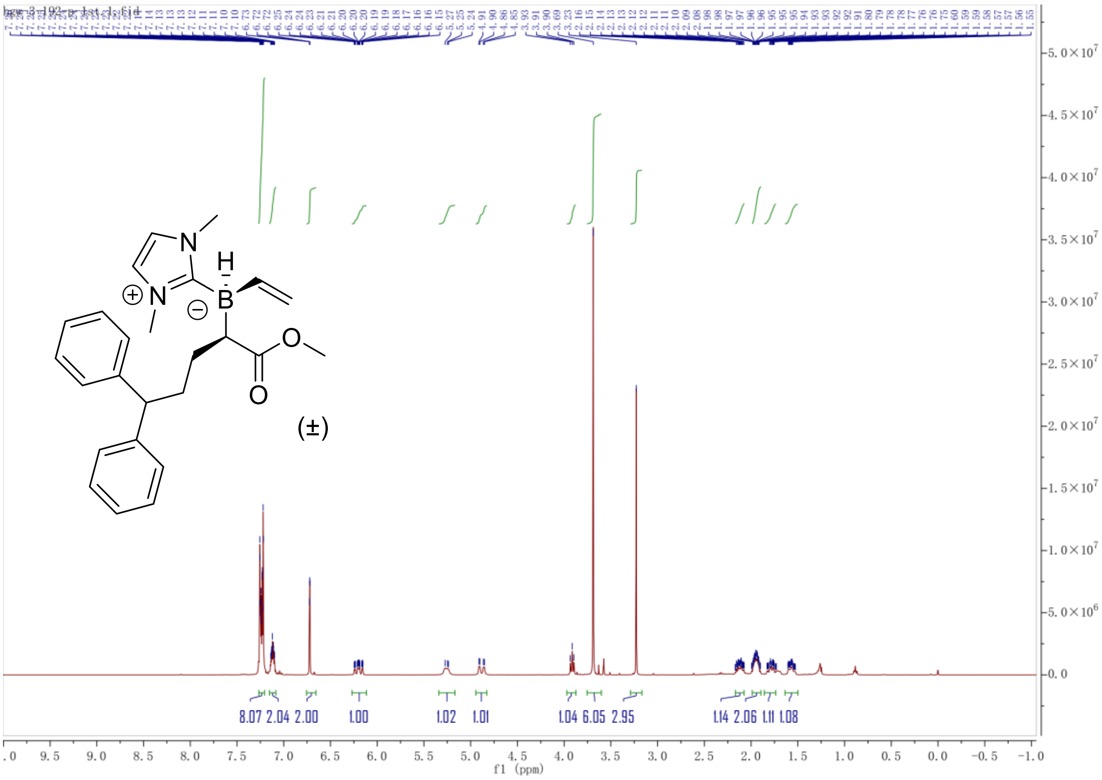
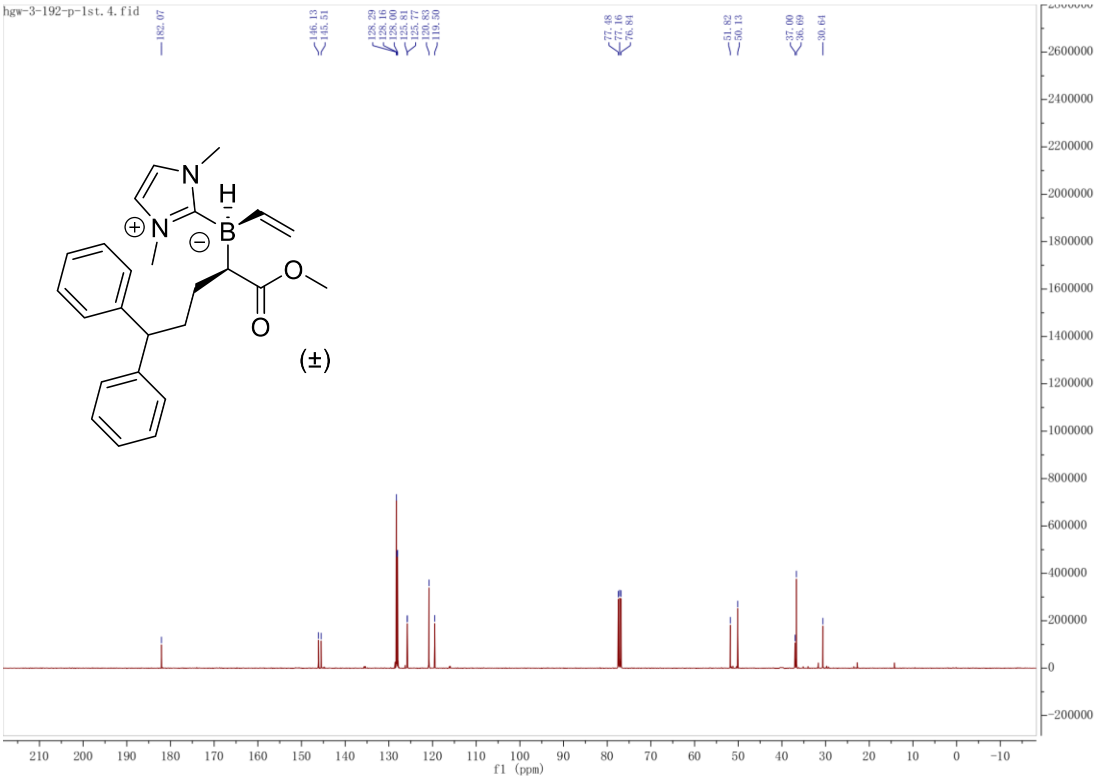
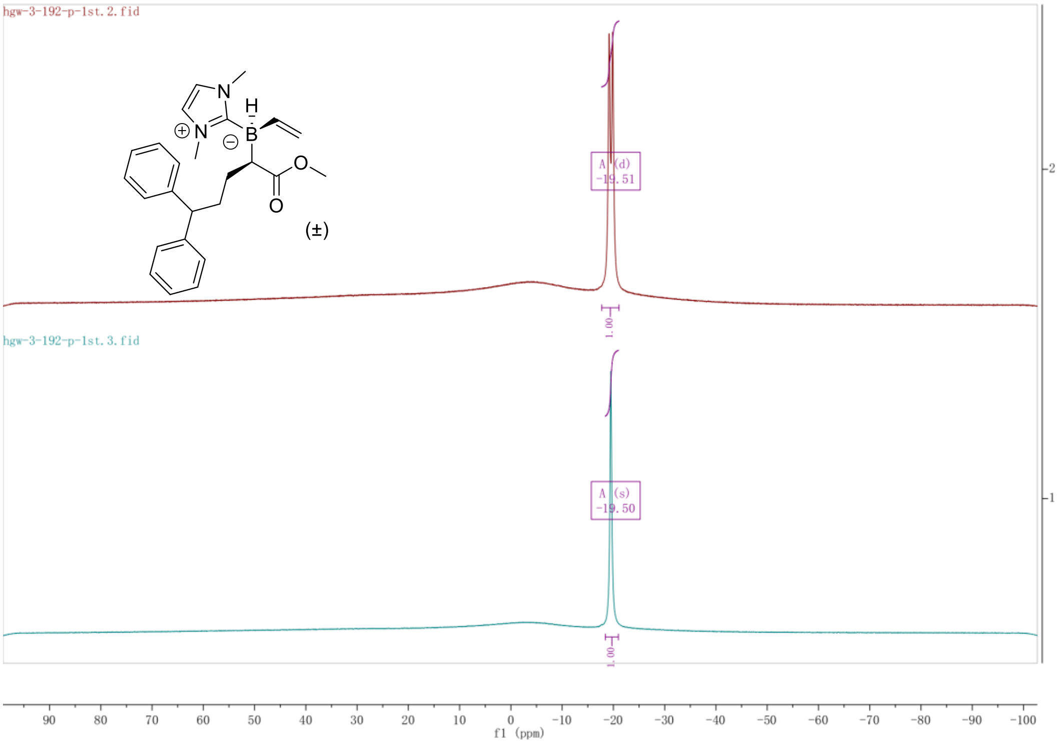


^{13}C NMR of 47



^{11}B NMR and ^{11}B {^{1}H} NMR of 47



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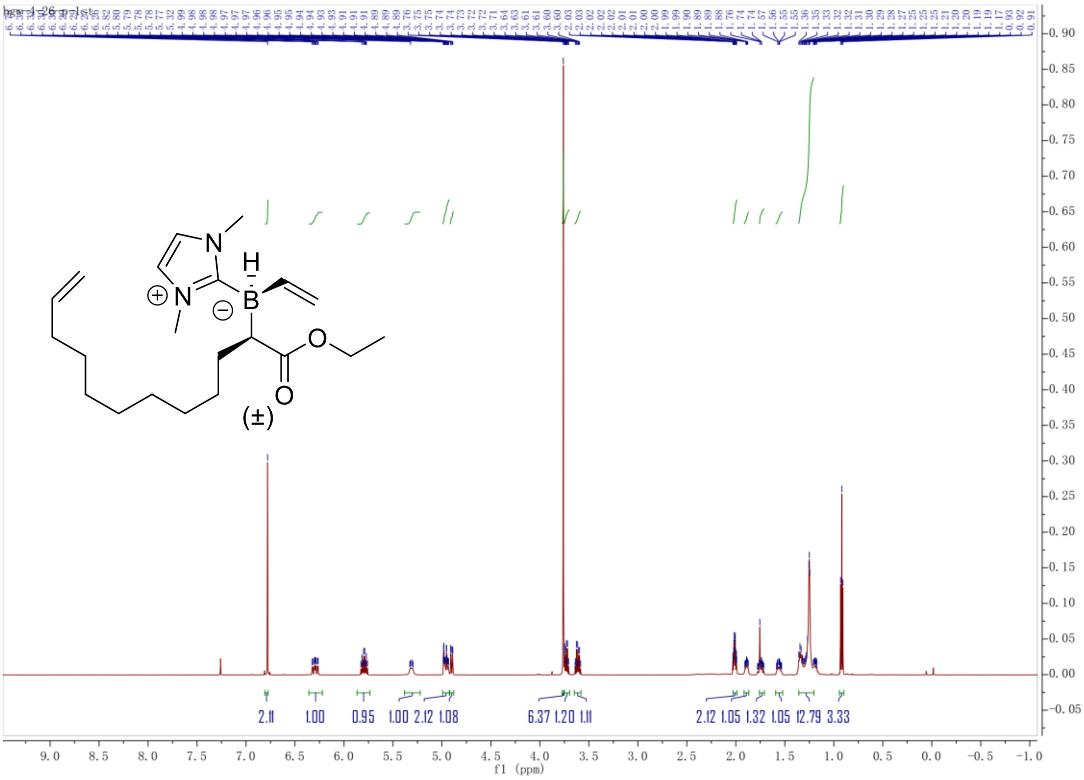
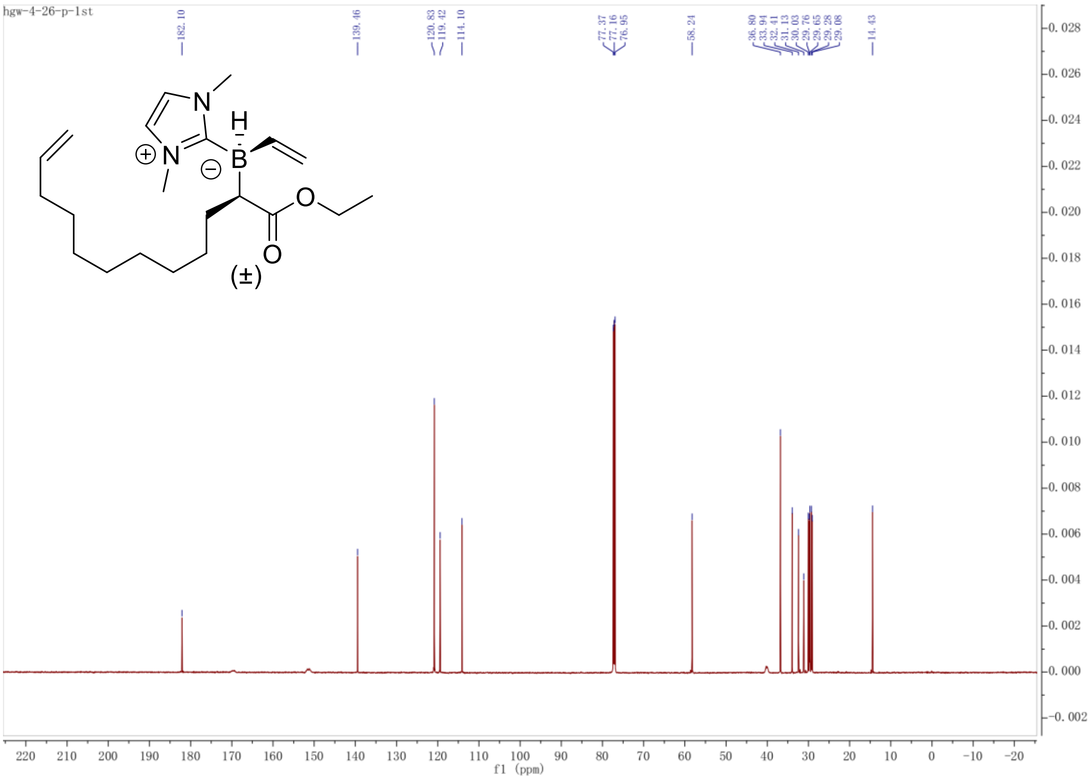
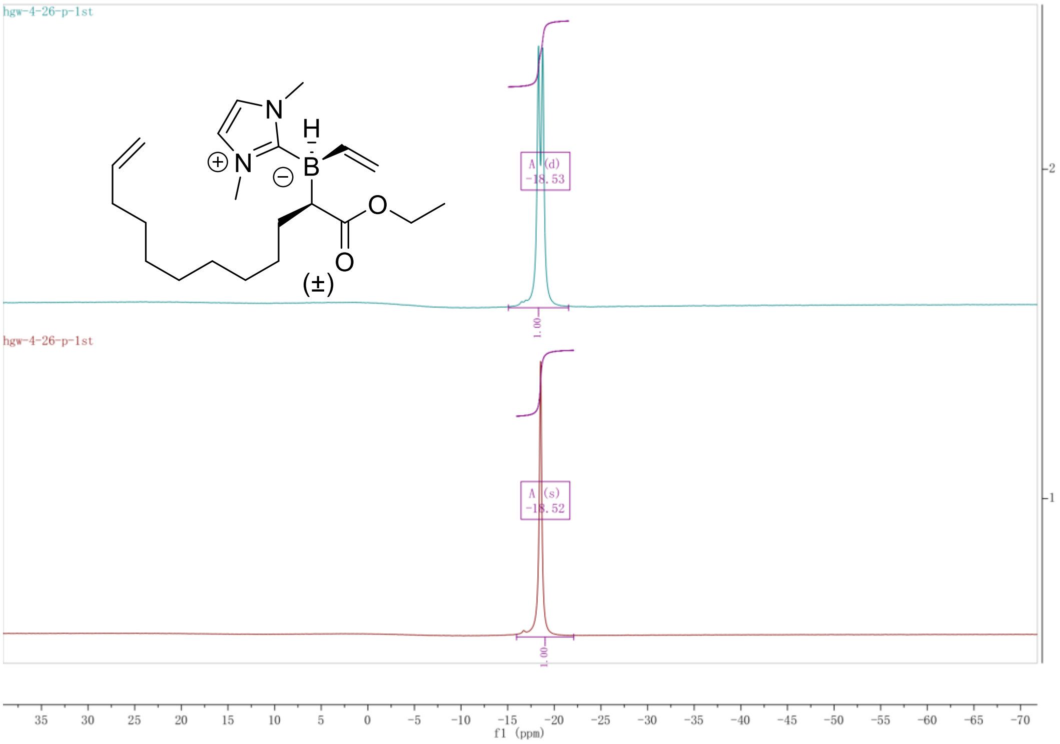


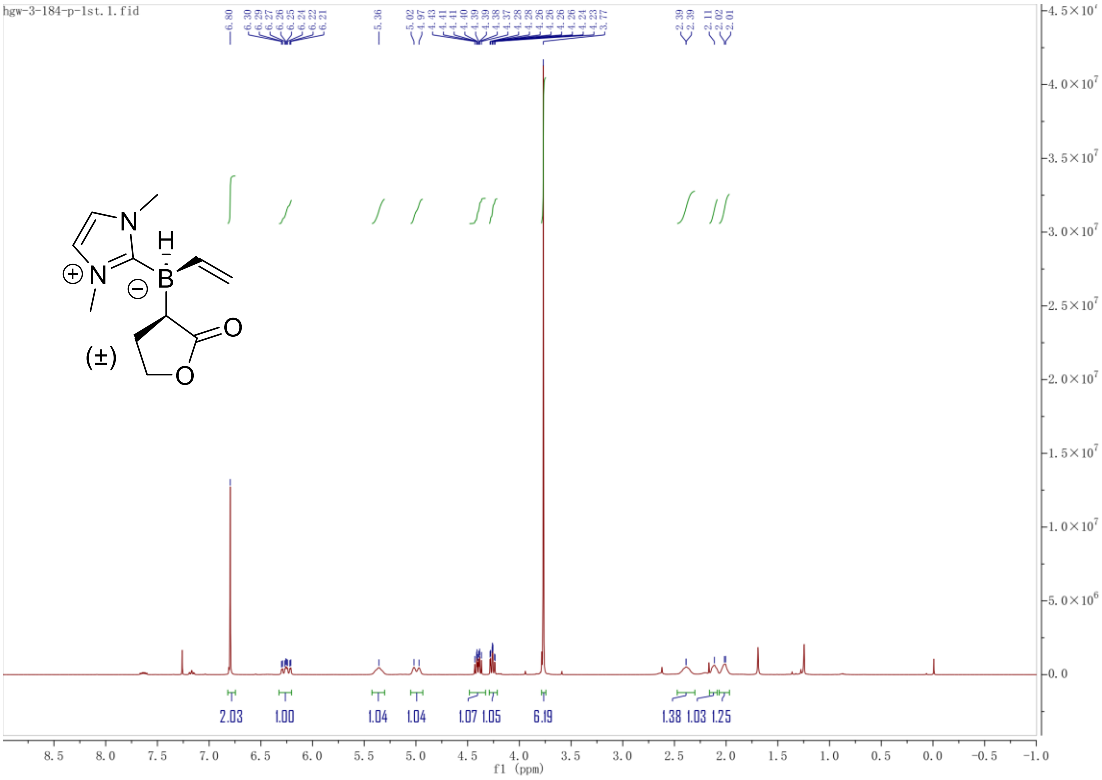
^{13}C NMR of 48



^{11}B NMR and ^{11}B {^{1}H} NMR of 48



^{1}H NMR of 49



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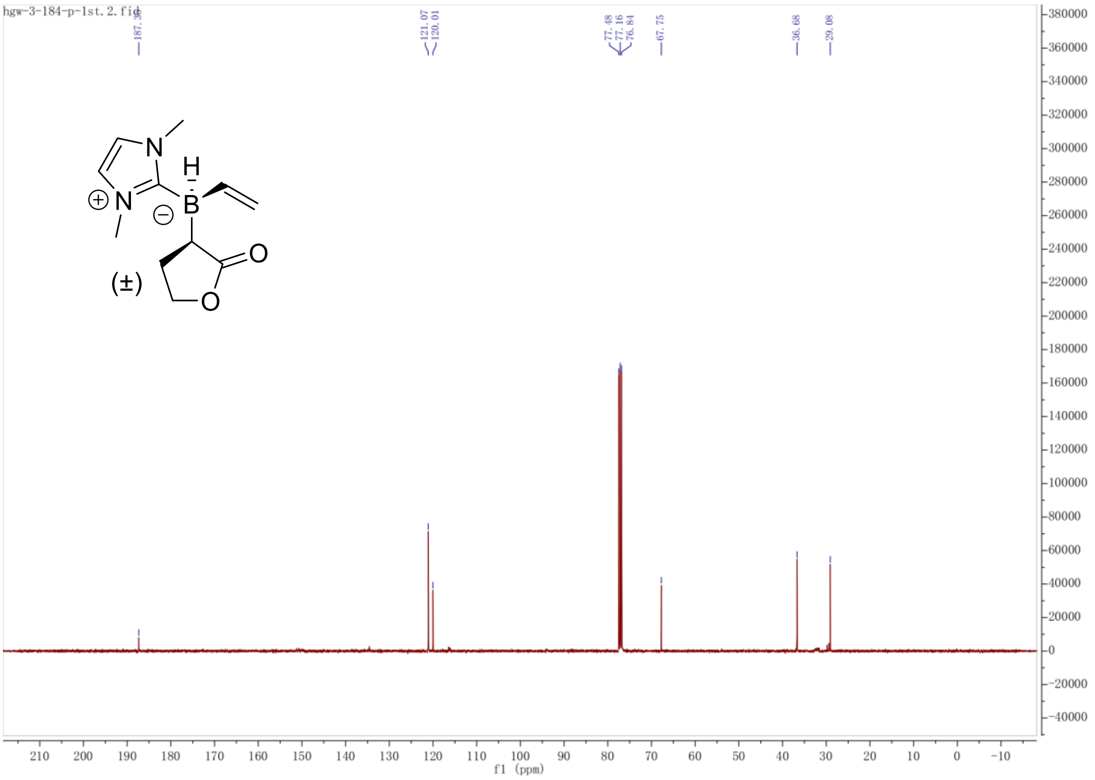
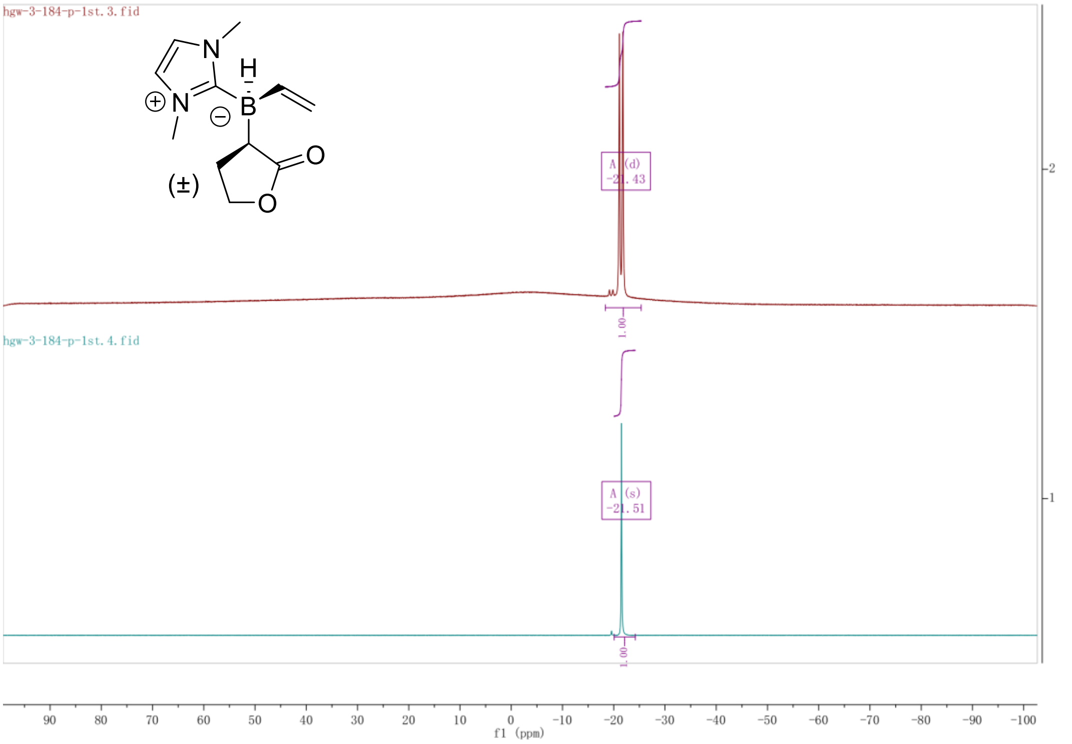


^{11}B NMR and ^{11}B {^{1}H} NMR of 49



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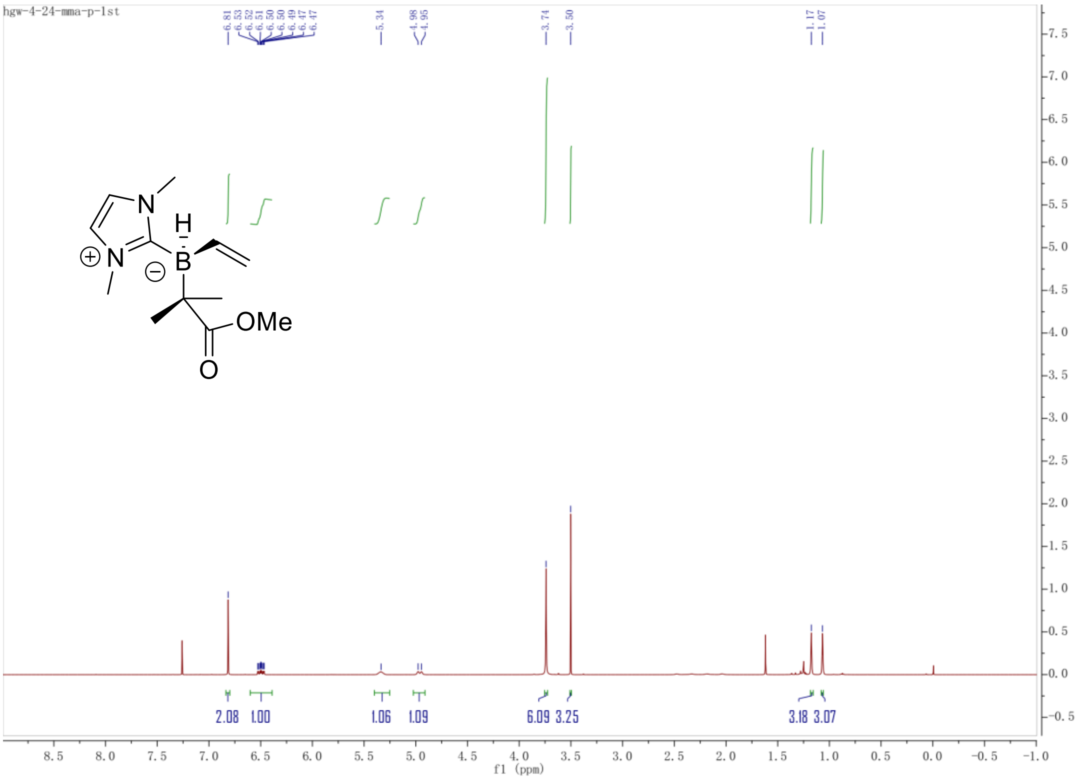

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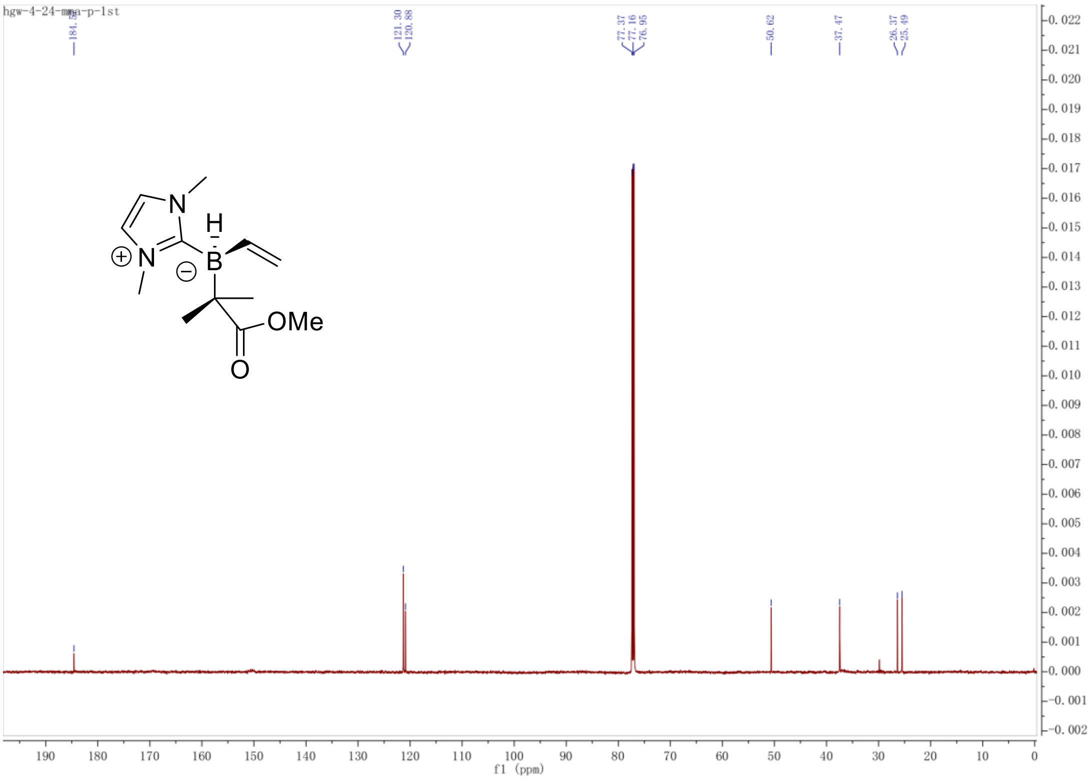

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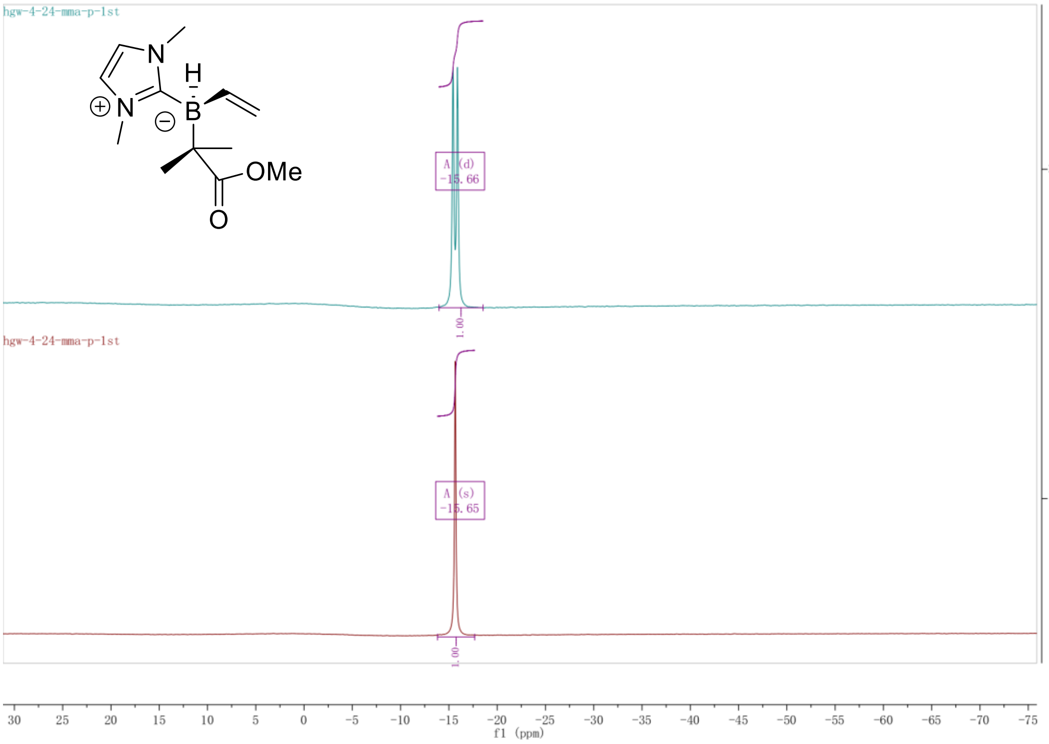

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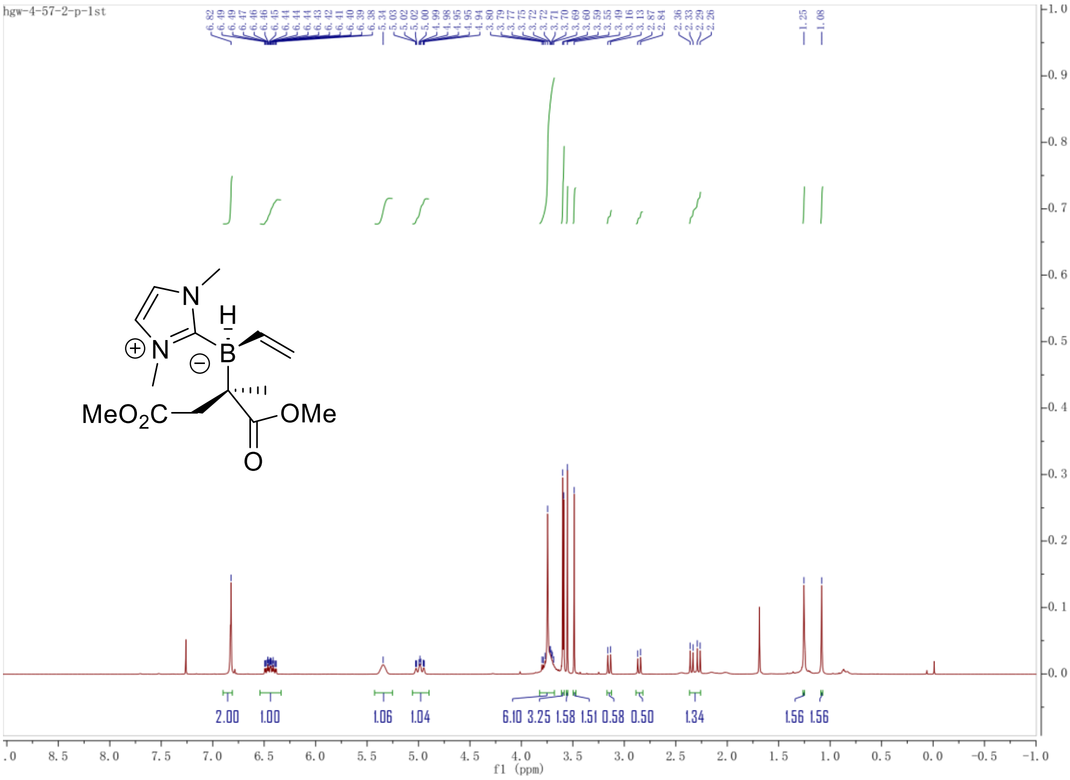
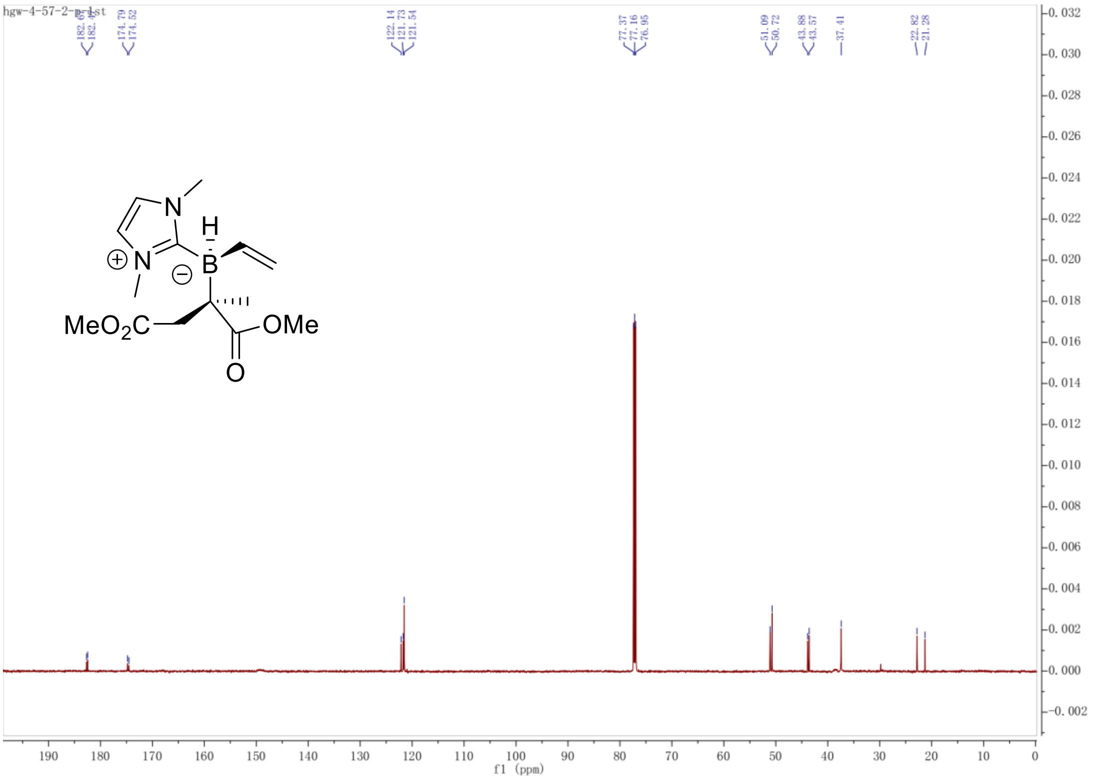


^{13}C NMR of 51



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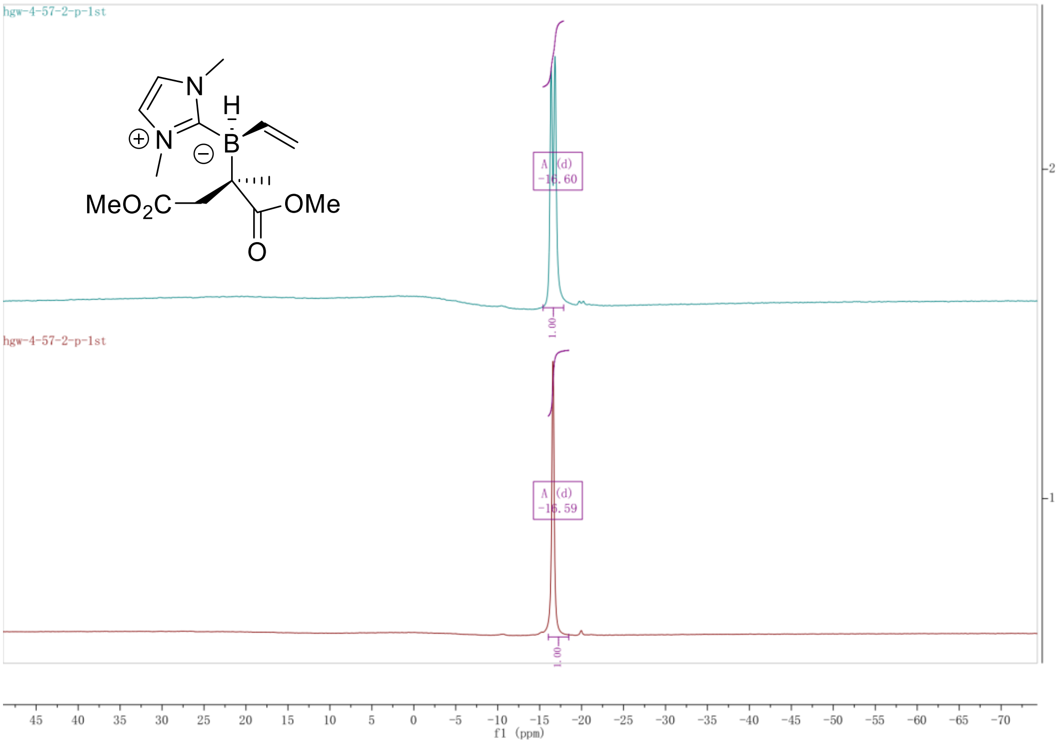
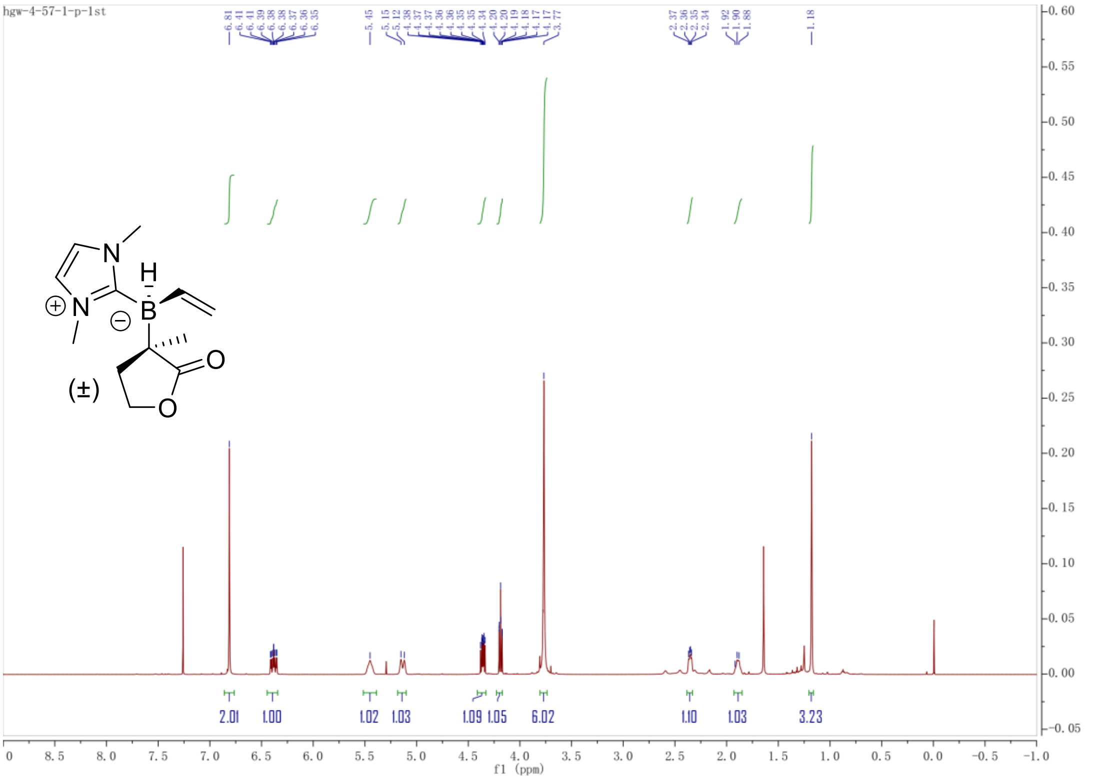


^{1}H NMR of 52



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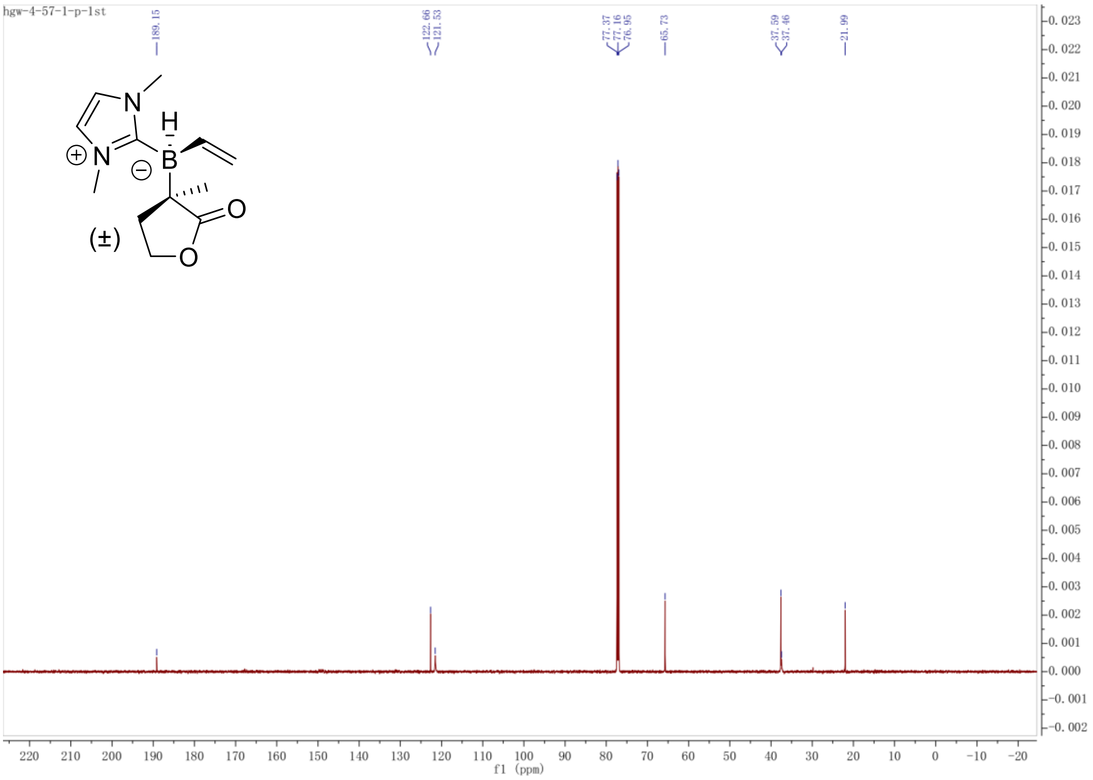

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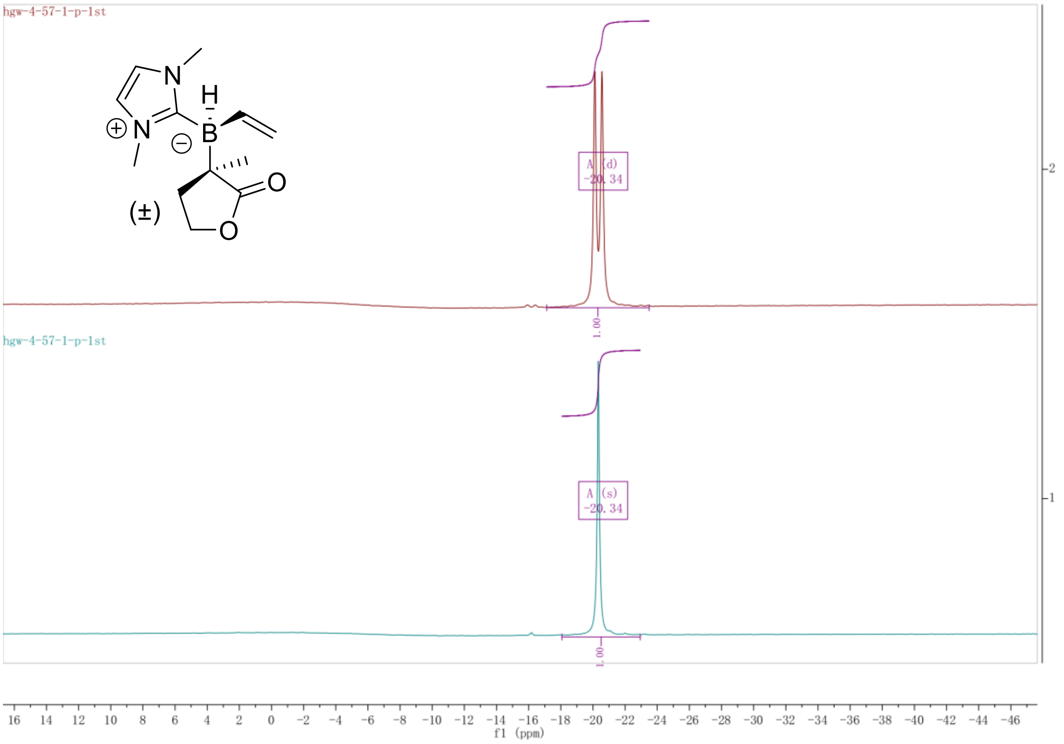

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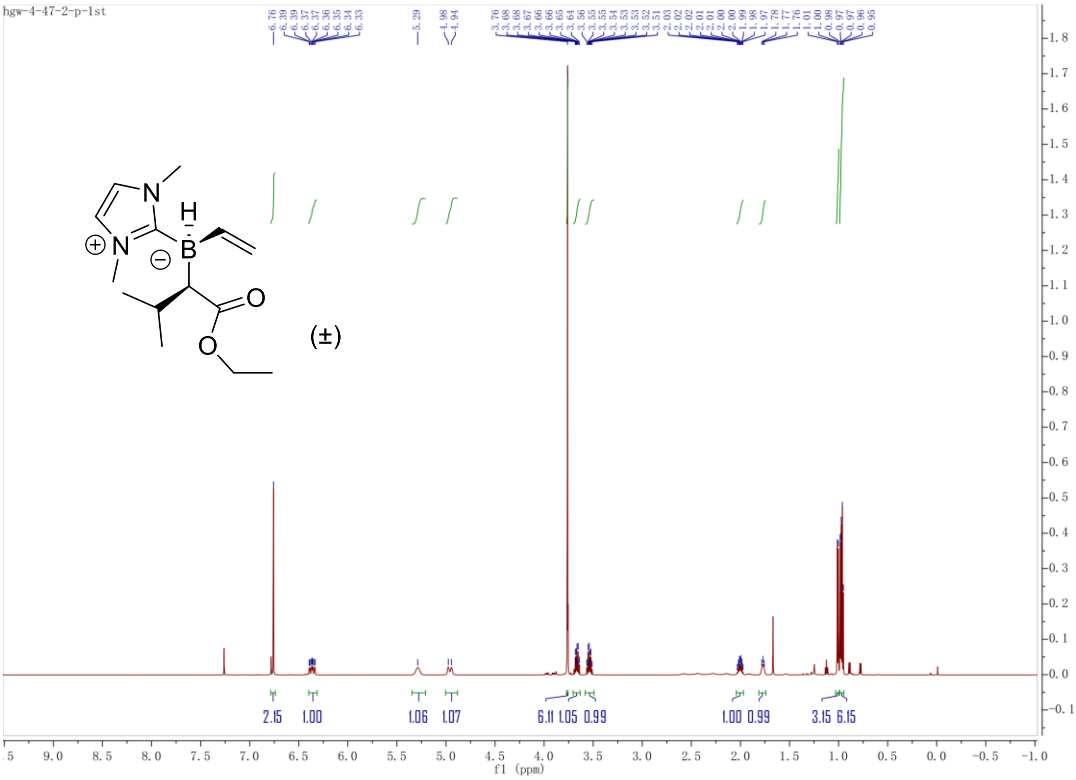

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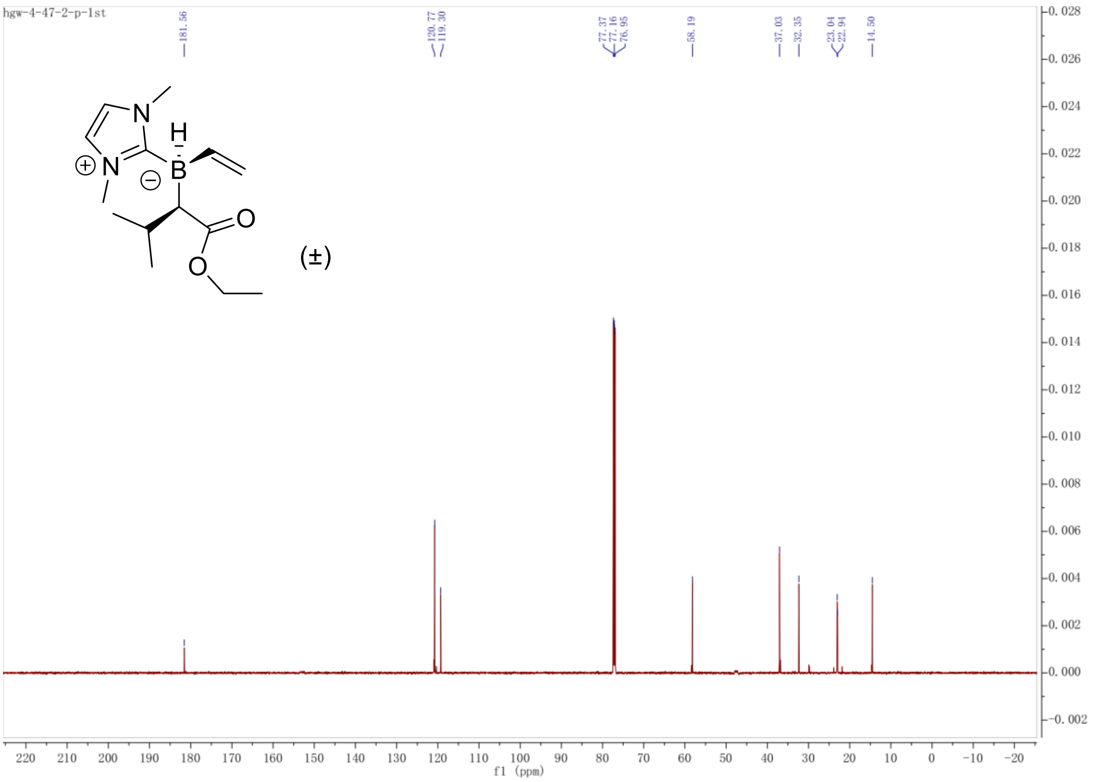

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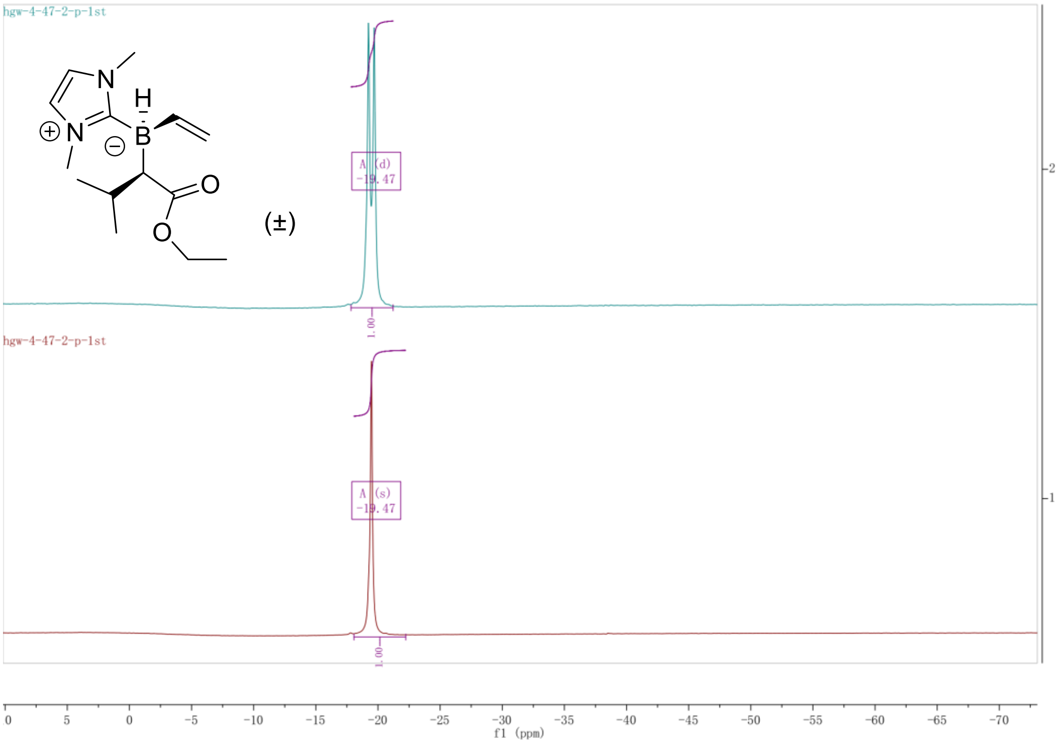
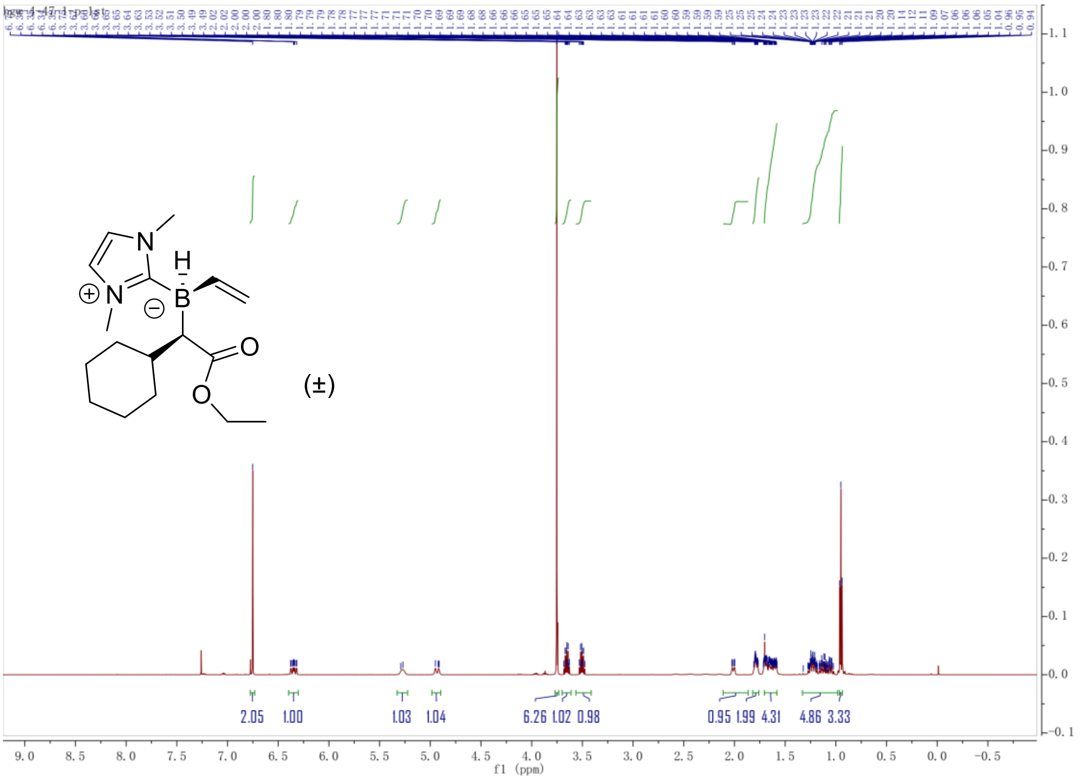
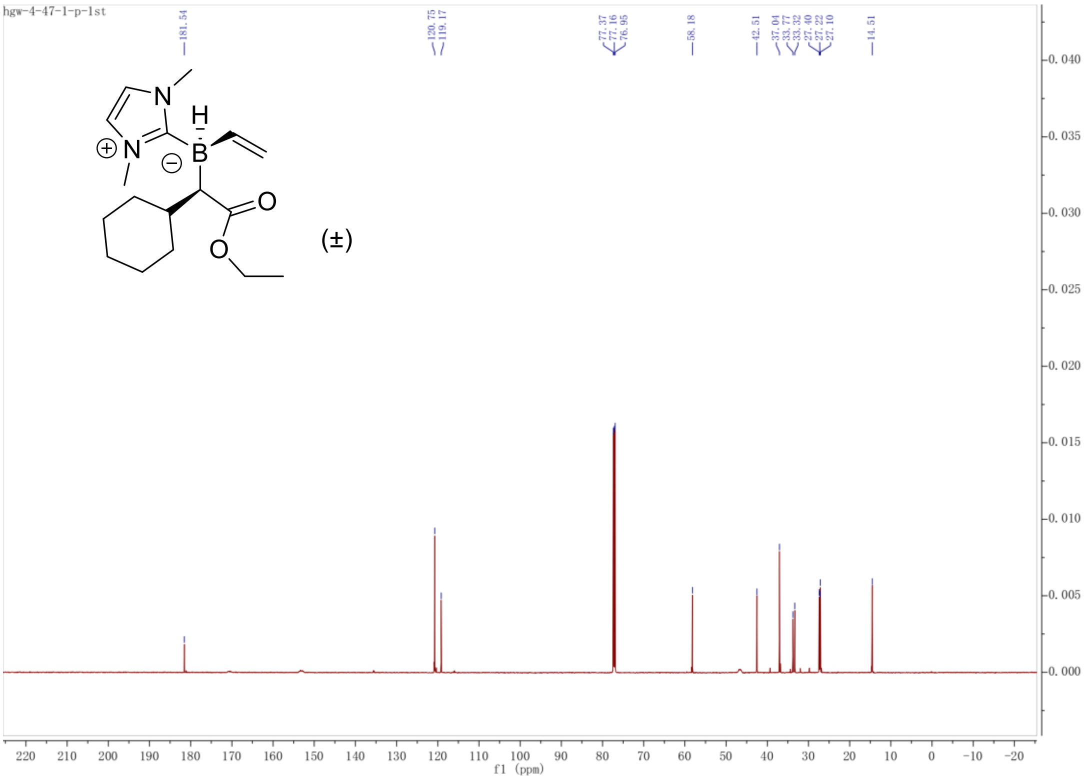


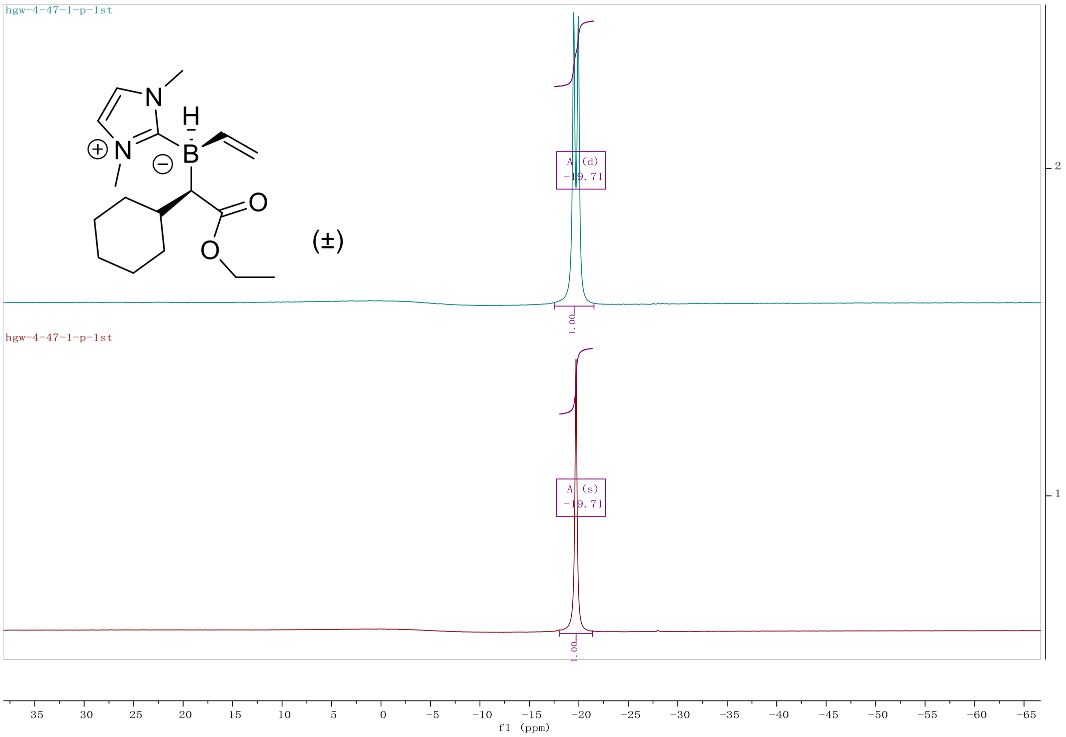
^{1}H NMR of 54



^{13}C NMR of 54



^{11}B NMR and ^{11}B {^{1}H} NMR of 54



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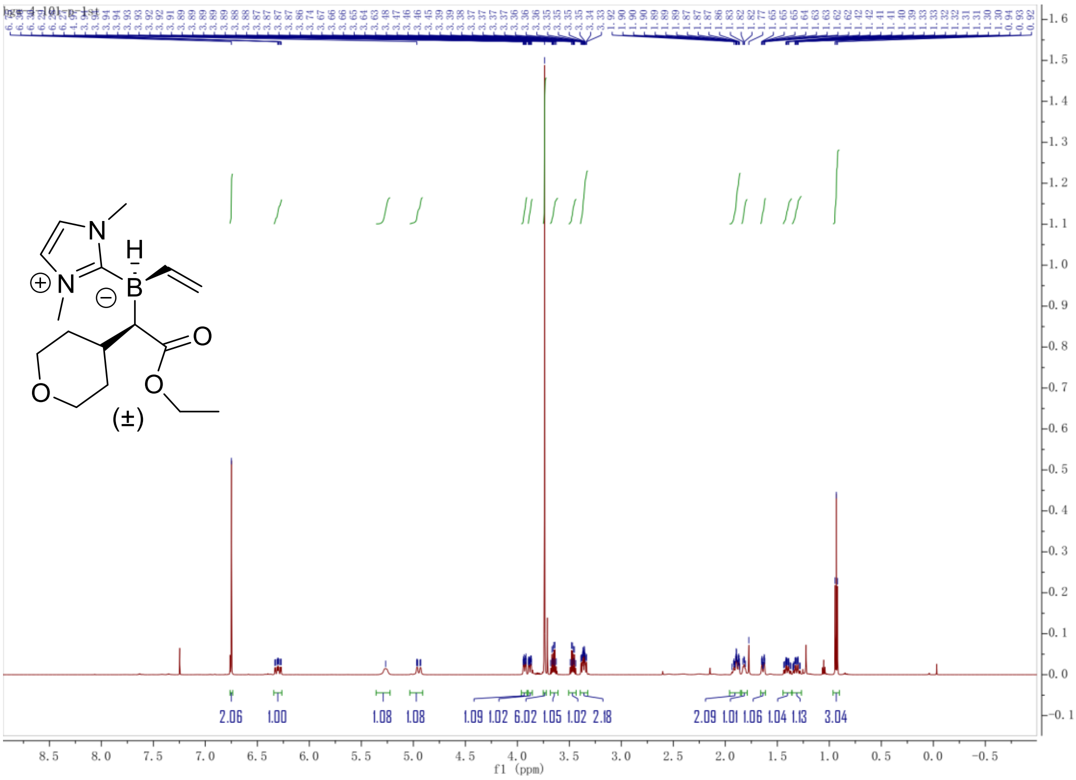

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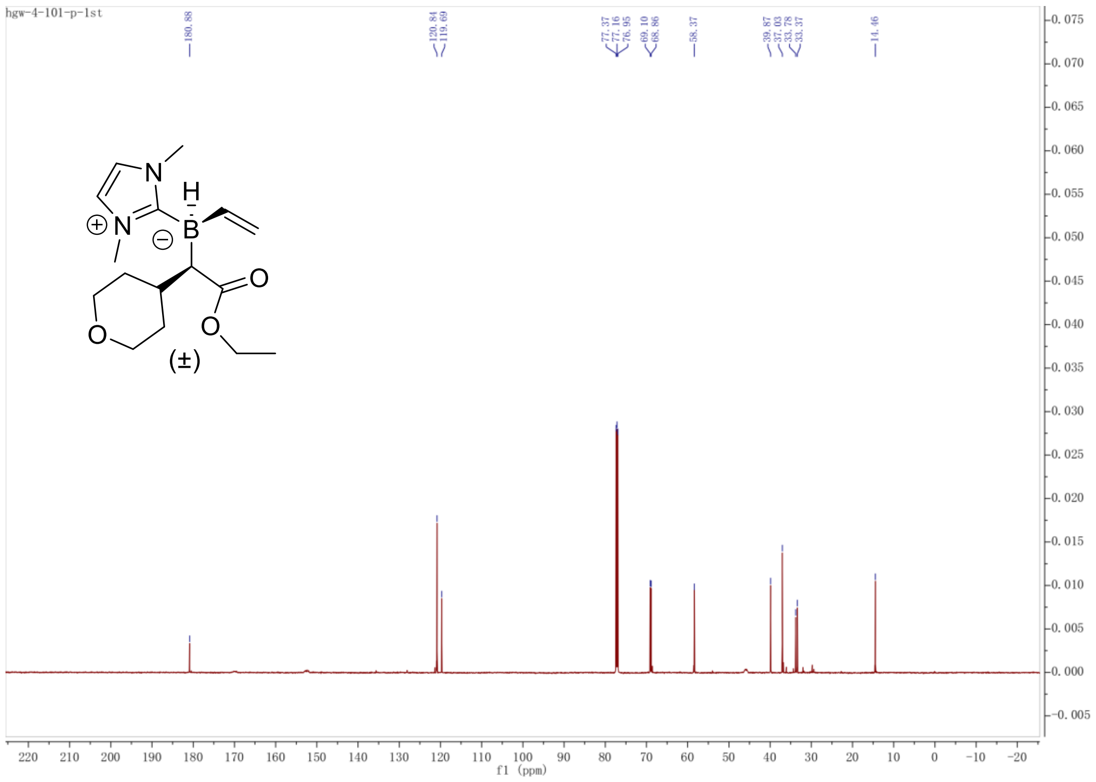

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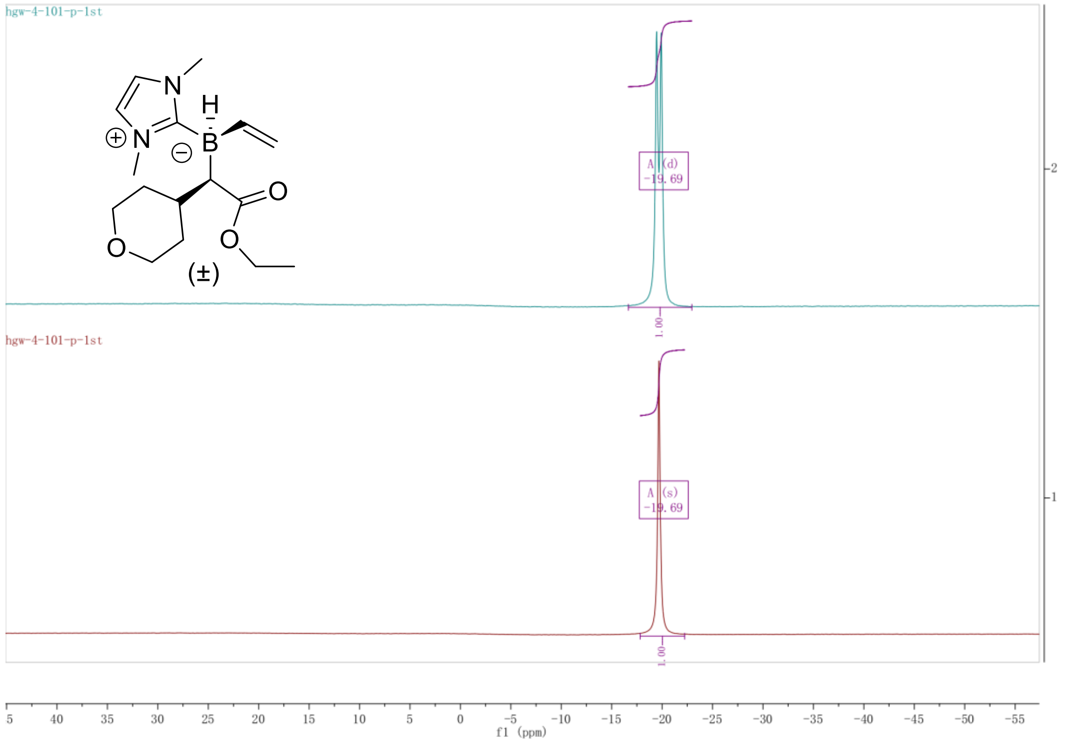

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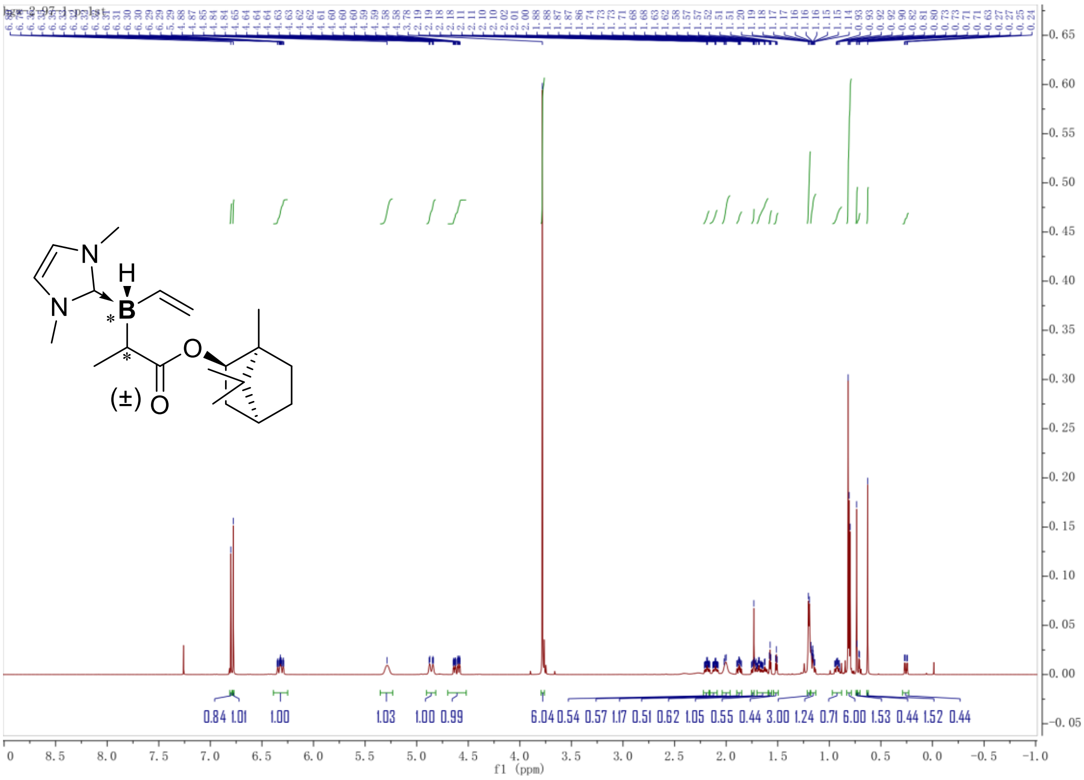

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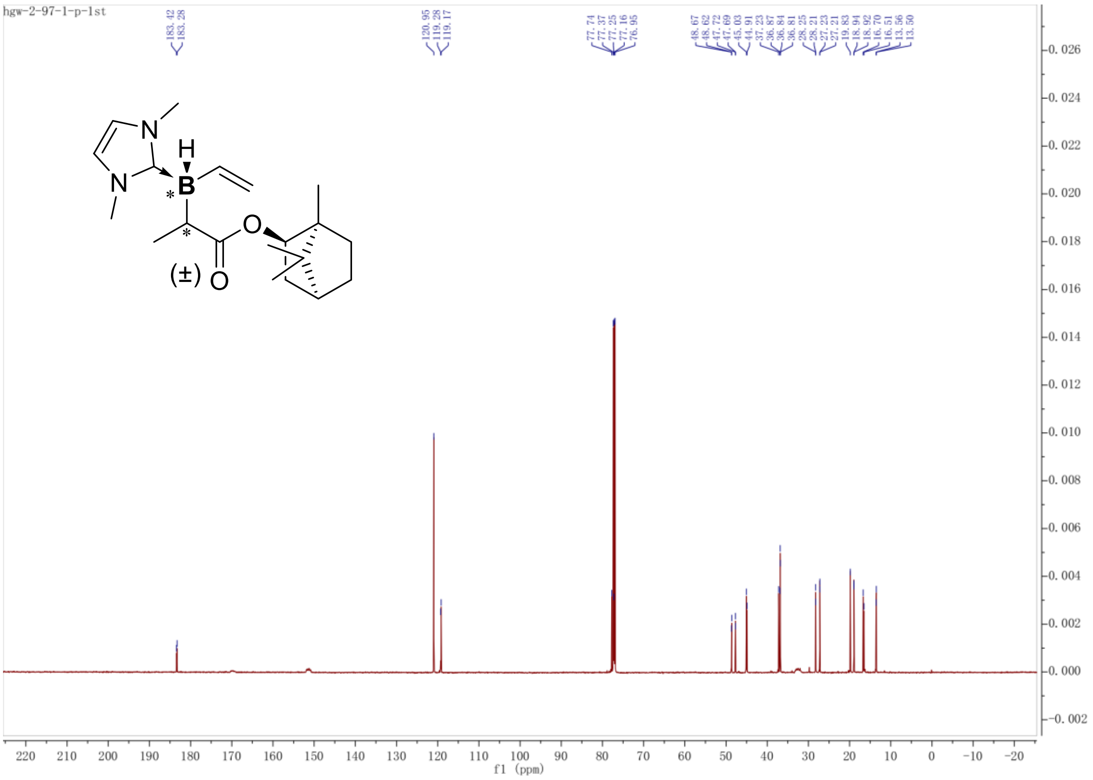
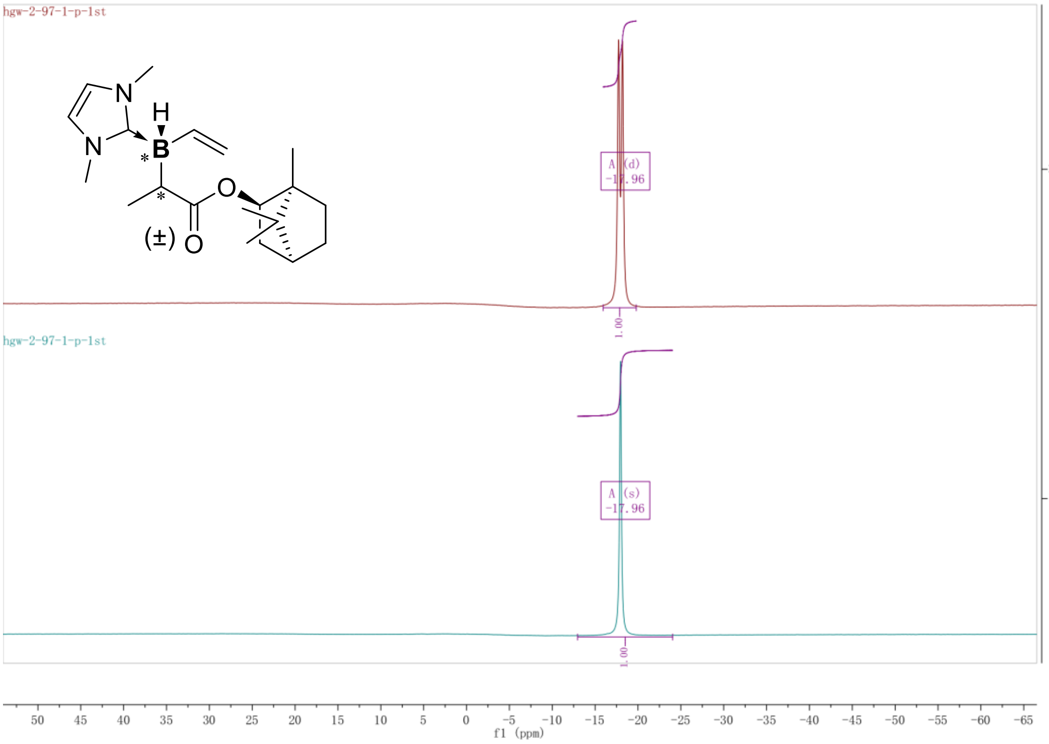


^{11}B NMR and ^{11}B {^{1}H} NMR of 56



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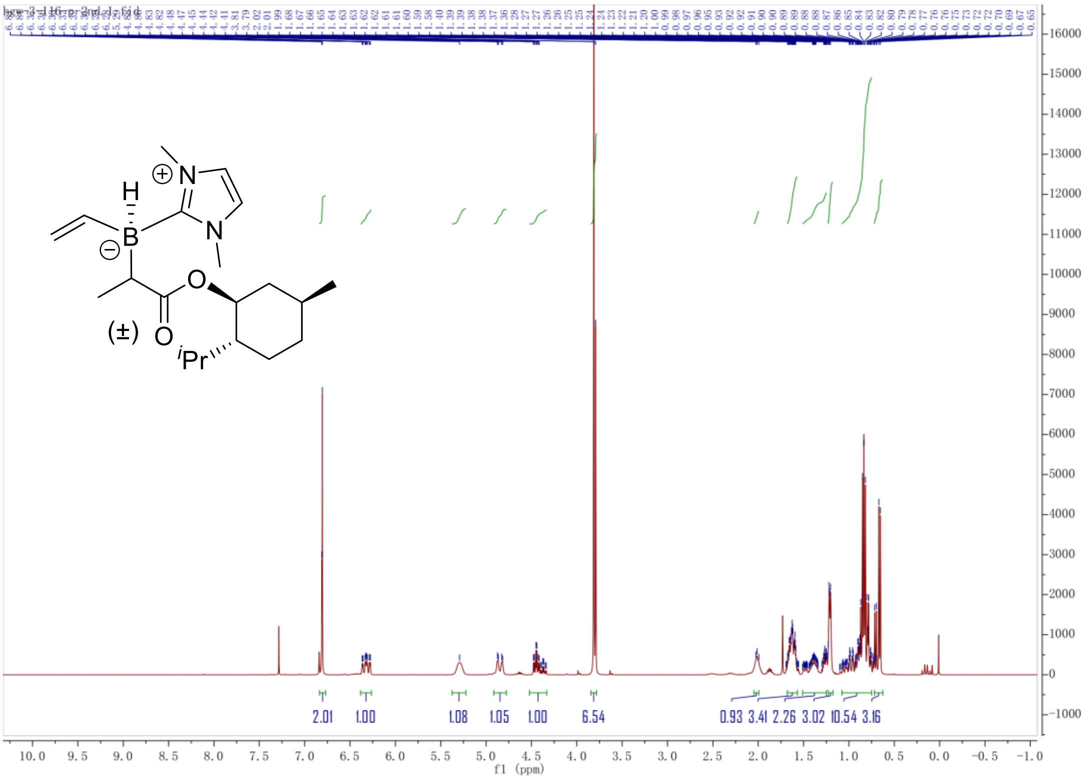

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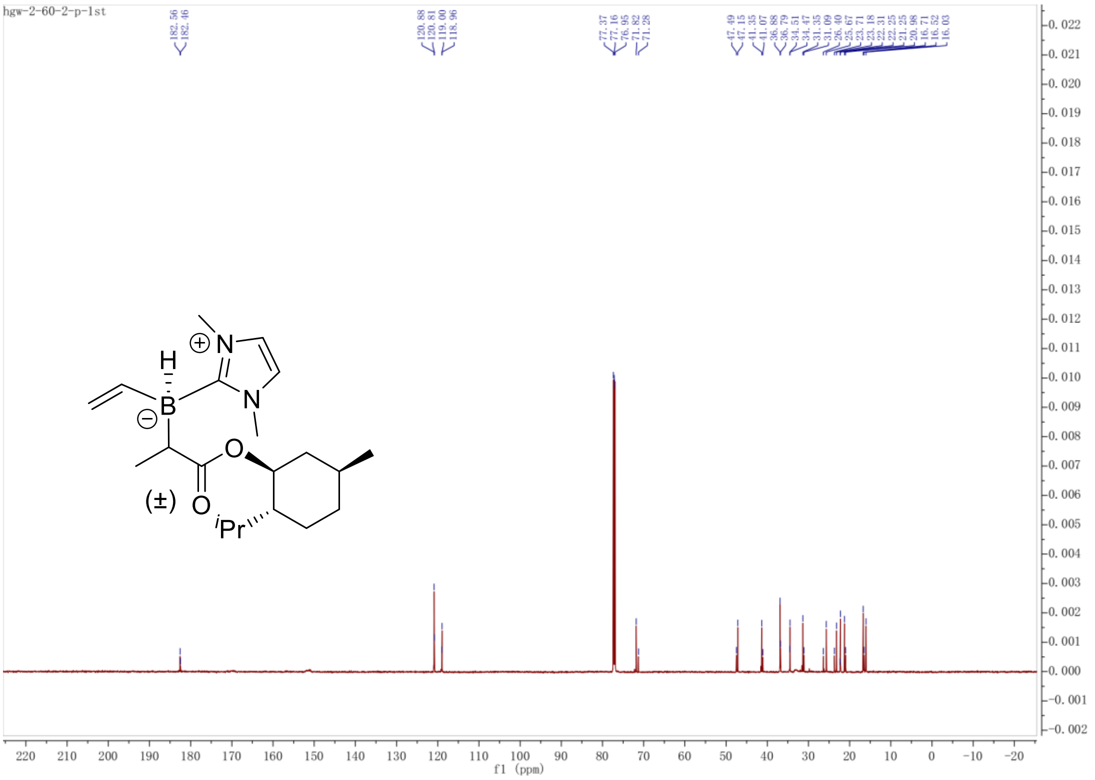

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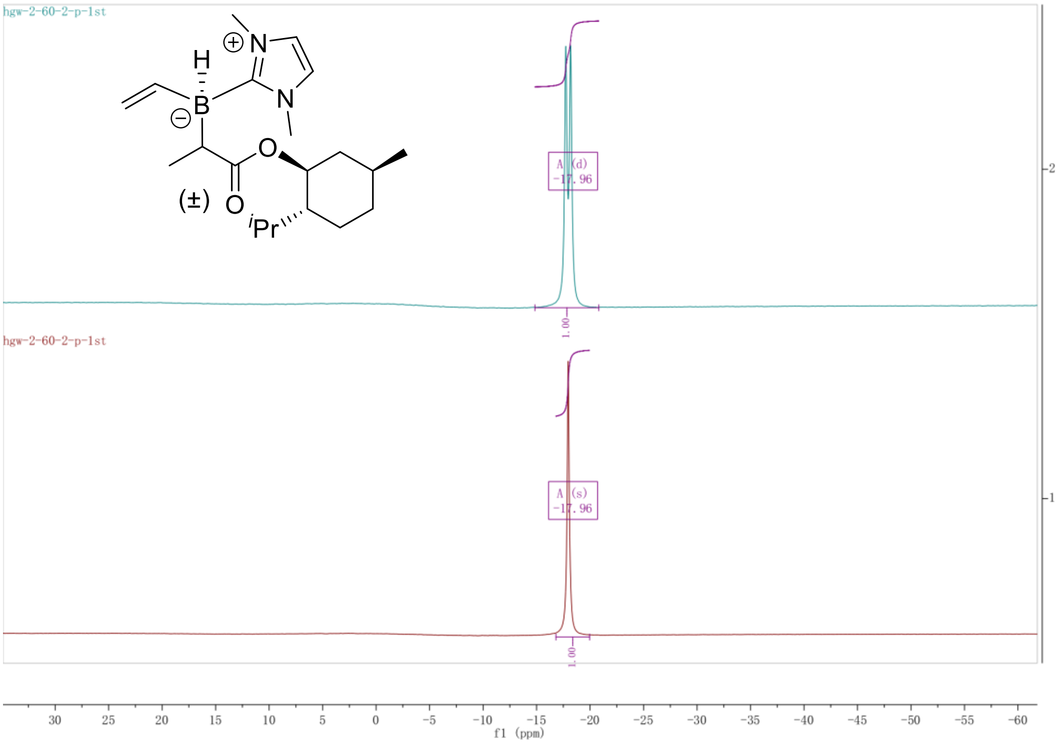

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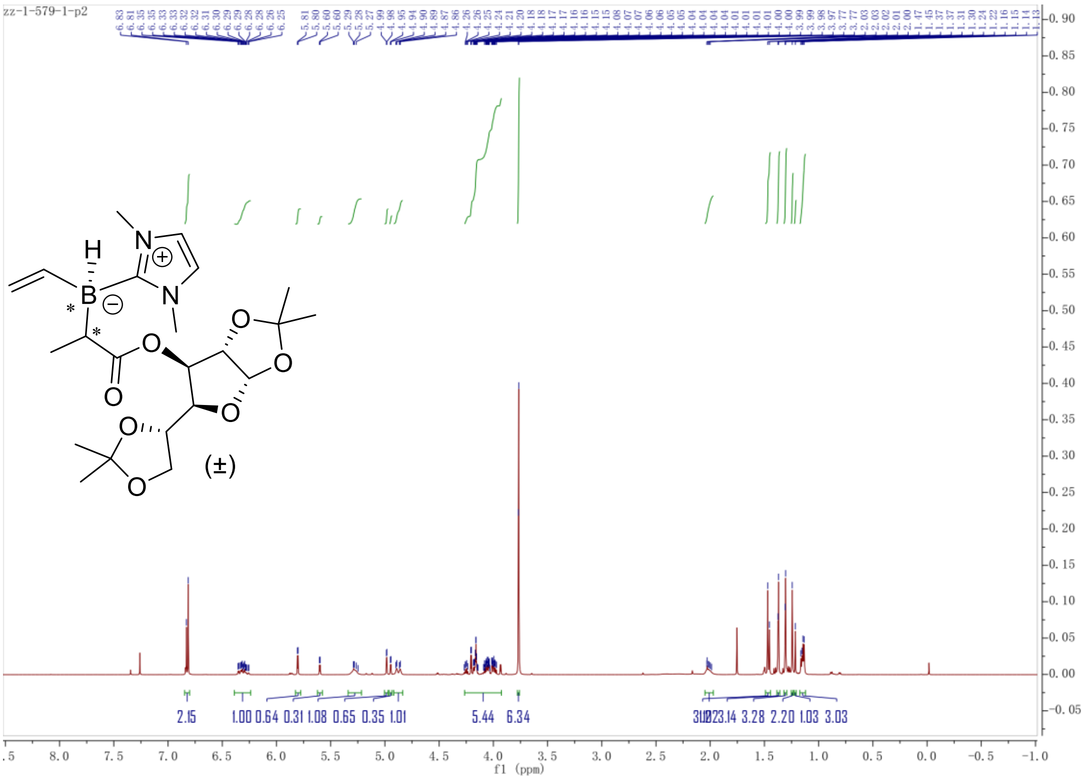

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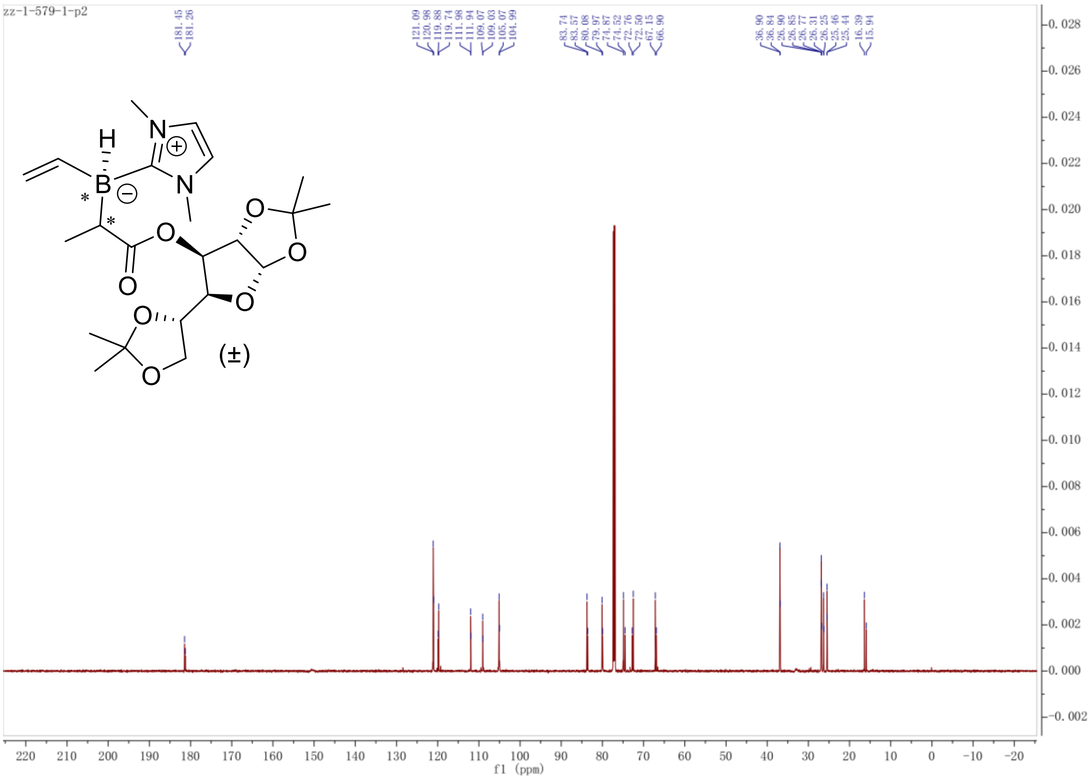
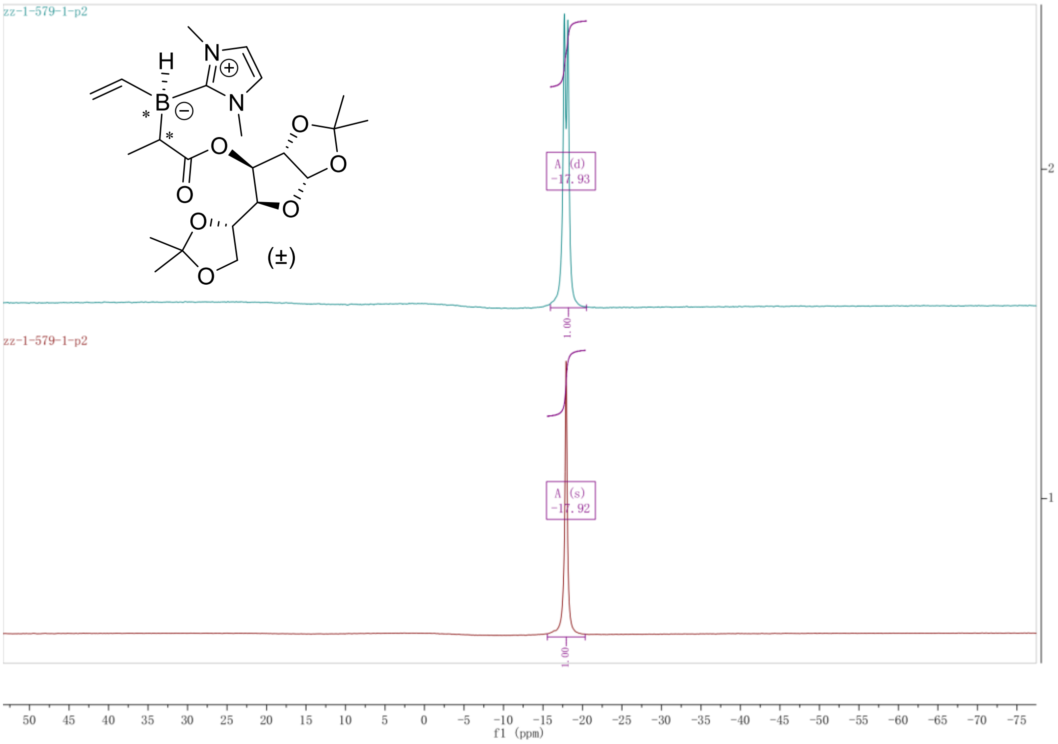
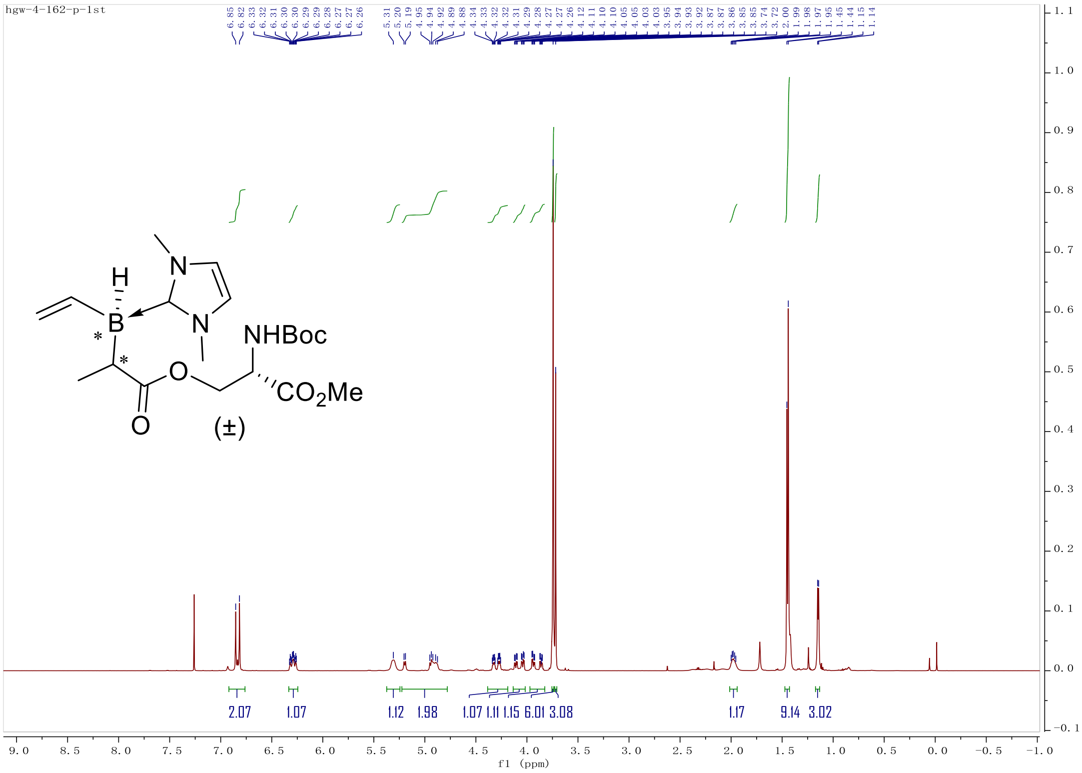


^{11}B NMR and ^{11}B {^{1}H} NMR of 58



^{1}H NMR of 59



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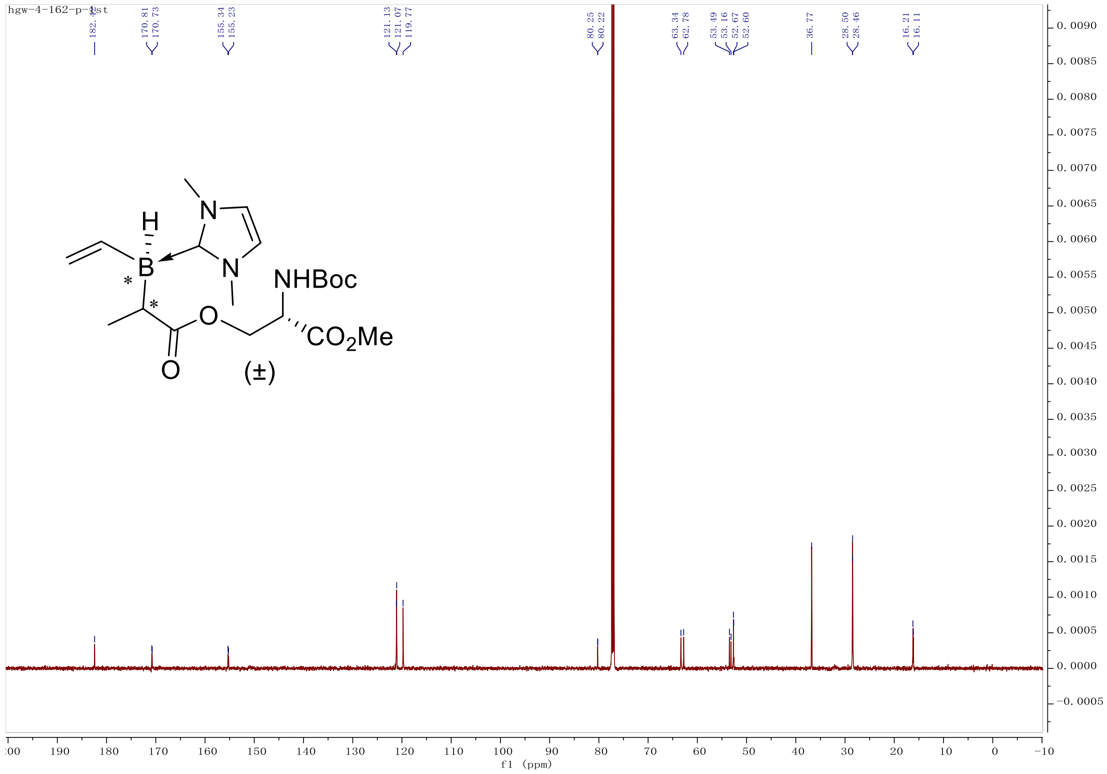

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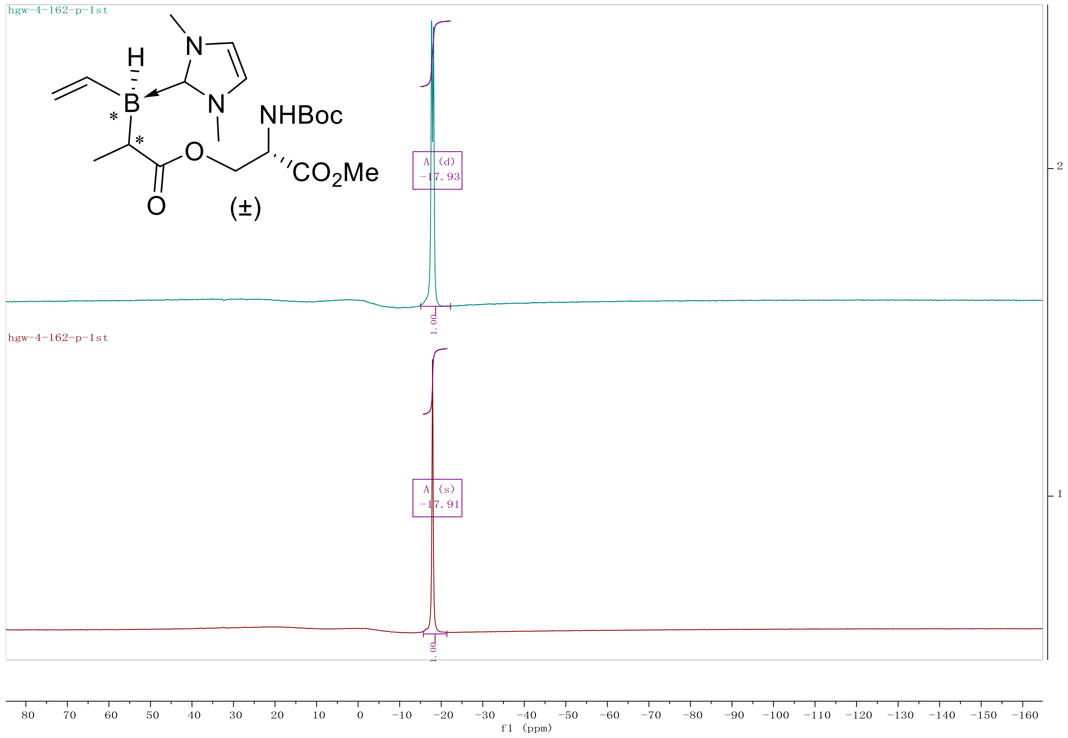

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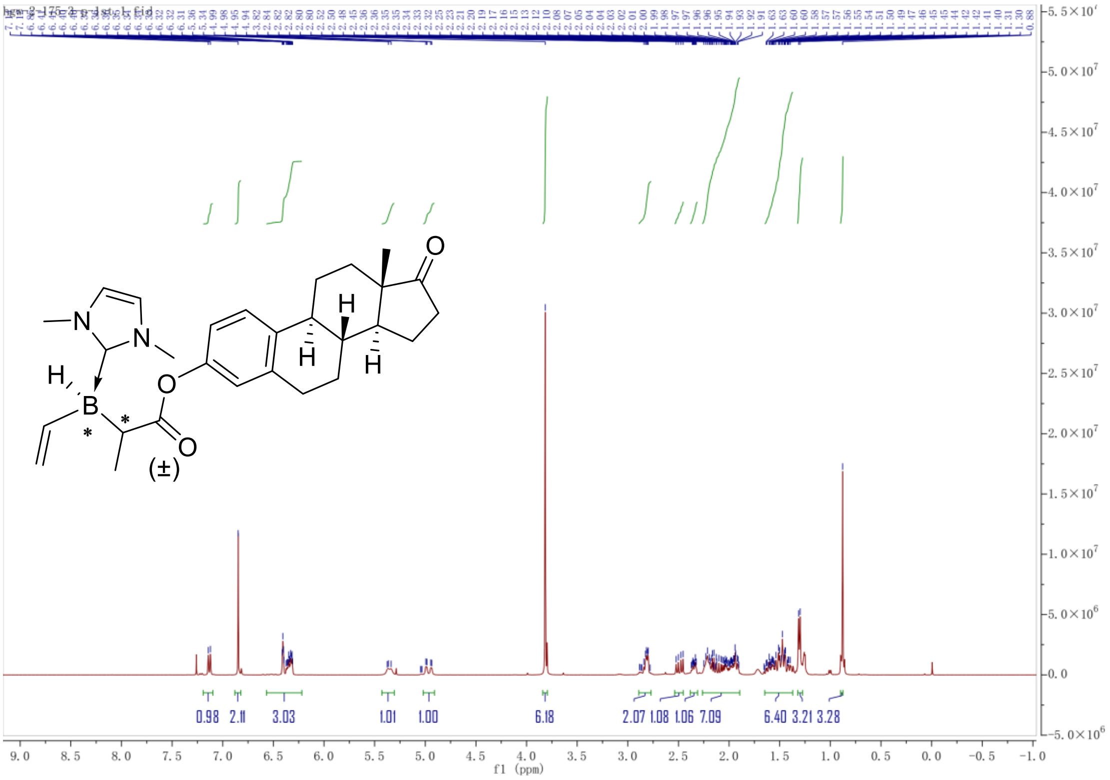
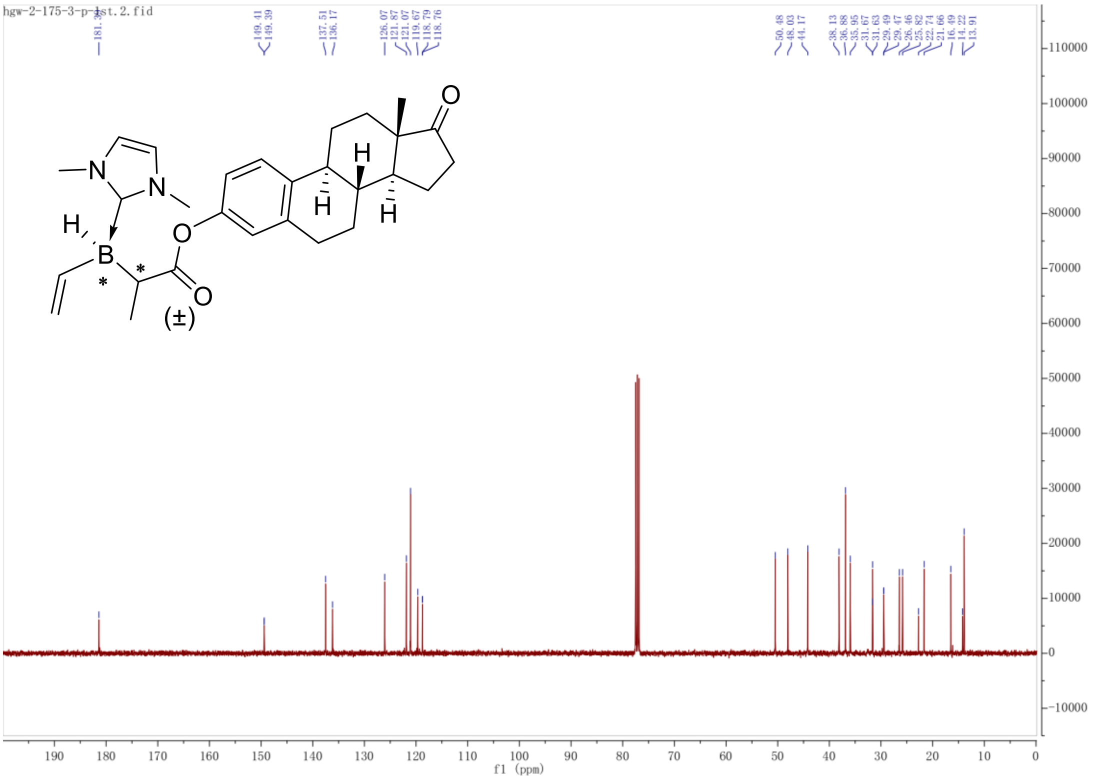
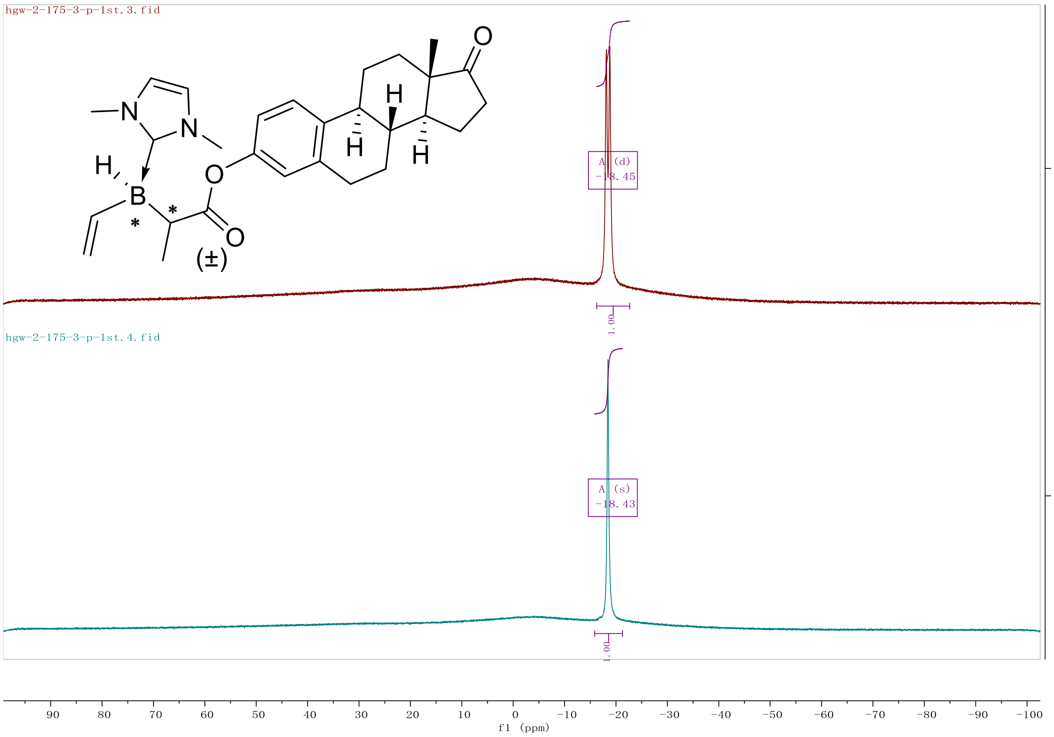


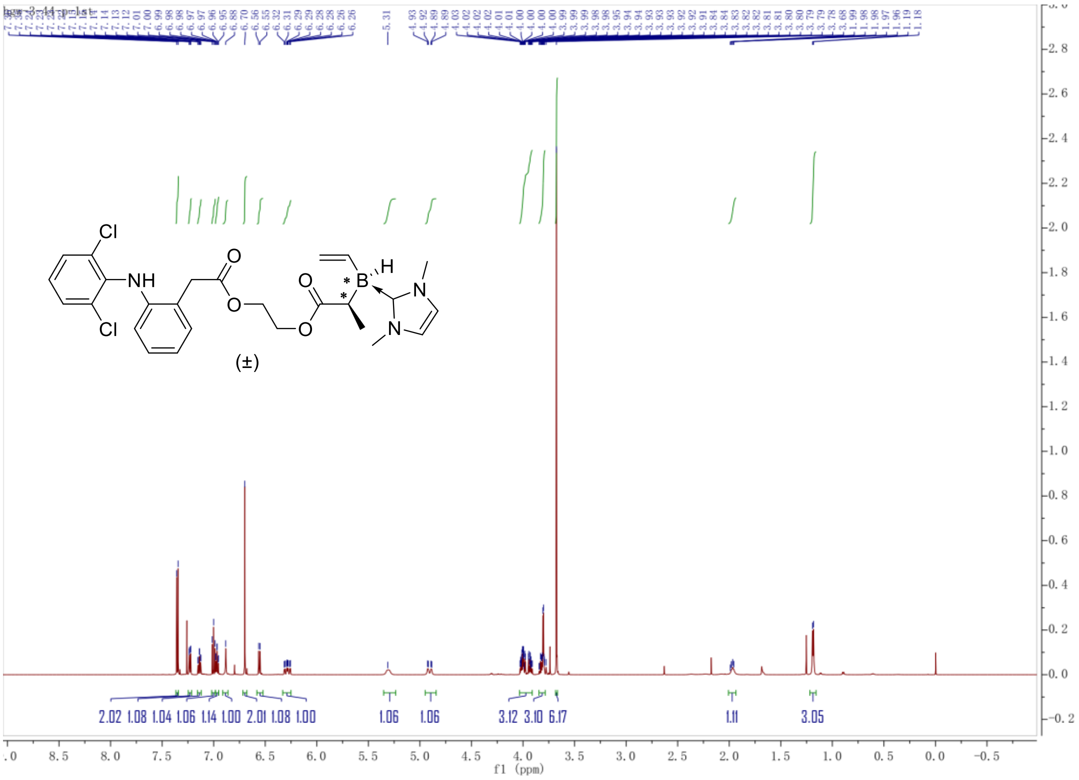
^{13}C NMR of 60



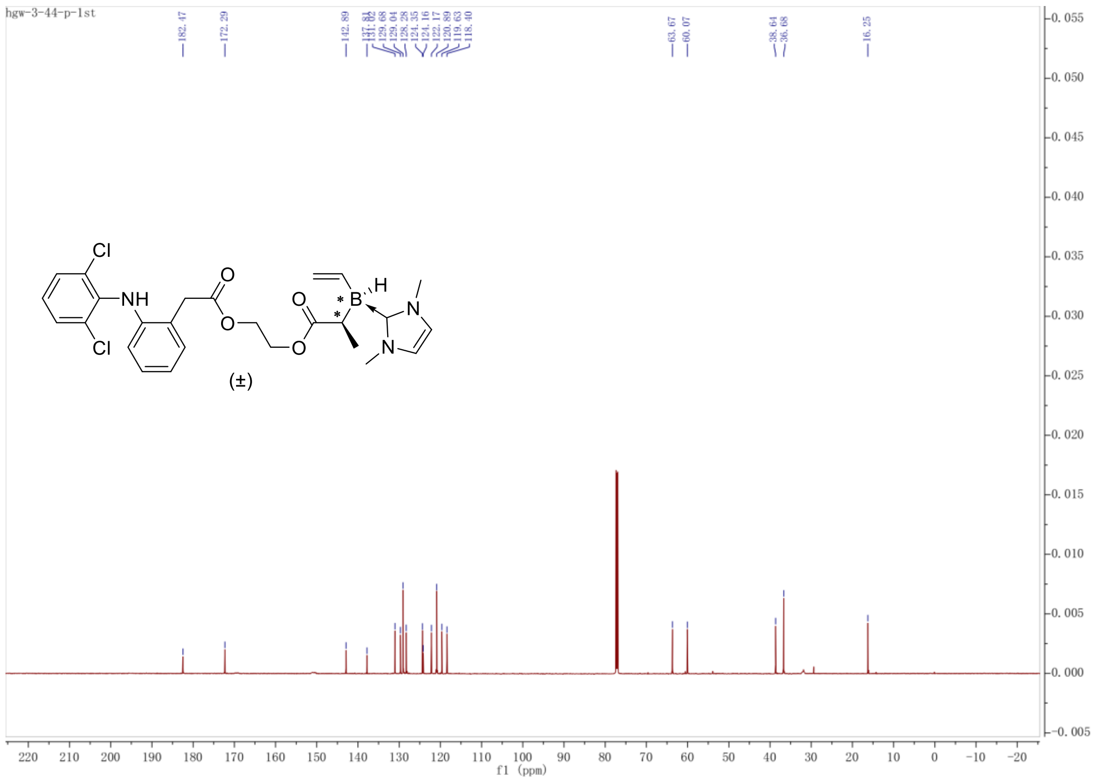
^{11}B NMR and ^{11}B {^{1}H} NMR of 60



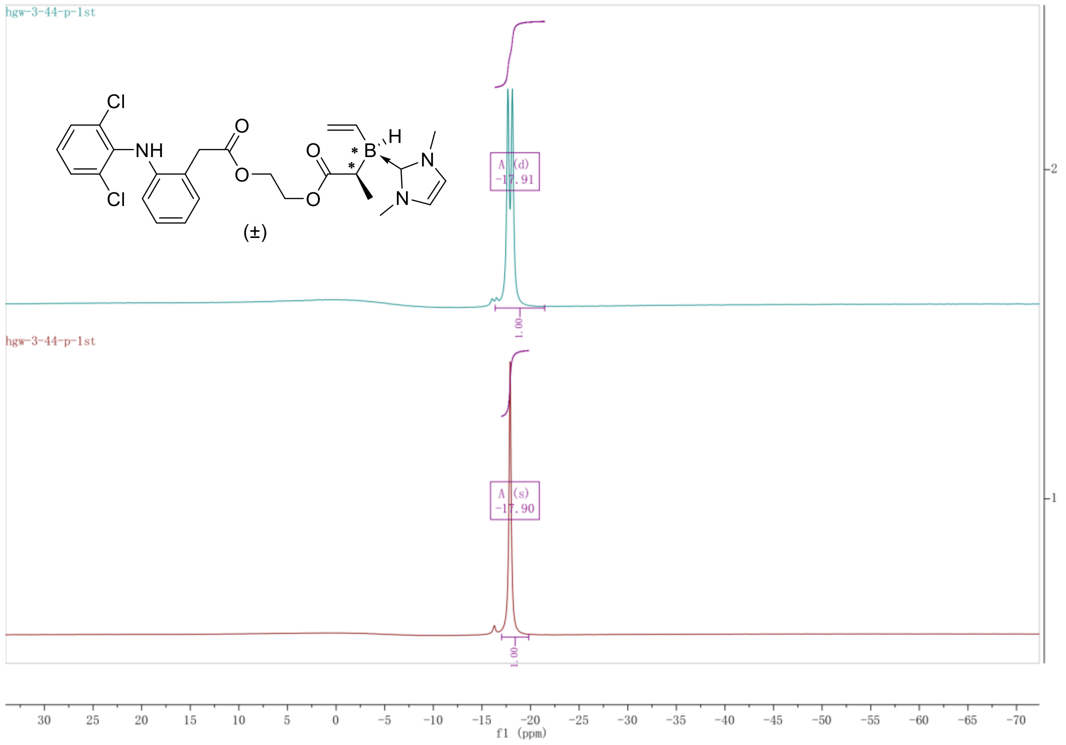
^{1}H NMR of 61



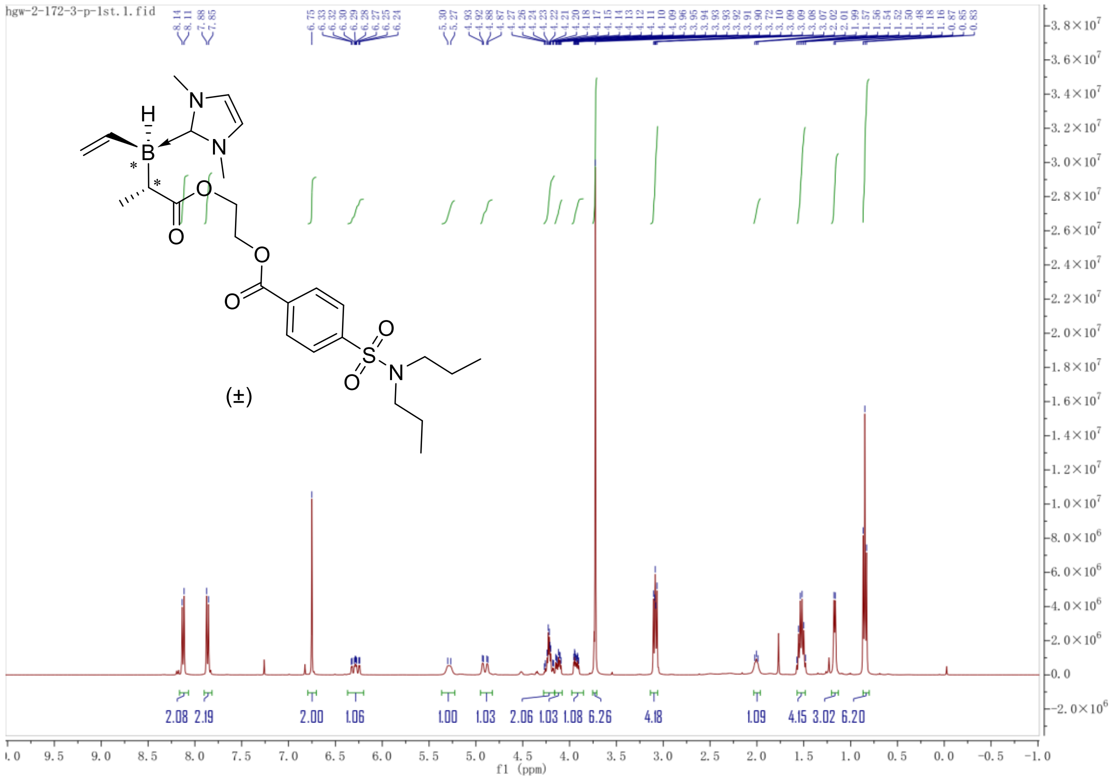
^{13}C NMR of 61



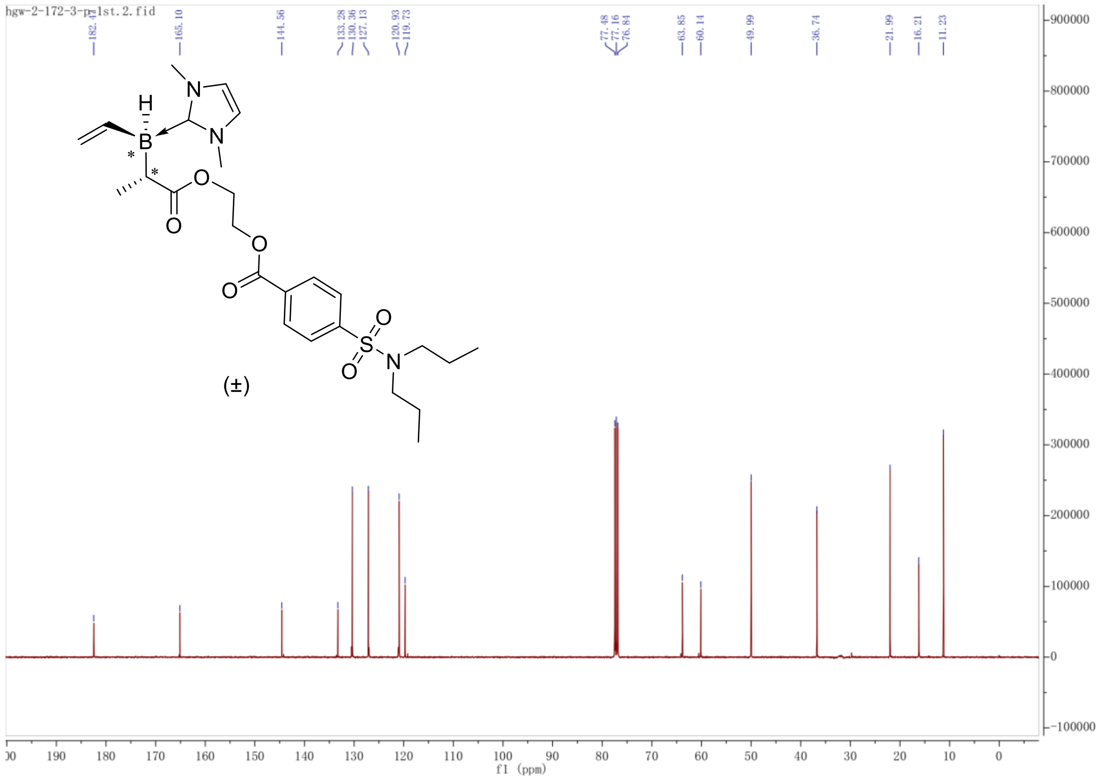
^{11}B NMR and ^{11}B {^{1}H} NMR of 61



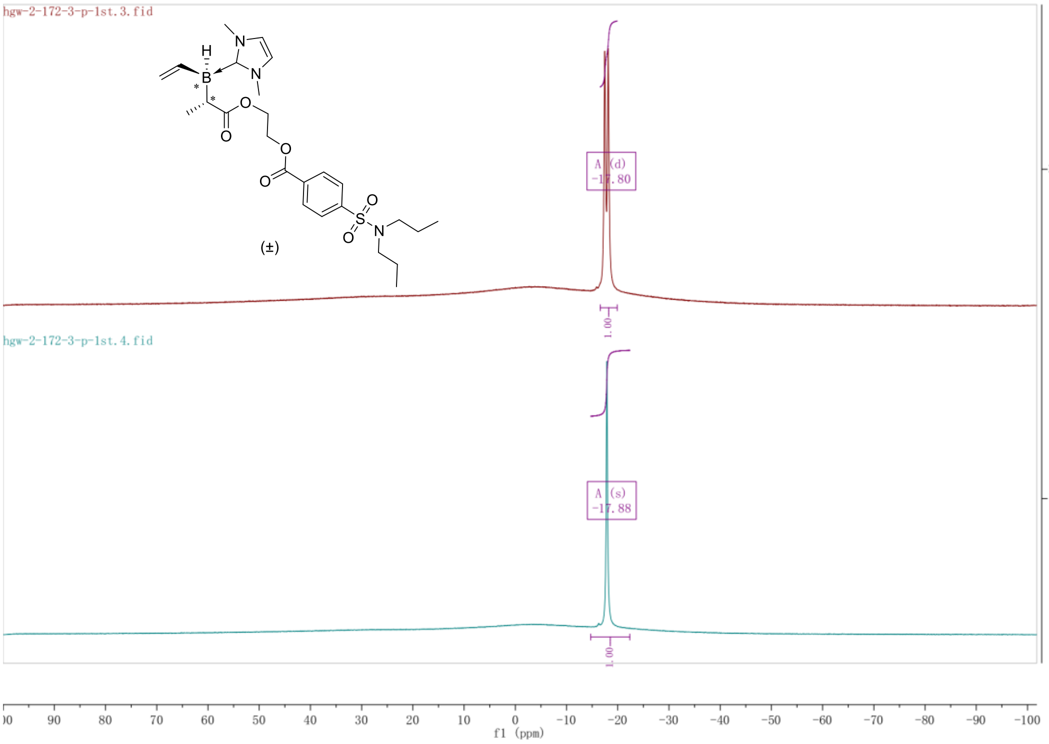
^{1}H NMR of 62



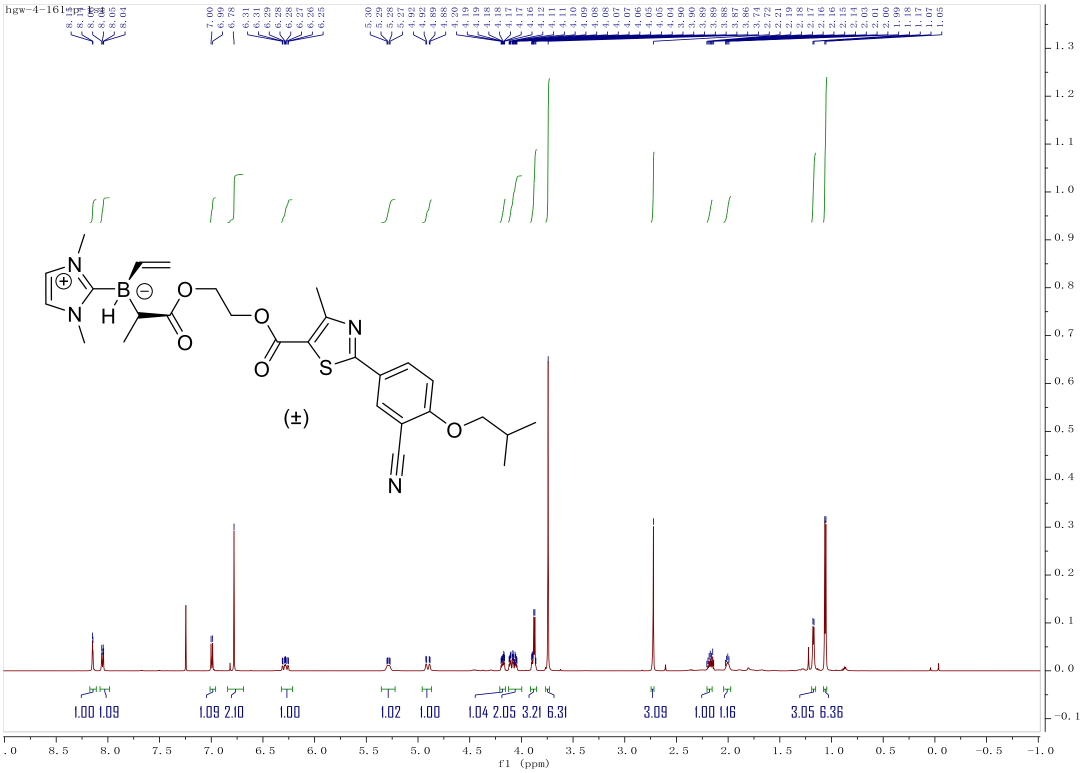
^{13}C NMR of 62



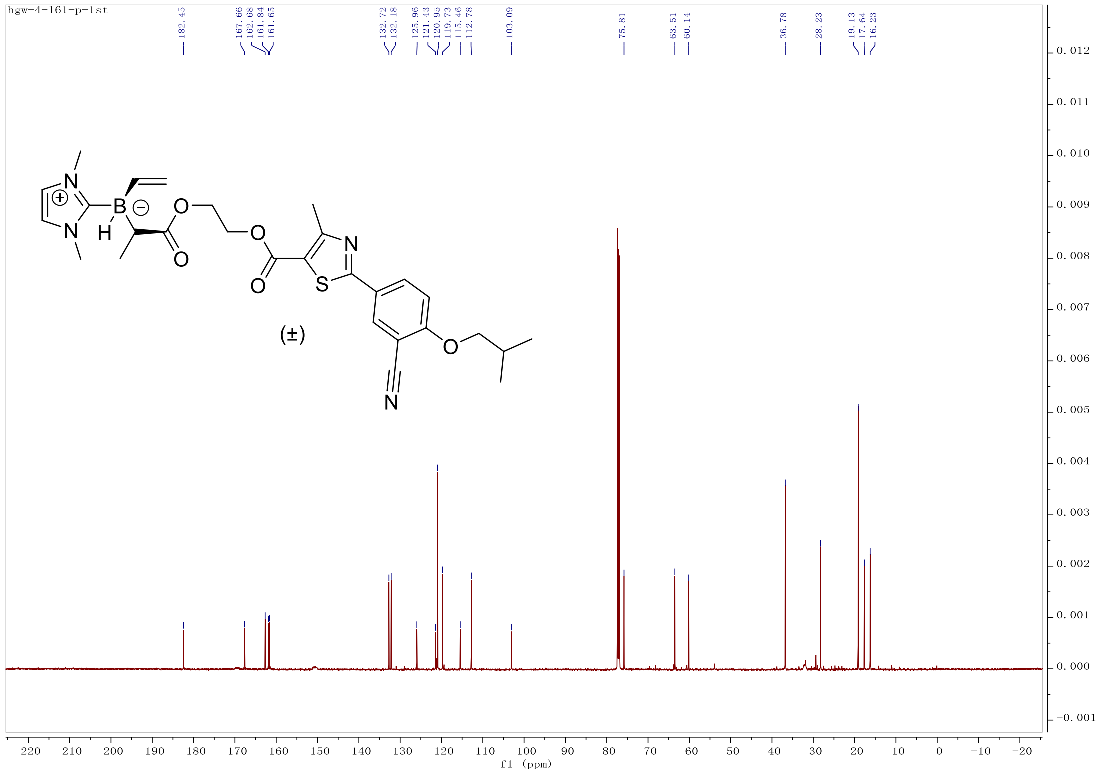
^{11}B NMR and ^{11}B {^{1}H} NMR of 62



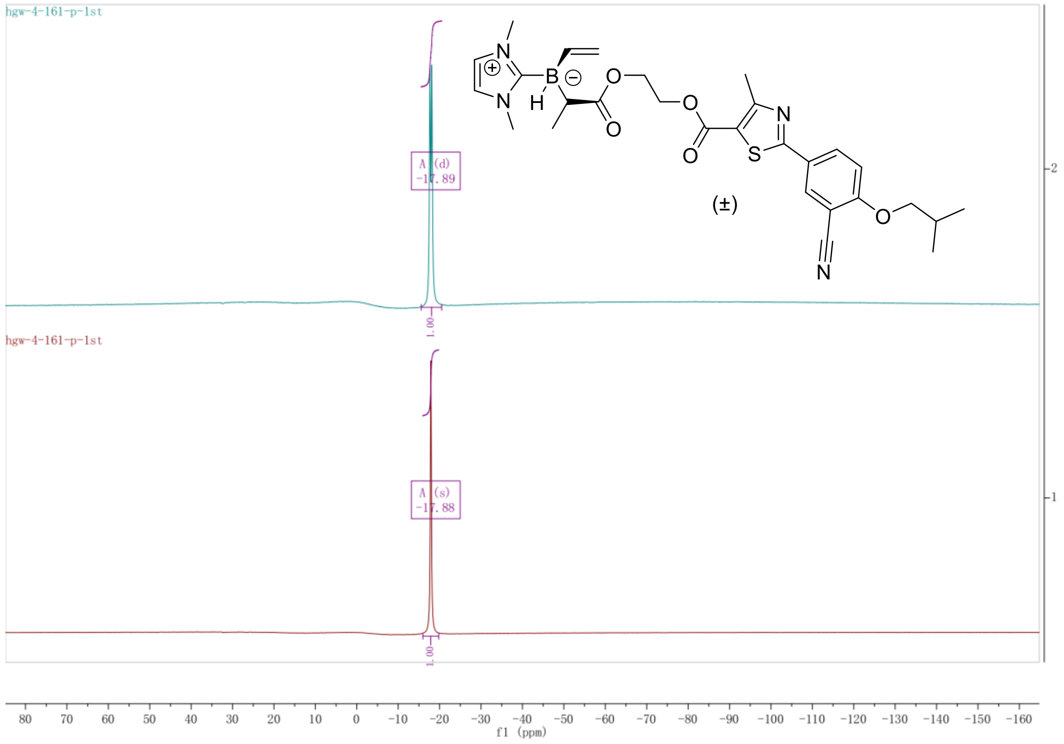
^{1}H NMR of 63



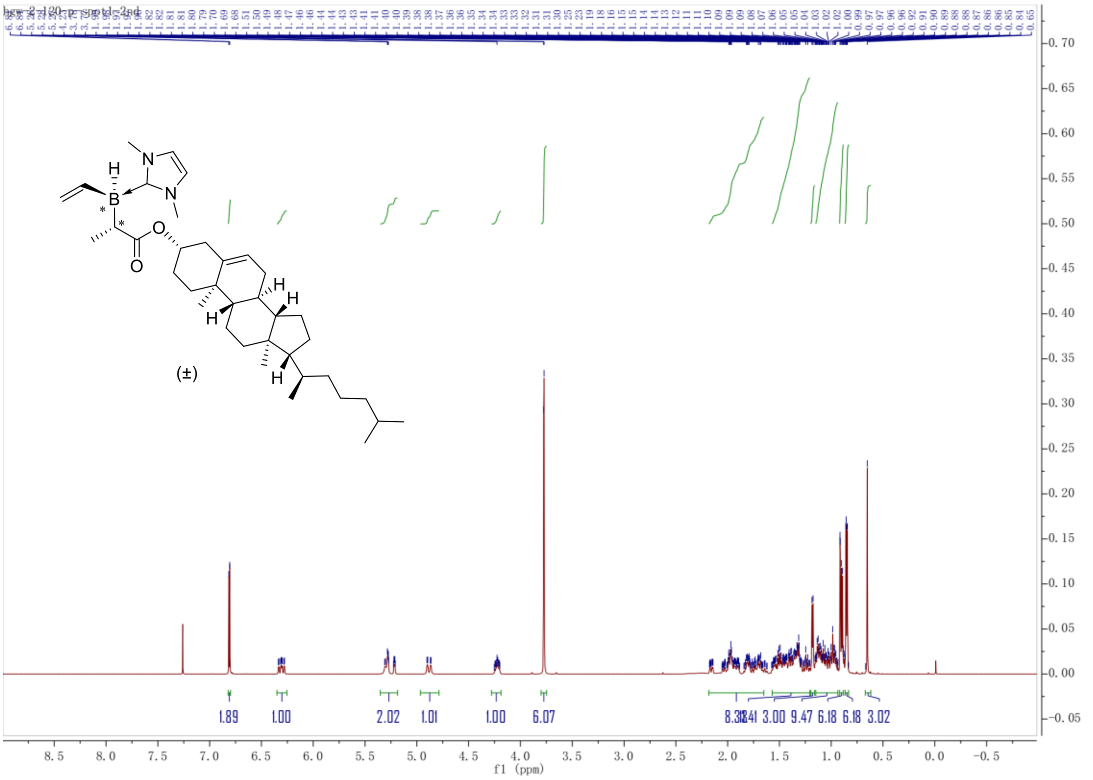
^{13}C NMR of 63



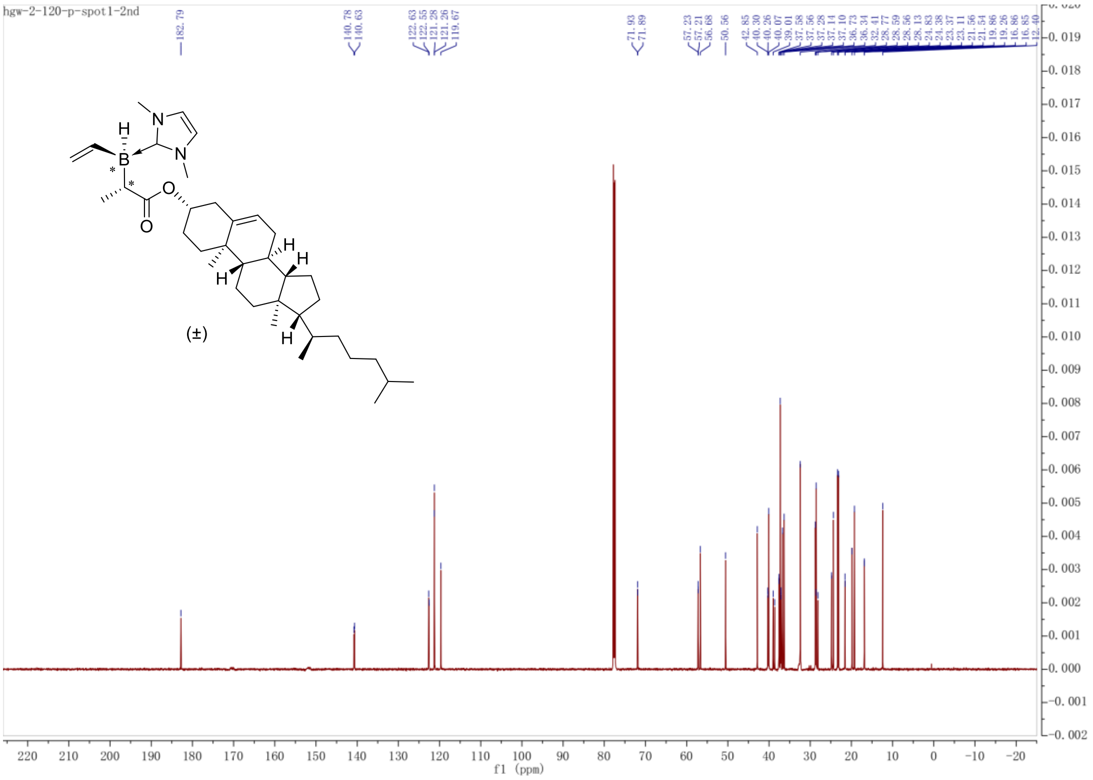
^{11}B NMR and ^{11}B {^{1}H} NMR of 63



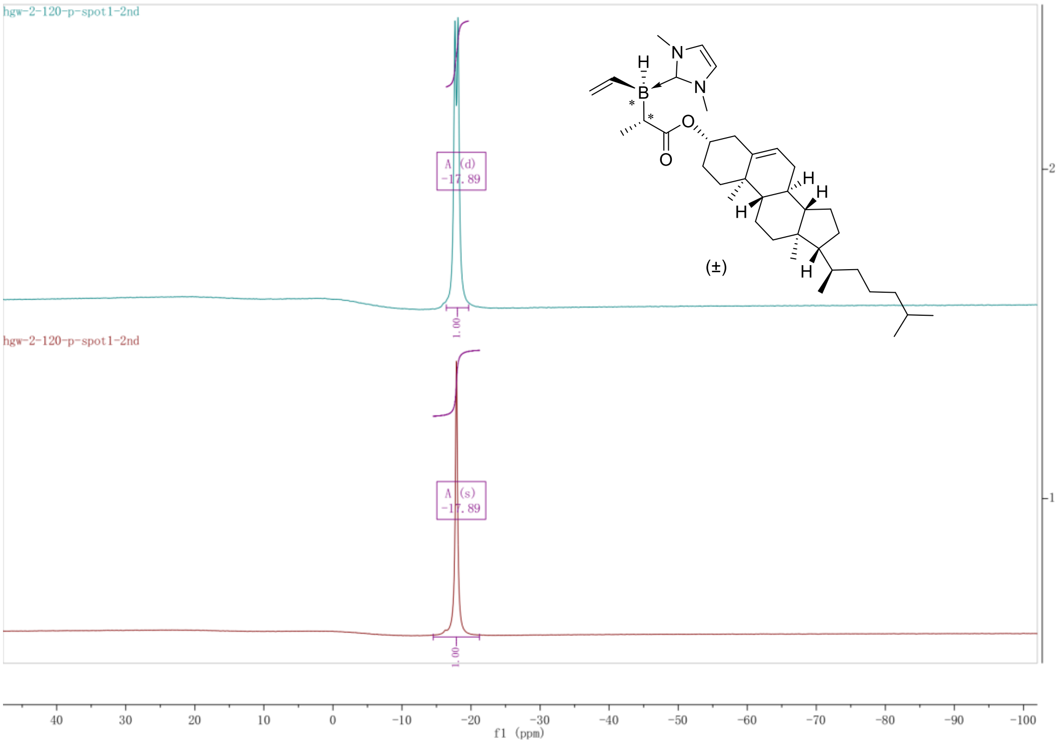
^{1}H NMR of 64



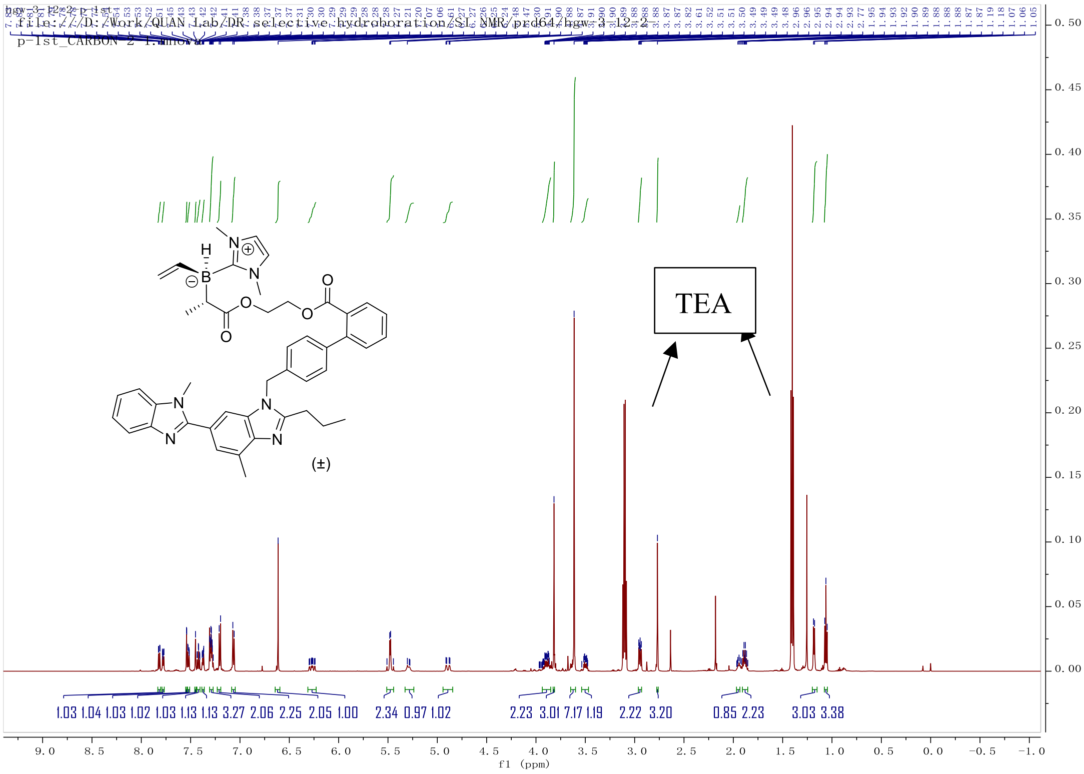
^{13}C NMR of 64



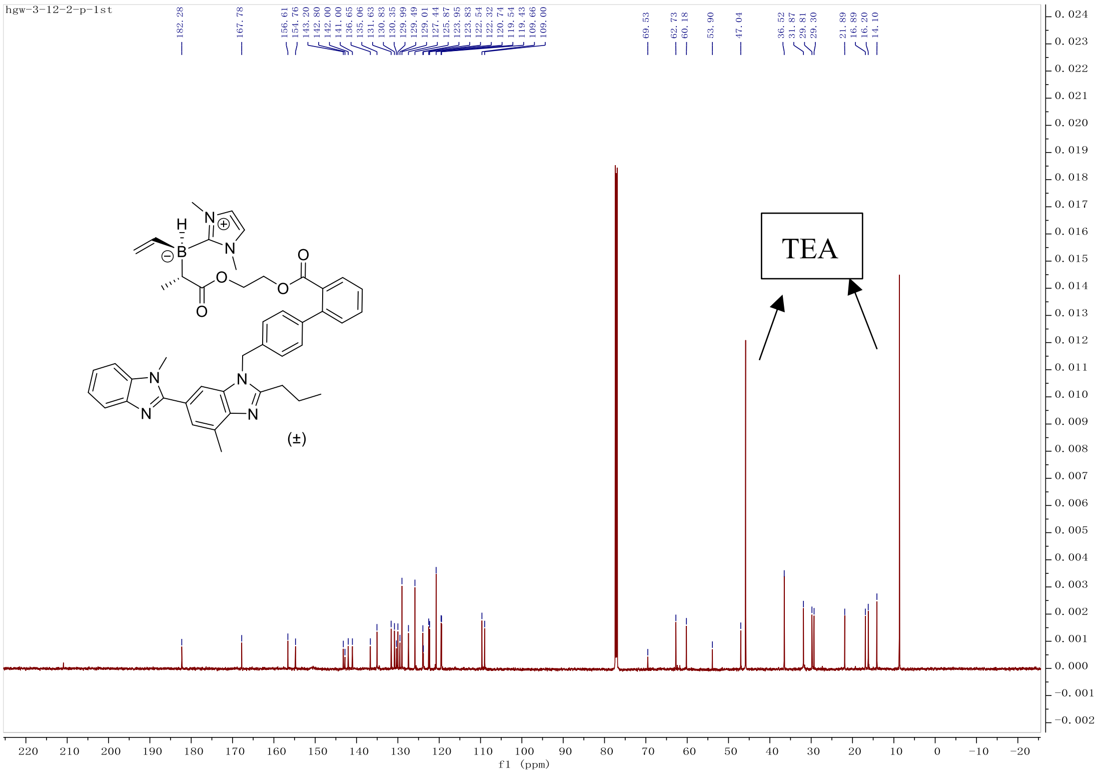
^{11}B NMR and ^{11}B {^{1}H} NMR of 64



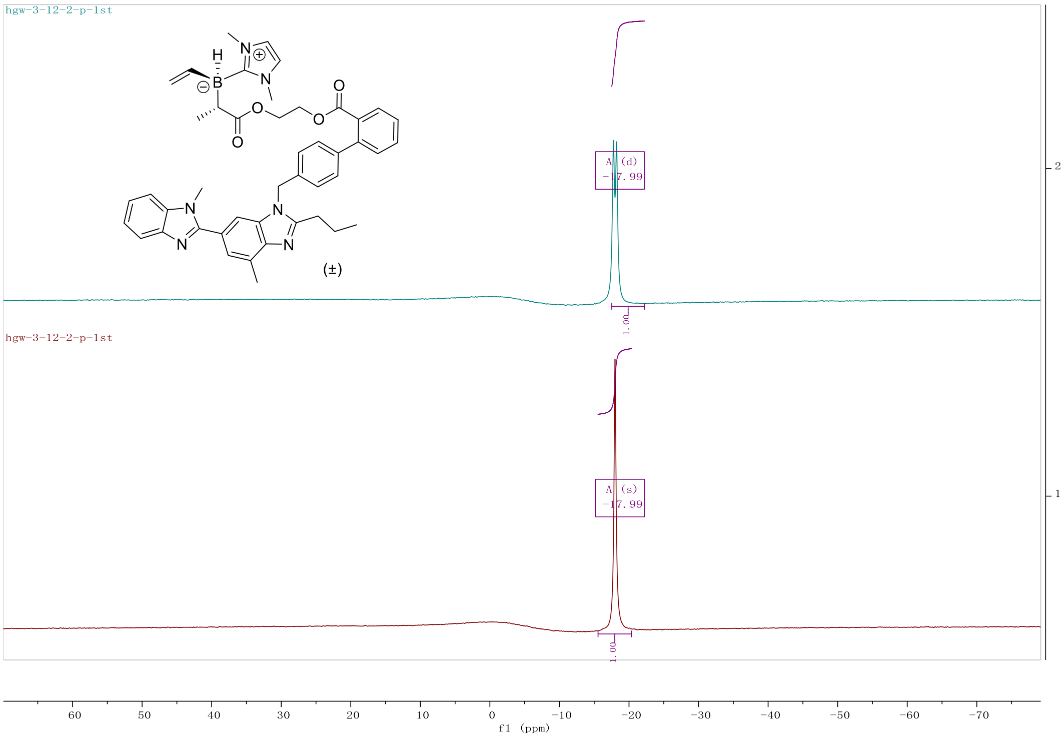
^{1}H NMR of 65



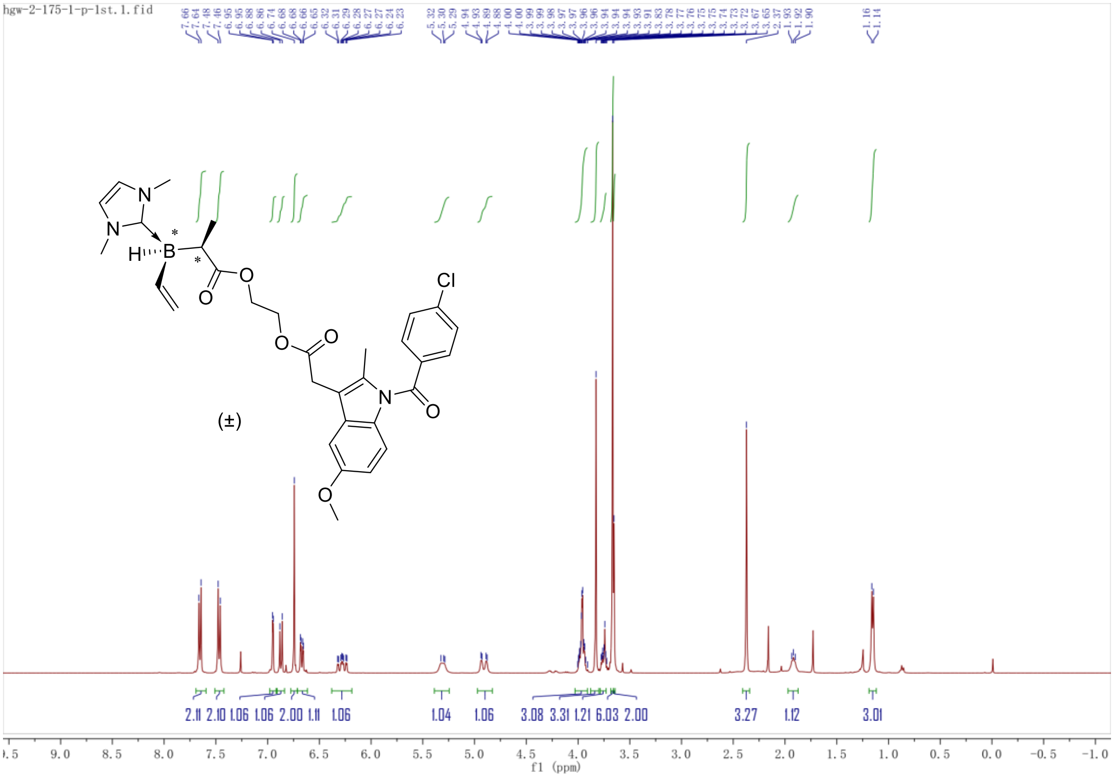
^{13}C NMR of 65



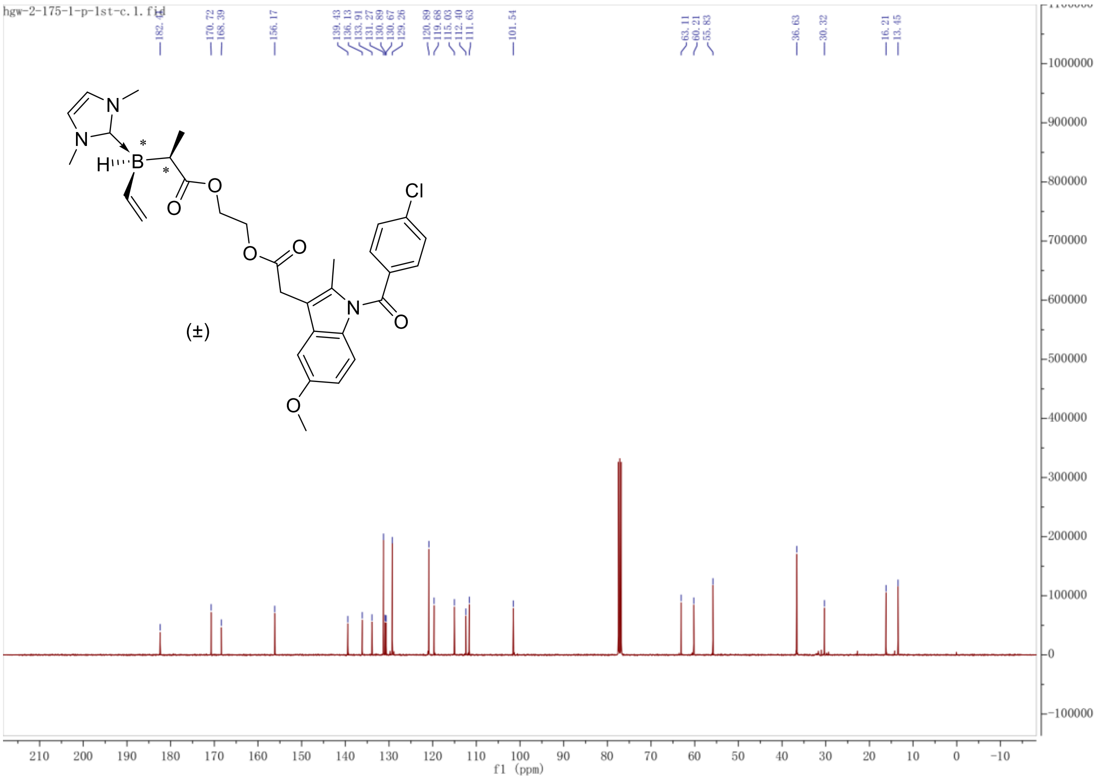
^{11}B NMR and ^{11}B {^{1}H} NMR of 65



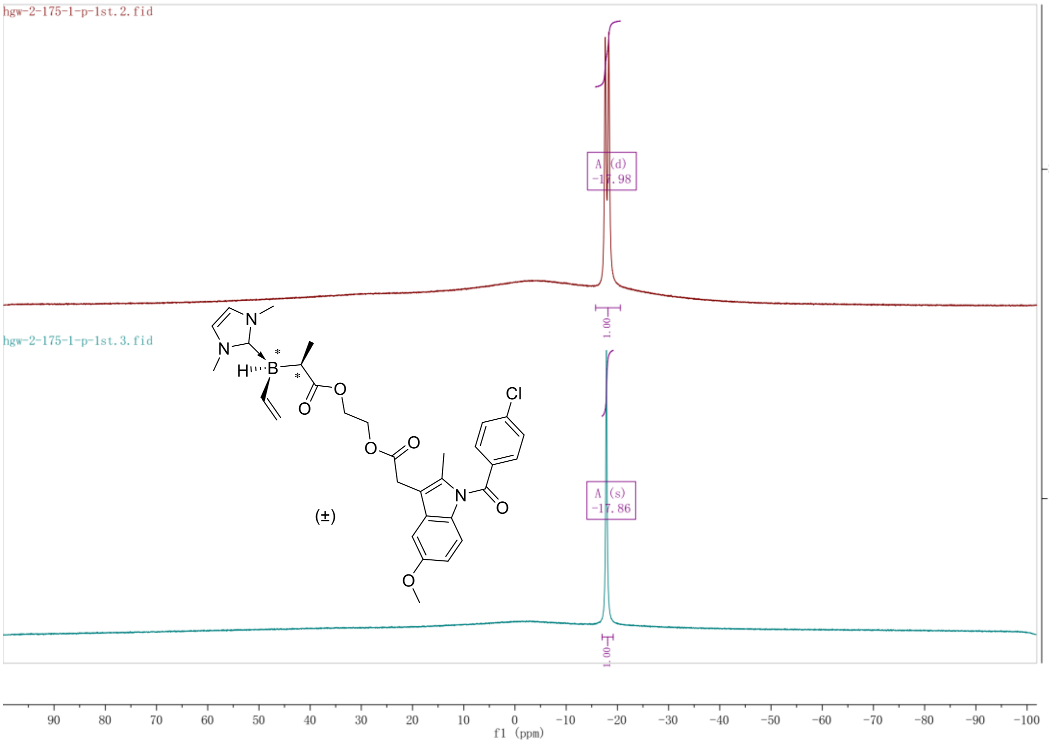
^{1}H NMR of 66



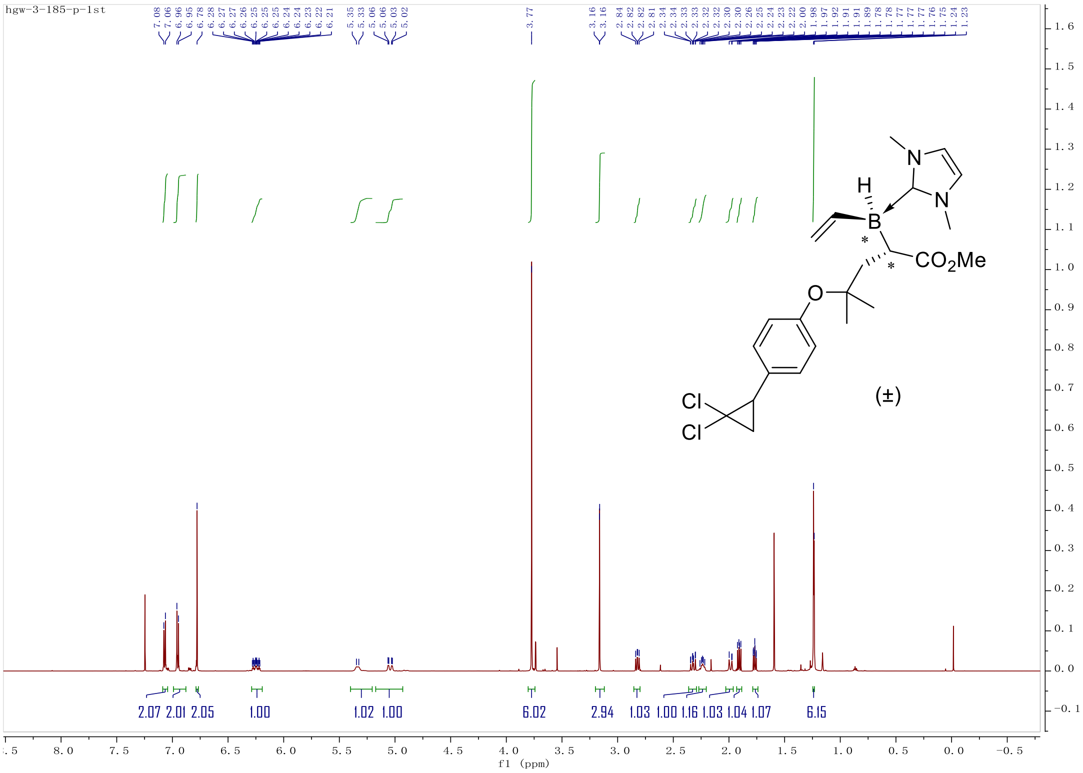
^{13}C NMR of 66



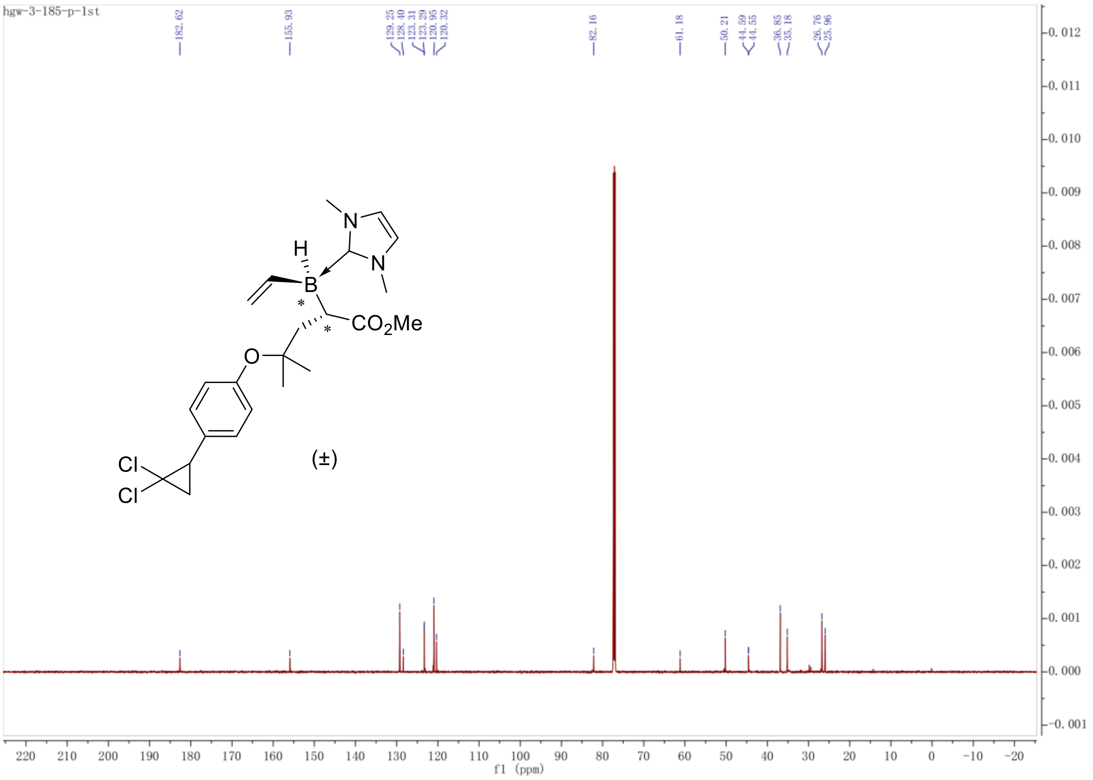
^{11}B NMR and ^{11}B {^1H} NMR of 66



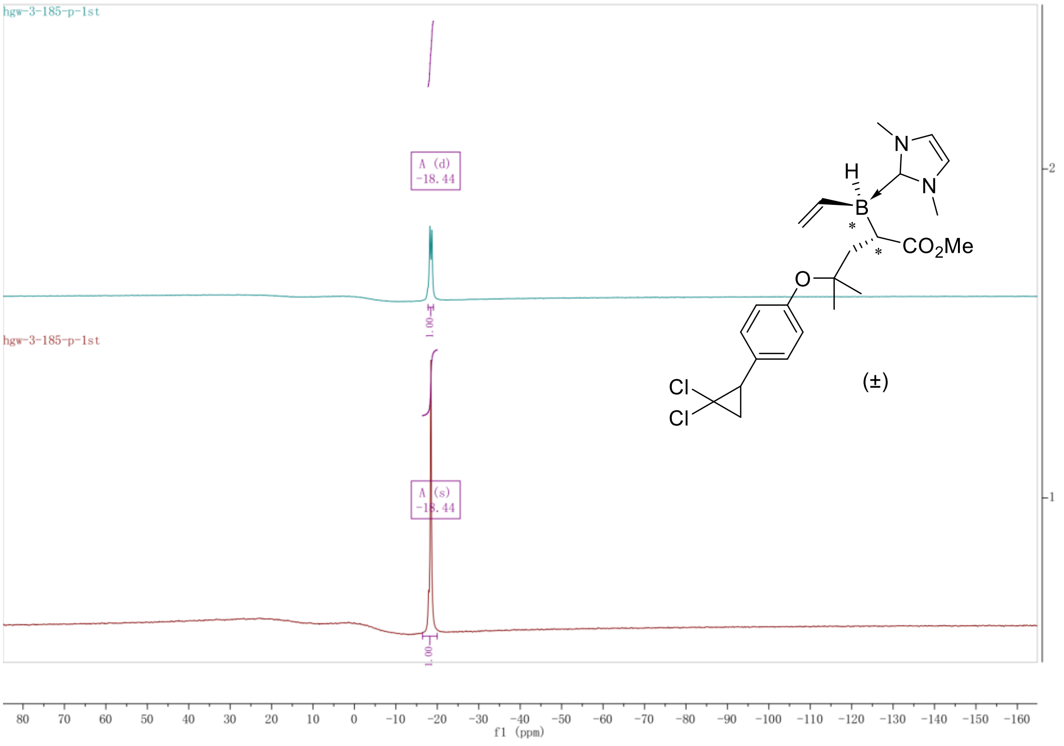
^1H NMR of 67



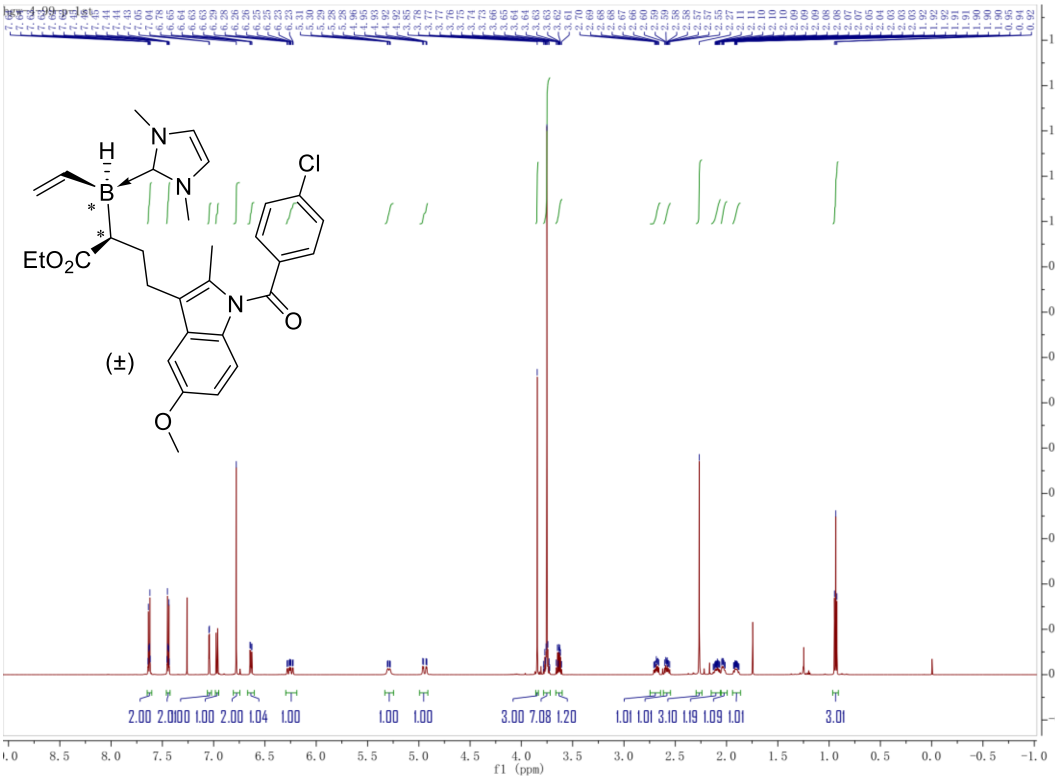
^{13}C NMR of 67



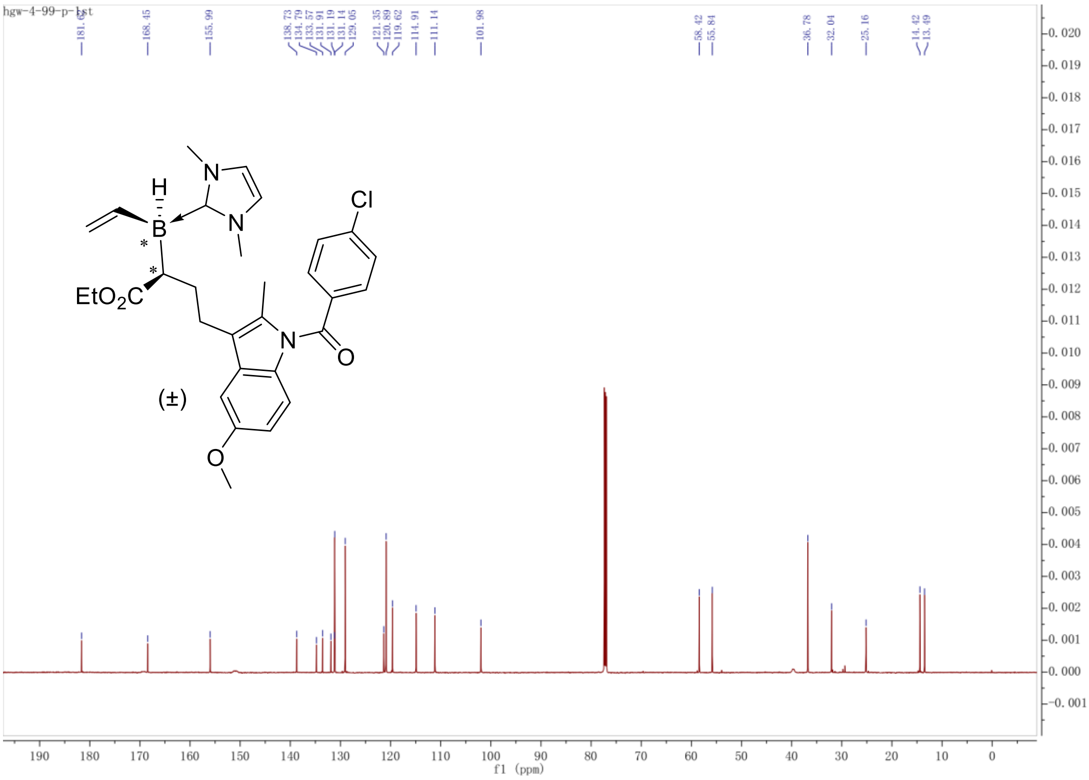
^{11}B NMR and ^{11}B {^{1}H} NMR of 67



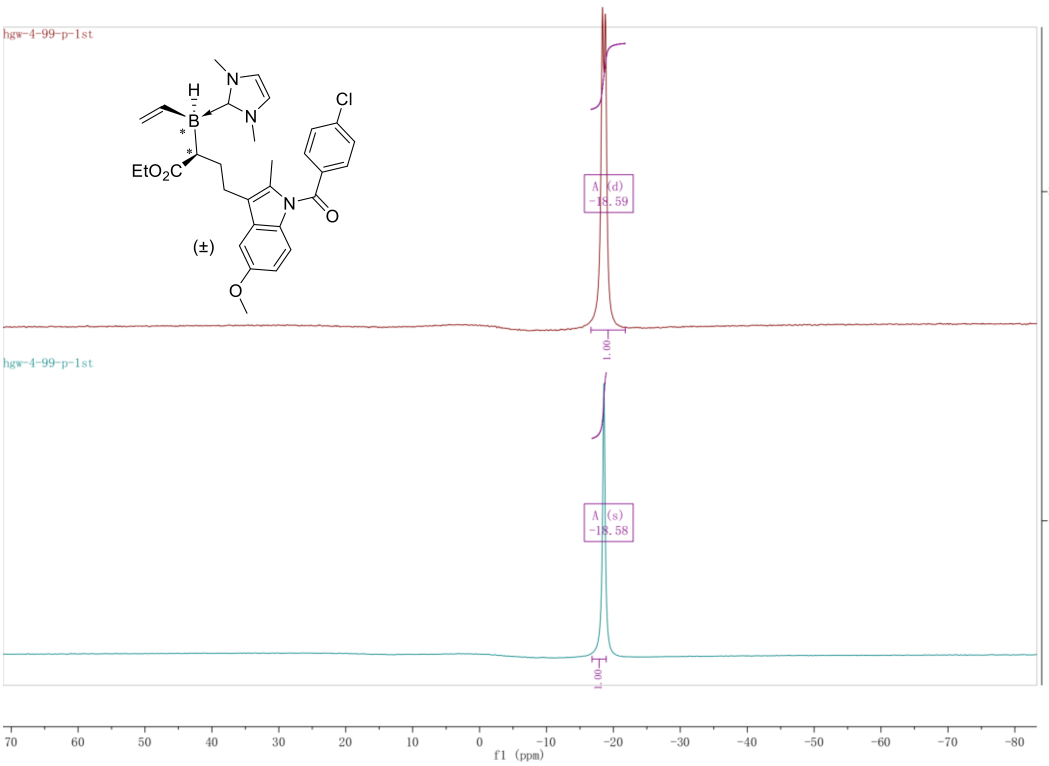
^{1}H NMR of 68



^{13}C NMR of 68



^{11}B NMR and ^{11}B {^{1}H} NMR of 68



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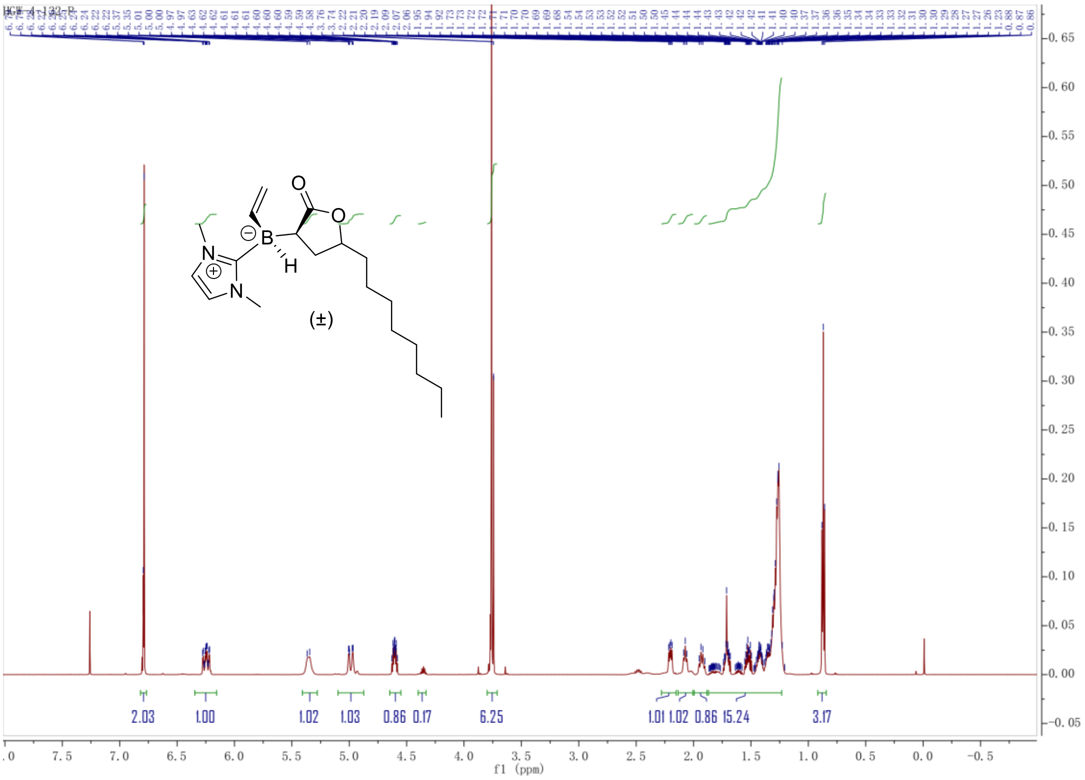
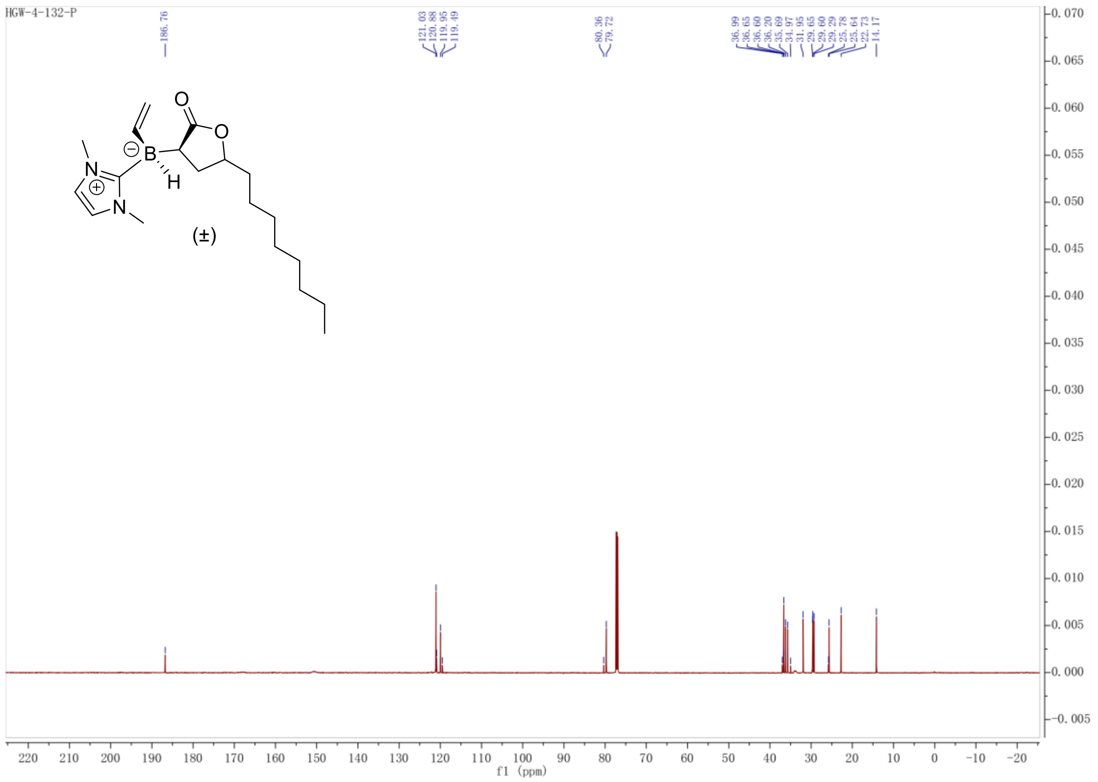
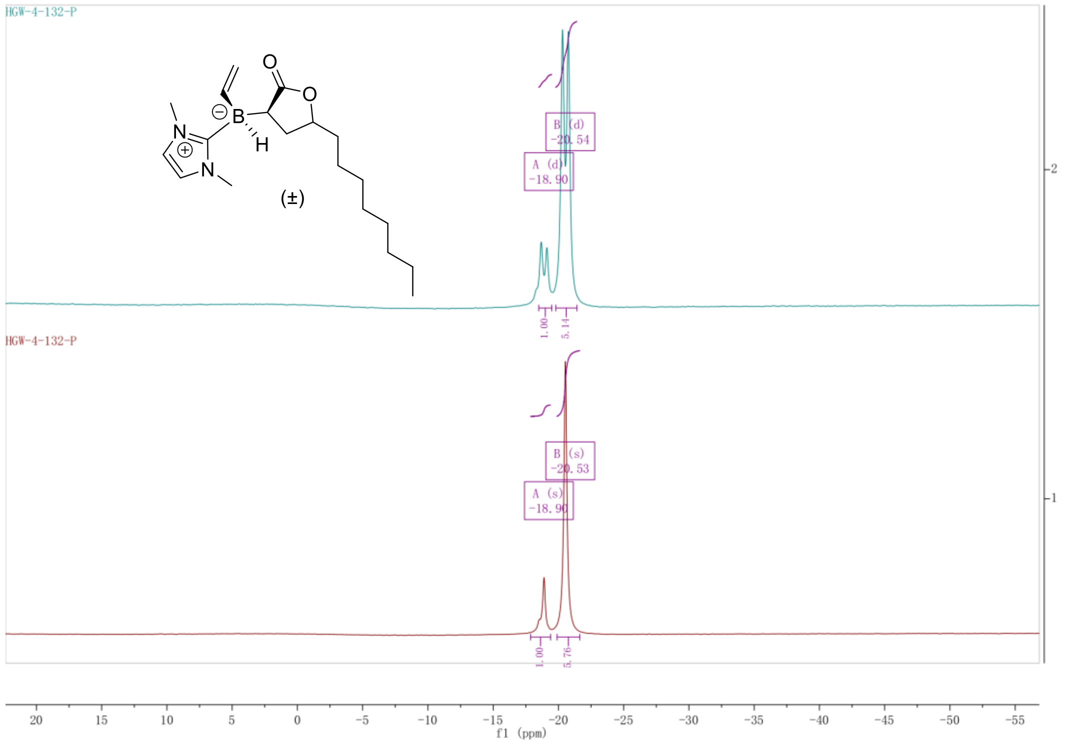


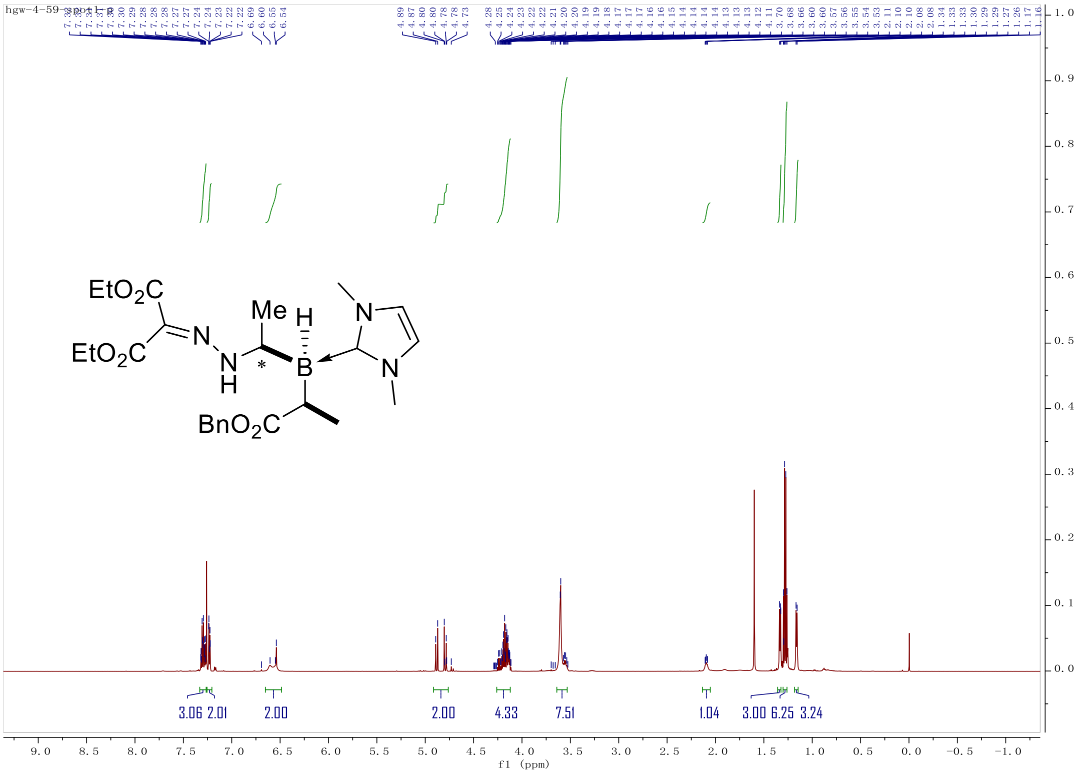
^{13}C NMR of 69

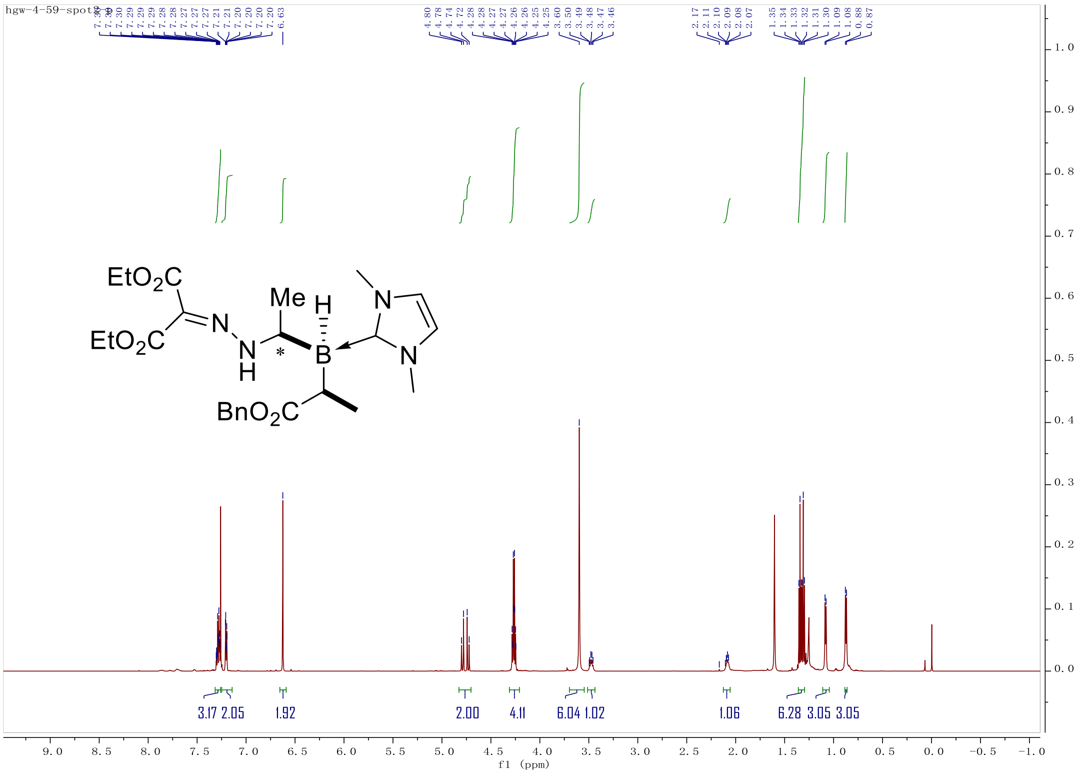


^{11}B NMR and ^{11}B {^{1}H} NMR of 69



^{1}H NMR of 70


hgw-4-59-spot1-p
7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.28 7.28 7.28 7.27 7.27 7.24 7.24 7.23 7.22 7.22 6.69 6.60 6.55 6.54
4.89 4.87 4.80 4.80 4.78 4.78 4.73
4.28 4.25 4.24 4.23 4.22 4.22 4.21 4.20 4.20 4.19 4.19 4.18 4.17 4.17 4.17 4.16 4.16 4.15 4.14 4.14 4.14 4.14 4.13 4.13 4.13 4.12 4.11 3.70 3.68 3.66 3.60 3.60 3.57 3.56 3.55 3.54 3.53 2.11 2.10 2.10 2.08 2.08 1.34 1.33 1.33 1.30 1.29 1.29 1.27 1.26 1.17 1.16
EtO2C
EtO2C
N
N
H
Me
H
*
B
N
N
BnO2C
3.06 2.01
2.00
2.00
4.33
7.51
1.04
3.00 6.25 3.24
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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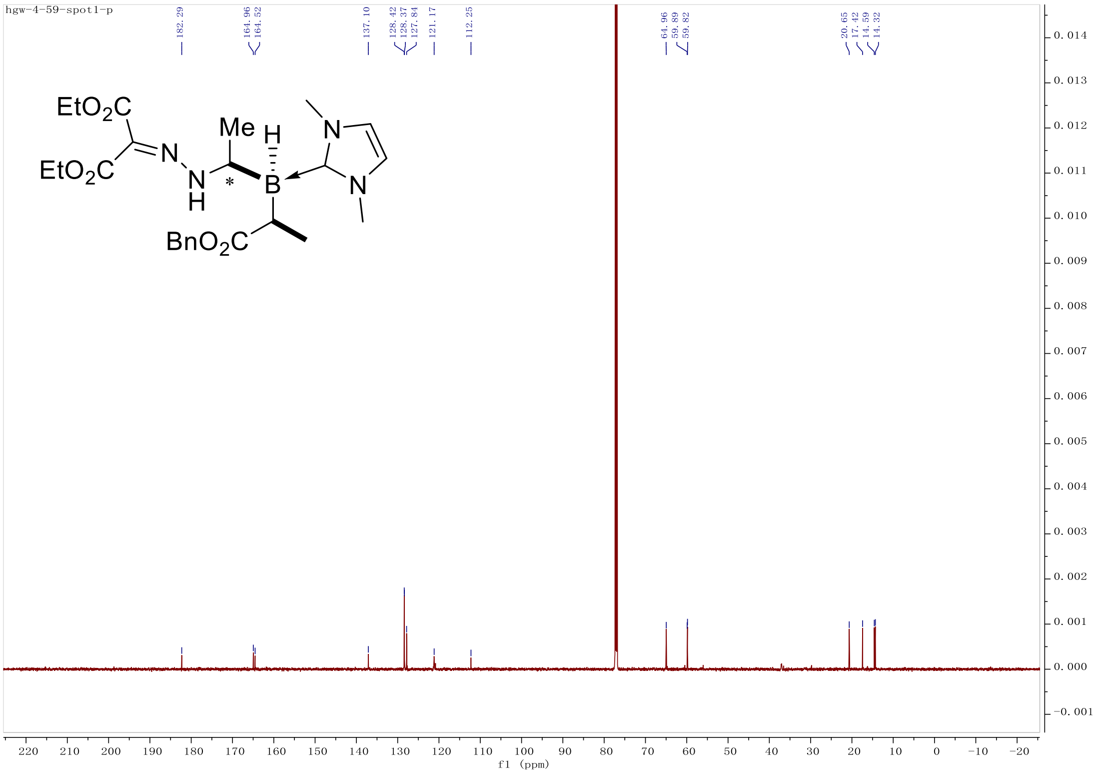
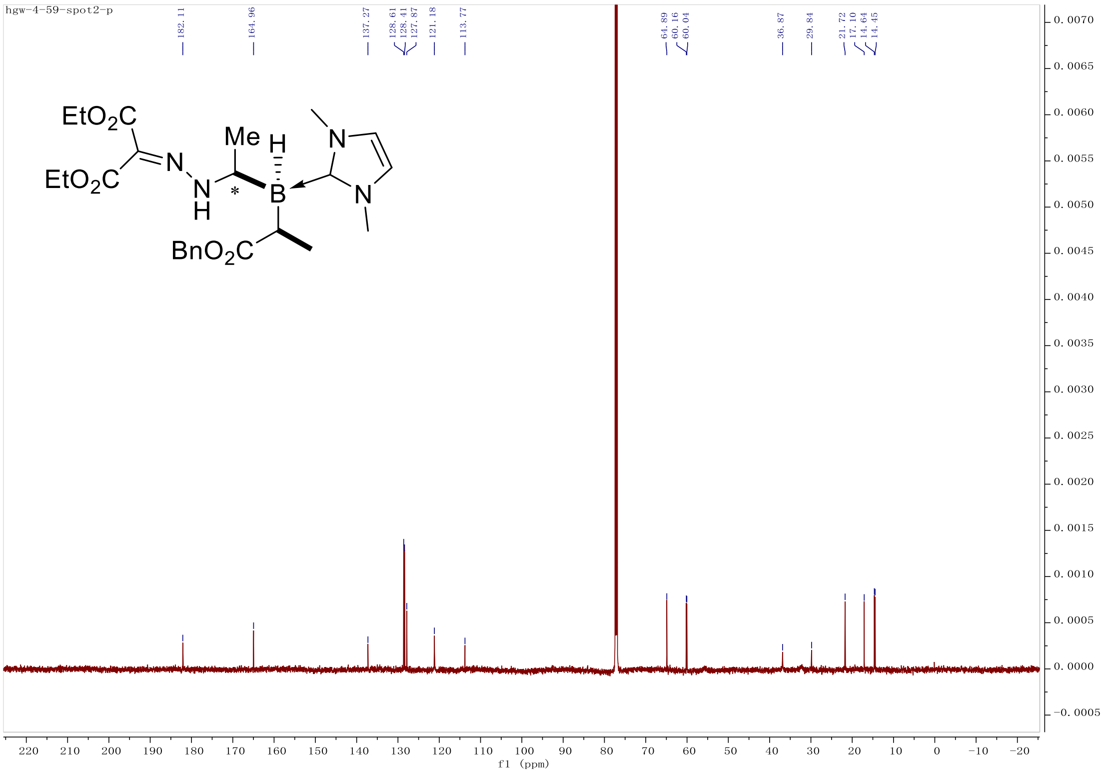
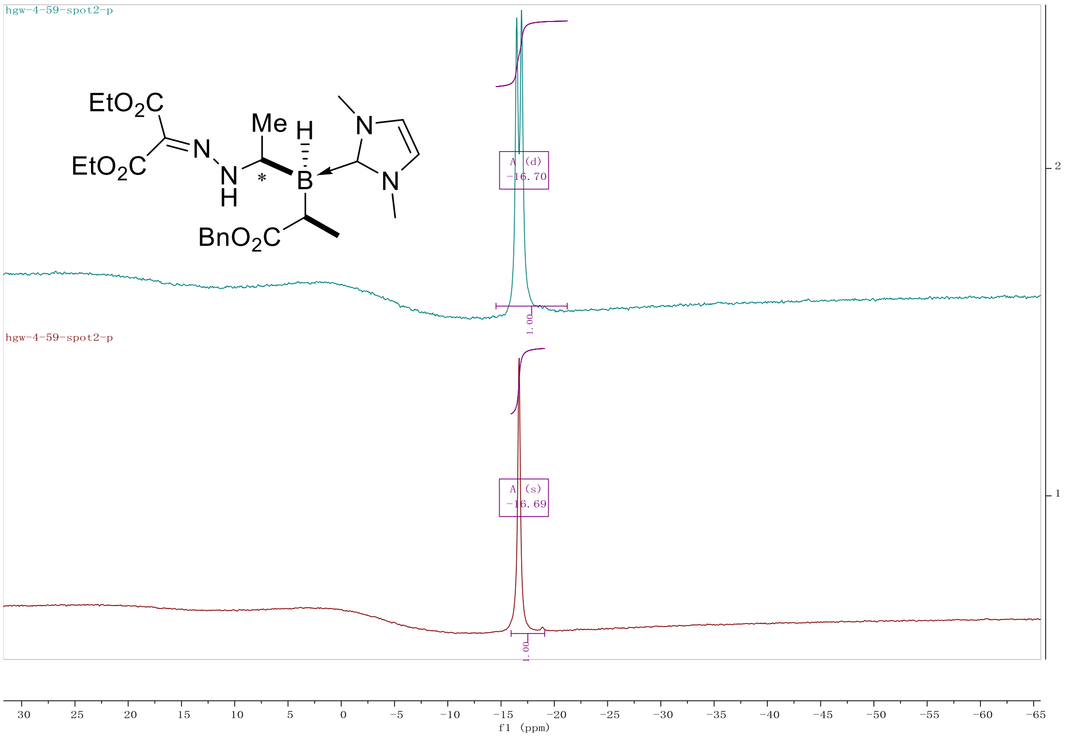
4.80 4.78 4.74 4.72 4.28 4.28 4.27 4.27 4.26 4.26 4.25 4.25 3.60 3.50 3.49 3.48 3.47 3.46
2.17 2.11 2.10 2.09 2.08 2.07
1.35 1.34 1.33 1.32 1.31 1.30 1.09 1.08 0.88 0.87
EtO2C
EtO2C
N
N
H
Me
H
*
B
N
N
BnO2C
3.17 2.05
1.92
2.00
4.11
6.04 1.02
1.06
6.28 3.05 3.05
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

^{13}C NMR of 70

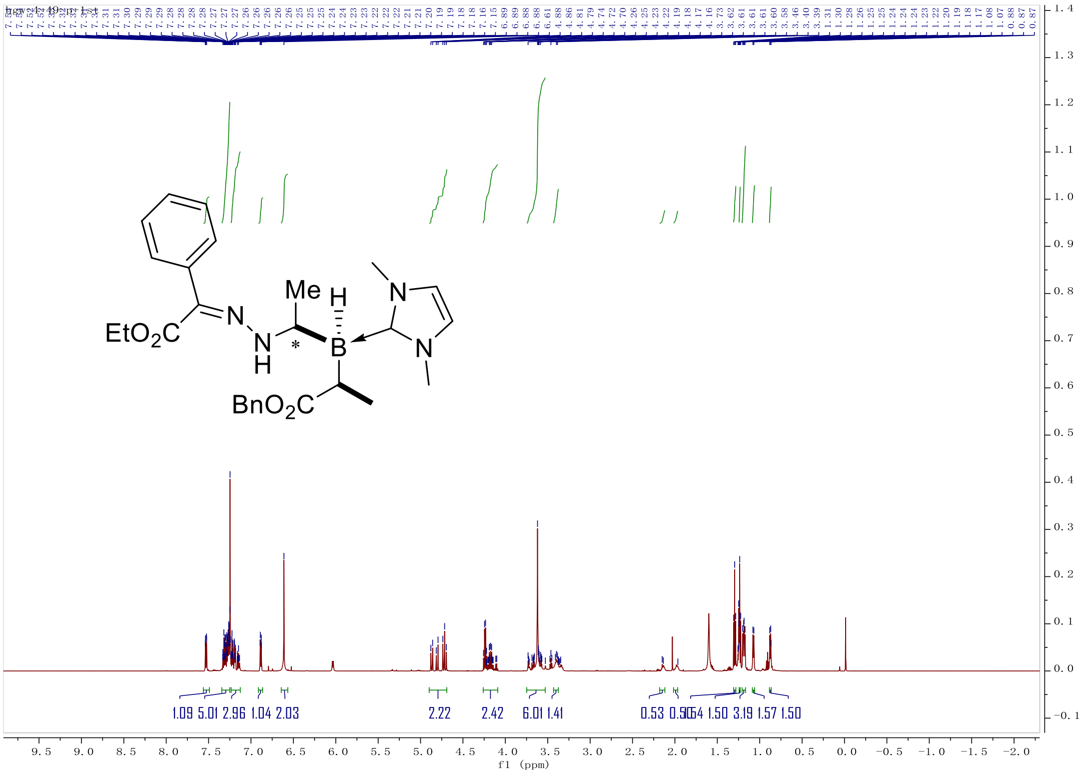

hgw-4-59-spot1-p
182.29
164.96
164.52
137.10
128.42
128.37
127.84
121.17
112.25
64.96
59.89
59.82
20.65
17.42
14.59
14.32
EtO2C
EtO2C
N
N
H
Me
H
B
*
N
N
BnO2C
f1 (ppm)


hgw-4-59-spot2-p
182.11
164.96
137.27
128.61
128.41
127.87
121.18
113.77
64.89
60.16
60.04
36.87
29.84
21.72
17.10
14.64
14.45
EtO2C
EtO2C
N
N
H
Me
H
B
*
N
N
BnO2C
f1 (ppm)

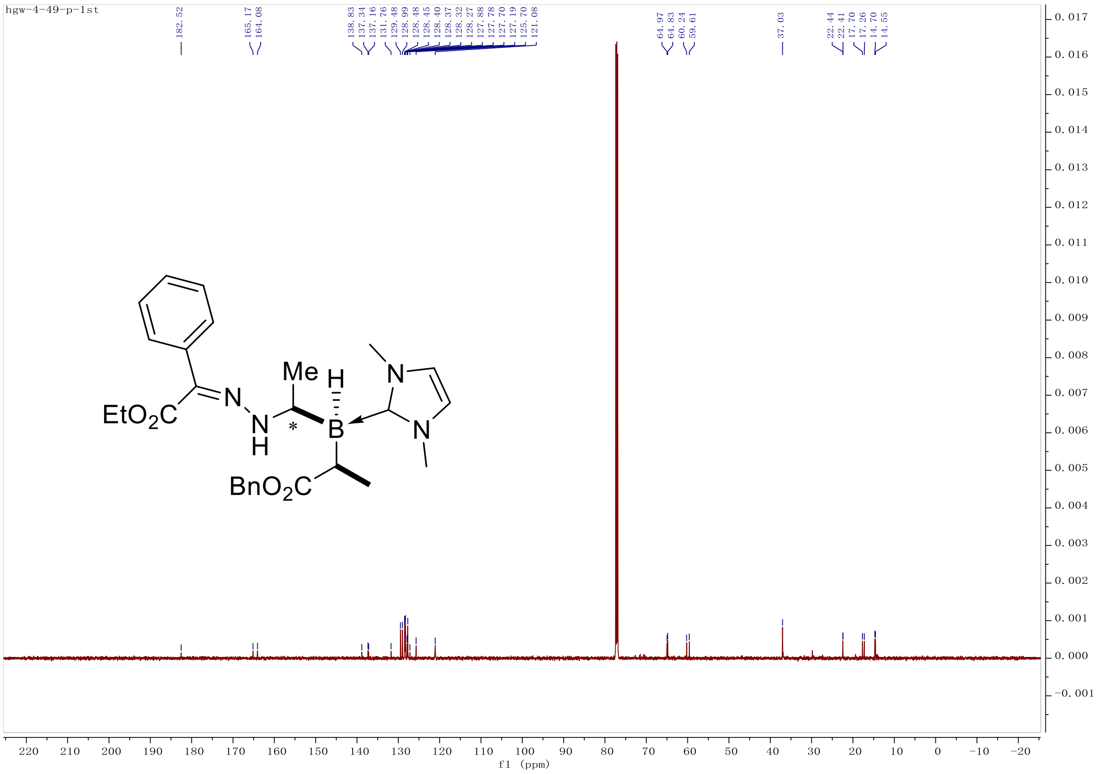
^{11}B NMR and ^{11}B {^{1}H} NMR of 70



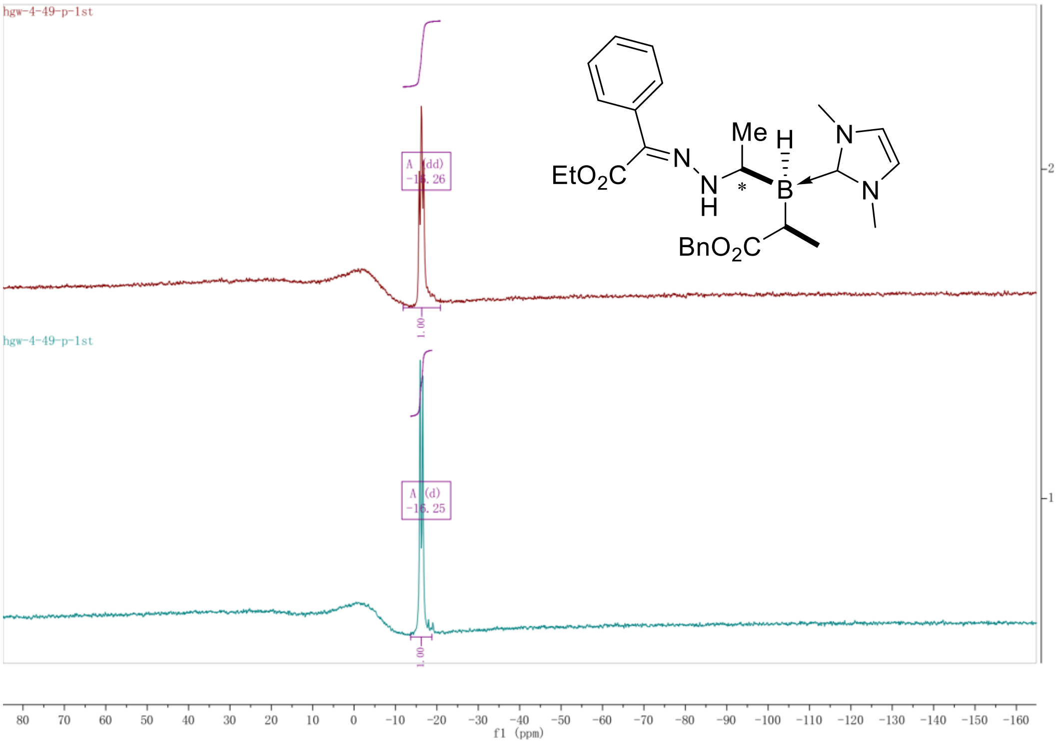
^{1}H NMR of 71



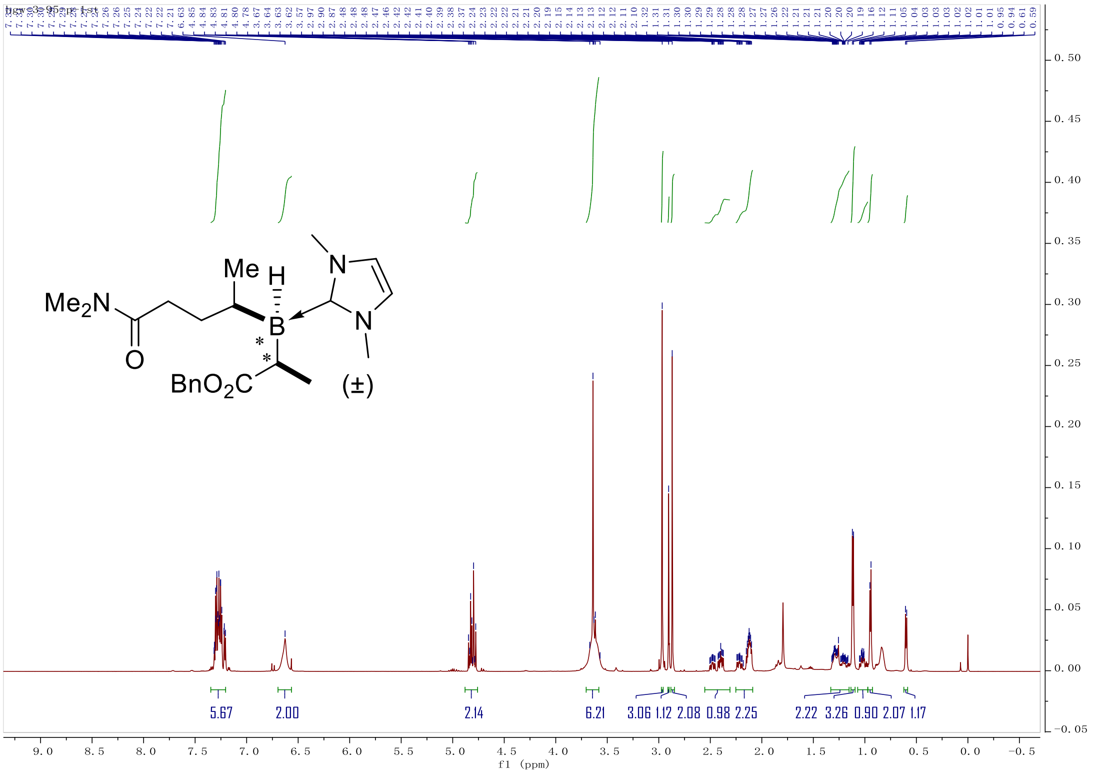
^{13}C NMR of 71



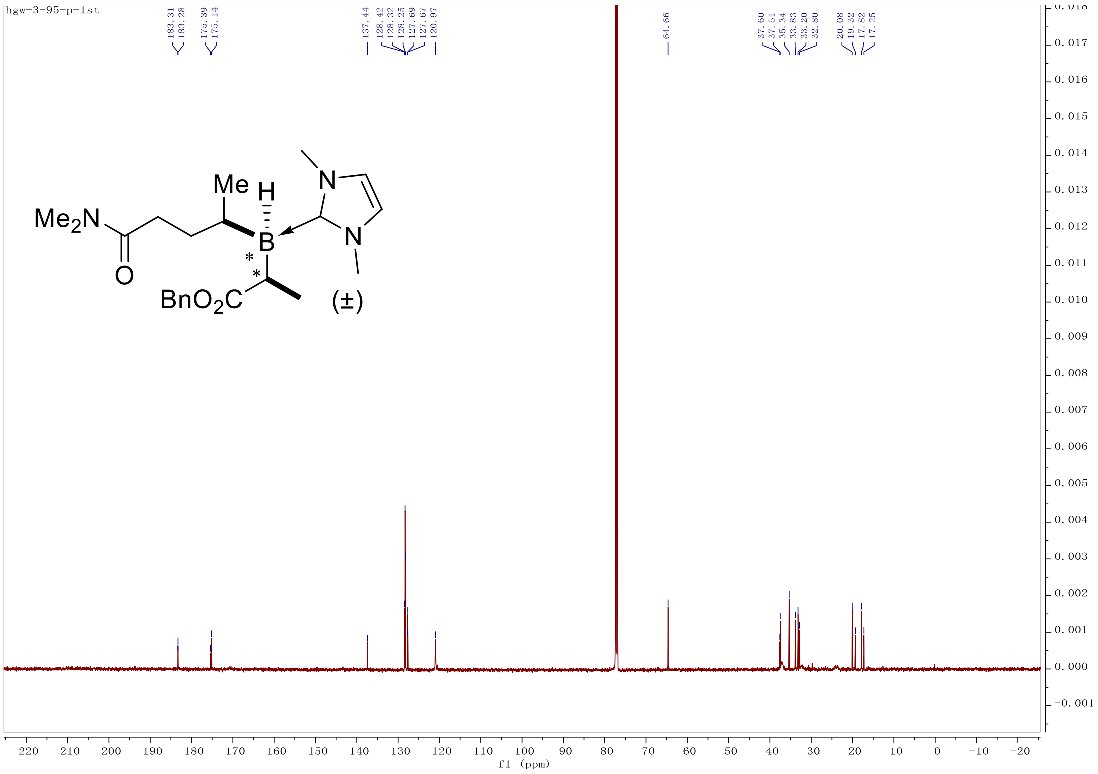
^{11}B NMR and ^{11}B {^{1}H} NMR of 71



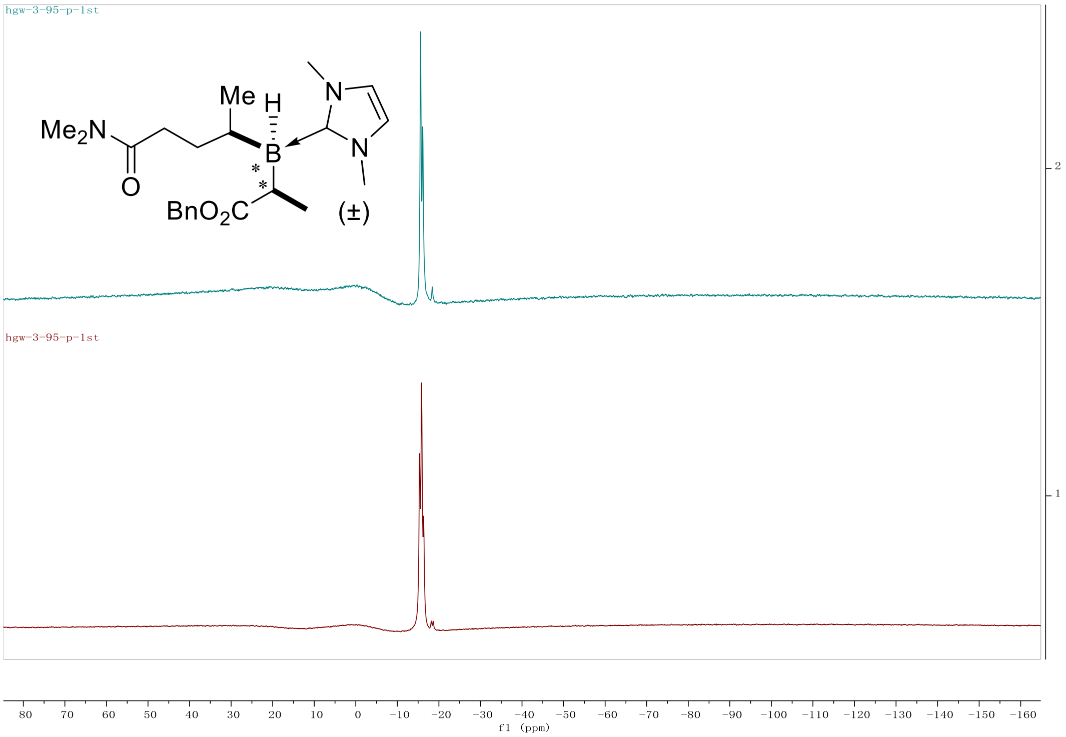
^{1}H NMR of 72



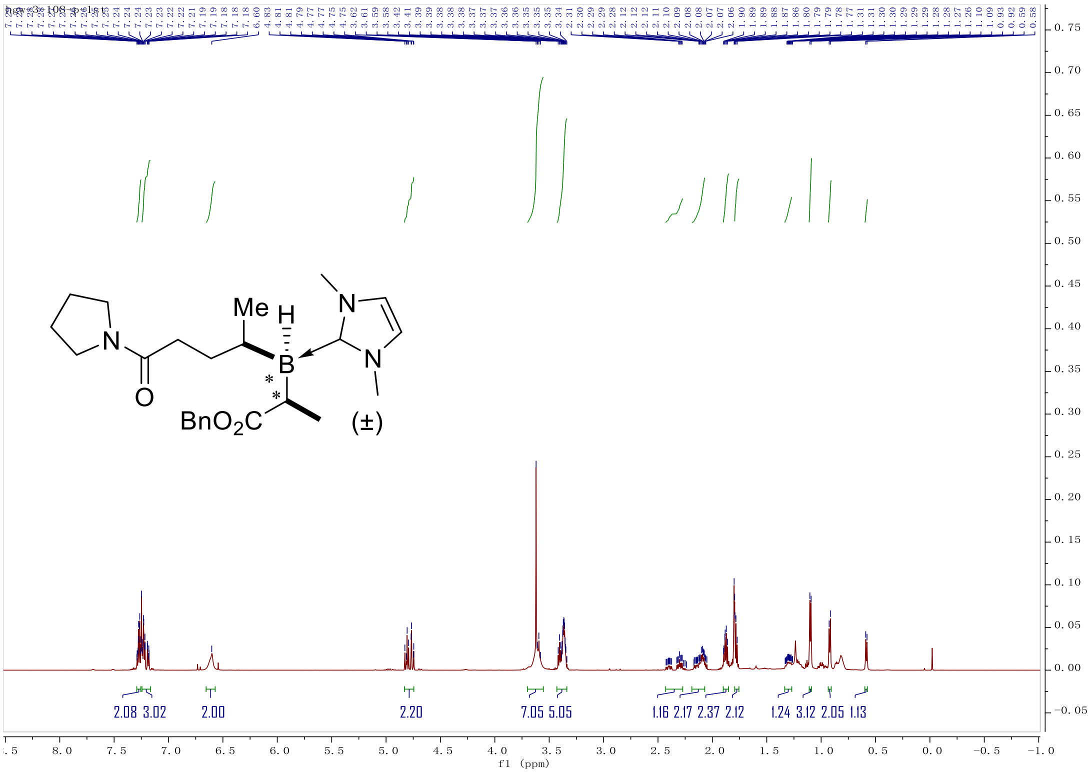
^{13}C NMR of 72



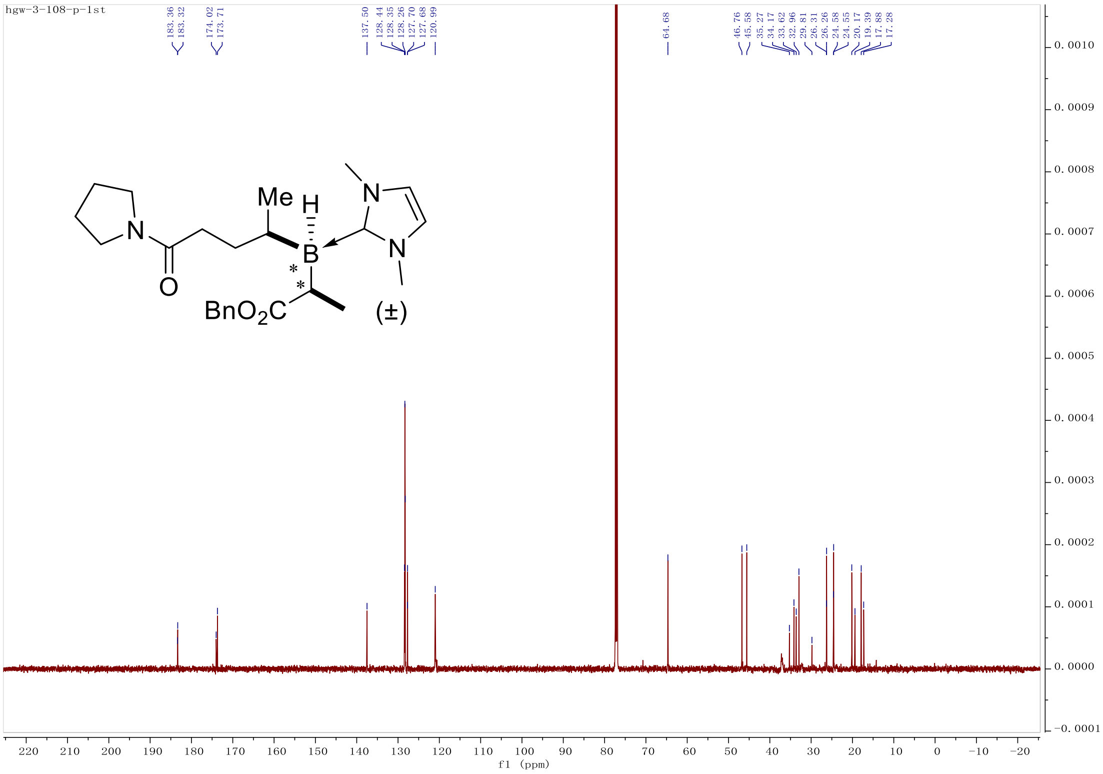
^{11}B NMR and ^{11}B {^{1}H} NMR of 72



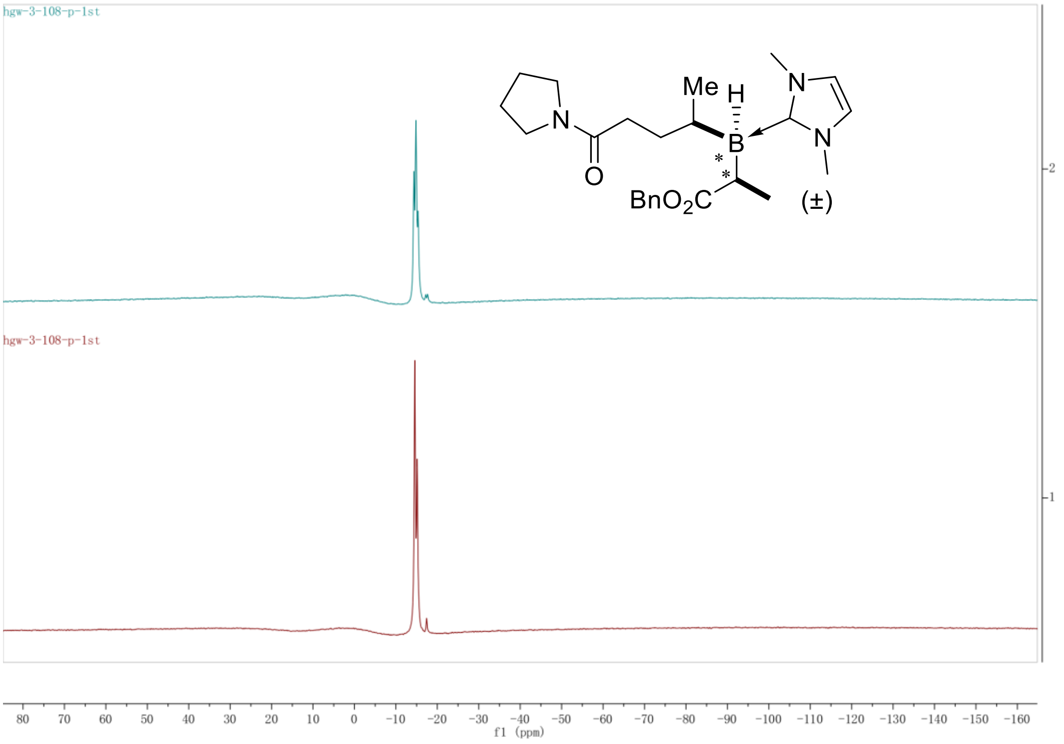
^{1}H NMR of 73



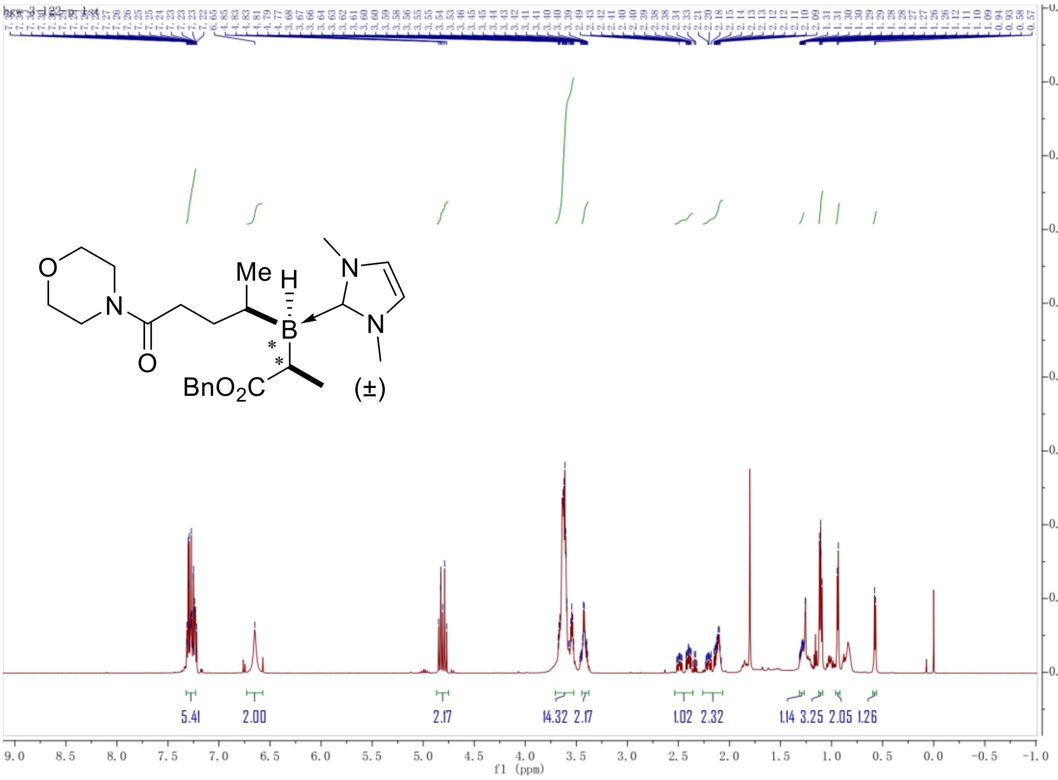
^{13}C NMR of 73



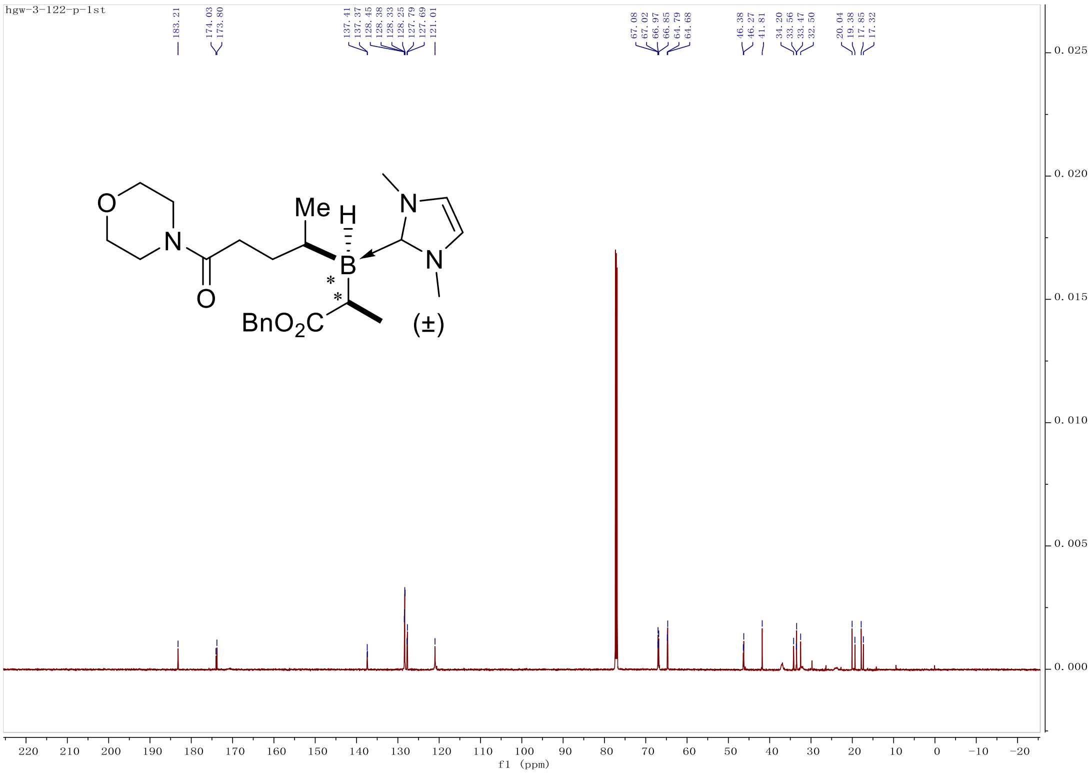
^{11}B NMR and ^{11}B {^{1}H} NMR of 73



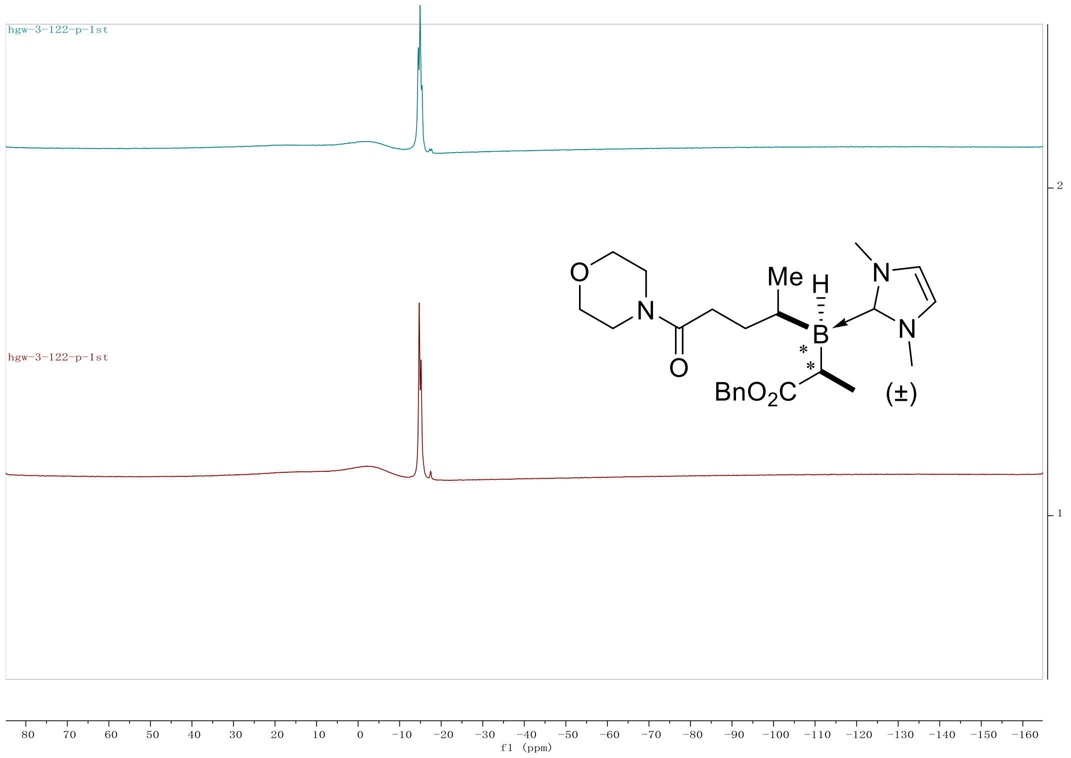
^{1}H NMR of 74



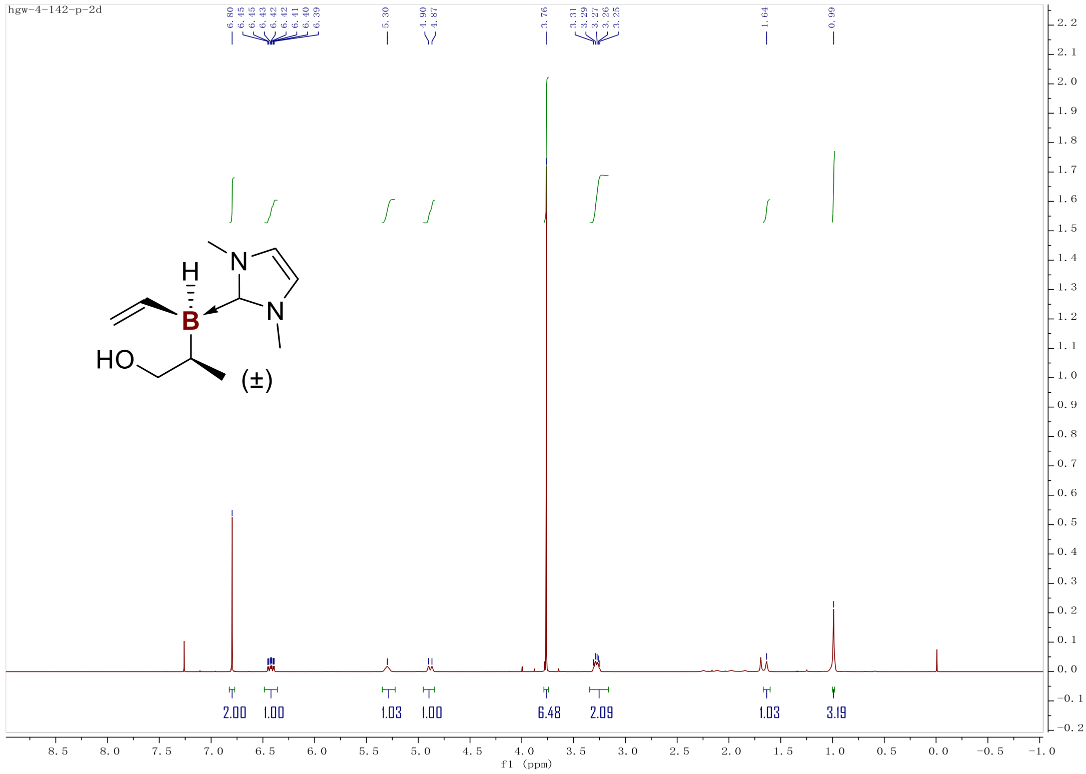
^{13}C NMR of 74



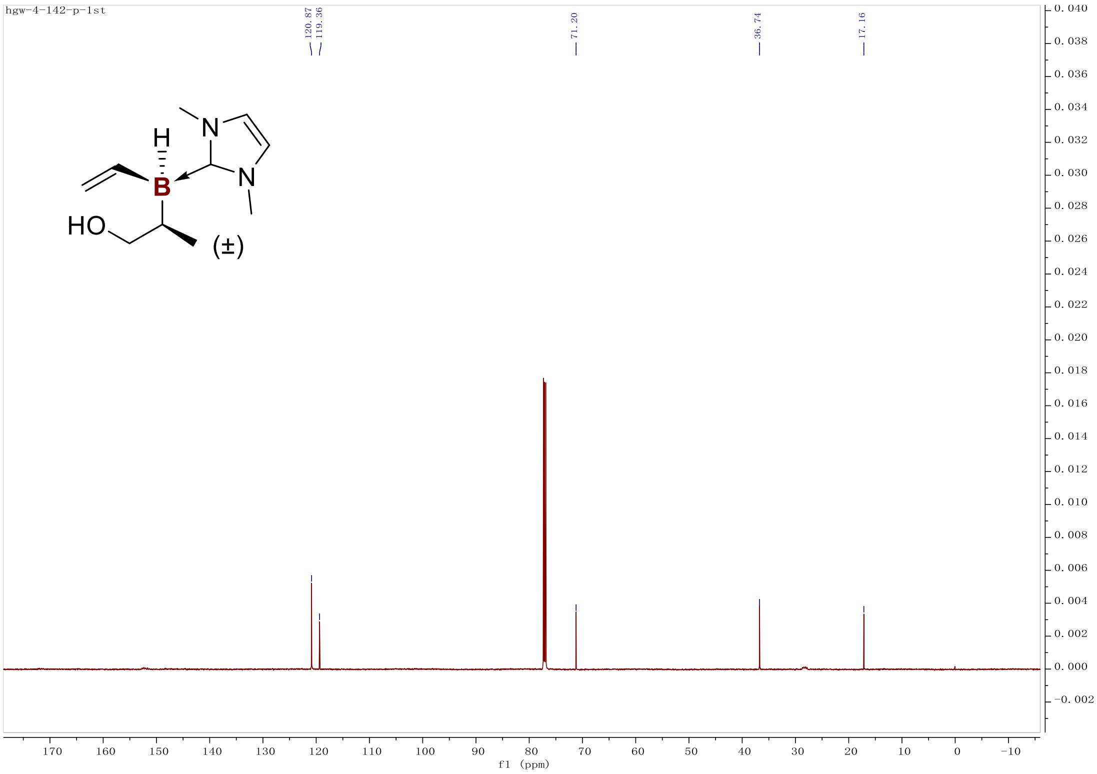
^{11}B NMR and ^{11}B {^{1}H} NMR of 74



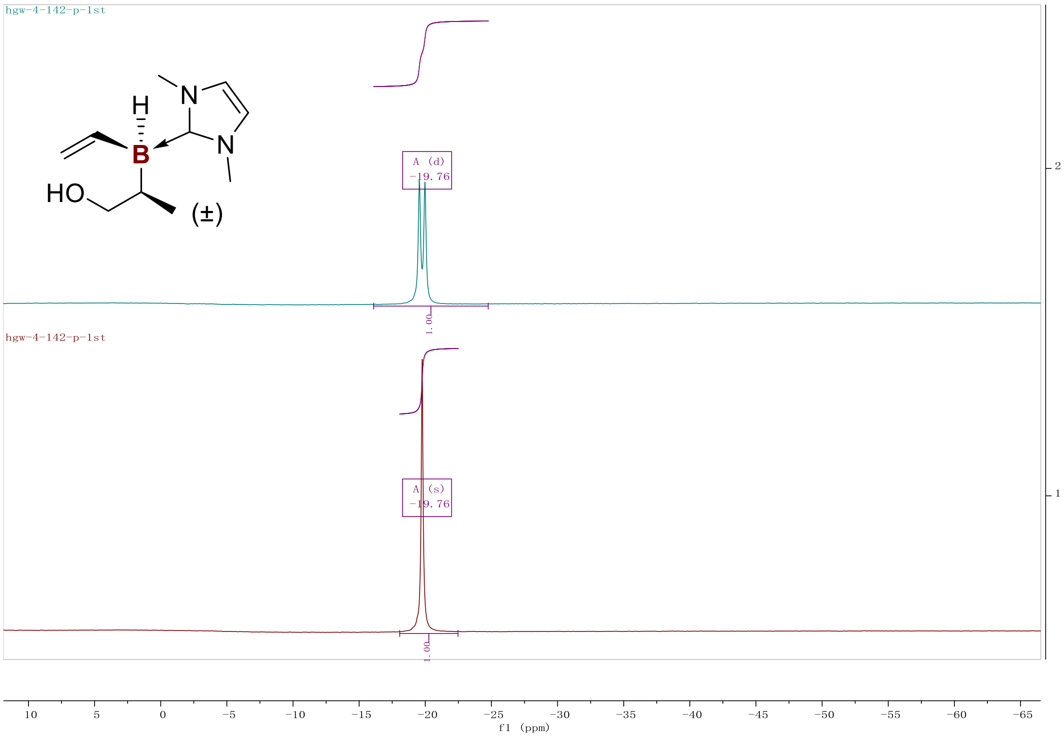
^{1}H NMR of 75



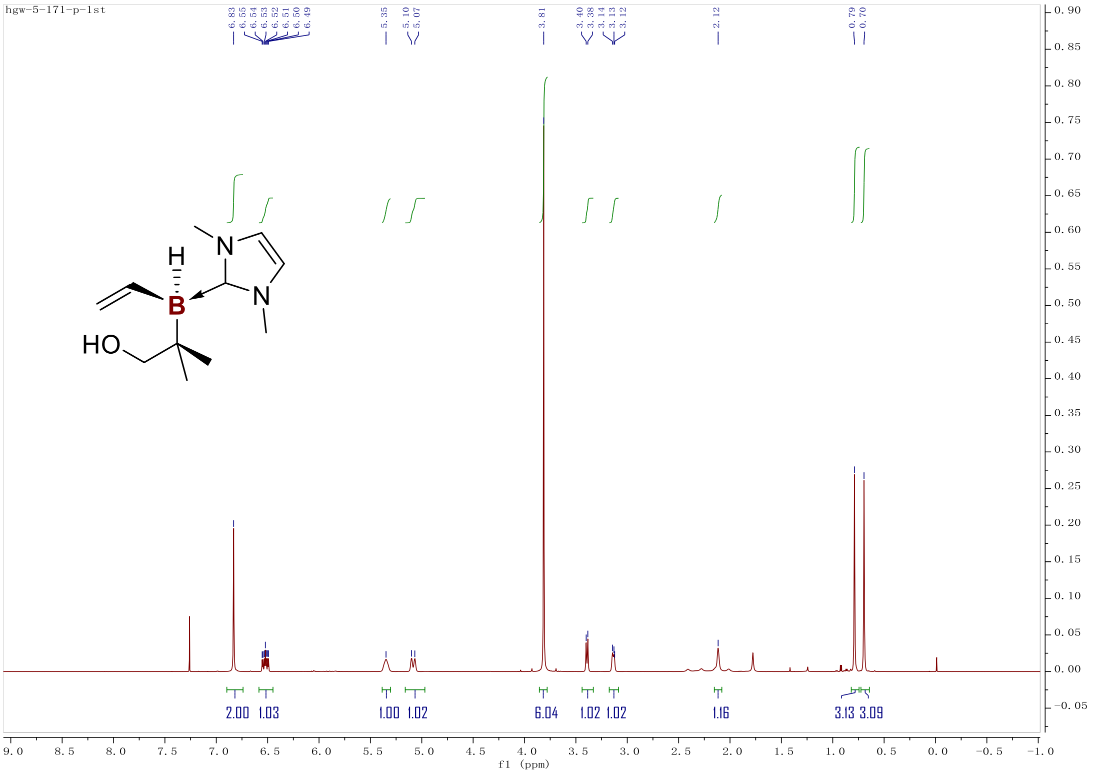
^{13}C NMR of 75



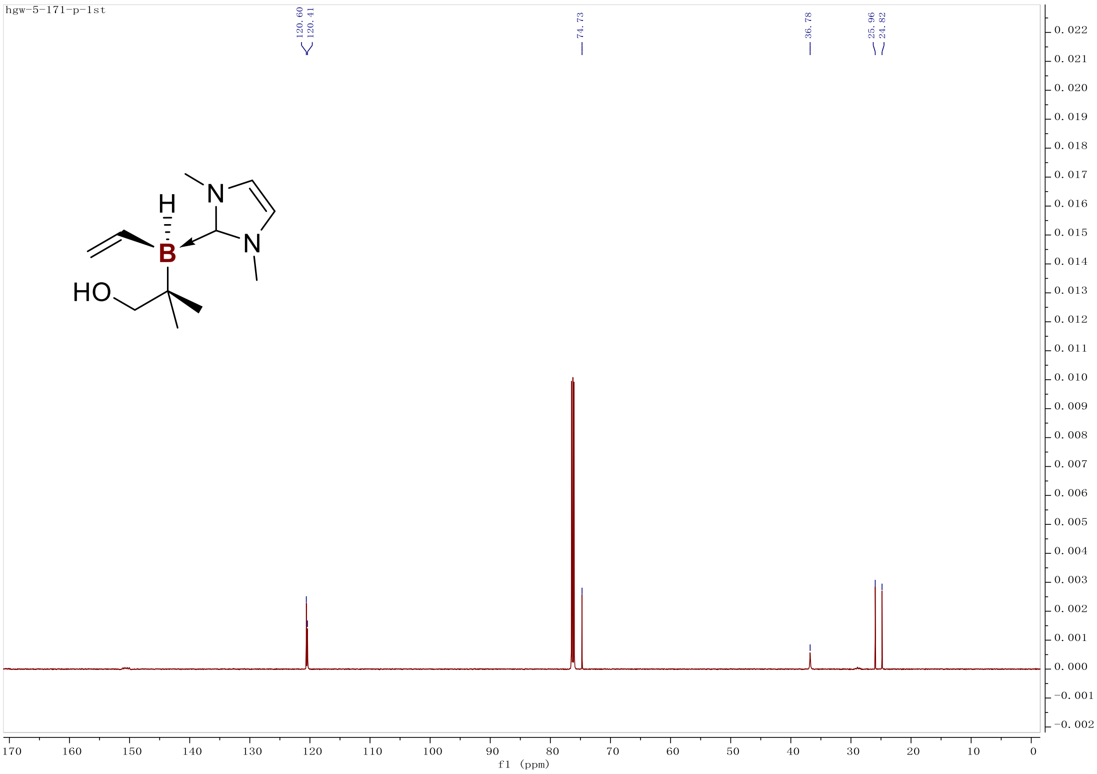
^{11}B NMR and ^{11}B {^{1}H} NMR of 75



^{1}H NMR of 76

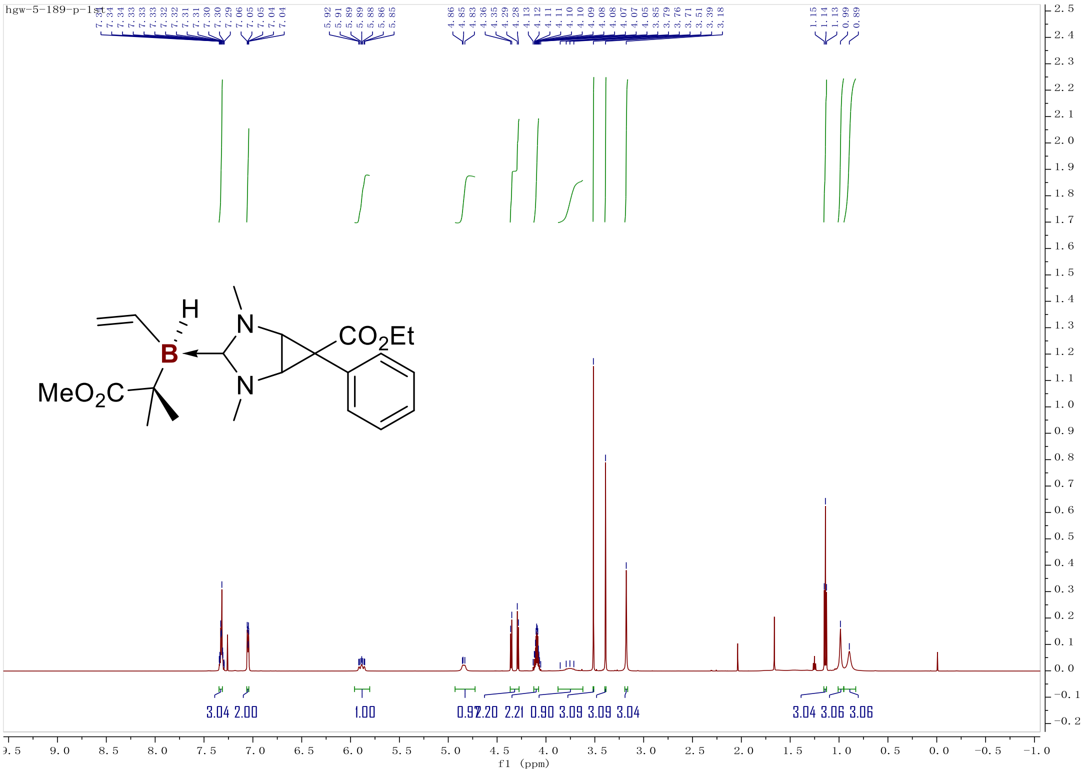


^{13}C NMR of 76

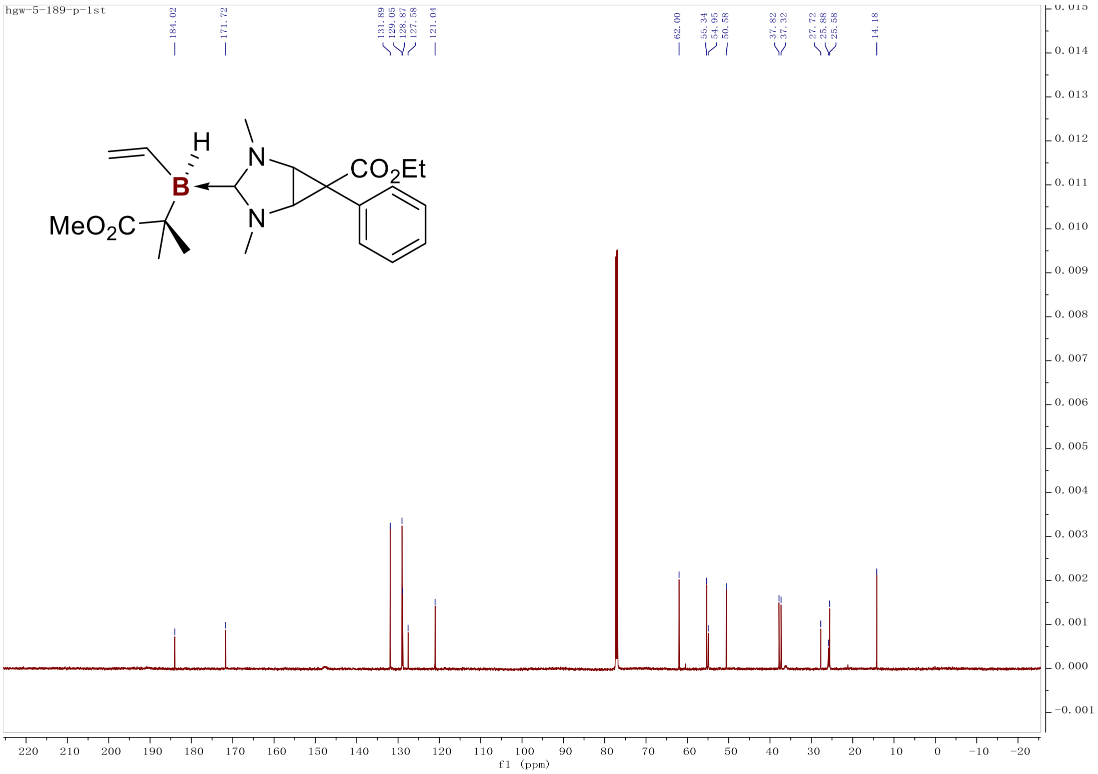


^{11}B NMR and ^{11}B {^{1}H} NMR of 76

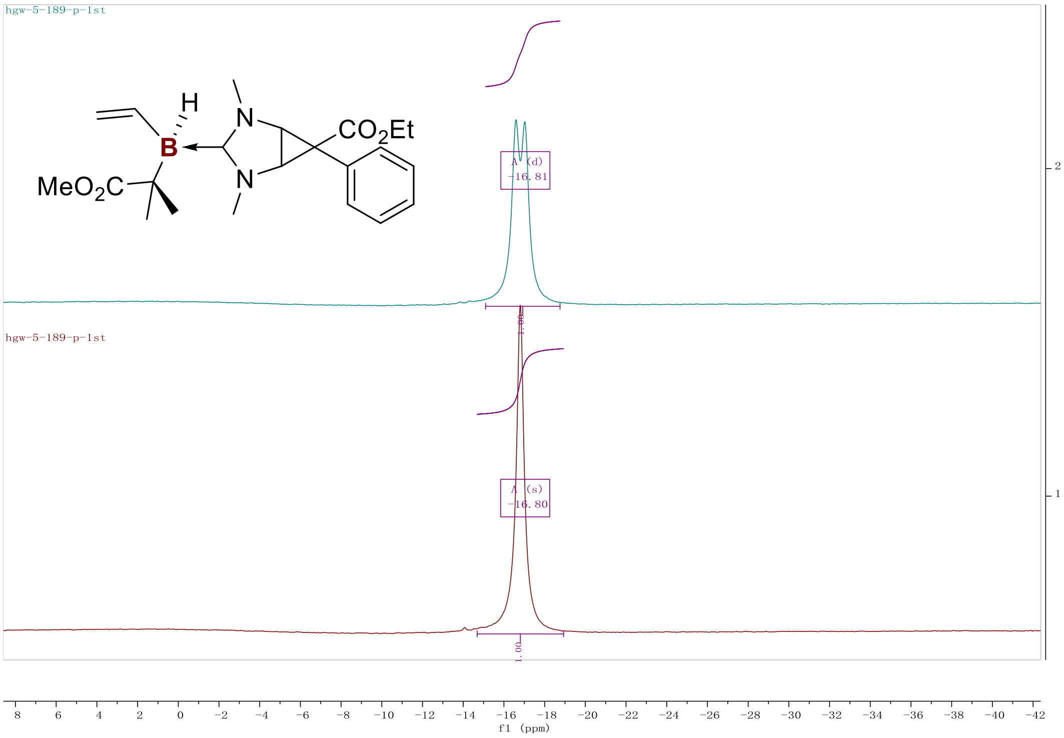
^{1}H NMR of 77



^{13}C NMR of 77



^{11}B NMR and ^{11}B {^{1}H} NMR of 77



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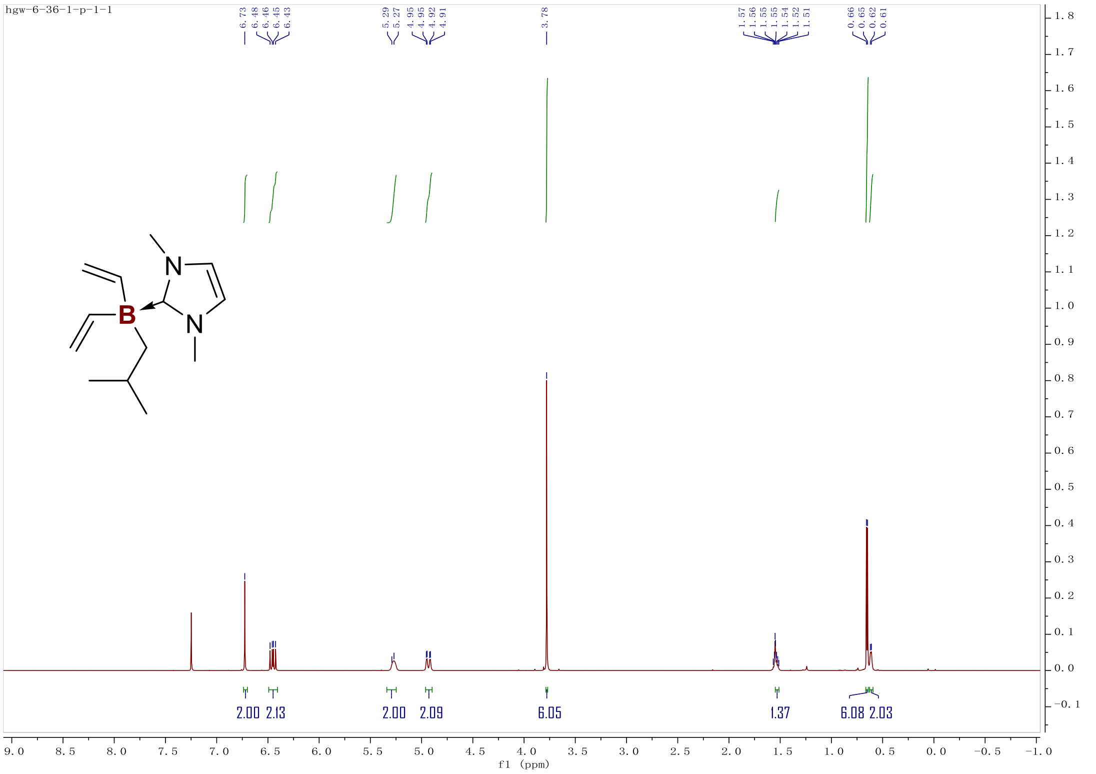
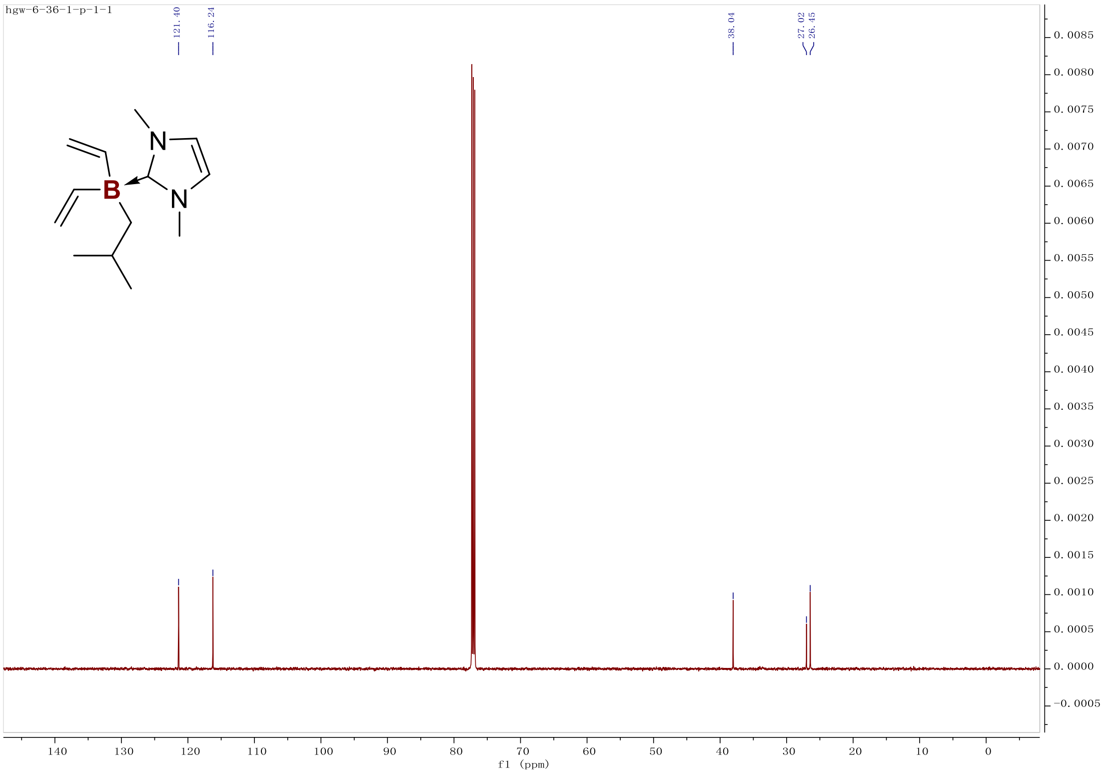
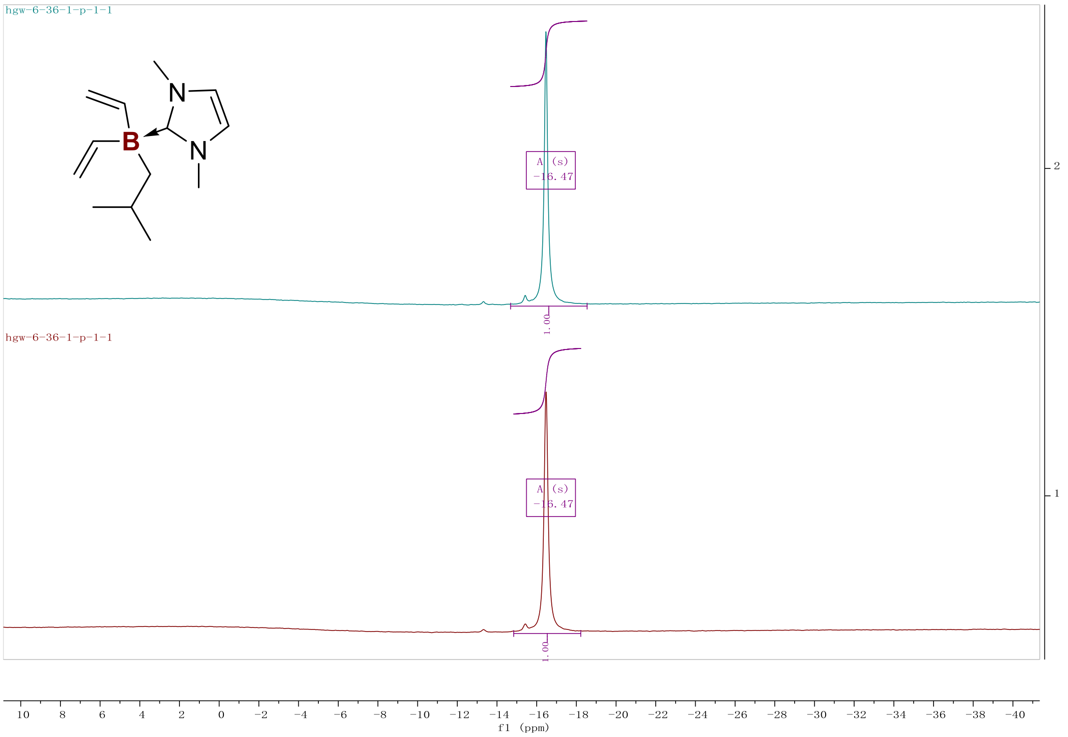


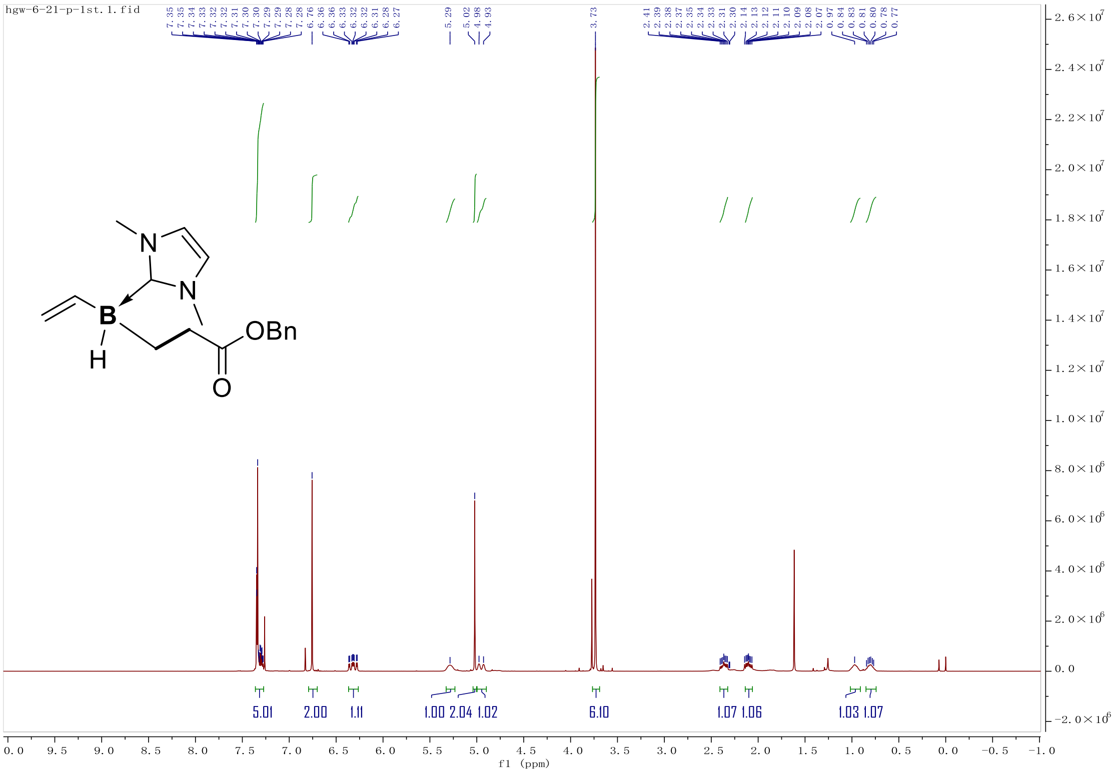
^{13}C NMR of 78



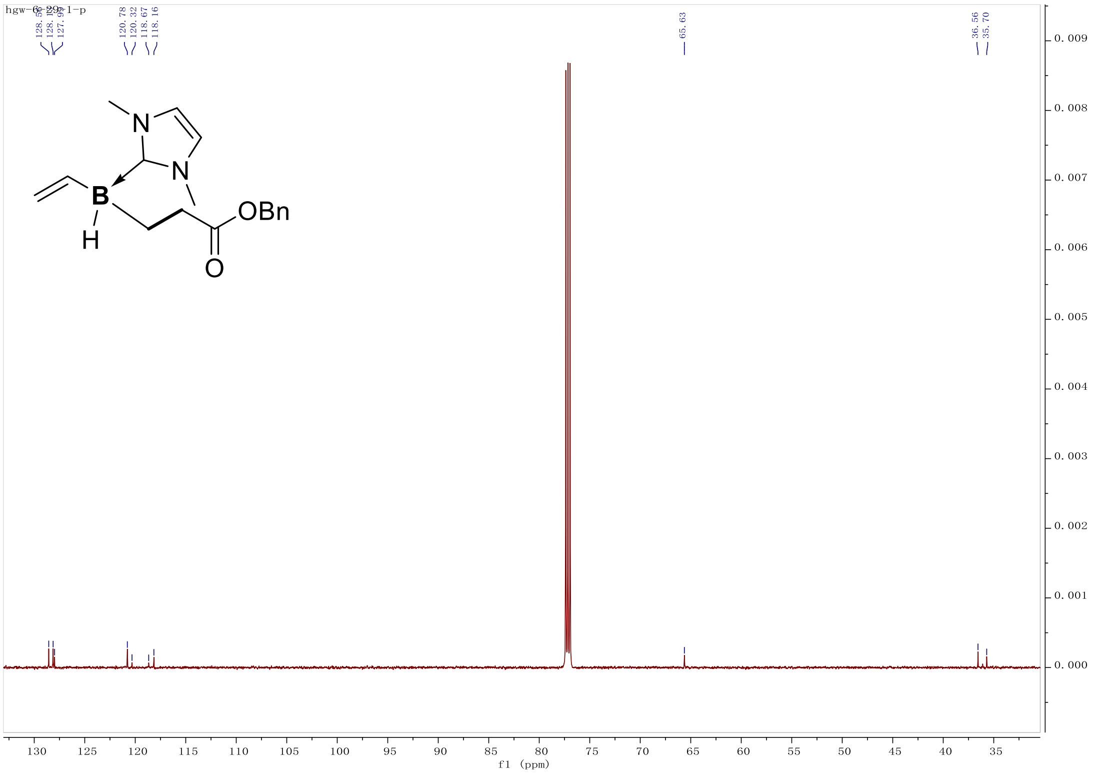
^{11}B NMR and ^{11}B {^{1}H} NMR of 78



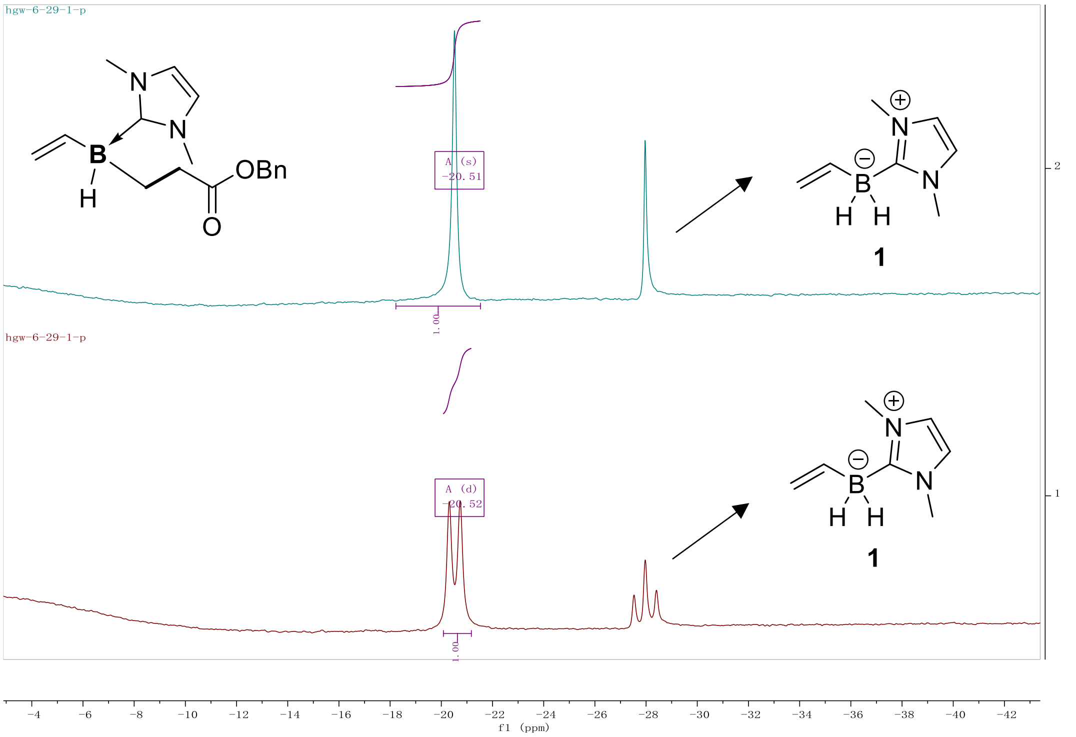
^{1}H NMR of S71



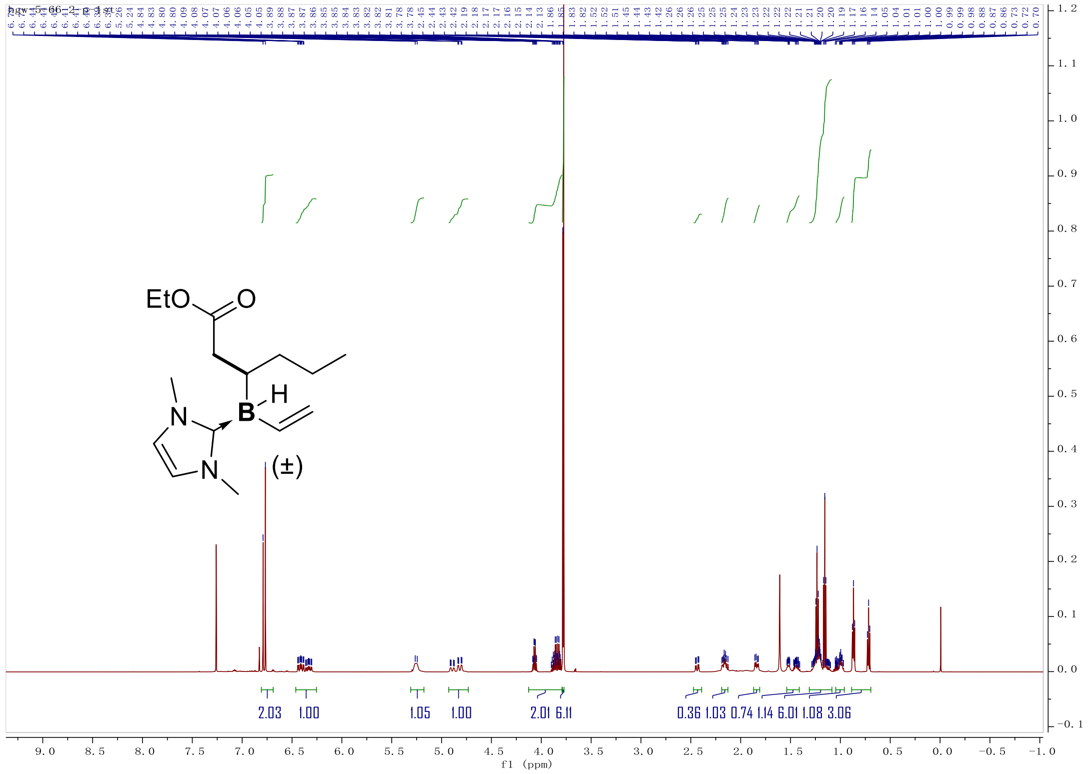
^{13}C NMR of S71



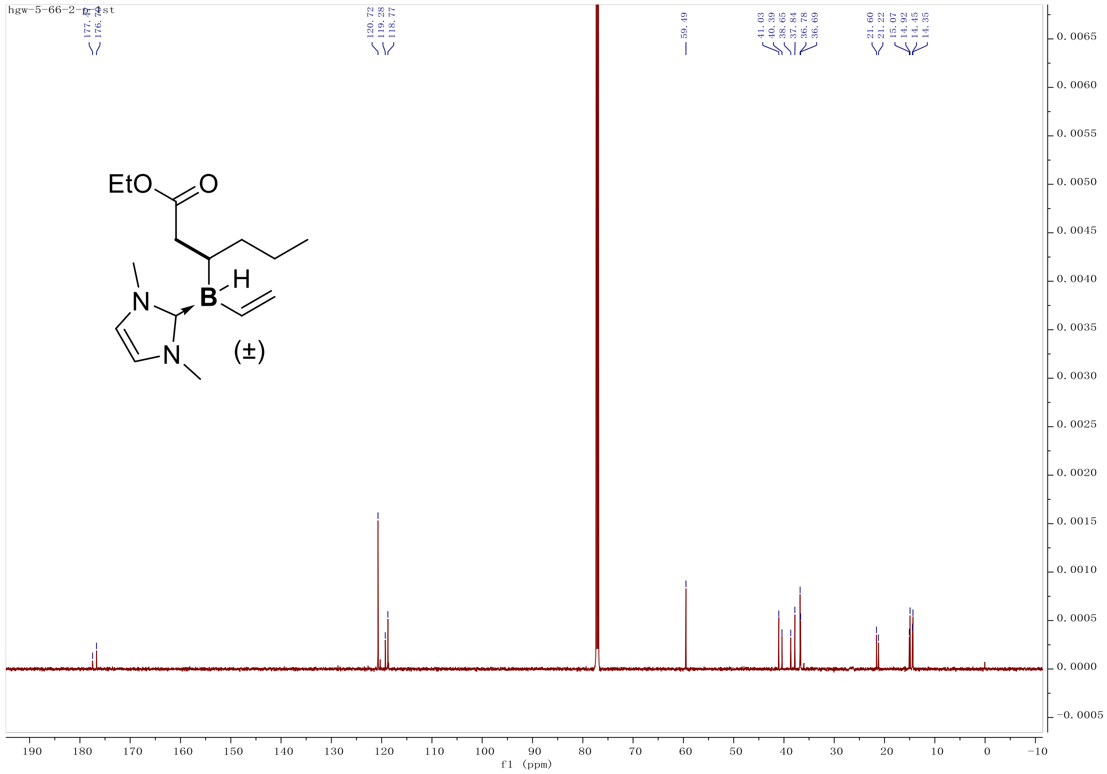
^{11}B NMR and ^{11}B {^{1}H} NMR of S71



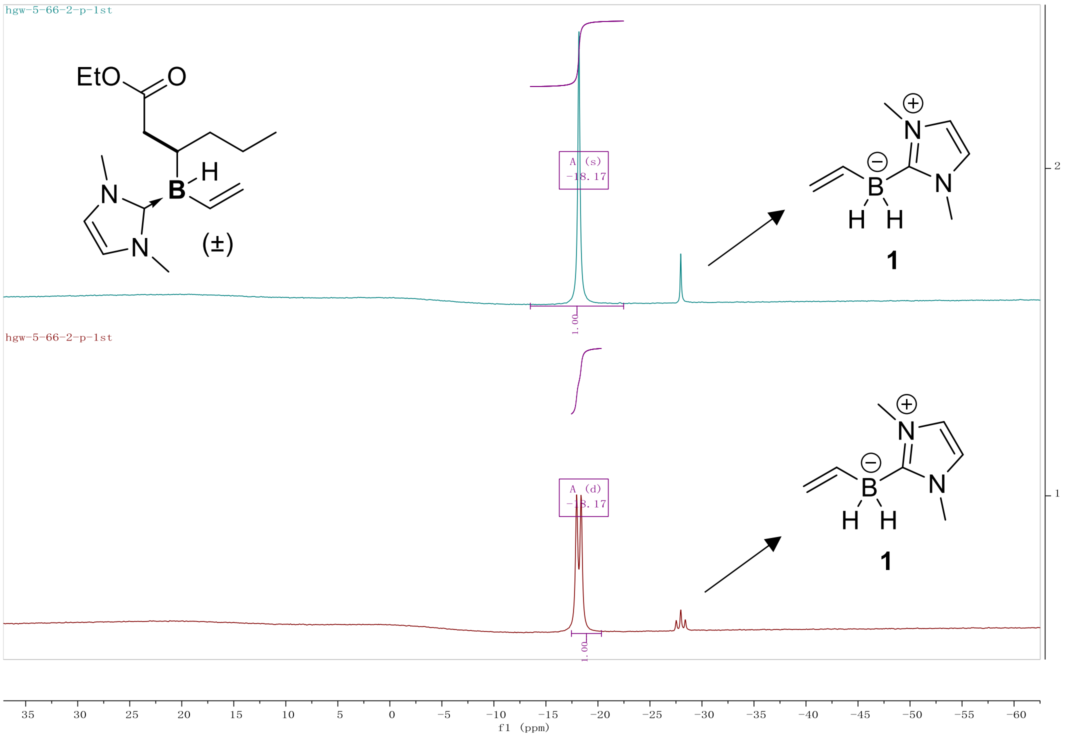
^{1}H NMR of S72



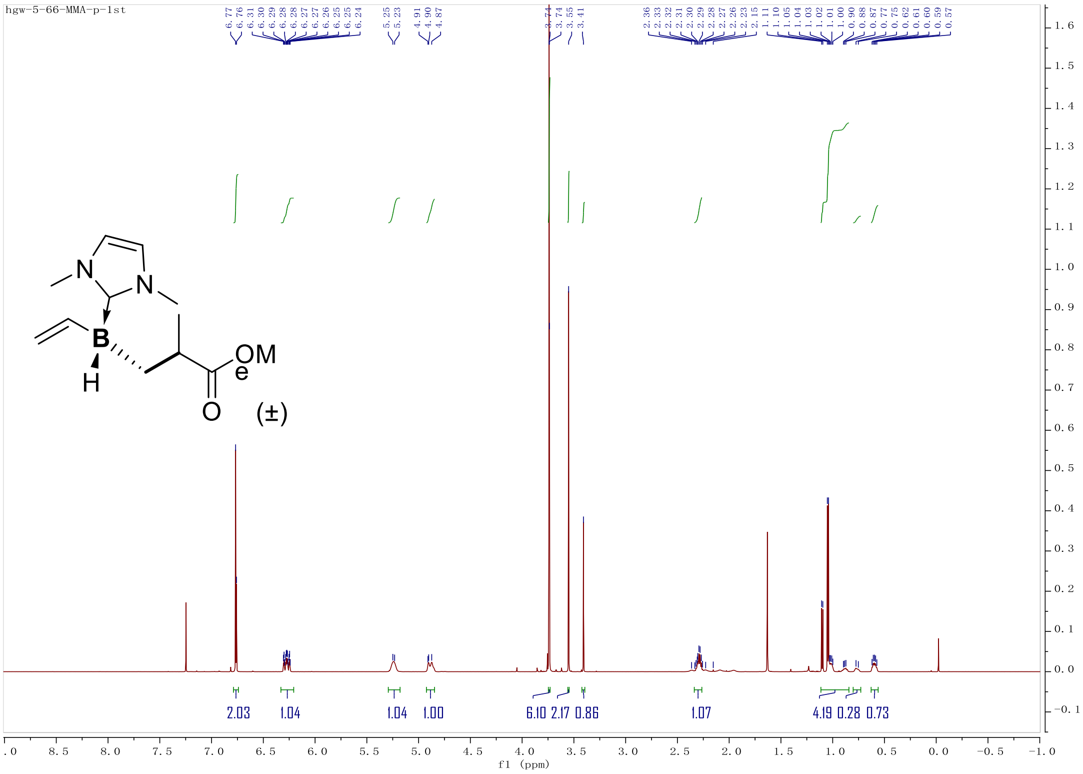
^{13}C NMR of S72



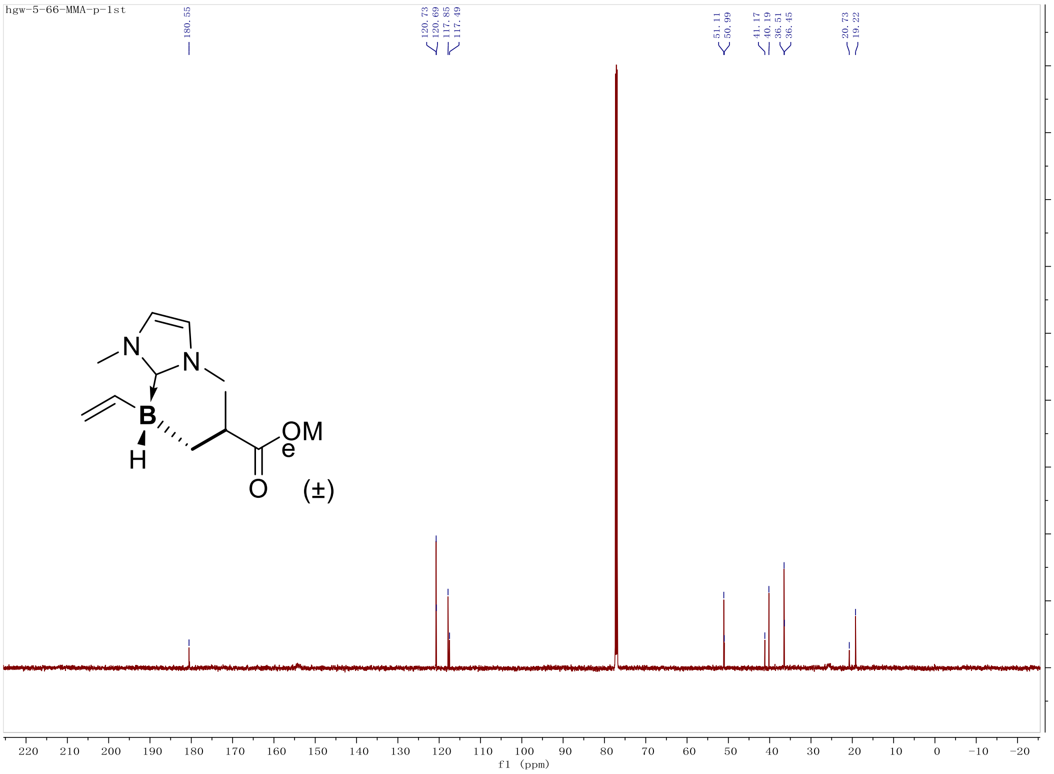
^{11}B NMR and ^{11}B {^{1}H} NMR of S72



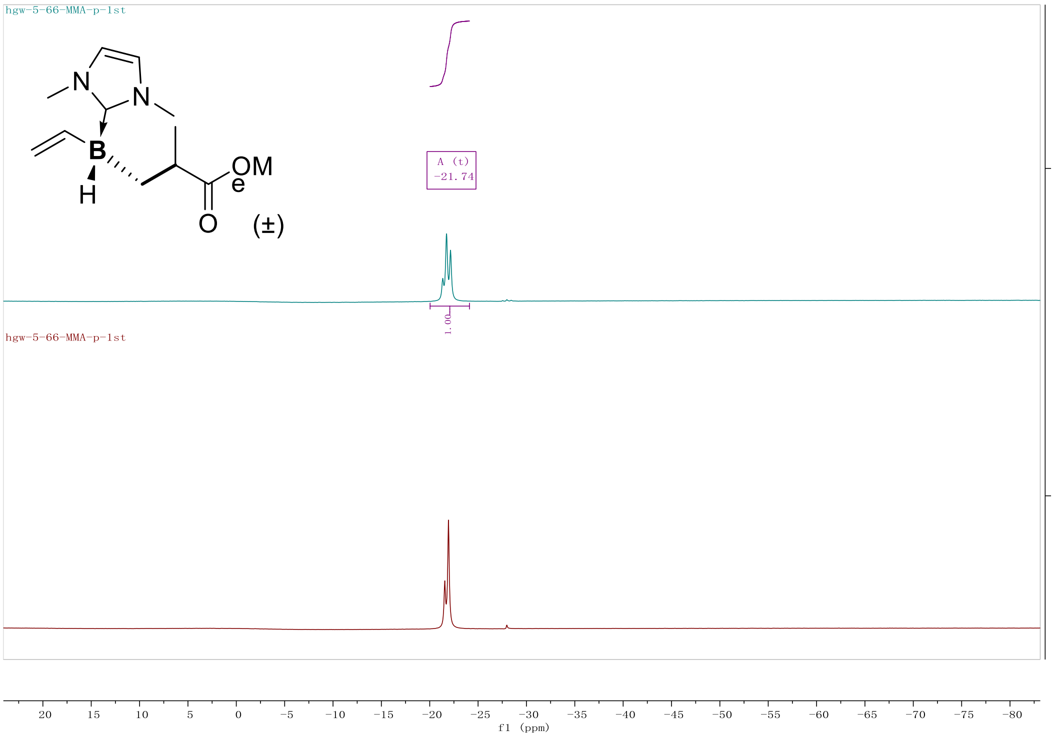
^{1}H NMR of S73



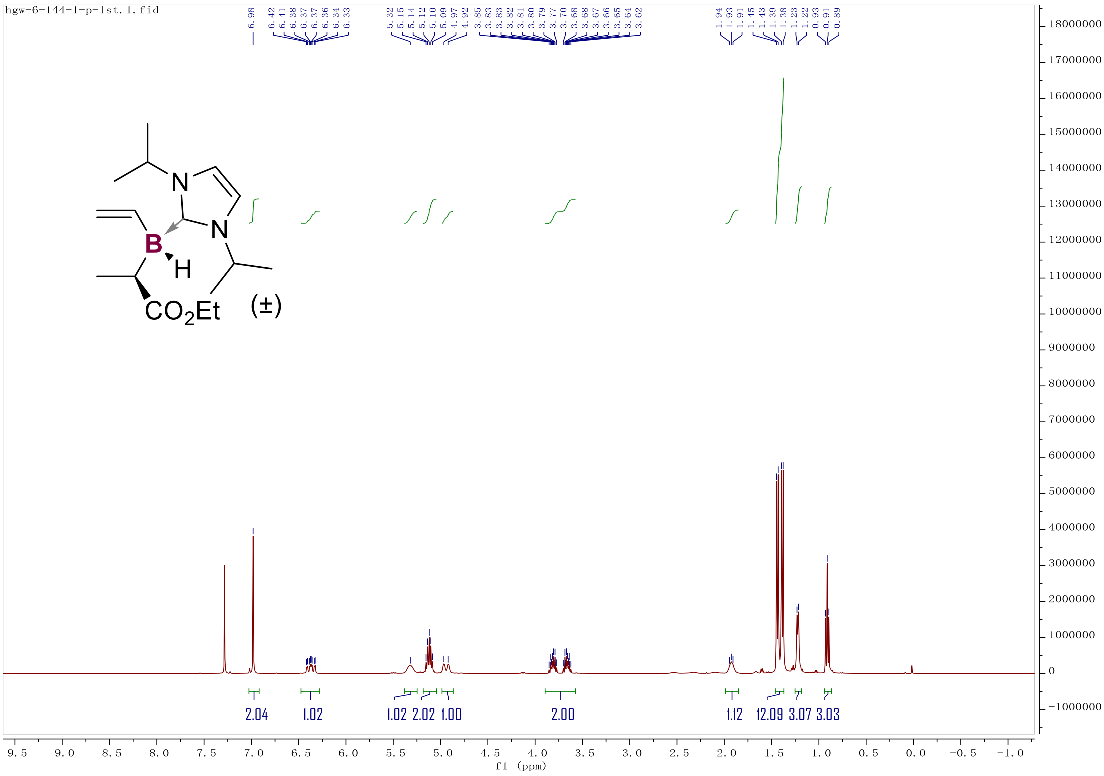
^{13}C NMR of S73



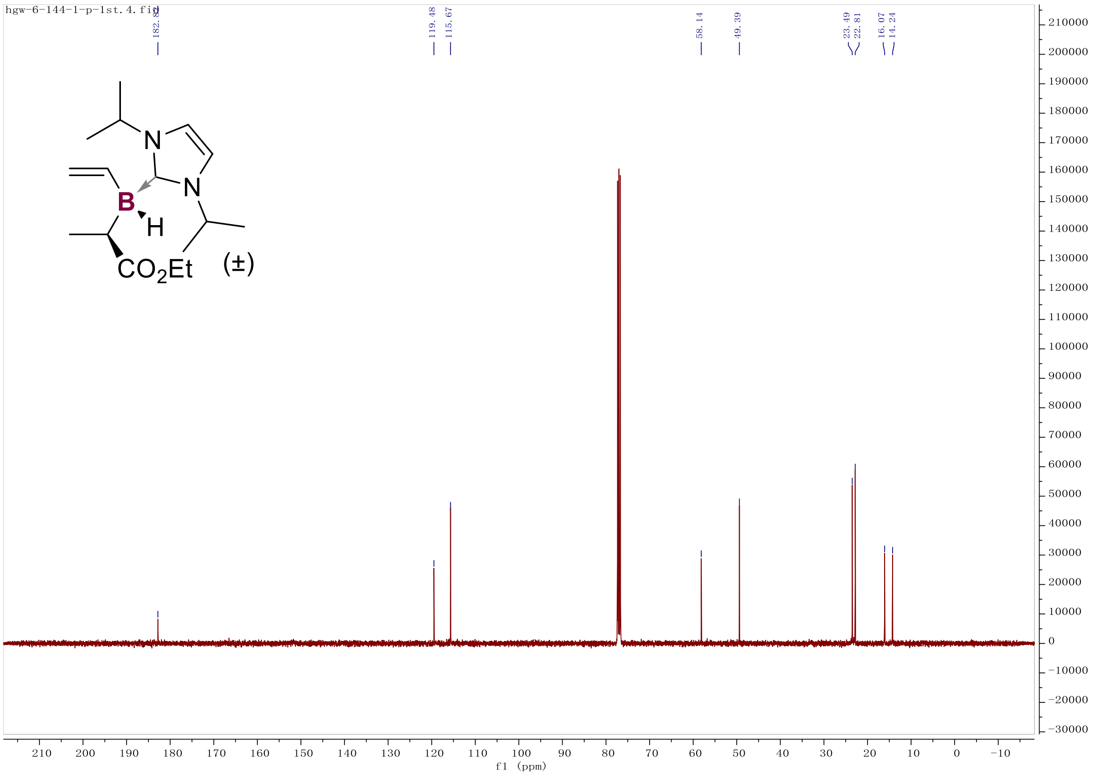
^{11}B NMR and ^{11}B {^{1}H} NMR of S73



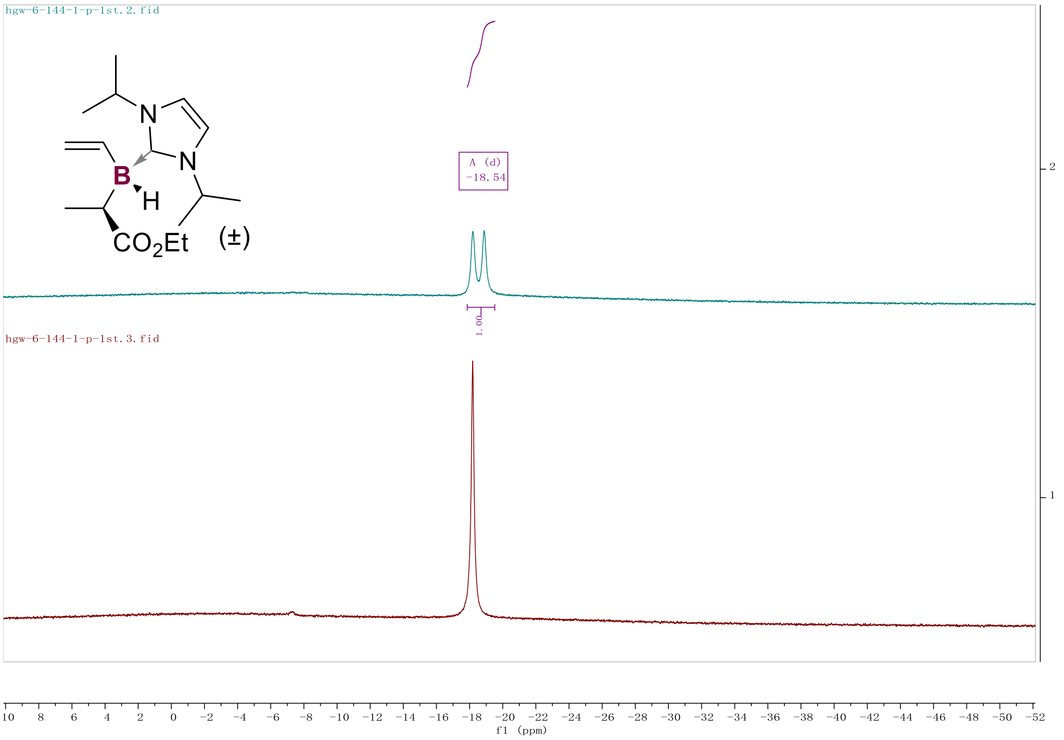
^{1}H NMR of S74



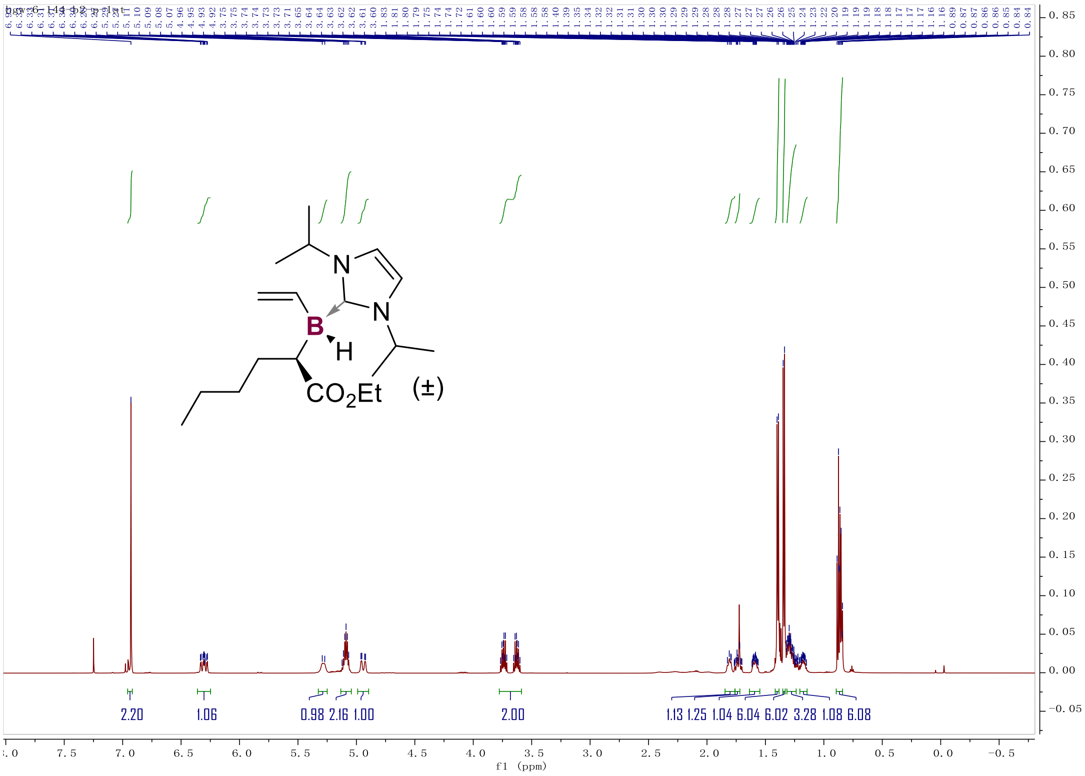
^{13}C NMR of S74



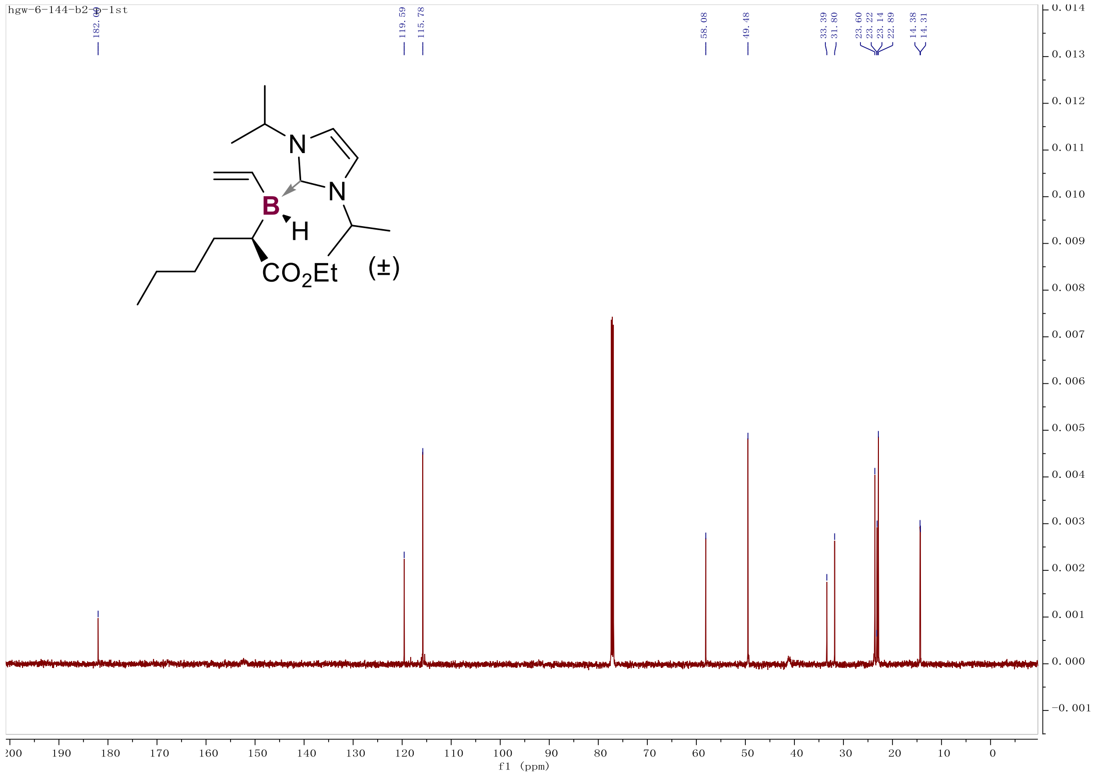
^{11}B NMR and ^{11}B {^{1}H} NMR of S74



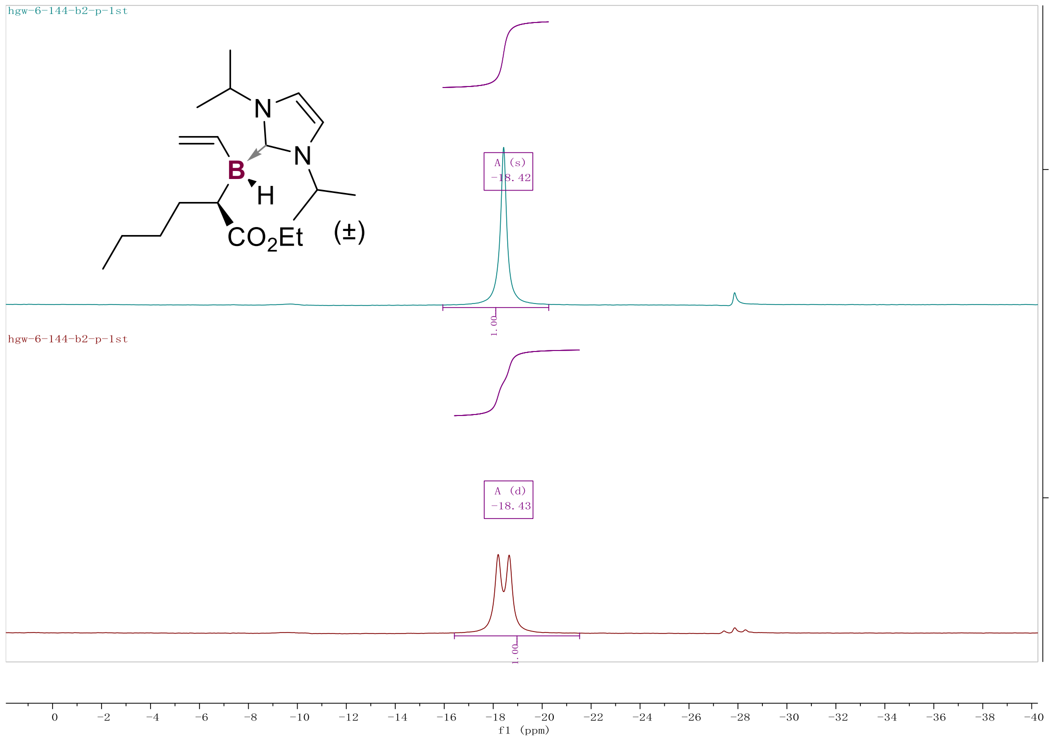
^{1}H NMR of S75



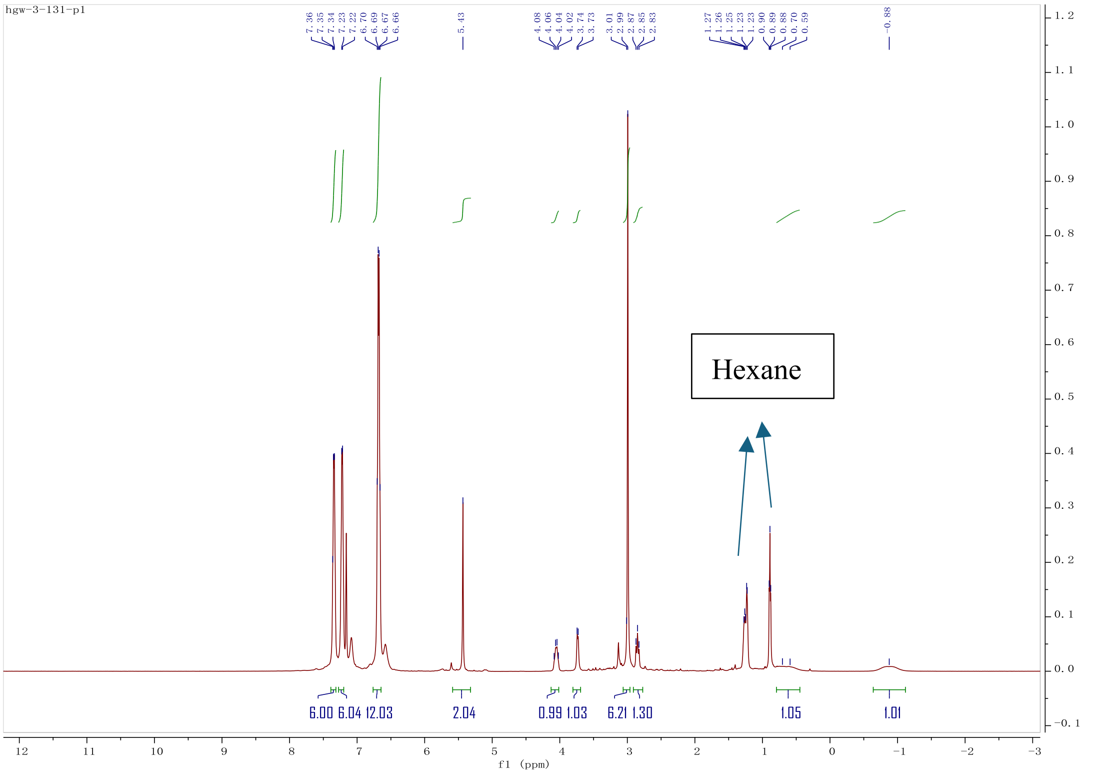
^{13}C NMR of S75



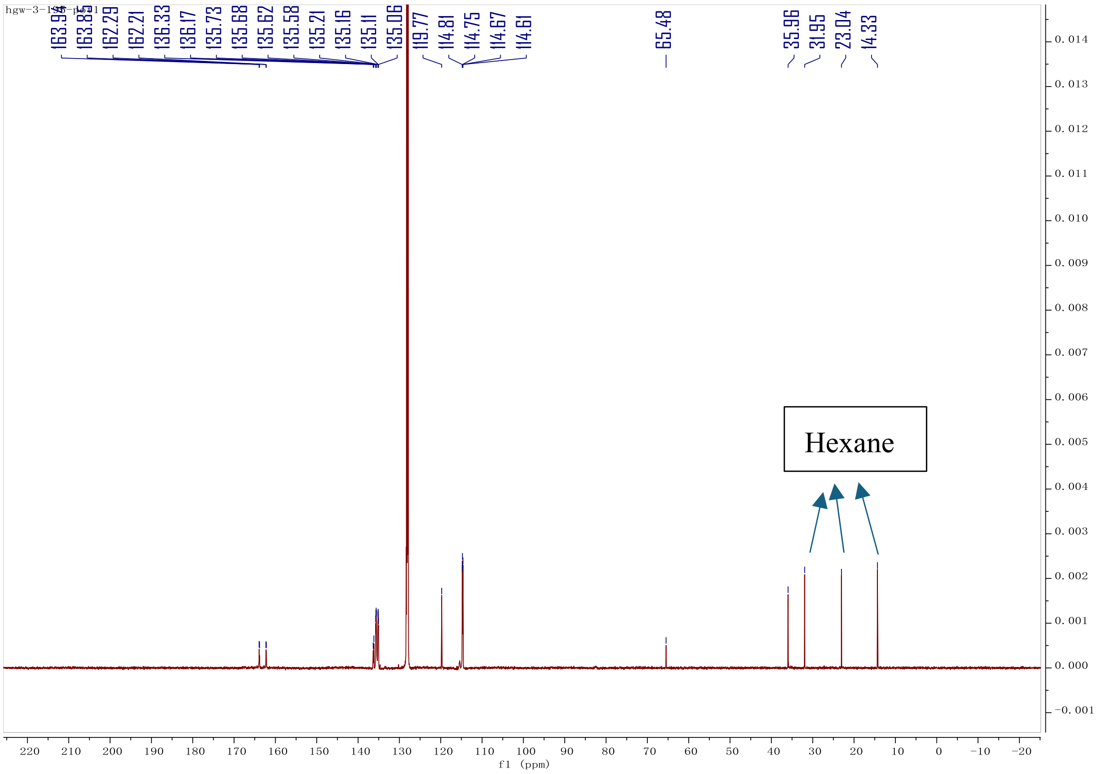
^{11}B NMR and ^{11}B {^{1}H} NMR of S75



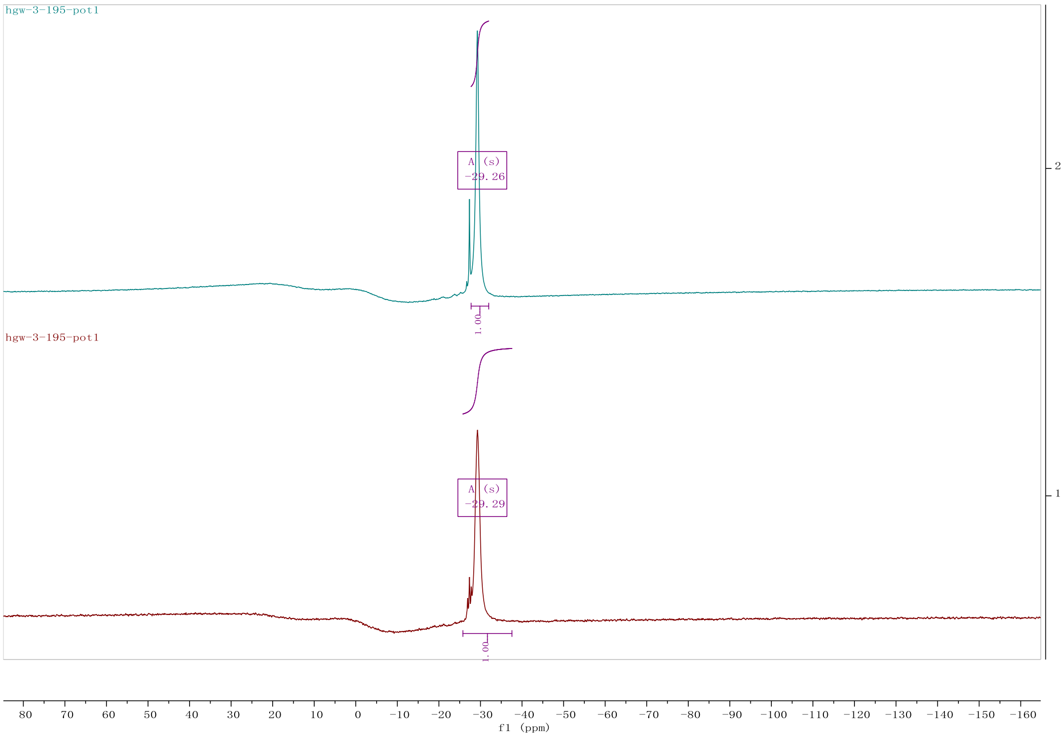
^{1}H NMR of INT1



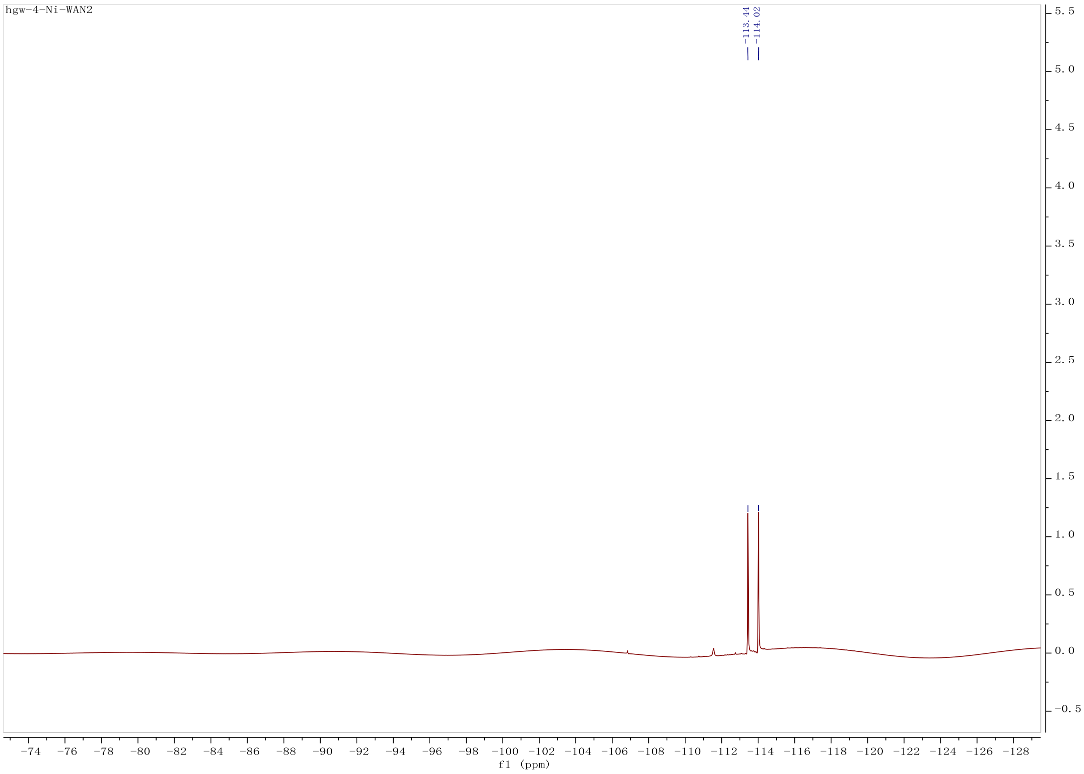
^{13}C NMR of INT1



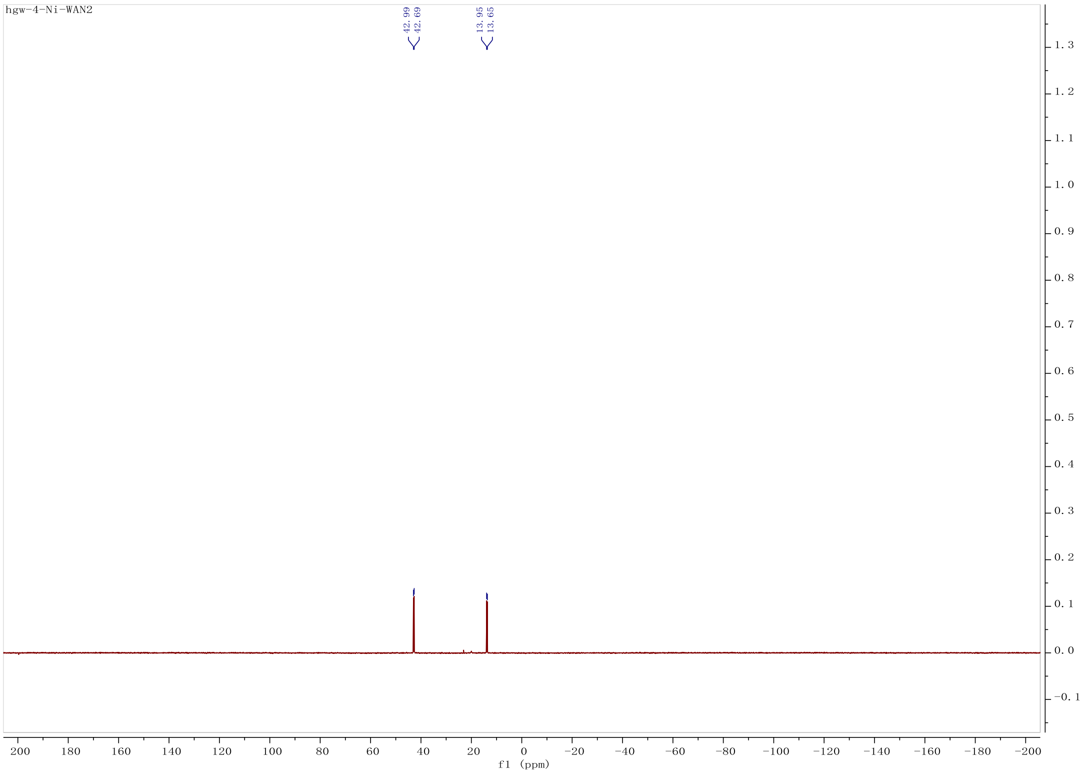
^{11}B NMR and ^{11}B {^{1}H} NMR of INT1



^{19}F NMR of INT1



^{31}P NMR of INT1



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