Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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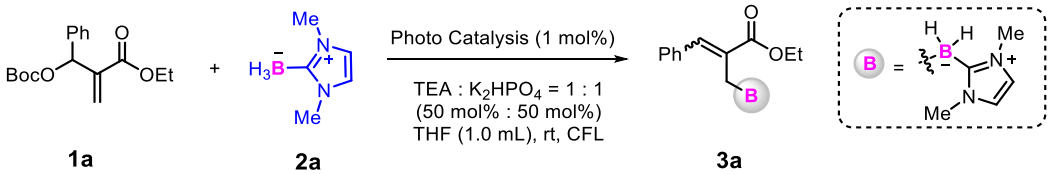
1. General Information

All the reactions were conducted in oven-dried Schlenk tubes under Argon atmosphere unless otherwise noted. All solvents and chemicals were obtained from commercial suppliers and used without further purification. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (300-400 mesh). ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F NMR spectra were recorded on 400 MHz and 500 MHz spectrometer in $CDCl_3$ at room temperature. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. High resolution mass spectra were obtained on a high–resolution mass spectrometer in the ESI positive mode. The 45 W blue LEDs light was purchased from Kessil (A360NE/WE) and the 36 W fluorescent light bulb were purchased from the supermarket. All NHC-boranes were known compounds and prepared according to the literature procedures. [1]

2. Optimization of the reaction conditions.

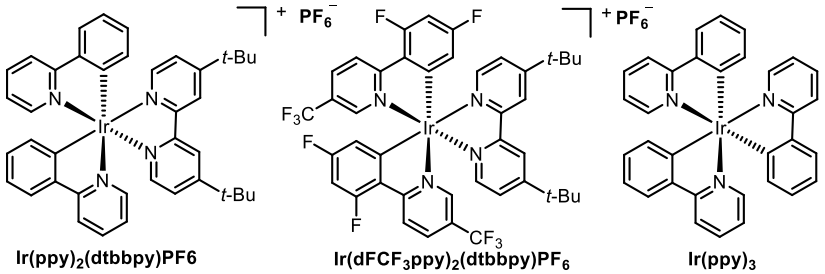
***Table 2.1*: Screening of photocatalyst**



1a **2a** **3a**

Entry	Photocatalyst	Yield[a]	*Z/E*
1	**$Ir(ppy)_2(dtbbpy)PF_6$**	**78%**	**4.2/1**
2	$Ir(ppy)_3$	10%	4.1/1
3	$IrdFCF_3(ppy)_2(dtbbpy)PF_6$	trace	-
4	$Ru(bpy)_3Cl_2$	trace	-
5	4CZIPN	trace	-
6	Eosin Y	10%	3.0/1

[a]Yield of isolated.



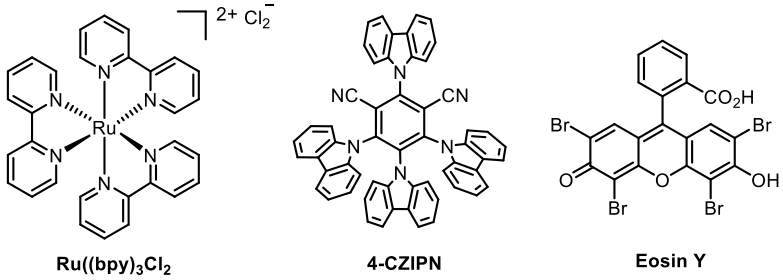
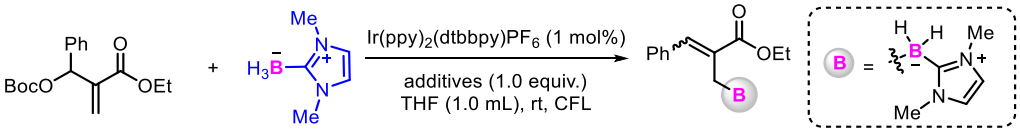


***Table 2.2*: Screening of additives**

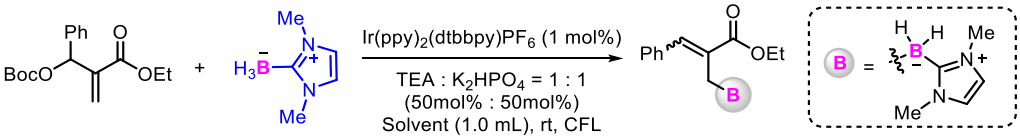


1a **2a** **3a**

Entry	Base	Equiv.	Yield[a]	Z/E
1	TEA	0.2	47%	4.0/1
2	K_2HPO_4	0.2	trace	-
3	K_2HPO_4	0.5	trace	-
4	TEA:K_2HPO_4 = 1:1	0.4	60%	4.0/1
5	**TEA:K_2HPO_4 = 1:1**	**1.0**	**78%**	**4.2/1**
6	TEA:K_2HPO_4 = 1:1	2.0	49%	4.2/1
7	TEA:K_3PO_4 = 1:1	1.0	63%	3.3/1
8	TEA:KH_2PO_4 = 1:1	1.0	56%	1.7/1
9	TEA:$KHCO_3$ = 1:1	1.0	59%	1.5/1
10	TEA:K_2CO_3 = 1:1	1.0	55%	1.4/1
11	TEA:$NaHCO_3$ = 1:1	1.0	56%	1/1
12	TEA:KF = 1:1	1.0	47%	3.3/1
13	TEA:Cs_2CO_3 = 1:1	1.0	trace	-
14	TEA:Pyridine = 1:1	1.0	50%	1.3/1

[a]Yield of isolated.

***Table 2.3*: Screening of solvents**

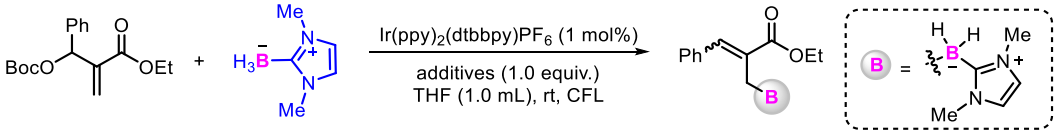


1a **2a** **3a**

Entry	Solvent	Yield[a]	Z/E
1	CH_3CN	58%	4.0/1
2	**THF**	**78%**	**4.2/1**
3	DMA	trace	-
4	DCM	trace	-
5	Toluene	trace	-
6	1,4-Dioxane	trace	-

[a]Yield of isolated.

***Table 2.4*: Another changes**



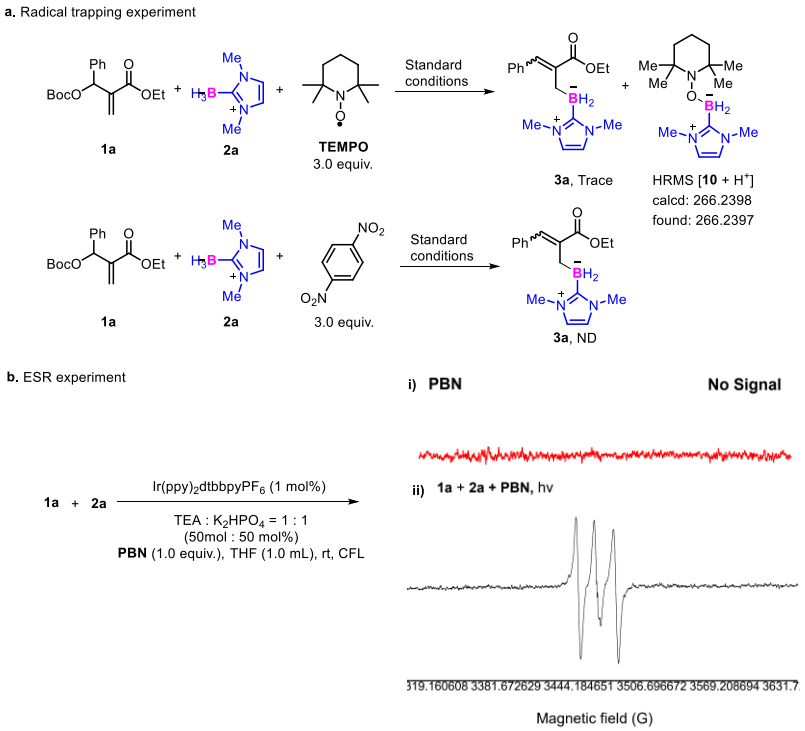
1a **2a** **3a**

Entry	Base	Equiv.	Solvent	Yield[a]
1	TEA:K_2HPO_4 = 1:1	0.4	CH_3CN	42%
2	TEA:K_2HPO_4 = 1:1	1.0	CH_3CN:THF (1:1)	50%

[a]Yield of isolated.

3. Investigation of the reaction mechanism

3.1 Radical inhibition experiments and ESR experiments



The reaction was completely inhibited by TEMPO, 1,4-Dinitrobenzene. The compounds **10** detected by HRMS suggested that the reaction might produce boron radical. For furture demonstrated the possible reaction mechanism, electron paramagnetic resonance (EPR) experiments with *N*-tert-butyl-α-phenylnitrone (PBN) as the electron-spin trapping reagent were carried out. A significant EPR signal was observed for the model reaction. Combining the above results indicating that the reaction probably proceeded via a radical process. [2]

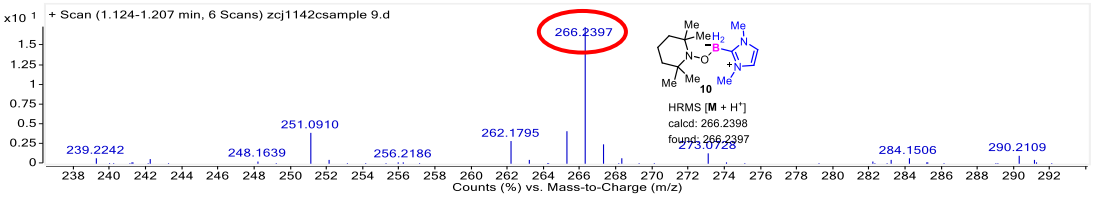


Figure S1. HRMS data of the reaction mixture.

3.2 The CV data of NHC-BH_3 (**2a**)

Redox potentials generally provide a starting point for the evaluation of the thermodynamic accessibility of a reaction, but solvent effects and errors in measurements always mean these should be taken only as guidelines. The oxidation potentials of NHC-BH_3 (**2a**) ($E_{1/2}^{oxidation}$ = 0.915 V vs SCE), the mixture of **2a** and K_2HPO_4 (0.5 eq.) ($E_{1/2}^{oxidation}$ = 0.801 V vs SCE). These results indicated that K_2HPO_4 probably can decrease the oxidation potentials of NHC-BH_3. It seems that Ir(III)* cannot oxidize NHC-BH_3. However, some parts of overlap between the excited $Ir(ppy)_2(dtbbpy)PF_6$ ($E1/2^{oxidation}$ = 0.66V vs SCE) with NHC-BH_3 was observed. Thus, the first sluggish oxidation of NHC-BH_3 is reasonable.

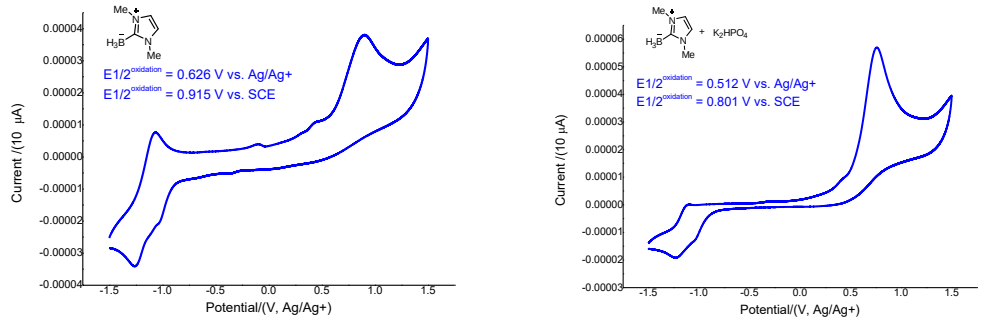
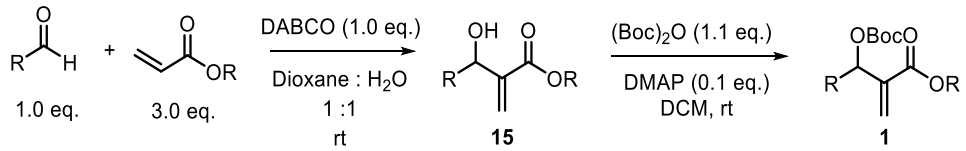


Figure S2. The CV data of NHC-BH_3 (**2a**), the mixture of **2a** and K_2HPO_4 (0.5 eq.) measured in acetonitrile containing 0.1 mol/L tetrabutylammonium hexafluorophosphate.

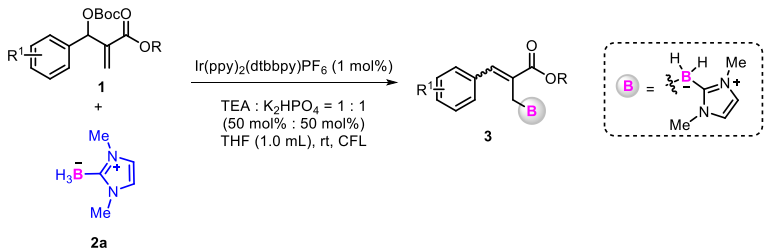
4. General procedure for the preparation of Morita–Baylis–Hillman adducts[3]



To a solution of aldehyde (10 mmol) and acrylate (30 mmol) in Dioxane : H_2O = (1 : 1) (10 mL), DABCO (10 mmol) was added at room temperature. The stirring continued all starting materials had been consumed (monitored by TLC). The reaction was quenched by H_2O, and water layer was extracted with ethyl acetate (20 mL × 3). Combined organic layers, then dried over Na_2SO_4. The residue was purified by column chromatography on silica gel to obtain the desired product **15**.

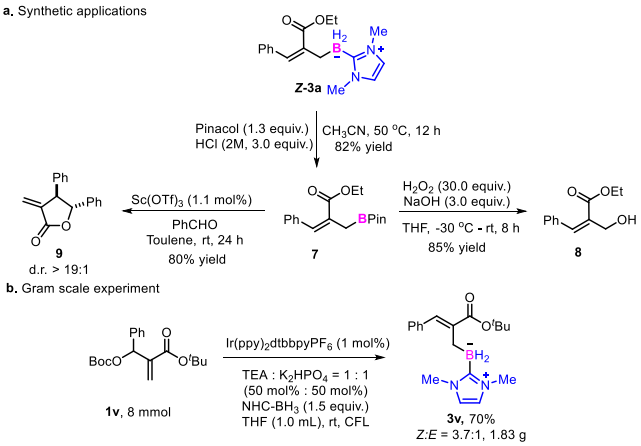
To a solution of **15** (0.5 mmol) and $(Boc)_2O$ (0.55 mmol) in DCM (10 mL), DMAP (0.1 mmol) was added at room temperature. The stirring continued all starting materials had been consumed (monitored by TLC). The reaction was quenched by H_2O, and water layer was extracted with DCM (10 mL × 3). Combined organic layers and dried over Na_2SO_4. The residue was purified by column chromatography on silica gel to obtain the desired product **1**.

5. General procedure for reaction of NHC-Borane with Morita–Baylis–Hillman Esters



An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, Morita–Baylis–Hillman Esters (**1**) (1.0 equiv., 0.2 mmol), NHC-borane (**2a**) (1.5 equiv., 0.3 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (1 mol%), TEA (0.5 equiv., 0.1 mmol), K_2HPO_4 (0.5 equiv., 0.1 mmol). The flask was evacuated and backfilled with Ar for 3 times. 1 mL THF was added with syringe under Ar. The tube was placed exposed to 36 W fluorescent light bulb at room temperature. After the reaction was finished, the reaction was quenched by water (2 mL), extracted by ethyl acetate (3 × 10 mL), dried by anhydrous Na_2SO_4, filtered and collected organic solvent. The organic solvent was removed under the reduced pressure. The residue was purified by column chromatography on silica gel to obtain the desired product **3**.

6. Synthetic applications and gram scale experiment.[4]

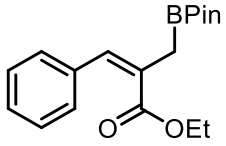


(*Z*)-(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-(ethoxycarbonyl)-3-phenylallyl)dihydroborate ((*Z*)-**3a**, 1.0 mmol, 298 mg) and pinacol (1.3 mmol, 138 mg) in CH_3CN (5 mL) was added 2 M aqueous HCl (1.5 mL, 3.0 mmol), and the resulting

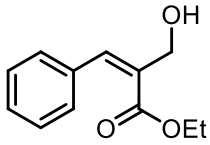
mixture was stirred at 50 °C for 12 h. After finish, the reaction was quenched by water (5 mL), extracted by ethyl acetate (3 × 10 mL), dried by anhydrous Na_2SO_4, filtered and collected organic solvent. The residue was purified by column chromatography on silica gel to obtain the desired product **7**.

The product **7** can be converted into arylallyl alcohol **8** in 85% yields by using H_2O_2 as the oxidant. Moreover, **7** could react with benzaldehyde use $Sc(OTf)_3$ as catalyst, and the resulting homoallylic alcohol intermediate cyclizes in situ with the carboxy ester group to form a lactone product **9** in 80% isolated yields.

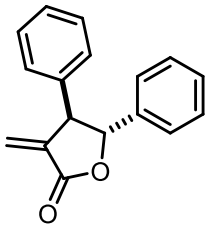
The gram scale experiment was carried out with the standard conditions in 8 mmol scale. After normal work-up can give the titled product **3v** as 1.83 g (70% yield).



ethyl (Z)-3-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (**7**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 1H), 7.26 – 7.19 (m, 4H), 6.74 (d, *J* = 1.6 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.04 (d, *J* = 1.4 Hz, 2H), 1.26 (s, 12H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.5, 136.9, 134.4, 131.2, 128.4, 127.8, 127.3, 83.6, 60.5, 24.8, 13.8.^{11}B NMR (160 MHz, Chloroform-*d*) δ 38.6. HRMS (ESI): m/z Calcd for $C_{18}H_{25}BNaO_4^+$ [M+Na^+]: 339.1738, found 339.1731.



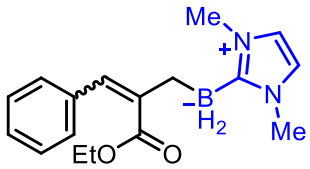
ethyl (Z)-2-(hydroxymethyl)-3-phenylacrylate (**8**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 5H), 6.99 (s, 1H), 4.43 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 1H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.2, 136.6, 135.4, 132.8, 128.6, 128.3, 128.0, 65.4, 60.9, 13.8.



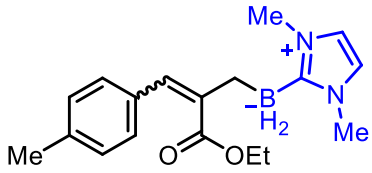
3-methylene-4,5-diphenyldihydrofuran-2(3H)-one (**9**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 7.36 – 7.32 (m, 4H), 7.23 – 7.19 (m, 2H), 7.19 – 7.16 (m, 2H), 6.45 (d, *J* = 3.3 Hz, 1H), 5.46 (d, *J* = 3.0 Hz, 1H), 5.38 (d, *J* = 7.7 Hz, 1H), 4.05 (dt, *J* = 7.8, 3.1 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.6, 139.9, 138.3, 138.2, 129.2, 128.8, 128.7, 128.5, 128.0, 125.5, 124.1, 85.9, 55.5.

7. Characterization of products

Note: In the ^{1}H NMR spectral data, the protons on boron are not listed due to quadrupole broadening and spin–spin coupling with boron.



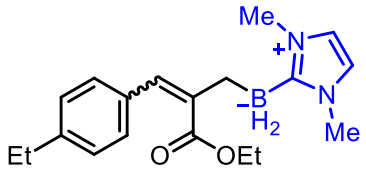
(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-(ethoxycarbonyl)-3-phenylallyl)dihydroborate (**3a**). 0.2 mmol scale, light yellow oil; (47.0 mg, 78%, *Z : E* = 4.2 : 1 (detected by ^{1}H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 – 7.59 (m, 0.5H), 7.33 (t, *J* = 7.7 Hz, 0.5H), 7.24 – 7.17 (m, 2.75H), 7.14 – 7.10 (m, 1H), 7.08 (dd, *J* = 7.8, 1.2 Hz, 2H), 6.80 (s, 2H), 6.72 (s, 0.5H), 6.09 (s, 1H), 4.08 – 3.97 (m, 2.5H), 3.76 (s, 6H), 3.70 (s, 1.5H), 1.96 (s, 0.5H), 1.76 (s, 2H), 1.23 (t, *J* = 7.1 Hz, 0.75H), 1.08 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.1, 170.5, 143.6, 142.0, 137.9, 137.7, 130.7, 129.8, 128.0, 127.5, 126.9, 126.2, 125.2, 120.2, 120.1, 60.2, 60.1, 36.0, 35.9, 14.4, 13.9. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.3, -22.5. HRMS (ESI): m/z Calcd for $C_{17}H_{23}BN_2NaO_2^+$ [M+Na$^+$]: 321.1745, found 321.1743.



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-(ethoxycarbonyl)-3-(p-tolyl)allyl)dihydroborate (**3b**). 0.2 mmol scale, colorless oil; (41.0 mg, 66%, *Z* : *E* = 1.3 : 1 (separated)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1).

(*Z*-**3b**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.00 (q, *J* = 8.2 Hz, 4H), 6.80 (s, 2H), 6.04 (s, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 6H), 2.28 (s, 3H), 1.75 (s, 2H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.2, 142.7, 135.8, 135.0, 128.6, 127.4, 125.2, 120.1, 60.0, 36.0, 21.1, 14.0. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.3. HRMS (ESI): m/z Calcd for $C_{18}H_{25}BN_2NaO_2^+$ [M+Na$^+$]: 335.1901, found 335.1899.

(*E*-**3b**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 5.0 Hz, 2H), 7.15 (s, 1H), 6.73 (s, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 6H), 2.35 (s, 3H), 1.96 (s, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.5, 141.0, 136.8, 134.8, 131.0, 129.9, 128.8, 120.0, 60.1, 35.9, 21.3, 14.4. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.6. HRMS (ESI): m/z Calcd for $C_{18}H_{25}BN_2NaO_2^+$ [M+Na$^+$]: 335.1901, found 335.1896.

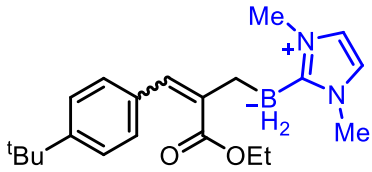


(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-(ethoxycarbonyl)-3-(4-ethylphenyl)allyl)dihydroborate (**3c**). 0.2 mmol scale, yellow oil; (40.0 mg, 61%, Z : E = 3 : 1 (separated)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1).

(*Z*-**3c**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.02 (q, *J* = 8.3 Hz, 4H), 6.80 (s, 2H), 6.05 (s, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 6H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.75 (s, 2H), 1.19 (t, *J* = 7.6 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.2, 142.7, 142.2, 135.2, 127.5, 127.4, 125.3, 120.1, 60.0, 36.0, 28.5, 15.5, 13.9. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.3. HRMS (ESI): m/z Calcd for $C_{19}H_{27}BN_2NaO_2^+$ [M+Na$^+$]: 349.2058, found 349.2052.

(*E*-**3c**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.17 (m, 3H), 6.73 (s, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 6H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.97

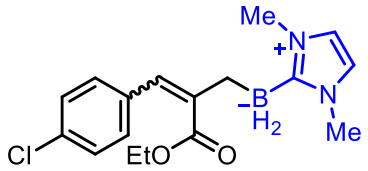
(s, 2H), 1.26 – 1.20 (m, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.6, 143.1, 141.0, 135.0, 131.0, 130.0, 127.6, 120.0, 60.1, 35.9, 28.7, 15.6, 14.4. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.6. HRMS (ESI): m/z Calcd for $C_{19}H_{27}BN_2NaO_2^+$ [M+Na$^+$]: 349.2058, found 349.2055.



(3-(4-(tert-butyl)phenyl)-2-(ethoxycarbonyl)allyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3d**). 0.2 mmol scale, colorless oil; (42.0 mg, 59%, *Z* : *E* = 2.6 : 1 (separated)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1).

(*Z*-**3d**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.80 (s, 2H), 6.06 (s, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 6H), 1.74 (s, 2H), 1.27 (s, 9H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.2, 149.0, 142.8, 135.0, 127.2, 125.2, 124.8, 120.1, 60.0, 36.0, 34.4, 31.3, 13.9. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.3. HRMS (ESI): m/z Calcd for $C_{21}H_{31}BN_2NaO_2^+$ [M+Na$^+$]: 377.2371, found 377,2368.

(*E*-**3d**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.18 (s, 1H), 6.72 (s, 2H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 6H), 1.98 (s, 2H), 1.33 (s, 9H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.6, 149.9, 141.2, 134.8, 130.9, 129.7, 125.0, 120.0, 60.1, 35.9, 34.6, 31.3, 14.4. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.6. HRMS (ESI): m/z Calcd for $C_{21}H_{31}BN_2NaO_2^+$ [M+Na$^+$]: 377.2371, found 377.2370.

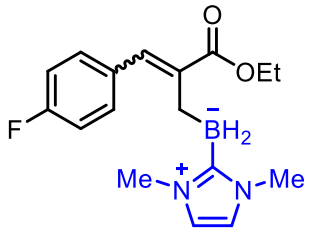


(3-(4-chlorophenyl)-2-(ethoxycarbonyl)allyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3e**). 0.2 mmol scale, light yellow oil; (34.0 mg, 51%, *Z* : *E* = 2.4 : 1 (separated)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1).

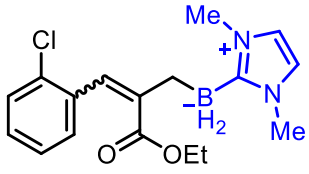
(*Z*-**3e**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.17 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.81 (s, 2H), 6.06 (s, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 6H), 1.74 (s, 2H),

1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.7, 144.5, 136.4, 131.8, 128.8, 128.0, 124.0, 120.2, 60.2, 36.0, 14.0. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.4. HRMS (ESI): m/z Calcd for $C_{17}H_{22}BClN_2NaO_2^+$ [M+Na$^+$]: 355.1355, found 355.1352.

(*E*-**3e**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.13 (s, 1H), 6.75 (s, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 6H), 1.92 (s, 2H), 1.23 (q, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.2, 142.6, 136.1, 132.6, 131.2, 129.4, 128.2, 120.1, 60.3, 35.92, 14.4. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.7. HRMS (ESI): m/z Calcd for $C_{17}H_{22}BClN_2NaO_2^+$ [M+Na$^+$]: 355.1355, found 355.1352.



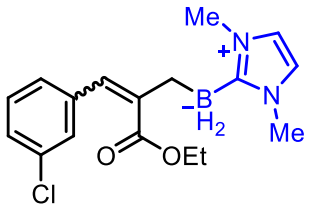
(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-(ethoxycarbonyl)-3-(4-fluorophenyl)allyl)dihydroborate (**3f**). 0.2 mmol scale, light yellow oil; (45.0 mg, 71%, *Z* : *E* = 2 : 1 (detected by ^{1}H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (dd, *J* = 8.6, 5.7 Hz, 1H), 7.15 (s, 0.5H), 7.08 – 6.98 (m, 3H), 6.88 (t, *J* = 8.8 Hz, 2H), 6.80 (s, 2H), 6.75 (s, 1H), 6.08 (s, 1H), 4.05 – 3.96 (m, 3H), 3.76 (s, 6H), 3.72 (s, 3H), 1.91 (s, 1H), 1.72 (s, 2H), 1.21 (t, *J* = 7.2 Hz, 1.5H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.9, 170.3, 161.7 (d, *J* = 245.4 Hz), 161.4 (d, *J* = 245.1 Hz) 143.6, 141.6, 134.0 (d, *J* = 3.2 Hz), 133.7 (d, *J* = 3.3 Hz), 131.6 (d, *J* = 7.7 Hz), 129.7, 129.1 (d, *J* = 7.9 Hz), 124.2, 120.2, 120.1, 120.0, 115.0, 114.8, 114.6, 60.2, 60.1, 36.0, 35.9, 14.4, 13.9. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.4, -22.6. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -114.9, -116.5. HRMS (ESI): m/z Calcd for $C_{17}H_{22}BFN_2NaO_2^+$ [M+Na$^+$]: 339.1651, found 339.1645.



(3-(2-chlorophenyl)-2-(ethoxycarbonyl)allyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3g**). 0.2 mmol scale, colorless oil; (40.0 mg, 60%, *Z* : *E* = 3 : 1 (separated)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1).

(*Z*-**3g**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.25 (m, 1H), 7.16 – 7.07 (m, 3H), 6.82 (s, 2H), 6.19 (s, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 6H), 1.85 (s, 2H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.1, 145.9, 136.8, 132.6, 129.7, 128.8, 127.5, 126.2, 122.8, 120.3, 60.0, 36.1, 13.8. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.5. HRMS (ESI): m/z Calcd for $C_{17}H_{22}BClN_2NaO_2^+$ [M+Na$^+$]: 355.1355, found 355.1354.

(*E*-**3g**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.31 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.14 (td, *J* = 7.7, 1.7 Hz, 1H), 6.69 (s, 2H), 4.10 (q, *J* = 15.4, 7.2 Hz, 2H), 3.67 (s, 6H), 1.90 (s, 2H), 1.30 – 1.25 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.2, 143.7, 135.8, 133.8, 131.2, 129.1, 127.9, 126.8, 126.2, 120.2, 60.3, 35.9, 14.4. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.4. HRMS (ESI): m/z Calcd for $C_{17}H_{22}BClN_2NaO_2^+$ [M+Na$^+$]: 355.1355, found 355.1352.

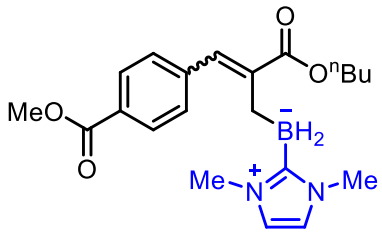


(3-(3-chlorophenyl)-2-(ethoxycarbonyl)allyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3h**). 0.2 mmol scale, light yellow oil; (46.0 mg, 69%, *Z* : *E* = 3.6 : 1 (separated)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1).

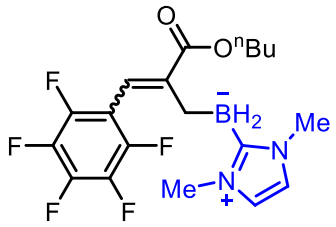
(*Z*-**3h**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.13 (t, *J* = 7.6 Hz, 1H), 7.11 – 7.05 (m, 2H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.82 (s, 2H), 6.05 (s, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 6H), 1.75 (s, 2H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.6, 145.3, 139.8 133.7, 129.1, 127.5, 126.1, 125.7, 123.7 120.2, 60.3 36.0, 13.9. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.3. HRMS (ESI): m/z Calcd for $C_{17}H_{22}BClN_2NaO_2^+$ [M+Na$^+$]: 355.1355, found 355.1350.

(*E*-**3h**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (s, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.24 (m, 1), 7.18 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H), 7.09 (s, 1H), 6.75 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2), 3.74 (s, 6), 1.91 (s, 2), 1.28 – 1.17 (m, 3). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.2, 143.6, 139.6, 133.7, 129.3, 129.2, 128.8, 128.0, 126.72, 120.1,

60.4, 35.9, 14.4. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.7. HRMS (ESI): m/z Calcd for $C_{17}H_{22}BClN_2NaO_2^+$ [M+Na$^+$]: 355.1355, found 355.1352.

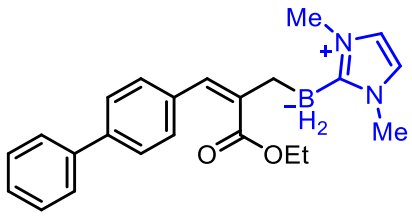


(2-(butoxycarbonyl)-3-(4-(methoxycarbonyl)phenyl)allyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3i**). 0.2 mmol scale, light yellow oil; (46.0 mg, 60%, *Z* : *E* = 1.4 : 1 (detected by ^{1}H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.4 Hz, 1.4H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 1.4H), 7.15 (s, 0.7H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.81 (s, 2H), 6.73 (s, 1.4H), 6.08 (s, 1H), 4.01 – 3.95 (m, 3.4H), 3.90 (s, 2.1H), 3.87 (s, 3H), 3.76 (s, 6H), 3.71 (s, 4.2H), 1.95 (s, 1.4H), 1.77 (s, 2H), 1.64 – 1.57 (m, 1.4H), 1.47 – 1.36 (m, 3.4H), 1.20 – 1.11 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 2.1H), 0.80 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.8, 170.1, 167.1, 167.0, 146.5, 144.6, 142.8, 142.5, 129.6, 129.4, 129.3, 129.1, 127.6, 127.3, 127.0, 123.9, 120.2, 120.1, 64.4, 64.3, 52.0, 51.9, 36.0, 35.9, 30.8, 30.4, 19.3, 19.0, 13.8, 13.7. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.3, -22.6. HRMS (ESI): m/z Calcd for $C_{21}H_{29}BN_2NaO_4^+$ [M+Na$^+$]: 407.2113, found 407.2109.



(2-(butoxycarbonyl)-3-(perfluorophenyl)allyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3j**). 0.2 mmol scale, light yellow oil; (46.5 mg, 56%, *Z* : *E* = 1 : 1.7 (detected by ^{1}H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.82 (s, 1.2H), 6.72 (s, 2H), 6.60 (d, *J* = 1.8 Hz, 1H), 5.76 (d, *J* = 1.8 Hz, 0.6H), 4.06 (t, *J* = 6.7 Hz, 2H), 3.95 (t, *J* = 6.7 Hz, 1.2H), 3.74 (s, 3.6H), 3.63 (s, 6H), 1.87 (s, 1.2H), 1.69 (s, 2H), 1.65 – 1.60 (m, 2H), 1.51 – 1.44 (m, 1.2H), 1.44 – 1.38 (m, 2H), 1.23 – 1.19 (m, 1.2H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 1.8H).

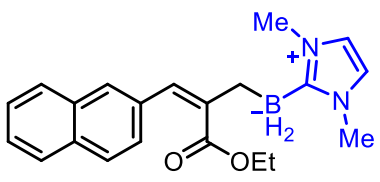
^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.1, 168.5, 151.6, 150.7, 145.9 – 142.1 (m), 137.4 (d, *J* = 251.2 Hz), 120.3, 120.2, 112.9, 109.5, 64.6, 64.4, 35.9, 35.7, 30.7, 30.4, 19.2, 19.1, 13.8, 13.6. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.1, -22.6. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -138.1 – -138.2 (m), -141.6 – -141.7 (m), -157.2 (t, *J* = 20.9 Hz), -158.3 (t, *J* = 20.8 Hz), -163.2 (td, *J* = 22.3, 7.4 Hz), -164.0 (td, *J* = 22.3, 7.4 Hz). HRMS (ESI): m/z Calcd for $C_{19}H_{22}BF_5N_2NaO_2^+$ [M+Na$^+$]: 439.1587, found 439.1586.



(3-([1,1'-biphenyl]-4-yl)-2-(ethoxycarbonyl)allyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3k**). 0.2 mmol scale, light yellow oil; (34.0 mg, 51%, *Z* : *E* = 2.4 : 1 (separated)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1).

(*Z*-**3k**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 – 7.55 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.82 (s, 2H), 6.12 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 6H), 1.80 (s, 2H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.1, 143.9, 140.9, 138.8, 136.9, 128.7, 128.0, 127.1, 126.9, 126.6, 124.8, 120.2, 60.2, 36.1, 14.0. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.3. HRMS (ESI): m/z Calcd for $C_{23}H_{27}BN_2NaO_2^+$ [M+Na$^+$]: 397.2058, found 397.2055.

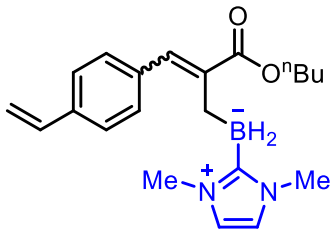
(*E*-**3k**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.57 (m, 4H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.31 (m, 1H), 7.23 (s, 1H), 6.74 (s, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 6H), 2.02 (s, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.4, 142.1, 140.9, 139.5, 136.73, 130.4 130.4, 128.8, 127.2, 127.0, 126.7, 120.1, 60.2, 36.0, 14.4. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.5. HRMS (ESI): m/z Calcd for $C_{23}H_{27}BN_2NaO_2^+$ [M+Na$^+$]: 397.2058, found 397.2056.



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-(ethoxycarbonyl)-3-(naphthalen-2-yl)allyl)dihydroborate (**3l**). 0.2 mmol scale, colorless oil; (44.0 mg, 63%, *Z* : *E* = 2.2 : 1 (separated)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1).

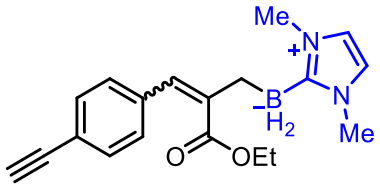
(*Z*-**3l**) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 – 7.70 (m, 2H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.53 (s, 1H), 7.46 – 7.35 (m, 2H), 7.27 – 7.22 (m, 1H), 6.80 (s, 2H), 6.26 (s, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 6H), 1.83 (s, 2H), 1.07 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.1, 144.2, 135.5, 133.4, 132.1, 127.8, 127.5, 127.3, 126.2, 126.1, 125.9, 125.4, 125.2, 120.2, 60.2, 36.0, 14.0. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.2. HRMS (ESI): m/z Calcd for $C_{21}H_{25}BN_2NaO_2^+$ [M+Na$^+$]: 371.1901, found 371.1897.

(*E*-**3l**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.88 – 7.69 (m, 4H), 7.49 – 7.40 (m, 2H), 7.34 (s, 1H), 6.79 (s, 2H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.73 (s, 6H), 2.06 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.4, 142.5, 135.3, 133.4, 132.4, 130.7, 128.8, 128.3, 128.1, 127.5, 127.3, 125.8, 125.8, 120.0, 60.2, 35.9, 14.4. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.5. HRMS (ESI): m/z Calcd for $C_{21}H_{25}BN_2NaO_2^+$ [M+Na$^+$]: 371.1901, found 371.1900.



(2-(butoxycarbonyl)-3-(4-vinylphenyl)allyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3m**). 0.2 mmol scale, light yellow oil; (45.0 mg, 58%, *Z* : *E* = 1 : 1.7 (detected by ^{1}H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.3 Hz, 0.8H), 7.41 – 7.38 (m, 0.8H), 7.27 – 7.23 (m, 2H), 7.17 (s, 0.4H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.80 (s, 2H), 6.72 (s, 0.8H), 6.72 – 6.69 (m, 0.4H), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.03 (s, 1H), 5.75 (dd, *J* = 17.6, 1.0 Hz, 0.4H), 5.68 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.23 (dd, *J* = 10.9, 0.9 Hz, 0.4H), 5.17 (dd, *J* = 10.8, 1.0 Hz, 1H), 4.00 – 3.93 (m, 2.8H), 3.76 (s, 6H), 3.72 (s, 2.4H), 1.98 (s, 0.8H), 1.75 (s, 2H), 1.62 – 1.55 (m, 0.8H), 1.49 – 1.44 (m, 2H), 1.42 – 1.36 (m, 0.8H), 1.21 – 1.14 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 1.2H), 0.82 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 170.4, 143.9, 142.1, 137.6, 137.3, 136.7, 136.6, 136.1, 135.5, 130.4, 130.1, 127.6, 125.9, 125.9, 124.7, 120.2, 120.1, 113.6, 113.0, 64.2, 64.1, 36.0, 35.9,

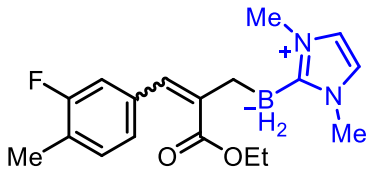
30.9, 30.4, 19.3, 19.1, 13.8, 13.7. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.3, -22.5. HRMS (ESI): m/z Calcd for $C_{21}H_{29}BN_2NaO_2^+$ [M+Na$^+$]: 375.2214, found 375.2209.



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-(ethoxycarbonyl)-3-(4-ethynylphenyl)allyl)dihydroborate (**3n**). 0.2 mmol scale, light yellow oil; (34.0 mg, 53%, *Z* : *E* = 7.5 : 1 (separated)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1).

(*Z*-**3n**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.81 (s, 2H), 6.07 (s, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 6H), 3.05 (s, 1H), 1.75 (s, 2H), 1.10 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.8, 145.0, 138.5, 131.8, 131.7, 129.7, 127.4, 124.3, 120.2, 120.1, 119.6, 83.9, 77.1, 60.3, 36.0, 13.9. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.3. HRMS (ESI): m/z Calcd for $C_{19}H_{23}BN_2NaO_2^+$ [M+Na$^+$]: 345.1745, found 345.1745.

(*E*-**3n**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.14 (s, 1H), 6.74 (s, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 6H), 3.10 (s, 1H), 1.95 (s, 2H), 1.25 – 1.22 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.7, 138.3, 131.8, 129.7, 120.1, 83.31, 58.9, 35.9, 14.9. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.7. HRMS (ESI): m/z Calcd for $C_{19}H_{23}BN_2NaO_2^+$ [M+Na$^+$]: 345.1745, found 345.1747.

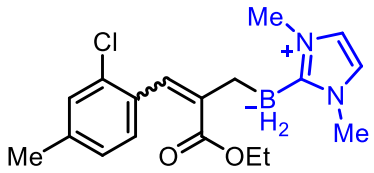


(Z)-(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-(ethoxycarbonyl)-3-(3-fluoro-4-methylphenyl)allyl)dihydroborate (**3o**). 0.2 mmol scale, colorless oil; (40.0 mg, 61%, *Z* : *E* = 3 : 1 (separated)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1).

(*Z*-**3o**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.03 – 6.97 (m, 1H), 6.81 (s, 2H), 6.77 – 6.71 (m, 2H), 5.99 (s, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 6H), 2.20 (d, *J* = 1.8 Hz, 3H), 1.73 (s, 2H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.8, 161.0 (d, *J* = 243.3 Hz), 144.1, 137.4 (d, *J* = 7.7 Hz), 130.8 (d, *J* = 5.6 Hz), 123.9, 123.1

(d, *J* = 2.9 Hz), 122.5 (d, *J* = 17.4 Hz), 120.2, 113.8 (d, *J* = 22.6 Hz), 60.2, 36.0, 14.3 (d, *J* = 3.4 Hz), 14.0. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.4. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -118.8. HRMS (ESI): m/z Calcd for $C_{18}H_{24}BFN_2NaO_2^+$ [M+Na$^+$]: 353.1807, found 353.1805.

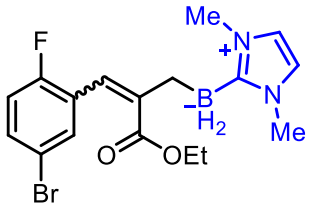
(***E*-3o**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 (dd, *J* = 11.6, 1.7 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.17 – 7.09 (m, 2H), 6.75 (s, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 6H), 2.27 (d, *J* = 1.8 Hz, 3H), 1.92 (s, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.3, 161.03 (d, *J* = 243.3 Hz), 142.3, 137.2 (d, *J* = 7.9 Hz), 130.8 (d, *J* = 5.7 Hz), 129.6 (d, *J* = 2.4 Hz), 125.5 (d, *J* = 3.0 Hz), 120.1, 116.0, 115.8, 60.3, 35.9, 14.5 (d, *J* = 3.3 Hz), 14.4. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.7. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -118.5. HRMS (ESI): m/z Calcd for $C_{18}H_{24}BFN_2NaO_2^+$ [M+Na$^+$]: 353.1807, found 353.1804.



(3-(2-chloro-4-methylphenyl)-2-(ethoxycarbonyl)allyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3p**). 0.2 mmol scale, light yellow oil; (48.0 mg, 69%, *Z* : *E* = 2.2 : 1 (separated)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1).

(*Z*-**3p**) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.08 (s, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.90 – 6.86 (m, 1H), 6.79 (s, 2H), 6.12 (s, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 6H), 2.25 (s, 3H), 1.82 (s, 2H), 1.06 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.3, 145.2, 137.7, 133.7, 132.3, 129.4, 129.3, 127.0, 122.7, 120.3, 60.0, 36.1, 20.8, 13.9. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.5. HRMS (ESI): m/z Calcd for $C_{18}H_{24}BClN_2NaO_2^+$ [M+Na$^+$]: 369.1512, found 369.1511.

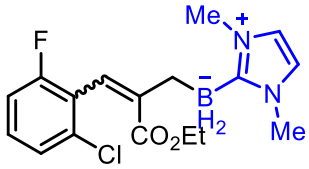
(*E*-**3p**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.25 (s, 1H), 7.15 (d, *J* = 1.0 Hz, 1H), 7.06 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.71 (s, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 6H), 2.32 (s, 3H), 1.89 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.3, 142.9, 138.1, 133.7, 132.7, 131.0, 129.6, 127.0, 126.9, 120.1, 60.3, 35.9, 21.0, 14.4. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.4. HRMS (ESI): m/z Calcd for $C_{18}H_{24}BClN_2NaO_2^+$ [M+Na$^+$]: 369.1512, found 369.1509.



(3-(5-bromo-2-fluorophenyl)-2-(ethoxycarbonyl)allyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3q**). 0.2 mmol scale, light yellow oil; (45.0 mg, 57%, *Z* : *E* = 3.5 : 1 (separated)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1).

(*Z*-**3q**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 – 7.18 (m, 2H), 6.82 (t, *J* = 9.0 Hz, 1H), 6.81 (s, 2H), 6.02 (s, 1H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 6H), 1.80 (s, 2H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.7, 158.8 (d, *J* = 246.5 Hz), 147.6, 132.3 (d, *J* = 3.6 Hz), 130.4 (d, *J* = 8.4 Hz), 128.2 (d, *J* = 16.1 Hz), 120.3, 120.2, 116.9 (d, *J* = 2.7 Hz), 116.8, 116.6, 115.9 (d, *J* = 3.2 Hz), 60.3, 36.0, 13.9. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.3. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -118.7. HRMS (ESI): m/z Calcd for $C_{17}H_{21}BBrFN_2NaO_2^+$ [M+Na$^+$]: 417.0756, found 417.0751.

(*E*-**3q**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 6.8, 2.6 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.12 (s, 1H), 6.88 (dd, *J* = 9.8, 8.7 Hz, 1H), 6.74 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 6H), 1.85 (s, 2H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.7, 159.4 (d, *J* = 248.6 Hz), 145.4, 133.5 (d, *J* = 3.3 Hz), 130.9 (d, *J* = 8.4 Hz), 127.7 (d, *J* = 14.3 Hz), 120.3 (d, *J* = 4.6 Hz), 120.2, 116.7 (d, *J* = 23.8 Hz), 116.0 (d, *J* = 3.7 Hz), 60.5, 36.0, 14.4. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.6. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -117.2. HRMS (ESI): m/z Calcd for $C_{17}H_{21}BBrFN_2NaO_2^+$ [M+Na$^+$]: 417.0756, found 417.0756.

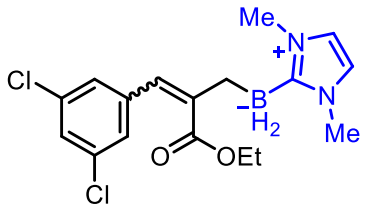


(3-(2-chloro-6-fluorophenyl)-2-(ethoxycarbonyl)allyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3r**). 0.2 mmol scale, light yellow oil; (44.0 mg, 63%, *Z* : *E* = 1 : 3 (separated)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1).

(*Z*-**3r**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.11 – 7.07 (m, 1H), 7.07 – 7.03 (m, 1H), 6.86 (ddd, *J* = 9.5, 7.9, 1.5 Hz, 1H), 6.79 (s, 2H), 6.00 (s, 1H), 3.95 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 6H), 1.91 (s, 2H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-

d) δ 169.6, 160.2 (d, *J* = 247.4 Hz), 148.1, 134.0 (d, *J* = 5.3 Hz), 127.6 (d, *J* = 9.5 Hz), 126.0 (d, *J* = 18.9 Hz), 124.6 (d, *J* = 3.4 Hz), 120.3, 117.5, 113.5 (d, *J* = 23.7 Hz), 60.0, 36.1, 13.8. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.1. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -110.8. HRMS (ESI): m/z Calcd for $C_{17}H_{21}BClFN_2NaO_2^+$ [M+Na$^+$]: 373.1261, found 373.1259.

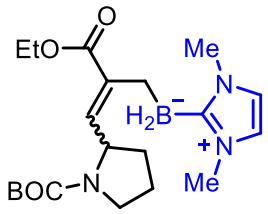
(*E*-**3r**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.11 (td, *J* = 3.7, 2.6 Hz, 2H), 6.96 – 6.90 (m, 1H), 6.79 (s, 1H), 6.65 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.56 (s, 6H), 1.71 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.4, 159.6 (d, *J* = 249.3 Hz), 147.4, 134.7 (d, *J* = 5.5 Hz), 128.0 (d, *J* = 9.3 Hz), 125.3 (d, *J* = 19.6 Hz), 124.8 (d, *J* = 3.4 Hz), 120.2, 120.1, 113.9 (d, *J* = 23.2 Hz), 60.4, 35.7, 14.4. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.6. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -107.3. HRMS (ESI): m/z Calcd for $C_{17}H_{21}BClFN_2NaO_2^+$ [M+Na$^+$]: 373.1261, found 373.1260.



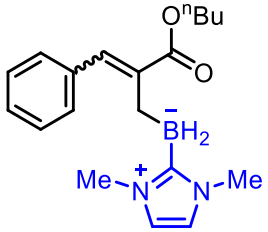
(3-(3,5-dichlorophenyl)-2-(ethoxycarbonyl)allyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3s**). 0.2 mmol scale, light yellow oil; (35.0 mg, 48%, *Z* : *E* = 2.5 : 1 (separated)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1).

(*Z*-**3s**) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.11 (t, *J* = 1.9 Hz, 1H), 6.99 – 6.94 (m, 2H), 6.82 (s, 2H), 6.00 (s, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 6H), 1.74 (s, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.2, 147.0, 140.9, 134.3, 126.0, 125.9, 122.3, 120.3, 60.4, 36.0, 13.9. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.4. HRMS (ESI): m/z Calcd for $C_{17}H_{21}BCl_2N_2NaO_2^+$ [M+Na$^+$]: 389.0965, found 389.0968.

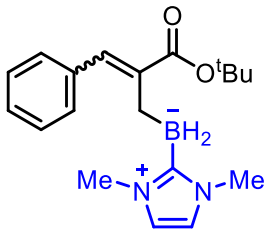
(*E*-**3s**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 1.9 Hz, 2H), 7.19 (t, *J* = 1.9 Hz, 1H), 7.01 (s, 1H), 6.77 (s, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 6H), 1.85 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.7. HRMS (ESI): m/z Calcd for $C_{17}H_{21}BCl_2N_2NaO_2^+$ [M+Na$^+$]: 389.0965, found 389.0966.



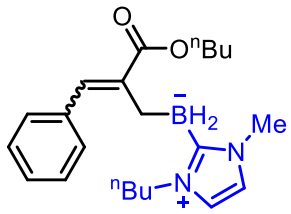
(3-(1-((l1-boranyl)carbonyl)pyrrolidin-2-yl)-2-(ethoxycarbonyl)allyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3t**). 0.2 mmol scale, light yellow oil; (64.0 mg, 82%, *Z* : *E* = 9 : 1 (detected by ^{1}H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.76 (s, 2H), 6.13 (d, *J* = 9.0 Hz, 1H), 4.61 (s, 1H), 3.97 – 3.88 (m, 2H), 3.73 (s, 6H), 3.40 – 3.34 (m, 1H), 2.25 – 2.16 (m, 1H), 1.92 – 1.82 (m, 1H), 1.82 – 1.75 (m, 1H), 1.73 – 1.67 (m, 2H), 1.36 (s, 9H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.6, 139.2 135.8 120.0, 79.1 59.7, 56.5, 55.5 46.4 35.9 33.2, 28.5, 24.0, 14.3. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -21.9, 22.2. HRMS (ESI): m/z Calcd for $C_{20}H_{34}BN_3NaO_4^+$ [M+Na$^+$]: 414.2535, found 414.2530.



(2-(butoxycarbonyl)-3-phenylallyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3u**). 0.2 mmol scale, light yellow oil; (45.0 mg, 69%, *Z* : *E* = 2.4 : 1 (detected by 1H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.5 Hz, 0.85H), 7.33 (t, *J* = 7.7 Hz, 0.89H), 7.23 – 7.18 (m, 2.46H), 7.17 (s, 0.43H), 7.13 – 7.09 (m, 1H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.80 (s, 2H), 6.71 (s, 0.82H), 6.06 (s, 1H), 3.99 – 3.92 (m, 2.87H), 3.76 (s, 6H), 3.70 (s, 2.47H), 1.96 (s, 0.87H), 1.75 (s, 2H), 1.62 – 1.56 (m, 0.88H), 1.45 – 1.41 (m, 2H), 1.40 – 1.36 (m, 0.89H), 1.20 – 1.11 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 1.36H), 0.81 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.2, 170.5, 143.8, 142.1, 138.0, 137.7, 130.6, 129.8, 128.0, 127.9, 127.4, 126.9, 126.1, 125.1, 120.2, 120.1, 77.3, 77.1, 76.8, 64.2, 64.1, 36.0, 35.9, 30.9, 30.4, 19.3, 19.0, 13.8, 13.7. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.3, -22.5. HRMS (ESI): m/z Calcd for $C_{19}H_{27}BN_2O_2^+$ [M+Na$^+$]: 349.2059, found 349.2055.

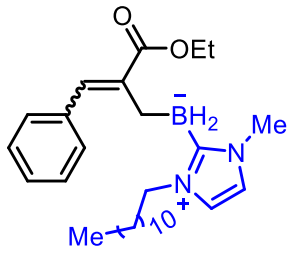


(2-(tert-butoxycarbonyl)-3-phenylallyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3v**). 0.2 mmol scale, light yellow oil; (48.0 mg, 74%, *Z* : *E* = 3.7 : 1 (detected by ^{1}H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.3 Hz, 0.58H), 7.31 (t, *J* = 7.7 Hz, 0.6H), 7.22 – 7.17 (m, 2.27H), 7.13 – 7.11 (m, 1H), 7.11 – 7.08 (m, 2H), 6.81 (s, 2H), 6.70 (s, 0.52H), 5.89 (s, 1H), 3.77 (s, 6H), 3.68 (s, 1.66H), 1.94 (s, 0.58H), 1.80 – 1.65 (m, 2H), 1.41 (s, 2.64H), 1.35 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.2, 169.7, 145.2, 143.7, 138.3, 137.9, 129.8, 129.7, 127.9, 127.8, 127.6, 126.6, 126.0, 123.8, 120.2, 120.1, 80.1, 79.2, 36.0, 35.9, 28.2, 27.9, 27.8. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.4. HRMS (ESI): m/z Calcd for $C_{19}H_{27}BN_2NaO_2^+$ [M+Na$^+$]: 349.2058, found 349.2054.

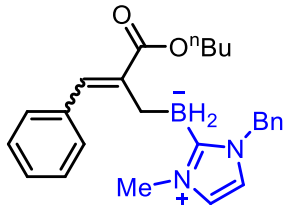


(2-(butoxycarbonyl)-3-phenylallyl)(3-butyl-1-methyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3w**). 0.2 mmol scale, colorless oil; (68.0 mg, 92%, *Z* : *E* = 2.5 : 1 (detected by ^{1}H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.3 Hz, 0.8H), 7.32 (t, *J* = 7.7 Hz, 0.8H), 7.22 – 7.20 (m, 0.4H), 7.20 – 7.17 (m, 2.5H), 7.13 – 7.10 (m, 1H), 7.10 – 7.06 (m, 2H), 6.82 (dd, *J* = 14.3, 1.9 Hz, 2H), 6.74 (dd, *J* = 13.1, 2.0 Hz, 0.8H), 6.08 (s, 1H), 4.16 – 4.10 (m, 2H), 4.08 – 4.04 (m, 0.8H), 4.02 – 3.94 (m, 2.8H), 3.75 (s, 3H), 3.72 (s, 1.2H), 1.93 (s, 0.8H), 1.75 – 1.67 (m, 3.3H), 1.64 – 1.56 (m, 1H), 1.47 – 1.40 (m, 3H), 1.39 – 1.29 (m, 4H), 1.21 – 1.10 (m, 2H), 1.02 – 0.87 (m, 5.6H), 0.81 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.2, 170.4, 143.6, 141.4, 138.0, 137.7, 131.9, 130.8, 129.9, 128.0, 127.9, 127.6, 126.8, 126.1, 125.2, 120.3, 120.2, 118.7, 118.5, 60.1, 48.7, 36.0, 35.8, 31.9, 30.7, 30.5, 29.6, 29.5, 29.4, 29.2, 26.6, 22.7, 14.4, 14.1, 13.9. ^{11}B NMR

(160 MHz, Chloroform-*d*) δ -22.4. HRMS (ESI): m/z Calcd for $C_{22}H_{33}BN_2NaO_2^+$ [M+Na^+]: 391.2527, found 391.2527.

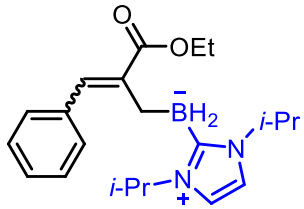


(3-dodecyl-1-methyl-1H-imidazol-3-ium-2-yl)(2-(ethoxycarbonyl)-3-phenylallyl)dihydroborate (**3x**). 0.2 mmol scale, light yellow oil; (71.0 mg, 78%, *Z* : *E* = 2 : 1 (detected by ^{1}H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.23 – 7.18 (m, 3H), 7.15 – 7.11 (m, 1H), 7.11 – 7.08 (m, 2H), 6.82 (dd, *J* = 15.5, 1.9 Hz, 2H), 6.76 (dd, *J* = 13.1, 1.9 Hz, 1H), 6.11 (s, 1H), 4.16 – 4.10 (m, 2H), 4.08 – 4.05 (m, 1H), 4.05 – 4.00 (m, 3H), 3.77 (s, 3H), 3.74 (s, 1.5H), 1.94 (s, 1H), 1.82 – 1.69 (m, 2H), 1.60 (s, 6H), 1.27 – 1.18 (m, 24H), 1.09 (t, *J* = 7.1 Hz, 1.5H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.2, 170.4, 143.6, 141.4, 138.0, 137.7, 131.9, 130.8, 129.9, 128.0, 127.9, 127.6, 126.8, 126.1, 125.2, 120.3, 120.2, 118.7, 118.5, 60.1, 60.1, 48.7, 36.0, 35.8, 31.9, 30.7, 30.5, 29.6, 29.6, 29.5, 29.4, 29.2, 26.6, 22.7, 14.4, 14.1, 13.9. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.4. HRMS (ESI): m/z Calcd for $C_{28}H_{45}BN_2NaO_2^+$ [M+Na^+]: 475.3466, found 475.3467.

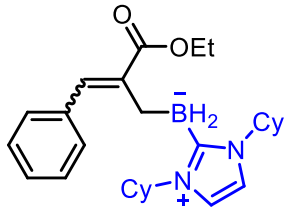


(1-benzyl-3-methyl-1H-imidazol-3-ium-2-yl)(2-(butoxycarbonyl)-3-phenylallyl)dihydroborate (**3y**). 0.2 mmol scale, colorless oil; (57.0 mg, 71%, *Z* : *E* = 3 : 1 (detected by ^{1}H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.6 Hz, 0.7H), 7.35 – 7.28 (m, 5H), 7.28 – 7.18 (m, 5.5H), 7.18 – 7.12 (m, 1H), 7.11 – 7.08 (m, 2H), 6.81 (d, *J* = 2.0 Hz, 1H), 6.72 (d, *J* = 2.0 Hz, 0.33H), 6.69 (d, *J* = 2.0 Hz, 1H), 6.60 (d, *J* = 2.0 Hz, 0.33H), 6.09 (s, 1H), 5.36 (s, 2H), 5.29 (s, 0.7H), 4.04 – 3.95 (m, 2.7H), 3.81 (s, 3H), 3.77 (s, 1H), 2.02 (s,

0.7H), 1.78 (s, 2H), 1.64 – 1.57 (m, 1H), 1.48 – 1.36 (m, 2.7H), 1.23 – 1.06 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 1H), 0.79 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.4, 170.5, 143.8, 142.0, 138.0, 137.7, 135.9, 135.8, 130.8, 129.8, 128.9, 128.5, 128.4, 128.3, 128.0, 127.9, 127.5, 126.9, 126.2, 125.0, 120.7, 120.6, 118.8, 118.6, 64.2, 64.1, 52.1, 52.0, 36.0, 35.9, 30.9, 30.4, 19.3, 19.1, 13.9, 13.7. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.2. HRMS (ESI): m/z Calcd for $C_{25}H_{31}BN_2NaO_2^+$ [M+Na$^+$]: 425.2371, found 425.2367.

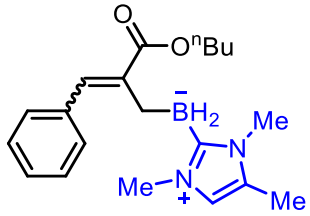


(1,3-diisopropyl-1H-imidazol-3-ium-2-yl)(2-(ethoxycarbonyl)-3-phenylallyl)dihydroborate (**3z**). 0.2 mmol scale, light yellow oil; (56.0 mg, 79%, *Z* : *E* = 2 : 1 (detected by ^{1}H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.27 (s, 0.5H), 7.23 (t, *J* = 1.3 Hz, 0.5H), 7.21 – 7.17 (m, 2H), 7.14 – 7.08 (m, 3H), 6.95 (s, 2H), 6.92 (s, 1H), 6.14 (s, 1H), 5.32 – 5.08 (m, 3H), 4.23 – 3.96 (m, 3H), 1.87 (s, 1H), 1.71 (s, 2H), 1.40 – 1.35 (m, 15H), 1.27 – 1.22 (m, 1.6H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.4, 170.4, 143.6, 142.0, 137.9, 137.8, 130.6, 129.9, 127.9, 127.8, 127.6, 126.8, 126.1, 124.9, 115.3, 115.2, 60.1, 49.1, 49.1, 23.3, 23.2, 14.4, 13.9. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.5. HRMS (ESI): m/z Calcd for $C_{21}H_{31}BN_2NaO_2^+$ [M+Na$^+$]: 377.2371, found 377.2371.

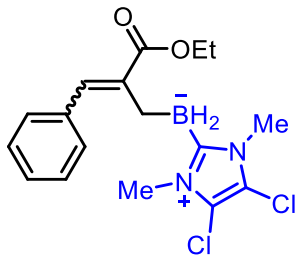


(1,3-dicyclohexyl-1H-imidazol-3-ium-2-yl)(2-(ethoxycarbonyl)-3-phenylallyl)dihydroborate (**3aa**). 0.2 mmol scale, light yellow oil; (68.0 mg, 78%, *Z* : *E* = 2.2 : 1 (detected by ^{1}H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.3 Hz, 0.9H), 7.32 (t, *J* = 7.7 Hz, 0.9H),

7.23 (s, 0.5H), 7.22 – 7.21 (m, 0.5H), 7.21 – 7.17 (m, 2H), 7.14 – 7.14 (m, 1H), 7.13 – 7.08 (m, 2H), 6.91 (s, 2H), 6.88 (s, 0.9H), 6.14 (s, 1H), 4.94 – 4.64 (m, 3.2H), 4.21 – 3.97 (m, 3.2H), 2.10 – 1.97 (m, 6H), 1.86 – 1.77 (m, 6H), 1.77 – 1.66 (m, 6H), 1.52 – 1.36 (m, 14H), 1.31 – 1.21 (m, 1.3H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.4, 170.4, 143.7, 142.2, 137.9, 137.8, 130.2, 129.8, 127.9, 127.8, 127.6, 126.7, 126.0, 124.7, 115.7, 115.6, 60.1, 56.6, 56.4, 33.9, 33.8, 25.5, 25.4, 25.3, 25.2, 14.5, 14.0. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.4. HRMS (ESI): m/z Calcd for $C_{27}H_{39}BN_2O_2^+$ [M+Na$^+$]: 457.2997, found 457.3001.



(2-(butoxycarbonyl)-3-phenylallyl)(1,3,5-trimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3bb**). 0.2 mmol scale, colorless oil; (50.0 mg, 73%, Z : E = 2.5 : 1 (detected by ^{1}H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (d, J = 7.3 Hz, 0.8H), 7.31 (t, J = 7.7 Hz, 0.8H), 7.19 (t, J = 7.5 Hz, 2.5H), 7.14 (s, 0.4H), 7.13 – 7.09 (m, 1H), 7.08 – 7.05 (m, 2H), 6.54 (d, J = 1.2 Hz, 1H), 6.44 (d, J = 1.4 Hz, 0.4H), 6.06 (s, 1H), 4.03 – 3.90 (m, 2.8H), 3.70 (s, 3H), 3.64 (s, 3H), 3.63 (s, 1.2H), 3.54 (s, 1.2H), 2.16 (d, J = 1.1 Hz, 3H), 2.08 (d, J = 1.2 Hz, 1.2H), 1.96 (s, 0.8H), 1.73 (s, 2H), 1.64 – 1.55 (m, 1H), 1.45 – 1.37 (m, 3H), 1.21 – 1.10 (m, 2H), 0.94 (t, J = 7.4 Hz, 1.2H), 0.81 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.6, 143.1, 141.0, 135.0, 131.0, 130.0, 127.6, 120.0, 60.1, 35.9, 28.7, 15.6, 14.4. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -22.1, -22.2. HRMS (ESI): m/z Calcd for $C_{20}H_{29}BN_2NaO_2^+$ [M+Na$^+$]: 363.2214, found 363.2213.



(2-(butoxycarbonyl)-3-phenylallyl)(4,5-dichloro-1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3cc**). 0.2 mmol scale, colorless oil; (60.0 mg, 82%, *Z* : *E* = 5 : 1 (detected by ^{1}H NMR)); Rf = 0.25 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.46 (m, 0.4H), 7.32 (t, *J* = 7.7 Hz, 0.4H), 7.22 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.17 (s, 0.2H), 7.16 – 7.12 (m, 1H), 7.08 (dd, *J* = 7.7, 1.3 Hz, 2H), 6.21 (s, 1H), 4.09 (q, *J* = 7.1 Hz, 0.4H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 6H), 3.65 (s, 1.2H), 1.99 (s, 0.4H), 1.75 (s, 2H), 1.28 – 1.25 (m, 0.6H), 1.06 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.9, 170.3, 143.0, 141.5, 137.8, 137.4, 130.9, 129.4, 128.0, 127.9, 127.5, 126.9, 126.3, 126.0, 116.2, 116.0, 60.2, 33.8, 33.6, 14.4, 13.8. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -21.3, -21.8. HRMS (ESI): m/z Calcd for $C_{17}H_{21}BCl_2N_2NaO_2^+$ [M+Na$^+$]: 389.0965, found 389.0962.

References

(1) (a) Brahmi, M. M.; Monot, J.; Desage-El Murr, M.; Curran, D. P.; Fensterbank, L.; Lacôte, E.; Malacria, M. Preparation of NHC Borane Complexes by Lewis Base Exchange with Amine− and Phosphine−Boranes. *J. Org. Chem.* **2010**, *75*, 6983; (b) Solovyev, A.; Ueng, S.H.; Monot, J.; Fensterbank, L.; Malacria, M.; Lacôte, E.; Curran, D. P. Estimated Rate Constants for Hydrogen Abstraction from N-Heterocyclic Carbene−Borane Complexes by an Alkyl Radical†. *Org. Lett.* **2010**, *12*, 2998; (c) Kawamoto, T.; Geib, S. J.; Curran, D. P. Radical Reactions of N-Heterocyclic Carbene Boranes with Organic Nitriles: Cyanation of NHC-Boranes and Reductive Decyanation of Malononitriles. *J. Am. Chem. Soc.* **2015**, *137*, 8617.

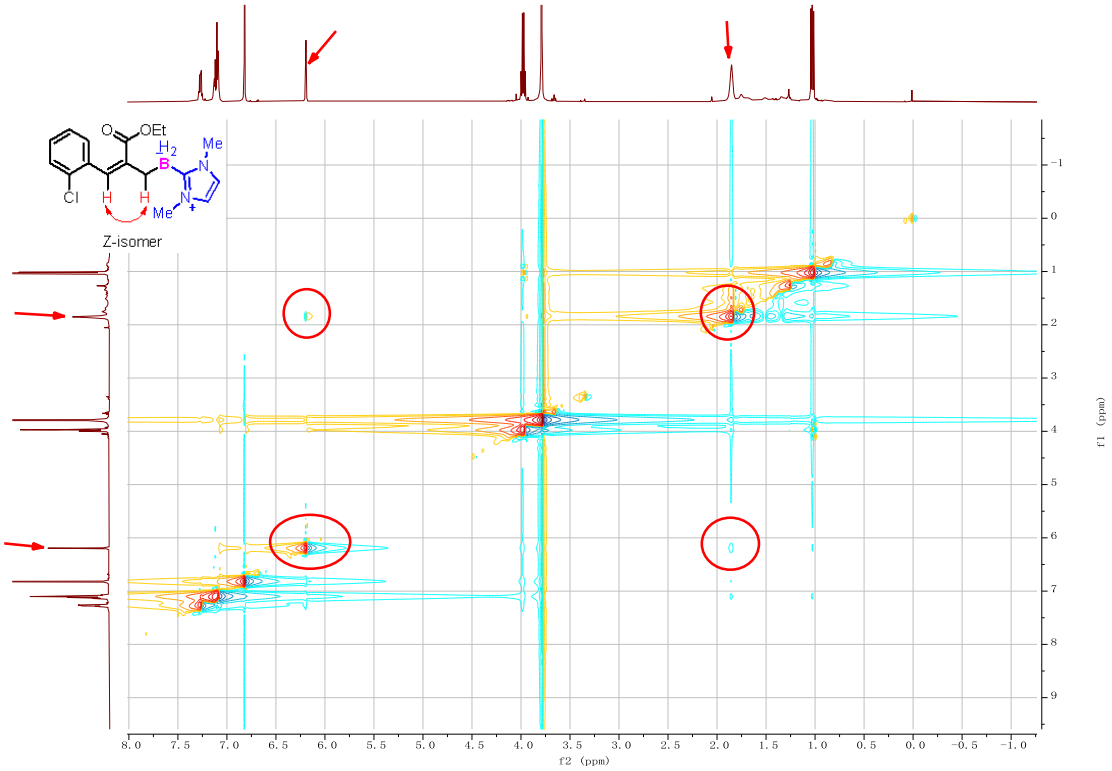
(2) Frogneux, X.; Hippolyte, L.; Mercier, D.; Portehault, D.; Chanac, C.; Sanchez, C.; Marcus, P.; Ribot, F.; Fensterbank, L.; Carenco, S. Direct Synthesis of N-Heterocyclic Carbene-Stabilized Copper Nanoparticles from an N-Heterocyclic Carbene–Borane. *Chem. Eur. J.* **2019**, *25*, 11481.

(3) Feng, J.; Lu, X.; Kong, A.; Han, X. A highly regio- and stereo-selective [3+2] annulation of allylic compounds and 2-substituted 1,1-dicyanoalkenes through a catalytic carbon–phosphorus ylide reaction. *Tetrahedron*. **2007**, *63*, 6035.

(4) (a) Mann, G.; John, K. D.; Baker, R. T. Platinum-Catalyzed Diboration Using a Commercially Available Catalyst: Diboration of Aldimines to α-Aminoboronate Esters. *Org. Lett.* **2000**, *2*, 2105; (b) Cho, H. Y.; Yu, Z.Y.; Morken, J. P. Stereoselective Borylative Ketone-Diene Coupling. *Org. Lett.* **2011**, *13*, 5267. (c) Kennedy, J. W. J.; Hall, D. G. Lewis Acid Catalyzed Allylboration: Discovery, Optimization, and Application to the Formation of Stereogenic Quaternary Carbon Centers. *J. Org. Chem.* **2004**, *69*, 4412.

NMR spectra

^{1}H -^{1}H Noesy Spectra of ***Z*-3e**



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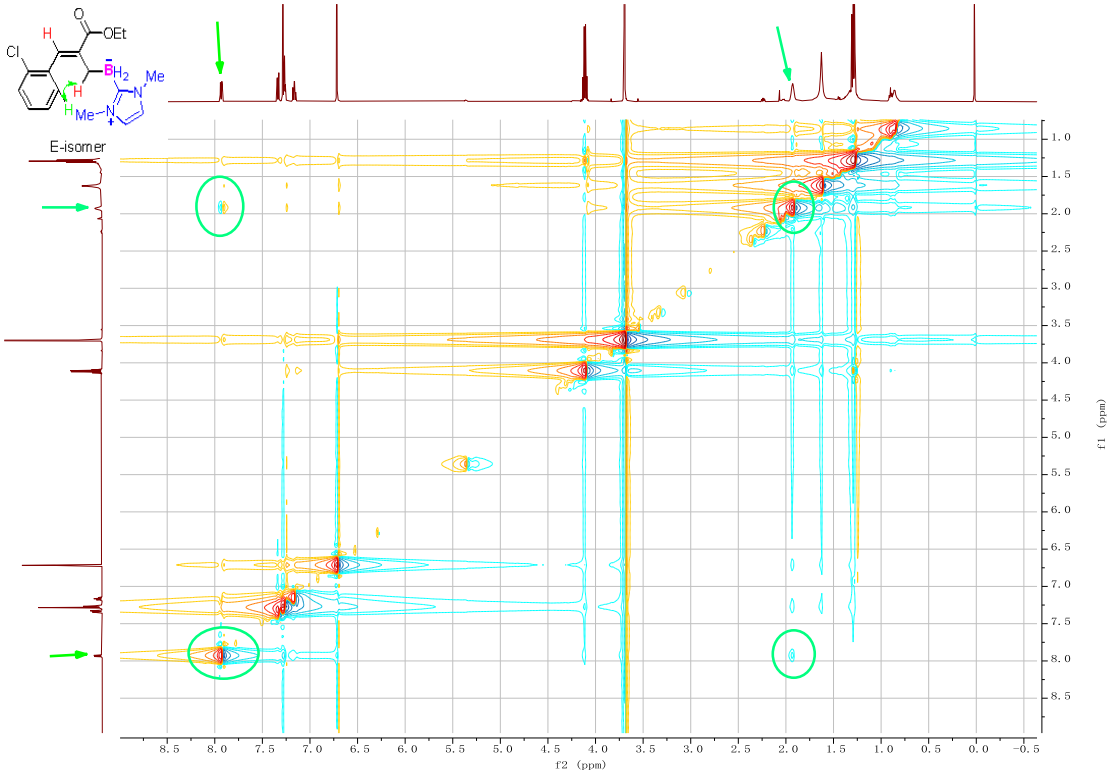

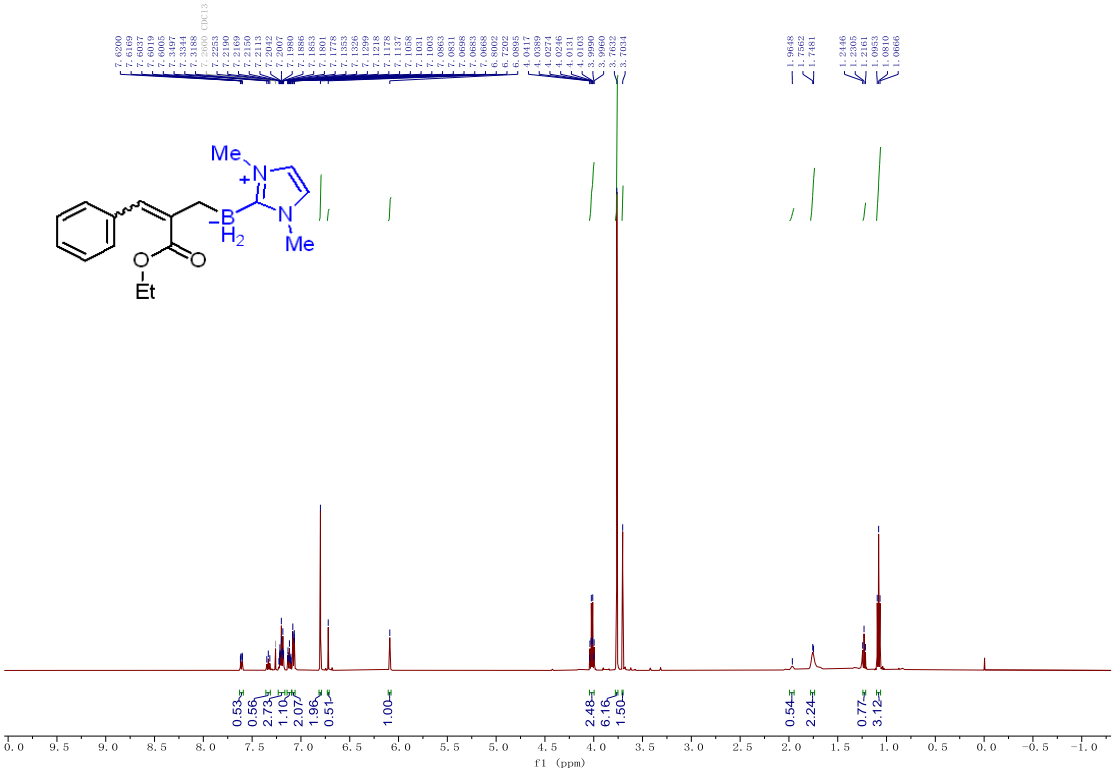
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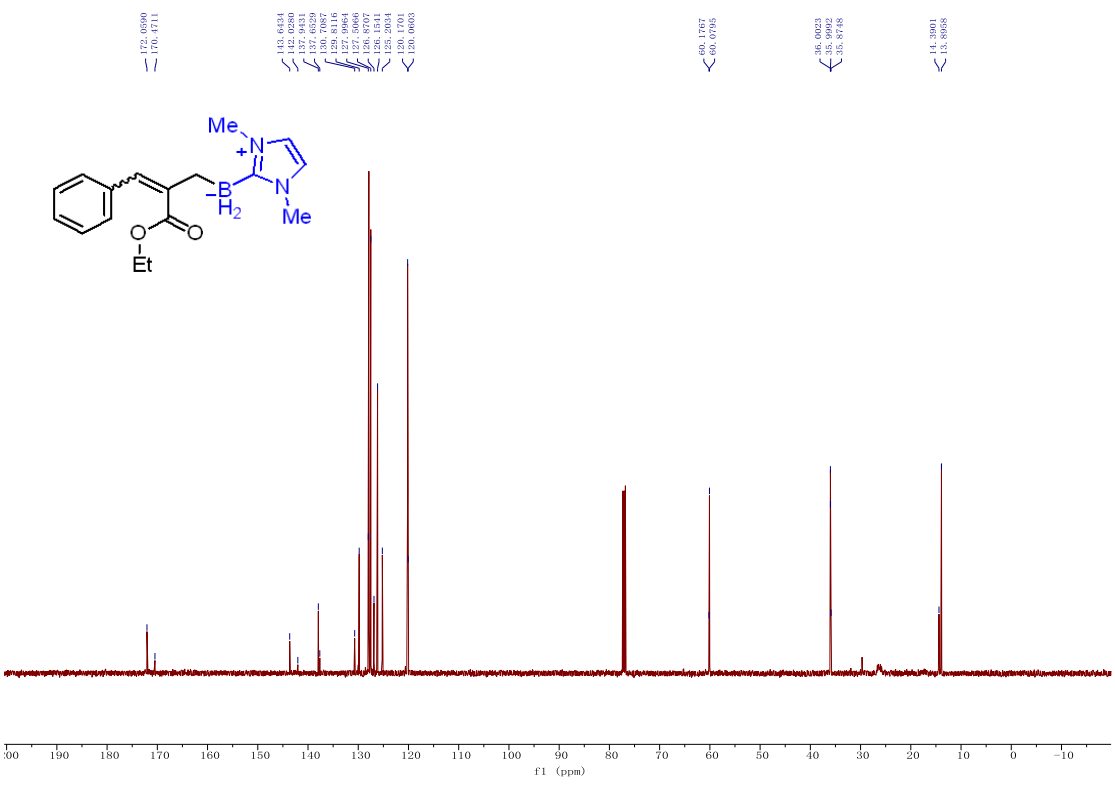
B
H2
N
Me
O
O
Et
f1 (ppm)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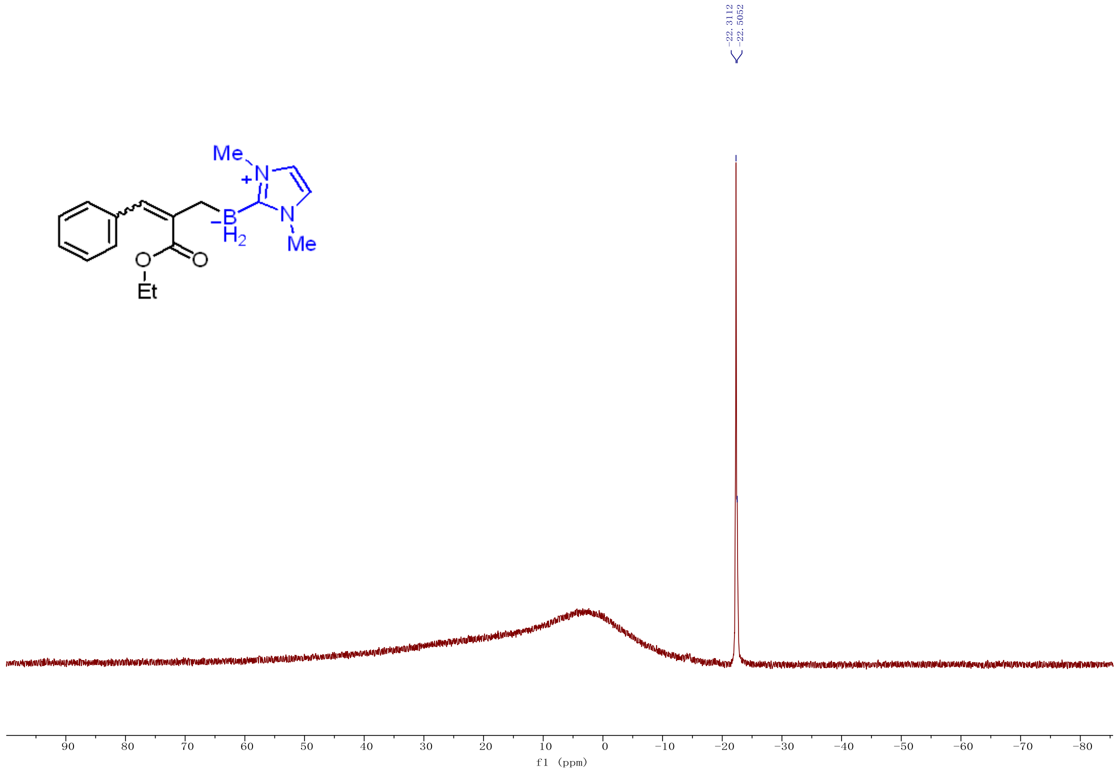

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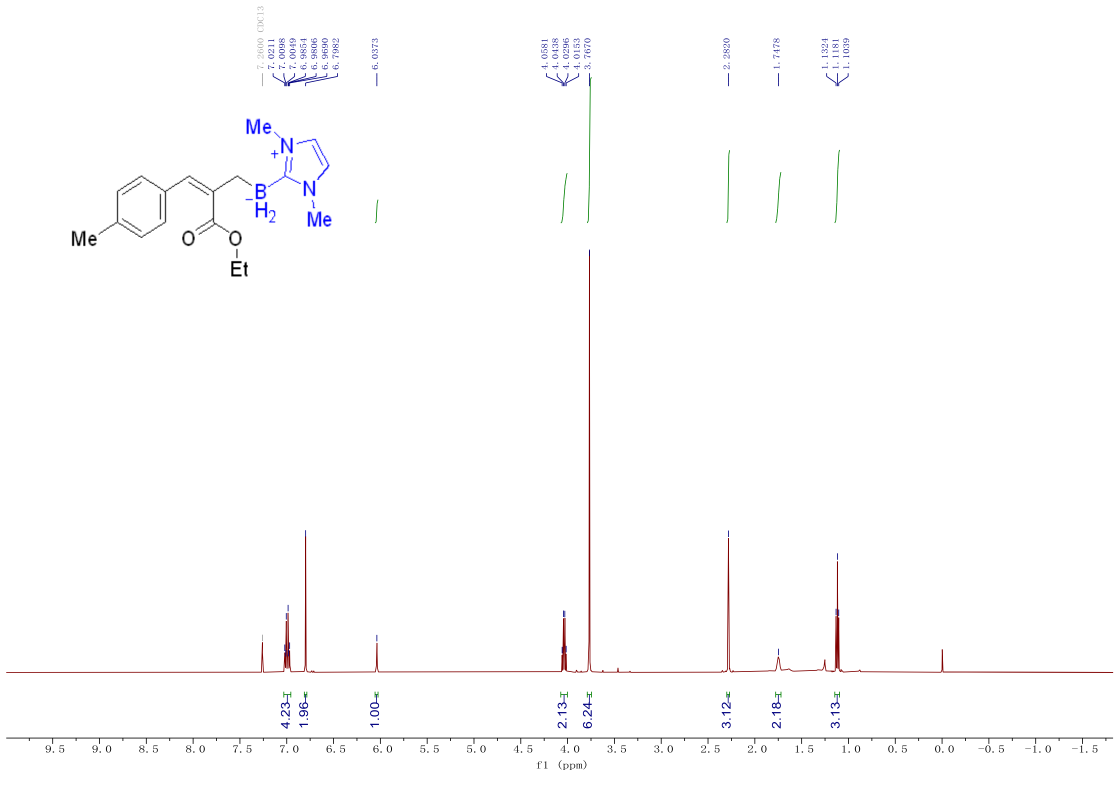
f1 (ppm)



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Me
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O
Et
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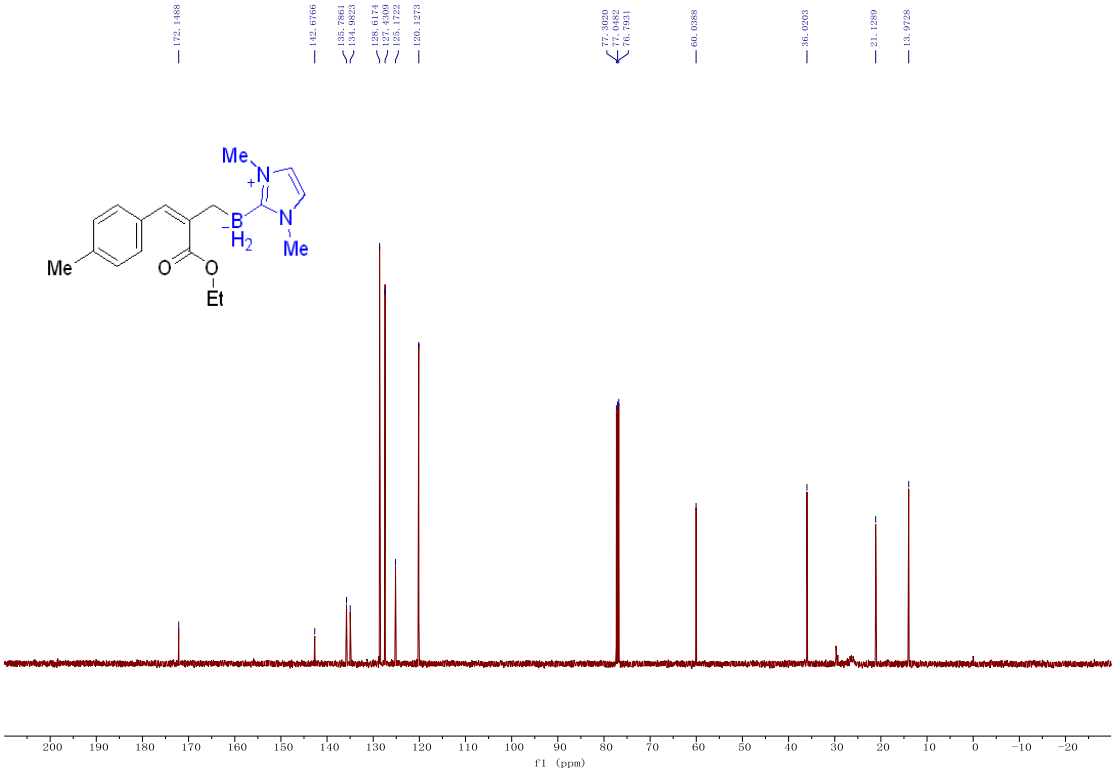
f1 (ppm)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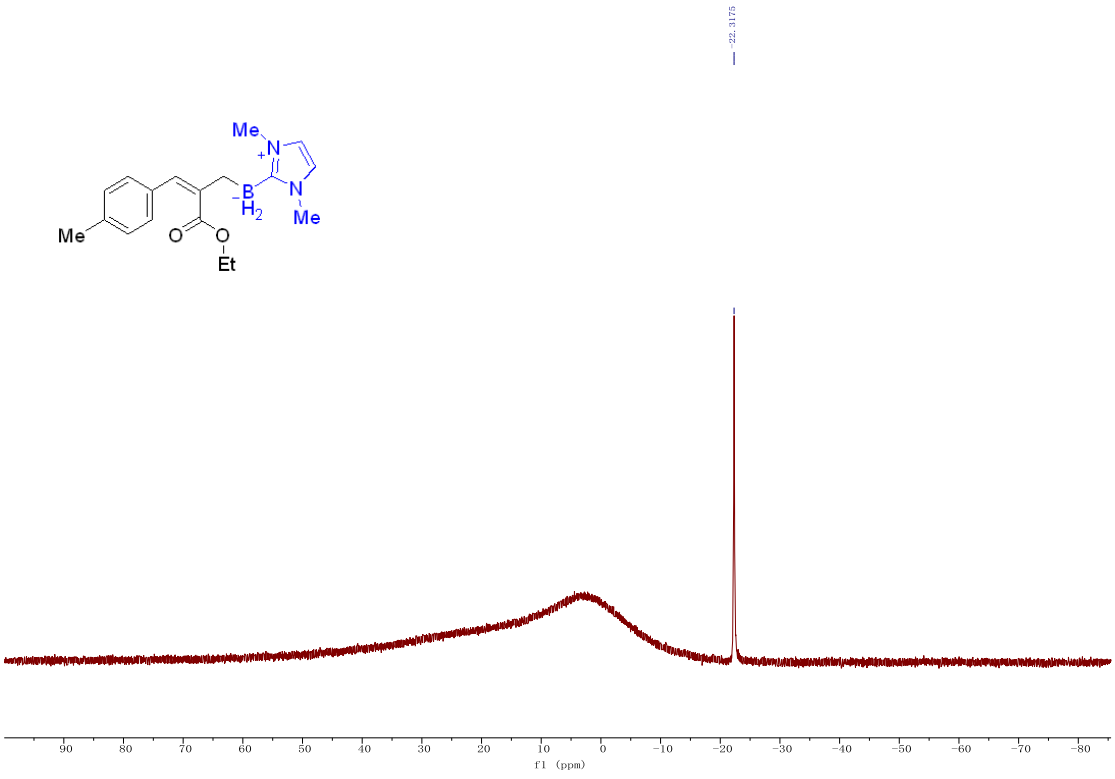
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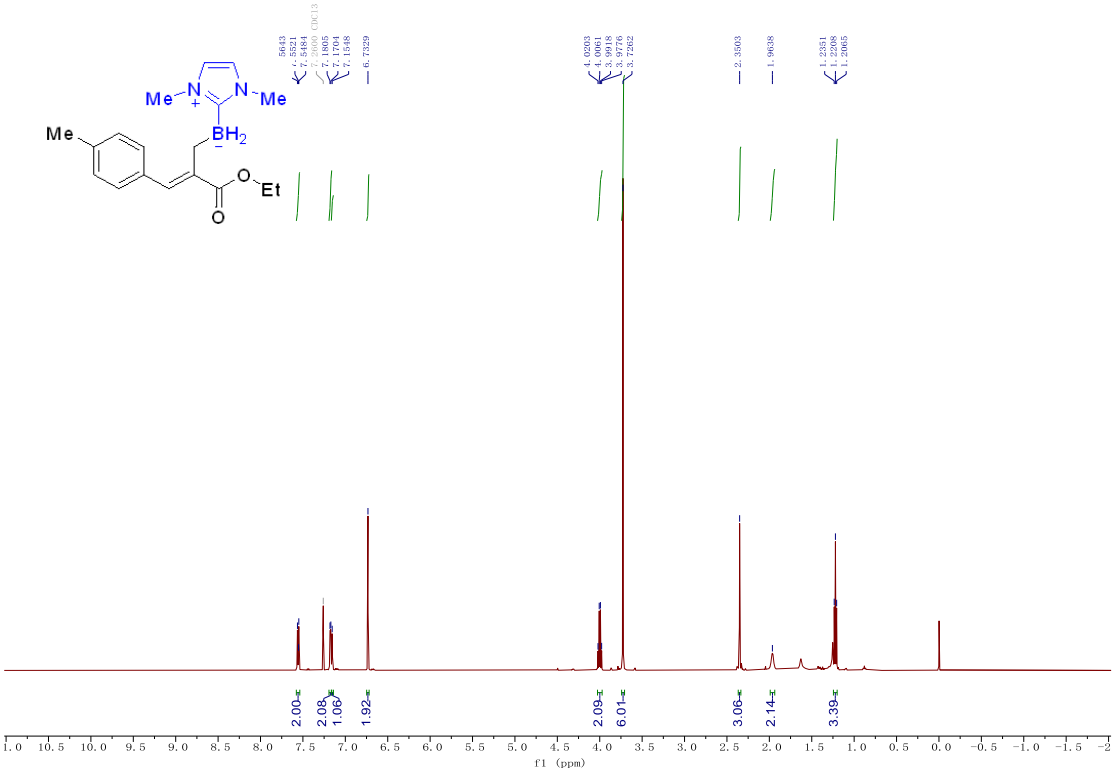
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N
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BH2
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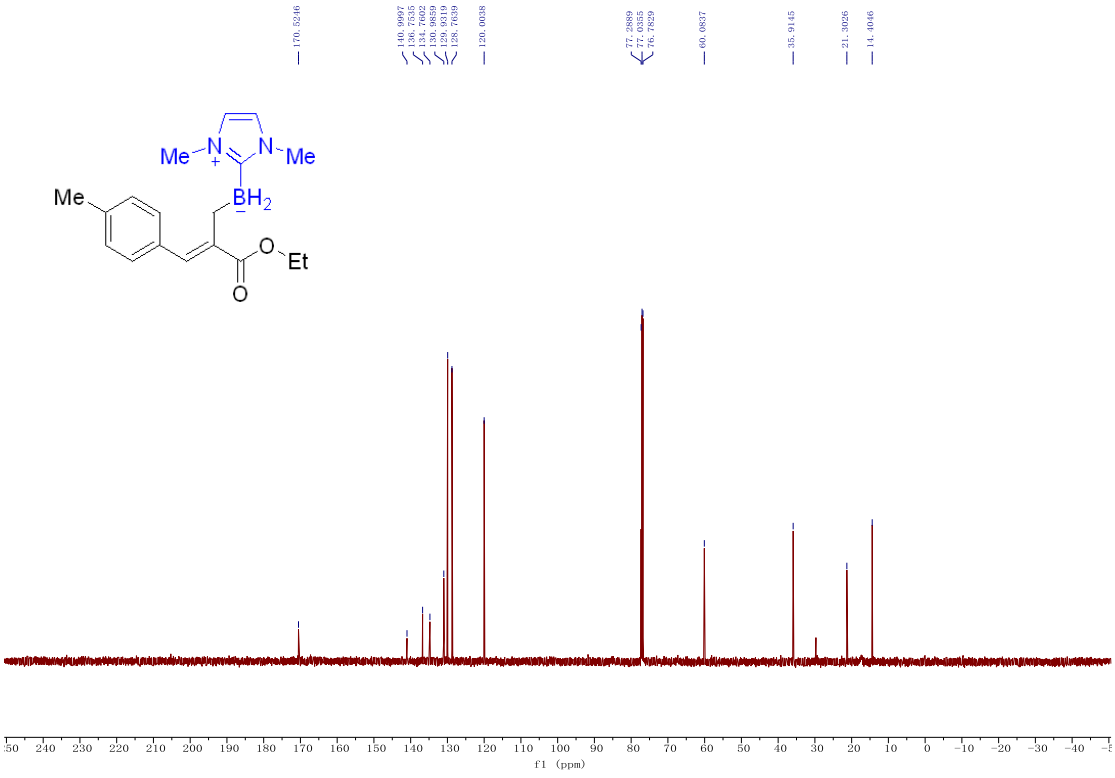
f1 (ppm)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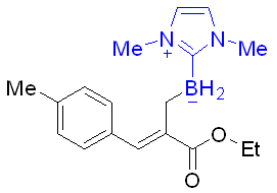
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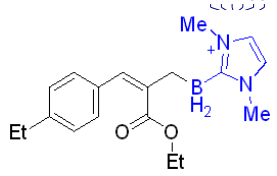
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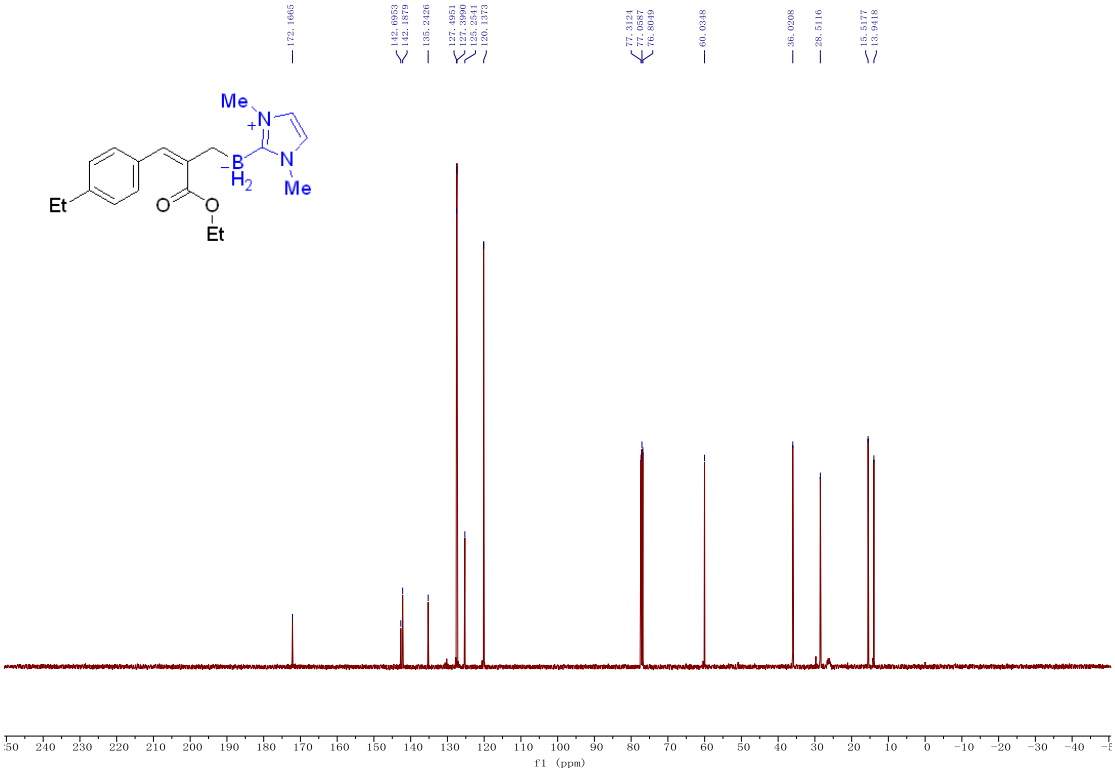
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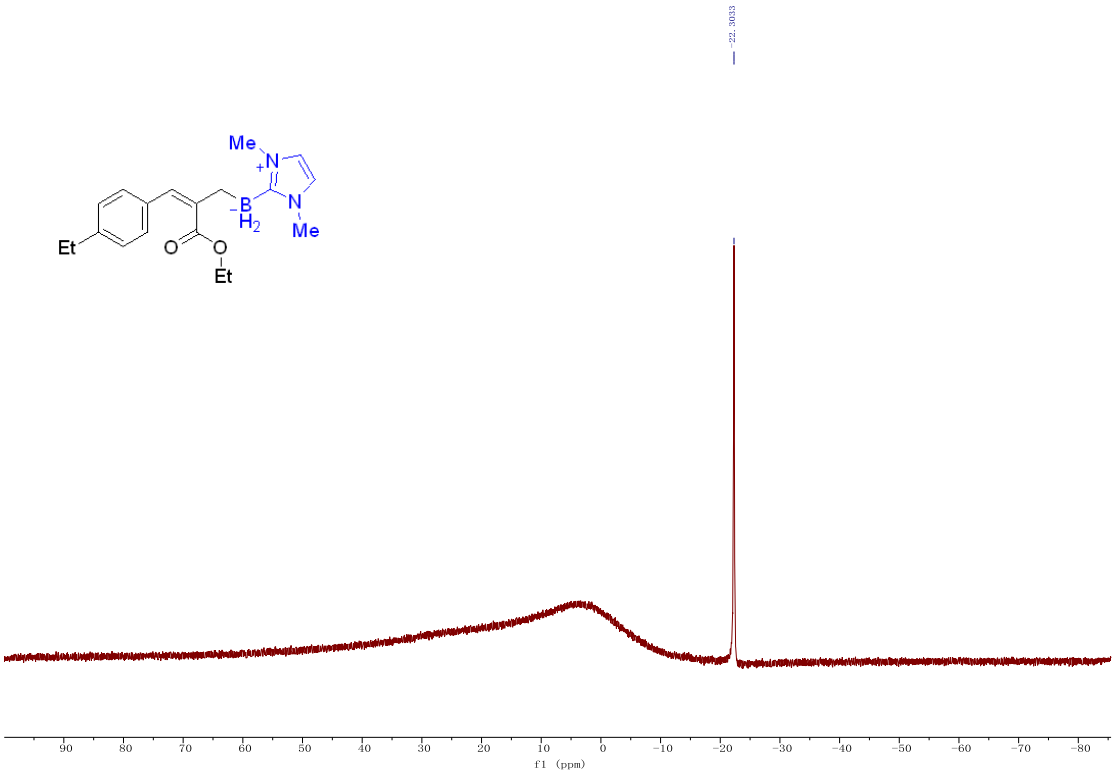
Et
f1 (ppm)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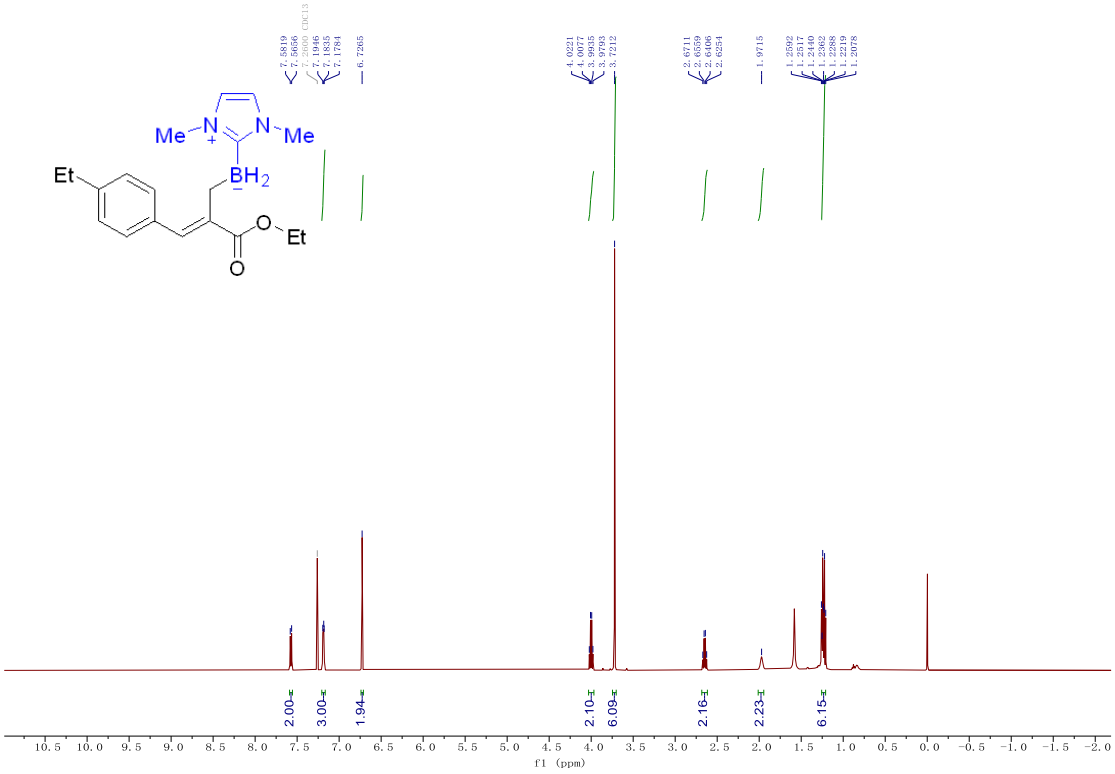
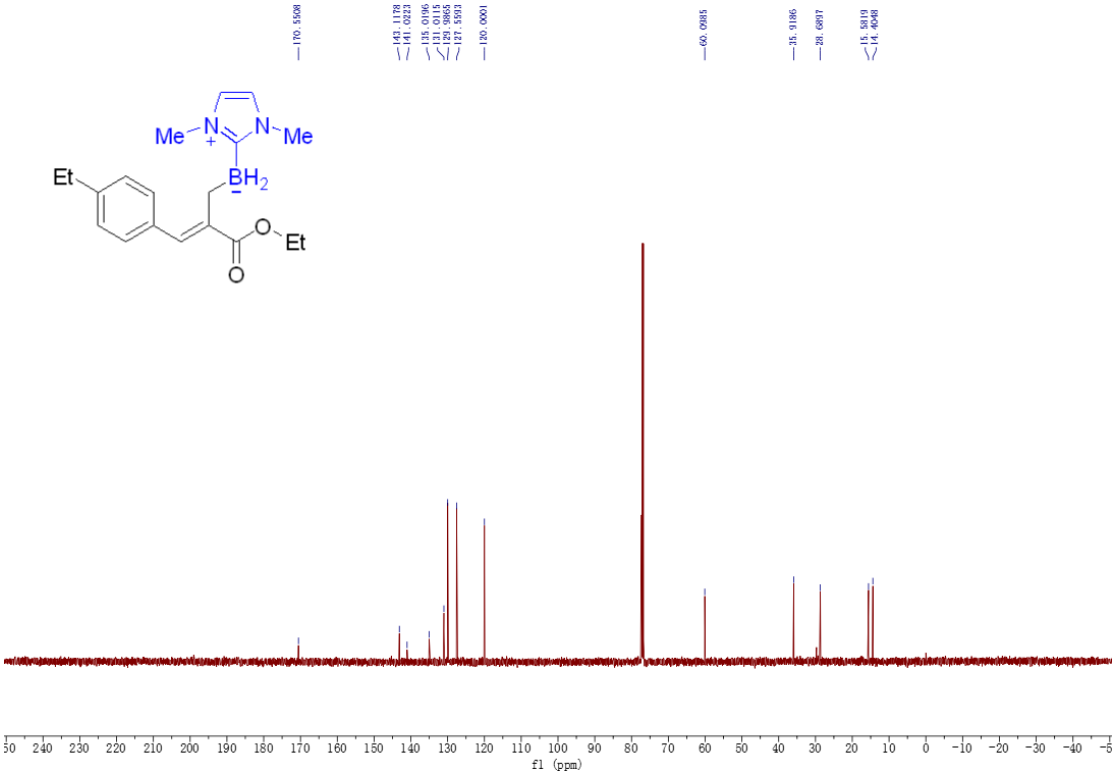
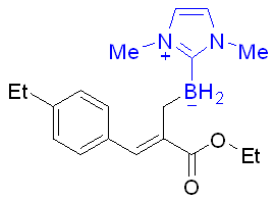
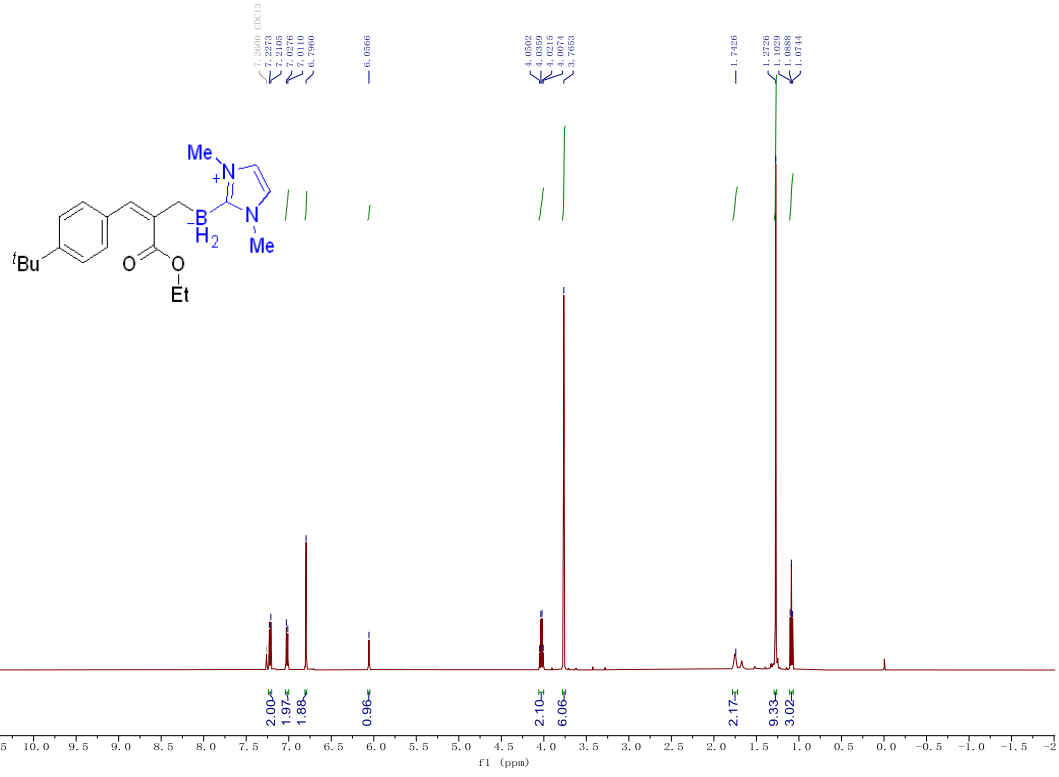
N
B
H2
N
Me
Et
O
O
Et
f1 (ppm)


Me
N
N
Me
BH2
Et
O
Et
O
f1 (ppm)

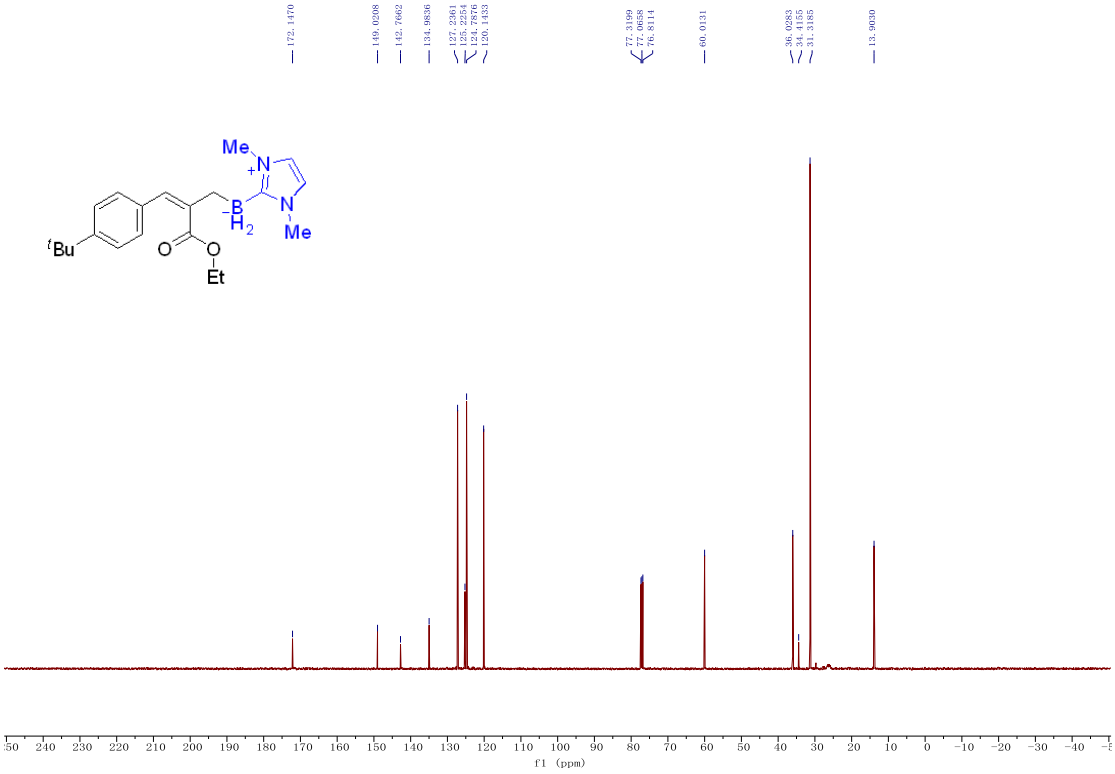

Me
N
N
Me
BH2
Et
O
Et
O
f1 (ppm)

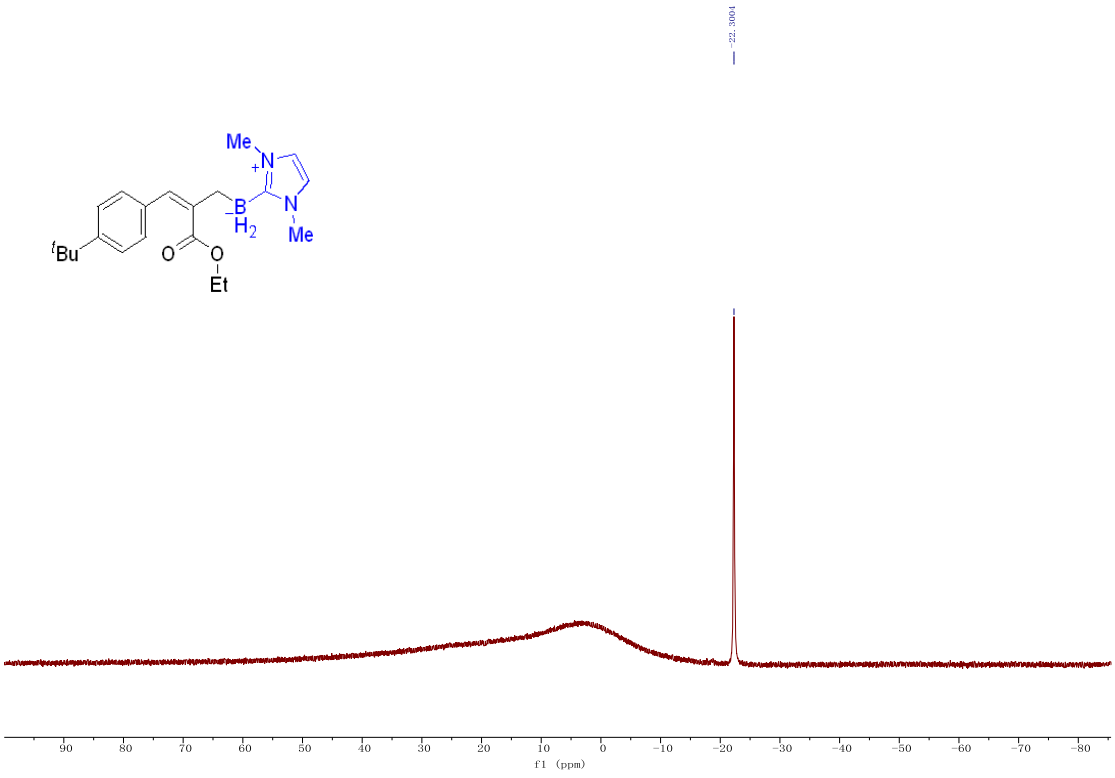

Me
N
N
Me
BH2
Et
O
Et
O

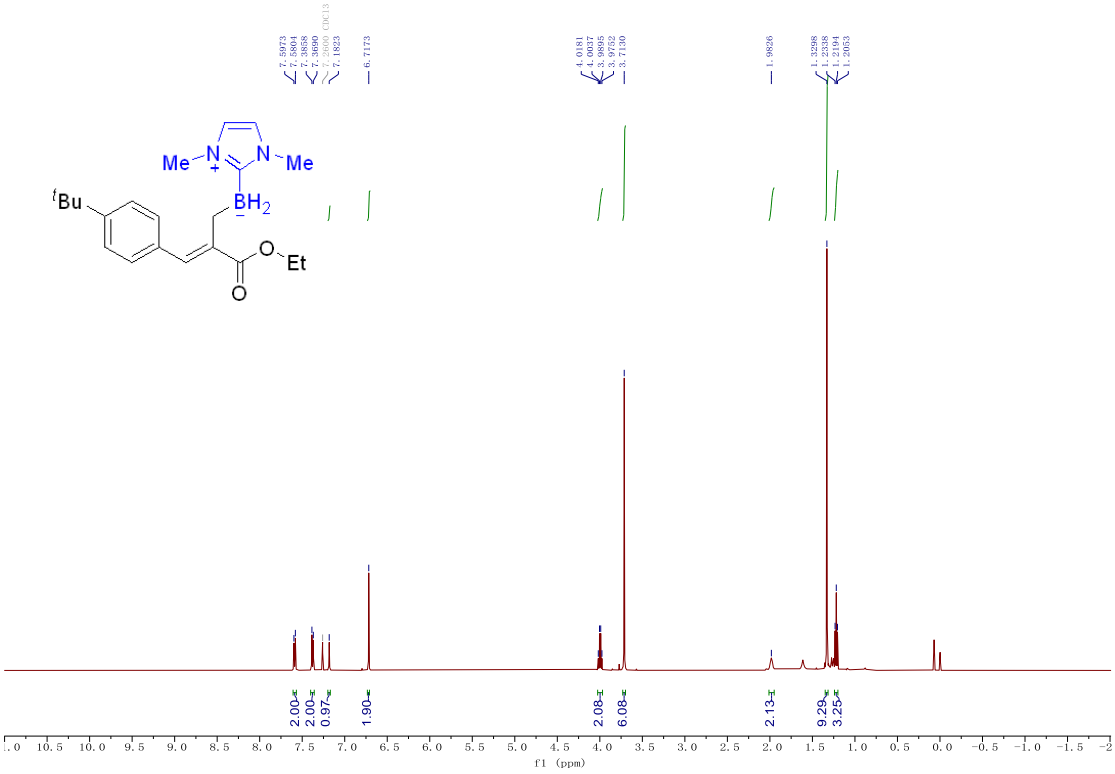
-22.5781
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

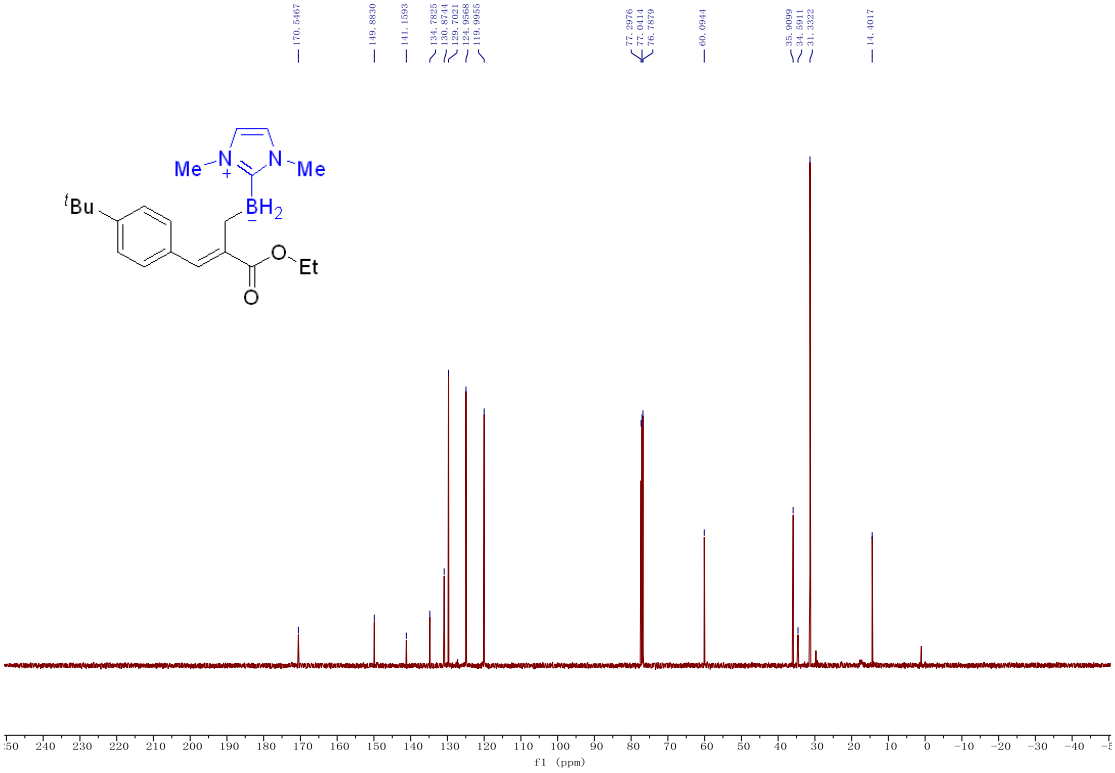

7.2600 CDCl3
7.2978
7.2105
7.0276
7.0110
6.7960
6.0566
4.0502
4.0359
4.0215
4.0074
3.7653
1.7426
1.2726
1.1029
1.0888
1.0744
2.00
1.97
1.88
0.96
2.10
6.06
2.17
9.33
3.02
f1 (ppm)

Me
N
B
H2
N
Me
tBu
O
O
Et


172.1470
149.0208
142.7662
134.9836
127.2361
125.2554
124.7876
120.1433
77.3199
77.0658
76.8114
60.0131
36.0283
34.4455
31.3185
13.9030
Me
N
B
H2
N
Me
tBu
O
O
Et
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


-22.3004
Me
N
B
H2
N
Me
tBu
O
O
Et
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)


7.5973
7.5804
7.3858
7.3690
7.1910
CDCl3
7.1823
6.7173
4.0181
4.0007
3.9895
3.9732
3.7130
1.9836
1.3298
1.2338
1.2194
1.2053
Me
N
N
Me
BH2
tBu
O
Et
O
2.00
2.00
0.97
1.90
2.08
6.08
2.13
9.29
3.25
f1 (ppm)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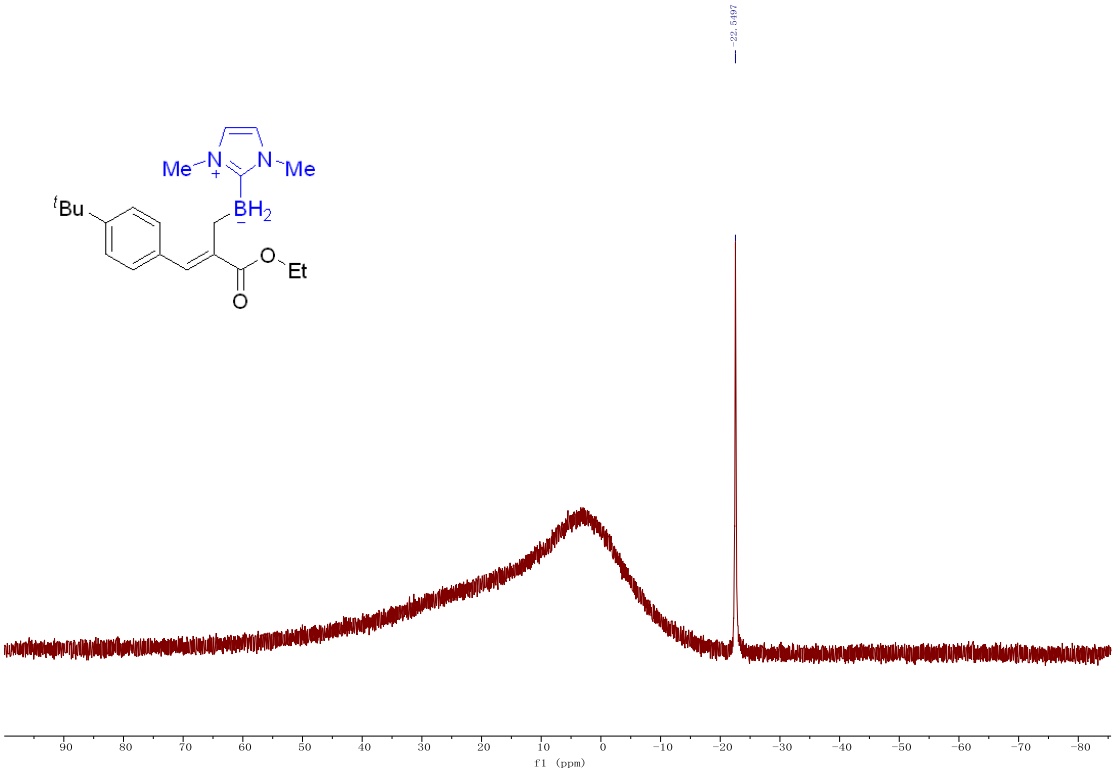
141.1593
134.7825
130.8744
129.7021
124.9588
118.9065
77.2976
77.0414
76.7879
60.0944
35.9099
34.5911
31.3322
14.4017
Me
N
N
Me
BH2
tBu
O
Et
O
f1 (ppm)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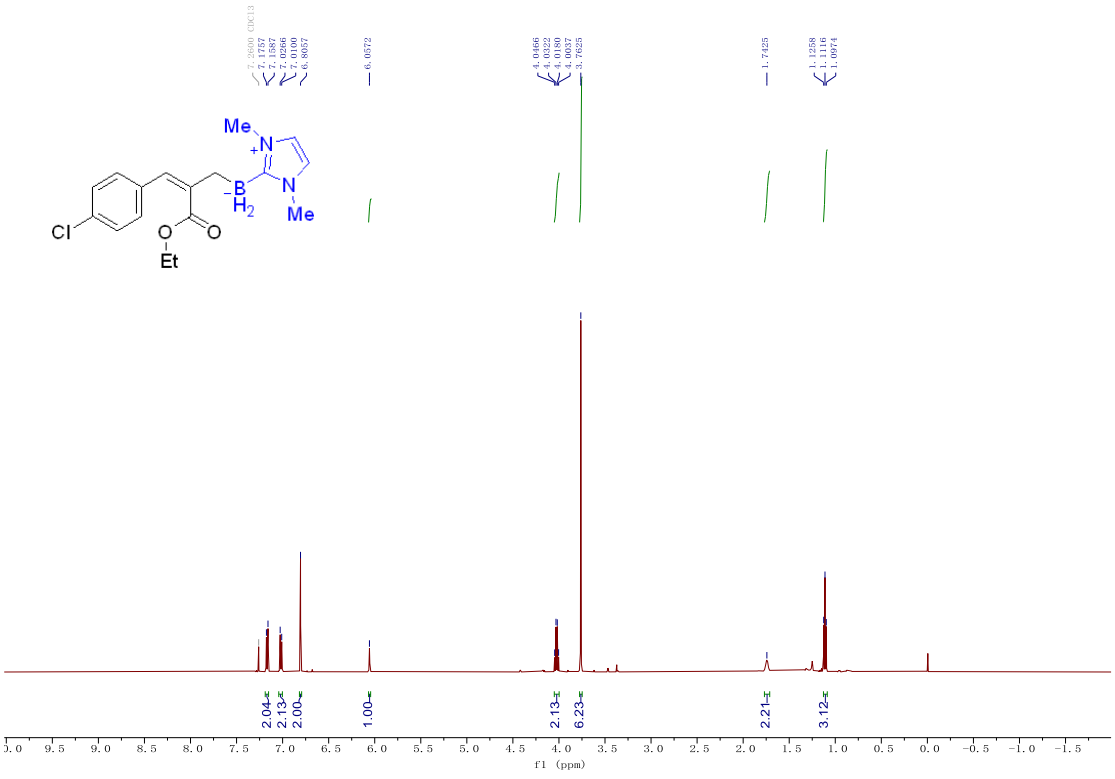
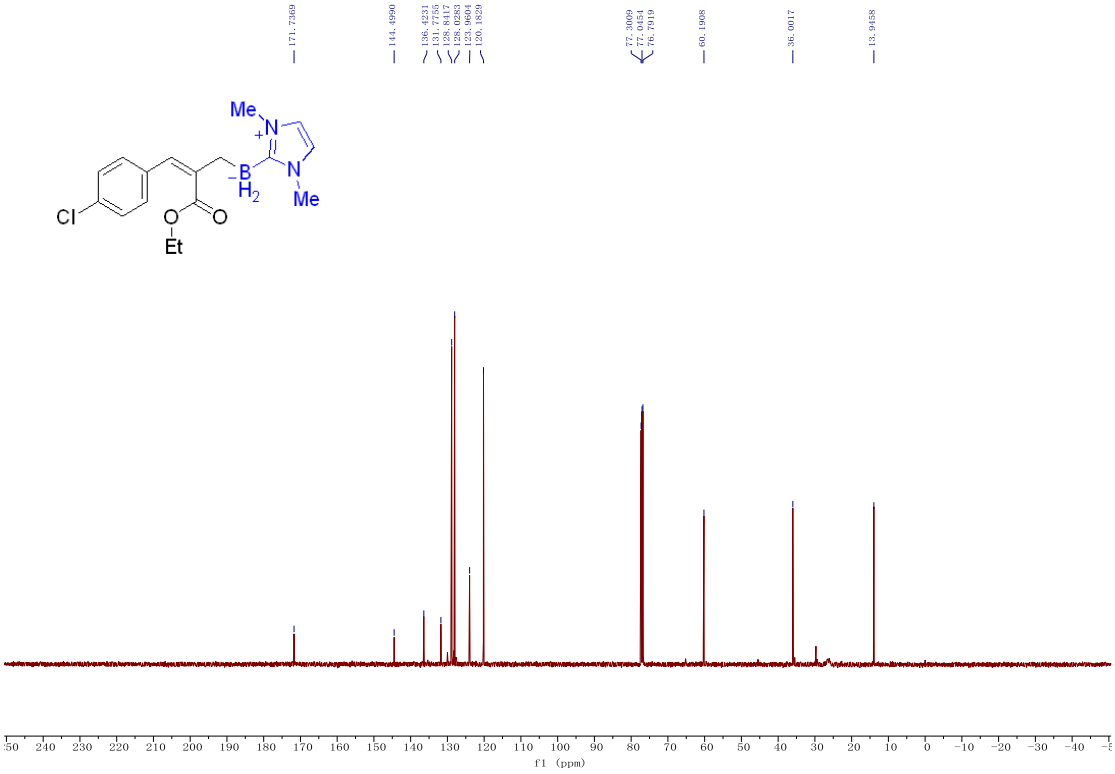
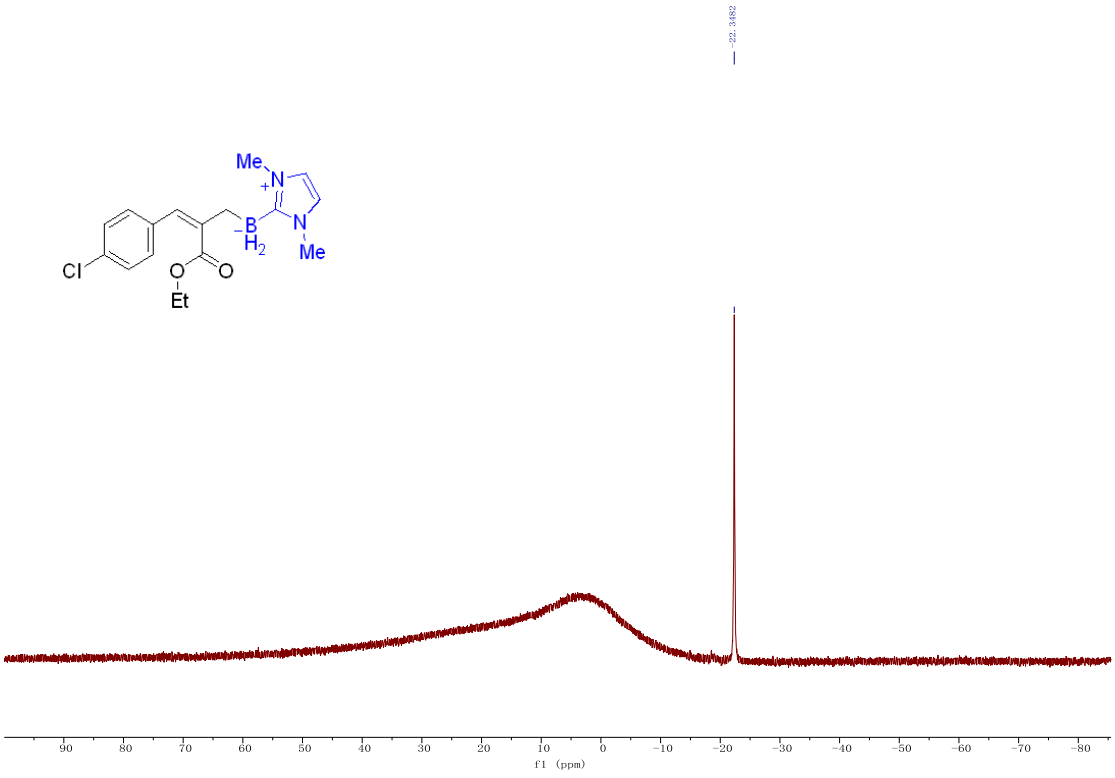
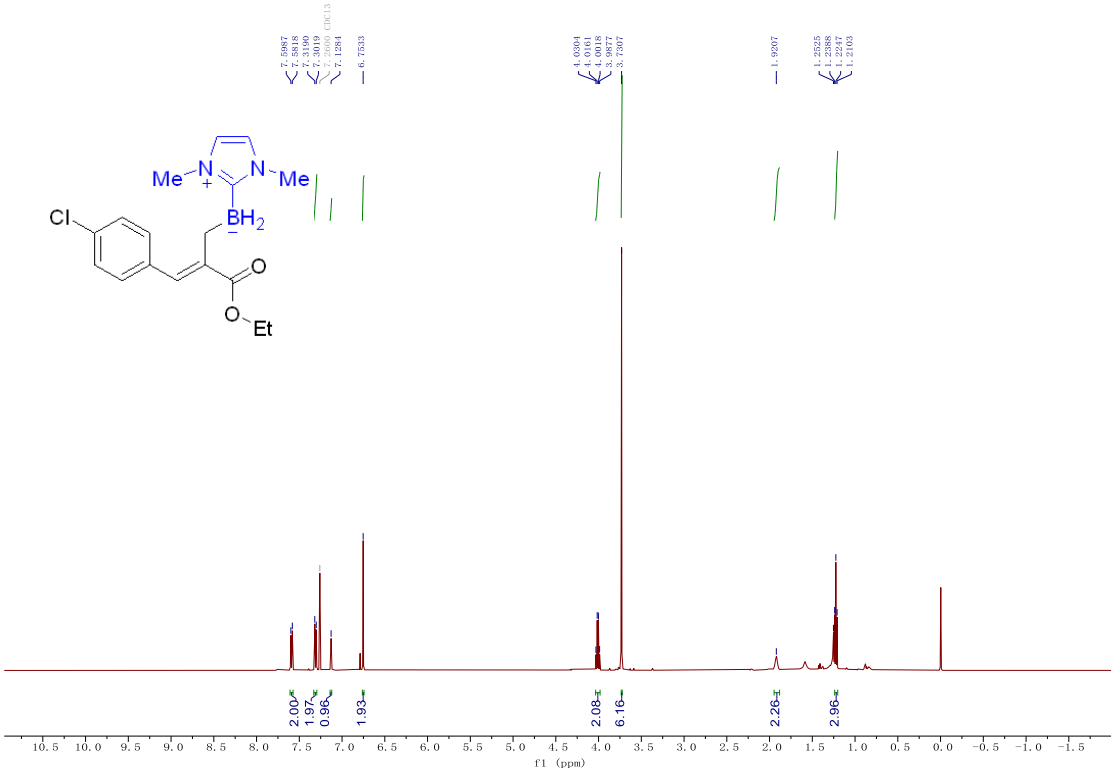
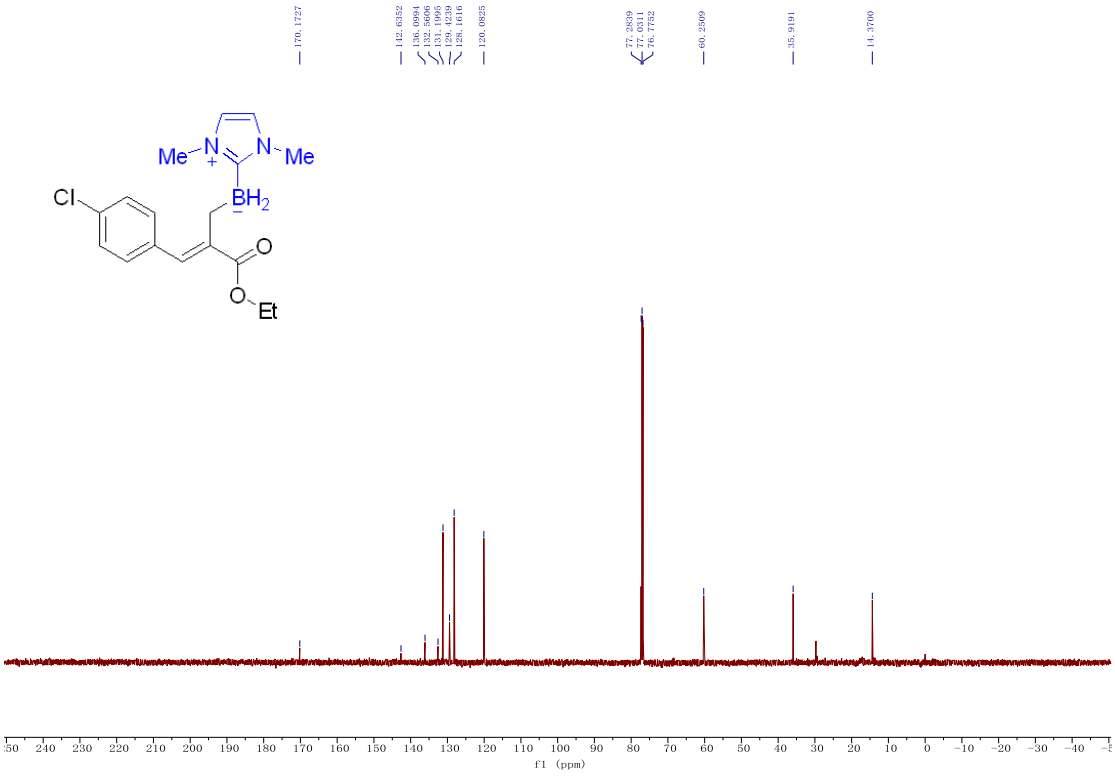
Me
N
N
Me
BH2
tBu
O
Et
O
f1 (ppm)

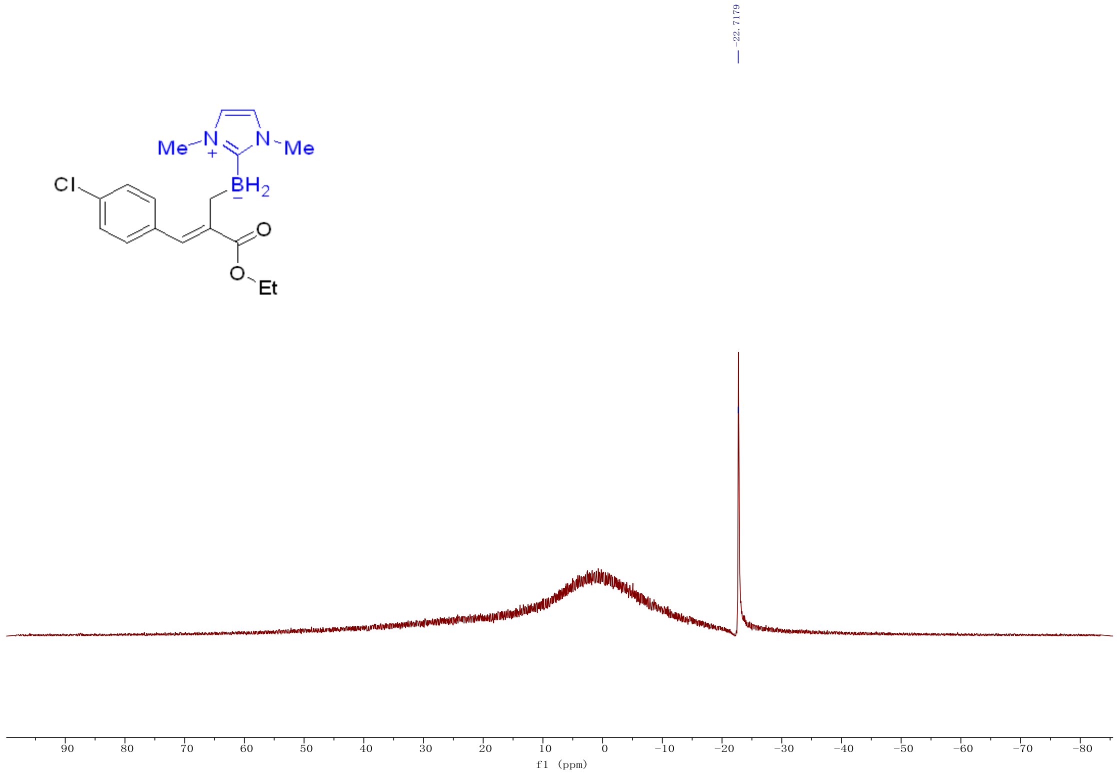

7.2600 CDCl3
7.1757
7.1587
7.0266
7.0100
6.8057
6.0572
4.0466
4.0322
4.0180
4.0037
3.7625
1.7425
1.1258
1.1116
1.0974
Me
N
B
H2
N
Me
Cl
O
O
Et
2.04
2.13
2.00
1.00
2.13
6.23
2.21
3.12
f1 (ppm)

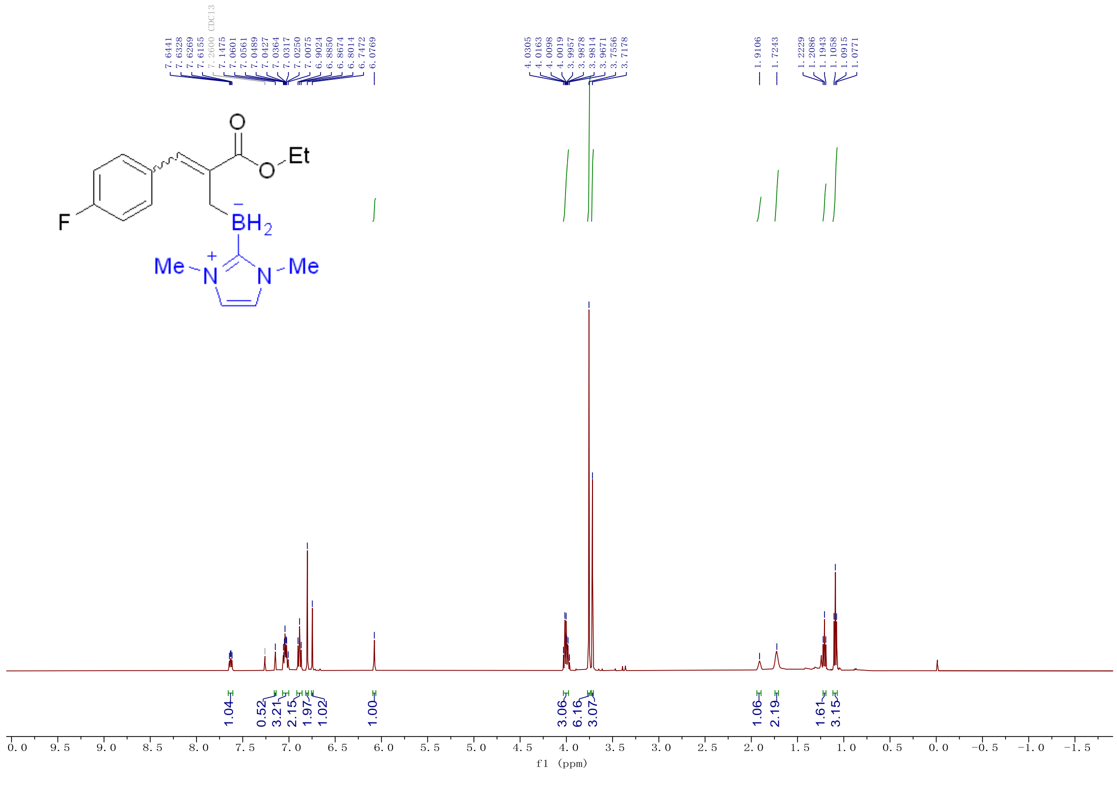

171.7369
144.4990
136.4231
133.7765
128.8417
128.0283
123.9604
120.1829
77.3099
77.0454
76.7919
60.1908
36.0017
13.9458
Me
N
B
H2
N
Me
Cl
O
O
Et
f1 (ppm)

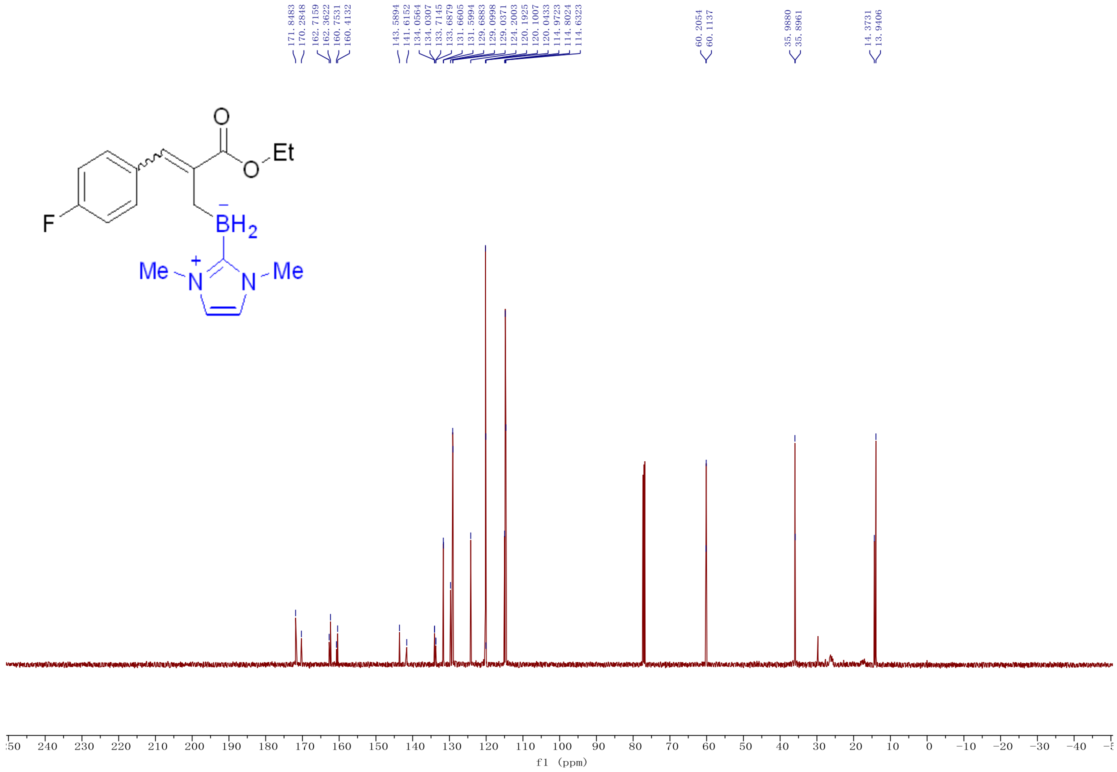

-22.3482
Me
N
B
H2
N
Me
Cl
O
O
Et
f1 (ppm)


7.5987
7.5838
7.3190
7.3019
7.2900 CDCl3
7.1084
6.7533
4.0394
4.0161
4.0018
3.9877
3.7507
1.9207
1.2525
1.2398
1.2247
1.2103
Me
N
N
Me
BH2
Cl
O
O
Et
2.00
1.97
0.96
1.93
2.08
6.16
2.26
2.96
f1 (ppm)


170.1727
142.6352
136.0994
132.5606
131.1995
130.1458
128.1616
120.0825
77.2839
77.0311
76.7782
60.2569
35.9191
14.3700
Me
N
N
Me
BH2
Cl
O
O
Et
f1 (ppm)



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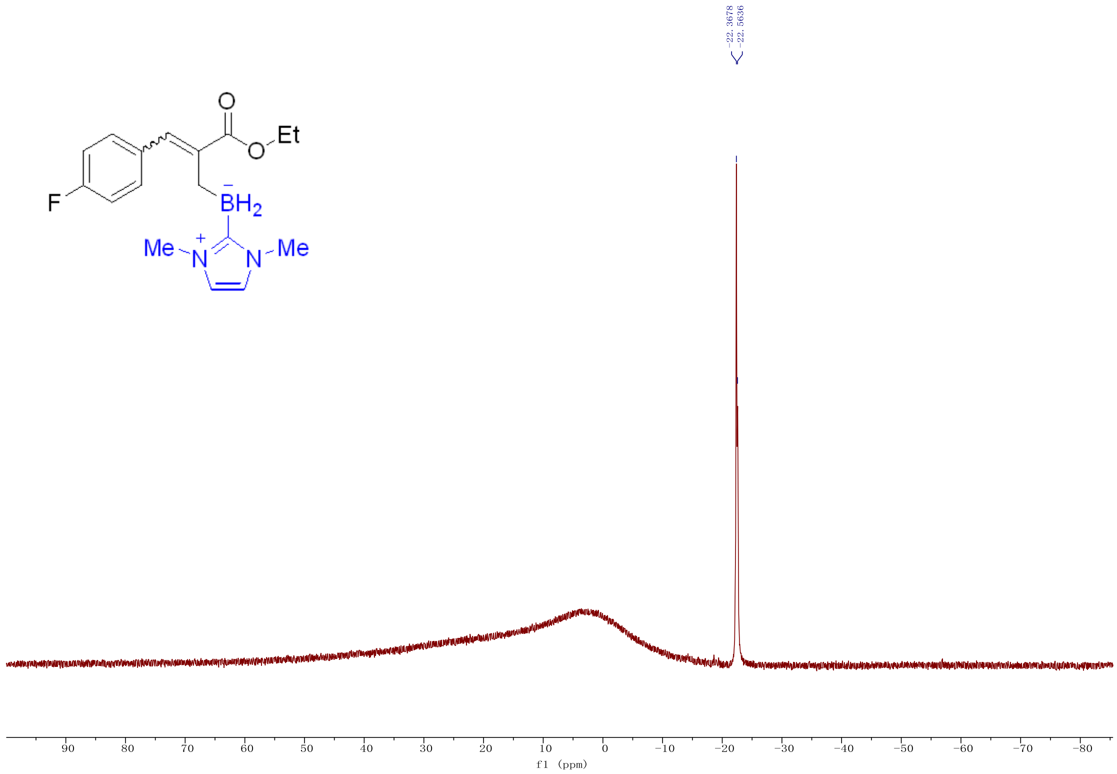
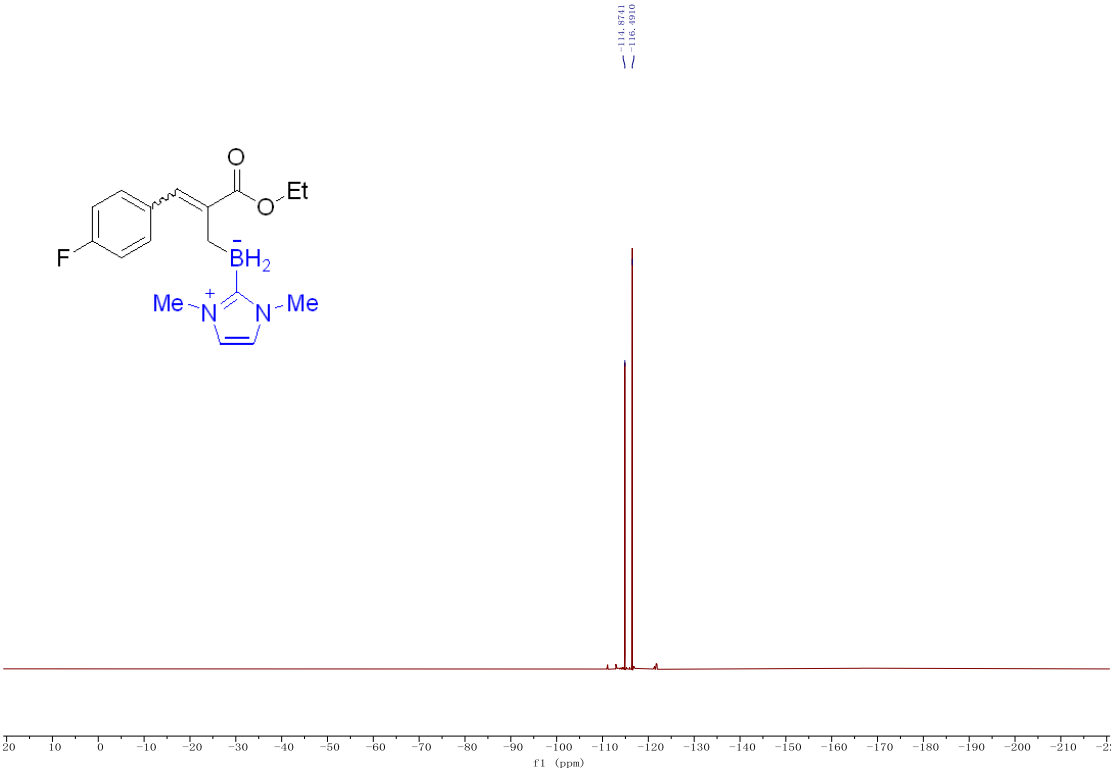
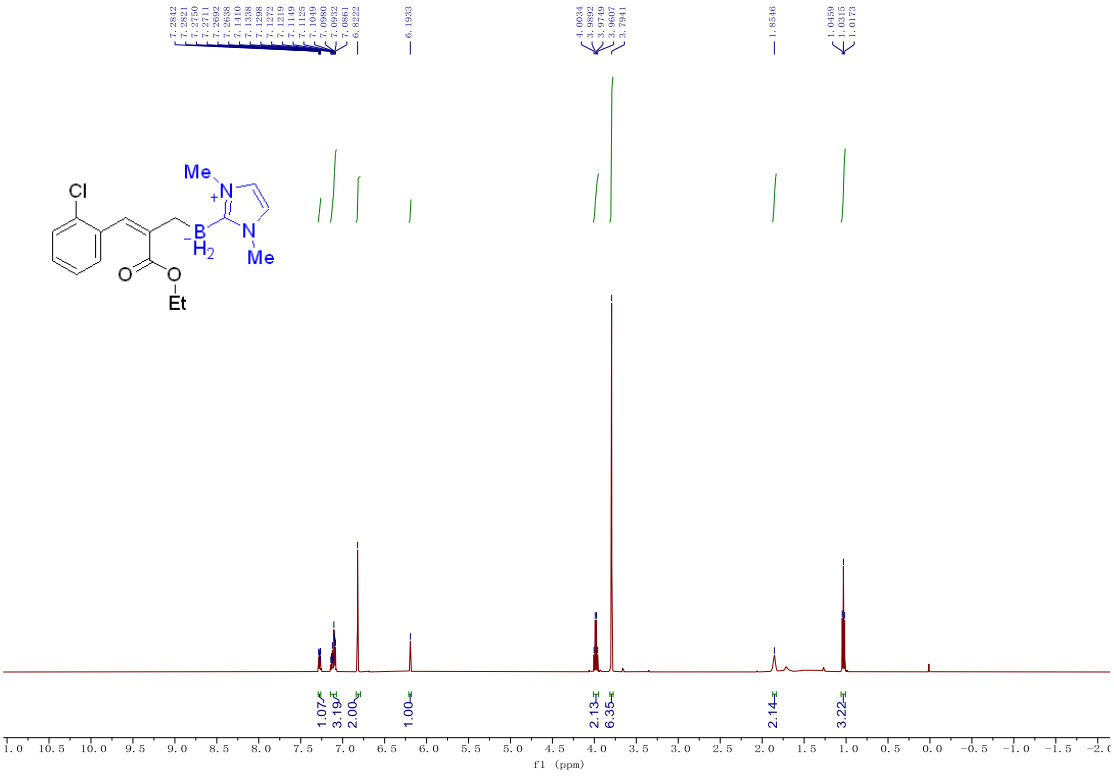
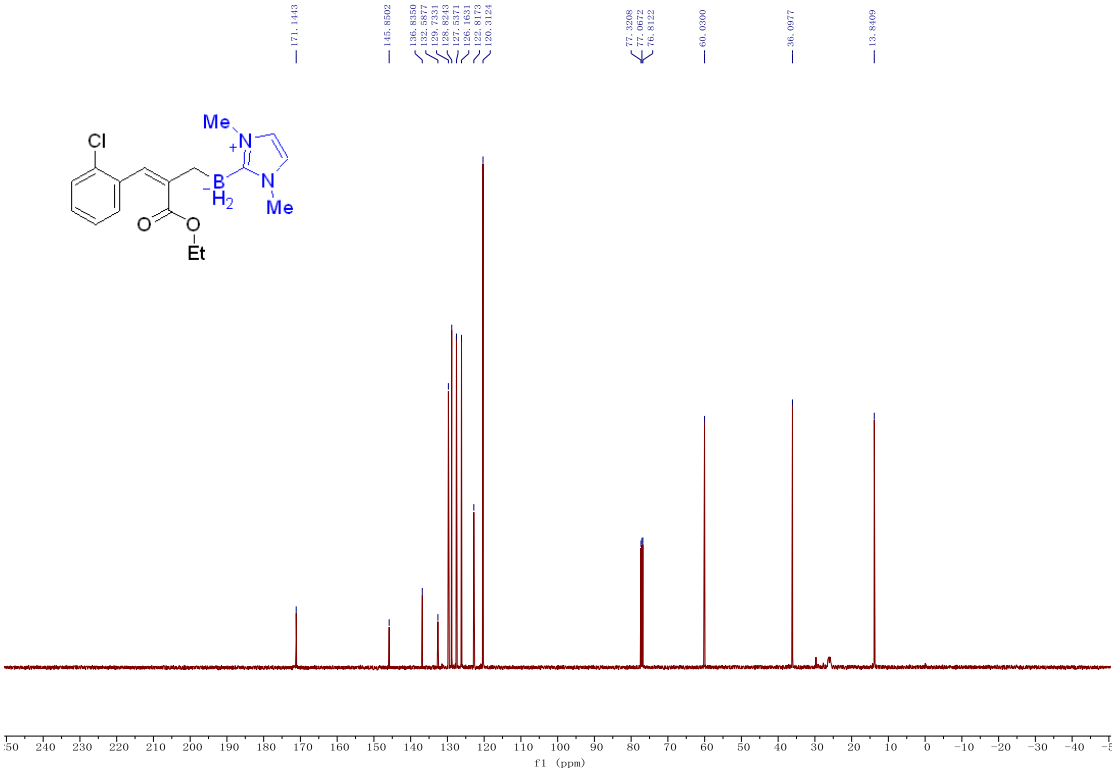
162.7159
162.3622
160.7531
160.4132
143.5894
141.6152
134.0564
134.0307
133.7145
133.6879
131.6605
131.5994
129.6883
129.0998
129.0371
124.2003
120.1925
120.1007
120.0133
114.9723
114.8924
114.6323
60.2054
60.1137
35.9880
35.8961
14.3731
13.9406
O
Et
O
F
BH2
Me
N
N
Me
f1 (ppm)


-22.3678
-22.5636
O
Et
O
F
BH2
Me
N
N
Me
f1 (ppm)


O
Et
O
F
BH2
Me
N
N
Me
-114.8741
-116.4910
f1 (ppm)


Cl
Me
N
B
H2
N
Me
O
O
Et
7.2812
7.2821
7.2500
7.2711
7.2692
7.2638
7.1410
7.1338
7.1272
7.1239
7.1149
7.1125
7.1049
7.0990
7.0932
7.0861
6.8222
6.1933
4.0834
3.9892
3.9510
3.9607
3.7941
1.8546
1.0459
1.0405
1.0173
1.07
3.19
2.00
1.00
2.13
6.35
2.14
3.22
f1 (ppm)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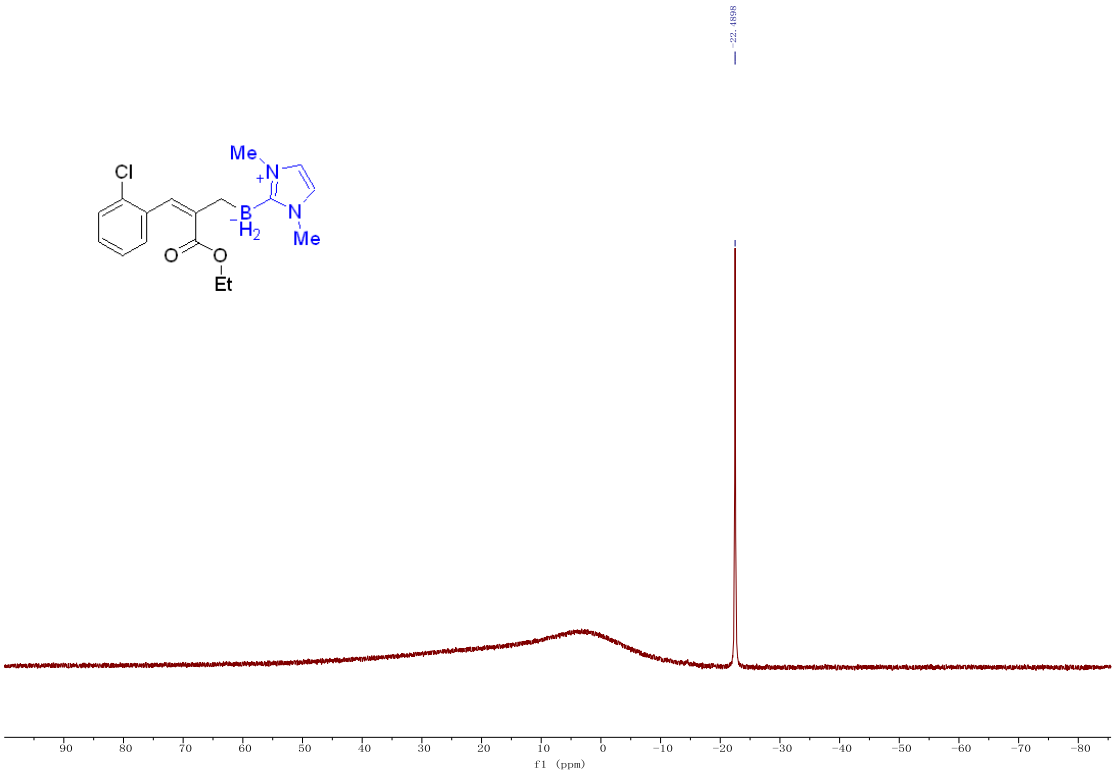
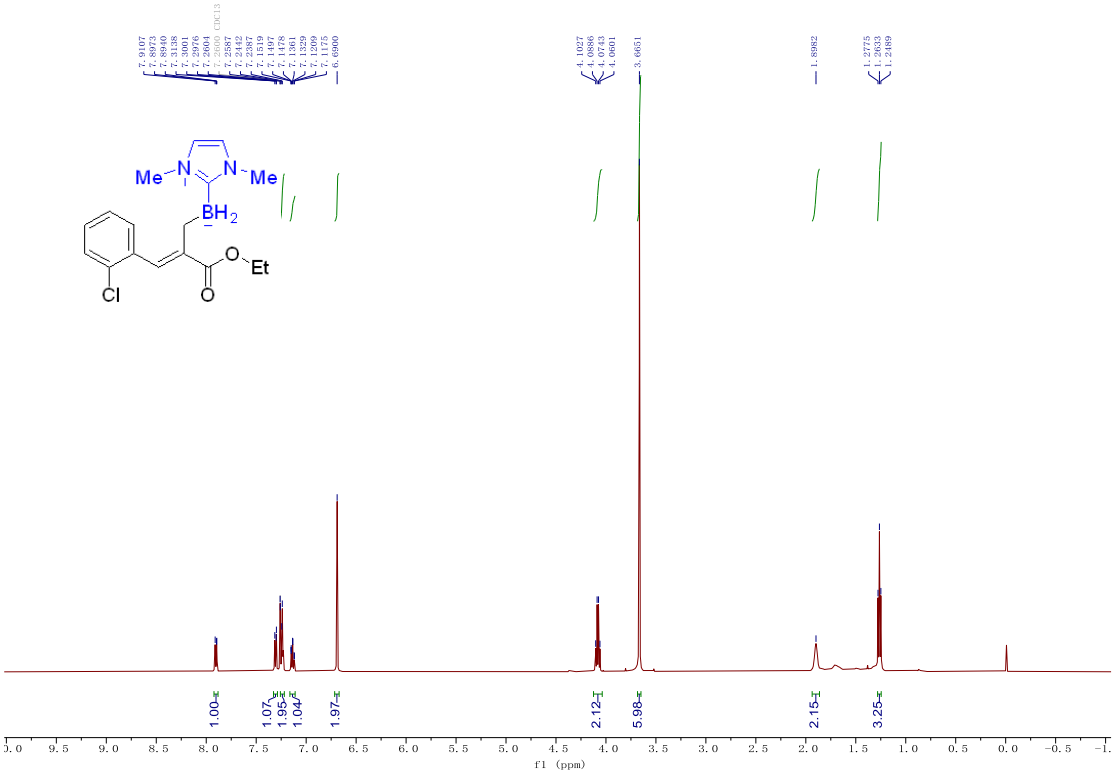
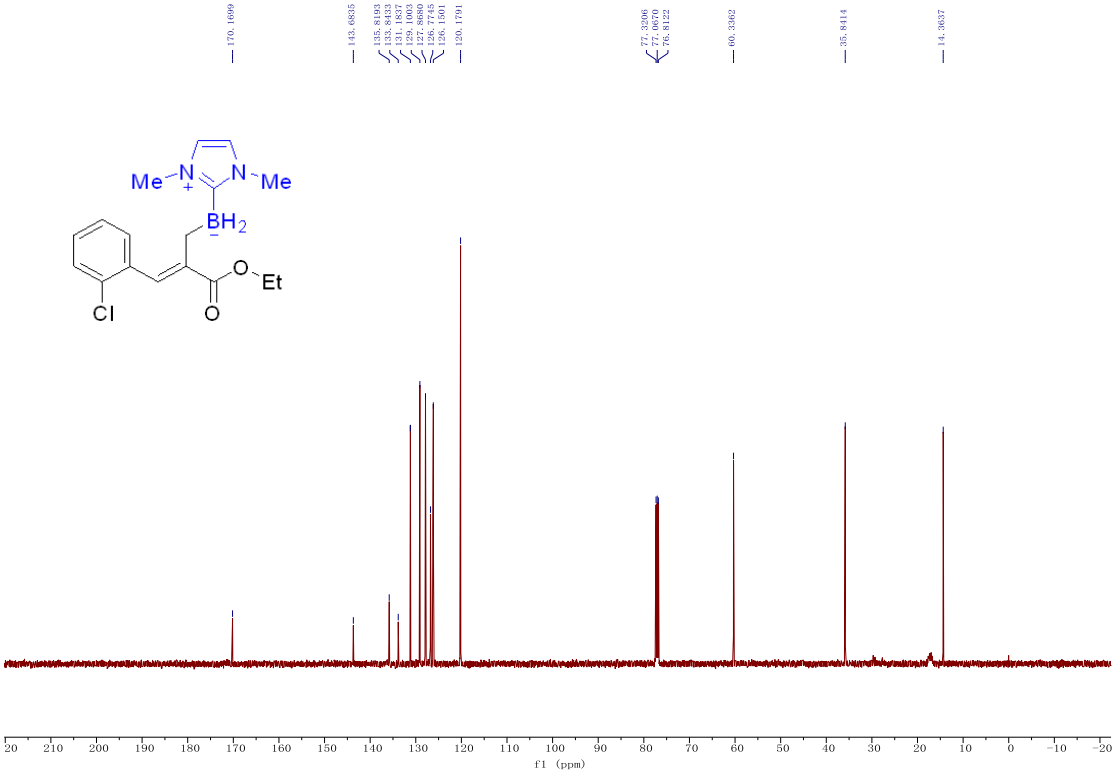
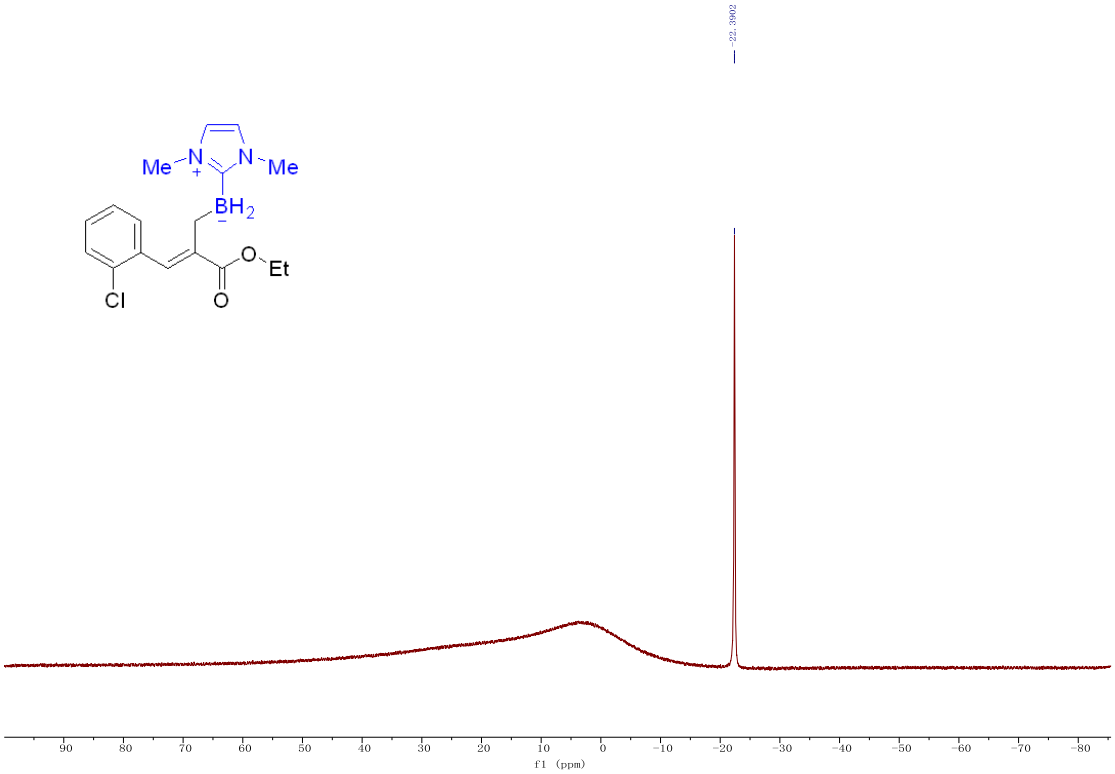
132.5877
130.7251
128.8243
127.5371
126.1631
125.8772
120.3124
77.3208
77.0672
76.8122
60.0300
36.0977
13.8469
Cl
Me
N
B
H2
N
Me
O
O
Et
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


22.4898
Cl
Me
N
B
H2
N
Me
O
O
Et
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)


Me
N
N
Me
BH2
O
Et
Cl
O
f1 (ppm)


Me
N
N
Me
BH2
O
Et
Cl
O
f1 (ppm)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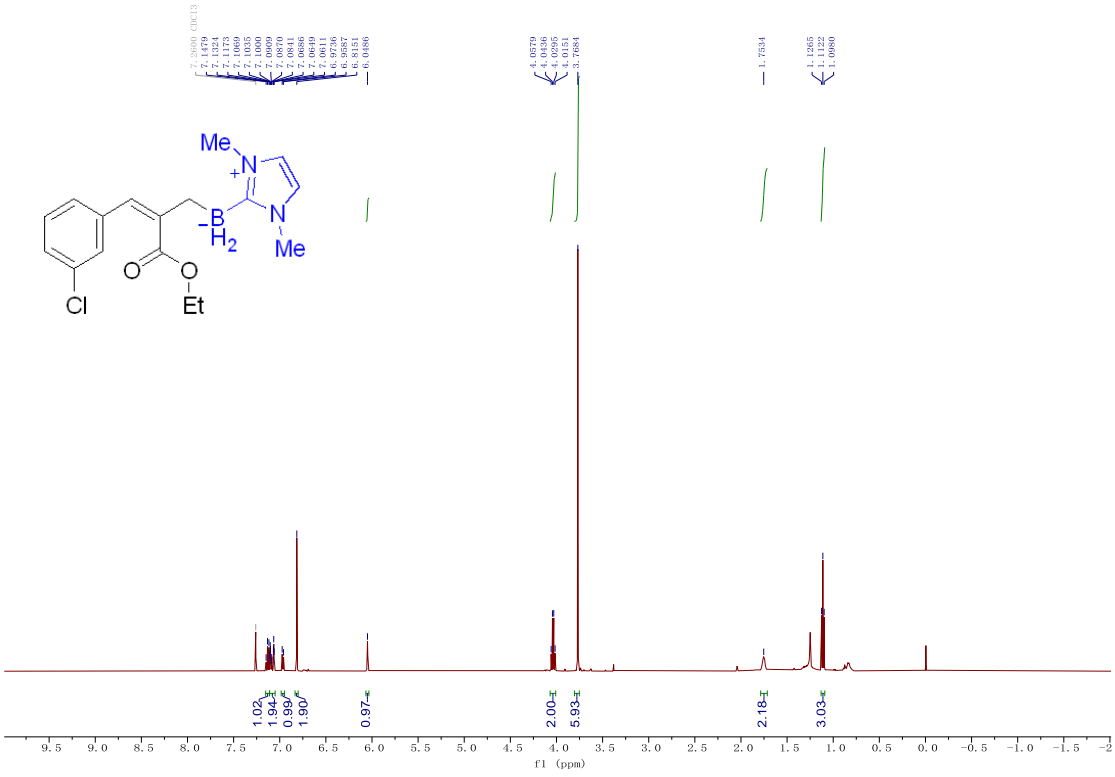
N
Me
BH2
O
Et
Cl
O
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)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7.1173
7.1069
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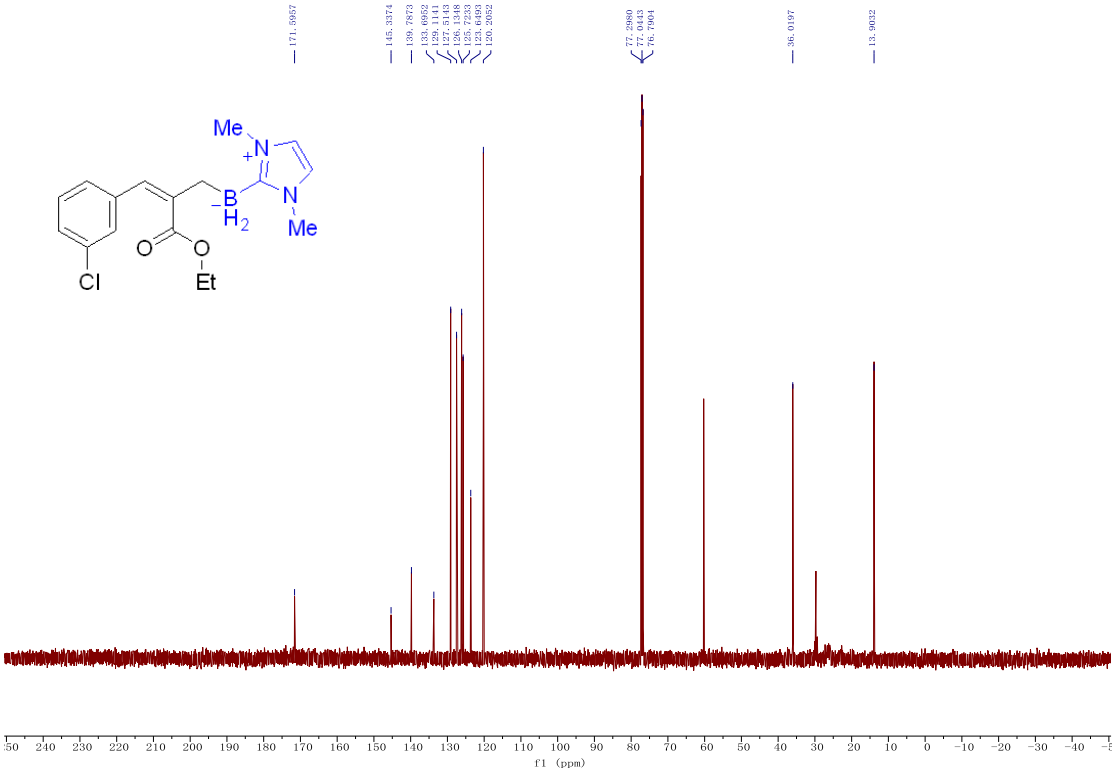
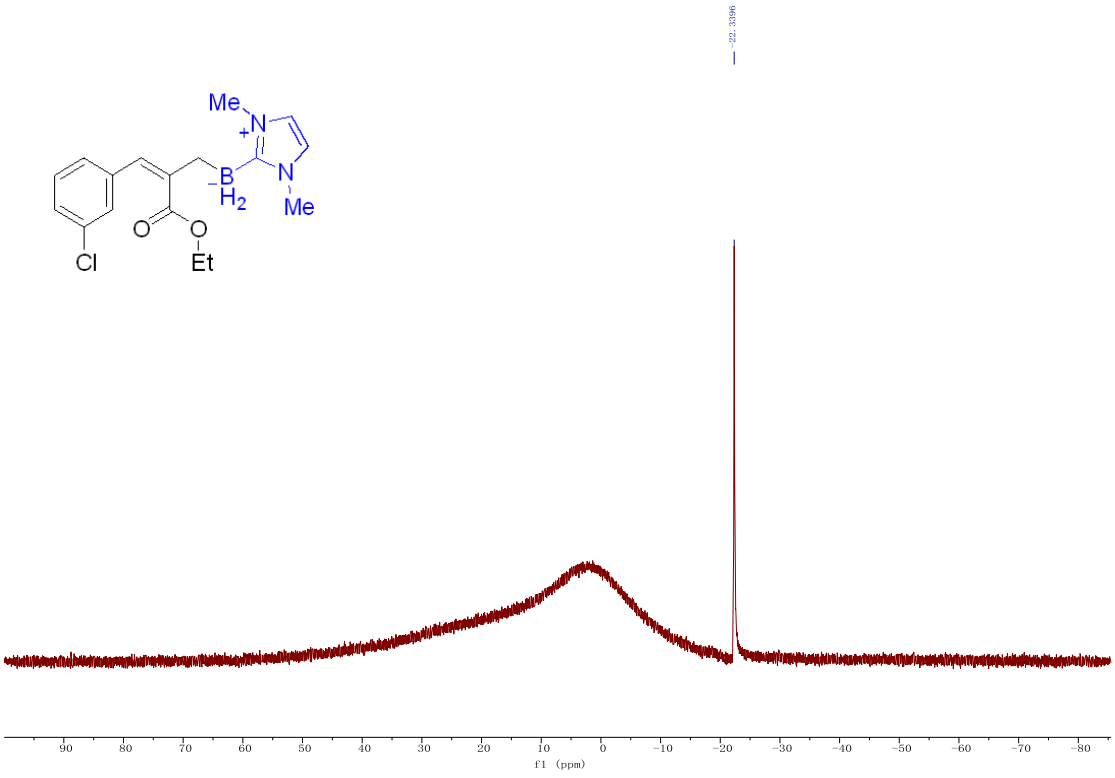
7.1000
7.0959
7.0870
7.0841
7.0686
7.0649
7.0611
6.9736
6.9587
6.8151
6.6466
4.0579
4.0436
4.0295
4.0151
3.7684
1.7534
1.1265
1.1122
1.0980
Me
N
B
H2
N
Me
O
O
Cl
Et
1.02
1.94
0.99
1.90
0.97
2.00
5.93
2.18
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2
f1 (ppm)


171.0957
145.3374
139.7873
133.6652
132.1141
127.5143
126.1348
125.7233
123.6693
120.2952
77.2980
77.0443
76.7904
36.0197
13.9032
Me
N
+
B
H2
N
Me
O
O
Et
Cl
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)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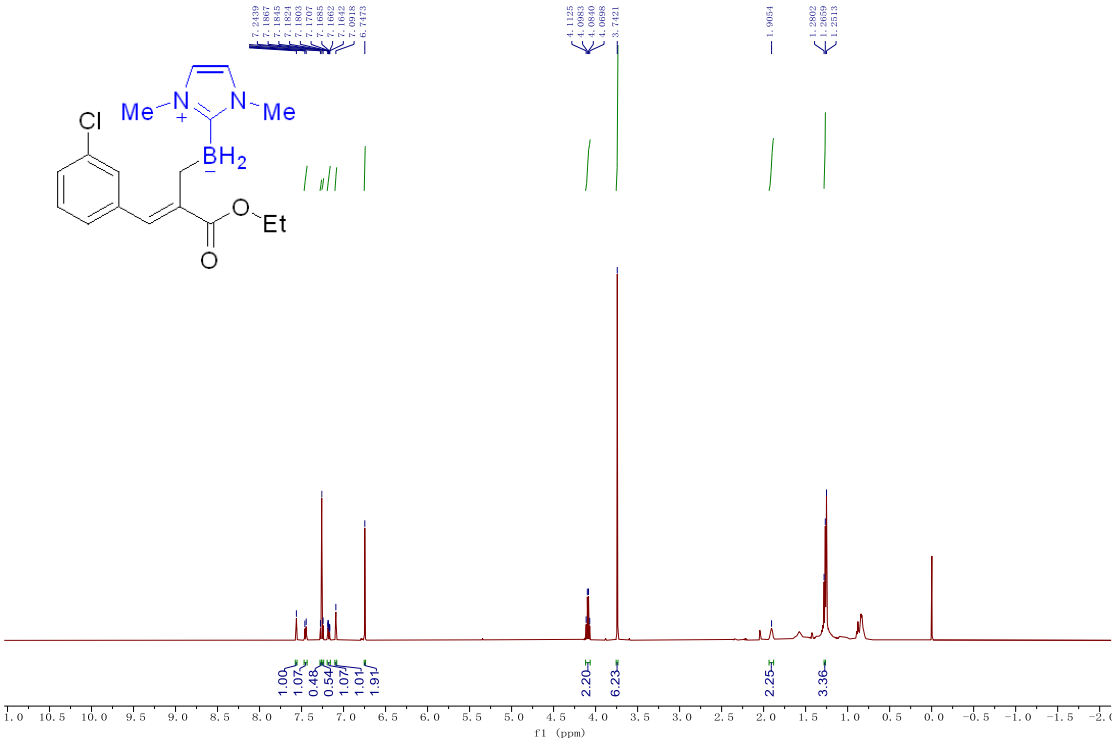
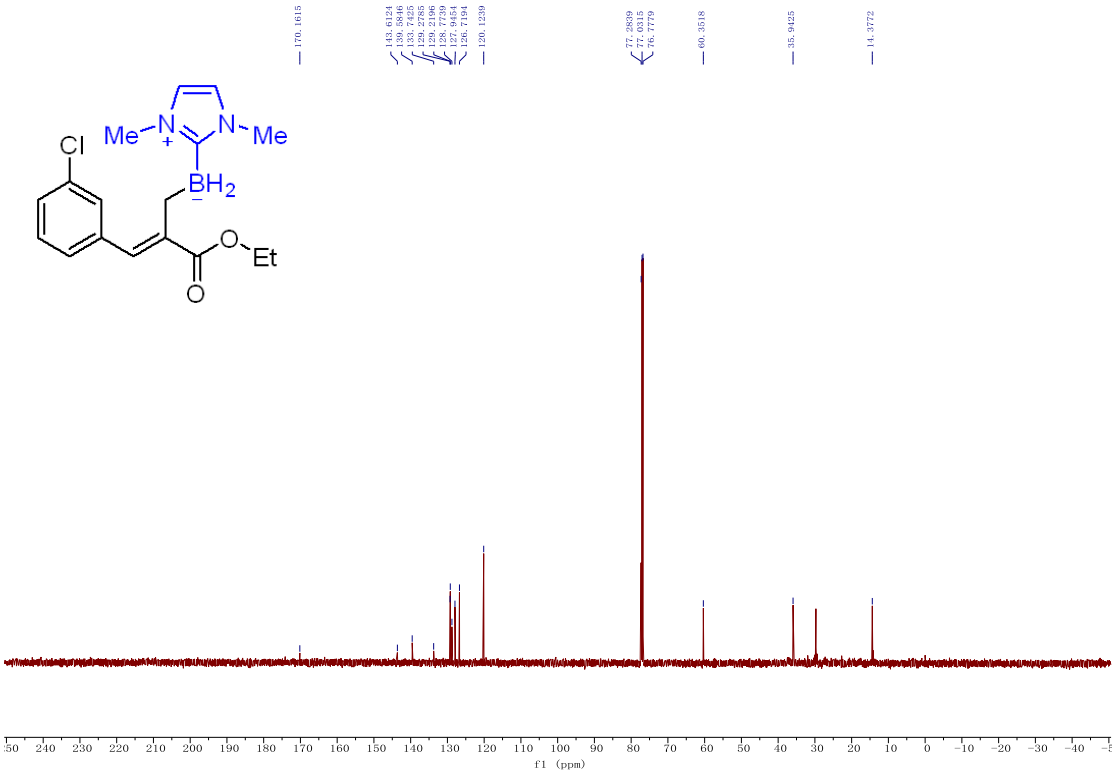
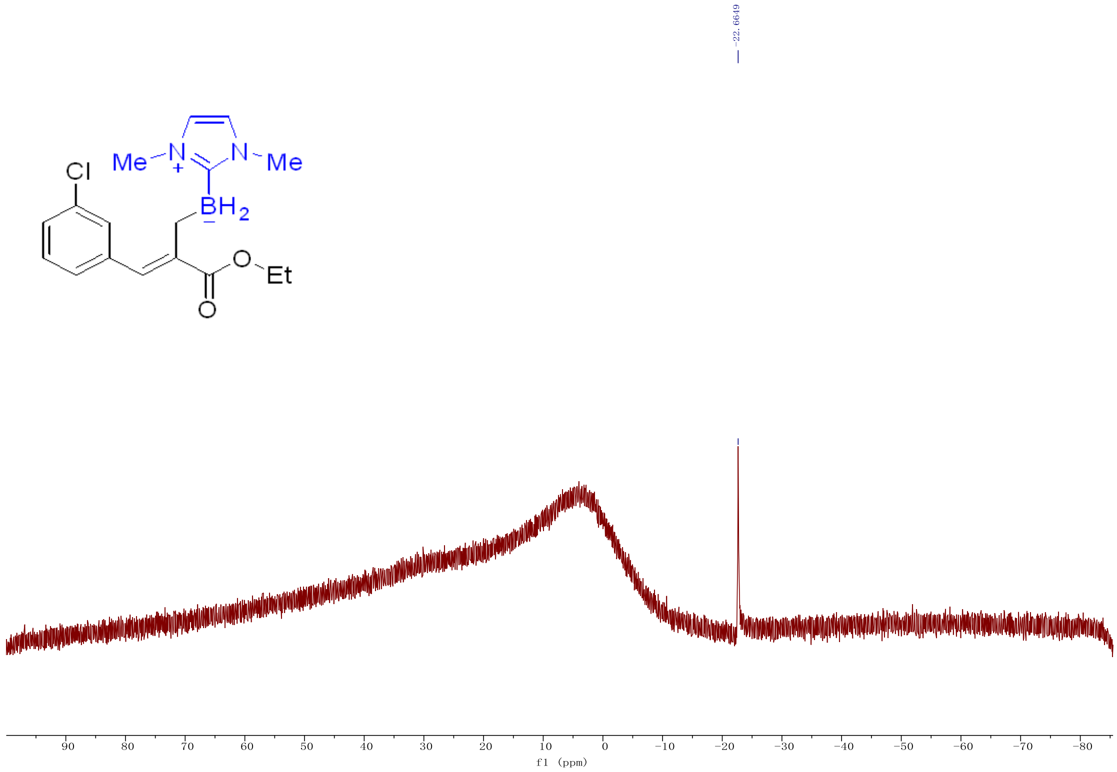
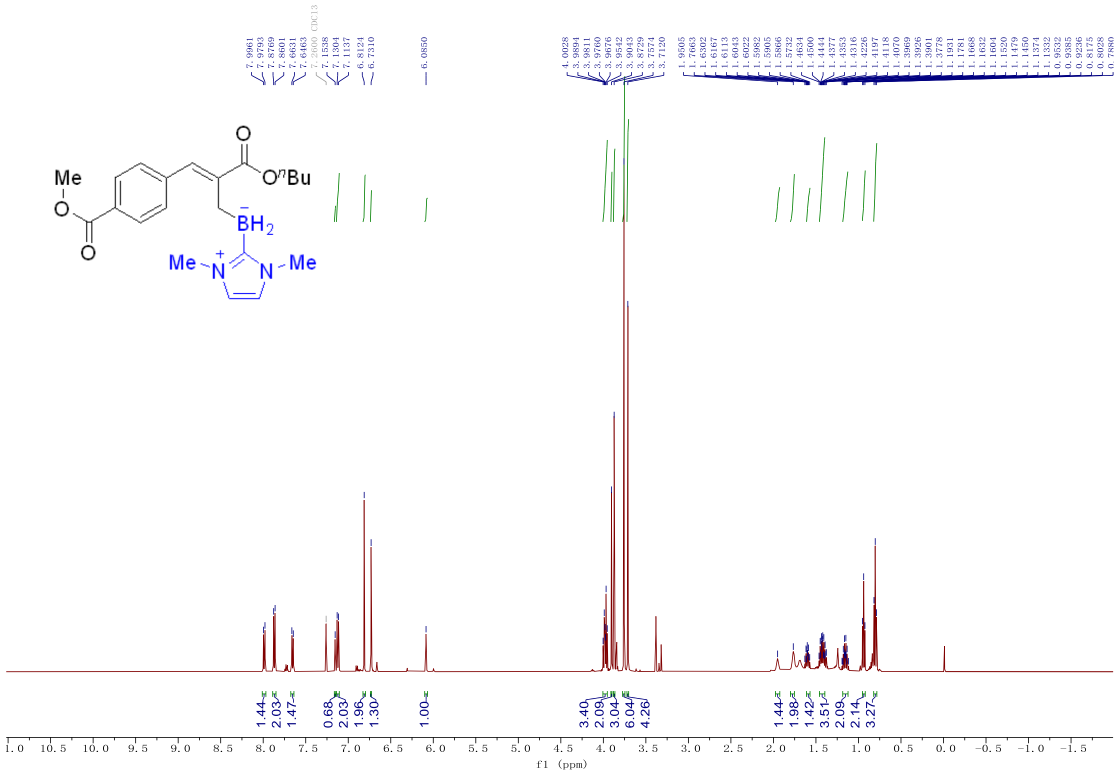
Me
N
+
B
H2
N
Me
O
O
Et
Cl
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)


Cl
Me
N
N
Me
BH2
O
Et
O
1.00
1.07
0.48
0.54
1.07
1.01
1.91
2.20
6.23
2.25
3.36
f1 (ppm)

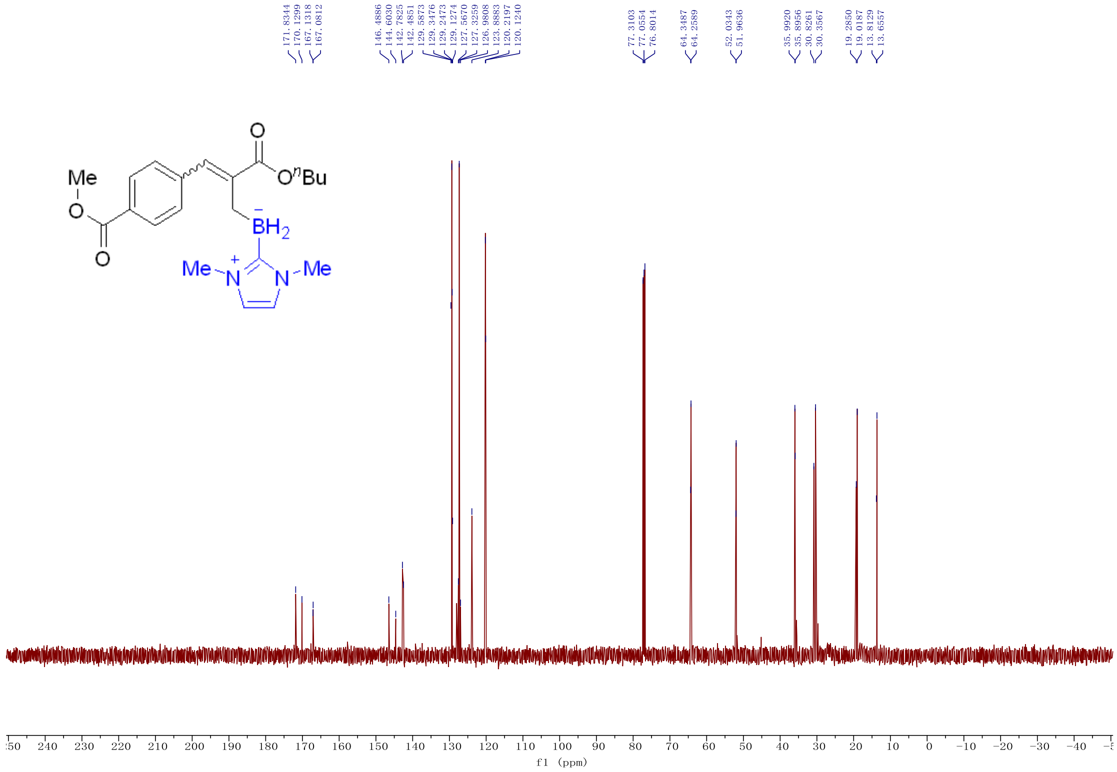

Cl
Me
N
N
Me
BH2
O
Et
O
f1 (ppm)



Cl
Me
N
N
Me
BH2
O
Et
O
f1 (ppm)



Me
O
O
O
O
nBu
BH2
Me
N
N
Me
f1 (ppm)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167.0812
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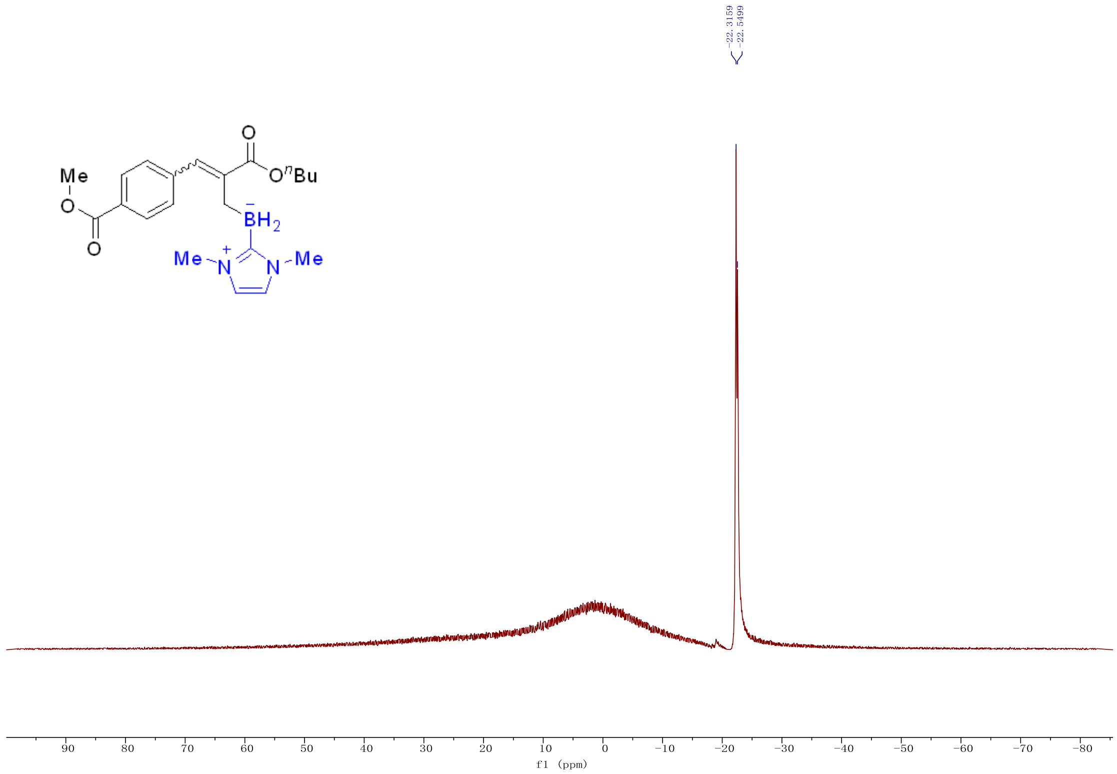
144.6030
142.7825
142.4851
129.5873
129.3476
129.2473
129.1274
127.5670
127.3259
126.9808
123.8883
120.2197
120.1240
77.3103
77.0554
76.8014
64.3487
64.2589
52.0343
51.9636
35.9920
35.8956
30.8261
30.3567
19.2850
19.0187
13.8129
13.6557
Me
O
O
O
O^nBu
BH2
Me
N
N
Me
f1 (ppm)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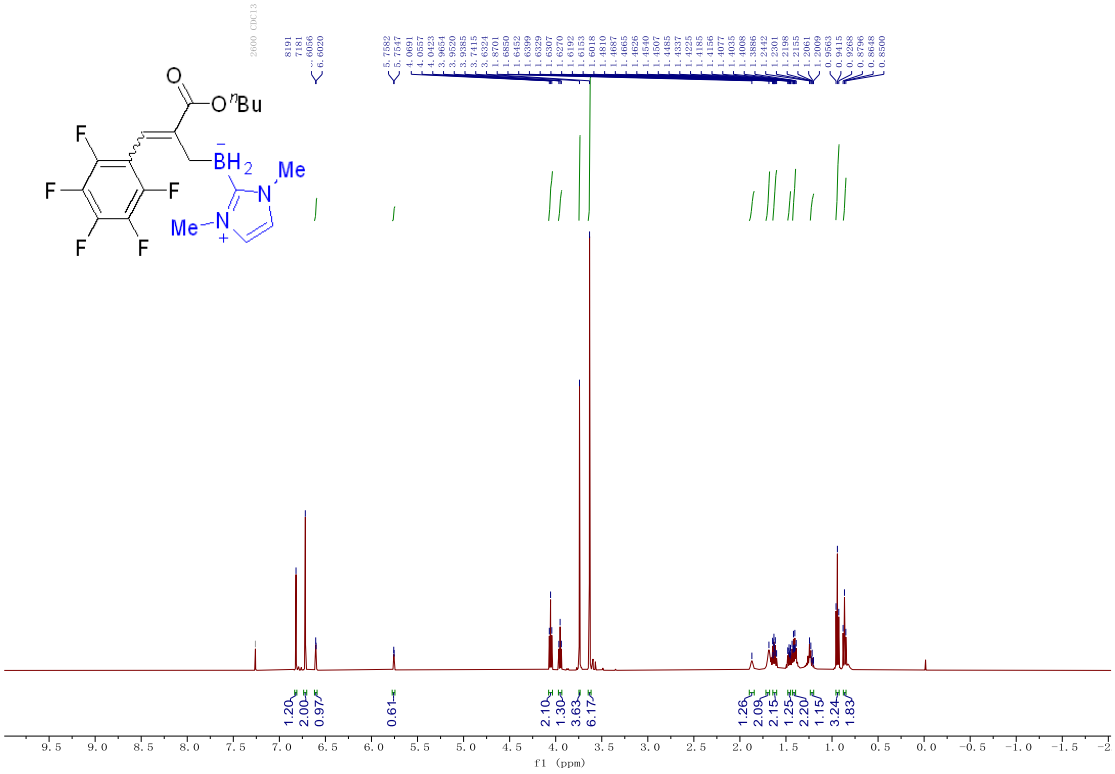
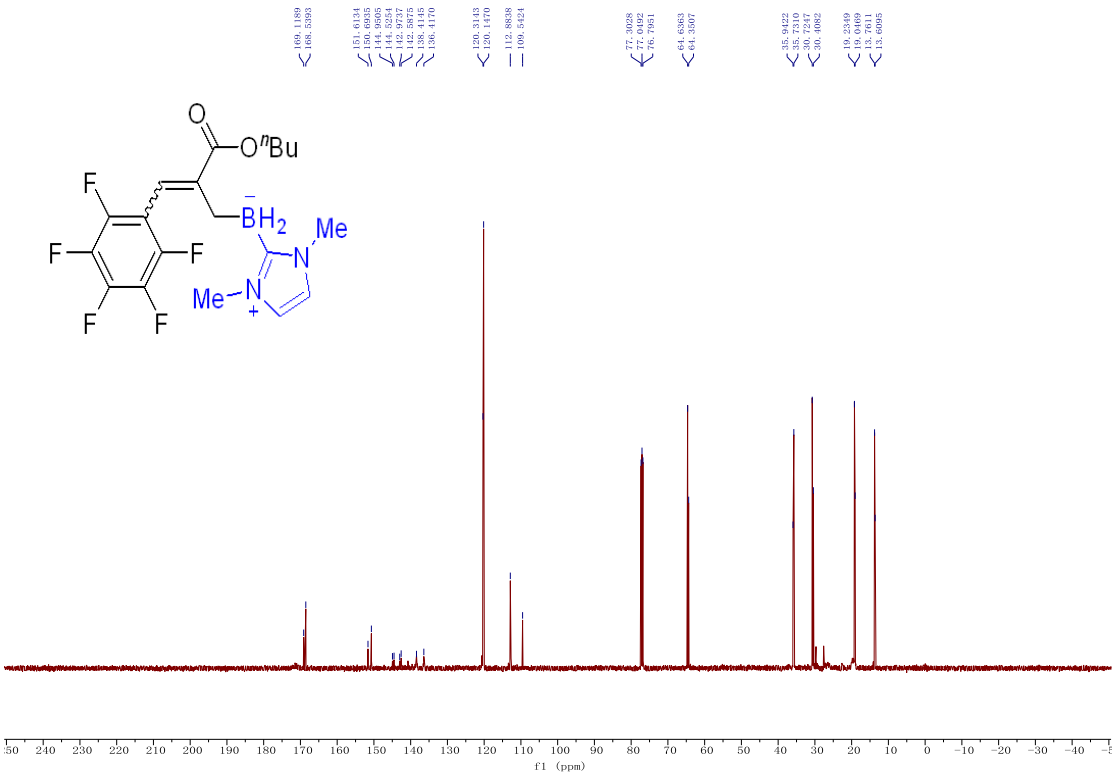
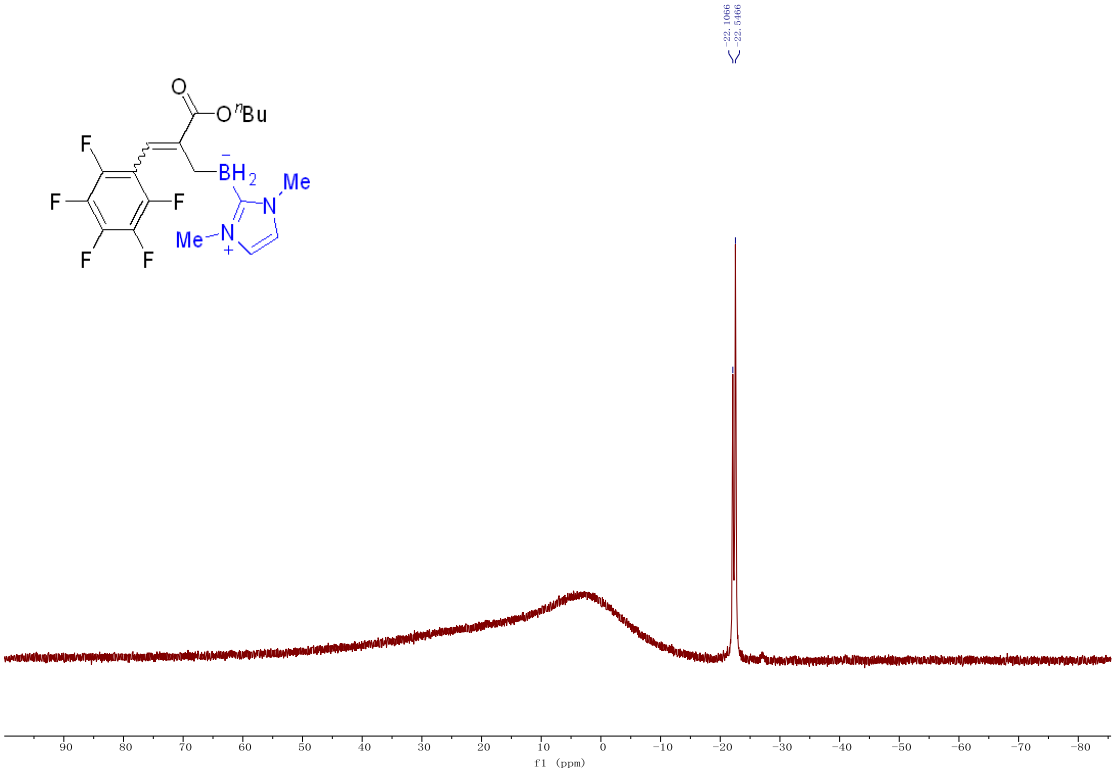
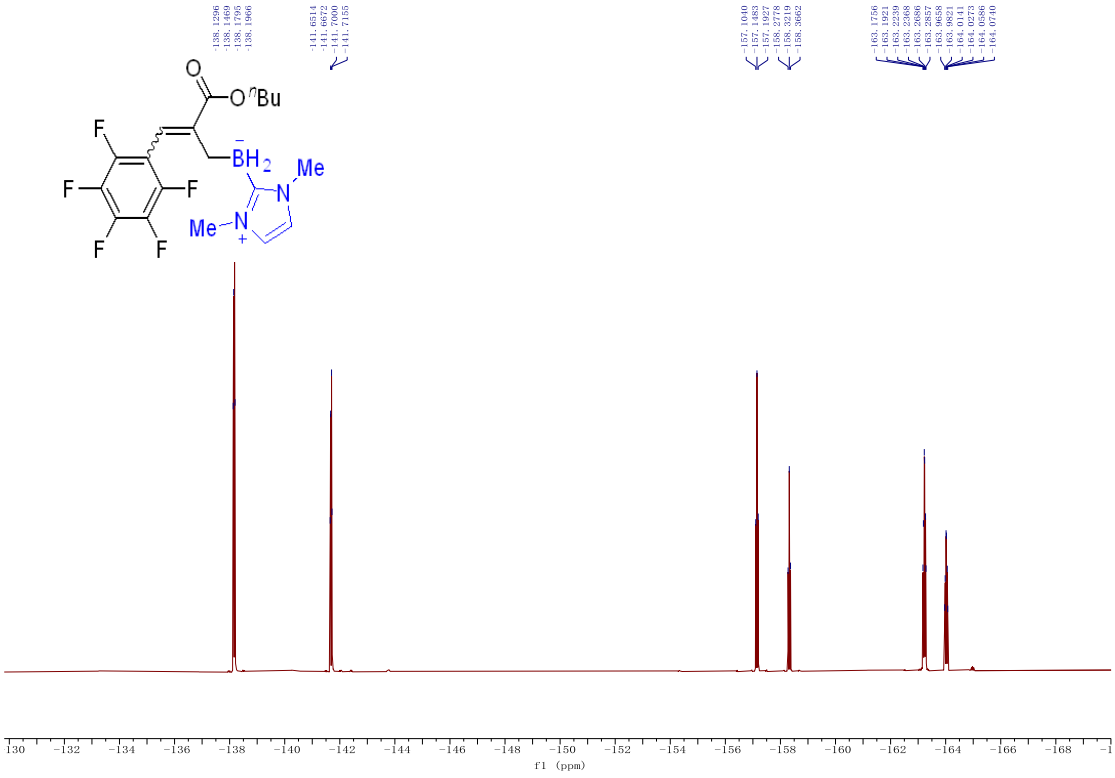
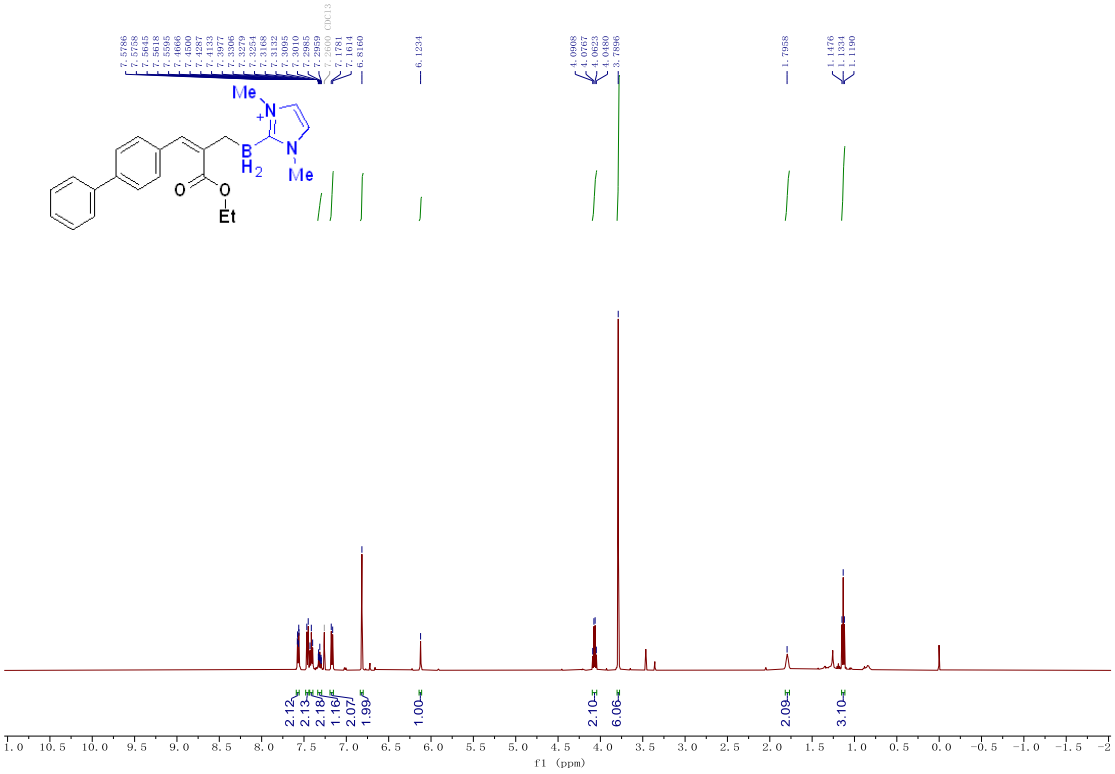
-22.5499
Me
O
O
O
O^nBu
BH2
Me
N
N
Me
f1 (ppm)

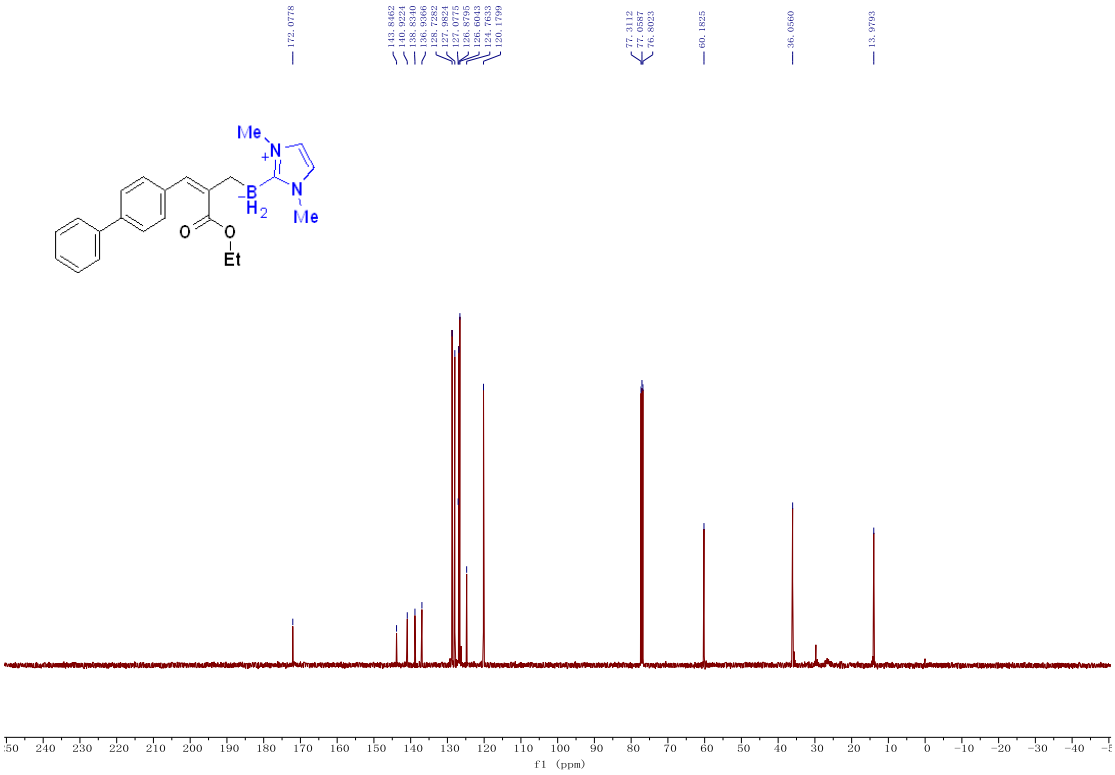

2600 CDCl3
O
O
nBu
F
F
F
F
F
BH2
N
Me
Me
N
+
f1 (ppm)

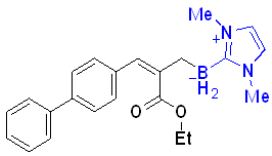

O
O
nBu
F
F
F
F
F
BH2
N
Me
Me
N
+
f1 (ppm)


-22.1066
-22.5466
O
O
nBu
F
F
F
F
F
BH2
N
Me
Me
N
+
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

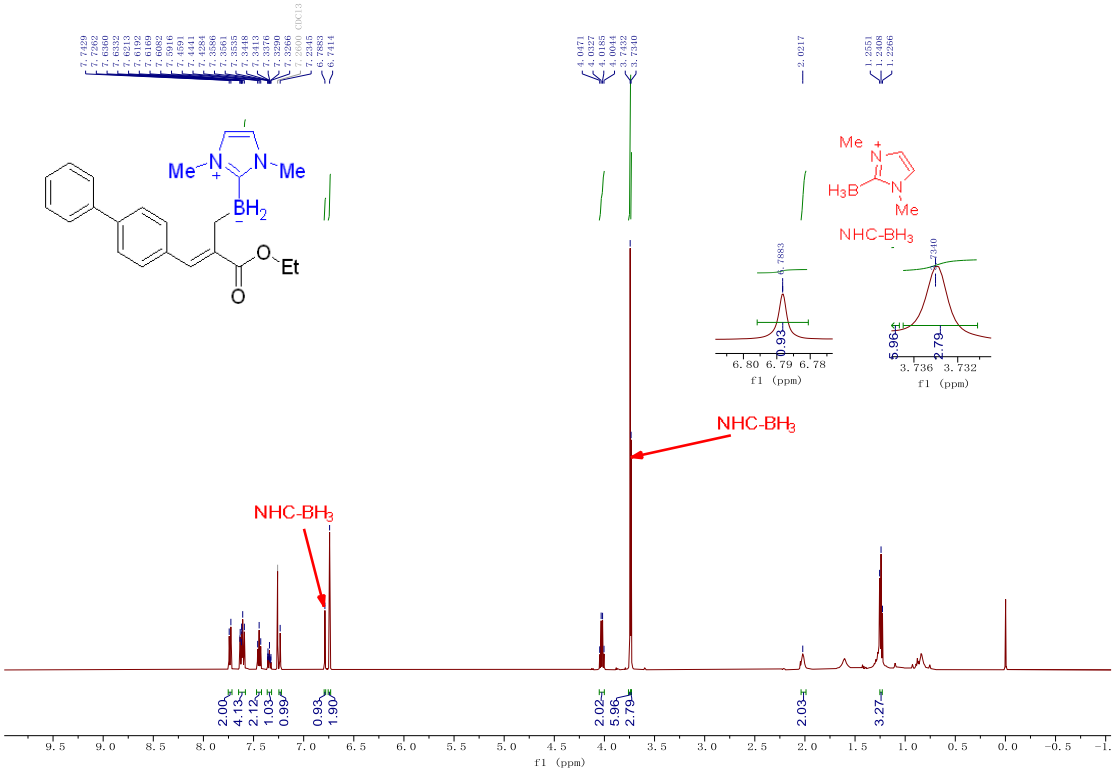

-138.1296
-138.1469
-138.1635
-138.1966
-141.6514
-141.6672
-141.7000
-141.7155
-157.1040
-157.1483
-157.1927
-158.2778
-158.3219
-158.3662
-163.1756
-163.1921
-163.2239
-163.2368
-163.2686
-163.2857
-163.9698
-163.9821
-164.0141
-164.0273
-164.0596
-164.0740
O
O
nBu
F
F
F
F
F
BH2
N
Me
Me
N
+
130 −132 −134 −136 −138 −140 −142 −144 −146 −148 −150 −152 −154 −156 −158 −160 −162 −164 −166 −168 −1
f1 (ppm)

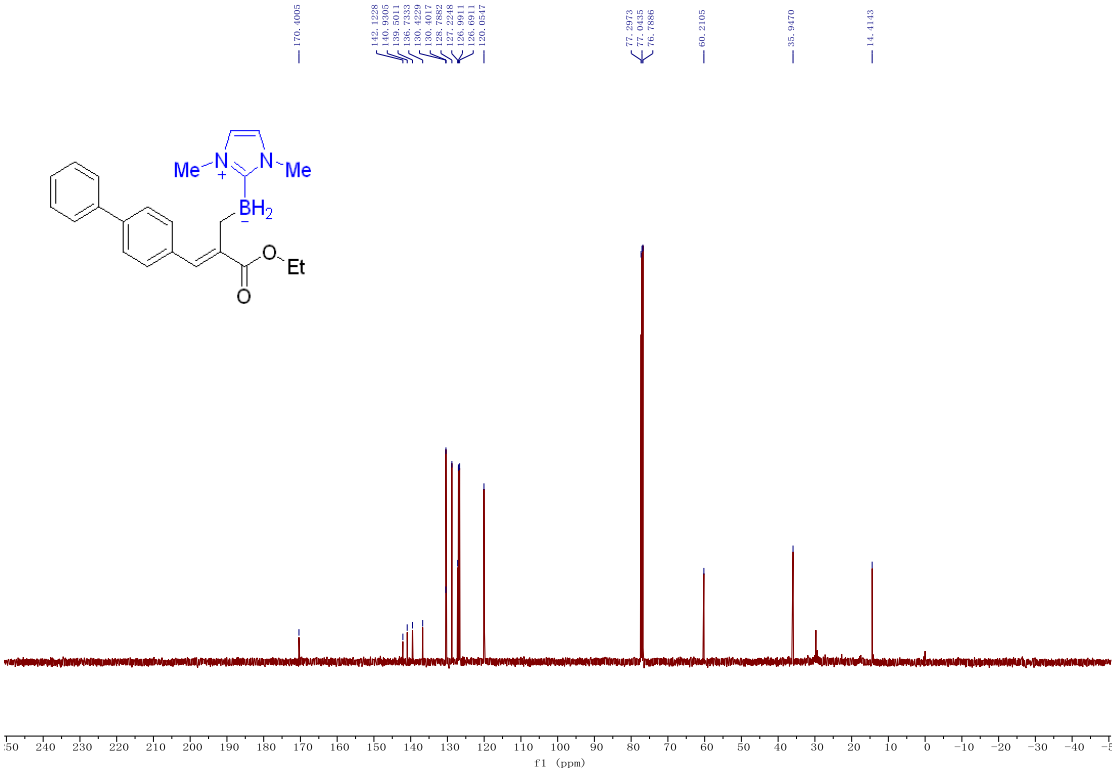

7.5786
7.5758
7.5645
7.5618
7.5595
7.4666
7.4590
7.4497
7.4135
7.3977
7.3306
7.3279
7.3254
7.3168
7.3132
7.3095
7.3010
7.2985
7.2959
7.2900 CDCl3
7.1781
7.1614
6.8160
6.1234
4.0908
4.0767
4.0623
4.0480
3.7986
1.7958
1.1476
1.1334
1.1190
Me
N
B
H2
N
Me
O
O
Et
2.12
2.13
2.18
1.16
2.07
1.99
1.00
2.10
6.06
2.09
3.10
f1 (ppm)

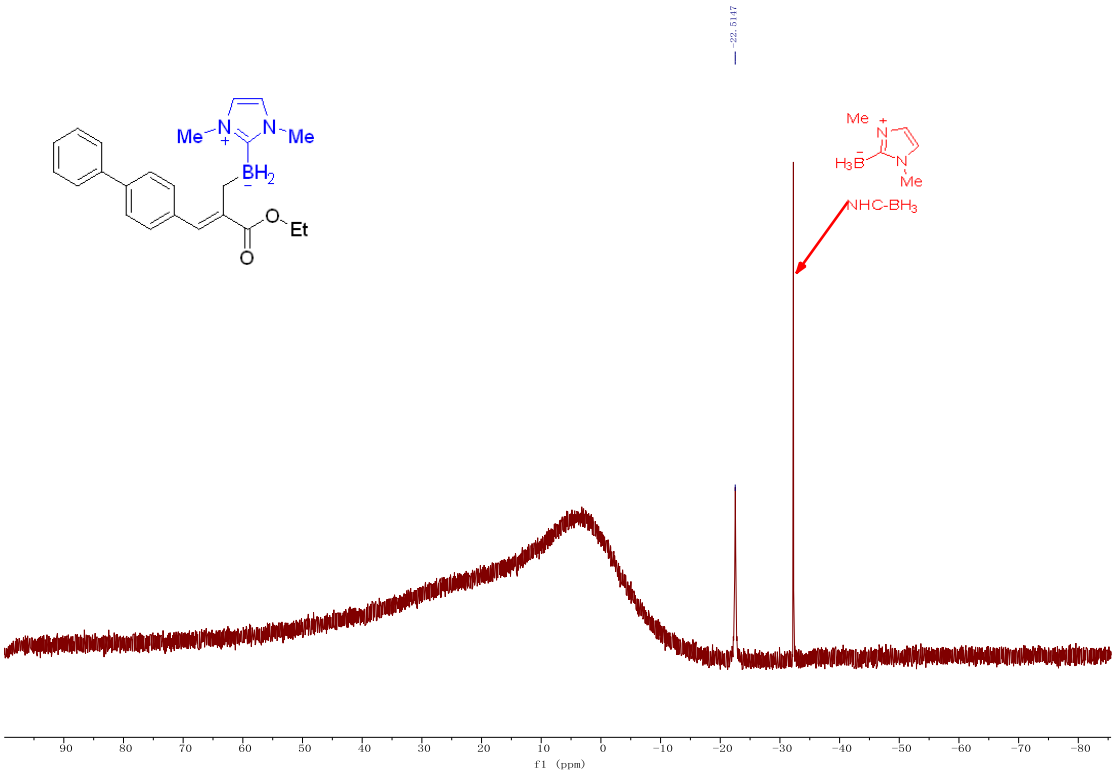

172.0778
143.8462
140.9224
138.8340
136.9366
128.7262
127.9824
127.0775
126.8795
126.6043
124.7633
120.1799
77.3112
77.0587
76.8023
60.1825
36.0560
13.9793
Me
N
B
H2
N
Me
O
O
Et
f1 (ppm)

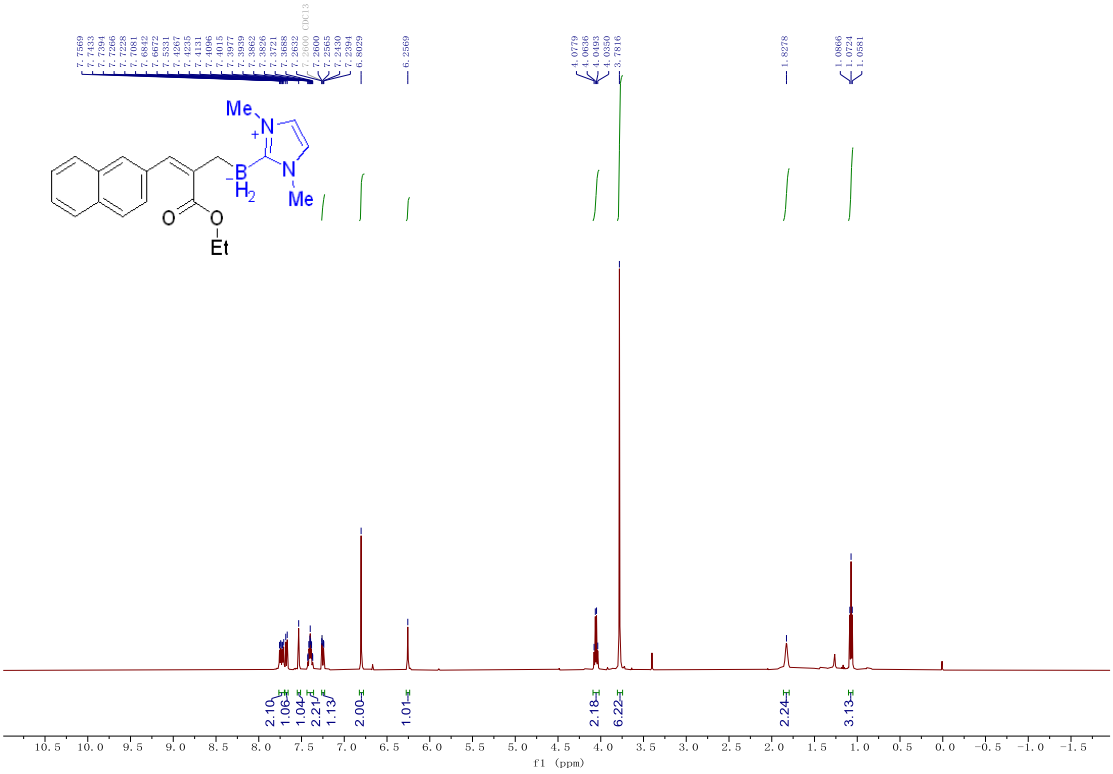

Me
N
+
B
H2
N
Me
O
O
Et

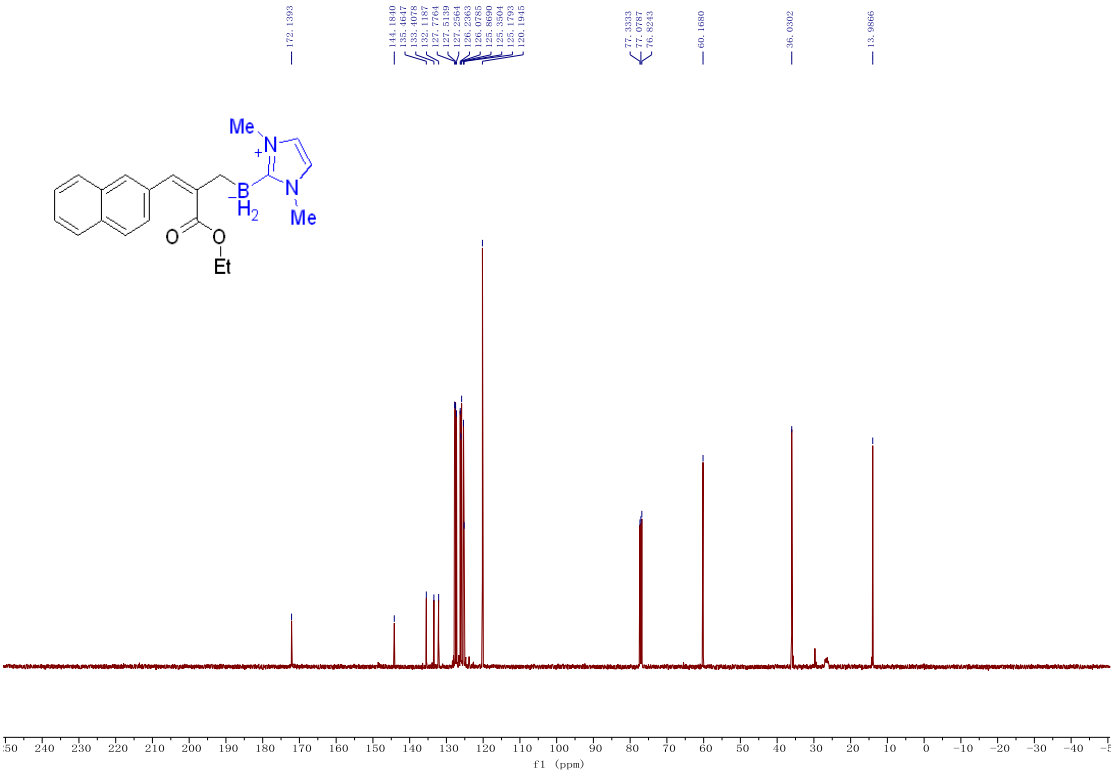
-22.2672
f1 (ppm)

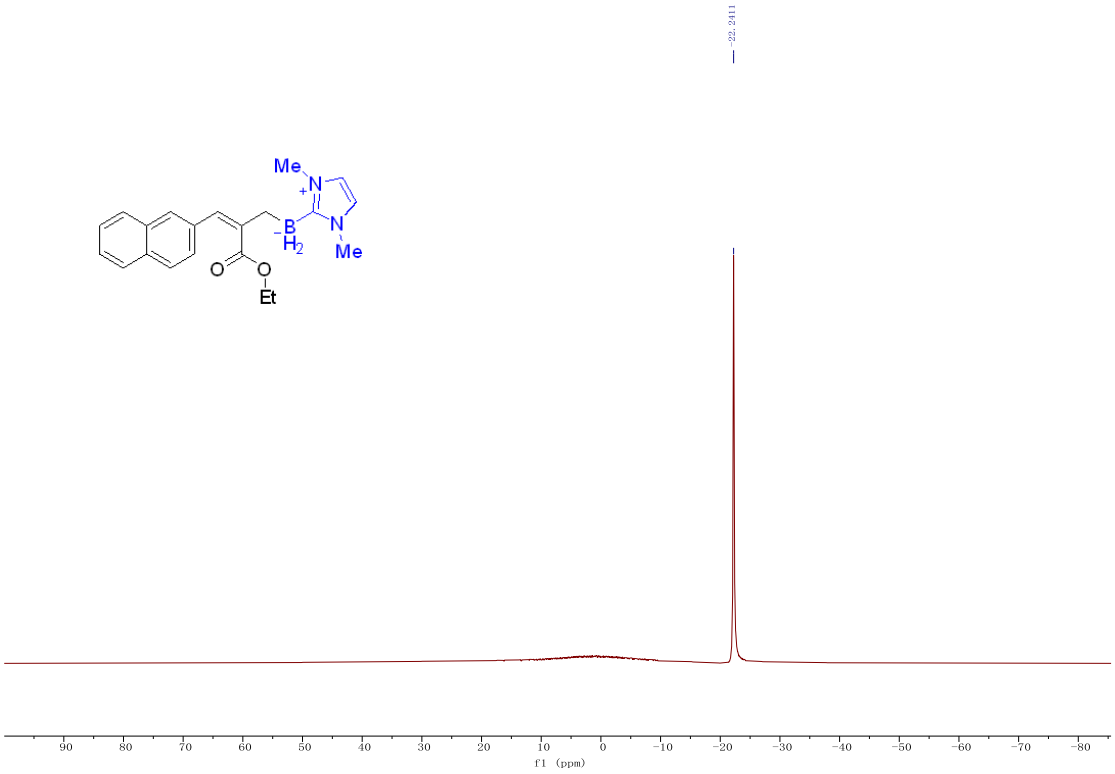

Me
N
+
N
Me
BH2
O
Et
O
NHC-BH3
NHC-BH3
f1 (ppm)

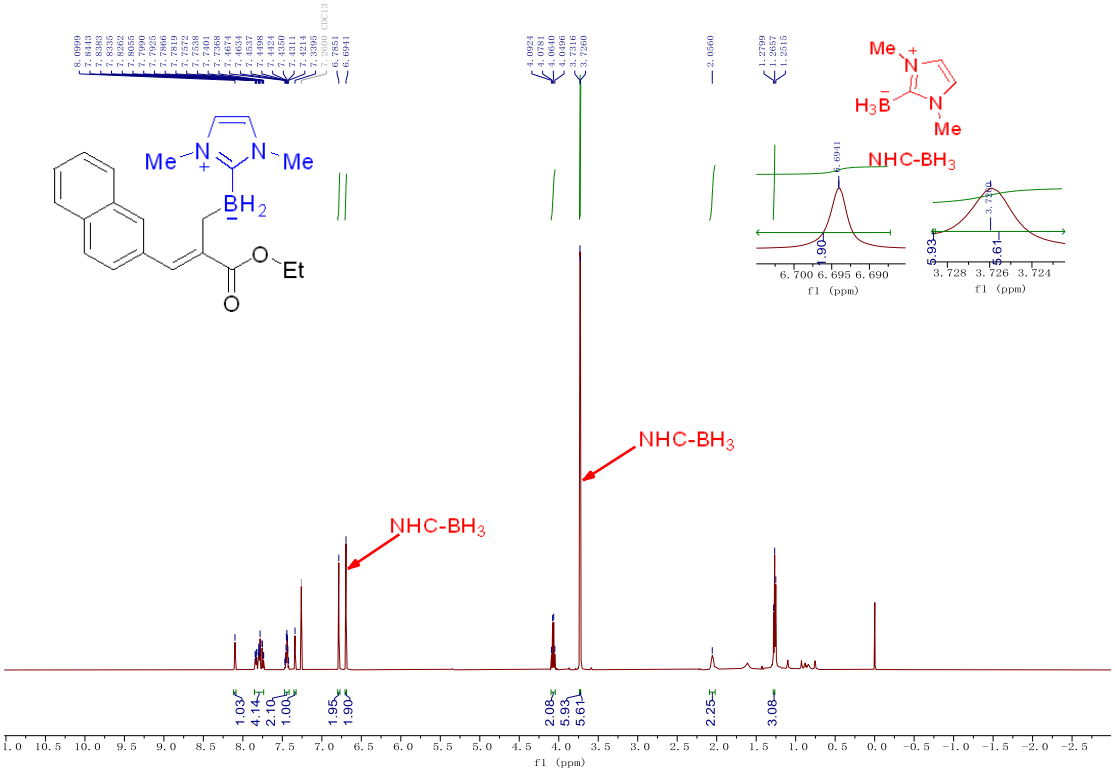

170.4005
142.1228
140.9305
139.5041
136.7253
130.4229
130.4017
128.7882
127.2940
126.6911
120.0547
77.2973
77.0435
76.7886
60.2105
35.9470
14.4143
Me
N
N
Me
BH2
O
Et
O
f1 (ppm)


-22.5147
Me
N
H3B
N
Me
NHC-BH3
Me
N
N
Me
BH2
O
Et
O
f1 (ppm)


Me
N
B
H2
N
Me
O
O
Et
f1 (ppm)


Me
N
B
H2
N
Me
O
O
Et
f1 (ppm)


-22.2411
Me
N
B
H2
N
Me
O
O
Et
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)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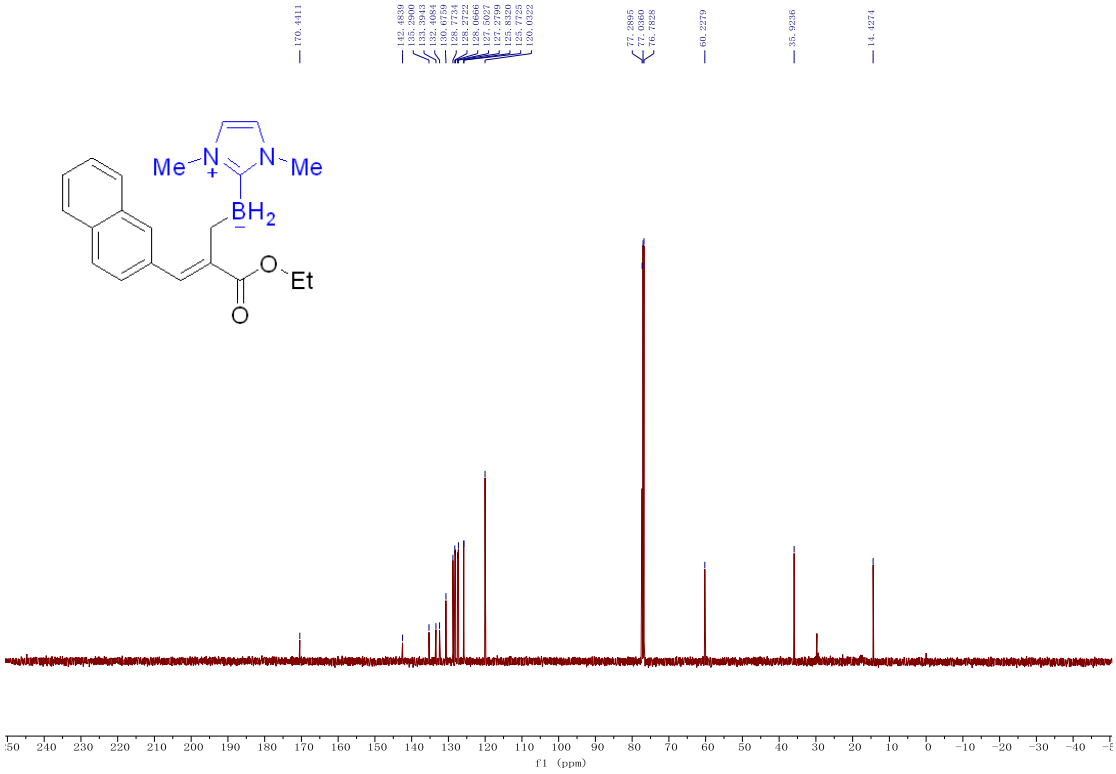
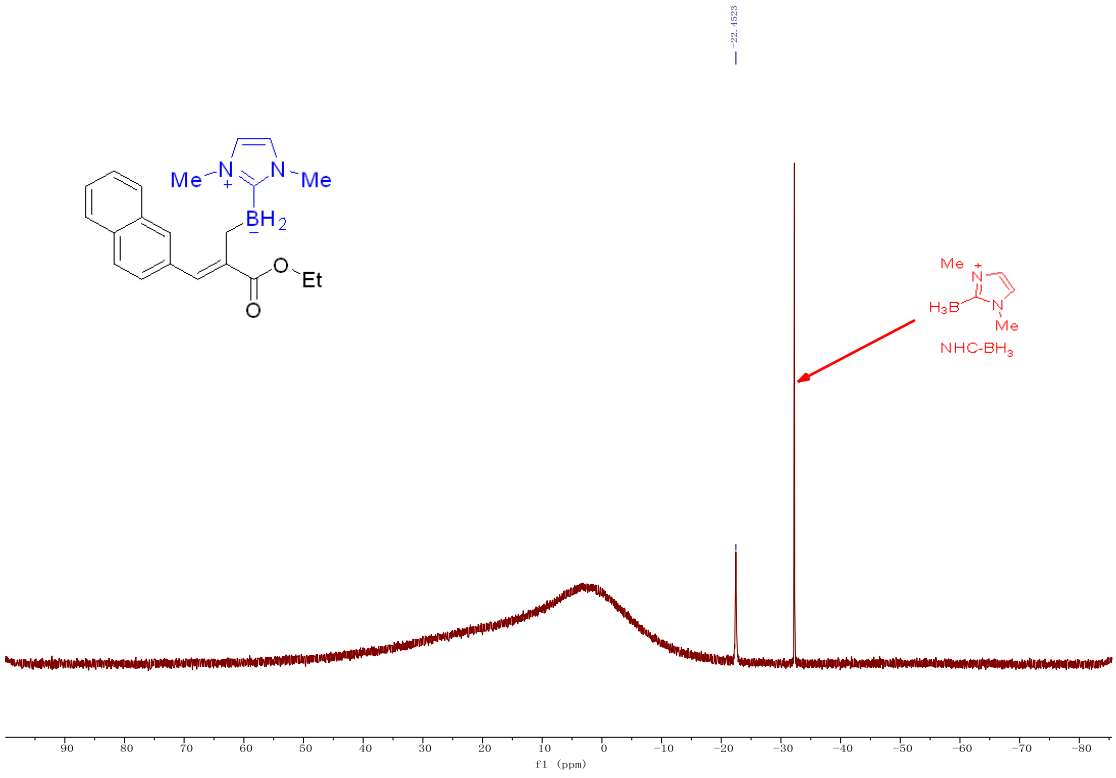
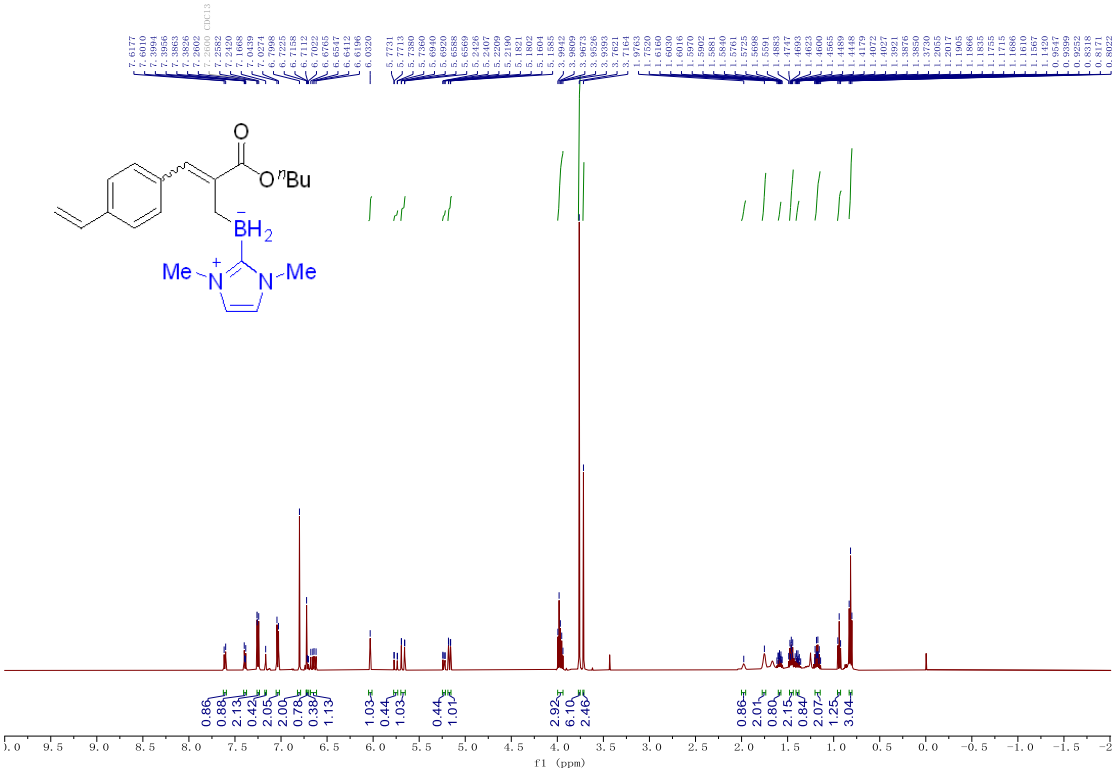
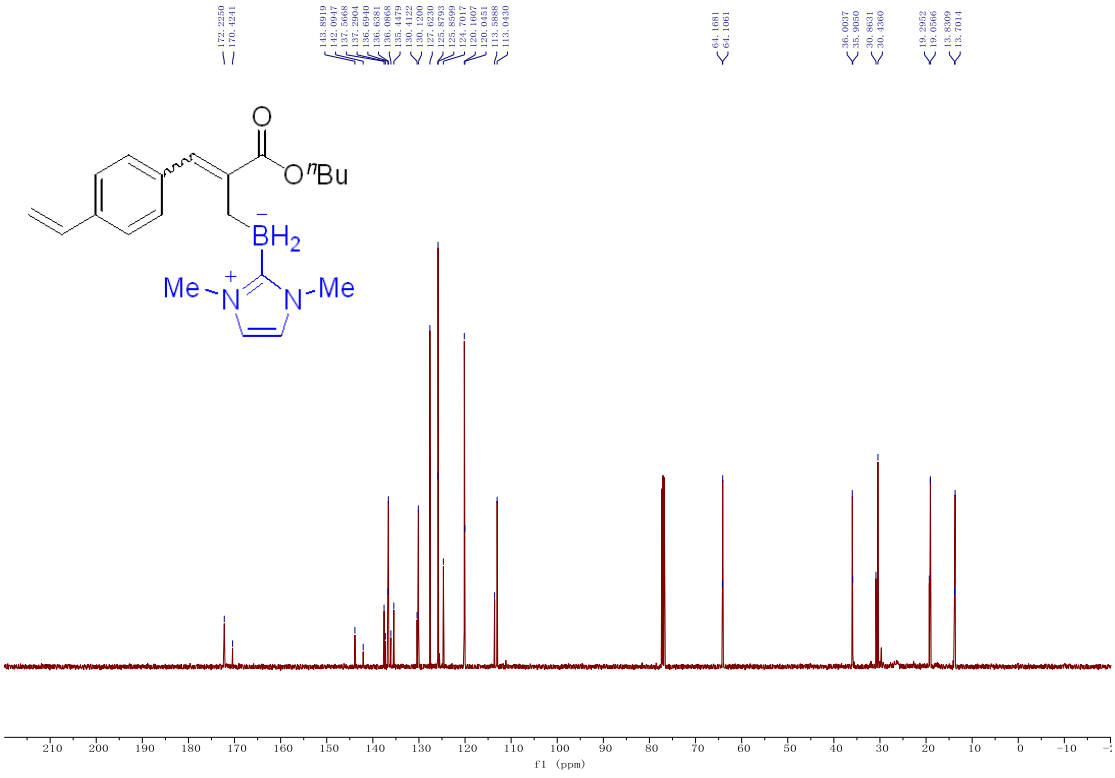
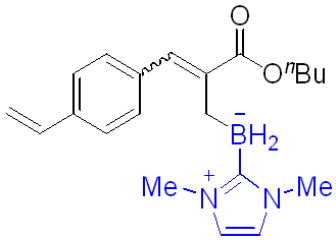
7.8368
7.8335
7.8262
7.8055
7.7990
7.7925
7.7866
7.7819
7.7572
7.7538
7.7401
7.7368
7.4674
7.4644
7.4537
7.4498
7.4424
7.4390
7.4311
7.4214
7.3395
CDCl3
6.7851
6.6941
4.0924
4.0781
4.0640
4.0496
3.7316
3.7260
2.0560
1.2799
1.1657
1.1516
Me
N
B
H2
N
Me
O
O
Et
NHC-BH3
6.6941
1.90
6.700 6.695 6.690
f1 (ppm)
3.7260
5.93
5.61
3.728 3.726 3.724
f1 (ppm)
NHC-BH3
NHC-BH3
1.03
4.14
2.10
1.00
1.95
1.90
2.08
5.93
5.61
2.25
3.08
1.0 10.5 10.0 9.5 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 -1.5 -2.0 -2.5
f1 (ppm)


170.4411
142.4839
135.2900
133.3041
132.4084
130.6750
128.7734
128.2772
128.0666
127.5027
127.2799
125.8320
125.7252
120.0322
77.2895
77.0360
76.7828
60.2279
35.9236
14.4274
Me
N
N
Me
BH2
O
Et
O
f1 (ppm)

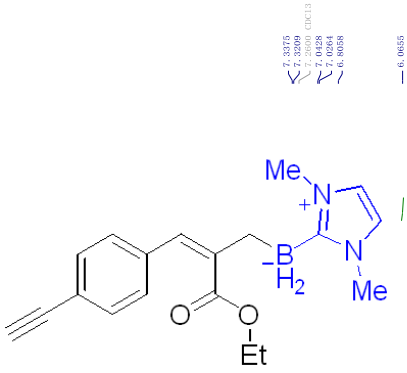

22.4523
Me
N
N
Me
BH2
O
Et
O
Me
N
H3B
N
Me
NHC-BH3
f1 (ppm)


O
nBu
BH2
Me
N
N
Me
f1 (ppm)

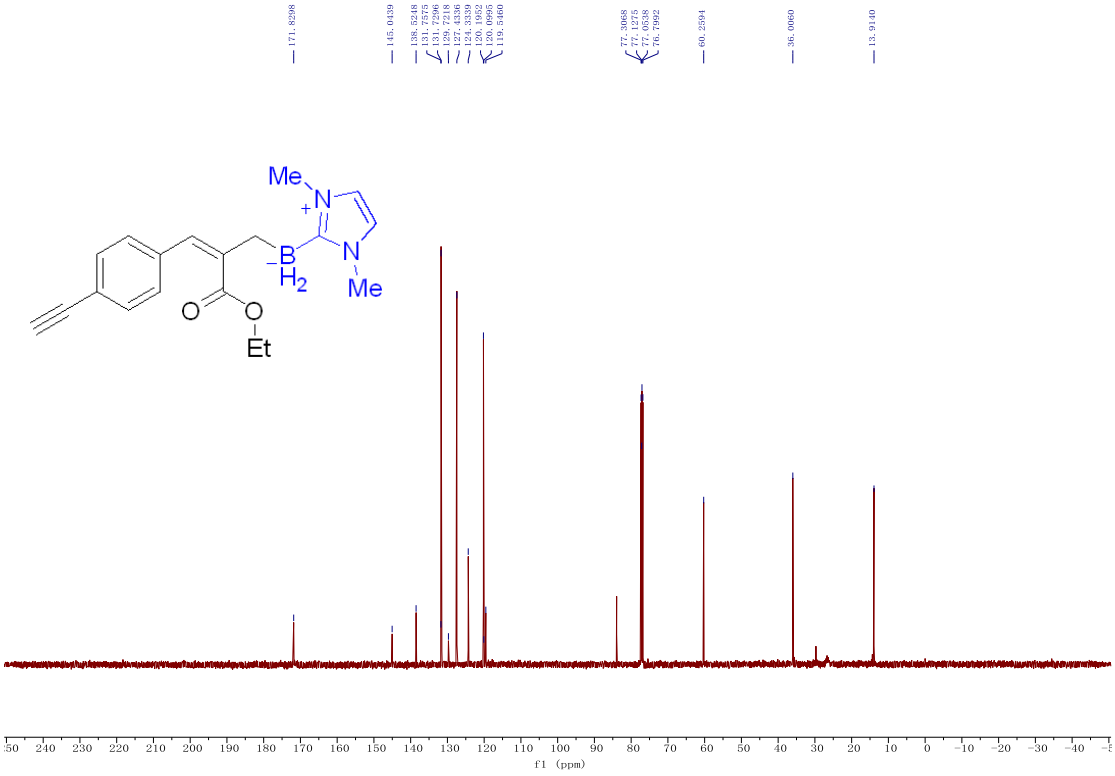

O
nBu
BH2
Me
N
N
Me
f1 (ppm)


O
O^{n}Bu
BH$_2$
Me
N
N
Me

-22.3117
-22.5240
f1 (ppm)


Me
N
B
H$_2$
N
Me
O
O
Et

7.3375
7.3209
7.0428
7.0264
6.8658
6.0655
4.0498
4.0356
4.0212
4.0070
3.7569
3.0964
3.0515
1.7343
1.1178
1.1035
1.0891
2.00
2.03
1.97
0.97
2.15
6.06
0.91
2.09
3.01
f1 (ppm)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138.5248
131.7575
131.7296
129.7218
127.4336
124.3339
120.1952
120.0995
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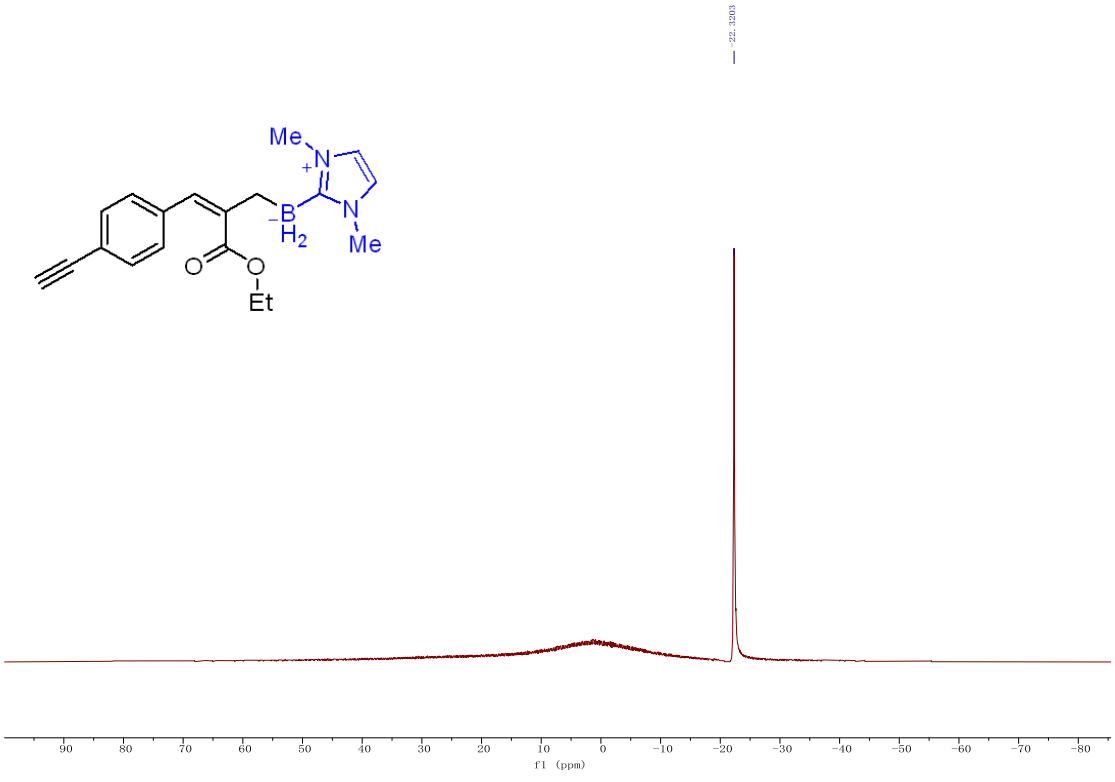
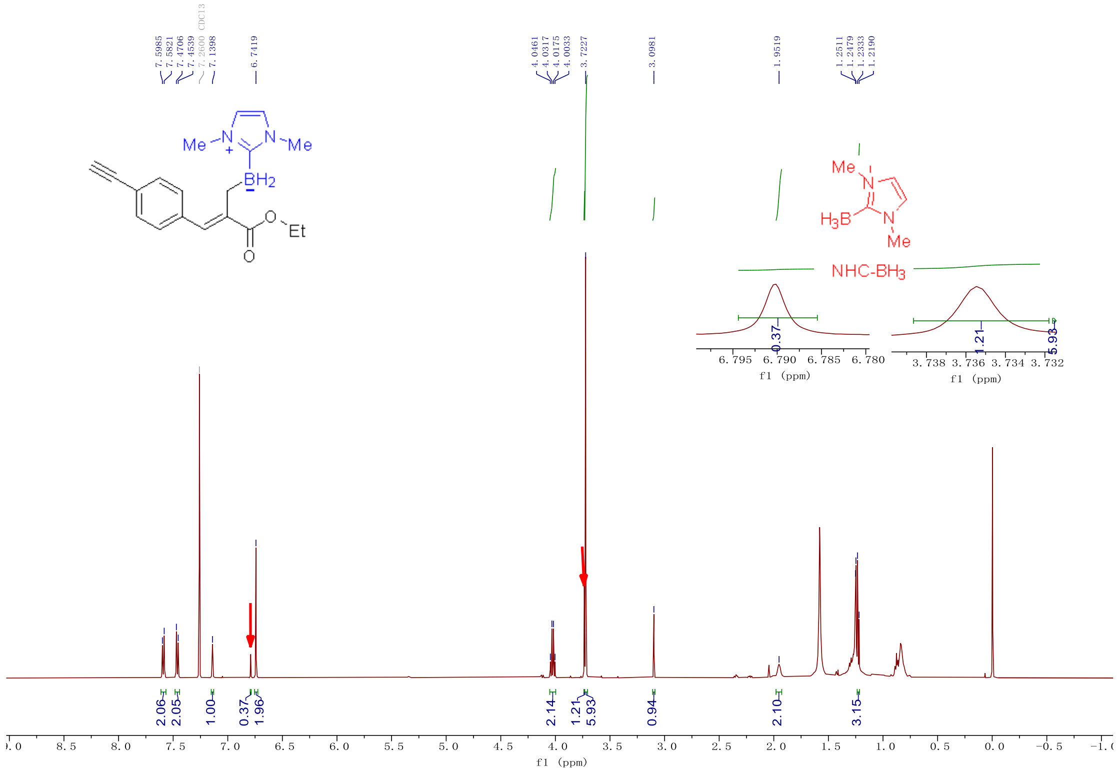
77.3068
77.1275
77.0958
76.7992
60.2594
36.0060
13.9140
Me
N
+
B
H2
N
Me
O
O
Et
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


22.3203
Me
N
+
B
H2
N
Me
O
O
Et
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)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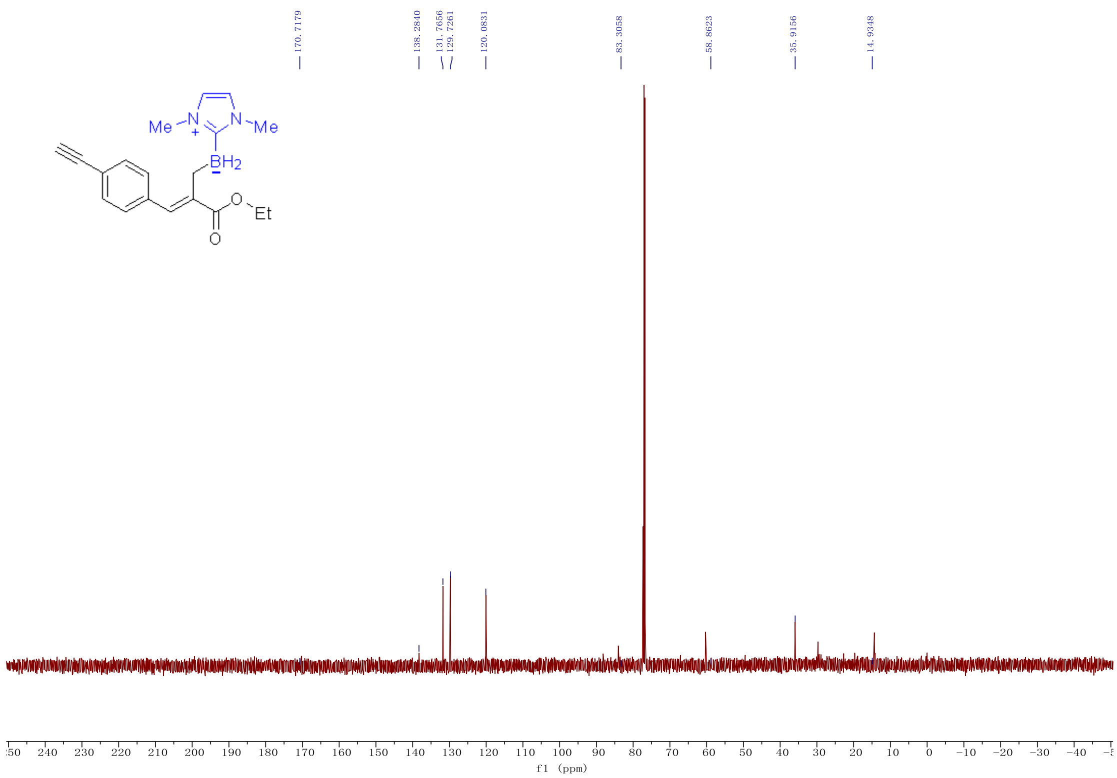
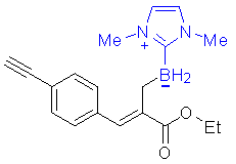
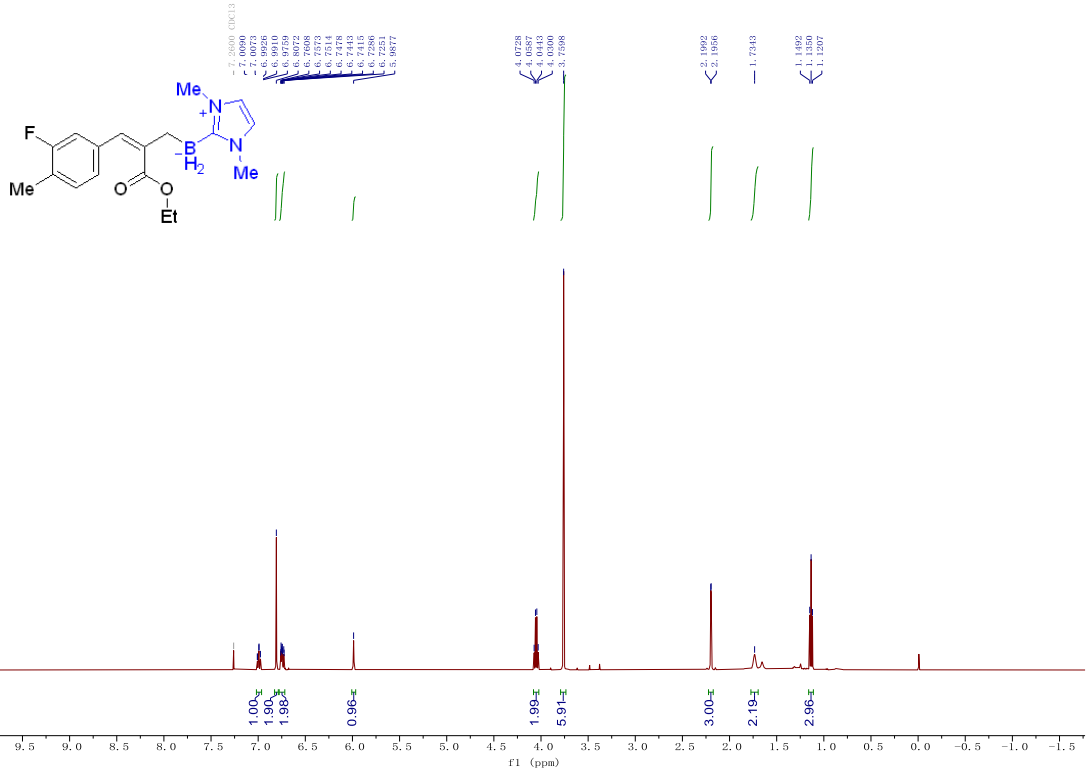
7.5821
7.4706
7.4539
7.2600 CDCl3
7.1398
6.7419
4.0461
4.0317
4.0175
4.0033
3.7227
3.0981
1.9519
1.2511
1.2479
1.2333
1.2190
Me
N
N
Me
BH2
O
Et
O
H3B
NHC-BH3
0.37
1.21
5.93
2.06
2.05
1.00
1.96
2.14
0.94
2.10
3.15
f1 (ppm)


170.7179
138.2840
131.7656
129.7261
120.0831
83.3058
58.8623
35.9156
14.9348
Me
N
N
Me
BH2
O
Et
O
f1 (ppm)


Me
N
N
Me
BH2
O
Et
O

-22.6513
f1 (ppm)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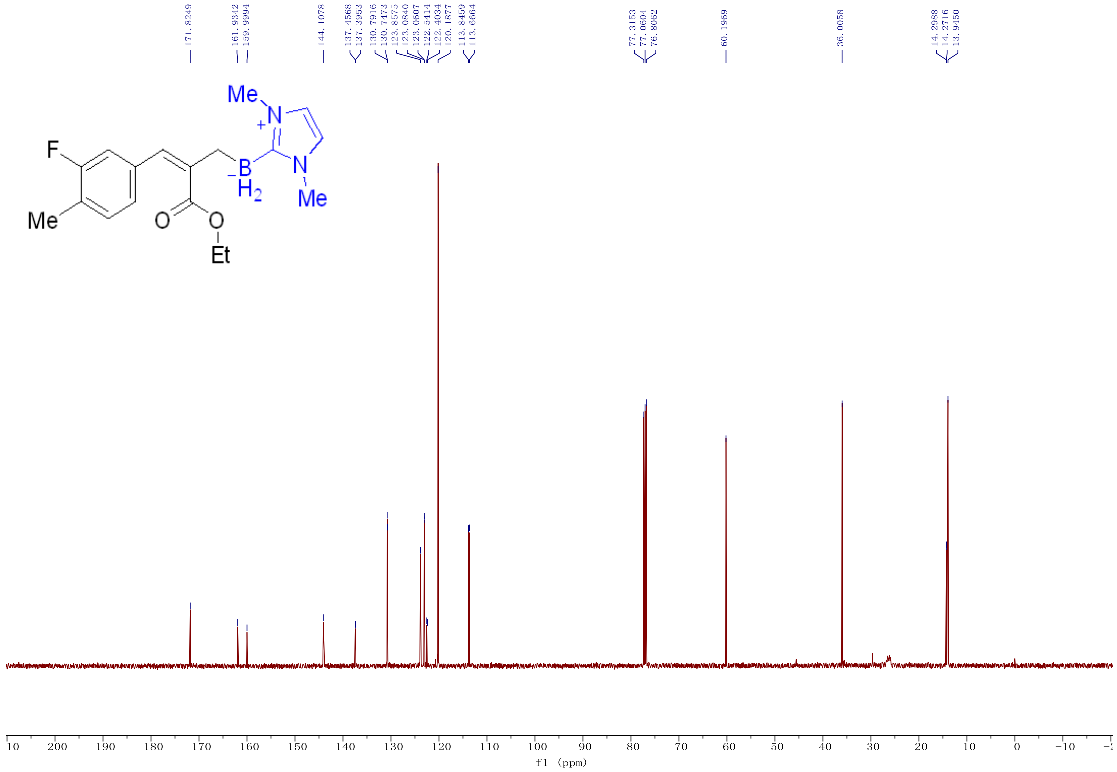
7.0096
7.0073
6.9926
6.9910
6.9759
6.9742
6.9672
6.7608
6.7573
6.7514
6.7478
6.7443
6.7415
6.7286
6.7251
6.0877
4.0728
4.0587
4.0443
4.0300
4.0156
3.7598
2.1992
2.1956
1.7343
1.1492
1.1350
1.1207
Me
N
N
Me
F
Me
B
H2
O
O
Et
1.00
1.90
1.98
0.96
1.99
5.91
3.00
2.19
2.96
f1 (ppm)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144.1078
137.4568
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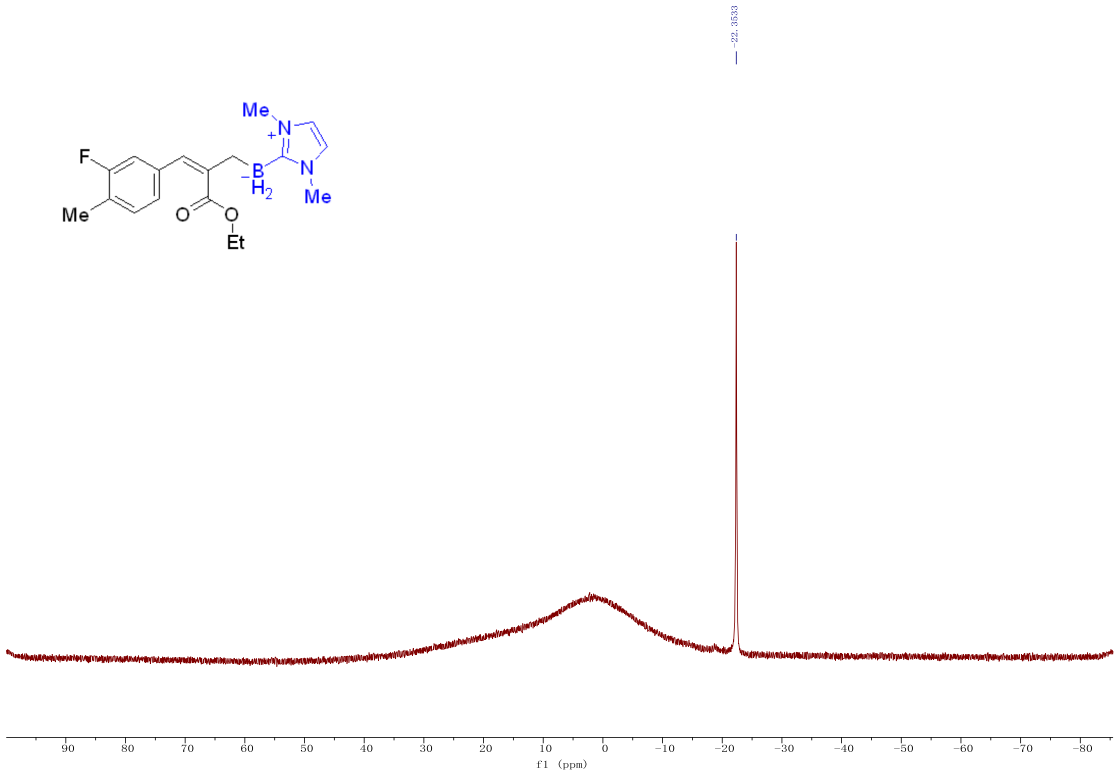
130.7916
130.7473
123.8575
123.0840
123.0607
122.5414
122.4034
120.1877
113.8459
113.6664
77.3153
77.0604
76.8062
60.1969
36.0058
14.2988
14.2716
13.9450
Me
N
H2
B
N
Me
F
Me
O
O
Et
f1 (ppm)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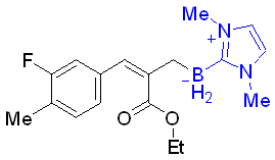
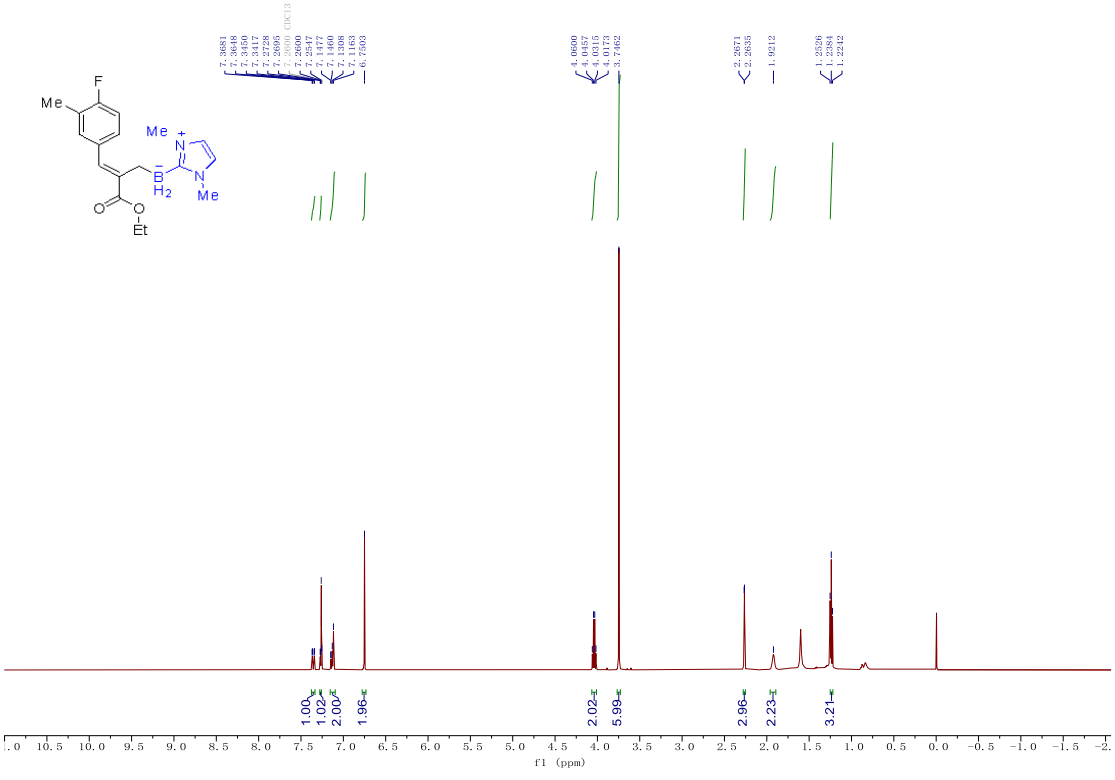
Me
N
F
B
H2
N
Me
Me
O
O
Et
f1 (ppm)


Me
N
+
F
B
H2
N
Me
Me
O
O
Et

-118.7849
f1 (ppm)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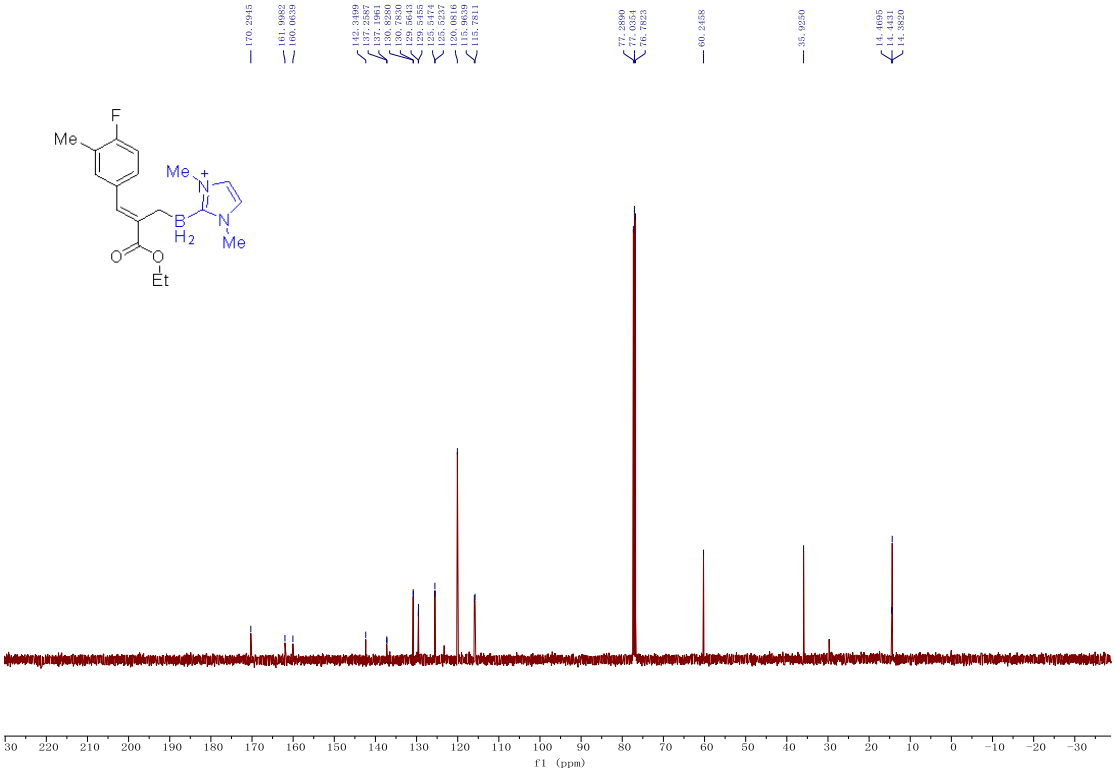
7.3648
7.3450
7.3417
7.2736
7.2695
7.2600 CDCl3
7.2547
7.1477
7.1460
7.1398
7.1365
6.7503
4.0600
4.0457
4.0315
4.0173
3.7462
2.2671
2.2635
1.9212
1.2526
1.2384
1.2242
1.00
1.02
2.00
1.96
2.02
5.99
2.96
2.23
3.21
f1 (ppm)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160.0639
142.3499
137.2957
137.1981
130.8280
130.7830
129.5643
129.5555
125.5474
125.5237
120.0816
115.8669
115.7811
77.2890
77.0354
76.7823
60.2458
35.9250
14.4695
14.4431
14.3820
F
Me
Me
B
H2
N
N
Me
O
O
Et
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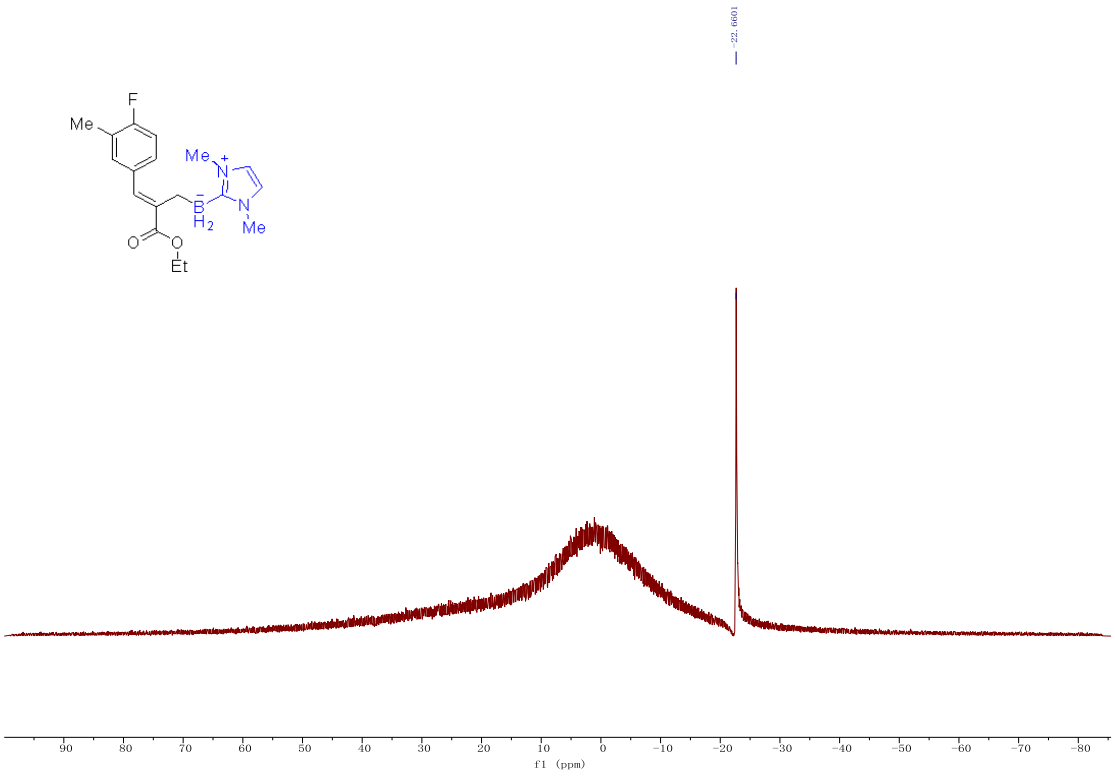
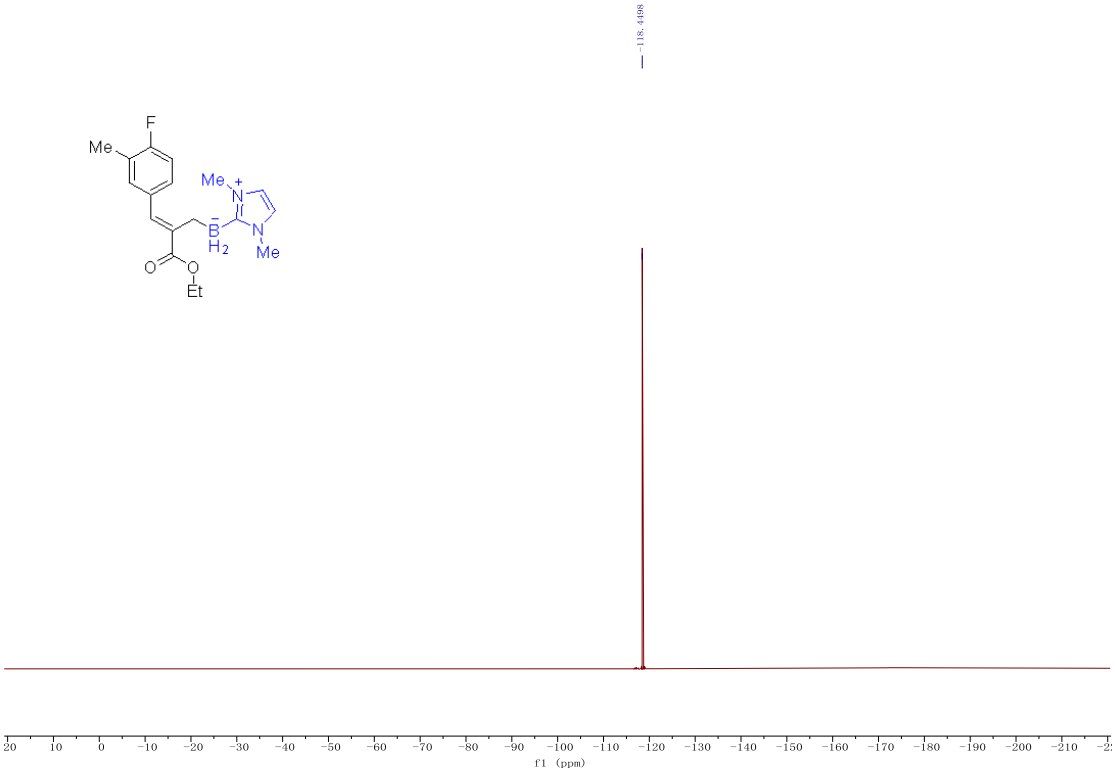
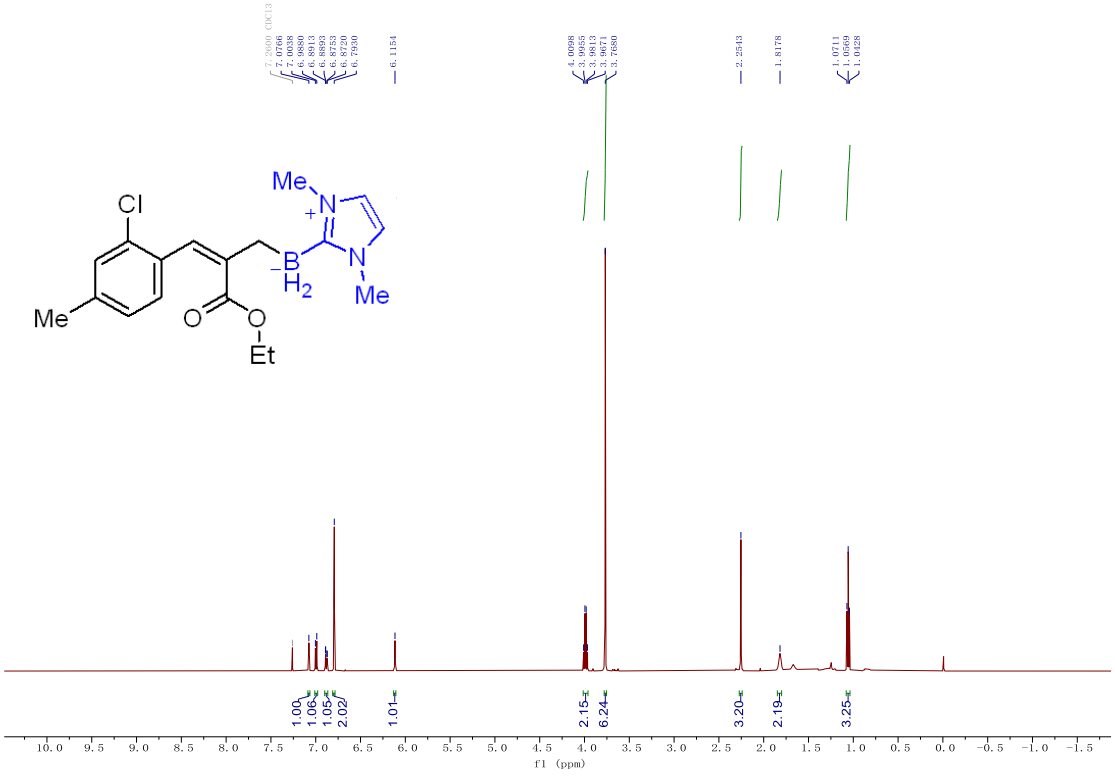
f1 (ppm)


22.6601
F
Me
Me
B
H2
N
N
Me
O
O
Et
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)


F
Me
Me
N
+
B
H2
N
Me
O
O
Et
-118.4498
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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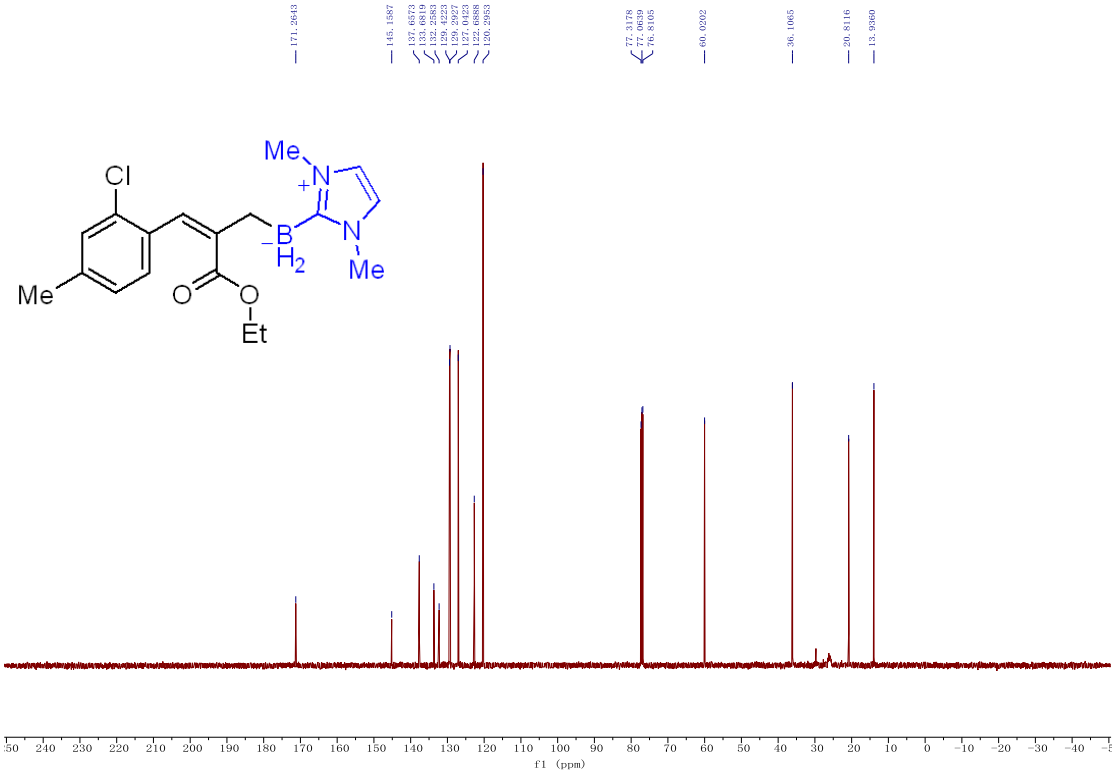
6.8720
6.7930
6.1154
4.0098
3.9955
3.9813
3.9671
3.7680
2.2543
1.8178
1.0711
1.0569
1.0428
Cl
Me
Me
N
+
B
H2
N
Me
O
O
Et
1.00
1.06
1.05
2.02
1.01
2.15
6.24
3.20
2.19
3.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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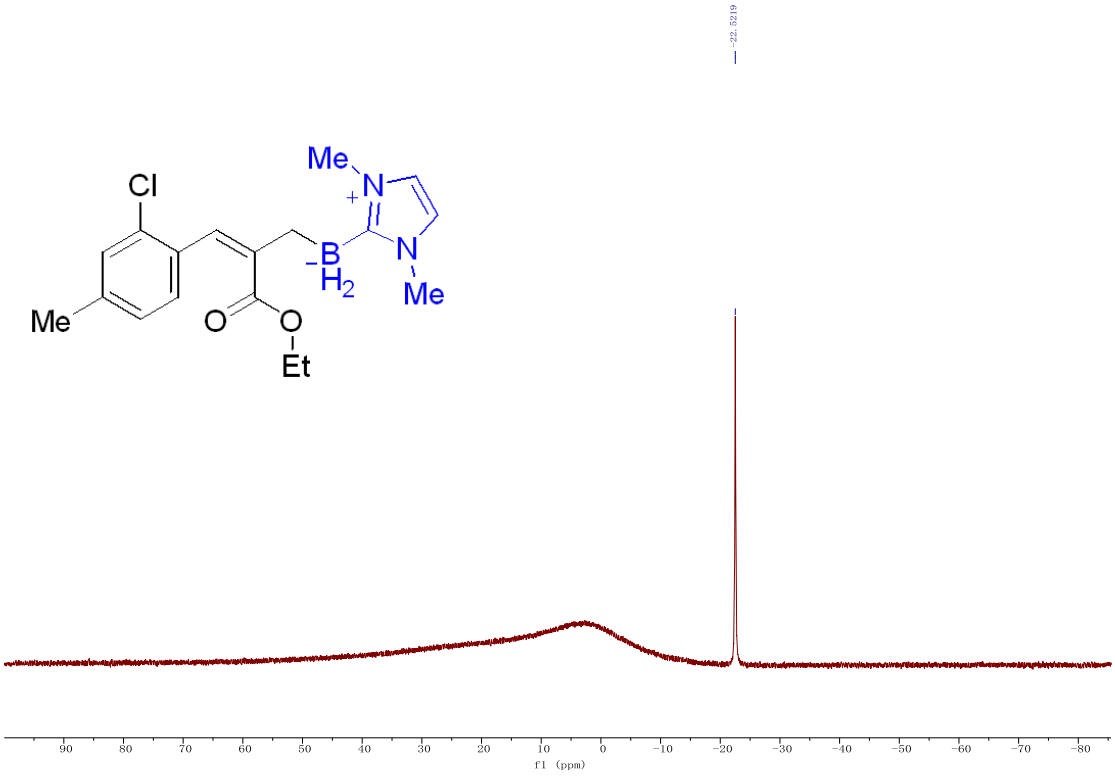
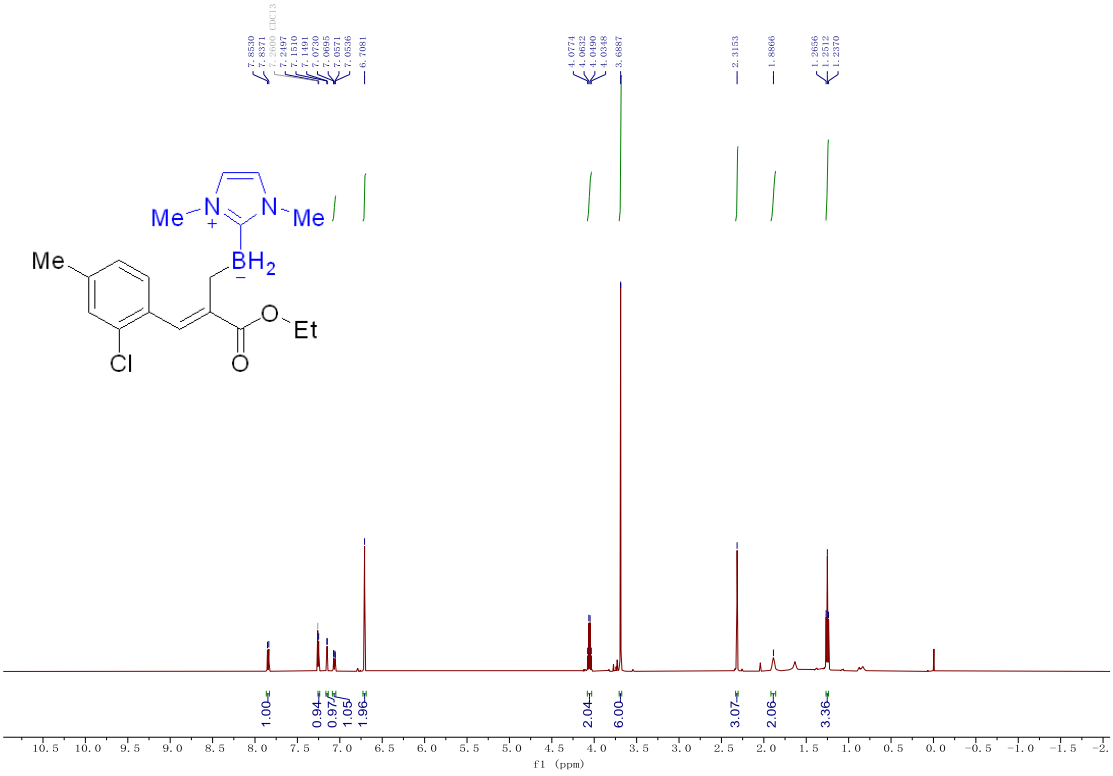
132.2585
129.4223
129.2927
127.0423
125.8988
120.2953
77.3178
77.0639
76.8105
60.0202
36.1065
20.8116
13.9360
Cl
Me
O
O
Et
Me
N
+
B
H2
N
Me
f1 (ppm)


22.5219
Cl
Me
O
O
Et
Me
N
+
B
H2
N
Me
f1 (ppm)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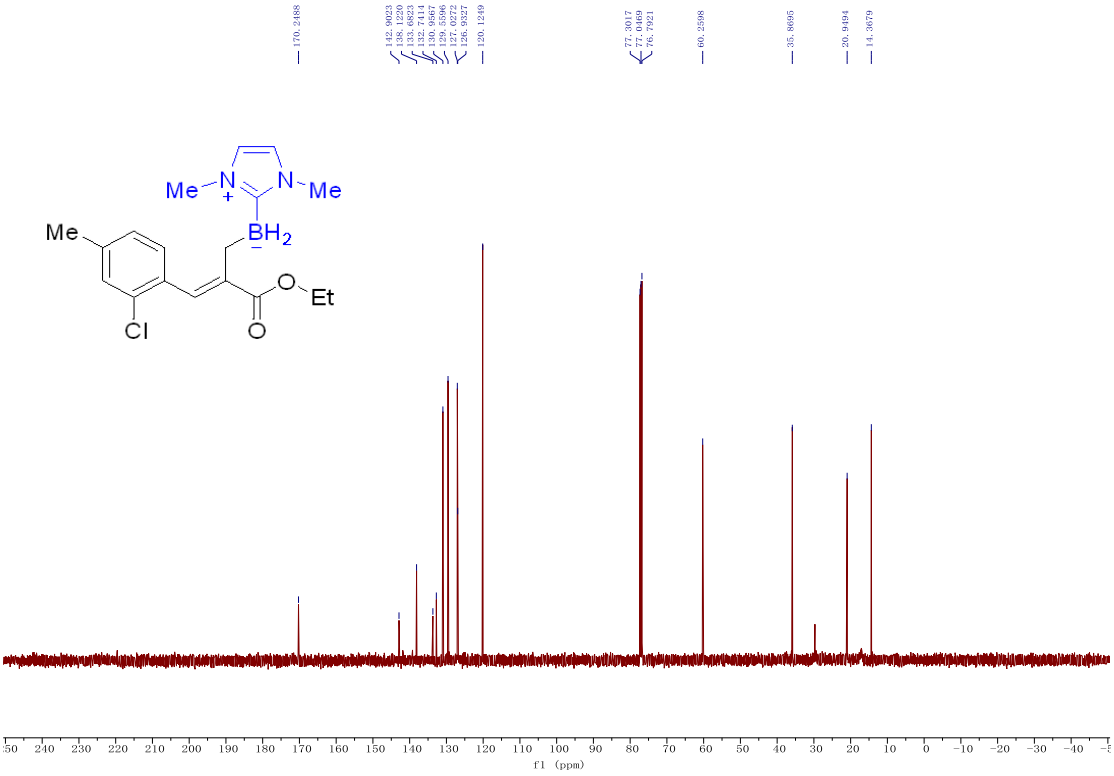
N
N
Me
BH2
Me
Cl
O
Et
O
f1 (ppm)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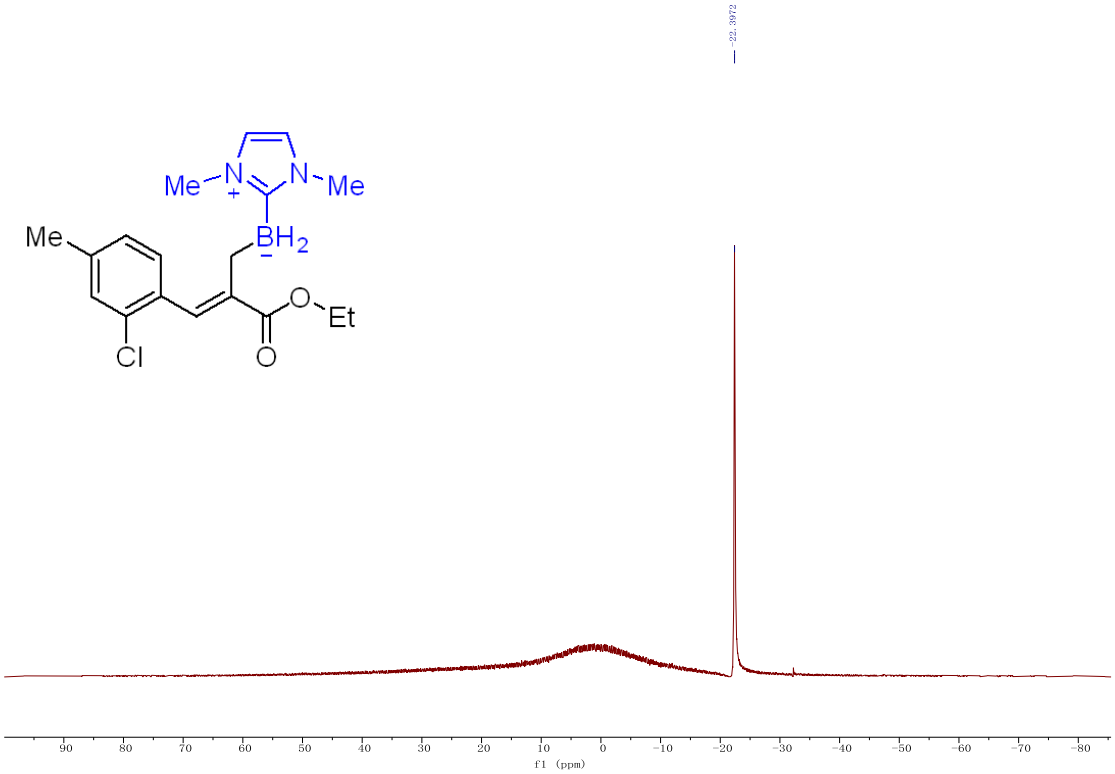
N
Me
BH2
Me
Cl
O
Et
O
f1 (ppm)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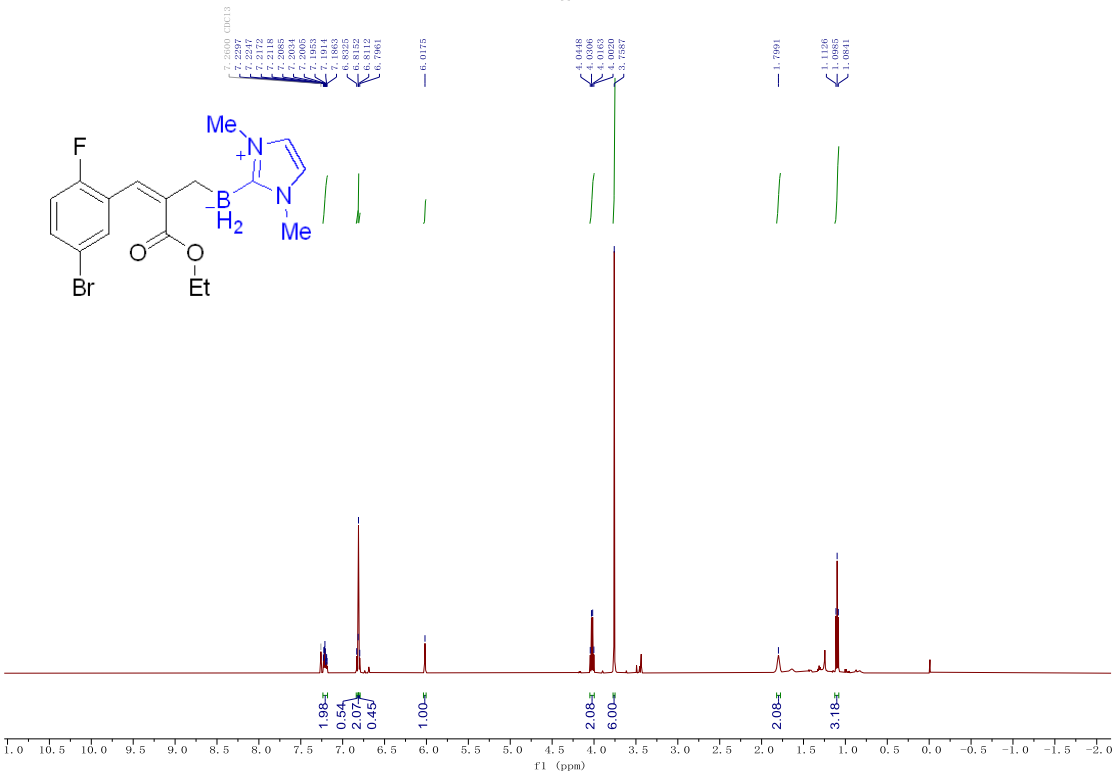
Me
BH2
Me
O
Et
Cl
O
-22.3972
f1 (ppm)


F
Me
N
B
H2
N
Me
O
O
Et
Br
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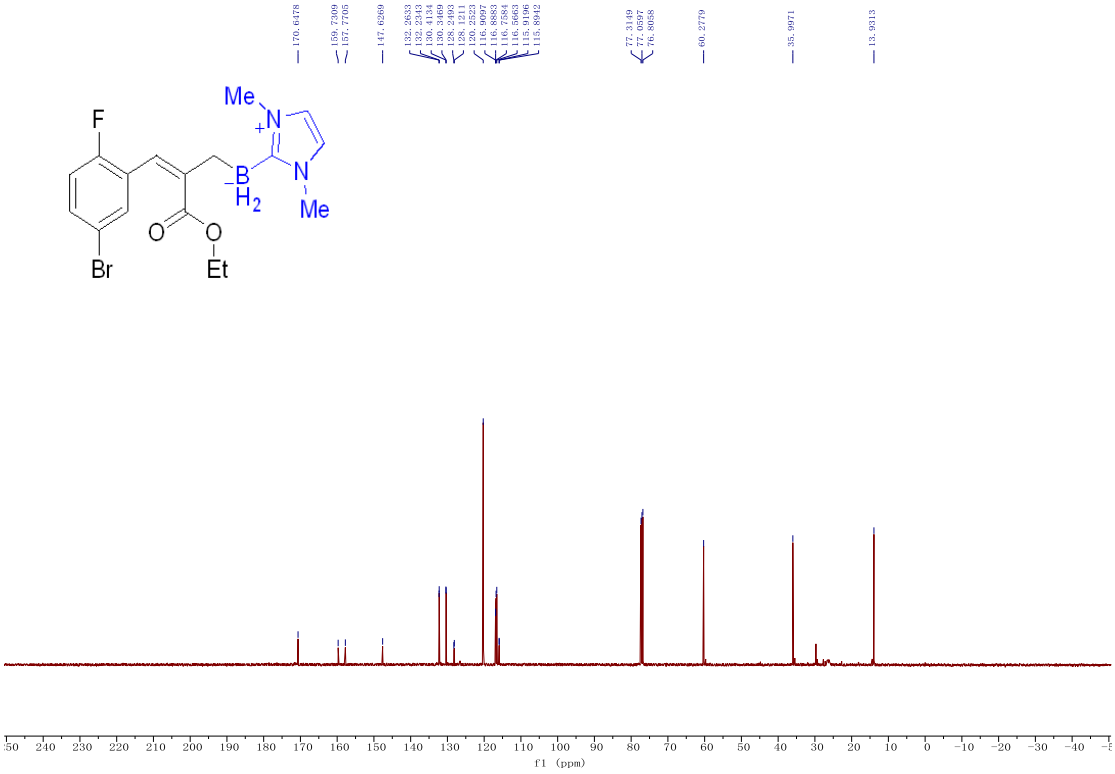
7.2297
7.2247
7.2172
7.2118
7.2085
7.2034
7.2005
7.1953
7.1914
7.1863
6.8325
6.8152
6.8012
6.7981
6.0175
4.0448
4.0306
4.0163
4.0020
3.7587
1.7991
1.1126
1.0985
1.0841
1.98
0.54
2.07
0.45
1.00
2.08
6.00
2.08
3.18
f1 (ppm)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128.1111
120.2523
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116.8883
116.7564
116.5663
115.9196
115.8942
77.3149
77.0597
76.8058
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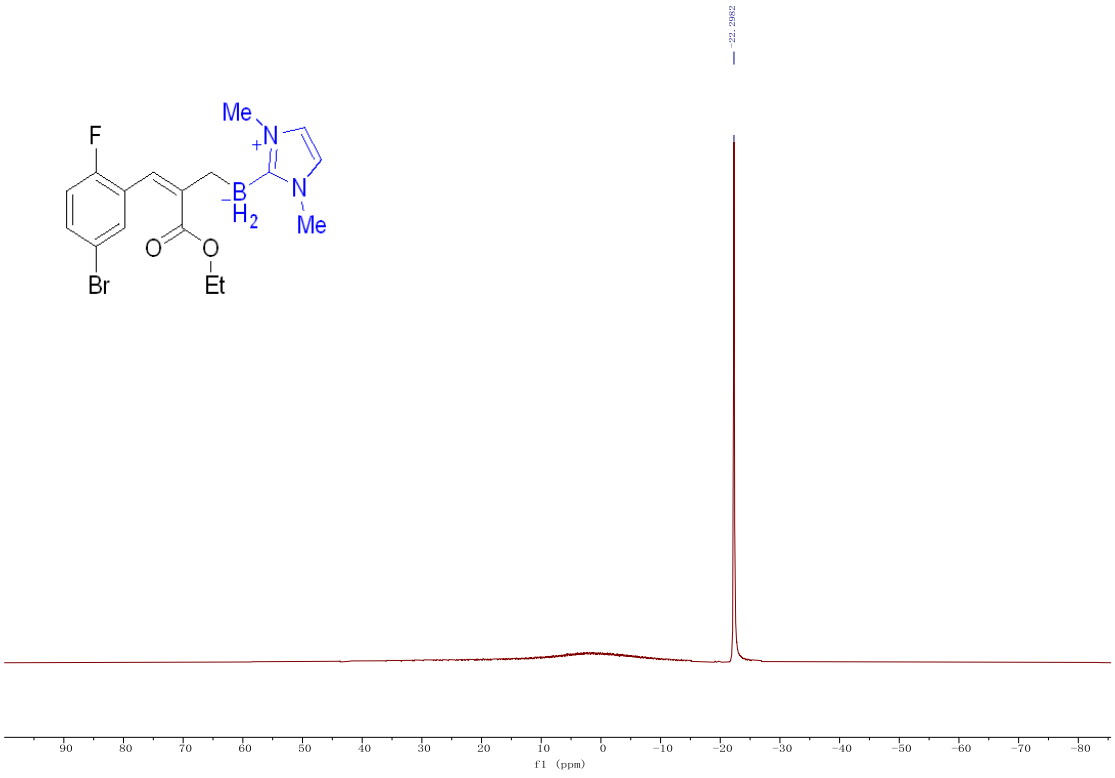
13.9313
F
Me
N
B
H2
N
Me
O
O
Et
Br
f1 (ppm)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Me
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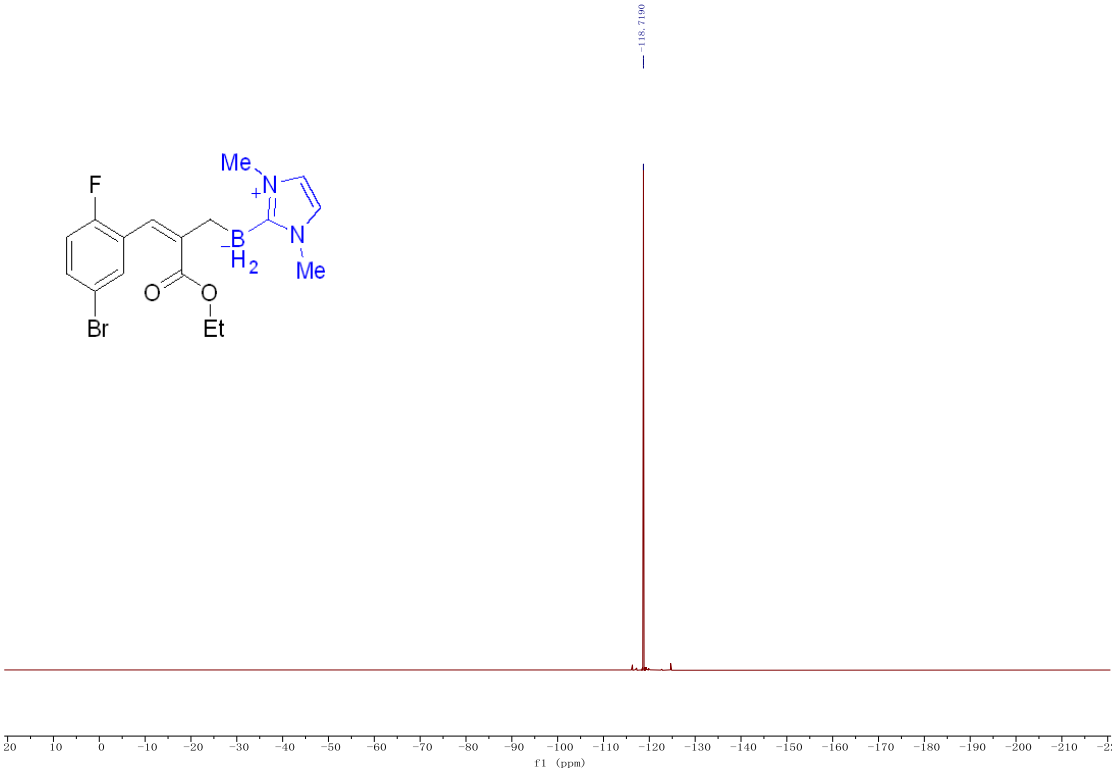
B
H2
N
Me
O
O
Et
Br
f1 (ppm)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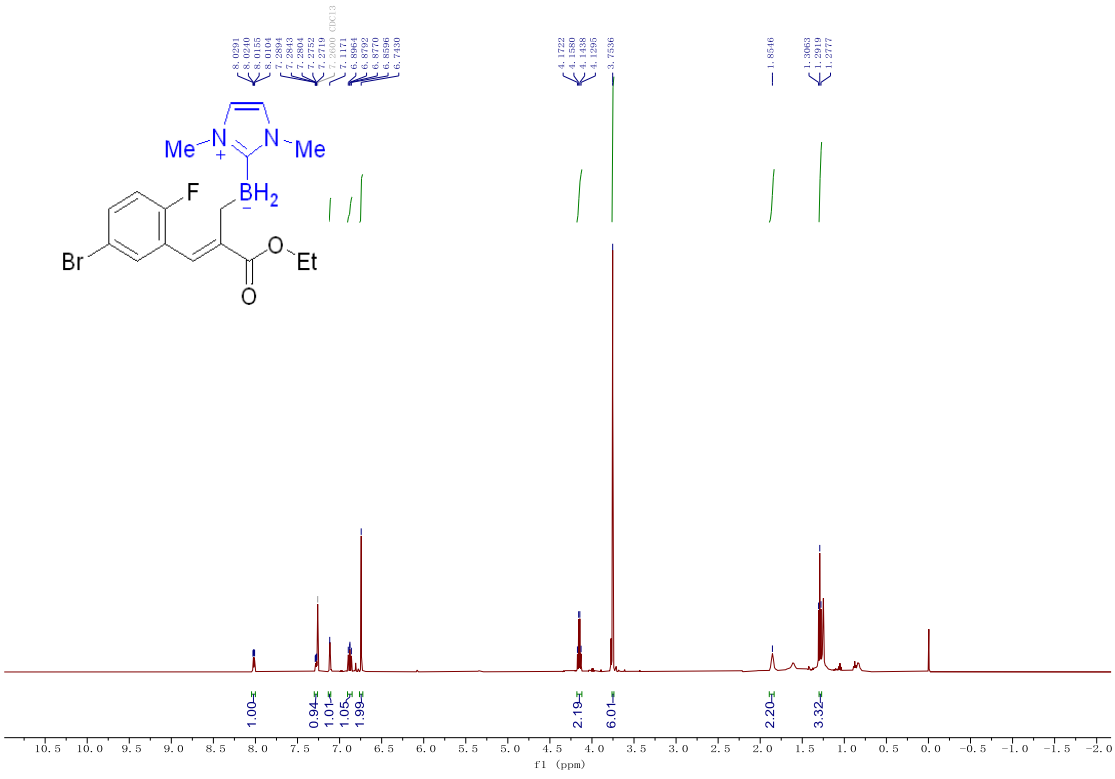
N
+
F
B
H2
N
Me
O
O
Br
Et
f1 (ppm)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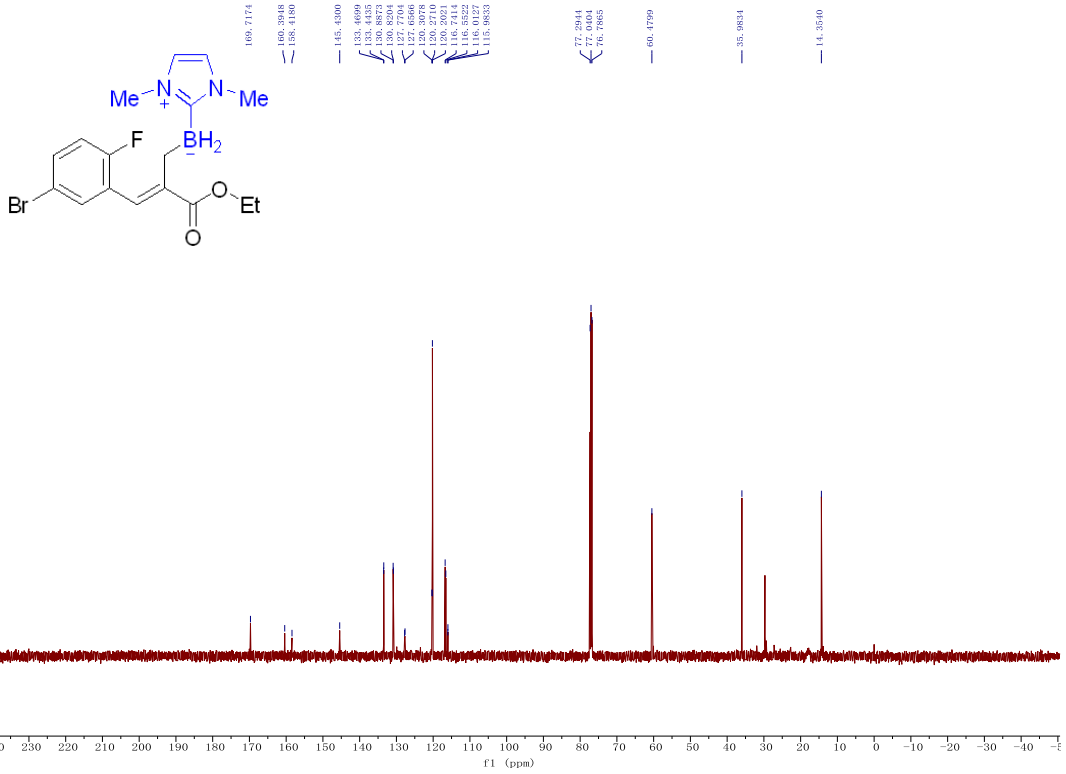
8.0240
8.0155
8.0104
7.2994
7.2843
7.2804
7.2752
7.2710
7.2660 CDCl3
7.1171
6.8964
6.8770
6.8596
6.7430
4.1722
4.1589
4.1438
4.1295
3.7536
1.8546
1.3063
1.2919
1.2777
Me
N
+
N
Me
F
BH2
Br
O
Et
O
1.00
0.94
1.01
1.05
1.99
2.19
6.01
2.20
3.32
f1 (ppm)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148.4300
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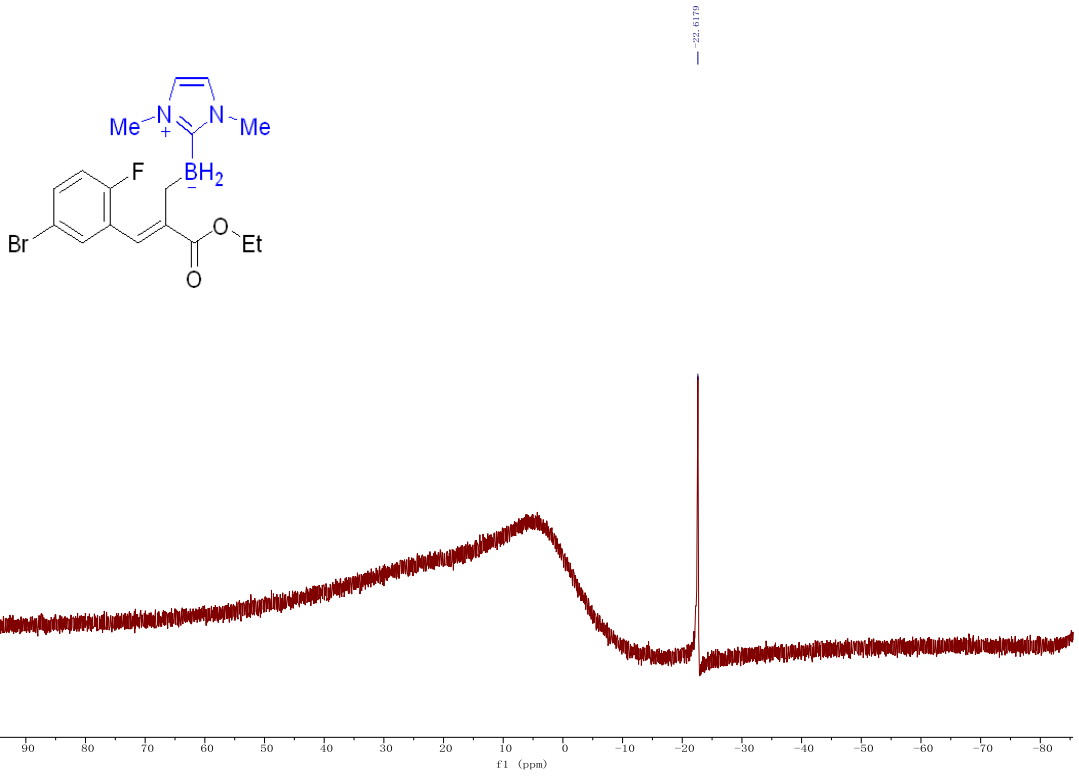
130.8873
130.8204
127.7704
127.6946
120.3078
120.2710
120.2021
116.5714
116.5322
116.0127
115.9833
77.2944
77.0404
76.7865
60.4799
35.9834
14.3540
Me
N
N
Me
BH2
F
Br
O
Et
O
f1 (ppm)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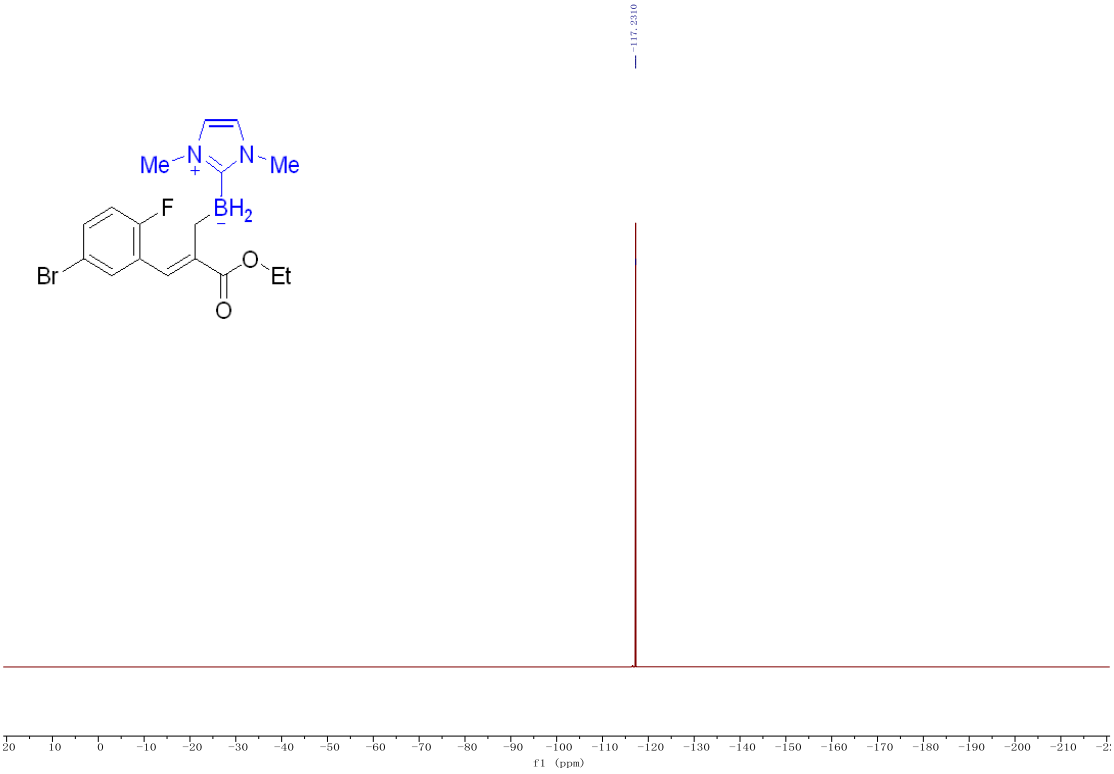
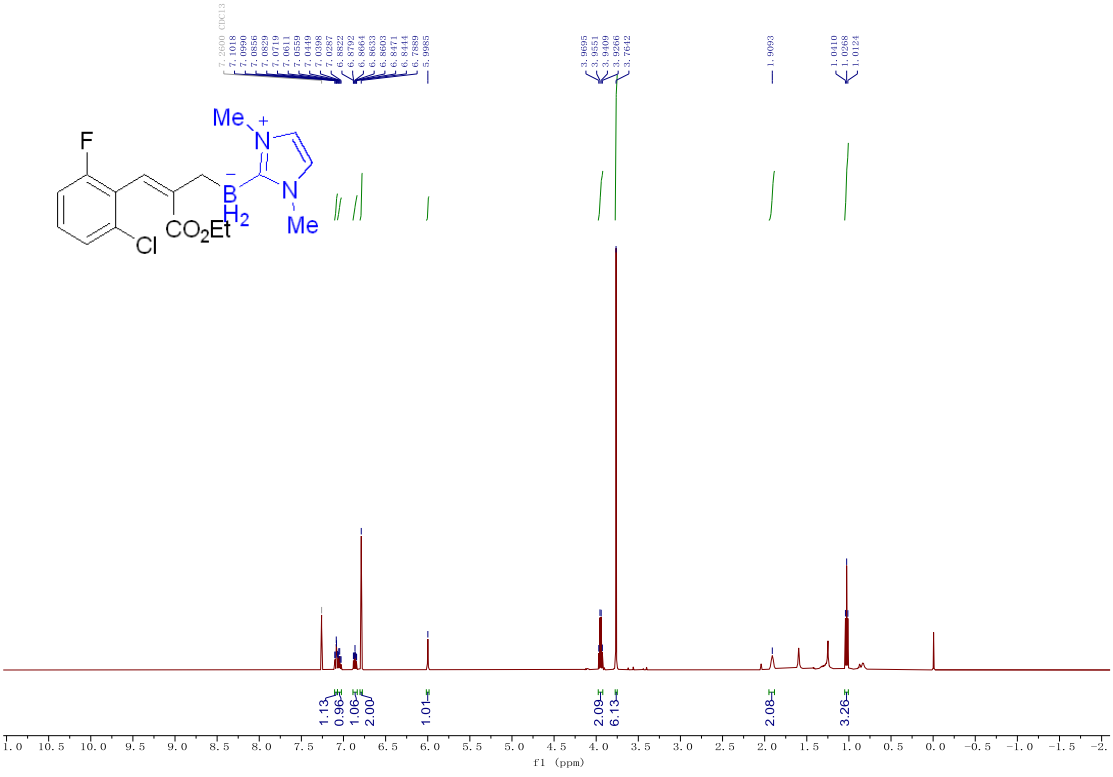
N
N
Me
BH2
F
Br
O
Et
O
f1 (ppm)


-117.2310
Me
N
N
Me
F
BH2
Br
O
Et
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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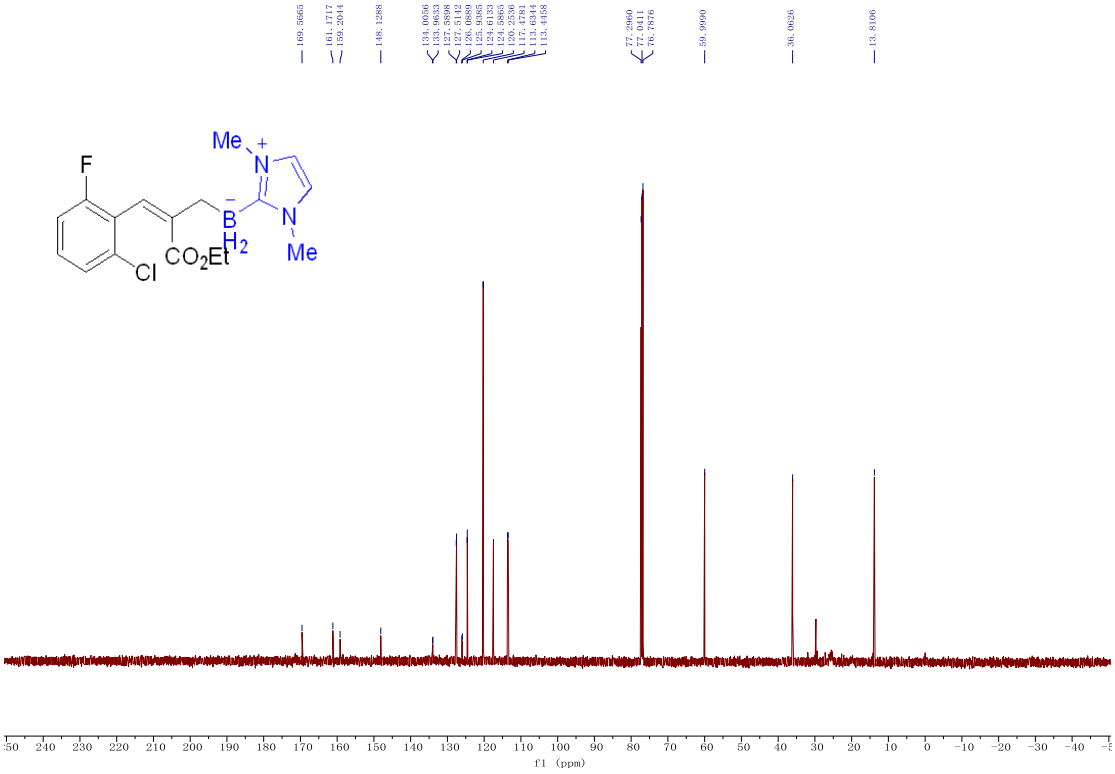
7.0539
7.0449
7.0398
7.0287
6.8822
6.8797
6.8664
6.8633
6.8603
6.8471
6.8444
6.7889
5.9985
3.9695
3.9551
3.9409
3.9266
3.7642
1.9693
1.0410
1.0268
1.0124
Me
N
F
B
H2
N
Me
CO2Et
Cl
1.13
0.96
1.06
2.00
1.01
2.09
6.13
2.08
3.26
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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127.5898
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126.0889
125.9385
124.6135
124.5865
120.2536
117.4781
115.6544
113.4458
77.2960
77.0411
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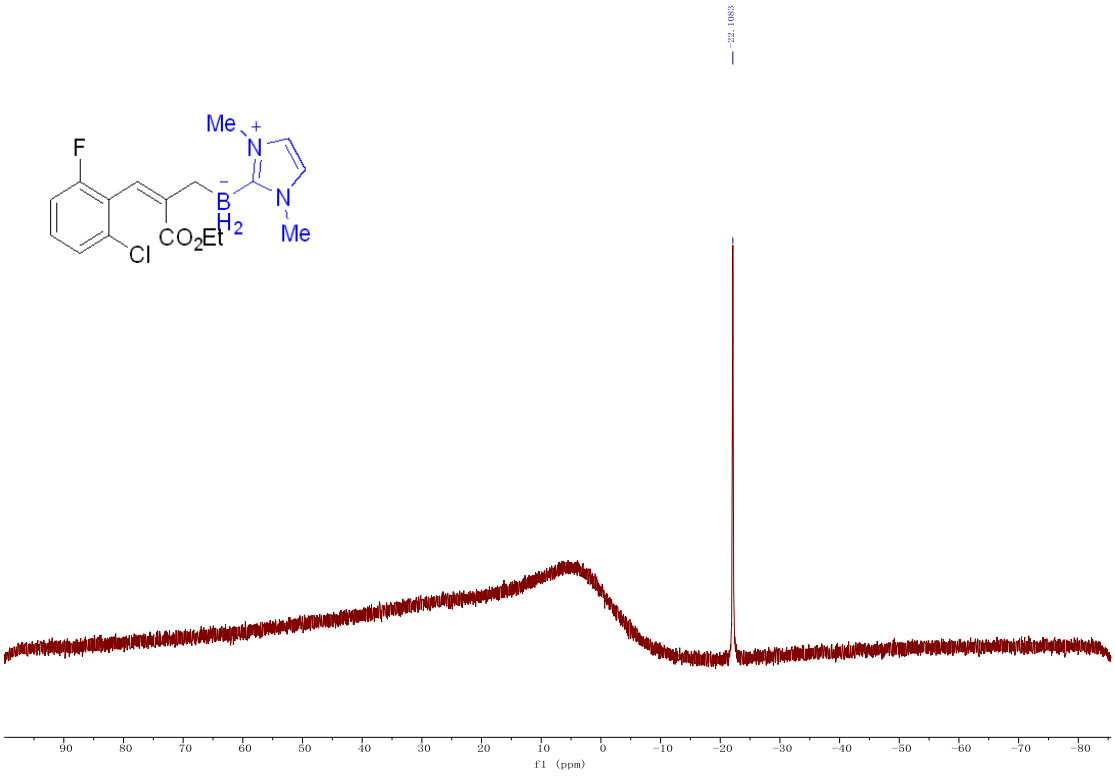
59.9990
36.0626
13.8106
Me
N
F
B
H2
N
Me
CO2Et
Cl
f1 (ppm)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N
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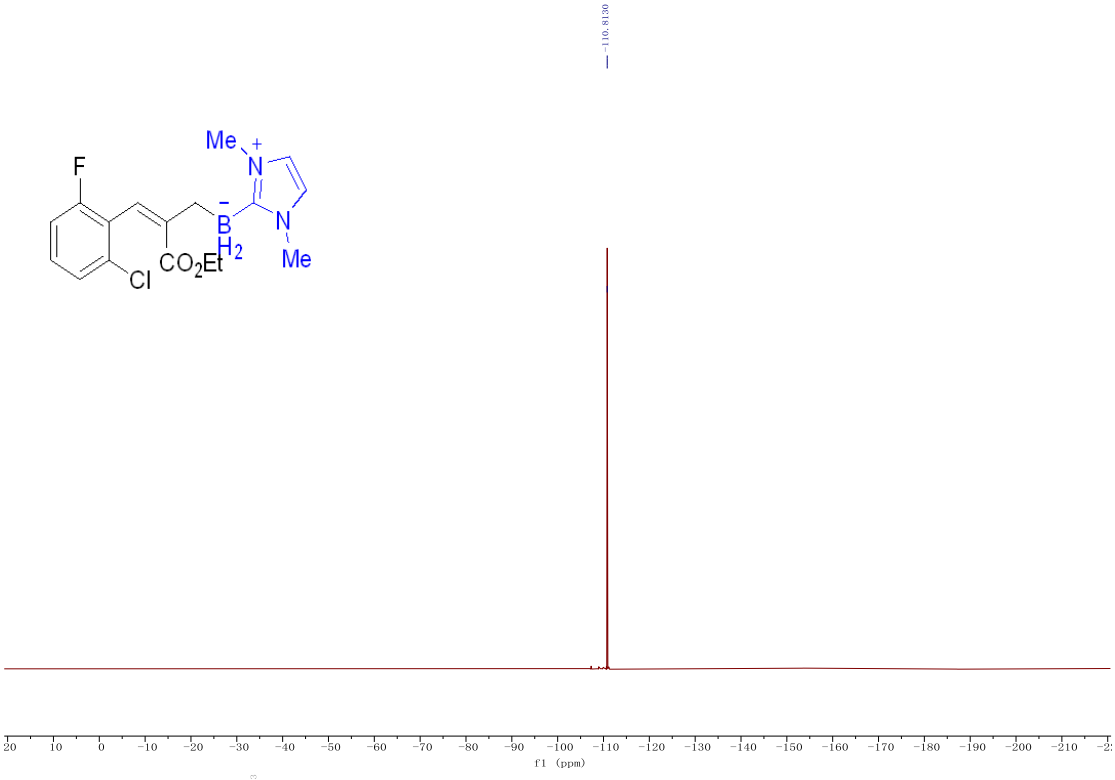
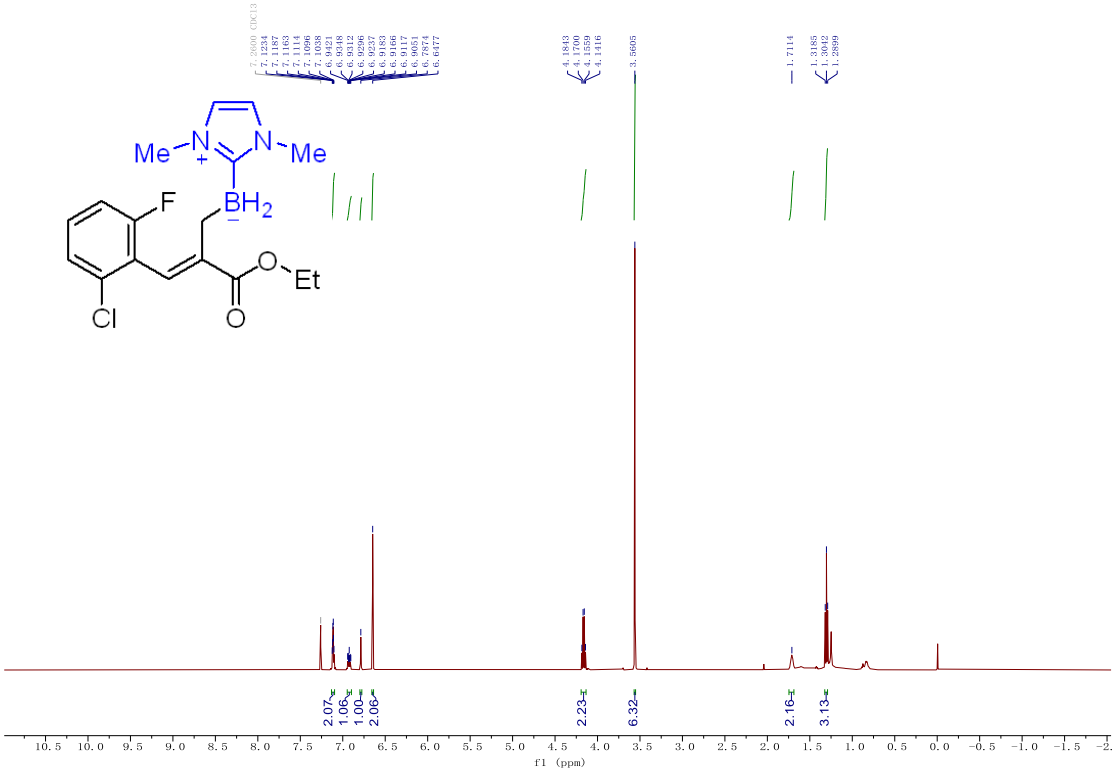
B
H2
N
Me
CO2Et
Cl
f1 (ppm)


-110.8130
f1 (ppm)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7.1144
7.1096
7.1038
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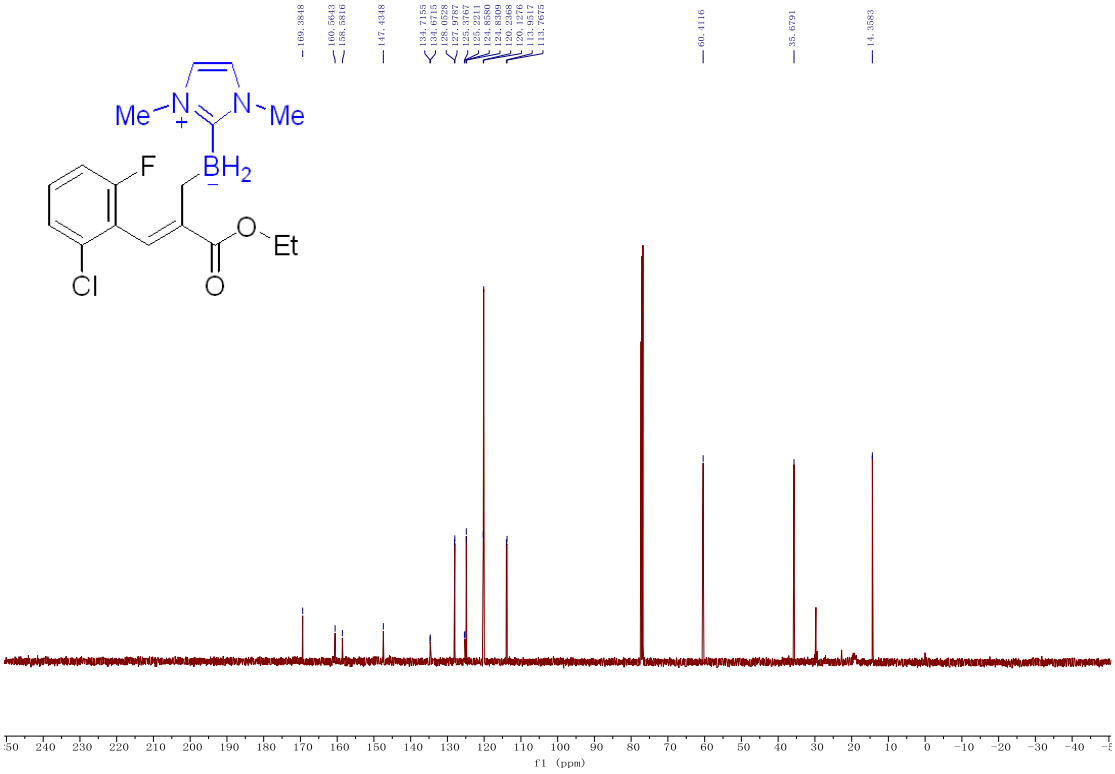
6.9348
6.9312
6.9296
6.9237
6.9183
6.9166
6.9146
6.9117
6.9051
6.7874
6.6477
4.1843
4.1730
4.1559
4.1416
3.5605
1.7114
1.3185
1.3042
1.2899
2.07
1.06
1.00
2.06
2.23
6.32
2.16
3.13
f1 (ppm)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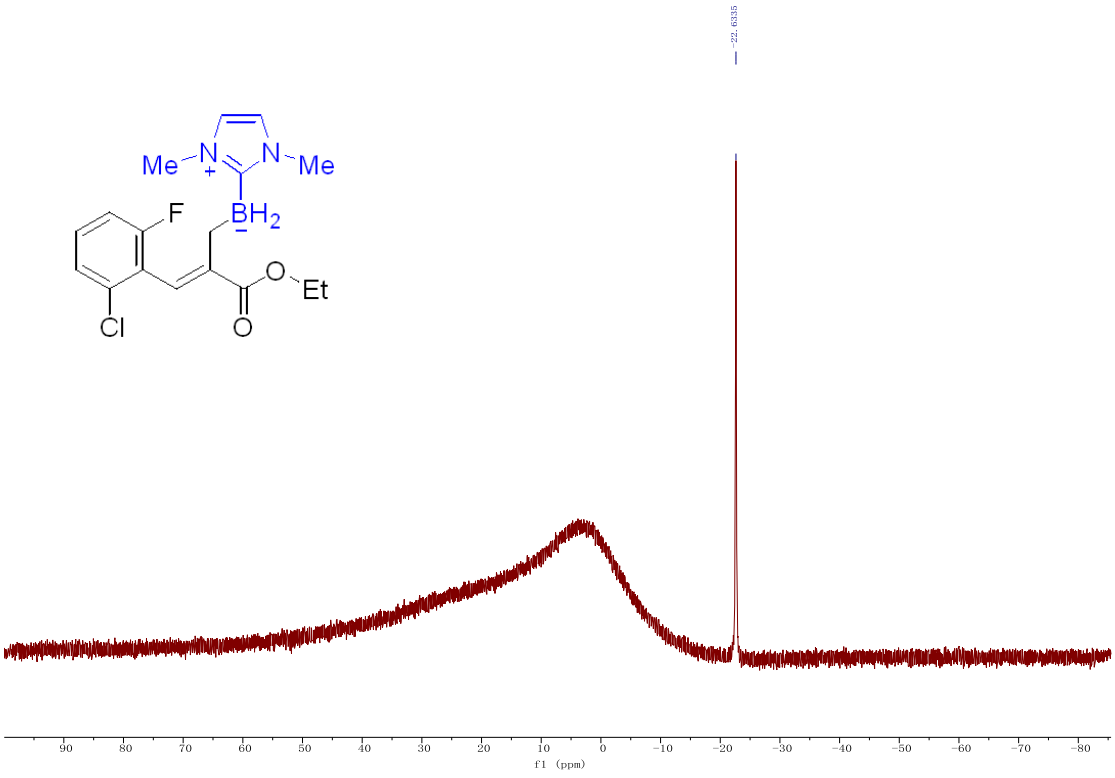
128.0528
127.9787
125.3767
125.2711
124.8580
124.8309
120.2368
119.1787
113.9517
113.7675
60.4116
35.6791
14.3583
Me
N
N
Me
BH2
F
Cl
O
Et
O
f1 (ppm)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Et
O
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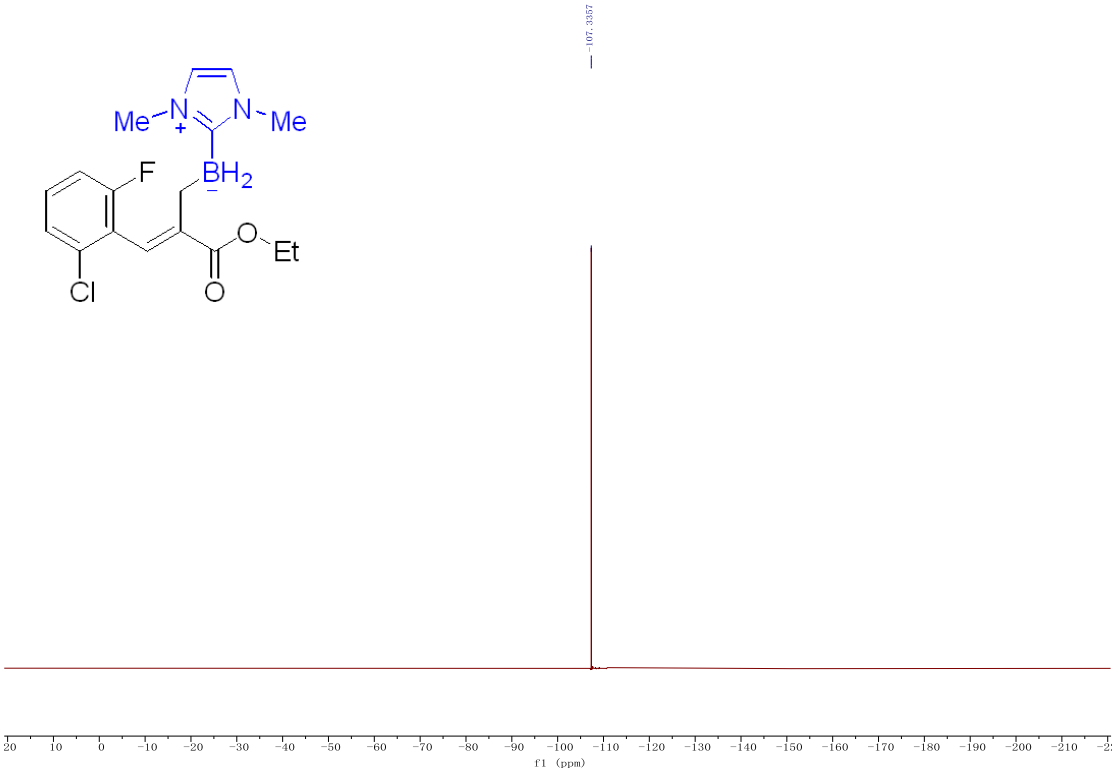
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Me
F
BH2
O
Et
Cl
O
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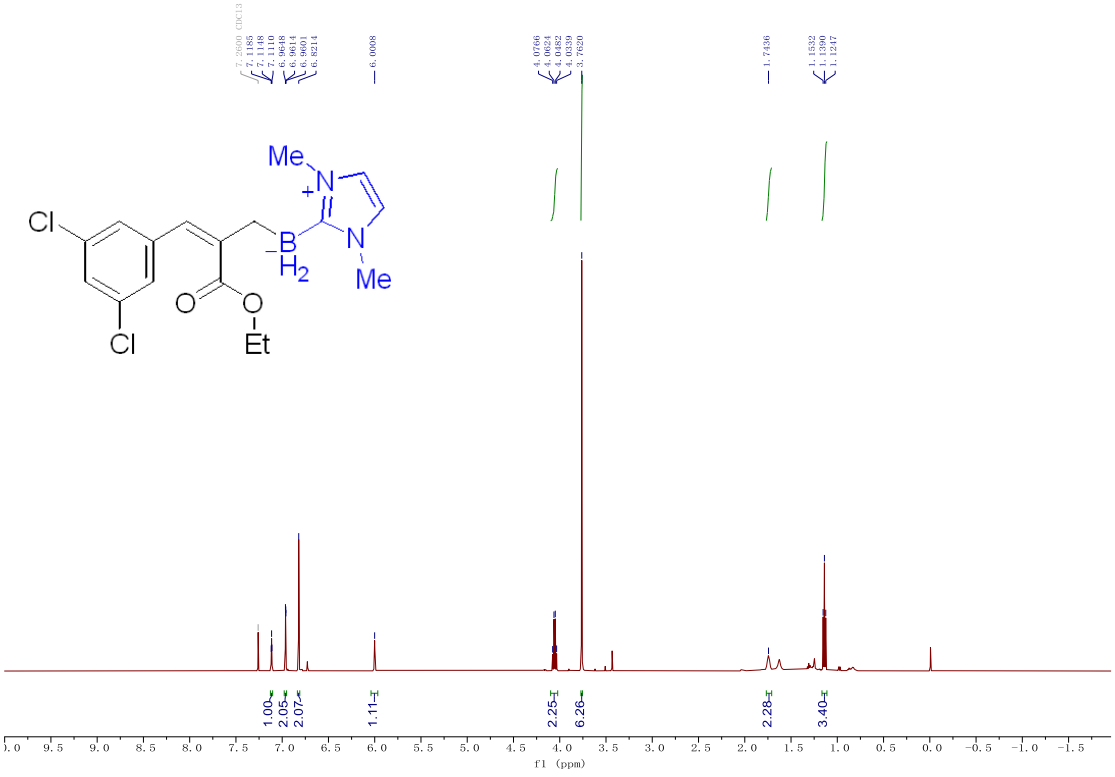
f1 (ppm)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N
+
Cl
B
H2
N
Me
Cl
O
O
Et
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6.9648
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6.8214
6.0008
4.0766
4.0684
4.0482
4.0339
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1.7436
1.1532
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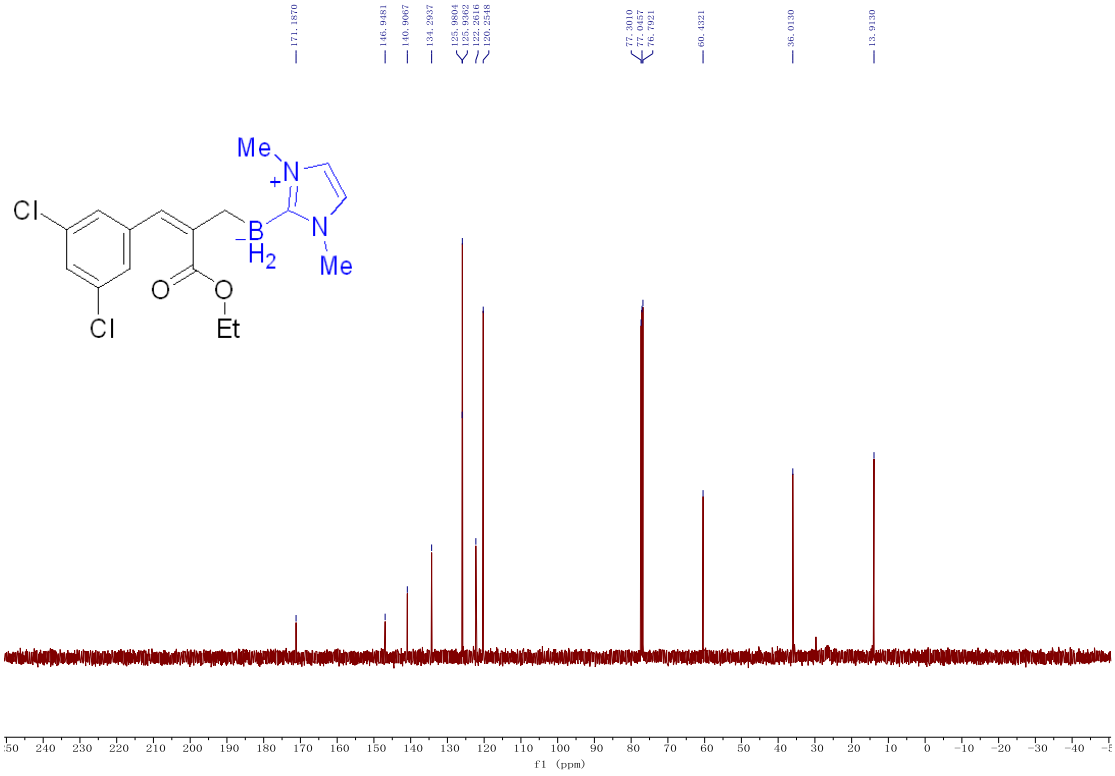
1.11
2.25
6.26
2.28
3.40
f1 (ppm)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76.7921
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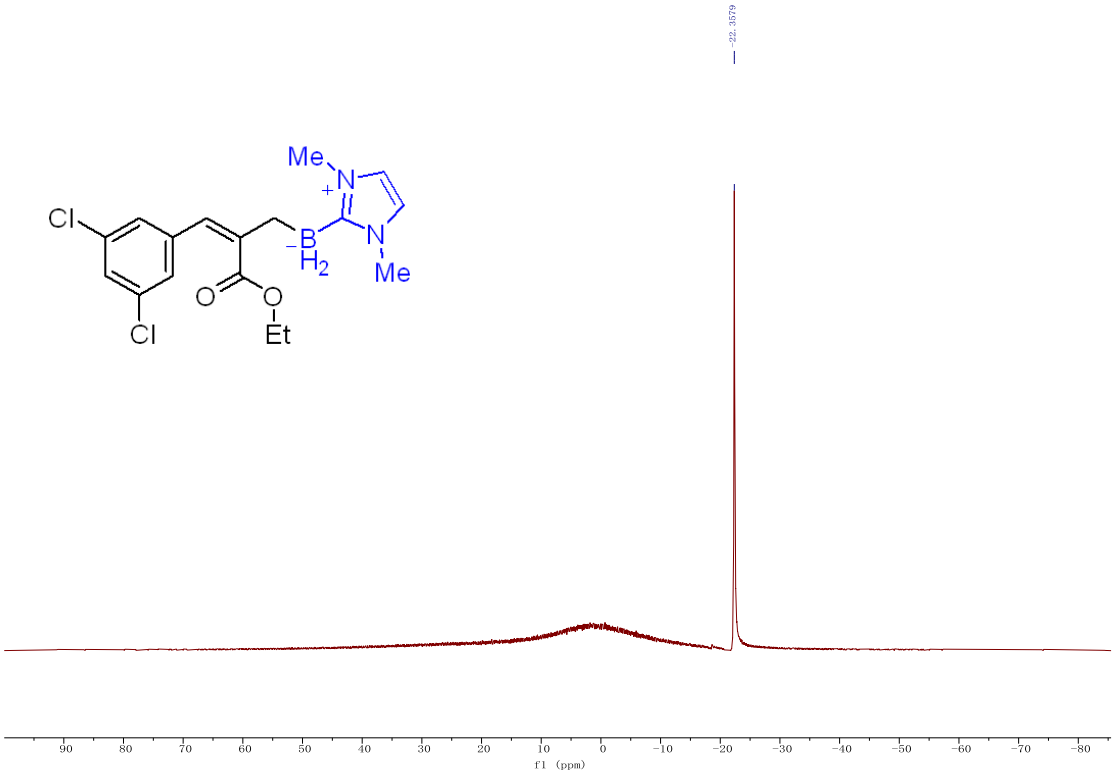
36.0130
13.9130
Me
N
+
B
H2
N
Me
Cl
Cl
O
O
Et
f1 (ppm)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Me
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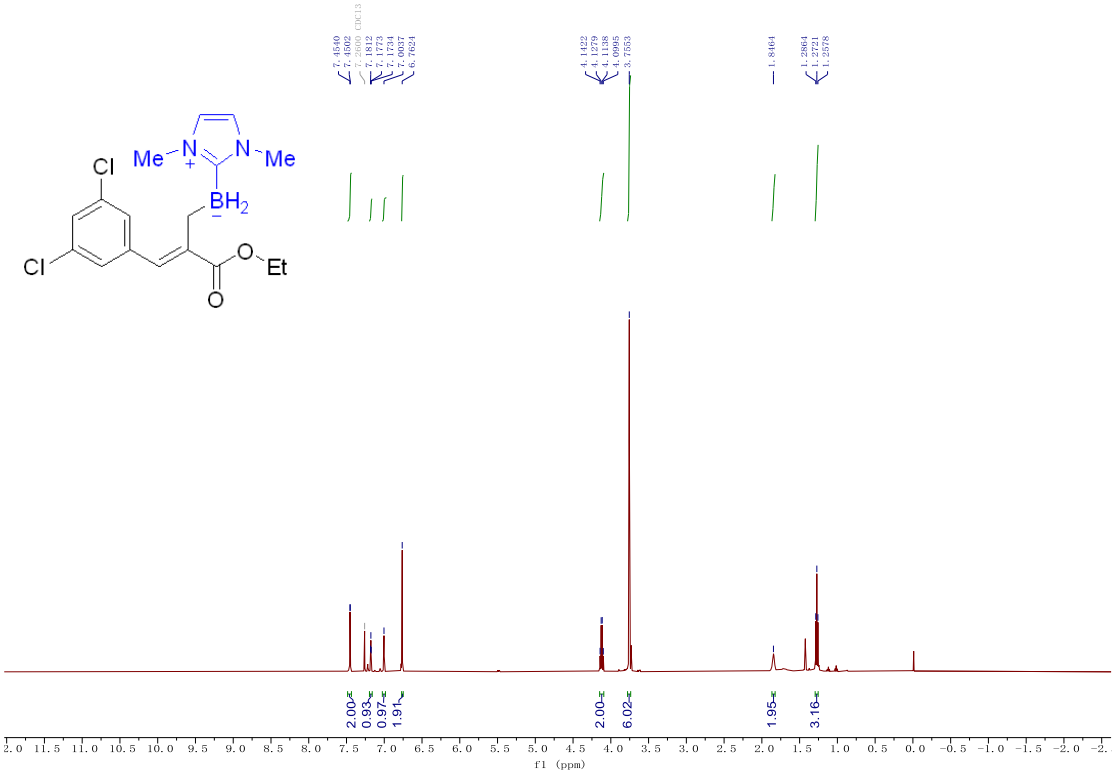
Cl
O
O
Et
f1 (ppm)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7.1779
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6.7624
4.1422
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1.8464
1.2864
1.2721
1.2578
Me
N
N
Me
BH2
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0.97
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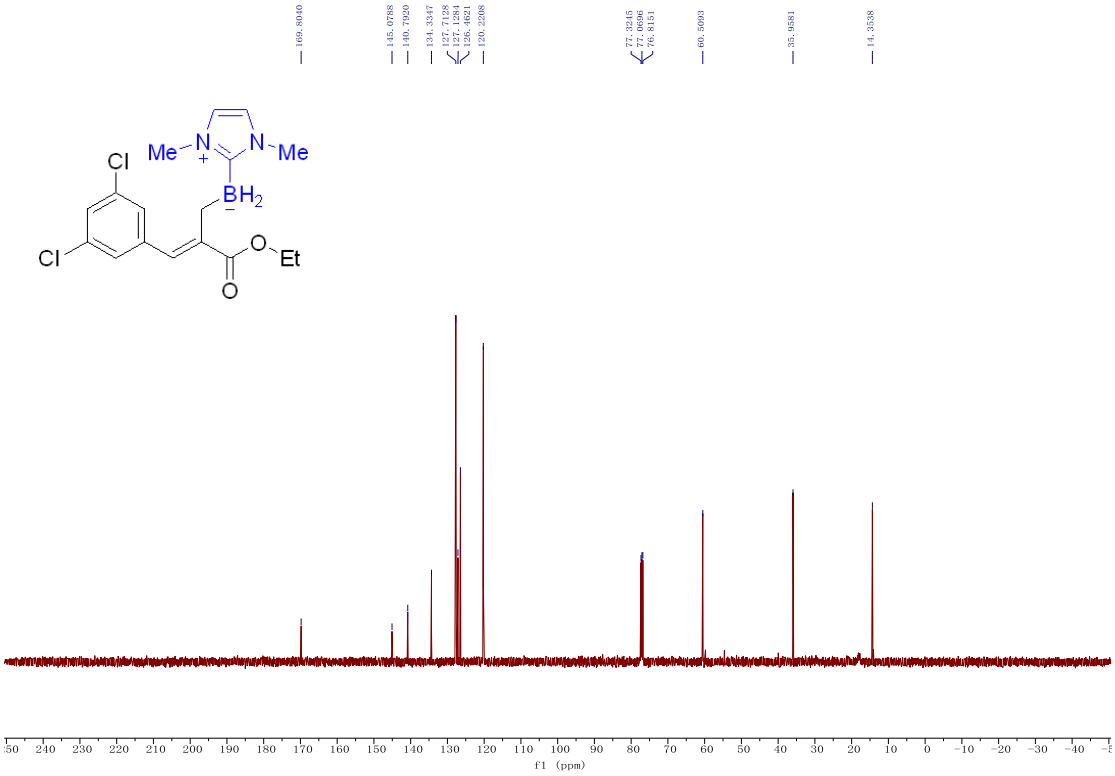
2.00
6.02
1.95
3.16
f1 (ppm)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126.4621
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14.3538
Me
N
N
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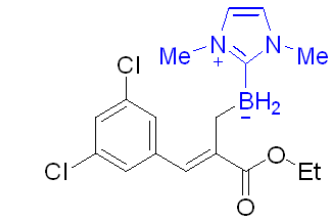
BH2
Cl
Cl
O
Et
O
f1 (ppm)


Cl
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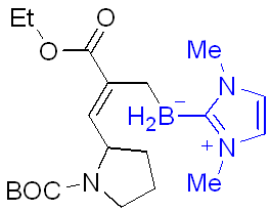
N
Me
BH2
Cl
O
Et
O

-22.7210
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)


Et
O
O
Me
N
H2B
N
Me
BOC
N

7.2600 CDCl3
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6.1392
6.1211
4.6120
3.9535
3.9483
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3.9320
3.9249
3.9176
3.9104
3.7336
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1.7071
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1.6831
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1.1455
1.1412
1.1270
2.00
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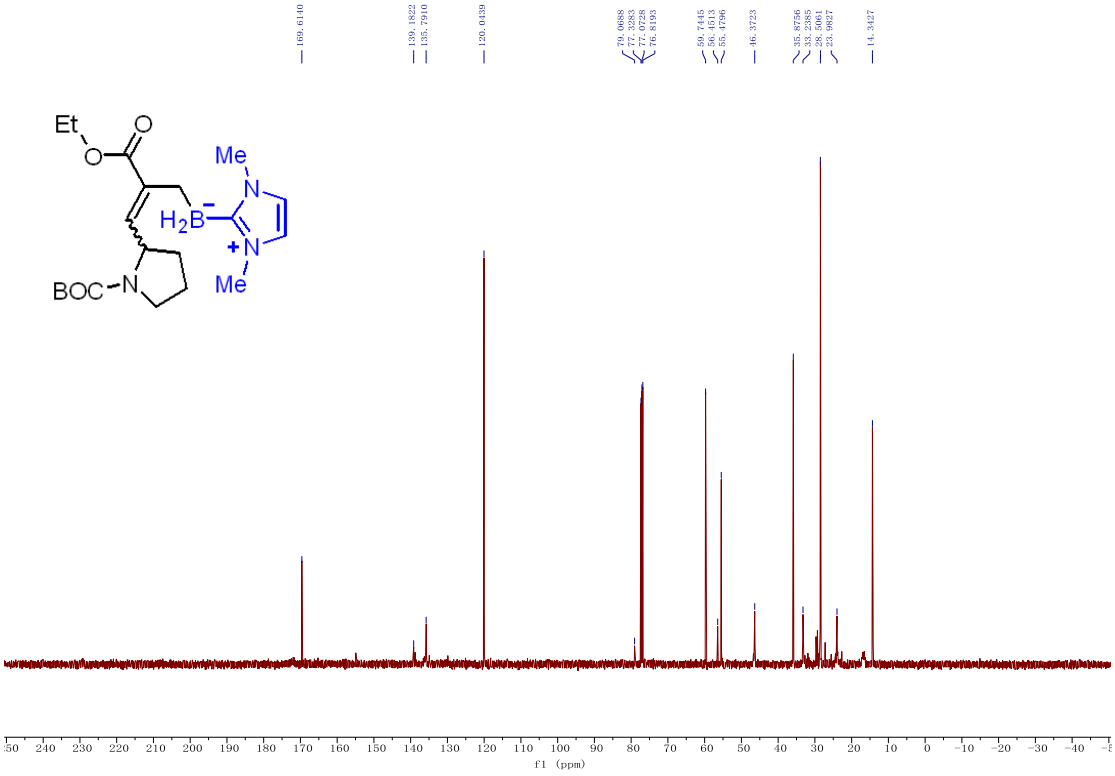
1.02
2.11
6.11
1.22
0.94
1.26
1.33
2.04
9.07
2.93
f1 (ppm)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77.0728
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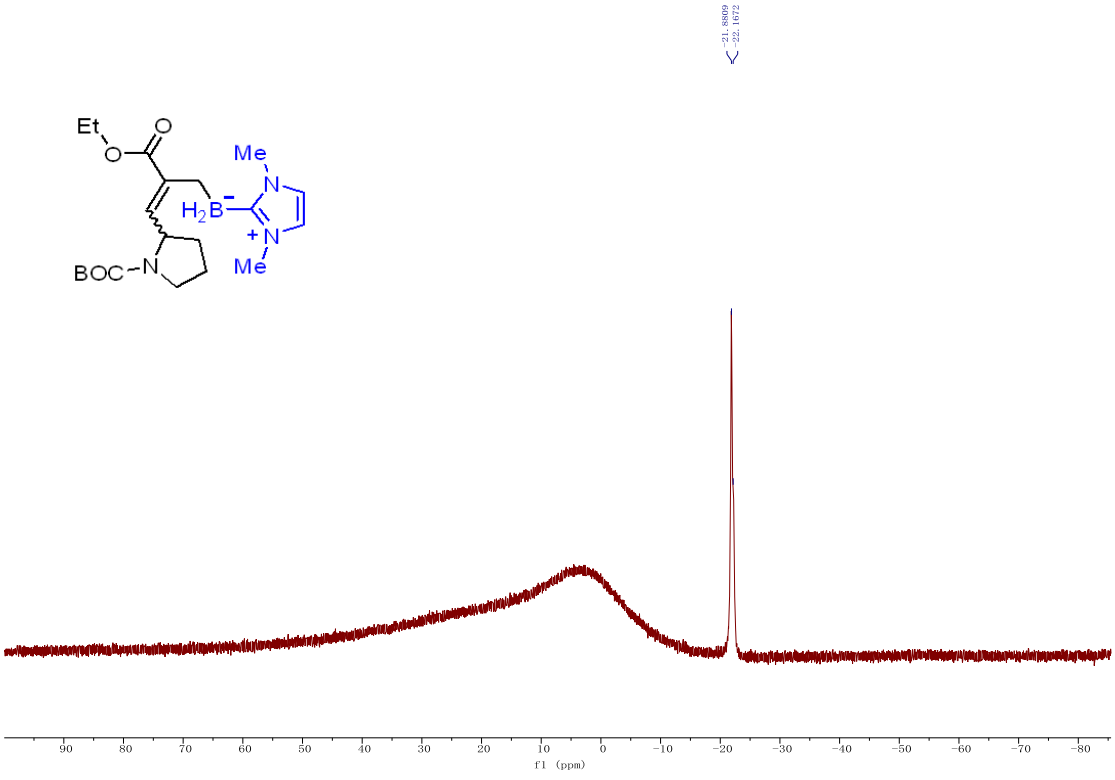
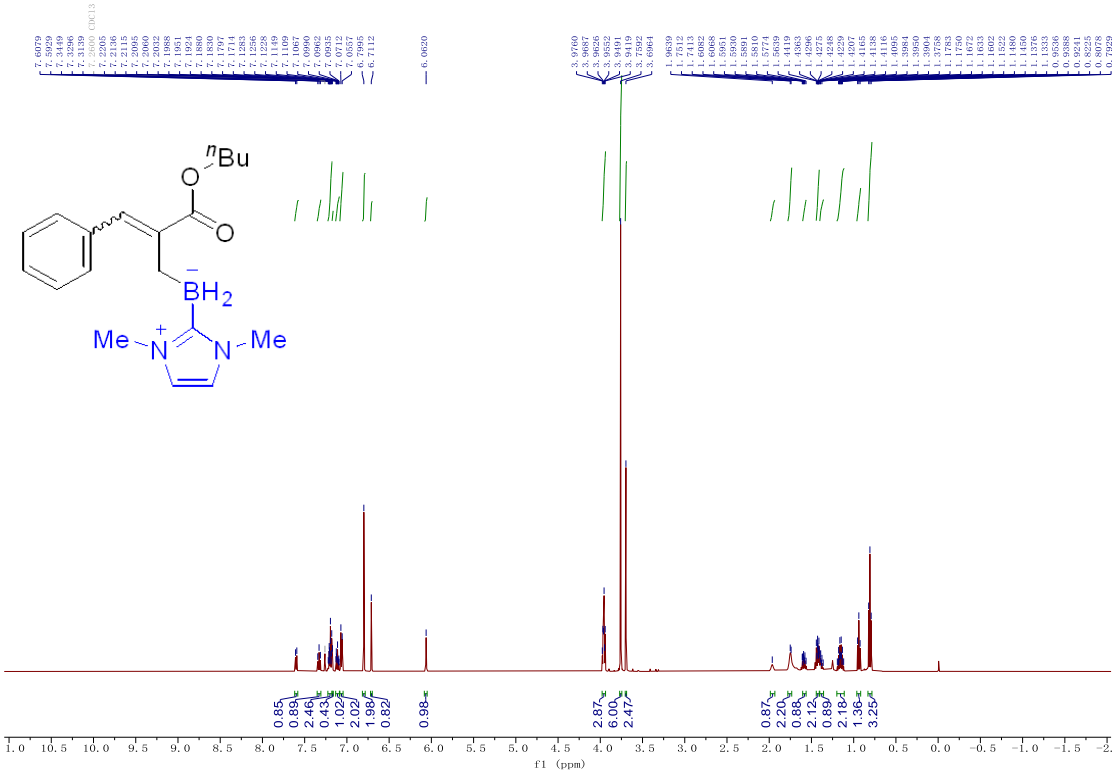
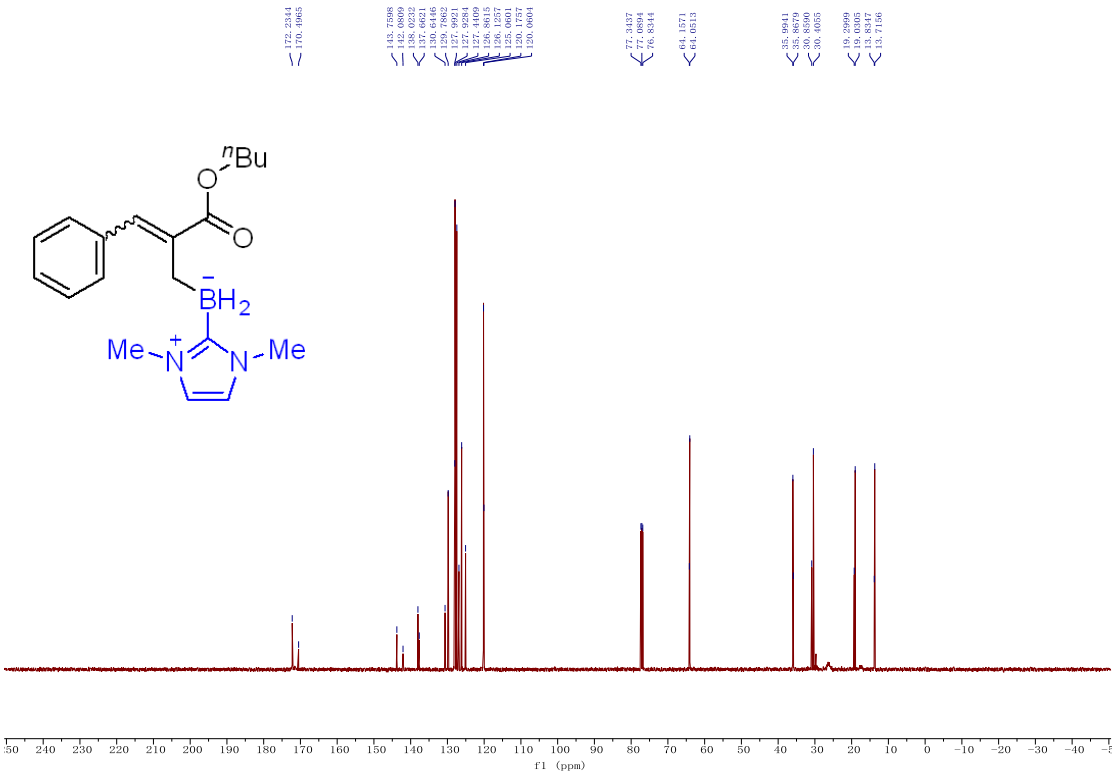
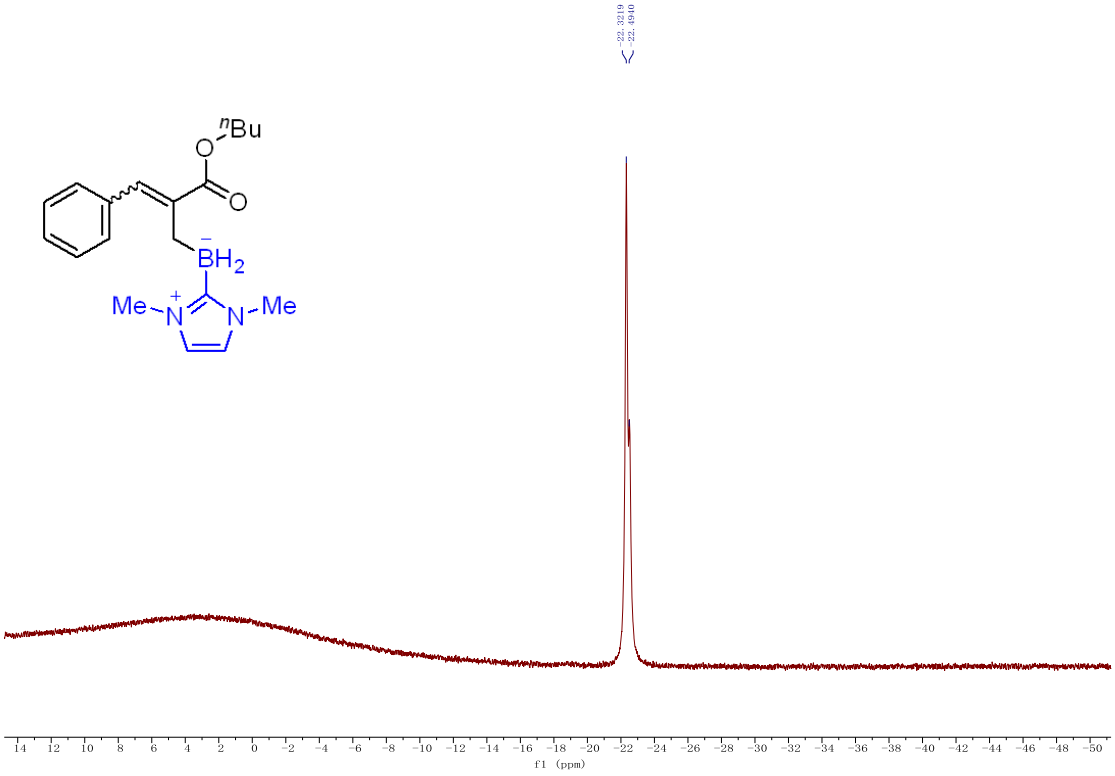
56.4513
55.4796
46.3723
35.8756
33.2385
28.5061
23.9827
14.3427
Et
O
O
Me
N
H2B
+N
Me
BOC
N
f1 (ppm)

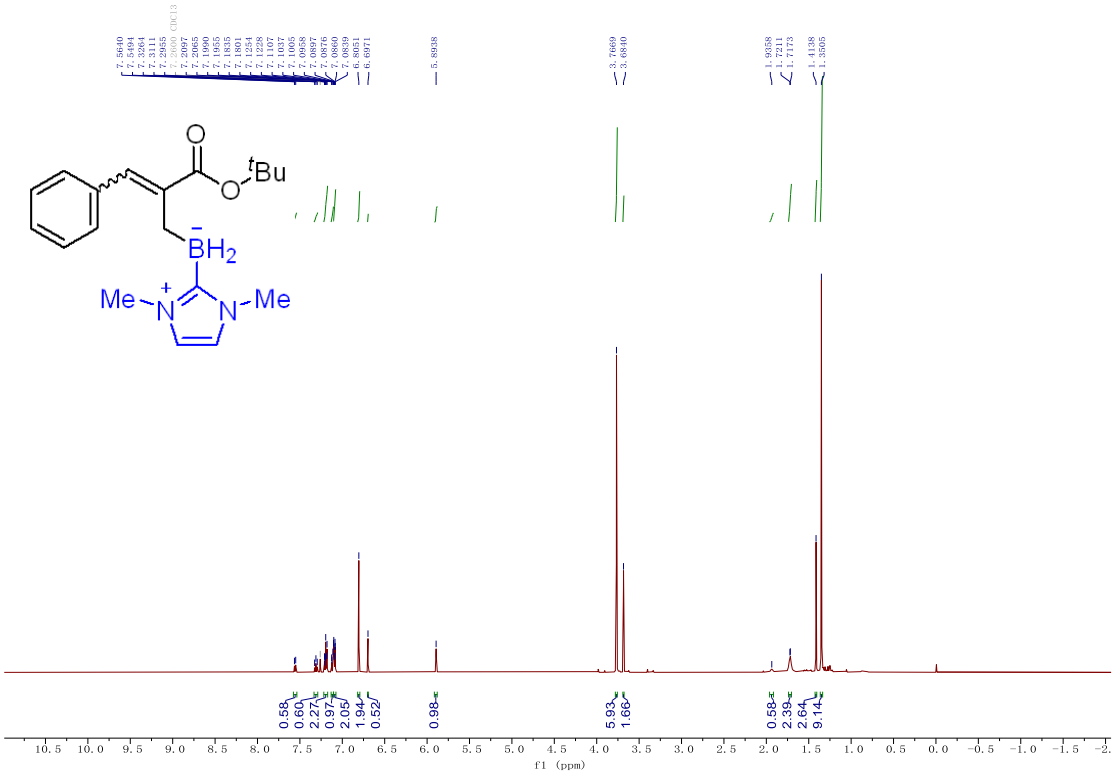

-21.8809
-22.1672
Et
O
O
Me
N
H2B
+N
Me
BOC
N
f1 (ppm)

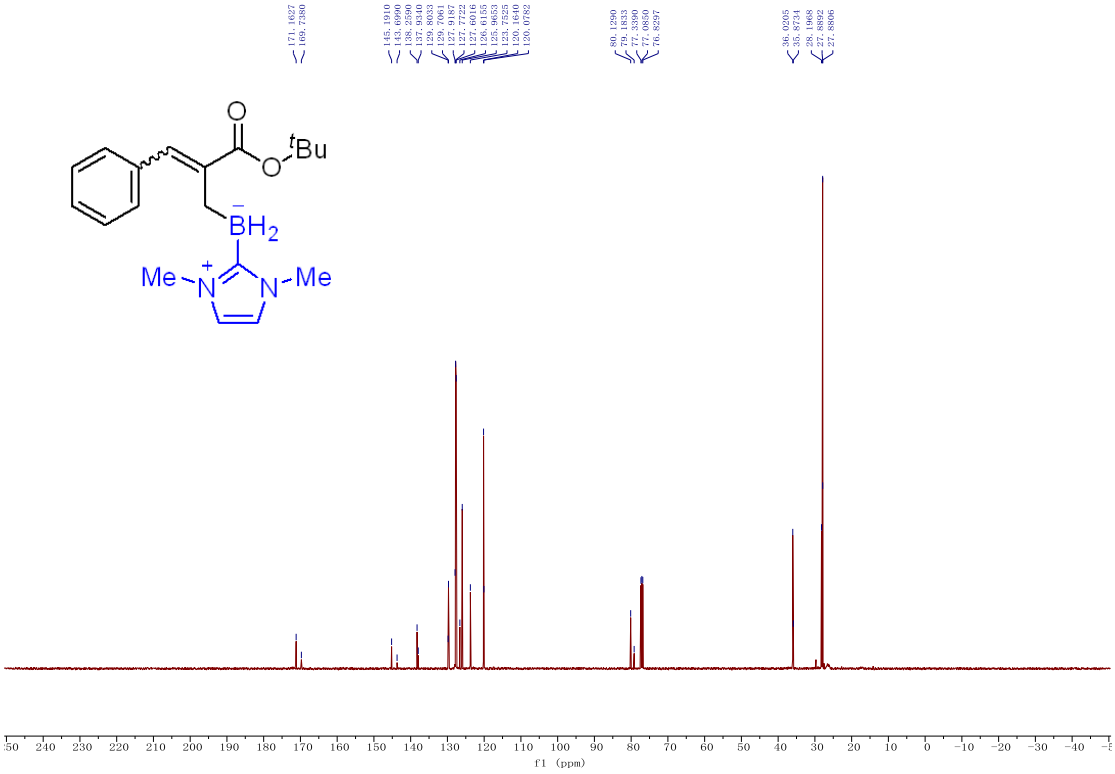

nBu
O
O
BH2
Me
N
N
Me

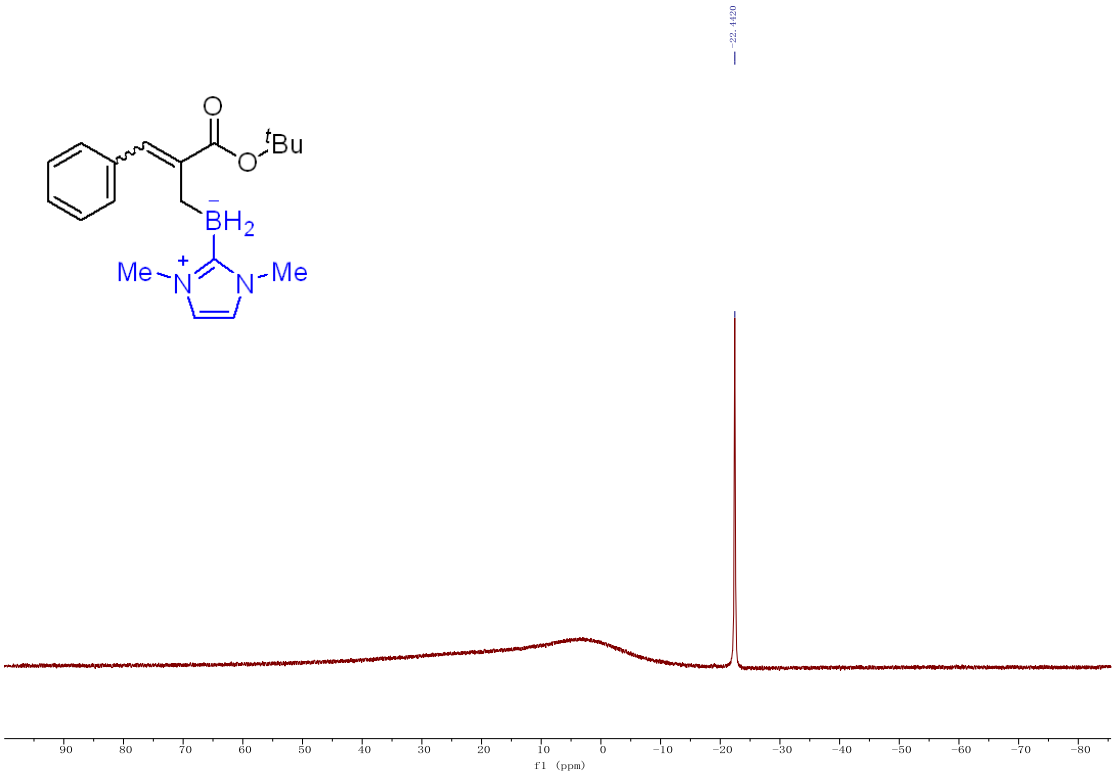

f1 (ppm)

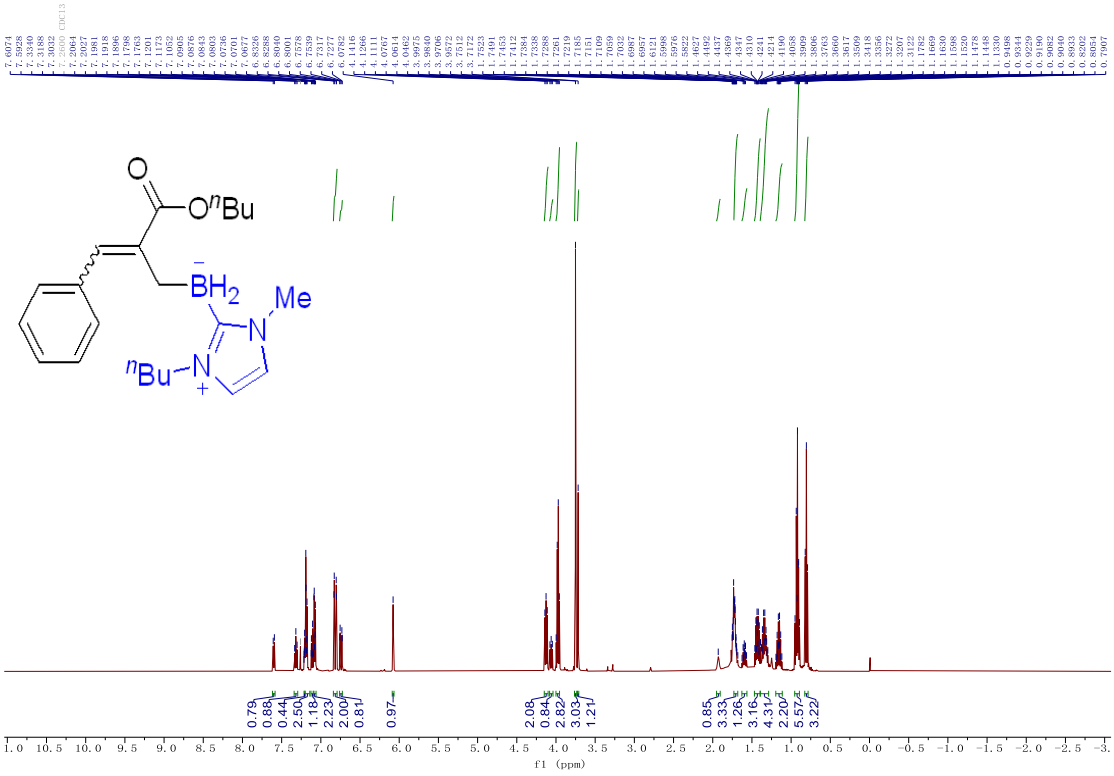
f1 (ppm)

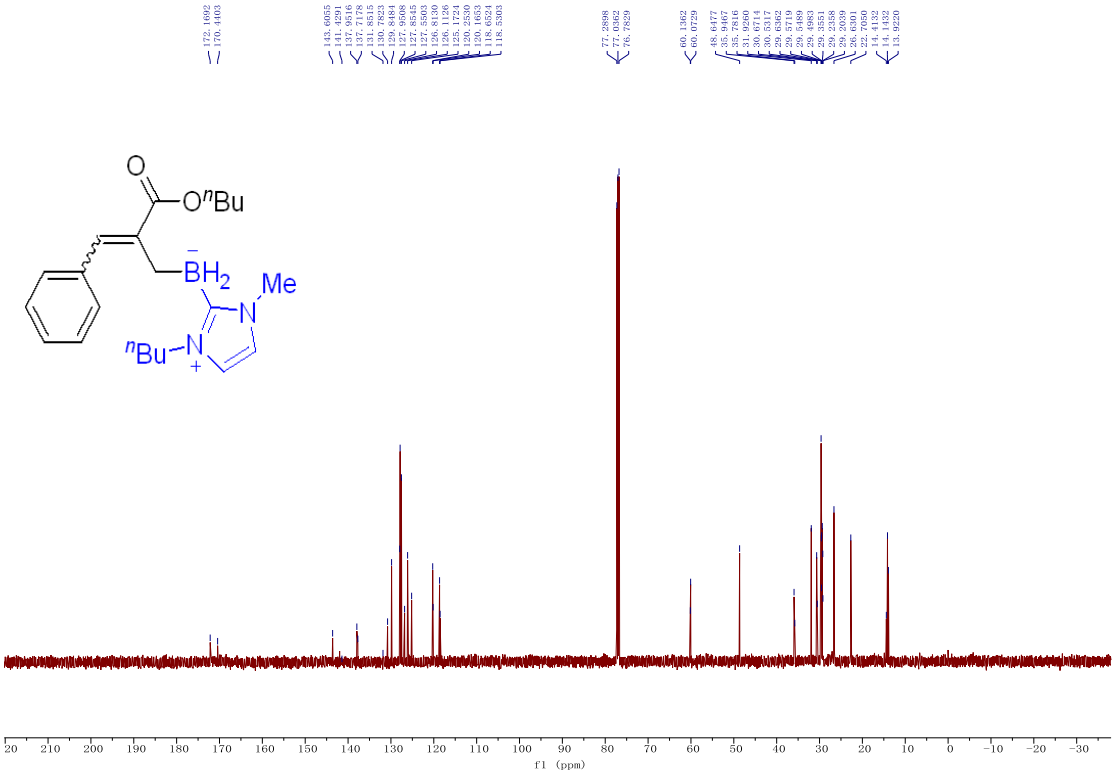

-221.3219
-221.4940
nBu
O
O
BH2
Me
N
N
Me
14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32 -34 -36 -38 -40 -42 -44 -46 -48 -50
f1 (ppm)

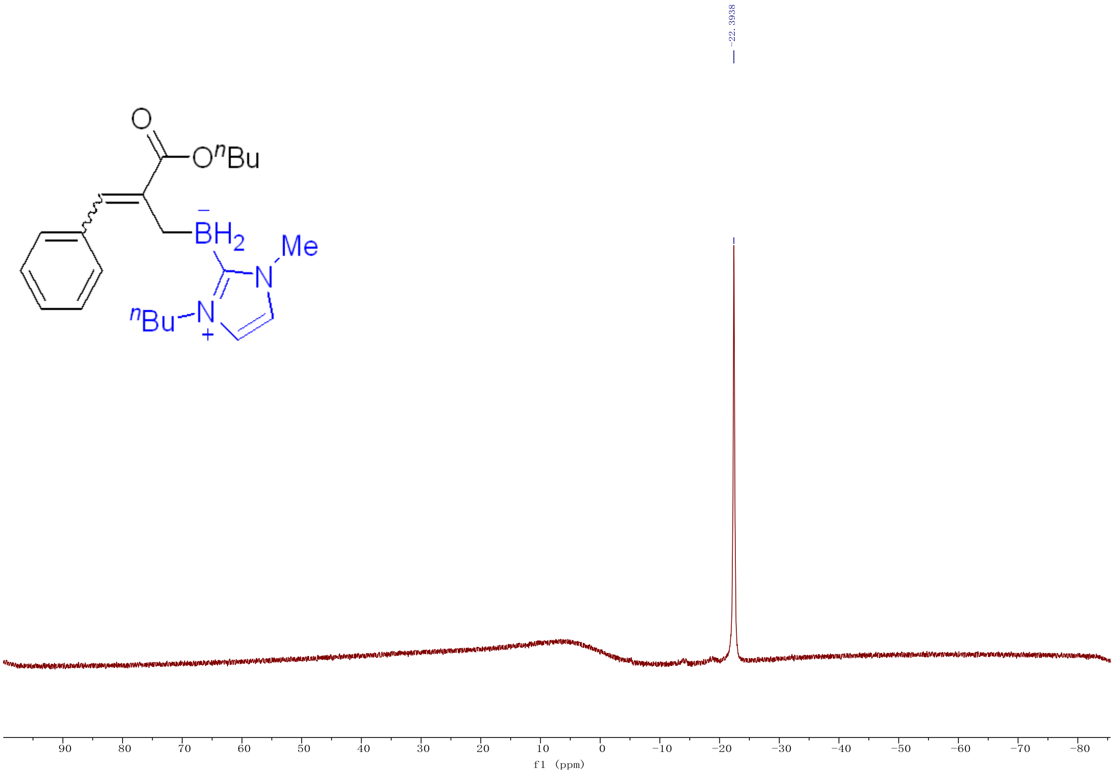

7.5640
7.5494
7.3264
7.3111
7.2955
7.2600 CDCl3
7.2097
7.2065
7.1990
7.1955
7.1835
7.1801
7.1254
7.1228
7.1107
7.1077
7.1005
7.0958
7.0897
7.0876
7.0860
7.0839
6.8051
6.6971
5.8938
3.7669
3.6840
1.9358
1.7211
1.7173
1.4138
1.3505
O
O
tBu
BH2
Me
N
N
Me
0.58
0.60
2.27
0.97
2.05
1.94
0.52
0.98
5.93
1.66
0.58
2.39
2.64
9.14
10.5 10.0 9.5 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 -1.5 -2.
f1 (ppm)

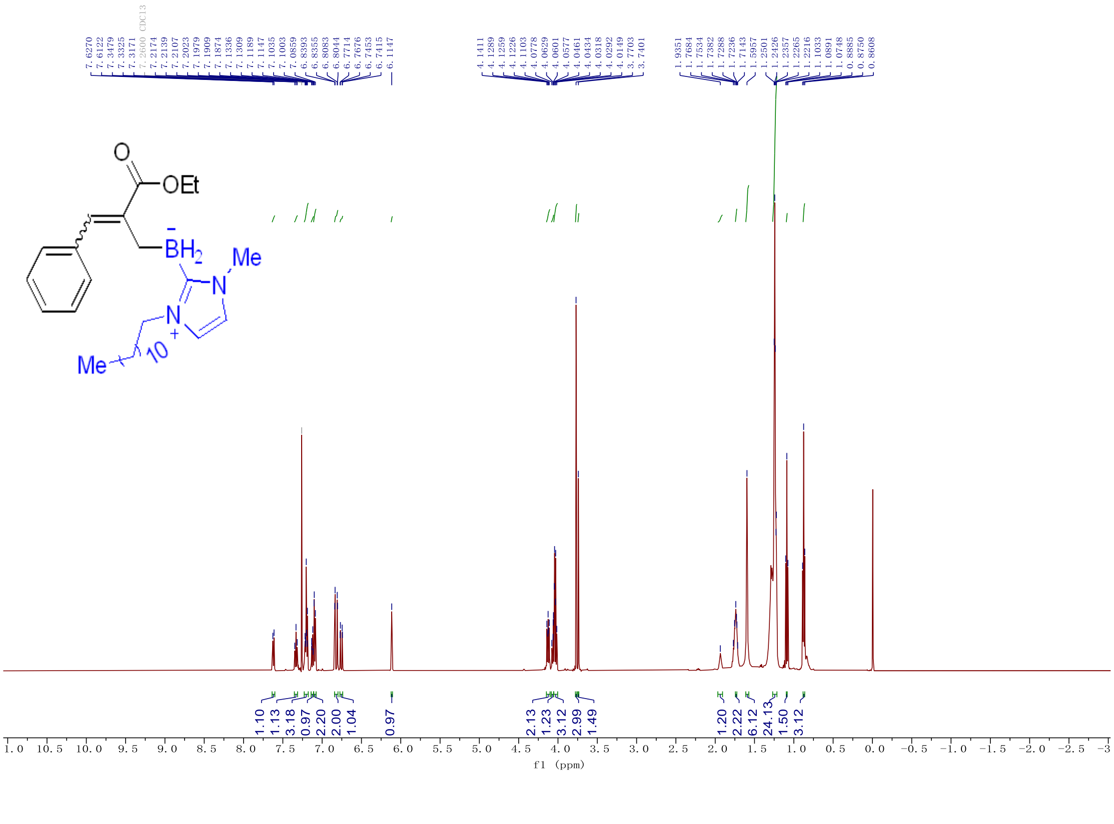

171.1627
169.7380
145.1910
143.6990
138.2360
137.9430
129.8033
129.7061
127.9187
127.7722
127.6016
126.6155
125.9653
125.7553
120.1640
120.0782
80.1290
79.1833
77.3390
77.0860
76.8297
36.0205
35.8734
28.1968
27.8892
27.8806
O
tBu
O
BH2
Me
N
N
Me
f1 (ppm)

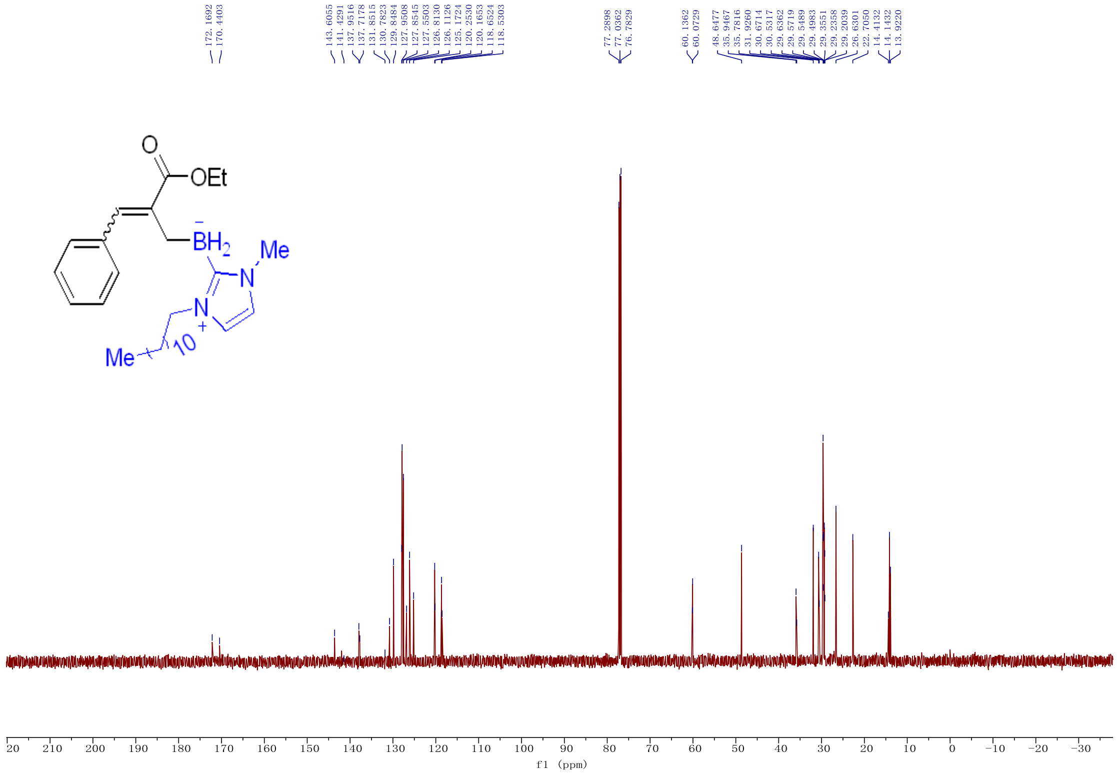

-22.4420
O
tBu
O
BH2
Me
N
N
Me
f1 (ppm)

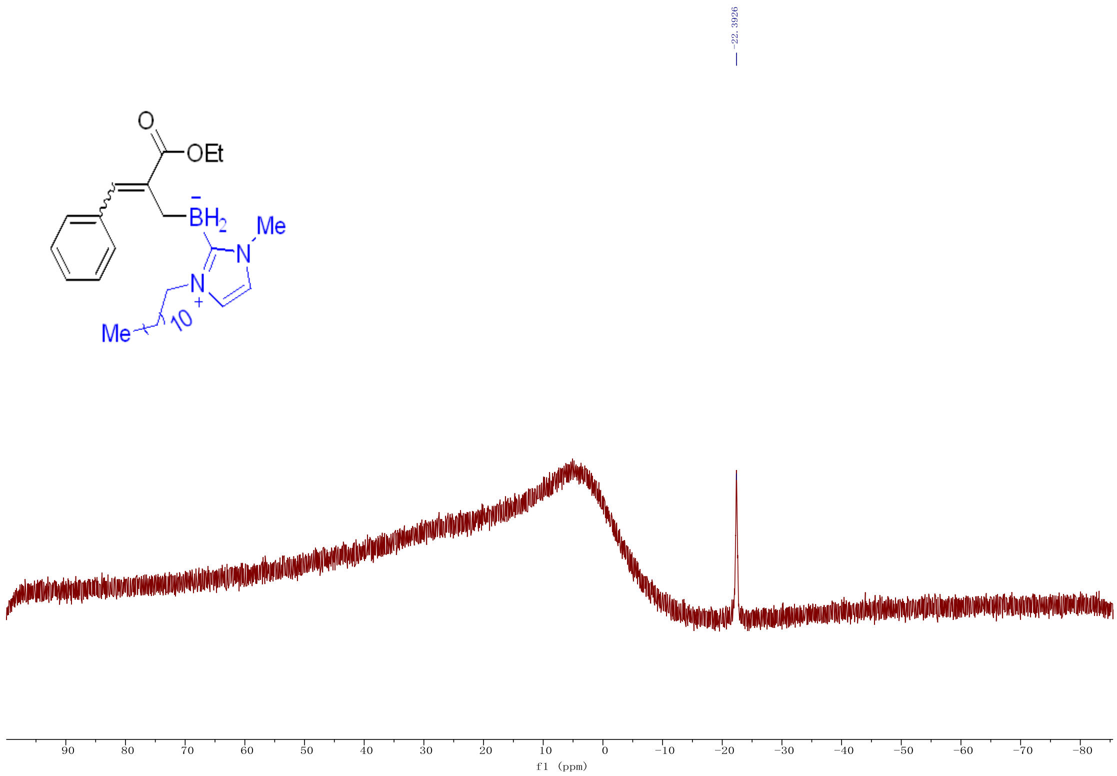

O
O^{n}Bu
BH$_2$
Me
N
^{n}Bu–N
+
0.79
0.88
0.44
2.50
1.18
2.23
2.00
0.81
0.97
2.08
0.84
2.82
3.03
1.21
0.85
3.33
1.26
3.16
4.31
2.20
5.57
3.22
f1 (ppm)

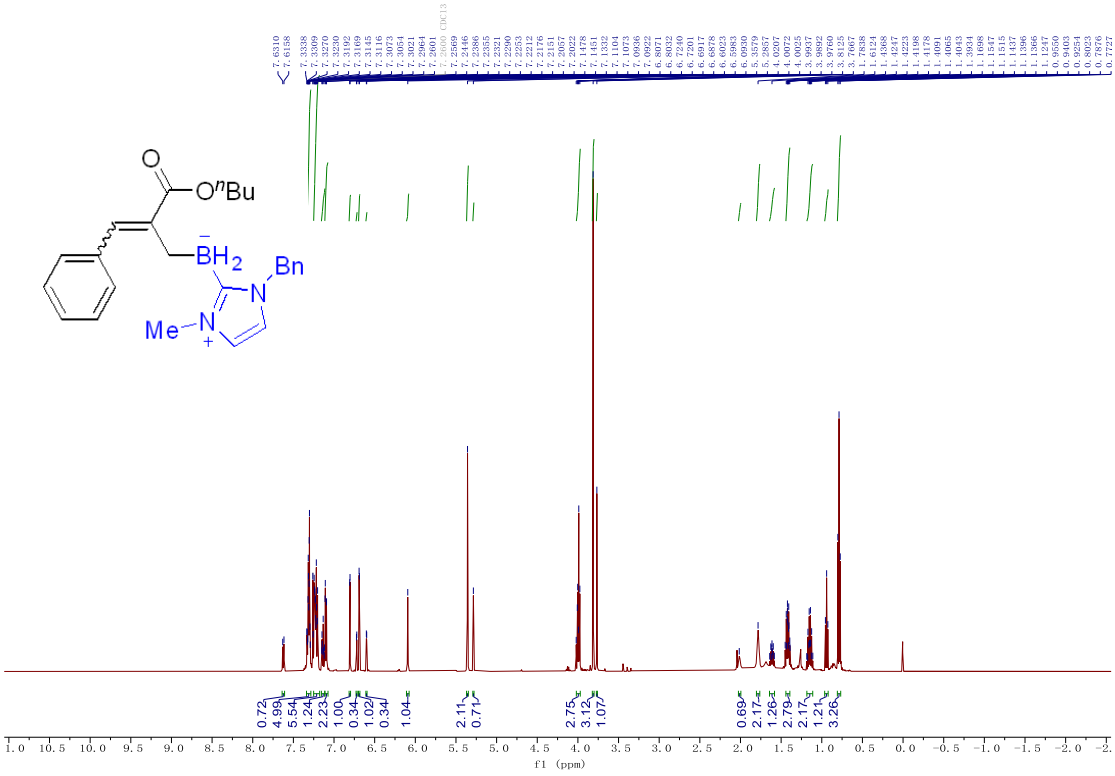

O
O^{n}Bu
BH$_2$
Me
N
^{n}Bu–N
+
f1 (ppm)

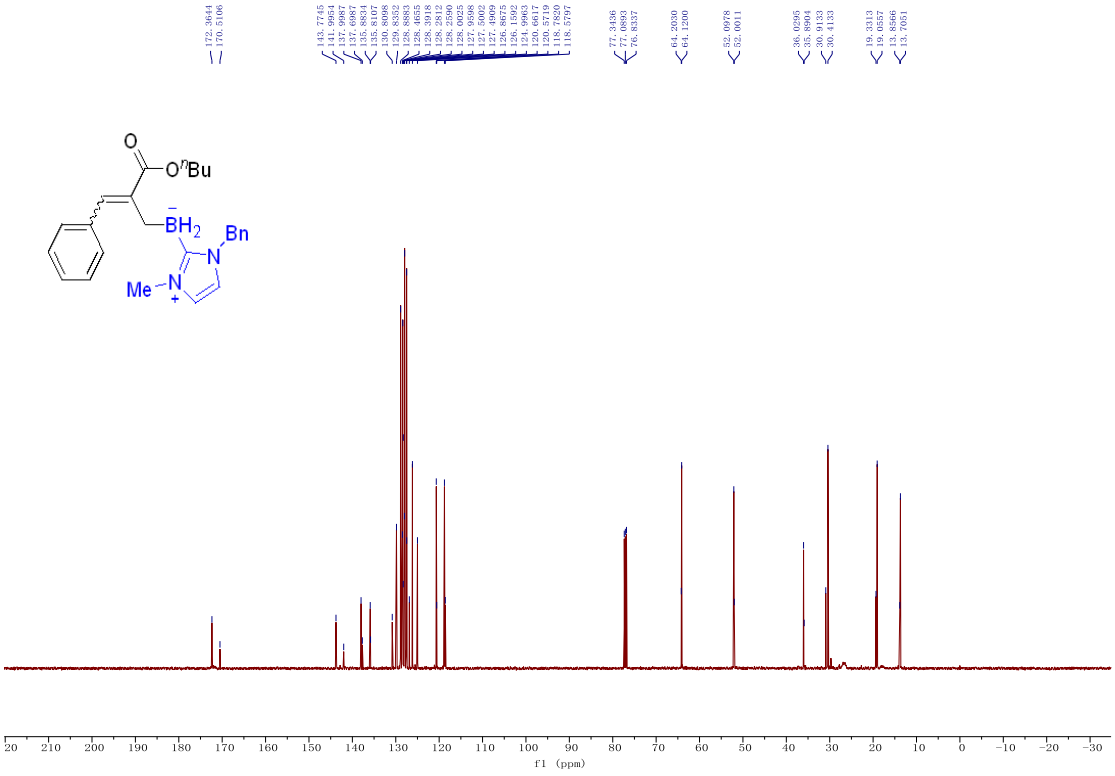

O
O^{n}Bu
BH$_2$
Me
^{n}Bu
-22.3938
f1 (ppm)

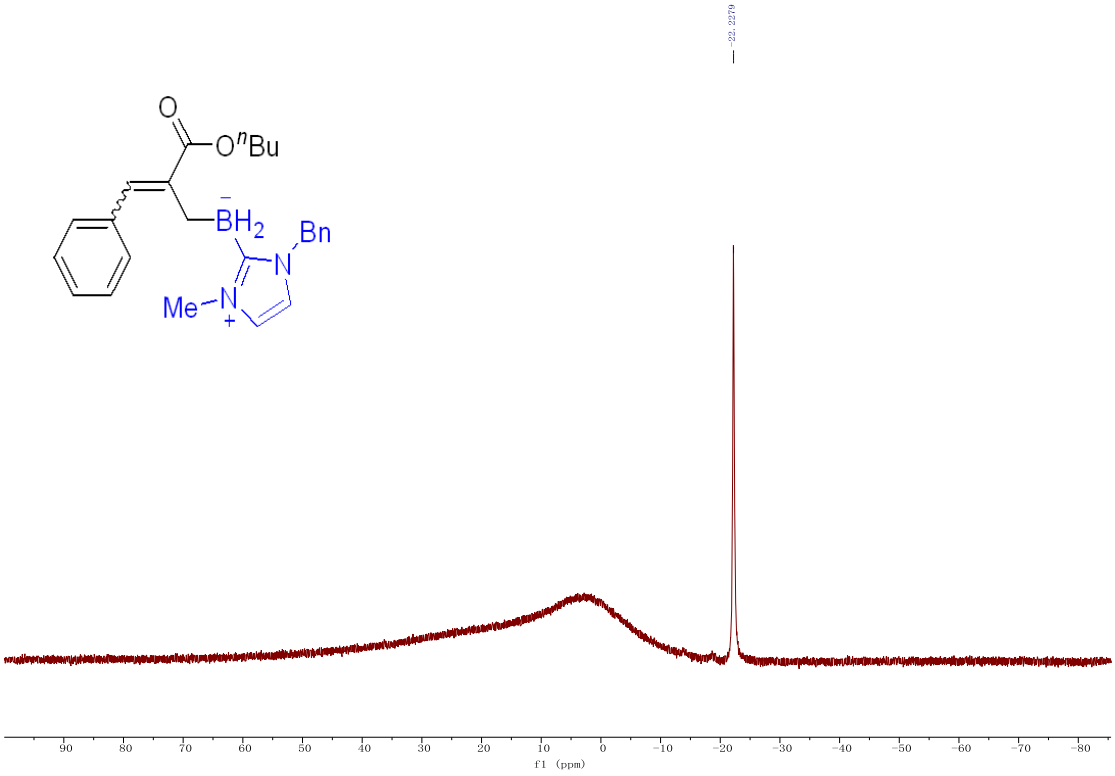

O
OEt
BH$_2$
Me
Me
10
f1 (ppm)

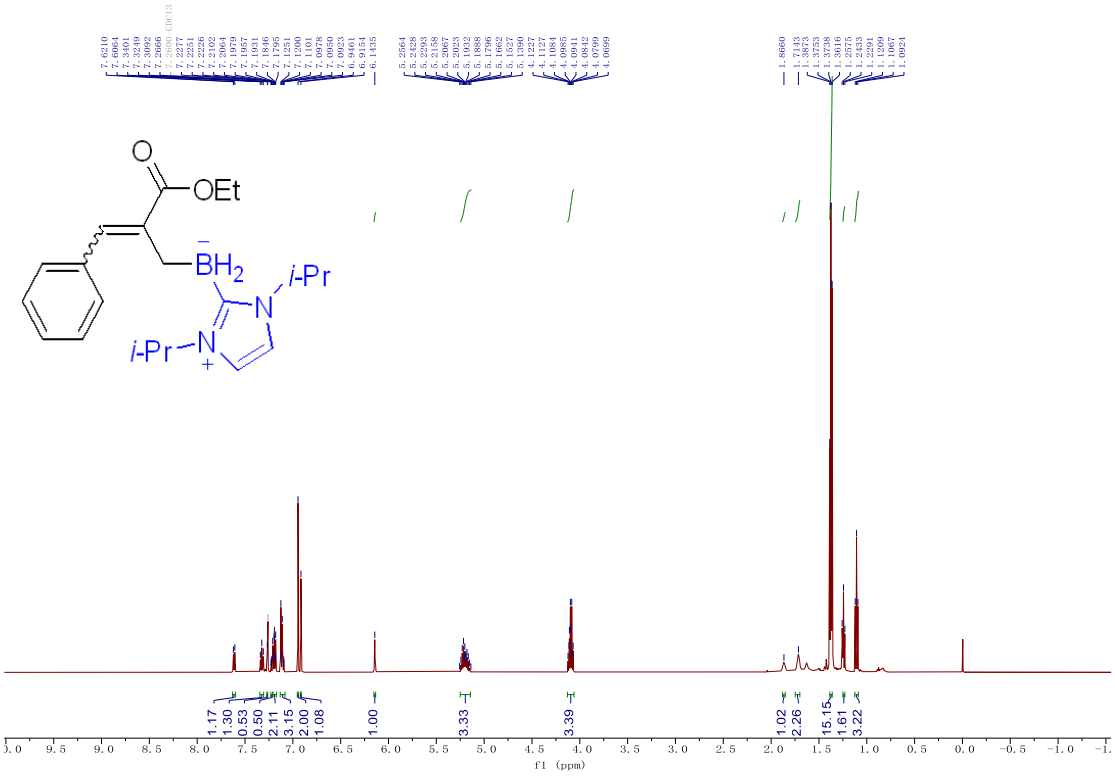

172.1692
170.4403
143.6955
141.4291
137.9516
137.7178
131.8515
130.7823
129.8484
127.9508
127.8545
127.5503
126.8130
126.1126
125.1724
120.2530
120.1653
118.6524
118.5303
77.2898
77.0362
76.7829
60.1362
60.0729
48.6477
35.9467
35.7816
31.9260
30.6714
30.5317
29.6362
29.5719
29.5489
29.4983
29.3551
29.2358
29.2039
26.6301
22.7050
14.4132
14.1432
13.9220
OEt
O
BH2
Me
N
N
Me
10
f1 (ppm)

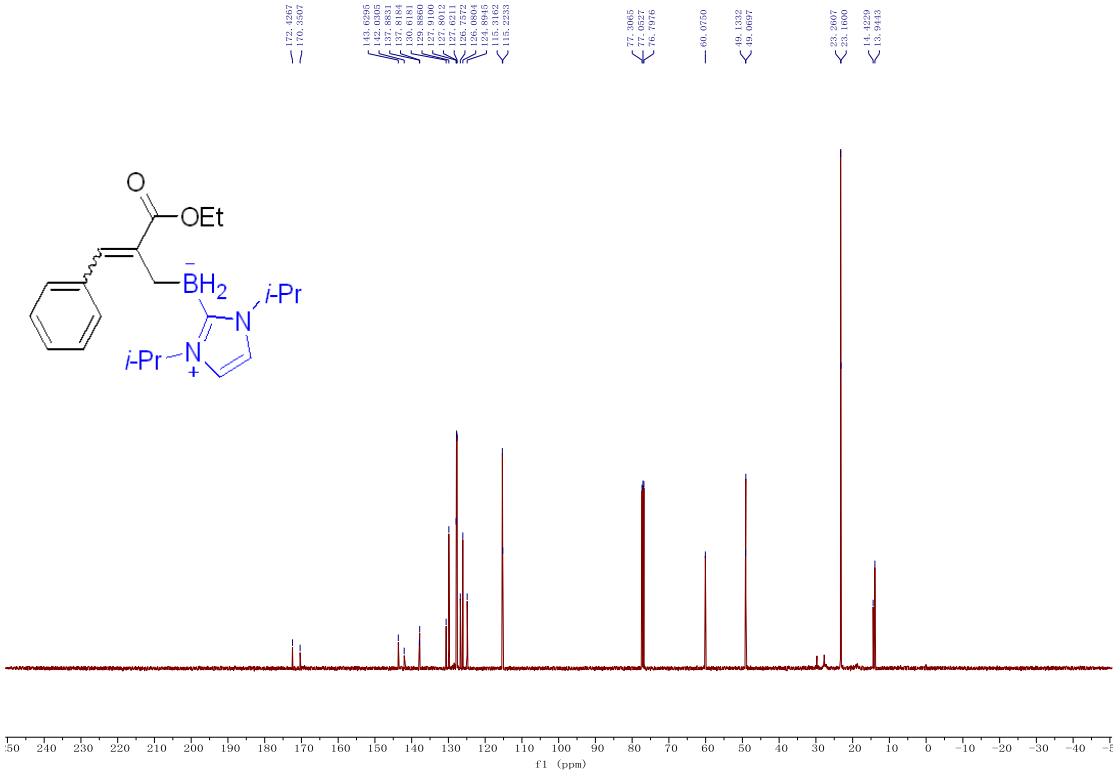

-22.3926
OEt
O
BH2
Me
N
N
Me
10
f1 (ppm)

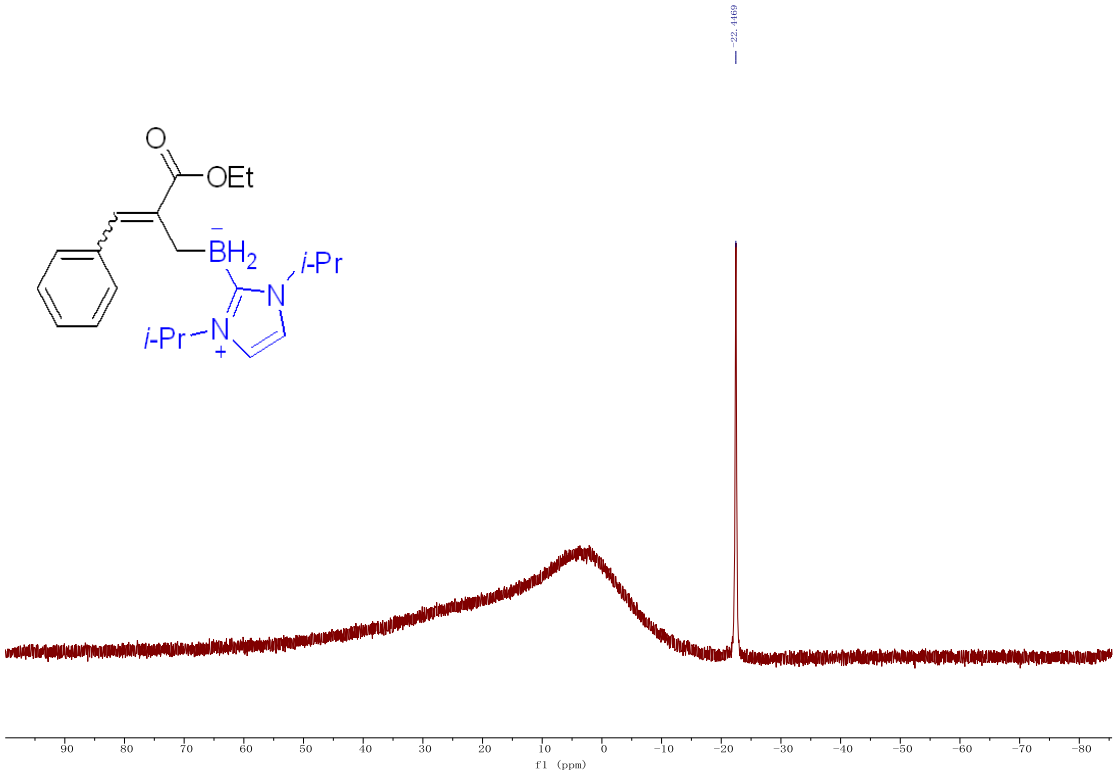

O
O^{n}Bu
$\bar{B}H_2$
Bn
N
Me–N$^+$
f1 (ppm)

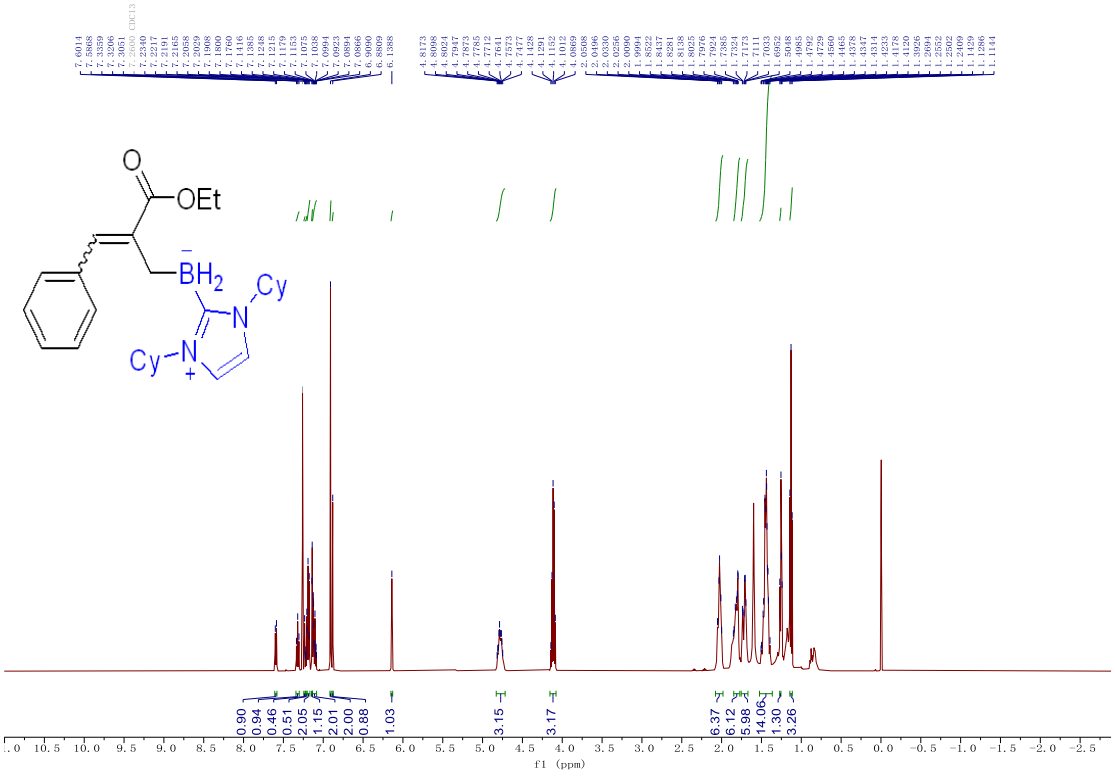

O
O^{n}Bu
$\bar{B}H_2$
Bn
N
Me–N$^+$
f1 (ppm)

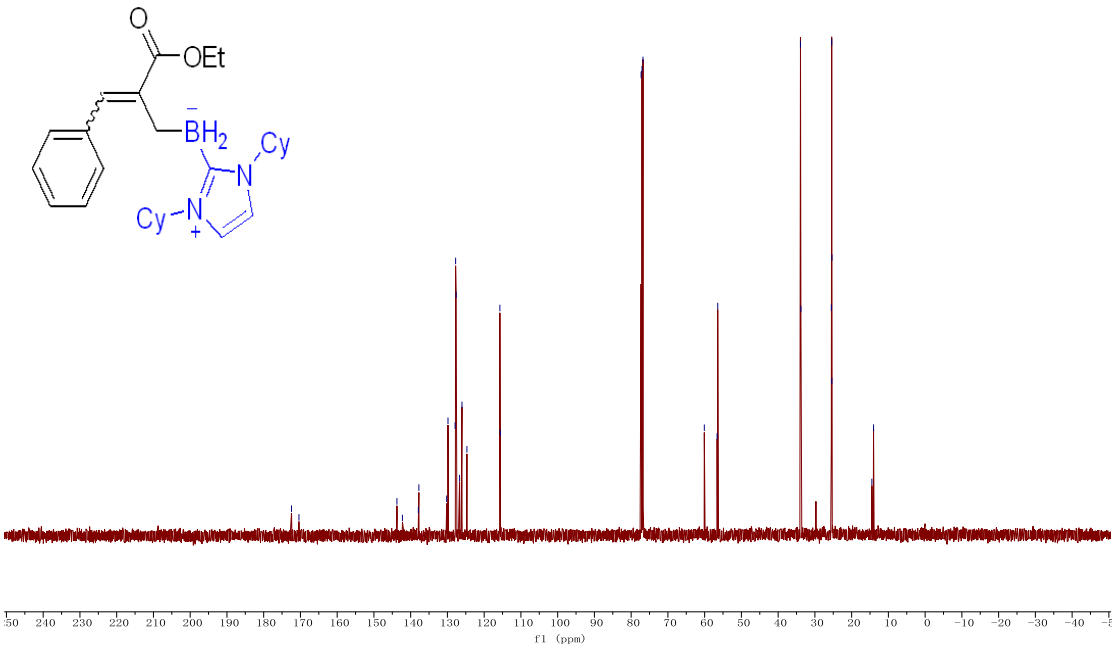

O
O^{n}Bu
BH$_2$
Bn
N
Me
N
+
-22.2279
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

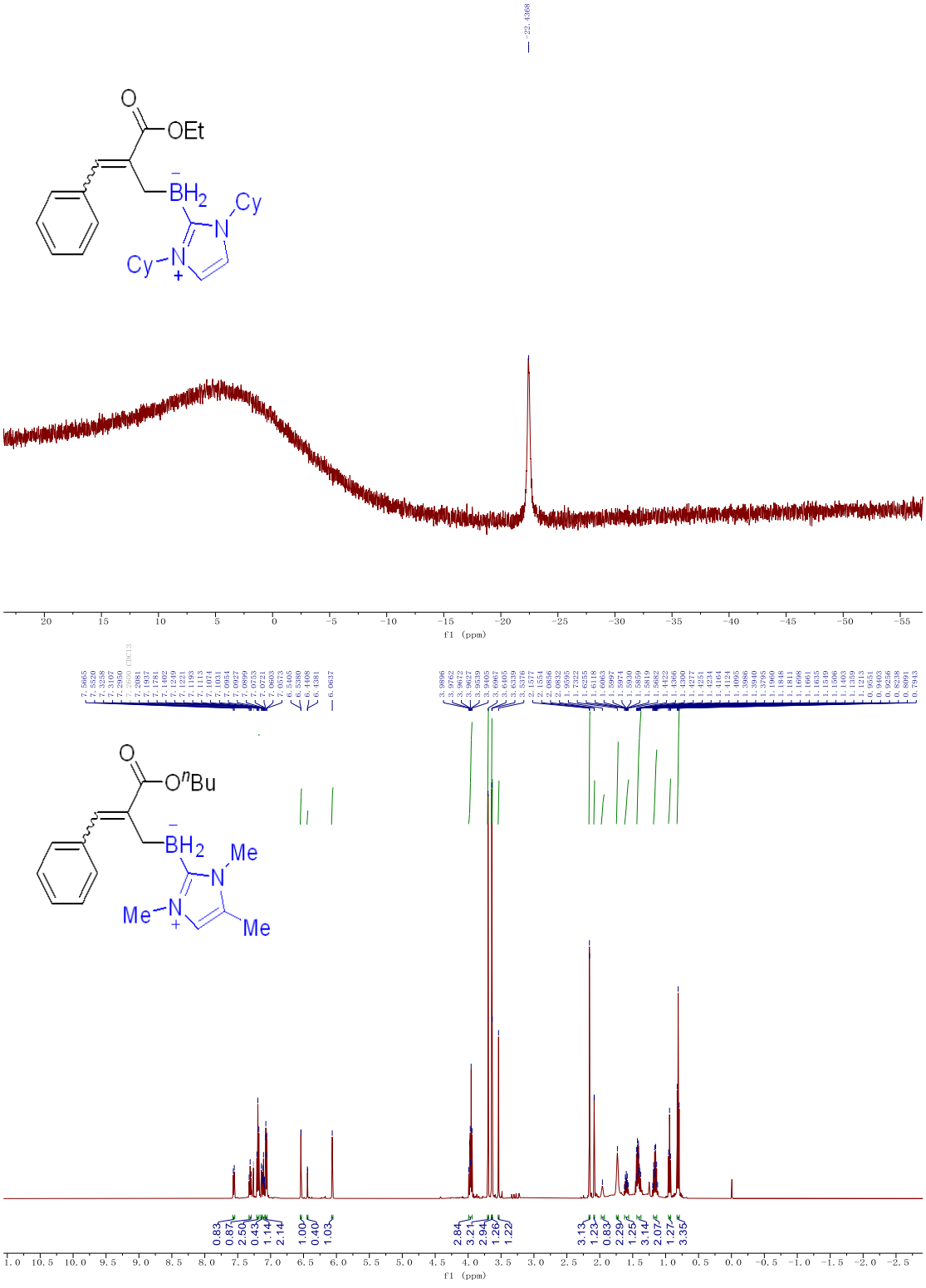

O
OEt
BH$_2$
i-Pr
N
i-Pr
N
+
1.17
1.30
0.53
0.50
2.11
3.15
2.00
1.08
1.00
3.33
3.39
1.02
2.26
15.15
1.61
3.22
f1 (ppm)

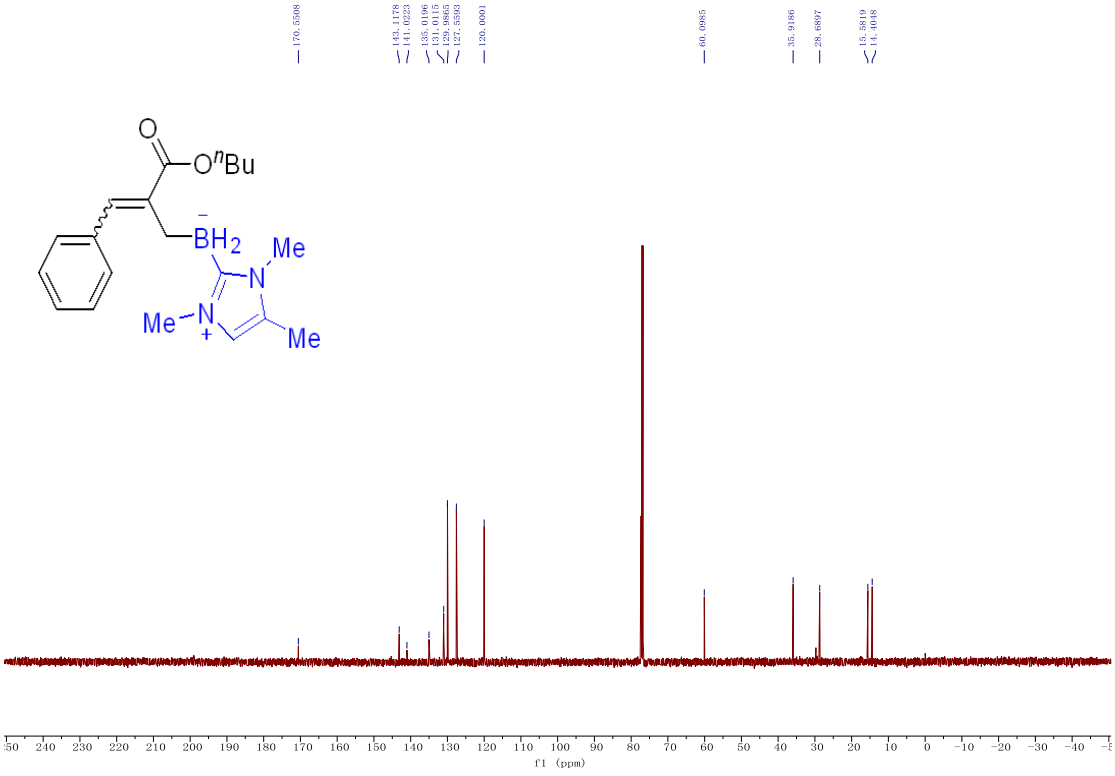

172.4267
170.3507
143.6295
142.0305
137.8831
137.8184
130.6491
129.8860
127.9100
127.8012
127.6211
126.7572
126.0804
124.8945
116.3162
115.2253
77.3065
77.0527
76.7976
60.0750
49.1332
49.0697
23.2607
23.1600
14.4229
13.9443
O
OEt
BH2
i-Pr
N
i-Pr
N
+
f1 (ppm)

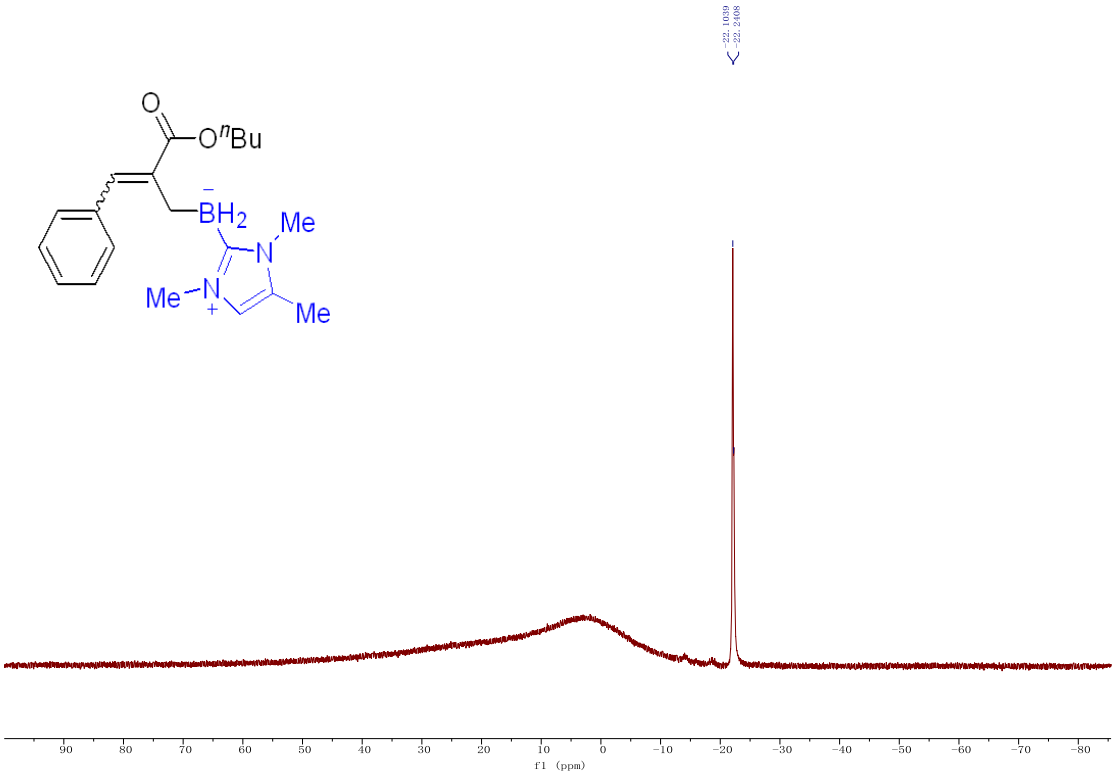

22.4469
O
OEt
BH2
i-Pr
N
i-Pr
N
+
f1 (ppm)

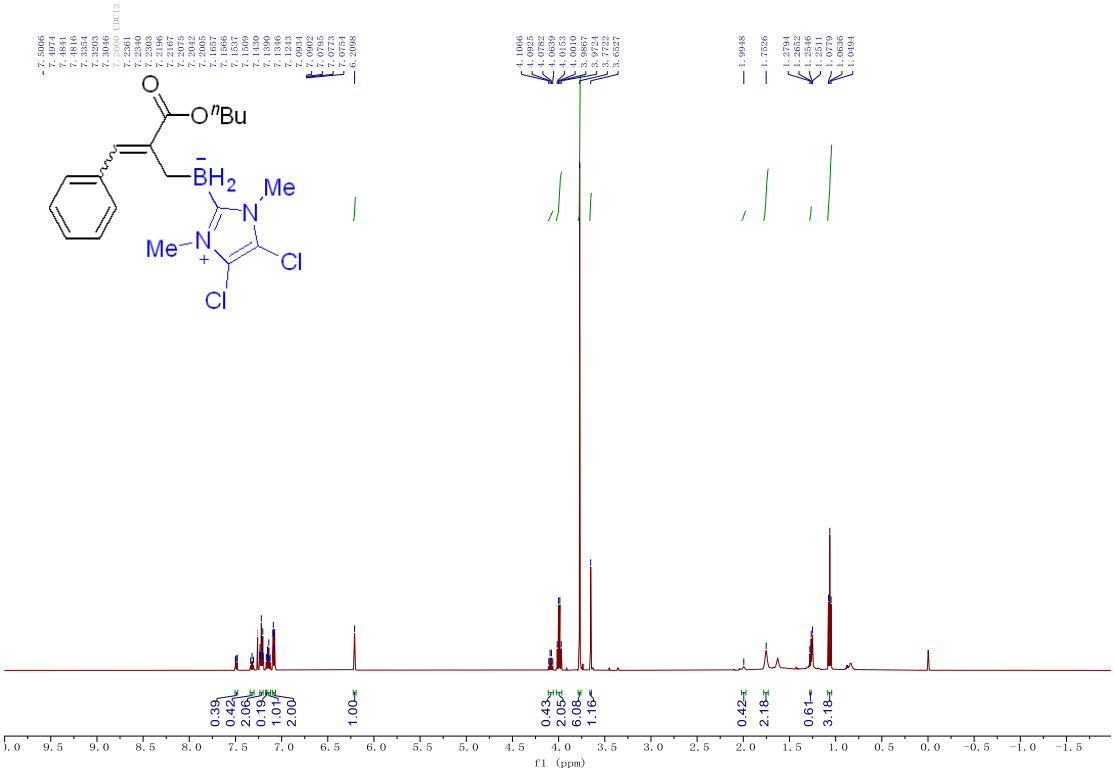

O
OEt
BH2
Cy
N
Cy
N
+
f1 (ppm)

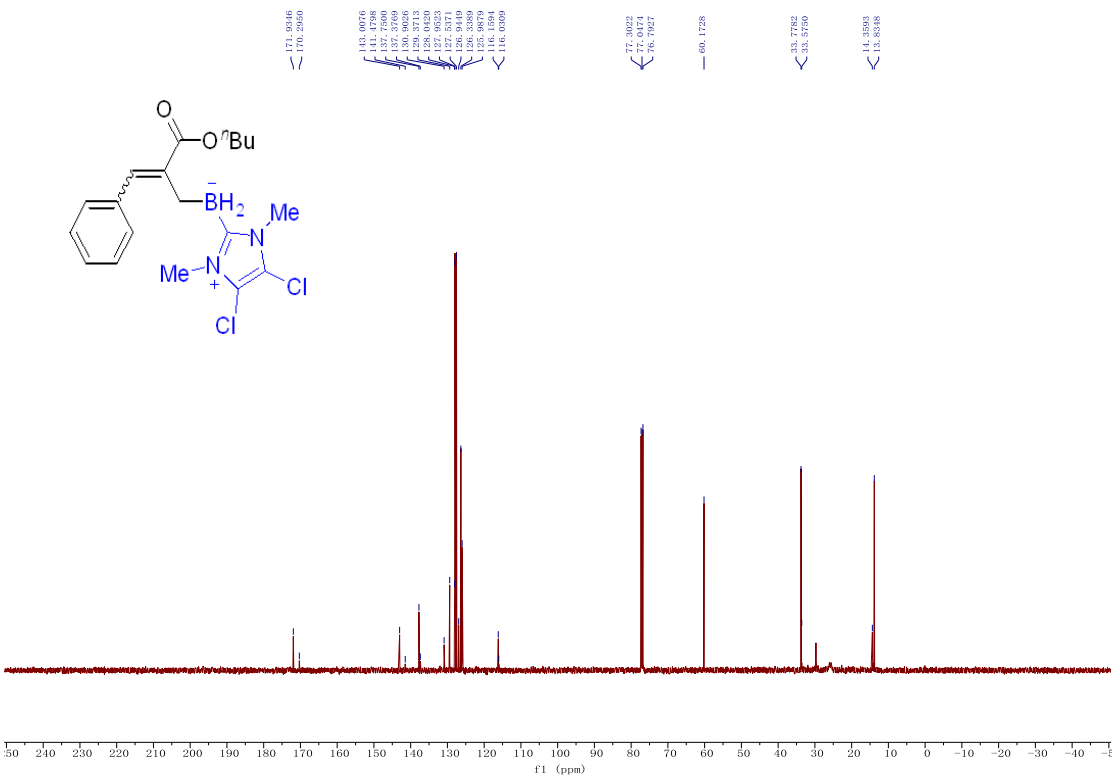

O
OEt
BH2
Cy
N
Cy
N
+
f1 (ppm)

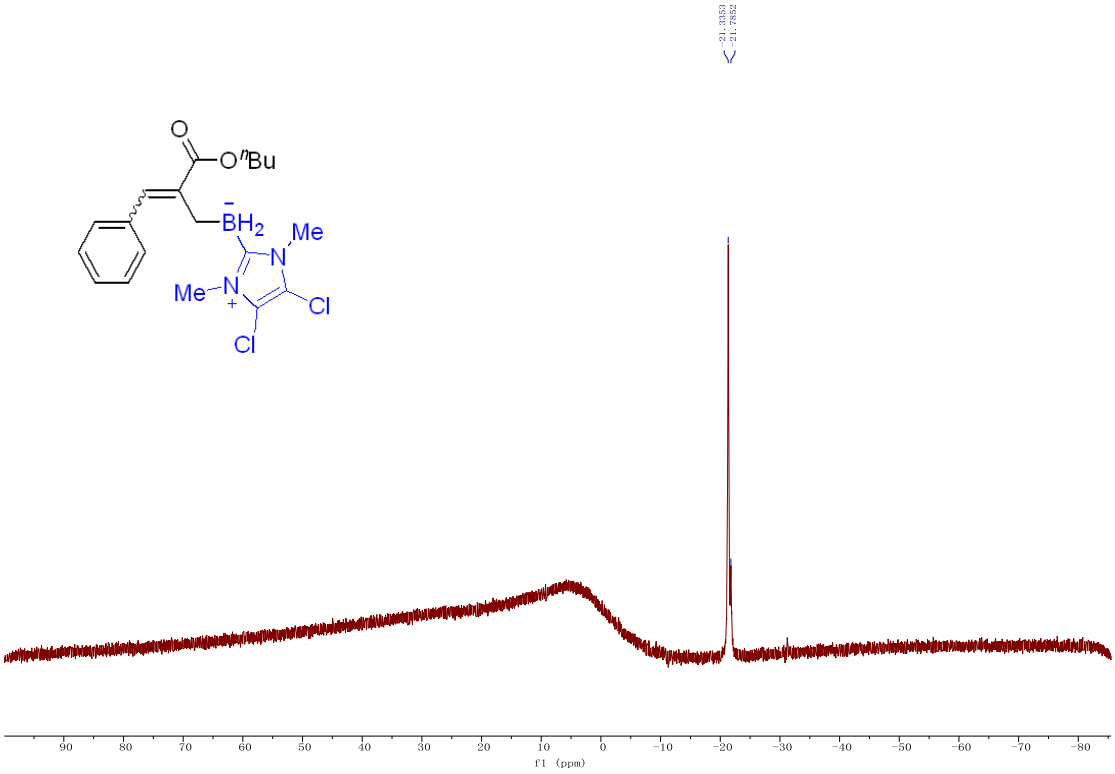

-22.4368
O
OEt
BH2
Cy
N
Cy
N
+
f1 (ppm)
O
OnBu
BH2
Me
N
Me
N
+
Me
0.83
0.87
2.50
0.43
1.14
2.14
1.00
0.40
1.03
2.84
3.21
2.94
1.26
1.22
3.13
1.23
0.83
2.29
1.25
3.14
2.07
1.27
3.35
f1 (ppm)

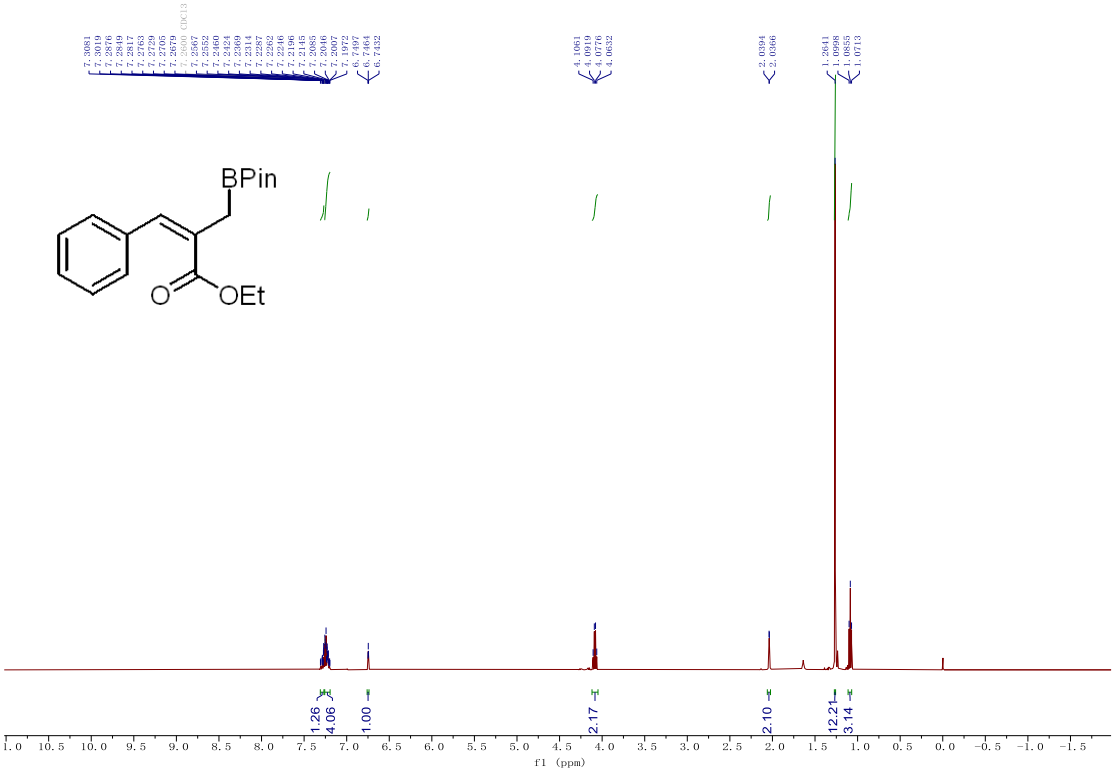

170.5508
143.1178
141.0223
138.0196
131.0415
129.9865
127.5593
120.0001
60.0985
35.9186
28.6897
15.5819
14.4048
O
O^{n}Bu
BH$_2$
Me
N
Me
N
+
Me
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)

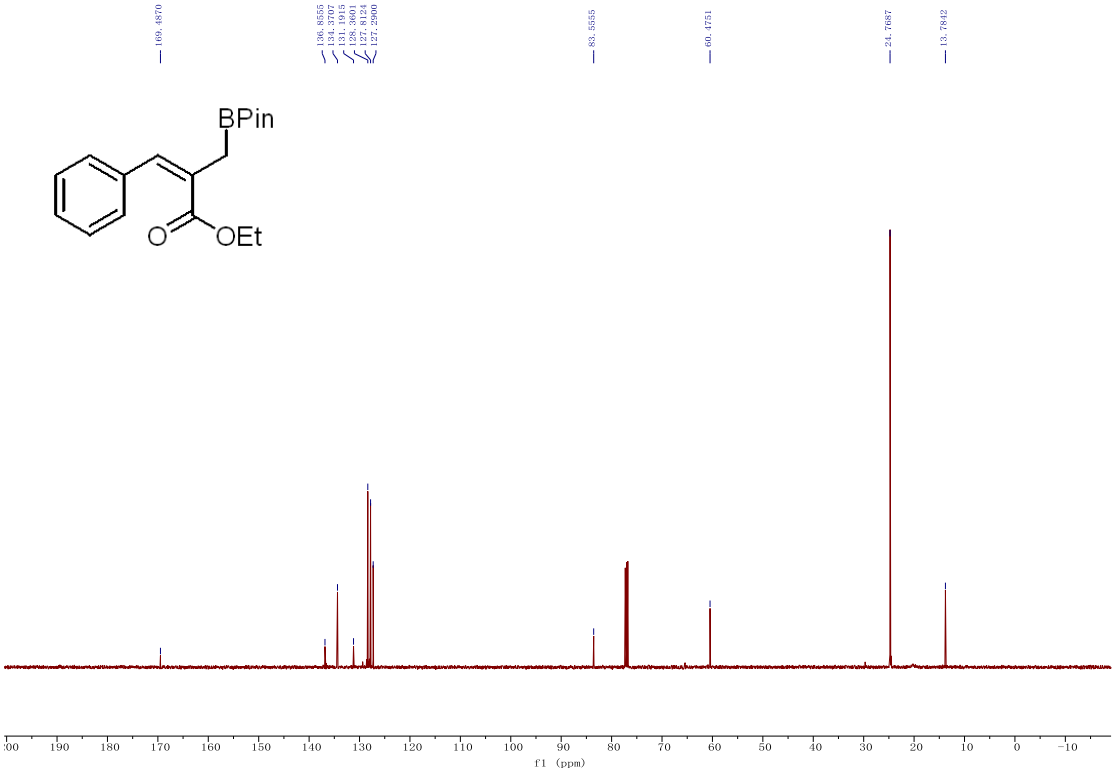

22.1039
22.2408
O
O^{n}Bu
BH$_2$
Me
N
Me
N
+
Me
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

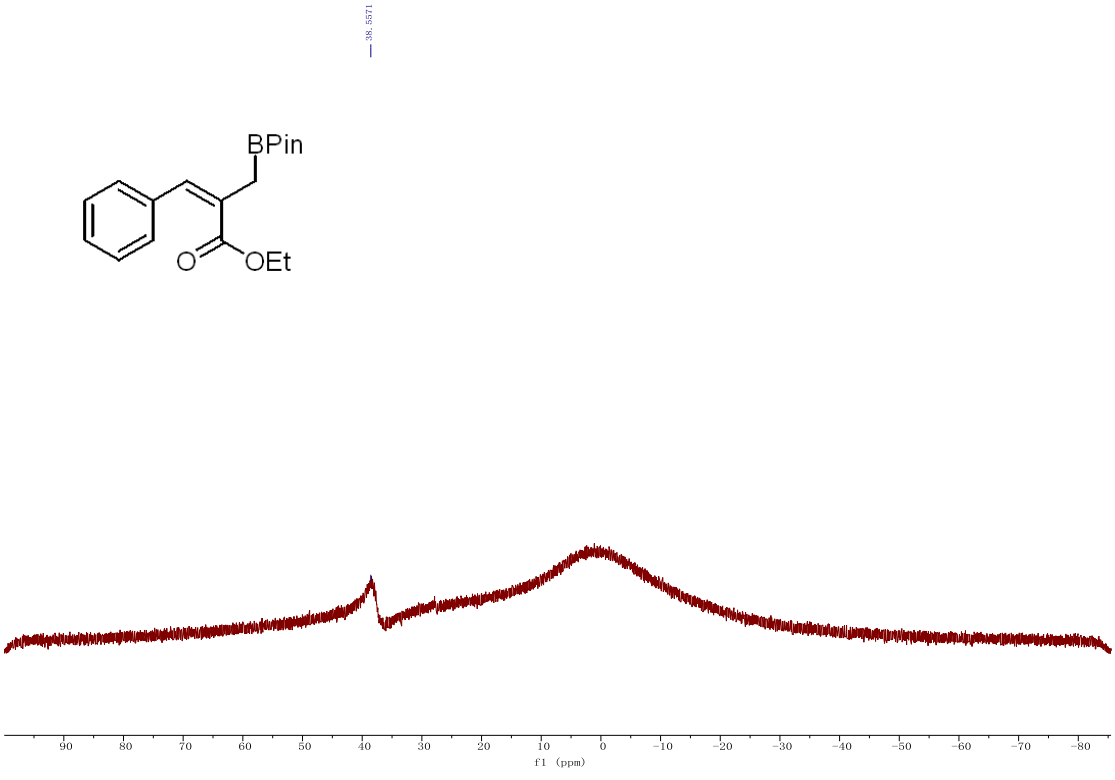

O
O^{n}Bu
$^-$BH$_2$
Me
N
Me
N
$^+$
Cl
Cl
f1 (ppm)

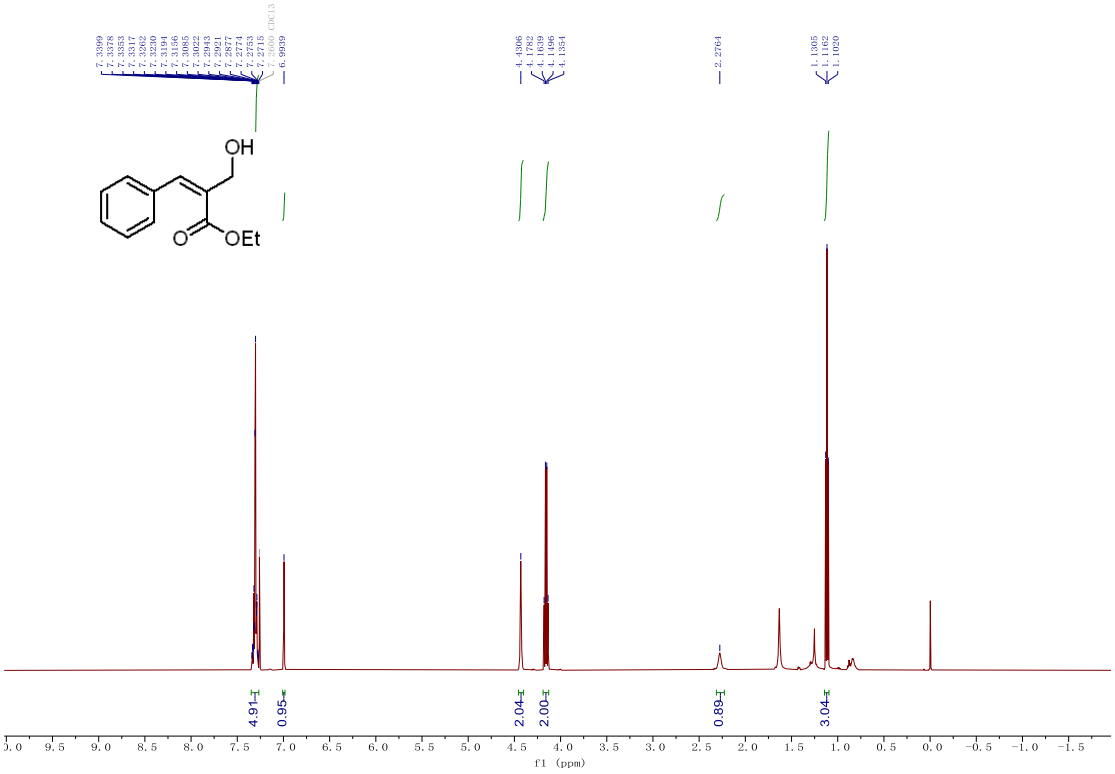

O
O^{n}Bu
$^-$BH$_2$
Me
N
Me
N
$^+$
Cl
Cl
f1 (ppm)

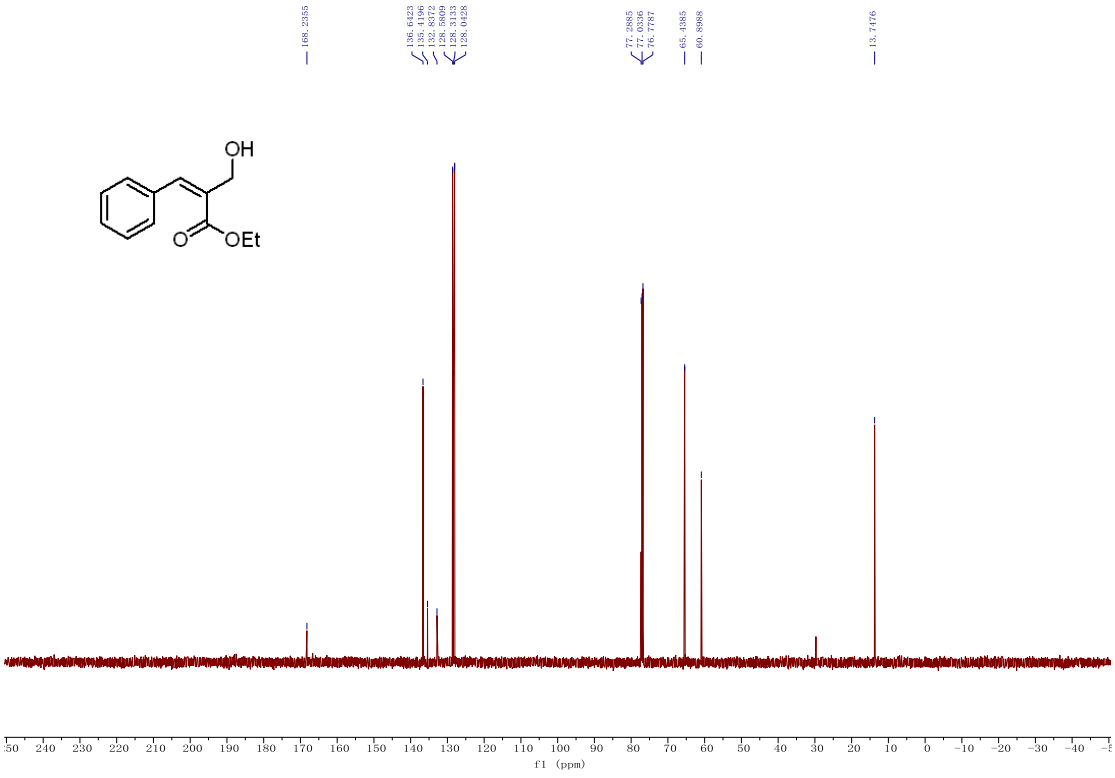

-21.3353
-21.7852
O
O^{n}Bu
BH$_2$
Me
N
Me
N
+
Cl
Cl
f1 (ppm)

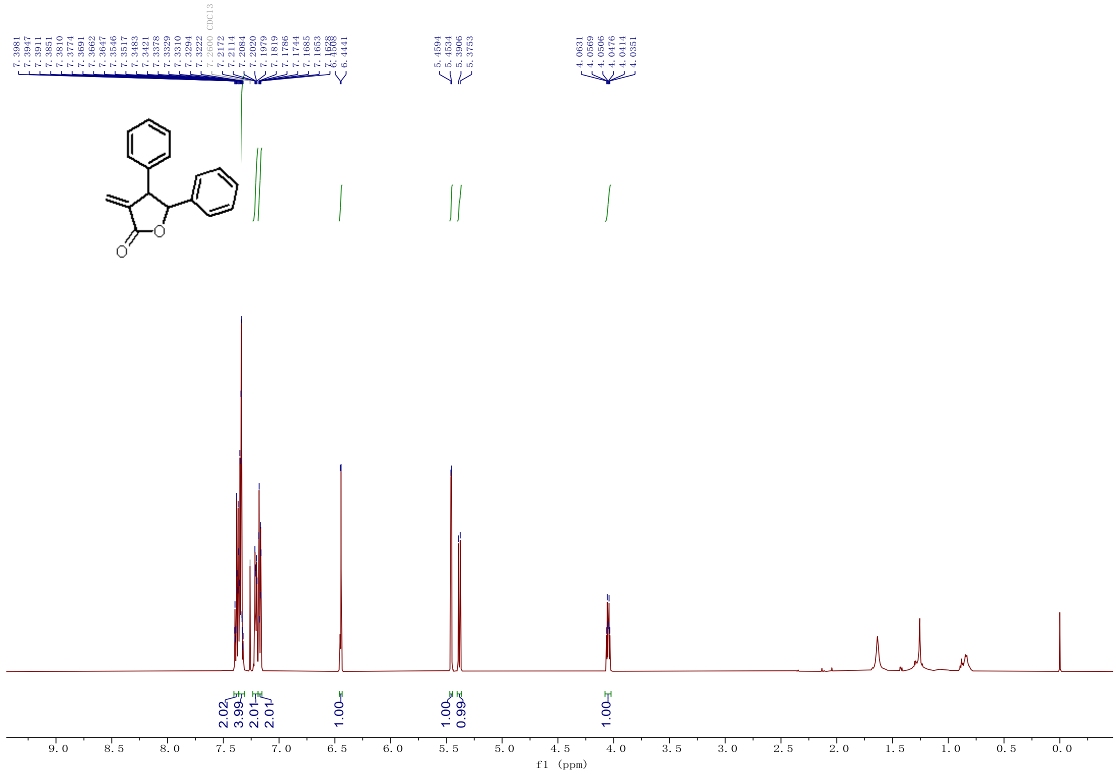

BPin
O
OEt
1.26
4.06
1.00
2.17
2.10
12.21
3.14
f1 (ppm)


169.4870
136.8555
134.3707
131.1915
129.5904
128.8124
127.2900
83.5555
60.4751
24.7687
13.7842
BPin
O
OEt
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


38.5571
BPin
O
OEt
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)


7.3399
7.3378
7.3353
7.3317
7.3293
7.3250
7.3194
7.3156
7.3085
7.3052
7.2943
7.2921
7.2877
7.2774
7.2753
7.2715
7.2690 CDCl3
6.9939
4.4306
4.1782
4.1639
4.1496
4.1354
2.2764
1.1305
1.1162
1.1020
OH
O
OEt
4.91
0.95
2.04
2.00
0.89
3.04
f1 (ppm)


168.2355
136.6423
135.1196
132.8372
128.5809
128.3133
126.0426
77.2885
77.0336
76.7787
65.4385
60.8988
13.7476
OH
O
OEt
f1 (ppm)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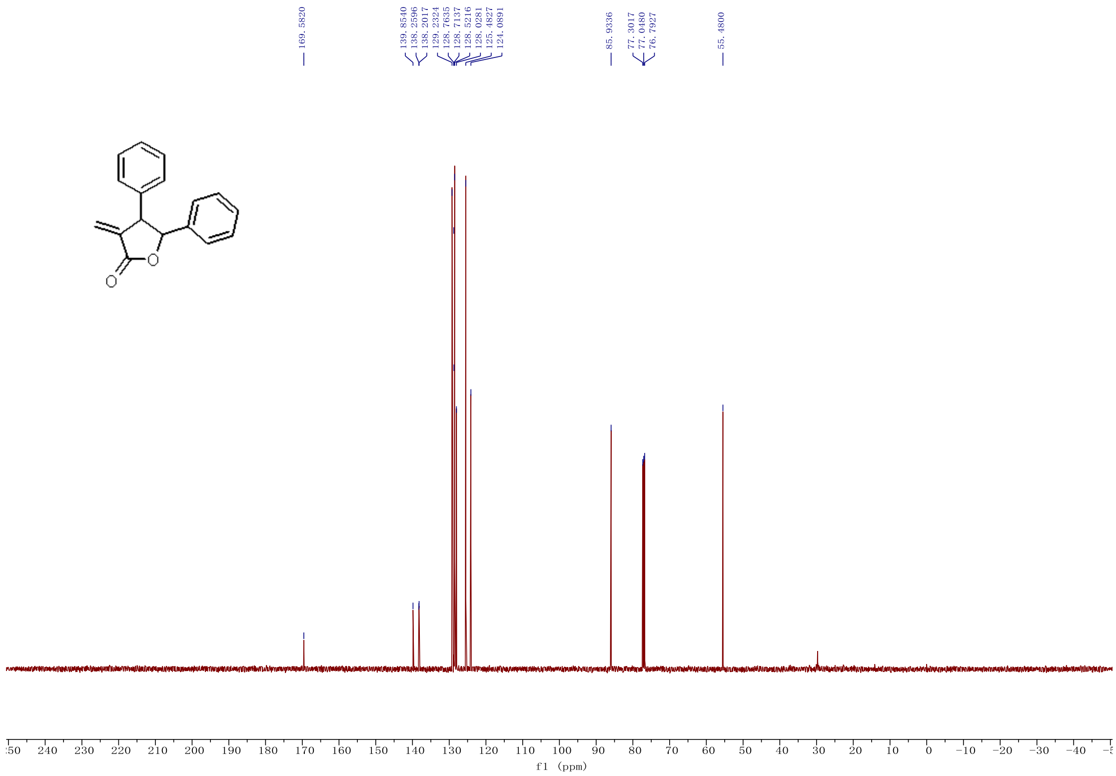
7.3947
7.3911
7.3851
7.3810
7.3774
7.3691
7.3662
7.3647
7.3546
7.3517
7.3483
7.3421
7.3378
7.3329
7.3310
7.3294
7.3222
7.2600 CDCl3
7.2172
7.2114
7.2084
7.2020
7.1979
7.1819
7.1786
7.1744
7.1685
7.1653
6.4508
6.4441
5.4594
5.4534
5.3906
5.3753
4.0631
4.0569
4.0506
4.0476
4.0414
4.0351
2.02
3.99
2.01
2.01
1.00
1.00
0.99
1.00
f1 (ppm)


169.5820
139.8540
138.2596
138.2017
129.2324
128.7635
128.7137
128.5216
128.0281
125.4827
124.0891
85.9336
77.3017
77.0180
76.7927
55.4800
f1 (ppm)