Supporting information

Visible-light-driven PhSSPh-catalysed regioselective hydroborylation of α,β-unsaturated carbonyl compounds with NHC-boranes

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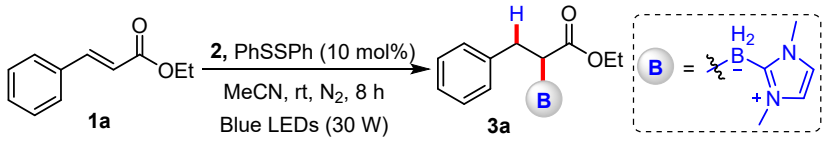
Table of contents

1. General Information

Unless otherwise declared, all the reagents were bought from commercial suppliers and used without additional purification. A glass tube (35 mL) with a rubber plug was used in hydroboration reactions unless otherwise noted. NHC-boranes reagent was prepared according to a previously reported procedure[1]. Thin layer chromatography (TLC) was performed on commercial silica gel plates and flash column chromatography was performed with 300-400 mesh silica gel cartridge. Visualization of TLC achieved using ultraviolet light (254 nm) or staining with Iodine. NMR spectra were recorded on a BRUKER AVANCE III 400 spectrometer (400 MHz for ^{1}H; 376 MHz for ^{19}F; 100 MHz for ^{13}C) instruments and are referenced relative to $CDCl_3$ (δ 7.26 ppm for ^{1}H, 77.16 ppm for ^{13}C) using TMS as internal standard. Resonances of hydrogen or carbon atoms bonded to the boron atom are weak (sometimes absent) in both ^{1}H or ^{13}C NMR spectra. Note: The protons on boron atom in the ^{1}H-NMR spectrum and the carbene carbon atom attached to the boron atom in the ^{13}C NMR spectrum are not detected owing to quadrupole broadening and spin–spin coupling with boron. Data are recorded as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet, brs = broad singlet), coupling constant (*J*) in Hertz (Hz), and integration. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer with electro spray ionization (ESI) as the ion source.

2. Optimization of reaction conditions

Table S1. Optimization of reaction conditions.[a]

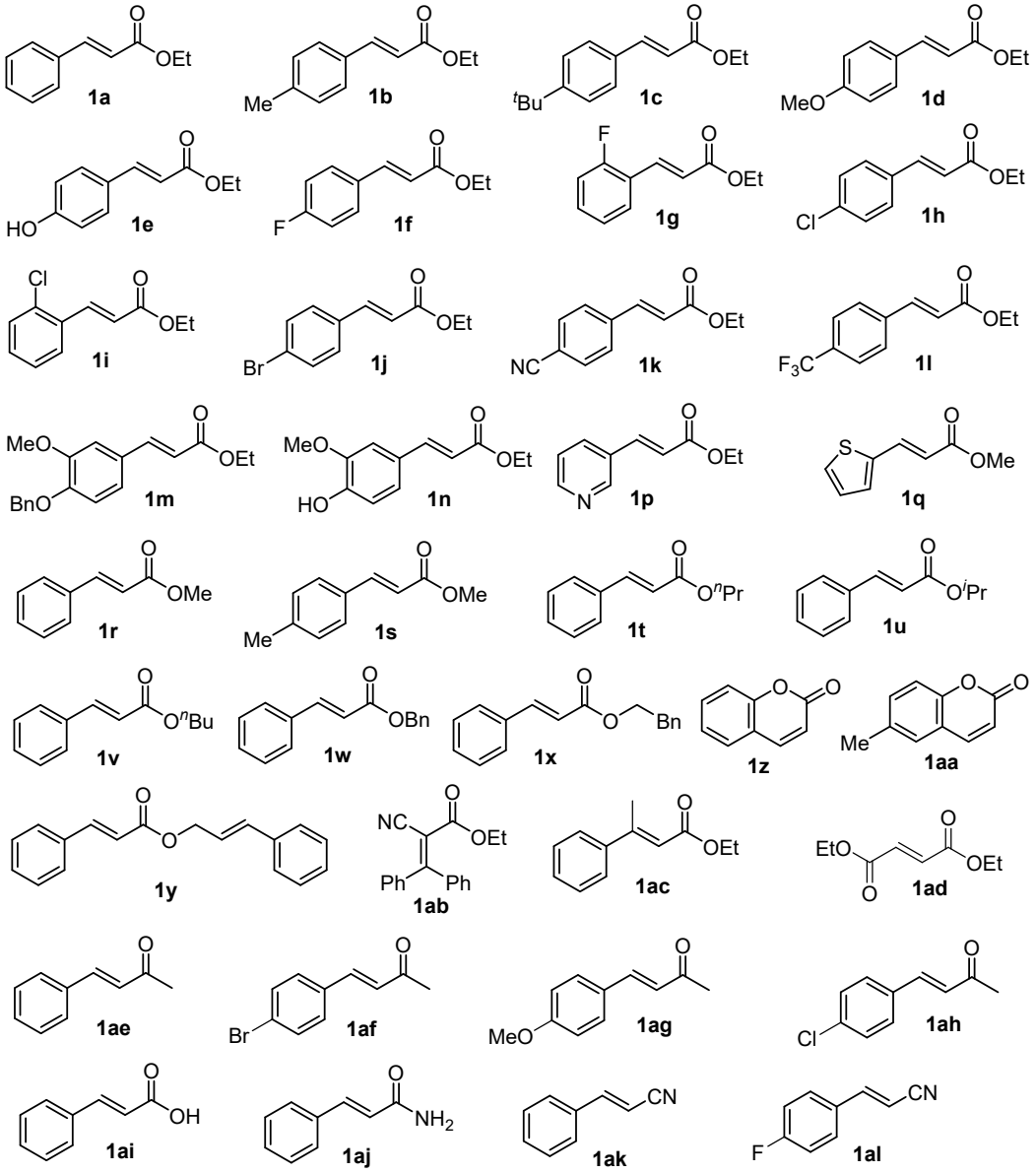


Entry	Variation of standard conditions	Yield [%][b]
1	**none**	**95**
2	MeOH instead of MeCN	91
3	DCE instead of MeCN	20
4	THF instead of MeCN	24
5	toluene instead of MeCN	66
6	1,4-dioxane instead of MeCN	27
7	DMF instead of MeCN	48
8	DCM instead of MeCN	26
9	BnSSBn instead of PhSSPh	NR
10	1.0 equiv of **2**	79
11	30 W CFL	21
12	5 mol% of PhSSPh	34
13	without PhSSPh	NR
14	no light irradiation	NR
15	without N_2	trace

[a] Standard reaction conditions: ethyl cinnamate **1a** (0.3 mmol), 1,3-dimethylimidazol-2-ylidene borane **2** (0.45 mmol), PhSSPh (10 mol%), blue LEDs (30 W), and solvent (2 mL), at room temperature for 8 h under N_2 atmosphere. The reaction was conducted at room temperature, but the solution temperature was increased to 30°C upon the irradiation by blue LEDs. [b] Isolated yield. NR = no reaction.

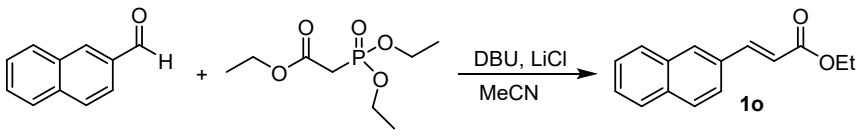
3. Experimental section

(1) Starting substrates were commercially available as below:



(2) Synthesis of Substrates.

Synthesis of Substrate 1o:

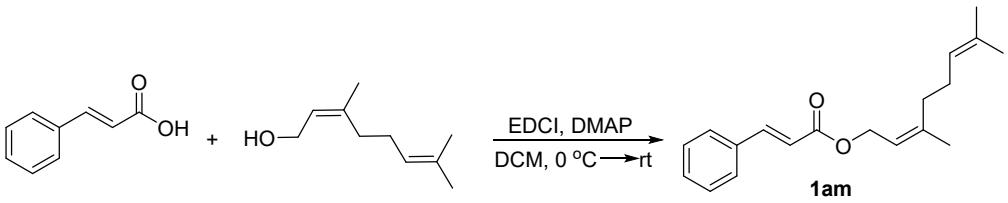


To a stirred slurry of LiCl (0.67 g, 14.2 mmol) in MeCN (80 mL) was added triethyl phosphonoacetate (2.9 mL, 12.8 mmol) and 2-naphthaldehyde (2.0 g, 12.8 mmol) at 0°C. After stirring for 5 minutes at 0°C, DBU (1.9 mL, 12.8 mmol) was added and then the reaction mixture was stirred at room temperature overnight. The resulting

slurry was diluted with diethyl ether (200 mL), washed with sat. NH_4Cl (100 mL), brine (100 mL), dried over anhydrous $MgSO_4$, filtered through celite (diethyl ether) and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc – 20/1) to yield the corrsponding compound **1o**. The spectral data are in good agreement with previous reports.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.87-7.81 (m, 4H), 7.66 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.53-7.48 (m, 2H), 6.55 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 143.6, 133.2, 132.2, 130.9, 128.9, 127.6, 127.5, 126.7, 126.2, 125.7, 122.5, 117.4, 59.5, 13.3 ppm.

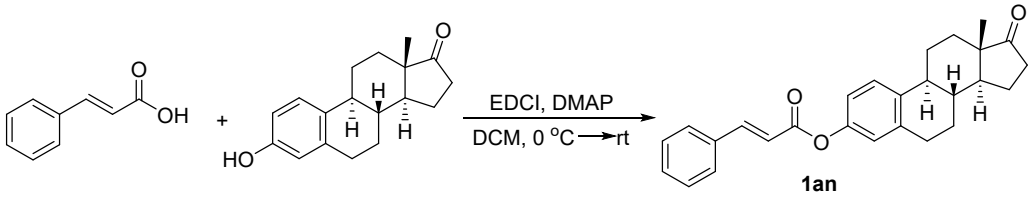
Synthesis of Substrate 1am[3]:



To a 50 mL round bottom flask, cinnamic acid (6.75 mmol, 1.0 g), nerol (8.10 mmol, 1.3 g) and DCM (15 mL) was added under N_2 atmosphere. After the solution was stirred at 0 °C for 5 min, EDCI (8.10 mmol, 1.6 g) and DMAP (0.675 mmol, 82.0 mg) were added, then the reaction mixture was stirred at room temperature. After completion of the reaction as indicated by TLC, anhydrous Na_2SO_4 was added. After filtration, the filtrate was concentrated in vacuo to afford crude product which was further purified by column chromatography (SiO_2, PE: EA = 100:1) to afford the desired product **1am**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.52-7.50 (m, 2H), 7.38-7.36 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 5.44 (t, *J* = 7.2 Hz, 1H), 5.12 (t, *J* = 7.0 Hz, 1H), 4.70 (d, *J* = 7.2 Hz, 2H), 2.18-2.10 (m, 4H), 1.79 (d, *J* = 0.9 Hz, 3H), 1.69 (s, 3H), 1.61 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 144.6, 142.7, 134.4, 132.1, 130.2, 128.8, 128.0, 123.5, 119.2, 118.2, 61.1, 32.2, 26.6, 25.7, 23.5, 17.6 ppm.

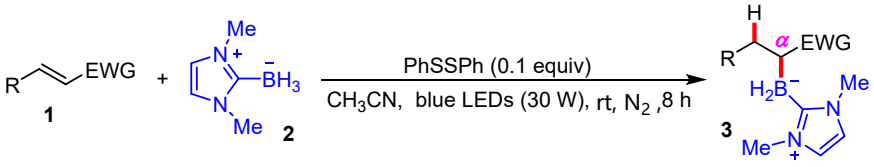
Synthesis of Substrate 1an[3]:



To a 50 mL round bottom flask, cinnamic acid (6.75 mmol, 1.0 g), estrone (8.10 mmol, 2.2 g) and DCM (15 mL) was added under N_2 atmosphere. After the solution was stirred at 0 °C for 5 min, EDCI (8.10 mmol, 1.6 g) and DMAP (0.675 mmol, 82.0 mg) were added, then the reaction mixture was stirred at room temperature. After completion of the reaction as indicated by TLC, anhydrous Na_2SO_4 was added. After filtration, the filtrate was concentrated in vacuo to afford crude product which was further purified by column chromatography (SiO_2, PE: EA = 8:1) to afford the desired product **1am**.

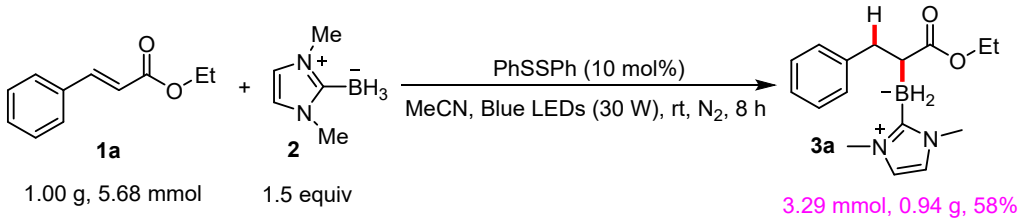
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 16.0 Hz, 1H), 7.57 (s, 2H), 7.41 (s, 3H), 7.30 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.90 (s, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 2.93-2.91 (m, 2H), 2.53-2.47 (m, 1H), 2.42-2.39 (m, 1H), 2.31-2.27 (m, 1H), 2.16-1.95 (m, 4H), 1.62-1.45 (m, 6H), 0.91 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 148.6, 146.4, 138.0, 137.3, 134.2, 130.7, 129.0, 128.3, 126.4, 121.6, 118.8, 117.3, 50.4, 47.9, 44.1, 38.0, 35.9, 31.5, 29.4, 26.3, 25.7, 21.6, 13.8 ppm.

(3) General procedure for this regioselective hydroborylation of α,β-unsaturated carbonyl compounds with NHC-BH_3.



A dry glass tube (35 mL, 18 x 180 mm) equipped with a rubber plug and magnetic stir bar was charged with the electron-deficient alkenes **1** (0.30 mmol), NHC-BH_3 **2** (0.45 mmol), PhSSPh (6.6 mg, 10 mol%), and CH_3CN (2 mL). The tube was evacuated and backfilled with N_2 for three times, then was tied up nitrogen balloons and placed approximately 5 cm from a 30 W blue LEDs light. The mixture was stirred at around 30 °C for 8 hours. The resulting mixture was then concentrated in vacuo to afford crude product which was further purified by column chromatography (SiO_2) to afford the desired product.

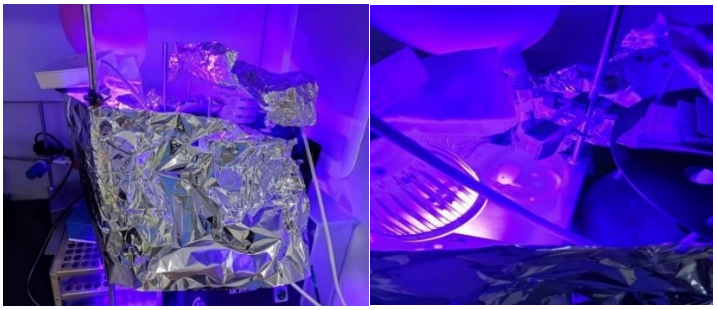
(4) Gram Scale Reaction



1a
1.00 g, 5.68 mmol

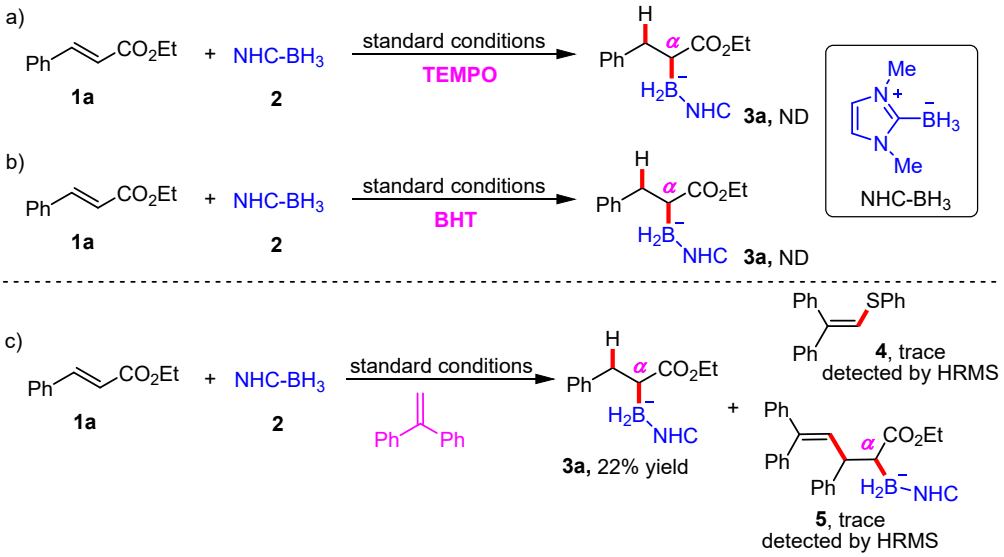
2
1.5 equiv

3.29 mmol, 0.94 g, 58%



Add **1a** (1.00 g, 5.7 mmol), NHC-BH_3 (937 mg, 8.5 mmol), PhSSPh (124 mg, 10 mol%), and CH_3CN (50 mL) to an eggplant flask (250 mL), then pump nitrogen three times, and finally tie up nitrogen ballon and placed approximately 3 cm from a 30 W blue LEDs light. The mixture was stirred at around 30 °C for 8 hours. The resulting mixture was then concentrated in vacuo to afford crude product which was further purified by column chromatography (SiO_2) to afford the desired product **3a** as pale-yellow oil; yield: 58% (0.94 g, 3.3 mmol).

(5) Control Experiments



Three dry glass tubes (35 mL, 18 x 180 mm) equipped with rubber plugs and magneticstir bar was charged with the cinnamate **1a** (0.30 mmol), NHC-borane **2** (0.45 mmol), PhSSPh (6.6 mg, 10 mol%), and MeCN (2 mL), respectively. Under the standard conditions, (a) adding 4.0 equiv. of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) into the reaction system; (b) adding 4.0 equiv. of BHT (2,6-di-tert-butyl-4-methylphenol) into the reaction system; (c) adding 4.0 equiv. of radical scavenger 1,1-diphenylethylene into the reaction system. After the reactions were completed, the desired product **3a** could not be observed in reaction (a) and (b). While, product **3a** could be isolated in 22% yield in reaction (c). Additionally, adducts **4** and **5** was detected in reaction (c) by HRMS.

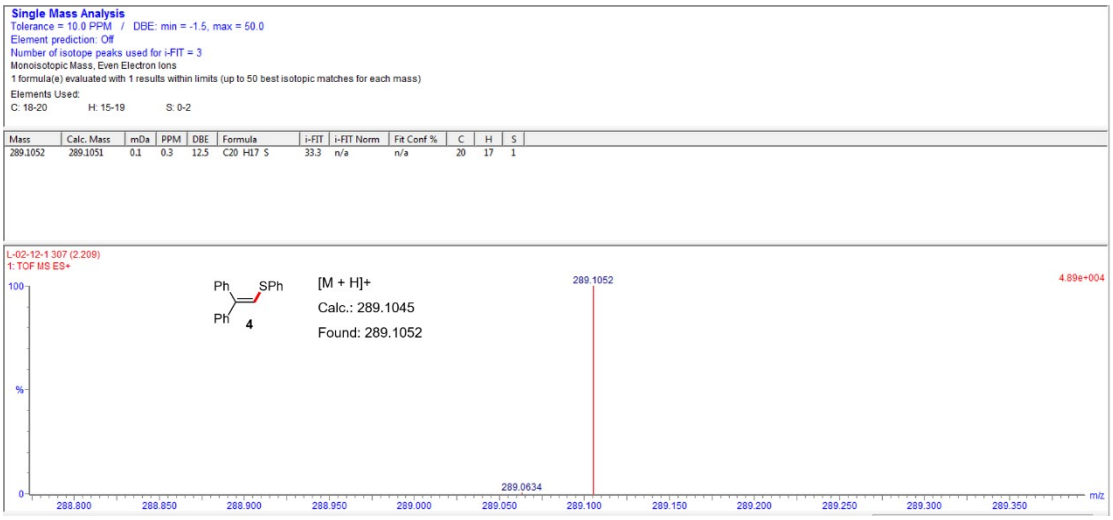


Fig. S1 HRMS spectrum of compound **4**.

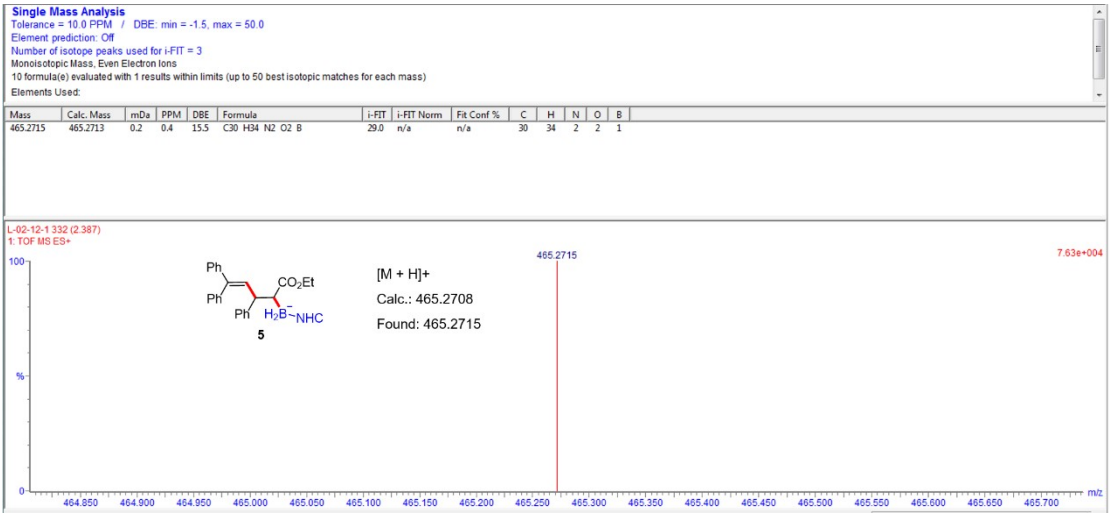


Fig. S2 HRMS spectrum of compound **5**.

(6) Determination of Quantum yield

According to previous reported procedures,[4-6] the actinometry measurements were determined by standard ferrioxalate actinometry.

Preparation of potassium ferrioxalate solution (0.15 M): Potassium ferrioxalate trihydrate (0.737 g) and 95~98% H_2SO_4 (27 μL) were added to a 10 mL volumetric flask and filled to the mark with distilled water. The solution was stored in the dark.

Preparation of buffer solution: Dissolving 5.0 mg of phenanthroline and 1.13 g of sodium acetate in 5.0 mL of 0.5 M H_2SO_4 solution. The solution was stored in the dark.

The actinometry measurements: To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated with 30W blue LEDs (λ ≈ 440 nm) for 90.0 seconds. After irradiation, 0.35 mL of buffer solution was added to the cuvette. The solution was then stored in the dark for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. In a similar method, a blank solution (a non-irradiated sample) was also prepared. The absorbance of irradiated and non-irradiated samples at λ = 510 nm was measured by UV-Vis spectrophotometry. Conversion was calculated using **Eq 1**,

$$mol\ of\ Fe^{2+} = \frac{V*\Delta A}{l*\varepsilon} = \frac{(0.00235\ L) * 2.532}{1\ cm*11100\ \frac{L}{mol}\ cm^{-1}} = 5.361*10^{-7}\ mol \qquad \textbf{(1)}$$

Where:

V = the total volume () of the solution after addition of phenanthroline;

ΔA = the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions;

l = the path length (**l** = 1 cm);

ε = the molar absorptivity at 510 nm (**ε** = 11100 $L*mol^{-1}*cm^{-1}$).

Then, the photon flux can be calculated using **Eq 2**,

$$Photon\ flux = \frac{\text{mol of } Fe^{2+}}{\Phi * t * f} = \frac{\text{mol of } Fe^{2+}}{\Phi * t * (1-10^{-A})} = \frac{5.361*10^{-7}\ \text{mol}}{1.01*90\text{s}*0.999} = 5.904*10^{-9}\ \text{einstein/s} \quad \textbf{(2)}$$

Where:

Φ = the quantum yield for the ferrioxalate actinometer (**Φ** = 1.01 at λ = 436 nm);

t = irradiation time (**t** = 90 s);

A = the measured absorbance of the ferrioxalate actinometer solution at 440 nm (**A** = 3.000).

Reaction quantum yield: A dry glass tube equipped with a rubber plug and magnetic stir bar was charged with the ethyl cinnamate **1a** (0.20 mmol), NHC-BH_3 **2** (0.30 mmol), PhSSPh (4.4 mg, 10 mol%), and CH_3CN (2 mL). The tube was evacuated and backfilled with N_2 for three times, then was tied up nitrogen balloons. The reaction mixture was stirred at room temperature (around 30 °C) for 60 min under 30W blue LEDs irradiation (λ ≈ 440 nm). The solvent was removed in vacuo and the yield of product **3a** was determined by ^1H NMR based on 1,3,5-trimethoxybenzene as internal standard to be 17% (0.034 mmol). The quantum yield was determined using **Eq 3**,

$$\Phi = \frac{\text{mol of product}}{\text{flux} * t * f} = \frac{\text{mol of product}}{\text{flux} * t * (1-10^{-A})} = \frac{0.034*10^{-3}}{5.904*10^{-9}*3600*0.332} = 4.8 \quad \textbf{(3)}$$

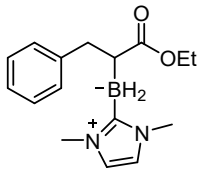
Where:

A = the measured absorbance of the reaction solution at 440 nm (**A** = 0.175).

The quantum yield (Φ) of this photoreaction was determined to be 4.8, which suggesting the reaction is proceed in a radical-chain mechanism.

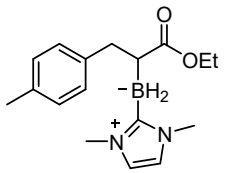
4. Analytical Data for Products

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-ethoxy-1-oxo-3-phenylpropan-2-yl)dihydroborate[7] (3a)



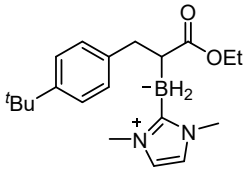
Yellow oil (95%, 81.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.17 (m, 4H), 7.12-7.06 (m, 1H), 6.79 (s, 2H), 3.84-3.79 (m, 2H), 3.71 (s, 6H), 3.12 (dd, *J* = 14.3, 10.2 Hz, 1H), 2.71 (dd, *J* = 14.3, 4.2 Hz, 1H), 2.18 (brs, 1H), 0.98 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6 (*C*O_2Et), 143.8, 127.5, 126.8, 124.0, 119.4, 57.5 (*C*$H_2$$CH_3$), 38.1 (N*C*$H_3$), 34.9 (Ar*C*$H_2$-), 13.3 ($CH_2$*C*$H_3$) ppm.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-ethoxy-1-oxo-3-(*p*-tolyl)propan-2-yl)dihydroborate[7] (3b)



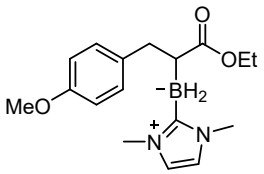
Yellow oil (96%, 86.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.80 (s, 2H), 3.84-3.75 (m, 2H), 3.73 (s, 6H), 3.08 (dd, *J* = 14.3, 10.3 Hz, 1H), 2.67 (dd, *J* = 14.3, 4.1 Hz, 1H), 2.27 (s, 3H), 2.17 (brs, 1H), 0.97 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7 (*C*O_2Et), 140.7, 133.2, 127.5, 127.3, 119.3, 57.5 (*C*$H_2$$CH_3$), 37.6 (N*C*$H_3$), 35.0 (Ar*C*$H_2$-), 20.3 (Ph-*C*$H_3$), 13.3 ($CH_2$*C*$H_3$) ppm.

(3-(4-(*tert*-Butyl)phenyl)-1-ethoxy-1-oxopropan-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3c)



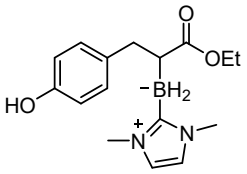
Yellow oil (93%, 94.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.79 (s, 2H), 3.87-3.77 (m, 2H), 3.72 (s, 6H), 3.11 (dd, *J* = 14.3, 10.2 Hz, 1H), 2.68 (dd, *J* = 14.3, 4.4 Hz, 1H), 2.19 (brs, 1H), 1.27 (s, 9H), 0.98 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7 (*C*O_2Et), 146.5, 140.7, 127.0, 123.7, 119.3, 57.5 (*C*$H_2$$CH_3$), 37.5 (N*C*$H_3$), 35.0 (Ar*C*$H_2$-), 33.2 (*C*$(CH_3)_3$), 30.4 (C(*C*$H_3$)$_3$), 13.3 ($CH_2$*C*$H_3$) ppm. HRMS (ESI) (m/z): calculated for $C_{20}H_{31}BN_2NaO_2^+$ $[M + Na]^+$ 365.2376; found, 365.2379.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-ethoxy-3-(4-methoxyphenyl)-1-oxopropan-2-yl)dihydroborate[7] (3d)



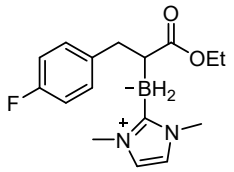
Yellow oil (92%, 87.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.12 (m, 2H), 6.81 (s, 2H), 6.77-6.73 (m, 2H), 3.85-3.78 (m, 2H), 3.75 (s, 3H), 3.74 (s, 6H), 3.05 (dd, *J* = 14.3, 10.2 Hz, 1H), 2.66 (dd, *J* = 14.3, 4.2 Hz, 1H), 2.15 (brs, 1H), 0.98 (t, *J* = 8.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7 (*C*O_2Et), 156.1, 136.1, 128.3, 119.3, 112.2, 57.5 (*C*$H_2$$CH_3$), 54.2 (O*C*$H_3$), 37.7 (N*C*$H_3$), 35.0 (Ar*C*$H_2$-), 13.3 ($CH_2$*C*$H_3$) ppm.

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



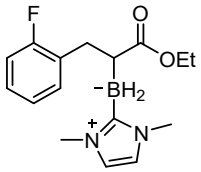
Yellow oil (45%, 40.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.4 Hz, 2H), 6.77 (s, 2H), 6.59 (d, *J* = 8.4 Hz, 2H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.7 (s, 6H), 3.03-2.96 (m, 1H), 2.65-2.61 (m, 1H), 2.20 (brs, 1H), 1.01 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.6 (*C*O_2Et), 152.7, 135.2, 128.3, 119.4, 113.8, 57.9 (*C*$H_2$$CH_3$), 37.1 (N*C*$H_3$), 35.0 (Ar*C*$H_2$-), 13.3 ($CH_2$*C*$H_3$) ppm. HRMS (ESI) (m/z): calculated for $C_{16}H_{23}BN_2NaO_3^+$ $[M + Na]^+$ 325.1708; found, 325.1702.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-ethoxy-3-(4-fluorophenyl)-1-oxopropan-2-yl)dihydroborate[8] (3f)



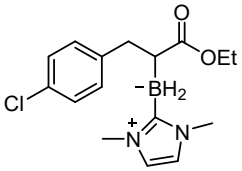
Yellow oil (92%, 86.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.13 (m, 2H), 6.90-6.85 (m, 2H), 6.82 (s, 2H), 3.84-3.76 (m, 2H), 3.74 (s, 6H), 3.07 (dd, *J* = 14.3, 10.3 Hz, 1H), 2.69 (dd, *J* = 14.3, 4.3 Hz, 1H), 2.14 (brs, 1H), 0.97 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4 (*C*O_2Et), 159.8 (d, J_{CF} = 240.0 Hz), 139.5, 128.8 (d, J_{CF} = 8.0 Hz), 119.4, 113.4 (d, J_{CF} = 21.0 Hz), 57.5 (*C*$H_2$$CH_3$), 37.3 (N*C*$H_3$), 35.9 (Ar*C*$H_2$-), 13.3 ($CH_2$*C*$H_3$) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.2 (s, 1F) ppm.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-ethoxy-3-(2-fluorophenyl)-1-oxopropan-2-yl)dihydroborate (3g)



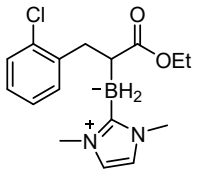
Yellow oil (91%, 82.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.27 (m, 4H), 6.82 (s, 2H), 3.86-3.77 (m, 2H), 3.74 (s, 6H), 3.16 (dd, *J* = 14.3 Hz, 10.2 Hz, 1H), 2.78 (dd, *J* = 14.3, 4.4 Hz, 1H), 2.18 (brs, 1H), 0.98 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2 (*C*O_2Et), 160.2 (d, J_{CF} = 242.1 Hz), 130.0 (d, J_{CF} = 5.6 Hz), 125.5 (d, J_{CF} = 8.1 Hz), 122.3 (d, J_{CF} = 3.4 Hz), 119.4, 113.4 (d, J_{CF} = 22.5 Hz), 57.7 (*C*$H_2$$CH_3$), 37.9 (N*C*$H_3$), 35.0 (Ar*C*$H_2$-), 13.2 ($CH_2$*C*$H_3$) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.7 (s, 1F) ppm. HRMS (ESI) (m/z): calculated for $C_{16}H_{22}BFKN_2O_2^+$ $[M + K]^+$ 343.1395; found, 343.1356.

(3-(4-Chlorophenyl)-1-ethoxy-1-oxopropan-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate[7] (3h)



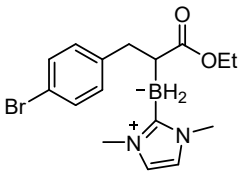
Yellow oil (92%, 88.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.13 (m, 4H), 6.82 (s, 2H), 3.84-3.76 (m, 2H), 3.74 (s, 6H), 3.06 (dd, *J* = 14.3, 10.3 Hz, 1H), 2.69 (dd, *J* = 14.3, 4.3 Hz, 1H), 2.14 (brs, 1H), 0.97 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3 (*C*O_2Et), 142.3, 129.5, 128.9, 126.8, 119.3, 57.6 (*C*$H_2$$CH_3$), 37.8 (N*C*$H_3$), 35.0 (Ar*C*$H_2$-), 13.3 ($CH_2$*C*$H_3$) ppm.

(3-(2-Chlorophenyl)-1-ethoxy-1-oxopropan-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (3i)



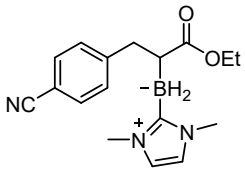
Yellow oil (90%, 86.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.27-7.24 (m, 1H), 7.12-7.02 (m, 2H), 6.83 (s, 2H), 3.85 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 6H), 3.13 (dd, *J* = 14.3, 10.6 Hz, 1H), 2.84 (dd, *J* = 14.3, 3.5 Hz, 1H), 1.01 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3 (*C*O_2Et), 141.0, 132.9, 129.9, 128.0, 125.5, 125.2, 119.3, 57.6 (*C*$H_2$$CH_3$), 35.6 (N*C*$H_3$), 35.0 (Ar*C*$H_2$-), 13.3 ($CH_2$*C*$H_3$) ppm. HRMS (ESI) (m/z): calculated for $C_{16}H_{22}BClN_2NaO_2^+$ $[M + Na]^+$ 343.1361; found, 343.1367.

(3-(4-Bromophenyl)-1-ethoxy-1-oxopropan-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (3j)



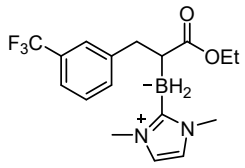
Yellow oil (76%, 83.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.82 (s, 2H), 3.85-3.76 (m, 2H), 3.74 (s, 6H), 3.05 (dd, *J* = 14.3, 10.3 Hz, 1H), 2.67 (dd, *J* = 14.3, 4.3 Hz, 1H), 2.13 (brs, 1H), 0.97 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100MHz, $CDCl_3$) δ 180.8 (*C*O_2Et), 142.9, 129.8, 129.4, 119.4, 117.6, 58.0 (*C*$H_2$$CH_3$), 37.5 (N*C*$H_3$), 35.0 (Ar*C*$H_2$-), 13.3 ($CH_2$*C*$H_3$) ppm. HRMS (ESI) (m/z): calculated for $C_{16}H_{22}BBrN_2NaO_2^+$ $[M + Na]^+$ 387.0855; found, 387.0844.

(3-(4-Cyanophenyl)-1-ethoxy-1-oxopropan-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate[7] (3k)



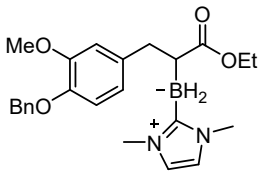
Yellow oil (68%, 63.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.84 (s, 2H), 3.82-3.72 (m, 2H), 3.75 (s, 6H), 3.15 (dd, *J* = 14.4, 10.3 Hz, 1H), 2.78 (dd, *J* = 14.4, 4.3 Hz, 1H), 2.16 (brs, 1H), 0.95 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9 (*C*O_2Et), 149.8, 130.7, 128.4, 119.4, 118.6, 107.7, 56.9 (*C*$H_2$$CH_3$), 37.9 (N*C*$H_3$), 35.0 (Ar*C*$H_2$-), 13.3 ($CH_2$*C*$H_3$) ppm.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-ethoxy-1-oxo-3-(3-(trifluoromethyl)phenyl)propan-2-yl)dihydroborate (3l)



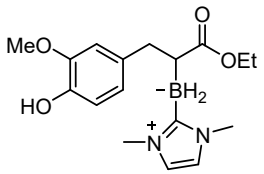
Yellow oil (65%, 69.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.27 (m, 4H), 6.82 (s, 2H), 3.86-3.77 (m, 2H), 3.74 (s, 6H), 3.16 (dd, *J* = 14.3, 10.2 Hz, 1H), 2.78 (dd, *J* = 14.3, 4.4 Hz, 1H), 2.18 (brs, 1H), 0.98 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1 (*C*O_2Et), 145.6, 132.1, 129.9 (q, J_{CF} = 31.5 Hz), 128.1, 125.1 (q, J_{CF} = 3.7 Hz), 124.5 (q, J_{CF} = 270.5 Hz, *C*F_3), 121.8 (q, J_{CF} = 3.8 Hz), 120.4, 58.6 (*C*$H_2$$CH_3$), 38.9 (N*C*$H_3$), 36.0 (Ar*C*$H_2$-), 14.2 ($CH_2$*C*$H_3$) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4 (s, 3F) ppm. HRMS (ESI) (m/z): calculated for $C_{17}H_{22}BF_3N_2NaO_2^+$ $[M + Na]^+$ 377.1624; found, 377.1623.

(3-(4-(Benzyloxy)-3-methoxyphenyl)-1-ethoxy-1-oxopropan-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate[7] (3m)



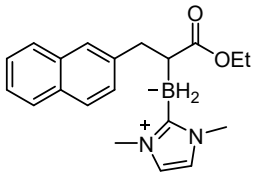
Yellow oil (89%, 117.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 6.80 (s, 1H), 6.78 (s, 2H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.67 (d, *J* = 8.2 Hz, 1H), 5.09 (s, 2H), 3.88-3.76 (m, 5H), 3.72 (s, 6H), 3.05 (dd, *J* = 14.4, 10.2 Hz, 1H), 2.65 (dd, *J* = 14.4, 4.3 Hz, 1H), 2.15 (brs, 1H), 0.98 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7 (*C*O_2Et), 148.1, 144.7, 137.5, 136.7, 127.4, 126.6, 126.3, 119.3, 119.2, 113.0, 111.6, 69.8 (O*C*H_2Ph), 57.5 (*C*$H_2$$CH_3$), 54.1 (O*C*$H_3$), 37.7 (N*C*$H_3$), 35.4 (Ar*C*$H_2$-), 13.4 ($CH_2$*C*$H_3$) ppm.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-ethoxy-3-(4-hydroxy-3-methoxyphenyl)-1-oxopropan-2-yl)dihydroborate (3n)



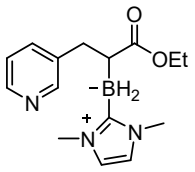
Yellow oil (68%, 71.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 2H), 6.76-6.66 (m, 3H), 3.86-3.76 (m, 5H), 3.73 (s, 6H), 3.04 (dd, *J* = 14.4, 10.3 Hz, 1H), 2.64 (dd, *J* = 14.3, 4.1 Hz, 1H), 2.15 (brs, 1H), 0.98 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100MHz, $CDCl_3$) δ 180.7 (*C*O_2Et), 144.9, 142.0, 136.0, 119.8, 119.3, 112.7, 110.4, 57.5 (*C*$H_2$$CH_3$), 54.8 (O*C*$H_3$), 37.8 (N*C*$H_3$), 35.0 (Ar*C*$H_2$-), 13.3 ($CH_2$*C*$H_3$) ppm. HRMS (ESI) (m/z): calculated for $C_{17}H_{25}BN_2NaO_4^+$ [M + Na] $^+$ 355.1805; found, 355.1800.

(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(1-ethoxy-3-(naphthalen-2-yl)-1-oxopropan-2-yl)dihydroborate[8] **(3o)**



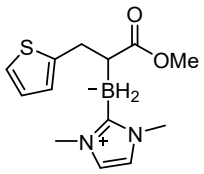
White solid (96%, 96.9 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (t, *J* = 7.0 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.64 (s, 1H), 7.40-7.33 (m, 3H), 6.74 (s, 2H), 3.83-3.74 (m, 2H), 3.72 (s, 6H), 3.27 (dd, *J* = 14.3, 10.2 Hz, 1H), 2.88 (dd, *J* = 14.4, 4.2 Hz, 1H), 2.29 (brs, 1H), 0.95 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5 (*C*O_2Et), 141.4, 132.6, 130.7, 127.0, 126.4, 126.4, 126.2, 125.2, 124.4, 123.5, 119.3, 57.5 (*C*$H_2$$CH_3$), 38.3 (N*C*$H_3$), 35.0 (Ar*C*$H_2$-), 13.3 ($CH_2$*C*$H_3$) ppm.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-ethoxy-1-oxo-3-(pyridin-3-yl)propan-2-yl)dihydroborate[7] (3p)



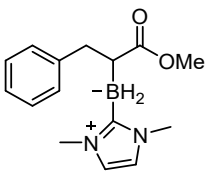
Yellow oil (63%, 54.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 45.6 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.14 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.84 (s, 2H), 3.84-3.76 (m, 2H), 3.74 (s, 6H), 3.12-3.06 (m, 1H), 2.75-2.70 (m, 1H), 2.15 (s, 1H), 0.97 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1 (*C*O_2Et), 149.1, 145.5, 138.9, 135.1, 121.9, 119.5, 57.6 (*C*$H_2$$CH_3$), 35.2, 35.0, 13.3 ($CH_2$*C*$H_3$) ppm.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-methoxy-1-oxo-3-(thiophen-2-yl)propan-2-yl)dihydroborate[7] (3q)



Yellow oil (36%, 30.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 5.1 Hz, 1H), 6.84 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.82 (s, 2H), 6.75 (d, *J* = 3.4 Hz, 1H), 3.75 (s, 6H), 3.43 (s, 3H), 3.31 (dd, *J* = 15.3, 11.1 Hz, 1H), 2.90 (dd, *J* = 15.3, 3.9 Hz, 1H), 2.20 (brs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.5 (*C*O_2Me), 148.0, 126.3, 123.5, 122.2, 120.4, 50.5 (*C*O_2*Me*), 36.0 (N*C*H_3), 33.3 (Ar*C*H_2-) ppm. HRMS (ESI) (m/z): calculated for $C_{13}H_{19}BN_2NaO_2S^+$ $[M + Na]^+$ 301.1153; found, 301.1122.

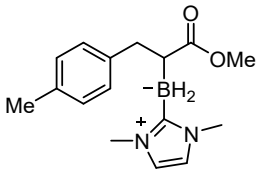
(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-methoxy-1-oxo-3-phenylpropan-2-yl)dihydroborate[7] (3r)



Yellow oil (93%, 76.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.19 (m, 4H), 7.12-7.05 (m, 1H), 6.80 (s, 2H), 3.72 (s, 6H), 3.37 (s, 3H), 3.11 (dd, *J* = 14.3, 10.1 Hz, 1H),

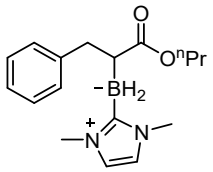
2.71 (dd, J = 14.3, 4.3 Hz, 1H), 2.20 (brs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.9 (CO$_2$Me), 143.7, 127.4, 126.9, 124.0, 119.4, 49.3 (CO$_2$*Me*), 38.1 (N*CH$_3$*), 35.0 (Ar*CH$_2$*-) ppm.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-methoxy-1-oxo-3-(*p*-tolyl)propan-2-yl)dihydroborate[7] (3s)



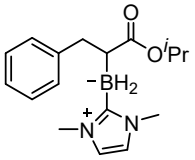
Yellow oil (91%, 78.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 7.9 Hz, 2H), 7.00 (d, J = 7.8 Hz, 2H), 6.80 (s, 2H), 3.73 (s, 6H), 3.37 (s, 3H), 3.07 (dd, J = 14.3, 10.3 Hz, 1H), 2.66 (dd, J = 14.3, 4.2 Hz, 1H), 2.27 (s, 3H), 2.18 (brs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.9 (CO$_2$Me), 140.6, 133.2, 127.6, 127.3, 119.4, 49.3 (CO$_2$*Me*), 37.6 (N*CH$_3$*), 35.0 (Ar*CH$_2$*-), 20.0 (Ph-*CH$_3$*) ppm.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-oxo-3-phenyl-1-propoxypropan-2-yl)dihydroborate[7] (3t)



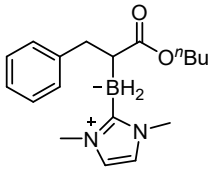
Yellow oil (90%, 81.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.19 (m, 4H), 7.10-7.06 (m, 1H), 6.79 (s, 2H), 3.80-3.76 (m, 1H), 3.73 (s, 6H), 3.69-3.63 (m, 1H), 3.12 (dd, J = 14.3, 10.2 Hz, 1H), 2.72 (dd, J = 14.3, 4.3 Hz, 1H), 2.20 (brs, 1H), 1.41-1.36 (m, 2H), 0.76 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6 (CO$_2$^{n}Pr), 143.8, 127.5, 126.8, 123.9, 119.3, 63.4 (CO$_2$*CH$_2$*CH$_2$CH$_3$), 38.1 (N*CH$_3$*), 35.0 (Ph*CH$_2$*-), 21.1 (CO$_2$CH$_2$*CH$_2$*CH$_3$), 9.4 (CO$_2$CH$_2$CH$_2$*CH$_3$*) ppm.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-isopropoxy-1-oxo-3-phenylpropan-2-yl)dihydroborate[7] (3u)



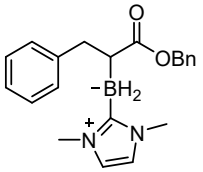
Yellow oil (79%, 71.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.19 (m, 4H), 7.10-7.05 (m, 1H), 6.79 (s, 2H), 4.75-4.65 (m, 1H), 3.74 (s, 6H), 3.14-3.08 (m, 1H), 2.74-2.69 (m, 1H), 2.18 (brs, 1H), 1.01 (d, J = 6.2 Hz, 3H), 0.87 (d, J = 6.3 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2 ($CO_2{}^i$Pr), 143.9, 127.5, 126.7, 123.9, 119.3, 64.0 ($CO_2CH(CH_3)_2$), 38.2 (NCH_3), 35.0 (PhCH_2-), 21.1 ($CO_2CH(CH_3)_2$), 20.7 ($CO_2CH(CH_3)_2$) ppm.

(1-Butoxy-1-oxo-3-phenylpropan-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate[7] (3v)



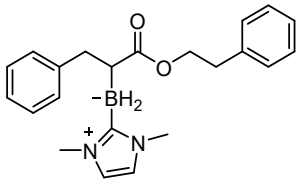
Yellow oil (96%, 89.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.19 (m, 4H), 7.12-7.06 (m, 1H), 6.80 (s, 2H), 3.85-3.79 (m, 1H), 3.73 (s, 6H), 3.72-3.69 (m, 1H), 3.11 (dd, J = 14.4, 10.2 Hz, 1H), 2.72 (dd, J = 14.4, 4.3 Hz, 1H), 2.20 (brs, 1H), 1.37-1.33 (m, 2H), 1.23-1.13 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7 ($CO_2{}^n$Bu), 143.8, 127.5, 126.8, 123.9, 119.3, 61.6 ($CO_2CH_2CH_2CH_2CH_3$), 38.1 (NCH_3), 35.0 (PhCH_2-), 30.3 ($CO_2CH_2CH_2CH_2CH_3$), 18.7 ($CO_2CH_2CH_2CH_2CH_3$), 12.8 ($CO_2CH_2CH_2CH_2CH_3$) ppm.

(1-(Benzyloxy)-1-oxo-3-phenylpropan-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborat[7] (3w)



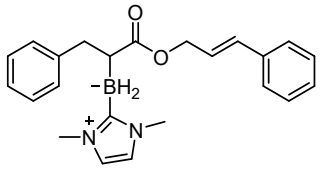
Yellow oil (35%, 36.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.18 (m, 7H), 7.14-7.07 (m, 3H), 6.67 (s, 2H), 4.9-4.8 (m, 2H), 3.62 (s, 6H), 3.15-3.08 (m, 1H), 2.76 (m, 1H), 2.28 (brs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3 (CO_2CH_2Ph), 143.7, 136.3, 127.5, 127.2, 126.9, 126.9, 126.4, 124.0, 119.2, 63.5 (CO_2CH_2Ph), 38.2 (NCH_3), 34.9 (PhCH_2-) ppm.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-oxo-1-phenethoxy-3-phenylpropan-2-yl)dihydroborate (3x)



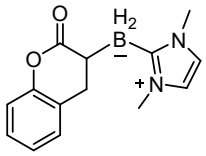
White solid (92%, 100.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.17 (m, 7H), 7.12 - 7.07 (m, 3H), 6.73 (s, 2H), 4.11-4.05 (m, 1H), 3.88-3.82 (m, 1H), 3.66 (s, 6H), 3.15-3.08 (m, 1H), 2.75-2.64 (m, 3H), 2.20 (brs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5 ($CO_2CH_2CH_2Ph$), 143.7, 137.6, 127.9, 127.5, 127.3, 126.8, 125.2, 124.0, 119.3, 62.6 ($CO_2CH_2CH_2Ph$), 38.1 (NCH_3), 34.9, 34.3 ppm. HRMS (ESI) (m/z): calculated for $C_{22}H_{27}BN_2NaO_2^+$ $[M + Na]^+$ 385.2058; found, 385.2062.

(1-(Cinnamyloxy)-1-oxo-3-phenylpropan-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate[7] (3y)



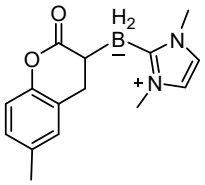
Yellow oil (69%, 77.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H), 7.24-7.17 (m, 5H), 7.10-7.07 (m, 1H), 6.69 (s, 2H), 6.41 (d, J = 15.9 Hz, 1H), 6.04-5.97 (m, 1H), 4.46-4.40 (m, 2H), 3.69 (s, 6H), 3.15 (m, 1H), 2.75 (m, 1H), 2.26 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2 (CO_2R), 143.7, 135.5, 131.5, 127.5, 126.9, 126.7, 125.4, 124.0, 123.7, 119.3, 62.2 (CO_2CH_2-), 38.1 (NCH_3), 35.0 ($PhCH_2$-) ppm.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-oxochroman-3-yl)dihydroborate[7] (3z)



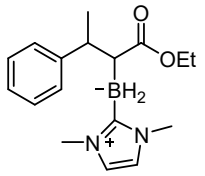
White solid (96%, 73.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.12 (m, 2H), 7.0 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.79 (s, 2H), 3.69 (s, 6H), 3.25 (s, 1H), 2.76-2.73(m, 1H), 2.38 (brs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0 (CO_2R), 151.3, 127.4, 125.8, 123.5, 122.3, 119.0, 114.1, 35.6 (NCH_3), 29.6 ($PhCH_2$-) ppm.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(6-methyl-2-oxochroman-3-yl)dihydrobor ate[7] **(3aa)**



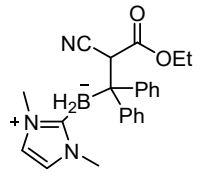
White solid (96%, 77.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97-6.93 (m, 2H), 6.82 (s, 1H), 6.79 (s, 2H), 3.69 (s, 6H), 3.23-3.21 (m, 1H), 2.72-2.68 (m, 1H), 2.36 (brs, 1H), 2.30 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5 (*C*O_2R), 149.2, 131.6, 128.0, 126.2, 122.6, 119.6, 114.1, 35.0 (N*C*H_3), 29.6 (Ph*C*H_2-), 19.8 (Ph*C*H_3) ppm.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-ethoxy-1-oxo-3-phenylbutan-2-yl)dihyd roborate (3ab)



Yellow oil (79%, 71.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.17 (m, 4H), 7.08-7.04 (m, 1H), 6.80 (s, 2H), 3.76 (s, 6H), 3.55-3.50 (m, 2H), 3.13-3.08 (dd, *J* = 10.5, 7.0 Hz, 1H), 2.15 (brs, 1H), 1.33 (d, *J* = 7.0 Hz, 3H), 0.74 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.9 (*C*O_2Et), 150.6, 127.7, 127.0, 124.9, 120.3, 58.1 (*C*$H_2$$CH_3$), 43.2, 35.9, 22.1, 14.0 (CH_2*C*H_3) ppm. HRMS (ESI) (m/z): calculated for $C_{17}H_{25}BN_2O_2Na^+$ $[M + Na]^+$ 323.1901; found, 323.1907.

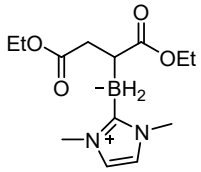
(2-Cyano-3-ethoxy-3-oxo-1,1-diphenylpropyl)(1,3-dimethyl-1H-imidazol-3-ium-2 -yl)dihydroborate[7] **(3ac)**



Yellow oil (96%, 111.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.3 Hz, 2H), 7.50 (d, *J* = 7.1 Hz, 2H), 7.28-7.09 (m, 6H), 6.81 (s, 2H), 4.70 (s, 1H), 3.93-3.77 (m, 2H), 3.64 (s, 6H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3

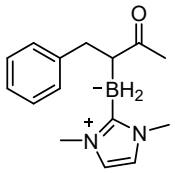
(*C*O_2Et), 144.5, 141.9, 130.6, 128.2, 127.9, 127.6, 126.4, 126.0, 125.3, 121.4, 60.6 (*CH*CO_2Et), 55.7 (*CH_2*CH_3), 36.7 (N*CH_3*), 13.8 (CH_2*CH_3*) ppm.

(1,4-Diethoxy-1,4-dioxobutan-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3ad)



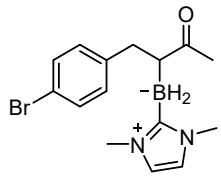
Yellow oil (36%, 30.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 2H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.95-3.83 (m, 2H), 3.76 (m, 6H), 2.85-2.78 (dd, *J* = 17.0, 10.2 Hz, 1H), 2.39 (dd, *J* = 17.0, 4.7 Hz, 1H), 2.24 (brs, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2 (*C*O_2Et), 175.1 (*C*O_2Et), 120.3, 59.8 (*CH_2*CH_3), 58.7 (*CH_2*CH_3), 37.5 (N*CH_3*), 35.9 (N*CH_3*), 14.3 (CH_2*CH_3*), 14.2 (CH_2*CH_3*) ppm. HRMS (ESI) (m/z): calculated for $C_{13}H_{23}BN_2O_4Na^+$ $[M + Na]^+$ 305.1643; found, 305.1647.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(3-oxo-1-phenylbutan-2-yl)dihydroborate[7] **(3ae)**



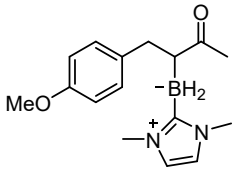
Yellow oil (44%, 33.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.5 Hz, 2H), 7.13-7.07 (m, 3H), 6.79 (s, 2H), 3.71 (s, 6H), 3.10 (dd, *J* = 14.5, 9.7 Hz, 1H), 2.65 (dd, *J* = 14.4, 4.6 Hz, 1H), 2.58 (brs, 1H), 2.00 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.4 (*C*OMe), 144.3, 128.2, 127.9, 125.0, 120.6, 38.2, 36.1, 28.2 (*CO**Me***) ppm. HRMS (ESI) (m/z): calculated for $C_{15}H_{21}BN_2ONa^+$ $[M + Na]^+$ 279.1639; found, 279.1621.

(1-(4-Bromophenyl)-3-oxobutan-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3af)



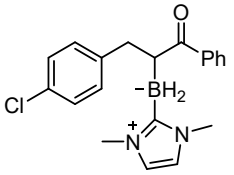
Yellow oil (61%, 61.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.82 (s, 2H), 3.71 (s, 6H), 3.02 (dd, *J* = 14.6, 9.9 Hz, 1H), 2.60-2.55 (m, 1H), 2.53 (brs, 1H), 1.97 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.0 (*C*OMe), 143.4, 130.8, 130.1, 120.6, 118.6, 37.6, 36.1, 28.4 (*CO**Me***) ppm. HRMS (ESI) (m/z): calculated for $C_{15}H_{21}BBrN_2O^+$ $[M + H]^+$ 335.0925; found, 335.0927.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-(4-methoxyphenyl)-3-oxobutan-2-yl)dihydroborate (3ag)



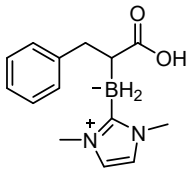
Yellow oil (82%, 70.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.6 Hz, 2H), 6.81 (s, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 3.74 (s, 3H), 3.71 (s, 6H), 3.02 (dd, *J* = 14.7, 10.0 Hz, 1H), 2.61-2.56 (m, 1H), 2.54 (brs, 1H), 2.00 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.6 (*C*OMe), 157.1, 136.5, 129.0, 120.5, 113.3, 55.1 (O*C*H_3), 37.3, 36.0, 28.2 (*CO**Me***) ppm. HRMS (ESI) (m/z): calculated for $C_{16}H_{24}BN_2O_2^+$ $[M + H]^+$ 287.1925; found, 287.1940.

(3-(4-Chlorophenyl)-1-oxo-1-phenylpropan-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3ah)



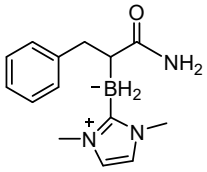
Yellow oil (30%, 31.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.6 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.26-7.24 (m, 2H), 7.14-7.12 (m, 4H), 6.63 (s, 2H), 3.56 (s, 6H), 3.47 (brs, 1H), 3.32 (dd, *J* = 14.0, 9.4 Hz, 1H), 2.79 (dd, *J* = 13.9, 3.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 131.1, 130.5, 130.0, 128.6, 127.9, 127.8, 127.4, 120.4, 38.0, 36.1 ppm.

(1-Carboxy-2-phenylethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate[8] **(3ai)**



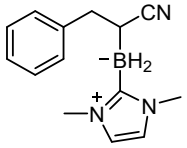
Yellow oil (91%, 70.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.19 (m, 4H), 7.13-7.09 (m, 1H), 6.68 (s, 2H), 3.63 (s, 6H), 3.07-3.01 (m, 1H), 2.75-2.70 (m, 1H), 2.17 (brs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.2 (*C*OOH), 143.7, 127.6, 126.8, 124.0, 119.4, 37.6 (N*CH*$_3$), 34.8 (Ph*CH*$_2$-) ppm.

(1-Amino-1-oxo-3-phenylpropan-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate[7] **(3aj)**



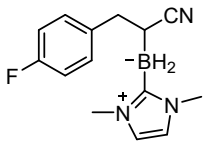
Yellow oil (46%, 35.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.20 (m, 4H), 7.13-7.08 (m, 1H), 6.78 (s, 2H), 5.24 (s, 2H), 3.74 (s, 6H), 2.97 (dd, *J* = 14.3, 10.1 Hz, 1H), 2.76 (dd, *J* = 14.4, 4.9 Hz, 1H), 2.12 (brs, 1H) ppm. ^{13}C NMR (100MHz, $CDCl_3$) δ 184.3 (*C*ONH_2), 142.7, 127.3, 127.0, 124.2, 119.5, 39.1 (N*CH*$_3$), 35.2 (Ph*CH*$_2$-) ppm.

(1-Cyano-2-phenylethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate[7] **(3ak)**



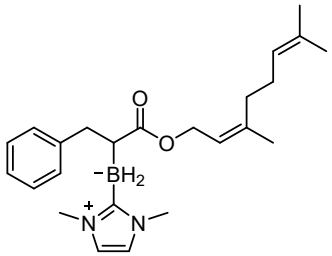
Yellow oil (75%, 53.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.28 (m, 4H), 7.21-7.16 (m, 1H), 6.86 (s, 2H), 3.84 (s, 6H), 2.90-2.78 (m, 2H), 1.87 (brs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 128.0, 127.5, 127.2, 124.9, 119.9, 39.0 (N*CH*$_3$), 35.4 (Ph*CH*$_2$-) ppm.

(1-Cyano-2-(4-fluorophenyl)ethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate[7] **(3al)**



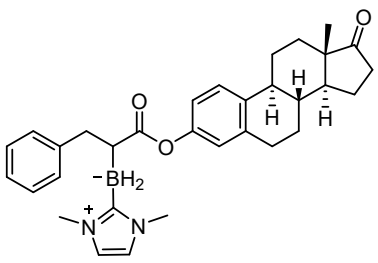
Yellow oil (87%, 67.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 8.6, 5.5 Hz, 2H), 6.96 (t, *J* = 8.8 Hz, 2H), 6.87 (s, 2H), 3.84 (s, 6H), 2.86-2.74 (m, 2H), 1.83 (brs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (d, J_{CF} = 241.4 Hz), 138.1, 129.8 (d, J_{CF} = 7.6 Hz), 128.8, 120.8, 114.8 (d, J_{CF} = 20.8 Hz), 39.1 (N*CH*$_3$), 36.3 (Ph*CH*$_2$-) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.8 (s, 1F) ppm.

(*Z*)-(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-1-oxo-3-phenylpropan-2-yl)dihydroborate (3am)



Yellow oil (76%, 89.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.16 (m, 4H), 7.09-7.06 (m, 1H), 6.77 (s, 2H), 5.04-5.00 (m, 2H), 4.30-4.28 (d, *J* = 6.8 Hz, 2H), 3.71 (s, 6H), 3.12 (dd, *J* = 14.2, 10.1 Hz, 1H), 2.72 (dd, *J* = 14.3, 4.2 Hz, 1H), 2.19 (brs, 1H), 2.00 (s, 4H), 1.68 (s, 3H), 1.66 (s, 3H), 1.57 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.4, 144.7, 140.4, 131.8, 128.5, 127.7, 124.9, 123.7, 120.5, 120.2, 59.4, 39.1, 35.9, 32.0, 26.6, 25.6, 23.4, 17.6 ppm. HRMS (ESI) (m/z): calculated for $C_{24}H_{35}BN_2O_2Na^+$ $[M + Na]^+$ 417.2684; found, 417.2698.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)-1-oxo-3-phenylpropan-2-yl)dihydroborate (3an)



Yellow oil (85%, 129.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.25 (m, 2H), 7.24-7.20 (m, 2H), 7.15-7.10 (m, 2H), 6.82 (s, 2H), 6.47-6.44 (m, 2H), 3.76 (s, 6H), 3.21 (dd, *J* = 14.3, 10.6 Hz, 1H), 2.83-2.80 (m, 3H), 2.52-2.33 (m, 3H), 2.14-1.91 (m, 5H), 1.60-1.39 (m, 7H), 0.88 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 149.4, 144.4, 137.3, 136.0, 128.5, 127.8, 125.8, 125.1, 121.7, 120.4, 118.7, 50.3, 47.8, 44.0, 39.2, 37.9, 36.1, 35.8, 31.5, 29.3, 26.3, 25.6, 21.5, 13.7 ppm. HRMS (ESI) (m/z): calculated for $C_{32}H_{40}BN_2O_3^+$ $[M + H]^+$ 511.3127; found, 511.3142.

5. Reference

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6. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

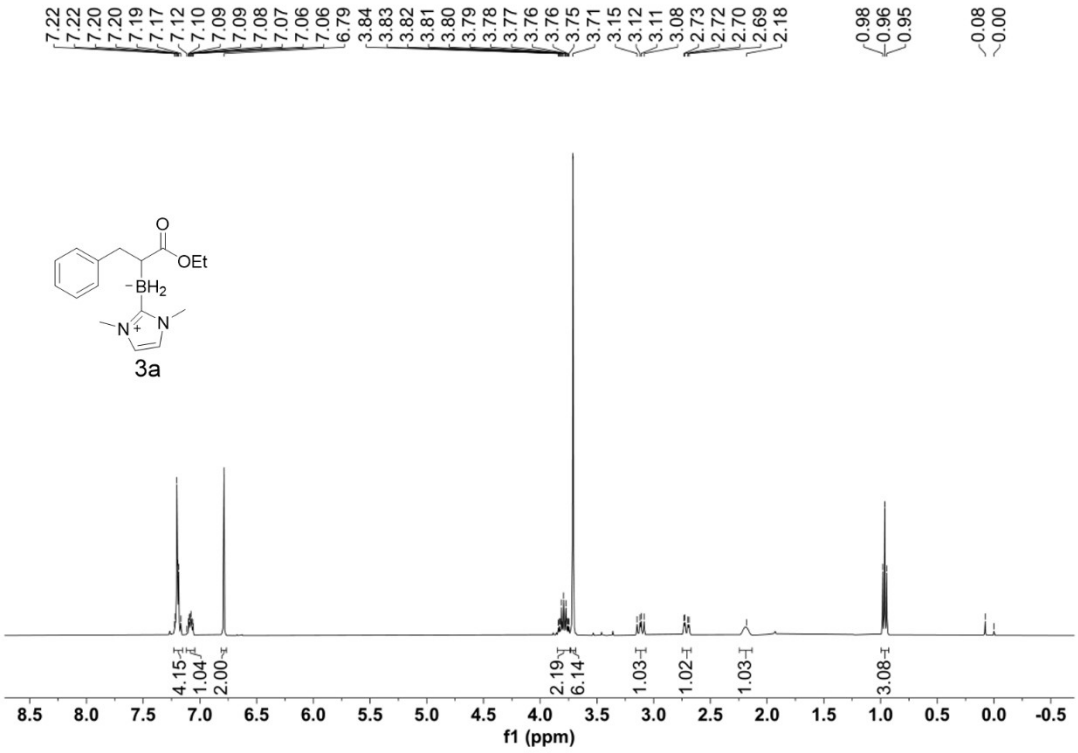

Fig. S3 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3a**.

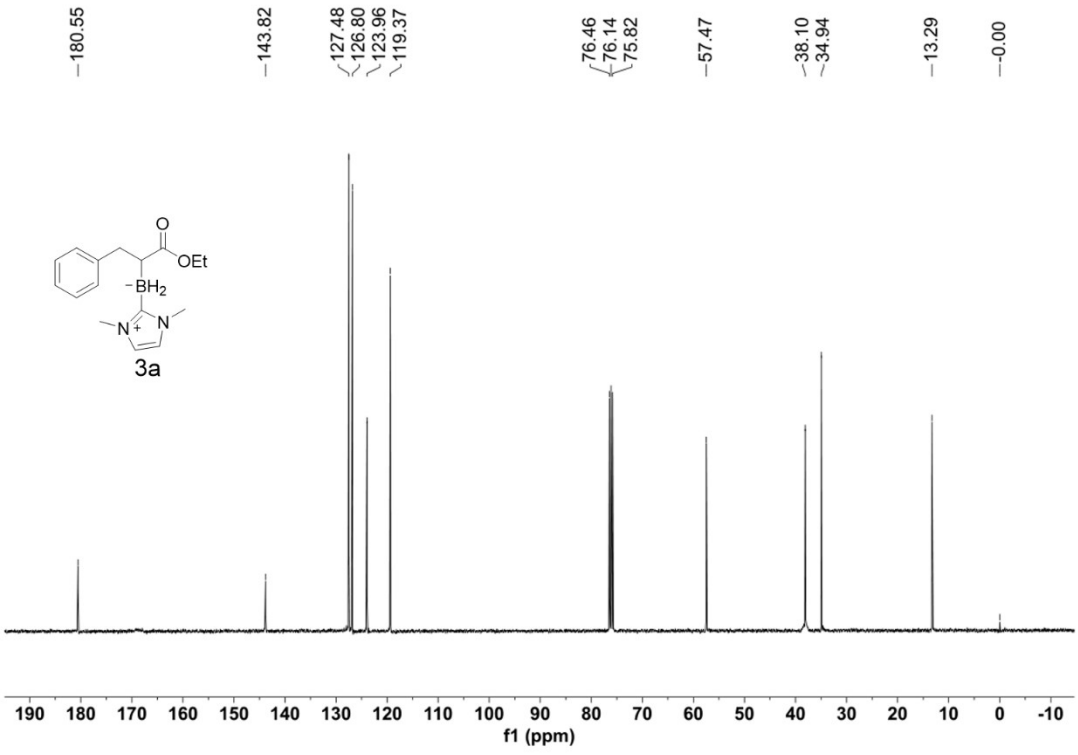

Fig. S4 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3a**.

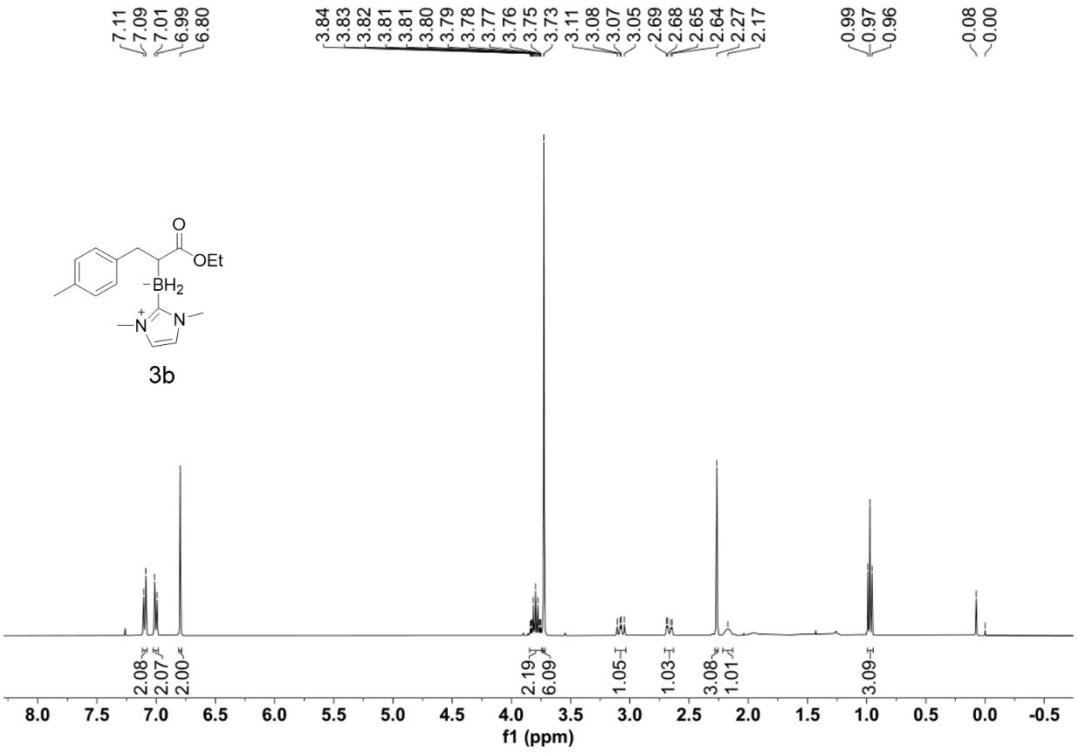

Fig. S5 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3b**.

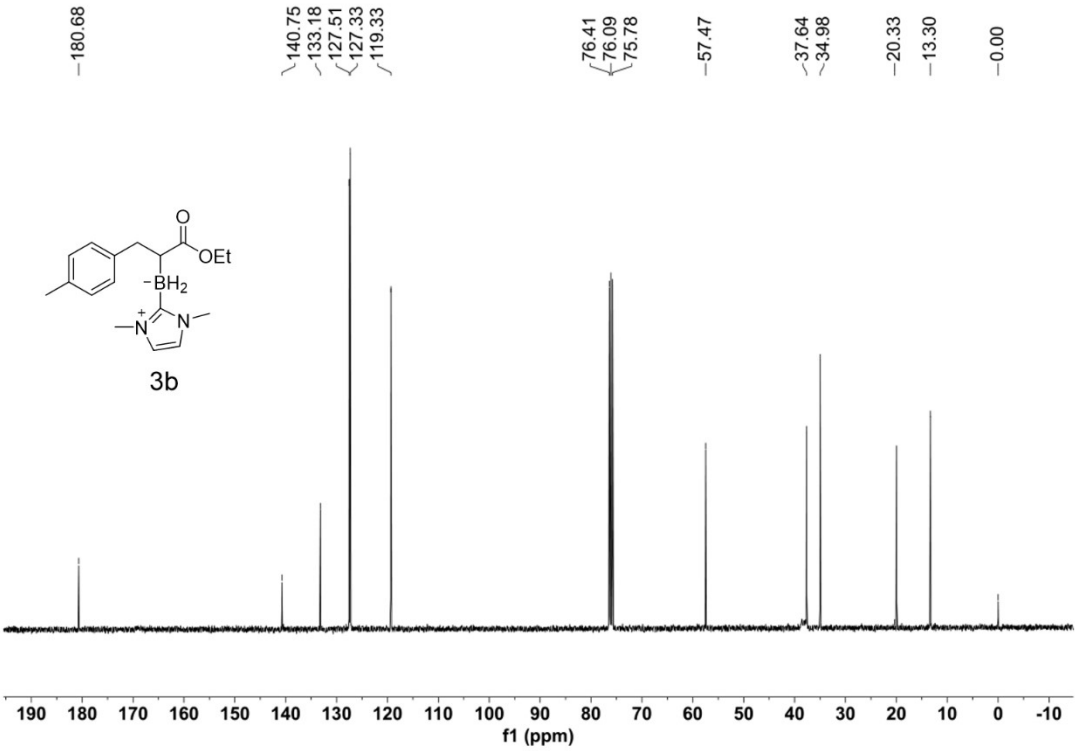

Fig. S6 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3b**.

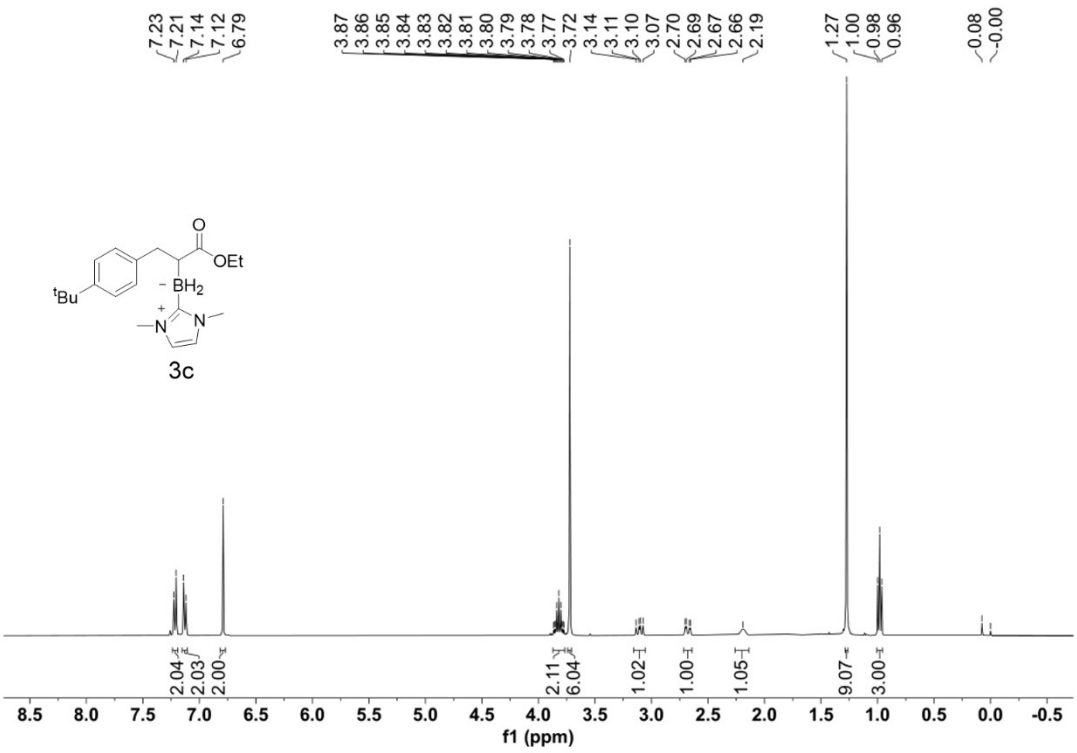

Fig. S7 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3c**.

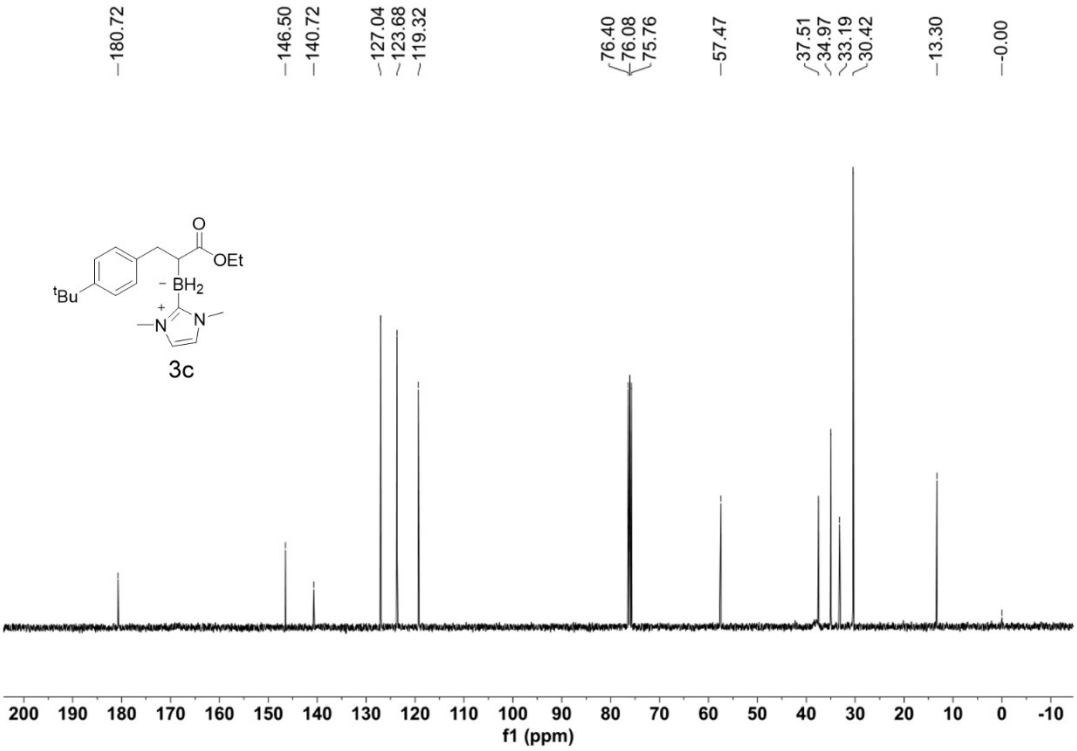

Fig. S8 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3c**.

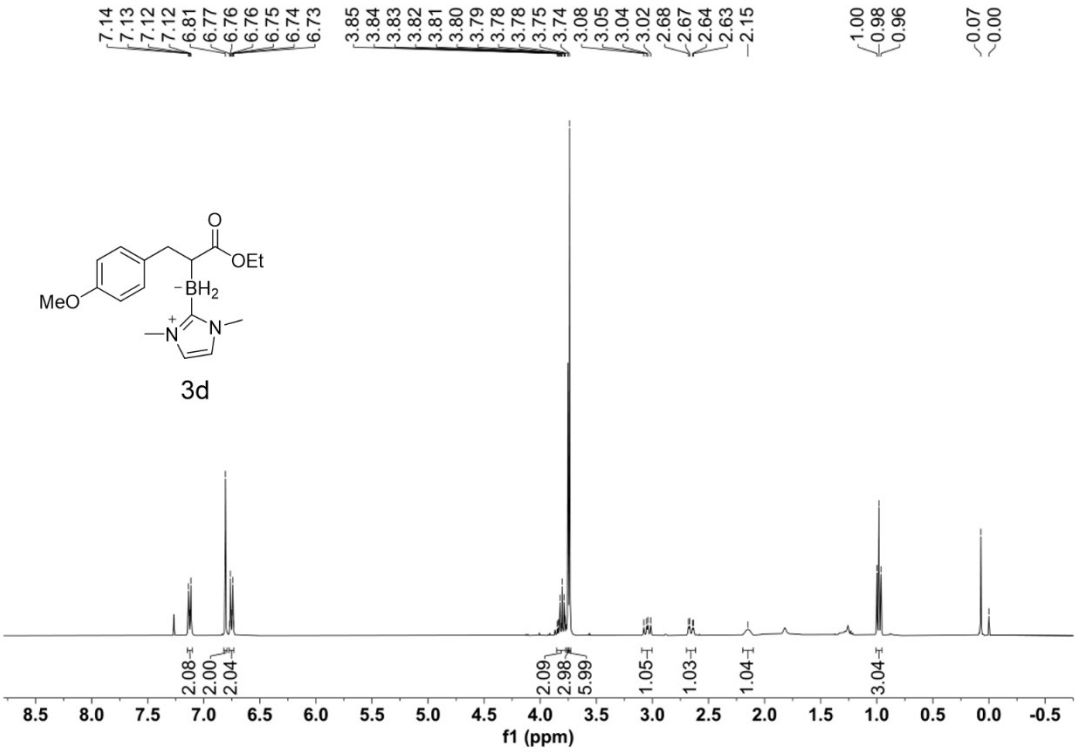

Fig. S9 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3d**.

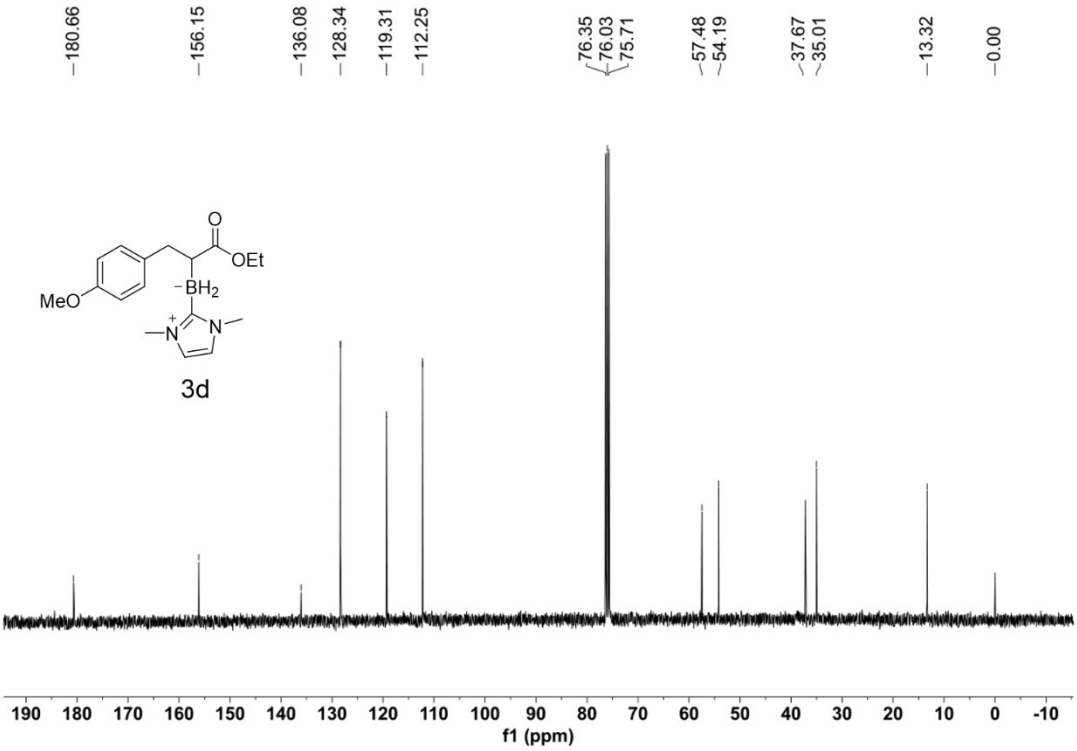

Fig. S10 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3d**.

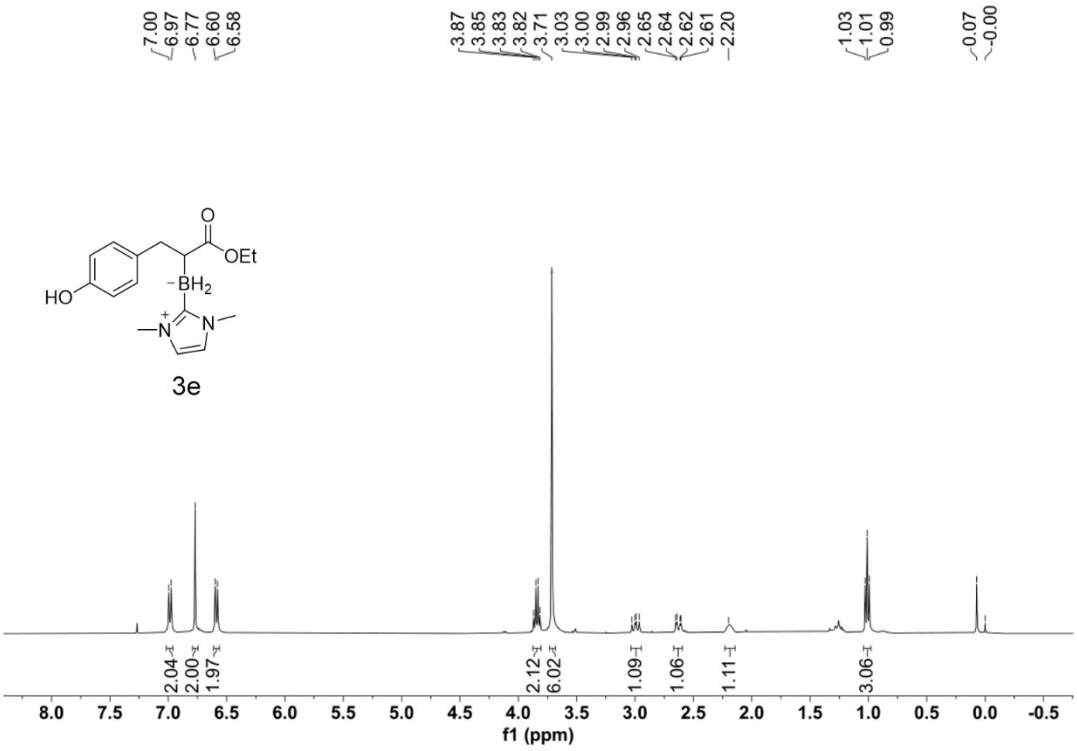

Fig. S11 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3e**.

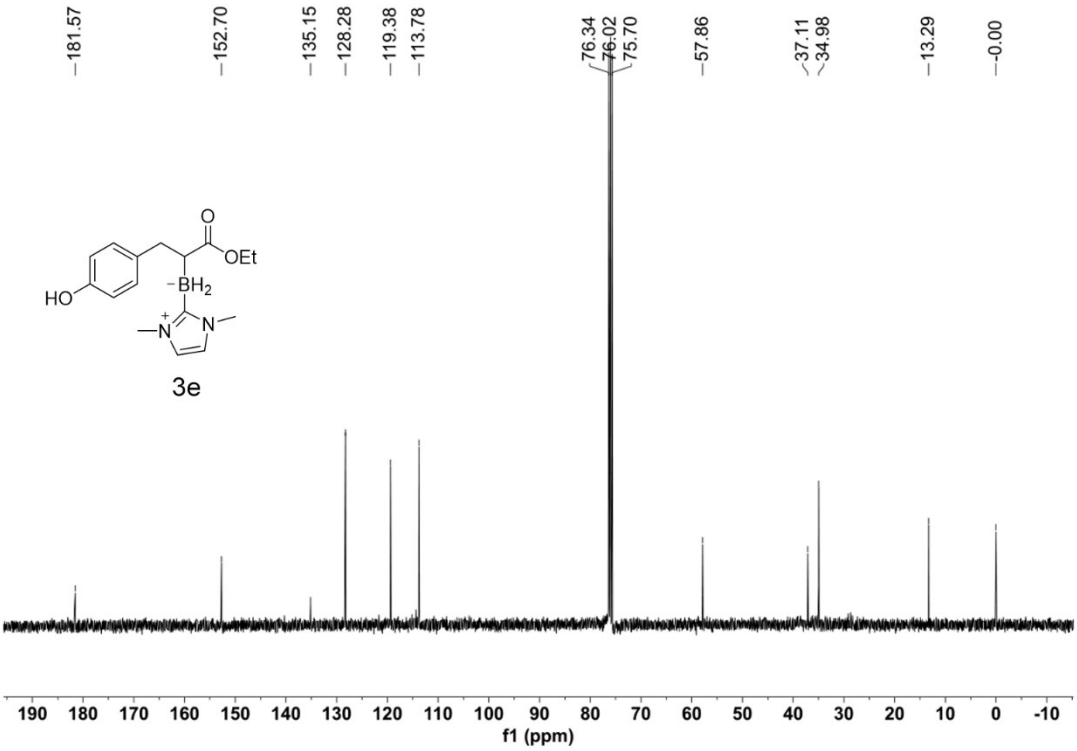

Fig. S12 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3e**.

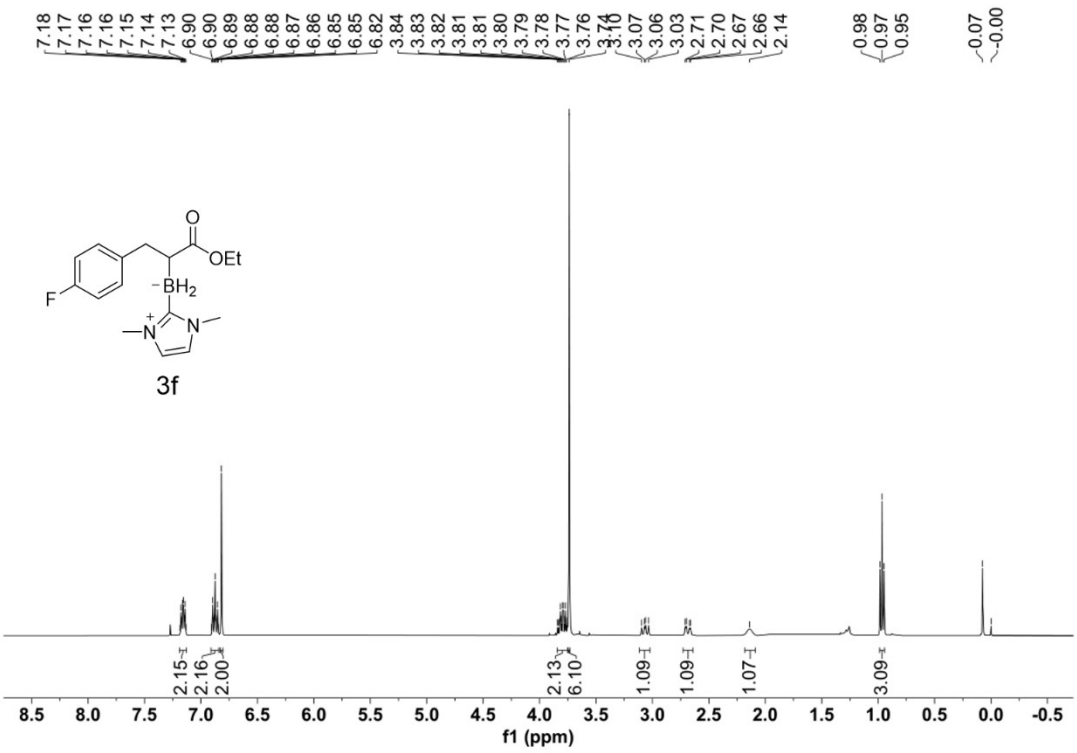

Fig. S13 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3f**.

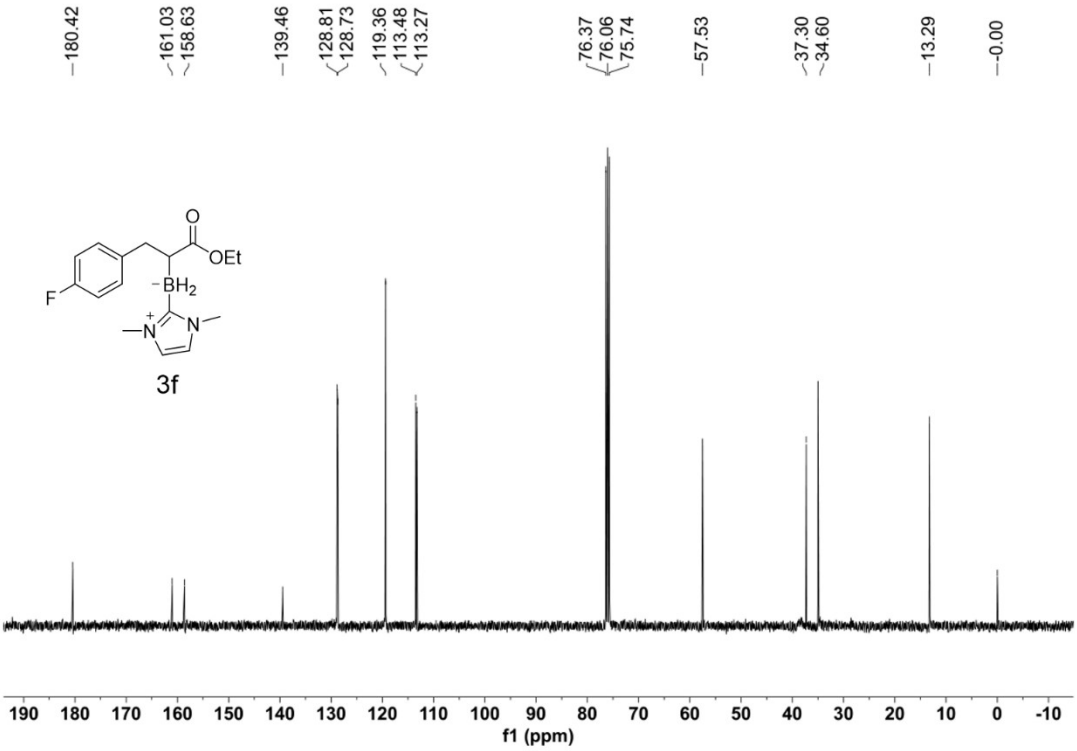

Fig. S14 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3f**.

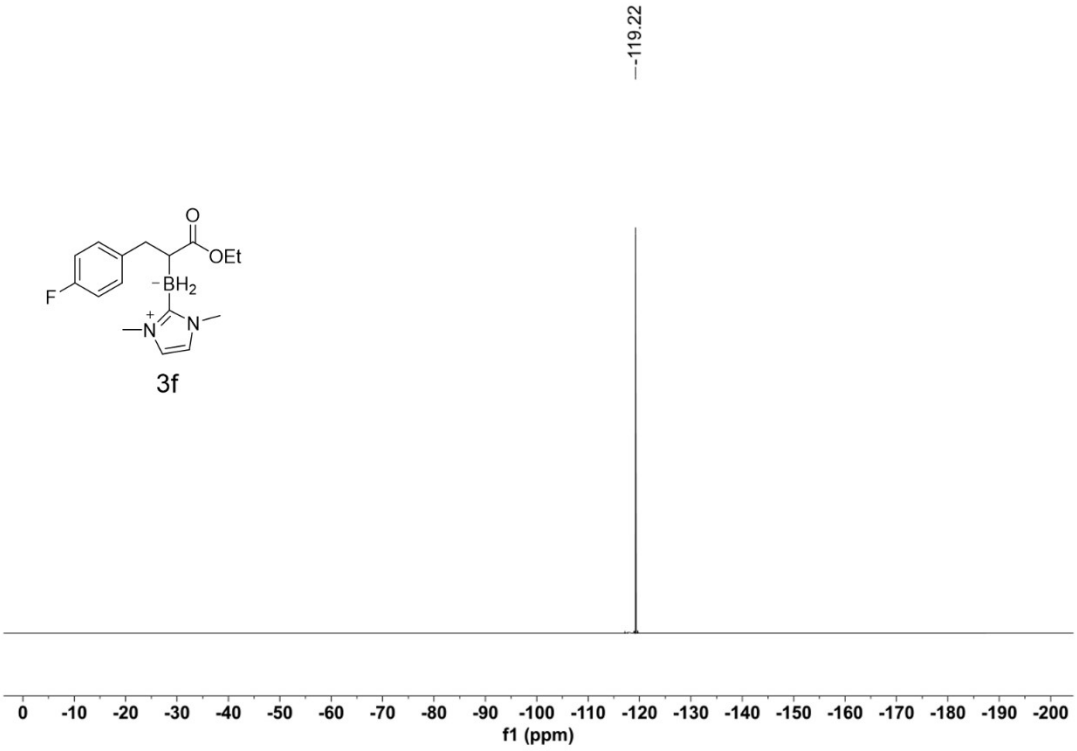

Fig. S15 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **3f**.

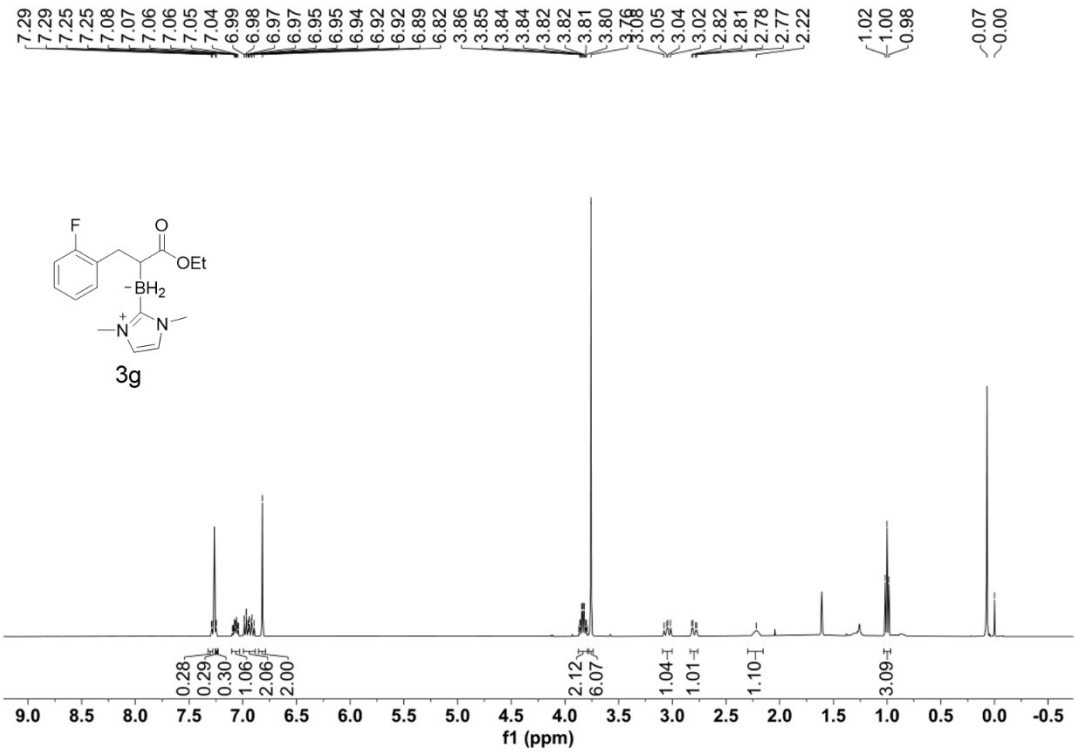

Fig. S16 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3g**.

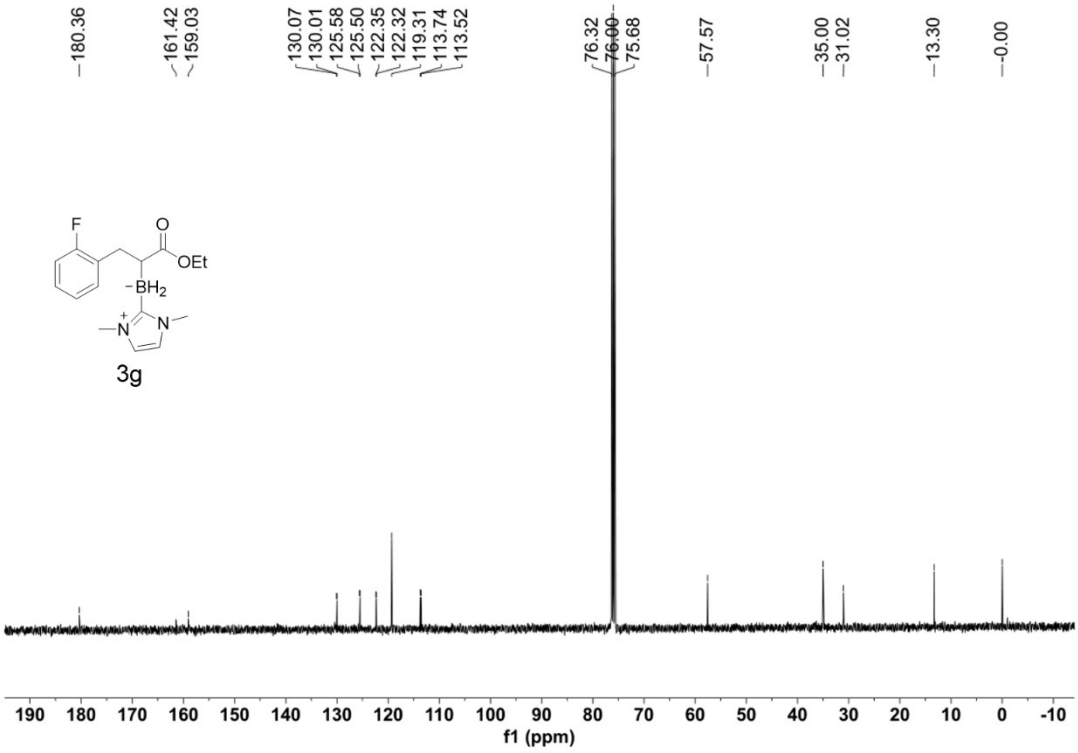

Fig. S17 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3g**.

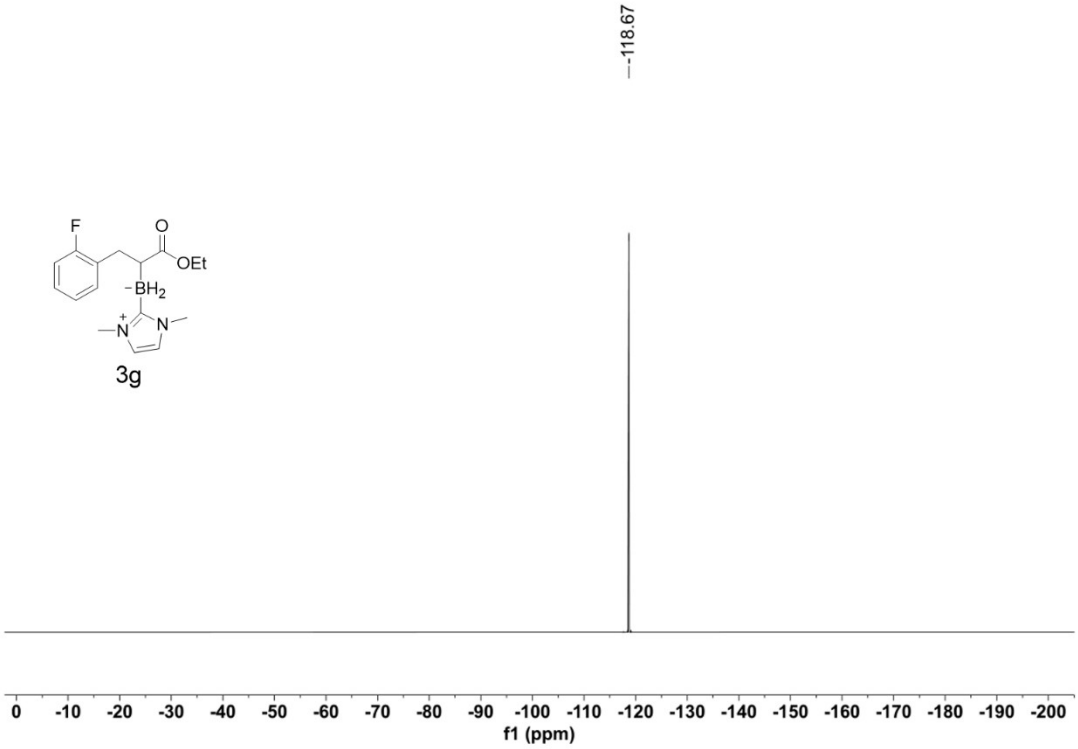

Fig. S18 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **3g**.

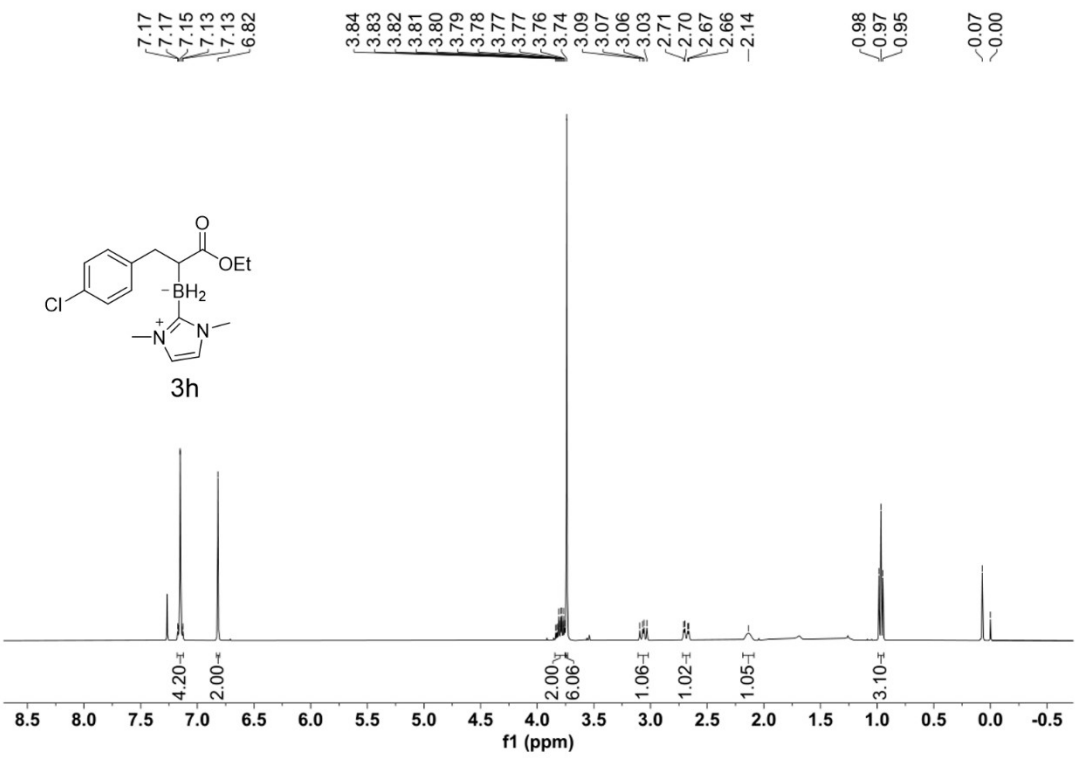

Fig. S19 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3h**.

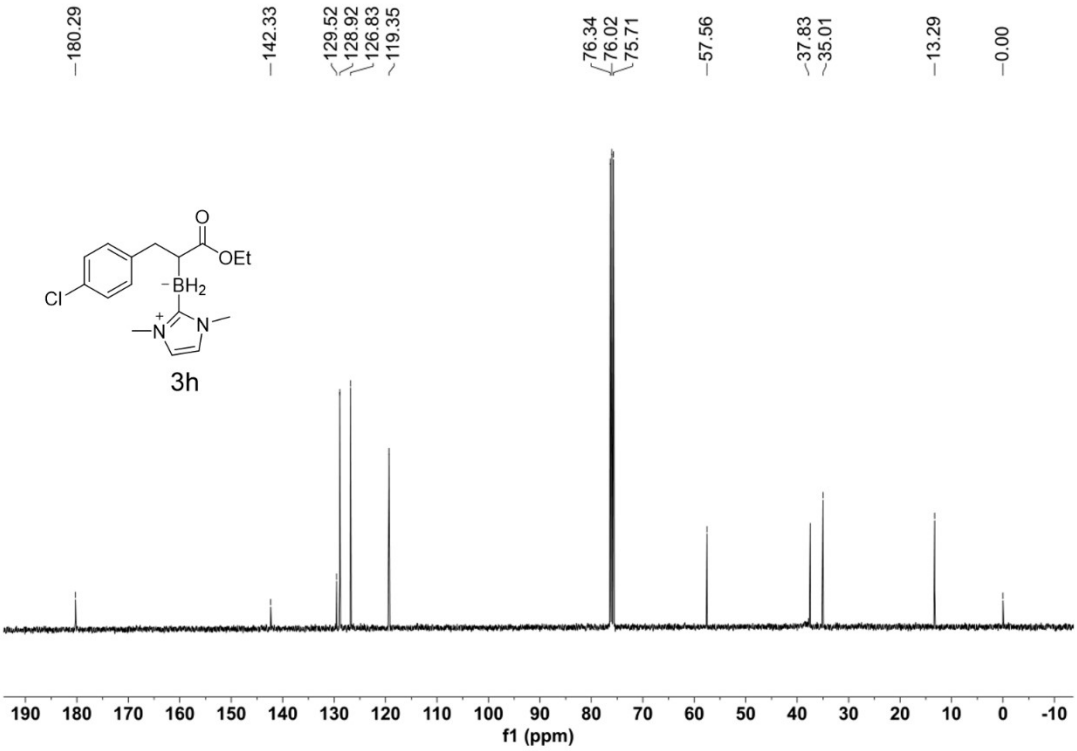

Fig. S20 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3h**.

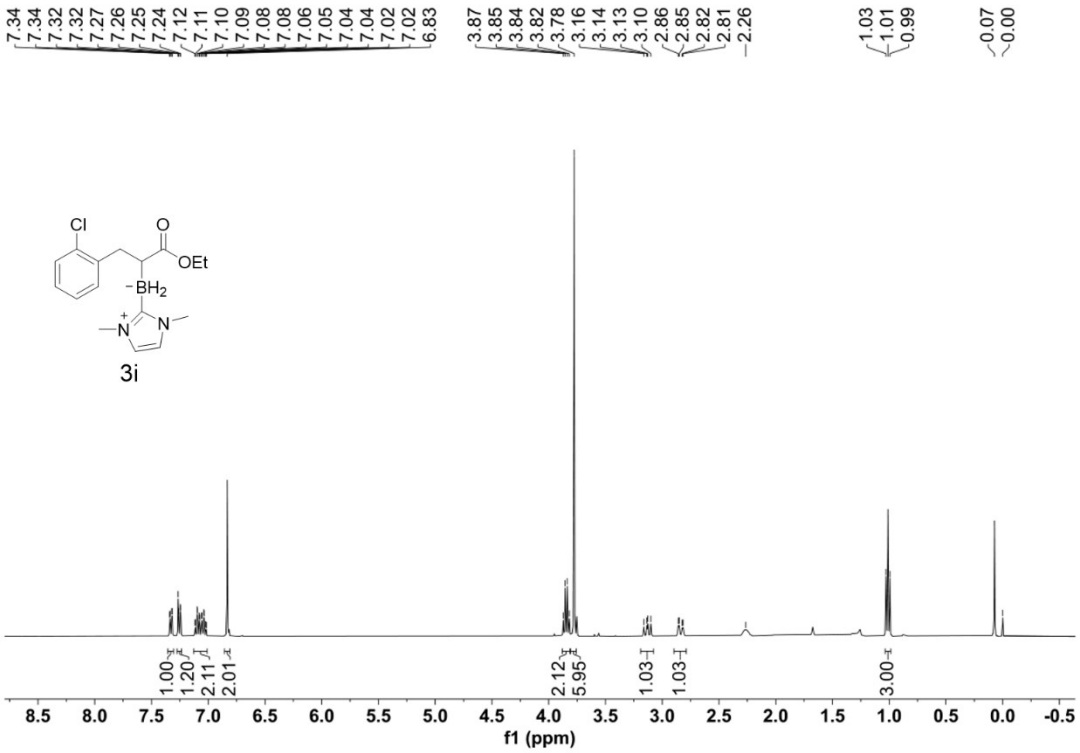

Fig. S21 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3i**.

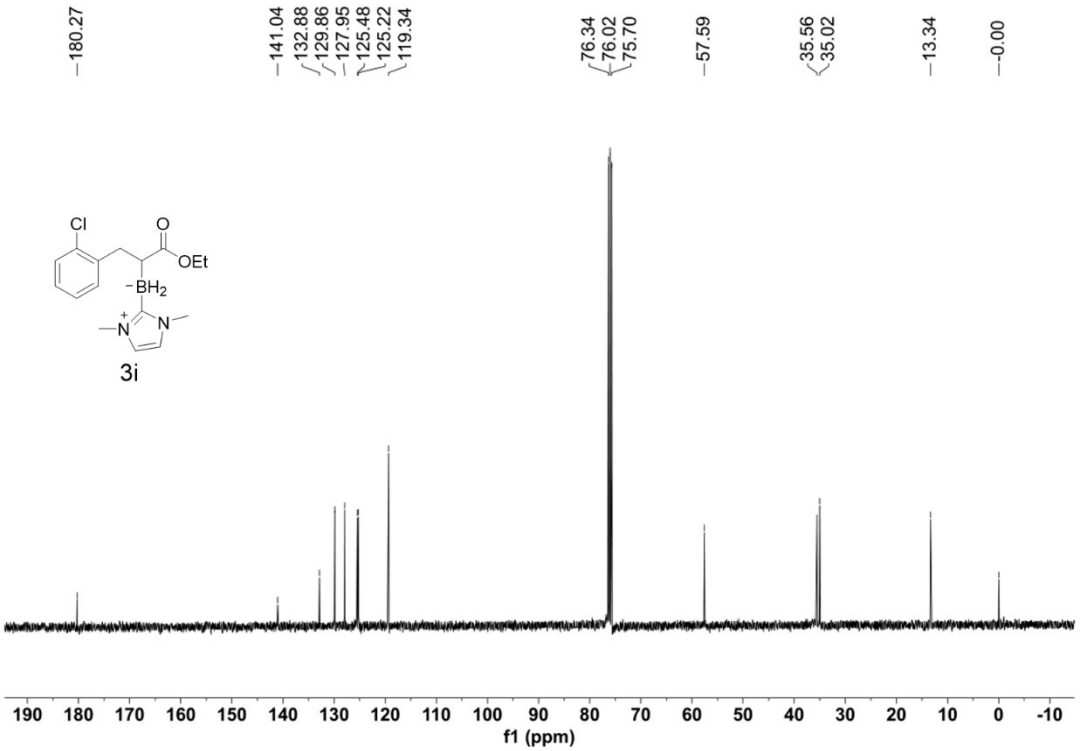

Fig. S22 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3i**.

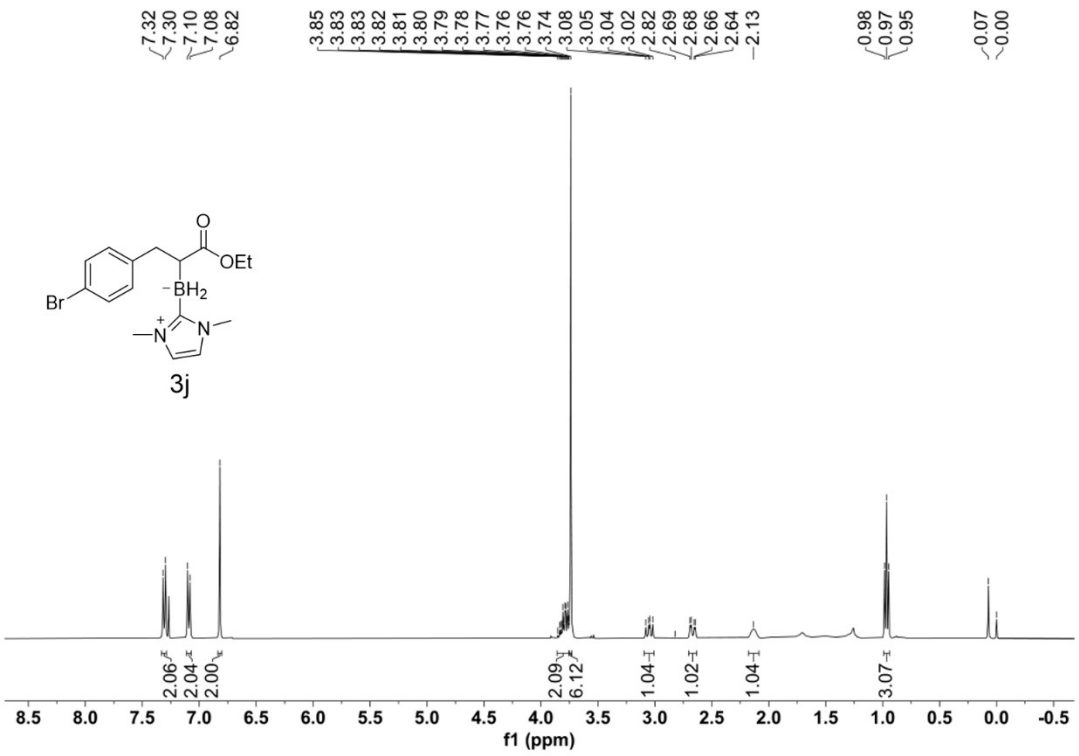

Fig. S23 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3j**.

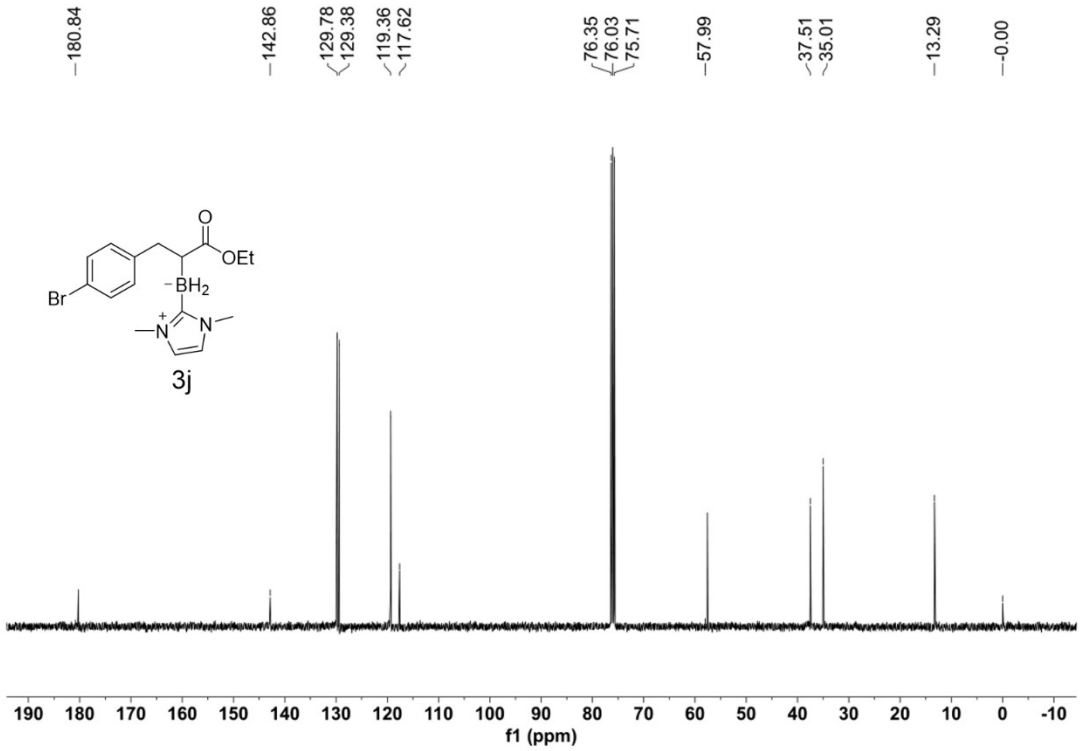

Fig. S24 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3j**.

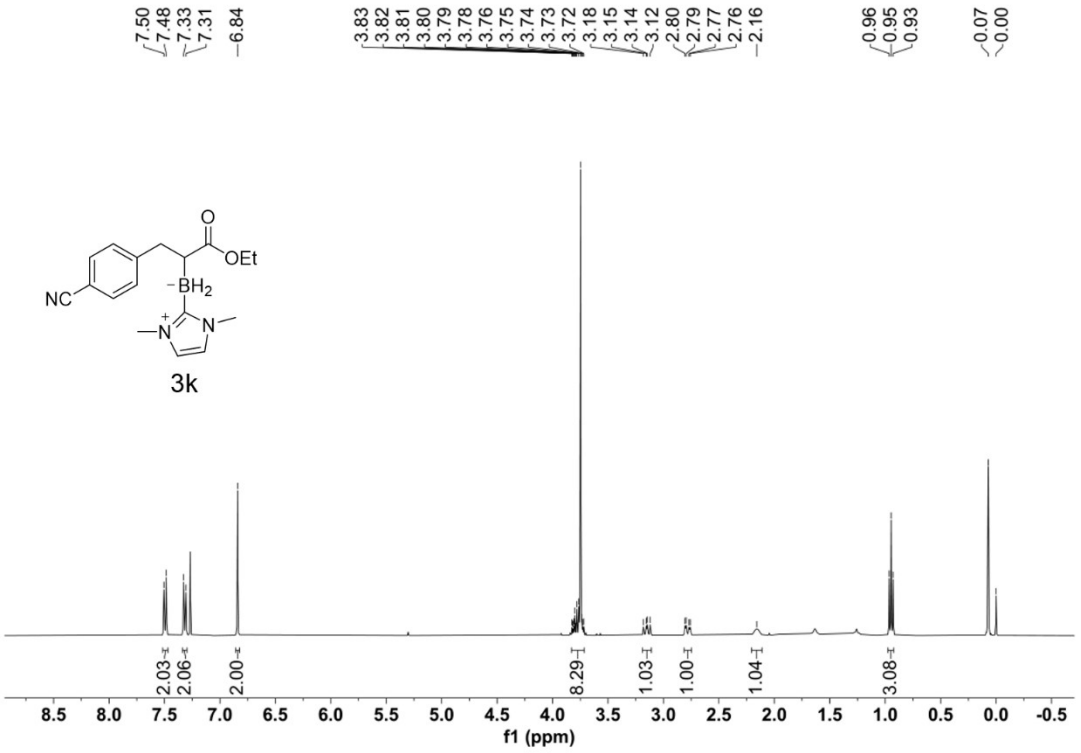

Fig. S25 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3k**.

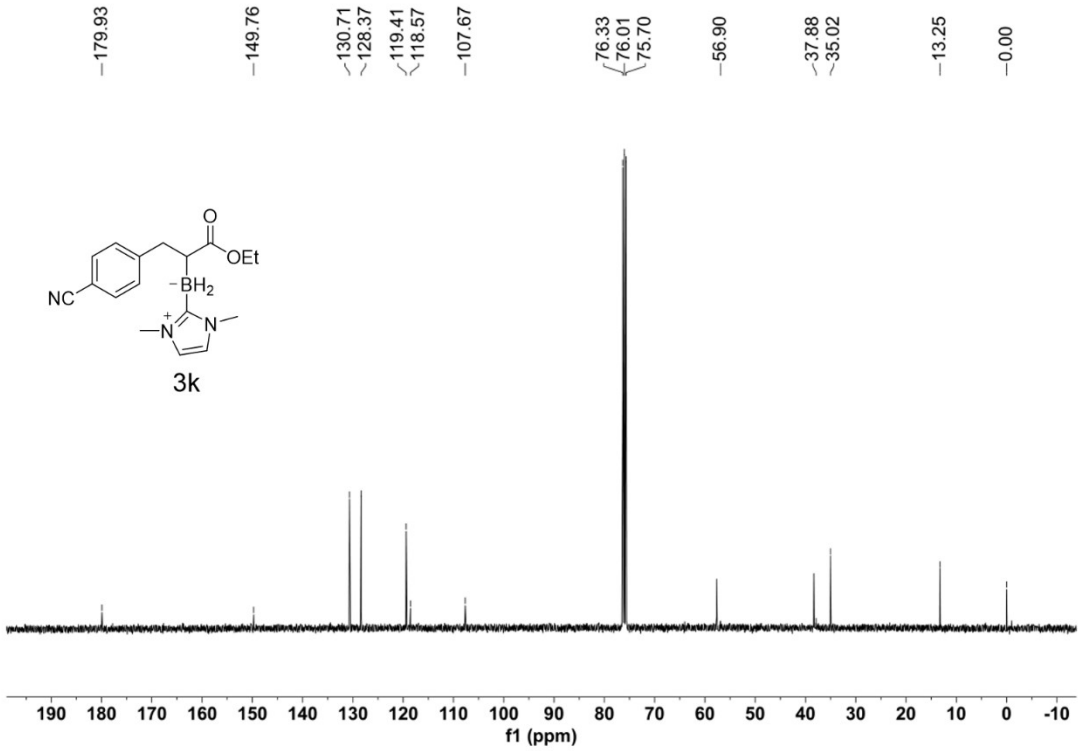

Fig. S26 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3k**.

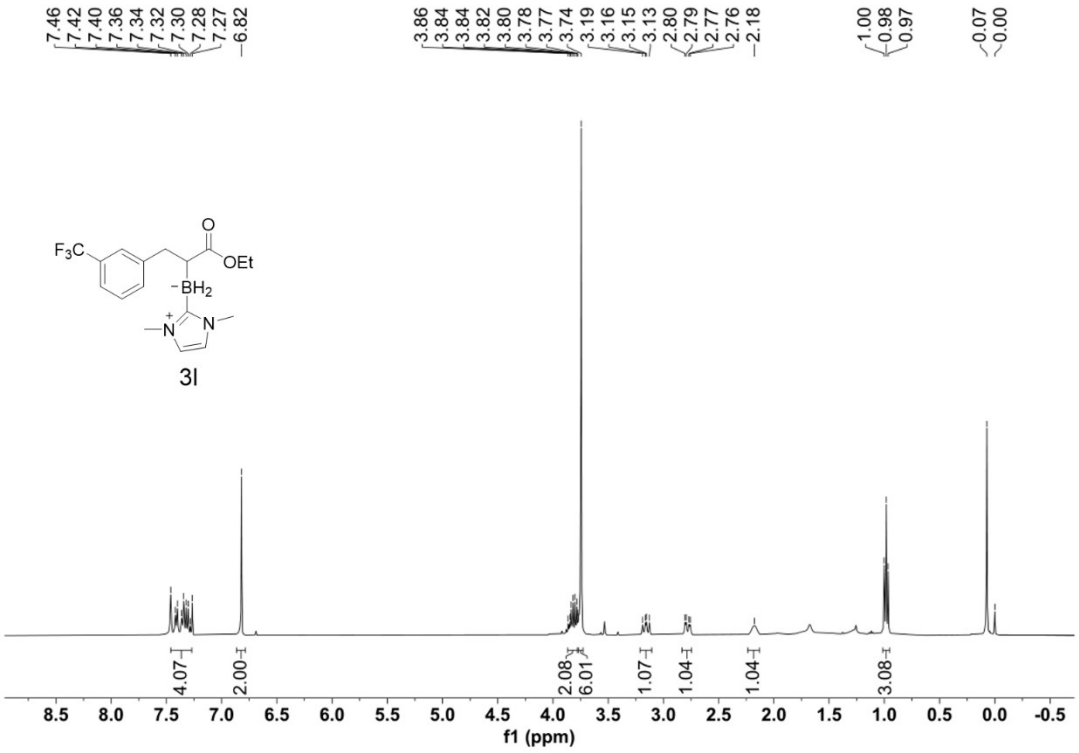

Fig. S27 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3l**.

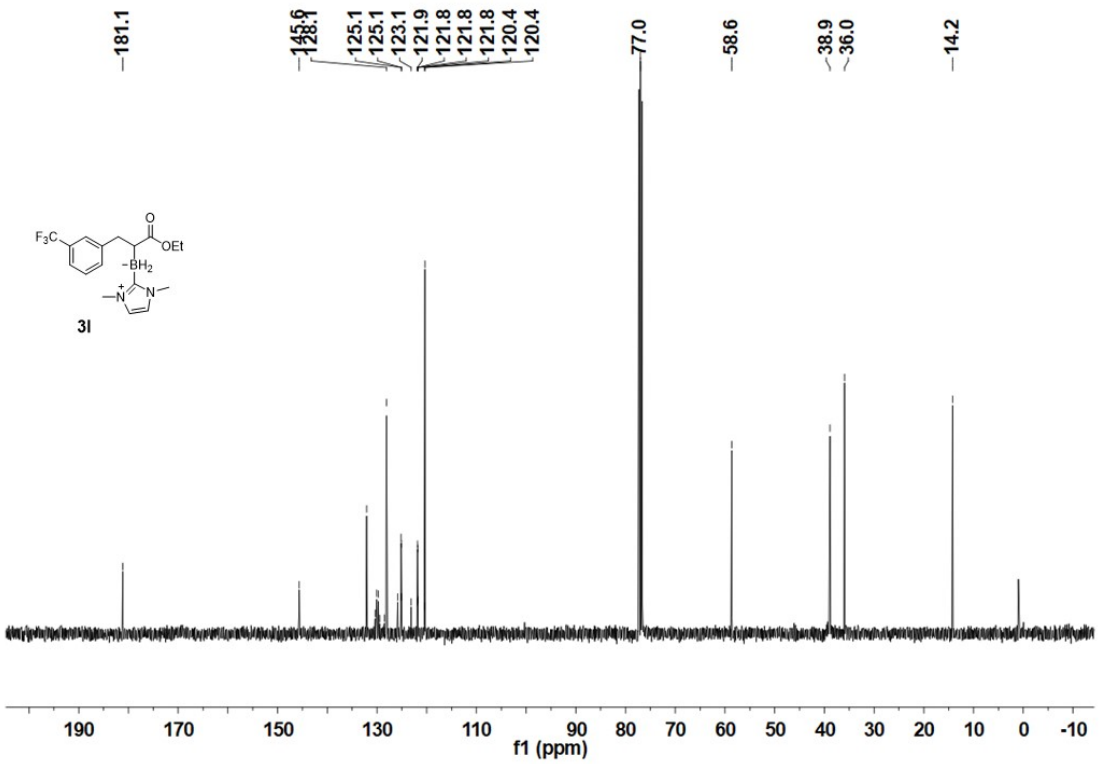

Fig. S28 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3l**.

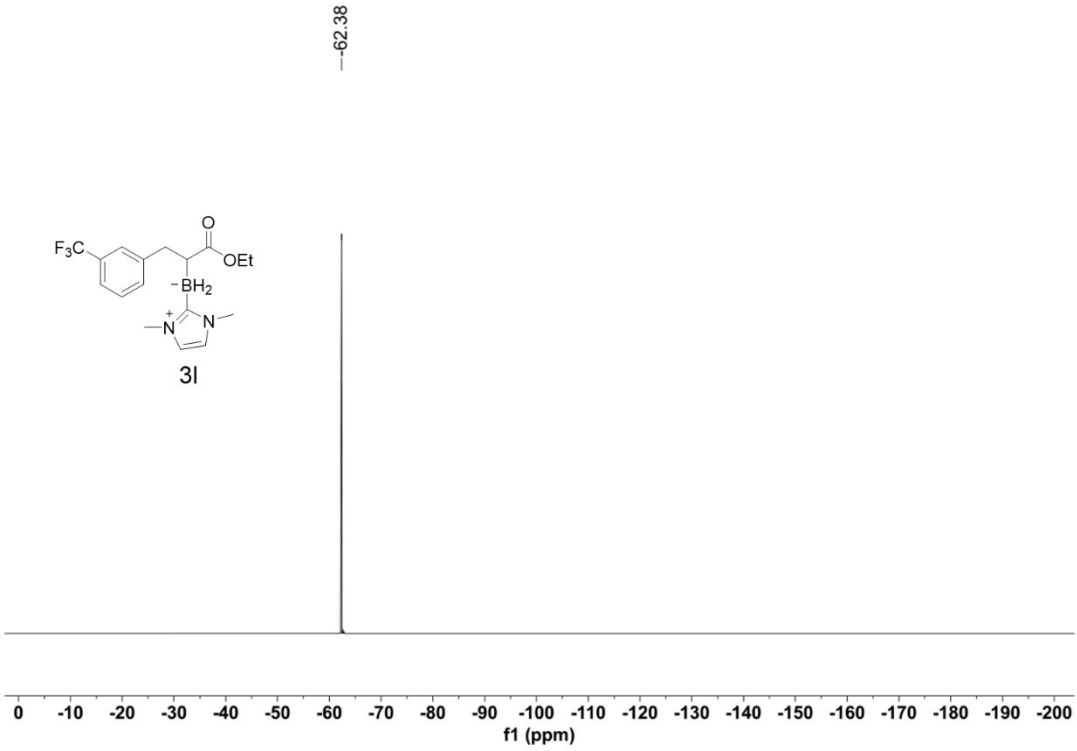

Fig. S29 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **3l**.

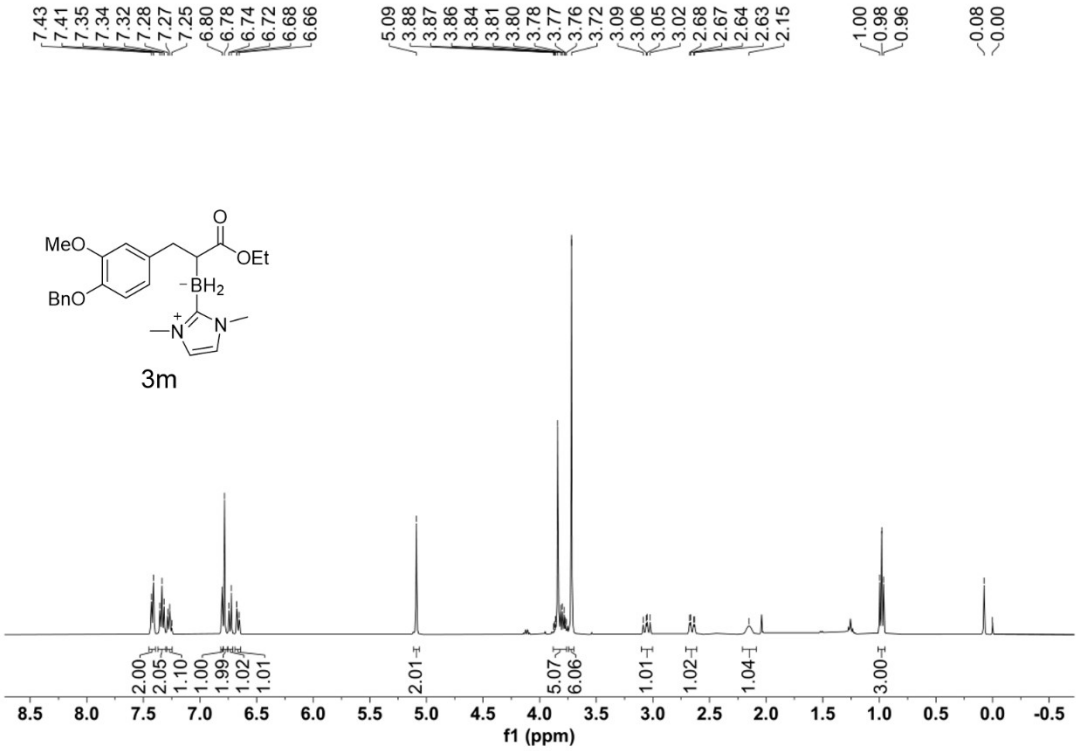

Fig. S30 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3m**.

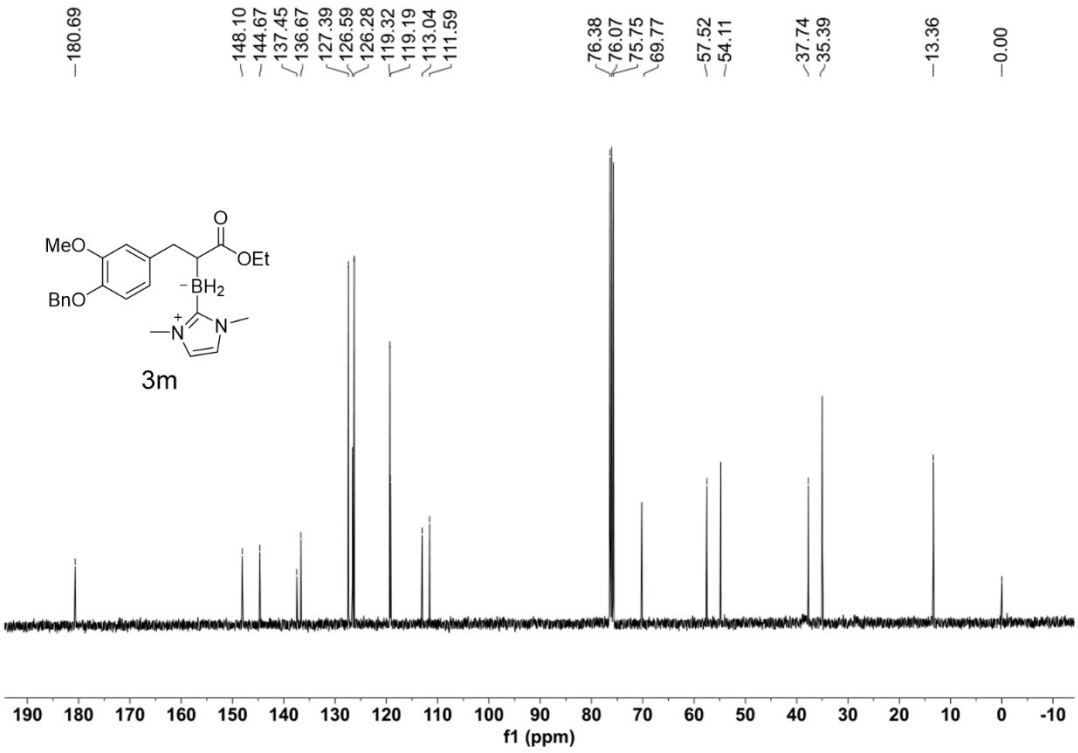

Fig. S31 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3m**.

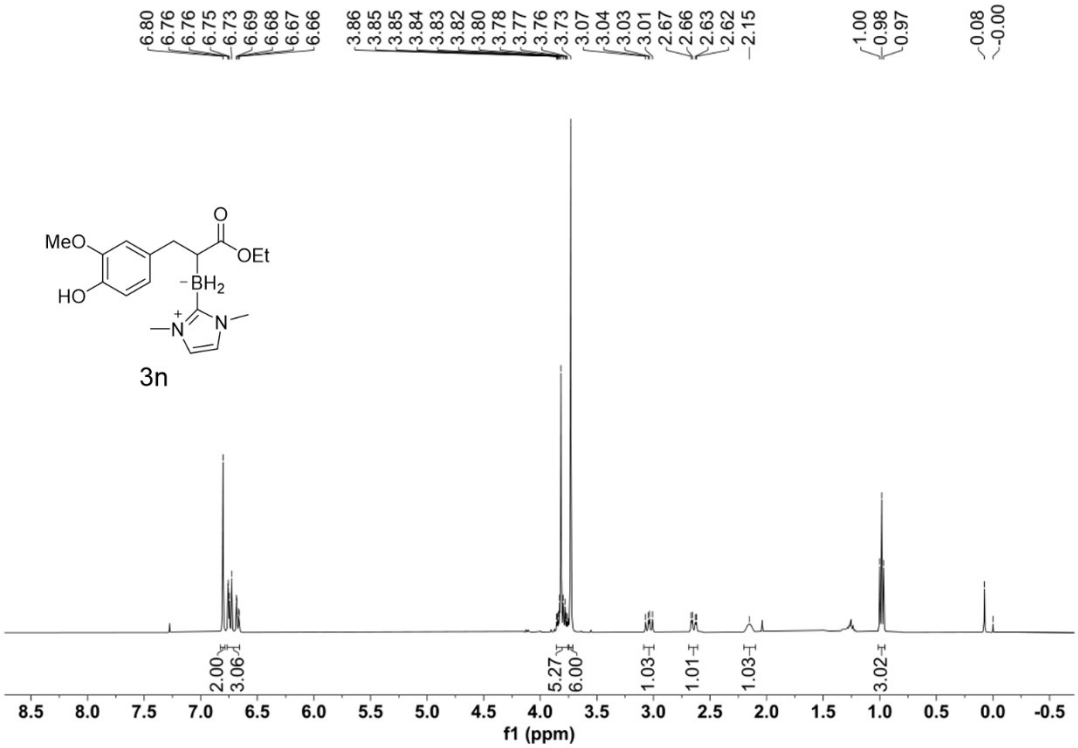

Fig. S32 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3n**.

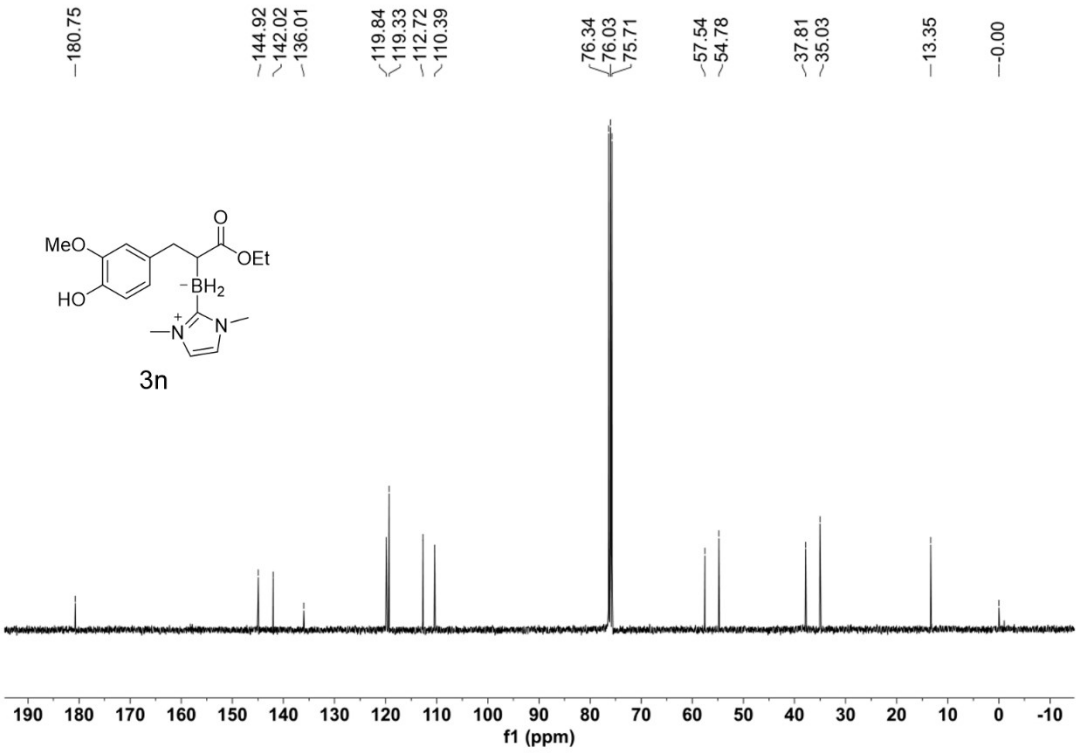

Fig. S33 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3n**.

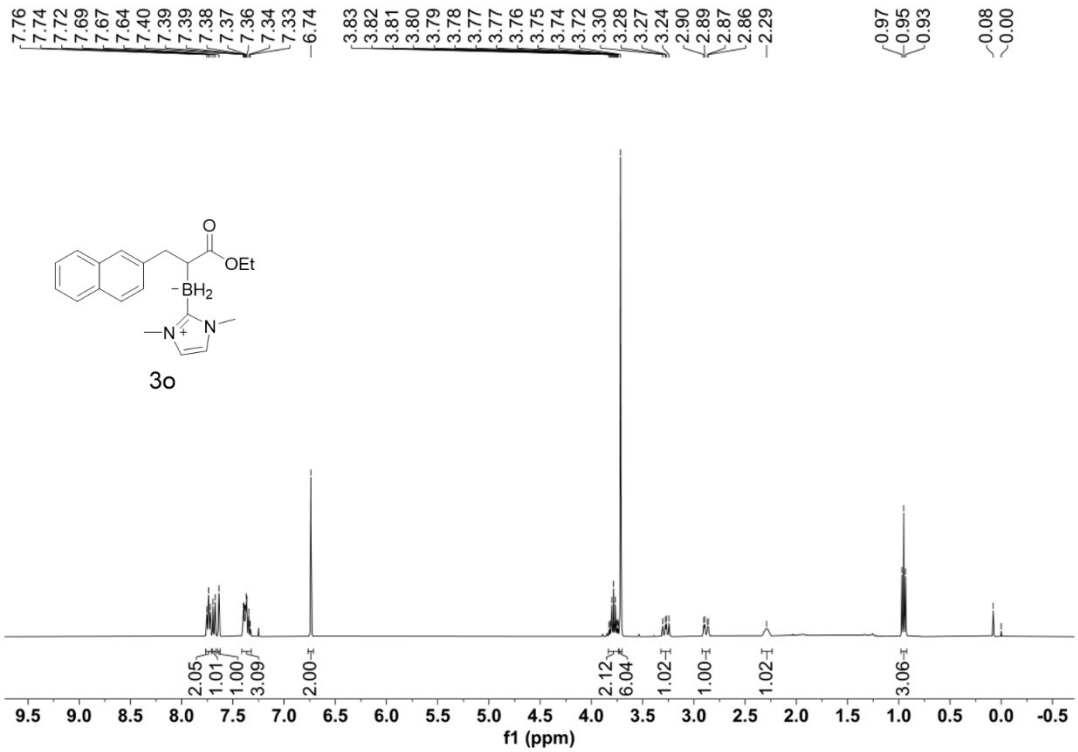

Fig. S34 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3o**.

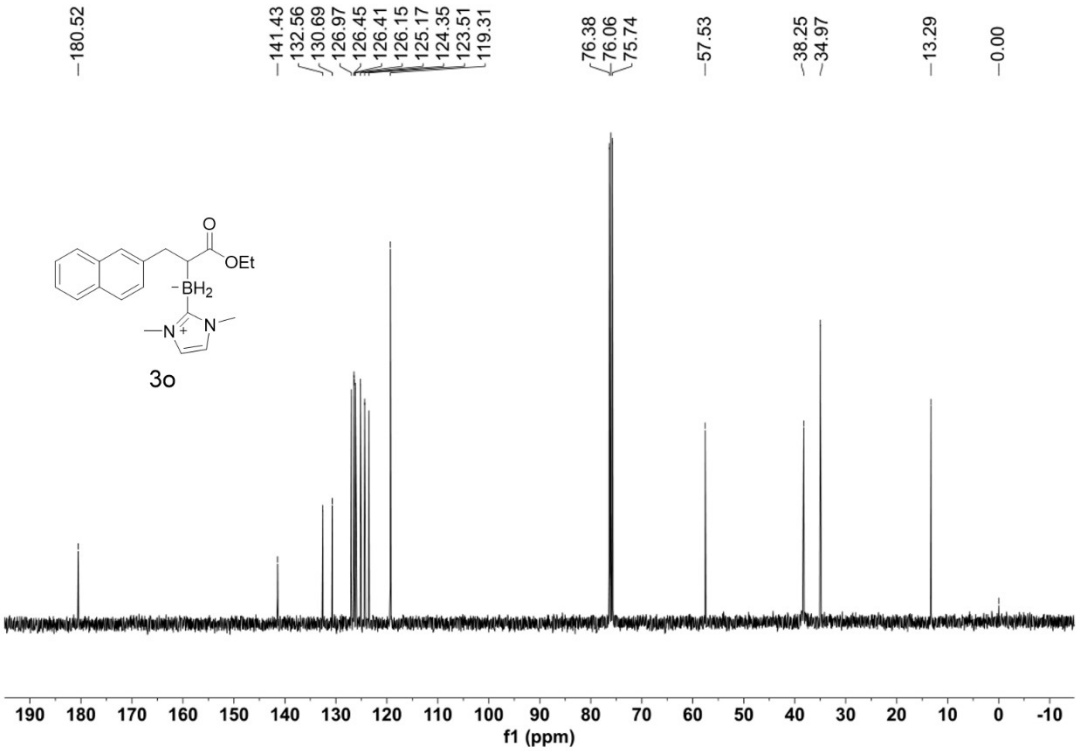

Fig. S35 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3o**.

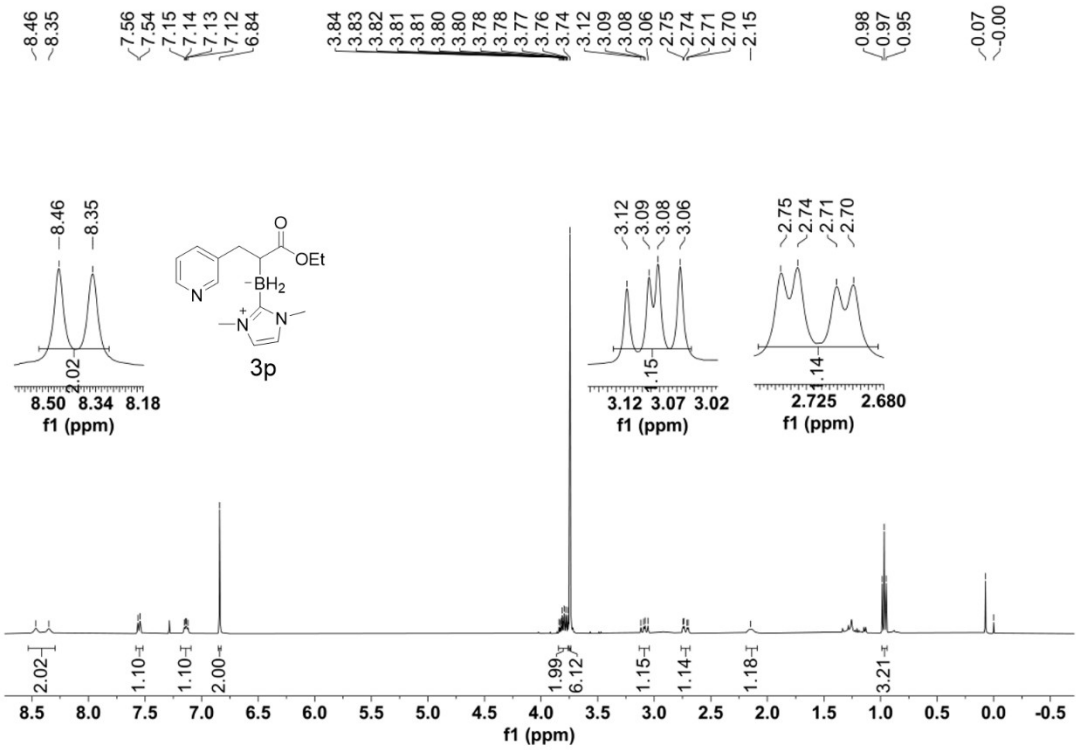

Fig. S36 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3p**.

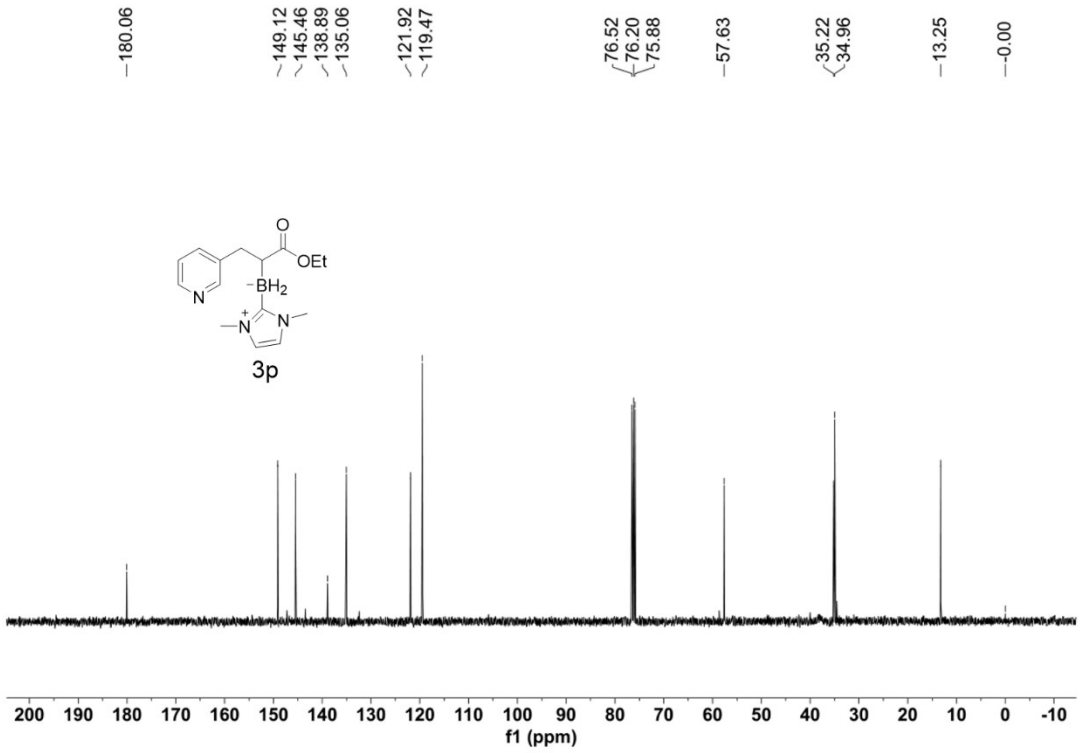

Fig. S37 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3p**.

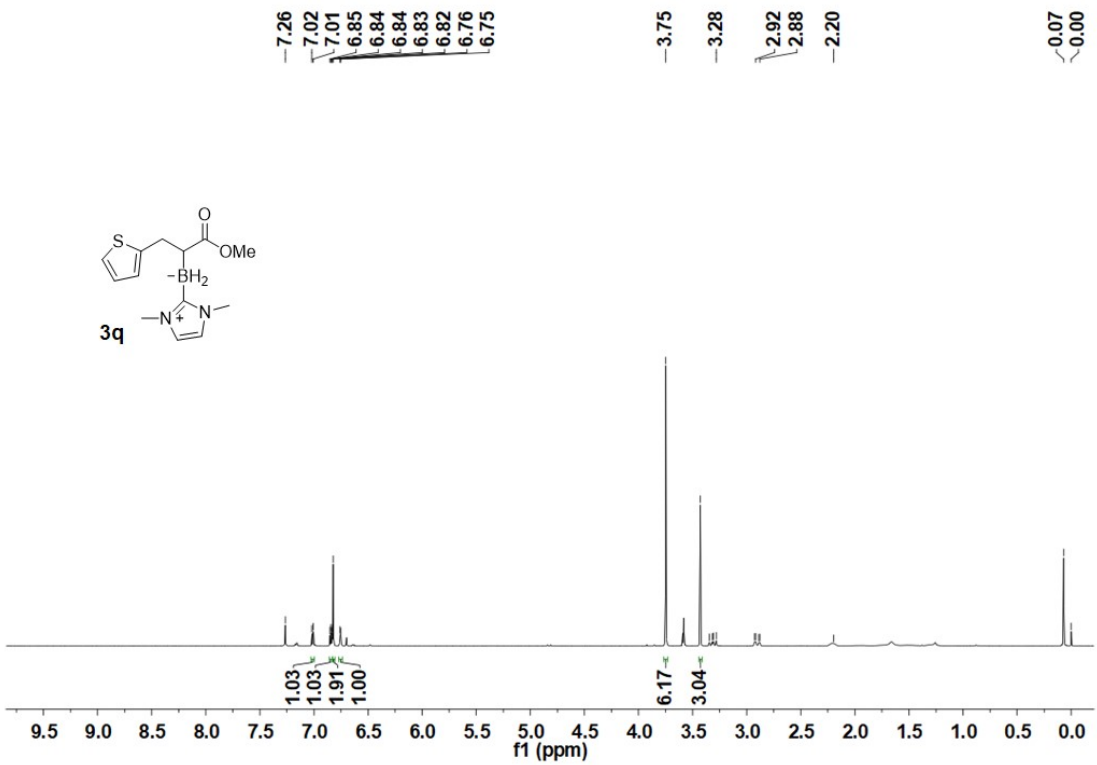

Fig. S38 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3q**.

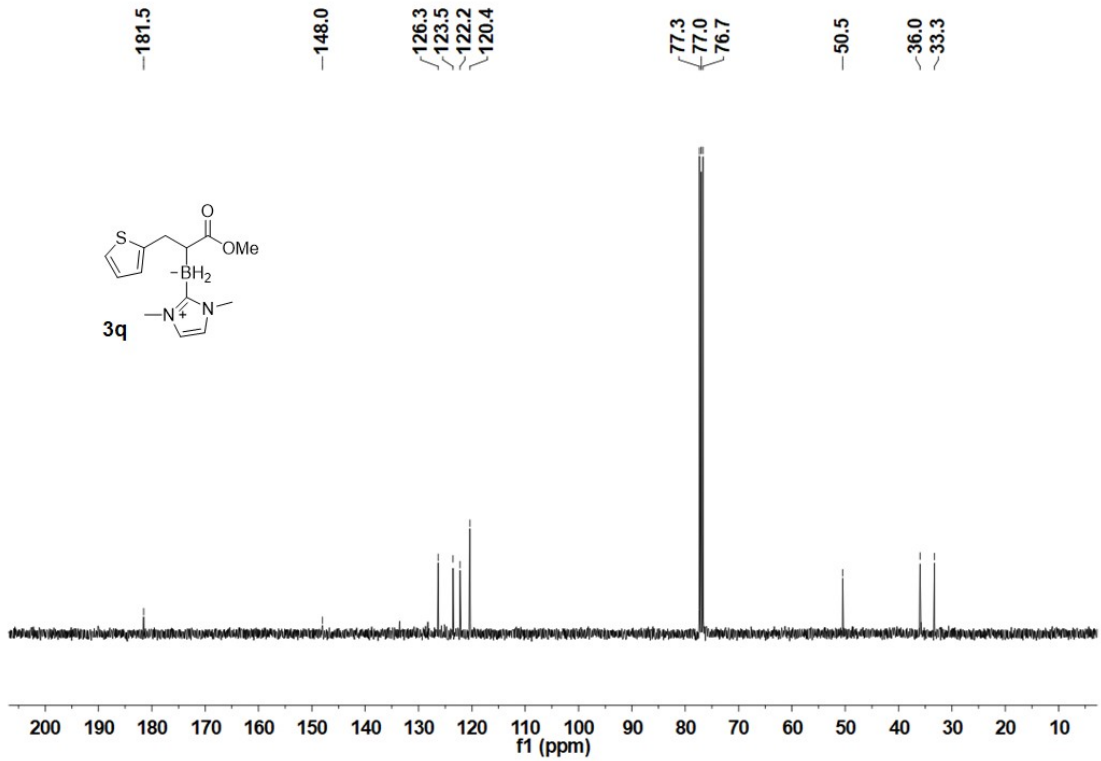

Fig. S39 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3q**.

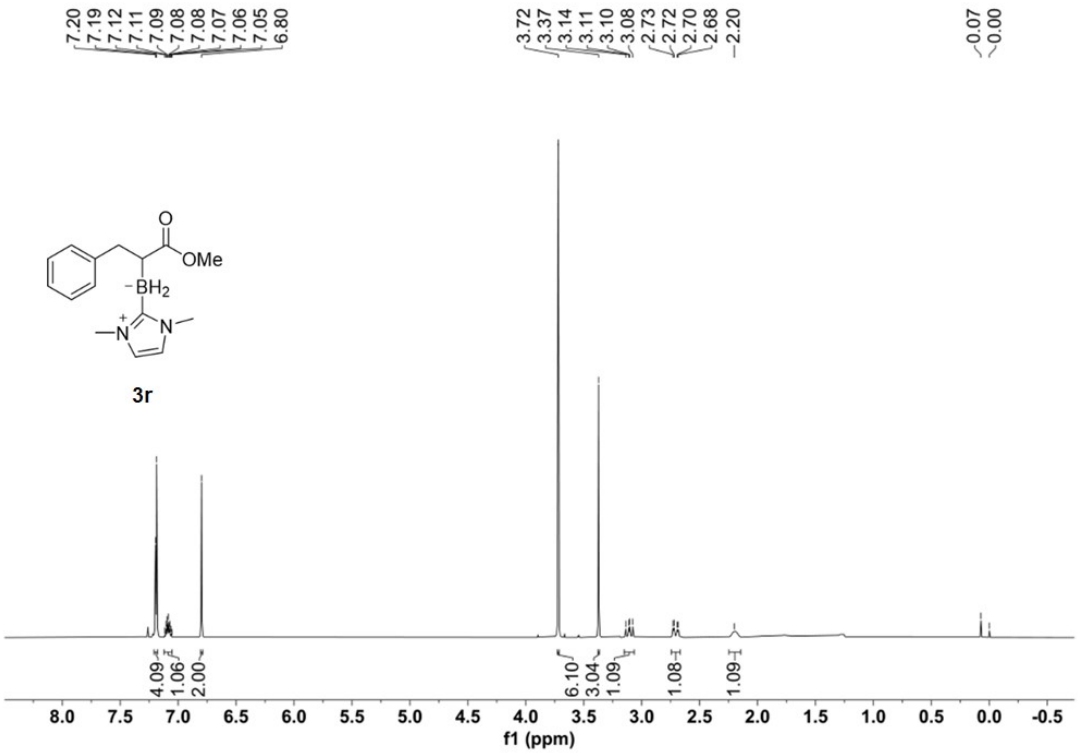

Fig. S40 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3r**.

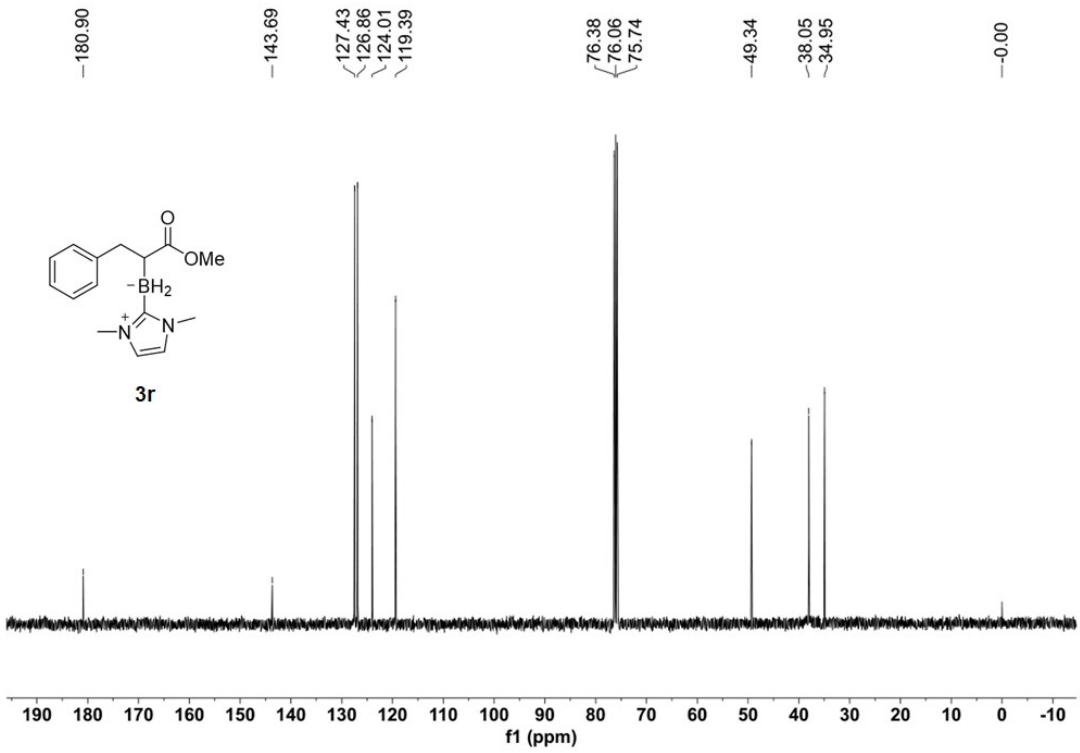

Fig. S41 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3r**.

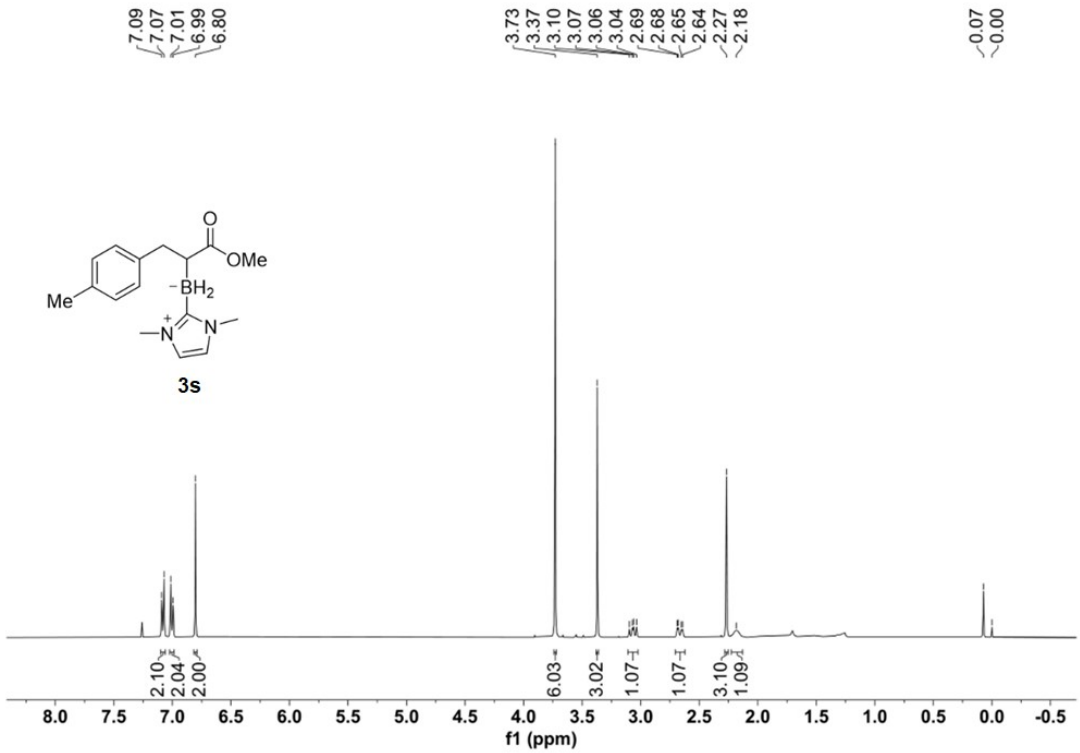

Fig. S42 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3s**.

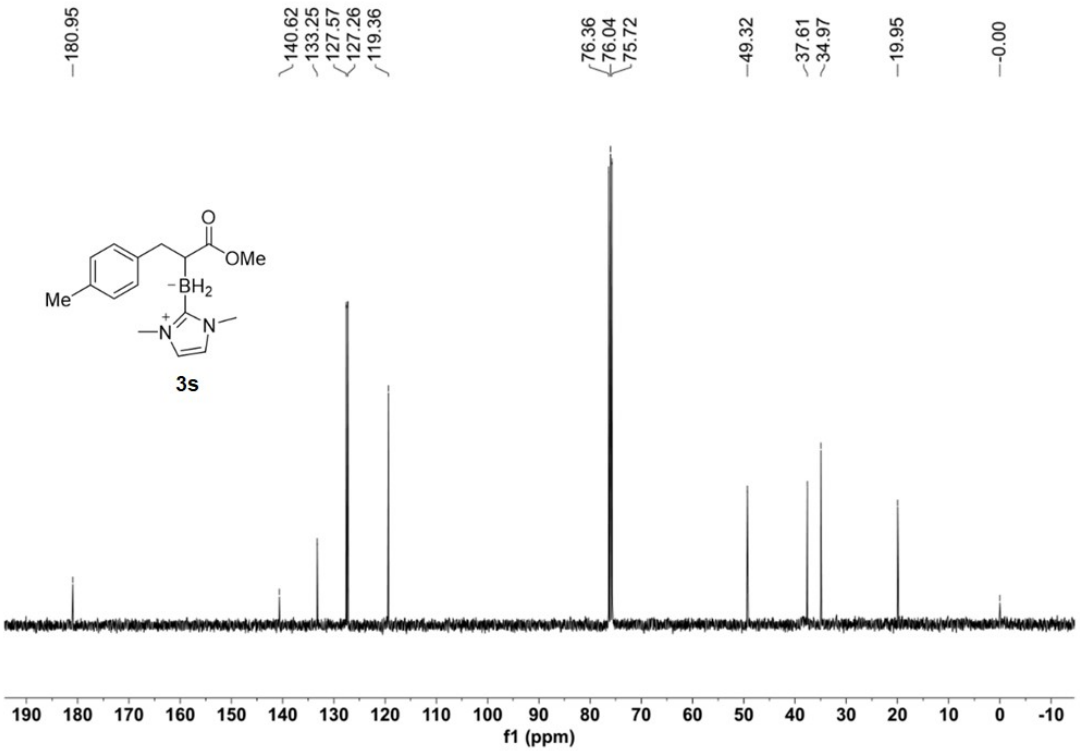

Fig. S43 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3s**.

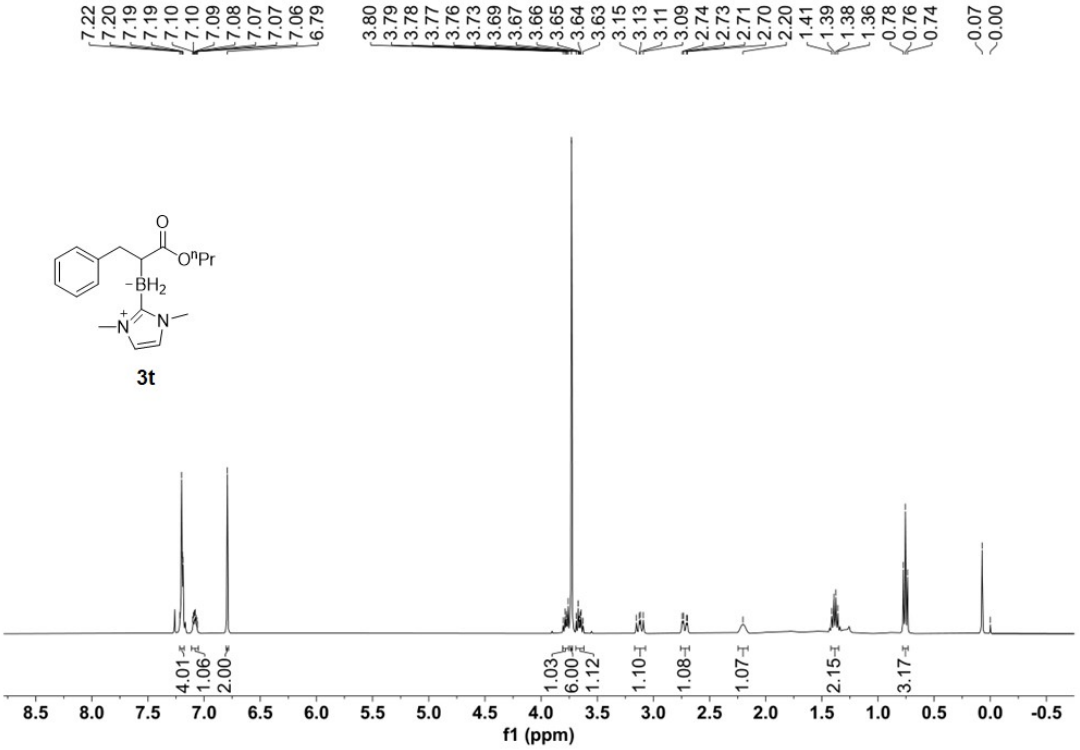

Fig. S44 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3t**.

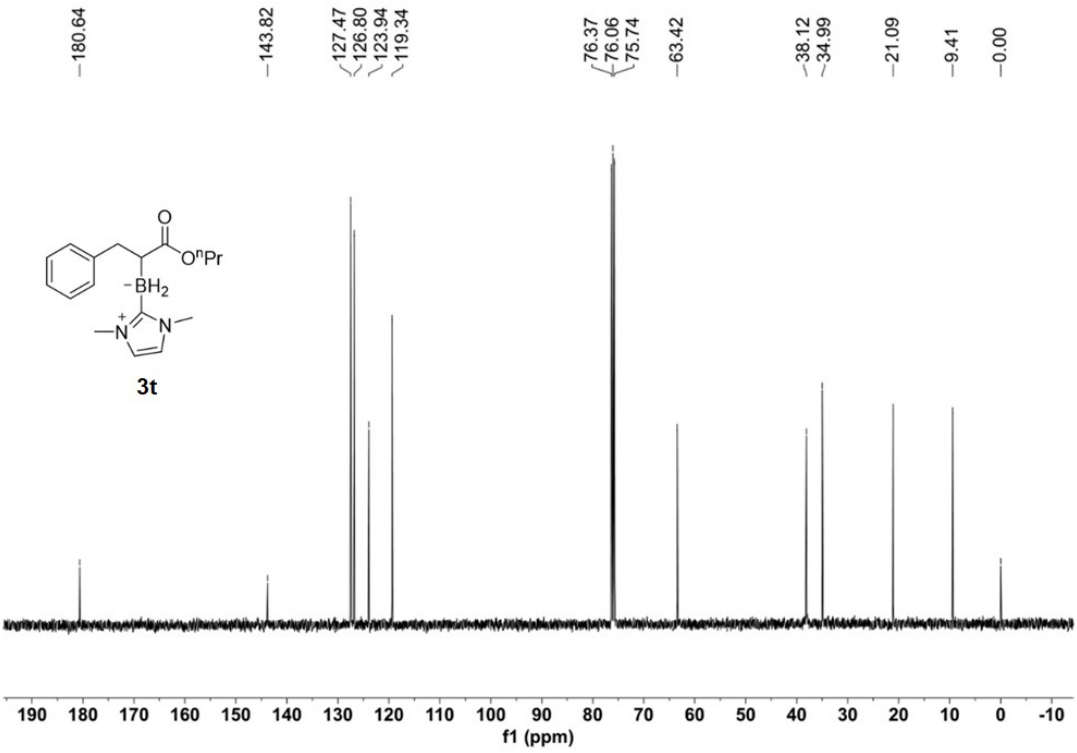

Fig. S45 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3t**.

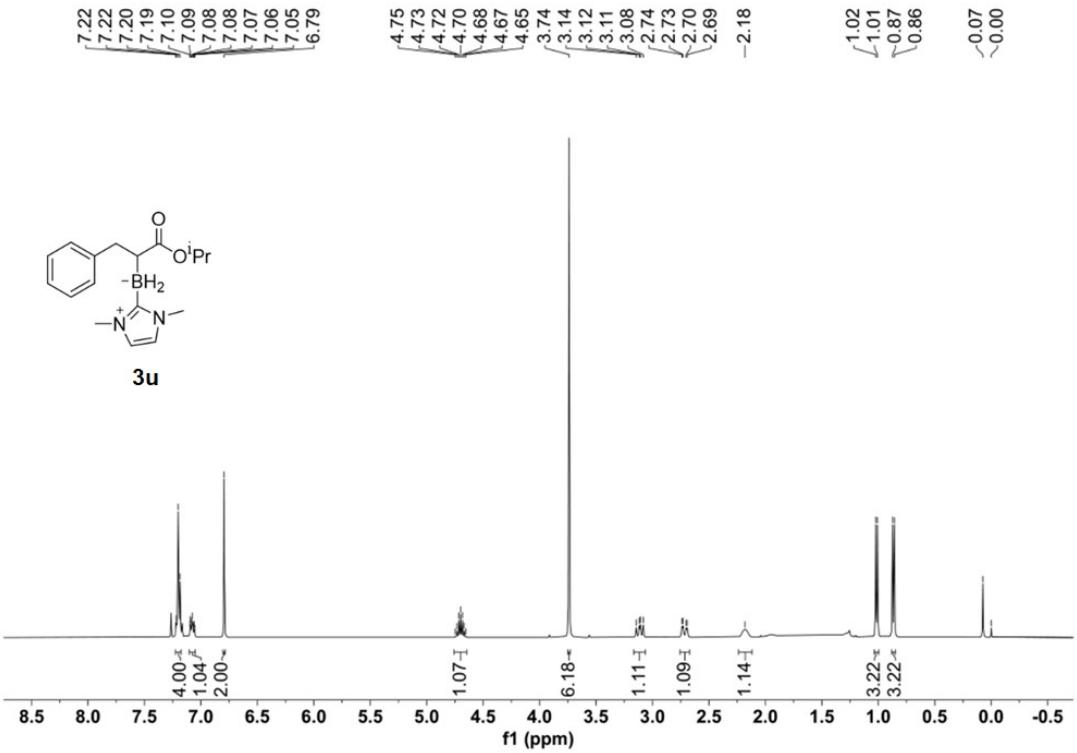

Fig. S46 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3u**.

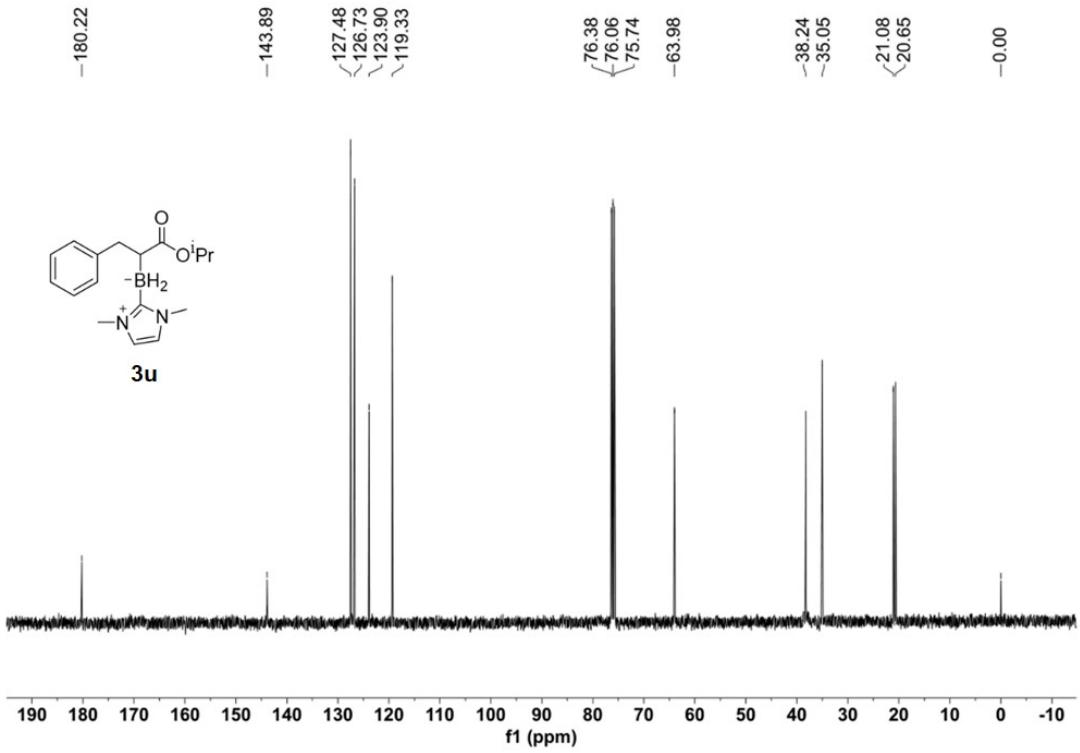

Fig. S47 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3u**.

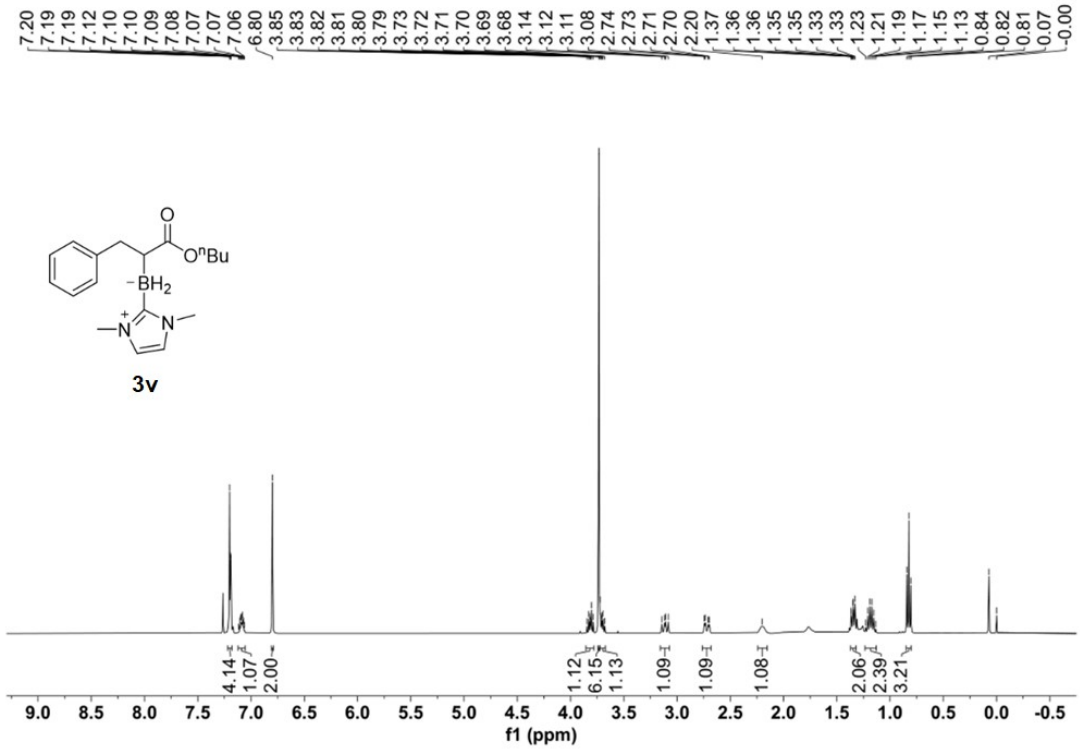

Fig. S48 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3v**.

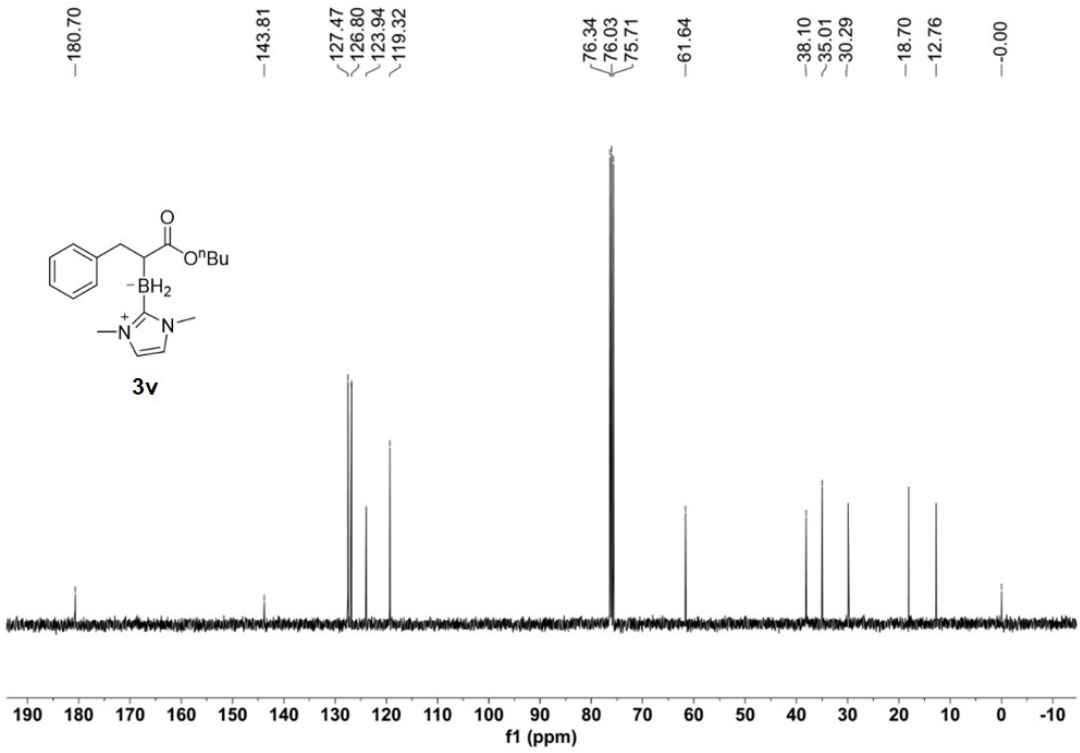

Fig. S49 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3v**.

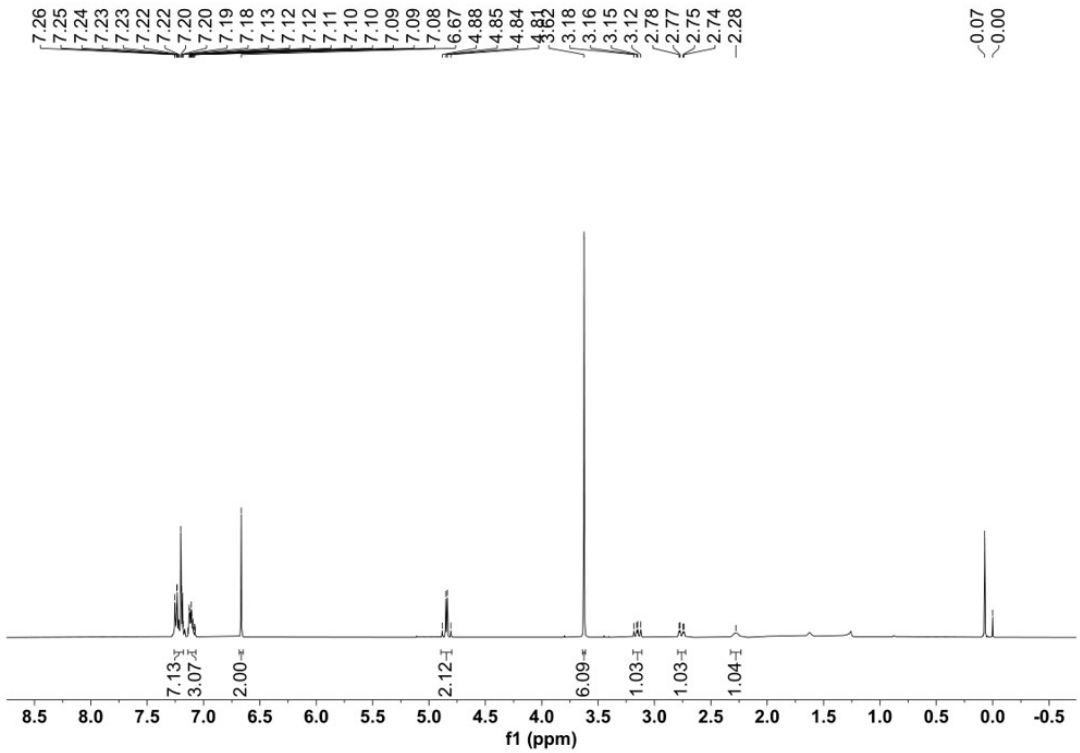

Fig. S50 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3w**.

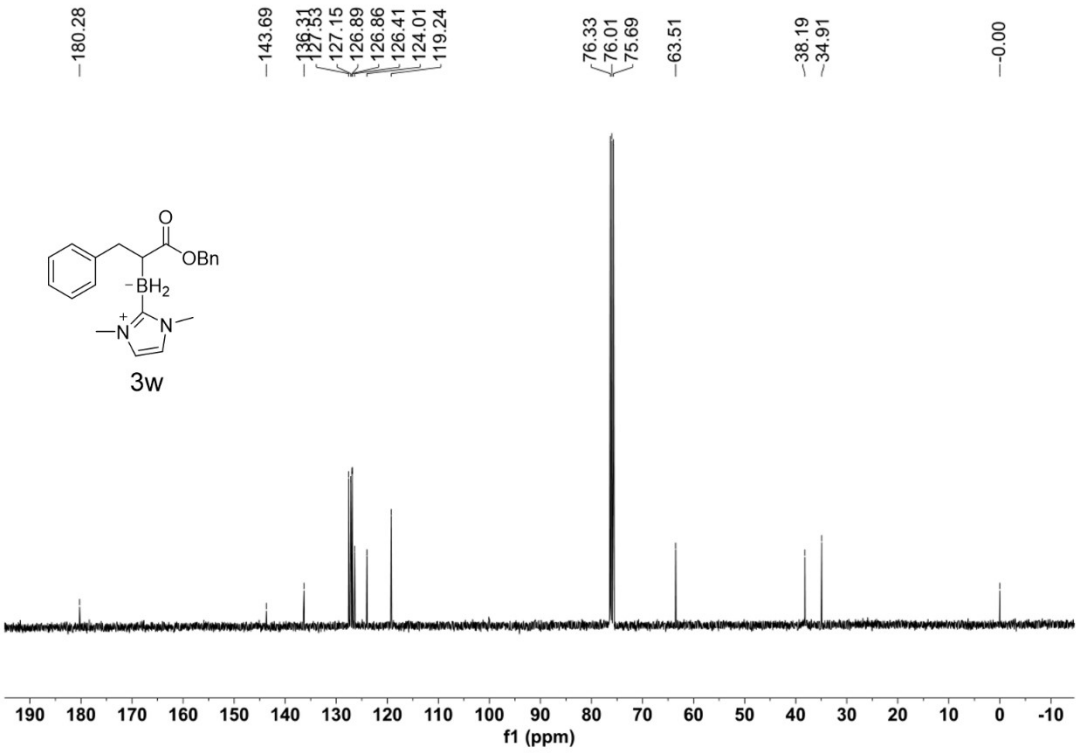

Fig. S51 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3w**.

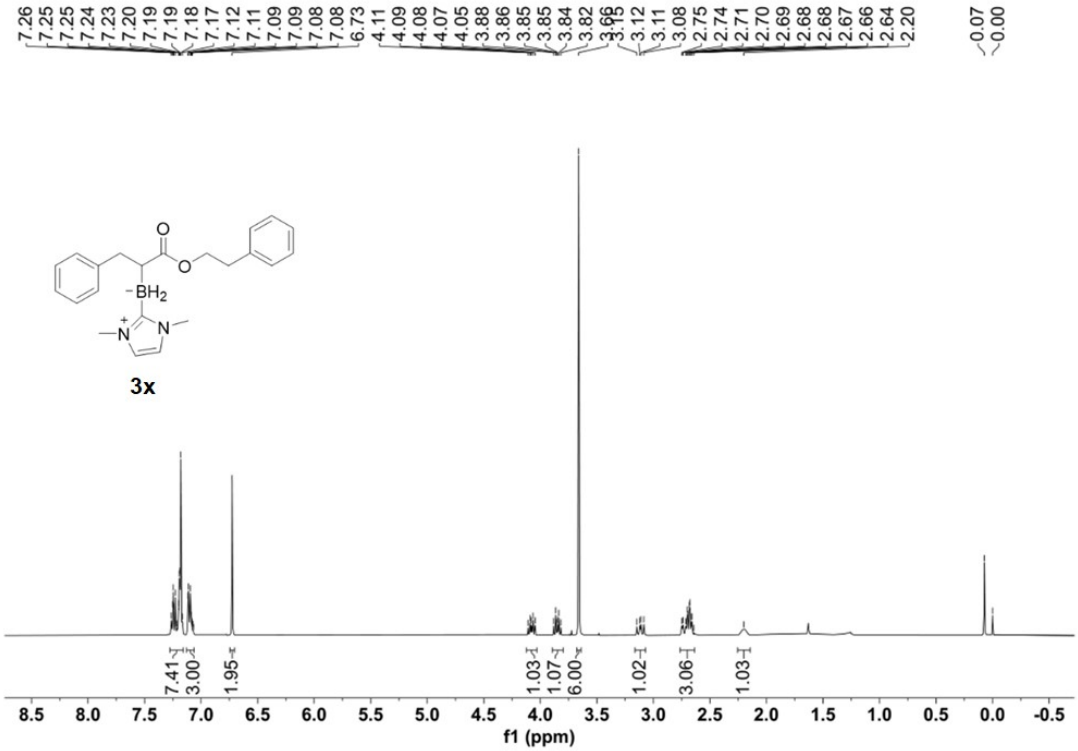

Fig. S52 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3x**.

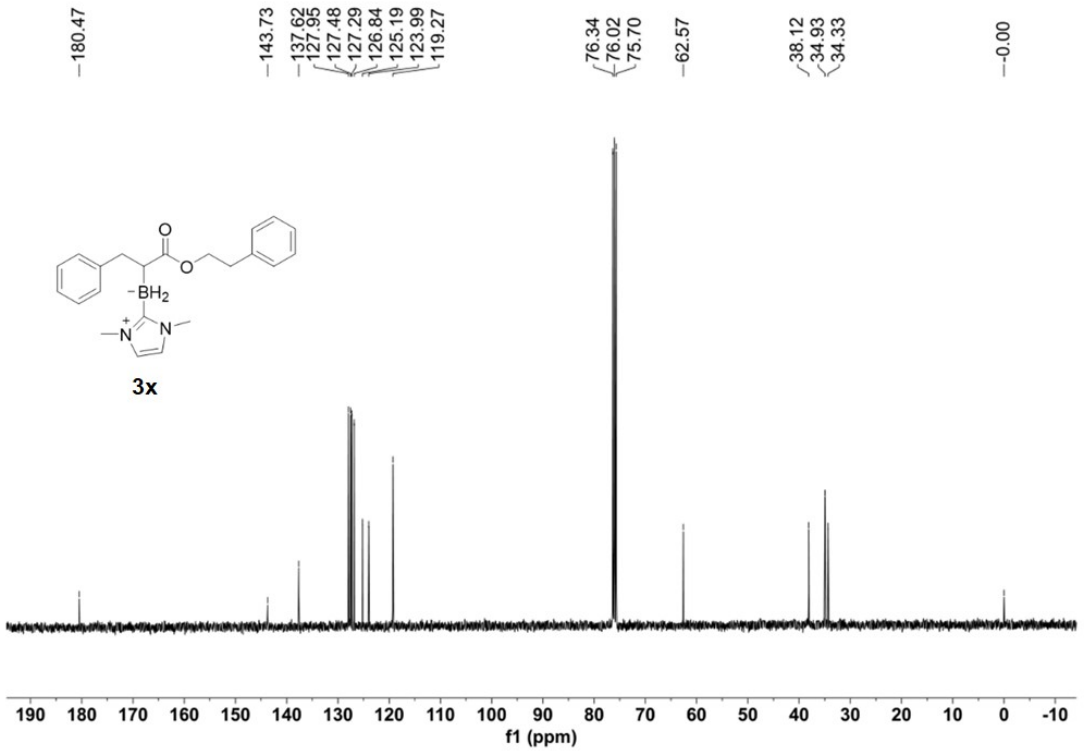

Fig. S53 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3x**.

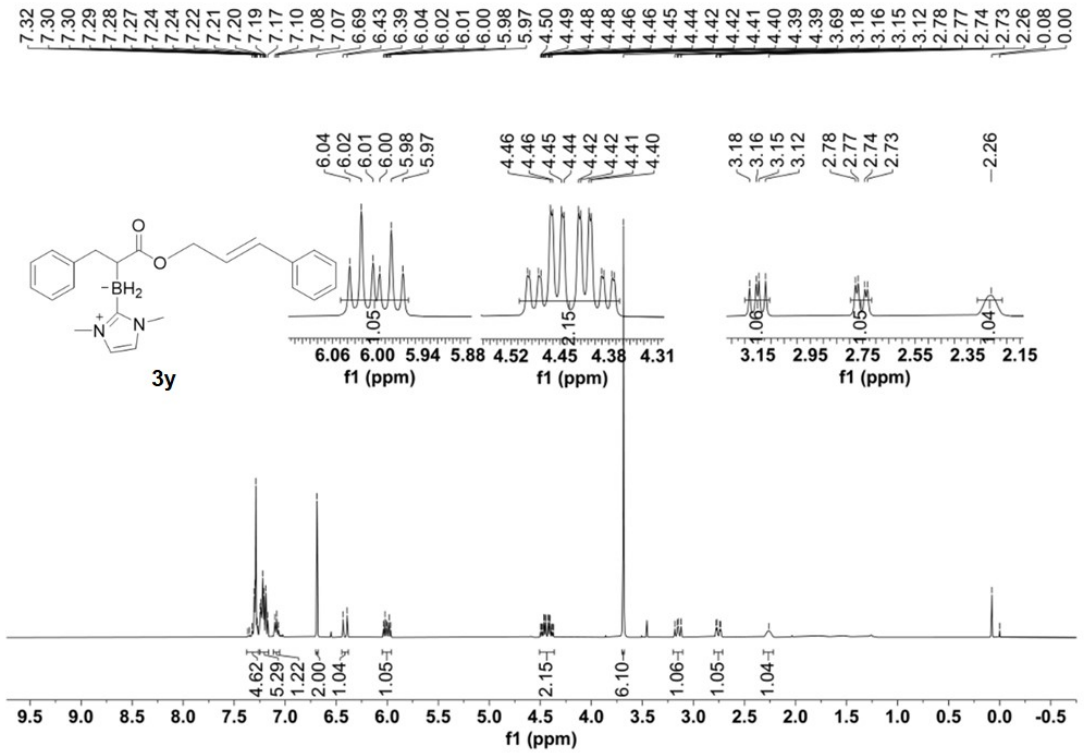

Fig. S54 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3y**.

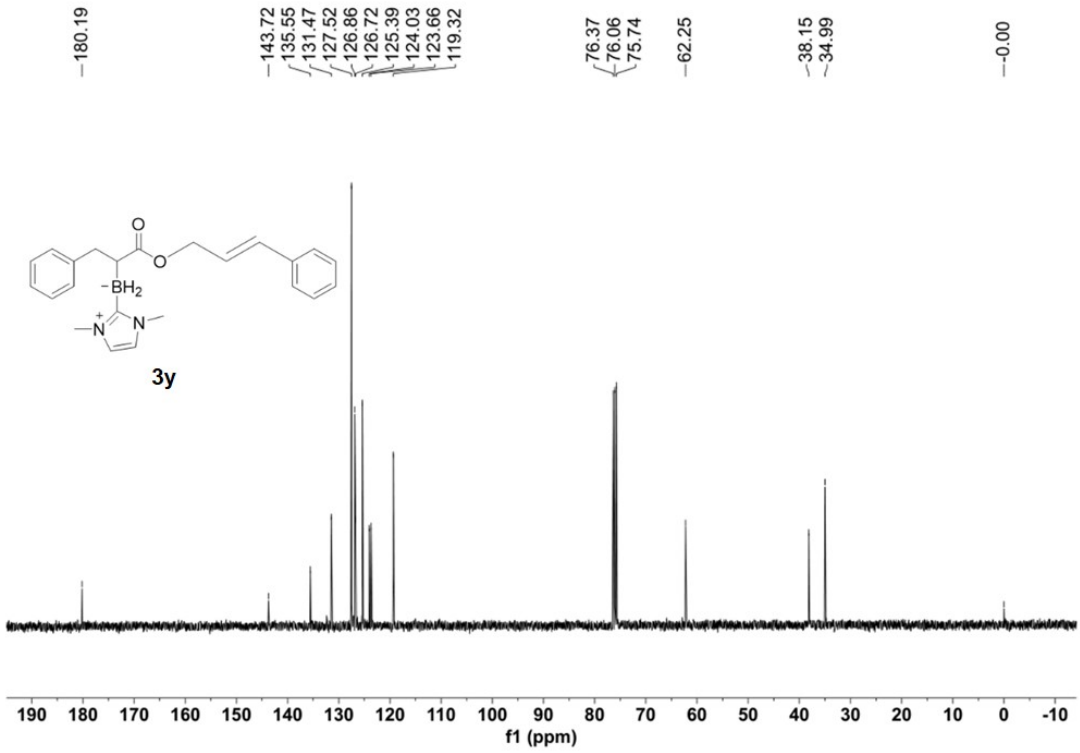

Fig. S55 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3y**.

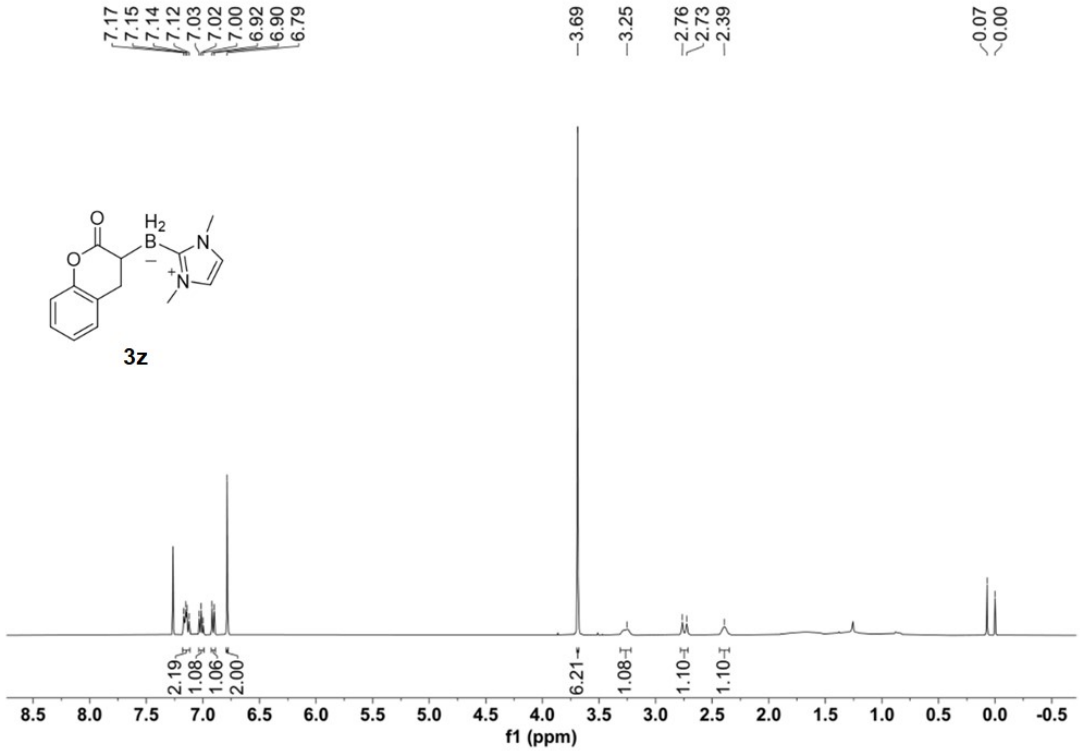

Fig. S56 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3z**.

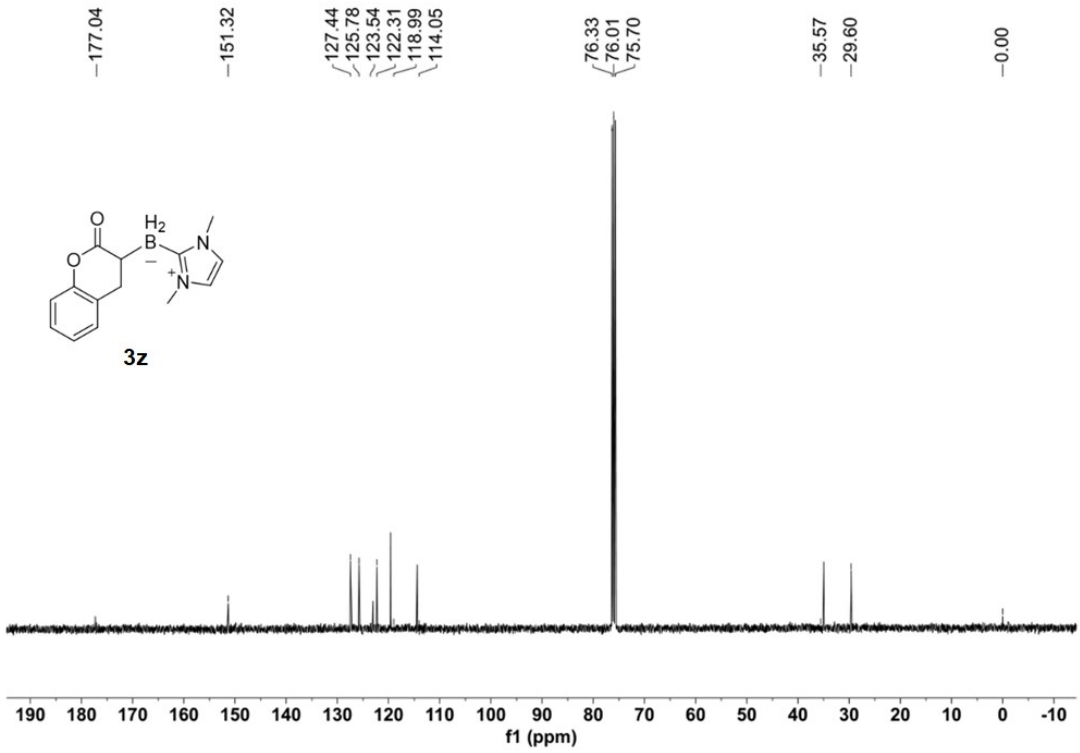

Fig. S57 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3z**.

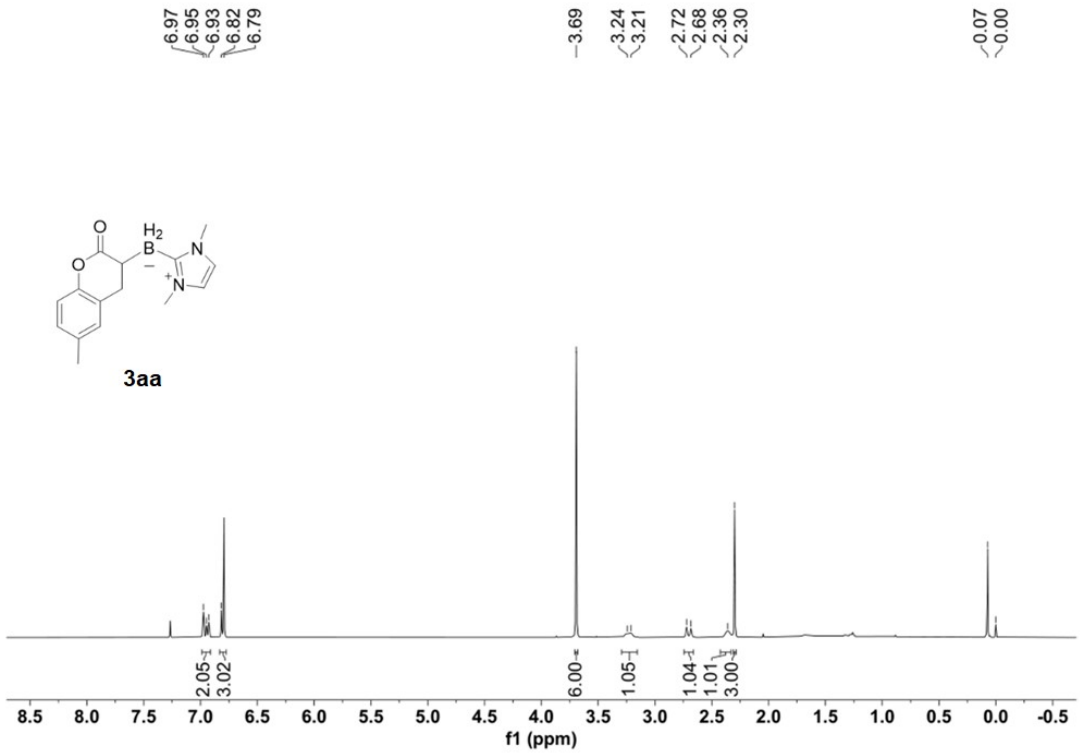

Fig. S58 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3aa**.

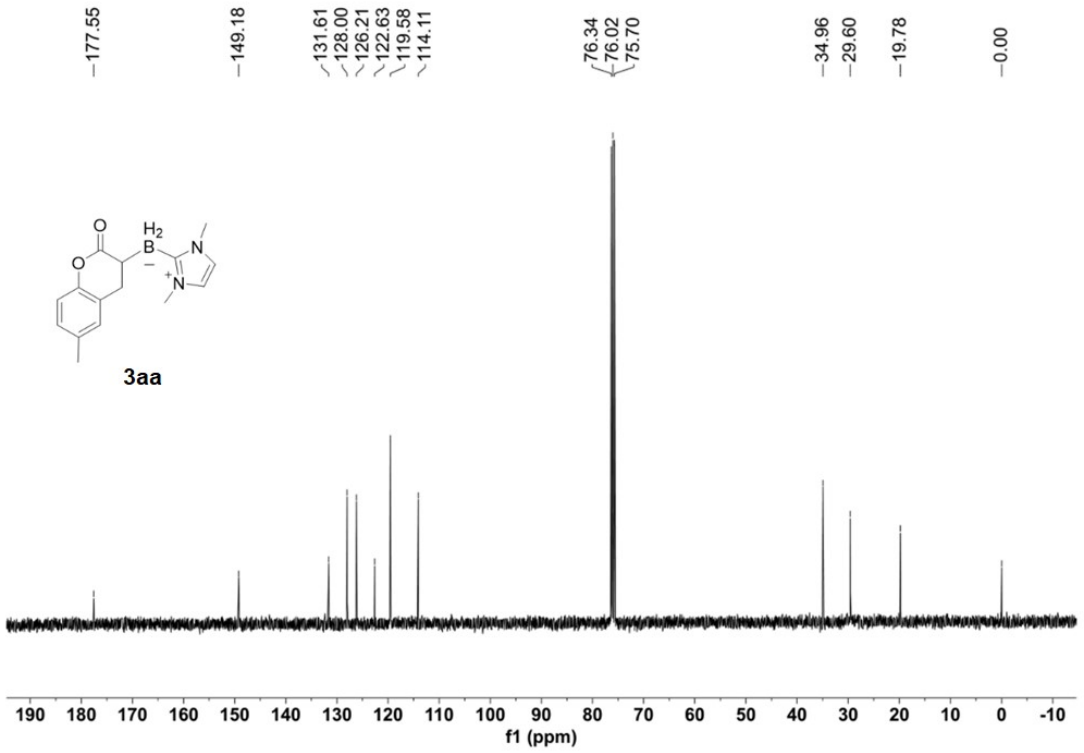

Fig. S59 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3aa**.

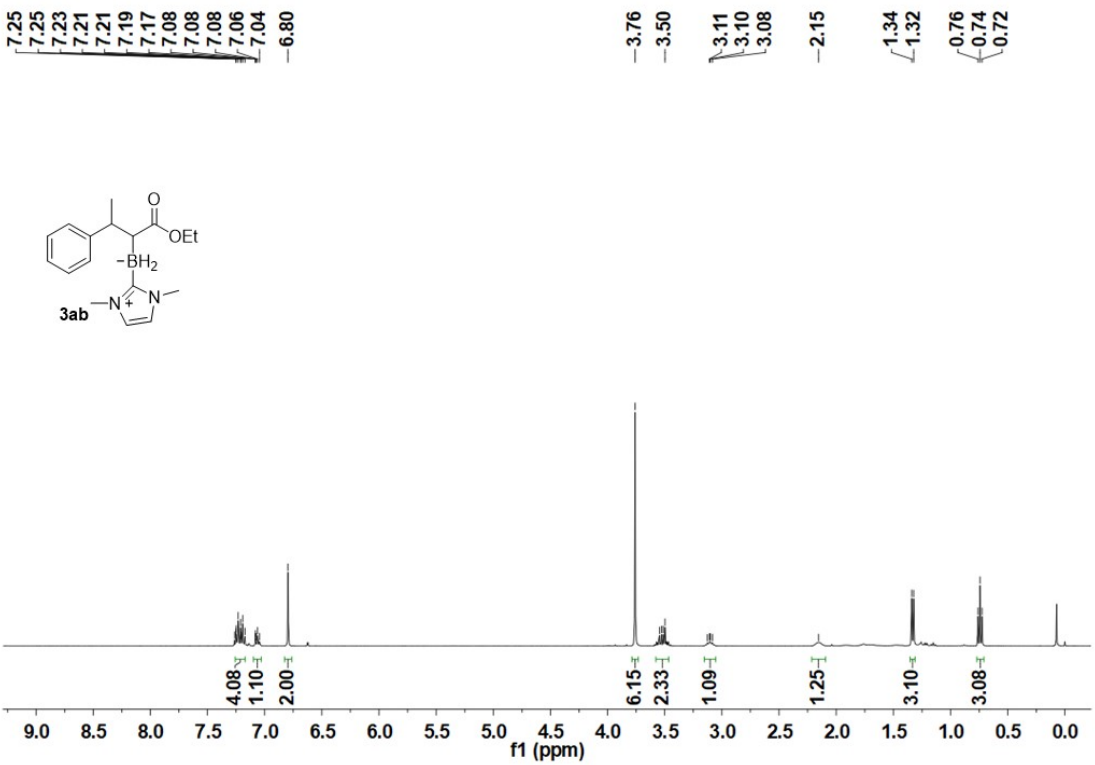

Fig. S60 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ab**.

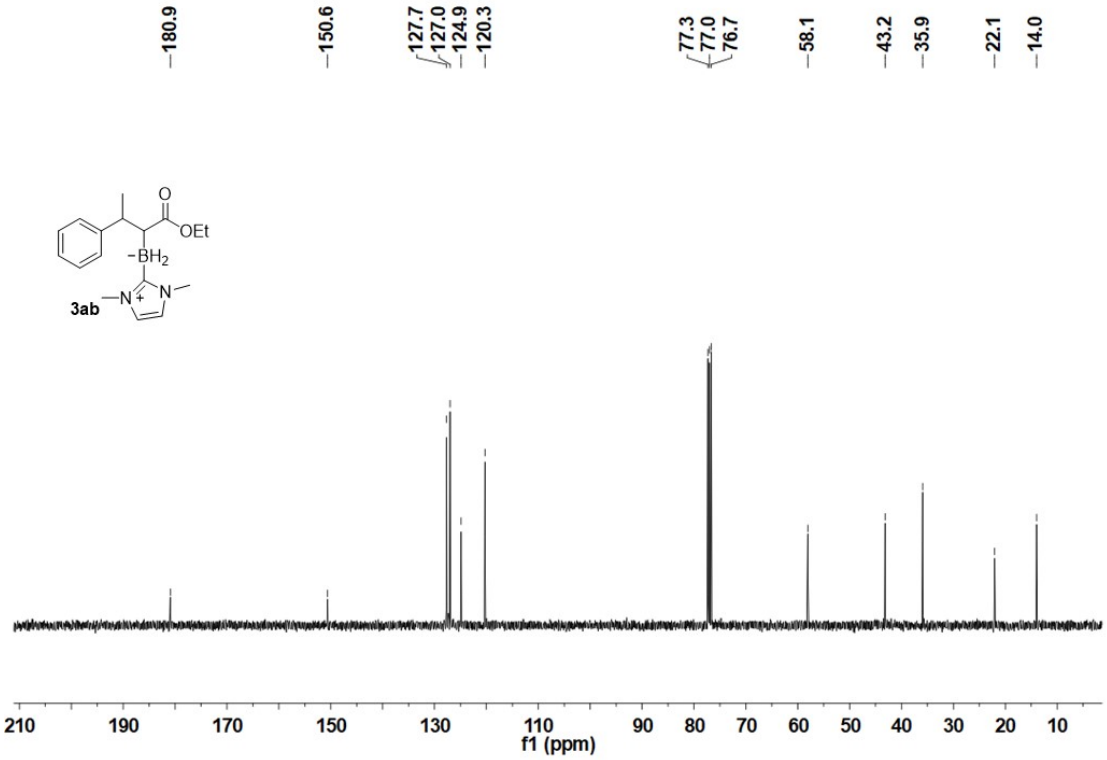

Fig. S61 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ab**.

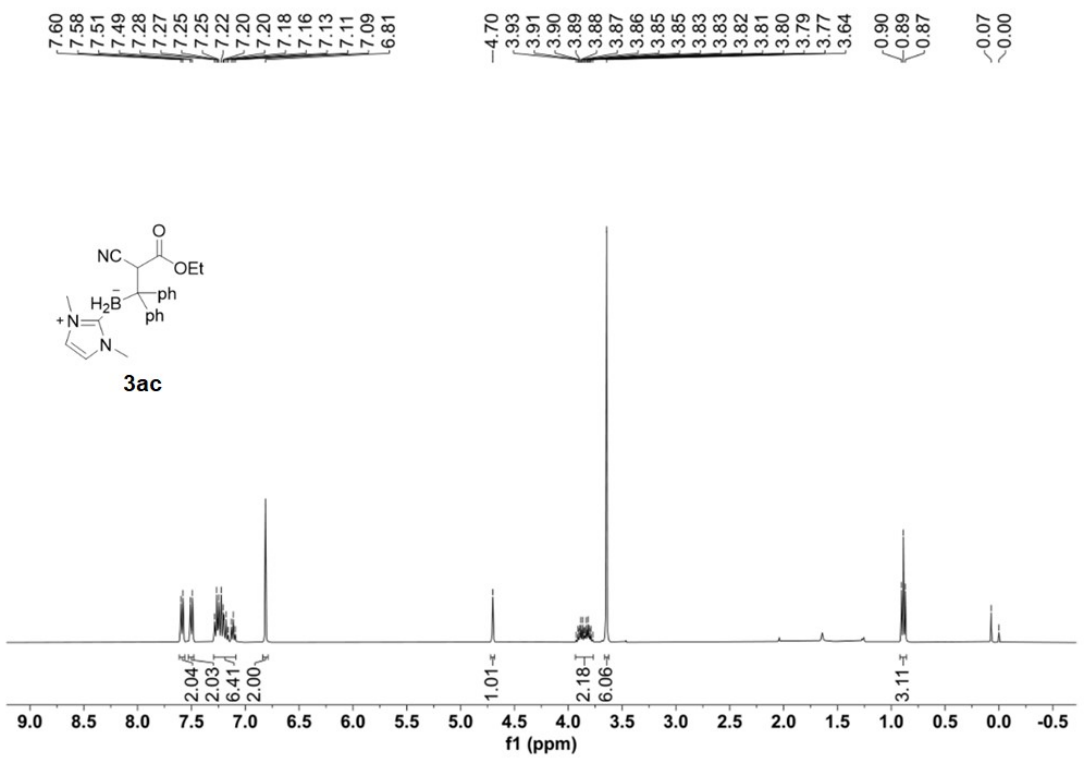

Fig. S62 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ac**.

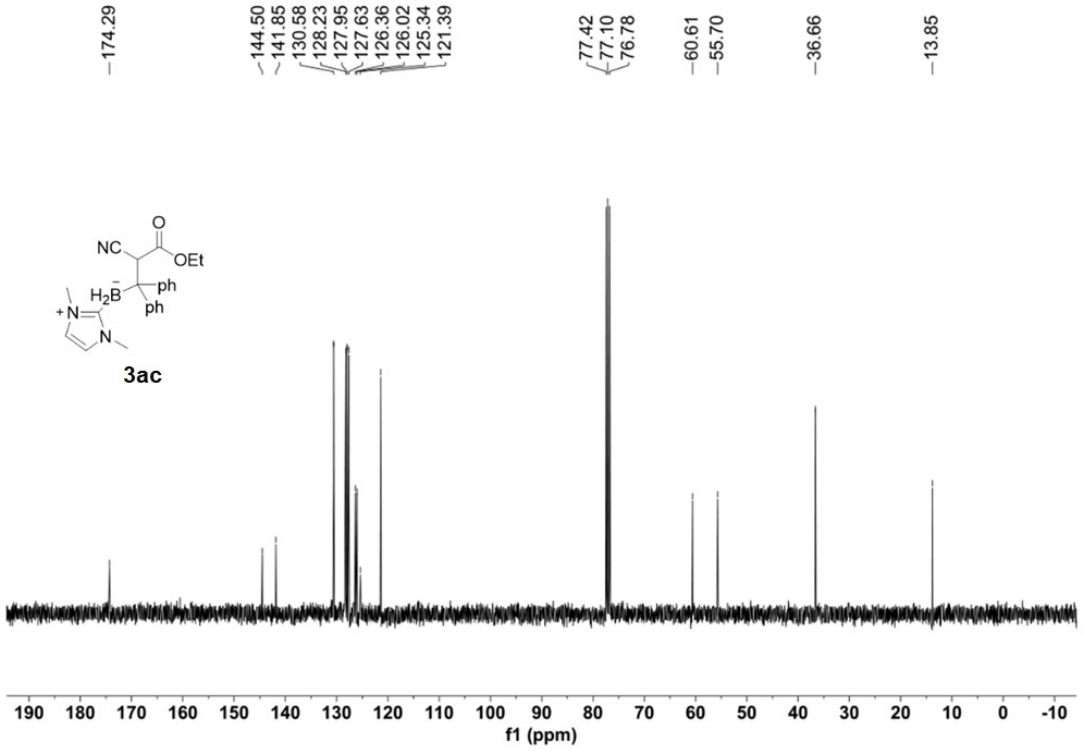

Fig. S63 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ac**.

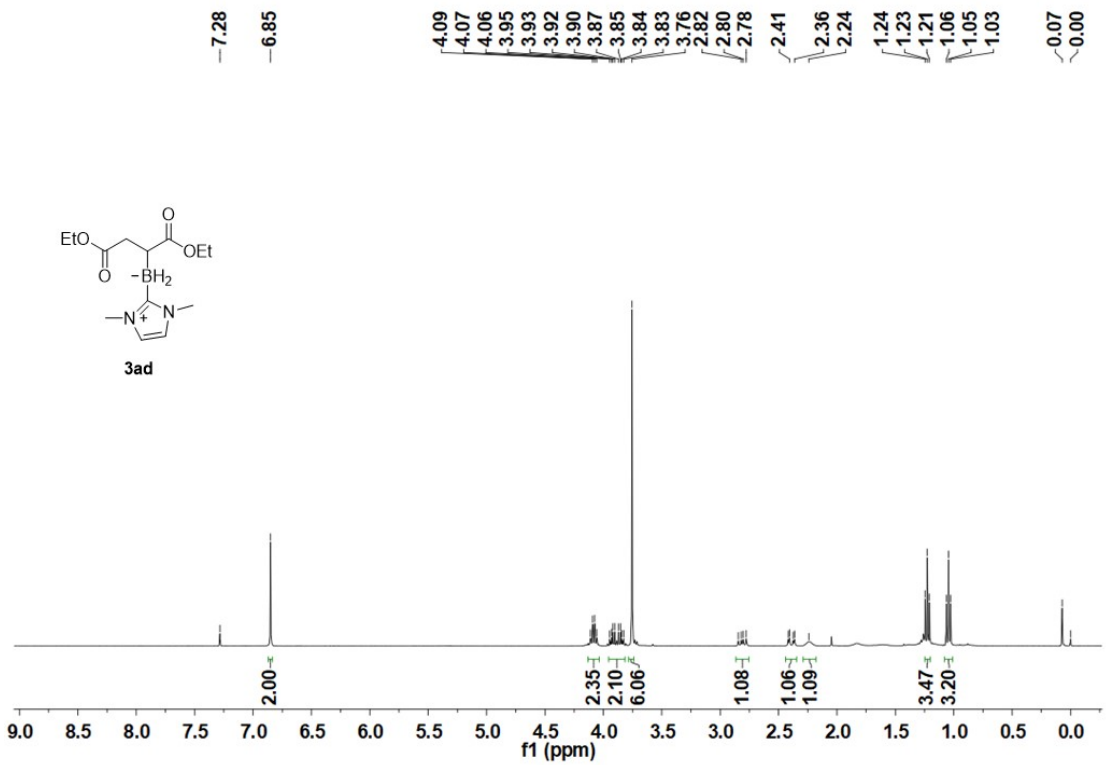

Fig. S64 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ad**.

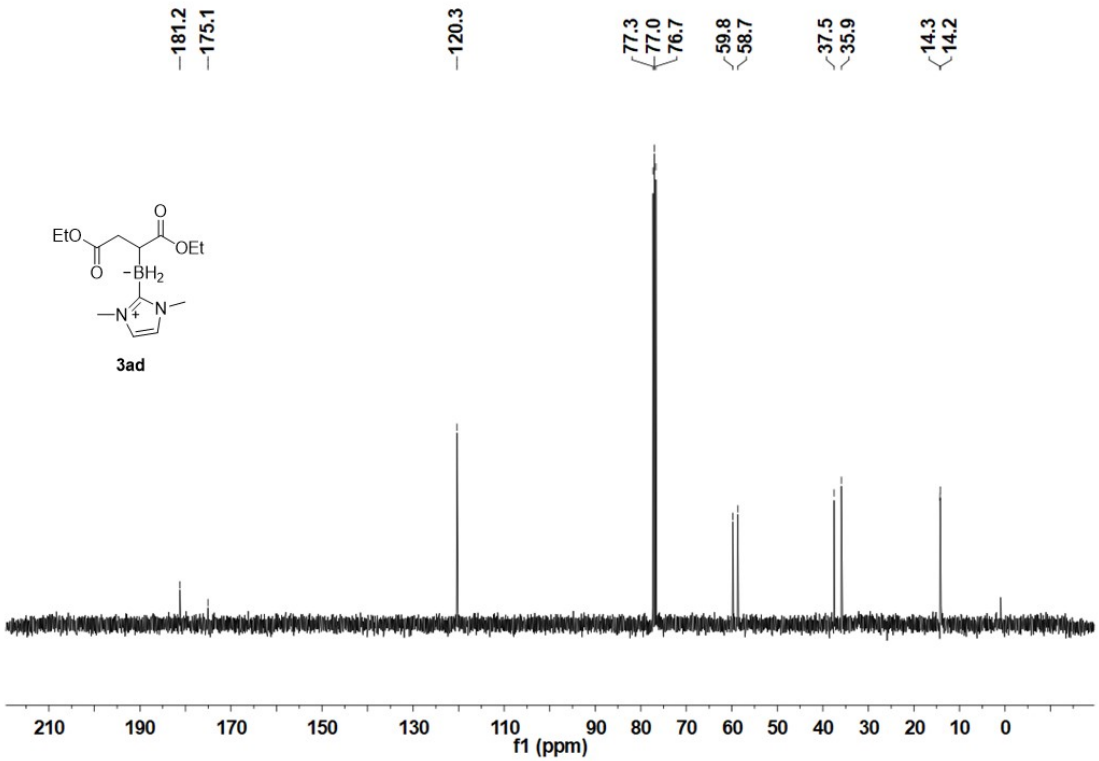

Fig. S65 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ad**.

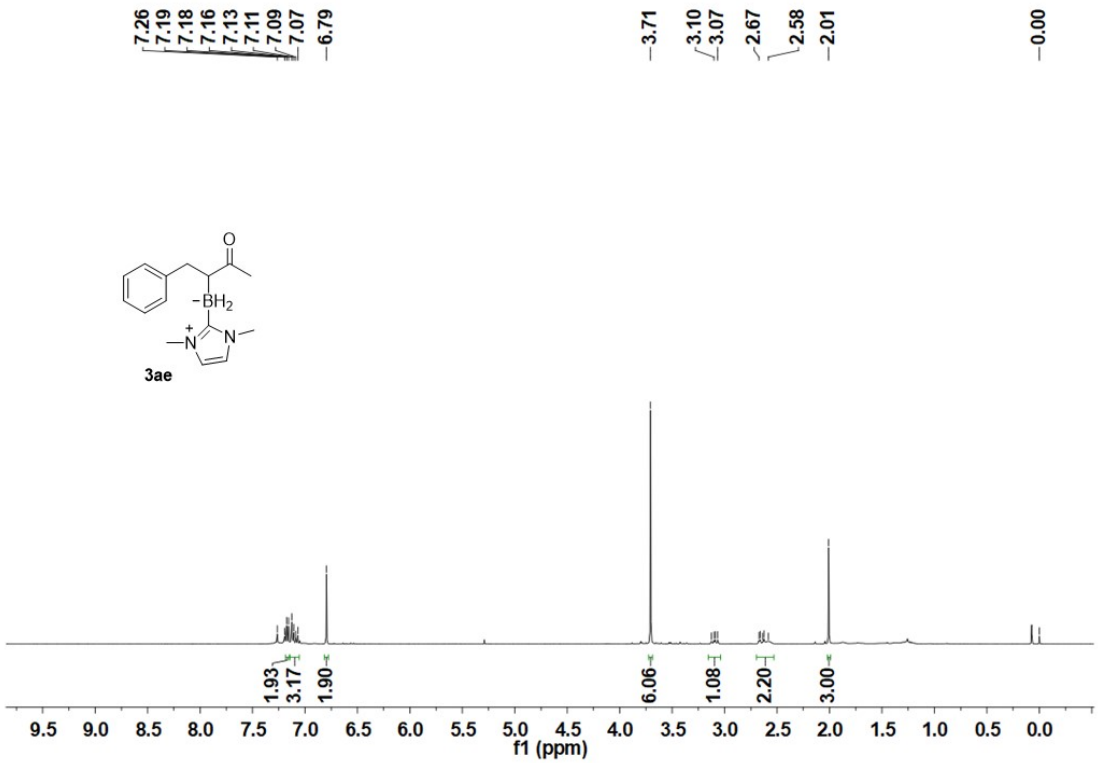

Fig. S66 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ae**.

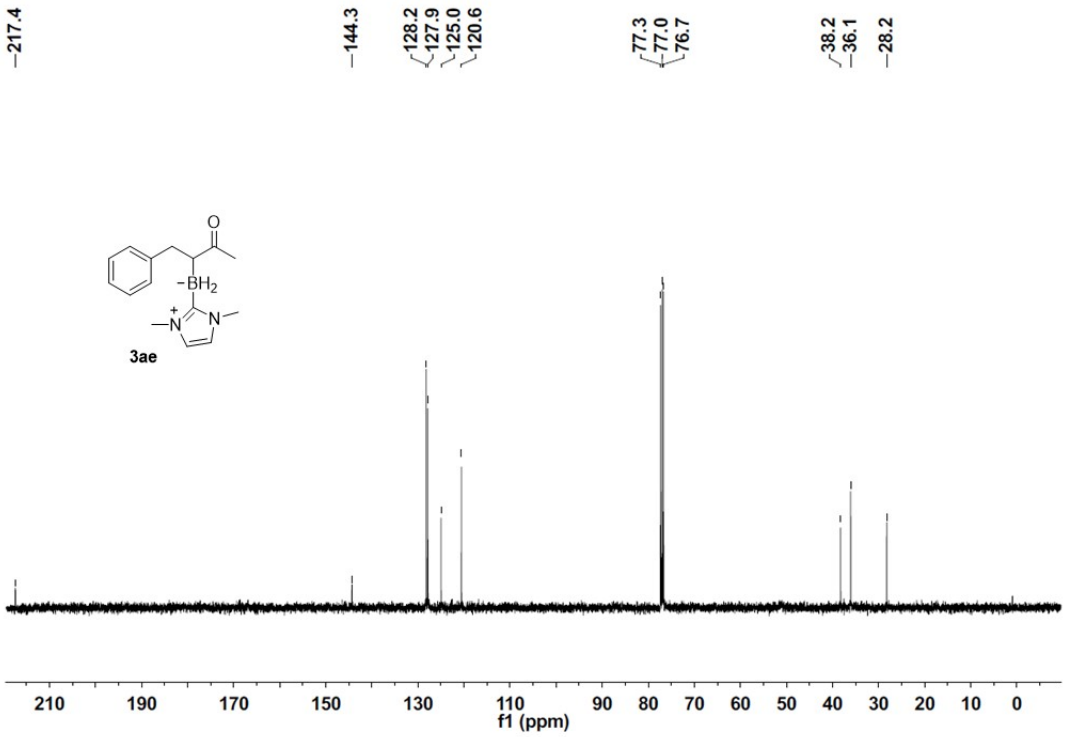

Fig. S67 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ae**.

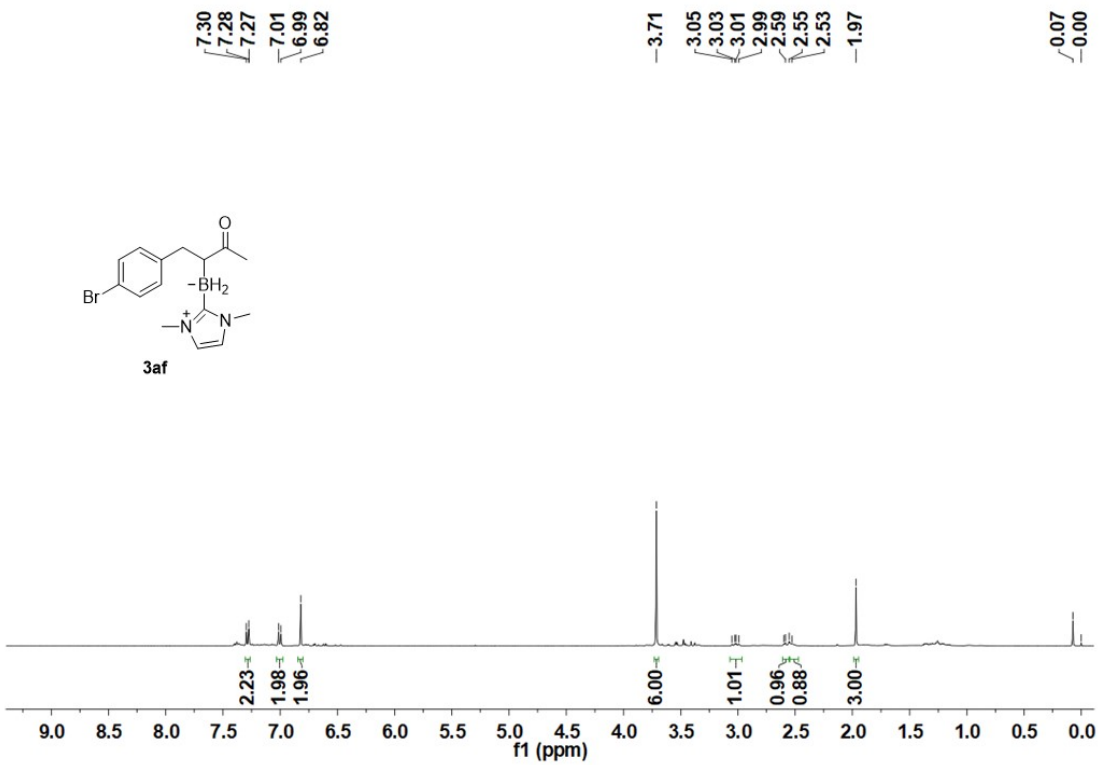

Fig. S68 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3af**.

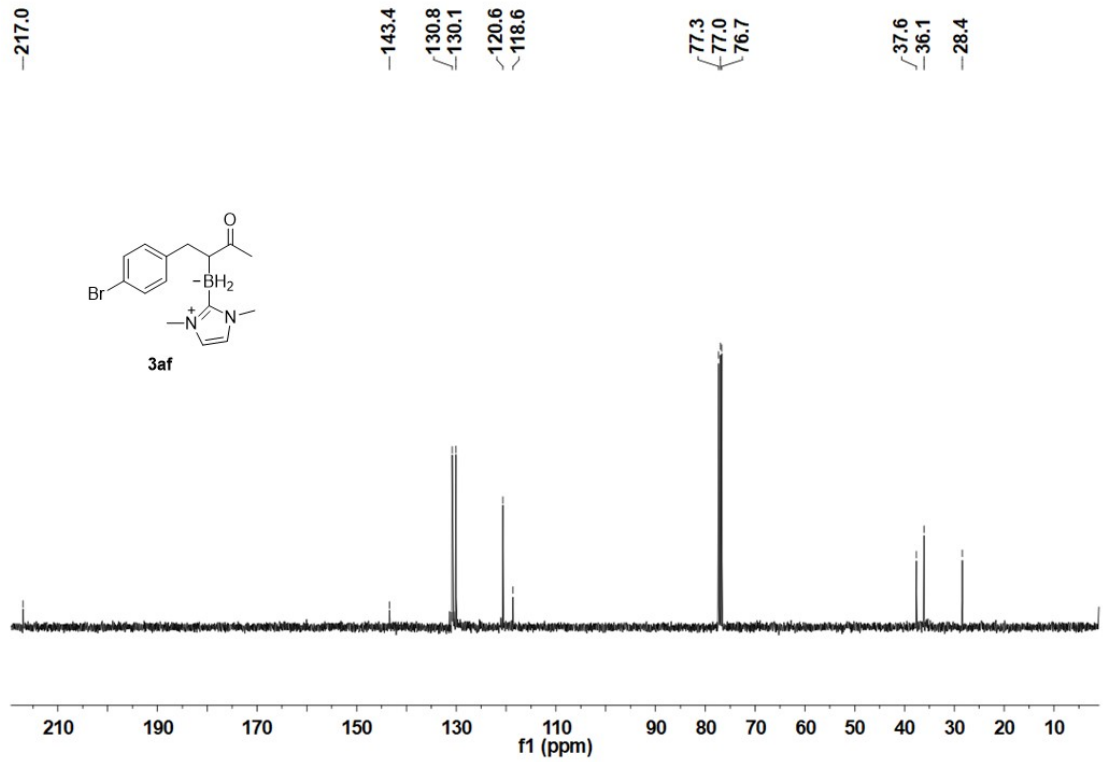

Fig. S69 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3af**.

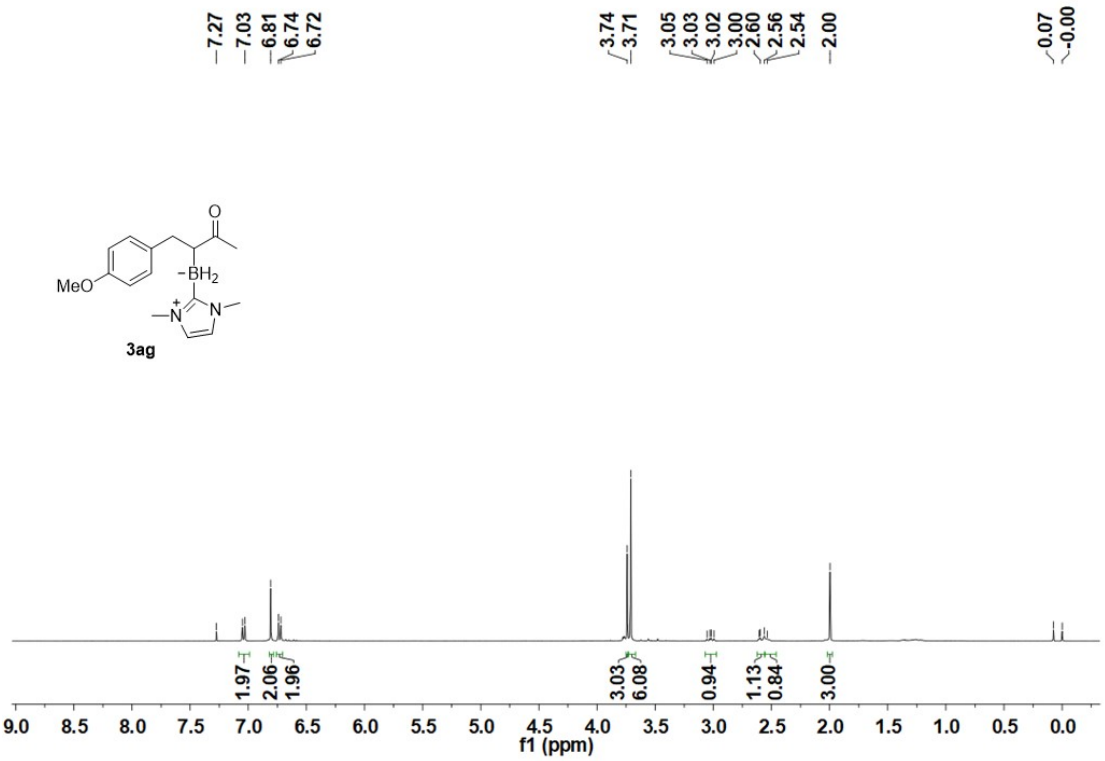

Fig. S70 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ag**.

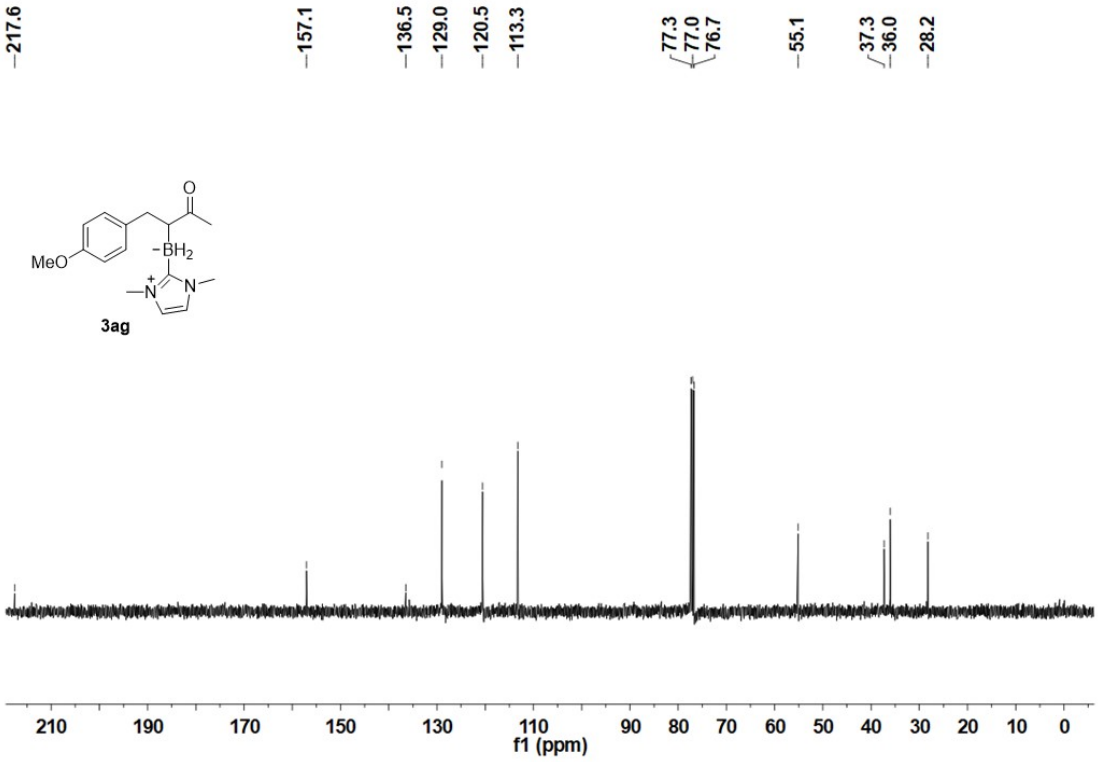

Fig. S71 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ag**.

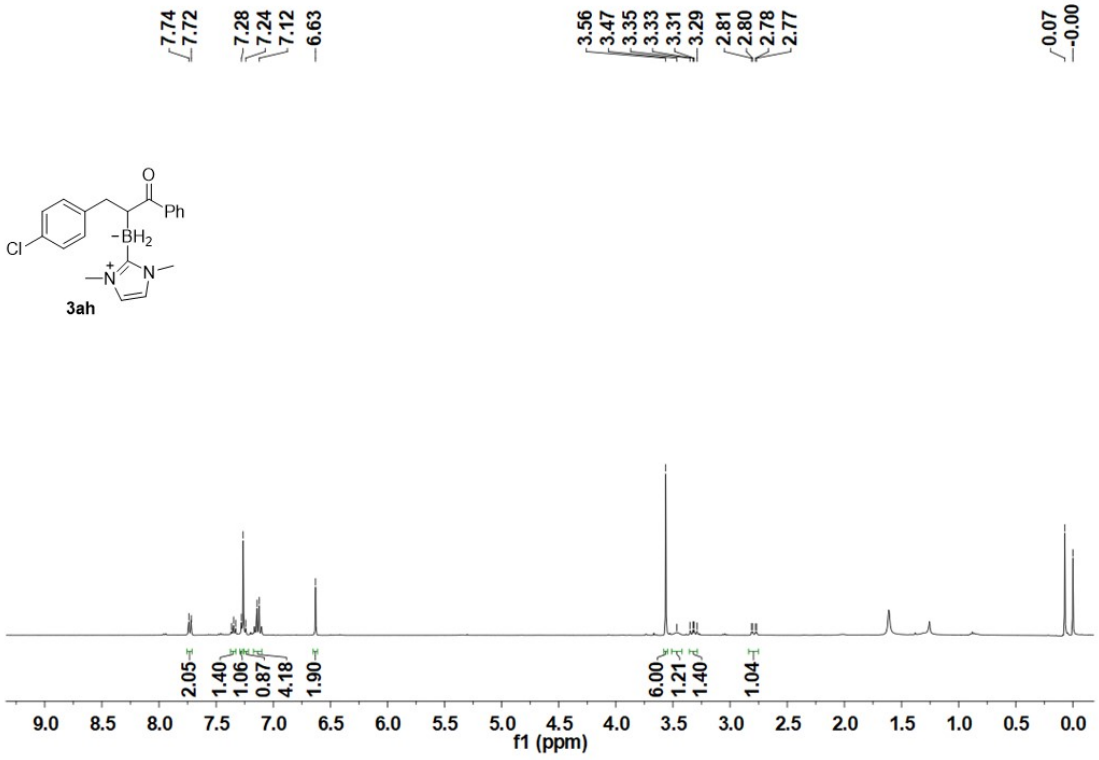

Fig. S72 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ah**.

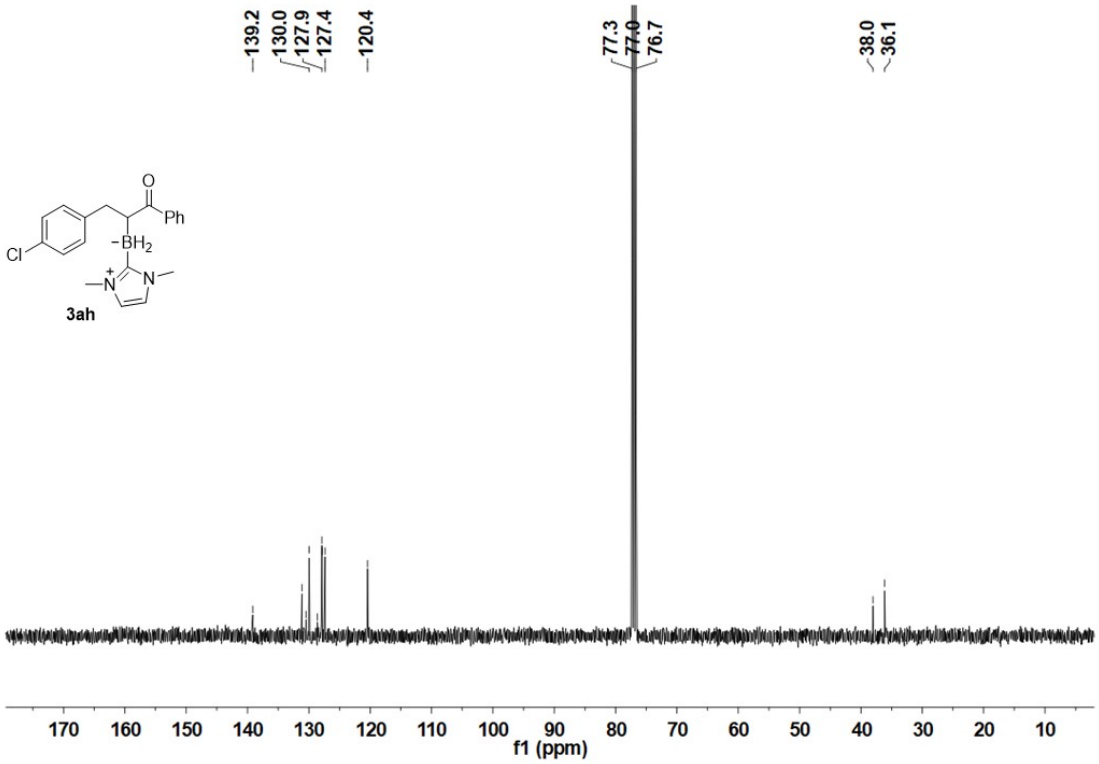

Fig. S73 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ah**.

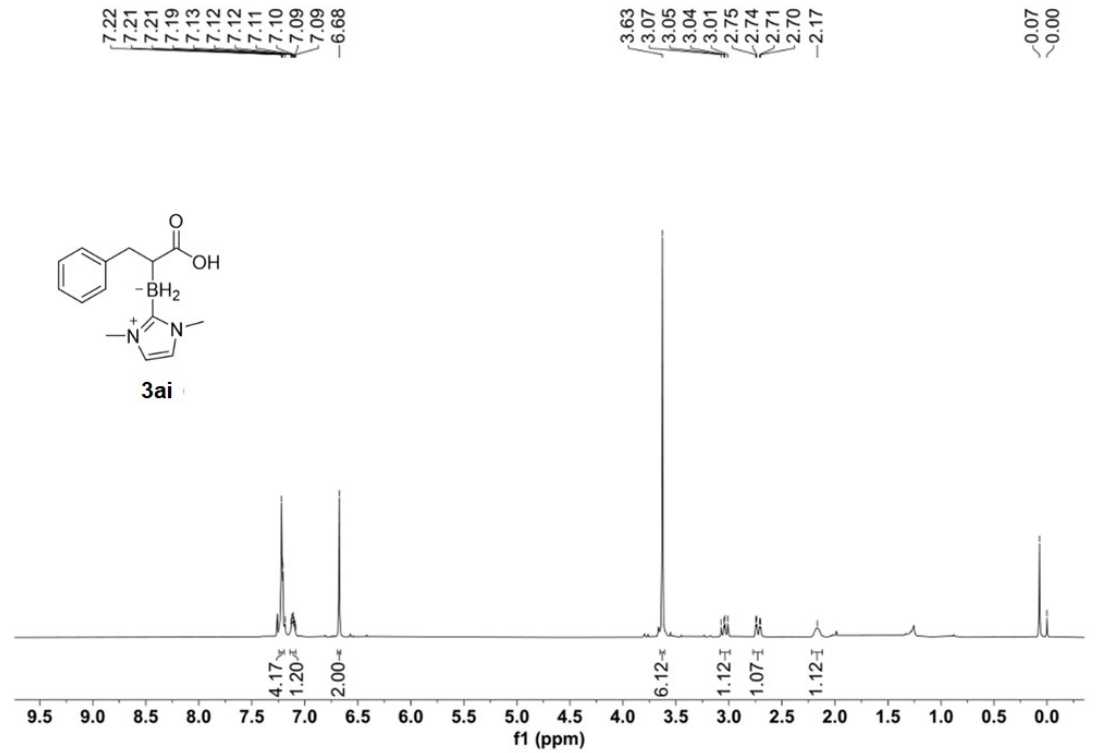

Fig. S74 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ai**.

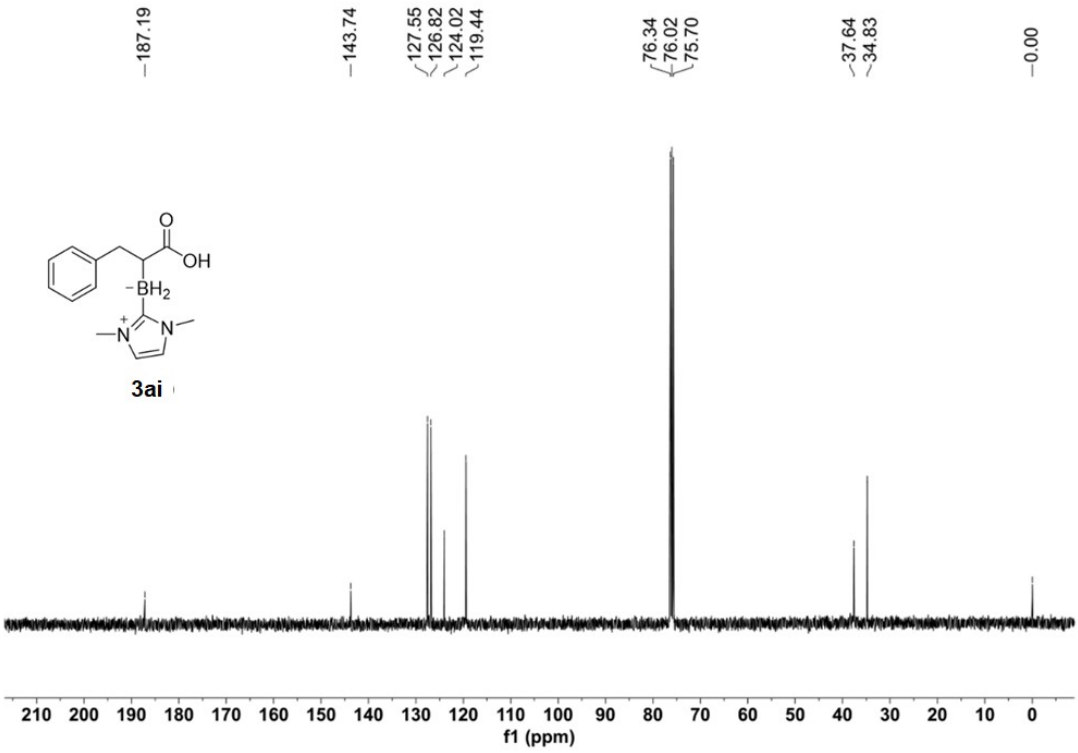

Fig. S75 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ai**.

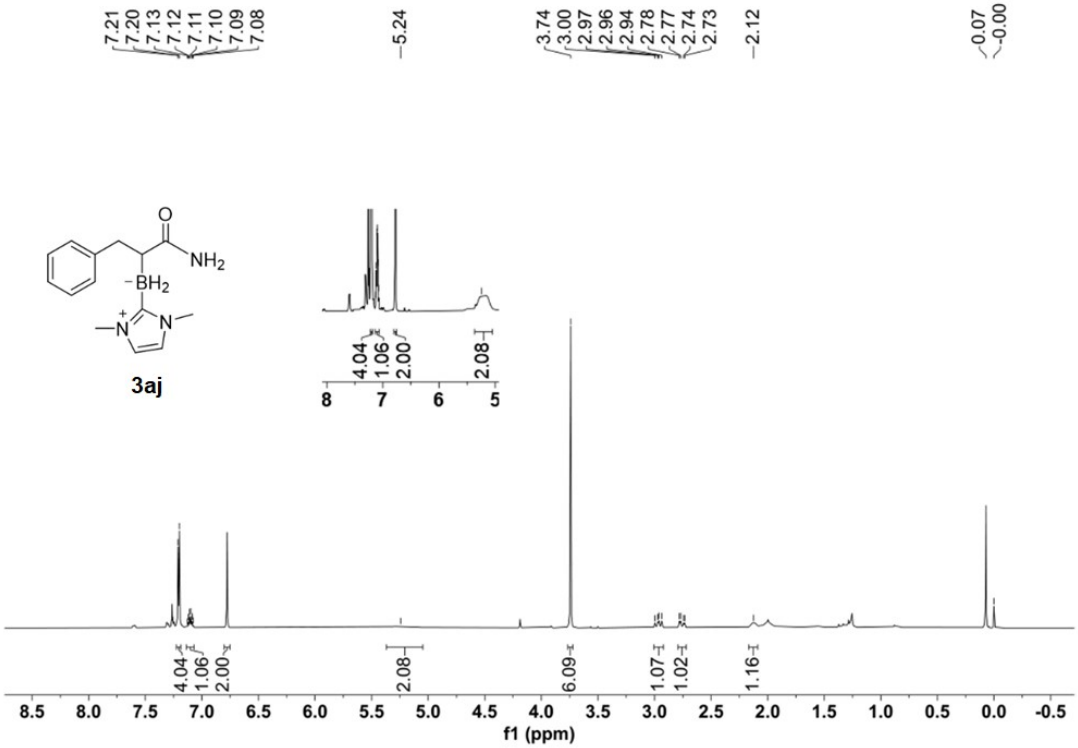

Fig. S76 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3aj**.

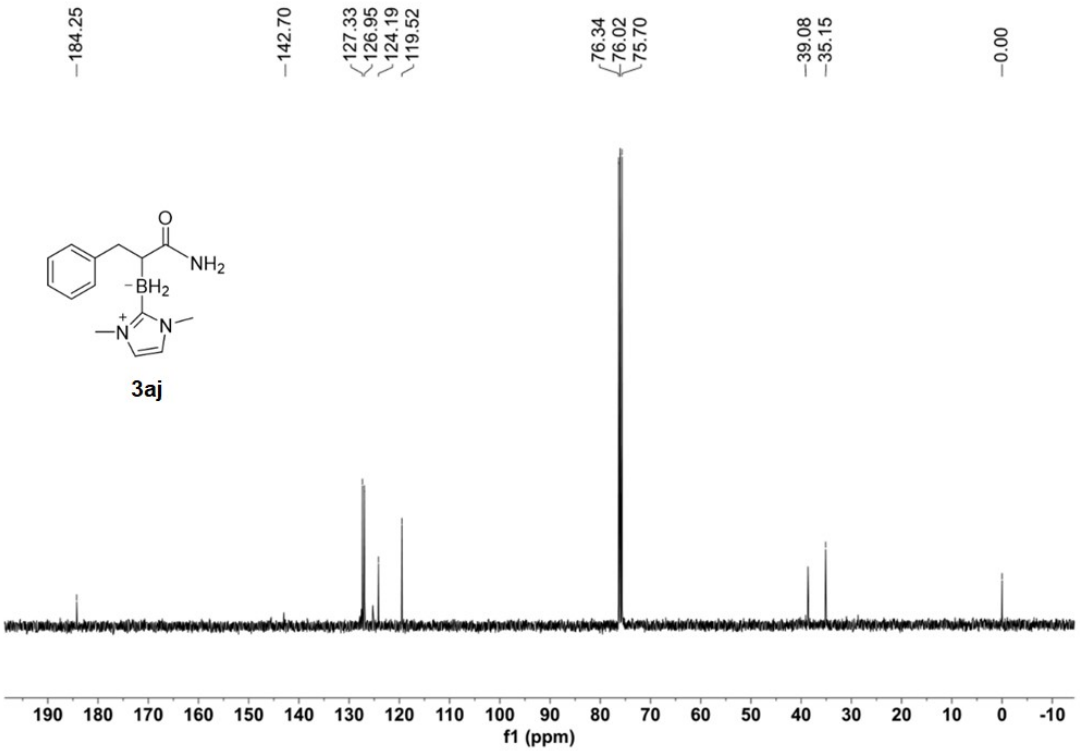

Fig. S77 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3aj**.

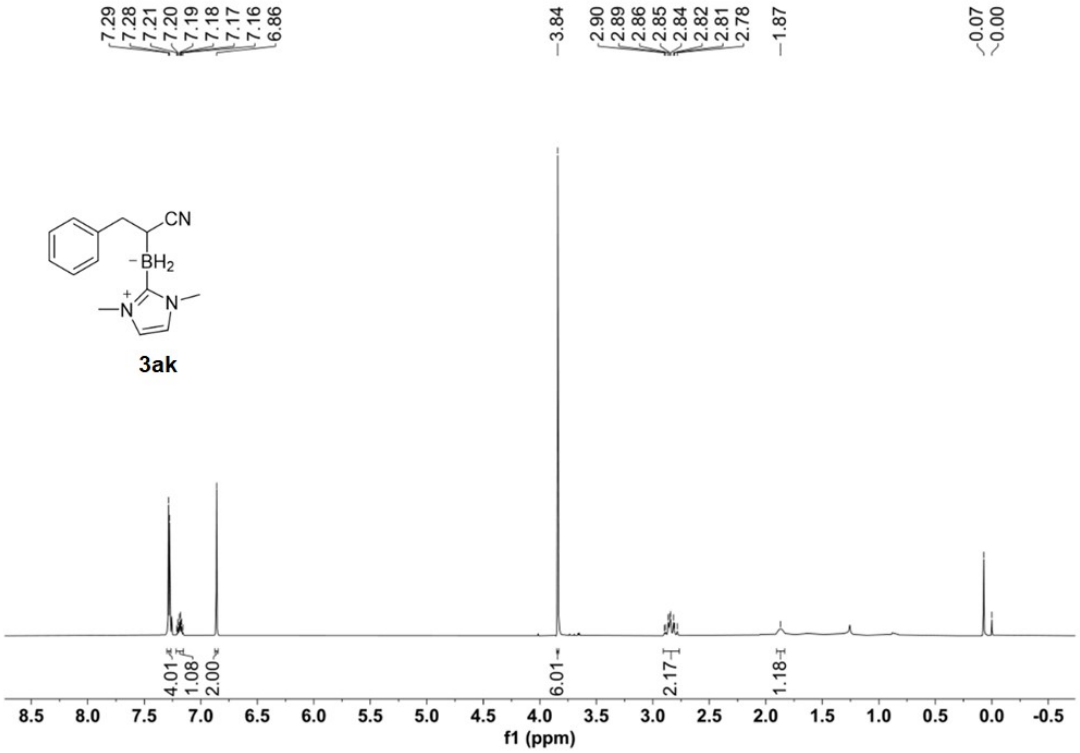

Fig. S78 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ak**.

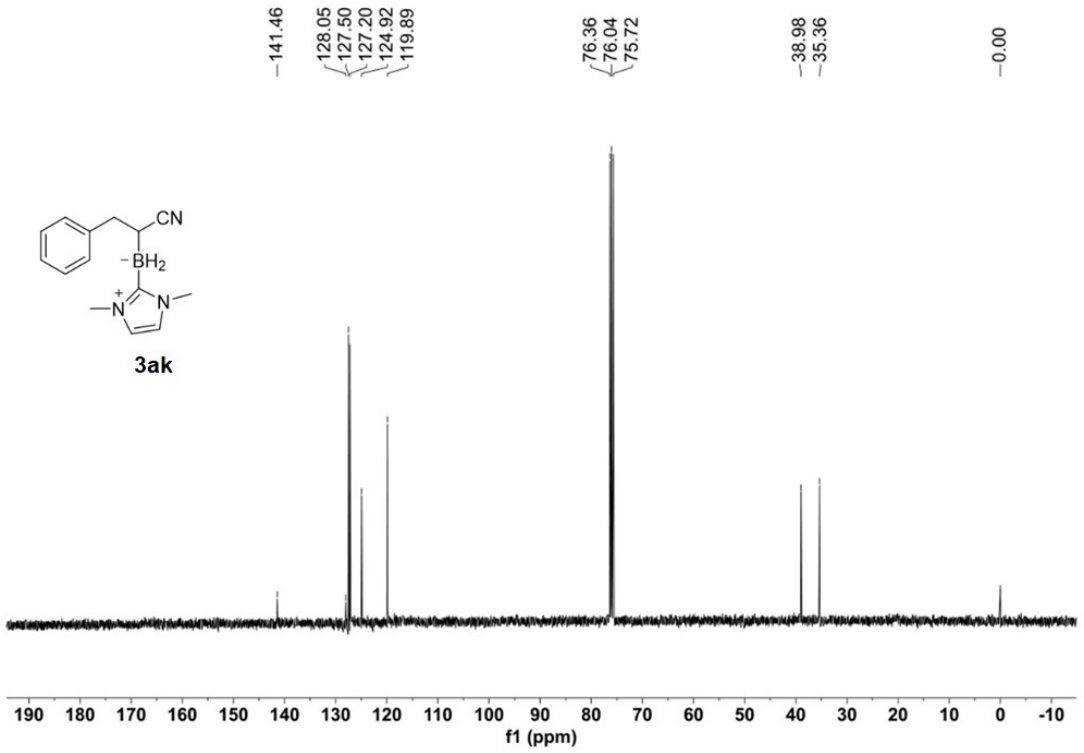

Fig. S79 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ak**.

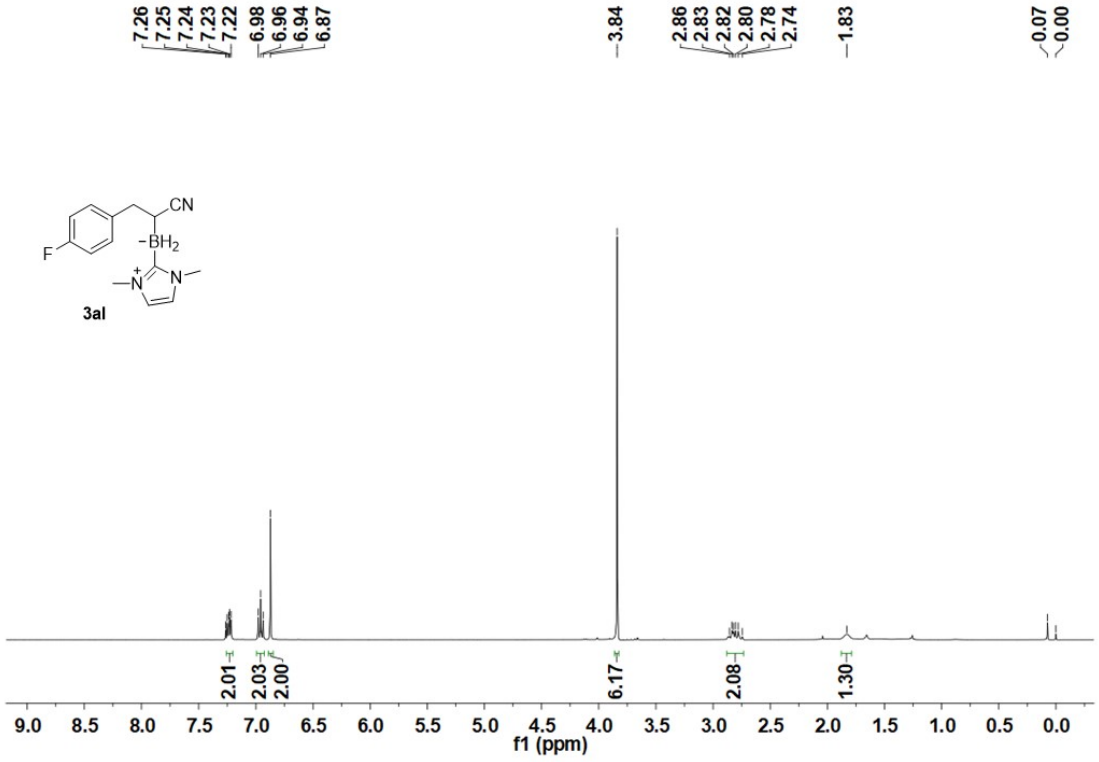

Fig. S80 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3al**.

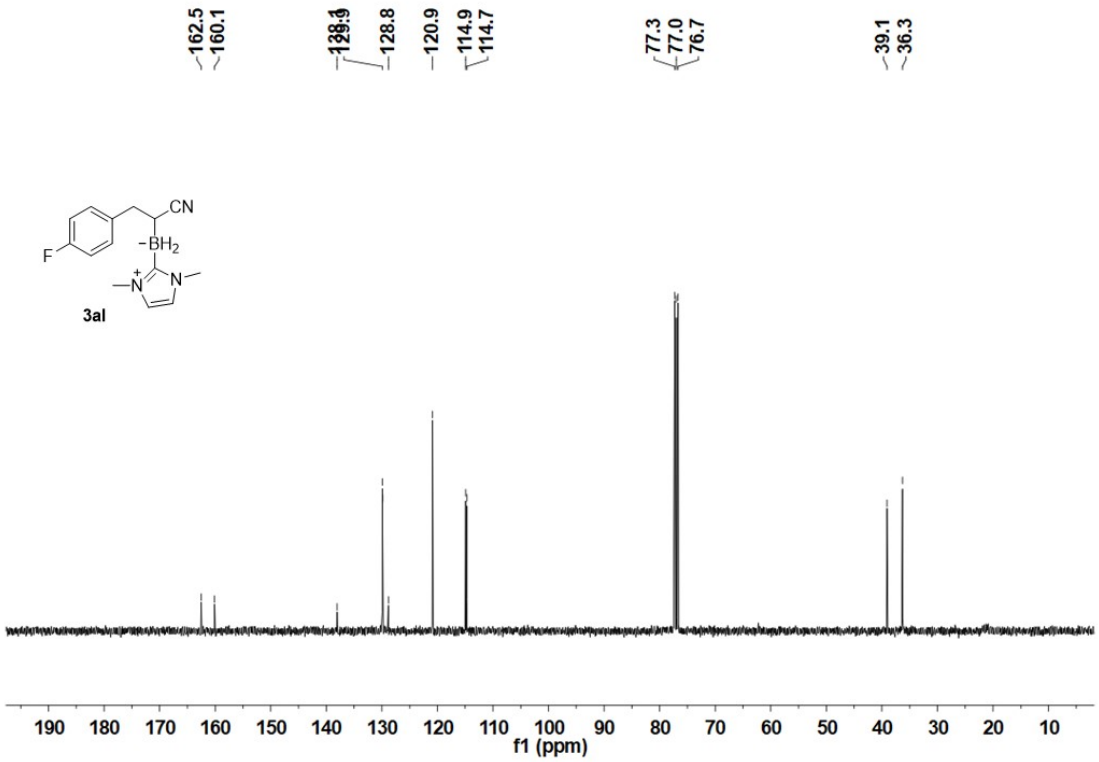

Fig. S81 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3al**.

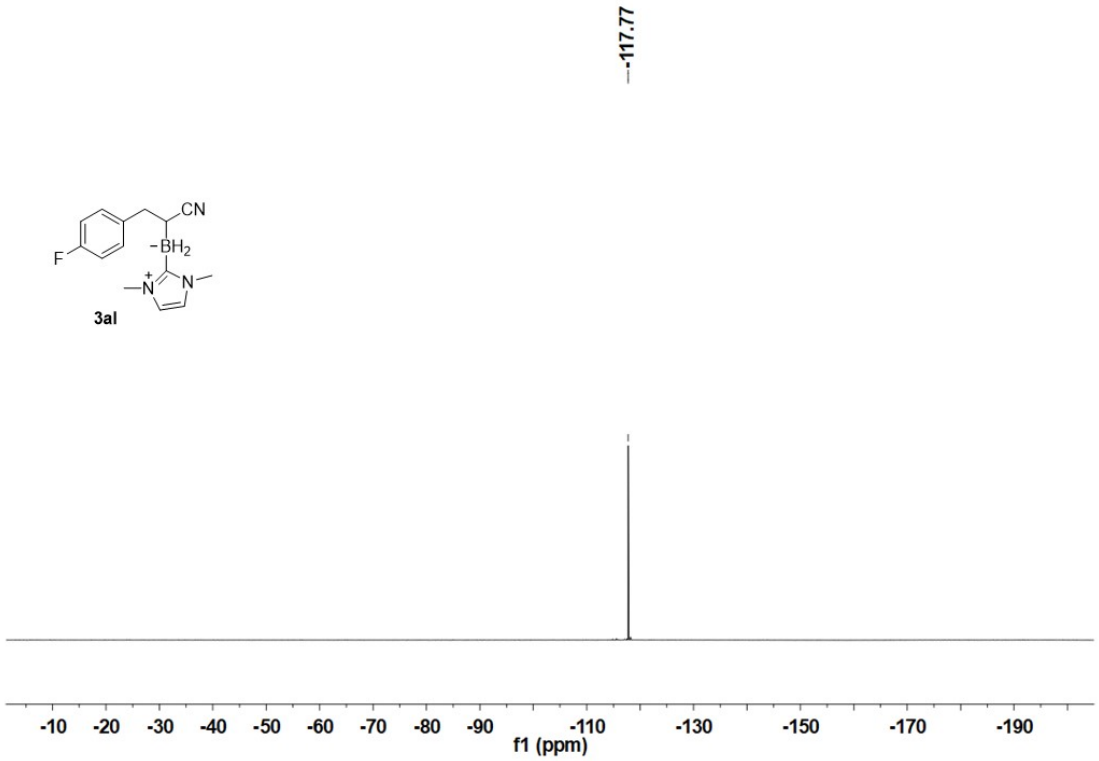

Fig. S82 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **3al**.

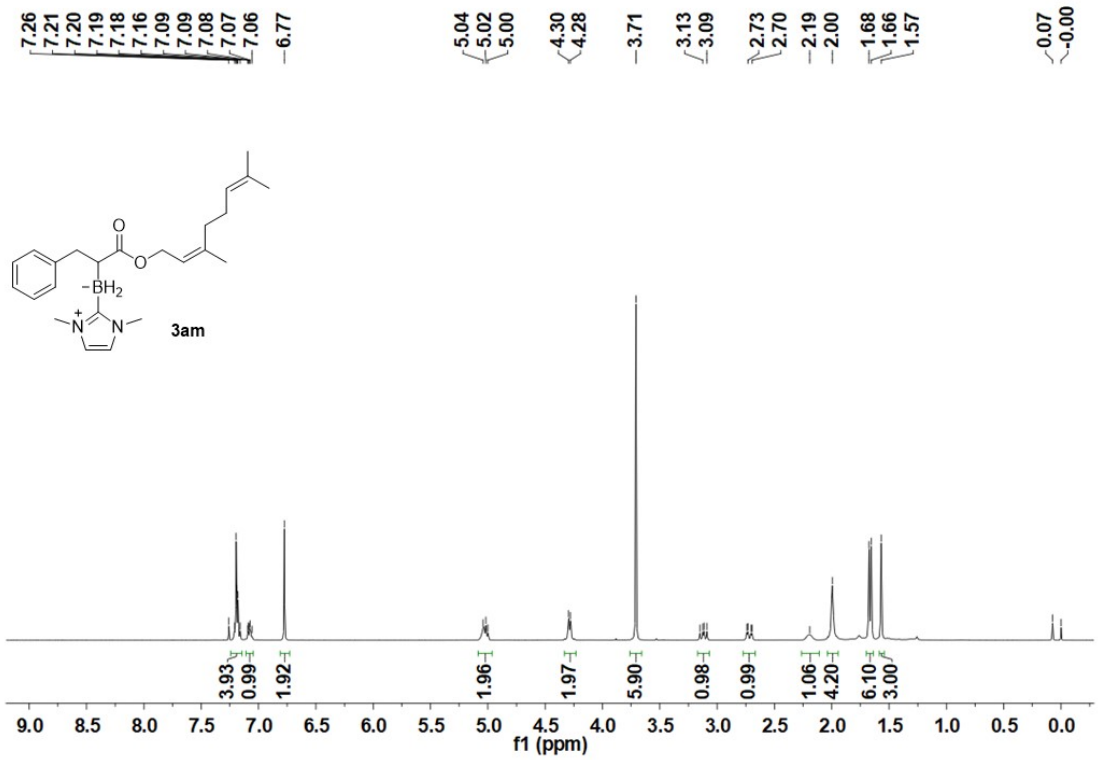

Fig. S83 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3am**.

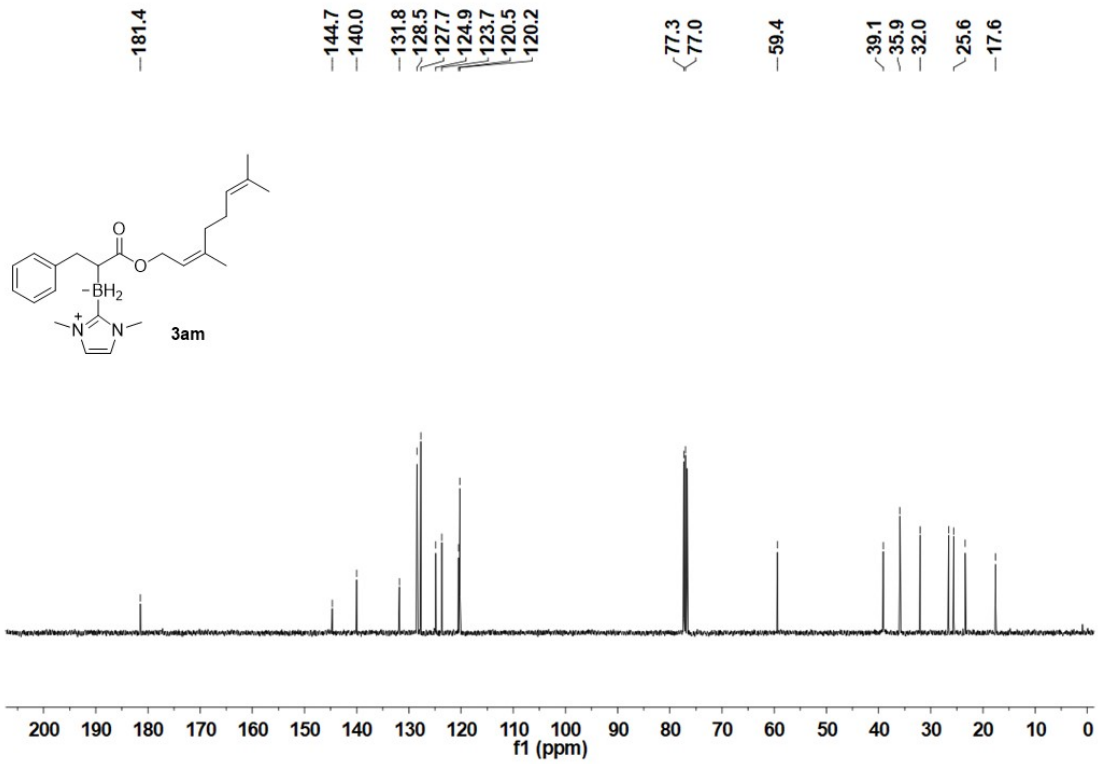

Fig. S84 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3am**.

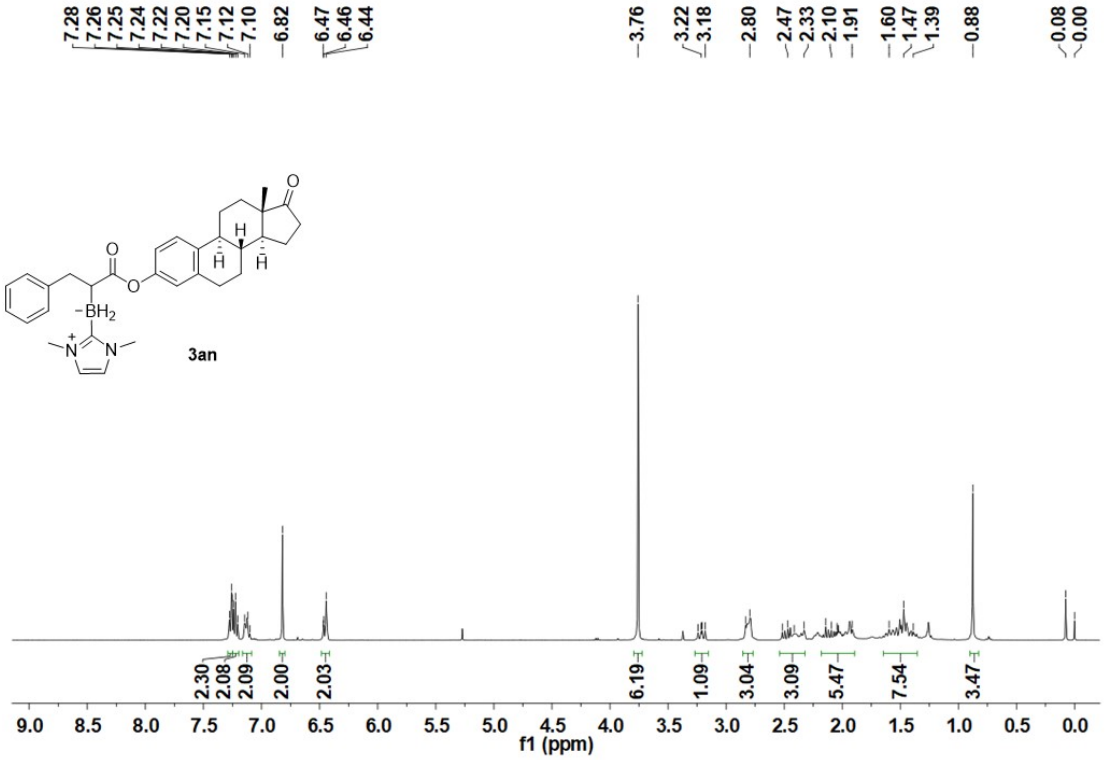

Fig. S85 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3an**.

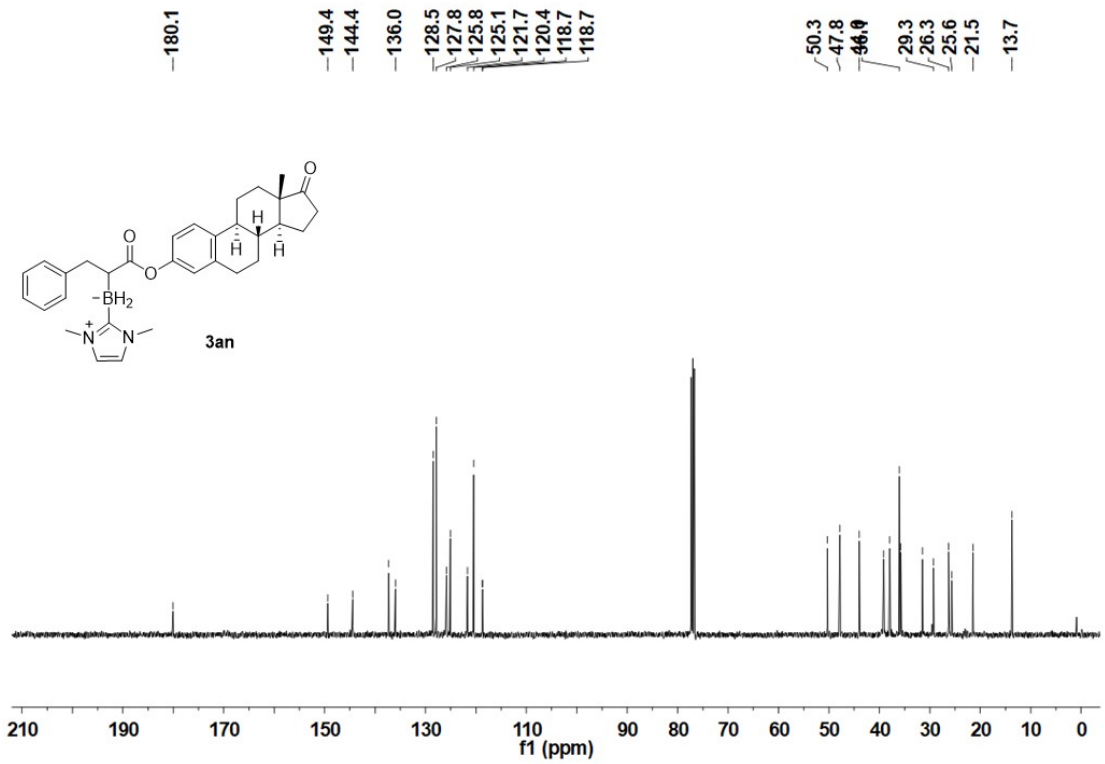

Fig. S86 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3an**.

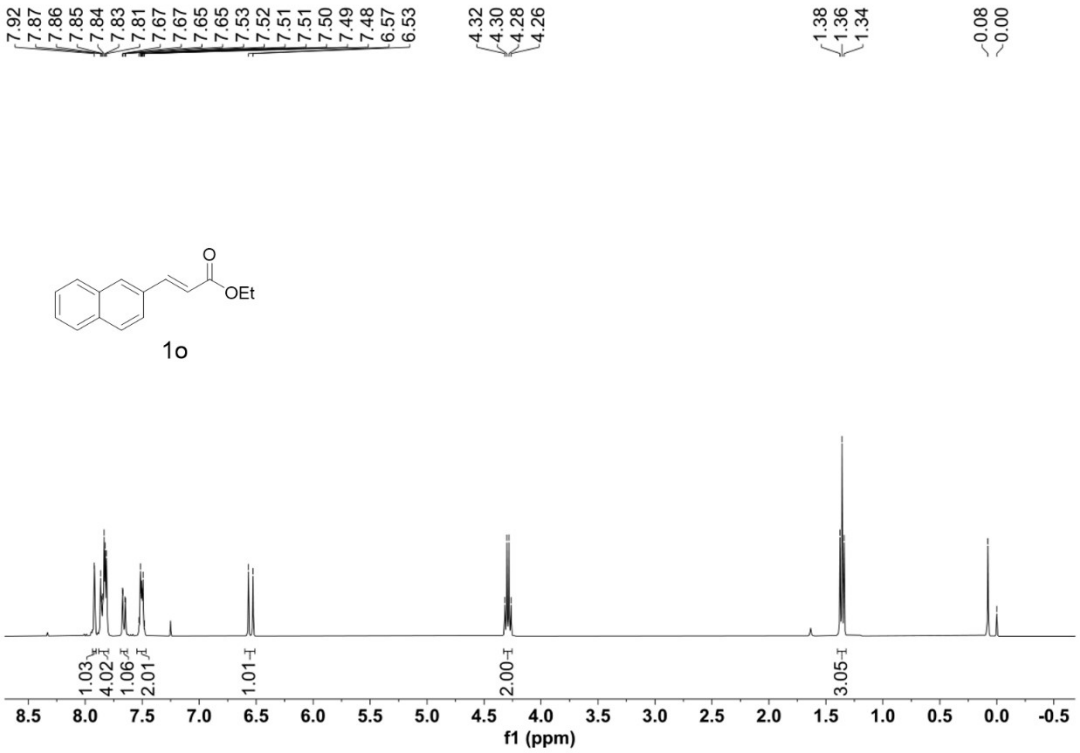

Fig. S87 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **1o**.

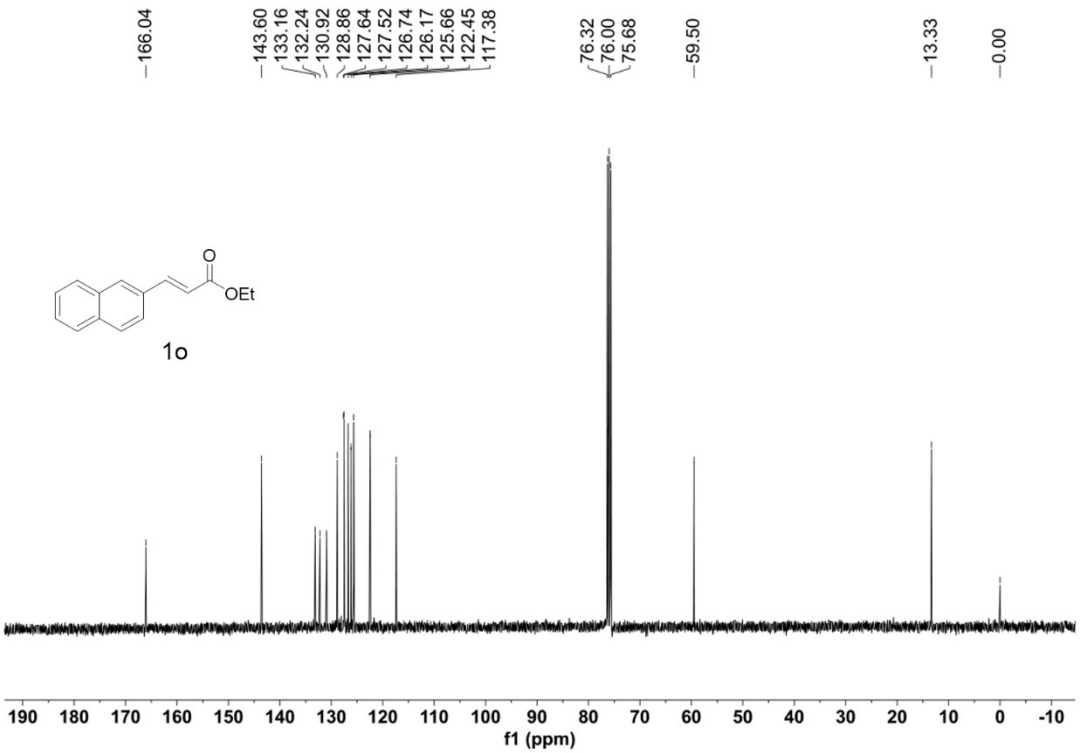

Fig. S88 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **1o**.

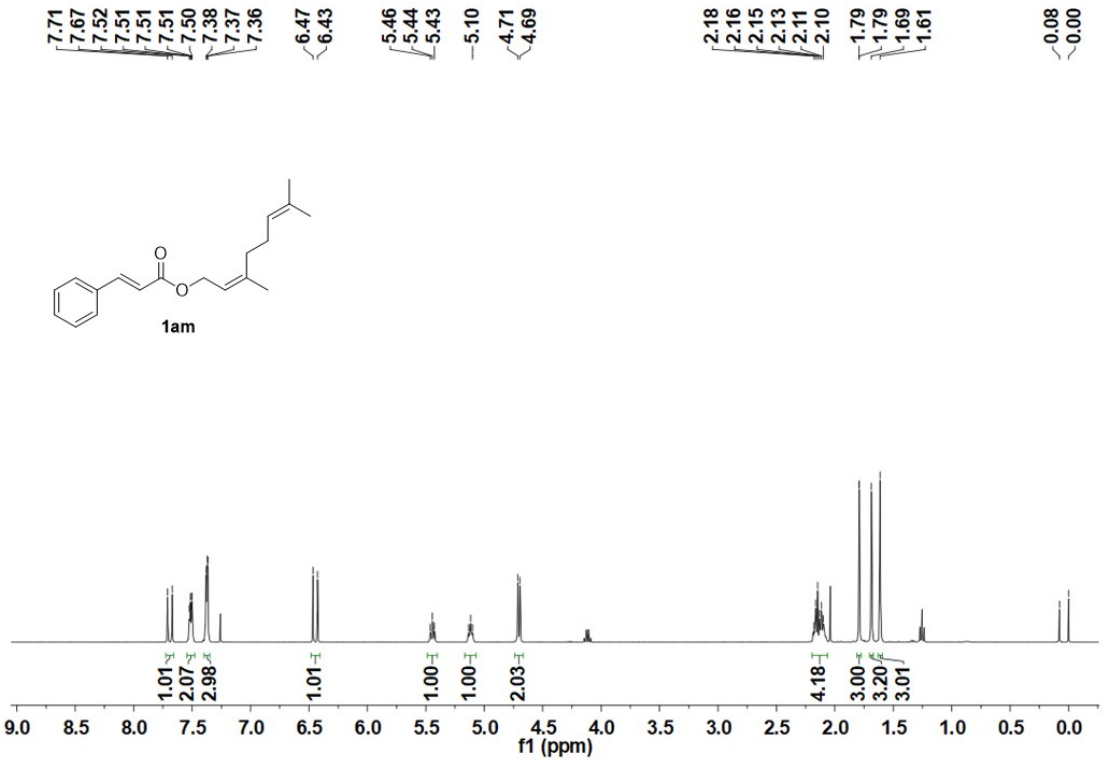

Fig. S89 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **1am**.

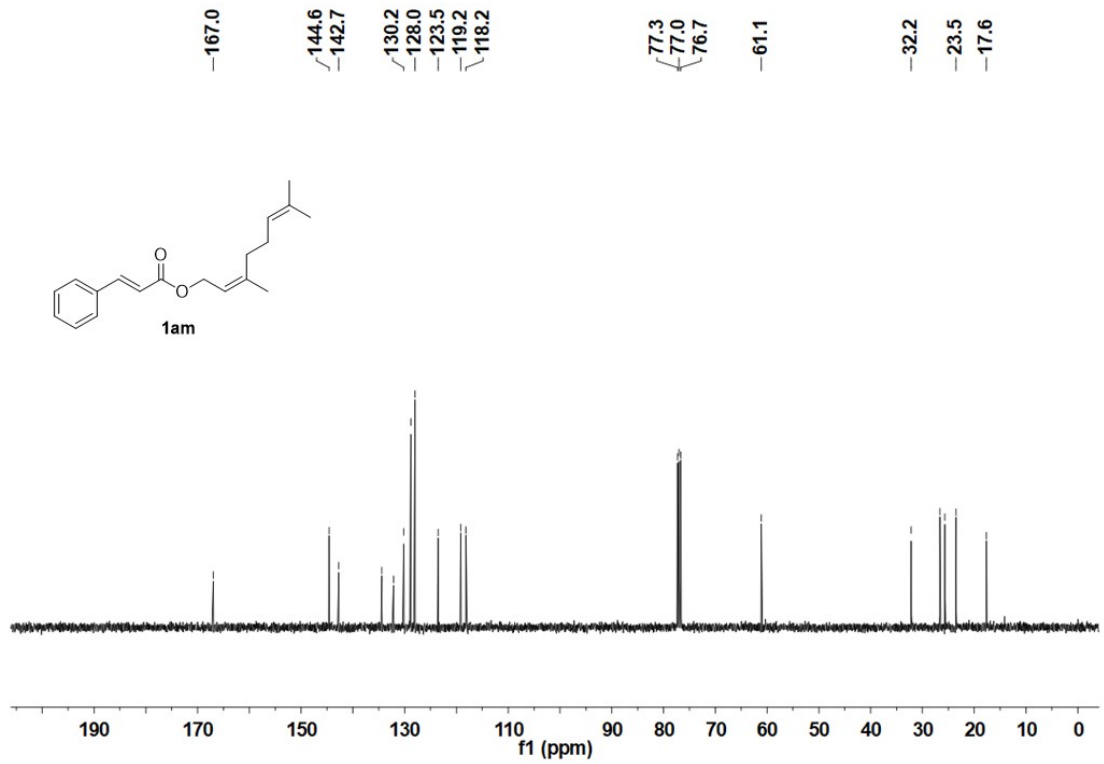

Fig. S90 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **1am**.

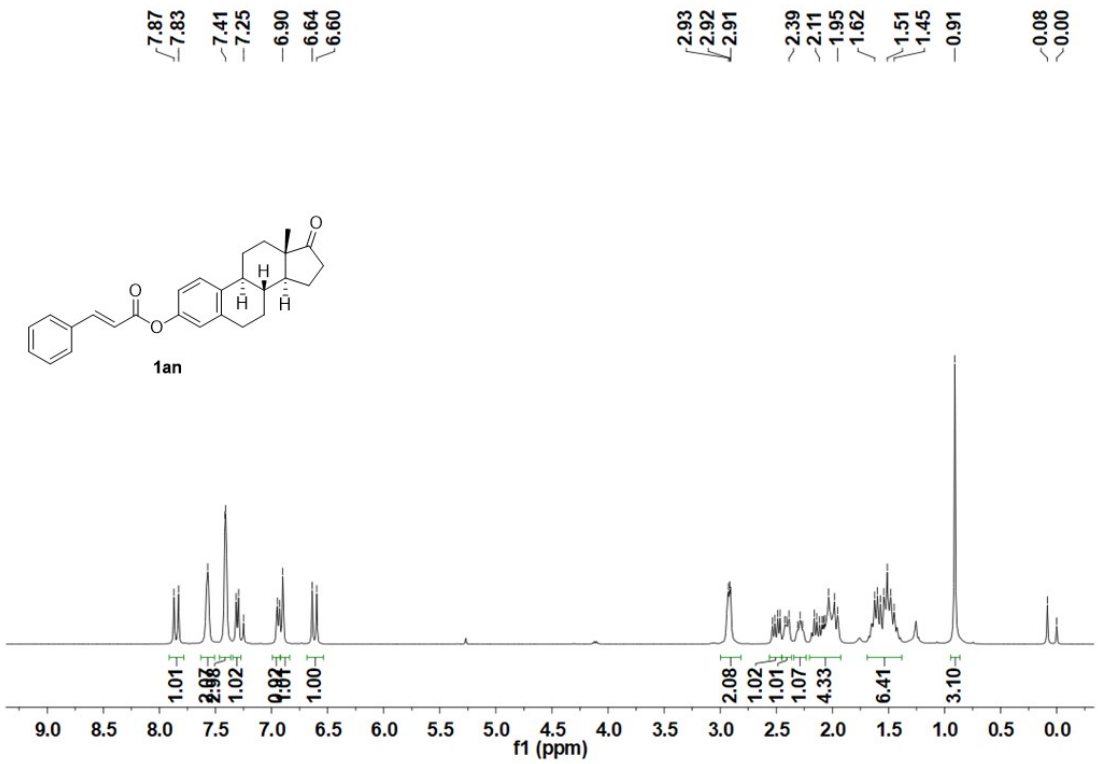

Fig. S91 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **1an**.

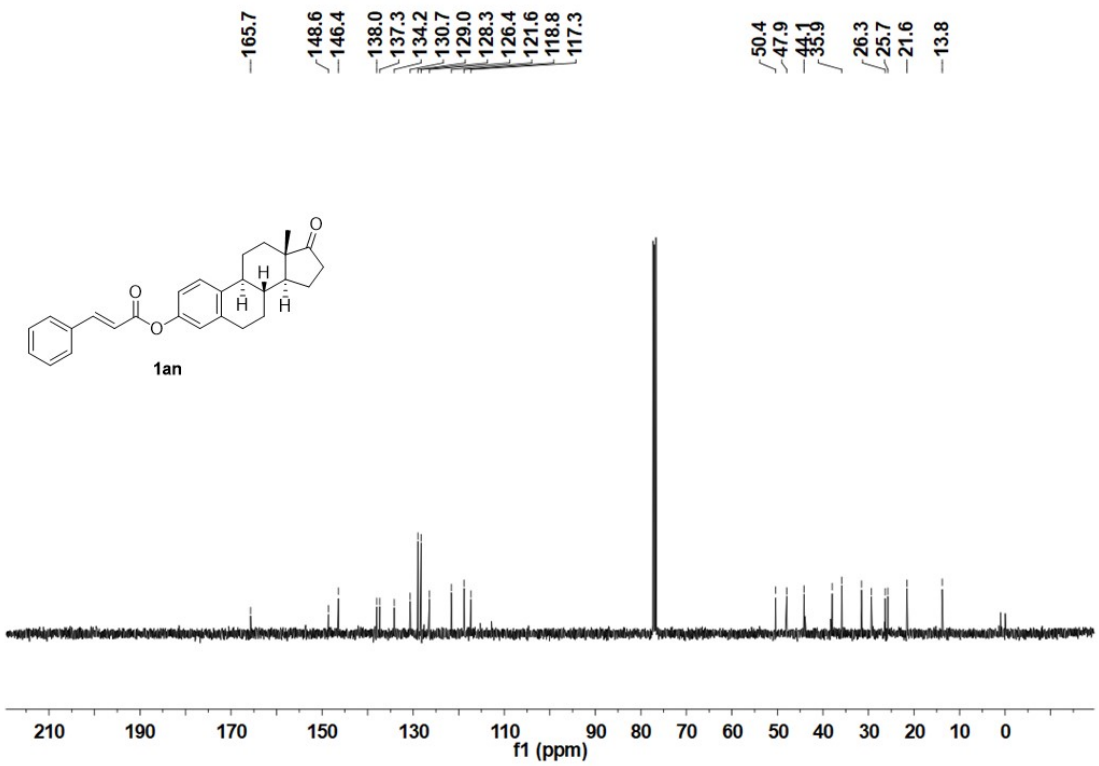

Fig. S92 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **1an**.