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Supporting Information

Photoredox dearomative *β*-hydroborylation of indoles for the synthesis of borylated indolines

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1. General Information

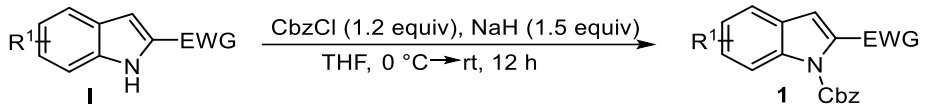
Unless otherwise noted, all commercially available components, as well as reagents and solvents, were obtained from suppliers and used without further purification. The starting materials were synthesized according to literature procedures. Photoreactions were carried out in 18 × 180 mm glass test tubes. 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.

^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{19}F NMR (376 MHz) and ^{11}B NMR (128 MHz) spectra were measured on Bruker AVIII 400M spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.16 ppm. All coupling constants (J values) were reported in Hertz (Hz). Data are reported as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, 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.

3. Preparation of Starting Materials

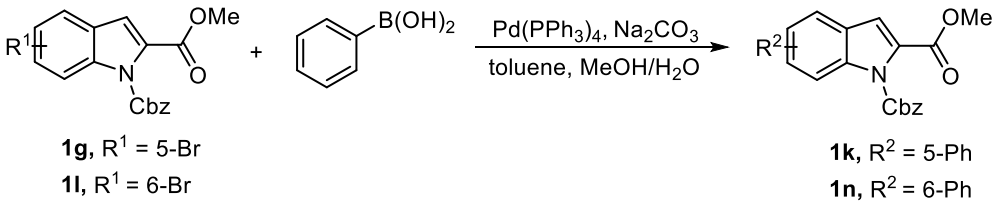
(1) Synthesis of indole-2-carboxylates 1.

General procedure for the synthesis of 1a, 1f-1j, 1l-1m, 1o-1r and 1t-1aa. [1-4]



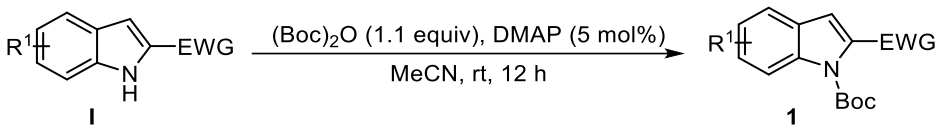
In a 250 mL round-bottom flask, 2-substituted indoles **I** (50 mmol, 1.0 equiv) and NaH (60% dispersion in paraffin liquid, 1.5 equiv) were dissolved in dry THF (100 mL) and the mixture was cooled to 0 °C. Benzyl chloroformate (1.2 equiv) was then added dropwise. After stirring for 12 h at room temperature, the reaction mixture was quenched by addition of water and extracted with CH_2Cl_2 for three times. The combined organic layer was then dried over Na_2SO_4. After filtration, the solvent was removed by evaporation. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate) to obtain desired products **1**.

Synthesis of 1k and 1n.[1]



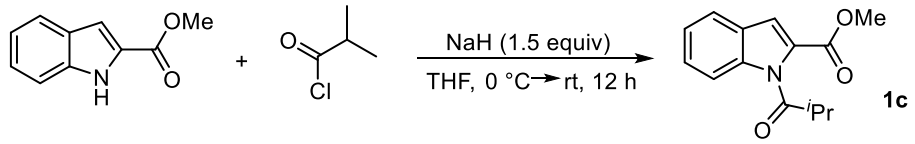
In a 25 mL round-bottom flask,**1g/1l** (0.80 mmol) and phenylboronic acid (187.8 mg, 1.50 mmol), $Pd(PPh_3)_4$ (89.0 mg, 10 mol%) and Na_2CO_3 (0.16 g, 1.50 mmol) were dissolved in toluene (5 mL) and a mixture solvent of MeOH/H_2O (1:1, 3 mL). The reaction mixture was stirred at 80 ºC for 6 h. After the reaction mixture was cooled to room temperature, the mixture was quenched by saturated $NaHCO_3$ aq. and extracted with EtOAc three times. The combined organic layer was then dried over Na_2SO_4. The crude material was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 50:1-32:1) to give the product **1k**/**1n**.

General procedure for the synthesis of 1b and 1s.[1-4]



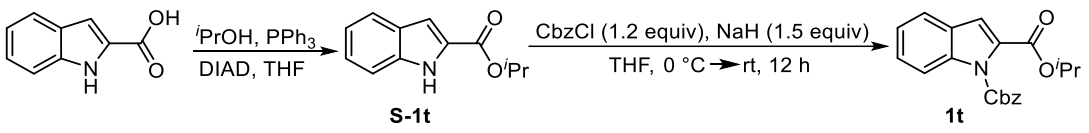
In a 25 mL round-bottom flask, 2-subsitiuted indoles (5.7 mmol, 1.0 equiv) and 4-dimethylaminopyridine (5 mol%) were dissolved in dry MeCN (10 mL), and the mixture was cooled to 0 °C under nitrogen atmosphere. Ditertbutyl dicarbonate (1.1 equiv) was then added dropwise. After stirred for 12 h at room temperature, the solvent was removed by evaporation. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate) to obtain desired product **1b**/ **1s**.

Experimental procedure for the synthesis of 1c.[1-4]



In a 25 mL round-bottom flask, methyl indole-2-carboxylate (0.50 g, 2.90 mmol) and NaH (176.0 mg, 60% dispersion in paraffin liquid, 4.40 mmol) were dissolved in dry THF (5 mL) and the mixture was cooled to 0 °C. Isobutyryl chloride (0.5 mL, 4.40 mmol) was then added dropwise. After stirring for 12 h at room temperature, the reaction mixture was quenched by addition of water and extracted with CH_2Cl_2 three times. The combined organic layer was then dried over Na_2SO_4. After filtration, the solvent was removed by evaporation. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 60:1-40:1) to obtain **1c** (0.60 g, 2.40 mmol, 81%) as a white solid.

Experimental procedure for the synthesis of 1t.[1,4]

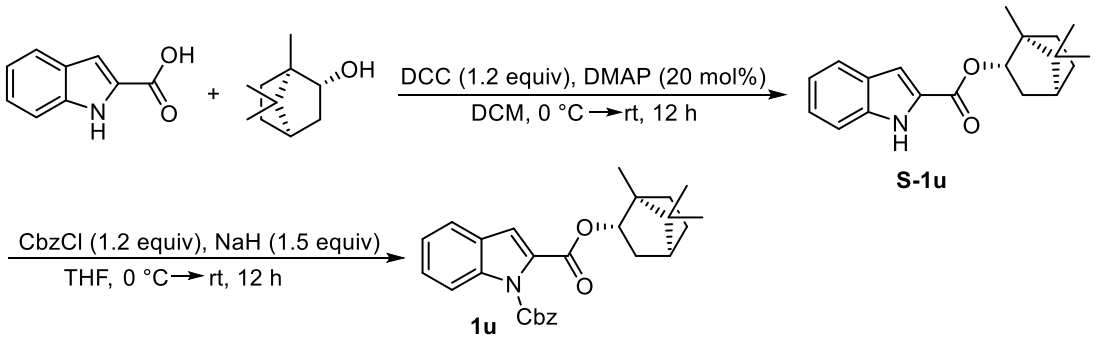


In a 50 mL round-bottom flask, indole-2-carboxylic acid (0.50 g, 3.10 mmol) and triphenylphosphine (0.98 g, 3.70 mmol) and ^{i}PrOH (236.8 μL, 3.10 mmol) were dissolved in dry THF (10 mL), and the mixture was cooled to 0 °C under nitrogen

atmosphere. Then diisopropyl azodicarboxylate (731.6 μL, 3.70 mmol) was added dropwise. After stirred for 48 h at room temperature, the reaction mixture was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 32:1) to obtain **S-1t** (0.56 g, 2.80 mmol, 89%) as a white solid.

In a 50 mL round-bottom flask, **S-1t** (0.50 g, 2.50 mmol) and NaH (0.15 g, 60% dispersion in paraffin liquid, 3.70 mmol) were dissolved in dry THF (10 mL) and the mixture was cooled to 0 °C. Benzyl chloroformate (414.6 μL, 3.00 mmol) was then added dropwise. After stirred for 12 h at room temperature, the reaction mixture was quenched by addition of water and extracted with CH_2Cl_2 three times. The combined organic layer was then dried over Na_2SO_4. After filtration, the solvents were removed by evaporation. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 32:1) to obtain **1t** (0.56 g, 1.70 mmol, 89%) as a white solid.

Synthesis of substrate 1u.[5,6]

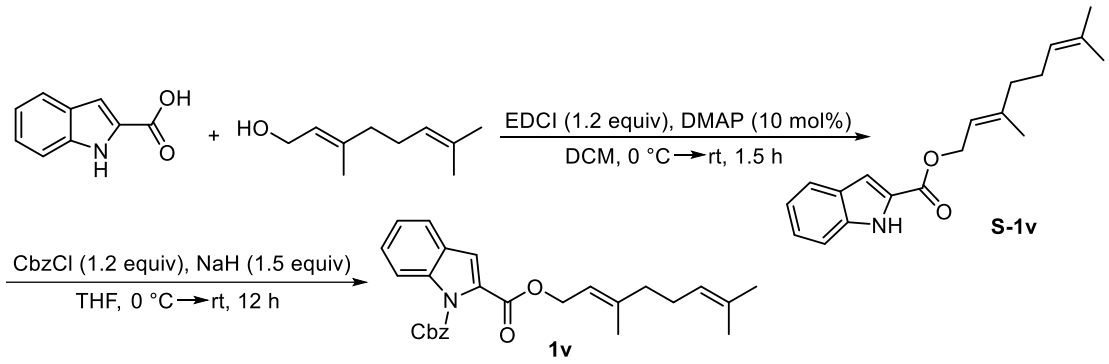


In a 25 mL round bottom flask, indole-2-carboxylic acid (0.50 g, 3.10 mmol), DMAP (63.5 mg, 0.50 mmol) and isoborneol (0.40 g, 2.60 mmol) were dissolved in DCM (5 mL), and the mixture was cooled to 0 °C under nitrogen atmosphere. DCC (0.64 g, 3.10 mmol) was then added, the reaction mixture was stirred for 12 h at room temperature. After completion, the mixture was concentrated in vacuo to afford crude product which was further purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 6:1) to obtain **S-1u** (0.57 g, 1.90 mmol, 73%) as a white solid.

In a 25 mL round bottomed flask, **S-1u** (0.30 g, 1.00 mmol) and NaH (60.0 mg, 60% dispersion in paraffin liquid, 1.50 mmol) were dissolved in dry THF (5 mL) and

the mixture was cooled to 0 °C. Benzyl chloroformate (168.9 μL, 1.20 mmol) was then added dropwise. After stirred for 12 h at room temperature, the reaction mixture was quenched by addition of water and extracted with CH_2Cl_2 three times. The combined organic layer was then dried over Na_2SO_4. After filtration, the solvents were removed by evaporation. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 50:1) to obtain **1u** (0.43 g, 1.00 mmol, 99%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.46-7.36 (m, 6H), 7.28-7.26 (m, 1H), 7.08 (s, 1H), 5.44-5.38 (m, 2H), 4.81 (t, *J* = 5.8 Hz, 1H), 1.84-1.83 (m, 2H), 1.78-1.67 (m, 2H), 1.58-1.55 (m, 1H), 1.20-1.05 (m, 2H), 1.01 (s, 3H), 0.88-0.86 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.2, 150.9, 137.9, 134.6, 131.3, 128.9, 128.8, 127.8, 127.1, 123.7, 122.3, 115.5, 115.1, 82.4, 69.8, 49.1, 47.1, 45.2, 38.7, 33.8, 27.2, 20.2, 20.1, 11.6 ppm.

Synthesis of substrate 1v.[5,6]

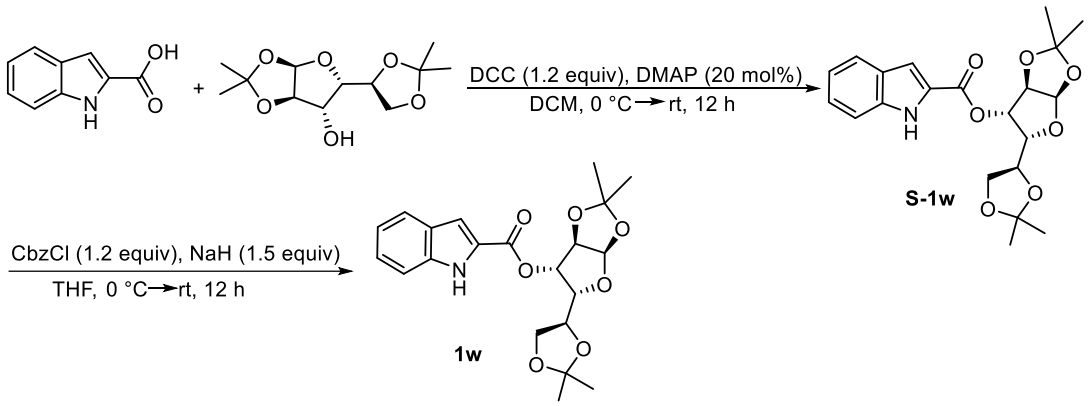


In a 50 mL round bottom flask, indole-2-carboxylic acid (0.50 g, 3.10 mmol) and nerol (0.57 g, 3.70 mmol) were dissolved in DCM (10 mL), and the mixture was cooled to 0 °C under nitrogen atmosphere. EDCI (0.71 g, 3.70 mmol) and DMAP (37.9 mg, 0.30 mmol) were then added. Then, the reaction mixture was stirred for 1.5 h at room temperature, 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, petroleum ether/ethyl acetate, 32:1) to obtain **S-1v** (0.68 g, 2.30 mmol, 73%) as a white solid.

In a 25 mL round bottomed flask, **S-1v** (0.30 g, 1.00 mmol), NaH (60.0 mg, 60% dispersion in paraffin liquid, 1.50 mmol) was dissolved in dry THF (5 mL) and the

mixture was cooled to 0 °C. Benzyl chloroformate (168.0 μL, 1.20 mmol) was then added dropwise. After stirred for 12 h at room temperature, the reaction mixture was quenched by addition of water and extracted with CH_2Cl_2 three times. The combined organic layer was then dried over Na_2SO_4. After filtration, the solvents were removed by evaporation. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 50:1) to obtain **1v** (0.43 g, 1.00 mmol, 98%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.46-7.34 (m, 6H), 7.29-7.23 (m, 1H), 7.13 (s, 1H), 5.41 (s, 2H), 5.37-5.33 (m, 1H), 5.13-5.06 (m, 1H), 4.67 (d, *J* = 7.2 Hz, 2H), 2.15-2.05 (m, 4H), 1.76 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.9, 150.9, 143.2, 137.8, 134.7, 132.4, 130.8, 128.9, 128.8, 127.8, 127.1, 123.7, 122.3, 118.9, 115.7, 115.2, 69.7, 62.2, 32.3, 26.8, 25.8, 23.7, 17.8 ppm.

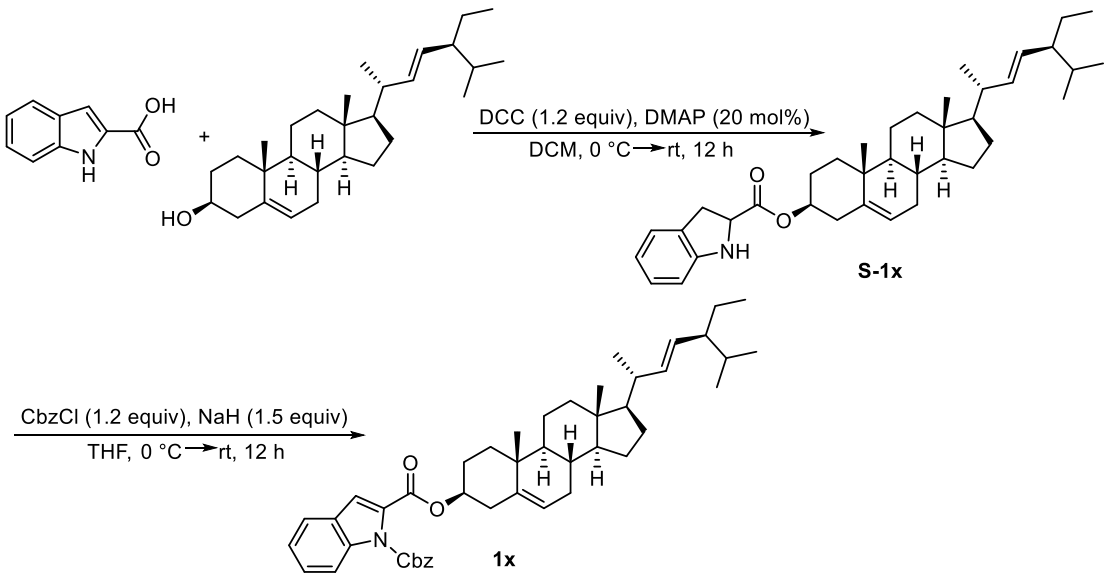
Synthesis of substrate 1w.[5,6]



In a 25 mL round bottom flask, indole-2-carboxylic acid (0.30 g, 1.85 mmol), DMAP (37.9 mg, 0.31 mmol) and diacetone-d-glucose (0.40 g, 1.54 mmol) were dissolved in DCM (5 mL), and the mixture was cooled to 0 °C under nitrogen atmosphere. DCC (0.38 g, 1.85 mmol) was then added, the reaction mixture was stirred for 12 h at room temperature. After completion, the mixture was concentrated in vacuo to afford crude product which was further purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 6:1) to obtain **S-1w** (0.50 g, 1.23 mmol, 98%) as a colorless oil.

In a 25 mL round bottomed flask, **S-1w** (0.30 g, 0.74 mmol), NaH (44.4 mg, 60% dispersion in paraffin liquid, 1.11 mmol) was dissolved in dry THF (5 mL) and the mixture was cooled to 0 °C. Benzyl chloroformate (125.0 μL, 1.20 mmol) was then added dropwise. After stirred for 12 h at room temperature, the reaction mixture was quenched by addition of water and extracted with CH_2Cl_2 three times. The combined organic layer was then dried over Na_2SO_4. After filtration, the solvents were removed by evaporation. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 10:1) to obtain **1w** (0.32 g, 0.59 mmol, 98%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.49-7.36 (m, 6H), 7.32-7.26 (m, 1H), 7.19 (s, 1H), 5.84-5.82 (m, 1H), 5.44 (s, 2H), 5.40-5.38 (m, 1H), 4.71-4.70 (m, 1H), 4.56-4.54 (m, 1H), 4.33-4.32 (m, 1H), 4.32-4.25 (m, 2H), 1.55 (s, 3H), 1.42 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.3, 150.8, 137.8, 137.8, 134.5, 129.8, 129.0, 128.9, 128.8, 128.7, 127.8, 127.6, 127.1, 124.0, 122.6, 117.0, 115.3, 83.0, 80.0, 77.4, 72.7, 70.0, 67.4, 27.0, 26.9, 26.5, 25.4 ppm.

Synthesis of substrate 1x.[5,6]



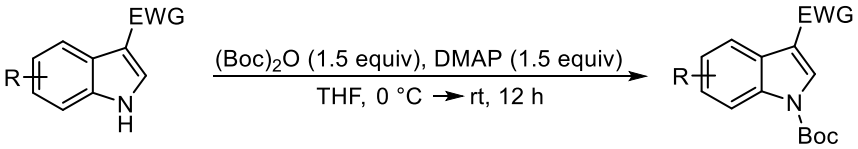
In a 25 mL round bottom flask, indole-2-carboxylic acid (186.9 mg, 1.20 mmol), DMAP (23.2 mg, 0.20 mmol) and stigmasterol (0.40 g, 1.00 mmol) were dissolved in DCM (5 mL), and the mixture was cooled to 0 °C under nitrogen atmosphere. DCC (0.24 g, 1.20 mmol) was then added, the reaction mixture was stirred for 12 h at room

temperature. After completion, the mixture was concentrated in vacuo to afford crude product which was further purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 32:1) to obtain **S-1x** (0.49 g, 0.90 mmol, 90%) as a white solid.

In a 25 mL round bottomed flask, **S-1x** (0.30 g, 0.50 mmol) and NaH (32.0 mg, 60% dispersion in paraffin liquid, 0.80 mmol) were dissolved in dry THF (5 mL) and the mixture was cooled to 0 °C. Benzyl chloroformate (90.0 μL, 0.60 mmol) was then added dropwise. After stirred for 12 h at room temperature, the reaction mixture was quenched by addition of water and extracted with CH_2Cl_2 three times. The combined organic layer was then dried over Na_2SO_4. After filtration, the solvents were removed by evaporation. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 50:1) to obtain **1x** (0.36 g, 0.50 mmol, 98%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.48-7.35 (m, 6H), 7.29-7.24 (m, 1H), 7.12 (s, 1H), 5.42-5.37 (m, 3H), 5.22-5.12 (m, 1H), 5.03-5.01 (m, 1H), 4.70-4.72 (m, 1H), 2.37-2.35 (m, 2H), 2.14-1.94 (m, 2H), 1.90-1.80 (m, 1H), 1.58-1.40 (m, 9H), 1.32-1.10 (m, 11H), 1.05-1.02 (m, 3H), 0.89-0.75 (m, 12H), 0.71-0.68 (m, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.3, 150.9, 139.6, 138.5, 137.8, 134.7, 129.4, 128.9, 128.8, 128.5, 127.9, 127.1, 123.7, 123.0, 122.3, 115.5, 115.2, 75.5, 69.7, 58.6, 56.9, 56.1, 51.4, 50.2, 42.4, 40.7, 39.8, 38.1, 37.1, 36.8, 32.0, 29.1, 27.8, 25.6, 24.5, 21.4, 21.2, 19.5, 19.1, 18.6, 12.4, 12.2 ppm.

(2) (1) Synthesis of indole-3-carboxylates 4.

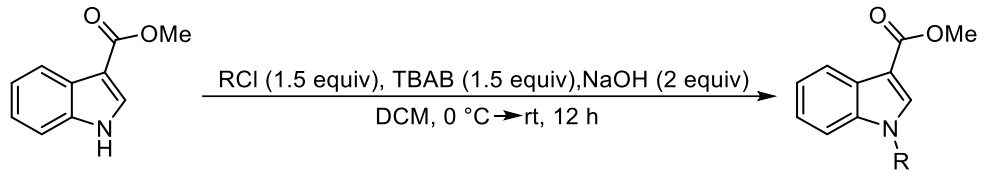
General procedure for the synthesis of 4a, 4h-4q.[7,8]



In a 150 mL round bottomed flask, 3-subsitiuted indoles (30 mmol) and DMAP (1.5 equiv) were dissolved in dry THF (50 mL) and the mixture was cooled to 0 °C. $(Boc)_2O$ (1.5 equiv) was then added dropwise under N_2 atmosphere. After stirred for 12 h at room temperature, the solvent was removed by evaporation. The crude product was

purified by column chromatography (SiO_2, petroleum ether/ethyl acetate) to obtain desired products.

Experimental procedure for the synthesis of 4b-4e.[7,8]

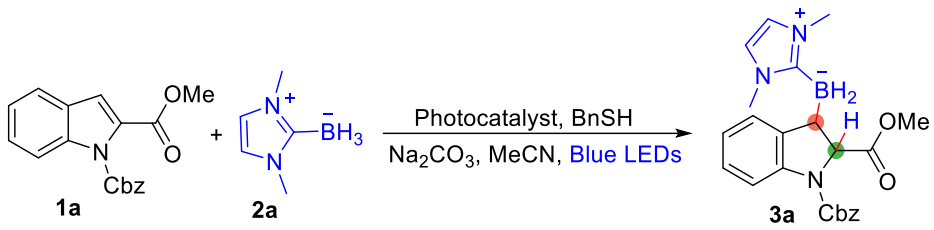


In a 25 mL round bottomed flask, methyl indole-3-carboxylate (0.50 g, 2.90 mmol), NaOH (0.20 g, 5.80 mmol) and TBAB (5.40 g, 44.00 mmol) were dissolved in dry DCM (10 mL), and the mixture was cooled to 0 °C. RCl (1.5 equiv) was then added dropwise. After stirred for 12 h at room temperature. The reaction was then diluted by 2 M HCl (5 mL) and extracted with DCM (3 × 10 mL). The combined organic phase was dried over Na_2SO_4. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate) to obtain desired products.

3. Optimization of Reaction Conditions

(1) Optimization of dearomative *β*-hydroborylation of 2-substituted indoles.

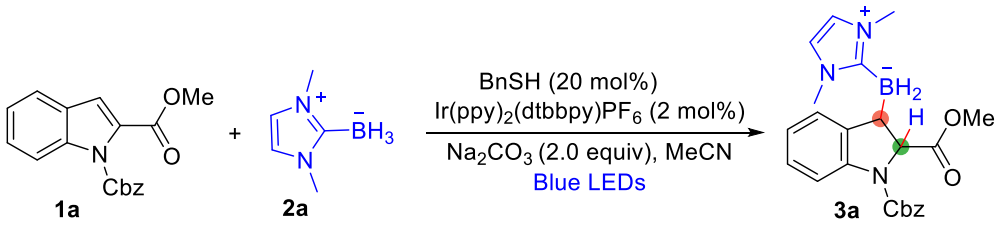
Table S1 Screening of different photocatalysts.[a]



Entry	Photocatalyst	Yield (%)[b]
1	*fac*-Ir(ppy)$_3$	trace
2	Ir(ppy)$_2$(dtbbpy)PF$_6$	86
3	[Ir(cod)Cl]$_2$	trace
4	Ru(bpy)$_3$Cl$_2$·6H$_2$O	20

[a]Reaction conditions: **1a** (1.2 equiv), **2a** (0.2 mmol), photocatalyst (2 mol%), BnSH (20 mol%), Na_2CO_3 (2.0 equiv), anhydrous MeCN (2 mL), 30 W blue LEDs (λ = 440-450 nm), rt, 12 h, N_2 atmosphere. [b]Yield were determined by ^{1}H NMR with triphenyl methane as internal standard.

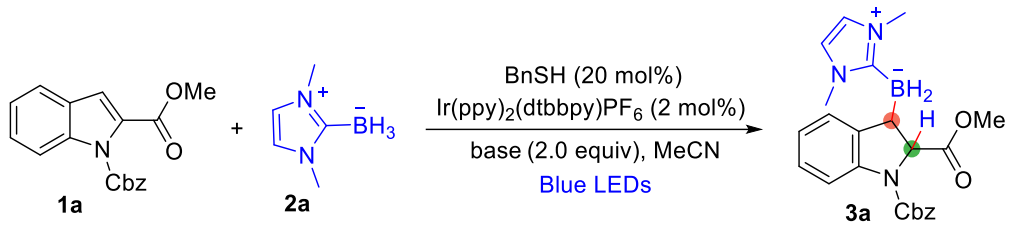
Table S2 Control experiments.[a]



Entry	Photocatalyst	Additive	Base	Yield (%)[b]
1	Ir(ppy)$_2$(dtbbpy)PF$_6$	—	Na_2CO_3	76
2	Ir(ppy)$_2$(dtbbpy)PF$_6$	BnSH	—	80
3[c]	Ir(ppy)$_2$(dtbbpy)PF$_6$	BnSH	Na_2CO_3	59
4	—	BnSH	Na_2CO_3	nr
5[d]	Ir(ppy)$_2$(dtbbpy)PF$_6$	BnSH	Na_2CO_3	nr

[a]Reaction conditions: **1a** (1.2 equiv), **2a** (0.2 mmol), Ir(ppy)$_2$(dtbbpy)PF$_6$ (2 mol%), BnSH (20 mol%), Na_2CO_3 (2.0 equiv), anhydrous MeCN (2 mL), 30 W blue LEDs (λ = 440-450 nm), rt, 12 h, N_2 atmosphere. [b]Yields were determined by ^{1}H NMR with triphenyl methane as internal standard, nr means no reaction. [c]Reaction was set up in the air. [d]In dark.

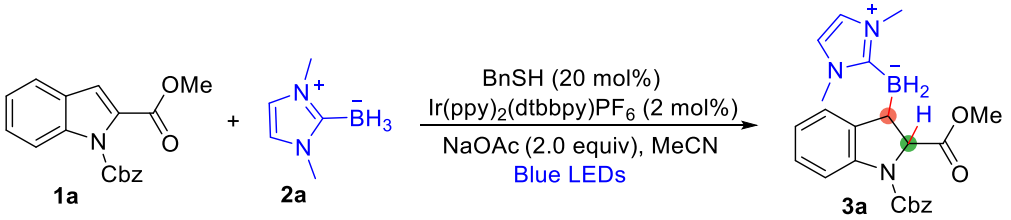
Table S3 Screening of different bases.[a]



Entry	Base	Yield (%)[b]
1	NaOH	41
2[c]	^{t}BuOK	15
3	NaOMe	55
4	DMAP	24
5	Py	70
6	DIPEA	41
7[c]	NaH	32
8	DBU	79
9	DABCO	57
10	NaOAc	88

[a]Reaction conditions: **1a** (1.2 equiv), **2a** (0.2 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%), BnSH (20 mol%), base (2.0 equiv), anhydrous MeCN (2 mL), 30 W blue LEDs (λ = 440-450 nm), rt, 12 h, N_2 atmosphere. [b]Yields were determined by ^{1}H NMR with triphenyl methane as internal standard. [c]Reaction for 18 h.

Table S4 Screening of equivalents of **1a**/**2a**.[a]

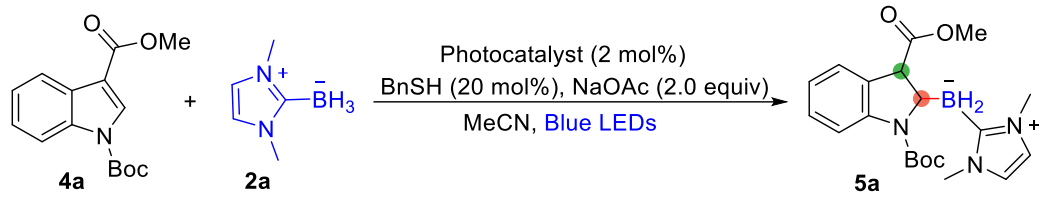


Entry	**1a**/**2a**	Yield (%)[b]
1	1.0/1.0	89
2	1.0/1.2	96(95[c])
3	1.0/1.5	98

[a]Reaction conditions: **1a**, **2a**, $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%), BnSH (20 mol%), NaOAc (2.0 equiv), anhydrous MeCN (2 mL), 30 W blue LEDs (λ = 440-450 nm), rt, 12 h, N_2 atmosphere. [b]Yields were determined by ^{1}H NMR with triphenyl methane as internal standard. [c]Isolated yield.

(2) Optimization of dearomative *β*-hydroborylation of 3-substituted indoles.

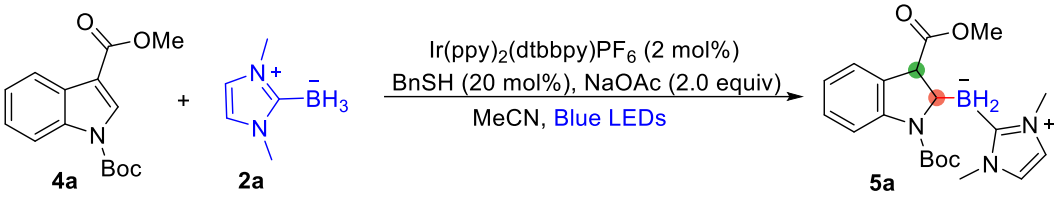
Table S5 Screening of different photocatalysts.[a]



Entry	Variation	Yield (%)[b]	dr
1	none	95	2.5:1
2	$Ru(bpy)_3Cl_2·6H_2O$ instead of $Ir(ppy)_2(dtbbpy)PF_6$	26	>99:1
3	$Ru(bpy)_3(PF_6)_2$ instead of $Ir(ppy)_2(dtbbpy)PF_6$	38	>99:1
4	$Ru(dtbpy)_3(PF_6)_2$ instead of $Ir(ppy)_2(dtbbpy)PF_6$	29	>99:1
5	$Ru(bpz)_3(PF_6)_2$ instead of $Ir(ppy)_2(dtbbpy)PF_6$	trace	—
6	$Ru(bpm)_3(PF_6)_2$ instead of $Ir(ppy)_2(dtbbpy)PF_6$	trace	—
7	4-CzIPN instead of $Ir(ppy)_2(dtbbpy)PF_6$	94	2.5:1
8	*fac*-$Ir(ppy)_3$ instead of $Ir(ppy)_2(dtbbpy)PF_6$	nr	—

[a]Reaction conditions: **4a** (0.2 mmol), **2a** (1.5 equiv), photocatalyst (2 mol%), BnSH (20 mol%), NaOAc (2.0 equiv), anhydrous MeCN (2 mL), 30 W blue LEDs (λ = 440-450 nm), rt, 12 h, N_2 atmosphere. [b]Isolated yields. nr = no reaction.

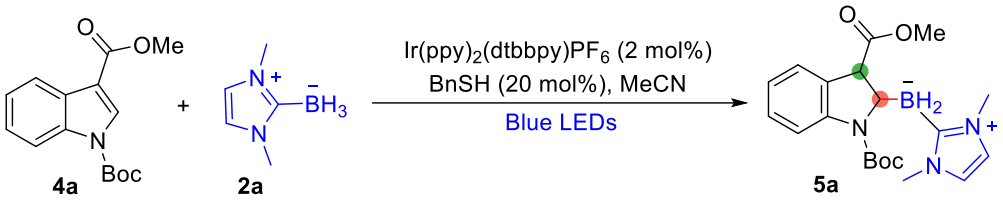
Table S6 Control experiments.[a]



Entry	Photocatalyst	Additive	Base	Yield (%)[b]	dr
1	—	BnSH	NaOAc	nr	—
2[c]	$Ir(ppy)_2(dtbbpy)PF_6$	BnSH	NaOAc	nr	—
3	$Ir(ppy)_2(dtbbpy)PF_6$	—	NaOAc	43	15.7:1
4	$Ir(ppy)_2(dtbbpy)PF_6$	BnSH	—	96	32.3:1
5[d]	$Ir(ppy)_2(dtbbpy)PF_6$	BnSH	NaOAc	53	40:1

[a]Reaction conditions: **4a** (1.0 equiv), **2a** (1.5 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%), BnSH (20 mol%), NaOAc (2.0 equiv), anhydrous MeCN (2 mL), 30 W blue LEDs (λ = 440-450 nm), rt, 12 h, N_2 atmosphere. [b]Isolated yields. [c]In dark. [d]Reaction was set up in the air. nr = no reaction.

Table S7 Screening of equivalents of **4a**/**2a**.[a]

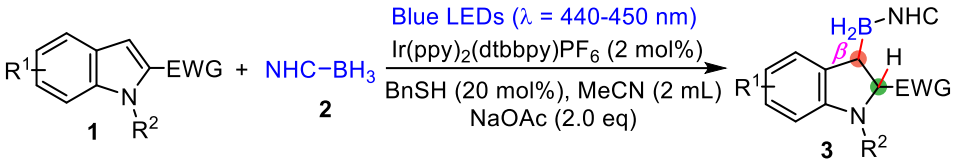


Entry	**4a/2a**	Yield (%)[b]	dr
1	1.0/1.0	95	3.2:1
2	1.5/1.0	45	>99:1
3	1.0/2.0	99	>99:1

[a]Reaction conditions: **4a**, **2a**, $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%), BnSH (20 mol%), NaOAc (2.0 equiv), anhydrous MeCN (2 mL), 30 W blue LEDs (λ = 440-450 nm), rt, 12 h, N_2 atmosphere. [b]Isolated yields.

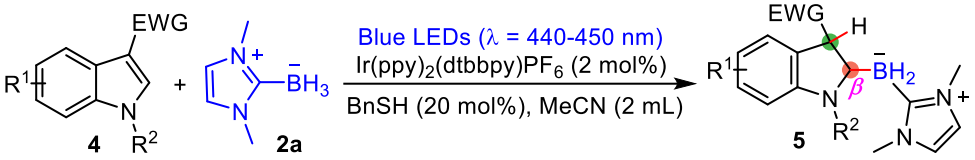
4. General Experimental Procedures

General procedure for the dearomative *β*-hydroborylation of 2-substituted indoles.



A dry glass tube (35 mL, 18 x 180 mm) charged with **1** (0.20 mmol, 1.0 equiv), **2** (0.24 mmol, 1.2 equiv), $[Ir(ppy)_2(dtbbpy)]PF_6$ (3.7 mg, 2 mol%), NaOAc (32.8 mg, 0.40 mmol), BnSH (4.7 μL, 20 mol%) and MeCN (2 mL) was evacuated and backfilled with N_2 for three times, then was tied up nitrogen balloon and placed approximately 5 cm from a 30 W blue LEDs (λ = 440-450 nm) light. The mixture was stirred at room temperature for 12 h. As the reaction completed, the reaction solvent was removed by vacuum and the crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate) to provide the desired product **3**.

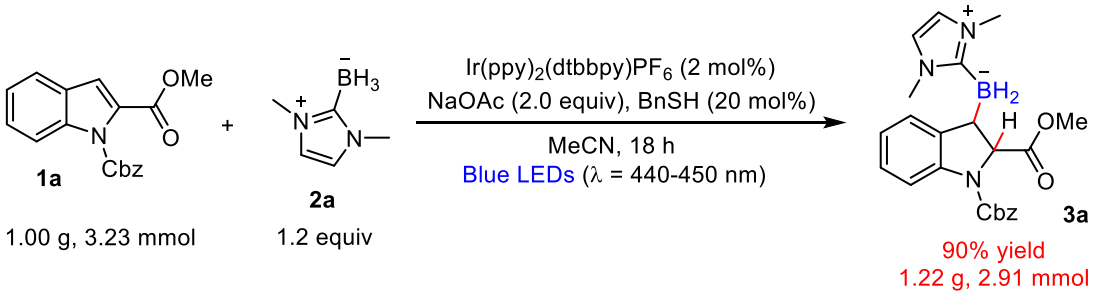
General procedure for the dearomative *β*-hydroborylation of 3-substituted indoles.

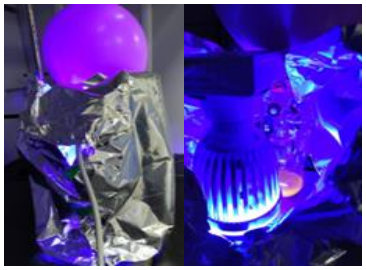


A dry glass tube (35 mL, 18 x 180 mm) charged with **4** (0.20 mmol, 1.0 equiv), **2a** (44.0 mg, 2.0 equiv), $[Ir(ppy)_2(dtbbpy)]PF_6$ (3.7 mg, 2 mol%), BnSH (4.7 μL, 20 mol%) and MeCN (2 mL) was evacuated and backfilled with N_2 for three times, then was tied up nitrogen balloon and placed approximately 5 cm from a 30 W blue LEDs (λ = 440-450 nm) light. The mixture was stirred at room temperature for 12 h. As the reaction completed, the solvent was removed by vacuum and the crude product was purified by

column chromatography (SiO_2, petroleum ether/ethyl acetate) to provide the desired product **5**.

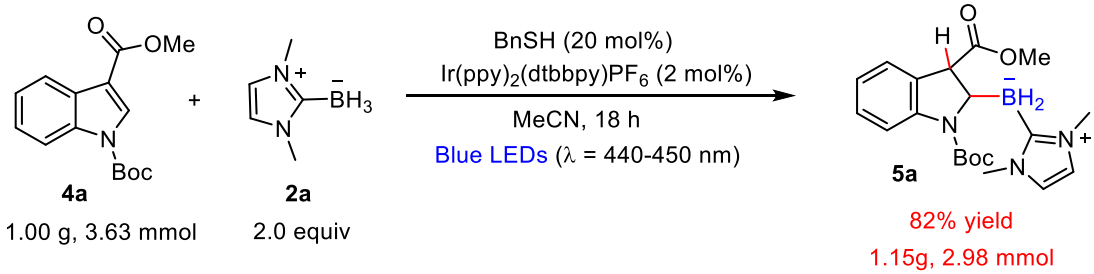
Gram scale reaction of 1a.





In a 100 mL round-bottom flask charged with **1a** (1.00 g, 3.23 mmol), **2a** (0.42 g, 3.84 mmol), $[Ir(ppy)_2(dtbbpy)]PF_6$ (58.5 mg, 0.064 mmol), NaOAc (0.50 g, 6.40 mmol), BnSH (75.1 μL, 0.64 mmol) and 30 mL MeCN was evacuated and backfilled with N_2 for three times, and finally tie up nitrogen balloon and placed approximately 3 cm from a 30 W blue LEDs (λ = 440-450 nm) light. The mixture was stirred at room temperature for 18 hours. Then filtration, the solvent was removed by evaporation. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 2:1) to obtain **3a** in 95% yield.

Gram scale reaction of 4a.

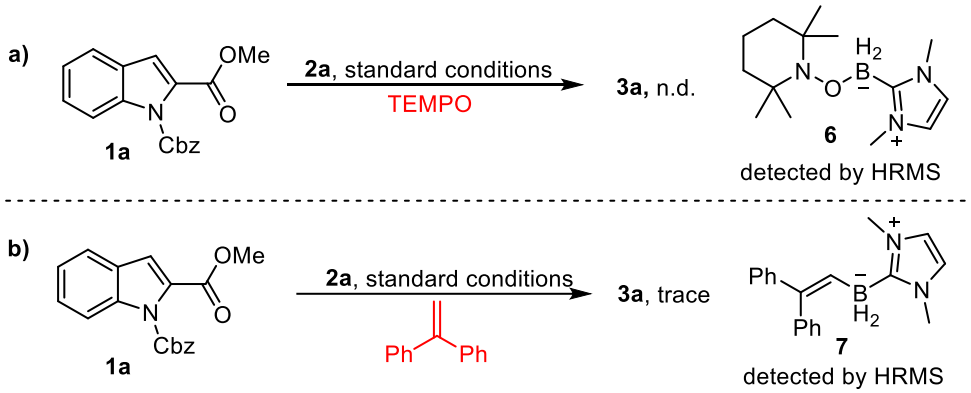


In a 100 mL round bottom flask charged with **4a** (1.00 g, 3.60 mmol), **2a** (0.80 g, 7.2 mmol), $[Ir(ppy)_2(dtbbpy)]PF_6$ (65.8 mg, 0.072 mmol), BnSH (84.5 μL, 0.72 mmol)

and 40 mL MeCN was evacuated and backfilled with N_2 for three times, and finally tie up nitrogen balloon and placed approximately 3 cm from a 30 W blue LEDs (λ = 440-450 nm) light. The mixture was stirred at room temperature for 18 hours. Then filtration, the solvent was removed by evaporation. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 2:1) to obtain **5a** in 82% yield.

5. Mechanism Studies

(1) Radical trapping experiments.



Two dry glass tubes (35 mL, 18 × 180 mm) equipped with rubber plugs and magneticstir bar was charged with **1a** (0.20 mmol), **2a** (0.24 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.7 mg, 2 mol%), NaOAc (32.8 mg, 2.0 equiv), BnSH (4.7 μL, 20 mol%), anhydrous 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 radical scavenger 1,1-diphenylene into the reaction system. After stirred at room temperature for 12 hours, it was found that both reaction (a) and (b) were hindered. The desired product **3a** could not be observed in reaction (a), and only trace amount of **3a** could be detected by HRMS (b). Additionally, intermediates **6** and **7** were detected in reaction (a) and (b) by HRMS, respectively.

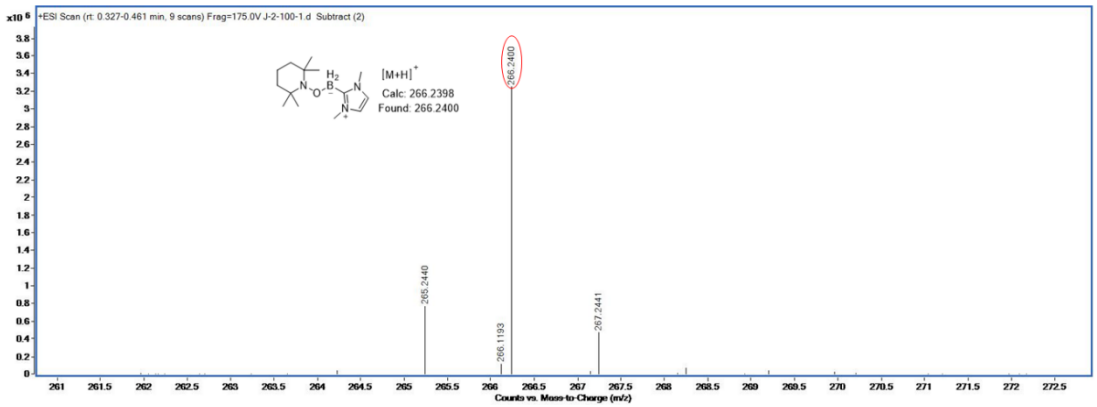


Fig. S1 HRMS spectrum of compound **6**.

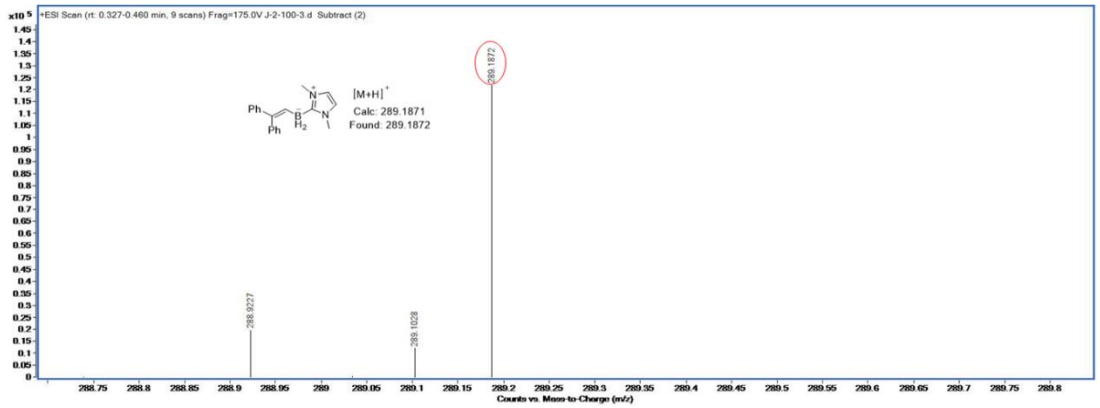
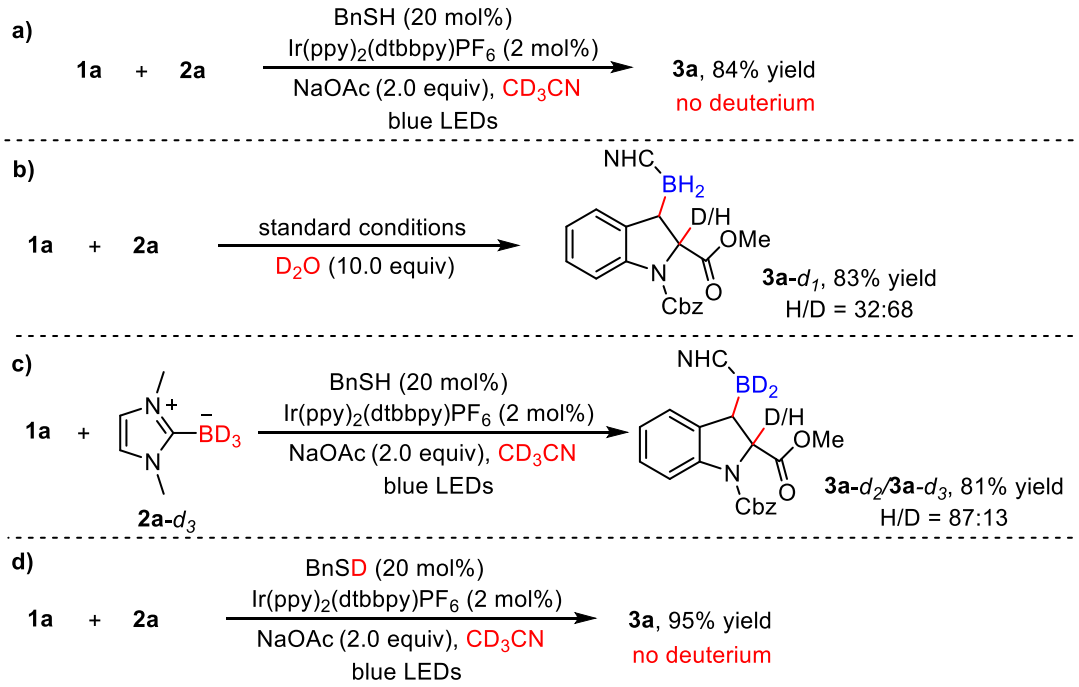


Fig. S2 HRMS spectrum of compound **7**.

(2) Isotopic labelling experiments.



Reaction a)： A dry glass tube (35 mL, 18 × 180 mm) charged with **1a** (0.20 mmol), **2a** (0.24 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%), BnSH (20 mol%), NaOAc (2.0 equiv) and anhydrous CD_3CN (2 mL) was evacuated and backfilled with N_2 three times, and finally tie up nitrogen balloon. The reaction mixture was stirred at 30 W blue LEDs (λ = 440-450 nm) light at room temperature for 12 h. The yield was determined by ^1H NMR.

Reaction b)： A dry glass tube (35 mL, 18 × 180 mm) charged with **1a** (0.20 mmol), **2a** (0.24 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%), BnSH (20 mol%), NaOAc (2.0 equiv), D_2O (10.0 equiv) and anhydrous CH_3CN (2 mL) was evacuated and backfilled with N_2 three times, and finally tie up nitrogen balloon. The reaction mixture was stirred at 30 W blue LEDs (λ = 440-450 nm) light at room temperature for 12 h. The yield and H/D ratio were determined by ^1H NMR.

Reaction c)： A dry glass tube (35 mL, 18 × 180 mm) charged with **1a** (0.20 mmol), **2a**-d_3 (0.24 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%), BnSH (20 mol%), NaOAc (2.0 equiv) and anhydrous CD_3CN (2 mL) was evacuated and backfilled with N_2 three times, and finally tie up nitrogen balloon. The reaction mixture was stirred at 30 W blue LEDs (λ = 440-450 nm) light at room temperature for 12 h. The yield and H/D ratio were determined by ^1H NMR.

Reaction d)： A dry glass tube (35 mL, 18 × 180 mm) charged with **1a** (0.20 mmol), **2a** (0.24 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%), BnDH (20 mol%), NaOAc (2.0 equiv) and anhydrous CD_3CN (2 mL) was evacuated and backfilled with N_2 three times, and finally tie up nitrogen balloon. The reaction mixture was stirred at 30 W blue LEDs (λ = 440-450 nm) light at room temperature for 12 h. The yield was determined by ^1H NMR.

(3) Light/dark experiments.

Six dry glass tubes (35 mL, 18 × 180 mm) charged with **1a** (0.20 mmol), **2a** (0.24 mmol), $[Ir(ppy)_2(dtbbpy)]PF_6$ (2 mol%), NaOAc (32.8 mg, 2.0 equiv), BnSH (4.7 μL, 20 mol%) and MeCN (2 mL) were evacuated and backfilled with N_2 for three times. The reaction was alternatively irradiated with a 30 W blue LEDs (λ = 440-450 nm) and

kept in the dark in 2 h intervals. After each interval, one vial was taken out, the solvent was removed under reduced pressure, and the yield was determined by ^{1}H NMR based on a triphenyl methane as an internal standard.

Table S8 Yields of light/dark experiment.[a]

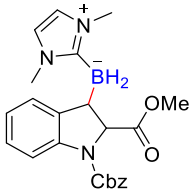
Vial	Time (h)/Condition						Yield (%)[b]
1	0-2/*hv*						19
2	0-2/*hv*	2-4/*dark*					19
3	0-2/*hv*	2-4/*dark*	4-6/*hv*				63
4	0-2/*hv*	2-4/*dark*	4-6/*hv*	6-8/*dark*			63
5	0-2/*hv*	2-4/*dark*	4-6/*hv*	6-8/*dark*	8-10/*hv*		83
6	0-2/*hv*	2-4/*dark*	4-6/*hv*	6-8/*dark*	8-10/*hv*	10-12/*dark*	83

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (1.2 equiv), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%), NaOAc (2.0 equiv), BnSH (20 mol%), MeCN (2 mL), 30 W blue LEDs (λ = 440-450 nm), rt, 12 h, N_2 atmosphere. [b]Yields were determined by ^{1}H NMR with triphenyl methane as internal standard.

6. Analytical Data for Products

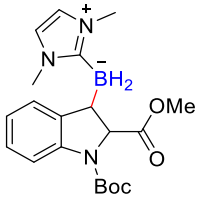
NMR spectra for most of all hydroborylative products contain conformational isomers, which is caused by the restricted C-N bond rotation around the carbamate group.

(1-((Benzyloxy)carbonyl)-2-(methoxycarbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-2-yl)dihydroborate (3a)



Colorless oil (95%, 79.6 mg, 2.9:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.44-7.20 (m, 5H), 7.01-6.97 (m, 1H), 6.76 (s, 2H), 6.73-6.69 (m, 1H), 6.14 (d, *J* = 7.4 Hz, 1H), 5.39-5.05 (m, 2H), 4.64-4.62 (m, 1H), 3.70-3.37 (m, 9H), 2.65 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.2 (*C*OOMe), 153.1 (*C*=O), 141.1, 141.0, 136.7, 128.5, 128.2, 128.0 and 127.9 (a pair of s, *C*H), 124.9, 122.3, 121.7, 120.6, 114.2, 68.6 and 68.4 (a pair of s, CH_2), 66.7, 51.9, 35.9 (NCH_3) ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ -25.5 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{20}H_{28}BN_3O_4$, 442.1909; found, 442.1919.

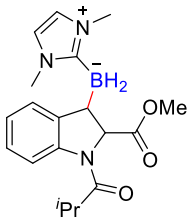
(1-(*tert*-Butoxycarbonyl)-2-(methoxycarbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-2-yldihydroborate (3b)



Colorless oil (97%, 74.6 mg, 3.0:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 1H), 6.98-6.94 (m, 1H), 6.83 (s, 2H), 6.68-6.64 (m, 1H), 6.06 (d, *J* = 7.3 Hz, 1H), 4.55-4.53 (m, 1H), 3.72-3.48 (m, 9H), 2.60 (brs, 1H), 1.58 and 1.48 (a pair of s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.5 (*C*OOMe), 152.6 (*C*=O), 141.5, 140.8, 124.8, 121.7, 121.5, 120.7 and 120.6 (a pair of s, *C*H), 113.9, 80.3, 68.9, 51.7, 36.2 and

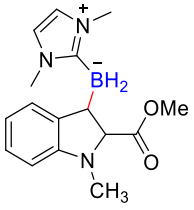
35.9 (a pair of s, N*C*H$_3$), 28.4 ppm. **HRMS-ESI** (m/z): [M+Na]$^+$ calcd for $C_{20}H_{28}BN_3O_4$, 408.2065; found, 408.2071.

(1,3-Dimethyl-1*H*-imidazol-2-yl)(1-isobutyryl-2-(methoxycarbonyl)indolin-3-yl)-dihydroborate (3c)



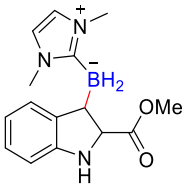
Colorless oil (67%, 47.7 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.02-6.95 (m, 1H), 6.82 (s, 2H), 6.70-6.66 (m, 1H), 5.87 (d, *J* = 7.3 Hz, 1H), 4.74-4.73 (m, 1H), 3.68-3.42 (m, 9H), 2.71 (brs, 1H), 2.62-2.54 (m, 1H), 1.26 (d, *J* = 6.7 Hz, 3H), 1.18 (d, *J* = 6.4 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.7 (*C*OOMe), 174.3 (*C*=O), 141.7, 124.7, 122.9, 120.9, 120.5, 117.2, 69.0, 52.3, 35.8 (N*C*H$_3$), 33.5, 20.1, 19.0 ppm. **HRMS-ESI** (m/z): [M+Na]$^+$ calcd for $C_{19}H_{26}BN_3O_3$, 378.1959; found, 378.1964.

(1,3-Dimethyl-1*H*-imidazol-2-yl)(2-(methoxycarbonyl)-1-methylindolin-3-yl)dihydroborate (3d)



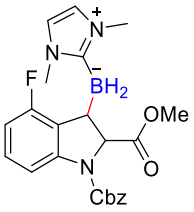
Colorless oil (77%, 46.9 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94-6.91 (m, 1H), 6.84 (s, 2H), 6.58-6.44 (m, 2H), 6.37 (d, *J* = 7.7 Hz, 1H), 3.77-3.76 (m, 1H), 3.69 (s, 6H), 3.60 (s, 3H), 2.77 (s, 3H), 2.66 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.7 (*C*OOMe), 151.8 (*C*=O), 139.3, 125.3, 122.1, 120.4, 117.7, 106.2, 51.8, 36.2 (N*C*H$_3$), 35.2 ppm. **HRMS-ESI** (m/z): [M+H]$^+$ calcd for $C_{16}H_{22}BN_3O_2$, 300.1878; found, 300.1881.

Methyl 3-((1,3-dimethyl-1*H*-imidazol-2-yl)boraneyl)indoline-2-carboxylate (3e)



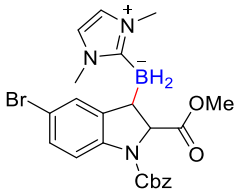
Colorless oil (46%, 26.3 mg, 1.4:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.85-6.83 (m, 1H), 6.82 (s, 2H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.50-6.48 (m, 1H), 6.13 (d, *J* = 7.2 Hz, 1H), 4.09-4.07 (m, 1H), 3.65 (s, 3H), 3.56 (s, 6H), 2.84 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0 (*C*OOMe), 123.3, 121.8, 120.6, 119.1, 115.0, 110.2, 51.3, 35.7 (N*C*H_3) ppm. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{15}H_{20}BN_3O_2$, 308.1541; found, 308.1547.

(1-((Benzyloxy)carbonyl)-4-fluoro-2-(methoxycarbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3f)



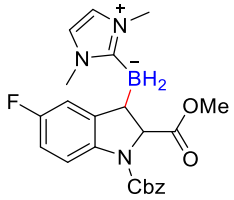
Colorless oil (83%, 72.4 mg, 3.5:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.41-7.19 (m, 5H), 6.98-6.92 (m, 1H), 6.76 (s, 2H), 6.41-6.37 (m, 1H), 5.34-5.14 (m, 2H), 4.77-4.75 (m, 1H), 3.69-3.46 (m, 9H), 2.79 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8 (*C*OOMe), 157.5 (d, *J* = 237.7 Hz), 153.2 (*C*=O), 143.8, 143.7, 136.4, 128.6 and 128.5 (a pair of s, *CH*), 128.3 and 128.0 (a pair of s, *C*H), 127.8 and 127.7 (a pair of s, *CH*), 126.4 (d, *J* = 7.0 Hz), 120.5, 110.3 (d, *J* = 2.8 Hz), 109.0 (d, *J* = 21.1 Hz), 69.3 and 69.1 (a pair of s, *C*H_2), 66.9, 52.1 and 52.0 (a pair of s, O*C*H_3), 35.7 (N*C*H_3) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -125.6 and -126.8 (a pair of s, F). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{23}H_{25}BFN_3O_4$, 460.1814; found, 460.1820.

(1-((Benzyloxy)carbonyl)-5-bromo-2-(methoxycarbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3g)



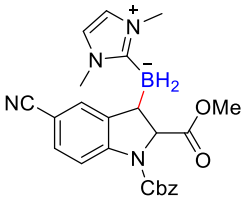
Colorless oil (82%, 82.3 mg, 3.4:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 1H), 7.43-7.19 (m, 5H), 7.12-7.09 (m, 1H), 6.83 and 6.82 (a pair of s, 2H), 6.16 (s, 1H), 5.32-5.11 (m, 2H), 4.64-4.62 (m, 1H), 3.68-3.45 (m, 9H), 2.60 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8 (*C*OOMe), 153.0 (*C*=O), 143.8, 140.3, 136.4, 128.5, 128.1, 127.9, 127.4, 124.8, 120.7, 115.5, 114.8, 68.5, 67.0, 52.0, 35.9 (N*C*H$_3$) ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ -25.5 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{23}H_{25}BBrN_3O_4$, 520.1014; found, 520.1022.

(1-((Benzyloxy)carbonyl)-5-fluoro-2-(methoxycarbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3h)



Colorless oil (95%, 83.5 mg, 3.0:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76-7.72 (m, 1H), 7.42-7.28 (m, 5H), 6.80 (s, 2H), 6.70-6.66 (m, 1H), 5.92 (d, *J* = 8.8 Hz, 1H), 5.30-5.13 (m, 2H), 4.64-4.61 (m, 1H), 3.69-3.51 (m, 9H), 2.62 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.0 (*C*OOMe), 159.2 (d, *J* = 237.3 Hz), 153.1 (*C*=O), 143.4, 137.1, 136.6, 128.5, 128.3, 128.1 and 127.9 (a pair of s, *C*H), 120.7, 114.5 (d, *J* = 8.5 Hz), 110.6 (d, *J* = 22.8 Hz), 109.1 (d, *J* = 24.1 Hz), 68.7, 66.9, 52.0, 36.0 (N*C*H$_3$) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.58 and 122.61 (a pair of s, F). **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{23}H_{25}BFN_3O_4$, 460.1814; found, 460.1820.

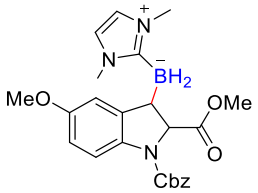
(1-((Benzyloxy)carbonyl)-5-cyano-2-(methoxycarbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3i)



Colorless oil (44%, 38.6 mg, 2.6:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.41-7.27 (m, 6H), 6.87 (s, 2H), 6.35 (s, 1H), 5.34-5.14 (m, 2H), 4.65-4.64 (m, 1H), 3.75-3.42 (m, 9H), 2.62 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$)

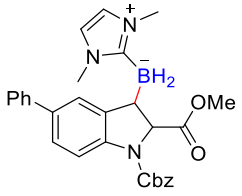
δ 173.4 (*C*OOMe), 152.9 (*C*=O), 145.4, 136.0, 130.4, 128.6, 128.3, 128.0, 124.8, 120.9, 120.1, 114.4, 104.8, 68.8, 67.4, 52.1, 36.0 (N*C*H$_3$) ppm. **HRMS-ESI** (m/z): [M+Na]$^+$ calcd for $C_{24}H_{25}BN_4O_4$, 467.1861; found, 467.1862.

(1-((Benzyloxy)carbonyl)-5-methoxy-2-(methoxycarbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3j)



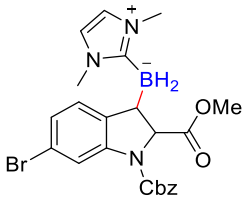
Green oil (90%, 81.3 mg, 2.7:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.6 Hz, 1H), 7.41-7.27 (m, 5H), 6.78 and 6.77 (a pair of s, 2H), 6.55-6.52 (m, 1H), 5.81 (s, 1H), 5.31-5.11 (m, 2H), 4.62-4.58 (m, 1H), 3.67-3.47 (m, 12H), 2.62 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.2 (*C*OOMe), 155.7 (*C*=O), 153.0, 142.7, 136.8, 134.9, 128.6 and 128.5 (a pair of s, *C*H), 128.2, 127.9, 120.6, 114.7 and 114.4 (a pair of s, *C*H), 109.3 and 109.1 (a pair of s, *C*H), 108.8, 68.8 and 68.6 (a pair of s, *C*H$_2$), 66.6, 55.6, 51.9, 36.0 and 35.9 (a pair of s, N*C*H$_3$) ppm. **HRMS-ESI** (m/z): [M+Na]$^+$ calcd for $C_{24}H_{28}BN_3O_5$, 472.2014; found, 472.2022.

(1-((Benzyloxy)carbonyl)-2-(methoxycarbonyl)-5-phenylindolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3k)



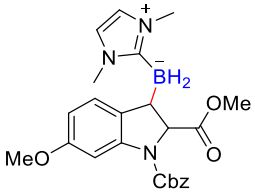
Colorless oil (85%, 84.2 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 1H), 7.39-7.13 (m, 11H), 6.69 and 6.64 (a pair of s, 2H), 6.33-6.32 (m, 1H), 5.26-5.08 (m, 2H), 4.61-4.58 (m, 1H), 3.56-3.39 (m, 9H), 2.62 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1 (*C*OOMe), 153.1 (*C*=O), 141.7, 141.6, 140.7, 136.6, 135.3, 128.6, 128.3, 128.5, 128.0, 127.9, 126.6, 126.5, 124.0, 120.6 and 120.4 (a pair of s, *C*H), 114.3, 68.7, 66.9, 51.9, 35.9 (N*C*H$_3$) ppm. **HRMS-ESI** (m/z): [M+H]$^+$ calcd for $C_{29}H_{30}BN_3O_4$, 496.2402; found, 496.2399.

(1-((Benzyloxy)carbonyl)-6-bromo-2-(methoxycarbonyl)indolin-3-yl)(1,3-dimeth yl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3l)



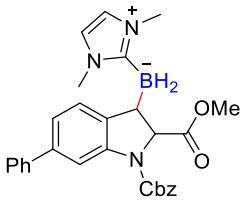
Colorless oil (72%, 72.0 mg, 3.6:1 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 1.9 Hz, 1H), 7.46-7.28 (m, 5H), 6.84-6.82 (m, 1H), 6.79 (s, 2H), 6.00 (d, *J* = 7.8 Hz, 1H), 5.38-5.10 (m, 2H), 4.62-4.58 (m, 1H), 3.64-3.44 (m, 9H), 2.57 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8 (*C*OOMe), 153.0 (*C*=O), 142.5, 140.4, 136.4, 128.5, 128.1, 127.9, 125.0, 122.8, 120.7, 117.9, 117.3, 68.8, 67.0, 52.0, 36.0 (N*C*H$_3$) ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{23}H_{25}BBrN_3O_4$, 520.1014; found, 520.1019.

Benzyl 2-methyl 3-((1,3-dimethyl-1*H*-imidazol-2-yl)boraneyl)-6-methoxyindoline 1,2-dicarboxylate (3m)



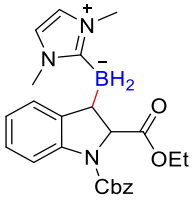
Colorless oil (30%, 26.8 mg, 1.8:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56-7.55 (m, 1H), 7.48-7.30 (m, 5H), 6.81 and 6.78 (a pair of s, 2H), 6.32-6.29 (m, 1H), 6.01 (d, *J* = 8.1 Hz, 1H), 5.33-5.15 (m, 2H), 4.65-4.60 (m, 1H), 3.77-3.25 (m, 12H), 2.57 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.2 (*C*OOMe), 158.8 and 157.8 (a pair of s, *C*), 153.0 (*C*=O), 142.1, 136.6, 134.3, 128.7, 128.5, 128.0 and 127.8 (a pair of s, *C*H), 123.9 and 121.8 (a pair of s,*C*H), 120.5 and 120.4 (a pair of s, *C*H), 111.9 and 108.5 (a pair of s, *C*H), 100.6 and 98.9 (a pair of s, *C*H), 69.2 and 68.8 (a pair of s, *C*H$_2$), 66.7, 55.6 and 55.5 (a pair of s, CO*C*H$_3$), 51.8 and 51.6 (a pair of s, O*C*H$_3$), 36.1 and 35.9 (a pair of s, N*C*H$_3$) ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{24}H_{28}BN_3O_5$, 472.2014; found, 472.2017.

(1-((Benzyloxy)carbonyl)-2-(methoxycarbonyl)-6-phenylindolin-3-yl)(1,3-dimeth yl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3n)



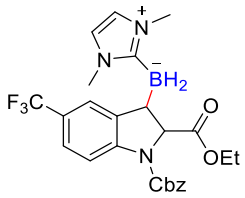
Colorless oil (74%, 73.3 mg, 2.4:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.35-7.17 (m, 8H), 6.96-6.90 (m, 1H), 6.68 (s, 2H), 6.14 (d, *J* = 7.7 Hz, 1H), 5.23-5.07 (m, 2H), 4.61-4.57 (m, 1H), 3.56-3.40 (m, 9H), 2.60 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.2 (*C*OOMe), 153.1 (*C*=O), 141.9, 141.8, 140.5, 138.2, 136.7, 128.6, 128.5, 128.0, 127.9, 127.1, 126.7, 121.9, 121.3, 120.6, 113.0, 68.8, 66.8, 51.9, 36.0 (N*C*H$_3$) ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{29}H_{30}BN_3O_4$, 518.2222; found, 518.2229.

1-Benzyl 2-ethyl 3-((1,3-dimethyl-1*H*-imidazol-2-yl)boraneyl)indoline-1,2-dicarboxylate (3o)



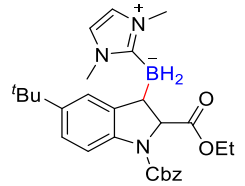
Colorless oil (94%, 81.7 mg, 2.8:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.43-7.26 (m, 5H), 7.00-6.81 (m, 1H), 6.77 (s, 2H), 6.73-6.70 (m, 1H), 6.18 (d, *J* = 7.3 Hz, 1H), 5.31-5.16 (m, 2H), 4.61-4.58 (m, 1H), 4.01 (q, *J* = 7.1, 2H), 3.53 and 3.45 (a pair of s, 6H), 2.64 (brs, 1H), 1.08 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.7 (*C*OOMe), 153.1 (*C*=O), 141.2, 141.0, 136.6, 128.6 and 128.5 (a pair of s, *C*H), 128.2, 127.9 and 127.8 (a pair of s, *C*H), 124.8, 122.3, 121.8, 120.5, 114.1, 68.7 and 68.5 (a pair of s, *C*H$_2$), 66.7, 60.5, 36.0 and 35.9 (a pair of s, N*C*H$_3$), 14.2 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{24}H_{28}BN_3O_4$, 456.2065; found, 456.2074.

(1-((Benzyloxy)carbonyl)-2-(ethoxycarbonyl)-5-(trifluoromethyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3p)



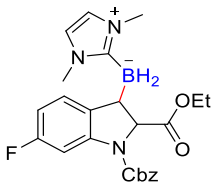
Colorless oil (84%, 84.2 mg, 3.8:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 1H), 7.44-7.26 (m, 6H), 6.82 (s, 2H), 6.16 (s, 1H), 5.34-5.17 (m, 2H), 4.69-4.67 (m, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.57-3.40 (m, 6H), 2.62 (brs, 1H), 1.09 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.3 (*C*OOMe), 153.2 (*C*=O), 144.4, 142.1, 136.3, 128.6, 128.4 (q, *J* = 238 Hz), 128.1, 127.9, 123.7 (q, *J* = 31 Hz), 122.5 (q, *J* = 4 Hz), 120.7, 118.3, 113.6, 68.9, 67.2, 60.8, 35.9 (N*C*H$_3$), 14.2 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.3 and -61.4 (a pair of s, 3F). **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{25}H_{27}BF_3N_3O_4$, 524.1939; found, 524.1946.

(1-((Benzyloxy)carbonyl)-5-(*tert*-butyl)-2-(ethoxycarbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**3q**)



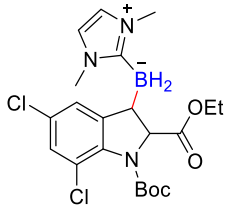
Colorless oil (88%, 86.2 mg, 2.6:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 1H), 7.43-7.26 (m, 5H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.78 (s, 2H), 6.15 and 6.14 (a pair of s, 1H), 5.30-5.16 (m, 2H), 4.63-4.60 (m, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.70-3.45 (m, 6H), 2.62 (brs, 1H), 1.20 and 1.19 (a pair of s, 9H), 1.17-1.08 (m, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8 (*C*OOMe), 153.1 (*C*=O), 144.8, 140.5, 138.8, 136.8, 128.4, 128.2 and 128.1 (a pair of s, *C*H), 127.9 and 127.8 (a pair of s, *C*H), 121.6, 120.5, 118.8, 113.4, 68.7, 66.7, 60.5, 35.9 (N*C*H$_3$), 34.2, 31.8, 14.3 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{28}H_{36}BN_3O_4$, 512.2691; found, 512.2698.

(1-((Benzyloxy)carbonyl)-2-(ethoxycarbonyl)-6-fluoroindolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3r)



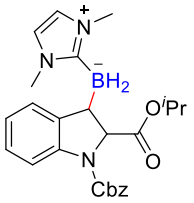
Colorless oil (81%, 72.7 mg, 3.4:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 10.5 Hz, 1H), 7.43-7.26 (m, 5H), 6.80 (s, 2H), 6.47-6.40 (m, 1H), 6.11-6.08 (m, 1H), 5.32-5.15 (m, 2H), 4.60-4.57 (m, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.61 and 3.52 (a pair of s, 6H), 2.58 (brs, 1H), 1.08 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5 (*C*OOMe), 161.2 (d, *J* = 237.6 Hz), 153.0 (*C*=O), 142.4, 142.3, 136.4 and 136.3 (a pair of s, *C*), 128.7 and 128.5 (a pair of s, *C*H), 128.3, 128.1 and 127.9 (a pair of s, *C*H), 121.7 (d, *J* = 9.3 Hz), 120.6, 108.2 (d, *J* = 22.2 Hz), 102.6 (d, *J* = 28.6 Hz), 69.3, 67.0, 60.7, 36.0 (N*C*H$_3$), 14.22 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.6 and -118.7 (a pair of s, F). **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{24}H_{27}BFN_3O_4$, 474.1971; found, 474.1979.

(1-(*tert*-Butoxycarbonyl)-5,7-dichloro-2-(methoxycarbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3s)



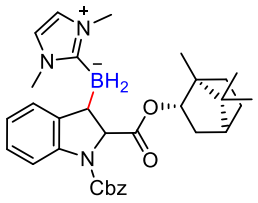
Colorless oil (74%, 67.2 mg, 3.8:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 6.87 (s, 2H), 6.19 (s, 1H), 4.66-4.64 (m, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.61 (s, 6H), 2.59 (brs, 1H), 1.52 (s, 9H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5 (*C*OOMe), 154.1 (*C*=O), 148.9, 138.0, 129.0, 125.4, 124.0, 120.8, 120.2, 81.3, 71.4, 60.7, 36.0 (N*C*H$_3$), 28.3, 14.2 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{20}H_{26}BCl_2N_3O_4$, 476.1286; found, 476.1289.

(1-((Benzyloxy)carbonyl)-2-(isopropoxycarbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3t)



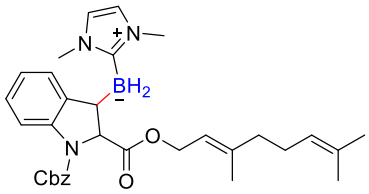
Colorless oil (95%, 84.9 mg, 3.5:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.43-7.26 (m, 5H), 7.01-6.97 (m, 1H), 6.77 (s, 2H), 6.74-6.70 (m, 1H), 6.22 (d, *J* = 7.3 Hz, 1H), 5.20 (s, 2H), 4.96-4.87 (m, 1H), 4.57-4.53 (m, 1H), 3.70-3.48 (m, 6H), 2.61 (brs, 1H), 1.17-1.05 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.1 (*C*OOMe), 153.1 (*C*=O), 141.3, 141.1, 136.6, 128.4, 128.2, 127.9 and 127.8 (a pair of s, *C*H), 124.8, 122.3, 121.9, 120.6, 114.1, 68.6, 67.7, 66.8, 35.9 (N*C*H$_3$), 21.7 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{25}H_{30}BN_3O_4$, 470.2222; found, 470.2225.

(1-((Benzyloxy)carbonyl)-2-((((1*S*,2*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)carbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3u)



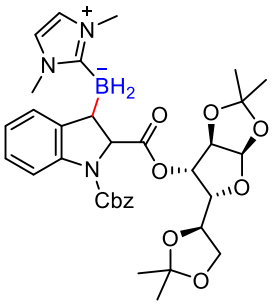
Colorless oil (73%, 79.2 mg, 3.7:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.77 (m, 1H), 7.45-7.27 (m, 5H), 6.99-6.94 (m, 1H), 6.78 (s, 2H), 6.76-6.66 (m, 1H), 6.09-6.03 (m, 1H), 5.29-5.15 (m, 2H), 4.61-4.46 (m, 2H), 3.51-3.41 (m, 6H), 2.62 (brs, 1H), 1.71-1.57 (m, 3H), 1.56-1.42 (m, 2H), 1.06-0.93 (m, 2H), 0.76-0.67 (m, 6H), 0.58-0.47 (m, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.1 (*C*OOMe), 153.1(*C*=O), 141.3, 136.6, 128.5, 128.1, 128.0, 124.7, 122.2, 121.5 and 121.4 (a pair of s, *C*H), 120.5, 114.2, 81.1 and 80.9 (a pair of s, O*C*H), 68.7 and 68.5 (a pair of s, *C*H$_2$), 66.8, 48.6-48.4 (a pair of s, *C*), 46.8, 45.0, 38.9 and 38.6 (a pair of s, *C*H$_2$), 35.8 (N*C*H$_3$), 33.6, 27.0, 20.1, 19.6 and 19.4 (a pair of s, *C*H$_3$), 11.3 and 11.9 (a pair of s, *C*H$_3$) ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{32}H_{40}BN_3O_4$, 564.3004; found, 564.3010.

(*E*)-(1-((Benzyloxy)carbonyl)-2-(((3,7-dimethylocta-2,6-dien-1-yl)oxy)carbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3v)



Green oil (74%, 80.6 mg, 3.0:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.43 -7.26 (m, 5H), 7.00-6.96 (m, 1H), 6.75 (s, 2H), 6.71-6.69 (m, 1H), 6.19 (d, *J* = 7.3 Hz, 1H), 5.30-5.17 (m, 3H), 5.06-5.02 (m, 1H), 4.62-4.43 (m, 3H), 3.55 and 3.45 (a pair of s, 6H), 2.66 (brs, 1H), 2.04-1.99 (m, 4H), 1.72-1.66 (m, 6H), 1.57 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.6 (*C*OOMe), 153.1(*C*=O), 141.7, 141.2, 141.1, 136.7, 132.1, 128.5, 127.9, 127.7, 124.8, 123.7, 122.3, 121.8, 120.5, 119.5, 114.2, 68.5, 66.7, 61.3, 35.9 (N*C*H_3), 32.3, 26.7, 25.8, 23.6, 17.7 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{32}H_{40}BN_3O_4$, 564.3004; found, 564.3010.

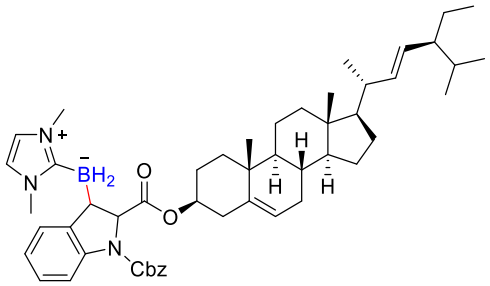
(1-((Benzyloxy)carbonyl)-2-((((3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)carbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3w)



Colorless oil (79%, 102.1 mg, 2.4:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.46-7.30 (m, 5H), 7.01-6.97 (m, 1H), 6.81 and 6.79 (a pair of s, 2H), 6.72-6.65 (m, 1H), 6.15-5.84 (m, 1H), 5.52-5.09 (m, 4H), 4.68-4.66 (m, 1H), 4.59-4.00 (m, 4H), 3.82-3.63 (m, 1H), 3.59-3.42 (m, 6H), 2.67 (brs, 1H), 1.50-1.44 (m, 3H), 1.38-1.25 (m, 6H), 1.20-1.09 (m, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2 (*C*OOMe), 152.9 and 152.8 (a pair of s, *C*=O), 141.1 and 140.9 (a pair of s, *C*), 140.6, 136.4 and 136.3 (a pair of s, *C*), 128.6, 128.3 and 128.1 (a pair of s, *C*H), 128.0, 125.0, 122.4 and 122.2 (a pair of s, *C*H), 121.3 and 120.6 (a pair of s, *C*H), 120.6, 114.1, 112.2, 109.2 and 108.9 (a pair of s, *C*H), 105, 83.2 and 83.0 (a apir of s, O*C*H), 79.7 and 79.6 (a pair

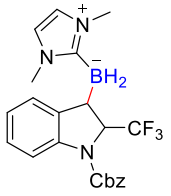
of s, *C*H), 76.1 and 75.9 (a pair of s, *C*H), 72.6 and 72.2 (a pair of s, *C*H), 68.5 and 68.2 (a pair of s, *C*H), 67.2 and 67.1 (a pair of s, CH_2), 66.8 and 66.7 (a pair of s, *C*H), 36.0 and 35.8 (a pair of s, NCH_3), 27.0-26.8 (a pair of s, CH_3), 26.3, 25.6, 25.1 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{34}H_{42}BN_3O_9$, 670.2906; found, 670.2916.

(1-((Benzyloxy)carbonyl)-2-((((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,5*S*,*E*)-5-ethyl-6-methylhet-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)oxy)carbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3x)



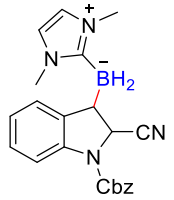
Colorless oil (34%, 54.8 mg, 3.0:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.44-7.29 (m, 5H), 7.24-7.00 (m, 1H), 6.79 (s, 2H), 6.75-6.71 (m, 1H), 6.23 (t, *J* = 7.0, 1H), 5.31-5.12 (m, 4H), 5.04-4.98 (m, 1H), 4.57-4.49 (m, 2H), 3.61-3.49 (m, 6H), 2.63 (brs, 1H), 2.15-2.10 (m, 1H), 2.00-1.93 (m, 2H), 1.79-1.62 (m, 2H), 1.55-1.38 (m, 9H), 1.26-1.01 (m, 11H), 0.98-0.96 (m, 3H), 0.85-0.78 (m, 12H), 0.69-0.66 (m, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.1 (*C*OOMe), 153.2 (*C*=O), 141.3, 141.0, 139.8, 138.5, 136.6, 129.4, 128.5, 128.3, 128.0, 124.9, 122.6, 122.3, 121.9, 120.6, 114.2, 74.0, 68.6, 66.8, 56.9, 56.0, 51.3, 50.1, 42.3, 40.7, 39.7, 38.0, 37.0, 36.8, 36.0 (NCH_3), 32.0, 31.9, 29.1, 27.6, 25.5, 24.5, 21.3, 21.2, 21.1, 19.5. 19.1, 12.4, 12.2 ppm. **HRMS-ESI** (m/z): $[M+H]^+$ calcd for $C_{51}H_{70}BN_3O_4$, 800.5532; found, 800.5523.

(1-((Benzyloxy)carbonyl)-2-(trifluoromethyl)indolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3y)



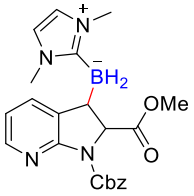
Colorless oil (51%, 43.6 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.37-7.29 (m, 5H), 7.14-7.11 (m, 2H), 6.97-6.93 (m, 1H), 6.57 (s, 2H), 5.12-4.80 (m, 2H), 3.46 (s, 6H), 3.45-3.44 (m, 1H), 3.18-3.14 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.7 (*C*=O), 143.1, 136.2, 131.1, 129.0, 128.4, 127.0, 126.9 (q, J = 269.2 Hz), 124.3, 122.7, 120.5, 116.0, 67.3, 41.2 (q, J = 24.3 Hz), 36.1 (N*C*H$_3$) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.4 (s, 3F). **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{22}H_{23}BF_3N_3O_2$, 452.1728; found, 452.1731.

(1-((Benzyloxy)carbonyl)-2-cyanoindolin-3-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3z)



Colorless oil (75%, 57.9 mg, 1.5:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 7.5 Hz, 2H), 6.78 (s, 2H), 6.76-6.72 (m, 1H), 7.00 (d, J = 7.6 Hz), 6.78-6.72 (m, 3H). 6.00 (d, J = 7.4 Hz, 1H), 5.32 (s, 2H), 4.88-4.86 (m, 1H), 3.74-3.39 (m, 6H), 2.84 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.5 (*C*=O), 136.1, 129.0, 128.7, 128.3, 128.1, 127.5, 125.3, 123.0, 121.6, 120.7, 114.9, 67.7, 56.3, 36.2 and 35.9 (a pair of s, N*C*H$_3$) ppm. **HRMS-ESI** (m/z): $[M+H]^+$ calcd for $C_{24}H_{31}BN_4O_2$, 419.2613; found, 419.2604.

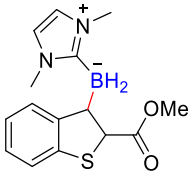
(1-((Benzyloxy)carbonyl)-2-(methoxycarbonyl)-2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)(1,3-dimethyl-1*H*-imidazol-2-yl)dihydroborate (3aa)



Colorless oil (96%, 80.8 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, J = 5.9 Hz, 1H), 7.41 (d, J = 7.4 Hz, 2H), 7.36-7.26 (m, 3H), 6.82 (s, 2H), 6.68-6.63 (m, 1H), 6.63-6.51 (m, 1H), 5.38-5.15 (m, 2H), 4.58-4.57 (m, 1H), 3.53 (s, 6H), 3.51 (s, 3H), 2.55 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.7 (*C*OOMe), 155.1

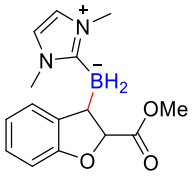
(*C*=O), 144.2, 136.5, 135.0, 129.4, 128.4, 128.1, 127.9, 120.8, 117.6, 67.1, 67.0, 51.9, 36.0 (N*C*H$_3$) ppm. **HRMS-ESI** (m/z): [M+Na]$^+$ calcd for $C_{22}H_{25}BN_4O_4$, 443.1861; found, 443.1867.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-(methoxycarbonyl)-2,3-dihydrobenzo[*b*]dihydrobenzo[b]thiophen-3-yl)dihydroborate (3ab)



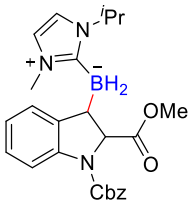
Colorless oil (93%, 56.3 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.7 Hz, 1H), 6.92-6.88 (m, 1H), 6.80 (s, 2H), 6.75-6.71 (m, 1H), 6.14 (d, *J* = 7.4 Hz, 1H), 4.90-4.88 (m, 1H), 3.74 (s, 3H), 3.49 (s, 6H), 3.07 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4 (*C*OOMe), 150.0, 139.4, 124.8, 123.6, 121.7, 121.6, 120.4, 59.6, 52.0 (O*C*H$_3$), 35.8 (N*C*H$_3$) ppm. **HRMS-ESI** (m/z): [M+Na]$^+$ calcd for $C_{15}H_{19}BN_2O_2S$, 325.1153; found, 325.1161.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-(methoxycarbonyl)-2,3-dihydrobenzofuran-3-yl)dihydroborate (3ac)



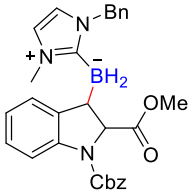
Colorless oil (47%, 26.9 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.93-6.89 (m, 1H), 6.85 (s, 2H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.60-6.56 (m, 1H), 5.95 (d, *J* = 7.2 Hz, 1H), 5.36-5.34 (m, 1H), 3.81 (s, 3H), 3.51 (s, 6H), 3.00 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3 (*C*OOMe), 158.2, 137.9, 125.3, 121.6, 120.5, 120.2, 109.2, 86.6, 51.5, 36.0 (N*C*H$_3$) ppm. **HRMS-ESI** (m/z): [M+Na]$^+$ calcd for $C_{15}H_{19}BN_2O_3$, 309.1381; found, 309.1389.

(1-((Benzyloxy)carbonyl)-2-(methoxycarbonyl)indolin-3-yl)(1-isopropyl-3-methyl 1*H*-imidazol-3-ium-2-yl)dihydroborate (3ad)



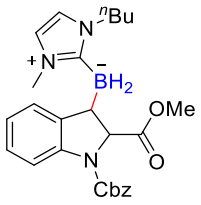
Colorless oil (99%, 93.9 mg, 3.4:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.42-7.28 (m, 5H), 7.00-6.96 (m, 1H), 6.91 and 6.80 (a pair of s,2H), 6.72-6.68 (m, 1H), 6.13 (d, *J* = 7.3 Hz, 1H), 5.32-5.27 (m, 2H), 4.99-4.89 (m, 1H), 4.64-4.61 (m, 1H), 3.62-3.36 (m, 6H), 2.62 (brs, 1H), 1.33 (d, *J* = 6.7 Hz, 3H), 1.25 (d, *J* = 6.7 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.2 (*C*OOMe), 153.1 (*C*=O), 141.1, 141.0, 136.6, 128.5, 127.9 and 127.8 (a pair of s, *C*H), 124.9, 122.3, 121.7, 121.2, 115.2, 114.2, 68.5, 66.7, 51.8, 49.8, 35.6 (N*C*H$_3$), 23.4, 22.7 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{25}H_{30}BN_3O_4$, 470.2222; found, 470.2230.

1-Benzyl-3-methyl-1*H*-imidazol-3-ium-2-yl)(1-((benzyloxy)carbonyl)-2-(methoxy carbonyl)dihydroborate (3ae)



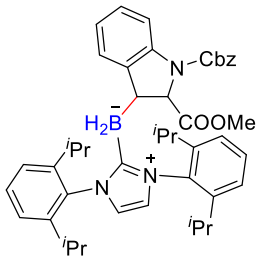
Colorless oil (83%, 82.7 mg, 2.3:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.43-7.27 (m, 9H), 7.18-7.15 (m, 2H), 7.04-7.00 (m, 1H), 6.76-6.65 (m, 2H), 6.20 (d, *J* = 7.4 Hz, 1H), 5.35-4.94 (m, 4H), 4.67-4.65 (m, 1H), 3.64-3.45 (m, 6H), 2.64 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.2 (*C*OOMe), 153.1 (*C*=O), 141.2, 141.0, 136.7, 135.5, 129.0, 128.6 and 128.5 (a pair of s, *C*H), 128.3 and 128.4 (a pair of s, *C*H), 128.0, 127.9, 125.0, 122.4, 121.9, 121.0, 119.2, 114.3, 68.5, 66.8, 52.1, 51.9, 36.0 (N*C*H$_3$) ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{29}H_{30}BN_3O_4$, 518.2222; found, 518.2227.

(1-((Benzyloxy)carbonyl)-2-(methoxycarbonyl)indolin-3-yl)(1-butyl-3-methyl-1*H* -imidazol-3-ium-2-yl)dihydroborate (3af)



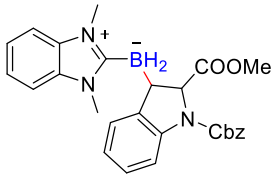
Colorless oil (99%, 92.1 mg, 3.4:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.36-7.18 (m, 5H), 6.91-6.89 (m, 1H), 6.81-6.70 (m, 1H), 6.64 and 6.60 (a pair of s, 2H), 6.06 (d, *J* = 7.3 Hz, 1H), 5.24-5.19 (m, 2H), 4.57-4.54 (m, 1H), 3.97-3.73 (m, 2H), 3.54-3.31 (m, 6H), 2.56 (brs, 1H), 1.58-1.49 (m, 2H), 1.24-1.14 (m, 2H), 0.80 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.2 (*C*OOMe), 153.1 (*C*=O), 141.1, 141.0, 136.6, 128.4, 128.1, 127.9 and 127.8 (a pair of s, *C*H), 124.8, 122.3 and 121.7 (a pair of s, *C*H), 120.7, 119.0, 114.1, 68.5, 66.8, 52.1, 51.9, 36.0 (N*C*H_3) ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{26}H_{32}BN_3O_4$, 484.2378; found, 484.2384.

(1-((Benzyloxy)carbonyl)-2-(methoxycarbonyl)indolin-3-yl)(1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium-2-yl)dihydroborate (3ag)



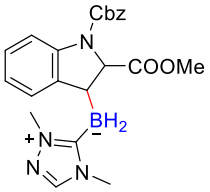
White solid (29%, 14.9 mg, 2.7:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.49-7.22 (m, 10H), 7.09 (s, 2H), 6.85 (t, *J* = 7.7 Hz, 1H), 6.75-6.71 (m, 1H), 6.05 (d, *J* = 7.4 Hz, 1H), 5.29-5.18 (m, 1H), 4.87-4.84 (m, 1H), 4.36-4.28 (m, 1H), 3.29 (s, 3H), 2.79-2.61 (m, 4H), 2.08 (brs, 1H), 1.28-1.11 (m, 24H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.7 (*C*OOMe), 152.8, 145.9, 145.6, 142.1, 140.7, 136.7, 134.2, 130.4, 128.4, 128.3, 127.9, 124.3, 124.2, 124.1, 123.2, 122.9, 122.5, 113.6, 69.7, 66.6, 51.3, 28.9 and 28.8 (a pair of s, *C*H), 26.3 and 26.0 (a pair of s, *C*H_3), 22.6 and 22.5 (a pair of s, *C*H_3) ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{45}H_{54}BN_3O_4$, 734.4100; found, 734.4105.

(1-((Benzyloxy)carbonyl)-2-(methoxycarbonyl)indolin-3-yl)(1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium-2-yl)dihydroborate (3ah)



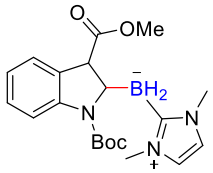
Colorless oil (86%, 80.4 mg, 2.3:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.46-7.25 (m, 9H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.64-6.60 (m, 1H), 6.08 (d, *J* = 7.4 Hz, 1H), 5.38-5.09 (m, 2H), 4.72-4.68 (m, 1H), 3.89-3.71 (m, 6H), 3.46 (s, 3H), 2.77 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1 (*C*OOMe), 153.1 (*C*=O), 141.2, 140.6, 136.6, 133.0, 128.5, 128.1 and 128.0 (a pair of s, *C*H), 127.8, 125.1, 124.6, 122.3, 121.6, 114.3, 110.1, 68.6, 66.8, 51.9, 32.2 (N*C*H$_3$) ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{27}H_{28}BN_3O_4$, 492.2065; found, 492.2069.

(1-((Benzyloxy)carbonyl)-2-(methoxycarbonyl)indolin-3-yl)(1,4-dimethyl-4*H*-1,2,4-triazol-1-ium-5-yl)dihydroborate (3ai)



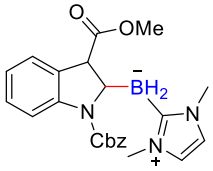
Colorless oil (76%, 63.8 mg, 2.4:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83-7.70 (m, 2H), 7.38-7.26 (m, 5H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.80-6.72 (m, 1H), 6.28 (d, *J* = 7.3 Hz, 1H), 5.31-5.13 (m, 2H), 4.60-4.58 (m, 1H), 3.77 and 3.73 (a pair of s, 3H), 3.62-3.39 (m, 6H), 2.68 (brs, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.9 (*C*OOMe), 153.0 (*C*=O), 141.7, 141.1, 140.3, 136.5, 128.5, 128.3 and 128.1 (a pair of s, *C*H), 127.9, 125.3, 122.6, 121.8, 114.3, 68.3, 66.9, 52.0, 38.2, 33.6 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{22}H_{25}BN_4O_4$, 443.1861; found, 443.1867.

(1-(*tert*-Butoxycarbonyl)-3-(methoxycarbonyl)indolin-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (5a)



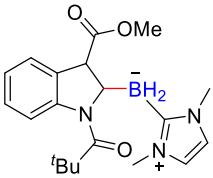
White solid (99%, 76.1 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70-7.44 (m, 1H), 7.34-7.32 (m, 1H), 7.19-7.15 (m, 1H), 6.95-6.92 (m, 1H), 6.80 (s, 2H), 4.37 (brs, 1H), 3.79-3.77 (m, 1H), 3.70 (s, 6H), 3.64 (s, 3H), 1.34 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.6 (*C*OOMe), 152.1 (*C*=O), 142.4, 131.9, 127.9, 125.9, 121.8, 120.2, 116.0, 79.0, 52.7, 51.9, 35.9 (N*C*H$_3$), 28.4 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ -25.5. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{20}H_{28}BN_3O_4$, 408.2065; found, 408.2068.

(1-((Benzyloxy)carbonyl)-3-(methoxycarbonyl)indolin-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (5b)



Colorless oil (99%, 83.0 mg, 3.8:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16-7.83 (m, 1H), 7.36-7.22 (m, 7H), 6.99-6.95 (m, 1H), 6.53 (s, 2H), 5.09 (s, 1H), 4.47-4.45 (m, 2H), 3.84-3.82 (m, 1H), 3.66 (s, 3H), 3.44 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.5 (*C*OOMe), 152.8 (*C*=O), 145.6, 136.5, 131.5, 128.4, 128.2, 128.1, 126.0, 122.4, 120.1, 115.9, 66.9, 53.0, 52.1, 35.7 (N*C*H$_3$) ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{23}H_{26}BN_3O_4$, 442.1909; found, 442.1911.

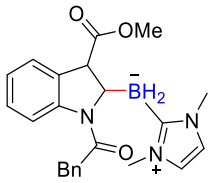
(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(3-(methoxycarbonyl)-1-pivaloylindolin-2-yl)dihydroborate (5c)



White solid (50%, 40.0 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.04-6.95 (m, 2H), 6.61 (s, 2H), 4.80 (brs,

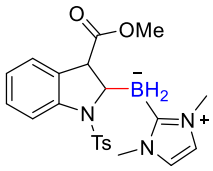
1H), 4.38-4.36 (m, 1H), 3.81 (s, 3H), 3.57 (s, 6H), 1.26 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.9 (*C*OOMe), 172.3 (*C*=O), 145.3, 132.3, 126.7, 125.2, 123.4, 120.6, 118.5, 51.9, 51.5, 40.3, 36.3 (N*C*H$_3$), 28.0 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{20}H_{28}BN_3O_3$, 392.2116; found, 392.2111.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(3-(methoxycarbonyl)-1-(2-phenylacetyl)indolin-2-yl)dihydroborate (5d)



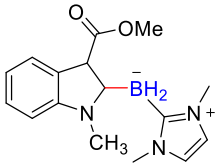
Colorless oil (98%, 78.7 mg, 2.6:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 1H), 7.32-7.19 (m, 6H), 7.12-7.08 (m, 1H), 6.92-6.88 (m, 1H), 6.70 (s, 2H), 4.52 (brs, 1H), 3.82-3.78 (m, 1H), 3.71-3.69 (m, 1H), 3.68 (s, 6H), 3.49 (s, 3H), 3.38-3.34 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.9 (*C*OOMe), 168.6 (*C*=O), 142.6, 135.8, 131.4, 129.6, 128.4, 128.2, 126.6, 125.0, 123.5, 121.0, 117.8, 53.0, 52.1, 41.6, 36.2 (N*C*H$_3$) ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{23}H_{26}BN_3O_3$, 426.1959; found, 426.1956.

1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(3-(methoxycarbonyl)-1-tosylindolin-2-yl)dihydroborate (5e)



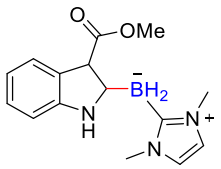
Colorless oil (99%, 86.8 mg, 2.2:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.29-7.21 (m, 2H), 7.14-7.09 (m, 3H), 6.90 (s, 2H), 4.22 (brs, 1H), 3.81 (s, 6H), 3.74 (s, 4H), 3.72-3.70 (m, 1H), 2.34 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5 (*C*OOMe), 143.3, 142.4, 135.9, 134.6, 129.4, 127.7, 126.8, 126.7, 126.1, 120.6, 118.8, 51.5, 50.8, 36.2 (N*C*H$_3$), 21.6 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{22}H_{26}BSN_3O_4$, 462.1629; found, 462.1632.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(3-(methoxycarbonyl)-1-methylindolin-2-yl)dihydroborate (5f)



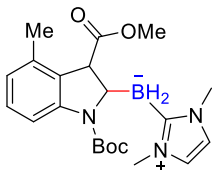
White solid (84%, 50.4 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.07-7.03 (m, 1H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.81 (s, 2H), 6.59-6.55 (m, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 3.81 (s, 6H), 3.60 (s, 3H), 3.58-3.57 (m, 1H), 3.09-3.03 (m, 1H), 2.80 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.6 (*C*OOMe), 155.7, 129.6, 127.9, 122.9, 120.7, 116.9, 108.0, 54.4, 51.7, 36.3 (N*C*H$_3$), 35.3 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{16}H_{22}BN_3O_2$, 322.1697; found, 322.1705.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(3-(methoxycarbonyl)indolin-2-yl)dihydroborate (5g)



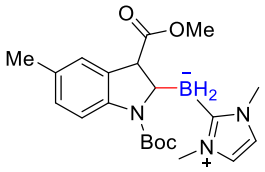
Colorless oil (58%, 30.1 mg, 1.3:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (brs, 1H), 8.11 (d, *J* = 6.9 Hz, 1H), 7.31-7.26 (m, 1H), 7.18-7.06 (m, 2H), 6.80 and 6.78 (a pair of s, 2H), 3.88-3.86 (m, 2H), 3.66-3.53 (m, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7 (*C*OOMe), 141.6, 128.5, 121.4 and 121.2 (a pair of s, *C*H), 120.9 and 120.8 (a pair of s, *C*H), 120.3, 113.0, 110.1, 50.7, 50.3, 36.4 and 36.0 (a pair of s, N*C*H$_3$) ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{16}H_{20}BN_3O_2$, 308.1541; found, 308.1540.

(1-(*tert*-Butoxycarbonyl)-3-(methoxycarbonyl)-4-methylindolin-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (5h)



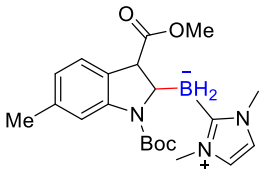
White solid (98%, 78.3 mg, 5.5:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.51 (m, 1H), 7.03-6.99 (m, 1H), 6.70 (s, 2H), 6.69-6.68 (m, 1H), 4.17 (brs, 1H), 3.67-3.66 (m, 1H), 3.61 (s, 6H), 3.55 (s, 3H), 2.20 (s, 3H), 1.29 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.8 (*C*OOMe), 135.4, 130.8, 128.0, 123.5, 120.2, 113.6, 51.8, 36.0 (N*C*H$_3$), 28.5, 18.8 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{21}H_{30}BN_3O_4$, 422.2222; found, 422.2220.

(1-(*tert*-Butoxycarbonyl)-3-(methoxycarbonyl)-5-methylindolin-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (5i)



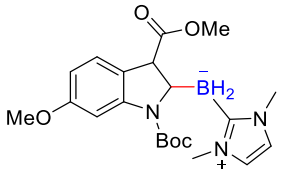
White solid (99%, 79.3 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.13 (s, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.78 (s, 2H), 4.33 (brs, 1H), 3.72-3.69 (m, 1H), 3.68 (s, 6H), 3.63 (s, 3H), 2.29 (s, 3H), 1.32 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.8 (*C*OOMe), 131.9, 131.3, 128.5, 126.6, 120.2, 115.7, 52.7, 51.9, 35.9 (N*C*H$_3$), 28.4, 21.0 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{21}H_{30}BN_3O_4$, 422.2222; found, 422.2218.

(1-(*tert*-Butoxycarbonyl)-3-(methoxycarbonyl)-6-methylindolin-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (5j)



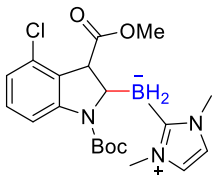
White solid (97%, 77.1 mg, 49:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.73 (s, 2H), 6.70-6.67 (m, 1H), 4.26 (brs, 1H), 3.65-3.63 (m, 1H), 3.63 (s, 6H), 3.55 (s, 3H), 2.24 (s, 3H), 1.24 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.8 (*C*OOMe), 137.8, 129.0, 125.5, 122.8, 120.3, 120.0, 116.9, 52.5, 51.9, 36.0 (N*C*H$_3$), 28.4, 21.9 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{21}H_{30}BN_3O_4$, 422.2222; found, 422.2219.

(1-(*tert*-Butoxycarbonyl)-6-methoxy-3-(methoxycarbonyl)indolin-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (5k)



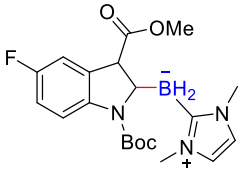
White solid (98%, 81.4 mg, 9:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (m, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 6.80 (s, 2H), 6.50-6.47 (m, 1H), 4.36 (brs, 1H), 3.78 (s, 3H), 3.70 (s, 6H), 3.69-3.67 (m, 1H), 3.63 (s, 3H), 1.34 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.0 (*C*OOMe), 160.0 (*C*=O), 143.1, 128.3, 126.2, 124.1, 120.2, 102.5, 59.3, 55.4, 51.9, 36.0 (N*C*H$_3$), 28.4 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{21}H_{30}BN_3O_5$, 438.2171; found, 438.2172.

(1-(*tert*-Butoxycarbonyl)-4-chloro-3-(methoxycarbonyl)indolin-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (5l)



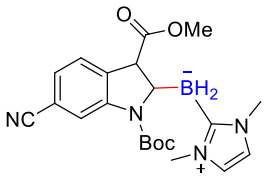
Colorless oil (99%, 84.0 mg, 4.5:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.32 (m, 1H), 7.13-7.09 (m, 1H), 6.91-6.89 (m, 1H), 6.79 (s, 2H), 4.18 (brs, 1H), 3.86-3.84 (m, 1H), 3.70 (s, 6H), 3.66 (s, 3H), 1.35 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1 (*C*OOMe), 152.0 (*C*=O), 144.8, 132.0, 130.4, 129.0, 123.0, 120.4, 114.5, 51.6, 51.5, 36.1 (N*C*H$_3$), 28.4 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{20}H_{27}BClN_3O_4$, 442.1675; found, 442.1682.

(1-(*tert*-Butoxycarbonyl)-5-fluoro-3-(methoxycarbonyl)indolin-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (5m)



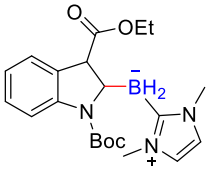
White solid (93%, 75.0 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.88-6.85 (m, 1H), 6.81 (s, 2H), 4.38 (brs, 1H), 3.72-3.70 (m, 1H), 3.69 (s, 6H), 3.66 (s, 3H), 1.32 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1 (*C*OOMe), 158.4 (d, *J* = 239.0 Hz), 133.6 (d, *J* = 8.3 Hz), 120.3, 116.4 (d, *J* = 4.4 Hz), 114.2 (d, *J* = 22.6 Hz), 113.4 (d, *J* = 24.2 Hz), 52.7, 52.1, 36.0 (N*C*H_3), 28.4 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.0 and -122.8 (a pair of s, F). **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{20}H_{27}BFN_3O_4$, 426.1971; found, 426.1967.

(1-(tert-butoxycarbonyl)-6-cyano-3-(methoxycarbonyl)indolin-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (5n)



White solid (90%, 73.5 mg, 49:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03-7.82 (m, 1H), 7.41-7.39 (m, 1H), 7.28-7.22 (m, 1H), 6.85 (s, 2H), 4.40 (brs, 1H), 3.82-3.80 (m, 1H), 3.70 (s, 6H), 3.66 (s, 3H), 1.34 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5 (*C*OOMe), 137.4, 128.3, 126.9, 126.1, 120.4, 119.7, 118.9, 111.6, 52.9, 52.3, 36.0 (N*C*H_3), 28.3 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{21}H_{27}BN_4O_4$, 433.2018; found, 433.2021.

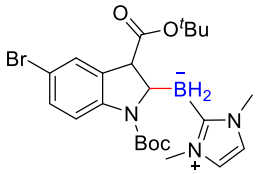
(1-(*tert*-Butoxycarbonyl)-3-(ethoxycarbonyl)indolin-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (5o)



White solid (99%, 79.1 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76-7.55 (m, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.18-7.14 (m, 1H), 6.94-6.90 (m, 1H), 6.79 (s, 2H), 4.37 (brs, 1H), 4.15-4.04 (m, 2H), 3.75-3.72 (m, 1H), 3.69 (s, 6H), 1.33 (s, 9H), 1.21 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1 (*C*OOMe), 132.1,

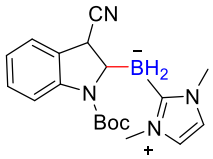
127.9, 125.9, 121.9, 120.3, 120.0, 116.0, 60.5, 52.9, 36.0 (N*C*H$_3$), 28.4, 14.3 ppm. **HR MS-ESI** (m/z): [M+Na]$^+$ calcd for $C_{21}H_{30}BN_3O_4$, 422.2222; found, 422.222.

(5-Bromo-1,3-bis(tert-butoxycarbonyl)indolin-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (5p)



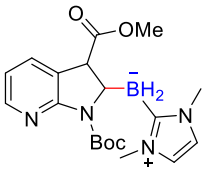
Colorless oil (99%, 100.2 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.42-7.41 (m, 1H), 7.28-7.22 (m, 1H), 6.81 (s, 2H), 4.35-4.30 (m, 2H), 3.69 and 3.66 (a pair of s, 6H), 1.56 (s, 9H), 1.40 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4 (*C*OOMe), 134.8, 130.5, 129.7, 128.7, 120.3, 117.2, 113.8, 80.4 and 80.3 (a pair of s, *C*), 60.4, 35.8 (N*C*H$_3$), 28.4, 28.0 ppm. **HRMS-ESI** (m/z): [M+Na]$^+$ calcd for $C_{23}H_{33}BBrN_3O_4$, 528.1640; found, 528.1647.

(1-(*tert*-Butoxycarbonyl)-3-cyanoindolin-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (5q)



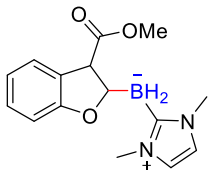
White solid (89%, 62.5 mg, 3.5:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.41 (m, 1H), 7.25-7.13 (m, 2H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.75 (s, 2H), 4.21 (brs, 1H), 3.80-3.78 (m, 1H), 3.60 (s, 6H), 1.26 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0 (*C*=O), 129.1, 128.4, 125.7, 122.6, 122.1, 120.5, 116.3, 79.8, 36.4, 36.0 (N*C*H$_3$), 28.4 ppm. **HRMS-ESI** (m/z): [M+Na]$^+$ calcd for $C_{19}H_{25}BN_4O_2$, 375.1963; found, 375.1959.

(1-(*tert*-Butoxycarbonyl)-3-(methoxycarbonyl)-2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridin-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (5r)



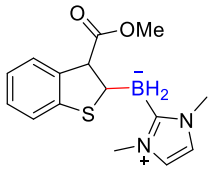
Colorless oil (61%, 47.4 mg, single diastereomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 6.9 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 6.85-6.82 (m, 1H), 6.77 (s, 2H), 4.28 (brs, 1H), 3.74-3.72 (m, 1H), 3.64 (s, 6H), 3.56 (s, 3H), 1.22 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.7 (*C*OOMe), 156.5 (*C*=O), 151.5, 147.7, 134.0, 126.0, 120.4, 117.4, 79.3, 52.1, 50.8, 36.2 (N*C*H$_3$), 28.2 ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{19}H_{27}BN_4O_4$, 409.2018; found, 409.2015.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(3-(methoxycarbonyl)-2,3-dihydrobenzofuran-2-yl)dihydroborate (5s)



White solid (62%, 35.7 mg, 1.6:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 7.4 Hz, 1H), 7.04-7.00 (m, 1H), 6.77 (s, 2H), 6.73-6.70 (m, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 4.59 (brs, 1H), 4.15-4.14 (m, 1H), 3.73 (s, 6H), 3.60 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1 (*C*OOMe), 162.5, 128.7, 128.5, 125.4, 120.7, 119.4, 109.4, 53.3, 51.3, 36.5 (N*C*H$_3$) ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{15}H_{19}BN_2O_3$, 309.1381; found, 309.1388.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(3-(methoxycarbonyl)-2,3-dihydrobenzo[*b*]thiophen-2-yl)dihydroborate (5t)



Colorless oil (85%, 51.1 mg, 2.1:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.8 Hz, 1H), 7.06-7.00 (m, 2H), 6.96-6.92 (m, 1H), 6.80 (s, 2H), 3.91 (brs, 1H), 3.79-3.77 (m, 1H), 3.74 (s, 6H), 3.67 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.8 (*C*OOMe), 139.5, 138.5, 131.1, 130.0, 127.0, 122.7, 121.6, 51.8, 48.9, 36.8 (N*C*H$_3$) ppm. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{15}H_{19}BN_2O_2S$, 325.1153; found, 325.1157.

7. References

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8. Crystal Data of Products *cis*-3z and *trans*-3z

Table S9 Crystal data and structure refinement for *cis*-**3z**.

Empirical formula	$C_{22}H_{23}BN_4O_2$
Formula weight	386.25
Temperature	193.00 K
Crystal system	triclinic
Space group	P-1
a/Å	9.5689(4)
b/Å	9.6362(4)
c/Å	10.9620(5)
α/°	97
β/°	90
γ/°	93
Volume/Å^3	1001.5(7)
Z	2
ρ_{calc}g/cm^3	1.281
μ/mm^{-1}	0.083
F(000)	408.0
Crystal size/mm^3	0.12 × 0.11 × 0.10
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.74 to 55.16
Index ranges	-12 <= h <= 12, -12 <= k <= 12, -14 <= l <= 10
Reflections collected	9586
Independent reflections	4593 [R_{int} = 0.0297, R_{sigma} = 0.0469]
Data / restraints / parameters	4593/0/272
Goodness-of-fit on F^2	1.022
Final *R* indices [I >= 2sigma (I)]	R_1 = 0.0472, wR_2 = 0.1110
Final *R* indices [all data]	R_1 = 0.0685, wR_2 = 0.1221
Largest diff. peak and hole/ e Å^{-3}	0.24 and -0.19
CCDC	2290532

Table S10 Crystal data and structure refinement for *trans*-**3z**.

Empirical formula	$C_{22}H_{21}BN_4O_2$
Formula weight	384.24
Temperature	249.00 K
Crystal system	triclinic
Space group	P-1
a/Å	7.2850(10)
b/Å	10.3394(14)
c/Å	15.038(2)
α/°	71.988(4)
β/°	76.430(4)
γ/°	75.074(4)
Volume/Å^3	1026.0(2)
Z	2
ρ_{calc}g/cm^3	1.244
μ/mm^{-1}	0.081
F(000)	404.0
Crystal size/mm^3	0.4 × 0.3 × 0.26
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.228 to 50.836
Index ranges	-8 <= h <= 8, -12 <= k <= 12, -18 <= l <= 18
Reflections collected	27513
Independent reflections	3746 [R_{int} = 0.0272, R_{sigma} = 0.0158]
Data / restraints / parameters	3746/0/264
Goodness-of-fit on F^2	1.060
Final R indices [I >= 2sigma (I)]	R_1 = 0.0512, wR_2 = 0.1554
Final R indices [all data]	R_1 = 0.0561, wR_2 = 0.1617
Largest diff. peak and hole/ e Å^{-3}	0.64 and -0.24
CCDC	2290538

Table S11 Crystal data and structure refinement for *trans*-**5i**.

Empirical formula	$C_{21}H_{30}BN_3O_4$
Formula weight	399.29
Temperature	193.00 K
Crystal system	orthorhombic
Space group	Pbca
a/Å	15.5158(5)
b/Å	14.5905(4)
c/Å	18.9569(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4291.5(2)
Z	8
ρ_{calc}g/cm^3	1.236
μ/mm^{-1}	0.687
F(000)	1712.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	9.33 to 137.118
Index ranges	-18 <= h <= 18, -17 <= k <= 17, -22 <= l <= 22
Reflections collected	93384
Independent reflections	3945 [R_{int} = 0.0460, R_{sigma} = 0.0176]
Data / restraints / parameters	3945/0/277
Goodness-of-fit on F^2	1.041
Final *R* indices [I >= 2sigma (I)]	R_1 = 0.0375, wR_2 = 0.1033
Final *R* indices [all data]	R_1 = 0.0400, wR_2 = 0.1054
Largest diff. peak and hole/ e Å^{-3}	0.25 and -0.21
CCDC	2304719

Table S12 Crystal data and structure refinement for *trans*-**5q**.

Empirical formula	$C_{19}H_{25}BN_4O_2$
Formula weight	352.24
Temperature	193.00 K
Crystal system	monolinic
Space group	$P2_1/c$
a/Å	9.5060(3)
b/Å	10.6586(4)
c/Å	18.9403(7)
α/°	90
β/°	94.531(2)
γ/°	90
Volume/Å^3	1913.05(12)
Z	4
ρ_{calc}g/cm^3	1.223
μ/mm^{-1}	0.641
F(000)	752.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	9.332 to 136.684
Index ranges	-11 <= h <= 11, -12 <= k <= 12, -22 <= l <= 22
Reflections collected	34581
Independent reflections	3508 [R_{int} = 0.0313, R_{sigma} = 0.0222]
Data / restraints / parameters	3508/0/248
Goodness-of-fit on F^2	1.046
Final *R* indices [I >= 2sigma (I)]	R_1 = 0.0344, wR_2 = 0.0936
Final *R* indices [all data]	R_1 = 0.0361, wR_2 = 0.0952
Largest diff. peak and hole/ e Å^{-3}	0.18 and -0.16
CCDC	2304720

9. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra

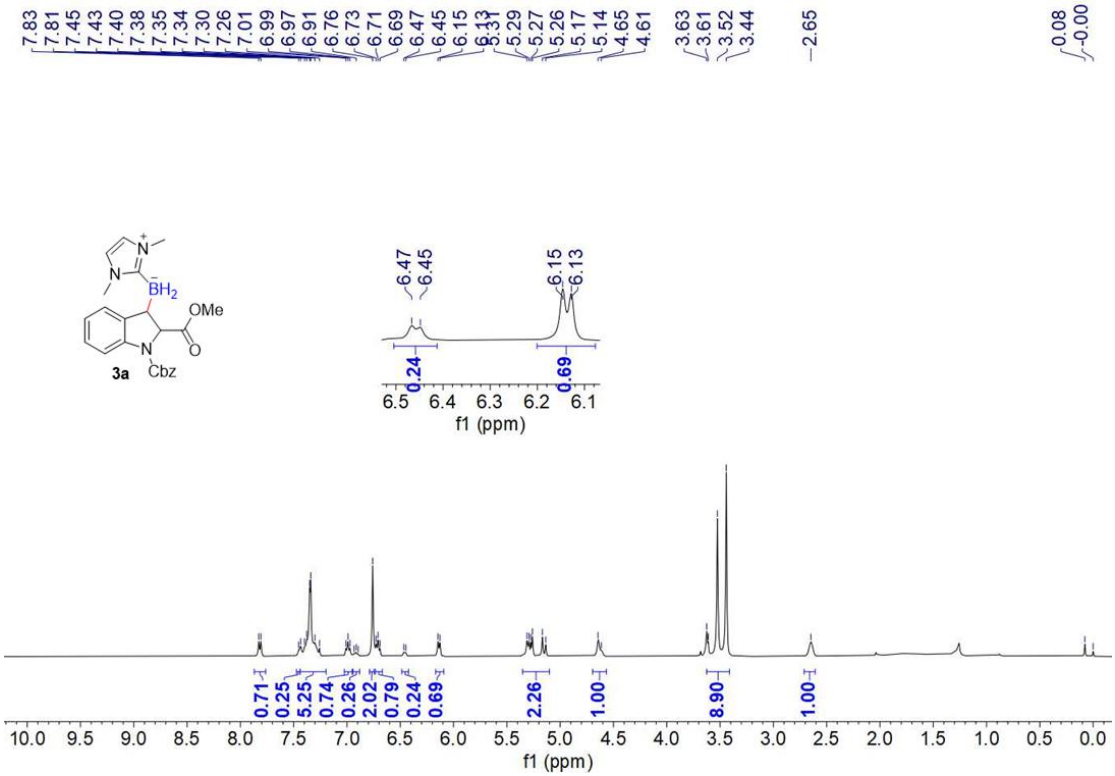

Fig. S3 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3a**.

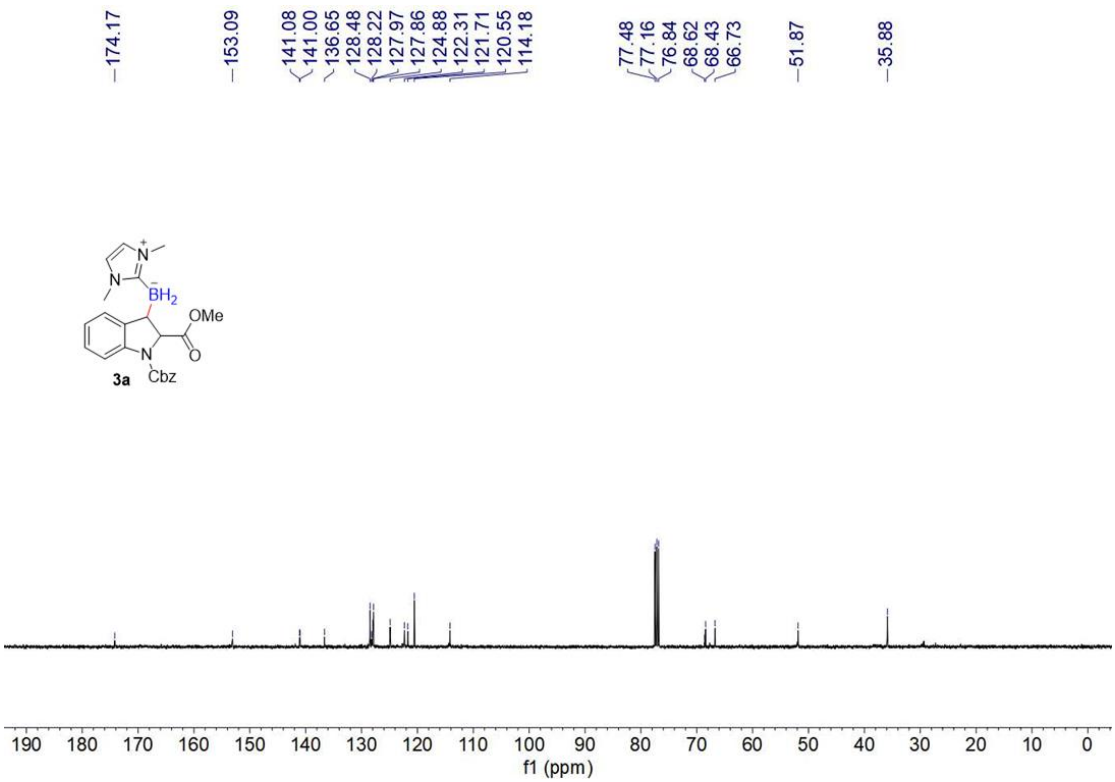

Fig. S4 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3a**.

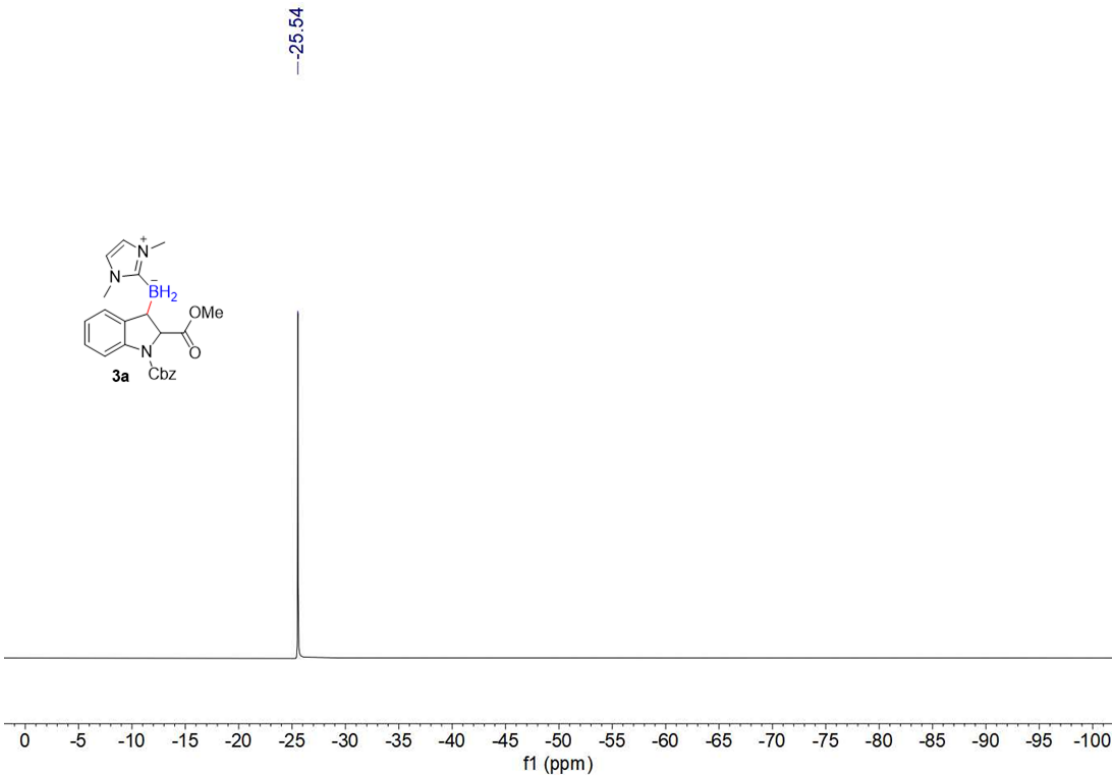

Fig. S5 ^{11}B NMR (128 MHz, $CDCl_3$) spectrum for **3a**.

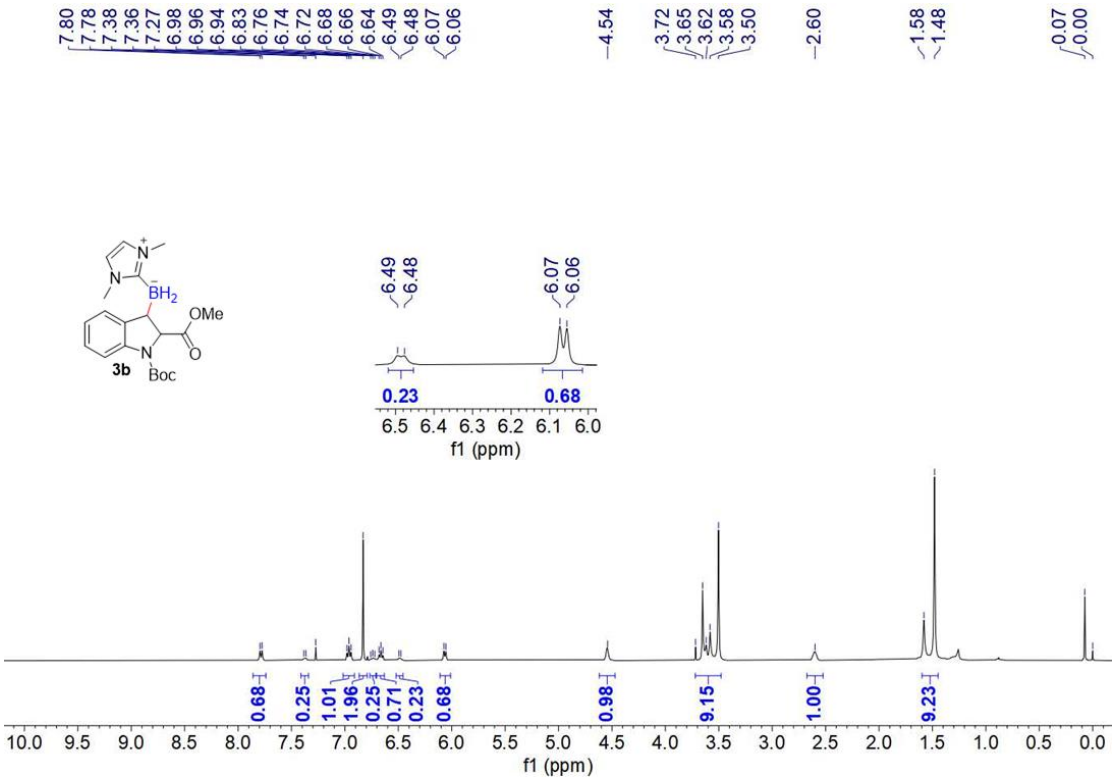

Fig. S6 ^{1}H NMR (100 MHz, $CDCl_3$) spectrum for **3b**.

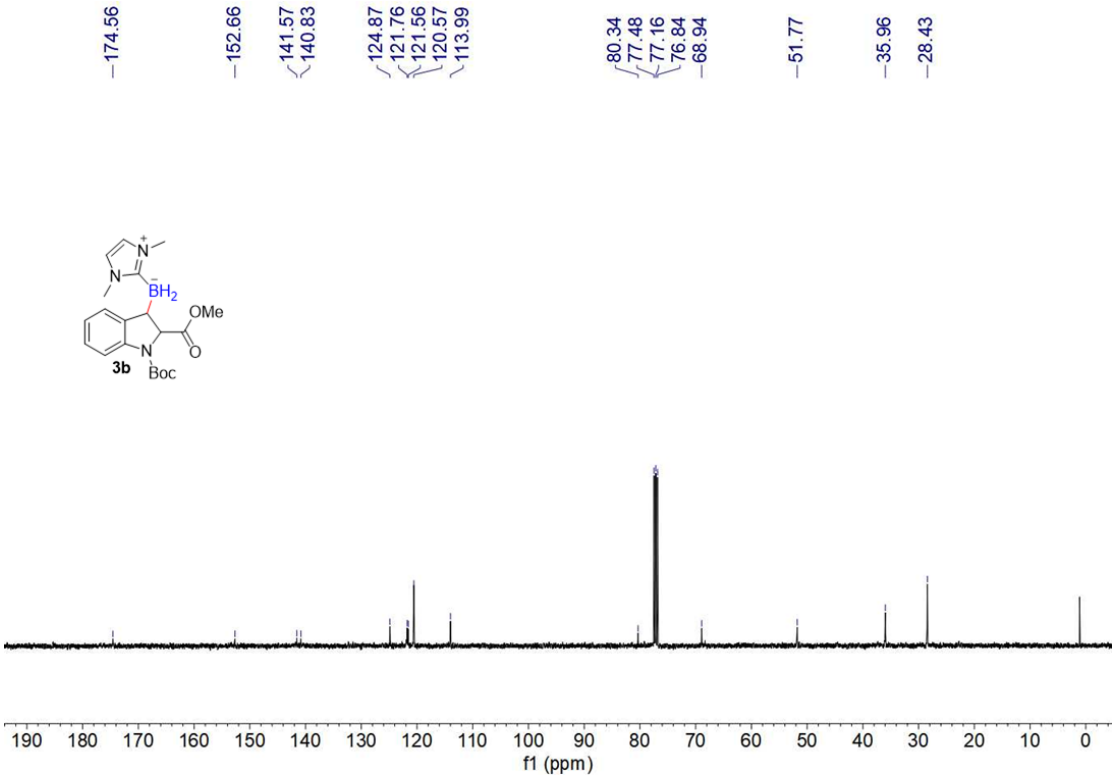

Fig. S7 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3b**.

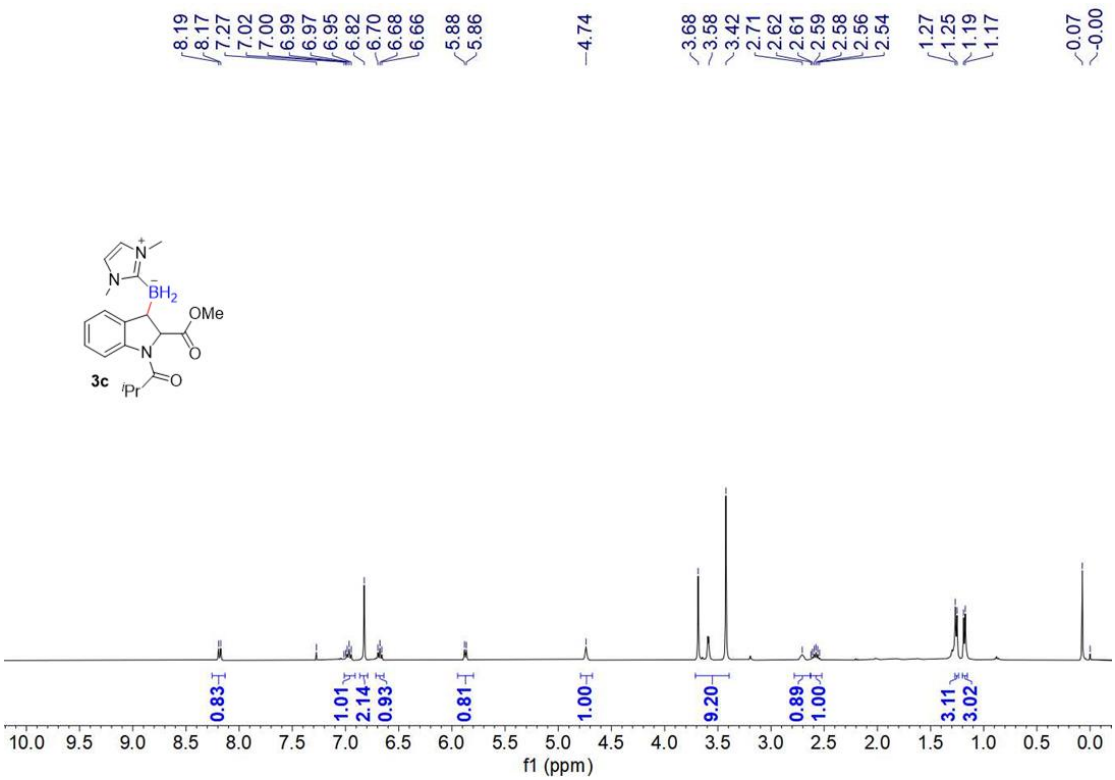

Fig. S8 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3c**.

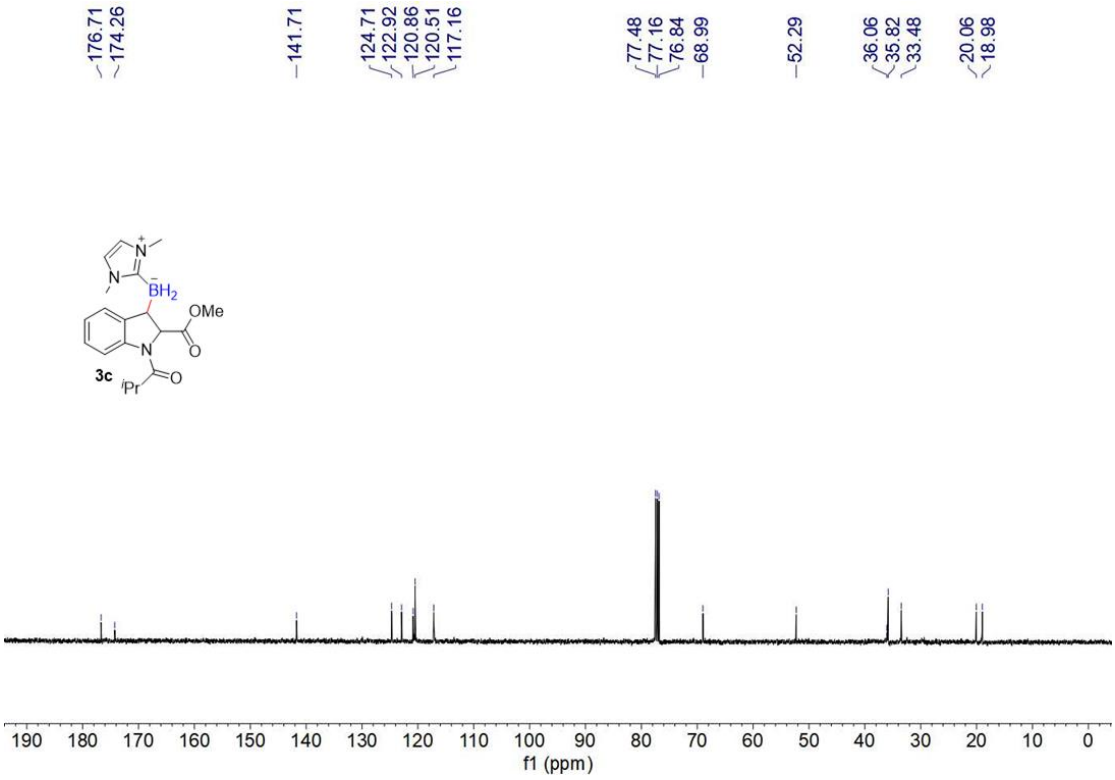

Fig. S9 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3c**.

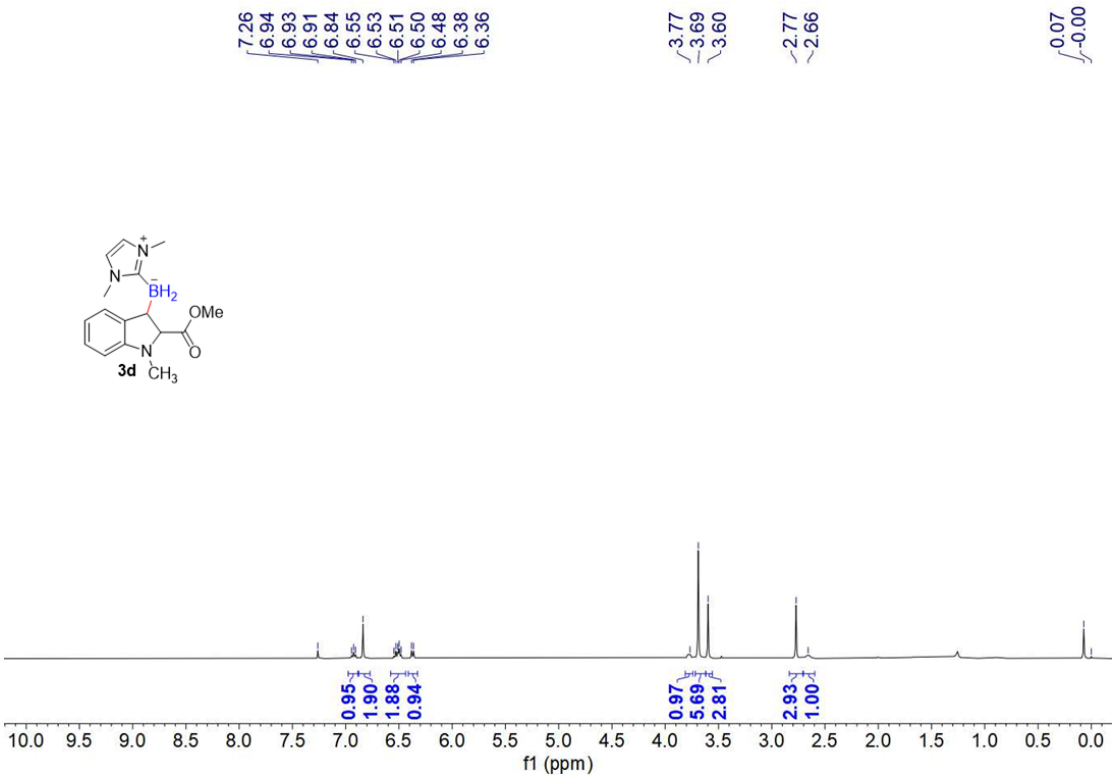

Fig. S10 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3d**.

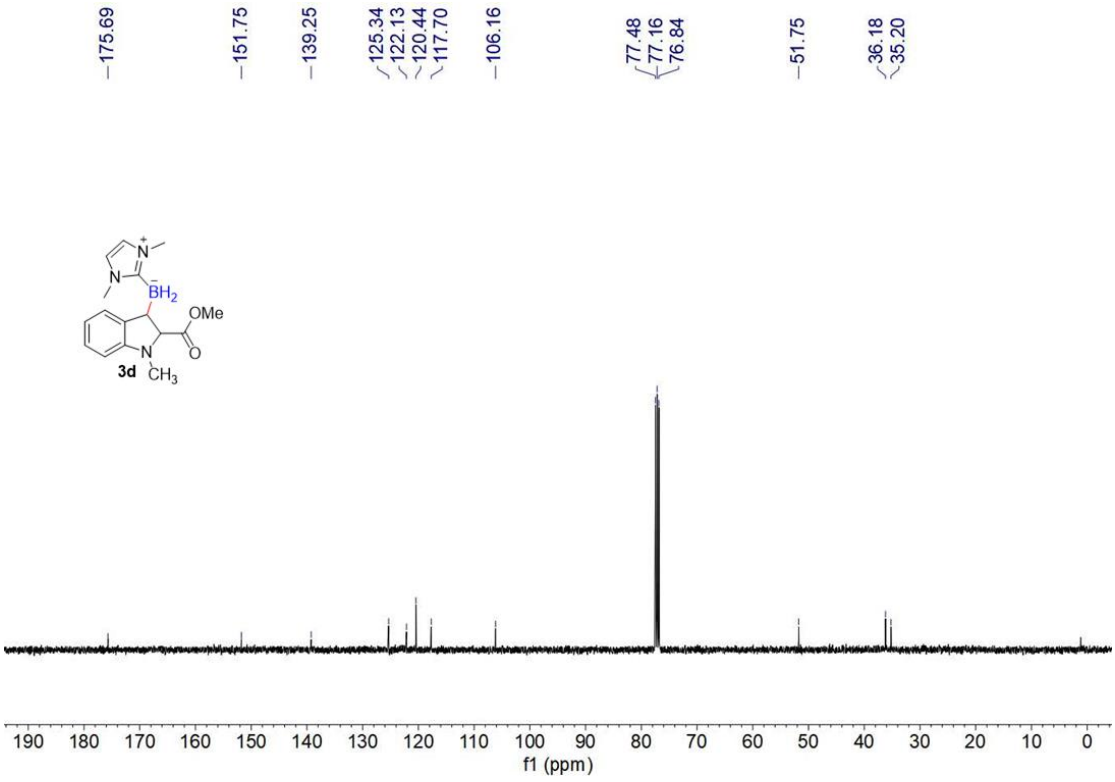

Fig. S11 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3d**.

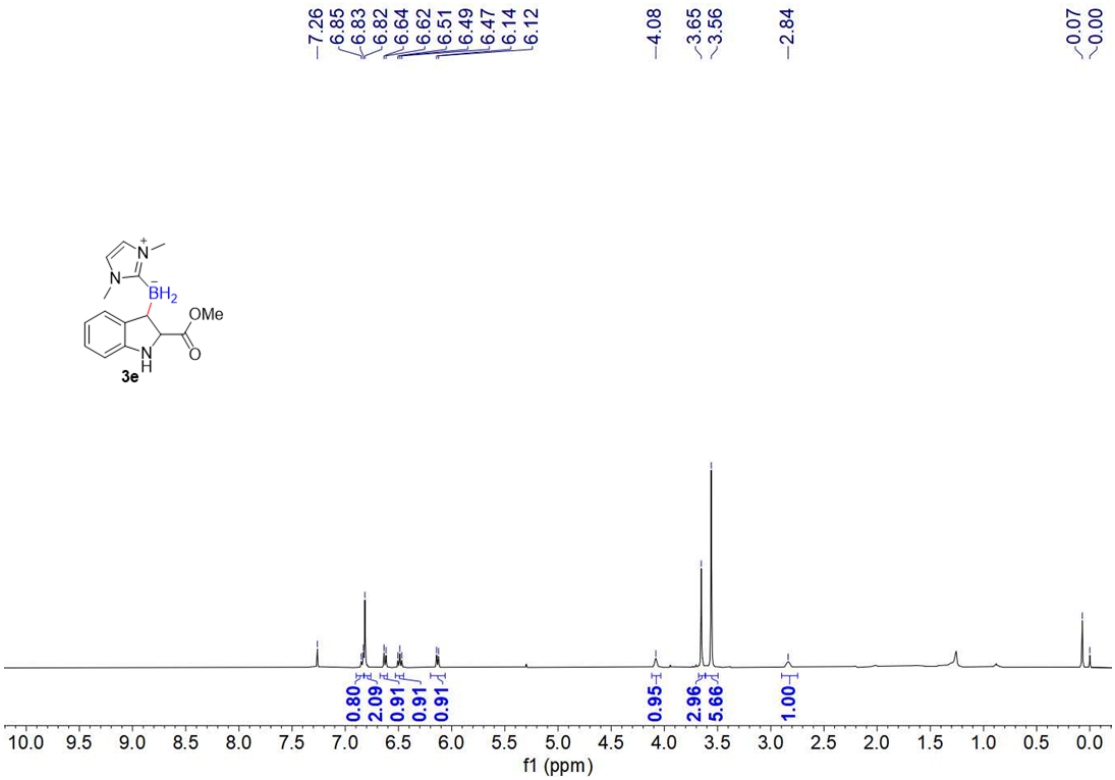

Fig. S12 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3e**.

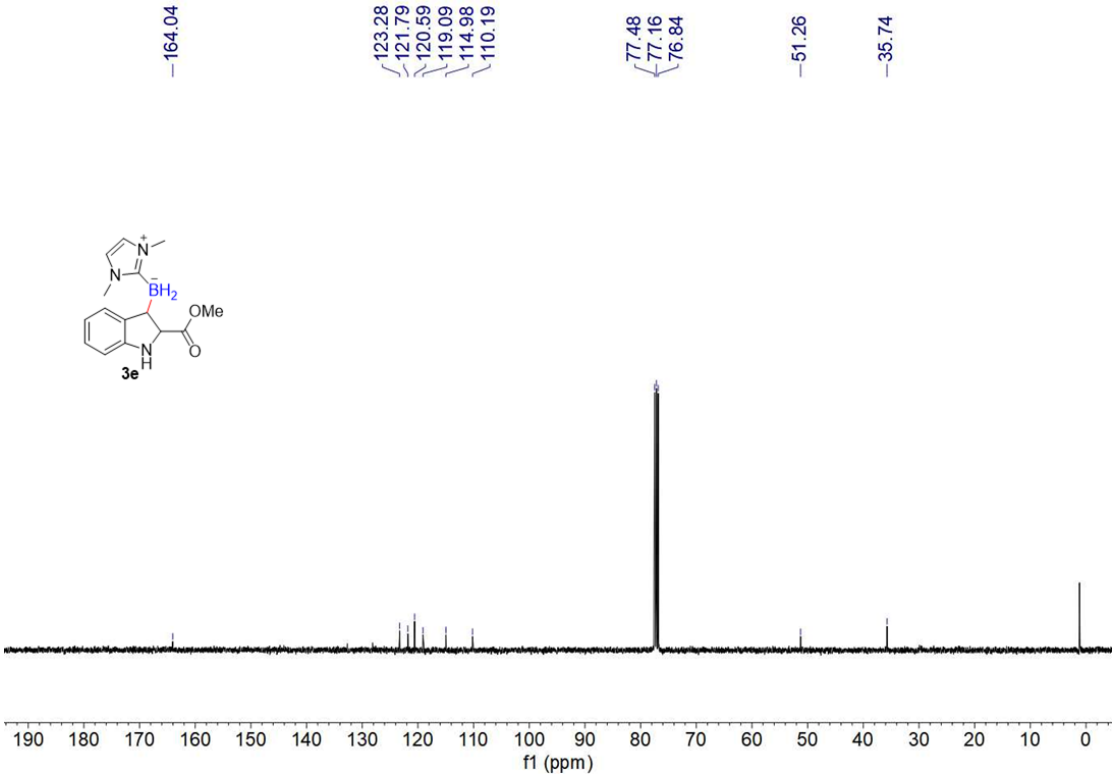

Fig. S13 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3e**.

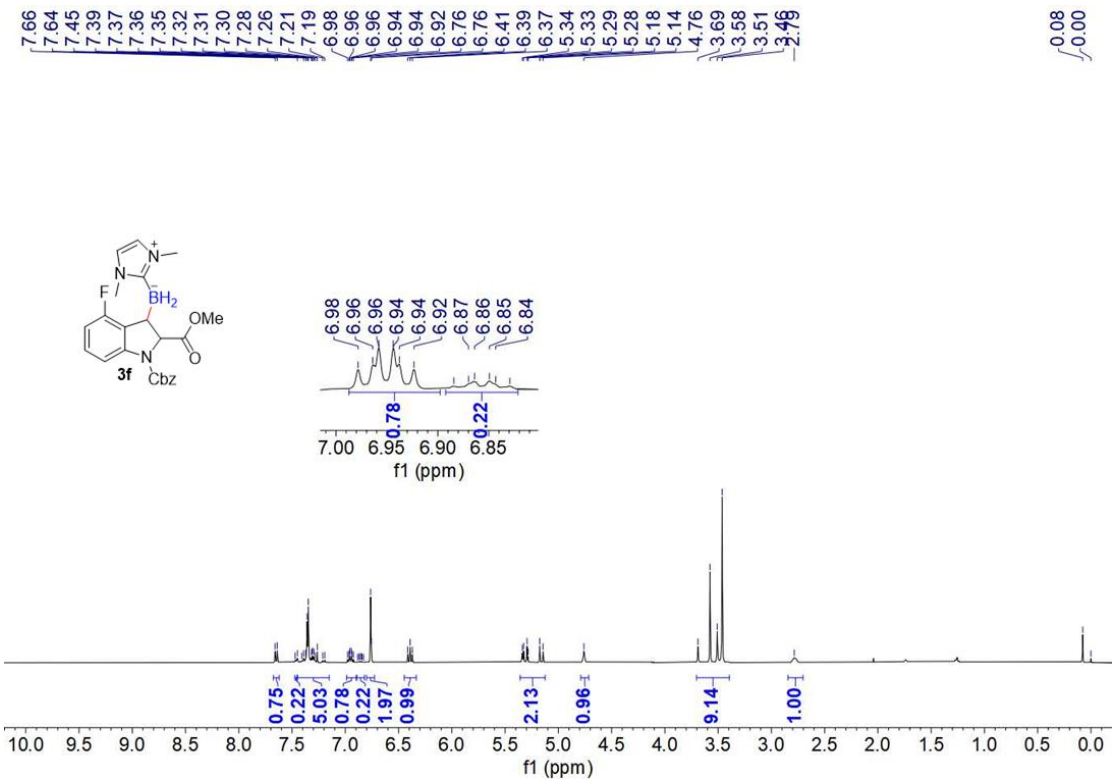

Fig. S14 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3f**.

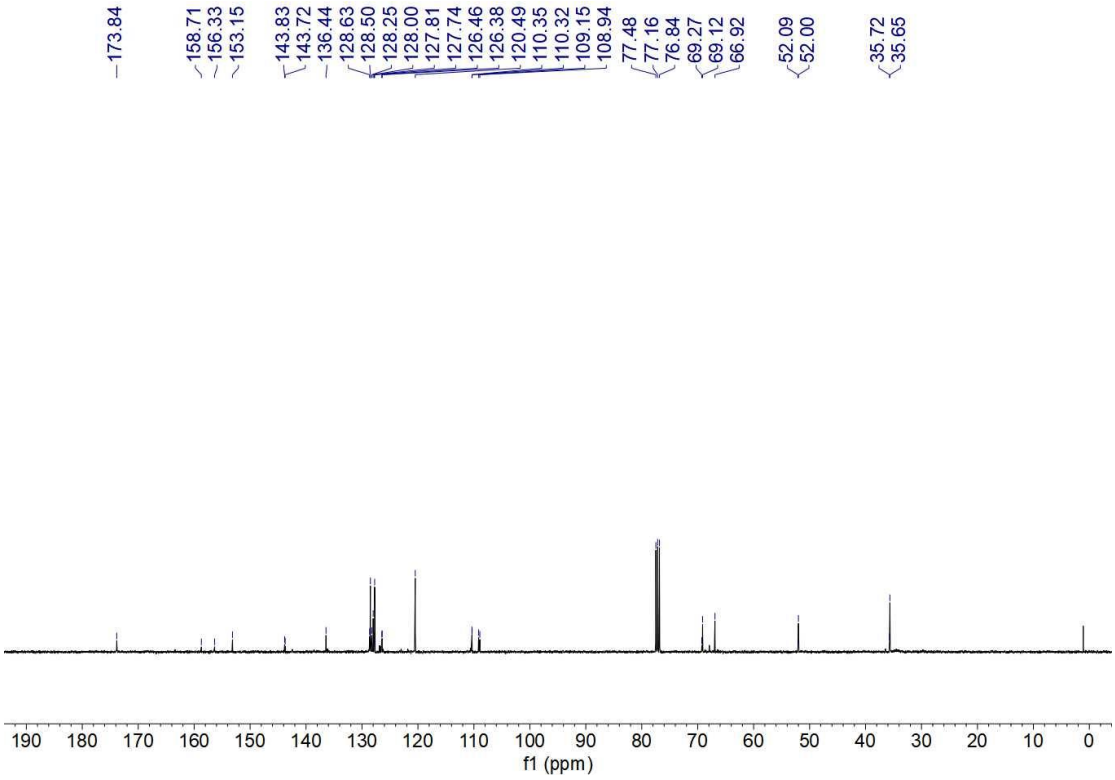

Fig. S15 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3f**.

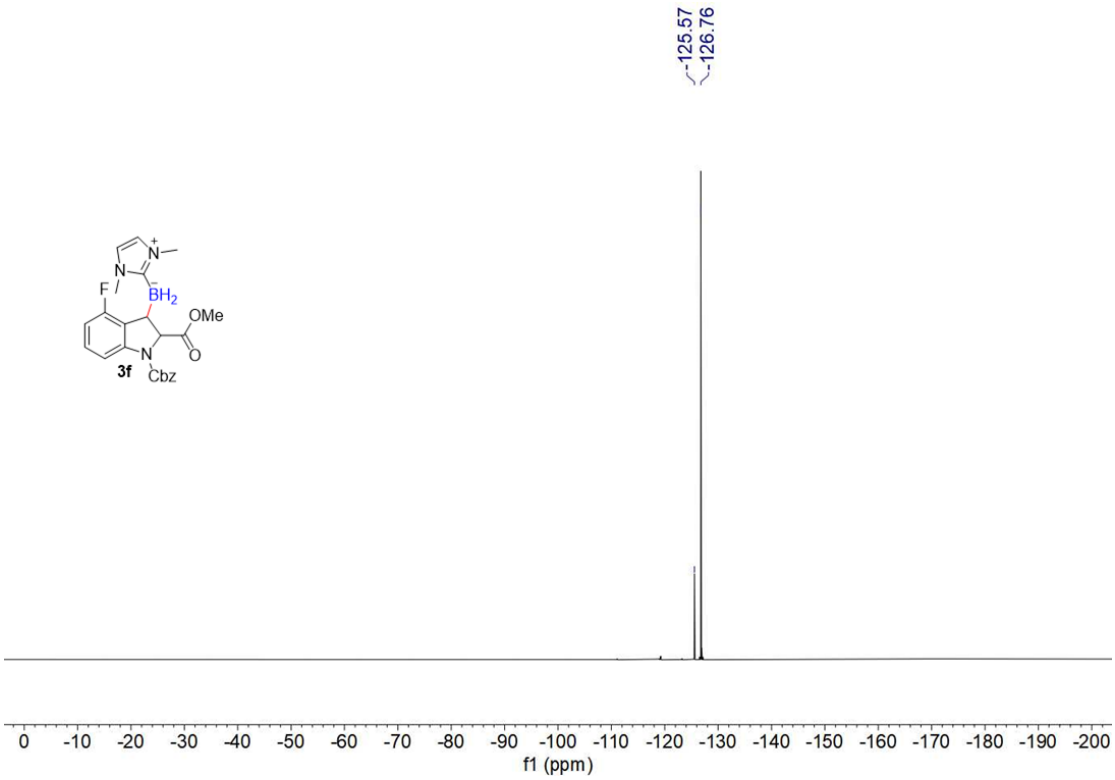

Fig. S16 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **3f**.

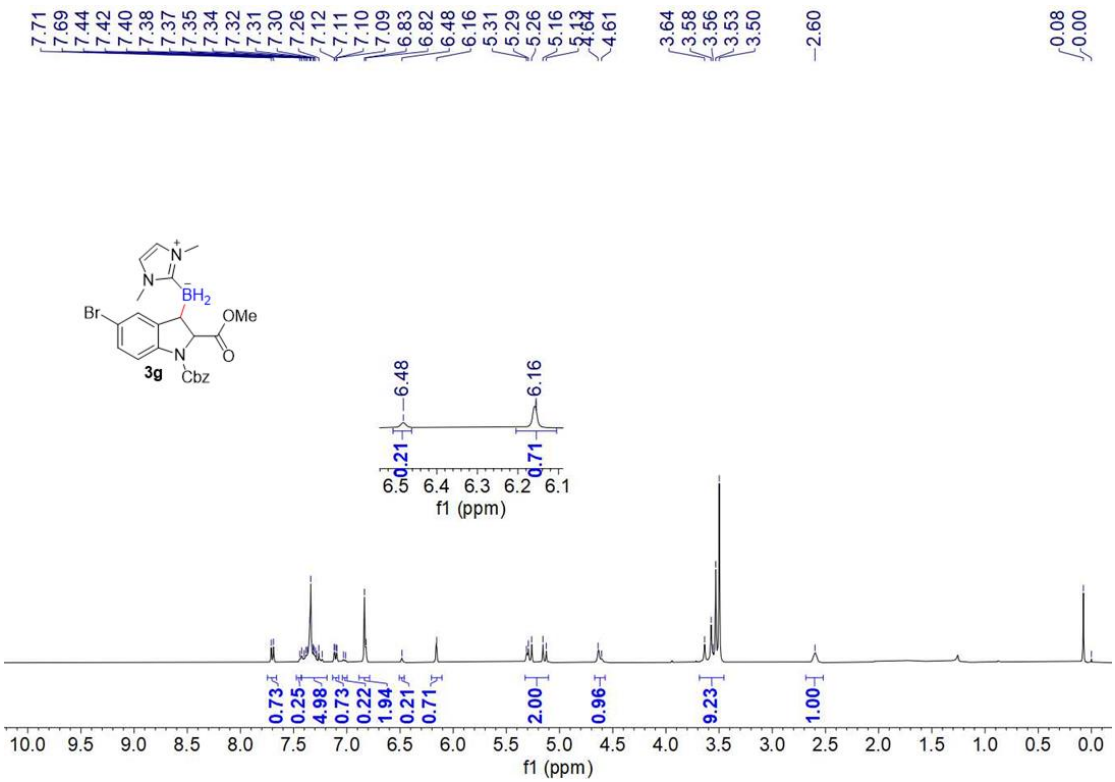

Fig. S17 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3g**.

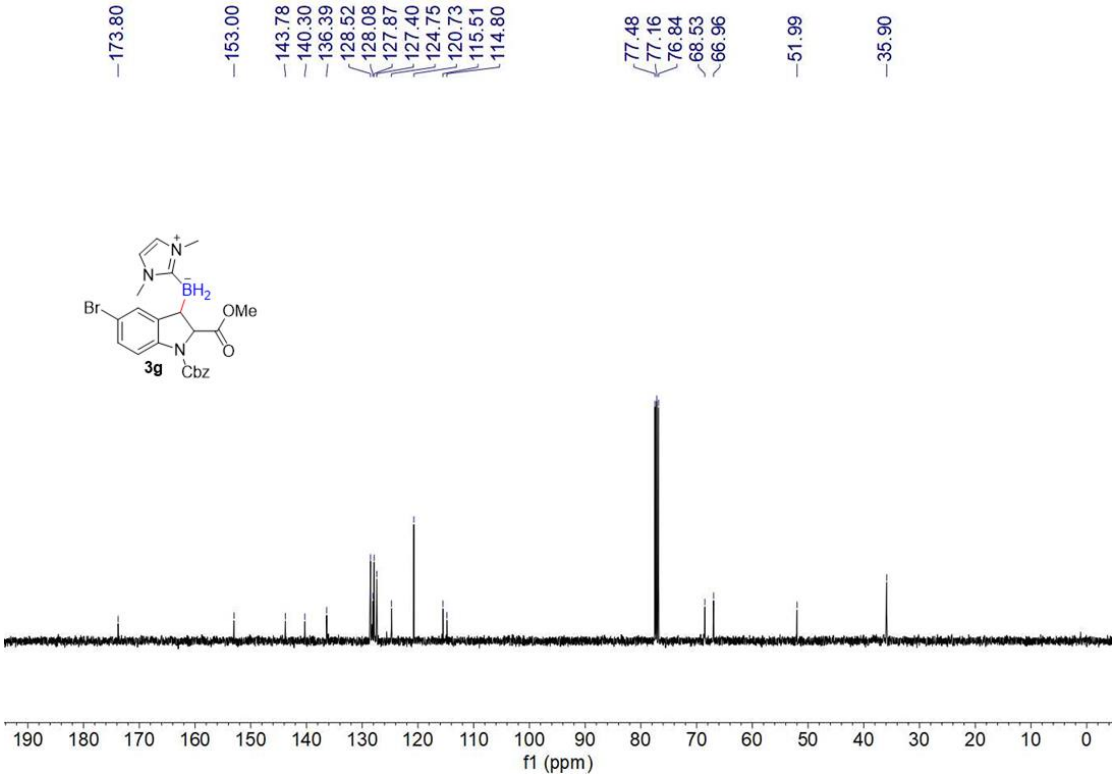

Fig. S18 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3g**.

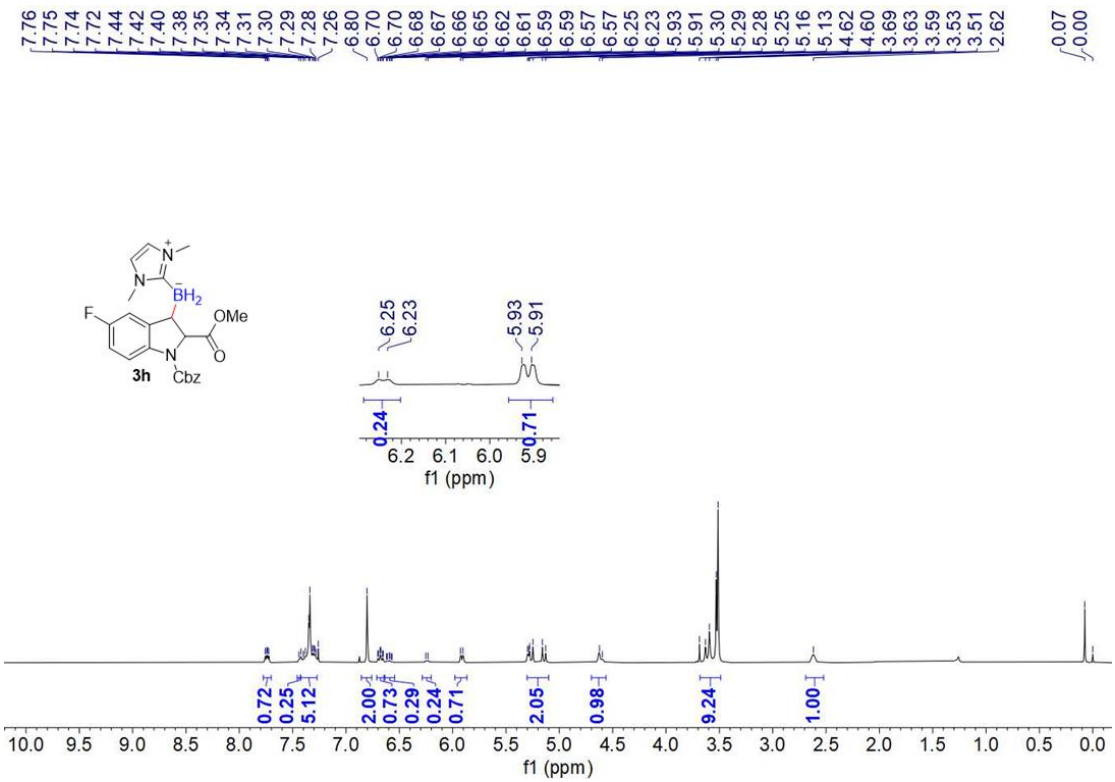

Fig. S19 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3h**.

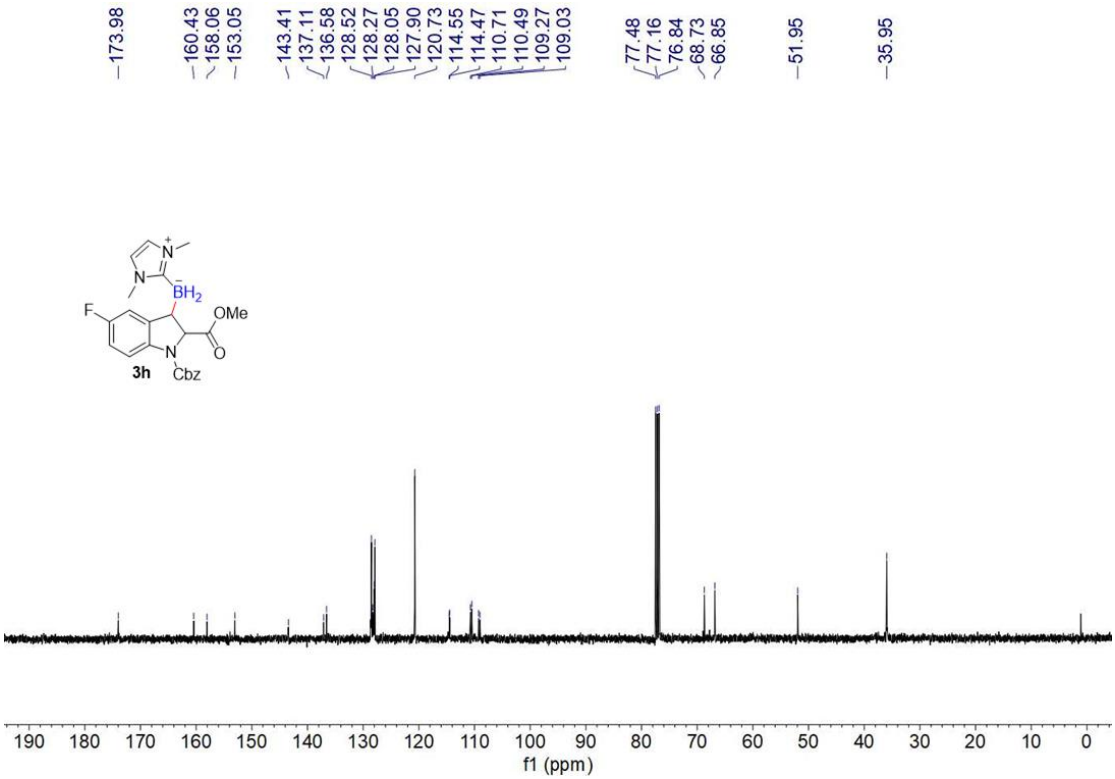

Fig. S20 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3h**.

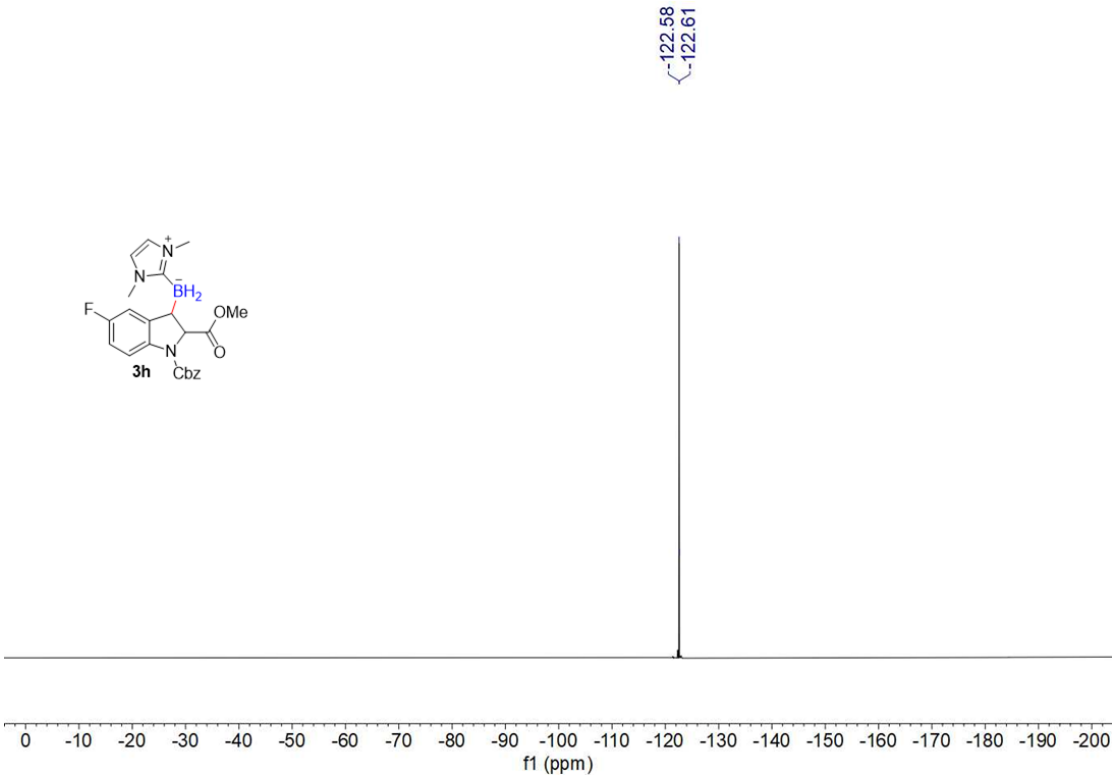

Fig. S21 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **3h**.

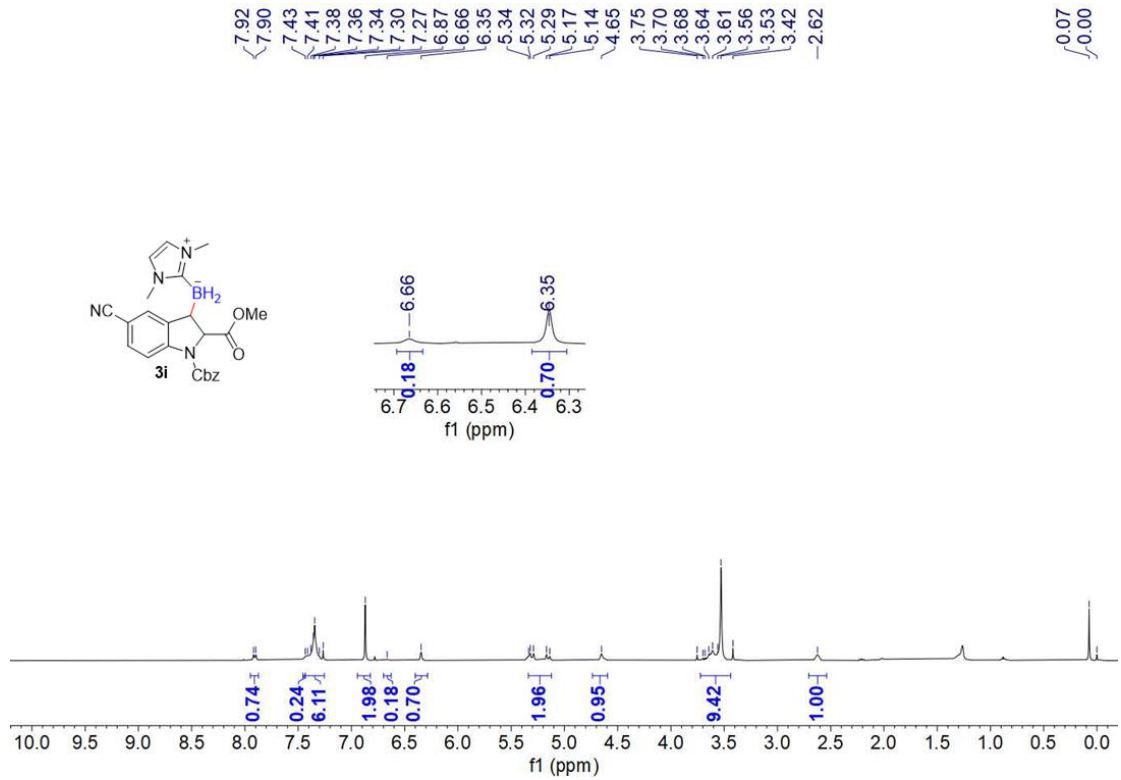

Fig. S22 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3i**.

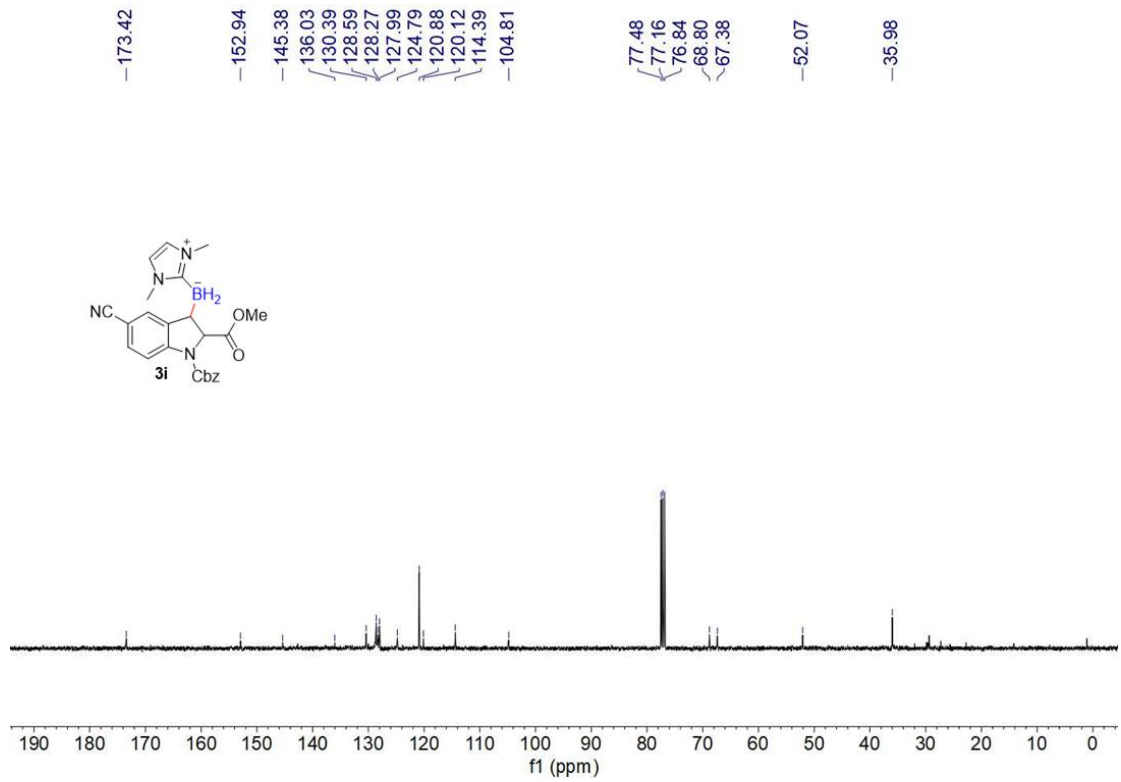

Fig. S23 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3i**

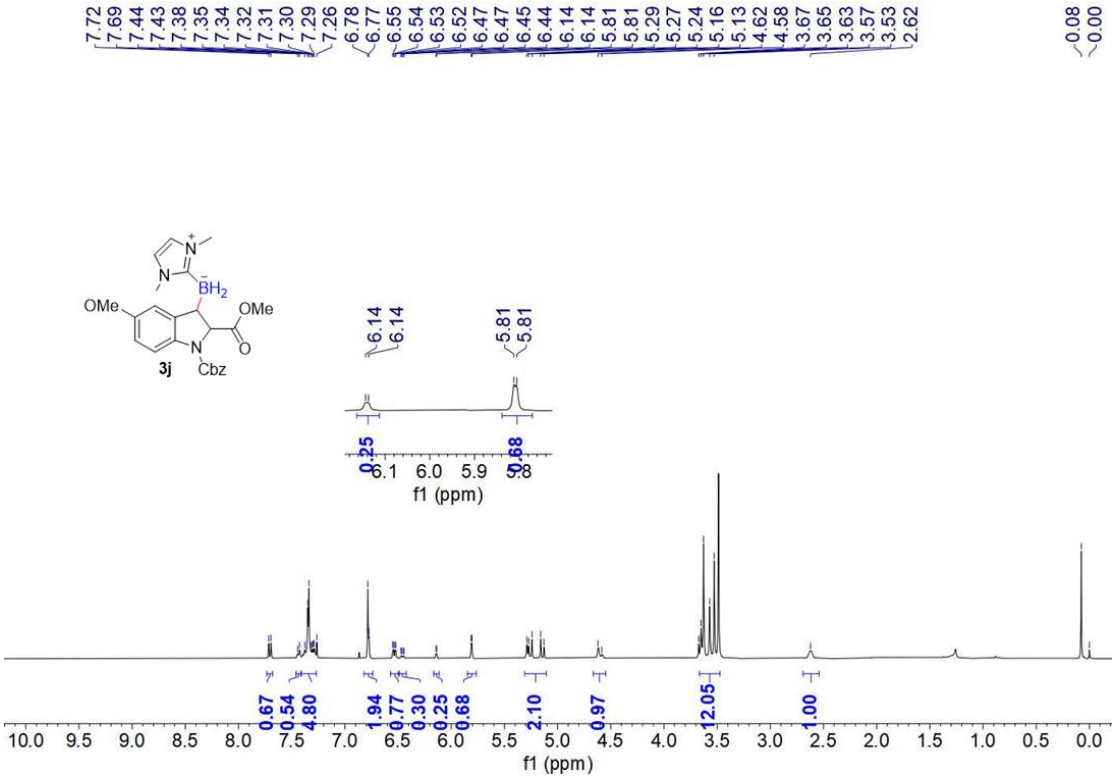

Fig. S24 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3j**.

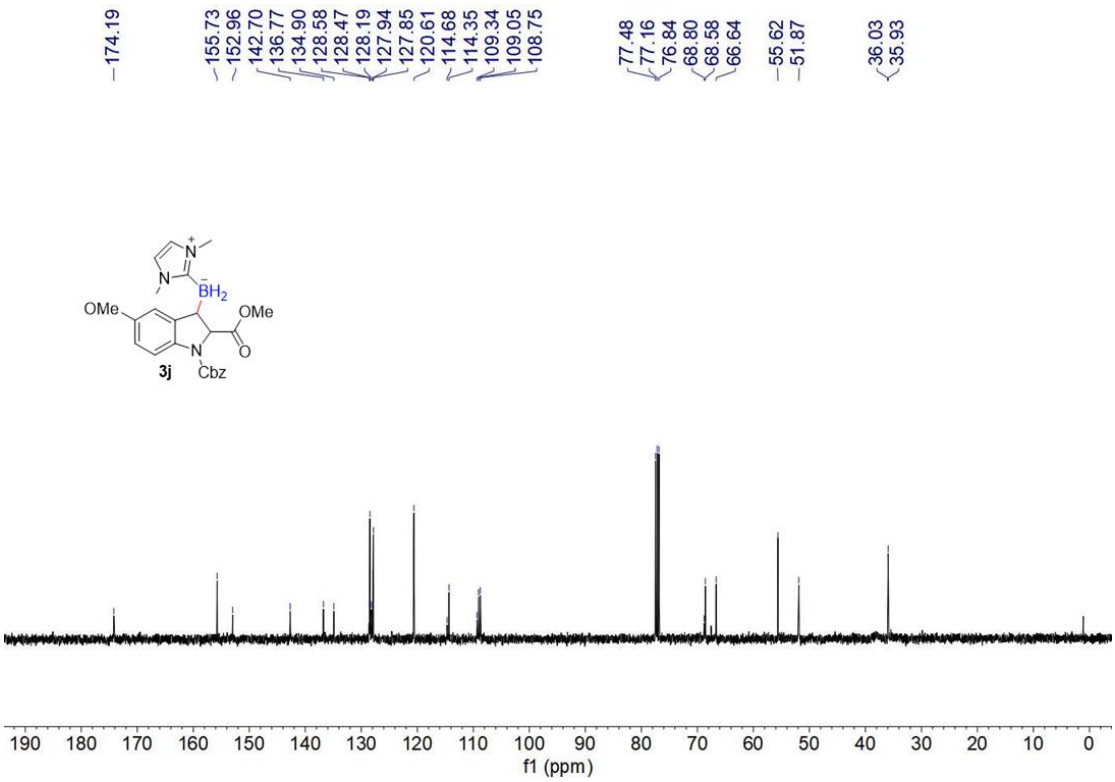

Fig. S25 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3j**.

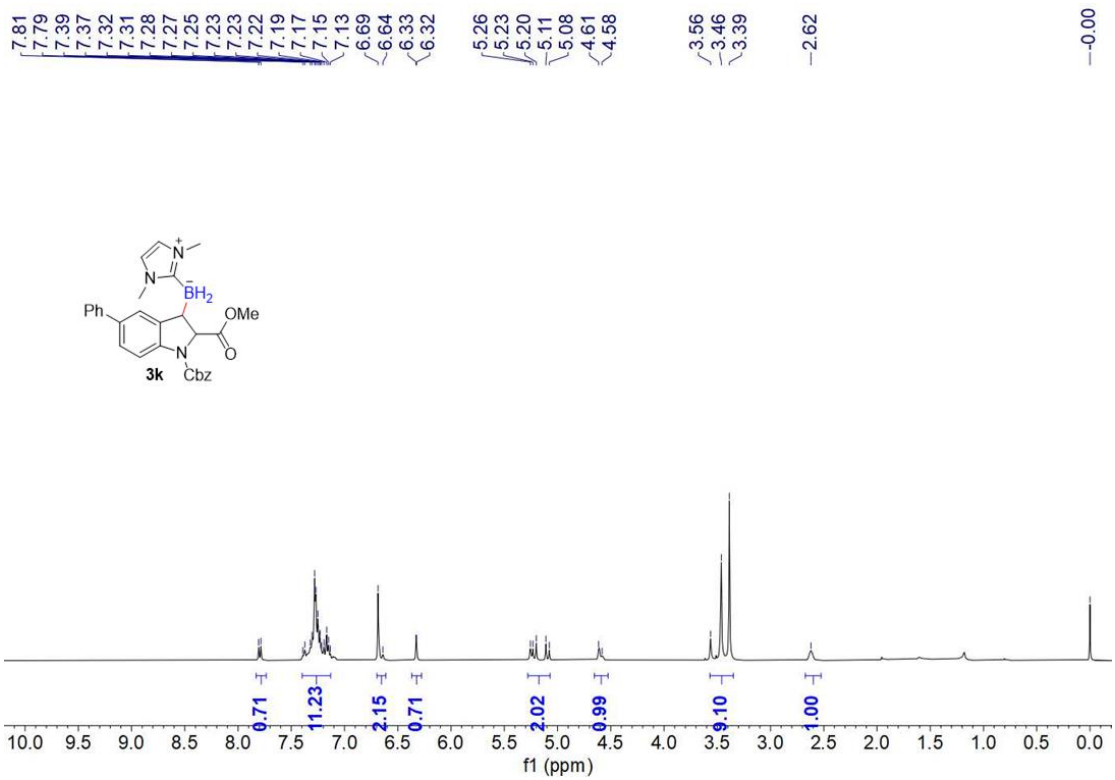

Fig. S26 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3k**.

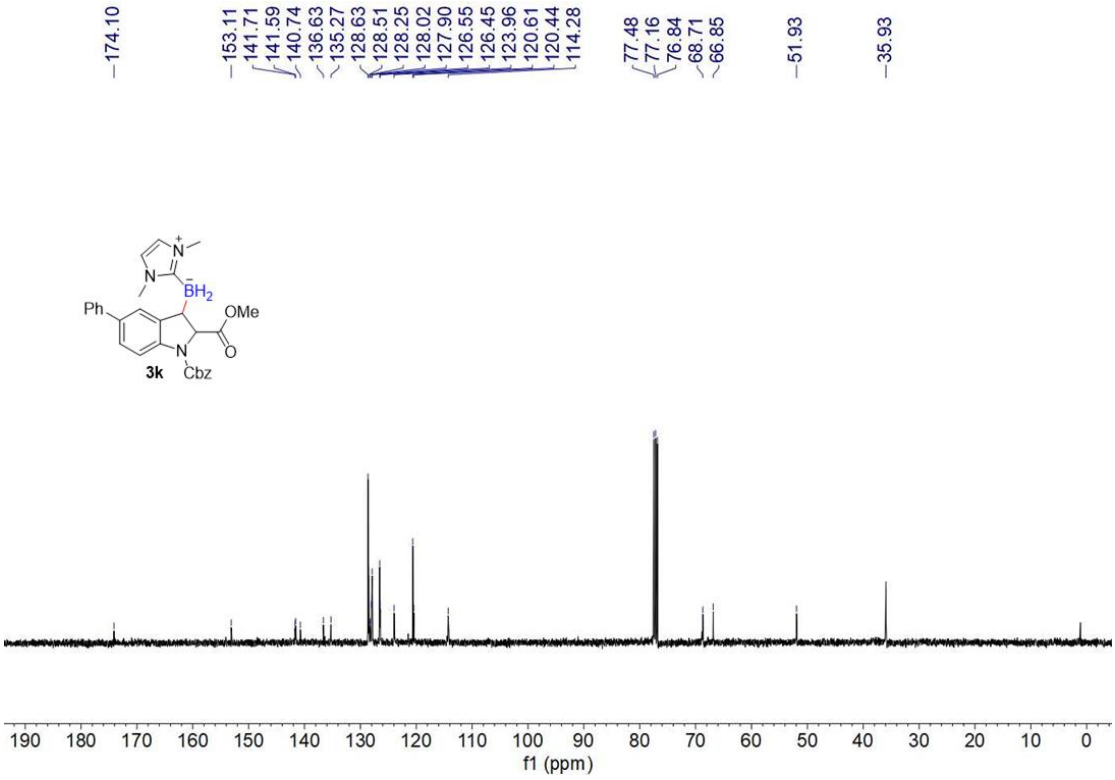

Fig. S27 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3k**.

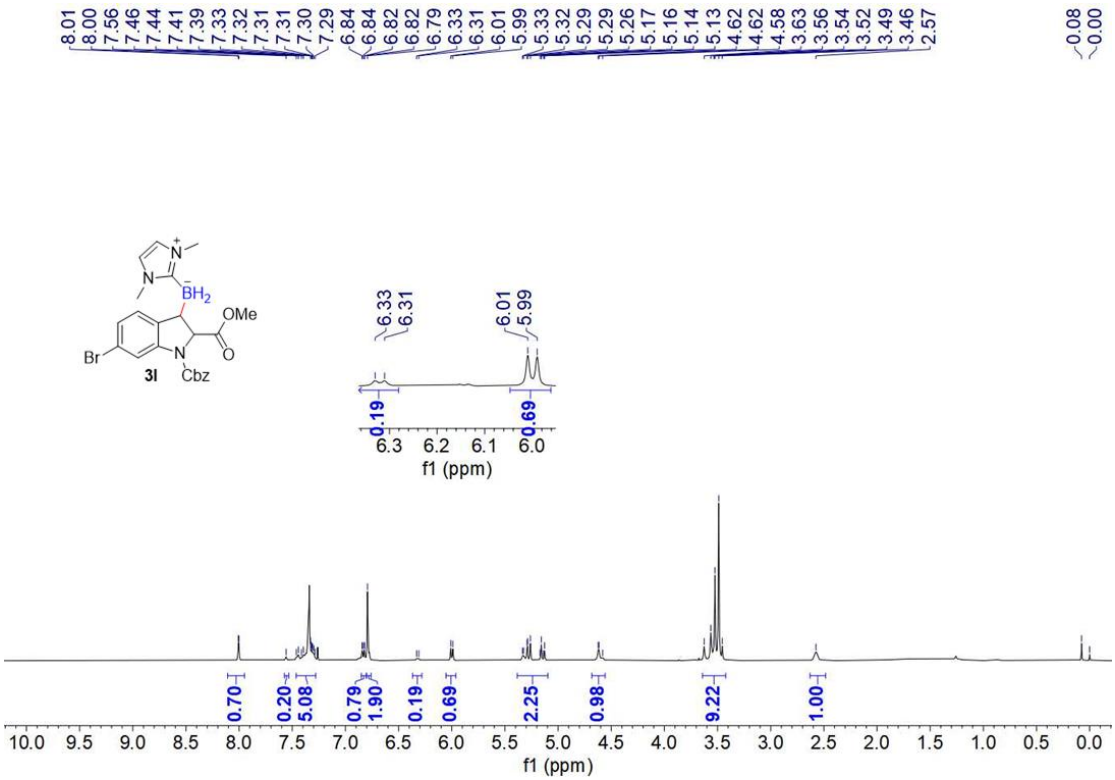

Fig. S28 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3l**.

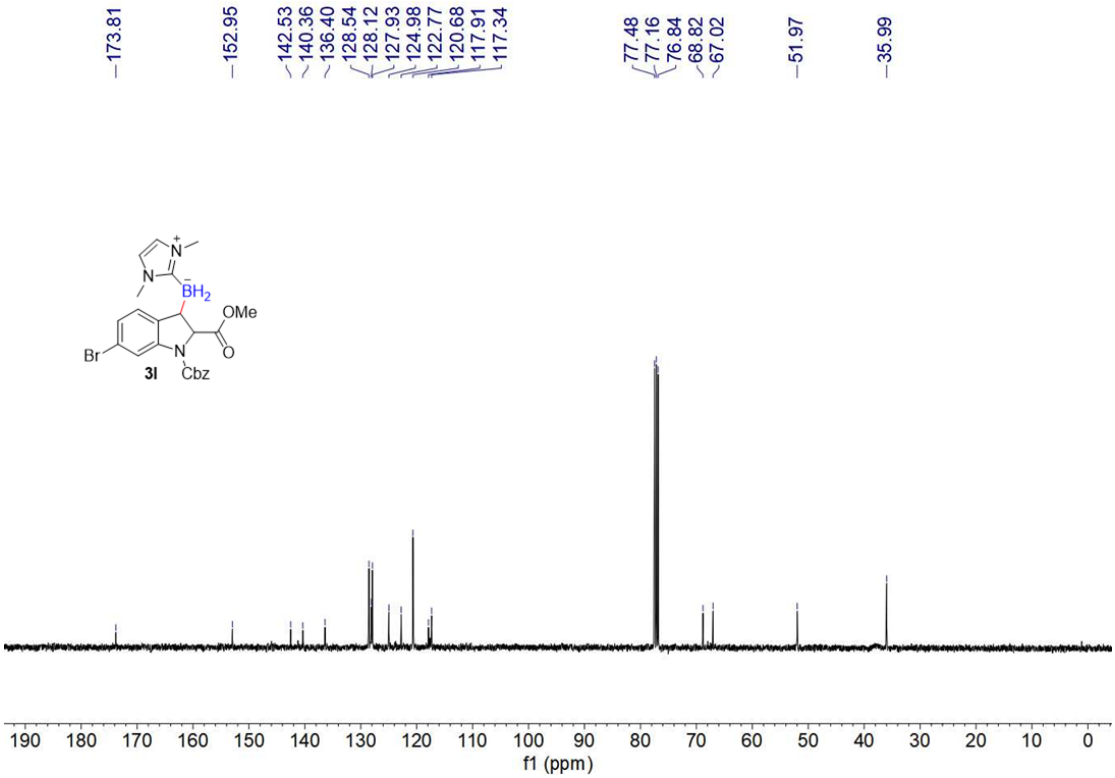

Fig. S29 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3l**.

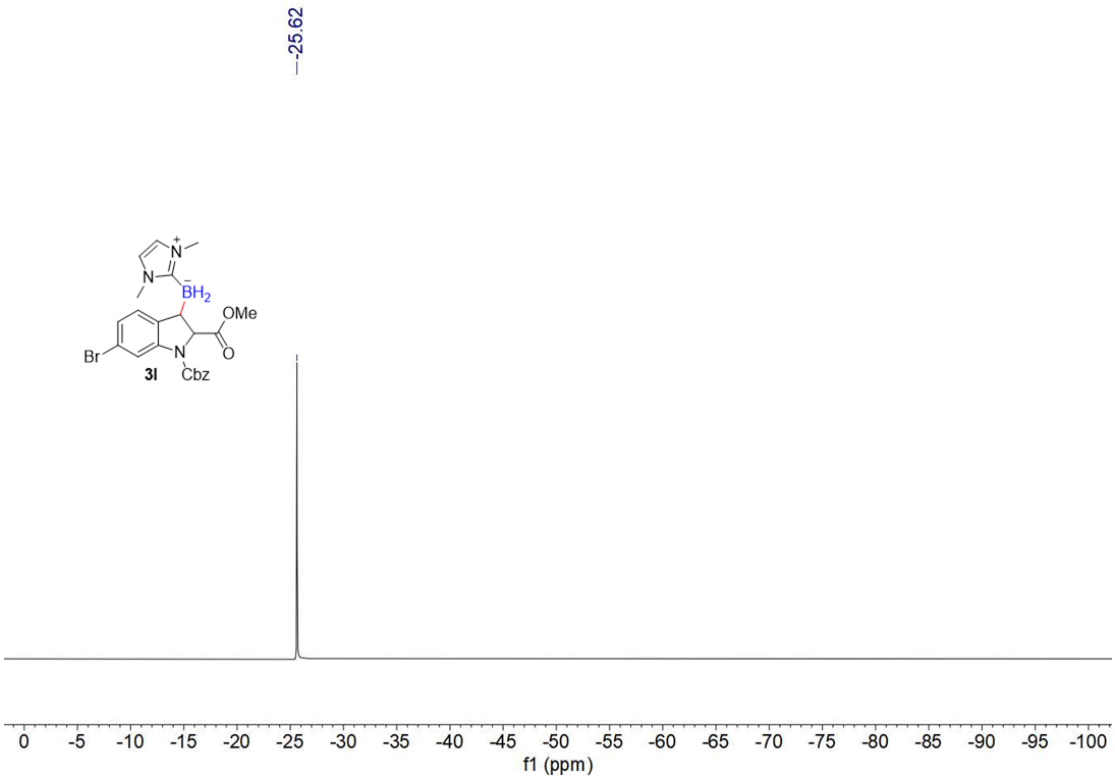

Fig. S30 ^{11}B NMR (128 MHz, $CDCl_3$) spectrum for **3l**.

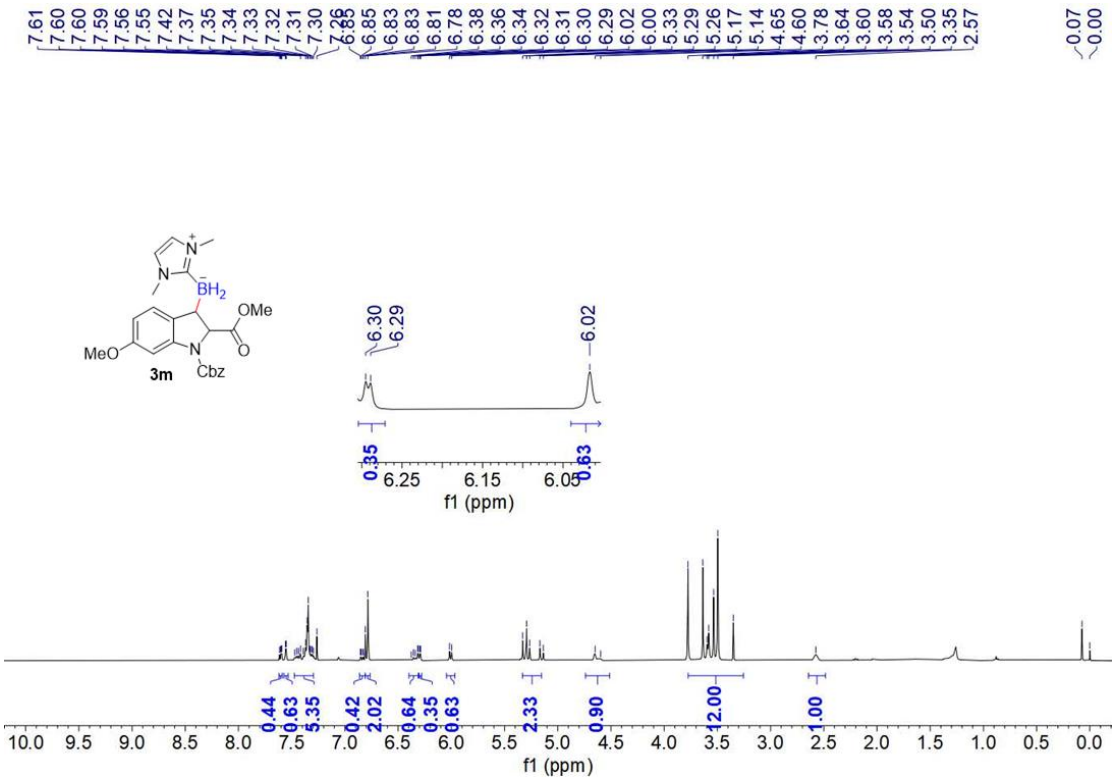

Fig. S31 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3m**.

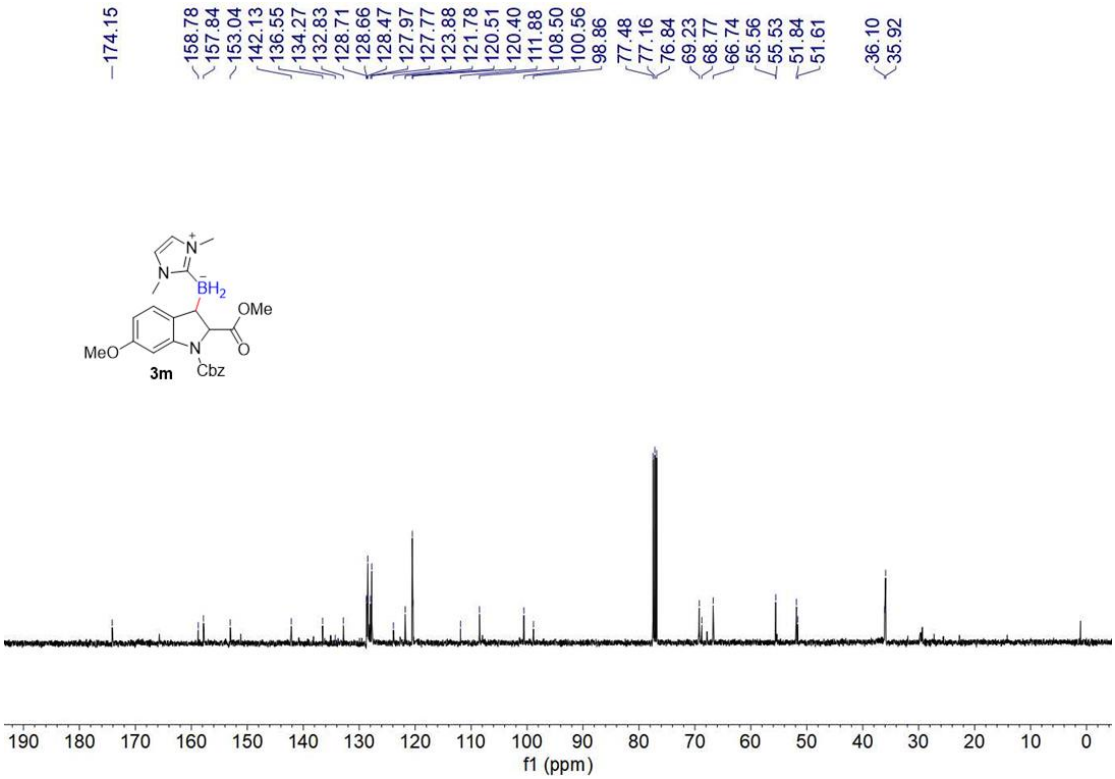

Fig. S32 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3m**.

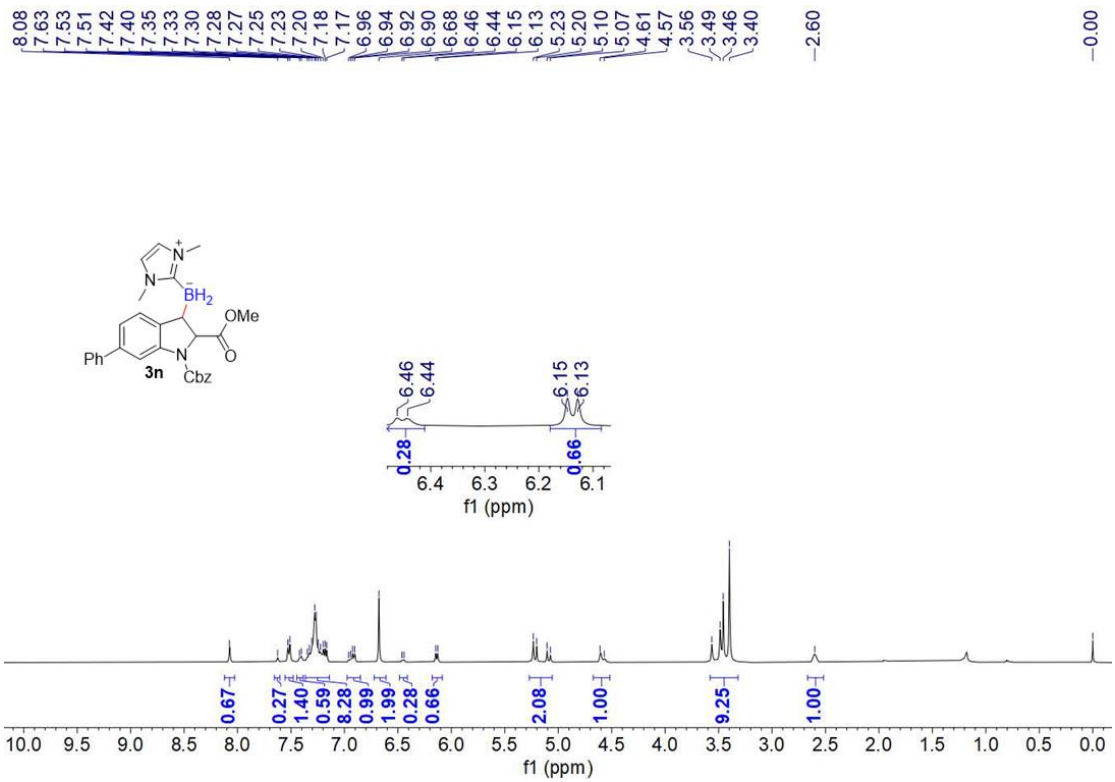

Fig. S33 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3n**.

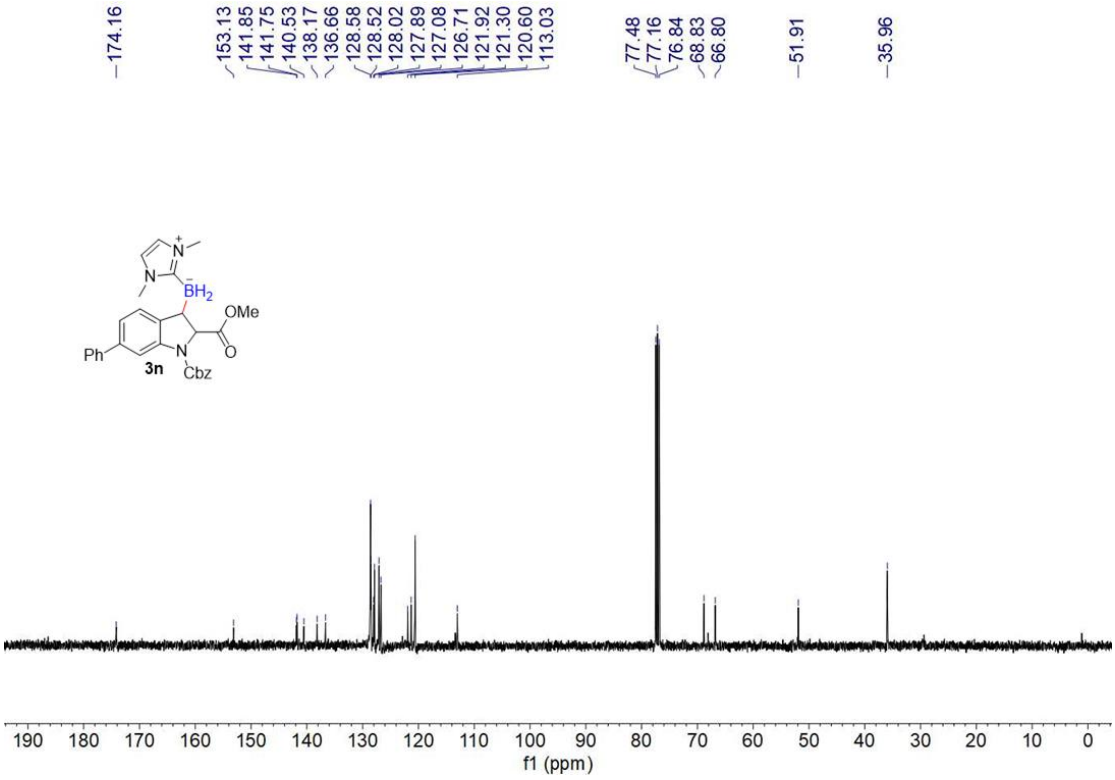

Fig. S34 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3n**.

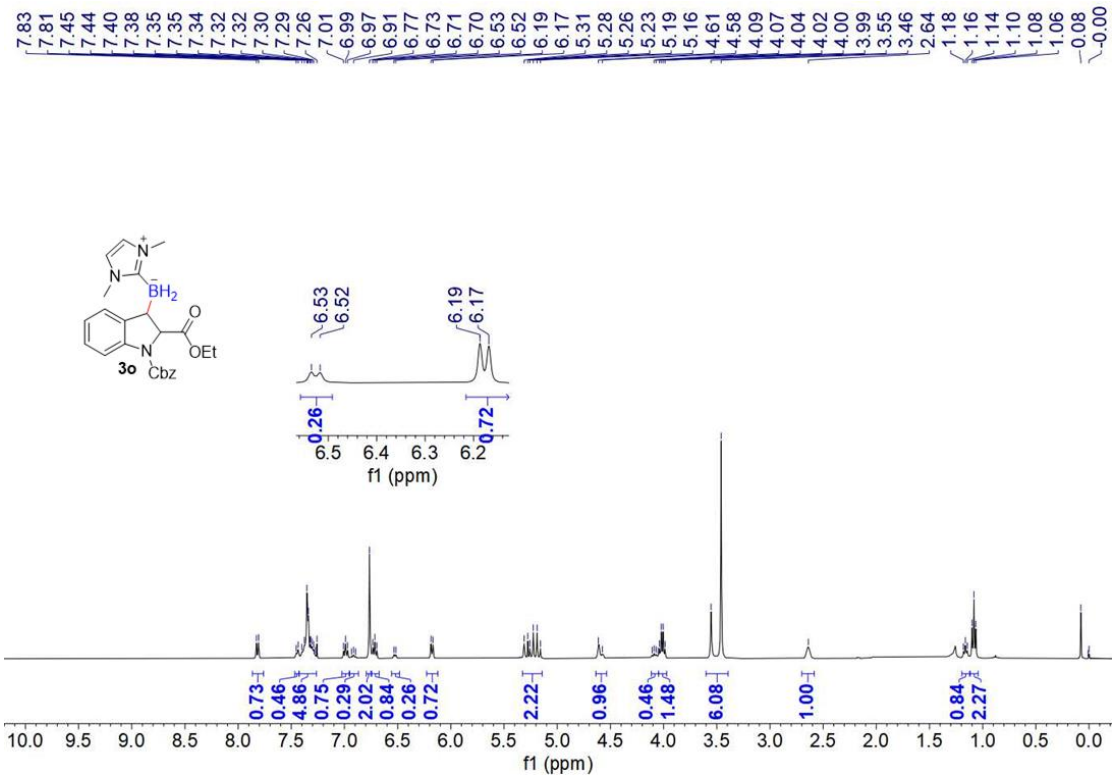

Fig. S35 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3o**.

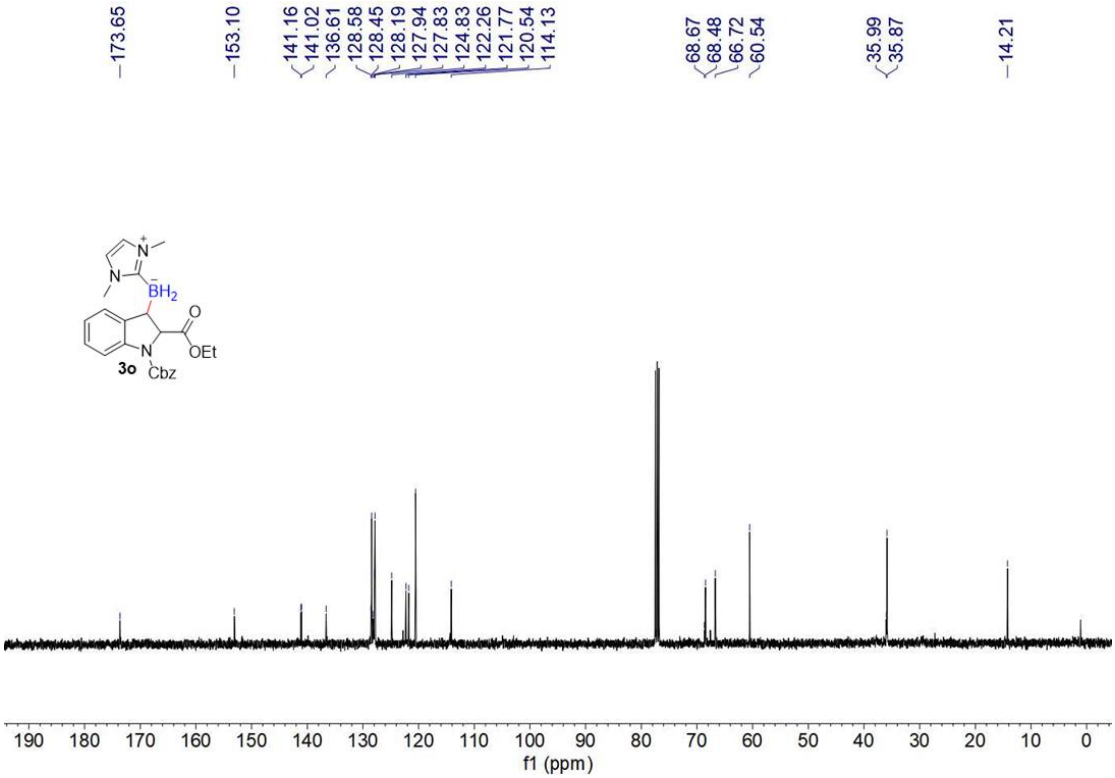

Fig. S36 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3o**.

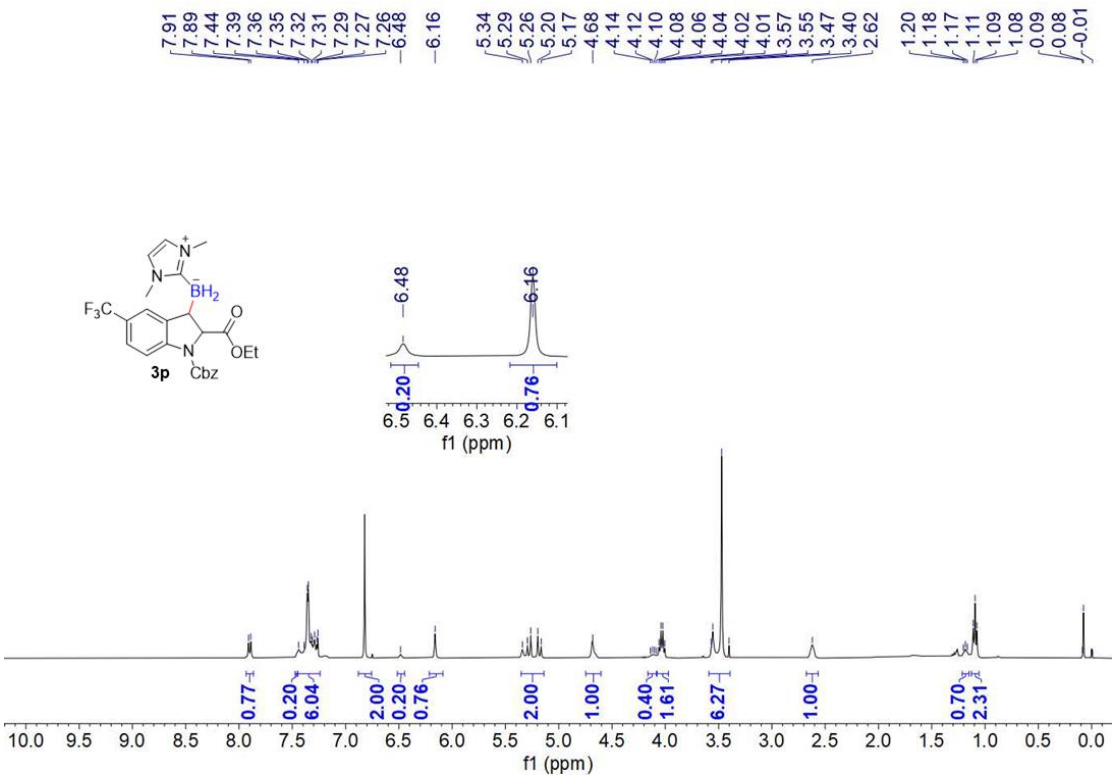

Fig. S37 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3p**.

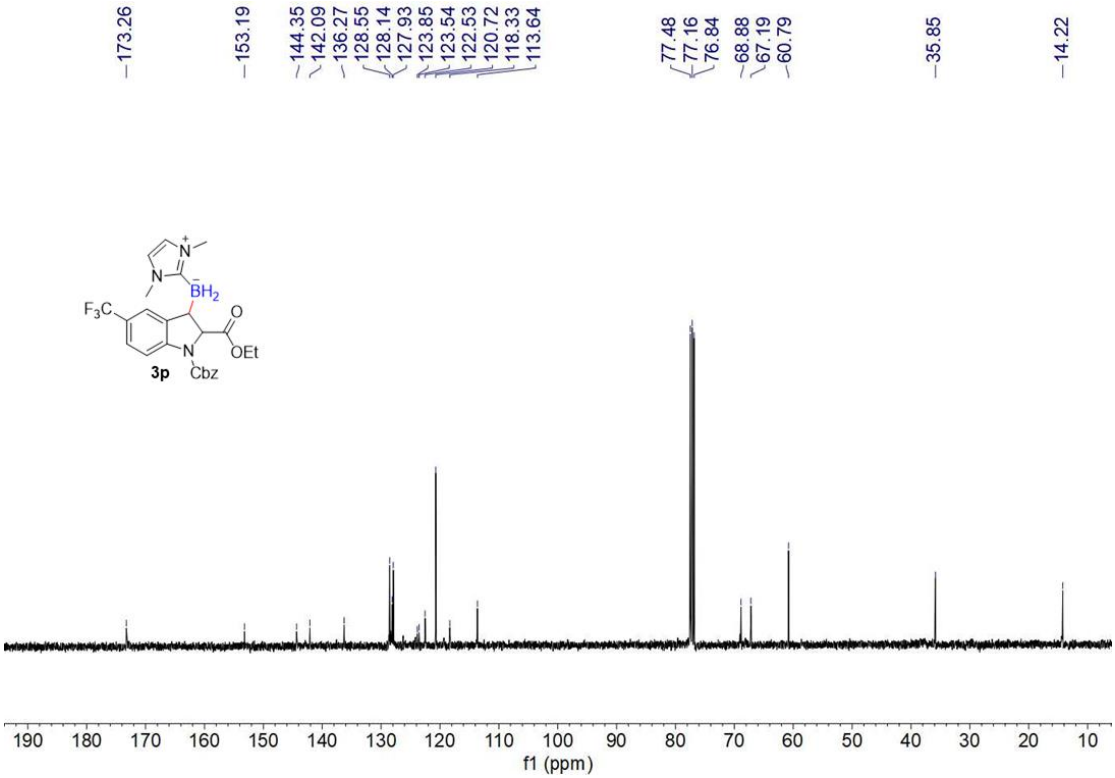

Fig. S38 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3p**.

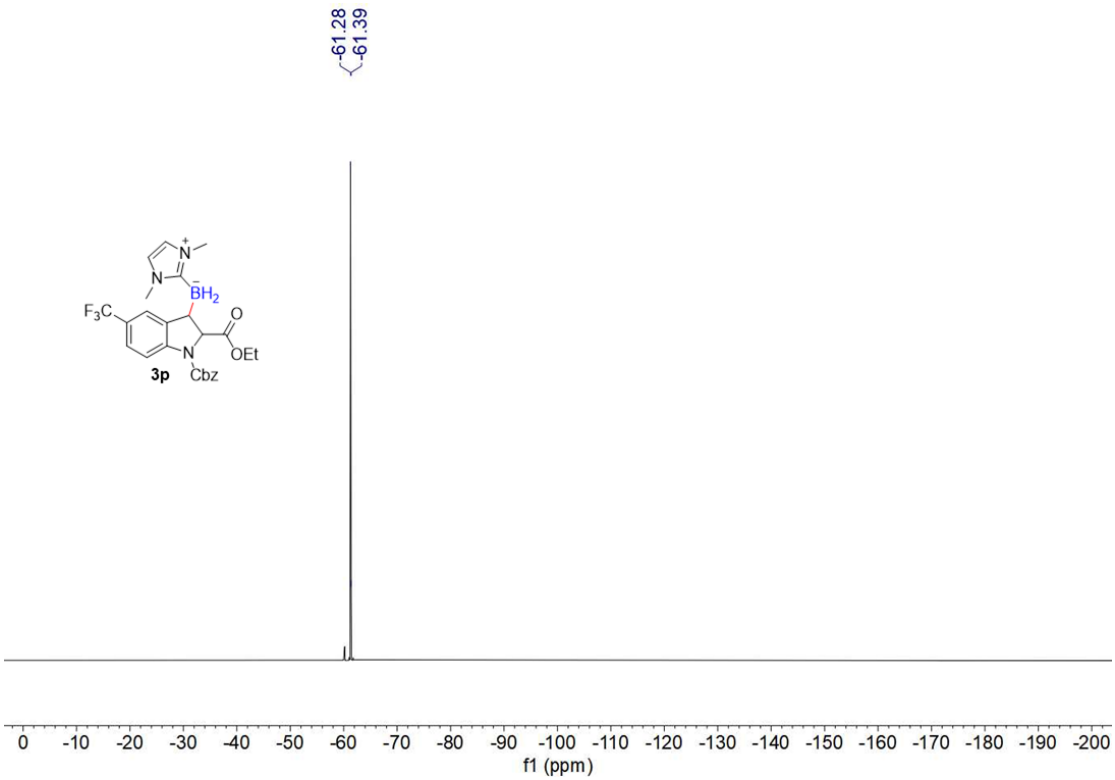

Fig. S39 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **3p**.

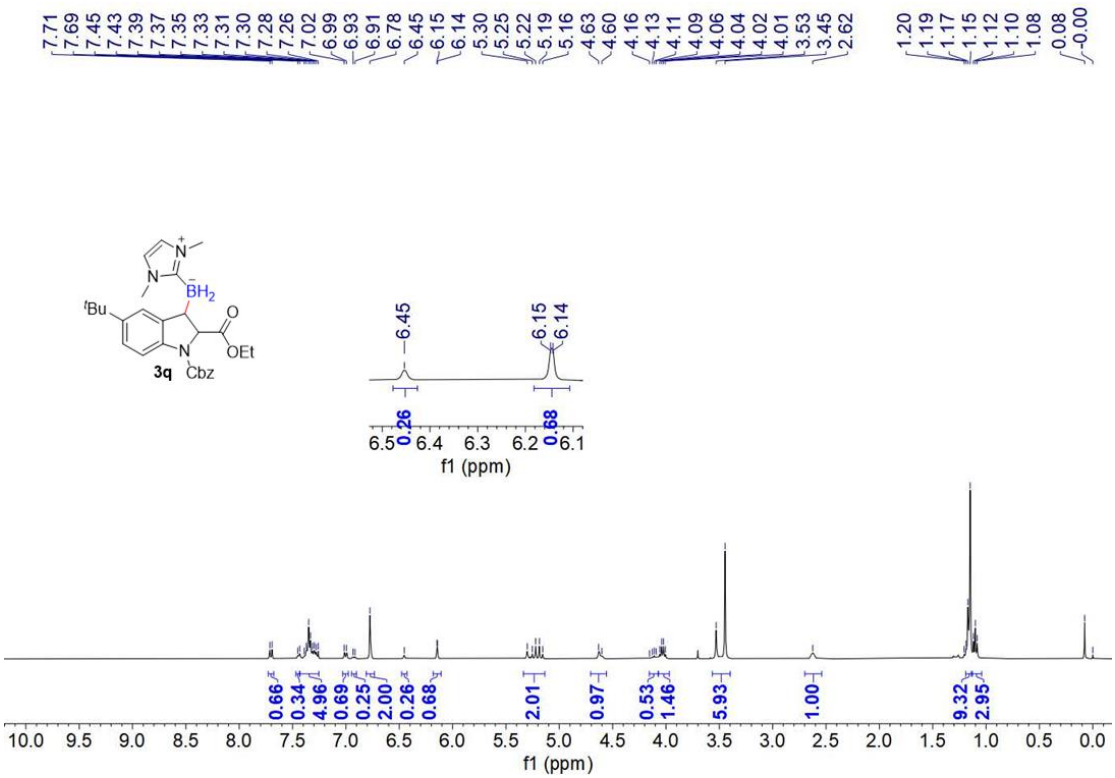

Fig. S40 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3q**.

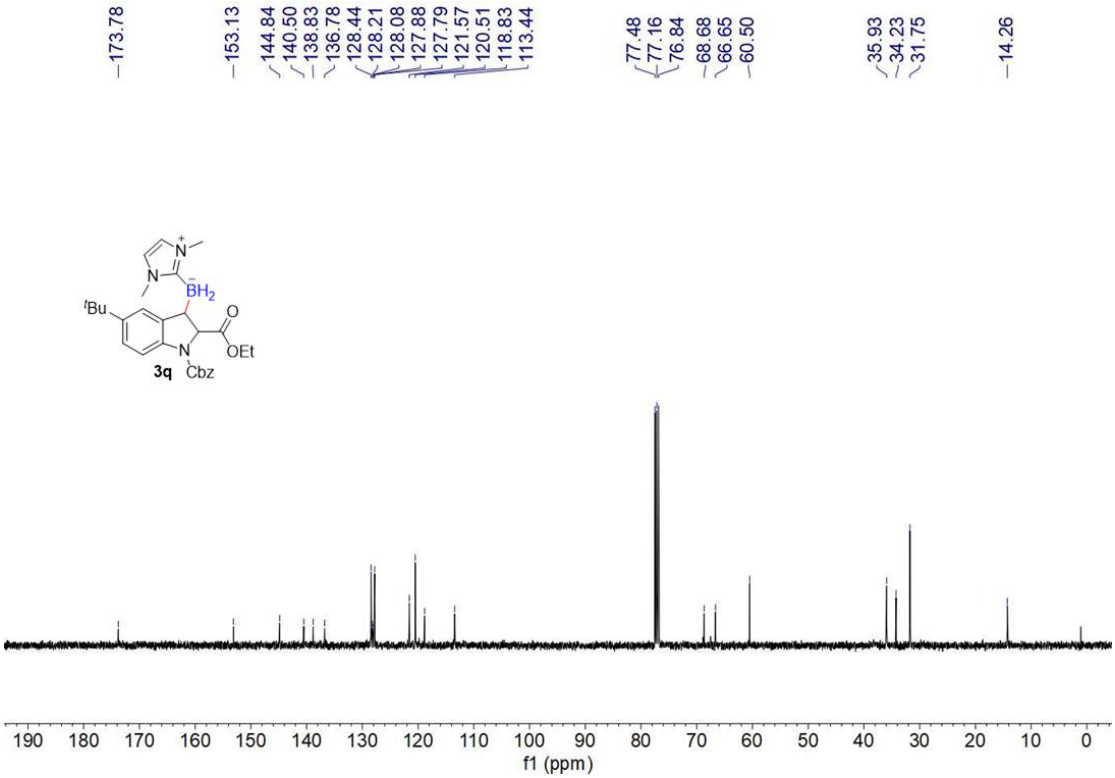

Fig. S41 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3q**.

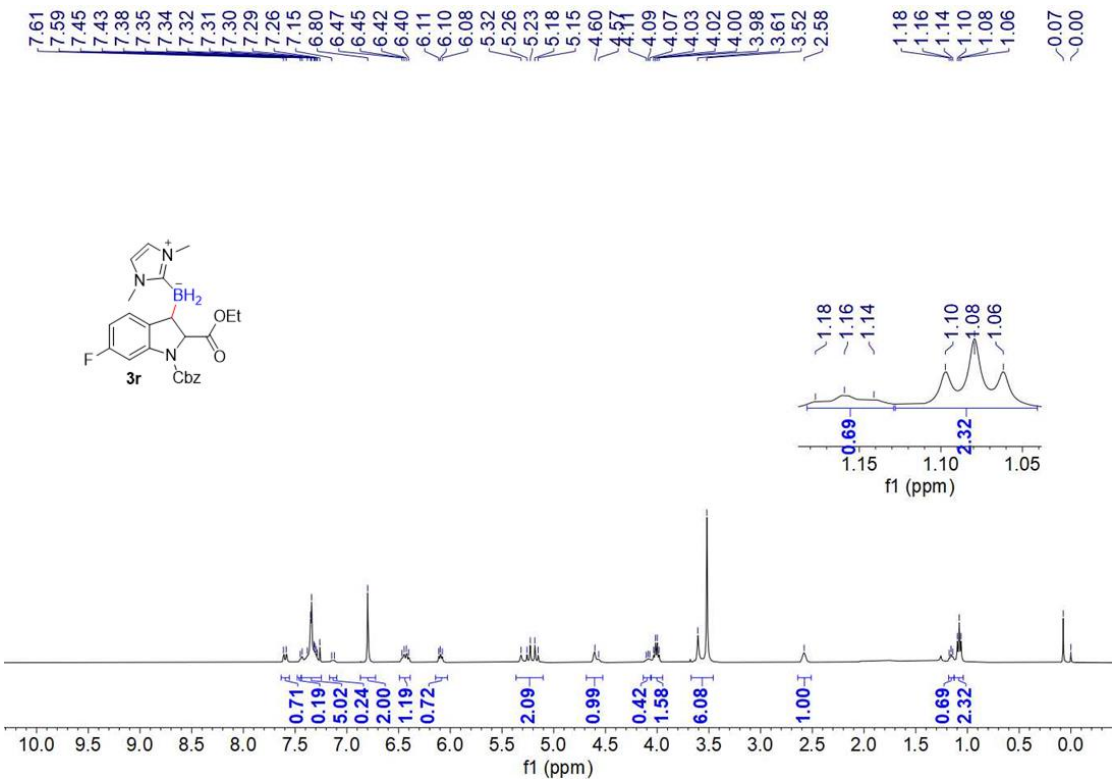

Fig. S42 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3r**.

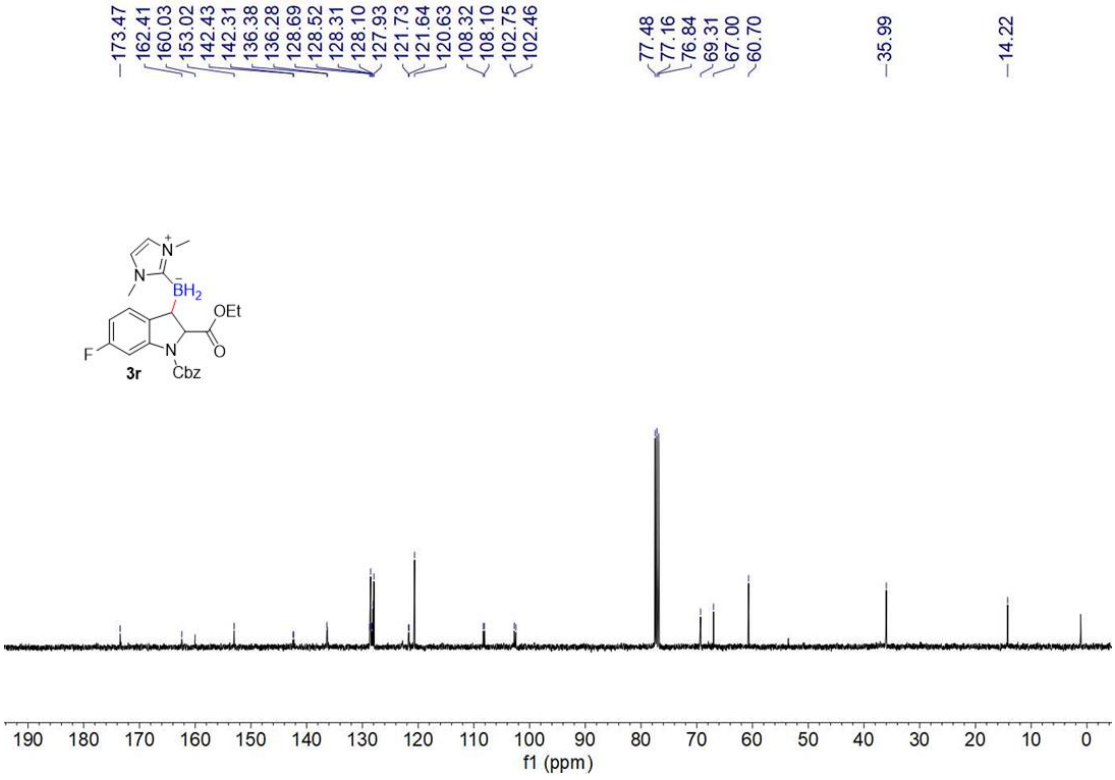

Fig. S43 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3r**.

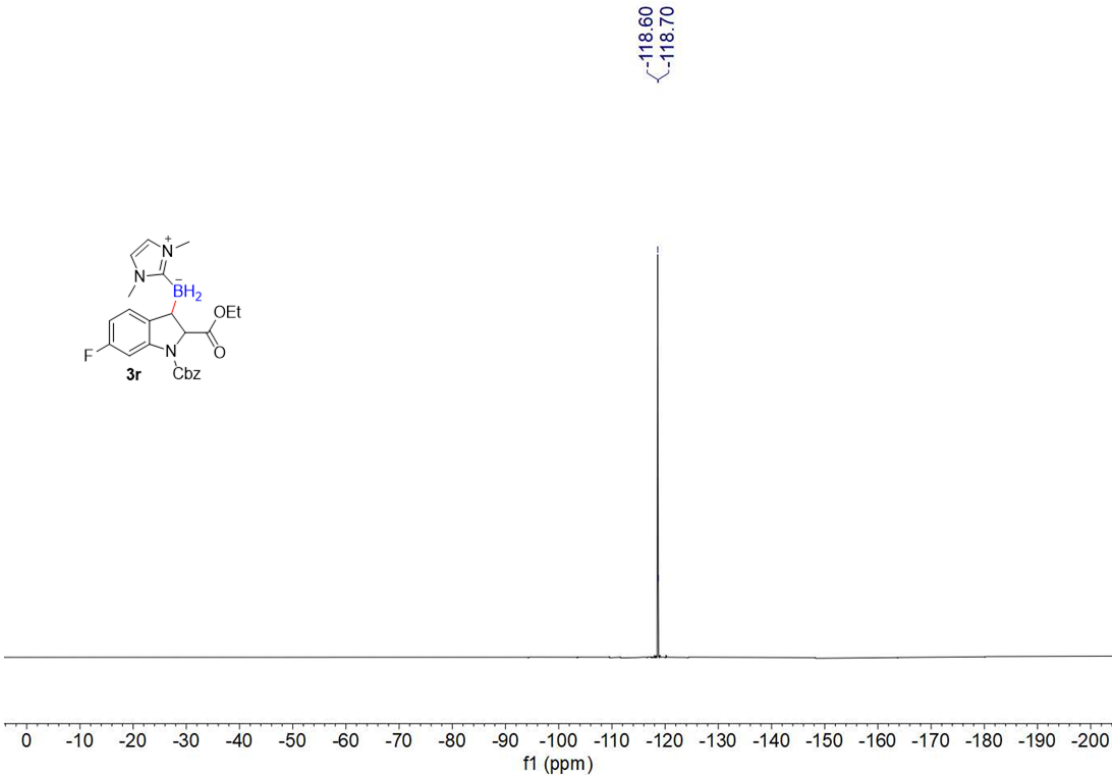

Fig. S44 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **3r**.

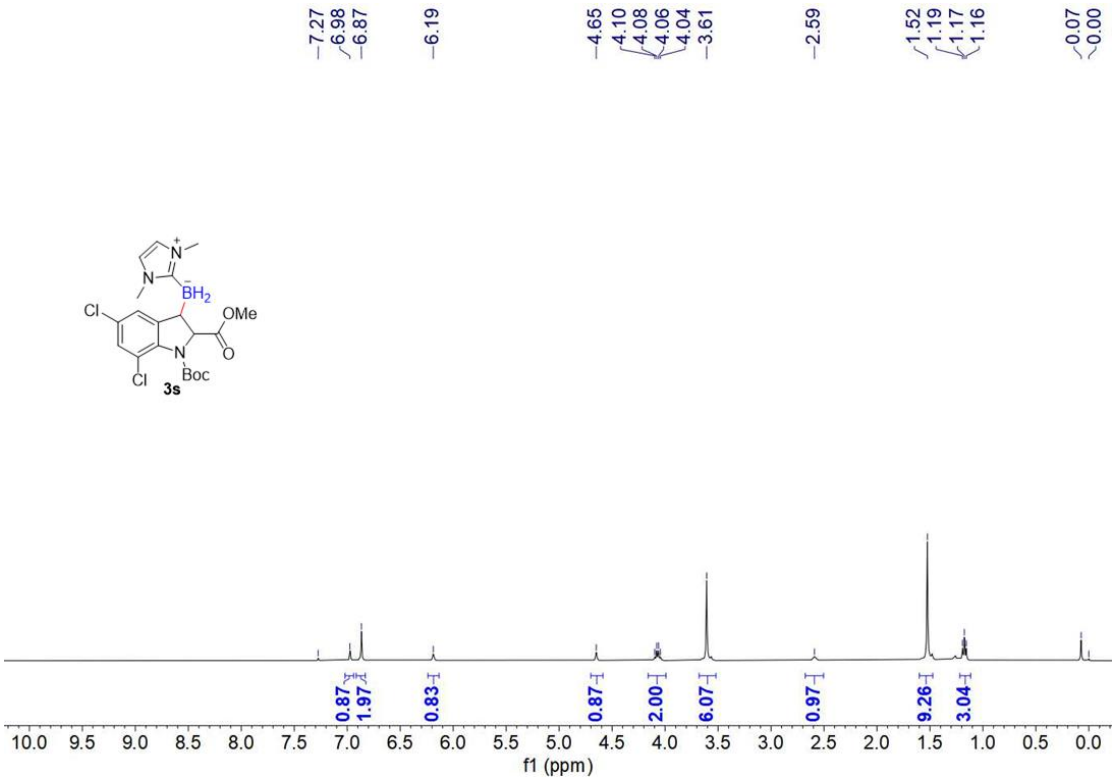

Fig. S45 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3s**.

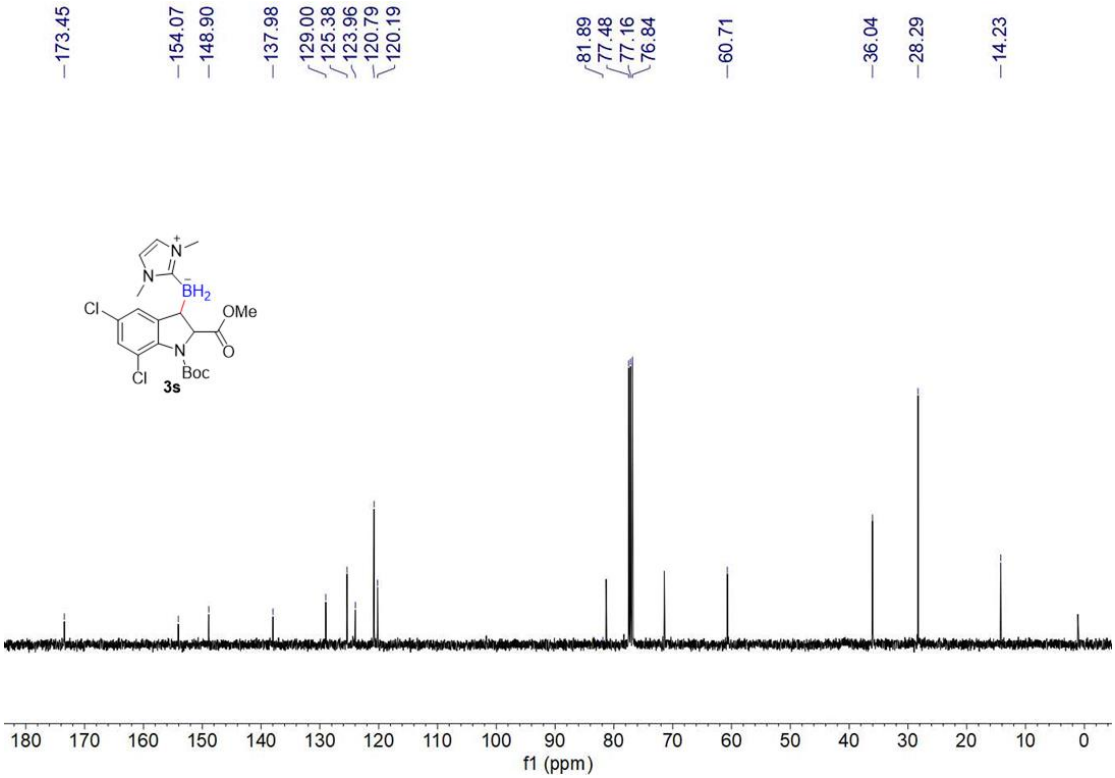

Fig. S46 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3s**.

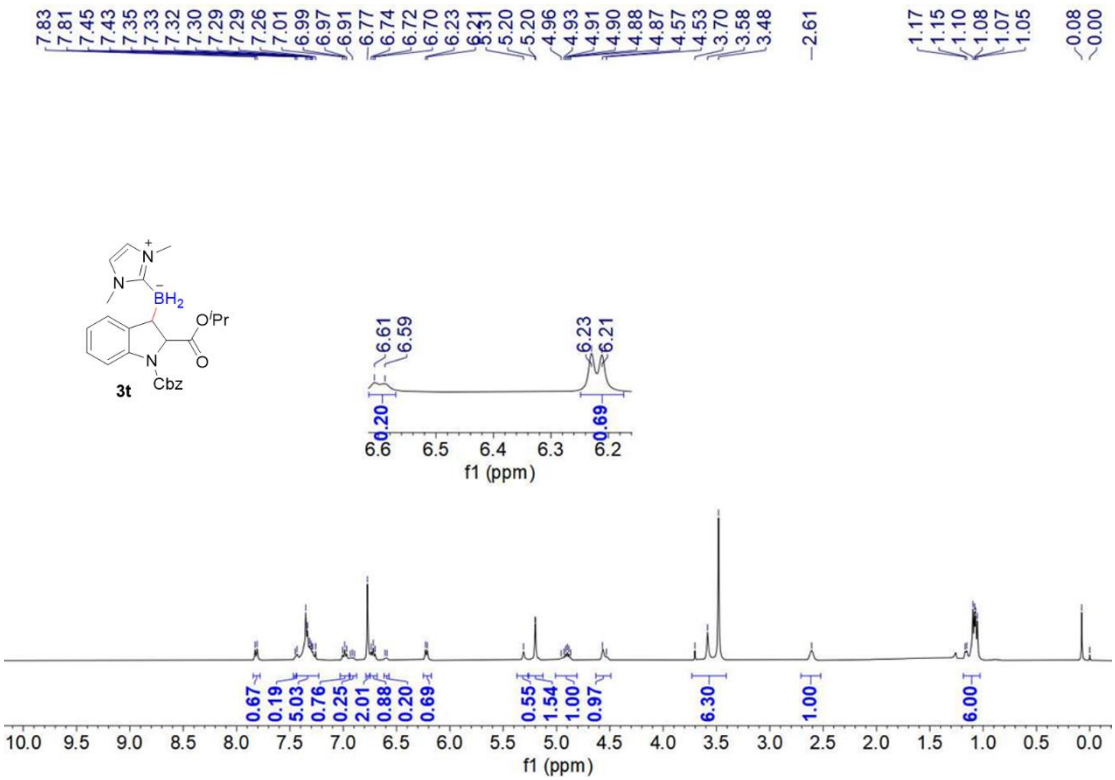

Fig. S47 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3t**.

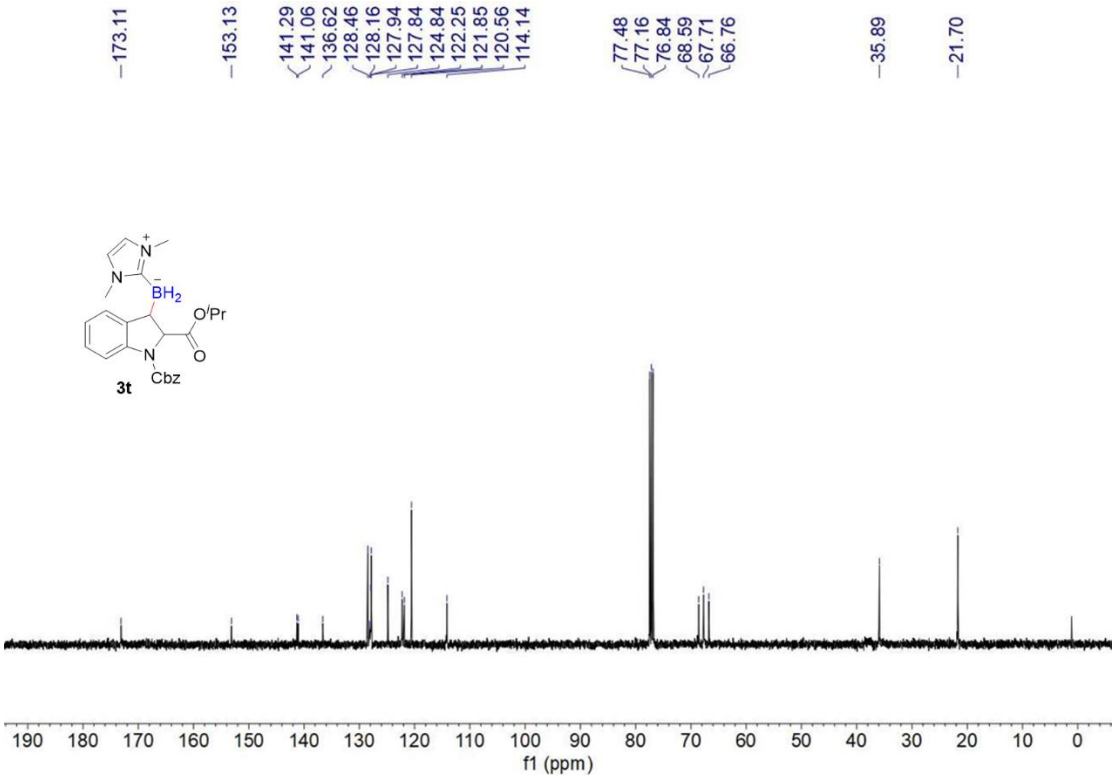

Fig. S48 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3t**.

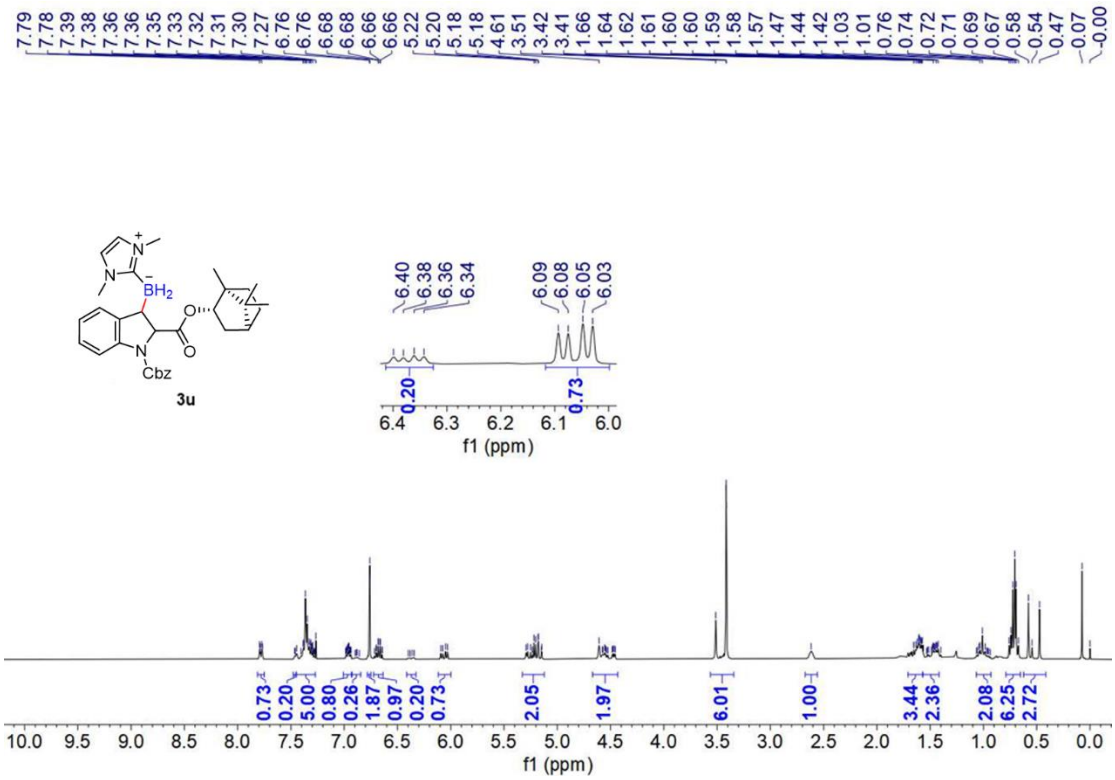

Fig. S49 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3u**.

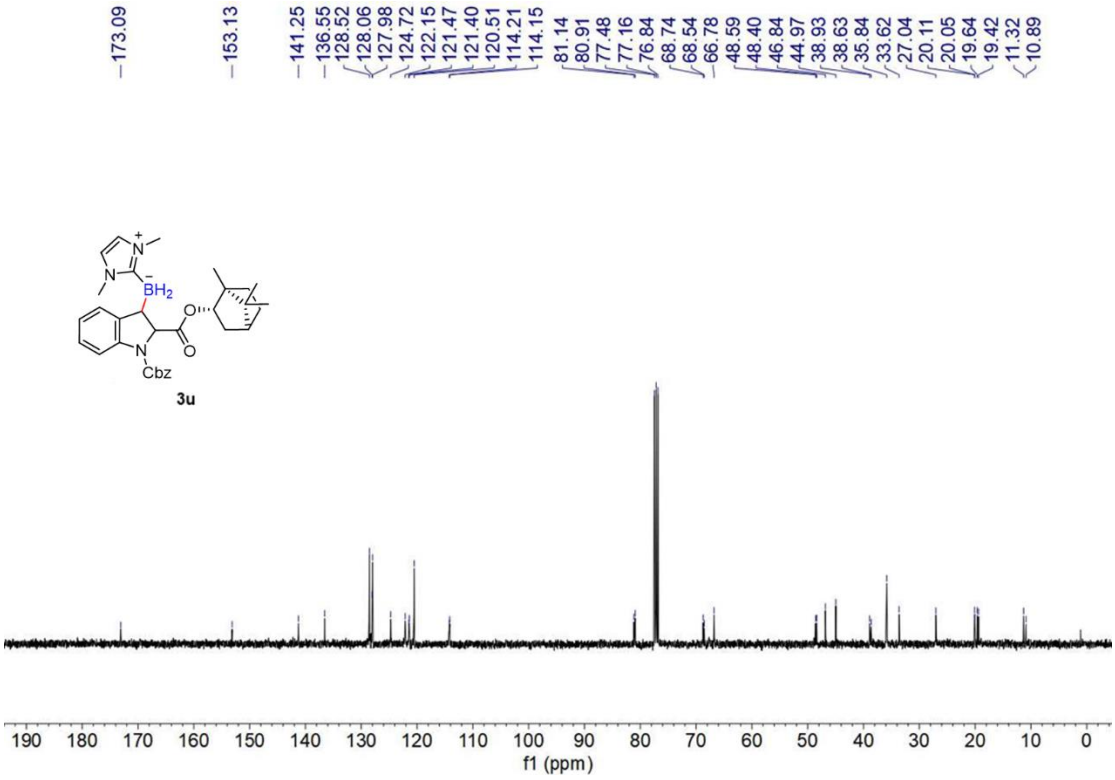

Fig. S50 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3u**.

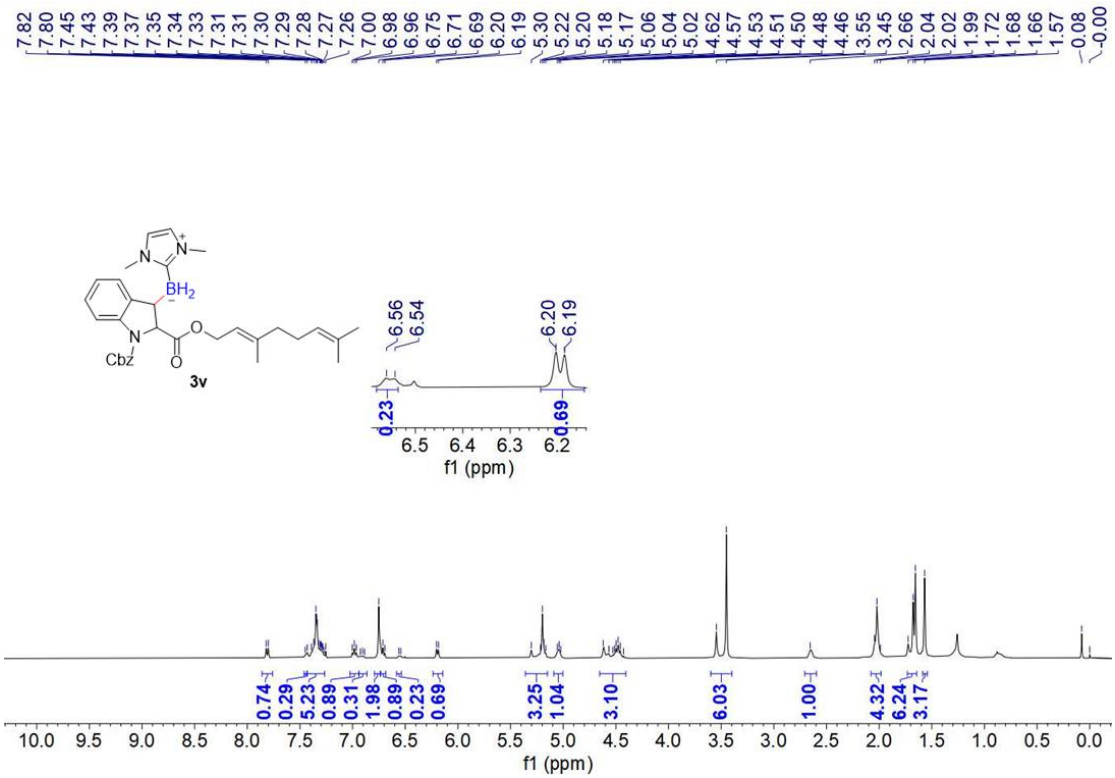

Fig. S51 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3v**.

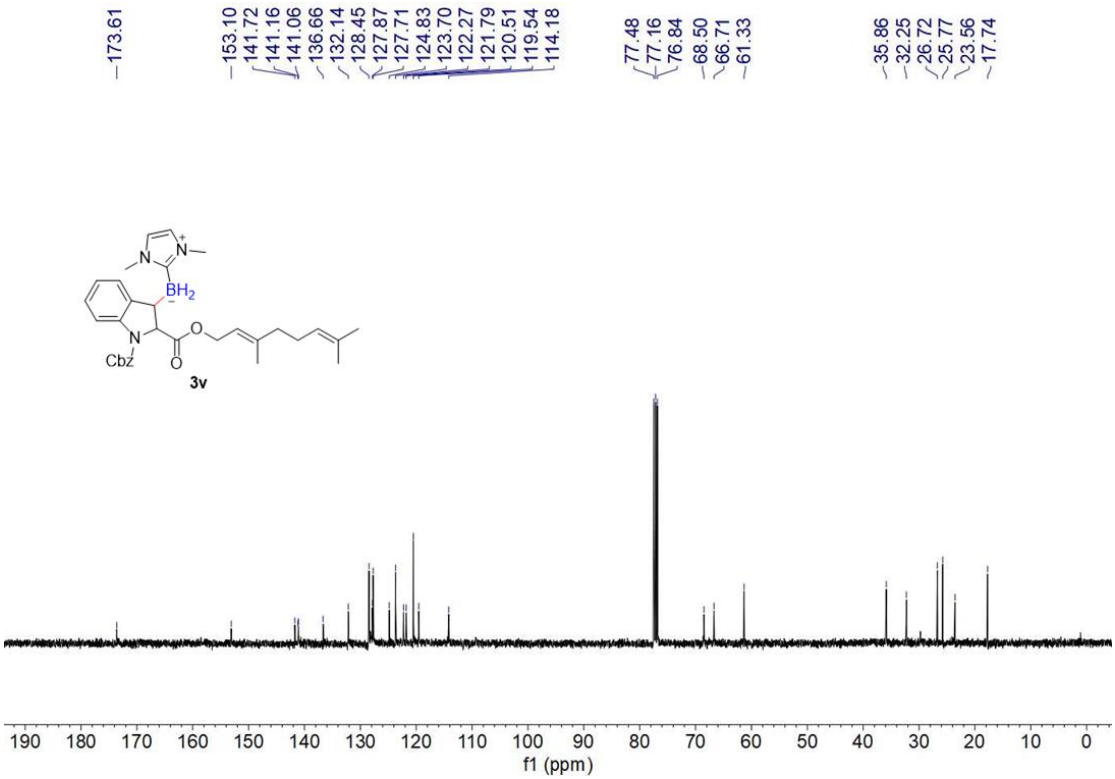

Fig. S52 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3v**.

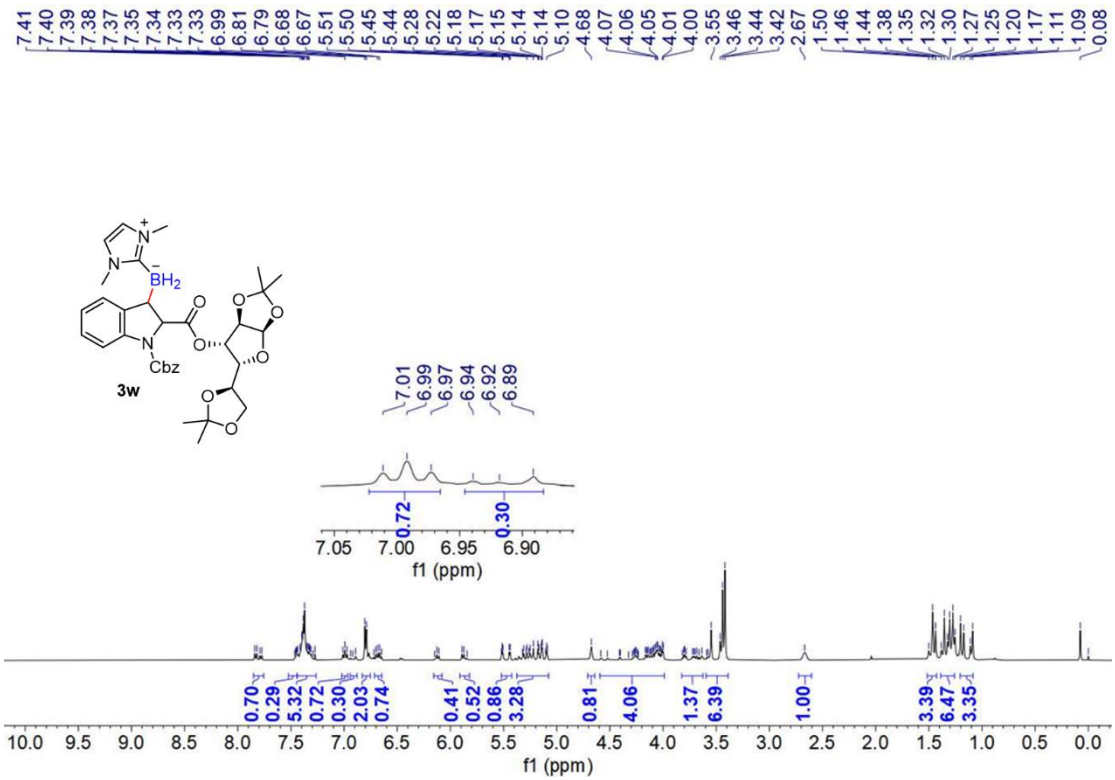

Fig. S53 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3w**.

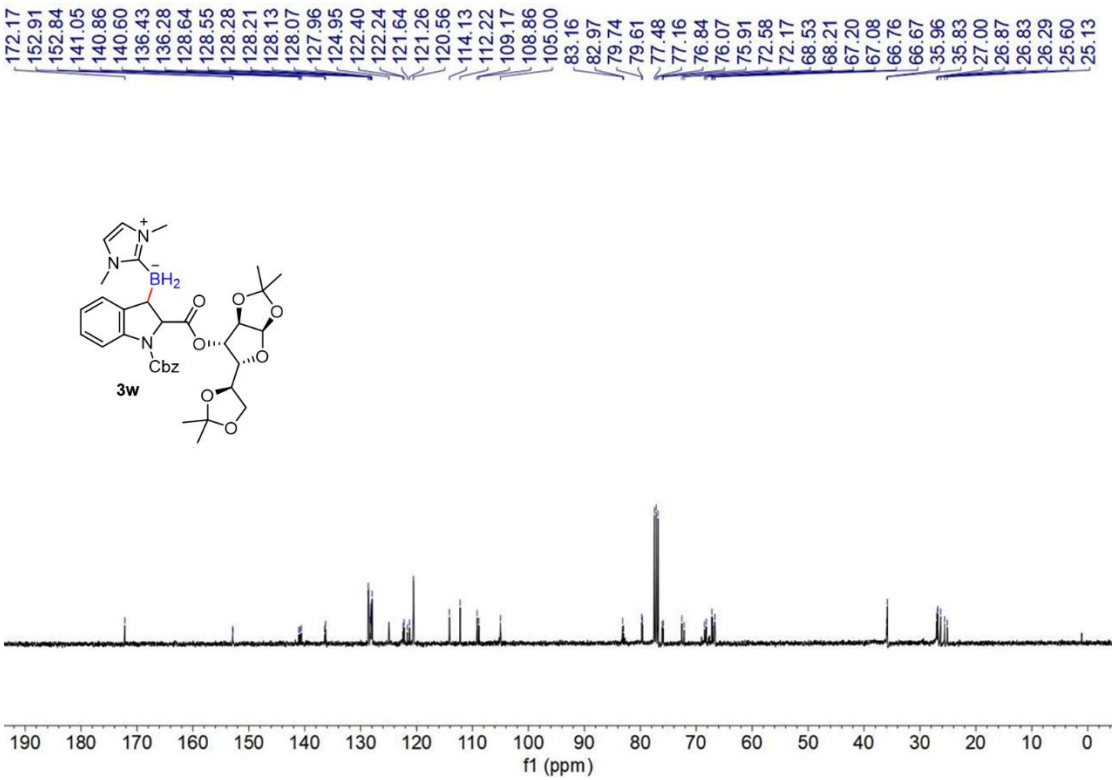

Fig. S54 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3w**.

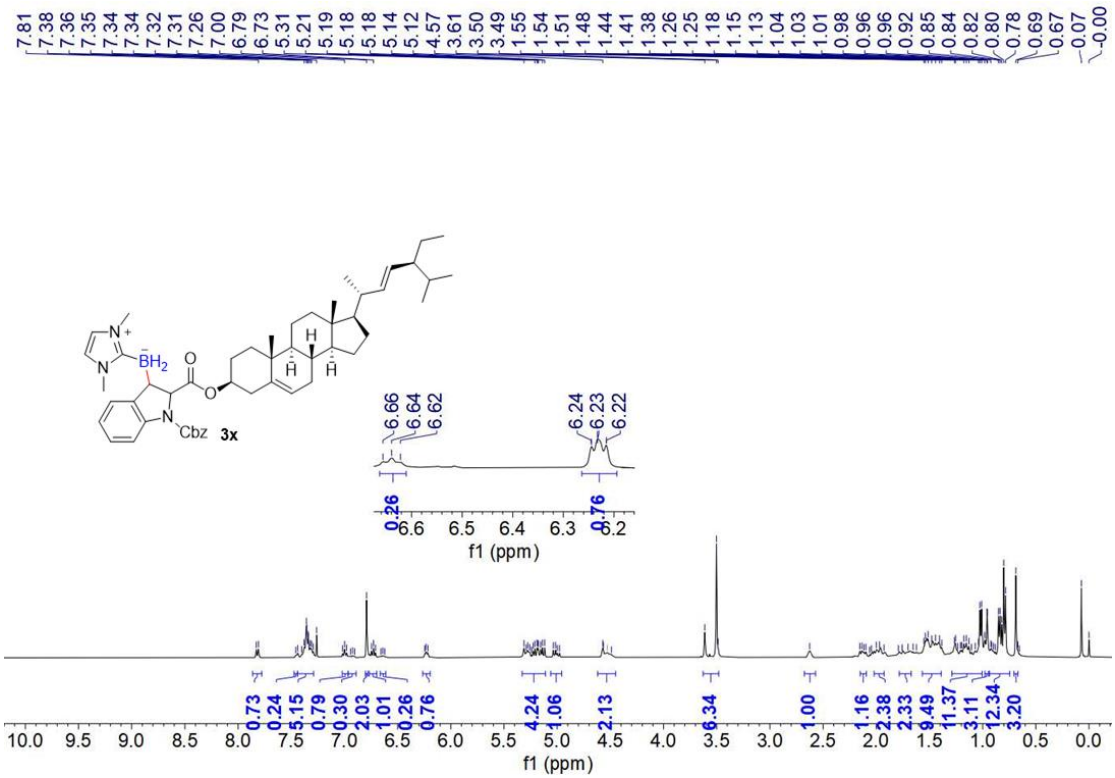

Fig. S55 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3x**.

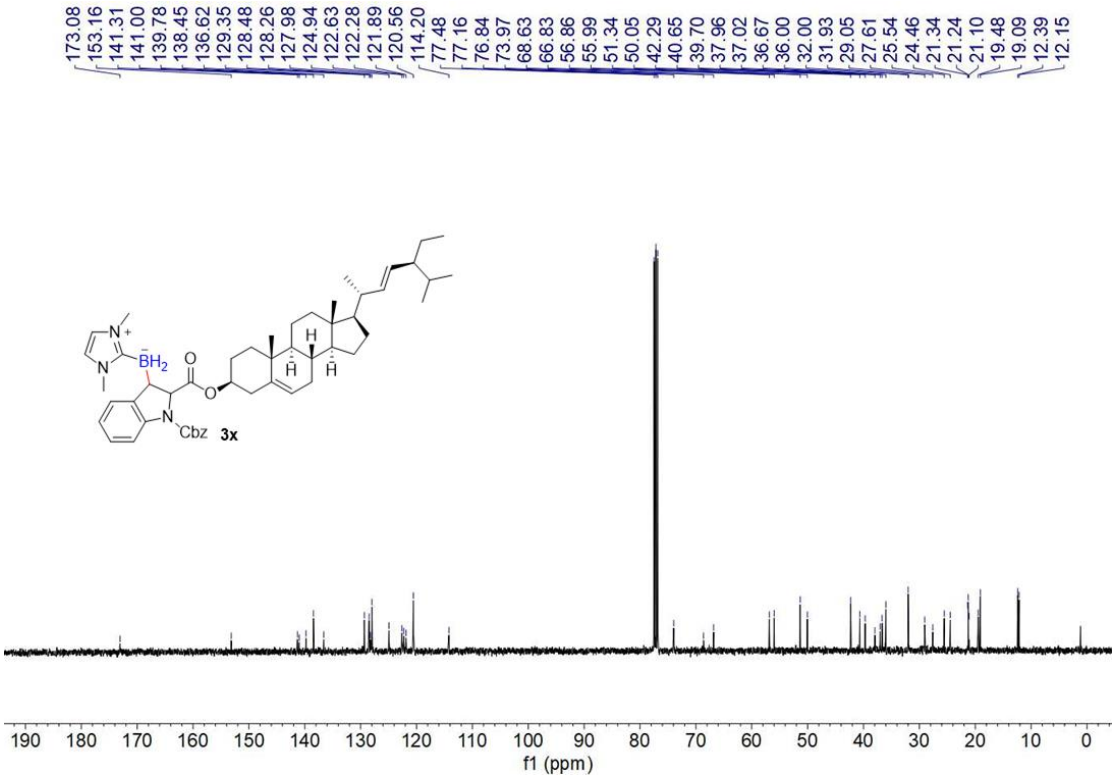

Fig. S56 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3x**.

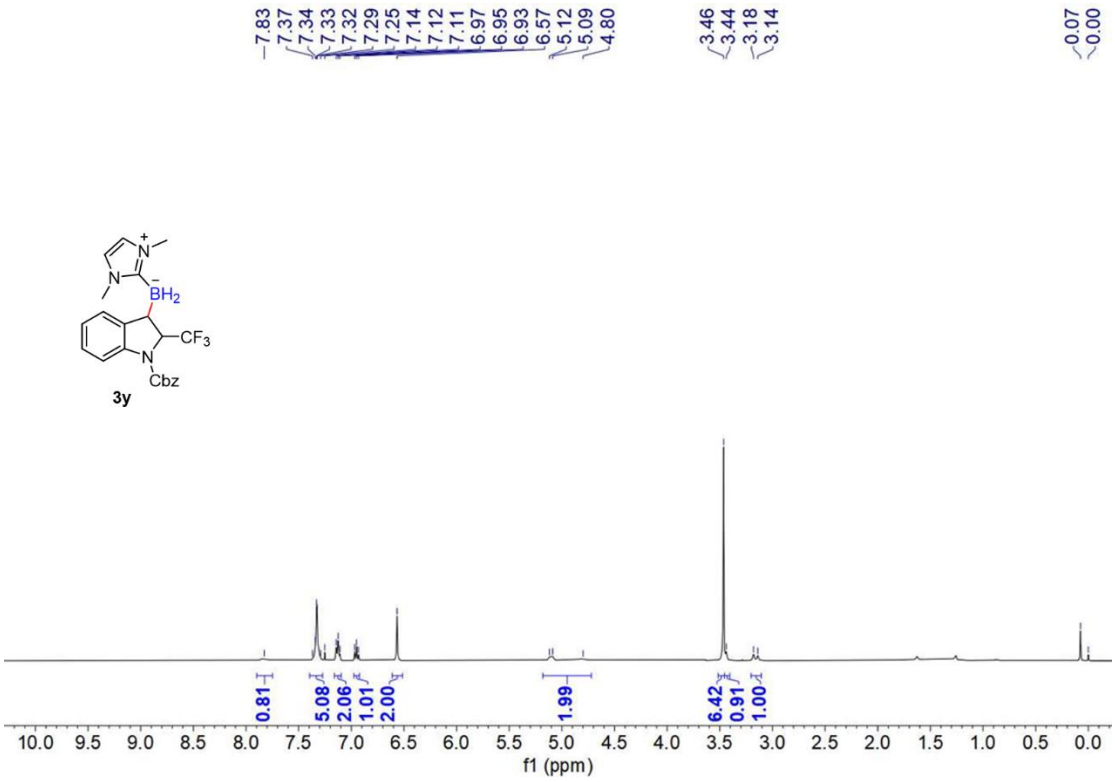

Fig. S57 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3y**.

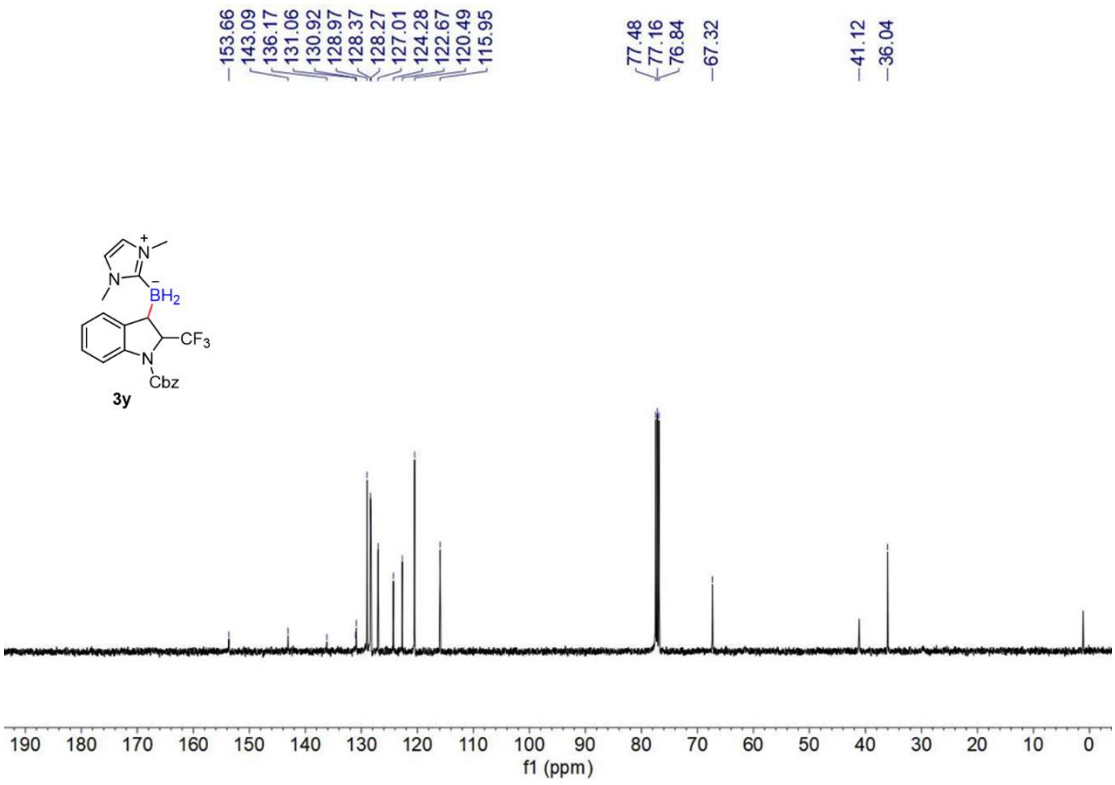

Fig. S58 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3y**.

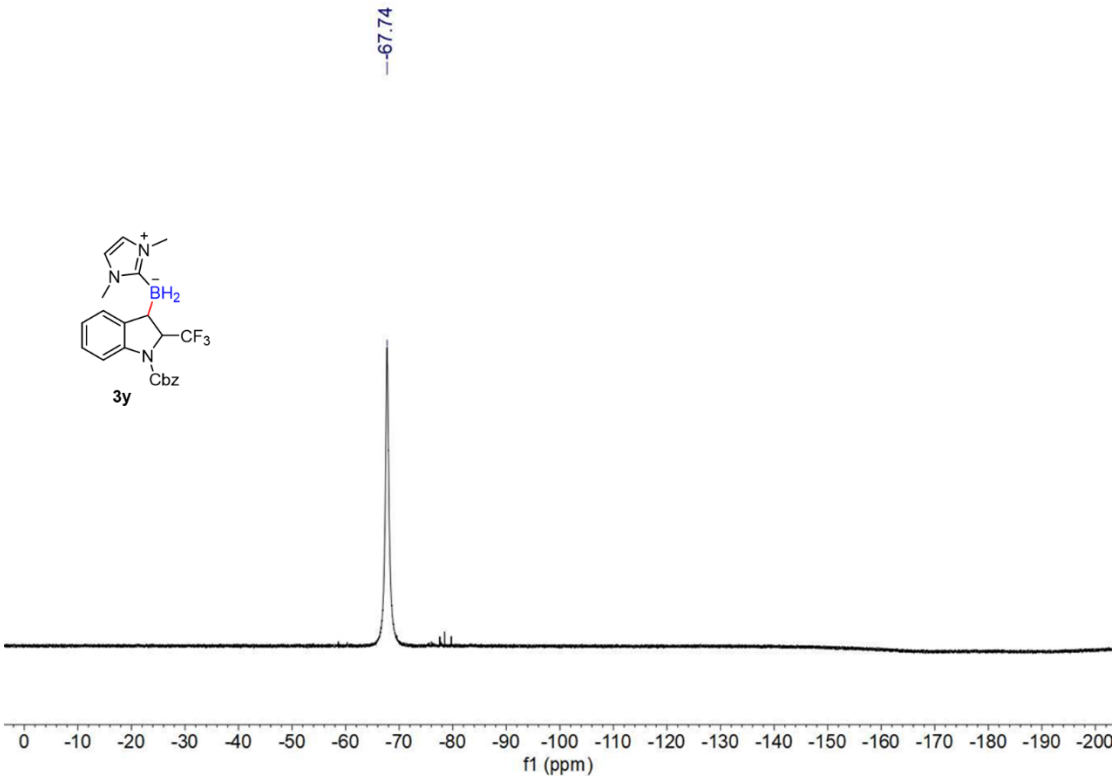

Fig. S59 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **3y**.

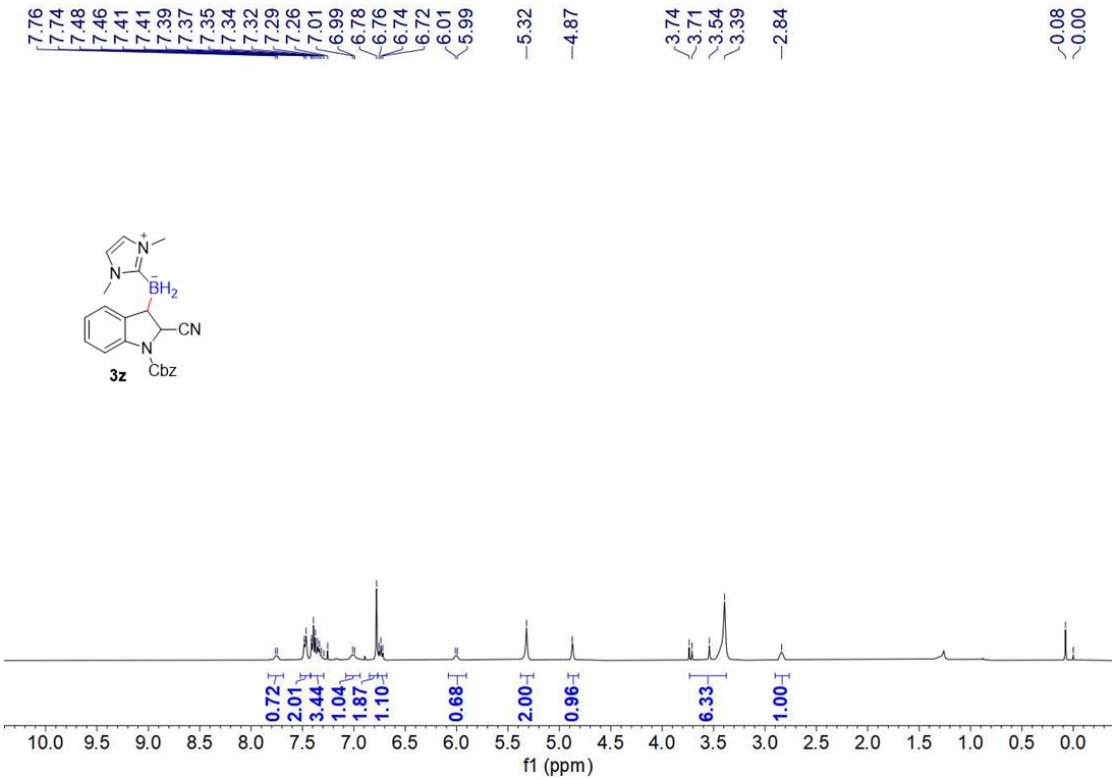

Fig. S60 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3z**.

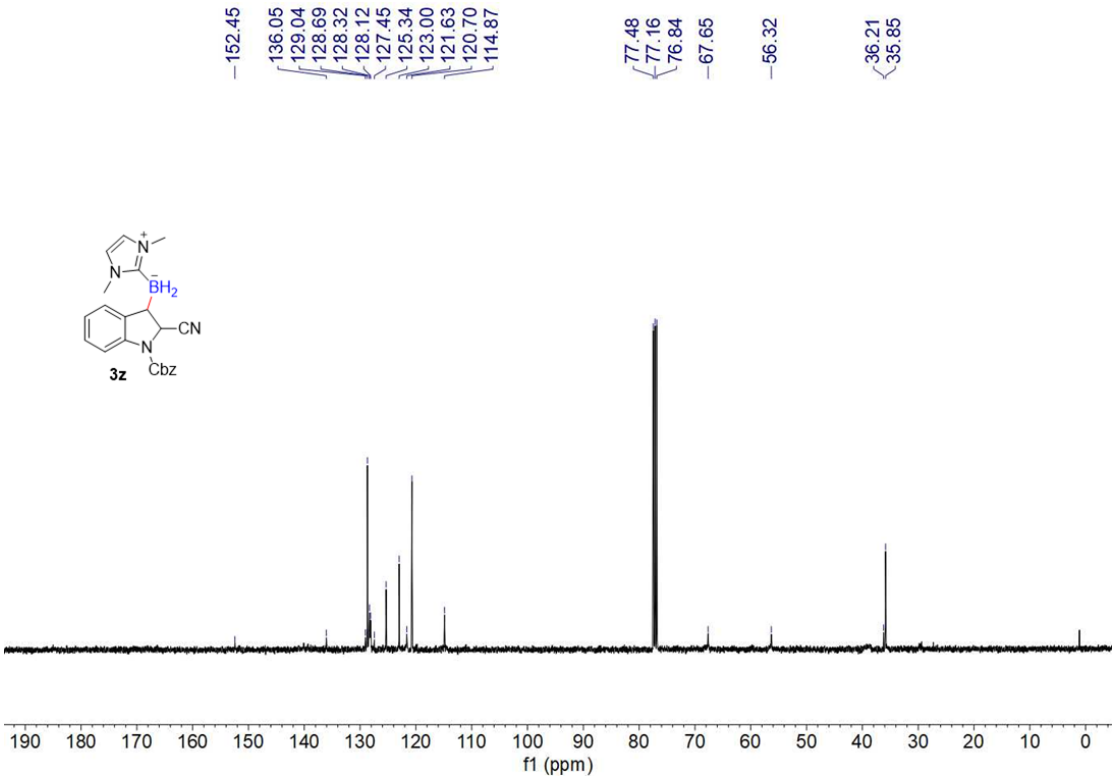

Fig. S61 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3z**.

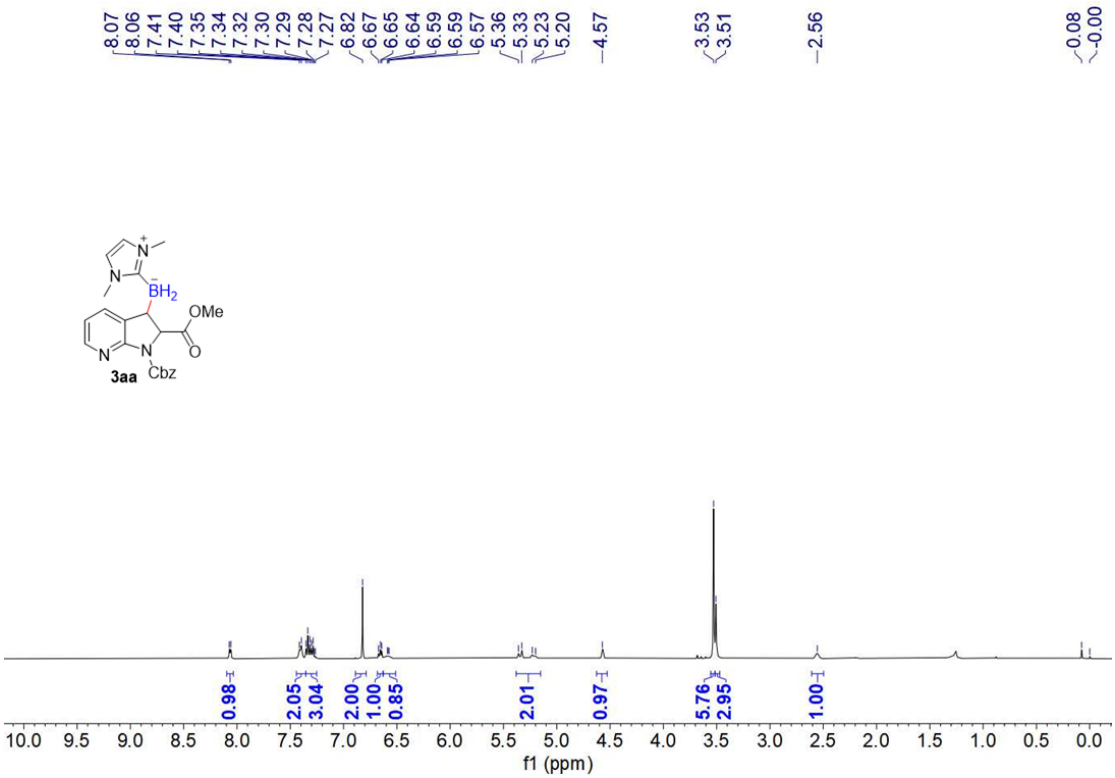

Fig. S62 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3aa**.

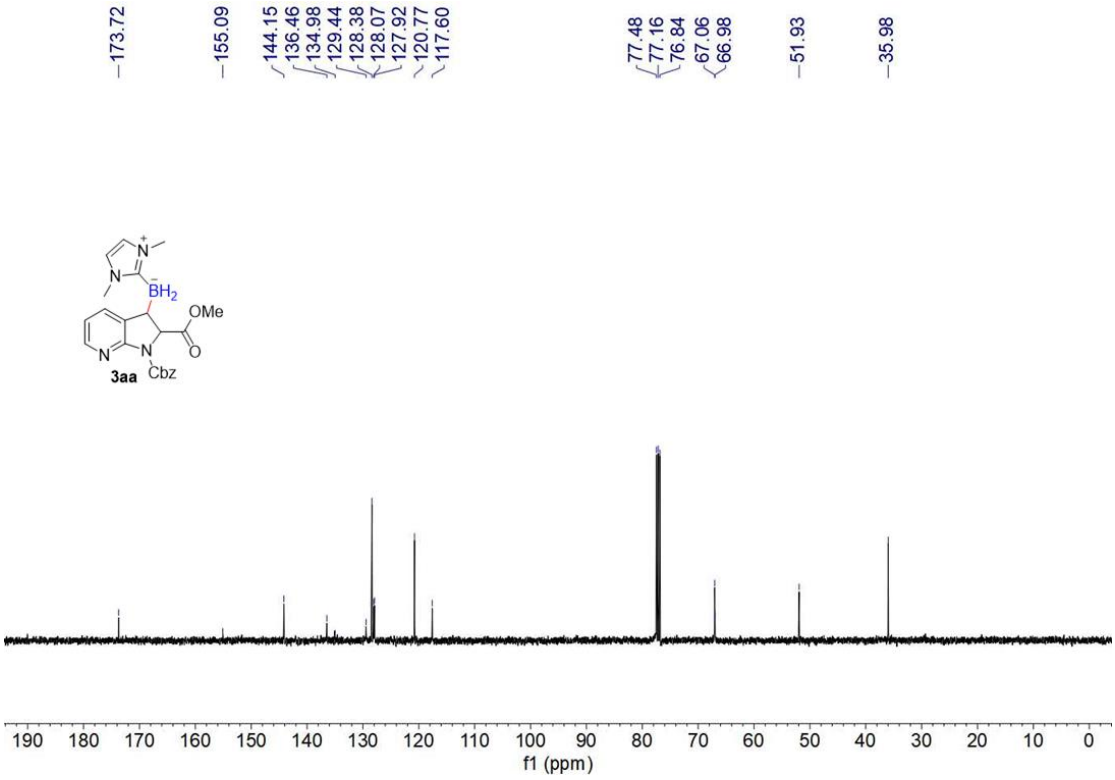

Fig. S63 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3aa**.

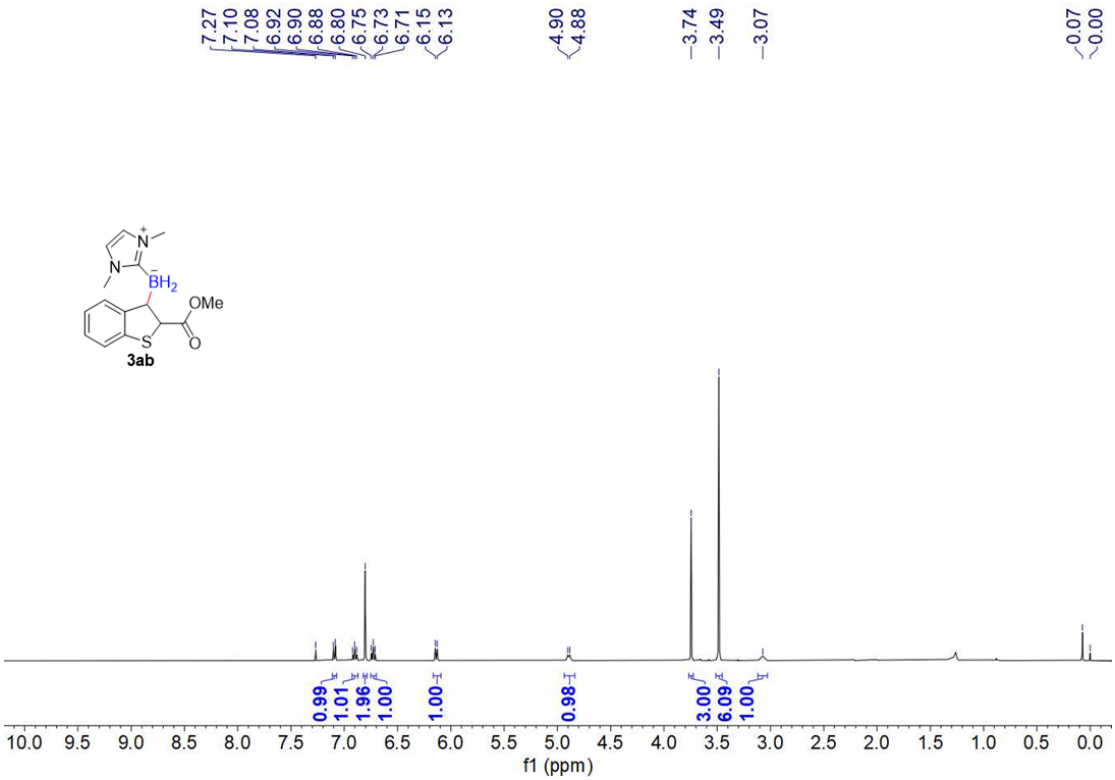

Fig. S64 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ab**.

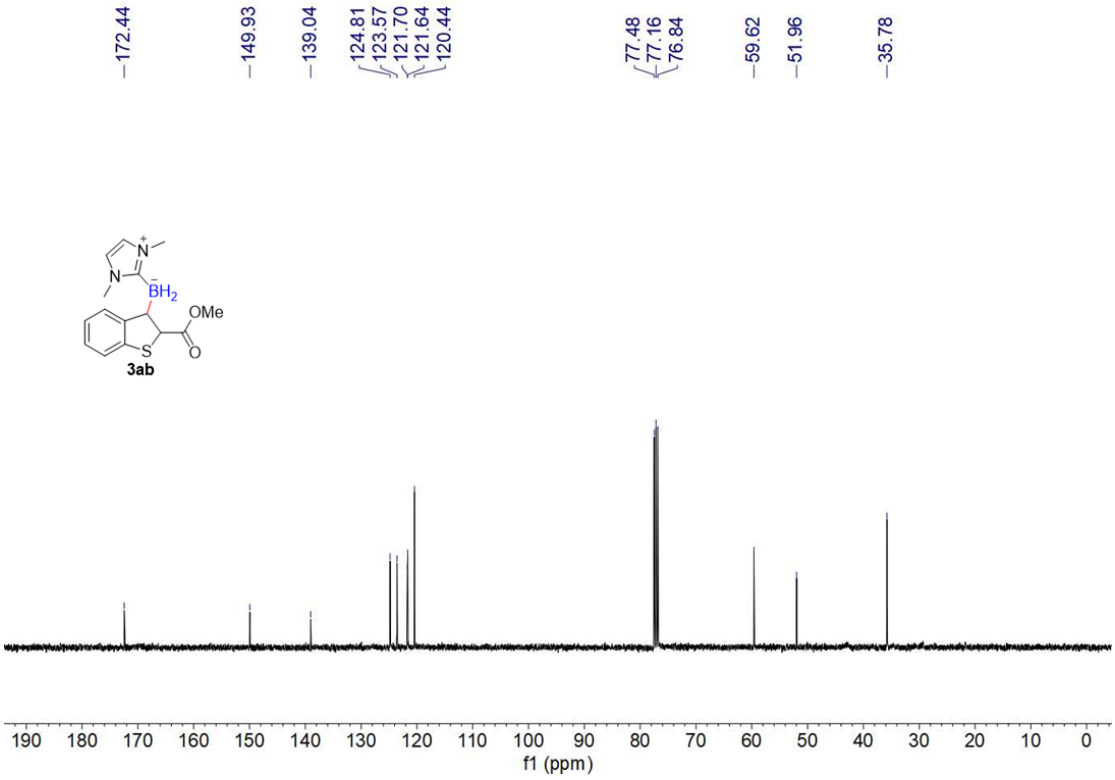

Fig. S65 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ab**.

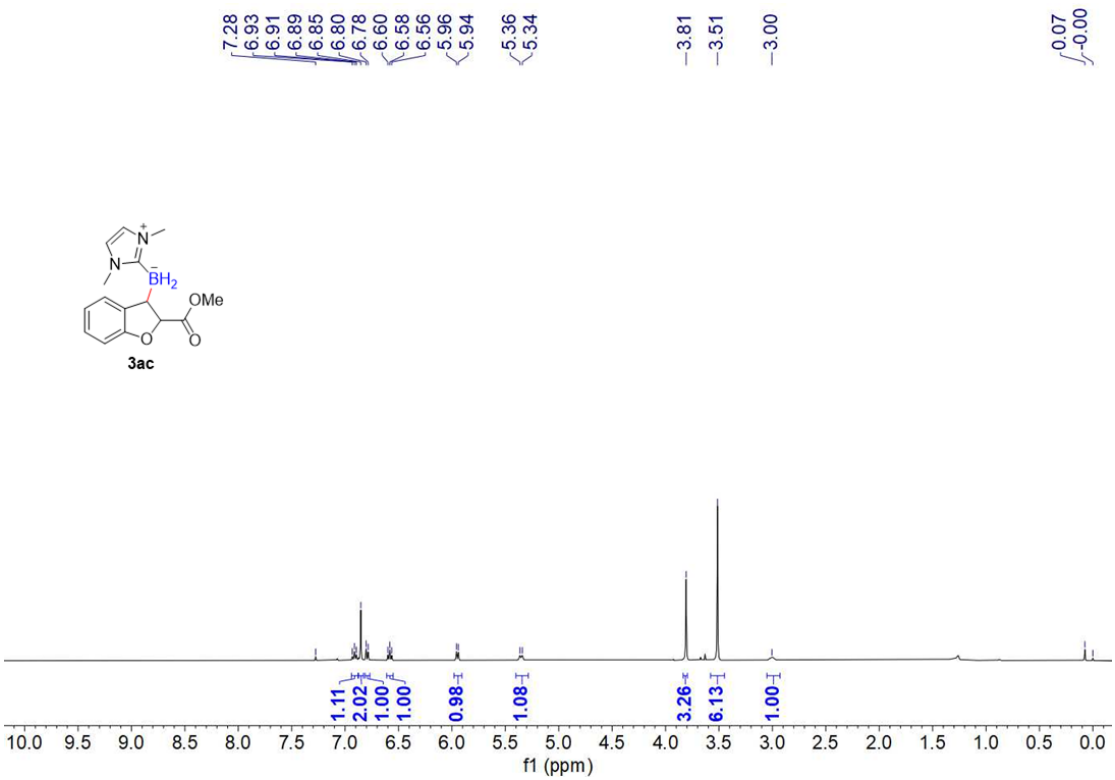

Fig. S66 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ac**.

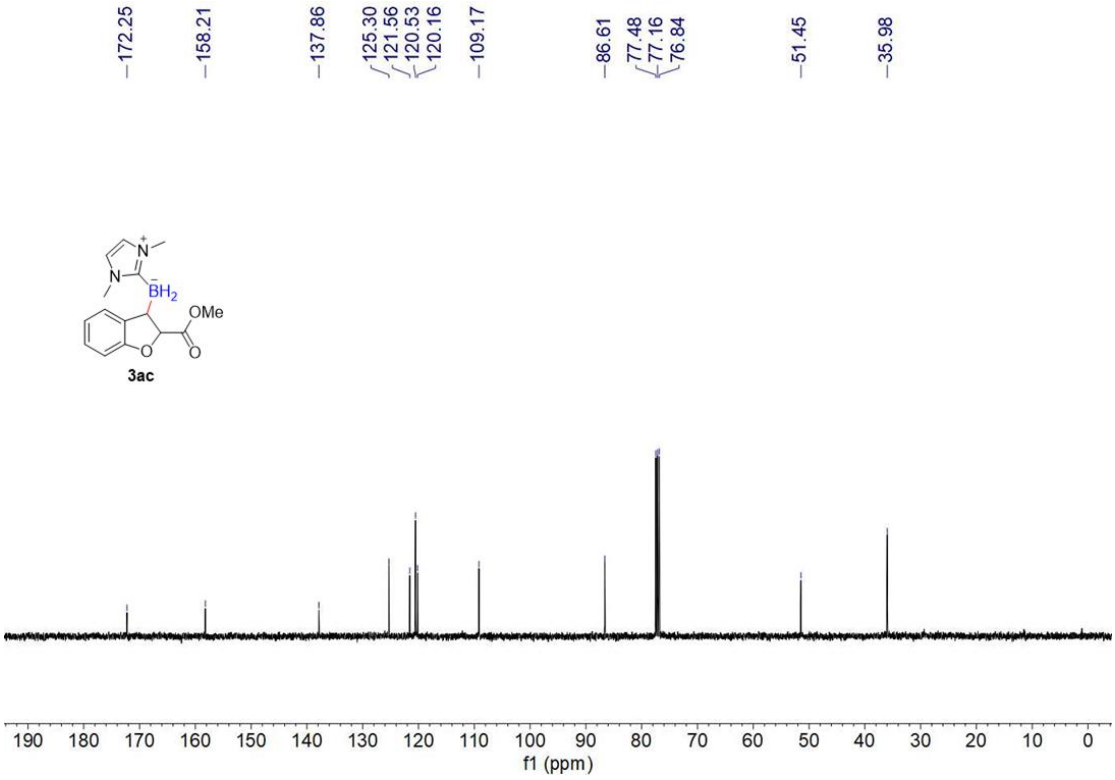

Fig. S67 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ac**.

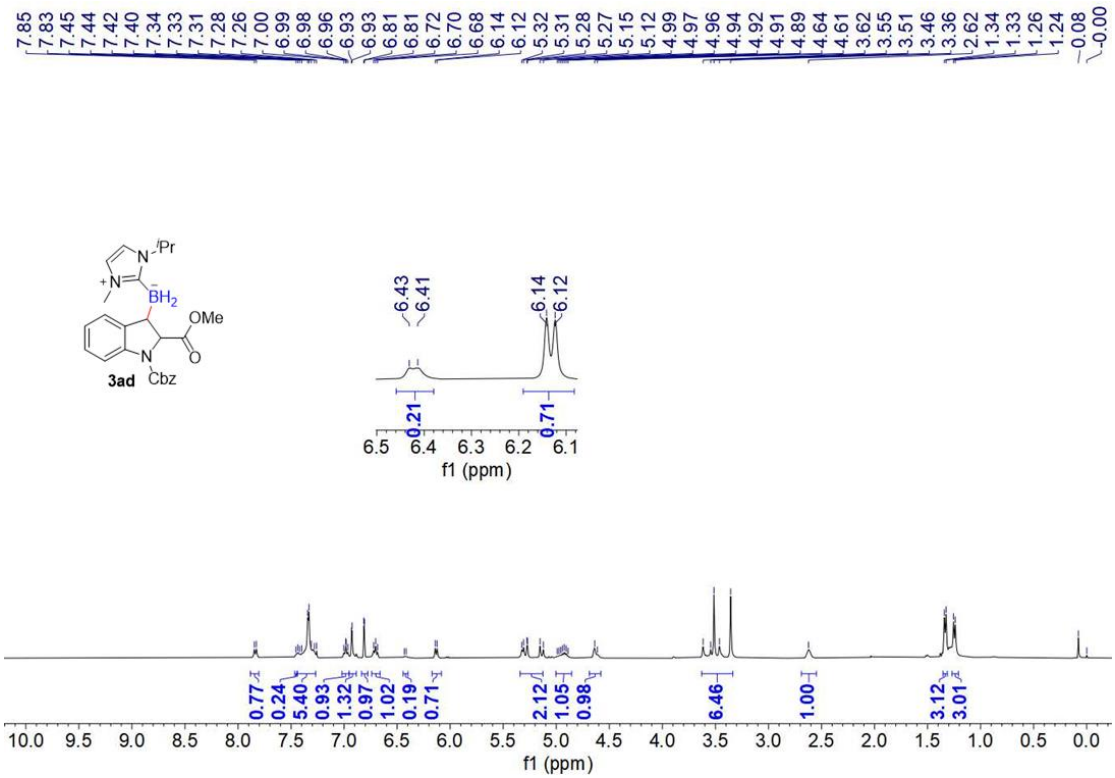

Fig. S68 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ad**.

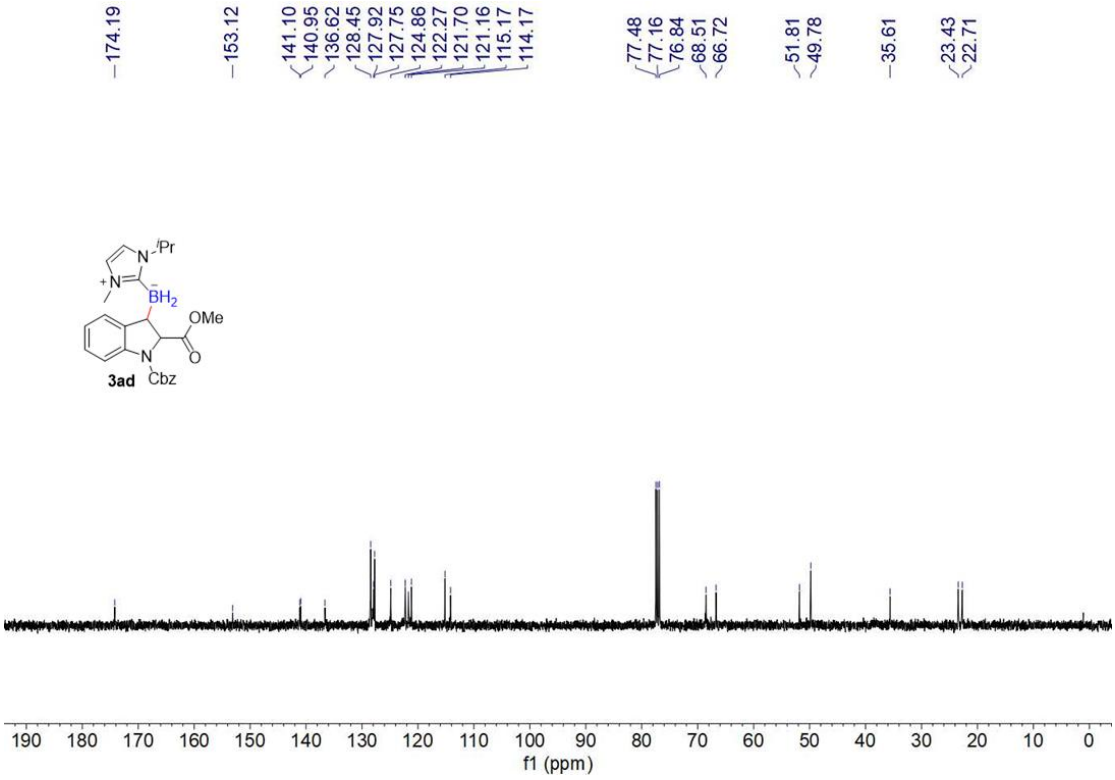

Fig. S69 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ad**.

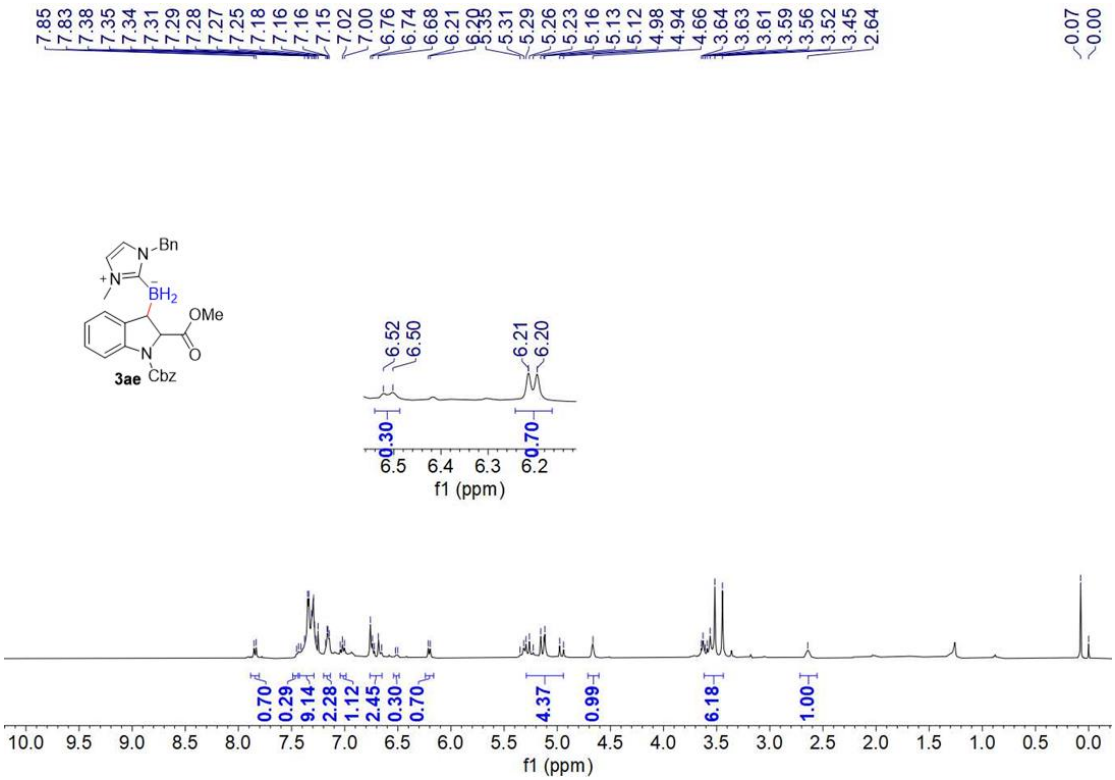

Fig. S70 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ae**.

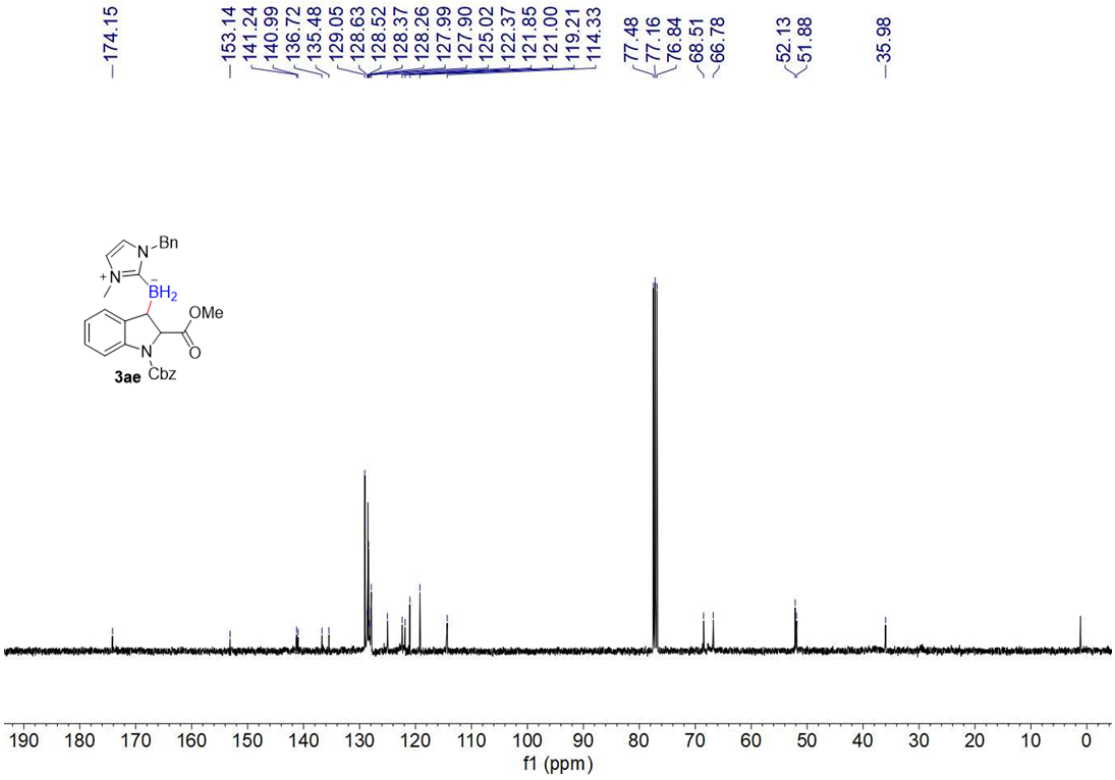

Fig. S71 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ae**.

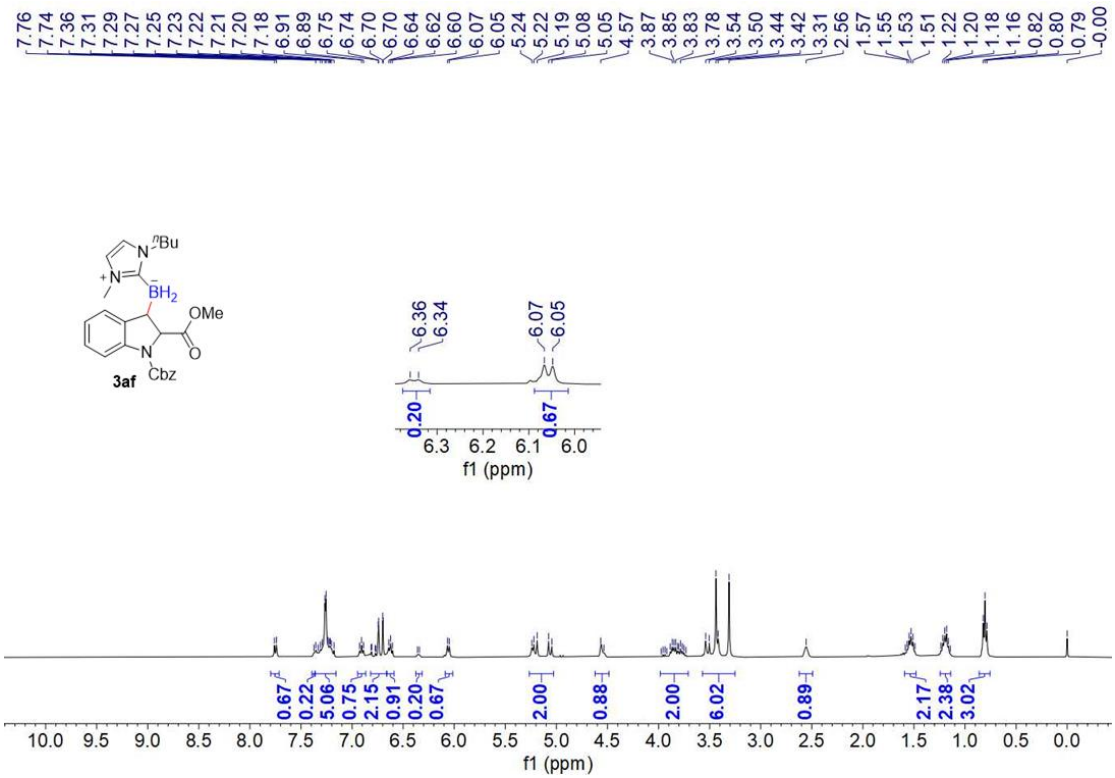

Fig. S72 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3af**.

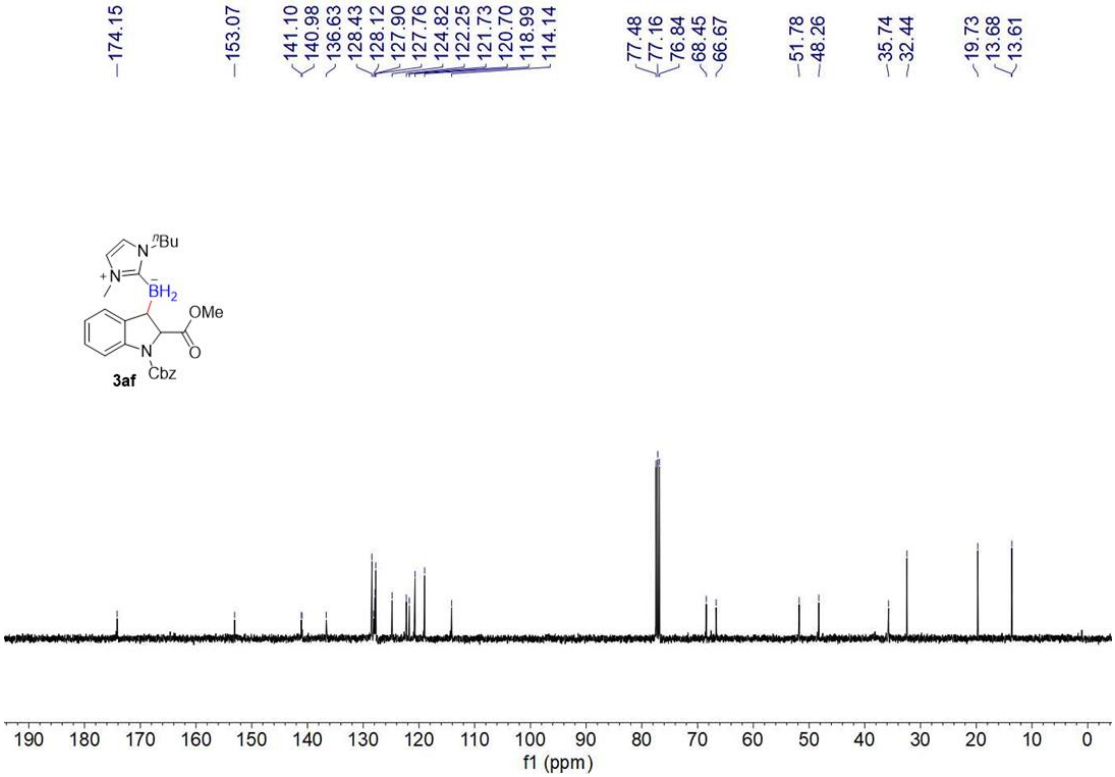

Fig. S73 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3af**.

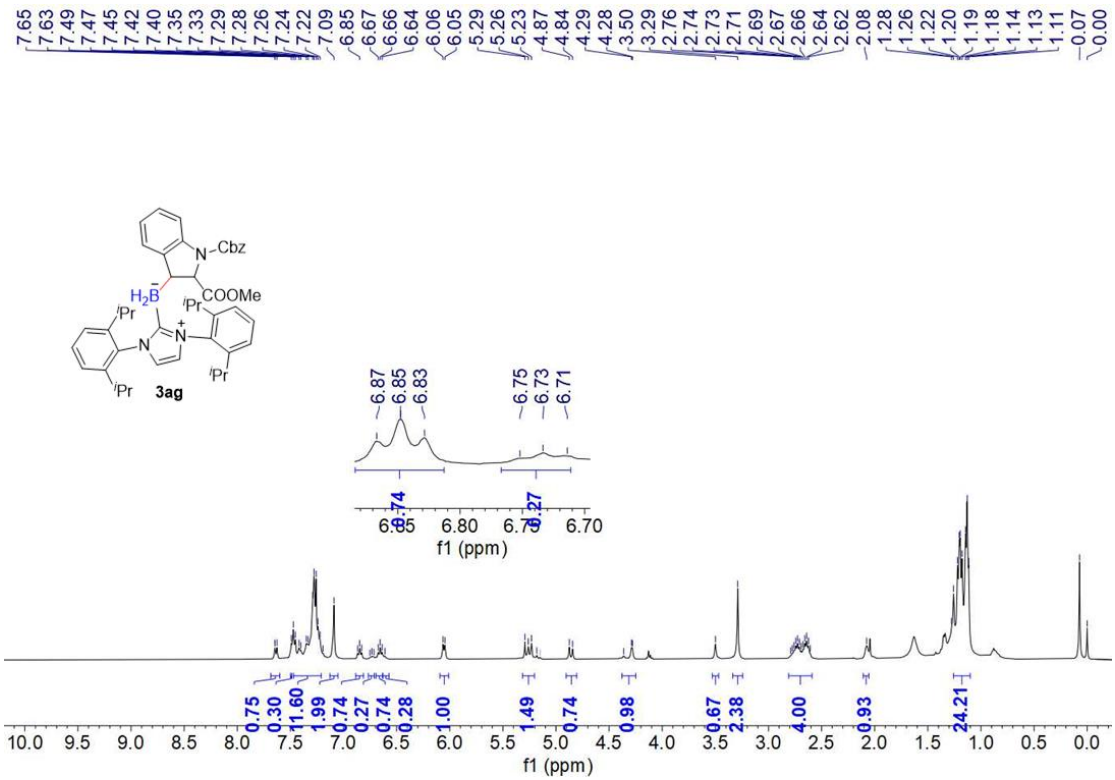

Fig. S74 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ag**.

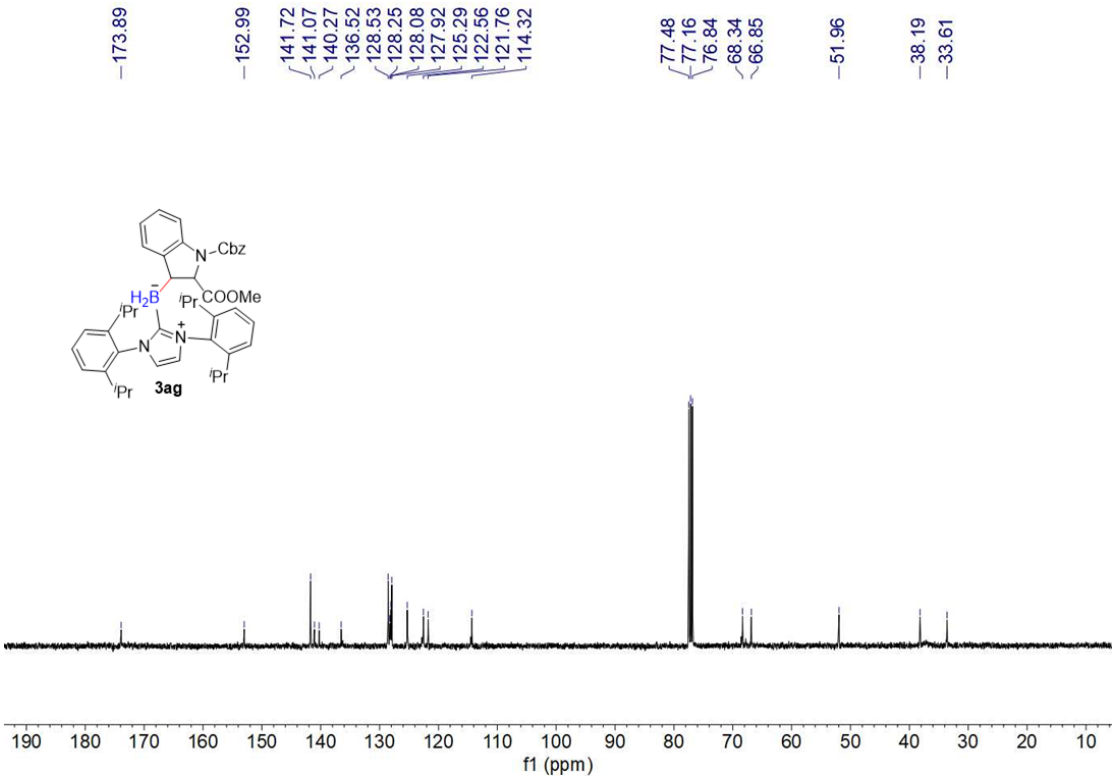

Fig. S75 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ag**.

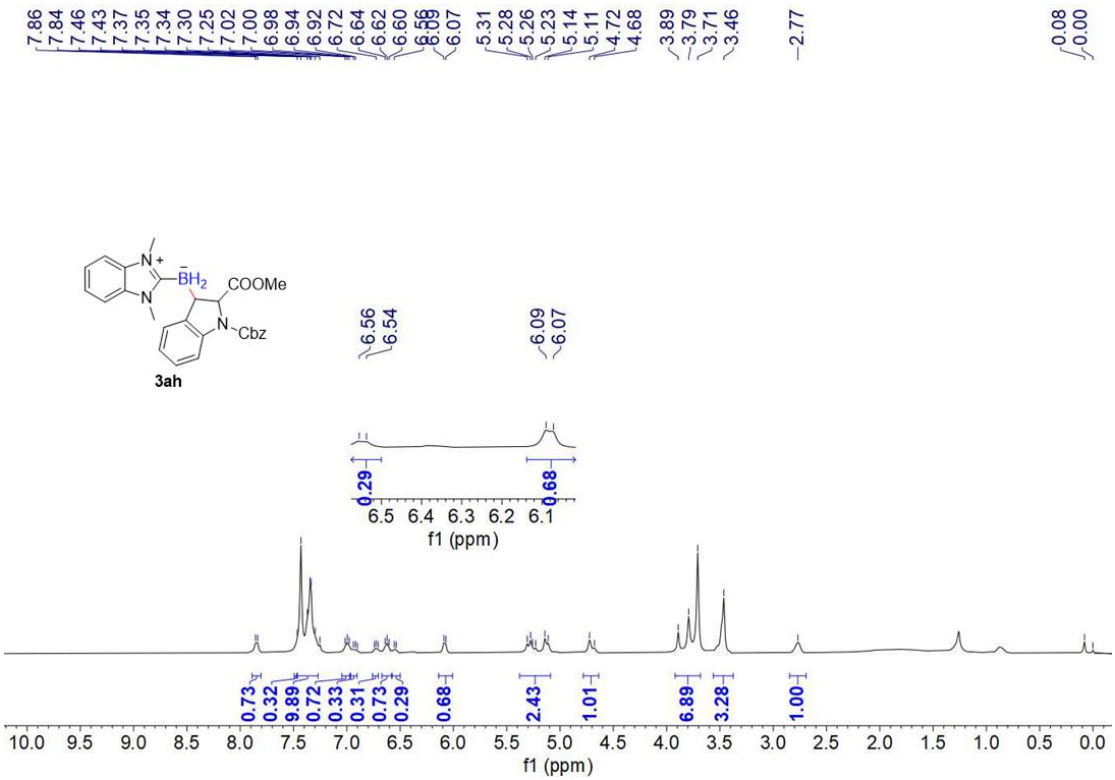

Fig. S76 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ah**.

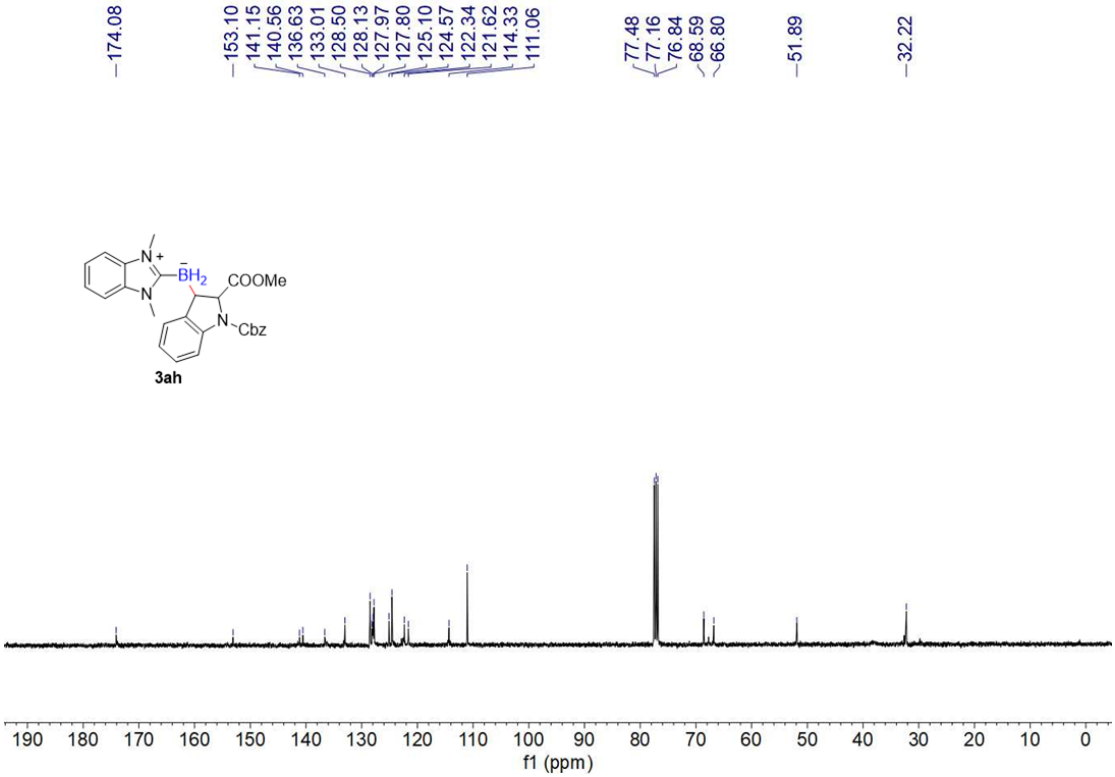

Fig. S77 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ah**.

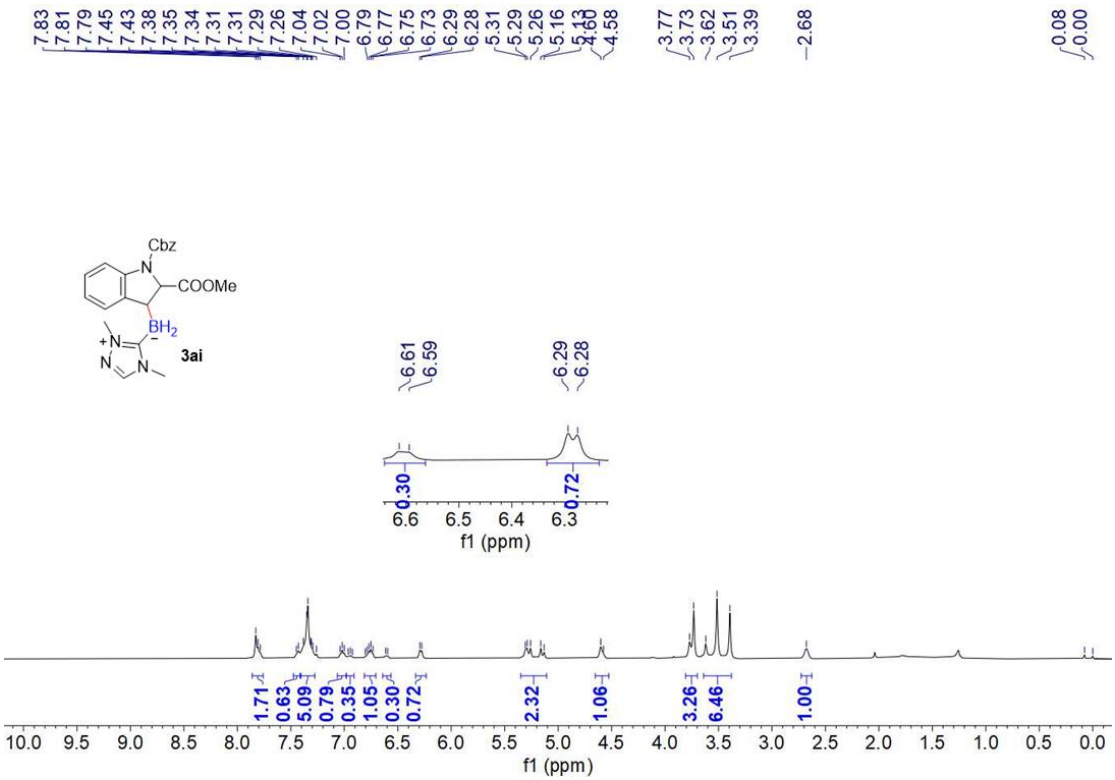

Fig. S78 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3ai**.

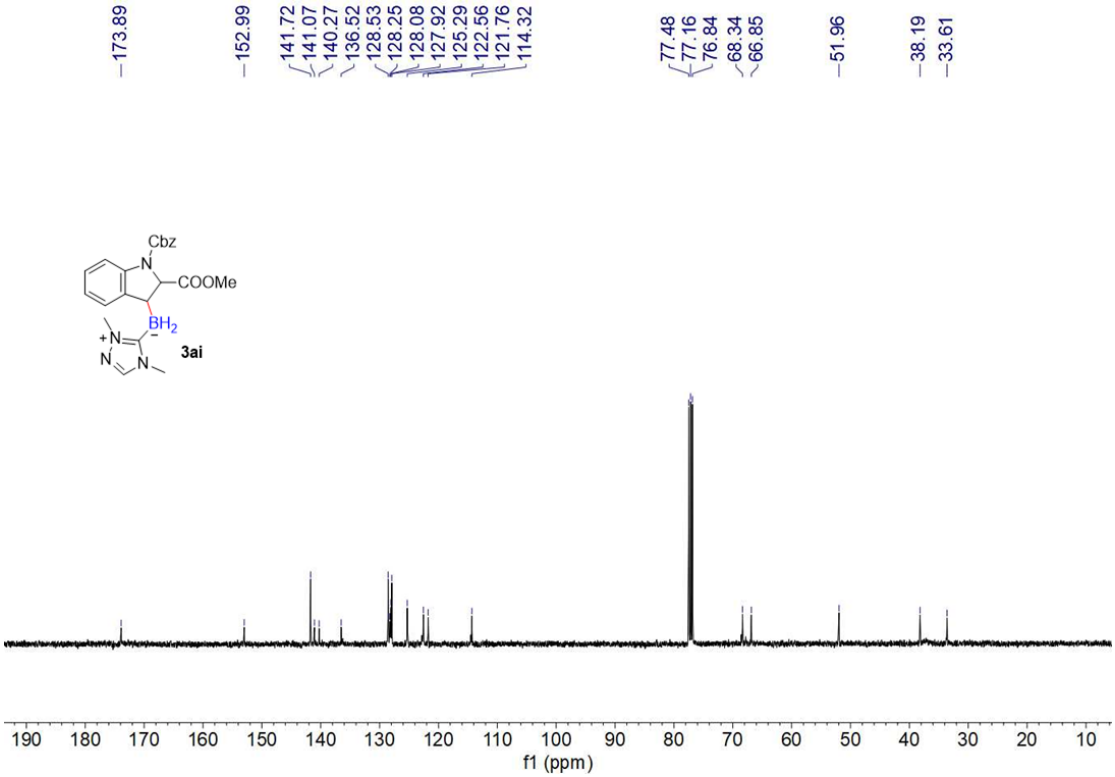

Fig. S79 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **3ai**.

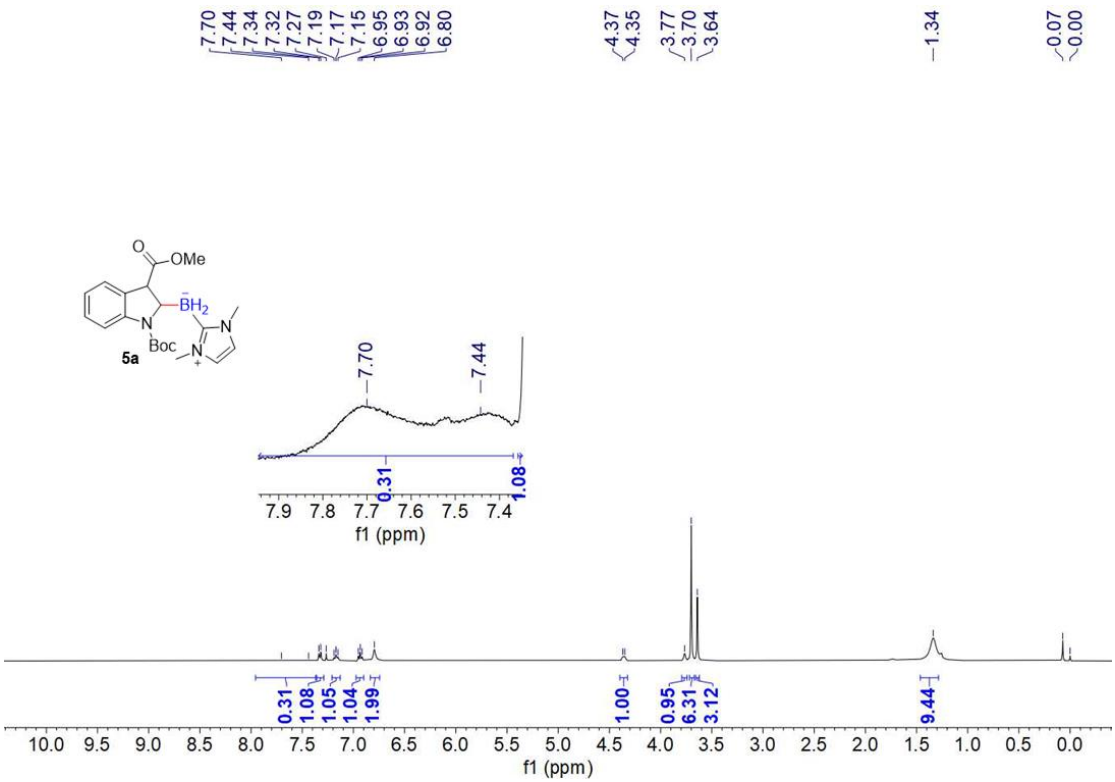

Fig. S80 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5a**.

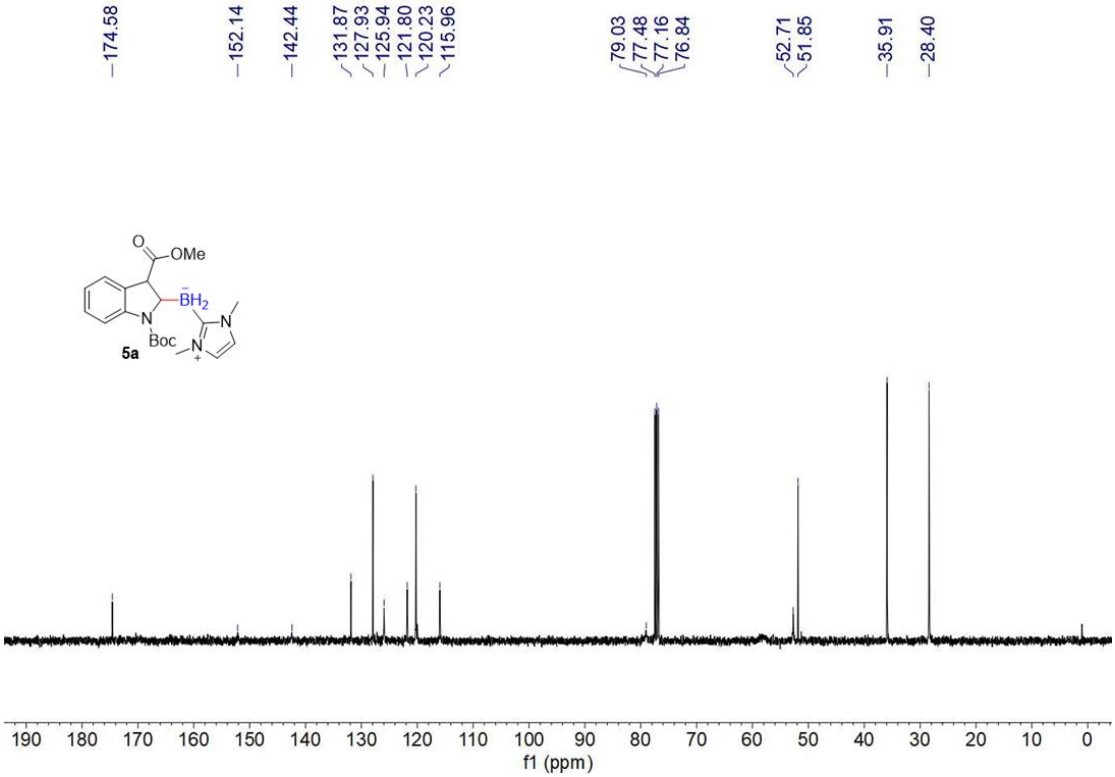

Fig. S81 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5a**.

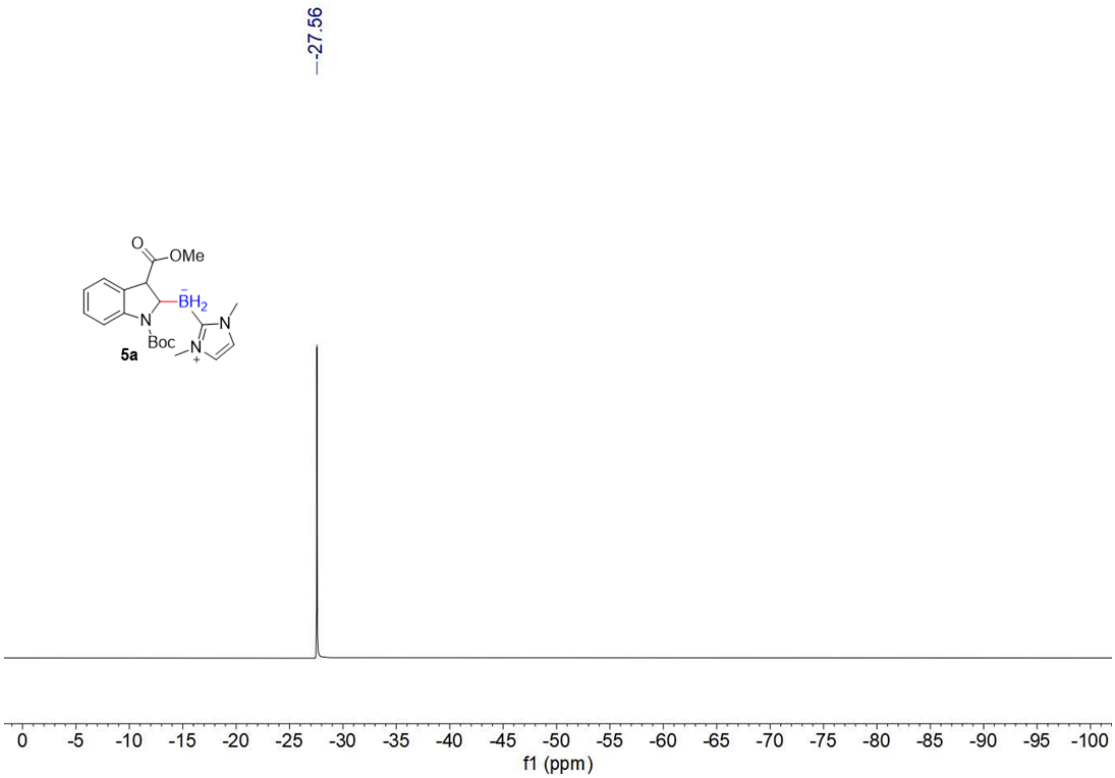

Fig. S82 ^{11}B NMR (128 MHz, $CDCl_3$) spectrum for **5a**.

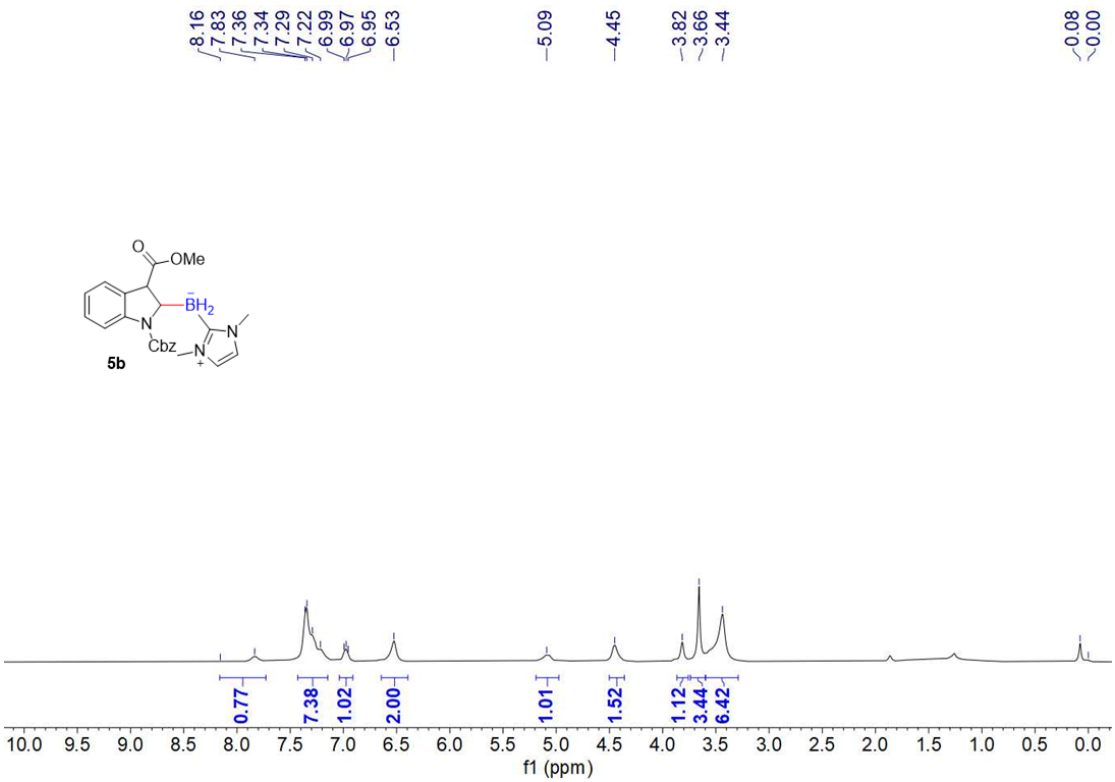

Fig. S83 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5b**.

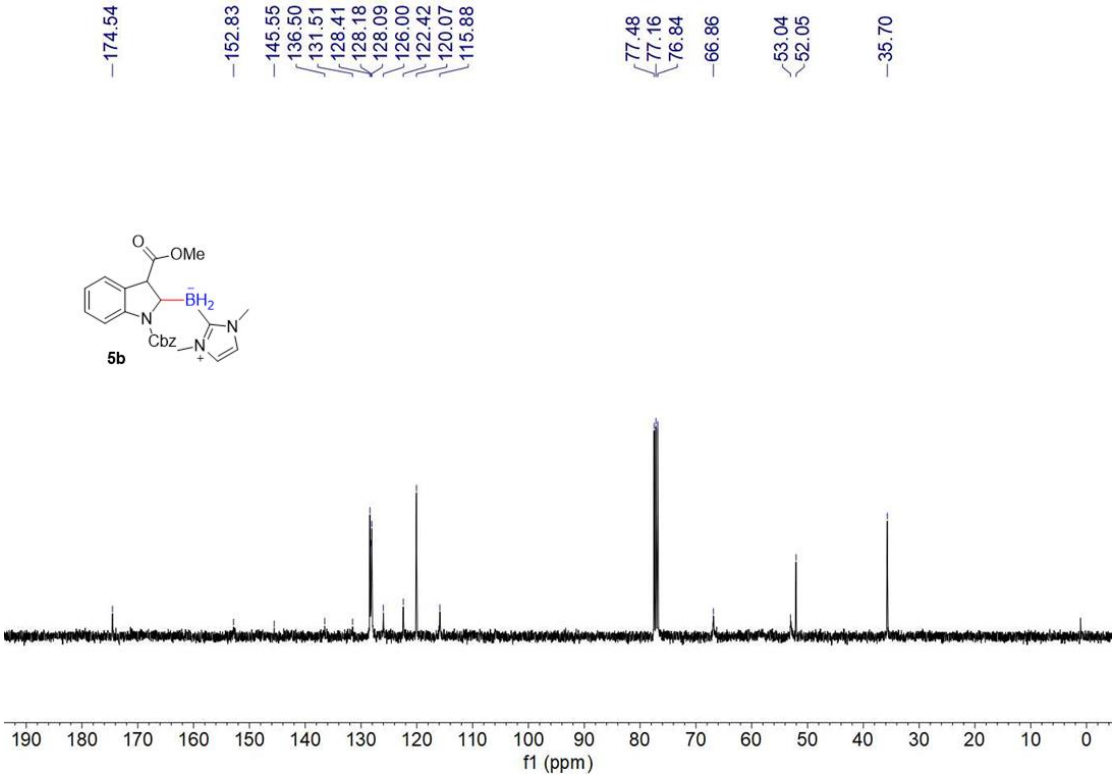

Fig. S84 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5b**.

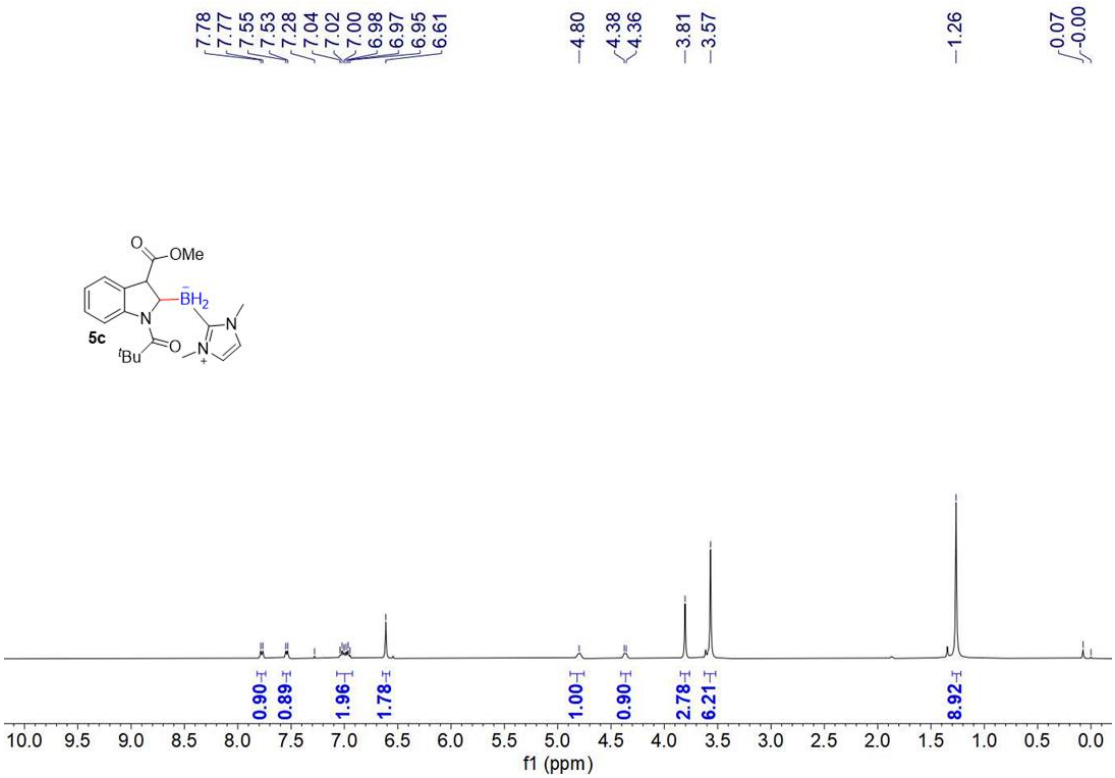

Fig. S85 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5c**.

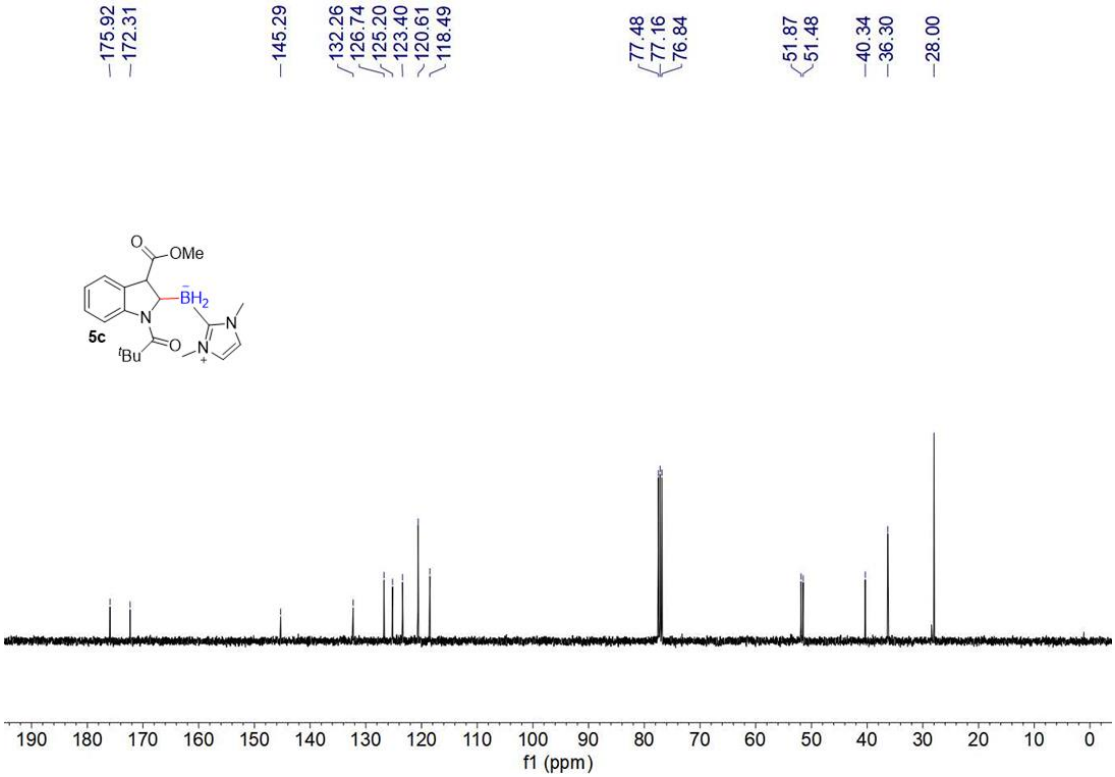

Fig. S86 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5c**.

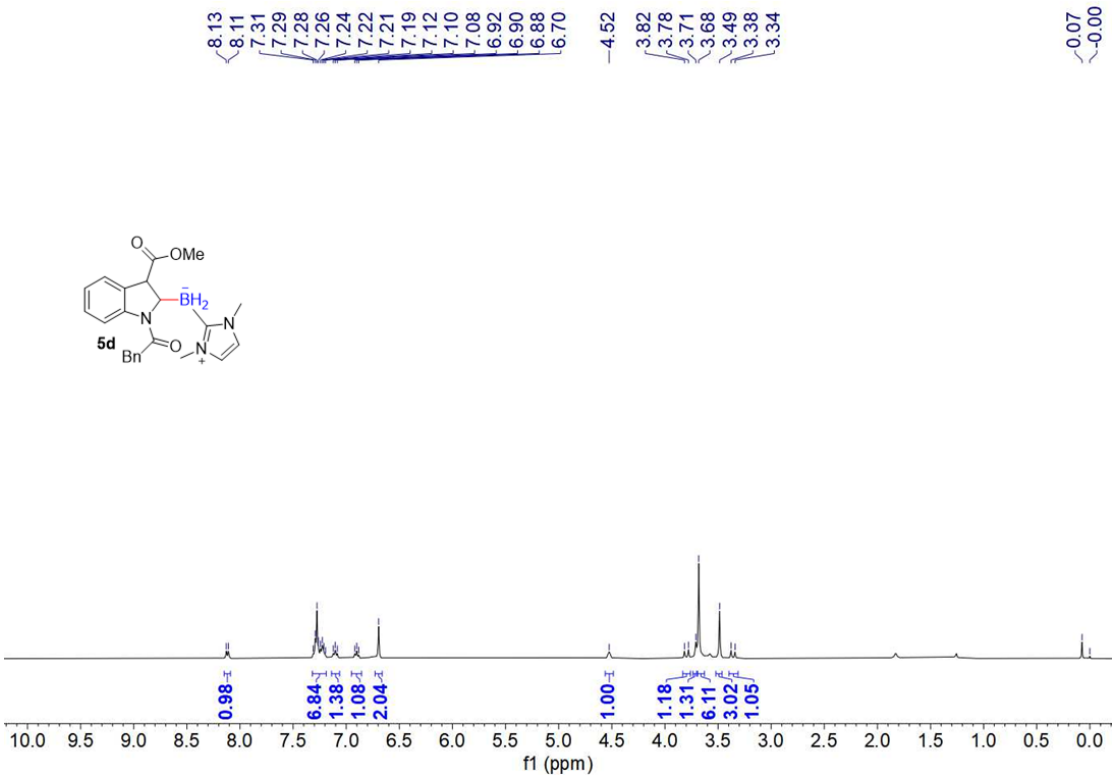

Fig. S87 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5d**.

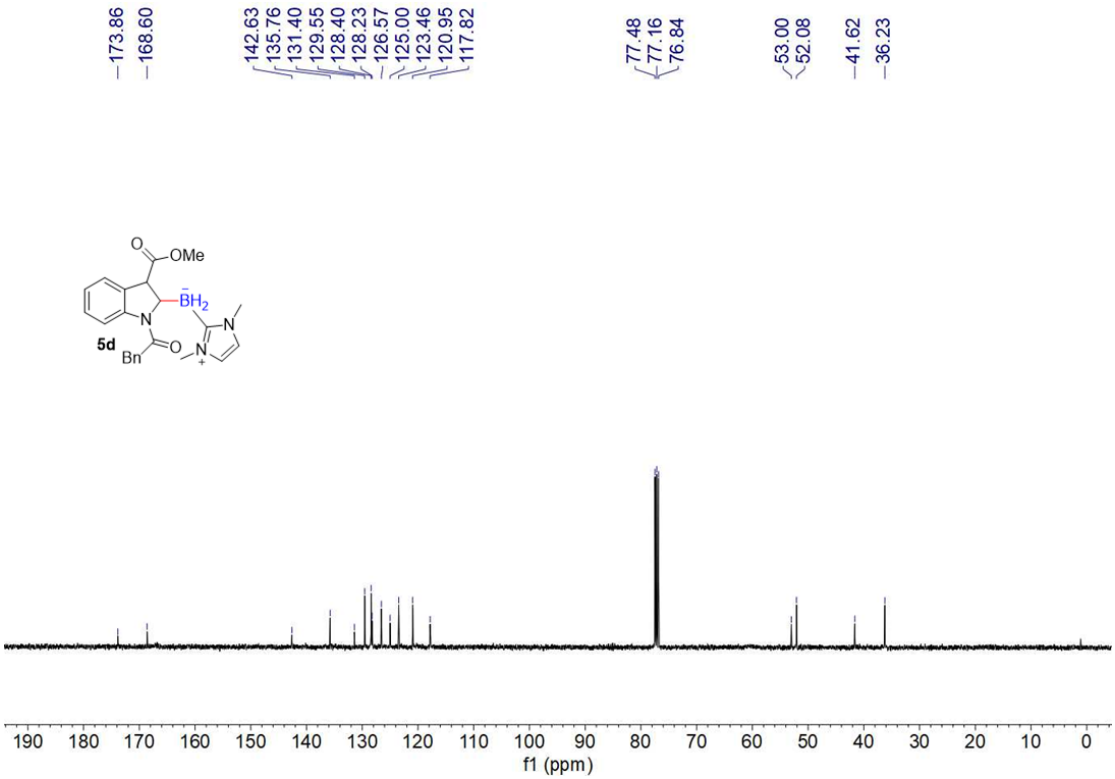

Fig. S88 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5d**.

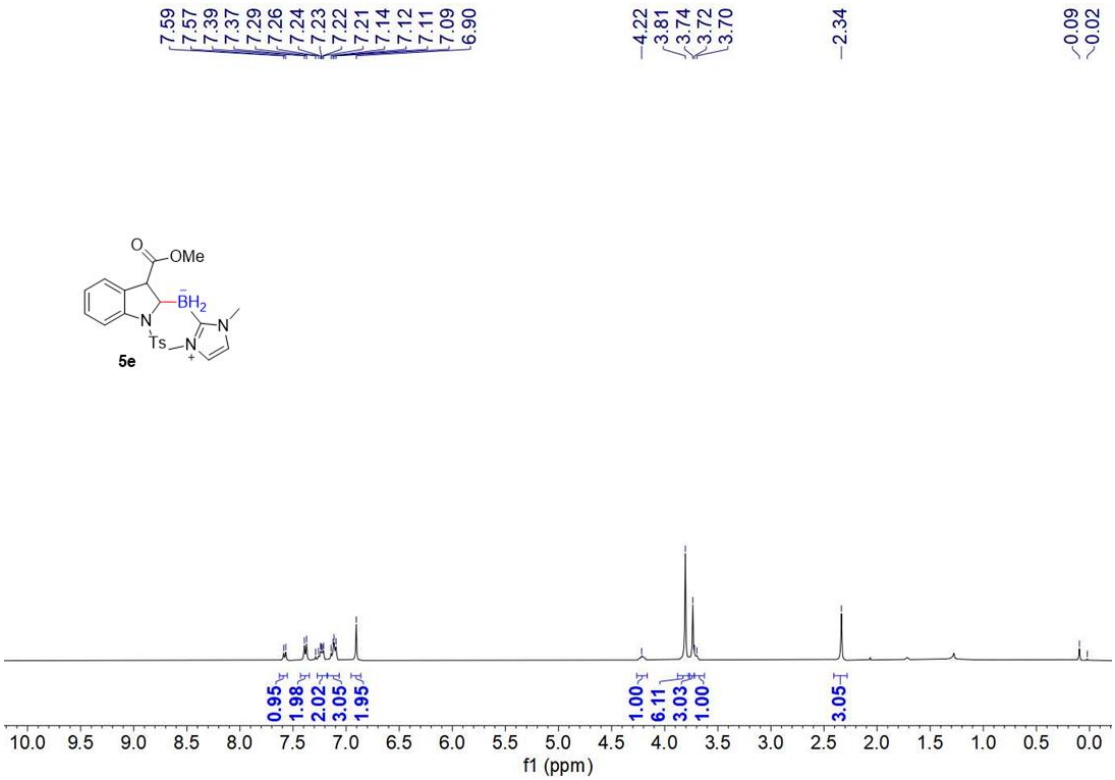

Fig. S89 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5e**.

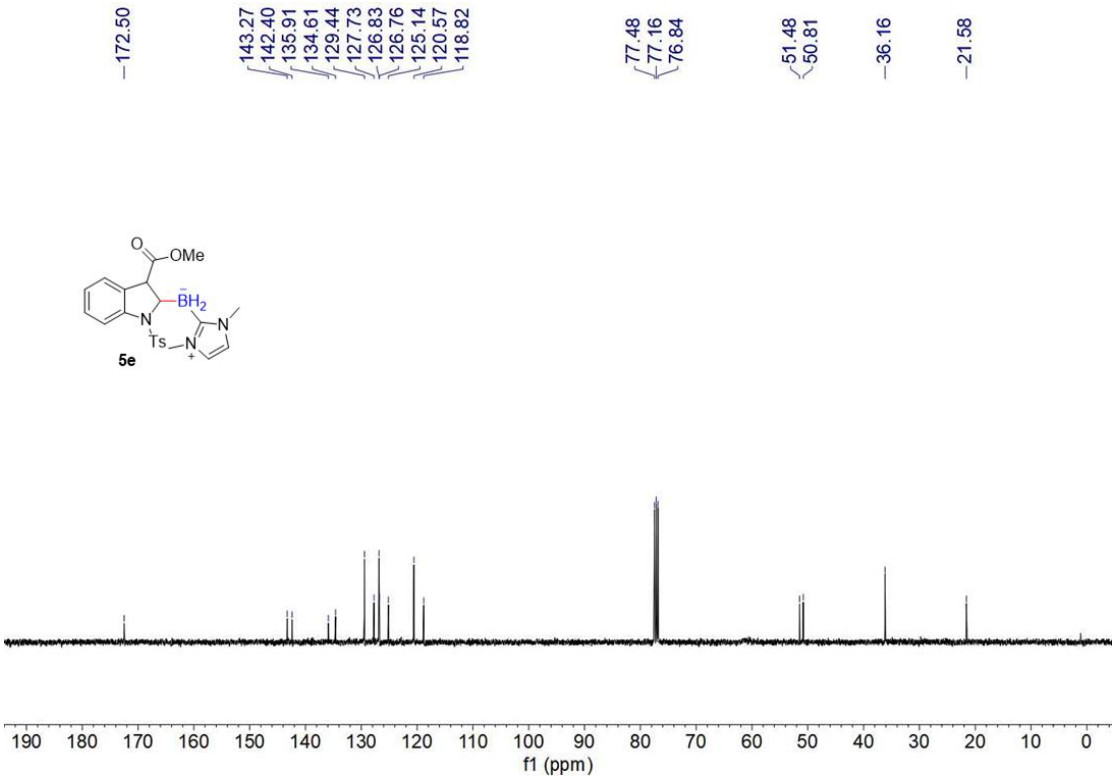

Fig. S90 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5e**.

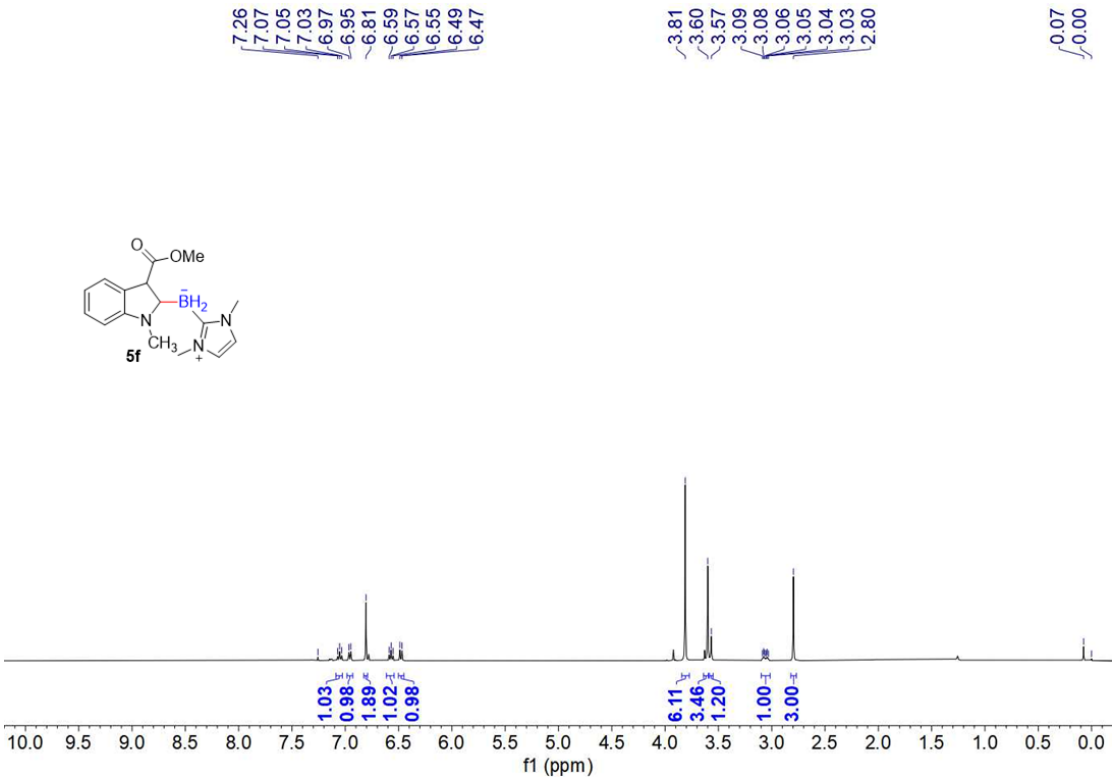

Fig. S91 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5f**.

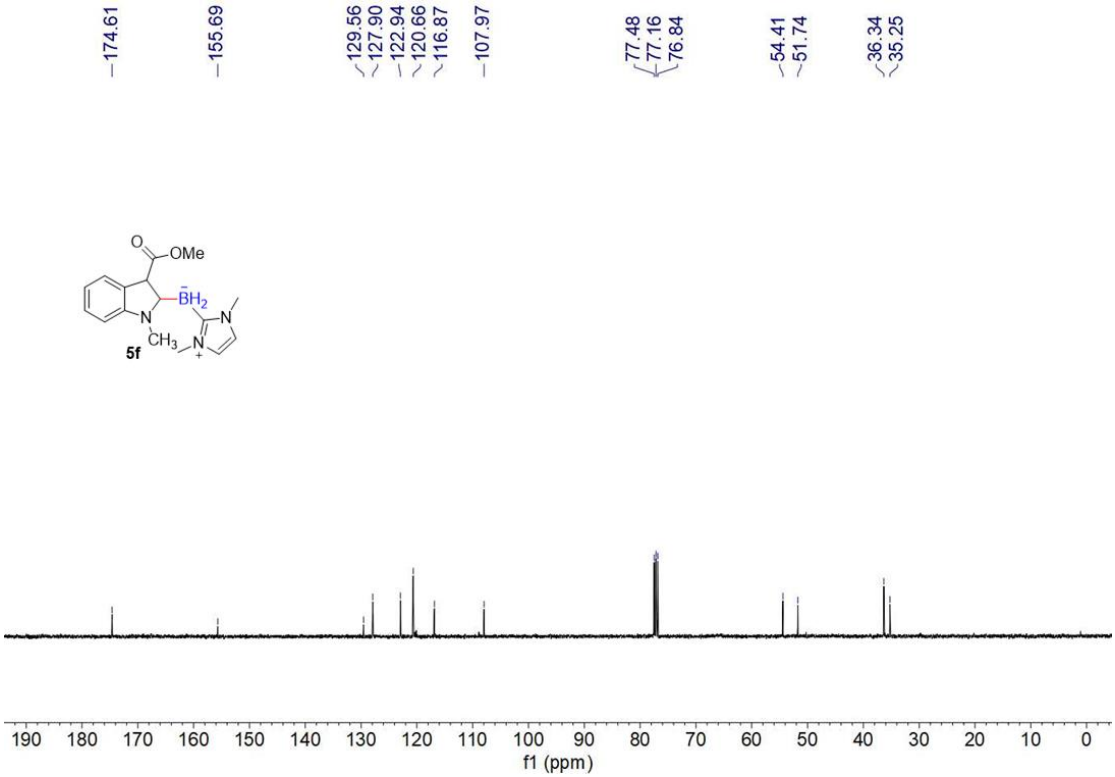

Fig. S92 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5f**.

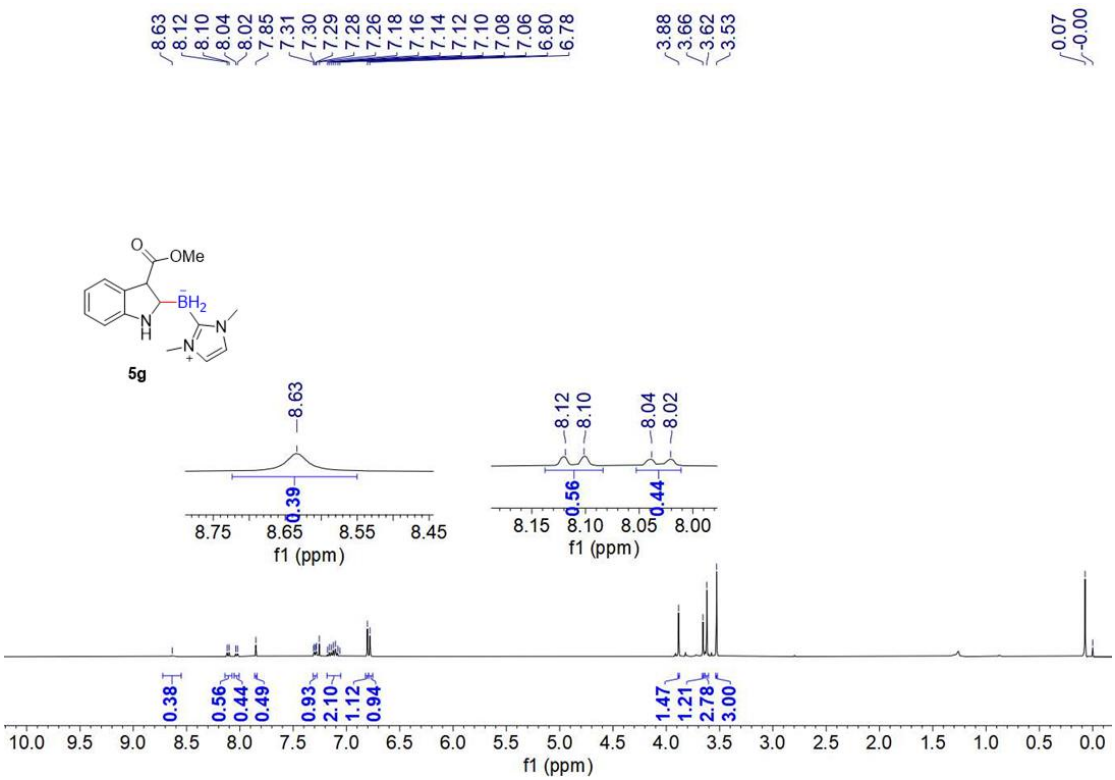

Fig. S93 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5g**.

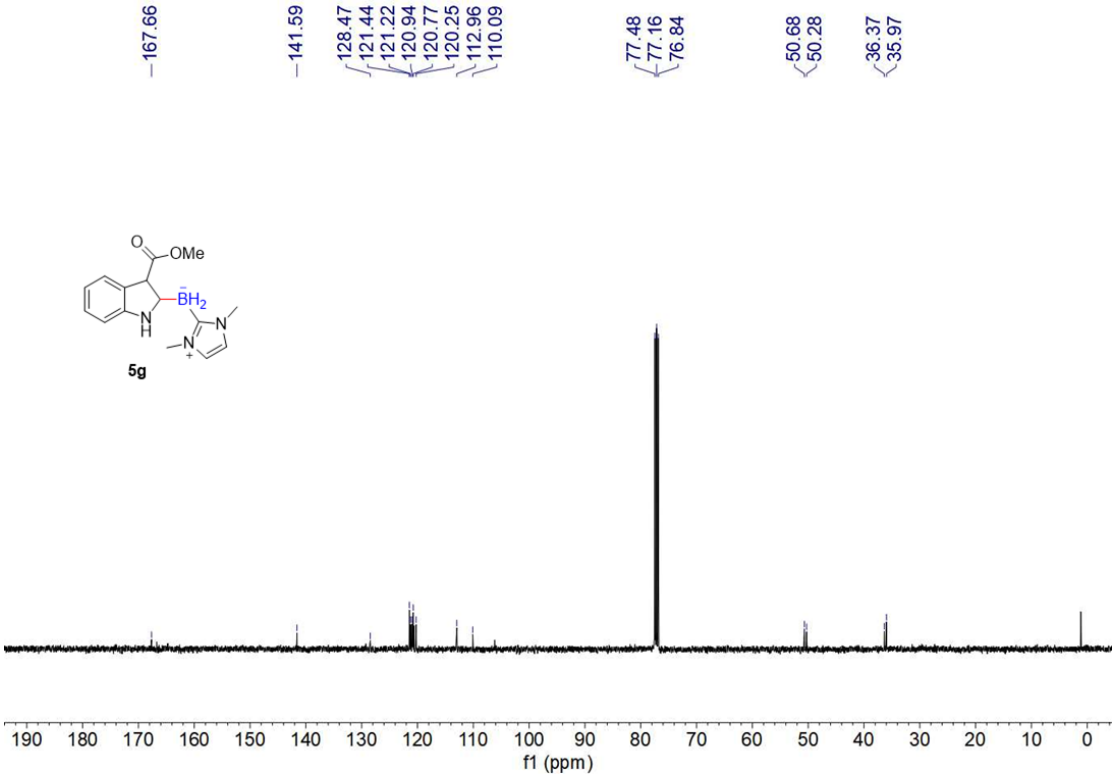

Fig. S94 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5g**.

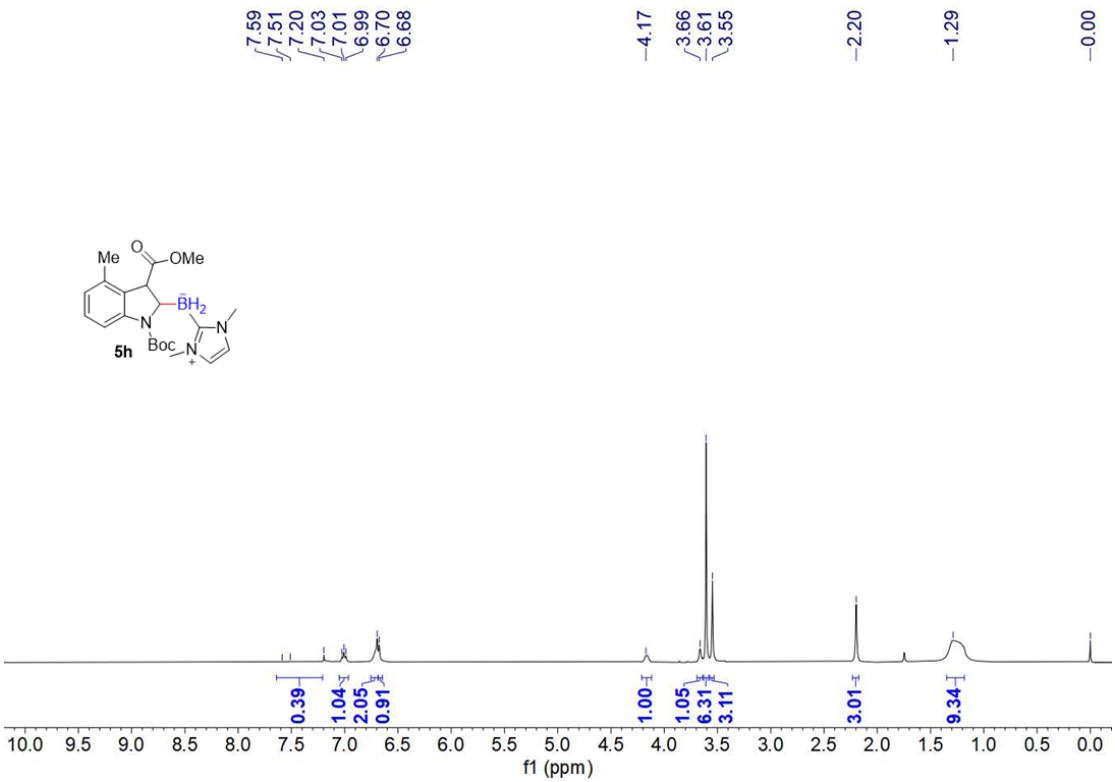

Fig. S95 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5h**.

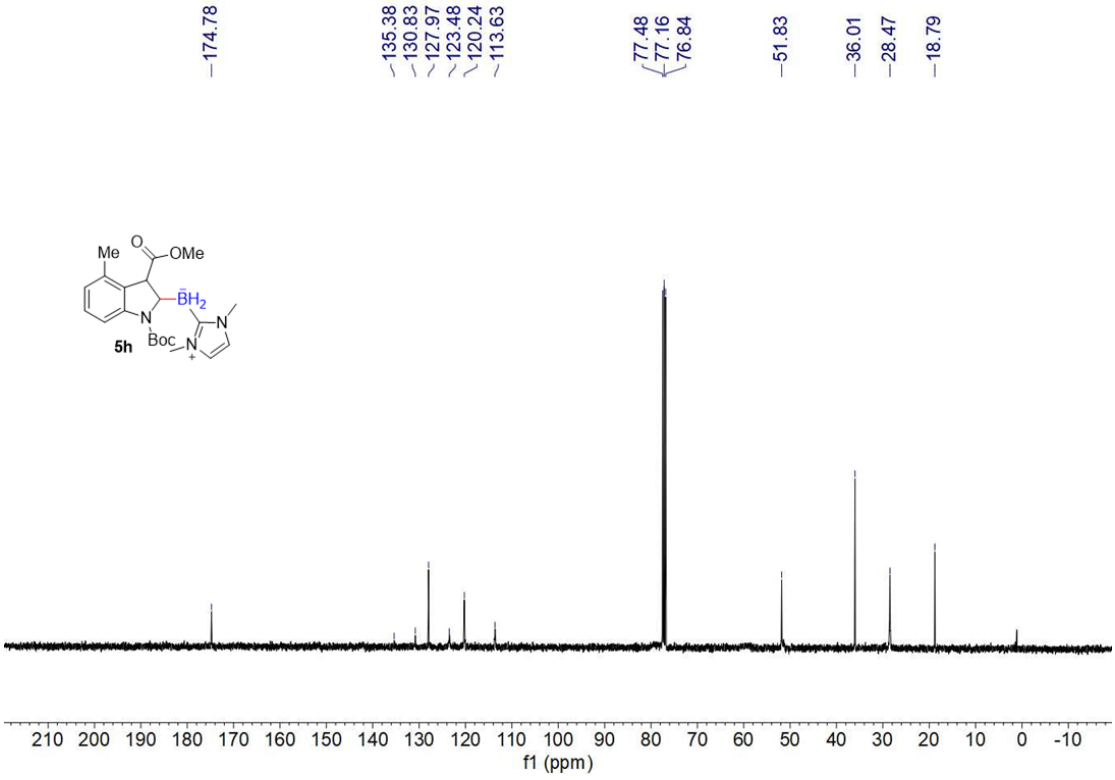

Fig. S96 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5h**.

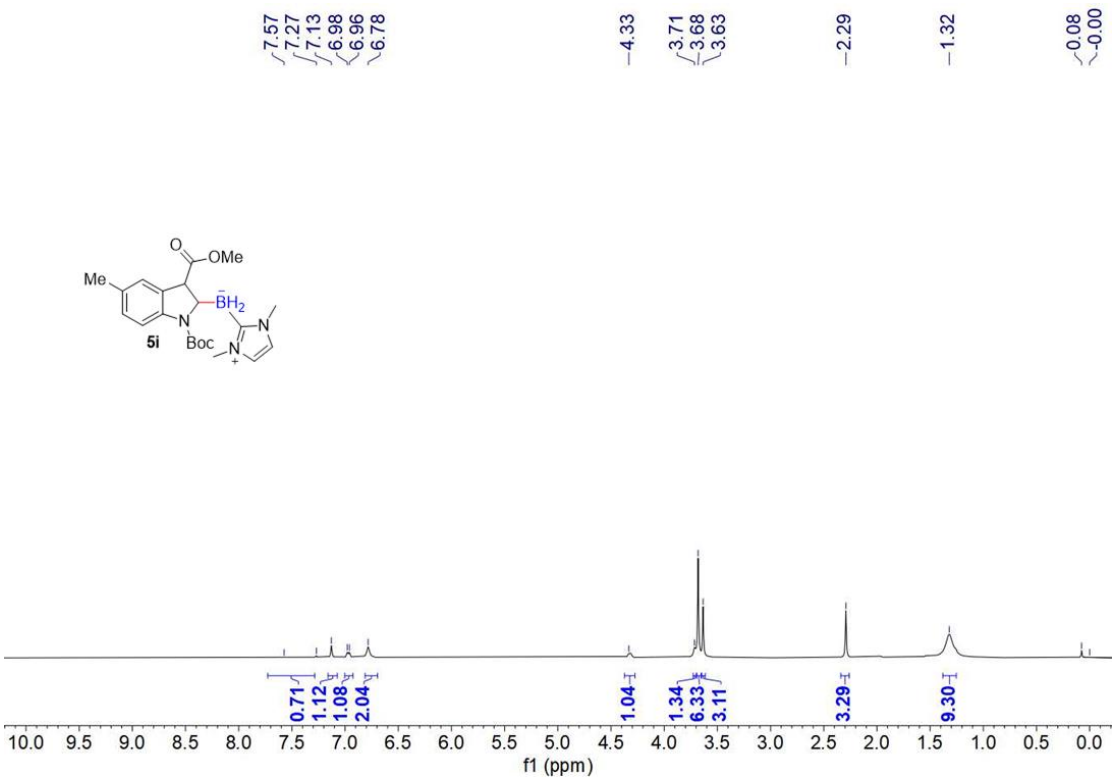

Fig. S97 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5i**.

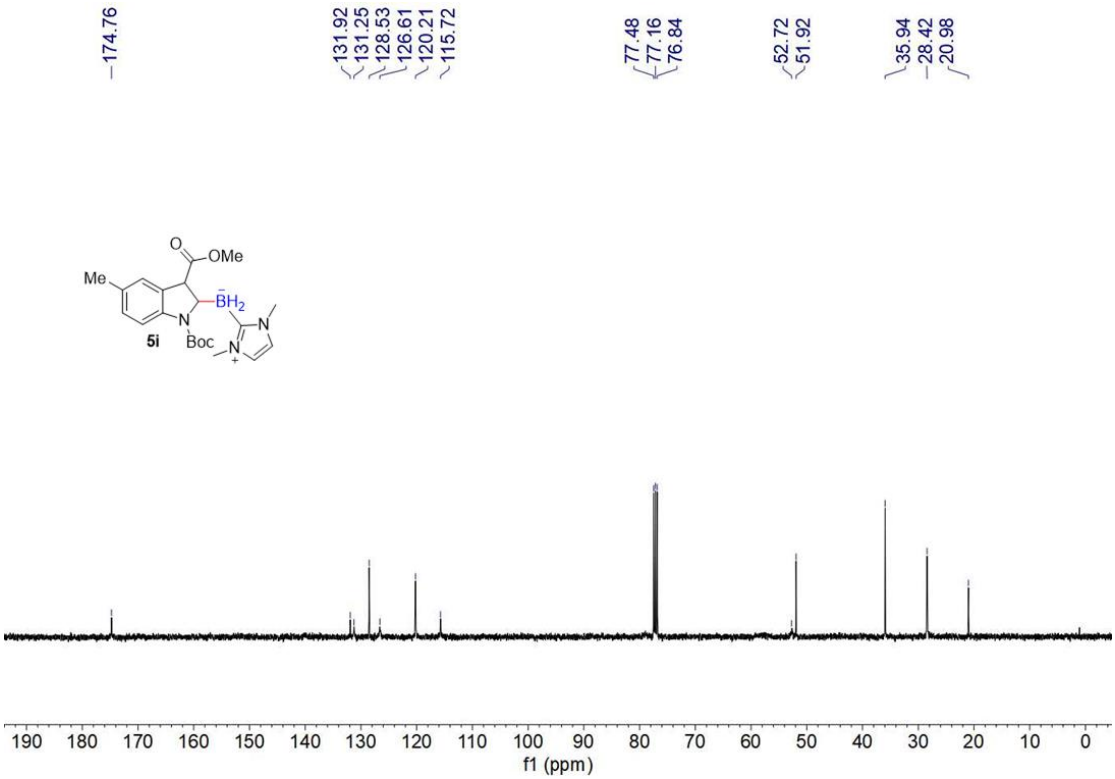

Fig. S98 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5i**.

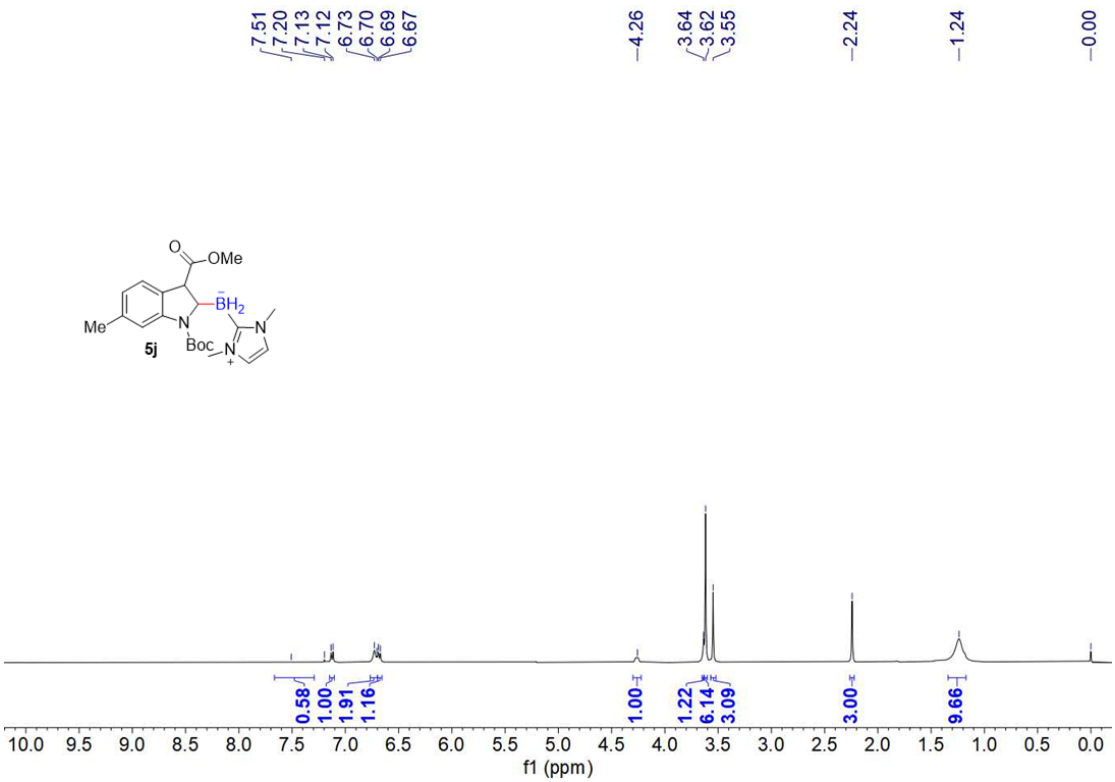

Fig. S99 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5j**.

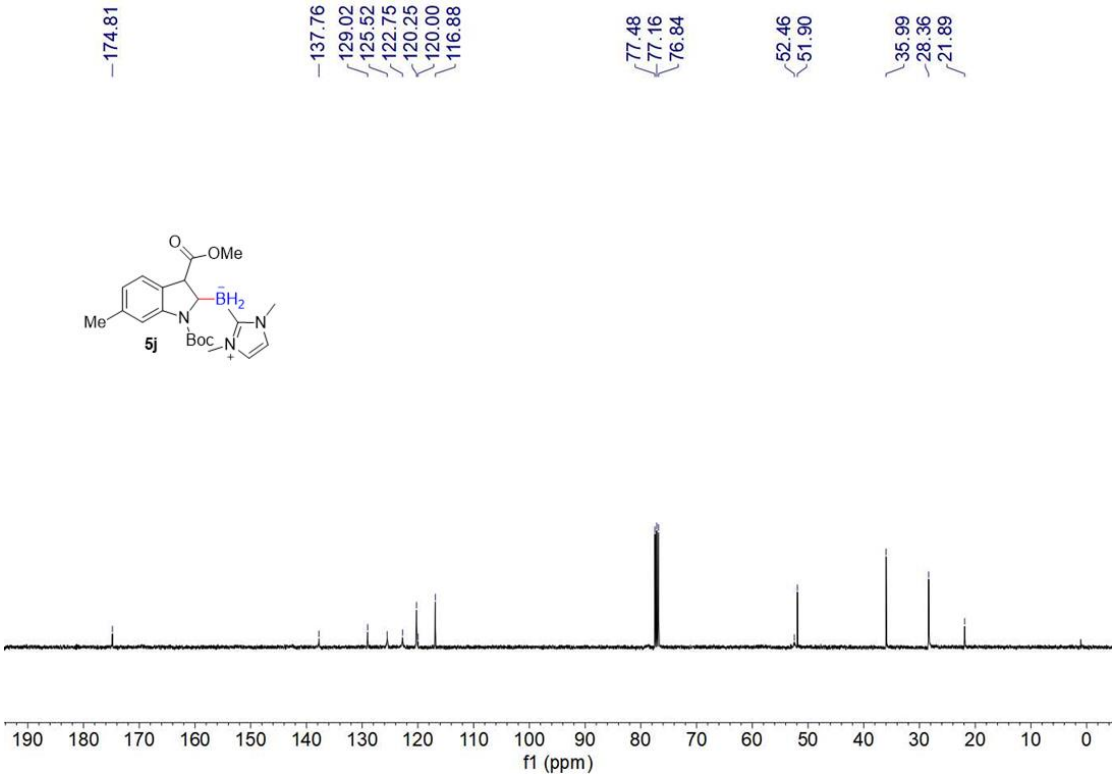

Fig. S100 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5j**.

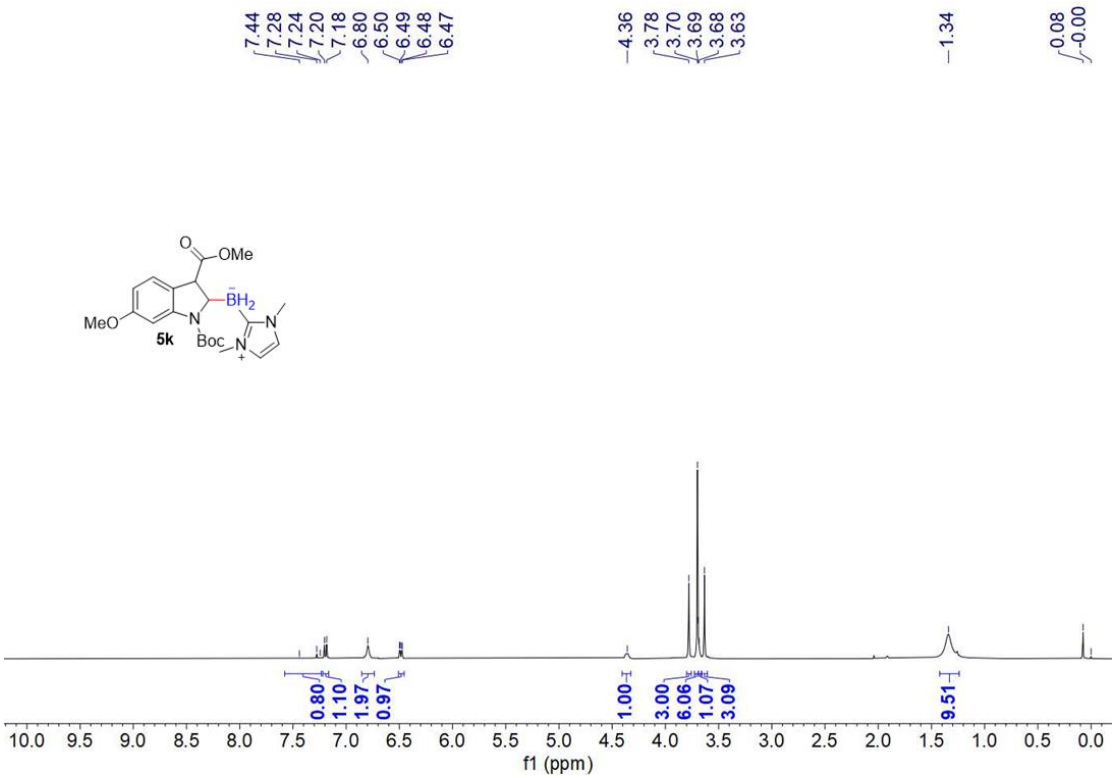

Fig. S101 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5k**.

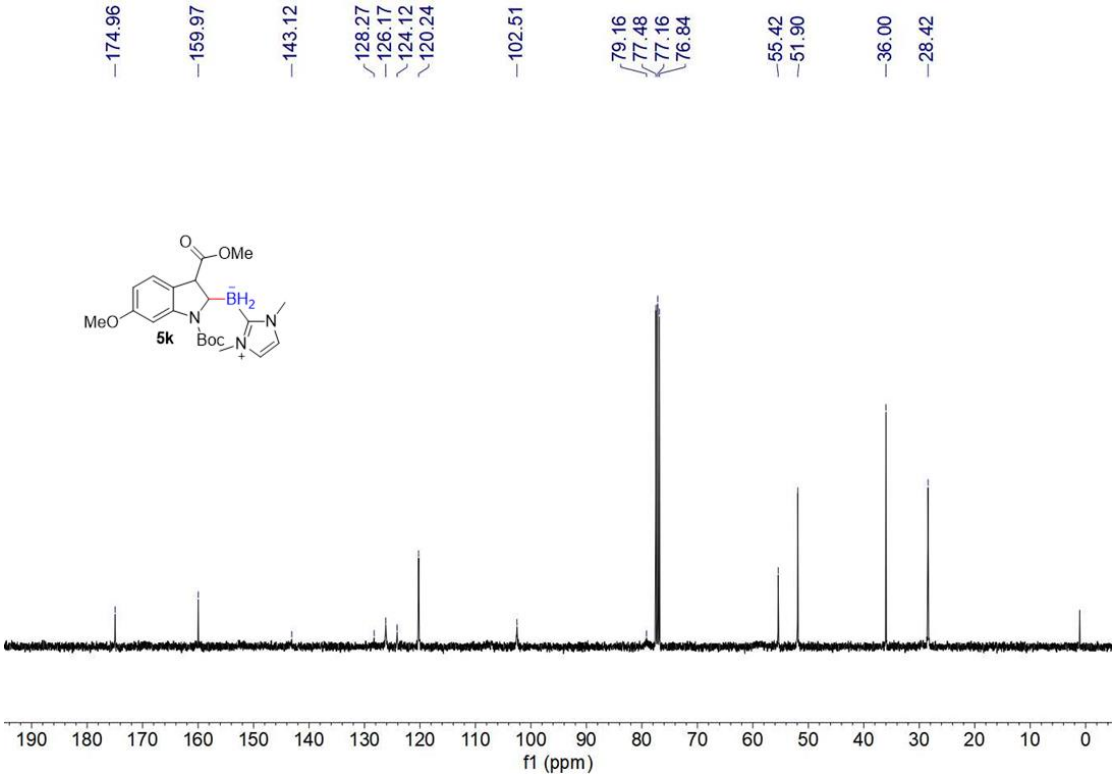

Fig. S102 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5k**.

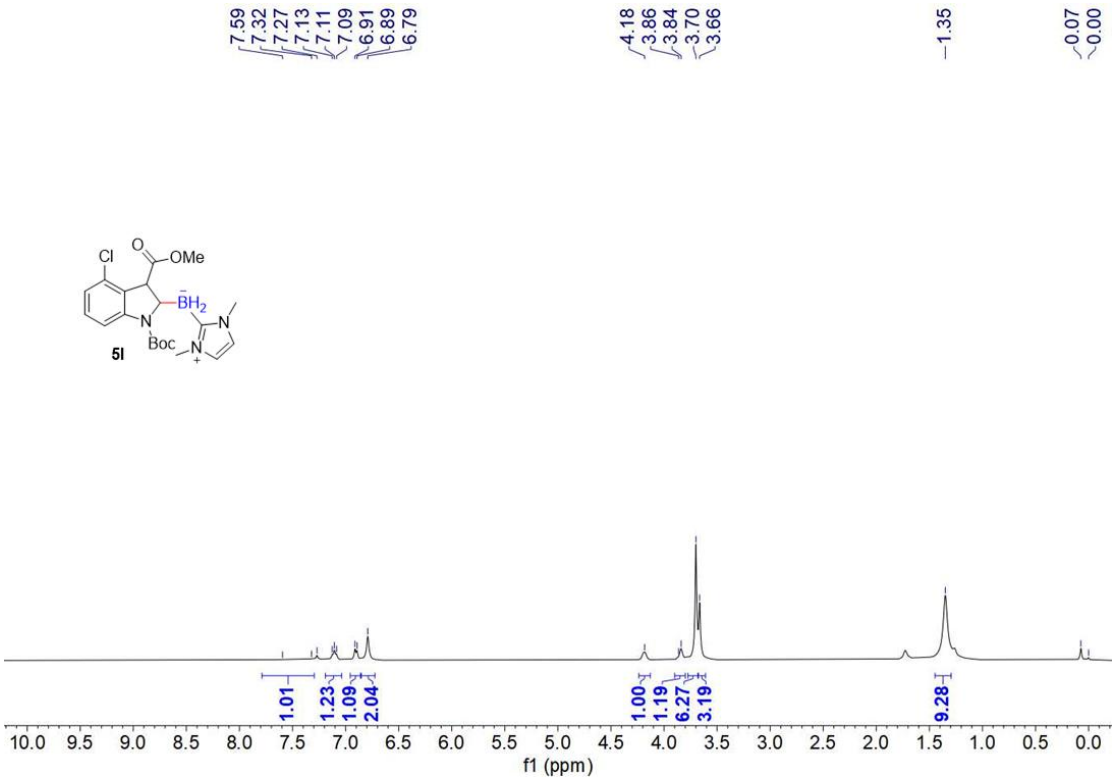

Fig. S103 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5l**.

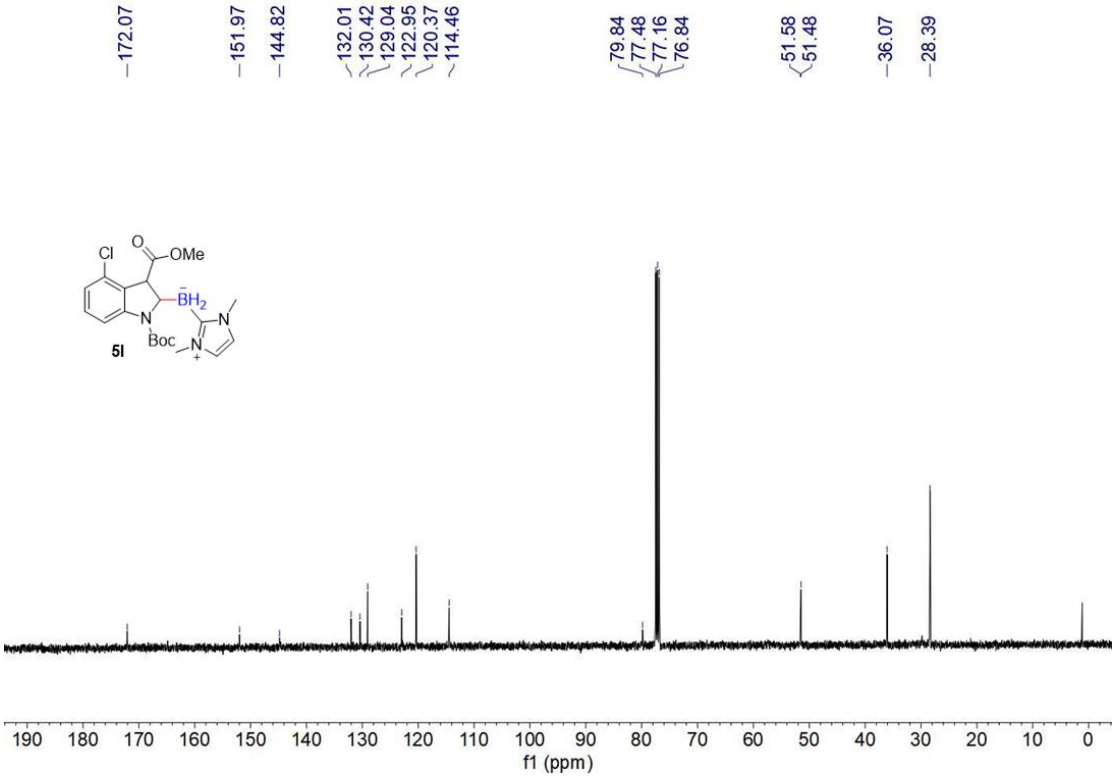

Fig. S104 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5l**.

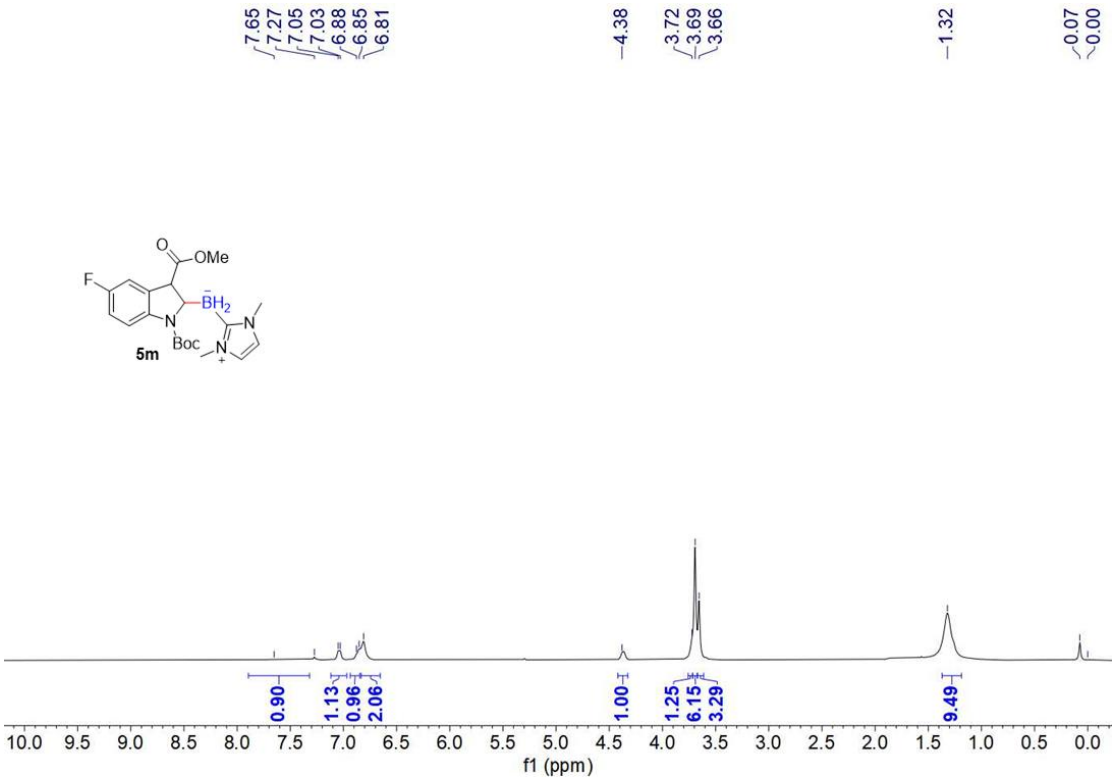

Fig. S105 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5m**.

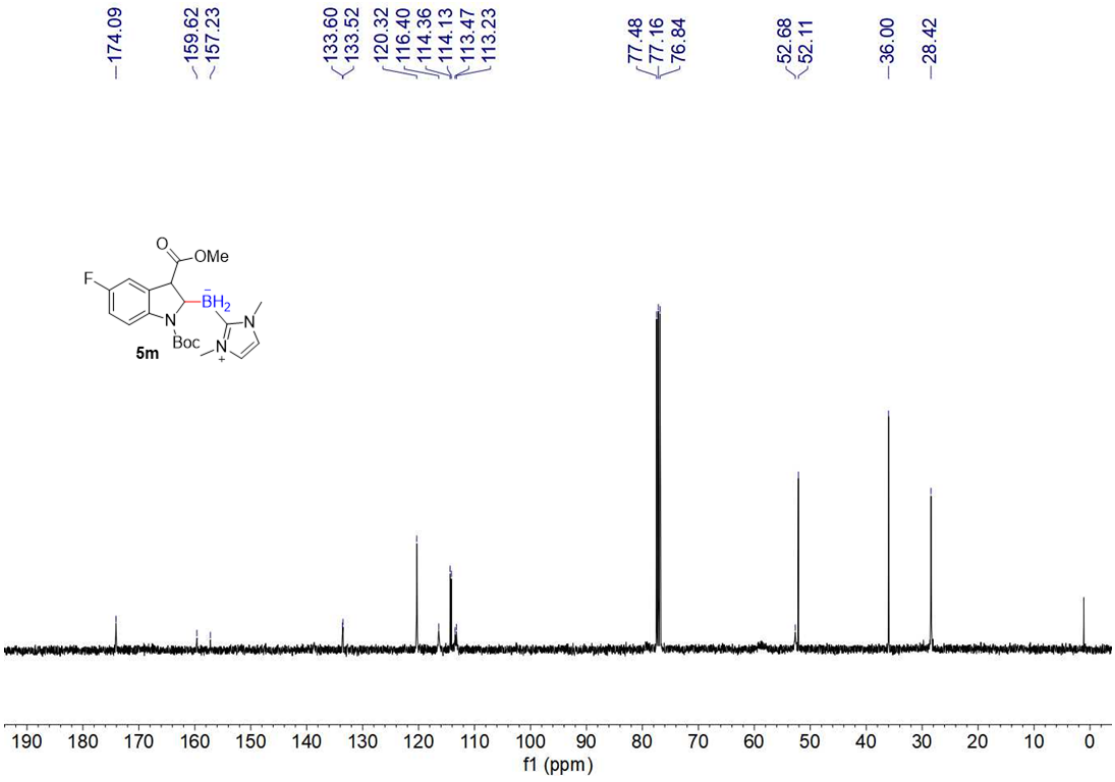

Fig. S106 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5m**.

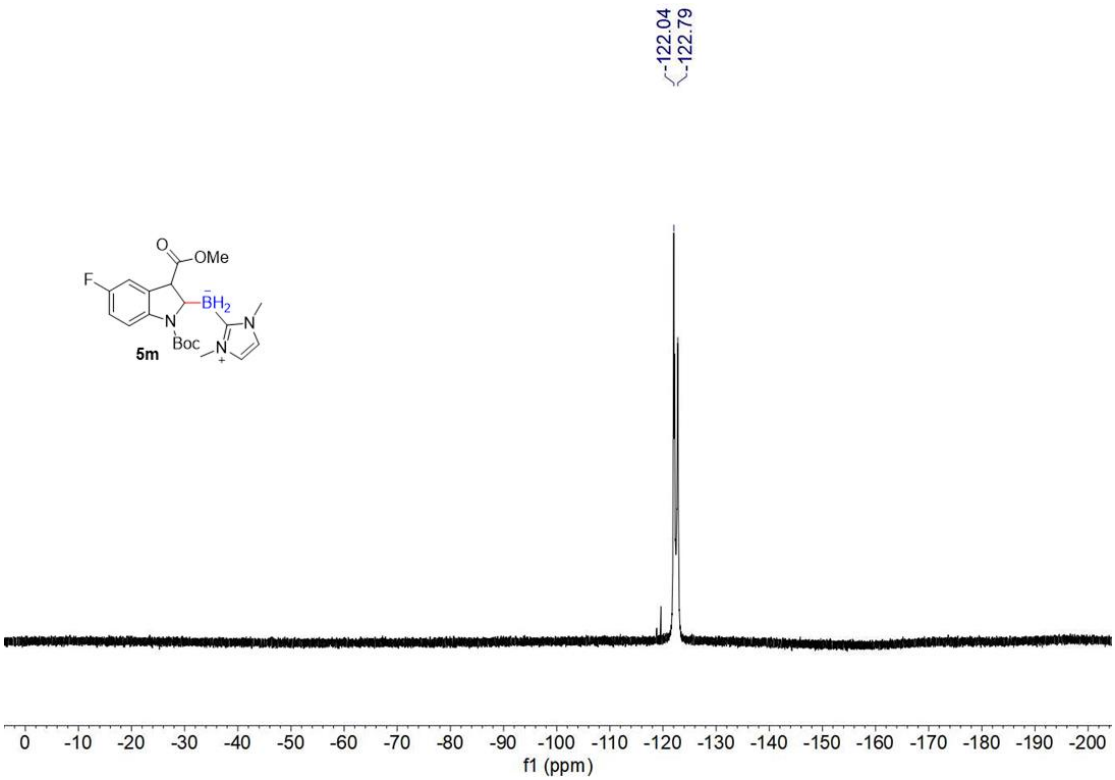

Fig. S107 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **5m**.

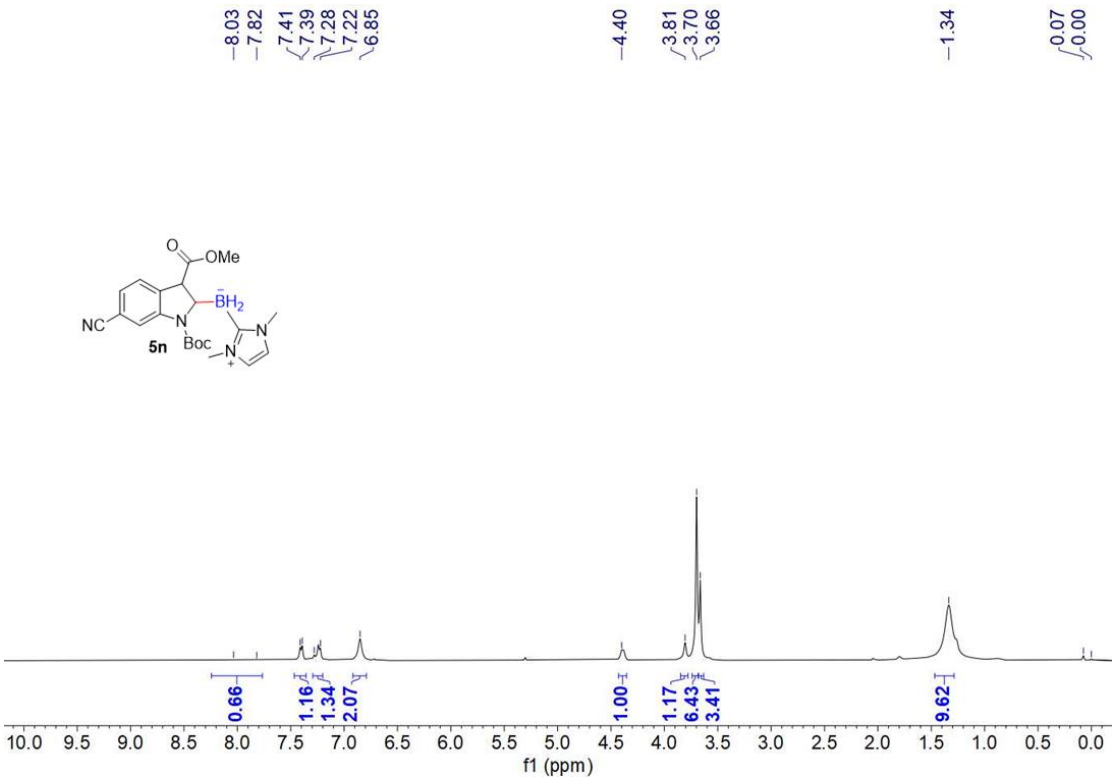

Fig. S108 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5n**.

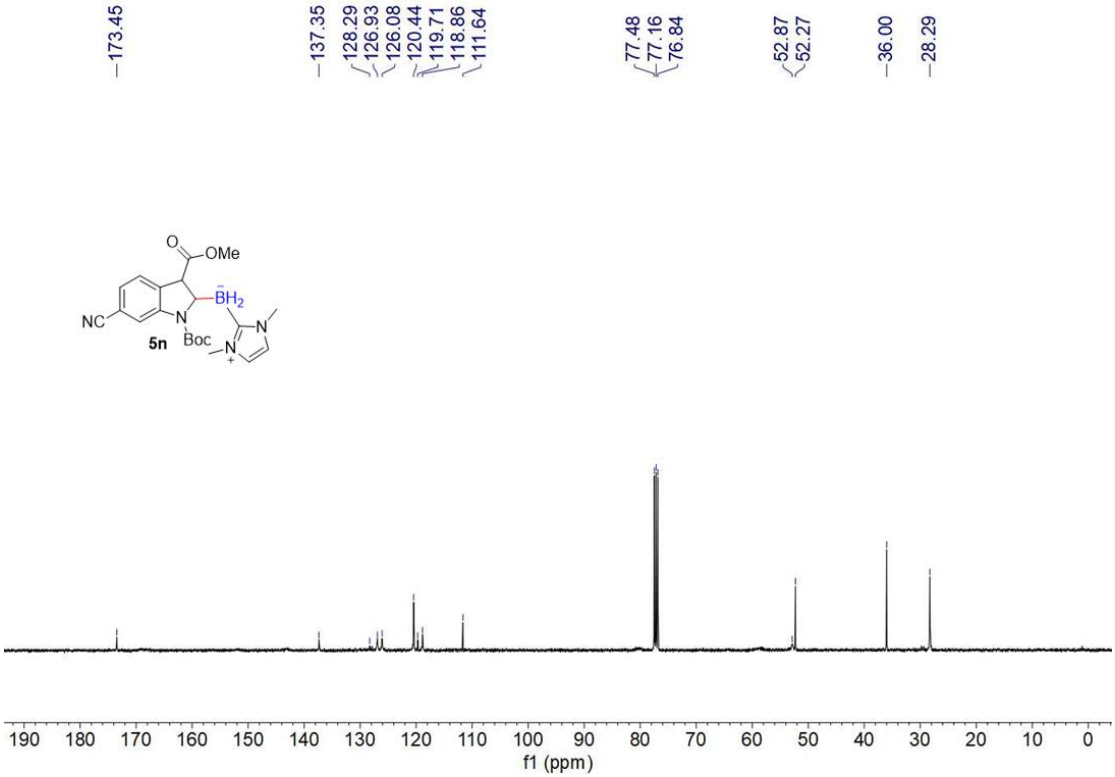

Fig. S109 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 5n.

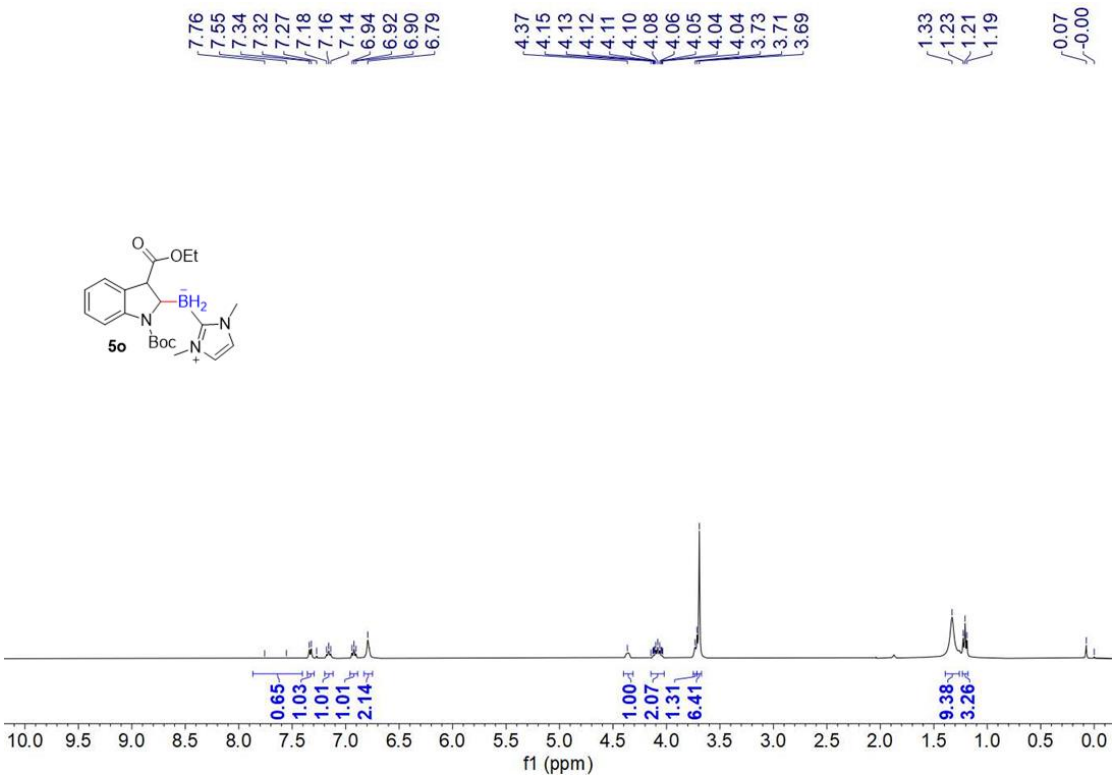

Fig. S110 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5o**.

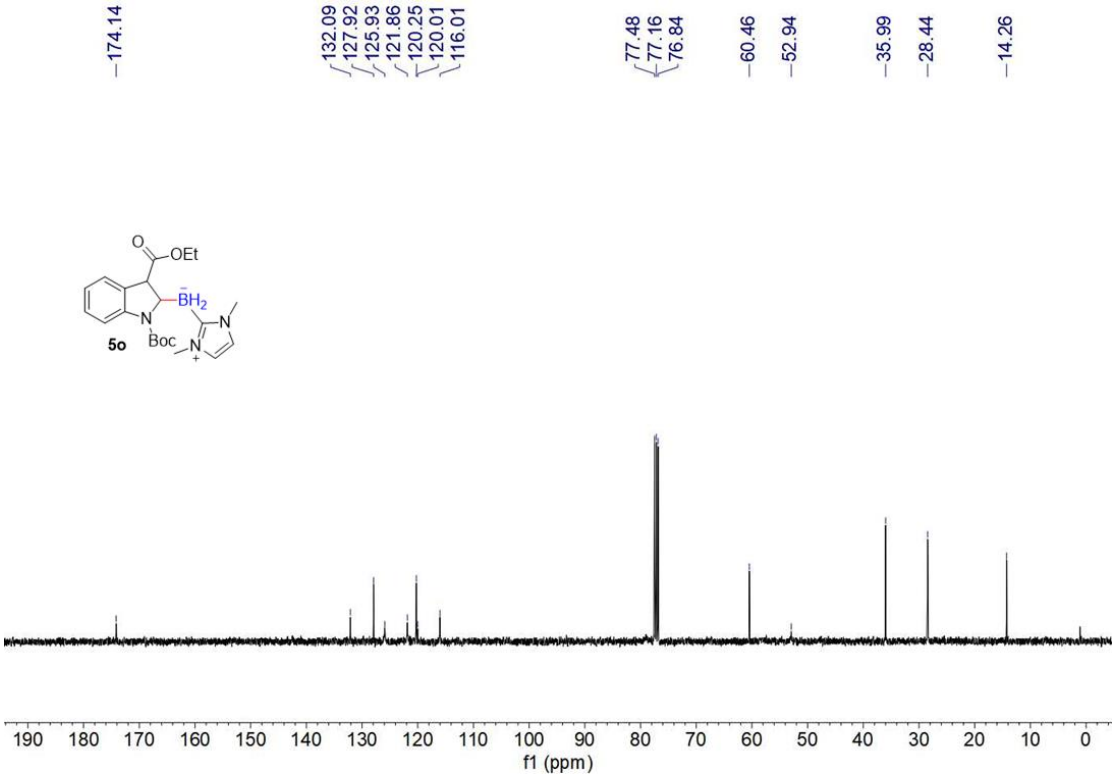

Fig. S111 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5o**.

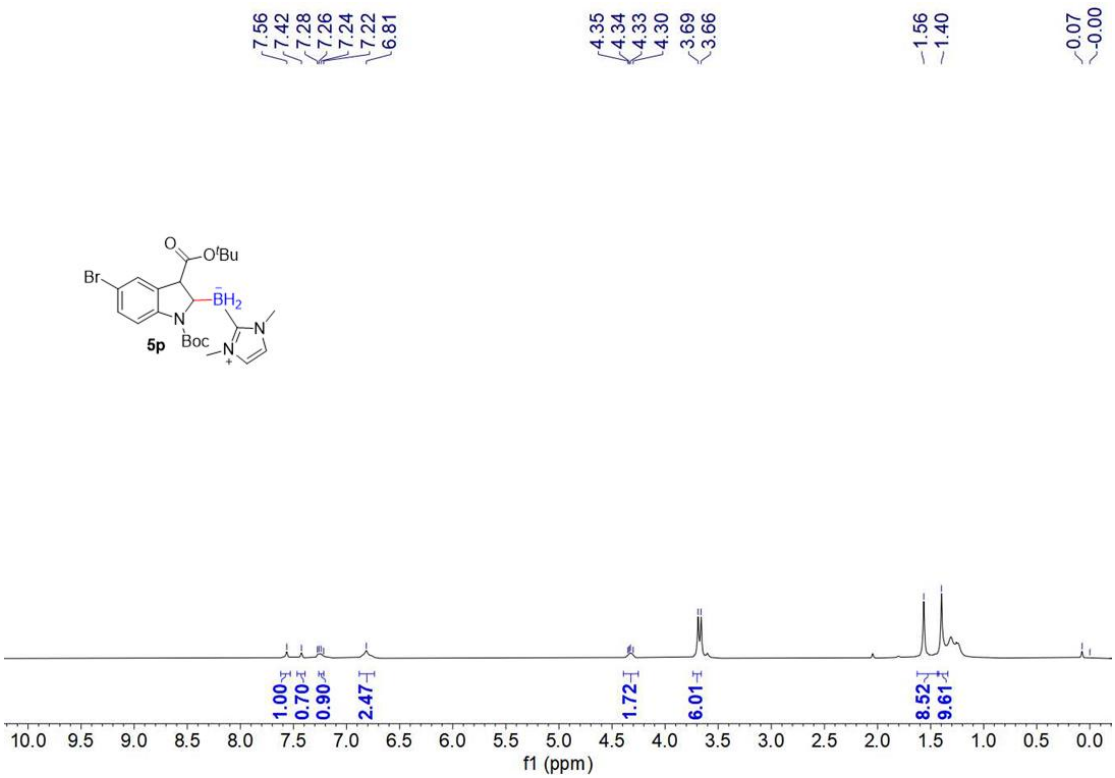

Fig. S112 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5p**.

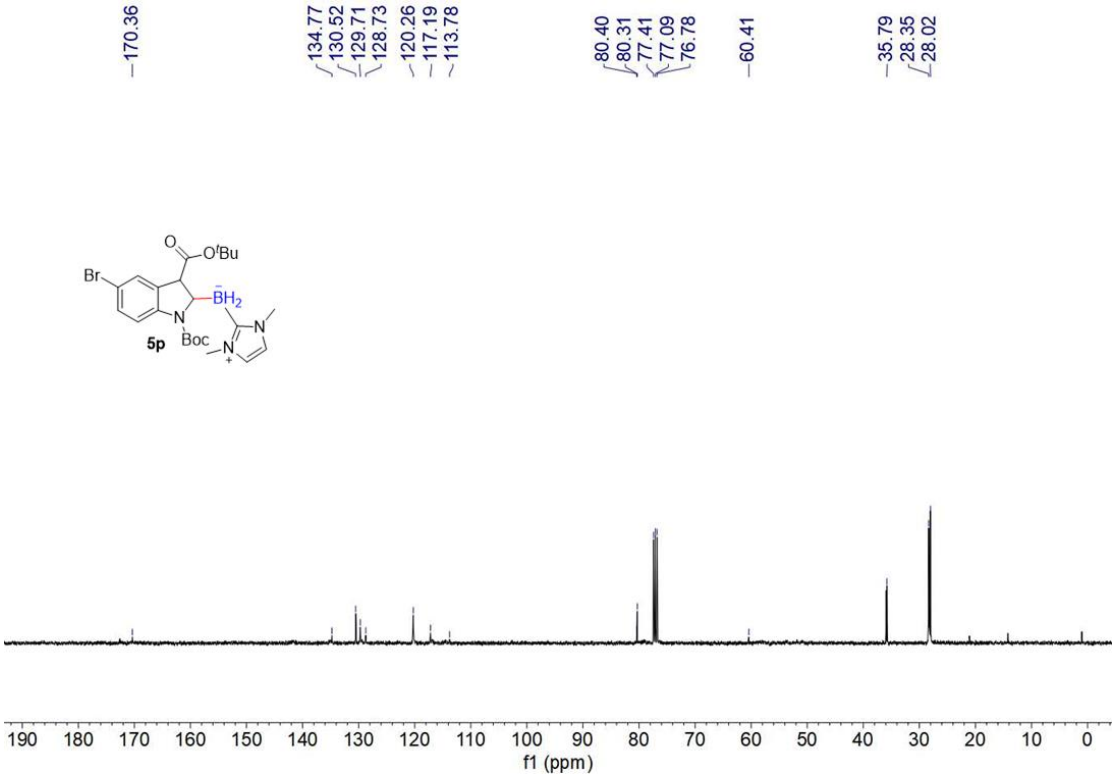

Fig. S113 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5p**.

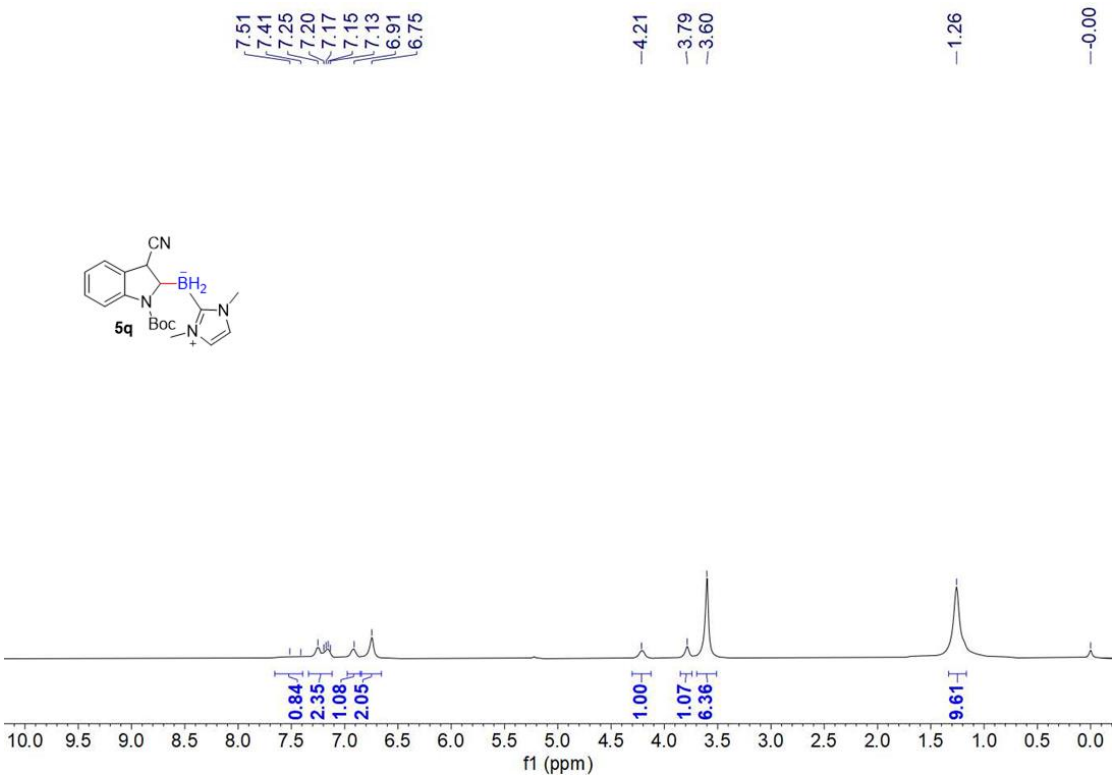

Fig. S114 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5q**.

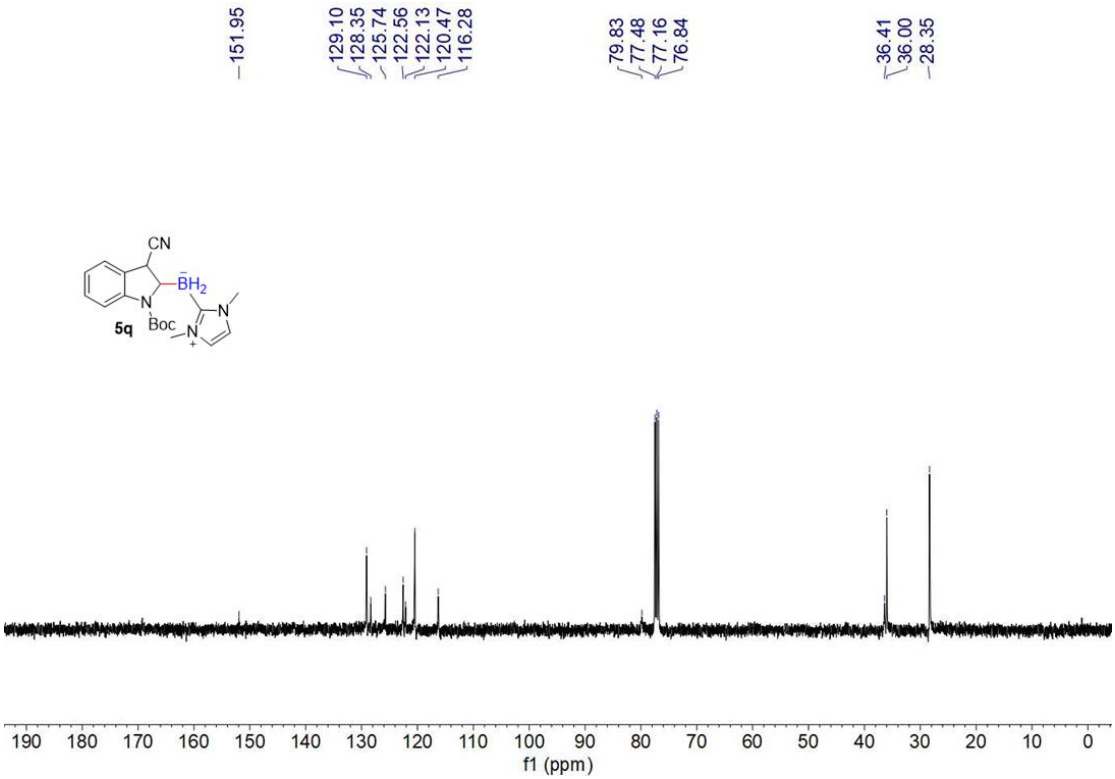

Fig. S115 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5q**.

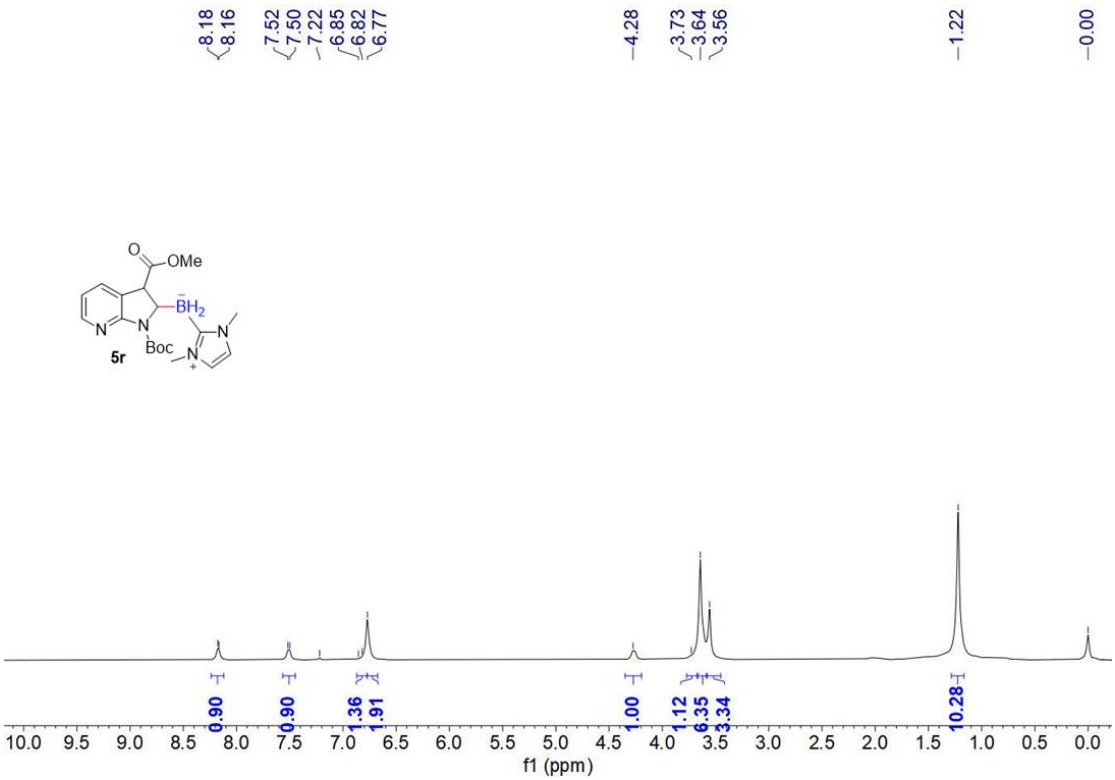

Fig. S116 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5r**.

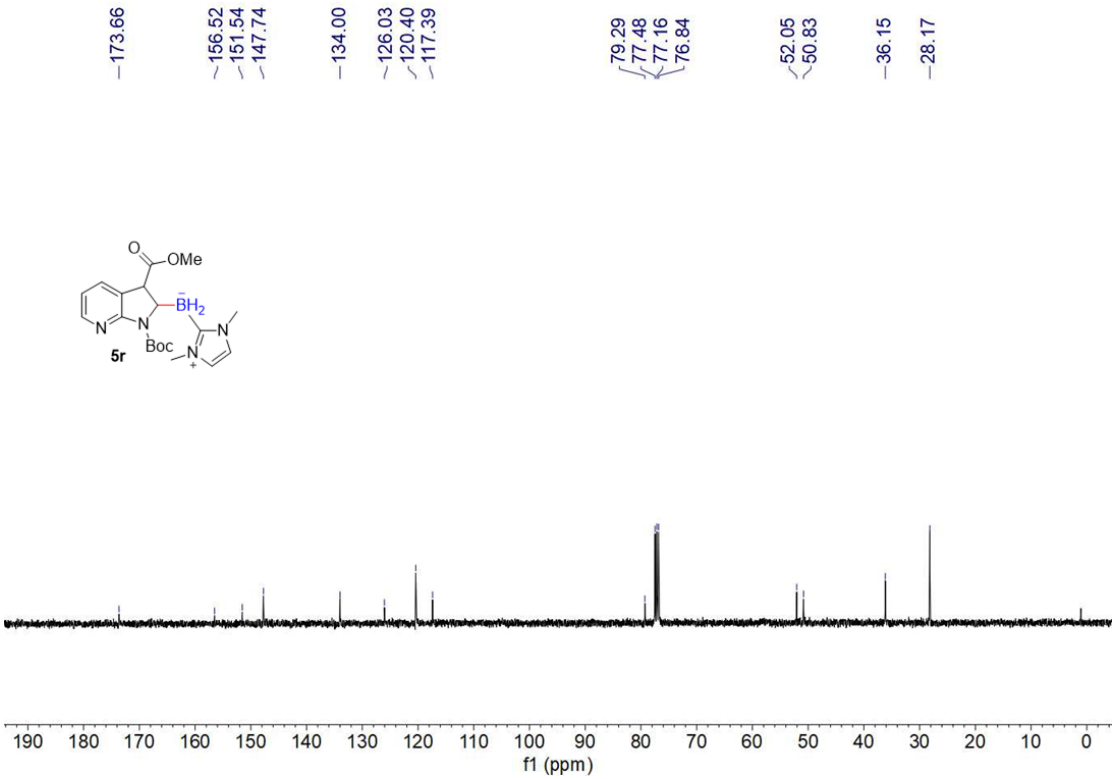

Fig. S117 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5r**.

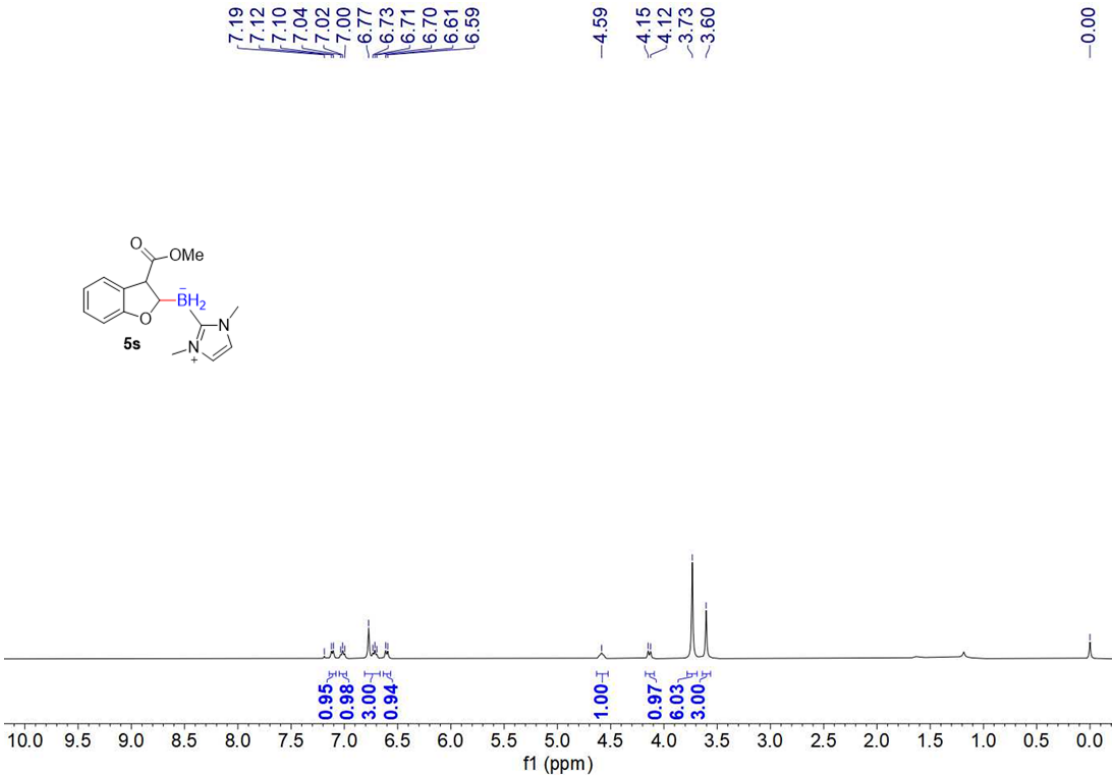

Fig. S118 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5s**.

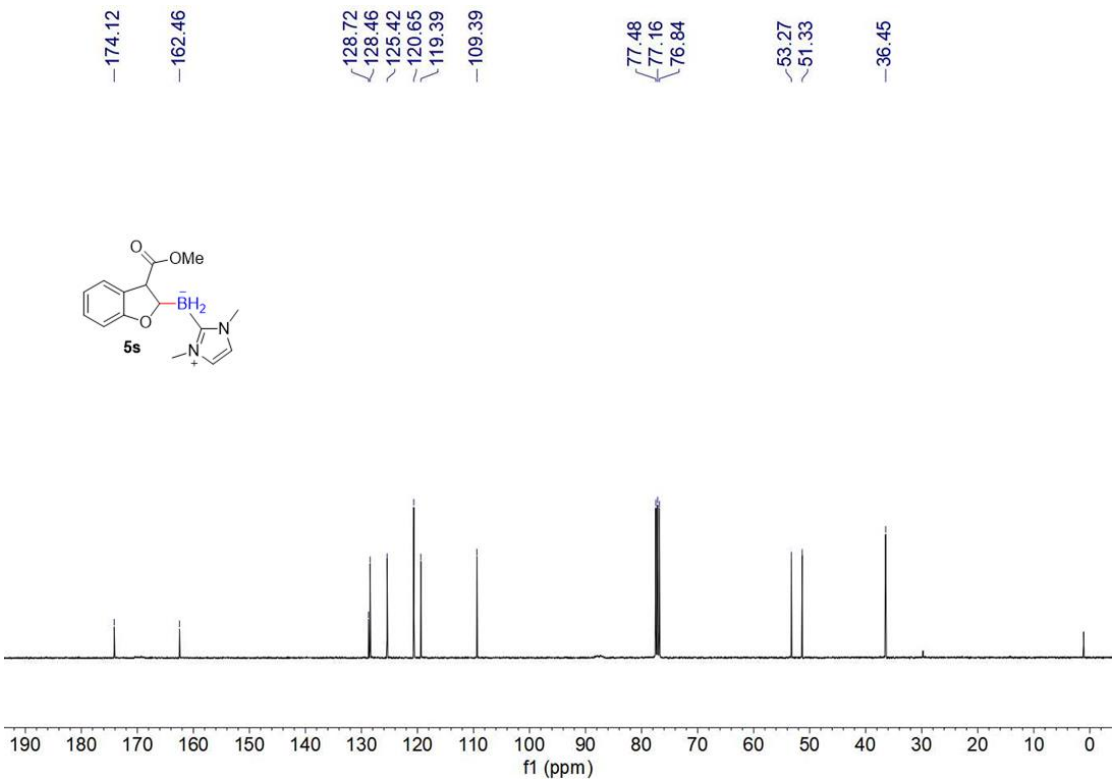

Fig. S119 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5s**.

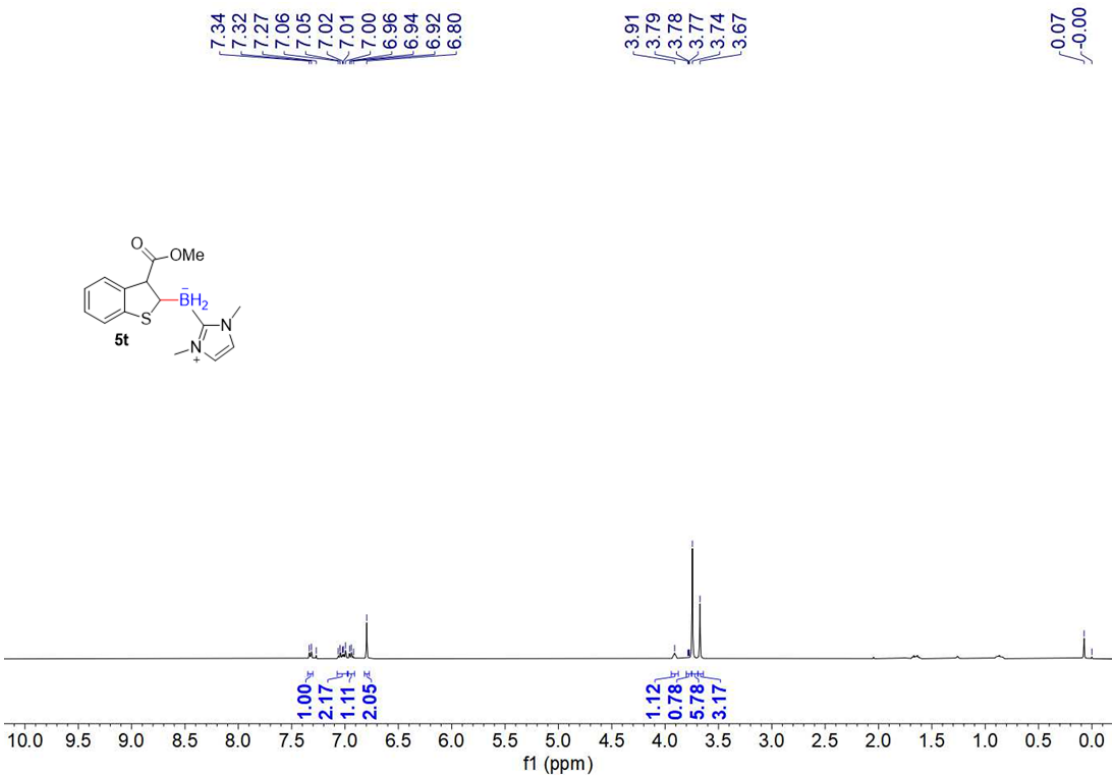

Fig. S120 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5t**.

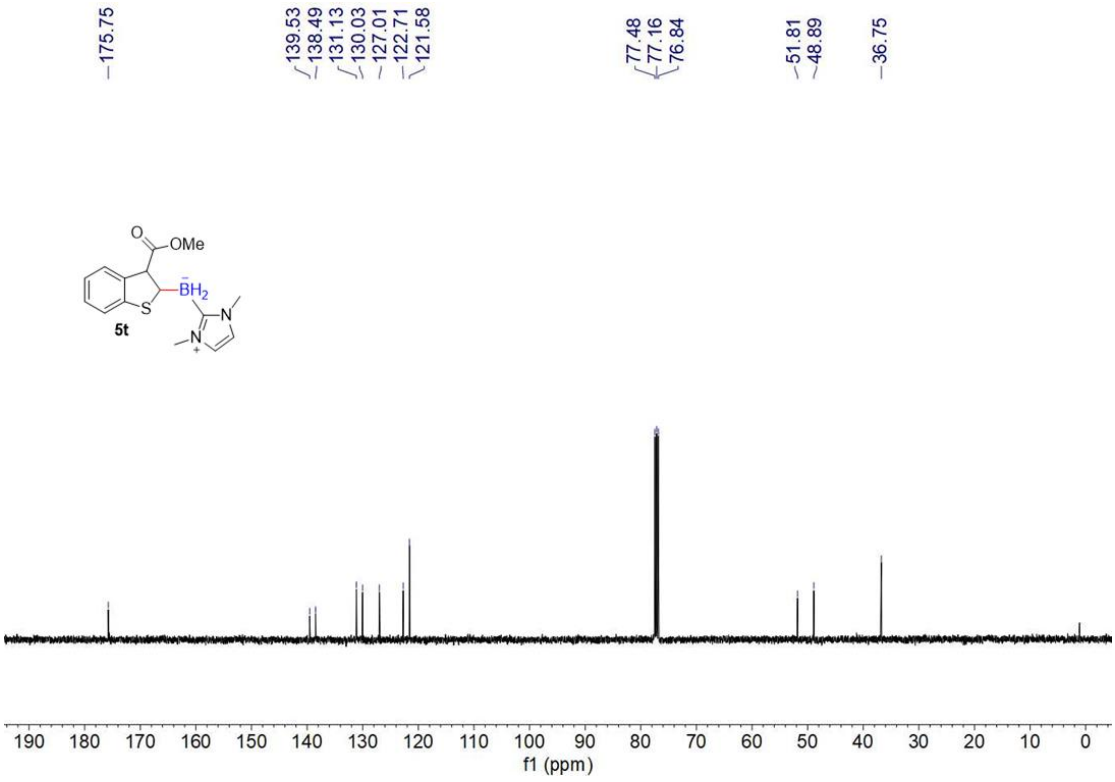

Fig. S121 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **5t**.