Supporting Information for

Electrochemical radical borylation of *N*-heterocycles with NHC-boranes: efficient access to B−N bond

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Contents

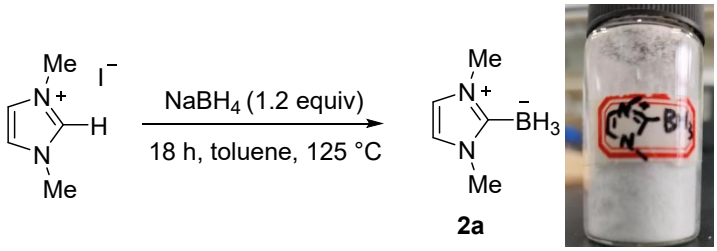
1. General

^{1}H NMR, ^{13}C NMR, ^{11}B NMR,^{19}F NMR spectra were recorded on 600 or 500 MHz NMR spectrometers and resonances (δ) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. HRMS were obtained on Agilent 6540 UHD Q-TOF or German Thermo Fisher Q Exactive high resolution Mass Spectrometer. The melting point was recorded on X-4BII and uncorrected. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60 F254 plates and viewed by UV light (254 nm). Flash column chromatography was performed on silica gel (200-300 mesh). The X-ray crystal-structures were obtained on a Bruker D8 VENTURE Single Crystal Diffractometer. Electrochemical reactions were performed on DC Power Supply (GPD-2303S). Continuous-flow reaction was performed in the microfluidic electrolysis cell and its components were purchased from Hangzhou Saiao Electrochemical Technology Co. Ltd., China. Cyclic voltammetry (CV) was carried out on a CHI660E electrochemical workstation (CH Instruments, Ins).

All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. The boranes compounds **2a** and **2b** were known compounds and prepared according to the literature procedures [1-2].

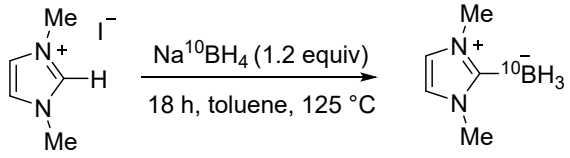
2. Experimental procedures

2.1 General procedure for the synthesis of 2a and 2b[1-2] and 2a-^{10}B



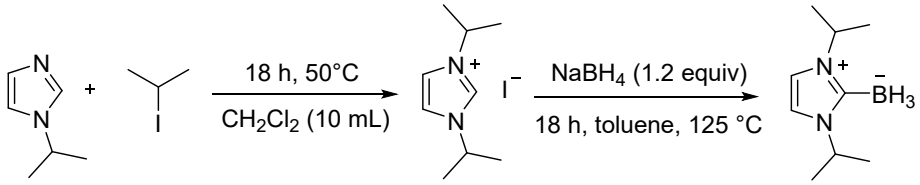
2a

A 250 mL eggplant shaped flask was charged with 1,3-dimethylimidazolium iodide (11.2 g, 50 mmol) and $NaBH_4$ (2.27 g, 60 mmol), followed by 50 mL toluene, and the reaction was carried out at 125 ℃ for 18 h. At the end of the reaction, hot toluene was poured out and washed three times with hot toluene, and the pooled hot toluene was cooled and evaporated to give the crude product. This sample was recrystallized once from water (about 14 mL/g) to give white solid **2a** in 47% yield.



2a-^{10}B

When $Na^{10}BH_4$ was used to replace $NaBH_4$, the corresponding **2a-^{10}B** compound can be generated. And it was detected by HRMS. (HRMS (ESI-Orbitrap) m/z calcd for $C_{15}H_{11}N_2{}^{10}BNa^+$ $[M+Na]^+$: 132.0944; found: 132.0945)

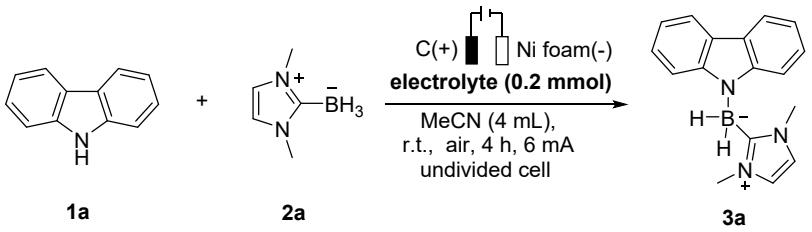


75% **2b**, 17%

The 1-isopropylimidazole (2.2 mL, 20 mmol) and 2-iodopropane (3 mL, 30 mmol) and CH_2Cl_2 10 mL were added to a round-bottomed flask fitted with a condenser tube, and the reaction was heated to 50 ℃ for 18 h. At the end of the reaction, the mixture was concentrated under reduced pressure. Then, 10 mL of *n*-hexane and 2 mL of CH_2Cl_2 were added. The product precipitated and was filtered under suction. After vacuum drying, the salt was obtained in 75% yield. Subsequently, compound **2b** was synthesized following the procedure for the preparation of **2a**, and the white solid **2b** was obtained in 17% yield.

2.2 Optimization of reaction conditions

Table S1 Screening of electrolytes[a]



1a 2a 3a

Entry	Electrolyte	Yield (%)[b]
1	Bu_4NBr	trace
2	KI	14
3	Et_4NCl	49
4	[BMMIm]Cl	52
5	$[C_{12}MIm]Cl$	36
6	[AMIm]Cl	17
7	Bu_4NPF_6	trace
8	Bu_4NClO_4	trace
9	Bu_4NHSO_4	trace
10	without electrolyte	n.r.

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), electrolyte (0.2 mmol), MeCN (4.0 mL), C anode, Ni foam cathode, constant current = 6 mA, 4 h, 4.5 F/mol, room temperature, under air, undivided cell. [b] Isolated yields. n.r. = no reaction.

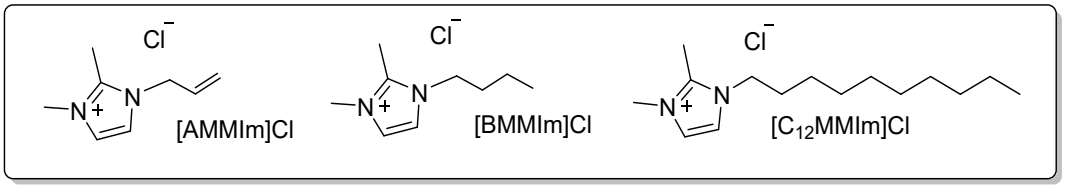
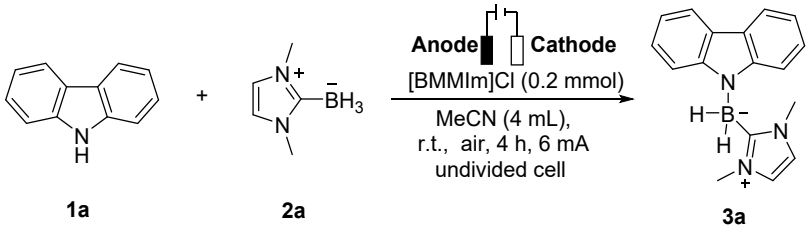


Table S2 Screening of electrodes[a]



1a 2a 3a

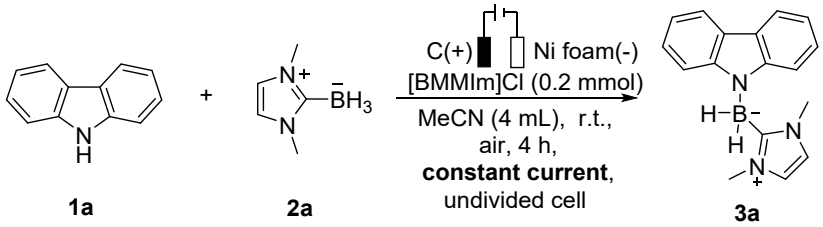
Entry	Anode	Cathode	Yield (%)[b]
1	C	Ni foam	51
2	C	Pt	46
3	C	C	trace
4	RVC	Ni foam	53
5	Cu	C	n.r.

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), [BMMIm]Cl (0.2 mmol), MeCN (4.0 mL), anode X, cathode Y, constant current = 6 mA, 4 h, 4.5 F/mol, room temperature, under air, undivided

cell. [b] Isolated yields.

Considering that the use of carbon electrodes is more economical than that of RVC electrodes, carbon electrodes were ultimately chosen for use.

Table S3 Screening of currents[a]

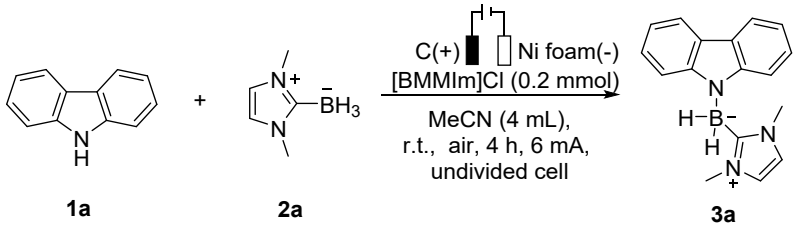


1a **2a** **3a**

Entry	Constant current (mA)	Yield (%)[b]
1	3	25
2	6	52
3	8	27
4	without current	n.r.

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), [BMMIm]Cl (0.2 mmol), MeCN (4.0 mL), C anode, Ni foam cathode, constant current = x mA, 4 h, 2.2/4.5/6.0 F/mol, room temperature, under air, undivided cell. [b] Isolated yields.

Table S4 Screening of feed radio[a]

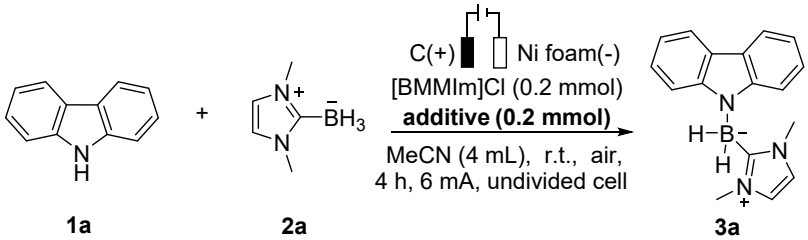


1a **2a** **3a**

Entry	2a (mmol)	Yield (%)[b]
1	0.1	trace
2	0.2	52
3	0.3	58
4	0.6	68

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (x mmol), [BMMIm]Cl (0.2 mmol), MeCN (4.0 mL), C anode, Ni foam cathode, constant current = 6 mA, 4 h, room temperature, under air, undivided cell. [b] Isolated yields.

Table S5 Screening of additive[a]

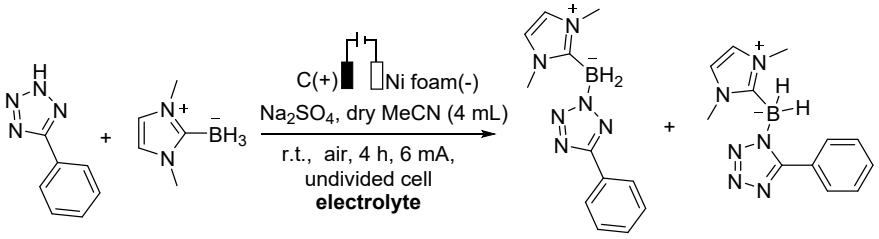


1a **2a** **3a**

Entry	Additive	Yield (%)[b]
1	Cs_2CO_3	20
2	DBU	n.r.
3	2-mercaptopyridine	31
4	2-methyl-3-furan mercaptan	18
5	4-chlorophenylthiophenol	16
6[c]	-	55
7[c]	Na_2SO_4	80
8[c]	4A MS	75
9[c]	$MgSO_4$	77

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), [BMMIm]Cl (0.2 mmol), additive (0.2 mmol）, MeCN (4.0 mL), C anode, Ni foam cathode, constant current = 6 mA, 4 h, 4.5 F/mol, room temperature, under air, undivided cell. [b] Isolated yields. [c] MeCN replaced with dry MeCN.

Table S6 Screening of electrolytes of 5a[a]



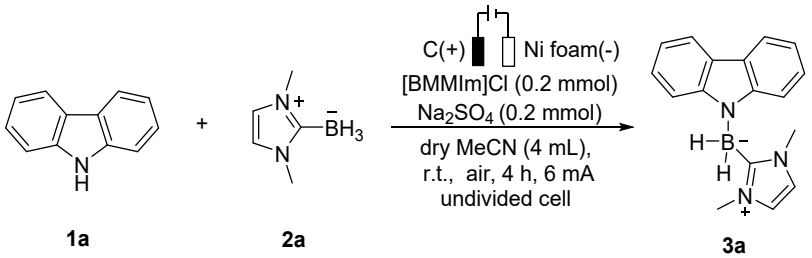
4a **2a** **5a** **5a'**

Entry	electrolyte	Yield (%)[b] 5a/5a'
1	[BMMIm]Cl	76:20
2	Choline chloride	80:14
3[c]	-	82:20
4[c,d]	-	n.r.

[a] Reaction conditions: **4a** (0.3 mmol), **2a** (0.9 mmol), electrolyte (0.3 mmol), Na_2SO_4 (0.3 mmol）, dry MeCN (4.0 mL), C anode, Ni foam cathode, constant current = 6 mA, 4 h, 3.0 F/mol, room temperature, under air, undivided cell. [b] Isolated yields. [c] Without Na_2SO_4. [d] Without current. n.r. = no reaction

2.3 General procedure for the synthesis for 3 and 5

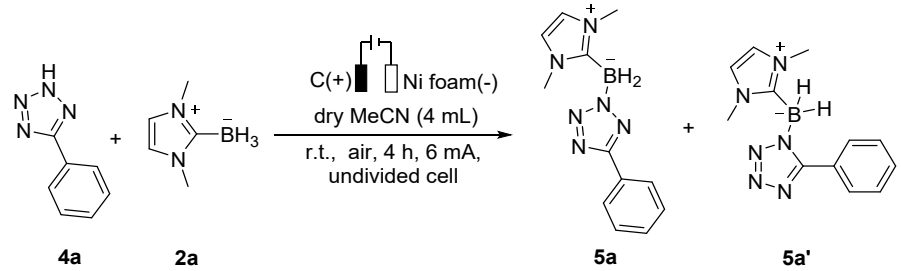
2.3.1 General procedure for the synthesis for 3 (3a as an example)



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

Under air, a mixture of carbazole **1a** (33.4 mg, 0.2 mmol), 1,3-dimethylimidazolylborane **2a** (66.0 mg, 0.6 mmol), [BMMIm]Cl (37.7 mg, 0.2 mmol), anhydrous sodium sulfate (28.4 mg, 0.2 mmol, 1.0 equiv.) and dry MeCN (4 mL) were added in an oven-dried undivided bottle (10 mL). The bottle was equipped with carbon chip (15 mm × 10 mm × 1 mm) as the anode (carbon electrodes are sandpapered and polished) and nickel foam (15 mm × 10 mm × 1 mm) as the cathode, the distance between the electrodes was 1 cm. The submerged anode and cathode height are approximately 7 mm. The resulting mixture was stirred and electrolyzed at a constant current of 6 mA at room temperature for 4 h, 4.5 F/mol. At the end of the reaction, purification by column chromatography on silica gel using petroleum ether (60-90 ℃)/ dichloromethane (3:1 v/v) as eluent afforded **3a** as a white solid (44.0 mg, 80% yield).

2.3.2 General procedure for the synthesis for 5 (5a as an example)



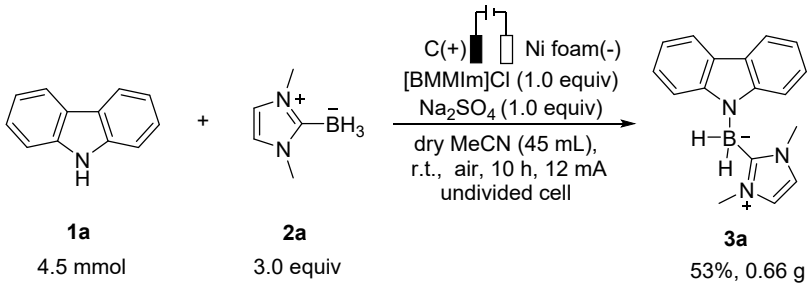
When performing tetrazolium substrate exploration, we found that the reaction could be performed without the addition of electrolytes. Under air, a mixture of tetrazole **4a** (44.0 mg, 0.3 mmol), 1,3-dimethylimidazolylborane **2a** (99.0 mg, 0.9 mmol) and dry MeCN (4 mL) were added in an oven-dried undivided bottle (10 mL). The bottle was equipped with carbon chip (15 mm × 10 mm × 1 mm) as the anode (carbon electrodes are sandpapered and polished) and nickel foam (15 mm × 10 mm × 1 mm) as the cathode, the distance between the electrodes was 1 cm. The submerged anode and cathode height are approximately 7 mm. The resulting mixture was stirred and electrolyzed at a constant current of 6 mA at room temperature for 4 h, 3.0 F/mol. At the end of the reaction, purification by column chromatography on silica gel using petroleum ether (60-90 ℃)/ethyl acetate (1:2 v/v) as eluent afforded **5a** as a white solid (62.0 mg, 82% yield).

2.4 Electrochemical reaction device

Figure S1. Electrochemical reaction equipment

2.5 Large-scale experiments

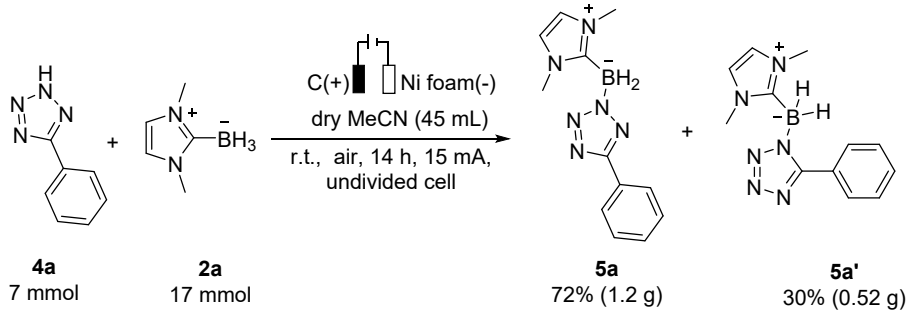
2.5.1 Large-scale experiment for 3a



Under air, a mixture of carbazole **1a** (4.5 mmol), 1,3-dimethylimidazolylborane **2a** (13.5 mmol), [BMMIm]Cl (4.5 mmol), anhydrous sodium sulfate (4.5 mmol) and dry MeCN (45 mL) were added in a three-necked flask (100 mL). The bottle was equipped with carbon chip (30 mm × 15 mm × 1 mm) as the anode and nickel foam (30 mm × 15 mm × 1 mm) as the cathode, the distance between the electrodes was 2.5 cm. The submerged anode and cathode height are approximately 15 mm. The resulting mixture was stirred and electrolyzed at a constant current of 12 mA at room temperature for 10 h, 1.0 F/mol. At the end of the reaction, purification by column chromatography on silica gel using petroleum ether (60-90 °C)/ dichloromethane (3:1 v/v) as eluent afforded **3a** as a white solid (0.66 g, 53% yield).

Figure S2. Electrochemical gram-scale reaction equipment for 3a in batch reactor

2.5.2 Large-scale experiment for 5a



Under air, a mixture of 5-Phenyl-1H-tetrazole **4a** (7 mmol), 1,3-dimethylimidazolylborane **2a** (17 mmol) and dry MeCN (45 mL) were added in a beaker (100 mL). The beaker was equipped with carbon chip (30 mm × 15 mm × 1 mm) as the anode and nickel foam (30 mm × 15 mm × 1 mm) as the cathode, the distance between the electrodes was 2.5 cm. The submerged anode and cathode height are approximately 15 mm. The resulting mixture was stirred and electrolyzed at a constant current of 15 mA at room temperature for 14 h, 1.1 F/mol. At the end of the reaction,

purification by column chromatography on silica gel using petroleum ether (60-90 ℃)/ ethyl acetate (1:2 v/v) as eluent afforded **5a** as a white solid (1.2 g, 72% yield) and **5a'** (0.52 g, 30%).

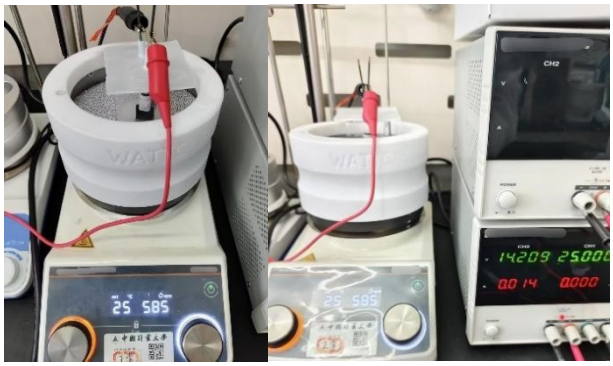
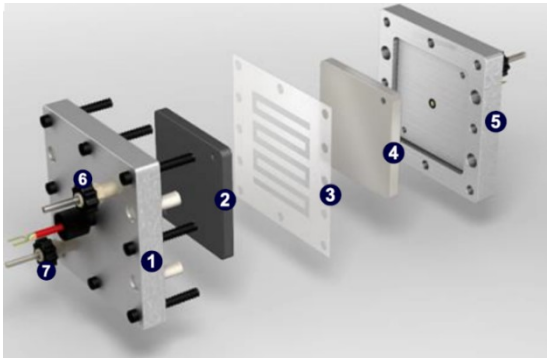


Figure S3. Electrochemical gram-scale reaction equipment for 5a in batch reactor

2.6 Flow electrochemical experiments

2.6.1 Flow electrochemical equipment



Design of electrochemical flow cell. ① and ⑤: Electrode holder. ②: Anode. ③:Fluorinated ethylene propylene (FEP) foil. ④: Cathode. ⑥ and ⑦: Inlet and outlet.

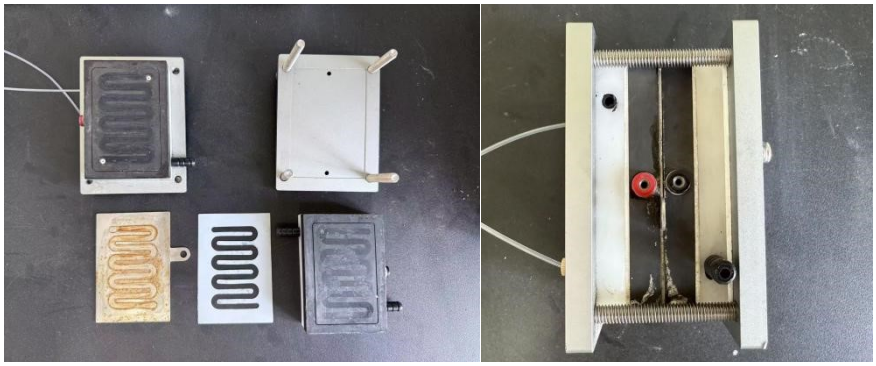
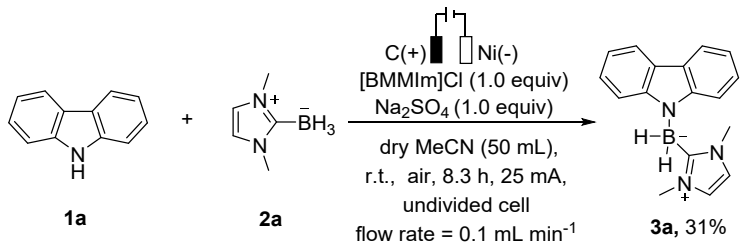


Figure S4. Flow electrochemical equipment

2.6.2 Flow electrochemical experiments for 3a



The substrates **1a** (0.33 g, 2 mmol), **2a** (0.66 g, 6 mmol) [BMMIM]Cl as well as Na_2SO_4 were added in dry CH_3CN and then flow electrochemical reactions were carried out at a flow rate of 0.1 mL min^{-1} for 8.3 h at a constant current of 25 mA, 3.9 F/mol. At the end of the reaction, purification by column chromatography on silica gel using petroleum ether (60-90 ℃)/ dichloromethane (3:1 v/v) as eluent afforded **3a** as a white solid (85 mg, 31% yield).

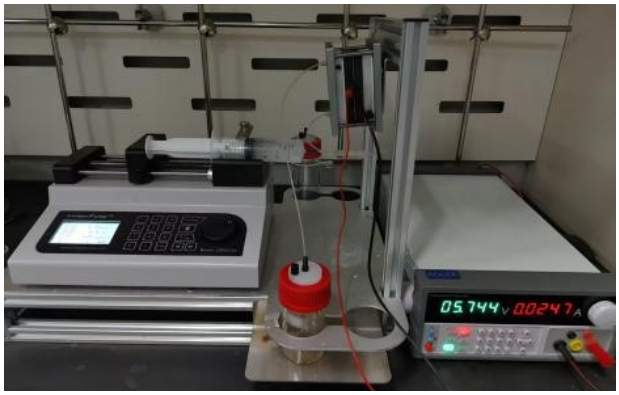
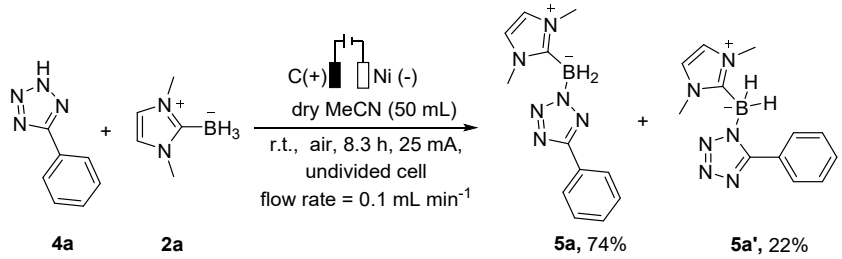


Figure S5. Electrochemical reaction equipment for 3a in continuous flow reactor

2.6.3 Flow electrochemical experiments for 5a



The substrates **4a** (0.3 g, 2 mmol) and **2a** (0.66 g, 6 mmol) were dissolved in dry CH_3CN and then flow electrochemical reactions were carried out at a flow rate of 0.1 mL min^{-1} for 8.3 h at a constant current of 25 mA, 3.9 F/mol. At the end of the reaction, purification by column chromatography on silica gel using petroleum ether (60-90 ℃)/ ethyl acetate (1:2 v/v) as eluent afforded **5a** as a white solid (0.19 g, 74% yield) and **5a'** (0.05 g, 22%).

Figure S6. Electrochemical reaction equipment for 5a in continuous flow reactor

2.7 Stability experiments

编号	**3a/5a**	试剂	days
1	1 mg/2 mg	CH_3CN	7
2	1 mg/2 mg	DMSO	7
3	1 mg/2 mg	H_2O	7
4	1 mg/2 mg	甲苯	7
5	1 mg/2 mg	1M HCl	7
6	1 mg/2 mg	1M NaOH	7

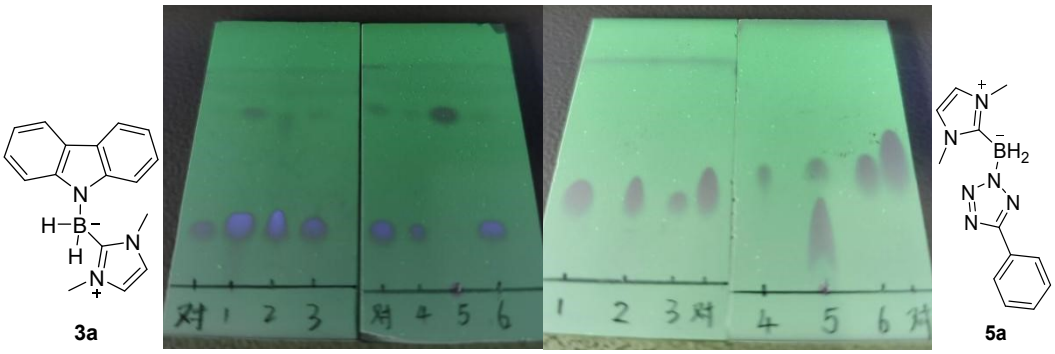
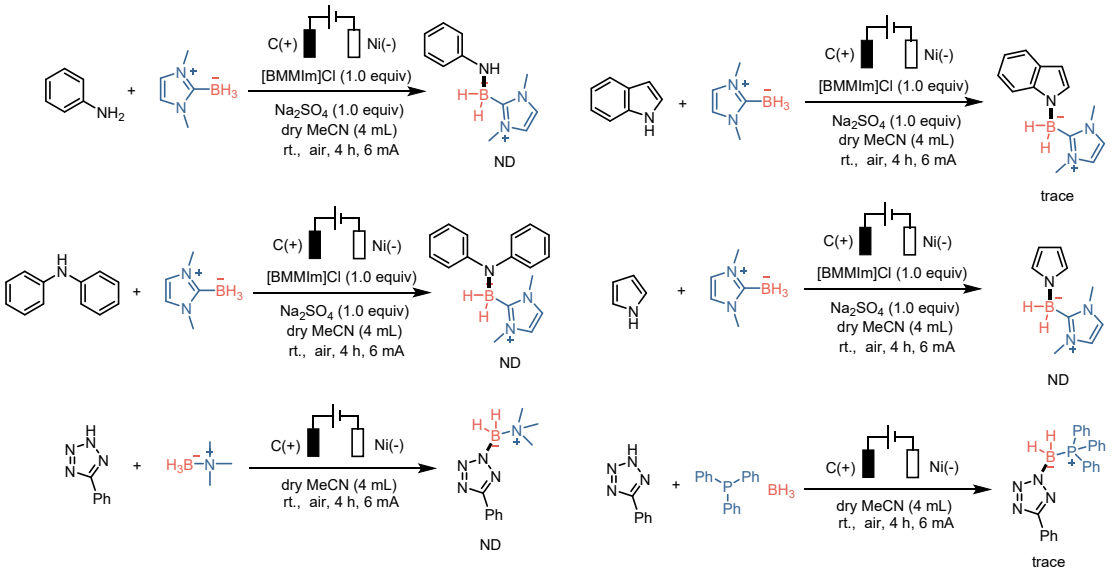


Figure S7. Stability experiments

3a and **5a** were added to seven centrifuge tubes, and then two sets of tubes were filled with CH_3CN, DMSO, H_2O, toluene, 1M HCl and 1M NaOH. After leaving for seven days, TLC assay revealed significant decomposition of the product with the addition of 1M HCl.

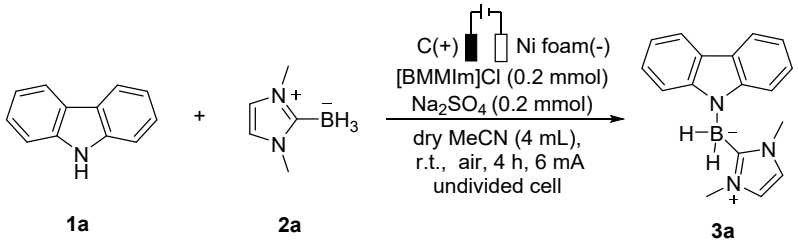
2.8 Failed examples

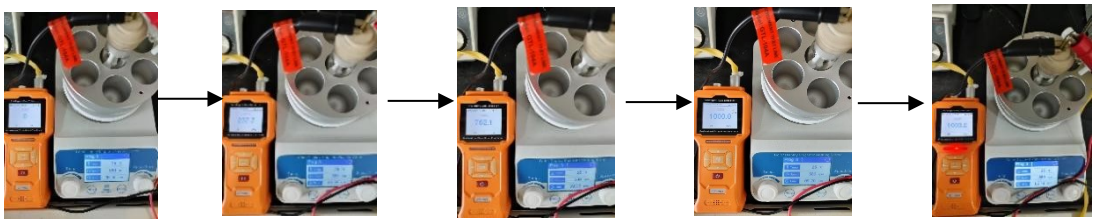


3. Mechanistic studies

3.1 H_2 detection experiments

3.1.1 H_2 detection experiments for 3a

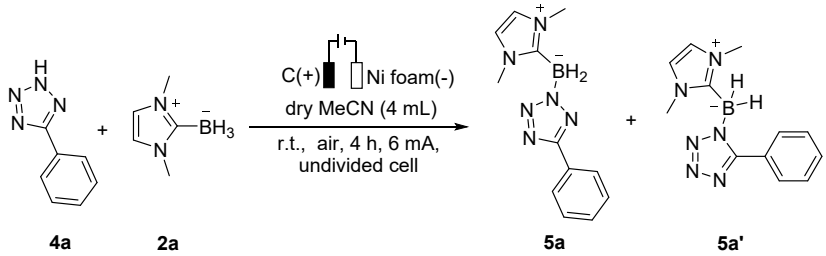


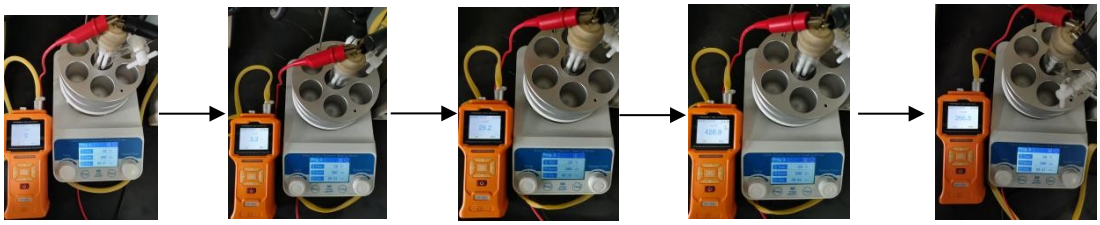


0 min 0 ppm 20 min 237.7 ppm 27 min 762.12 ppm 31 min 1000 ppm 3.5 h 1000 ppm

Figure S8. H_2 detection experiments for 3a

3.1.2 H_2 detection experiments for 5a



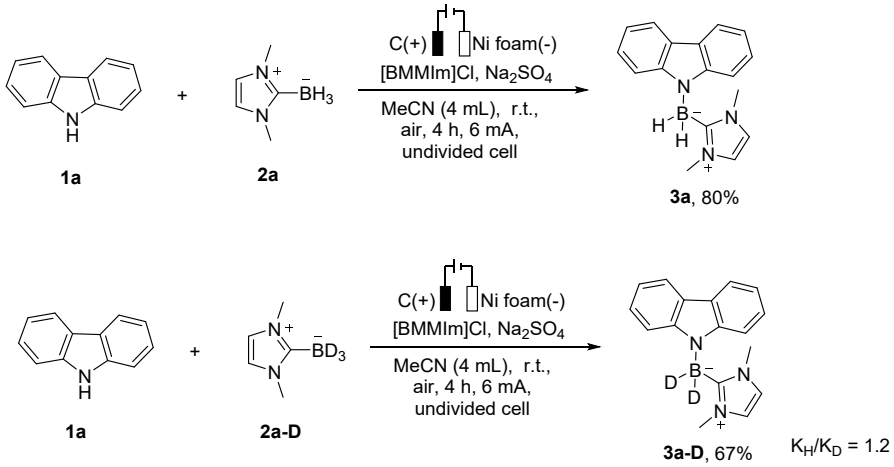


0 min 0 ppm 20 min 3.3 ppm 25 min 29.2 ppm 45 min 428.9 ppm 4 h 266.5 ppm

Figure S9. H_2 detection experiments for 5a

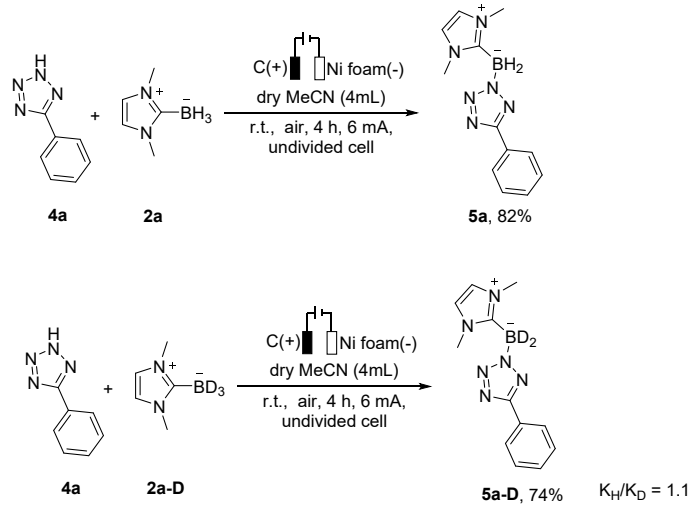
3.2 Kinetic experiments

3.2.1 Kinetic experiments for 3a and D-3a



Under air, a mixture of carbazole **1a** (33.4 mg, 0.2 mmol), 1,3-dimethylimidazolylborane **2a** (66.0 mg, 0.6 mmol), [BMMIm]Cl (37.7 mg, 0.2 mmol), anhydrous sodium sulfate (28.4 mg, 0.2 mmol, 1.0 equiv.) and dry MeCN (4 mL) were added in an oven-dried undivided bottle (10 mL). The rest of the conditions remained the same, and the other bottle had **2a-D** (67.8 mg, 0.6 mmol) instead of **2a**. Ultimately, **3a** and **3a-D** were obtained in 80% and 67% yields, respectively.

3.2.2 Kinetic experiments for 5a and D-5a



Under air, a mixture of 5-Phenyl-1H-tetrazole **4a** (0.3 mmol), 1,3-dimethylimidazolylborane **2a** (0.9 mmol) and dry MeCN (4 mL) were added in an oven-dried undivided bottle (10 mL). The rest of the conditions remained the same, and the other bottle had **2a-D** (0.9 mmol) instead of **2a**. Ultimately, **5a** and **5a-D** were obtained in 82% and 74% yields, respectively.

3.3 Switching current experiment

3.3.1 Switching current experiment for 3a

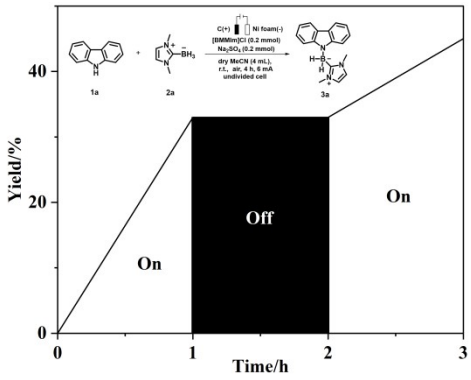


Figure S10. Switching current experiment for 3a

3.3.2 Switching current experiment for 5a

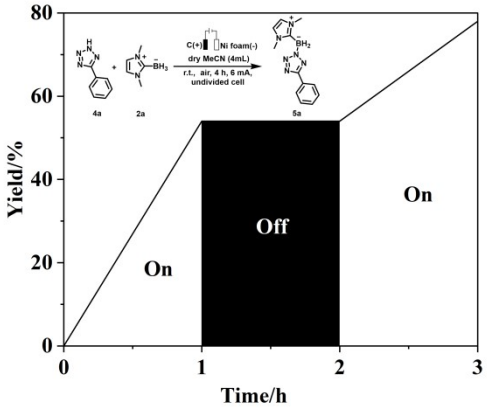
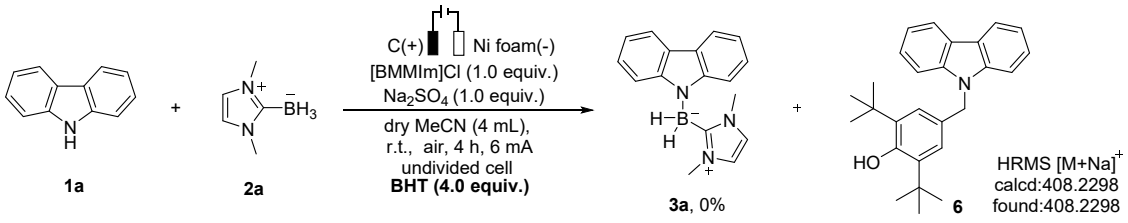


Figure S11. Switching current experiment for 5a

Three undivided electrolytic cells (No.1, No.2 and No.3) were selected and the reaction was carried out according to the general procedure, alternating between electrolysis and no current. The isolated products were obtained by column chromatography.

3.4 Free radical capture experiments



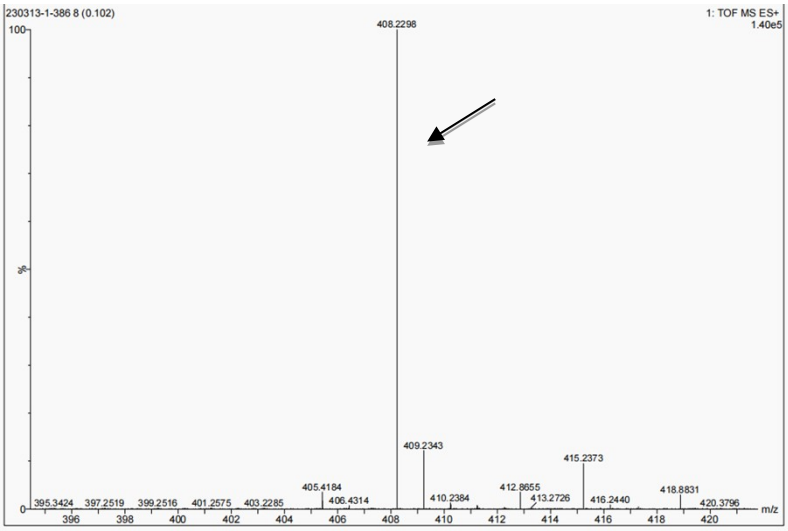
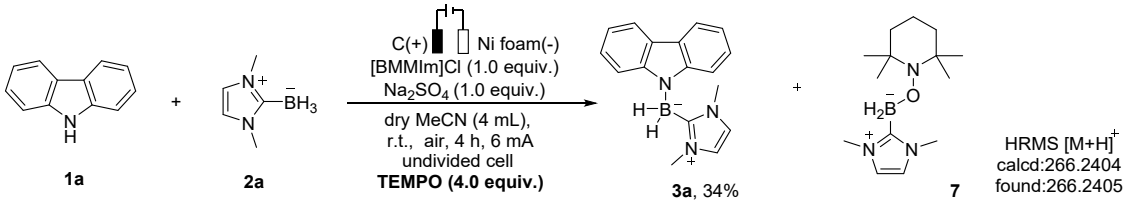


Figure S12. HRMS of the 6



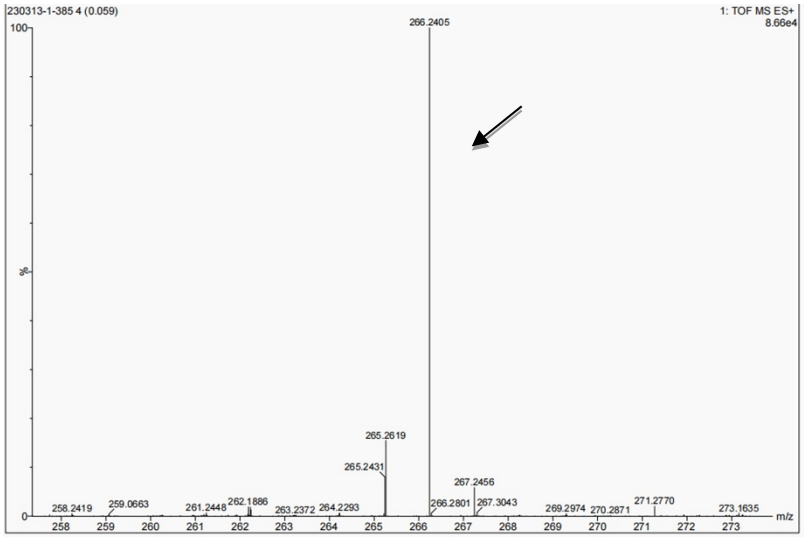
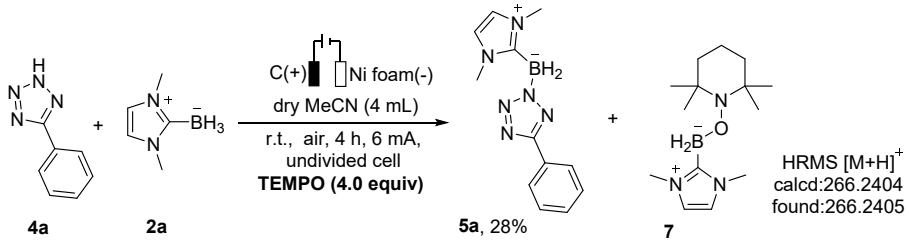


Figure S13. HRMS of the 7



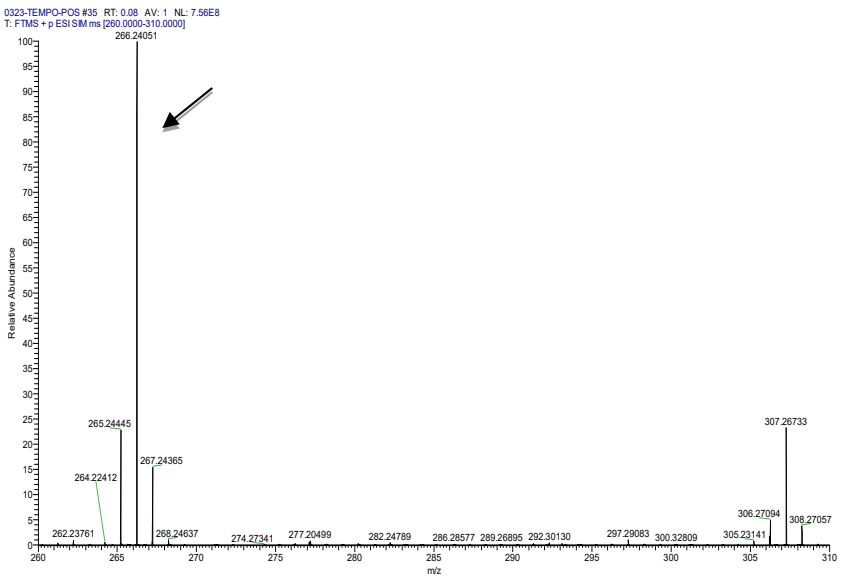


Figure S14. HRMS of the 7

3.5 Cyclic voltammetry experiments

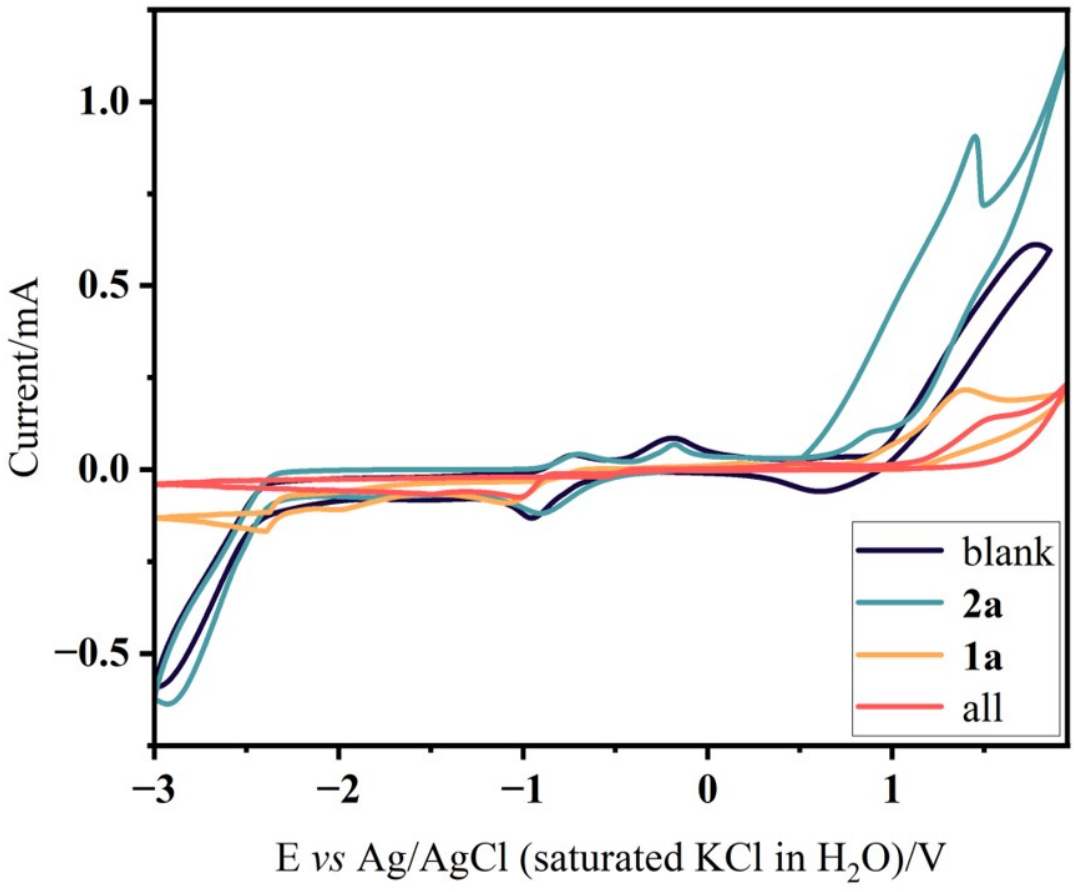


Figure S15. Cyclic voltammetry experiment of 3a

Cyclic voltammograms using a glassy carbon disk as work electrode, Pt disk and Ag/AgCl as counter and reference electrode, respectively, at 100 mV/s scan rate.

Black line (blank): [BMMIM]Cl+Na_2SO_4+dry CH_3CN;

Orange line (**1a**): **1a**+[BMMIM]Cl+Na_2SO_4+dry CH_3CN;

Green line (**2a**): **2a**+[BMMIM]Cl+Na_2SO_4+dry CH_3CN;

Red line (**1a**+**2a**): **1a**+**2a**+[BMMIM]Cl+Na_2SO_4+dry CH_3CN.

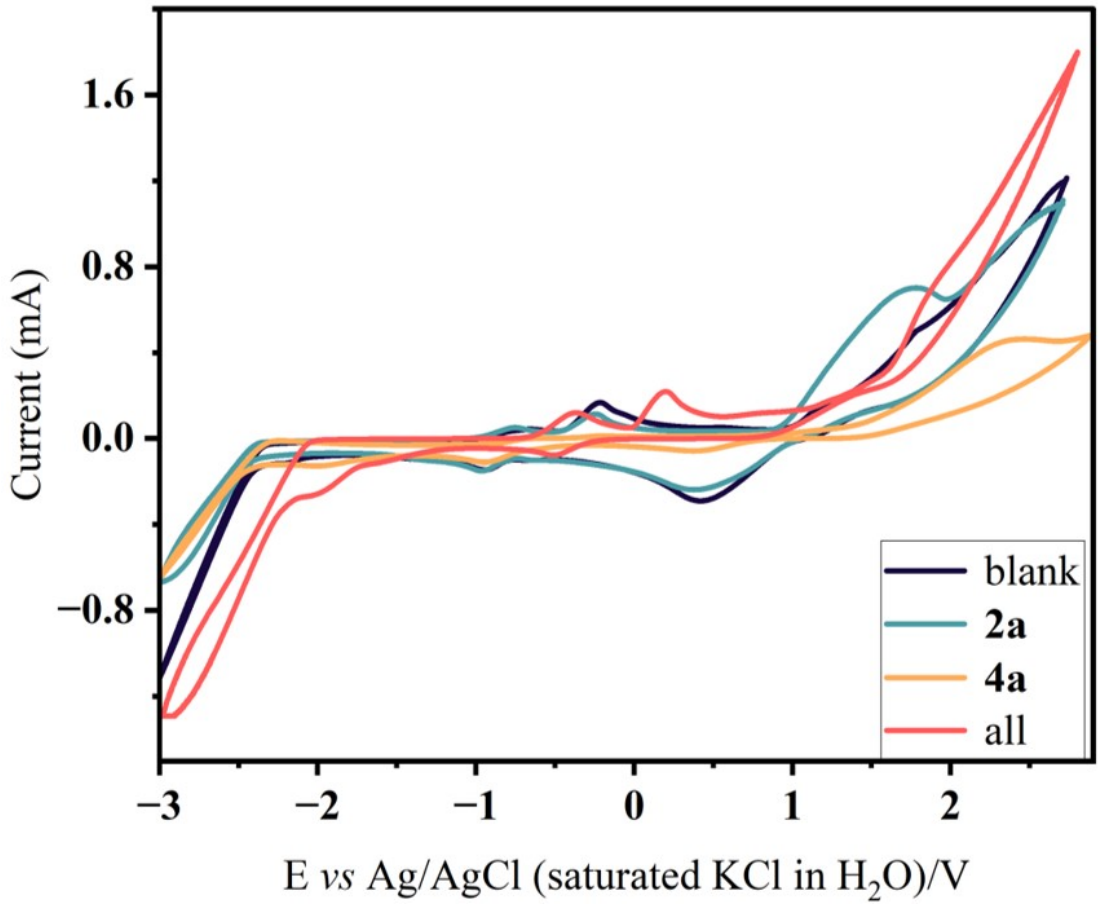
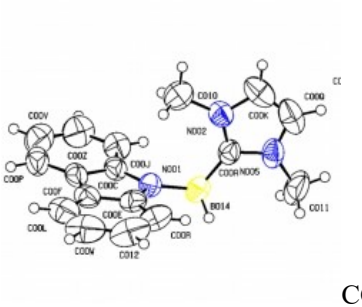


Figure S16. Cyclic voltammetry experiment of 5a

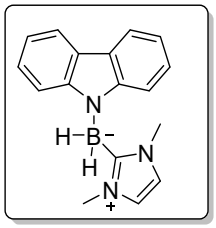
Cyclic voltammograms using a glassy carbon disk as work electrode, Pt disk and Ag/AgCl as counter and reference electrode, respectively, at 100 mV/s scan rate.
Black line (blank):dry CH_3CN;
Orange line (**4a**): **4a**+dry CH_3CN;
Green line (**2a**): **2a**+dry CH_3CN;
Red line (**4a**+**2a**): **4a**+**2a**+dry CH_3CN.

4. The crystallographic data

4.1 The crystallographic data of 3a



CCDC 2451381



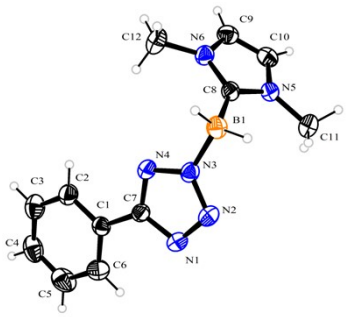
3a

Figure S17. Crystal data and structural refinement of **3a**

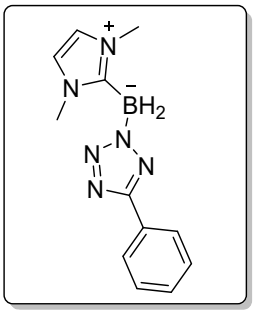
Compound	**3a**
Empirical formula	$C_{17}H_{18}BN_3$
Formula weight	275.15
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.575(5)
b/Å	8.029(3)
c/Å	25.514(8)
α/°	90
β/°	102.777(6)
γ/°	90
Volume/Å^3	3111.6(17)
Z	8
ρ_{calc}g/cm^3	1.175
μ/mm^{-1}	0.070
F(000)	1168.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.816 to 52.744
Index ranges	-15 ≤ h ≤ 19, -9 ≤ k ≤ 10, -31 ≤ l ≤ 31

Reflections collected	16821
Independent reflections	6326 [R_{int} = 0.0596, R_{sigma} = 0.0732]
Data/restraints/parameters	6326/0/383
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0715, wR_2 = 0.1826
Final R indexes [all data]	R_1 = 0.1560, wR_2 = 0.2315
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.16

4.2 The crystallographic data of 5a



CCDC 2406846



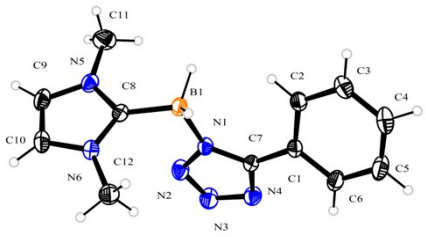
5a

Figure S18. Crystal data and structural refinement of **5a**

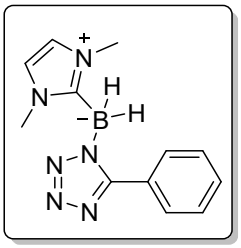
Compound	**5a**
Empirical formula	$C_{24}H_{30}B_2N_{12}$
Formula weight	508.22
Temperature/K	296.15
Crystal system	monoclinic
Space group	C2/c
a/Å	14.861(6)
b/Å	13.916(5)
c/Å	13.706(5)
α/°	90
β/°	107.314(6)
γ/°	90
Volume/$Å^3$	2705.9(18)
Z	4
$\rho_{calc}g/cm^3$	1.248
μ/mm^{-1}	0.080
F (000)	1072.0

Crystal size/mm^3	0.13 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.1 to 56.764
Index ranges	-19 ≤ h ≤ 19, -17 ≤ k ≤ 18, -18 ≤ l ≤ 18
Reflections collected	11956
Independent reflections	3373 [R_{int} = 0.0351, R_{sigma} = 0.0331]
Data/restraints/parameters	3373/0/175
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0472, wR_2 = 0.1371
Final R indexes [all data]	R_1 = 0.0712, wR_2 = 0.1550
Largest diff. peak/hole / e Å^{-3}	0.20/-0.17

4.3 The crystallographic data of 5a'



CCDC 2412782



5a'

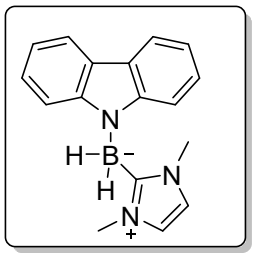
Figure S19. Crystal data and structural refinement of **5a'**

Compound	**5a'**
Empirical formula	$C_{12}H_{15}BN_6$
Formula weight	254.11
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.699(3)
b/Å	6.1877(13)
c/Å	14.634(3)
α/°	90
β/°	109.537(3)
γ/°	90
Volume/Å^3	1339.7(5)
Z	4
ρ_{calc}g/cm^3	1.260

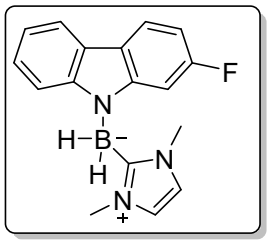
μ/mm^{-1}	0.081
F(000)	536.0
Crystal size/mm^3	0.2 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.506 to 62.842
Index ranges	$-22 \leq h \leq 22$, $-8 \leq k \leq 8$, $-21 \leq l \leq 20$
Reflections collected	13686
Independent reflections	4309 [R_{int} = 0.0286, R_{sigma} = 0.0283]
Data/restraints/parameters	4309/0/180
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0479, wR_2 = 0.1389
Final R indexes [all data]	R_1 = 0.0655, wR_2 = 0.1551
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.23

5. Spectroscopic data

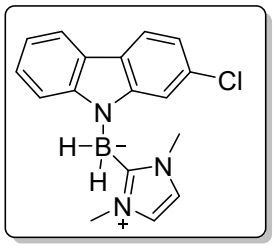
5.1 Spectroscopic data for 3a-3z



(9*H*-carbazol-9-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3a): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 44.0 mg, 80% yield. White solid; m.p.: 155-157 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05-8.16 (m, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.33-7.37 (m, 2H), 7.10-7.14 (m, 2H), 6.73 (s, 2H), 3.39 (s, 6H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 145.5 (2C), 125.1 (2C), 123.8(2C), 122.4 (2C), 121.0, 120.0 (2C), 117.2 (2C), 111.8 (2C), 35.4 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.89 (s). HRMS (ESI-Orbitrap) m/z calcd for $C_{17}H_{19}N_3B^+$ $[M+H]^+$: 276.1667; found: 276.1659.

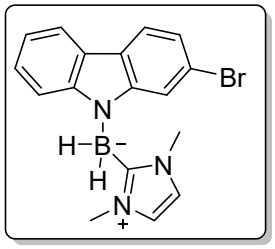


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(2-fluoro-9*H*-carbazol-9-yl)dihydroborate (3b): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 50.4 mg, 86% yield. Yellow solid; m.p.: 185-187 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, J = 7.6 Hz, 1H), 7.97 (dd, J = 8.4, 6.0 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.30 (t, J = 7.8 Hz, 1H), 7.11-7.14 (m, 2H), 6.83-6.86 (m, 1H), 6.73 (s, 2H), 3.37 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.0 (d, J_{C-F}= 87.0 Hz), 146.6 (d, J_{C-F}= 12.0 Hz), 146.3 (d, J_{C-F}= 1.5 Hz), 124.4, 124.0, 121.1 (2C), 120.7, 120.4 (d, J_{C-F}= 10.5 Hz), 119.4, 111.7, 105.1 (d, J_{C-F}= 24.0 Hz), 97.9 (d, J_{C-F}= 25.5 Hz), 35.7 (2C); **^{19}F NMR** (565 MHz, $CDCl_3$) δ -117.4; **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.88 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{17}H_{17}N_3BFNa^+$ $[M+Na]^+$: 316.1392; found: 316.1401.

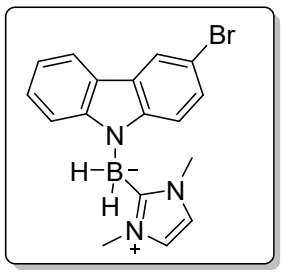


(2-chloro-9*H*-carbazol-9-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3c): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 45.7 mg, 74% yield. Yellow

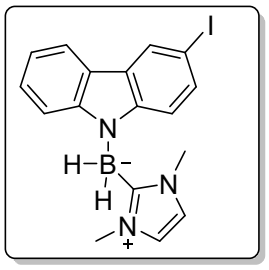
oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 1.8 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.36-7.30 (m, 1H), 7.16-7.09 (m, 1H), 7.07 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.67 (s, 2H), 3.33 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.4, 146.1, 130.4, 125.1, 123.7, 122.8, 121.2 (2C), 120.5, 119.7, 117.7, 117.4, 111.9, 111.7, 35.7 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.82 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{17}H_{17}N_3BClNa^+$ $[M+Na]^+$: 332.1097; found: 332.1102.



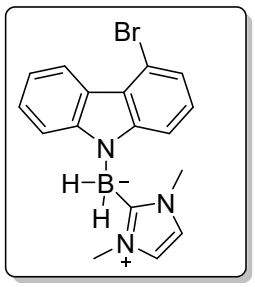
(2-bromo-9*H*-carbazol-9-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3d): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 33.2 mg, 47% yield. White oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 1.2 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 6.6 Hz, 1H), 7.25 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.66 (s, 2H), 3.35 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.7, 145.9, 125.2 (2C), 123.7, 123.1, 121.2 (2C), 120.9, 120.0, 119.8, 118.5, 117.7 (2C), 114.7, 112.0, 35.6 (2C),; **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.90 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{17}H_{17}N_3BBrNa^+$ $[M+Na]^+$: 376.0592; found: 376.0598.



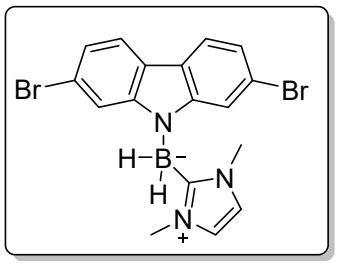
(3-bromo-9*H*-carbazol-9-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3e): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 52.3 mg, 74% yield. White solid. m.p.: 135-137 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.8 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.43-7.37 (m, 2H), 7.36-7.31 (m, 2H), 7.11(t, J = 7.2 Hz, 1H), 6.61 (s, 2H), 3.28 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.9, 144.2, 127.3, 125.9(2C), 125.5, 123.1, 122.3, 121.2(2C), 119.9, 117.5, 113.3, 112.0, 109.8, 35.6 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -22.0 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{17}H_{17}N_3BBrNa^+$ $[M+Na]^+$: 376.0592; found: 376.0598.



(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(3-iodo-9*H*-carbazol-9-yl)dihydroborate (3f): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 35.3 mg, 44% yield. Orange solid. m.p.: 179-181 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.37 (d, *J*=1.8 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.57 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.38-7.33 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.14-7.10 (m, 1H), 6.75 (s, 2H), 3.36 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.7, 144.8, 132.9, 128.6, 126.9, 125.5, 123.0, 121.3(2C), 120.0(2C), 117.7, 114.0, 111.9(2C), 35.8 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.93 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{17}H_{17}N_3BINa^+$ $[M+Na]^+$: 424.0453; found: 424.0457.

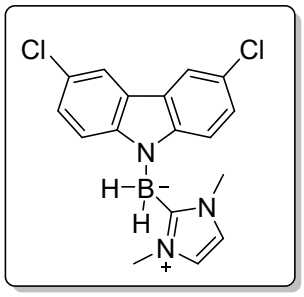


(4-bromo-9*H*-carbazol-9-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3g): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 36.0 mg, 51% yield. White solid. m.p.: 119-121 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.67 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.08 (m, 2H), 6.46 (s, 2H), 3.17 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.9, 145.8, 125.4, 125.1, 123.8, 122.6, 122.2 (2C), 121.2 (2C), 121.1, 117.3 (2C), 116.3, 111.8, 110.8, 35.6 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.82 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{17}H_{17}N_3BBrNa^+$ $[M+Na]^+$: 376.0592; found: 376.0598.

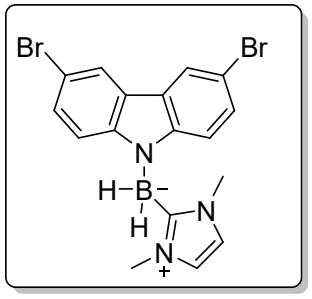


(2,7-dibromo-9*H*-carbazol-9-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3h): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 58.9 mg, 68% yield. White solid. m.p.: 206-208 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 1.2 Hz, 2H), 7.26 (dd, J = 8.4, 1.2 Hz, 2H), 6.74 (s, 2H), 3.36 (s, 6H); **^{13}C NMR** (150 MHz,

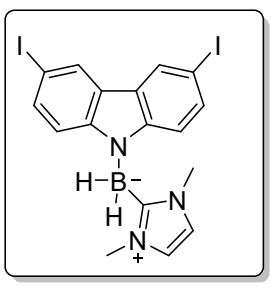
$CDCl_3$) δ 146.9 (2C), 122.6 (2C), 121.4 (2C), 120.9 (2C), 120.8 (2C), 119.0 (2C), 115.0 (2C), 35.6 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.87 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{17}H_{16}N_3BBr_2K^+$ $[M+K]^+$: 469.9436; found: 469.9447.



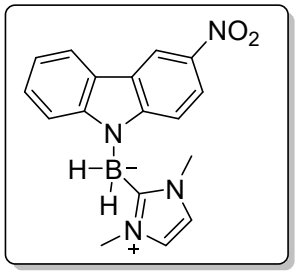
(3,6-dichloro-9*H*-carbazol-9-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborat (3i): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 53.5 mg, 78% yield. White solid. m.p.: 186-188 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 2.4 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 2H), 7.32 (dd, *J* = 9.0, 2.4 Hz, 2H), 6.73 (s, 2H), 3.31 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.4 (2C), 125.5 (2C), 124.3 (2C), 122.8 (2C), 121.3 (2C), 119.6 (2C), 113.1 (2C), 35.7 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.5 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{17}H_{16}N_3BCl_2Na^+$ $[M+Na]^+$: 366.0707; found: 366.0719.



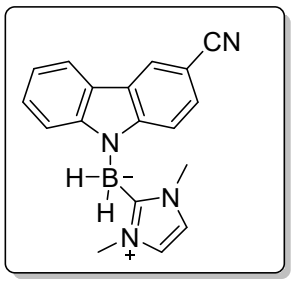
(3,6-dibromo-9*H*-carbazol-9-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3j): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 54.5 mg, 63% yield. White solid. m.p.: 199-201 ℃; **1H NMR** (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 1.8 Hz, 2H), 7.45 (dd, *J* = 9.0, 1.8 Hz, 2H), 7.35 (d, *J* = 9.0 Hz, 2H), 6.73 (s, 2H), 3.33 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.5 (2C), 128.1 (2C), 124.8 (2C), 122.6 (2C), 121.3 (2C), 113.6 (2C), 110.3 (2C), 35.7 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.92 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{17}H_{16}N_3BBr_2K^+$ $[M+K]^+$: 469.9436; found: 469.9447.



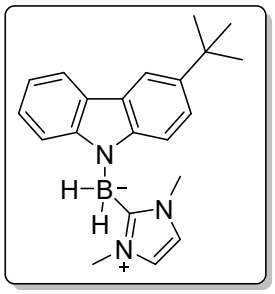
(3,6-diiodo-9*H*-carbazol-9-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3k): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 46.4 mg, 44% yield. White solid. m.p.: 204-206 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.8 Hz, 2H), 7.57 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.75 (s, 2H), 3.33 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.7 (2C), 133.7 (2C), 128.8 (2C), 125.6 (2C), 121.4 (2C), 114.2 (2C), 80.1 (2C), 35.8 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.89 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{17}H_{16}N_3BI_2Na^+$ $[M+Na]^+$: 549.9419; found: 549.9422.



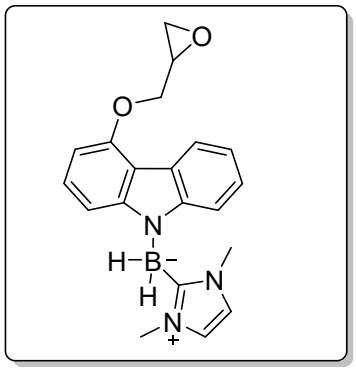
(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(3-nitro-9*H*-carbazol-9-yl)dihydroborate (3l): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 42.2 mg, 66% yield. Orange solid. m.p.: 184-186 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.02 (d, *J* = 2.4 Hz, 1H), 8.28 (dd, *J* = 9.0, 2.4 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.48 (d, J = 9.0 Hz, 2H), 7.44-7.41 (m, 1H), 7.26 (s, 1H), 6.82 (s, 2H), 3.41 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.3, 147.2, 139.2, 126.6, 124.5, 123.8, 121.5 (2C), 121.1, 120.5, 119.4, 117.2, 112.8, 111.2, 35.9 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.79 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{17}H_{17}N_4BO_2Na^+$ $[M+Na]^+$: 343.1337; found: 343.1343.



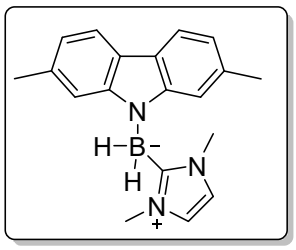
(3-cyano-9*H*-carbazol-9-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3m): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 37.8 mg, 63% yield. Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.36 (d, J = 1.2 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.56 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.42-7.38 (m, 1H), 7.23-7.17 (m, 1H), 6.73 (s, 2H), 3.34 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.5, 146.3, 128.0, 126.2, 124.8, 124.3, 123.4, 121.9, 121.4 (2C), 120.1, 118.8, 112.4 (2C), 99.0, 35.7 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -22.0 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{18}H_{17}N_4BNa^+$ $[M+Na]^+$: 323.1439; found: 323.1448.



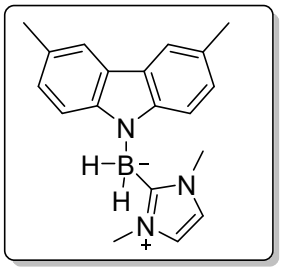
(3-tert-butyl-9*H*-carbazol-9-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3n): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 31.8 mg, 48% yield. Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 1.8 Hz, 2H), 7.46-7.40 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.31-7.34 (m, 1H), 7.11-7.05 (m, 1H), 6.71 (s, 2H), 3.40 (s, 6H), 1.43 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.1, 143.9, 139.8, 124.5, 124.4, 123.8, 122.7, 121.1 (2C), 119.6, 116.7, 115.8, 111.7, 111.1, 35.8 (2C), 34.7, 31.3 (3C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -22.15 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{21}H_{26}N_3BNa^+$ $[M+Na]^+$: 354.2112; found: 354.2122.



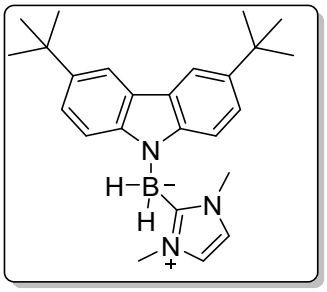
(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(4-(oxiran-2-ylmethoxy)-9*H*-carbazol-9-yl)dihydroborate (3o): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 31.9 mg, 46% yield. Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.27-7.23 (m, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 2H), 6.62 (s, 2H), 6.48 (d, *J* = 7.8 Hz, 1H), 4.35 (dd, *J* = 10.8, 3.6 Hz, 1H), 4.21 (dd, *J* = 10.8, 5.4 Hz, 1H), 3.49 (dt, *J* = 7.8, 3.6 Hz, 1H), 3.26 (s, 6H), 2.91 (t, *J* = 4.8 Hz, 1H), 2.83 (dd, *J* = 4.8, 3.0 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.0, 147.4, 145.0, 125.1 (2C), 124.0, 122.7, 121.1 (2C), 117.5 (2C), 113.4, 111.3, 105.7, 99.2, 68.7, 50.7, 45.2, 35.7 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.99 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{20}H_{22}N_3BO_2Na^+$ $[M+Na]^+$: 370.1698; found: 370.1698.



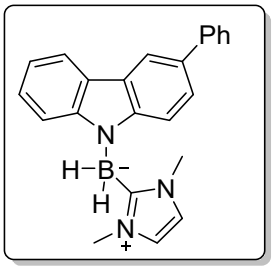
(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(2,7-dimethyl-9*H*-carbazol-9-yl)dihydroborate (3p): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 48.5 mg, 85% yield. White solid. m.p.: 161-163 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.22 (s, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.66 (s, 2H), 3.34 (s, 6H), 2.49 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.3 (2C), 133.9 (2C), 122.2 (2C), 121.1 (2C), 119.1 (2C), 118.5 (2C), 111.8 (2C), 35.7 (2C), 22.5 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.94 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{19}H_{22}N_3BNa^+$ $[M+Na]^+$: 326.1799; found: 326.1809.



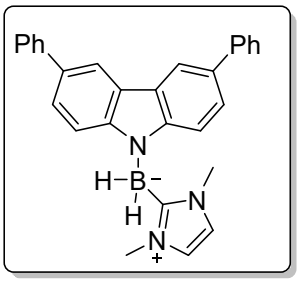
(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(3,6-dimethyl-9*H*-carbazol-9-yl)dihydroborate (3q): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 32.1 mg, 53% yield. White solid. m.p.: 197-199 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.57 (s, 2H), 3.27 (s, 6H), 2.43 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.2 (2C), 126.0 (2C), 125.7 (2C), 124.1 (2C), 121.1 (2C), 119.7 (2C), 111.3 (2C), 35.7 (2C), 21.6 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.81 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{19}H_{22}N_3BNa^+$ $[M+Na]^+$: 326.1799; found: 326.1809.



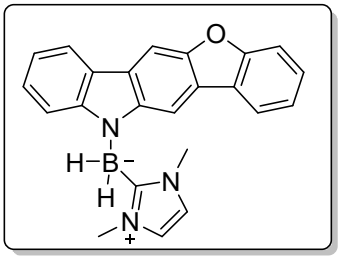
(3,6-di-tert-butyl-9*H*-carbazol-9-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3r): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 54.2 mg, 70% yield. Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.30 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.24 (d, J = 9.0 Hz, 2H), 6.51 (s, 2H), 3.28 (s, 6H), 1.47 (s, 18H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.2 (2C), 139.5 (2C), 123.9 (2C), 122.4 (2C), 121.0 (2C), 115.5 (2C), 110.9 (2C), 35.8 (2C), 34.7 (2C), 32.3 (6C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.51 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{25}H_{36}N_3B^+$ $[M+H]^+$: 388.2919; found: 388.2922.



(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(3-phenyl-9*H*-carbazol-9-yl)dihydroborate (3s): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 41.4 mg, 59% yield. Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.2 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.61 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.47-7.40 (m, 3H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.66 (s, 2H), 3.37 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.2, 145.3, 143.0, 130.3, 128.8 (2C), 127.2 (2C), 125.9, 124.9(2C), 124.7, 124.4, 124.3, 121.2, 119.8, 118.3, 117.3, 111.9(2C), 35.8 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.69 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{23}H_{22}N_3BNa^+$ $[M+Na]^+$: 374.1799; found: 374.1800.

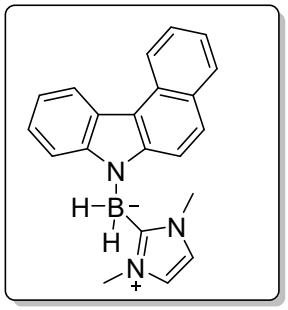


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(3,6-diphenyl-9*H*-carbazol-9-yl)dihydroborate (3t): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 51.2 mg, 60% yield. White solid. m.p.: 186-188 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.29 (d, *J* = 1.2 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 4H), 7.54 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 4H), 7.20 (t, J = 7.2 Hz, 2H), 6.53 (s, 2H), 3.27 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.8 (2C), 142.8 (2C), 130.5 (2C), 128.8 (4C), 127.2 (4C), 126.0 (2C), 124.9 (2C), 124.5 (2C), 121.2 (2C), 118.3 (2C), 112.1 (2C), 35.8 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.90 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{29}H_{26}N_3BNa^+$ $[M+Na]^+$: 450.2112; found: 450.2116.

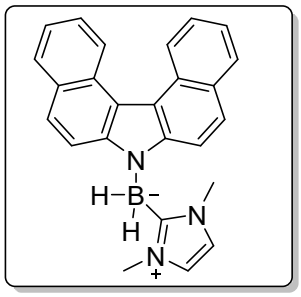


(11*H*-benzofuro[3,2-*b*]carbazol-11-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3u): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v).

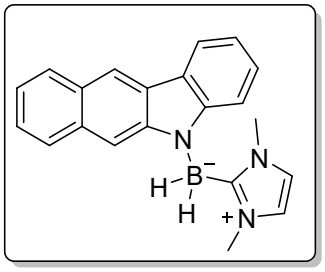
44.6 mg, 61% yield. White solid. m.p.: 107-109 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.44 (dd, *J* = 18.0, 8.4 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.29-7.22 (m, 2H), 7.18 (t, J = 7.2 Hz, 1H), 6.51 (s, 2H), 3.20 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.0, 151.8, 146.6, 145.2, 126.0, 124.5, 124.3, 122.6, 122.2, 121.9, 121.2 (2C), 119.2, 118.1, 116.6, 113.9, 112.0, 111.5, 109.1, 108.0, 35.6 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.72 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{23}H_{20}N_3BONa^+$ $[M+Na]^+$: 388.1592; found: 388.1594.



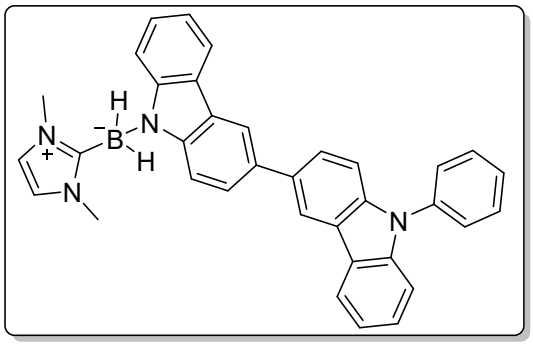
(7*H*-benzo[*c*]carbazol-7-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3v): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 37.1 mg, 57% yield. Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.81 (d, *J* = 8.4 Hz, 1H), 8.57 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 9.0 Hz), 7.66 - 7.62 (m, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.41-7.33 (m, 2H), 7.27 (t, *J* = 7.2 Hz, 1H), 6.56 (s, 2H), 3.23 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.6, 143.4, 130.5, 129.0, 128.5, 126.1, 125.9 (2C), 124.9, 123.1, 123.0, 121.7, 121.5, 121.1 (2C), 118.2, 115.7, 115.0, 112.6, 35.6 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.95 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{21}H_{20}N_3BNa^+$ $[M+Na]^+$: 348.1643; found: 348.1649.



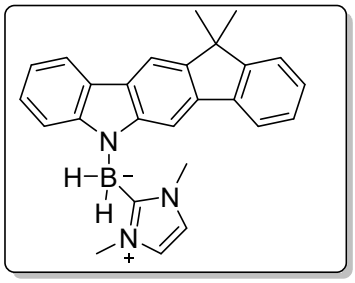
(7*H*-dibenzo[*c*,*g*]carbazol-7-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3w): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 45.0 mg, 60% yield. White solid; m.p.: 245-248 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.24 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 7.8 Hz, 2H), 7.87 (d, *J* = 9.0 Hz, 2H), 7.75 (d, *J* = 9.0 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 6.54 (s, 2H), 3.21 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 142.5 (2C), 129.6 (2C), 129.5 (2C), 128.9 (2C), 125.2 (2C), 125.1 (4C), 124.5 (2C), 122.3 (2C), 121.2 (2C), 118.2, 115.1 (2C), 35.5 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.36 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{25}H_{22}N_3BNa^+$ $[M+Na]^+$: 398.1799; found: 398.1805.



(5*H*-benzo[*b*]carbazol-5-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3x): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 38.4 mg, 59% yield. Yellow oil; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.63 (s, 1H), 8.23 (d, J = 7.2 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.72 (s, 1H), 7.38-7.42 (m, 1H), 7.35-7.38 (m, 2H), 7.34 (d, J = 10.8 Hz, 2H), 7.27-7.30 (m, 1H), 7.08-7.11 (m, 1H), 3.41 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.6, 146.0, 132.7, 128.4, 127.3, 127.2, 126.7, 124.1, 124.0, 121.4 (2C), 121.2, 120.6, 117.7, 117.0, 111.2, 105.9, 35.8 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.82 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{21}H_{20}N_3BNa^+$ $[M+Na]^+$: 348.1643; found: 348.1653.

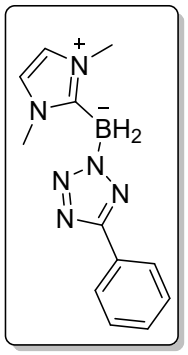


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(9'-phenyl-9*H*,9'*H*-[3,3'-bicarbazol]-9-yl)dihydroborate (3y): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 41.3 mg, 40% yield. White solid. m.p.: 175-178 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.37 (dd, J = 23.4, 1.2 Hz, 2H), 8.14 (dd, J = 21.0, 7.8 Hz, 2H), 7.73 (dd, J = 8.4, 1.2 Hz, 1H), 7.67 (dd, J = 8.4, 1.8 Hz, 1H), 7.56 (d, J = 4.2 Hz, 4H), 7.49 (d, J = 8.4 Hz, 1H), 7.36 (dd, J = 11.4, 5.4 Hz, 3H), 7.30 (t, J = 7.8 Hz, 2H), 7.23 (dd, J = 10.8, 3.6 Hz, 1H), 7.08 (t, J = 7.2 Hz, 2H), 6.71 (s, 2H), 3.38 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.2, 145.0, 141.4, 139.8, 138.1, 135.5, 131.2, 130.0 (2C), 129.6, 127.2 (2C), 126.0 (2C), 124.9 (2C), 124.7, 124.5, 124.0, 123.9, 121.2 (2C), 120.5, 120.0 (2C), 118.8, 118.4, 117.2, 112.0, 111.9, 110.0 (2C), 35.9 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.27 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{39}H_{30}N_4BNa^+$ $[M+Na]^+$: 539.2378; found: 539.2382.

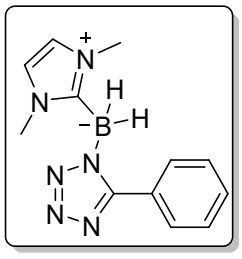


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(11,11-dimethylindeno[1,2-*b*]carbazol-5(11*H*)-yl)dihydroborate (3z): New compound. (Eluent: petroleum ether/ dichloromethane = 3:1, v/v). 45.4 mg, 58% yield. Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.45 (s, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.25-7.20 (m, 2H), 7.13 (dd, J = 7.2, 0.6 Hz, 1H), 7.05-7.01 (m, 1H), 6.51 (s, 2H), 3.24 (s, 6H), 1.44 (6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.3, 152.1, 146.4, 146.2, 140.9, 129.5, 127.0, 125.4, 124.5, 124.4, 123.7, 122.5, 121.1 (2C), 119.6, 119.0, 117.2, 111.7, 110.7, 105.8(2C), 46.5, 35.6 (2C), 28.5 (2C); **^{11}B NMR** (160 MHz, DMSO-d_6) δ -21.73 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{26}H_{26}N_3BNa^+$ $[M+Na]^+$: 414.2112; found: 414.2123.

5.2 Spectroscopic data for 5a-5ag

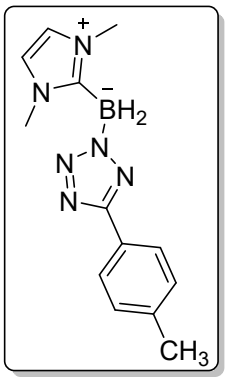


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-phenyl-2*H*-tetrazol-2-yl)dihydroborate 5a: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 42 mg, 82% yield. White solid; m.p.: 136-138 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.5 Hz, 2H), 7.40 (dt, *J* = 25.5, 7.5 Hz, 3H), 6.95 (s, 2H), 3.86 (s,6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.4, 129.2, 129.1, 128.6 (2C), 126.8 (2C), 121.6 (2C), 36.5 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -18.96 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{16}N_6B^+$ $[M+H]^+$: 255.1524; found: 255.1521.

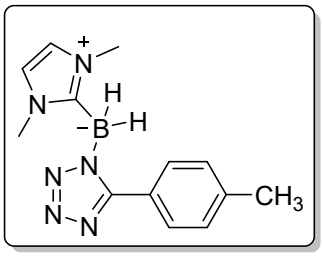


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-phenyl-1*H*-tetrazol-1-yl)dihydroborate 5a': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 10 mg, 20% yield. White solid;

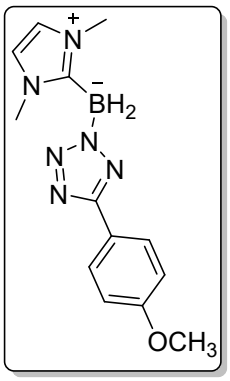
m.p.: 137-139 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 6.5 Hz, 2H), 7.49 (q, *J* = 6.0 Hz, 3H), 6.95 (s, 2H), 3.70 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.9, 129.7, 129.5, 128.3 (2C), 127.4 (2C), 121.5 (2C), 36.4 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -20.22 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{16}N_6B^+$ $[M+H]^+$: 255.1524; found: 255.1521.



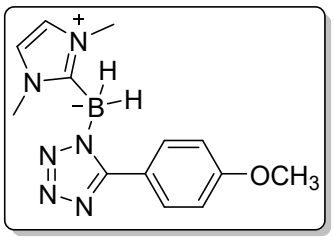
(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(p-tolyl)-2*H*-tetrazol-2-yl)dihydroborate 5b: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 52 mg, 65% yield. White solid; m.p.: 132-134 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 6.5 Hz, 2H), 7.25 (t, *J* = 12.5 Hz, 2H), 6.94 (d, *J* = 1.5 Hz, 2H), 3.85 (d, *J* = 3.0 Hz, 6H), 2.37 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.5, 139.1, 129.3, 126.7 (2C), 126.4 (2C), 121.6 (2C), 36.5 (2C), 21.5; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -19.01 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{18}N_6B^+$ $[M+H]^+$: 269.1681; found: 269.1678.



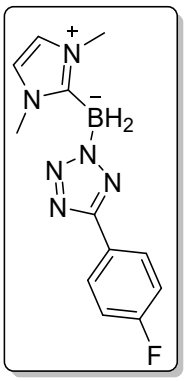
(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(5-(p-tolyl)-1H-tetrazol-1-yl)dihydroborate 5b': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 26 mg, 32% yield. White solid; m.p.: 170-172 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 9.0 Hz, 2H), 6.89 (s, 2H), 3.62 (s, 6H), 2.35 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.9, 139.7, 129.4, 129.0 (2C), 124.5 (2C), 121.5 (2C), 36.3 (2C), 21.6; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -20.15 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{18}N_6B^+$ $[M+H]^+$: 269.1681; found: 269.1685.



(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(4-methoxyphenyl)-2*H*-tetrazol-2-yl)dihydroborate 5c: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 61 mg, 72% yield. White solid; m.p.: 132-134 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 7.5 Hz, 4H), 3.85 (d, *J* = 10.0 Hz, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 164.3, 160.4, 128.2, 121.9 (2C), 121.6 (2C), 114.0 (2C), 55.4, 36.5 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -18.99 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{18}N_6BO^+$ $[M+H]^+$: 285.1630; found: 285.1620.

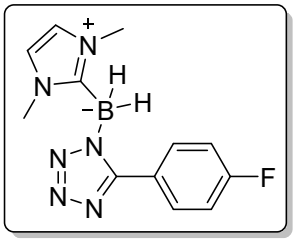


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(4-methoxyphenyl)-1*H*-tetrazol-1-yl)dihydroborate 5c': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 31 mg, 36% yield. White solid; m.p.: 163-165 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.95 (s, 2H), 3.88 (s, 3H), 3.71 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 169.2, 160.7, 131.0, 121.5 (2C), 113.8 (2C), 55.5, 36.4 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -20.19 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{18}N_6BO^+$ $[M+H]^+$: 285.1630; found: 285.1632.

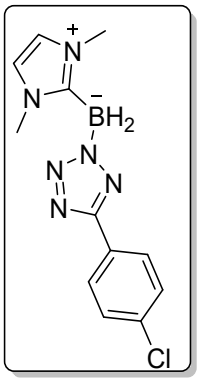


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(4-fluorophenyl)-2*H*-tetrazol-2-yl)dihydroborate 5d: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 64 mg, 78% yield. White solid; m.p.: 124-125 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.5, 5.5 Hz,

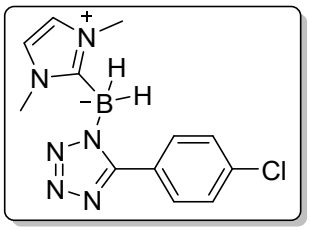
2H), 7.11 (t, *J* = 8.5 Hz, 2H), 6.97 (s, 2H), 3.88 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.4, 163.7, 162.5, 128.7, 128.6, 125.5, 125.5, 121.6, 115.7, 115.5 , 36.5 (2C); **^{19}F NMR** (471 MHz, $CDCl_3$) δ -112.3; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -18.98 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BF^+$ $[M+H]^+$: 273.1430; found: 273.1435.



(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(4-fluorophenyl)-1*H*-tetrazol-1-yl)dihydroborate 5d': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 23 mg, 28% yield. White solid; m.p.: 162-164 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.19 (t, *J* = 8.5 Hz, 2H), 6.99 (s, 2H), 3.71 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.1, 131.5, 131.5, 123.5, 123.5, 121.6, 115.5, 115.3, 36.3 (2C); **^{19}F NMR** (471 MHz, $CDCl_3$) δ -111.2; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -20.15 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BF^+$ $[M+H]^+$: 273.1430; found: 273.1443.

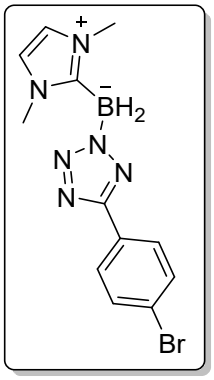


(5-(4-chlorophenyl)-2*H*-tetrazol-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5e: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 58 mg, 67% yield. White solid; m.p.: 132-133 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 - 8.08 (m, 2H), 7.42 (dd, *J* = 17.5, 7.5 Hz, 2H), 6.96 (d, *J* = 4.0 Hz, 2H), 3.87 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.6, 135.0, 128.9, 128.1 (2C), 126.8 (2C), 121.6 (2C), 36.5 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -18.96 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BCl^+$ $[M+H]^+$: 289.1135; found: 289.1134.

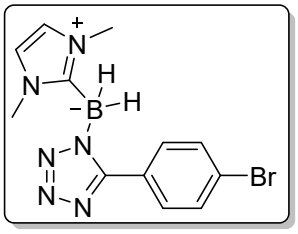


(5-(4-chlorophenyl)-1*H*-tetrazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5e': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 20 mg,

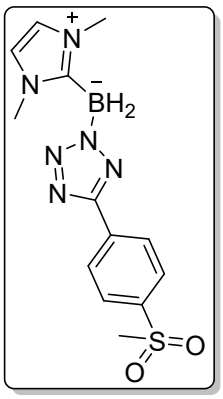
23% yield. White solid; m.p.: 154-156 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 13.5 Hz, 2H), 3.71 (d, *J* = 10.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.4, 129.2, 129.1, 128.6 (2C), 126.7 (2C), 121.6 (2C), 36.5 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -20.24 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BCl^+$ $[M+H]^+$: 289.1135; found: 289.1151.



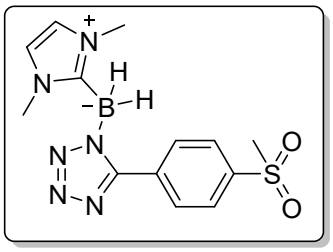
(5-(4-bromophenyl)-2*H*-tetrazol-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5f: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 71 mg, 71% yield. White solid; m.p.: 129-132 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.5 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz,1H), 6.96 (d, *J* = 4.0 Hz, 2H), 3.87 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.6, 131.8, 128.3, 126.8 (2C), 123.3 (2C), 121.6 (2C), 36.5 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -19.06 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BBr^+$ $[M+H]^+$: 333.0630; found: 333.0630.



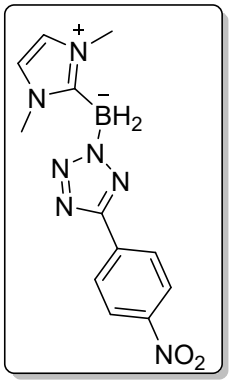
(5-(4-bromophenyl)-1*H*-tetrazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5f': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 13 mg, 13% yield. White solid; m.p.: 145-147 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 25.0, 7.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 14.5 Hz, 2H), 3.61 (d, *J* = 11.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.4, 129.2, 129.1, 128.7 (2C), 126.8 (2C), 121.6 (2C), 36.5 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -20.11 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BBr^+$ $[M+H]^+$: 333.0630; found: 333.0648.



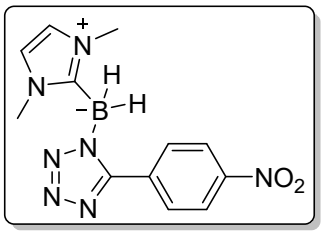
(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(4-(methylsulfonyl)phenyl)-2*H*-tetrazol-2-yl)dihydroborate 5g: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 60 mg, 60% yield. White solid; m.p.: 177-179 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (s, 2H), 7.41 (s, 2H), 6.95 (s, 2H), 3.83 (s, 8H), 3.07 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 164.2, 129.1, 128.5, 127.3 (2C), 126.6 (2C), 121.5 (2C), 44.4, 36.3 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -18.93 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{18}N_6BSO_2^+$ $[M+H]^+$: 333.1300; found: 333.1295.



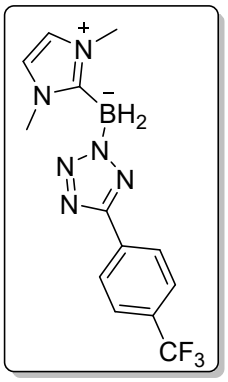
(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(5-(4-(methylsulfonyl)phenyl)-1H-tetrazol-1-yl)dihydroborate 5g': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 25 mg, 25% yield. White solid; m.p.: 126-128 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.29 (d, J = 7.5 Hz, 2H), 7.92 (d, J = 7.5 Hz, 2H), 6.90 (t, J = 12.5 Hz, 2H), 3.83 (s, 6H), 3.01 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 162.8, 140.5, 134.3, 128.6, 127.8, 127.4, 126.7, 121.7 (2C), 44.5, 36.5 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -19.67 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{18}N_6BSO_2^+$ $[M+H]^+$: 333.1300; found: 333.1296.



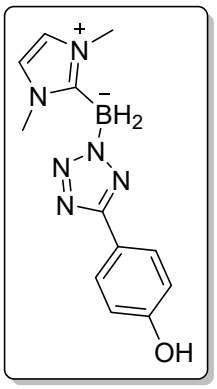
(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(4-nitrophenyl)-2*H*-tetrazol-2-yl)dihydroborate 5h: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 30 mg, 34% yield. Yellow solid; m.p.: 180-182 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 25.0, 8.5 Hz, 4H), 6.94 (s, 2H), 3.84 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 162.0, 148.2, 135.4, 127.5 (2C), 124.1 (2C), 121.7 (2C), 36.6 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -18.97 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_7BO_2^+$ $[M+H]^+$: 300.1375; found: 300.1373.



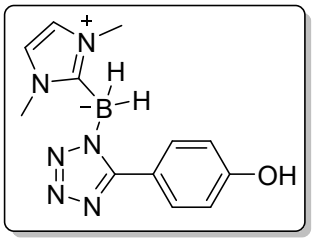
(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(4-nitrophenyl)-1*H*-tetrazol-1-yl)dihydroborate 5h': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 14 mg, 15% yield. Yellow solid; m.p.: 163-165 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 25.0, 9.0 Hz, 4H), 7.03 (s, 2H), 3.92 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 162.7, 148.1, 135.3, 127.4 (2C), 124.1 (2C), 121.7 (2C), 36.6 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -19.02 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_7BO_2^+$ $[M+H]^+$: 300.1375; found: 300.1380.



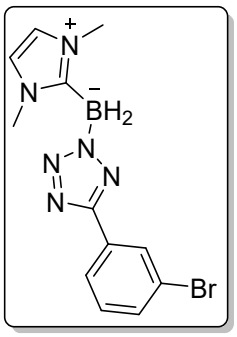
(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(4-(trifluoromethyl)phenyl)-2*H*-tetrazol-2-yl)dihydroborate 5i: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 54 mg, 56% yield. White solid; m.p.: 113-115 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 6.99 (s, 2H), 3.89 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 163.3, 132.6, 130.7, 127.0, 125.6, 125.6, 125.3, 123.1, 121.7, 36.5 (2C); **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.6; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -19.02 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_7BO_2^+$ $[M+H]^+$: 323.1398; found: 323.1392.



(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(4-hydroxyphenyl)-2*H*-tetrazol-2-yl)dihydroborate 5j: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 40 mg, 50% yield. White solid; m.p.: 208-209 ℃, **^{1}H NMR** (500 MHz, CD_3OD) δ 7.84 (d, *J* = 9.0 Hz, 2H), 7.30 (s, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 6H); **^{13}C NMR** (125 MHz, CD_3OD)) δ 164.0, 158.9, 127.7, 121.9 (2C), 119.4 (2C), 115.2 (2C), 35.1 (2C); **^{11}B NMR** (160 MHz, CD_3OD) δ -15.04 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{16}N_6BO^+$ $[M+H]^+$: 271.1474; found: 271.1472.

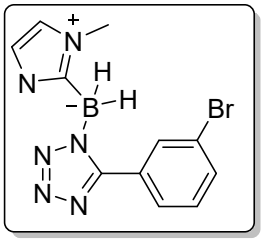


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(4-hydroxyphenyl)-1*H*-tetrazol-1-yl)dihydroborate 5j': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 31 mg, 38% yield. White solid; m.p.: 202-204 ℃, **^{1}H NMR** (500 MHz, CD_3OD) δ 7.84 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.28 (d, *J* = 26.0 Hz, 2H), 6.88 (dd, *J* = 24.0, 8.5 Hz, 2H), 3.85 (s, 2H), 3.63 (s, 4H); **^{13}C NMR** (125 MHz, CD_3OD)) δ 159.3, 158.0, 130.5, 127.7 (2C), 121.7 (2C), 114.8 (2C), 34.8 (2C); **^{11}B NMR** (160 MHz, CD_3OD) δ -20.13 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{16}N_6BO^+$ $[M+H]^+$: 271.1474; found: 271.1491.

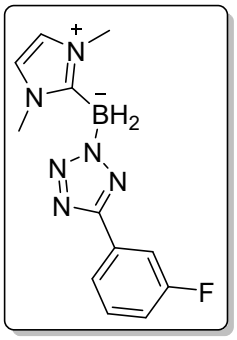


(5-(3-bromophenyl)-2*H*-tetrazol-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5k: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 62 mg, 62% yield. White solid; m.p.: 116-118 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.12 (dd, *J*

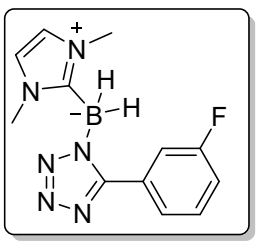
= 30.5, 6.5 Hz, 1H), 7.50 (d, *J* = 6.5 Hz, 1H), 7.30 (d, *J* = 7.0 Hz, 1H), 6.97 (s, 2H), 3.87 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 163.2, 132.1, 131.2, 130.3, 129.6, 128.6, 126.7, 125.3, 122.7, 121.6, 36.5 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -18.99 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BBr^+$ $[M+H]^+$: 333.0630; found: 333.0626.



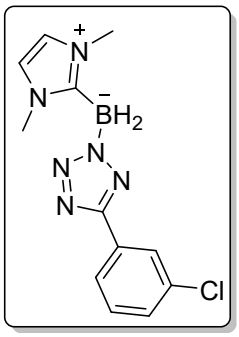
(5-(3-bromophenyl)-1*H*-tetrazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5k': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 21 mg, 21% yield. White solid; m.p.: 108-110 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 - 7.84 (m, 2H), 7.63 - 7.31 (m, 2H), 6.99 (s, 2H), 3.80 (d, *J* = 83.5 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 132.7, 132.1, 129.9, 129.4, 128.3, 128.0, 121.6, 121.5, 36.3 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -20.17 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BBr^+$ $[M+H]^+$: 333.0630; found: 333.0639.



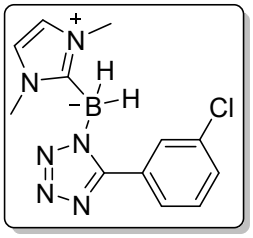
(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(3-fluorophenyl)-2*H*-tetrazol-2-yl)dihydroborate 5l: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 65 mg, 79% yield. White solid; m.p.: 153-155 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 9.5 Hz, 1H), 7.39 (dd, *J* = 14.0, 7.5 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.98 (s, 2H), 3.88 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 164.0, 163.5, 162.0, 131.3, 131.3, 130.3, 130.2, 122.4, 122.4, 121.6, 116.1, 116.0, 113.7, 113.5, 36.5 (2C); **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.1; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -19.05 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_7BF^+$ $[M+H]^+$: 273.1430; found: 273.1435.



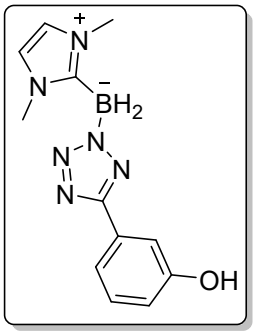
(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(3-fluorophenyl)-1*H*-tetrazol-1-yl)dihydroborate 5l': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 8 mg, 10% yield. White solid; m.p.: 146-148 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 34.0, 8.0 Hz, 2H), 7.47 (d, *J* = 6.5 Hz, 1H), 7.18 (d, *J* = 6.5 Hz, 1H), 7.02 (s, 2H), 3.71 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 163.4, 161.4, 156.8, 130.0, 129.9, 129.3, 125.1, 121.6, 116.7, 116.5, 116.4, 116.2, 36.2 (2C); **^{19}F NMR** (471 MHz, $CDCl_3$) δ -112.7; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -20.09 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_7BF^+$ $[M+H]^+$: 273.1430; found: 273.1431.



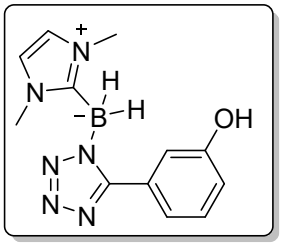
(5-(3-chlorophenyl)-2*H*-tetrazol-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5m: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 65 mg, 75% yield. White solid; m.p.: 106-108 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.04 (d, *J* = 5.5 Hz, 1H), 7.40 - 7.32 (m, 2H), 6.97 (d, *J* = 5.0 Hz, 2H), 3.87 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 163.3, 134.5, 130.9, 130.0, 129.1, 128.6, 126.7, 124.8, 121.6 (2C), 36.5 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -19.04 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BCl^+$ $[M+H]^+$: 289.1135; found: 289.1138.



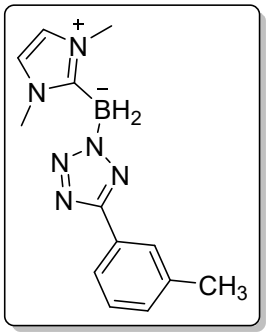
(5-(3-chlorophenyl)-1*H*-tetrazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5m': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 21 mg, 24% yield. White solid; m.p.: 99-102 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 66.0, 37.5 Hz, 2H), 7.38 (d, *J* = 15.5 Hz, 2H), 6.90 (d, *J* = 15.0 Hz, 2H), 3.79 (s, 1H), 3.60 (d, *J* = 13.5 Hz, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 156.7, 134.2, 129.7, 129.6, 129.3, 128.3, 127.6, 121.6 (2C), 36.3 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -20.12 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BCl^+$ $[M+H]^+$: 289.1135; found: 289.1137.



(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(3-hydroxyphenyl)-2*H*-tetrazol-2-yl)dihydroborate 5n: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 62 mg, 76% yield. Yellow solid; m.p.: 153-155 ℃, **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 7.49 - 7.46 (m, 2H), 7.29 (d, *J* = 15.0 Hz, 3H), 6.86 (d, *J* = 7.5 Hz, 1H), 3.86 (s, 6H); **^{13}C NMR** (125 MHz, CD_2Cl_2)) δ 167.9, 161.6, 133.6, 133.3, 125.8, 121.3 (2C), 120.3, 116.9, 39.0 (2C); **^{11}B NMR** (160 MHz, CD_2Cl_2) δ -15.13 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{16}N_6BO^+$ $[M+H]^+$: 271.1474; found: 271.1478.

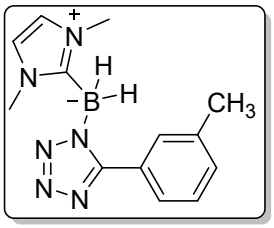


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(3-hydroxyphenyl)-1*H*-tetrazol-1-yl)dihydroborate 5n': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 13 mg, 25% yield. Yellow solid; m.p.: 135-136 ℃, **^{1}H NMR** (500 MHz, CD_3OD) δ 7.51 - 7.42 (m, 1H), 7.31 (dd, *J* = 10.0, 5.5 Hz, 1H), 7.22 (d, *J* = 10.0 Hz, 3H), 6.93 (d, *J* = 7.0 Hz, 1H), 3.86 (s, 1H), 3.62 (s, 5H); **^{13}C NMR** (125 MHz, CD_3OD)) δ 158.0, 157.3, 129.2, 127.5, 121.8 (2C), 120.0, 116.8, 115.7, 34.8 (2C); **^{11}B NMR** (160 MHz, CD_3OD) δ -20.15 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{16}N_6BO^+$ $[M+H]^+$: 271.1474; found: 271.1483.

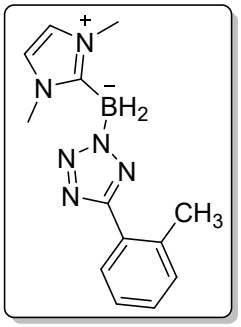


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(m-tolyl)-2*H*-tetrazol-2-yl)dihydroborate 5o: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 61 mg, 76% yield. White solid; m.p.: 130-132 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 20.5 Hz, 2H), 7.31 (s, 1H), 7.19 (s,

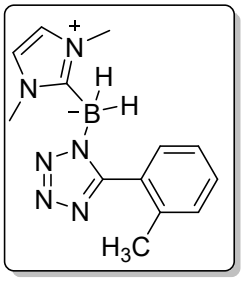
1H), 6.94 (s, 2H), 3.83 (s, 6H), 2.39 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 164.4, 138.2, 129.9, 128.9, 128.5, 127.3, 123.8, 121.5 (2C), 36.4 (2C), 21.4; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -18.97 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{18}N_6B^+$ $[M+H]^+$: 269.1681; found: 269.1675.



(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(m-tolyl)-1*H*-tetrazol-1-yl)dihydroborate 5o': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 23 mg, 28% yield. White solid; m.p.: 129-131 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.0 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.91 (s, 2H), 3.56 (s, 6H), 2.12 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 158.1, 138.2, 130.2, 130.0, 129.7, 127.9, 125.4, 121.5 (2C), 36.1 (2C), 19.8; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -21.07 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{18}N_6B^+$ $[M+H]^+$: 269.1681; found: 269.1680.

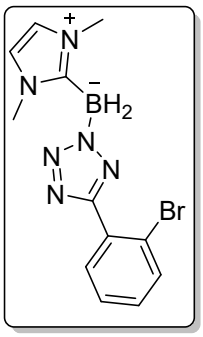


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(o-tolyl)-2*H*-tetrazol-2-yl)dihydroborate 5p: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 45 mg, 56% yield. White solid; m.p.: 97-99 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 6.5 Hz, 1H), 7.26 (s, 3H), 6.95 (s, 2H), 3.86 (s, 6H), 2.59 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 164.7, 137.0, 131.0, 129.5, 128.8, 128.3, 125.7, 121.5 (2C), 36.4 (2C), 21.7; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -19.07 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{18}N_6B^+$ $[M+H]^+$: 269.1681; found: 269.1679.

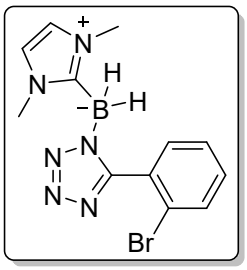


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(o-tolyl)-1*H*-tetrazol-1-yl)dihydroborate 5p': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 37 mg, 46% yield. White solid; m.p.: 95-97 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 - 7.75 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.28

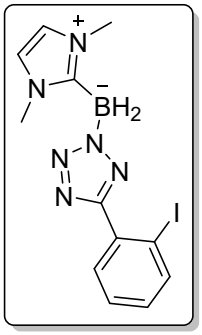
(d, *J* = 7.0 Hz, 1H), 6.96 (s, 2H), 3.68 (s, 6H), 2.43 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 158.0, 138.0, 130.4, 130.0, 128.2, 127.2, 126.5, 121.5 (2C), 36.3 (2C), 21.5; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -20.20 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{18}N_6B^+$ $[M+H]^+$: 269.1681; found: 269.1695.



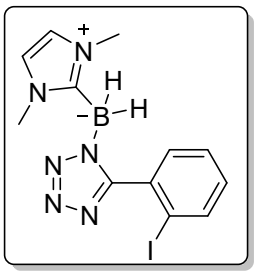
(5-(2-bromophenyl)-2*H*-tetrazol-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5q: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 50 mg, 50% yield. White solid; m.p.: 115-117 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.0 Hz, 1H), 7.81-7.67 (m, 1H), 7.40 (dt, *J* = 23.5, 6.0 Hz, 2H), 6.95 (s, 2H), 3.86 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 164.4, 133.7, 131.8, 130.3, 129.2, 128.6, 126.8, 121.6 (2C), 36.5 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -19.01 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BBr^+$ $[M+H]^+$: 333.0630; found: 333.0630.



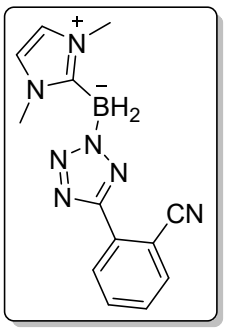
(5-(2-bromophenyl)-1*H*-tetrazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5q': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 27 mg, 27% yield. White solid; m.p.: 150-152 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99-7.66 (m, 1H), 7.51 - 7.31 (m, 3H), 6.97 (d, *J* = 21.5 Hz, 2H), 3.64 (d, *J* = 35.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 157.0, 131.5, 131.0, 129.4, 128.3, 126.3, 124.2, 121.6 (2C), 36.3 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -20.98 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BBr^+$ $[M+H]^+$: 333.0630; found: 333.0630.



(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(2-iodophenyl)-2*H*-tetrazol-2-yl)dihydroborate 5r: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 80 mg, 70% yield. Colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.5 Hz, 2H), 7.38 - 7.27 (m, 3H), 6.87 (s, 2H), 3.77 (d, *J* = 2.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 164.4, 140.3, 131.2, 130.4, 129.2, 129.1, 128.6, 126.7, 121.6, 96.3, 36.5 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -18.97 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BI^+$ $[M+H]^+$: 381.0491; found: 381.0534.

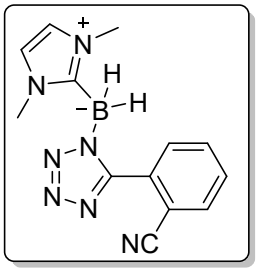


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(2-iodophenyl)-1*H*-tetrazol-1-yl)dihydroborate 5r': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 45 mg, 39% yield. Colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 - 7.91 (m, 1H), 7.51 - 7.41 (m, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.18 (td, *J* = 8.0, 1.5 Hz, 1H), 6.99 (s, 1H), 6.93 (s, 1H), 3.88 (s, 2H), 3.62 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 159.5, 139.1, 134.4, 131.3, 131.1, 128.7, 127.9, 126.8, 121.7, 98.6, 36.4 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -21.06 (d); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BI^+$ $[M+H]^+$: 381.0491; found: 381.0507.

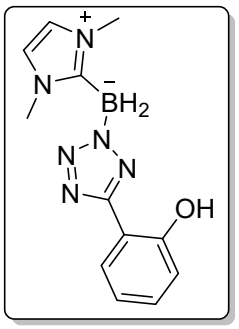


(5-(2-cyanophenyl)-2*H*-tetrazol-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5s: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 51 mg, 61% yield. White solid; m.p.: 170-172 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 55.0, 7.5

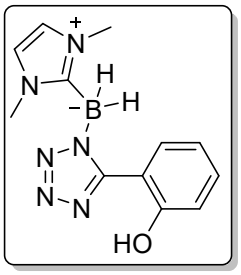
Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 30.5 Hz, 2H), 3.97 (s, 4H), 3.89 (s, 1H), 3.81 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 161.8, 134.5, 132.9, 131.7, 129.2, 126.8, 121.6 (2C), 118.5, 110.4, 36.7 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -18.98 (d); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{15}N_7B^+$ $[M+H]^+$: 280.1477; found: 280.1478.



(5-(2-cyanophenyl)-1*H*-tetrazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5s': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 11 mg, 14% yield. Colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 - 8.27 (m, 1H), 7.82 - 7.62 (m, 2H), 7.38 (d, *J* = 98.0 Hz, 1H), 6.99 (s, 2H), 3.96 - 3.70 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 155.6, 133.3, 132.5, 131.7, 131.4, 130.1, 121.8 (2C), 117.2, 113.2, 36.3 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -20.74 (d); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{15}N_7B^+$ $[M+H]^+$: 280.1477; found: 280.1477.

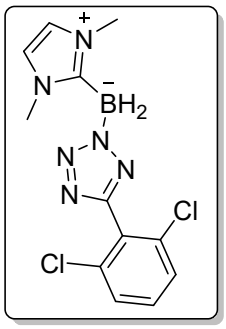


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(2-hydroxyphenyl)-2*H*-tetrazol-2-yl)dihydroborate 5t: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 32 mg, 40% yield. White solid; m.p.: 154-156 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.0 Hz, 1H), 7.29 (dd, *J* = 15.5, 7.5 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 7.00 - 6.92 (m, 3H), 3.89 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 163.3, 156.3, 131.0, 127.3, 121.7 (2C), 119.7, 117.1, 112.9, 36.6 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -18.88 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{16}N_6BO^+$ $[M+H]^+$: 271.1474; found: 271.1480.

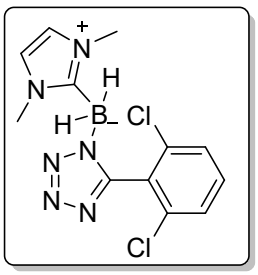


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(2-hydroxyphenyl)-1*H*-tetrazol-1-yl)dihydroborate 5t': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 2 mg, 2%

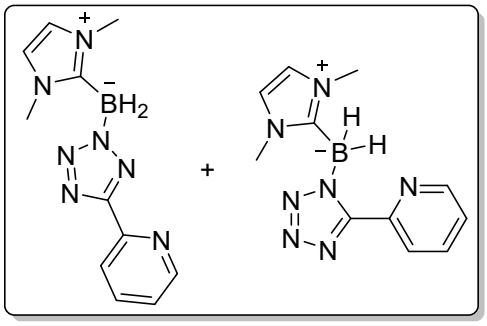
yield. White solid; m.p.: 158-160 ℃, **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 8.37 (s, 1H), 7.96 (s, 1H), 7.25 (d, *J* = 41.0 Hz, 1H), 6.95 (d, *J* = 22.5 Hz, 4H), 3.72 (d, *J* = 70.5 Hz, 6H); **^{13}C NMR** (125 MHz, CD_2Cl_2)) δ 157.5, 155.5, 131.5, 129.5, 121.7 (2C), 121.6, 118.7, 117.1, 36.2 (2C); **^{11}B NMR** (160 MHz, CD_2Cl_2) δ -19.32 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{16}N_6BO^+$ $[M+H]^+$: 271.1474; found: 271.1482.



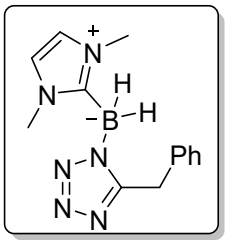
(5-(2,6-dichlorophenyl)-2*H*-tetrazol-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5u: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 40 mg, 41% yield. White solid; m.p.: 150-152 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 6.5 Hz, 1H), 7.40 (t, *J* = 10.5 Hz, 3H), 6.98 (d, *J* = 17.5 Hz, 2H), 3.87 (s, 3H), 3.66 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 136.2, 131.6, 129.2, 128.6 (2C), 127.9, 126.8, 121.7 (2C), 36.3 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -21.27 (d); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{13}N_6BCl_2Na^+$ $[M+Na]^+$: 345.0564; found: 345.0572.



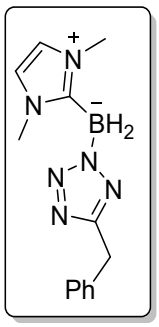
(5-(2,6-dichlorophenyl)-1*H*-tetrazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5u': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 12 mg, 13% yield. White solid; m.p.: 159-161 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 71.0 Hz, 1H), 7.43 (dd, *J* = 27.5, 17.5 Hz, 3H), 6.97 (dd, *J* = 15.5, 8.5 Hz, 2H), 3.94 - 3.61 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 131.5, 129.5, 129.2, 128.7, 127.9, 126.9, 121.7, 121.6, 36.4 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -21.25 (d); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{13}N_6BCl_2Na^+$ $[M+Na]^+$: 345.0564; found: 345.0567.



(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(pyridin-2-yl)-2*H*-tetrazol-2-yl)dihydroborate 5v +(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(pyridin-2-yl)-1*H*-tetrazol-1-yl)dihydroborate 5v': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 80 mg, 97% yield. White solid; m.p.: 130-132 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.0 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.30 (s, 1H), 6.97 (d, *J* = 1.0 Hz, 2H), 3.86 (d, *J* = 1.5 Hz, 6H), 3.24 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.4, 150.0, 148.6, 136.8, 123.8, 122.3, 121.6 (2C), 36.5 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -19.25 (d); HRMS (ESI-Orbitrap) m/z calcd for $C_{11}H_{15}N_7B^+$ $[M+H]^+$: 256.1477; found: 256.1485.

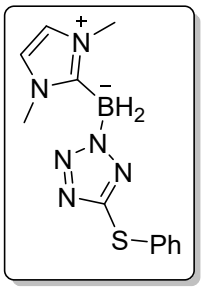


(5-benzyl-1*H*-tetrazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5w: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 53 mg, 66% yield. White solid; m.p.: 132-134 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.0 Hz, 2H), 7.16 (t, *J* = 7.0 Hz, 1H), 6.89 (s, 2H), 4.20 (s, 2H), 3.74 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.2, 138.1, 128.8, 128.3 (2C), 126.3 (2C), 121.5 (2C), 36.2 (2C), 31.7; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -18.99 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{18}N_6B^+$ $[M+H]^+$: 269.1681; found: 269.1687.



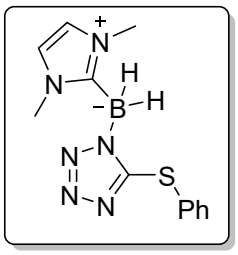
(5-benzyl-2*H*-tetrazol-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5w': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 35 mg, 44% yield. Colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 6.0 Hz, 4H), 7.18 (d, *J* = 6.0 Hz, 1H), 6.88 (s, 2H), 4.35 (s, 2H), 3.55 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.3, 136.9, 128.8, 128.4 (2C), 126.6 (2C),

121.5 (2C), 36.1 (2C), 30.2; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -21.38 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{18}N_6B^+$ $[M+H]^+$: 269.1681; found: 269.1678.



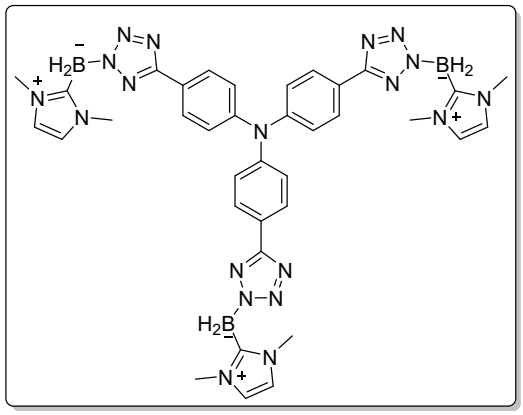
(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(phenylthio)-2*H*-tetrazol-2-yl)dihydroborate

5x: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 46 mg, 54% yield. White solid; m.p.: 132-134 °C, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 29.5, 7.0 Hz, 2H), 7.24 - 7.13 (m, 3H), 6.85 (d, *J* = 14.5 Hz, 2H), 4.44 (s, 1H), 3.66 (s, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 156.5, 137.0, 129.2, 128.6 (2C), 127.6 (2C), 121.6 (2C), 37.0, 36.5; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -21.66 (d); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BSNa^+$ $[M+Na]^+$: 309.1065; found: 309.1031.

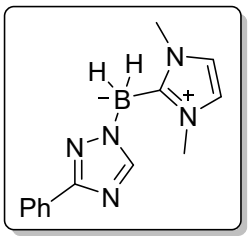


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(phenylthio)-1*H*-tetrazol-1-yl)dihydroborate

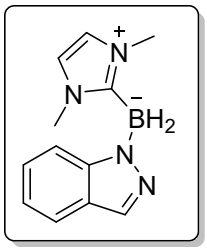
5x': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 24 mg, 28% yield. Colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.25 - 7.19 (m, 1H), 6.89 (s, 2H), 4.50 (s, 2H), 3.73 (s, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 156.5, 137.1, 129.3, 128.6 (2C), 127.6 (2C), 121.6 (2C), 37.0, 36.5; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -21.62 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{15}N_6BSNa^+$ $[M+Na]^+$: 309.1065; found: 309.1040.



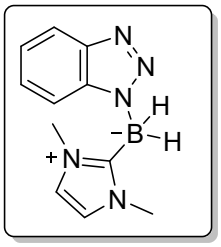
((nitrilotris(benzene-4,1-diyl))tris(2H-tetrazole-5,2-diyl))tris((1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate) 5y: New compound. (Eluent: dichloromethane/ ethanol = 20:1, v/v). 116 mg, 50% yield. Colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (s, 3H), 8.04 (d, *J* = 8.0 Hz, 4H), 7.18 (d, *J* = 8.0 Hz, 5H), 6.98 (s, 6H), 3.86 (s, 18H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 164.2 (3C), 148.1 (3C), 129.6 (6C), 127.9 (3C), 124.3 (6C), 121.6 (6C), 36.6 (6C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -20.52 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{36}H_{43}N_{19}B_3^+$ $[M+H]^+$: 774.4223; found: 774.4245.



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(3-phenyl-1H-1,2,4-triazol-1-yl)dihydroborate 5z: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 32 mg, 42% yield. Colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 - 8.06 (m, 3H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 6.86 (s, 2H), 3.78 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 163.2, 149.5, 132.6, 128.4 (2C), 128.2, 126.2 (2C), 121.3 (2C), 36.3 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -19.85 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{13}H_{17}N_5B^+$ $[M+H]^+$: 254.1572; found: 254.1585.

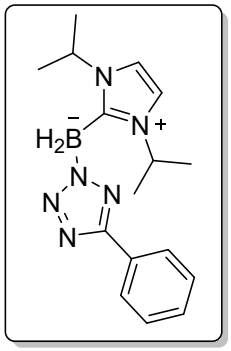


(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(1*H*-indazol-1-yl)dihydroborate 5aa: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:3, v/v). 42 mg, 62% yield. Yellow oil, **^{1}H NMR** (500 MHz, $CDCl_3$)δ 8.06 (s, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.17 - 7.08 (m, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.75 (s, 2H), 3.60 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 150.7, 129.2, 124.0, 122.5, 121.2 (2C), 120.1, 119.6, 117.0,, 36.0 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -17.68 (t); HRMS (ESI-Orbitrap) m/z calcd for $C_{12}H_{16}N_4B^+$ $[M+H]^+$: 227.1463; found:227.1458.

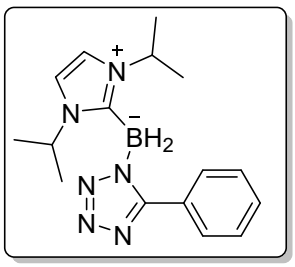


(1*H*-benzo[d][1,2,3]triazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5ab: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 35 mg, 52% yield.

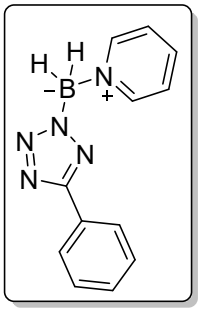
Colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.25 (dd, *J* = 13.0, 4.5 Hz, 1H), 6.91 (s, 2H), 3.76 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 146.0, 138.2, 125.0, 122.3, 121.3 (2C), 118.6, 112.5, 36.4 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -21.03 (t); HRMS (ESI-Orbitrap) m/z calcd for $C_{11}H_{15}N_5B^+$ $[M+H]^+$: 228.1416; found: 228.1423.



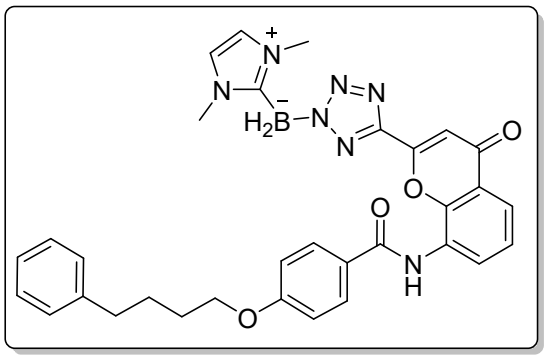
(1,3-diisopropyl-1*H*-imidazol-3-ium-2-yl)(5-phenyl-2*H*-tetrazol-2-yl)dihydroborate 5ac: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 48 mg, 78% yield. White solid; m.p.: 153-155 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.0 Hz, 1H), 7.40 (dd, *J* = 20.5, 7.0 Hz, 3H), 7.09 (s, 2H), 5.38 - 5.31 (m, 1H), 1.48 - 1.21 (m, 14H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 164.3, 129.3, 129.1, 128.6 (2C), 126.7 (2C), 116.8 (2C), 50.3 (2C), 23.2 (4C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -19.09 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{16}H_{24}N_6B^+$ $[M+H]^+$: 311.2150; found: 311.2159.



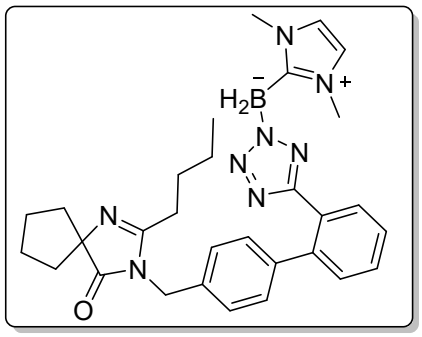
(1,3-diisopropyl-1*H*-imidazol-3-ium-2-yl)(5-phenyl-1*H*-tetrazol-1-yl)dihydroborate 5ac': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 12 mg, 20% yield. White solid; m.p.: 162-164 ℃, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.5 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 3H), 7.10 (s, 2H), 4.96 - 4.90 (m, 1H), 1.30 (dd, *J* = 32.0, 10.0 Hz, 14H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 157.7, 129.6, 129.5, 128.3 (2C), 127.5 (2C), 116.7 (2C), 50.3 (2C), 23.2 (4C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -20.30 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{16}H_{24}N_6B^+$ $[M+H]^+$: 311.2150; found: 311.2146.



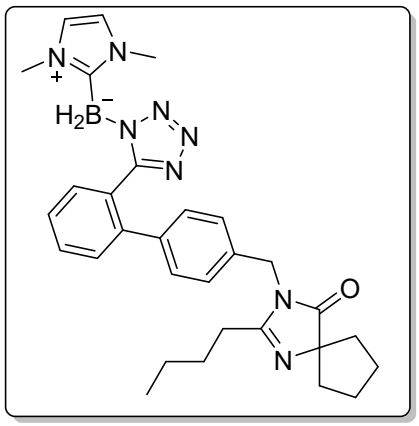
5ad: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 31 mg, 44% yield. Colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.5 Hz, 2H), 8.14 (dd, *J* = 22.0, 7.0 Hz, 3H), 7.77 - 7.63 (m, 2H), 7.42 (dd, *J* = 14.0, 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 165.1, 147.5, 142.1 (2C), 129.6, 128.8, 128.7 (2C), 127.0 (2C), 126.5 (2C); **^{11}B NMR** (160 MHz, $CDCl_3$) δ -2.46 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{11}H_{15}N_5B^+$ $[M+H]^+$: 238.1259; found: 238.1263.



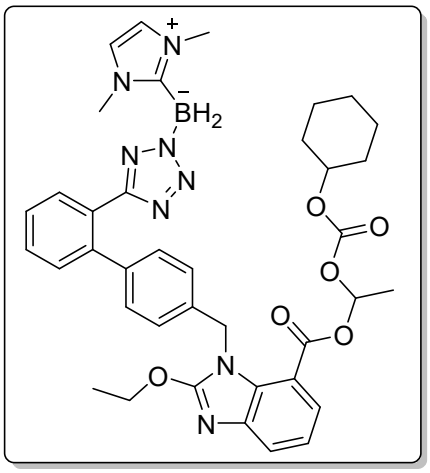
(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(5-(4-oxo-8-(4-(4-phenylbutoxy)benzamido)-4*H*-chromen-2-yl)-2*H*-tetrazol-2-yl)dihydroborate 5ae: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 85 mg, 48% yield. Colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.86 (d, *J* = 7.0 Hz, 1H), 8.08 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.93 - 7.88 (m, 1H), 7.45 (td, *J* = 8.0, 2.0 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.25 - 7.16 (m, 4H), 7.04 (dd, *J* = 9.0, 3.0 Hz, 2H), 6.99 (s, 2H), 4.06 (t, *J* = 5.5 Hz, 2H), 3.90 (d, *J* = 2.5 Hz, 6H), 2.71 (t, *J* = 7.0 Hz, 2H), 1.85 (d, *J* = 4.5 Hz, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 177.9, 164.9, 162.5, 153.7, 145.8, 142.2, 129.4 (2C), 128.6 (4C), 128.5, 128.4, 126.3, 126.0, 125.7 (2C), 124.2, 123.9, 121.8 (2C), 119.4, 114.8 (2C), 109.9, 68.2, 36.7, 35.7, 28.8, 27.9; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -18.72 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{32}H_{33}N_7BO_4^+$ $[M+H]^+$: 590.2682; found: 590.2758.



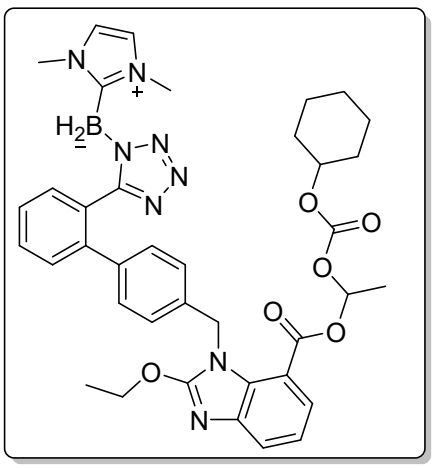
(5-(4'-((2-butyl-4-oxo-1,3-diazaspiro[4.4]non-1-en-3-yl)methyl)-[1,1'-biphenyl]-2-yl)-2*H*-tetrazol-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5af: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 71 mg, 44% yield. Colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.03 - 6.97 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 5.0 Hz, 1H), 4.67 (s, 2H), 3.62 (s, 5H), 3.35 (s, 1H), 2.29 (dd, *J* = 21.5, 14.0 Hz, 3H), 2.03 - 1.95 (m, 4H), 1.84 (s, 2H), 1.62 - 1.53 (m, 2H), 1.35 - 1.23 (m, 3H), 0.85 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 187.0, 164.1, 161.7, 141.3, 140.8, 134.4, 130.6, 130.4, 129.9 (2C), 129.1, 128.0, 127.4, 125.3 (2C), 121.4 (2C), 121.3, 76.6, 43.1, 37.4 (2C), 36.1, 28.6, 27.6, 26.1 (2C), 22.2, 13.7; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -19.34 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{30}H_{38}N_8BO^+$ $[M+H]^+$: 537.3257; found: 537.3324.



(5-(4'-((2-butyl-4-oxo-1,3-diazaspiro[4.4]non-1-en-3-yl)methyl)-[1,1'-biphenyl]-2-yl)-1*H*-tetrazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5af': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 84 mg, 52% yield. Colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 13.5 Hz, 2H), 7.06 - 6.90 (m, 3H), 6.86 (s, 2H), 4.62 (s, 2H), 3.62 (s, 1H), 3.35 (s, 5H), 2.35-2.24 (m, 2H), 2.01 - 1.93 (m, 4H), 1.81 (s, 2H), 1.61 - 1.52 (m, 2H), 1.36 - 1.23 (m, 4H), 0.86 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 186.7, 161.8, 158.0, 141.5, 139.9, 135.1, 130.8, 130.1, 129.9 (2C), 129.6, 127.1, 126.8, 126.1 (2C), 121.4 (2C), 76.5, 43.1, 37.4 (2C), 35.8, 28.7, 27.7, 26.1 (2C), 22.3, 13.8; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -21.58 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{30}H_{38}N_8BO^+$ $[M+H]^+$: 537.3257; found: 537.3277.



(5-(4'-((7-((1-(((cyclohexyloxy)carbonyl)oxy)ethoxy)carbonyl)-2-ethoxy-1*H*-benzo[d]imidazol-1-yl)methyl)-[1,1'-biphenyl]-2-yl)-2*H*-tetrazol-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5ag: New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 88 mg, 41% yield. Colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.52 (dd, *J* = 7.5 Hz, 1H), 7.34 - 7.25 (m, 2H), 7.22 - 7.16 (m, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.88 - 6.75 (m, 3H), 6.66 (d, *J* = 10.5 Hz, 2H), 5.53 (s, 2H), 4.56 (d, *J* = 7.0 Hz, 2H), 4.16 (d, *J* = 7.0 Hz, 1H), 3.37 (d, *J* = 3.5 Hz, 5H), 3.01 (s, 1H), 1.81 (s, 1H), 1.62 (s, 2H), 1.47 - 1.31 (m, 7H), 1.28 - 1.05 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 166.6, 164.2, 158.9, 158.8, 152.7, 142.0, 141.2, 135.4, 132.2, 130.7, 129.7, 129.6, 129.2 (2C), 127.4 (2C), 126.6, 126.3, 124.4, 123.8, 122.8, 121.9, 121.3, 116.4, 114.7, 91.8, 67.0, 61.5, 47.0, 36.1, 31.5 (2C), 25.2, 23.7 (2C), 19.7, 14.8, 14.3; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -19.91 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{38}H_{44}N_8BO_6^+$ $[M+H]^+$: 719.3472; found: 719.3567.



(5-(4'-((7-((1-(((cyclohexyloxy)carbonyl)oxy)ethoxy)carbonyl)-2-ethoxy-1*H*-benzo[d]imidazol-1-yl)methyl)-[1,1'-biphenyl]-2-yl)-1*H*-tetrazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate 5ag': New compound. (Eluent: petroleum ether/ ethyl acetate = 1:2, v/v). 108 mg, 50% yield. Colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 7.0 Hz, 1H), 7.42 - 7.36 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 1H),

7.06 (t, *J* = 6.5 Hz, 2H), 6.90 (dd, *J* = 8.0 Hz, 3H), 6.73 (dd, *J* = 13.5 Hz, 3H), 5.64 - 5.52 (m, 2H), 4.67 - 4.62 (m, 2H), 4.25 (d, *J* = 7.0 Hz, 1H), 3.47 (s, 1H), 3.11 (s, 5H), 1.92 (s, 1H), 1.73 (s, 2H), 1.50 (dd, *J* = 6.0 Hz, 7H), 1.27 (d, *J* = 9.0 Hz, 6H).; **^{13}C NMR** (125 MHz, $CDCl_3$)) δ 166.3, 164.0, 158.7, 157.9, 152.6, 141.8, 139.4, 136.0, 132.0, 130.9, 130.0 (2C), 129.5, 129.3, 126.9 (2C), 126.7, 124.1, 123.5, 122.7, 121.2, 120.8, 116.1, 114.4, 91.7, 66.8, 61.4, 46.8 , 35.9, 35.4, 31.3, 29.6, 25.0, 23.5, 19.6, 14.6, 14.2; **^{11}B NMR** (160 MHz, $CDCl_3$) δ -21.14 (s); HRMS (ESI-Orbitrap) m/z calcd for $C_{38}H_{44}N_8BO_6^+$ $[M+H]^+$: 719.3472; found: 719.3597.

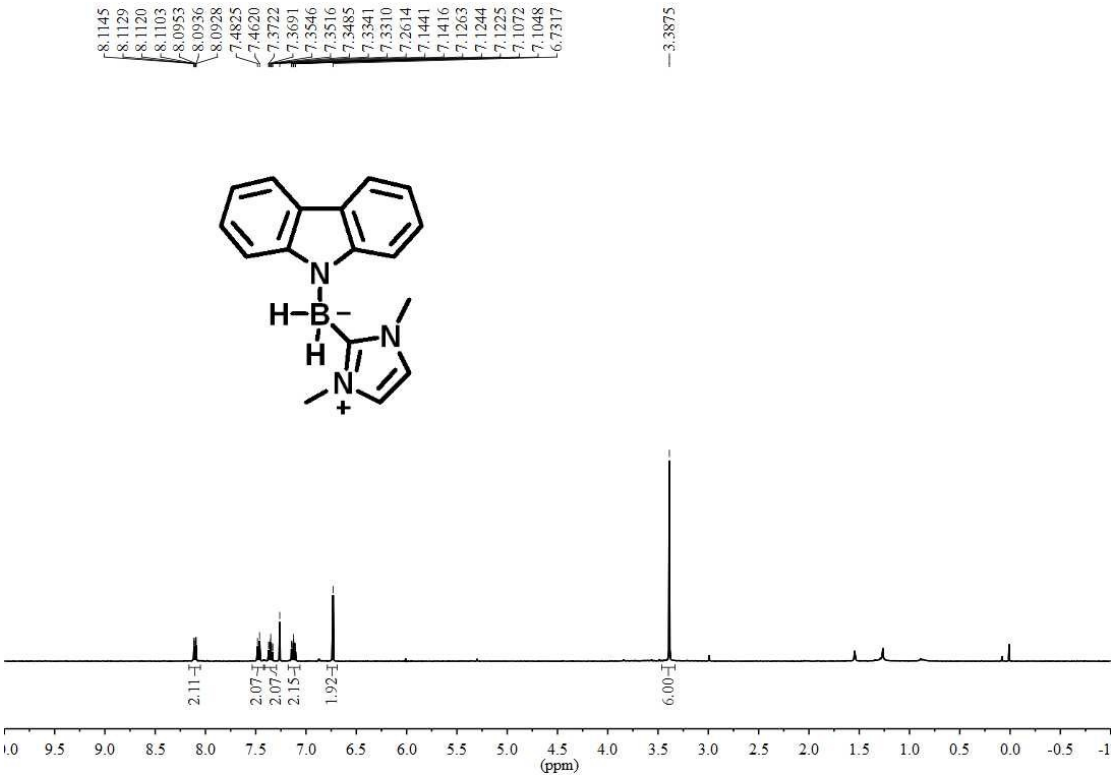
6. References

1. Gardner, S.; Kawamoto, T.; Curran, D. P. *J. Org. Chem.* **2015**, *80*, 9794-9797.

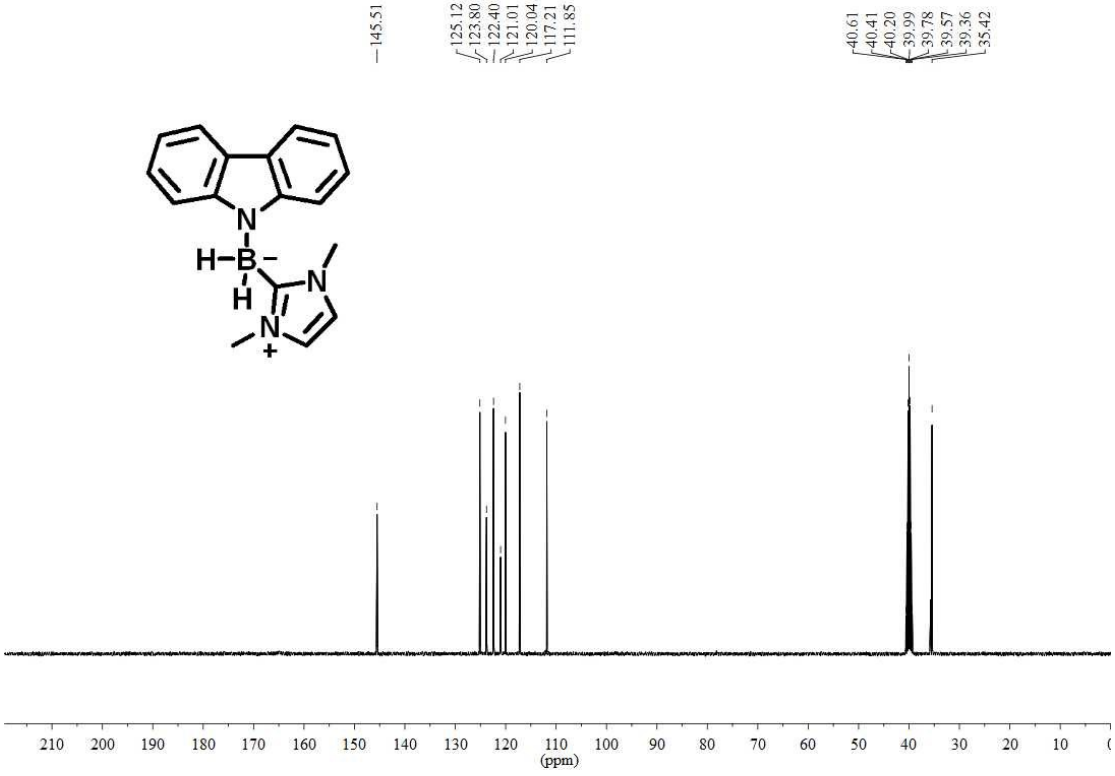
2. Hirano, K.; Urban, S.; Wang, C.; Glorius, F. *Org. Lett*. **2009**, *11*, 1019-1022.

7. Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{11}B NMR spectra

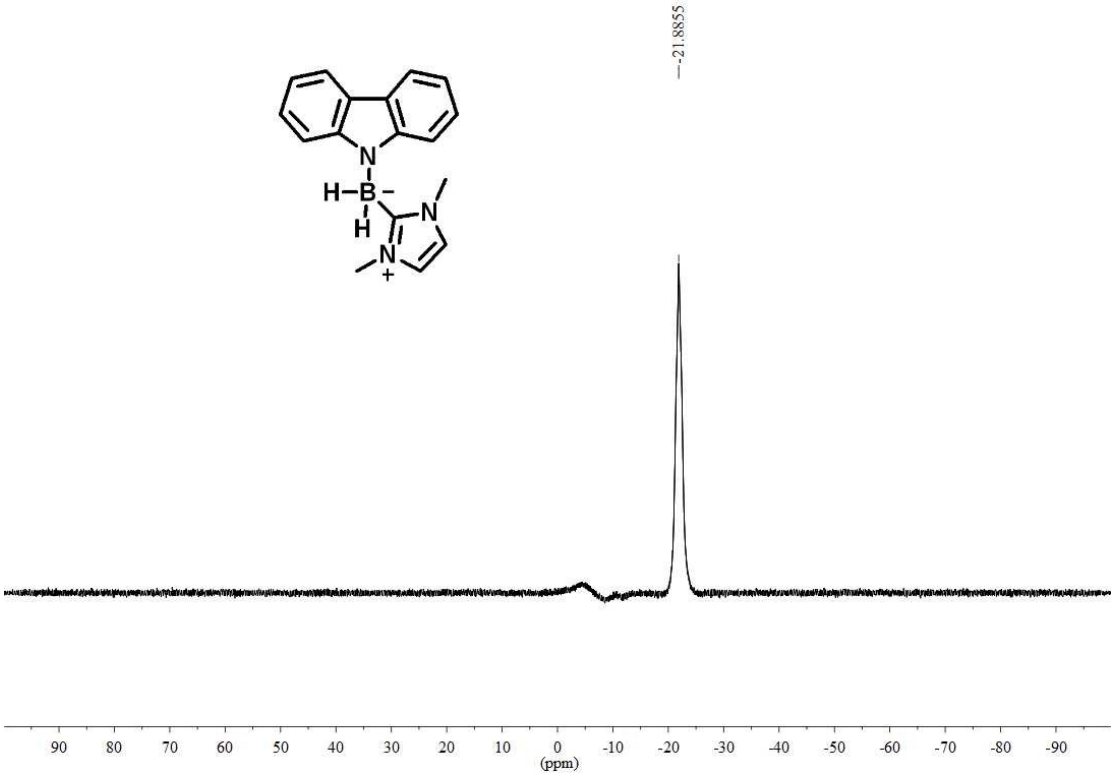
^{1}H NMR of product 3a in $CDCl_3$ (600 MHz)



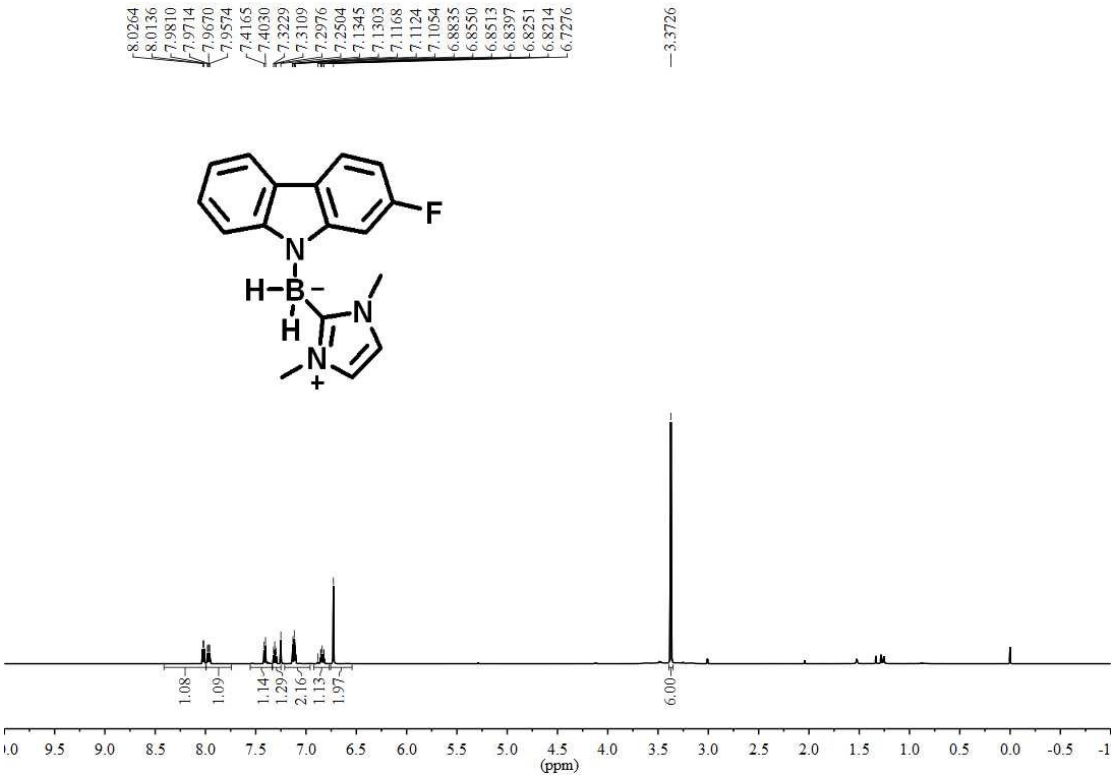
^{13}C NMR of product 3a in DMSO-d_6 (150 MHz)



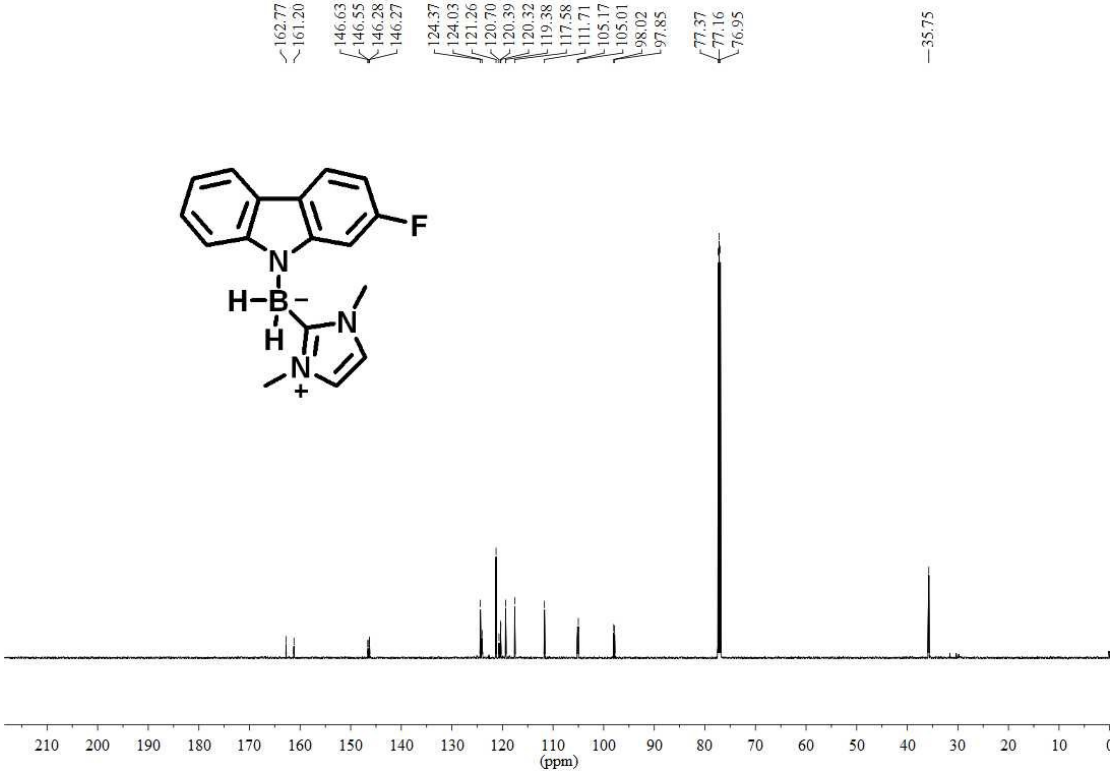
^{11}B NMR of product 3a in DMSO-d_6 (160 MHz)



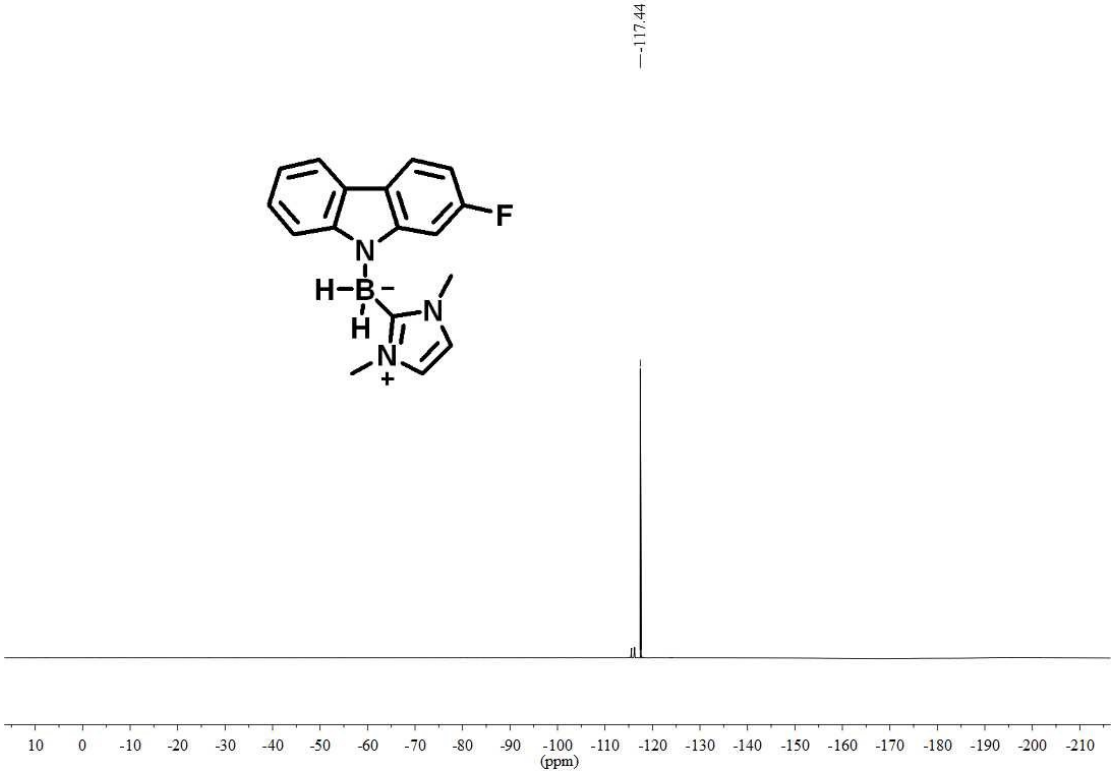
^{1}H NMR of product 3b in $CDCl_3$ (600 MHz)



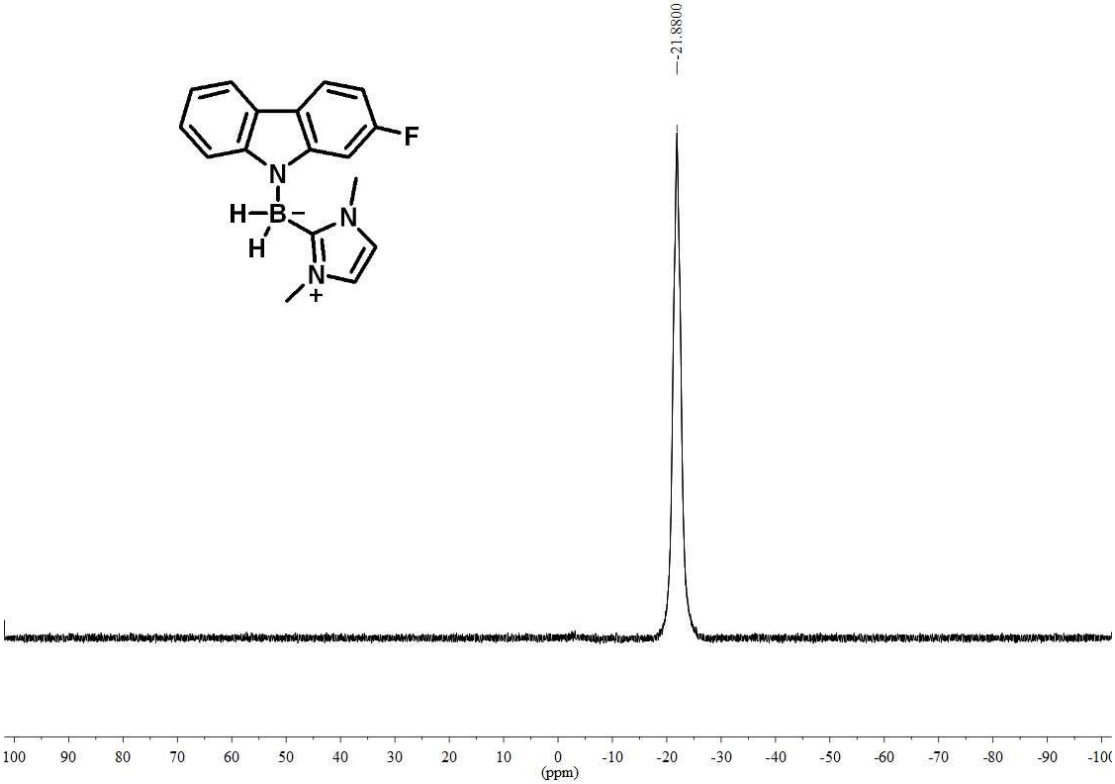
^{13}C NMR of product 3b in $CDCl_3$ (150 MHz)



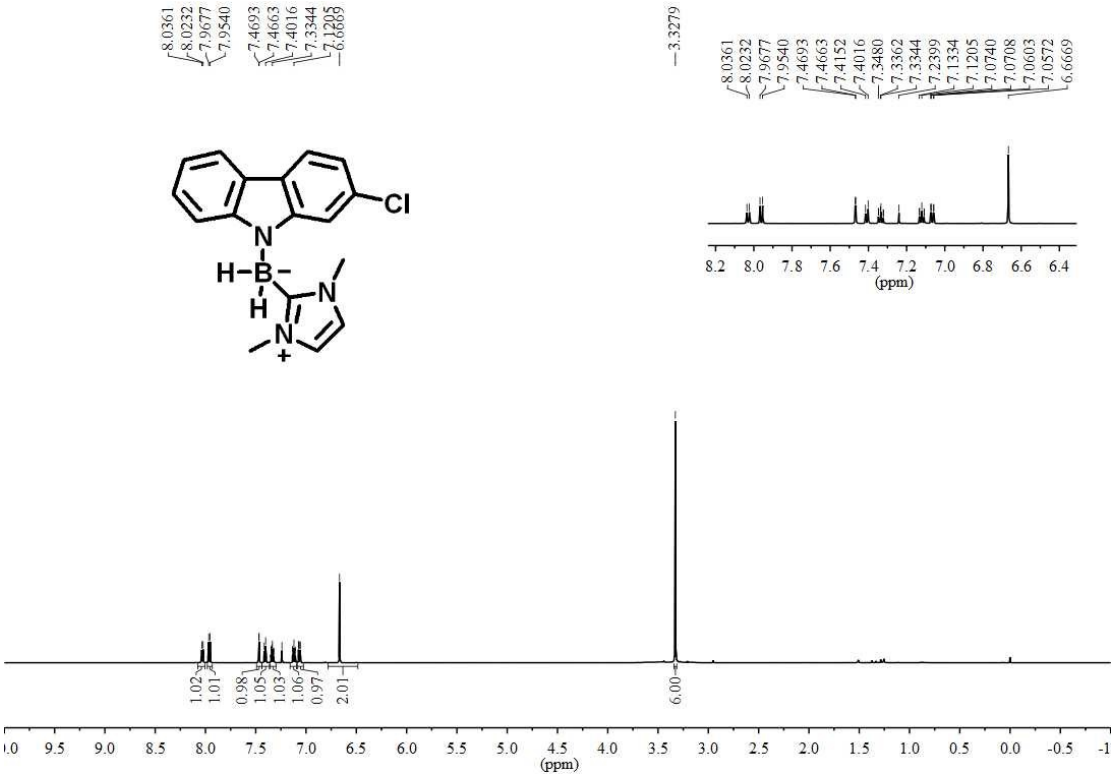
^{19}F NMR of product 3b in $CDCl_3$ (565 MHz)



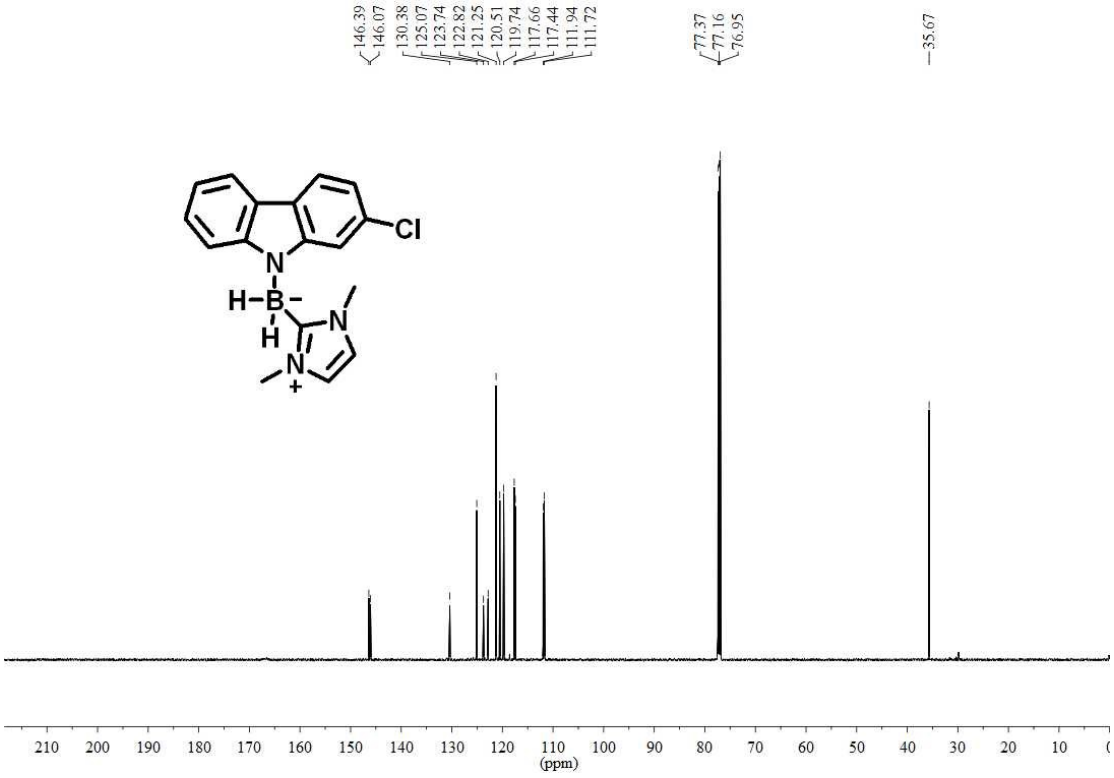
^{11}B NMR of product 3b in DMSO-d_6 (160 MHz)



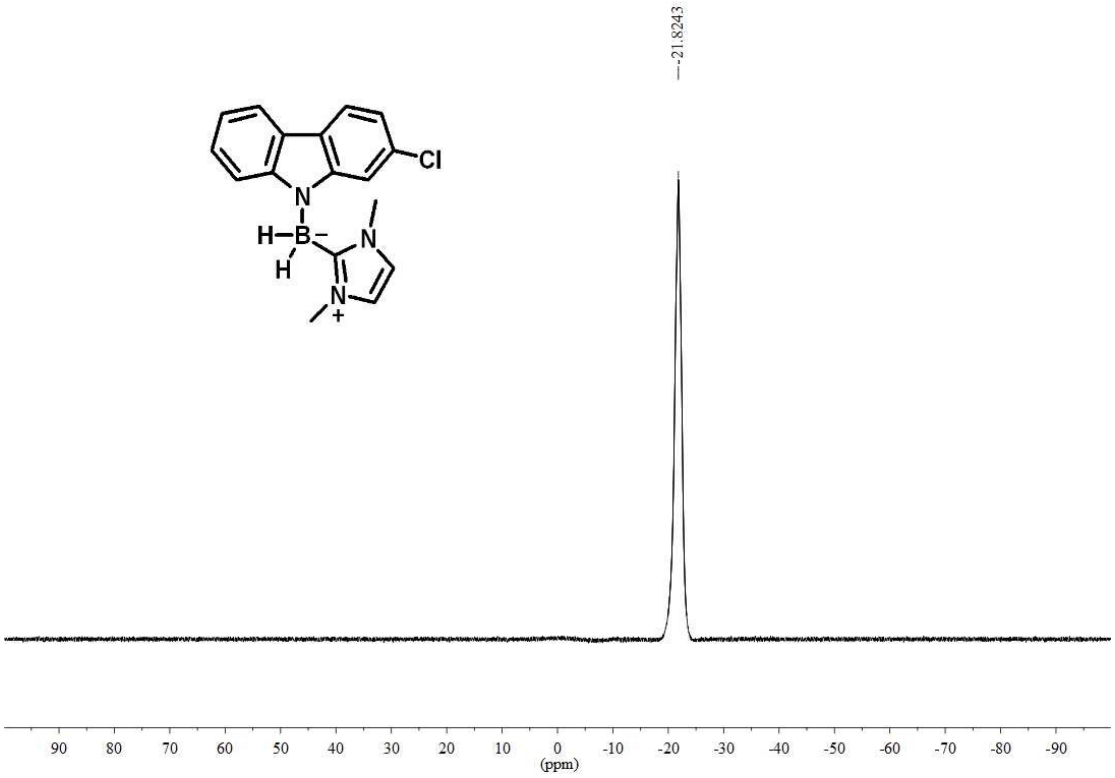
^{1}H NMR of product 3c in $CDCl_3$ (600 MHz)



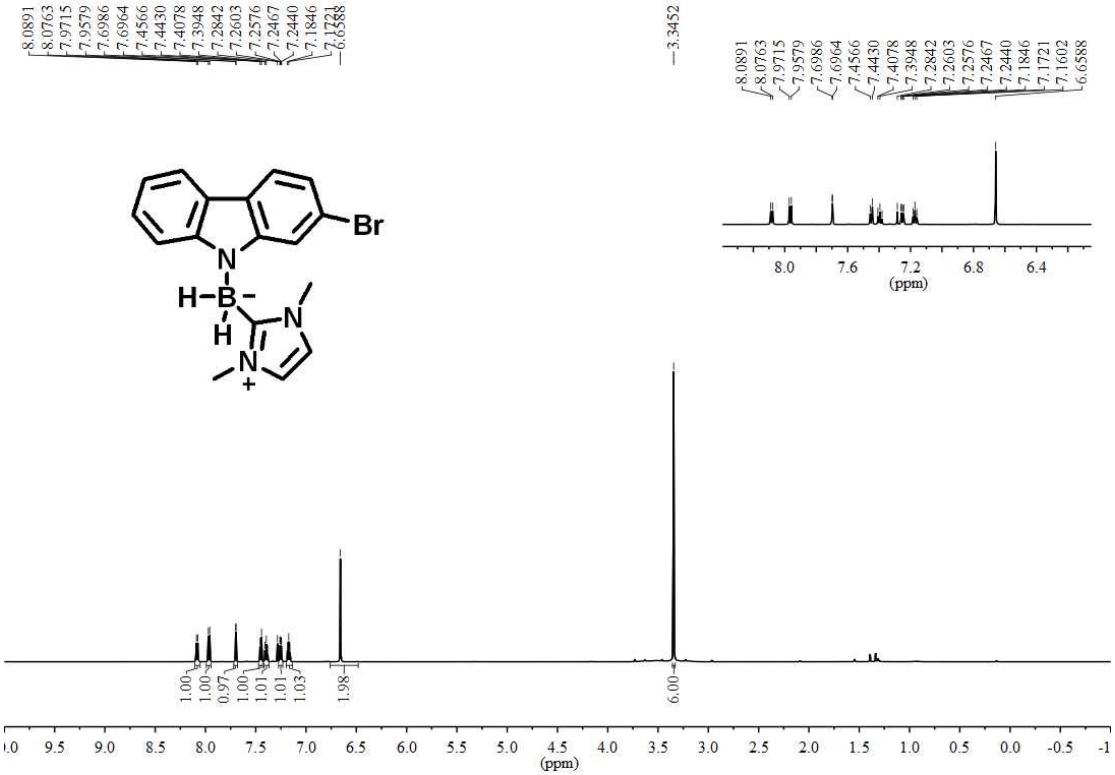
^{13}C NMR of product 3c in $CDCl_3$ (150 MHz)



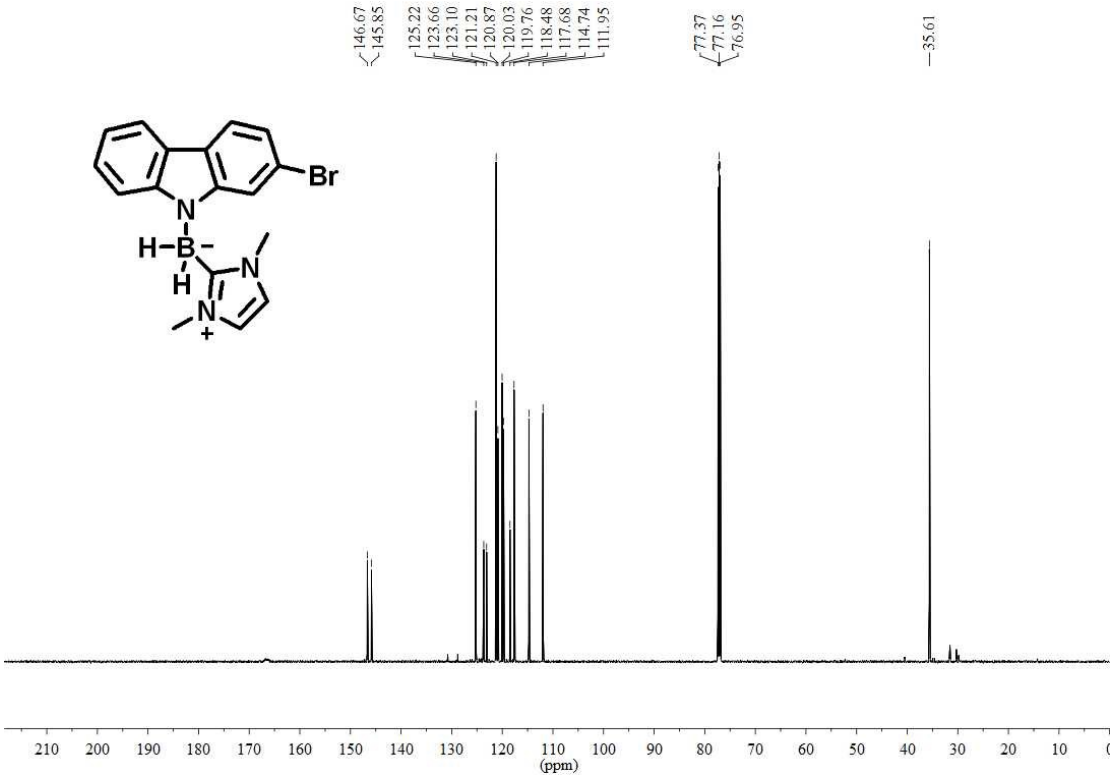
^{11}B NMR of product 3c in DMSO-d_6 (160 MHz)



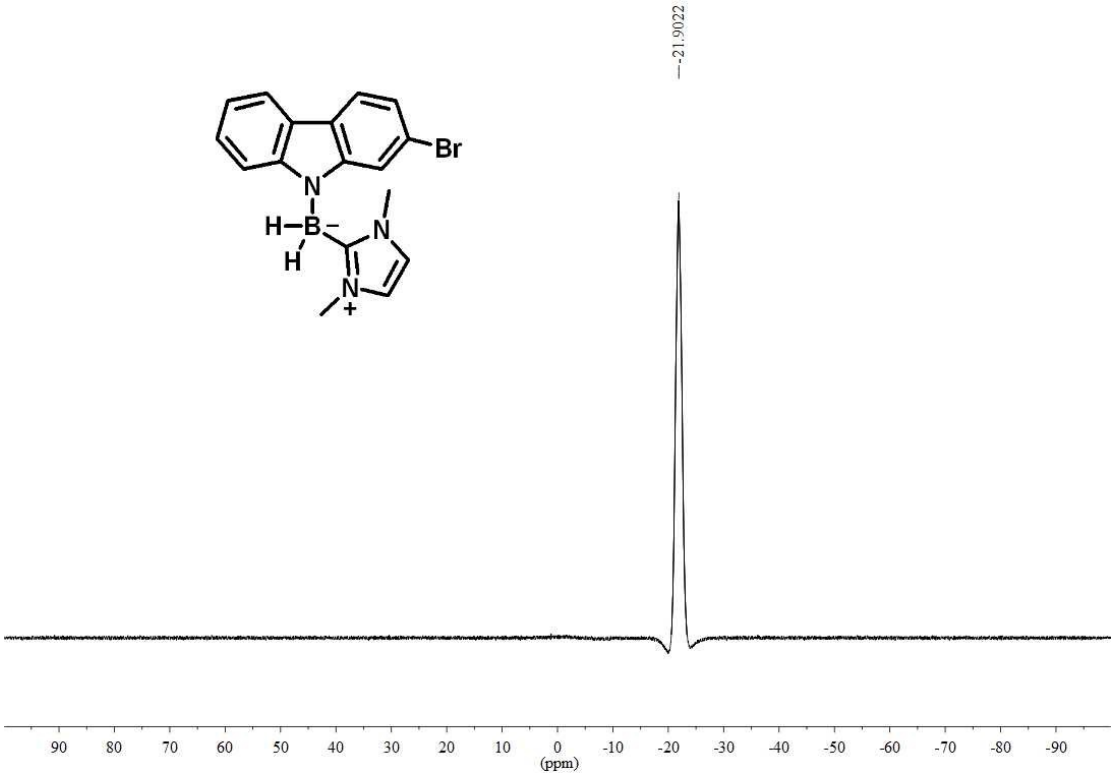
^{1}H NMR of product 3d in $CDCl_3$ (600 MHz)



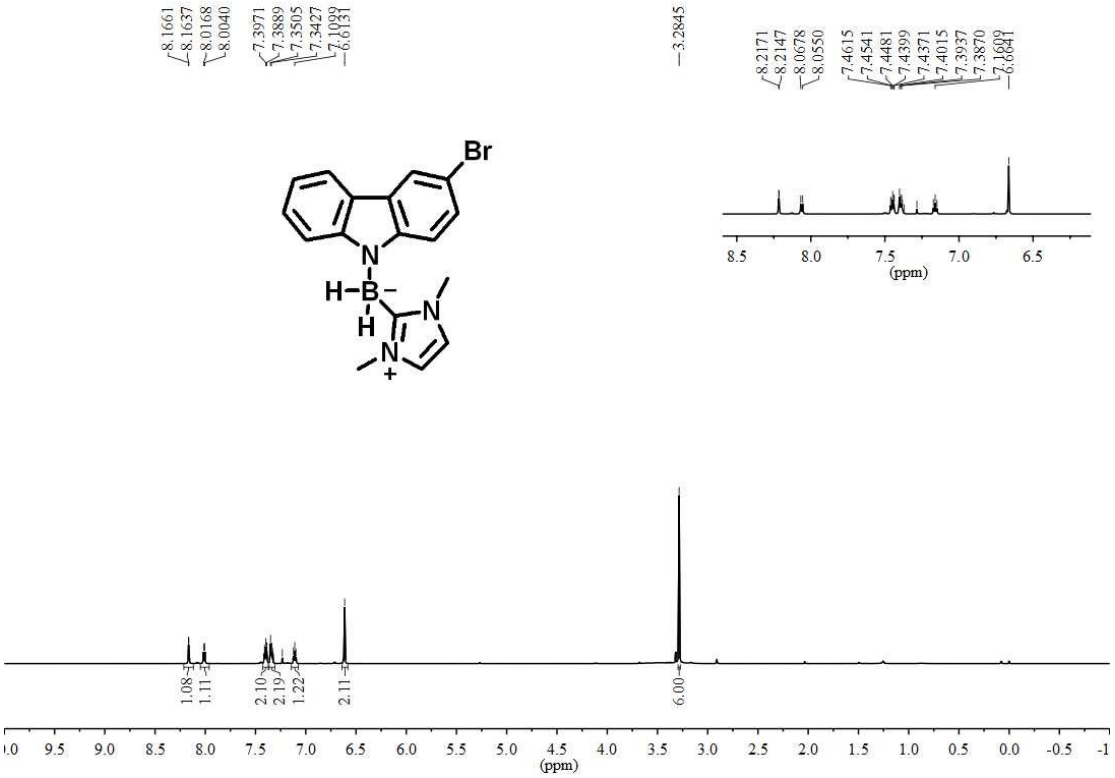
^{13}C NMR of product 3d in $CDCl_3$ (150 MHz)



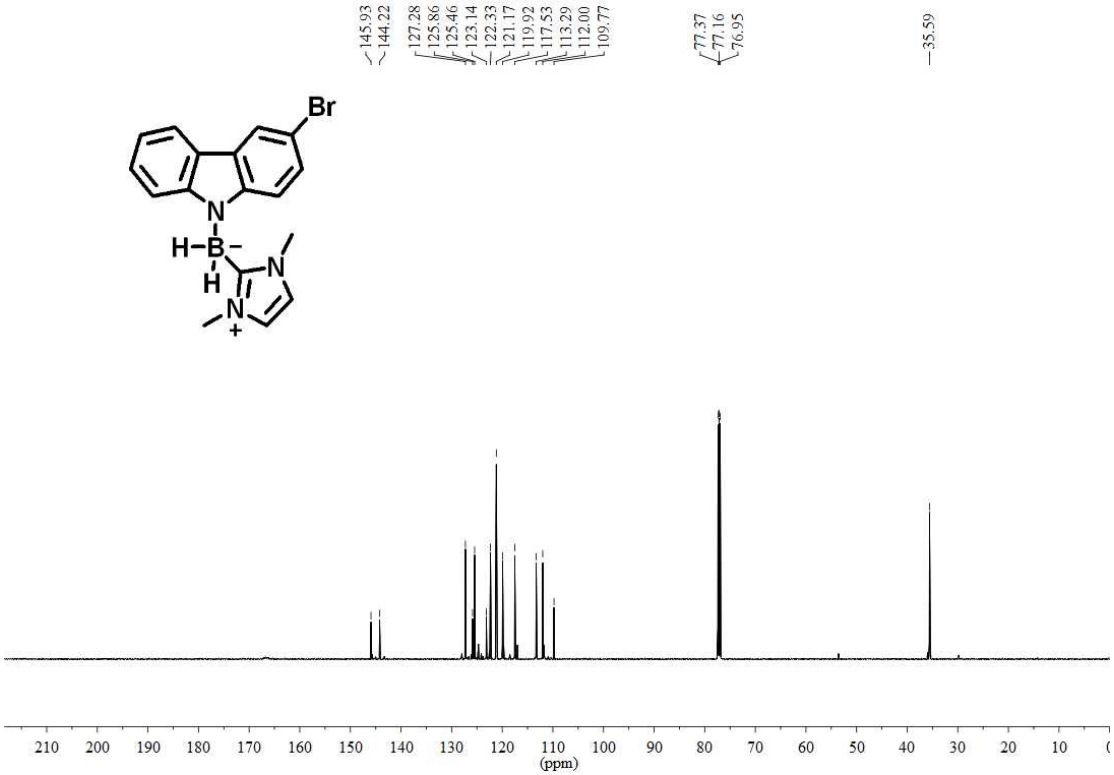
^{11}B NMR of product 3d in DMSO-d_6 (160 MHz)



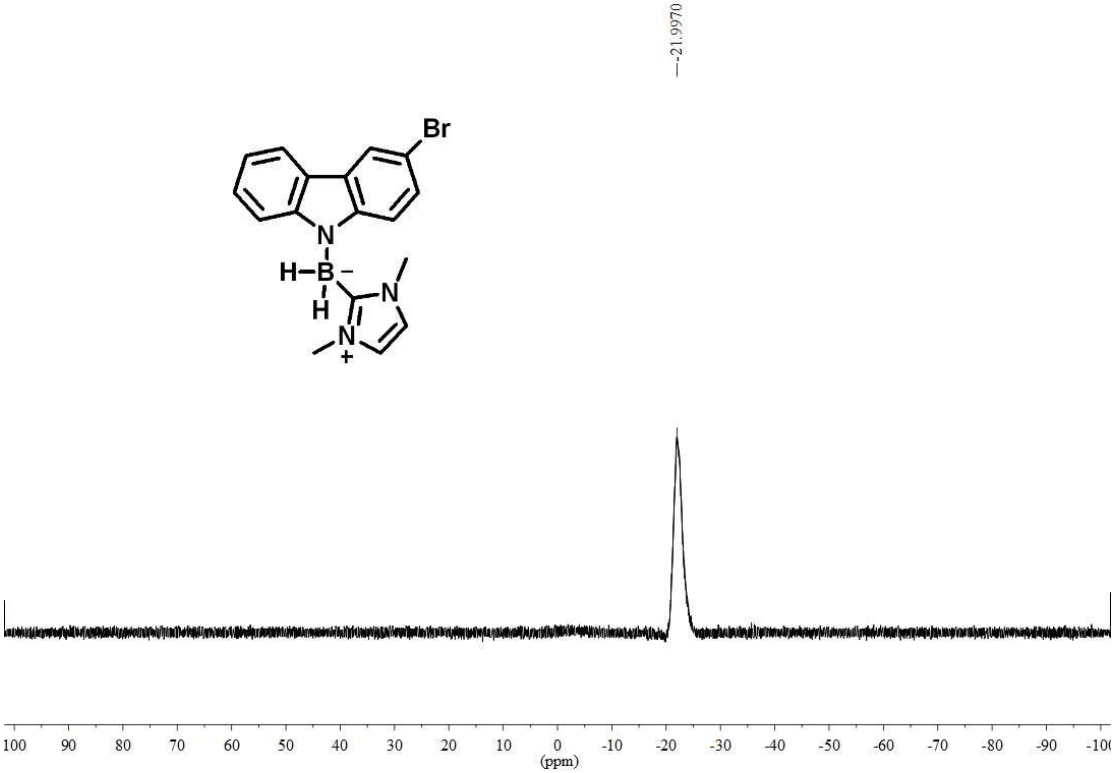
^{1}H NMR of product 3e in $CDCl_3$ (600 MHz)



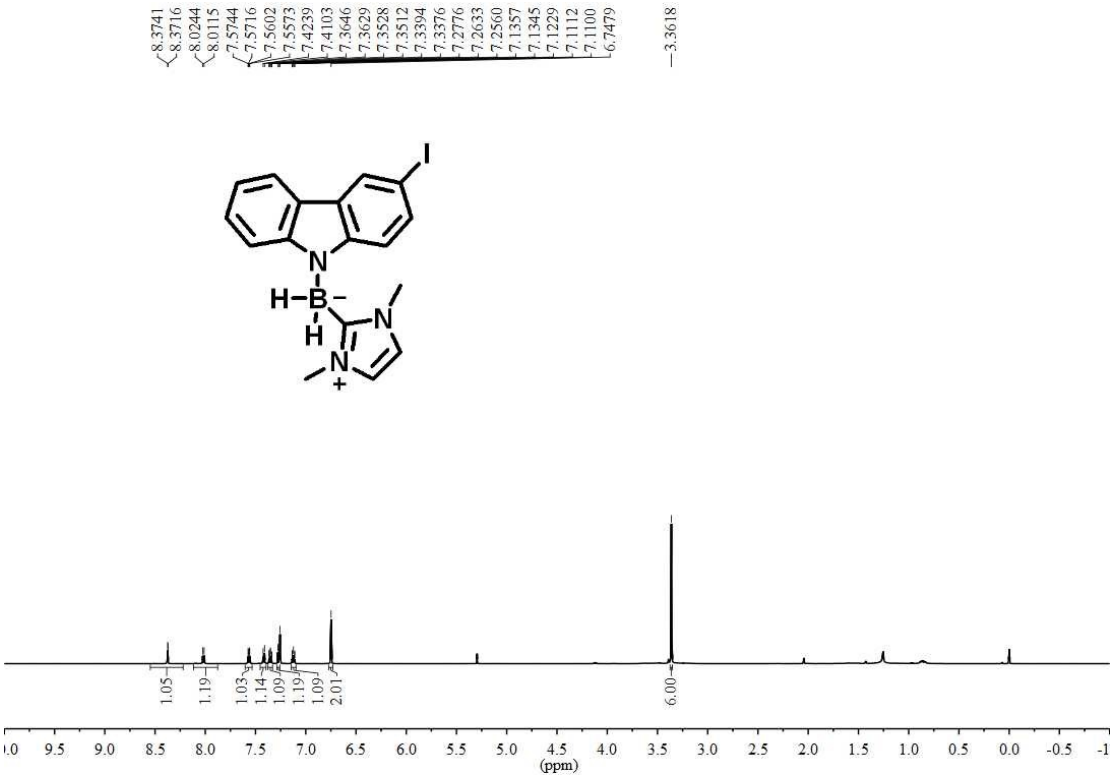
^{13}C NMR of product 3e in $CDCl_3$ (150 MHz)



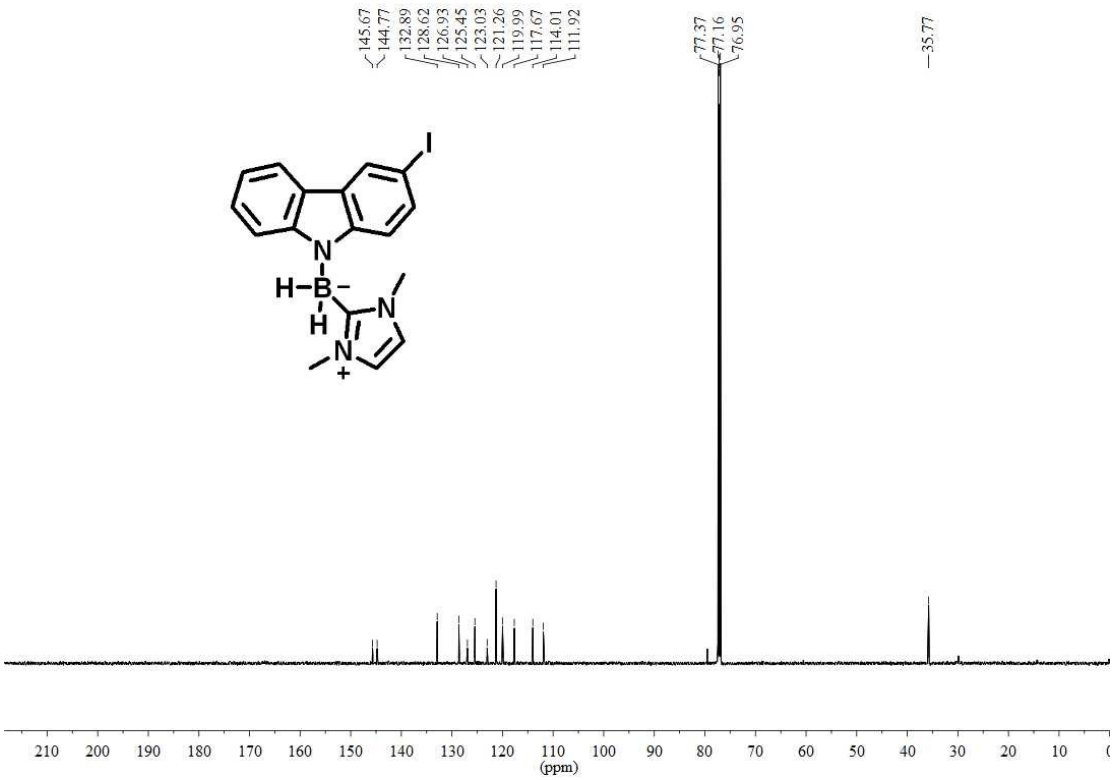
^{11}B NMR of product 3e in DMSO-d_6 (160 MHz)



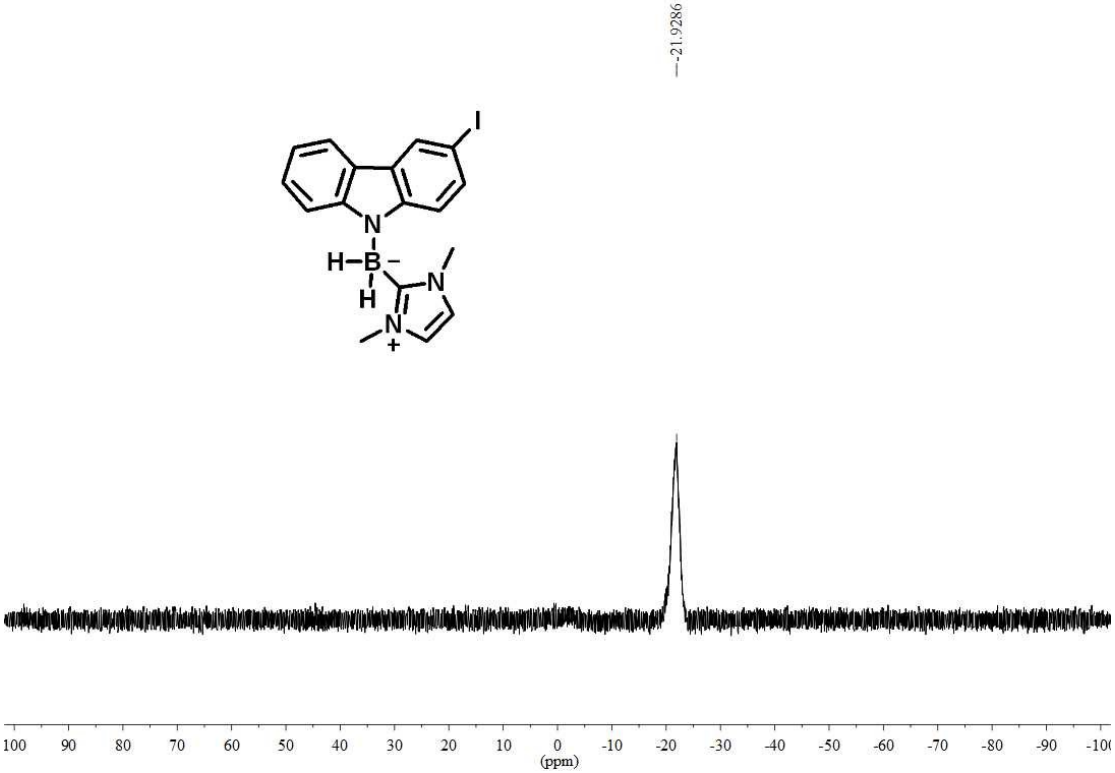
^{1}H NMR of product 3f in $CDCl_3$ (600 MHz)



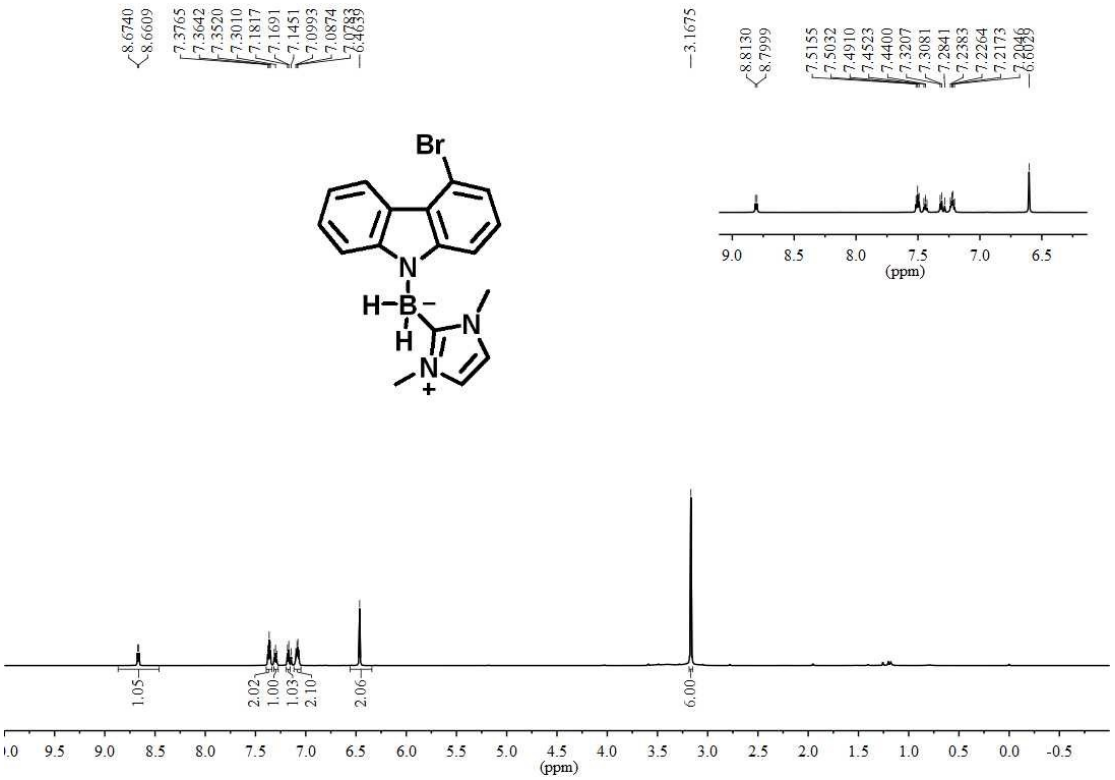
^{13}C NMR of product 3f in $CDCl_3$ (150 MHz)



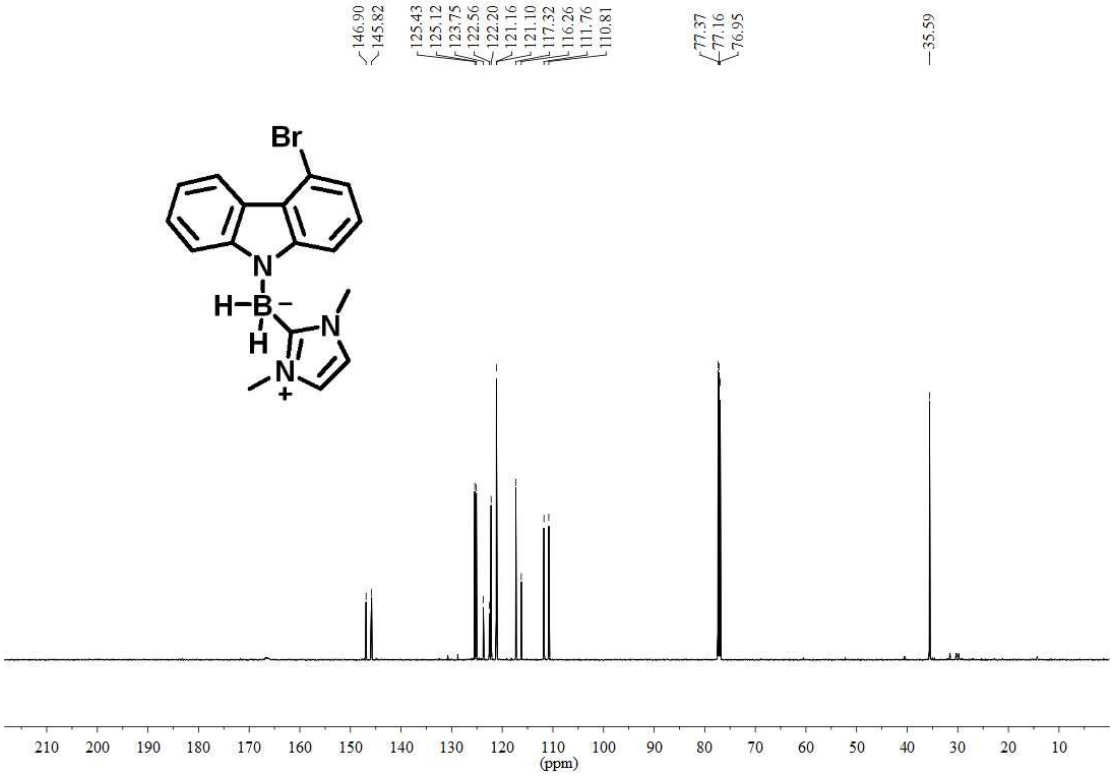
^{11}B NMR of product 3f in DMSO-d_6 (160 MHz)



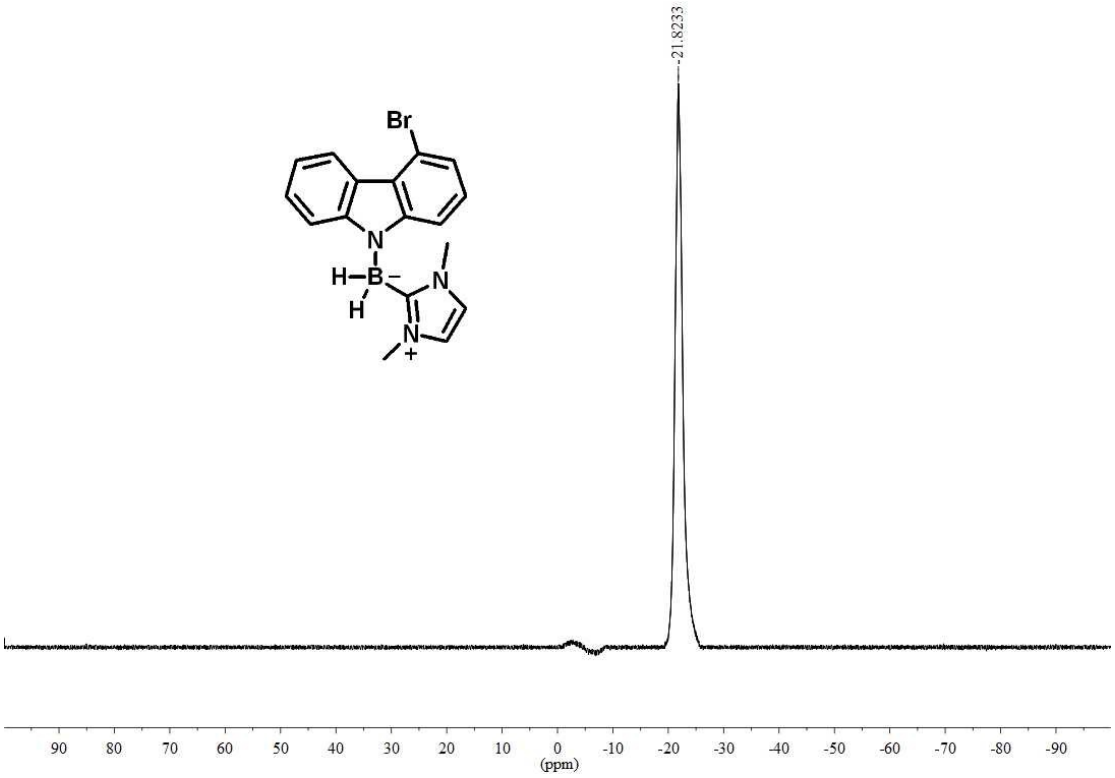
^{1}H NMR of product 3g in $CDCl_3$ (600 MHz)



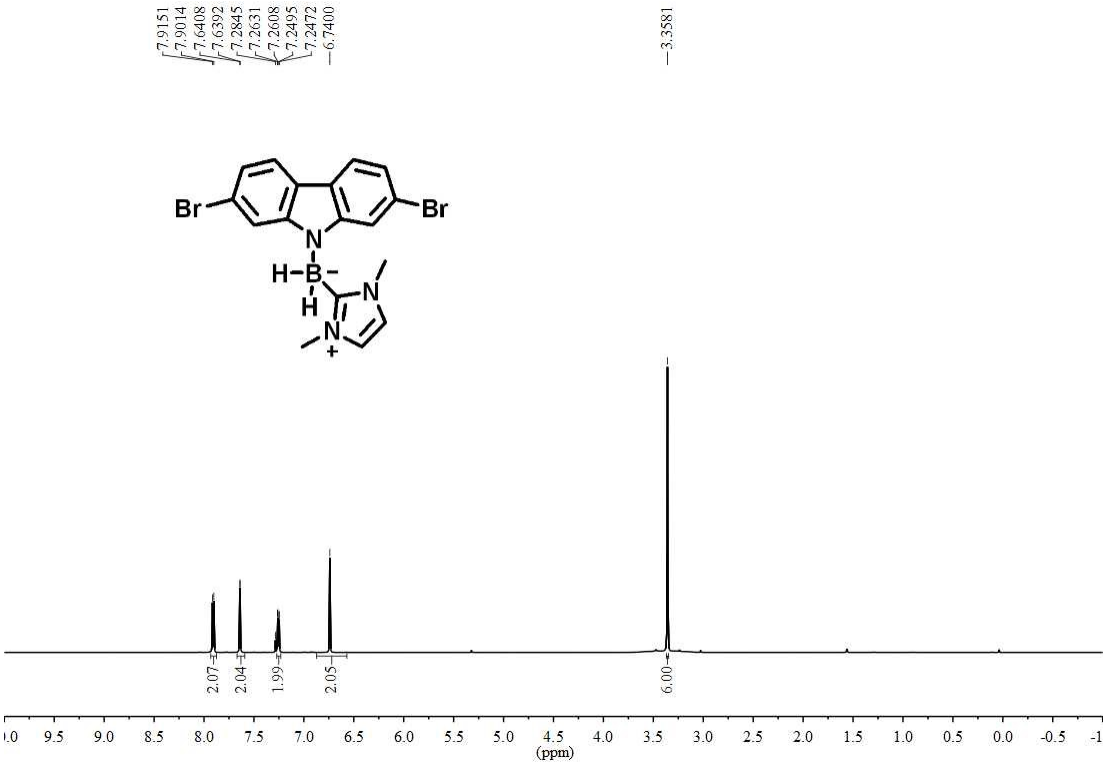
^{13}C NMR of product 3g in $CDCl_3$ (150 MHz)



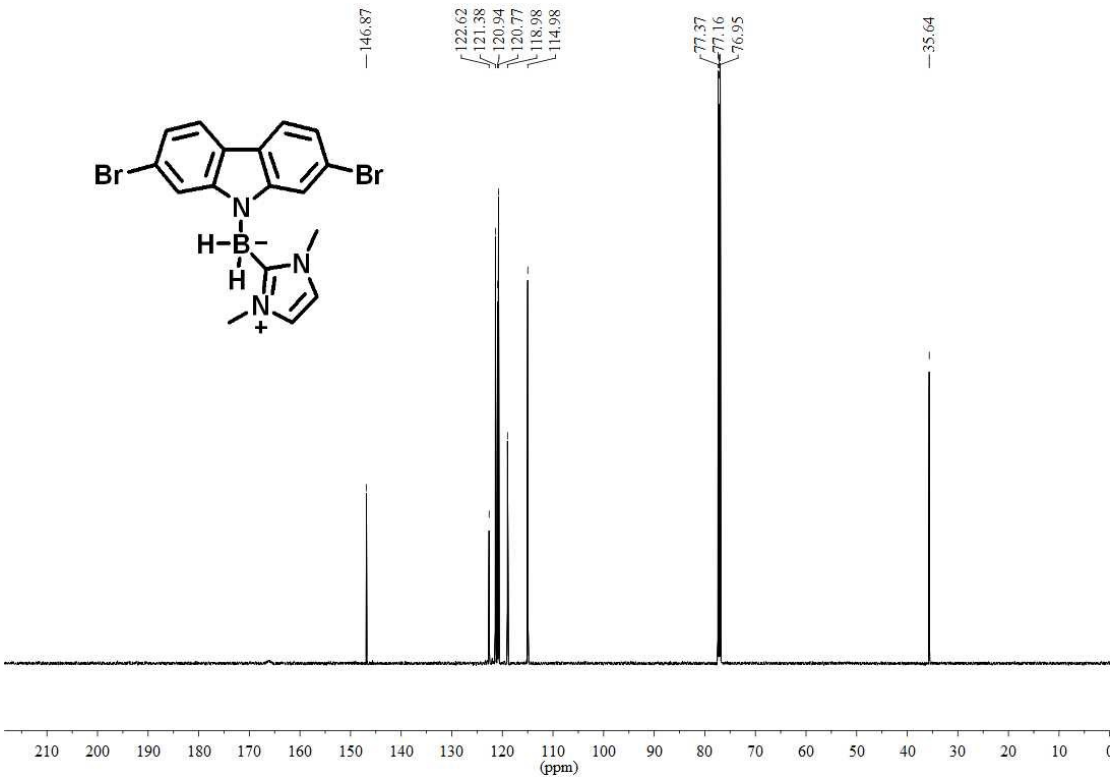
^{11}B NMR of product 3g in DMSO-d_6 (160 MHz)



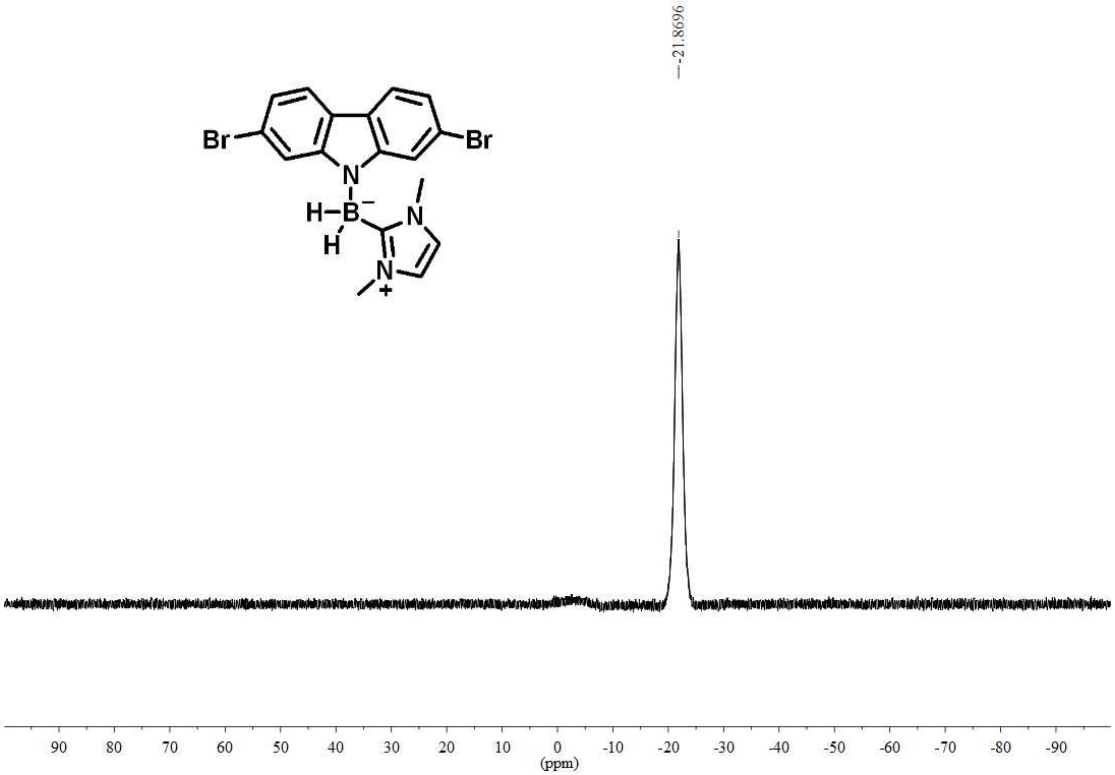
^{1}H NMR of product 3h in $CDCl_3$ (600 MHz)



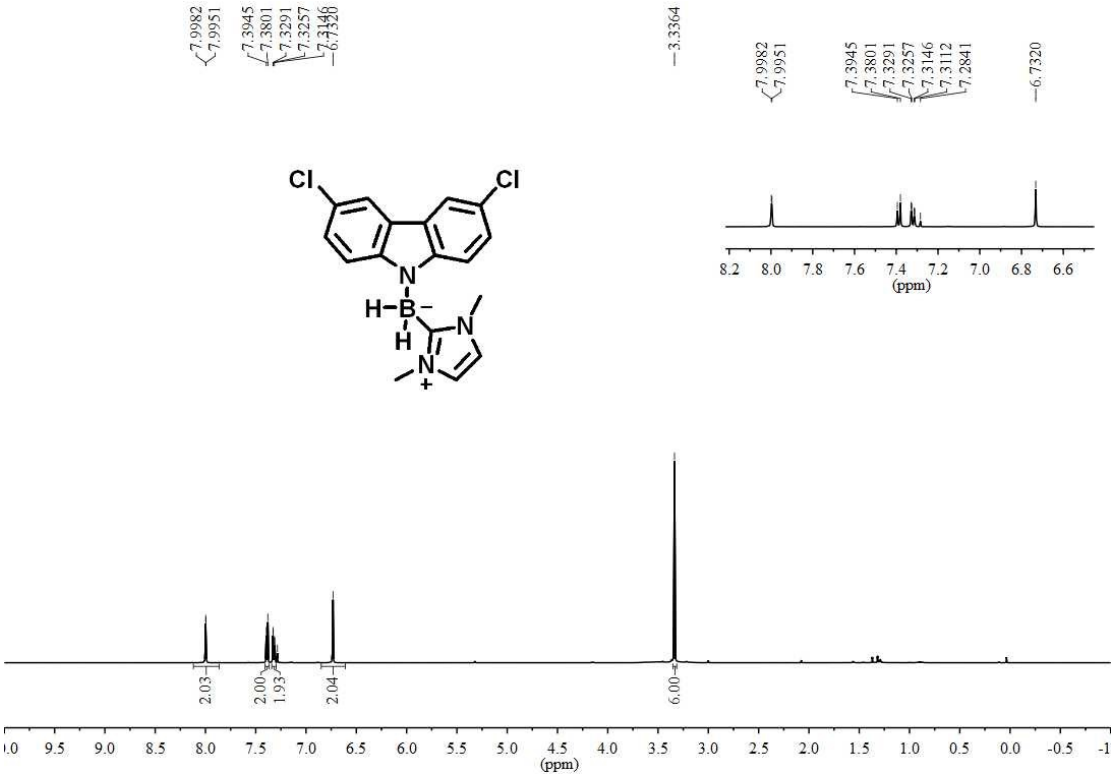
^{13}C NMR of product 3h in $CDCl_3$ (150 MHz)



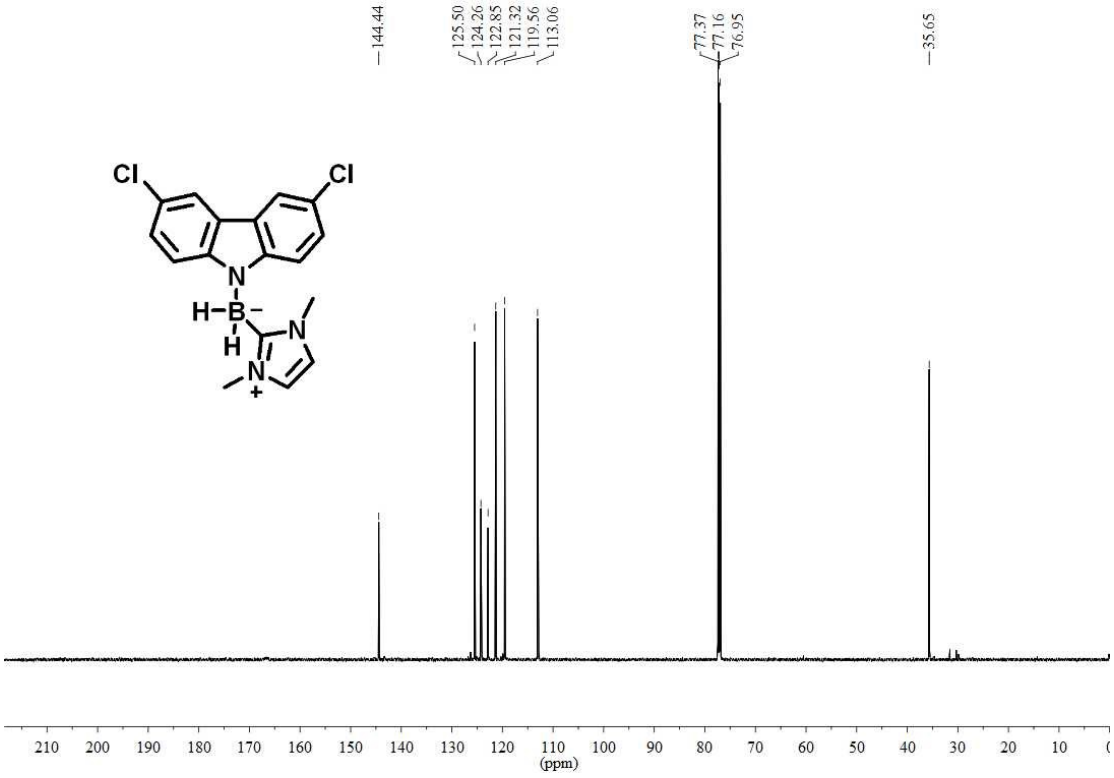
^{11}B NMR of product 3h in DMSO-d_6 (160 MHz)



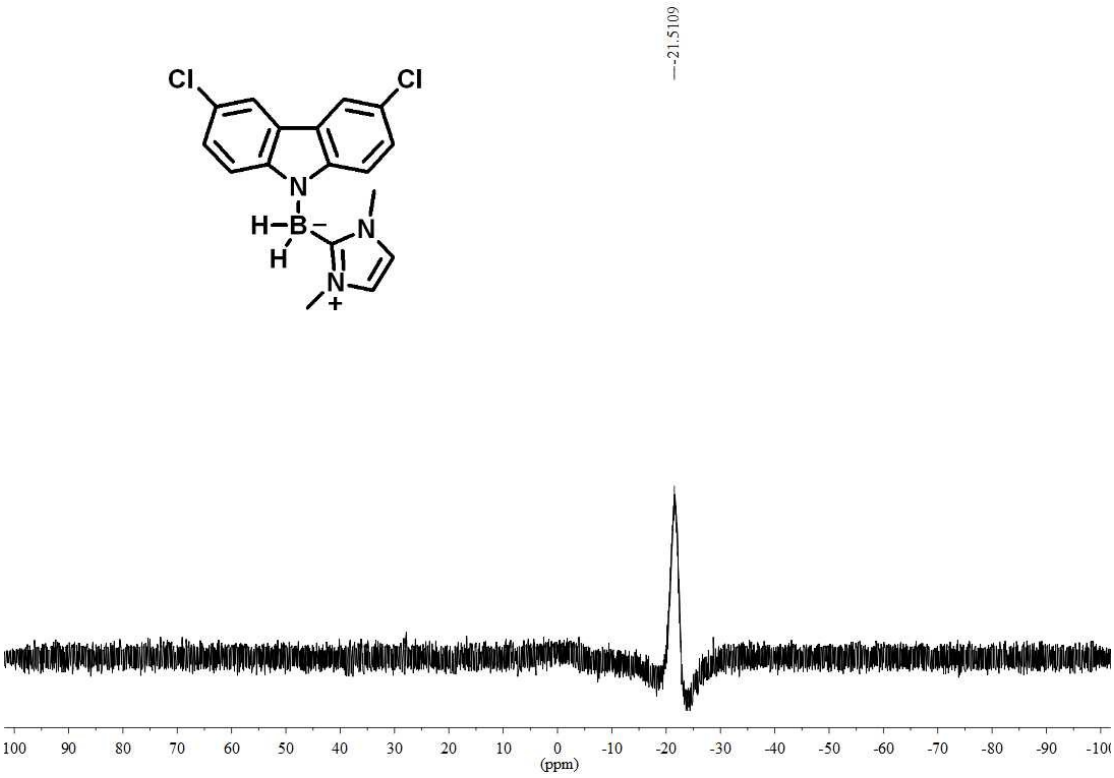
^{1}H NMR of product 3i in $CDCl_3$ (600 MHz)



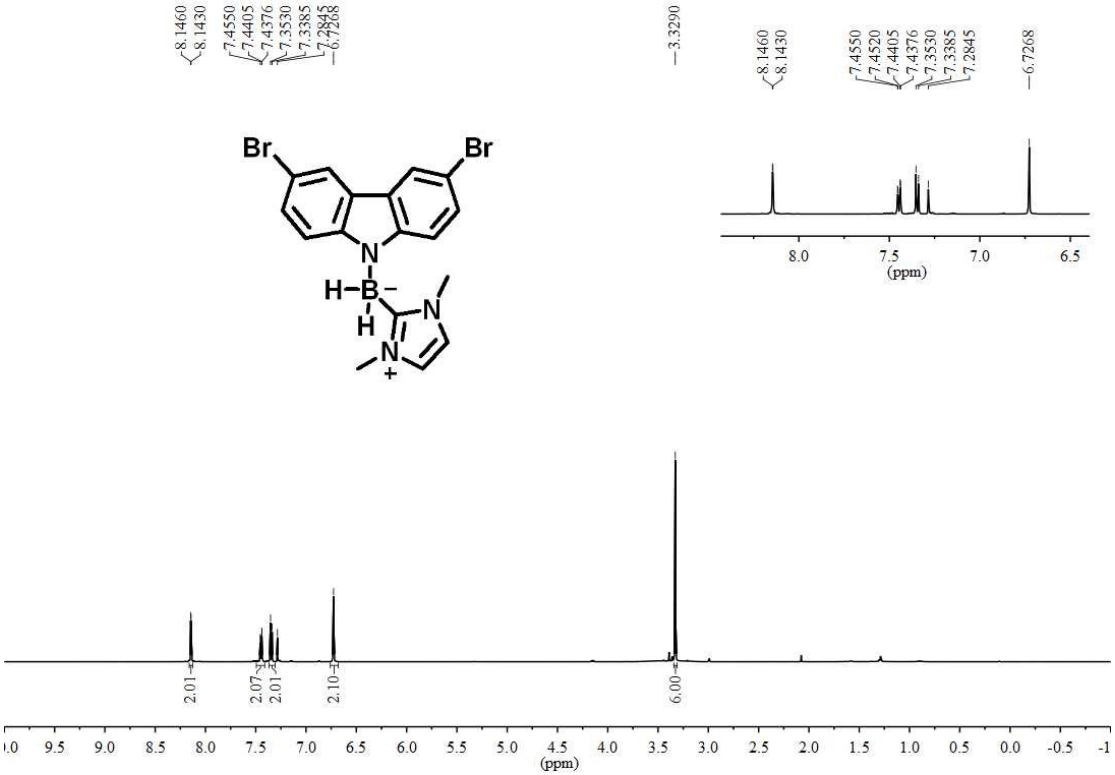
^{13}C NMR of product 3i in $CDCl_3$ (150 MHz)



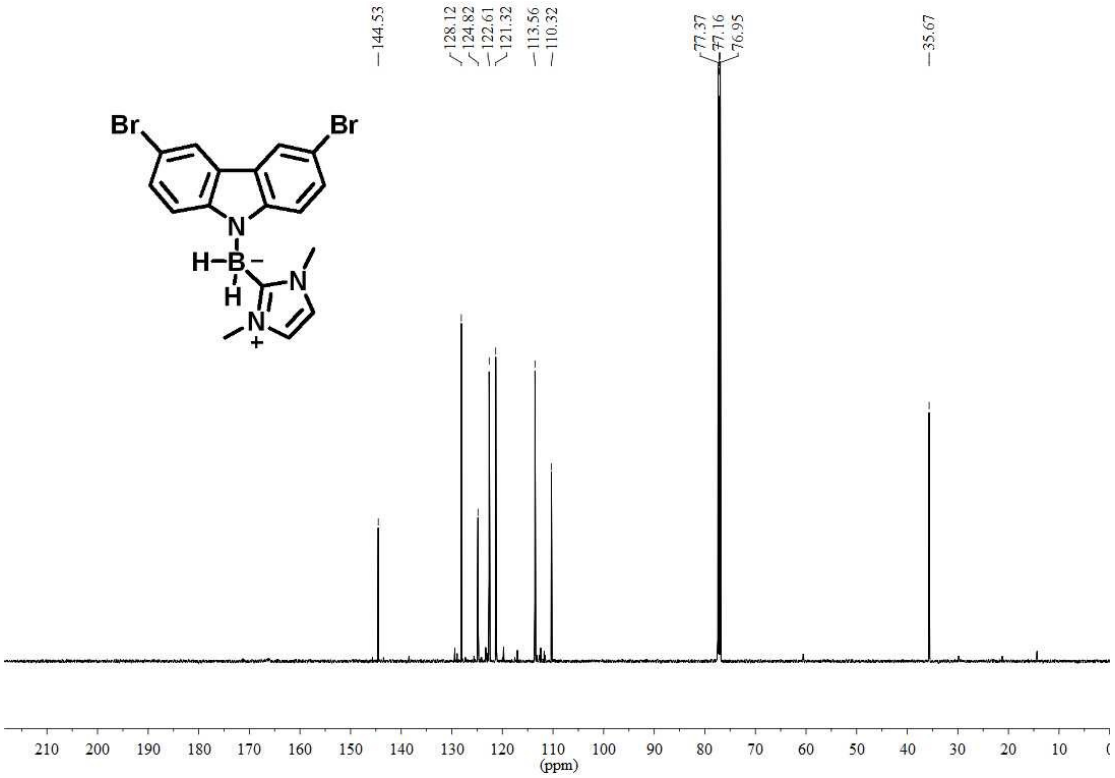
^{11}B NMR of product 3i in DMSO-d_6 (160 MHz)



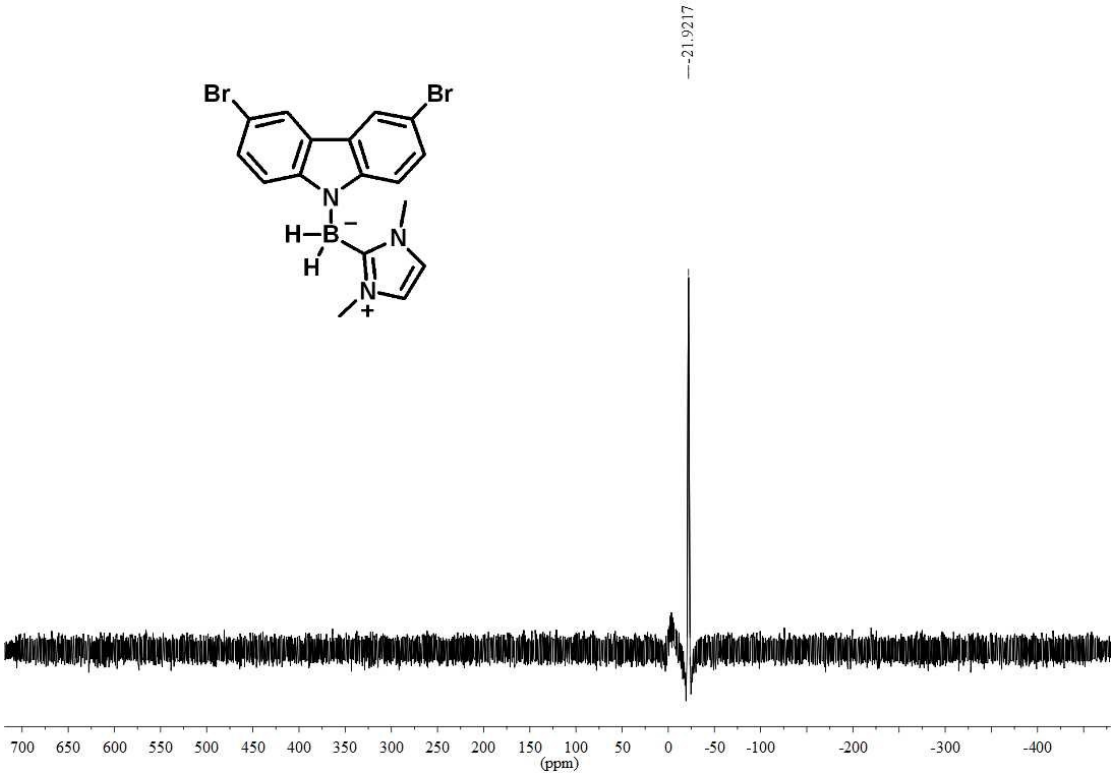
^{1}H NMR of product 3j in $CDCl_3$ (600 MHz)



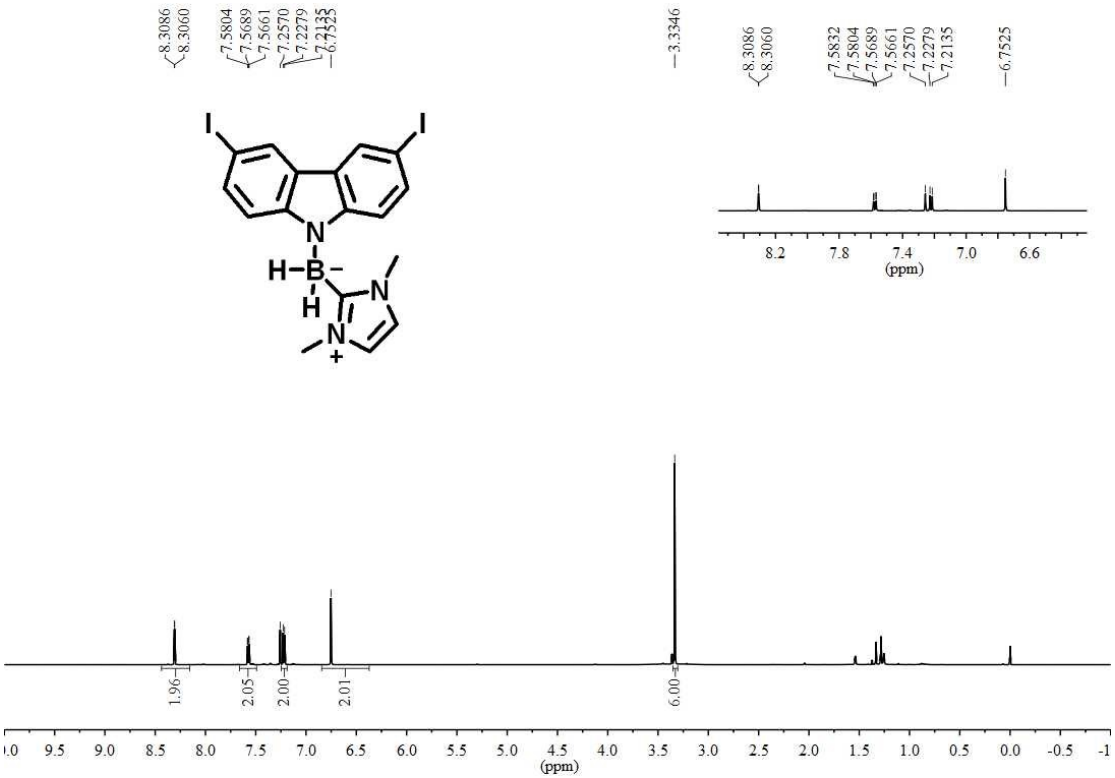
^{13}C NMR of product 3j in $CDCl_3$ (150 MHz)



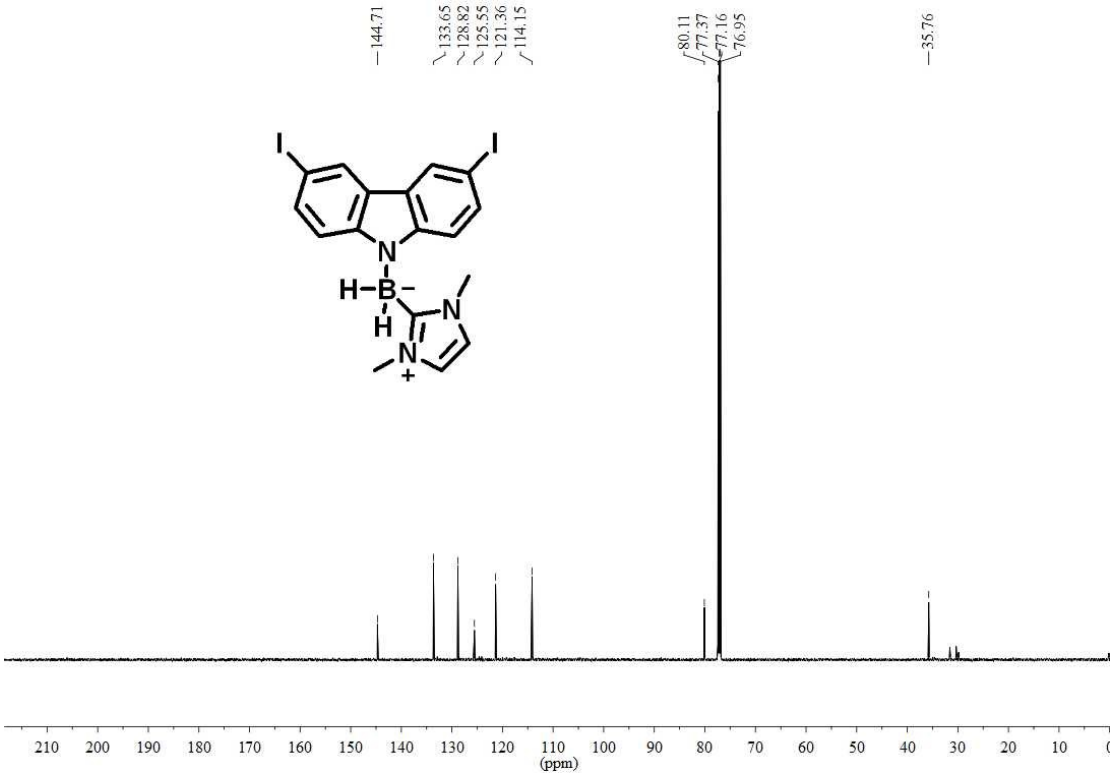
^{11}B NMR of product 3j in DMSO-d_6 (160 MHz)



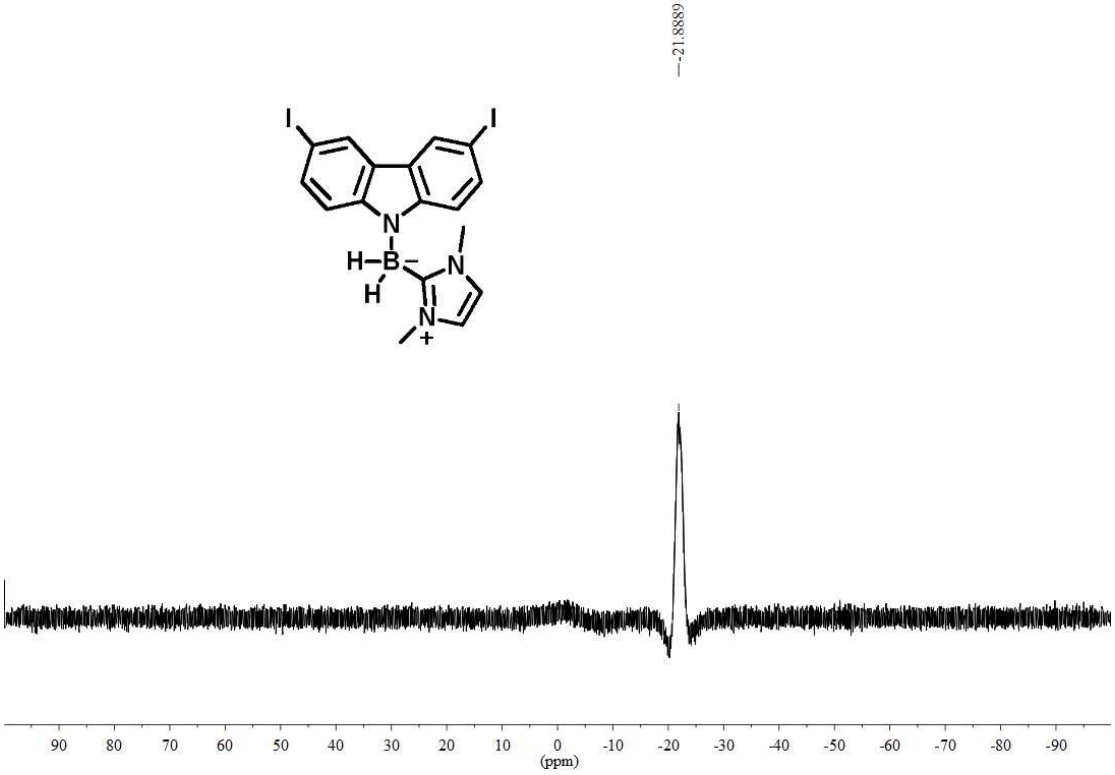
^{1}H NMR of product 3k in $CDCl_3$ (600 MHz)



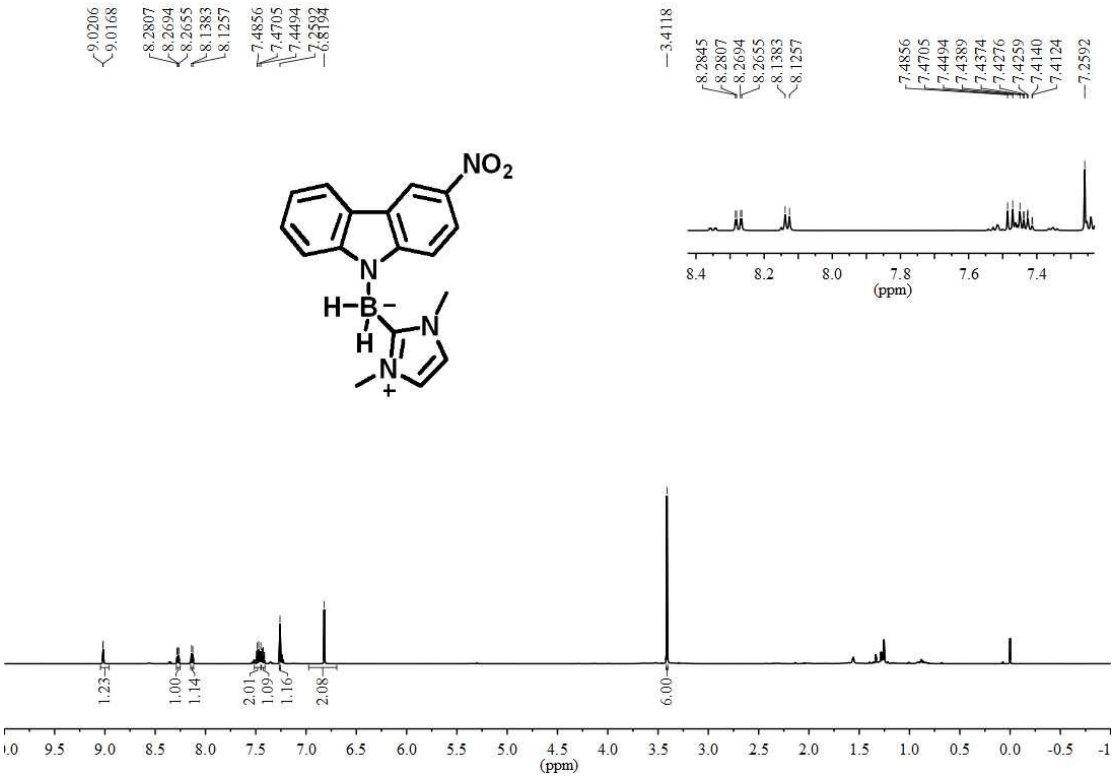
^{13}C NMR of product 3k in $CDCl_3$ (150 MHz)



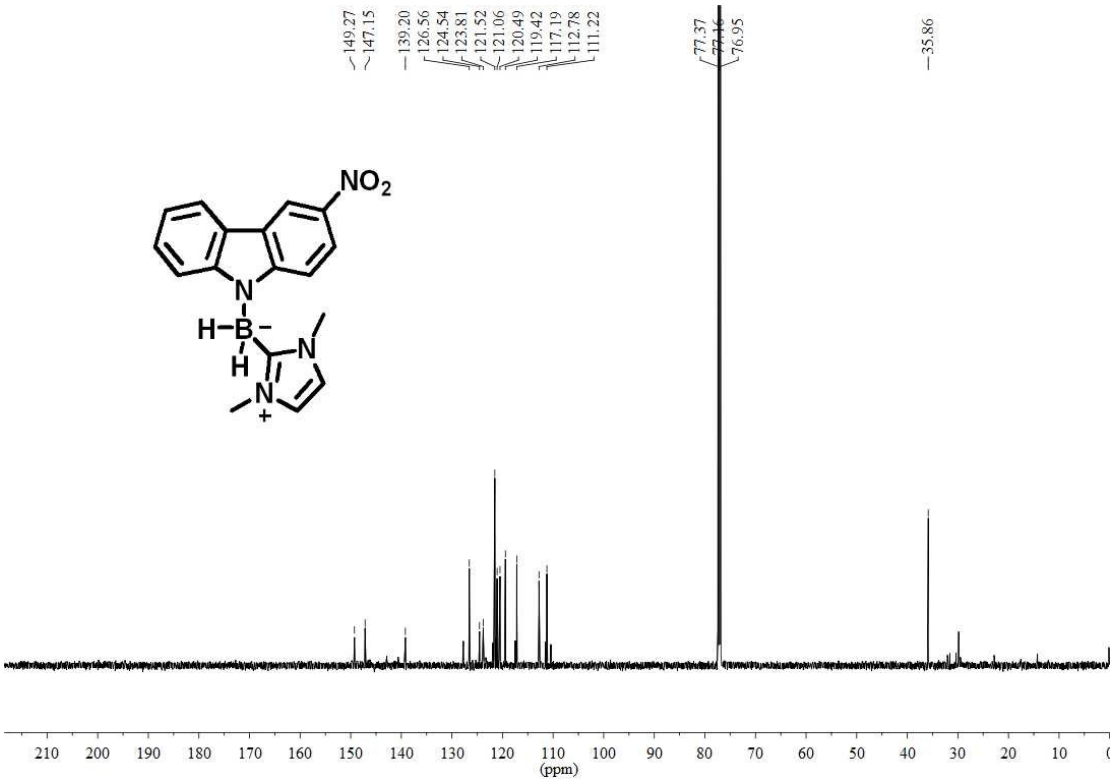
^{11}B NMR of product 3k in DMSO-d_6 (160 MHz)



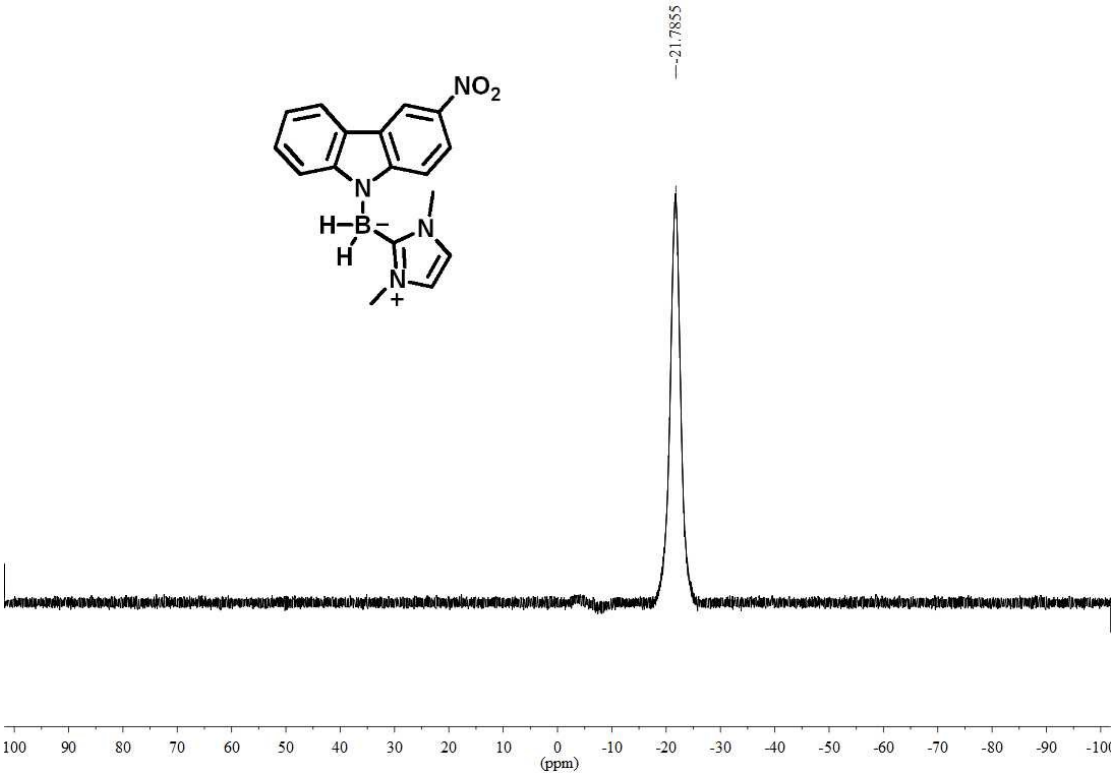
^{1}H NMR of product 3l in $CDCl_3$ (600 MHz)



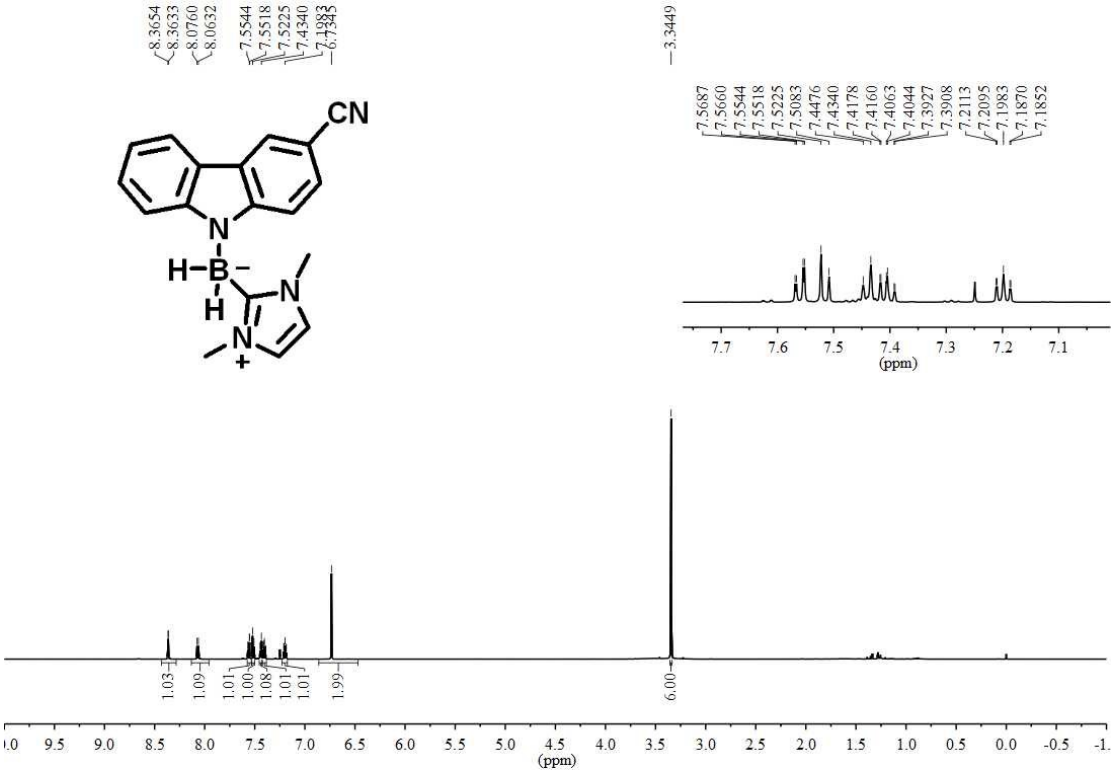
^{13}C NMR of product 3l in $CDCl_3$ (150 MHz)



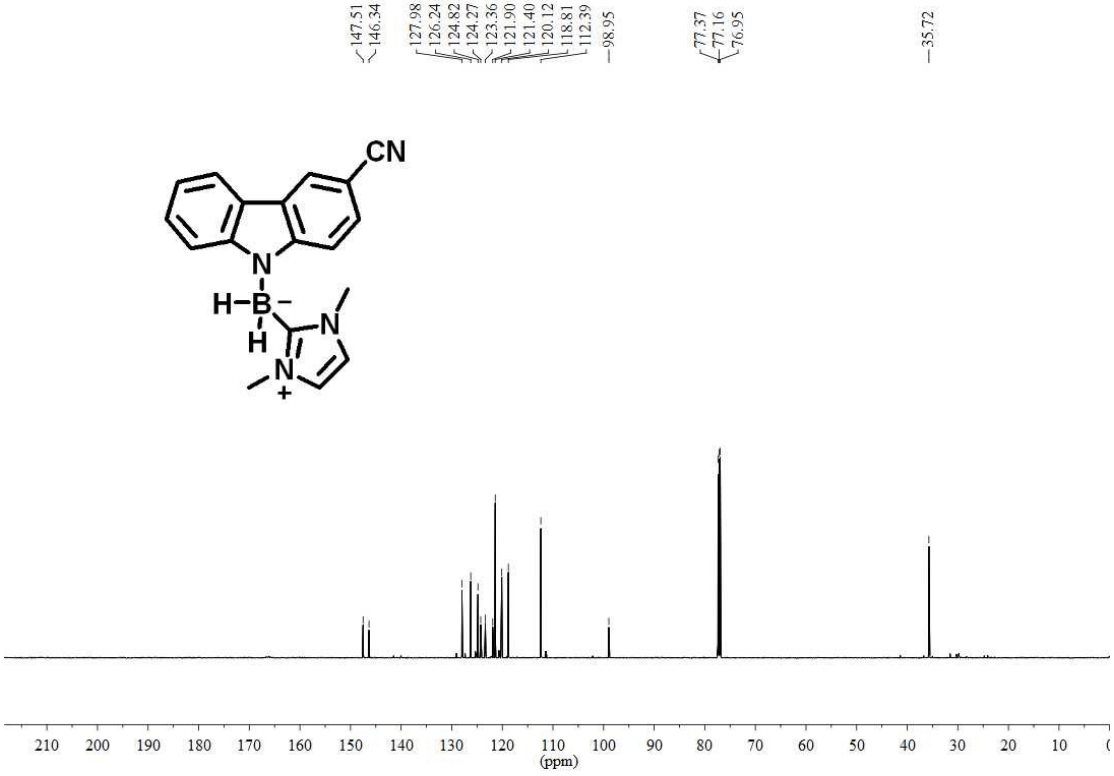
^{11}B NMR of product 3l in DMSO-d_6 (160 MHz)



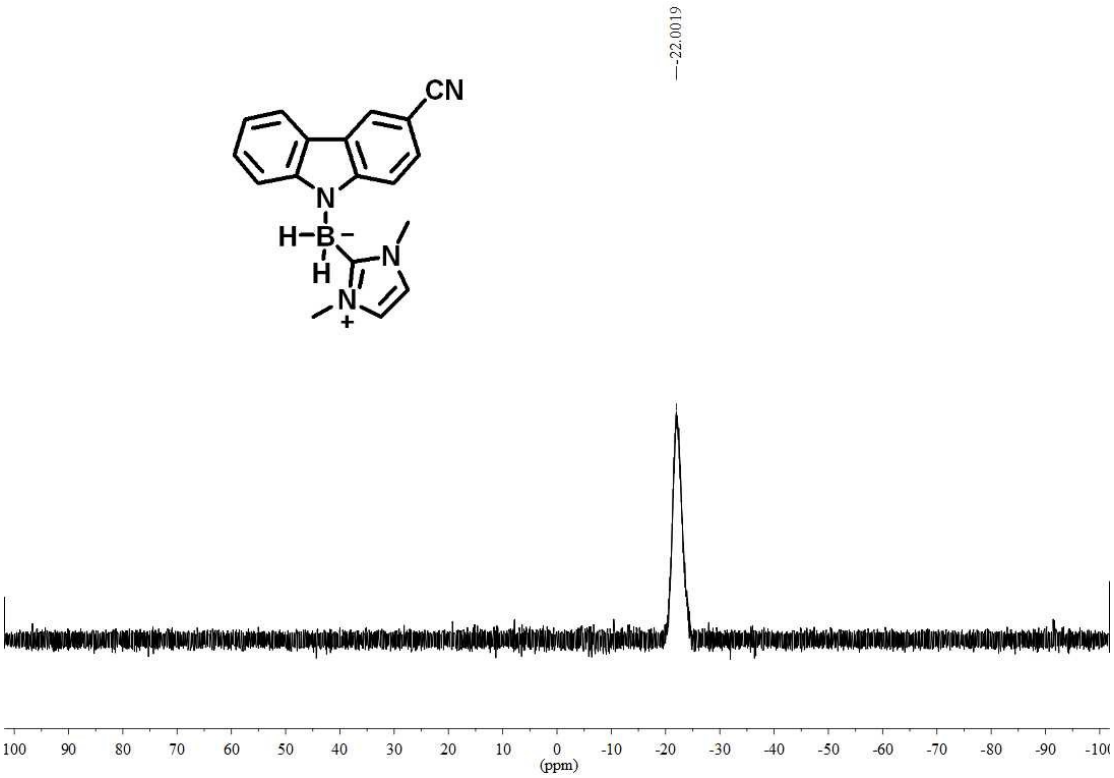
^{1}H NMR of product 3m in $CDCl_3$ (600 MHz)



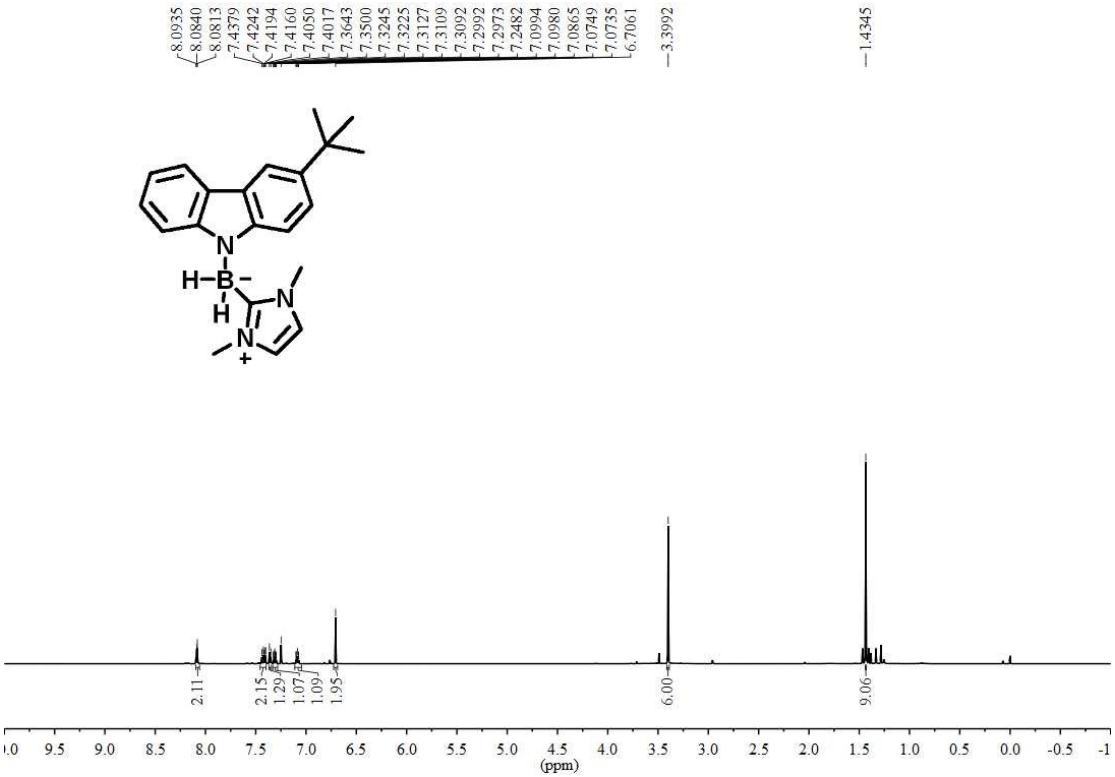
^{13}C NMR of product 3m in $CDCl_3$ (150 MHz)



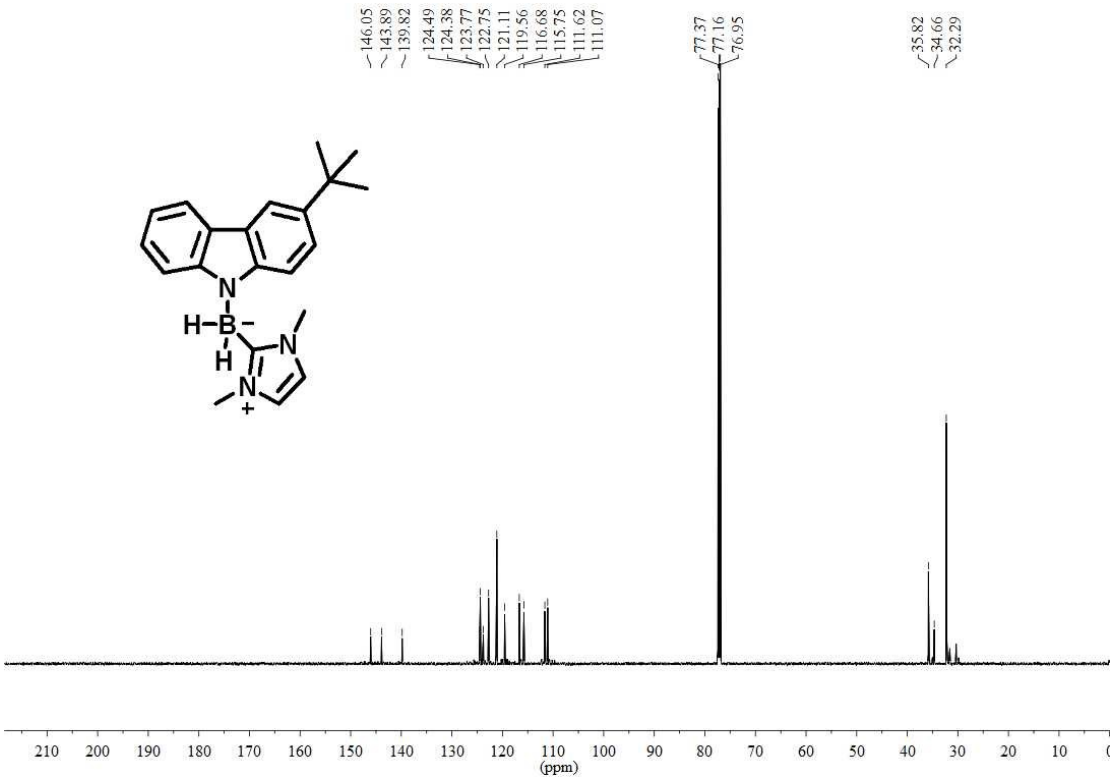
^{11}B NMR of product 3m in DMSO-d_6 (160 MHz)



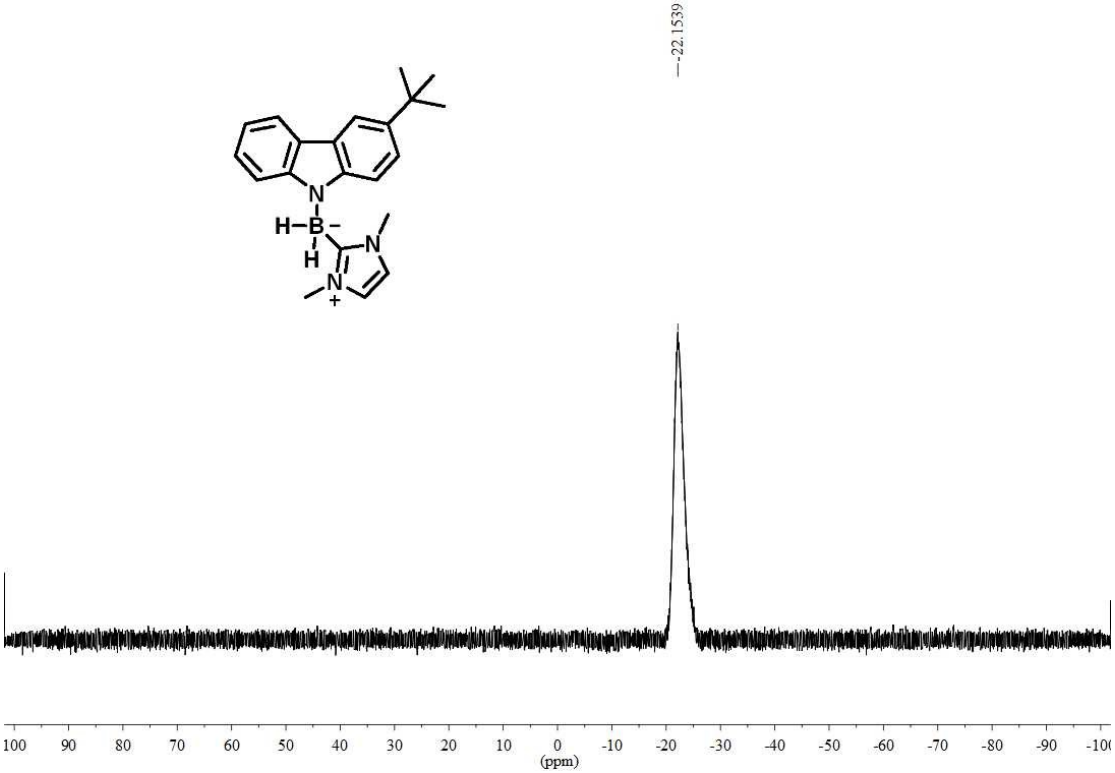
^{1}H NMR of product 3n in $CDCl_3$ (600 MHz)



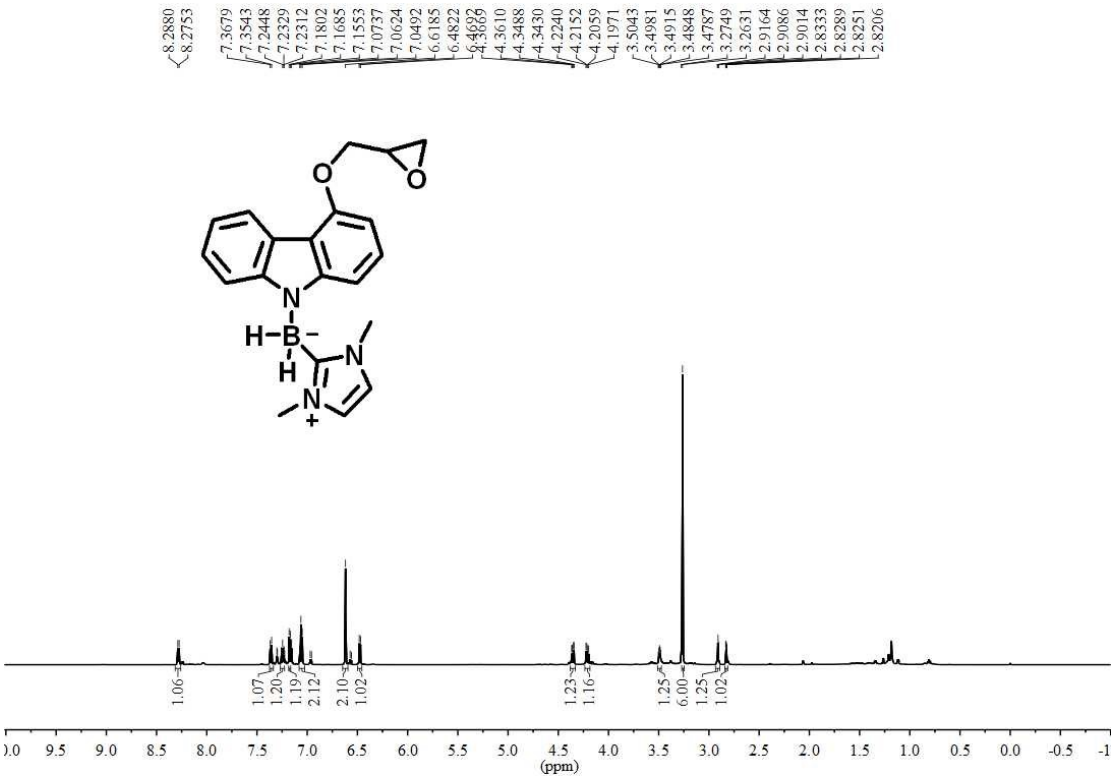
^{13}C NMR of product 3n in $CDCl_3$ (150 MHz)



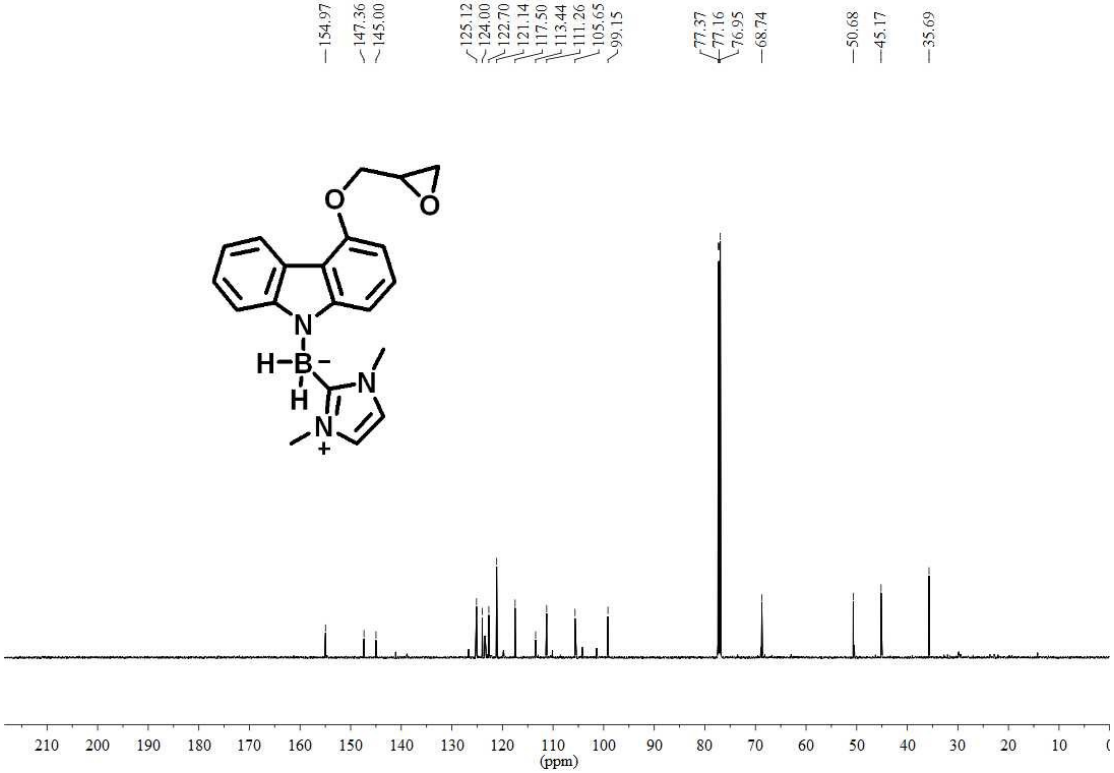
^{11}B NMR of product 3n in DMSO-d_6 (160 MHz)



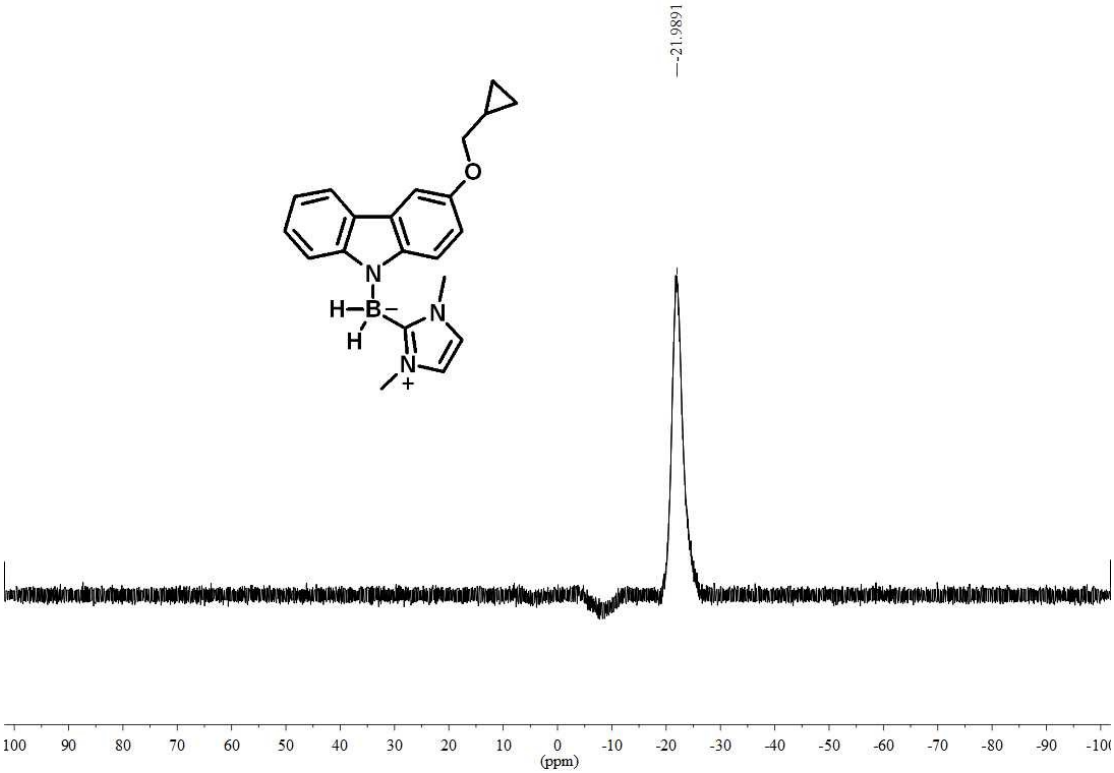
^{1}H NMR of product 3o in $CDCl_3$ (600 MHz)



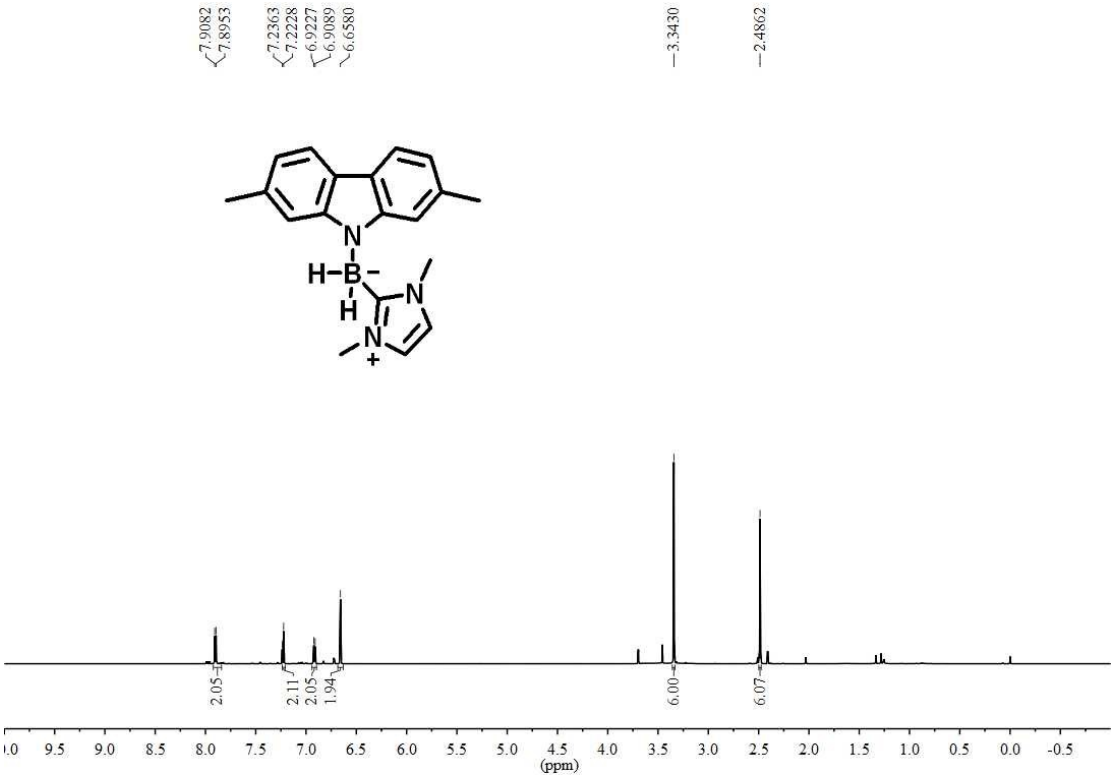
^{13}C NMR of product 3o in $CDCl_3$ (150 MHz)



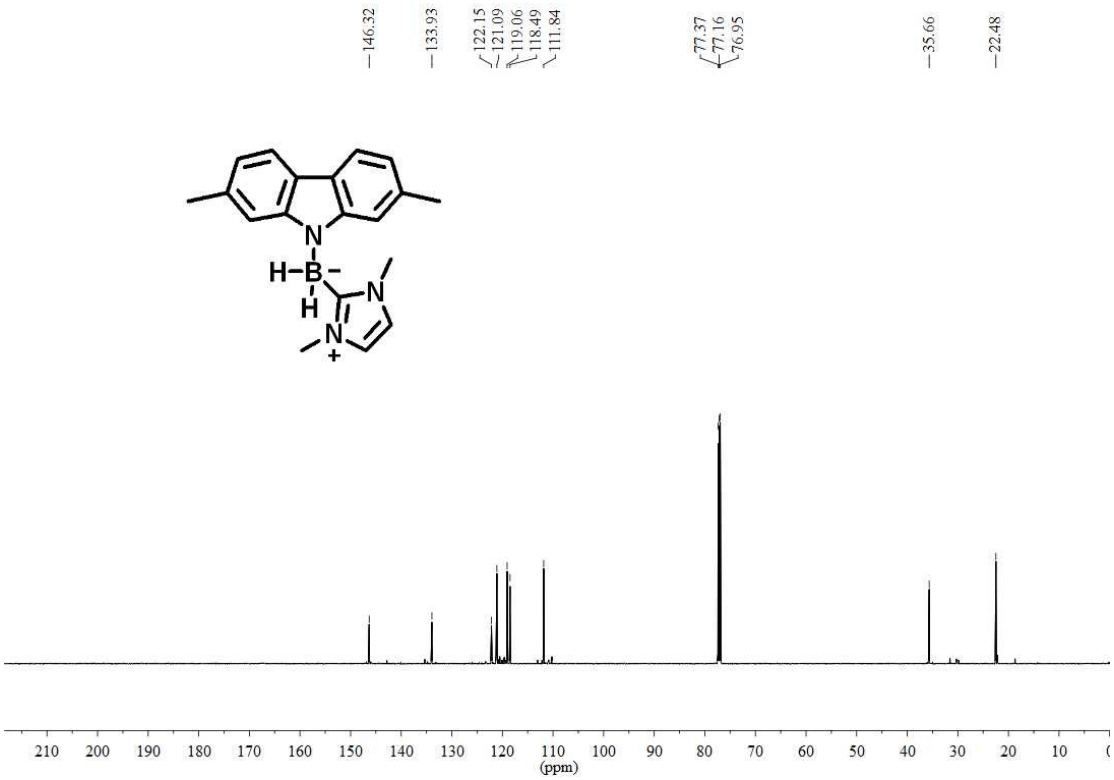
^{11}B NMR of product 3o in DMSO-d_6 (160 MHz)



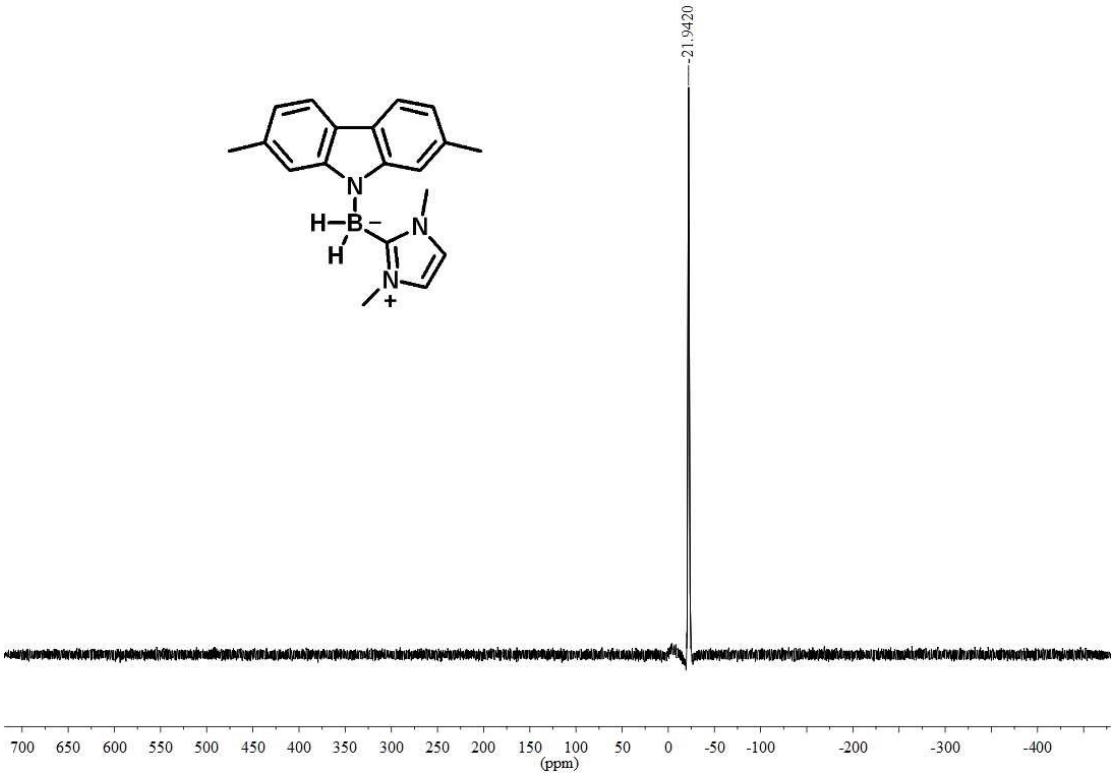
^{1}H NMR of product 3p in $CDCl_3$ (600 MHz)



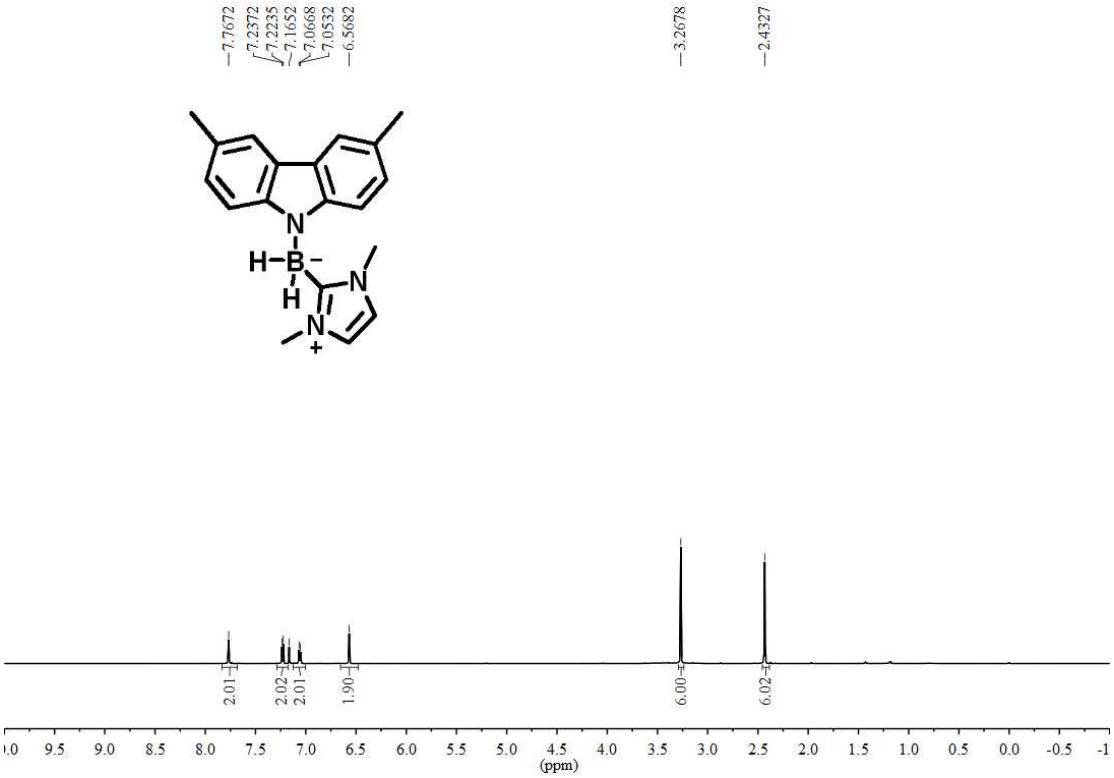
^{13}C NMR of product 3p in $CDCl_3$ (150 MHz)



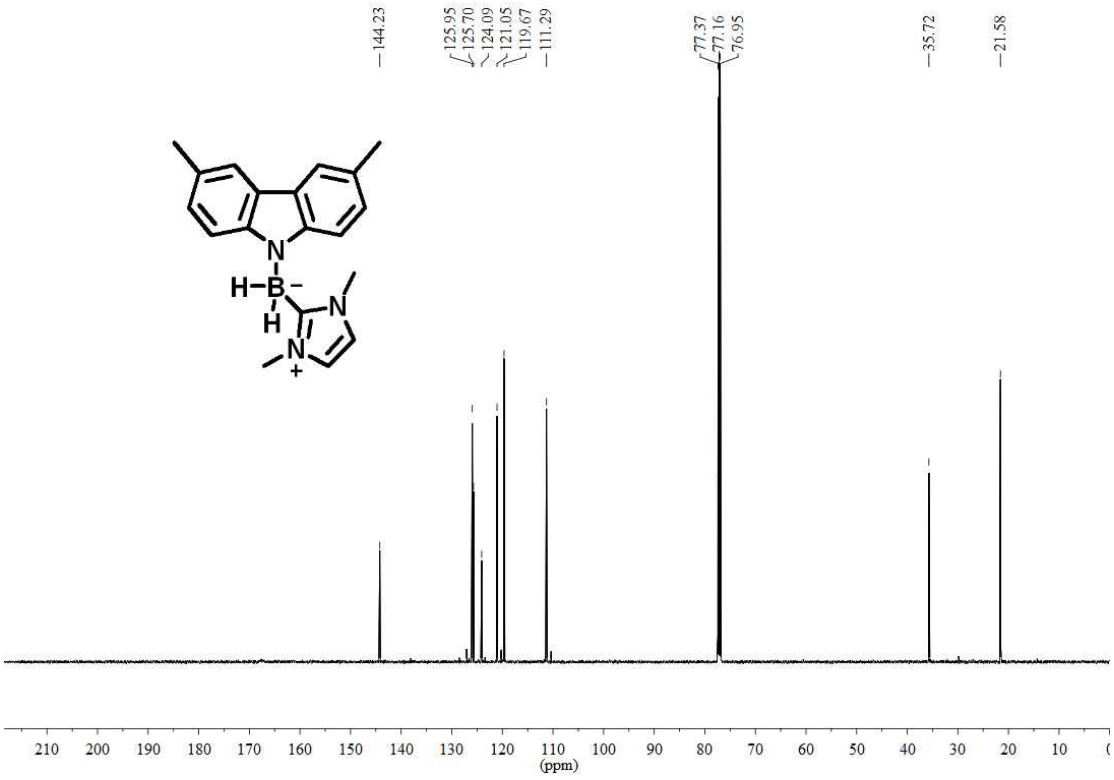
^{11}B NMR of product 3p in DMSO-d_6 (160 MHz)



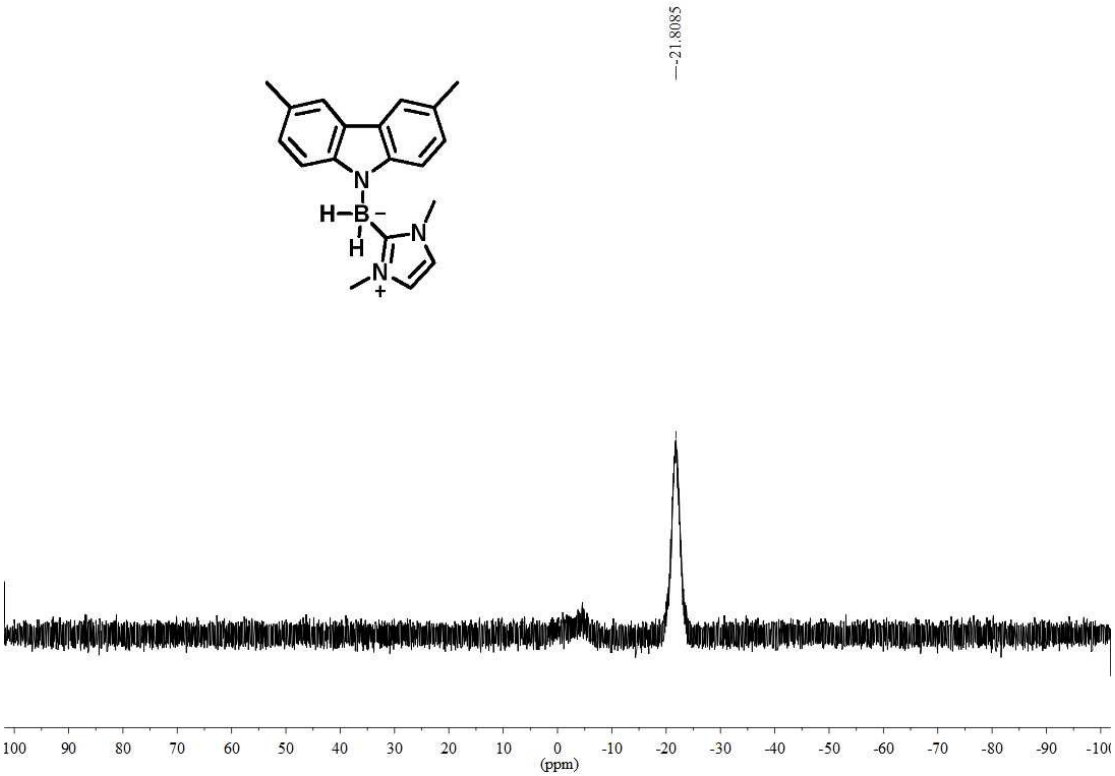
^{1}H NMR of product 3q in $CDCl_3$ (600 MHz)



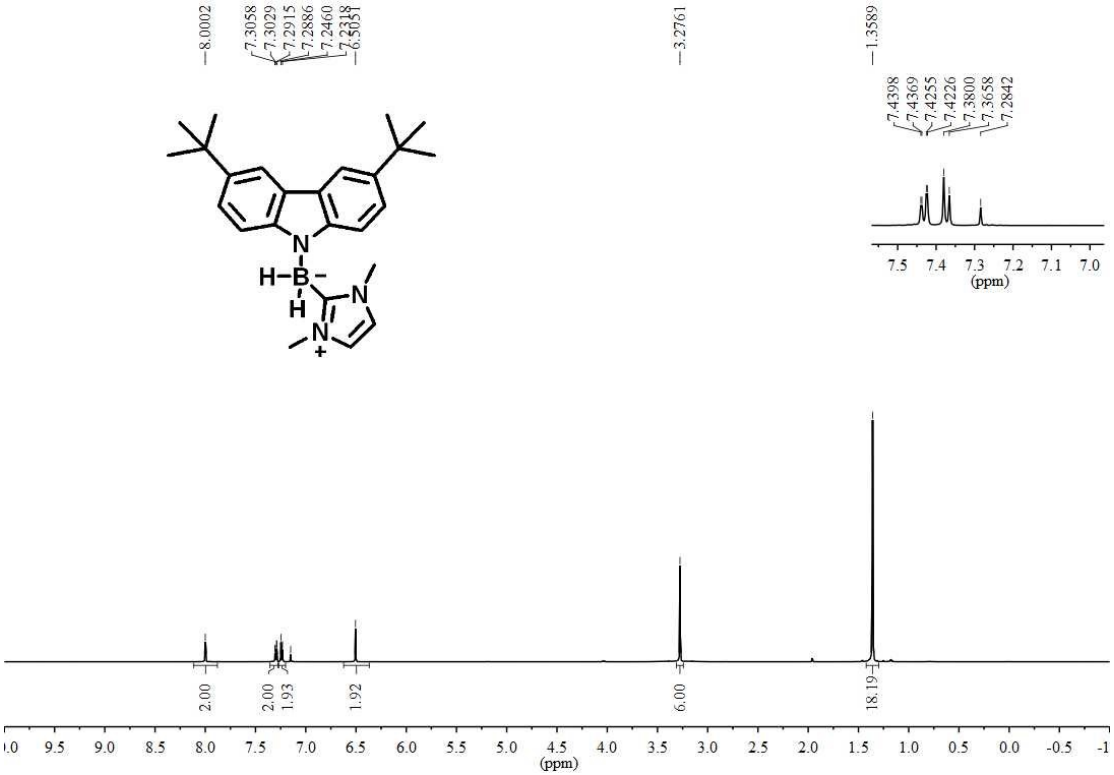
^{13}C NMR of product 3q in $CDCl_3$ (150 MHz)



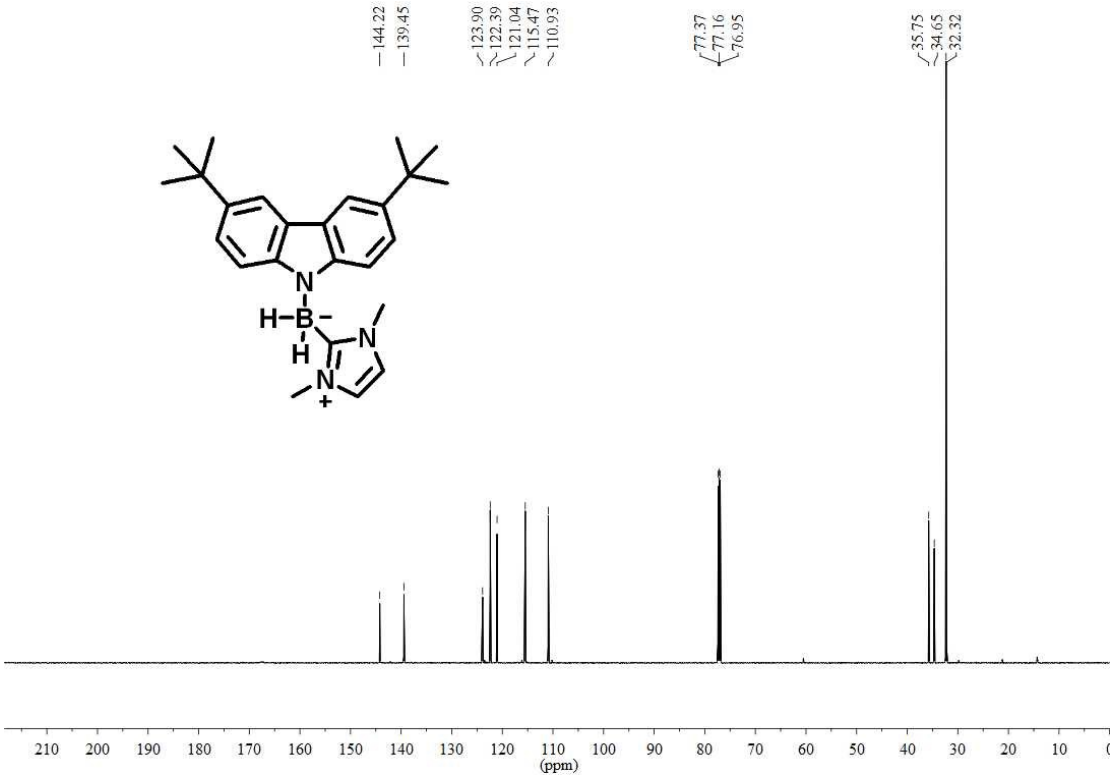
^{11}B NMR of product 3q in DMSO-d_6 (160 MHz)



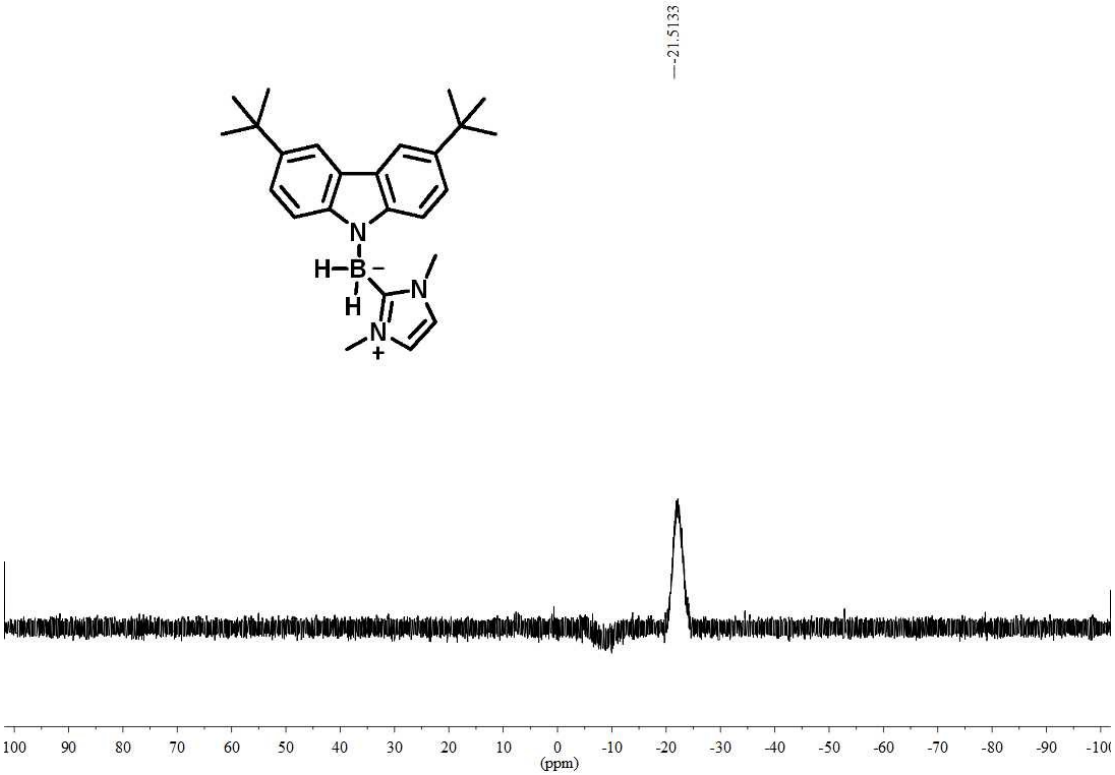
^{1}H NMR of product 3r in $CDCl_3$ (600 MHz)



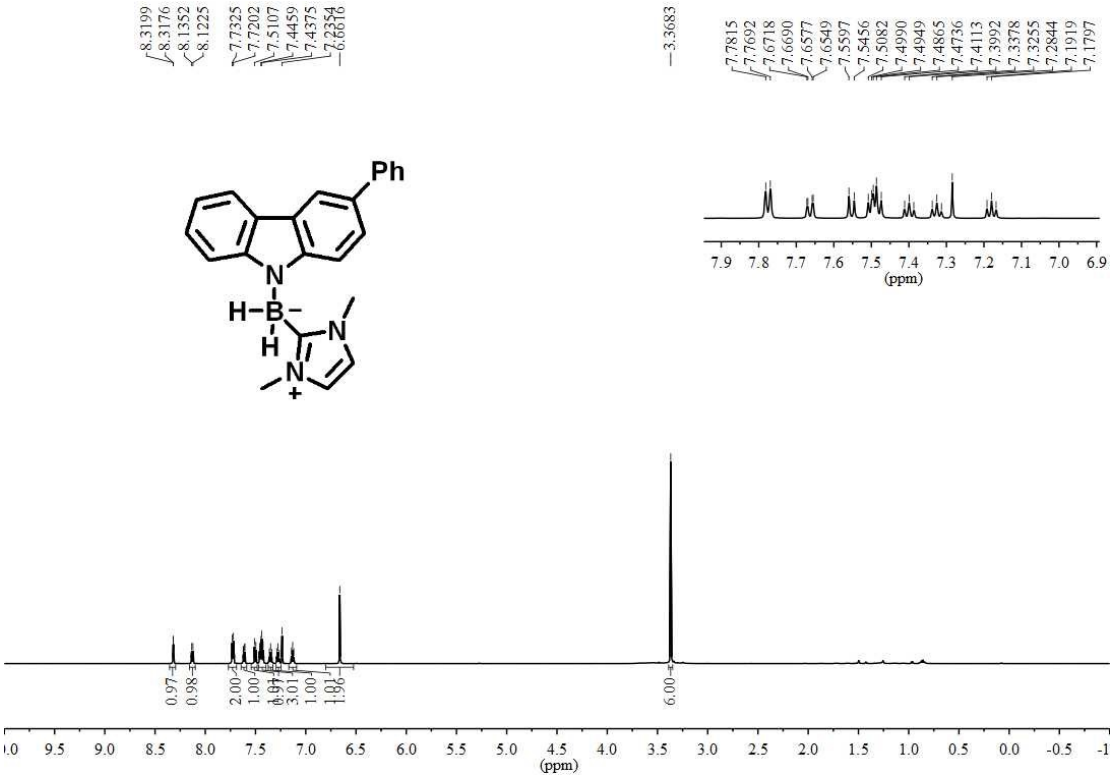
^{13}C NMR of product 3r in $CDCl_3$ (150 MHz)



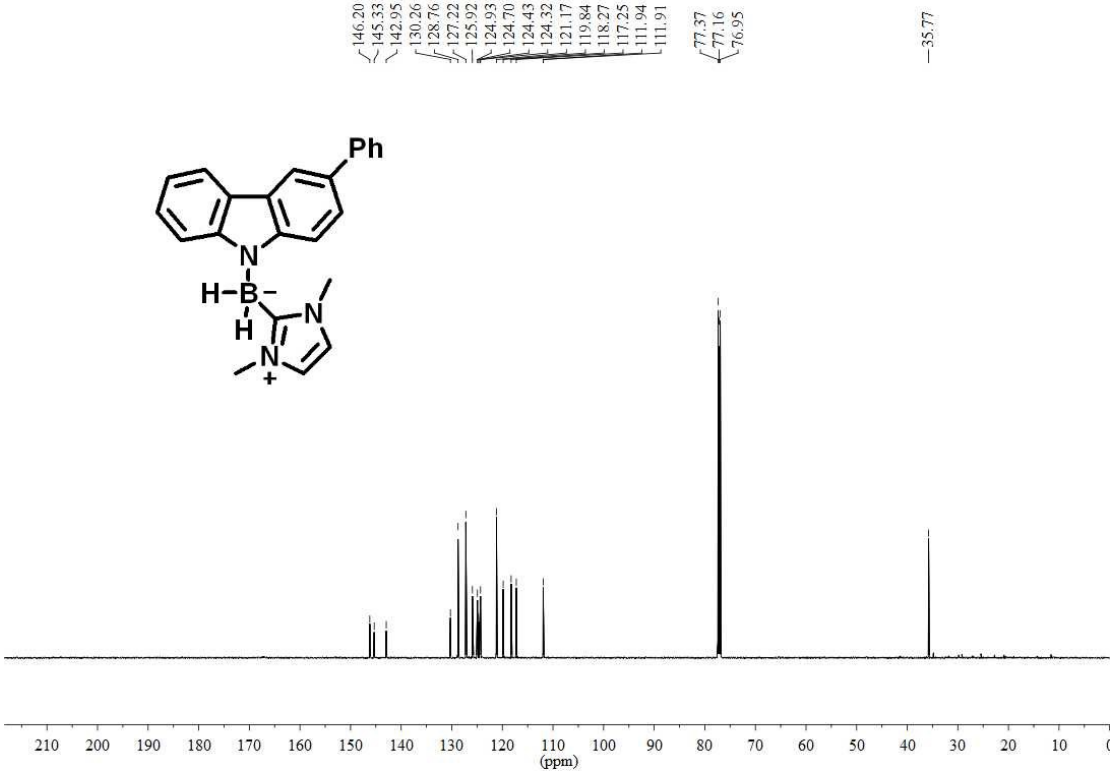
^{11}B NMR of product 3r in DMSO-d_6 (160 MHz)



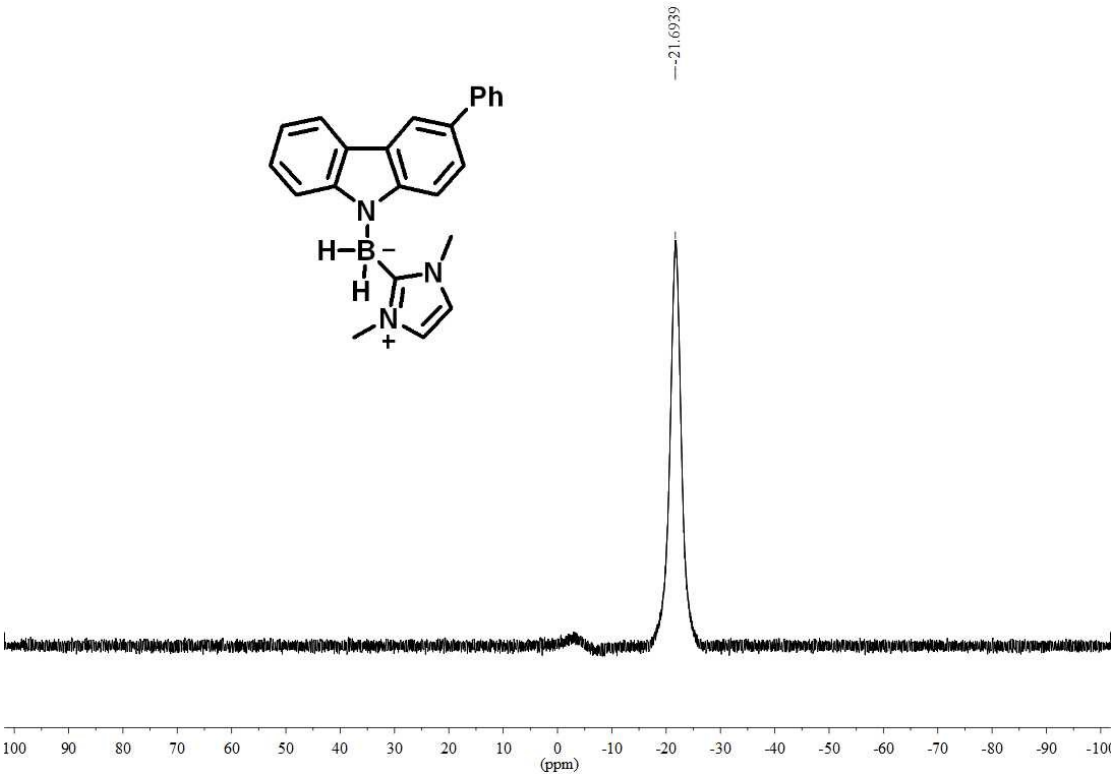
^{1}H NMR of product 3s in $CDCl_3$ (600 MHz)



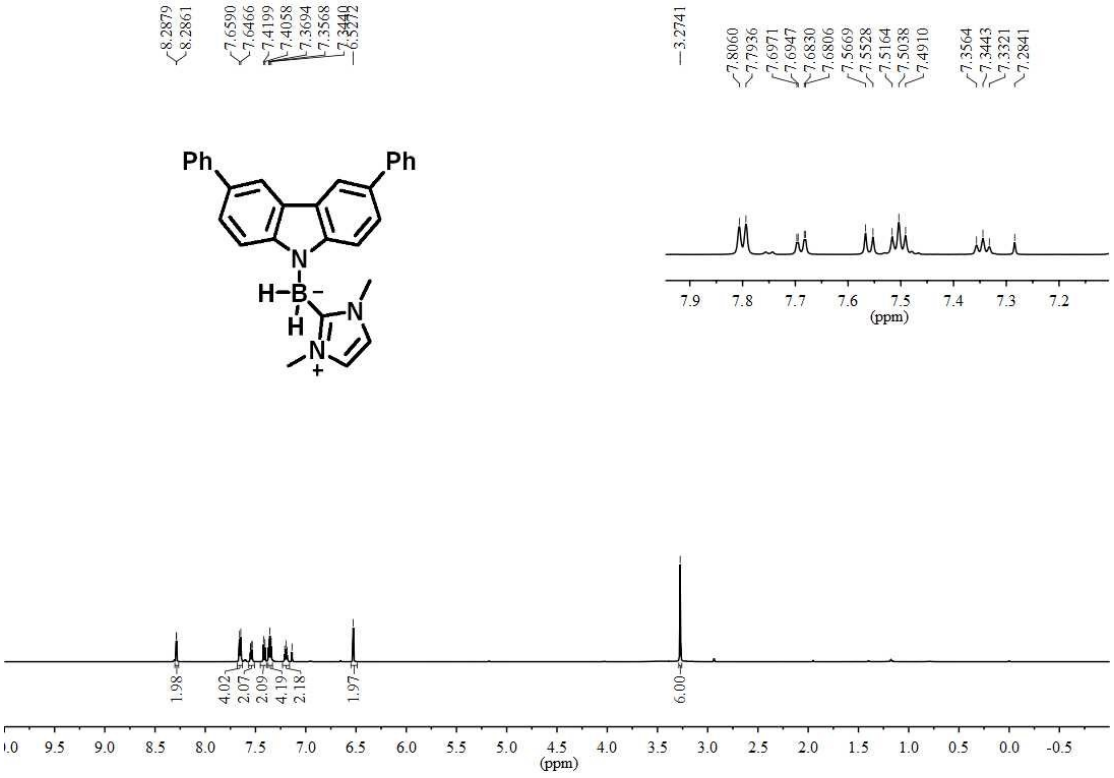
^{13}C NMR of product 3s in $CDCl_3$ (150 MHz)



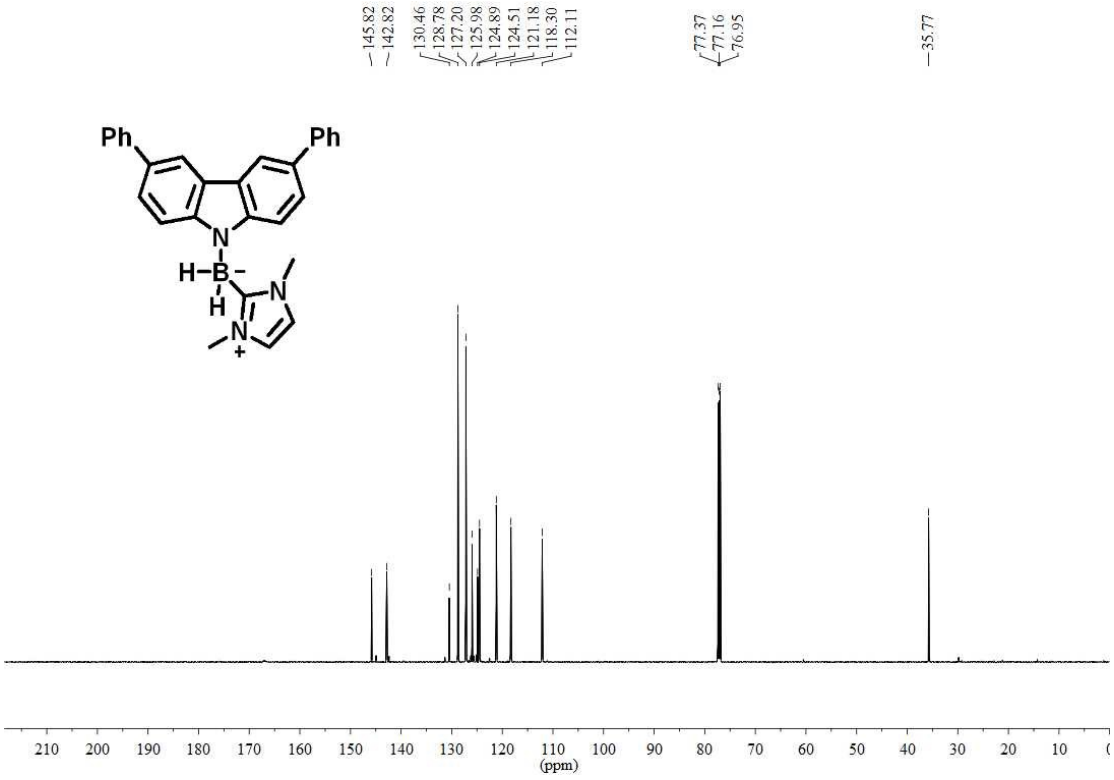
^{11}B NMR of product 3s in DMSO-d_6 (160 MHz)



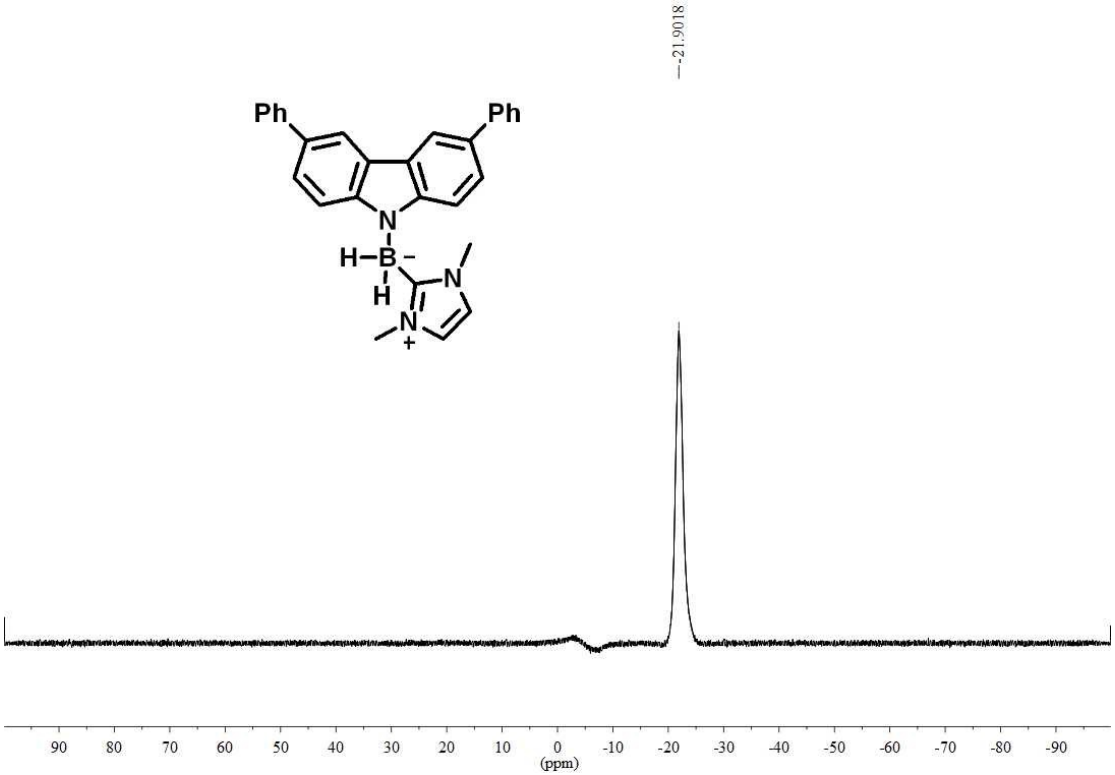
^{1}H NMR of product 3t in $CDCl_3$ (600 MHz)



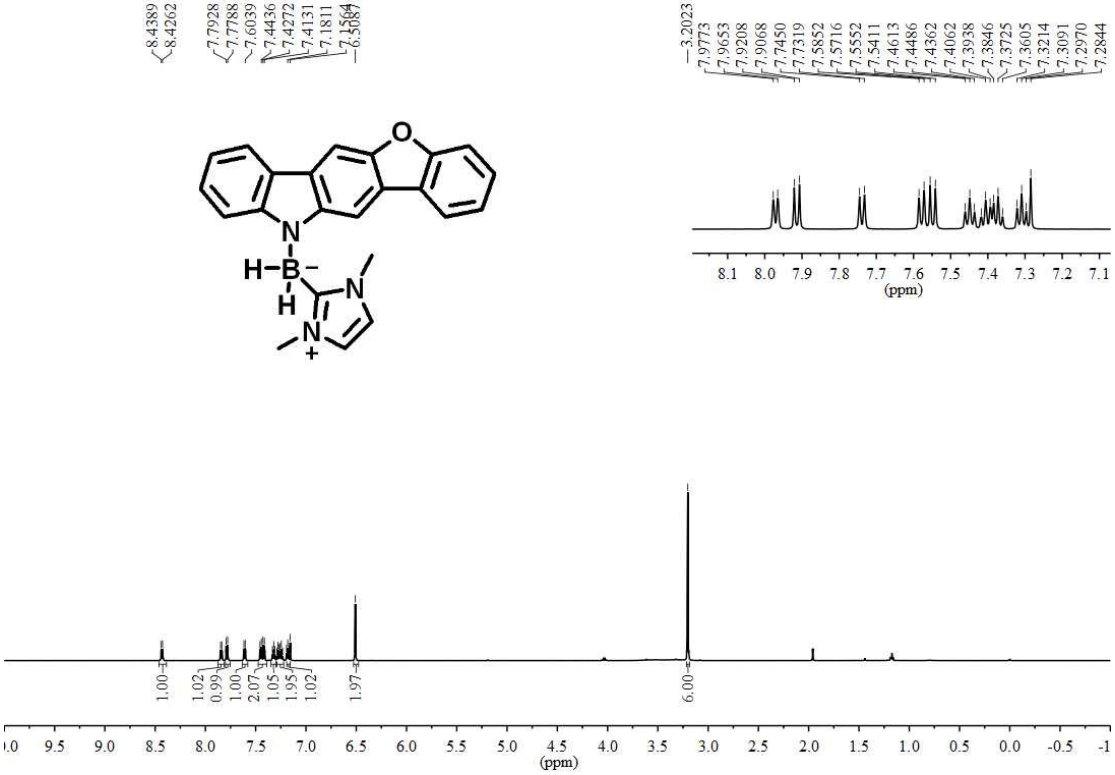
^{13}C NMR of product 3t in $CDCl_3$ (150 MHz)



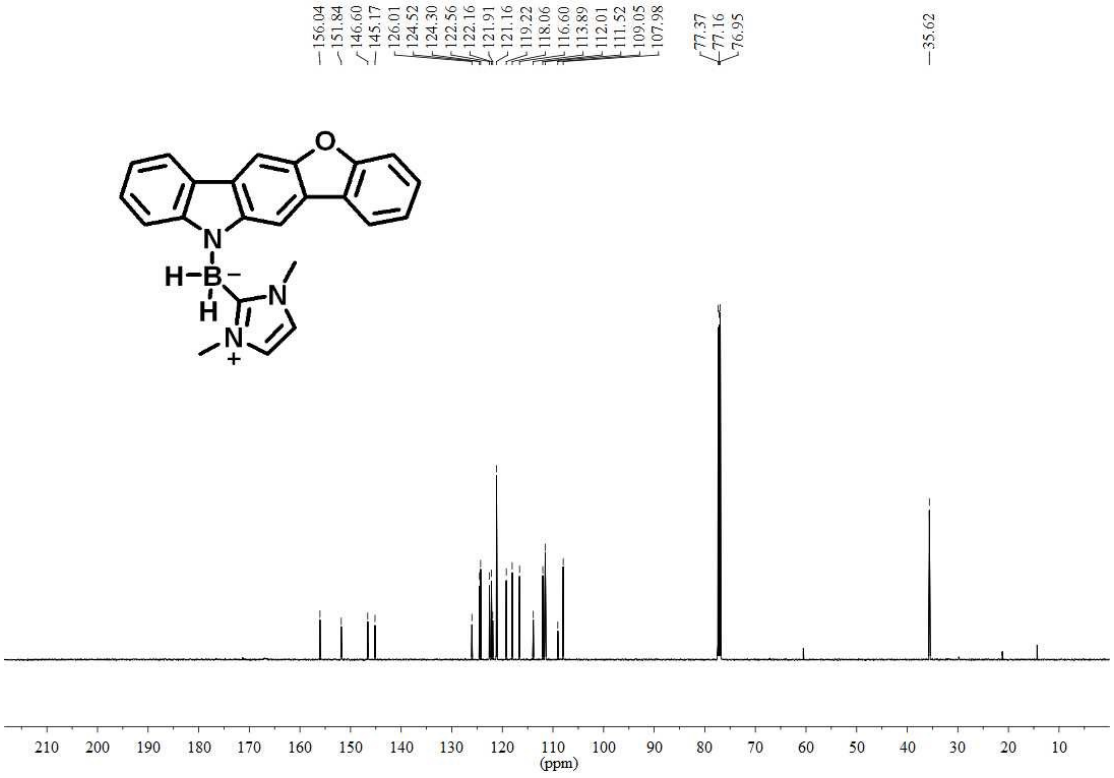
^{11}B NMR of product 3t in DMSO-d_6 (160 MHz)



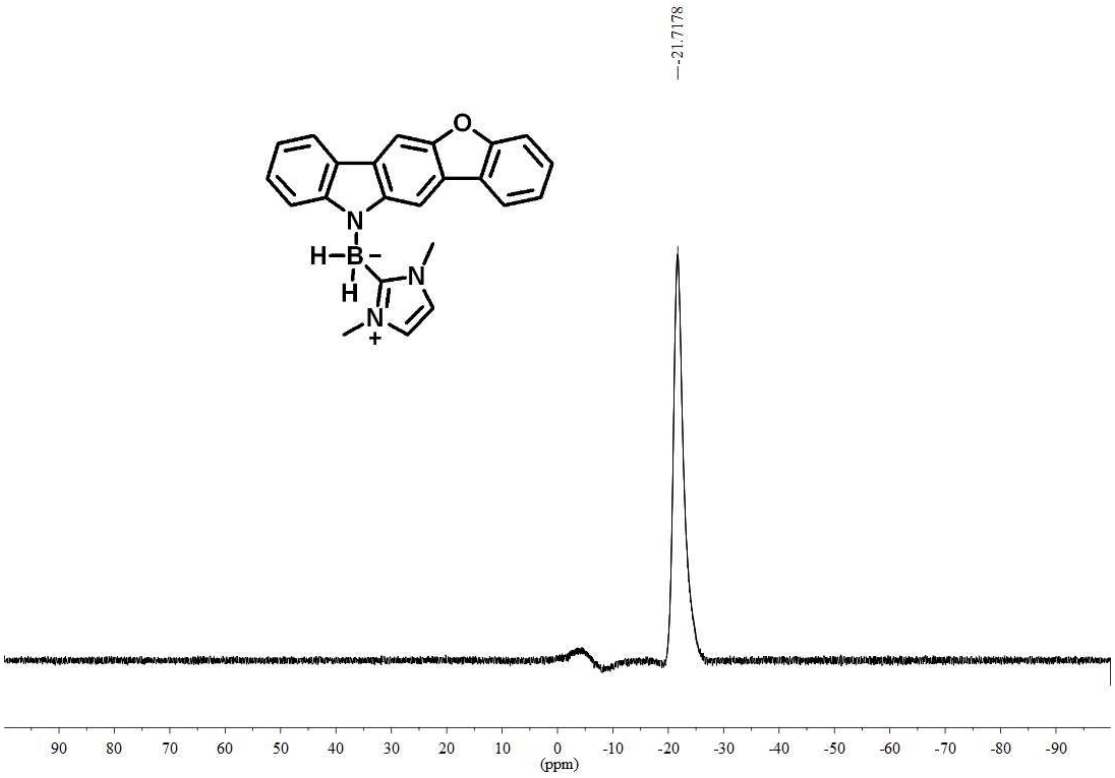
^{1}H NMR of product 3u in $CDCl_3$ (600 MHz)



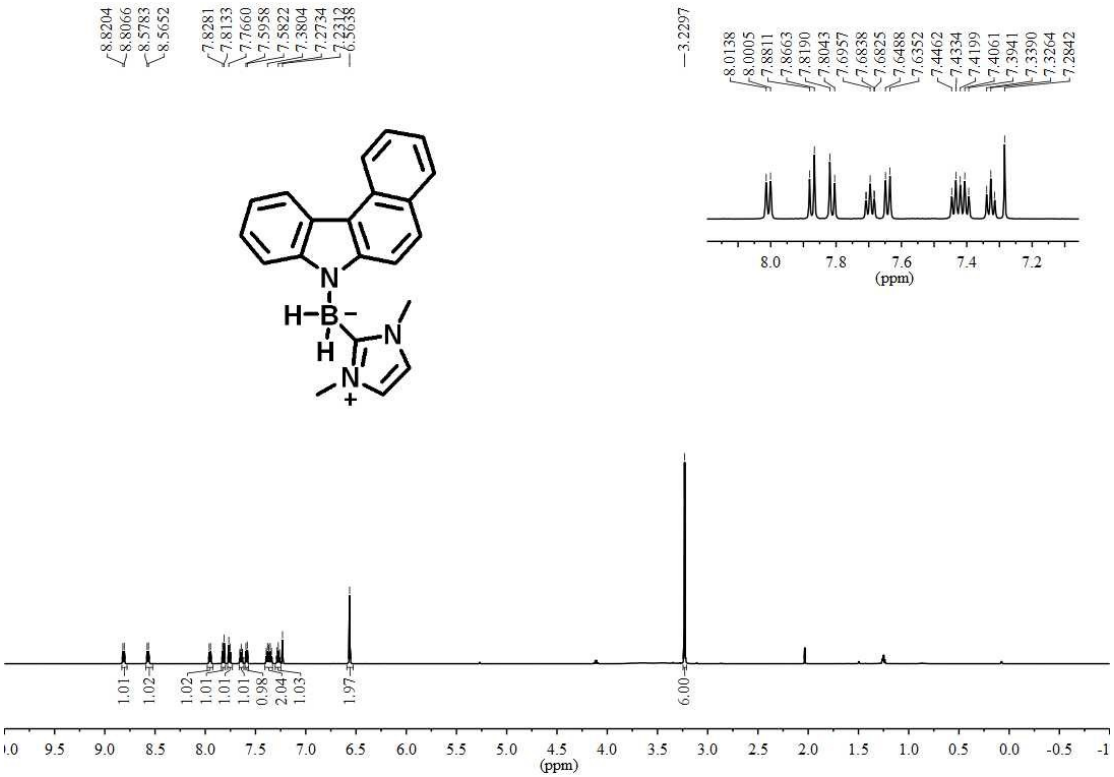
^{13}C NMR of product 3u in $CDCl_3$ (150 MHz)



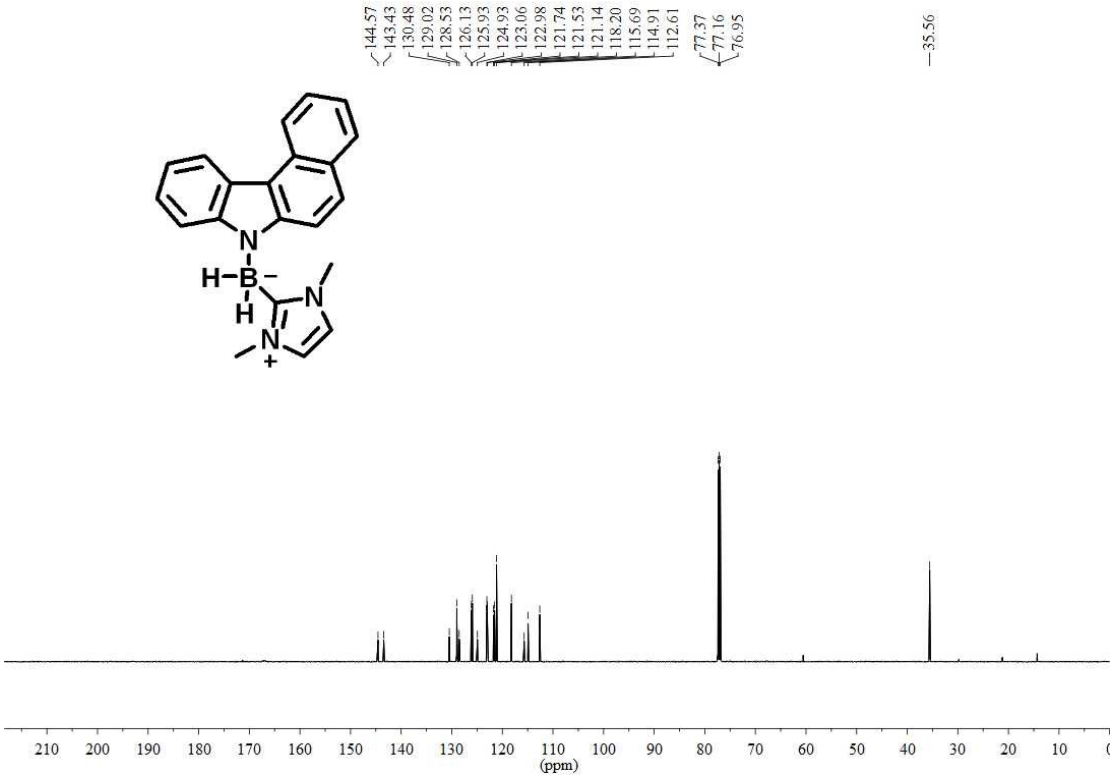
^{11}B NMR of product 3u in DMSO-d_6 (160 MHz)



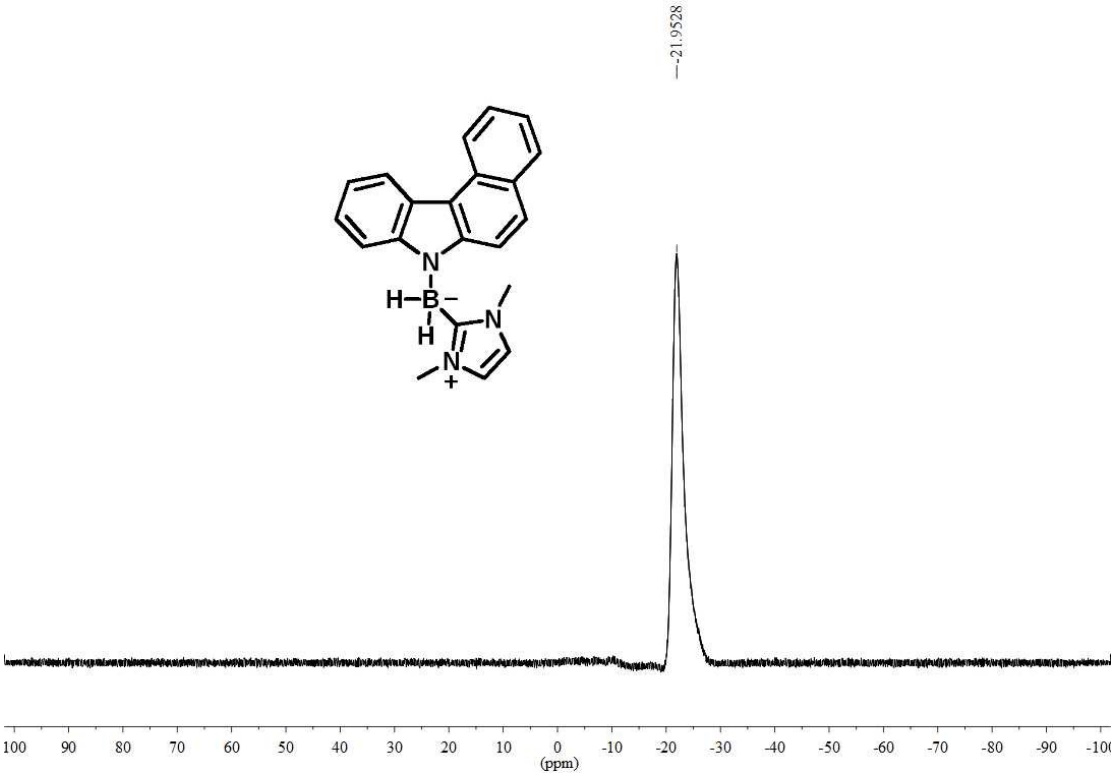
^{1}H NMR of product 3v in $CDCl_3$ (600 MHz)



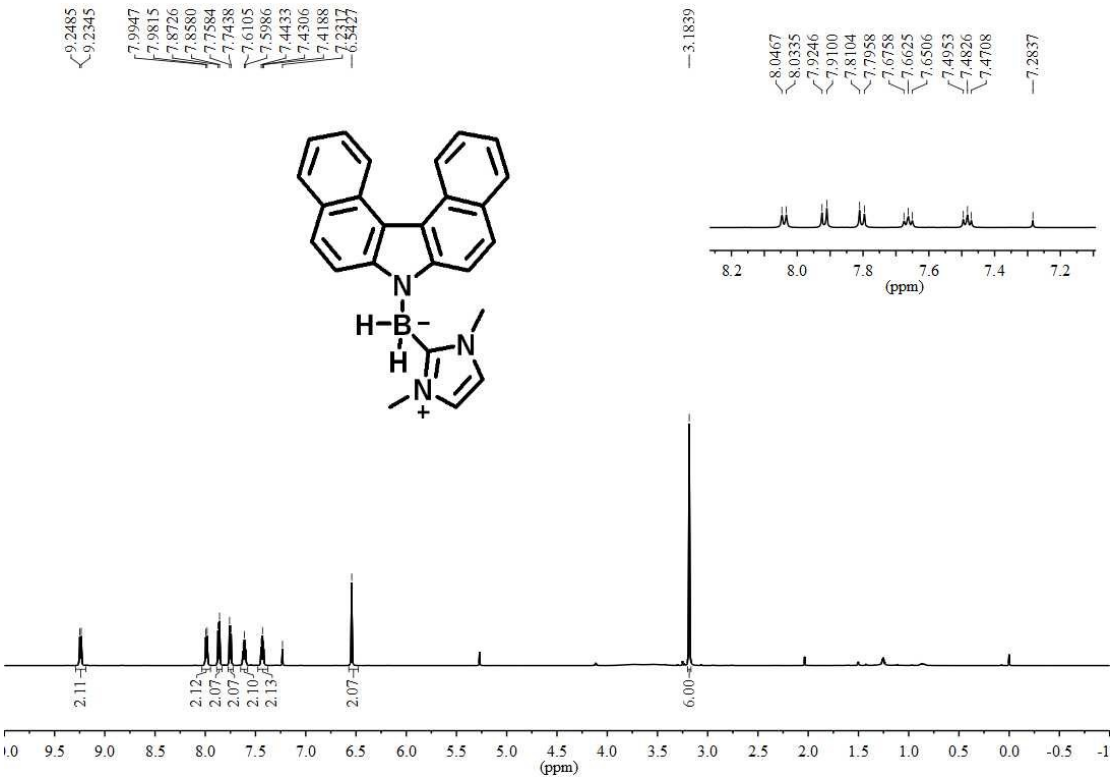
^{13}C NMR of product 3v in $CDCl_3$ (150 MHz)



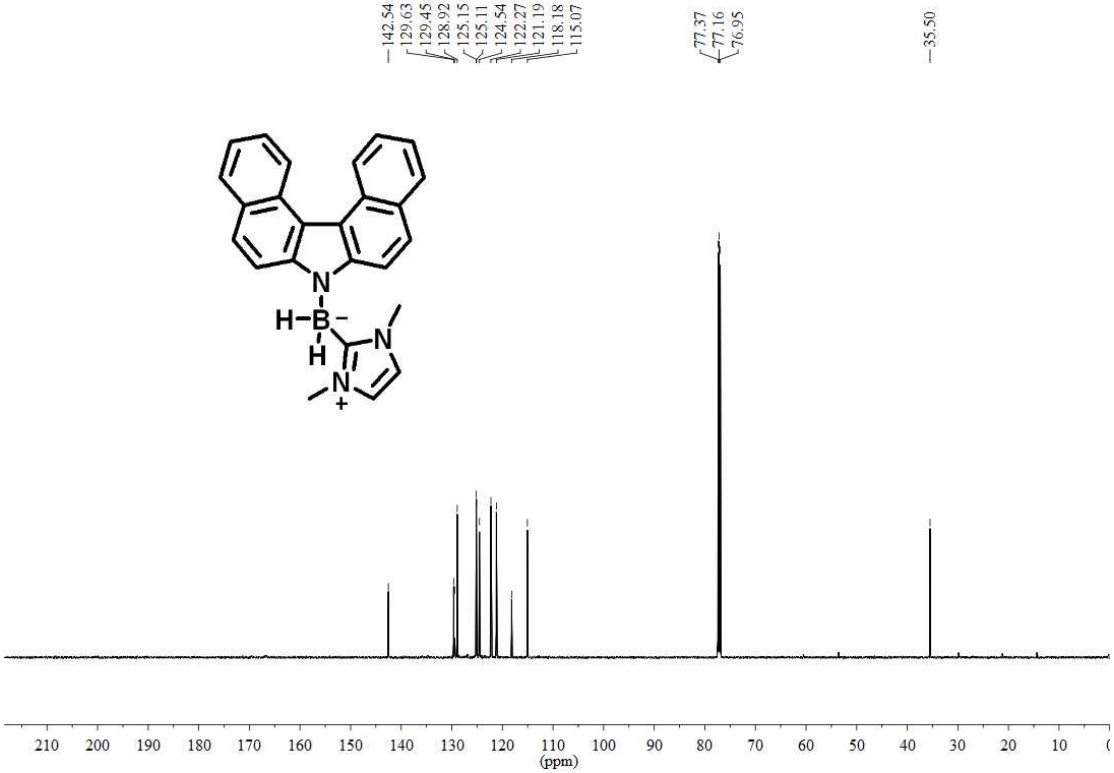
^{11}B NMR of product 3v in DMSO-d_6 (160 MHz)



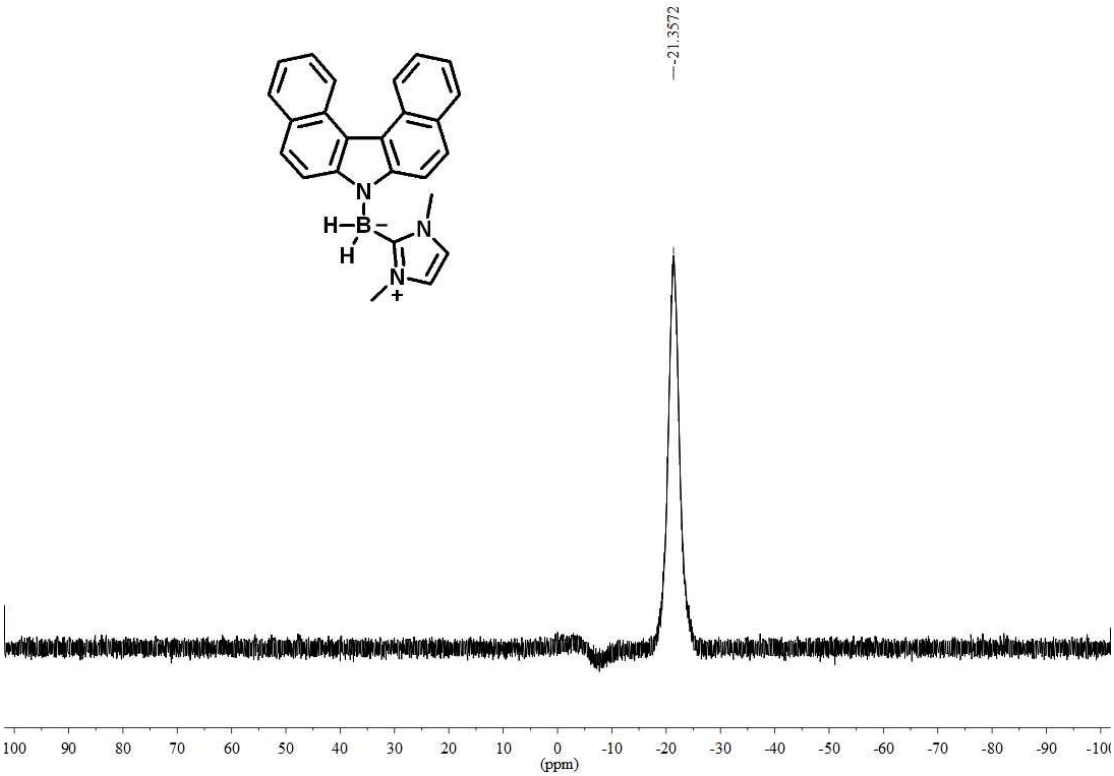
^{1}H NMR of product 3w in $CDCl_3$ (600 MHz)



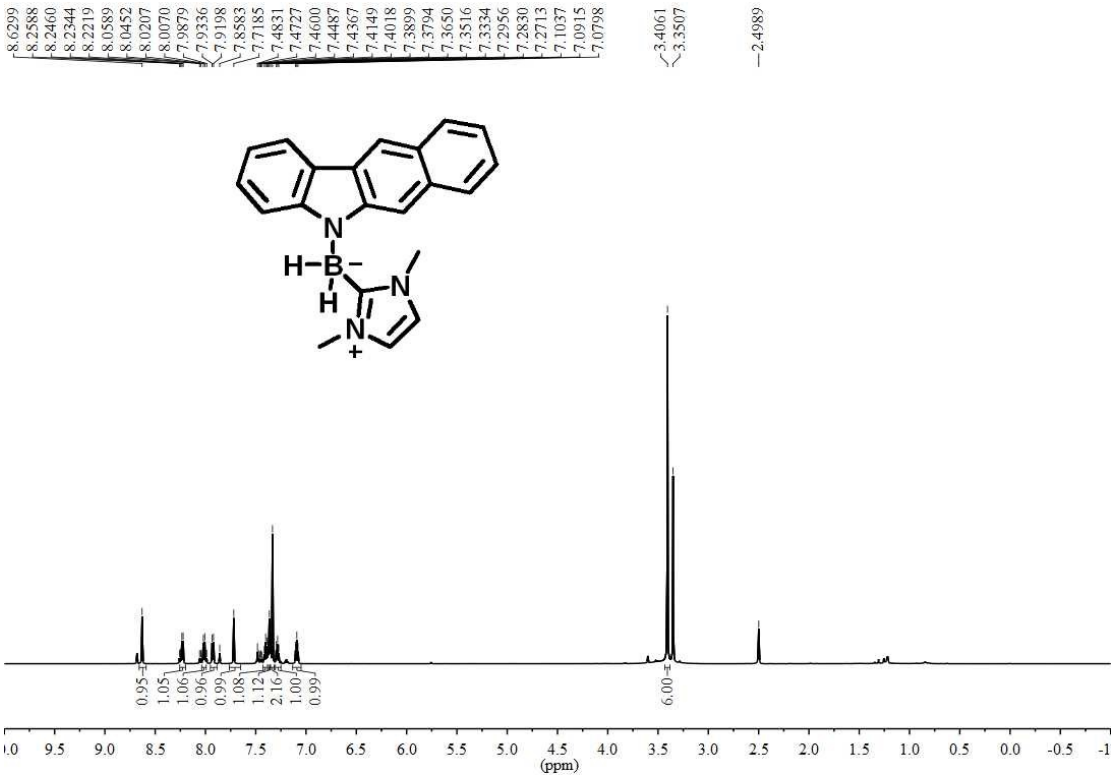
^{13}C NMR of product 3w in $CDCl_3$ (150 MHz)



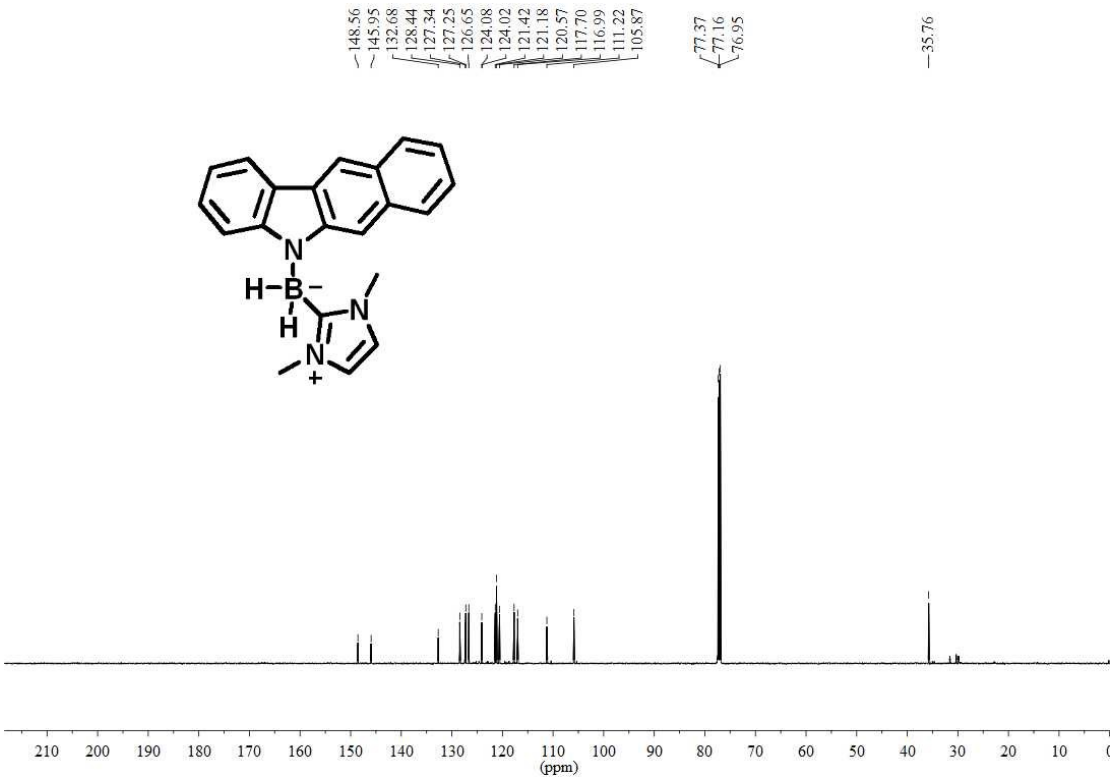
^{11}B NMR of product 3w in DMSO-d_6 (160 MHz)



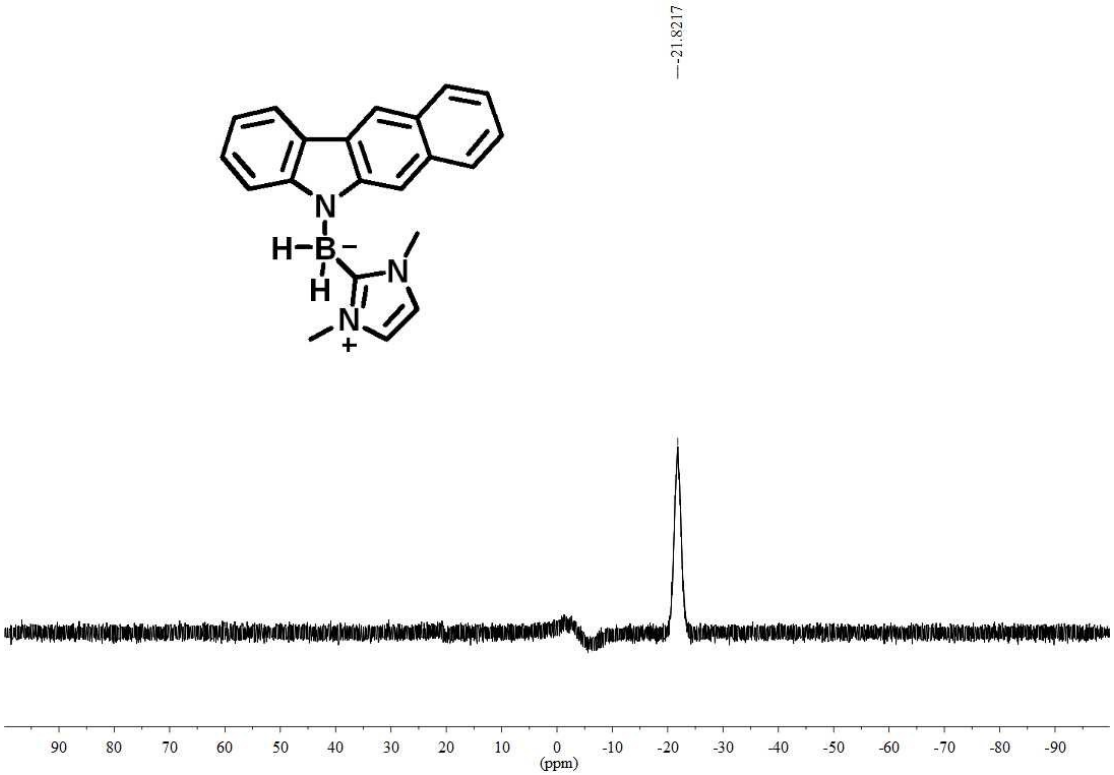
^{1}H NMR of product 3x in DMSO-d_6 (600 MHz)



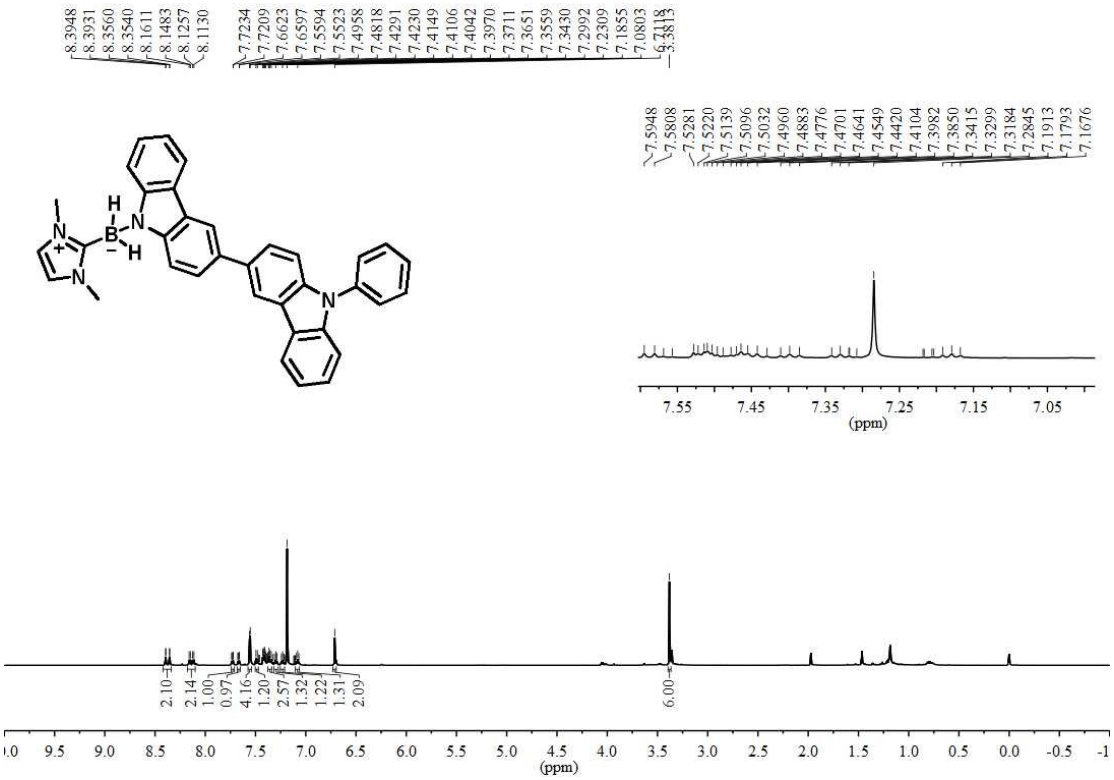
^{13}C NMR of product 3x in $CDCl_3$ (150 MHz)



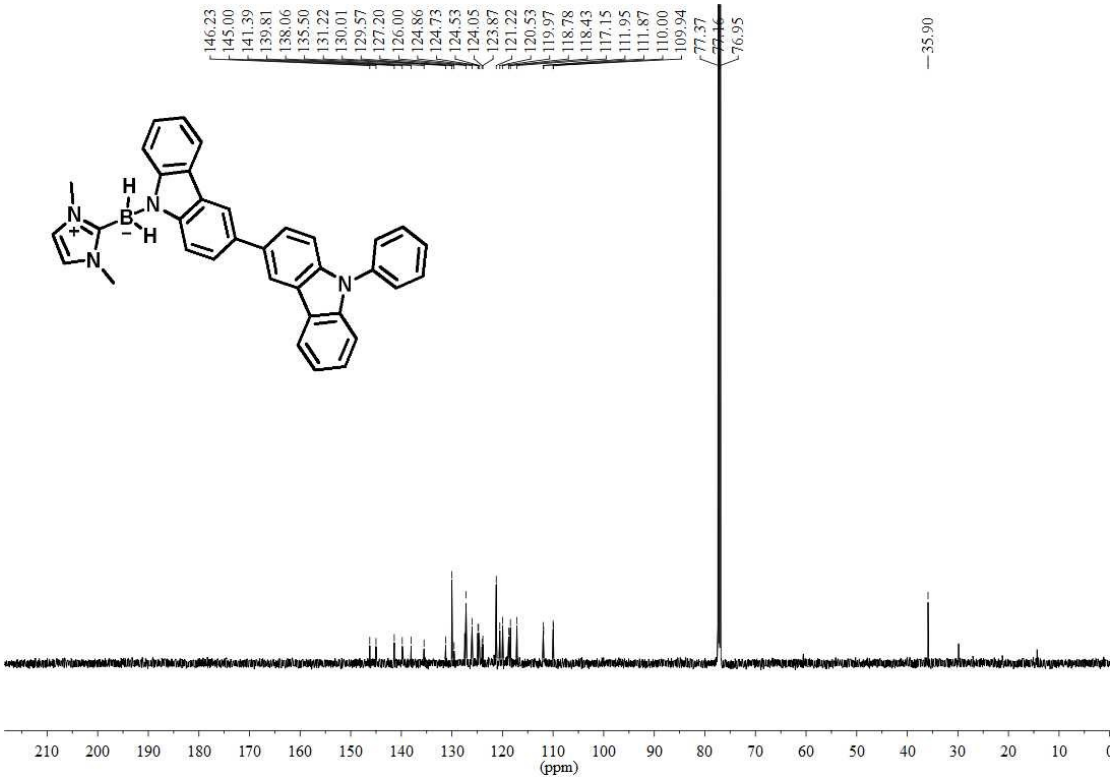
^{11}B NMR of product 3x in DMSO-d_6 (160 MHz)



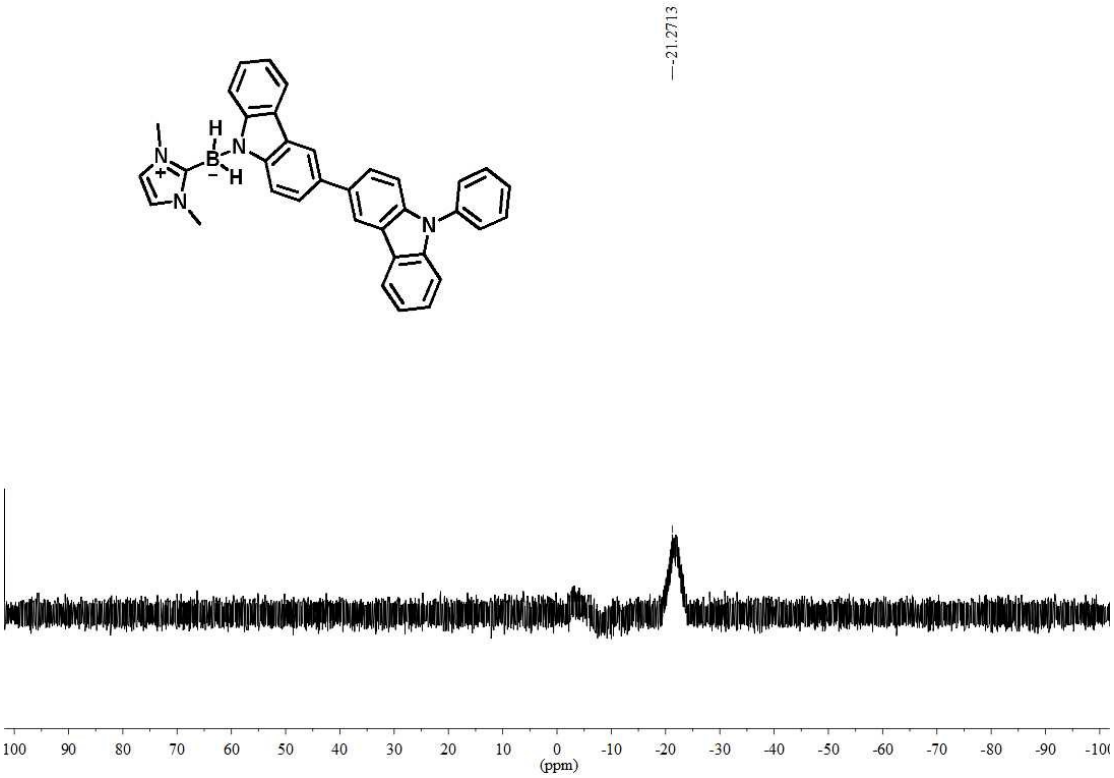
^{1}H NMR of product 3y in $CDCl_3$ (600 MHz)



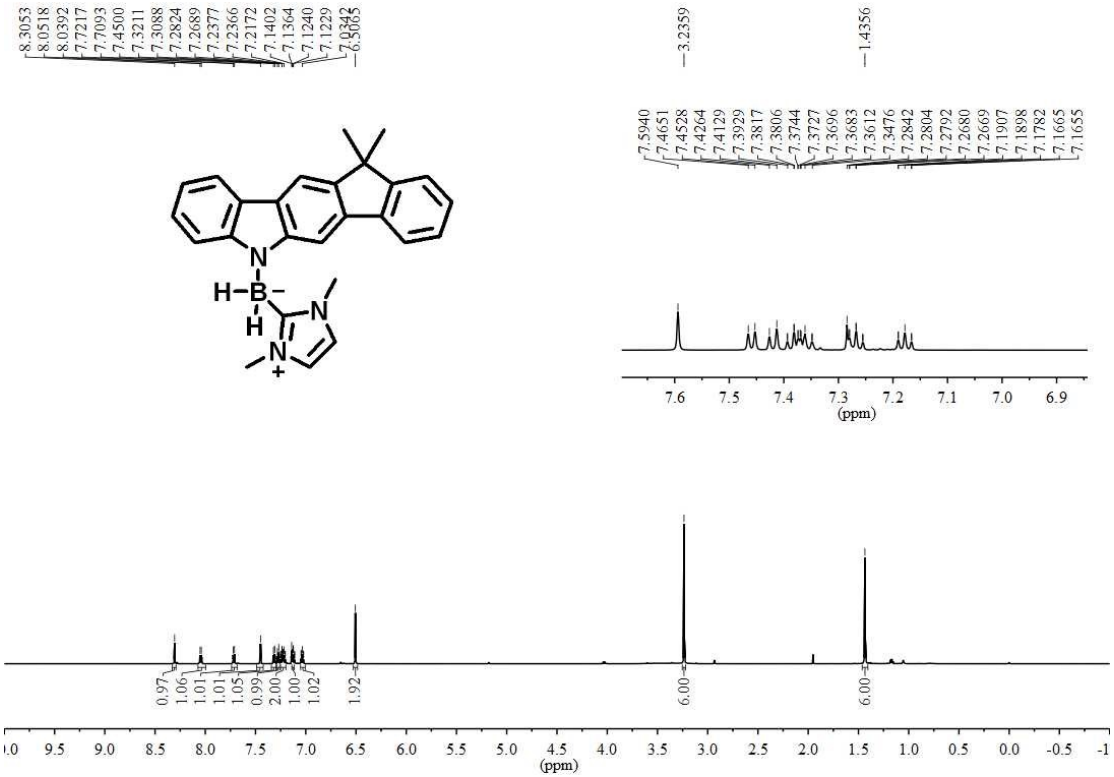
^{13}C NMR of product 3y in $CDCl_3$ (150 MHz)



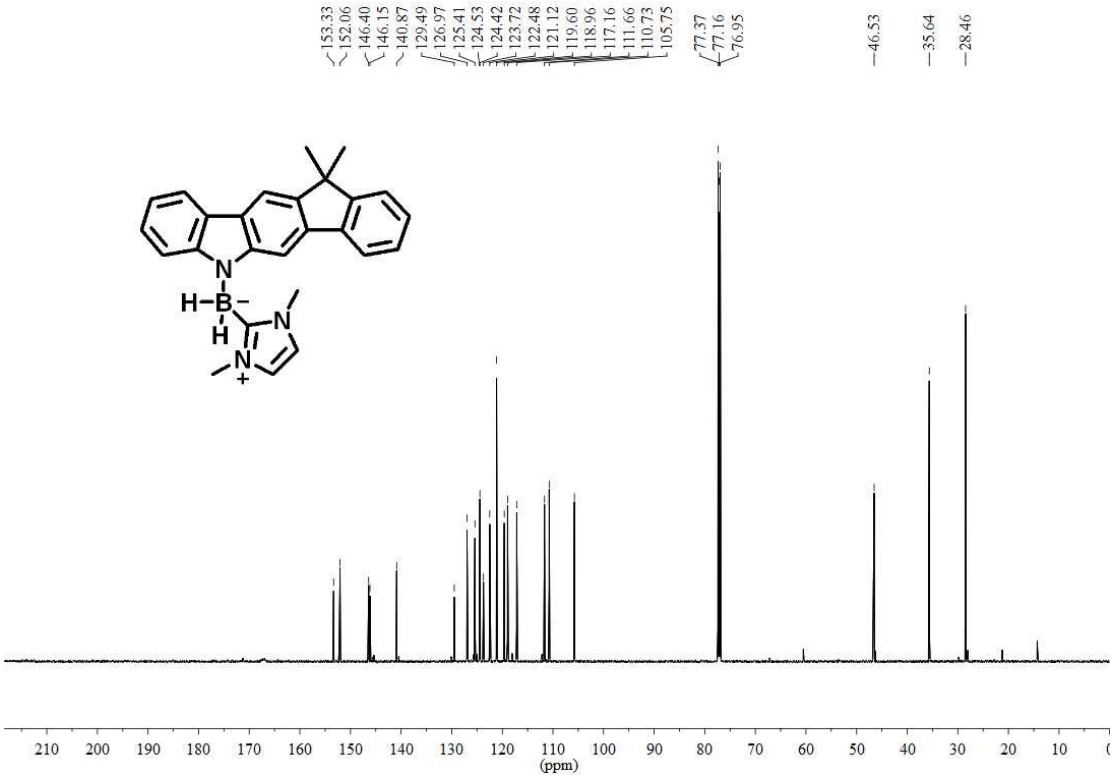
^{11}B NMR of product 3y in DMSO-d_6 (160 MHz)



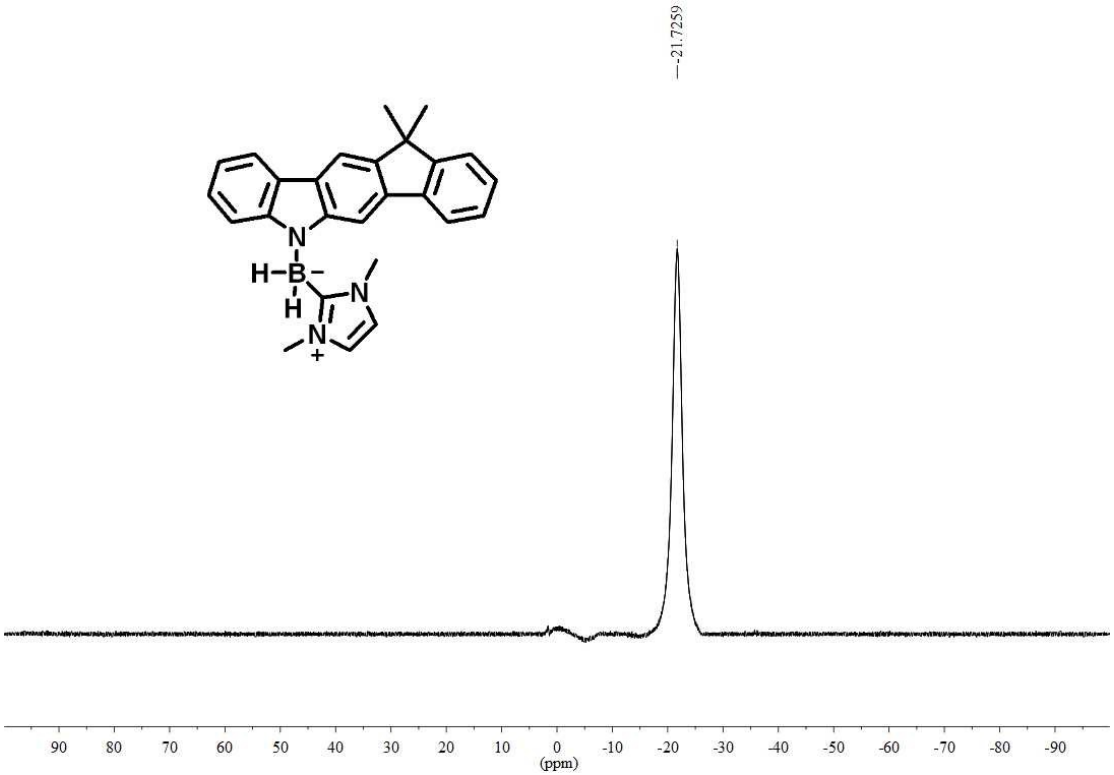
^{1}H NMR of product 3z in $CDCl_3$ (600 MHz)



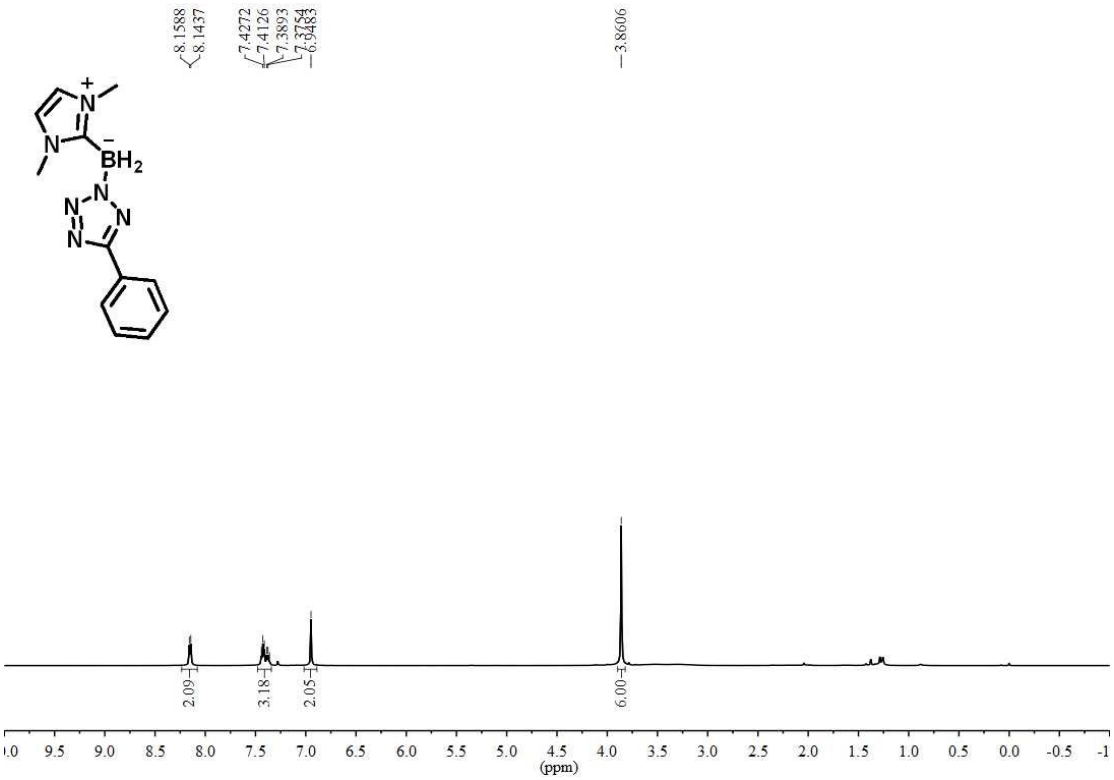
^{13}C NMR of product 3z in $CDCl_3$ (150 MHz)



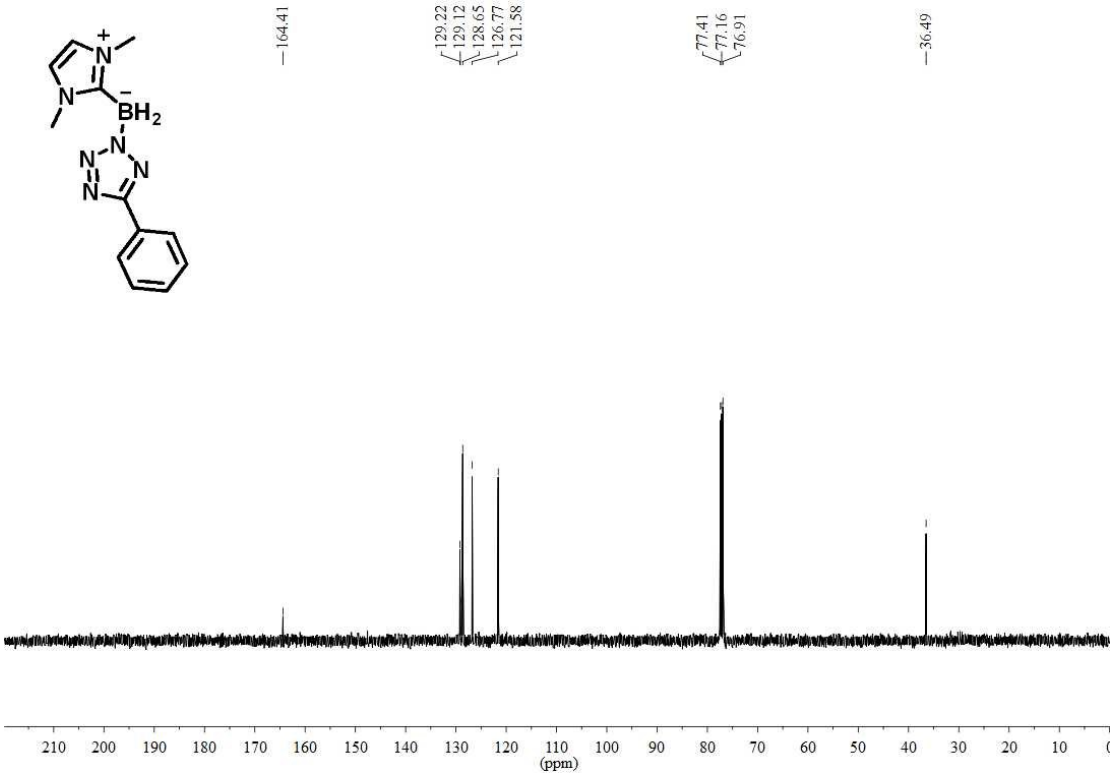
^{11}B NMR of product 3z in DMSO-d_6 (160 MHz)



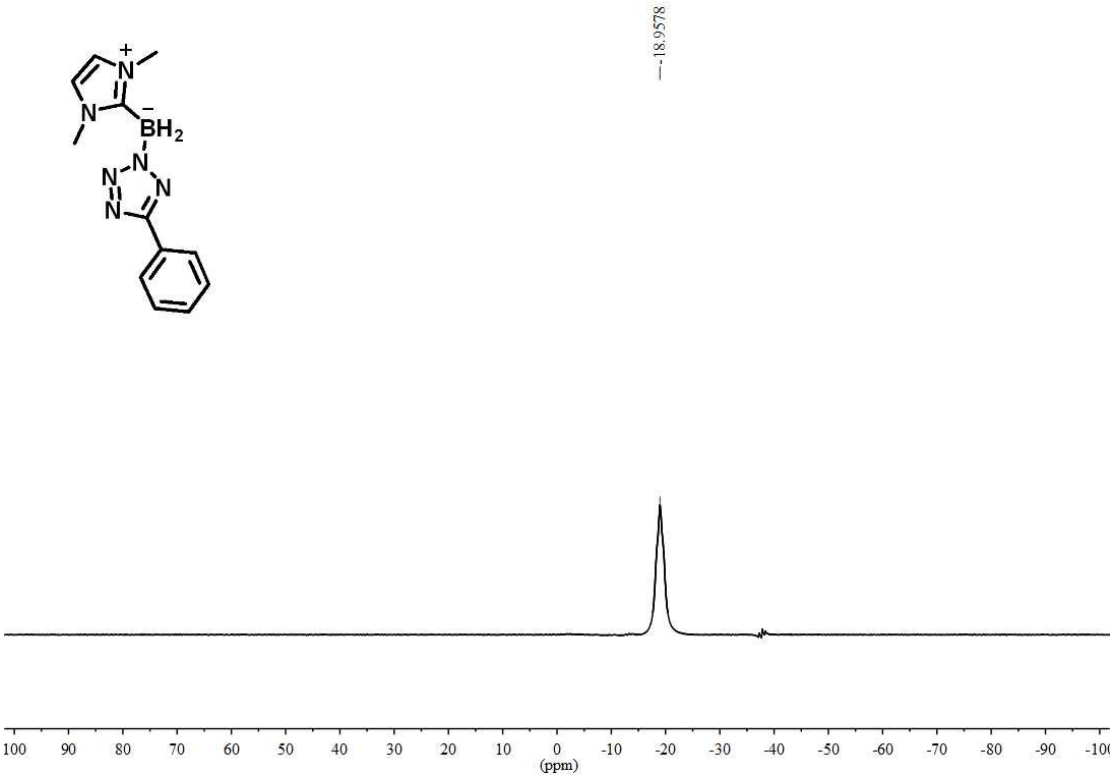
^{1}H NMR of product 5a in $CDCl_3$ (500 MHz)



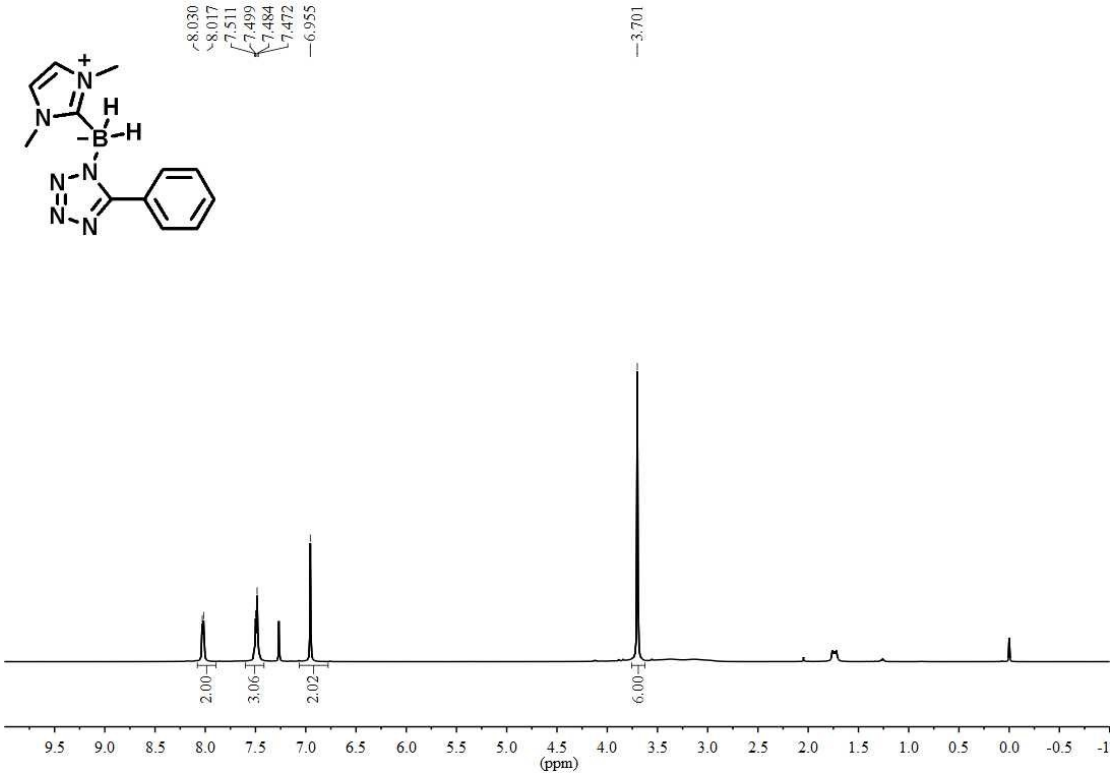
^{13}C NMR of product 5a in $CDCl_3$ (125 MHz)



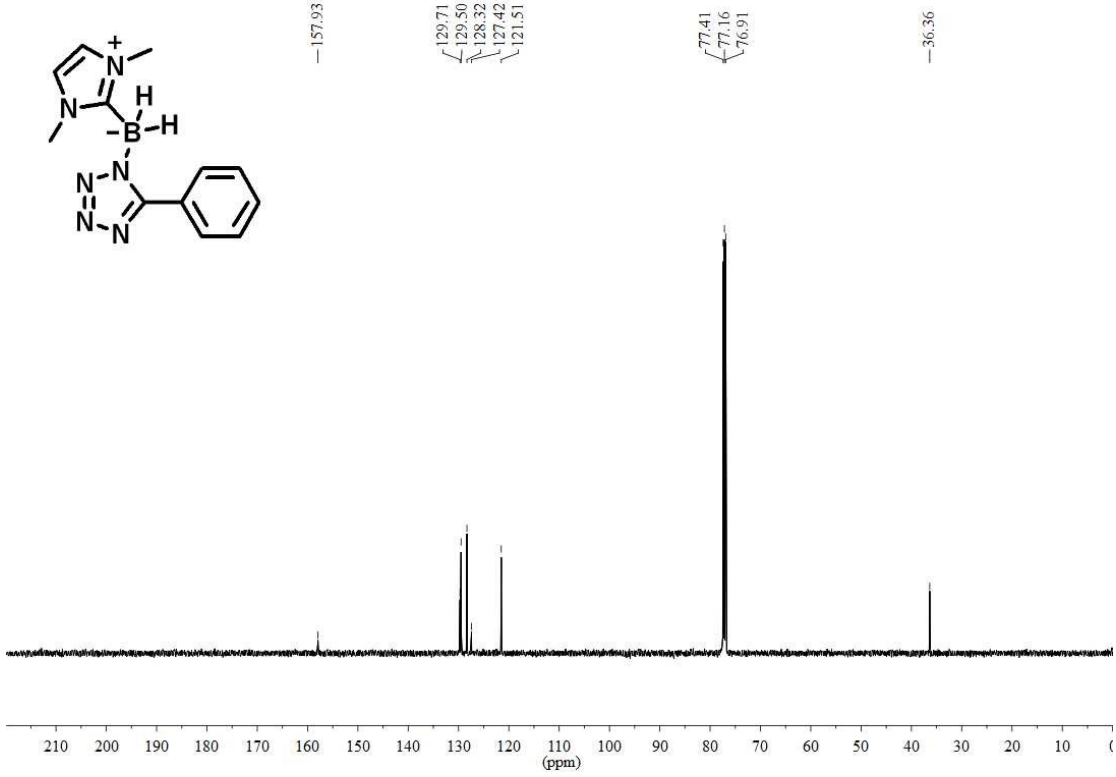
^{11}B NMR of product 5a in $CDCl_3$ (160 MHz)



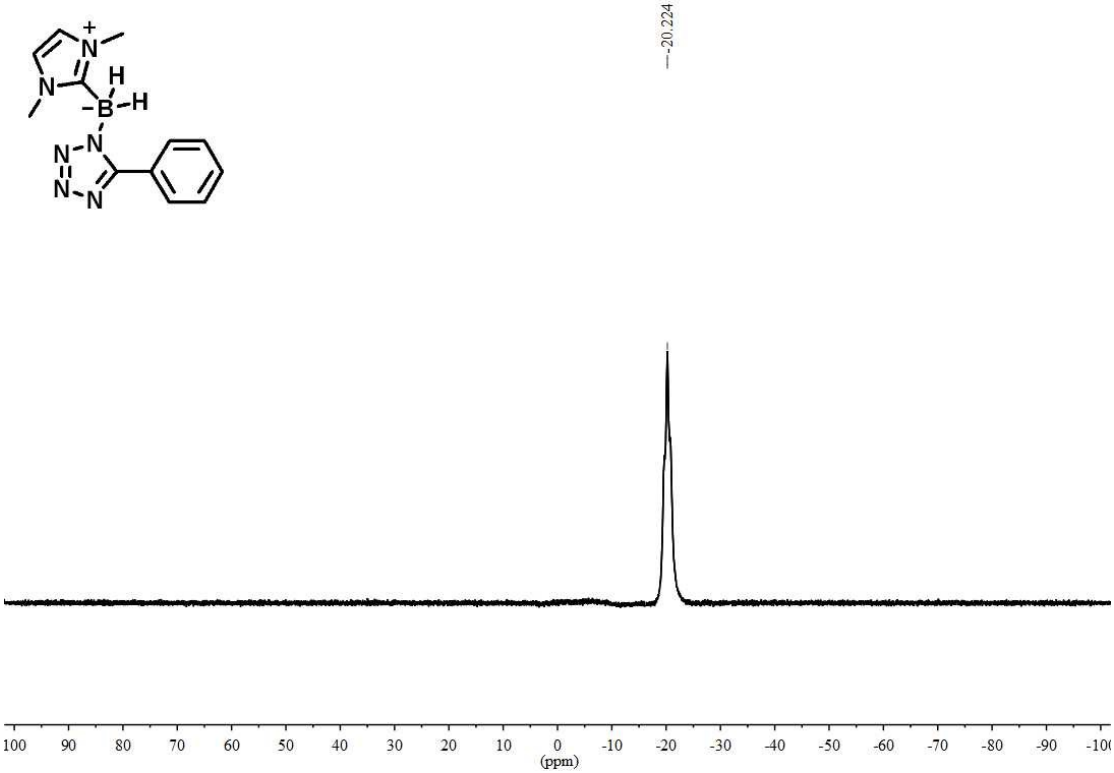
^{1}H NMR of product 5a' in $CDCl_3$ (500 MHz)



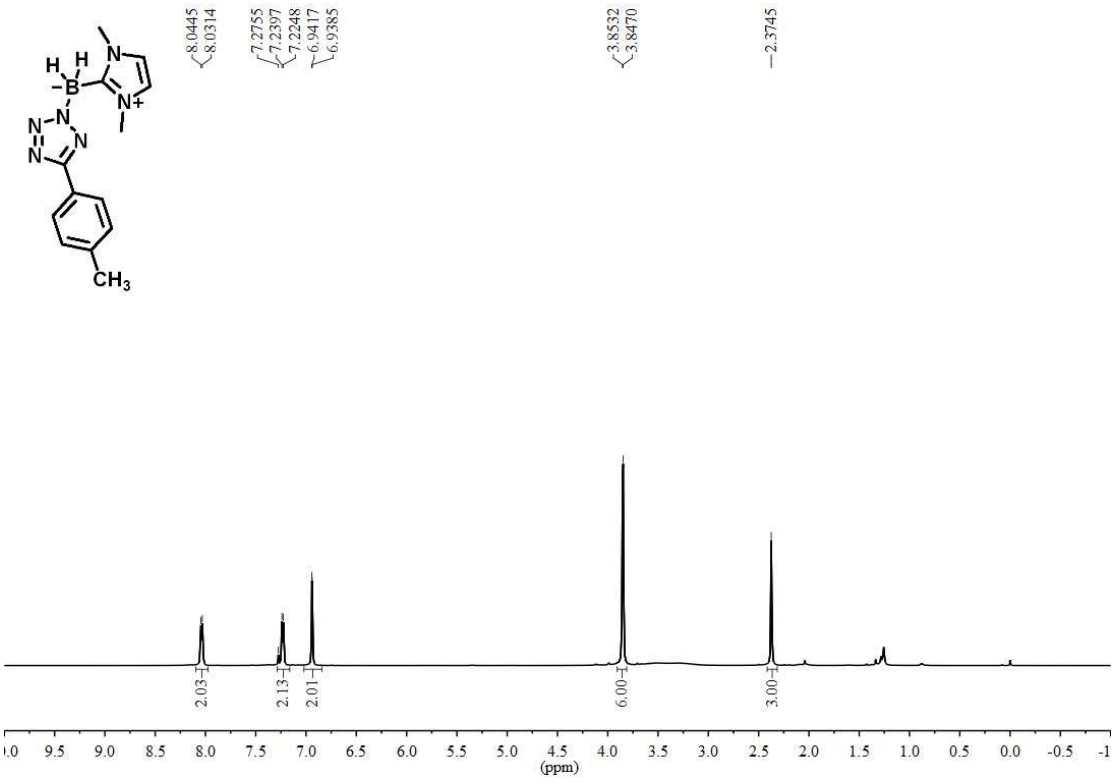
^{13}C NMR of product 5a' in $CDCl_3$ (125 MHz)



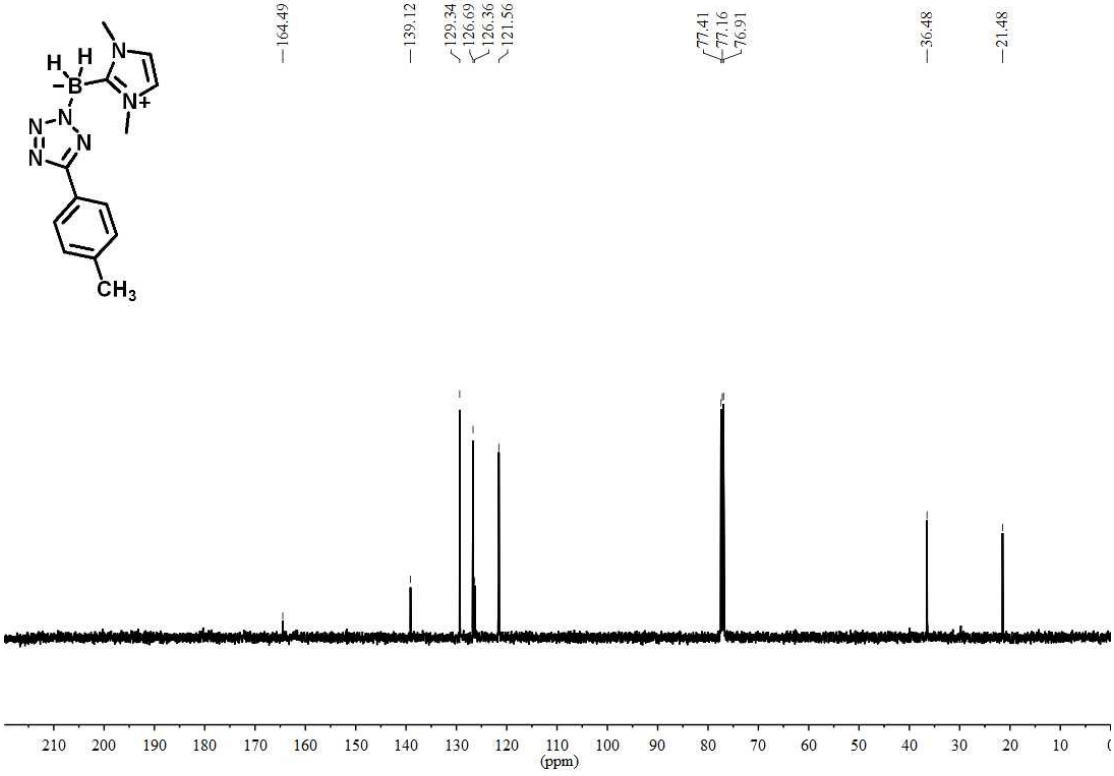
^{11}B NMR of product 5a' in $CDCl_3$ (160 MHz)



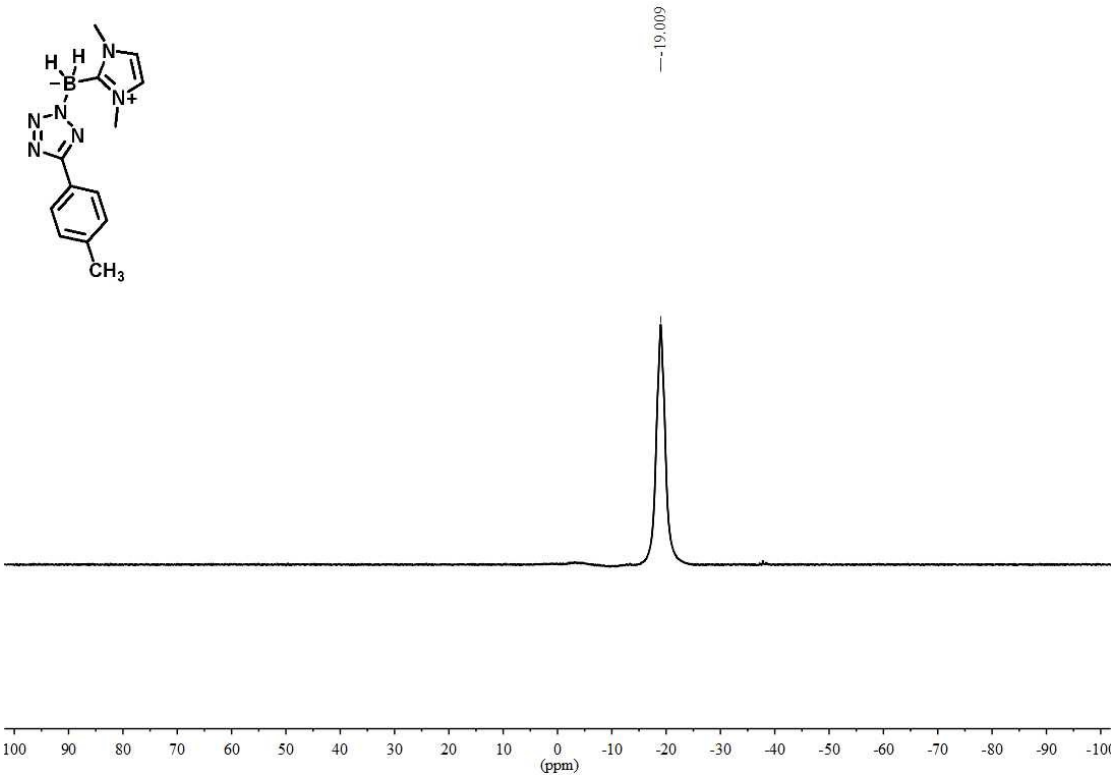
^{1}H NMR of product 5b in $CDCl_3$ (500 MHz)



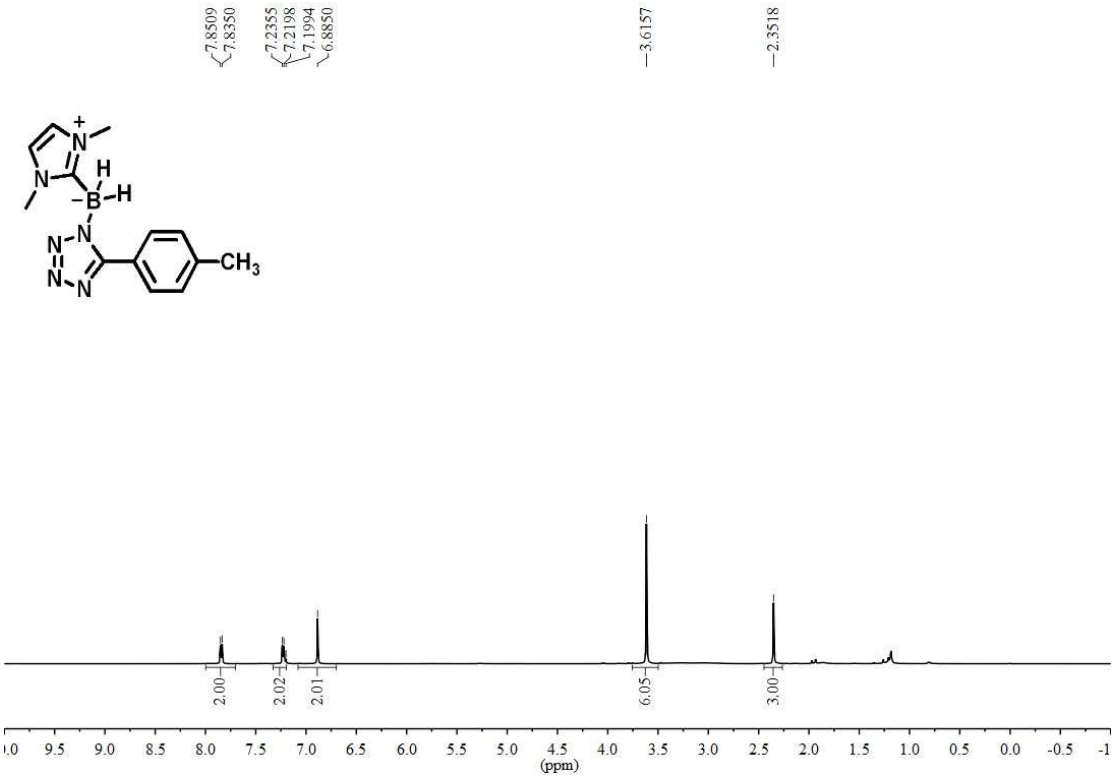
^{13}C NMR of product 5b in $CDCl_3$ (125 MHz)



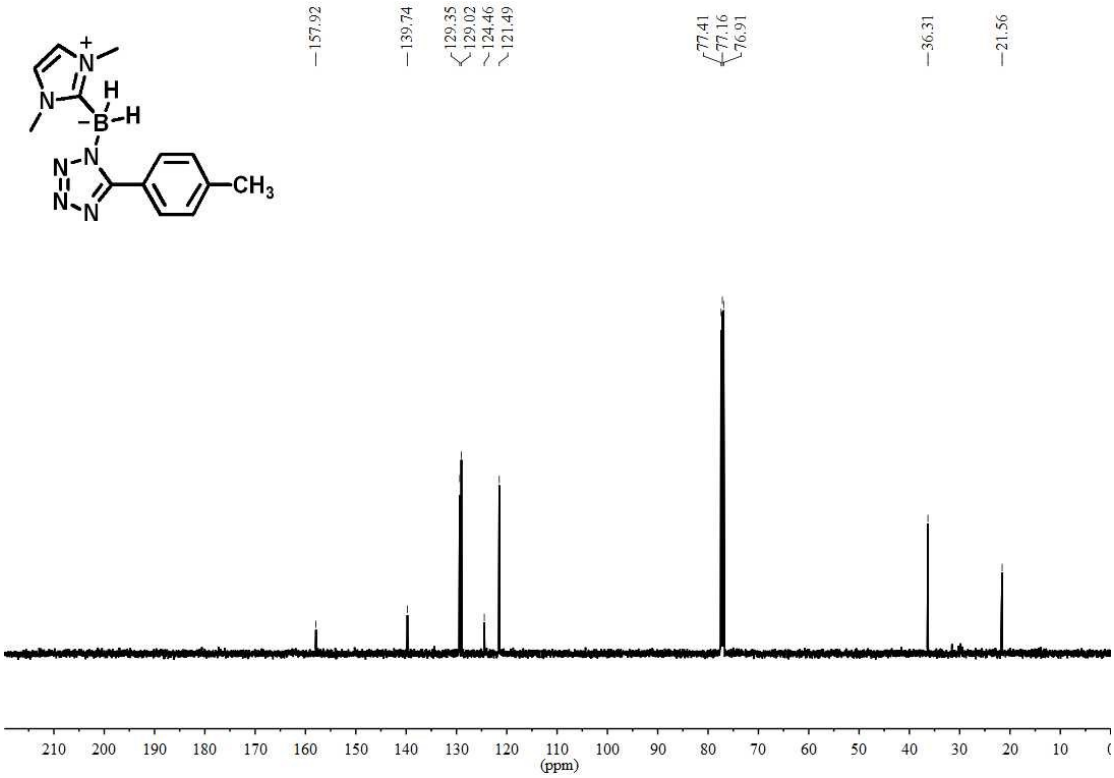
^{11}B NMR of product 5b in $CDCl_3$ (160 MHz)



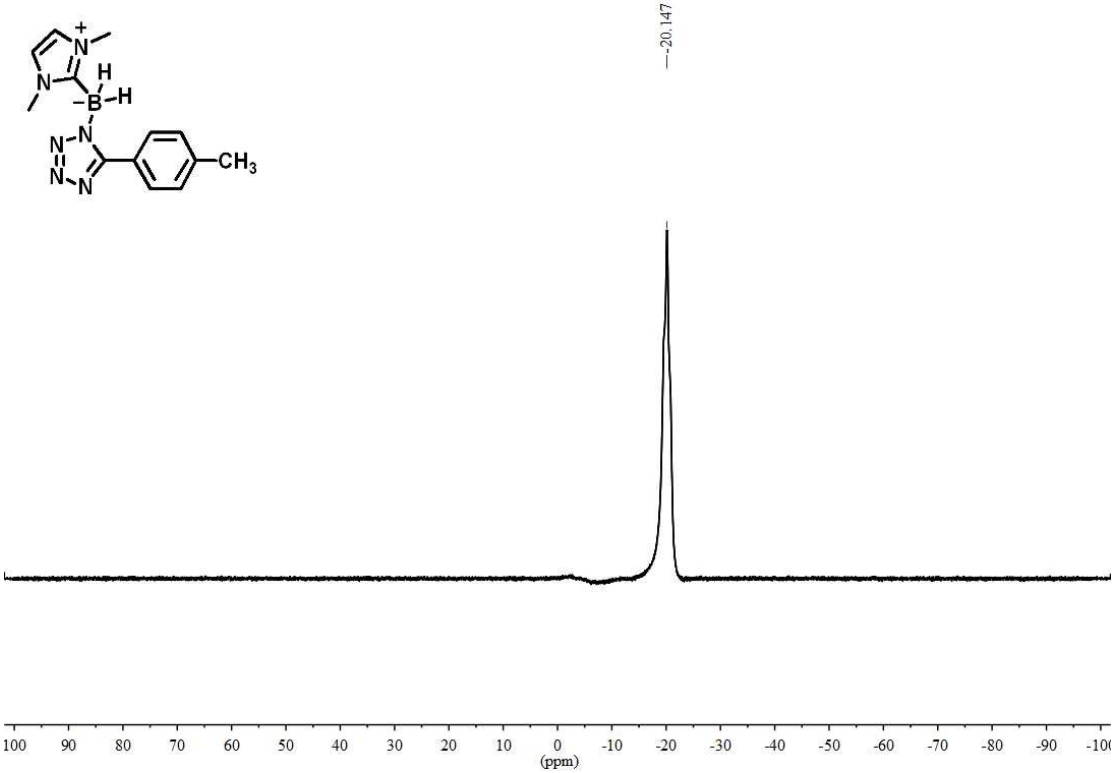
^{1}H NMR of product 5b' in $CDCl_3$ (500 MHz)



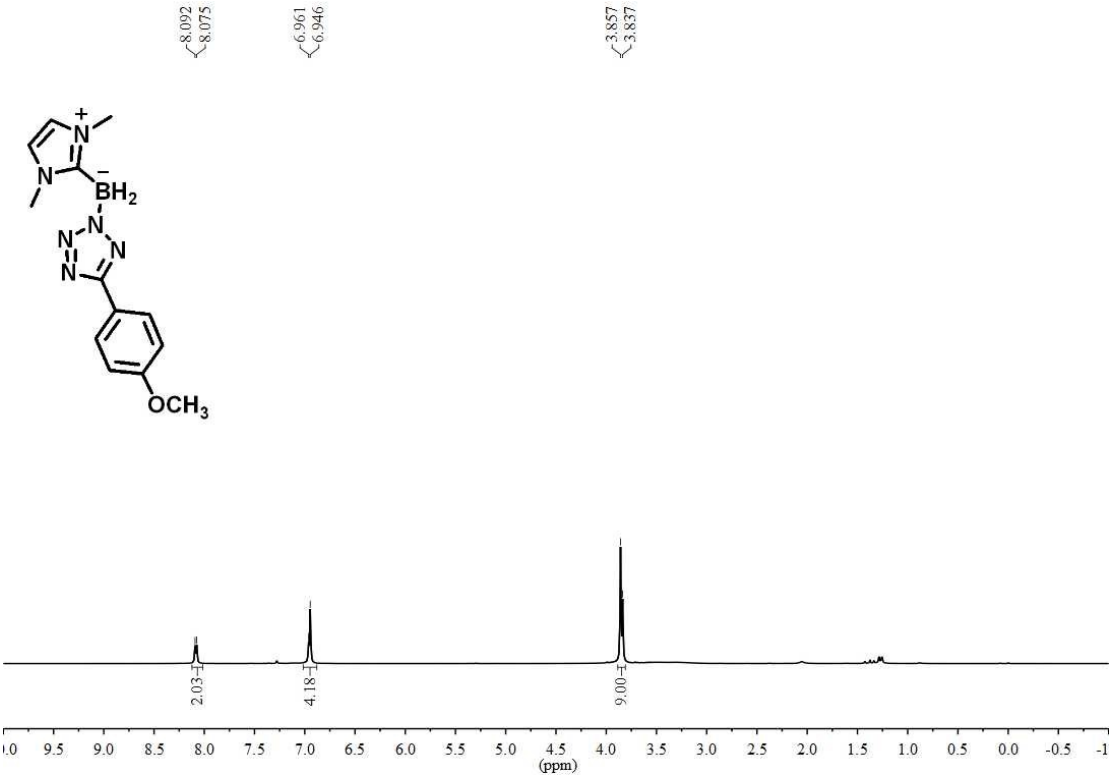
^{13}C NMR of product 5b' in $CDCl_3$ (125 MHz)



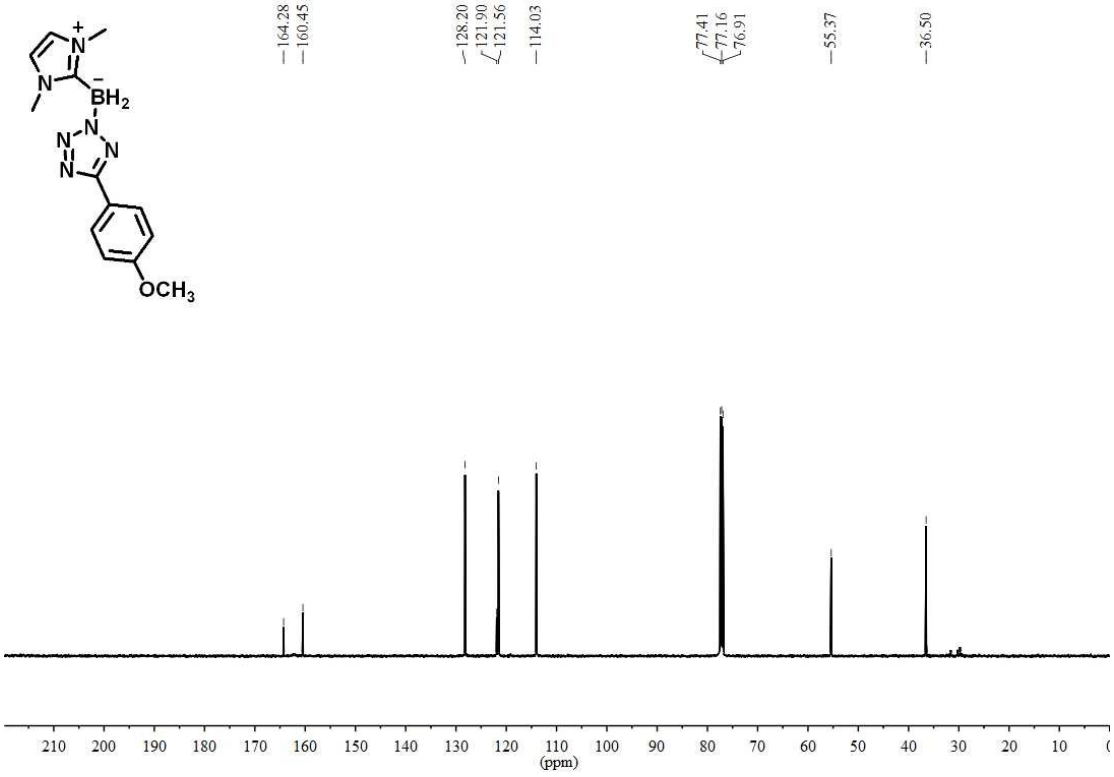
^{11}B NMR of product 5b' in $CDCl_3$ (160 MHz)



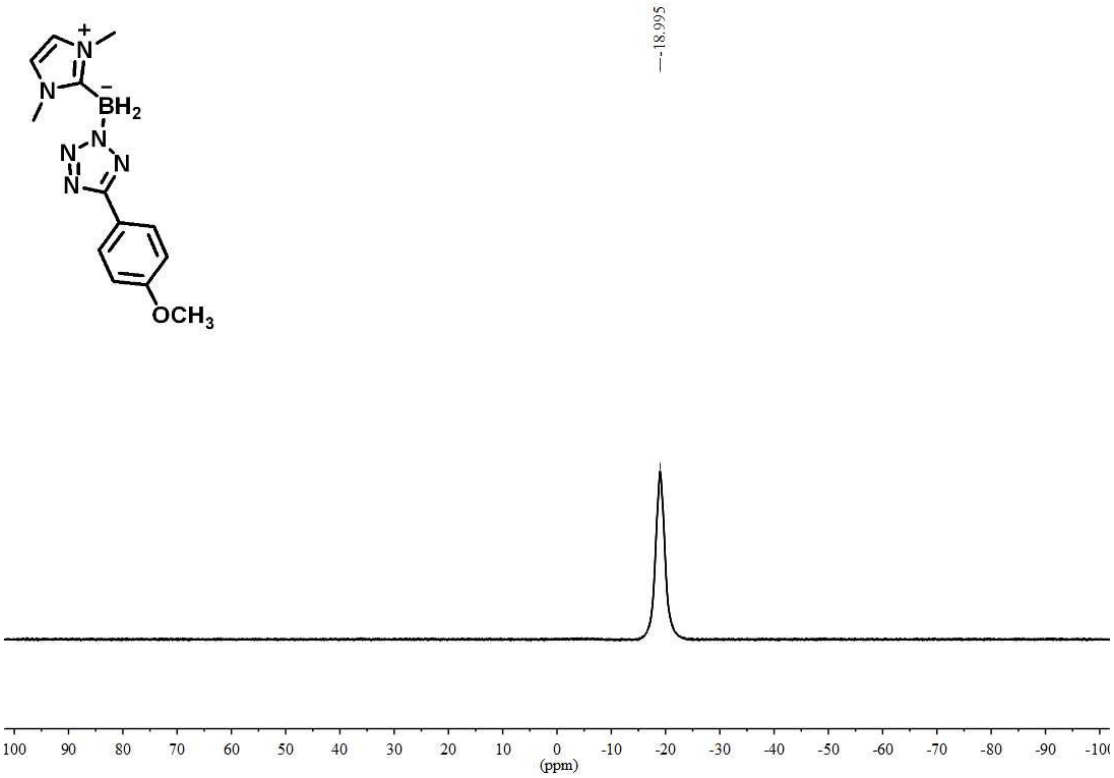
^{1}H NMR of product 5c in $CDCl_3$ (500 MHz)



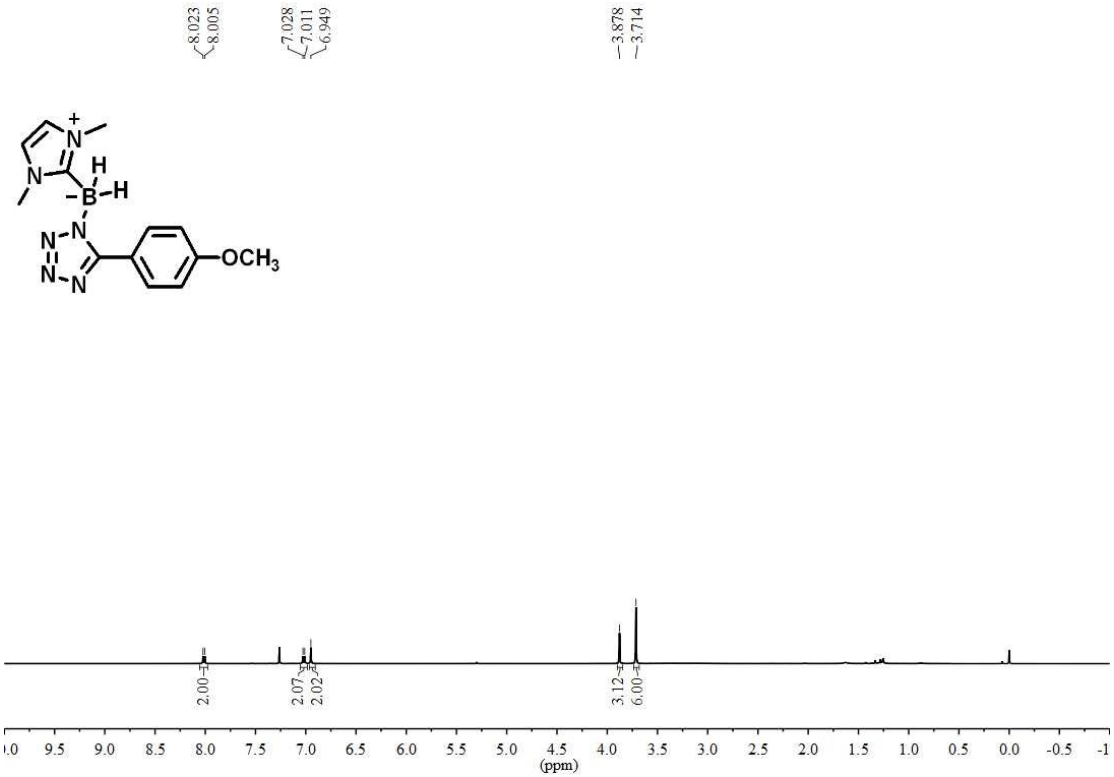
^{13}C NMR of product 5c in $CDCl_3$ (125 MHz)



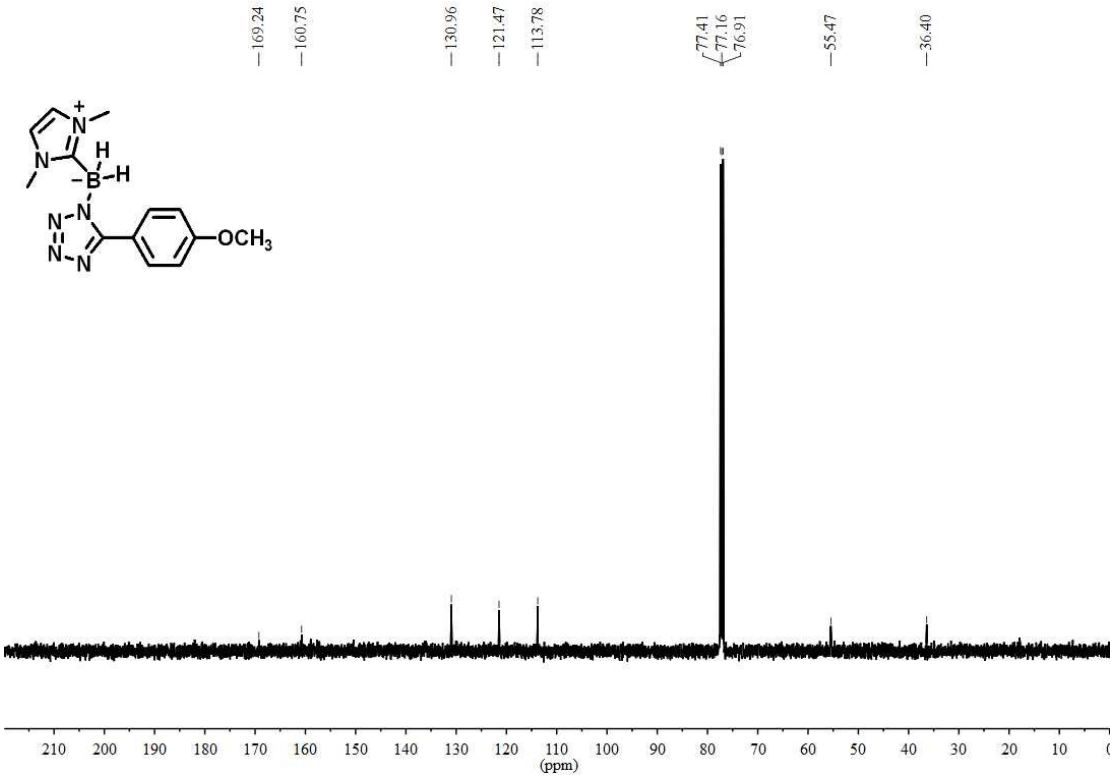
^{11}B NMR of product 5c in $CDCl_3$ (160 MHz)



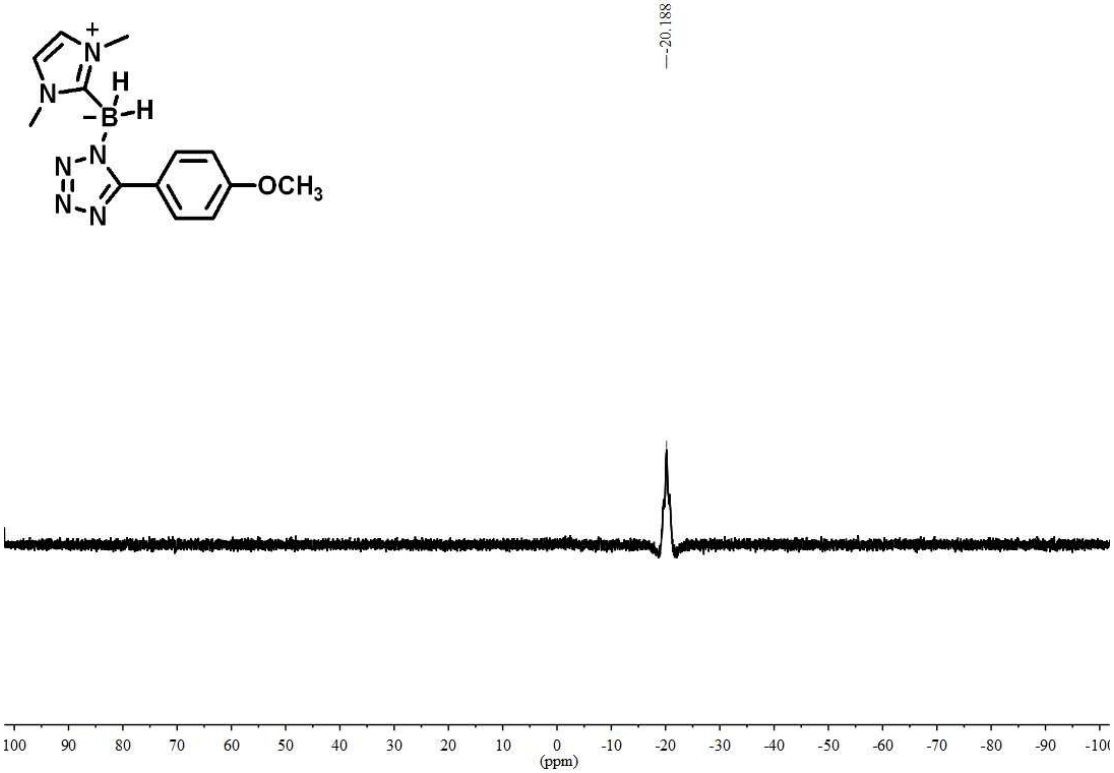
^{1}H NMR of product 5c' in $CDCl_3$ (500 MHz)



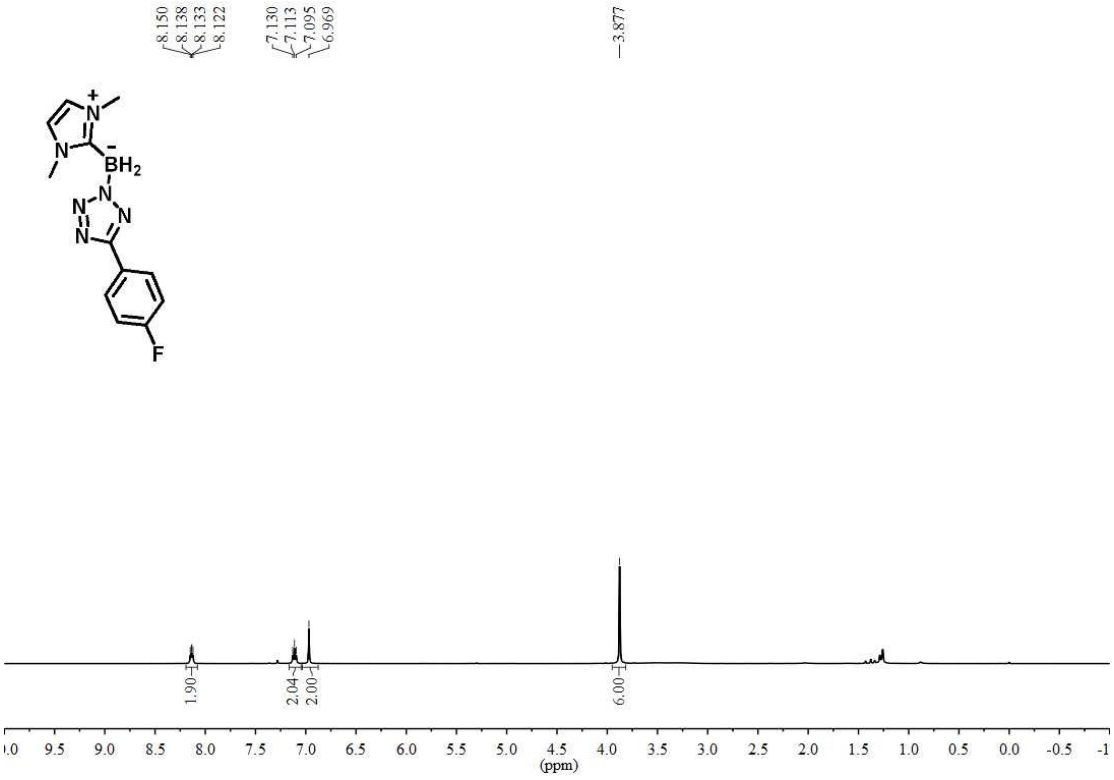
^{13}C NMR of product 5c' in $CDCl_3$ (125 MHz)



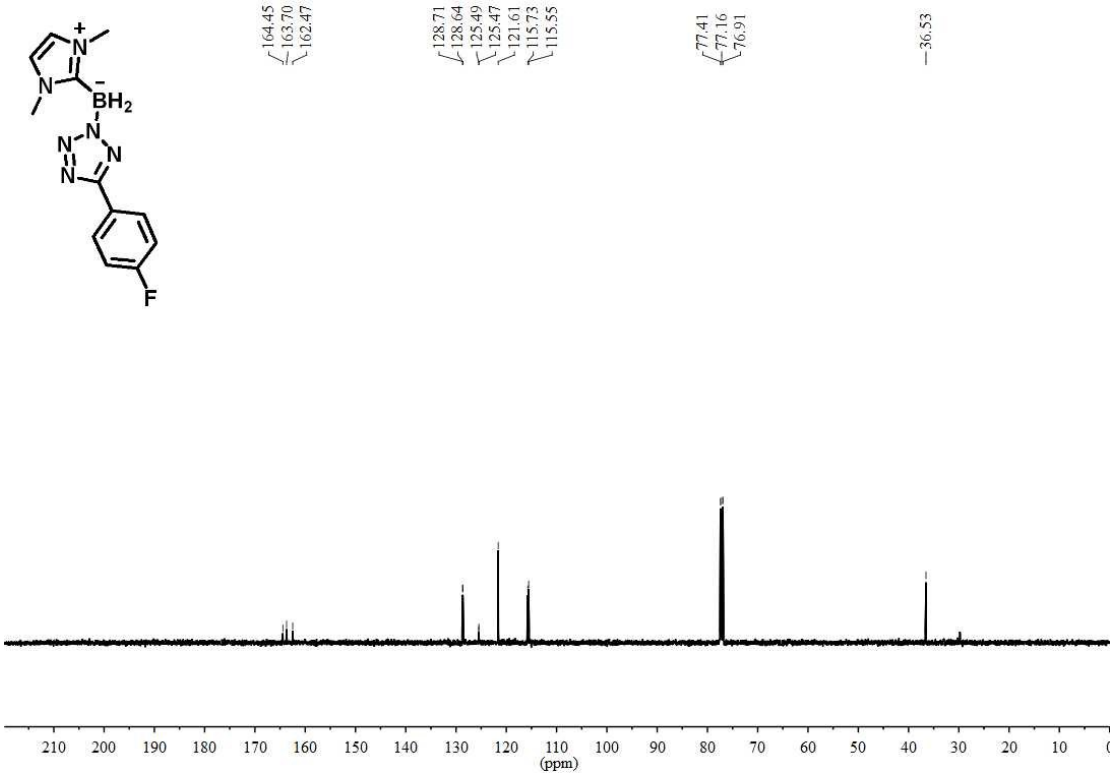
^{11}B NMR of product 5c' in $CDCl_3$ (160 MHz)



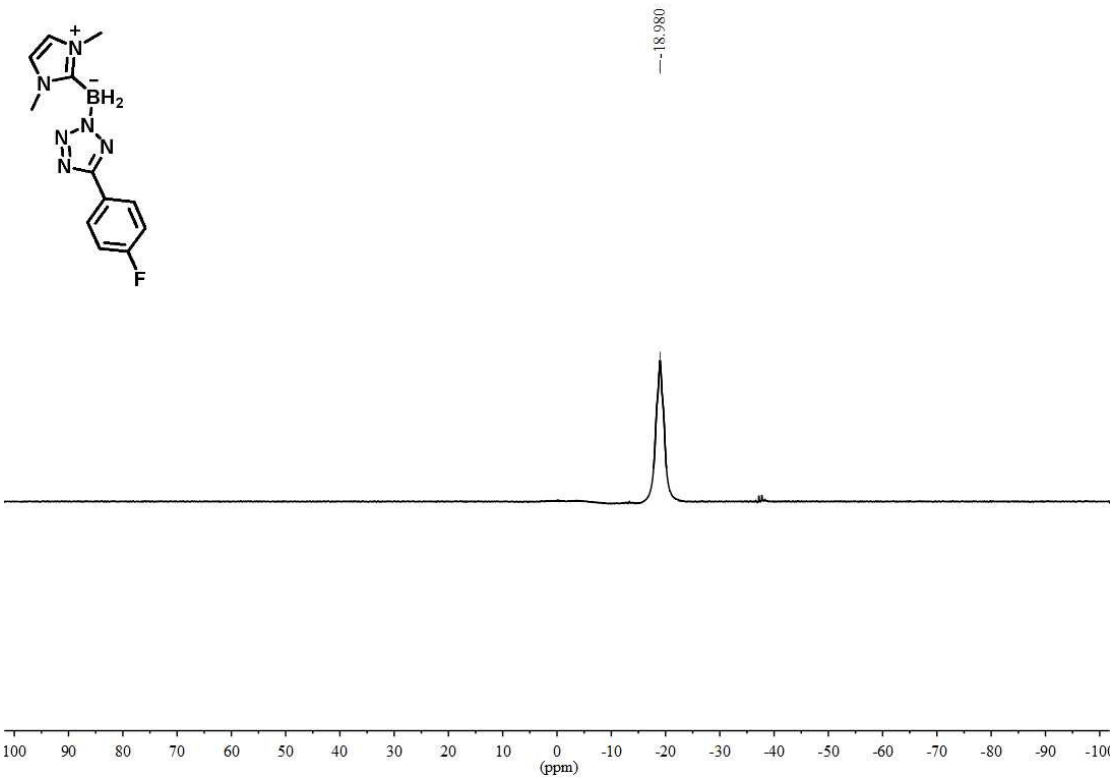
^{1}H NMR of product 5d in $CDCl_3$ (500 MHz)



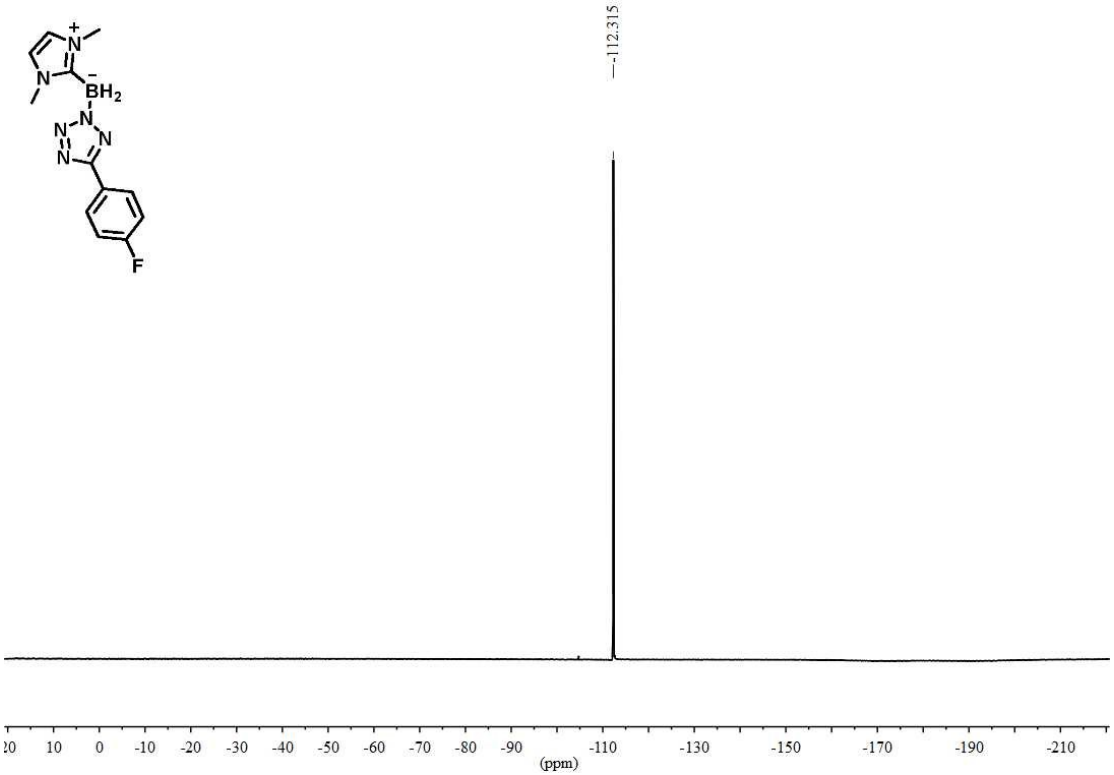
^{13}C NMR of product 5d in $CDCl_3$ (125 MHz)



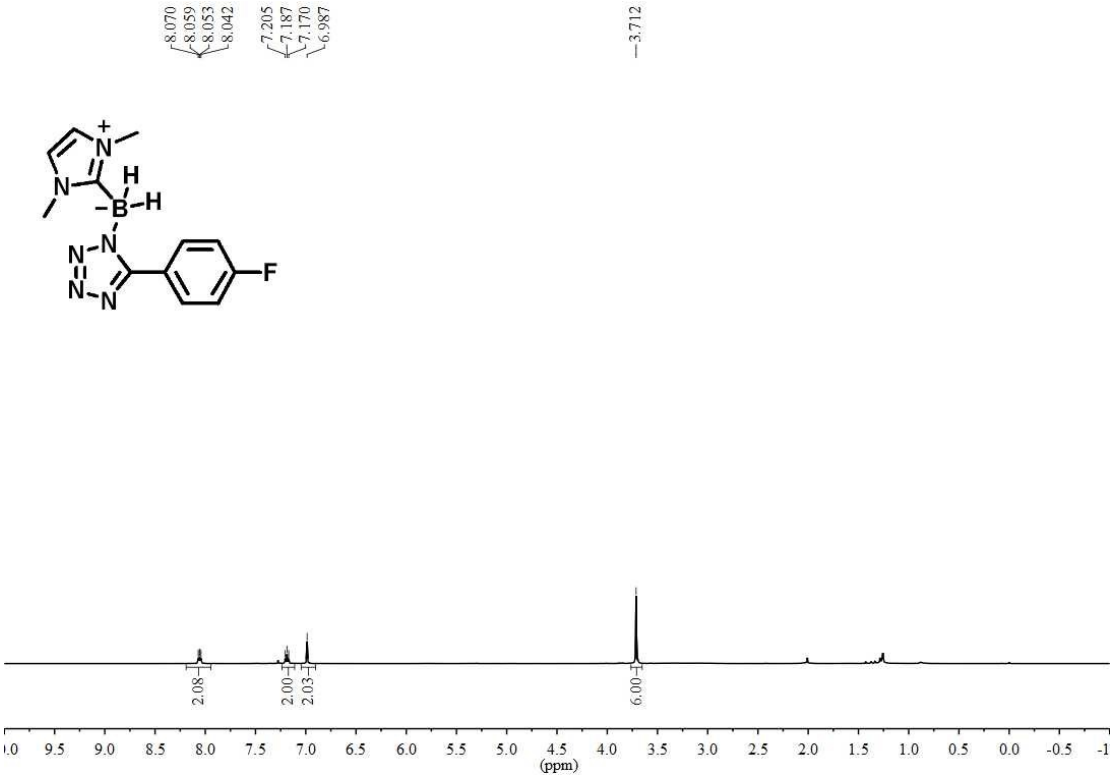
^{11}B NMR of product 5d in $CDCl_3$ (160 MHz)



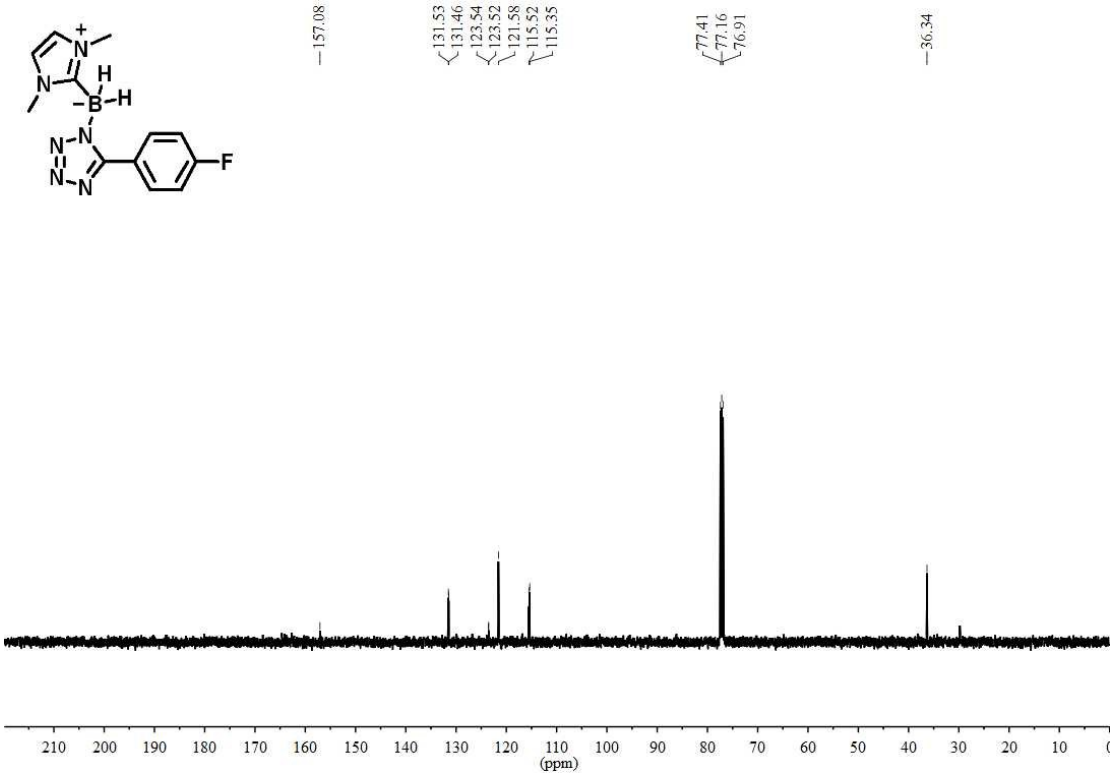
^{19}FNMR of product 5d in $CDCl_3$ (471 MHz)



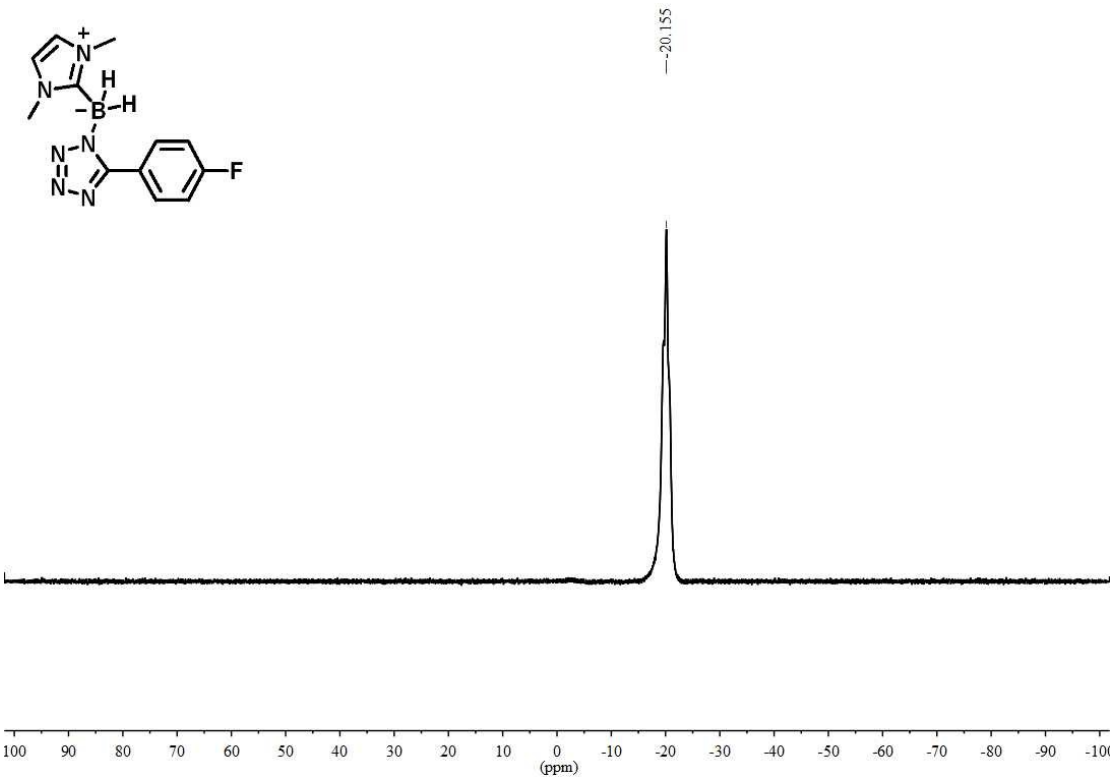
^{1}H NMR of product 5d' in $CDCl_3$ (500 MHz)



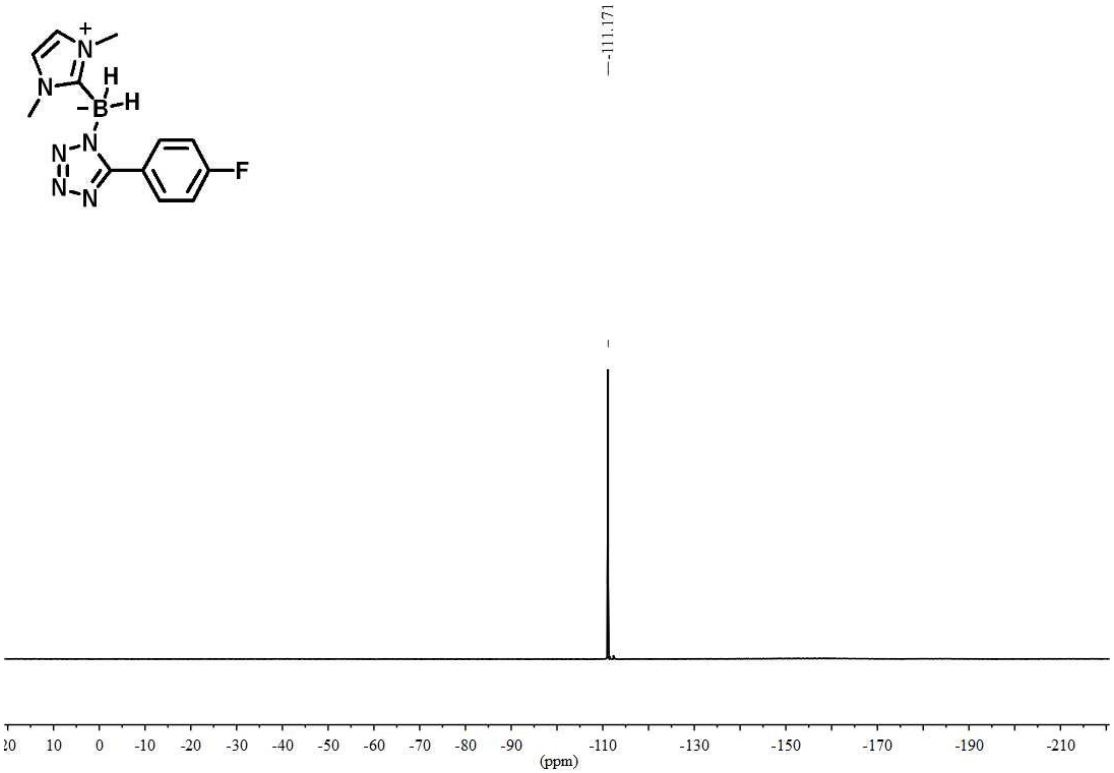
^{13}C NMR of product 5d' in $CDCl_3$ (125 MHz)



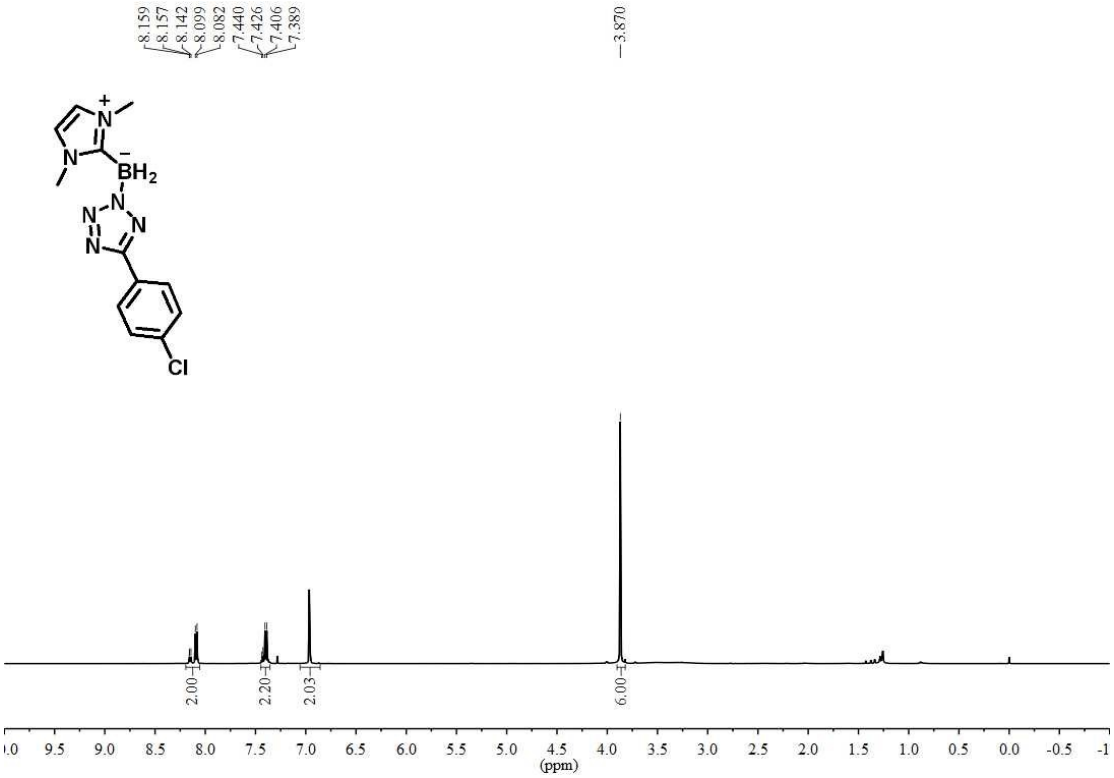
^{11}B NMR of product 5d' in $CDCl_3$ (160 MHz)



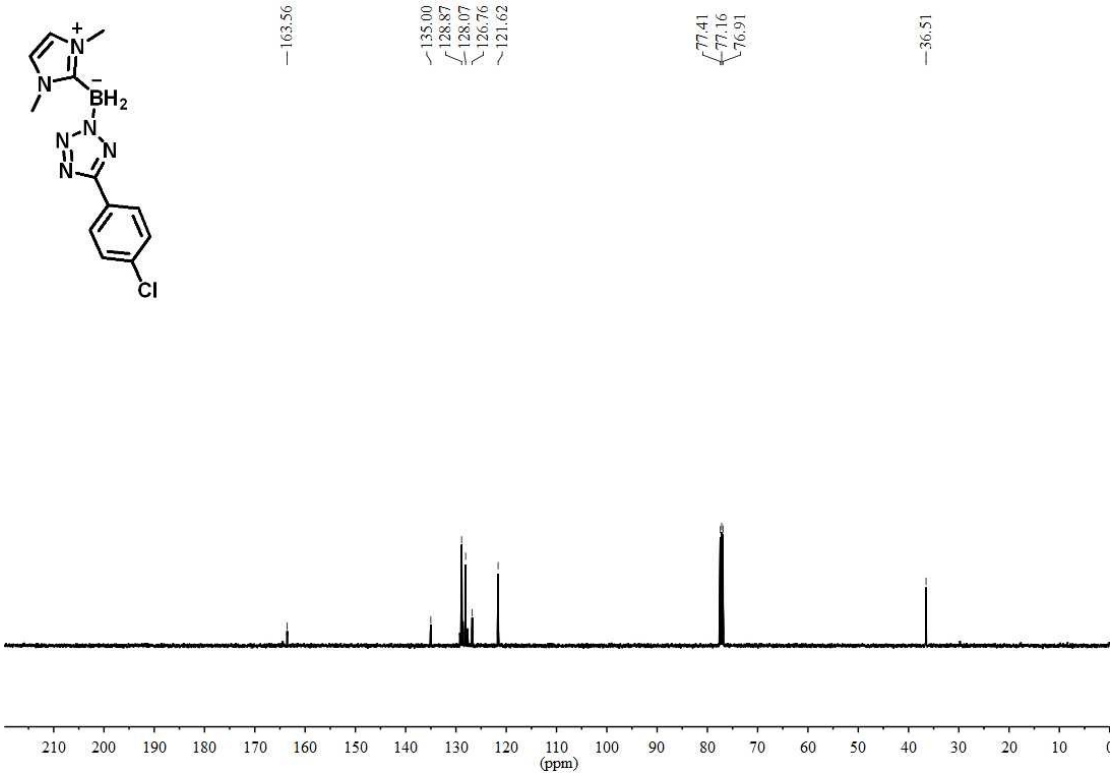
^{19}FNMR of product 5d' in $CDCl_3$ (471 MHz)



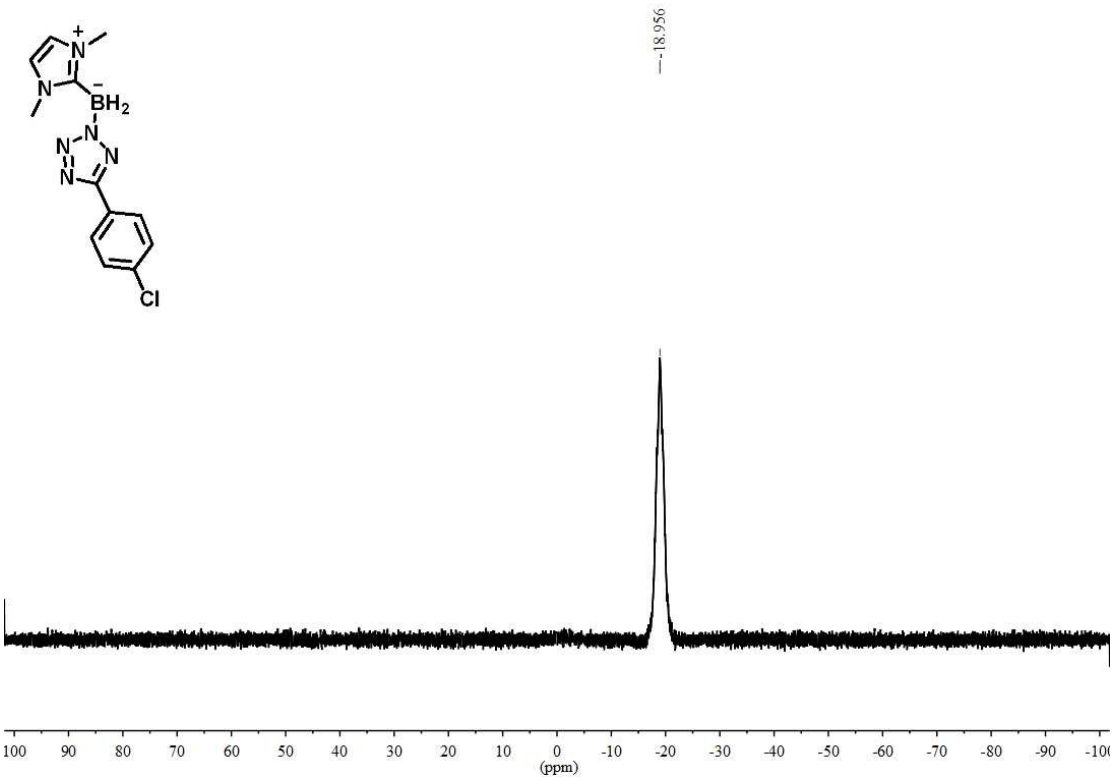
^{1}H NMR of product 5e in $CDCl_3$ (500 MHz)



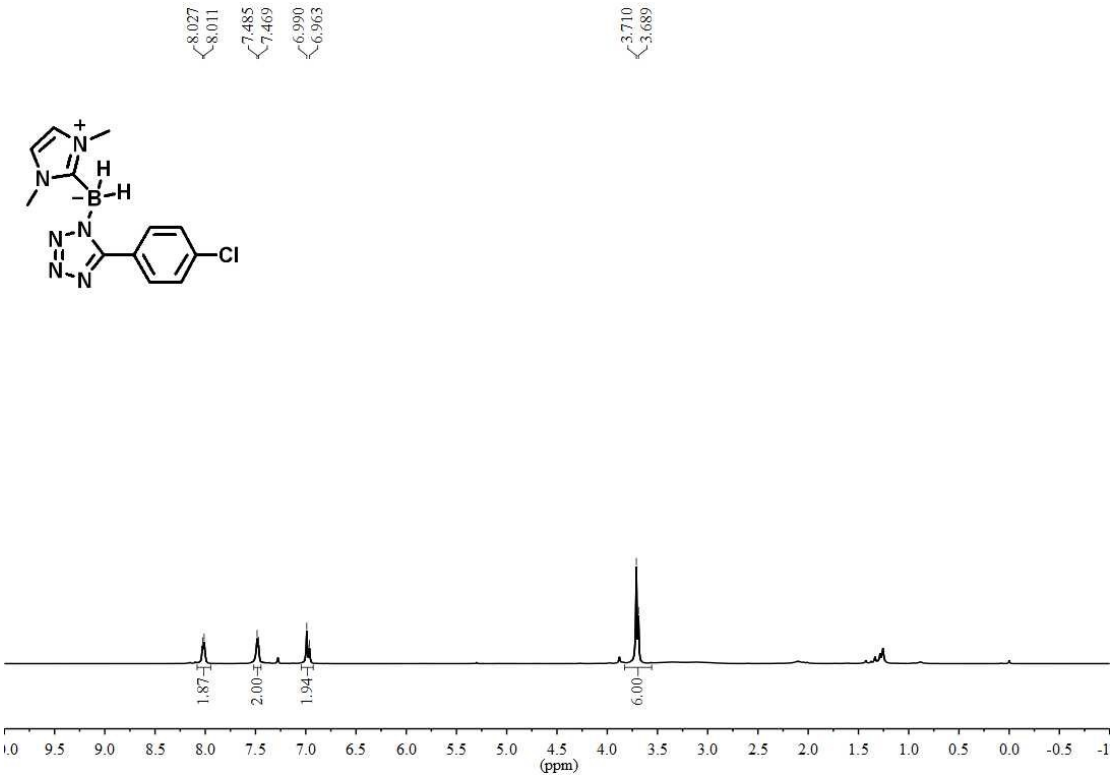
^{13}C NMR of product 5e in $CDCl_3$ (125 MHz)



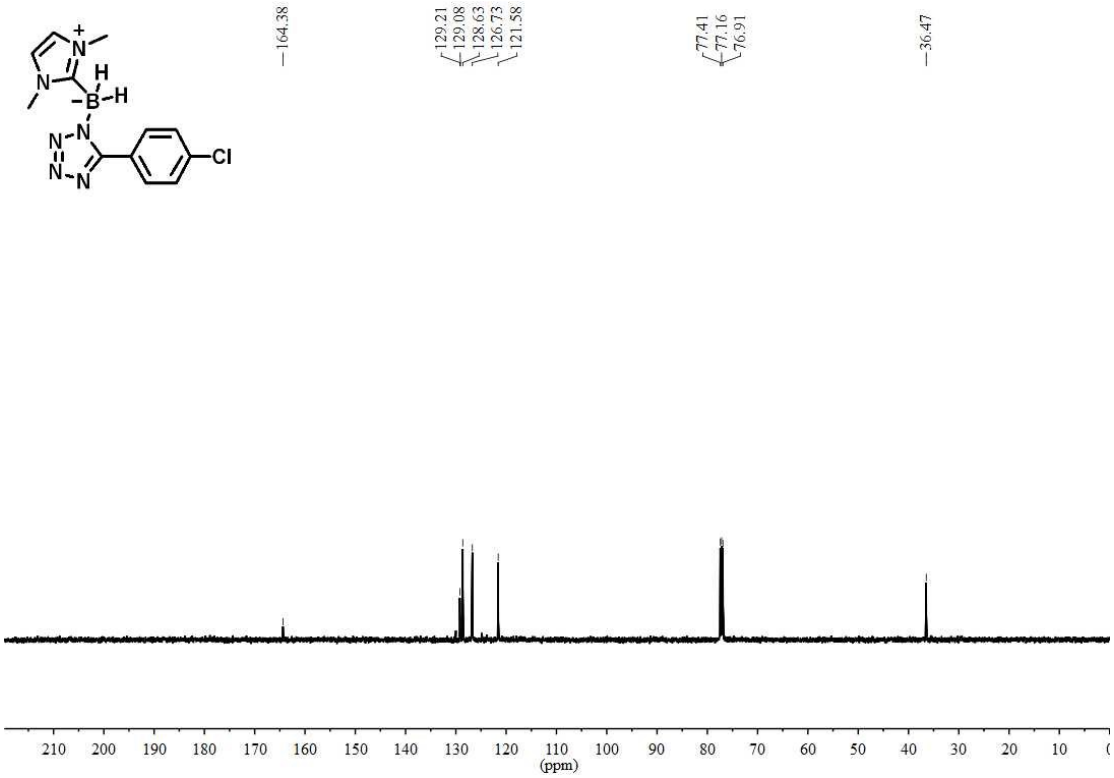
^{11}B NMR of product 5e in $CDCl_3$ (160 MHz)



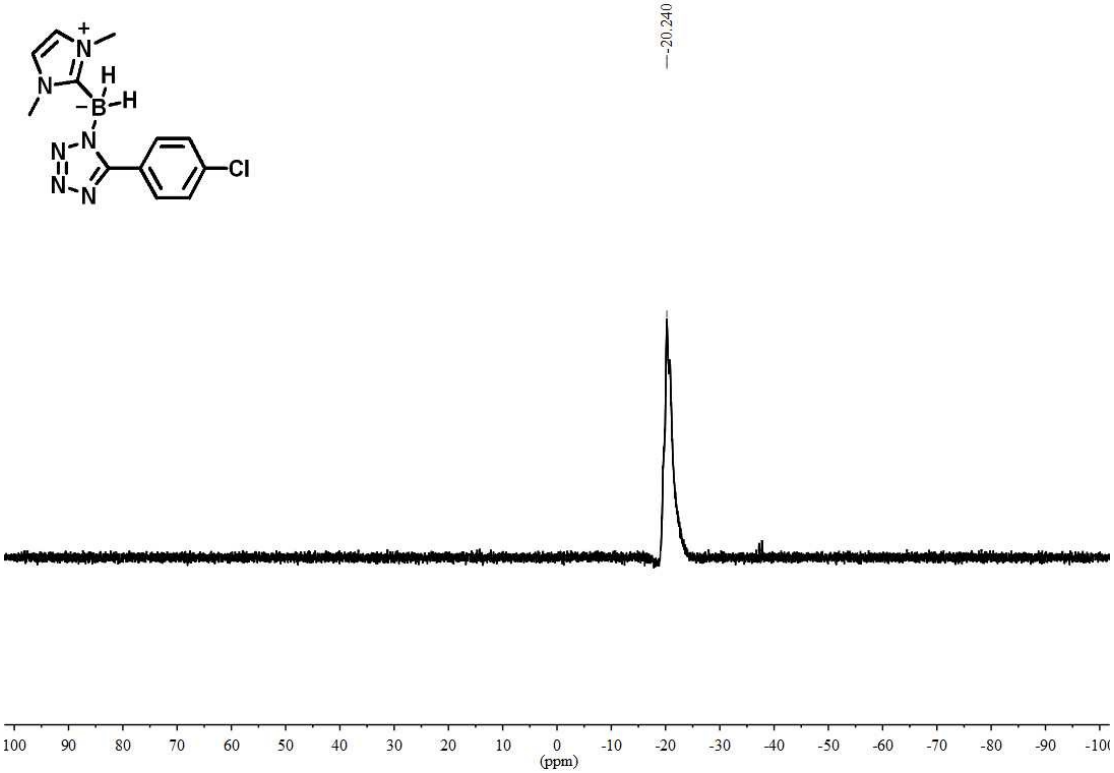
^{1}H NMR of product 5e' in $CDCl_3$ (500 MHz)



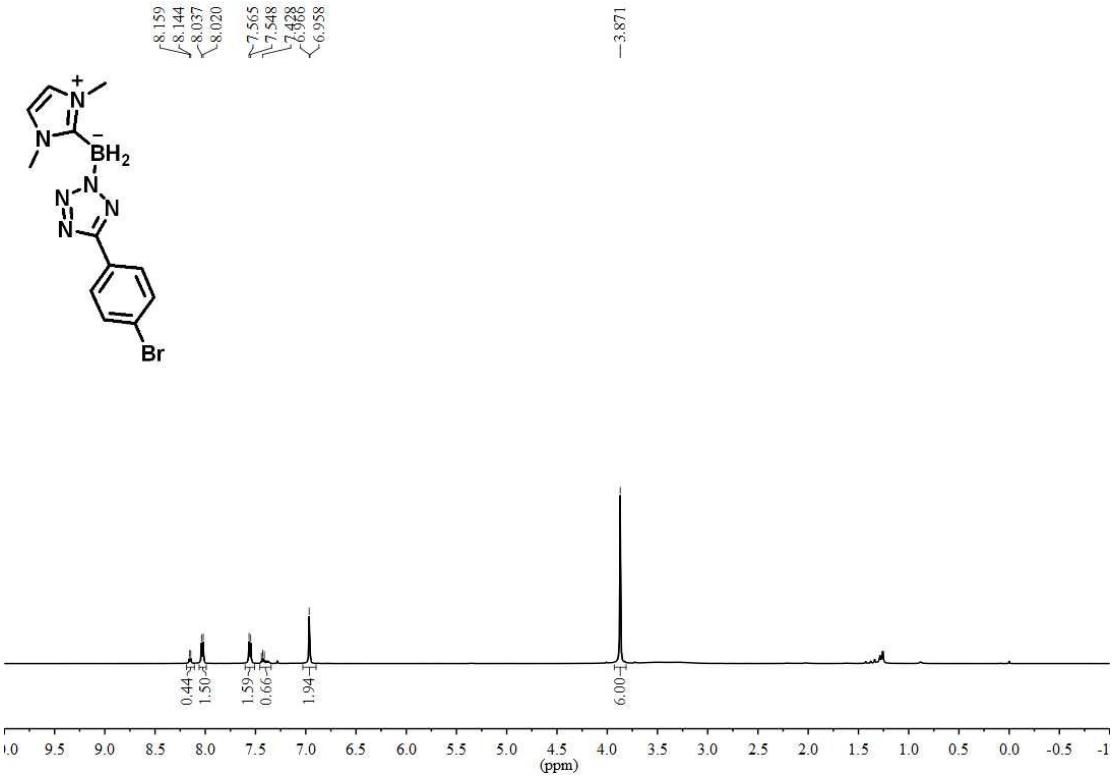
^{13}C NMR of product 5e' in $CDCl_3$ (125 MHz)



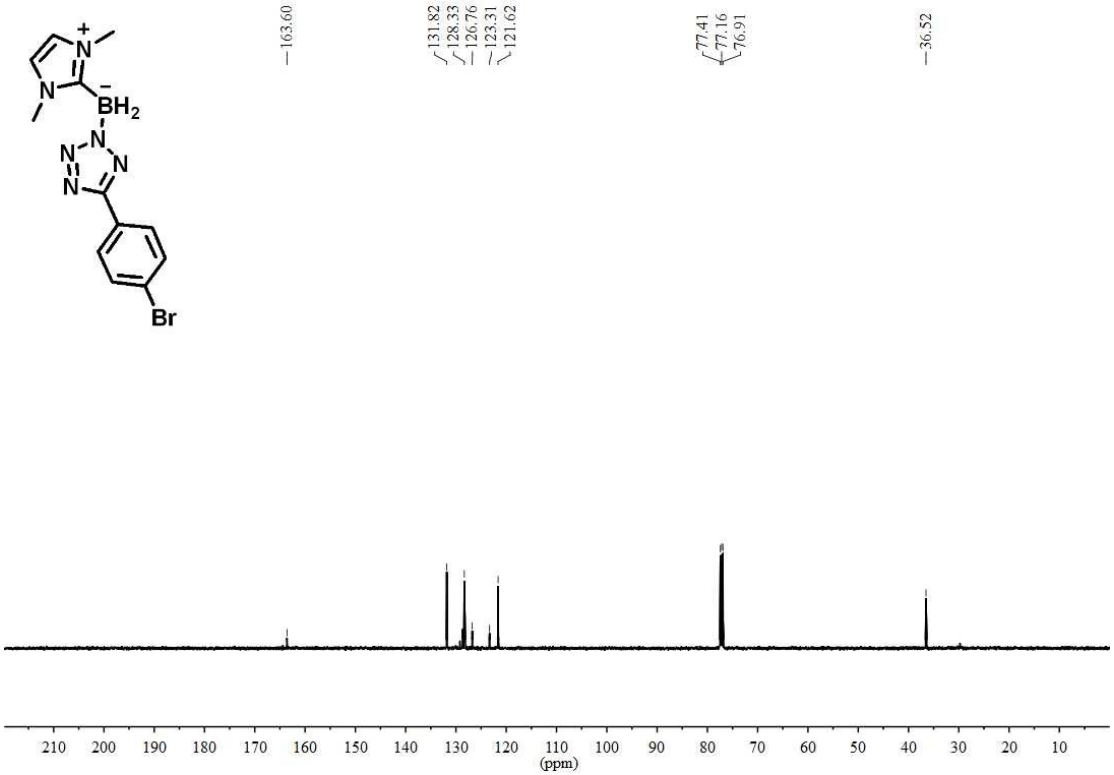
^{11}B NMR of product 5e' in $CDCl_3$ (160 MHz)



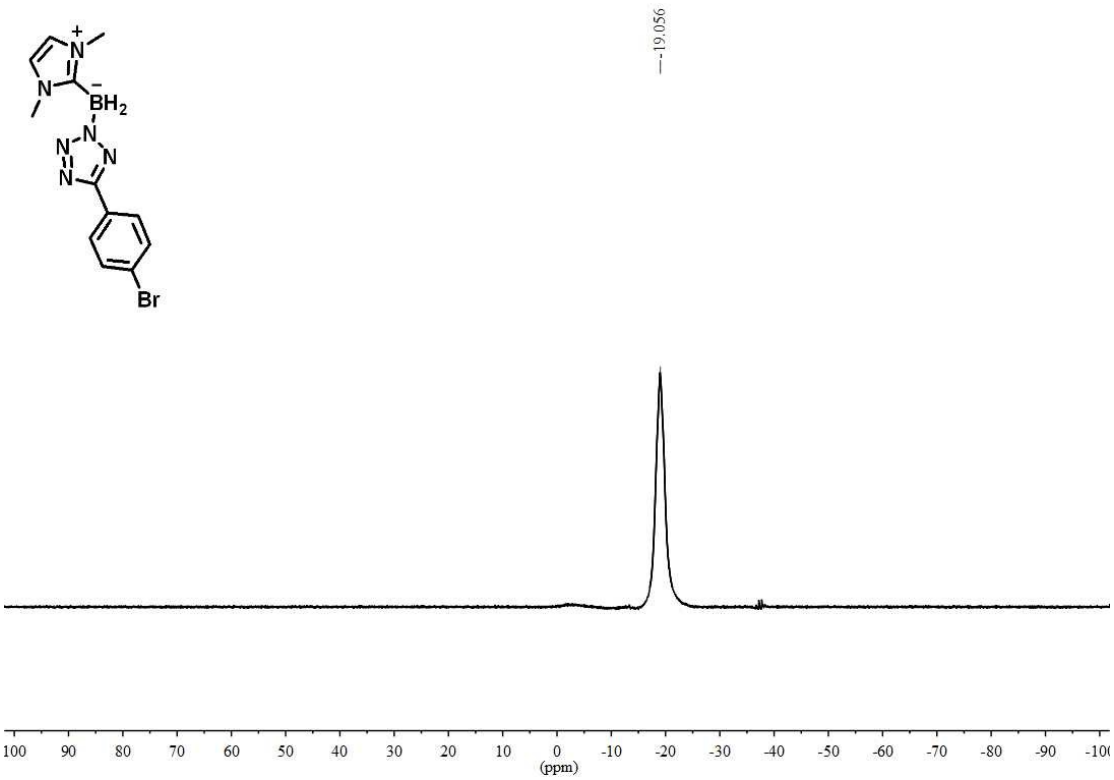
^{1}H NMR of product 5f in $CDCl_3$ (500 MHz)



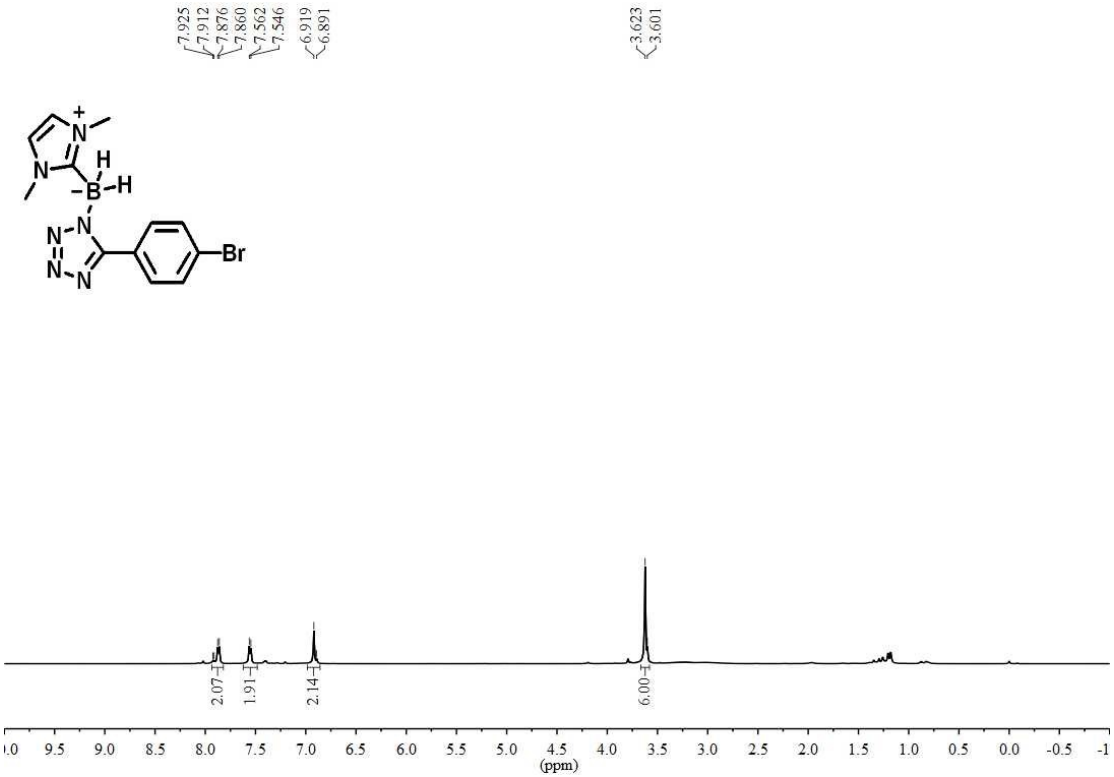
^{13}C NMR of product 5f in $CDCl_3$ (125 MHz)



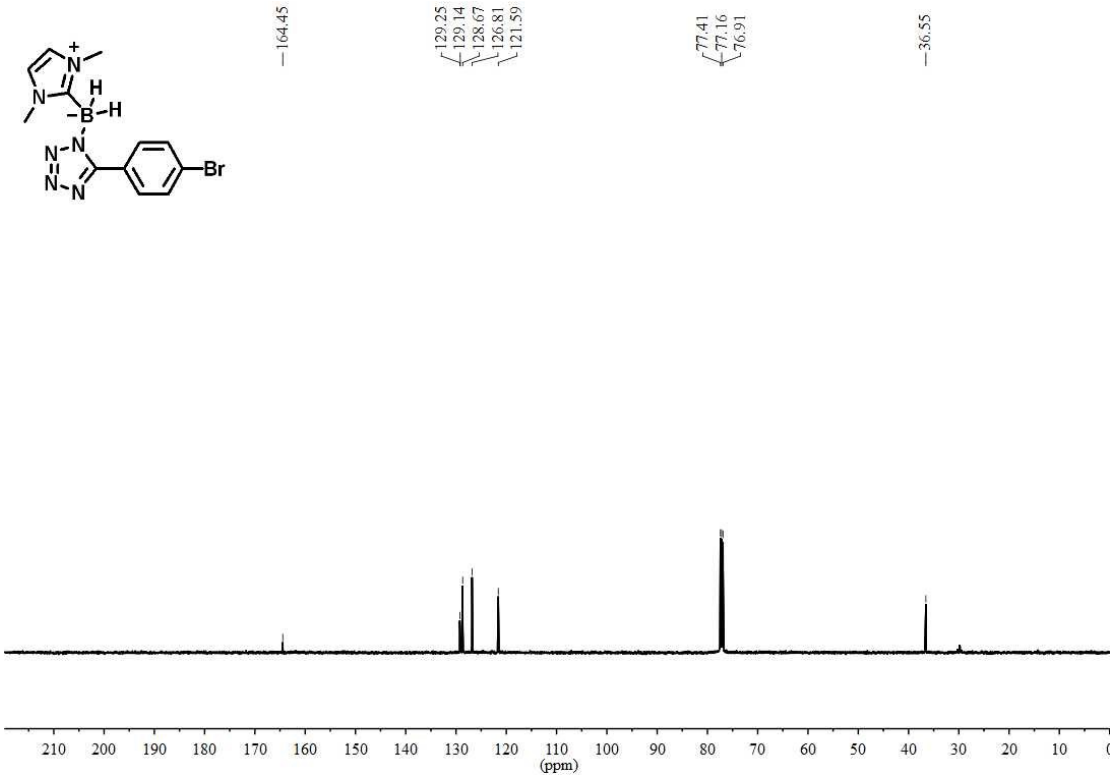
^{11}B NMR of product 5f in $CDCl_3$ (160 MHz)



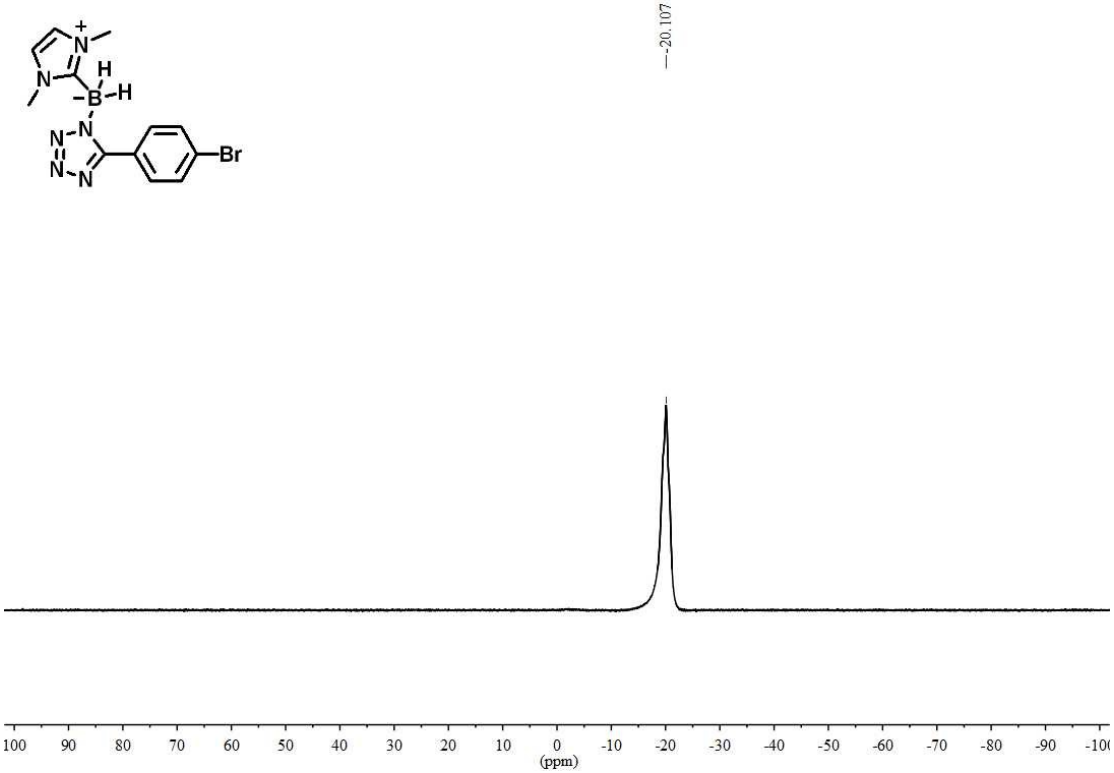
^{1}H NMR of product 5f' in $CDCl_3$ (500 MHz)



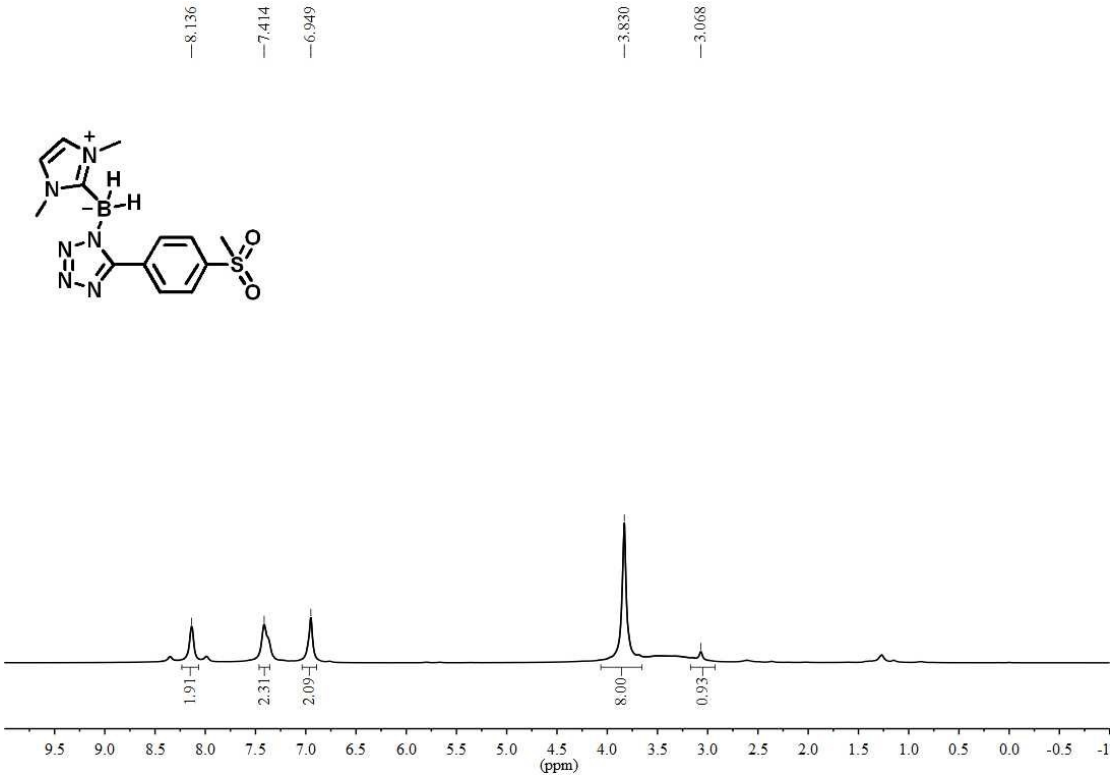
^{13}C NMR of product 5f' in $CDCl_3$ (125 MHz)



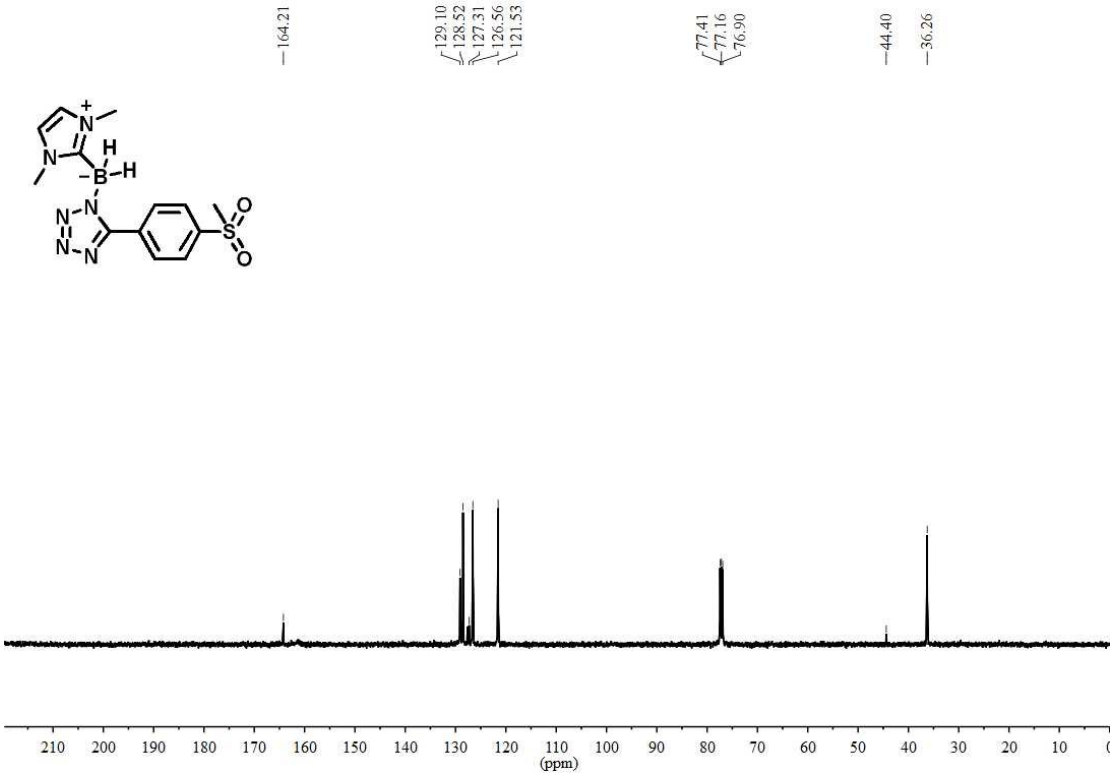
^{11}B NMR of product 5f' in $CDCl_3$ (160 MHz)



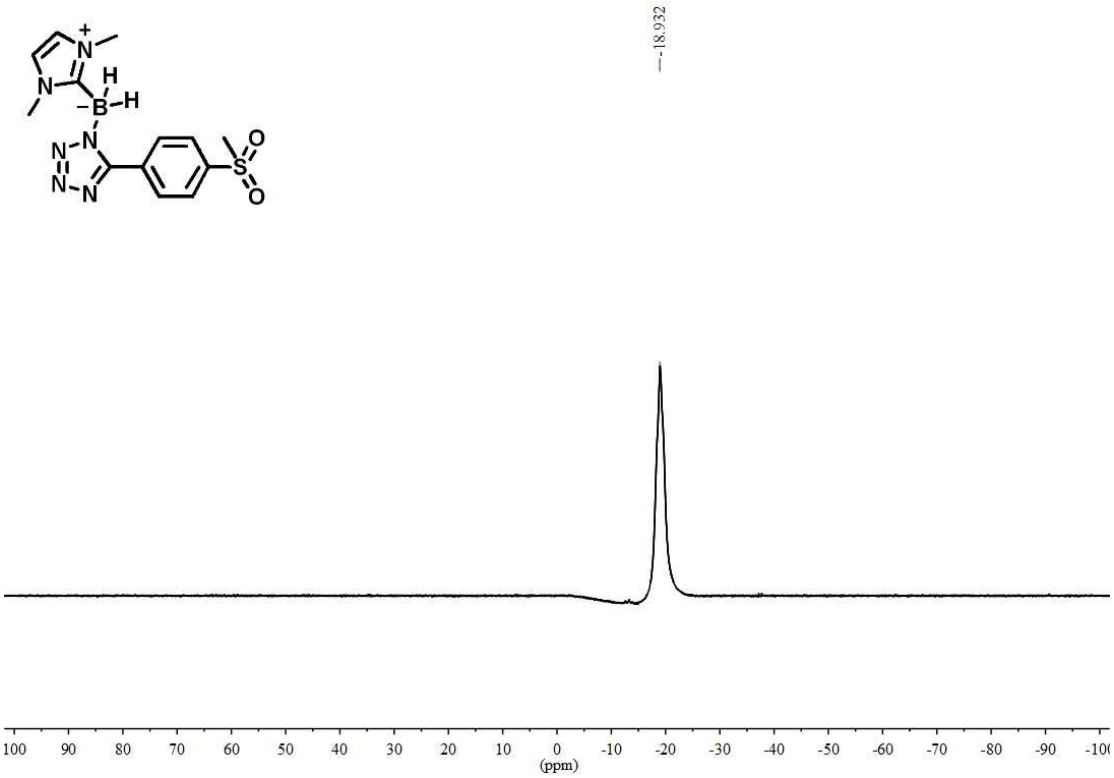
^{1}H NMR of product 5g in $CDCl_3$ (500 MHz)



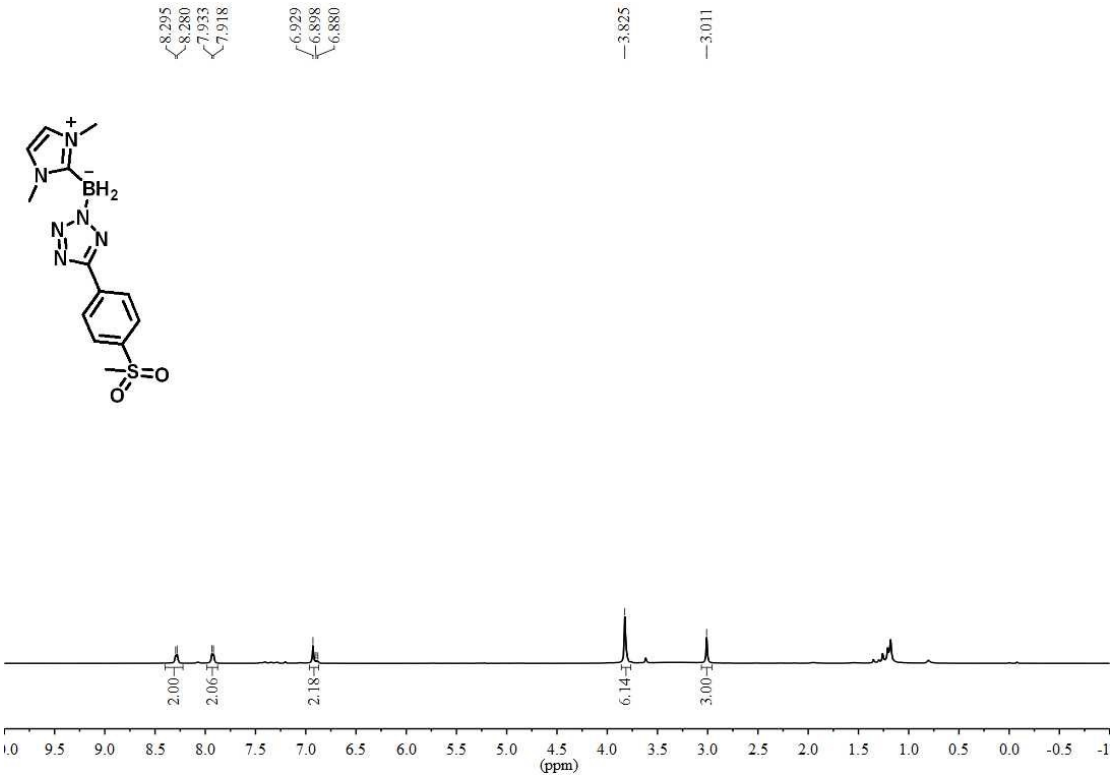
^{13}C NMR of product 5g in $CDCl_3$ (125 MHz)



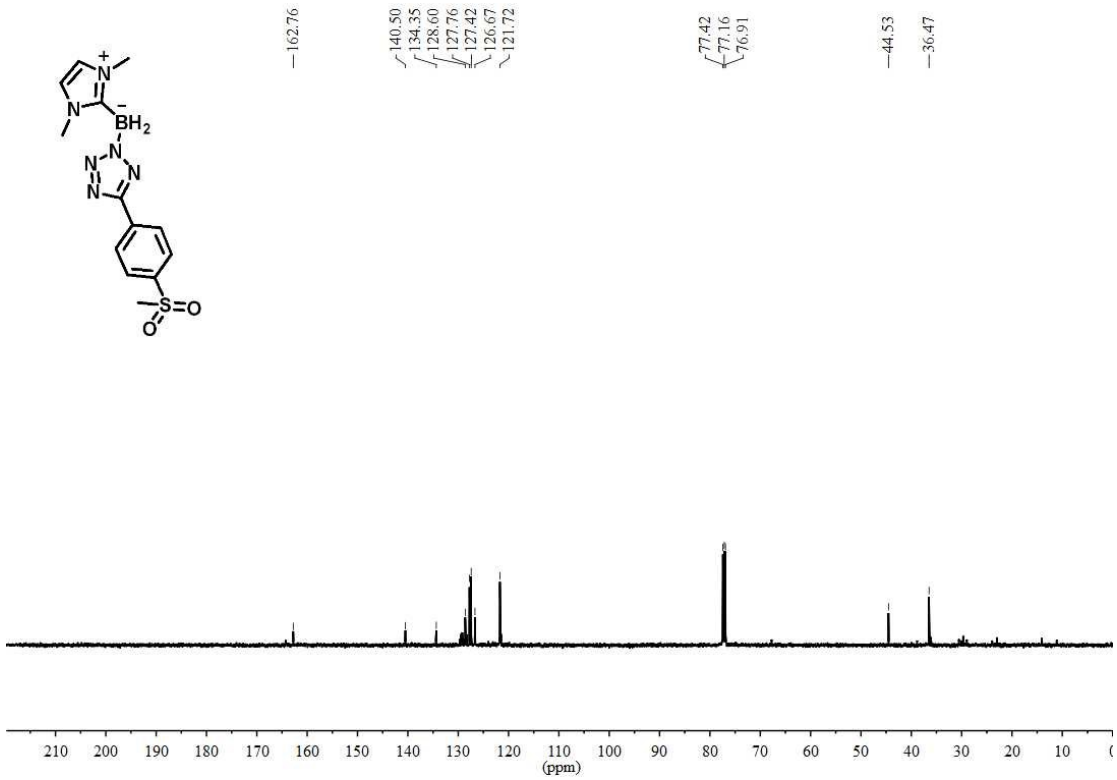
^{11}B NMR of product 5g in $CDCl_3$ (160 MHz)



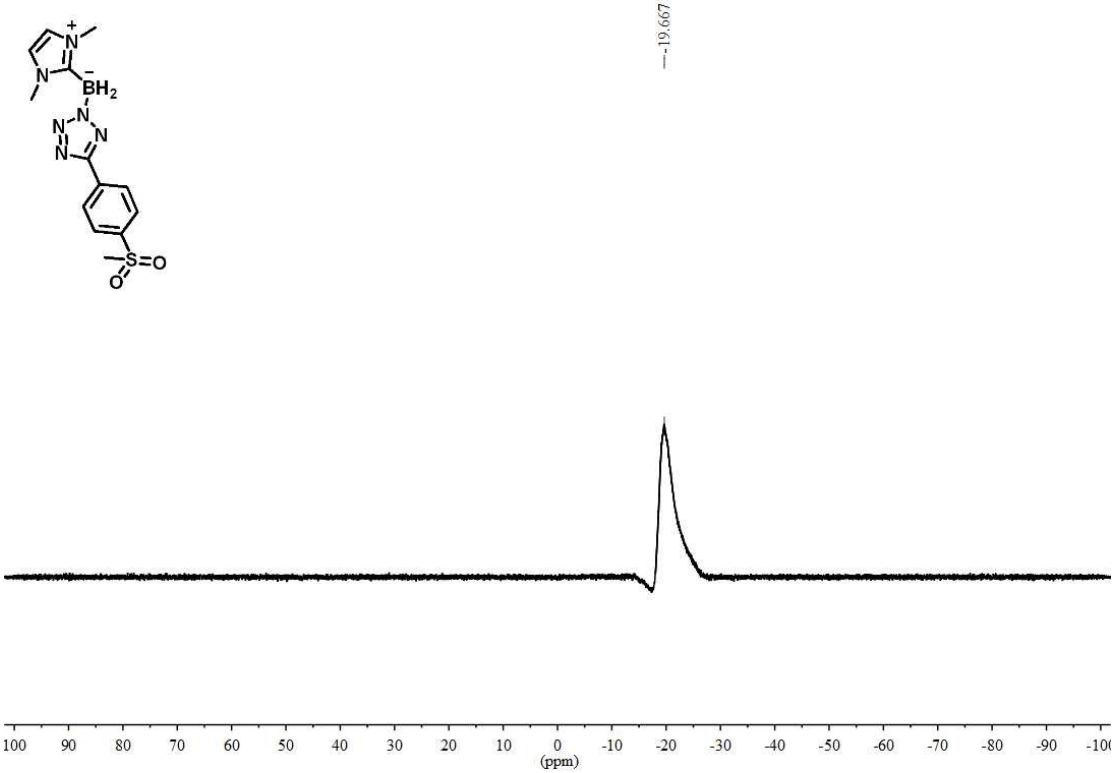
^{1}H NMR of product 5g' in $CDCl_3$ (500 MHz)



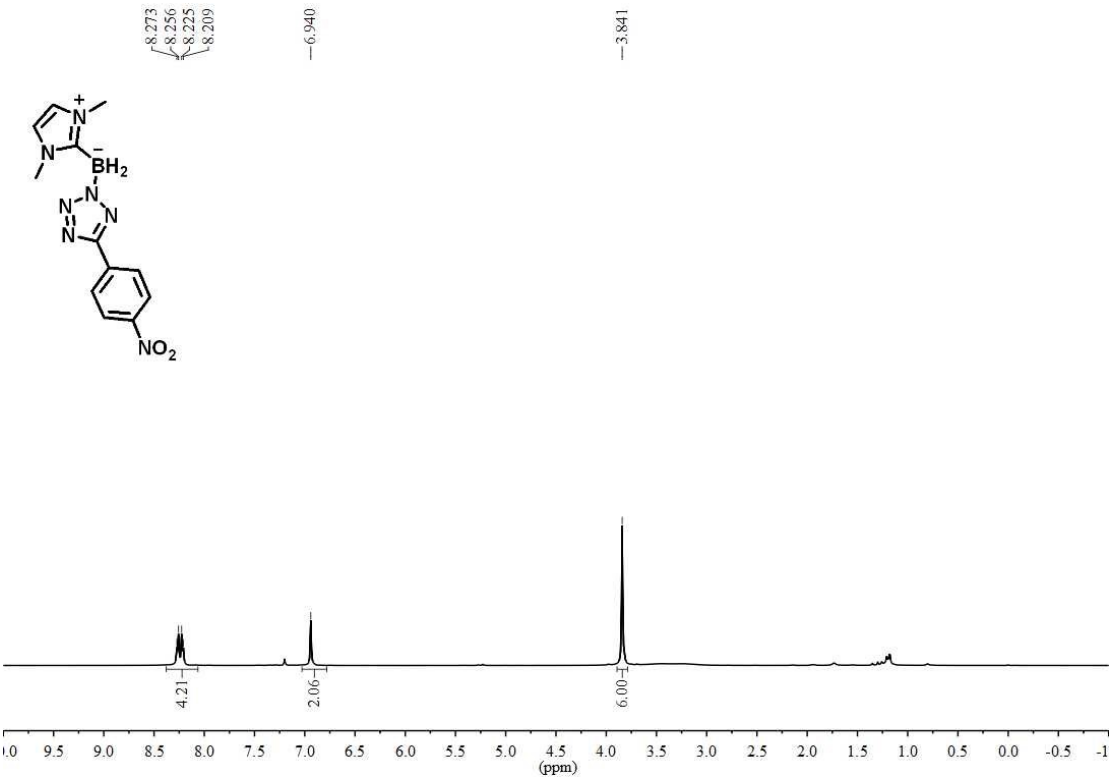
^{13}C NMR of product 5g' in $CDCl_3$ (125 MHz)



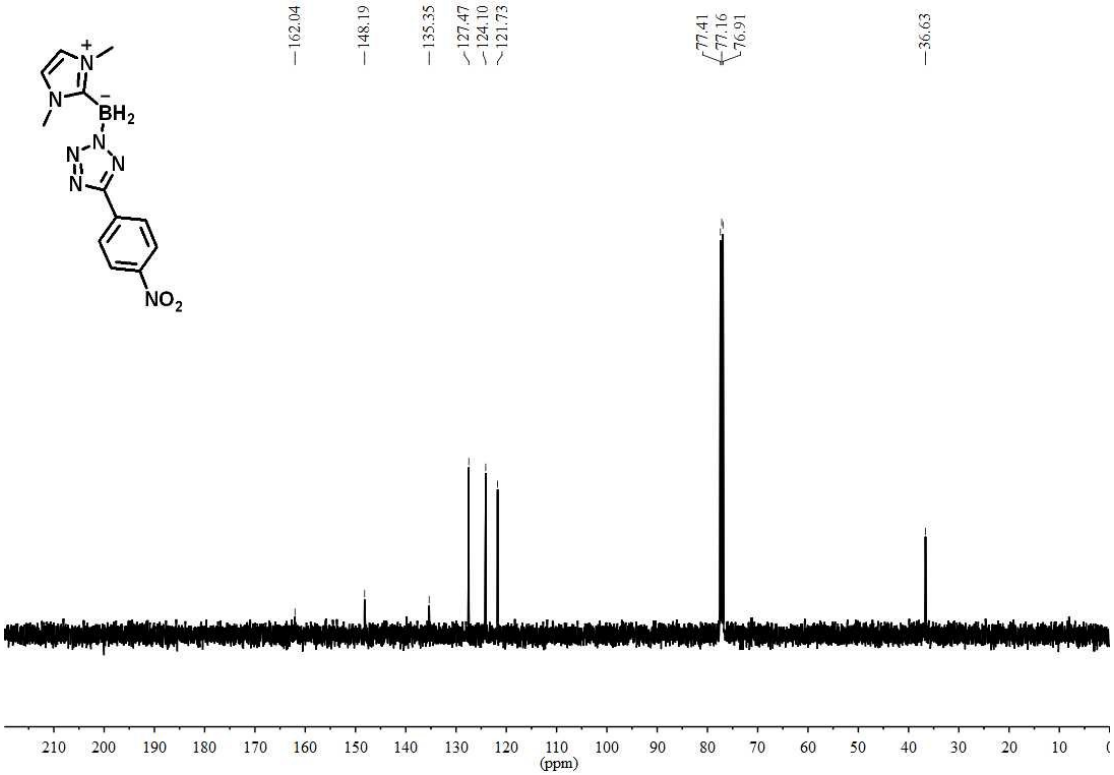
^{11}B NMR of product 5g' in $CDCl_3$ (160 MHz)



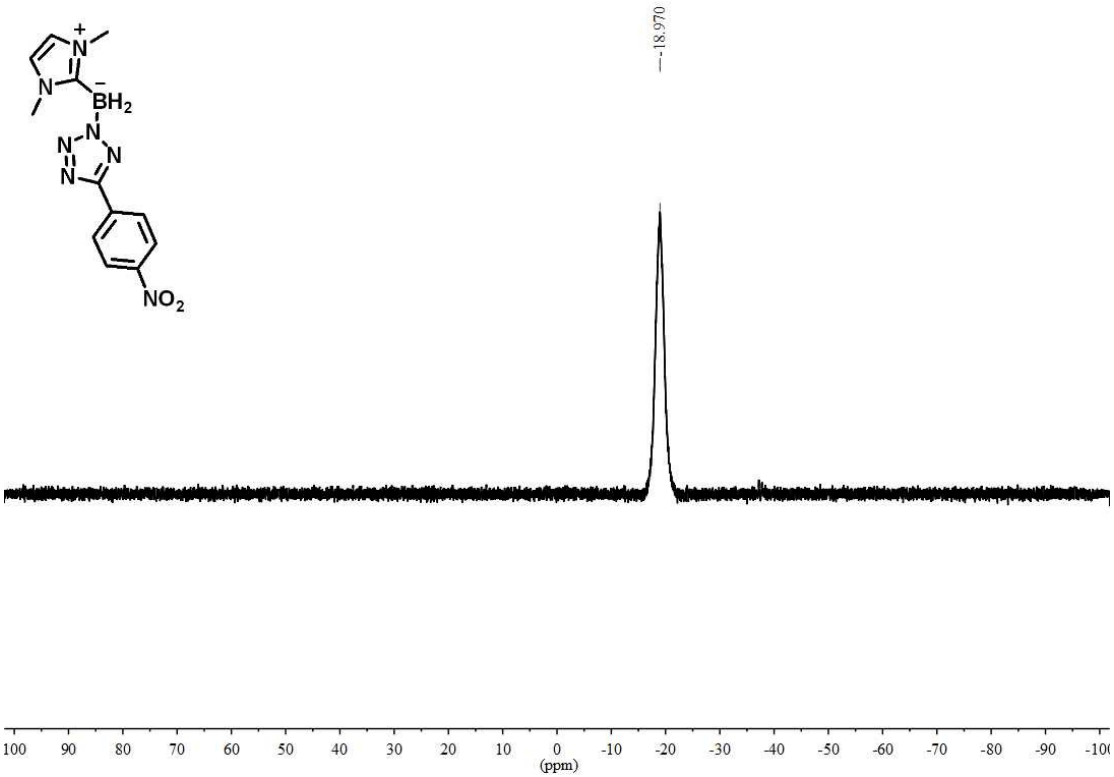
^{1}H NMR of product 5h in $CDCl_3$ (500 MHz)



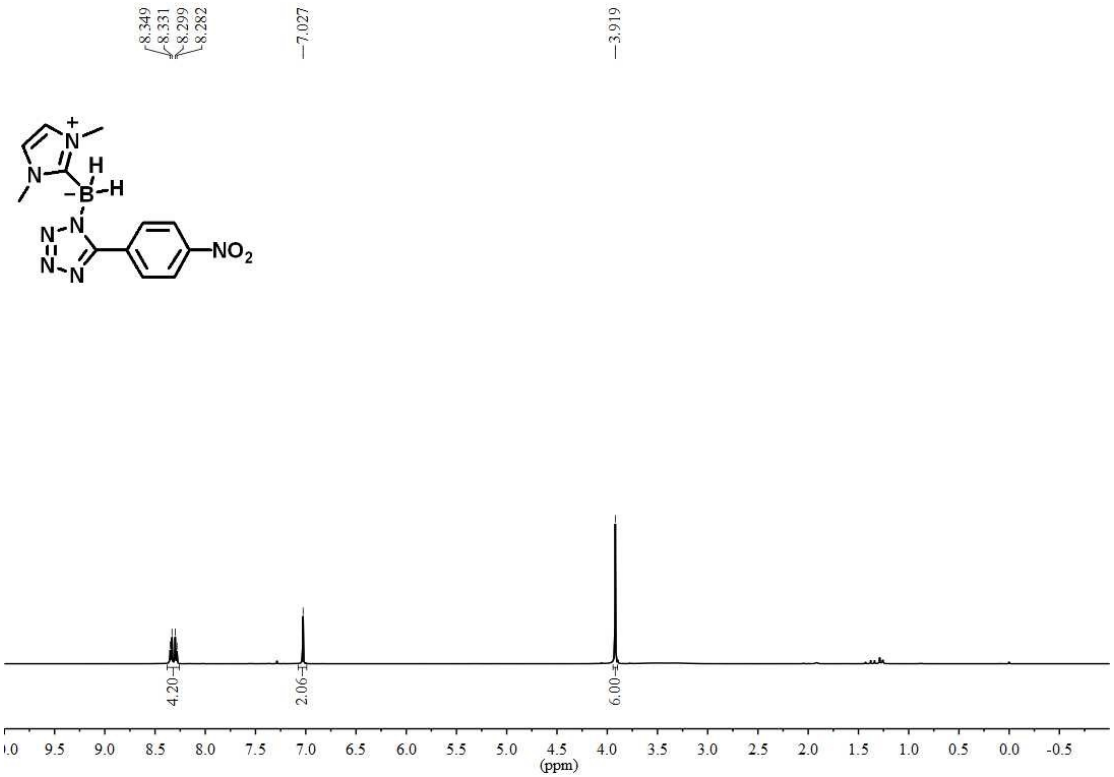
^{13}C NMR of product 5h in $CDCl_3$ (125 MHz)



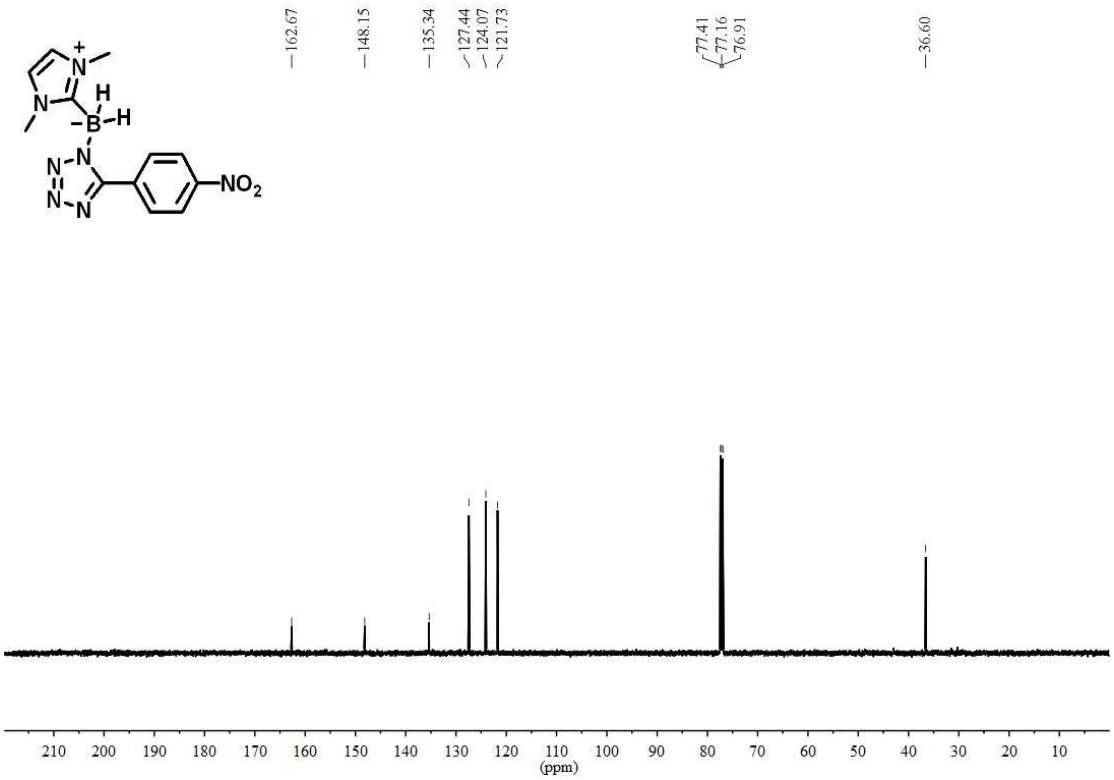
^{11}B NMR of product 5h in $CDCl_3$ (160 MHz)



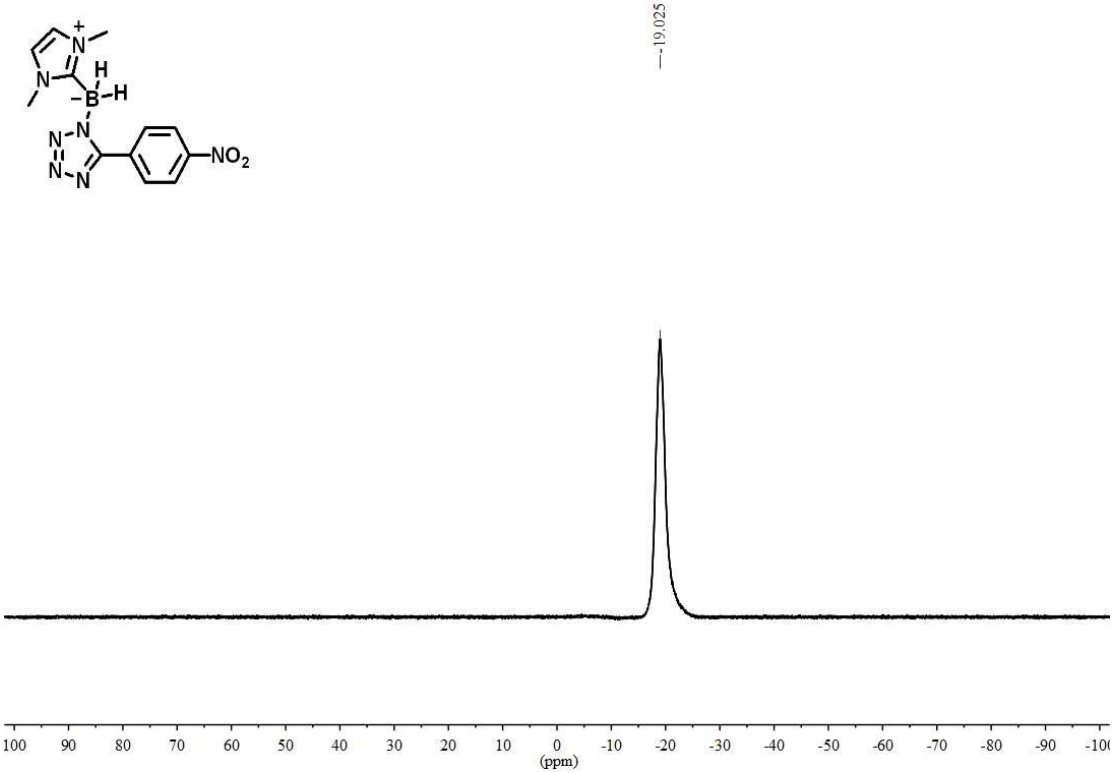
^{1}H NMR of product 5h' in $CDCl_3$ (500 MHz)



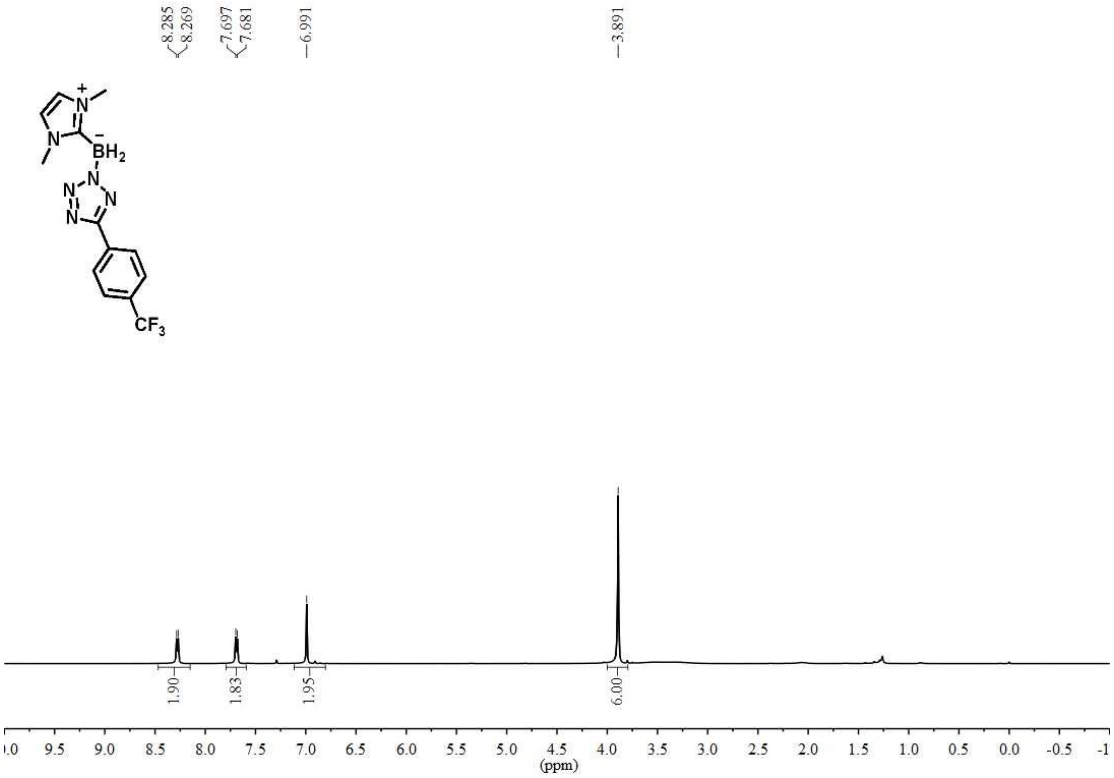
^{13}C NMR of product 5h' in $CDCl_3$ (125 MHz)



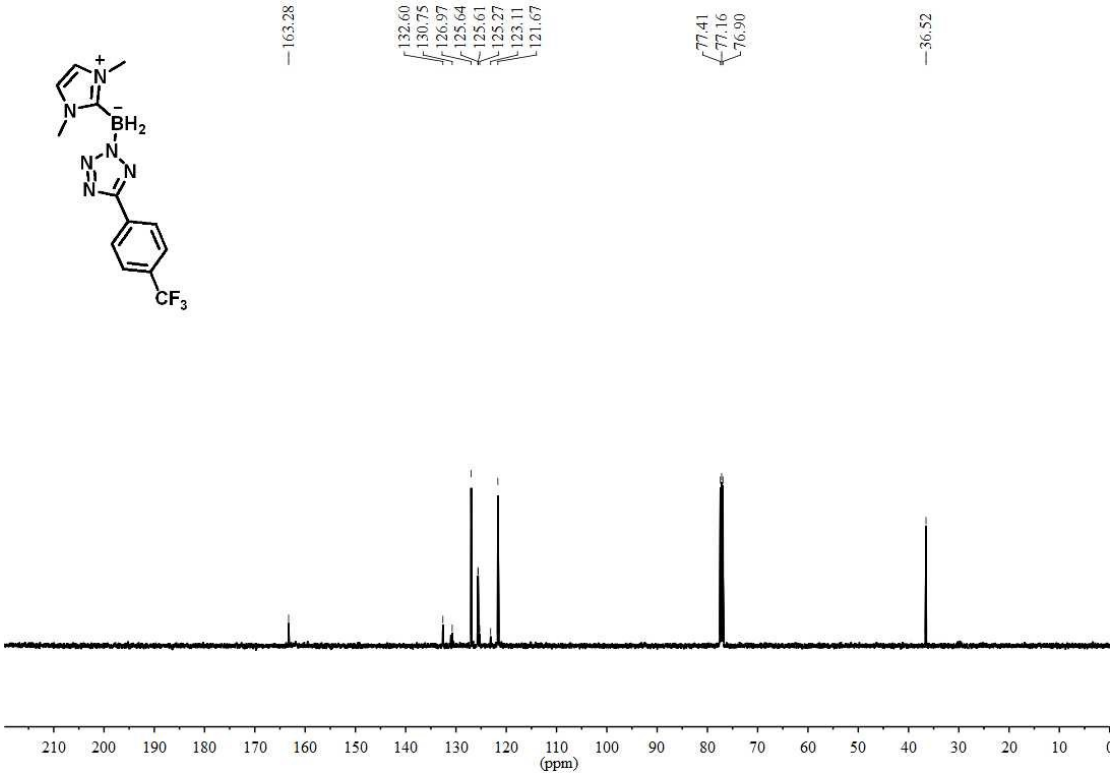
^{11}B NMR of product 5h' in $CDCl_3$ (160 MHz)



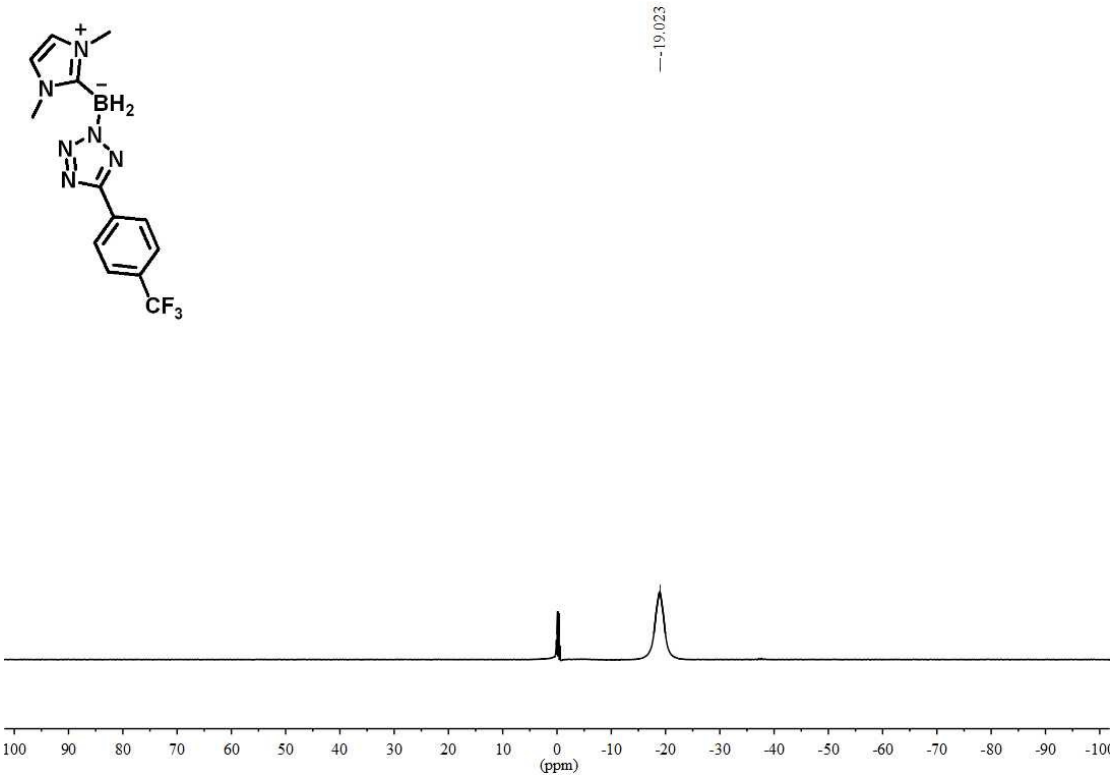
^{1}H NMR of product 5i in $CDCl_3$ (500 MHz)



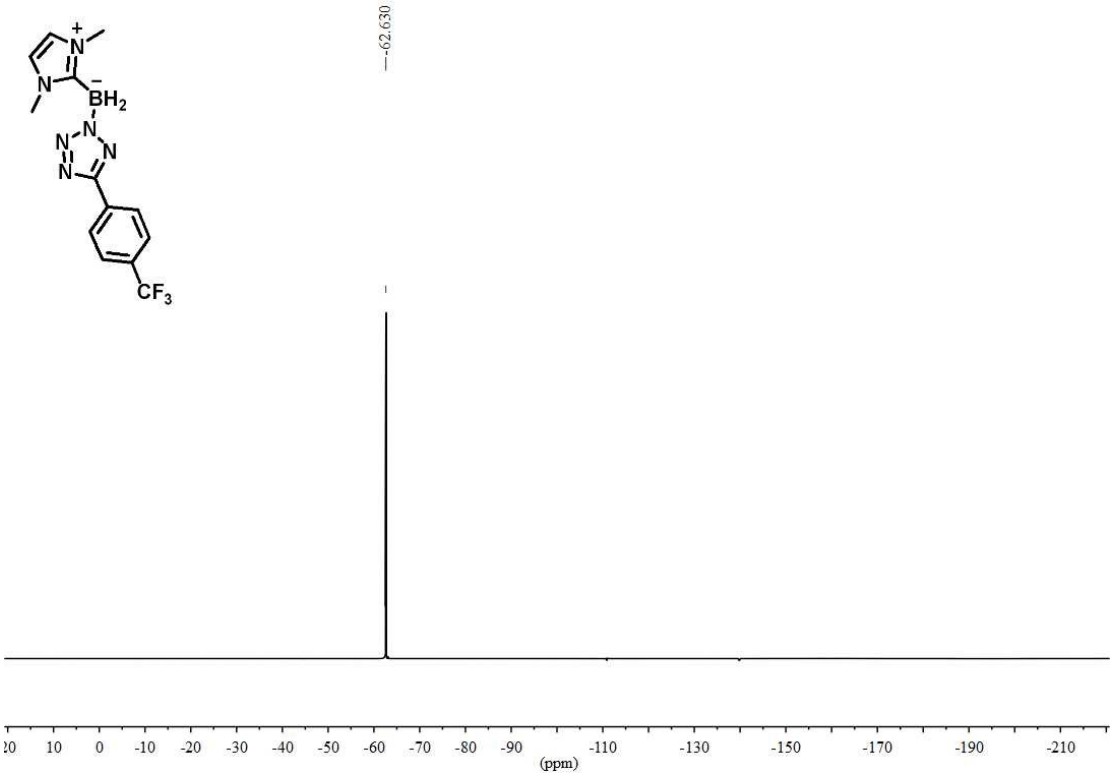
^{13}C NMR of product 5i in $CDCl_3$ (125 MHz)



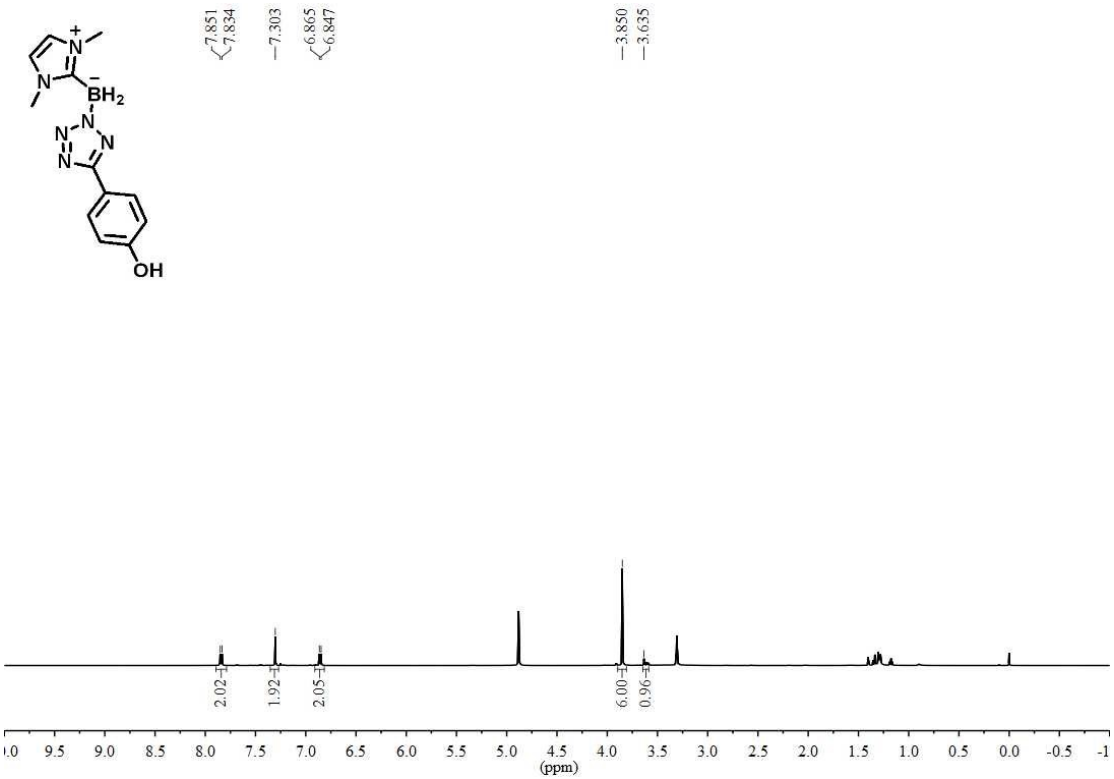
^{11}B NMR of product 5i in $CDCl_3$ (160 MHz)



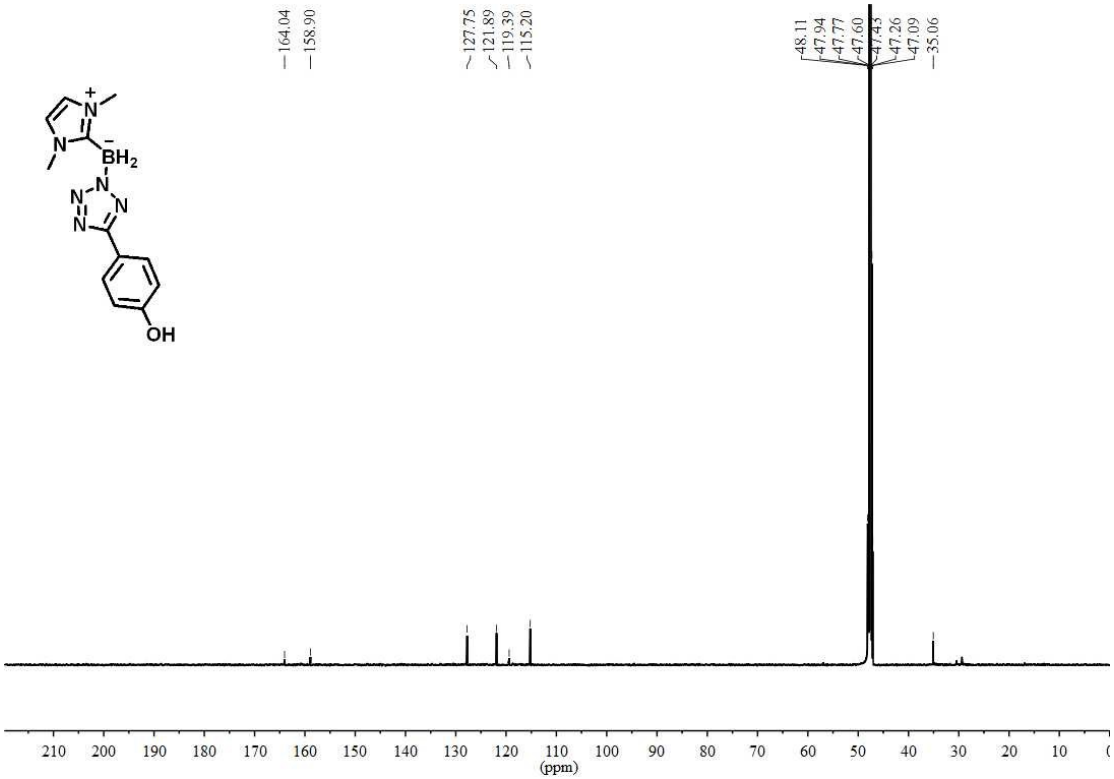
^{19}F NMR of product 5i in $CDCl_3$ (471 MHz)



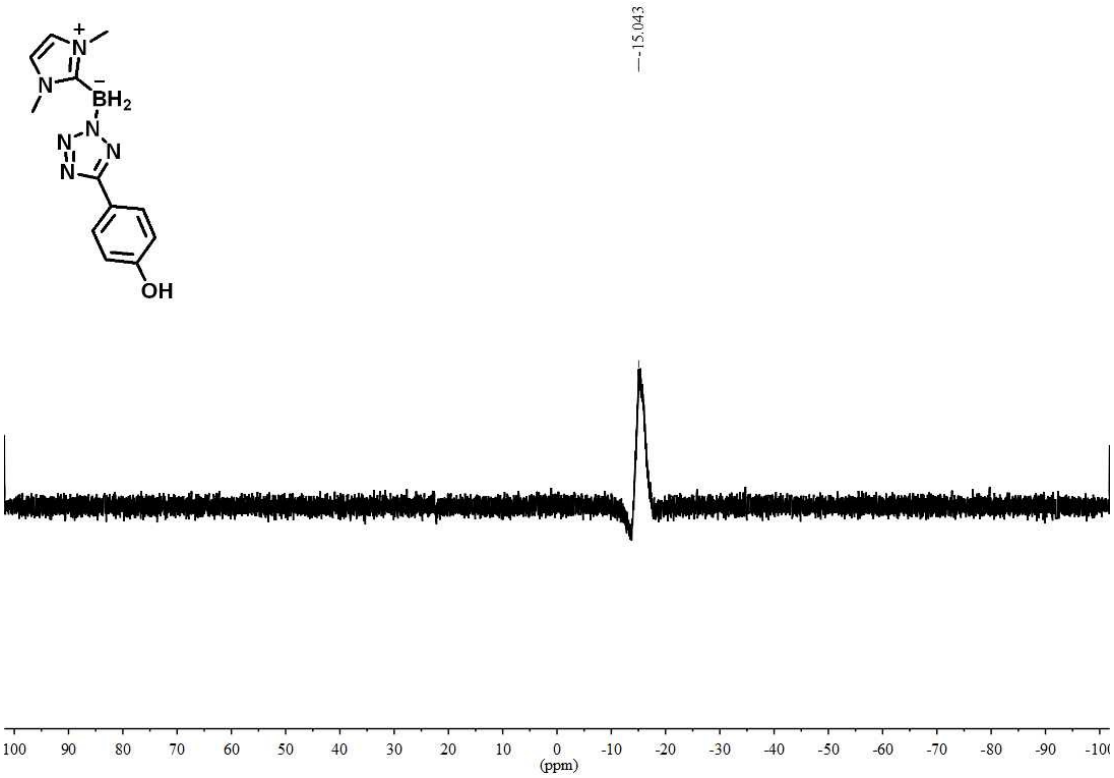
^{1}H NMR of product 5j in CD_3OD (500 MHz)



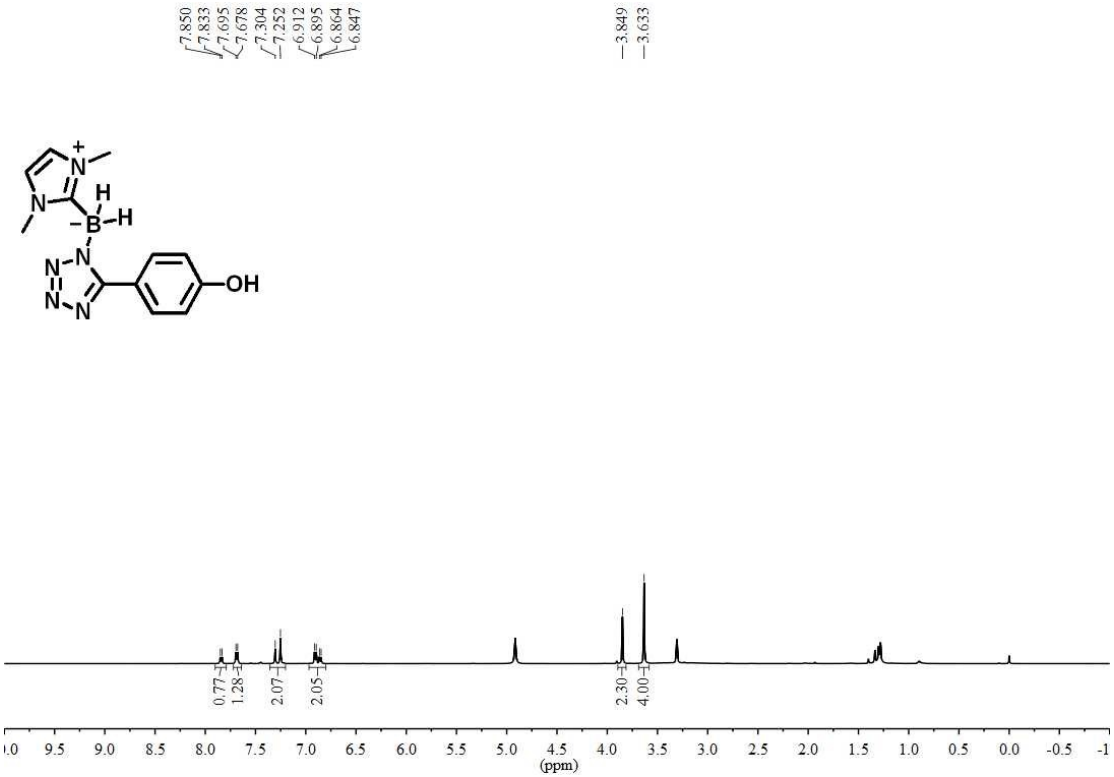
^{13}C NMR of product 5j in CD_3OD (125 MHz)



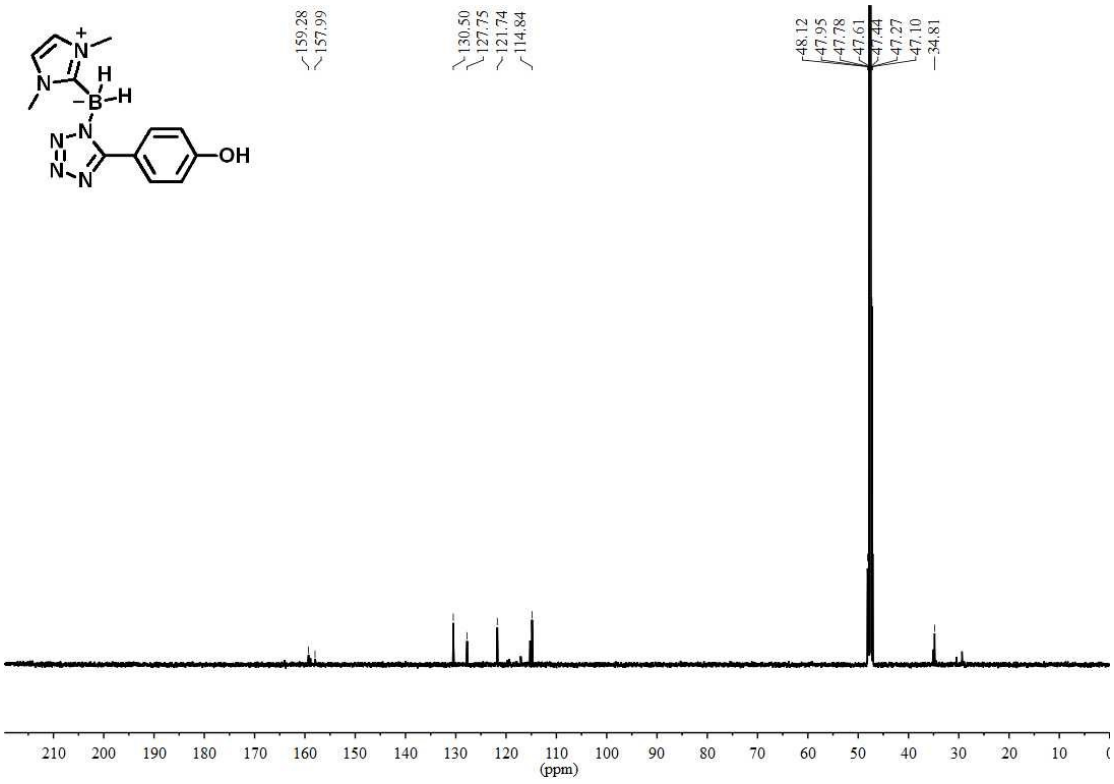
^{11}B NMR of product 5j in CD_3OD (160 MHz)



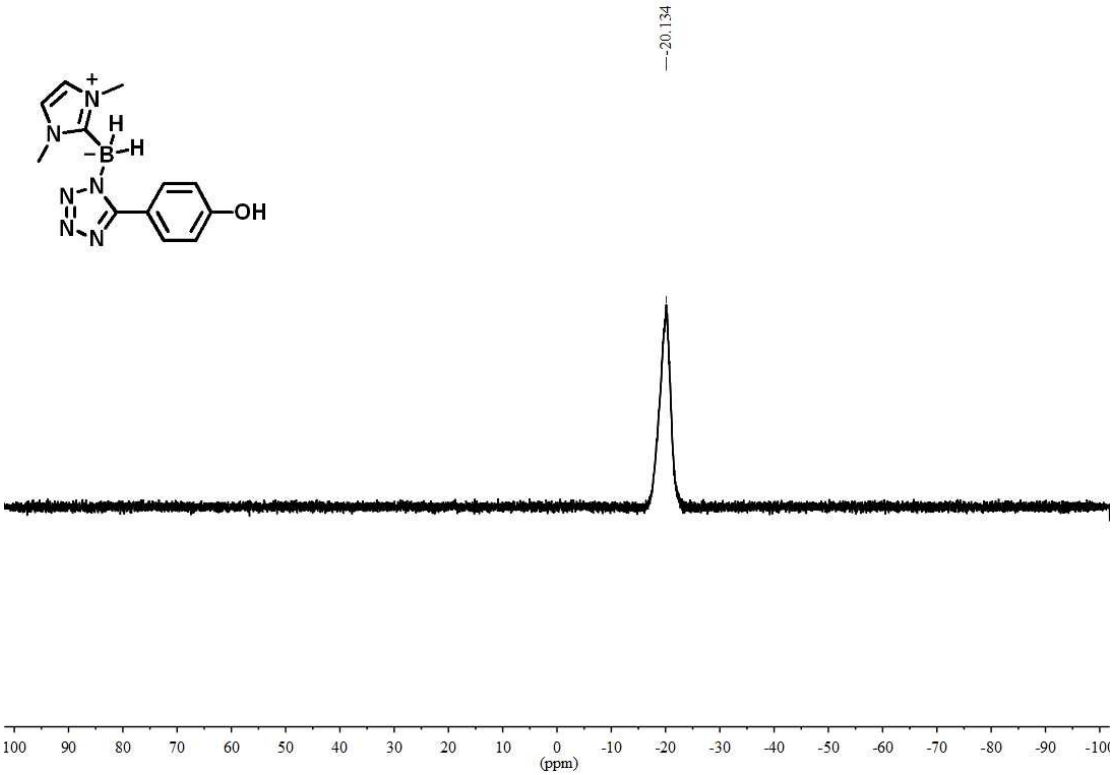
^{1}H NMR of product 5j' in CD_3OD (500 MHz)



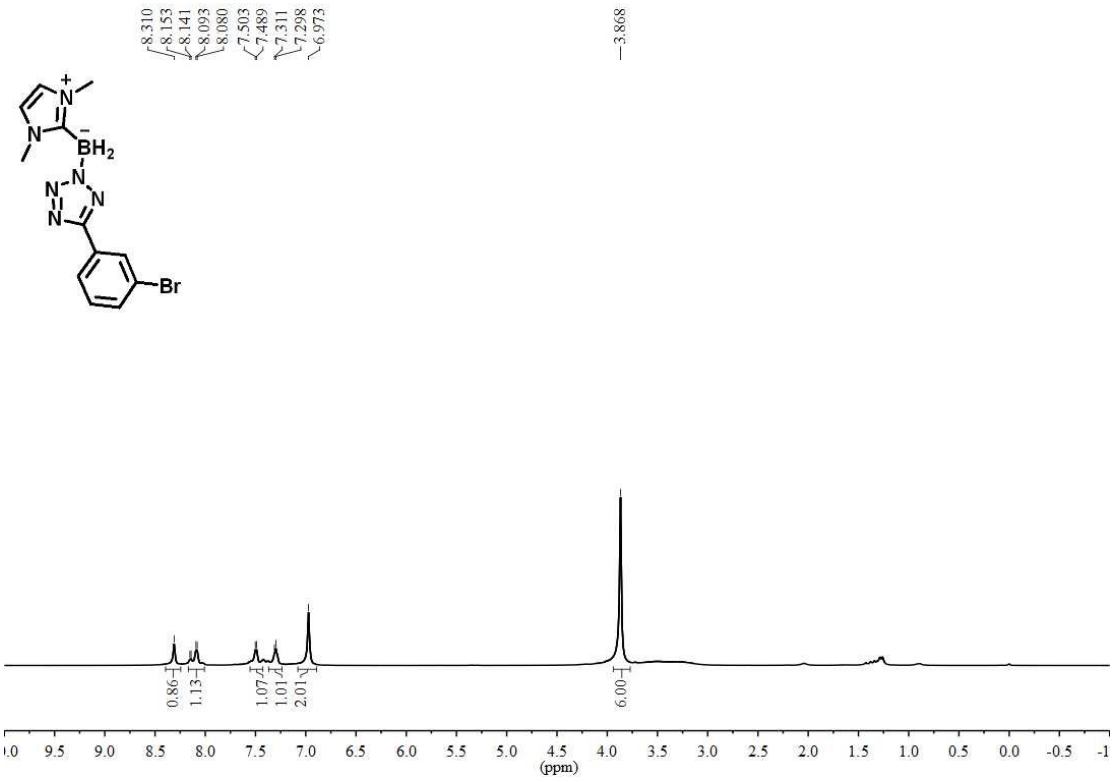
^{13}C NMR of product 5j' in CD_3OD (125 MHz)



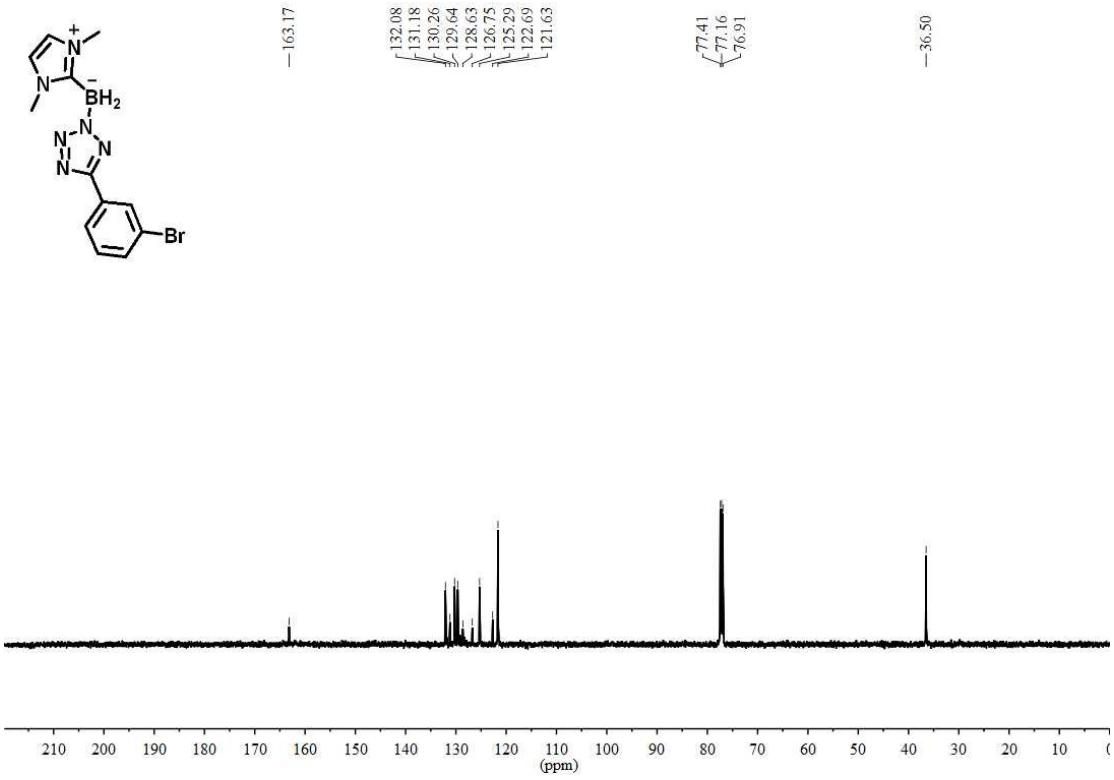
^{11}B NMR of product 5j' in CD_3OD (160 MHz)



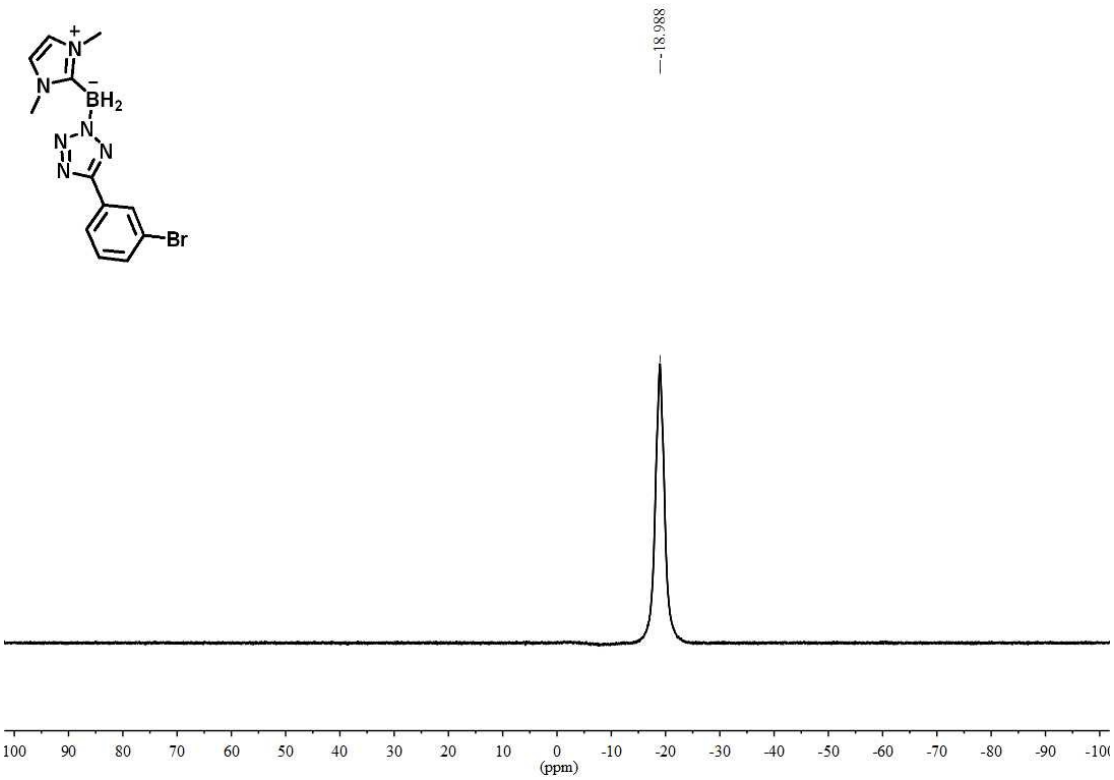
^{1}H NMR of product 5k in $CDCl_3$ (500 MHz)



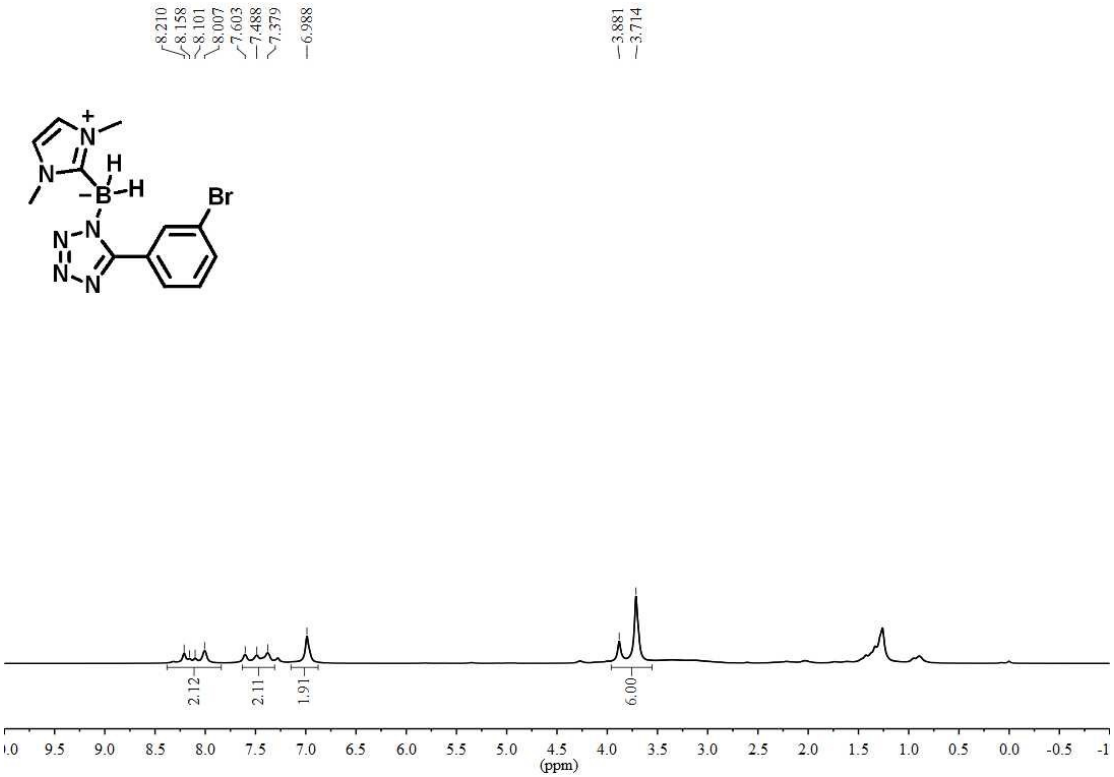
^{13}C NMR of product 5k in $CDCl_3$ (125 MHz)



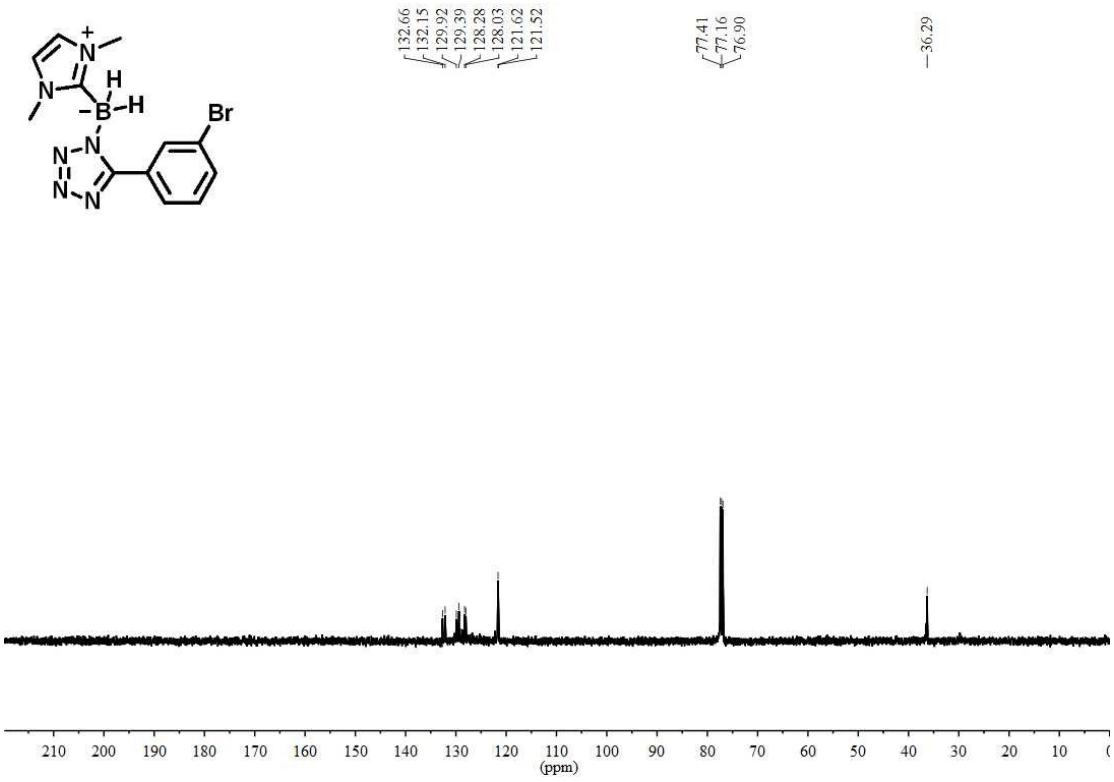
^{11}B NMR of product in 5k $CDCl_3$ (160 MHz)



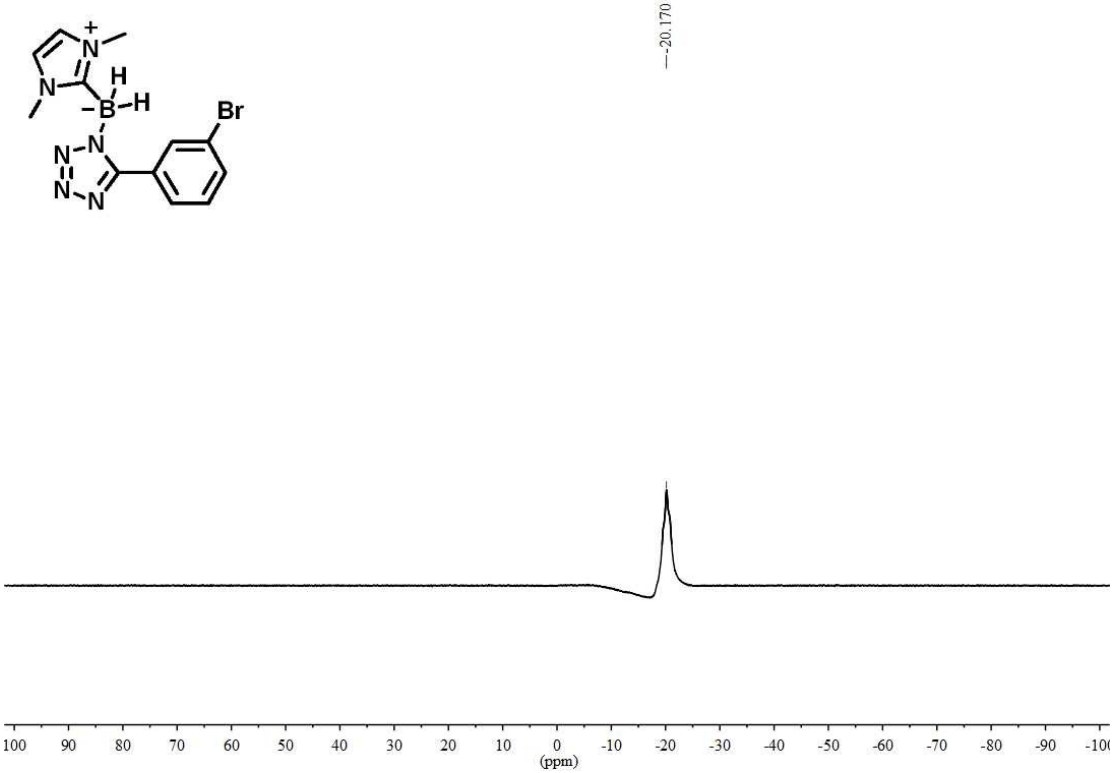
^{1}H NMR of product 5k' in $CDCl_3$ (500 MHz)



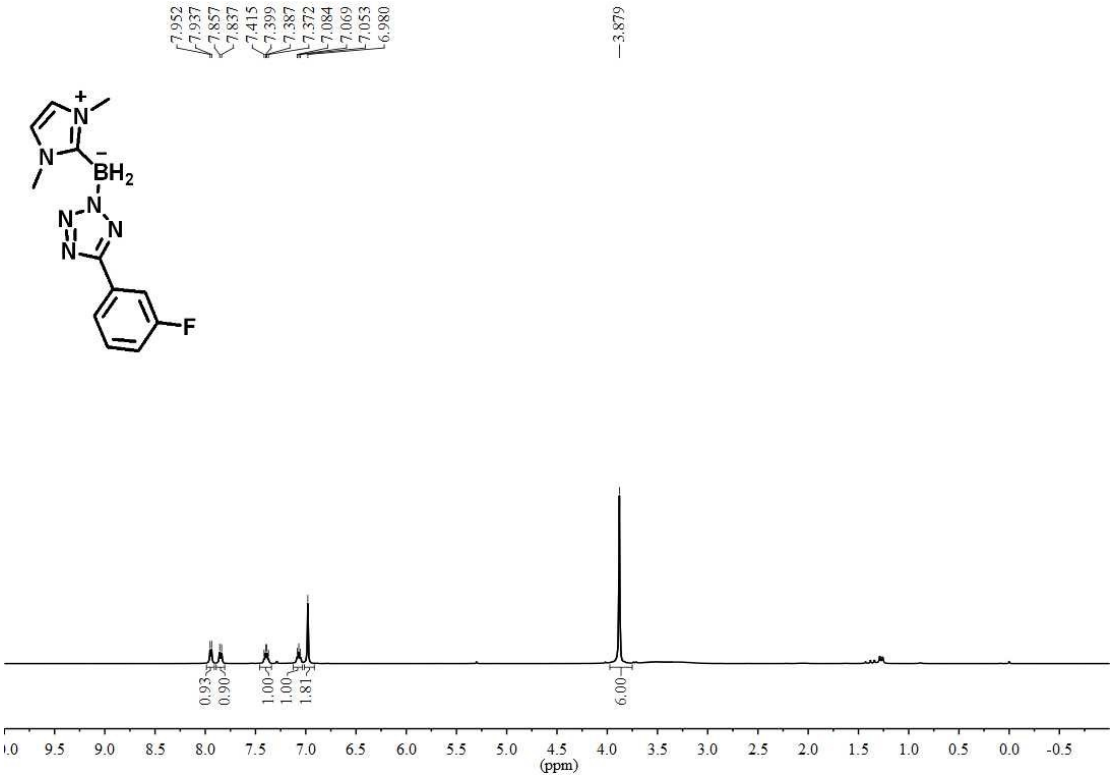
^{13}C NMR of product 5k' in $CDCl_3$ (125 MHz)



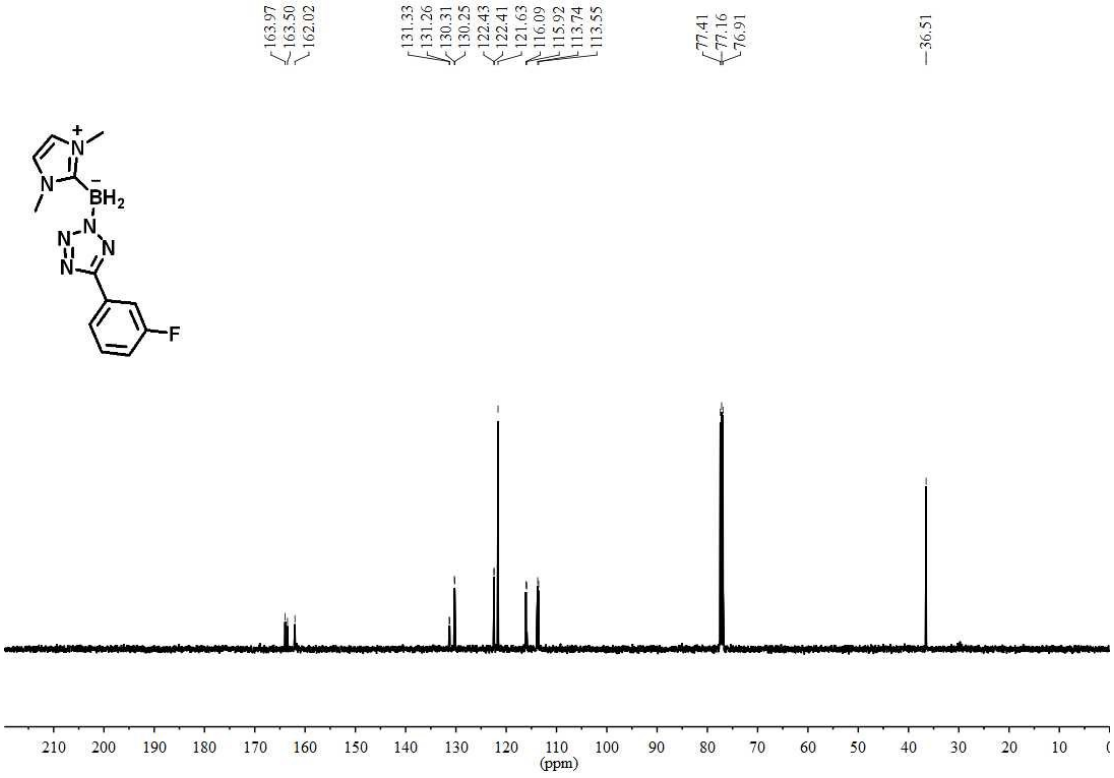
^{11}B NMR of product 5k' in $CDCl_3$ (160 MHz)



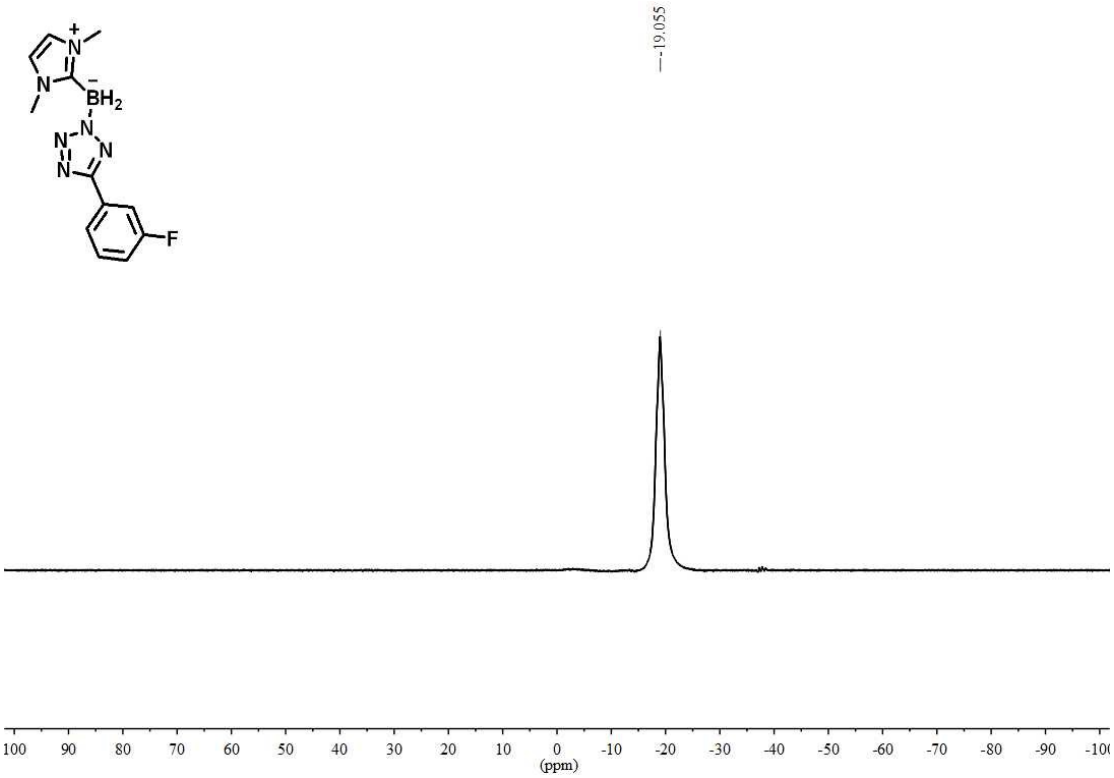
^{1}H NMR of product 5l in $CDCl_3$ (500 MHz)



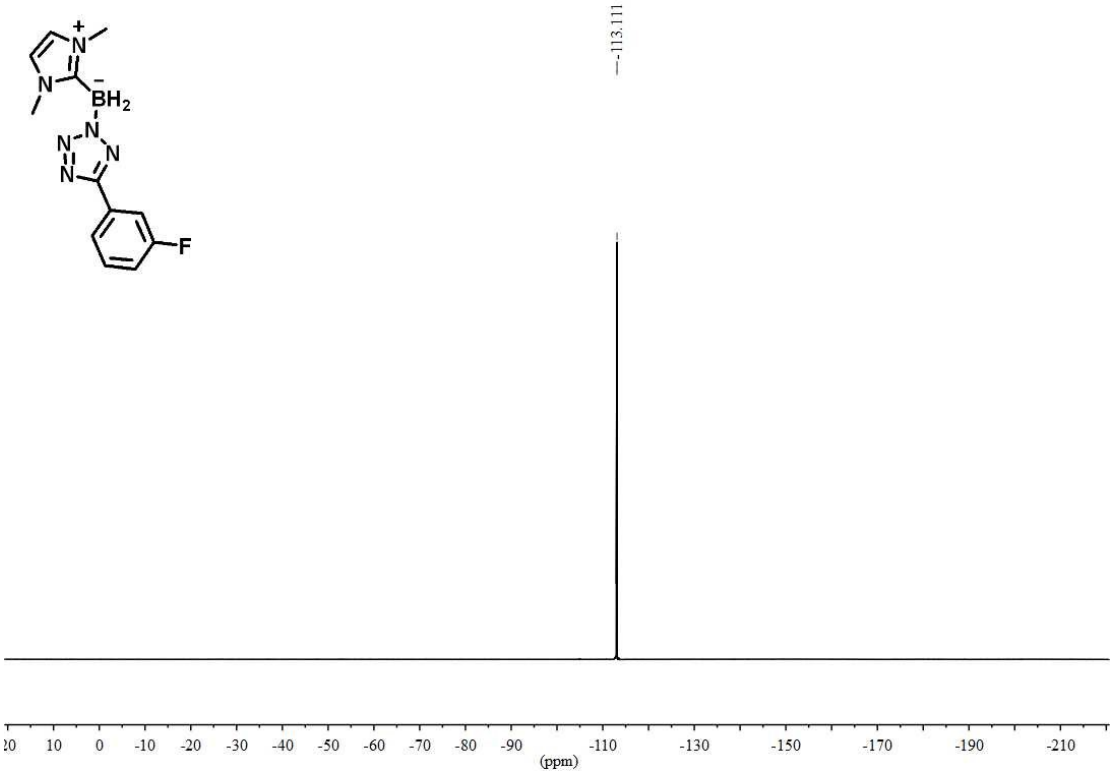
^{13}C NMR of product 5l in $CDCl_3$ (125 MHz)



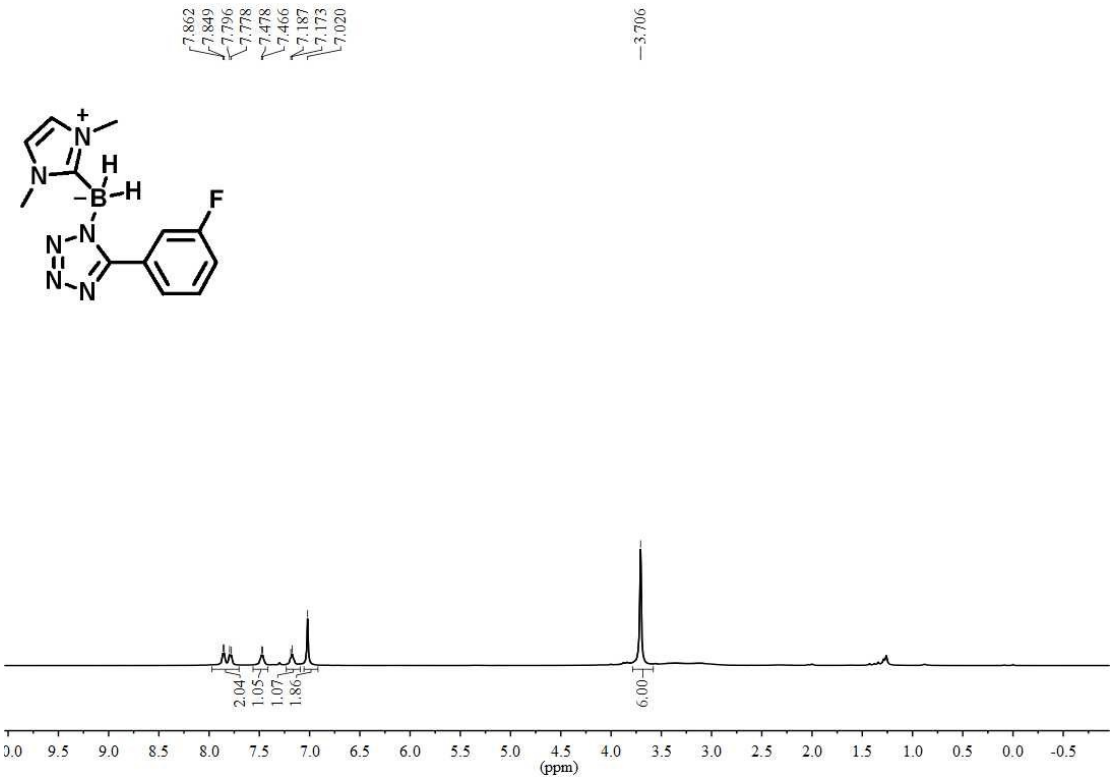
^{11}B NMR of product in 5l $CDCl_3$ (160 MHz)



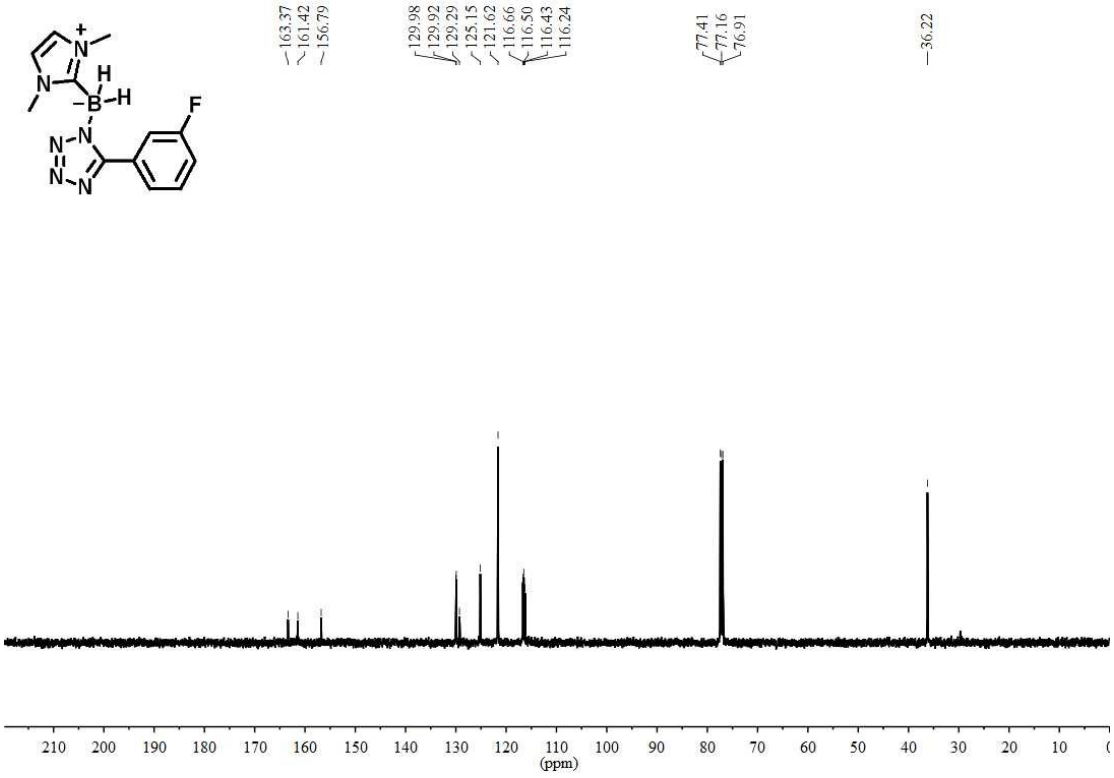
^{19}F NMR of product 5l in $CDCl_3$ (471 MHz)



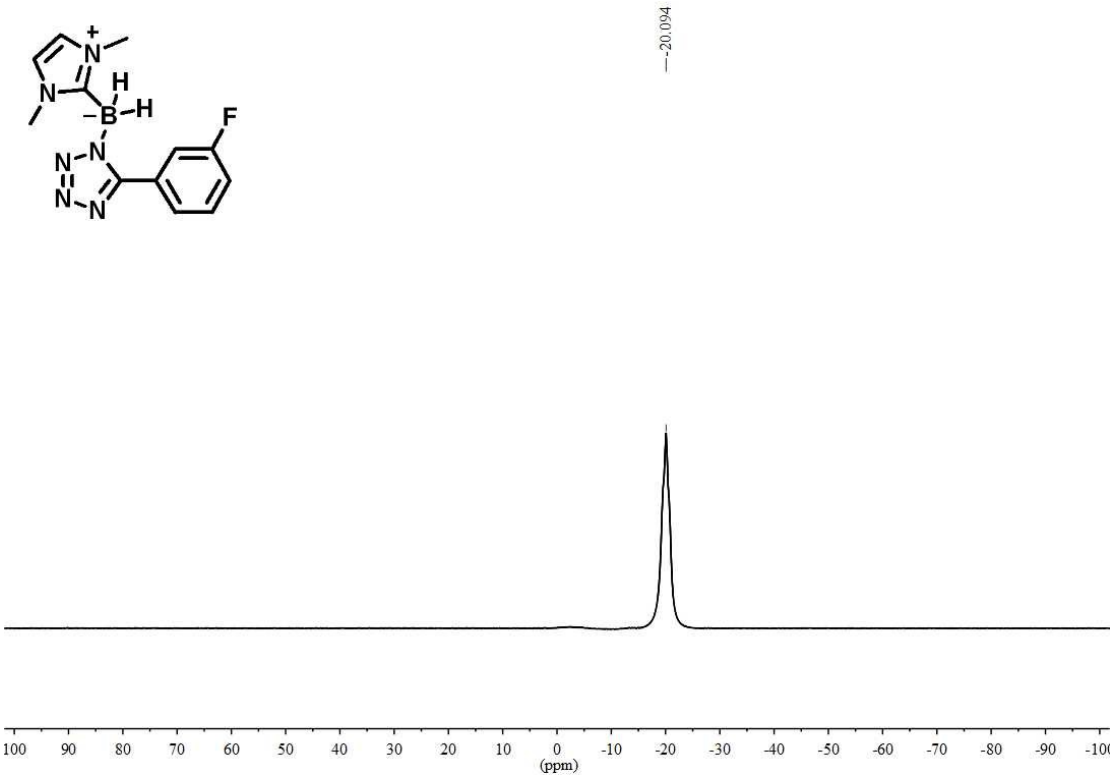
^{1}H NMR of product 5l' in $CDCl_3$ (500 MHz)



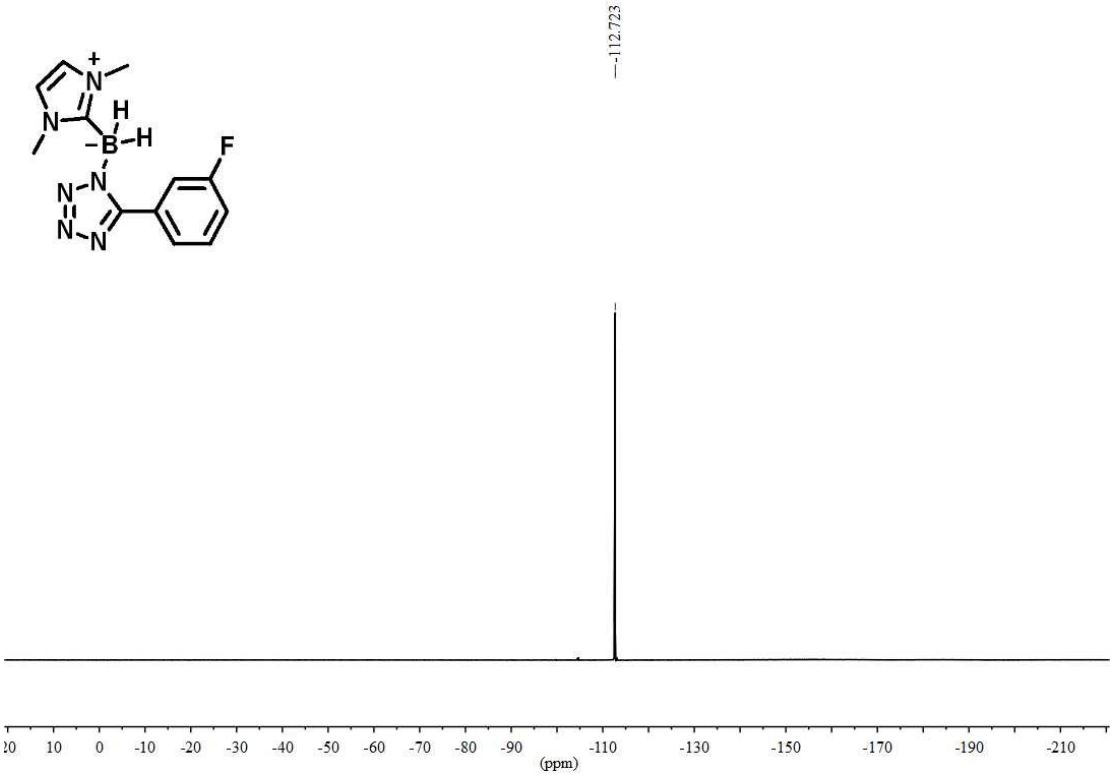
^{13}C NMR of product 5l' in $CDCl_3$ (125 MHz)



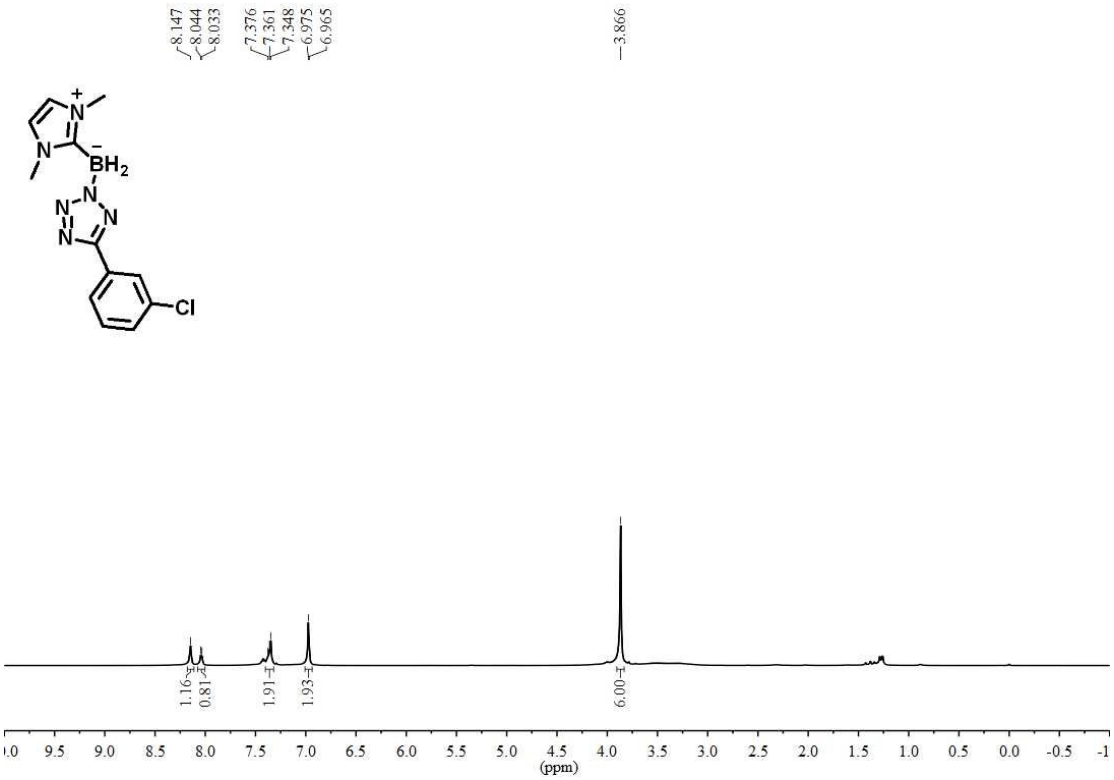
^{11}B NMR of product 5l' in $CDCl_3$ (160 MHz)



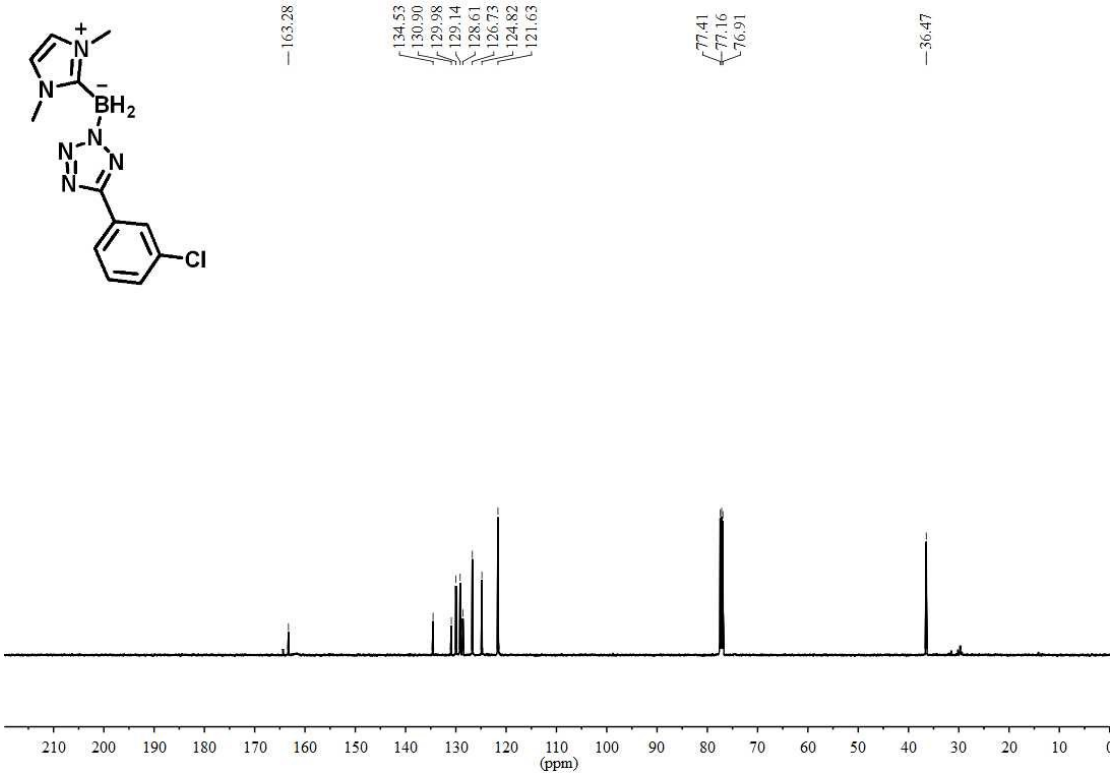
^{19}F NMR of product 5l'in $CDCl_3$ (471 MHz)



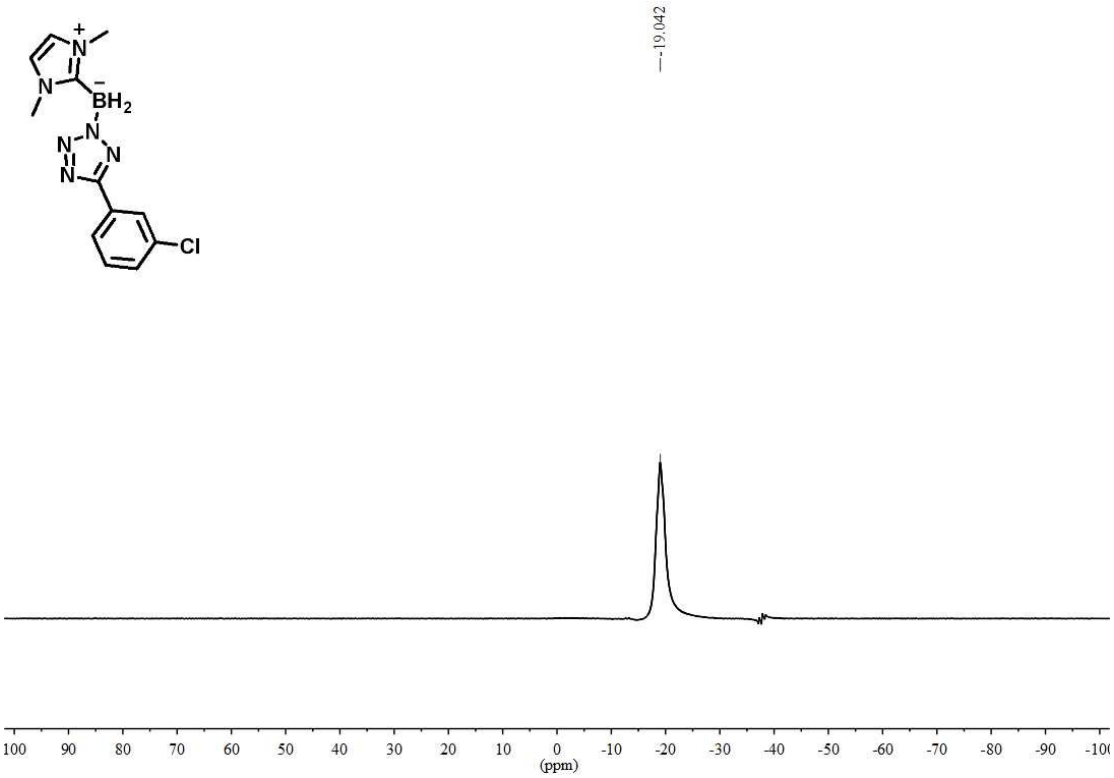
^{1}H NMR of product 5m in $CDCl_3$ (500 MHz)



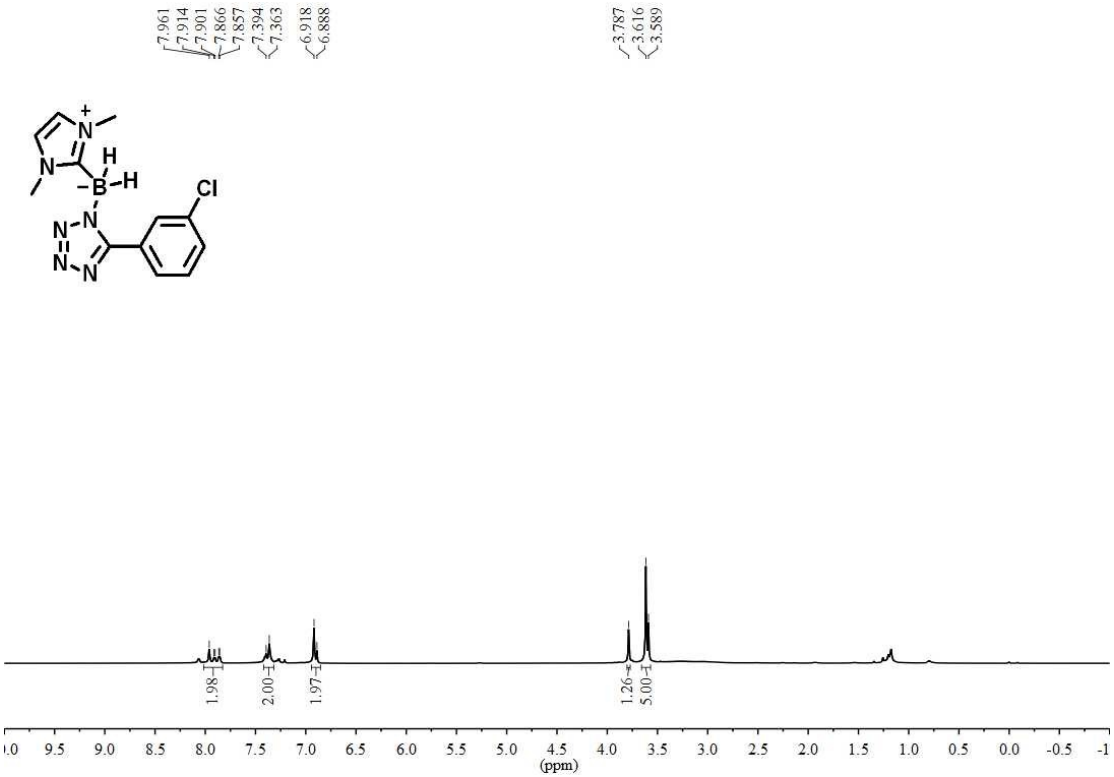
^{13}C NMR of product 5m in $CDCl_3$ (125 MHz)



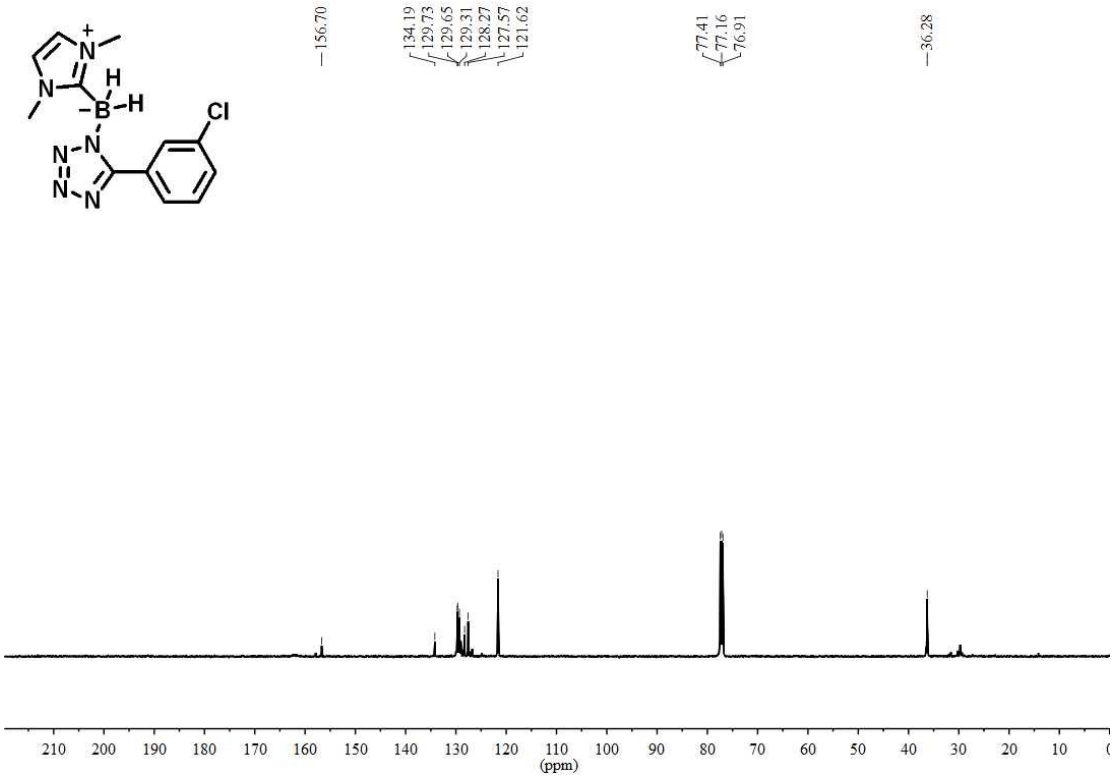
^{11}B NMR of product 5m in $CDCl_3$ (160 MHz)



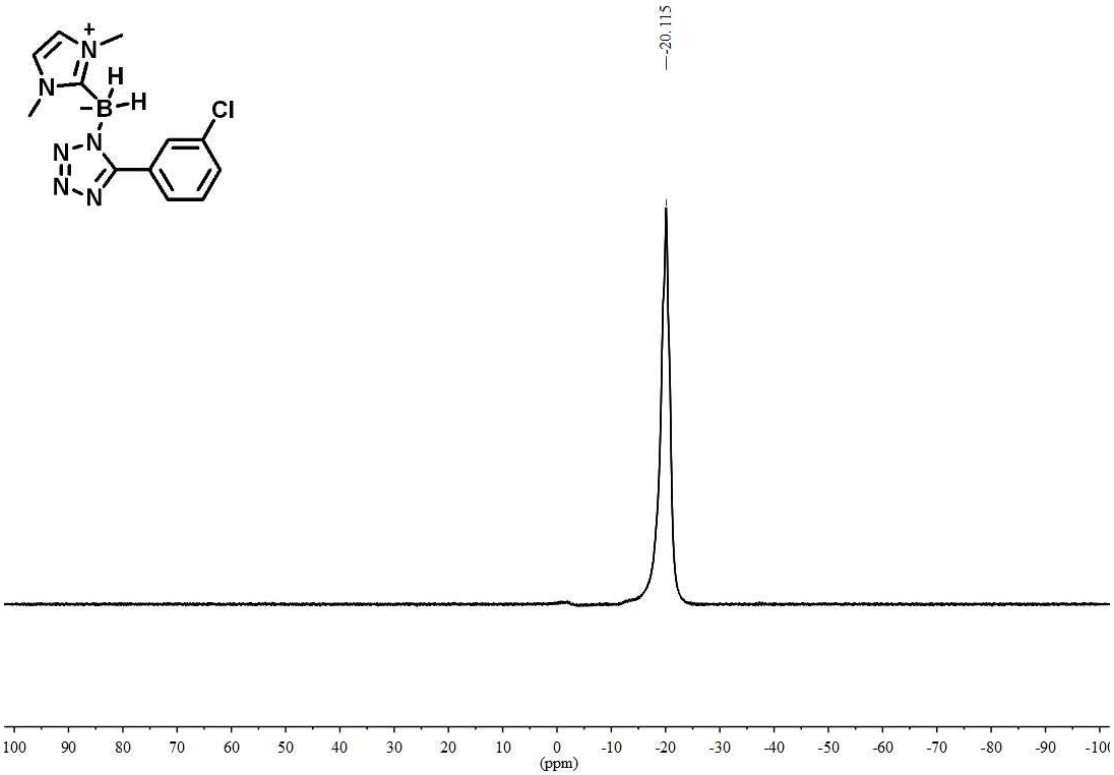
^{1}H NMR of product 5m' in $CDCl_3$ (500 MHz)



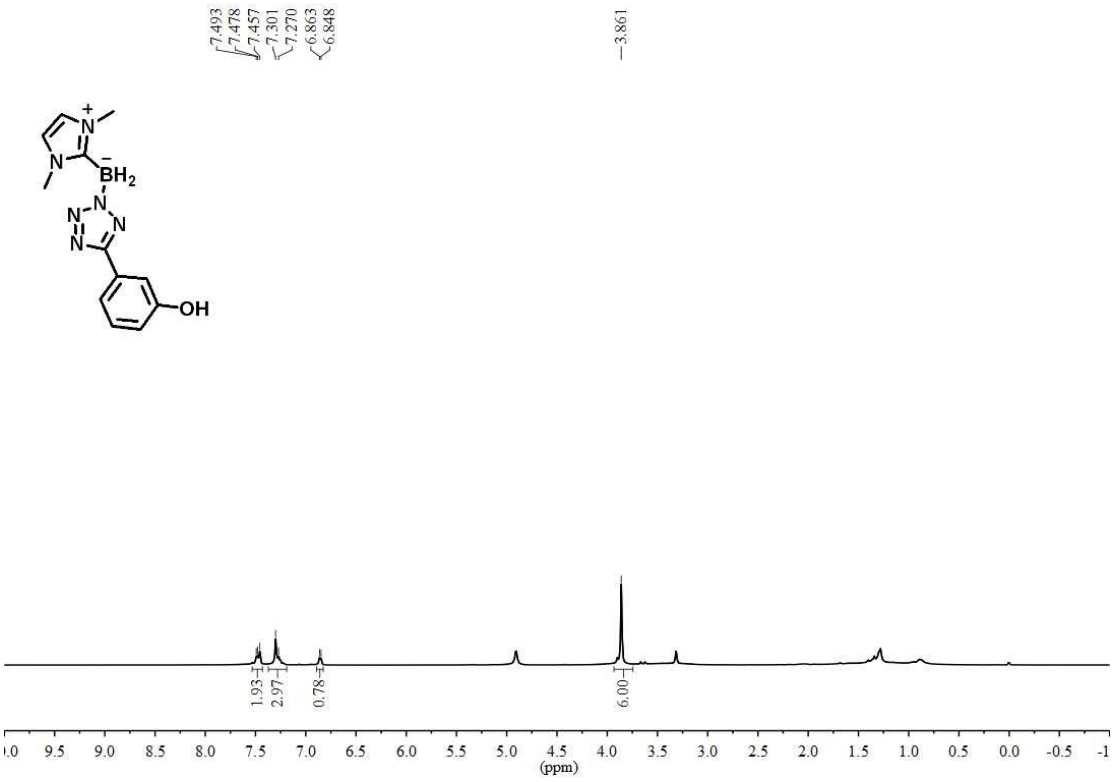
^{13}C NMR of product 5m' in $CDCl_3$ (125 MHz)



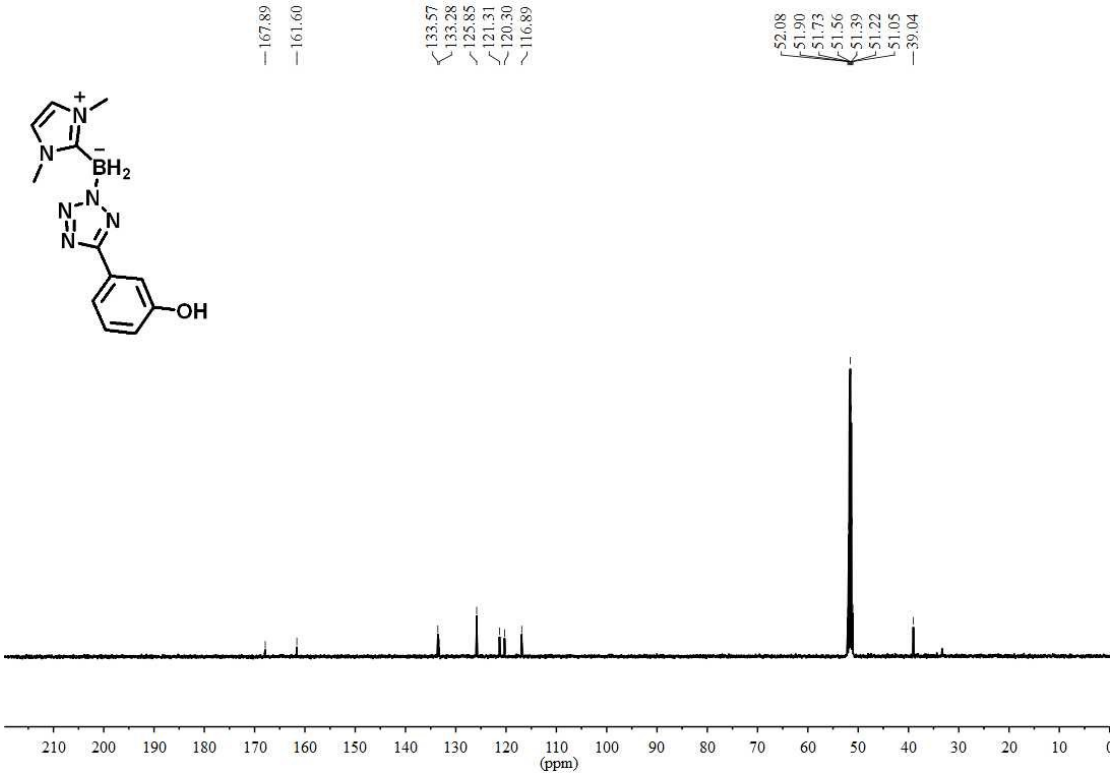
^{11}B NMR of product 5m' in $CDCl_3$ (160 MHz)



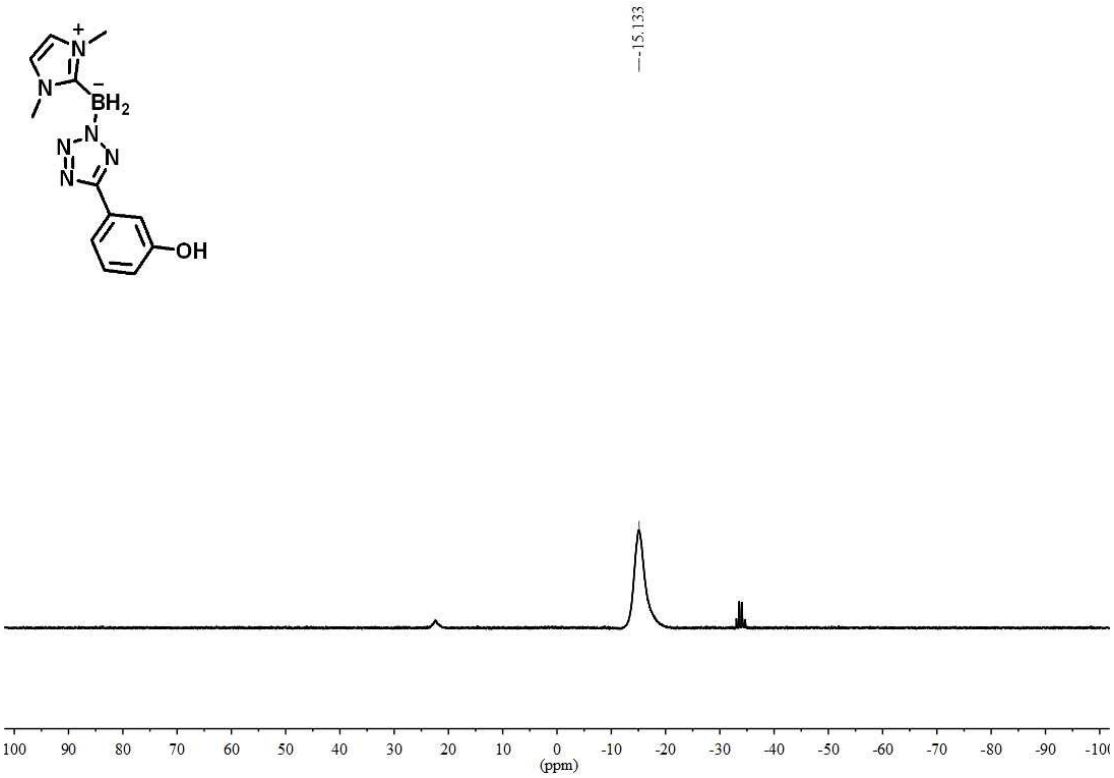
^{1}H NMR of product 5n in CD_2Cl_2 (500 MHz)



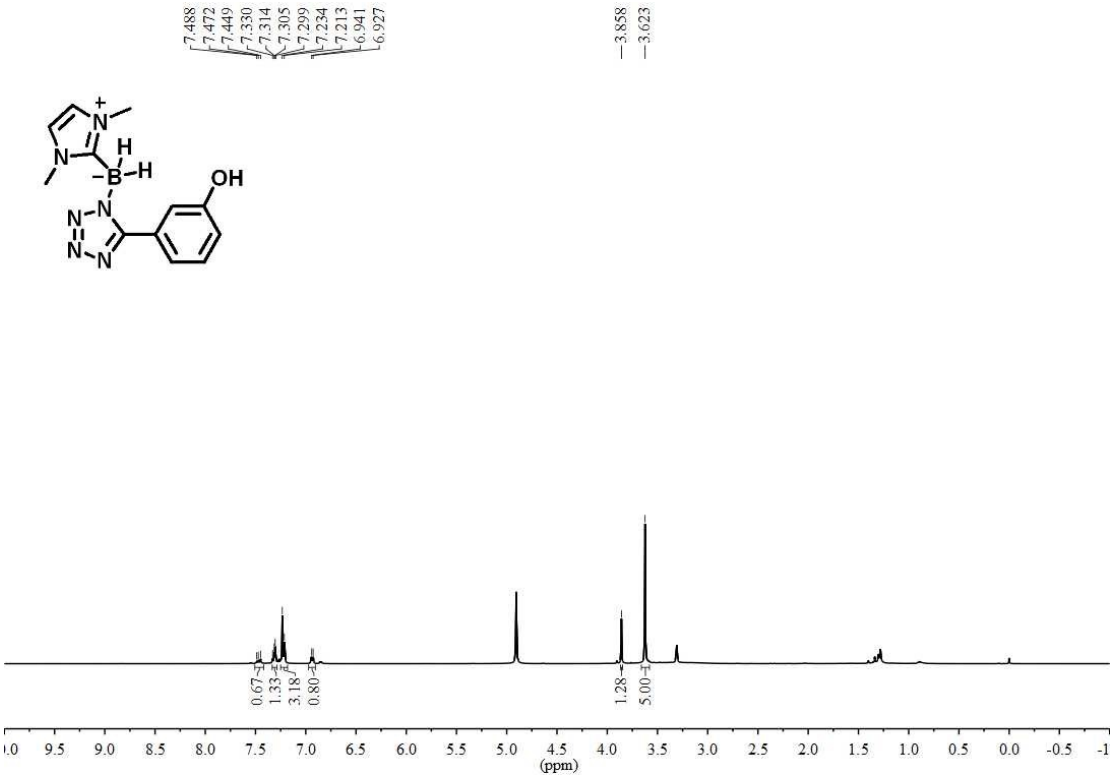
^{13}C NMR of product 5n in CD_2Cl_2 (125 MHz)



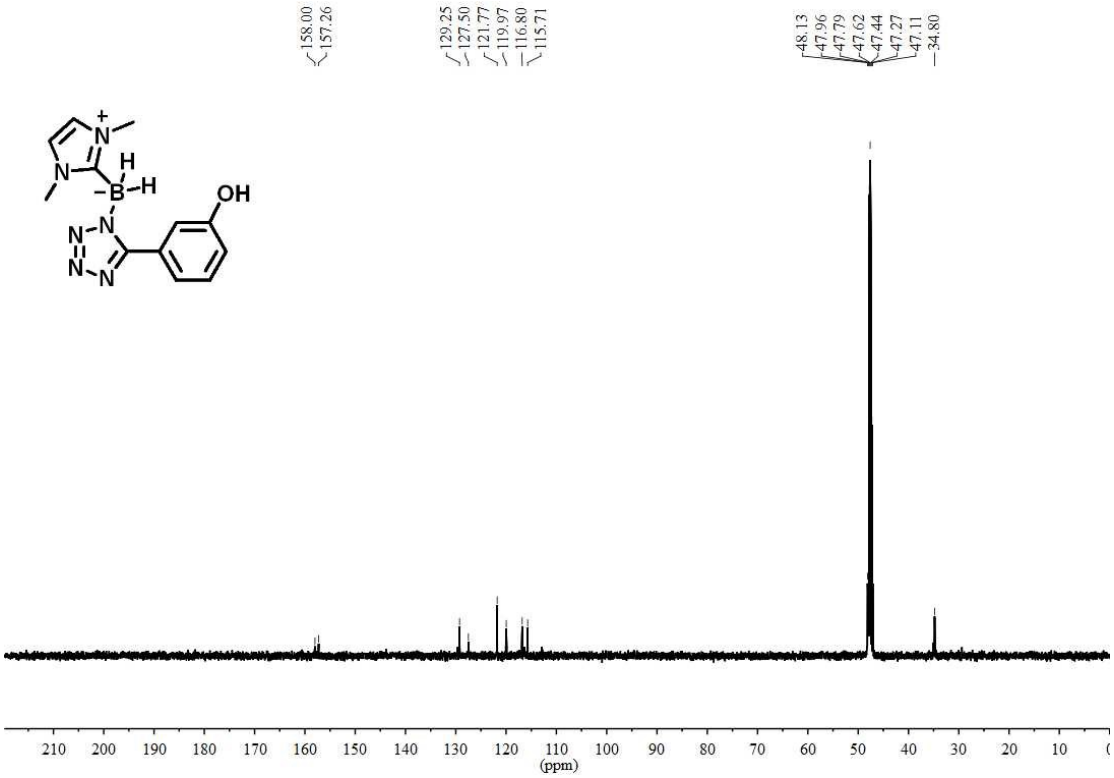
^{11}B NMR of product 5n in CD_2Cl_2 (160 MHz)



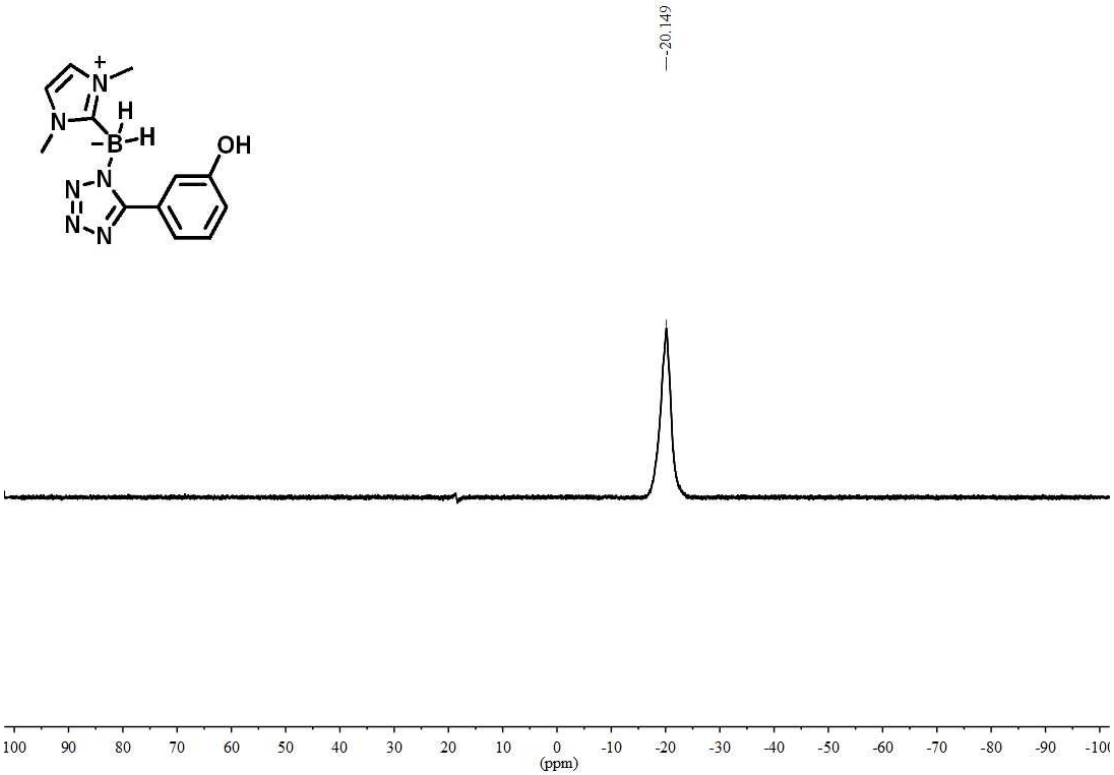
^{1}H NMR of product 5n' in CD_3OD (500 MHz)



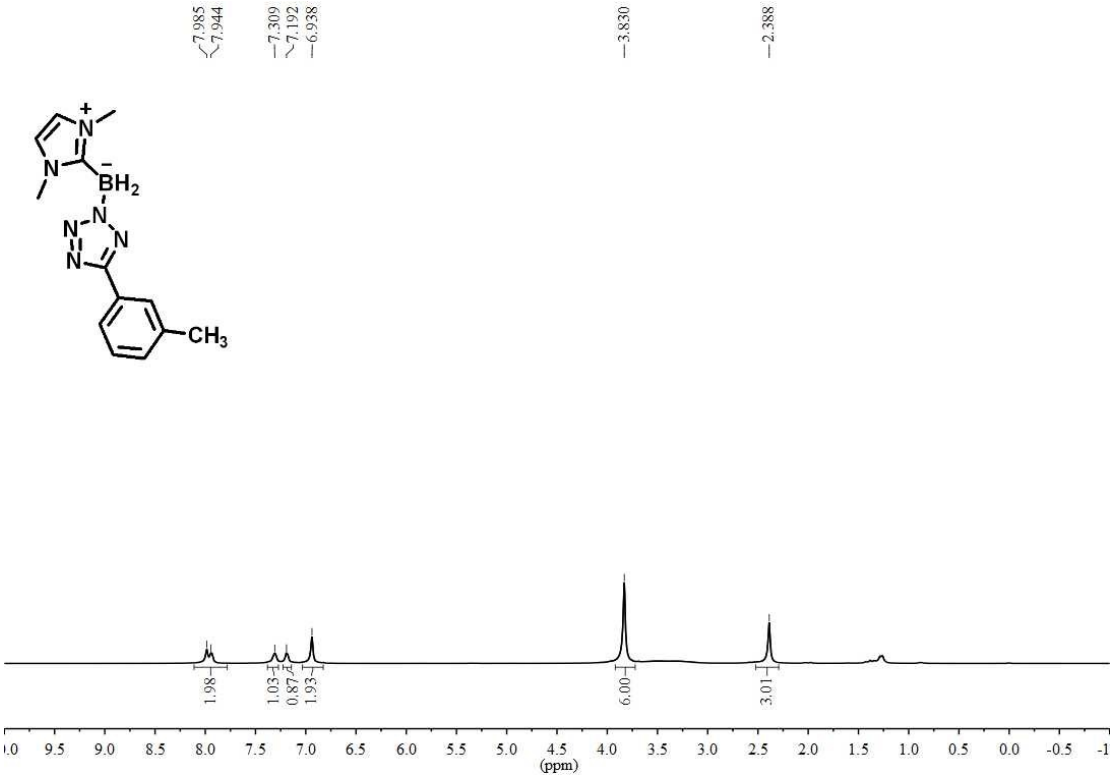
^{13}C NMR of product 5n' in CD_3OD (125 MHz)



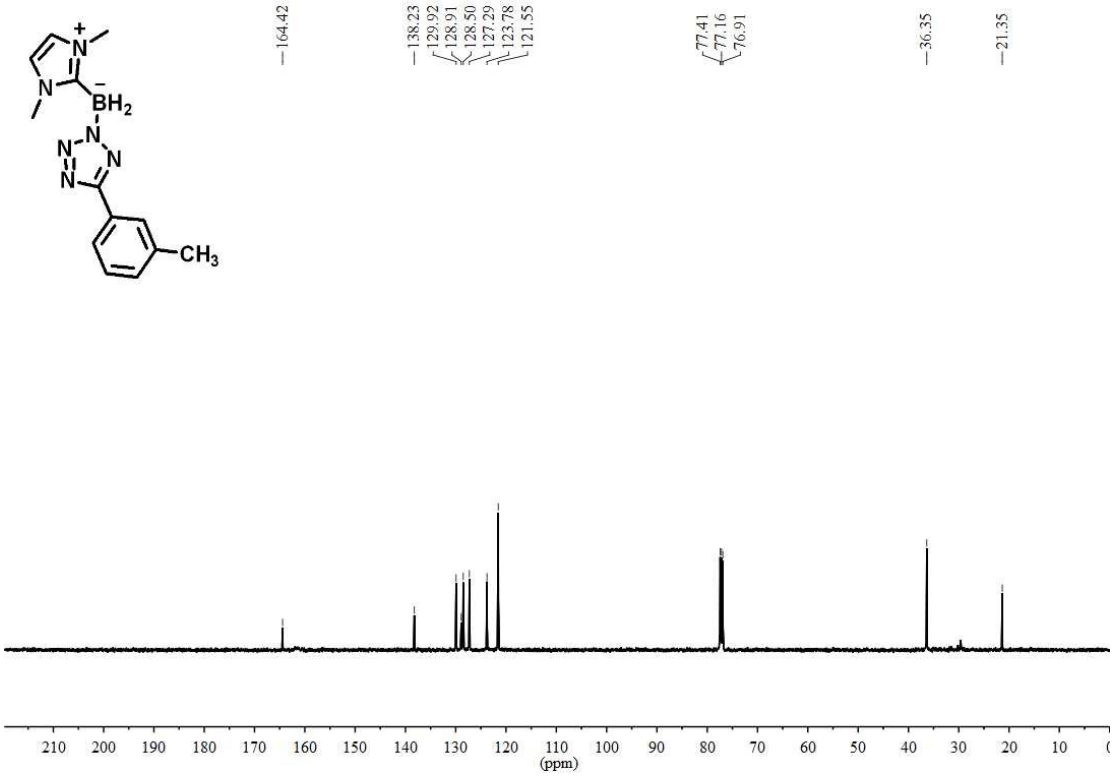
^{11}B NMR of product 5n' in CD_3OD (160 MHz)



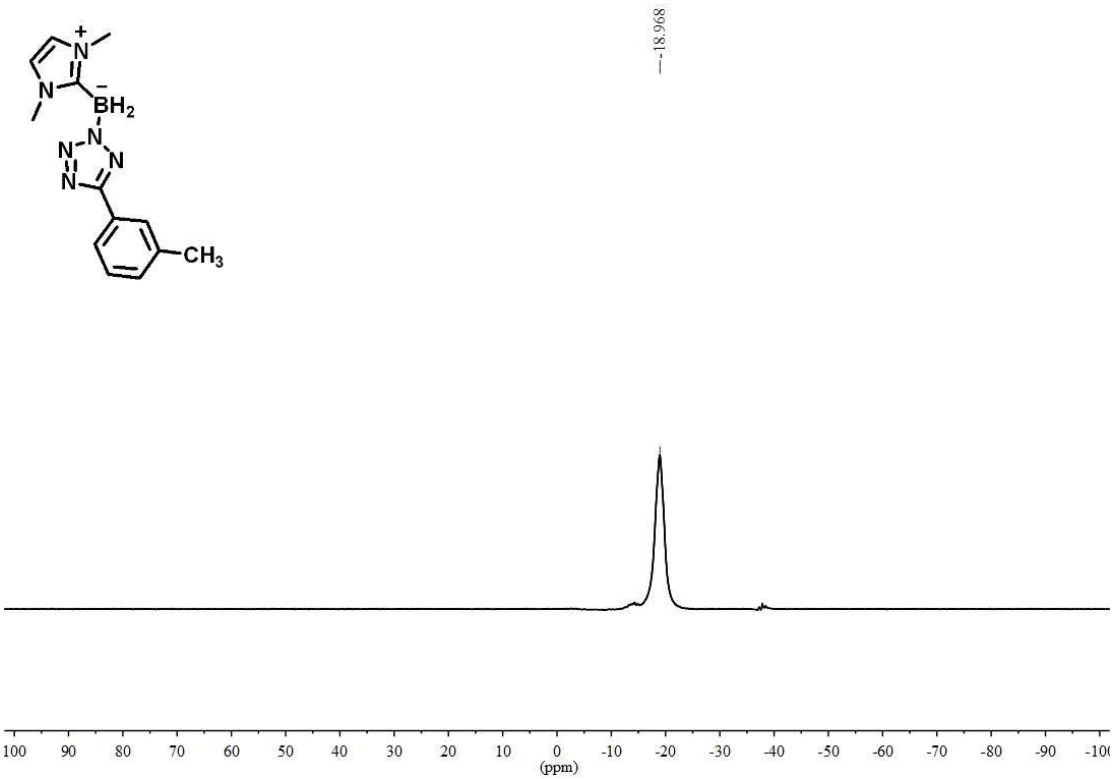
^{1}H NMR of product 5o in $CDCl_3$ (500 MHz)



^{13}C NMR of product 5o in $CDCl_3$ (125 MHz)



^{11}B NMR of product 5o in $CDCl_3$ (160 MHz)



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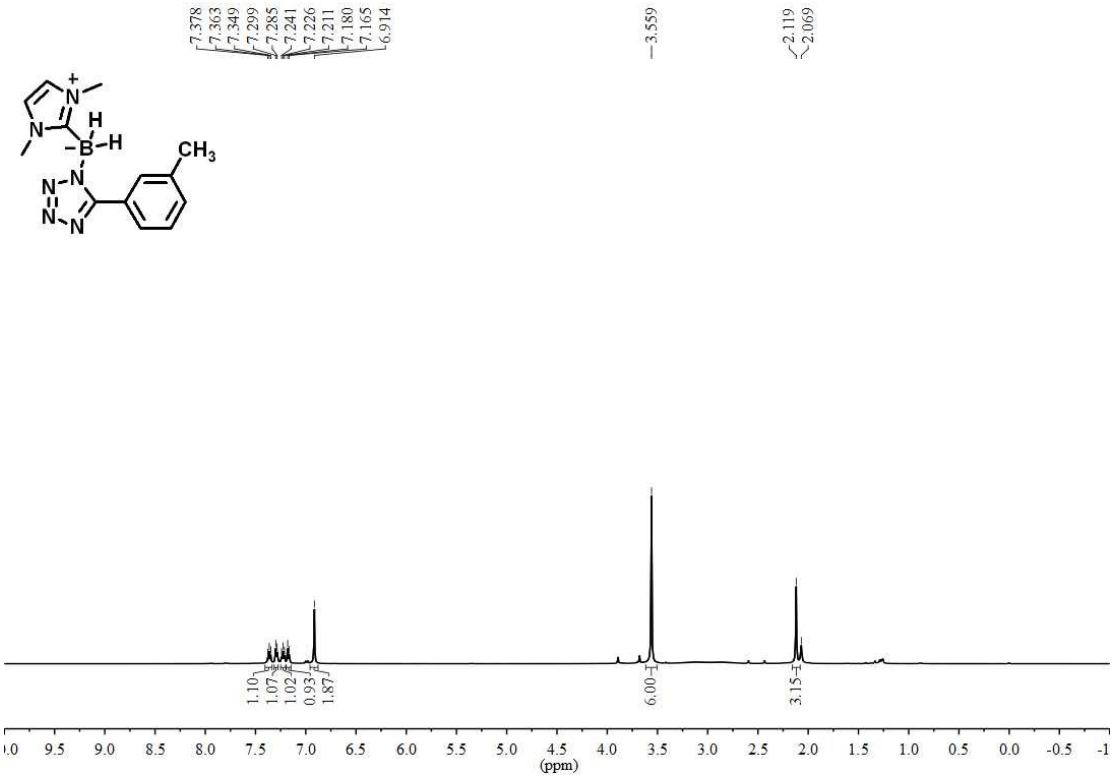
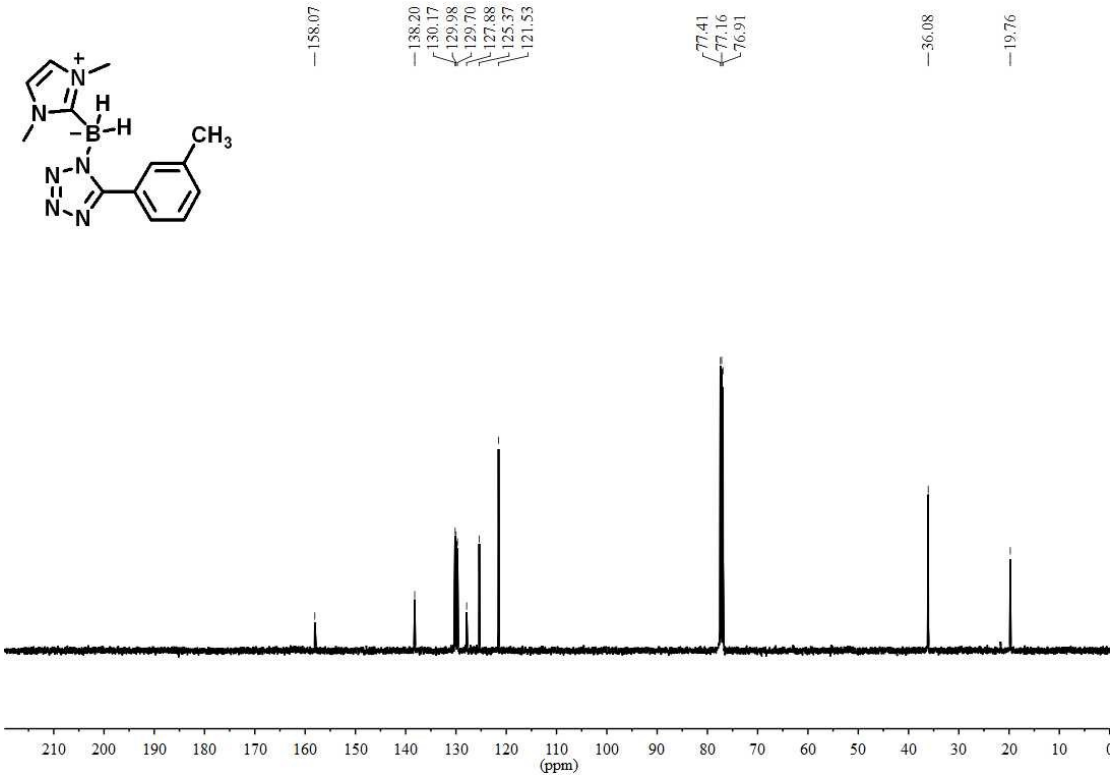
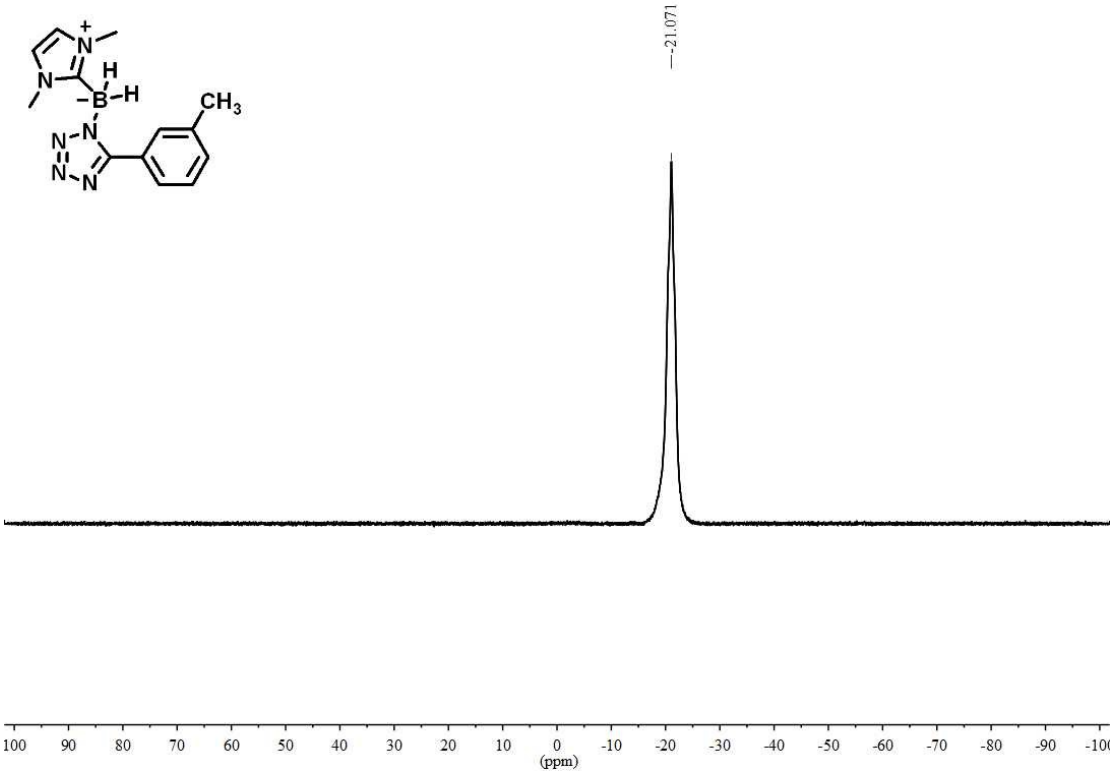


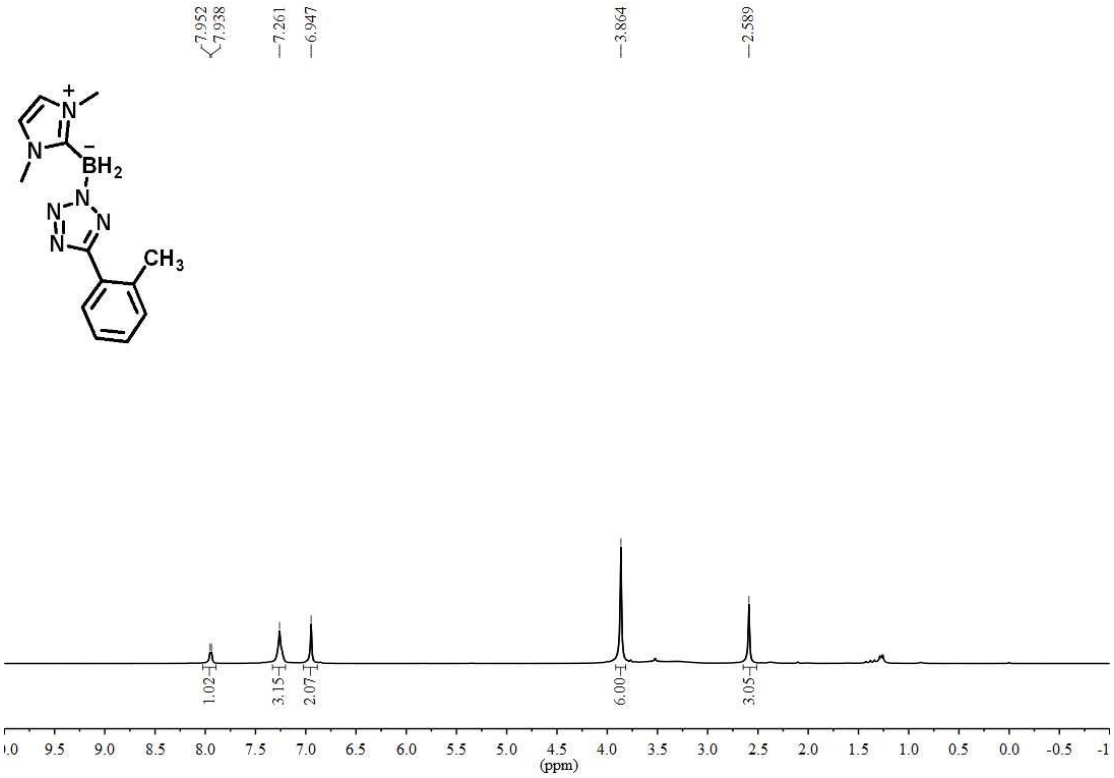
^{13}C NMR of product 5o' in $CDCl_3$ (125 MHz)



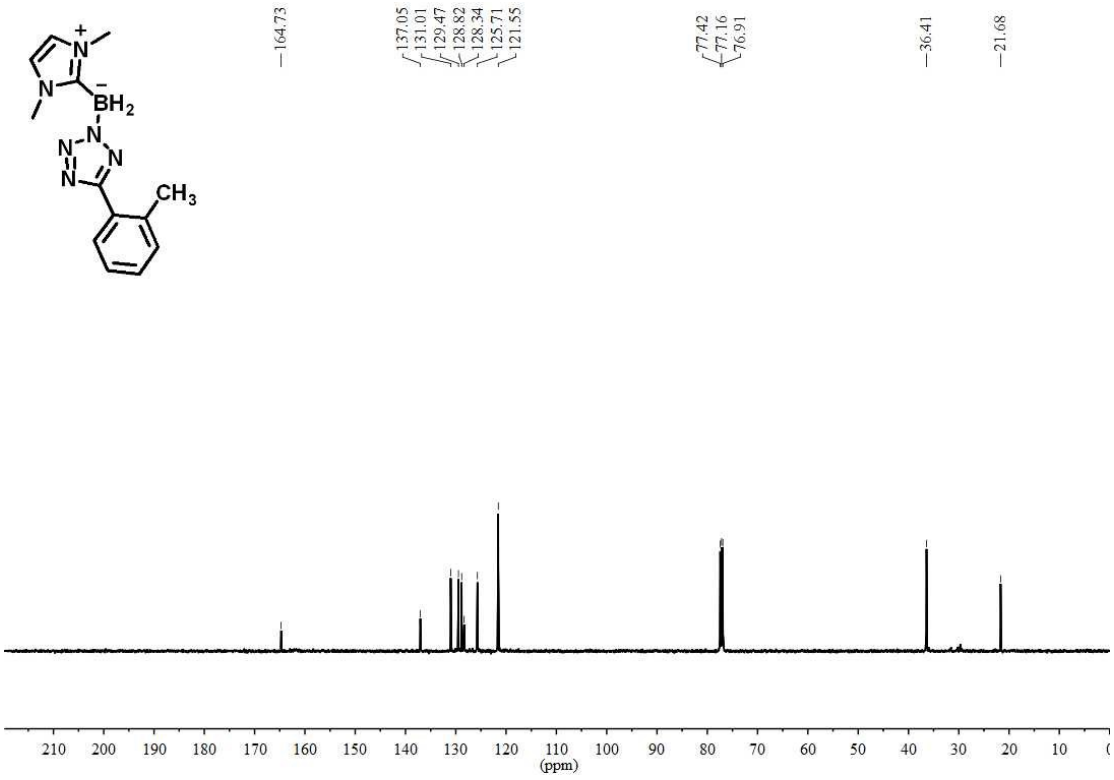
^{11}B NMR of product 5o' in $CDCl_3$ (160 MHz)



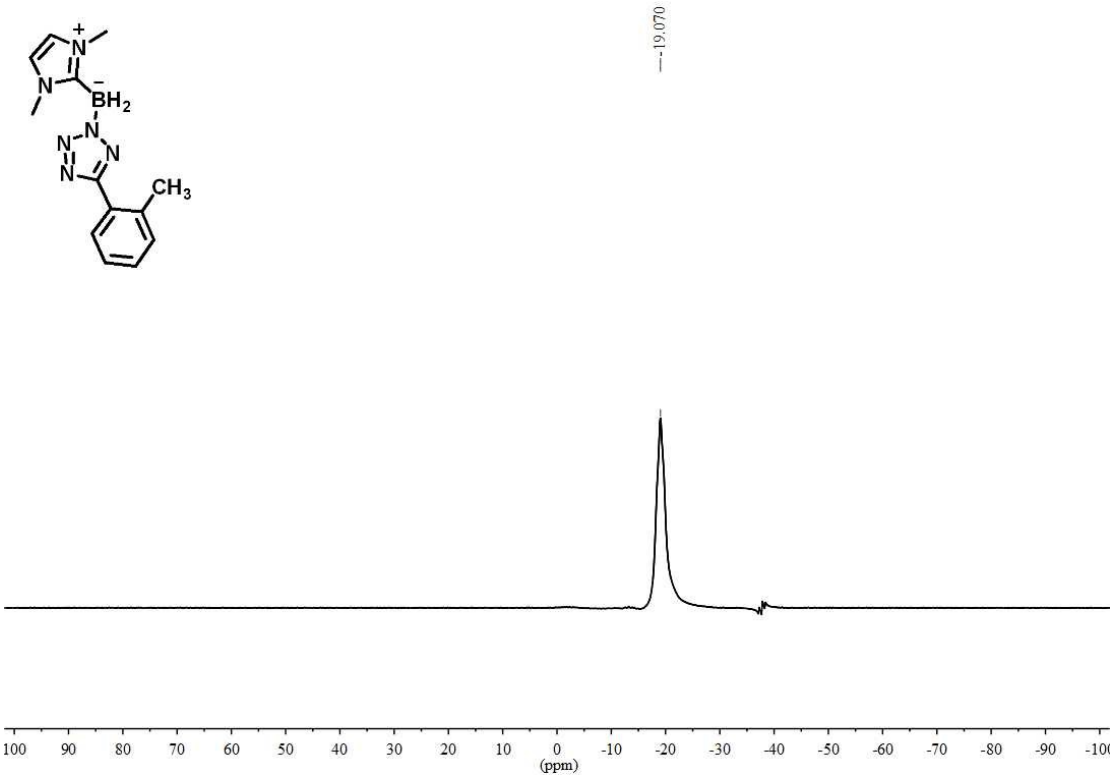
^{1}H NMR of product 5p in $CDCl_3$ (500 MHz)



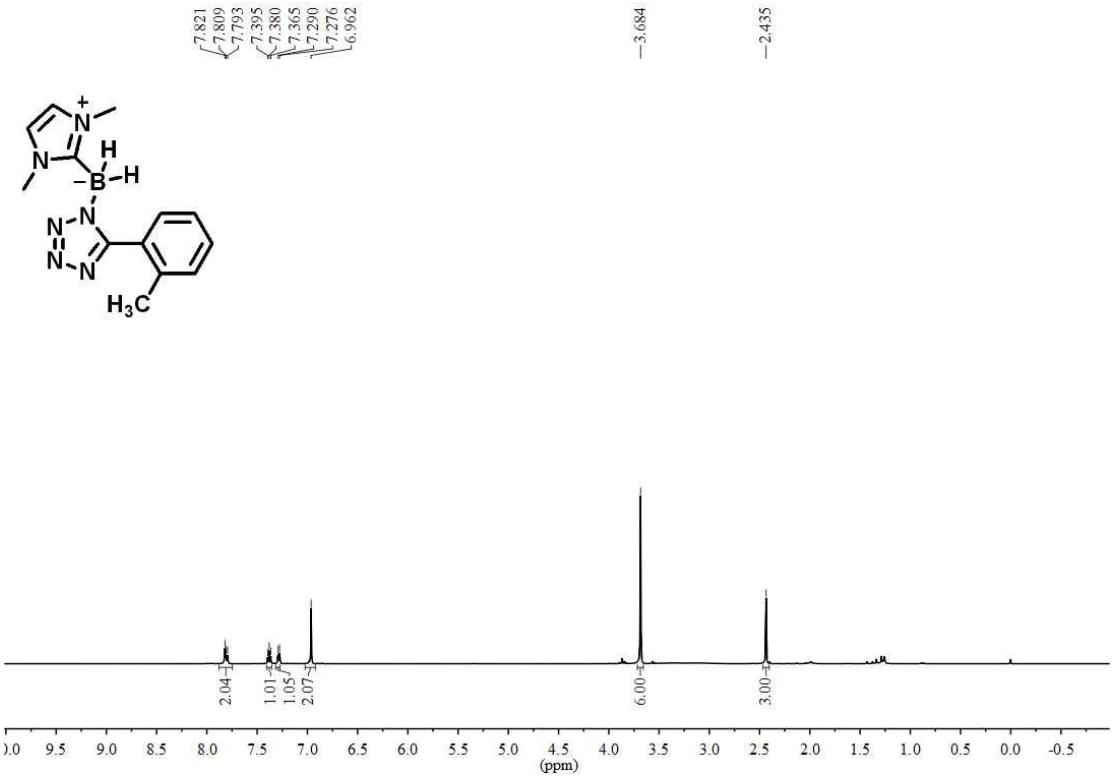
^{13}C NMR of product 5p in $CDCl_3$ (125 MHz)



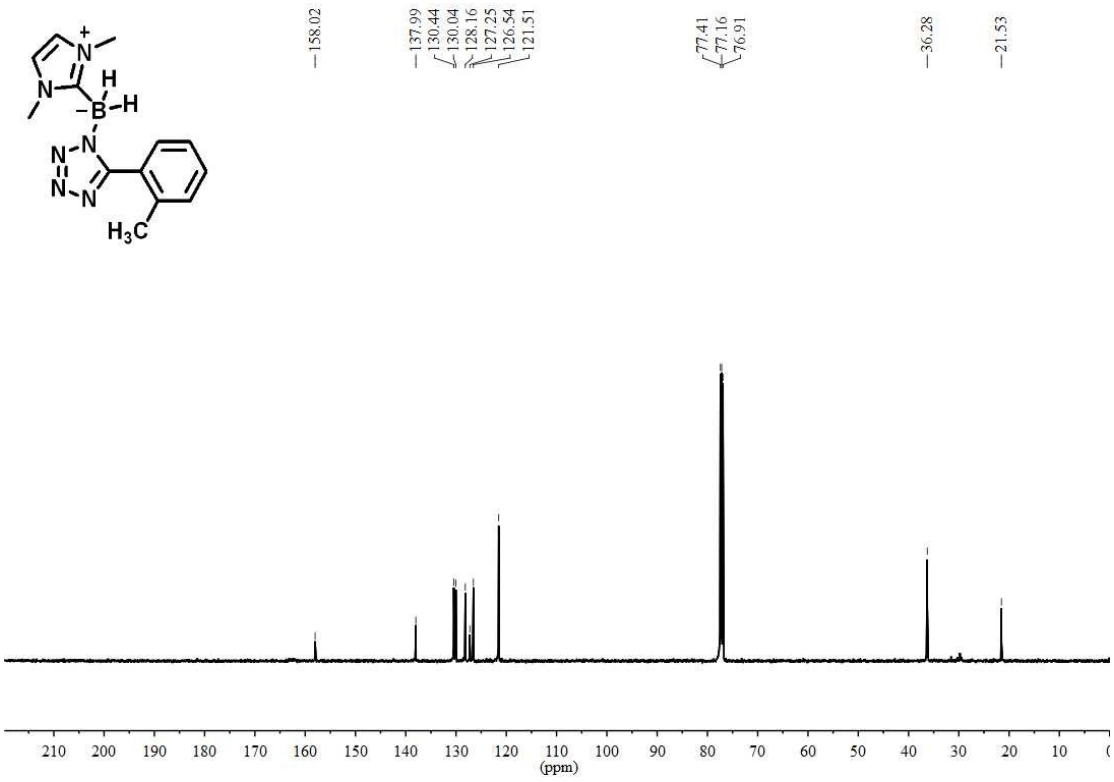
^{11}B NMR of product 5p in $CDCl_3$ (160 MHz)



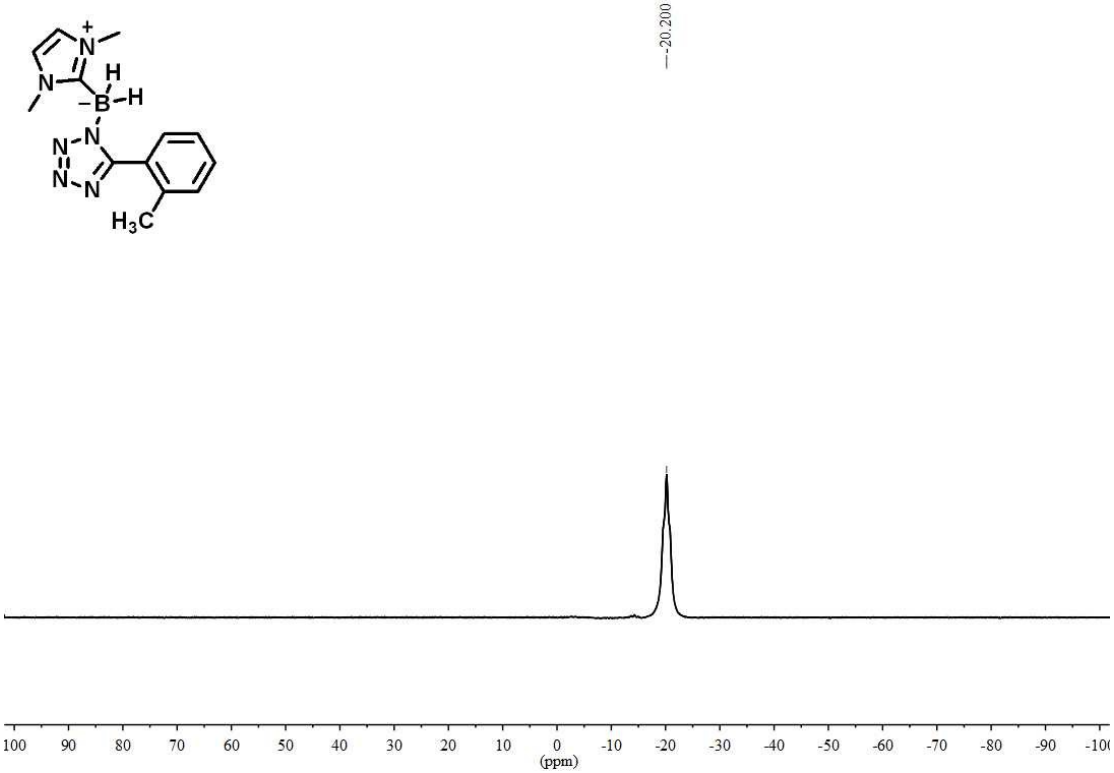
^{1}H NMR of product 5p' in $CDCl_3$ (500 MHz)



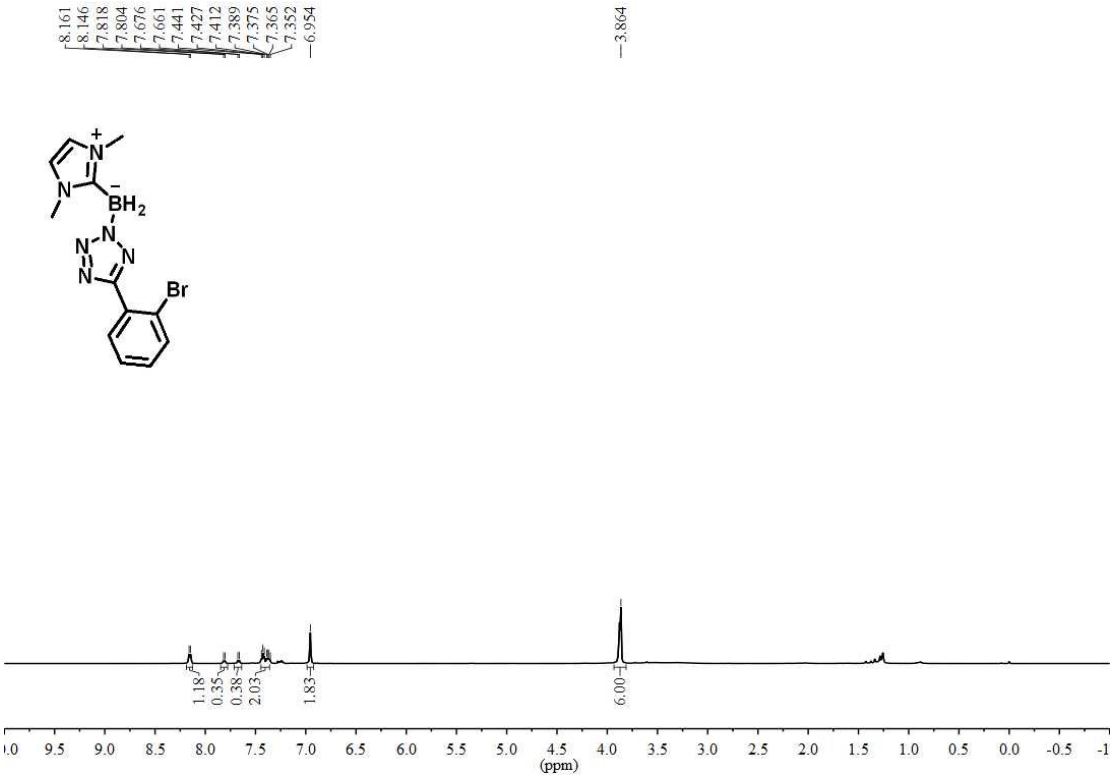
^{13}C NMR of product 5p' in $CDCl_3$ (125 MHz)



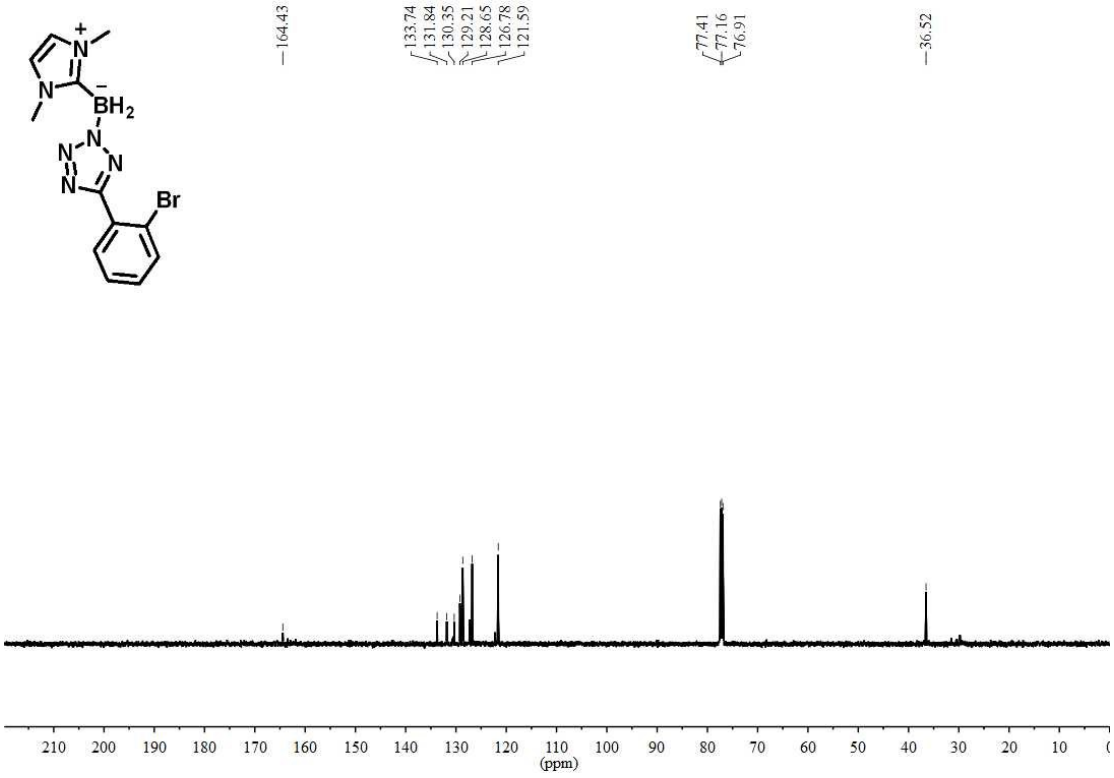
^{11}B NMR of product 5p' in $CDCl_3$ (160 MHz)



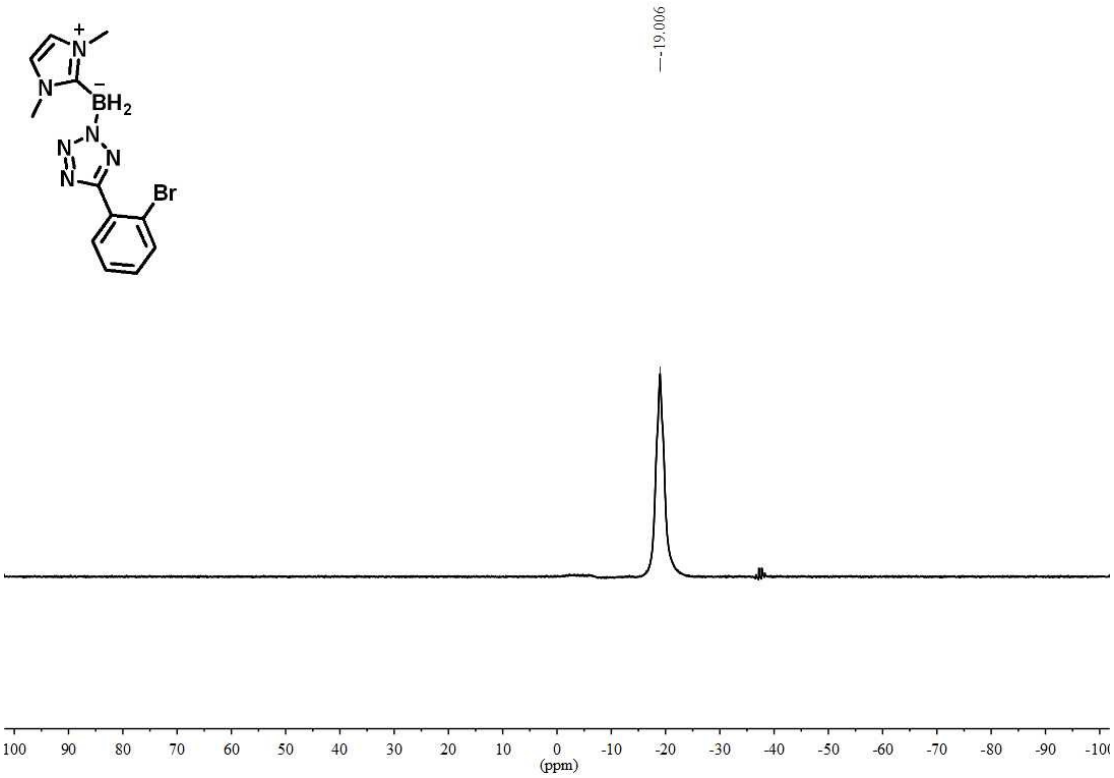
^{1}H NMR of product 5q in $CDCl_3$ (500 MHz)



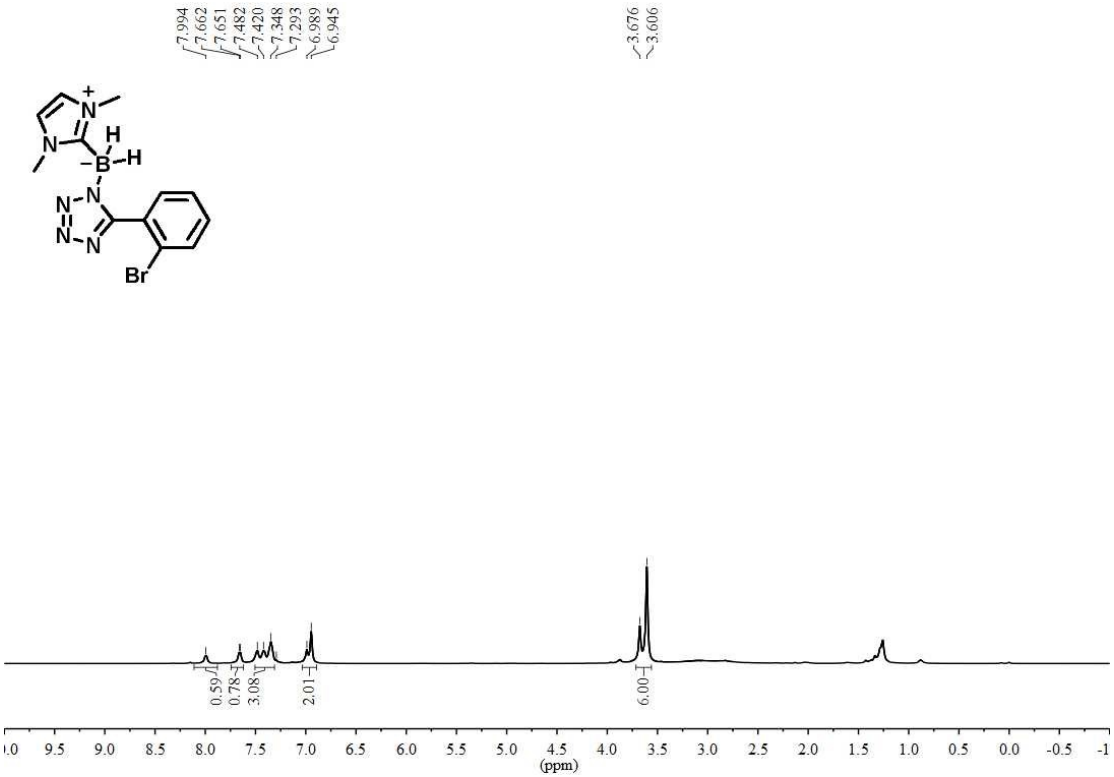
^{13}C NMR of product 5q in $CDCl_3$ (125 MHz)



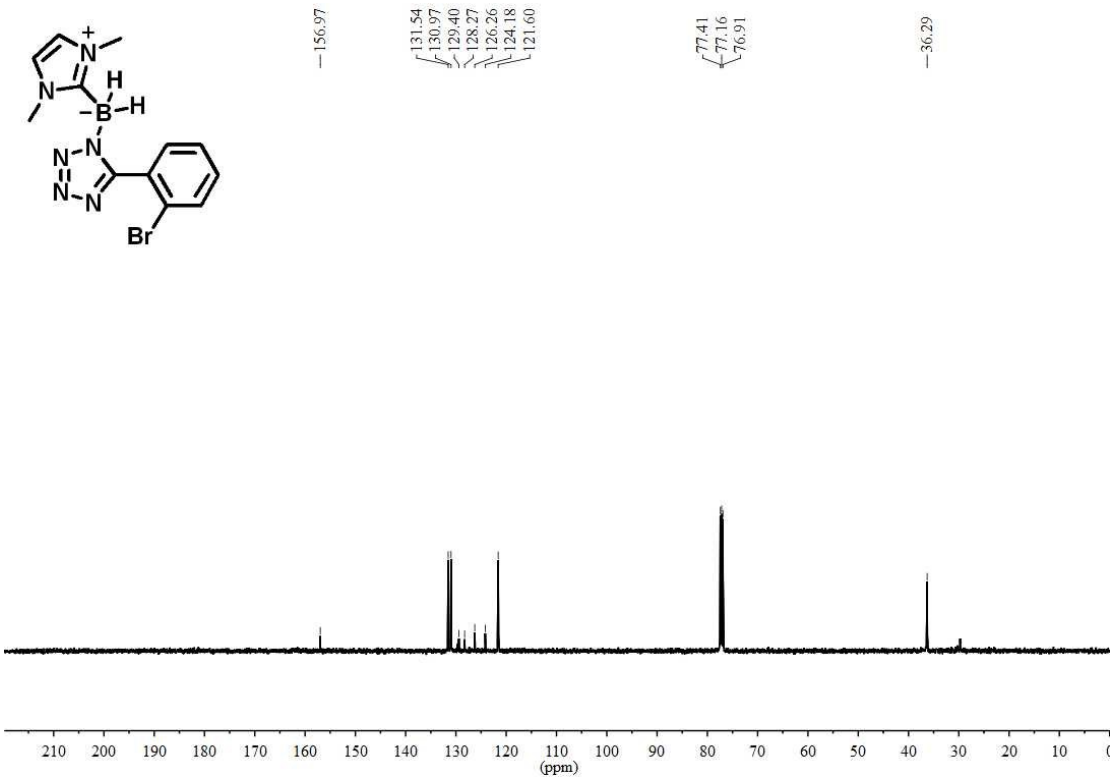
^{11}B NMR of product 5q in $CDCl_3$ (160 MHz)



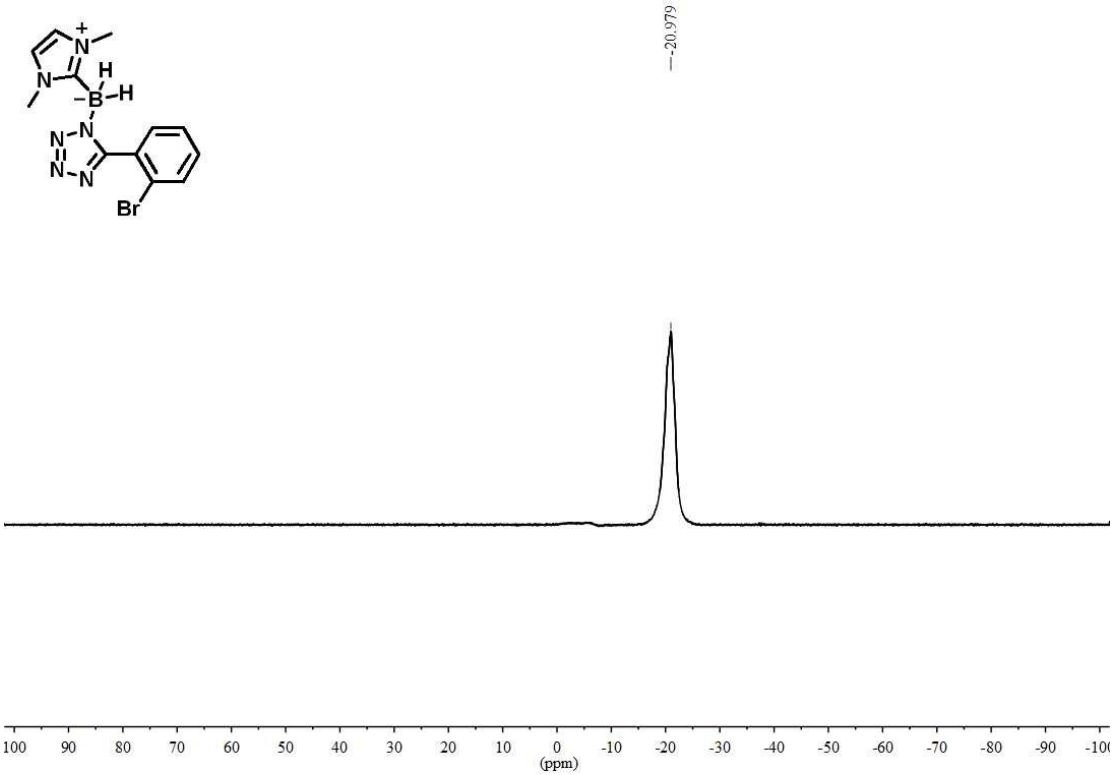
^{1}H NMR of product 5q' in $CDCl_3$ (500 MHz)



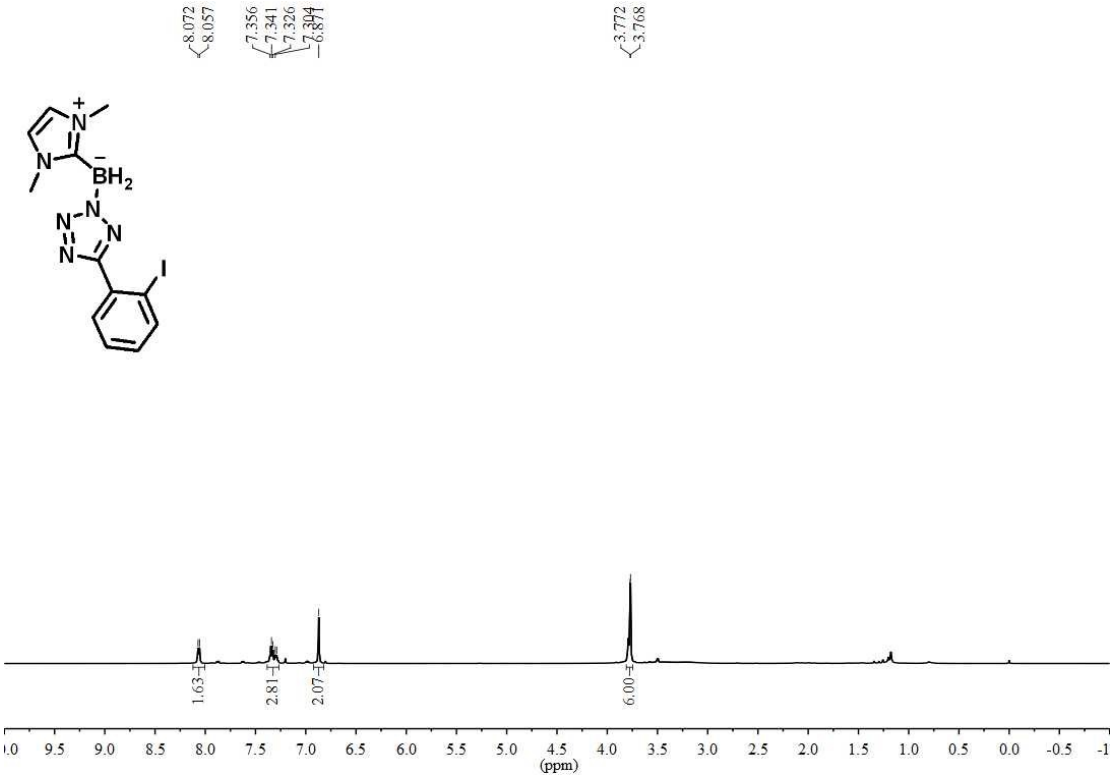
^{13}C NMR of product 5q' in $CDCl_3$ (125 MHz)



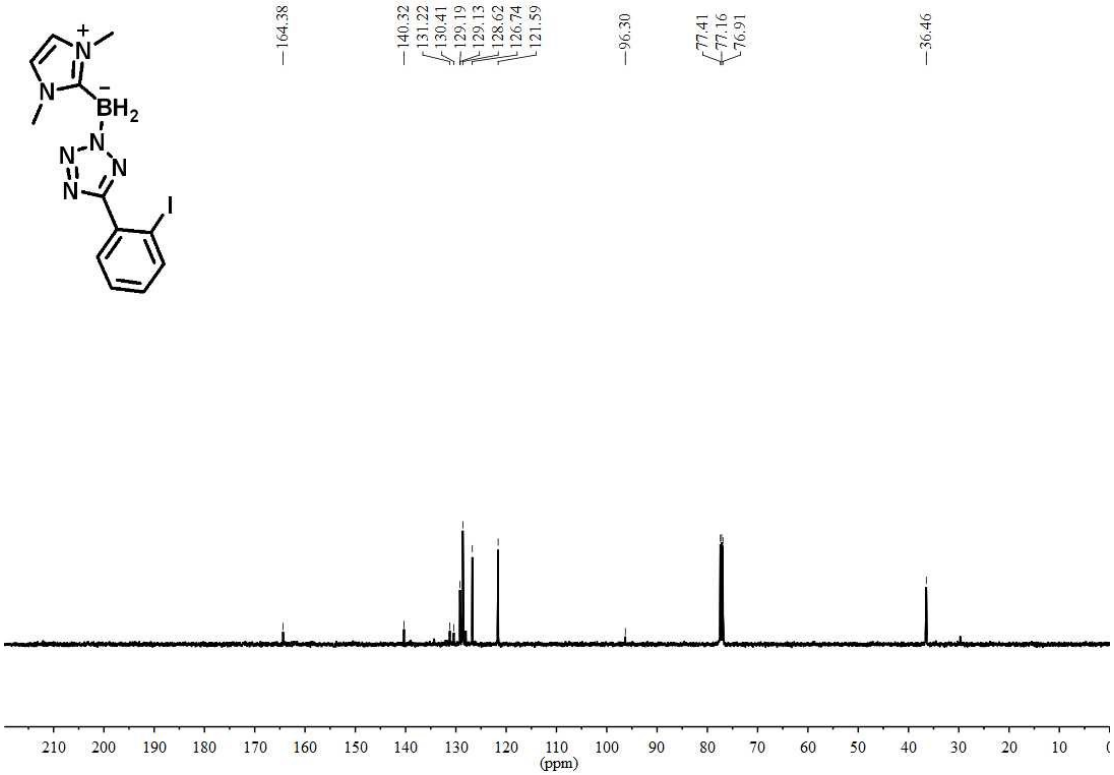
^{11}B NMR of product 5q' in $CDCl_3$ (160 MHz)



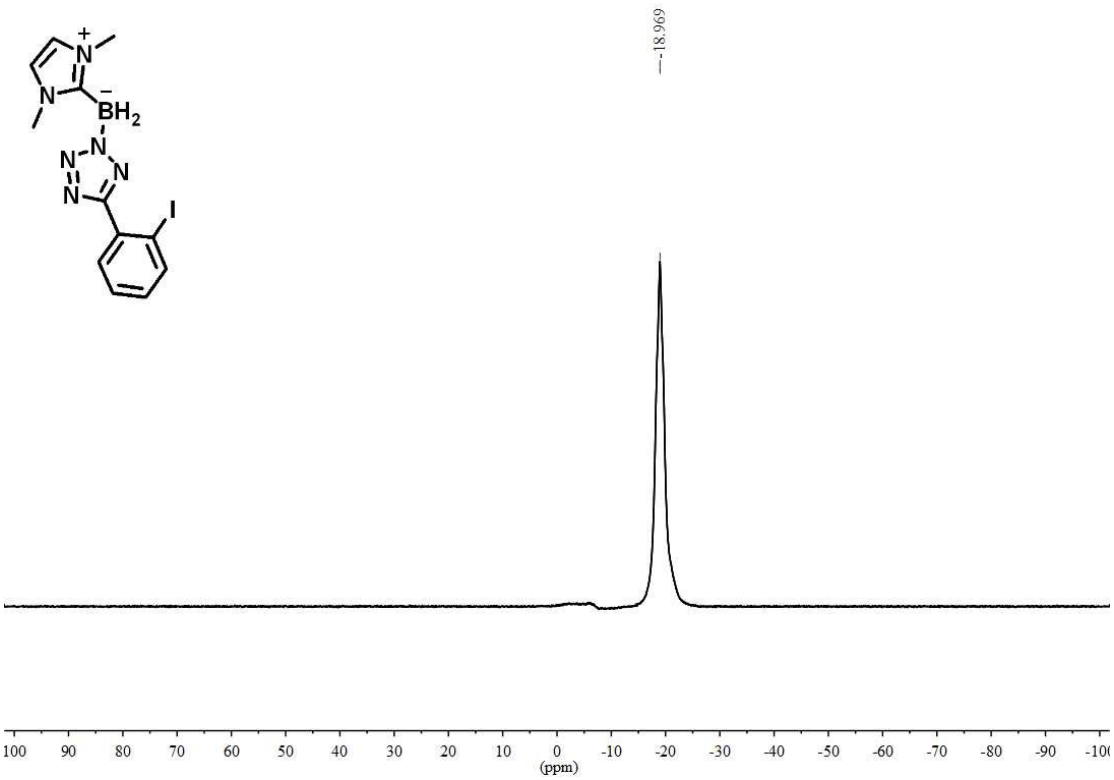
^{1}H NMR of product 5r in $CDCl_3$ (500 MHz)



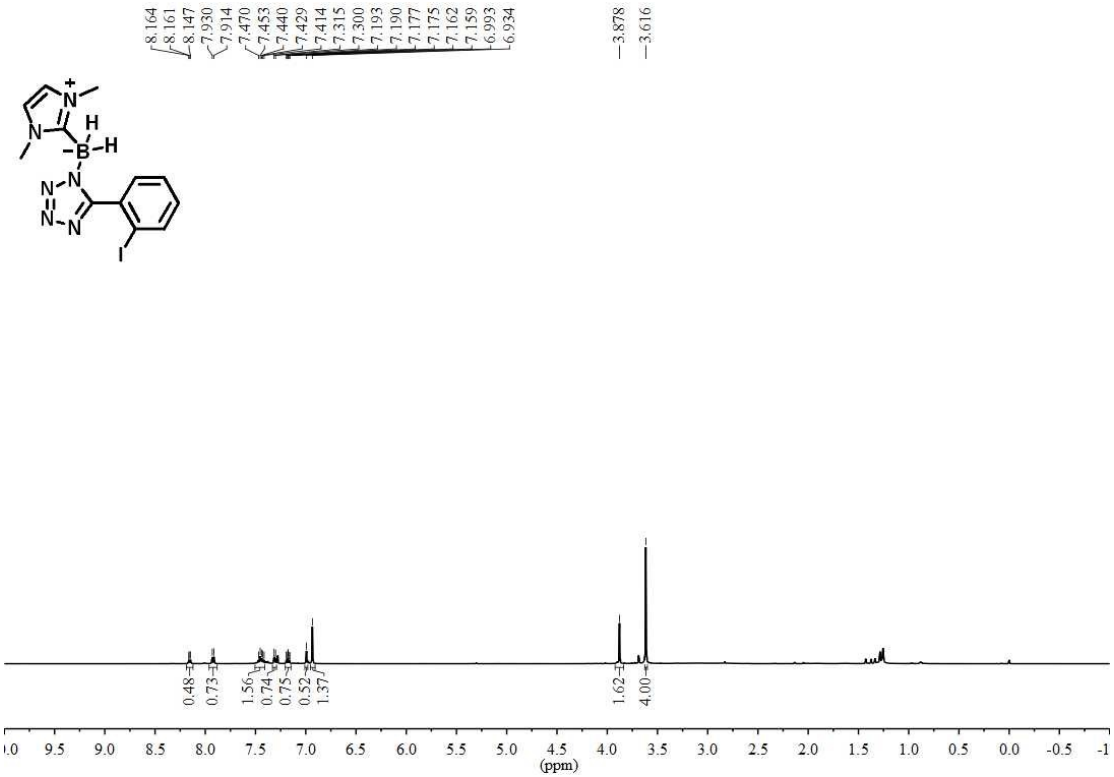
^{13}C NMR of product 5r in $CDCl_3$ (125 MHz)



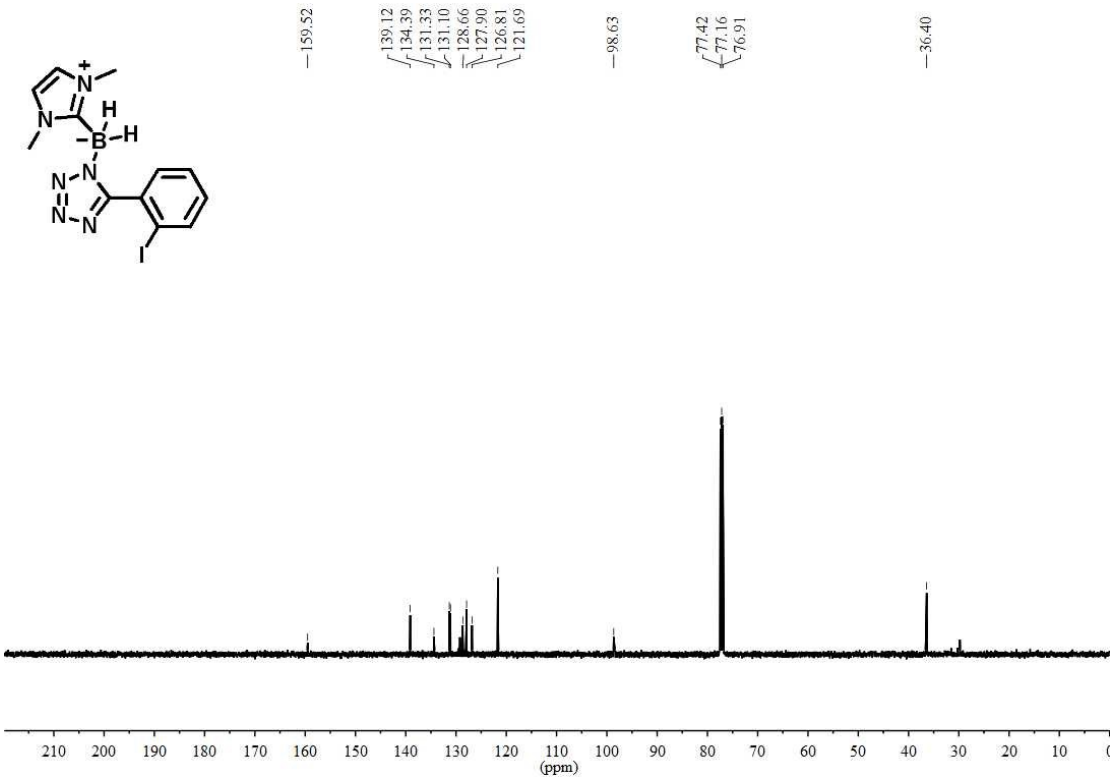
^{11}B NMR of product 5r in $CDCl_3$ (160 MHz)



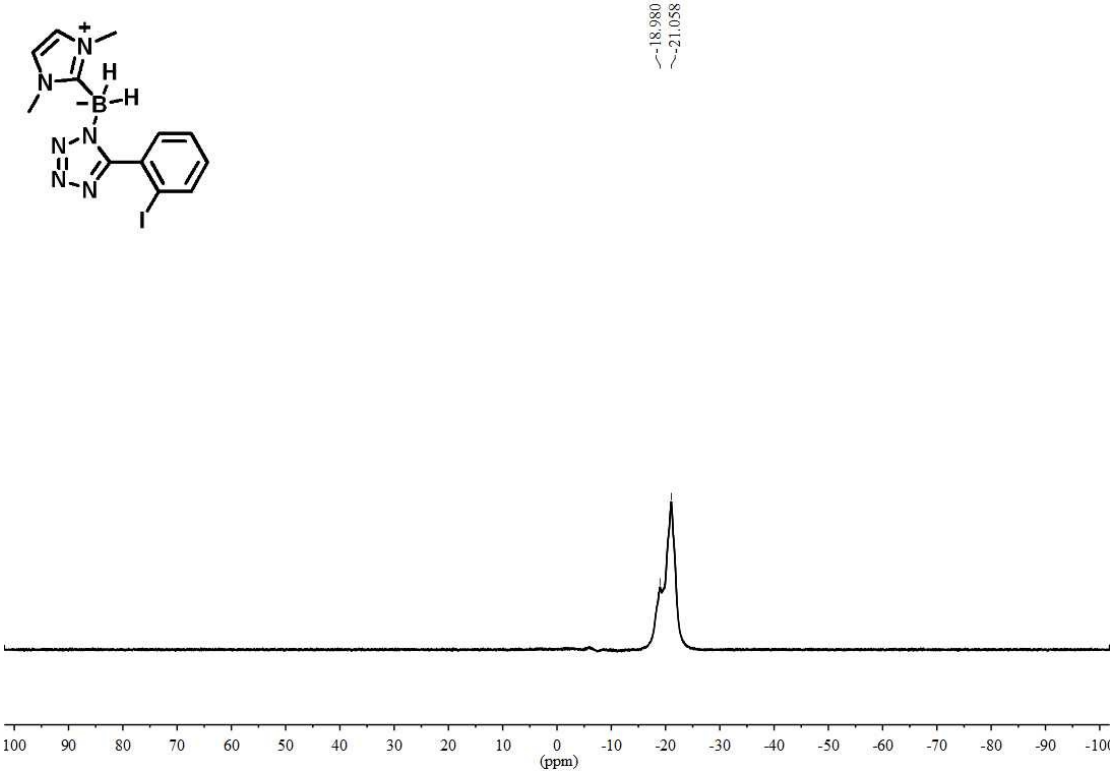
^{1}H NMR of product 5r' in $CDCl_3$ (500 MHz)



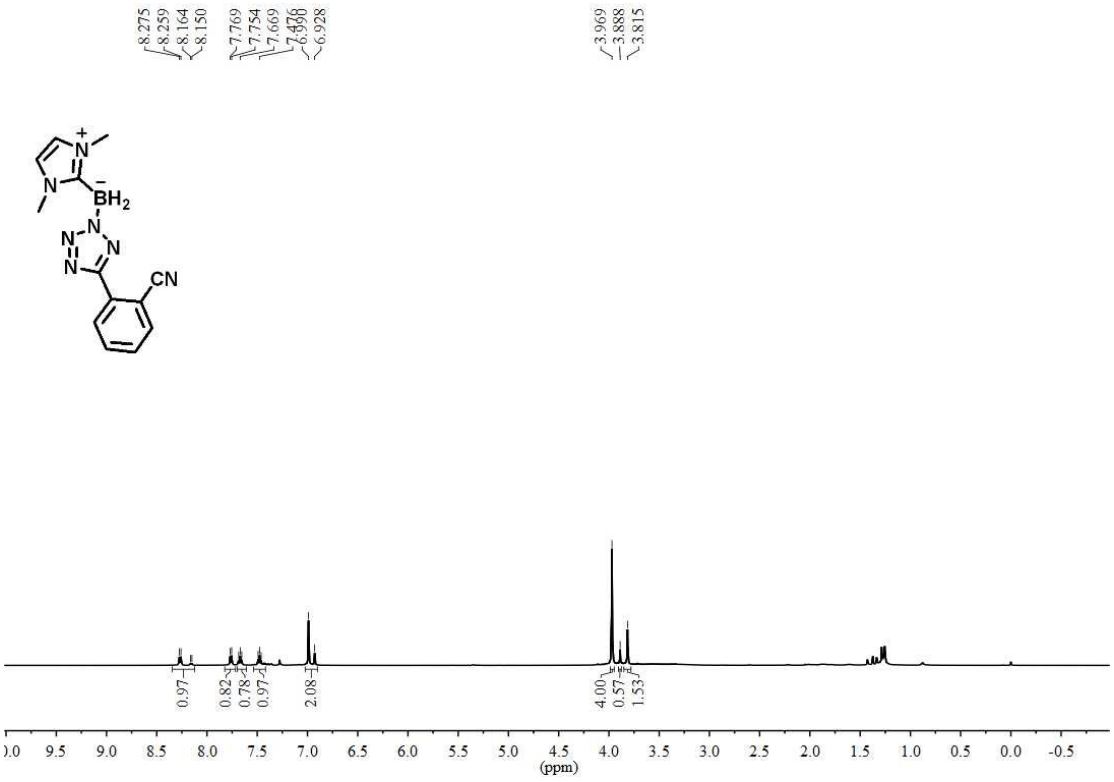
^{13}C NMR of product 5r' in $CDCl_3$ (125 MHz)



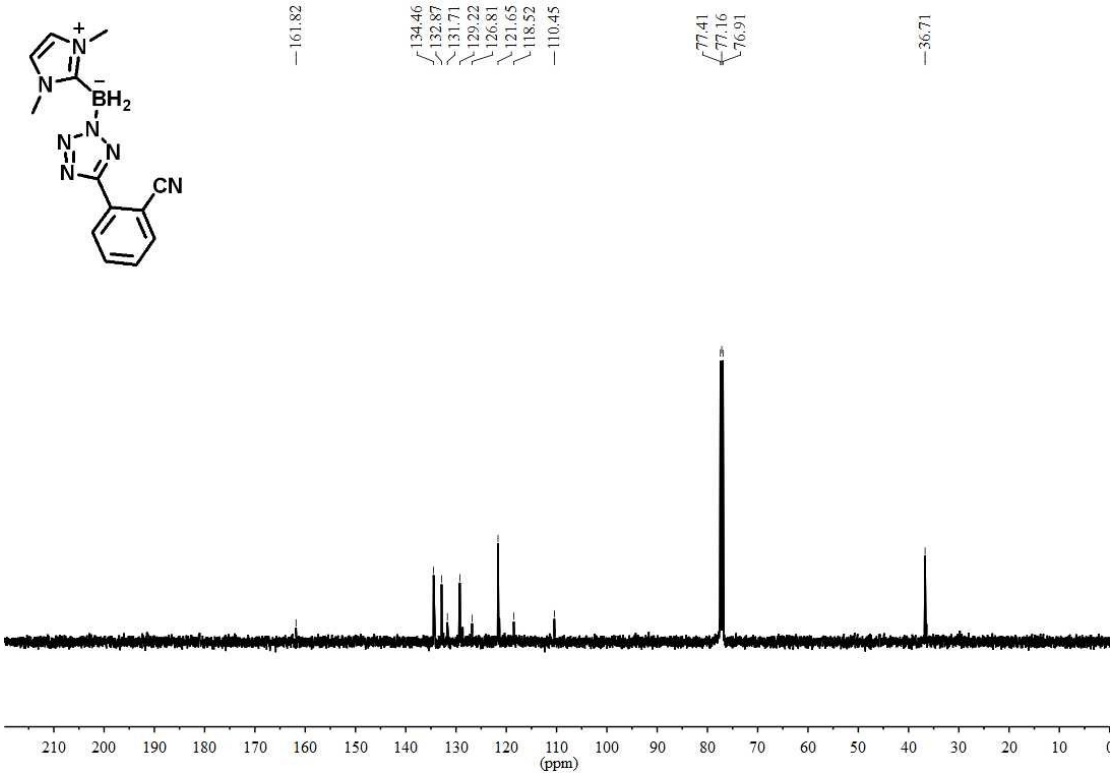
^{11}B NMR of product 5r' in $CDCl_3$ (160 MHz)



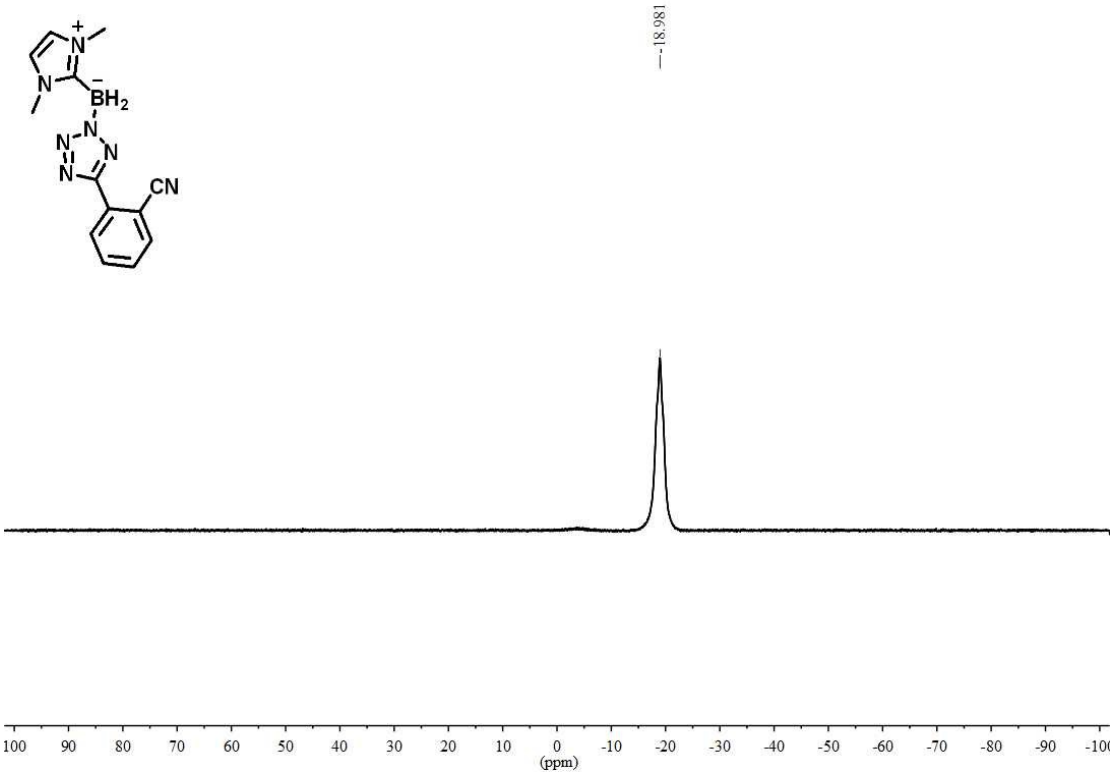
^{1}H NMR of product 5s in $CDCl_3$ (500 MHz)



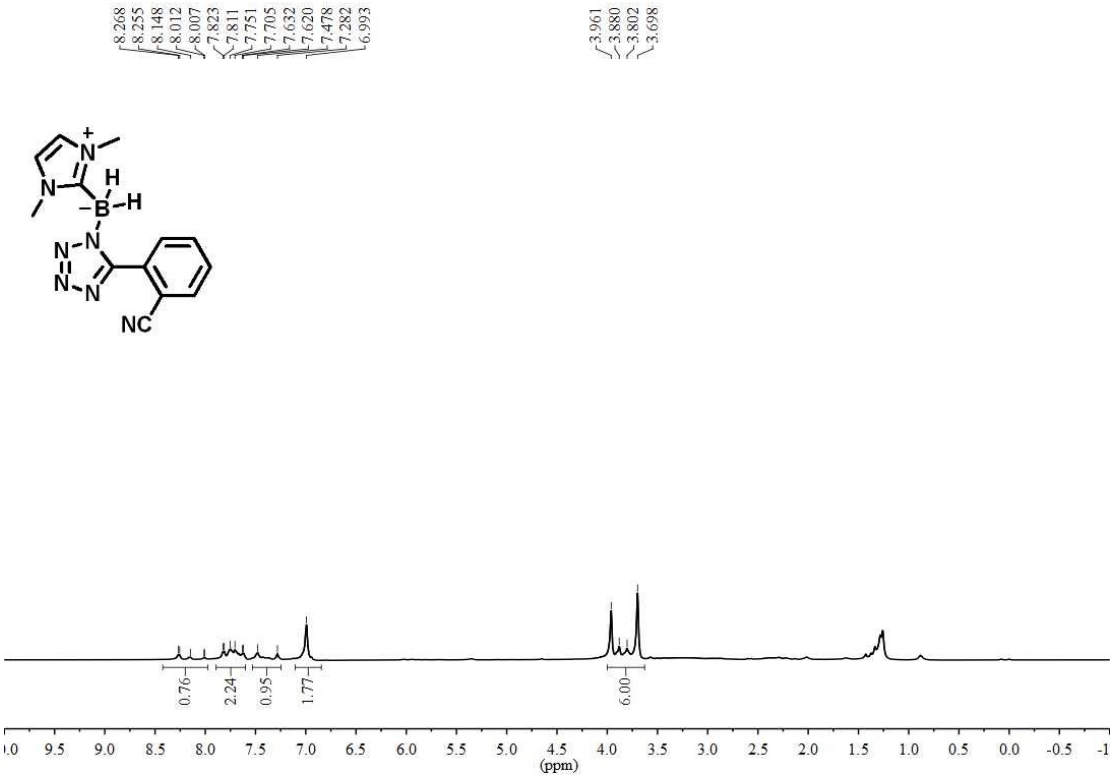
^{13}C NMR of product 5s in $CDCl_3$ (125 MHz)



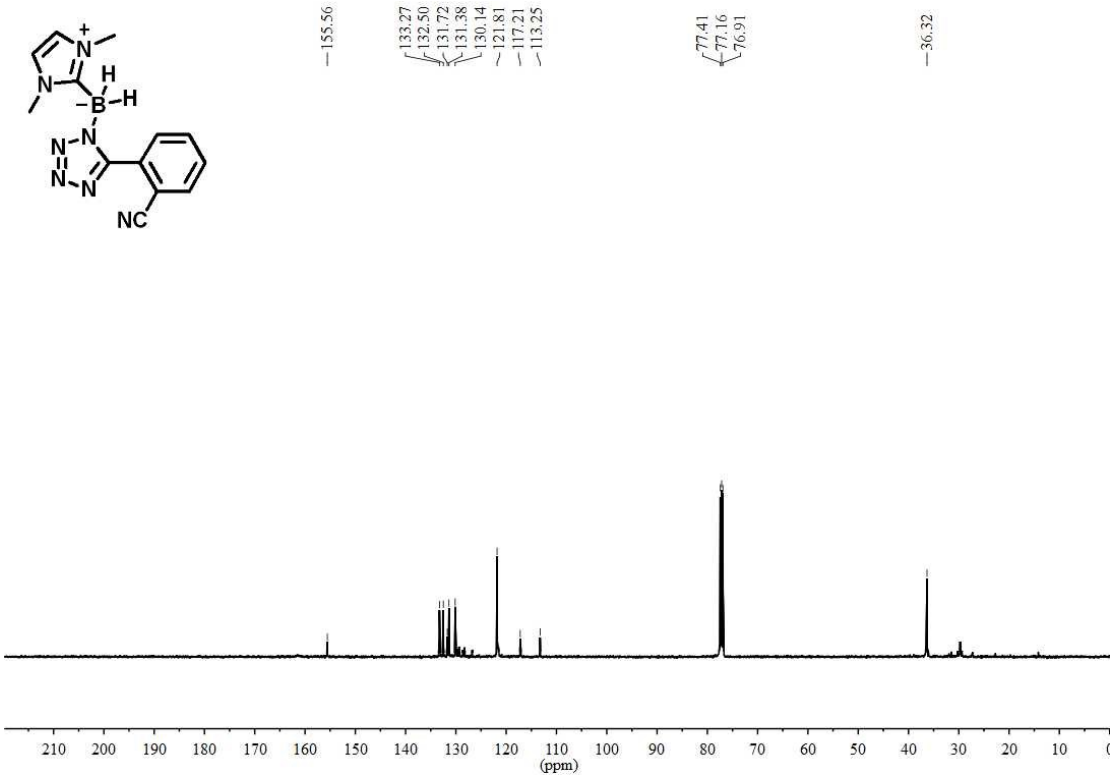
^{11}B NMR of product 5s in $CDCl_3$ (160 MHz)



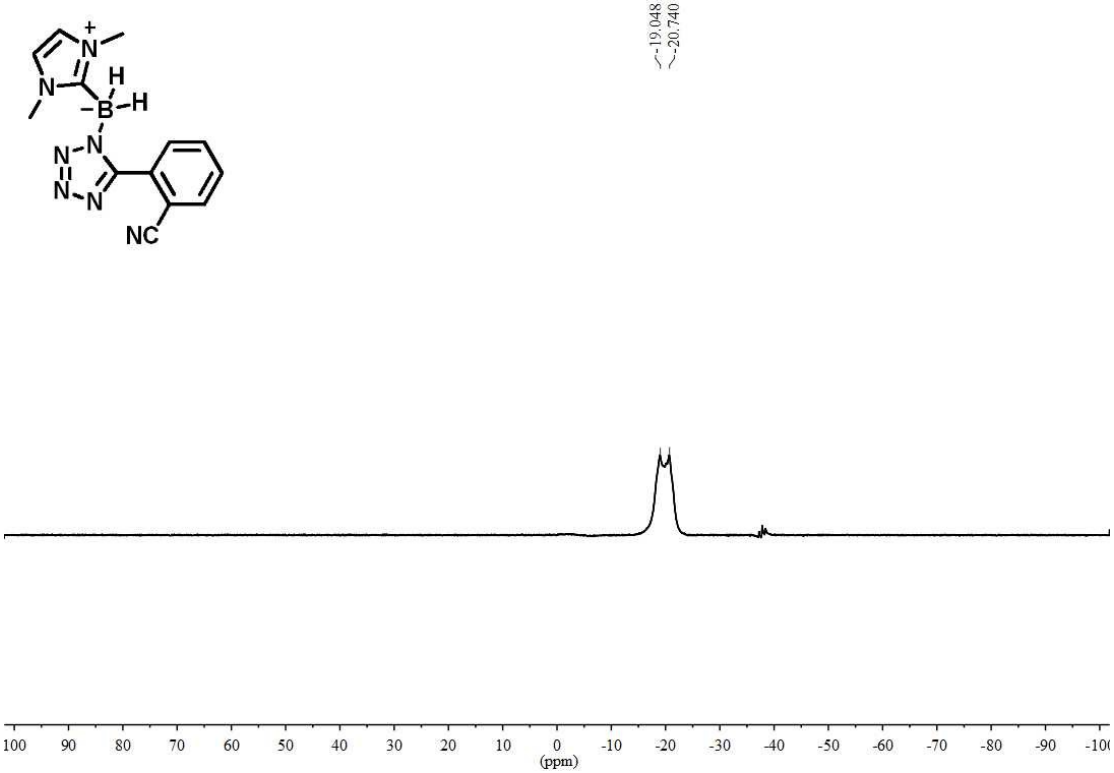
^{1}H NMR of product 5s' in $CDCl_3$ (500 MHz)



^{13}C NMR of product in 5s' $CDCl_3$ (125 MHz)



^{11}B NMR of product 5s' in $CDCl_3$ (160 MHz)



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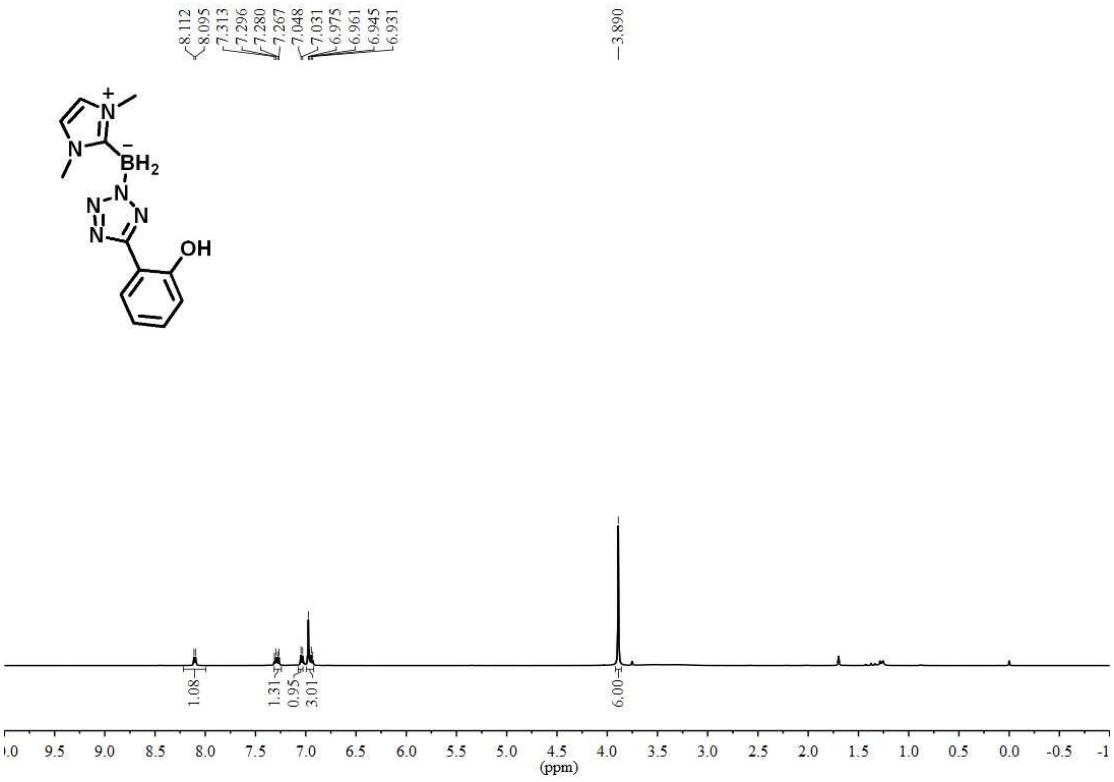
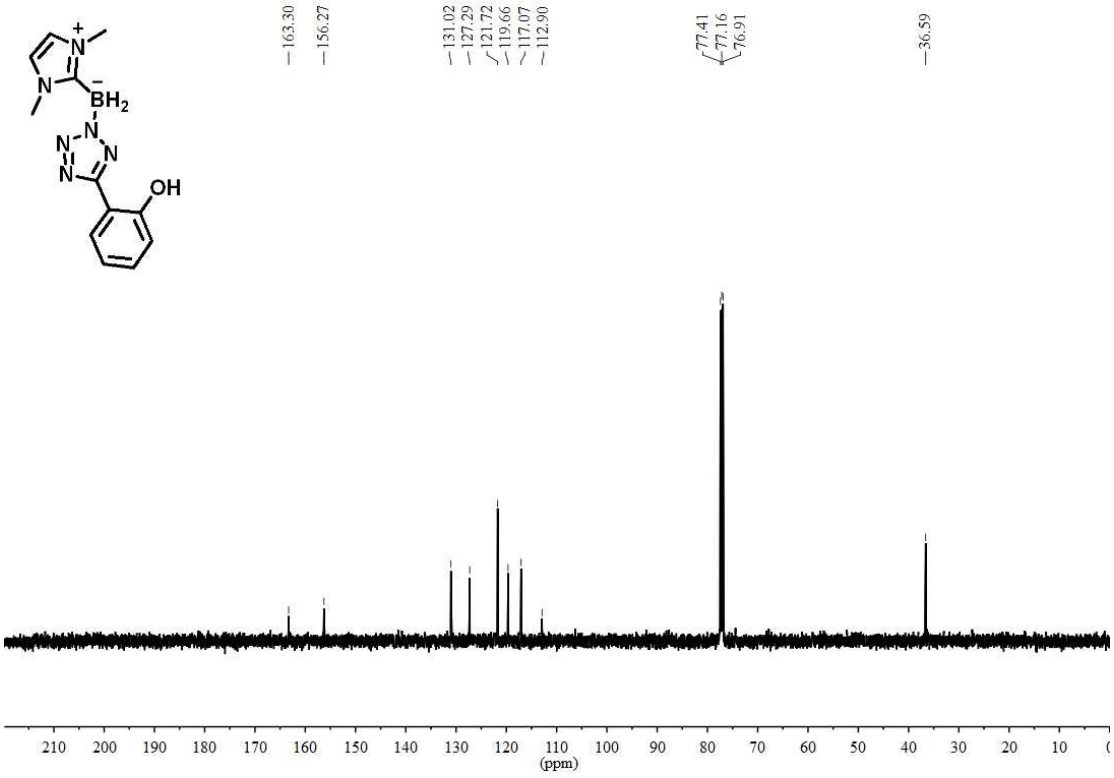
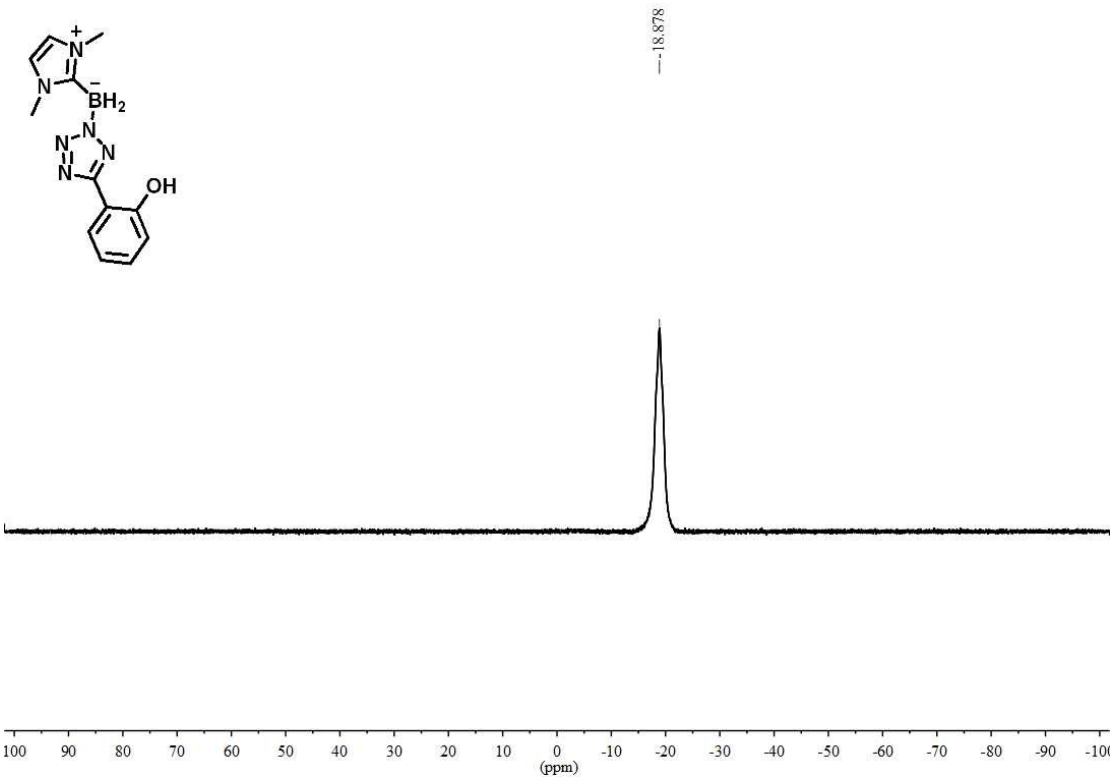


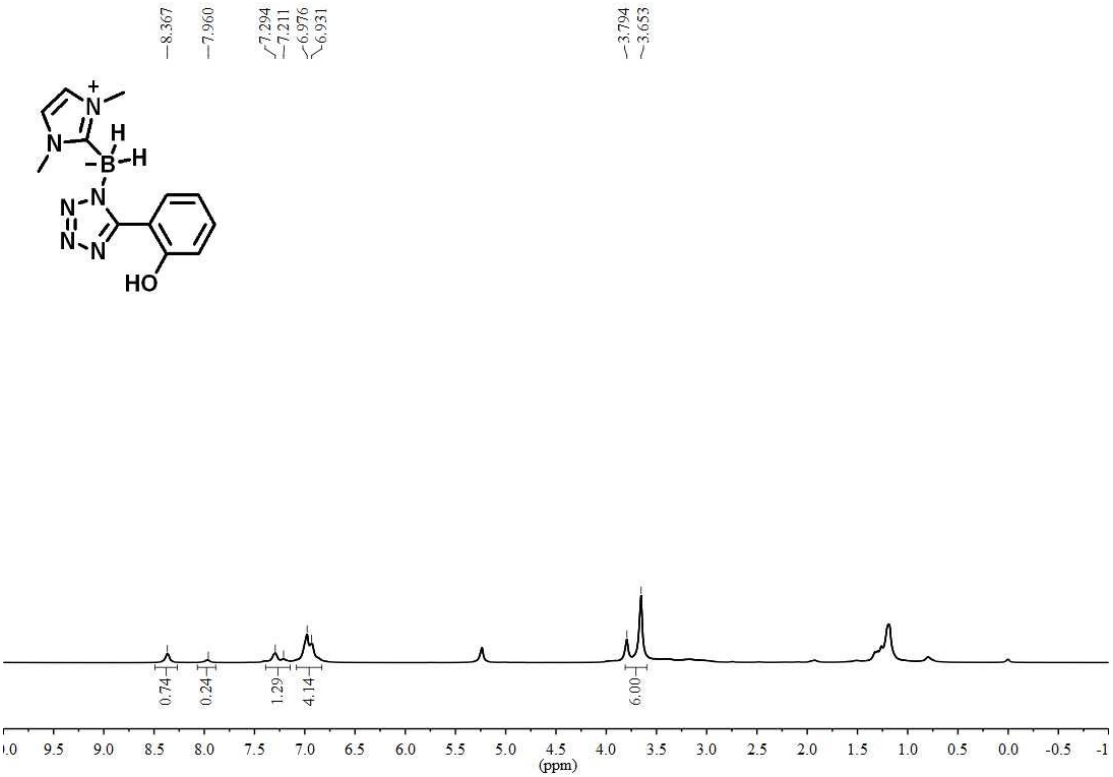
^{13}C NMR of product 5t in $CDCl_3$ (125 MHz)



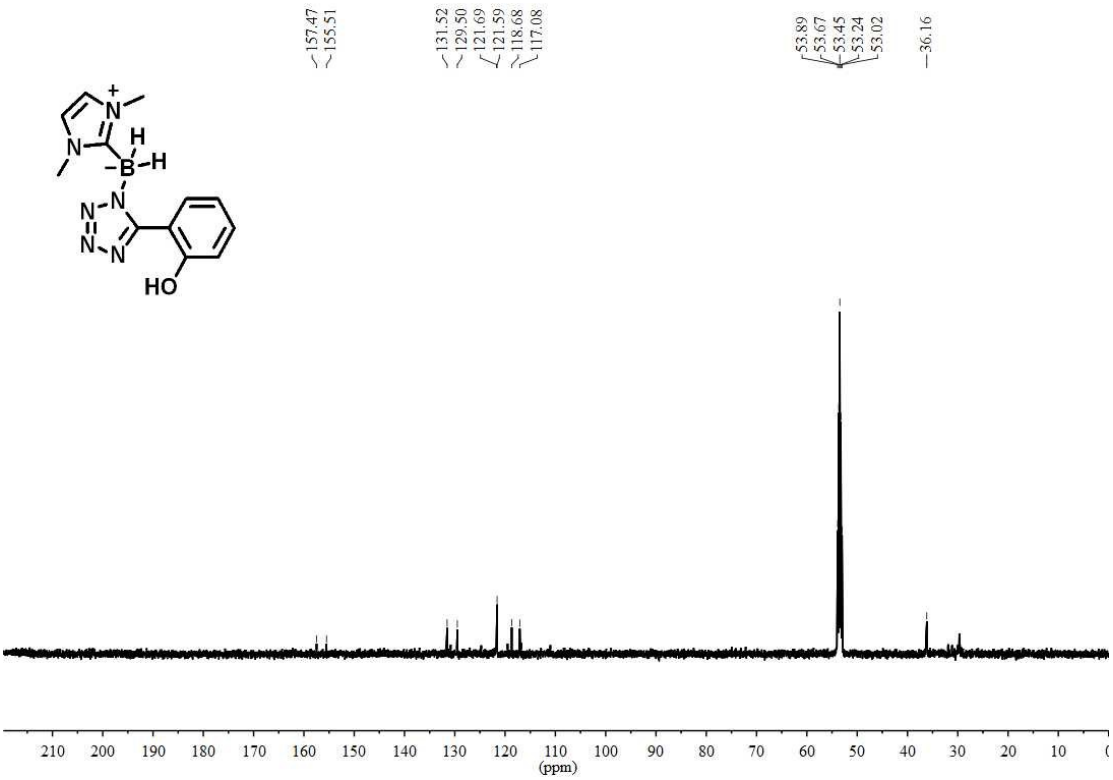
^{11}B NMR of product 5t in $CDCl_3$ (160 MHz)



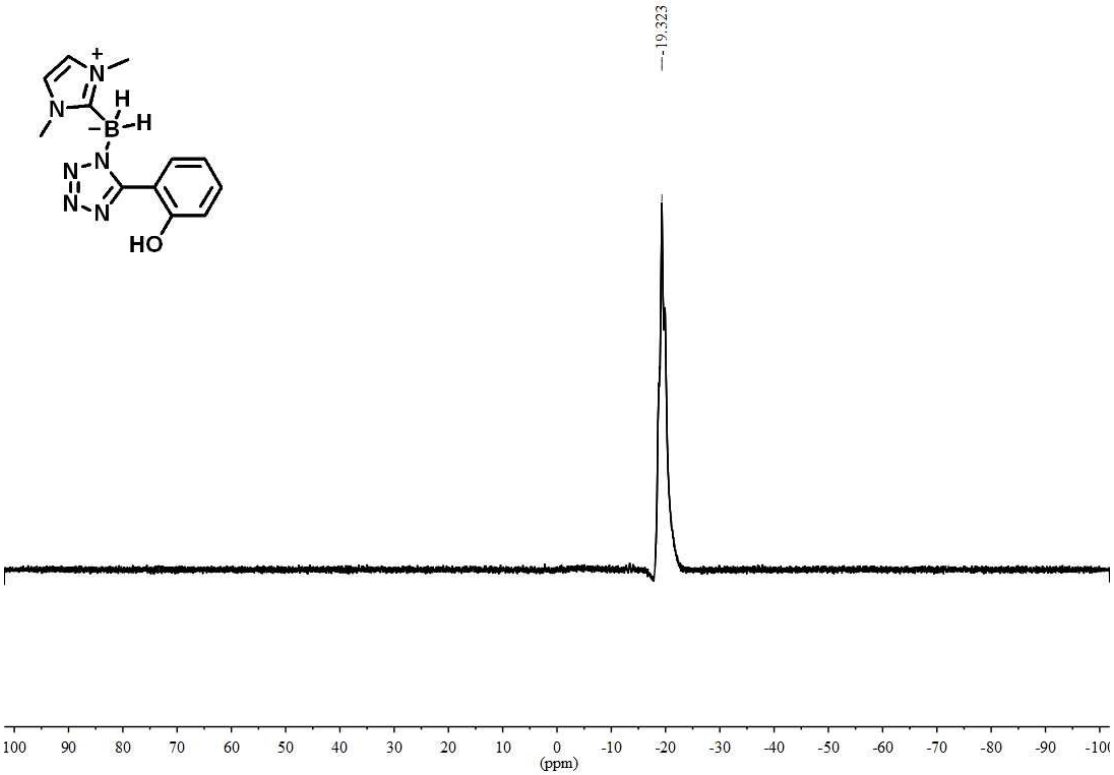
^{1}H NMR of product 5t' in CD_2Cl_2 (500 MHz)



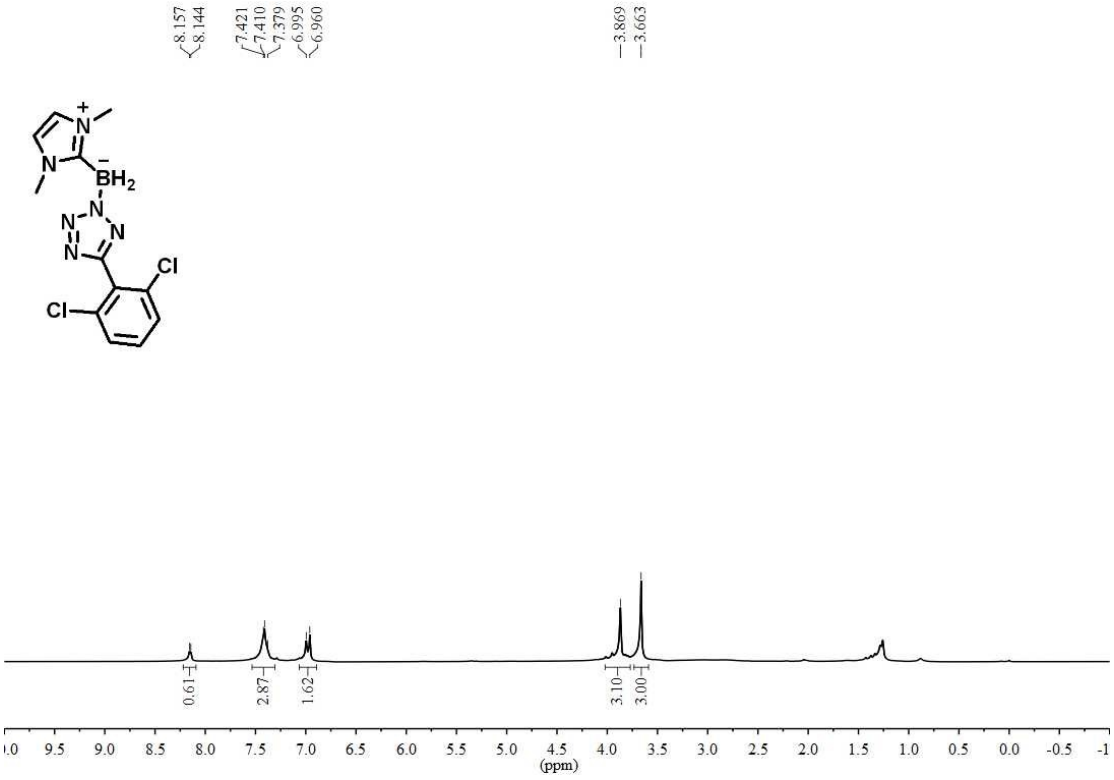
^{13}C NMR of product 5t' in CD_2Cl_2 (125 MHz)



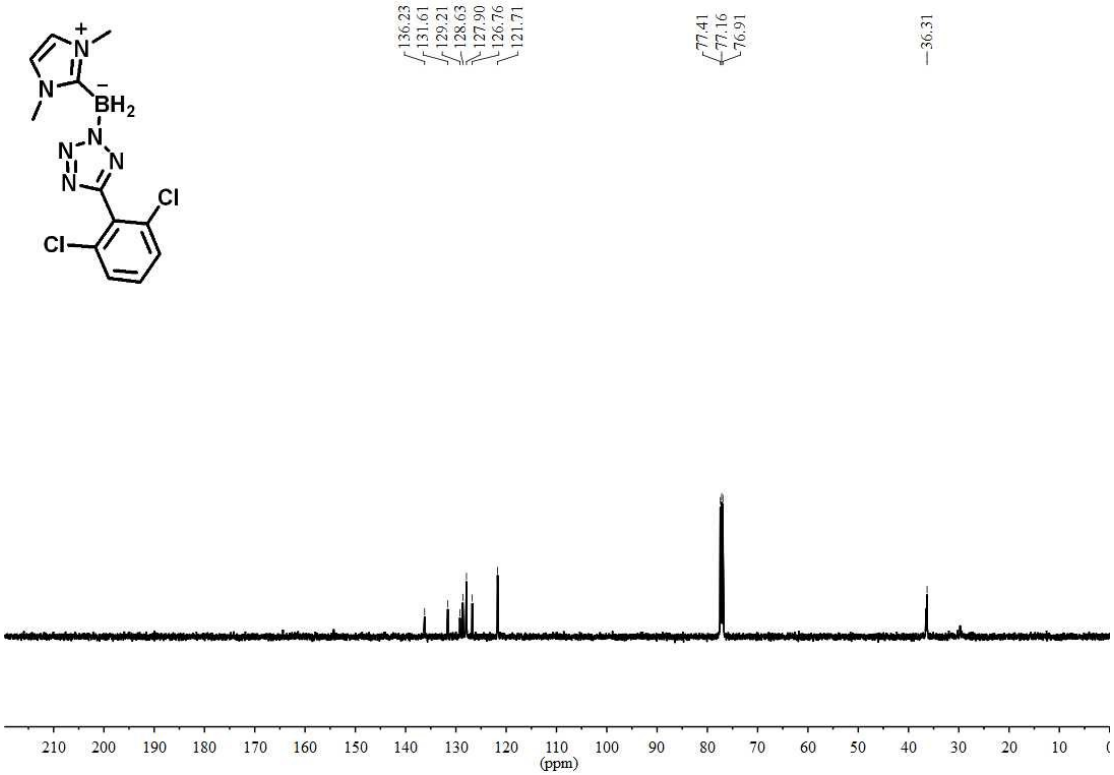
^{11}B NMR of product 5t' in CD_2Cl_2 (160 MHz)



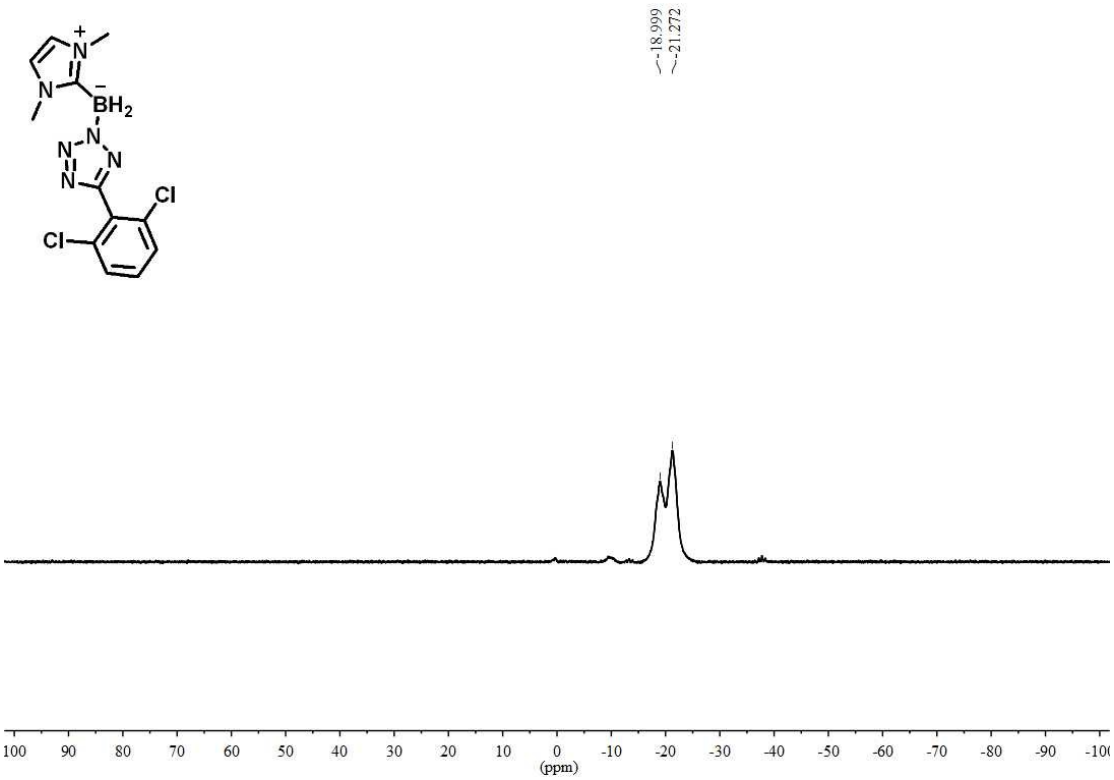
^{1}H NMR of product 5u in $CDCl_3$ (500 MHz)



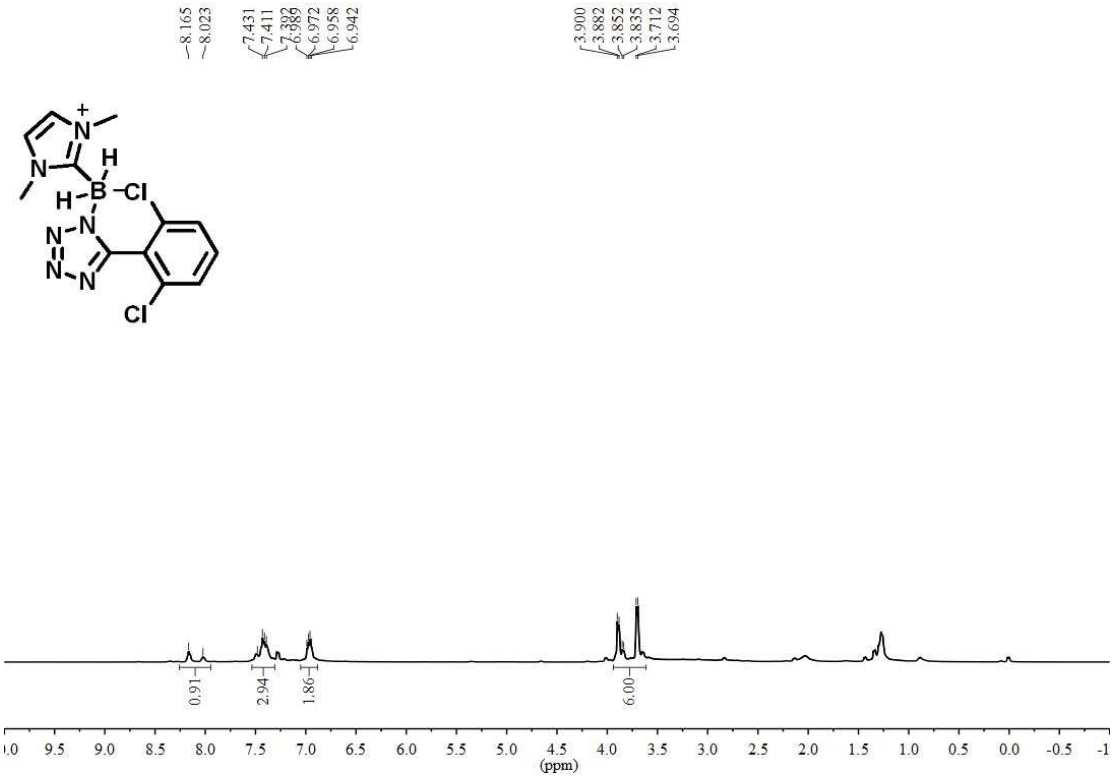
^{13}C NMR of product 5u in $CDCl_3$ (125 MHz)



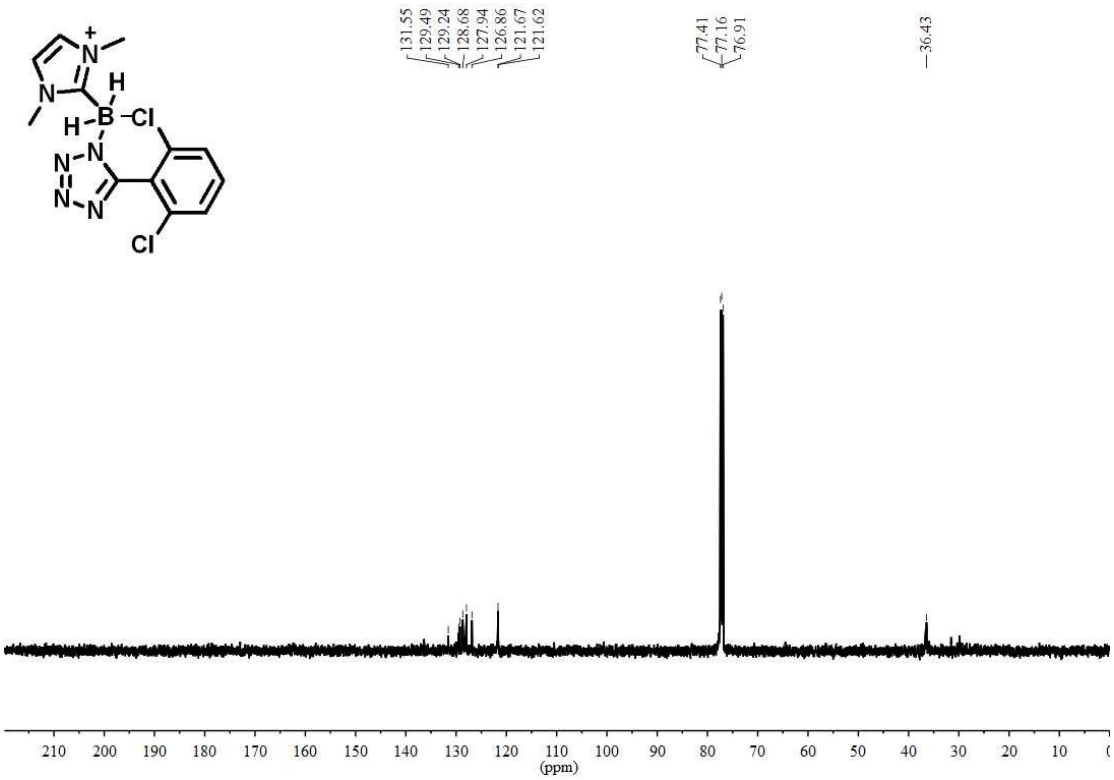
^{11}B NMR of product 5u in $CDCl_3$ (160 MHz)



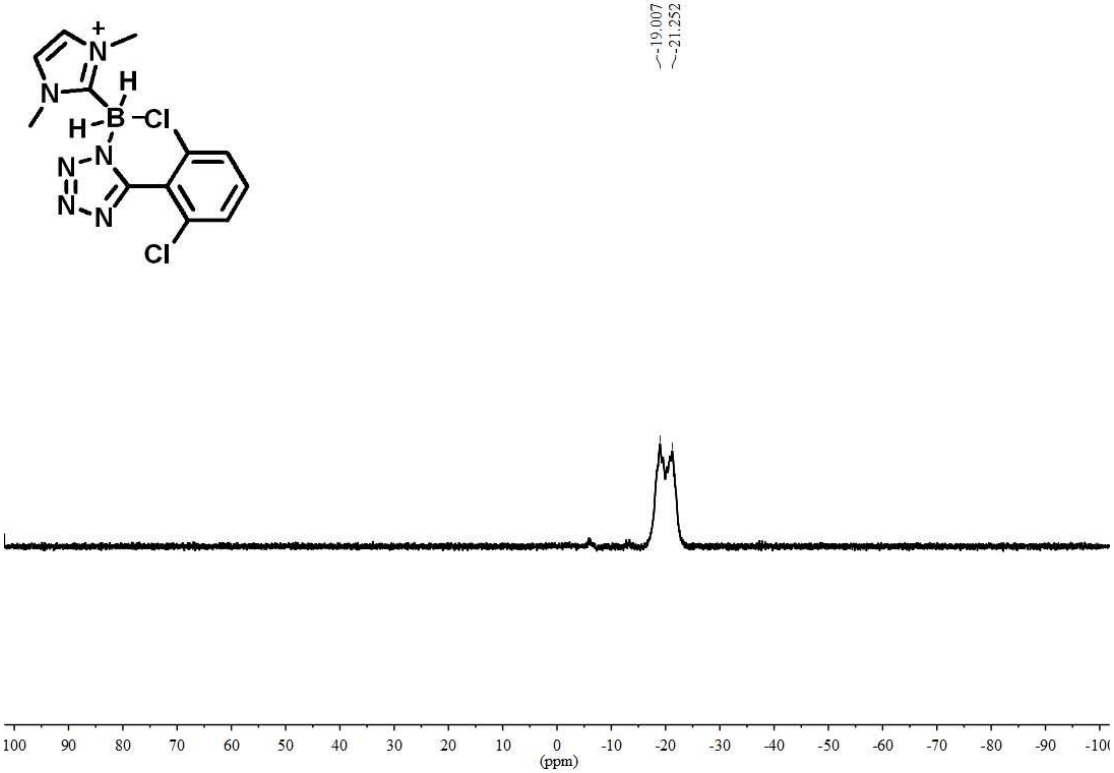
^{1}H NMR of product 5u' in $CDCl_3$ (500 MHz)



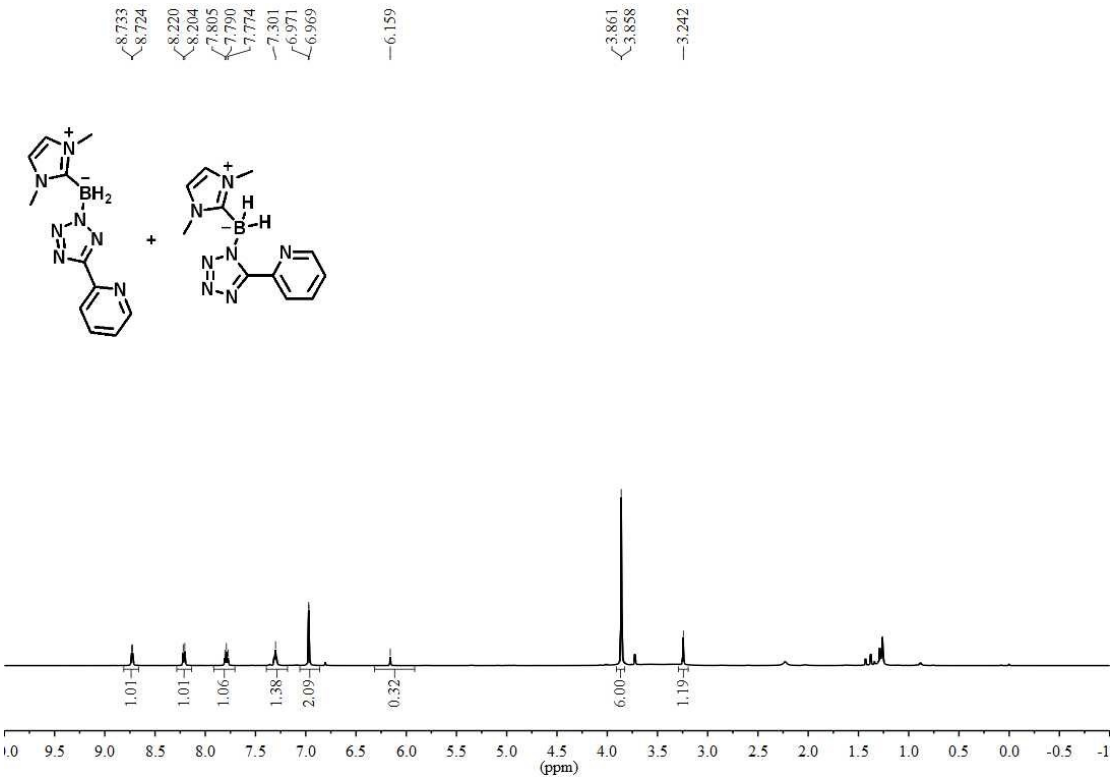
^{13}C NMR of product 5u' in $CDCl_3$ (125 MHz)



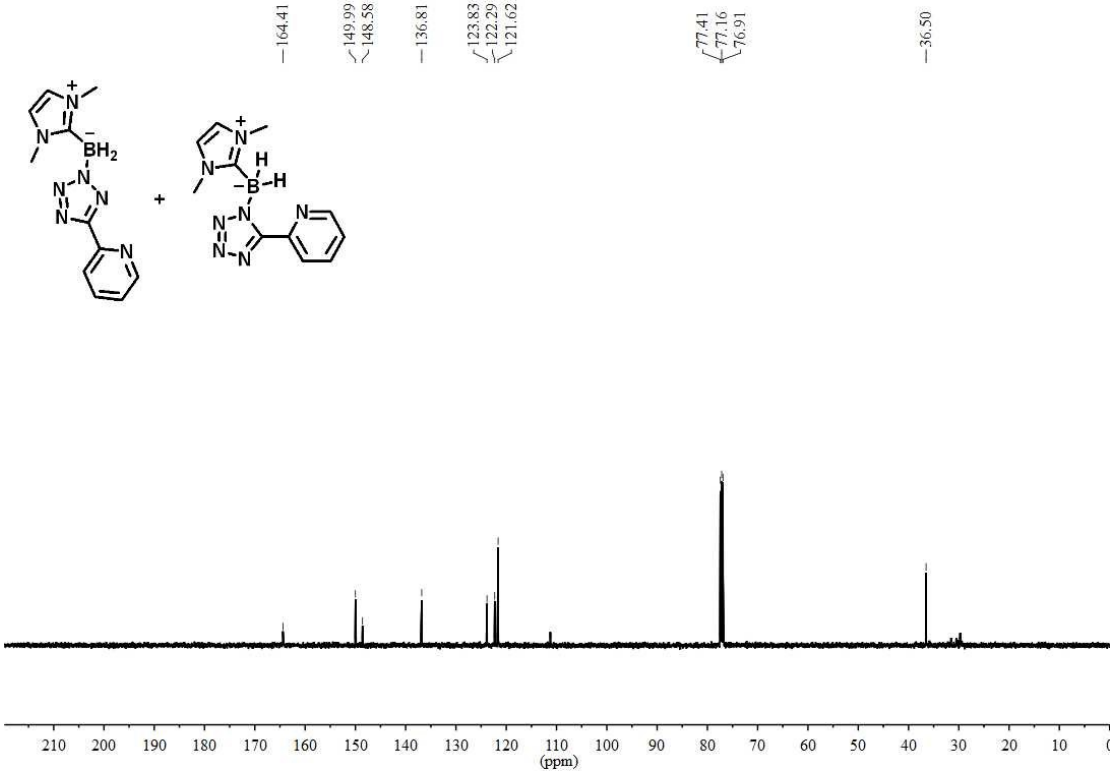
^{11}B NMR of product 5u' in $CDCl_3$ (160 MHz)



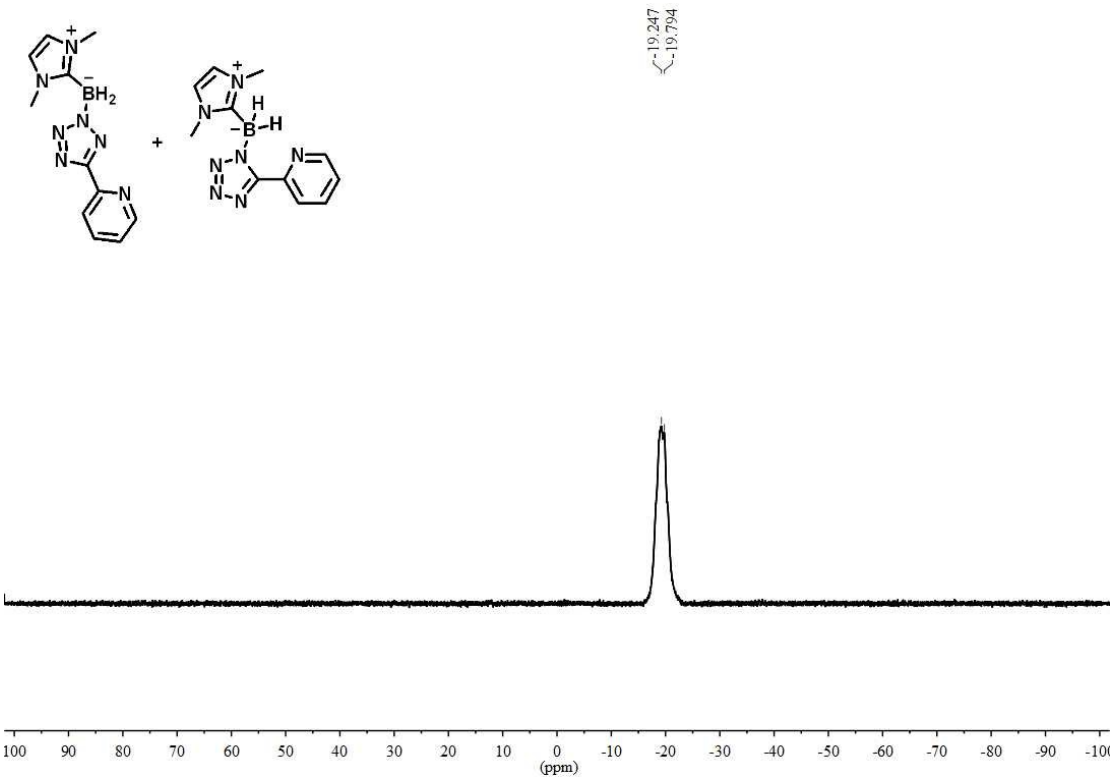
^{1}H NMR of product 5v+5v' in $CDCl_3$ (500 MHz)



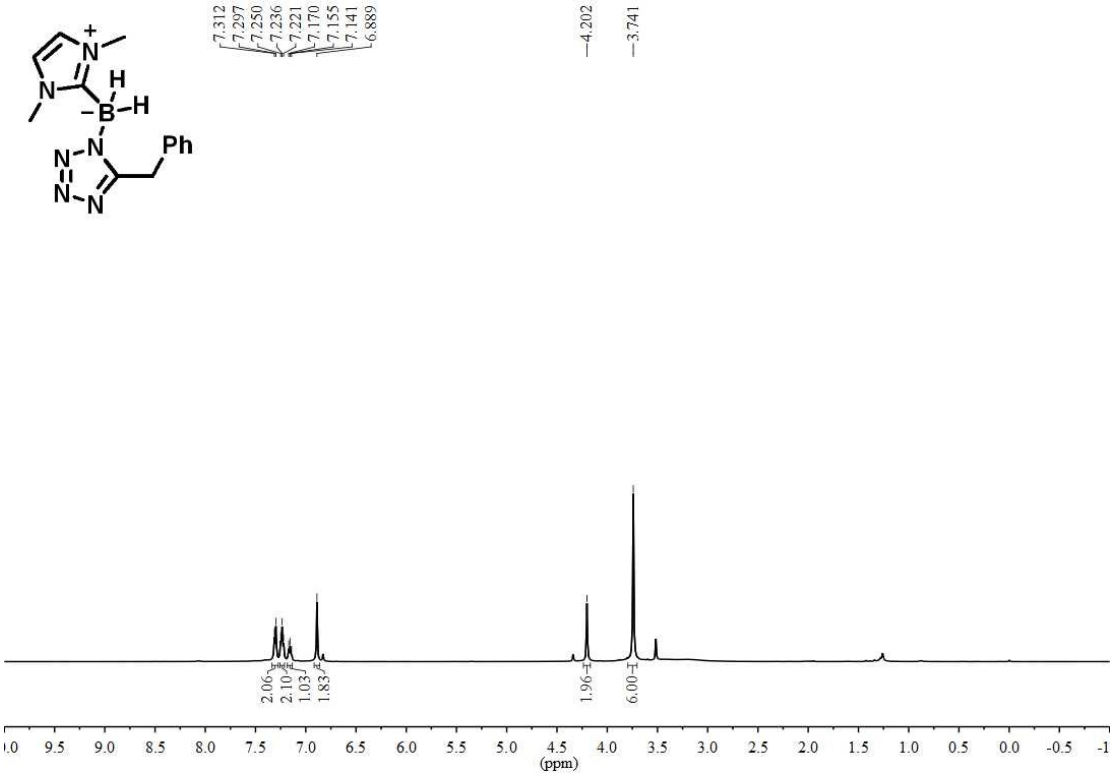
^{13}C NMR of product 5v+5v' in $CDCl_3$ (125 MHz)



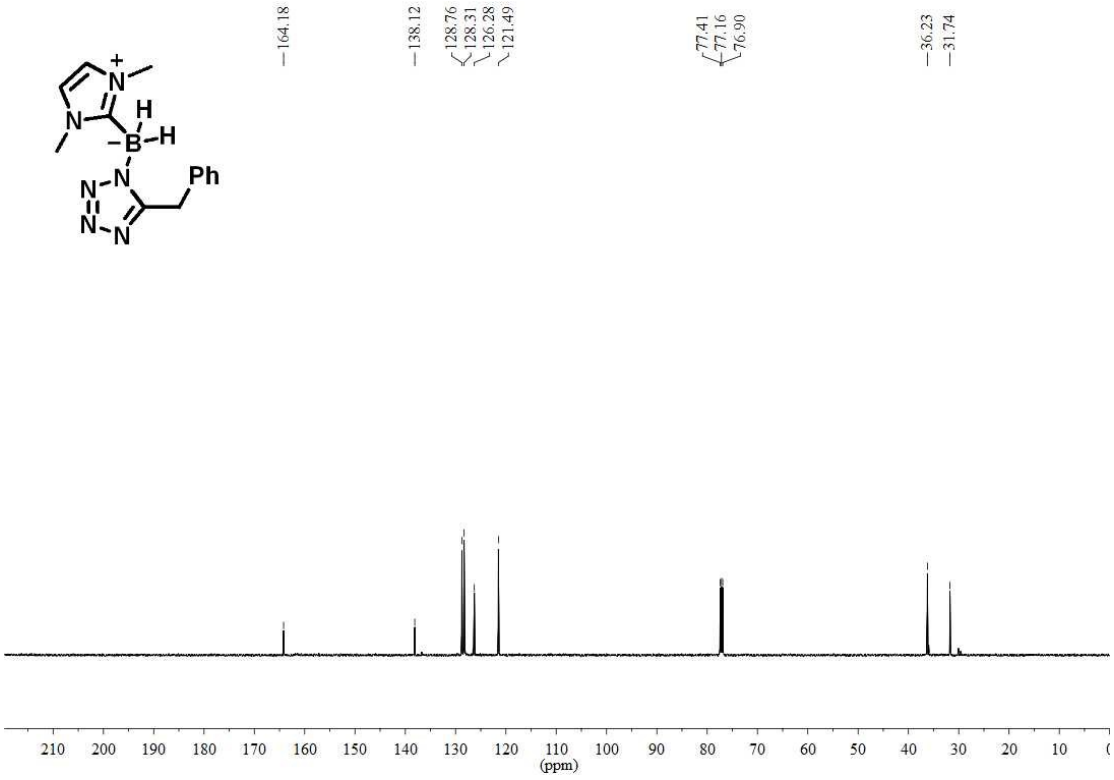
^{11}B NMR of product 5v+5v' in $CDCl_3$ (160 MHz)



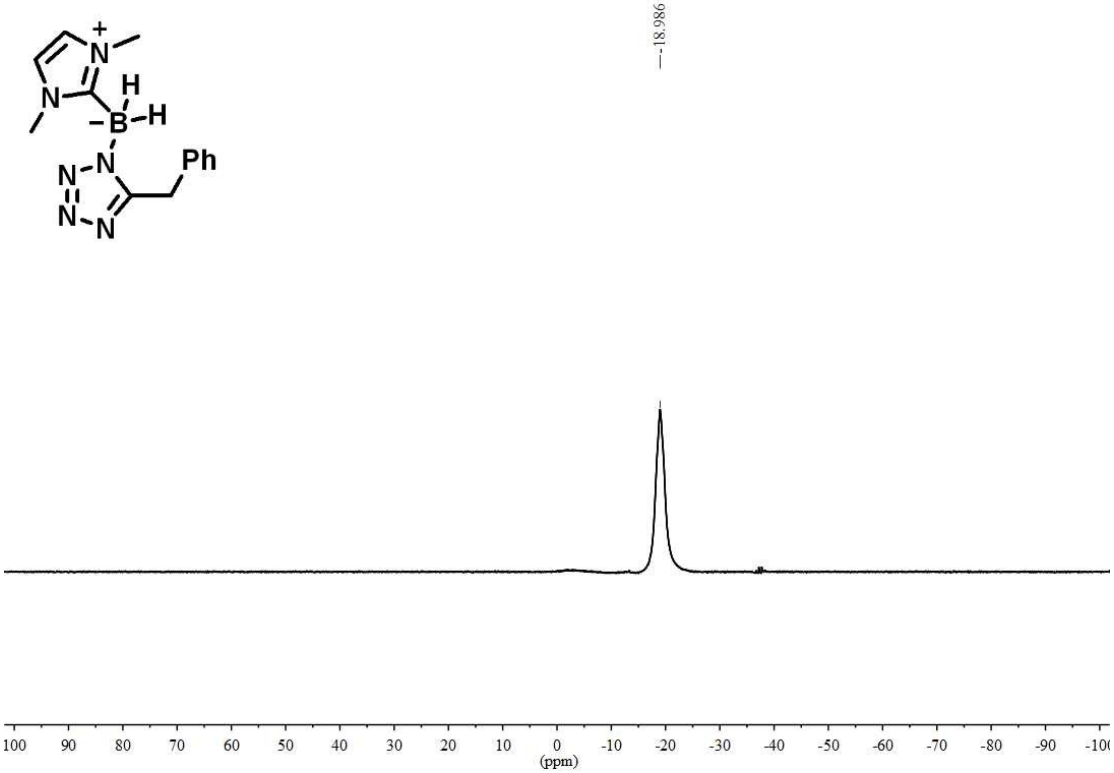
^{1}H NMR of product 5w in $CDCl_3$ (500 MHz)



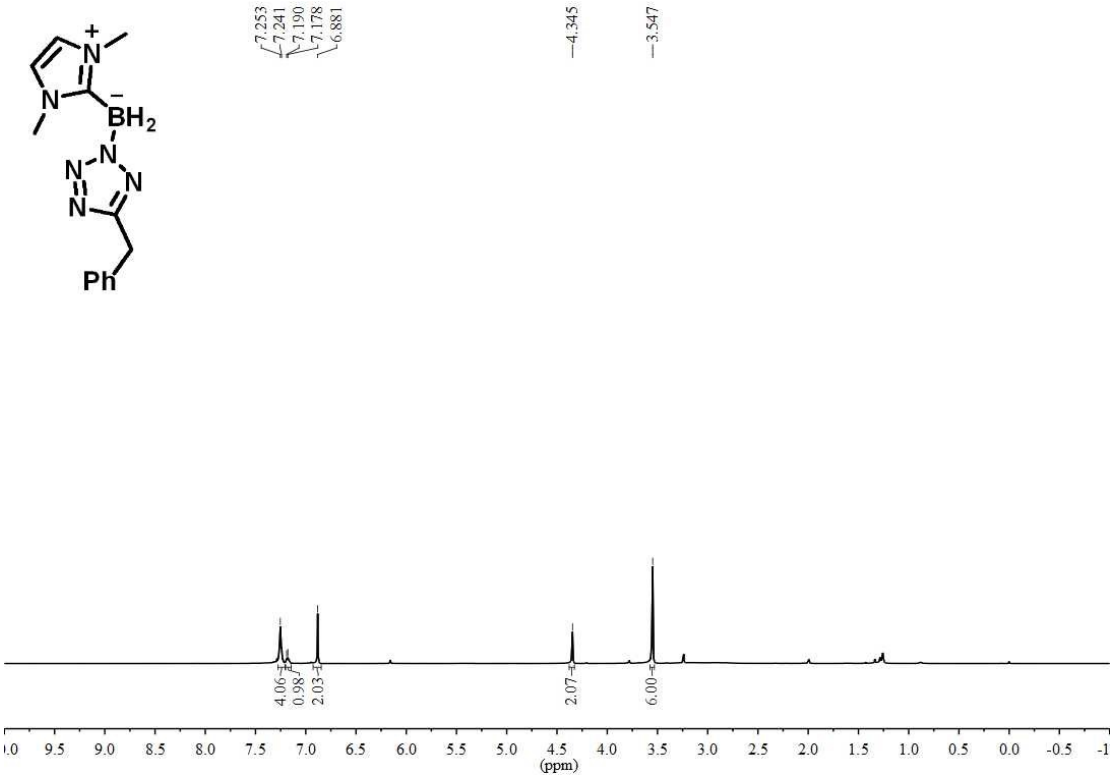
^{13}C NMR of product 5w in $CDCl_3$ (125 MHz)



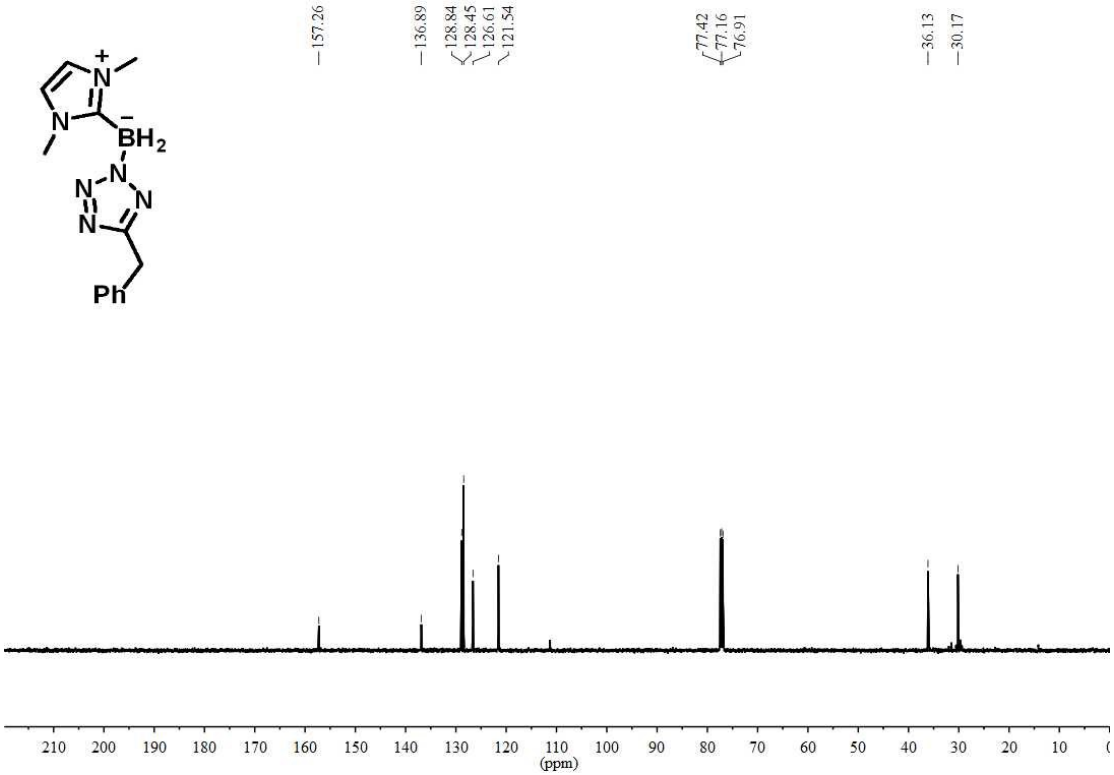
^{11}B NMR of product in 5w $CDCl_3$ (160 MHz)



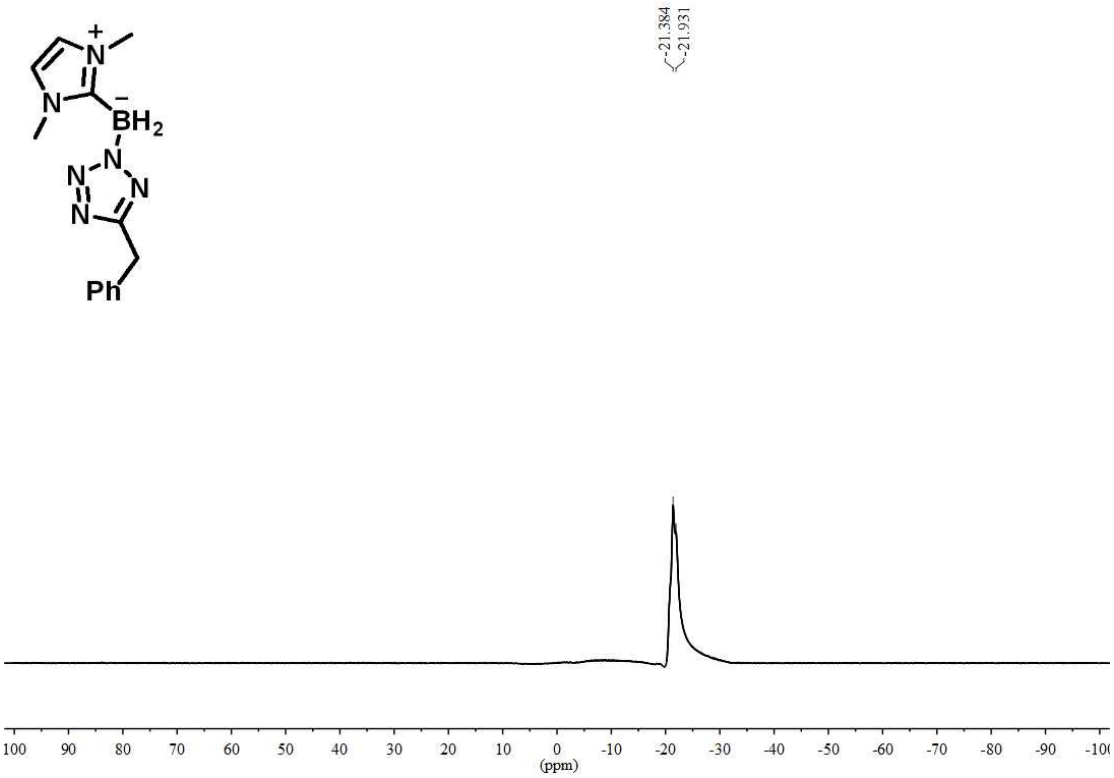
^{1}H NMR of product 5w' in $CDCl_3$ (500 MHz)



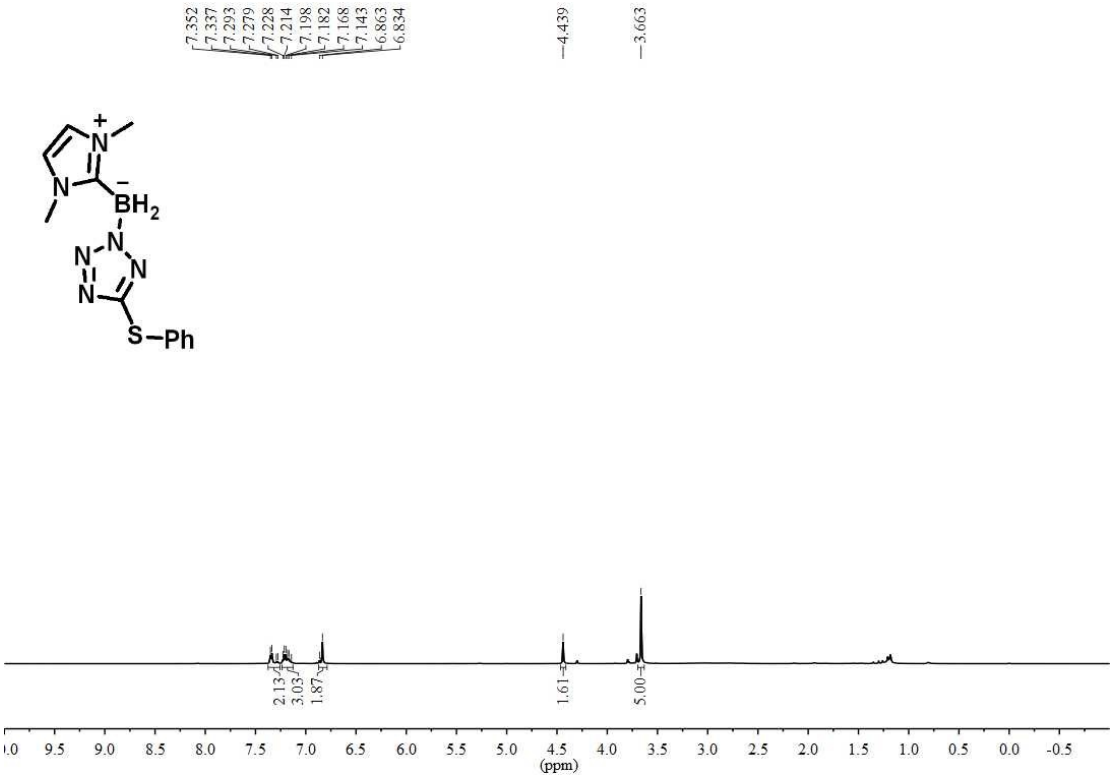
^{13}C NMR of product 5w' in $CDCl_3$ (125 MHz)



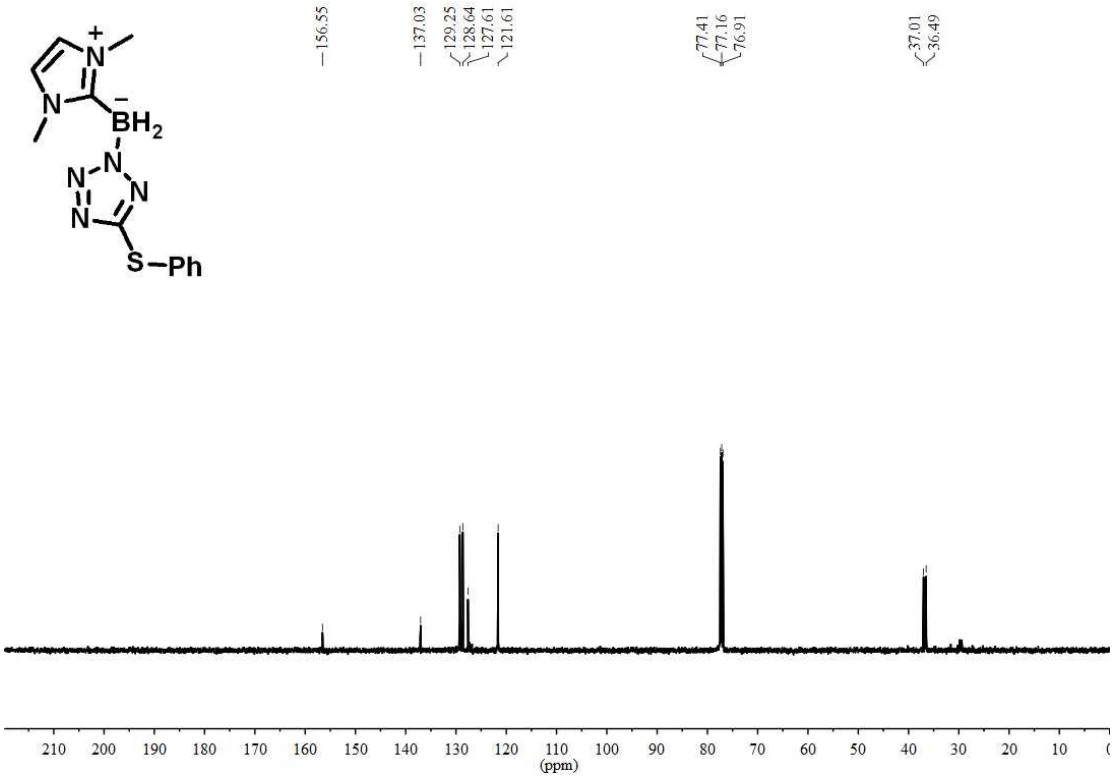
^{11}B NMR of product 5w' in $CDCl_3$ (160 MHz)



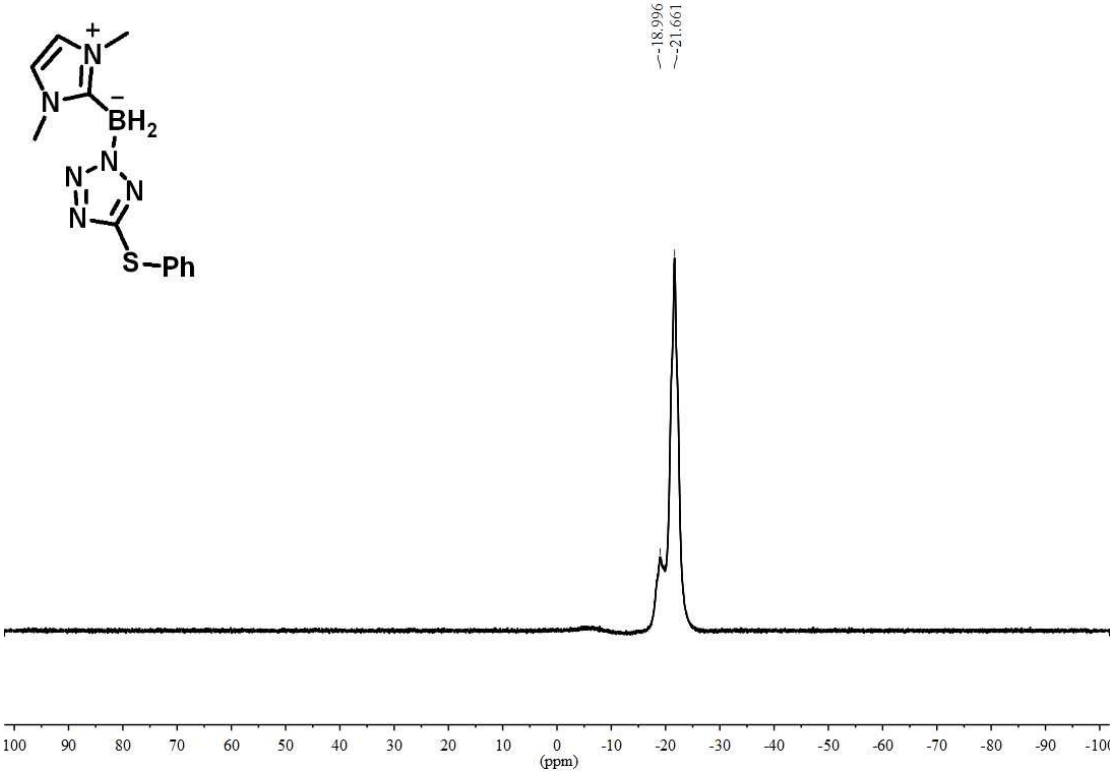
^{1}H NMR of product 5x in $CDCl_3$ (500 MHz)



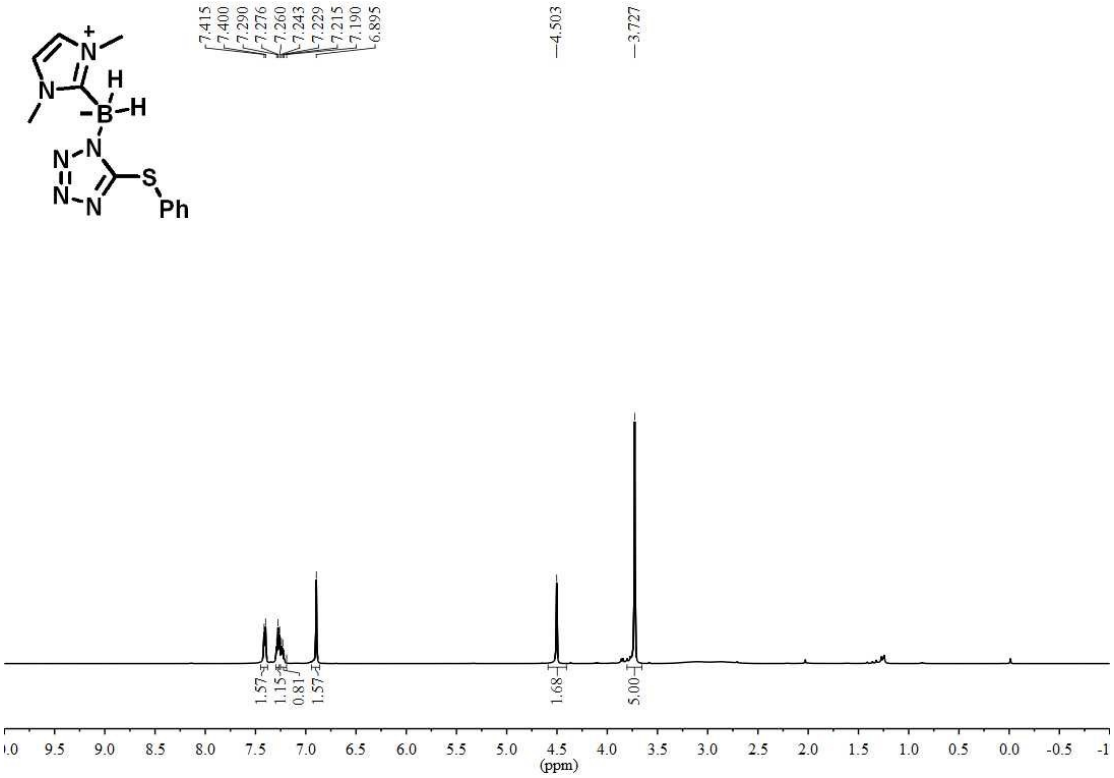
^{13}C NMR of product 5x in $CDCl_3$ (125 MHz)



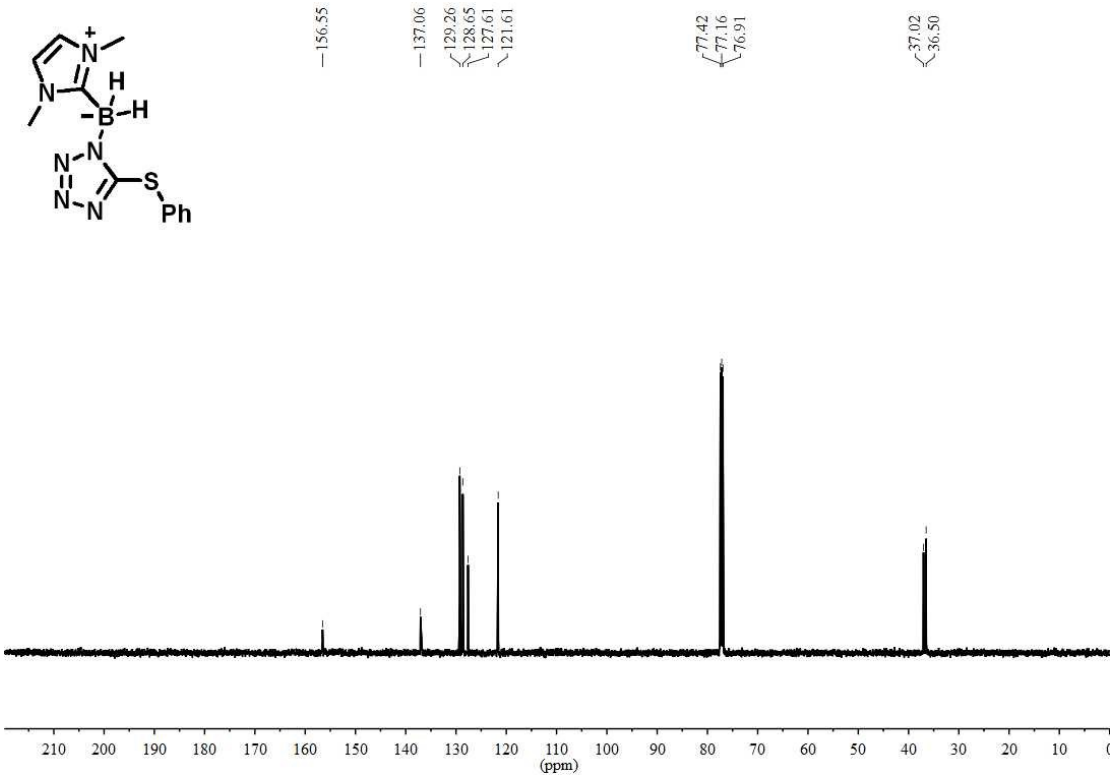
^{11}B NMR of product 5x in $CDCl_3$ (160 MHz)



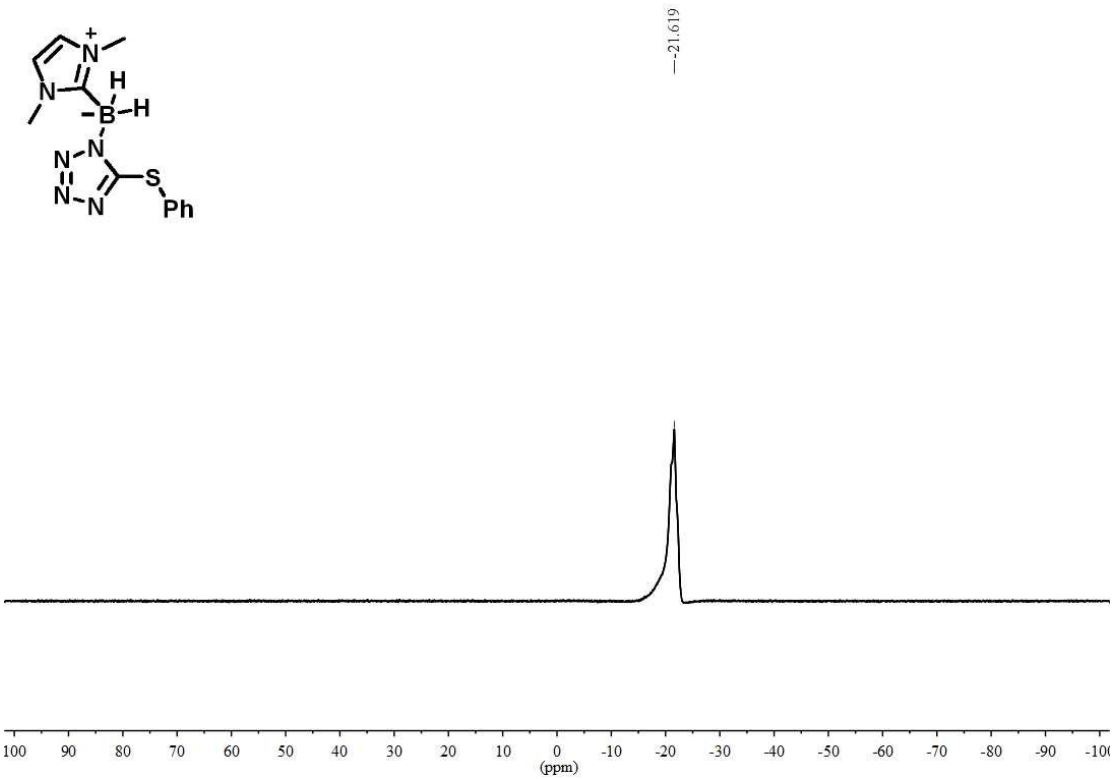
^{1}H NMR of product 5x' in $CDCl_3$ (500 MHz)



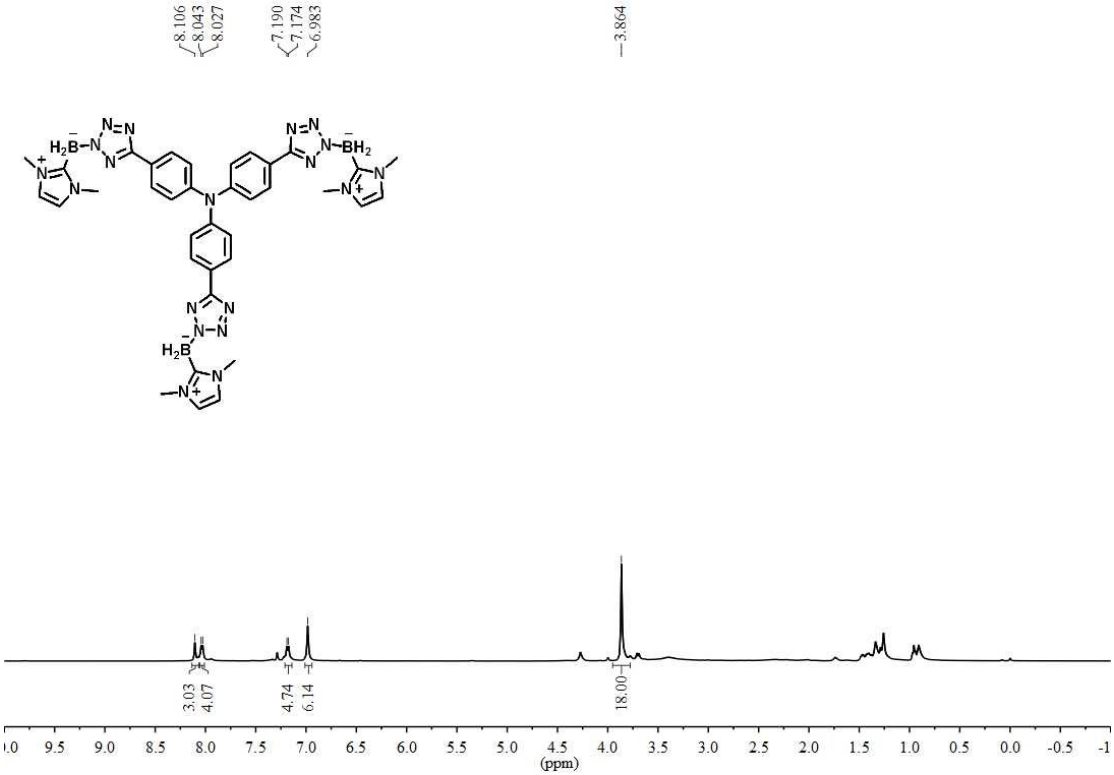
^{13}C NMR of product in 5x' $CDCl_3$ (125 MHz)



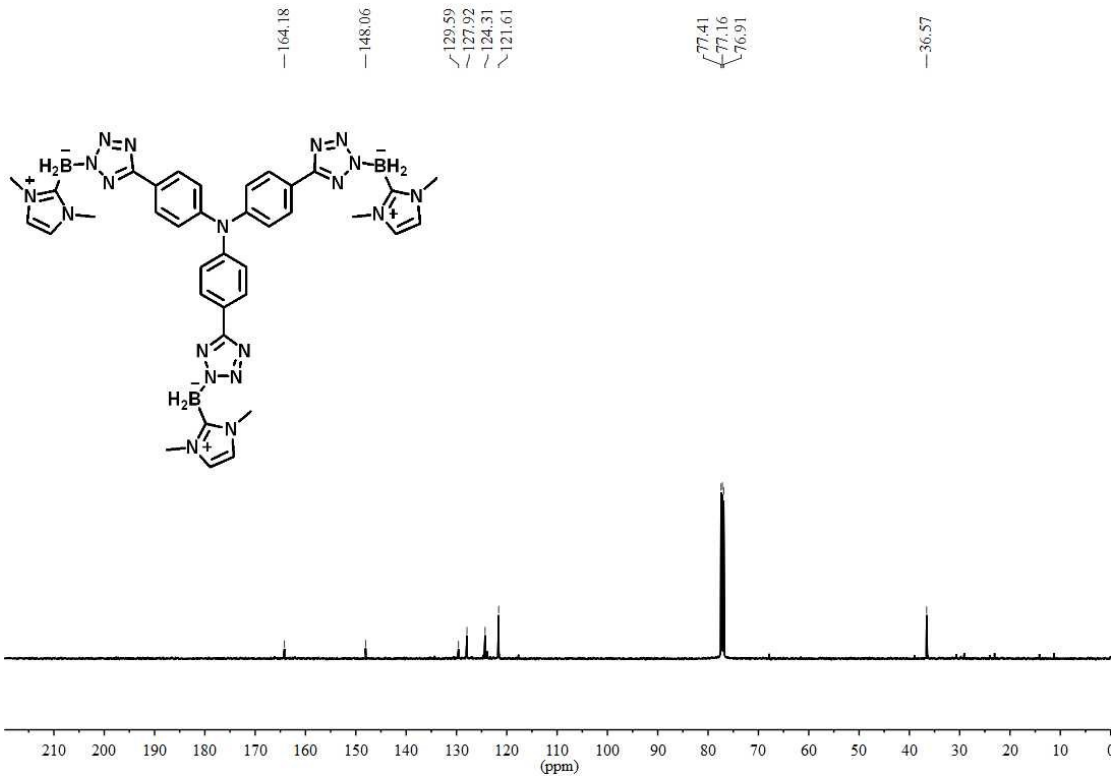
^{11}B NMR of product 5x' in $CDCl_3$ (160 MHz)



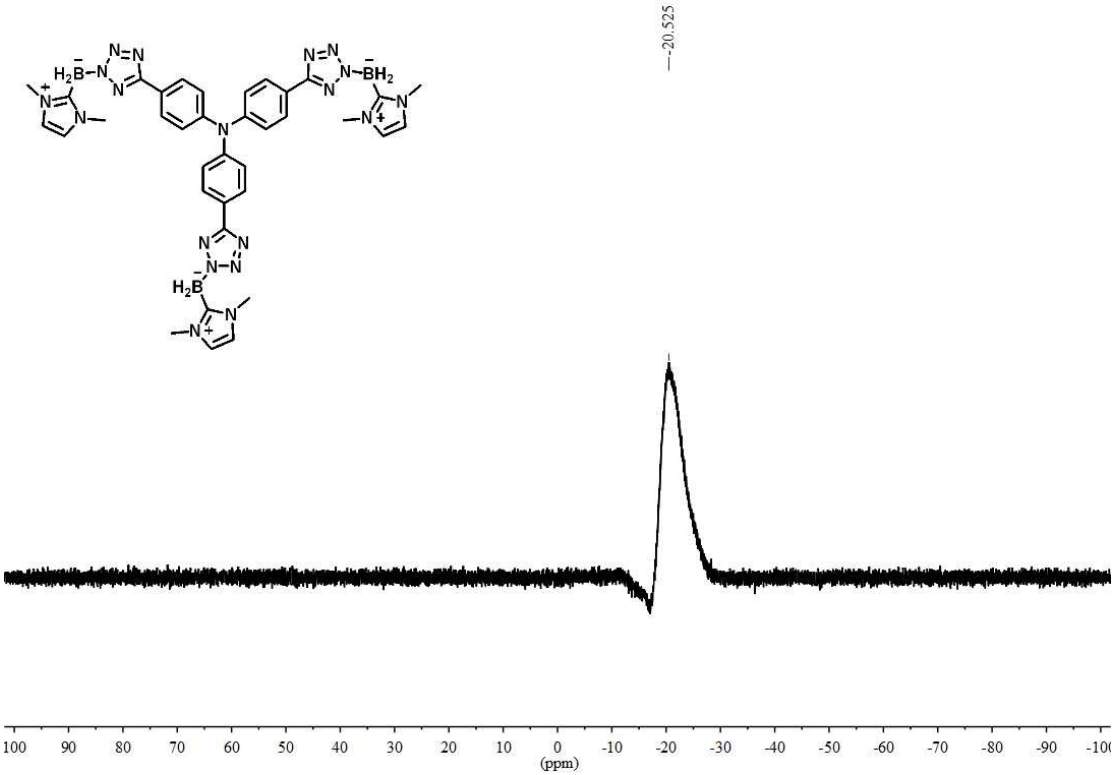
^{1}H NMR of product 5y in $CDCl_3$ (500 MHz)



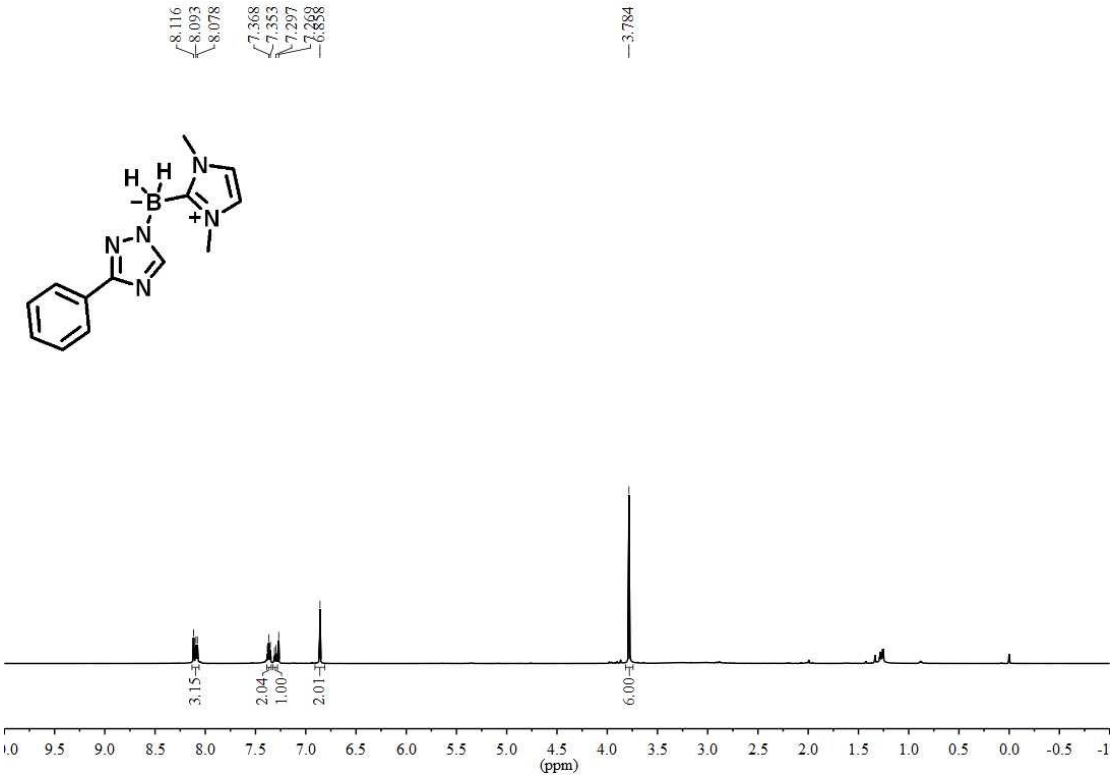
^{13}C NMR of product 5y in $CDCl_3$ (125 MHz)



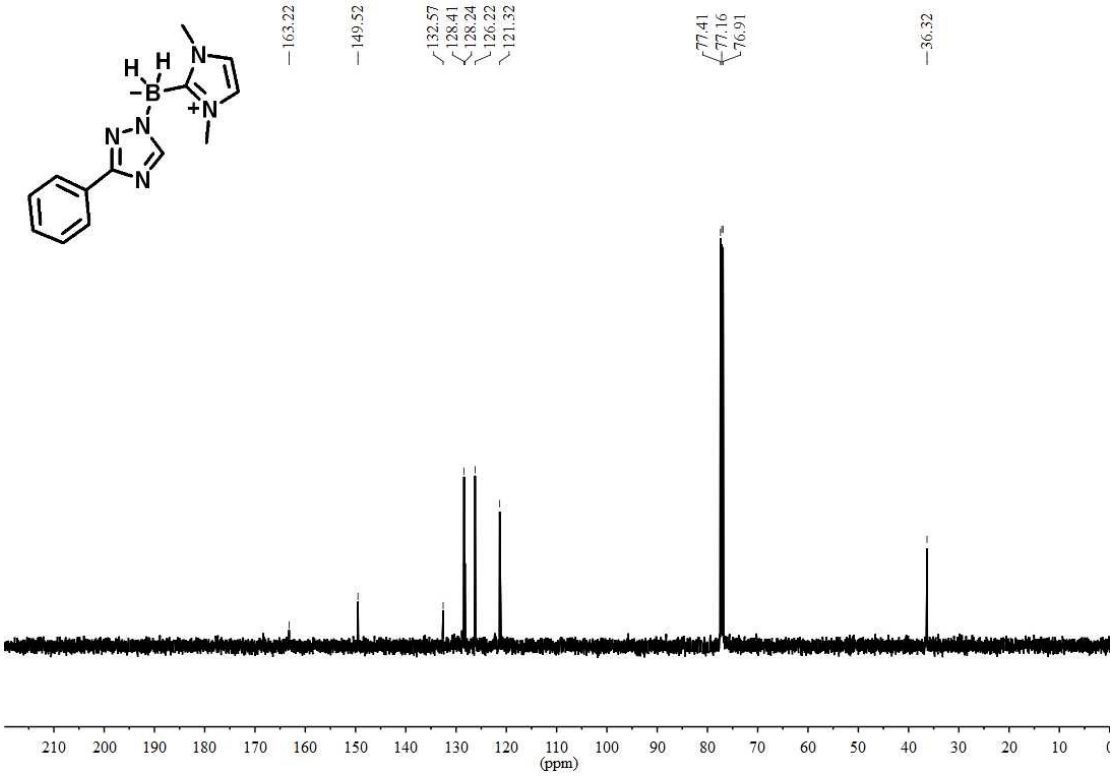
^{11}B NMR of product 5y in $CDCl_3$ (160 MHz)



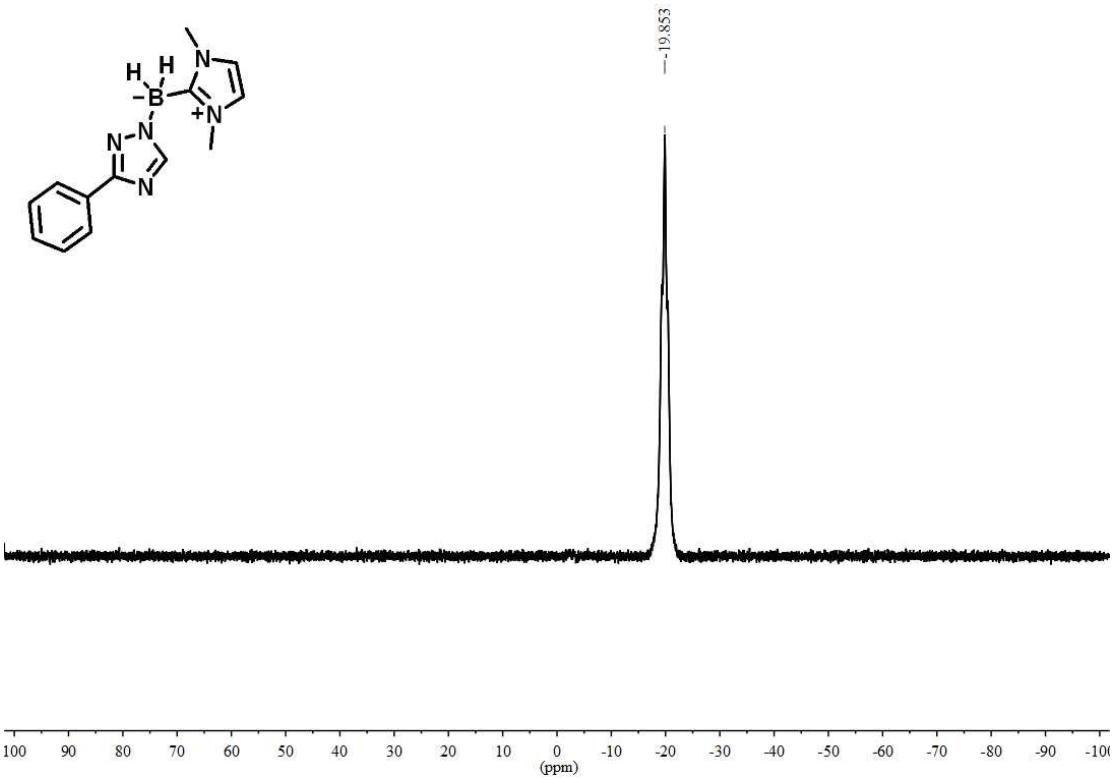
^{1}H NMR of product 5z in $CDCl_3$ (500 MHz)



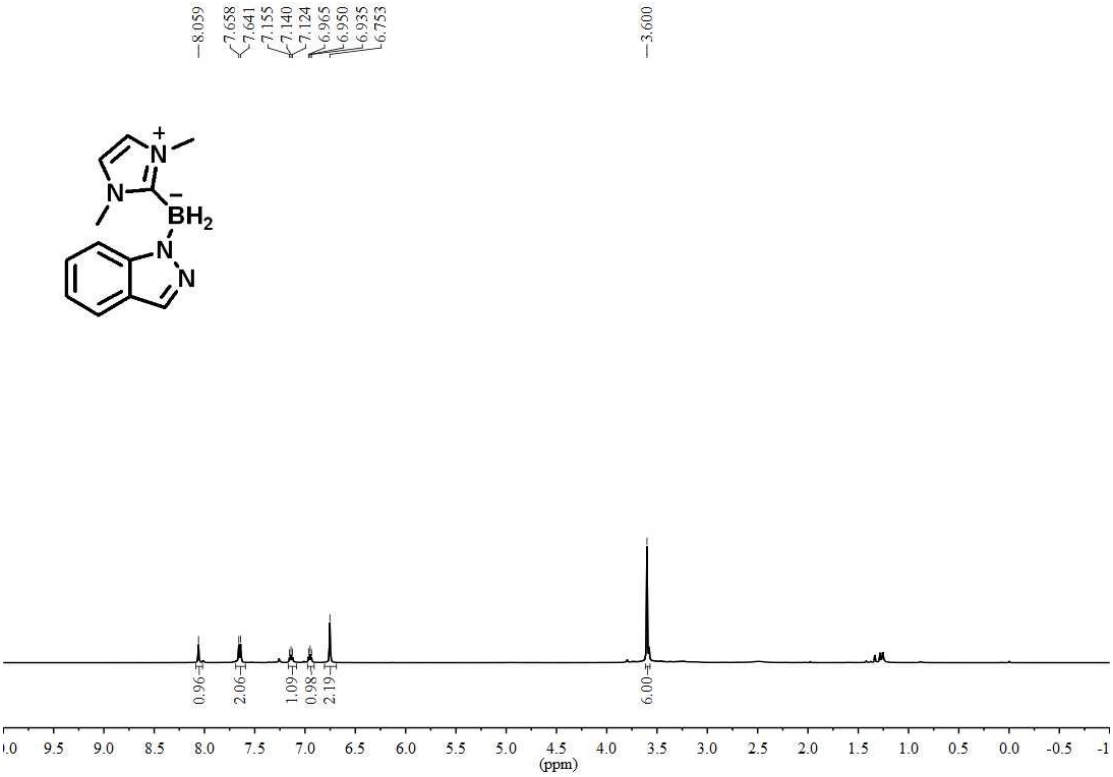
^{13}C NMR of product 5z in $CDCl_3$ (125 MHz)



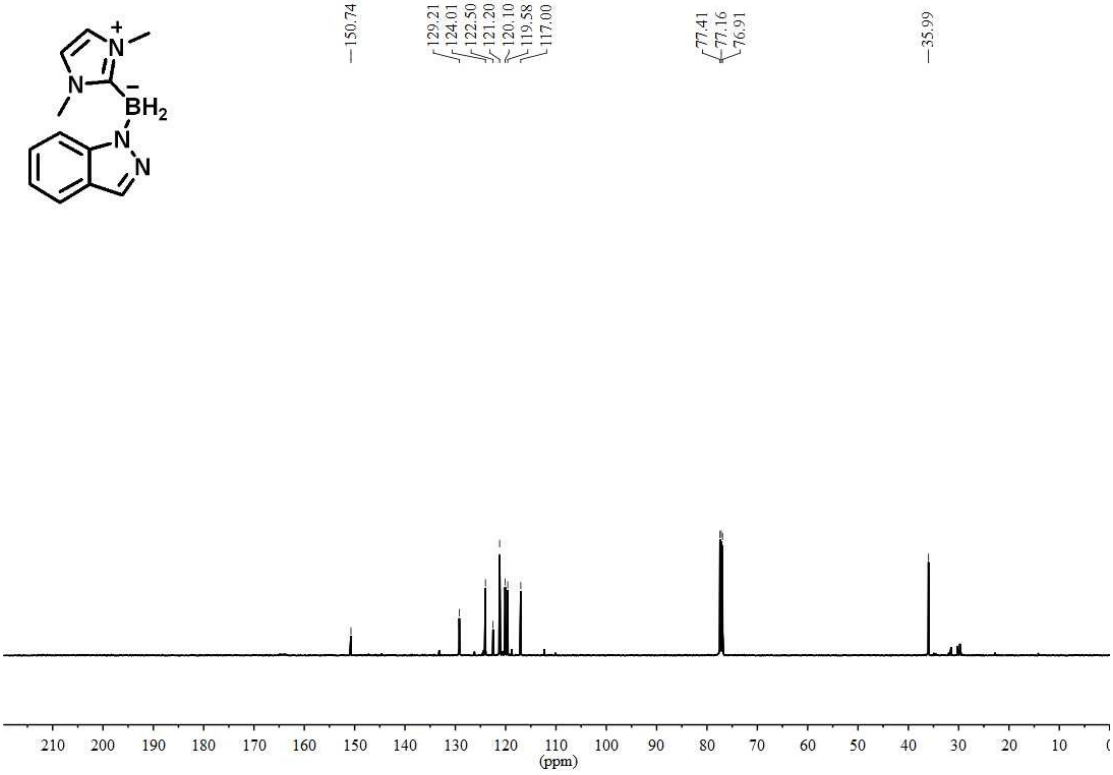
^{11}B NMR of product 5z in $CDCl_3$ (160 MHz)



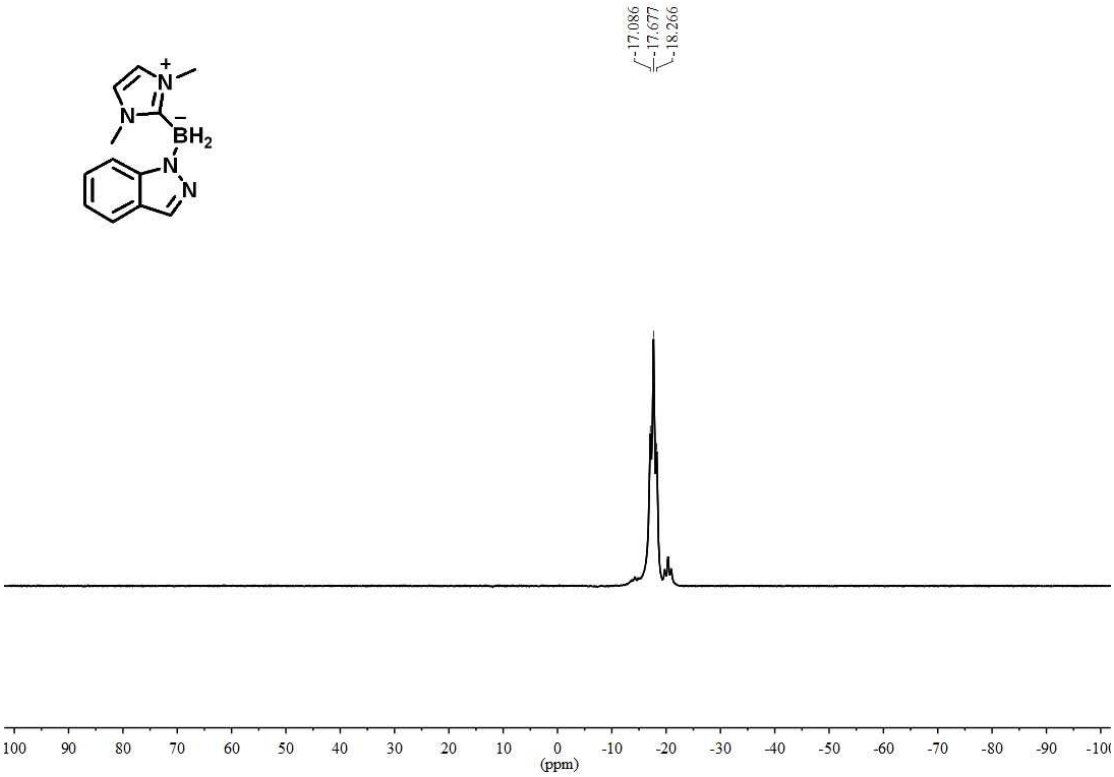
^{1}H NMR of product 5aa in $CDCl_3$ (500 MHz)



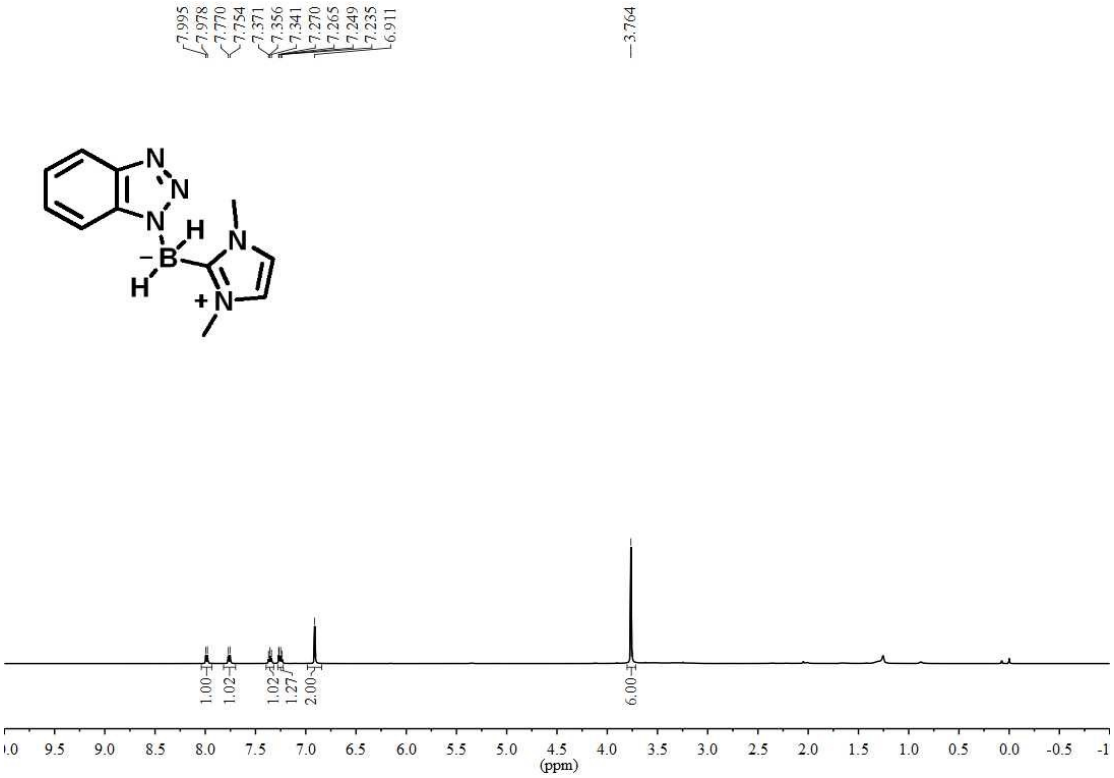
^{13}C NMR of product 5aa in $CDCl_3$ (125 MHz)



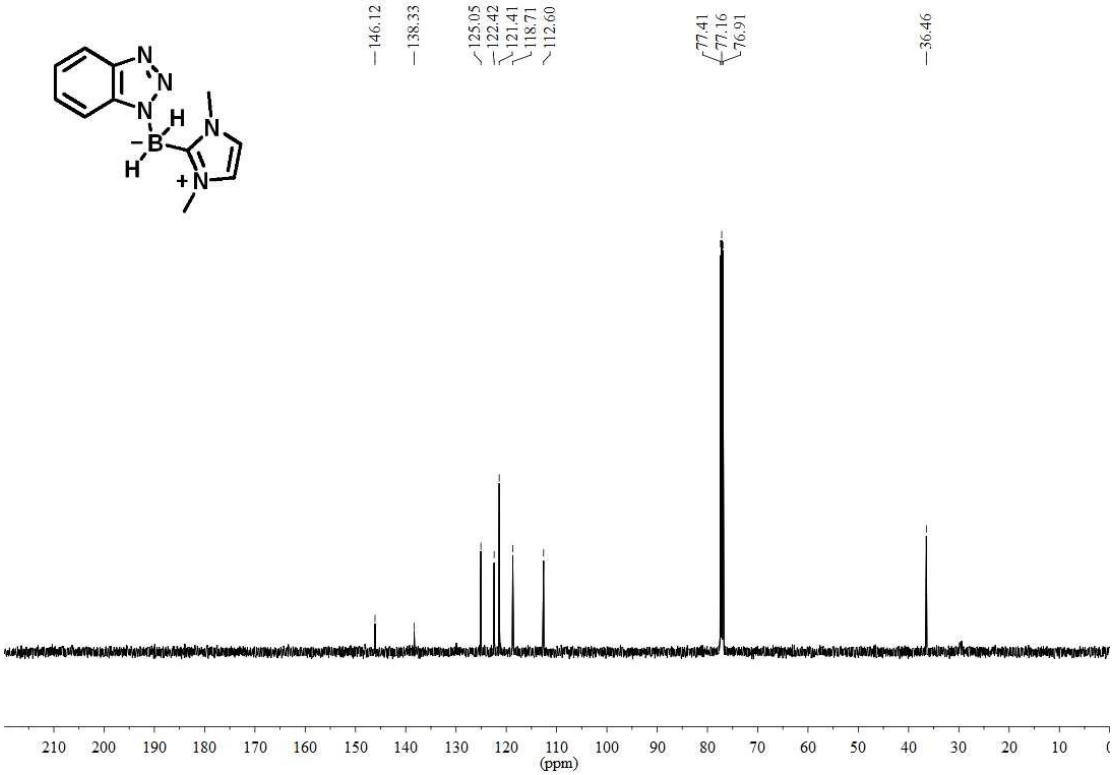
^{11}B NMR of product 5aa in $CDCl_3$ (160 MHz)



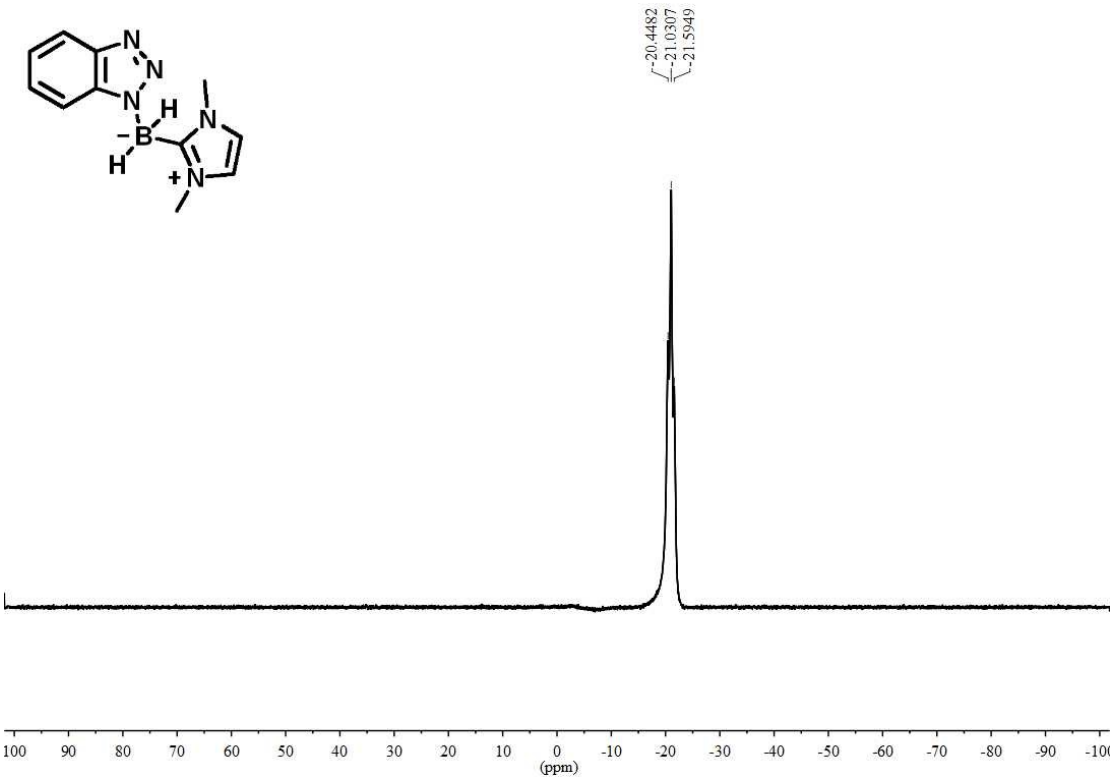
^{1}H NMR of product 5ab in $CDCl_3$ (500 MHz)



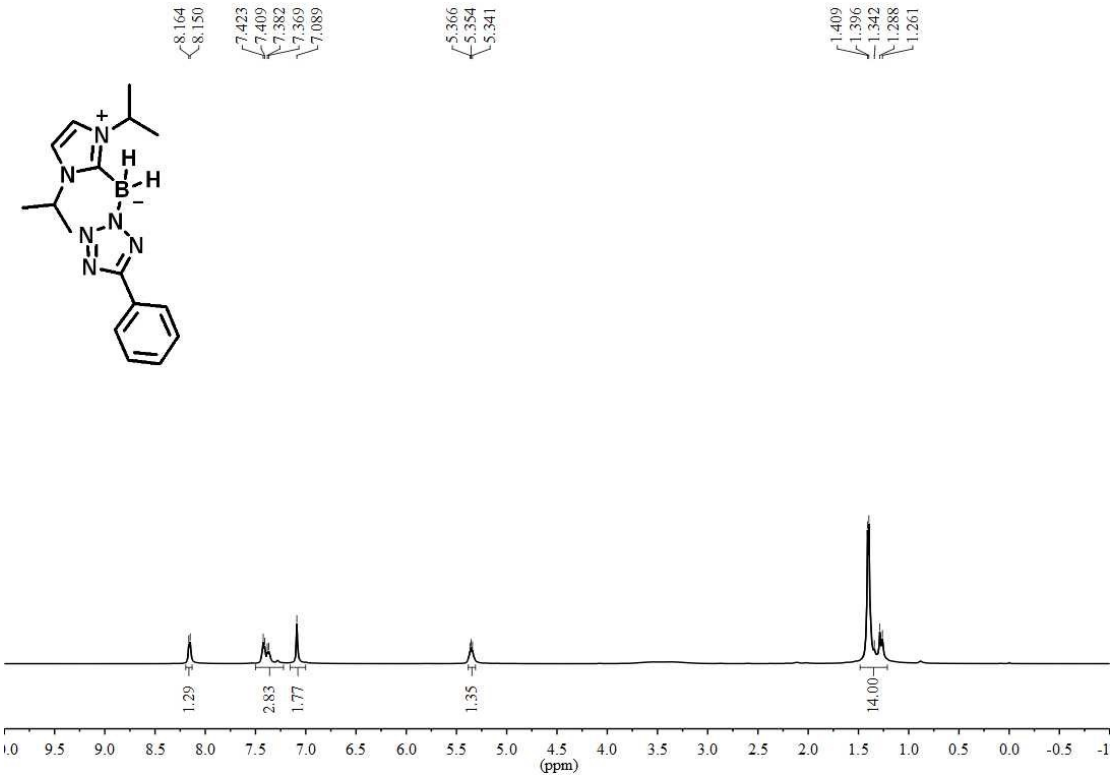
^{13}C NMR of product 5ab in $CDCl_3$ (125 MHz)



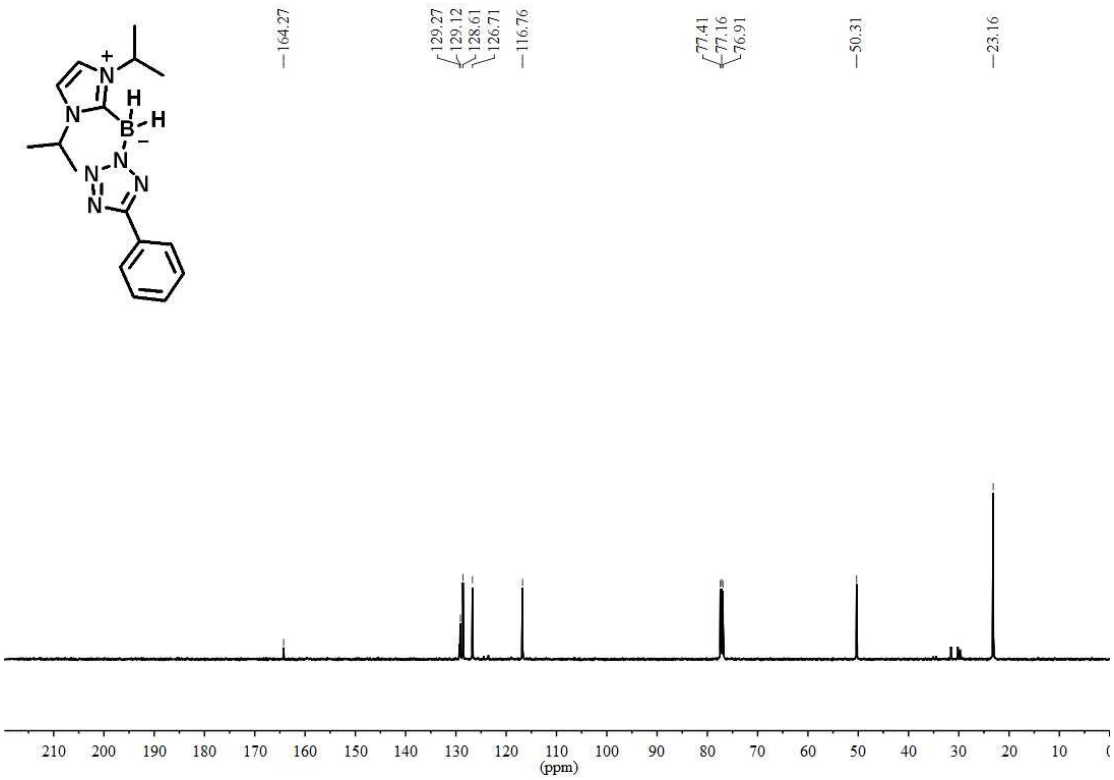
^{11}B NMR of product 5ab in $CDCl_3$ (160 MHz)



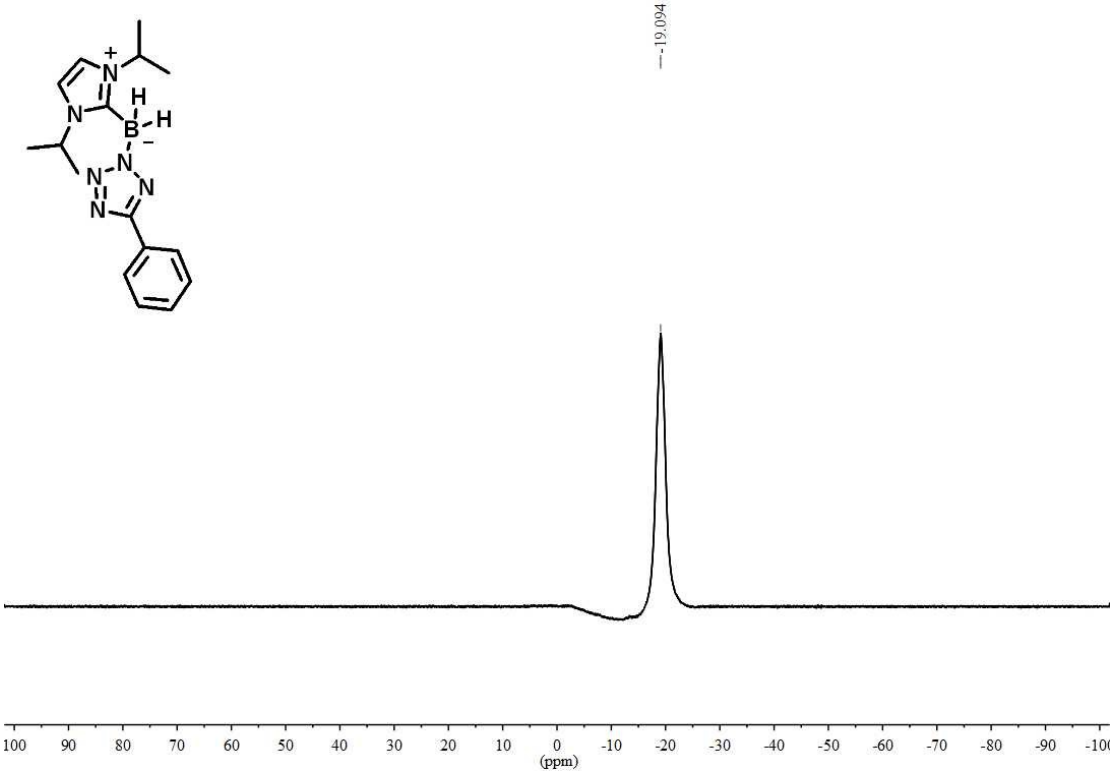
^{1}H NMR of product 5ac in $CDCl_3$ (500 MHz)



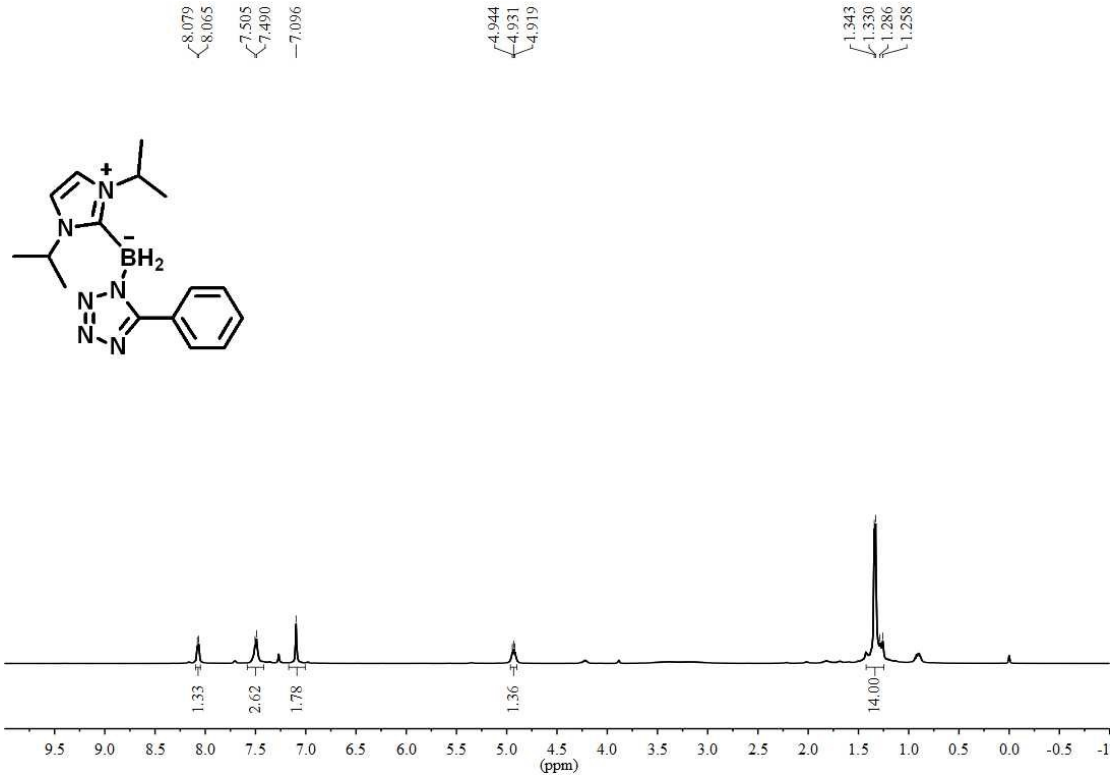
^{13}C NMR of product 5ac in $CDCl_3$ (125 MHz)



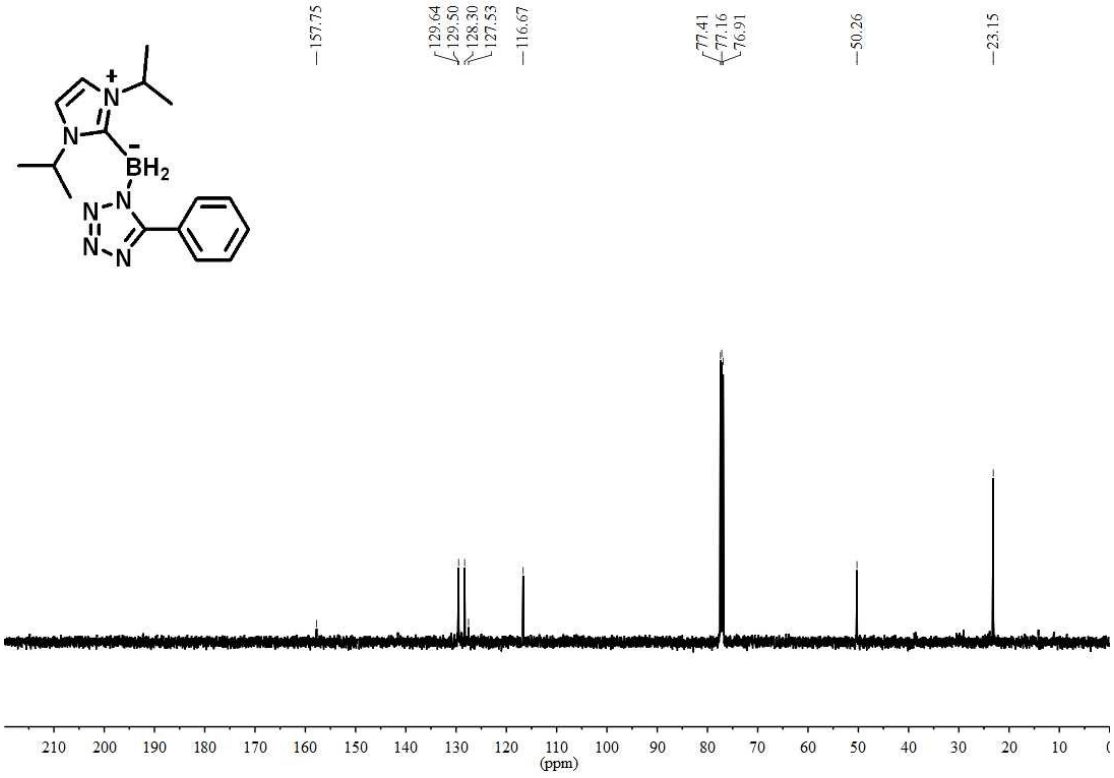
^{11}B NMR of product 5ac in $CDCl_3$ (160 MHz)



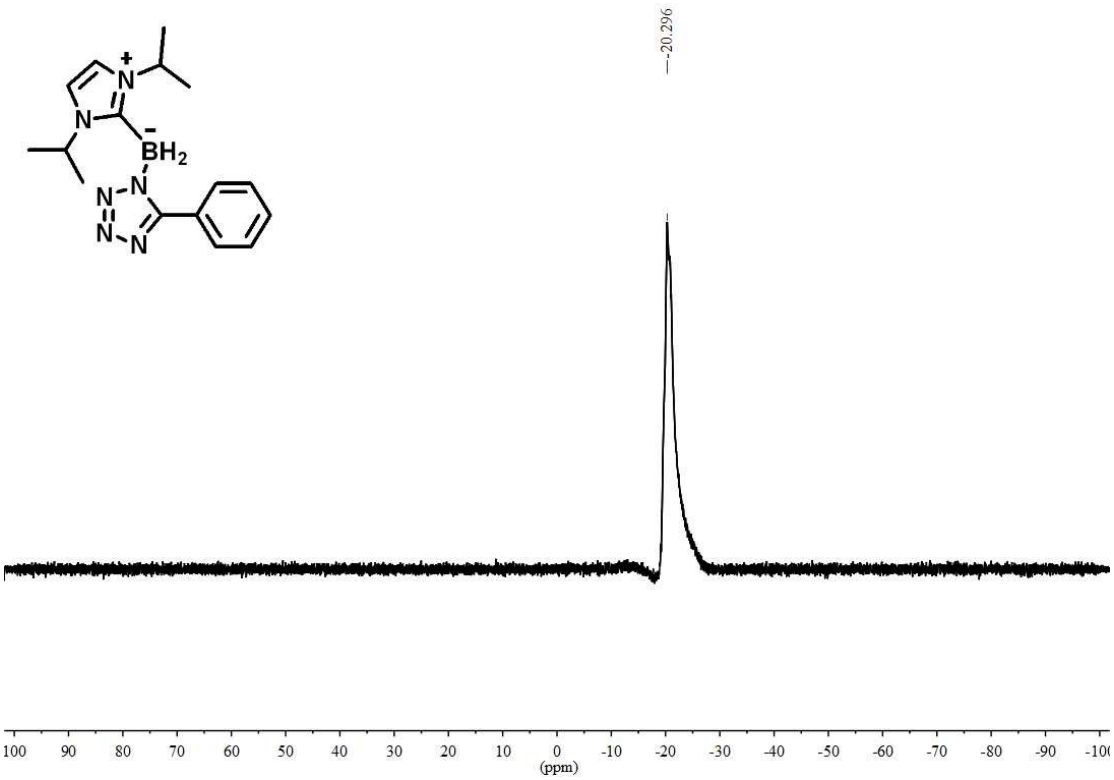
^{1}H NMR of product 5ac' in $CDCl_3$ (500 MHz)



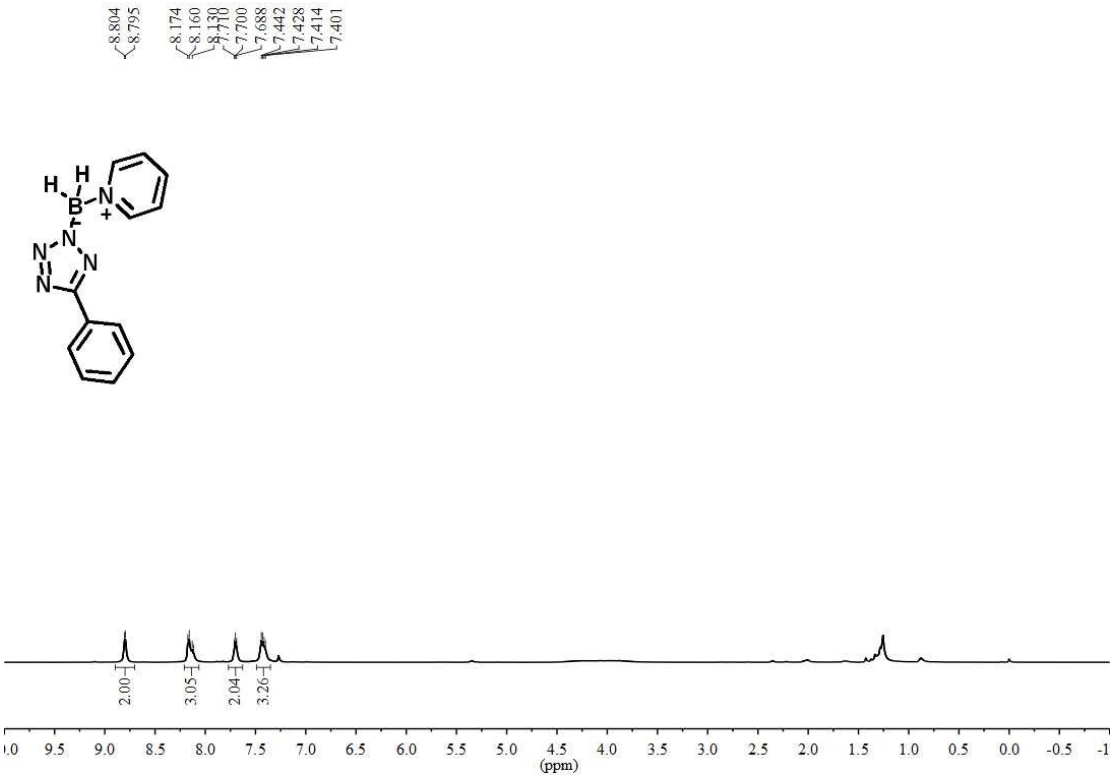
^{13}C NMR of product 5ac' in $CDCl_3$ (125 MHz)



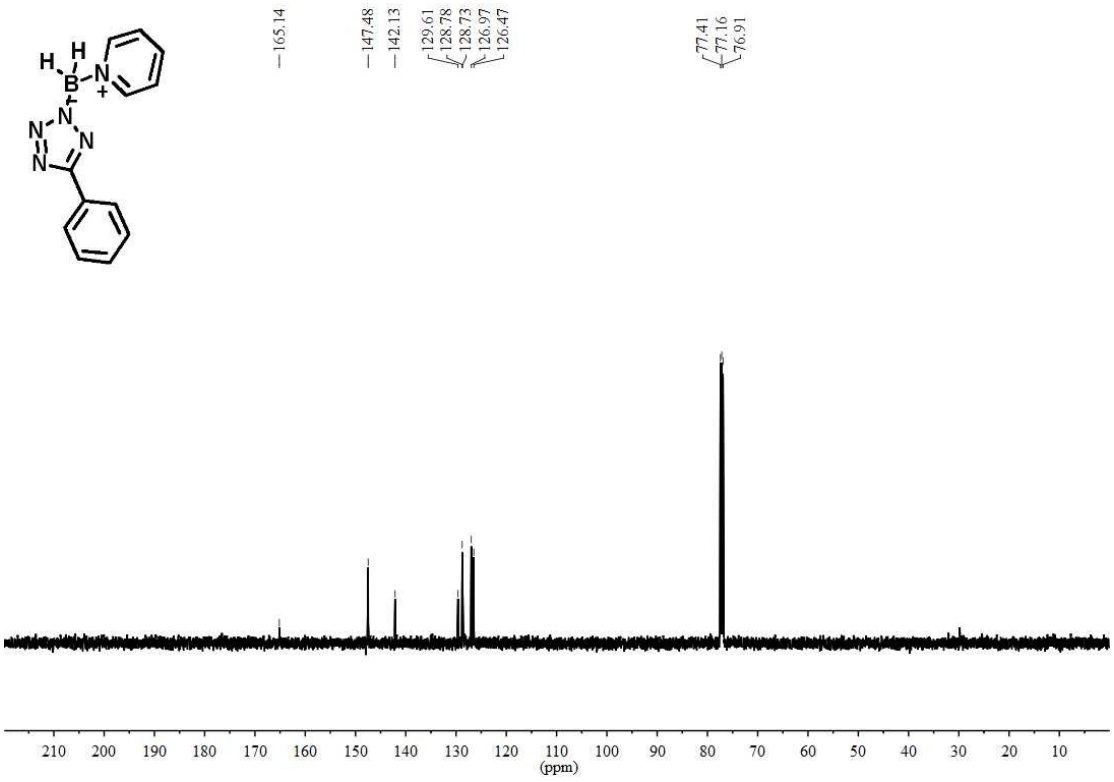
^{11}B NMR of product 5ac' in $CDCl_3$ (160 MHz)



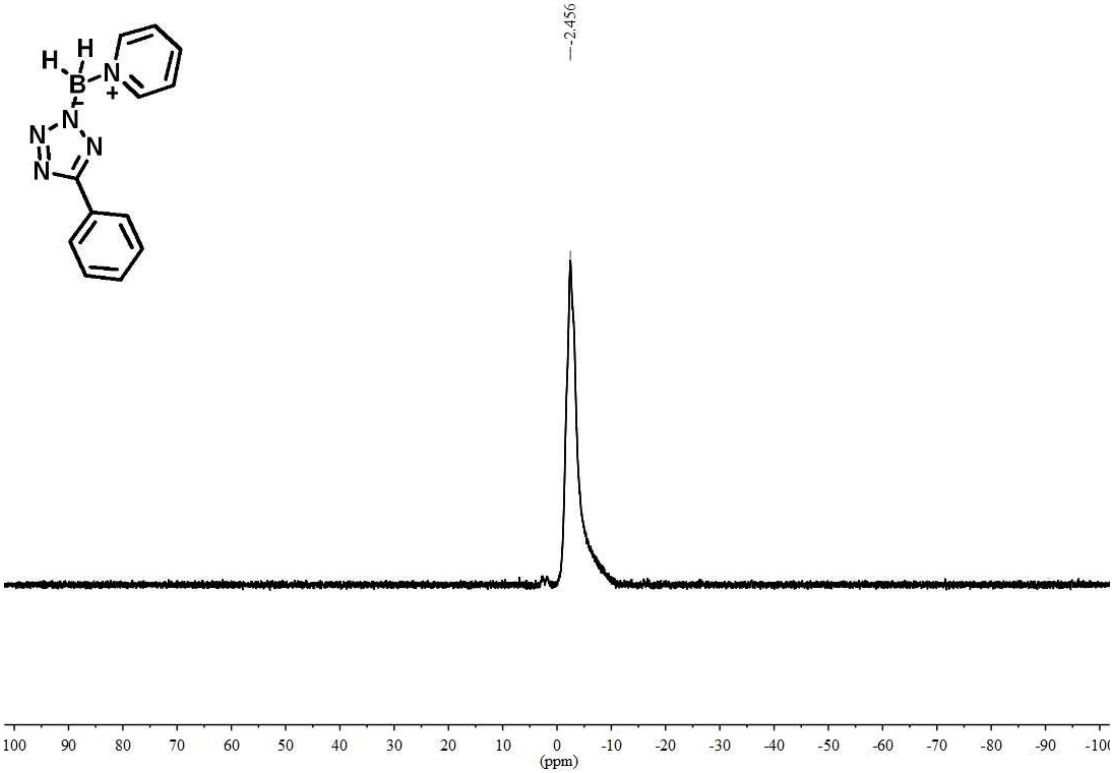
^{1}H NMR of product 5ad in $CDCl_3$ (500 MHz)



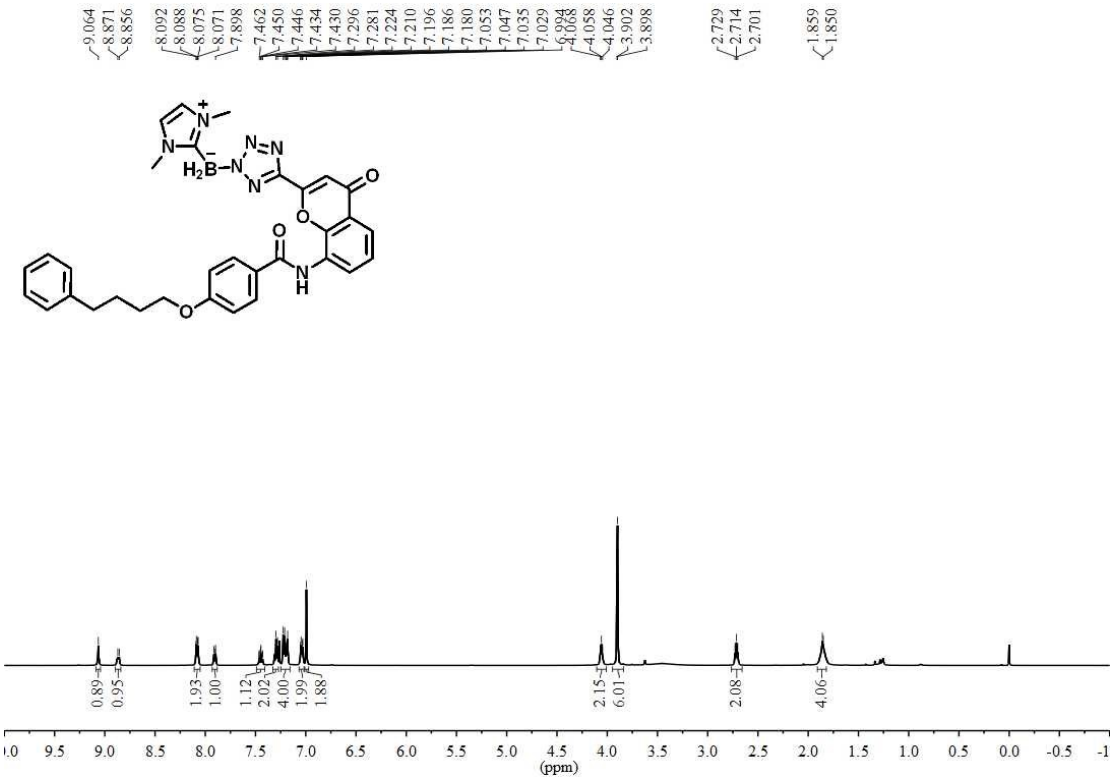
^{13}C NMR of product 5ad in $CDCl_3$ (125 MHz)



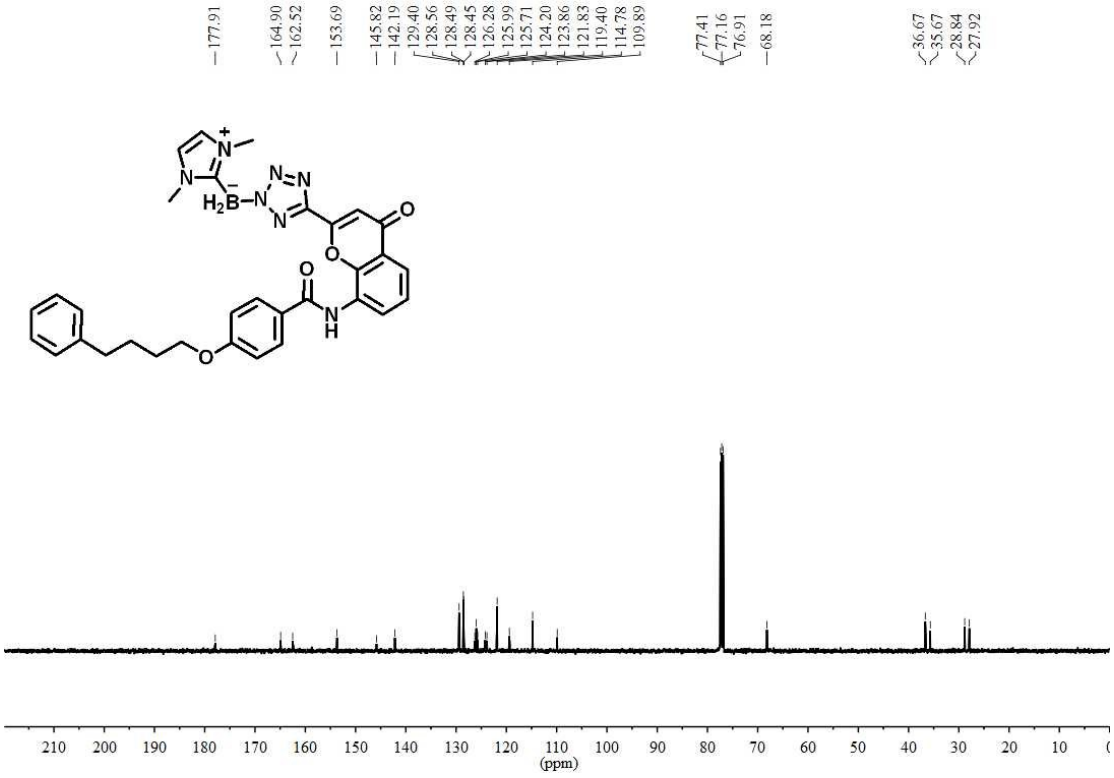
^{11}B NMR of product 5ad in $CDCl_3$ (160 MHz)



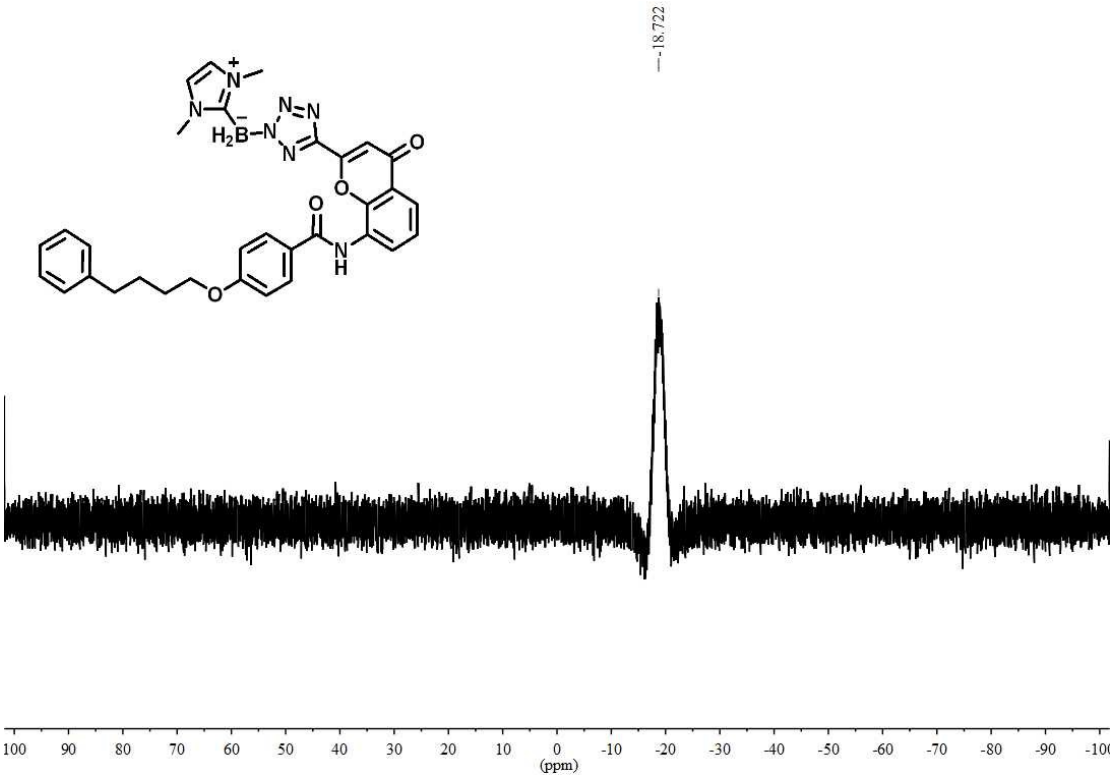
^{1}H NMR of product 5ae in $CDCl_3$ (500 MHz)



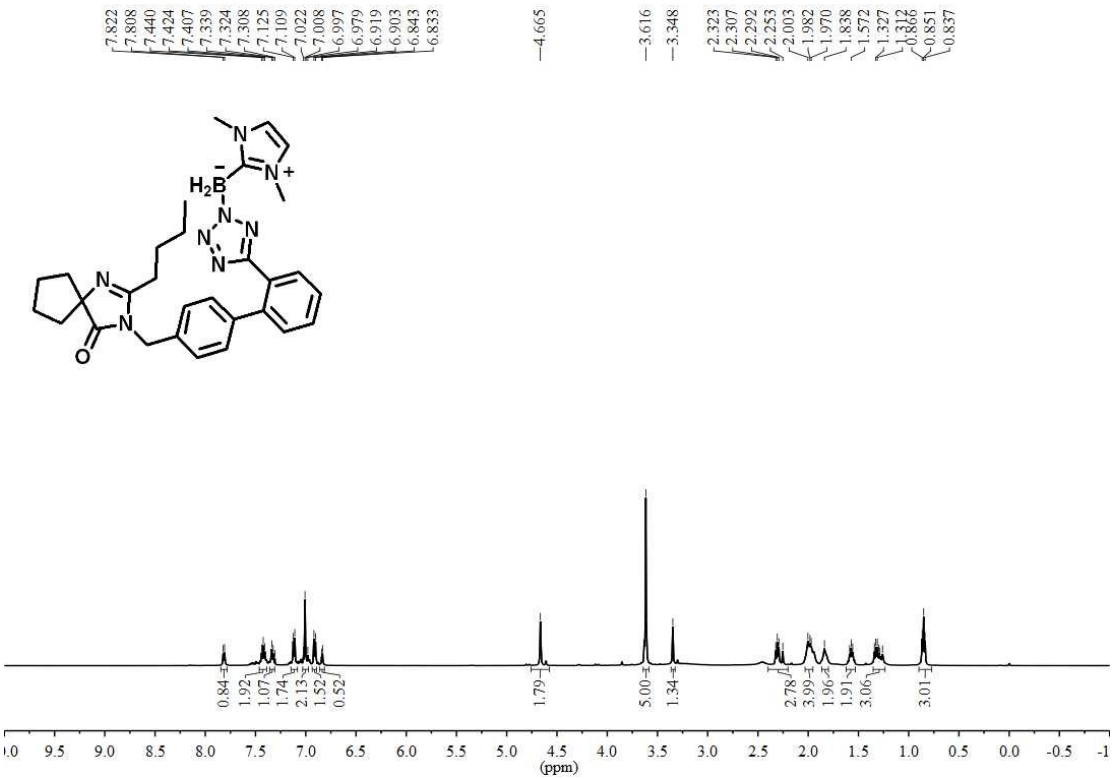
^{13}C NMR of product 5ae in $CDCl_3$ (125 MHz)



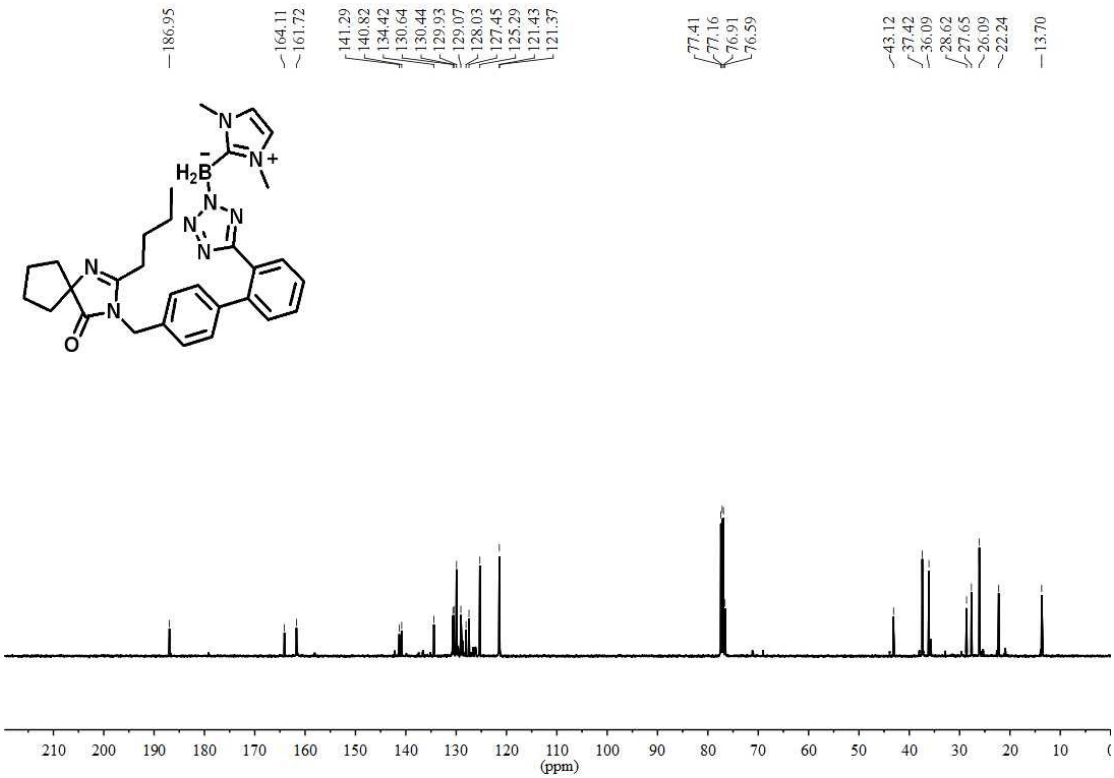
^{11}B NMR of product 5ae in $CDCl_3$ (160 MHz)



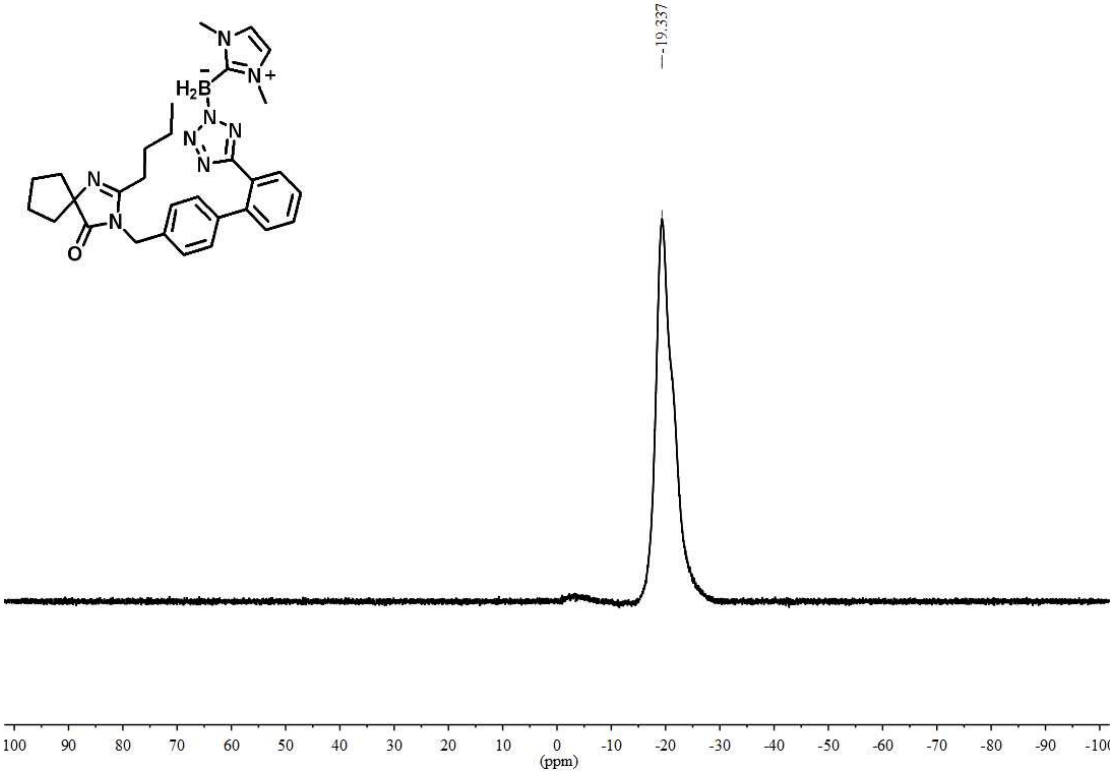
^{1}H NMR of product 5af in $CDCl_3$ (500 MHz)



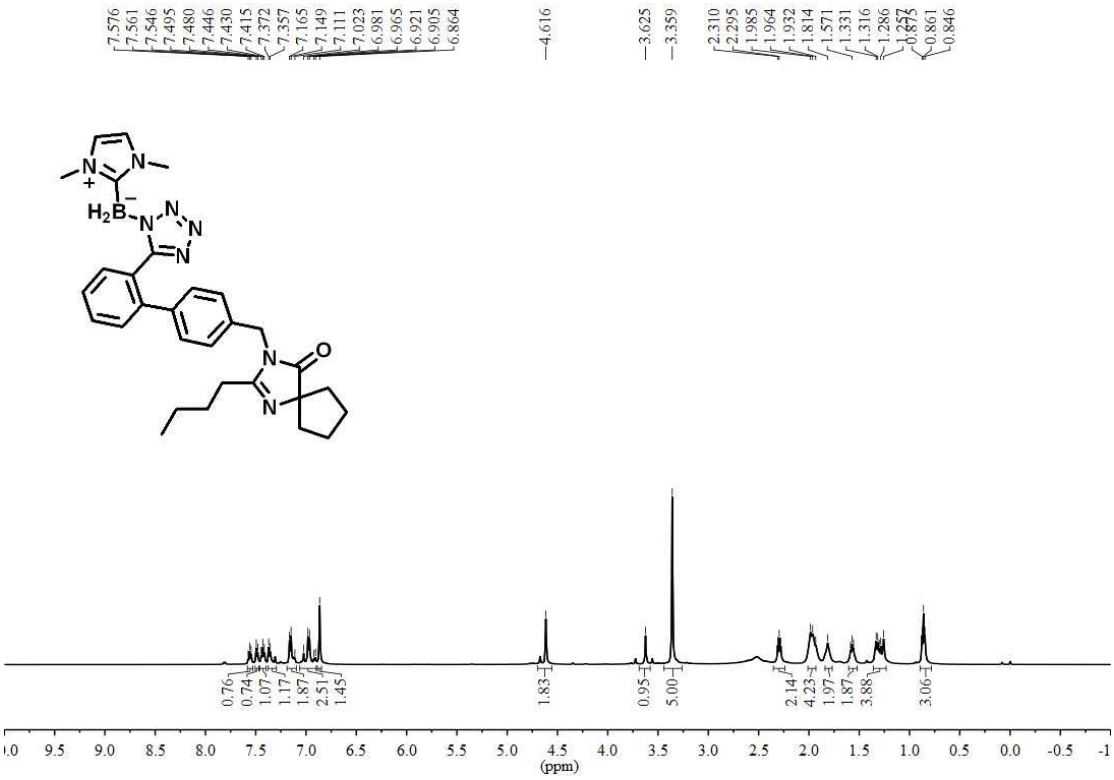
^{13}C NMR of product 5af in $CDCl_3$ (125 MHz)



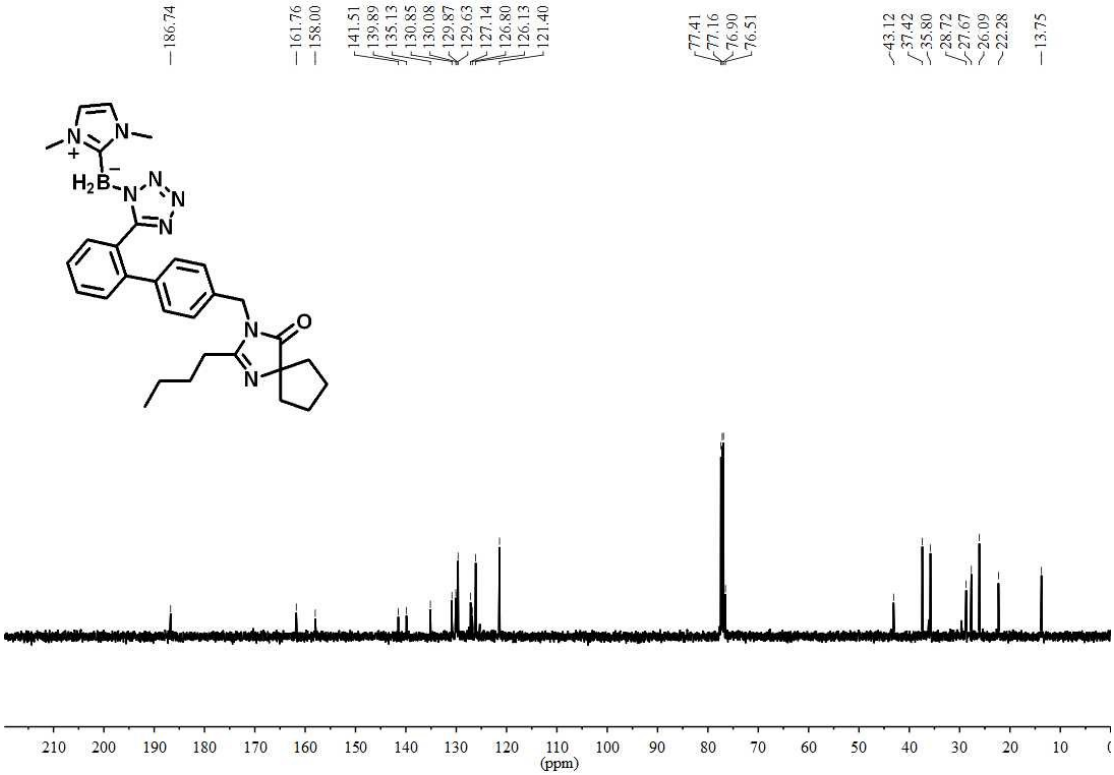
^{11}B NMR of product 5af in $CDCl_3$ (160 MHz)



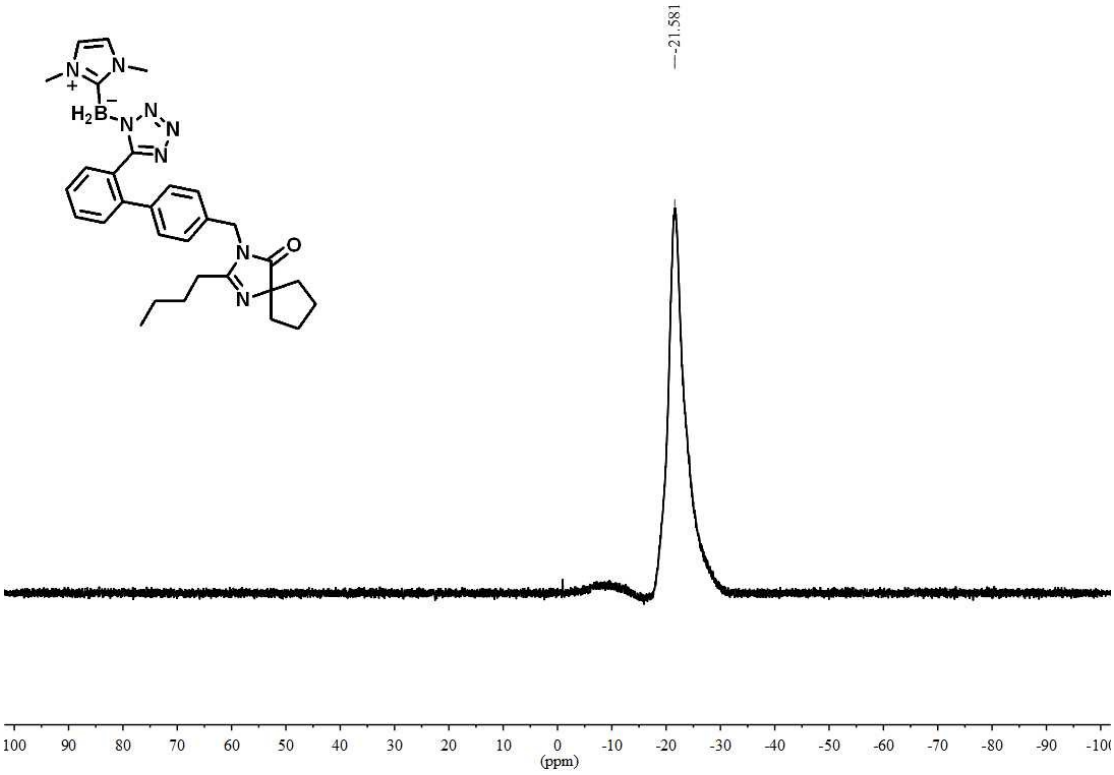
^{1}H NMR of product 5af' in $CDCl_3$ (500 MHz)



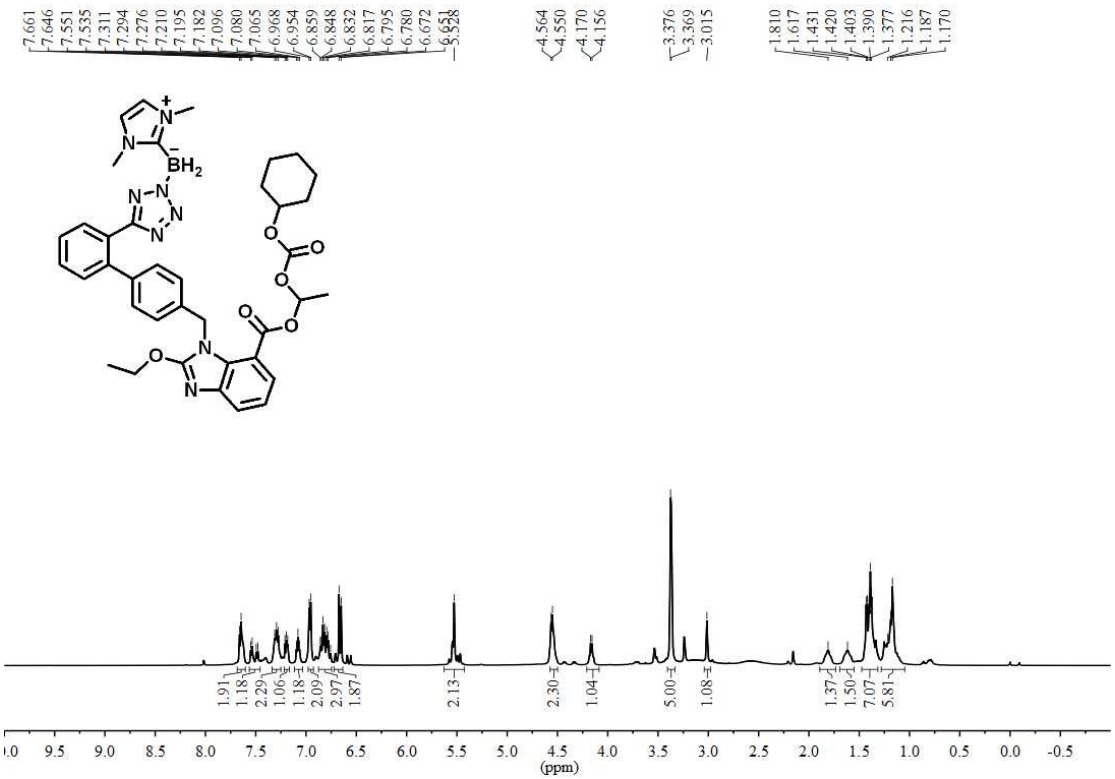
^{13}C NMR of product 5af' in $CDCl_3$ (125 MHz)



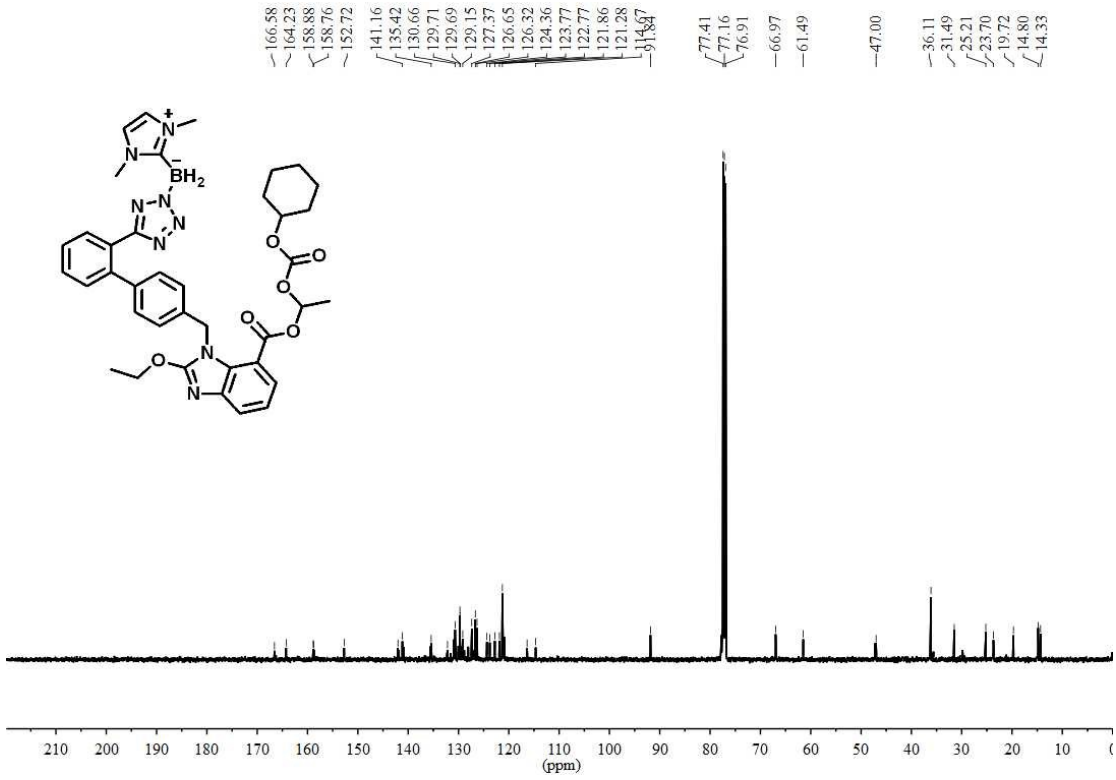
^{11}B NMR of product 5af' in $CDCl_3$ (160 MHz)



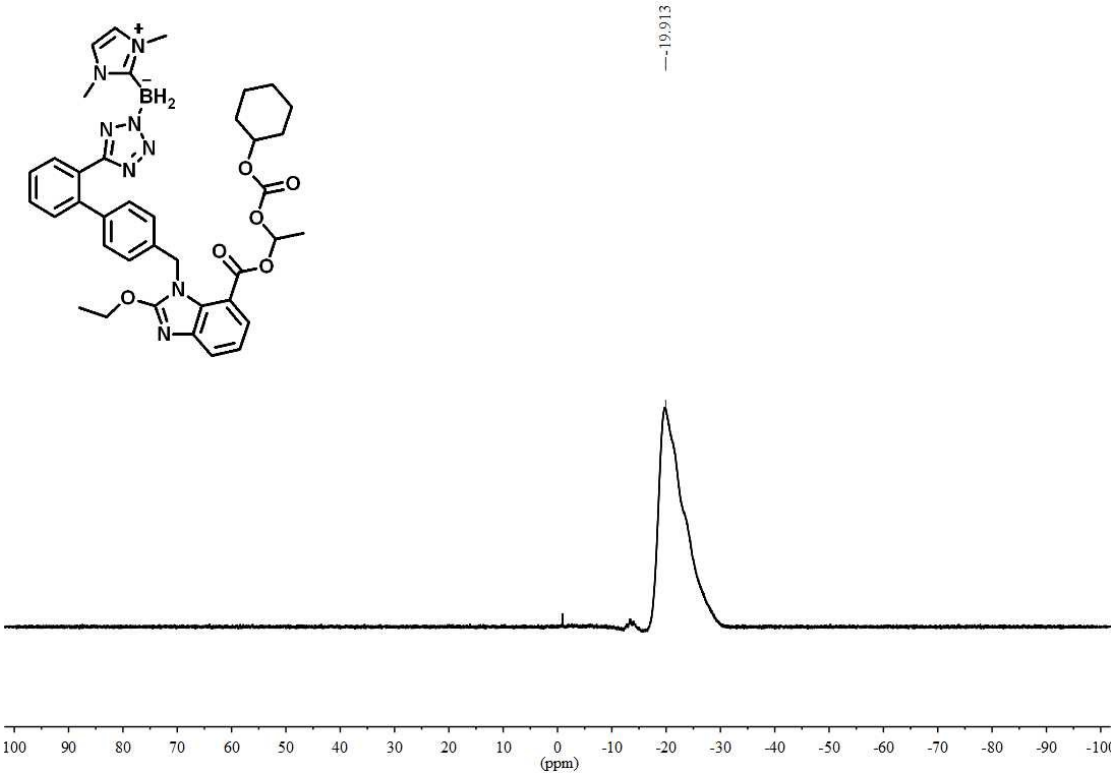
^{1}H NMR of product 5ag in $CDCl_3$ (500 MHz)



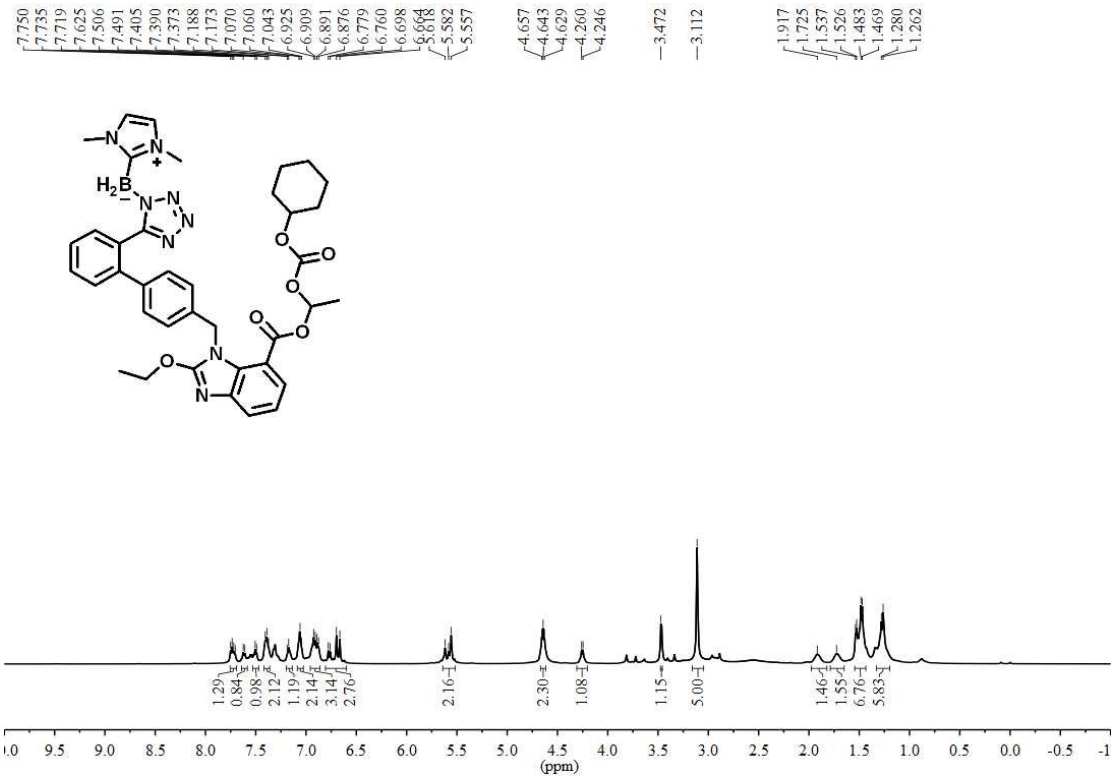
^{13}C NMR of product 5ag in $CDCl_3$ (125 MHz)



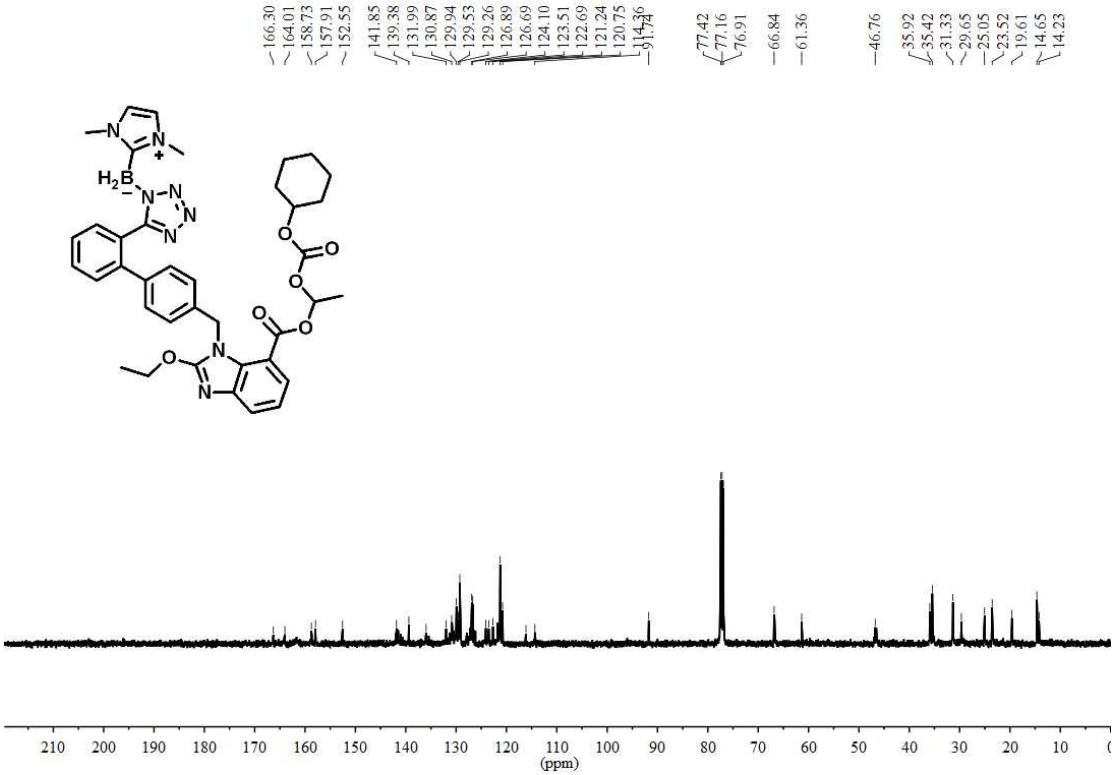
^{11}B NMR of product 5ag in $CDCl_3$ (160 MHz)



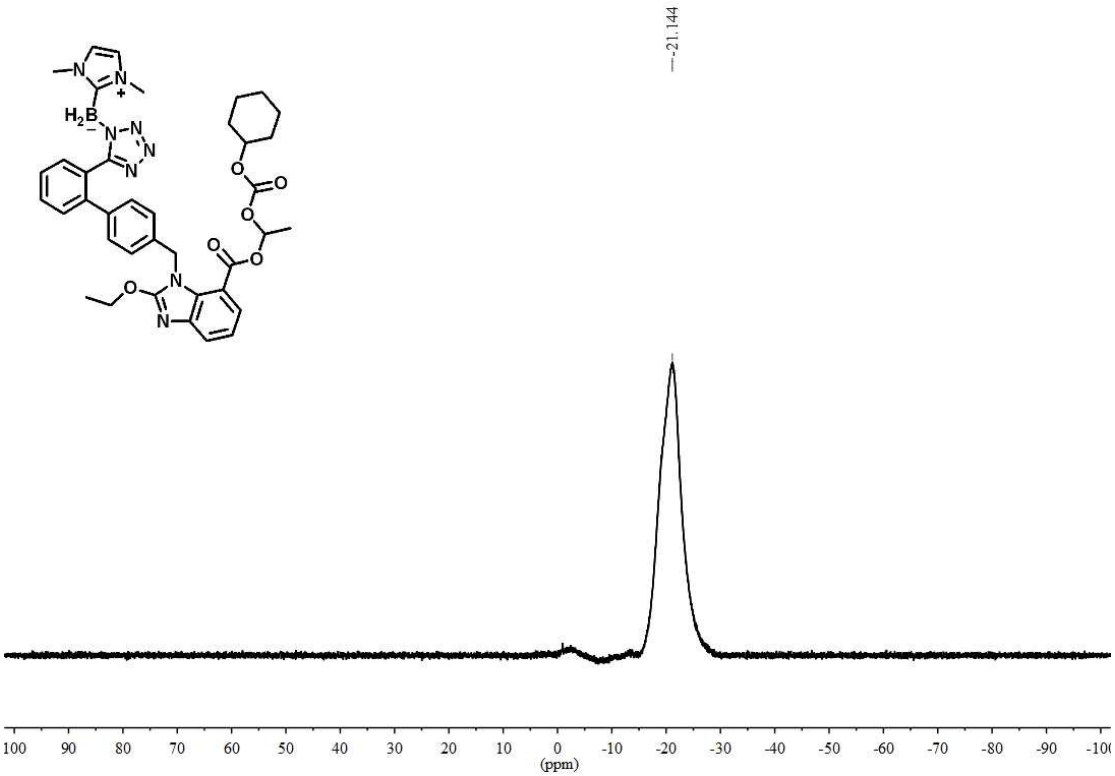
^{1}H NMR of product 5ag' in $CDCl_3$ (500 MHz)



^{13}C NMR of product 5ag' in $CDCl_3$ (125 MHz)



^{11}B NMR of product 5ag' in $CDCl_3$ (160 MHz)



8. Anti-proliferation assay

8.1 General procedures for anti-proliferation assay of 3a-3d, D-3a, 3f, 3i, 3m and 3w

Huh7 cells were seeded into a 96-well plate at a density of 5.0 × 10^3 cells per well, cultured in dulbecco's modified eagle medium (DMEM) (200 μL) with 10% Fetal Bovine Serum (FBS), and maintained at 37℃ for 24 h. The cells were then exposed to different concentrations of compounds **3a-3d, 3f, 3i, 3m**, and **3w** for 48 h. Following treatment, 10 μL of cell counting Kit-8 (CCK-8) reagent (5 mg/mL in PBS) was added to each well, and the plate was incubated for an additional 4 h. To solubilize the formazan crystals, 120 μL of DMSO was added per well, and the plate was left at room temperature for 10 min. Finally, absorbance at 450 nm was recorded using an HBS-1096A microplate reader (Detie, Nanjing, China) to assess cell viability (%).

Cell viability (%) = $(A_{treated} - A_{blank})/(A_{untreated} - A_{blank}) \times 100\%$

where $A_{treated}$, $A_{untreated}$ and A_{blank} represent the absorbance of treated cells, untreated cells and the medium, respectively.

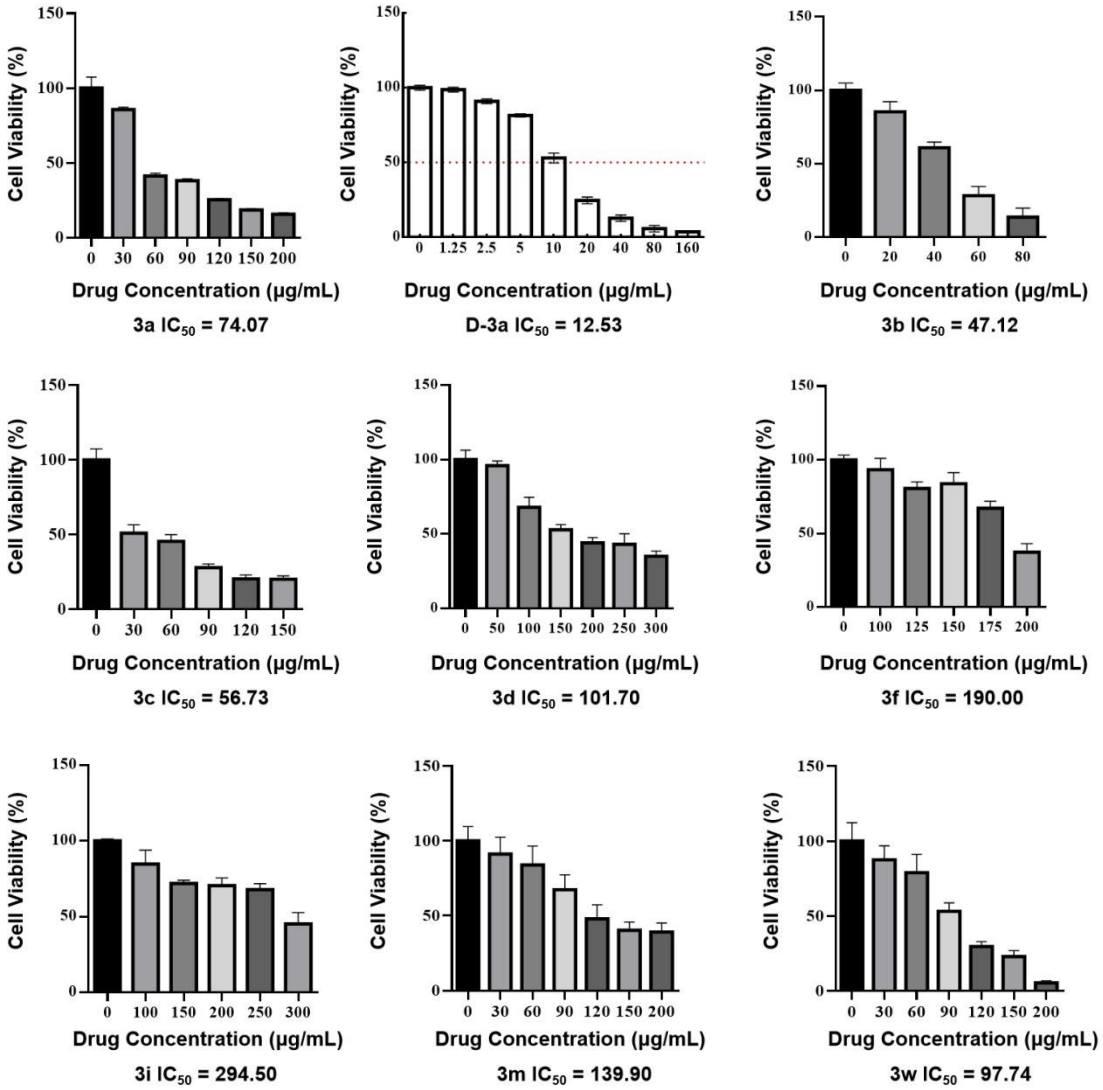
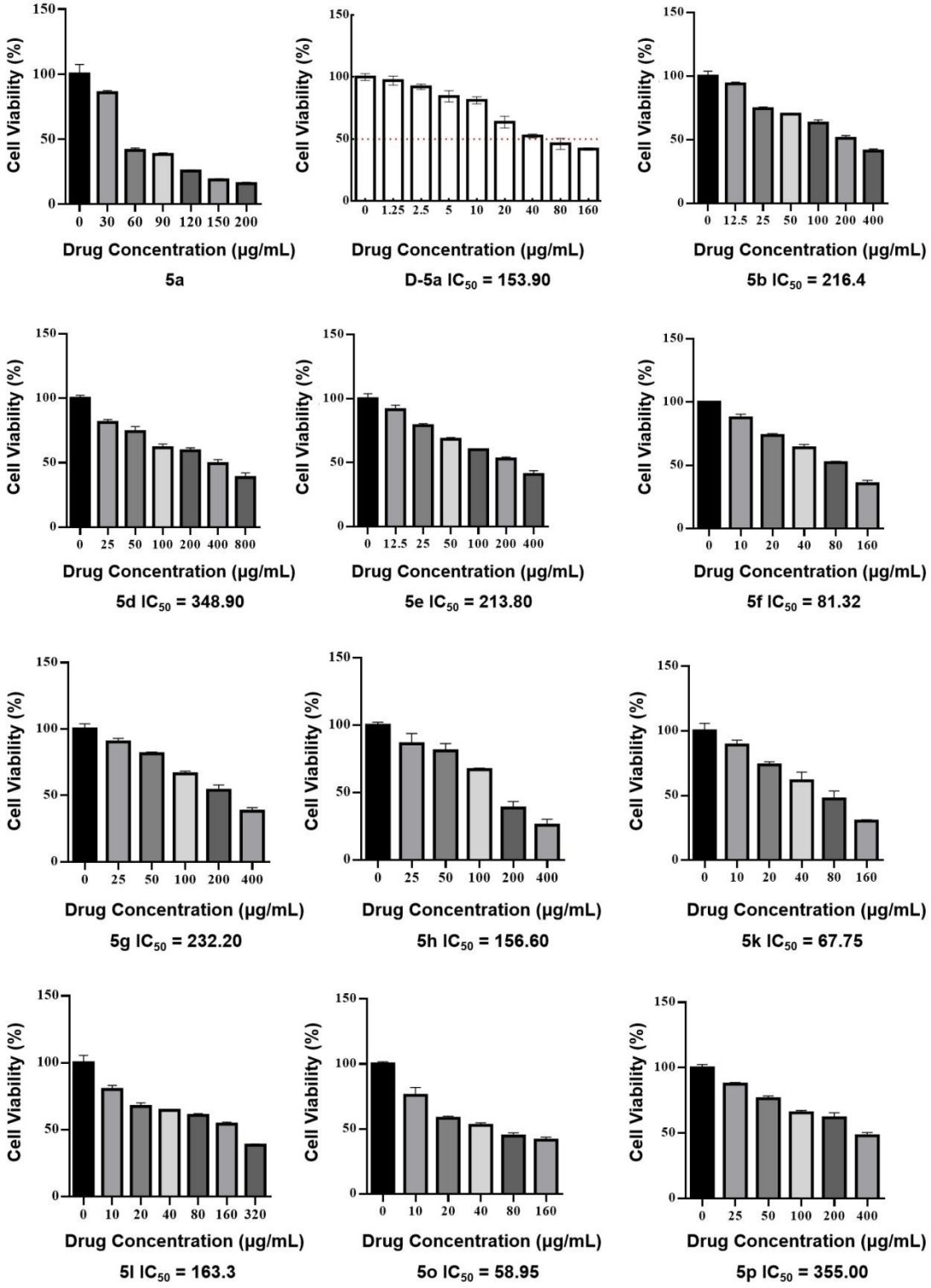


Figure S20. Anti-proliferation assay of 3a-3d, D-3a, 3f, 3i, 3m and 3w

8.2 Anti-proliferation assay of 5a-5b, D-5b, 5d-5h, 5k-5l, 5o-5q, 5u



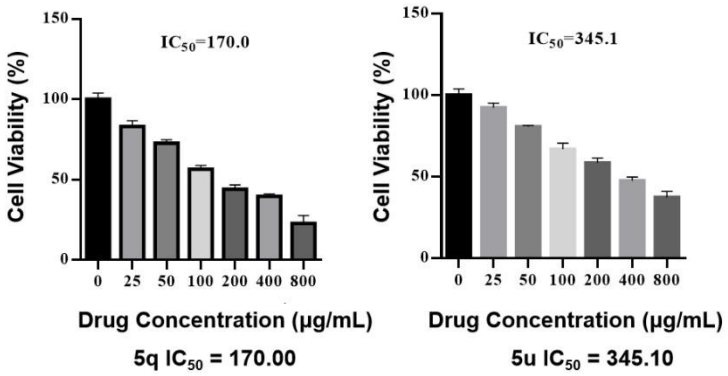
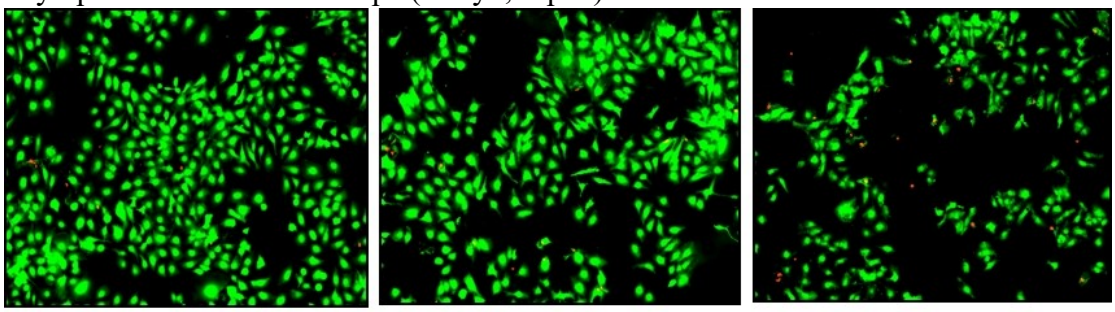


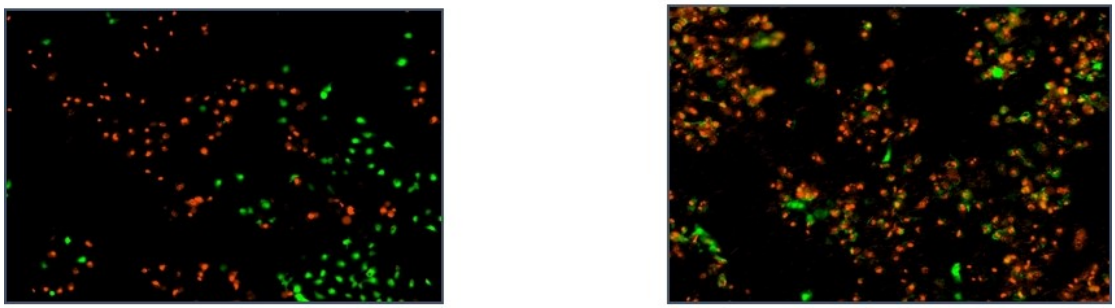
Figure S21. Anti-proliferation assay of 5a-5b, D-5b, 5d-5h, 5k-5l, 5o-5q, 5u

9. Live/dead cell staining assay

Briefly, Huh7 cells were plated in a 6-well plate (3.0×10^5 cells/well) and cultured at 37°C for 24 h. They were then treated with test compounds in serum-free DMEM for 6 h, followed by incubation in DMEM with 10% FBS for 48 h. After two PBS washes, the cells were stained with calcein AM and ethidium homodimer (20 min each) and rinsed three times with 1.0 mL PBS. Fluorescence imaging was performed using an Olympus IX73P1F microscope (Tokyo, Japan).



1a 3a D-3a



1c 3c

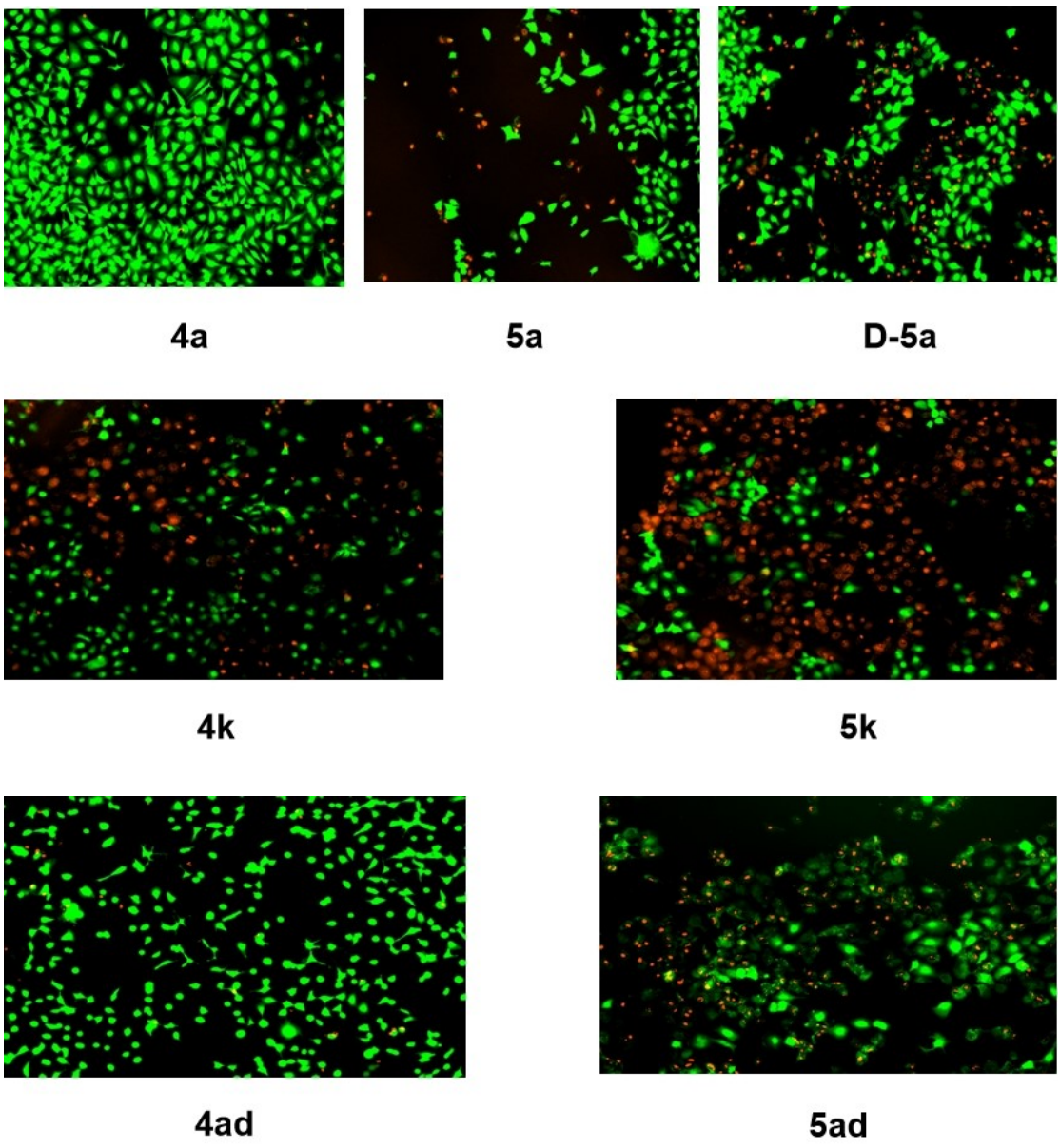


Figure S22. Live/dead cell staining assay