Supporting Information

Metal Free Visible-Light-Induced Borylative/Silylative Pyridylation of Vinylarenes

Yiting Zhou and Bin Liu*

School of Chemistry and Chemical Engineering, Nanchang University, Nanchang, Jiangxi 330031, P. R. China.

*Corresponding author, E-mail: liubin@ncu.edu.cn

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1. Experimental Section

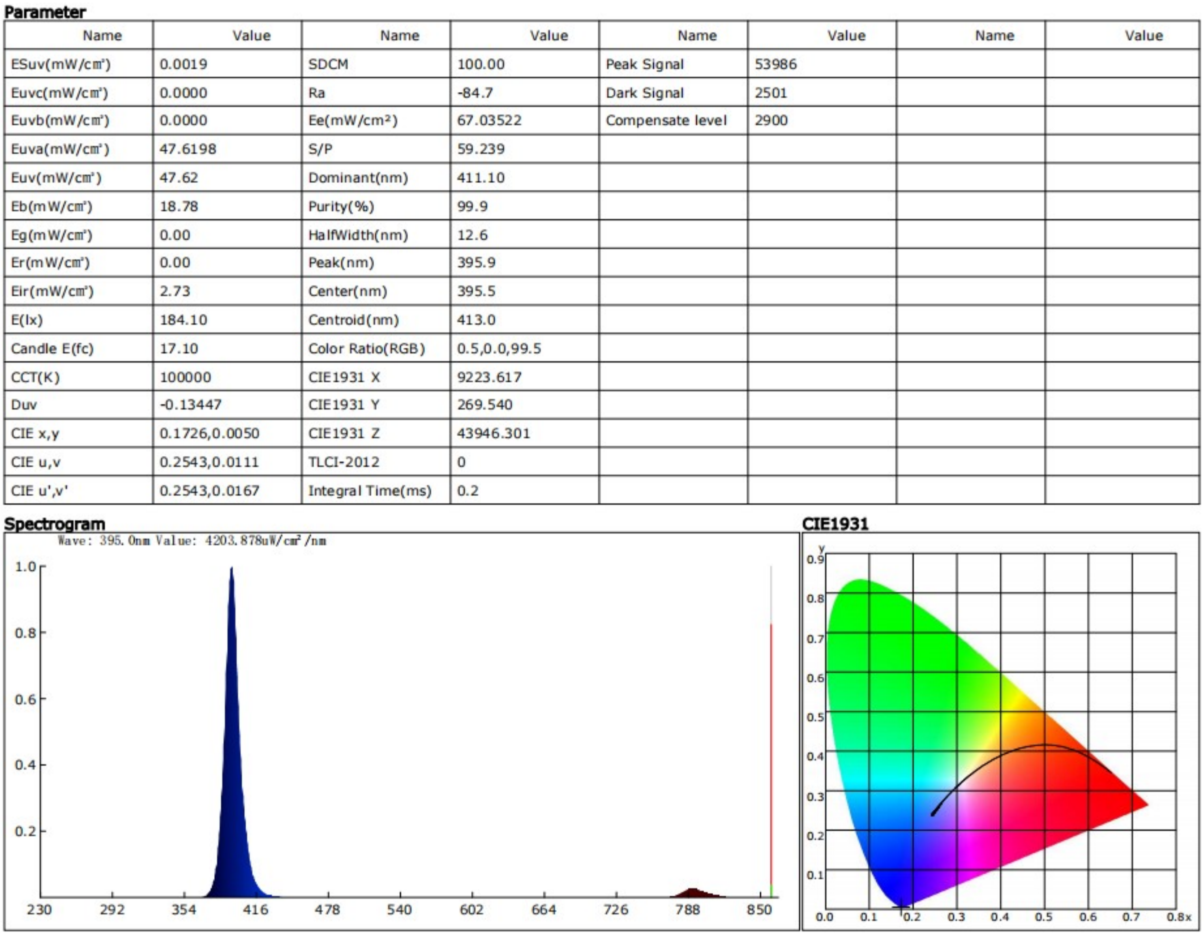
1.1. General Information

All air and water-sensitive reactions were carried out in oven-dried glassware under nitrogen atmosphere using standard Schlenk manifold technique. Commercially available compounds and solvents were purchased from Leyan, Adamas-beta, Bidepharm and used as received. All reactions were followed by thin-layer chromatography (TLC) and visualized under UV light. If the reaction product is not fluorescent under UV light, it is placed in an iodine bath for 5 minutes before observation. Flash column chromatography (FCC) was carried out using silica gel (*200 - 300 mesh*). ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, ^{11}B NMR, spectra were recorded on an Agilent *400MR DD2* (400 MHz) or *AVANCE III HD* (400MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to incompletely deuterated CDCl3 (s, 7.26 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), q (quartet). HRMS ESI measurements were tested by an Agilent *1260HpLC-6545Q-TOF LC-MS*. The microanalyte was dissolved in chromatography-grade methanol before the test. High resolution mass values are given in m/z.

Note: The resonances of hydrogen atoms connected to the boron atom could not be observed in 1H NMR spectra because of quadrupole broadening and spin–spin coupling.

1.2. Experimental Equipments

We used the RLH-18-bit photoreaction system, which was produced by Beijing Rogertech Ltd. The photoreactor has eight same 10 W LEDs. This blue light 10 W LEDs energy peak wavelength is 395.5 nm, 12.6 nm in half-height, and the irradiance of sample position is 18.78 mW./cm^2. The irradiation vessel is a borosilicate glass test tube, and the LED reaches the test tube through a high-reflection channel with a path length of 2 cm. There is no filter between the LED and the test tube. The spectra are as follows：



Parameter

Name	Value	Name	Value	Name	Value	Name	Value
ESuv(mW/cm^2)	0.0019	SDCM	100.00	Peak Signal	53986		
Euvc(mW/cm^2)	0.0000	Ra	-84.7	Dark Signal	2501		
Euvb(mW/cm^2)	0.0000	Ee(mW/cm^2)	67.03522	Compensate level	2900		
Euva(mW/cm^2)	47.6198	S/P	59.239				
Euv(mW/cm^2)	47.62	Dominant(nm)	411.10				
Eb(mW/cm^2)	18.78	Purity(%)	99.9				
Eg(mW/cm^2)	0.00	HalfWidth(nm)	12.6				
Er(mW/cm^2)	0.00	Peak(nm)	395.9				
Eir(mW/cm^2)	2.73	Center(nm)	395.5				
E(lx)	184.10	Centroid(nm)	413.0				
Candle E(fc)	17.10	Color Ratio(RGB)	0.5,0.0,99.5				
CCT(K)	100000	CIE1931 X	9223.617				
Duv	-0.13447	CIE1931 Y	269.540				
CIE x,y	0.1726,0.0050	CIE1931 Z	43946.301				
CIE u,v	0.2543,0.0111	TLCI-2012	0				
CIE u',v'	0.2543,0.0167	Integral Time(ms)	0.2				

Spectrogram

Wave: 395.0nm Value: 4203.878uW/cm^2/nm

CIE1931

Figure S1 Light Source Test Report

The main experimental equipments during the reaction is the photoreactor and magnetic stirrer, as shown in the figure below：

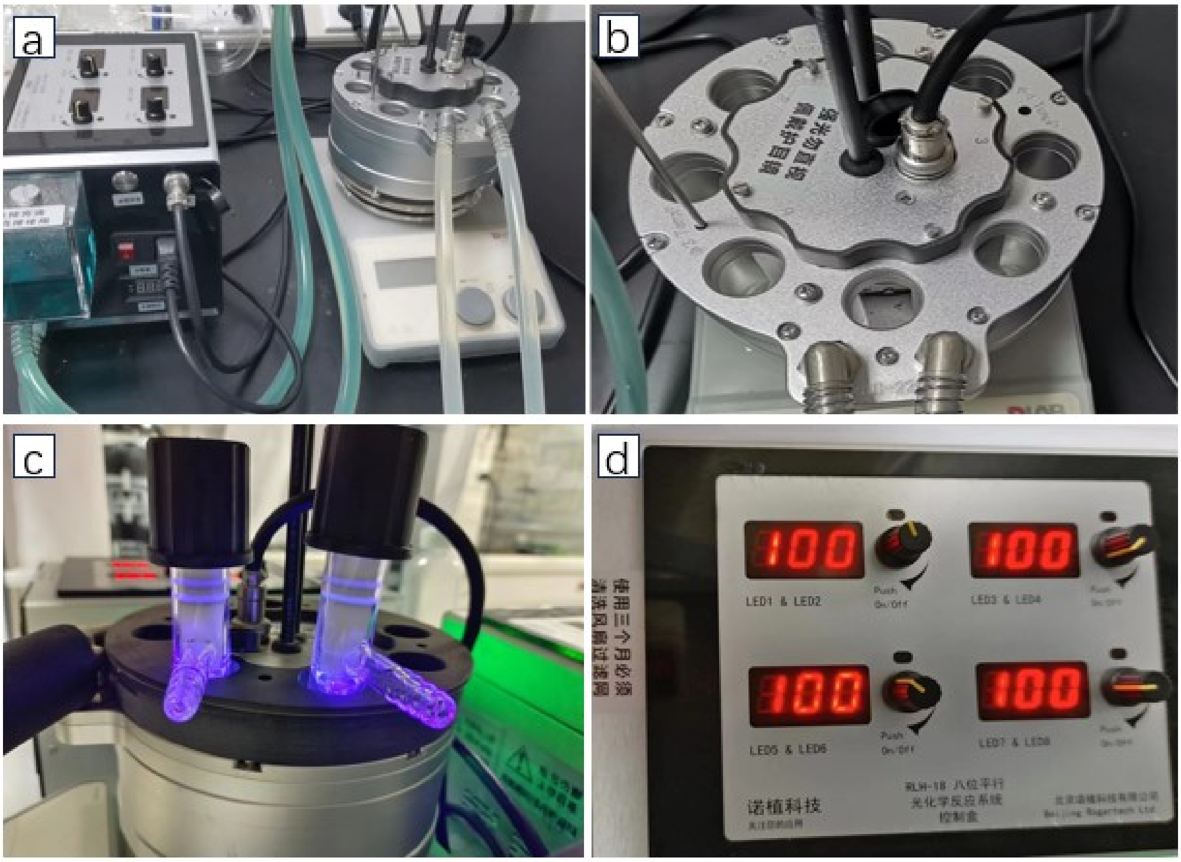
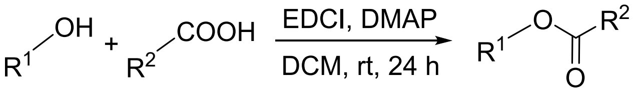


Figure S2 **a).** General view of photoreactor and agitator; **b).** Top view of reaction tube module; **c).** Operation status of the reaction tube module; **d).** Control switch

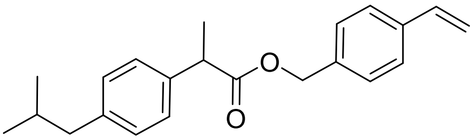
2. Methods for the synthesis of substrates

2.1. Synthesis of alkene

General procedure A[1]



To a stirred solution of carboxylic acid (3 mmol, 1 equiv.) and EDCI (1.73 g，9 mmol, 3 equiv.) in DCM (10 mL) were added DMAP (4-dimethylaminepyridine) (74 mg, 0.6 mmol, 0.2 equiv.) and alcohol (3 mmol, 1 equiv.). The reaction mixture was stirred at room temperature for 24 h. After completion of the reaction (TLC), the reaction was quenched with water and the mixture was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4. The reaction mixture was concentrated under reduced pressure and purified by flash chromatography afforded the product.

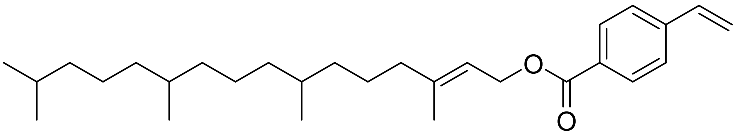


S1

Synthesized according to general procedure A. To a stirred solution of Ibuprofen (0.62 g, 3.0 mmol, 1.0 equiv.) and EDCI (1.73 g，9 mmol, 3.0 equiv.) in DCM (10 mL) were added DMAP (4-dimethylaminepyridine) (0.44 g, 3.6 mmol, 1.2 equiv.) and (4-vinylphenyl)methanol and (0.4 g, 3.0 mmol, 1.0 equiv.). Purification by flash column chromatography (SiO_2, PE:EA = 10:1) afford **S1** (0.83 g, 86%) as a white solid.

TLC (SiO_2): R_f (PE:EA = 10:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.8 Hz, 4H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.74 (d, *J* = 17.6 Hz, 1H), 5.29 – 5.24 (m, 1H), 5.10 (s, 2H), 3.76 (q, *J* = 7.2 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.91 – 1.82 (m, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 1.37 – 1.25 (m, 1H), 0.92 (d, *J* = 6.7 Hz, 6H).

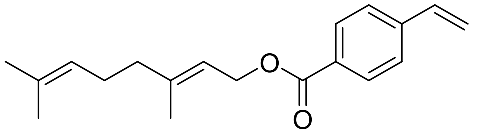


S2

Synthesized according to general procedure A. To a stirred solution of 4-vinylbenzoic acid (0.45 g, 3.0 mmol, 1.0 equiv.) and EDCI (1.73 g，9 mmol, 3.0 equiv.) in DCM (10 mL) were added DMAP (4-dimethylaminepyridine) (74 mg, 0.6 mmol, 0.2 equiv.) and phytol (0.89 g, 3.0 mmol, 1.0 equiv.). Purification by flash column chromatography (SiO_2, PE) afford **S2** (1.13 g, 88%) as a colorless liquid.

TLC (SiO_2): R_f (PE) = 0.6

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 6.75 (dd, J = 17.6, 10.9 Hz, 1H), 5.85 (d, J = 17.6 Hz, 1H), 5.47 (t, J = 7.2 Hz, 1H), 5.37 (d, J = 10.9 Hz, 1H), 4.84 (d, J = 7.0 Hz, 2H), 2.04 (t, J = 7.7 Hz, 2H), 1.57 – 1.47 (m, H), 1.45 – 1.33 (m, 4H), 1.31 – 1.22 (m, 7H), 1.17 – 1.12 (m, 2H), 1.11 – 1.02 (m, 2H), 0.90 – 0.82 (m, 13H).

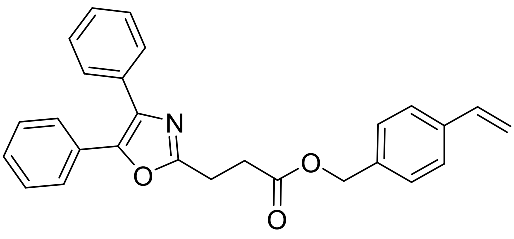


S3

Synthesized according to general procedure A. To a stirred solution of 4-vinylbenzoic acid (0.45 g, 3.0 mmol, 1.0 equiv.) and EDCI (1.73 g，9 mmol, 3.0 equiv.) in DCM (10 mL) were added DMAP (4-dimethylaminepyridine) (74 mg, 0.6 mmol, 0.2 equiv.) and geraniol (0.46 g, 3.0 mmol, 1.0 equiv.). Purification by flash column chromatography (SiO_2, PE) afford **S3** (0.48 g, 56%) as a colorless liquid.

TLC (SiO_2): R_f (PE) = 0.7

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 6.75 (dd, J = 17.6, 10.9 Hz, 1H), 5.85 (d, J = 17.6 Hz, 1H), 5.48 (t, J = 7.1 Hz, 1H), 5.37 (d, J = 10.9 Hz, 1H), 5.14 – 5.06 (m, 1H), 4.84 (d, J = 7.0 Hz, 2H), 2.18 – 2.04 (m, 4H), 1.77 (s, 3H), 1.68 (s, 3H), 1.61 (s, 3H).



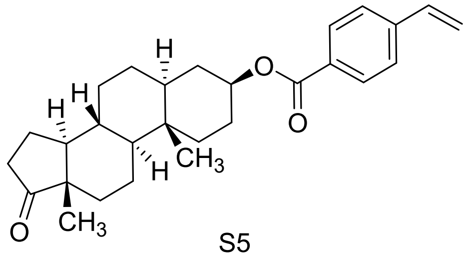
S4

Synthesized according to general procedure A. To a stirred solution of Oxaprozin (0.88 g, 3.0 mmol, 1.0 equiv.) and EDCI (1.73 g，9 mmol, 3.0 equiv.) in DCM (10 mL) were added

DMAP (4-dimethylaminepyridine) (0.44 g, 3.6 mmol, 1.2 equiv.) and (4-vinylphenyl)methanol and (0.4 g, 3.0 mmol, 1.0 equiv.). Purification by flash column chromatography (SiO_2, PE:EA = 1:1) afford **S4** (0.97 g, 79%) as a white solid.

TLC (SiO_2): R_f (PE:EA = 1:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 6.4 Hz, 2H), 7.56 (d, J = 6.3 Hz, 2H), 7.38 – 7.24 (m, 10H), 6.66 (dd, J = 17.6, 10.8 Hz, 1H), 5.70 (d, J = 17.9 Hz, 1H), 5.23 (d, J = 10.8 Hz, 1H), 5.14 (s, 2H), 3.19 (t, J = 7.3 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H).

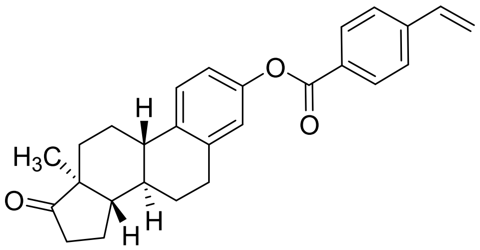


S5

Synthesized according to general procedure A. To a stirred solution of 4-vinylbenzoic acid (0.45 g, 3.0 mmol, 1.0 equiv.) and EDCI (1.73 g，9 mmol, 3.0 equiv.) in DCM (10 mL) were added DMAP (4-dimethylaminepyridine) (0.44 g, 3.6 mmol, 1.2 equiv.) and Epiandrosterone (0.87 g, 3.0 mmol, 1.0 equiv.). Purification by flash column chromatography (SiO_2, PE:EA = 5:1) afford **S5** (0.72 g, 57%) as a white solid.

TLC (SiO_2): R_f (PE:EA = 5:1) = 0.6

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 6.75 (dd, J = 17.6, 10.9 Hz, 1H), 5.85 (d, J = 17.7 Hz, 1H), 5.37 (d, J = 10.9 Hz, 1H), 4.94 (dt, J = 12.4, 6.7 Hz, 1H), 2.44 (dd, J = 19.3, 8.9 Hz, 1H), 2.08 (dt, J = 18.6, 8.8 Hz, 1H), 1.94 (s, 3H), 1.80 (d, J = 12.2 Hz, 4H), 1.69 (d, J = 13.8 Hz, 3H), 1.51 (s, 1H), 1.34 – 1.25 (m, 6H), 1.10 (d, J = 14.2 Hz, 2H), 1.01 (d, J = 11.3 Hz, 1H), 0.91 (s, 3H), 0.87 (s, 3H), 0.79 – 0.71 (m, 1H).



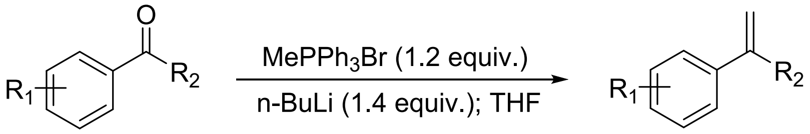
S6

Synthesized according to general procedure A. To a stirred solution of 4-vinylbenzoic acid (0.45 g, 3.0 mmol, 1.0 equiv.) and EDCI (1.73 g，9 mmol, 3.0 equiv.) in DCM (10 mL) were added DMAP (4-dimethylaminepyridine) (0.44 g, 3.6 mmol, 1.2 equiv.) and Estrone (0.81 g, 3.0 mmol, 1.0 equiv.). Purification by flash column chromatography (SiO_2, PE:EA = 5:1) afford **S6** (1.05 g, 87%) as a white solid.

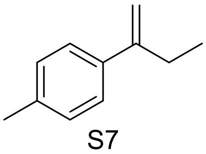
TLC (SiO_2): R_f (PE:EA = 5:1) = 0.6

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.01 – 6.93 (m, 2H), 6.79 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.91 (d, *J* = 17.6 Hz, 1H), 5.43 (d, *J* = 10.9 Hz, 1H), 3.00 – 2.88 (m, 2H), 2.52 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.43 (dd, *J* = 12.4, 4.4 Hz, 1H), 2.36 – 2.27 (m, 1H), 2.21 – 2.12 (m, 1H), 2.12 – 2.03 (m, 2H), 1.96 – 1.90 (m, 1H), 1.68 – 1.61 (m, 2H), 1.54 – 1.49 (m, 2H), 1.35 (d, *J* = 14.4 Hz, 1H), 1.14 – 1.06 (m, 1H), 0.93 (s, 3H).

General procedure B[2]



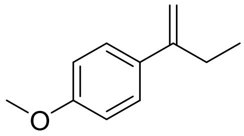
Synthesized according to general procedure B. To an oven-dried RBF charged with a stir bar, was added $MePPh_3Br$ (1.3 g, 3.6 mmol) and THF (7.5 mL) under an N_2 atmosphere. The solution was cooled to 0 °C before n-BuLi (1.7 mL, 4.2 mmol, 2.4 M in hexane) was added dropwise. The mixture was allowed to stir at 0 °C for 1 h before a solution of ketone (3 mmol) in THF (2.5 mL) was added. The reaction was stirred for 1 h at 0 °C then 1 h at rt. Before water (20 ml) and DCM (10 ml) were added. The phases were separated, and the aqueous phase was extracted with DCM. The combined organic phases were washed with water (10 ml) and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo and the crude product was purified via flash column chromatography on silica gel to obtain the pure alkenes.



S7

S7: Synthesized according to general procedure B, colourless liquid, 0.37 g, 84% yield.

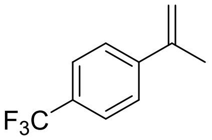
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 5.28 – 5.22 (m, 1H), 5.01 (q, *J* = 1.5 Hz, 1H), 2.50 (q, *J* = 7.4 Hz, 2H), 2.34 (s, 3H), 1.10 (t, *J* = 7.4 Hz, 3H).



S8

S8: Synthesized according to general procedure B, colourless liquid, 0.44 g, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.22 – 5.20 (m, 1H), 4.97 (q, *J* = 1.5 Hz, 1H), 3.80 (s, 3H), 2.51 – 2.46 (m, 2H), 1.10 (t, *J* = 7.4 Hz, 3H).



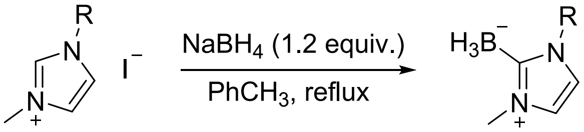
S9

S9: Synthesized according to general procedure B, colourless liquid, 0.17 g, 31% yield.

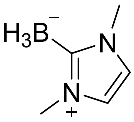
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 4H), 5.44 (s, 1H), 5.19 (s, 1H), 2.16 (s, 3H).

2.2. Synthesis of borane

General procedure C[3]



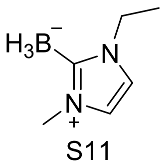
Synthesized according to general procedure C. imidazole iodide (5 mmol) was suspended in toluene (1 mL/mmol) and sodium borohydride (1.2 equiv.) was added in one portion. The mixture was refluxed overnight. The hot reaction solvent was decanted from the insoluble mixture, and the remaining residue was extracted with hot toluene (2×1 reaction volume), and concentrated under reduced pressure. Purification by flash chromatography on silica gel (PE:EA = 1:4) to give product as a white solid.



S10

S10: Synthesized according to general procedure C, white solid, 0.34 g, 62% yield.

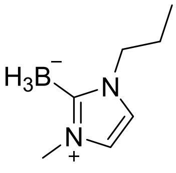
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 2H), 3.74 (s, 6H), 1.34 – 0.69 (m, 3H).



S11

S11: Synthesized according to general procedure C, colourless liquid, 0.27 g, 44% yield.

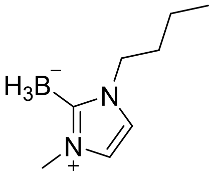
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 – 6.78 (m, 2H), 4.16 (q, *J* = 7.3 Hz, 2H), 3.73 (s, 3H), 1.39 (t, *J* = 7.3 Hz, 3H), 1.35 – 0.7 (m, 3H).



S12

S12: Synthesized according to general procedure C, colourless liquid, 0.22 g, 32% yield.

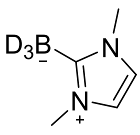
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 2H), 4.11 – 4.03 (m, 2H), 3.73 (s, 3H), 1.81 (m, 2H), 0.94 (m, 6H).



S13

S13: Synthesized according to general procedure C, colourless liquid, 0.36 g, 47% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (t, *J* = 1.7 Hz, 2H), 4.14 – 4.07 (m, 2H), 3.73 (s, 3H), 1.82 – 1.71 (m, 2H), 1.38 – 1.31 (m, 2H), 1.20 – 0.63 (m, 6H).



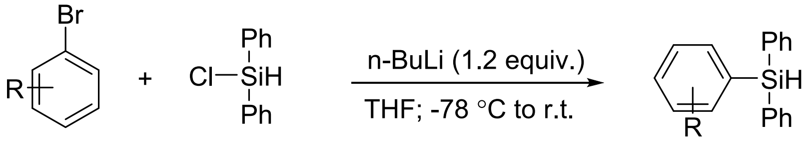
S14

S14: Synthesized according to general procedure C, colourless liquid, 0.23 g, 42% yield.

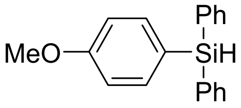
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 2H), 3.74 (s, 6H).

2.3. Synthesis of silane

General procedure D[4]



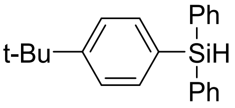
In a 100 mL reaction flask, aryl bromide (10 mmol, 1.0 equiv.) in THF (33 mL) was cooled to -78 °C under N_2. Then n-BuLi (2.4 M in hexanes, 12 mmol, 1.2 equiv.) was added dropwise slowly over 30 min. The resulting mixture was stirred at -78 °C for 2 h before the dropwise addition of diphenychlorosilane (12 mmol, 1.2 equiv.). The reaction was allowed to warm to room temperature and stirred for 8 h. The reaction mixture was quenched with NH_4Cl saturated solution and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, concentrated in vacuo. The crude product was purified by silica gel column chromatography to afford the corresponding hydrosilane.



S15

S15: Synthesized according to general procedure D, colourless liquid, 2.64 g, 91% yield.

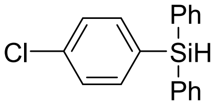
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.8, 1.7 Hz, 4H), δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.41 – 7.31 (m, 6H), δ 6.91 (d, *J* = 8.6 Hz, 2H), 5.46 (s, 1H), 3.76 (s, 3H).



S16

S16: Synthesized according to general procedure D, colourless liquid, 2.7 g, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 4H), 7.56 – 7.49 (m, 2H), 7.45 – 7.31 (m, 8H), 5.46 (s, 1H), 1.39 – 1.28 (m, 9H).



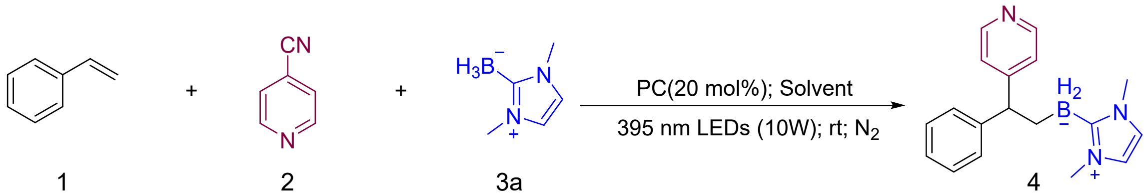
S17

S17: Synthesized according to general procedure D, white solid, 2.4 g, 82% yield.

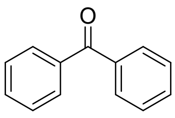
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 4H), 7.50 – 7.48 (m, 2H), 7.44 – 7.33 (m, 8H), 5.46 (d, *J* = 3.5 Hz, 1H).

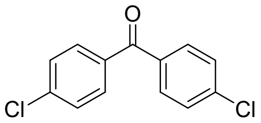
3. Optimization of the reaction conditions

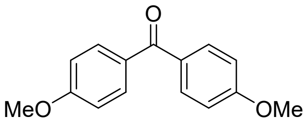
Table S 1

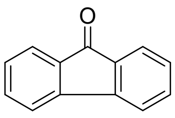


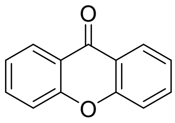
Entry	Time/h	PC	Equiv	*c*/M	Solvent	Yield/%
1	12	PC1	3	0.05	MeCN	53
2	24	PC1	3	0.05	MeCN	60
3	36	PC1	3	0.05	MeCN	78
4	48	PC1	3	0.05	MeCN	70
5	72	PC1	3	0.05	MeCN	69
6	36	PC2	3	0.05	MeCN	26
7	36	PC3	3	0.05	MeCN	8
8	36	PC4	3	0.05	MeCN	n.d.
9	36	PC5	3	0.05	MeCN	6
10	36	PC1	1	0.05	MeCN	28
11	36	PC1	2	0.05	MeCN	30
12	36	PC1	4	0.05	MeCN	69
13	36	PC1	5	0.05	MeCN	77
14	36	PC1	3	0.2	MeCN	50
15	36	PC1	3	0.1	MeCN	66
16	36	PC1	3	0.07	MeCN	57
17	36	PC1	3	0.05	DMSO	58
18	36	PC1	3	0.05	DMF	n.d.
19	36	PC1	3	0.05	DCM	n.d.
20	36	-	3	0.05	MeCN	n.d.
21[a]	36	PC1	3	0.05	MeCN	n.d.
22[b]	36	PC1	3	0.05	MeCN	46


PC1


PC2


PC3

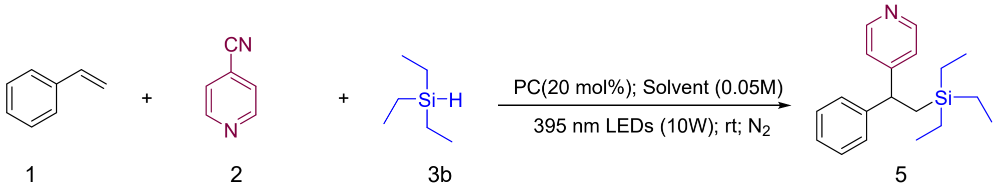

PC4


PC5

Reaction conditions: compound 1 (0.4mmol), compound 2 (0.2 mmol), compound 3a (X mmol), and PC

(20 mol%) in solvent (X mL), room temperature, 395 nm blue LEDs, and 36 h, with an isolated yield. [a] Dark. [b] Open to air.

Table S 2

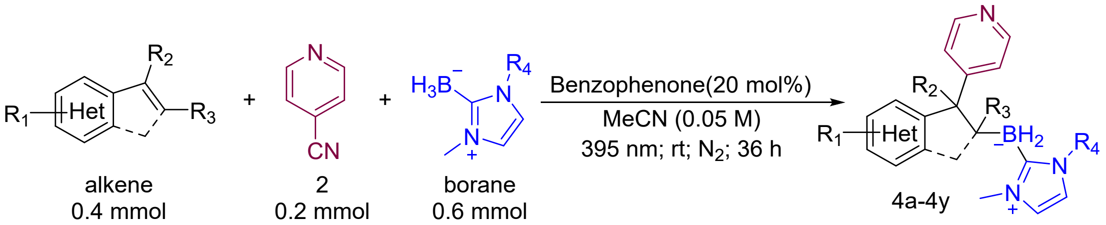


Entry	Time/h	PC	Equiv	Solvent	Yield/%
1	12	PC1	20	MeCN	45
2	24	PC1	20	MeCN	68
3	36	PC1	20	MeCN	90
4	48	PC1	20	MeCN	77
5	72	PC1	20	MeCN	72
6	36	PC2	20	MeCN	59
7	36	PC3	20	MeCN	n.d.
8	36	PC4	20	MeCN	n.d.
9	36	PC5	20	MeCN	n.d.
10	36	PC1	15	MeCN	63
11	36	PC1	10	MeCN	47
12	36	PC1	20	DMSO	35
13	36	PC1	20	DMF	29
14	36	PC1	20	DCM	n.d.
15	36	-	20	MeCN	n.d.
16[a]	36	PC1	20	MeCN	n.d.
17[b]	36	PC1	20	MeCN	55

Reaction conditions: compound 1 (0.4mmol), compound 2 (0.2 mmol), compound 3b (X mmol), and PC (20 mol%) in solvent (X mL), room temperature, 395 nm blue LEDs, and 36 h, with an isolated yield. [a] Dark. [b] Open to air.

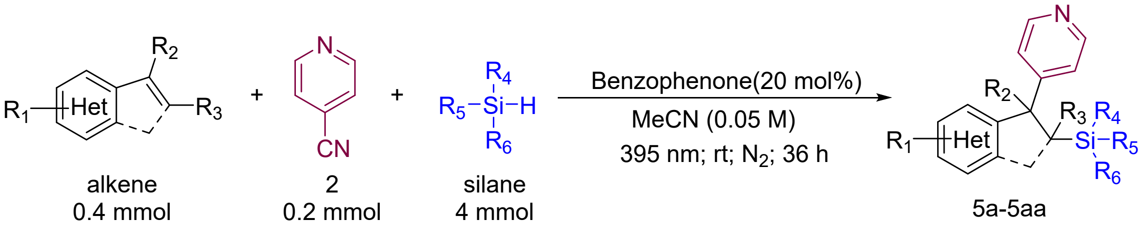
4. General procedure for the photoreactions

General procedure E



In a 10 mL Schlenk tube with a magnetic stir bar were placed 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) and borane (0.6 mmol, 3 equiv.). The reaction mixture was evacuated and purged with inert gas (N_2) three times. Under nitrogen atmosphere, alkene (0.4 mmol, 2.0 equiv.) and MeCN (0.05 M) were added, subsequently. The reaction was placed under blue light and irradiated for 36 h at rt. The solvent was removed under vacuum. Silica gel chromatography of the crude product afforded the desire compound.

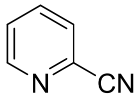
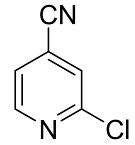
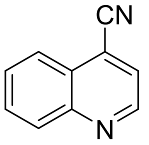
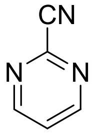
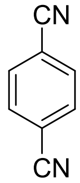
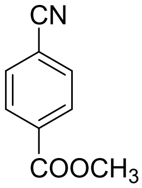
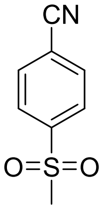
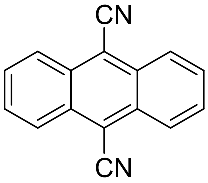
General procedure F



In a 10 mL Schlenk tube with a magnetic stir bar were placed 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.). The reaction mixture was evacuated and purged with inert gas (N_2) three times. Under nitrogen atmosphere, alkene (0.4 mmol, 2.0 equiv.), silane (4 mmol, 20 equiv.) and MeCN (0.05 M) were added, subsequently. The reaction was placed under blue light and irradiated for 36 h at rt. The solvent was removed under vacuum. Silica gel chromatography of the crude product afforded the desire compound.

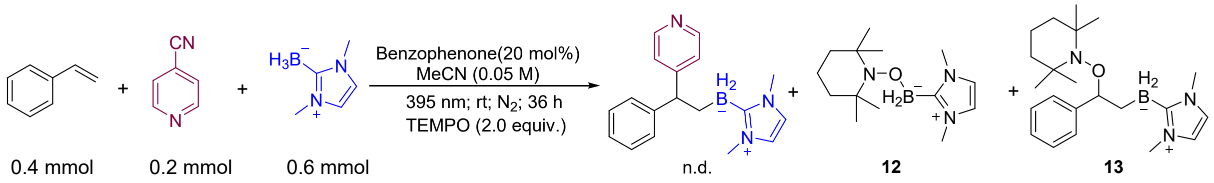
5. Substrate containing CN

Table S 3

 n.d.	 n.d.	 n.d.	 n.d.
 trace	 trace	 n.d.	 n.d.

6. Mechanistic experiments

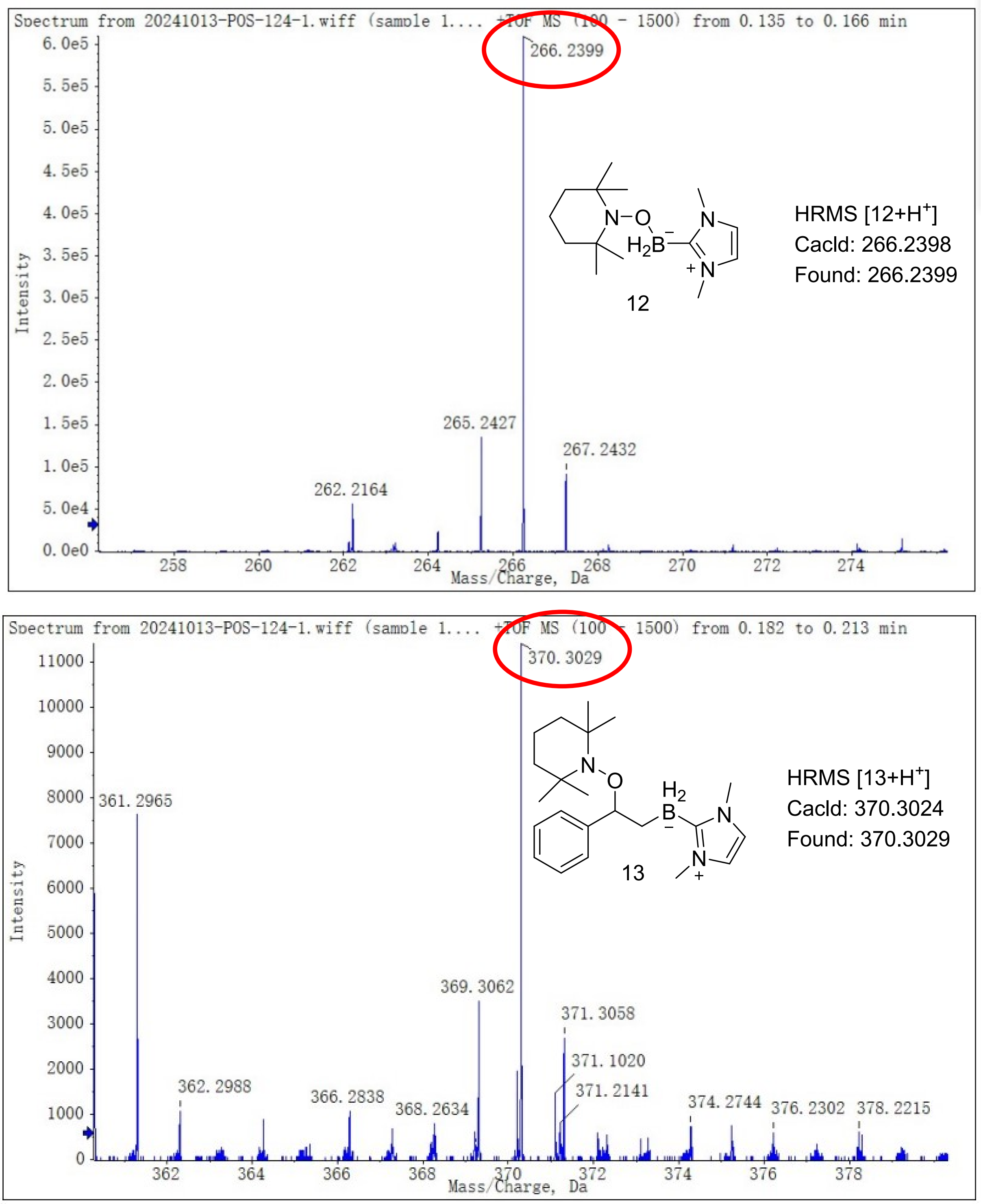
6.1. Radical quenching experiment with TEMPO



Synthesized according to general procedure E: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.), TEMPO (0.4 mmol, 62.4 mg, 2 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs.

HRMS (ESI) for 12: $C_{14}H_{28}BN_3OH^+$ $[M+H]^+$ Calcd 266.2398, Found 266.2399.

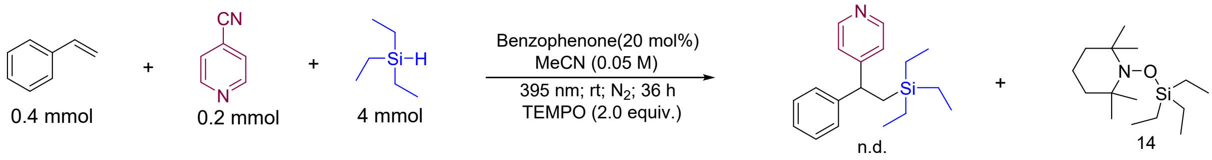
HRMS (ESI) for 13: $C_{22}H_{36}BN_3OH^+$ $[M+H]^+$ Calcd 370.3024, Found 370.3029.



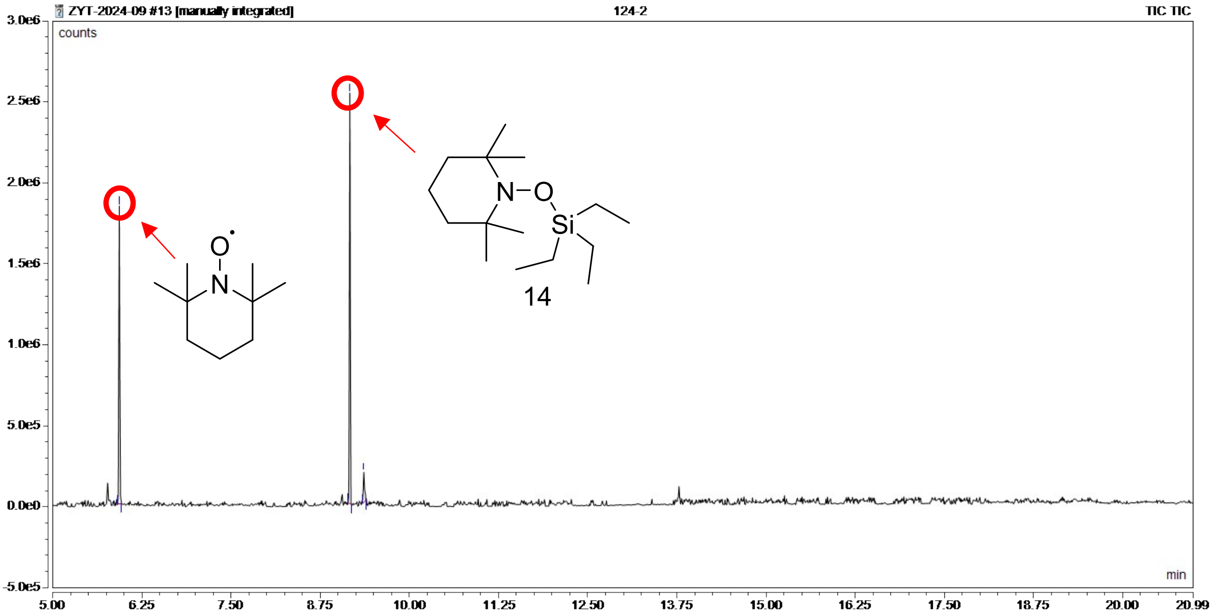
HRMS [12+H$^+$]
Cacld: 266.2398
Found: 266.2399

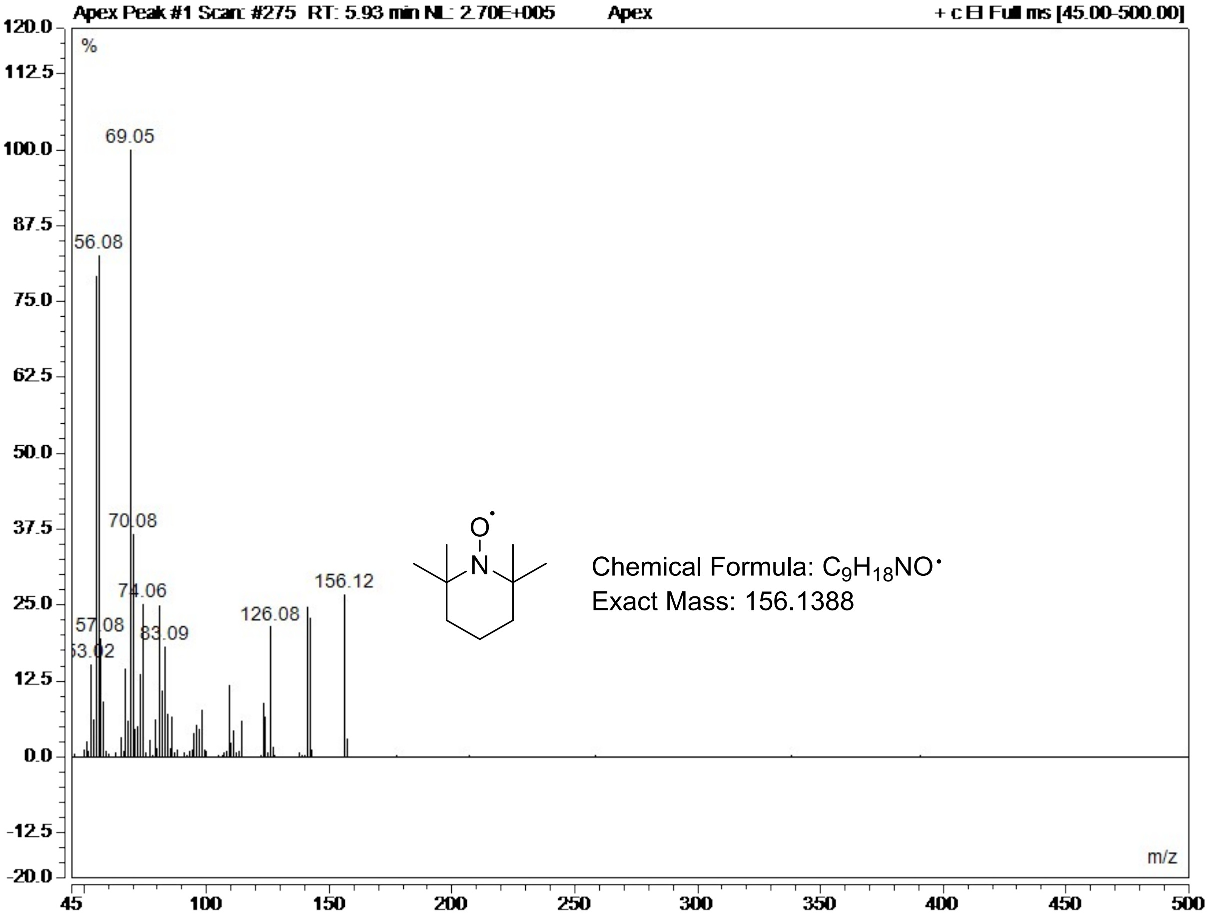
HRMS [13+H$^+$]
Cacld: 370.3024
Found: 370.3029

Figure S3 HRMS data of the reaction mixture



Synthesized according to general procedure F: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.), TEMPO (0.4 mmol, 62.4 mg, 2 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs.





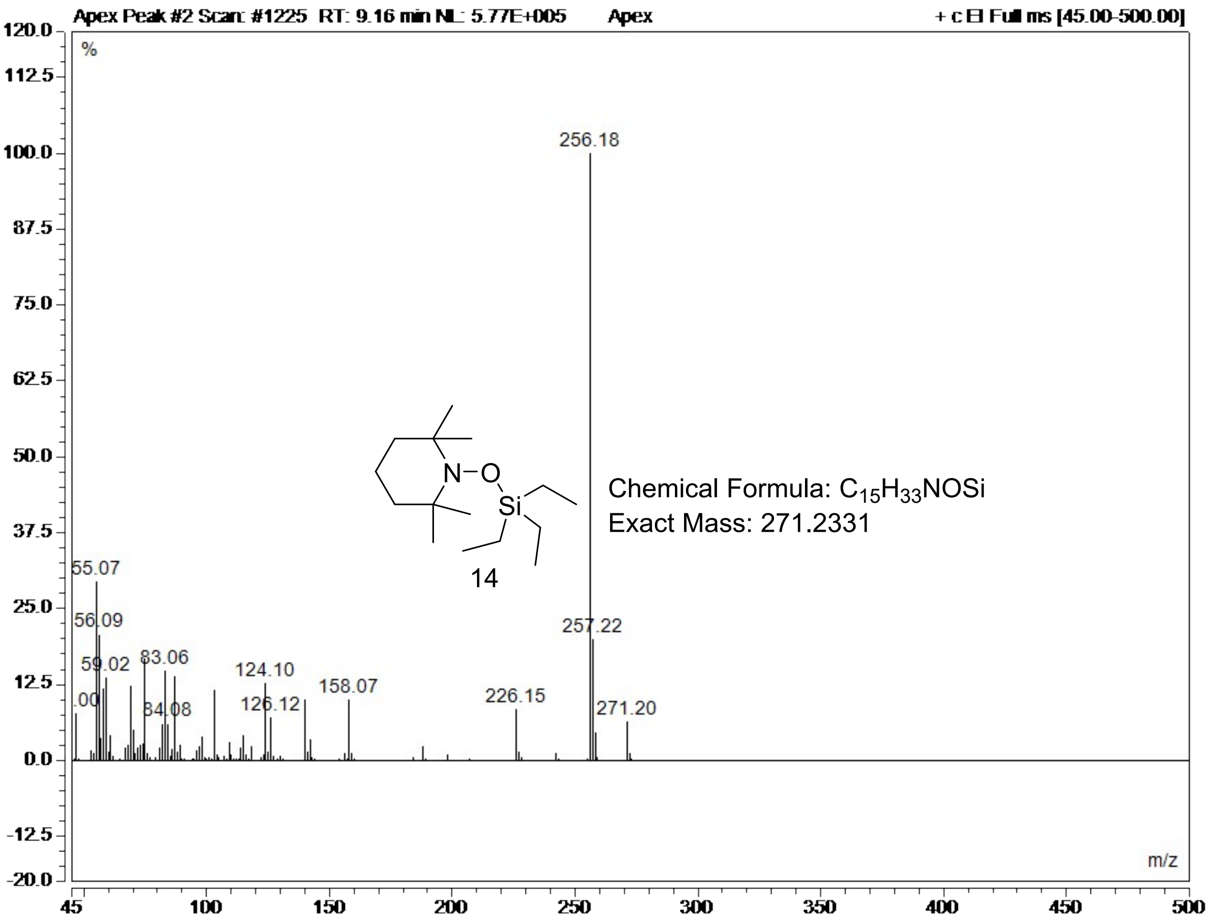
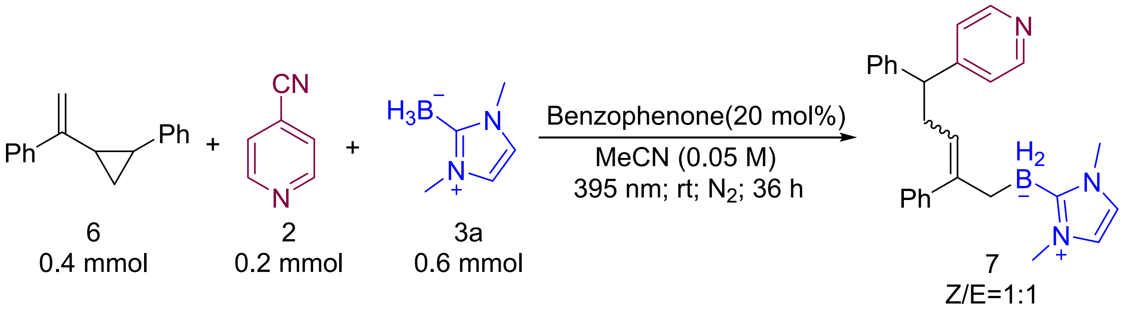
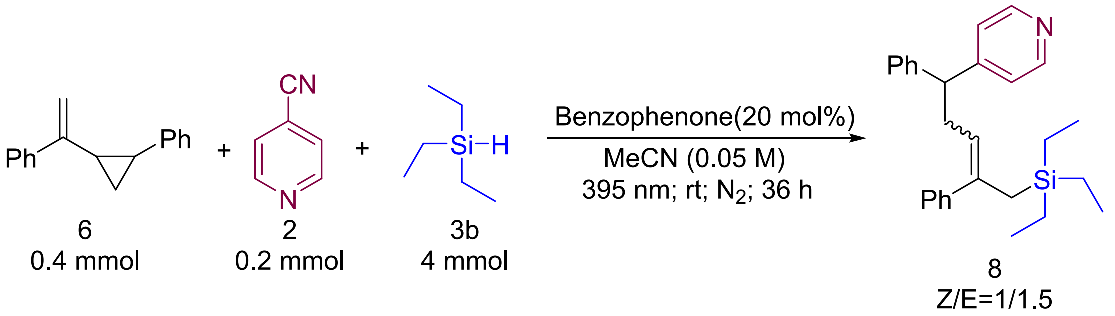


Figure S4 GCMS spectra of the reaction mixture

6.2. Radical clock experiment

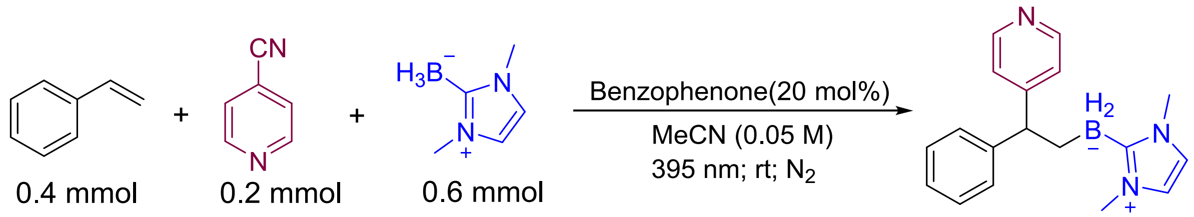


Synthesized according to general procedure E: Alkene **6** (0.4 mmol, 88 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.), and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 1:4) afforded **7** (44.6 mg, 55%) as a colorless liquid.



Synthesized according to general procedure F: Alkene (0.4 mmol, 88 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.), and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 7:1) afforded **8** (33.3 mg, 40%) as a colorless liquid.

6.3. Light on/off experiment



In six 10 mL Schlenk tube with a magnetic stir bar were placed 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), benzophenone **(**0.04 mmol, 7.3 mg, 0.2 equiv.) and borane **S10** (0.6 mmol, 66 mg, 3 equiv.). The reaction mixture was evacuated and purged with inert gas (N_2) three times. Under nitrogen atmosphere, alkene (0.4 mmol, 2.0 equiv.) and MeCN (0.05 M) were added, subsequently. The reaction was subjected to alternating intervals of irradiation with blue light and dark. The solvent was removed under vacuum. Silica gel chromatography of the crude product afforded the desire compound.

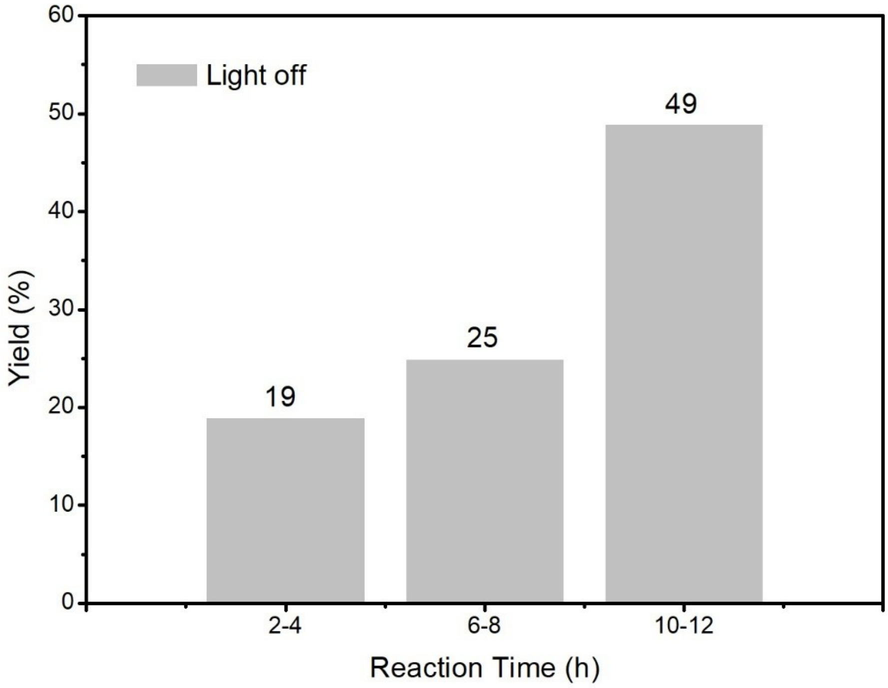
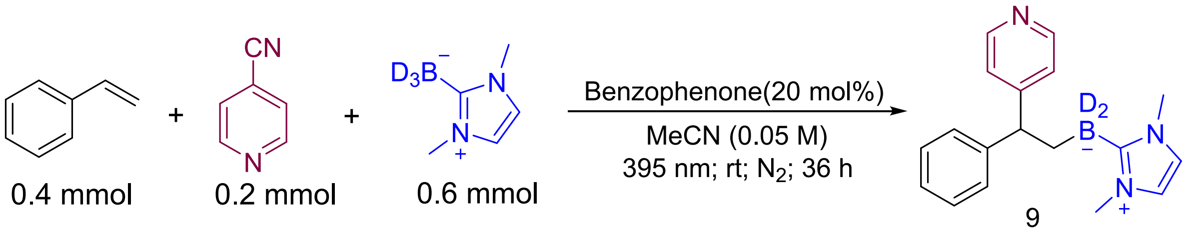


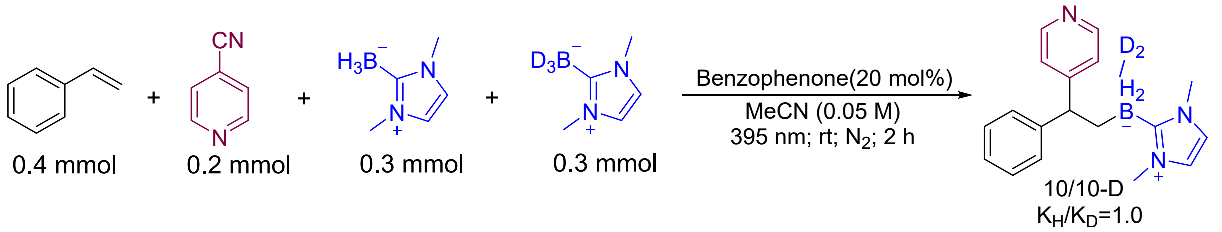
Figure S5 Light on/off experiment

6.4. Deuteration experiment



Synthesized according to general procedure E: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S14** (0.6 mmol, 67.8 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 1:4) afforded **9** (29.9 mg, 51%) as a colorless liquid.

6.5. KIE determination



Synthesized according to general procedure E: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.3 mmol, 33 mg, 1.5 equiv.), borane **S14** (0.3 mmol, 34 mg, 1.5 equiv.), and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 2 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 1:4) afforded **10/10-D** (10.2 mg, 18%) as a colorless liquid. **10/10-D** with a ratio of 1:1(determined by ^1H NMR).

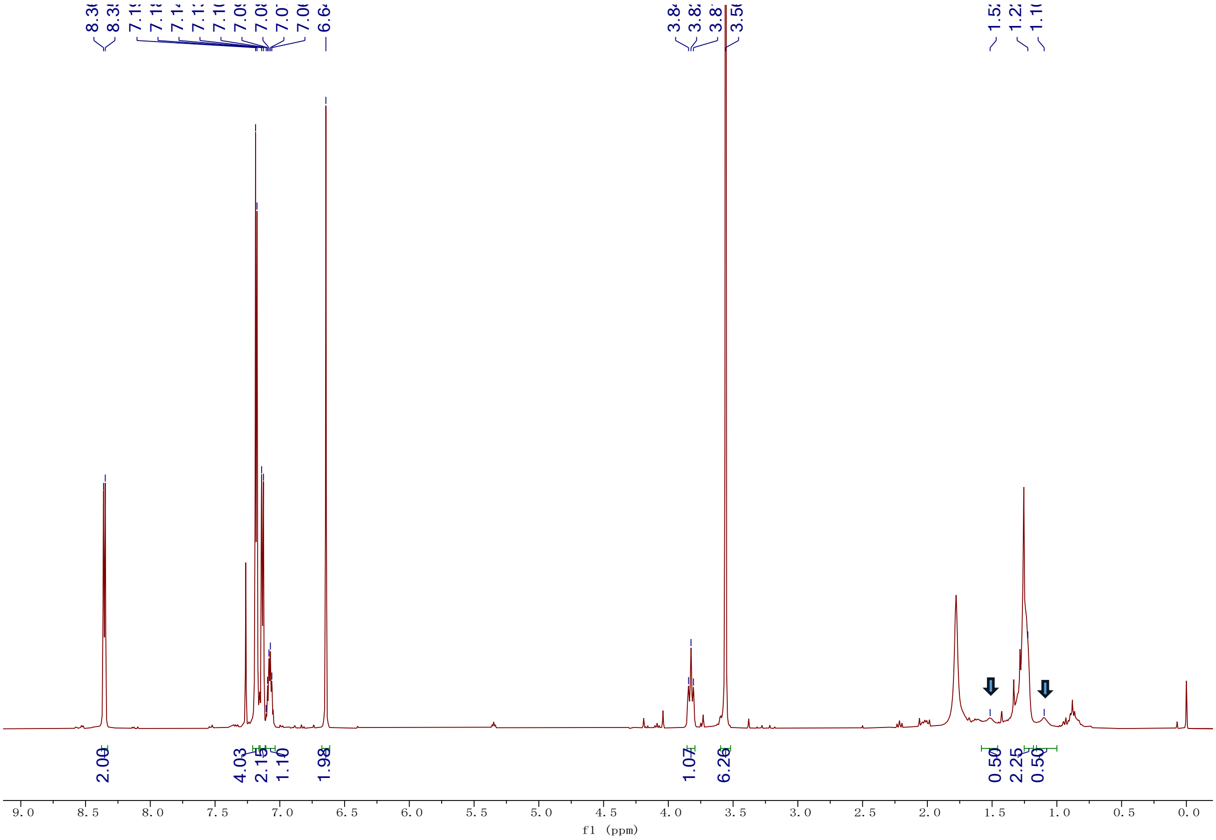


Figure S6 ^1H NMR spectrum of a mixture of **10/10-D**

6.6. Proposed mechanism

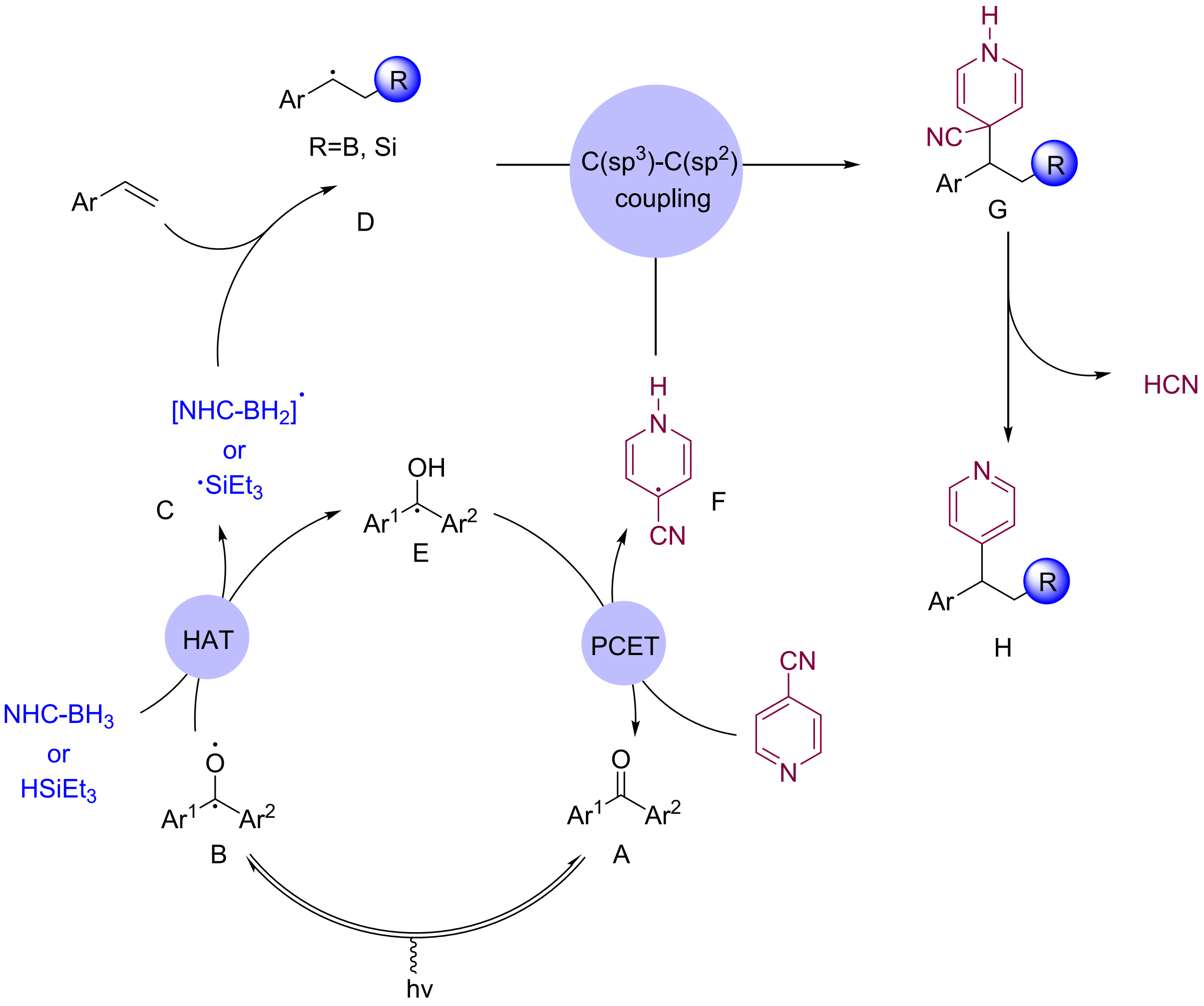
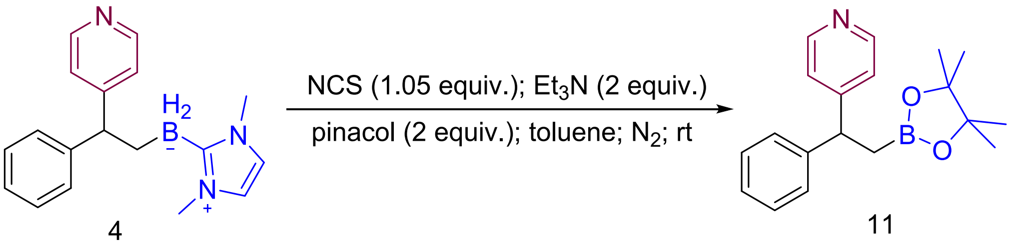


Figure S7 Proposed mechanism

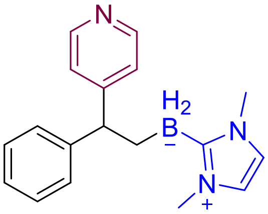
7. Synthetic application

General procedure G[5]



To an oven dried round bottomed-flask was added **4** (0.6 mmol, 175 mg, 1.0 equiv.), Et_3N (1.2 mmol, 0.166 mL, 2.0 equiv.), NCS (0.63 mmol, 84.1 mg, 1.05 equiv.) and pinacol (1.2 mmol, 142 mg, 2 equiv.) in toluene (6 mL). The resulting mixture was stirred at room temperature until TLC indicating the reaction complete. The reaction mixture was washed three times with water and extracted with ethyl acetate. The crude residue was purified by flash column chromatography on silica gel (Petroleum Ether:Ethyl Acetate = 3:1) to give **11** (92.4 mg, 50%) as a pale yellow liquid.

8. Characterization Data of the Products



4a

Synthesized according to General Procedure E: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Ethyl Acetate) afforded 4a (45.6 mg, 78%) as a white solid.

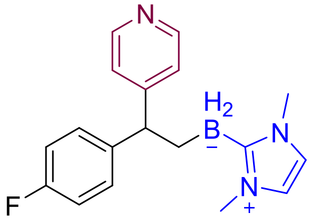
TLC (SiO_2): R_f (Ethyl Acetate) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 6.1 Hz, 2H), 7.18 (d, J = 4.9 Hz, 4H), 7.14 (d, J = 6.2 Hz, 2H), 7.10 – 7.04 (m, 1H), 6.63 (s, 2H), 3.83 (t, J = 7.5 Hz, 1H), 3.55 (s, 6H), 1.25 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.30, 149.16, 147.32, 128.05, 127.75, 125.55, 123.34, 119.97, 53.77, 35.74.

^{11}B NMR (128 MHz, $CDCl_3$) δ -28.11 (t, J = 83.7 Hz, 1B).

HRMS (ESI): $C_{18}H_{22}BN_3H^+$ $[M+H]^+$ Calcd 292.1980, Found 292.1981.



4b

Synthesized according to General Procedure E: 4-Fluorostyrene (0.4 mmol, 48.8 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 1:3) afforded 4b (44 mg, 71%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 1:3) = 0.5

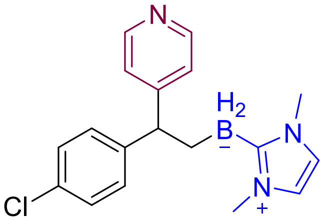
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.36 (d, *J* = 6.1 Hz, 2H), 7.18 – 7.13 (m, 2H), 7.11 (d, *J* = 6.2 Hz, 2H), 6.91 – 6.84 (m, 2H), 6.68 (s, 2H), 3.82 (t, *J* = 7.6 Hz, 1H)., 3.57 (s, 6H), 1.20 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 162.12 (d, J_{CF} = 243.4 Hz), 158.27, 149.20, 142.92, 129.14 (d, J_{CF} = 8.1 Hz), 123.22, 120.03, 114.78 (d, J_{CF} = 23.1 Hz) 52.91, 35.74, 29.72.

^{11}B NMR (128 MHz, CDCl$_3$) δ -28.16 (t, *J* = 83.8 Hz, 1B).

^{19}F NMR (376 MHz, CDCl$_3$) δ -118.11.

HRMS (ESI): $C_{18}H_{21}BFN_3H^+$ $[M+H]^+$ Calcd 310.1885, Found 310.1890.



4c

Synthesized according to General Procedure E: 4-Chlorostyrene (0.4 mmol, 55.2 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO$_2$, Petroleum Ether:Ethyl Acetate = 1:3) afforded 4c (42 mg, 65%) as a colourless liquid.

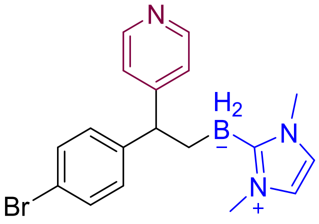
TLC (SiO$_2$): R$_f$ (Petroleum Ether:Ethyl Acetate = 1:3) = 0.5

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.37 (d, *J* = 6.1 Hz, 2H), 7.17 – 7.10 (m, 4H), 7.11 (d, *J* = 6.2 Hz, 2H), 6.68 (s, 2H), 3.81 (t, *J* = 7.5 Hz, 1H), 3.57 (s, 6H), 1.19 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 157.92, 149.20, 145.83, 131.10, 129.18, 128.07, 123.24, 120.06, 53.05, 35.75, 29.72.

^{11}B NMR (128 MHz, CDCl$_3$) δ -28.20 (t, *J* = 85.3 Hz, 1B).

HRMS (ESI): $C_{18}H_{21}BClN_3H^+$ $[M+H]^+$ Calcd 326.1590, Found 326.1591.



4d

Synthesized according to General Procedure E: 1-Bromo-4-vinylbenzene (0.4 mmol, 73.2 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Ethyl Acetate) afforded 4d (60 mg, 81%) as a colourless liquid.

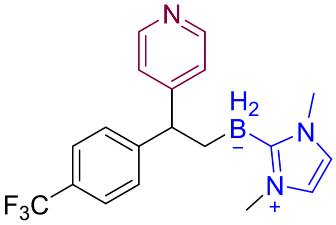
TLC (SiO_2): R_f (Ethyl Acetate) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 6.2 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 6.1 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.68 (s, 2H), 3.80 (t, *J* = 7.5 Hz, 1H), 3.57 (s, 6H), 1.18 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.74, 149.26, 146.38, 131.02, 129.62, 123.23, 120.06, 119.21, 53.11, 35.76.

^{11}B NMR (128 MHz, $CDCl_3$) δ -28.19 (t, *J* = 82.6 Hz, 1B).

HRMS (ESI): $C_{18}H_{21}BBrN_3H^+$ $[M+H]^+$ Calcd 370.1085, Found 370.1083.



4e

Synthesized according to General Procedure E: 4-(Trifluoromethyl)styrene (0.4 mmol, 68.8 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Ethyl Acetate) afforded 4e (54 mg, 75%) as a colourless liquid.

TLC (SiO_2): R_f (Ethyl Acetate) = 0.5

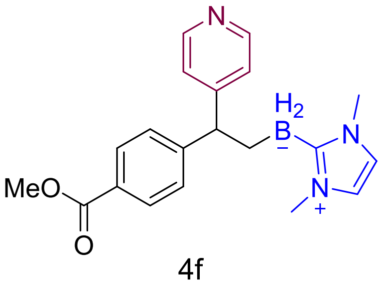
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 6.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 6.1 Hz, 2H), 6.67 (s, 2H), 3.91 (t, *J* = 7.5 Hz, 1H), 3.57 (s, 6H), 1.22 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.98, 151.34, 148.69, 128.14, 124.93 (q, J_{CF} = 3.9 Hz), 123.46, 120.11, 53.61, 35.71.

^{11}B NMR (128 MHz, $CDCl_3$) δ -28.22 (t, *J* = 84.7 Hz, 1B).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.24.

HRMS (ESI): $C_{19}H_{21}BF_3N_3H^+$ $[M+H]^+$ Calcd 360.1853, Found 360.1858.



4f

Synthesized according to General Procedure E: Methyl 4-vinylbenzoate (0.4 mmol, 64.8 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 1:4) afforded 4f (51 mg, 74%) as a colourless liquid.

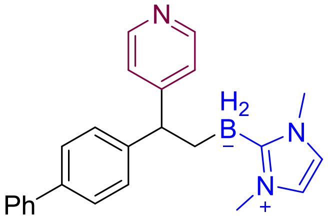
TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 1:4) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 6.1 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 6.2 Hz, 2H), 6.67 (s, 2H), 3.90 (t, *J* = 7.5 Hz, 1H), 3.87 (s, 3H), 3.57 (s, 6H), 1.23 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.18, 157.38, 152.93, 149.27, 129.43, 127.86, 127.41, 123.31, 120.08, 53.75, 51.97, 35.73.

^{11}B NMR (128 MHz, $CDCl_3$) δ -28.21 (t, *J* = 84.2 Hz, 1B).

HRMS (ESI): $C_{20}H_{24}BN_3O_2H^+$ $[M+H]^+$ Calcd 350.2034, Found 350.2041.



4g

Synthesized according to General Procedure E: 4-Vinylbiphenyl (0.4 mmol, 72 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Ethyl Acetate) afforded 4g (53 mg, 73%) as a colourless liquid.

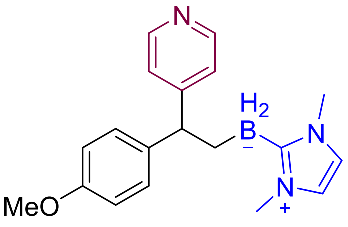
TLC (SiO_2): R_f (Ethyl Acetate) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 6.1 Hz, 2H), 7.52 (d, *J* = 7.0 Hz, 2H), 7.44 – 7.37 (m, 4H), 7.32 – 7.24 (m, 3H), 7.18 (d, *J* = 6.2 Hz, 2H), 6.62 (s, 2H), 3.88 (t, *J* = 7.5 Hz, 1H), 3.55 (s, 6H), 1.28 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.35, 149.15, 146.51, 141.06, 138.33, 128.74, 128.17, 127.01, 126.91, 126.76, 123.40, 120.01, 53.48, 35.74.

^{11}B NMR (128 MHz, $CDCl_3$) δ -28.04 (t, *J* = 83.9 Hz, 1B).

HRMS (ESI): $C_{24}H_{26}BN_3H^+$ $[M+H]^+$ Calcd 368.2293, Found 368.2301.



4h

Synthesized according to General Procedure E: 1-Methoxy-4-Vinylbenzene (0.4 mmol, 53.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 1:4) afforded 4h (18.7 mg, 30%) as a colourless liquid.

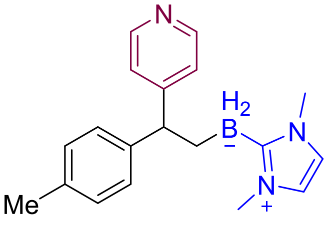
TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 1:4) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 6.1 Hz, 2H), 7.13 – 7.08 (m, 4H), 6.76 – 6.71 (m, 2H), 6.66 (s, 2H), 3.78 (t, *J* = 7.3 Hz, 1H), 3.74 (s, 3H), 3.57 (s, 6H), 1.22 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.86, 157.41, 149.06, 139.49, 128.60, 123.25, 119.97, 113.41, 55.22, 52.84, 35.75, 29.73.

^{11}B NMR (128 MHz, $CDCl_3$) δ -28.10 (t, *J* = 84.5 Hz, 1B).

HRMS (ESI): $C_{19}H_{24}BN_3OH^+$ $[M+H]^+$ Calcd 322.2085, Found 322.2090.



4i

Synthesized according to General Procedure E: *p*-Methylstyrene (0.4 mmol, 47.2 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 1:3) afforded 4i (40 mg, 66%) as a colourless liquid.

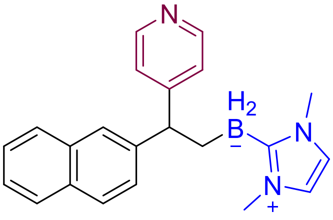
TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 1:3) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 6.1 Hz, 2H), 7.13 (d, *J* = 6.2 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.64 (s, 2H), 3.78 (t, *J* = 7.5 Hz, 1H), 3.56 (s, 6H), 2.25 (s, 3H), 1.23 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.52, 149.13, 144.46, 134.90, 128.75, 127.56, 123.32, 119.94, 53.33, 35.74, 20.98.

^{11}B NMR (128 MHz, $CDCl_3$) δ -28.12 (t, *J* = 84.1 Hz, 1B).

HRMS (ESI): $C_{19}H_{24}BN_3H^+$ $[M+H]^+$ Calcd 306.2136, Found 306.2141.



4j

Synthesized according to General Procedure E: 2-Vinylnaphthalene (0.4 mmol, 63.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Ethyl Acetate) afforded 4j (49 mg, 72%) as a colourless liquid.

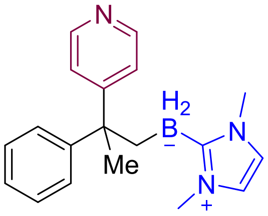
TLC (SiO_2): R_f (Ethyl Acetate) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 6.1 Hz, 2H), 7.71 (dt, *J* = 7.5, 2.3 Hz, 2H), 7.65 – 7.62 (m, 2H), 7.43 – 7.33 (m, 2H), 7.30 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.19 (d, *J* = 6.2 Hz, 2H), 6.52 (s, 2H), 3.99 (t, *J* = 7.4 Hz, 1H), 3.52 (s, 6H), 1.33 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.17, 149.19, 144.78, 133.51, 131.93, 127.59, 127.50, 126.90, 125.76, 125.66, 125.08, 123.49, 119.95, 53.77, 35.71, 29.74.

^{11}B NMR (128 MHz, $CDCl_3$) δ -28.08 (t, *J* = 83.5 Hz, 1B).

HRMS (ESI): $C_{22}H_{24}BN_3H^+$ $[M+H]^+$ Calcd 342.2136, Found 342.2138.



4k

Synthesized according to General Procedure E: alpha-Methylstyrene (0.4 mmol, 47.2 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 1:4) afforded 4k (33.7 mg, 55%) as a colourless liquid.

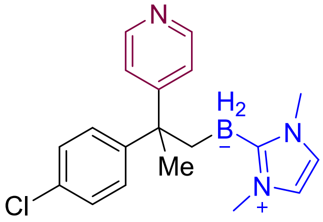
TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 1:4) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 6.3 Hz, 2H), 7.23 – 7.16 (m, 4H), 7.14 (d, J = 6.3 Hz, 2H), 7.09 – 7.03 (m, 1H), 6.62 (s, 2H), 3.52 (s, 6H), 1.69 (s, 3H), 1.33 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.82, 151.95, 148.69, 127.46, 127.39, 125.00, 123.05, 119.94, 47.17, 35.68, 29.73, 28.00.

^{11}B NMR (128 MHz, $CDCl_3$) δ -30.26 (t, J = 82.7 Hz, 1B).

HRMS (ESI): $C_{19}H_{24}BN_3H^+$ $[M+H]^+$ Calcd 306.2136, Found 306.2141.



4l

Synthesized according to General Procedure E: 4-Chloro-alpha-Methylstyrene (0.4 mmol, 60.8 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Ethyl Acetate) afforded 4l (52.1 mg, 76%) as a colourless liquid.

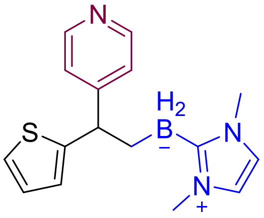
TLC (SiO_2): R_f (Ethyl Acetate) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 6.3 Hz, 2H), 7.14 (s, 4H), 7.12 (d, J = 6.3 Hz, 2H), 6.66 (s, 2H), 3.54 (s, 6H), 1.66 (s, 3H), 1.28 (s, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.34, 150.46, 148.84, 130.64, 128.92, 127.44, 122.91, 119.99, 46.95, 35.70, 28.01.

^{11}B NMR (128 MHz, $CDCl_3$) δ -30.34 (t, J = 84.8 Hz, 1B).

HRMS (ESI): $C_{19}H_{23}BClN_3H^+$ $[M+H]^+$ Calcd 340.1746, Found 340.1743.



4m

Synthesized according to General Procedure E: 2-Vinylthiophene (0.4 mmol, 44 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Ethyl Acetate) afforded 4m (42.2 mg, 71%) as a colourless liquid.

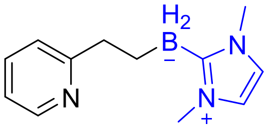
TLC (SiO_2): R_f (Ethyl Acetate) = 0.5

^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 6.1 Hz, 2H), 7.16 (d, J = 6.1 Hz, 2H), 7.04 (d, J = 3.9 Hz, 1H), 6.84 – 6.82 (m, 1H), 6.72 (d, J = 3.4 Hz, 1H), 6.66 (s, 2H), 4.08 (t, J = 7.4 Hz, 1H), 3.59 (s, 6H), 1.31 (s, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, CDCl3) δ 158.60, 152.19, 148.54, 126.33, 123.27, 123.23, 123.01, 120.08, 49.03, 35.75.

^{11}B NMR (128 MHz, $CDCl_3$) δ -28.17 (t, J = 83.3 Hz, 1B).

HRMS (ESI): $C_{16}H_{20}BN_3SH^+$ $[M+H]^+$ Calcd 298.1554, Found 298.1554.



4n

Synthesized according to General Procedure E: 2-Vinylpyridine (0.4 mmol, 42 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Ethyl Acetate) afforded 4n (23.3 mg, 54%) as a colourless liquid.

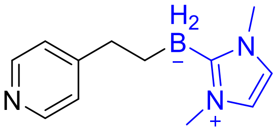
TLC (SiO_2): R_f (Ethyl Acetate) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 3.9 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.01 – 6.98 (m, 1H), 6.77 (s, 2H), 3.78 (s, 6H), 2.75 – 2.63 (m, 2H), 0.84 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.33, 148.52, 136.01, 122.21, 120.08, 119.99, 41.22, 35.98, 29.72.

^{11}B NMR (128 MHz, $CDCl_3$) δ -27.13 (t, *J* = 83.2 Hz, 1B).

HRMS (ESI): $C_{12}H_{18}BN_3H^+$ $[M+H]^+$ Calcd 216.1667, Found 216.1663.



4o

Synthesized according to General Procedure E: 4-Vinylpyridine (0.4 mmol, 42 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Ethyl Acetate) afforded 4o (20.1 mg, 47%) as a colourless liquid.

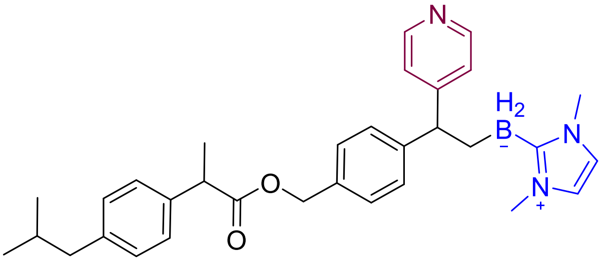
TLC (SiO_2): R_f (Ethyl Acetate) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 6.1 Hz, 2H), 7.11 (d, *J* = 6.1 Hz, 2H), 6.79 (s, 2H), 3.76 (s, 6H), 2.59 – 2.50 (m, 2H), 0.72 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.12, 149.08, 123.69, 120.14, 38.08, 35.93.

^{11}B NMR (128 MHz, $CDCl_3$) δ -27.20 (t, *J* = 83.5 Hz, 1B).

HRMS (ESI): $C_{12}H_{18}BN_3H^+$ $[M+H]^+$ Calcd 216.1667, Found 216.1663.



4p

Synthesized according to General Procedure E: **S1** (0.4 mmol, 123.2 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 1:4) afforded 4p (71.4 mg, 72%) as a colourless liquid.

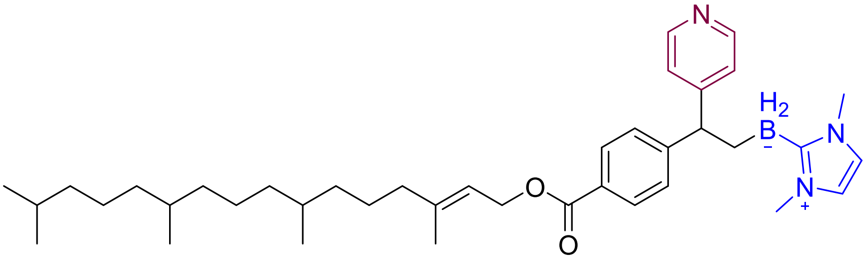
TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 1:4) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 6.1 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.14 – 7.07 (m, 5H), 7.07 – 7.01 (m, 3H), 6.56 (d, *J* = 4.2 Hz, 2H), 5.01 (d, *J* = 2.3 Hz, 2H), 3.81 (t, *J* = 7.5 Hz, 1H), 3.72 (q, *J* = 7.1 Hz, 1H), 3.51 (d, *J* = 2.1 Hz, 6H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.86 – 1.80 (m, 1H), 1.49 (d, *J* = 7.1 Hz, 4H), 1.22 (s, 2H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.63, 158.23, 149.10, 147.16, 147.13, 140.61, 137.67, 133.16, 129.35, 127.80, 127.65, 127.23, 123.29, 123.28, 119.97, 66.31, 53.52, 45.17, 45.15, 45.02, 35.68, 30.23, 22.41, 18.59, 18.55.

^{11}B NMR (128 MHz, $CDCl_3$) δ -28.13 (t, *J* = 86.8 Hz, 1B).

HRMS (ESI): $C_{32}H_{40}BN_3O_2H^+$ $[M+H]^+$ Calcd 510.3286, Found 510.3289.



4q

Synthesized according to General Procedure E: **S2** (0.4 mmol, 170.4 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 1:4) afforded 4q (94.4 mg, 77%) as a colourless liquid.

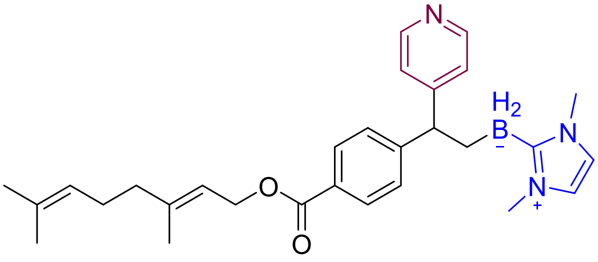
TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 1:4) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 6.2 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 6.1 Hz, 2H), 6.67 (s, 2H), 5.47 – 5.39 (m, 1H), 4.80 (d, *J* = 7.0 Hz, 2H), 3.89 (t, *J* = 7.4 Hz, 1H), 3.57 (s, 6H), 2.03 – 2.02 (m, 2H), 1.75 – 1.73 (s, 3H), 1.52 – 1.50 (m, 2H), 1.39 – 1.36 (m, 5H), 1.33 – 1.17 (m, 12H), 1.17 – 0.97 (m, 8H), 0.88 – 0.83 (m, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.72, 166.70, 157.59, 157.44, 152.78, 149.24, 149.11, 142.65, 129.44, 127.83, 127.79, 123.33, 123.30, 120.06, 118.22, 61.70, 53.76, 39.87, 39.35, 37.41, 37.34, 37.27, 36.63, 35.70, 32.77, 32.65, 27.96, 25.04, 24.79, 24.45, 22.74, 22.65, 19.77, 19.73, 16.46.

^{11}B NMR (128 MHz, CDCl$_3$) δ -28.17 (t, *J* = 83.3 Hz, 1B).

HRMS (ESI): $C_{39}H_{60}BN_3O_2H^+$ [M+H]$^+$ Calcd 614.4851, Found 614.4856.



4r

Synthesized according to General Procedure E: **S3** (0.4 mmol, 113.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO$_2$, Ethyl Acetate) afforded 4r (69.1 mg, 74%) as a colourless liquid.

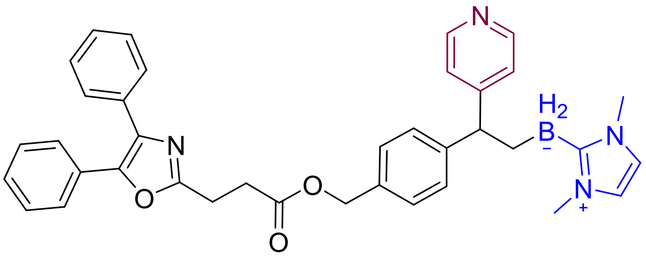
TLC (SiO$_2$): R$_f$ (Ethyl Acetate) = 0.5

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.37 (d, *J* = 6.1 Hz, 2H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 6.2 Hz, 2H), 6.67 (s, 2H), 5.47 – 5.41 (m, 1H), 5.12 – 5.05 (m, 1H), 4.80 (d, *J* = 7.0 Hz, 2H), 3.89 (t, *J* = 7.4 Hz, 1H), 3.57 (s, 6H), 2.18 – 2.01 (m, 4H), 1.75 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H), 1.23 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 166.71, 157.50, 152.78, 149.20, 142.17, 131.81, 131.80, 129.45, 127.80, 123.75, 123.43, 123.32, 120.09, 120.07, 118.49, 61.67, 53.76, 39.53, 35.71, 26.29, 25.69, 17.71, 16.55.

^{11}B NMR (128 MHz, CDCl$_3$) δ -28.32 (t, *J* = 88.3 Hz, 1B).

HRMS (ESI): $C_{29}H_{38}BN_3O_2H^+$ [M+H]$^+$ Calcd 472.3130 Found 472.3137.



4s

Synthesized according to General Procedure E: **S4** (0.4 mmol, 163.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Ethyl Acetate) afforded 4s (89.1 mg, 75%) as a colourless liquid.

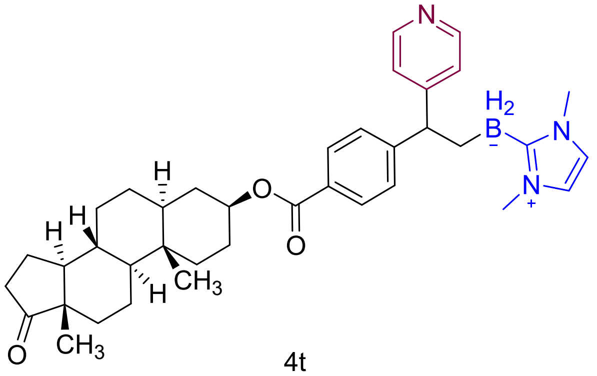
TLC (SiO_2): R_f (Ethyl Acetate) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 6.1 Hz, 2H), 7.63 – 7.60 (m, 2H), 7.57 – 7.53 (m, 2H), 7.38 – 7.28 (m, 7H), 7.14 (d, *J* = 1.8 Hz, 3H), 7.11 (d, *J* = 6.1 Hz, 2H), 6.62 (s, 2H), 5.08 (s, 2H), 3.81 (t, *J* = 7.5 Hz, 1H), 3.52 (s, 6H), 3.19 (t, *J* = 7.4 Hz, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 1.21 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.90, 161.73, 158.15, 149.07, 149.03, 147.53, 145.45, 135.09, 132.89, 132.44, 128.91, 128.69, 128.59, 128.52, 128.11, 127.93, 127.92, 127.90, 126.47, 123.37, 120.03, 66.50, 53.52, 35.68, 31.12, 23.51.

^{11}B NMR (128 MHz, $CDCl_3$) δ -28.1 (t, *J* = 89.6 Hz, 1B).

HRMS (ESI): $C_{37}H_{37}BN_4O_3H^+$ $[M+H]^+$ Calcd 597.3031 Found 597.3040.



4t

Synthesized according to General Procedure E: **S5** (0.4 mmol, 168 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Ethyl Acetate) afforded 4t (96.8 mg, 81%) as a colourless liquid.

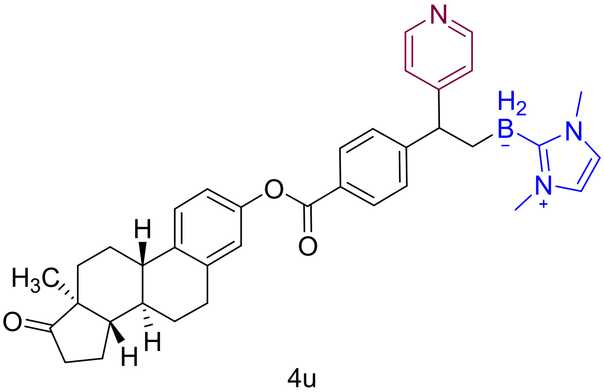
TLC (SiO_2): R_f (Ethyl Acetate) = 0.5

1H NMR (400 MHz, CDCl3) δ 8.36 (d, *J* = 6.2 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 6.2 Hz, 2H), 6.69 (s, 2H), 4.90 – 4.87 (m, 1H), 3.89 (t, *J* = 7.5 Hz, 1H), 3.58 (s, 6H), 2.50 – 2.37 (m, 1H), 2.14 – 2.00 (m, 2H), 1.98 – 1.86 (m, 3H), 1.85 – 1.72 (m, 4H), 1.72 – 1.62 (m, 3H), 1.53 – 1.50 (m, 5H), 1.41 – 1.17 (m, 12H), 1.15 – 0.93 (m, 3H), 0.87 (d, *J* = 9.5 Hz, 7H), 0.80 – 0.64 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 166.14, 157.54, 152.73, 149.11, 129.38, 128.12, 127.75, 123.32, 120.09, 60.39, 54.27, 53.72, 51.32, 47.78, 44.67, 36.72, 35.86, 35.71, 35.67, 35.00, 34.04, 31.51, 30.79, 28.28, 27.52, 21.77, 20.46, 13.83, 12.32, 12.28.

^{11}B NMR (128 MHz, CDCl$_3$) δ -28.2 (t, *J* = 81.9 Hz, 1B).

HRMS (ESI): $C_{38}H_{50}BN_3O_3H^+$ [M+H]$^+$ Calcd 608.4018 Found 608.4025.



4u

Synthesized according to General Procedure E: **S6** (0.4 mmol, 160 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO$_2$, Ethyl Acetate) afforded 4u (36.1 mg, 31%) as a colourless liquid.

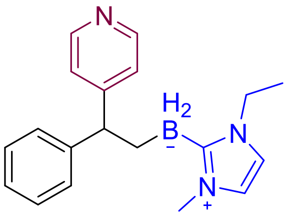
TLC (SiO$_2$): R$_f$ (Ethyl Acetate) = 0.5

^{1}H NMR (400 MHz, CDCl3) δ 8.39 (d, *J* = 6.1 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.34 (dd, *J* = 13.8, 8.4 Hz, 3H), 7.16 (d, *J* = 6.1 Hz, 2H), 6.96 – 6.90 (m, 2H), 6.71 (s, 2H), 3.94 (t, *J* = 7.4 Hz, 1H), 3.61 (s, 6H), 2.95 – 2.91 (m, 2H), 2.51 – 2.38 (m, 2H), 2.38 – 2.25 (m, 2H), 2.21 – 2.08 (m, 2H), 2.07 – 2.03 (m, 2H), 1.62 – 1.45 (m, 7H), 1.23 (s, 2H), 0.92 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 165.50, 157.36, 153.78, 149.21, 148.88, 138.04, 137.32, 130.07, 128.08, 126.90, 126.44, 123.38, 123.28, 121.75, 120.13, 118.91, 60.44, 53.83, 50.42, 47.98, 44.17, 43.24, 38.02, 35.90, 35.79, 31.56, 29.44, 26.37, 25.79, 21.61, 14.23, 13.86.

^{11}B NMR (128 MHz, CDCl$_3$) δ -28.19 (t, *J* = 82.6 Hz, 1B).

HRMS (ESI): $C_{37}H_{42}BN_3O_3H^+$ [M+H]$^+$ Calcd 588.3392 Found 588.3398.



4v

Synthesized according to General Procedure E: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S11** (0.6 mmol, 73.8 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 1:4) afforded 4v (40.1 mg, 66%) as a colourless liquid.

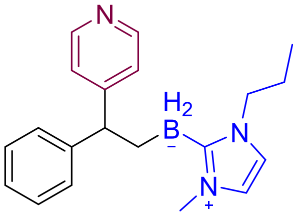
TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 1:4) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 6.1 Hz, 2H), 7.23 – 7.18 (m, 4H), 7.16 (d, J = 6.3 Hz, 2H), 7.11 – 7.05 (m, 1H), 6.71 (d, J = 1.9 Hz, 1H), 6.67 (d, J = 2.0 Hz, 1H), 3.99 – 3.96 (m, 2H), 3.84 (t, J = 7.5 Hz, 1H), 3.54 (s, 3H), 1.30 (t, J = 7.3 Hz, 3H), 1.21 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.42, 149.10, 147.46, 128.04, 127.83, 125.53, 123.48, 120.30, 117.99, 53.74, 43.32, 35.53, 15.86.

^{11}B NMR (128 MHz, $CDCl_3$) δ -28.16 (t, J = 84.9 Hz, 1B).

HRMS (ESI): $C_{19}H_{24}BN_3H^+$ $[M+H]^+$ Calcd 306.2136 Found 306.2141.



4w

Synthesized according to General Procedure E: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S12** (0.6 mmol, 82.8 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 1:4) afforded 4w (42.1 mg, 67%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 1:4) = 0.5

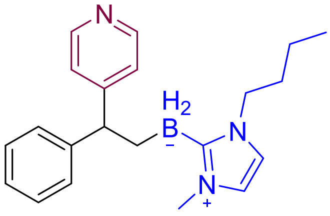
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 6.1 Hz, 2H), 7.24 – 7.18 (m, 4H), 7.16 (d, J = 6.2 Hz, 2H), 7.11 – 7.06 (m, 1H), 6.70 (d, J = 1.9 Hz, 1H), 6.67 (d, J = 2.0 Hz, 1H), 3.91 – 3.87

(m, 2H), 3.84 (t, *J* = 7.6 Hz, 1H), 3.56 (s, 3H), 1.73 – 1.67 (m, 2H), 1.20 (s, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 158.39, 149.11, 147.52, 128.03, 127.84, 125.51, 123.50, 120.07, 118.63, 53.70, 50.01, 35.57, 23.88, 11.02.

^{11}B NMR (128 MHz, CDCl$_3$) δ -28.15 (t, *J* = 84.2 Hz, 1B).

HRMS (ESI): $C_{20}H_{26}BN_3H^+$ [M+H]$^+$ Calcd 320.2293 Found 320.2294.



4x

Synthesized according to General Procedure E: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S13** (0.6 mmol, 91.8 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO$_2$, Petroleum Ether:Ethyl Acetate = 1:4) afforded 4x (48.3 mg, 72%) as a colourless liquid.

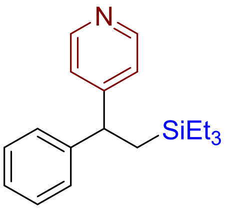
TLC (SiO$_2$): R$_f$ (Petroleum Ether:Ethyl Acetate = 1:4) = 0.5

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.36 (d, *J* = 6.1 Hz, 2H), 7.23 – 7.18 (m, 4H), 7.16 (d, *J* = 6.3 Hz, 2H), 7.11 – 7.06 (m, 1H), 6.70 (d, *J* = 2.0 Hz, 1H), 6.67 (d, *J* = 2.0 Hz, 1H), 3.93 – 3.89 (m, 2H), 3.84 (t, *J* = 7.4 Hz, 1H), 3.55 (s, 3H), 1.65 (p, *J* = 7.6 Hz, 2H), 1.32 – 1.25 (m, 2H), 1.20 (s, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 158.42, 149.09, 147.51, 128.03, 127.84, 125.51, 123.50, 120.11, 118.60, 53.70, 48.23, 35.55, 32.62, 19.73, 13.68.

^{11}B NMR (128 MHz, CDCl$_3$) δ -28.15 (t, *J* = 84.8 Hz, 1B).

HRMS (ESI): $C_{21}H_{28}BN_3H^+$ [M+H]$^+$ Calcd 334.2449 Found 334.2452.



5a

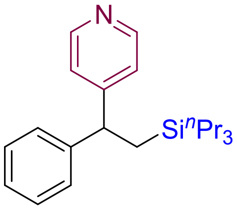
Synthesized according to General Procedure F: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 7:1) afforded 5a (54.1 mg, 90%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 7:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.3 Hz, 2H), 7.27 (d, *J* = 5.9 Hz, 4H), 7.21 (d, *J* = 4.3 Hz, 2H), 7.20 – 7.14 (m, 1H), 4.02 (t, *J* = 7.9 Hz, 1H), 1.46 – 1.33 (m, 2H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.35 (q, *J* = 7.8 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, cdcl$_3$) δ 156.27, 149.71, 145.17, 128.56, 127.56, 126.64, 122.76, 46.64, 18.31, 7.25, 3.43.

HRMS (ESI): $C_{19}H_{27}NSiH^+$ $[M+H]^+$ Calcd 298.1986 Found 298.1984.



5b

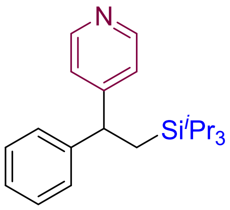
Synthesized according to General Procedure F: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), tri-*n*-propylsilane (4 mmol, 629.2 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 10:1) afforded 5b (48.4 mg, 71%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 10:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 6.2 Hz, 2H), 7.27 (d, *J* = 6.3 Hz, 4H), 7.21 (d, *J* = 6.2 Hz, 2H), 7.19 – 7.13 (m, 1H), 4.01 (dd, *J* = 8.8, 6.8 Hz, 1H), 1.44 – 1.30 (m, 2H), 1.26 – 1.19 – 1.13 (m, 6H), 0.86 (t, *J* = 7.2 Hz, 9H), 0.39 – 0.25 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.36, 149.71, 145.17, 128.62, 127.64, 126.67, 122.84, 46.75, 19.22, 18.59, 17.34, 15.38.

HRMS (ESI): $C_{22}H_{33}NSiH^+$ $[M+H]^+$ Calcd 340.2455 Found 340.2453.



5c

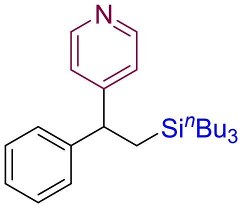
Synthesized according to General Procedure F: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), tri-*i*-propylsilane (4 mmol, 629.2 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 10:1) afforded 5c (52.1 mg, 77%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 10:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 6.2 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.29 – 7.23 (m, 4H), 7.22 – 7.15 (m, 1H), 4.13 (t, J = 7.3 Hz, 1H), 1.55 – 1.42(m, 2H), 1.12 (s, 1H), 1.00 – 0.90 (m, 20H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.67, 149.81, 145.61, 128.67, 127.59, 126.70, 122.80, 46.75, 18.80, 18.74, 16.69, 11.26.

HRMS (ESI): $C_{22}H_{33}NSiH^+$ $[M+H]^+$ Calcd 340.2455 Found 340.2460.



5d

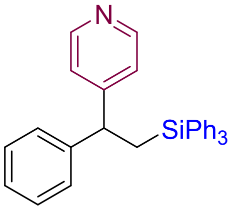
Synthesized according to General Procedure F: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), tributylsilane (4 mmol, 796 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 10:1) afforded 5d (64.5 mg, 85%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 10:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 6.1 Hz, 2H), 7.27 (d, J = 5.5 Hz, 4H), 7.21 (d, J = 6.3 Hz, 2H), 7.20 – 7.15 (m, Hz, 1H), 4.01 (dd, J = 8.7, 6.9 Hz, 1H), 1.44 – 1.32 (m, 2H), 1.26 – 1.19 (m, 6H), 1.17 – 1.10 (m, 6H), 0.83 (t, J = 7.1 Hz, 9H), 0.40 – 0.26 (m, 6H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.36, 149.74, 145.22, 128.61, 127.65, 126.67, 122.84, 46.76, 26.80, 25.98, 19.18, 13.79, 12.28.

HRMS (ESI): $C_{25}H_{39}NSiH^+$ $[M+H]^+$ Calcd 382.2925 Found 382.2925.



5e

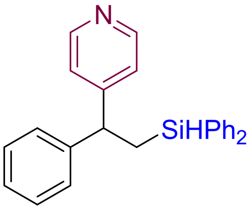
Synthesized according to General Procedure F: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triphenylsilane (4 mmol, 1036 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Dichloromethane:Ethyl Acetate = 40:1) afforded 5e (57.5 mg, 65%) as a colourless liquid.

TLC (SiO_2): R_f (Dichloromethane:Ethyl Acetate = 40:1) = 0.5

^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 6.2 Hz, 2H), 7.39 – 7.33 (m, 9H), 7.27 (dd, J = 8.1, 6.4 Hz, 6H), 7.18 – 7.07 (m, 5H), 7.00 (d, J = 6.1 Hz, 2H), 4.19 (t, J = 7.4 Hz, 1H), 2.33 – 2.20 (m, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.92, 149.78, 144.18, 135.08, 135.05, 133.57, 133.52, 129.83, 129.79, 128.65, 128.12, 128.10, 127.75, 126.82, 123.00, 46.58, 19.42.

HRMS (ESI): $C_{31}H_{27}NSiH^+$ $[M+H]^+$ Calcd 442.1986 Found 442.1991.



5f

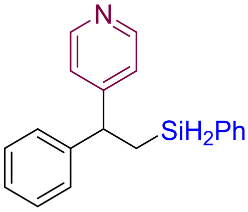
Synthesized according to General Procedure F: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), diphenylsilane (4 mmol, 728 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Dichloromethane:Ethyl Acetate = 40:1) afforded 5f (41.9 mg, 57%) as a colourless liquid.

TLC (SiO_2): R_f (Dichloromethane:Ethyl Acetate = 40:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 6.1 Hz, 2H), 7.49 – 7.43 (m, 4H), 7.42 – 7.36 (m, 2H), 7.35 – 7.30 (m, 4H), 7.28 – 7.22 (m, 2H), 7.21 – 7.14 (m, 3H), 7.11 (d, *J* = 6.1 Hz, 2H), 4.59 (t, *J* = 3.9 Hz, 1H), 4.06 (t, *J* = 8.0 Hz, 1H), 1.98 – 1.95 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.92, 149.78, 144.18, 135.08, 135.05, 133.57, 133.52, 129.83, 129.79, 128.65, 128.12, 128.10, 127.75, 126.82, 123.00, 46.58, 19.42.

HRMS (ESI): $C_{25}H_{23}NSiH^+$ $[M+H]^+$ Calcd 366.1673 Found 366.1675.



5g

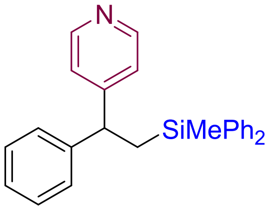
Synthesized according to General Procedure F: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), phenylsilane (4 mmol, 420 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Dichloromethane:Ethyl Acetate = 20:1) afforded 5g (9.8 mg, 17%) as a colourless liquid.

TLC (SiO_2): R_f (Dichloromethane:Ethyl Acetate = 20:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.3 Hz, 2H), 7.45 – 7.39 (m, 3H), 7.33 – 7.29 (m, 4H), 7.30 – 7.20 (m, 3H), 7.15 (d, *J* = 6.0 Hz, 2H), 4.14 (td, *J* = 3.7, 1.3 Hz, 2H), 4.08 (t, *J* = 8.1 Hz, 1H), 1.79 – 1.73 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.84, 149.83, 143.86, 135.24, 131.40, 129.84, 128.73, 128.11, 127.72, 126.93, 122.91, 47.10, 17.14.

HRMS (ESI): $C_{19}H_{19}NSiH^+$ $[M+H]^+$ Calcd 290.1360 Found 290.1357.



5h

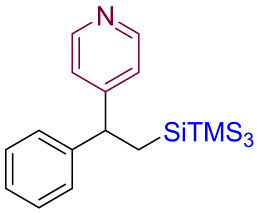
Synthesized according to General Procedure F: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), methyldiphenylsilane (4 mmol, 788 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Dichloromethane) afforded 5h (52.8 mg, 70%) as a colourless liquid.

TLC (SiO_2): R_f (Dichloromethane) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 5.1 Hz, 2H), 7.49 – 7.32 (m, 4H), 7.38 – 7.27 (m, 6H), 7.25 – 7.19 (m, 2H), 7.18 – 7.11 (m, 3H), 7.08 (d, *J* = 6.2 Hz, 2H), 4.01 (t, *J* = 7.9 Hz, 1H), 1.94 (dd, *J* = 7.9, 1.9 Hz, 2H), 0.15 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.53, 149.72, 144.61, 136.72, 136.31, 134.45, 134.35, 129.42, 129.35, 128.67, 127.98, 127.94, 127.76, 126.80, 122.95, 46.49, 21.11, -4.28.

HRMS (ESI): $C_{26}H_{25}NSiH^+$ $[M+H]^+$ Calcd 380.1829 Found 380.1836.



5i

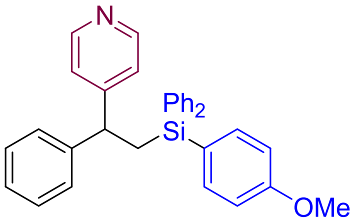
Synthesized according to General Procedure F: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), tris(trimethylsilyl)silane (4 mmol, 988 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 5:1) afforded 5i (70.5 mg, 82%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 5:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 6.1 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.30 – 7.22 (m, 3H), 7.20 (d, *J* = 6.2 Hz, 2H), 4.07 (dd, *J* = 8.4, 6.3 Hz, 1H), 1.79 – 1.61 (m, 2H), 0.11 (s, 27H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.55, 152.18, 147.02, 131.10, 129.82, 129.14, 124.88, 52.57, 17.76, 3.46.

HRMS (ESI): $C_{22}H_{39}NSi_4H^+$ $[M+H]^+$ Calcd 430.2232 Found 430.2232.



5j

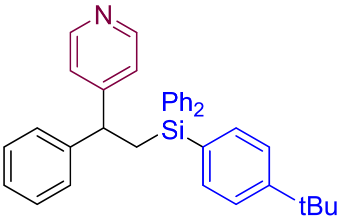
Synthesized according to General Procedure F: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), **S14** (4 mmol, 1160 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Dichloromethane:Ethyl Acetate = 30:1) afforded 5j (79 mg, 84%) as a colourless liquid.

TLC (SiO_2): R_f (Dichloromethane:Ethyl Acetate = 30:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 6.2 Hz, 2H), 7.38 – 7.32 (m, 6H), 7.28 – 7.22 (m, 6H), 7.17 – 7.09 (m, 5H), 7.00 (d, *J* = 6.2 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.18 (t, *J* = 7.4 Hz, 1H), 3.78 (s, 3H), 2.30 – 2.17 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.78, 155.29, 149.57, 145.06, 137.23, 135.62, 134.77, 129.48, 128.64, 127.88, 127.71, 126.63, 124.83, 123.07, 113.71, 55.09, 46.57, 20.61.

HRMS (ESI): $C_{32}H_{29}NOSiH^+$ $[M+H]^+$ Calcd 472.2091 Found 472.2086.



5k

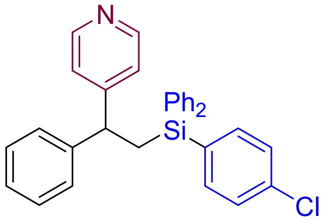
Synthesized according to General Procedure F: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), **S15** (4 mmol, 1264 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 5:1) afforded 5k (81 mg, 81%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 5:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 6.1 Hz, 2H), 7.41 – 7.33 (m, 6H), 7.30 – 7.24 (m, 8H), 7.17 – 7.07 (m, 5H), 6.99 (d, *J* = 6.2 Hz, 2H), 4.20 (t, *J* = 7.4 Hz, 1H), 2.32 – 2.18 (m, 2H), 1.31 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.20, 152.44, 149.52, 145.08, 135.65, 135.51, 134.57, 130.49, 129.46, 128.58, 127.84, 127.65, 126.56, 124.85, 123.03, 46.49, 34.71, 31.25, 20.42.

HRMS (ESI): $C_{35}H_{35}NSiH^+$ $[M+H]^+$ Calcd 498.2612 Found 498.2614.



5l

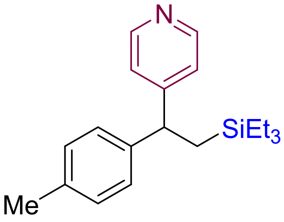
Synthesized according to General Procedure F: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), **S16** (4 mmol, 1176 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 5:1) afforded 5l (46.6 mg, 49%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 5:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 5.4 Hz, 2H), 7.39 – 7.33 (m, 6H), 7.32 – 7.27 (m, 4H), 7.24 (s, 4H), 7.16 – 7.11 (m, 3H), 7.10 – 7.05 (m, 2H), 7.02 (d, *J* = 6.2 Hz, 2H), 4.16 (t, *J* = 7.4 Hz, 1H), 2.31 – 2.18 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.14, 149.61, 144.60, 136.95, 135.97, 135.56, 135.51, 133.86, 133.71, 132.69, 129.75, 129.74, 128.67, 128.12, 128.02, 128.00, 127.67, 126.74, 122.93, 46.44, 20.32.

HRMS (ESI): $C_{31}H_{26}ClNSiH^+$ $[M+H]^+$ Calcd 476.1596 Found 476.1596.



5m

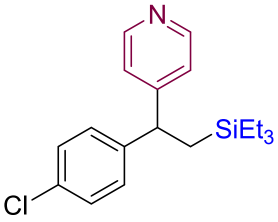
Synthesized according to General Procedure F: *p*-Methylstyrene (0.4 mmol, 47.2 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 5:1) afforded 5m (38.6 mg, 62%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 5:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 6.1 Hz, 2H), 7.20 (d, *J* = 6.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 3.98 (t, *J* = 7.9 Hz, 1H), 2.29 (s, 3H), 1.43 – 1.31 (m, 2H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.34 (q, *J* = 8.0 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.60, 149.75, 142.27, 136.25, 129.28, 127.42, 122.78, 46.28, 21.03, 18.30, 7.36, 3.47.

HRMS (ESI): $C_{20}H_{29}NSiH^+$ $[M+H]^+$ Calcd 312.2142 Found 312.2140.



5n

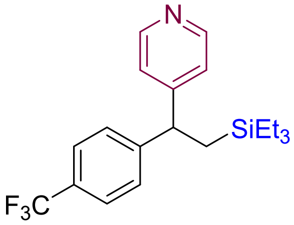
Synthesized according to General Procedure F: 1-(chloromethyl)-4-ethenylbenzene (0.4 mmol, 55.2 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 3:1) afforded 5n (27.2 mg, 41%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 3:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 6.2 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 6.2 Hz, 2H), 4.00 (t, *J* = 7.9 Hz, 1H), 1.44 – 1.29 (m, 2H), 0.84 (t, *J* = 7.9 Hz, 9H), 0.35 (q, *J* = 8.1 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.75, 149.90, 143.74, 132.41, 128.93, 128.74, 122.68, 46.06, 18.25, 7.33, 3.46.

HRMS (ESI): $C_{19}H_{26}ClNSiH^+$ $[M+H]^+$ Calcd 332.1596 Found 332.1594.



5o

Synthesized according to General Procedure F: 4-(Trifluoromethyl)styrene (0.4 mmol, 68.8 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 5:1) afforded 5o (49.1 mg, 67%) as a colourless liquid.

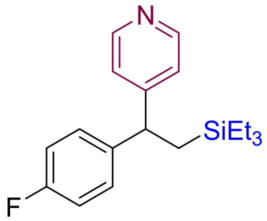
TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 5:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 6.2 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 6.2 Hz, 2H), 4.09 (t, *J* = 7.8 Hz, 1H), 1.40 (d, *J* = 7.9 Hz, 2H), 0.84 (t, *J* = 7.9 Hz, 9H), 0.35 (q, *J* = 8.2 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.02, 148.95, 148.36, 126.85, 124.55 (q, J_{CF} = 3.8Hz), 121.71, 45.50, 17.15, 6.23, 2.41.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.39.

HRMS (ESI): $C_{20}H_{26}F_3NSiH^+$ $[M+H]^+$ Calcd 366.1859 Found 366.1858.



5p

Synthesized according to General Procedure F: 4-Fluorostyrene (0.4 mmol, 48.8 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 3:1) afforded 5p (42.4 mg, 67%) as a colourless liquid.

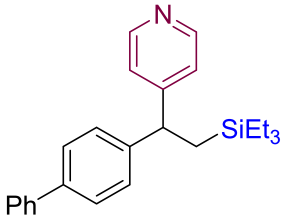
TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 3:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 6.2 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.18 (d, *J* = 6.2 Hz, 2H), 7.01 – 6.94 (m, 2H), 4.01 (dd, *J* = 8.8, 7.0 Hz, 1H), 1.42 – 1.30 (m, 2H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.37 – 0.31 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.79 (d, J_{CF} = 246.4Hz), 156.14, 149.84, 140.93 (d, J_{CF} = 3.3Hz), 129.06 (d, J_{CF} = 7.9Hz), 122.67, 115.52 (d, J_{CF} = 21.1Hz), 45.89, 18.45, 7.32, 3.44.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.19.

HRMS (ESI): $C_{19}H_{26}FNSiH^+$ $[M+H]^+$ Calcd 316.1891 Found 316.1889.



5q

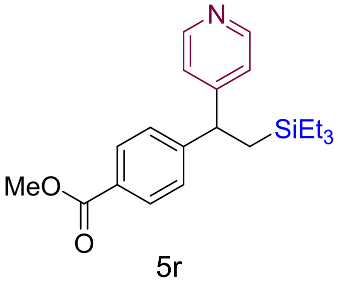
Synthesized according to General Procedure F: 4-Vinylbiphenyl (0.4 mmol, 72 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 5:1) afforded 5q (38 mg, 51%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 5:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 6.2 Hz, 2H), 7.56 (d, *J* = 7.0 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 3H), 7.25 (d, *J* = 6.2 Hz, 2H), 4.06 (t, *J* = 7.9 Hz, 1H), 1.50 – 1.35 (m, 2H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.43 – 0.31 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.19, 149.84, 144.39, 140.71, 139.59, 129.08, 128.78, 128.27, 128.00, 127.32, 127.26, 127.02, 122.88, 46.38, 18.37, 7.37, 3.51.

HRMS (ESI): $C_{25}H_{31}NSiH^+$ $[M+H]^+$ Calcd 374.2299 Found 374.2298.



5r

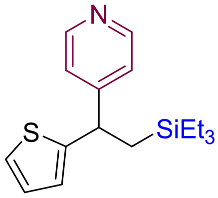
Synthesized according to General Procedure F: Methyl 4-vinylbenzoate (0.4 mmol, 64.8 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 5:1) afforded 5r (32.4 mg, 46%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 5:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 6.2 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 6.2 Hz, 2H), 4.08 (dd, *J* = 8.5, 7.2 Hz, 1H), 3.90 (s, 3H), 1.47 – 1.33 (m, 2H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.41 – 0.27 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.81, 154.31, 149.41, 148.85, 128.95, 127.56, 126.62, 121.71, 51.08, 45.64, 17.07, 6.26, 2.40.

HRMS (ESI): $C_{21}H_{29}NO_2SiH^+$ $[M+H]^+$ Calcd 356.2040 Found 356.2039.



5s

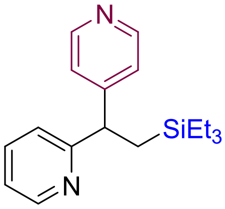
Synthesized according to General Procedure F: 2-Vinylthiophene (0.4 mmol, 44 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 5:1) afforded 5s (28.8 mg, 48%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 5:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 6.1 Hz, 2H), 7.23 (d, *J* = 6.2 Hz, 2H), 7.15 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.90 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.86 (d, *J* = 3.5 Hz, 1H), 4.26 (t, *J* = 7.8 Hz, 1H), 1.55 – 1.33 (m, 2H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.4 – 0.34 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.71, 149.93, 149.80, 126.69, 123.90, 122.57, 42.14, 20.62, 7.34, 3.36.

HRMS (ESI): $C_{17}H_{25}NSSiH^+$ $[M+H]^+$ Calcd 304.1550 Found 304.3558.



5t

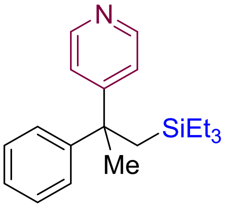
Synthesized according to General Procedure F: 2-Vinylpyridine (0.4 mmol, 42.1 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 2:1) afforded 5t (44 mg, 74%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 2:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 4.9 Hz, 1H), 8.47 (d, J = 6.1 Hz, 2H), 7.58 (td, J = 7.7, 1.9 Hz, 1H), 7.33 (d, J = 6.2 Hz, 2H), 7.21 (d, J = 7.9 Hz, 1H), 7.14 – 7.08 (m, 1H), 4.16 (dd, J = 8.9, 6.7 Hz, 1H), 1.66 (dd, J = 14.7, 8.9 Hz, 1H), 1.35 (dd, J = 14.6, 6.7 Hz, 1H), 0.83 (t, J = 7.9 Hz, 9H), 0.39 – 0.28 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.57, 155.05, 149.74, 149.45, 136.62, 123.02, 122.40, 121.81, 48.96, 17.84, 7.31, 3.40.

HRMS (ESI): $C_{18}H_{26}N_2SiH^+$ $[M+H]^+$ Calcd 299.1938 Found 299.1938.



5u

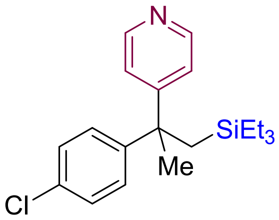
Synthesized according to General Procedure F: alpha-Methylstyrene (0.4 mmol, 47 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 5:1) afforded 5u (58 mg, 94%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 5:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 6.3 Hz, 2H), 7.29 – 7.18 (m, 5H), 7.16 (d, J = 6.4 Hz, 2H), 1.68 (s, 3H), 1.63 – 1.51 (m, 2H), 0.80 (t, J = 7.9 Hz, 9H), 0.32 – 0.21 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.13, 148.37, 127.04, 125.97, 125.11, 121.22, 43.97, 28.51, 24.56, 6.37, 3.27.

HRMS (ESI): $C_{20}H_{29}NSiH^+$ $[M+H]^+$ Calcd 312.2142 Found 312.2144.



5v

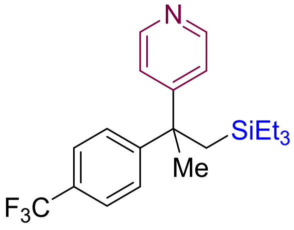
Synthesized according to General Procedure F: 4-Chloro-alpha-methylstyrene (0.4 mmol, 61.2 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 7:1) afforded 5v (59.3 mg, 86%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 7:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 6.3 Hz, 2H), 7.24 (d, J = 8.7 Hz, 2H), 7.18 – 7.12 (m, 4H), 1.66 (s, 3H), 1.54 (s, 2H), 0.81 (t, J = 7.9 Hz, 9H), 0.32 – 0.22 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.56, 149.54, 148.14, 132.00, 128.48, 128.20, 122.16, 44.79, 29.53, 25.61, 7.40, 4.35.

HRMS (ESI): $C_{20}H_{28}ClNSiH^+$ $[M+H]^+$ Calcd 346.1752 Found 346.1742.



5w

Synthesized according to General Procedure F: **S9** (0.4 mmol, 74.1 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 7:1) afforded 5w (60.2 mg, 79%) as a colourless liquid.

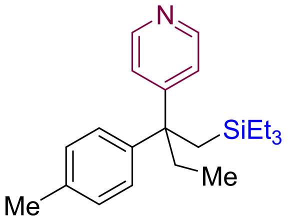
TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 7:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 6.3 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 6.3 Hz, 2H), 1.70 (s, 3H), 1.58 (s, 2H), 0.80 (t, J = 7.9 Hz, 9H), 0.32 – 0.22 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 159.92, 153.82, 153.81, 149.64, 127.37, 125.09 (q, J_{CF} = 3.7), 122.21, 45.26, 29.39, 25.58, 7.34, 4.33.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.38.

HRMS (ESI): $C_{21}H_{28}F_3NSiH^+$ $[M+H]^+$ Calcd 380.2016 Found 380.2016.



5x

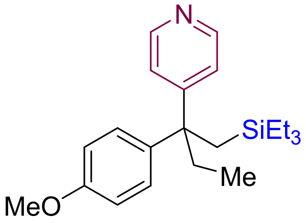
Synthesized according to General Procedure F: **S7** (0.4 mmol, 59.1 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 10:1) afforded 5x (36 mg, 53%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 10:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 6.3 Hz, 2H), 7.14 (d, *J* = 6.3 Hz, 2H), 7.05 (s, 4H), 2.31 (s, 3H), 2.14 (q, *J* = 7.2 Hz, 2H), 1.50 (s, 2H), 0.78 (t, *J* = 7.9 Hz, 9H), 0.63 (t, *J* = 7.3 Hz, 3H), 0.32 – 0.22 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.24, 149.17, 145.84, 135.52, 128.58, 127.56, 123.18, 48.23, 32.26, 21.41, 20.94, 9.02, 7.43, 4.13.

HRMS (ESI): $C_{22}H_{33}NSiH^+$ $[M+H]^+$ Calcd 340.2455 Found 340.2457.



5y

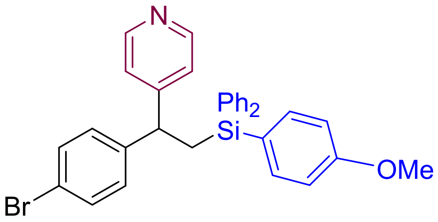
Synthesized according to General Procedure F: **S8** (0.4 mmol, 66.3 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 10:1) afforded 5y (23.4 mg, 33%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 10:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 6.3 Hz, 2H), 7.14 (d, *J* = 6.3 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 2.13 (q, *J* = 7.7, 6.8 Hz, 2H), 1.49 (d, *J* = 5.5 Hz, 2H), 0.78 (t, *J* = 7.9 Hz, 9H), 0.63 (t, *J* = 7.3 Hz, 3H), 0.27 – 0.17 (m, 6H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.32, 157.69, 149.14, 141.03, 128.67, 123.16, 113.17, 55.24, 47.94, 32.41, 21.54, 9.02, 7.44, 4.13.

HRMS (ESI): $C_{22}H_{33}NOSiH^+$ $[M+H]^+$ Calcd 356.2404 Found 356.2406.



5z

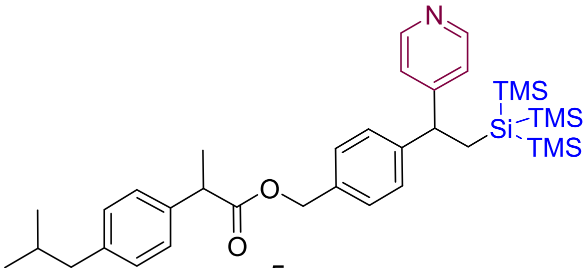
Synthesized according to General Procedure F: 1-Bromo-4-vinylbenzene (0.4 mmol, 73.2 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), **S14** (4 mmol, 1160 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 3:1) afforded 5z (63.2 mg, 57%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 3:1) = 0.5

^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 5.9 Hz, 2H), 7.39 – 7.34 (m, 6H), 7.30 – 7.25 (m, 6H), 7.22 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 6.0 Hz, 2H), 6.91 (d, J = 8.3 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 4.15 (t, J = 7.6 Hz, 1H), 3.81 (s, 3H), 2.19 (d, J = 7.5 Hz, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.81, 154.85, 149.75, 143.63, 137.11, 135.52, 135.50, 134.53, 134.47, 131.55, 129.53, 129.51, 129.48, 127.93, 127.91, 124.50, 122.78, 120.42, 113.71, 113.66, 55.10, 45.97, 20.52.

HRMS (ESI): $C_{32}H_{28}BrNOSiH^+$ $[M+H]^+$ Calcd 550.1196 Found 550.1191.



5aa

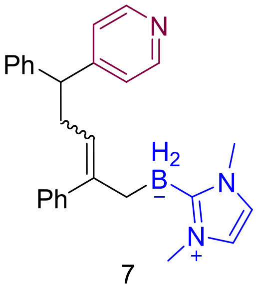
Synthesized according to General Procedure F: **S1** (0.4 mmol, 123.2 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), tris(trimethylsilyl)silane (4 mmol, 988 mg, 20 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 5:1) afforded 5aa (117 mg, 92%) as a colourless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 5:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 6.2 Hz, 2H), 7.25 – 7.19 (m, 6H), 7.19 (d, *J* = 6.1 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 5.08 (s, 2H), 4.05 (t, *J* = 7.3 Hz, 1H), 3.76 (q, *J* = 7.1 Hz, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 1.94 – 1.81 (m, 1H), 1.74 – 1.61 (m, 2H), 1.53 (d, *J* = 7.2 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 6H), 0.11 (s, 27H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 176.68, 158.42, 152.00, 146.93, 146.91, 142.76, 139.79, 139.78, 137.03, 131.53, 130.62, 129.82, 129.44, 124.90, 68.10, 52.31, 47.34, 47.24, 32.42, 24.61, 20.63, 17.78, 3.46.

HRMS (ESI): $C_{35}H_{55}NO_2Si_4H^+$ $[M+H]^+$ Calcd 648.3539 Found 648.3536.



7

Synthesized according to general procedure E: Alkene **6** (0.4 mmol, 88 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S10** (0.6 mmol, 66 mg, 3 equiv.), and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 1:4) afforded 7 (44.6 mg, 55%) as a colourless liquid.

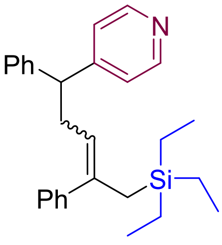
TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 1:4) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 6.1 Hz, 1H), 8.40 (d, *J* = 6.1 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.26 – 7.11 (m, 6H), 7.10 – 7.06 (m, 2H), 7.00 – 6.96 (m, 2H), 6.58 (s, 1H), 6.48 (s, 1H), 5.17 (t, *J* = 6.5 Hz, 0.5H), 5.05 (t, *J* = 7.0 Hz, 0.5H), 4.07 (t, *J* = 7.9 Hz, 0.5H), 3.85 (t, *J* = 7.7 Hz, 0.5H), 3.52 (s, 3H), 3.50 (s, 3H), 2.93 – 2.80 (m, 1H), 2.69 – 2.58 (m, 1H), 1.99 (s, 1H), 1.83 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.42, 153.98, 150.24, 149.60, 149.46, 148.89, 145.22, 143.89, 143.67, 143.40, 128.52, 128.43, 128.14, 128.08, 128.04, 127.54, 127.44, 126.52, 126.43, 125.68, 125.66, 125.54, 123.68, 119.81, 119.80, 118.88, 117.72, 51.68, 51.08, 35.73, 34.72, 33.93.

^{11}B NMR (128 MHz, $CDCl_3$) δ -28.04 (t, *J* = 83.9 Hz, 1B).

HRMS (ESI): $C_{17}H_{30}BN_3H^+$ $[M+H]^+$ Calcd 408.2606 Found 408.2602.



8

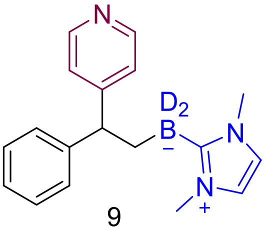
Synthesized according to general procedure F: Alkene (0.4 mmol, 88 mg, 2.0 equiv.), 4-Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), triethylsilane (4 mmol, 460 mg, 20 equiv.), and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 7:1) afforded **8** (33.3 mg, 40%) as a colorless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 7:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 6.1 Hz, 0.7H), 8.43 (d, *J* = 6.1 Hz, 1.3H), 7.31 – 7.17 (m, 8H), 7.11 – 7.00 (m, 4H), 5.31 (t, *J* = 6.7 Hz, 0.4H), 5.16 (t, *J* = 7.1 Hz, 0.6H), 4.03 (t, *J* = 7.8 Hz, 0.4H), 3.91 (t, *J* = 7.8 Hz, 0.6H), 2.87 (t, *J* = 7.3 Hz, 0.7H), 2.70 (t, *J* = 7.4 Hz, 1.3H), 1.92 (s, 1H), 1.77 (s, 1H), 0.80 (t, *J* = 7.9 Hz, 3H), 0.73 (t, *J* = 7.9 Hz, 5H), 0.34 (q, *J* = 7.9 Hz, 2H), 0.28 (q, *J* = 7.9 Hz, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.74, 153.63, 149.74, 149.55, 144.67, 142.94, 142.86, 142.16, 140.64, 140.39, 128.69, 128.54, 128.32, 128.01, 127.98, 126.80, 126.76, 126.65, 126.60, 123.52, 123.47, 122.59, 121.89, 51.52, 50.84, 34.68, 34.61, 24.51, 16.65, 7.29, 7.22, 3.80, 3.37.

HRMS (ESI): $C_{28}H_{35}NSiH^+$ $[M+H]^+$ Calcd 414.2612 Found 414.2610.



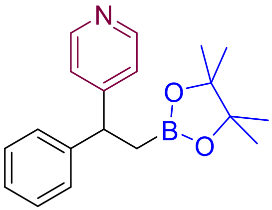
9

Synthesized according to general procedure E: Styrene (0.4 mmol, 41.6 mg, 2.0 equiv.), 4- Cyanopyridine (0.2 mmol, 20.8 mg, 1.0 equiv.), borane **S14** (0.6 mmol, 67.8 mg, 3 equiv.) and benzophenone (0.04 mmol, 7.3 mg, 0.2 equiv.) in MeCN (0.05 M, 4 mL), room temperature, 36 h, 10 W 395 nm blue LEDs. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 1:4) afforded **9** (29.9 mg, 51%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 6.1 Hz, 2H), 7.18 (d, *J* = 5.0 Hz, 4H), 7.14 (d, *J* = 6.1 Hz, 2H), 7.07 (ddd, *J* = 8.6, 4.9, 3.3 Hz, 1H), 3.82 (t, *J* = 7.7 Hz, 1H), 3.55 (s, 6H), 1.22 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.40, 149.11, 147.32, 128.04, 127.76, 125.55, 123.36, 119.98, 53.75, 35.68.

HRMS (ESI): $C_{18}H_{20}D_2BN_3H^+$ $[M+H]^+$ Calcd 294.2105 Found 294.2101.



11

4 (0.6 mmol, 175 mg, 1.0 equiv.), Et_3N (1.2 mmol, 0.166 mL, 2.0 equiv.), NCS (0.63 mmol, 84.1 mg, 1.05 equiv.) and pinacol (1.2 mmol, 142 mg, 2 equiv.) in toluene (6 mL). The resulting mixture was stirred at room temperature until TLC indicating the reaction complete. Purification by flash chromatography (SiO_2, Petroleum Ether:Ethyl Acetate = 3:1) afforded **11** (92.4 mg, 50%) as a colorless liquid.

TLC (SiO_2): R_f (Petroleum Ether:Ethyl Acetate = 3:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 6.2 Hz, 2H), 7.30 – 7.19 (m, 5H), 7.18 (d, *J* = 6.2 Hz, 2H), 4.25 (t, *J* = 8.4 Hz, 1H), 1.58 (d, *J* = 8.4 Hz, 2H), 1.07 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.44, 149.68, 144.69, 128.50, 127.71, 126.54, 123.03, 83.37, 45.95, 24.58.

9. Reference

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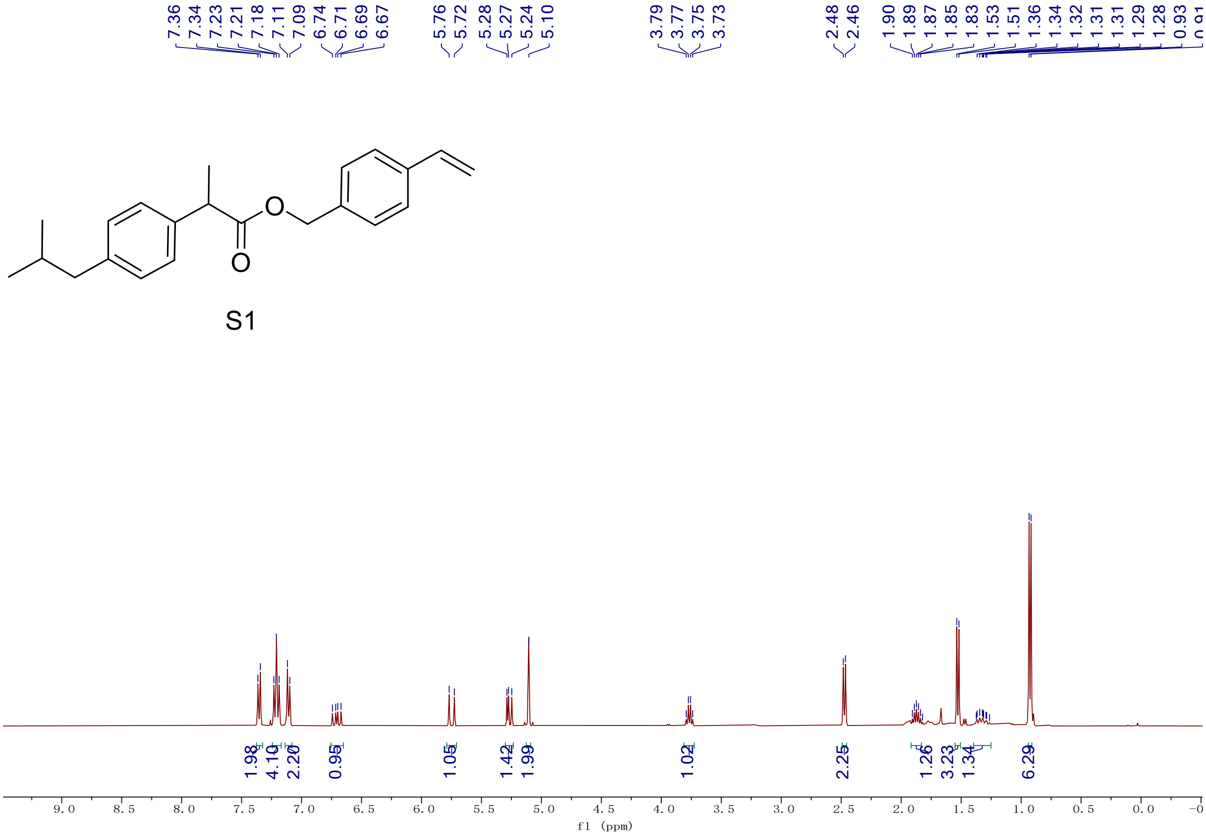
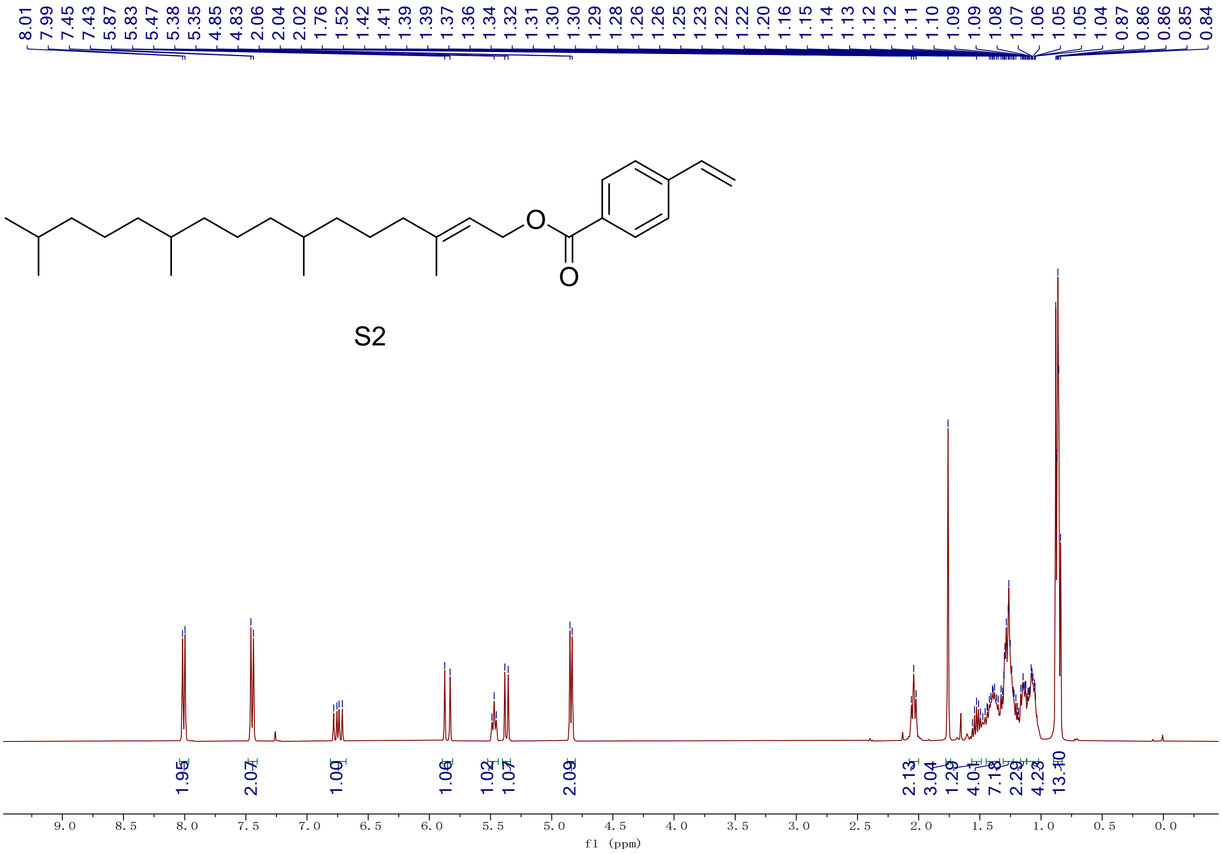
10. NMR Spectra for the products

^{1}H NMR spectra of compound **S1** (400 MHz, $CDCl_3$)

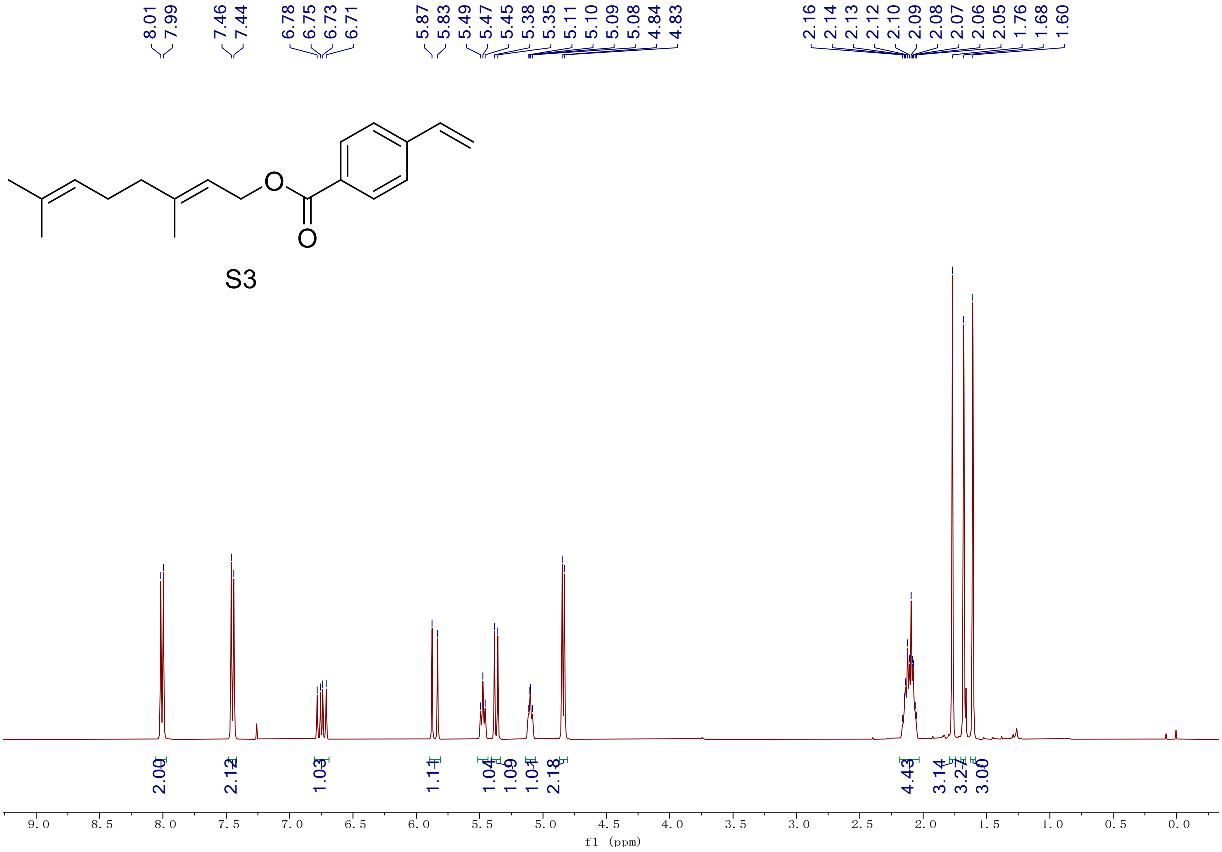


^{1}H NMR spectra of compound **S2** (400 MHz, $CDCl_3$)



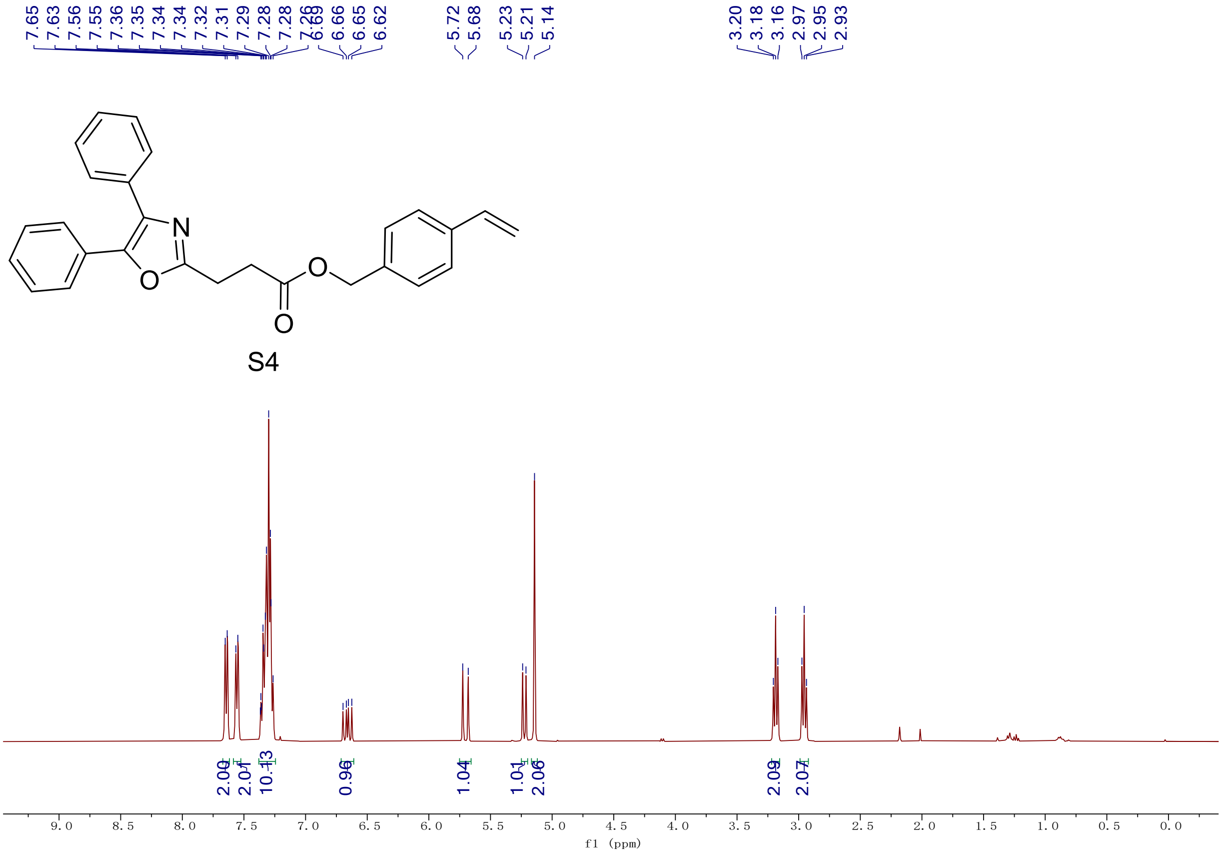
S2

^{1}H NMR spectra of compound **S3** (400 MHz, CDCl$_3$)

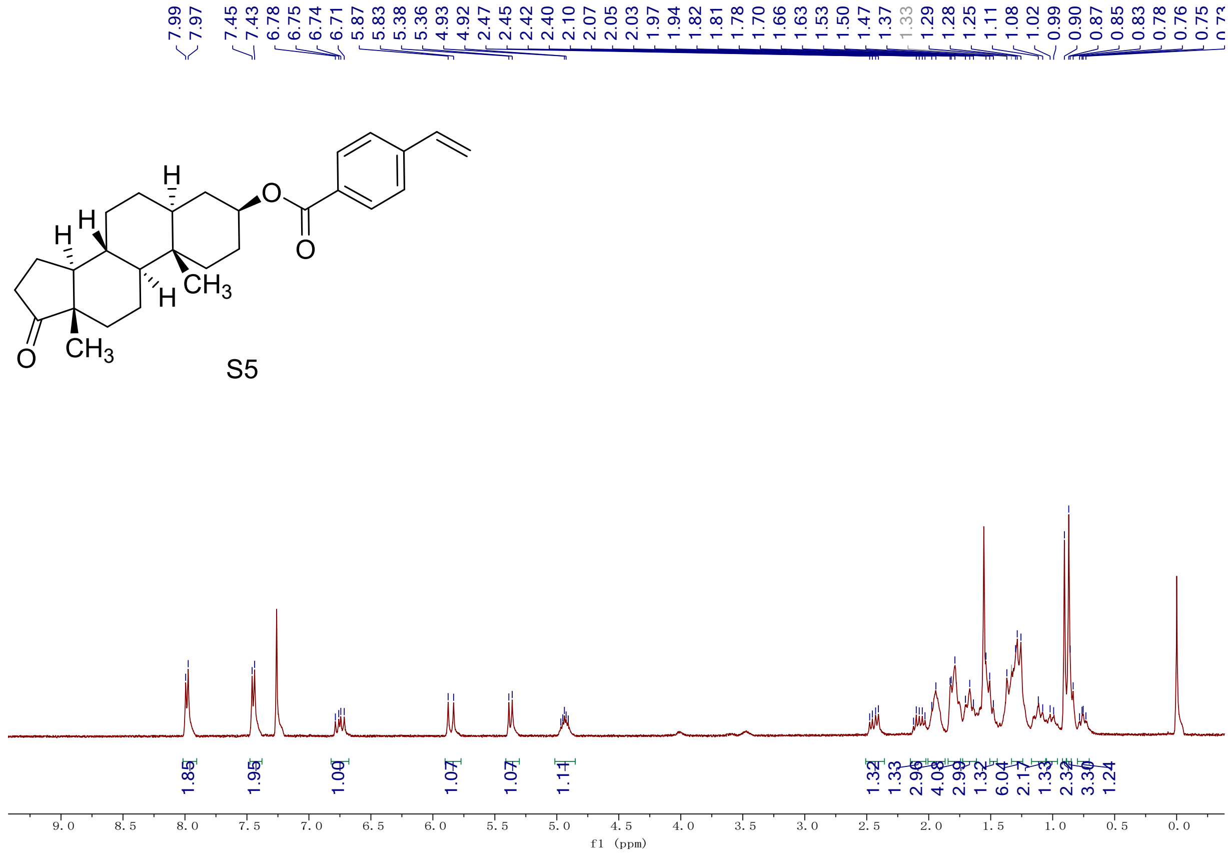


S3

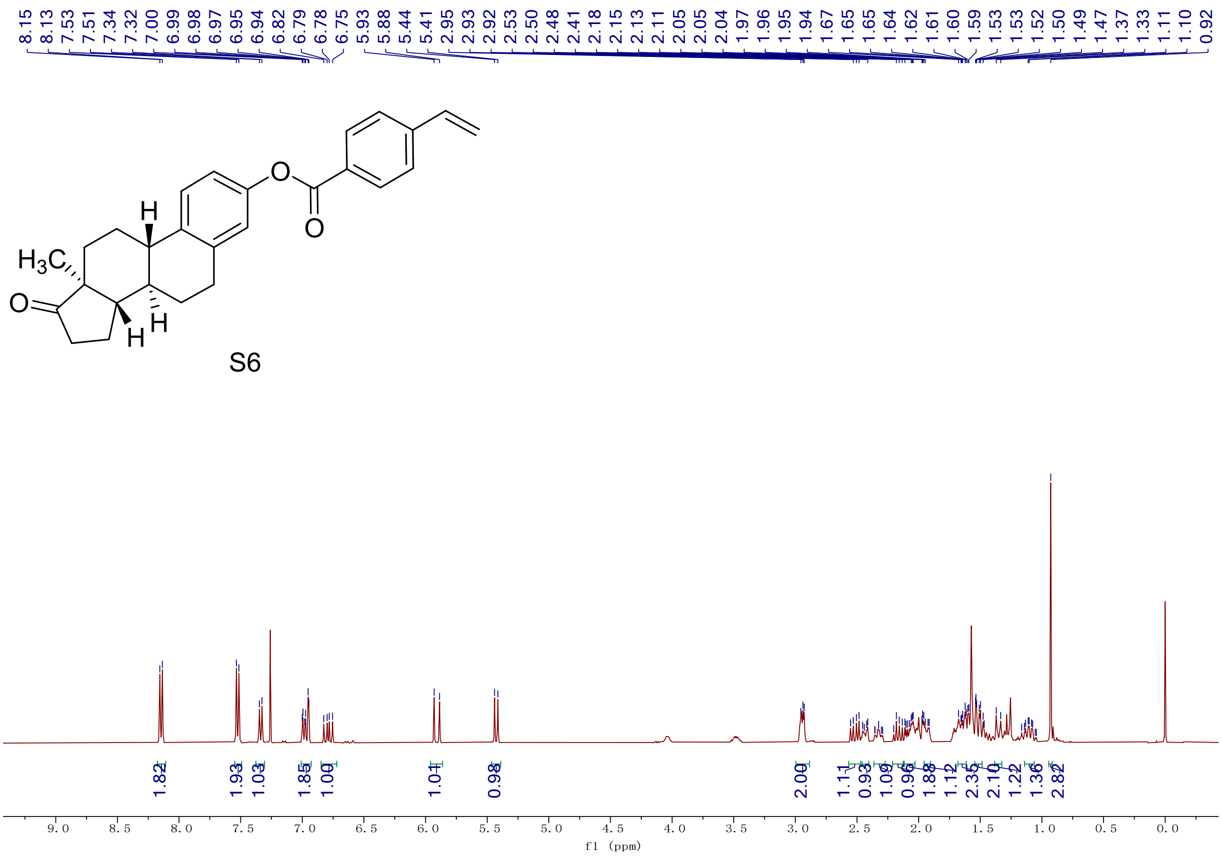
^{1}H NMR spectra of compound **S4** (400 MHz, CDCl$_3$)



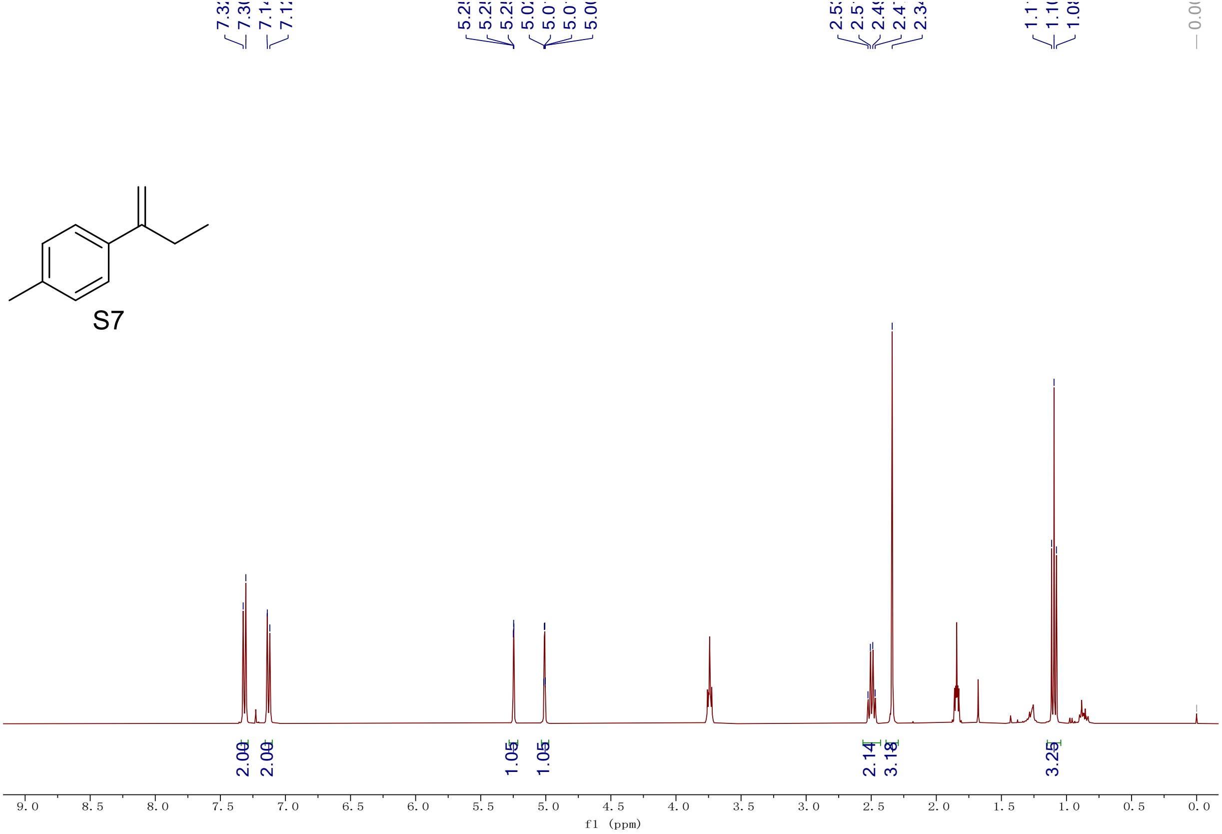
^{1}H NMR spectra of compound **S5** (400 MHz, $CDCl_3$)



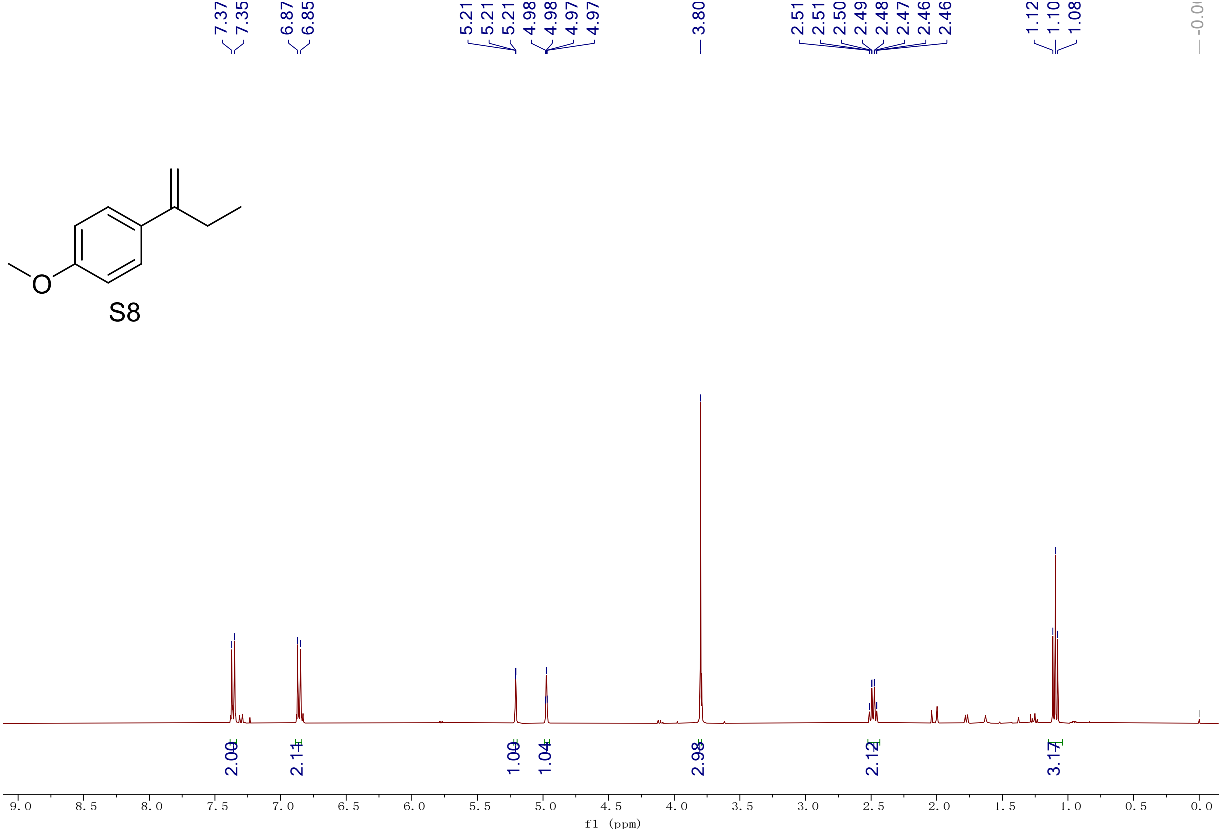
^{1}H NMR spectra of compound **S6** (400 MHz, CDCl$_3$)



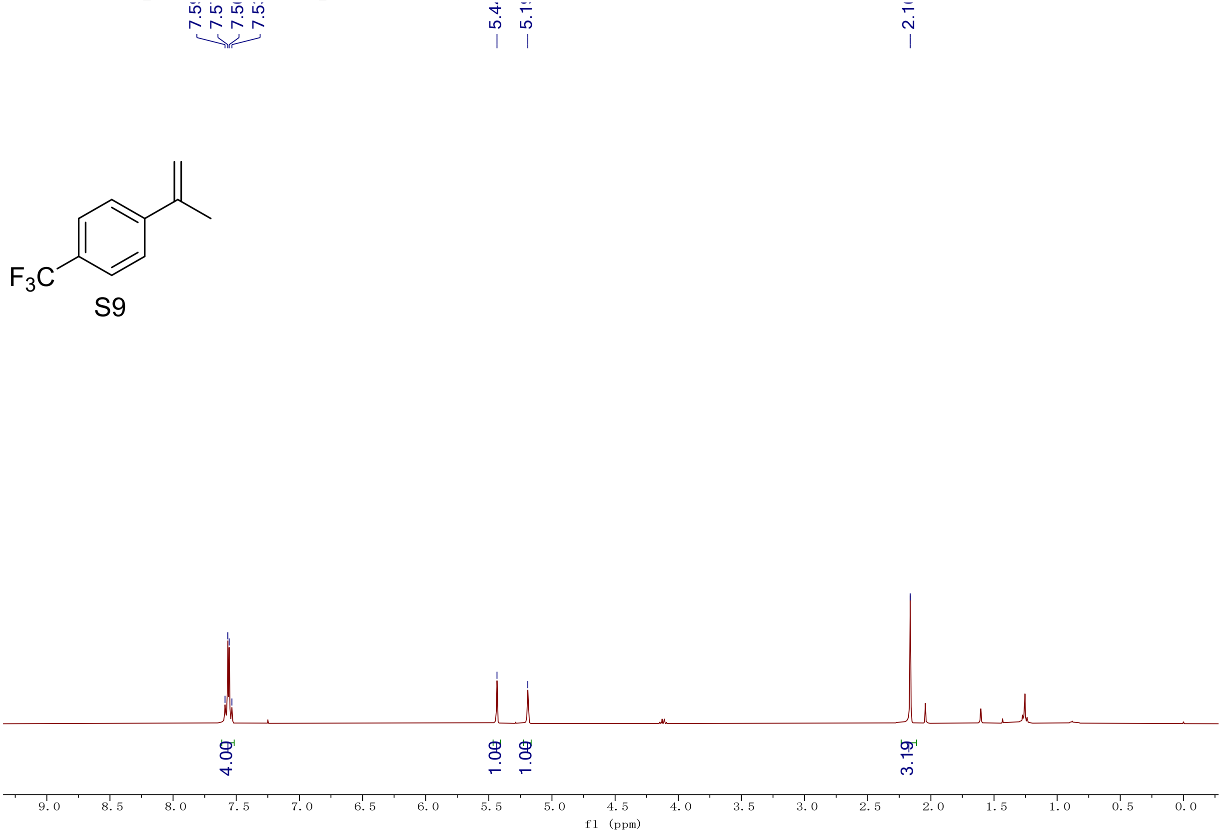
^{1}H NMR spectra of compound S7 (400 MHz, CDCl$_3$)



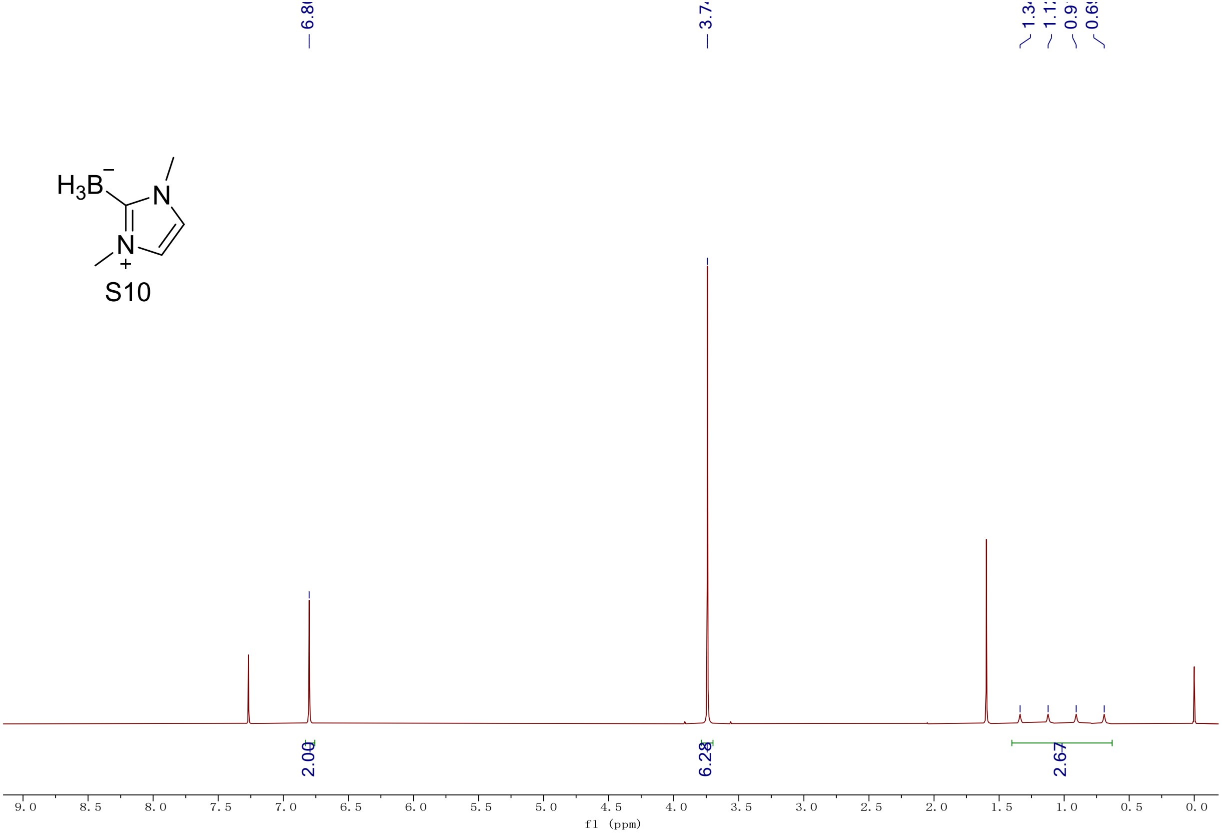
^{1}H NMR spectra of compound S8 (400 MHz, CDCl$_3$)



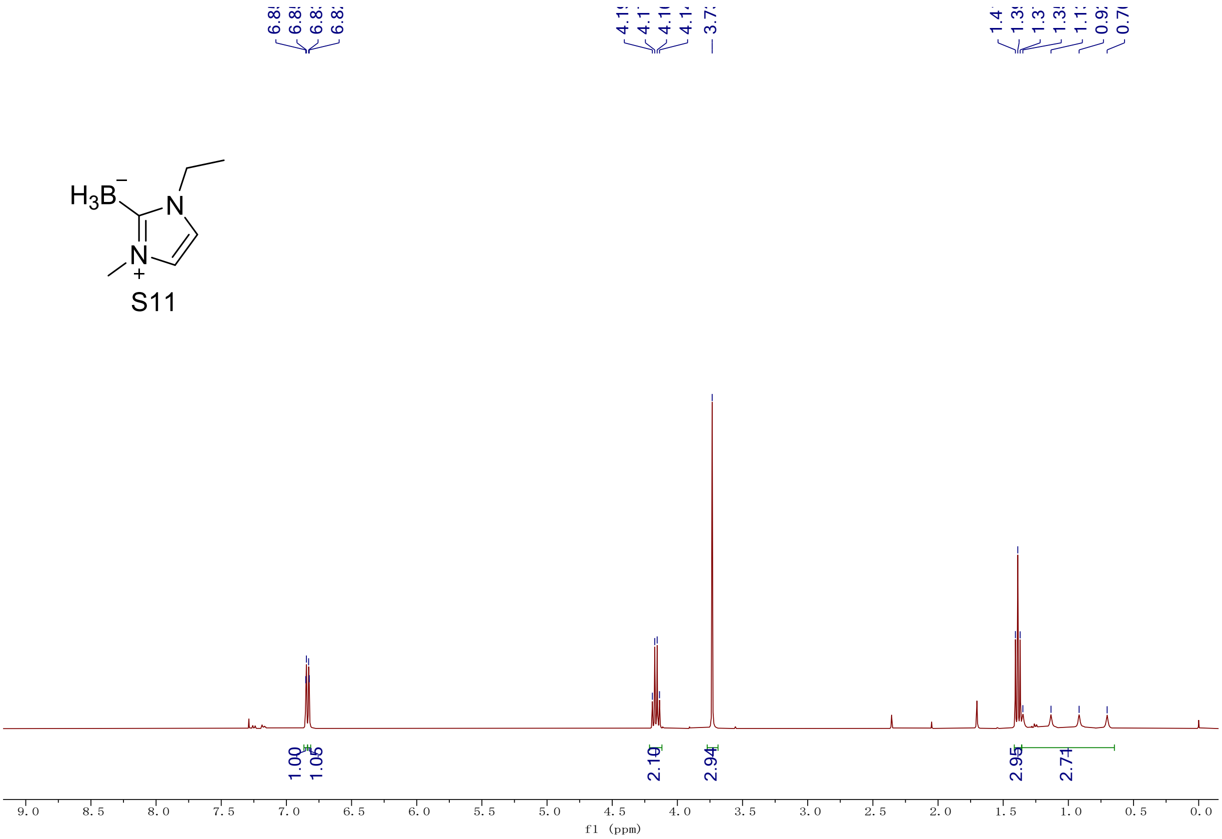
^{1}**H NMR** spectra of compound **S9** (400 MHz, $CDCl_3$)



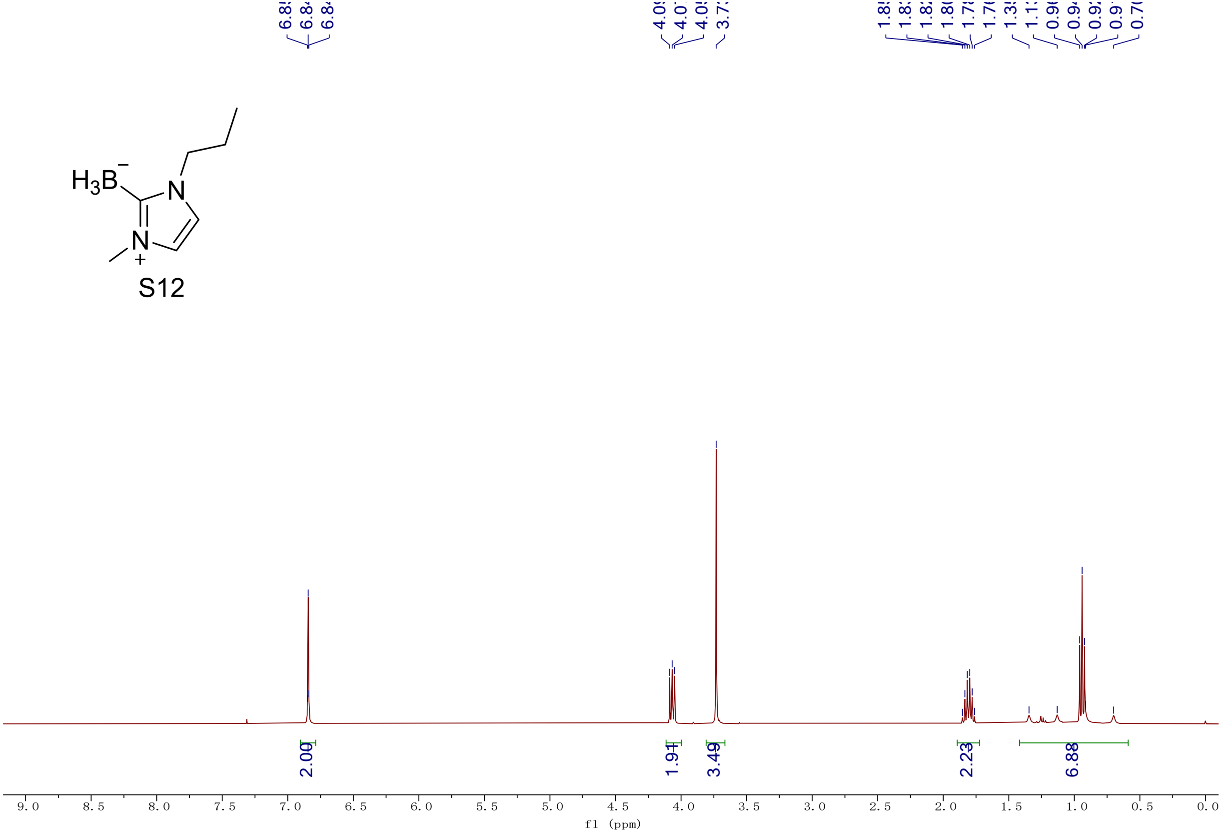
^{1}**H NMR** spectra of compound **S10** (400 MHz, $CDCl_3$)



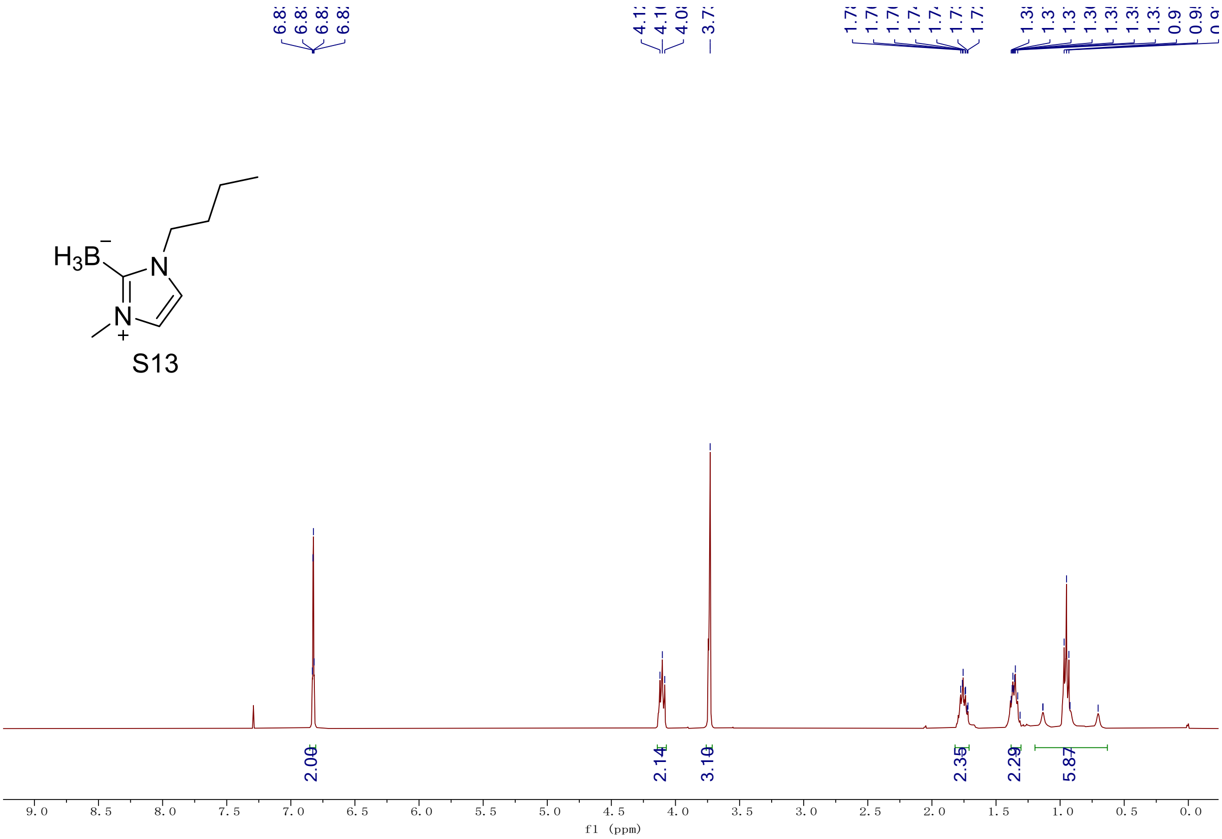
^{1}**H NMR** spectra of compound **S11** (400 MHz, $CDCl_3$)



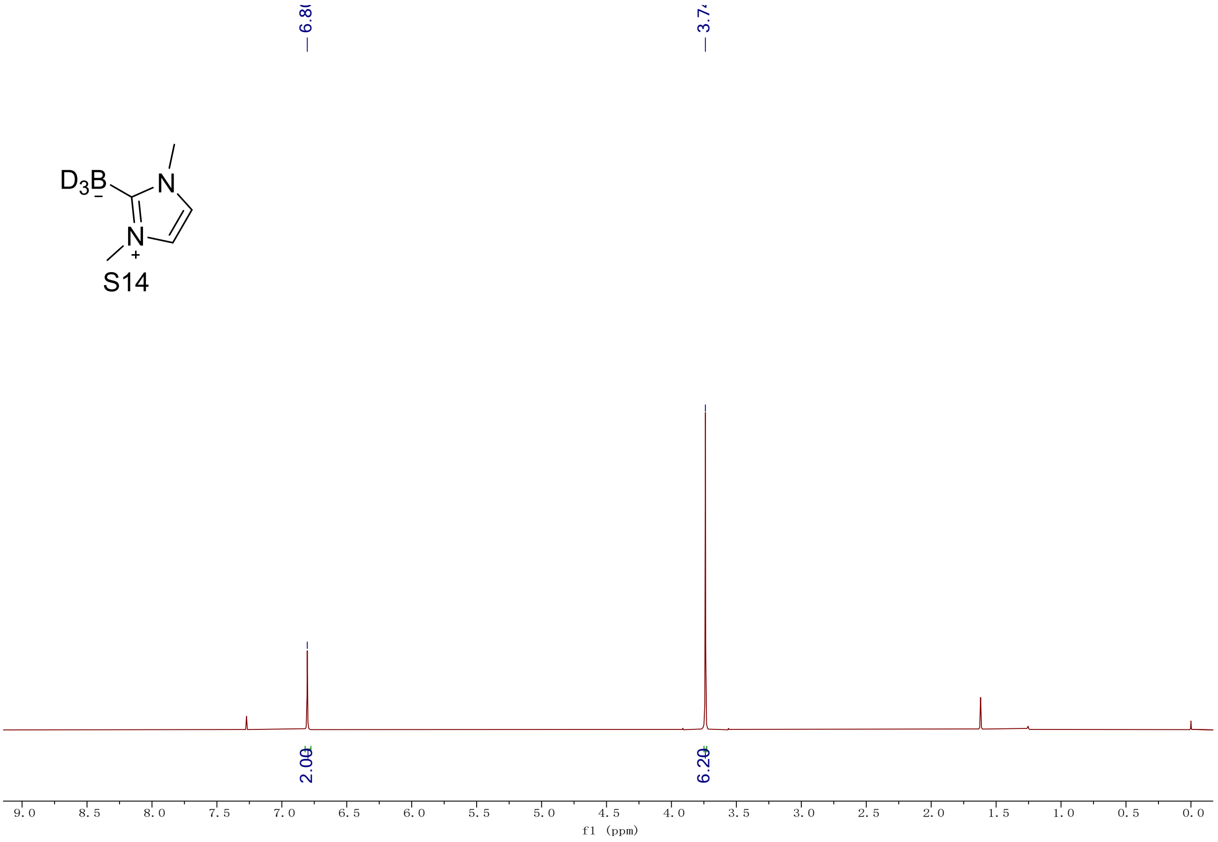
^{1}H NMR spectra of compound **S12** (400 MHz, $CDCl_3$)



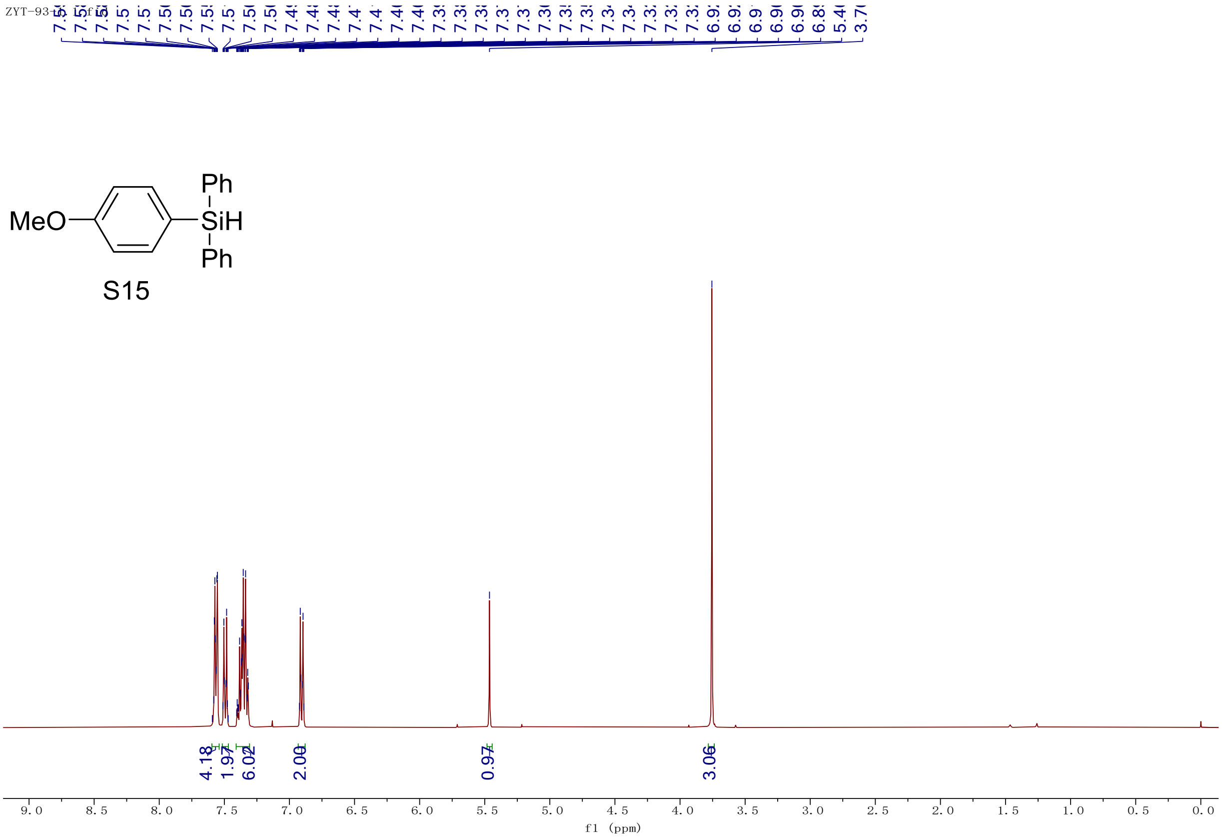
^{1}H NMR spectra of compound **S13** (400 MHz, $CDCl_3$)



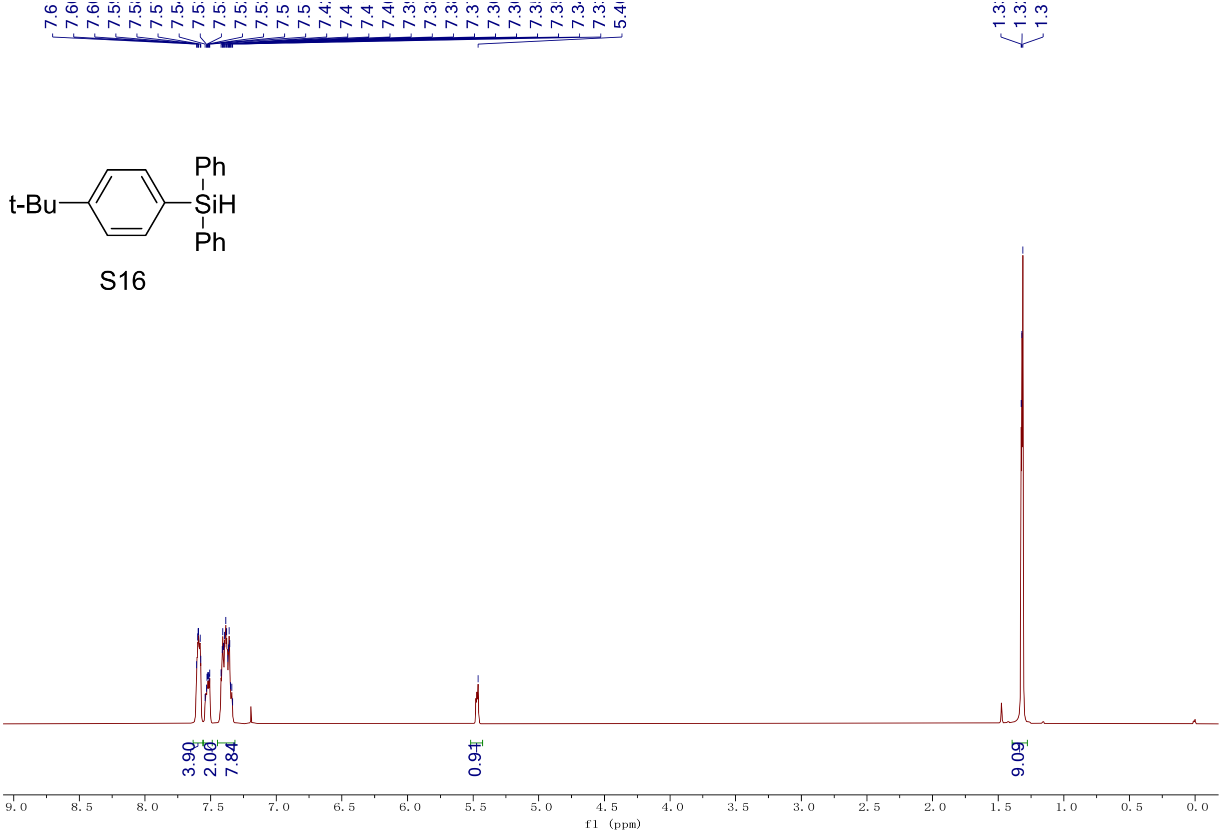
^{1}**H NMR** spectra of compound **S14** (400 MHz, $CDCl_3$)



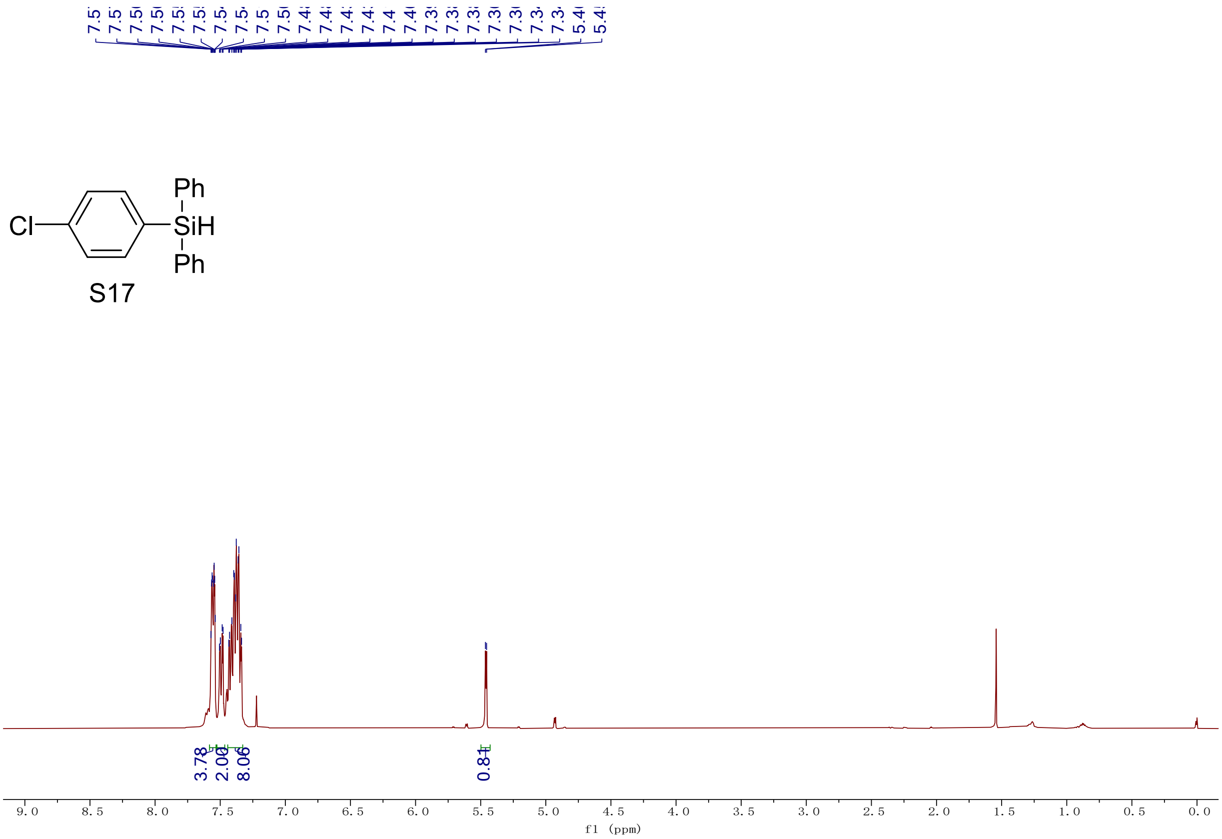
^{1}**H NMR** spectra of compound **S15** (400 MHz, $CDCl_3$)



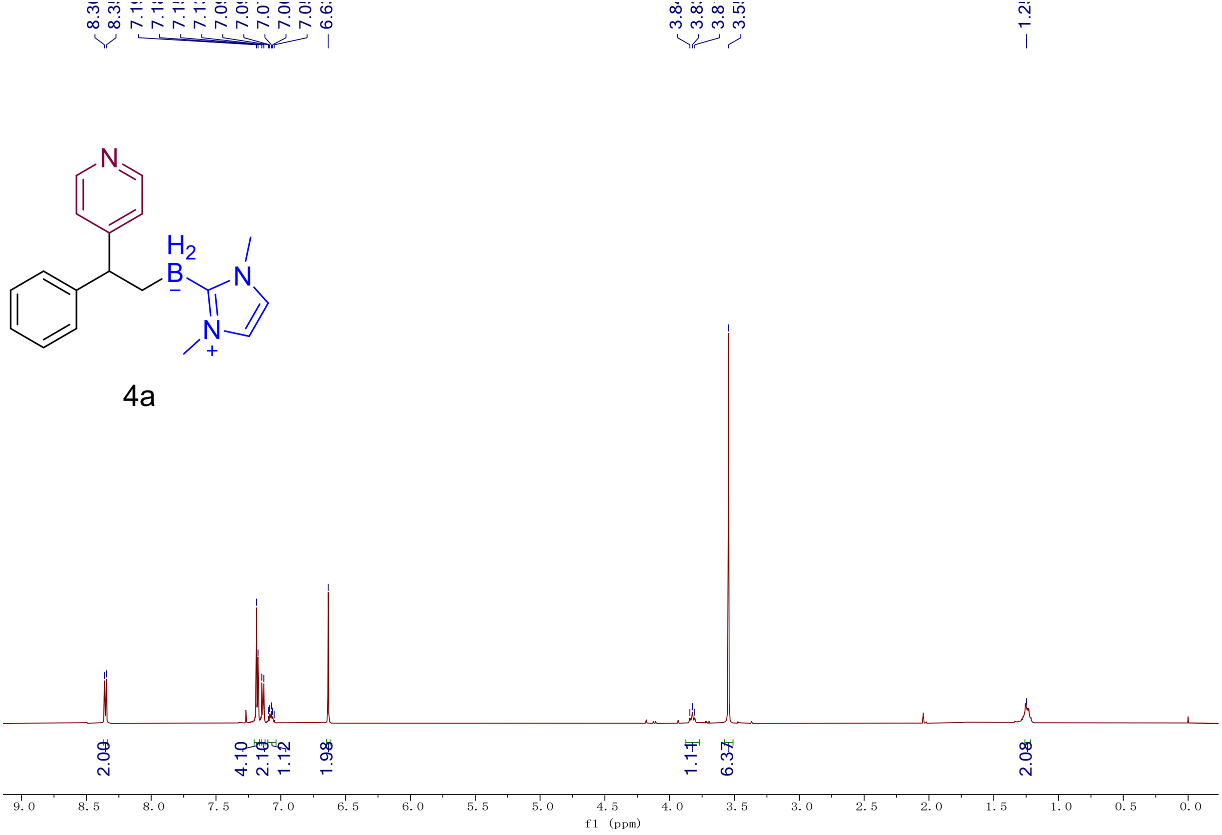
^{1}H NMR spectra of compound **S16** (400 MHz, $CDCl_3$)



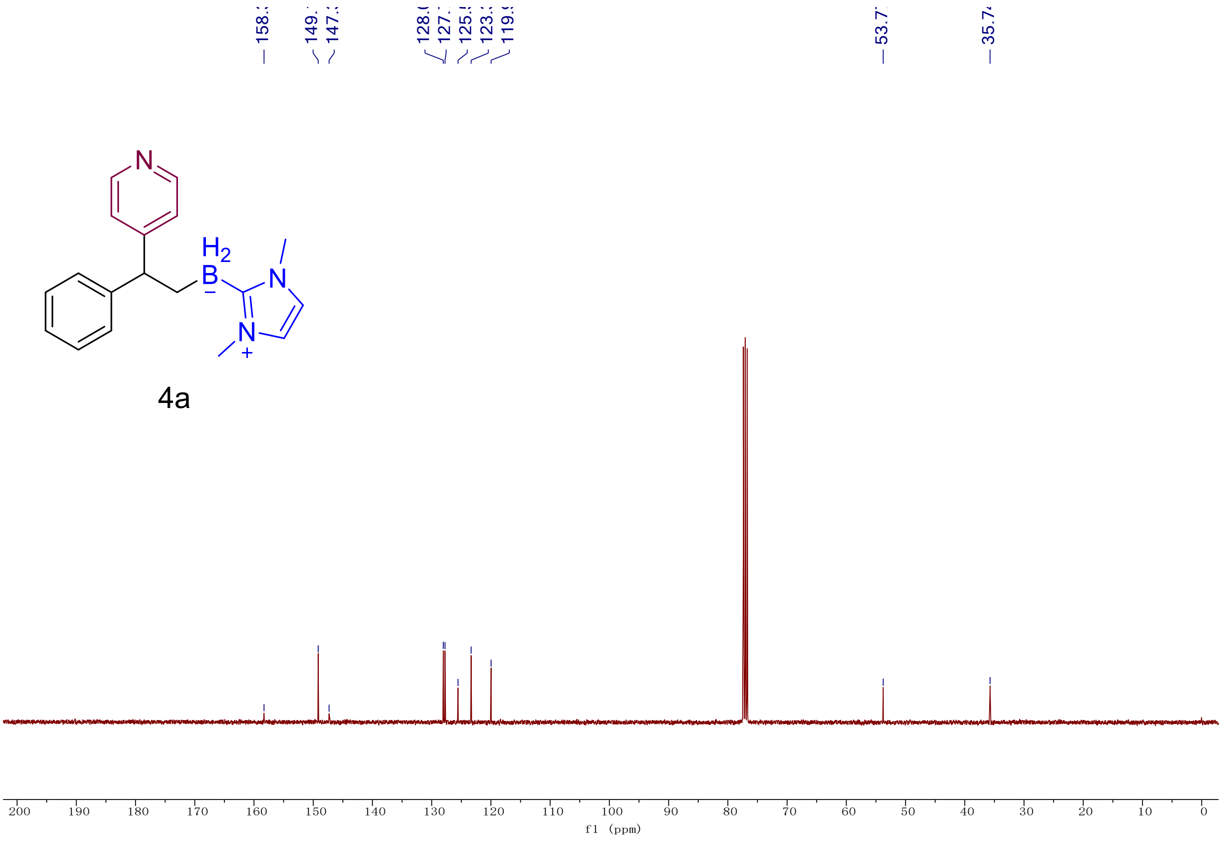
^{1}H NMR spectra of compound **S17** (400 MHz, $CDCl_3$)



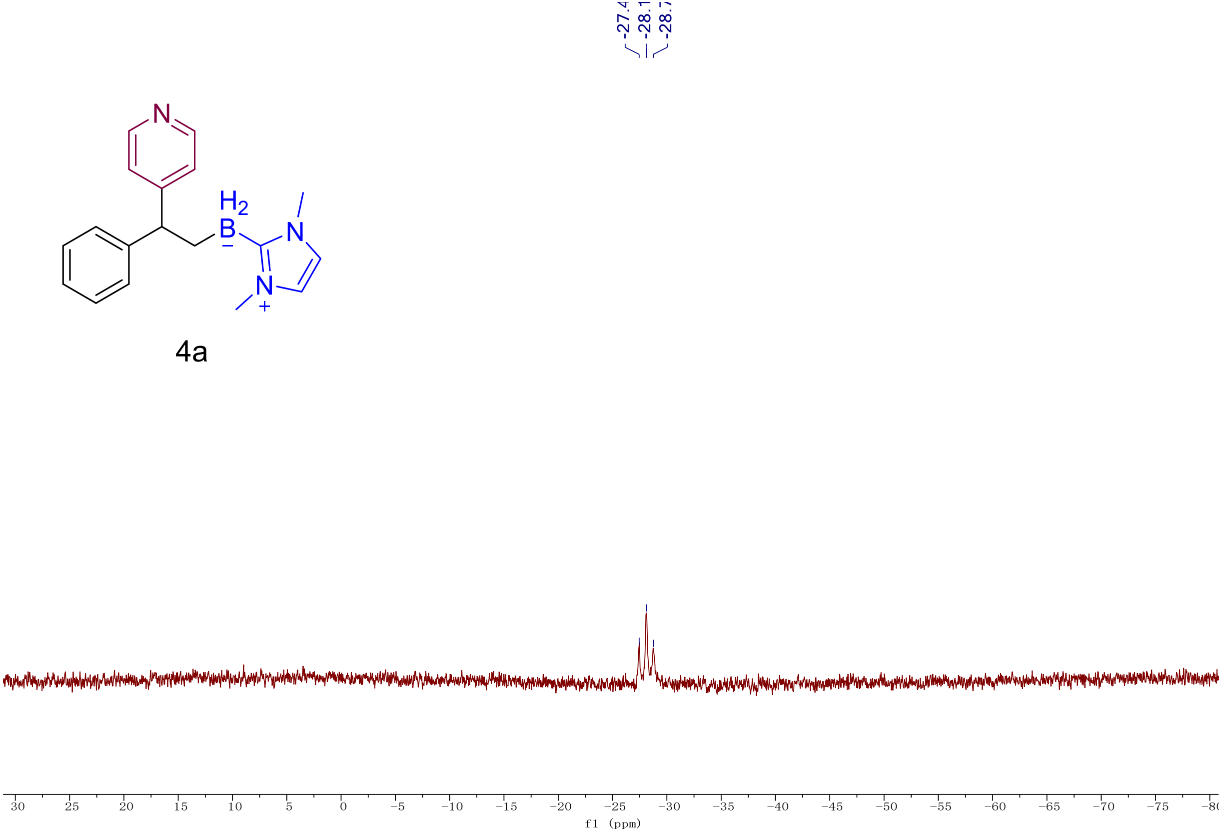
^{1}H NMR spectra of compound **4a** (400 MHz, $CDCl_3$)



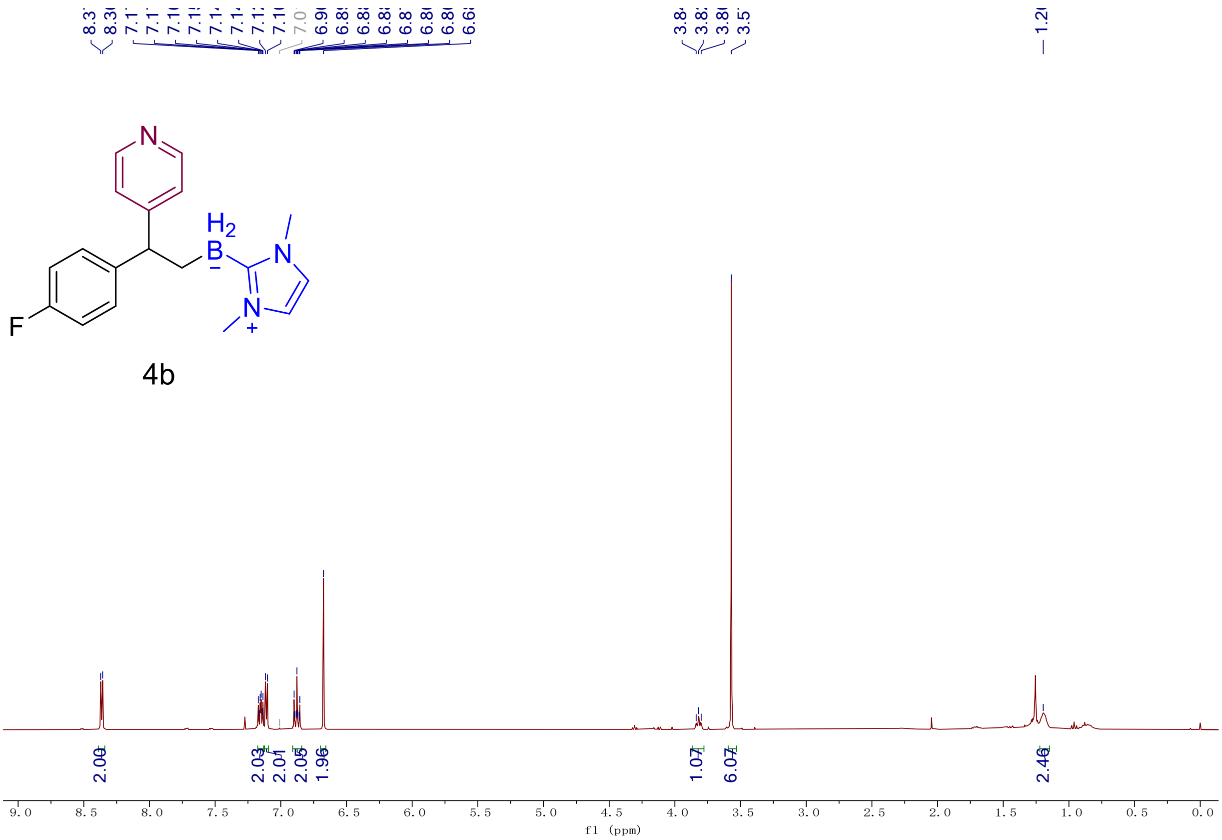
^{13}C NMR spectra of compound **4a** (101 MHz, $CDCl_3$)



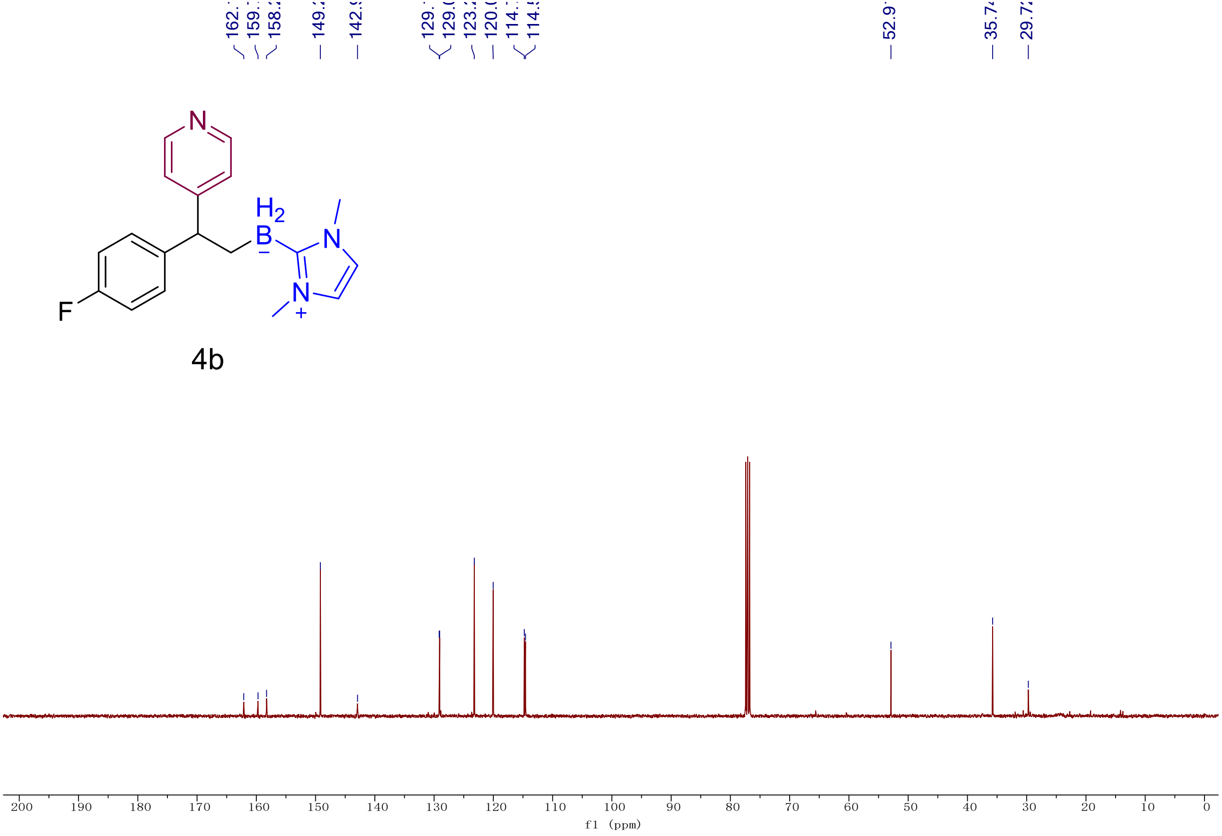
^{11}**B NMR** spectra of compound **4a** (128 MHz, $CDCl_3$)



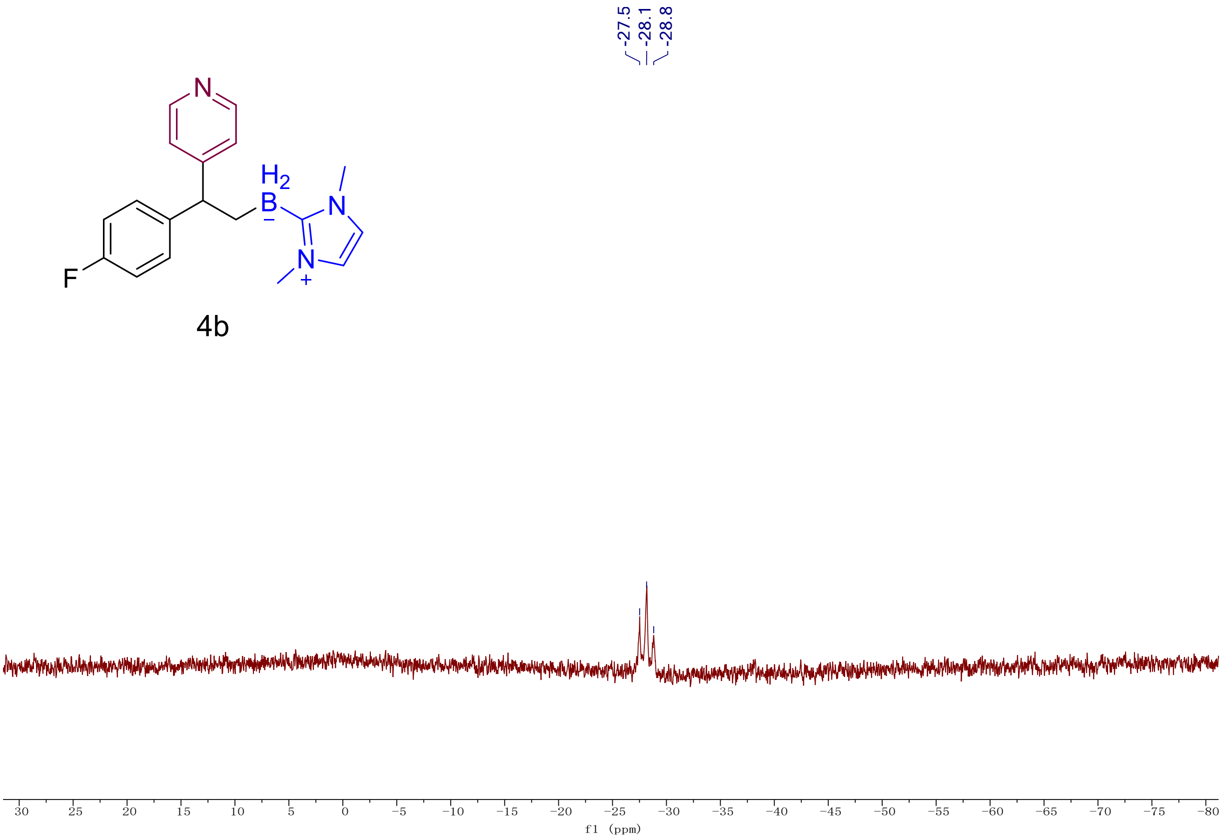
^{1}**H NMR** spectra of compound **4b** (400 MHz, $CDCl_3$)



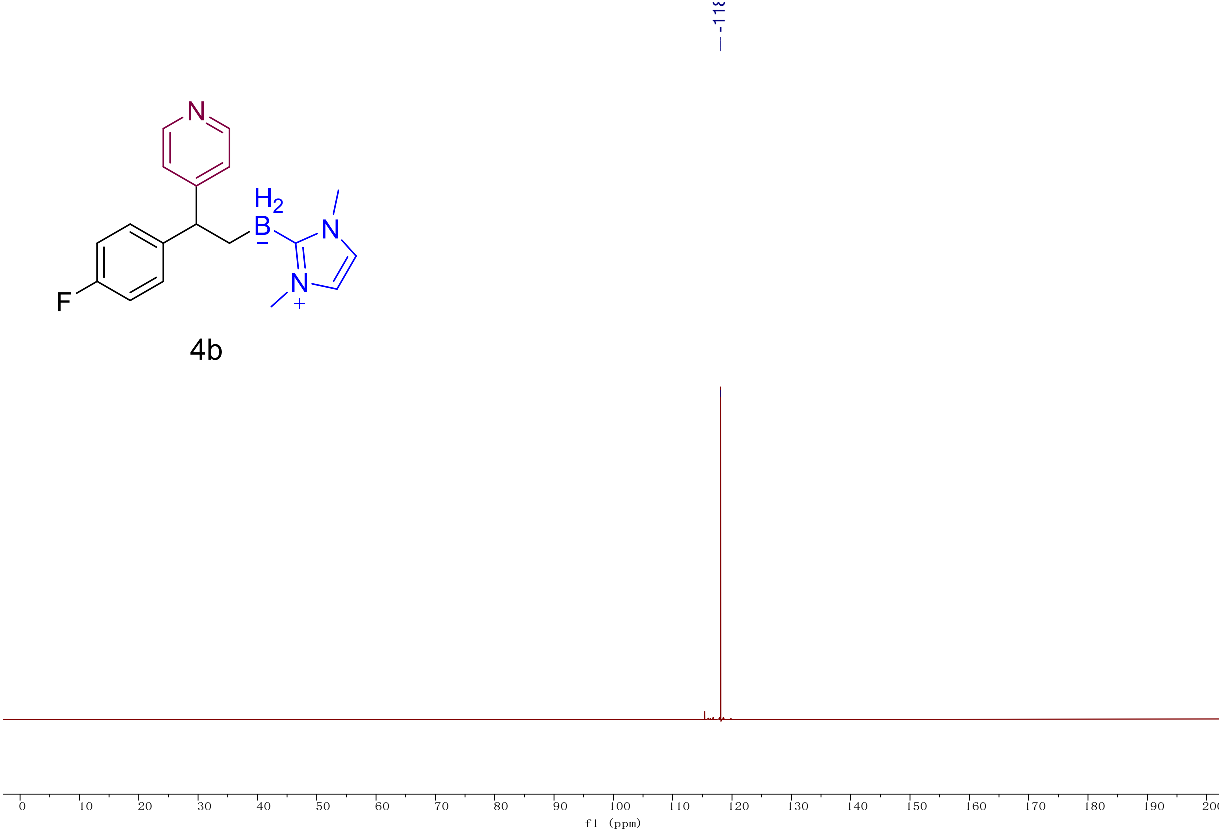
^{13}**C NMR** spectra of compound **4b** (101 MHz, $CDCl_3$)



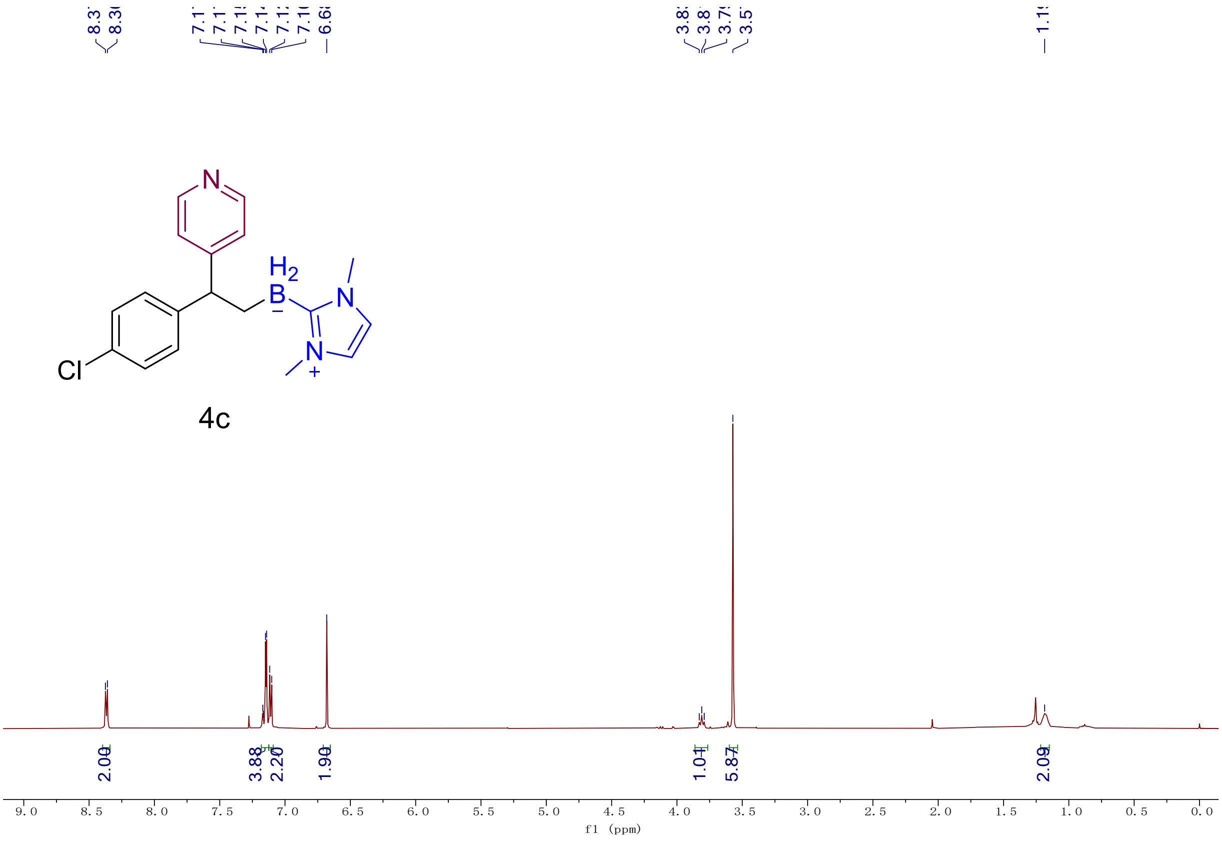
^{11}**B NMR** spectra of compound **4b** (128 MHz, $CDCl_3$)



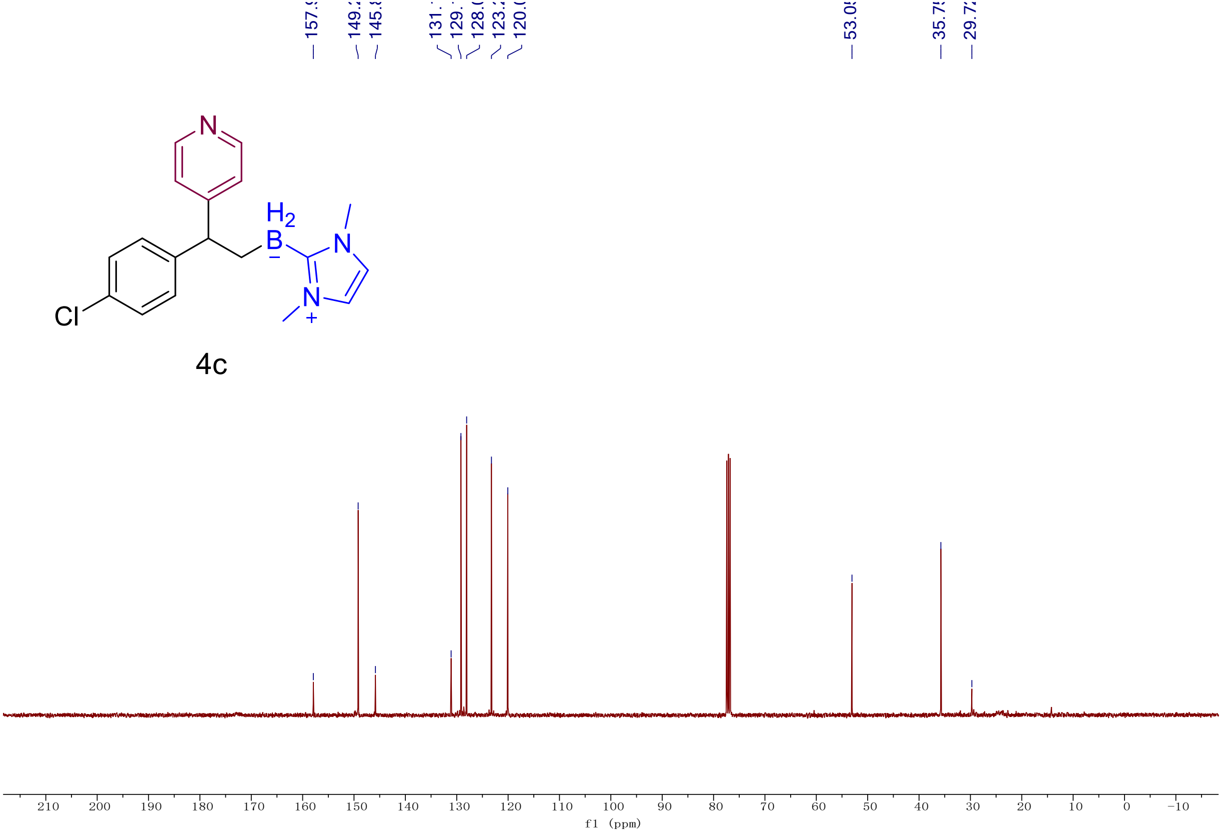
^{19}**F NMR** spectra of compound **4b** (376 MHz, CDCl$_3$)



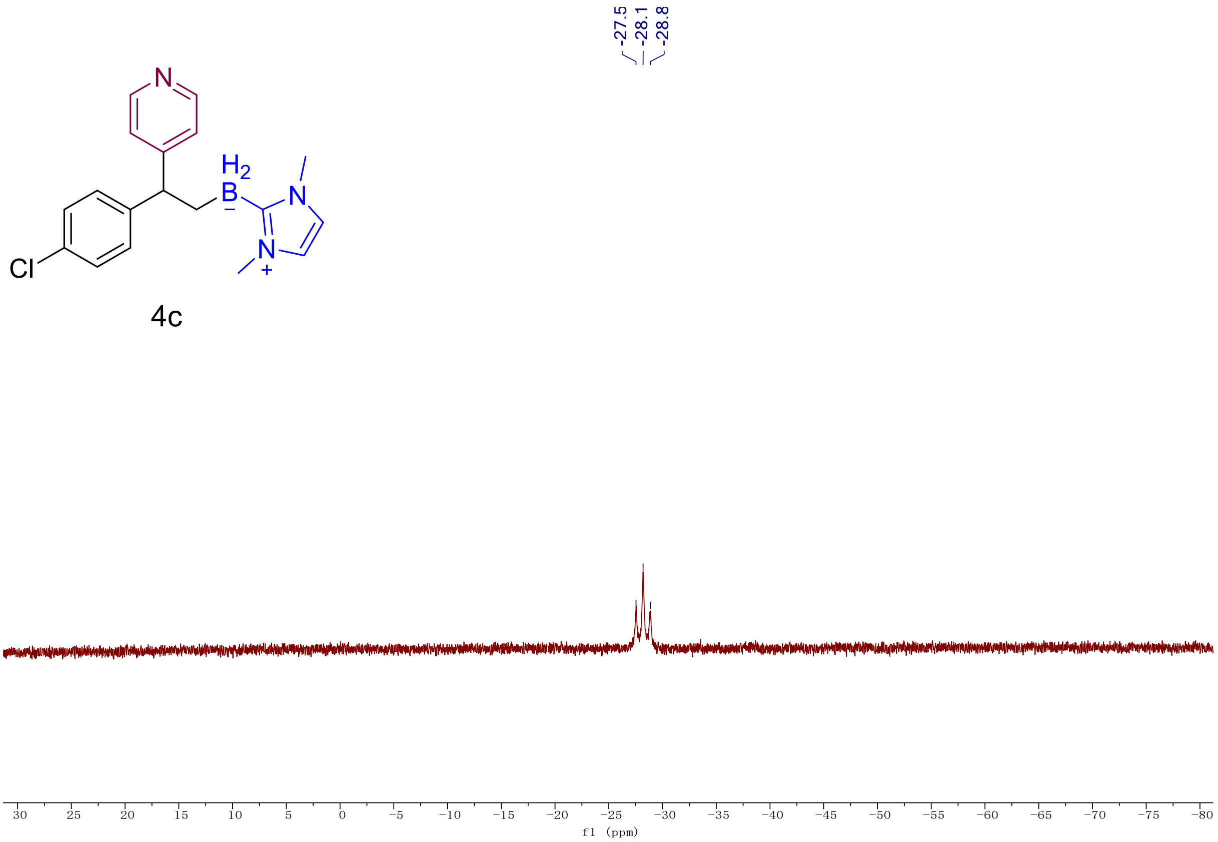
^{1}**H NMR** spectra of compound **4c** (400 MHz, CDCl$_3$)



^{13}C NMR spectra of compound **4c** (101 MHz, $CDCl_3$)

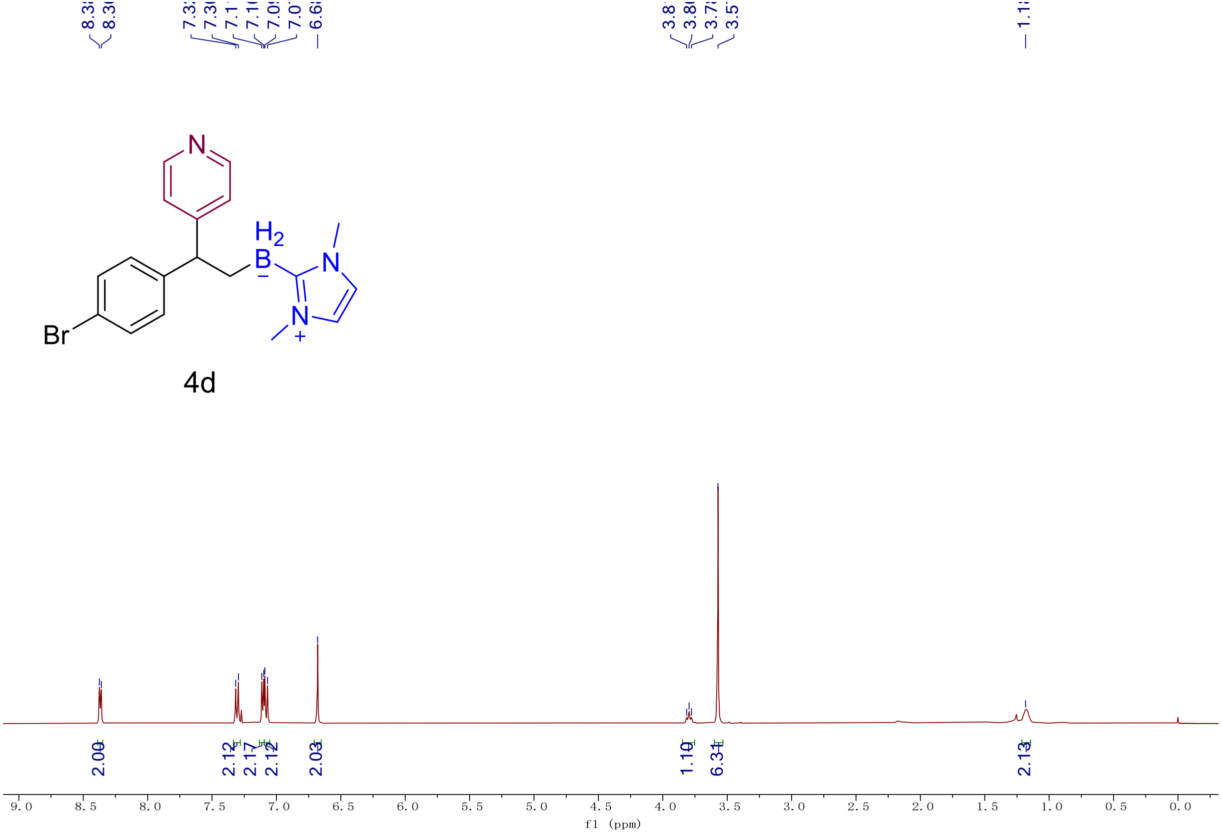


^{11}B NMR spectra of compound **4c** (128 MHz, $CDCl_3$)



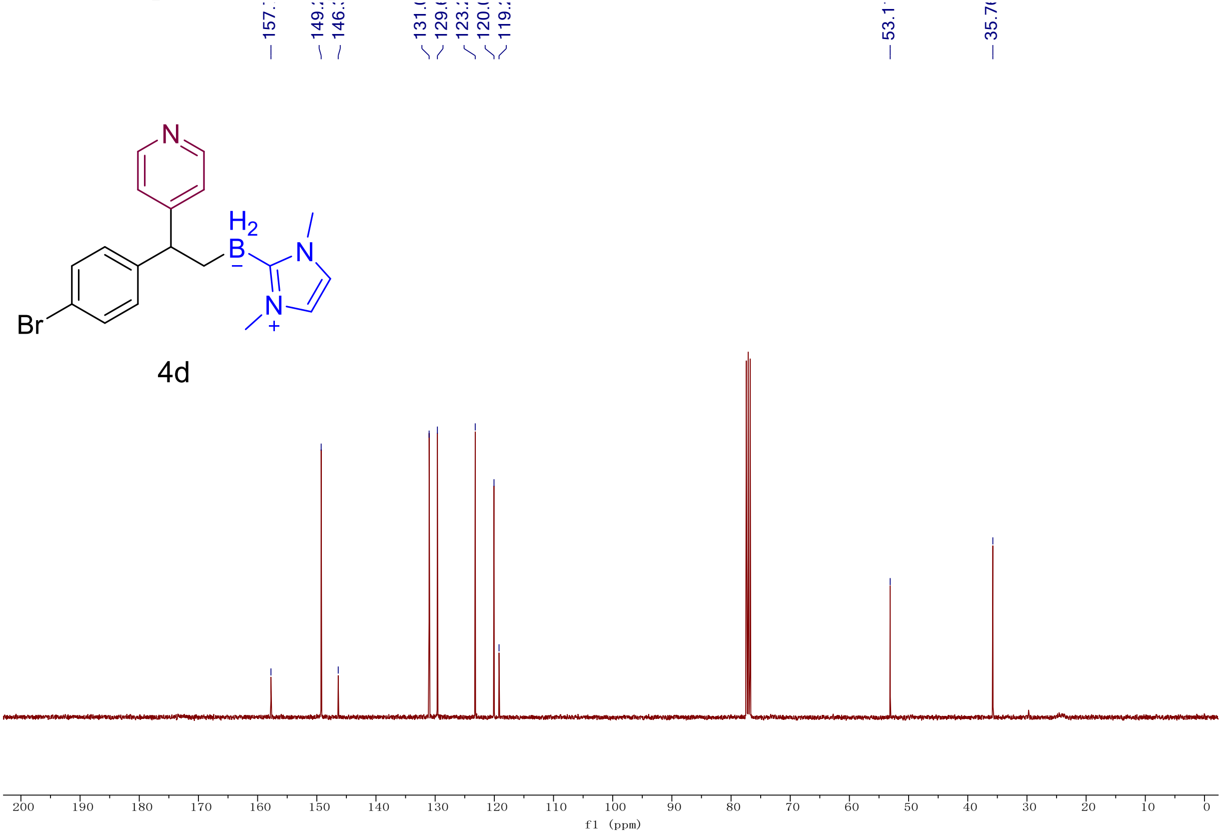
4c

^{1}H NMR spectra of compound 4d (400 MHz, $CDCl_3$)

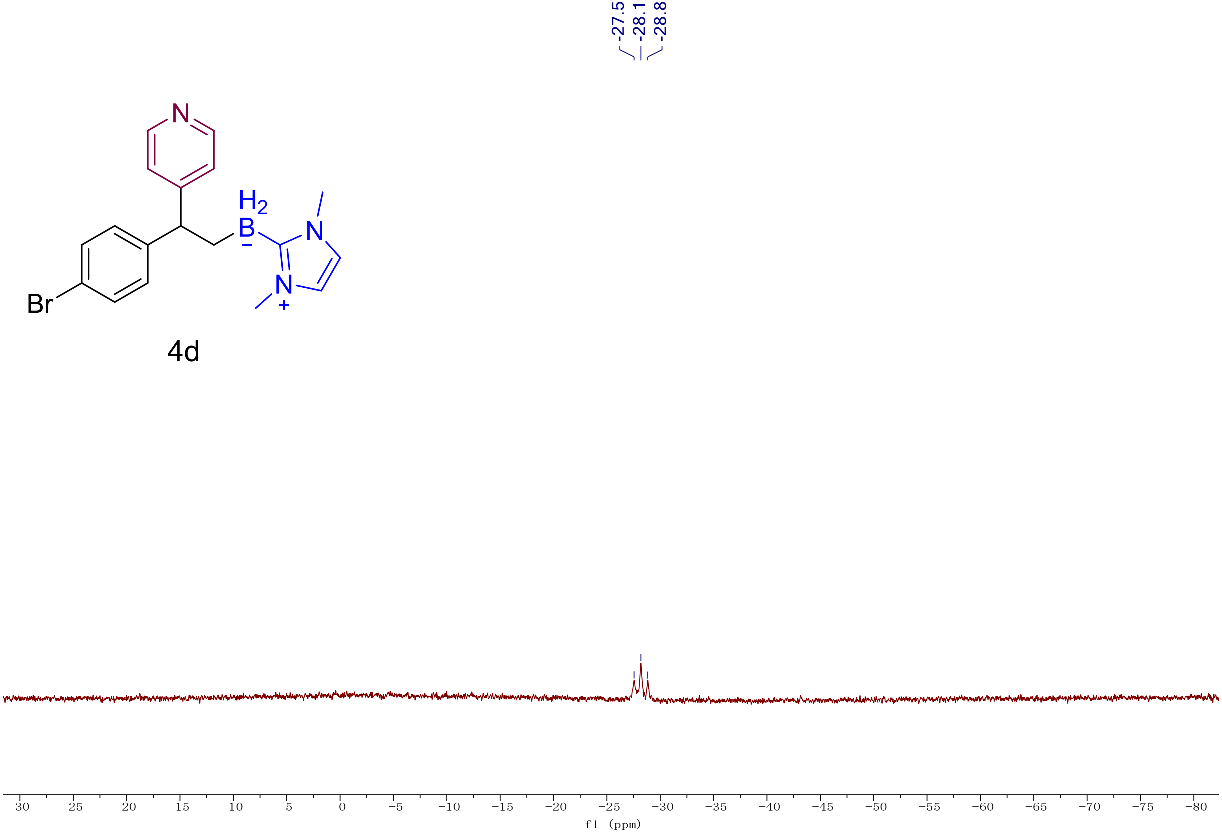


4d

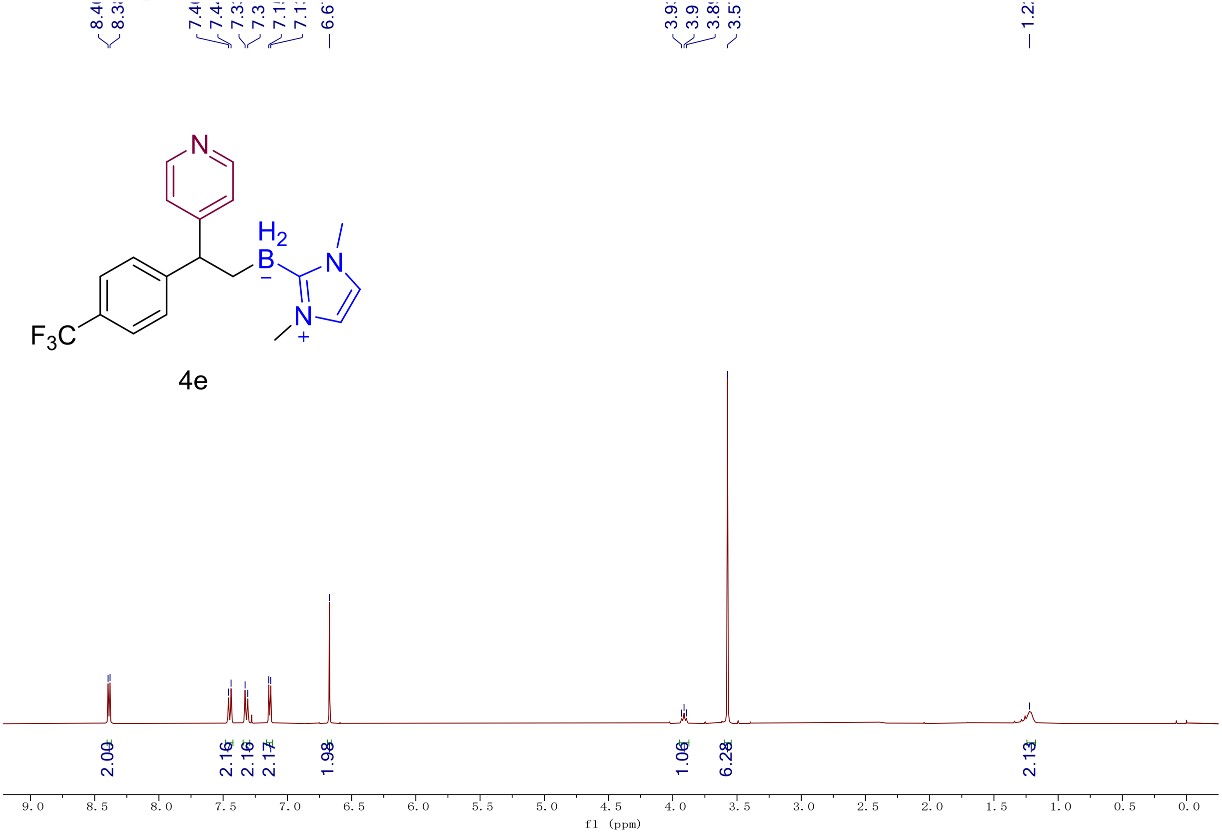
^{13}C **NMR** spectra of compound **4d** (101 MHz, CDCl$_3$)



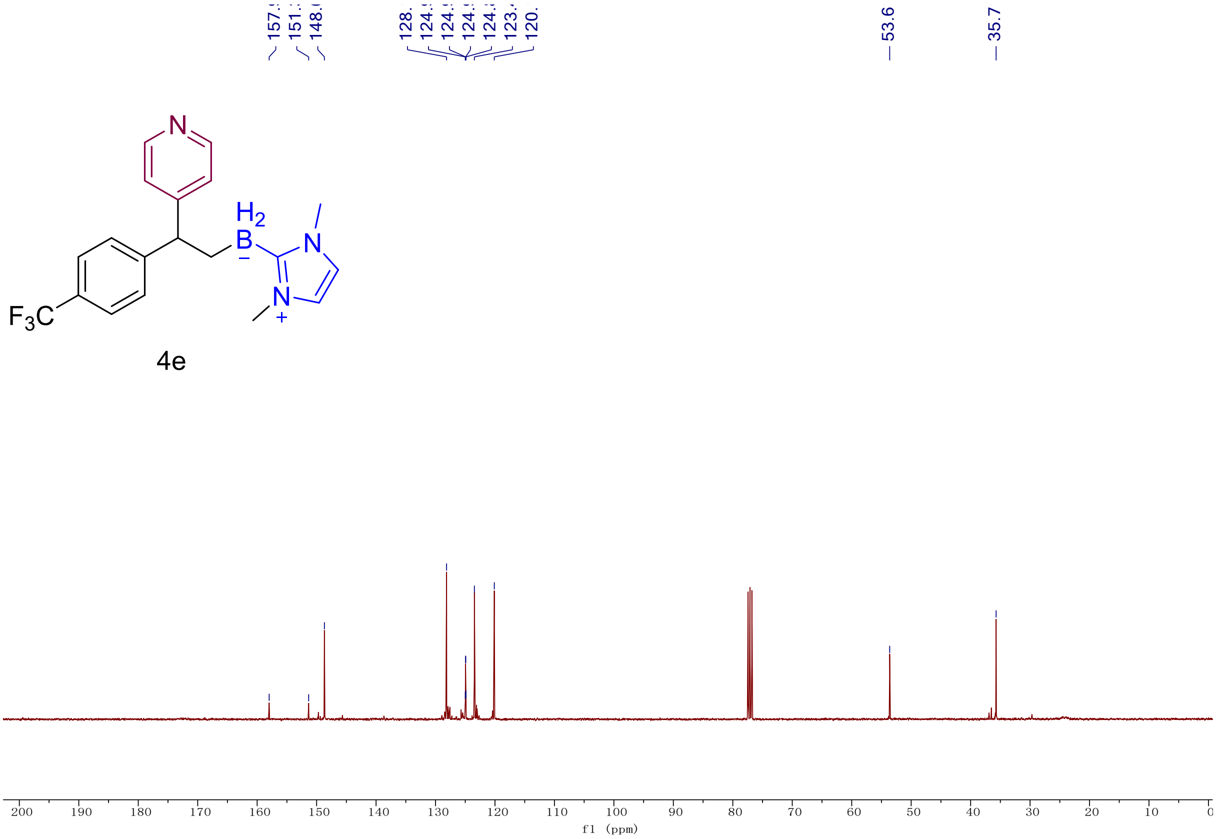
^{11}B **NMR** spectra of compound **4d** (128 MHz, CDCl$_3$)



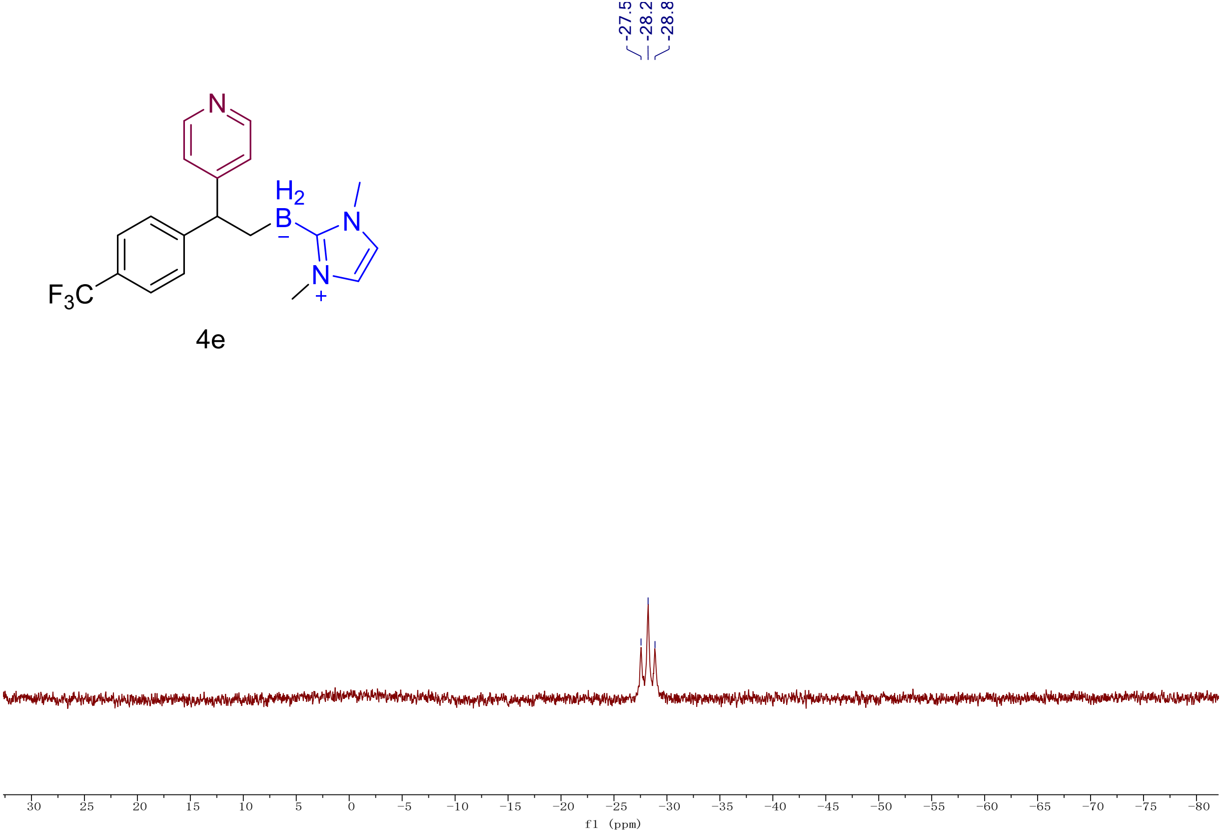
^{1}**H NMR** spectra of compound **4e** (400 MHz, $CDCl_3$)



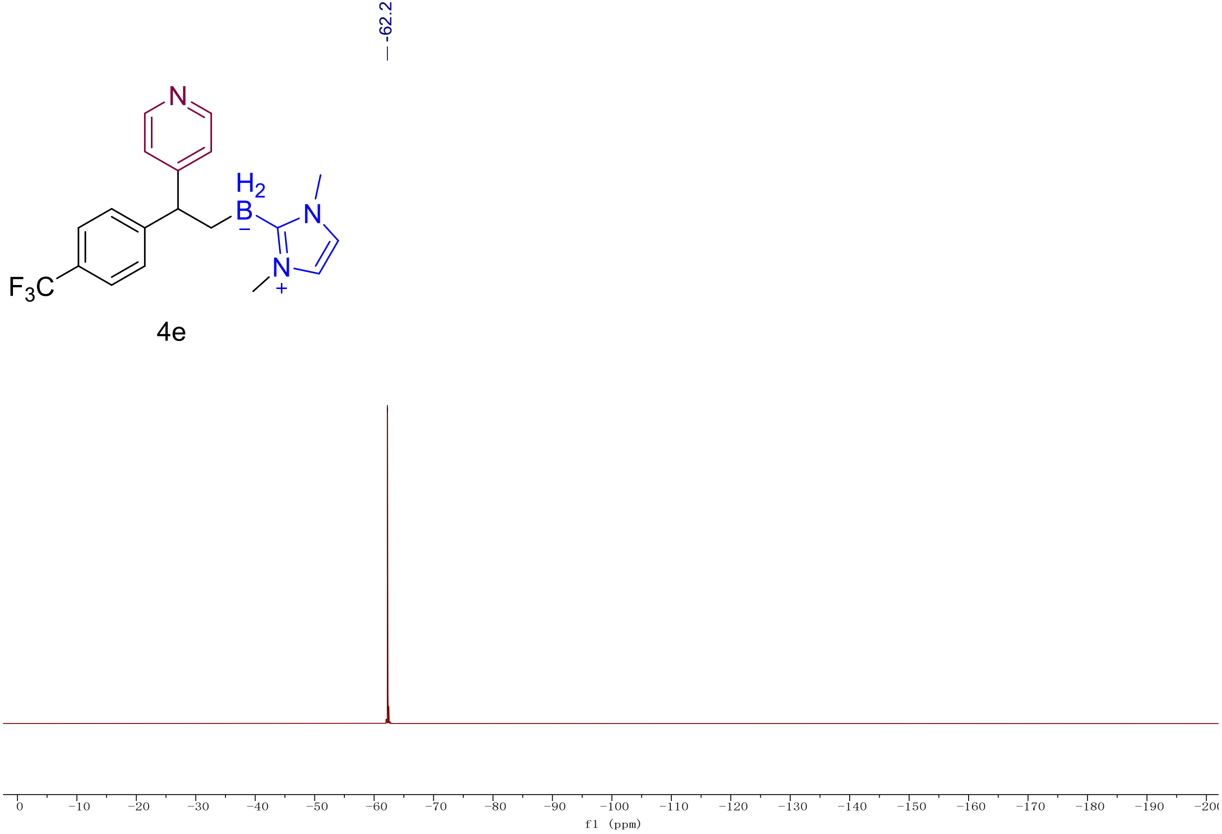
^{13}**C NMR** spectra of compound **4e** (101 MHz, $CDCl_3$)



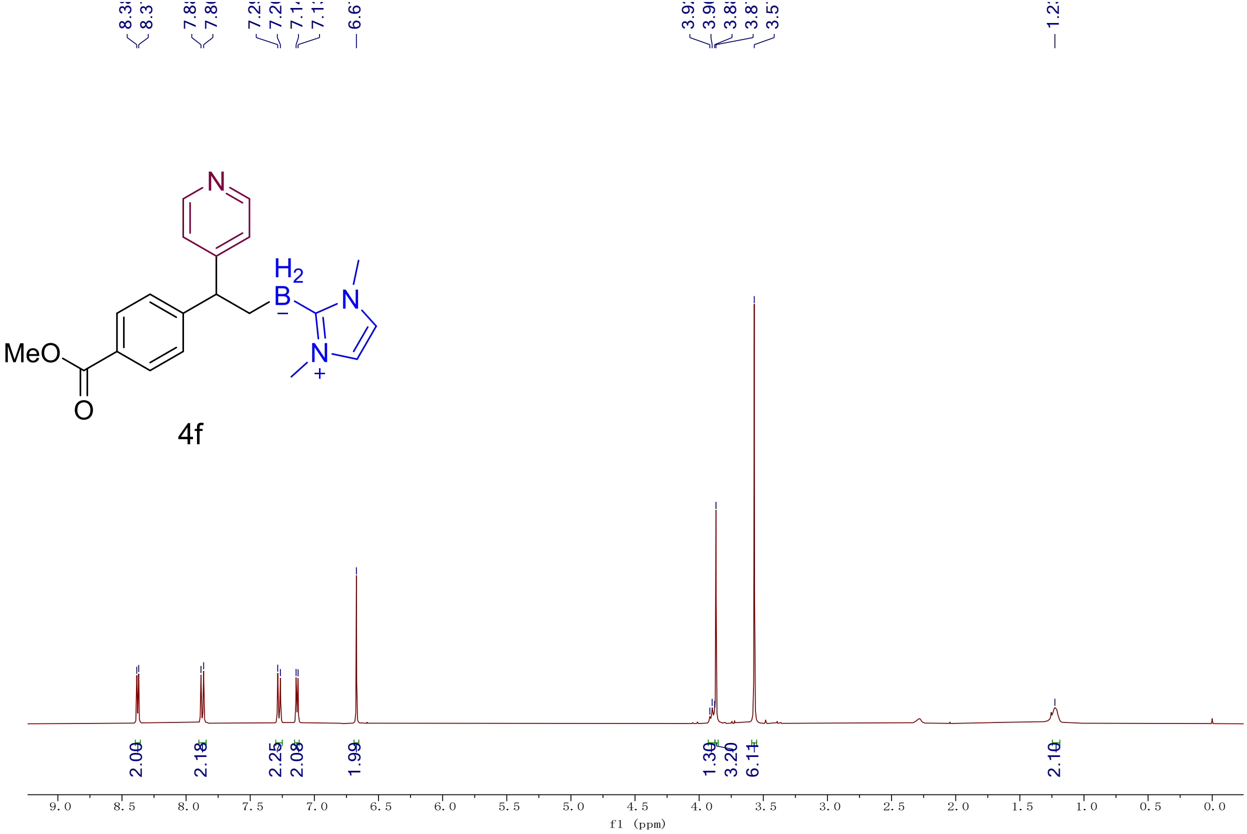
^{11}**B NMR** spectra of compound **4e** (128 MHz, $CDCl_3$)



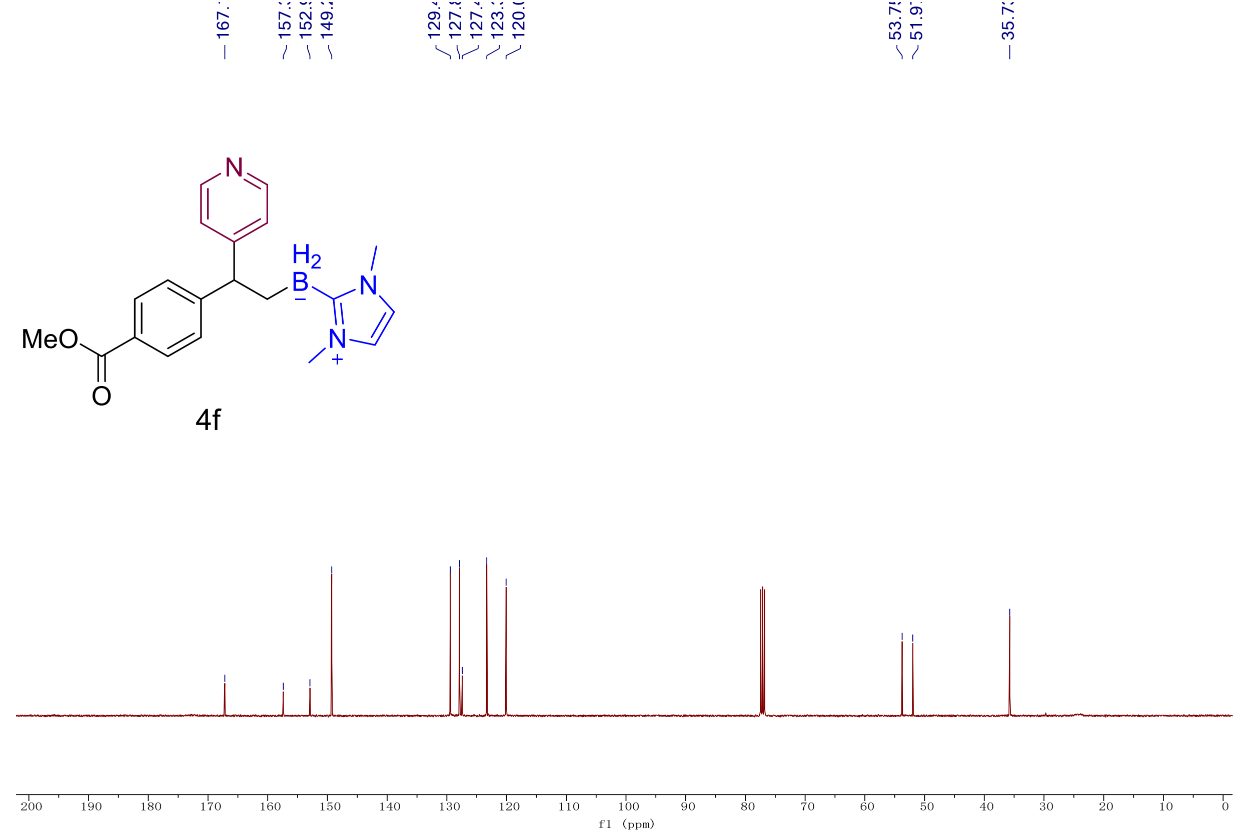
^{19}**F NMR** spectra of compound **4e** (376 MHz, $CDCl_3$)



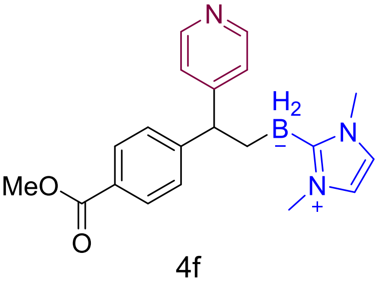
^{1}H NMR spectra of compound **4f** (400 MHz, $CDCl_3$)



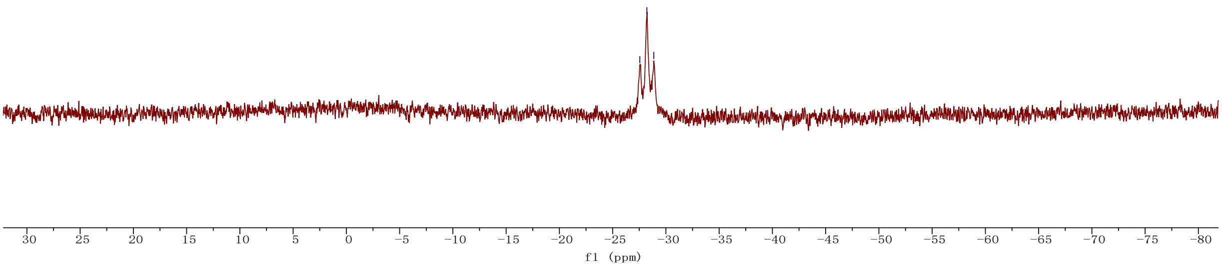
^{13}C NMR spectra of compound **4f** (101 MHz, $CDCl_3$)



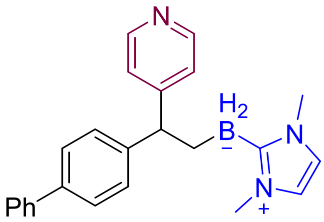
^{11}B NMR spectra of compound **4f** (128 MHz, $CDCl_3$)



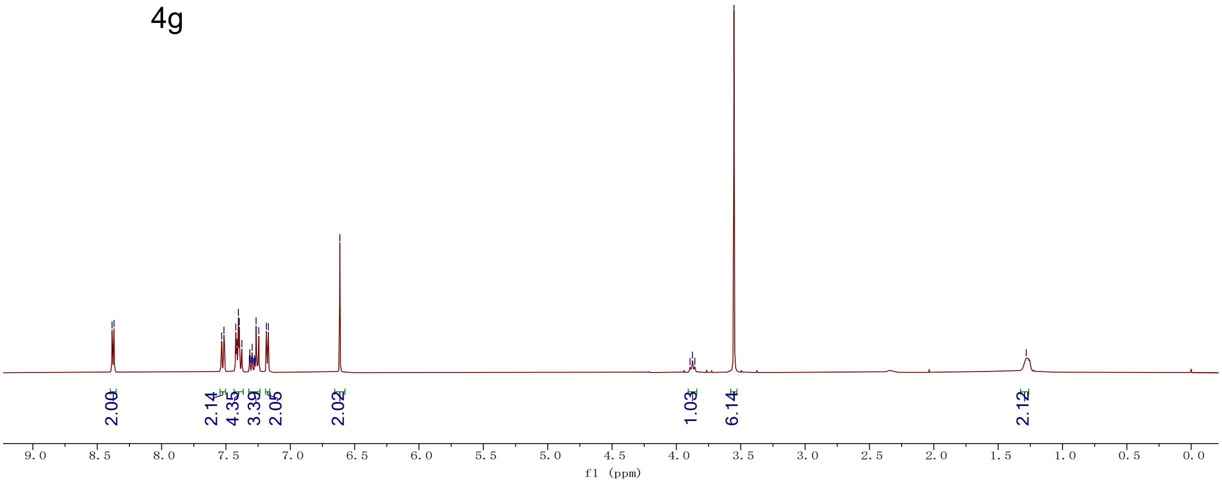
4f



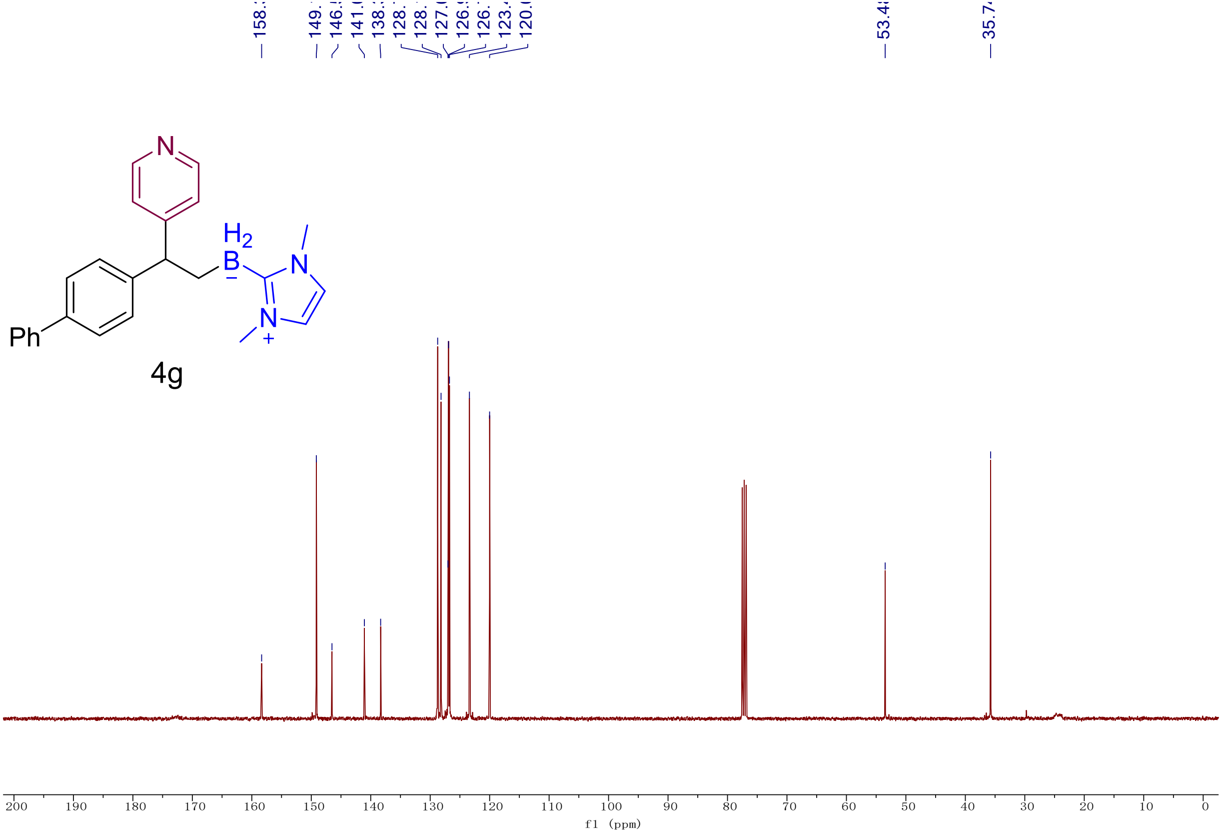
^{1}H NMR spectra of compound **4g** (400 MHz, $CDCl_3$)



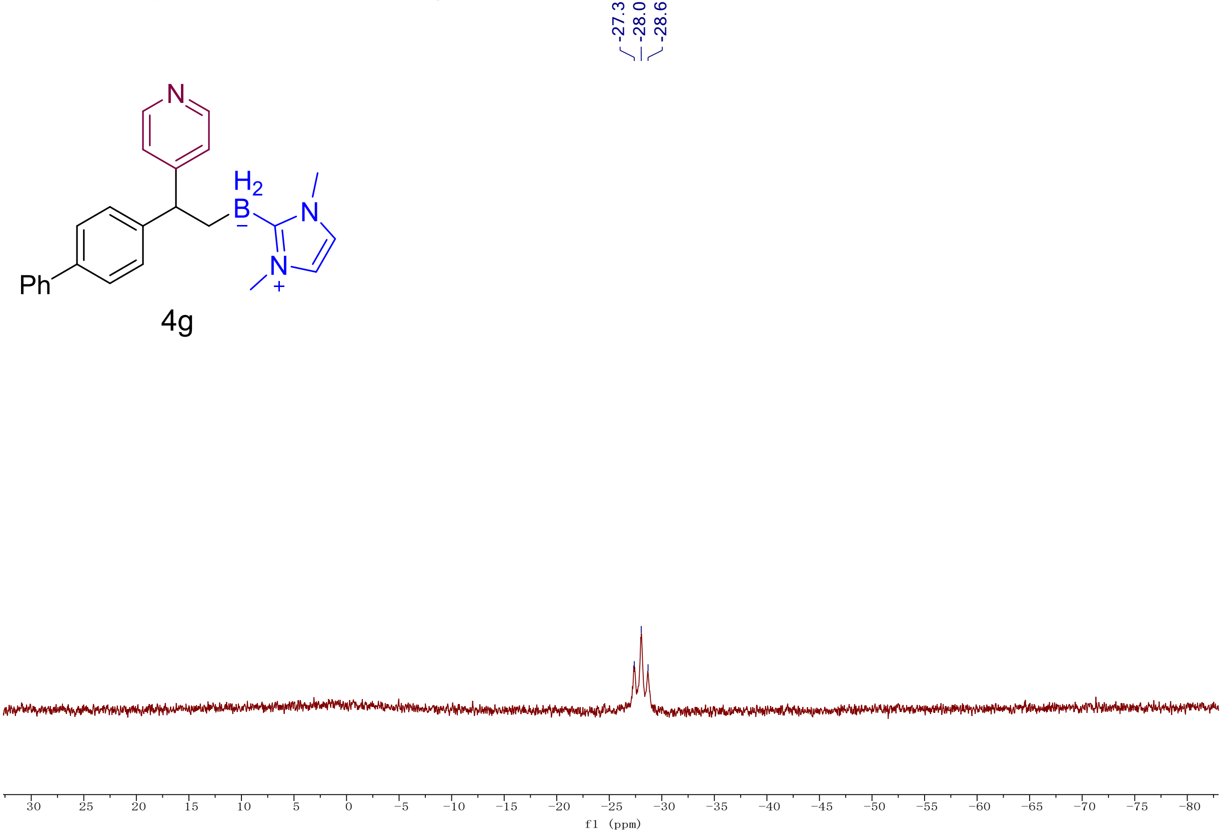
4g



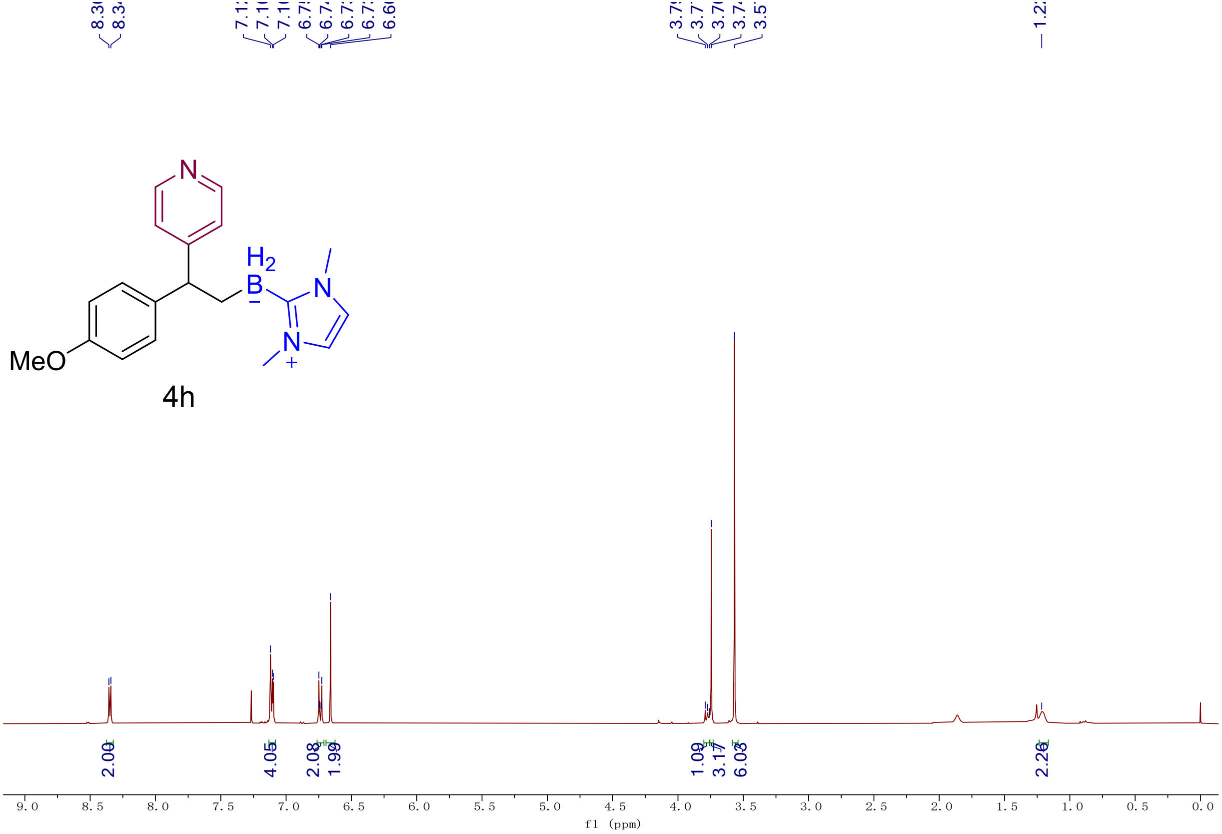
^{13}C NMR spectra of compound **4g** (101 MHz, $CDCl_3$)



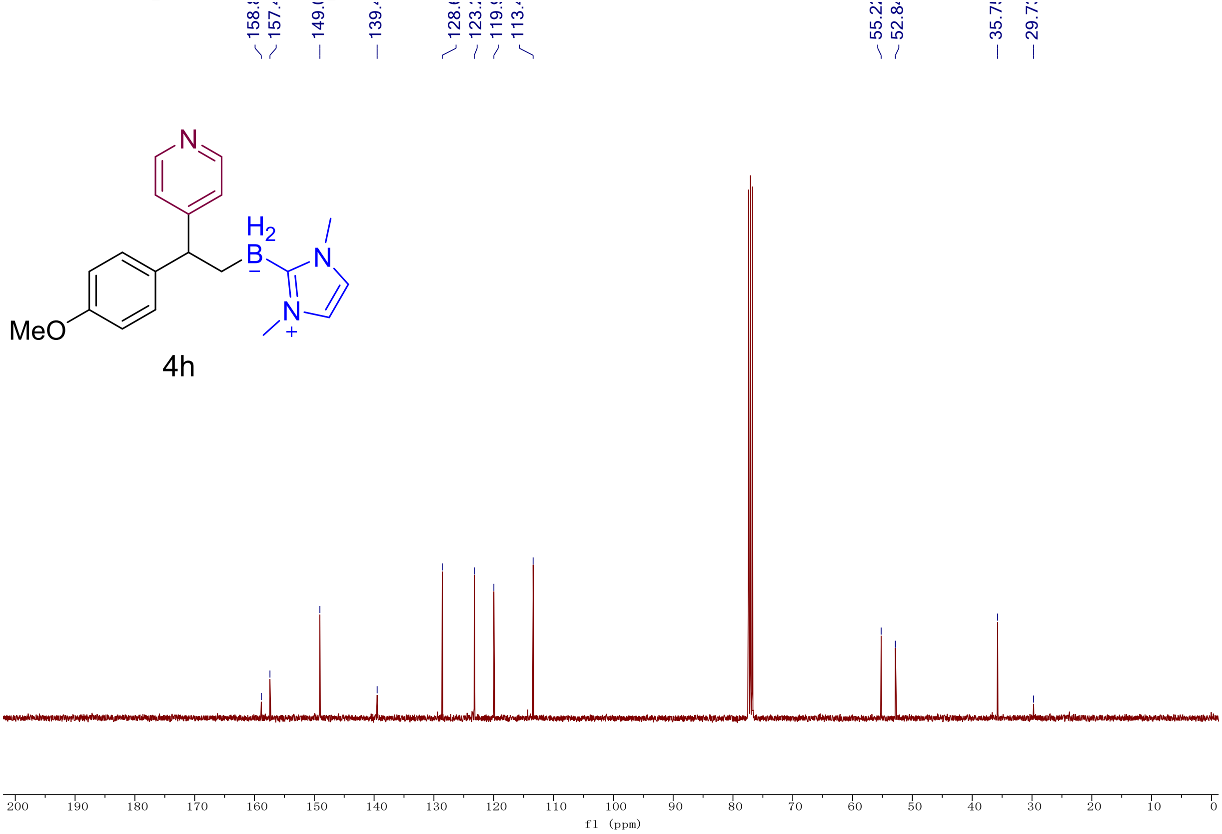
^{11}B NMR spectra of compound **4g** (128 MHz, $CDCl_3$)



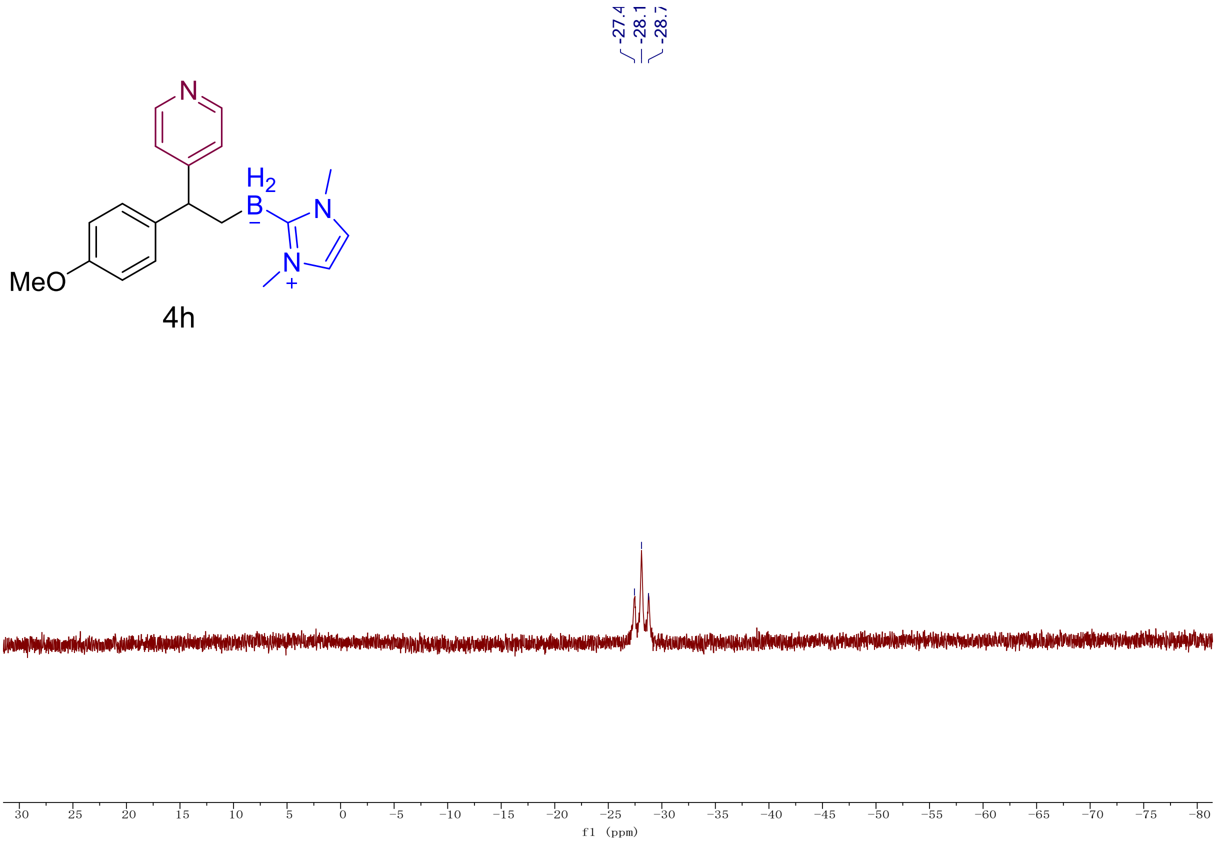
^{1}H NMR spectra of compound **4h** (400 MHz, CDCl$_3$)



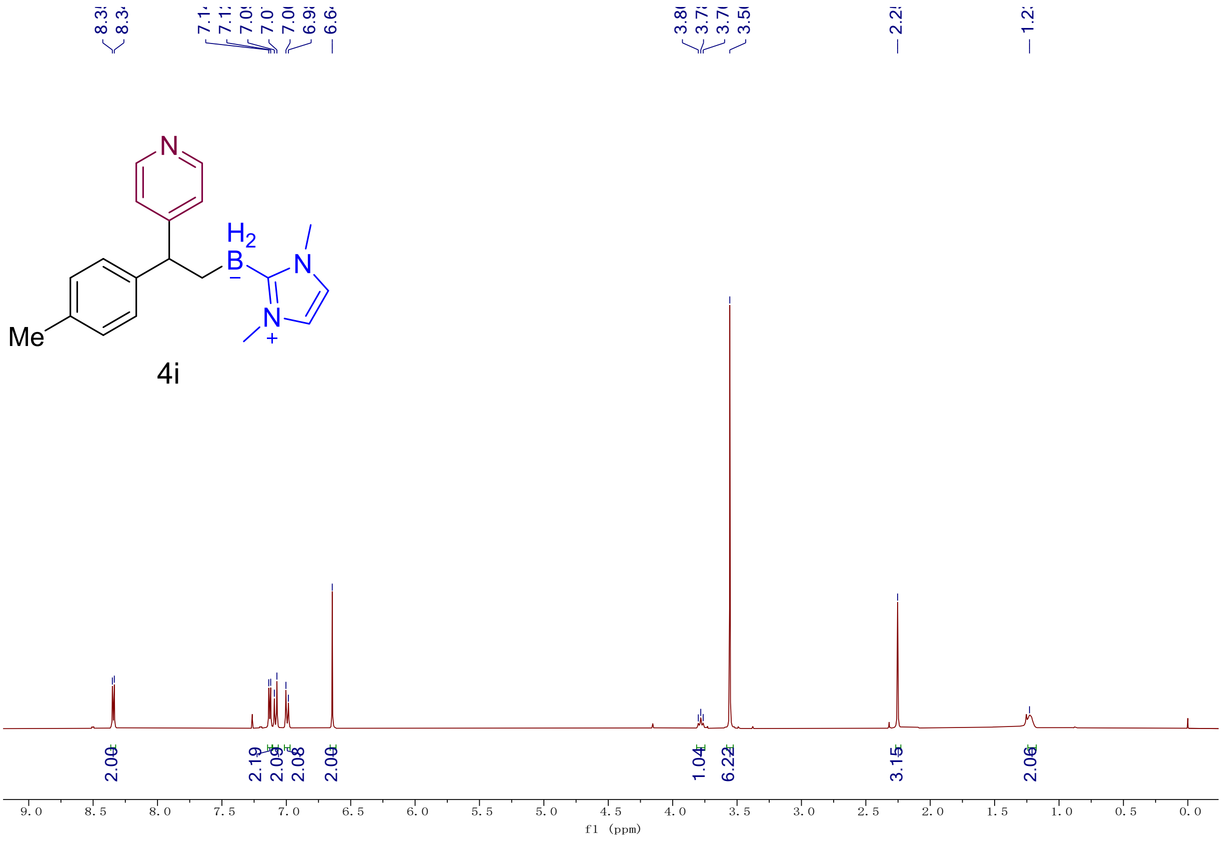
^{13}C NMR spectra of compound **4h** (101 MHz, CDCl$_3$)



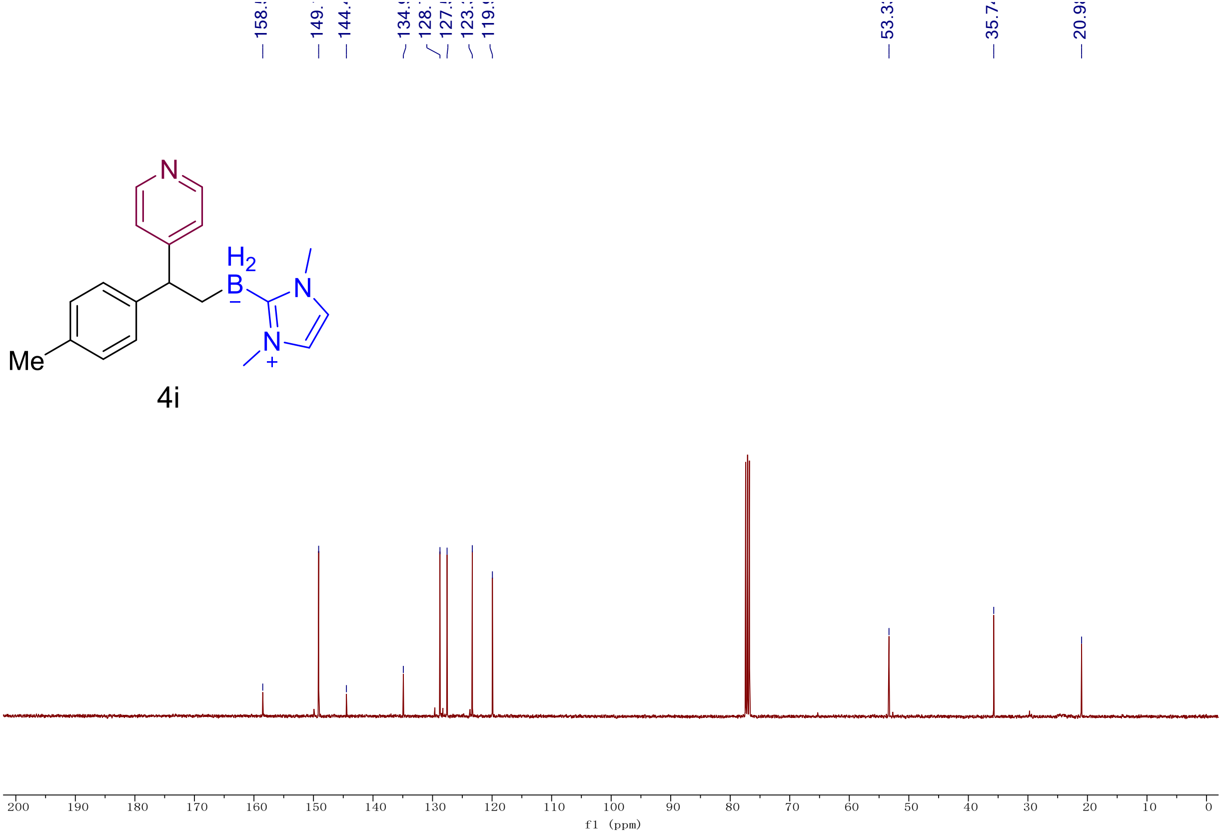
^{11}B NMR spectra of compound **4h** (128 MHz, $CDCl_3$)



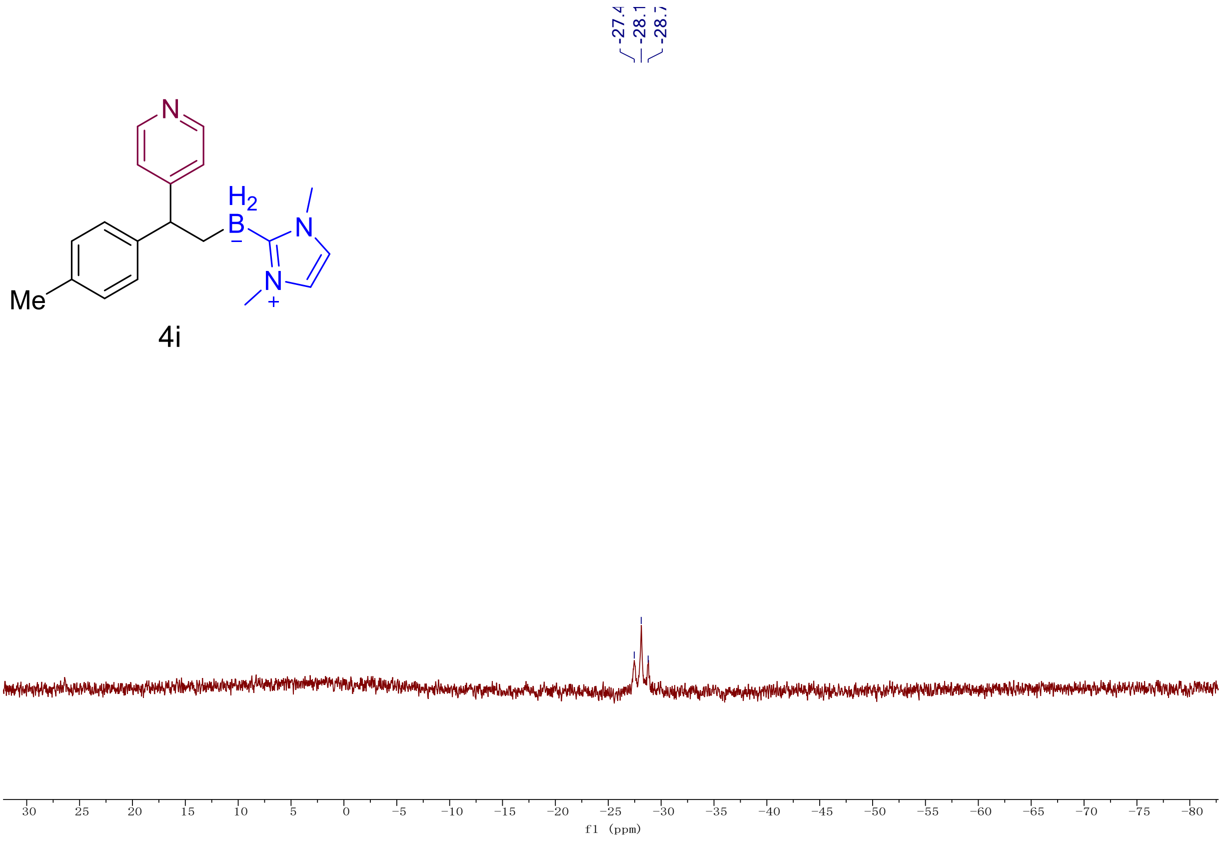
^{1}H NMR spectra of compound **4i** (400 MHz, $CDCl_3$)



^{13}C NMR spectra of compound **4i** (101 MHz, $CDCl_3$)

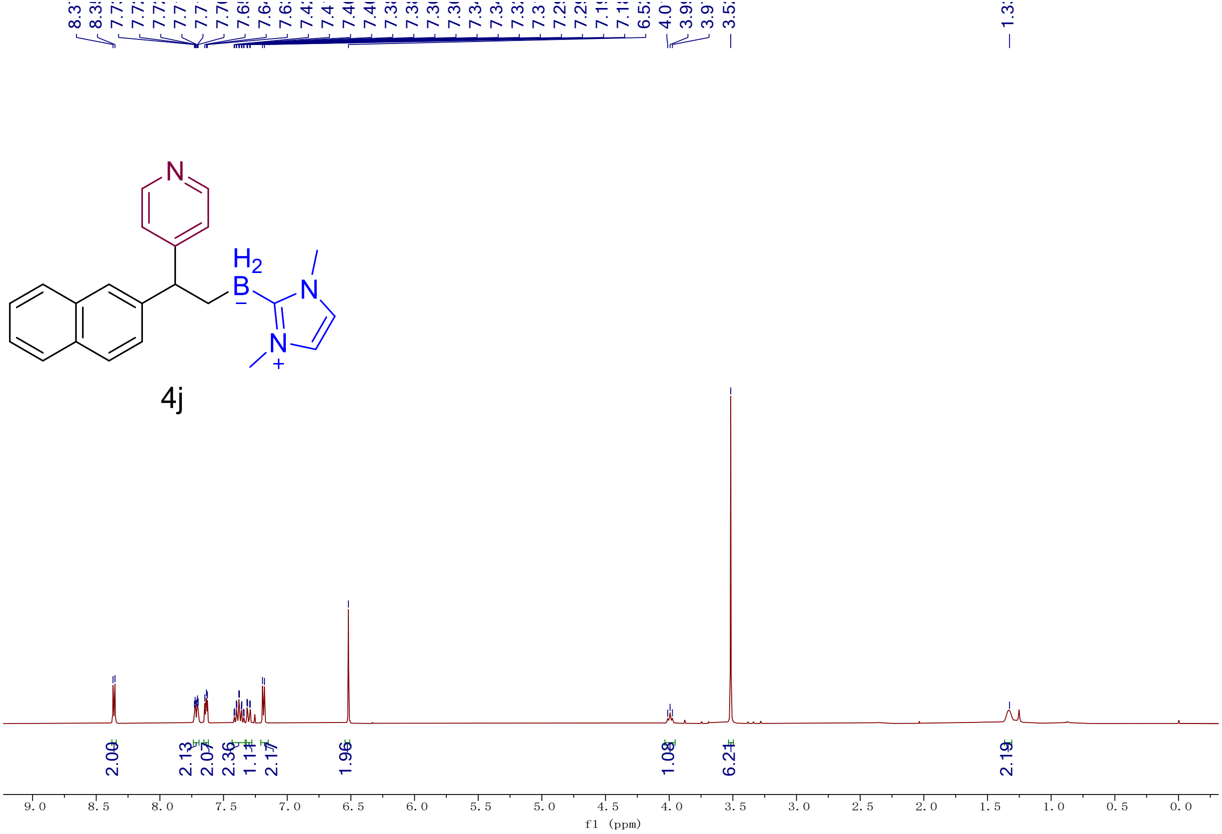


^{11}B NMR spectra of compound **4i** (128 MHz, $CDCl_3$)



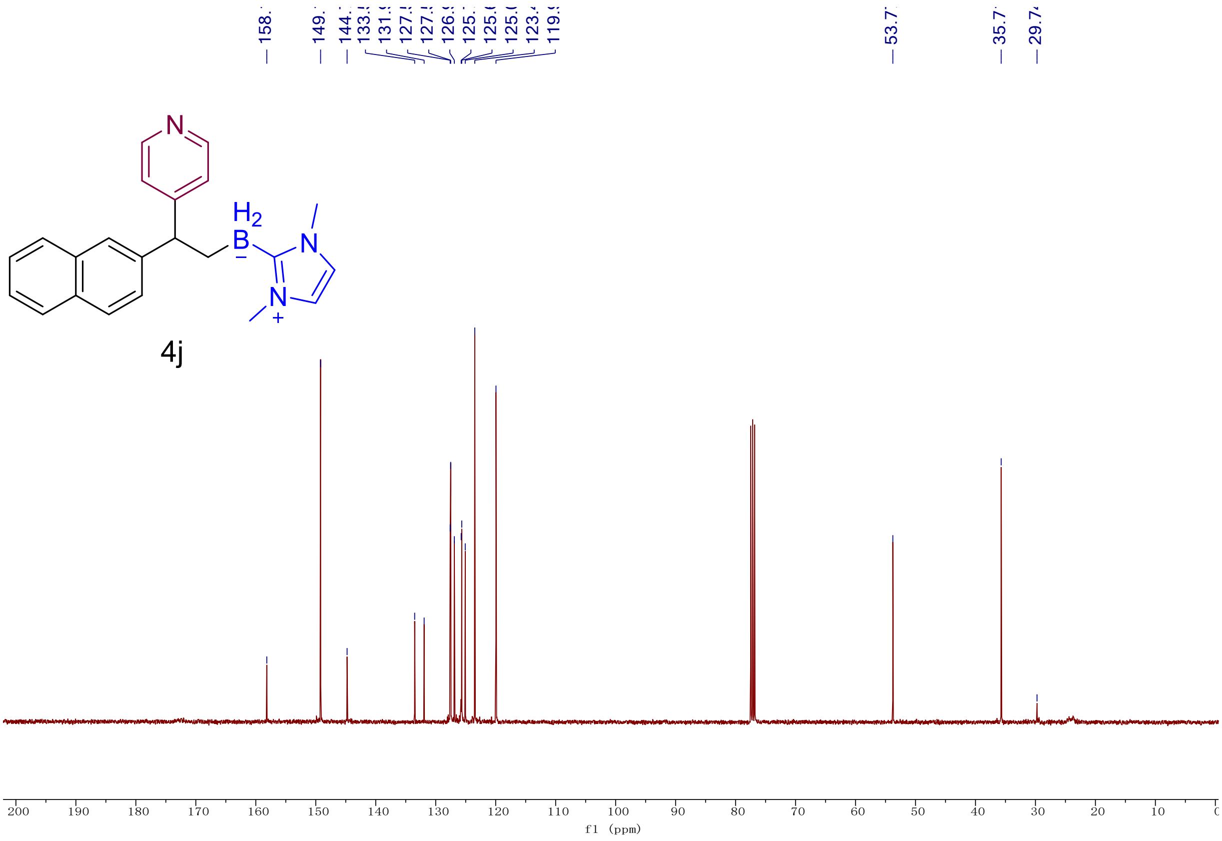
4i

^{1}H NMR spectra of compound **4j** (400 MHz, $CDCl_3$)

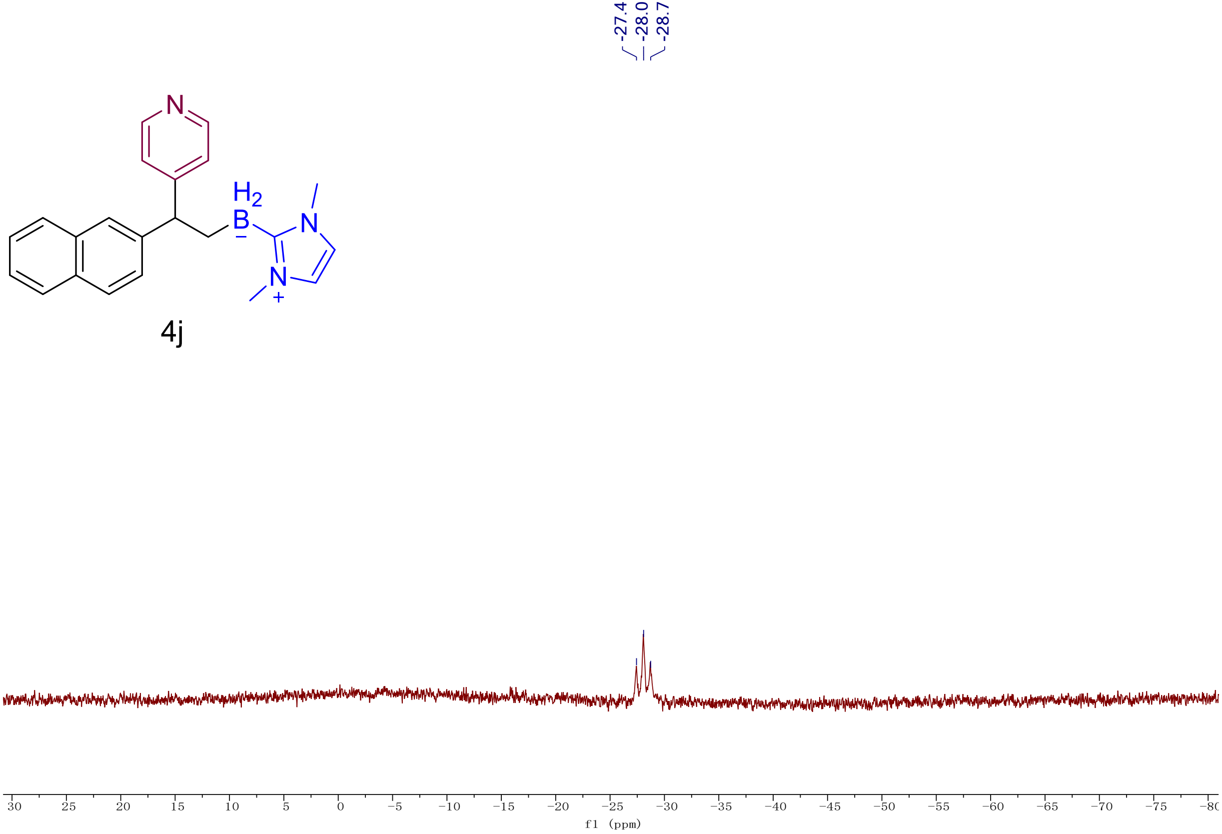


4j

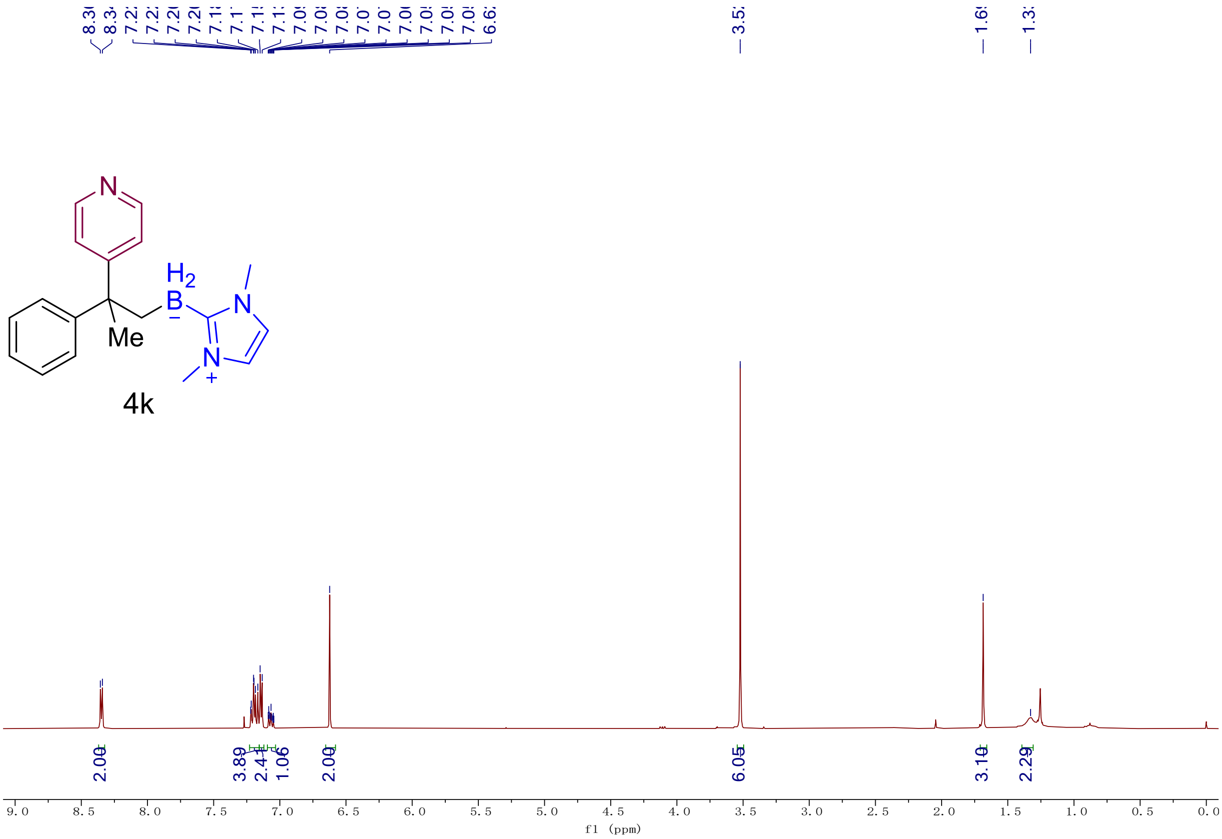
^{13}C NMR spectra of compound **4j** (101 MHz, $CDCl_3$)



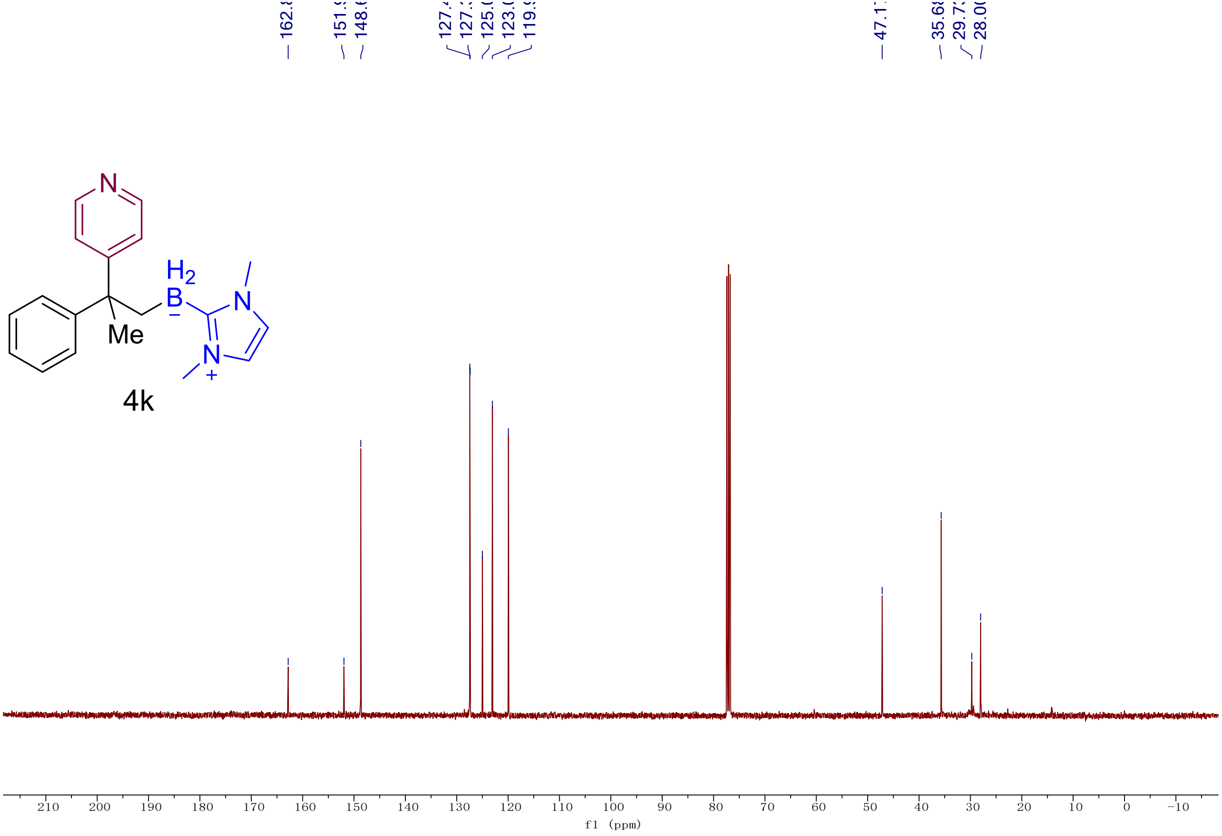
^{11}B NMR spectra of compound **4j** (128 MHz, CDCl$_3$)



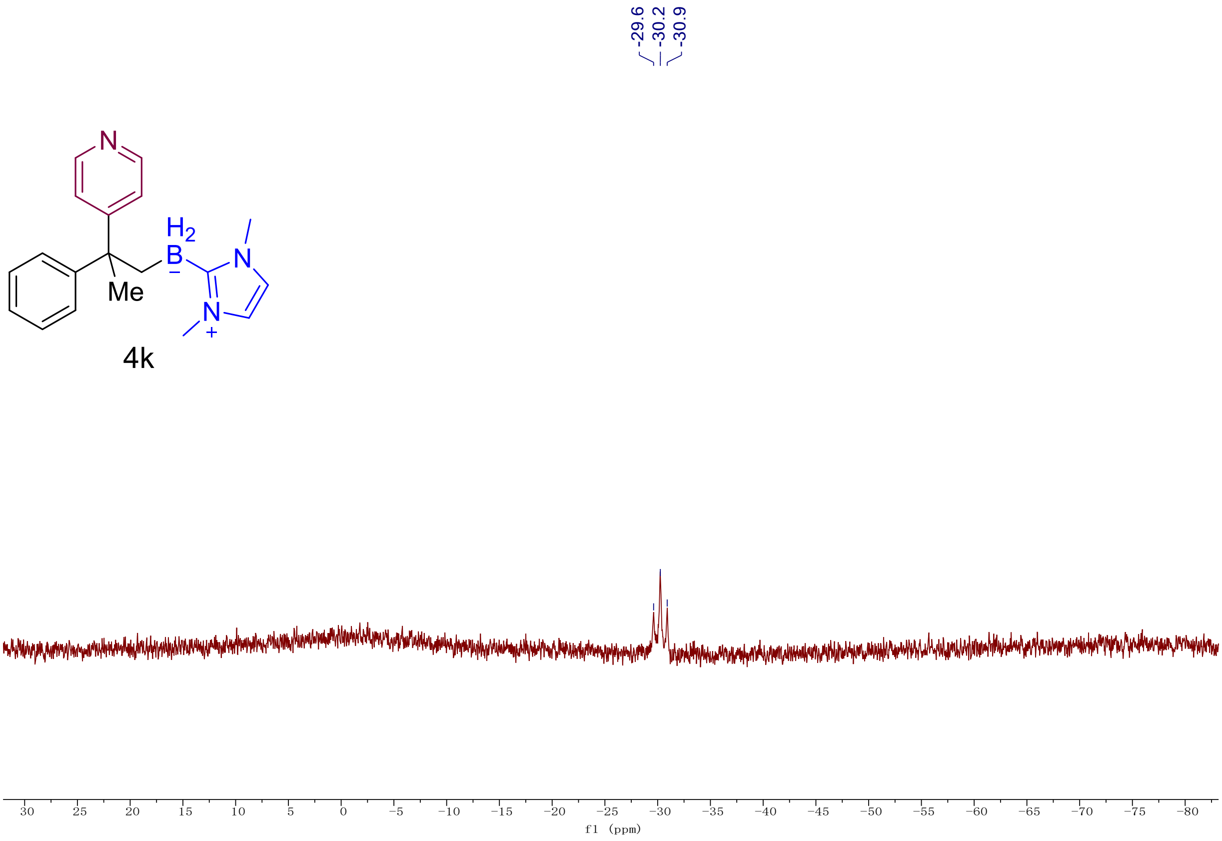
^{1}H NMR spectra of compound **4k** (400 MHz, CDCl$_3$)



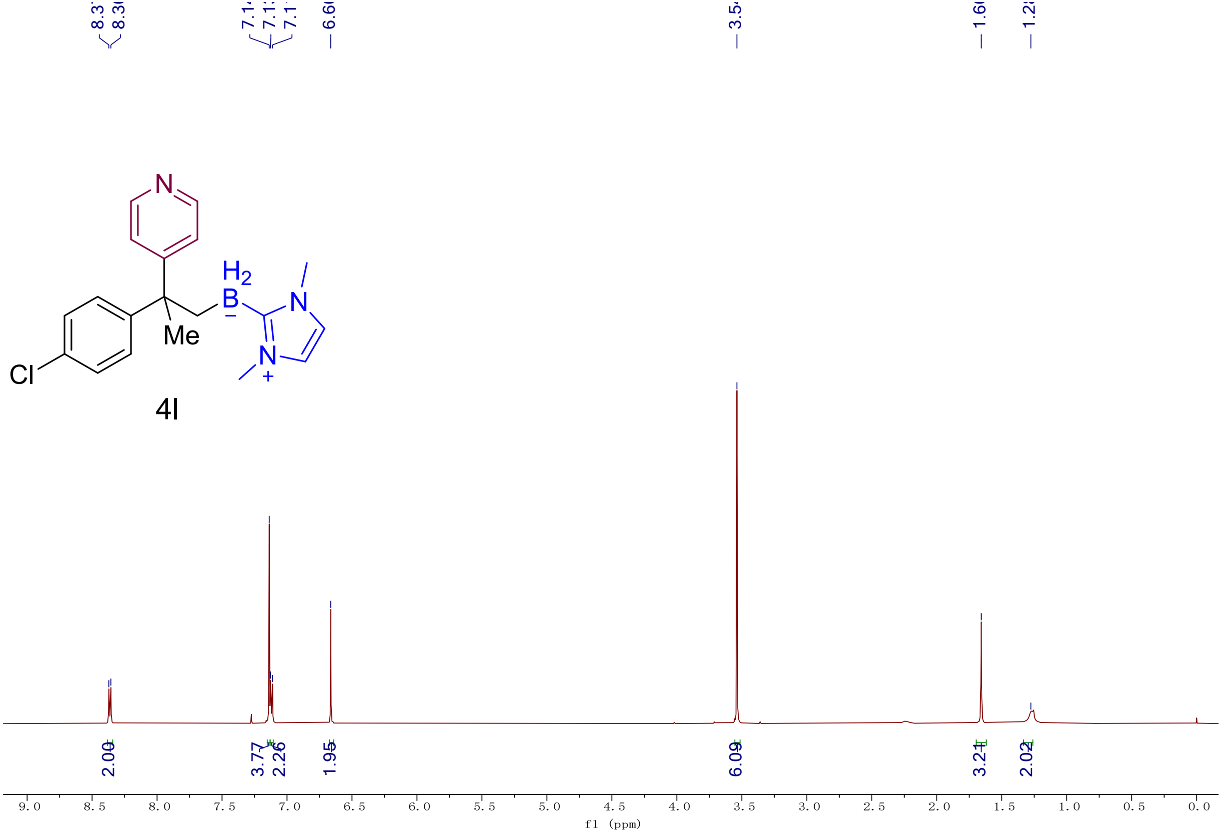
^{13}C NMR spectra of compound **4k** (101 MHz, $CDCl_3$)



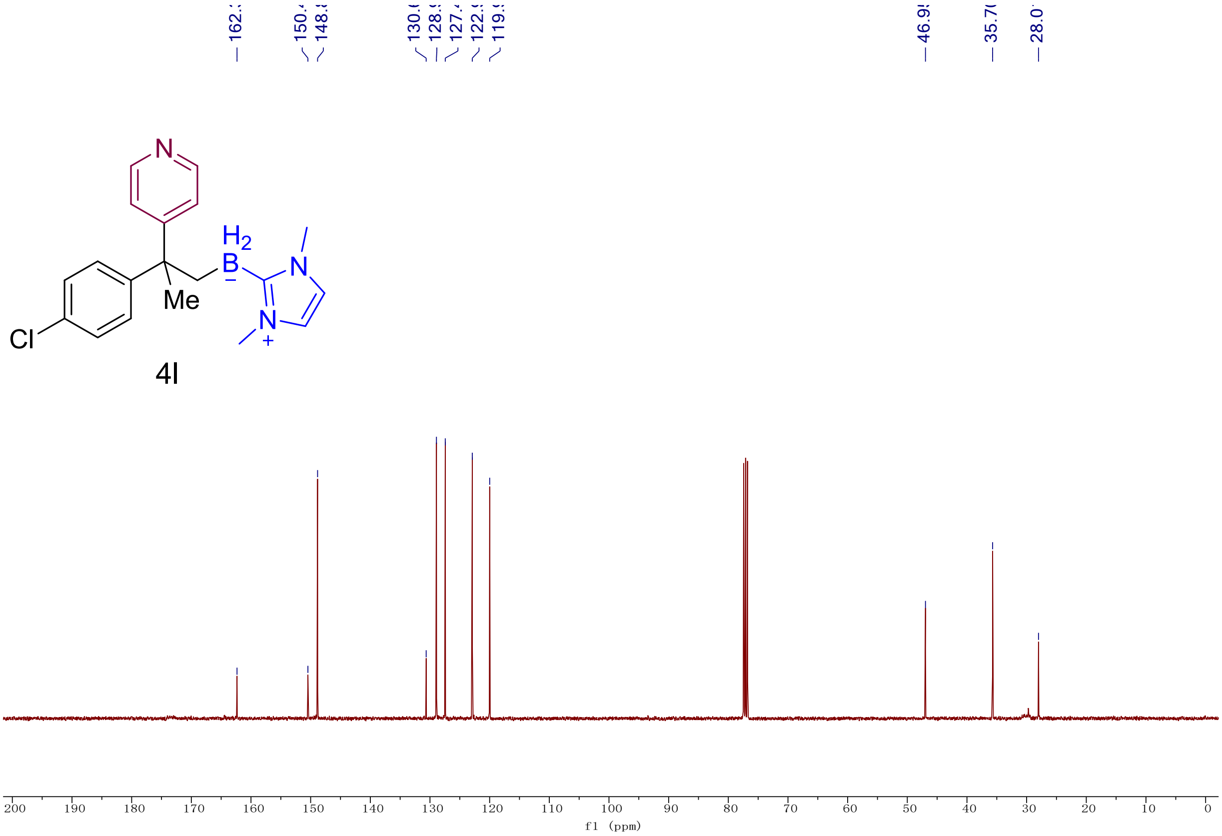
^{11}B NMR spectra of compound **4k** (128 MHz, $CDCl_3$)



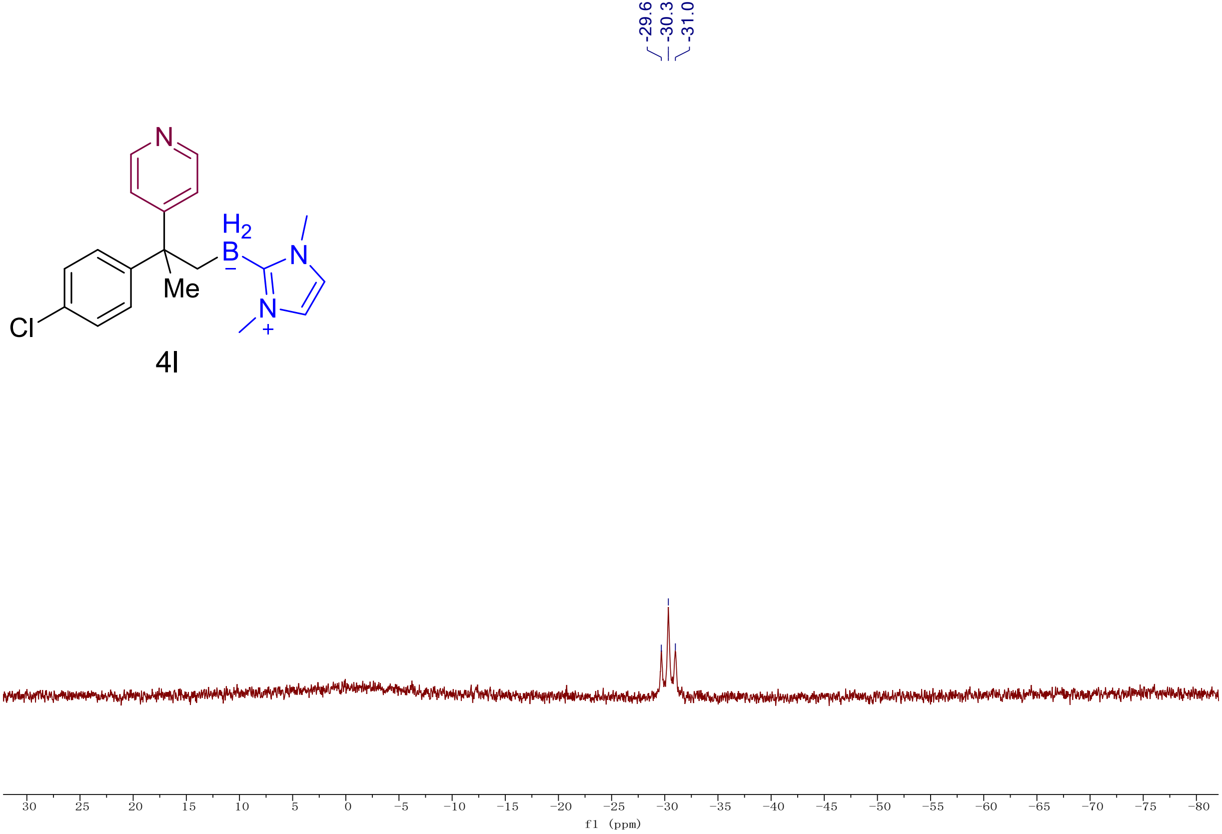
^{1}H NMR spectra of compound **4l** (400 MHz, $CDCl_3$)



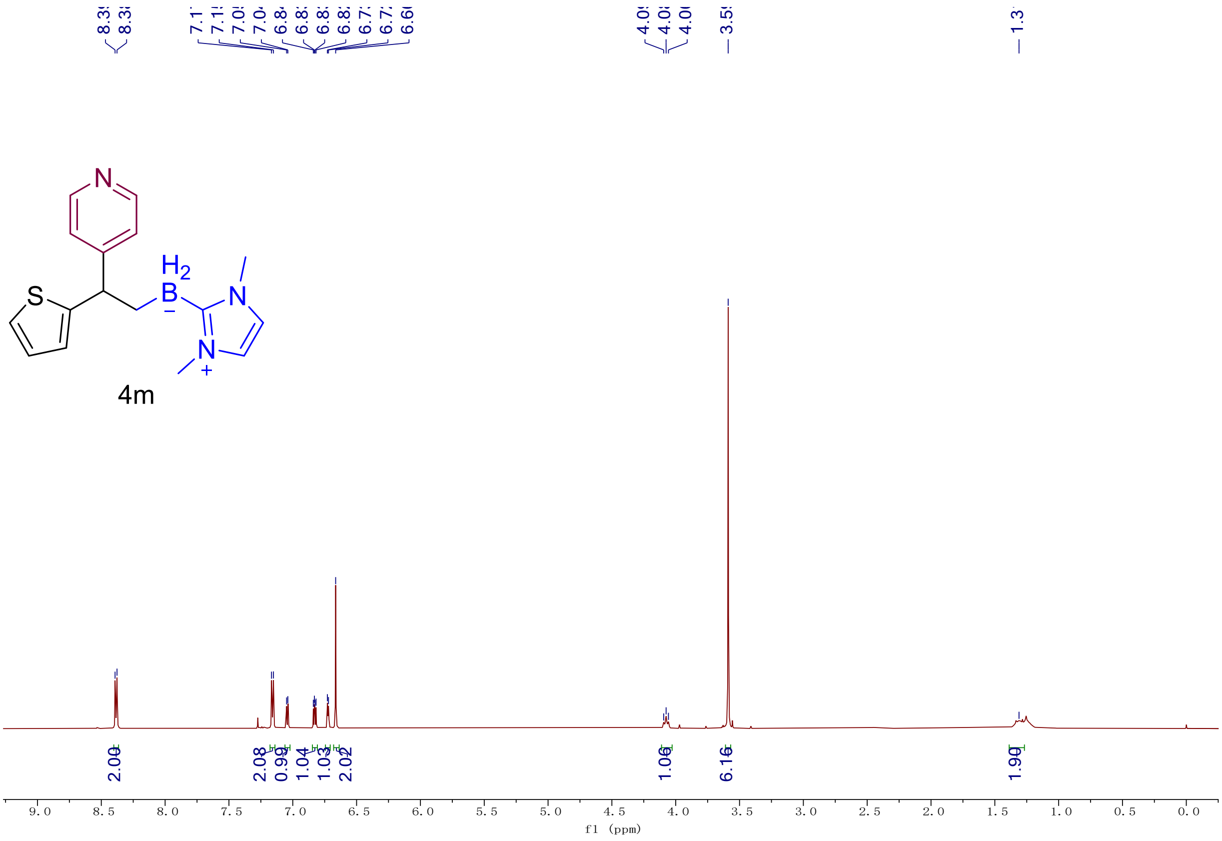
^{13}C NMR spectra of compound **4l** (101 MHz, $CDCl_3$)



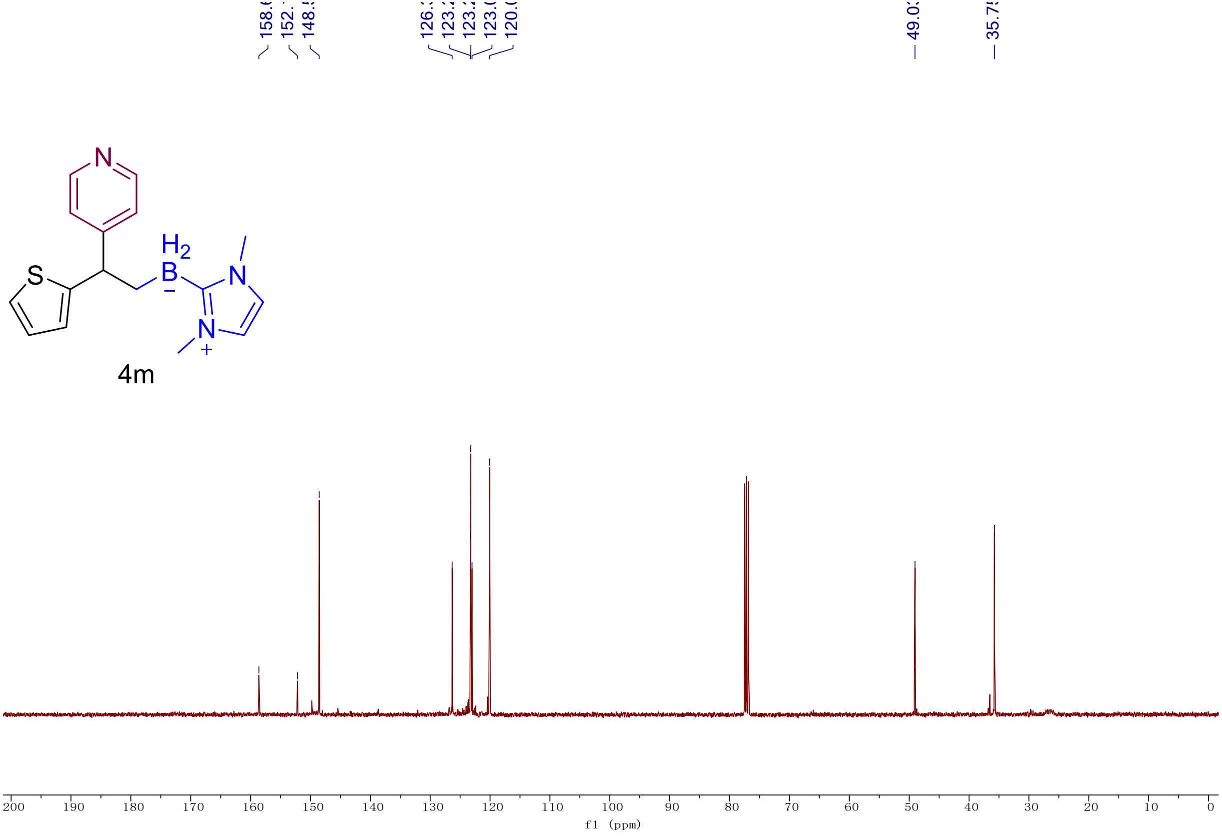
^{11}B NMR spectra of compound **4l** (128 MHz, $CDCl_3$)



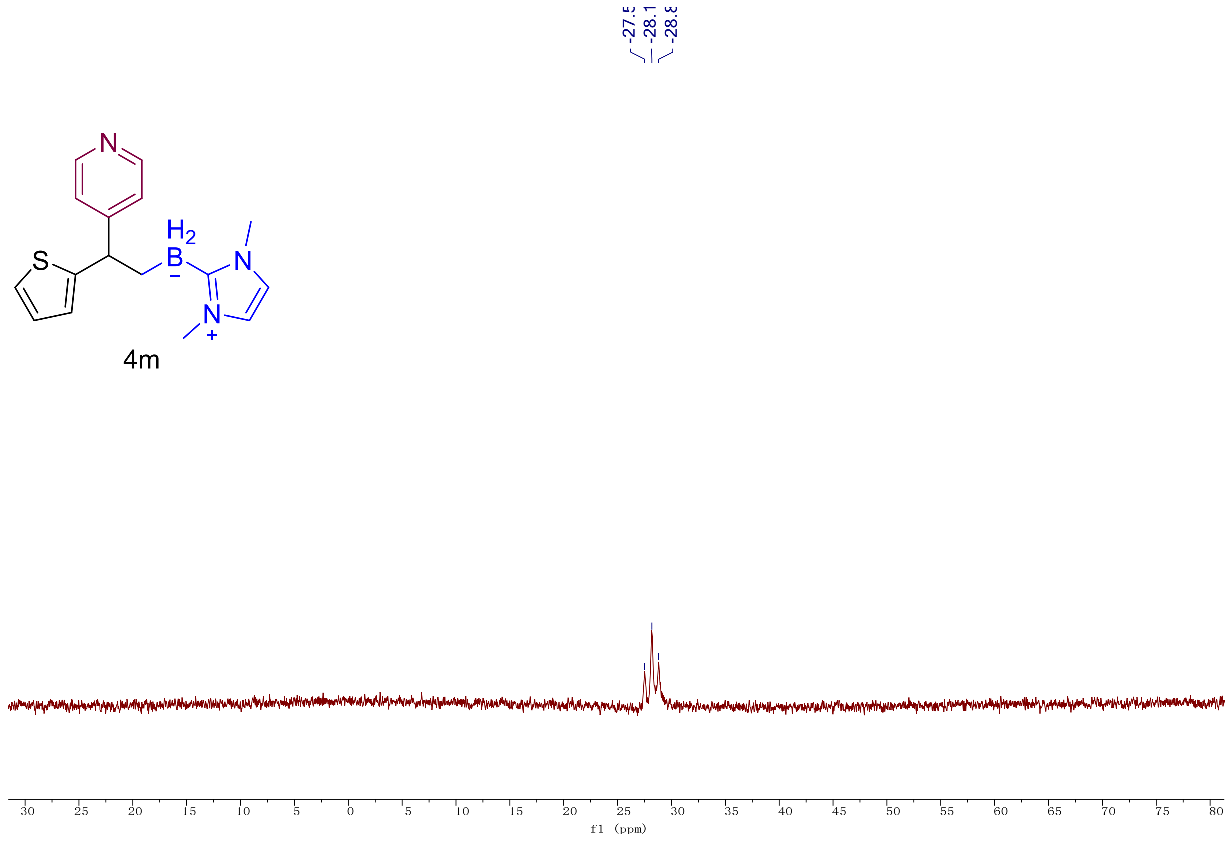
^{1}H NMR spectra of compound **4m** (400 MHz, $CDCl_3$)



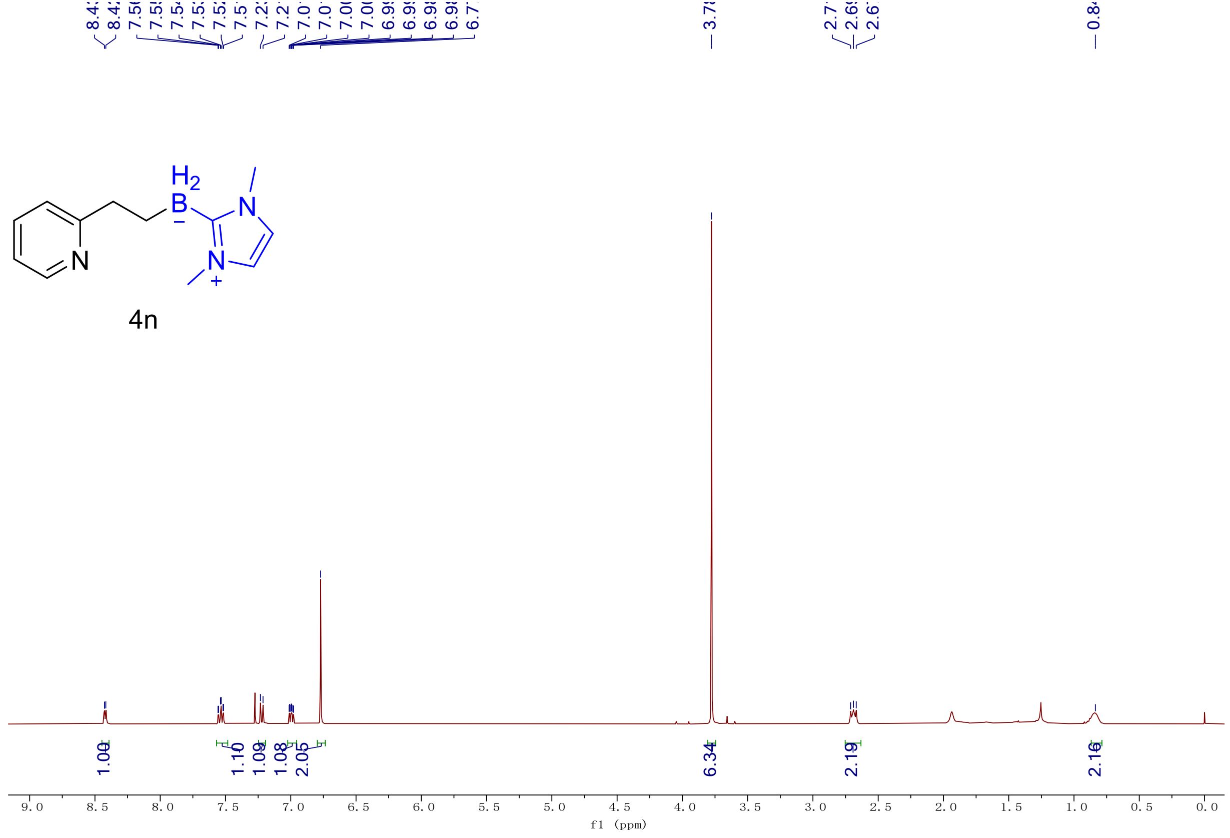
^{13}**C NMR** spectra of compound **4m** (101 MHz, $CDCl_3$)



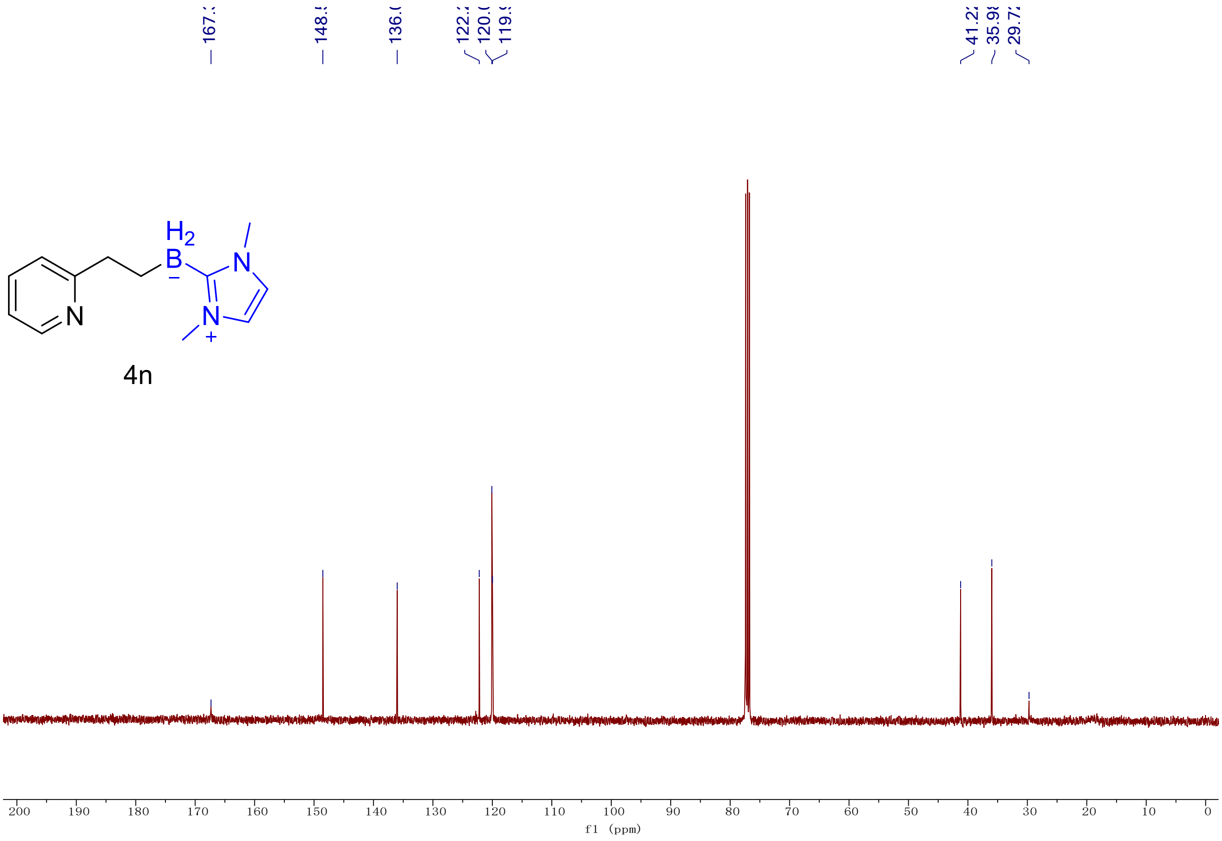
^{11}**B NMR** spectra of compound **4m** (128 MHz, $CDCl_3$)



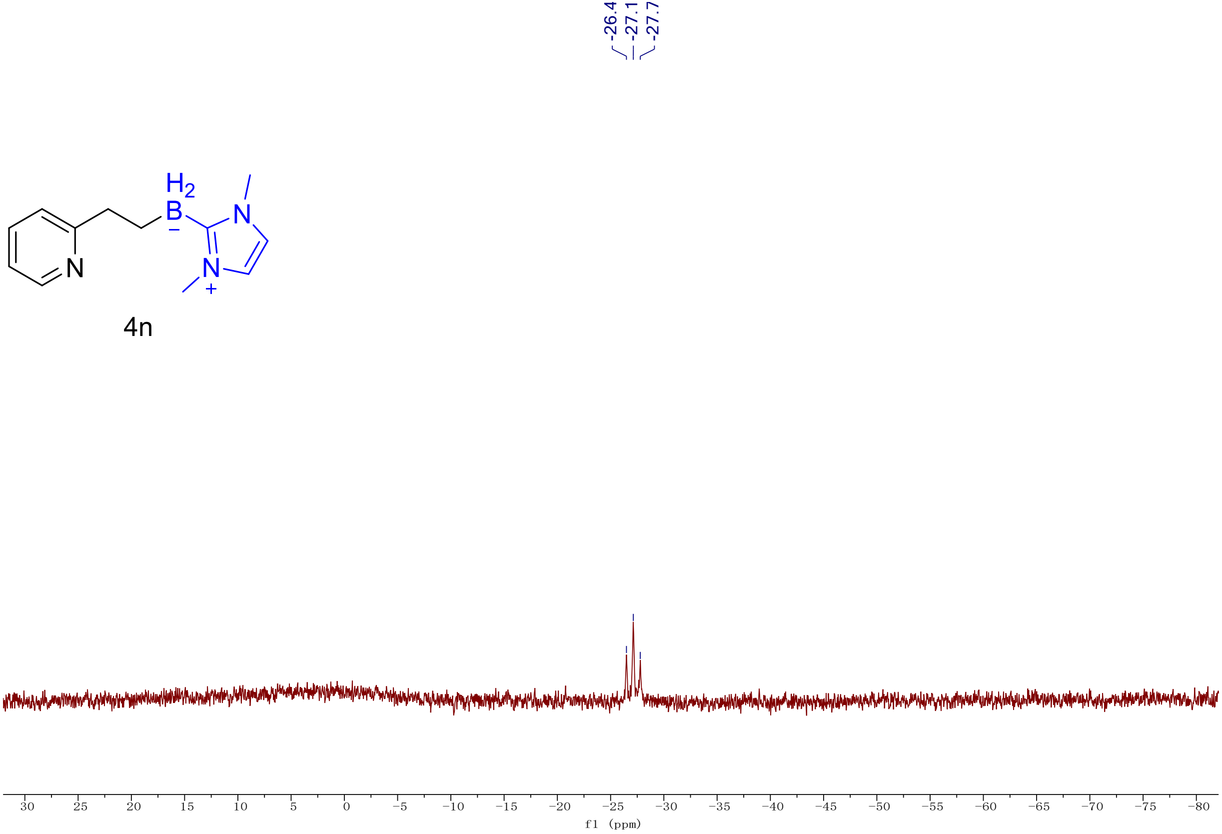
^{1}**H NMR** spectra of compound **4n** (400 MHz, $CDCl_3$)



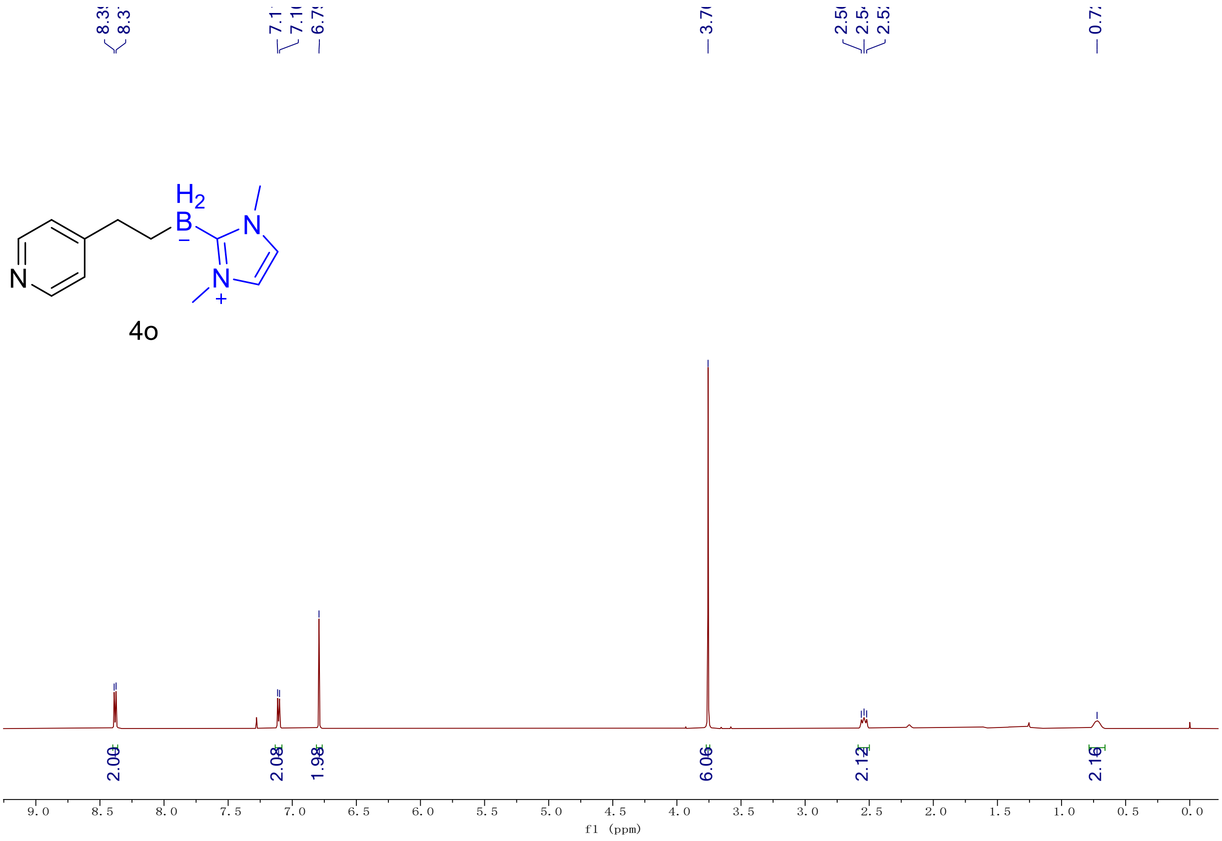
^{13}**C NMR** spectra of compound **4n** (101 MHz, $CDCl_3$)



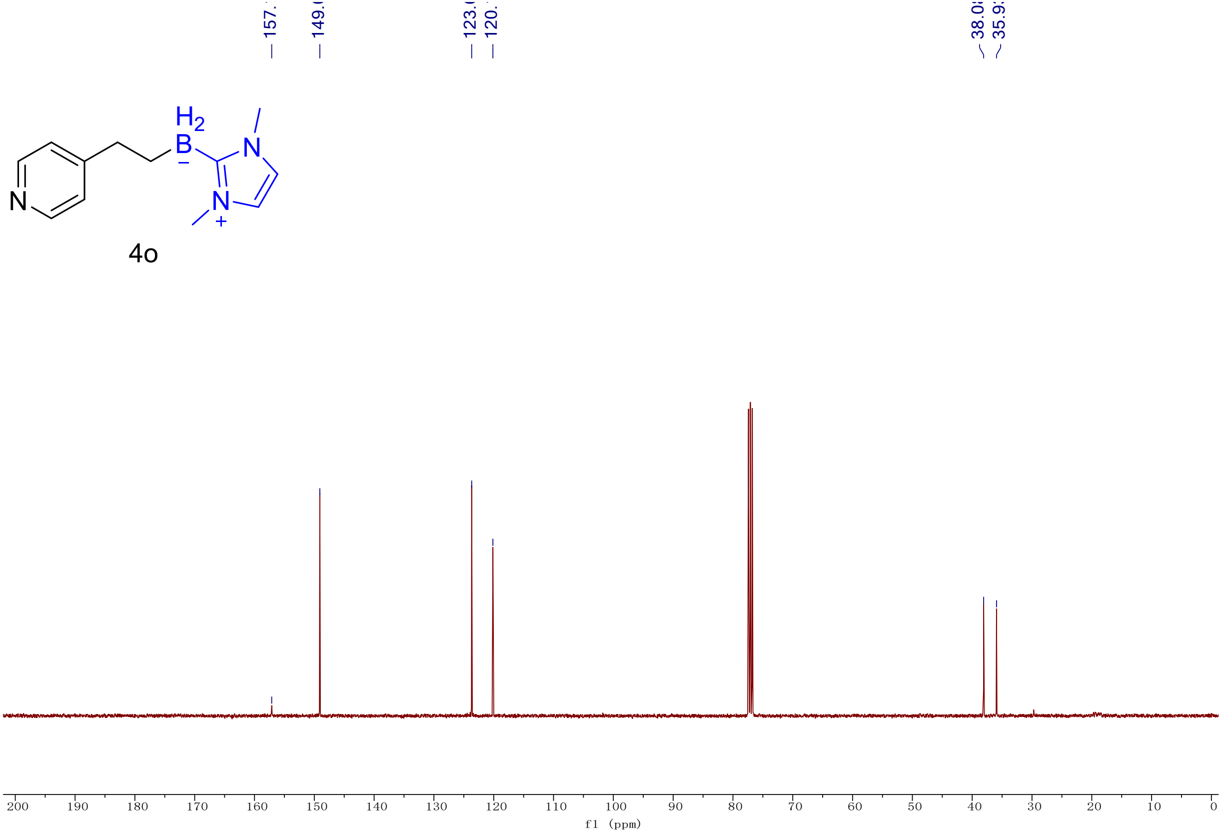
^{11}**B NMR** spectra of compound **4n** (128 MHz, $CDCl_3$)



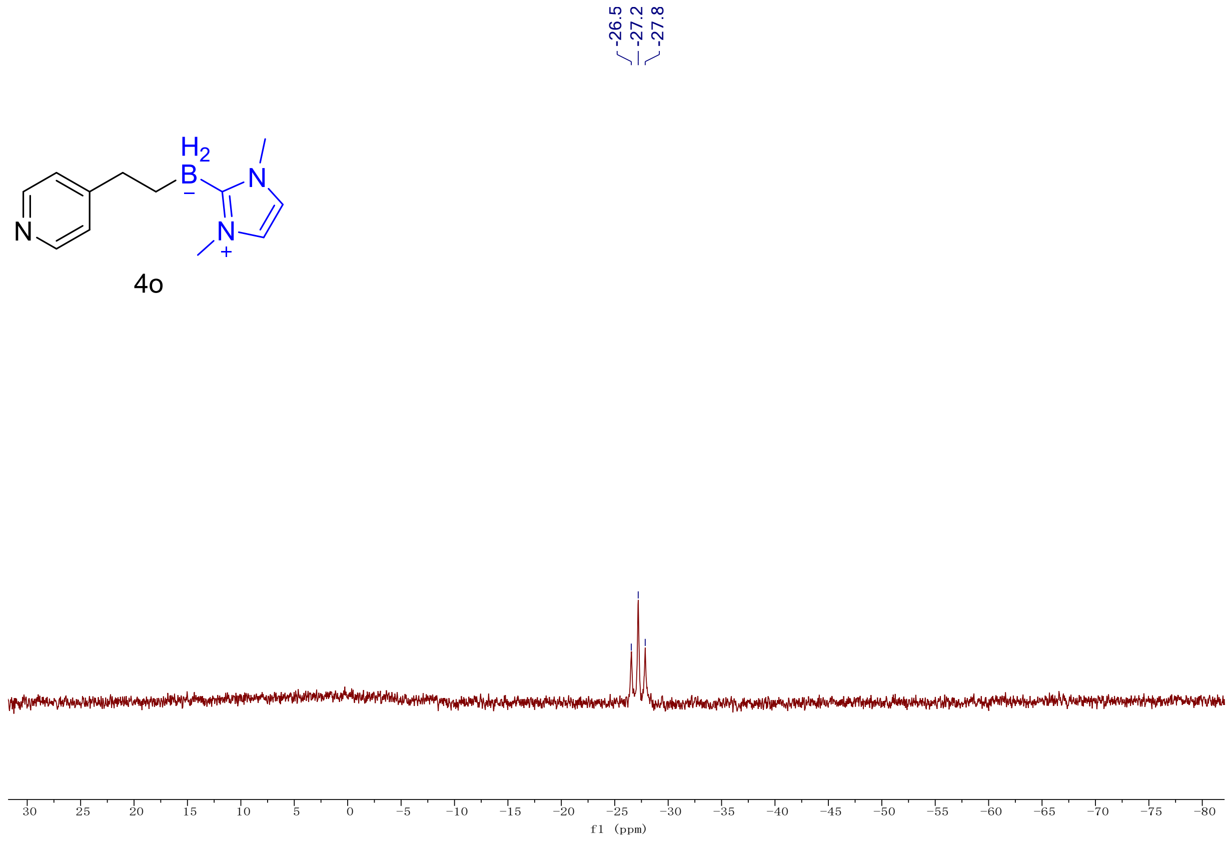
^{1}**H NMR** spectra of compound **4o** (400 MHz, $CDCl_3$)



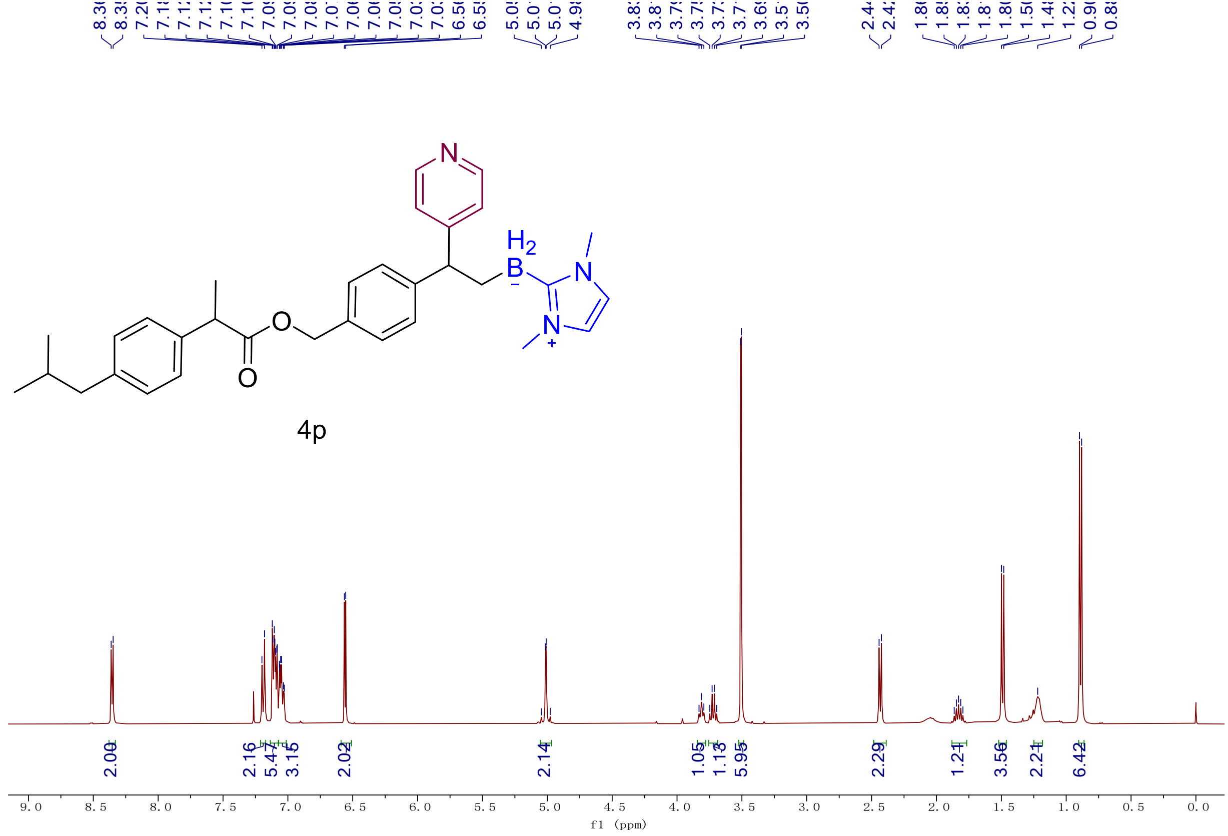
^{13}C NMR spectra of compound **4o** (101 MHz, $CDCl_3$)



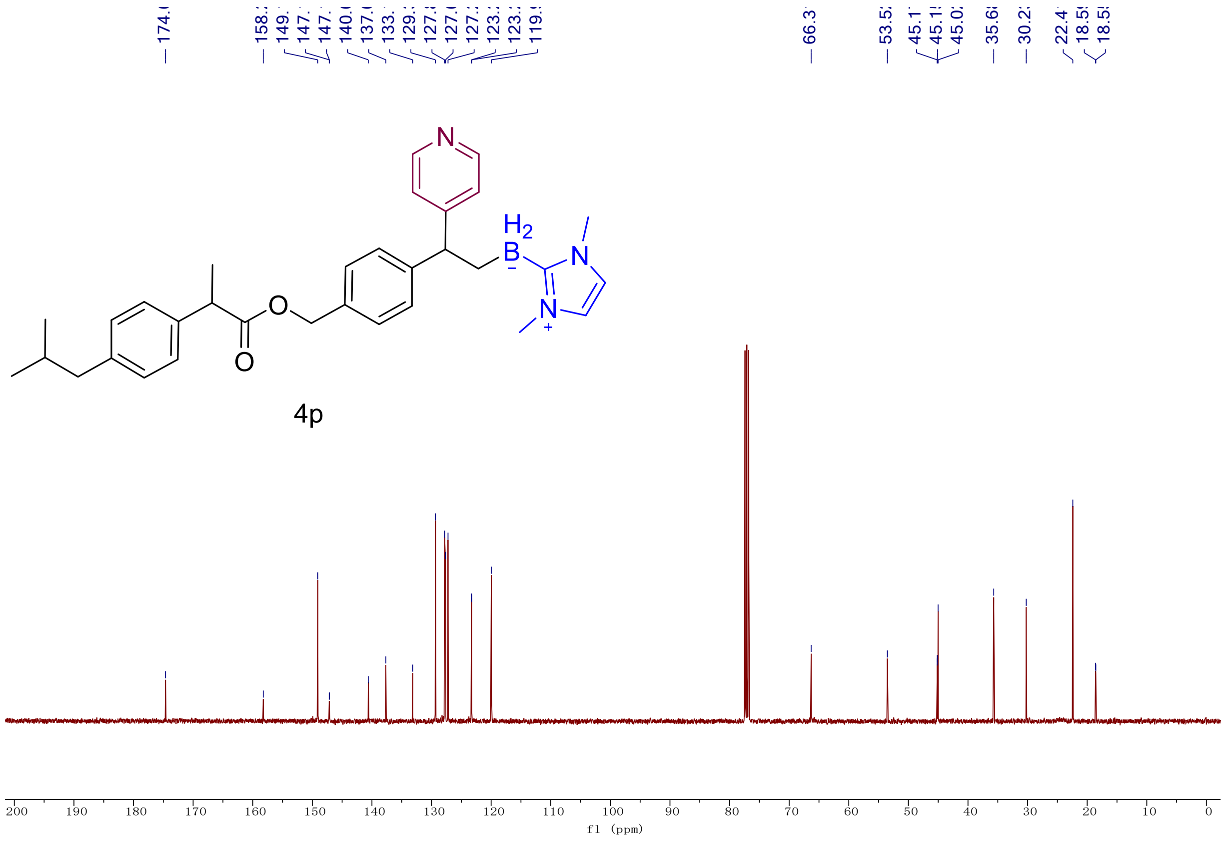
^{11}B NMR spectra of compound **4o** (128 MHz, $CDCl_3$)



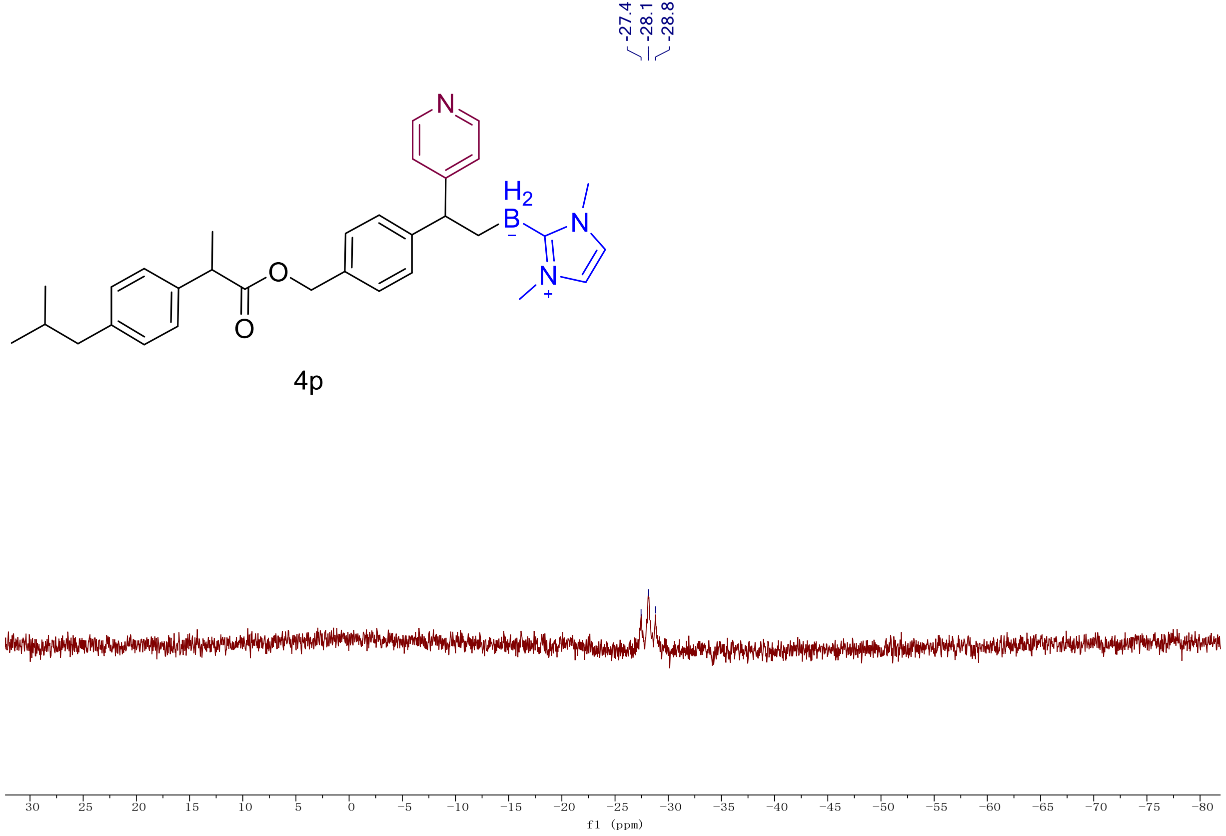
^{1}H NMR spectra of compound **4p** (400 MHz, $CDCl_3$)



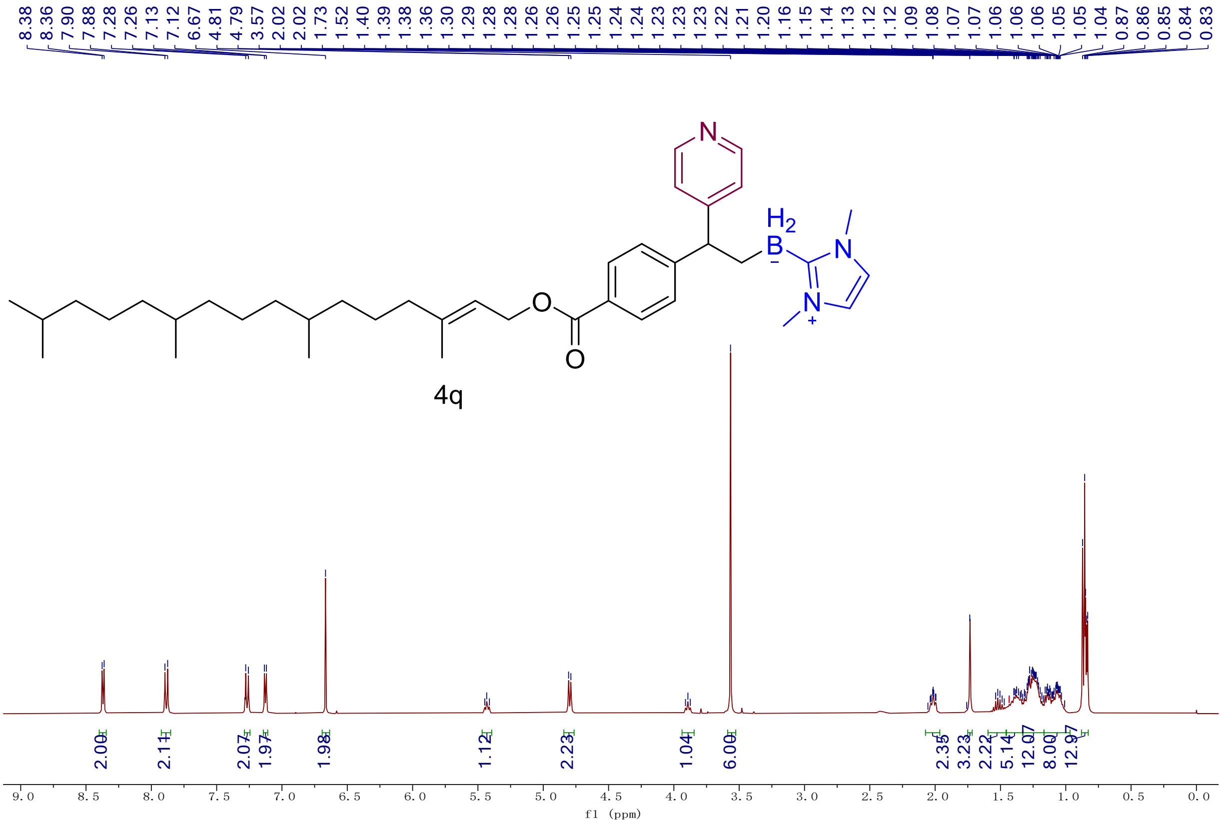
^{13}C NMR spectra of compound **4p** (101 MHz, $CDCl_3$)



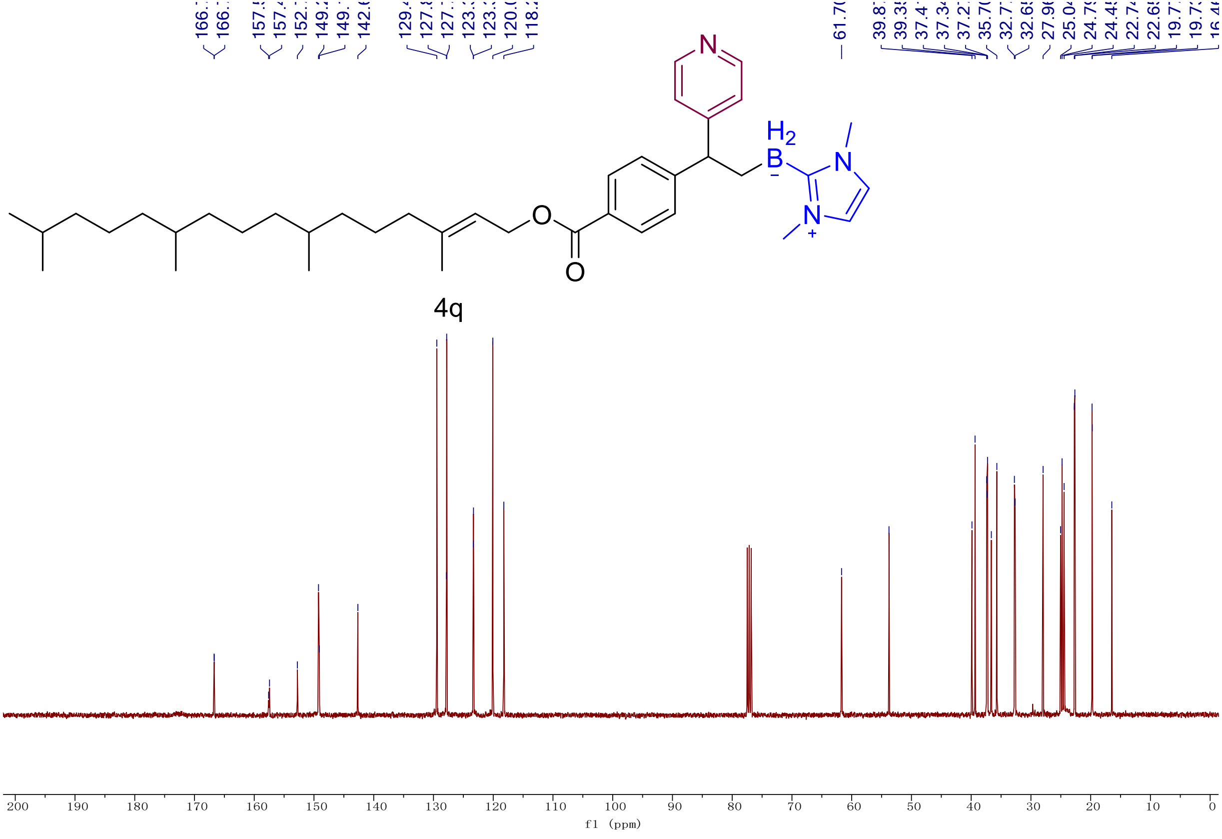
^{11}B NMR spectra of compound **4p** (128 MHz, $CDCl_3$)



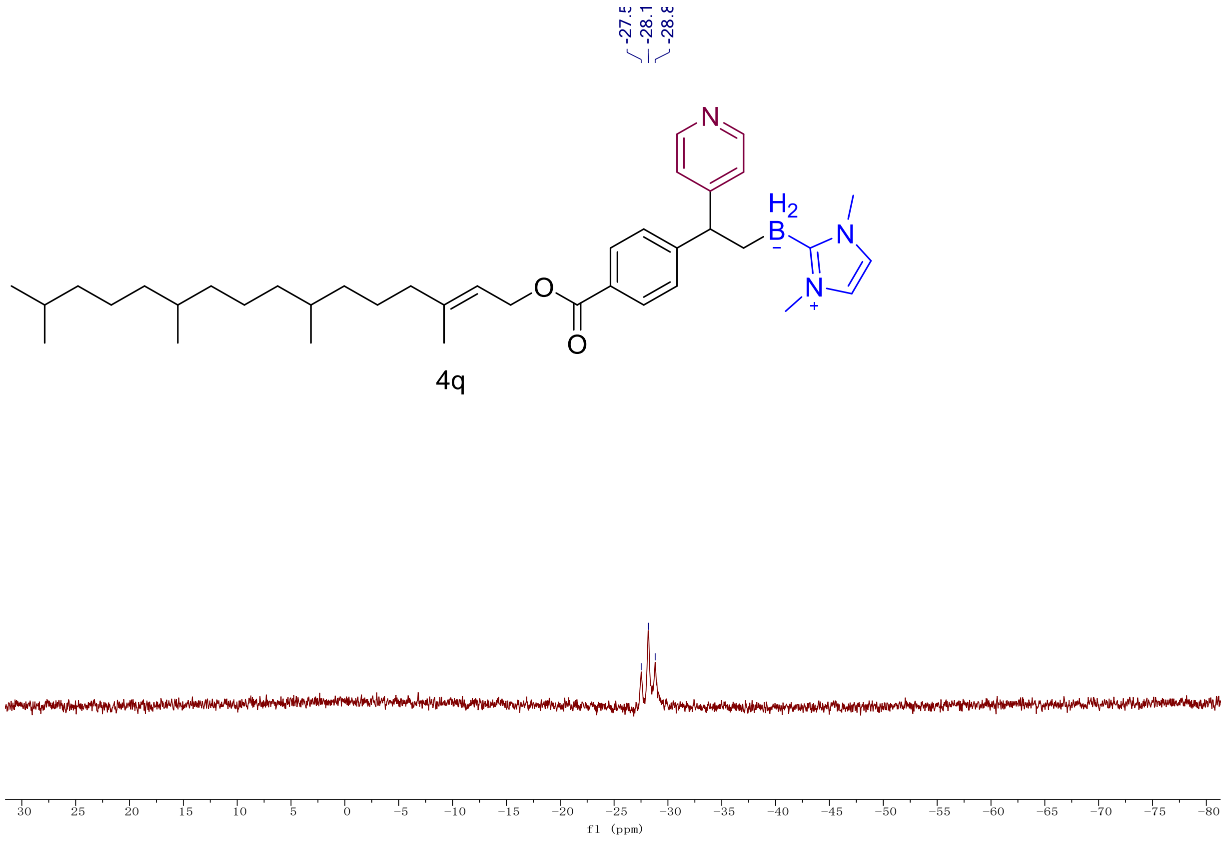
^{1}H NMR spectra of compound **4q** (400 MHz, $CDCl_3$)



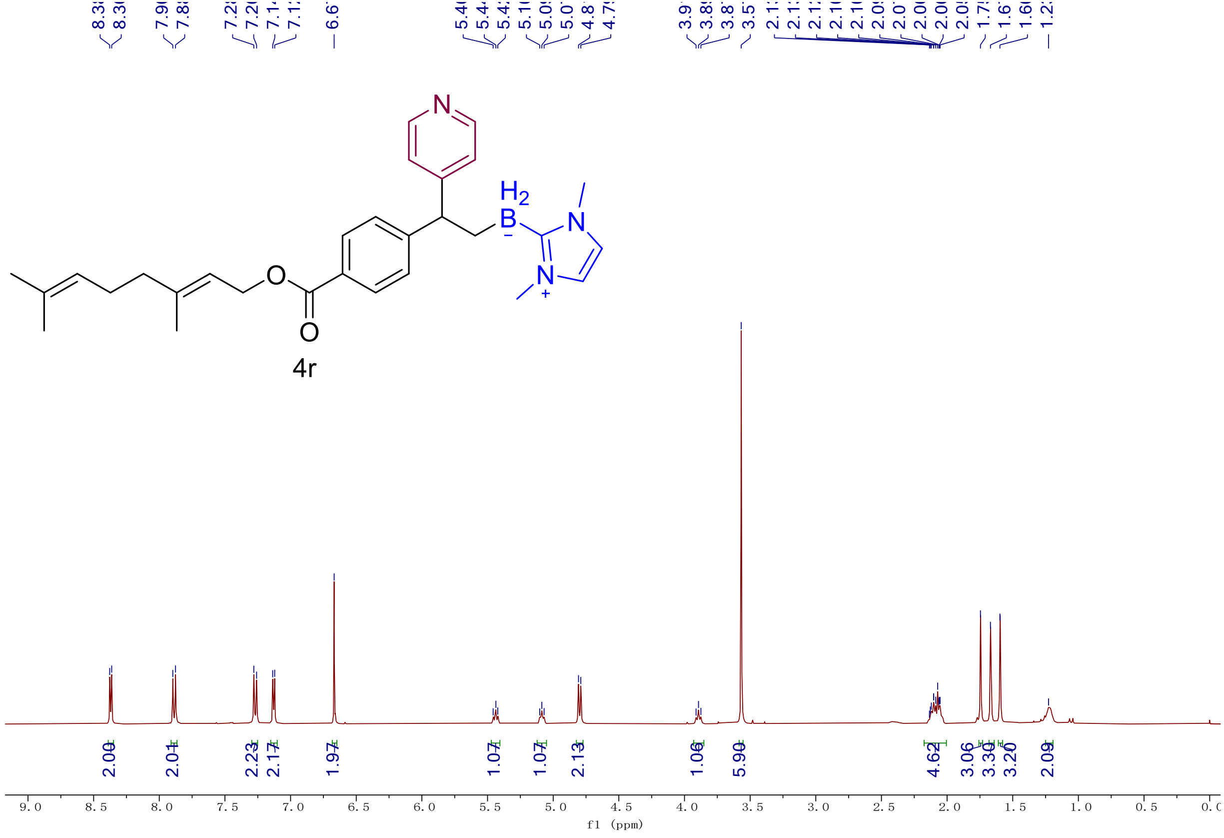
^{13}C NMR spectra of compound **4q** (101 MHz, CDCl$_3$)



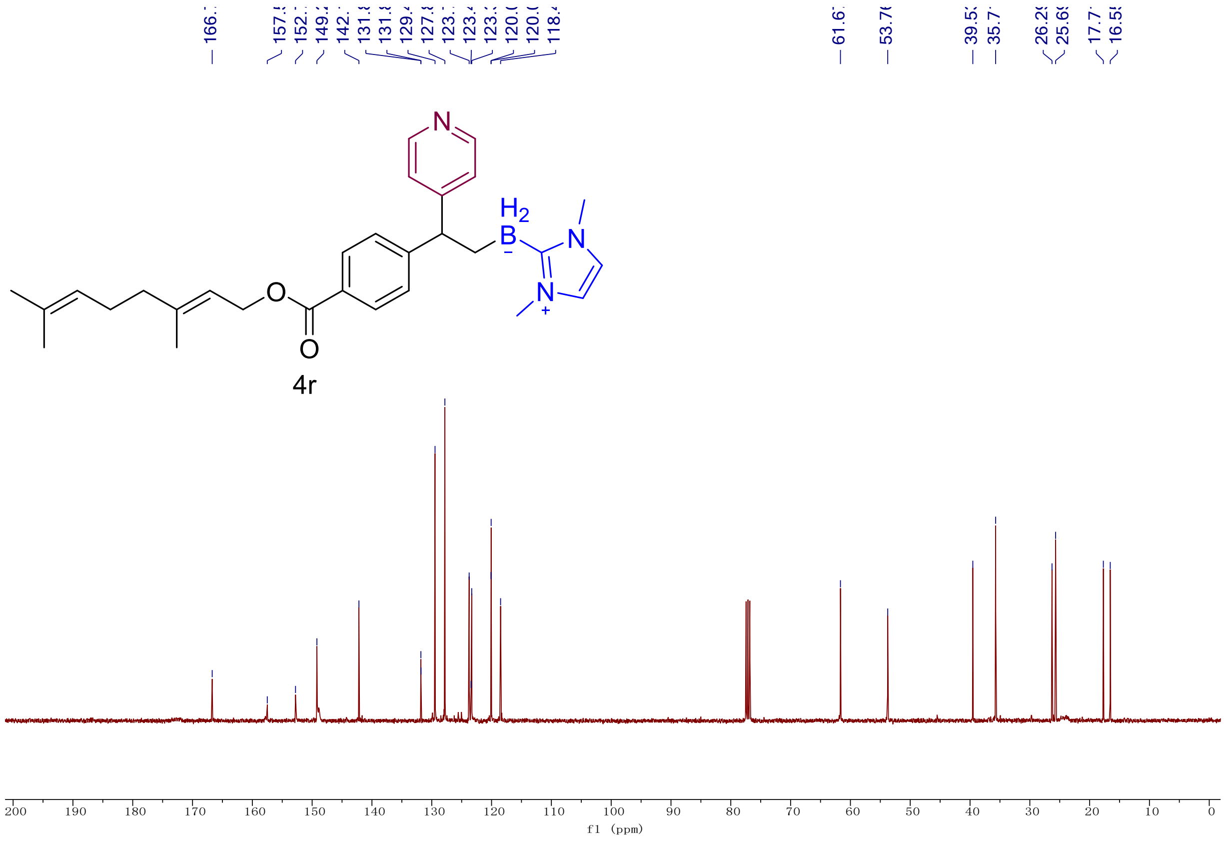
^{11}B NMR spectra of compound **4q** (128 MHz, CDCl$_3$)



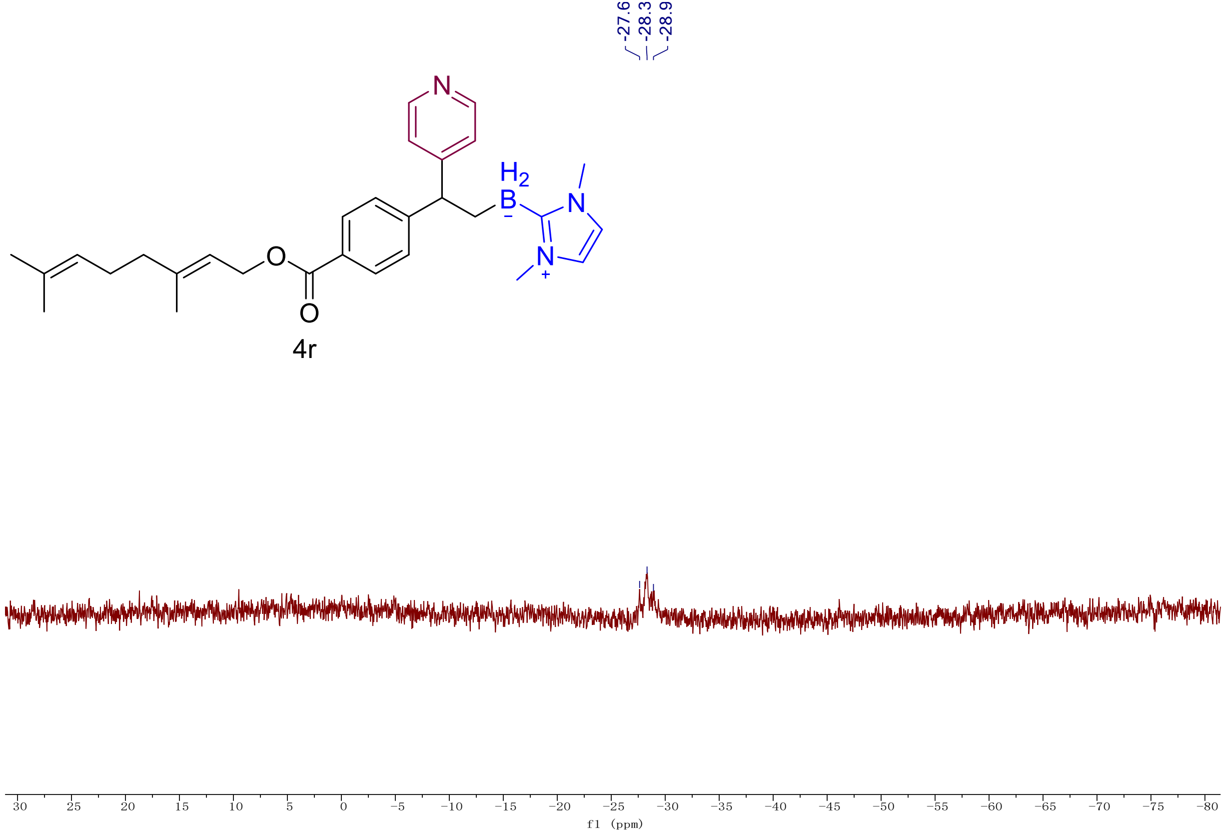
^{1}H NMR spectra of compound **4r** (400 MHz, $CDCl_3$)



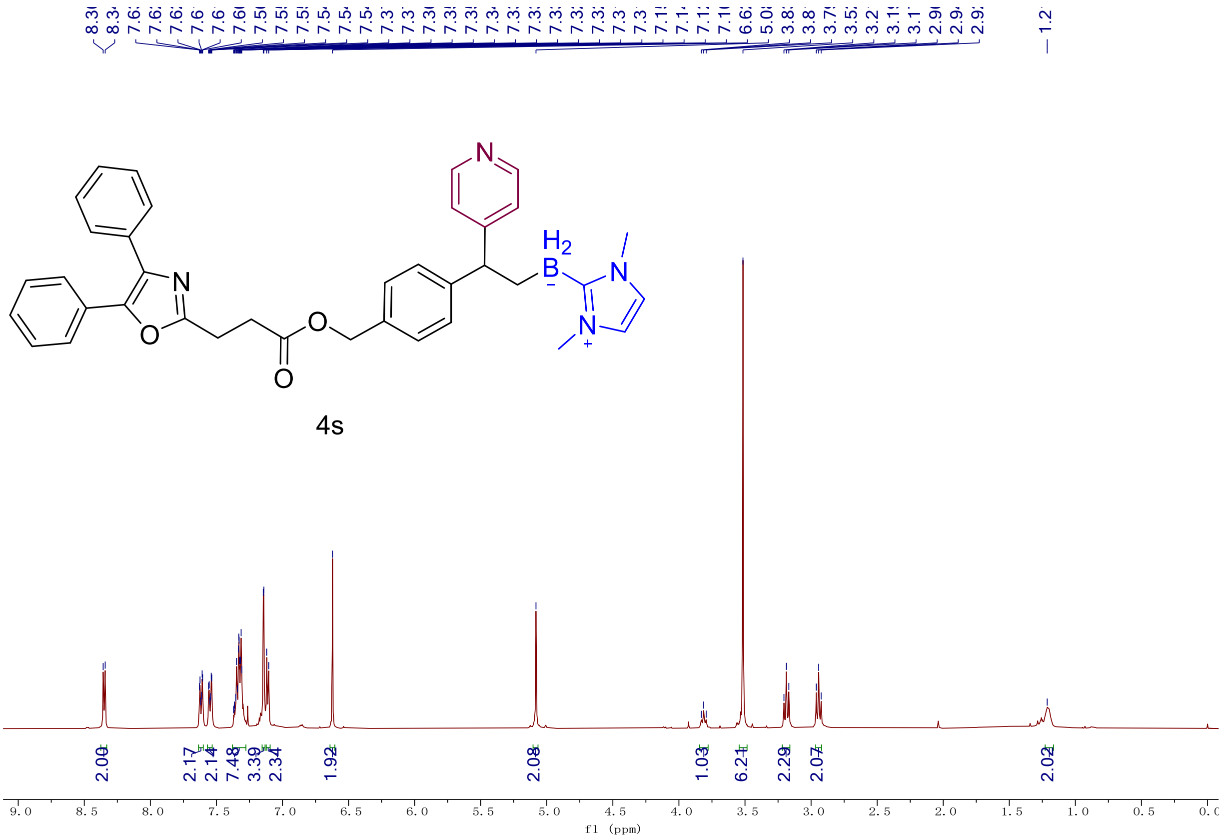
^{13}C NMR spectra of compound **4r** (101 MHz, $CDCl_3$)



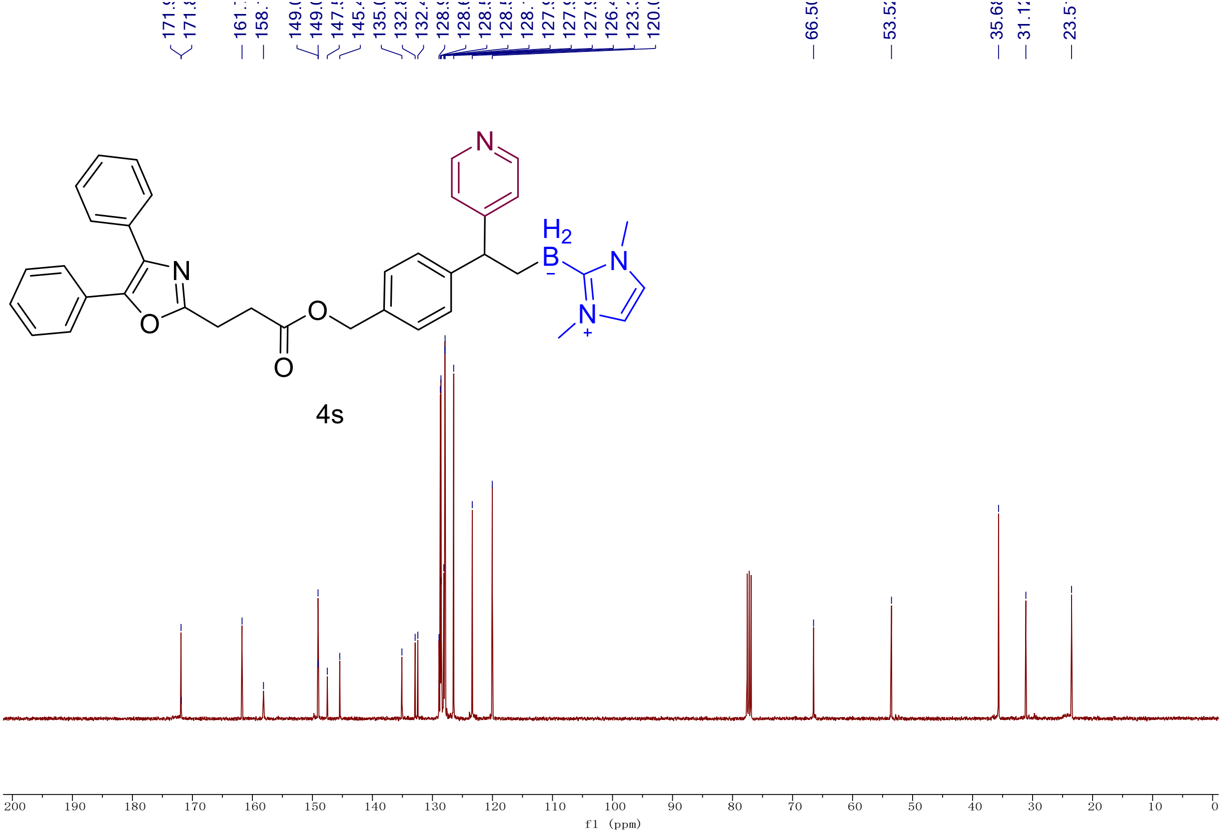
^{11}B NMR spectra of compound **4r** (128 MHz, $CDCl_3$)



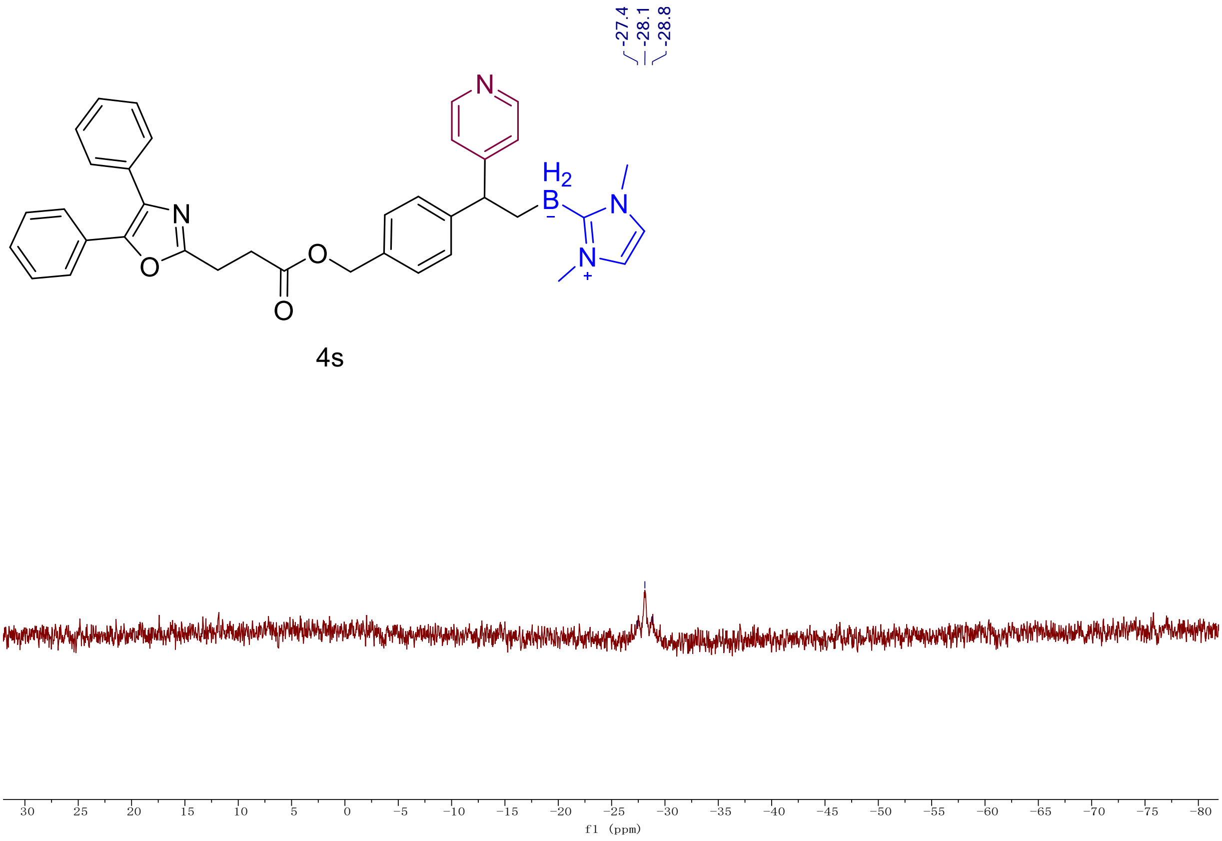
^{1}H NMR spectra of compound **4s** (400 MHz, $CDCl_3$)



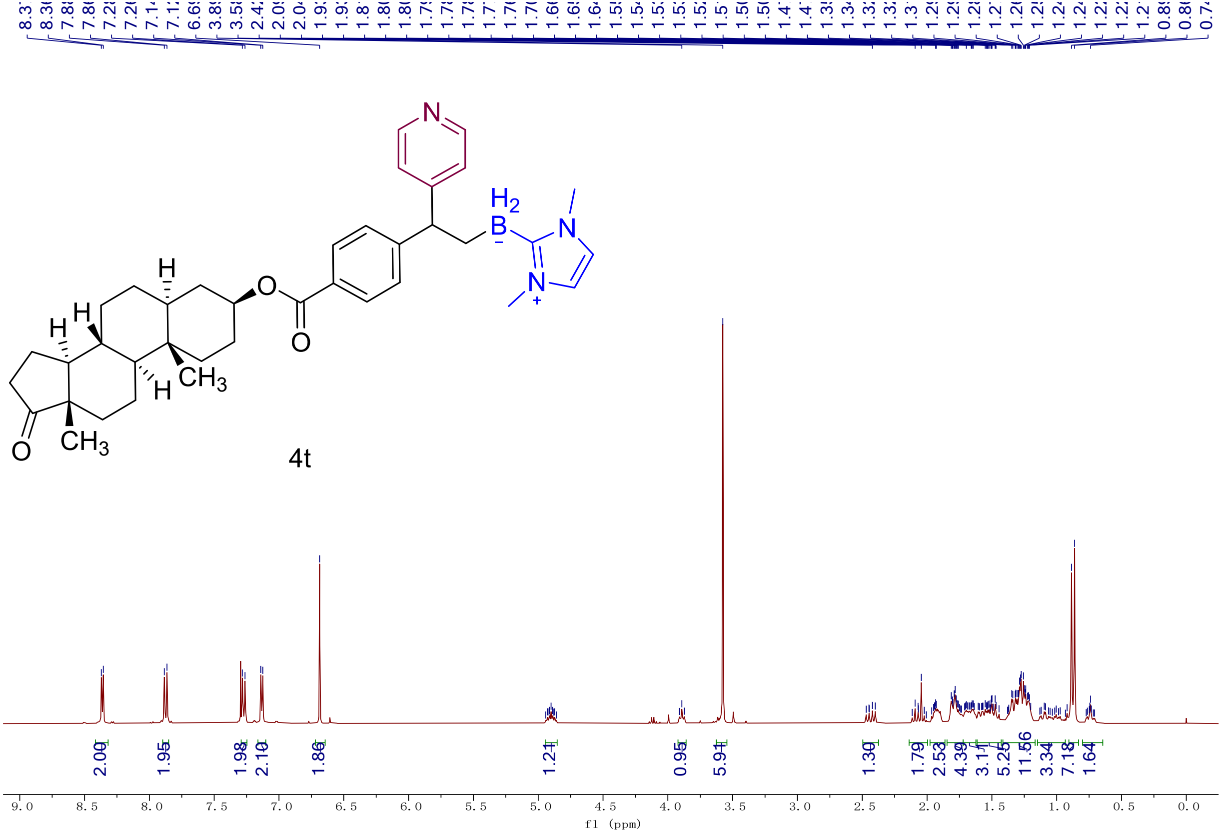
^{13}C NMR spectra of compound **4s** (101 MHz, $CDCl_3$)



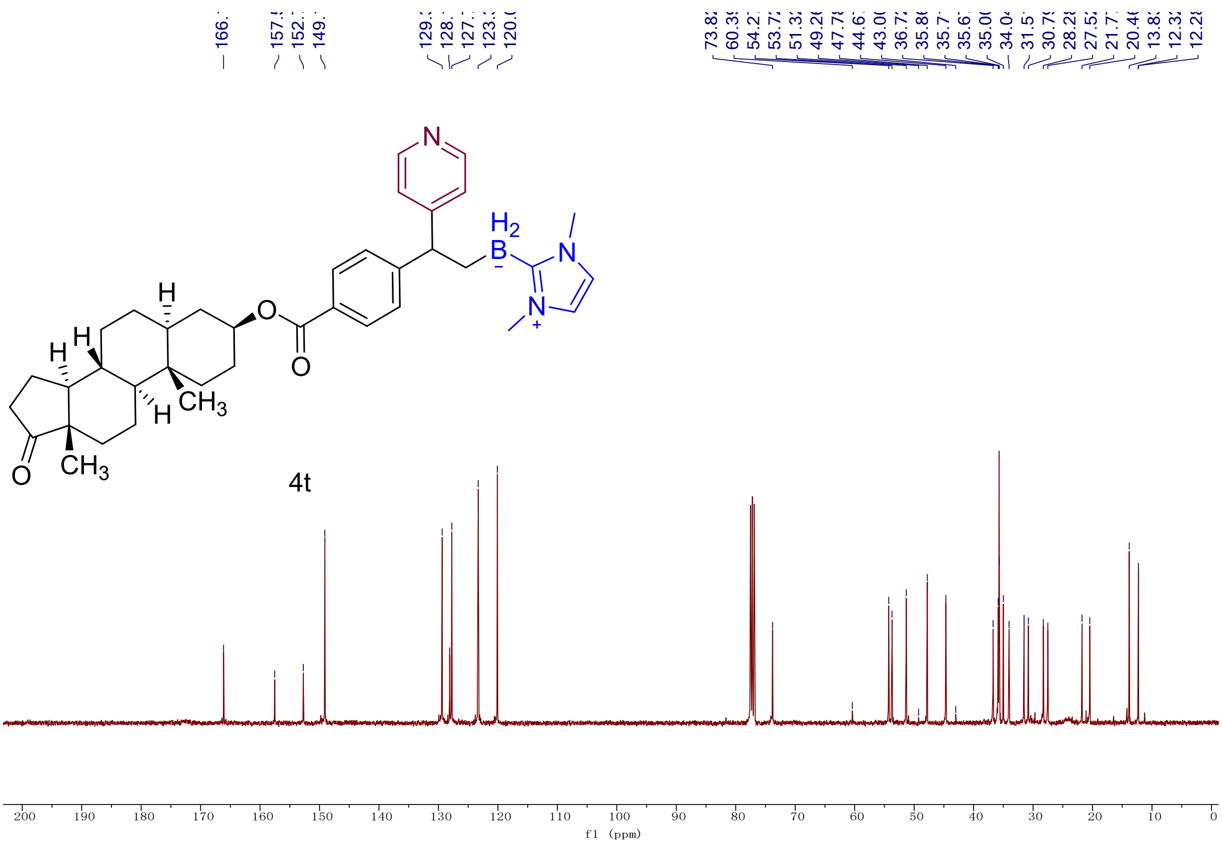
^{11}B NMR spectra of compound **4s** (128 MHz, $CDCl_3$)


4s

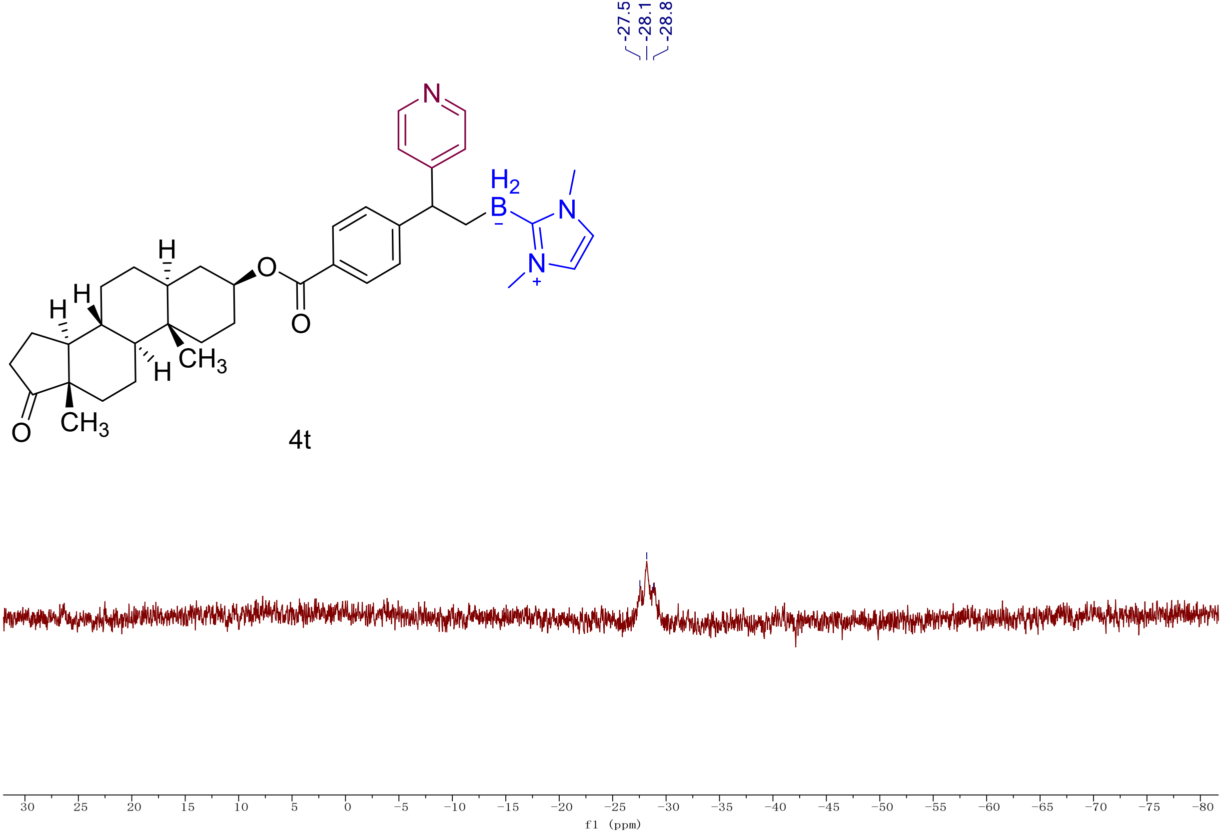
^{1}H NMR spectra of compound **4t** (400 MHz, $CDCl_3$)


4t

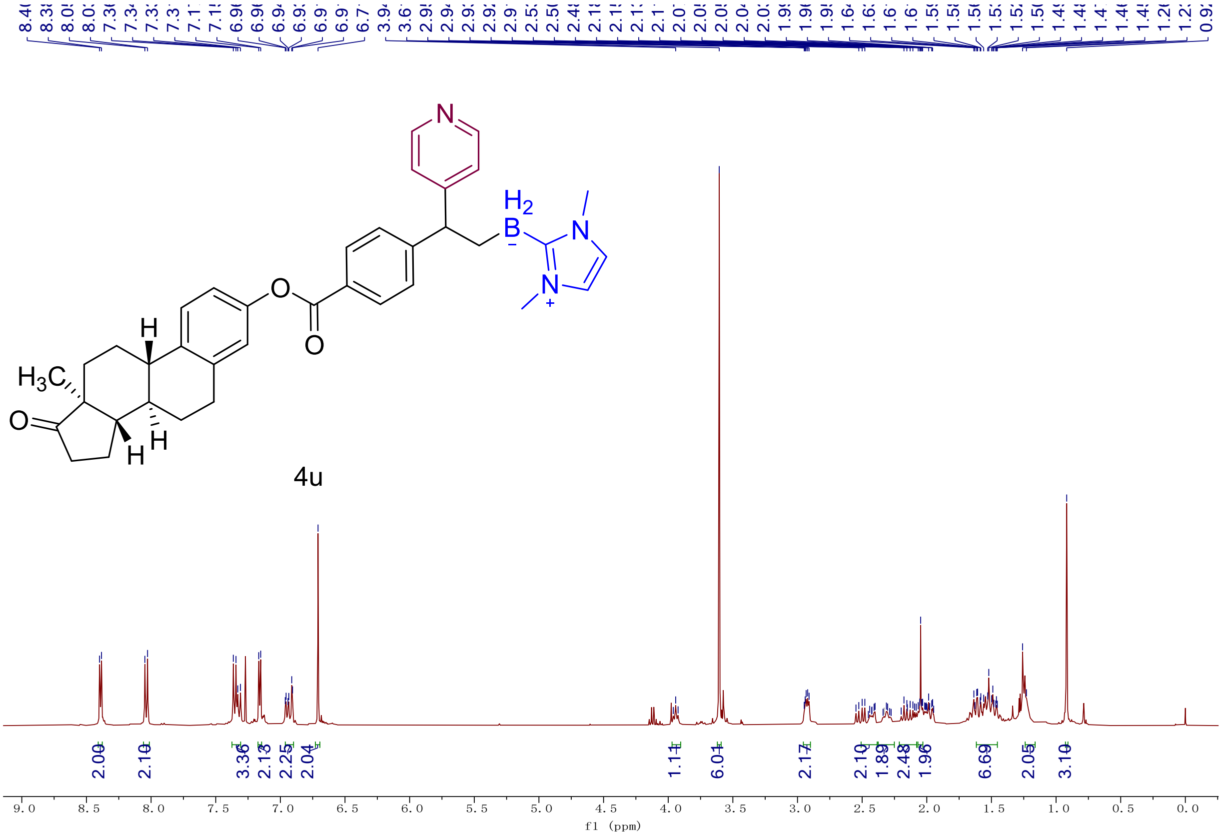
^{13}C NMR spectra of compound **4t** (101 MHz, $CDCl_3$)



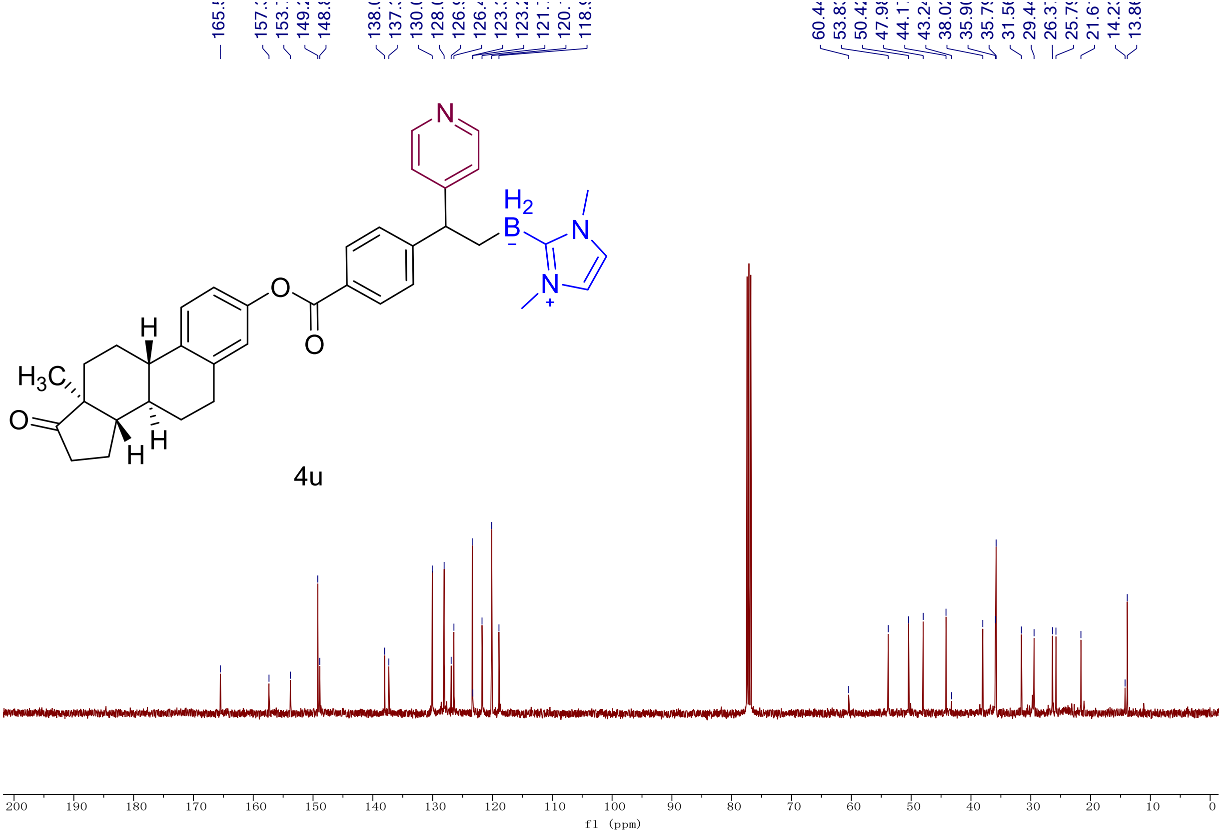
^{11}**B NMR** spectra of compound **4t** (128 MHz, CDCl$_3$)



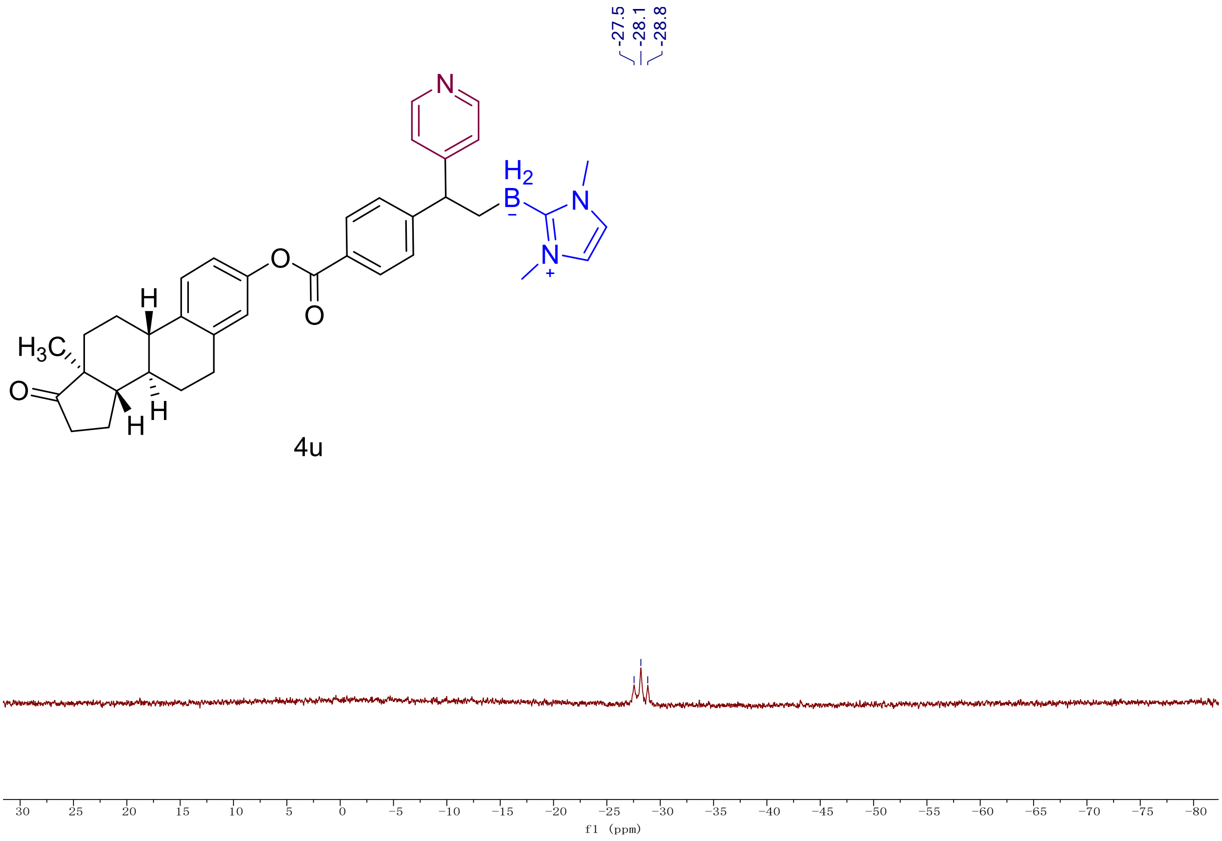
^{1}**H NMR** spectra of compound **4u** (400 MHz, CDCl$_3$)



^{13}C NMR spectra of compound **4u** (101 MHz, CDCl$_3$)

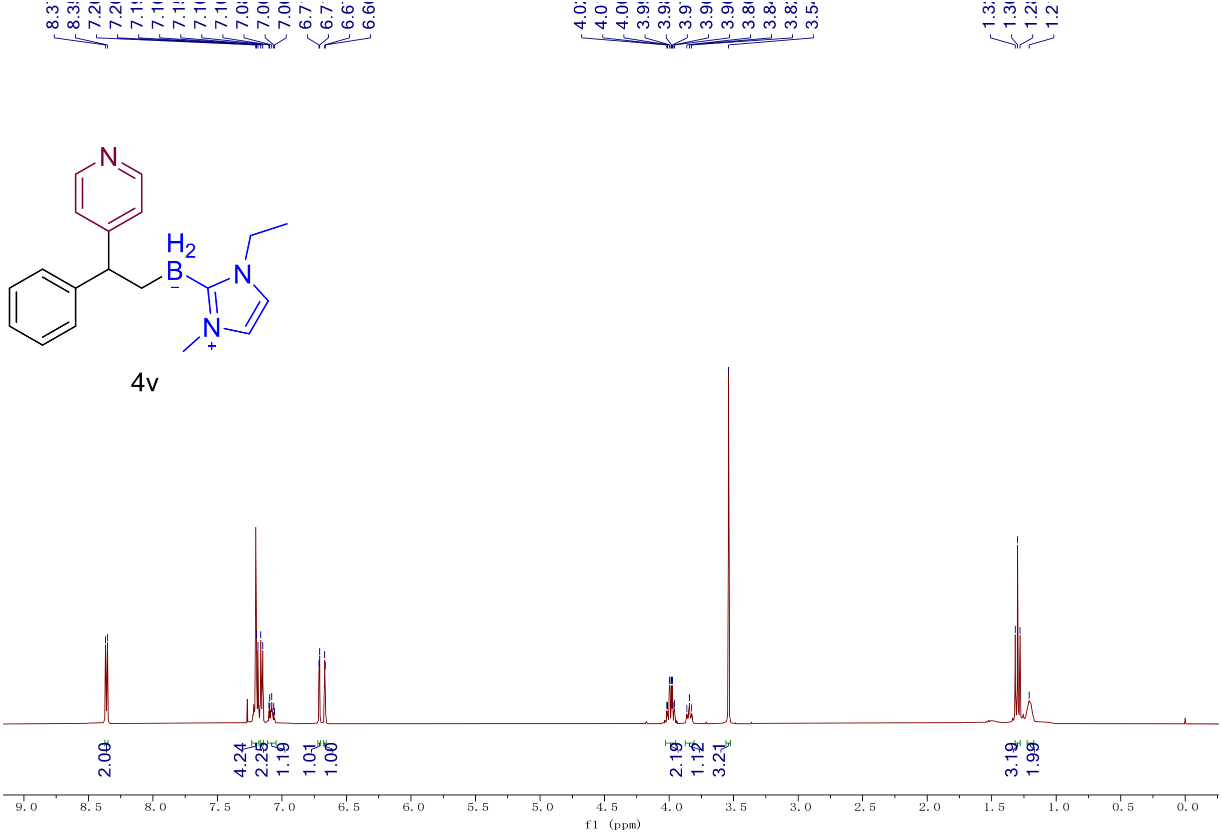


^{11}B NMR spectra of compound **4u** (128 MHz, CDCl$_3$)



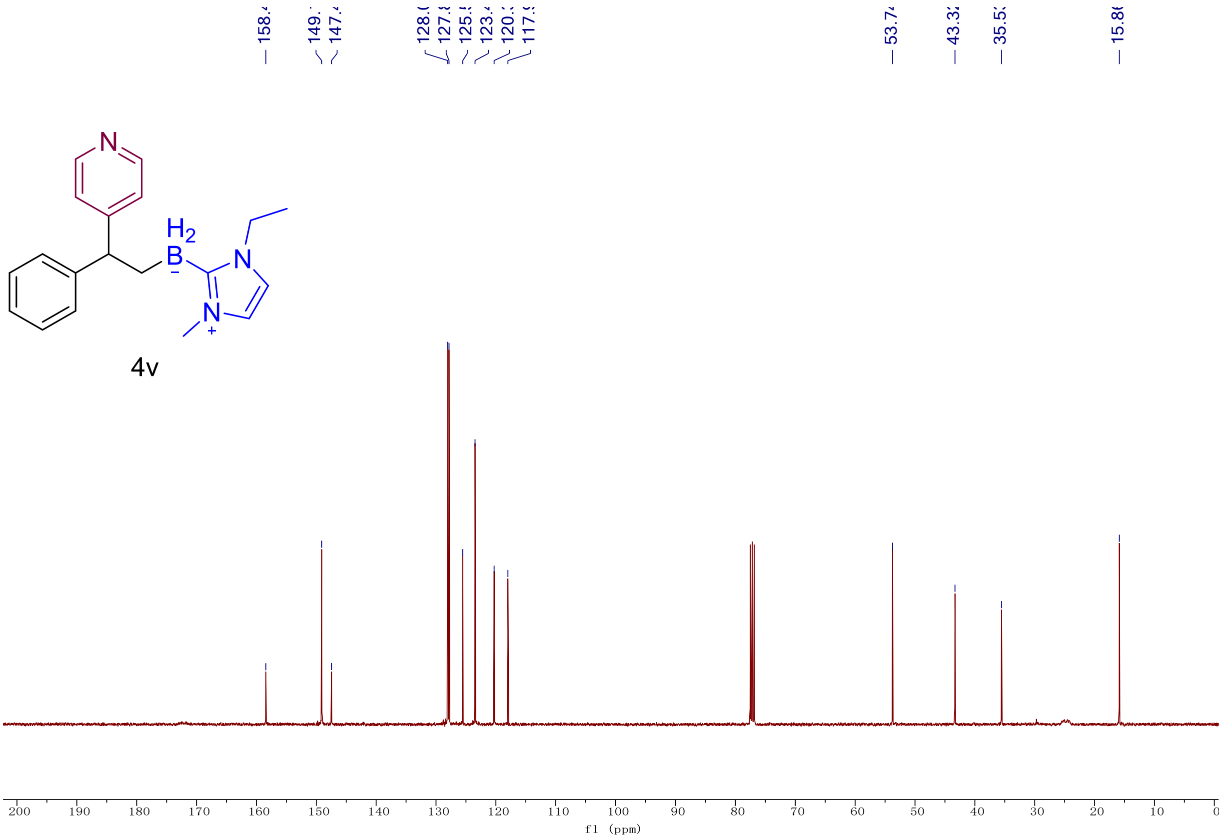
4u

^{1}H NMR spectra of compound **4v** (400 MHz, CDCl$_3$)

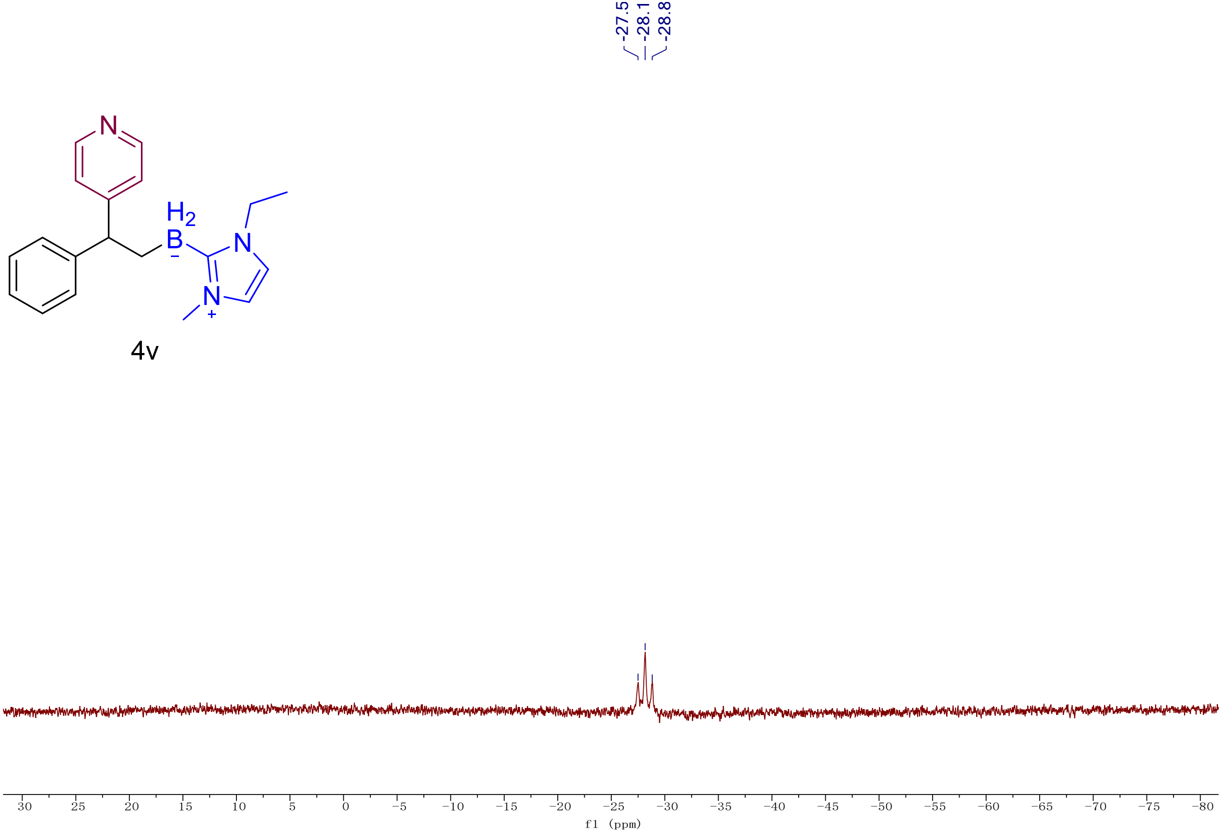


4v

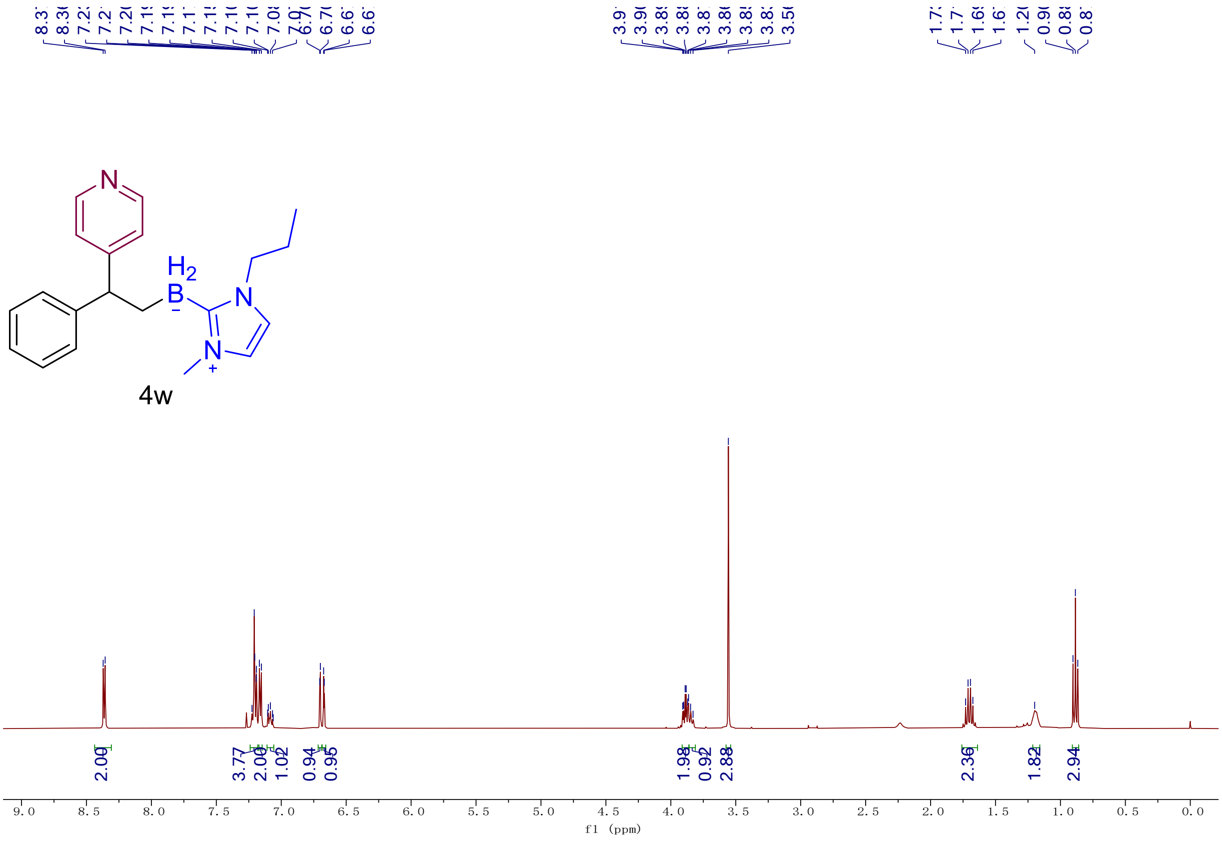
^{13}C NMR spectra of compound **4v** (101 MHz, CDCl$_3$)



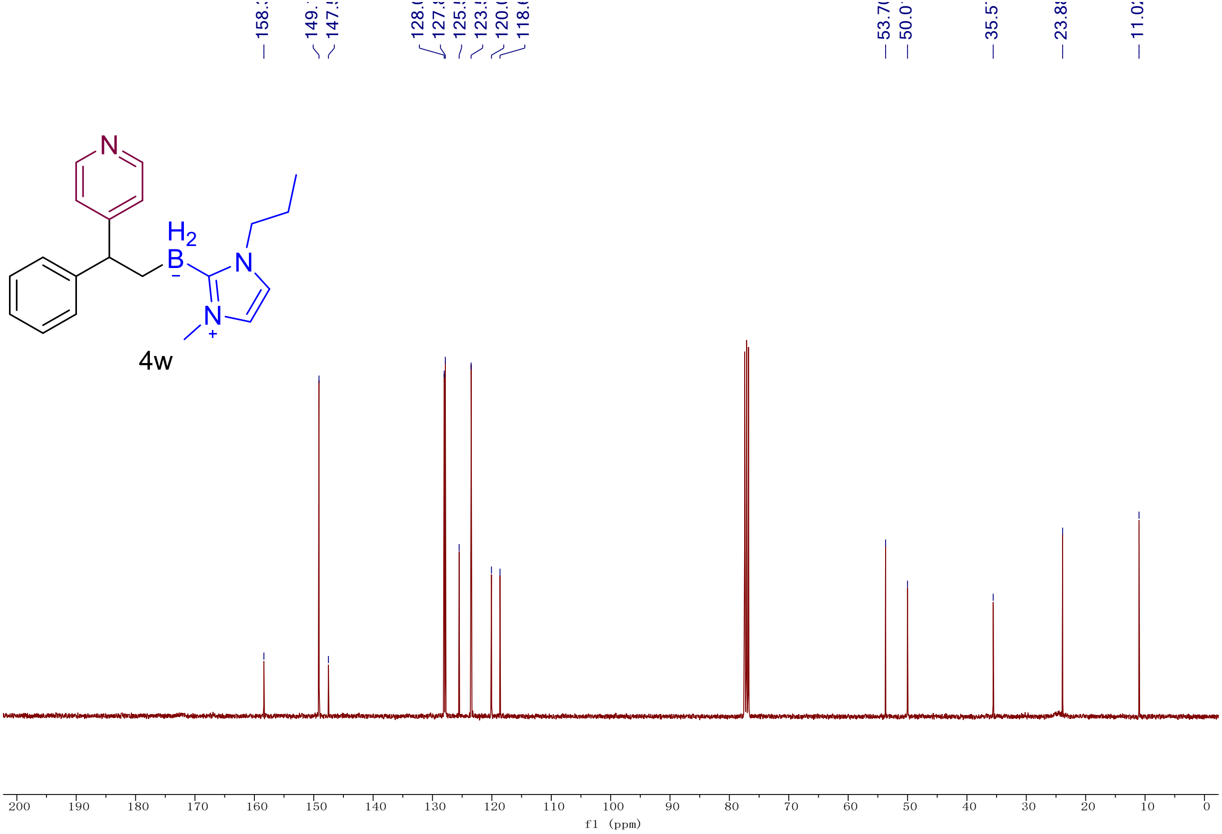
^{11}B NMR spectra of compound **4v** (128 MHz, CDCl$_3$)



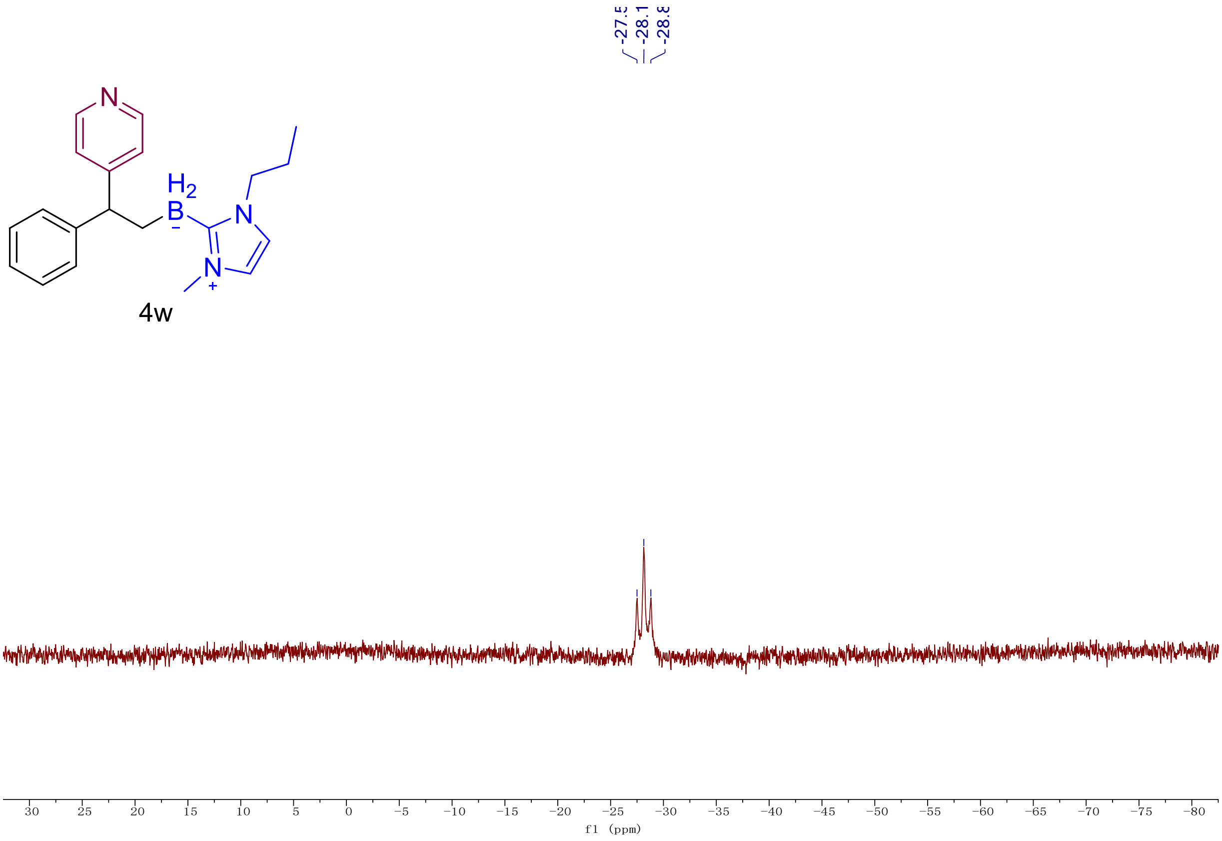
^{1}H NMR spectra of compound **4w** (400 MHz, CDCl$_3$)



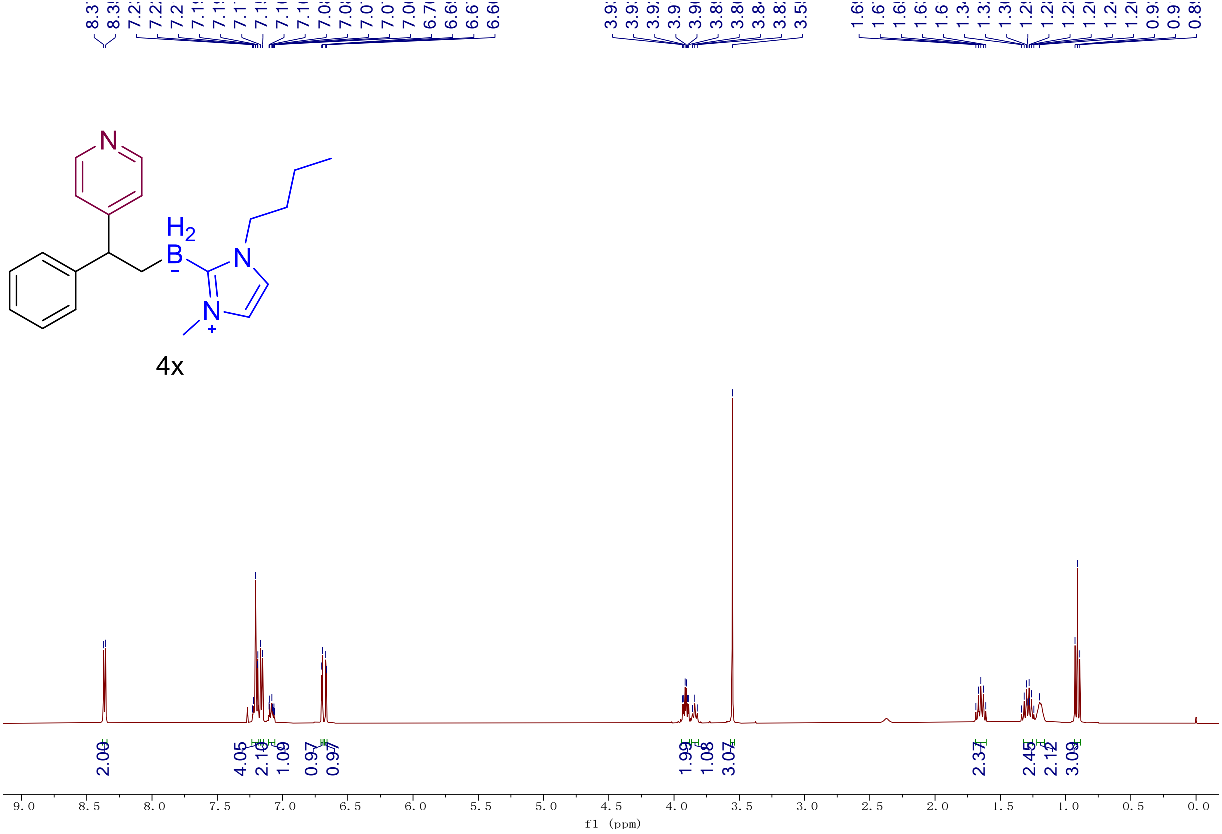
^{13}C NMR spectra of compound **4w** (101 MHz, CDCl$_3$)



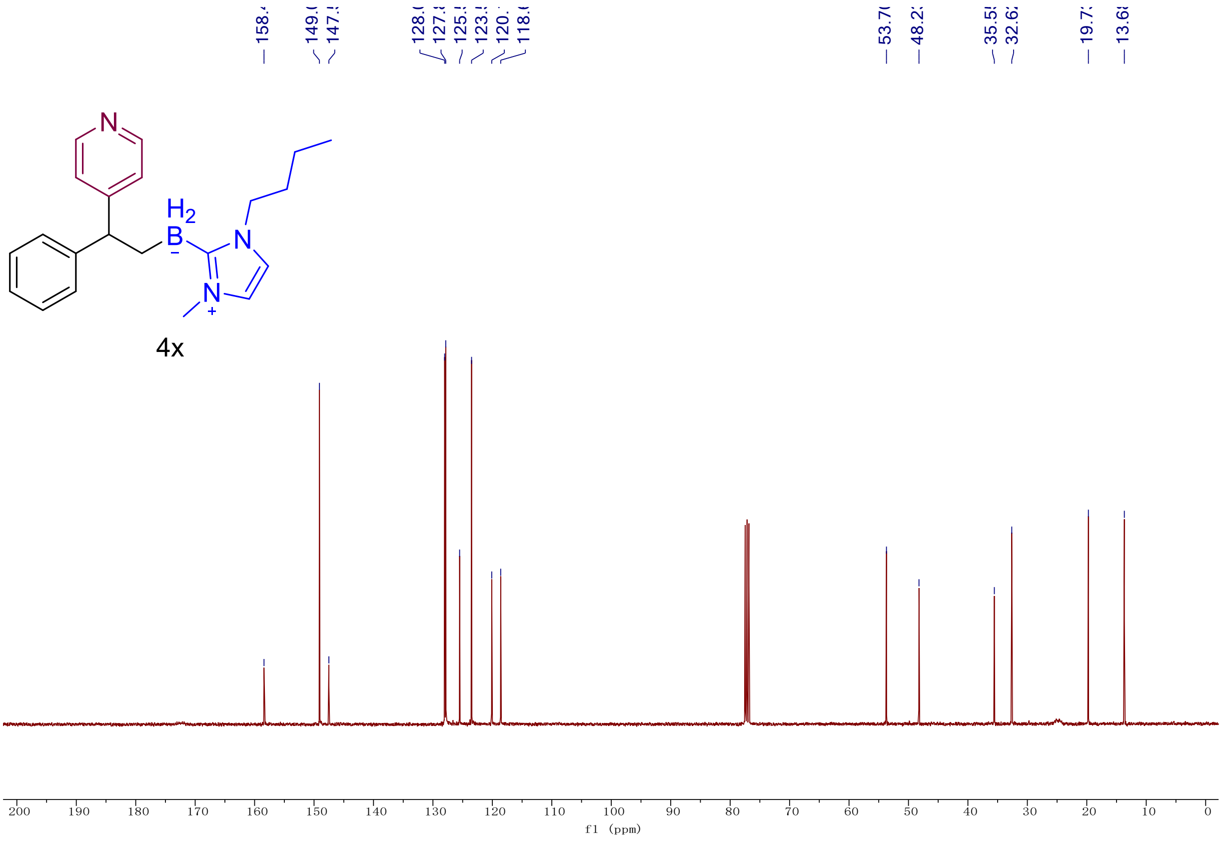
^{11}B NMR spectra of compound **4w** (128 MHz, CDCl$_3$)



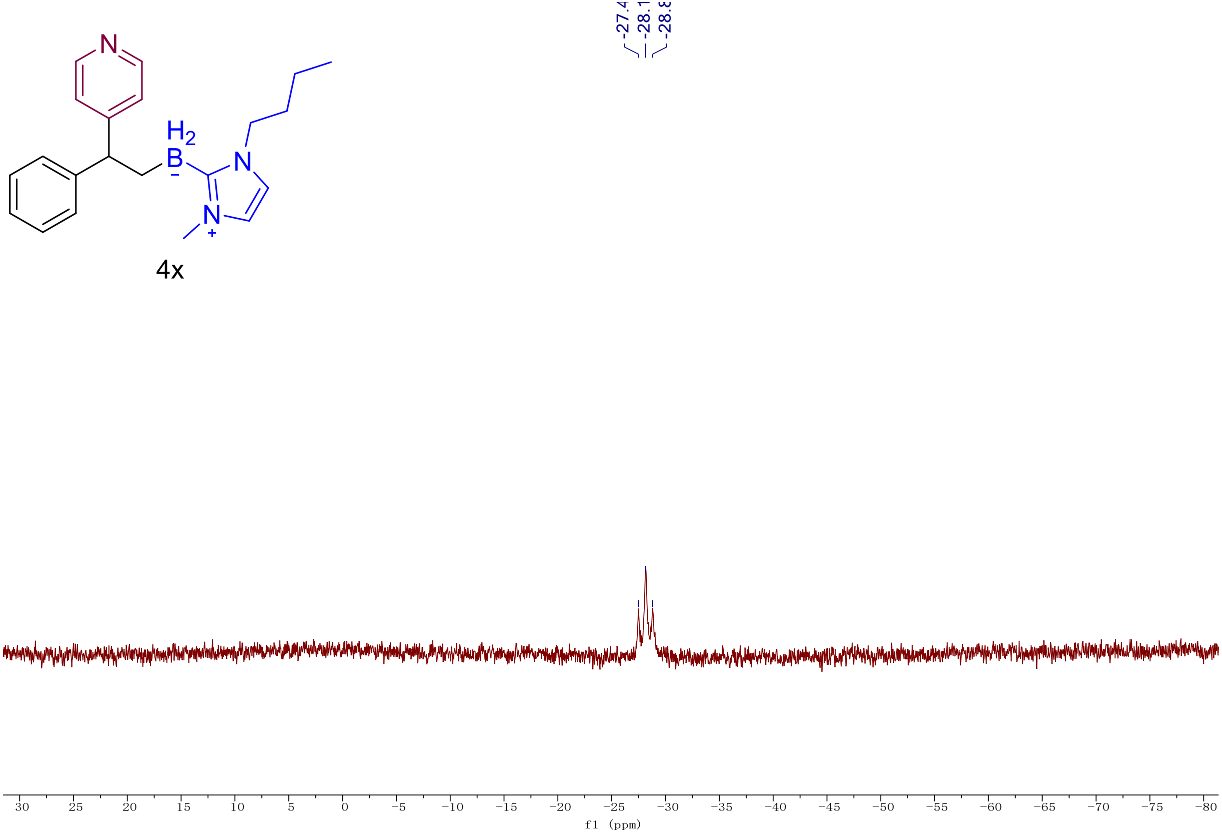
¹H NMR spectra of compound **4x** (400 MHz, $CDCl_3$)



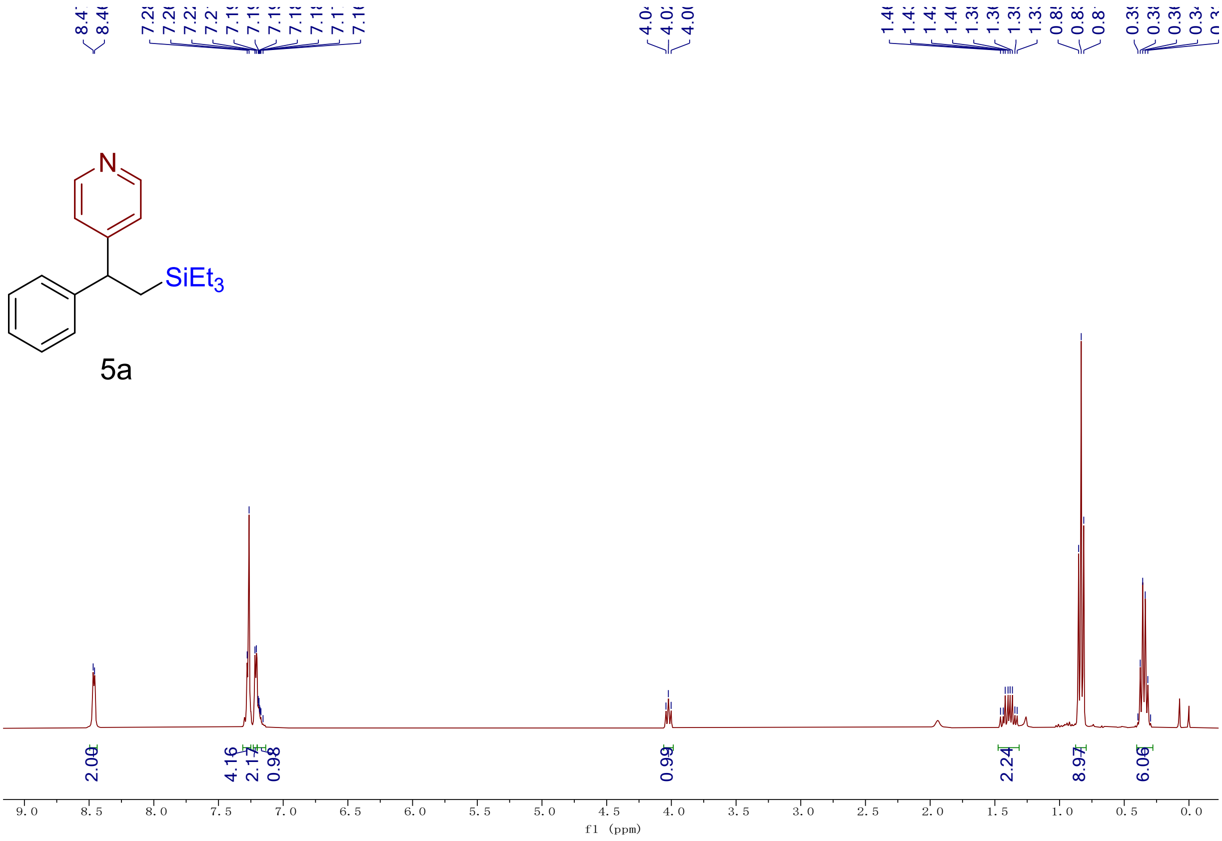
¹³C NMR spectra of compound **4x** (101 MHz, $CDCl_3$)



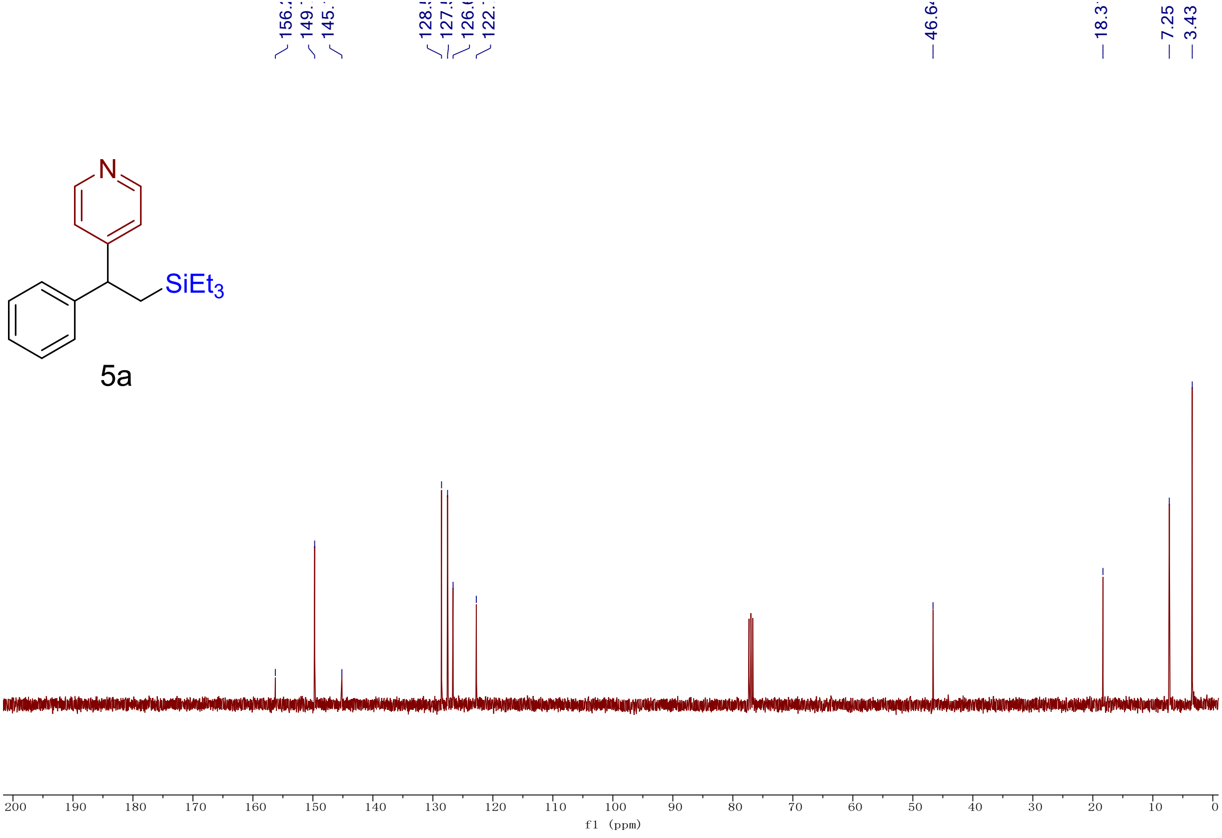
^{11}B NMR spectra of compound **4x** (128 MHz, $CDCl_3$)



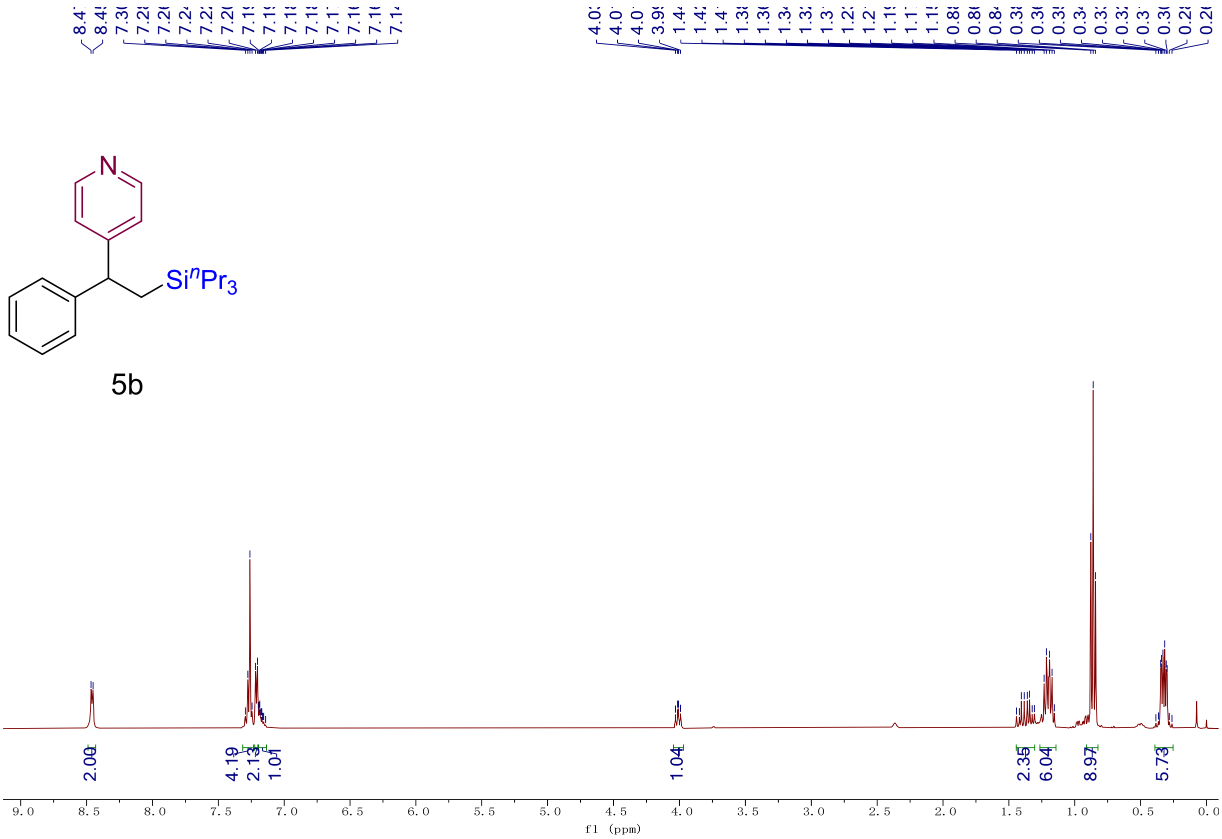
^{1}H NMR spectra of compound **5a** (400 MHz, $CDCl_3$)



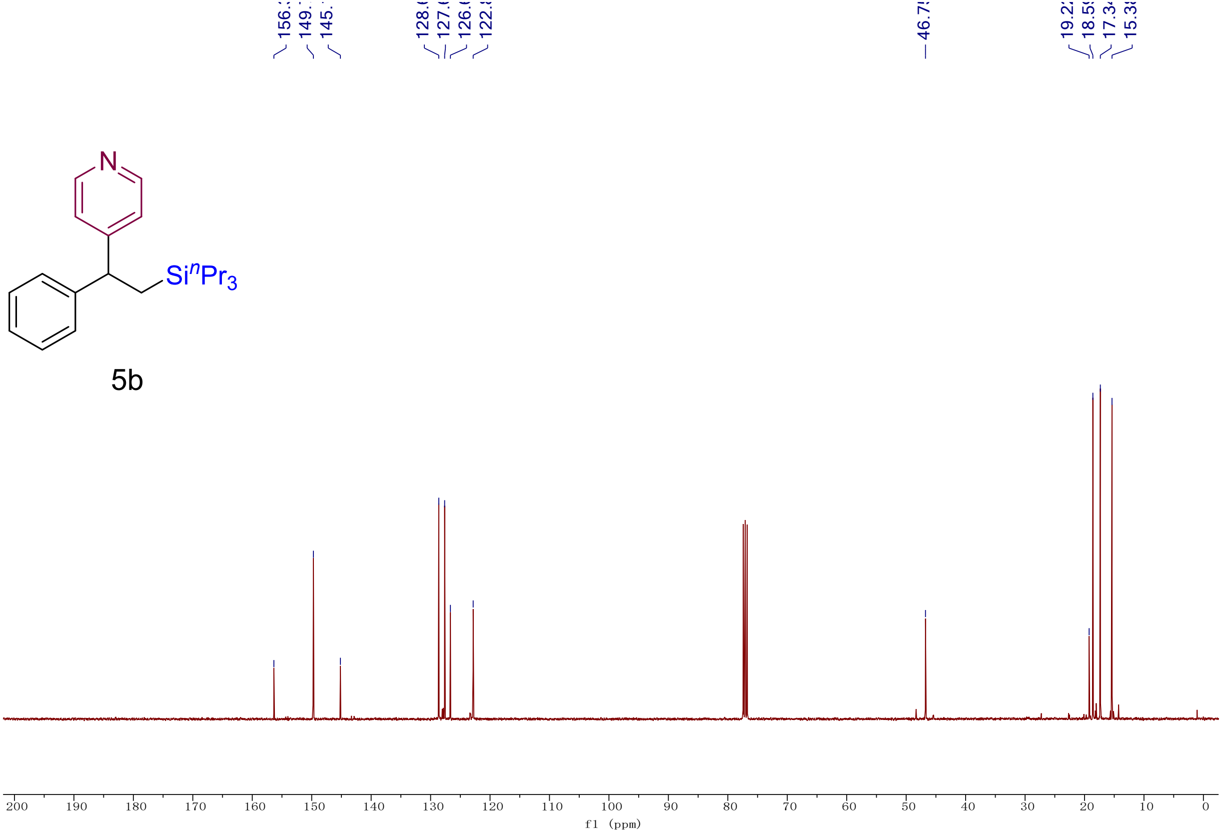
^{13}C NMR spectra of compound **5a** (101 MHz, CDCl$_3$)



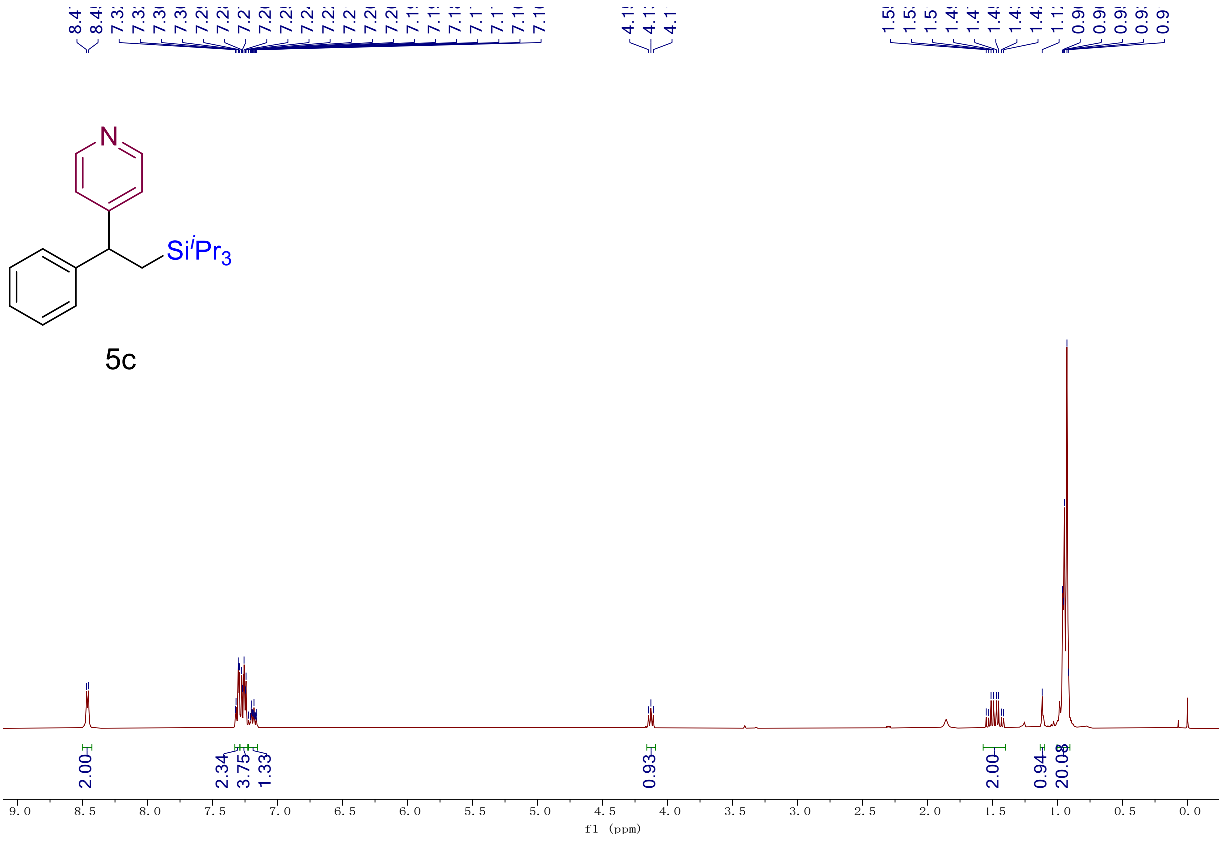
^{1}H NMR spectra of compound **5b** (400 MHz, CDCl$_3$)



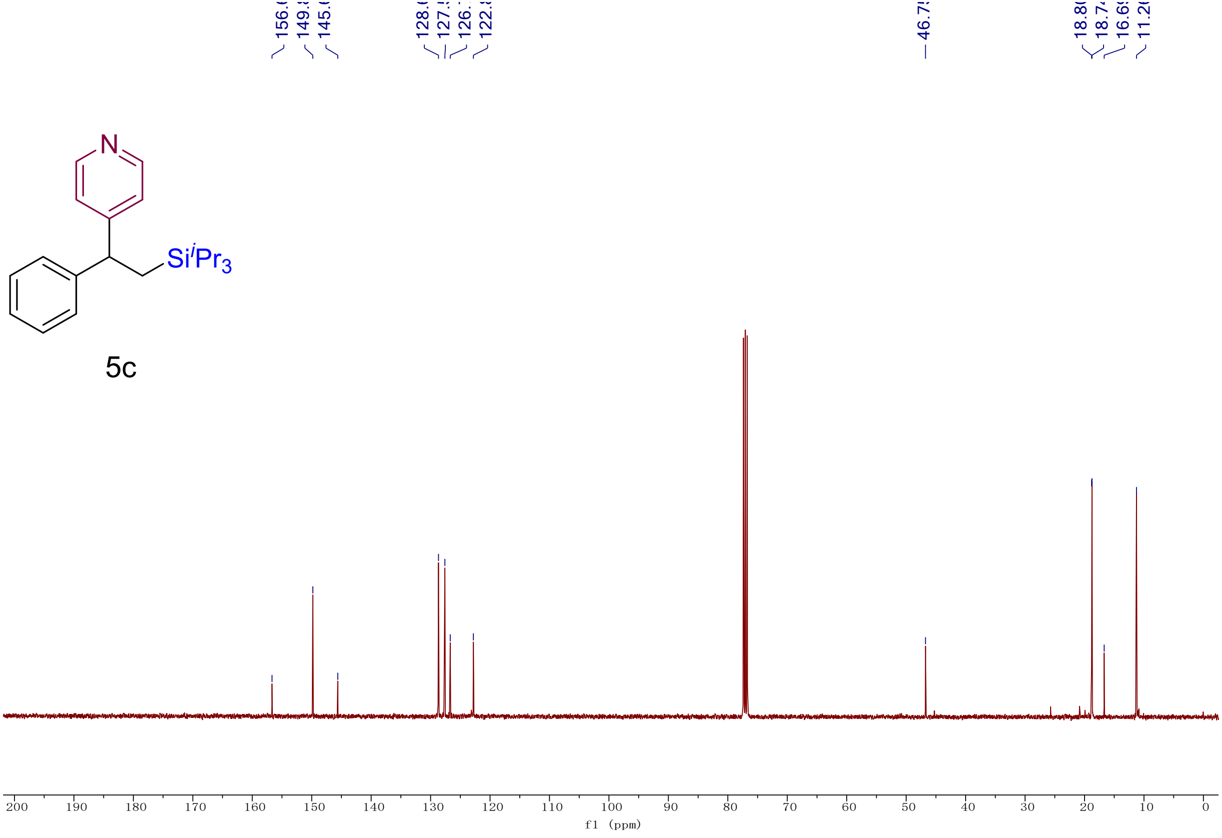
^{13}C NMR spectra of compound **5b** (101 MHz, CDCl$_3$)



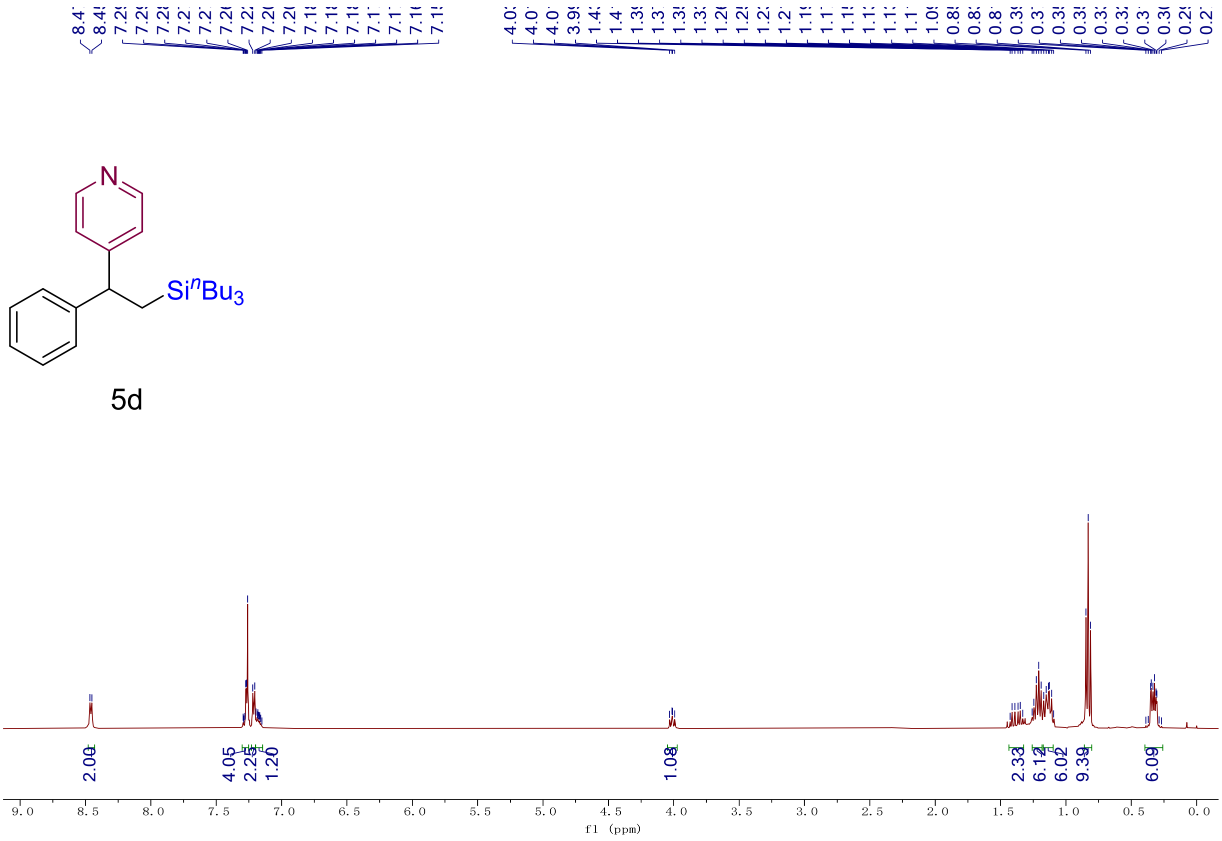
^{1}H NMR spectra of compound **5c** (400 MHz, CDCl$_3$)



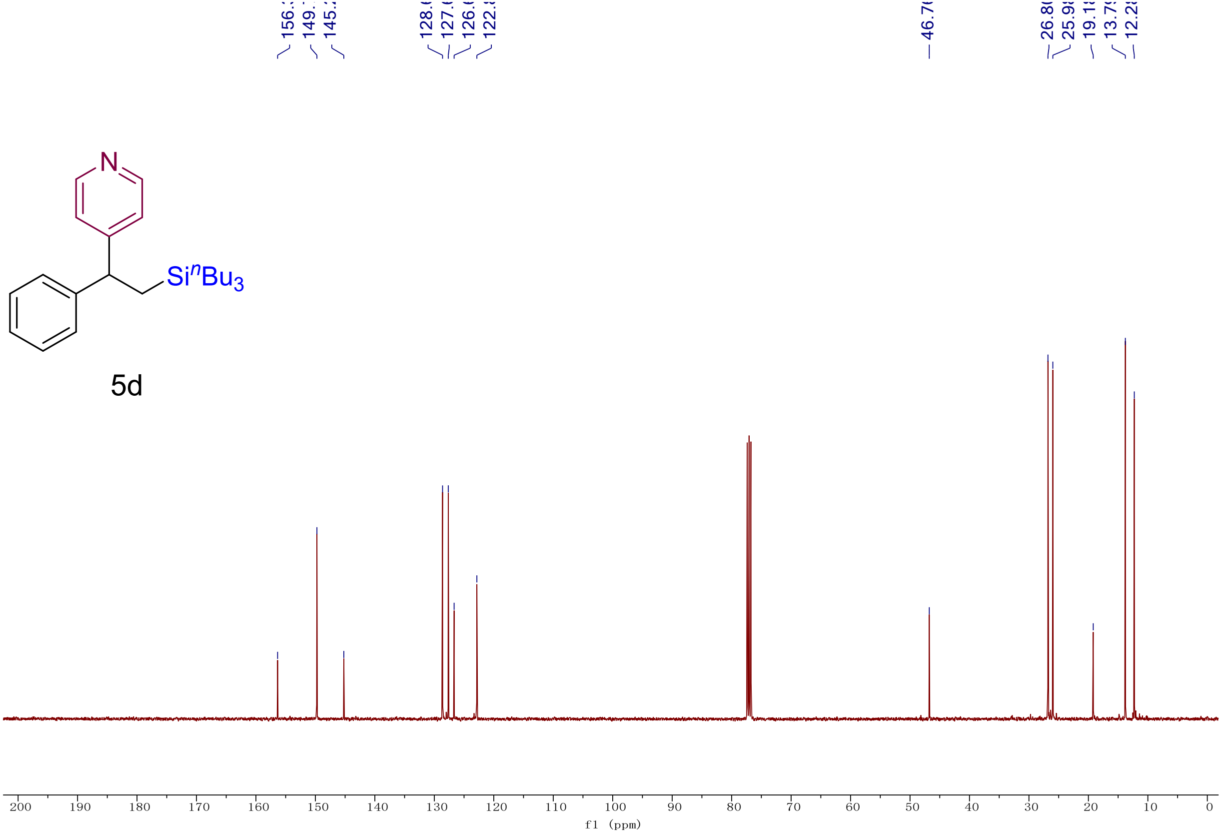
^{13}C NMR spectra of compound **5c** (101 MHz, CDCl$_3$)



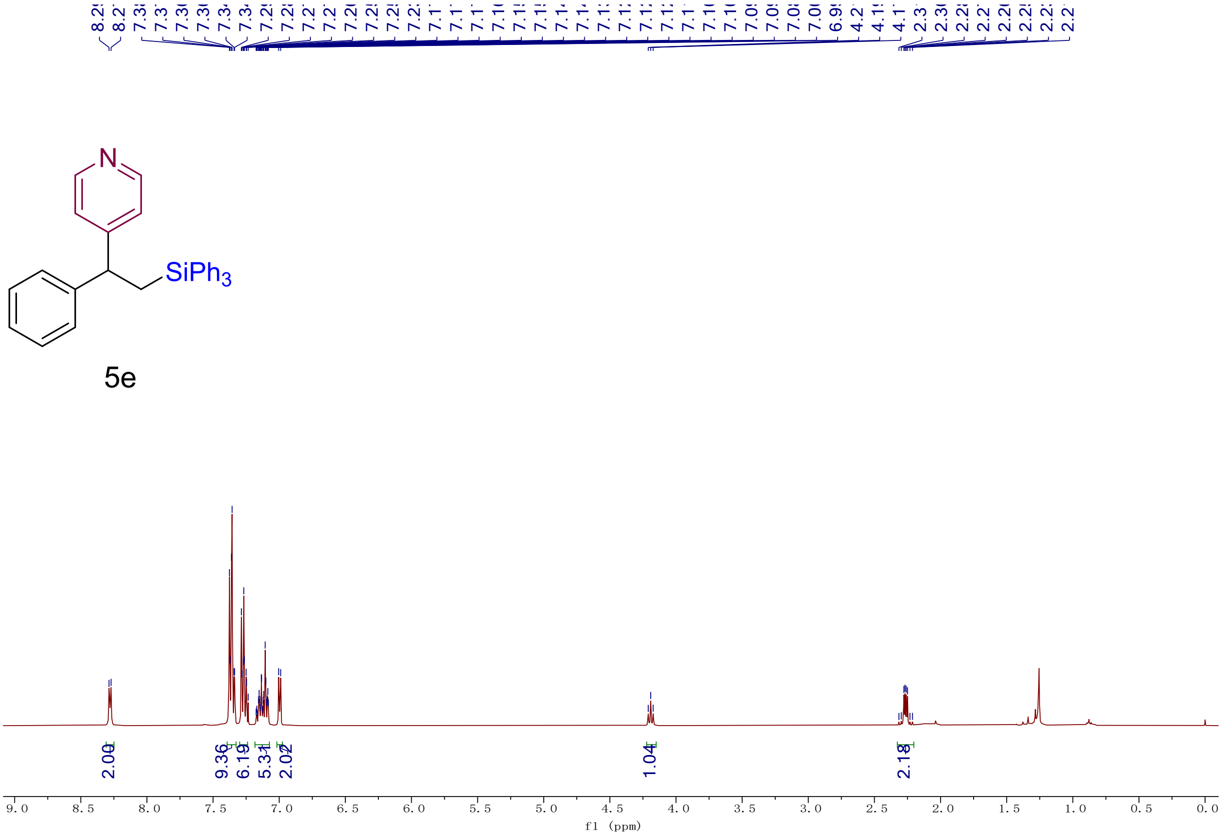
^{1}H NMR spectra of compound **5d** (400 MHz, CDCl$_3$)



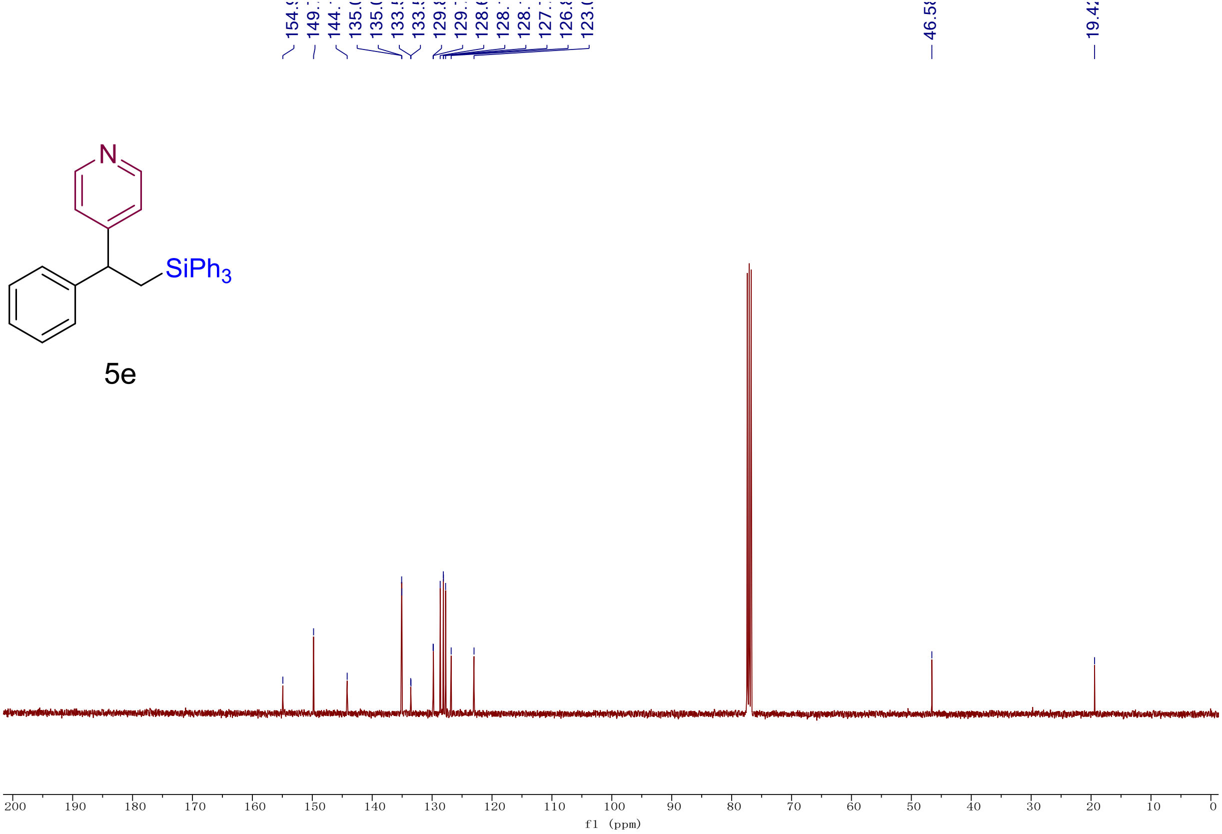
^{13}C NMR spectra of compound **5d** (101 MHz, $CDCl_3$)



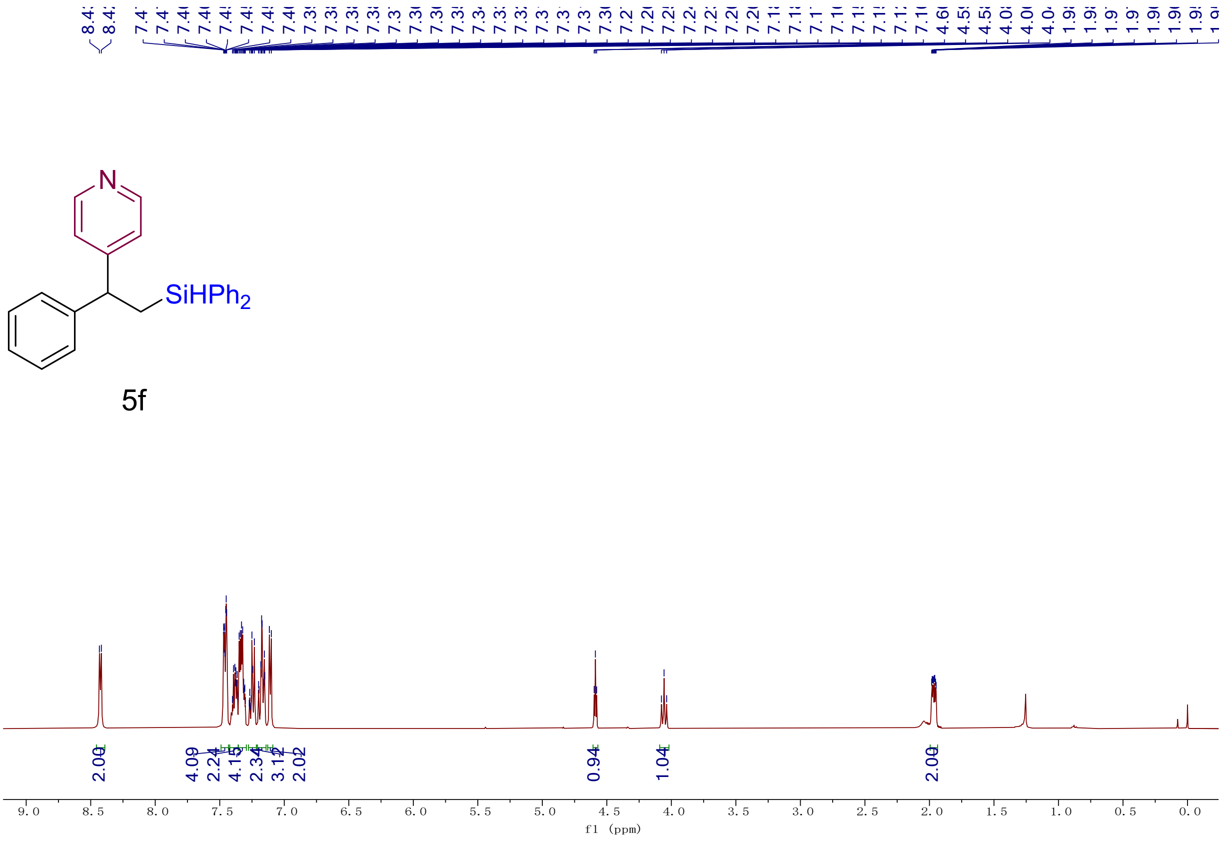
^{1}H NMR spectra of compound **5e** (400 MHz, $CDCl_3$)



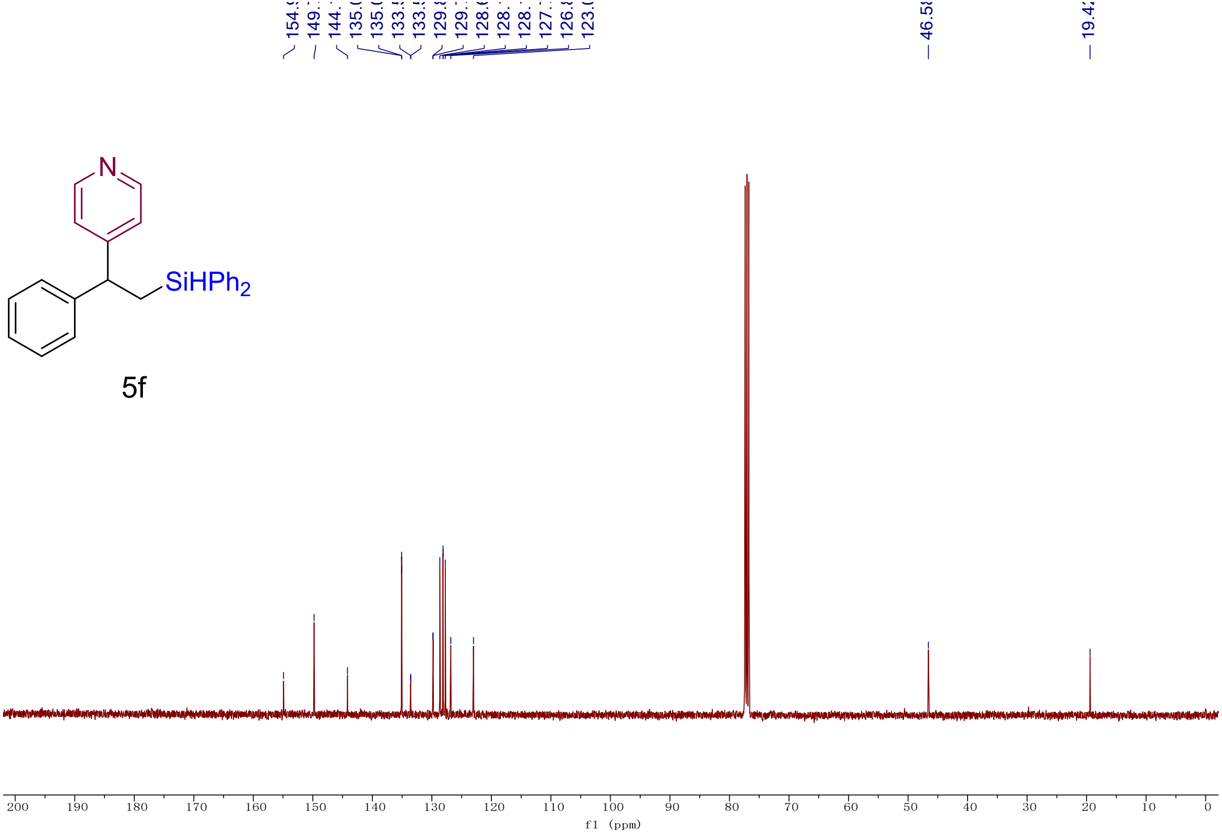
^{13}C NMR spectra of compound **5e** (101 MHz, $CDCl_3$)



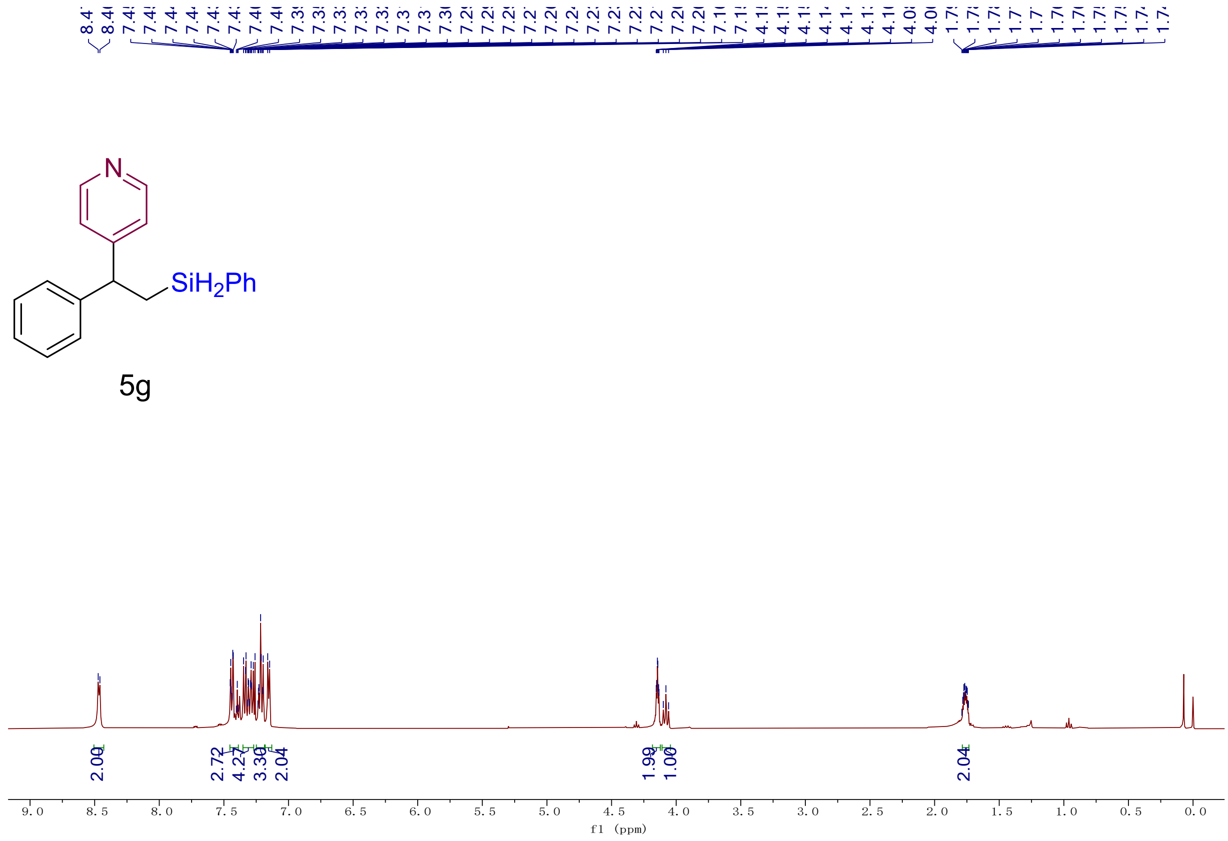
^{1}H NMR spectra of compound **5f** (400 MHz, $CDCl_3$)



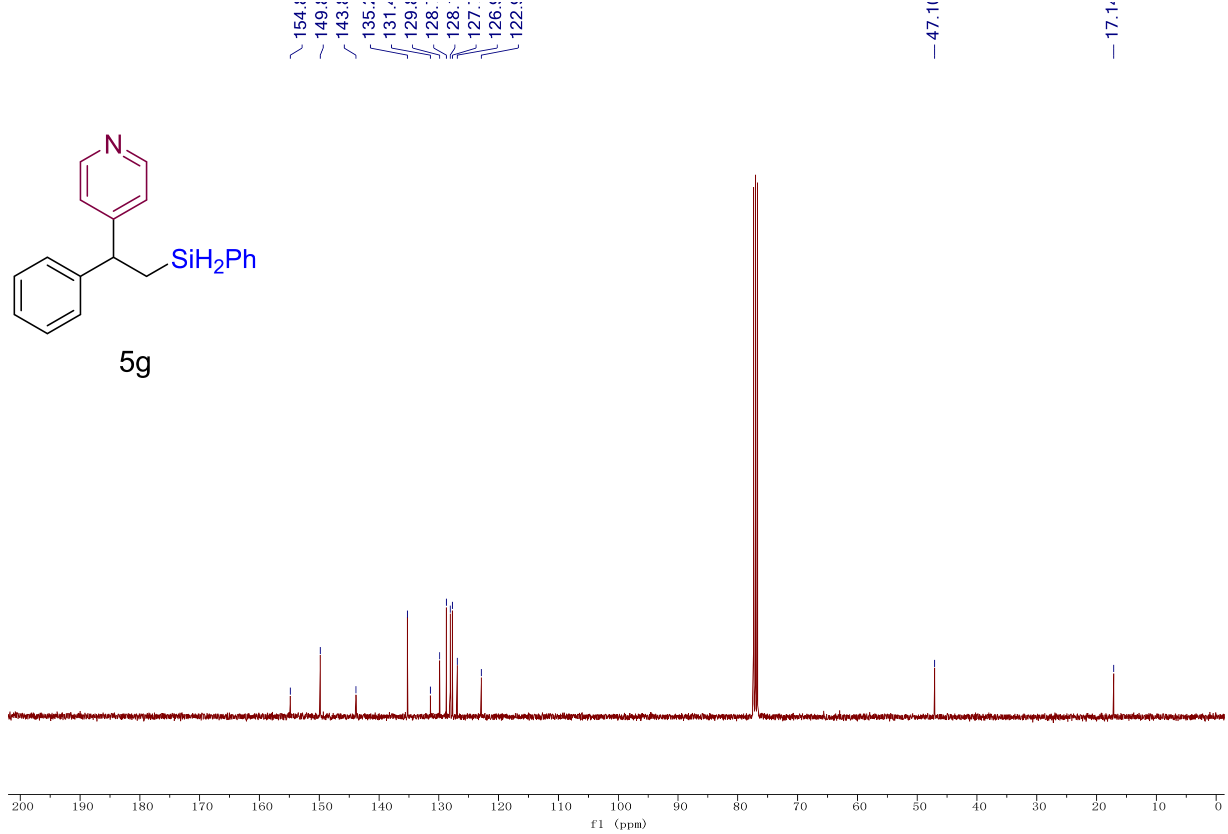
^{13}C NMR spectra of compound **5f** (101 MHz, $CDCl_3$)



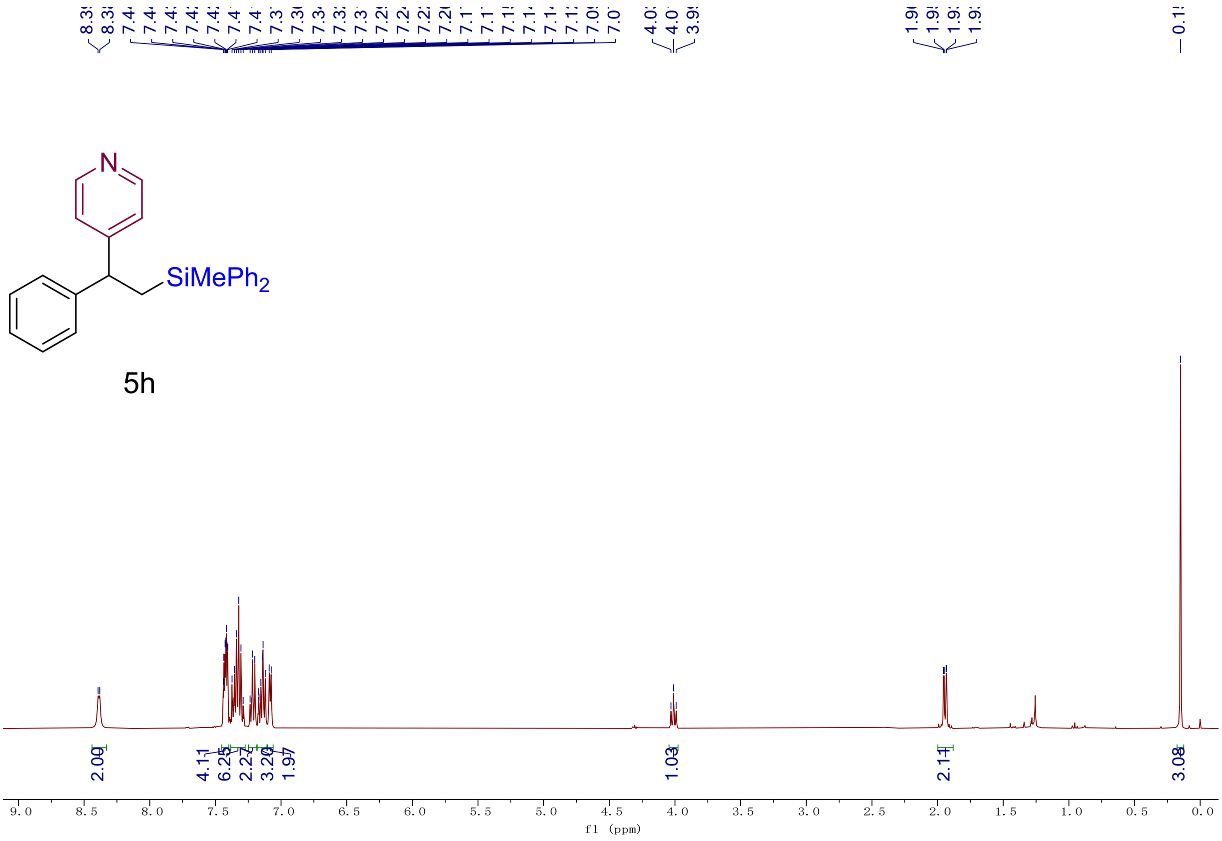
^{1}H NMR spectra of compound **5g** (400 MHz, $CDCl_3$)



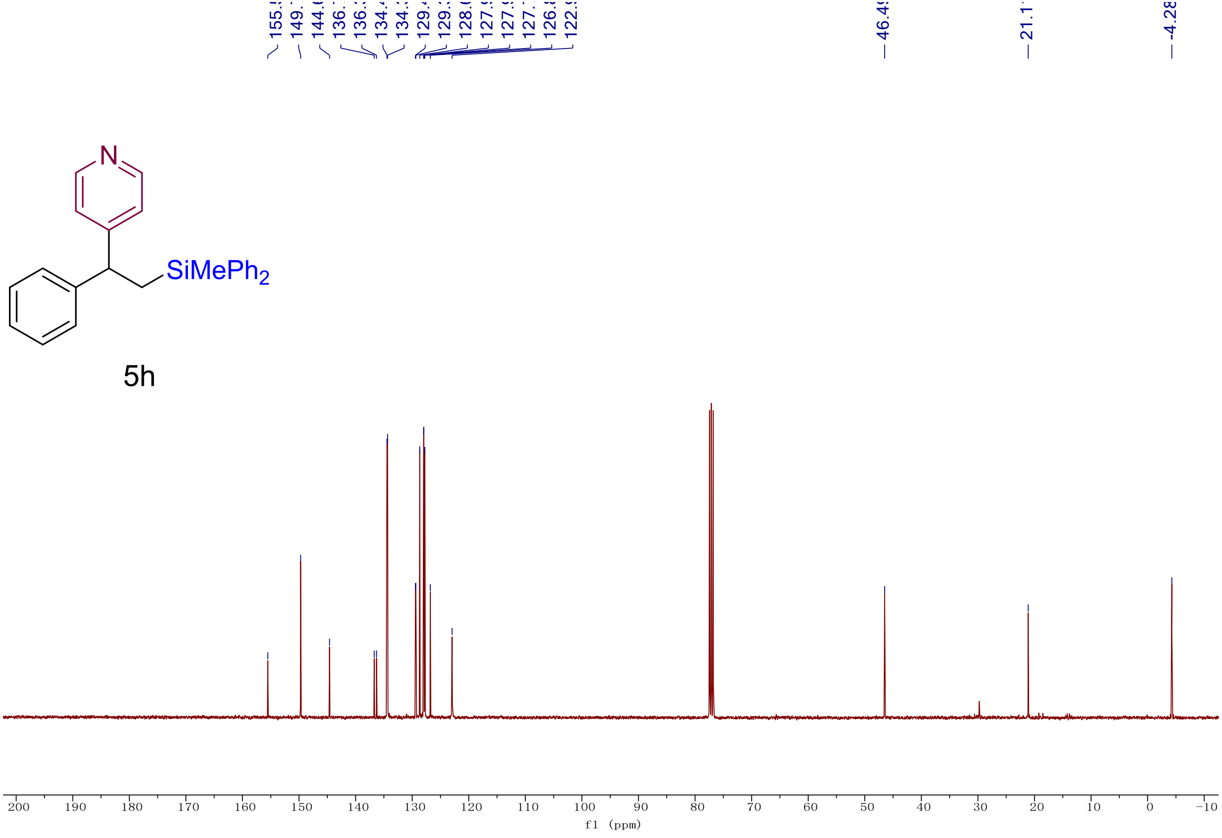
^{13}**C NMR** spectra of compound **5g** (101 MHz, $CDCl_3$)



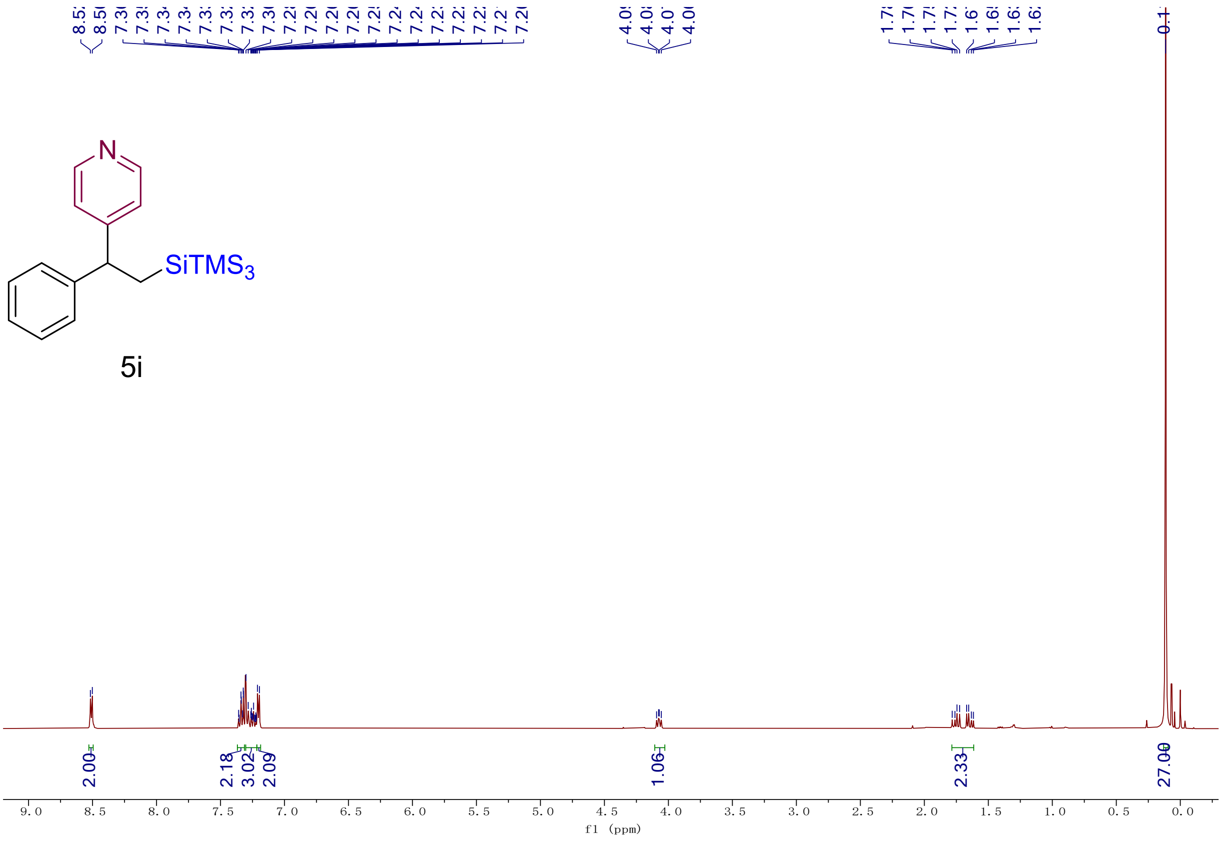
^{1}**H NMR** spectra of compound **5h** (400 MHz, $CDCl_3$)



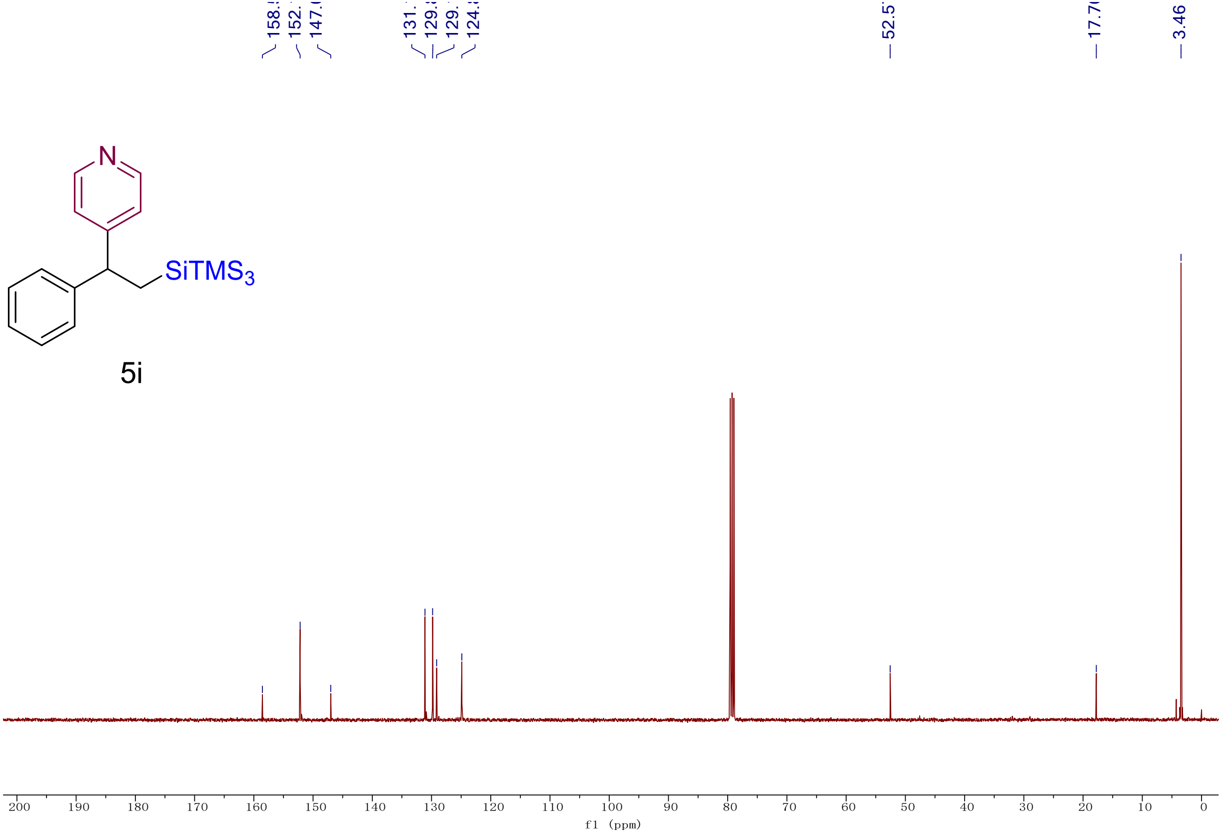
^{13}**C NMR** spectra of compound **5h** (101 MHz, $CDCl_3$)



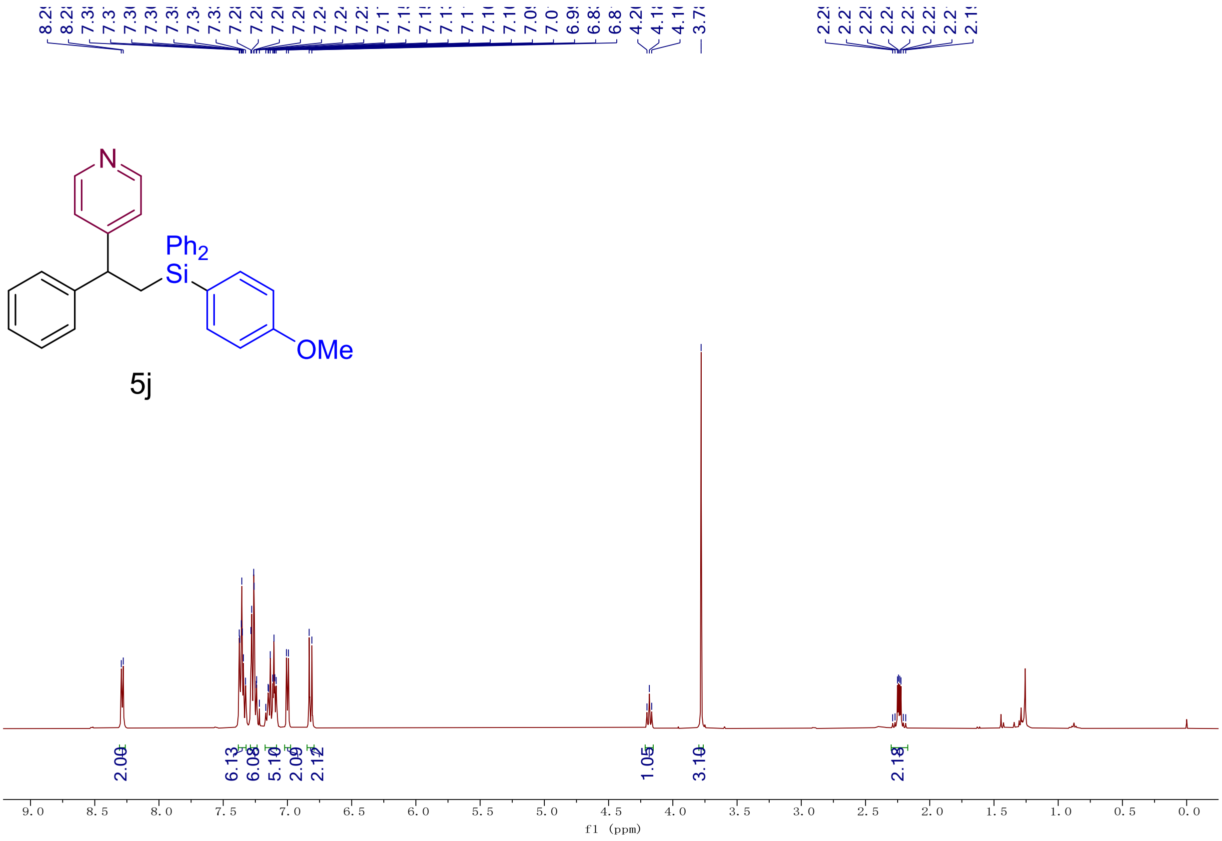
^{1}**H NMR** spectra of compound **5i** (400 MHz, $CDCl_3$)



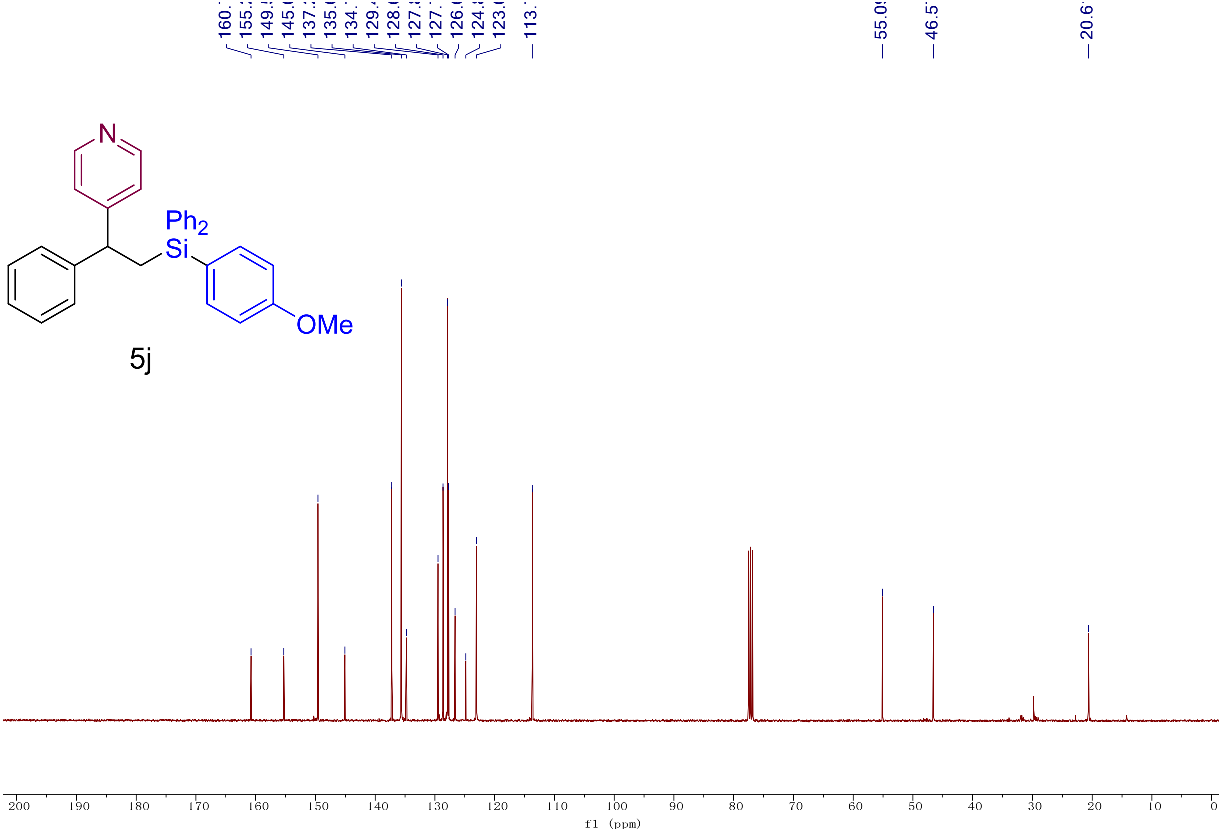
^{13}C NMR spectra of compound **5i** (101 MHz, CDCl$_3$)



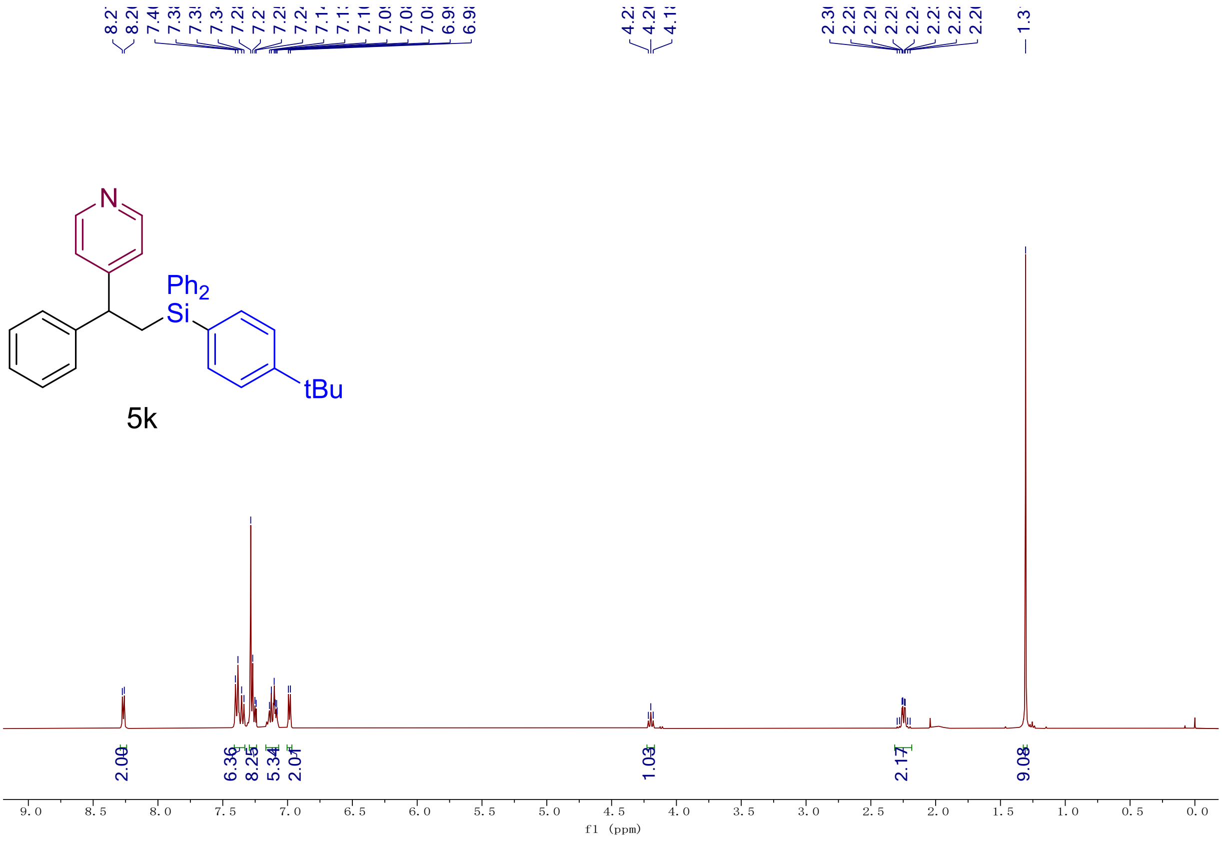
^{1}H NMR spectra of compound **5j** (400 MHz, CDCl$_3$)



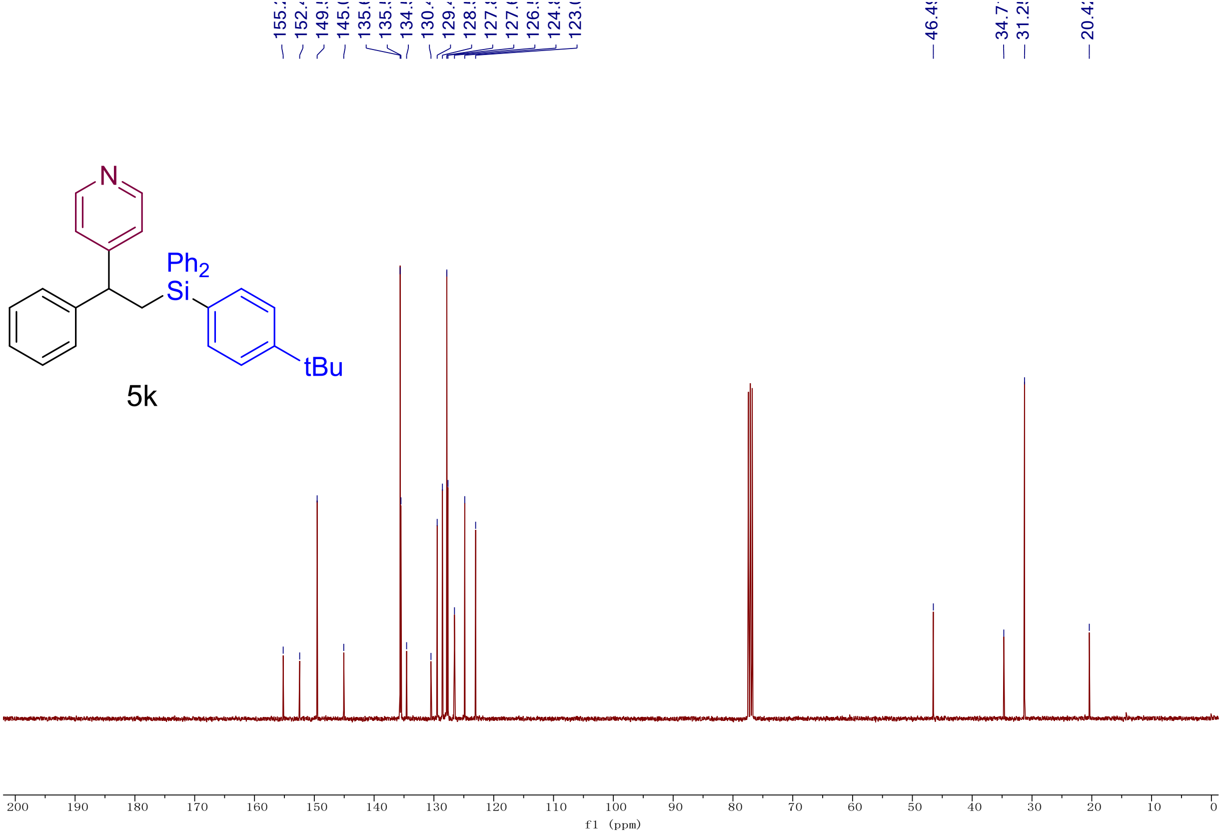
^{13}C NMR spectra of compound **5j** (101 MHz, $CDCl_3$)



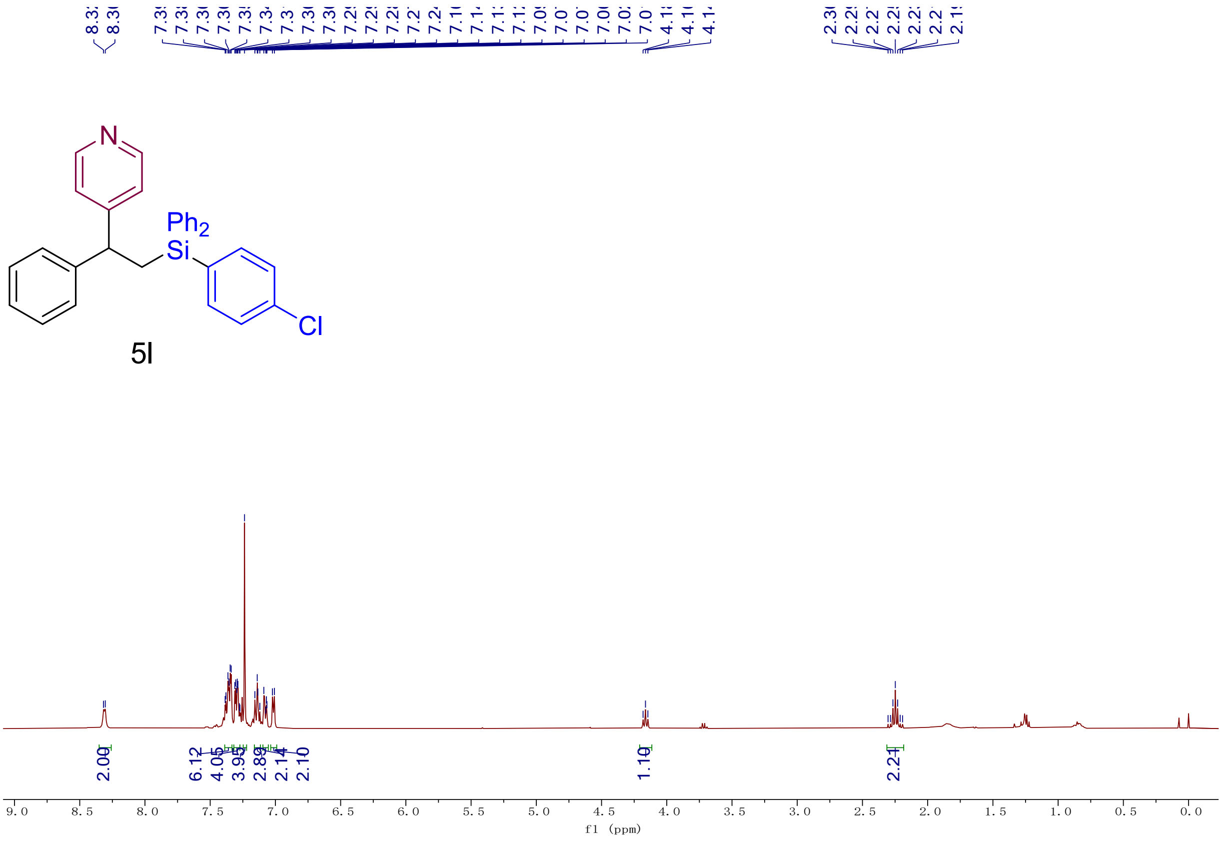
^{1}H NMR spectra of compound **5k** (400 MHz, $CDCl_3$)



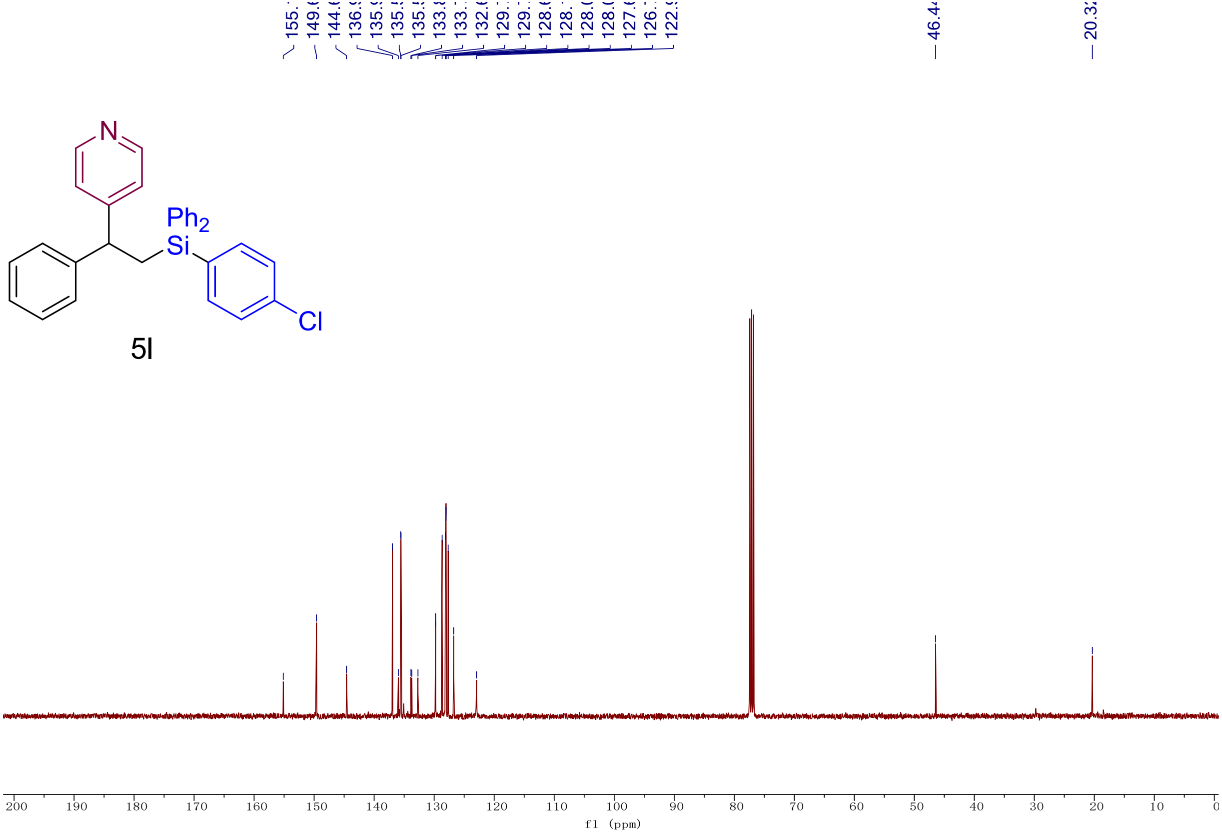
^{13}C NMR spectra of compound **5k** (101 MHz, $CDCl_3$)



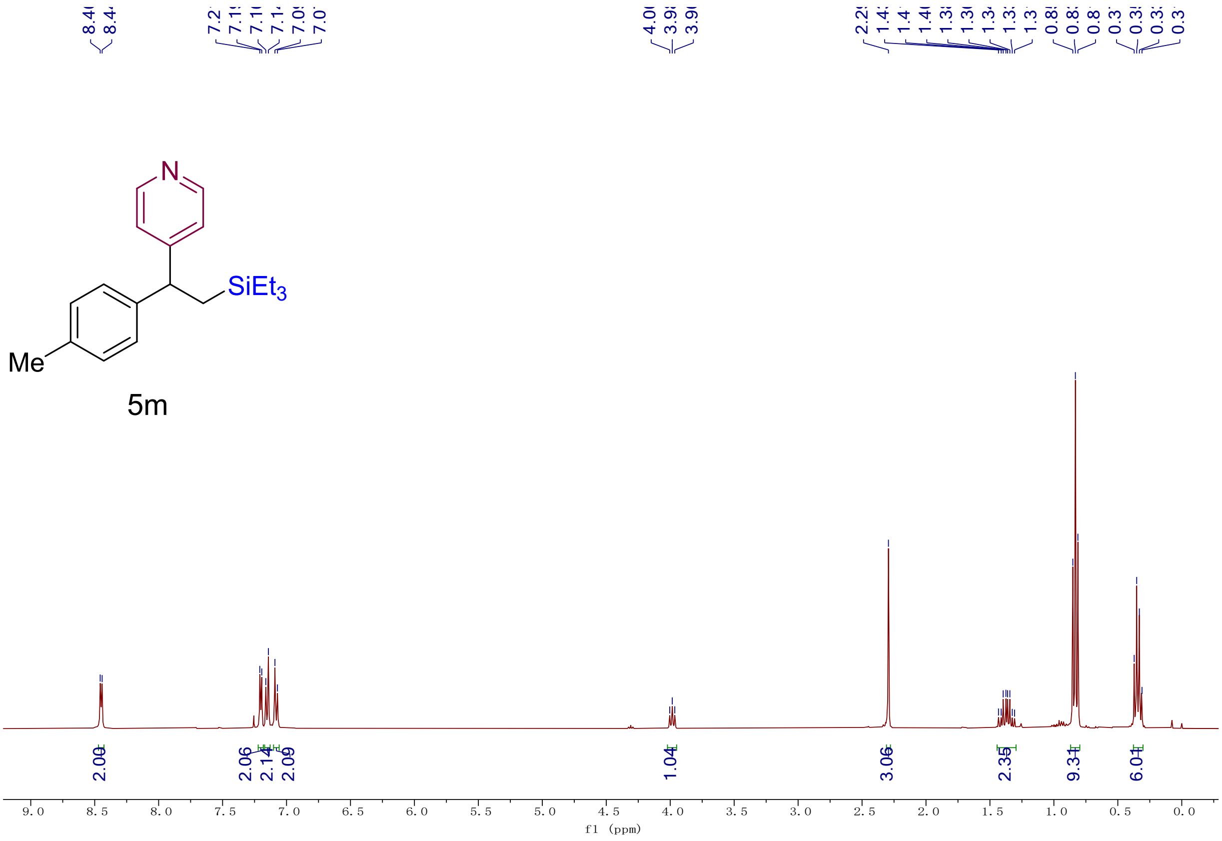
^{1}H NMR spectra of compound **5l** (400 MHz, $CDCl_3$)



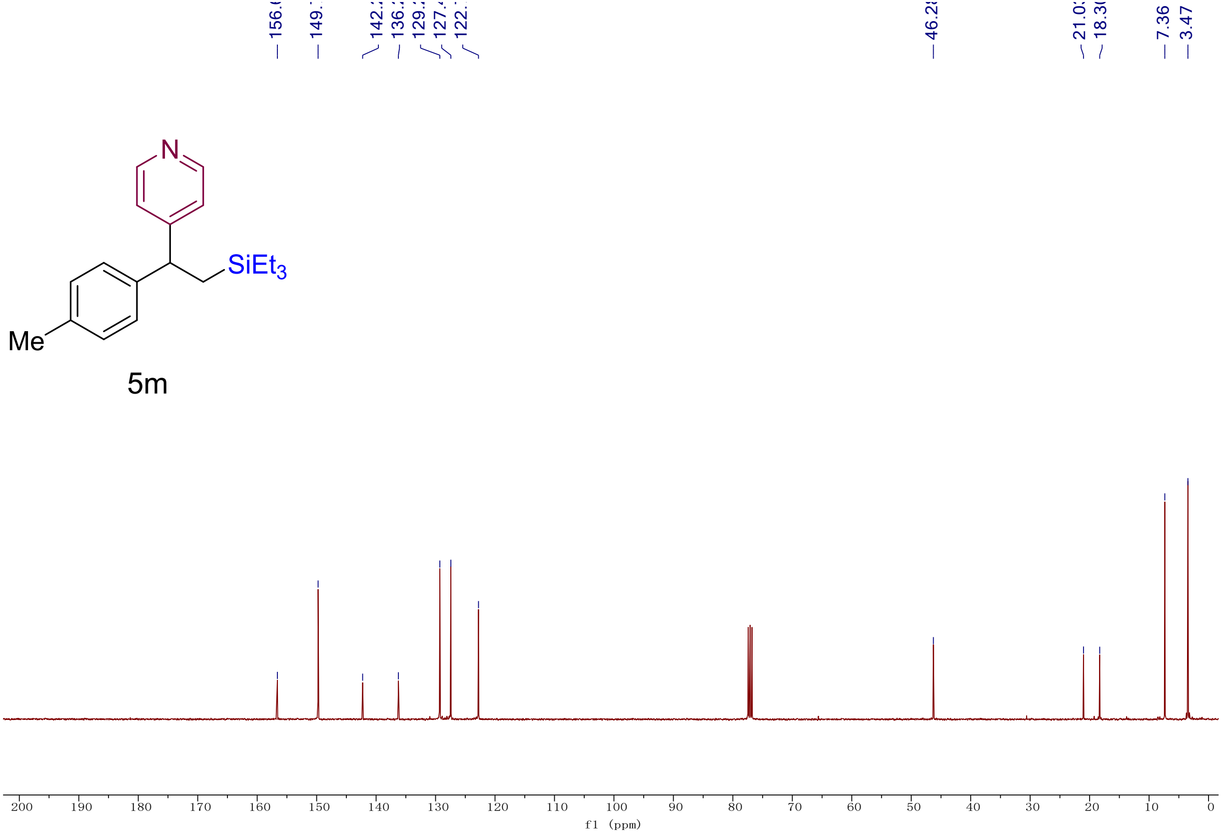
^{13}C NMR spectra of compound **5l** (101 MHz, $CDCl_3$)



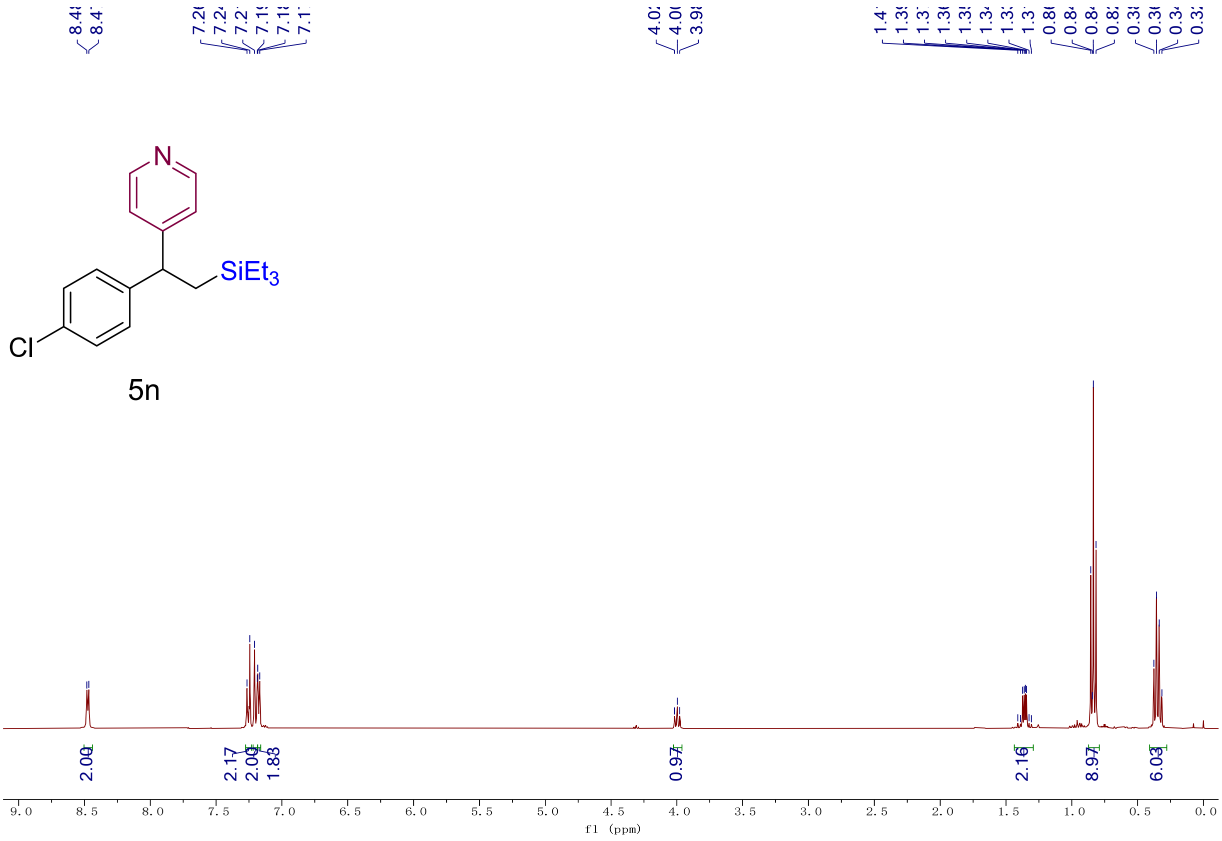
^{1}H NMR spectra of compound **5m** (400 MHz, $CDCl_3$)



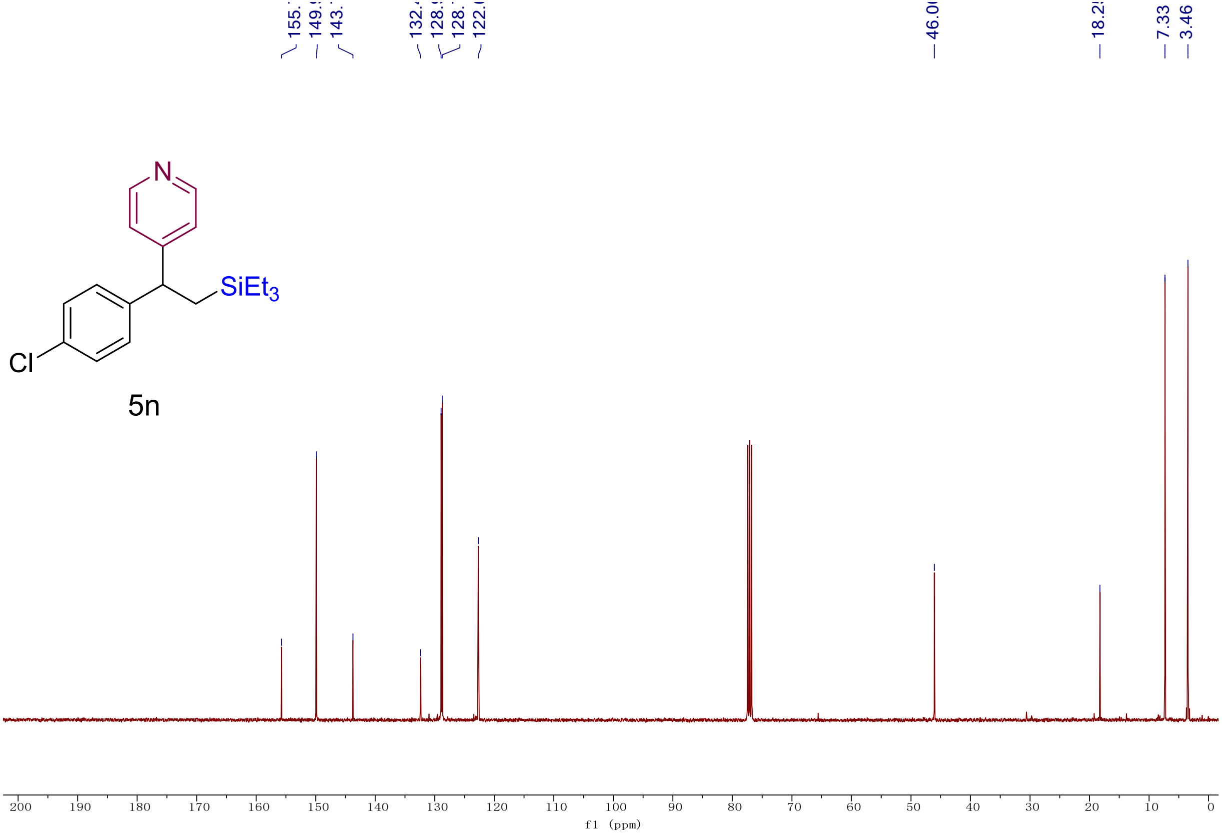
^{13}C NMR spectra of compound **5m** (101 MHz, CDCl$_3$)



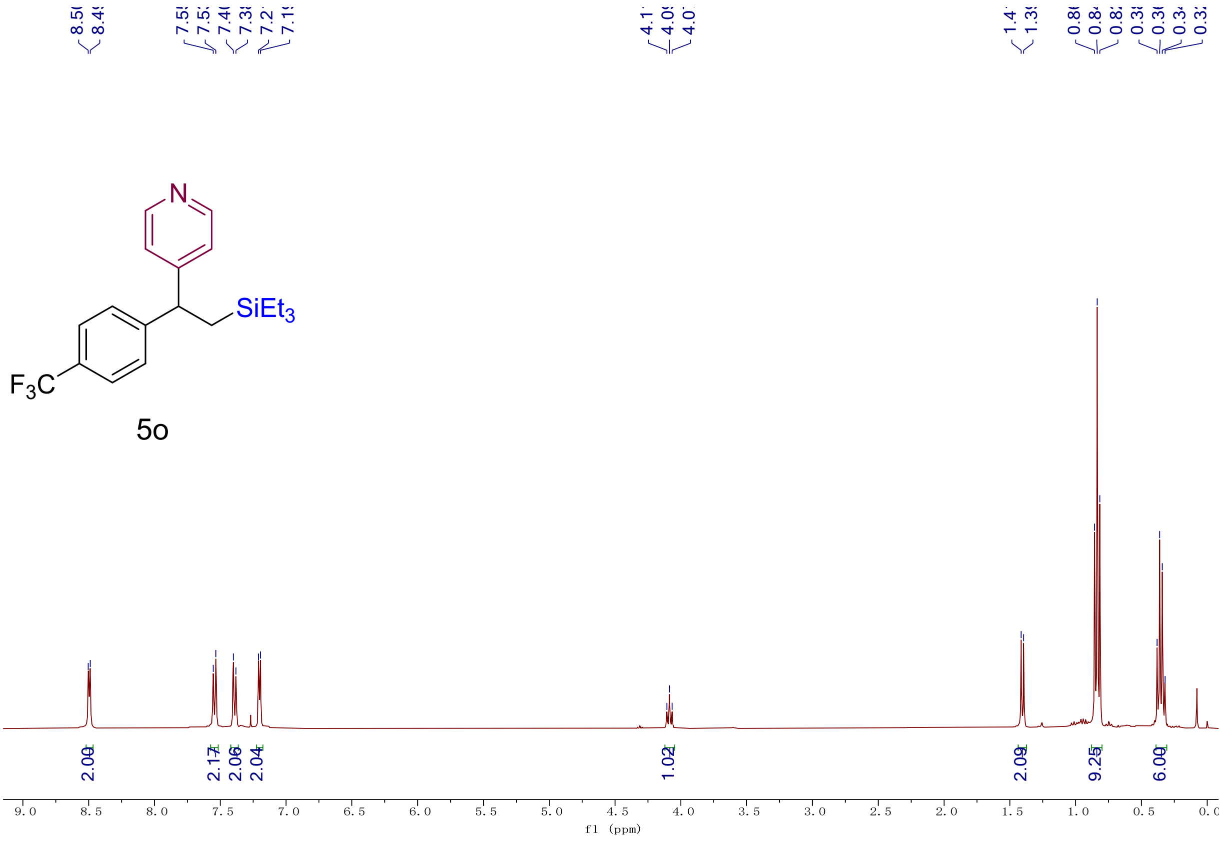
^{1}H NMR spectra of compound **5n** (400 MHz, CDCl$_3$)



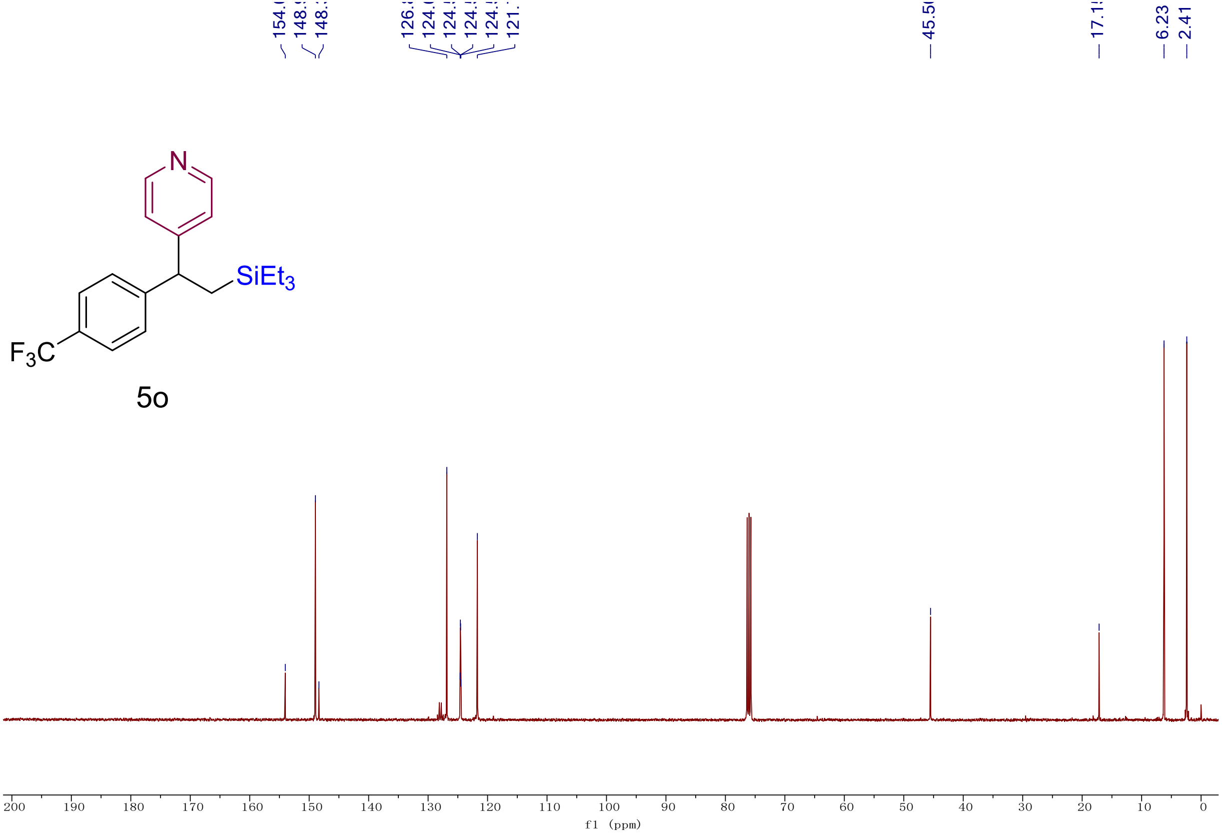
^{13}C NMR spectra of compound **5n** (101 MHz, CDCl$_3$)



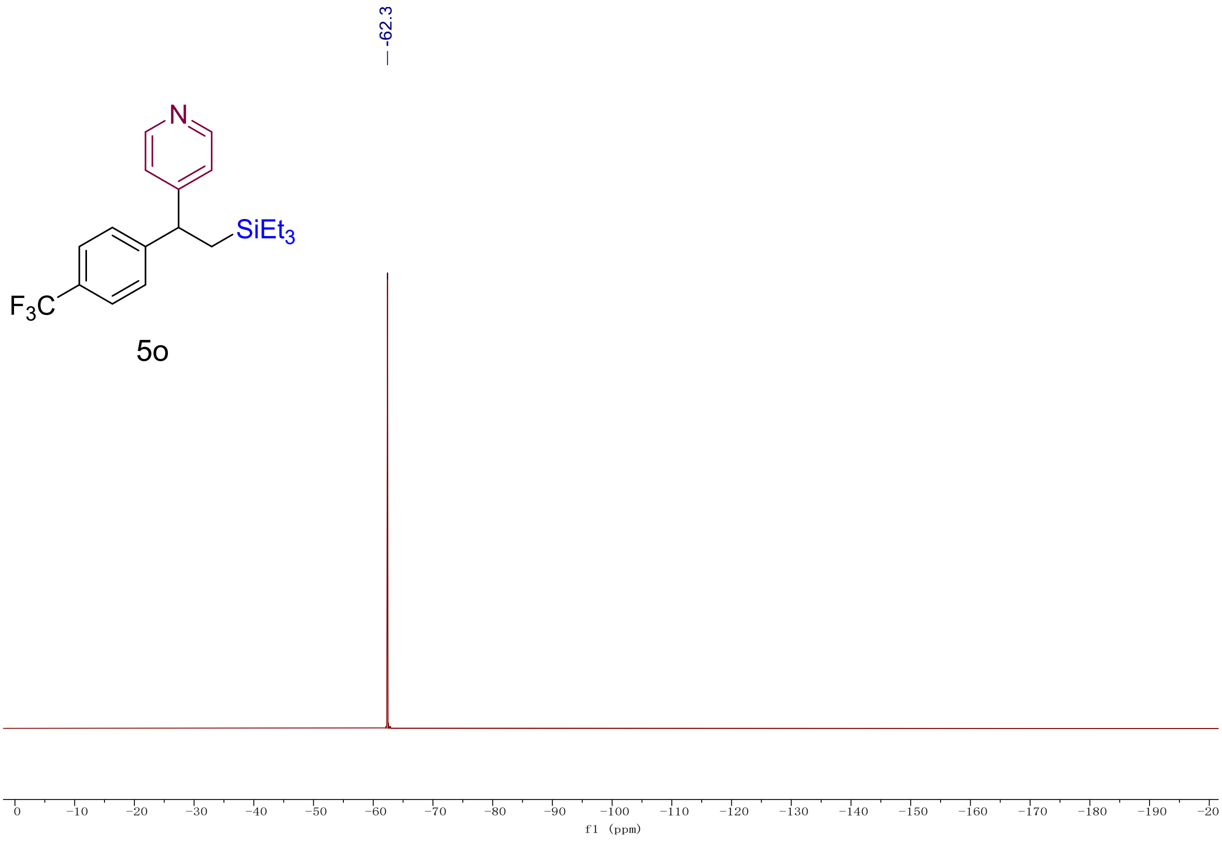
^{1}H NMR spectra of compound **5o** (400 MHz, CDCl$_3$)



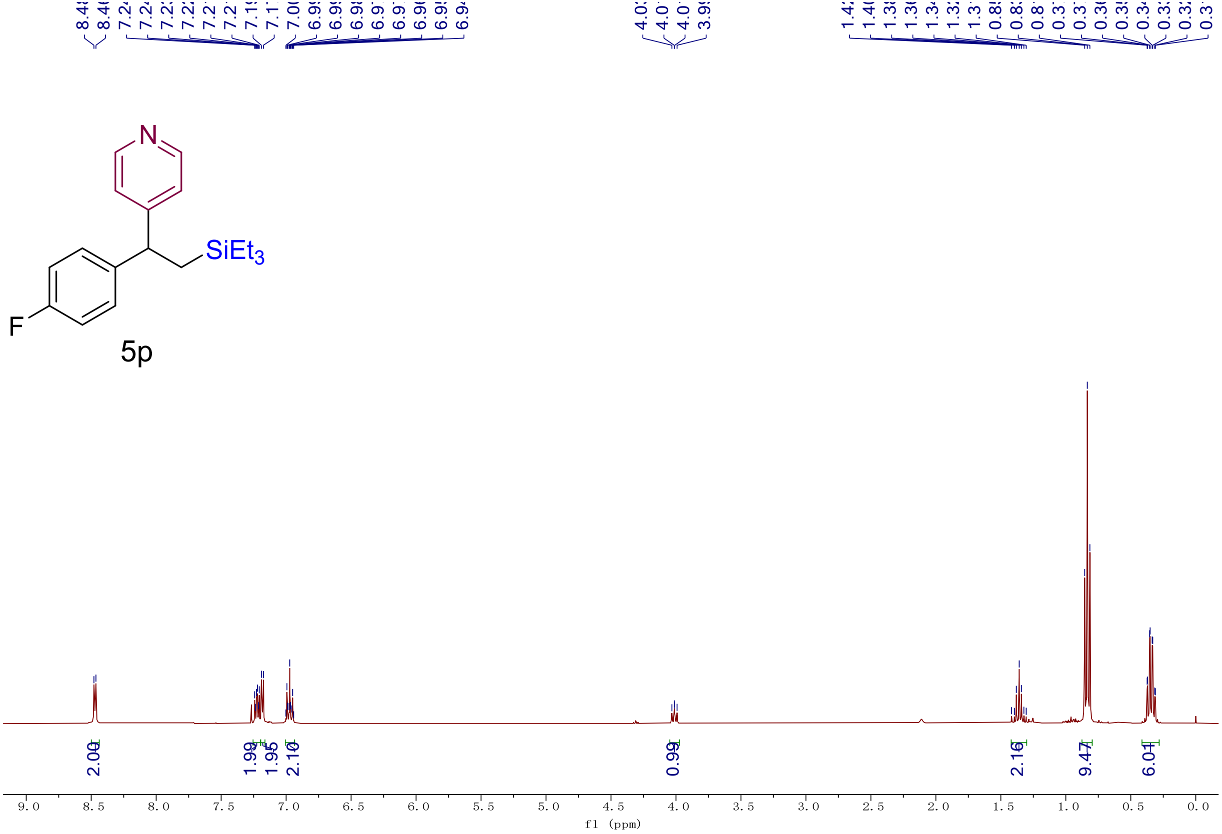
^{13}**C NMR** spectra of compound **5o** (101 MHz, $CDCl_3$)



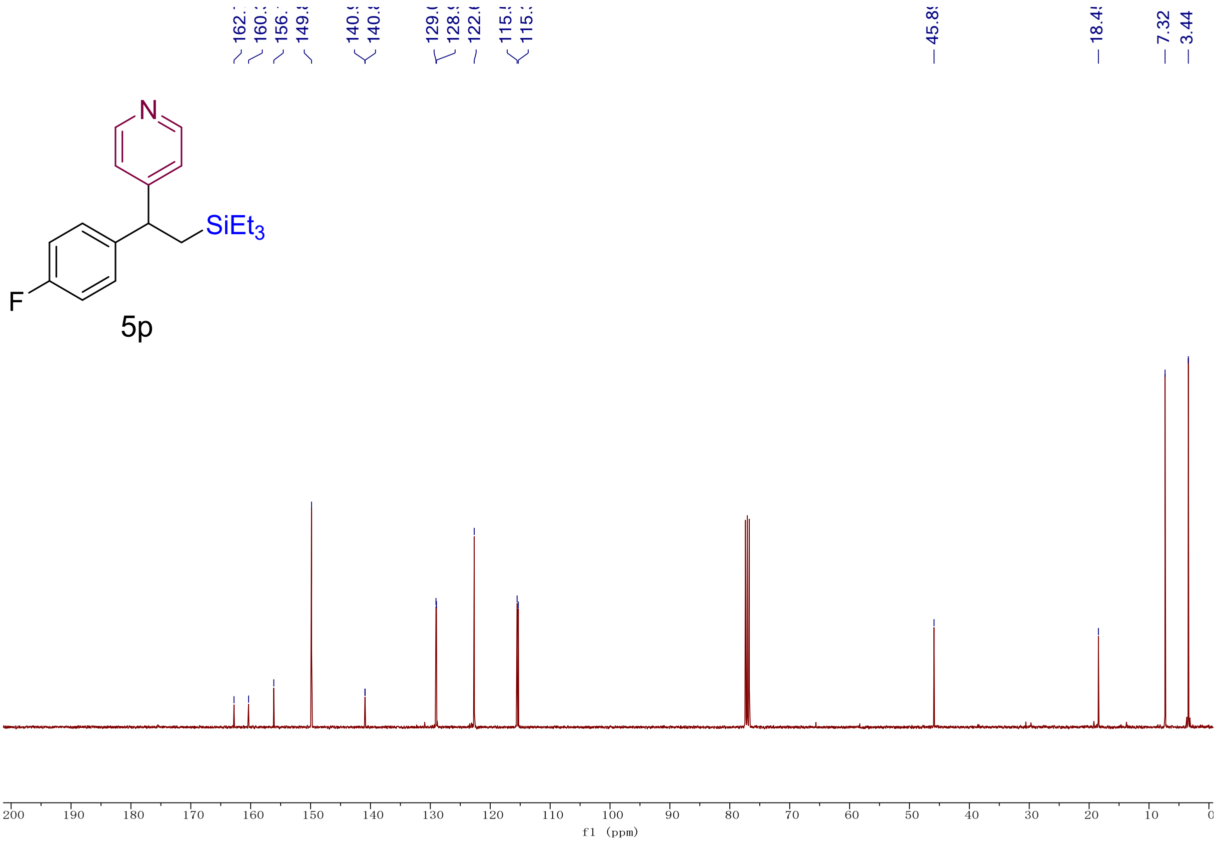
^{19}**F NMR** spectra of compound **5o** (376 MHz, $CDCl_3$)



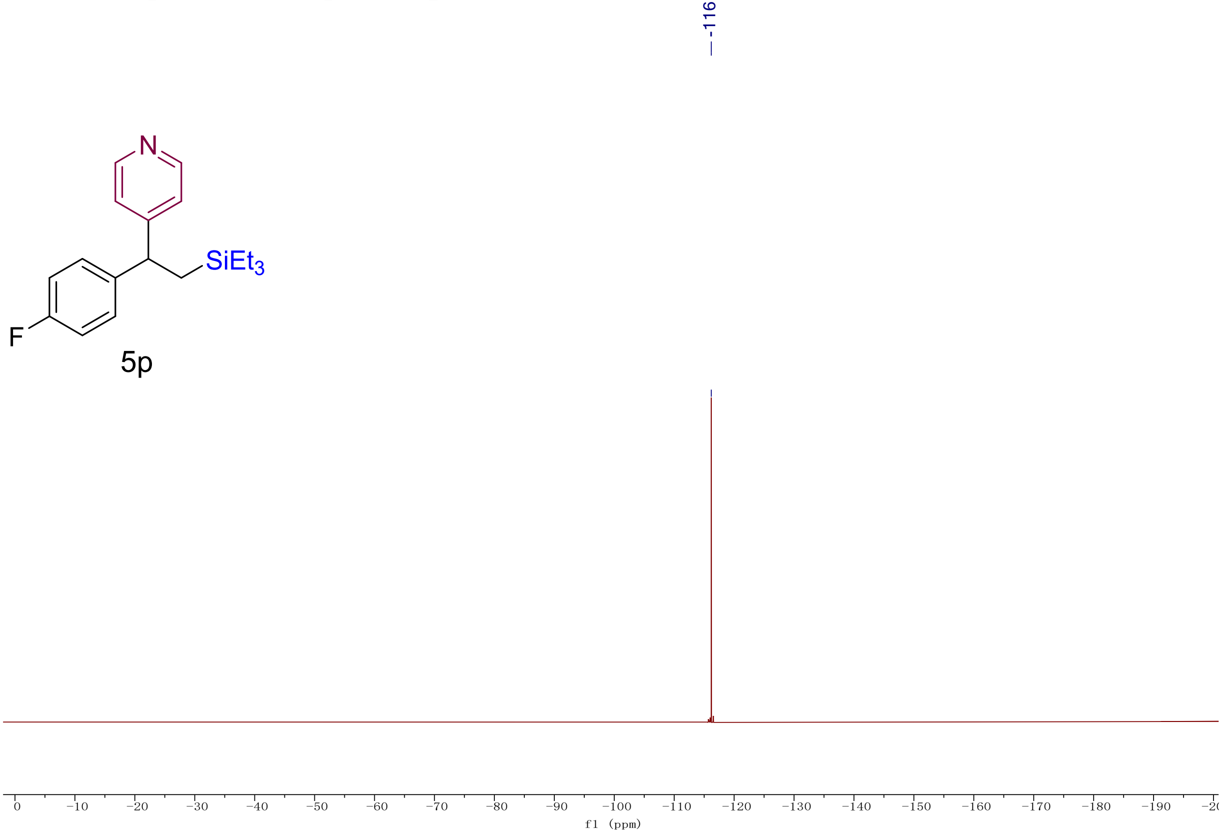
^{1}H NMR spectra of compound **5p** (400 MHz, $CDCl_3$)



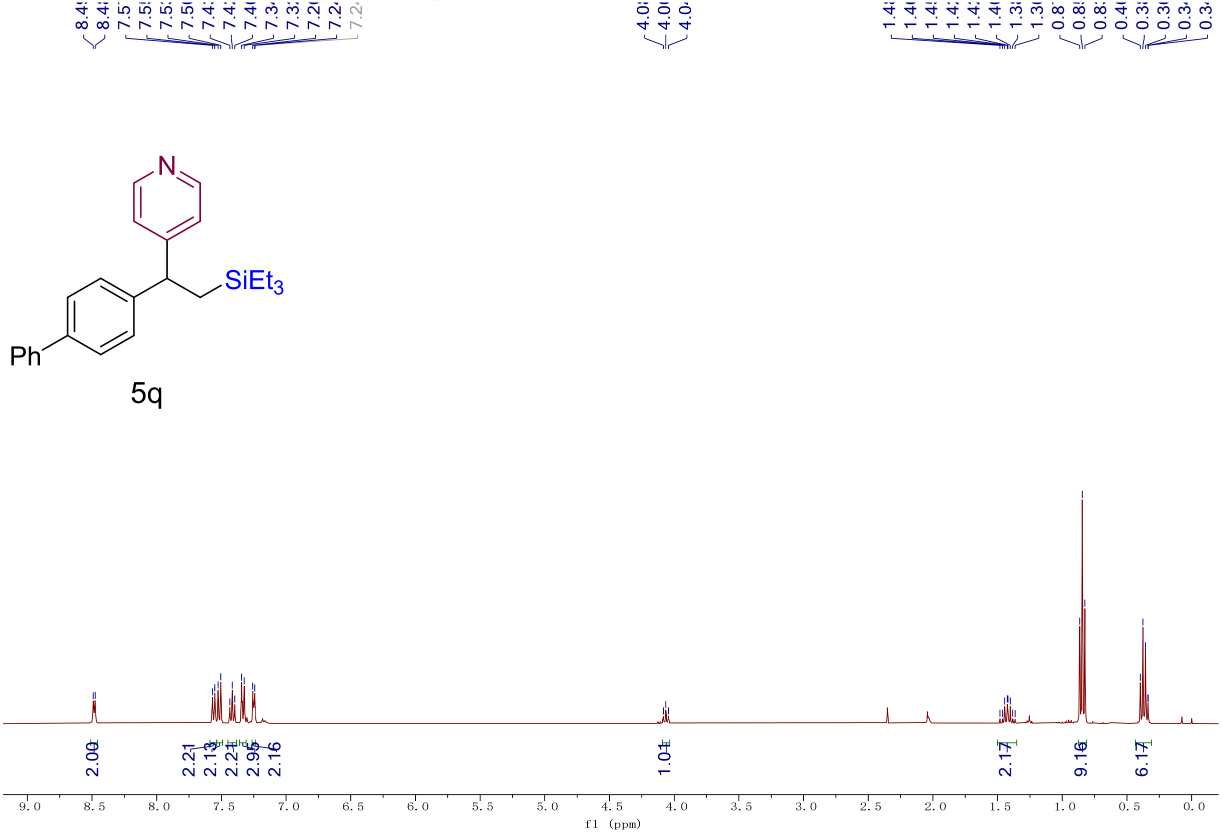
^{13}C NMR spectra of compound **5p** (101 MHz, $CDCl_3$)



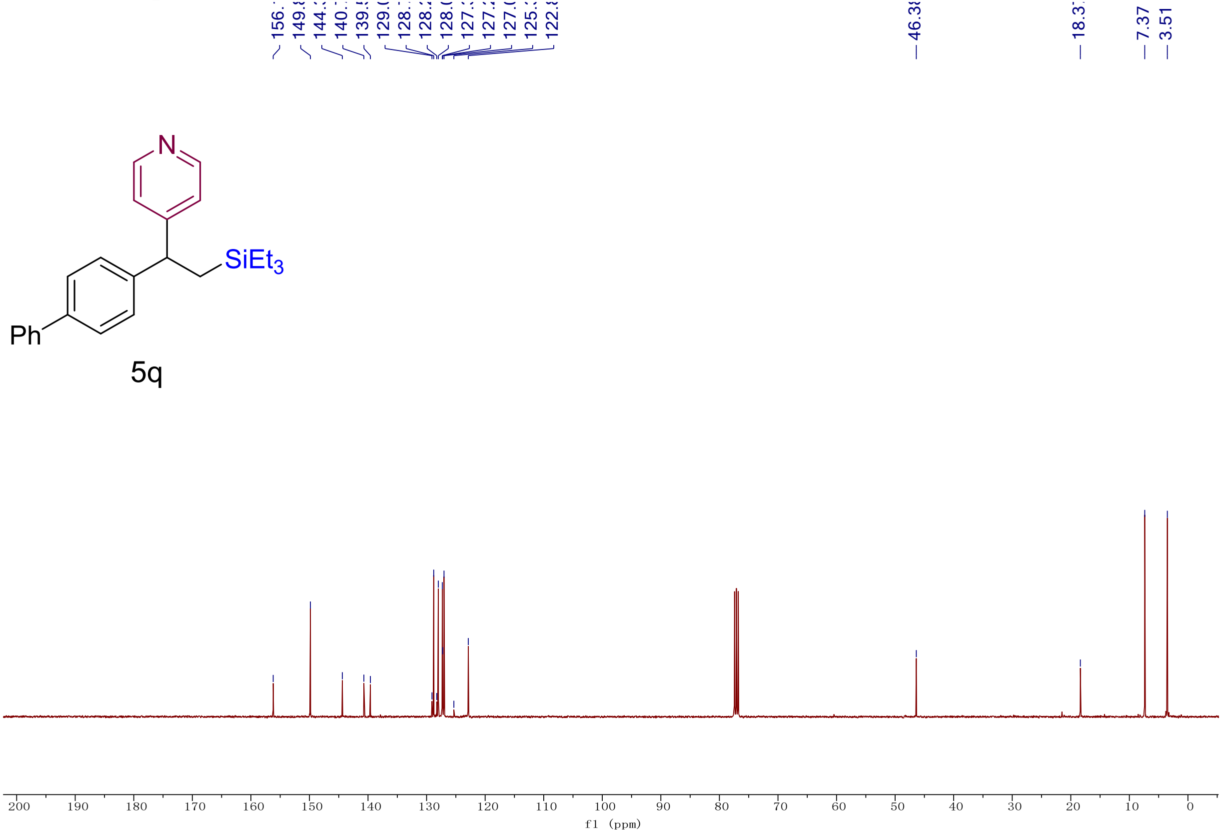
^{19}**F NMR** spectra of compound **5p** (376 MHz, $CDCl_3$)



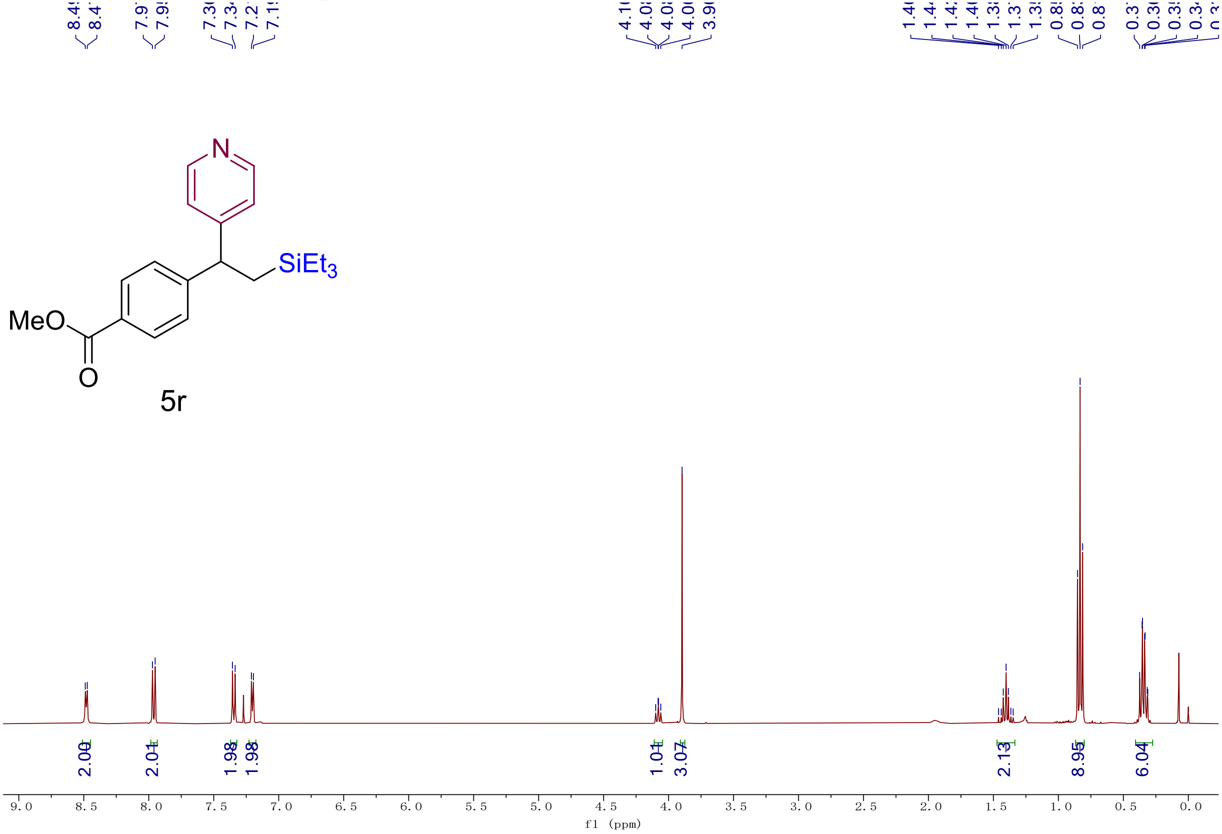
^{1}**H NMR** spectra of compound **5q** (400 MHz, CDCl$_3$)



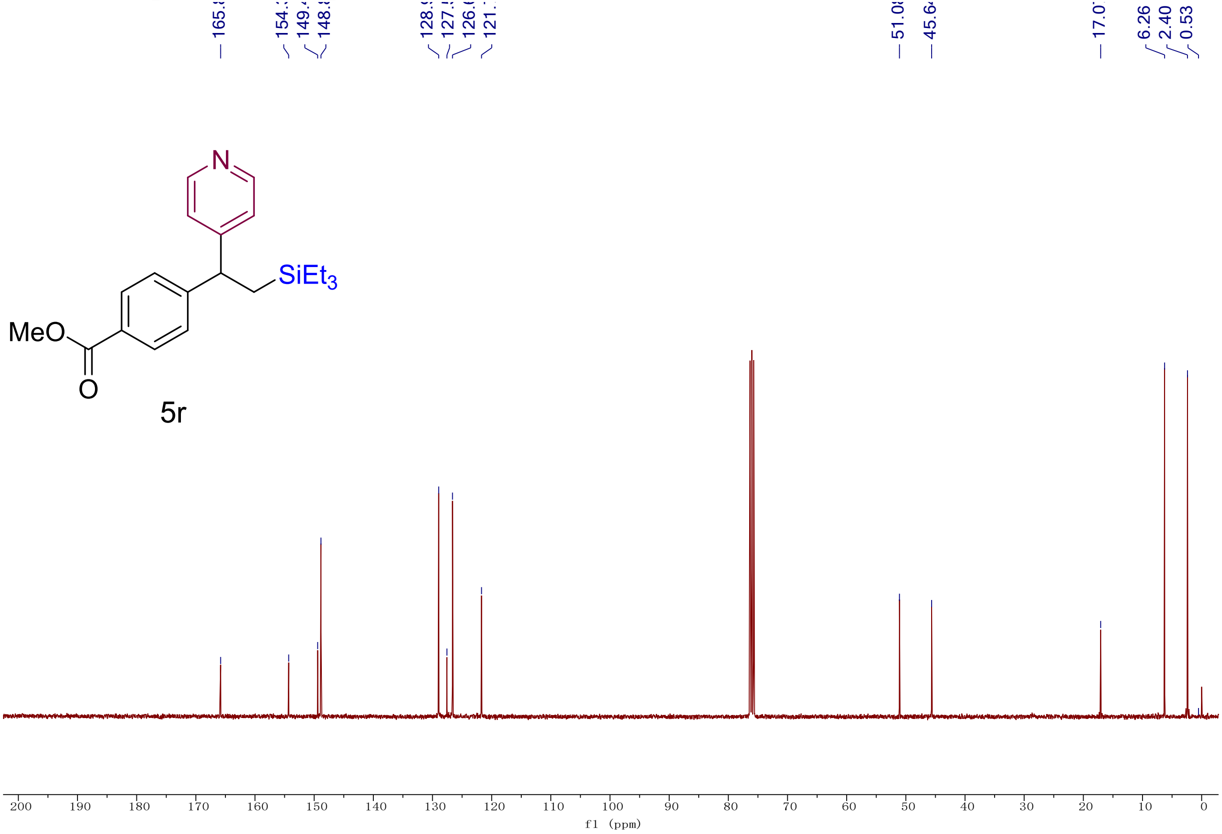
^{13}**C NMR** spectra of compound **5q** (101 MHz, CDCl$_3$)



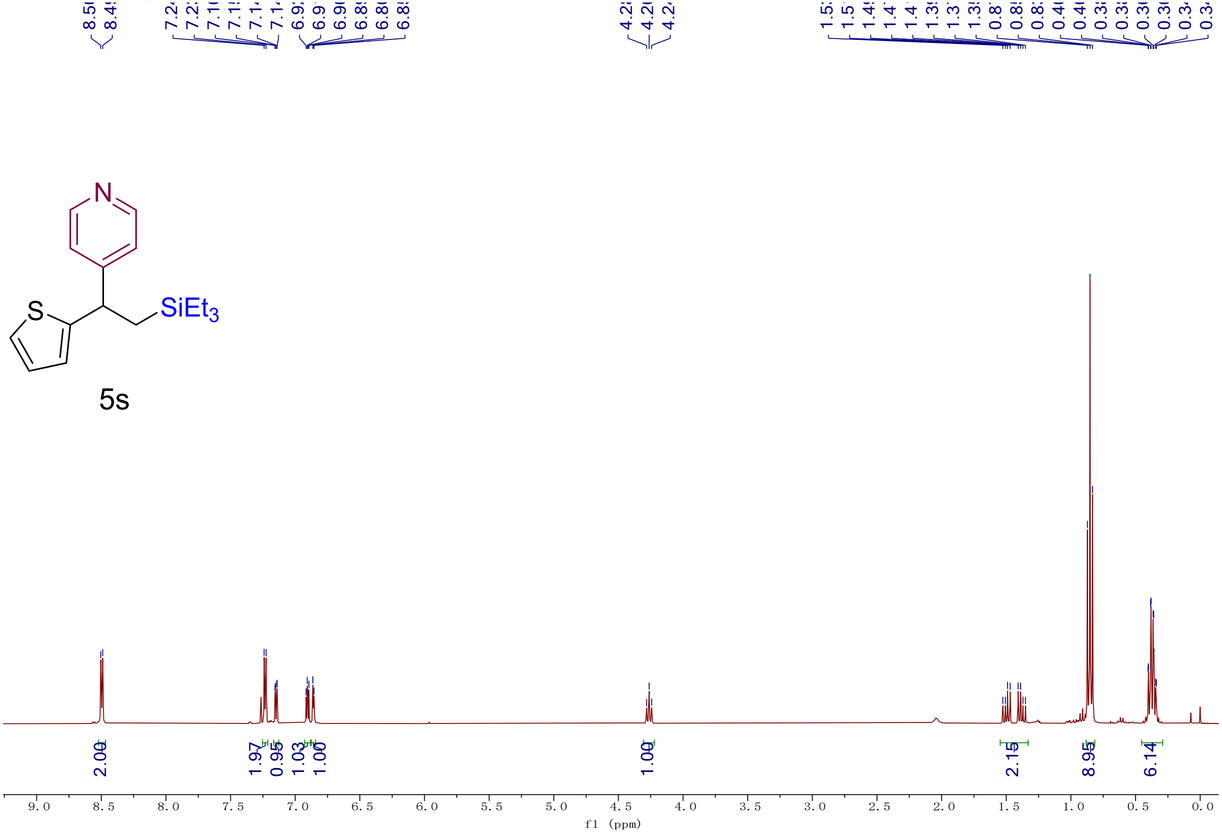
^{1}H NMR spectra of compound **5r** (400 MHz, $CDCl_3$)



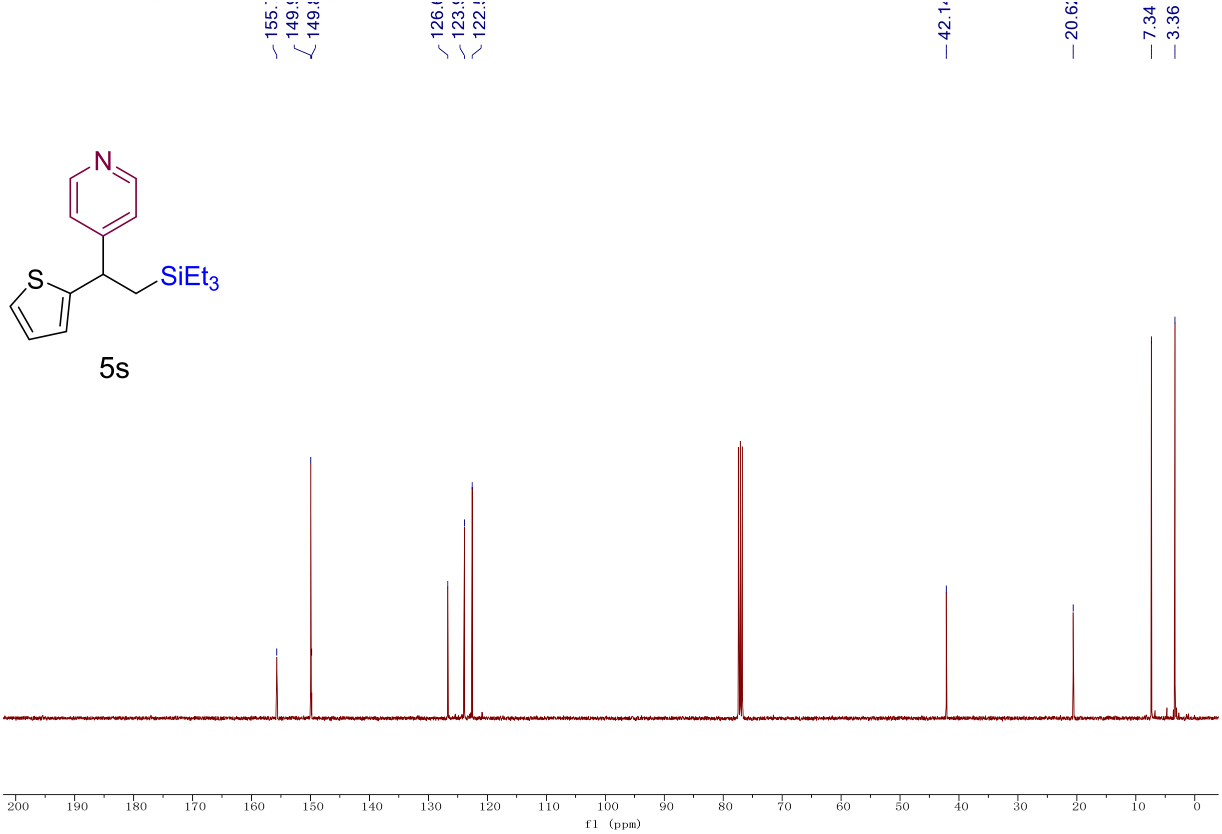
^{13}C NMR spectra of compound **5r** (101 MHz, $CDCl_3$)



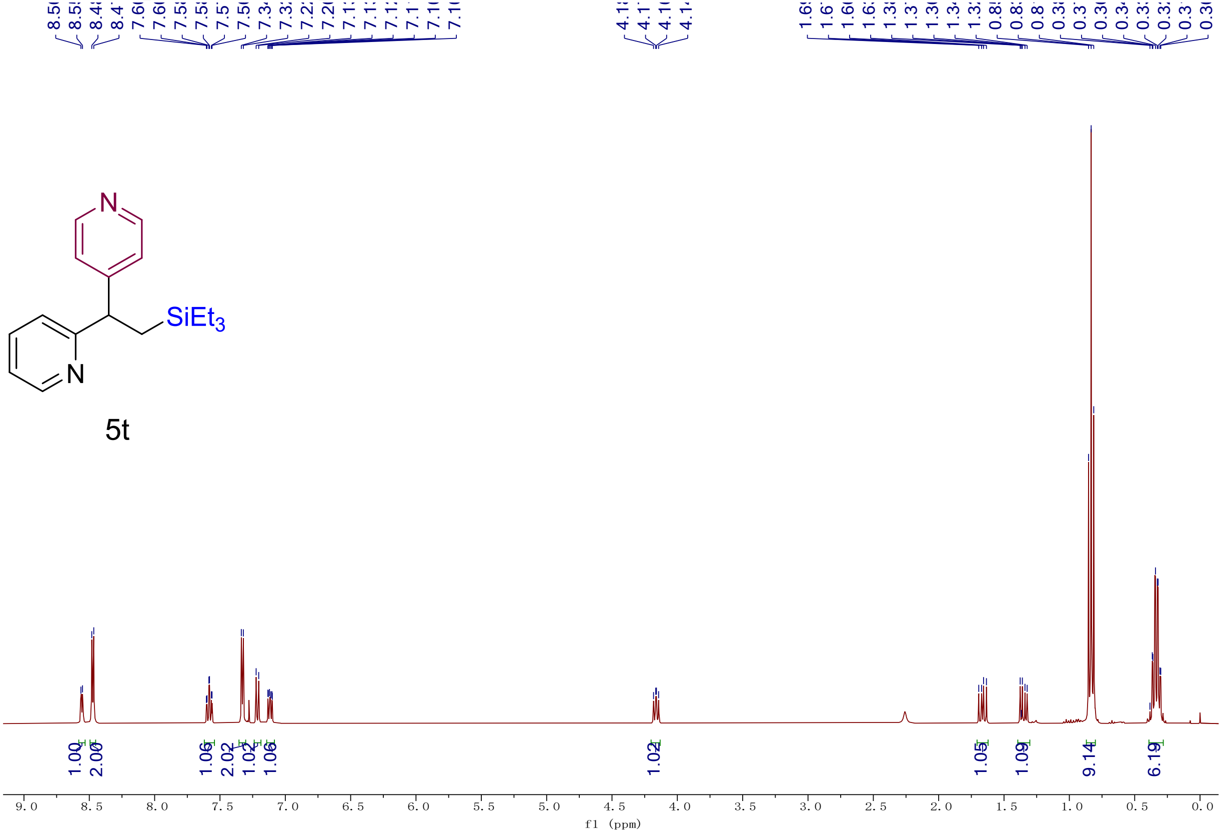
^{1}H NMR spectra of compound **5s** (400 MHz, $CDCl_3$)



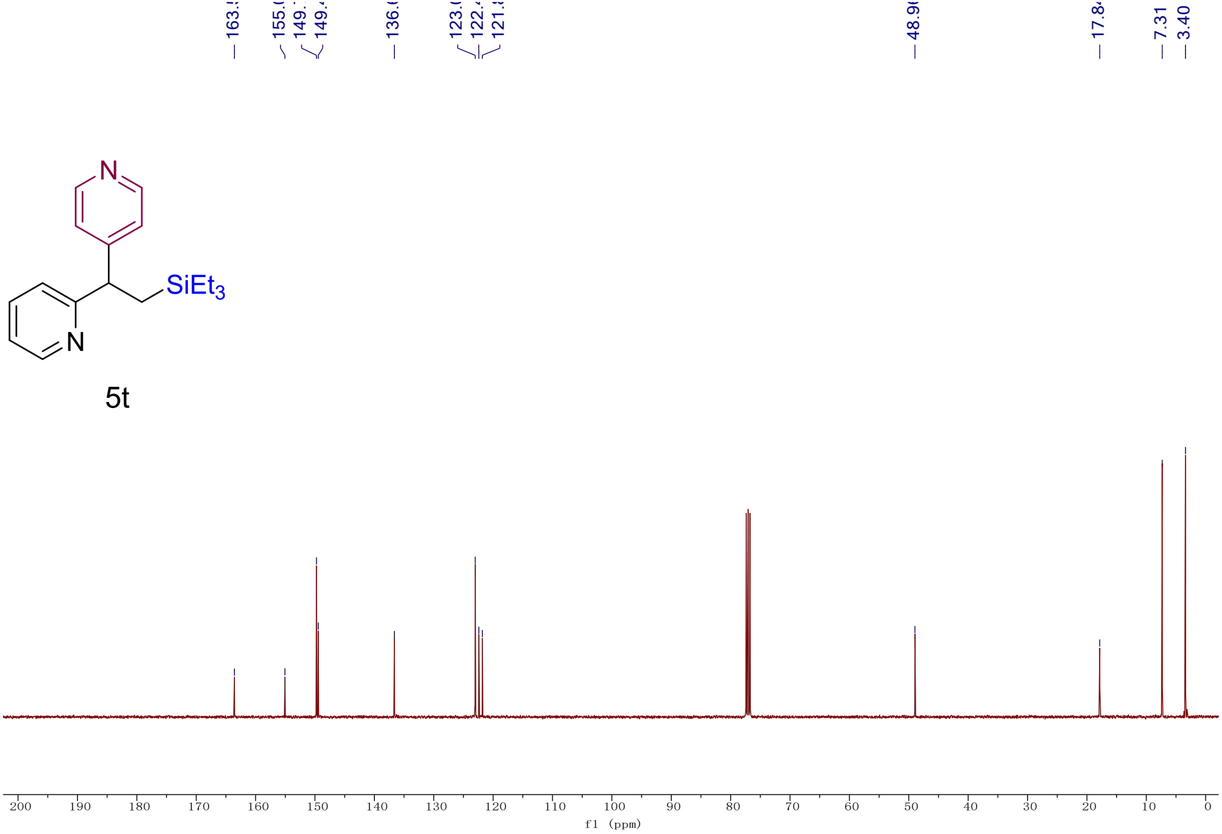
^{13}C NMR spectra of compound **5s** (101 MHz, $CDCl_3$)



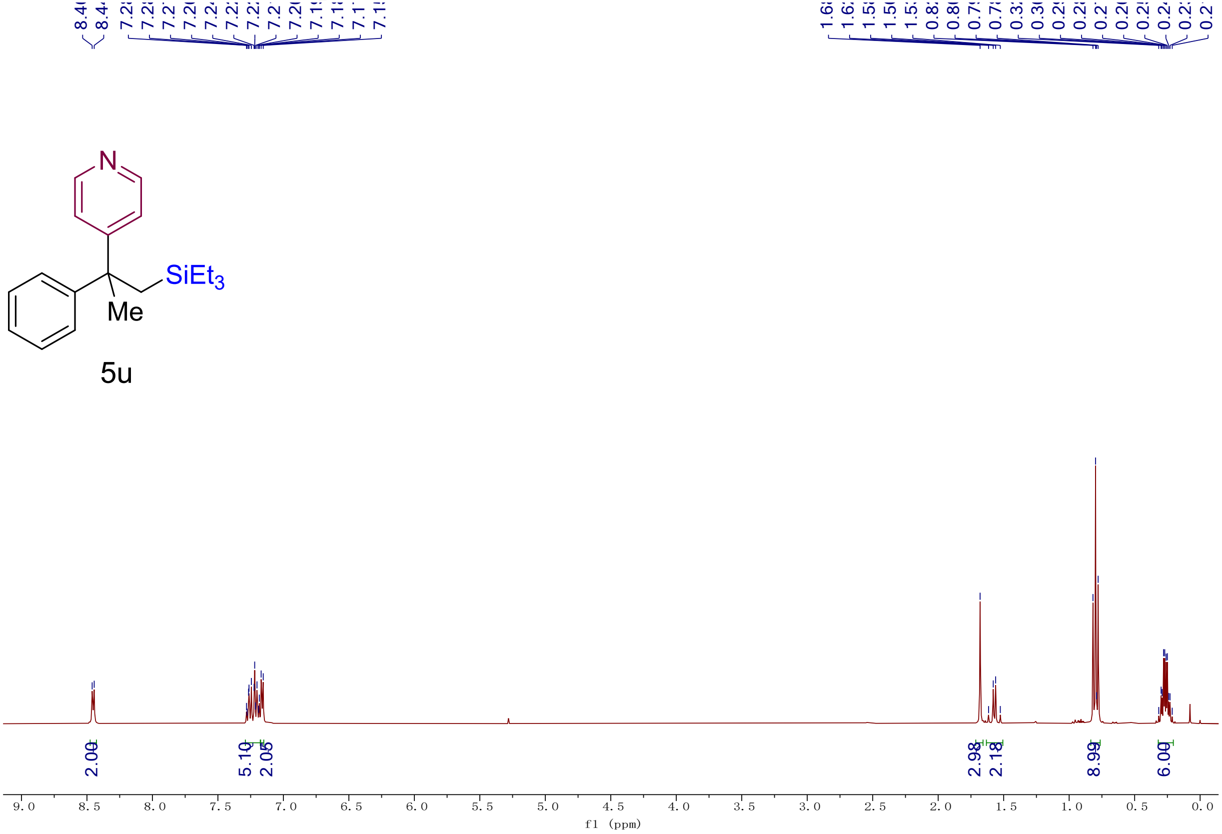
^{1}H NMR spectra of compound **5t** (400 MHz, $CDCl_3$)



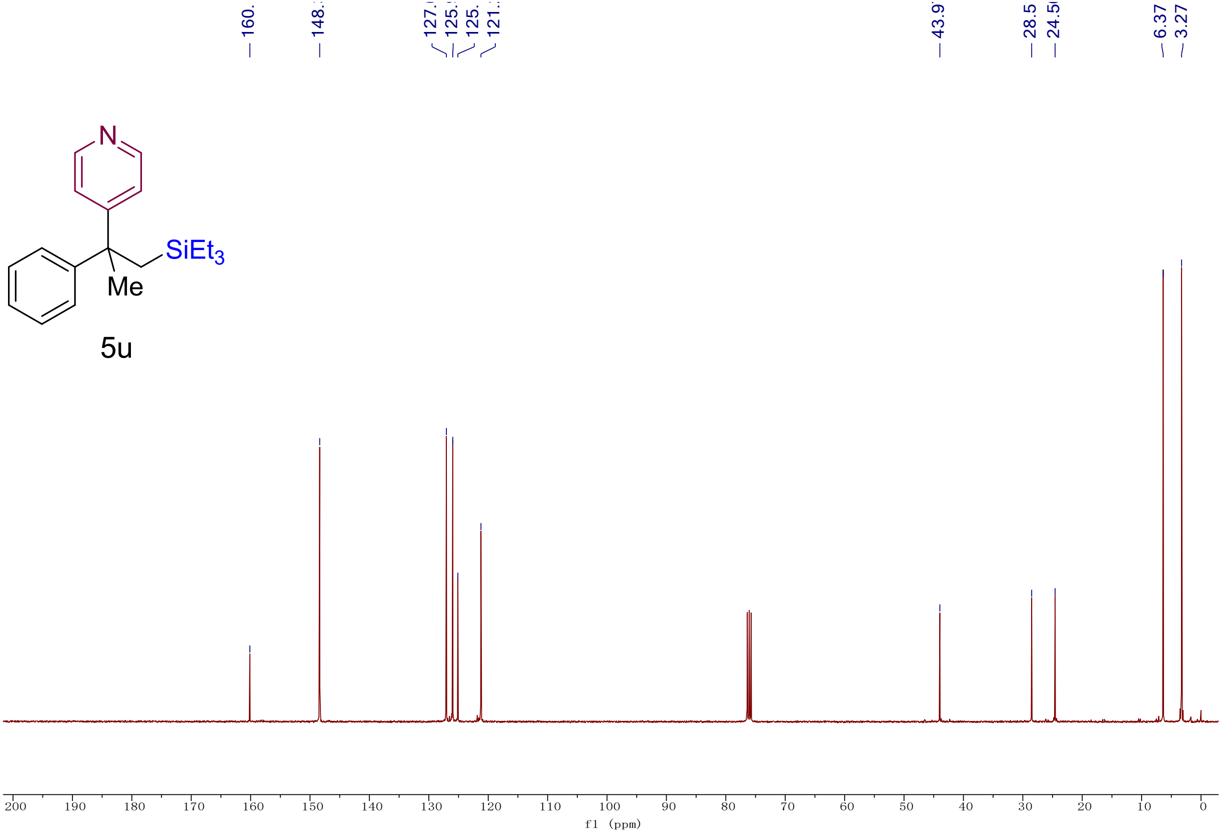
^{13}C NMR spectra of compound **5t** (101 MHz, $CDCl_3$)



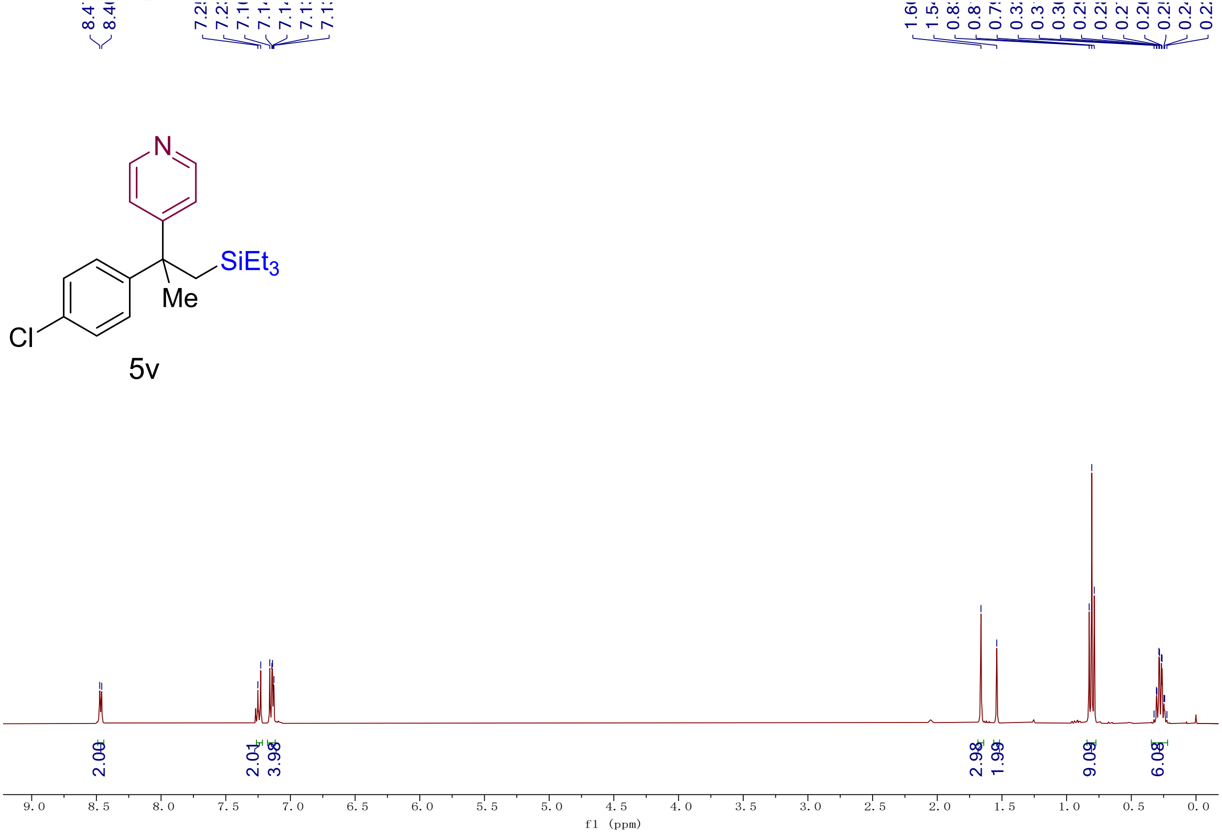
^{1}**H NMR** spectra of compound **5u** (400 MHz, $CDCl_3$)



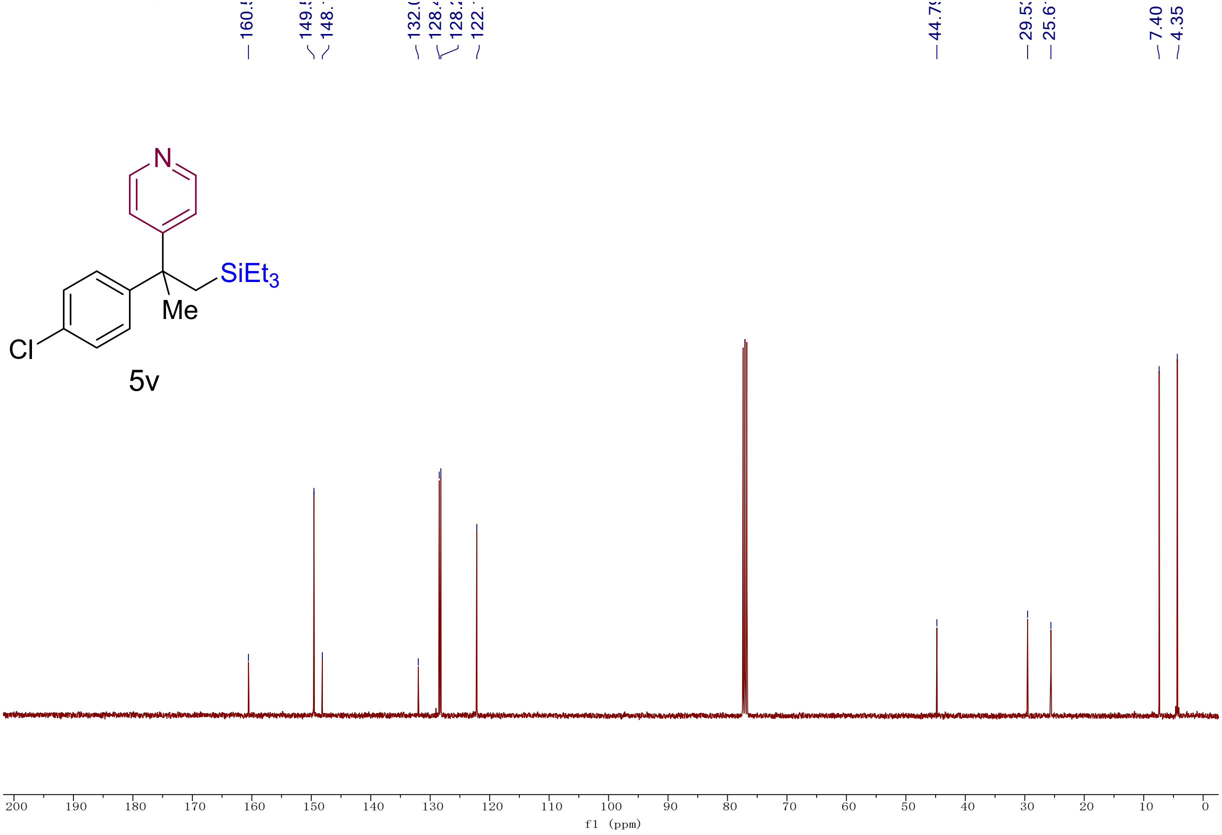
^{13}**C NMR** spectra of compound **5u** (101 MHz, $CDCl_3$)



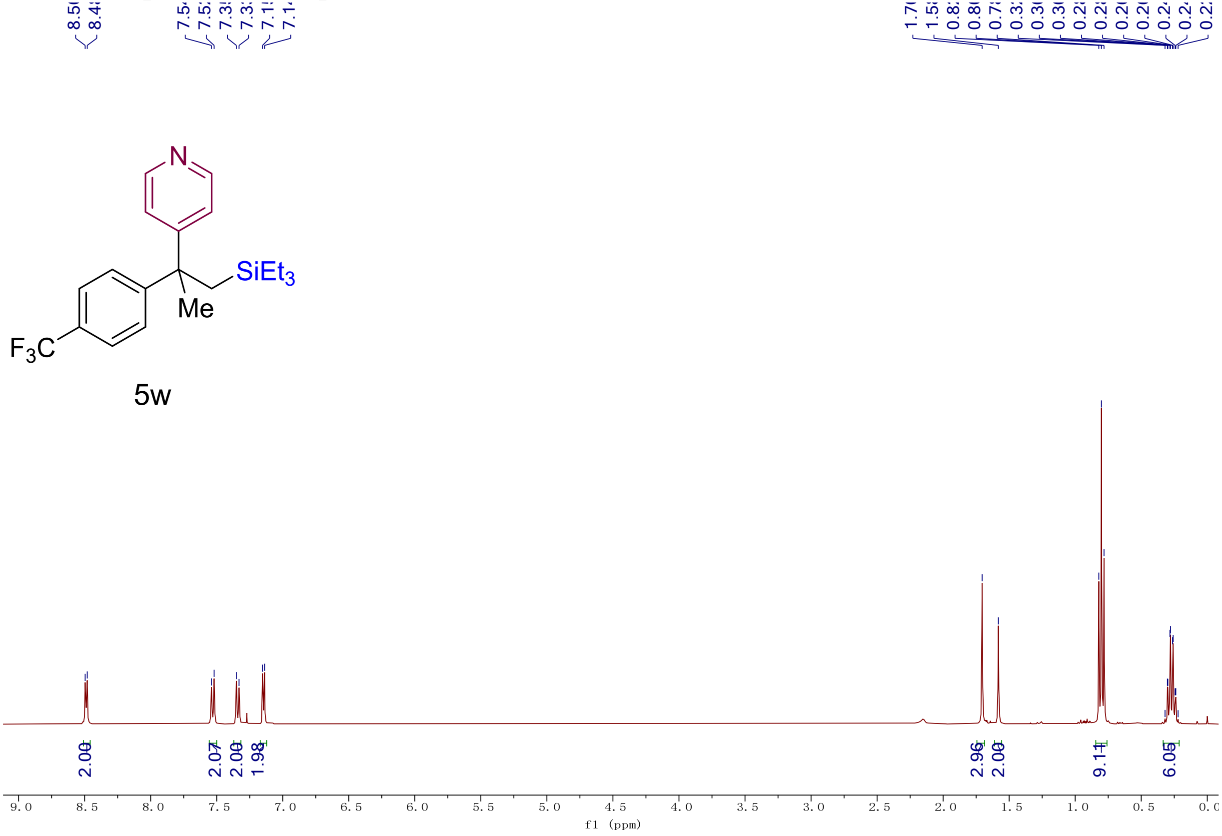
^{1}H NMR spectra of compound **5v** (400 MHz, $CDCl_3$)



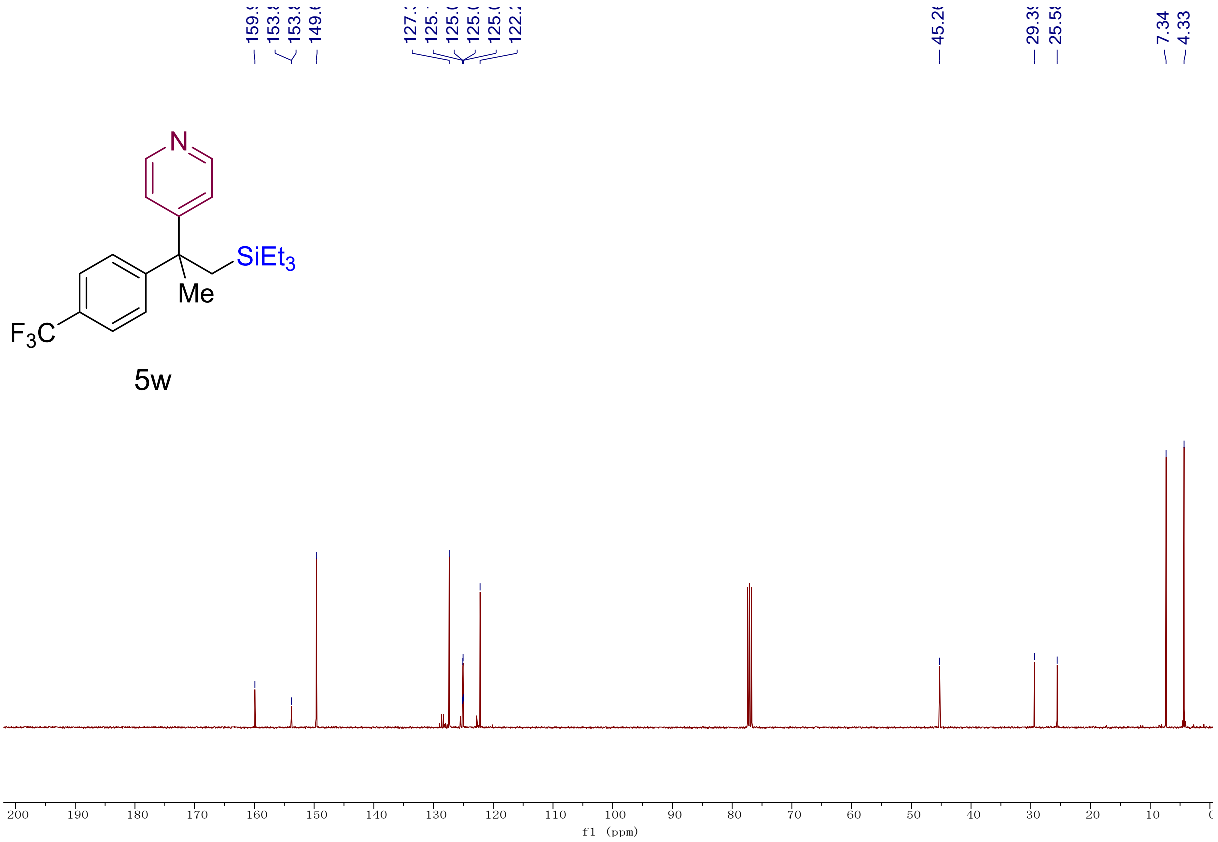
^{13}C NMR spectra of compound **5v** (101 MHz, $CDCl_3$)



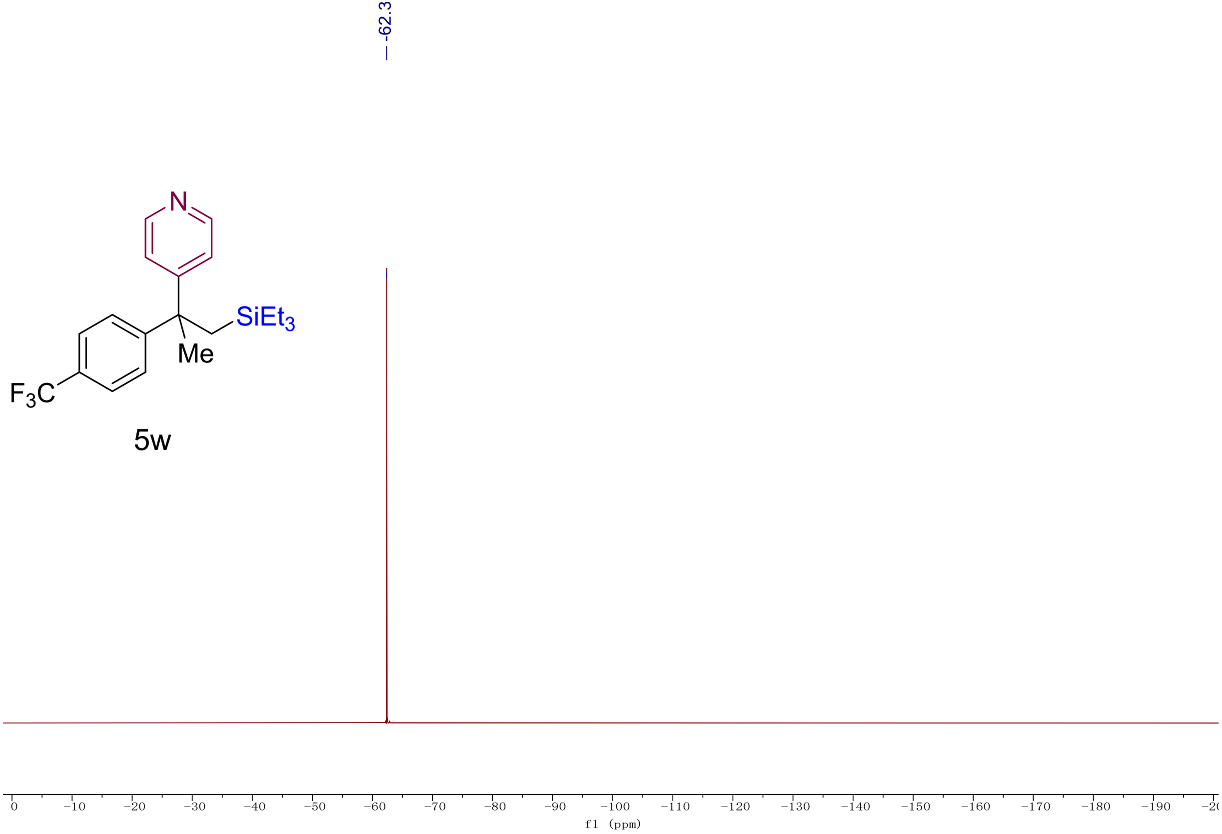
^{1}H NMR spectra of compound **5w** (400 MHz, $CDCl_3$)


5w

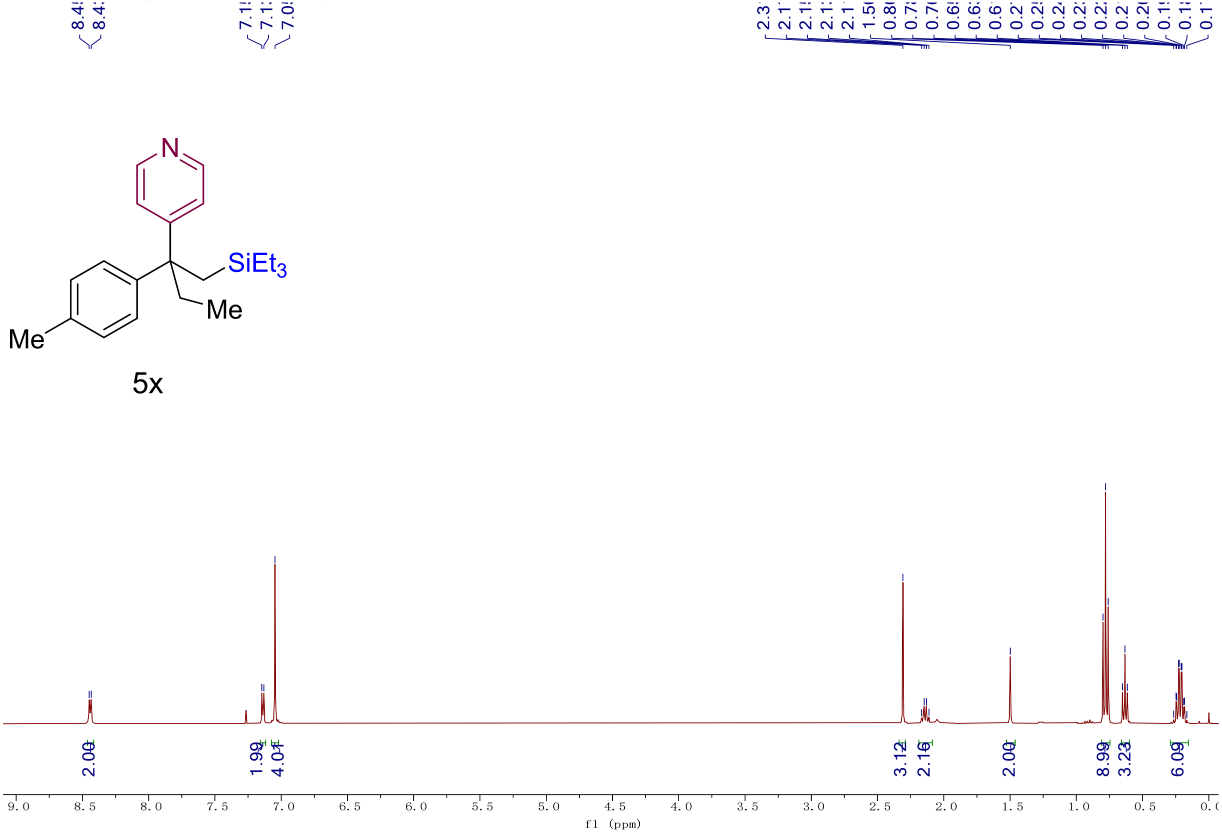
^{13}C NMR spectra of compound **5w** (101 MHz, $CDCl_3$)



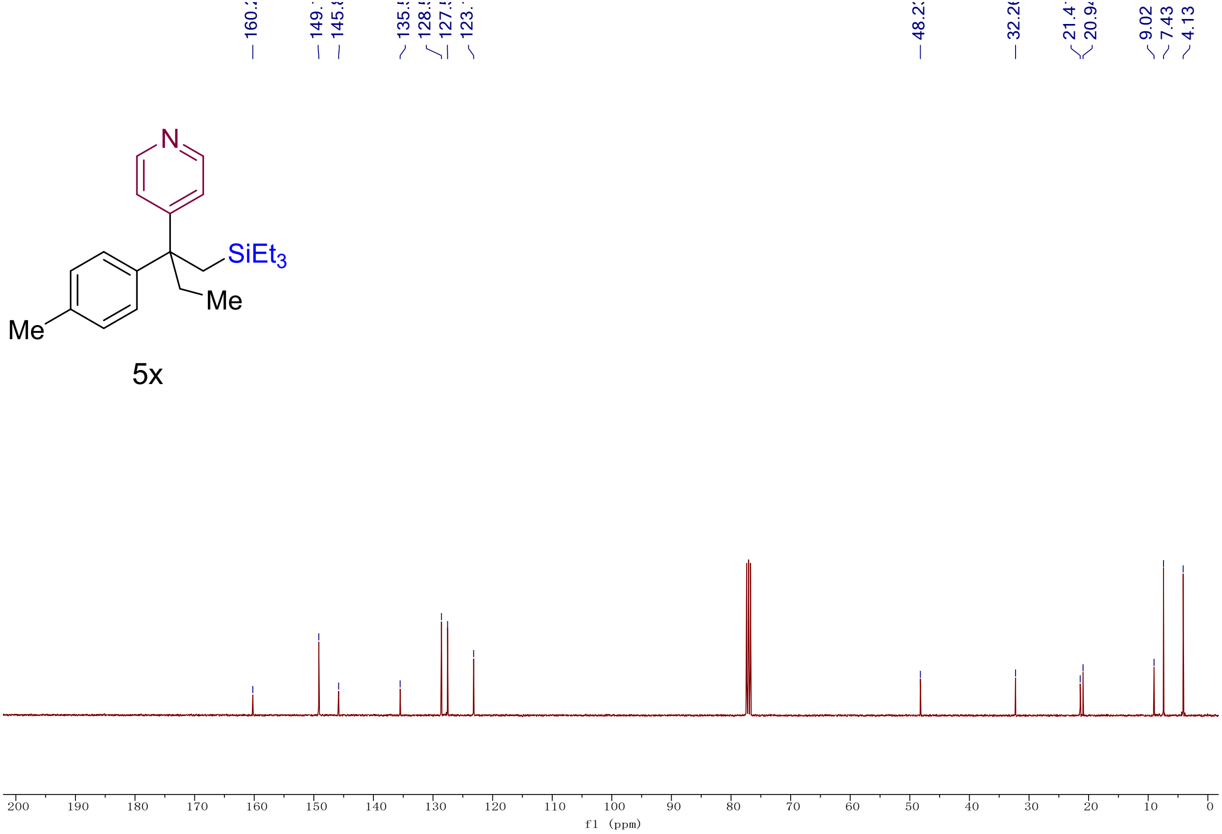
^{19}F NMR spectra of compound **5w** (376 MHz, $CDCl_3$)



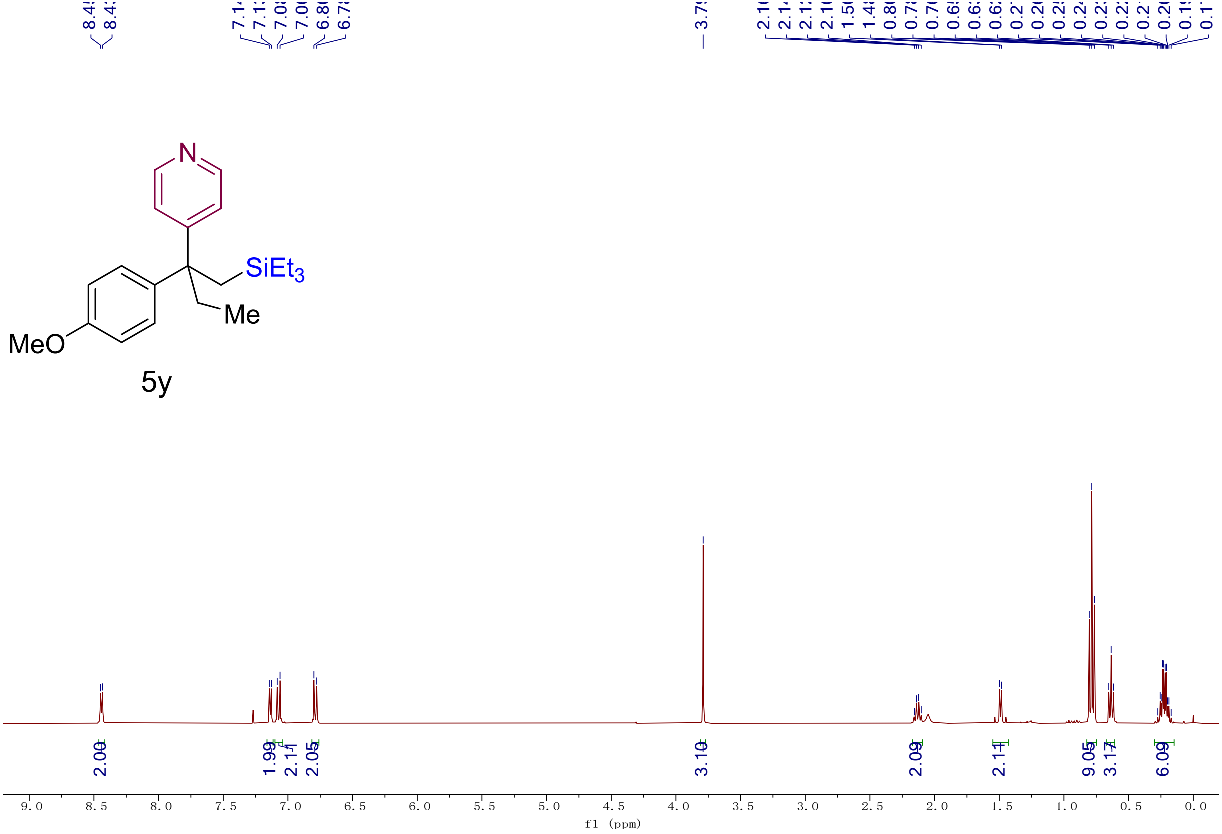
^{1}H NMR spectra of compound **5x** (400 MHz, CDCl$_3$)



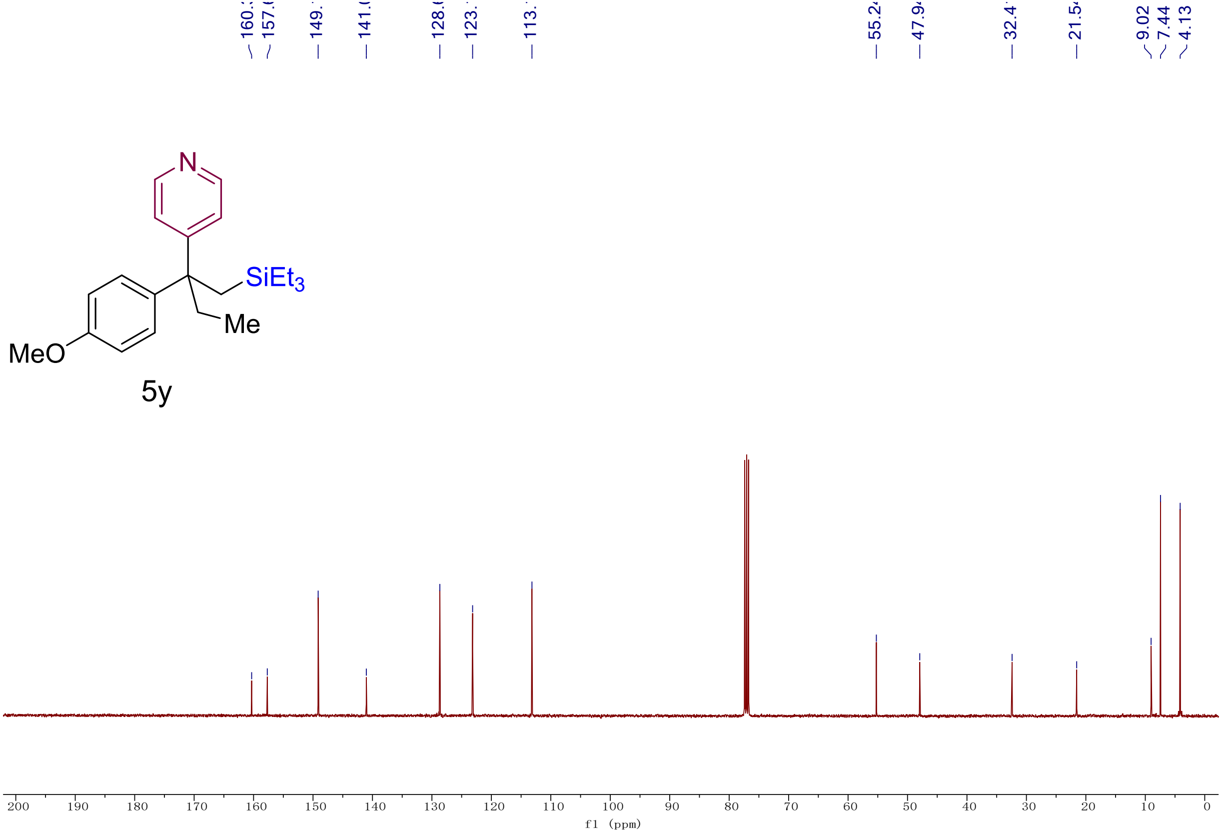
^{13}C NMR spectra of compound **5x** (101 MHz, CDCl$_3$)



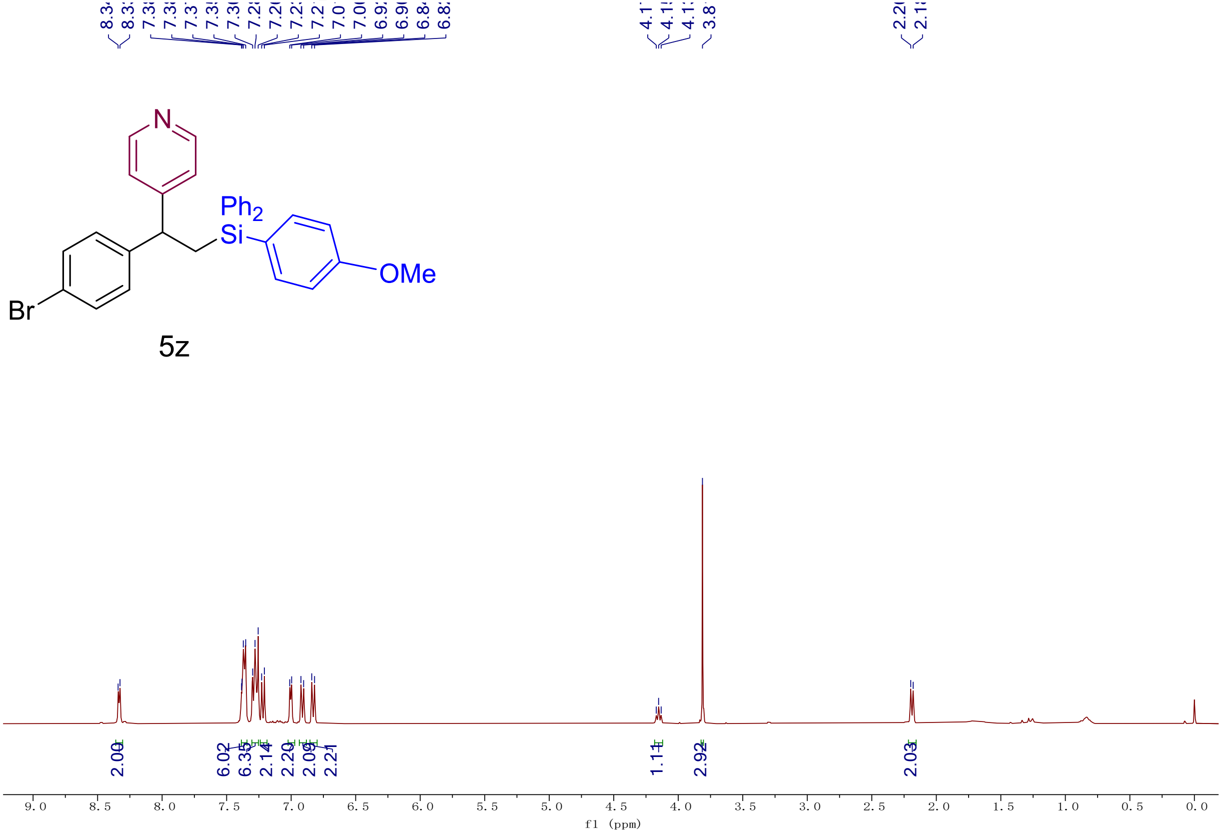
^{1}H NMR spectra of compound **5y** (400 MHz, CDCl$_3$)



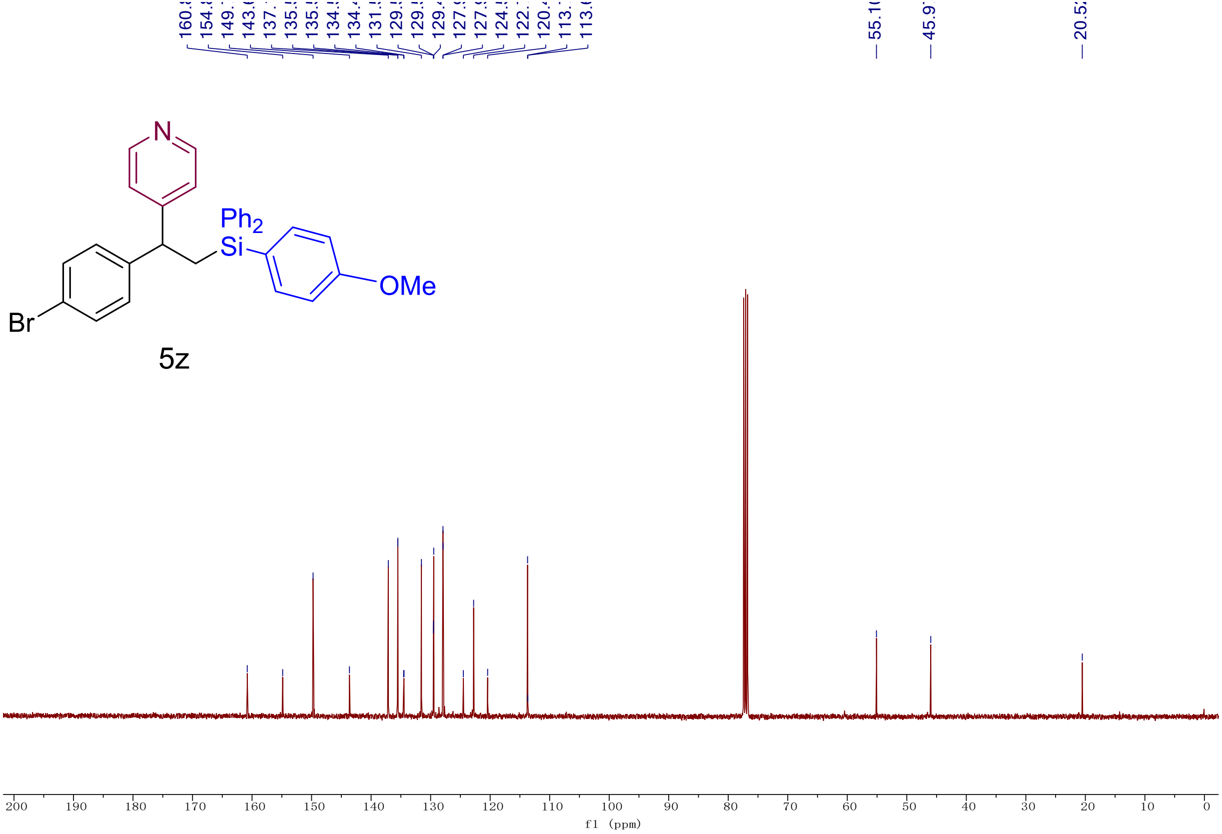
^{13}C NMR spectra of compound **5y** (101 MHz, CDCl$_3$)



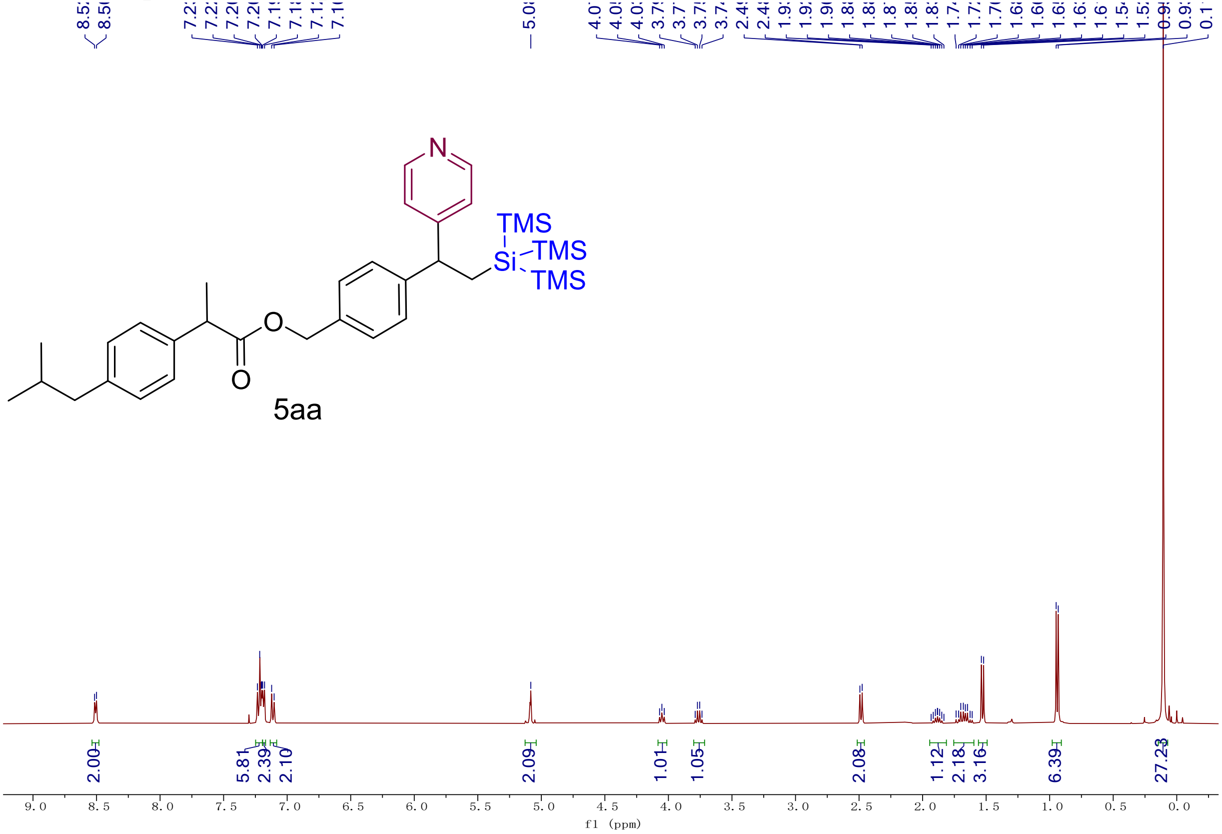
^{1}H NMR spectra of compound **5z** (400 MHz, CDCl$_3$)



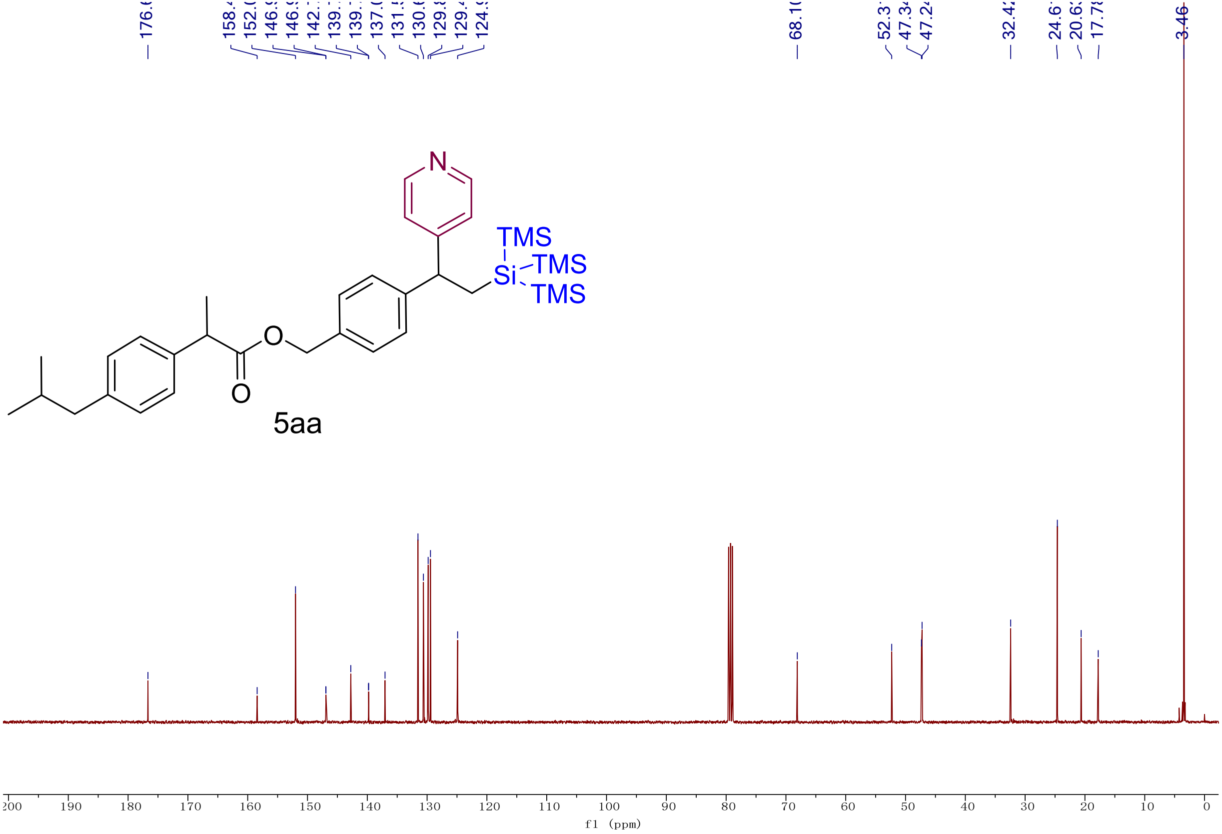
^{13}C NMR spectra of compound **5z** (101 MHz, CDCl$_3$)



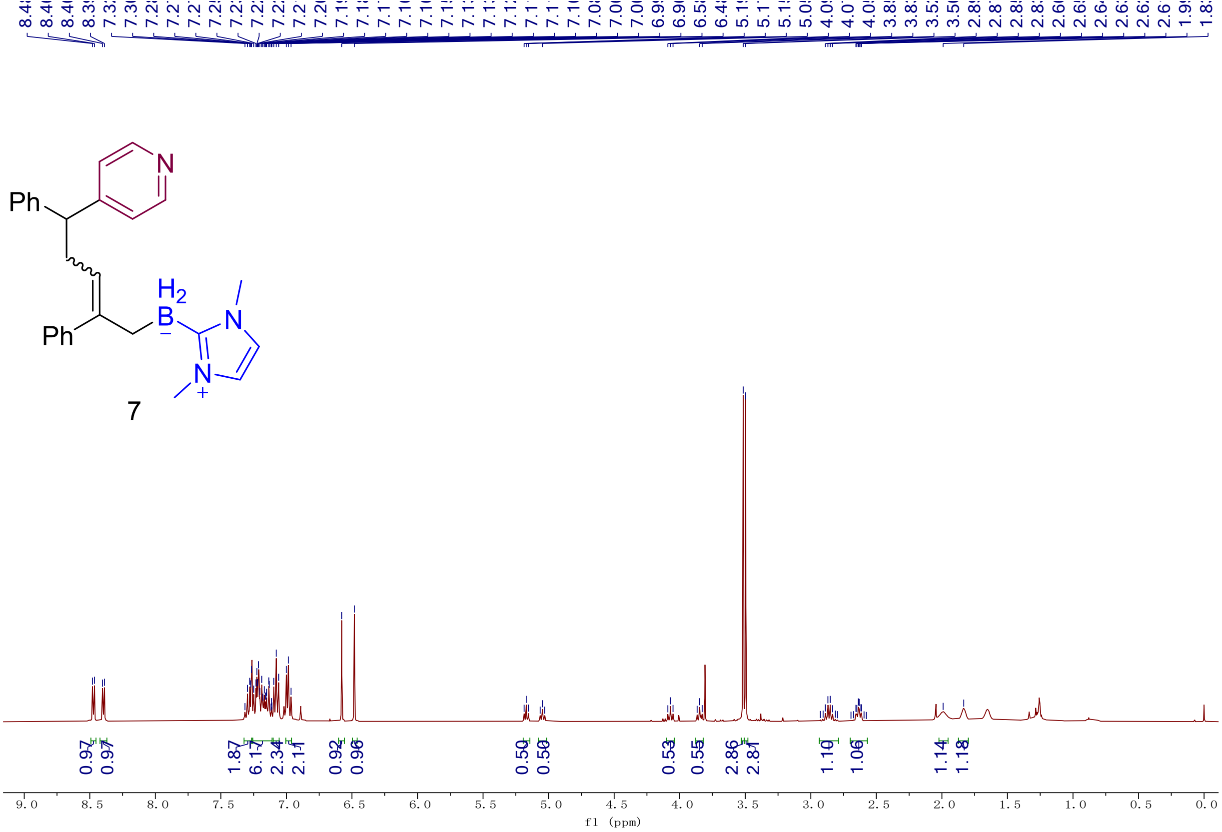
^{1}H NMR spectra of compound **5aa** (400 MHz, $CDCl_3$)



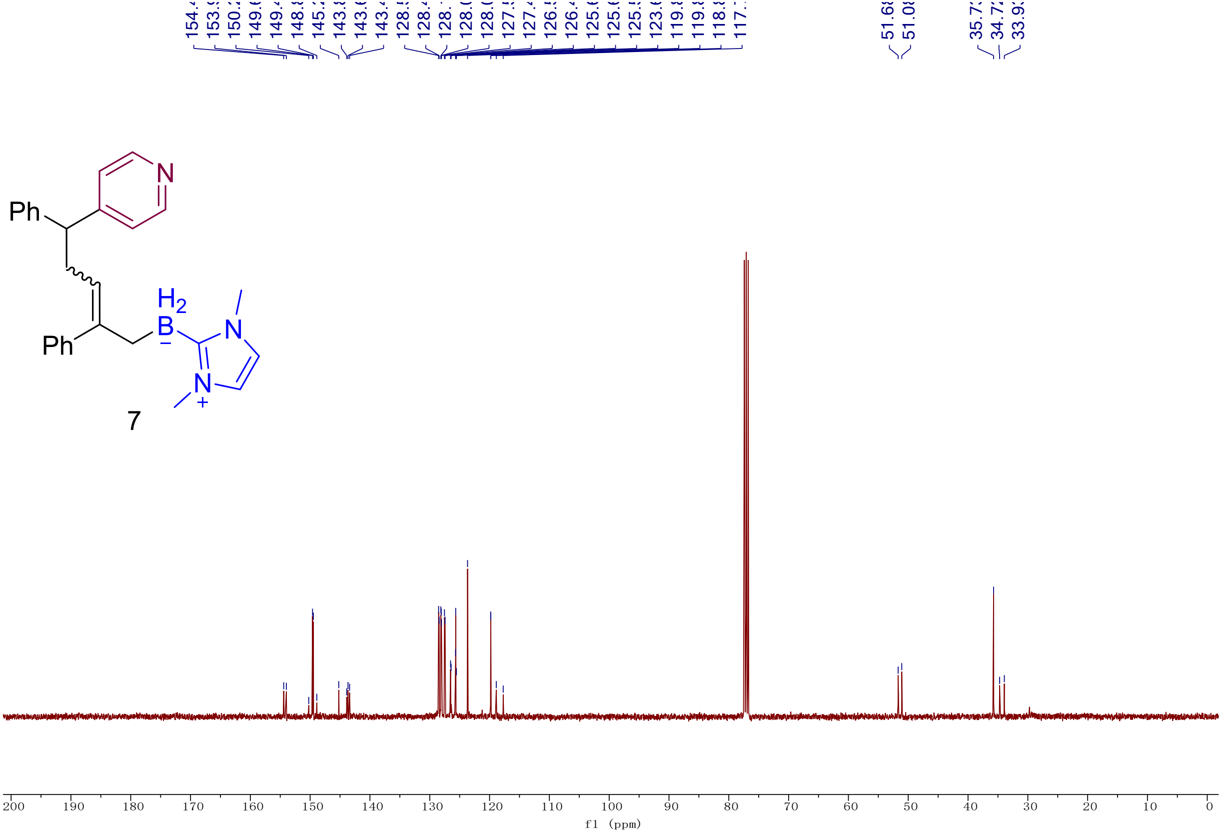
^{13}C NMR spectra of compound **5aa** (101 MHz, $CDCl_3$)



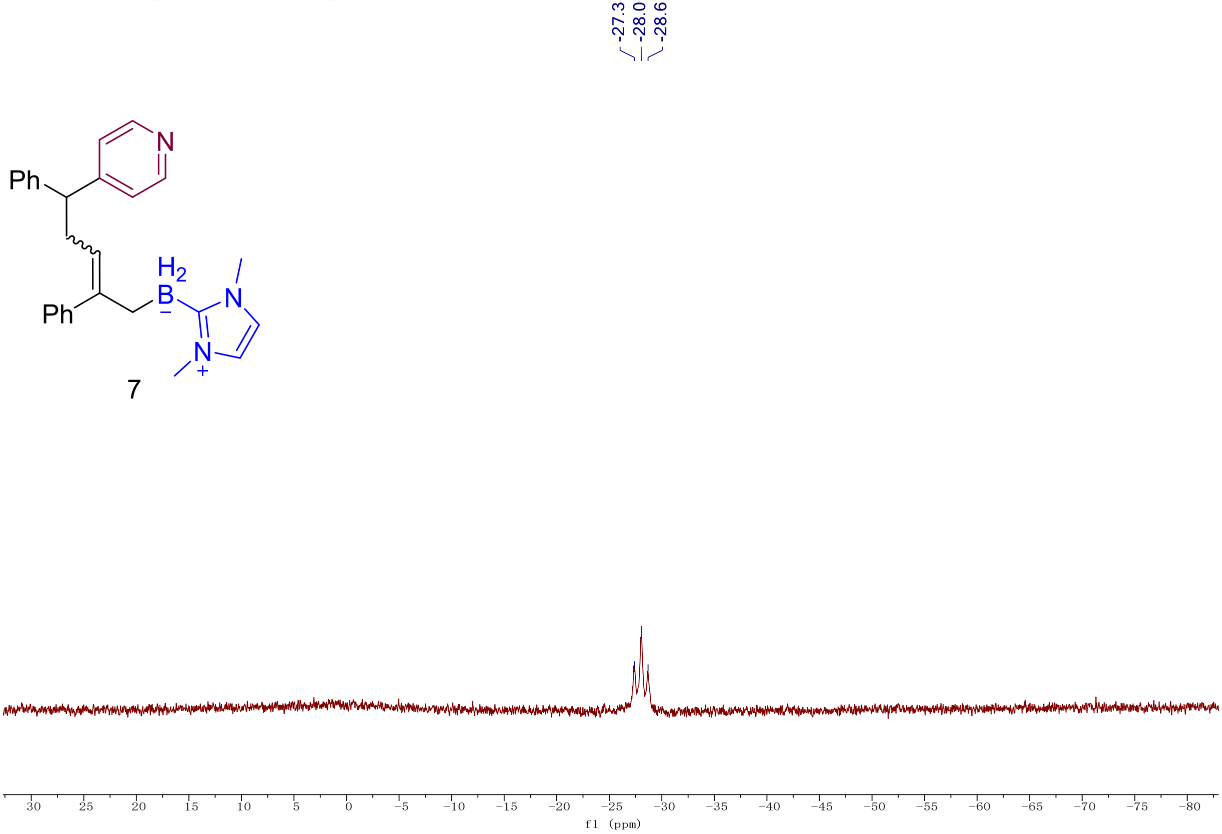
^{1}H **NMR** spectra of compound **7** (400 MHz, CDCl$_3$)



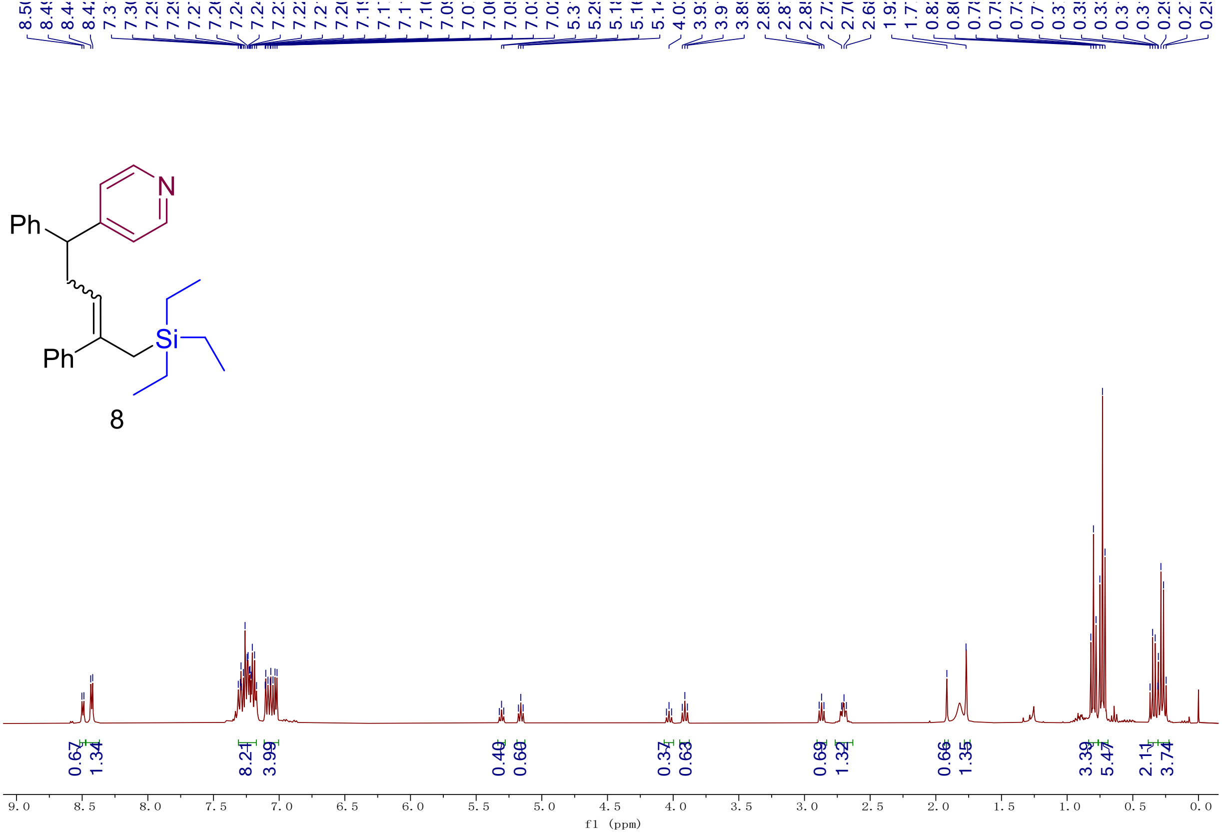
^{13}C **NMR** spectra of compound **7** (101 MHz, CDCl$_3$)



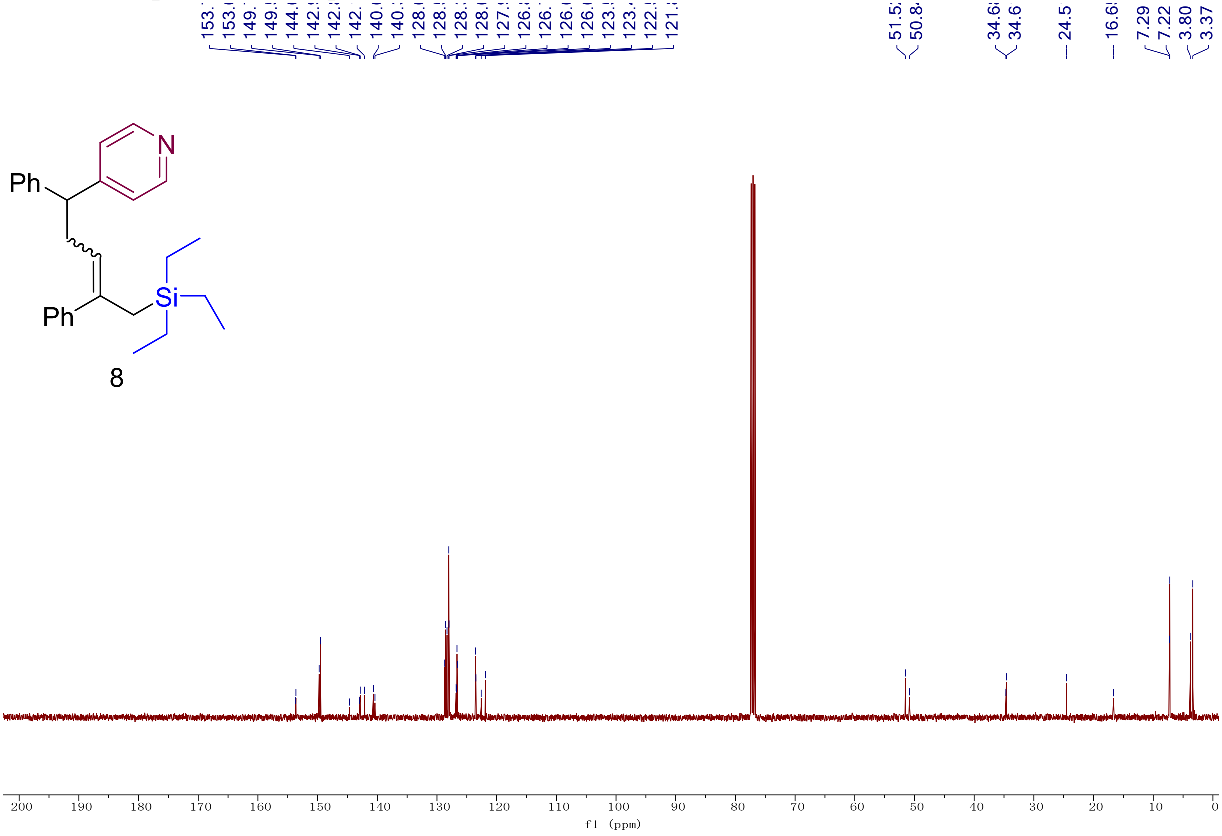
^{11}B NMR spectra of compound 7 (128 MHz, CDCl$_3$)



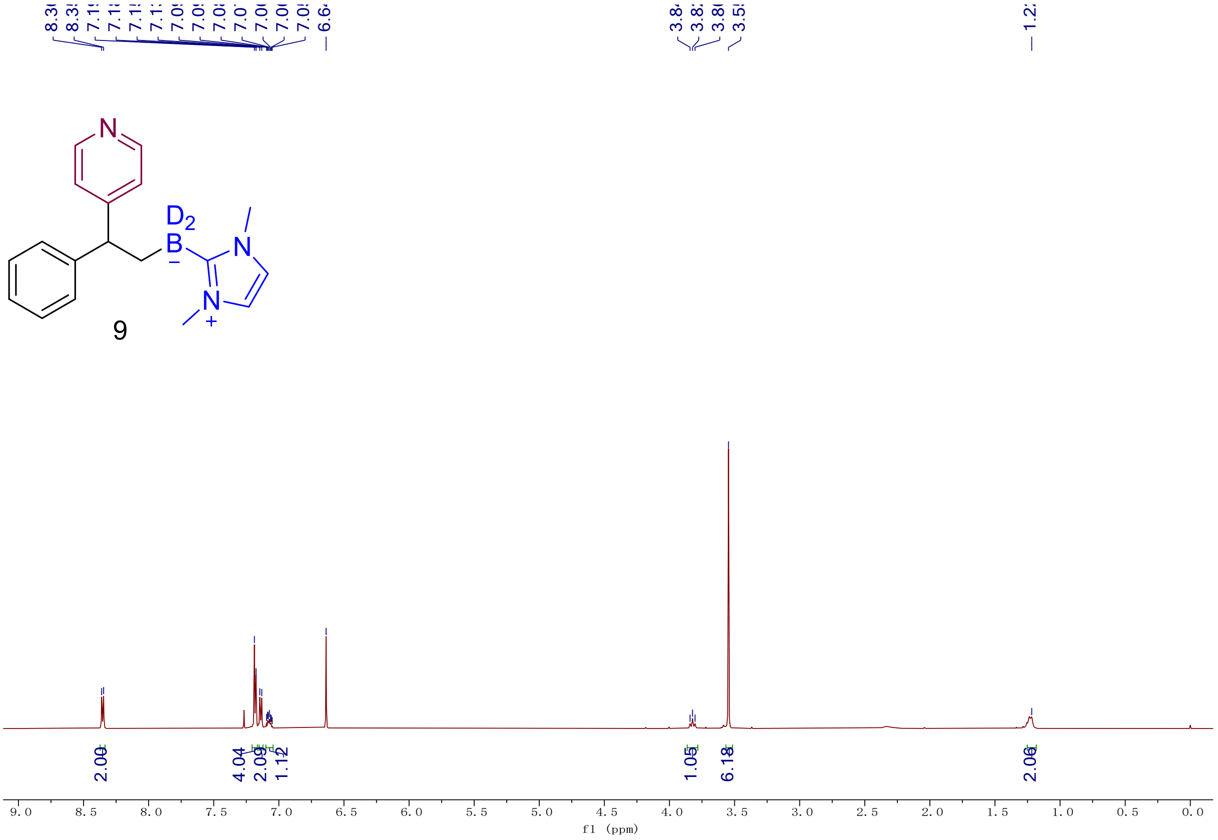
^{1}H NMR spectra of compound 8 (400 MHz, CDCl$_3$)



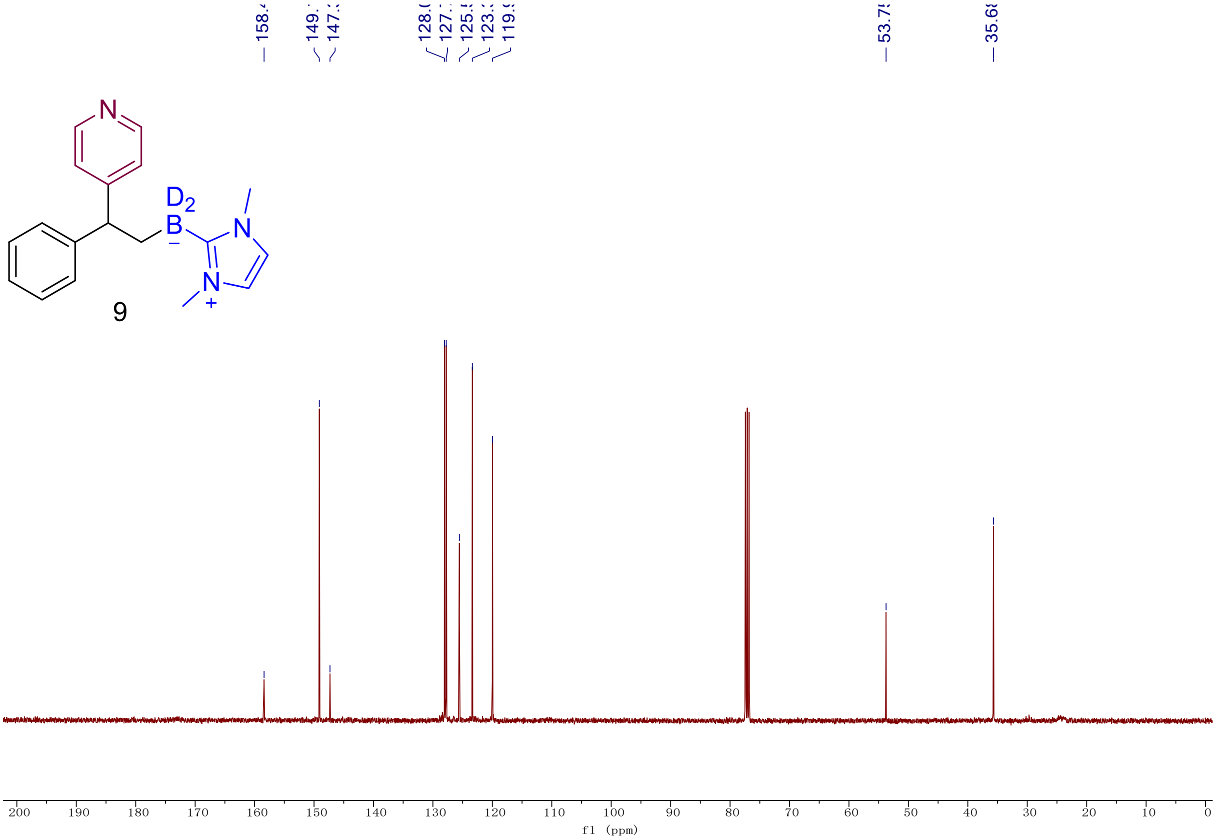
^{13}C NMR spectra of compound **8** (101 MHz, CDCl$_3$)



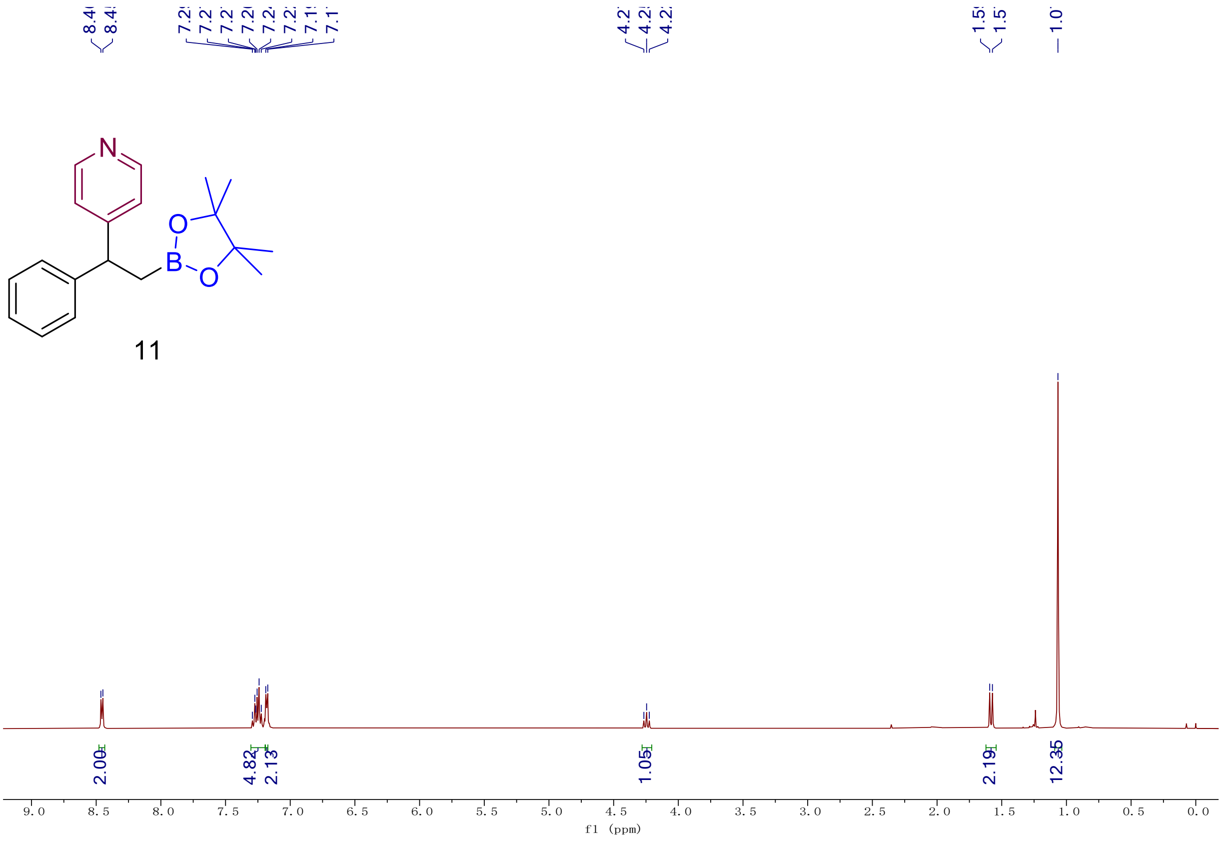
^{1}H NMR spectra of compound **9** (400 MHz, CDCl$_3$)



^{13}C NMR spectra of compound **9** (101 MHz, $CDCl_3$)



^{1}H NMR spectra of compound **11** (400 MHz, $CDCl_3$)



^{13}C NMR spectra of compound **11** (101 MHz, $CDCl_3$)