Supporting information

Organophotocatalytic Silyl Transfer of Silylboranes Enabled by Methanol Association: A Versatile Strategy for C-Si Bond Construction

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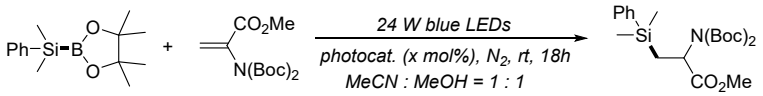
Optimization of Reaction Conditions

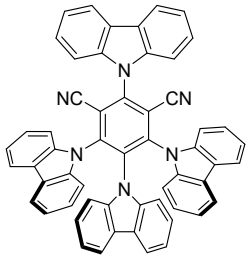
Table S1 Optimization of photocatalyst. [a]



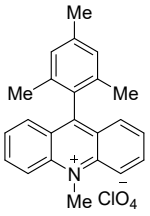
1a **2a** **3a**

Entry	Catalyst	Yield [b]
1	**P1** (3 mol%)	82%
2	**P2** (3 mol%)	n.d [c]
3	**P3** (1 mol%)	70%
4	**P4** (1 mol%)	25%
5	**P5** (1 mol%)	n.d [c]
6	**P6** (1 mol%)	n.d [c]
7	**P1** (1 mol%)	55%
8	**P1** (5 mol%)	80%

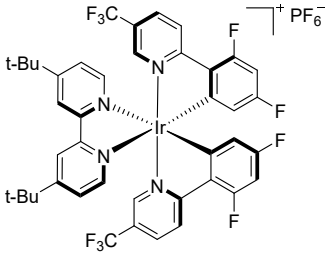
[a] Reaction conditions: 24 W blue LEDs, **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), MeCN : MeOH = 1 : 1 (4 mL), N_2, rt, 18 h, unless otherwise noted.
[b] Yields were determined by ^{1}H NMR using 1,3,5-Trimethylbenzene as internal standard. [c] Not detected.



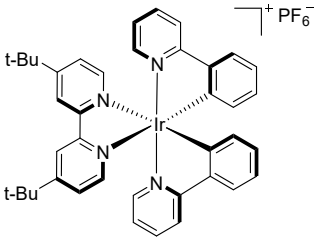
4CzIPN
P1



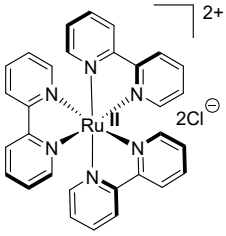
Mes-Acr-Me
P2



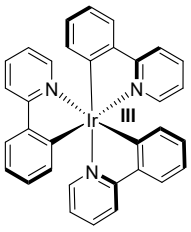
Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$
P3



Ir[ppy]$_2$(dtbbpy)PF$_6$
P4

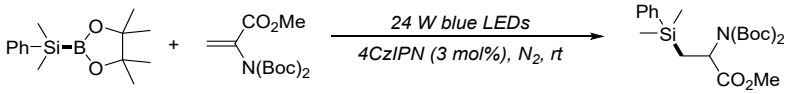


Ru(bpy)$_3$Cl$_2$.6H$_2$O
P5



Ir(ppy)$_3$
P6

Table S2 Optimization of reaction solvent and time. [a]

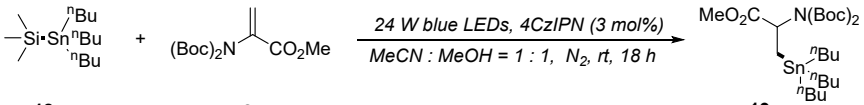


1a **2a** **3a**

Entry	Solvent	Time	Yield [b]
1	MeCN : MeOH = 1 : 1	18 h	82%
2	DCM : MeOH = 1 : 1	18 h	35%
3	Acetone : MeOH = 1 : 1	18 h	80%
4	DMF : MeOH = 1 : 1	18 h	35%
5	DMSO : MeOH = 1 : 1	18 h	22%
6	THF : MeOH = 1 : 1	18 h	70%
7	MeCN : MeOH = 1 : 1	24 h	78%
8	MeCN : MeOH = 1 : 1	12 h	60%
9	MeCN : MeOH = 1 : 1	18 h	72% [c]
10	MeCN : MeOH = 1 : 1	18 h	82% [d]

[a] Reaction conditions: 24 W blue LEDs, **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), 4CzIPN (0.006 mmol, 3 mol%), solvent (4 mL), N_2, rt, unless otherwise noted. [b] Yields were determined by ^{1}H NMR using 1,3,5-Trimethylbenzene as internal standard. [c] 1.0 equiv. of **1a** was employed. [d] 2.0 equiv. of **1a** was employed.

Table S3 Validation of reaction conditions for the synthesis of **19a**. [a]

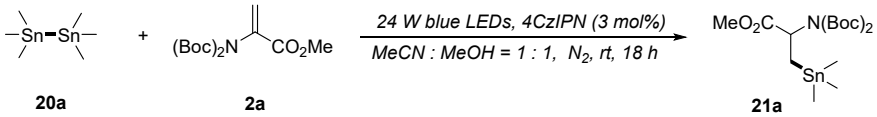


18a **2a** **19a**

Entry	Change From Optimal Conditions	Yield [b]
1	none	78%
2	in the absence of photocatalyst	n.d [c]
3	in darkness	n.d [c]
4	in the absence of MeOH	66%

[a] Reaction conditions: 24 W blue LEDs, **18a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), 4CzIPN (0.006 mmol, 3 mol%), MeCN : MeOH = 1 : 1 (4 mL), N_2, rt, 18 h, unless otherwise noted. [b] Isolated yields were reported. [c] Not detected.

Table S4 Validation of reaction conditions for the synthesis of **21a**. [a]

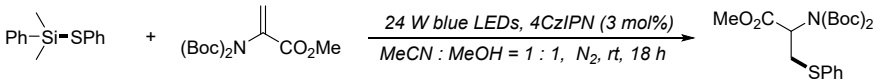


20a **2a** **21a**

Entry	Change From Optimal Conditions	Yield [b]
1	none	80%
2	in the absence of photocatalyst	n.d [c]
3	in darkness	n.d [c]
4	in the absence of MeOH	72%

[a] Reaction conditions: 24 W blue LEDs, **20a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), 4CzIPN (0.006 mmol, 3 mol%), MeCN : MeOH = 1 : 1 (4 mL), N_2, rt, 18 h, unless otherwise noted. [b] Isolated yields were reported. [c] Not detected.

Table S5 Validation of reaction conditions for the synthesis of **23a**. [a]



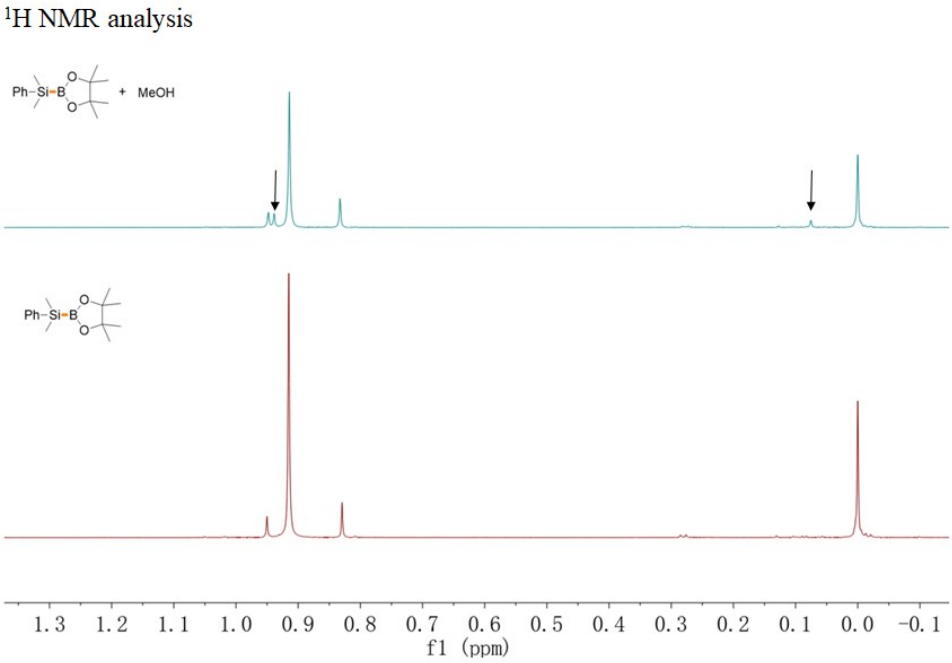
22a **2a** **23a**

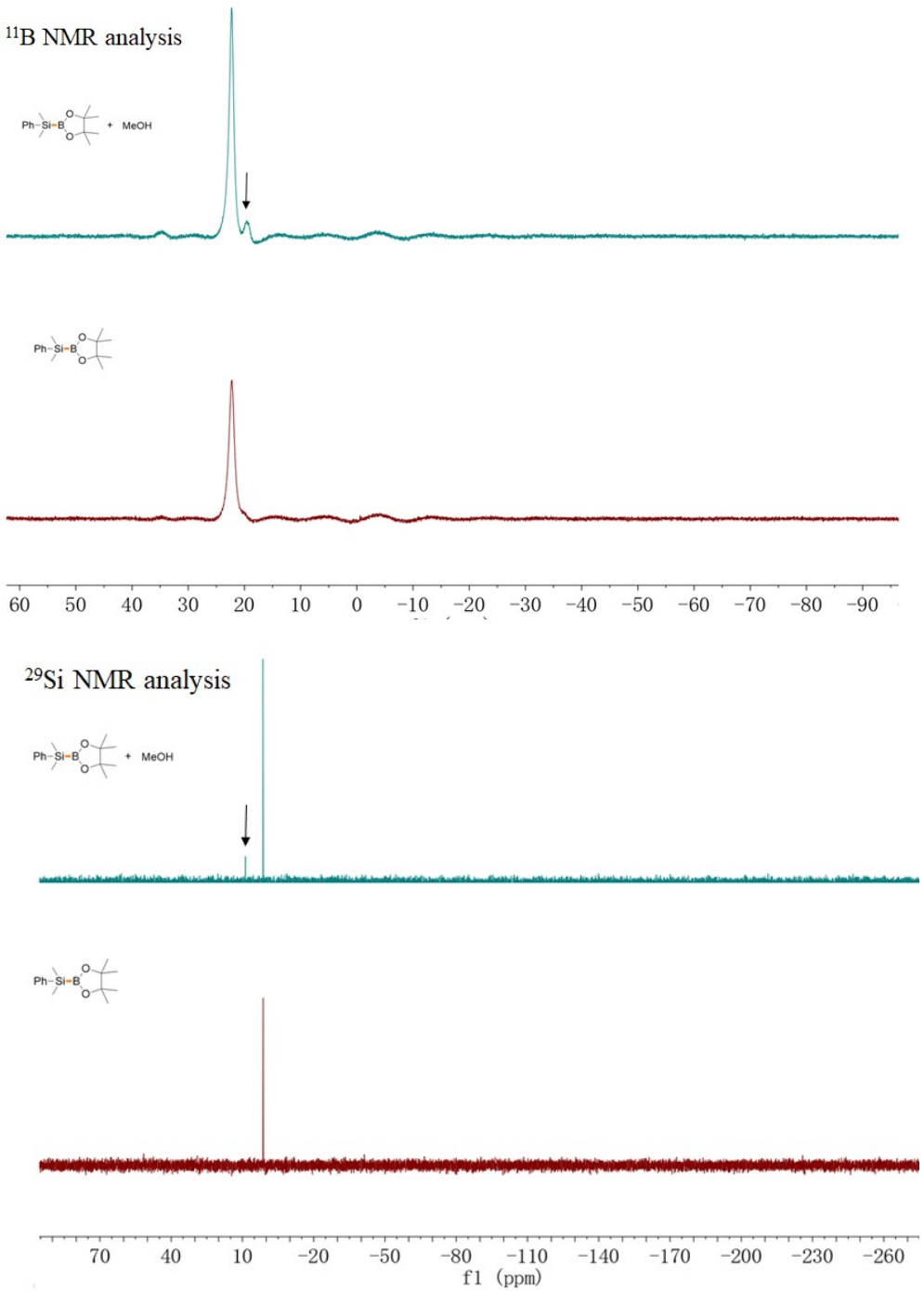
Entry	Change From Optimal Conditions	Yield [b]
1	none	80%
2	in the absence of photocatalyst	n.d [c]
3	in darkness	n.d [c]
4	in the absence of MeOH	70%

[a] Reaction conditions: 24 W blue LEDs, **22a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), 4CzIPN (0.006 mmol, 3 mol%), MeCN : MeOH = 1 : 1 (4 mL), N_2, rt, 18 h, unless otherwise noted. [b] Isolated yields were reported. [c] Not detected.

Mechanistic Investigations

Figure S1 Study of association of methanol with $PhMe_2Si$-BPin **1a** by NMR spectra



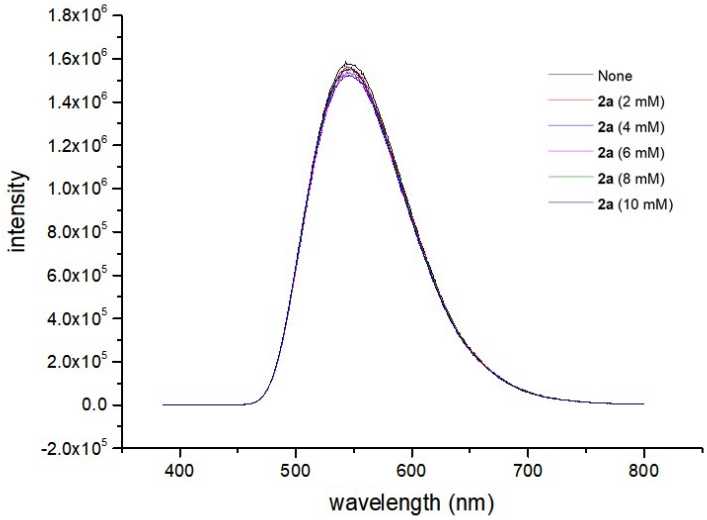


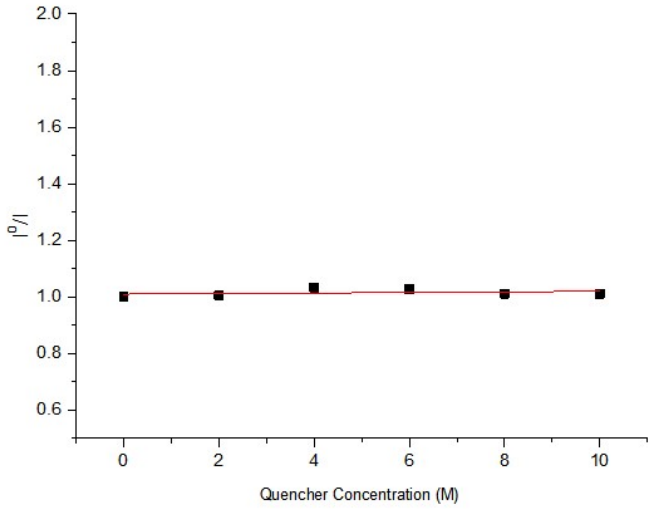
Notes: 1 equiv. of $PhMe_2Si$-BPin **1a** and 5.0 equiv. of MeOH were dissolved into d^6-DMSO. The NMR spectra data of this sample was then collected. According to the NMR data, it is reasonable to conclude that methanol could associate with $PhMe_2Si$-BPin **1a**.

Figure S2 Stern-Volmer fluorescence quenching experiments

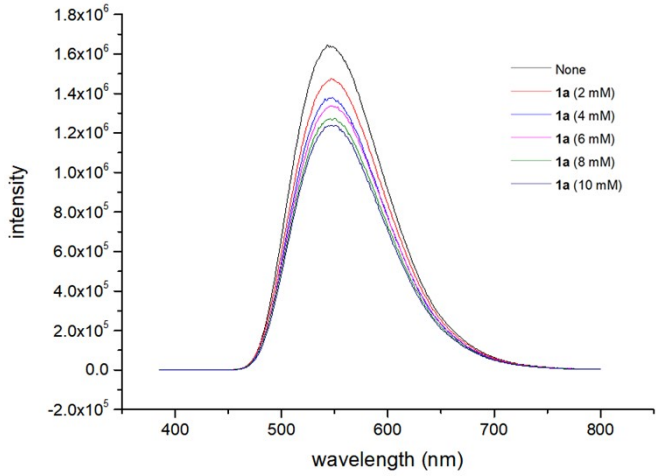
Emission intensities were recorded using a FluoroMax-4 Spectrophotometer. All quenching data was recorded using a 1.00 cm quartz cuvette, PMT voltage 500 v, scan speed 1200 nm/min. In a typical experiment, the solution of photocatalyst (30 μM) in anhydrous MeCN or a solvent mixture (anhydrous MeCN/MeOH = 1 : 1) was added the appropriate amount of quenchers. Then the emission spectrum of the sample was collected.

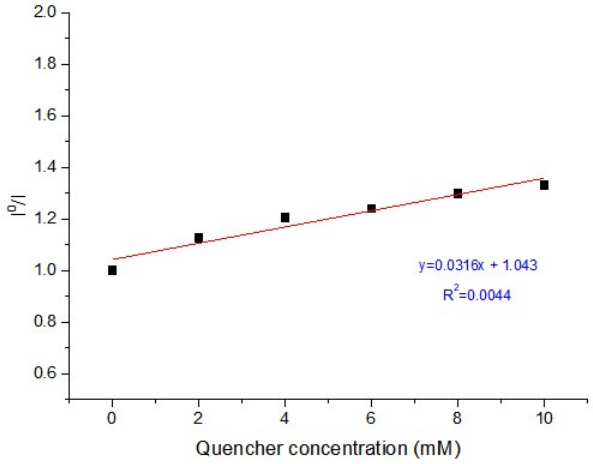
A. Emission quenching by **2a** in anhydrous MeCN



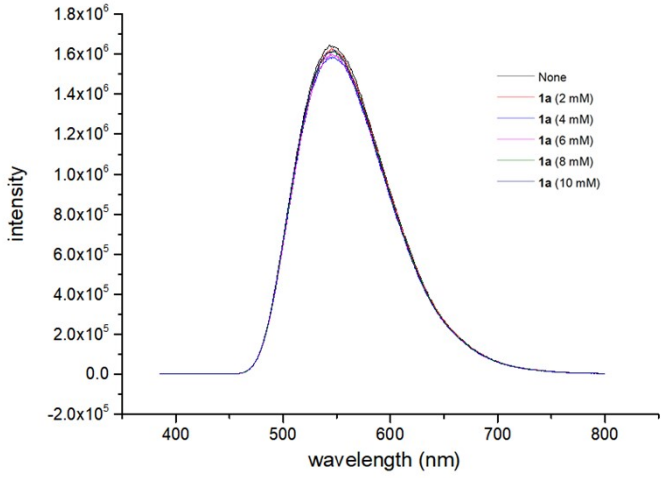


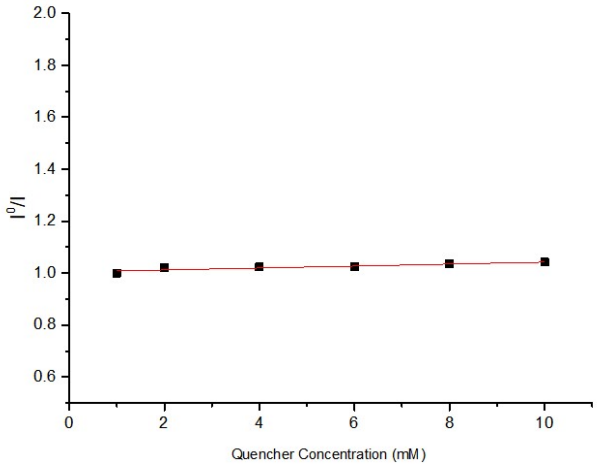
B. Emission quenching by **1a** in a solvent mixture (anhydrous MeCN/MeOH = 1 : 1)





C. Emission quenching by **1a** in anhydrous MeCN





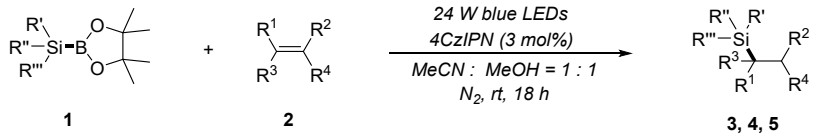
Notes: Both **1a** and **2a** could not quench the emission of 4CzIPN using anhydrous MeCN as solvent, while significant quenching effect of **1a** has been detected using anhydrous MeCN/MeOH (1 : 1) as solvent. Furthermore, the quenching by **2a** has not been detected even if using anhydrous MeCN/MeOH (1 : 1) as solvent (data not shown here). These results, as well as the results in Figure **S1**, reveal that methanol could associate with **1a** and the newly formed complex could quench the emission of 4CzIPN efficiently.

Experiment Procedures and Product Characterization

General Information

Unless stated otherwise, commercial reagents were used as received, reactions were conducted in oven–dried glassware under an atmosphere of nitrogen using anhydrous solvents. Thin–layer chromatography (TLC) was conducted with 0.25 mm silica gel plates (Qingdao Haiyang Chemical China), and the compounds were visualized exposure to UV light (254 nm) or by potassium permanganate staining. Flash chromatography was performed on silica gel 200–300 mesh (purchased from Qingdao Haiyang Chemical China) with commercial solvents (purchased from Adamas–beta®). Data for ^{1}H NMR spectra (recorded on a Bruker AM 400 Spectrometer at 400Hz) are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Among these parameters, multiplicities were given as s (singlet), d (doublet), t (triplet), dd (double of doublet), and m (multiplets). ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker Spectrometers (at 100 or 151 MHz). Data for ^{13}C NMR and ^{19}F NMR spectra are reported in terms of chemical shift. Blue LEDs were purchased from http://shenzhen0920428.11467.com/. High–resolution mass spectrometry (HRMS) was recorded on Waters LCT Premier XE spectrometer.

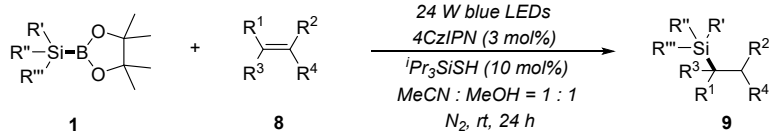
General Procedure A



1 2 3, 4, 5

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. After that CH_3CN (2.0 mL), MeOH (2.0 mL), **2** (0.2 mmol) and **1** (0.3 mmol) were added sequentially by means of syringe. The resulting solution was degassed for 15 min by bubbling N_2 stream, then stirred at room temperature under the irradiation of 24 W blue LED for 18 hours. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by flash silica-gel column chromatography (petroleum ether/ethyl acetate = 50 : 1 – 5 : 1) to give the products **3**, **4**, **5**.

General Procedure B

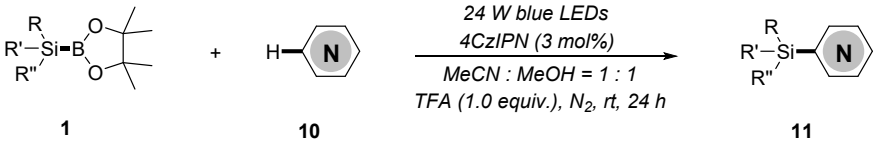


1 8 9

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the 4CzIPN (4.7 mg, 0.006 mmol). After that CH_3CN (2.0 mL), MeOH (2.0 mL), **8** (0.2 mmol), **1** (0.3 mmol) and $^{i}Pr_3SiSH$ (3.8 mg, 0.02 mmol) were added sequentially by means of syringe. The resulting solution was degassed for 15 min by bubbling N_2 stream. Then the reaction was placed under blue LEDs (24 W) for 24 hours.

The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by flash silica-gel column chromatography (petroleum ether/ethyl acetate = 50 : 1 – 5 : 1) to give the products **9**.

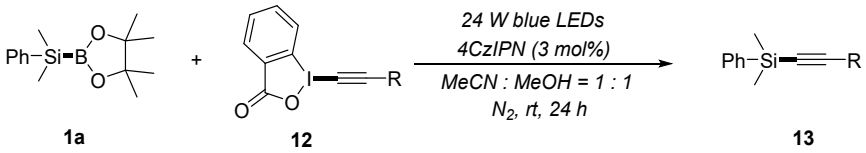
General Procedure C



1 10 11

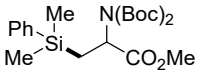
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the 4CzIPN (4.7 mg, 0.006 mmol). After that CH_3CN (2.0 mL), MeOH (2.0 mL), **10** (0.2 mmol), **1** (0.3 mmol) and TFA (23 mg, 0.2 mmol) were added sequentially by means of syringe. The resulting solution was degassed for 15 min by bubbling N_2 stream, then stirred at room temperature under the irradiation of 24 W blue LED for 24 hours. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by flash silica-gel column chromatography (petroleum ether/ethyl acetate = 100 : 1 – 5 : 1) to give the products **11**.

General Procedure D



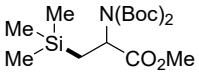
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the 4CzIPN (4.7 mg, 0.006 mmol). After that CH_3CN (2.0 mL), MeOH (2.0 mL), **12** (0.2 mmol) and **1a** (0.3 mmol) were added sequentially by means of syringe. The resulting solution was degassed for 15 min by bubbling N_2 stream, then stirred at room temperature under the irradiation of 24 W blue LED for 24 hours. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by flash silica-gel column chromatography (petroleum ether/ethyl acetate = 100 : 1 – 10 : 1) to give the products **13**.

Product Characterization



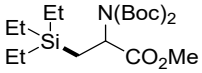
Methyl 3–(dimethyl(phenyl)silyl)–2–methylpropanoate (3a)

According to the general procedure **A**, **2a** (60 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 70 mg of **3a** was obtained as a colorless oil in 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) 7.52 – 7.48 (m, 2H), 7.35 – 7.33 (m, 3H), 5.00 (dd, *J* = 9.8, 5.7 Hz, 1H), 3.67 (s, 3H), 1.69 (dd, *J* =15.4, 5.7Hz, 1H), 1.54 (dd, *J* =15.4, 9.8 Hz, 1H), 1.46 (s, 18H), 0.33(s, 3H), 0.32(s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ177.3, 152.0, 138.6, 133.5, 129.0, 127.8, 83.1, 55.5, 53.5, 28.0, 17.2, –2.6. HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{35}NO_6SiNa$ 460.2131; Found 460.2134



Methyl 3–(dimethyl(phenyl)silyl)–2–methylpropanoate (3b)

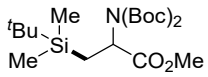
According to the general procedure **A**, **2a** (60 mg, 0.2 mmol, 1.0 equiv.), **1b** (60 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 54 mg of **3b** was obtained as a colorless oil in 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.92 (dd, *J* = 8.8, 4.5 Hz, 1H), 3.67 (s, 3H), 1.90 (dd, *J* = 14.6, 8.8 Hz, 1H), 1.48 (s, 18H), 1.00 (dd, *J* = 14.6, 4.4 Hz, 1H), 0.16 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 151.0, 81.8, 56.8, 51.1, 26.9, 8.7, 0.0; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{33}NO_6SiNa$ 398.1975; Found 398.1971.



Methyl 2–(bis(tert–butoxycarbonyl)amino)–3–(triethylsilyl)propanoate (3c)

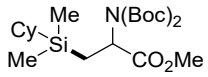
According to the general procedure **A**, **2a** (60 mg, 0.2 mmol, 1.0 equiv.), **1c** (72 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude

product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 65 mg of **3c** was obtained as a colorless oil in 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.98 (dd, *J* = 9.6, 5.5 Hz, 1H), 3.70 (s, 3H), 1.50 (s, 18H), 1.47 – 1.43 (m, 1H), 1.29 – 1.22 (m, 1H), 0.93 (d, *J* = 7.9 Hz, 9H), 0.61 – 0.52 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 152.1, 82.9, 55.5, 52.3, 28.0, 12.9, 7.3, 3.4. HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{39}NO_6SiNa$ 440.2444; Found 440.2438.



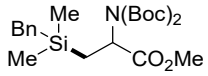
Methyl 2–(bis(tert–butoxycarbonyl)amino)–3–(cyclohexyldimethylsilyl)propanoate (3d)

According to the general procedure **A**, **2a** (60 mg, 0.2 mmol, 1.0 equiv.), **1d** (72 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 63 mg of **3d** was obtained as a colorless oil in 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.02 (dd, *J* = 9.8, 5.7 Hz, 1H), 3.74 (s, 3H), 1.54 (s, 18H), 1.51 – 1.46 (m, 1H), 1.33 – 1.27 (m, 1H), 0.91 (s, 9H), 0.07 (s, 3H), 0.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 152.0, 82.9, 55.6, 52.3, 28.0, 26.3, 16.5, 13.4, –6.0, –6.2. HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{39}NO_6SiNa$ 440.2444; Found 440.2437.



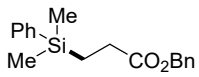
Methyl 2–(bis(tert–butoxycarbonyl)amino)–3–(cyclohexyldimethylsilyl)propanoate (3e)

According to the general procedure **A**, **2a** (60 mg, 0.2 mmol, 1.0 equiv.), **1e** (80 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 58 mg of **3e** was obtained as a colorless oil in 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.02 (dd, *J* = 10.1, 5.4 Hz, 1H), 1.81 – 1.69 (m, 5H), 1.55 (s, 18H), 1.48 – 1.07 (m, 9H), 0.03 (s, 3H), 0.00 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 152.1, 82.9, 55.6, 53.4, 28.0, 27.3, 26.9, 25.2, 14.9, –5.0; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{41}NO_6SiNa$ 466.2601; Found 466.2605.



Methyl 3–(benzyldimethylsilyl)–2–(bis(tert–butoxycarbonyl)amino)propanoate (3f)

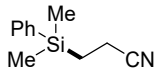
According to the general procedure **A**, **2a** (60 mg, 0.2 mmol, 1.0 equiv.), **1f** (83 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 56 mg of **3f** was obtained as a colorless oil in 62% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 2H), 7.12 – 6.98 (m, 3H), 5.04 (dd, *J* = 8.8, 5.9 Hz, 1H), 3.72 (s, 3H), 2.15 (s, 2H), 1.50 (s, 18H), 1.47 – 1.43 (m, 1H), 1.33 – 1.29 (m, 1H), 0.04 (s, 3H), 0.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 152.0, 139.9, 128.2, 128.1, 124.0, 83.1, 55.5, 52.3, 28.0, 25.7, 16.6, –3.2. HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{37}NO_6SiNa$ 474.2288; Found 474.2285.



Benzyl 3–(dimethyl(phenyl)silyl)propanoate (4a)

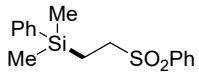
According to the general procedure **A**, **2a1** (32 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5

equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 50 mg of **3a2** was obtained as a colorless oil in 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.37 – 7.31 (m, 8H), 5.06 (s, 2H), 2.35 – 2.30 (m, 2H), 1.13 – 1.09 (m, 2H), 0.28 (s, 6H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ 174.7, 138.1, 136.0, 133.6, 129.1, 128.5, 128.2, 127.9, 66.3, 28.9, 10.8, –3.3; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{22}O_2SiNa$ 321.1287; Found 321.1282.



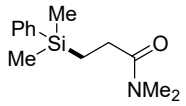
3–(Dimethyl(phenyl)silyl)propanenitrile (4b)

According to the general procedure **A**, **2b** (11 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 50 : 1) and 23 mg of **3b** was obtained as a colorless oil in 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.40 – 7.38 (m, 3H), 2.28 – 2.24 (m, 2H), 1.17– 1.13 (m, 2H), 0.36 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.7, 132.6, 127.3, 120.3, 11.3, 11.1, -4.4; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{15}NSiNa$ 212.0871; Found 212.0866.



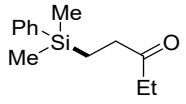
Dimethyl(phenyl)(2–(phenylsulfonyl)ethyl)silane (4c)

According to the general procedure **A**, **2c** (33 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) and 44 mg of **4c** was obtained as a colorless oil in 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.54 – 7.56 (m, 1H), 7.48 – 7.44 (m, 2H), 7.32 – 7.24 (m, 5H), 2.91 – 2.86 (m, 2H), 1.11 – 1.06 (m, 2H), 0.20 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.7, 136.6, 133.7, 133.5, 129.7, 129.3, 128.3, 128.2, 120.4, 115.5, 77.2, 52.6, 8.6, –3.3; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{20}O_2SSiNa$ 327.0851; Found 327.0855.



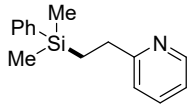
3–(dimethyl(phenyl)silyl)–N,N–dimethylpropanamide (4d)

According to the general procedure **A**, **2d** (20 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) and 35 mg of **4d** was obtained as a colorless oil in 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.32 – 7.28 (m, 3H), 2.91 (s, 3H), 2.90 (s, 3H), 2.28 – 2.23 (m, 2H), 1.11 – 1.07 (m, 2H), 0.30 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 133.8, 128.8, 124.3, 48.7, 32.4, 30.8, 23.0, 6.1, –7.9; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{21}NOSiNa$ 258.1290; Found 258.1286.



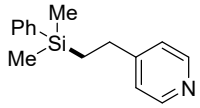
1–(Dimethyl(phenyl)silyl)pentan–3–one (4e)

According to the general procedure **A**, **2e** (16 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 32 mg of **4e** was obtained as a colorless oil in 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 2H), 7.36 – 7.34 (m, 3H), 2.40 – 2.32 (m, 4H), 1.04 – 0.96 (m, 5H), 0.28 (s, 6H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ 212.4, 138.4, 133.6, 133.0, 129.3, 127.9, 36.7, 35.2, 9.3, 8.0, –3.2; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}OSiNa$ 243.1181; Found 243.1176.



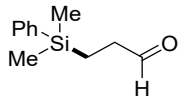
2–(2–(Dimethyl(phenyl)silyl)ethyl)pyridine (4f)

According to the general procedure **A**, **2f** (21 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) and 35 mg of **4f** was obtained as a colorless oil in 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 – 8.42 (m, 1H), 7.57 – 7.51 (m, 3H), 7.41 – 7.30 (m, 3H), 7.13 – 7.10 (m, 1H), 7.07 – 7.05 (m, 1H), 2.87 – 2.74 (m, 2H), 1.25 – 1.15 (m, 2H), 0.31 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.1, 149.0, 138.8, 136.3, 133.6, 128.9, 122.0, 120.8, 32.5, 29.7, –3.2; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{19}NSiNa$ 264.1184; Found 264.1182.



4–(2–(Dimethyl(phenyl)silyl)ethyl)pyridine (4g)

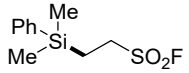
According to the general procedure **A**, **2g** (21 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) and 37 mg of **4g** was obtained as a colorless oil in 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 – 8.44 (m, 2H), 7.54 – 7.50 (m, 2H), 7.39 – 7.35 (m, 3H), 7.12 – 7.07 (m, 2H), 2.62 – 2.58 (m, 2H), 1.13 – 1.08 (m, 2H), 0.31 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.6, 133.6, 132.3, 130.6, 129.8, 129.2, 124.7, 123.4, 29.7, 16.6, -3.2; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{19}NSiNa$ 264.1184; Found 264.1182.



3–(Dimethyl(phenyl)silyl)propanal (4h)

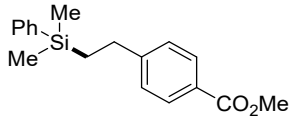
According to the general procedure **A**, **2h** (11 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 27 mg of **4h** was obtained as a colorless oil in 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72–9.70 (m, 1H),7.52 – 7.48 (m, 2H), 7.37 – 7.33 (m, 3H), 2.40 – 2.35 (m, 2H), 1.03 – 0.99 (m, 2H), 0.30 (s, 6H); **^{13}C NMR**

(400 MHz, $CDCl_3$) δ 168.0, 133.2, 131.5, 129.2, 127.9, 126.6, 125.2, 125.0, 25.9, 25.6, 16.2, –7.3; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{16}OSiNa$ 215.0868; Found 215.0874.



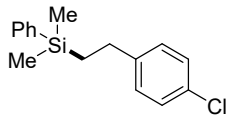
2–(Dimethyl(phenyl)silyl)ethane–1–sulfonyl fluoride (4i)

According to the general procedure **A**, **2i** (22 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 37 mg of **4i** was obtained as a colorless oil in 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.42 – 7.38 (m, 3H), 3.25 – 3.16 (m, 2H), 1.42 – 1.36 (m, 2H), 0.38 (s, 6H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ 135.5, 133.4, 130.0, 128.4, 47.8, 29.7, 10.0, –3.6; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{15}FO_2SSiNa$ 269.0444; Found 269.0440.



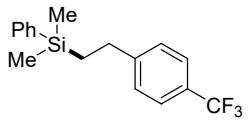
methyl 4–(2–(dimethyl(phenyl)silyl)ethyl)benzoate (4j)

According to the general procedure **A**, **2j** (32 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 49 mg of **4j** was obtained as a colorless oil in 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.72 – 7.67 (m, 2H), 7.55 – 7.47 (m, 3H), 7.38 – 7.35 (m, 2H), 3.89 (s, 3H), 2.69 – 2.65 (m, 2H), 1.14 – 1.10 (m, 2H), 0.30 (s, 6H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ167.1, 149.6, 139.5, 133.6, 129.2, 128.7, 128.2, 127.6, 51.9, 32.0, 15.1, -2.1; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{22}O_2SiNa$ 321.1287; Found 321.1290.



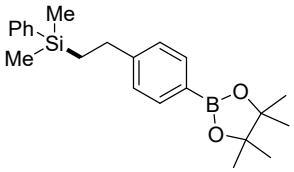
(4–Chlorophenethyl)dimethyl(phenyl)silane (4k)

According to the general procedure **A**, **2k** (28 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 50 : 1) and 36 mg of **4k** was obtained as a colorless oil in 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 2H), 7.39 – 7.35 (m, 3H), 7.22 – 7.18 (m, 2H), 7.10 – 7.08 (m, 2H), 2.67 – 2.53 (m, 2H), 1.14 – 1.04 (m, 2H), 0.29 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.3, 138.2, 134.2, 131.1, 129.1, 129.0, 128.3, 127.8, 29.7, 17.7, -3.1; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{19}ClSiNa$ 297.0842; Found 297.0844.



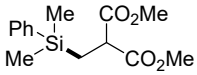
Dimethyl(phenyl)(4–(trifluoromethyl)phenethyl)silane (4l)

According to the general procedure **A**, **2l** (34 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 50 : 1) and 48 mg of **4l** was obtained as a colorless oil in 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 4H), 7.38 – 7.36 (m, 3H), 7.28 – 7.24 (m, 2H), 2.70 – 2.64 (m, 2H), 1.14 – 1.08 (m, 2H), 0.30 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.3, 138.9, 133.8, 129.3 (q, $^2J_{CF}$ = 31.6 Hz), 128.3 (q, $^3J_{CF}$ = 4.1 Hz), 125.5(q, $^1J_{CF}$ = 270.0 Hz), 30.2, 17.9, -2.9; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{19}F_3SiNa$ 331.1106; Found 331.1102.



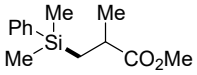
Dimethyl(phenyl)(4–(4,4,5,5–tetramethyl–1,3,2–dioxaborolan–2–yl)phenethyl)silane (4m)

According to the general procedure **A**, **2m** (46 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 50 : 1) and 54 mg of **4m** was obtained as a colorless oil in 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.30 – 7.26 (m, 3H), 7.11 (d, *J* = 7.8 Hz, 2H), 2.58 – 2.54 (m, 2H), 1,26 (s, 12H), 1.06 – 1.02 (m, 2H), 0.21 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.5, 141.9, 137.3, 136.7, 134.3, 132.3, 132.1, 131.4, 131.0, 86.6, 32.5, 28.1, 20.8, 0.0; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{31}BO_2SiNa$ 389.2084; Found 389.2090.



Dimethyl 2–((dimethyl(phenyl)silyl)methyl)malonate (4n)

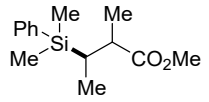
According to the general procedure **A**, **2n** (29 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 48 mg of **4n** was obtained as a colorless oil in 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.37 – 7.33 (m, 3H), 3.60 (s, 6H), 3.36 (t, *J* = 7.8 Hz, 1H), 1.43 (d, *J* = 7.8 Hz, 2H), 0.30 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.1, 136.8, 133.0, 128.6, 127.2, 51.8, 46.8, 14.8, -3.7; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{20}O_4SiNa$ 303.1029; Found 303.1025.



Methyl 3–(dimethyl(phenyl)silyl)–2–methylpropanoate (4o)

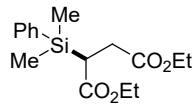
According to the general procedure **A**, **2o** (20 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 37 mg of **4o** was obtained as a colorless oil in 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.37 – 7.33 (m, 3H), 3.54 (s, 3H), 2.56 – 2.51 (m, 2H), 1.14 (d, *J* = 9.8 Hz, 1H), 0.96 – 0.90 (m, 2H), 0.29

(s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.9, 138.6, 133.5, 129.0, 127.8, 51.5, 35.5, 29.7, 20.9, 20.7, -2.6; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}O_2SiNa$ 259.1130; Found 259.1135.



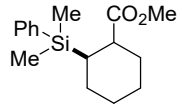
Methyl–3–(dimethyl(phenyl)silyl)–2–methylbutanoate (4p)

According to the general procedure **A**, **2p** (23 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA =20 : 1) and 36 mg of **4p** was obtained as a colorless oil in 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.37 – 7.33 (m, 3H), 3.58 (s, 3H), 2.54 – 2.50 (m, 1H), 1.29 – 1.25 (m, 1H), 1.10 (d, J = 7.0 Hz, 3H), 0.97 (d, J = 7.6 Hz, 3H), 0.31(s, 3H), 0.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.9, 138.7, 133.9, 128.9, 127.7, 51.6, 41.9, 24.3, 17.2, 12.9, -3.7; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{22}O_2SiNa$ 273.1287; Found 273.1288.



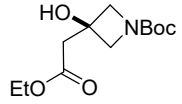
Diethyl 2–(dimethyl(phenyl)silyl)succinate (4q)

According to the general procedure **A**, **2q** (34 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 49 mg of **4q** was obtained as a colorless oil in 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 2H), 7.39 – 7.34 (m, 3H), 4.09 – 4.03 (m, 4H), 2.84 – 2.66 (m, 2H), 2.24 (dd, J = 16.8, 2.9 Hz, 1H), 1.21 – 1.15 (m, 6H), 0.41 (s, 3H), 0.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 168.1, 130.6, 129.1, 125.0, 123.2, 55.9, 55.4, 28.0, 26.9, 24.4, 9.5, -8.5, -9.6; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{24}O_4SiNa$ 331.1342; Found 331.1346.



Methyl 2–(dimethyl(phenyl)silyl)cyclohexane–1–carboxylate (4r)

According to the general procedure **A**, **2r** (28 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 41 mg of **4r** was obtained as a colorless oil in 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.35 – 7.32 (m, 3H), 3.52 (s, 3H), 2.68 – 2.66 (m, 1H), 1.98 – 1.95 (m, 1H), 1.76 – 1.68 (m, 2H), 1.60 – 1.48 (m, 4H), 1.16 – 1.10 (m, 2H), 0.29 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.7, 139.3, 133.9, 128.7, 127.6, 51.7, 41.1, 30.0, 28.1, 27.3, 24.0, 22.9, -3.7, -3.8; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{24}O_2SiNa$ 299.1443; Found 299.1438.

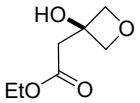


Tert-Butyl-3-(dimethyl(phenyl)silyl)-3-(2-methoxy-2-oxoethyl)azetidine-1-carboxylate (4s′)

According to general procedure A, **2s** (48 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) and 23 mg of **4s** was obtained as a colorless oil in 30% yield.

A vial containing **4s** (23 mg, 0.06 mmol) was filled with N_2. CH_2Cl_2 (1.0 mL) and $HBF_4 \cdot Et_2O$ (0.2 mL, 0.09 mmol) were sequentially added at 0 °C. After 2 h stirring at 0 °C, the mixture was quenched with water. The aqueous layer was extracted with hexane (three times). The combined organic layer was washed with water and brine, and then was dried and concentrated to provide the fluorinated product without other purification.

The fluorinated compound was placed in a screw-top test tube. THF (0.5 mL), MeOH (1.0 mL), KF (7.0 mg, 0.12 mmol), $KHCO_3$ (30.0 mg, 0.3 mmol), 30% H_2O_2 aq. (0.6 mmol) were sequentially added at 25 °C. After being stirred for 24 h, the mixture was quenched with $Na_2S_2O_3$ aq. The aqueous layer was extracted with ethyl acetate (three times). The combined organic layer was washed with water and brine, and then was dried and concentrated. Crude product was purified by flash column chromatography on silica gel (PE/EA = 2 : 1) and 10 mg of **4s′** was obtained as a colorless oil in 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.20 (q, *J* = 7.2, 2H), 3.93 (d, *J* = 9.4 Hz, 2H), 3.82 (d, *J* = 9.4 Hz, 2H), 2.81 (s, 2H), 1.44 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 156.4, 82.9, 79.8, 67.7, 61.3, 42.6, 28.3, 14.1. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_{21}NO_5$ 259.1420; Found 259.1415.

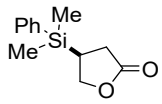


Methyl 2–(3–(dimethyl(phenyl)silyl)oxetan–3–yl)acetate (4t′)

According to general procedure A, **4t** (28 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) and 20 mg of **4t** was obtained as a colorless oil in 36% yield.

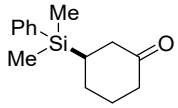
A vial containing **4t** (20 mg, 0.072 mmol) was filled with N_2. CH_2Cl_2 (1.0 mL) and $HBF_4 \cdot Et_2O$ (0.25 mL, 0.12 mmol) were sequentially added at 0 °C. After 2 h stirring at 0 °C, the mixture was quenched with water. The aqueous layer was extracted with hexane (three times). The combined organic layer was washed with water and brine, and then was dried and concentrated to provide the fluorinated product without other purification.

The fluorinated compound was placed in a screw-top test tube. THF (0.5 mL), MeOH (1.0 mL), KF (8.7 mg, 0.15 mmol), $KHCO_3$ (40 mg, 0.4 mmol), 30% H_2O_2 aq. (0.8 mmol) were sequentially added at 25 °C. After being stirred for 24 h, the mixture was quenched with $Na_2S_2O_3$ aq. The aqueous layer was extracted with ethyl acetate (three times). The combined organic layer was washed with water and brine, and then was dried and concentrated. Crude product was purified by flash column chromatography on silica gel (PE/EA = 2 : 1) and 8 mg of **4s′** was obtained as a colorless oil in 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.68 (d, *J* = 6.9 Hz, 2H), 4.49 (d, *J* = 6.9 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 1H), 2.93 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.1, 82.1, 71.0, 60.4, 41.1, 13.3. HRMS (EI) m/z: $[M]^+$ Calcd for $C_7H_{12}O_4$ 160.0736; Found 160.0740.



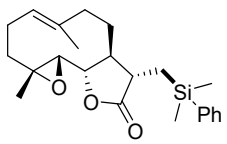
4–(Dimethyl(phenyl)silyl)dihydrofuran–2(3H)–one (4v)

According to the general procedure **A**, **2v** (17 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 18 mg of **4v** was obtained as a colorless oil in 42% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.44 – 7.36 (m, 3H), 4.45 – 4.40 (m, 1H), 4.14 – 4.08 (m, 1H), 2.54 – 2.46 (m, 1H), 2.33 – 2.27 (m, 1H), 2.09 – 2.01 (m, 1H), 0.37 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.1, 135.1, 133.7, 129.1, 128.4, 115.3, 70.9, 30.4, 23.9, -4.8; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{16}O_2SiNa$ 243.0817; Found 243.0812.



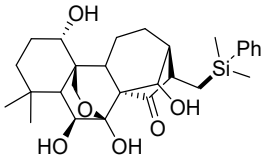
3–(Dimethyl(phenyl)silyl)cyclohexan–1–one (4w)

According to the general procedure **A**, **2w** (19 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 27 mg of **4w** was obtained as a colorless oil in 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.38 – 7.34 (m, 3H), 2.38 – 2.06 (m, 5H), 1.83 – 1.79 (m, 1H), 1.72 – 1.66 (m, 1H), 1.48 – 1.38 (m, 2H), 1.32– 1.24 (m, 2H), 0.31(s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 212.8, 136.6, 133.9, 129.3, 127.9, 53.5, 42.4, 41.9, 29.8, 27.7, 26.1, -5.3, -5.4; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{20}OSiNa$ 255.1181; Found 255.1185.



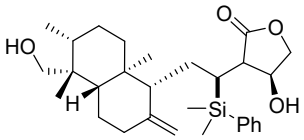
(3S,3aS,9aR,10aS,10bS,E)–3–((dimethyl(phenyl)silyl)methyl)–6,9a–dimethyl–3a,4,5,8,9,9a,10a,10b–octahydrooxireno[2',3':9,10]cyclodeca[1,2–b]furan–2(3H)–one (5a)

According to the general procedure **A**, **Parthenolide** (50 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 5 : 1) and 65 mg of **5a** was obtained as a colorless oil in 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.38 – 7.34 (m, 3H), 5.02 – 4.96 (m, 1H), 3,69 (t, J = 9.1 Hz, 1H), 3.48 (s, 3H), 2.54 (d, J = 8.9 Hz, 1H), 2.34 – 2.28 (m, 2H), 2.16 – 2.02 (m, 3H), 1.84 – 1.76 (m, 1H), 1.72 – 1.66 (m, 1H), 1.62 (s, 3H), 1.58 – 1.54 (m, 1H), 1.48 – 1.42 (m, 1H), 1.23 (s, 3H), 1.20 – 1.10 (m, 3H), 0.41(s, 3H), 0.39(s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.7, 136.7, 136.0, 131.5, 130.3, 127.2, 84.3, 68.6, 63.7, 54.1, 46.6, 42.9, 38.9, 31.9, 26.3, 19.4, 19.1, 17.3, 0.4, 0.0; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{32}O_3SiNa$ 407.2018; Found 407.2021.



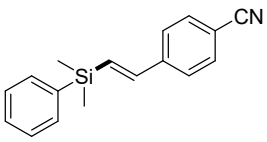
(1S,5S,6R,6aS,8S,9S)–8–((Dimethyl(phenyl)silyl)methyl)–1,5,6–trihydroxy–4,4–dimethyl–14–(l3–oxidaneylidene)–2,3,4,4a,5,6,8,9,10,11,11a,11b–dodecahydro–11bl5–6,11b–(epoxymethano)–6a,9–methanocyclohepta[c]naphthalen–7(1H)–one (5b)

According to the general procedure **A**, **Oridonin** (73 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (DCM/MeOH = 50 : 1) and 70 mg of **5b** was obtained as a colorless oil in 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.38 – 7.32 (m, 3H), 6.24 (d, *J* =11.4Hz, 1H), 5.64 (s, 1H), 4.89 (s, 1H), 4.44 (s, 1H), 4.21 (d, *J* =7.1Hz, 1H), 4.12 (dd, *J* =10.8, 5.6 Hz, 1H), 4.02 (d, *J* =10.8Hz, 1H), 3.65 (dd, *J* =11.4, 6.5 Hz, 1H), 3.43 (dd, *J* =11.2, 5.7 Hz, 1H), 3.04 – 2.99 (m, 1H), 1.94 (s, 1H), 1.98 – 1.92 (m, 1H), 1.70 – 152 (m, 4H), 1.52 – 1.34 (m, 4H), 1.28 – 1.18 (m, 4H), 1.10 – 1.05 (m, 6H), 0.78 (dd, *J* = 15.1, 11.1 Hz, 1H), 0.32 (s, 6H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 227.2, 140.4, 135.5, 131.2, 130.0, 98.7, 95.2, 75.2, 75.1, 73.6, 64.9, 62.6, 62.4, 54.9, 48.8, 41.2, 40.5, 40.1, 35.5, 34.6, 31.4, 23.5, 21.6, 20.5, 13.4, -0.6; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{40}O_6SiNa$ 523.2492; Found 523.2486.



(4S)–3–((S)–1–(Dimethyl(phenyl)silyl)–2–((1R,4aS,5R,6R,8aS)–5–(hydroxymethyl)–5,6,8a–trimethyl–2–methylenedecahydronaphthalen–1–yl)ethyl)–4–hydroxydihydrofuran–2(3H)–one (5c)

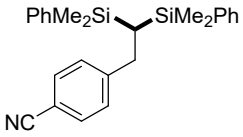
According to the general procedure **A**, **Andrographolide** (70 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 2 : 1) and 53 mg of **5c** was obtained as a colorless oil in 55% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.40 – 7.32 (m, 3H), 6.73 (s, 1H), 4.76 – 4.72 (m, 3H), 4.31 (s, 1H), 4.09 (d, *J* =11.1Hz, 1H), 4.36 – 4.32 (m, 2H), 4.31 (s, 1H), 2.89 (s, 1H), 2.70 (s, 1H), 2.36 – 2.30 (m, 1H), 2.26 – 2.20 (m, 1H), 2.04 (s, 1H), 1.90 – 1.82 (m, 1H), 1.74 – 1.66 (m, 6H), 1.74 – 1.66 (m, 6H), 1.26 – 1.22 (m, 9H), 1.16 (s, 3H), 0.94 – 0.82 (m, 2H), 0.50 (s, 2H),0.32(s, 3H), 0.28(s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.7 , 143.0, 142.9, 136.1, 133.0, 132.3, 129.4, 124.7, 123.1, 102.7, 75.9, 65.5, 59.4, 50.9, 50.4, 48.7, 38.0, 34.6, 33.1, 31.6, 23.5, 20.5, 20.1, 19.1, 17.9, 10.2, –10.4; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{44}O_4SiNa$ 507.2907; Found 507.2901.



(E)–4–(2–(Dimethyl(phenyl)silyl)vinyl)benzonitrile (7a)

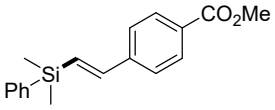
According to the general procedure **A**, **6a** (51 mg, 0.4 mmol, 2.0 equiv.), **1a** (52 mg, 0.2 mmol, 1.0

equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 39 mg of **7a** was obtained as a colorless oil in 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.56 – 7.52 (m, 2H), 7.50 (d, *J* = 8.5 Hz, 3H), 7.40 – 7.37 (m, 3H), 6.91 (d, *J* = 19.1 Hz, 1H), 6.74 (d, *J* = 19.1 Hz, 1H), 0.45 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.3, 143.4, 135.0, 133.7, 133.5, 131.0, 130.4, 129.1, 128.1, 120.0, 112.3, -1.7; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{18}NSi$ 264.1209; Found 264.1208.



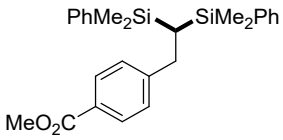
4–(2,2–Bis(dimethyl(phenyl)silyl)ethyl)benzonitrile (7a′)

According to the general procedure **A**, **6a** (26mg, 0.2 mmol, 1.0 equiv.), **1a** (156 mg, 0.6 mmol, 3.0 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 48 mg of **7a′** was obtained as a colorless oil in 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 – 7.17 (m, 4H), 7.15 – 7.12 (m, 2H), 7.11 – 7.06 (m, 6H), 6.62 (d, *J* = 8.1 Hz, 2H), 2.58 (d, *J* = 6.6 Hz, 2H), 0.58 (t, *J* = 6.6 Hz, 1H), 0.05 (s, 6H), 0.00 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.7, 140.4, 134.7, 132.6, 130.0, 129.9, 128.8, 120.2, 110.0, 33.2, 16.3, 0.0, -1.4; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{29}NSi_2Na$ 422.1736; Found 422.1732.



Methyl (E)-4-(2-(dimethyl(phenyl)silyl)vinyl)benzoate (7b)

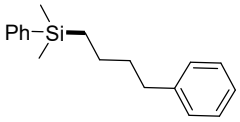
According to the general procedure **A**, **6b** (64 mg, 0.4 mmol, 2.0 equiv.), **1a** (52 mg, 0.2 mmol, 1.0 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 47 mg of **7b** was obtained as a colorless oil in 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.65 – 7.54 (m, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.37 (dd, *J* = 4.9, 1.9 Hz, 3H), 6.95 (d, *J* = 19.1 Hz, 1H), 6.72 (d, *J* = 19.1 Hz, 1H), 3.90 (s, 3H), 0.45 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 146.6, 144.8, 140.5, 136.4, 133.4, 132.4, 131.9, 131.7, 130.4, 128.9, 54.6, 0.2; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{20}O_2SiNa$ 319.1130; Found 319.1136.



Methyl 4-(2,2-bis(dimethyl(phenyl)silyl)ethyl)benzoate (7b′)

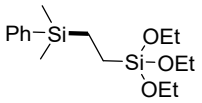
According to the general procedure **A**, **7b** (32mg, 0.2 mmol, 1.0 equiv.), **1a** (156 mg, 0.6 mmol, 3.0 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 57 mg of **7b′** was obtained as a colorless oil in 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H),

7.28 – 7.21 (m, 4H), 7.18 – 7.08 (m, 6H), 6.74 (d, *J* = 8.2 Hz, 2H), 3.72 (s, 3H), 2.65 (d, *J* = 6.6 Hz, 2H), 0.66 (t, *J* = 6.6 Hz, 1H), 0.00 (s, 6H), -0.01 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 151.0, 140.9, 135.0, 130.6, 130.1, 129.6, 129.0, 53.2, 33.3, 16.4, 0.0, -0.8; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{32}O_2Si_2Na$ 455.1839; Found 455.1841.



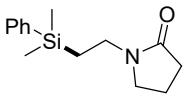
Dimethyl(phenyl)(4–phenylbutyl)silane (9a)

According to the general procedure **B**, **8a** (26 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), $^{i}Pr_3SiSH$ (3.8 mg, 0.02 mmol, 10 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 100 : 1) and 33 mg of **9a** was obtained as a colorless oil in 62% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.37 – 7.33 (m, 3H), 7.28 – 7.24 (m, 2H), 7.18 – 7.12 (m, 3H), 2.60 – 2.56 (m, 2H), 1.67 – 1.60 (m, 2H), 1.42 – 1.36 (m, 2H), 0.80 – 0.75 (m, 2H), 0.25 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.8, 138.2, 132.5, 127.8, 127.4, 127.2, 126.7, 124.5, 34.6, 34.3, 30.2, 28.7, 22.6, 14.5, -4.1. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{24}Si$ 268.1647; Found 268.1640.



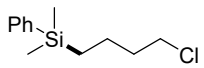
Dimethyl(phenyl)(4–phenylbutyl)silane (9b)

According to the general procedure **B**, **8b** (38 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), $^{i}Pr_3SiSH$ (3.8 mg, 0.02 mmol, 10 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 52 mg of **9b** was obtained as a colorless oil in 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.35 – 7.33 (m, 3H), 3.80 (q, *J* = 7.0 Hz, 6H), 1.21 (t, J = 7.0 Hz, 9H), 0.80 – 0.75 (m, 2H), 0.57 – 0.54 (m, 2H), 0.26 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.8, 132.7, 129.3, 127.7, 47.1, 29.0, 9.3, -4.3. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{30}O_3Si_2$ 326.1733; Found 326.1738.



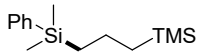
1–(2–(Dimethyl(phenyl)silyl)ethyl)pyrrolidin–2–one (9c)

According to the general procedure **B**, **8c** (22 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), $^{i}Pr_3SiSH$ (3.8 mg, 0.02 mmol, 10 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) and 35 mg of **9c** was obtained as a colorless oil in 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 2H), 7.36 – 7.34 (m, 3H), 3.37 – 3.32 (m, 2H), 3.28 – 3.25 (m, 2H), 2.30 – 2.25 (m, 2H), 1.87 – 1.82 (m, 2H), 1.07 – 1.02 (m, 2H), 0.32 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ174.3, 138.3, 133.4, 129.1, 127.8, 46.2, 38.4, 31.2, 17.6, 14.4, -3.2; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{21}NOSi$ 247.1392; Found 247.1390.



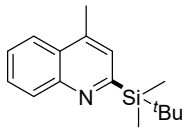
(4–Chlorobutyl)dimethyl(phenyl)silane (9d)

According to the general procedure **B**, **8d** (18 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), $^{i}Pr_3SiSH$ (3.8 mg, 0.02 mmol, 10 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 100 : 1) and 33 mg of **9d** was obtained as a colorless oil in 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.36 – 7.33 (m, 3H), 3.53 – 3.50 (m, 2H), 1.81 – 1.76 (m, 2H), 1.50 – 1.44 (m, 2H), 0.78 – 0.74 (m, 2H), 0.27 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.2, 133.5, 128.9, 127.8, 44.7, 36.1, 21.2, 15.0, -3.1. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_{19}ClSi$ 226.0945; Found 226.0948.



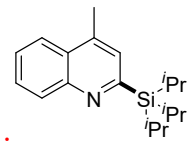
(3–(dimethyl(phenyl)silyl)propyl)trimethylsilane (9e)

According to the general procedure **B**, **8e** (23 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), $^{i}Pr_3SiSH$ (3.8 mg, 0.02 mmol, 10 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 100 : 1) and 27 mg of **9e** was obtained as a colorless oil in 54% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.41 – 7.36 (m, 3H), 1.46 – 1.40 (m, 2H), 0.88 – 0.84 (m, 2H), 0.62 – 0.58 (m, 2H), 0.30 (s, 6H), 0.00 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.4, 135.1, 130.2, 129.2, 31.2, 22.8, 21.7, 19.9, 2.6, -1.4. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{26}Si_2$ 250.1573; Found 250.1578.



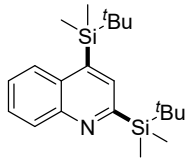
2–(tert–Butyldimethylsilyl)–4–methylquinoline (11a)

According to the general procedure **C**, **10a** (29 mg, 0.2 mmol, 1.0 equiv.), **1d** (82 mg, 0.3 mmol, 1.5 equiv.), TFA (23 mg, 0.2 mmol, 1.0 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 50 : 1) and 36 mg of **11a** was obtained as a colorless oil in 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 8.4, 0.5 Hz, 1H), 7.99 (dd, J = 8.3, 0.7 Hz, 1H), 7.70 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.55 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.44 (s, 1H), 2.73 (s, 3H), 1.02 (s, 9H), 0.45 (s, 6H);**^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.6, 148.4, 140.2, 130.8, 128.4, 127.3, 127.0, 126.0, 123.6, 26.7, 18.6, 17.2, –6.2; HRMS (ESI–TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{24}NSi$ 258.1678; Found 258.1668.



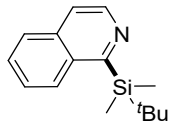
4–methyl–2–(triisopropylsilyl)quinoline (11b)

According to the general procedure **C**, **10a** (29 mg, 0.2 mmol, 1.0 equiv.), **1g** (85 mg, 0.3 mmol, 1.5 equiv.), TFA (23 mg, 0.2 mmol, 1.0 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 50 : 1) and 39 mg of **11b** was obtained as a colorless oil in 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 – 8.05 (m, 1H), 7.91 – 7.87 (m, 1H), 7.60 – 7.56 (m, 1H), 7.46 – 7.42 (m, 1H), 7.29 (s, 1H), 2.60 (s, 3H), 1.54 – 1.46 (m, 3H), 1.08 (d, *J* = 8.3, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.3, 147.5, 138.7, 129.8, 127.2, 126.7, 126.2, 124.9, 122.6, 28.7, 17.7, 10.2, -7.2; HRMS (ESI–TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{30}NSi$ 300.2148; Found 300.2155.



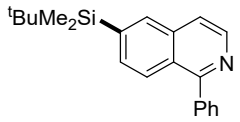
2,4–bis(tert–butyldimethylsilyl)quinoline (11c)

According to the general procedure **C**, **10c** (26 mg, 0.2 mmol, 1.0 equiv.), **1d** (82 mg, 0.3 mmol, 1.5 equiv.), TFA (23 mg, 0.2 mmol, 1.0 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 50 : 1) and 46 mg of **11c** was obtained as a colorless oil in 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 – 8.17 (m, 1H), 8.02 – 8.00 (m, 1H), 7.66 (s, 1H), 7.73 – 7.63 (m, 1H), 7.50 – 7.44 (m, 1H), 0.96 (s, 9H), 0.93 (s, 9H), 0.51 (s, 6H), 0.41 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 148.2, 141.9, 134.3, 131.4, 129.0, 128.1, 125.7, 27.0, 26.7, 17.7, 17.3, –3.3, –6.2; HRMS (ESI–TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{36}NSi_2$ 358.2381; Found 358.2387.



1–(tert–Butyldimethylsilyl)isoquinoline (11d)

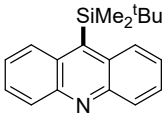
According to the general procedure **C**, **10d** (26 mg, 0.2 mmol, 1.0 equiv.), **1d** (82 mg, 0.3 mmol, 1.5 equiv.), TFA (23 mg, 0.2 mmol, 1.0 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 50 : 1) and 35 mg of **11d** was obtained as a colorless oil in 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.6 Hz, 1H), 8.25 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.84 – 7.76 (m, 1H), 7.65 – 7.61 (m, 1H), 7.58 – 7.54 (m, 1H), 0.96 (s, 9H), 0.56 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 141.7, 133.2, 132.9, 132.1, 128.4, 127.8, 126.8, 125.5, 119.0, 26.2, 17.1, –3.9; HRMS (ESI–TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{22}NSi$ 244.1522; Found 2244.1526.



6–(tert–Butyldimethylsilyl)–1–phenylisoquinoline (11e)

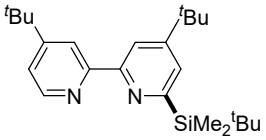
According to the general procedure **C**, **10e** (41 mg, 0.2 mmol, 1.0 equiv.), **1d** (82 mg, 0.3 mmol, 1.5 equiv.), TFA (23 mg, 0.2 mmol, 1.0 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 41 mg of **11e** was obtained as a colorless oil in 65% yield. **^{1}H NMR**

(400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 5.7 Hz, 1H), 8.10 – 7.99 (m, 2H), 7.74 – 7.66 (m, 2H), 7.66 – 7.60(m, 2H), 7.57 – 7.47 (m, 3H), 0.92 (s, 9H), 0.38 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.2, 141.7, 140.9, 139.0, 135.5, 133.5, 131.9, 129.5, 128.2, 127.9, 125.4, 119.6, 26.1, 16.6, –6.6; HRMS (ESI–TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{26}NSi$ 320.1835; Found 320.1837.



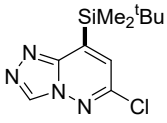
9–(tert–Butyldimethylsilyl)acridine (11f)

According to the general procedure **C**, **10f** (36 mg, 0.2 mmol, 1.0 equiv.), **1d** (82 mg, 0.3 mmol, 1.5 equiv.), TFA (23 mg, 0.2 mmol, 1.0 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 29 mg of **11f** was obtained as a colorless oil in 50% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.7, 2H), 8.25 (d, *J* = 8.7, 2H), 7.76 – 7.70 (m, 2H), 7.54 – 7.48 (m, 2H), 1.18 (s, 9H), 0.69 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.8, 142.6, 132.6, 129.2, 128.8, 127.6, 126.4, 126.1, 119.1, 27.1, 26.7, 17.2, -6.1; HRMS (ESI–TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}NSi$ 294.1678; Found 294.1683.



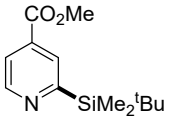
4,4'–di–tert–Butyl–6–(tert–butyldimethylsilyl)–2,2'–bipyridine (11g)

According to the general procedure **C**, **10g** (54 mg, 0.2 mmol, 1.0 equiv.), **1d** (82 mg, 0.3 mmol, 1.5 equiv.), TFA (23 mg, 0.2 mmol, 1.0 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 40 mg of **11g** was obtained as a colorless oil in 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.58 (d, *J* = 5.2 Hz, 1H), 8.33 (s, 1H), 7.49 (s, 1H), 7.28 (d, *J* = 5.2, 1H), 1.39 (s, 9H), 1.38 (s, 9H), 1.00 (s, 69H), 0.37 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ165.3, 158.1, 157.2, 155.5, 126.4, 120.5, 118.7, 116.6, 30.7, 30.5, 26.7, 17.0, –6.1; HRMS (ESI–TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{39}N_2Si$ 383.2883; Found 383.2887.



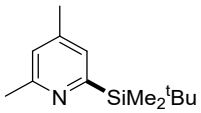
8–(tert–butyldimethylsilyl)–6–chloro–[1,2,4]triazolo[4,3–b]pyridazine (11h)

According to the general procedure **C**, **10h** (31 mg, 0.2 mmol, 1.0 equiv.), **1d** (82 mg, 0.3 mmol, 1.5 equiv.), TFA (23 mg, 0.2 mmol, 1.0 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) and 31 mg of **11h** was obtained as a colorless oil in 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.20 (s, 1H), 0.92 (s, 9H), 0.46 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.8, 134.0, 133.6, 133.0, 129.1, 115.5, 101.5, 26.7, –6.9; HRMS (ESI–TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{18}ClN_4Si$ 269.0984; Found 269.0988.



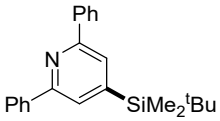
methyl 2–(tert–Butyldimethylsilyl)isonicotinate (11i)

According to the general procedure **C**, **10i** (27 mg, 0.2 mmol, 1.0 equiv.), **1d** (82 mg, 0.3 mmol, 1.5 equiv.), TFA (23 mg, 0.2 mmol, 1.0 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 30 mg of **11i** was obtained as a colorless oil in 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 5.0 Hz, 1H), 8.00 (s, 1.0 Hz), 7.71 (d, *J* = 5.0 Hz, 1H), 3.94 (s, 3H), 0.90 (s, 9H), 0.34 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 166.4, 150.5, 134.7, 128.3, 121.4, 52.6, 26.5, 17.0, –6.3; HRMS (ESI–TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{22}NO_2Si$ 252.1414; Found 252.1417.



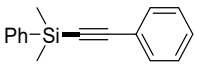
2–(tert–Butyldimethylsilyl)–4,6–dimethylpyridine (11j)

According to the general procedure **C**, **10j** (21 mg, 0.2 mmol, 1.0 equiv.), **1d** (82 mg, 0.3 mmol, 1.5 equiv.), TFA (23 mg, 0.2 mmol, 1.0 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 23 mg of **11j** was obtained as a colorless oil in 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (s, 1H), 6.86 (s, 1H), 2.51 (s, 3H), 2.27 (s, 3H), 0.91 (s, 9H), 0.28 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.3, 157.8, 128.1, 123.0, 38.1, 31.2, 26.7, 20.9, –6.2; HRMS (ESI–TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{24}NSi$ 222.1678; Found 222.1680.



4–(tert–Butyldimethylsilyl)–2,6–diphenylpyridine (11k)

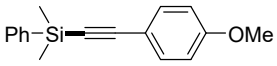
According to the general procedure A, **10k** (46 mg, 0.2 mmol, 1.0 equiv.), **1d** (82 mg, 0.3 mmol, 1.5 equiv.), TFA (23 mg, 0.2 mmol, 1.0 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 33 mg of **11k** was obtained as a colorless oil in 48% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 4H), 7.70 (m, 2H), 7.45 – 7.41 (m, 4H), 7.39 – 7.35 (m, 2H), 0.88 (s, 9H), 0.31 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ155.9, 149.2, 135.8, 128.8, 128.6, 124.3, 122.5, 118.6, 26.5, 13.1, –7.3; HRMS (ESI–TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{28}NSi$ 346.1986; Found 346.1995.



Dimethyl(phenyl)(phenylethynyl)silane (13a)

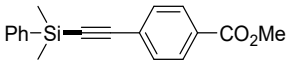
According to the general procedure **D**, **12a** (70 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 100 : 1) and 35 mg of

13a was obtained as a colorless oil in 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H), 7.52 – 7.49 (m, 2H), 7.42 – 7.38 (m, 3H), 7.32 – 7.28 (m, 3H), 0.49 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.8, 134.6, 132.9, 130.2, 129.5, 129.0, 128.7, 123.7, 107.6, 92.8, 0.0; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{17}Si$ 226.1021; Found 226.1026.



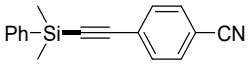
((4–Methoxyphenyl)ethynyl)dimethyl(phenyl)silane (13b)

According to the general procedure **D**, **12b** (76 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 100 : 1) and 30 mg of **13b** was obtained as a colorless oil in 56% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.67 (m, 2H), 7.46 – 7.42 (m, 2H), 7.40 – 7.36 (m, 3H), 6.84 – 6.82 (m, 2H), 3.81 (s, 3H), 0.48 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.8, 138.2, 134.7, 134.5, 130.3, 128.8, 116.0, 114.7, 107.8, 91.3, 56.2, –0.2; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{18}OSi$ 266.1127; Found 266.1135.



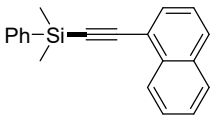
((4–Methoxyphenyl)ethynyl)dimethyl(phenyl)silane (13c)

According to the general procedure **D**, **12c** (81 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 48 mg of **13c** was obtained as a colorless oil in 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H), 7.68 – 7.64 (m, 2H), 7.68 – 7.64 (m, 2H), 7.48 – 7.44 (m, 2H), 7.41 – 7.36 (m, 3H), 3.99 (s, 3H), 0.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 139.3, 134.2, 132.4, 130.5, 129.8, 128.7, 128.0, 83.1, 80.4, 52.6, –3.6; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{18}O_2Si$ 294.1076; Found 294.1084.



4–((Dimethyl(phenyl)silyl)ethynyl)benzonitrile (13d)

According to the general procedure **D**, **12d** (74 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 40 mg of **13d** was obtained as a colorless oil in 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.54 – 7.50 (m, 2H), 7.40 – 7.36 (m, 2H), 7.33 – 7.28 (m, 3H), 0.32(s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.0, 133.9, 132.1, 128.4, 127.7, 127.0, 118.3, 112.3, 81.9, 81.6, –3.9; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{15}NSi$ 261.0974; Found 261.0978.

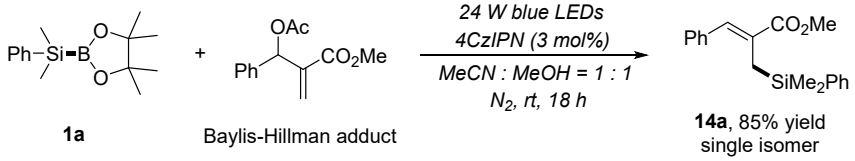


Dimethyl(naphthalen–1–ylethynyl)(phenyl)silane (13e)

According to the general procedure **D**, **12e** (80 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude

product was purified by flash column chromatography on silica gel (PE/EA = 50 : 1) and 34 mg of **13e** was obtained as a colorless oil in 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 – 8.33 (m, 1H), 7.85 – 7.81 (m, 2H), 7.79 – 7.72 (m, 3H), 7.58 – 7.52 (m, 2H), 7.52 – 7.49 (m, 1H), 7.74 – 7.40 (m, 4H), 0.58 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.2, 133.0, 132.6, 132.2, 130.2, 128.6, 127.4, 126.8, 126.1, 125.6, 125.3, 124.2, 119.7, 103.9, 96.4, –1.5; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{18}Si$ 286.1178; Found 286.1185.

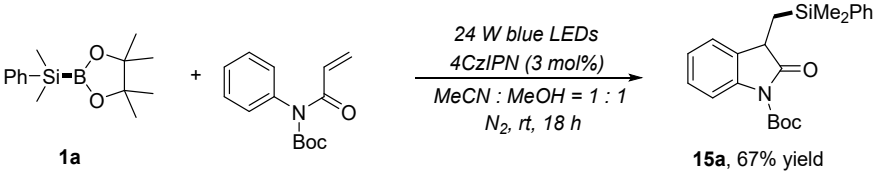
Synthesis of methyl (Z)–2–((dimethyl(phenyl)silyl)methyl)–3–phenylacrylate (14a)



1a Baylis-Hillman adduct **14a**, 85% yield single isomer

According to the general procedure A, **Bayils–Hillman adduct** (47 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) and 53 mg of **14a** was obtained as a colorless oil in 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.40 – 7.36 (m, 3H), 7.38 – 7.30 (m, 2H), 7.28 – 7.25 (m, 1H), 7.22 – 7.18 (m, 2H), 6.38 (s, 1H), 3.46 (s, 3H), 2.13 (s, 2H), 0.36 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.7, 132.6, 132.1, 130.2, 129.2, 128.8, 127.7, 127.2, 126.3, 126.1, 53.4, 51.4, 27.0, 26.7, 25.2, -3.3, -6.2; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{22}O_2SiNa$ 333.1287; Found 333.1282.

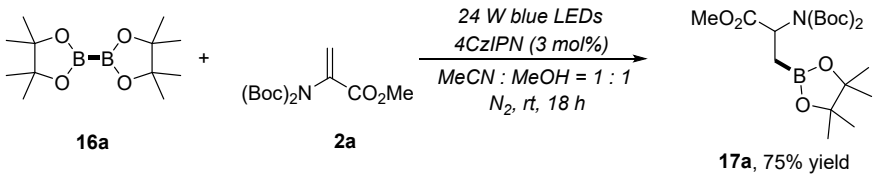
Synthesis of 3–((dimethyl(phenyl)silyl)methyl)–1,3–dimethylindolin–2–one (15a)



1a **15a**, 67% yield

According to the general procedure A, **alkene** (35 mg, 0.2 mmol, 1.0 equiv.), **1a** (78 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 3 mol%), CH_3CN (2.0 mL), MeOH (2.0 mL) were used. Crude product was purified by flash column chromatography on silica gel (PE/EA =10 : 1) and 41 mg of **15a** was obtained as a colorless oil in 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.17 (m, 6H), 7.07 (d, J = 7.3 Hz, 1H), 6.97 – 6.93 (m, 1H), 6.70 (d, J = 7.3 Hz, 1H), 2.90 (s, 3H), 2.04 (d, J = 14.7 Hz, 1H), 1.64 (d, J = 14.7 Hz,1H), 1.38 (s, 3H), –0.05 (s, 3H), –0.11 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.1, 135.1, 133.7, 133.1, 130.0, 128.4, 115.3, 70.9, 30.4, 23.9, 0.0, -3.6; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{23}NOSiNa$ 332.1447; Found 332.1440.

Synthesis of methyl 2–(bis(tert–butoxycarbonyl)amino)–3–(4,4,5,5–tetramethyl–1,3,2–dioxaborolan–2–yl)propanoate (17a)

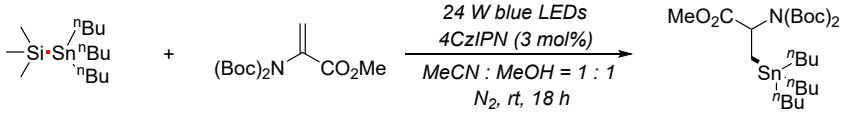


16a **2a** **17a**, 75% yield

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the 4CzIPN (4.7 mg, 0.006

mmol). After that CH_3CN (2.0 mL), MeOH (2.0 mL), **2a** (0.2 mmol), **16a** (0.3 mmol) and were added sequentially by means of syringe. The resulting solution was degassed for 15 min by bubbling N_2 stream, then stirred at room temperature under the irradiation of 24 W blue LED for 18 hours. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by flash silica–gel column chromatography (PE/EA = 20 : 1) to give the products **17a** (64mg) as a colorless oil in 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.17 (dd, *J* = 10.4, 5.2 Hz, 1H), 3.69 (s, 3H), 1.70 (dd, *J* = 15.4, 10.4 Hz, 1H), 1.49 (s, 18H), 1.23 (d, *J* = 10.6 Hz, 12H), 1.13 (dd, *J* = 15.4, 5.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 151.8, 83.8, 82.9, 55.7, 52.2, 28.0, 24.8, 24.6; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{36}NBO_8SiNa$ 452.2432; Found 452.2426.

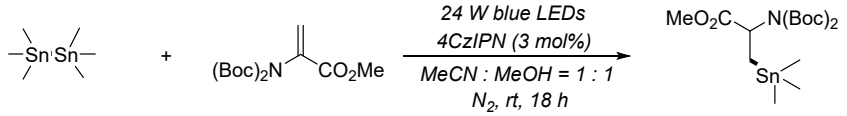
Synthesis of methyl 2–(bis(tert–butoxycarbonyl)amino)–3–(tributylstannyl)propanoate (19a)



18a **2a** **19a**, 78% yield

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the 4CzIPN (4.7 mg, 0.006 mmol). After that CH_3CN (2.0 mL), MeOH (2.0 mL), **2a** (0.2 mmol), **18a** (0.3 mmol) and were added sequentially by means of syringe. The resulting solution was degassed for 15 min by bubbling N_2 stream, then stirred at room temperature under the irradiation of 24 W blue LED for 18 hours. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by flash silica–gel column chromatography (PE/EA = 20 : 1) to give the products **19a** (92mg) as a colorless oil in 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) 5.03 (dd, *J* = 9.9, 6.8 Hz, 1H), 3.70 (s, 3H), 1.56 (dd, *J* = 12.8, 9.9 Hz, 1H), 1.50 (s, 18H), 1.50 – 1.39 (m, 4H), 1.35 – 1.25 (m, 6H), 1.16 (dd, *J* = 12.8, 6.8 Hz, 1H), 0.97 – 0.75 (m, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 151.9, 82.8, 58.0, 52.3, 29.1, 28.0, 27.4, 13.7, 10.7, 9.6; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{51}NO_6SnNa$ 616.2636; Found 616.2645.

Synthesis of methyl 2–(bis(tert–butoxycarbonyl)amino)–3–(trimethylstannyl)propanoate (21a)

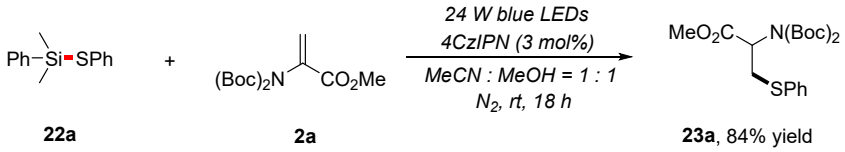


20a **2a** **21a**, 80% yield

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the 4CzIPN (4.7 mg, 0.006 mmol). After that CH_3CN (2.0 mL), MeOH (2.0 mL), **2a** (0.2 mmol), **20a** (0.3 mmol) and were added sequentially by means of syringe. The resulting solution was degassed for 15 min by bubbling N_2 stream, then stirred at room temperature under the irradiation of 24 W blue LED for 18 hours. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by flash silica–gel column chromatography (PE/EA = 20 : 1) to give the products **21a** (75mg) as a colorless oil in 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.94 (dd, *J* = 10.2, 6.6 Hz, 1H), 3.59 (s, 3H), 1.50 (dd, *J* = 12.7, 10.2 Hz, 1H), 1.40 (s, 18H), 1.07 (dd, *J* = 12.7, 6.6 Hz, 1H), 0.00 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9 , 151.1 , 82.1 , 57.0 , 27.2 , 12.2 , –9.9; **^{13}C NMR** (100 MHz, $CDCl_3$) δ

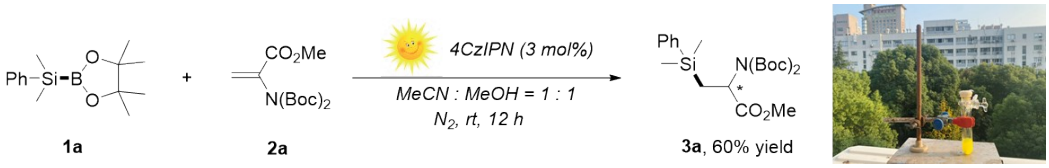
171.8, 151.1, 82.1, 57.0, 27.2, 12.2, -9.9; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{33}NO_6SnNa$ 490.1228; Found 490.1234.

Synthesis of methyl N,N–bis(tert–butoxycarbonyl)–S–phenylcysteinate (23a)



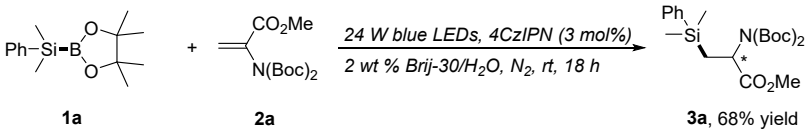
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the 4CzIPN (4.7 mg, 0.006 mmol). After that CH_3CN (2.0 mL), MeOH (2.0 mL), **2a** (0.2 mmol), **22a** (0.3 mmol) and were added sequentially by means of syringe. The resulting solution was degassed for 15 min by bubbling N_2 stream, then stirred at room temperature under the irradiation of 24 W blue LED for 18 hours. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by flash silica–gel column chromatography (PE/EA = 20 : 1) to give the products **23a** (66mg) as a colorless oil in 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 2H), 7.32 – 7.23 (m, 2H), 7.23 – 7.16 (m, 1H), 5.10 (dd, J = 9.9, 4.6 Hz, 1H), 3.76 – 3.72 (m, 1H), 3.73 (s, 3H), 3.47 (dd, J = 14.6, 9.9 Hz, 1H), 1.45 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.2, 150.8, 134.7, 128.7, 128.0, 125.4, 82.3, 56.8, 51.4, 33.8, 26.9; HRMS (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{29}NO_6SNa$ 434.1613; Found 434.1620.

Investigation of the model reaction under the irradiation of sunlight



On November 8th of 2022, the model reaction was performed following the general procedure A outside the window of the school of Pharmacy, East China University of Science and Technology, Shanghai. **1a** and **2a** were used as starting materials and employing natural sunlight irradiation for 12h. The exposure started at 6:00 and was stopped at 18:00.

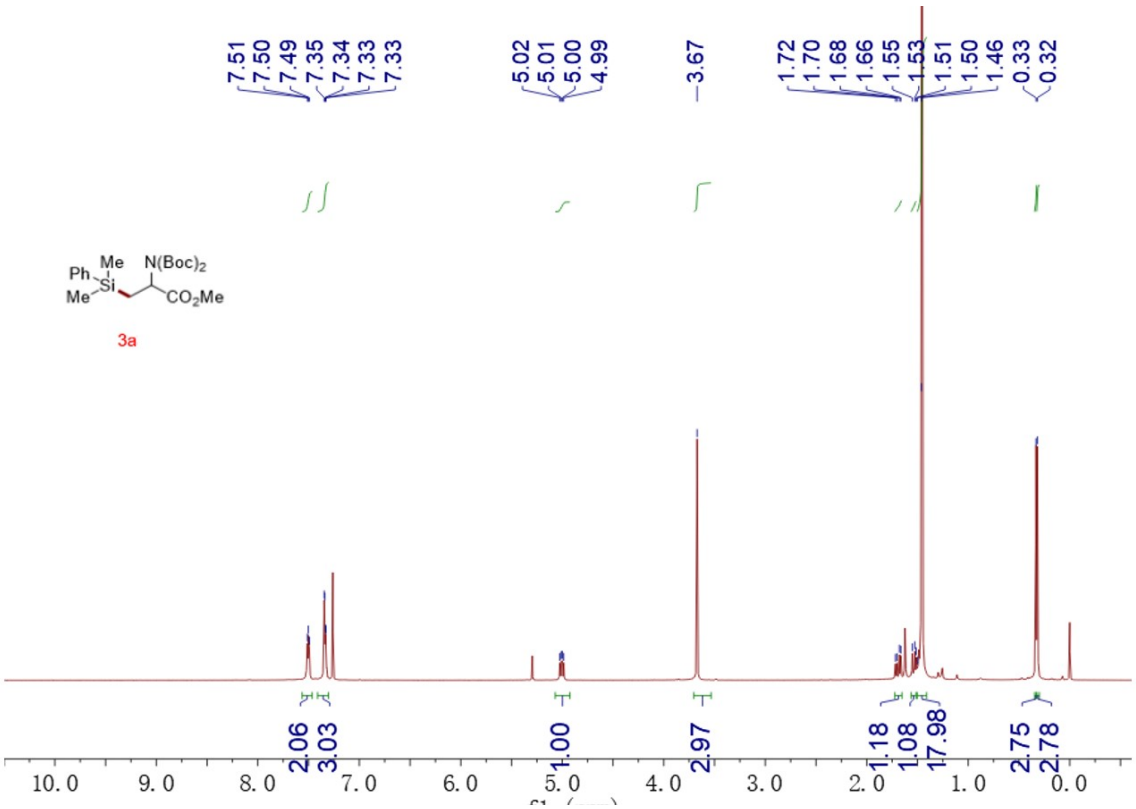
Investigation of the model reaction using water as alternative solvent



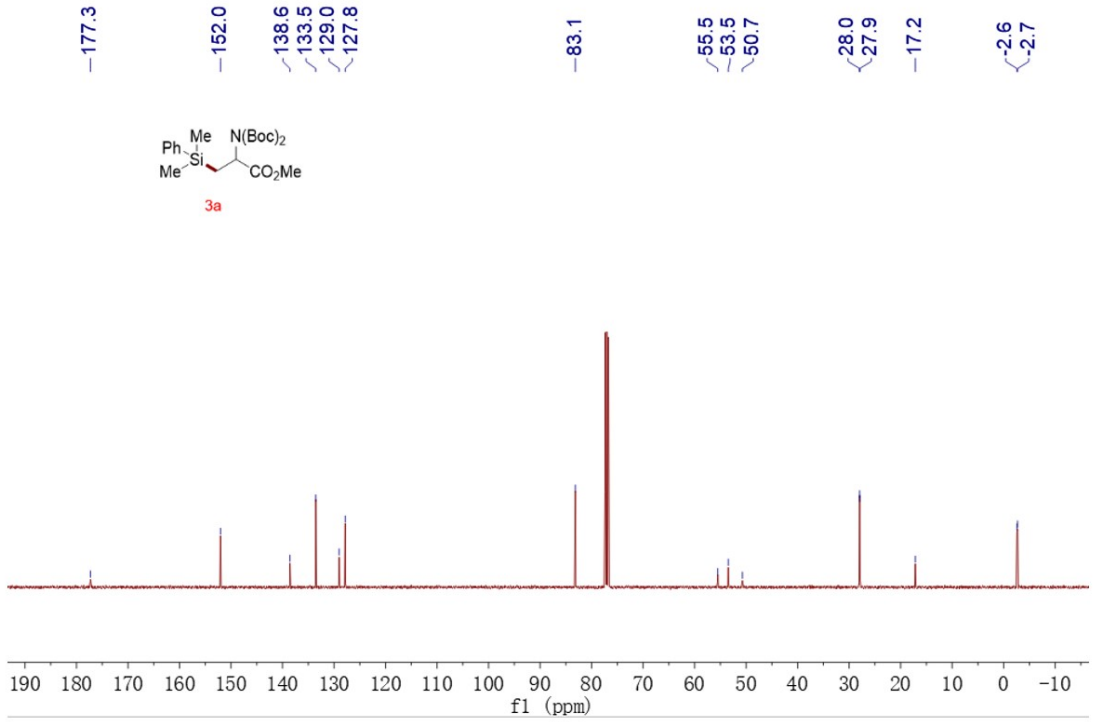
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the 4CzIPN (4.7 mg, 0.006 mmol). After that, aqueous solution of 2 wt % Brij-30 (2 mL), **2a** (0.2 mmol), **1a** (0.3 mmol) and were added sequentially by means of syringe. The resulting solution was degassed for 15 min by bubbling N_2 stream, then stirred at room temperature under the irradiation of 24 W blue LED for 18 hours. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by flash silica–gel column chromatography (PE/EA = 20 : 1) to give the products **3a** (60mg) as a colorless oil in 68% yield.

NMR Spectra

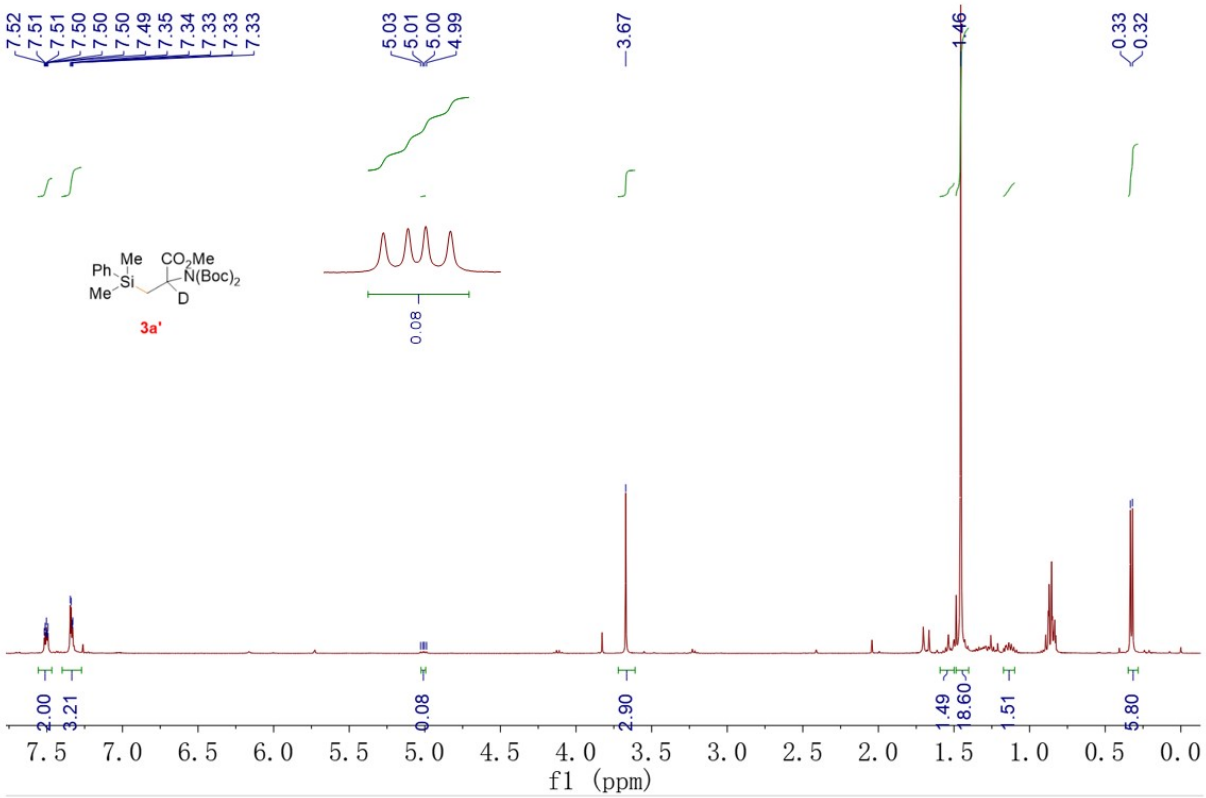
^{1}H NMR spectra of 3a (400 MHz, $CDCl_3$)



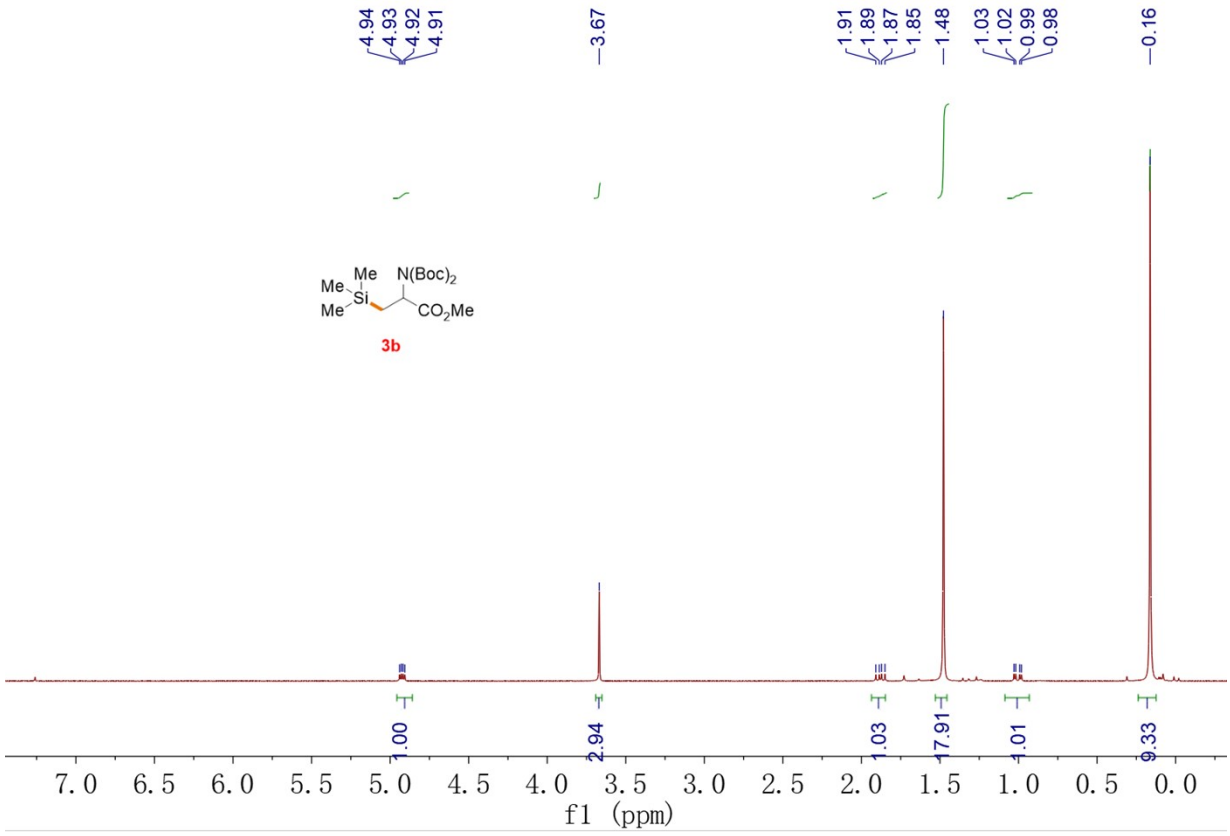
^{13}C NMR spectra of 3a (100 MHz, $CDCl_3$)



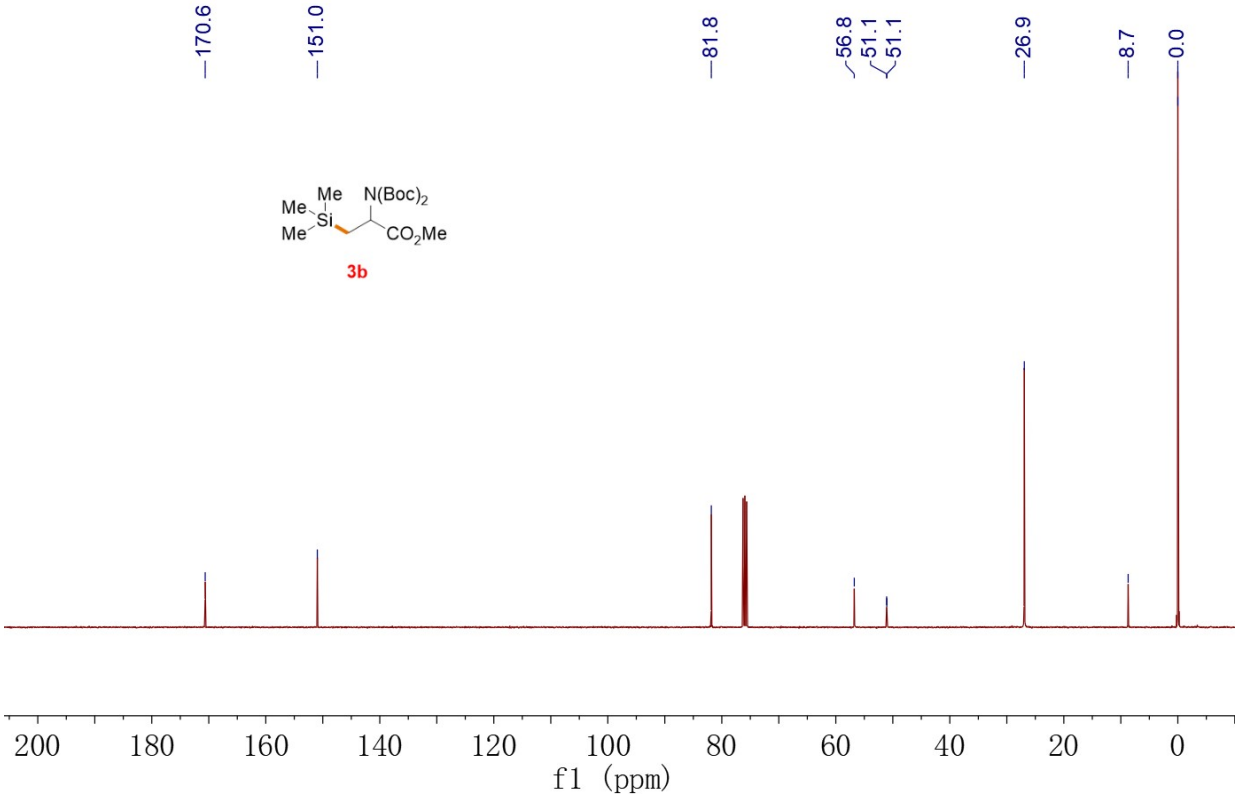
^{1}H NMR spectra of 3a′ (400 MHz, $CDCl_3$)



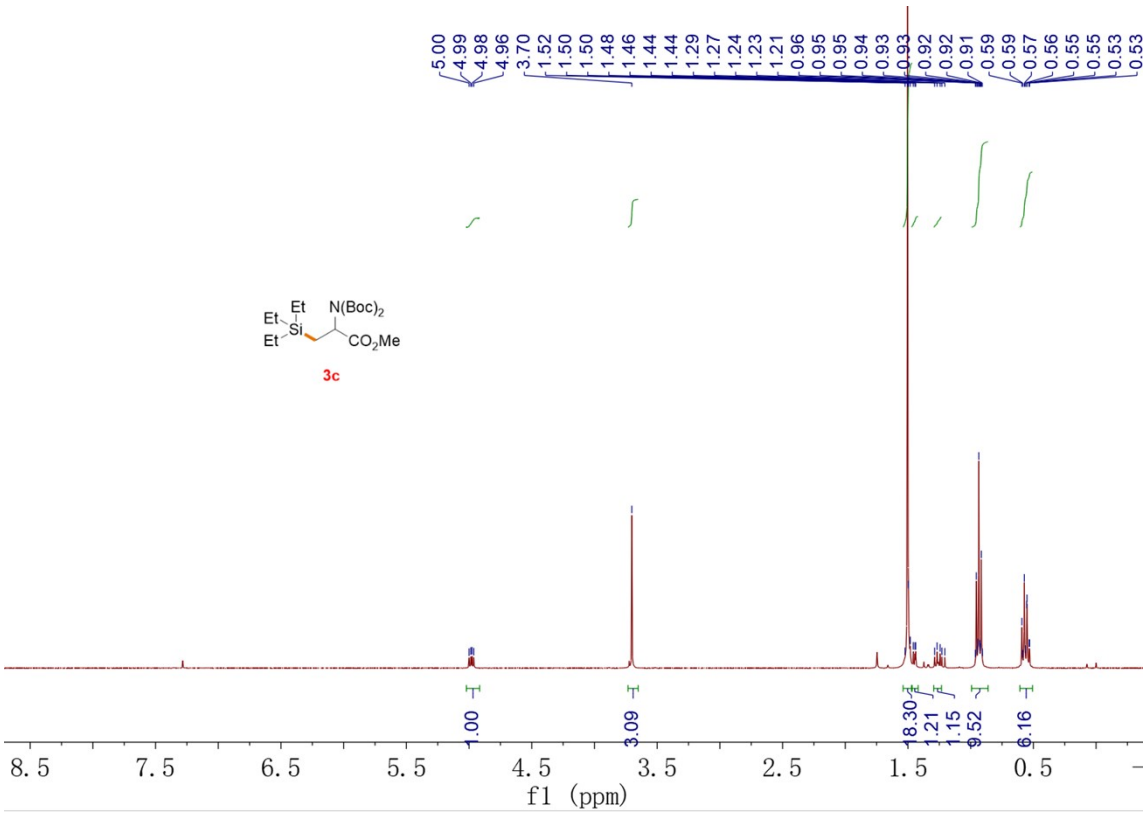
^{1}H NMR spectra of 3b (400 MHz, $CDCl_3$)



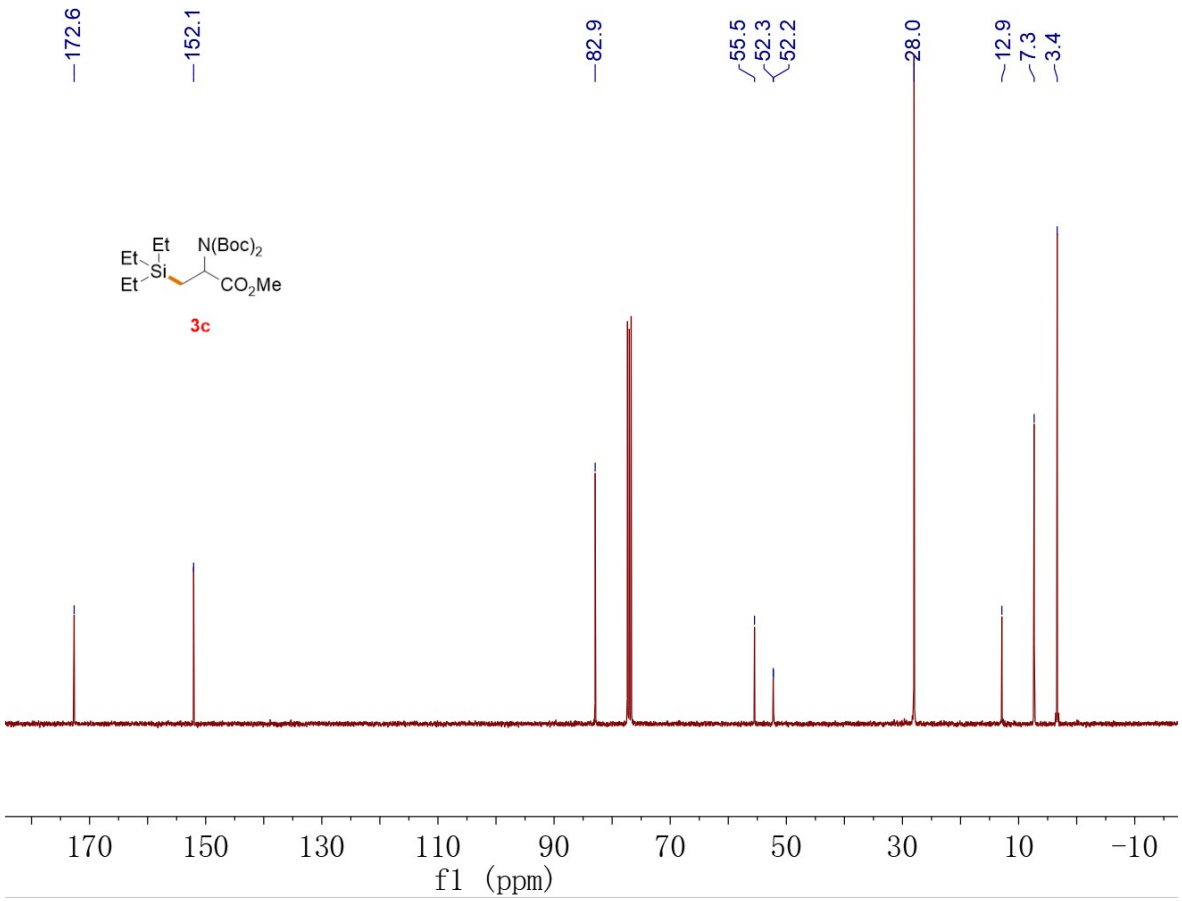
^{13}C NMR spectra of 3b (100 MHz, $CDCl_3$)



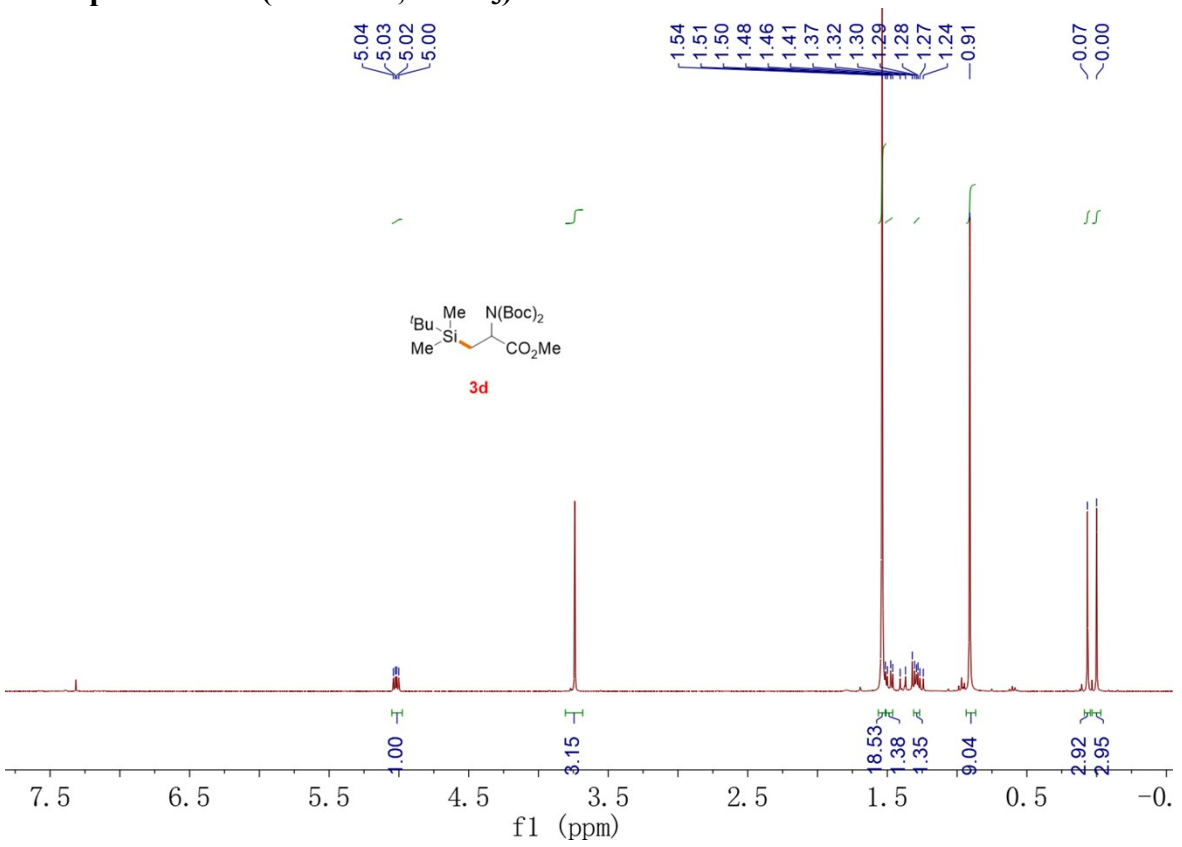
^{1}H NMR spectra of 3c (400 MHz, $CDCl_3$)



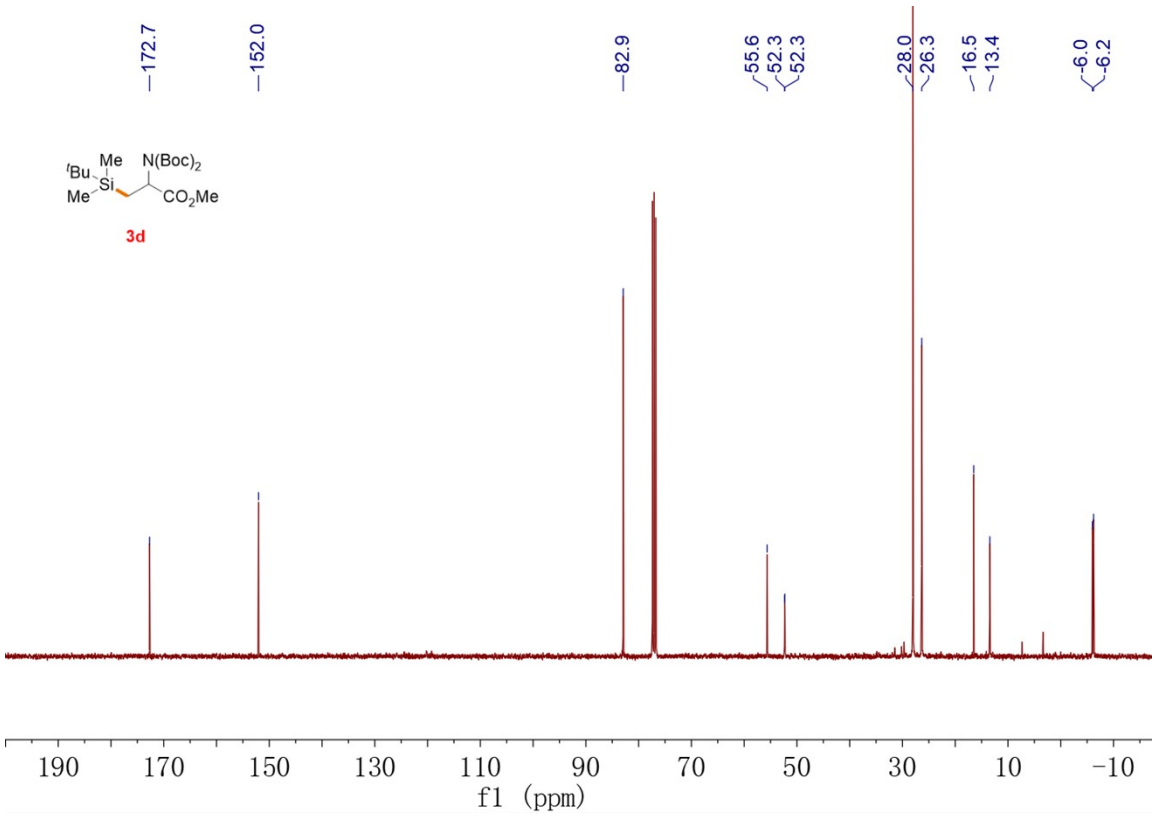
^{13}C NMR spectra of 3c (100 MHz, $CDCl_3$)



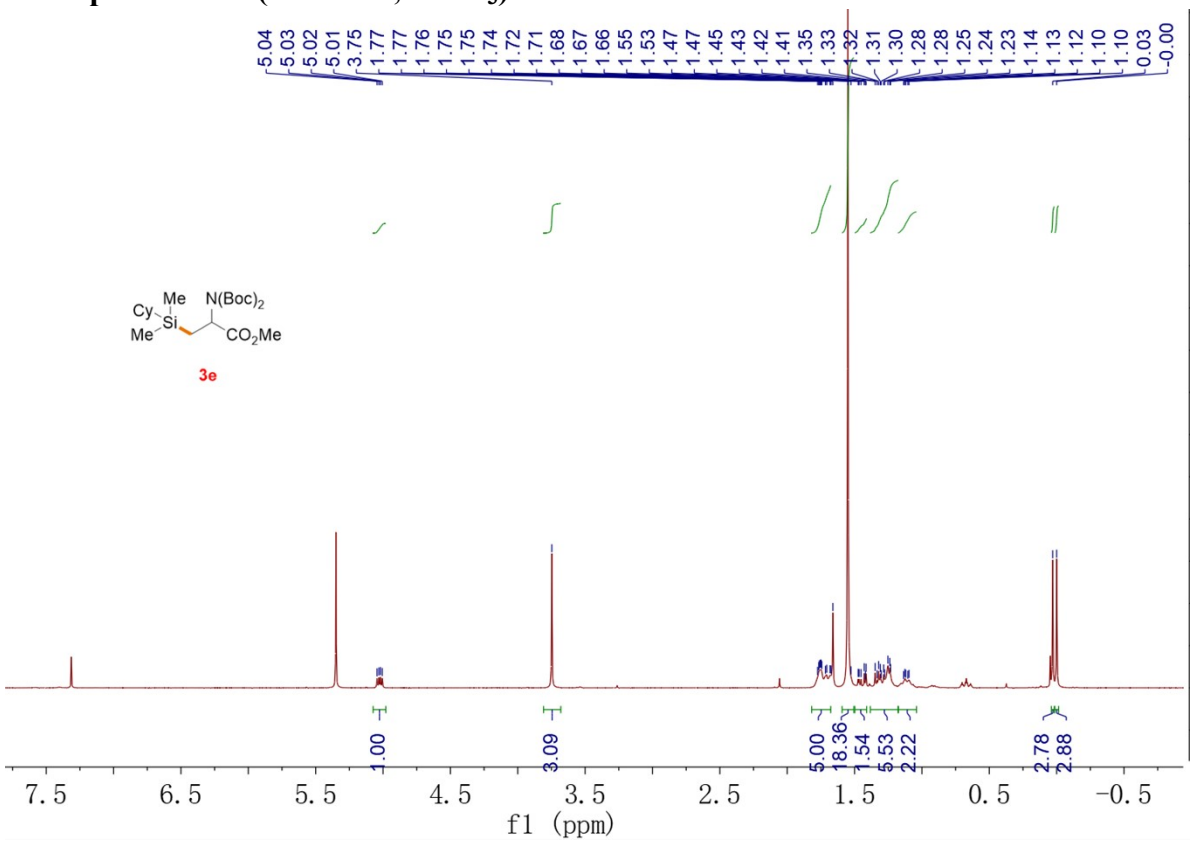
^{1}H NMR spectra of 3d (400 MHz, $CDCl_3$)



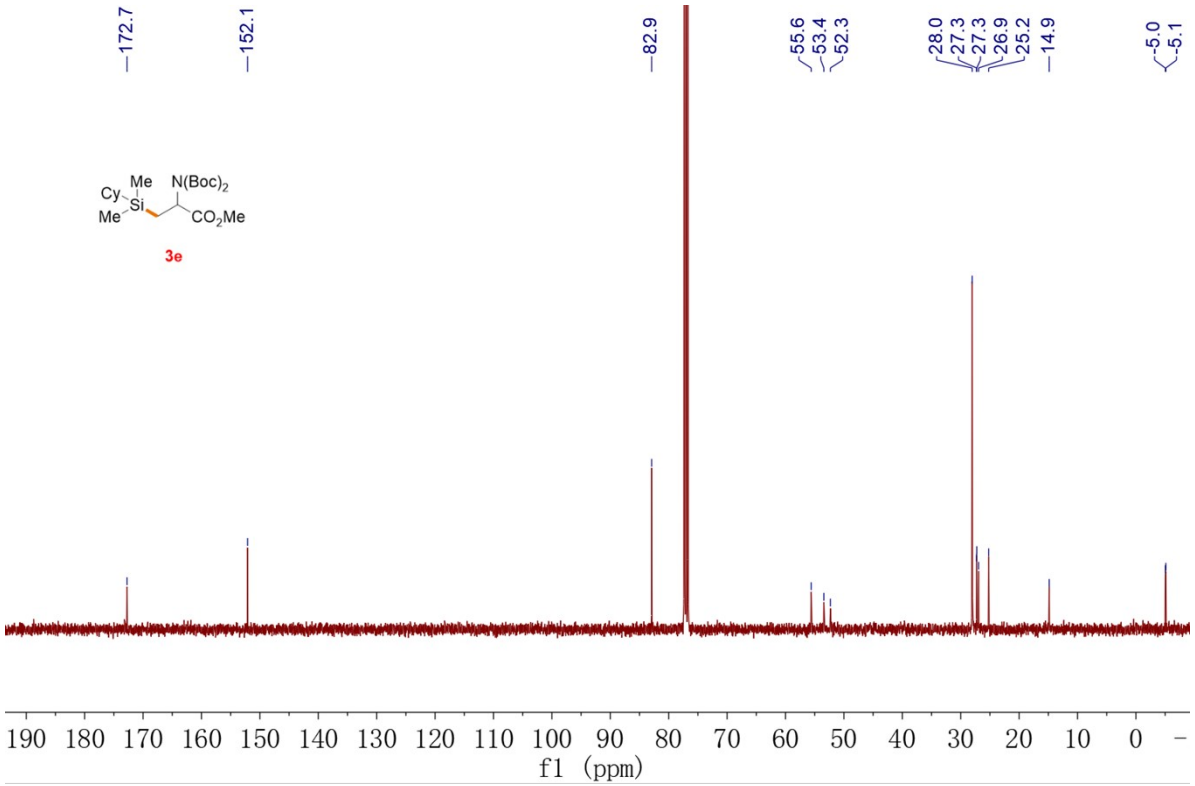
^{13}C NMR spectra of 3d (100 MHz, $CDCl_3$)



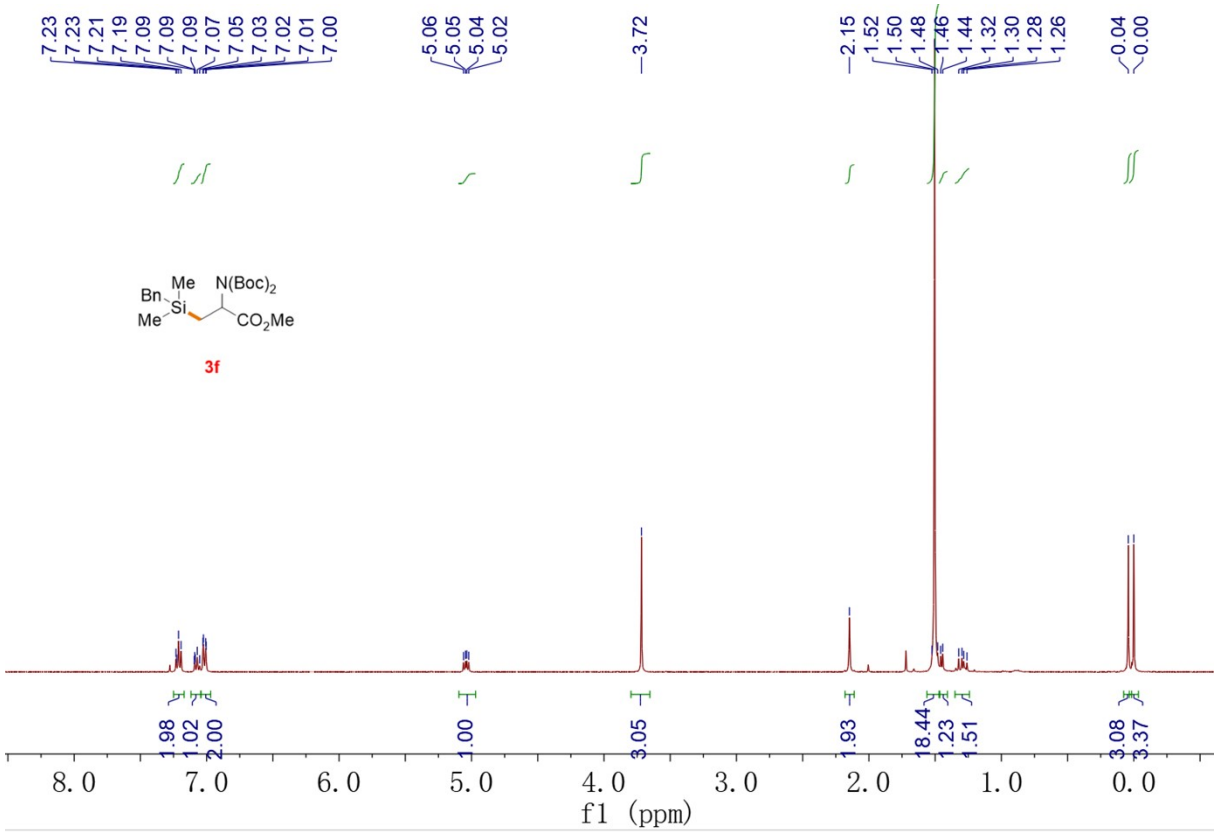
^{1}H NMR spectra of 3e (400 MHz, $CDCl_3$)



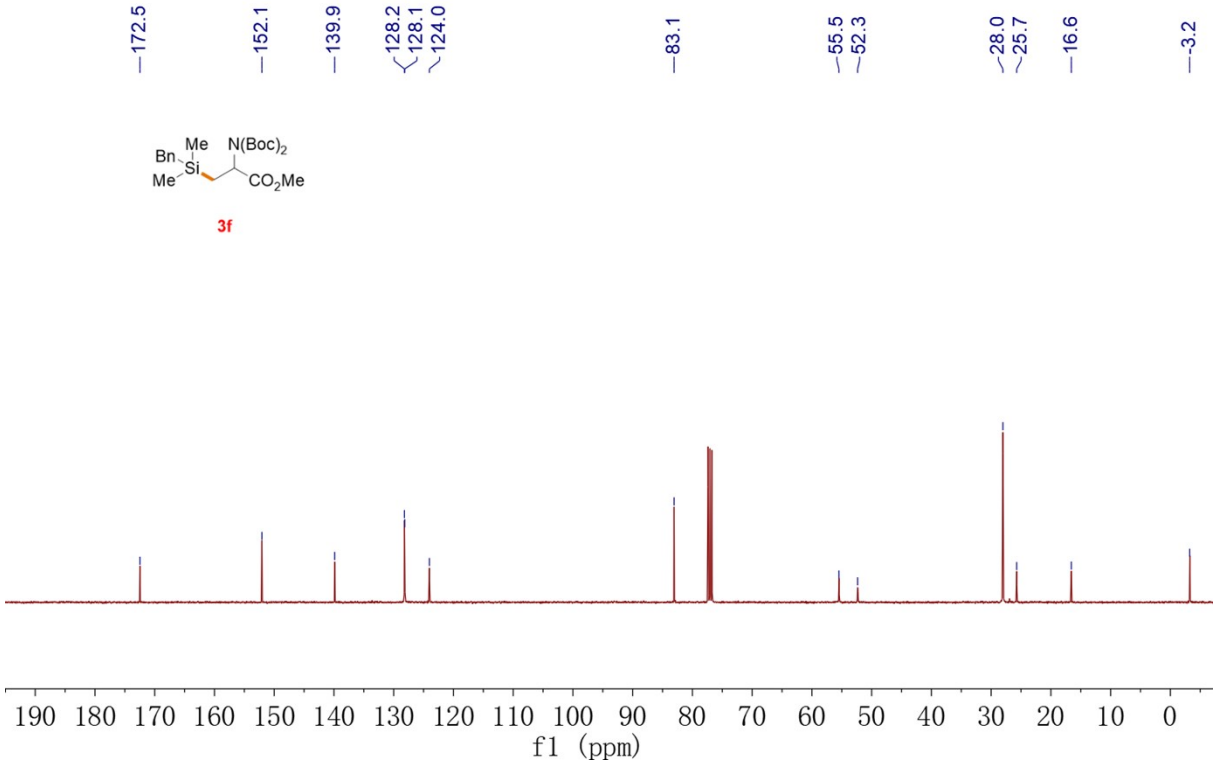
^{13}C NMR spectra of 3e (100 MHz, $CDCl_3$)



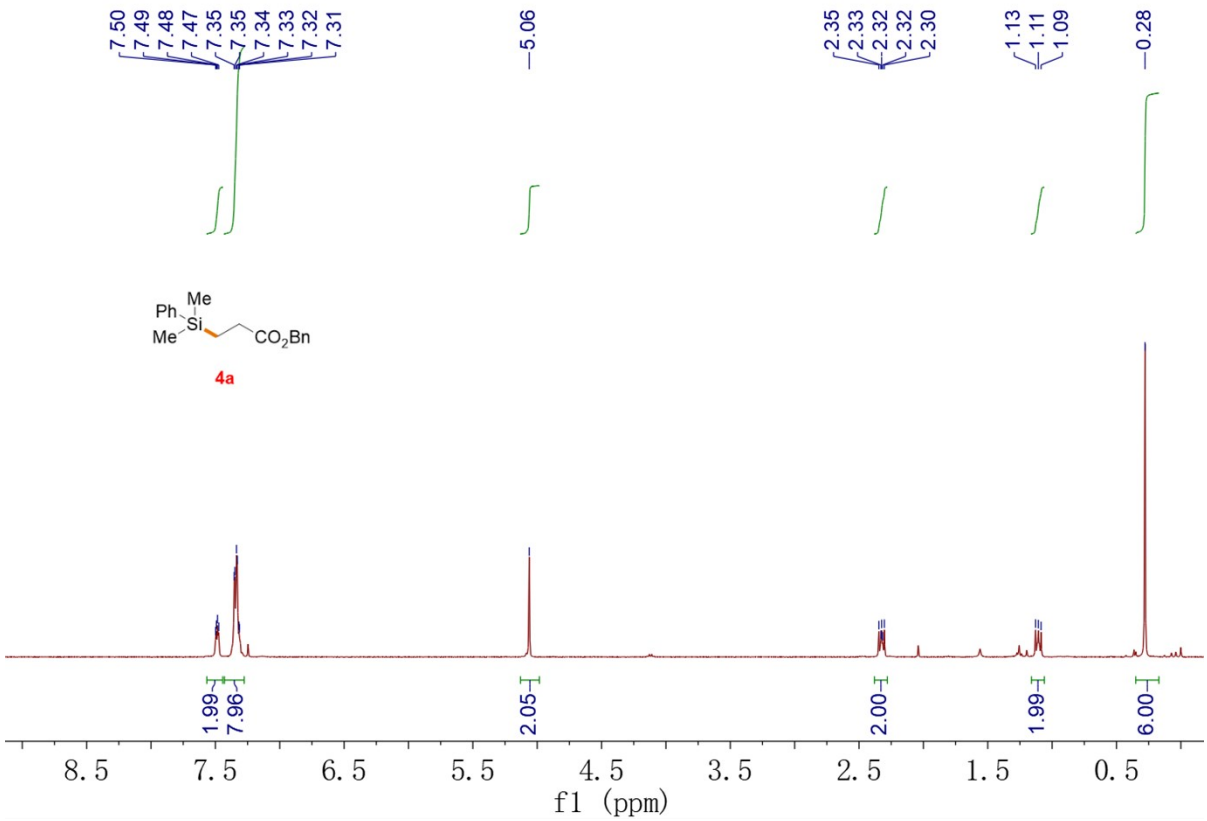
^{1}H NMR spectra of 3f (400 MHz, $CDCl_3$)



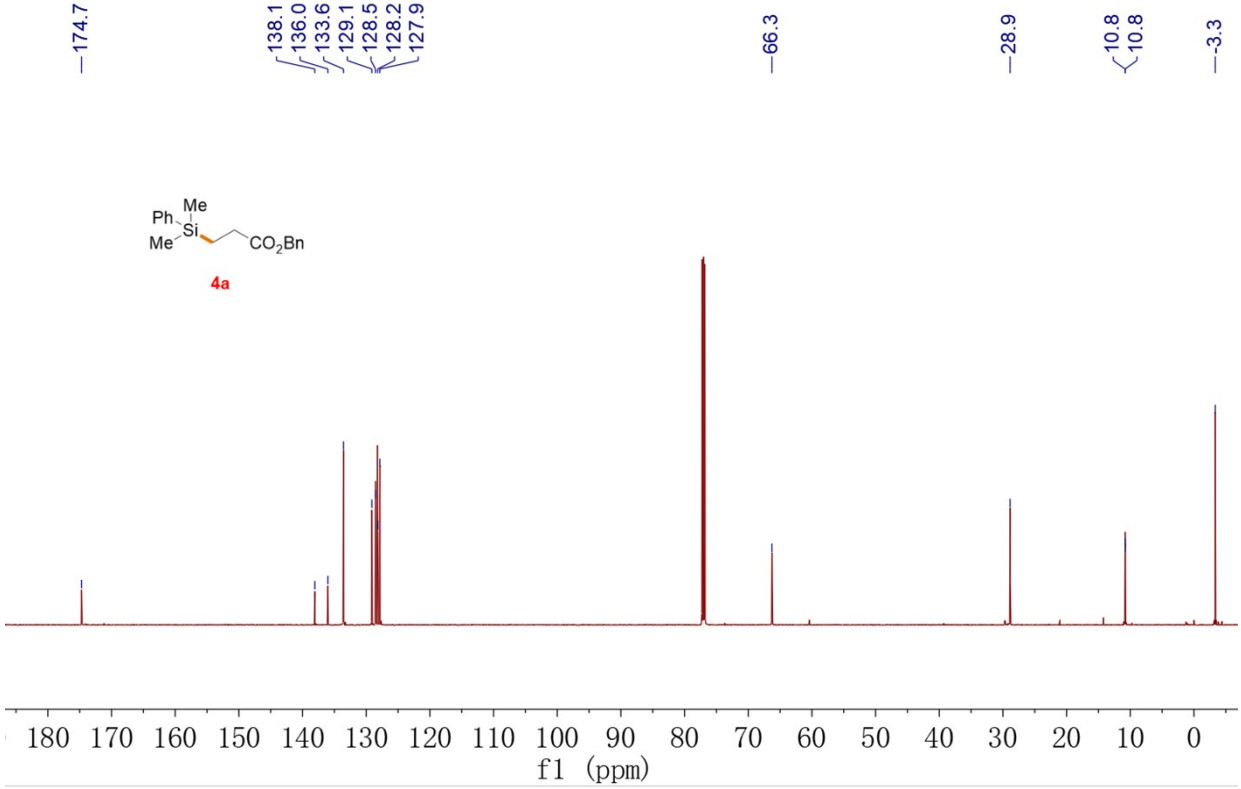
^{13}C NMR spectra of 3f (100 MHz, $CDCl_3$)



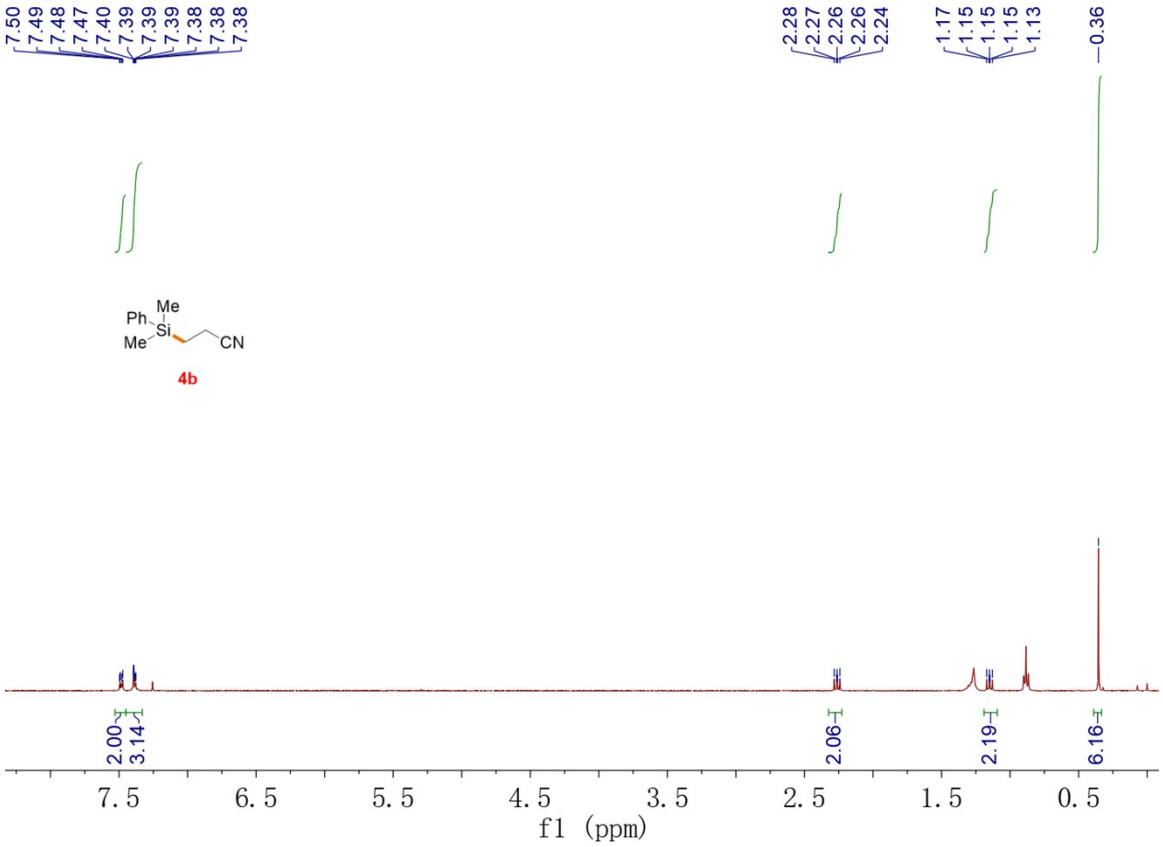
^{1}H NMR spectra of 4a (400 MHz, $CDCl_3$)



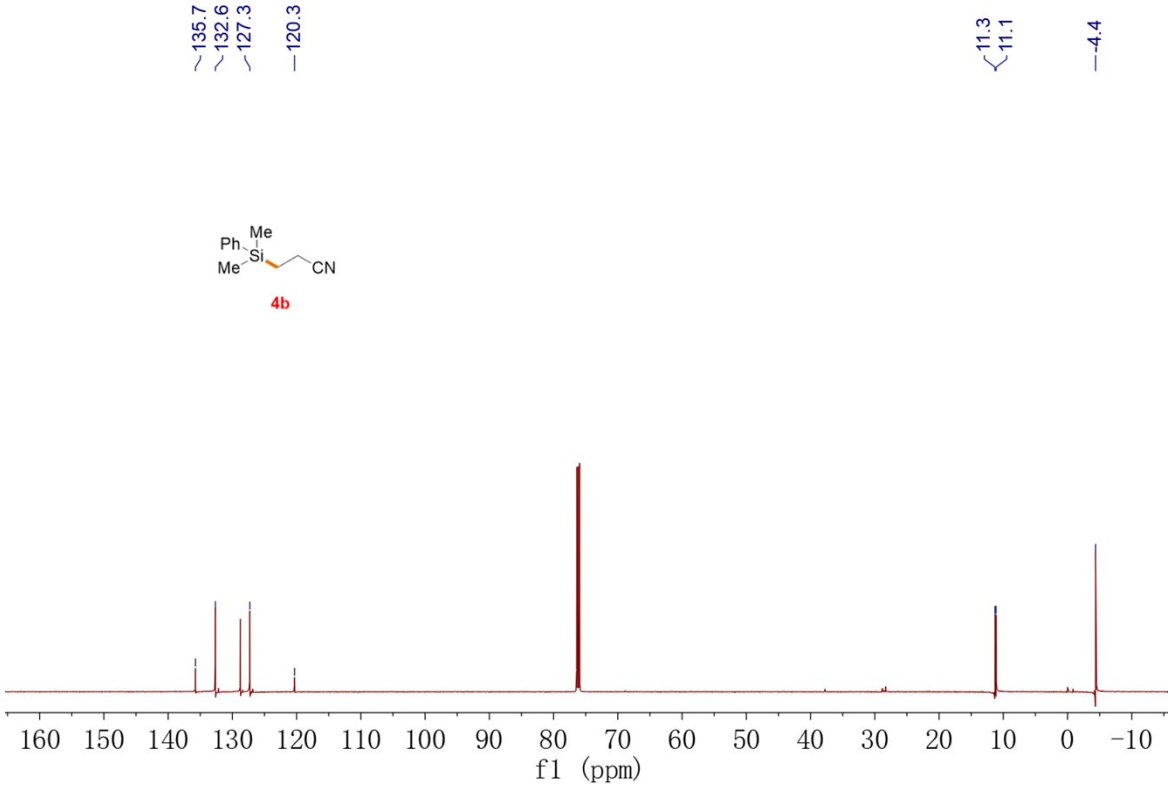
^{13}C NMR spectra of 4a (100 MHz, $CDCl_3$)



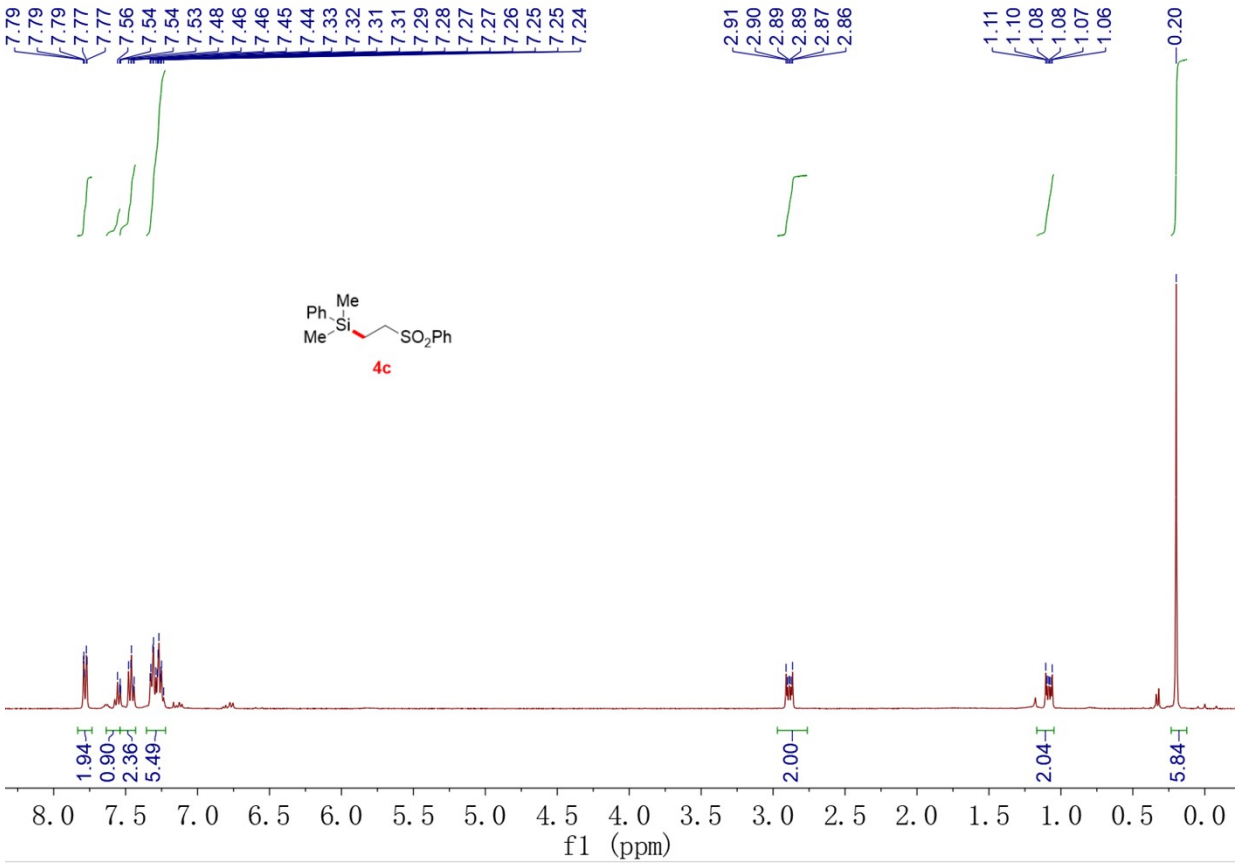
^{1}H NMR spectra of 4b (400 MHz, $CDCl_3$)



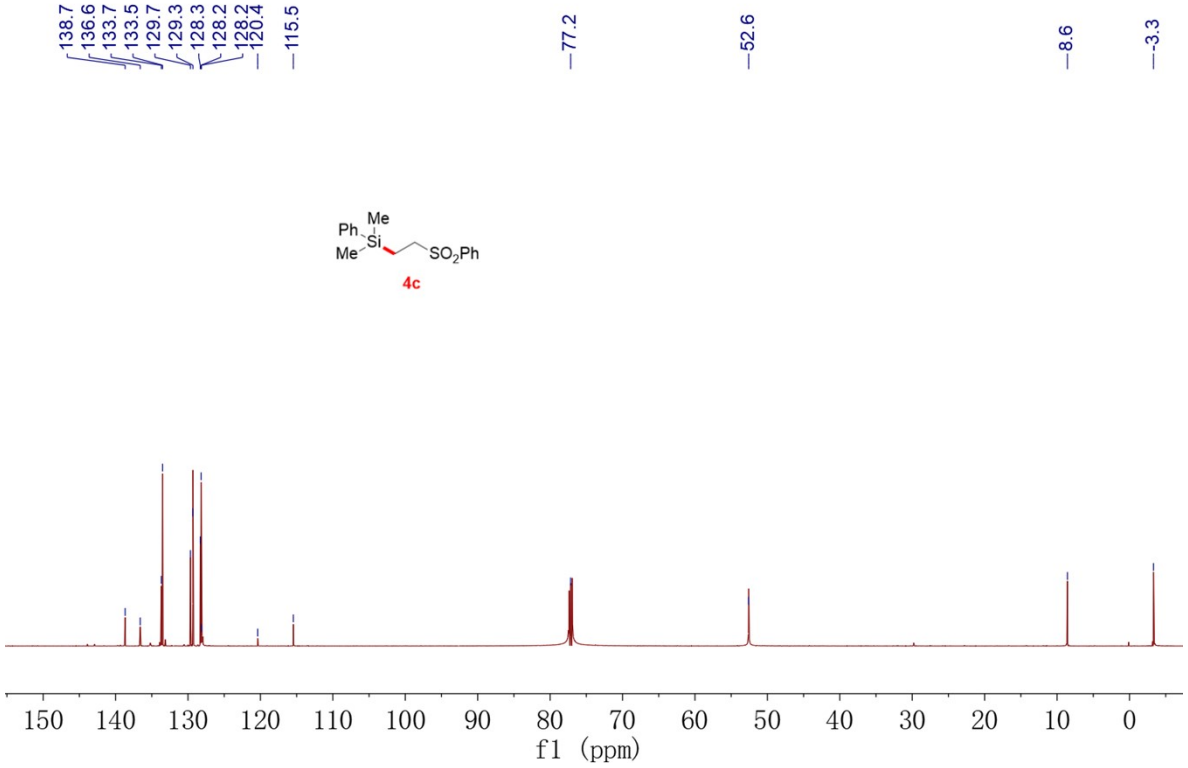
^{13}C NMR spectra of 4b (100 MHz, $CDCl_3$)



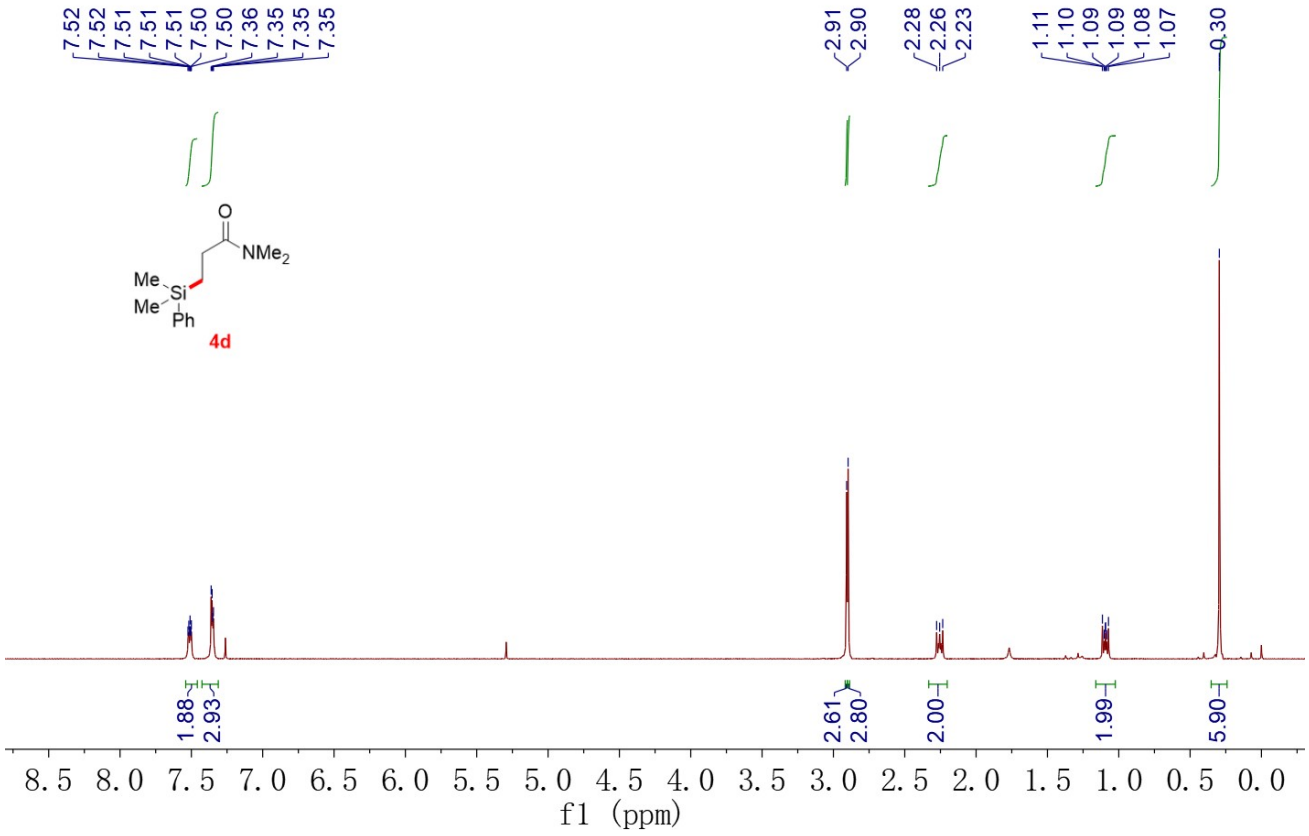
^{1}H NMR spectra of 4c (400 MHz, $CDCl_3$)



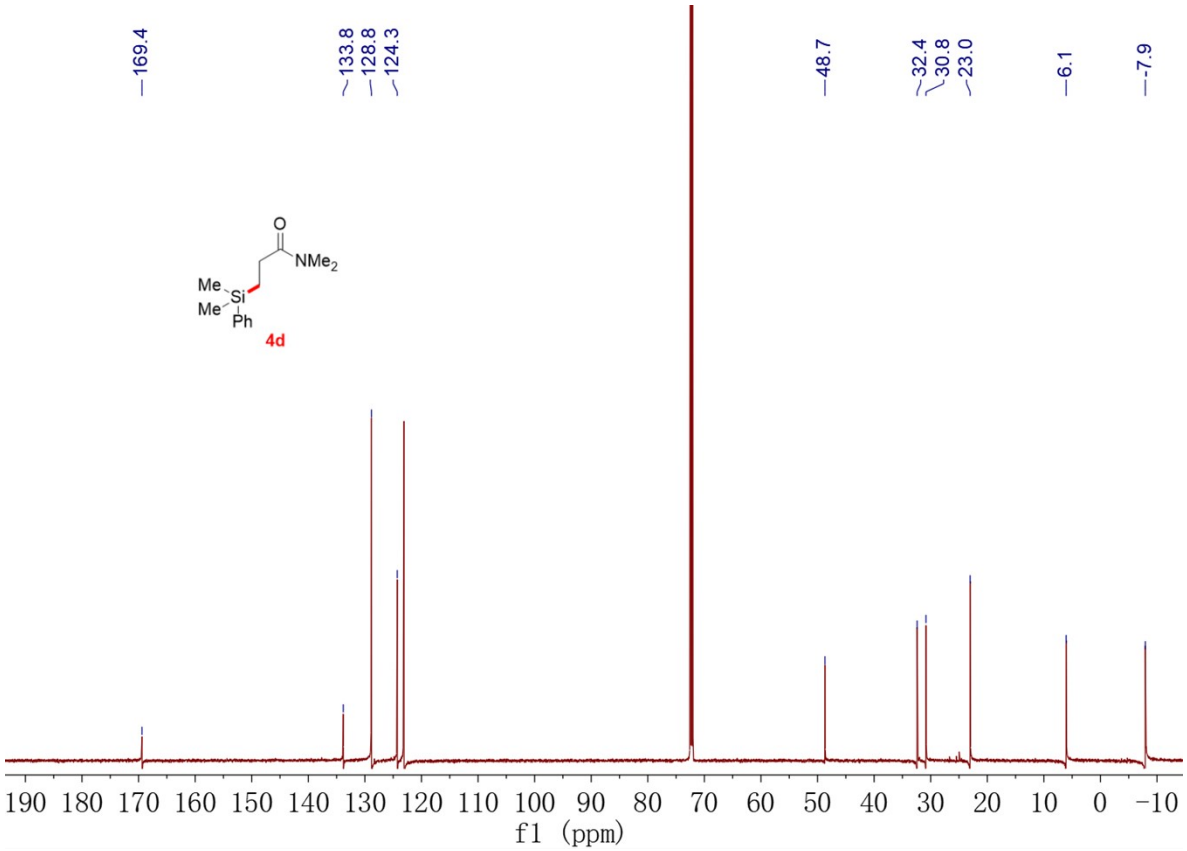
^{13}C NMR spectra of 4c (100 MHz, $CDCl_3$)



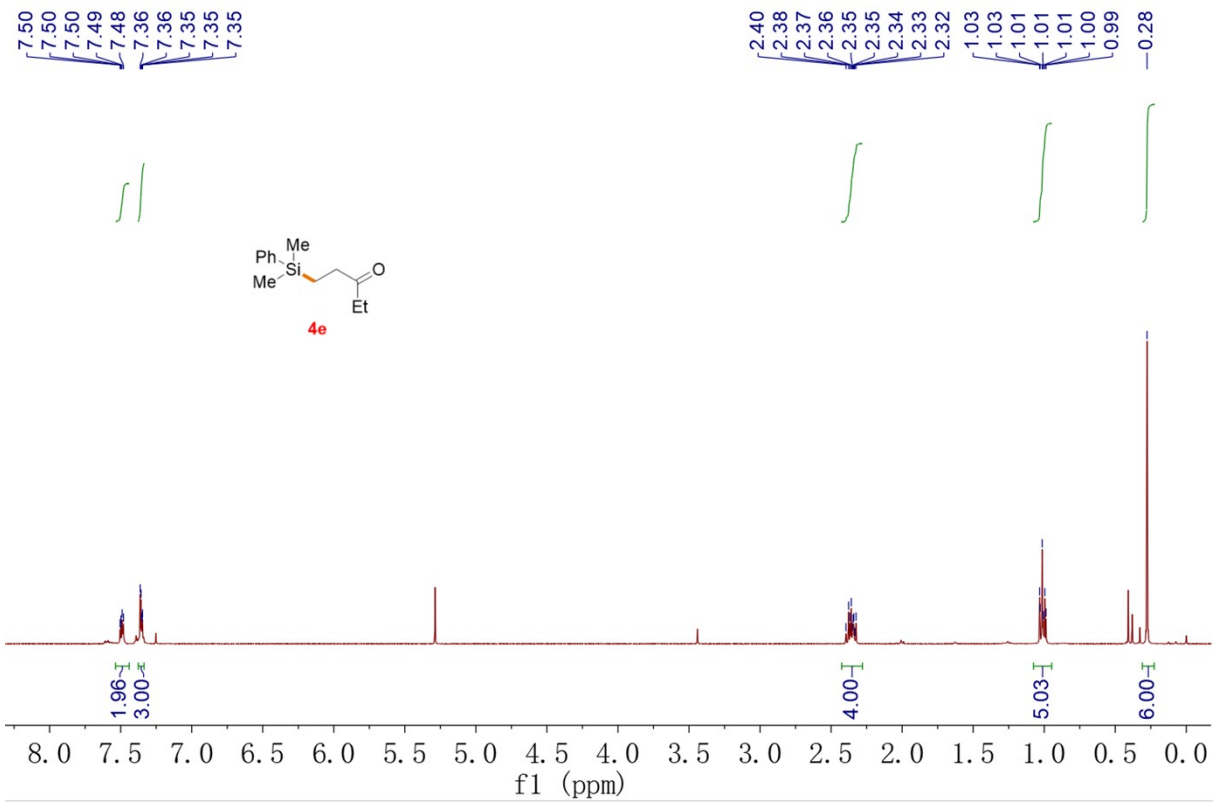
^{1}H NMR spectra of 4d (400 MHz, $CDCl_3$)



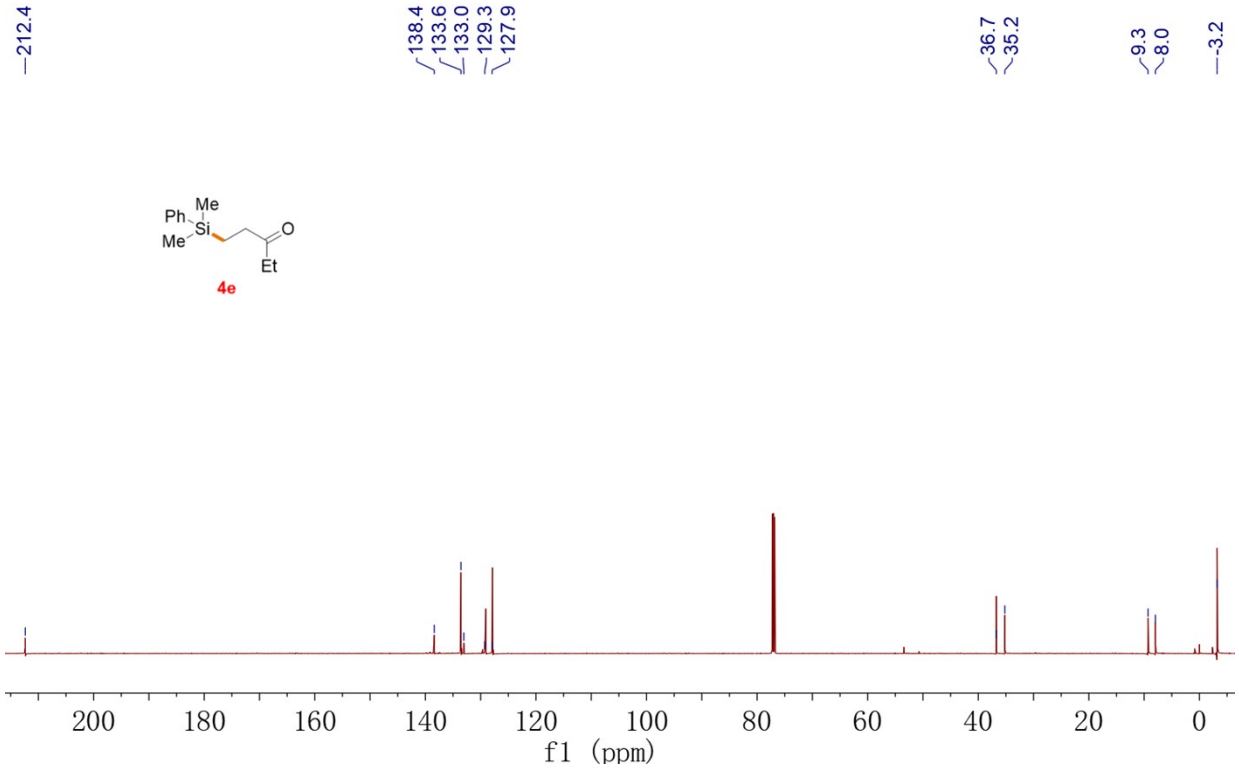
^{13}C NMR spectra of 4d (100 MHz, $CDCl_3$)



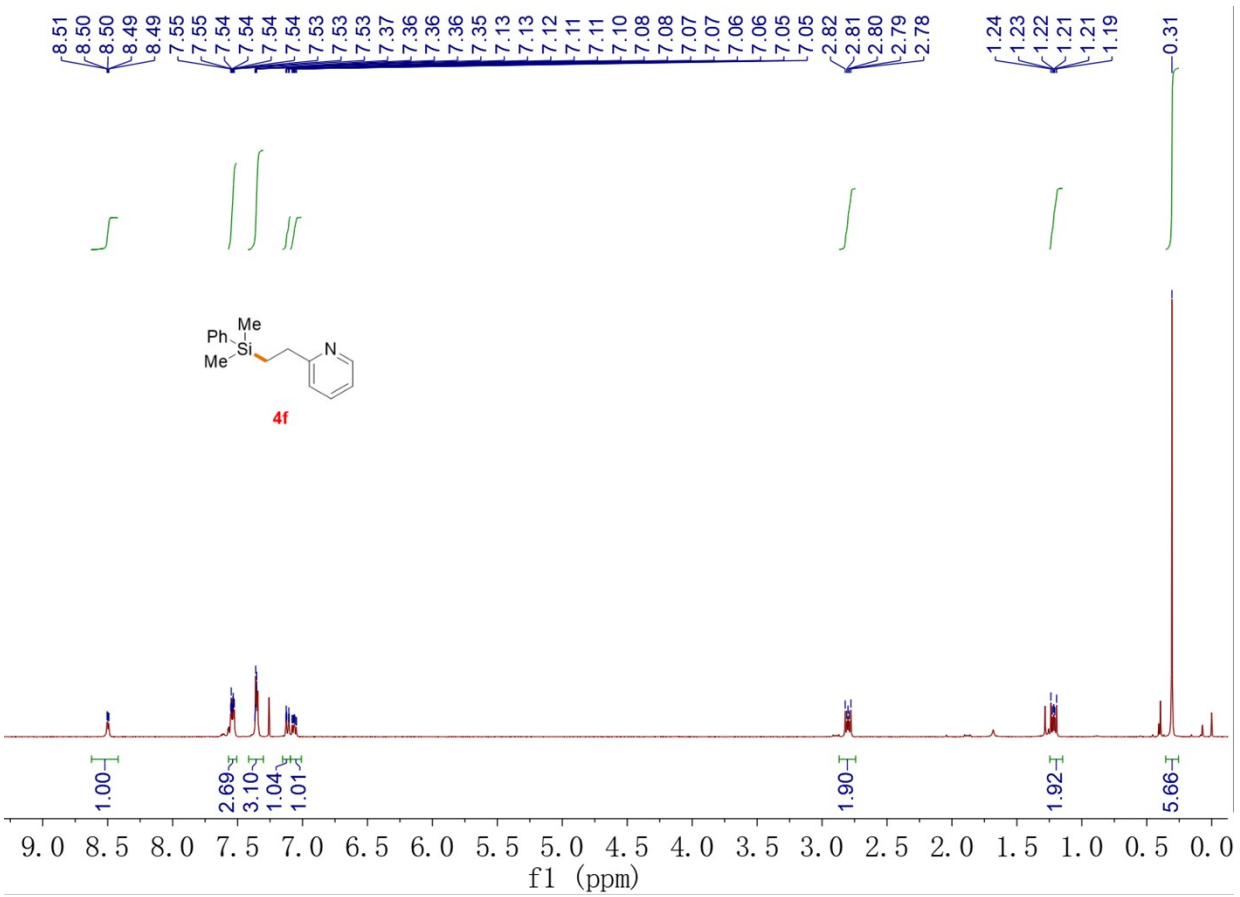
^{1}H NMR spectra of 4e (400 MHz, $CDCl_3$)



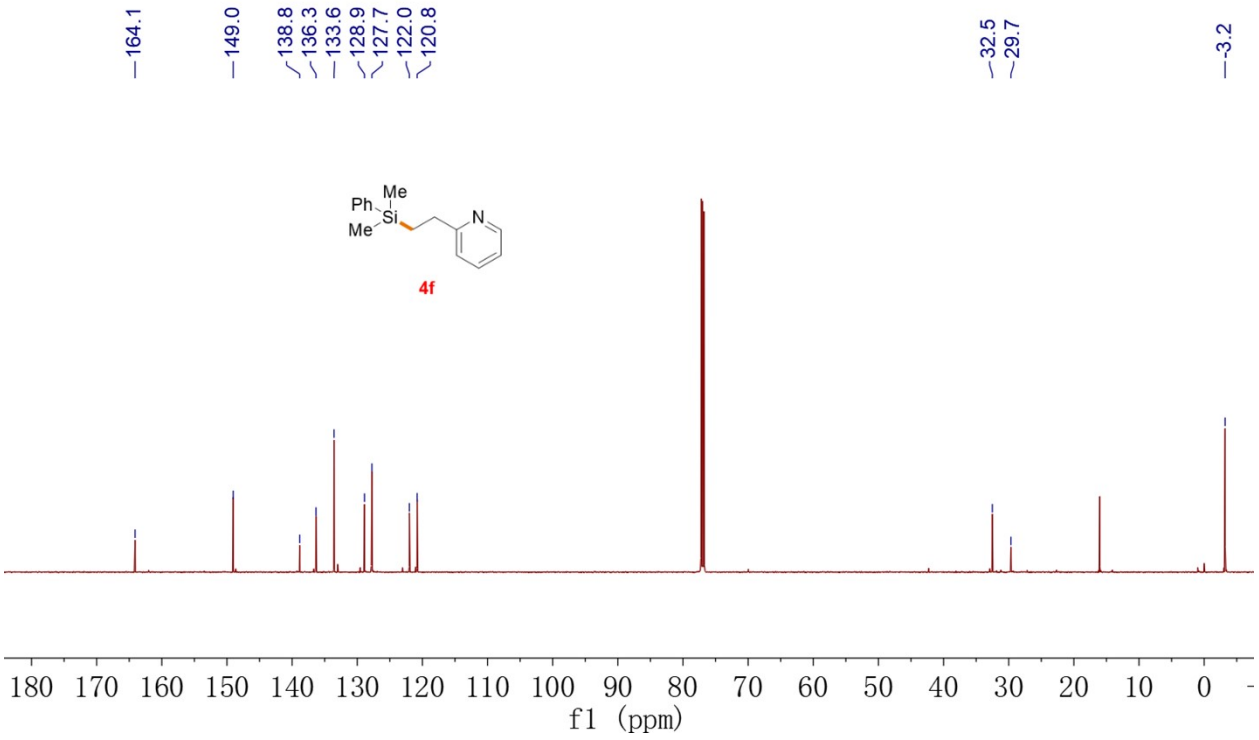
^{13}C NMR spectra of 4e (100 MHz, $CDCl_3$)



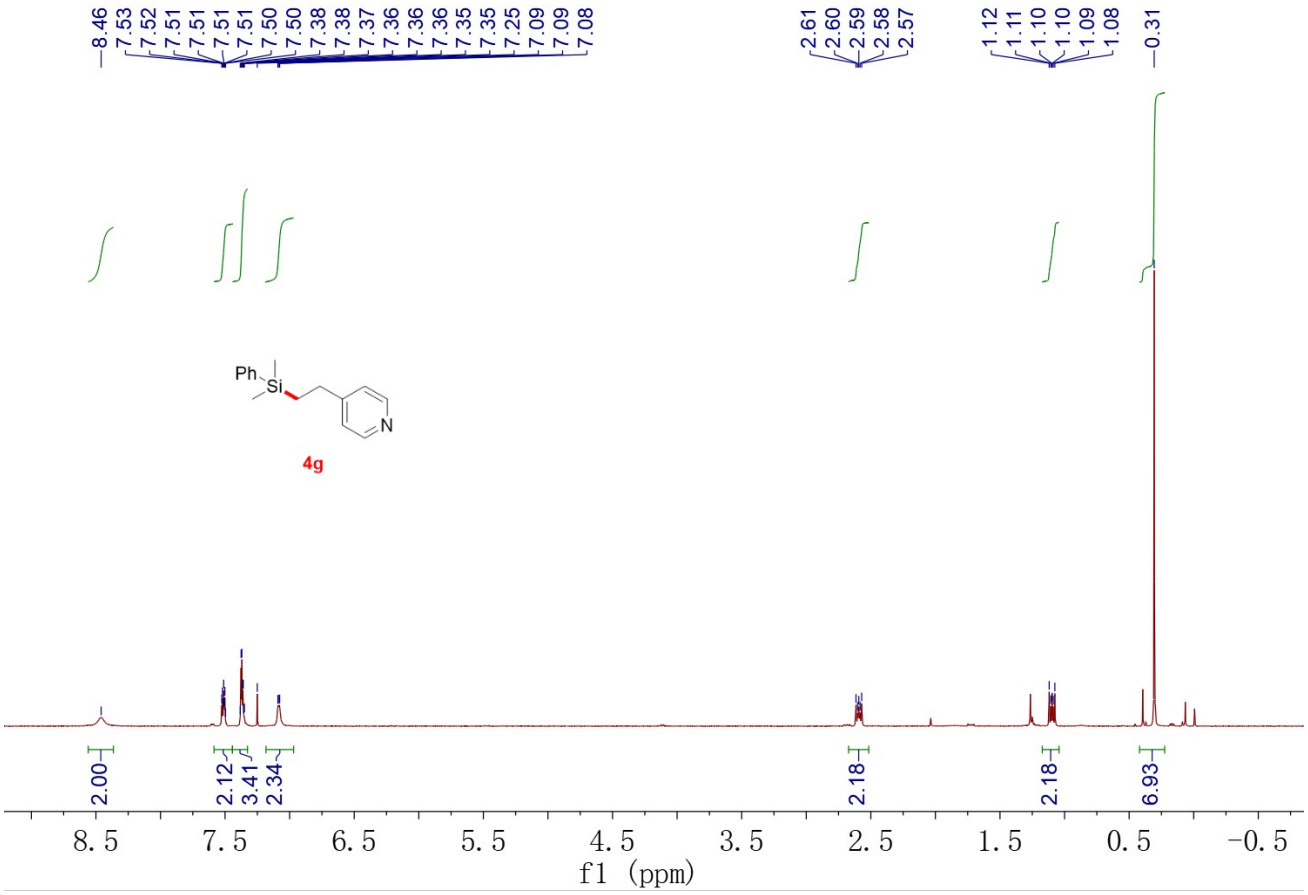
^{1}H NMR spectra of 4f (400 MHz, $CDCl_3$)



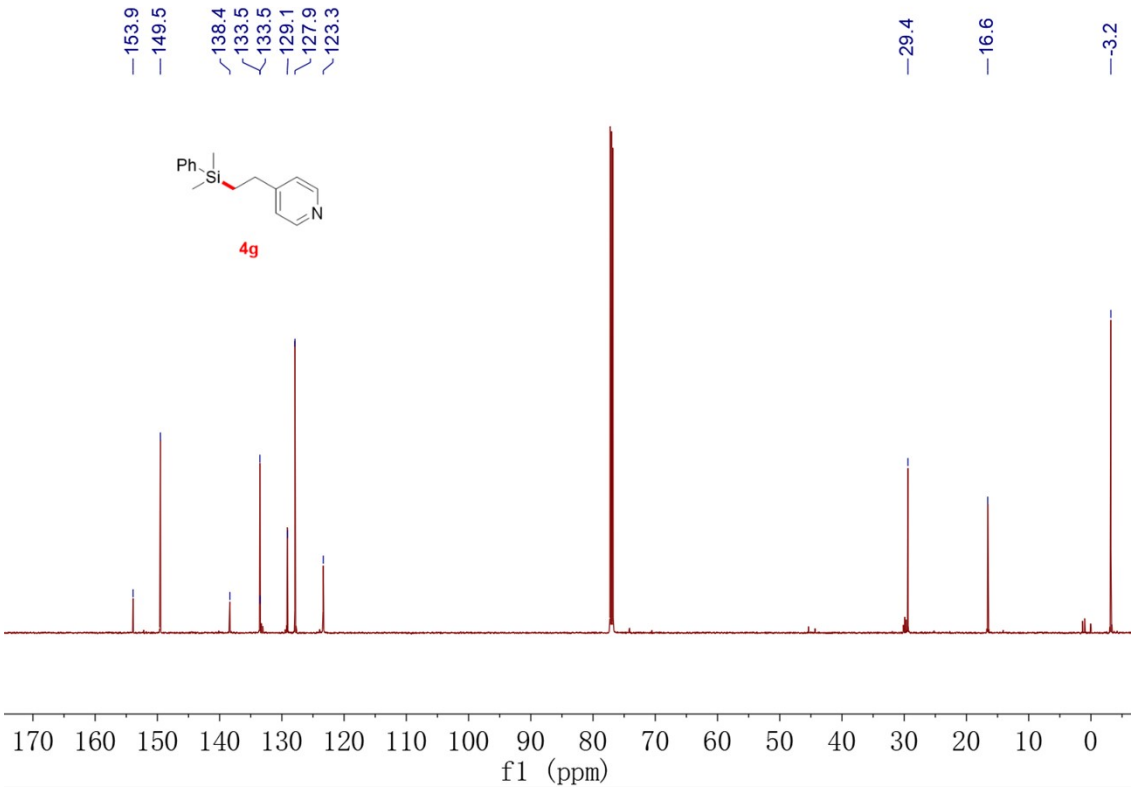
^{13}C NMR spectra of 4f (100 MHz, $CDCl_3$)



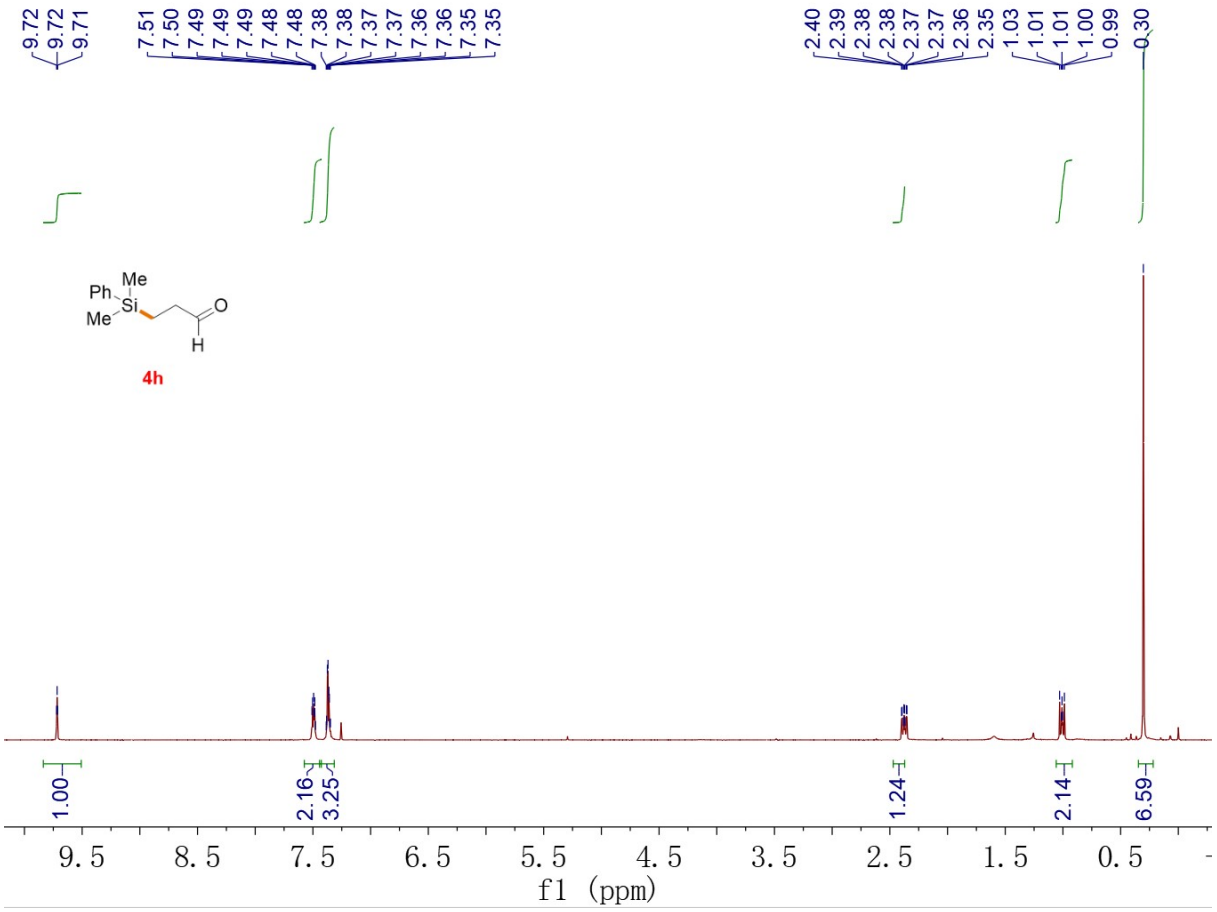
^{1}H NMR spectra of 4g (400 MHz, $CDCl_3$)



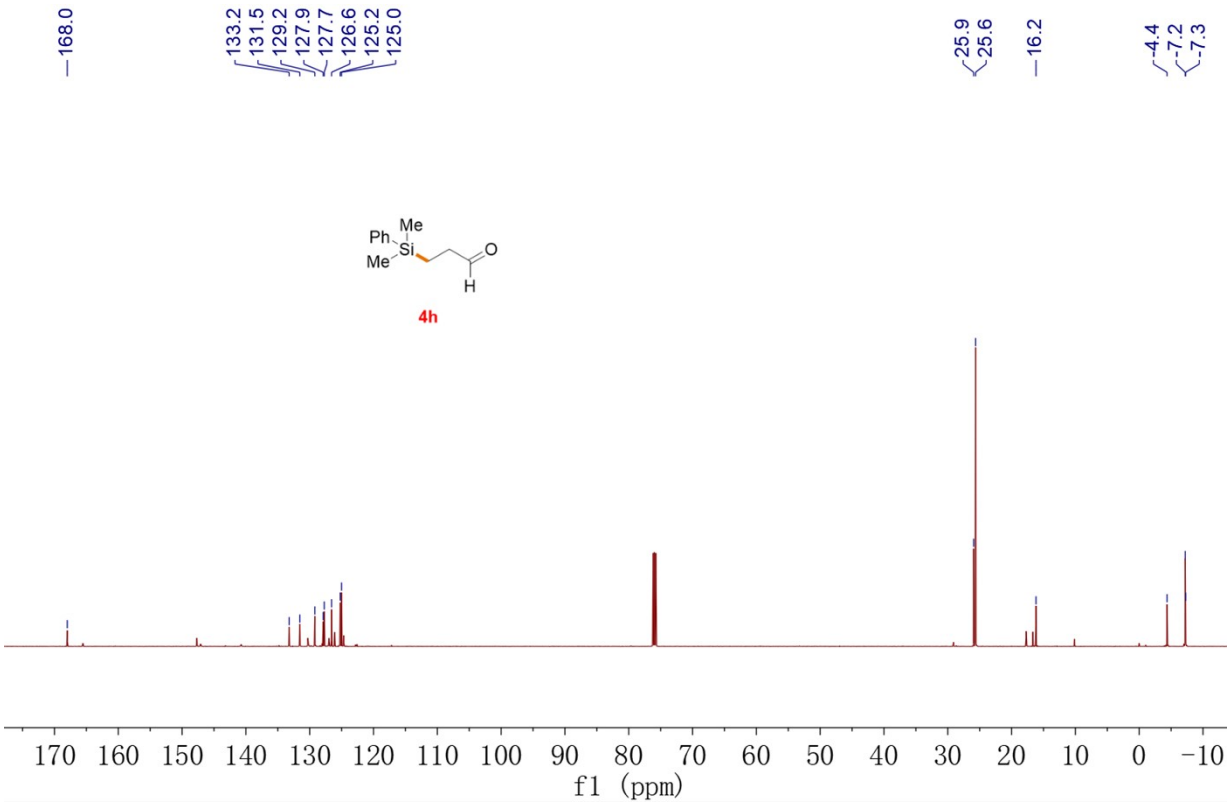
^{13}C NMR spectra of 4g (100 MHz, $CDCl_3$)



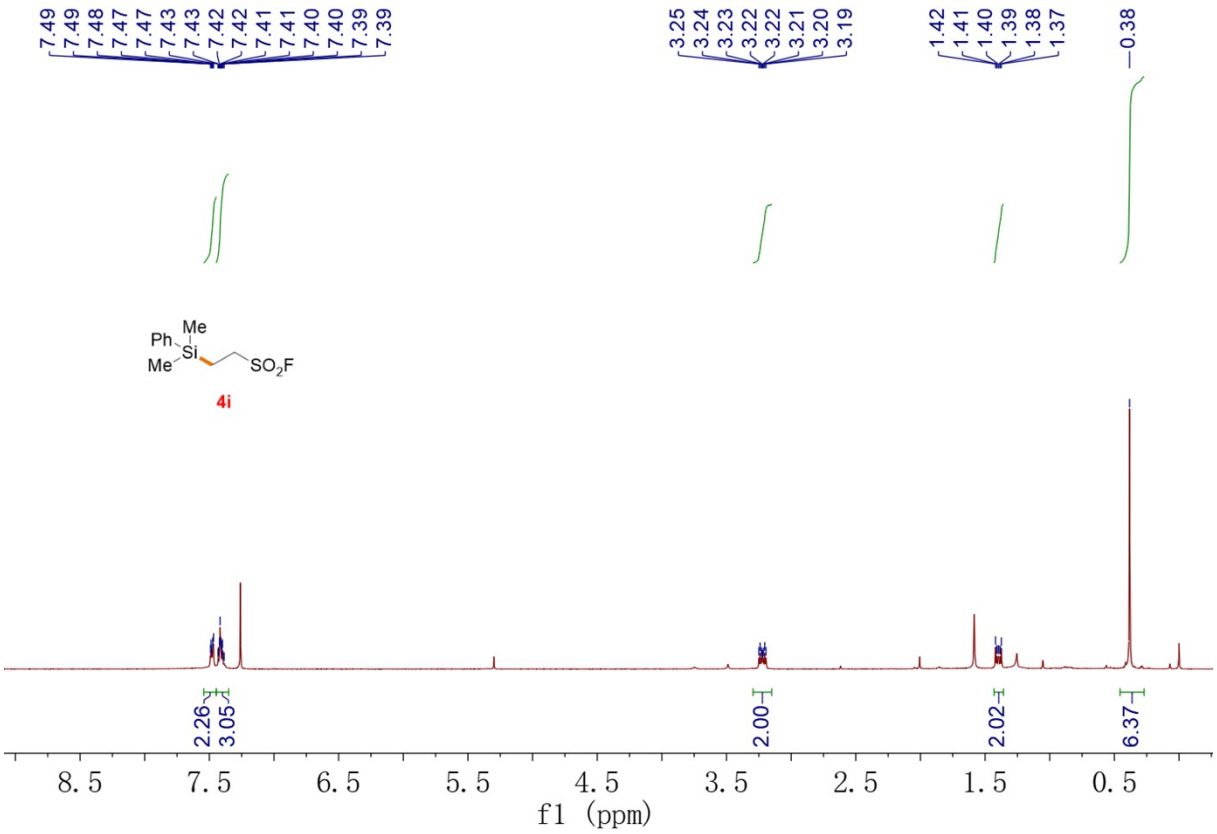
^{1}H NMR spectra of 4h (400 MHz, $CDCl_3$)



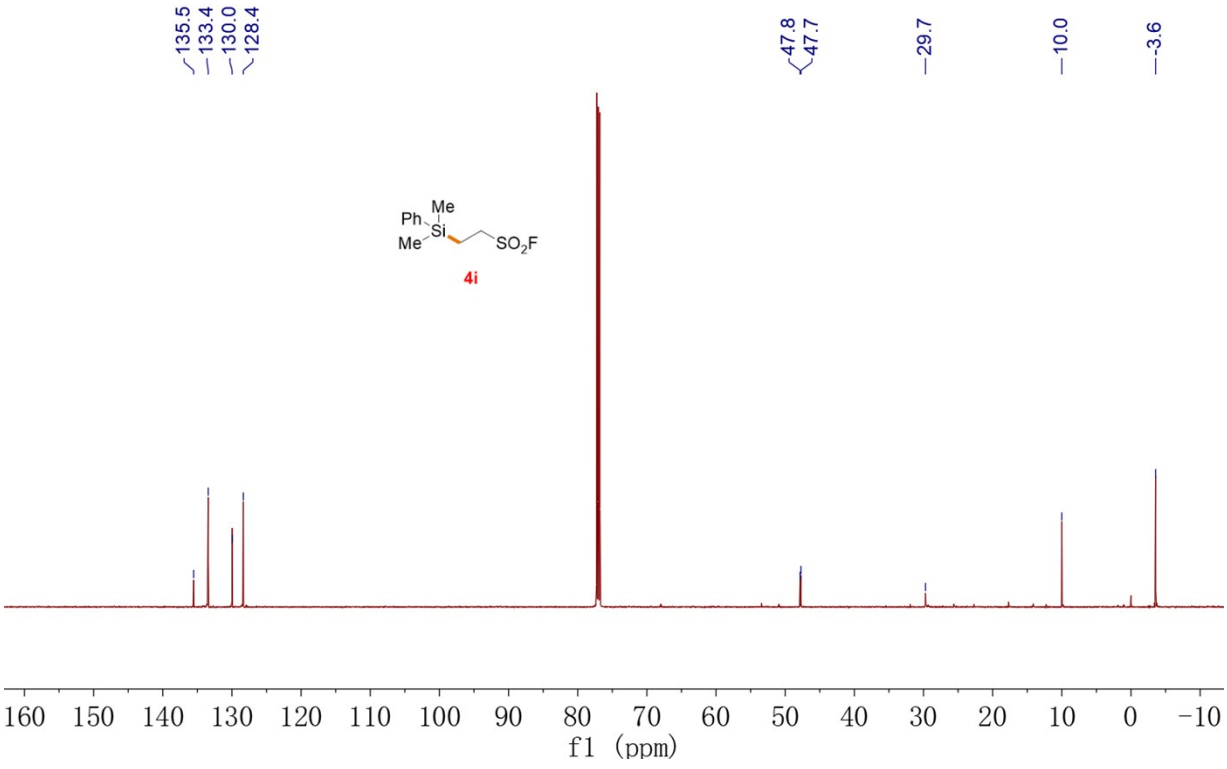
^{13}C NMR spectra of 4h (100 MHz, $CDCl_3$)



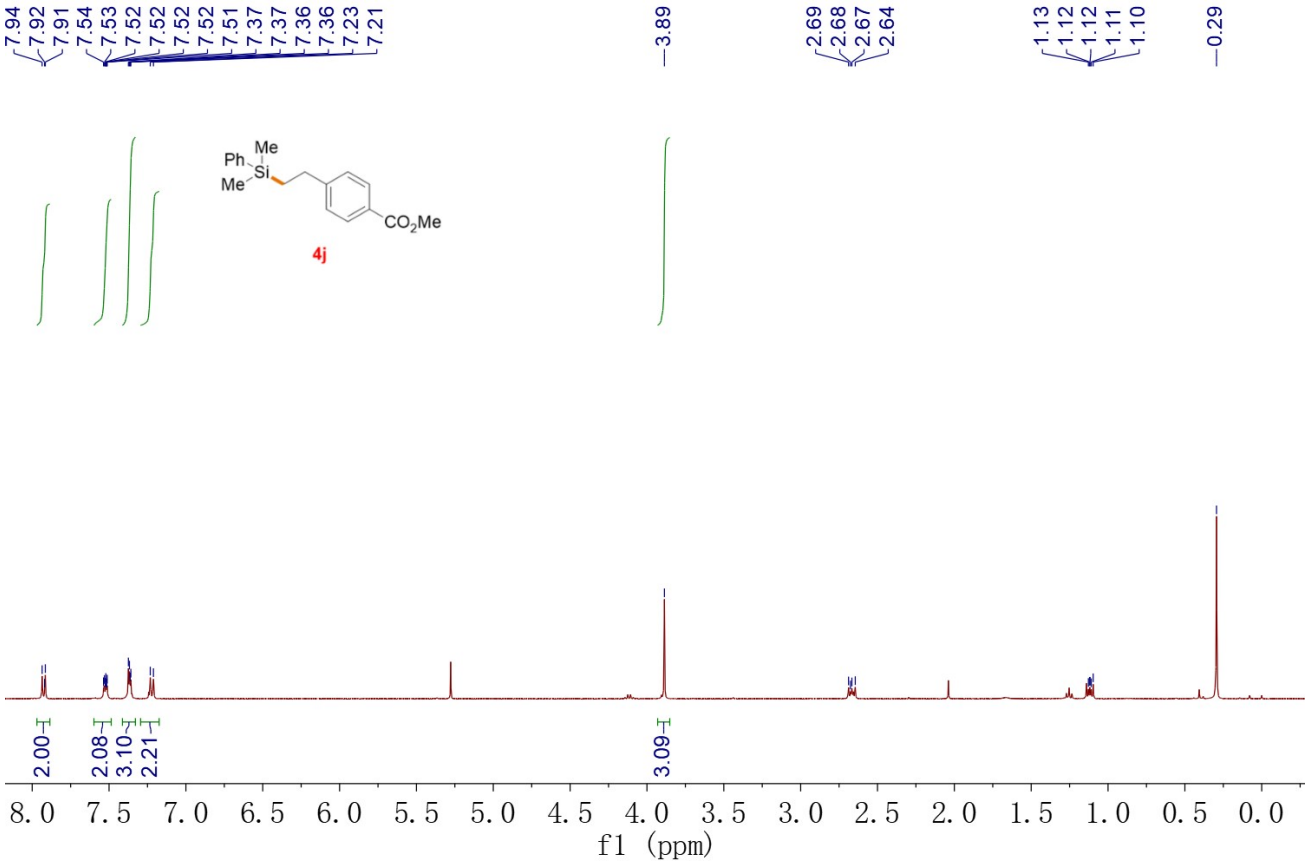
^{1}H NMR spectra of 4i (400 MHz, $CDCl_3$)



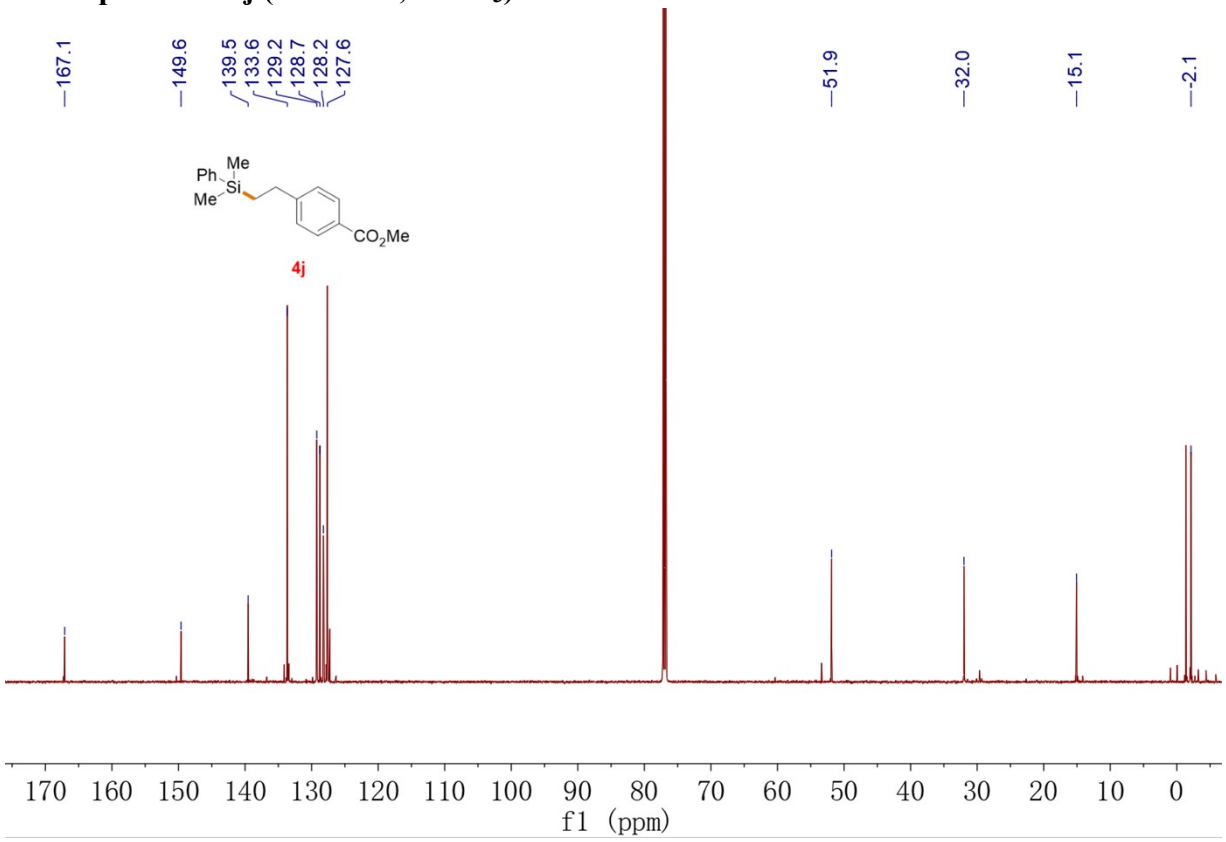
^{13}C NMR spectra of 4i (100 MHz, $CDCl_3$)



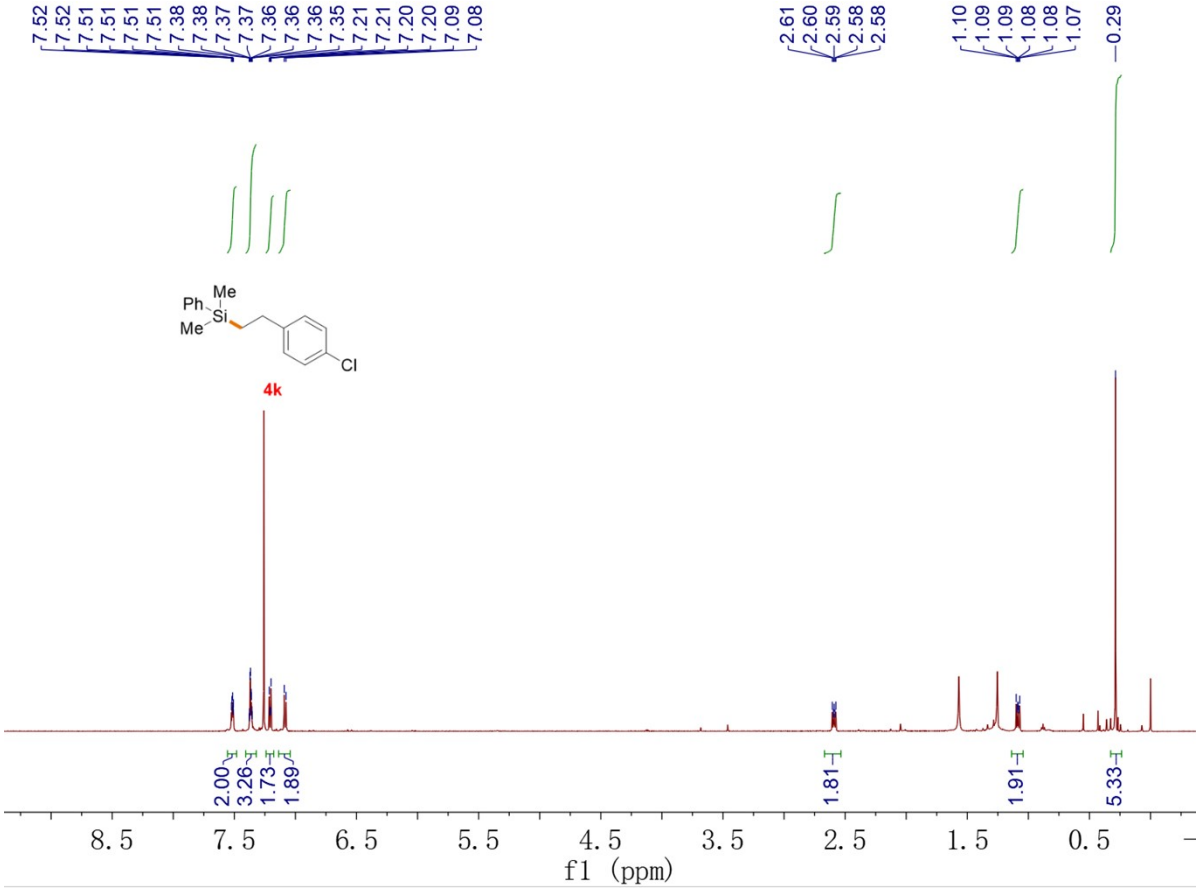
^{1}H NMR spectra of 4j (400 MHz, $CDCl_3$)



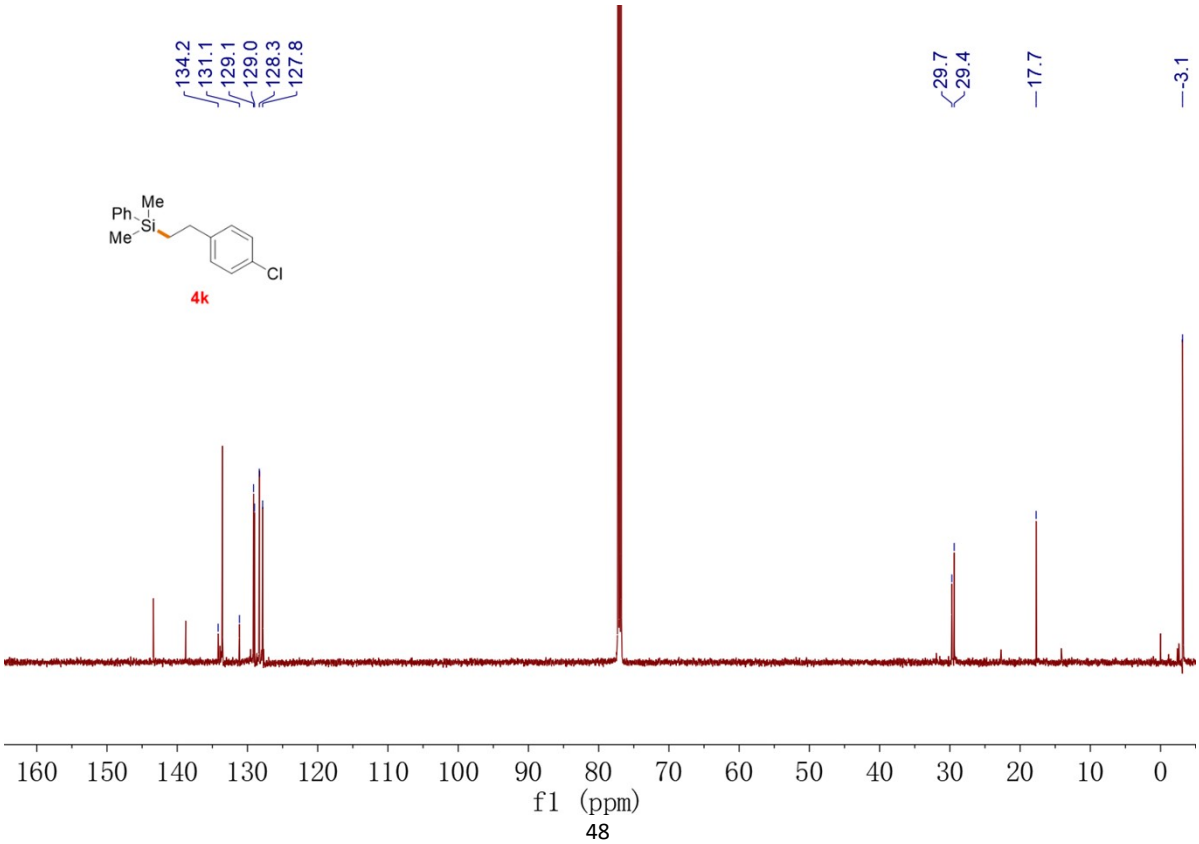
^{13}C NMR spectra of 4j (100 MHz, $CDCl_3$)



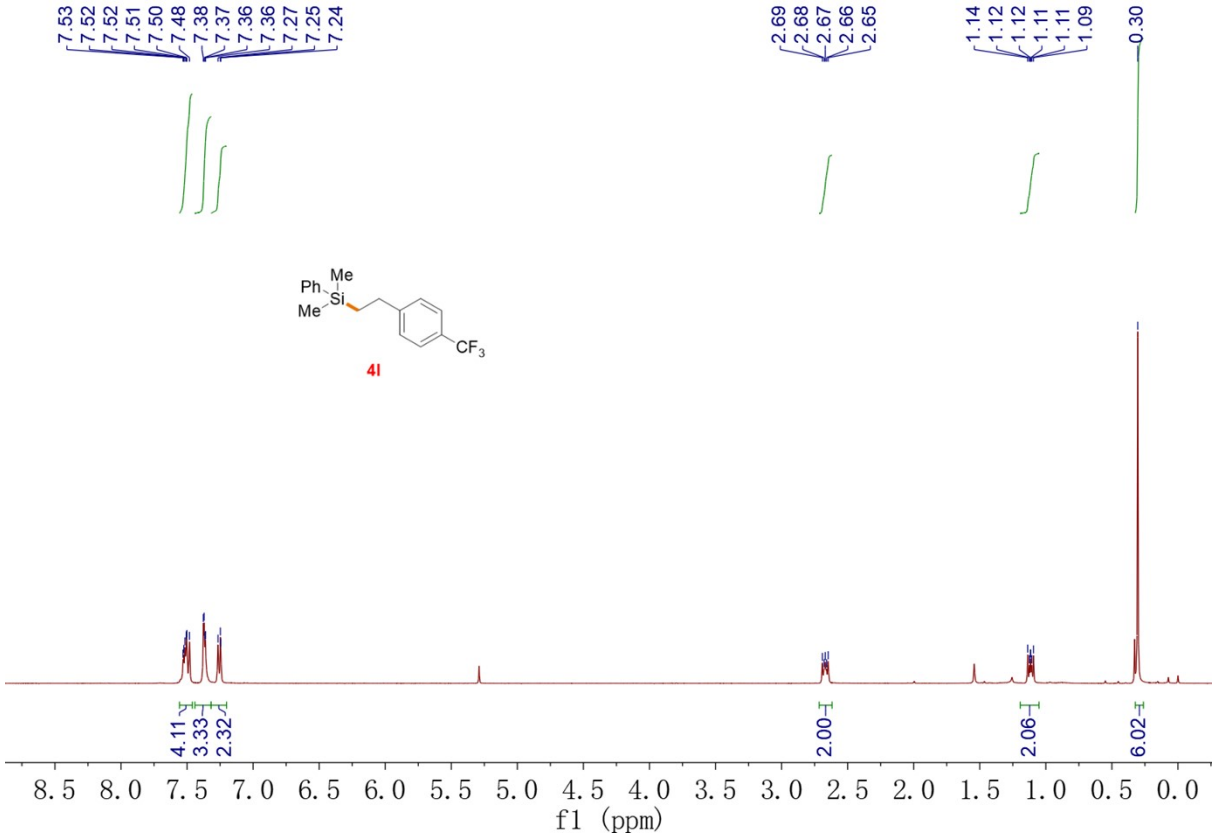
^{1}H NMR spectra of 4k (400 MHz, $CDCl_3$)



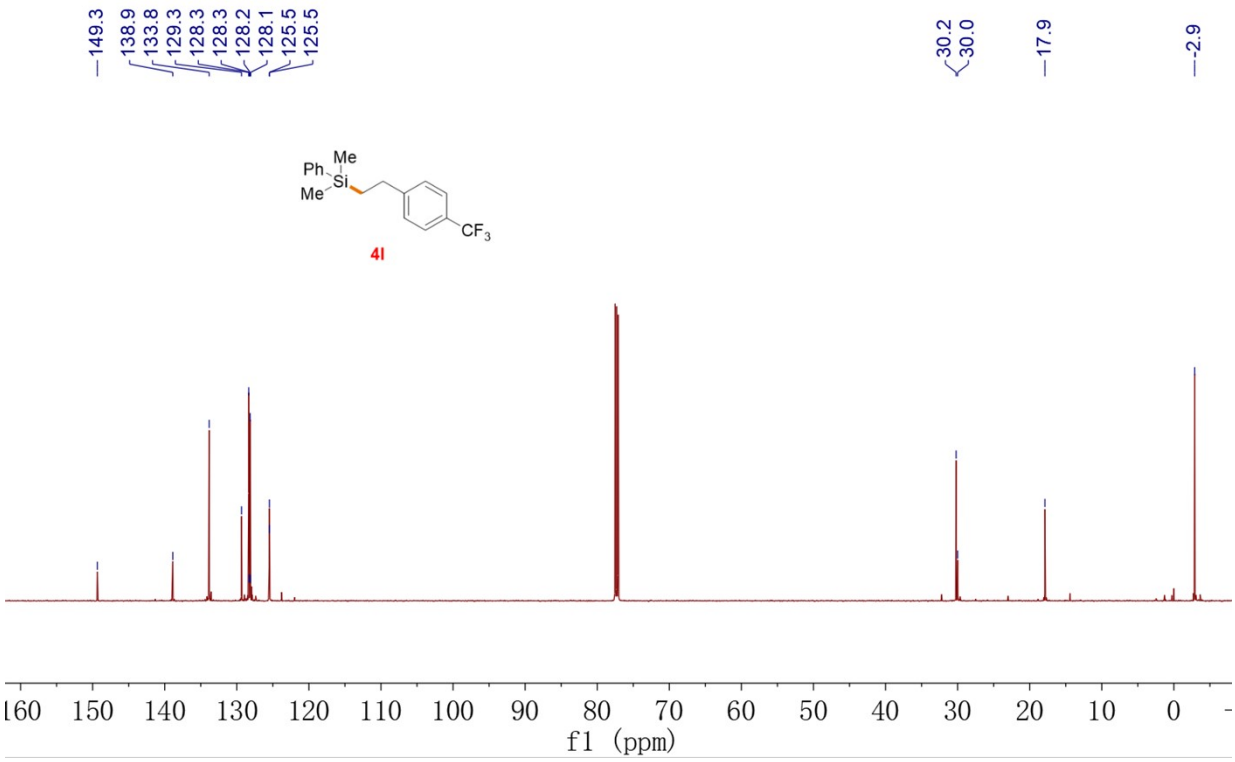
^{13}C NMR spectra of 4k (100 MHz, $CDCl_3$)



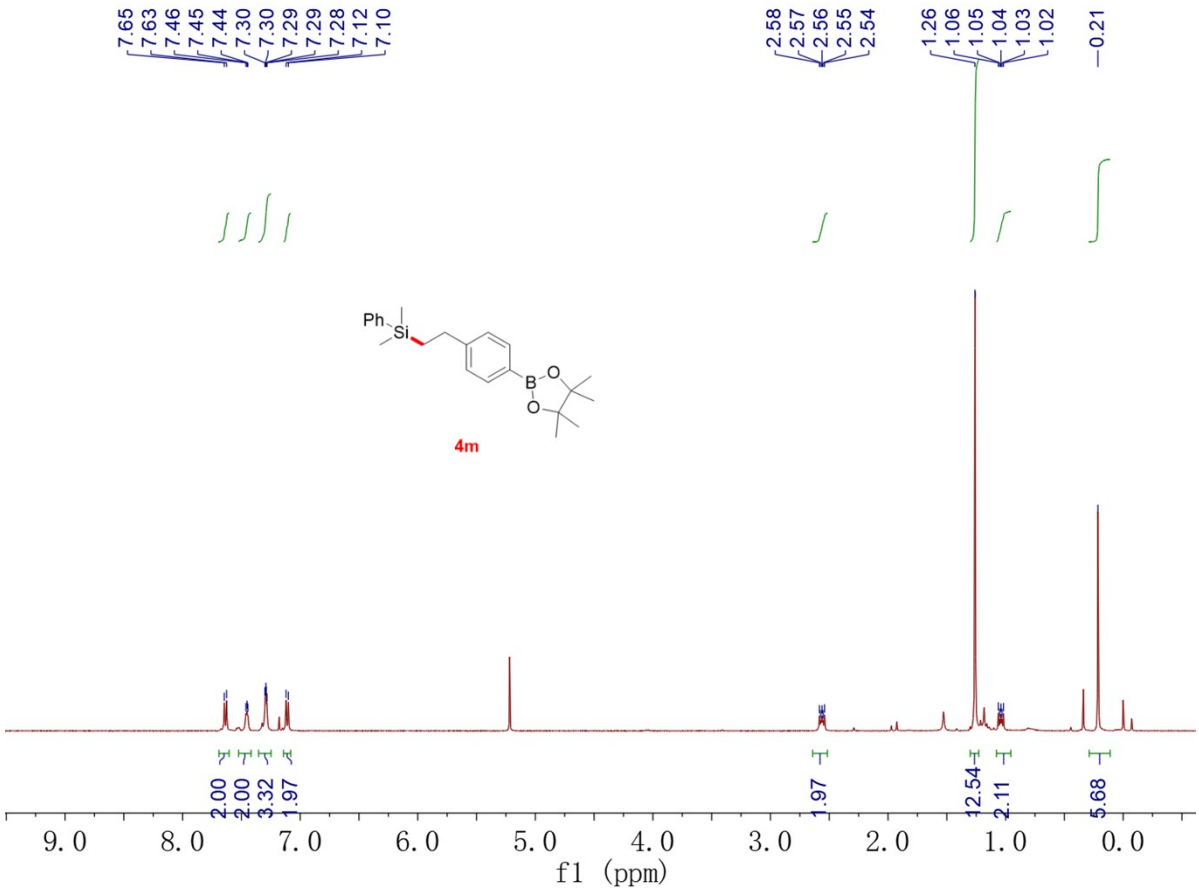
^{1}H NMR spectra of 4l (400 MHz, $CDCl_3$)



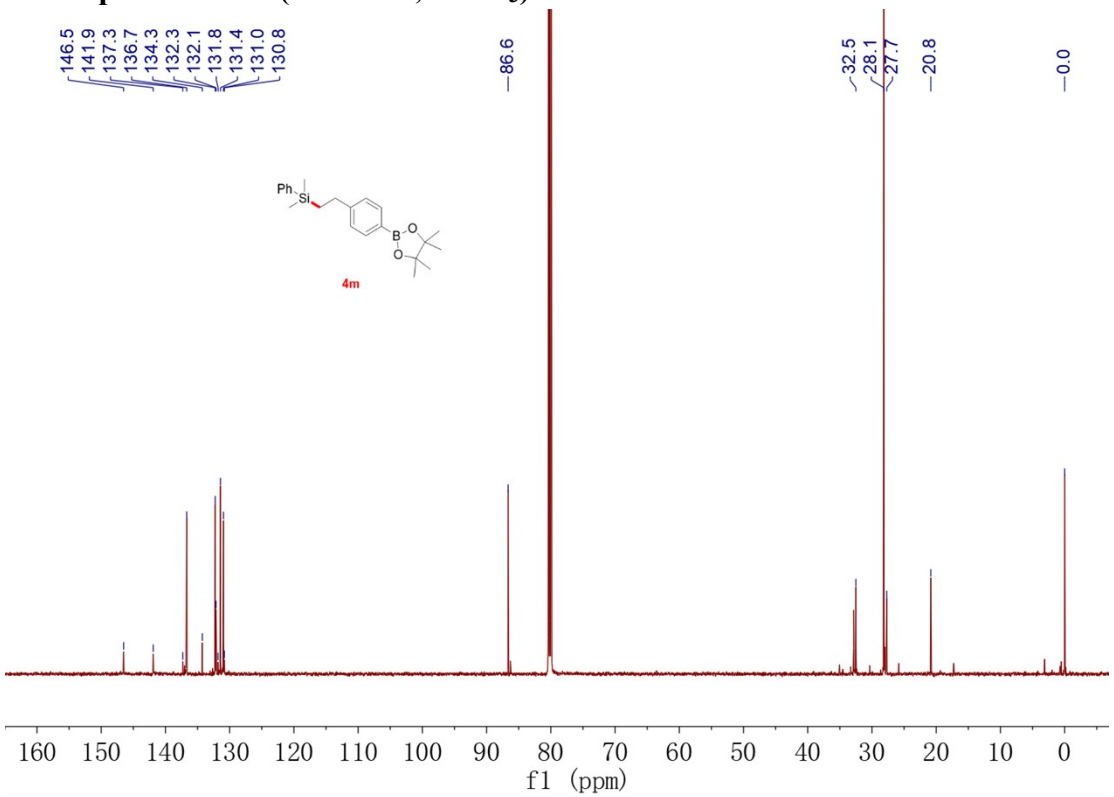
^{13}C NMR spectra of 4l (100 MHz, $CDCl_3$)



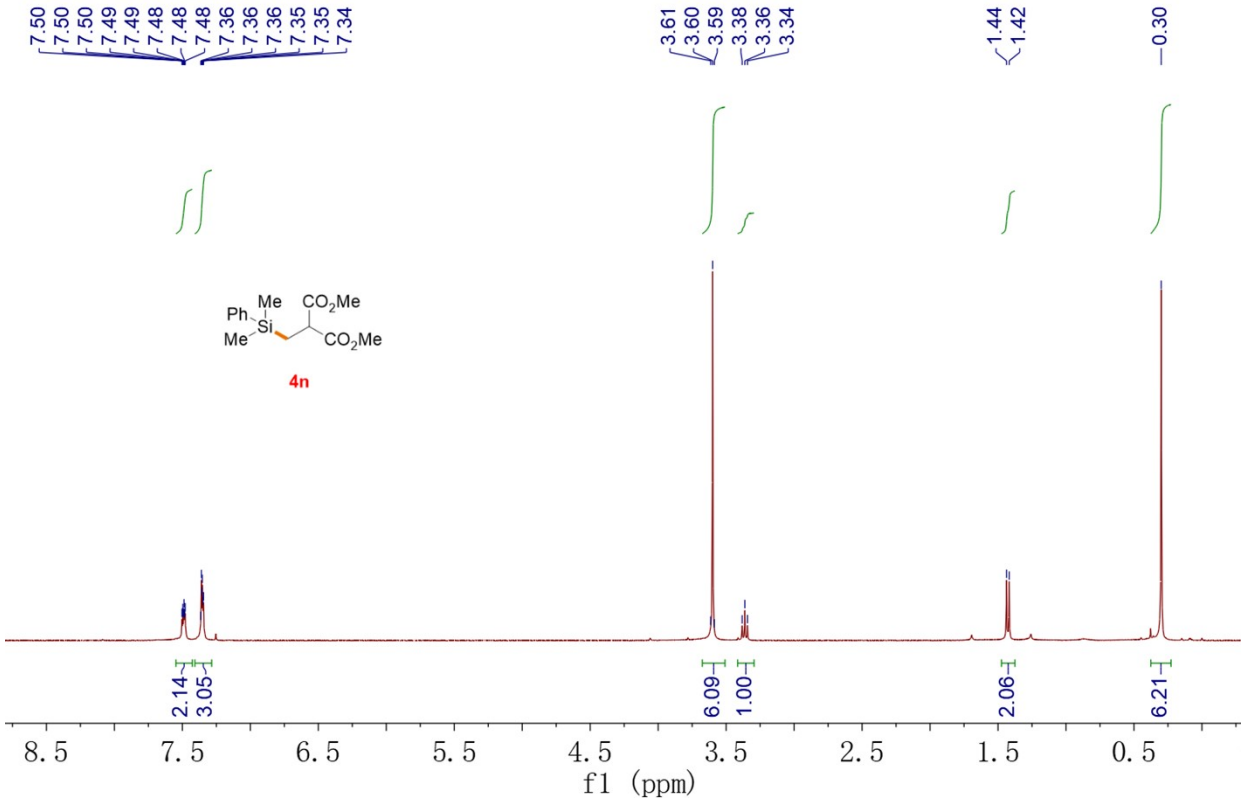
^{1}H NMR spectra of 4m (400 MHz, $CDCl_3$)



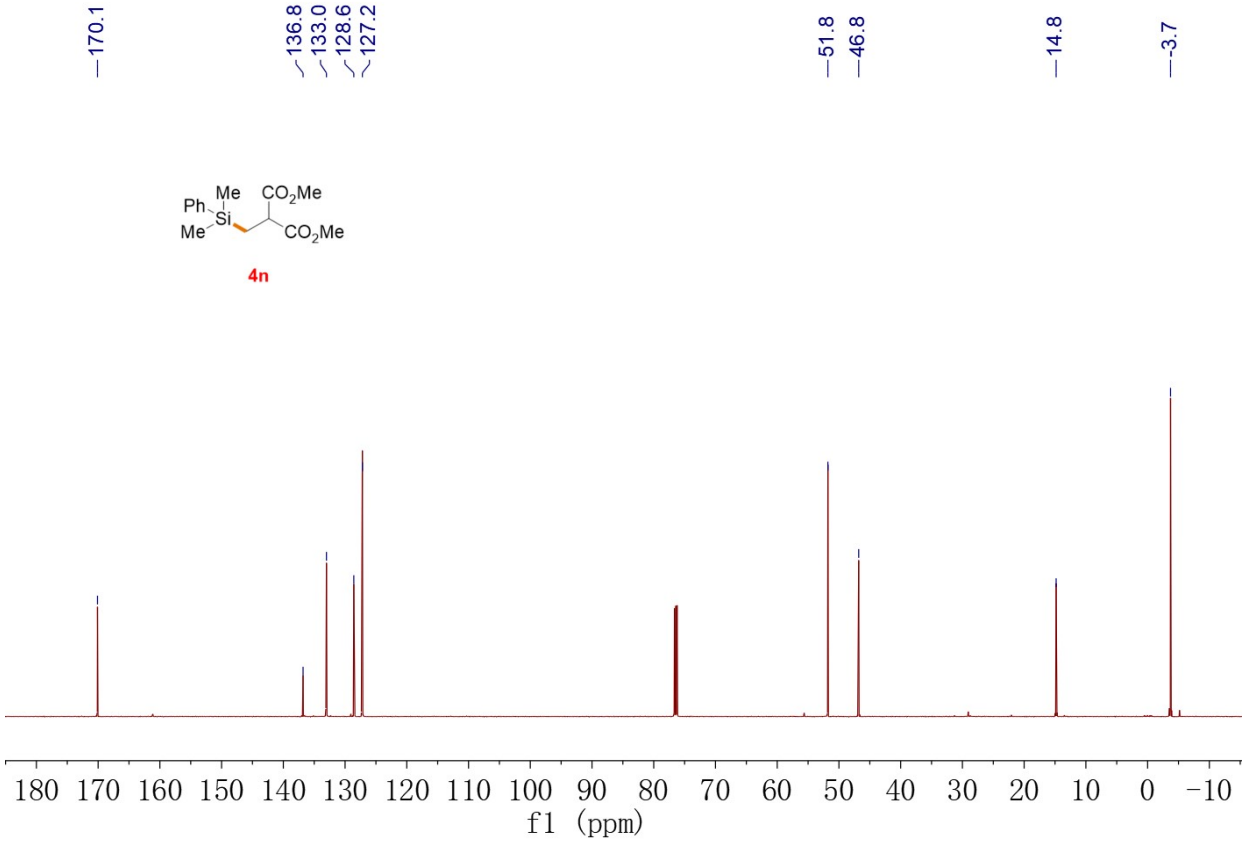
^{13}C NMR spectra of 4m (100 MHz, $CDCl_3$)



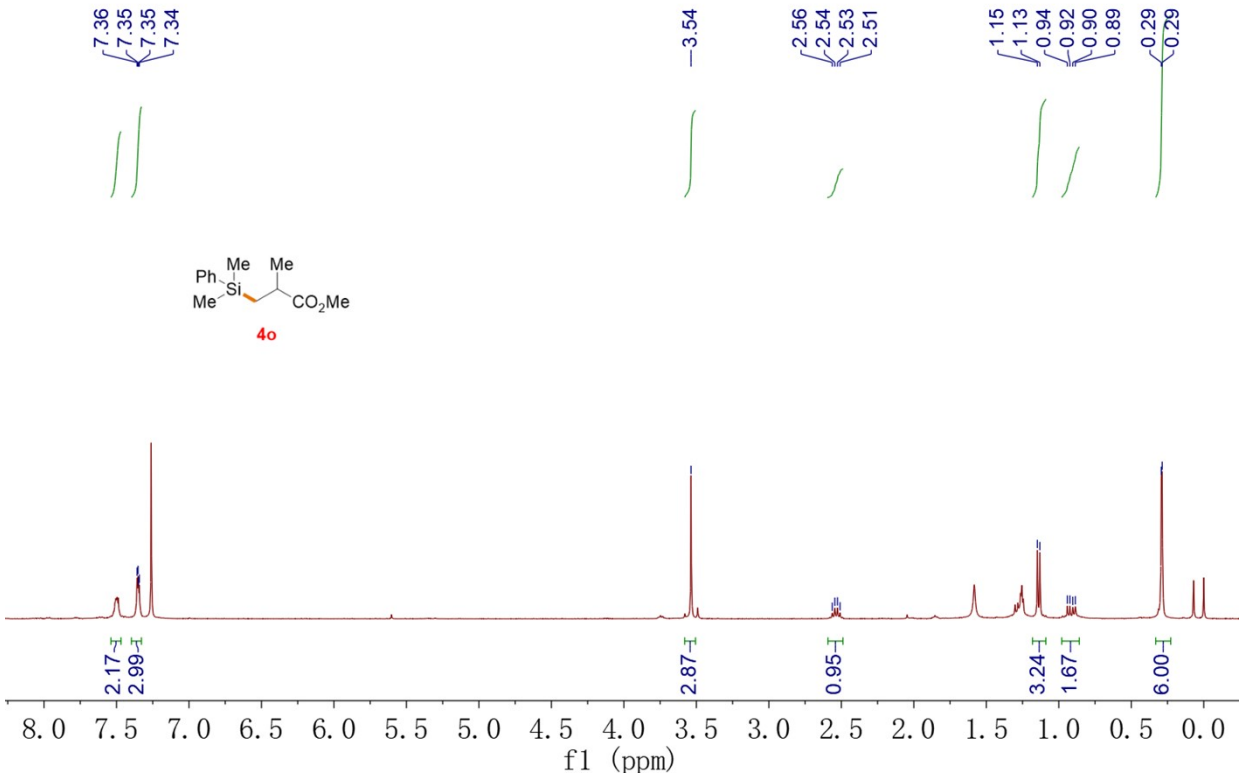
^{1}H NMR spectra of 4n (400 MHz, $CDCl_3$)



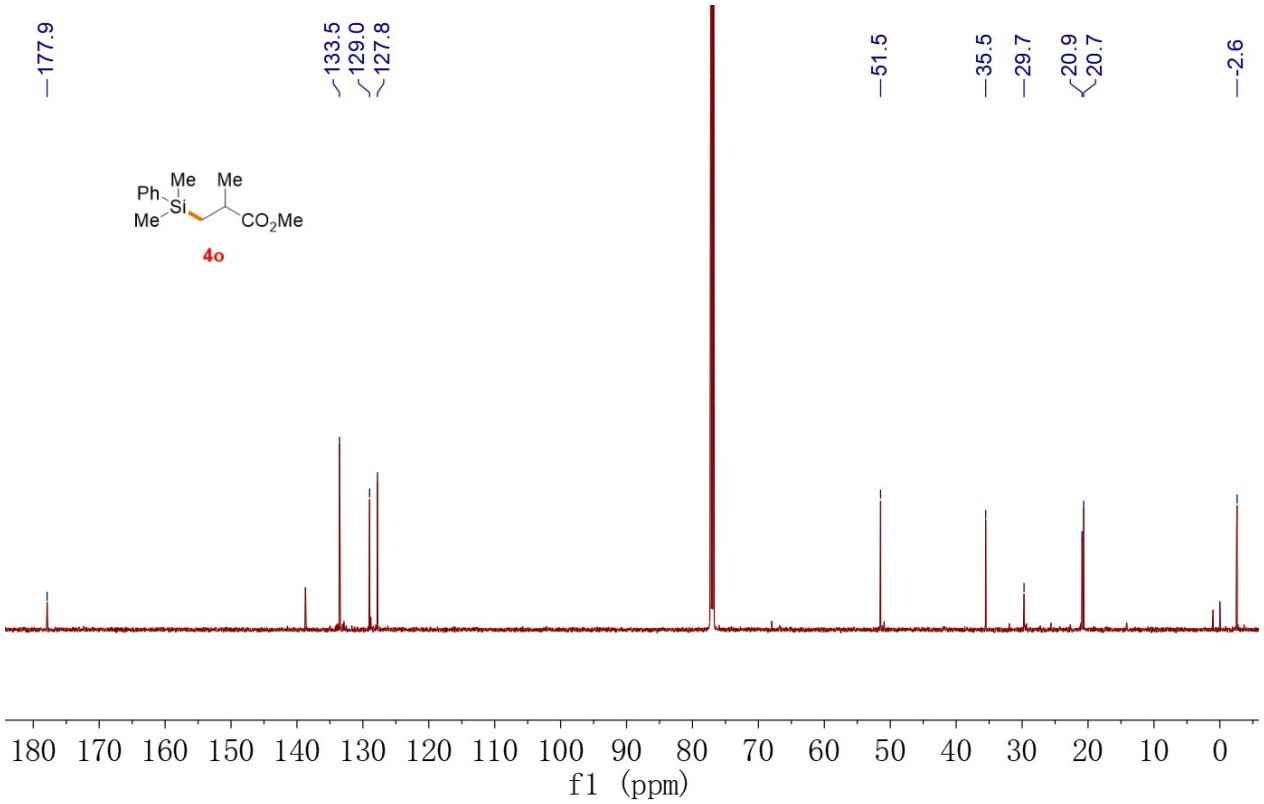
^{13}C NMR spectra of 4n (100 MHz, $CDCl_3$)



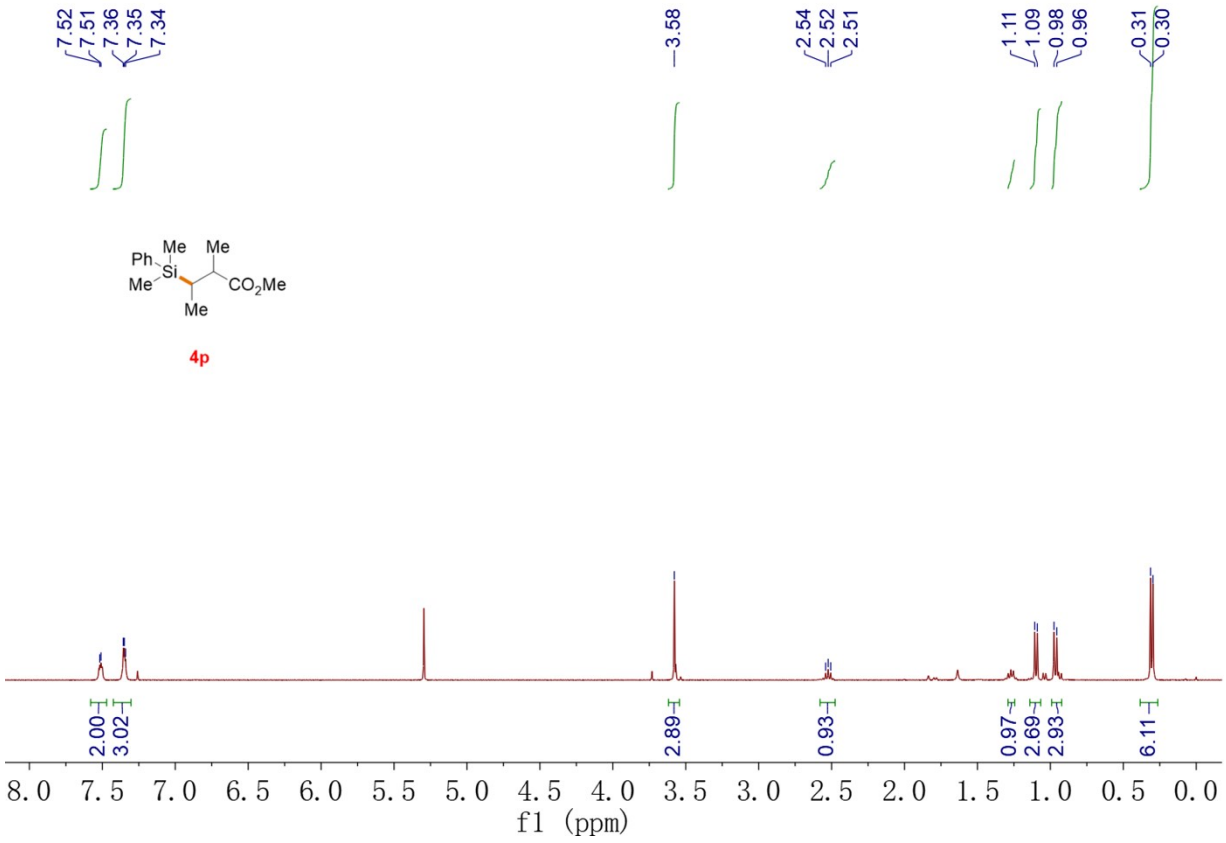
^{1}H NMR spectra of 4o (400 MHz, $CDCl_3$)



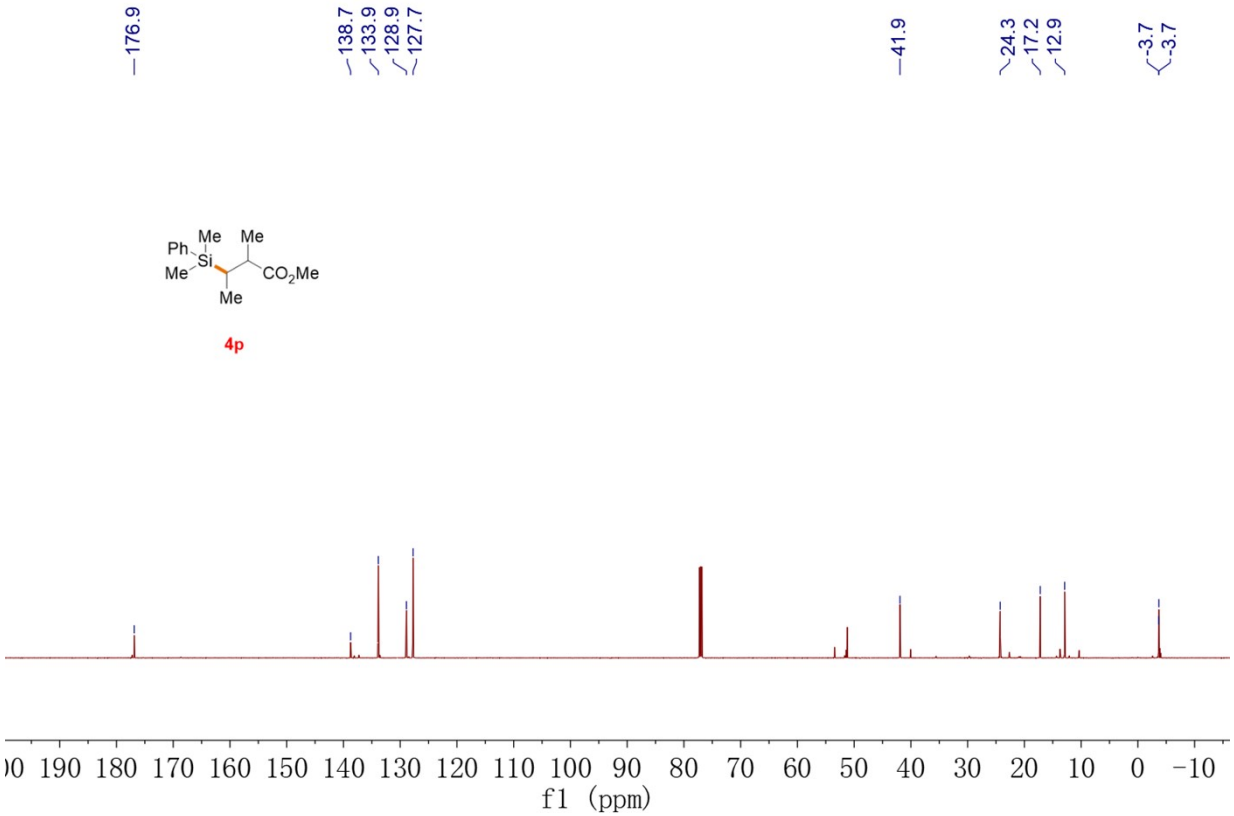
^{13}C NMR spectra of 4o (100 MHz, $CDCl_3$)



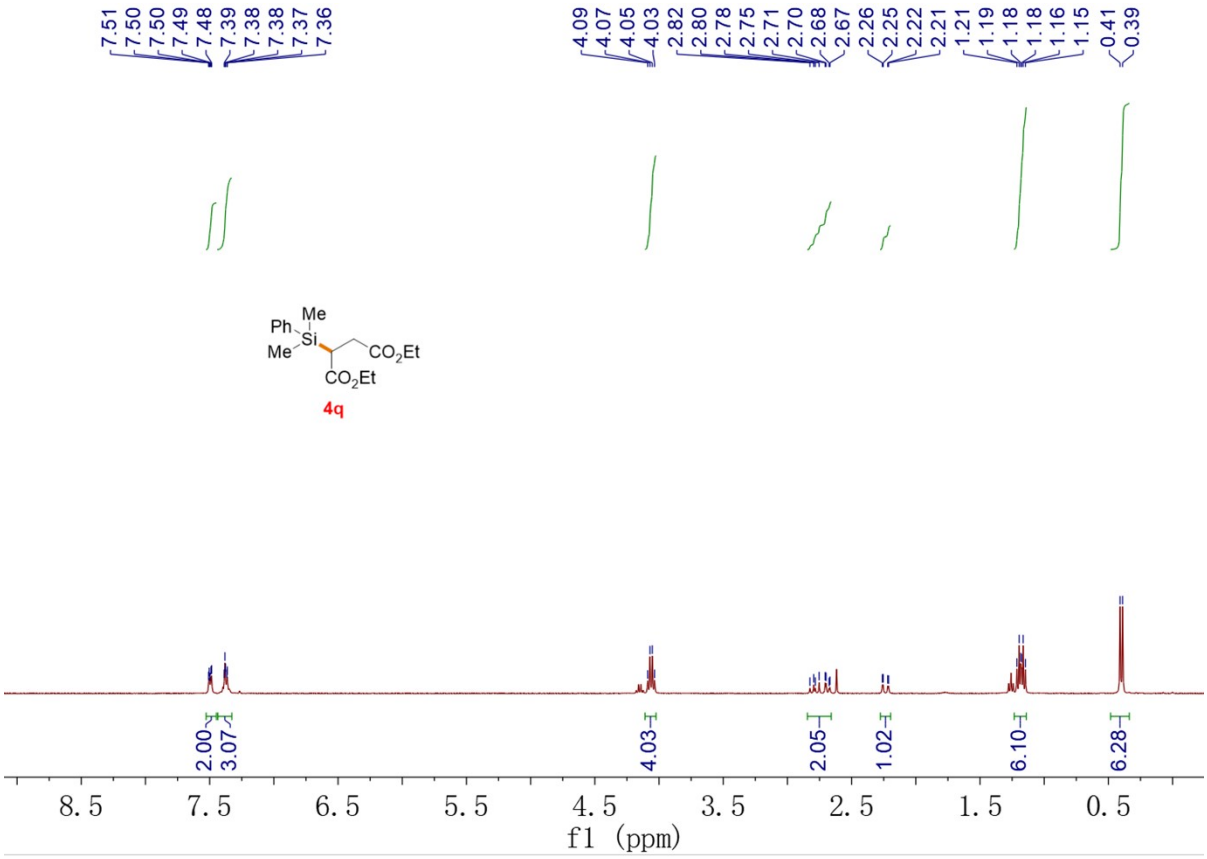
^{1}H NMR spectra of 4p(400 MHz, $CDCl_3$)



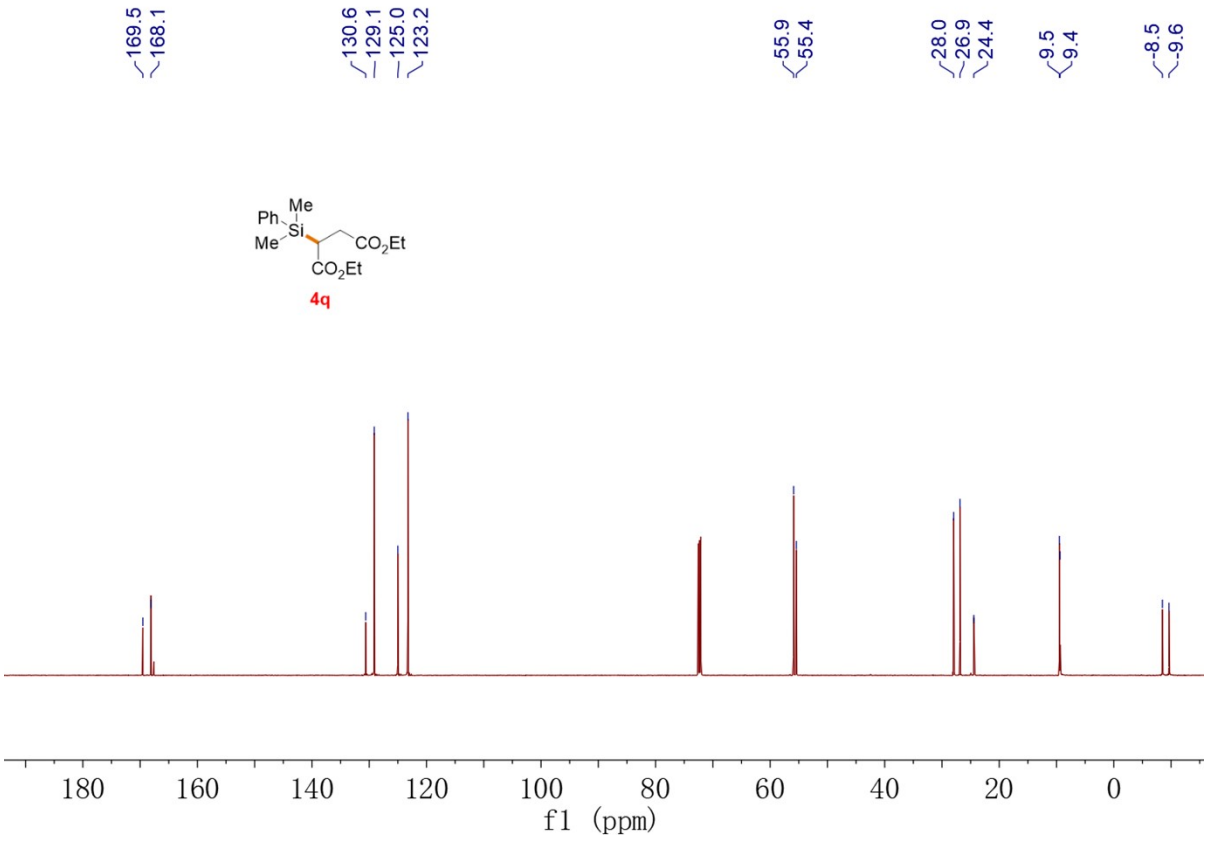
^{13}C NMR spectra of 4p (100 MHz, $CDCl_3$)



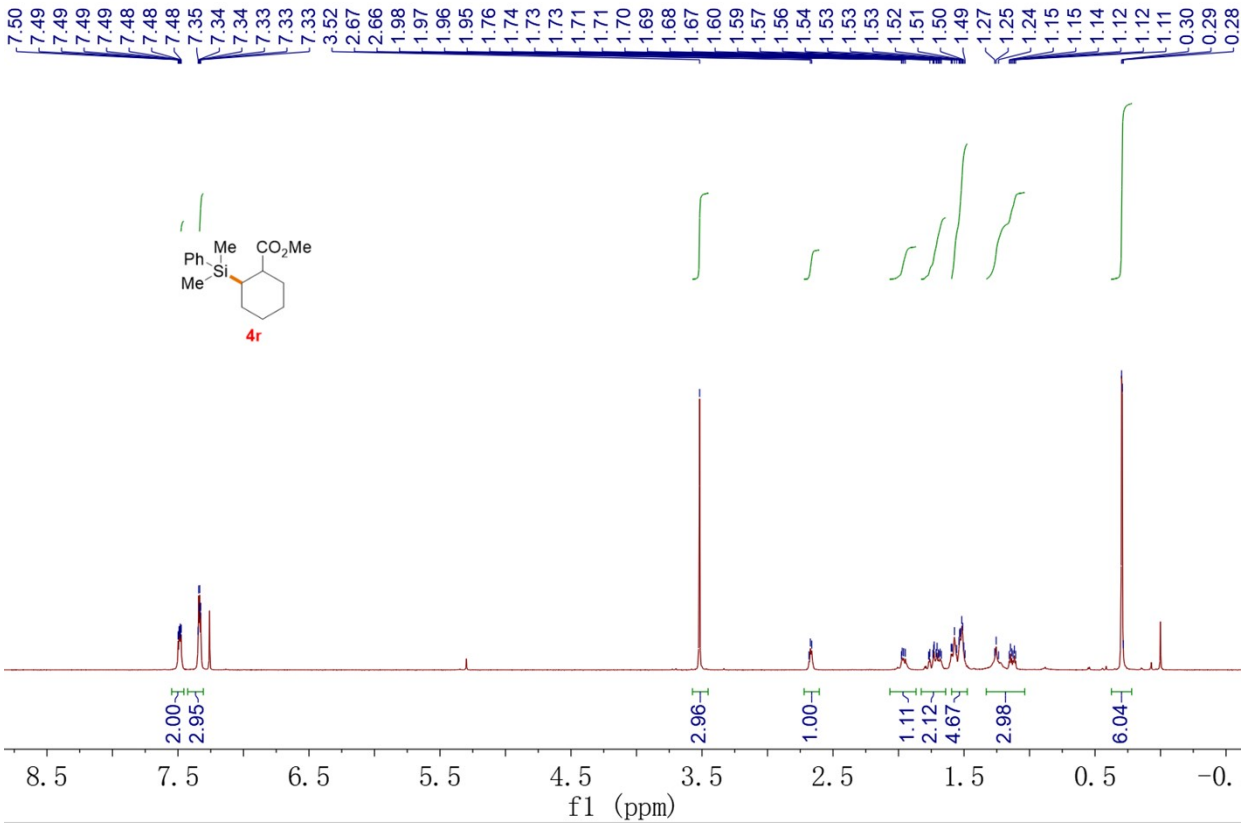
^{1}H NMR spectra of 4q (400 MHz, $CDCl_3$)



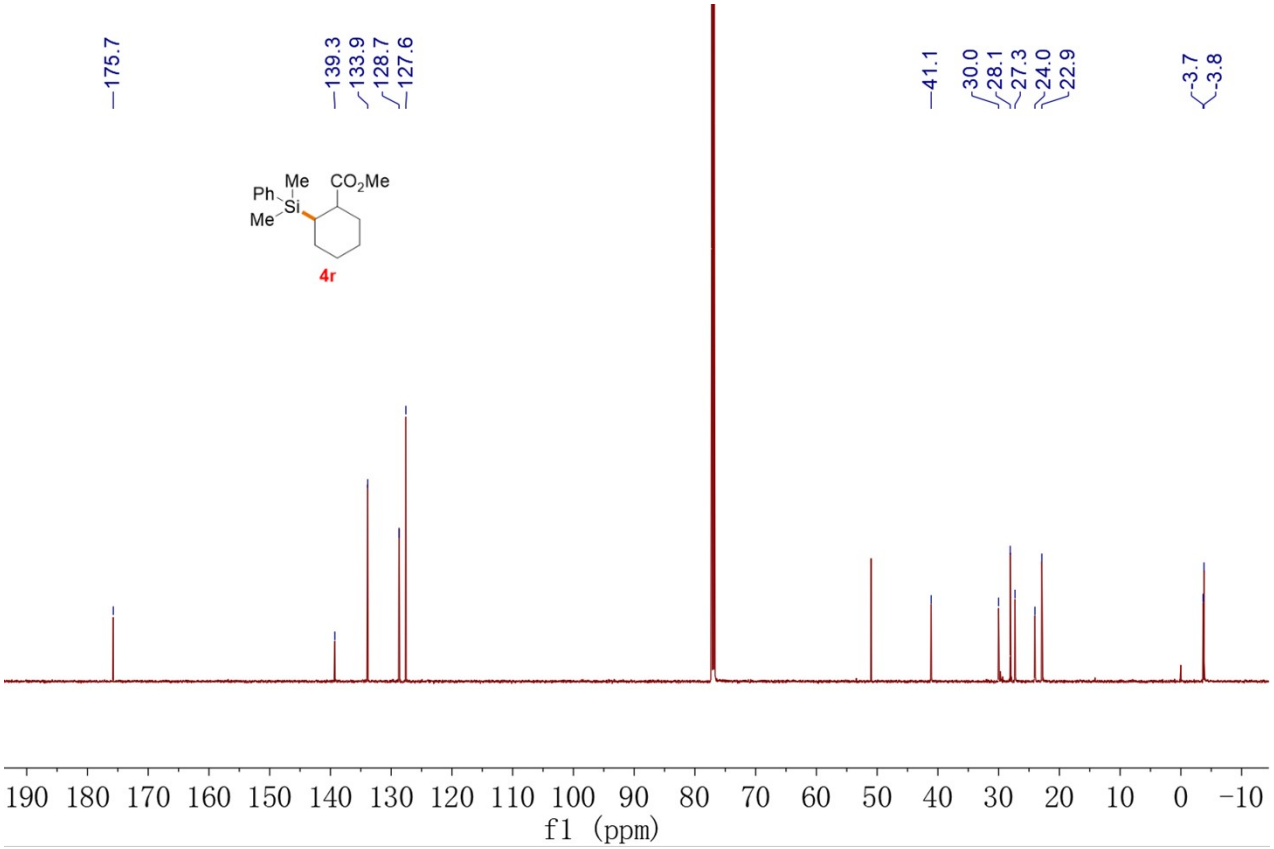
^{13}C NMR spectra of 4q (100 MHz, $CDCl_3$)



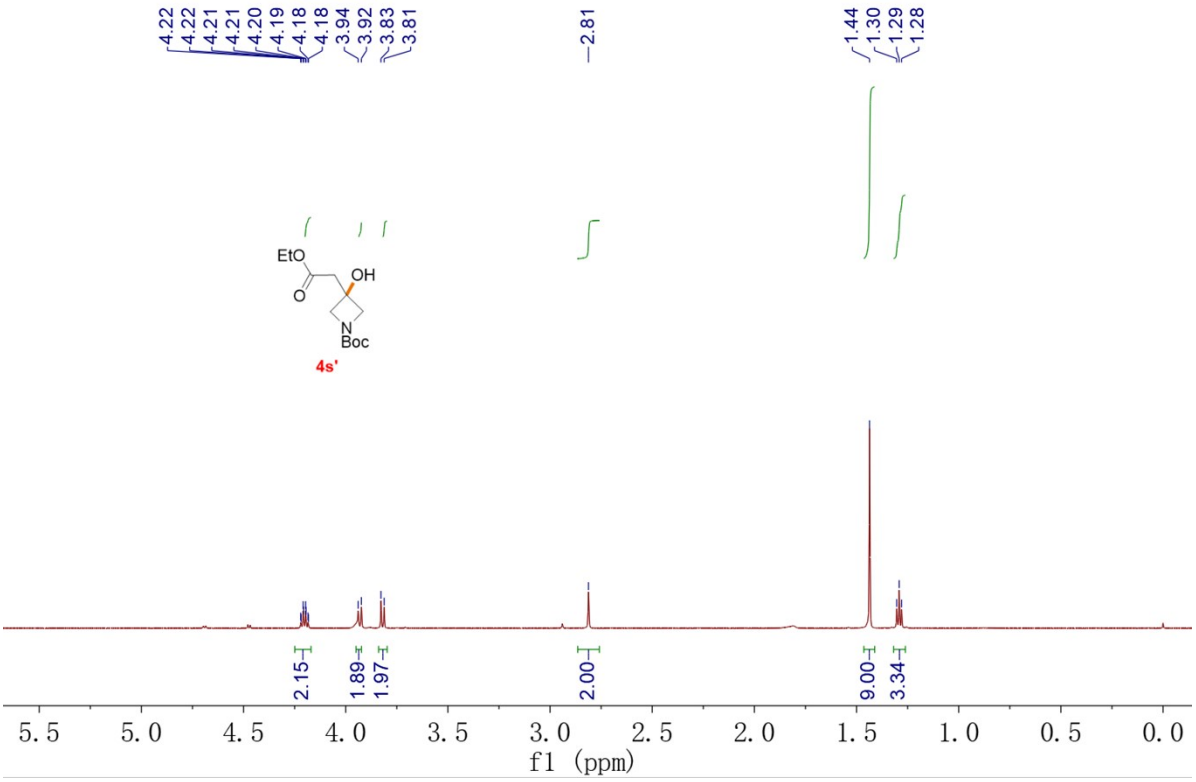
^{1}H NMR spectra of 4r (400 MHz, $CDCl_3$)



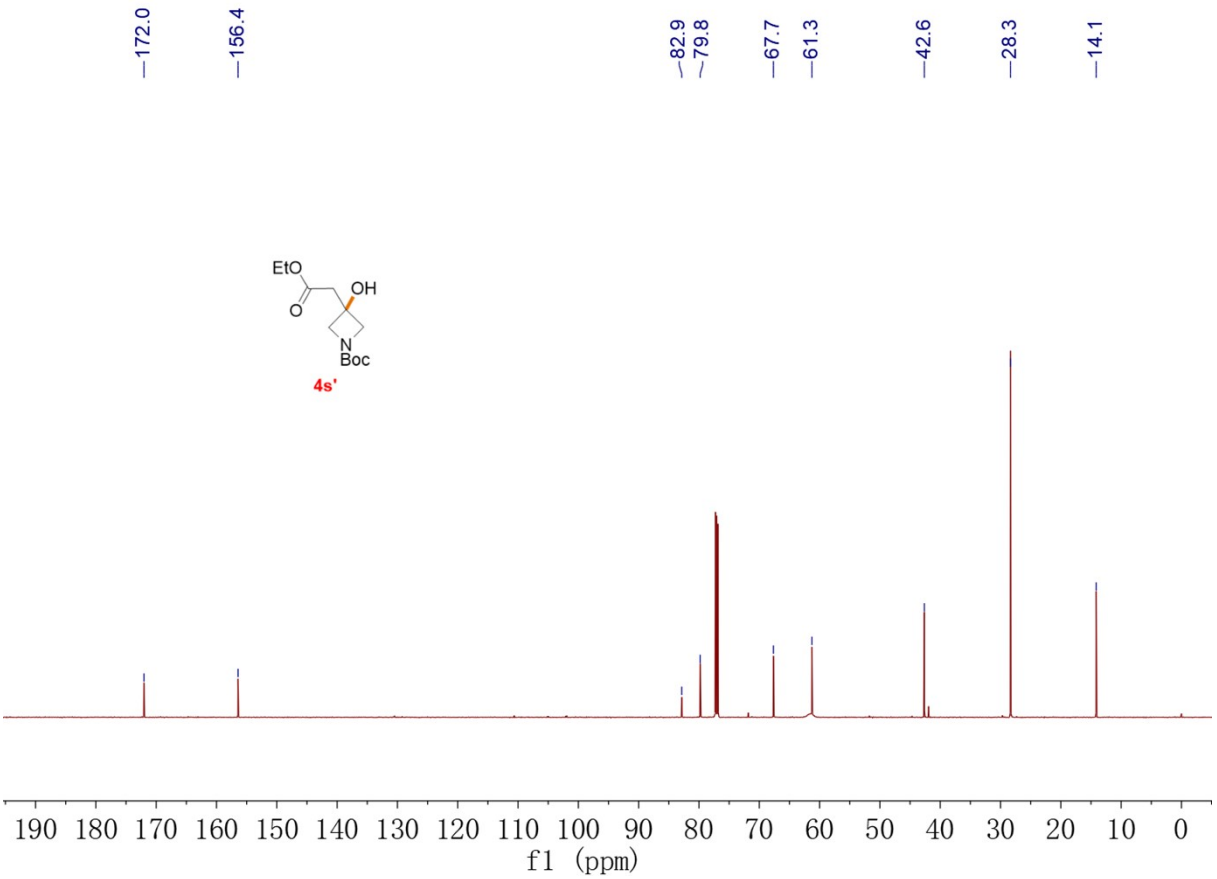
^{13}C NMR spectra of 4r (100 MHz, $CDCl_3$)



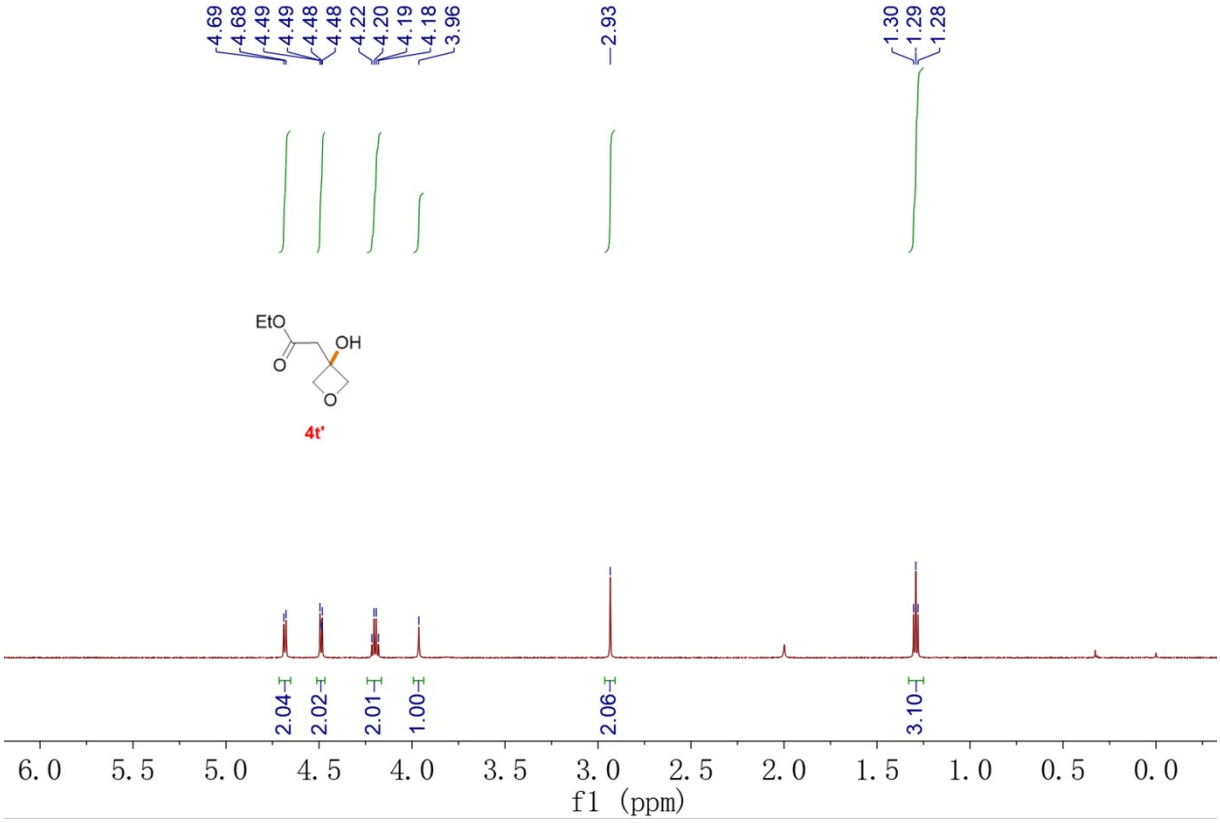
^{1}H NMR spectra of 4s′ (400 MHz, $CDCl_3$)



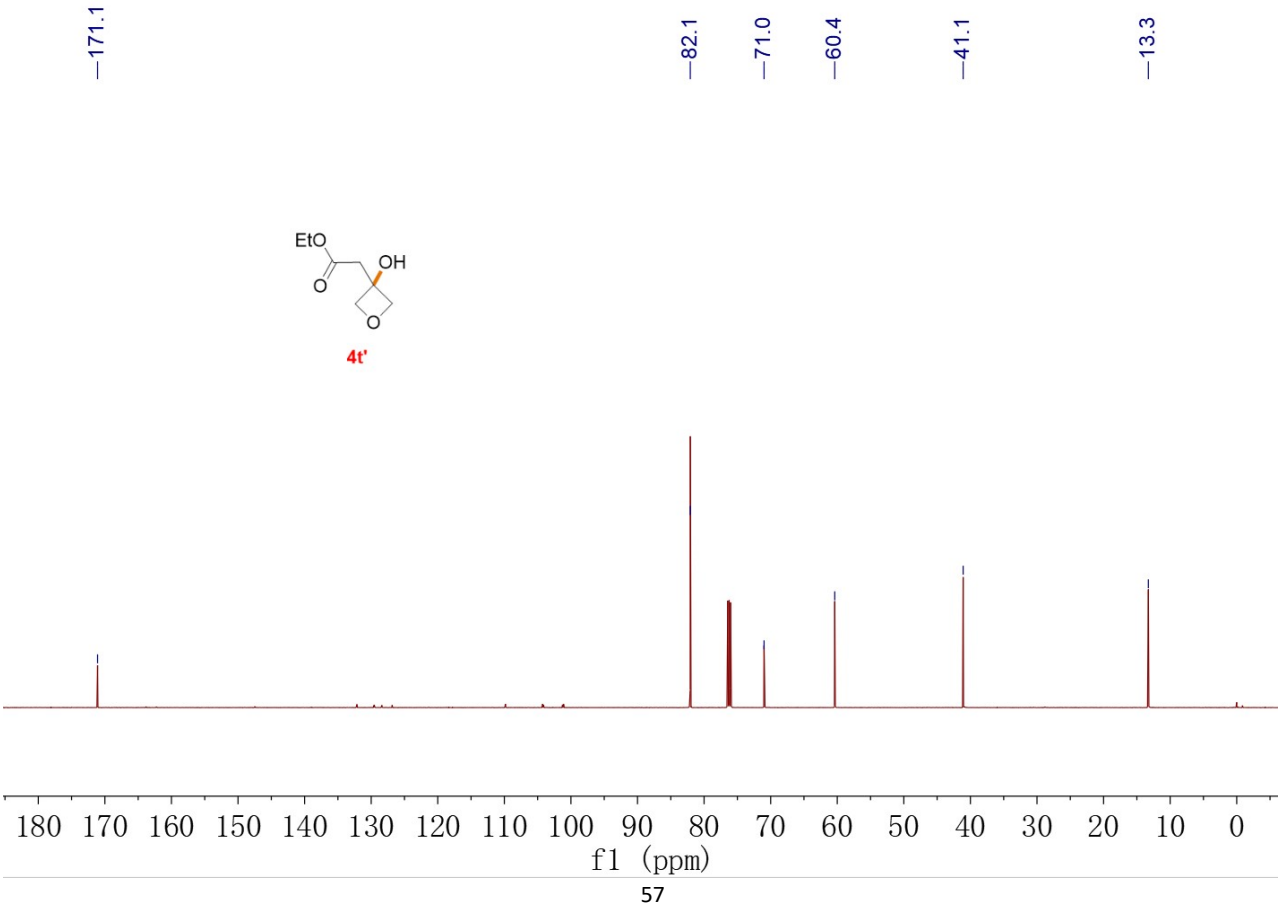
^{13}C NMR spectra of 4s′ (100 MHz, $CDCl_3$)



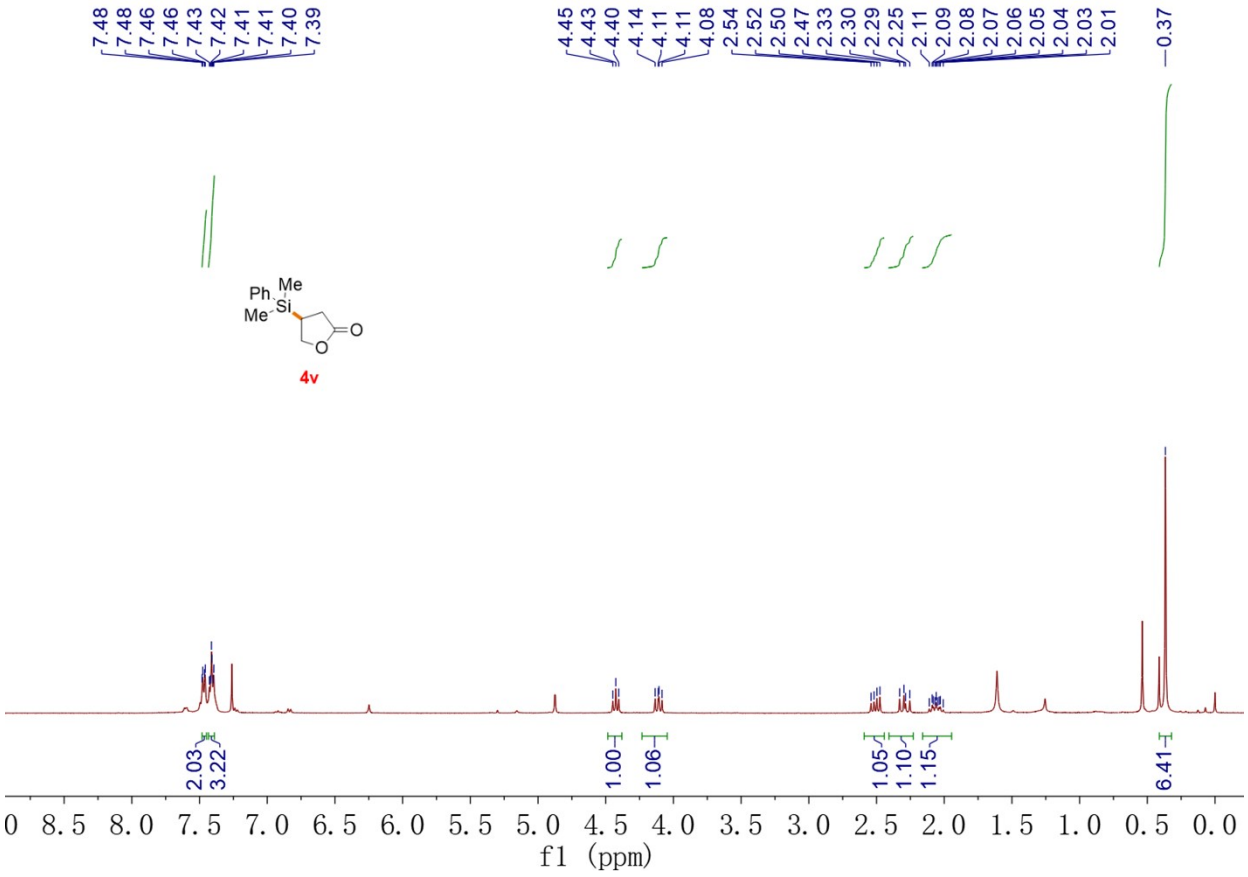
^{1}H NMR spectra of 4t′ (400 MHz, $CDCl_3$)



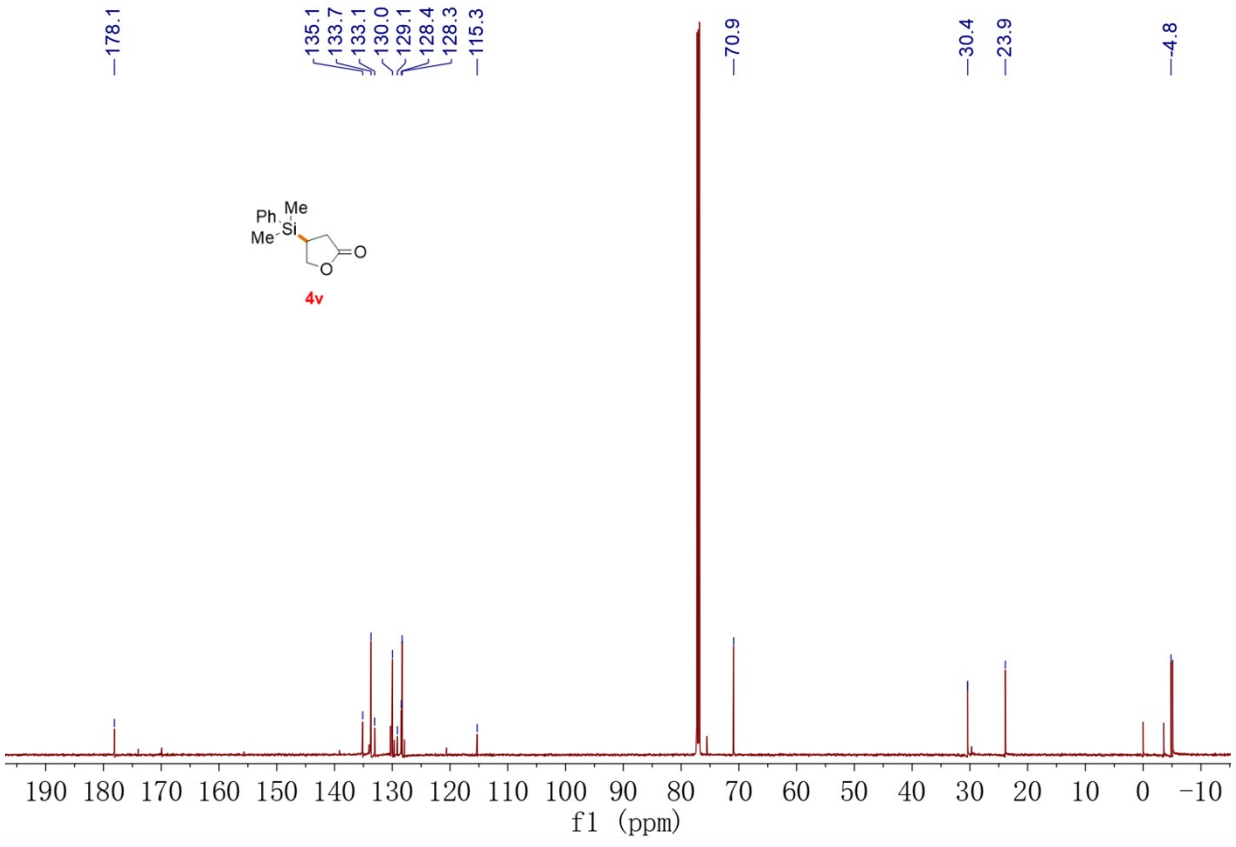
^{13}C NMR spectra of 4t′ (100 MHz, $CDCl_3$)



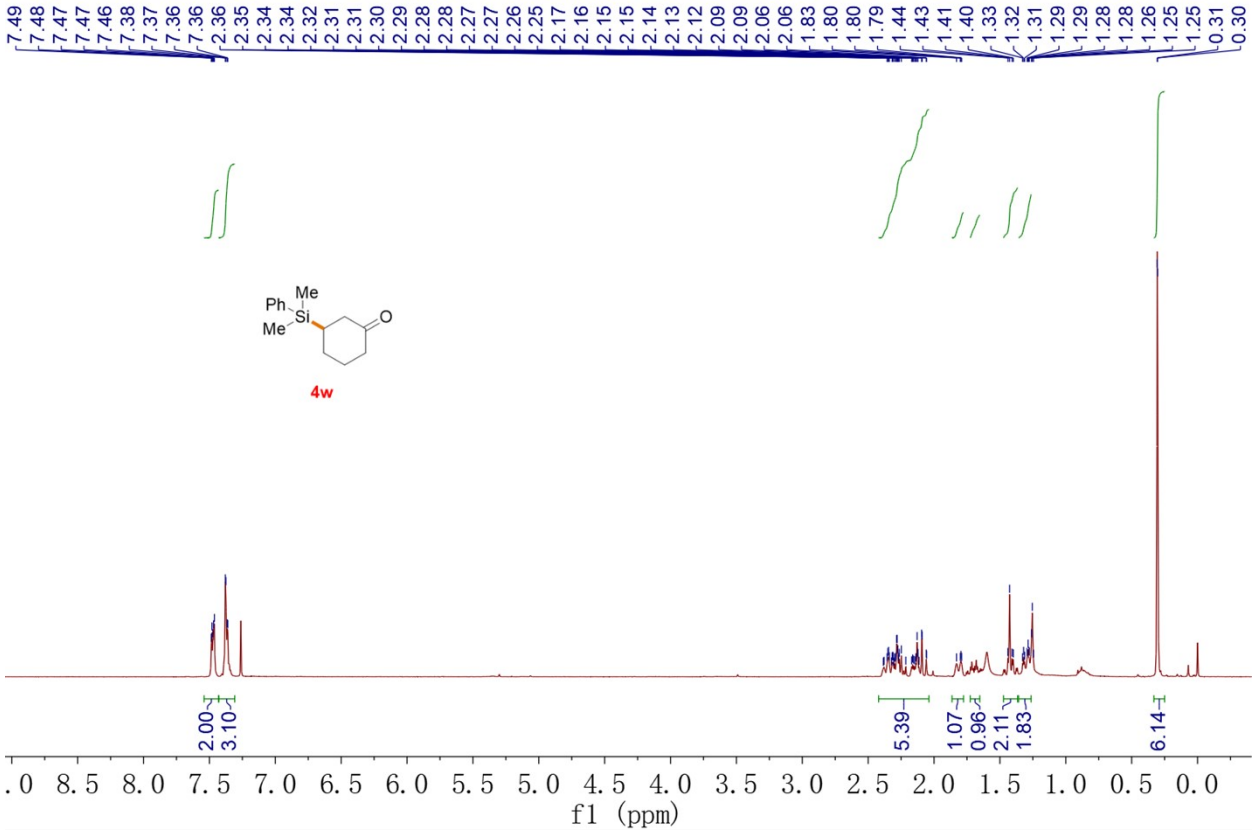
^{1}H NMR spectra of 4v (400 MHz, $CDCl_3$)



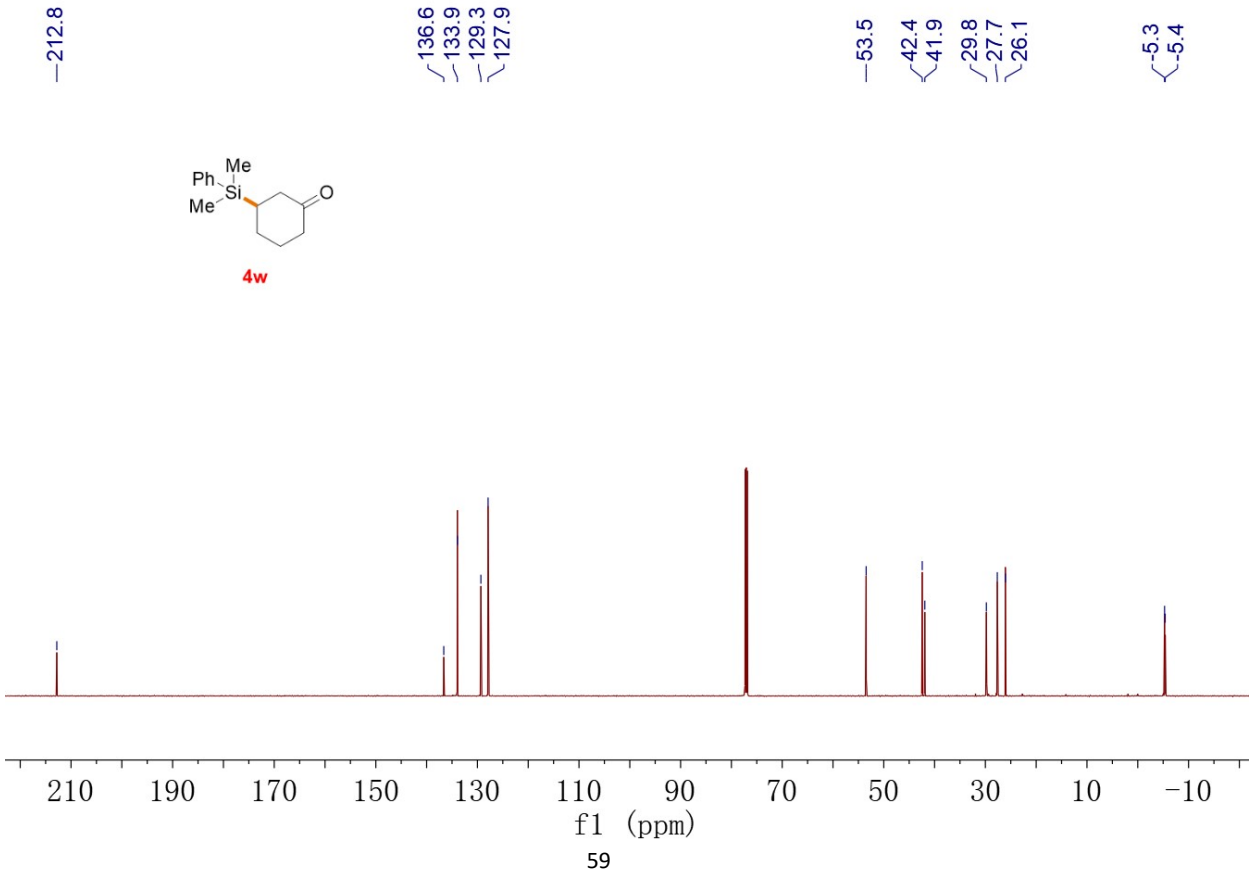
^{13}C NMR spectra of 4v (100 MHz, $CDCl_3$)



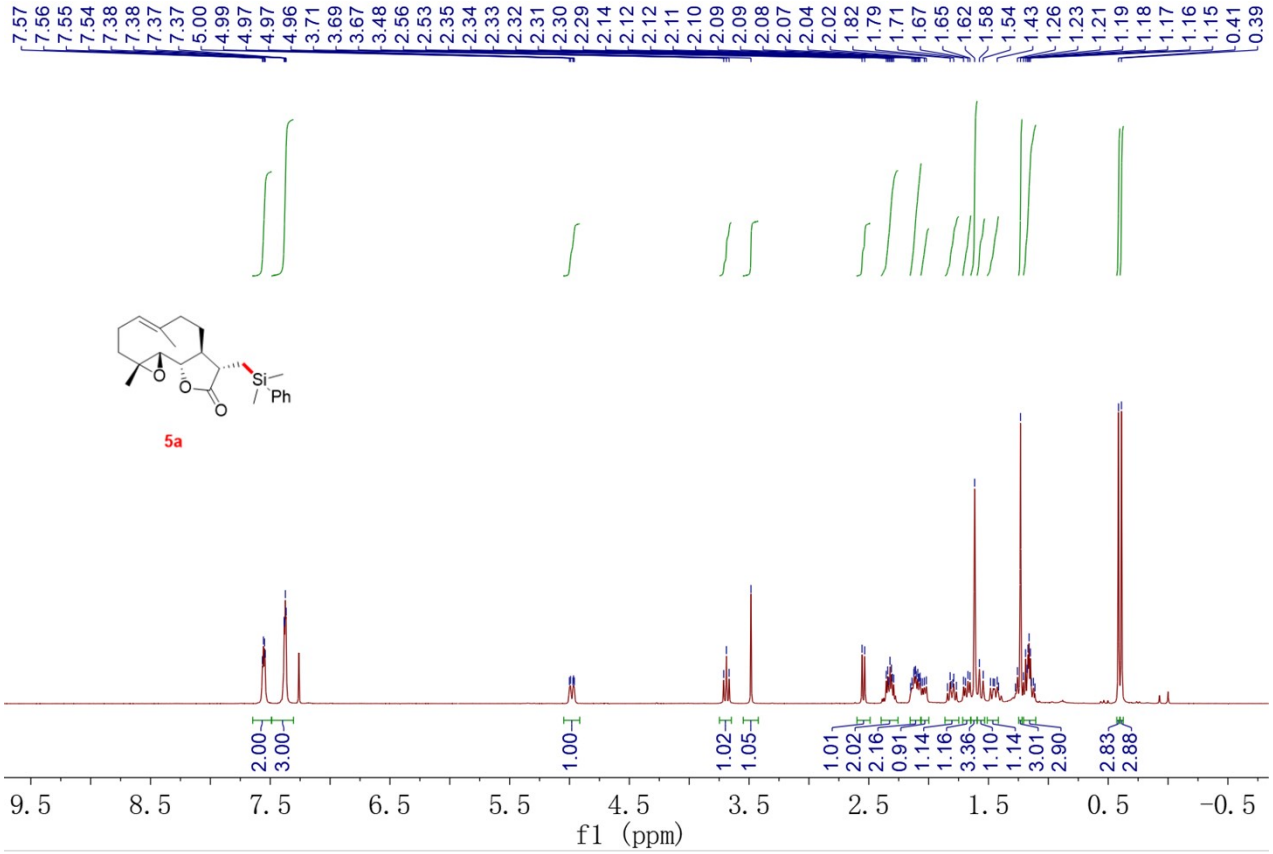
^{1}H NMR spectra of 4w (400 MHz, $CDCl_3$)



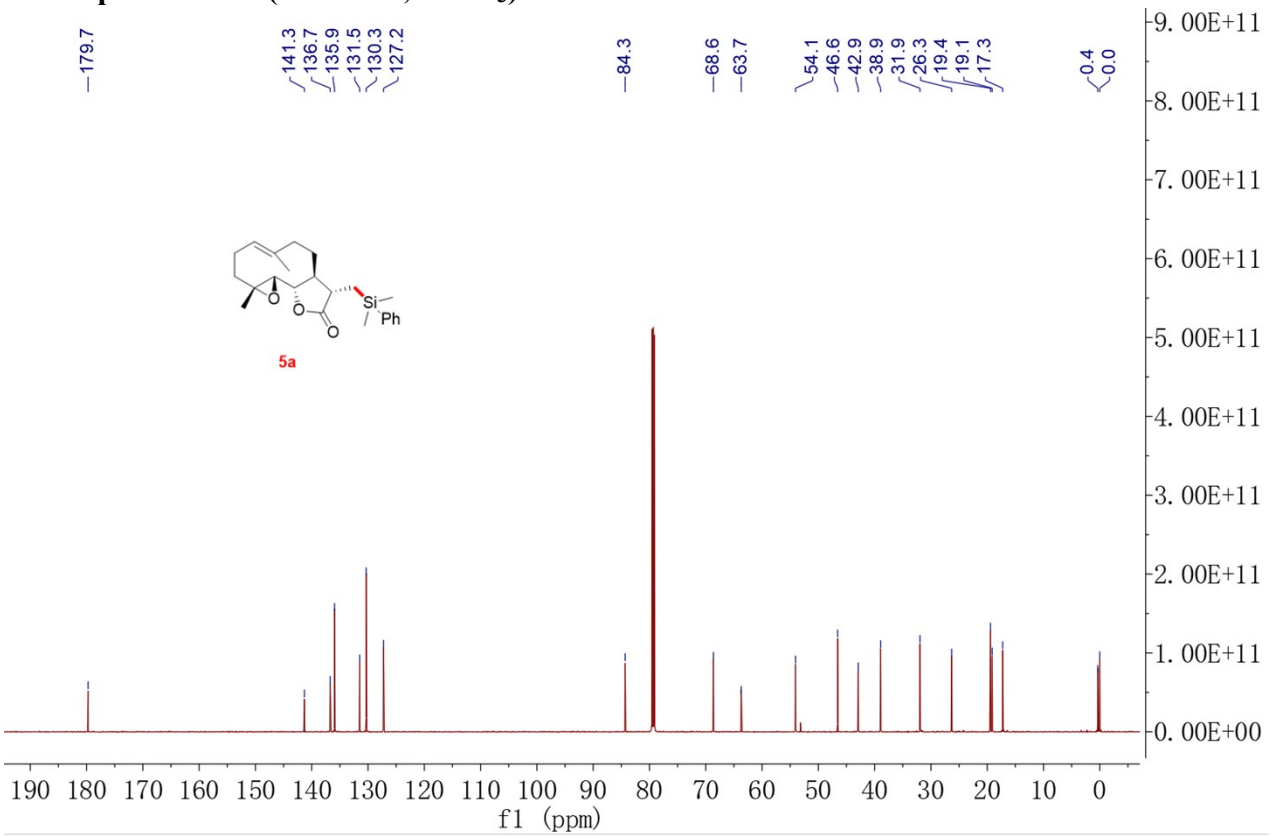
^{13}C NMR spectra of 4w (100 MHz, $CDCl_3$)



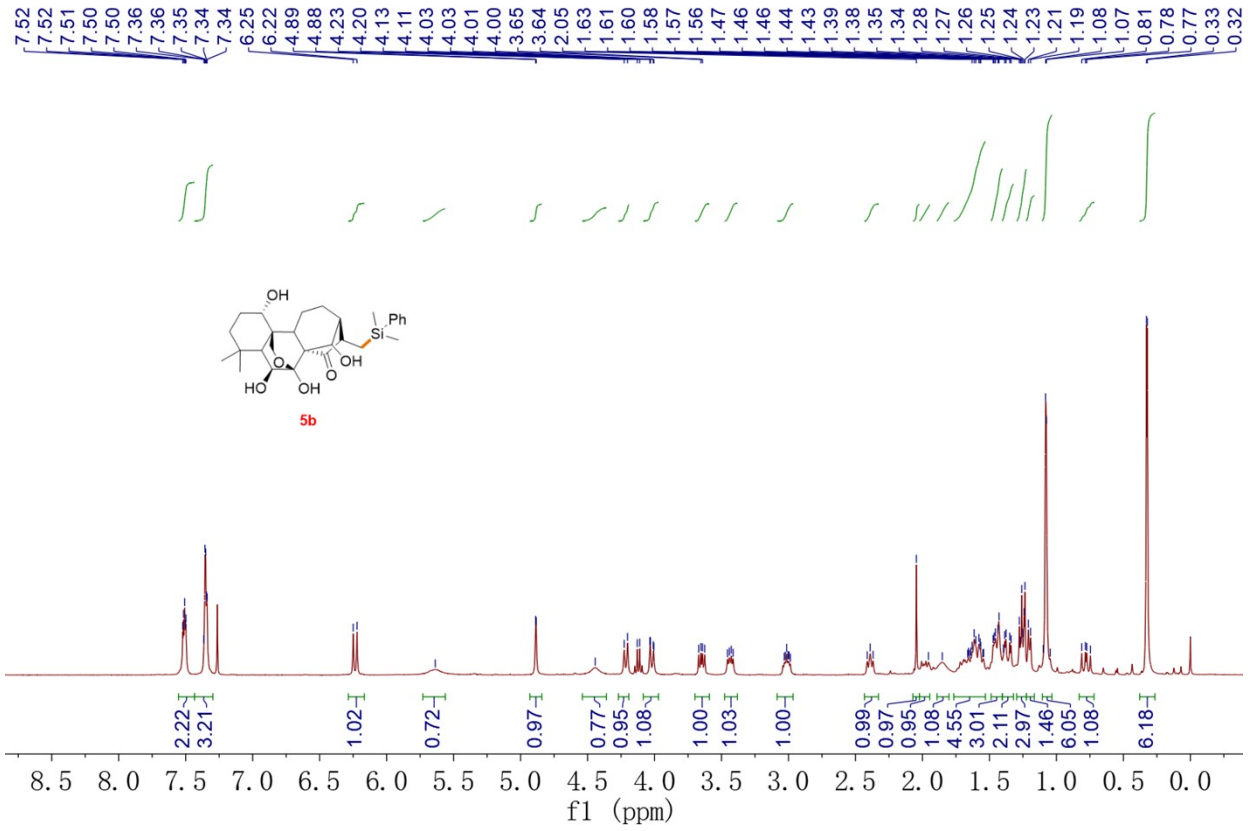
^{1}H NMR spectra of 5a (400 MHz, $CDCl_3$)



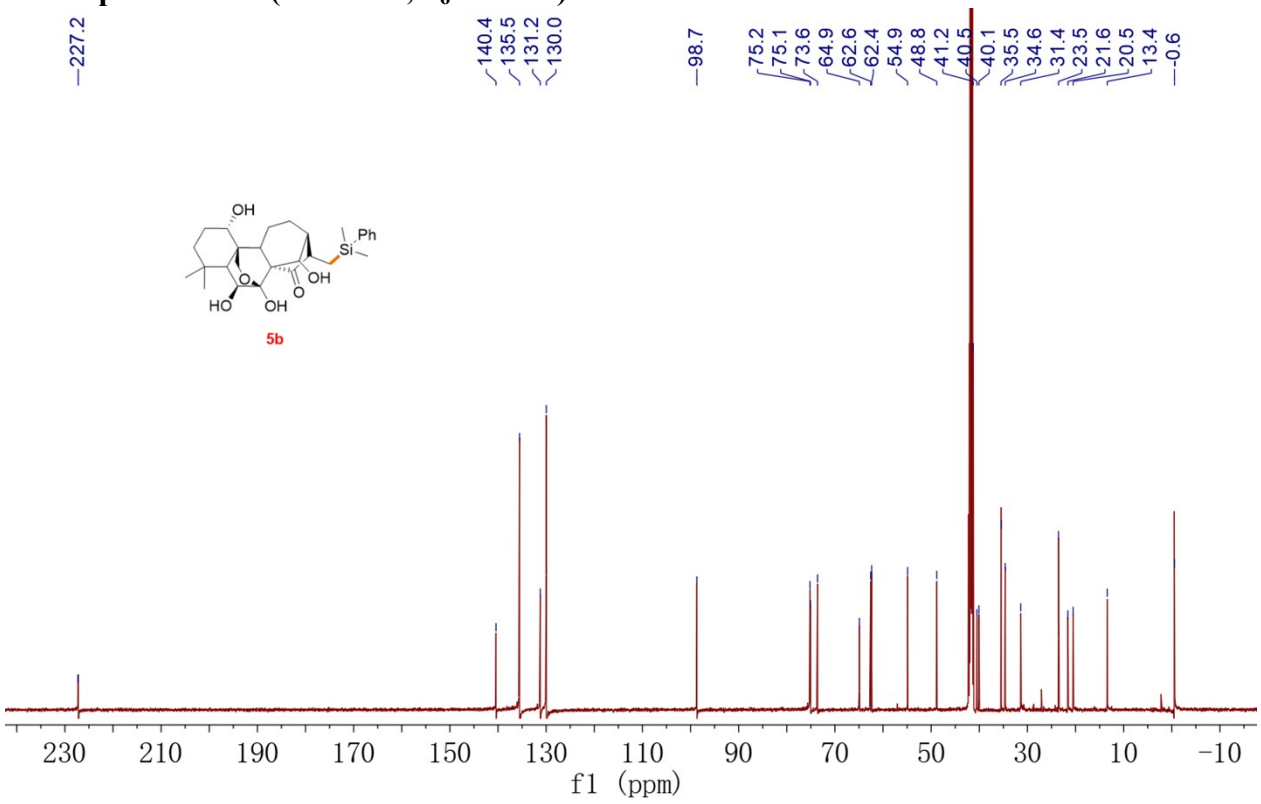
^{13}C NMR spectra of 5a (100 MHz, $CDCl_3$)



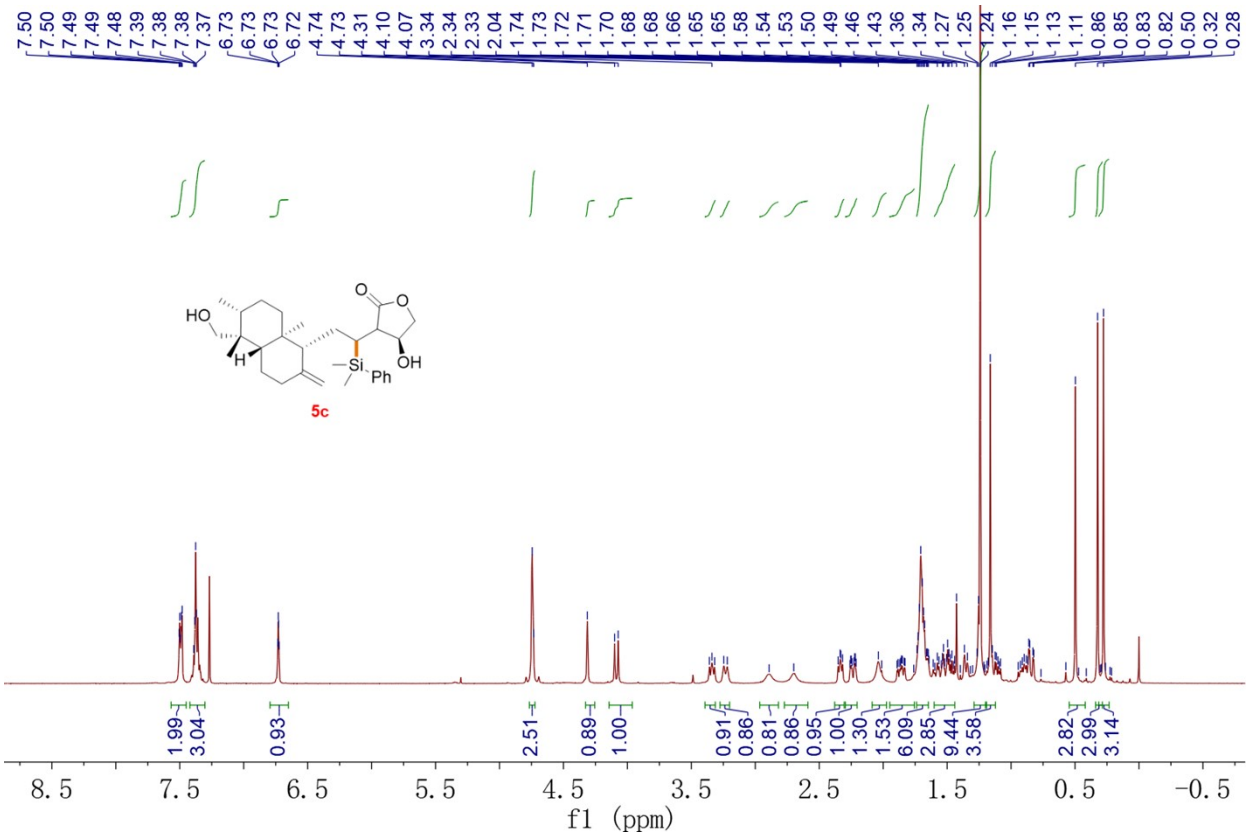
^{1}H NMR spectra of 5b (400 MHz, $CDCl_3$)



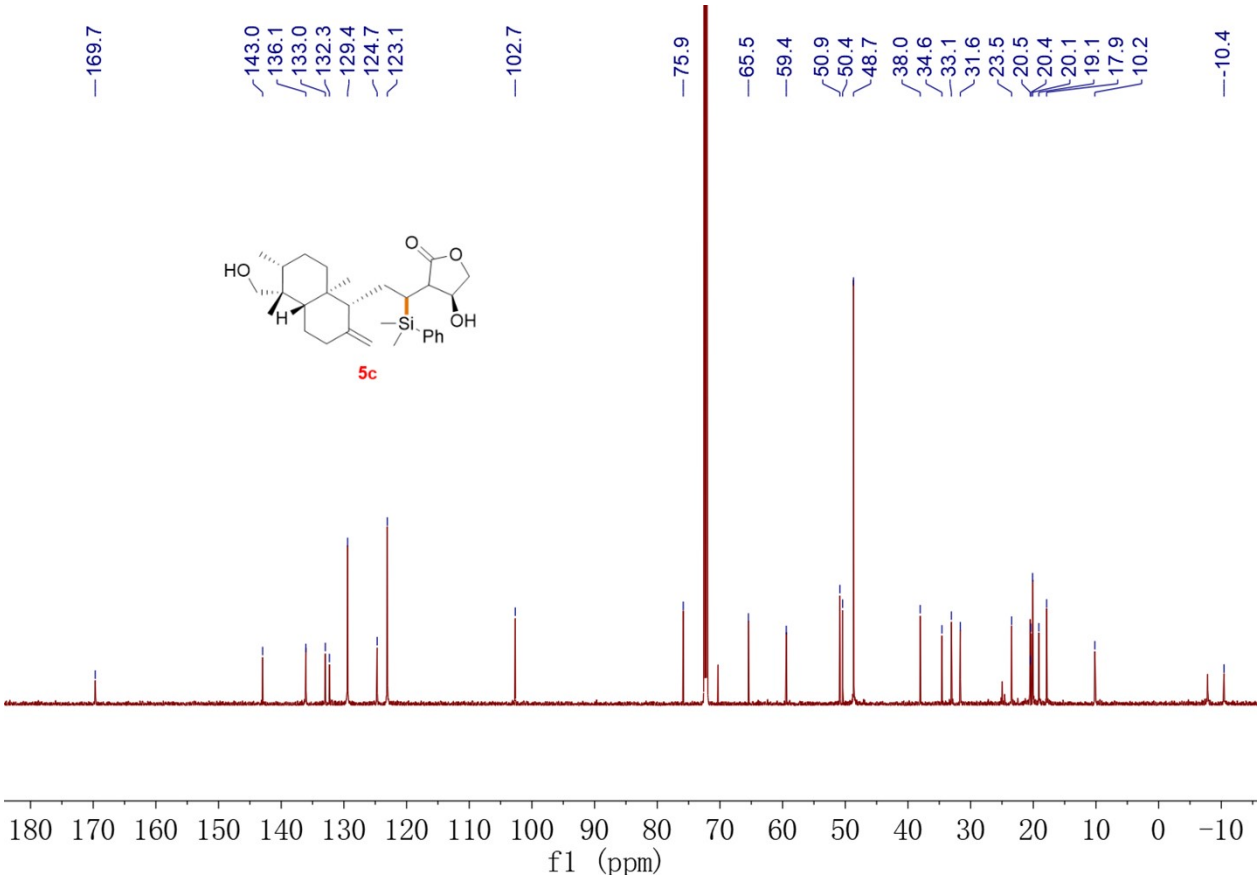
^{13}C NMR spectra of 5b (100 MHz, d_6-DMSO)



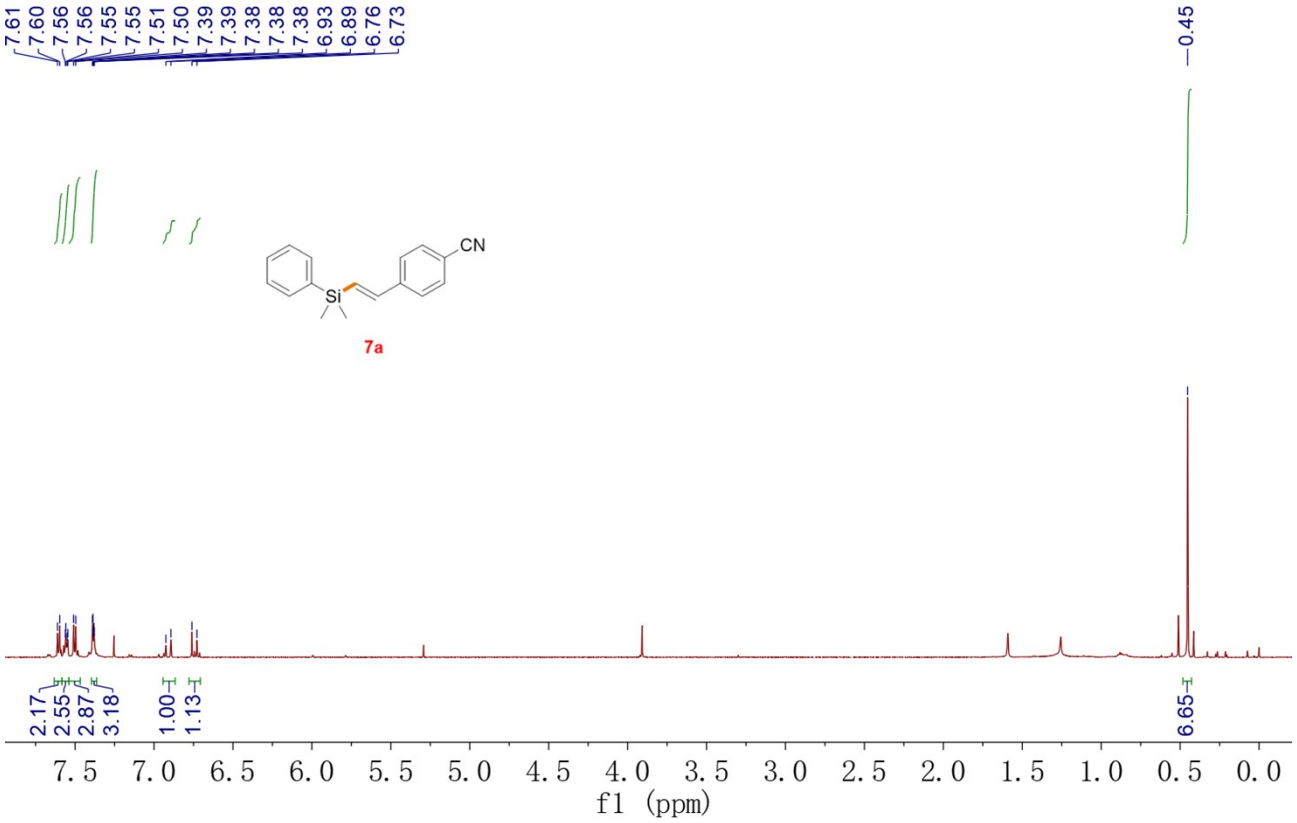
^{1}H NMR spectra of 5c (400 MHz, $CDCl_3$)



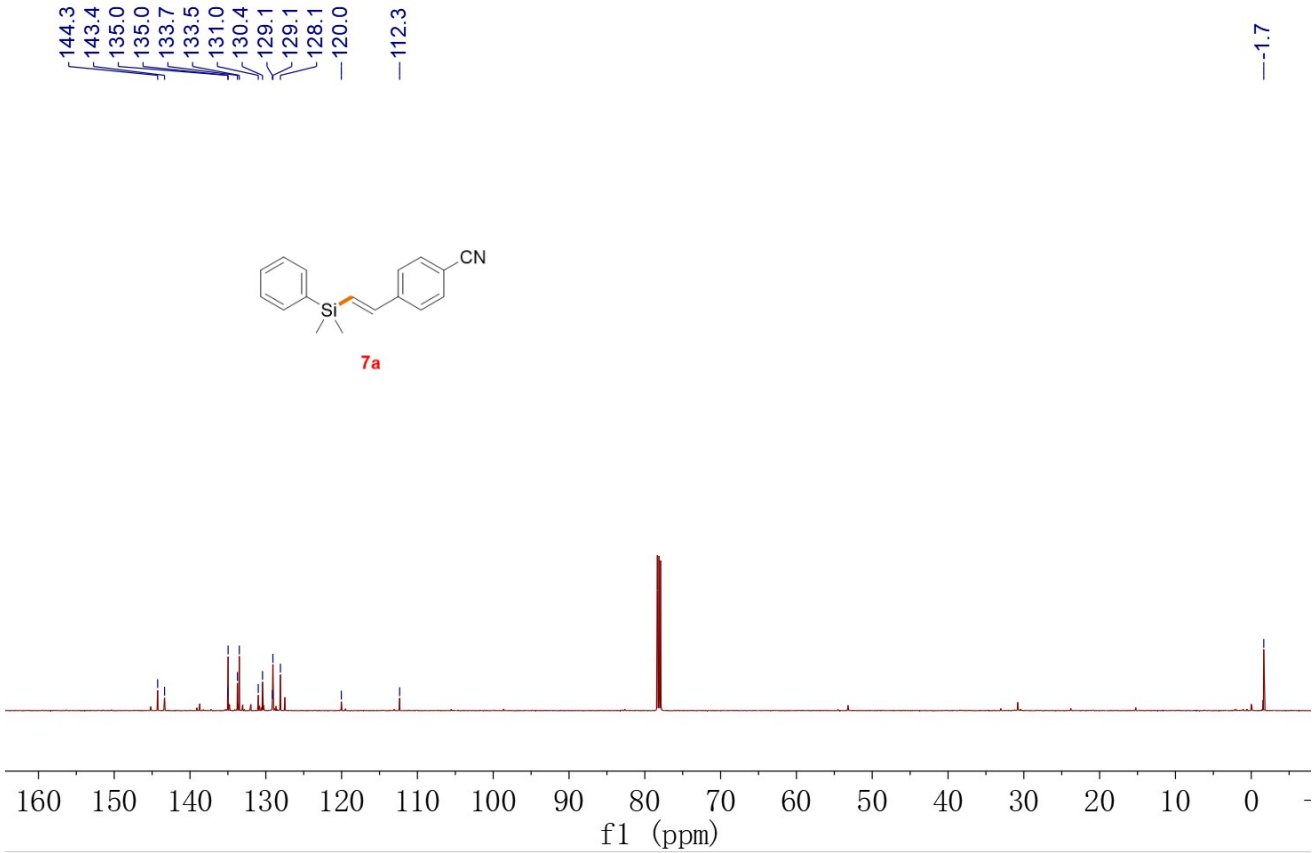
^{13}C NMR spectra of 5c (100 MHz, $CDCl_3$)



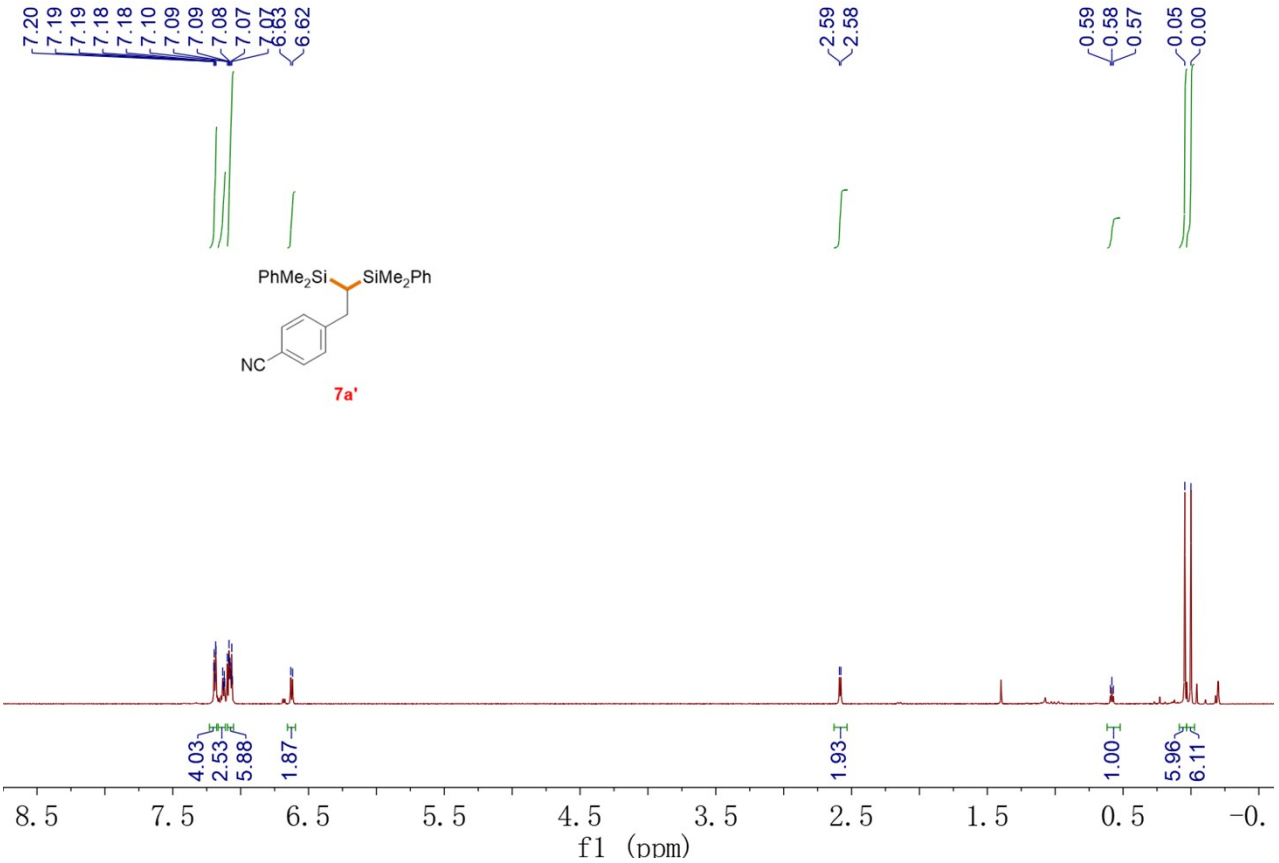
^{1}H NMR spectra of 7a (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 7a (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 7a′ (400 MHz, $CDCl_3$)



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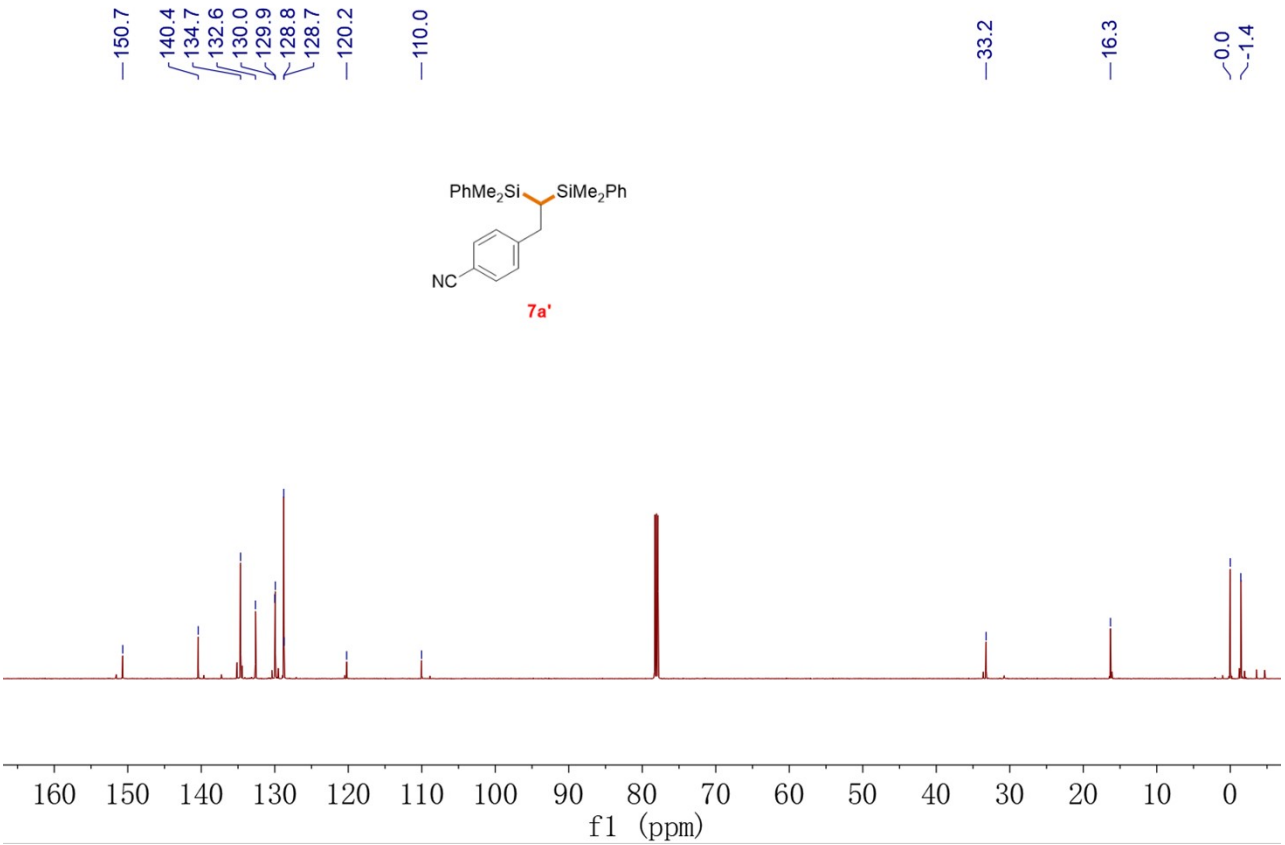
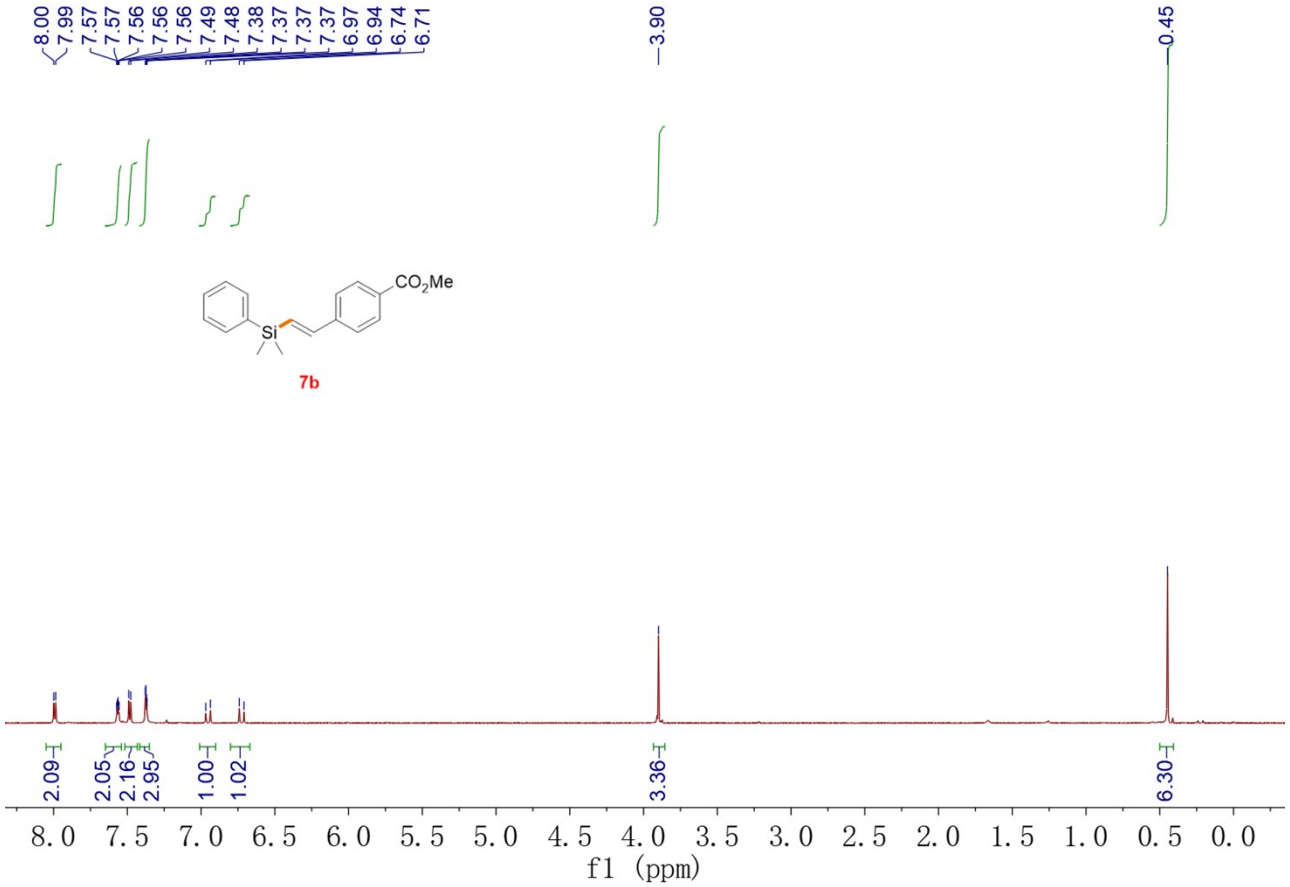
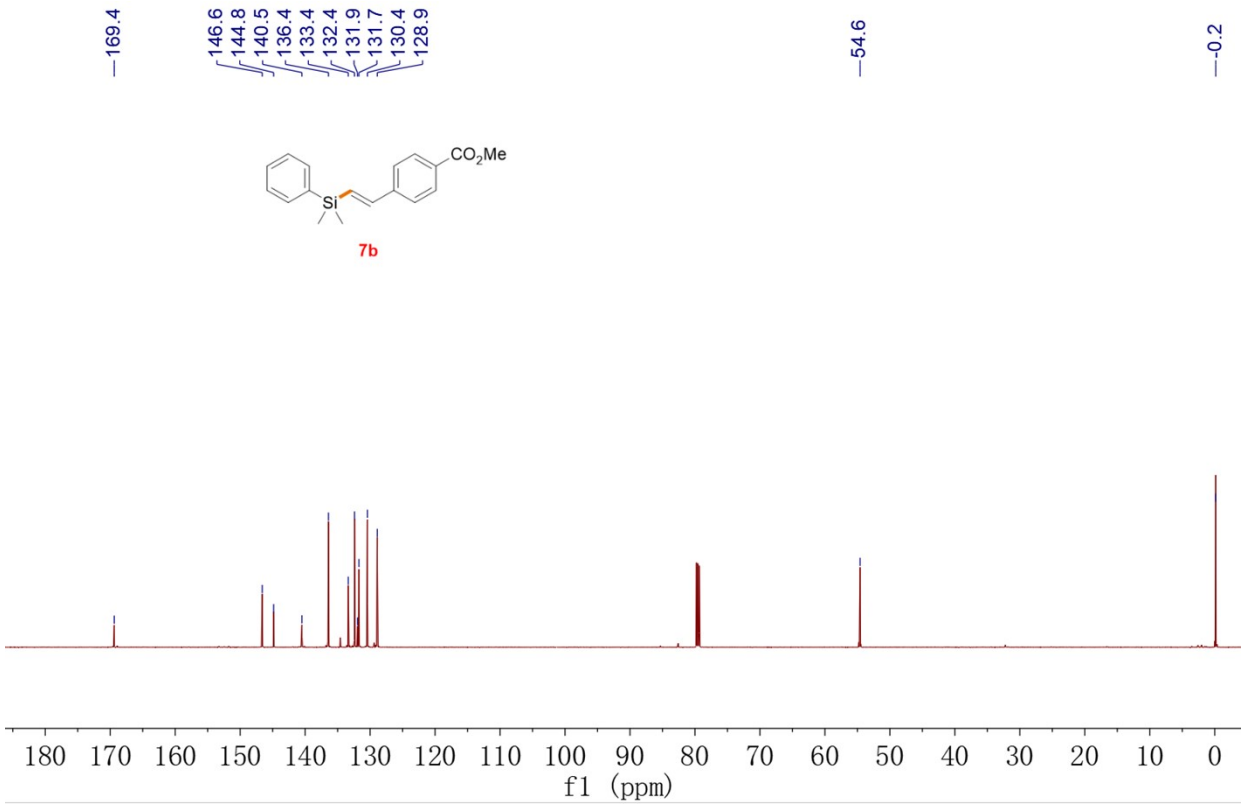


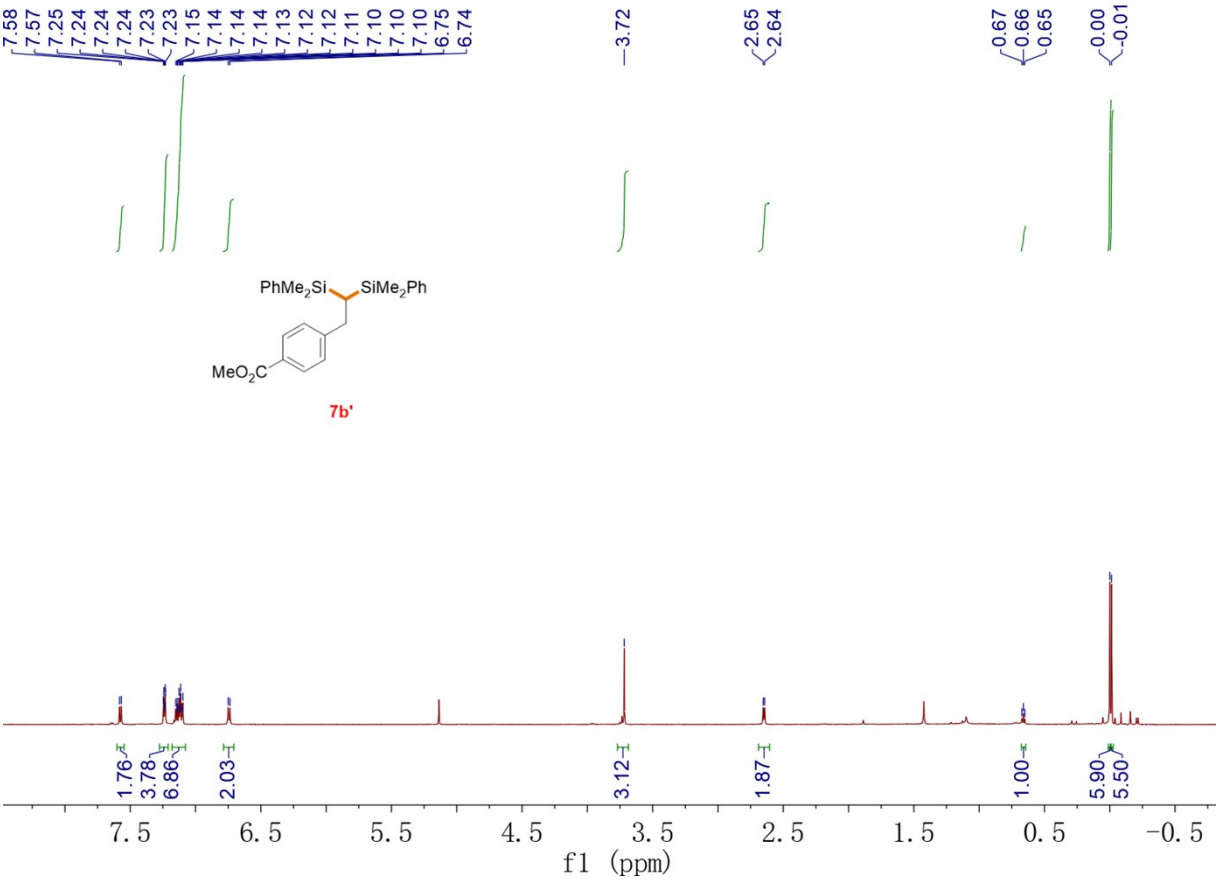
^{1}H NMR spectra of 7b (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 7b (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 7b′ (400 MHz, $CDCl_3$)



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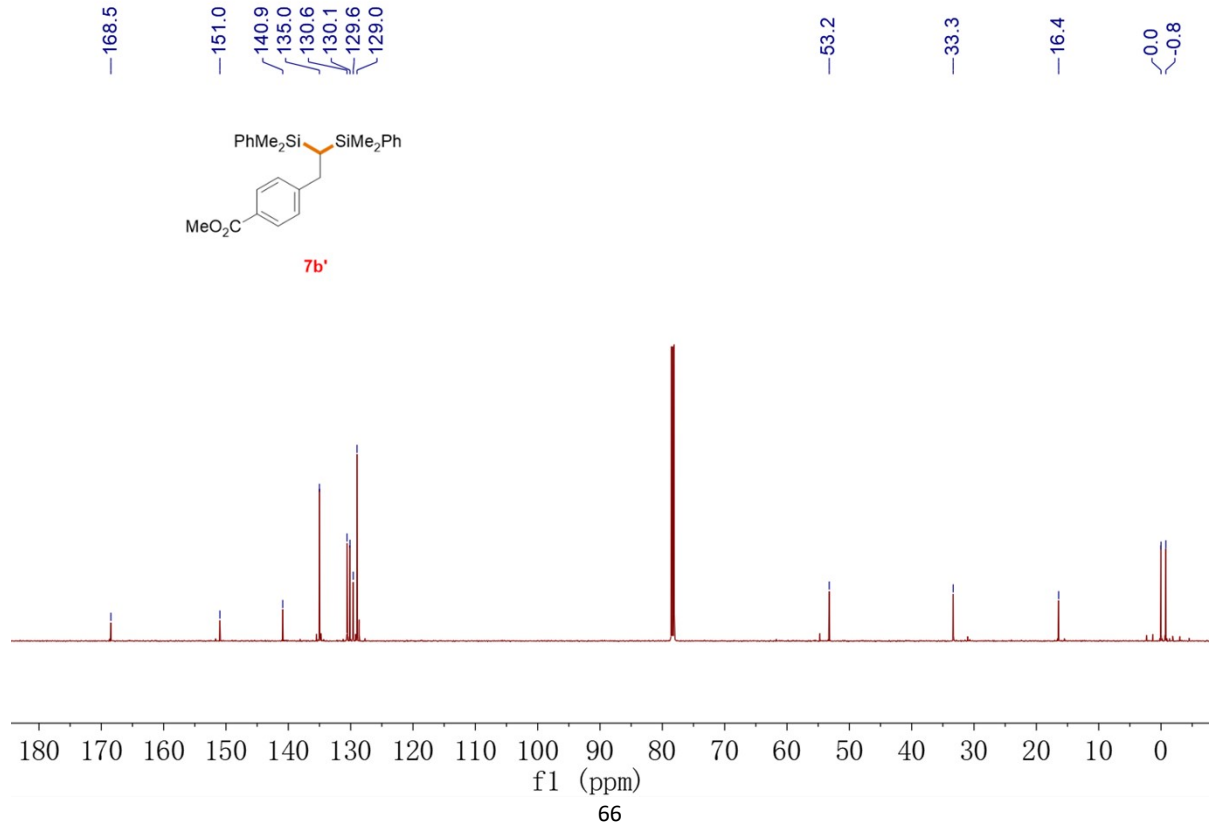
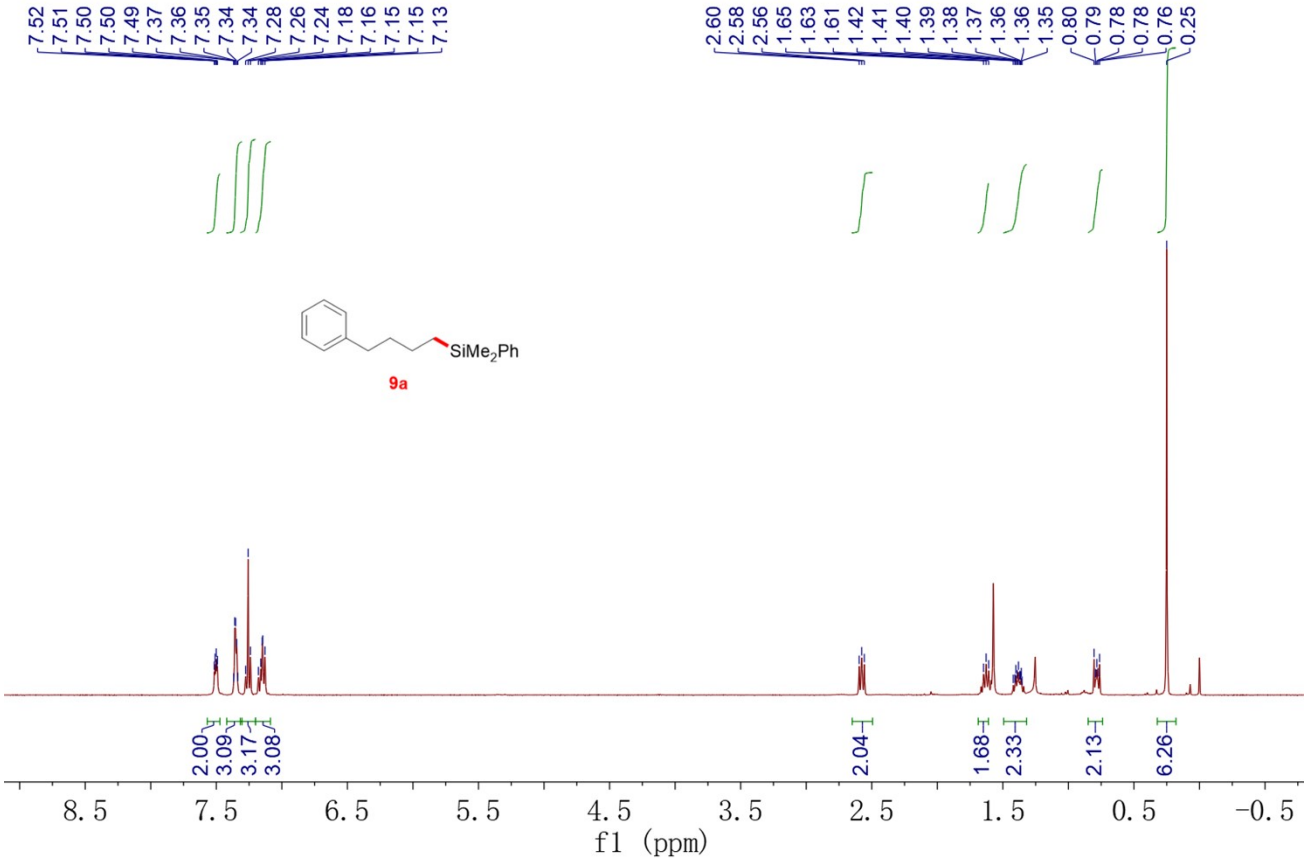
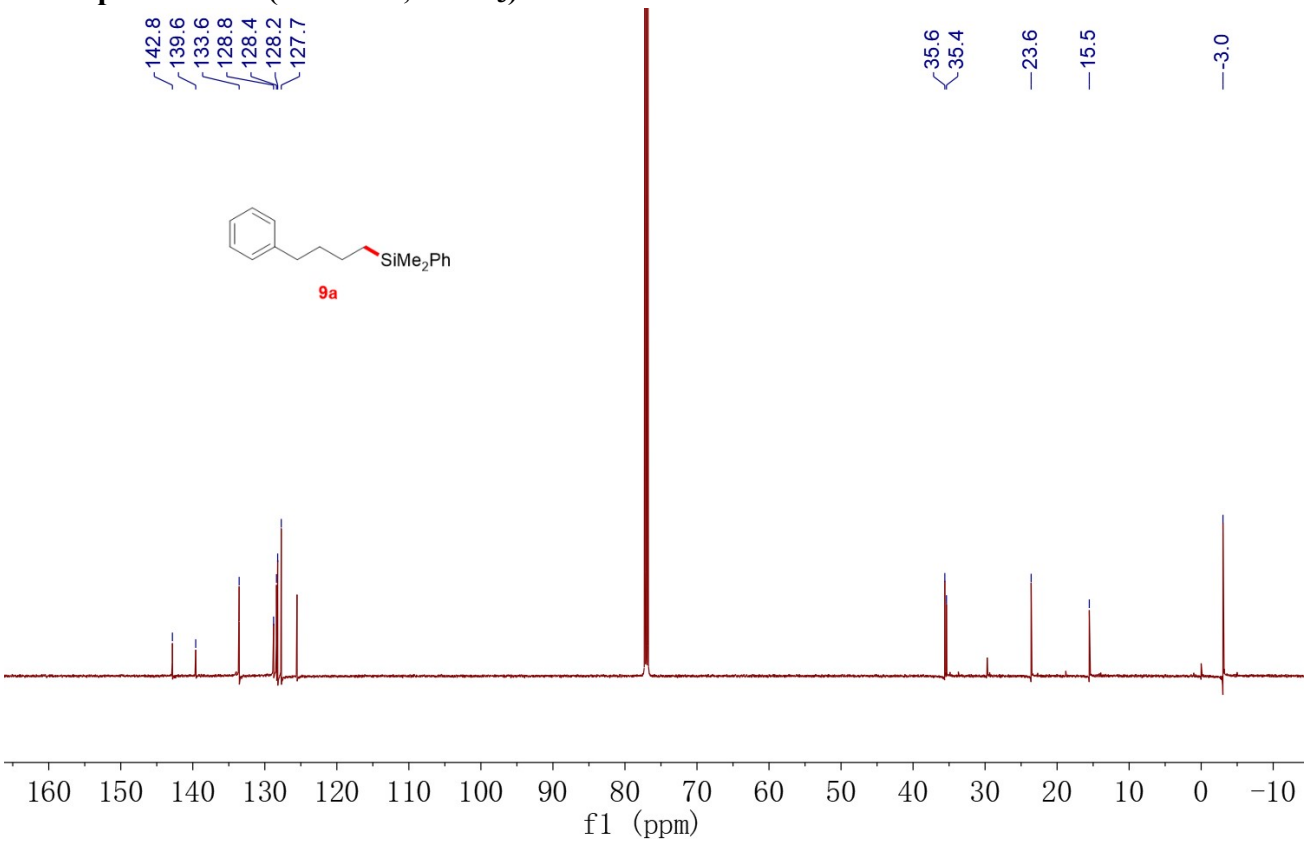


^{1}H NMR spectra of 9a (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 9a (100 MHz, $CDCl_3$)



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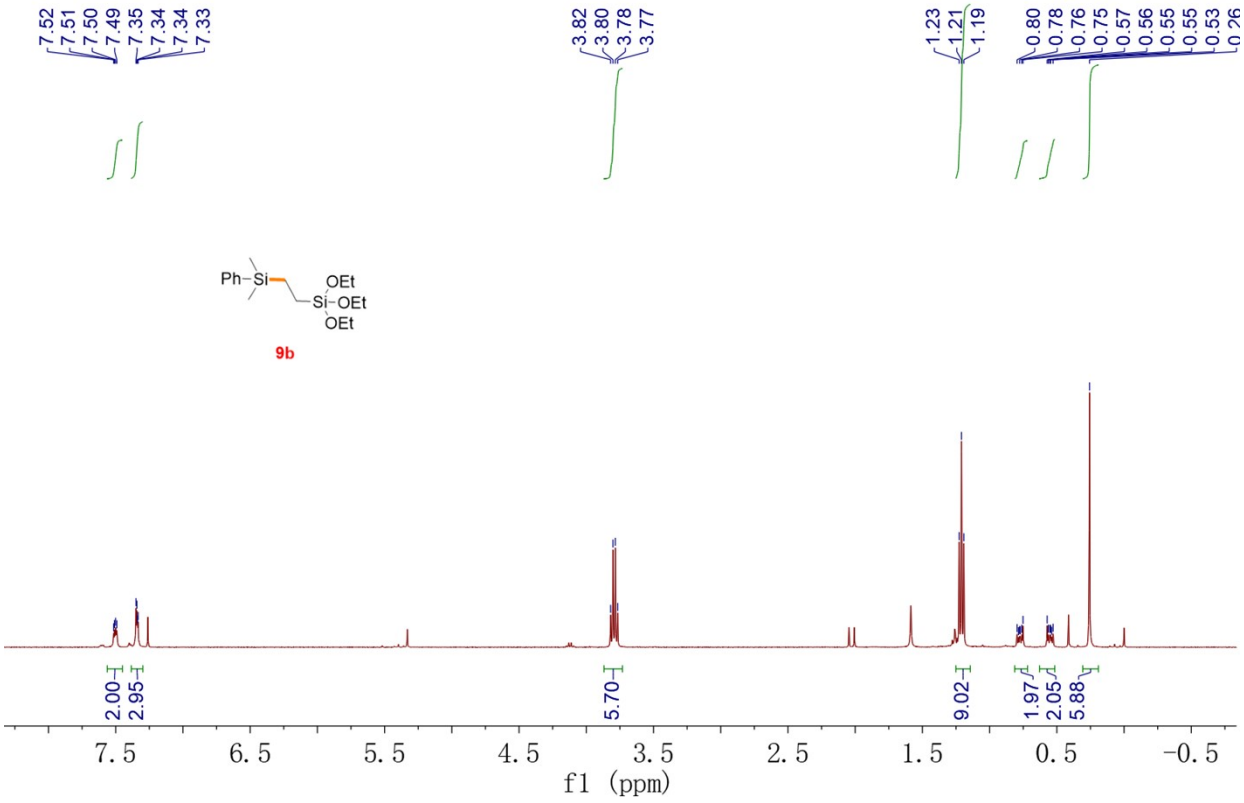

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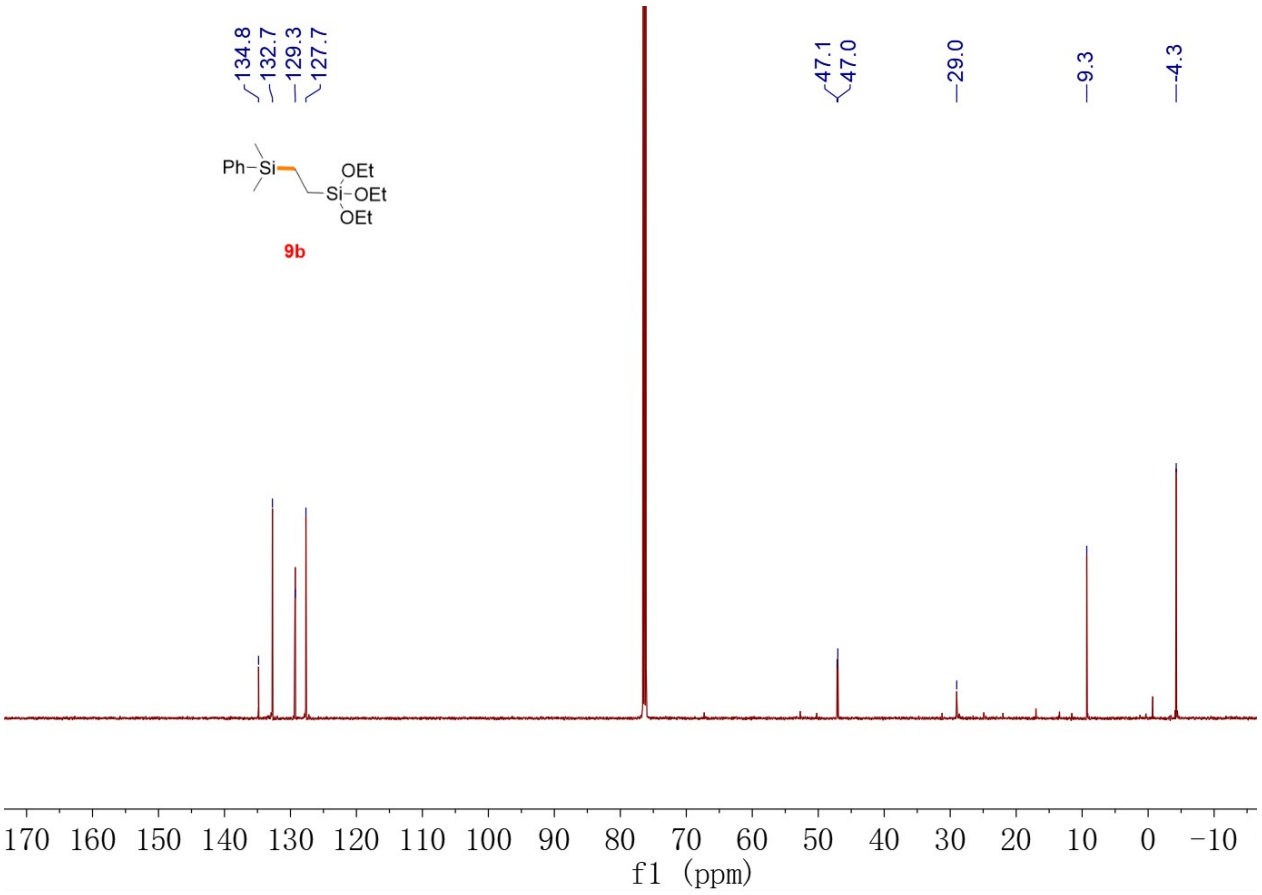
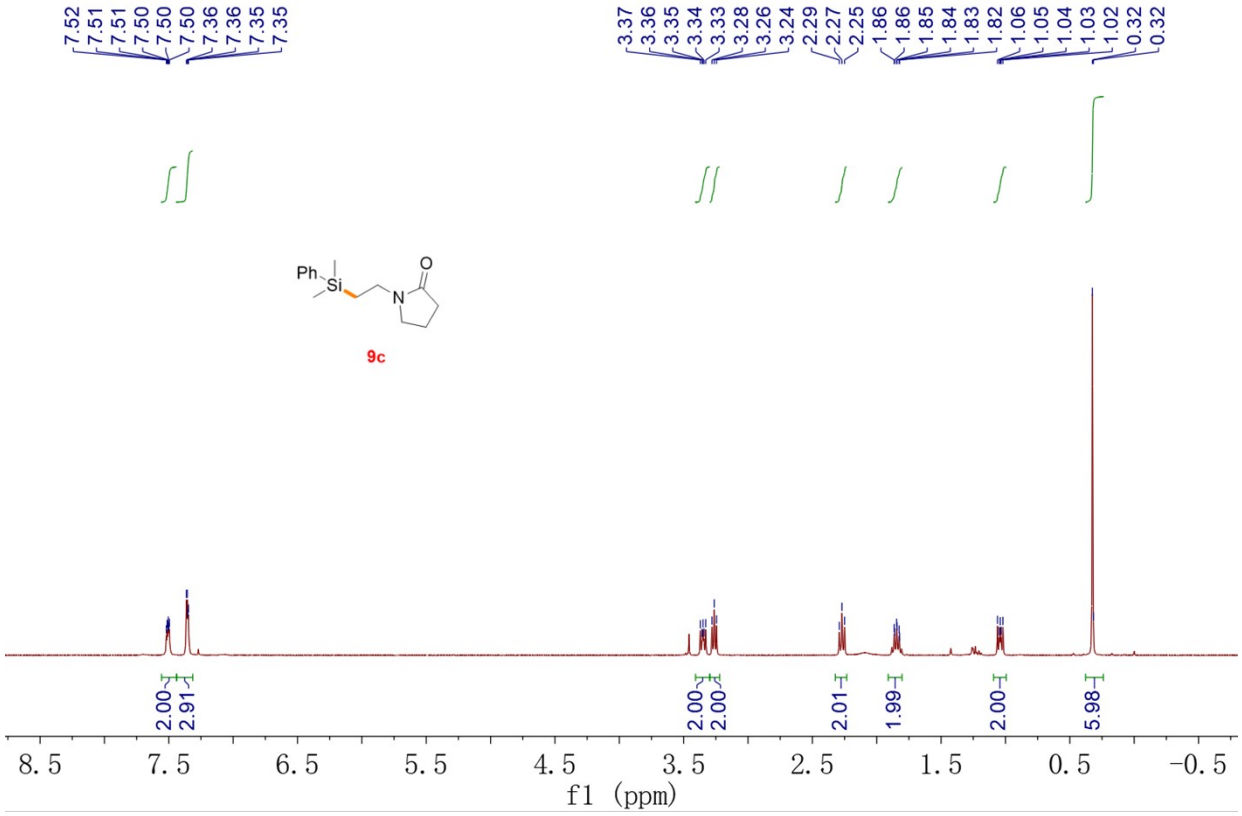


^{1}H NMR spectra of 9c (400 MHz, $CDCl_3$)



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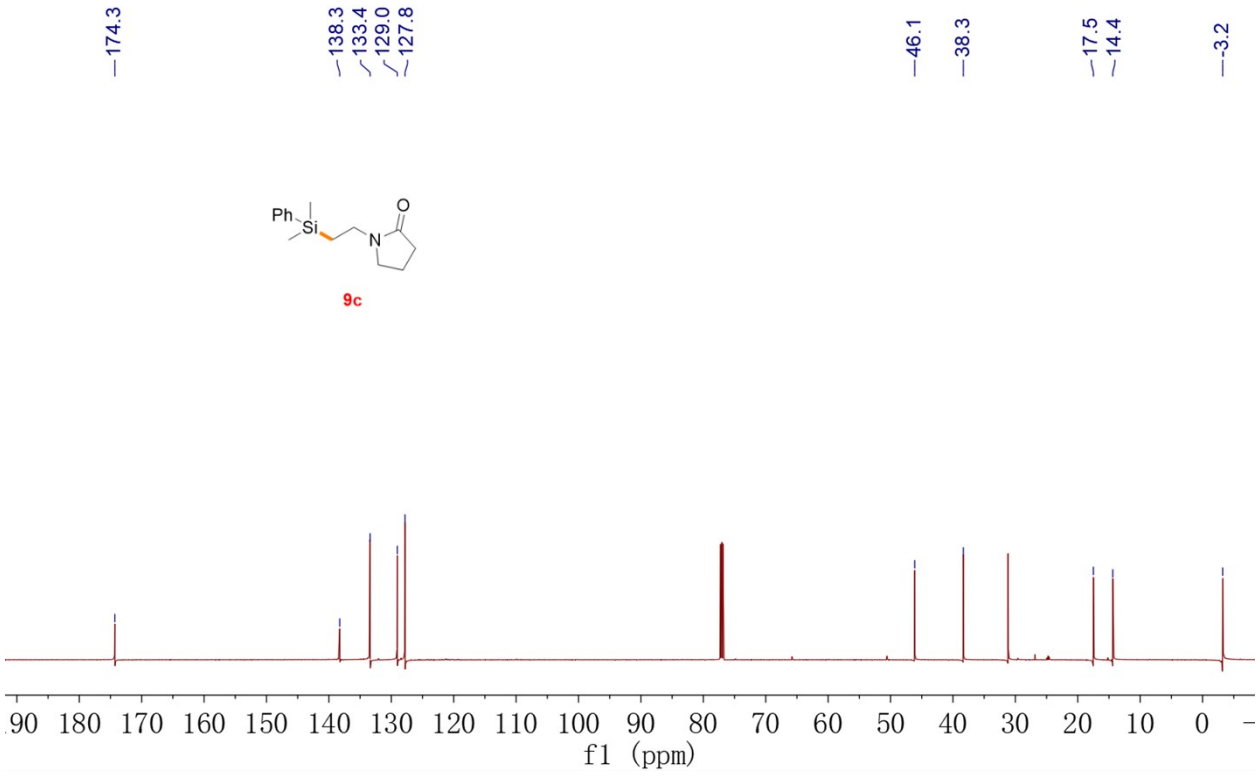

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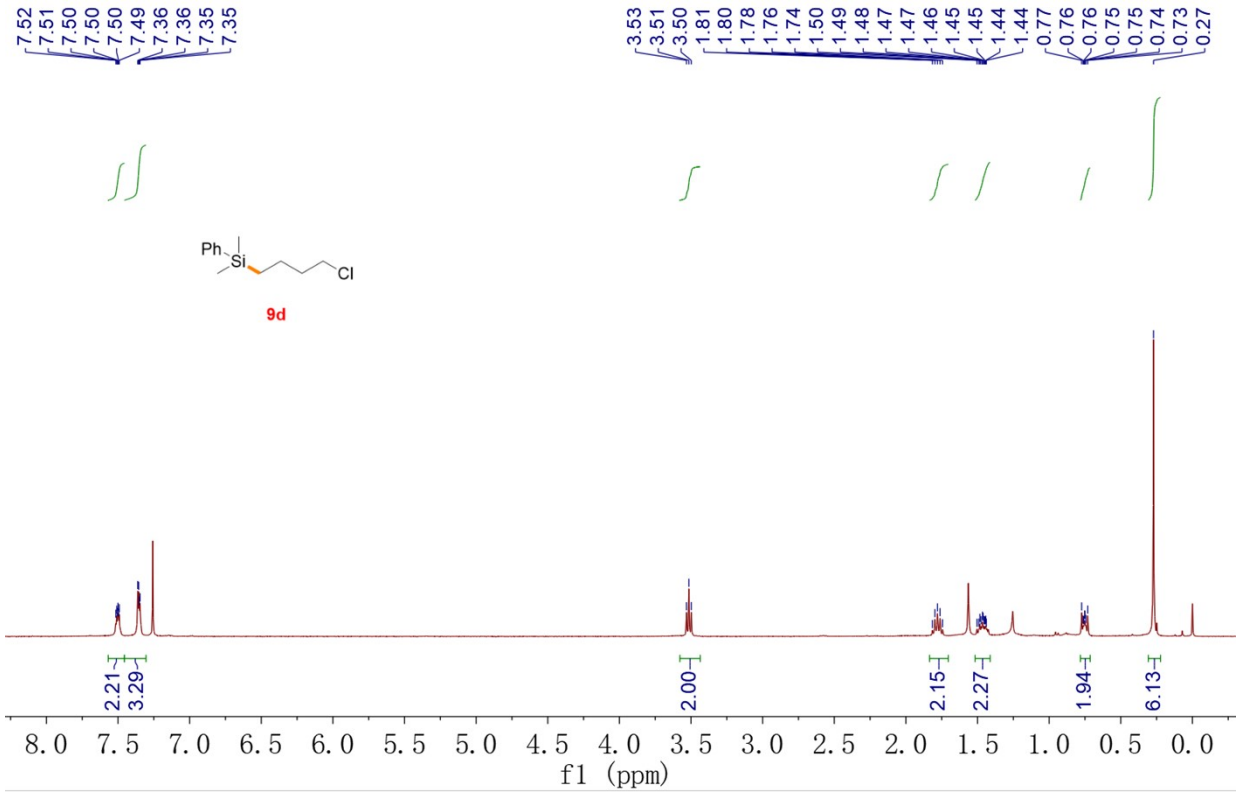
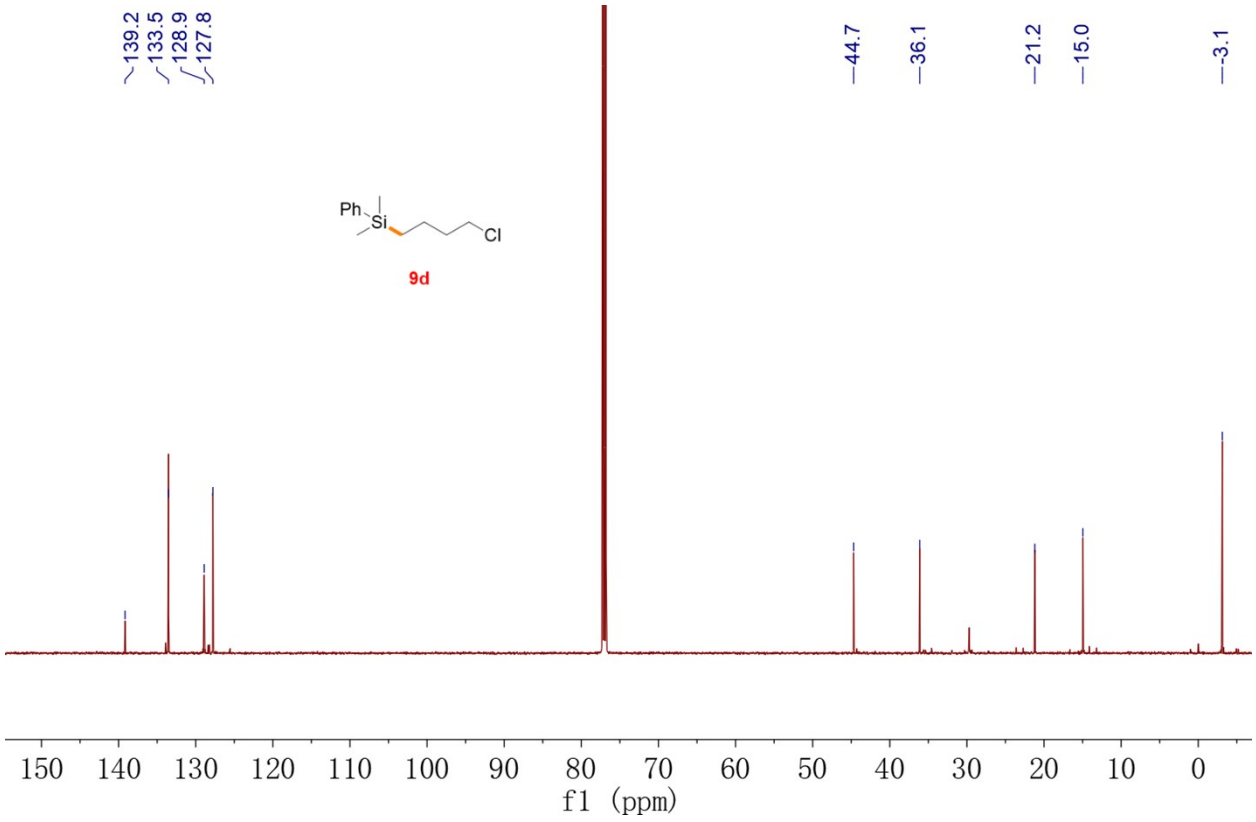
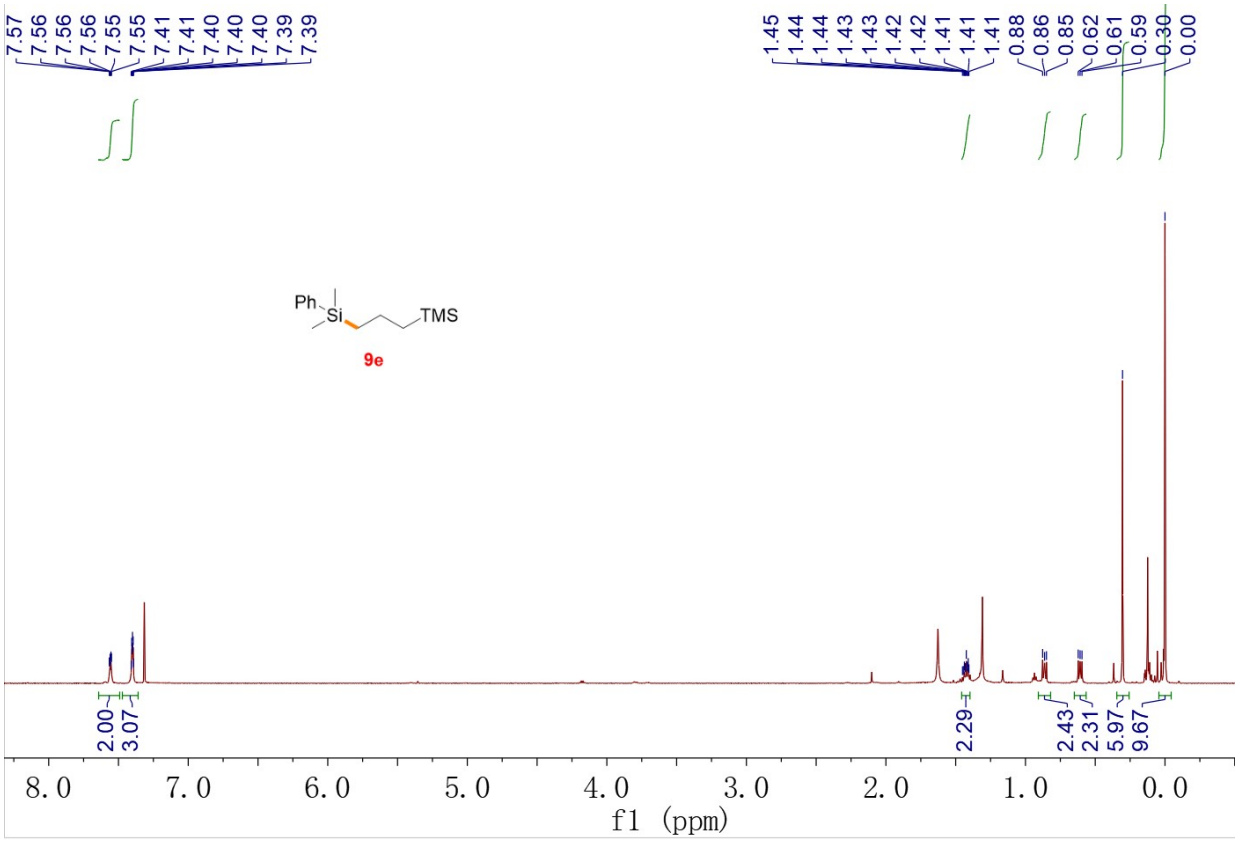


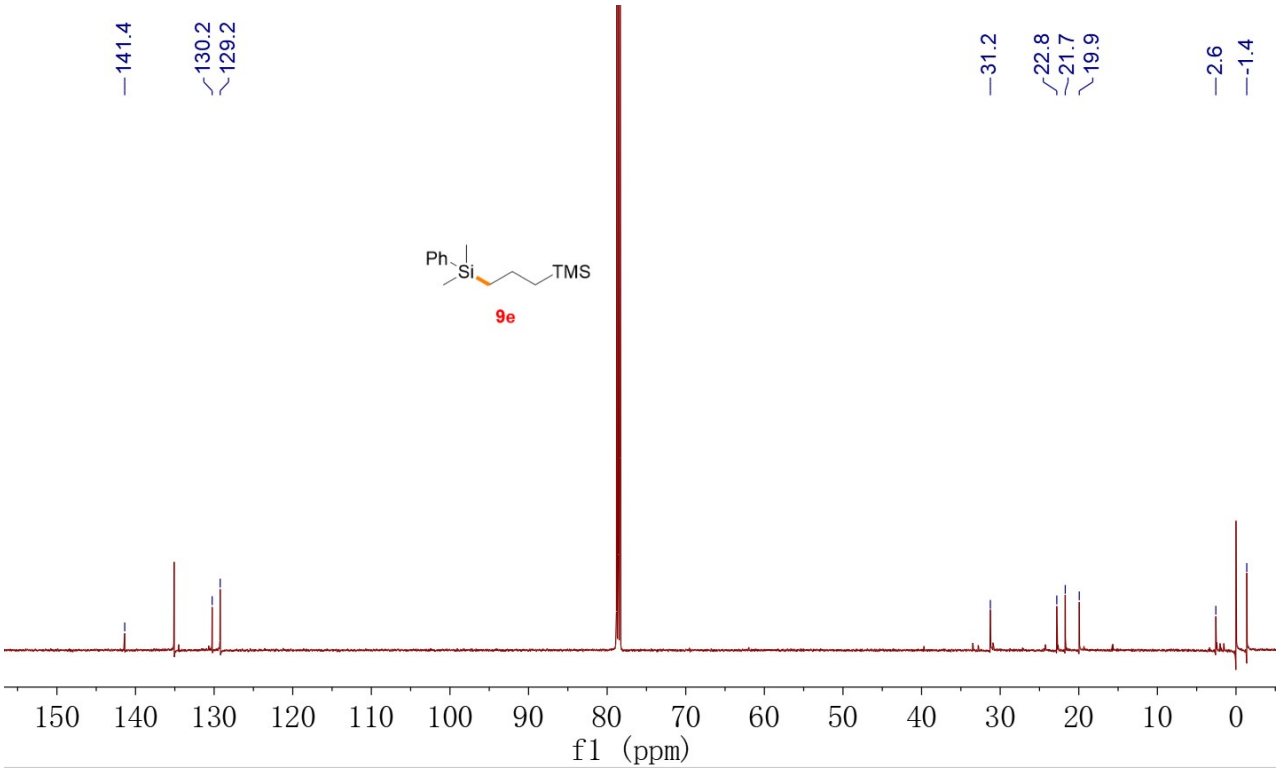
^{13}C NMR spectra of 9d (100 MHz, $CDCl_3$)



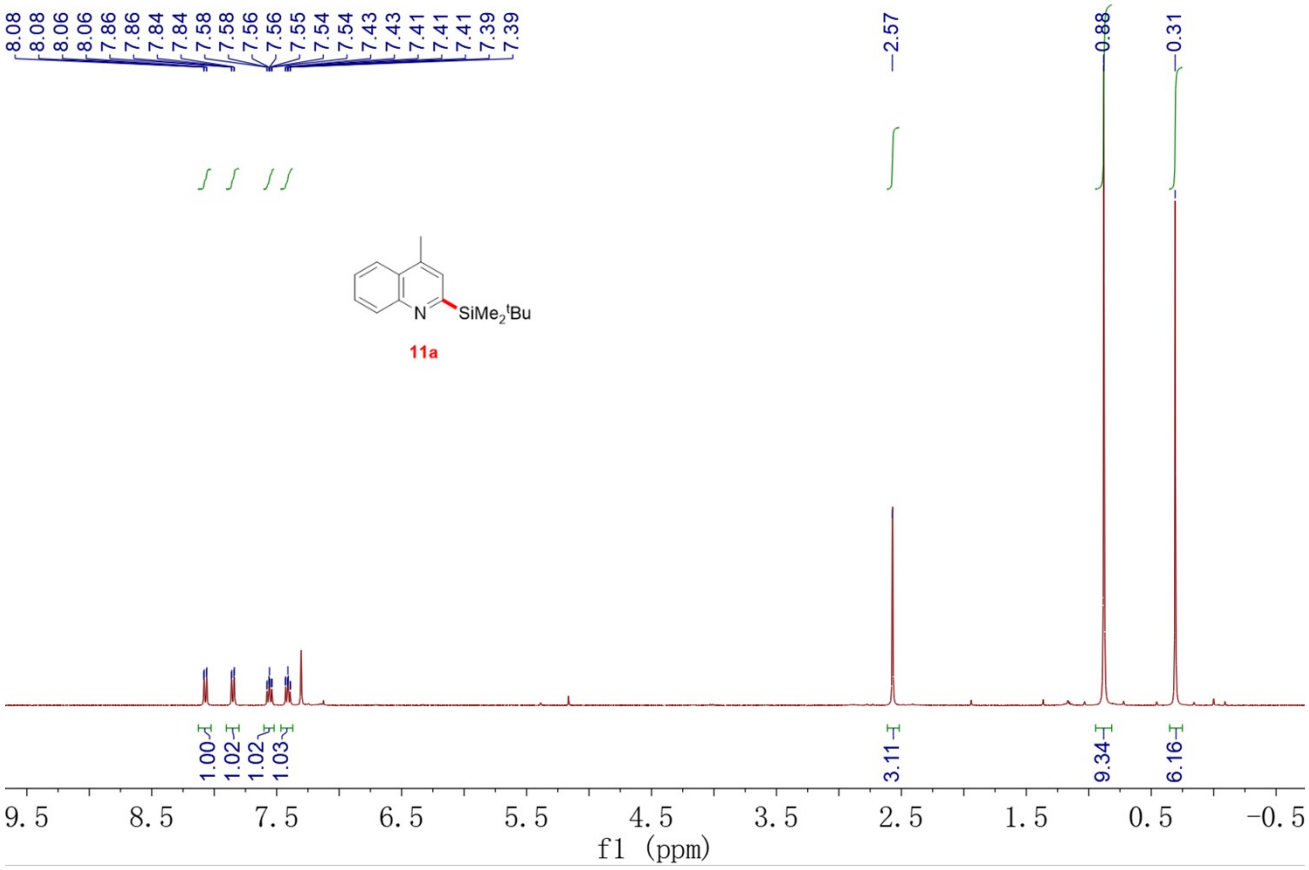
^{1}H NMR spectra of 9e (400 MHz, $CDCl_3$)



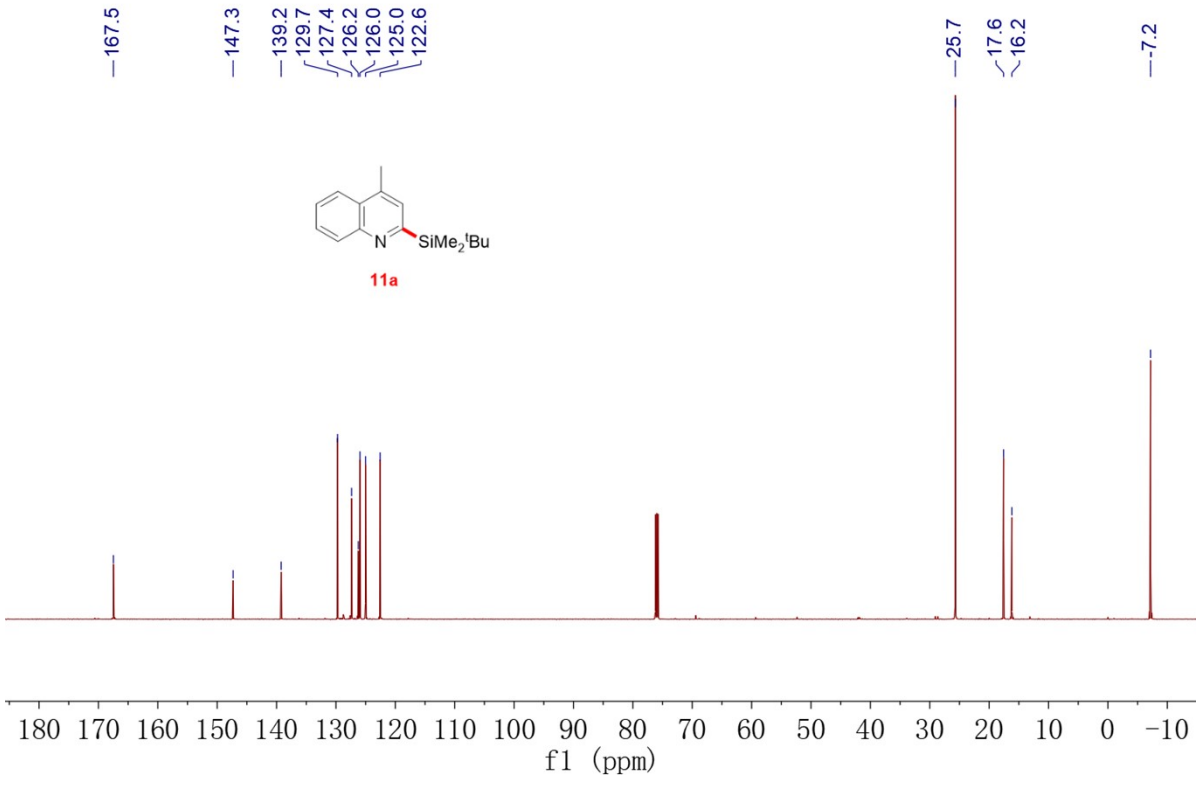
^{13}C NMR spectra of 9e (100 MHz, $CDCl_3$)



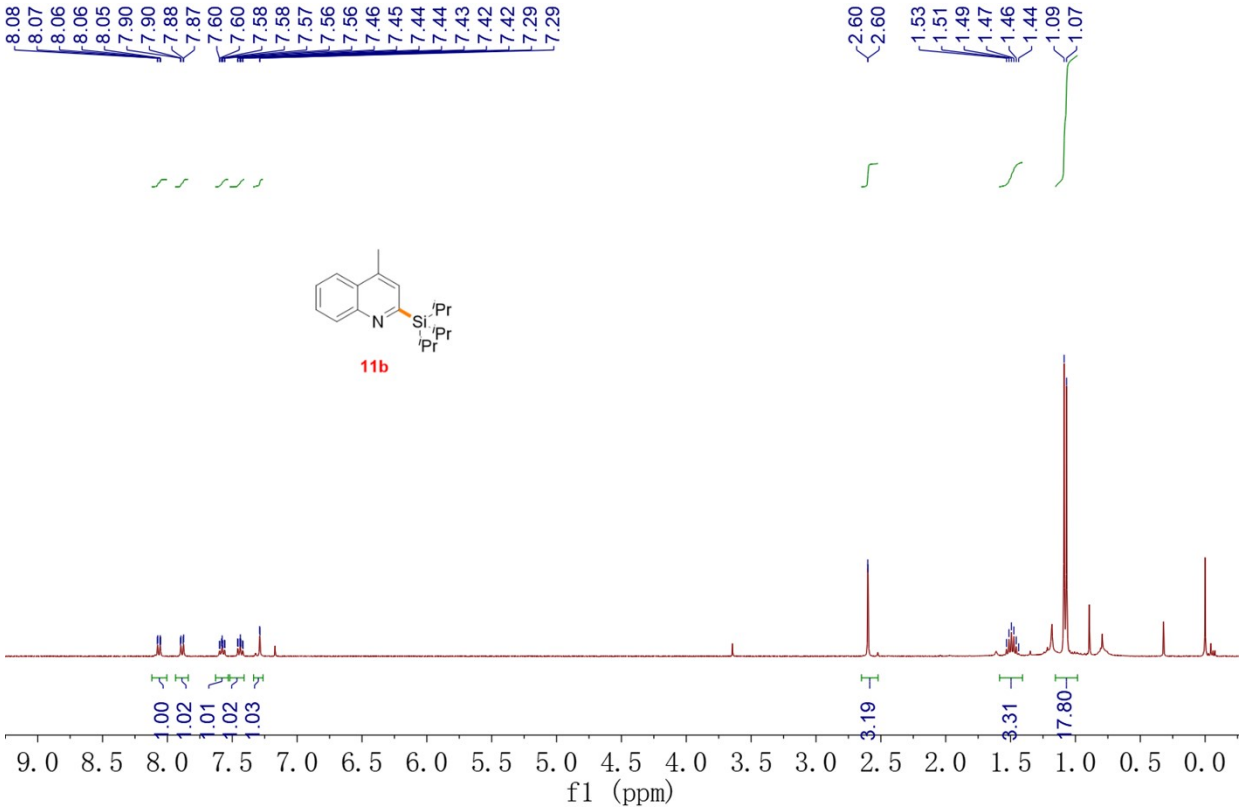
^{1}H NMR spectra of 11a (400 MHz, $CDCl_3$)



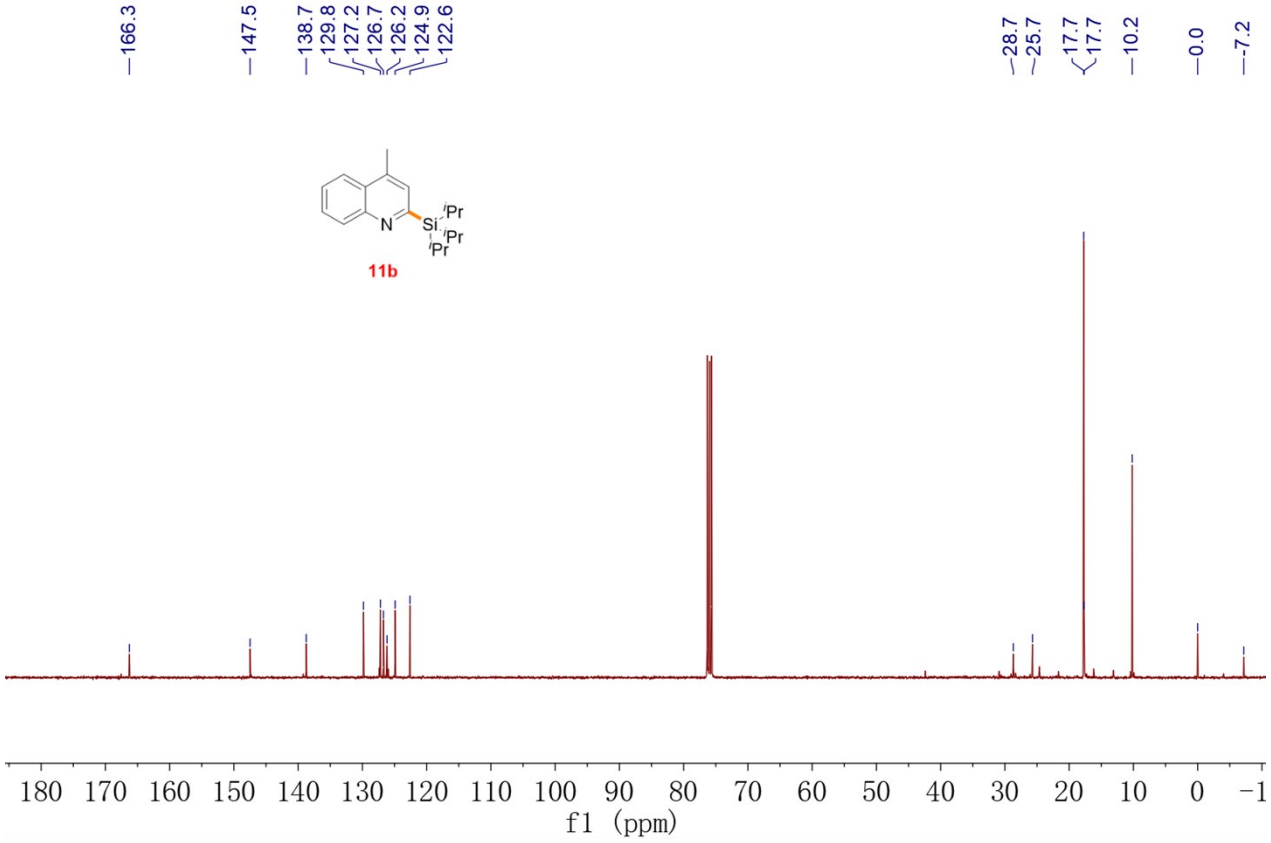
^{13}C NMR spectra of 11a (100 MHz, $CDCl_3$)



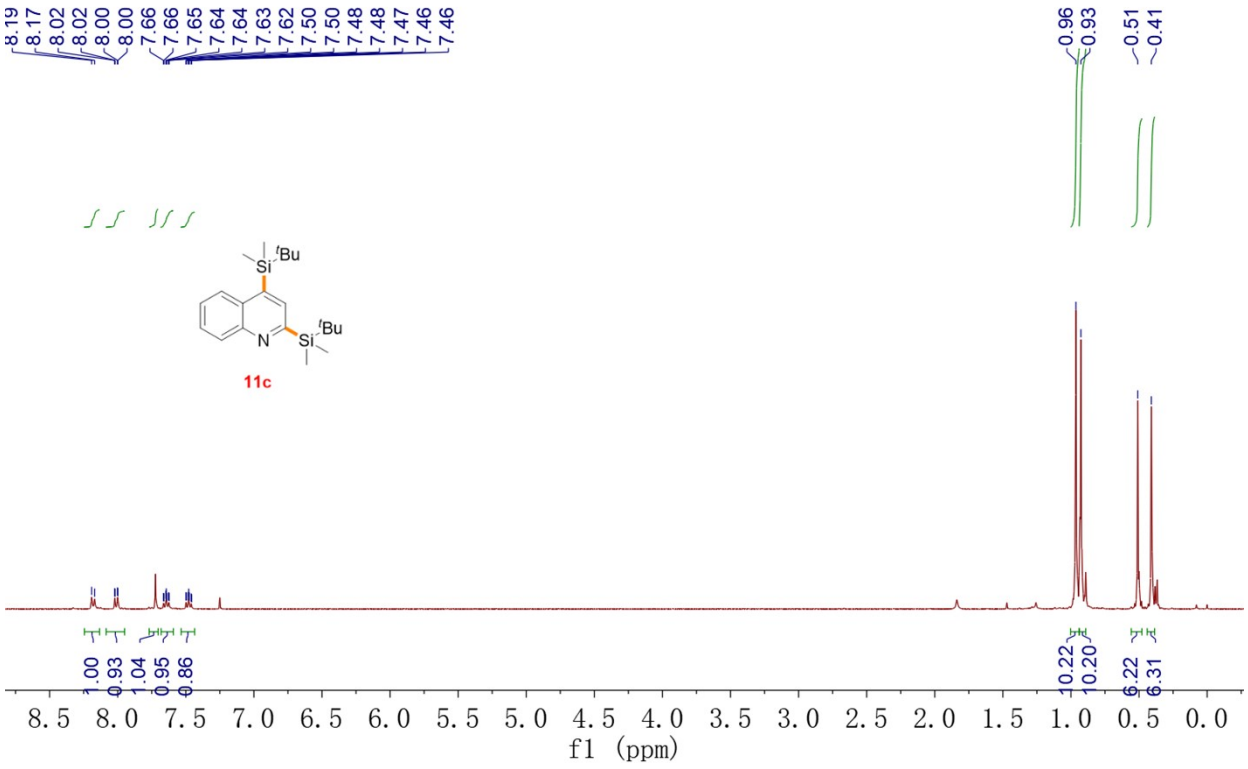
^{1}H NMR spectra of 11b (400 MHz, $CDCl_3$)



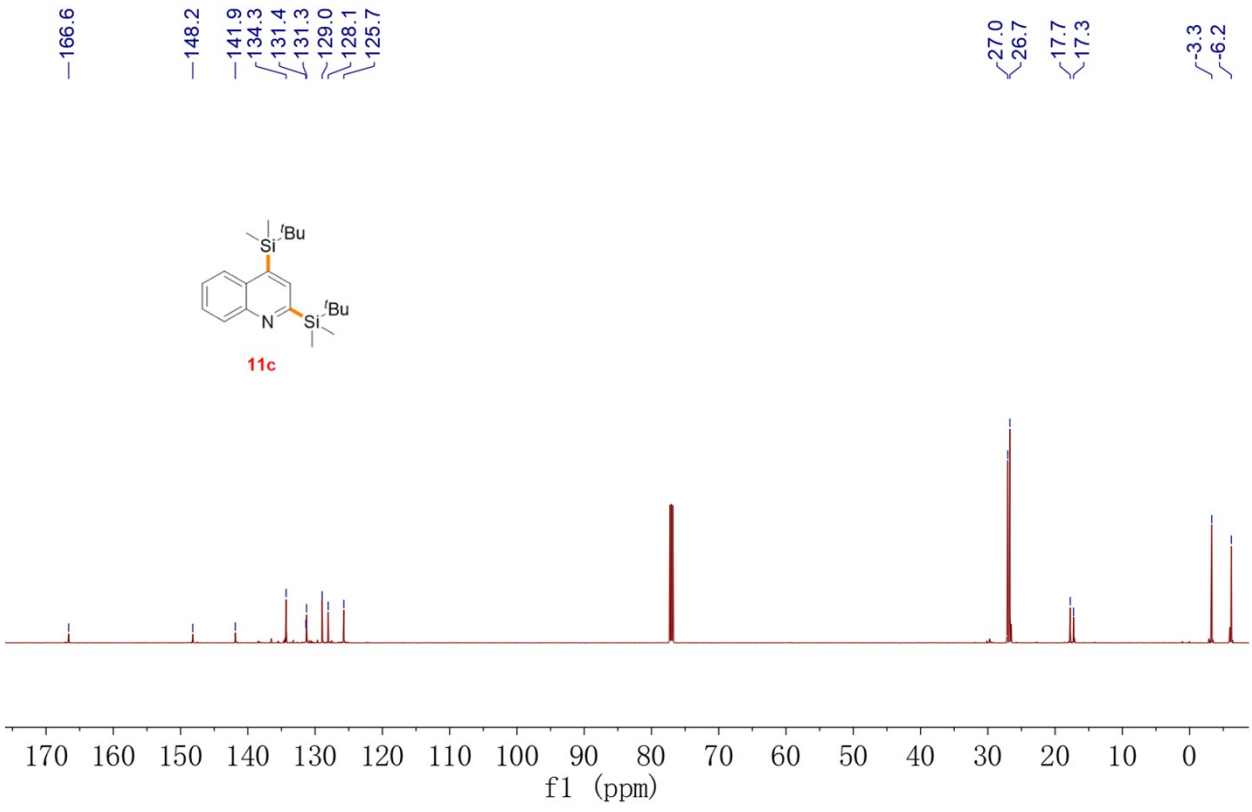
^{13}C NMR spectra of 11b (100 MHz, $CDCl_3$)



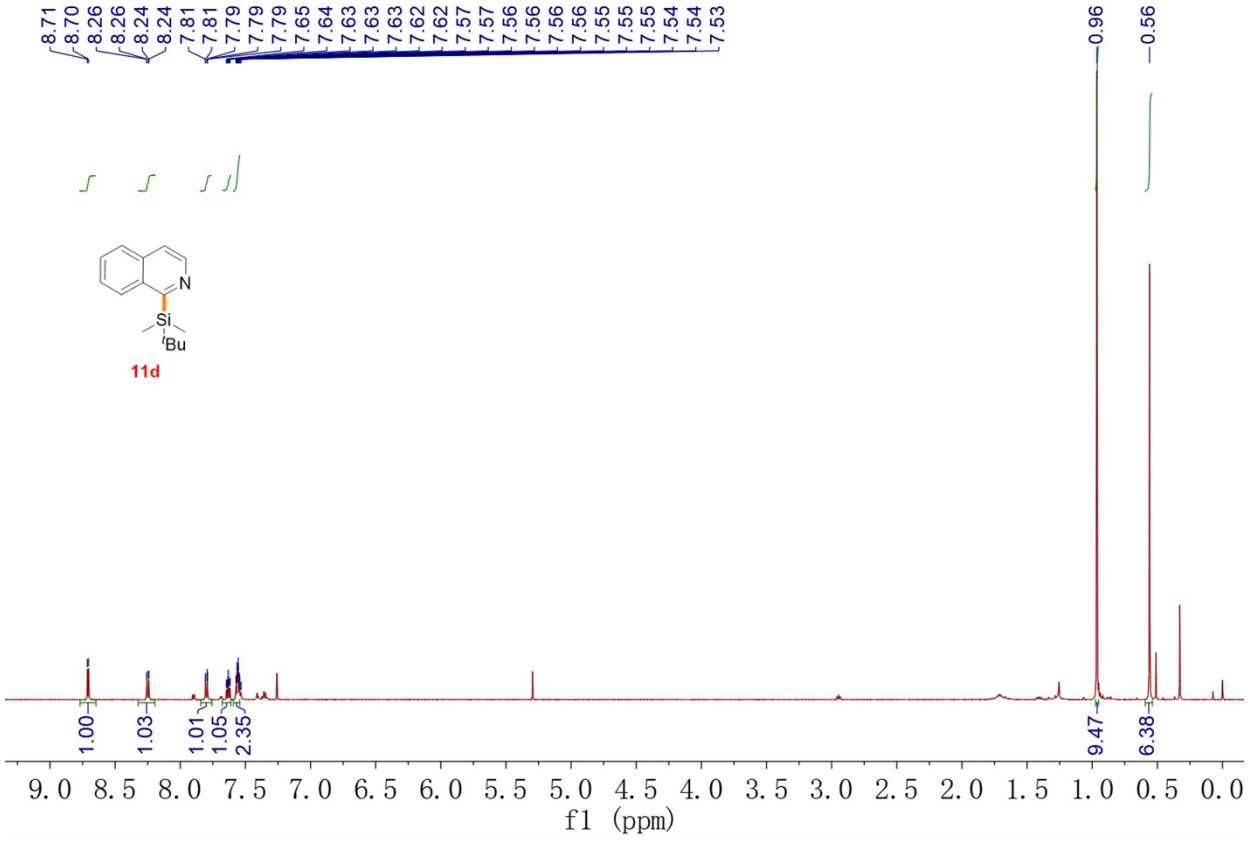
^{1}H NMR spectra of 11c (400 MHz, $CDCl_3$)



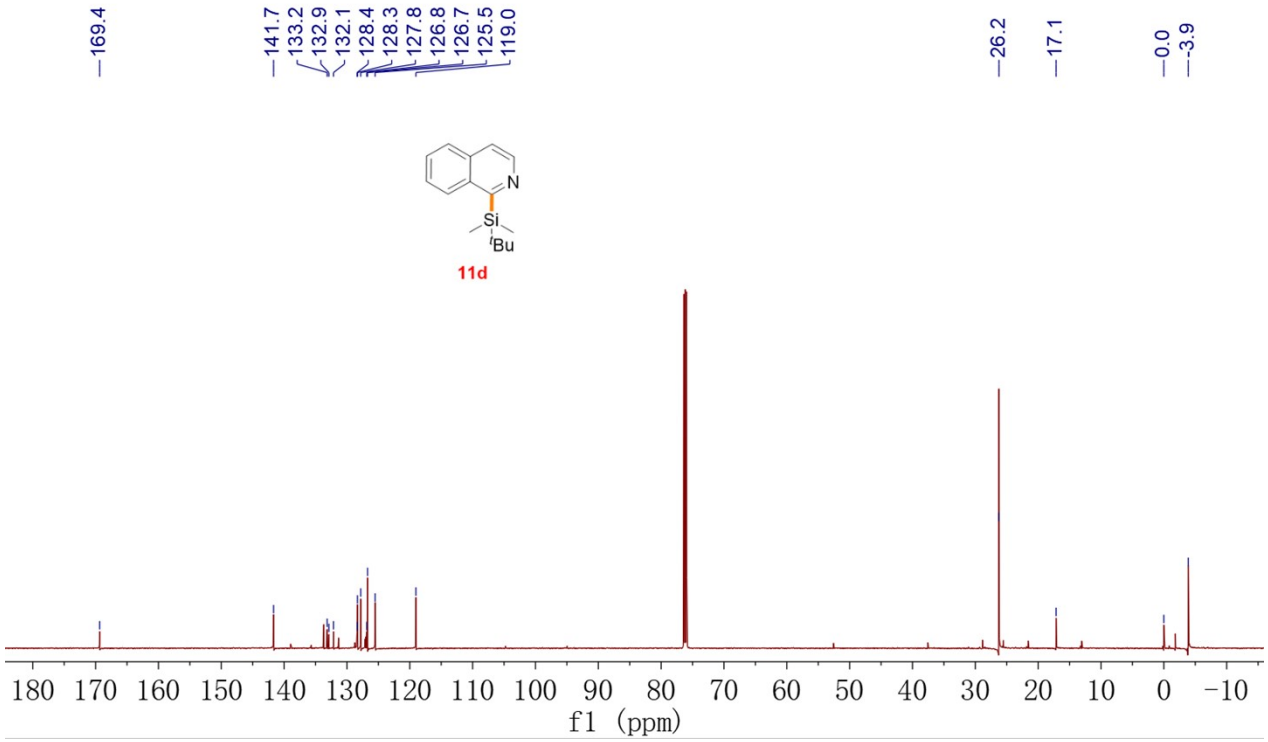
^{13}C NMR spectra of 11c (100 MHz, $CDCl_3$)



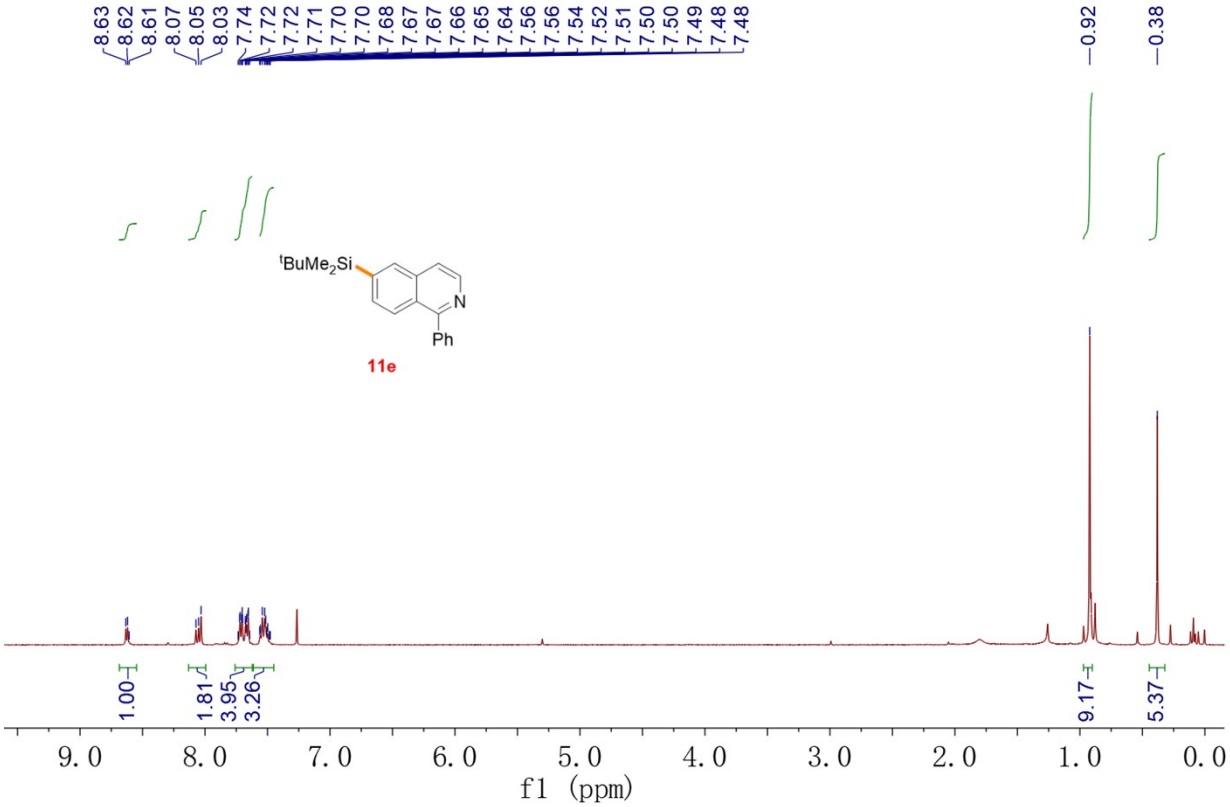
^{1}H NMR spectra of 11d (400 MHz, $CDCl_3$)



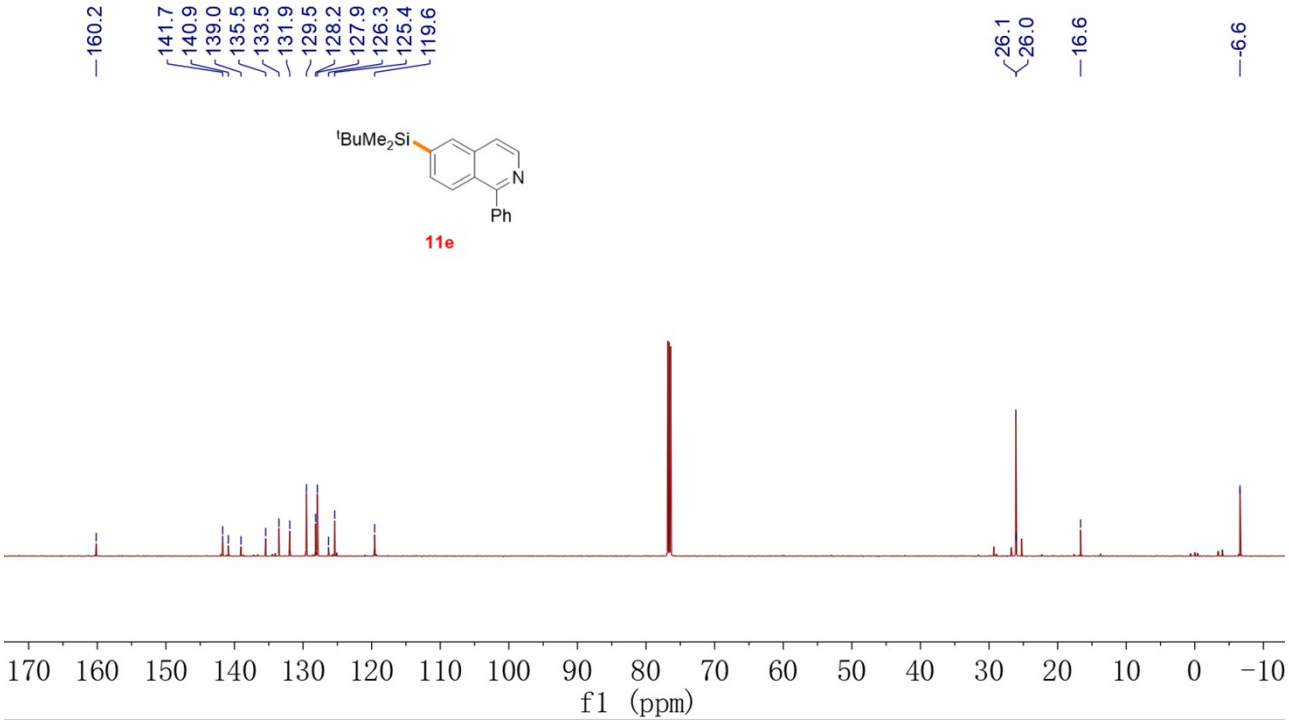
^{13}C NMR spectra of 11d (100 MHz, $CDCl_3$)



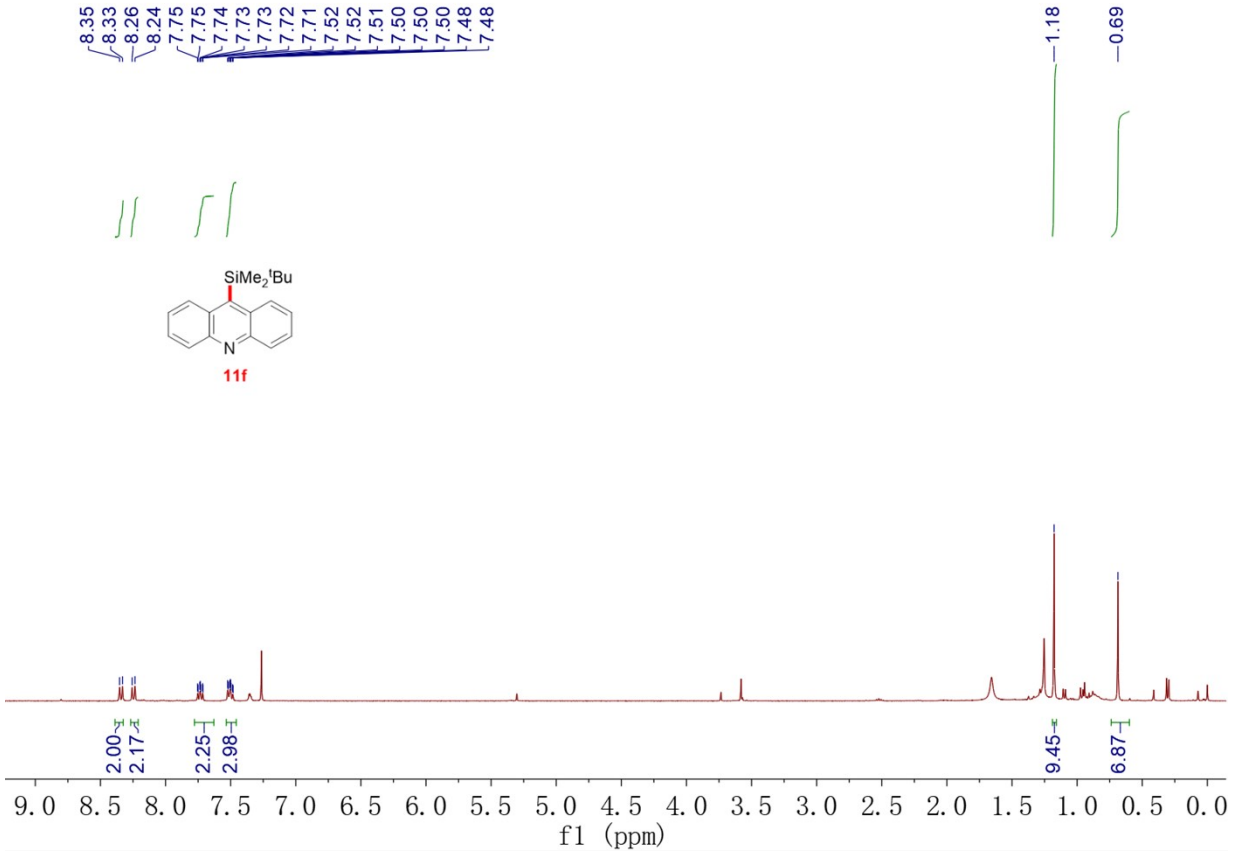
^{1}H NMR spectra of 11e (400 MHz, $CDCl_3$)



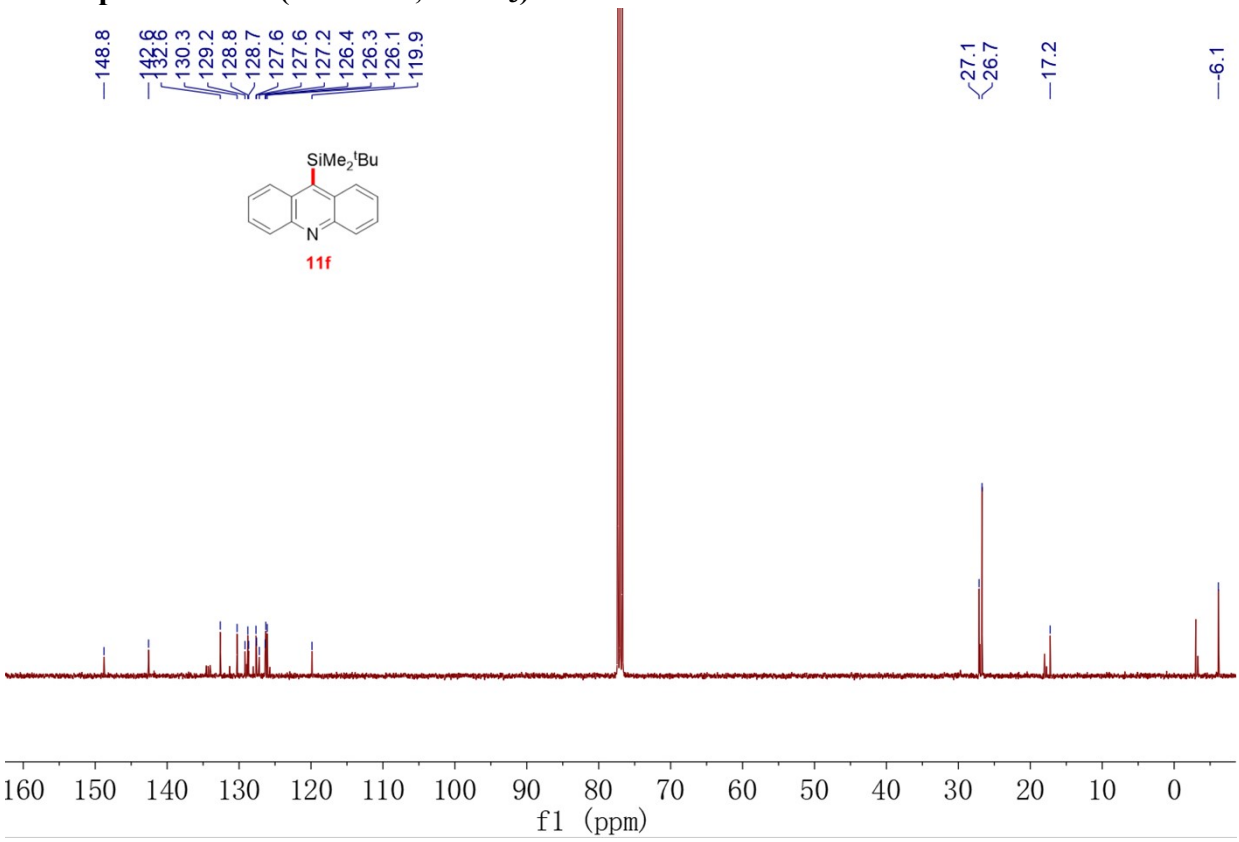
^{13}C NMR spectra of 11e (100 MHz, $CDCl_3$)



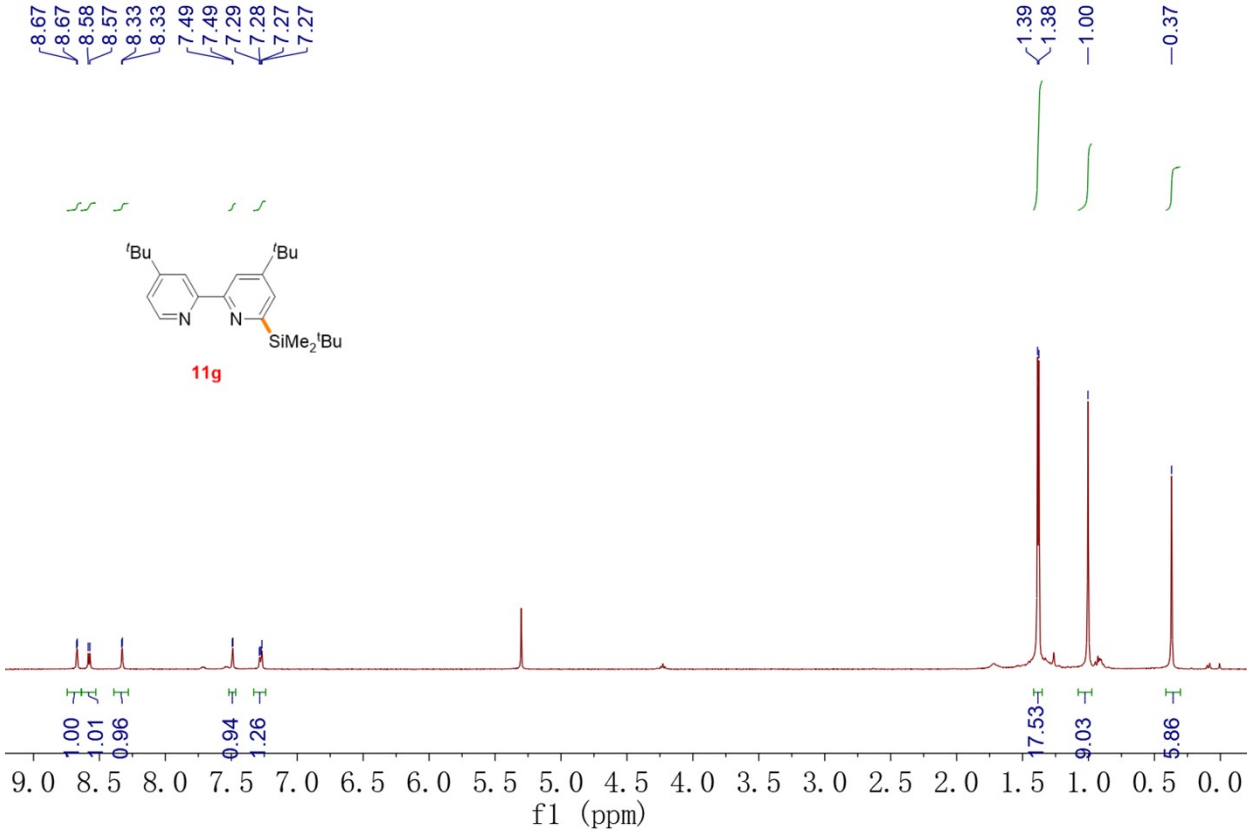
^{1}H NMR spectra of 11f (400 MHz, $CDCl_3$)



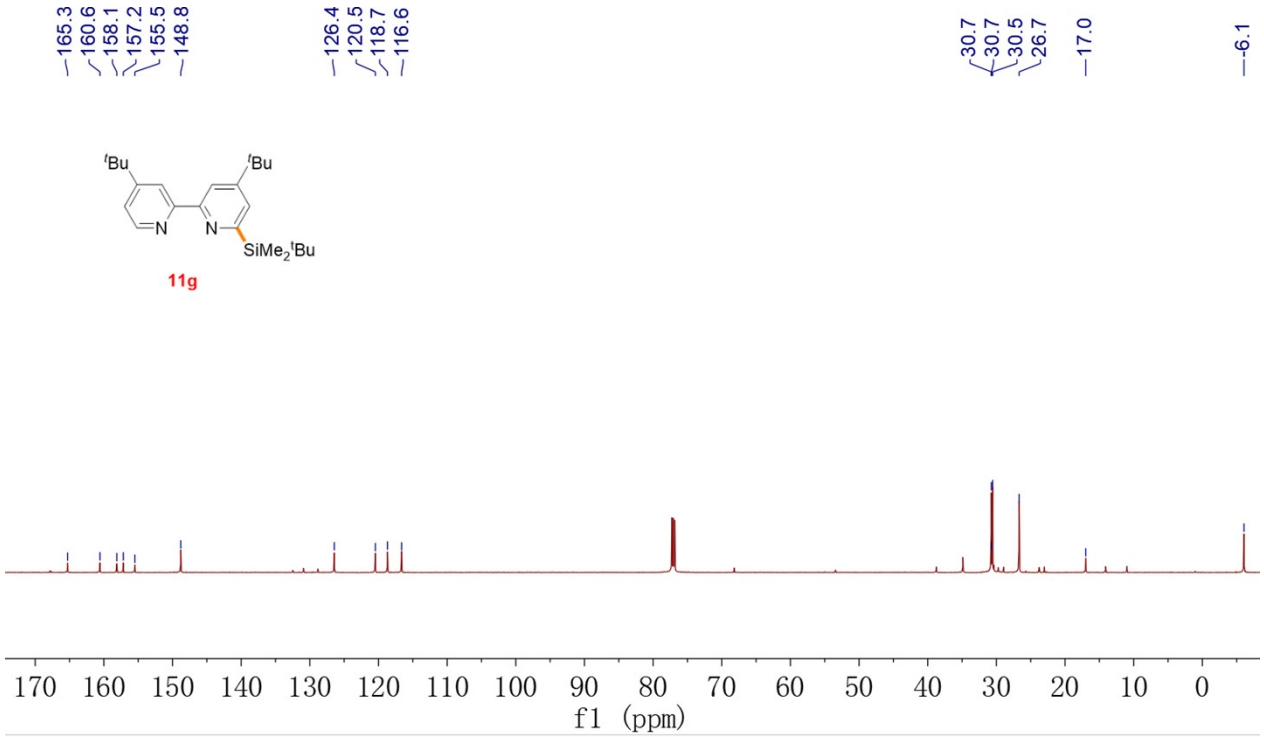
^{13}C NMR spectra of 11f (100 MHz, $CDCl_3$)



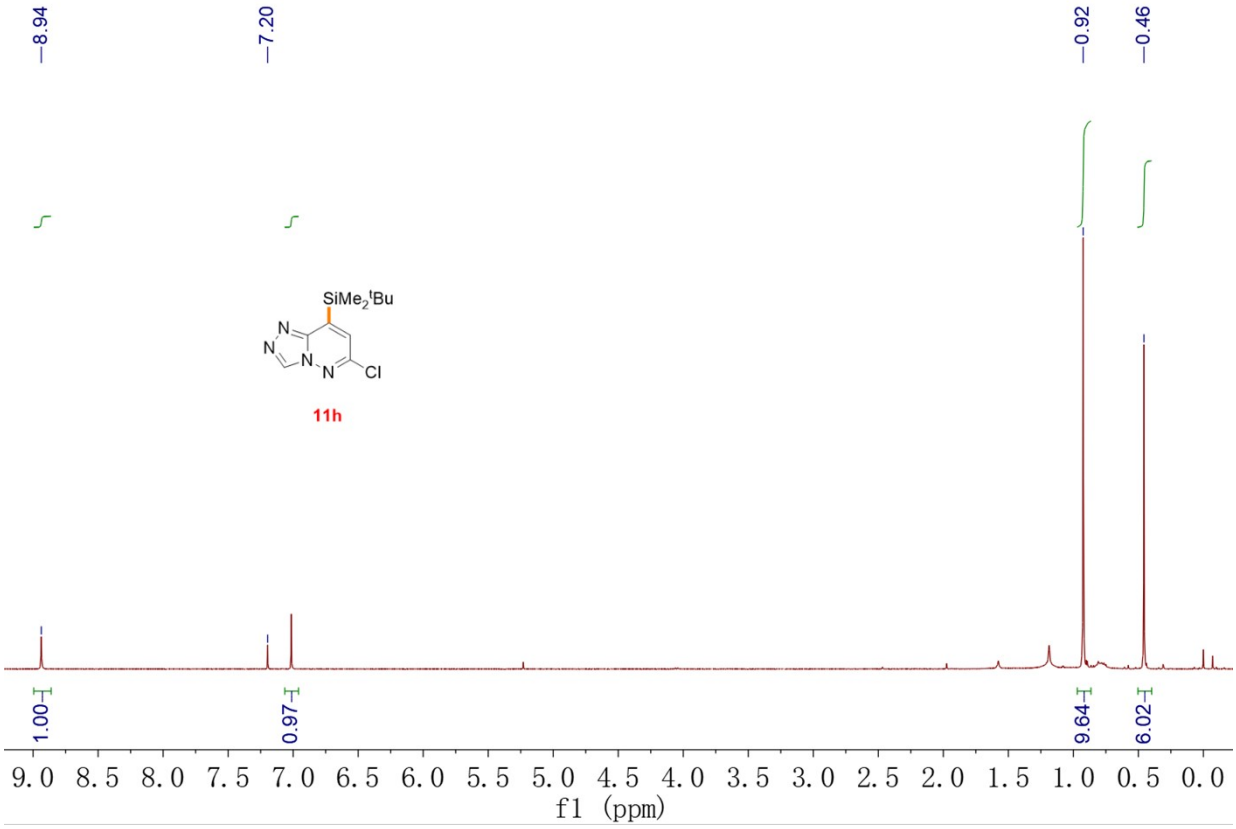
^{1}H NMR spectra of 11g (400 MHz, $CDCl_3$)



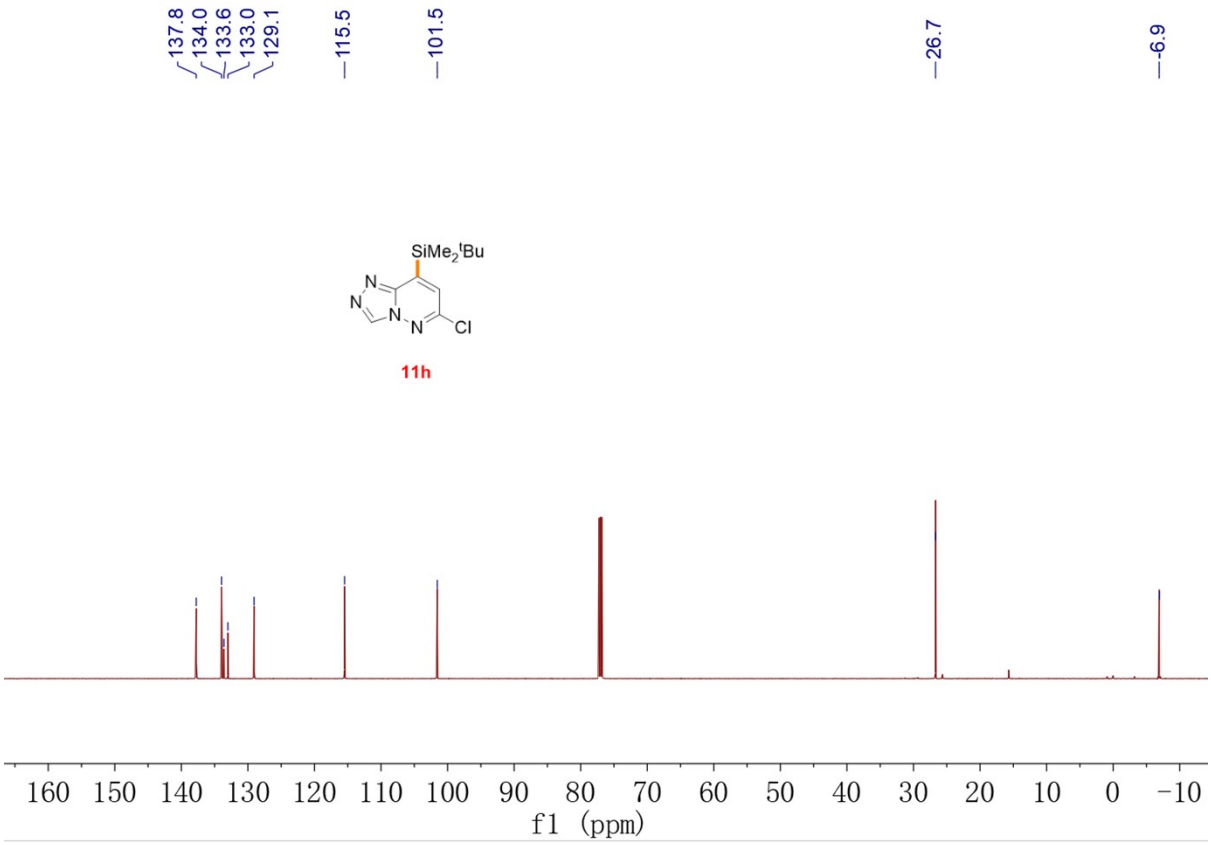
^{13}C NMR spectra of 11g (100 MHz, $CDCl_3$)



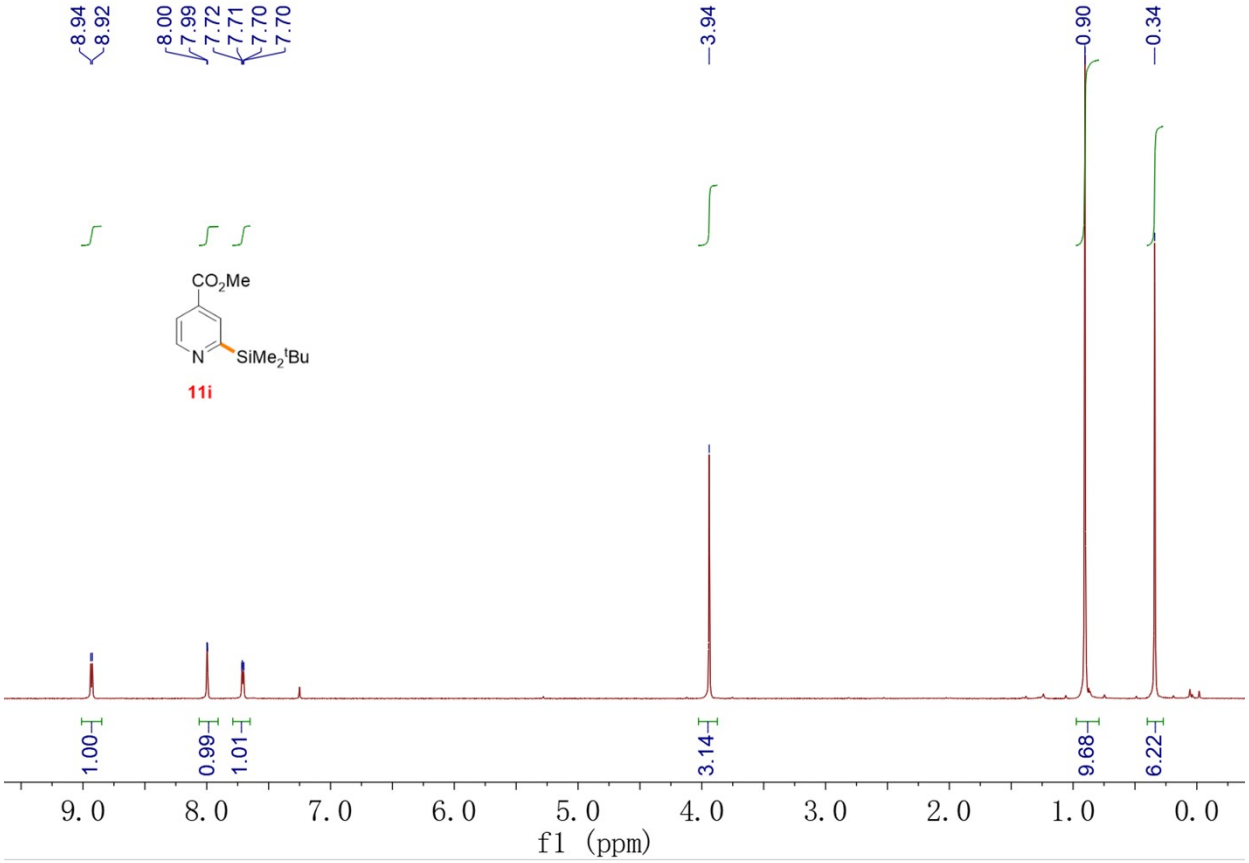
^{1}H NMR spectra of 11h (400 MHz, $CDCl_3$)



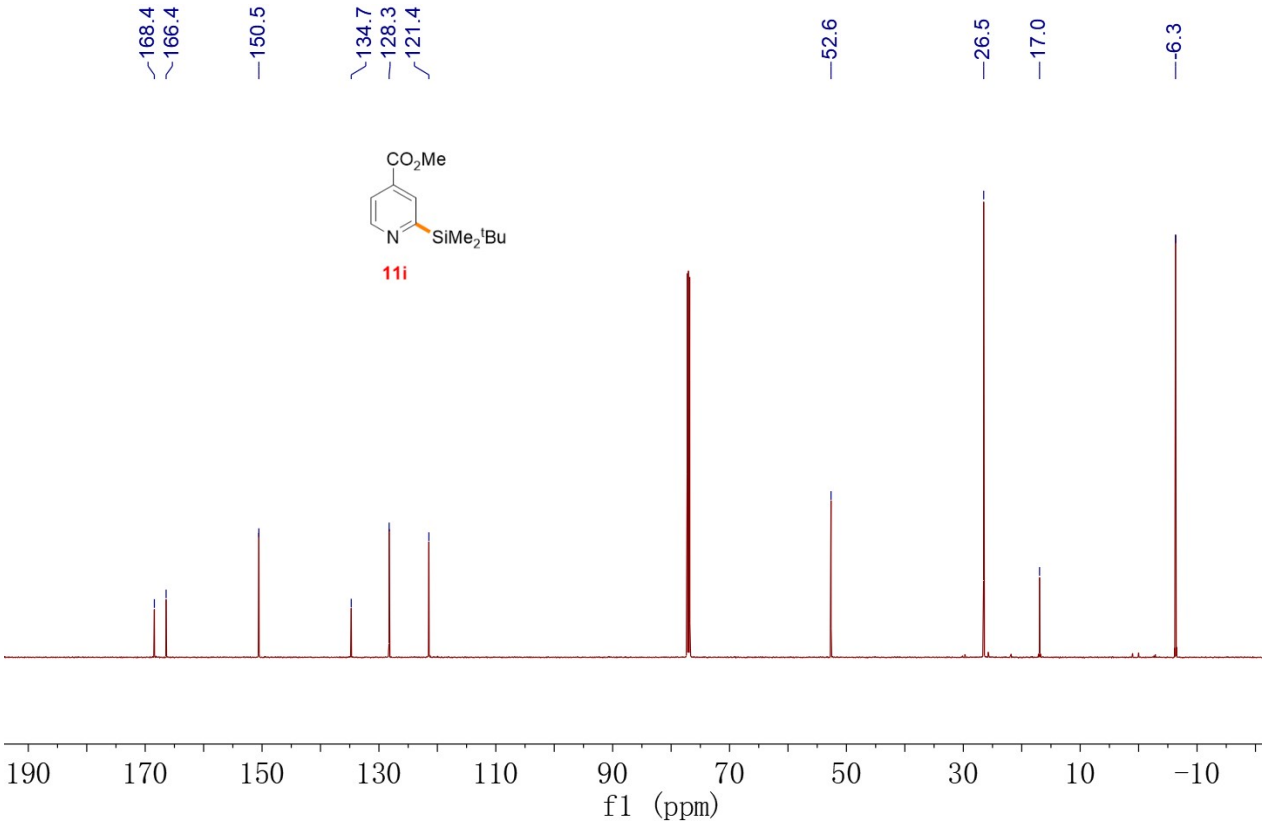
^{13}C NMR spectra of 11h (100 MHz, $CDCl_3$)



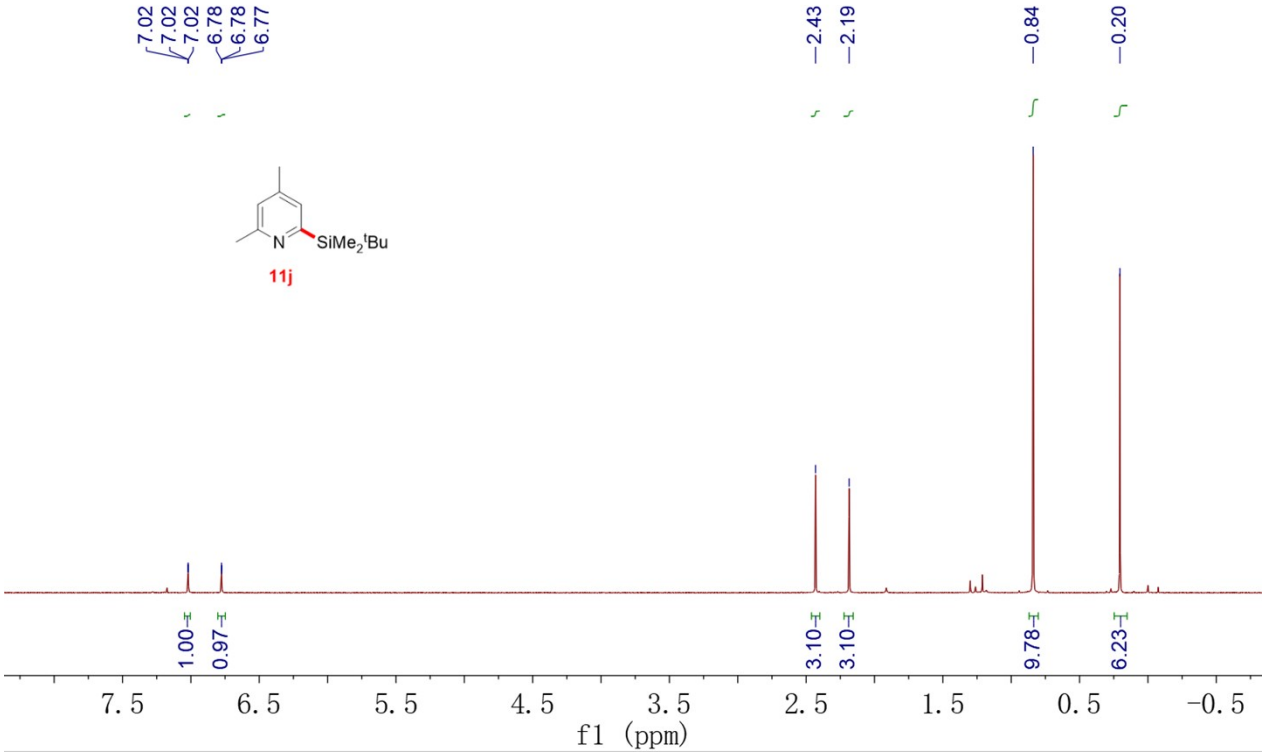
^{1}H NMR spectra of 11i (400 MHz, $CDCl_3$)



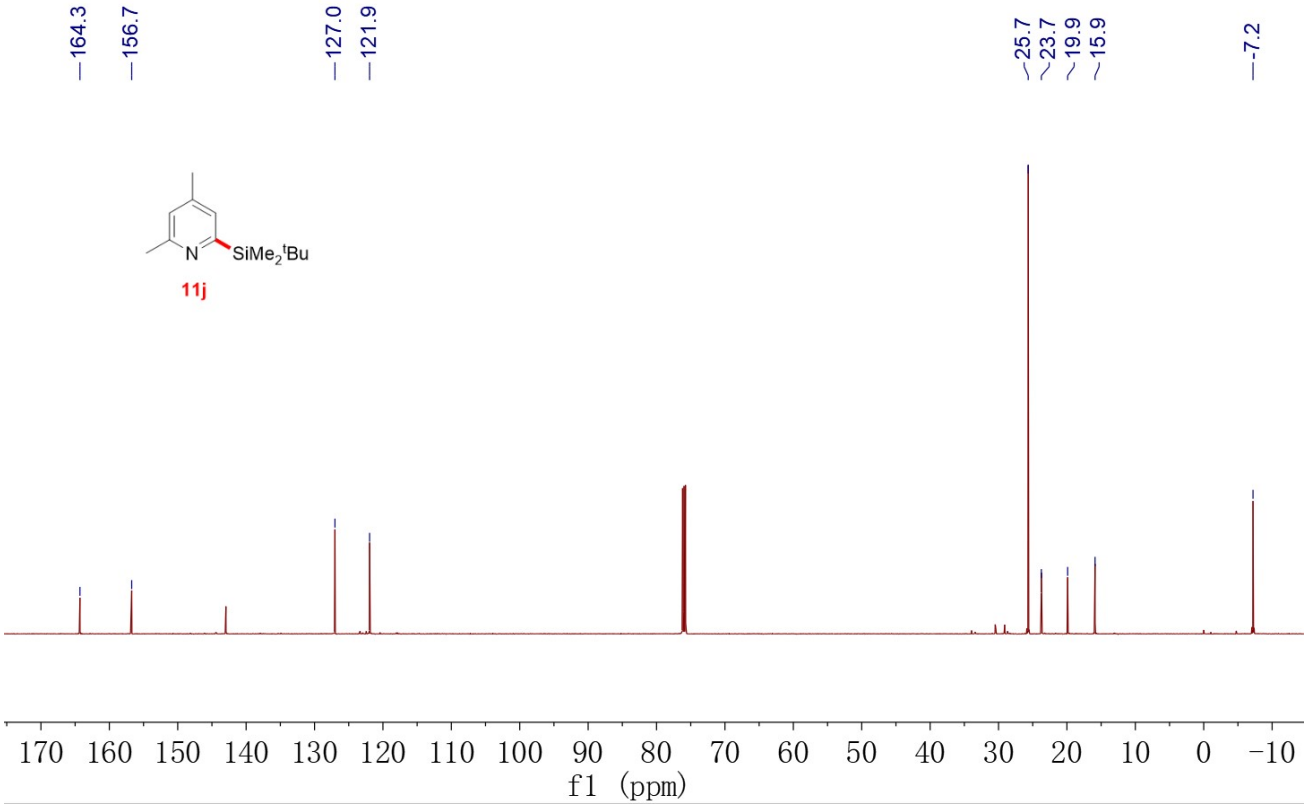
^{13}C NMR spectra of 11i (100 MHz, $CDCl_3$)



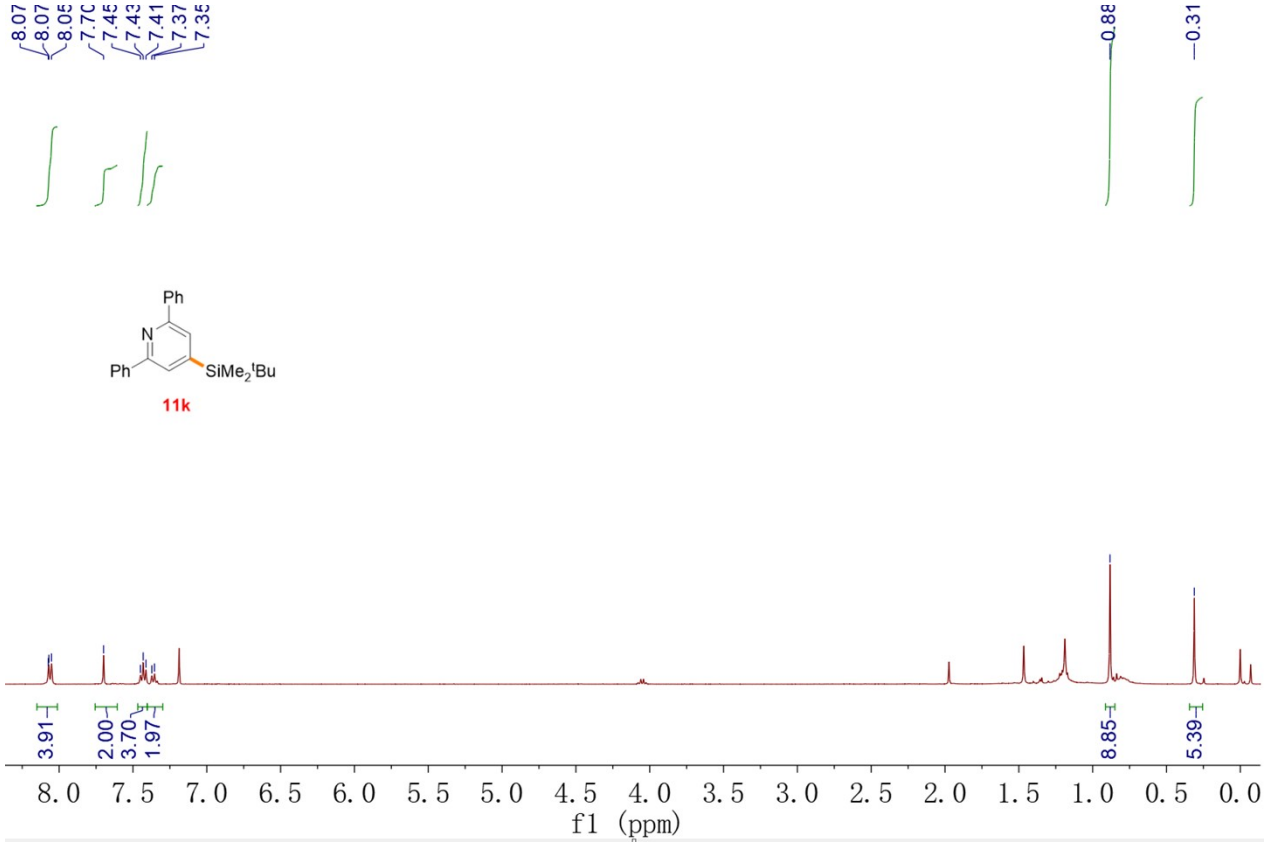
^{1}H NMR spectra of 11j (400 MHz, $CDCl_3$)



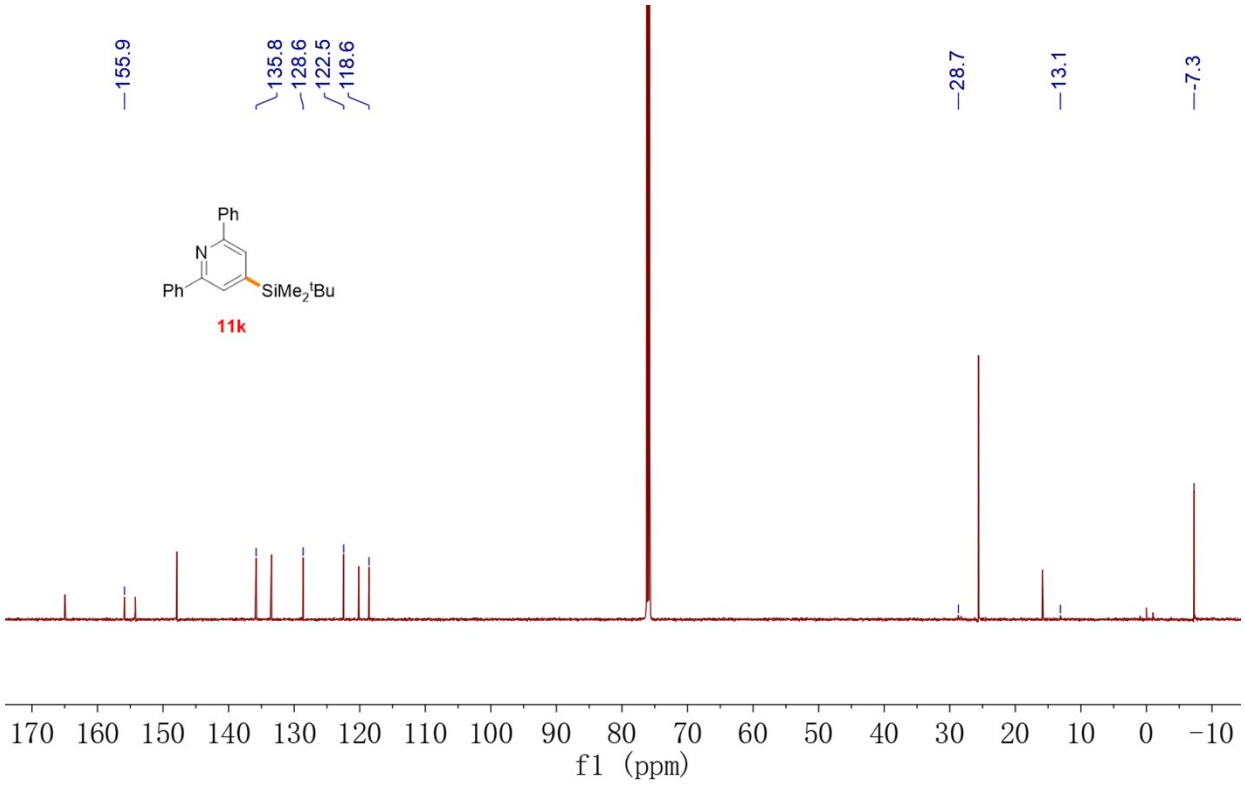
^{13}C NMR spectra of 11j (100 MHz, $CDCl_3$)



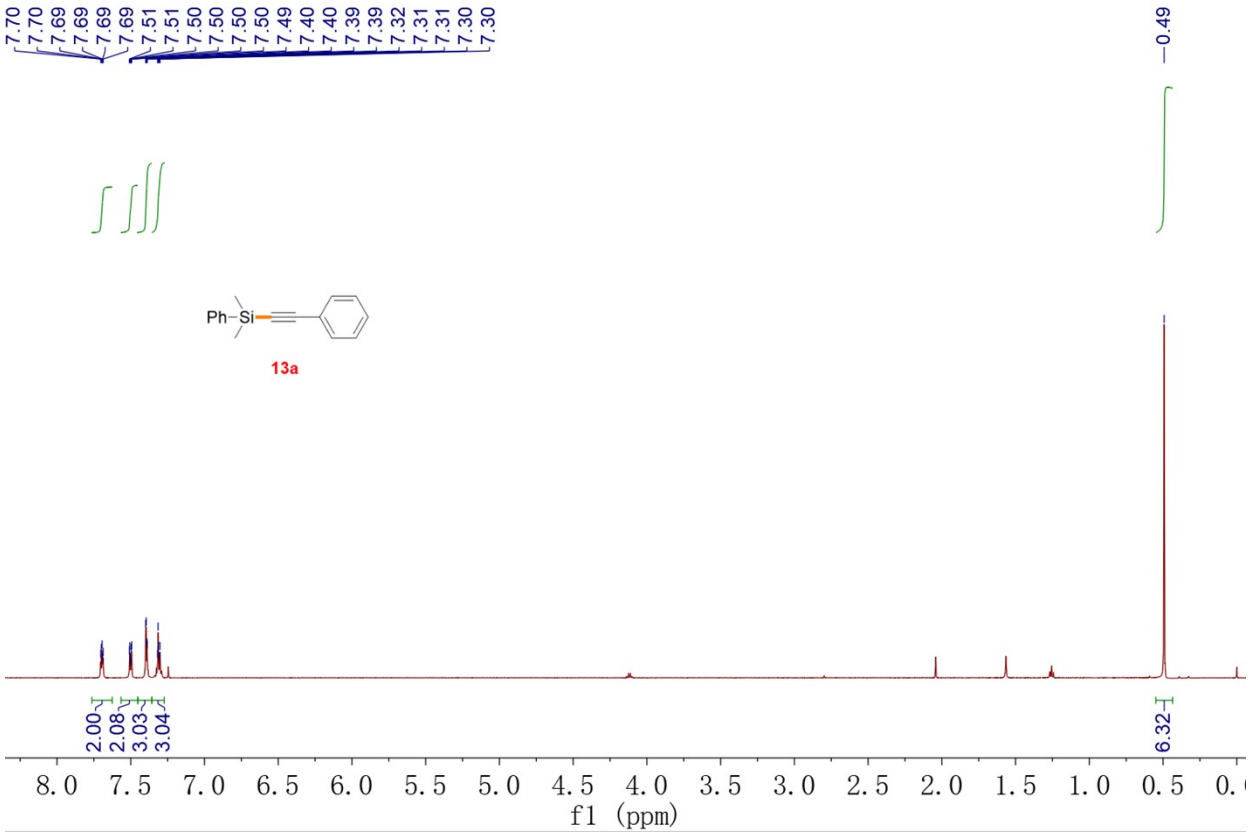
^{1}H NMR spectra of 11k (400 MHz, $CDCl_3$)



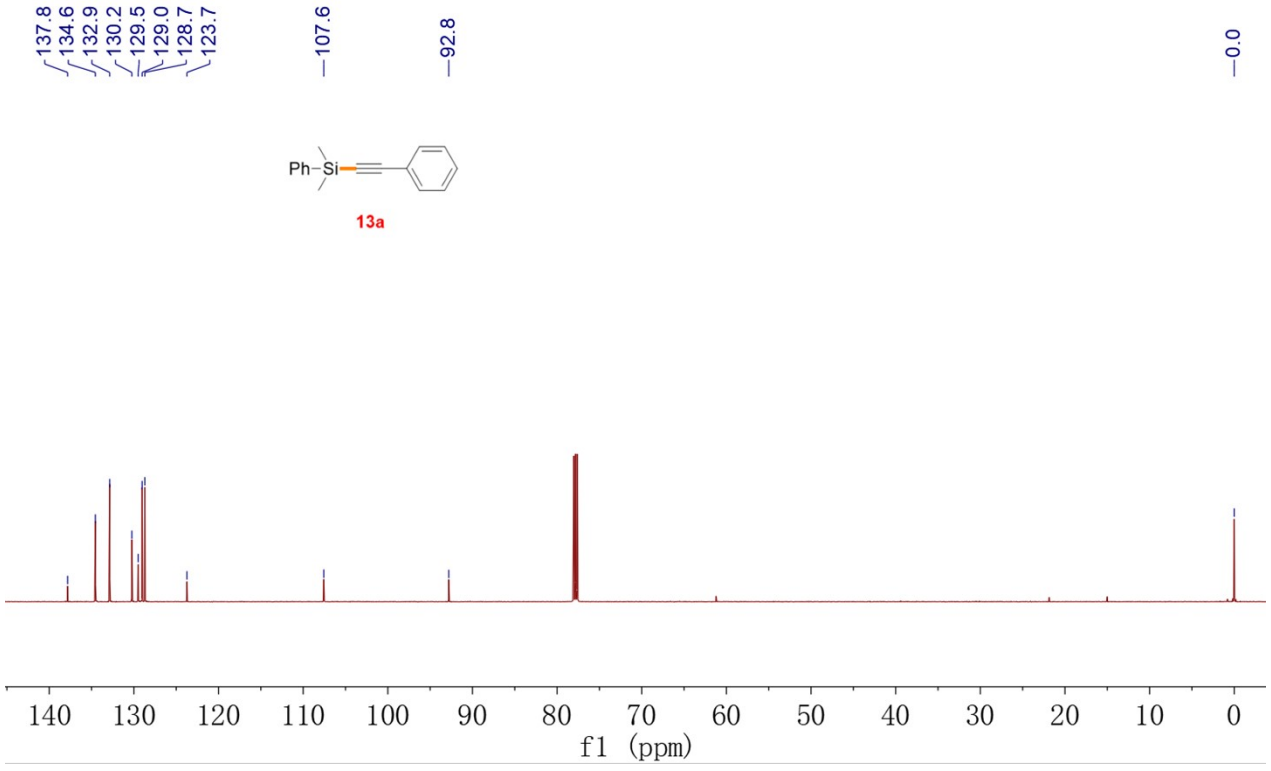
^{13}C NMR spectra of 11k (100 MHz, $CDCl_3$)



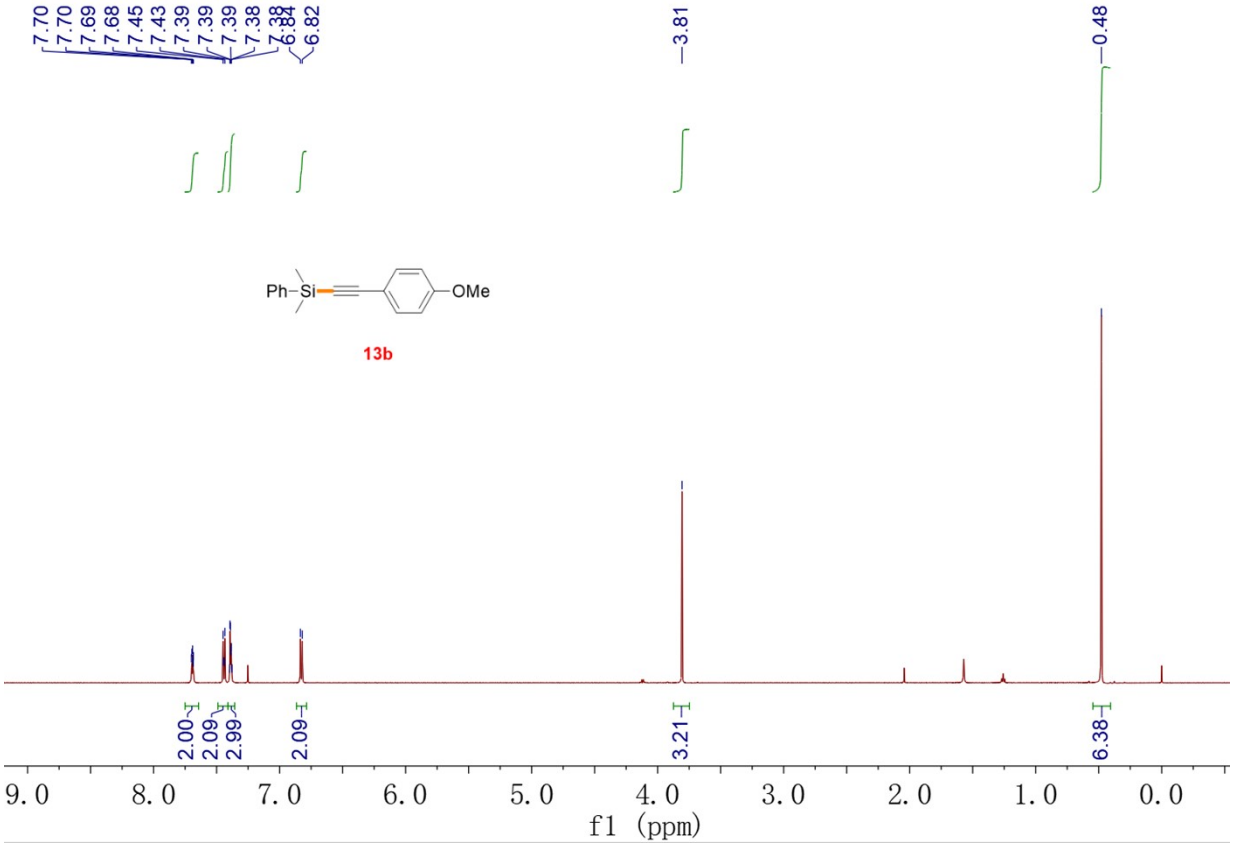
^{1}H NMR spectra of 13a (400 MHz, $CDCl_3$)



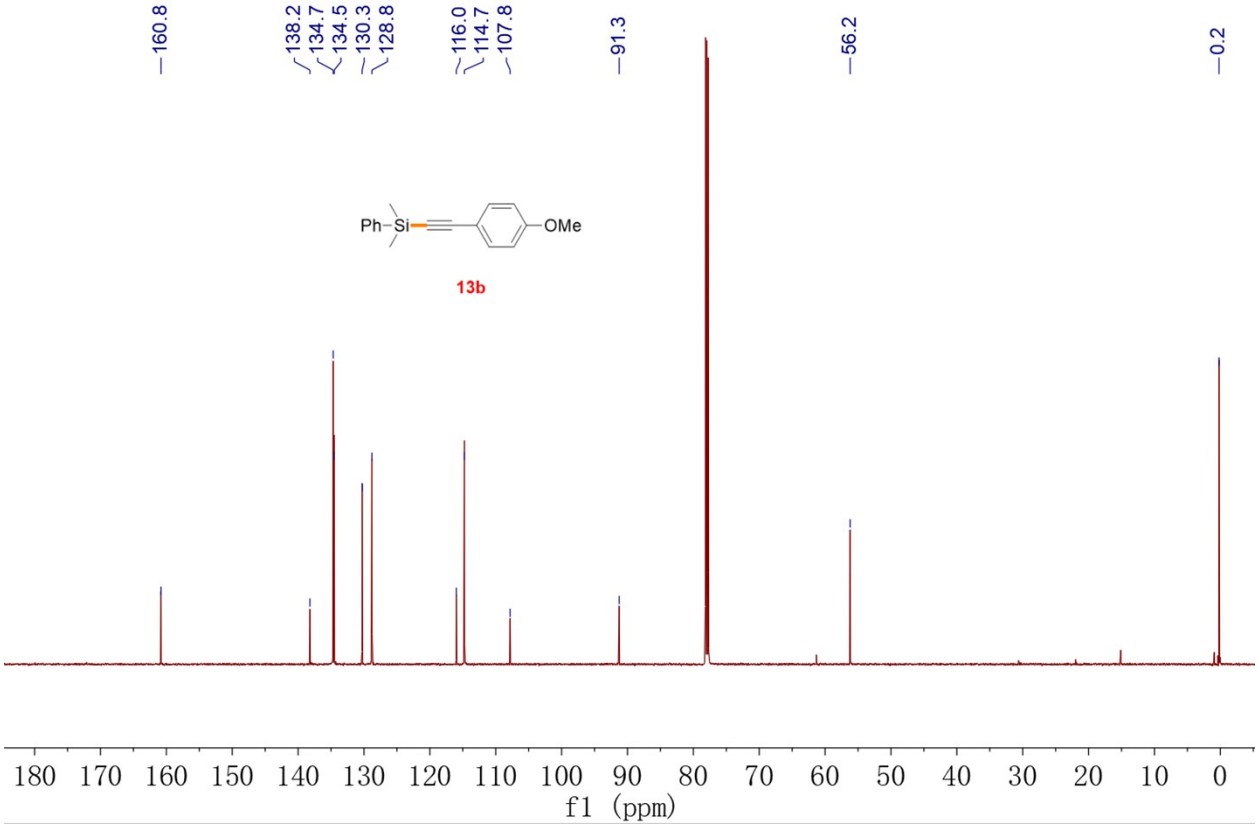
^{13}C NMR spectra of 13a (100 MHz, $CDCl_3$)



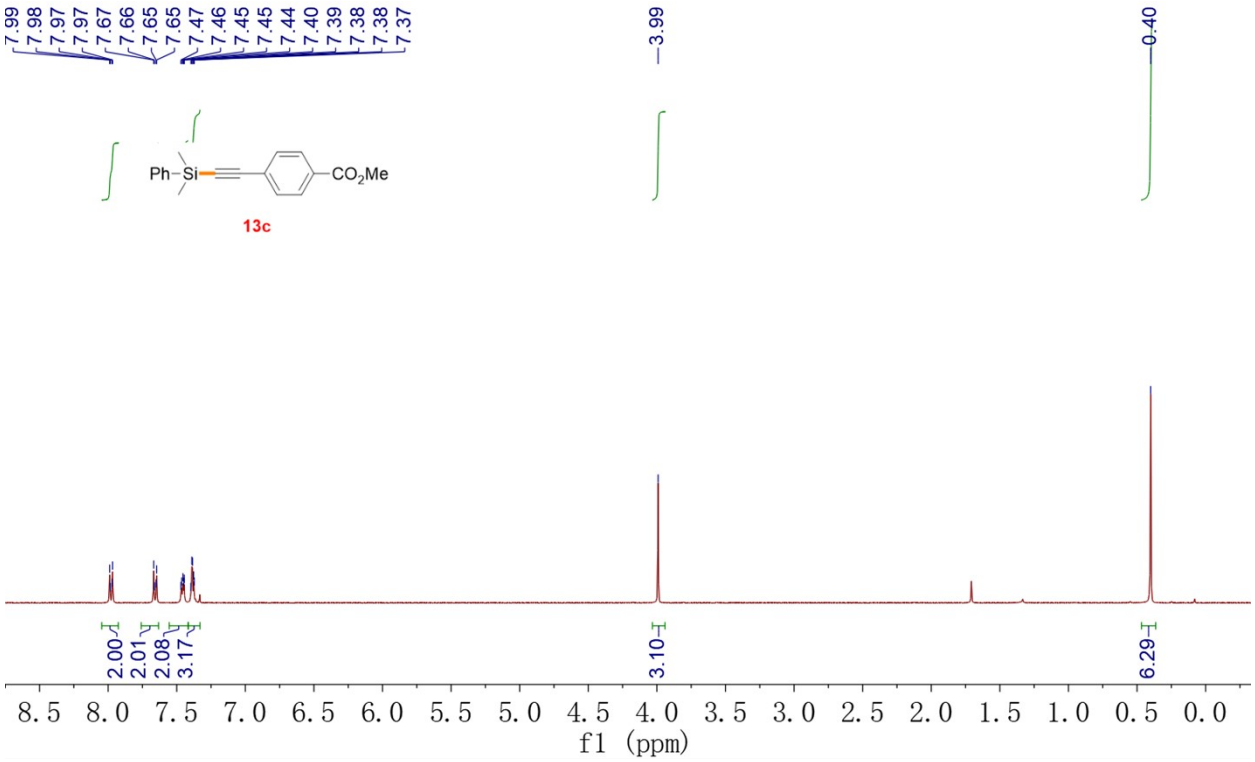
^{1}H NMR spectra of 13b (400 MHz, $CDCl_3$)



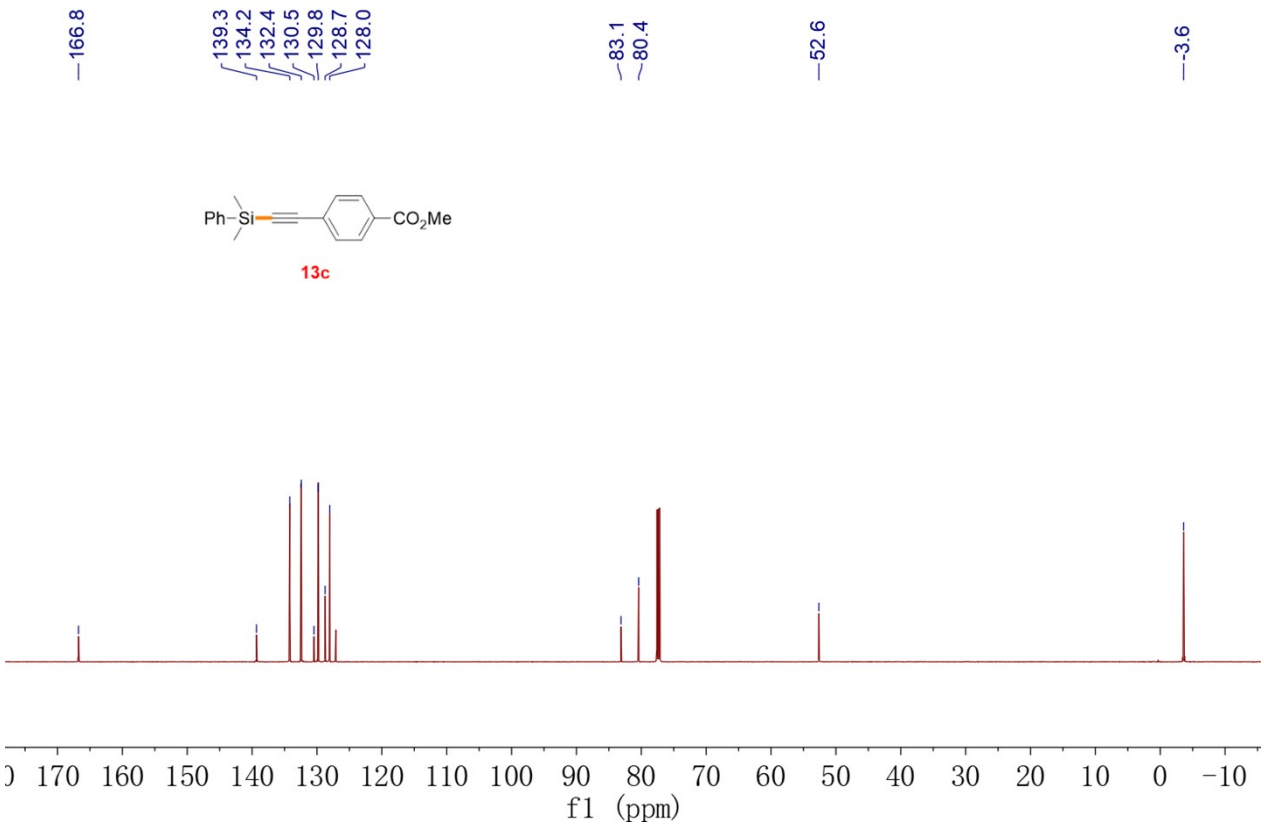
^{13}C NMR spectra of 13b (100 MHz, $CDCl_3$)



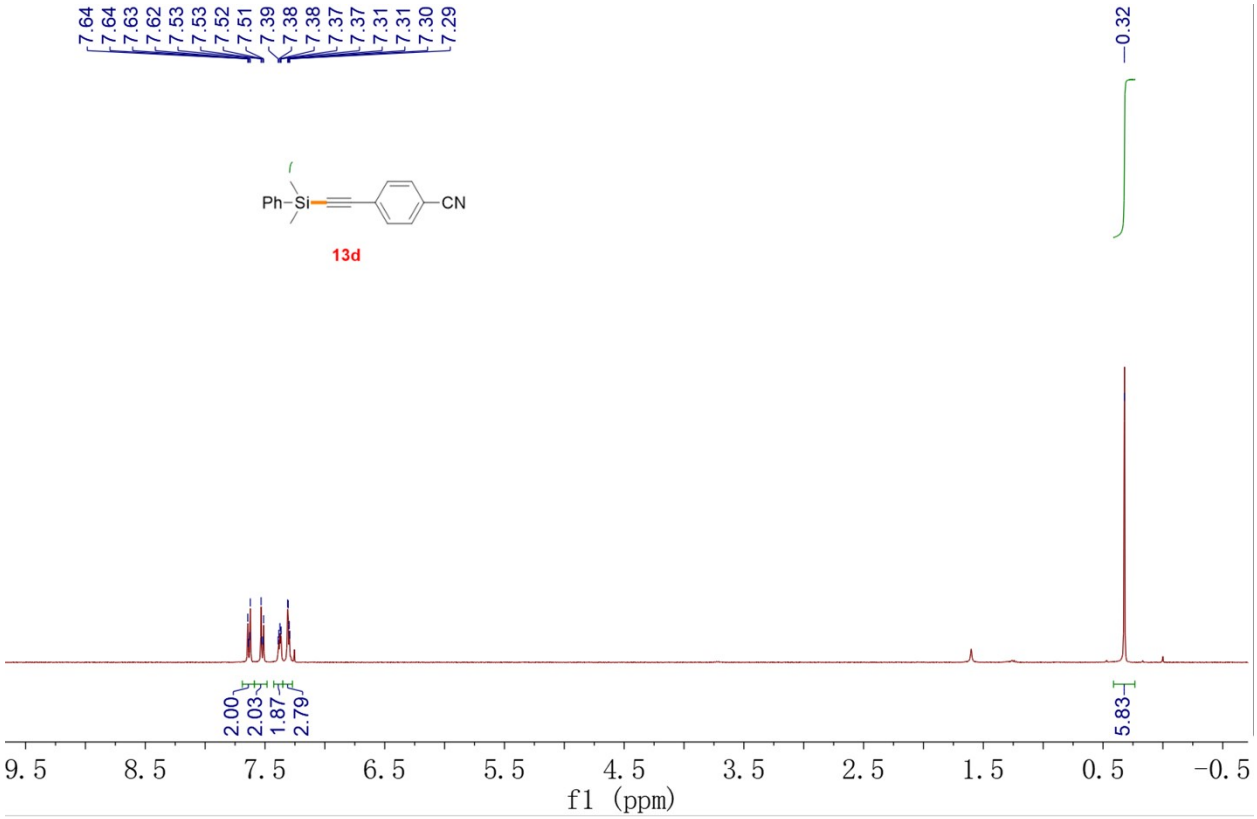
^{1}H NMR spectra of 13c (400 MHz, $CDCl_3$)



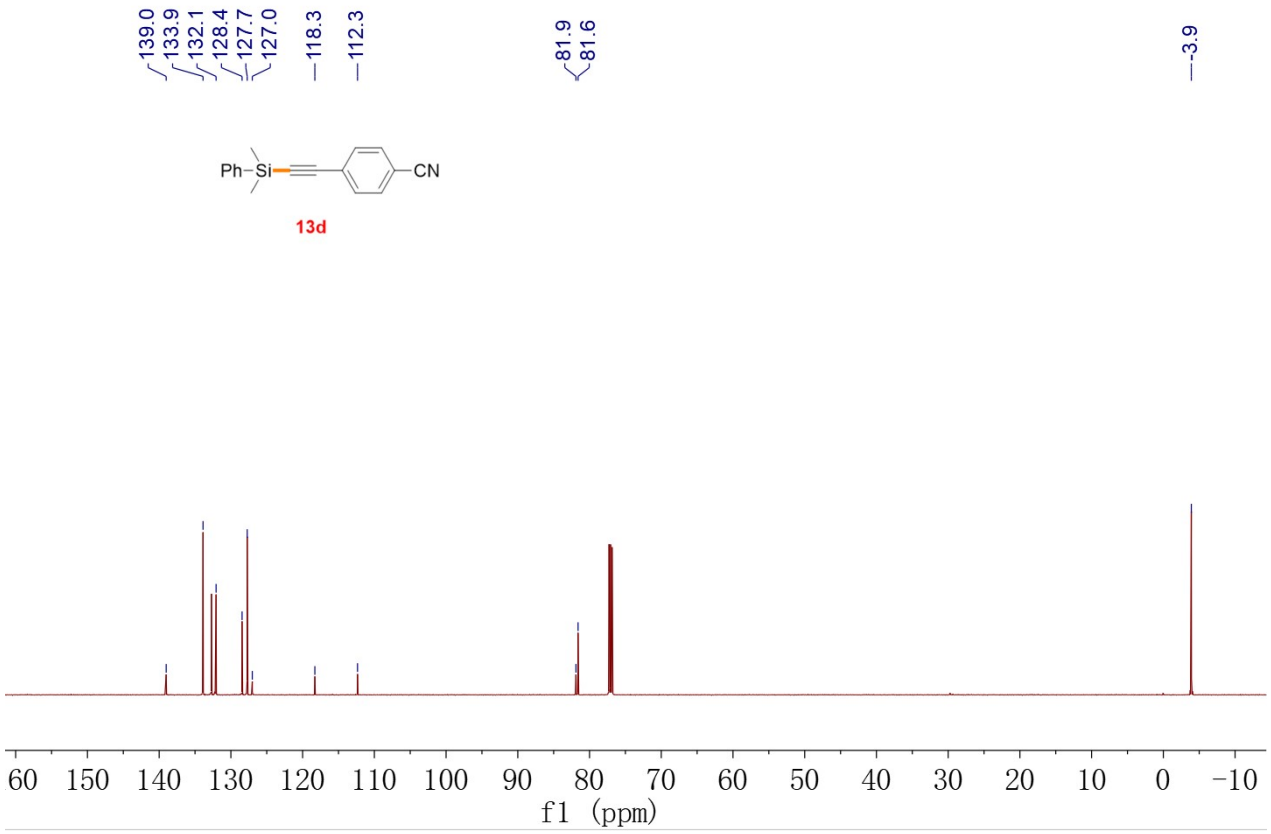
^{13}C NMR spectra of 13c (100 MHz, $CDCl_3$)



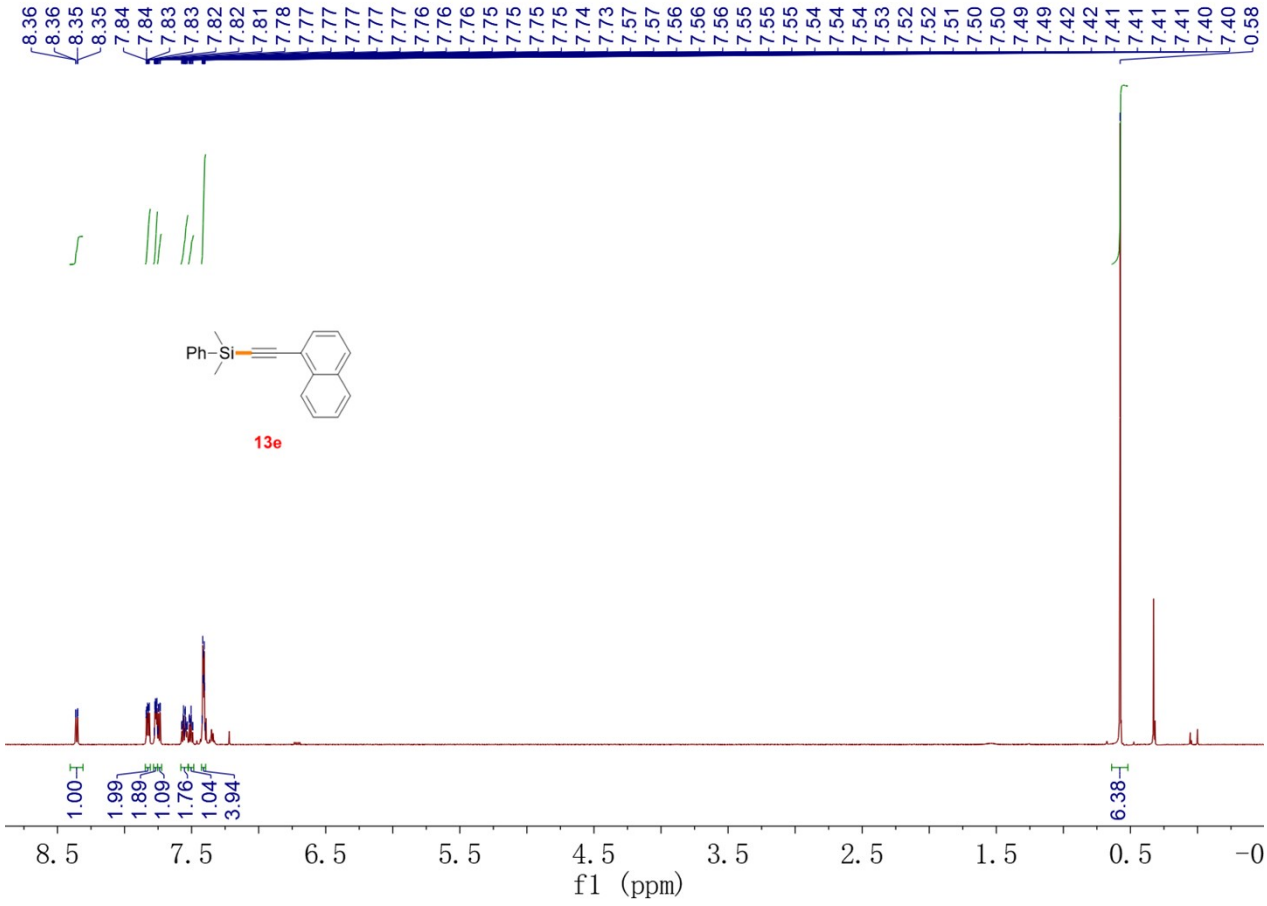
^{1}H NMR spectra of 13d (400 MHz, $CDCl_3$)



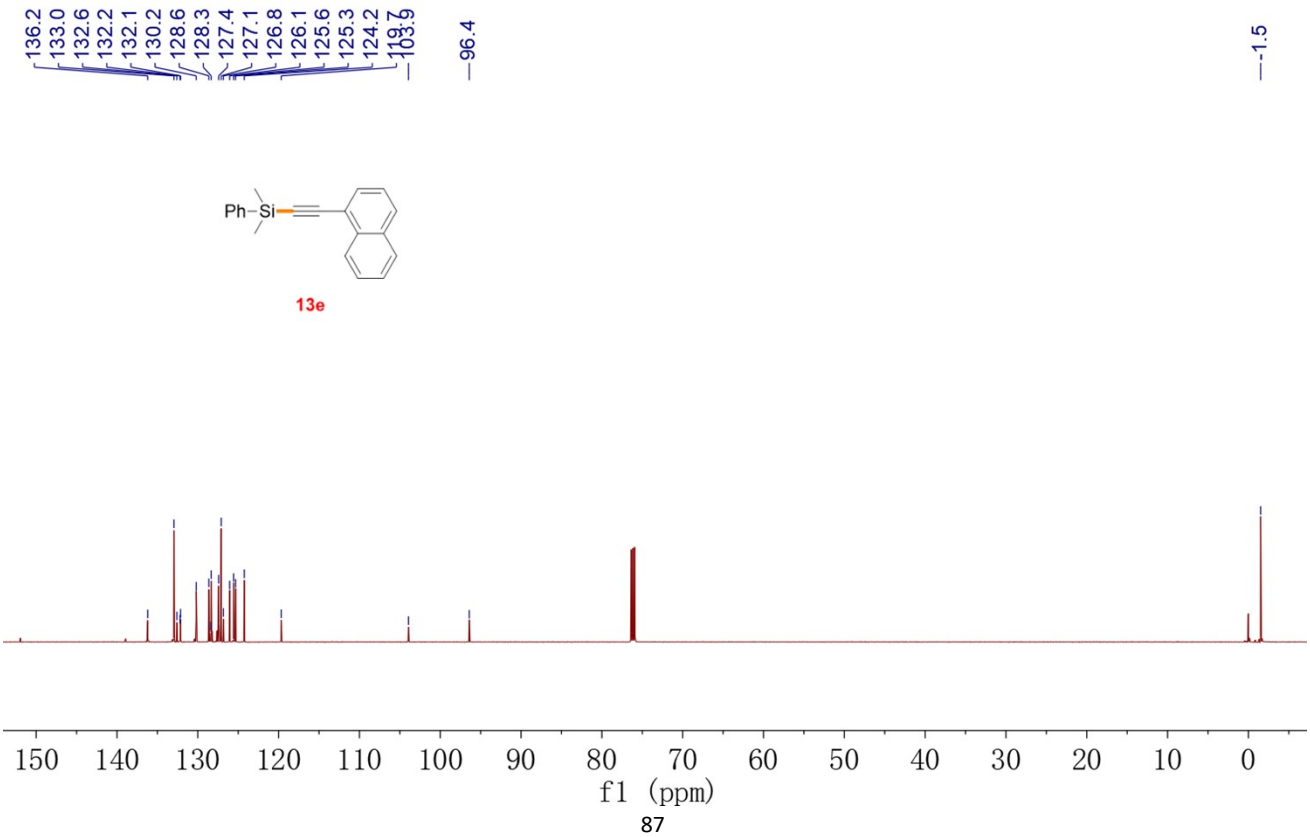
^{13}C NMR spectra of 13d (100 MHz, $CDCl_3$)



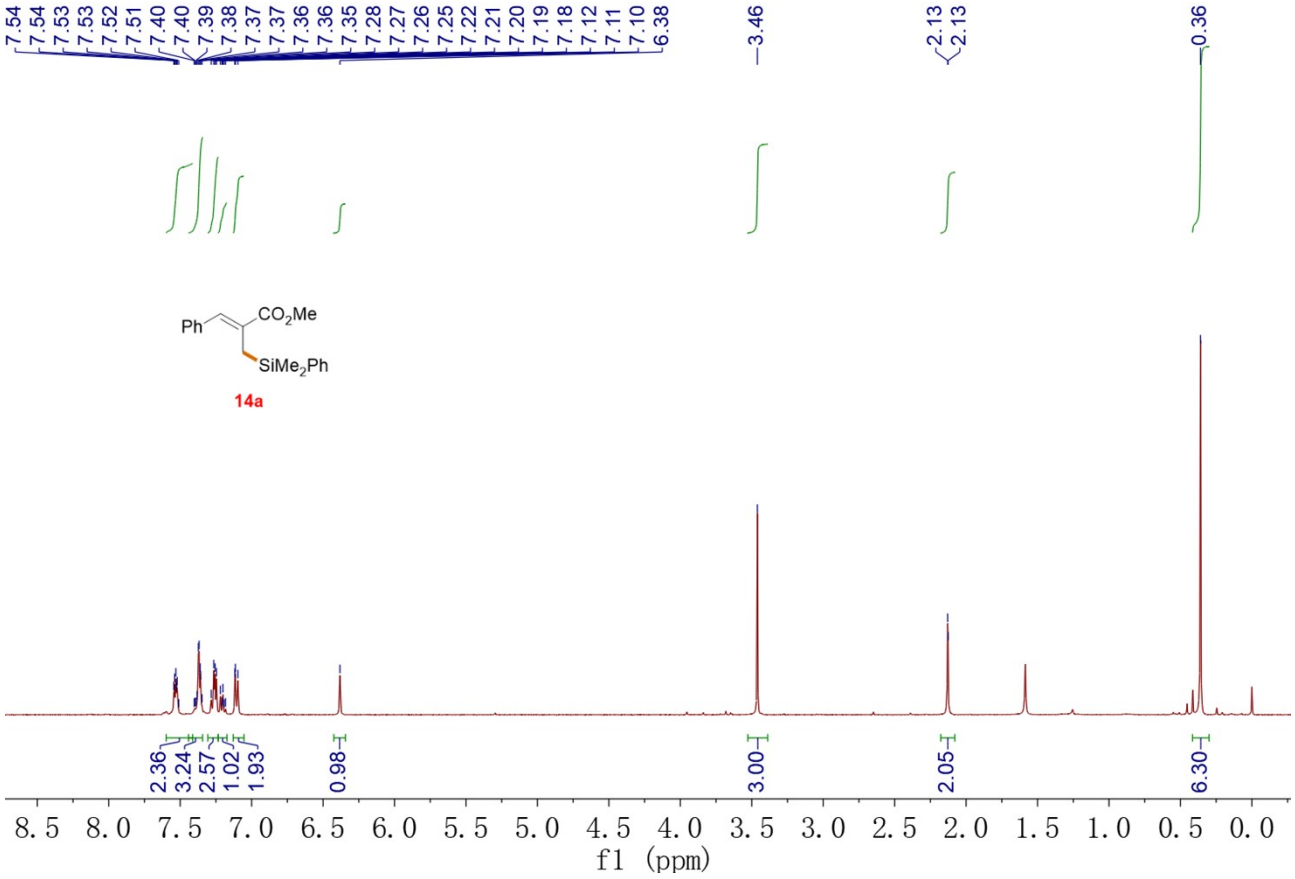
^{1}H NMR spectra of 13e (400 MHz, $CDCl_3$)



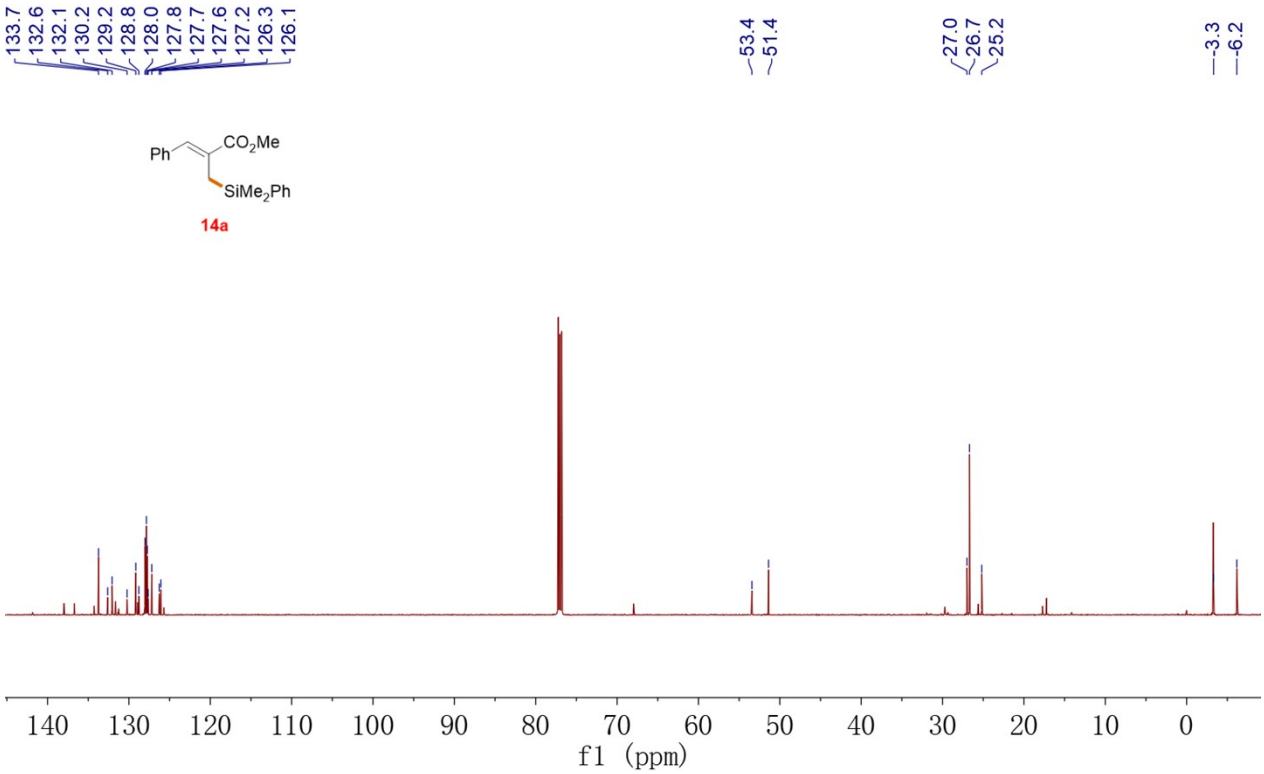
^{13}C NMR spectra of 13e (100 MHz, $CDCl_3$)



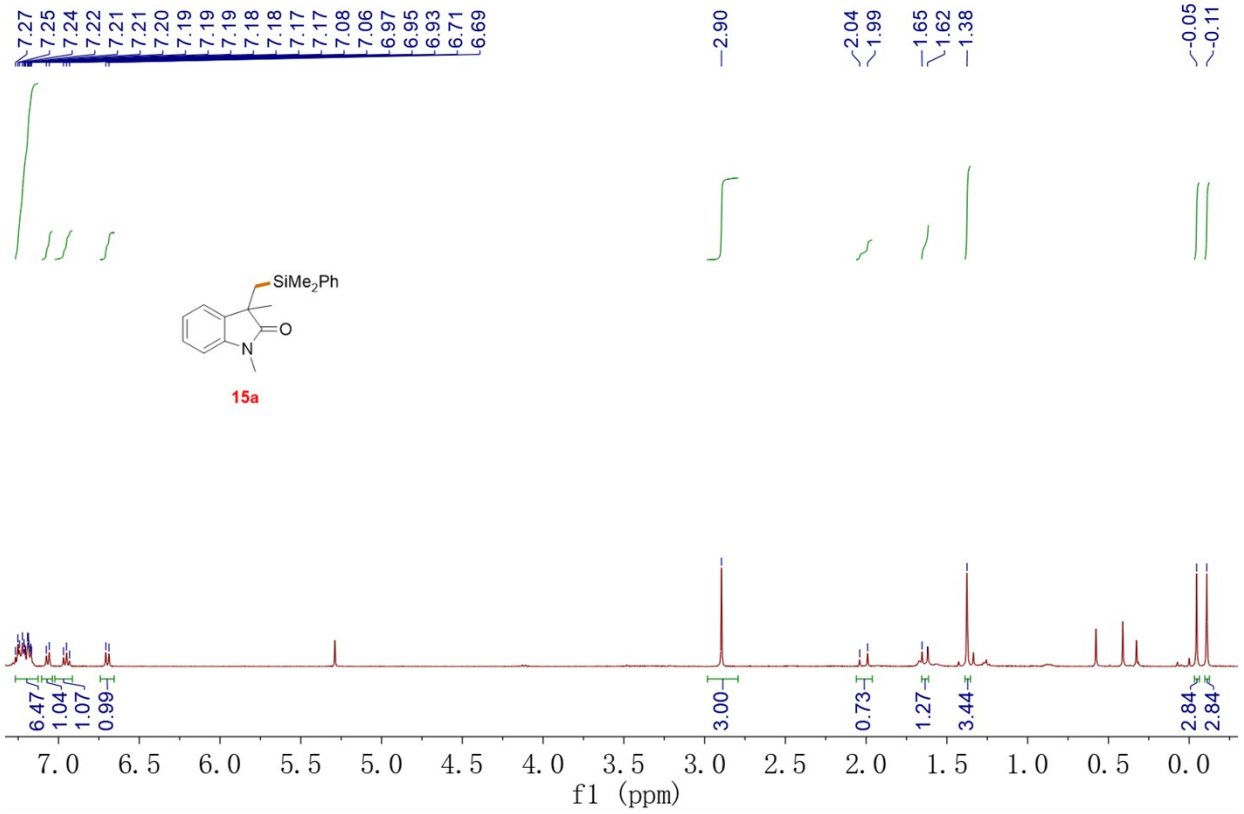
^{1}H NMR spectra of 14a (400 MHz, $CDCl_3$)



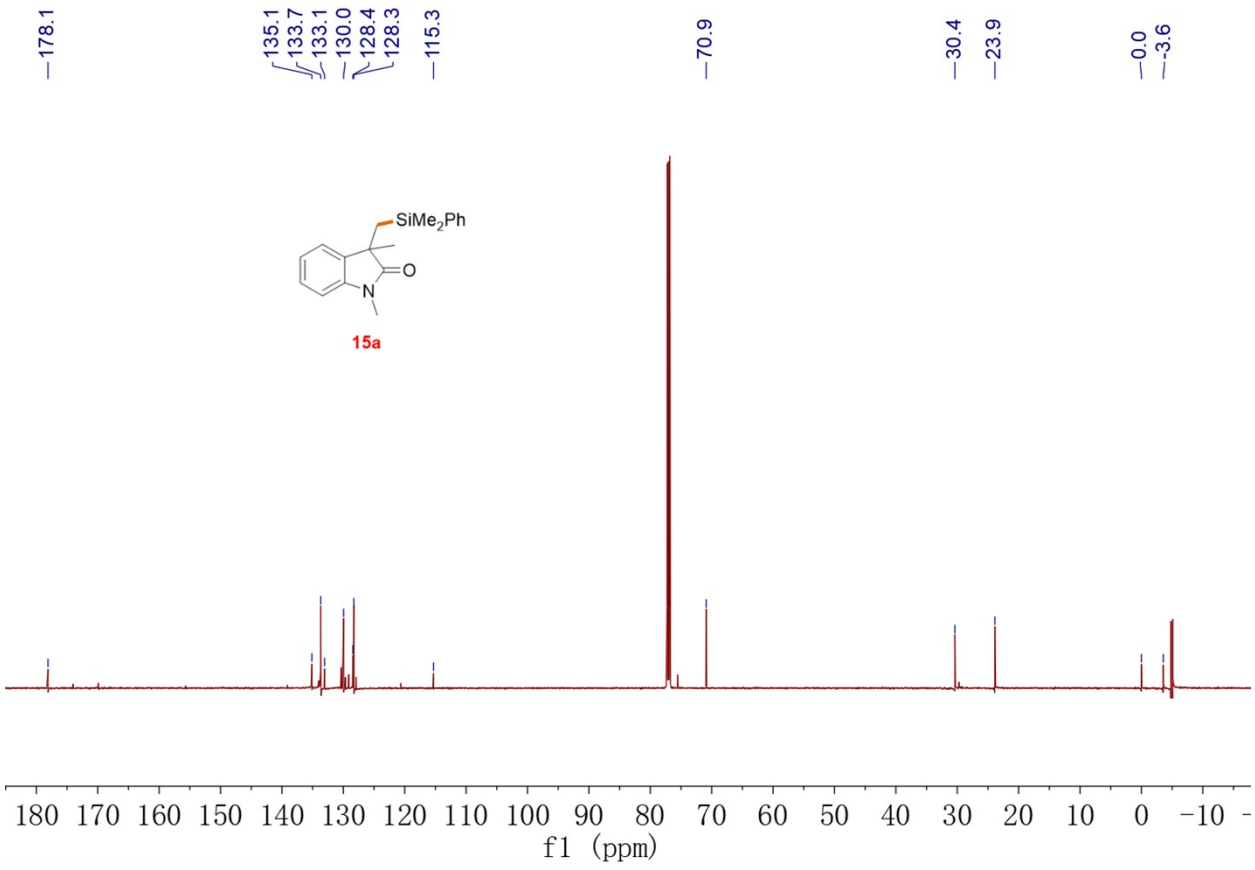
^{13}C NMR spectra of 14a (100 MHz, $CDCl_3$)



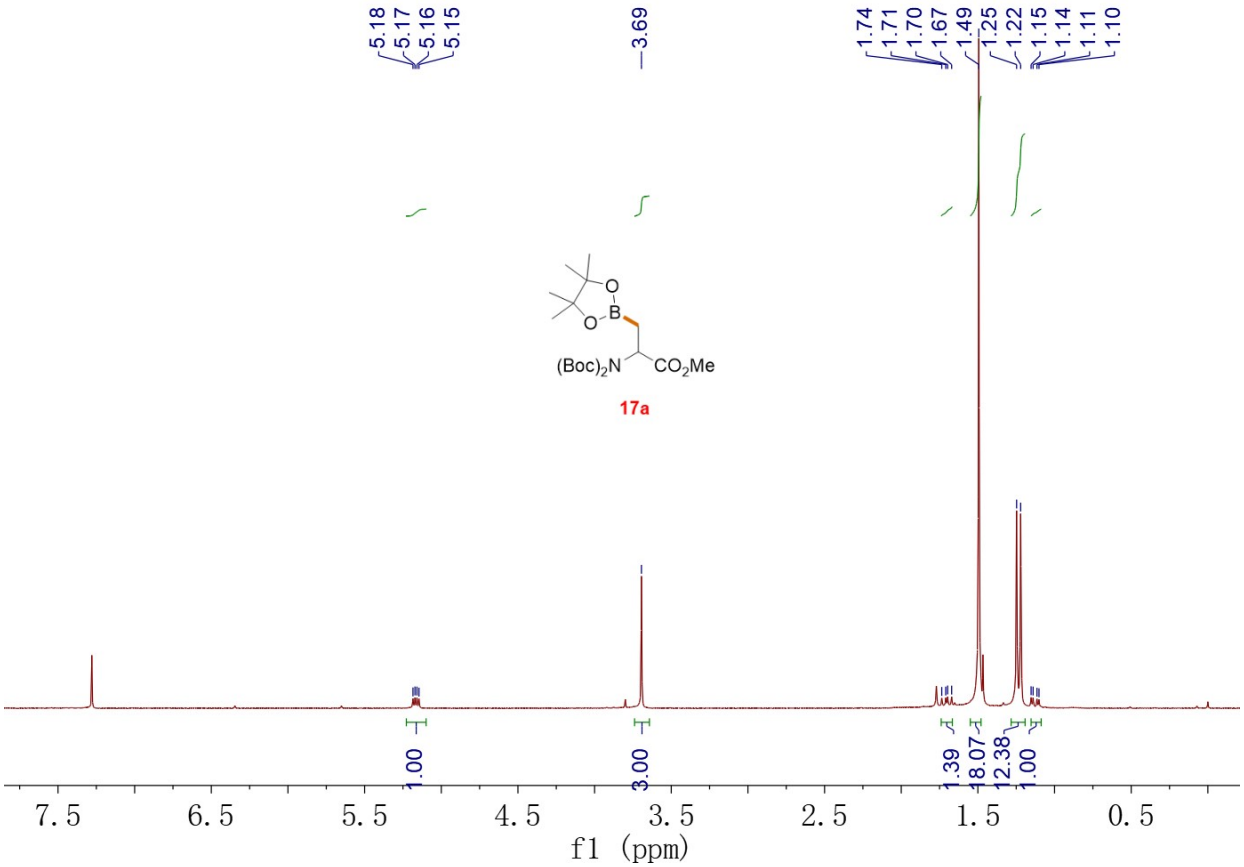
^{1}H NMR spectra of 15a (400 MHz, $CDCl_3$)



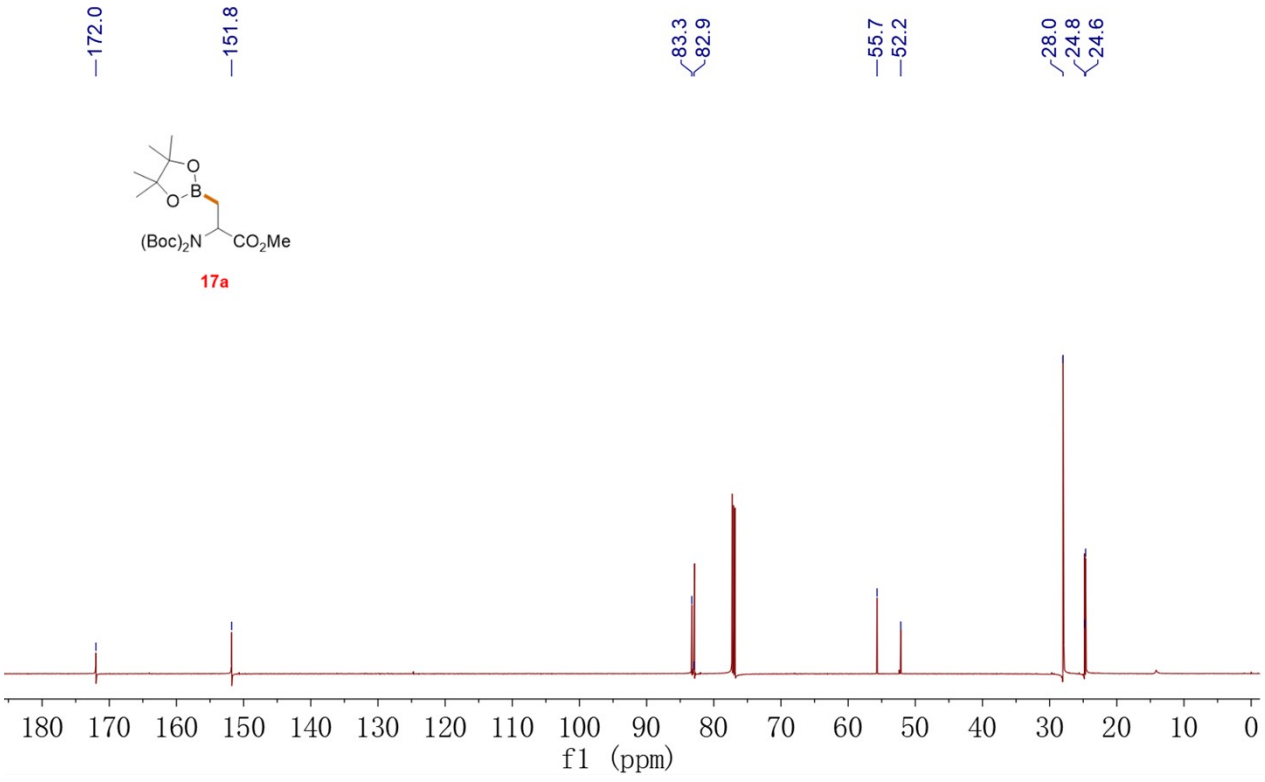
^{13}C NMR spectra of 15a (100 MHz, $CDCl_3$)



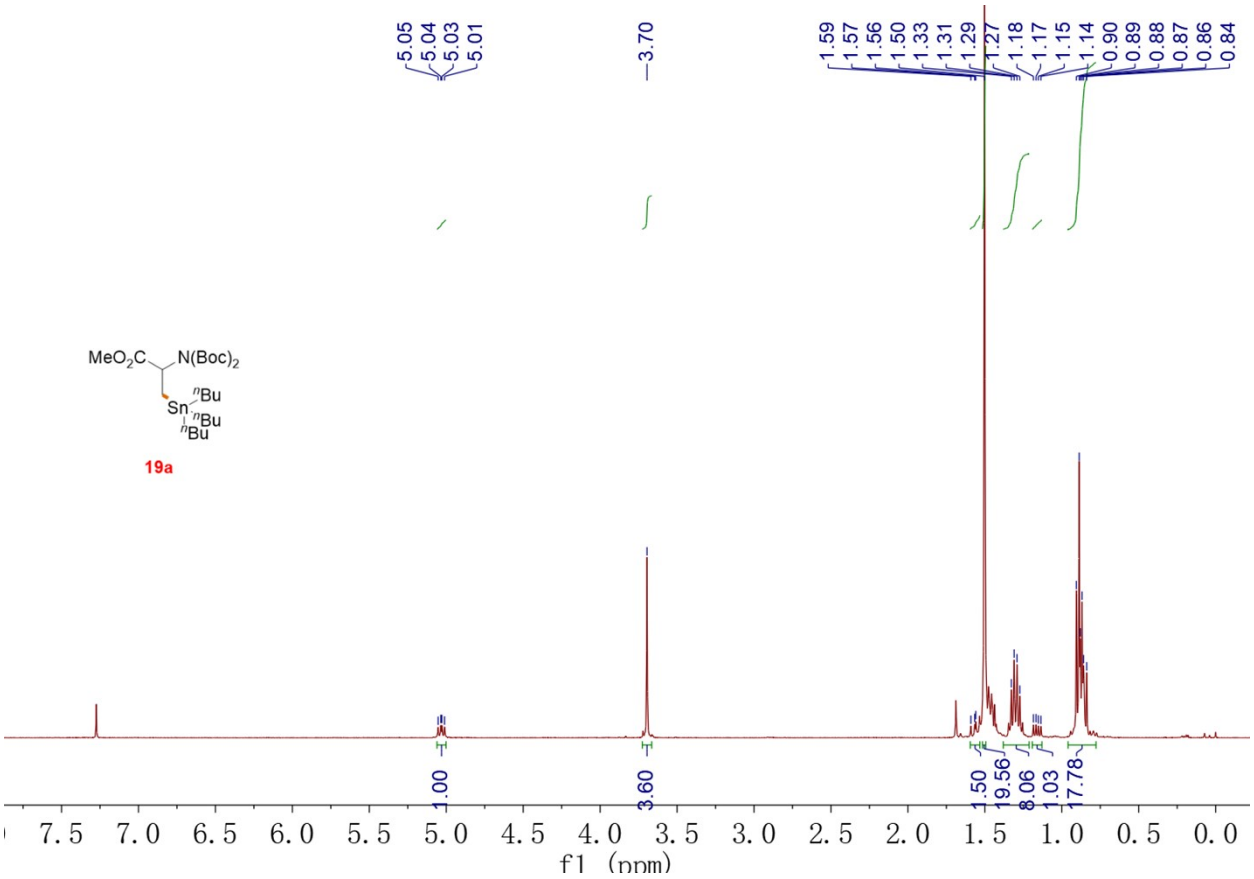
^{1}H NMR spectra of 17a (400 MHz, $CDCl_3$)



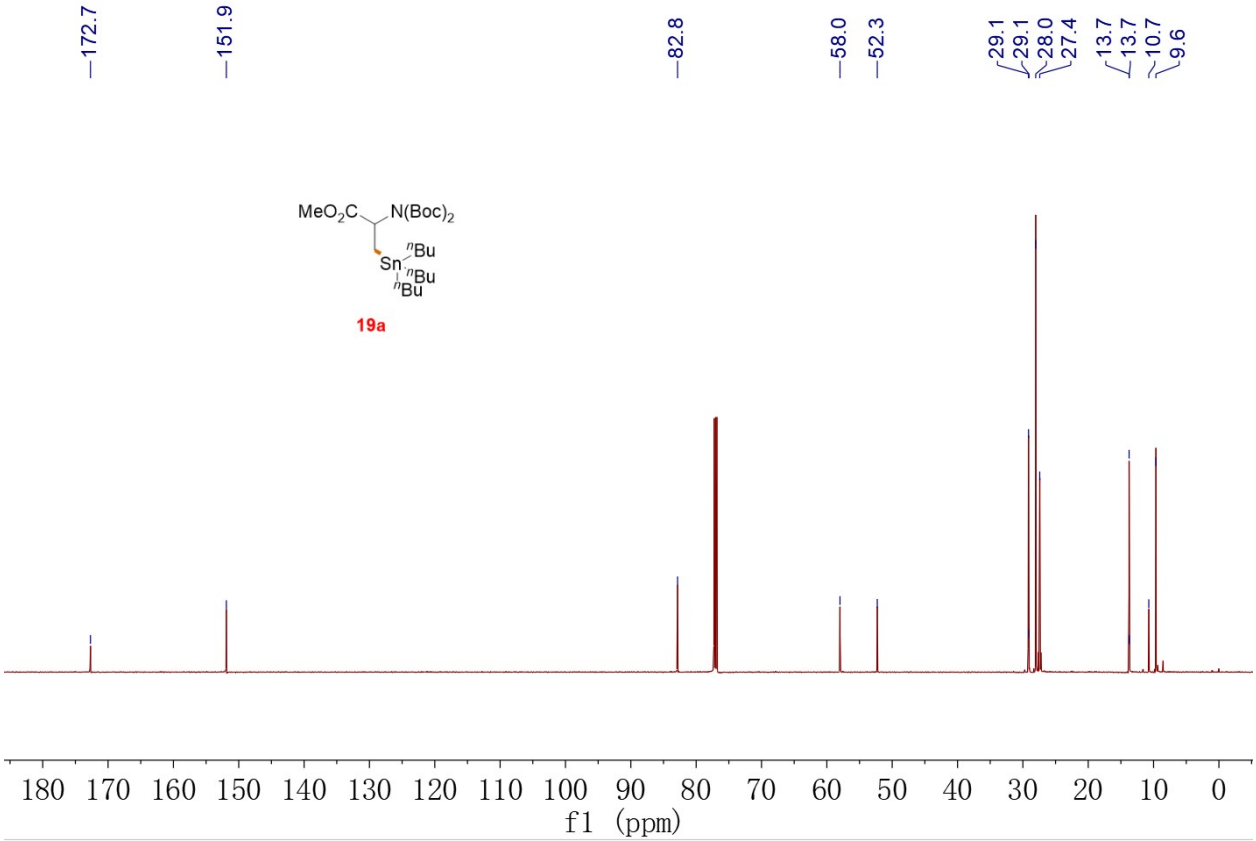
^{13}C NMR spectra of 17a (100 MHz, $CDCl_3$)



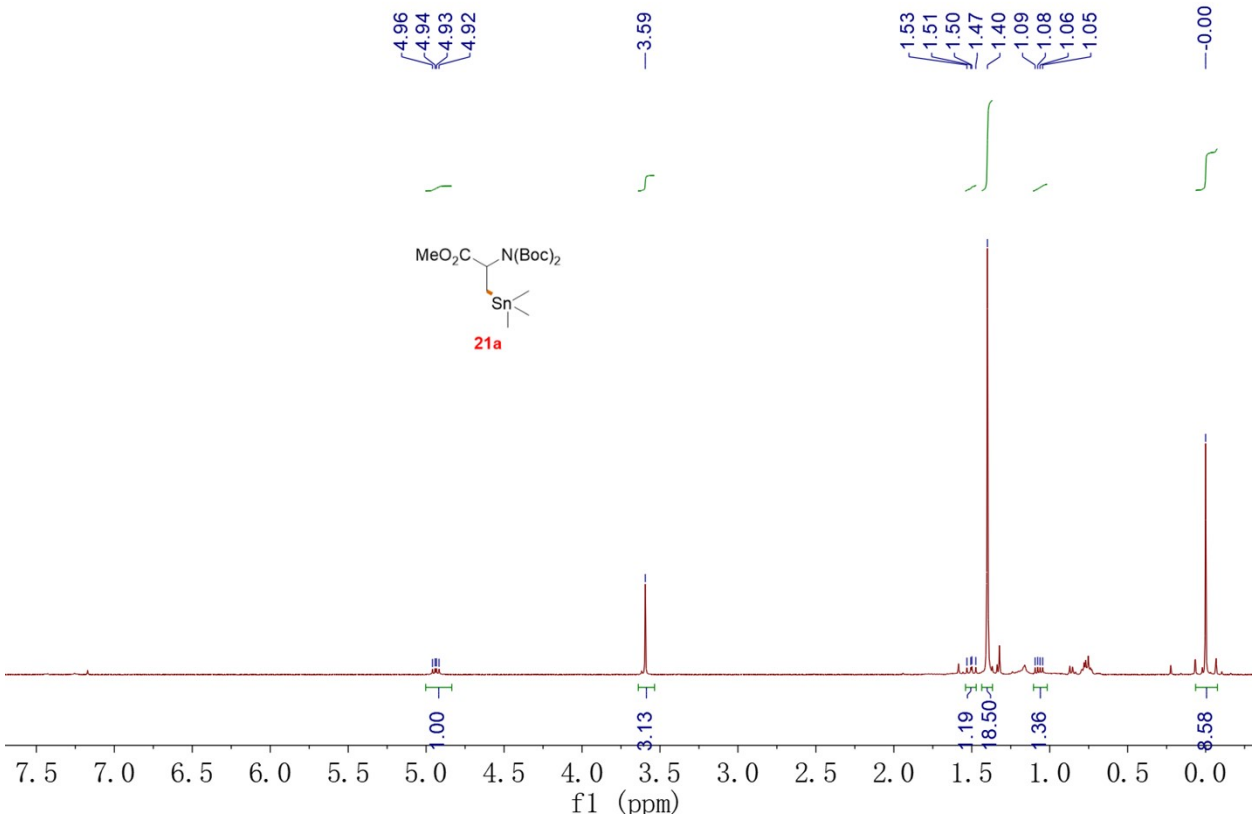
^{1}H NMR spectra of 19a (400 MHz, $CDCl_3$)



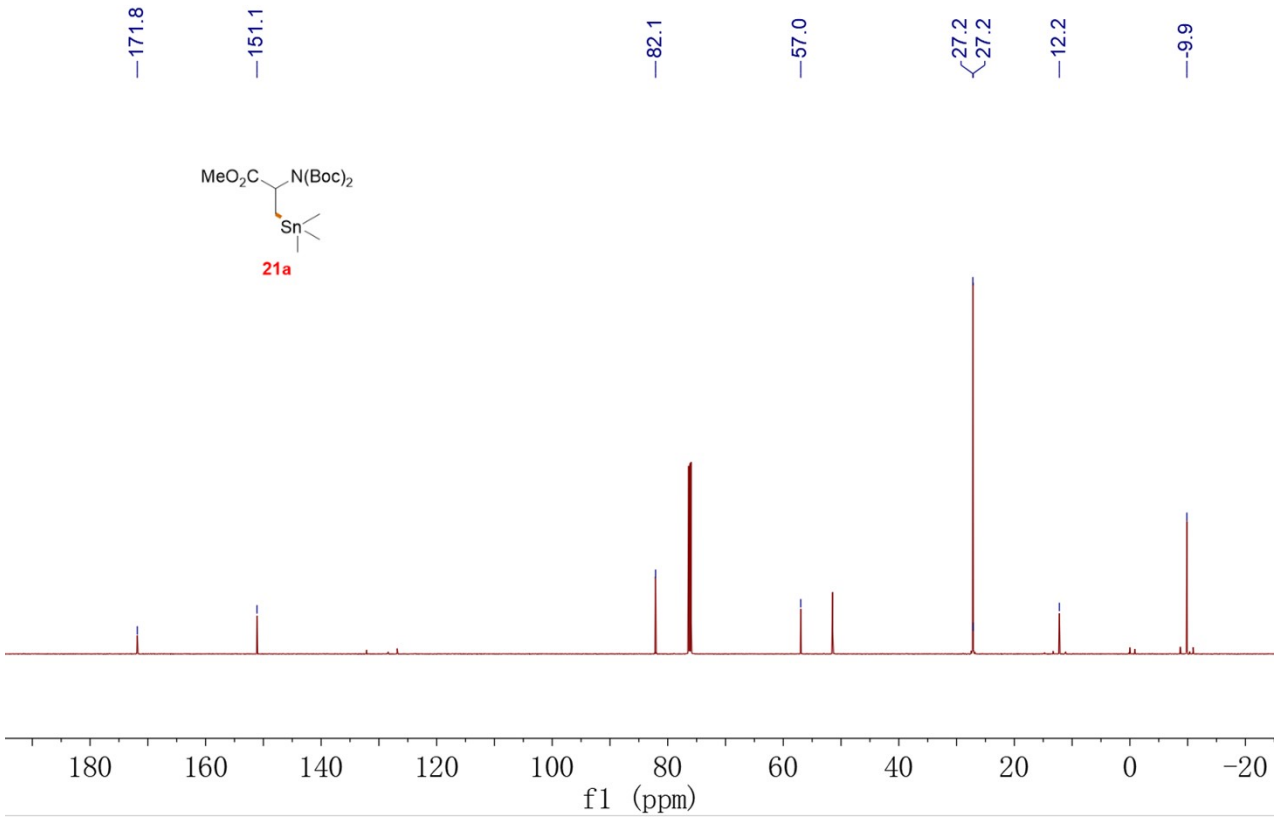
^{13}C NMR spectra of 19a (100 MHz, $CDCl_3$)



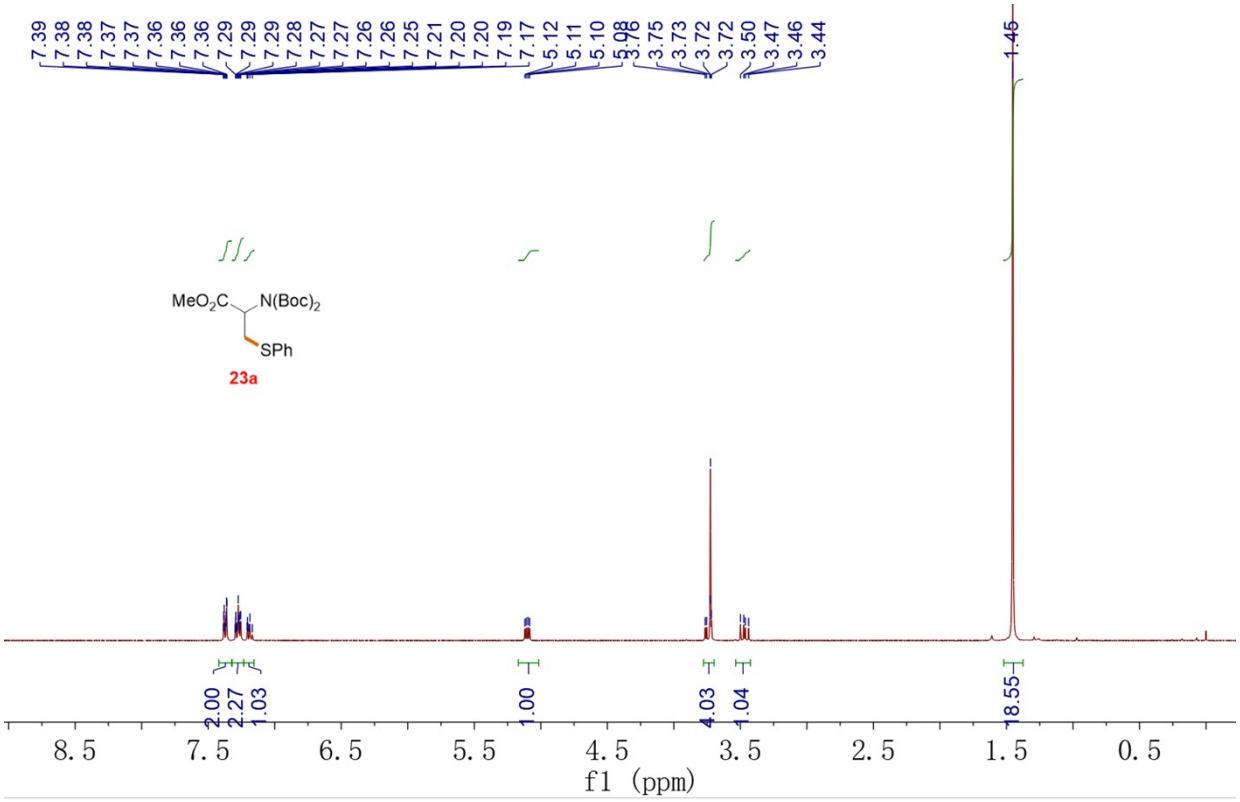
^{1}H NMR spectra of 21a (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 21a (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 23a (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 23a (100 MHz, $CDCl_3$)