Supporting Information

for

TBADT/nickel co-catalyzed arylation of hydrosilanes with aryl halides

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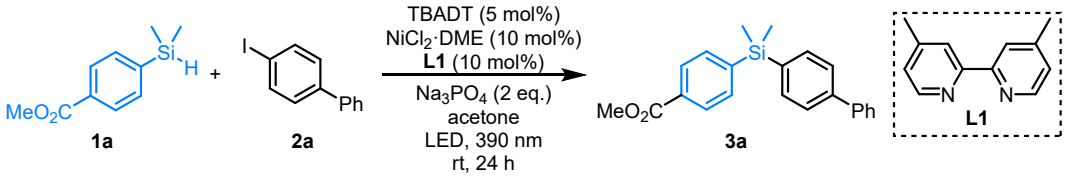
1. General Information

Unless otherwise stated, ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton ($CDCl_3$ δ 7.26), carbon ($CDCl_3$ δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet, bs = broad singlet, etc.), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were obtained on IonSpec FT-ICR or Waters Micromass Q-TOF micro Synapt High-Definition Mass Spectrometer. Flash chromatography was carried out with silica gel 300-400 mesh. All the key reactions were carried out under nitrogen atmosphere with a stir bar in a sealed vial. Acetone used for the key reactions was purchased from Sinopharm Chemical Reagent Company and were used as received. $NiCl_2$•DME were purchased from Annaiji Medical Company and were used as received. All the ligands were purchased from Leyan Medical Company and were used as received.

2. Experimental Procedures

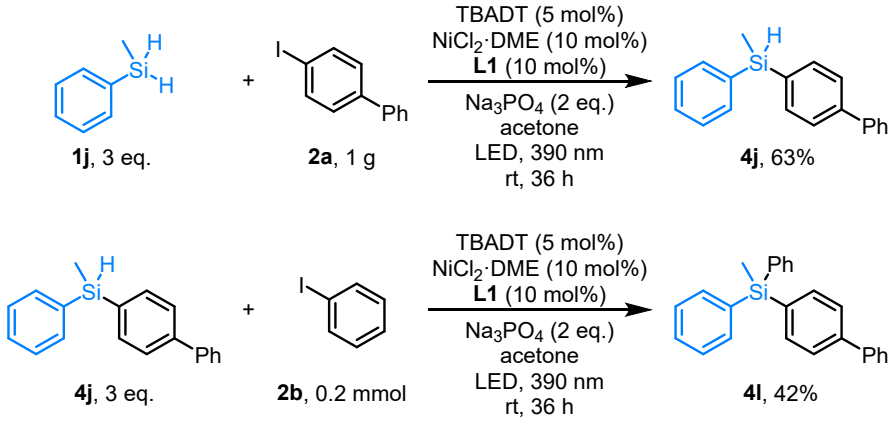
2.1 General procedure A: the arylation of silanes



In a N_2 filled glovebox, a 4 mL baked vial charged with a stir bar was added 4.4 mg of $NiCl_2$•DME (0.02 mmol), 3.6 mg of **L1** (0.02 mmol), followed by the addition of 1.0 mL of acetone. The resulting solution was stirred for 10 minutes before TBADT (33.2 mg, 0.01 mmol), Na_3PO_4 (65.6 mg, 0.4 mmol), **2a** (58.0 mg, 0.2 mmol) and **1a** (116.6 mg, 0.6 mmol) were subsequently added. The vial was then tightly capped, removed from the glovebox, placed under 390 nm blue LEDs and stirred at room temperature for 36 h. The actual temperature of reaction vial is 30 ℃. The reaction

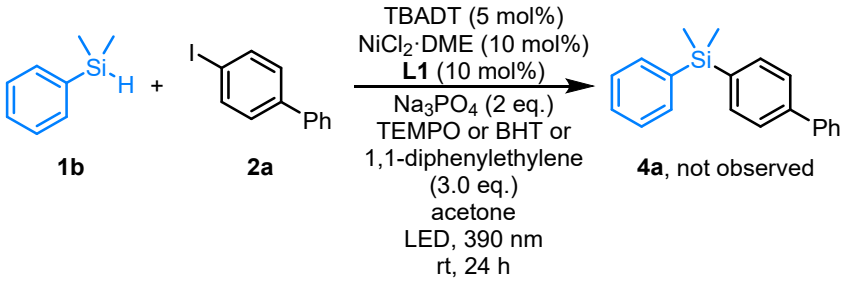
mixture was directly purified by column chromatography on silica gel to give the pure product **3a**.

2.2 General procedure B: Gram-scale reaction and successive arylation



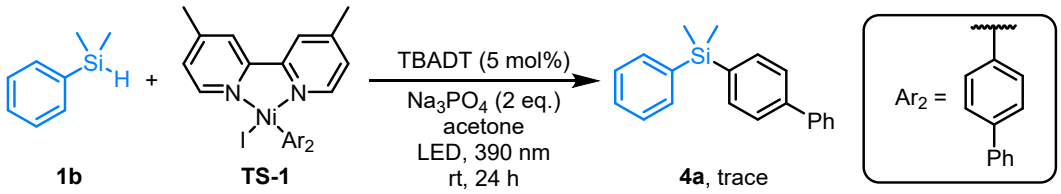
In a N_2 filled glovebox, a 30 mL baked vial charged with a stir bar was added 87.6 mg of $NiCl_2$•DME (0.4 mmol), 73.2 mg of **L1** (0.4 mmol), followed by the addition of 20 mL of acetone. The resulting solution was stirred for 30 minutes before TBADT (664 mg, 0.2 mmol), Na_3PO_4 (1.3 g, 8 mmol), **2a** (1.12 g, 4 mmol) and **1j** (1.46 g, 12 mmol) were subsequently added. The vial was then tightly capped, removed from the glovebox, placed under 390 nm blue LEDs and stirred at room temperature for 36 h. The reaction mixture was filtrated through Celite, evaporate to remove all volatiles. Purified by column chromatography on silica gel to give the pure product **4j**. Then, with the pure product **4j**, the successive arylation could be conducted. In a N_2 filled glovebox, a 4 mL baked vial charged with a stir bar was added 4.4 mg of $NiCl_2$•DME (0.02 mmol), 3.6 mg of **L1** (0.02 mmol), followed by the addition of 1.0 mL of acetone. The resulting solution was stirred for 10 minutes before TBADT (33.2 mg, 0.01 mmol), Na_3PO_4 (65.6 mg, 0.4 mmol), **2b** (40.8 mg, 0.2 mmol) and **4j** (164.7 mg, 0.6 mmol) were subsequently added. The vial was then tightly capped, removed from the glovebox, placed under 390 nm blue LEDs and stirred at room temperature for 36 h. The reaction mixture was directly purified by column chromatography on silica gel to give the pure product **4l**.

2.3 General procedure C: the radical inhibition experiment



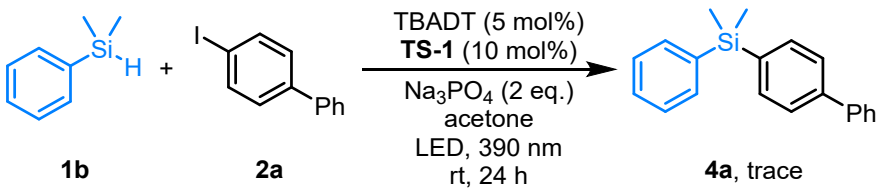
In a N_2 filled glovebox, a 4 mL baked vial charged with a stir bar was added 2.2 mg of $NiCl_2$•DME (0.01 mmol), 1.8 mg of **L1** (0.01 mmol), followed by the addition of 0.5 mL of acetone. The resulting solution was stirred for 10 minutes before TBADT (16.6 mg, 0.05 mmol), Na_3PO_4 (32.8 mg, 0.2 mmol), **2a** (28.0 mg, 0.1 mmol), **1b** (58.3 mg, 0.3 mmol) and TEMPO/BHT/1,1-diphenylethylene (3.0 eq.) were subsequently added. The vial was then tightly capped, removed from the glovebox, placed under 390 nm blue LEDs and stirred at room temperature for 36 h. The reaction mixture was monitored by HRMS.

2.4 Experimental procedure D: the stoichiometric experiment with pre-synthesized TS-1



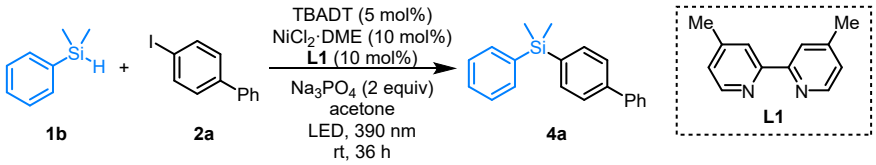
In a N_2 filled glovebox, a 4 mL baked vial charged with a stir bar was added 51.8 mg of **TS-1** (0.01 mmol), followed by the addition of 0.5 mL of acetone. The resulting solution was stirred for 10 minutes before TBADT (16.6 mg, 0.05 mmol), Na_3PO_4 (32.8 mg, 0.2 mmol) and **1b** (40.8 mg, 0.3 mmol) were subsequently added. The vial was then tightly capped, removed from the glovebox, placed under 390 nm blue LEDs and stirred at room temperature for 36 h. The reaction mixture was monitored by GC-MS.

2.5 Experimental procedure E: catalytic experiment with pre-synthesized TS-1



In a N_2 filled glovebox, a 4 mL baked vial charged with a stir bar was added 5.2 mg of **TS-1** (0.01 mmol), followed by the addition of 0.5 mL of acetone. The resulting solution was stirred for 10 minutes before TBADT (16.6 mg, 0.05 mmol), Na_3PO_4 (32.8 mg, 0.2 mmol), **2a** (28.0 mg, 0.1 mmol) and **1b** (40.8 mg, 0.3 mmol) were subsequently added. The vial was then tightly capped, removed from the glovebox, placed under 390 nm blue LEDs and stirred at room temperature for 36 h. The reaction mixture was monitored by GC-MS.

2.6 Experimental procedure F: Light on and off study



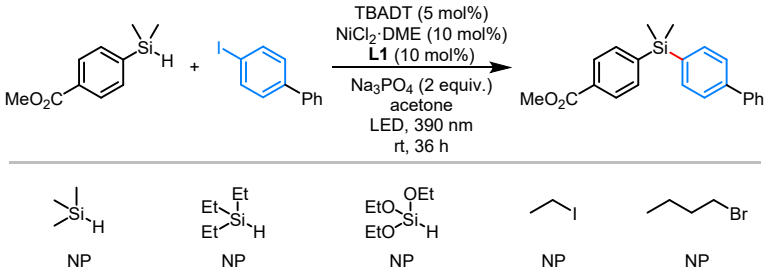
In a N_2 filled glovebox, a 4 mL baked vial charged with a stir bar was added 2.2 mg of $NiCl_2$•DME (0.01 mmol), 1.8 mg of **L1** (0.01 mmol), followed by the addition of 0.5 mL of acetone. The resulting solution was stirred for 10 minutes before TBADT (16.6 mg, 0.05 mmol), Na_3PO_4 (32.8 mg, 0.2 mmol), **2a** (28.0 mg, 0.1 mmol) and **1b** (40.8 mg, 0.3 mmol) were subsequently added. The vial was then tightly capped, removed from the glovebox, placed under 390 nm blue LEDs and stirred at room temperature for 8 h. After 8 h the reaction mixture sample was directly monitored by GC. Then stirred in the dark for 4 h, the reaction mixture sample was directly monitored by GC. Repeat the process for 3 times.

3. Additional Details for Scope Studies

A series of alkenes were tested under standard conditions, which were showed as Figure **S1**. It is depressing that trialkyl-substituted silanes, such as trimethylsilane and triethylsilane, as well as triethoxysilane were completely unreactive, in contrast to aryl-

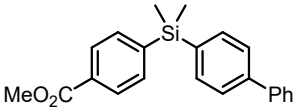
substituted silanes. This lack of reactivity may be attributed to the fact that the π electrons in aryl substitutes could help stabilize silyl radicals. Meanwhile, the reactivity of alkyl halides was also tested. Both iodide and n-butyl bromide showed no reactivity, which may be attributed to the low oxidative addition activity of alkyl halides.

Table S1. Unreactive Substances.[a,b]

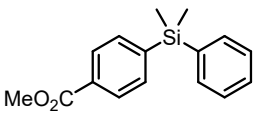


[a]**1** (3.0 eq.), **2** (0.1 mmol), $NiCl_2$•DME (10 mol%), **L1** (10 mol%), TBADT (5 mol%), Na_3PO_4 (2.0 equiv.) in acetone (0.5 mL) at rt under irradiation of LEDs (40 W, 390 nm) for 36 hours. [b]Yields were determined by GC analysis using n-dodecane as the internal standard of the crude reaction mixture. NP = no product.

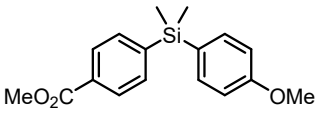
4. Characterization Data of Products



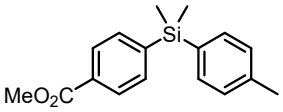
3a: Synthesized from **2a** by following general procedure A on a 0.2 mmol scale. 58.9 mg obtained, 85% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.4 Hz, 2H), 7.68-7.60 (m, 8H), 7.47 (t, J = 7.4 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 3.94 (s, 3H), 0.64 (s, 6H). ^{13}C NMR (400 MHz, CDCl3) δ 167.25, 144.62, 142.17, 140.94, 136.08, 134.66, 130.65, 128.81, 128.61, 127.18, 126.69, 52.14, -2.49. HRMS (EI) calcd. for $C_{22}H_{22}O_2Si$ $[M]^+$: 346.1389, Found: 346.1382.



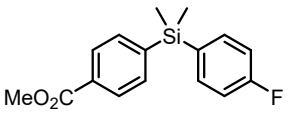
3b: Synthesized from **2b** by following general procedure A on a 0.2 mmol scale. 46.3 mg obtained, 86% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.9 Hz, 2H), 7.60 (d, J = 7.9 Hz, 2H), 7.51 (d, J = 6.7 Hz, 2H), 7.37 (d, J = 6.6 Hz, 3H), 3.92 (s, 3H), 0.58 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.70, 137.35, 134.19, 130.58, 129.40, 128.58, 127.97, 52.15, -2.54. HRMS (EI) calcd. for $C_{16}H_{18}O_2Si$ $[M]^+$: 269.0998, Found: 269.0986.



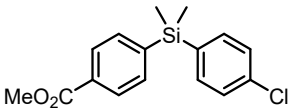
3c: Synthesized from **2c** by following general procedure A on a 0.2 mmol scale. 45.1 mg obtained, 75% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 3.91 (s, 3H), 3.81 (s, 3H), 0.55 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.63, 163.04, 147.54, 138.00, 136.48, 132.83, 130.89, 130.41, 116.09, 57.41, 54.48. HRMS (EI) calcd. for $C_{17}H_{20}O_3Si$ $[M]^+$: 300.1182, Found: 300.1173.



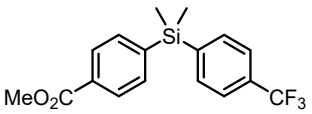
3d: Synthesized from **2d** by following general procedure A on a 0.2 mmol scale. 37.0 mg obtained, 65% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 7.5 Hz, 2H), 3.91 (s, 3H), 2.35 (s, 3H), 0.55 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.76, 147.47, 141.81, 136.69, 136.63, 136.12, 132.98, 131.28, 131.01, 54.59, 23.97. HRMS (EI) calcd. for $C_{17}H_{20}O_2Si$ $[M]^+$: 284.1233, Found: 284.1237.



3e: Synthesized from **2e** by following general procedure A on a 0.2 mmol scale. 39.2 mg obtained, 68% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.49-7.44 (m, 2H), 7.05 (t, *J* = 8.8 Hz, 2H), 3.91 (s, 3H), 0.56 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.63, 167.58, 138.59, 138.51, 136.55, 135.31, 135.27, 133.17, 131.08, 117.70, 117.51, 54.59. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.38. HRMS (EI) calcd. for $C_{16}H_{16}FO_2Si$ $[M]^+$: 288.0982, Found: 288.0973.

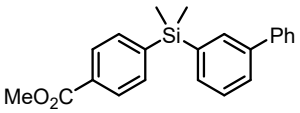


3f: Synthesized from **2f** by following general procedure A on a 0.2 mmol scale. 37.1 mg obtained, 61% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 2H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 3.92 (s, 3H), 0.57 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.16, 144.01, 135.79, 135.71, 135.50, 134.11, 130.78, 128.65, 128.22, 52.17. HRMS (EI) calcd. for $C_{16}H_{17}ClO_2Si$ $[M]^+$: 304.0686, Found: 304.0682.

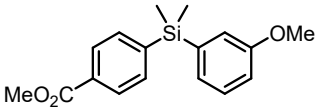


3g: Synthesized from **2g** by following general procedure A on a 0.2 mmol scale. 34.5 mg obtained, 51% isolated yield,

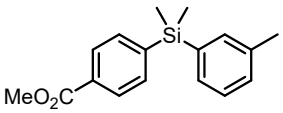
colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.63-7.56 (m, 6H), 3.92 (s, 3H), 0.60 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.12, 143.39, 134.42, 134.13, 131.48, 131.16, 130.95, 128.73, 124.52, 124.48, 124.44, 52.20, -2.74. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.97. HRMS (EI) calcd. for $C_{17}H_{17}F_3O_2Si$ $[M]^+$: 338.0950, Found: 338.0945.



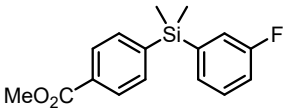
3h: Synthesized from **2h** by following general procedure A on a 0.2 mmol scale. 41.6 mg obtained, 60% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 6.8 Hz, 2H), 7.71 (s, 1H), 7.64-7.58 (m, 3H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 6.1 Hz, 1H), 7.46-7.40 (m, 3H), 7.33 (t, *J* = 7.3 Hz, 1H), 3.90 (s, 3H), 0.61 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.71, 147.03, 143.82, 143.26, 140.41, 136.68, 135.59, 135.37, 133.14, 131.27, 131.11, 130.84, 130.82, 129.80, 129.76, 54.60. HRMS (EI) calcd. for $C_{22}H_{22}O_3Si$ $[M]^+$: 346.1389, Found: 346.1379.



3i: Synthesized from **2i** by following general procedure A on a 0.2 mmol scale. 31.9 mg obtained, 53% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.1 Hz, 1H), 7.04 (s, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 3.92 (s, 3H), 3.79 (s, 3H), 0.58 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.25, 159.07, 144.55, 139.00, 134.17, 130.62, 129.21, 128.58, 126.42, 119.86, 114.42, 52.13, -2.56. HRMS (EI) calcd. for $C_{17}H_{20}O_3Si$ $[M]^+$: 300.1182, Found: 300.1175.

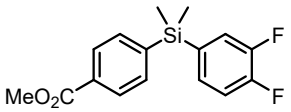


3j: Synthesized from **2j** by following general procedure A on a 0.2 mmol scale. 30.2 mg obtained, 53% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.29 (s, 2H), 7.25-7.16 (m, 2H), 3.89 (s, 3H), 2.32 (s, 3H), 0.55 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.29, 144.87, 137.33, 137.17, 134.78, 134.19, 131.22, 130.53, 128.55, 127.89, 52.14, 21.55, -2.51. HRMS (EI) calcd. for $C_{17}H_{20}O_2Si$ $[M]^+$: 284.1233, Found: 284.1227.

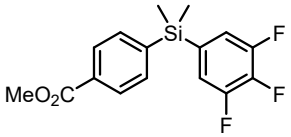


3k: Synthesized from **2k** by following general procedure A on a 0.2 mmol scale. 27.7 mg obtained, 48% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 7.7

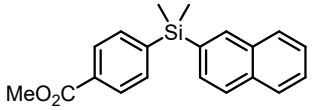
Hz, 2H), 7.38-7.33 (m, 1H), 7.28 (s, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.07 (t, *J* = 8.2 Hz, 1H), 3.94 (s, 3H), 0.60 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.18, 163.85, 143.80, 140.58, 134.13, 130.81, 129.82, 129.75, 129.68, 129.66, 128.68, 120.55, 116.22, 52.19, -2.67. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.40. HRMS (EI) calcd. for $C_{16}H_{17}FO_2Si$ $[M]^+$: 288.0982, Found: 288.0974.



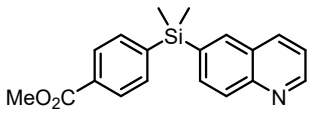
3l: Synthesized from **2l** by following general procedure A on a 0.2 mmol scale. 31.9 mg obtained, 52% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.27-7.14 (m, 3H), 3.92 (s, 3H), 0.57 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.11, 152.60, 152.47, 151.68, 151.56, 150.11, 149.98, 149.07, 143.45, 134.88, 134.81, 134.07, 130.94, 130.51, 130.41, 128.73, 122.70, 122.56, 117.42, 117.26, 52.20, -2.61. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -136.68, -138.86. HRMS (EI) calcd. for $C_{16}H_{16}F_2O_2Si$ $[M]^+$: 306.0888, Found: 306.0880.



3m: Synthesized from **2m** by following general procedure A on a 0.2 mmol scale. 33.1 mg obtained, 51% isolated yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.03 (t, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 0.57 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.98, 141.45, 133.00, 130.16, 125.65, 116.61, 116.43, 51.20, -3.82. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -134.64, -159.17. for $C_{16}H_{15}F_3O_2Si$ $[M]^+$: 324.0793, Found: 324.0788.

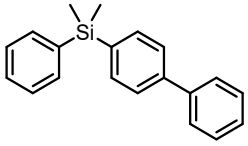


3n: Synthesized from **2n** by following general procedure A on a 0.2 mmol scale. 29.5 mg obtained, 46% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.2 Hz, 3H), 7.82 (d, *J* = 8.2 Hz, 3H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.45 (m, 2H), 3.90 (s, 3H), 0.65 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.73, 147.14, 137.48, 137.23, 136.73, 136.32, 135.39, 133.13, 132.68, 131.09, 130.60, 130.23, 129.71, 129.10, 128.56, 54.61, 0.00. HRMS (EI) calcd. for $C_{20}H_{20}O_2Si$ $[M]^+$: 320.1233, Found: 320.1223.

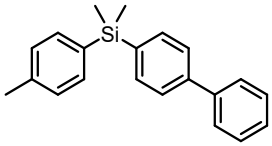


3o: Synthesized from **2o** by following general procedure A on a 0.2 mmol scale. 32.8 mg obtained, 51% isolated yield,

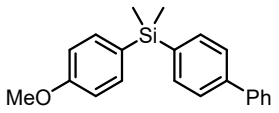
colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.11 (dd, *J* = 18.7, 8.3 Hz, 2H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.96 (s, 1H), 7.81 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.91 (s, 3H), 0.67 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.17, 151.04, 148.67, 143.99, 136.28, 136.25, 134.89, 134.21, 133.96, 130.84, 128.70, 128.68, 52.17, -2.53. HRMS (EI) calcd. for $C_{19}H_{19}NO_2Si$ $[M]^+$: 321.1185, Found: 321.1178.



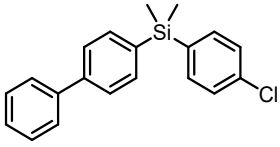
4a: Synthesized from **1b** by following general procedure A on a 0.2 mmol scale. 43.3 mg obtained, 75% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 8H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.41 – 7.28 (m, 4H), 0.59 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.22, 143.42, 140.51, 139.35, 137.02, 136.54, 131.50, 131.11, 130.20, 129.73, 129.51, 128.91, 0.00. HRMS (EI) calcd. for $C_{20}H_{20}Si$ $[M]^+$: 288.1334, Found: 288.1331.



4b: Synthesized from **1c** by following general procedure A on a 0.2 mmol scale. 41.7 mg obtained, 69% isolated yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.3 Hz, 6H), 7.50 – 7.44 (m, 4H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 2H), 2.38 (s, 3H), 0.60 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.04, 143.35, 141.32, 139.53, 136.91, 136.71, 136.51, 131.02, 130.97, 129.62, 129.42, 128.79, 23.75, 0.00. HRMS (EI) calcd. for $C_{14}H_{16}Si$ $[M]^+$: 302.1491, Found: 302.1483.

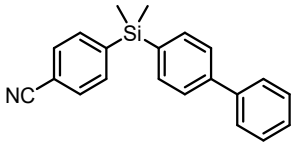


4c: Synthesized from **1d** by following general procedure A on a 0.2 mmol scale. 43.3 mg obtained, 68% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (m, *J* = 7.8 Hz, 6H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 2H), 3.81 (s, 3H), 0.56 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.67, 143.91, 143.23, 139.59, 137.80, 136.77, 131.04, 130.89, 129.50, 129.29, 128.66, 115.78, 57.16, 0.00. HRMS (EI) calcd. for $C_{21}H_{22}OSi$ $[M]^+$: 318.1440, Found: 318.1435.

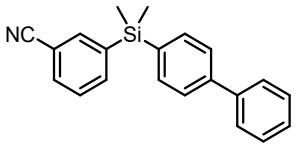


4d: Synthesized from **1e** by following general procedure A on a 0.2 mmol scale. 42.6 mg obtained, 66% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m,

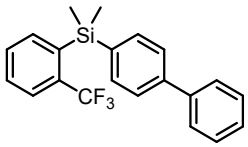
6H), 7.45 (q, *J* = 7.9 Hz, 4H), 7.35 (t, *J* = 7.9 Hz, 3H), 0.57 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.47, 143.33, 138.92, 138.74, 137.94, 137.91, 136.99, 131.18, 129.85, 129.54, 129.03, 0.00. HRMS (EI) calcd. for $C_{20}H_{19}ClSi$ $[M]^+$: 322.0945, Found: 322.0943.



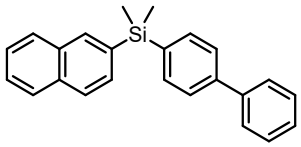
4e: Synthesized from **1f** by following general procedure A on a 0.2 mmol scale. 40.7 mg obtained, 65% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 10H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 0.61 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.34, 142.45, 140.79, 135.16, 134.65, 134.62, 131.10, 128.86, 127.62, 127.17, 126.82, 119.01, 112.74, -2.66. HRMS (EI) calcd. for $C_{21}H_{19}NSi$ $[M]^+$: 313.1287, Found: 313.1281.



4f: Synthesized from **1j** by following general procedure A on a 0.2 mmol scale. 35.7 mg obtained, 57% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.75 (d, *J* = 6.9 Hz, 1H), 7.66 – 7.56 (m, 7H), 7.46 (t, *J* = 7.5 Hz, 3H), 7.37 (t, *J* = 7.9 Hz, 1H), 0.62 (d, *J* = 1.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.50, 140.82, 140.68, 138.25, 137.69, 135.11, 134.60, 132.53, 128.85, 128.42, 127.60, 127.20, 126.86, 119.20, 112.20, -2.61. HRMS (EI) calcd. for $C_{21}H_{19}NSi$ $[M]^+$: 313.1287, Found: 313.1280.

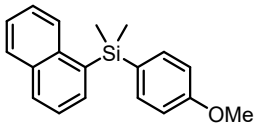


4g: Synthesized from **1h** by following general procedure A on a 0.2 mmol scale. 34.2 mg obtained, 48% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.60 (td, *J* = 13.5, 7.1 Hz, 7H), 7.45 (t, *J* = 7.7 Hz, 3H), 7.36 (t, *J* = 7.3 Hz, 1H), 0.61 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.72, 141.91, 138.29, 135.52, 131.62, 130.22, 129.71, 128.36, 128.09, 127.44, 127.14, 127.11, 127.05, 127.00, 30.65, 0.03, 0.00, -0.03, -0.06. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.70. HRMS (EI) calcd. for $C_{21}H_{19}F_3Si$ $[M]^+$: 356.1208, Found: 356.1199.

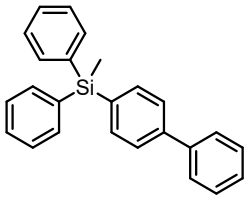


4h: Synthesized from **1i** by following general procedure A on a 0.2 mmol scale. 30.5 mg obtained, 45% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.83

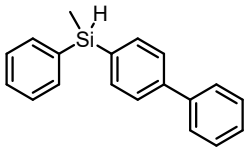
(d, J = 7.2 Hz, 3H), 7.64 – 7.57 (m, 7H), 7.49 – 7.41 (m, 4H), 7.34 (t, J = 7.3 Hz, 1H), 0.66 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.32, 139.24, 137.19, 137.02, 136.05, 135.19, 132.66, 131.04, 130.39, 129.99, 129.67, 129.44, 129.35, 128.87, 128.72, 128.22. HRMS (EI) calcd. for $C_{24}H_{22}Si$ [M]$^+$: 338.1491, Found: 338.1479.



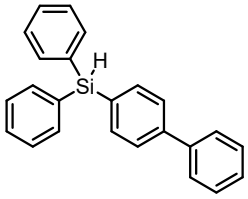
4i: Synthesized from **1j** by following general procedure A on a 0.2 mmol scale. 23.9 mg obtained, 41% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.3 Hz, 1H), 7.87 (dd, J = 14.3, 8.1 Hz, 2H), 7.71 (d, J = 6.8 Hz, 1H), 7.48 – 7.42 (m, 4H), 7.36 (t, J = 7.3 Hz, 1H), 6.88 (d, J = 8.5 Hz, 2H), 3.80 (s, 3H), 0.68 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.15, 137.70, 136.83, 136.38, 135.35, 134.15, 130.88, 130.41, 129.69, 129.38, 126.34, 126.07, 125.83, 114.42, 55.75, 0.00. HRMS (EI) calcd. for $C_{19}H_{20}OSi$ [M]$^+$: 292.1283, Found: 292.1274.



4j: Synthesized from **1k** by following general procedure A on a 0.2 mmol scale. 29.5 mg obtained, 42% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.52 (m, 10H), 7.47 – 7.32 (m, 9H), 0.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.11, 140.99, 136.09, 135.78, 135.31, 134.87, 129.45, 128.80, 127.91, 127.47, 127.18, 126.59, -3.31. HRMS (EI) calcd. for $C_{25}H_{22}Si$ [M]$^+$: 350.1491, Found: 350.1495.



4k: Synthesized from **1l** by following general procedure A on a 0.2 mmol scale. 42.8 mg obtained, 78% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 8H), 7.44 (ddd, J = 25.5, 17.4, 7.2 Hz, 6H), 5.15 – 4.93 (m, 1H), 0.71 (d, J = 2.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.26, 139.91, 134.29, 134.24, 133.82, 133.01, 128.54, 127.75, 126.98, 126.44, 126.13, 125.68, -5.99. HRMS (EI) calcd. for $C_{19}H_{18}Si$ [M]$^+$: 274.1178, Found: 274.1175.

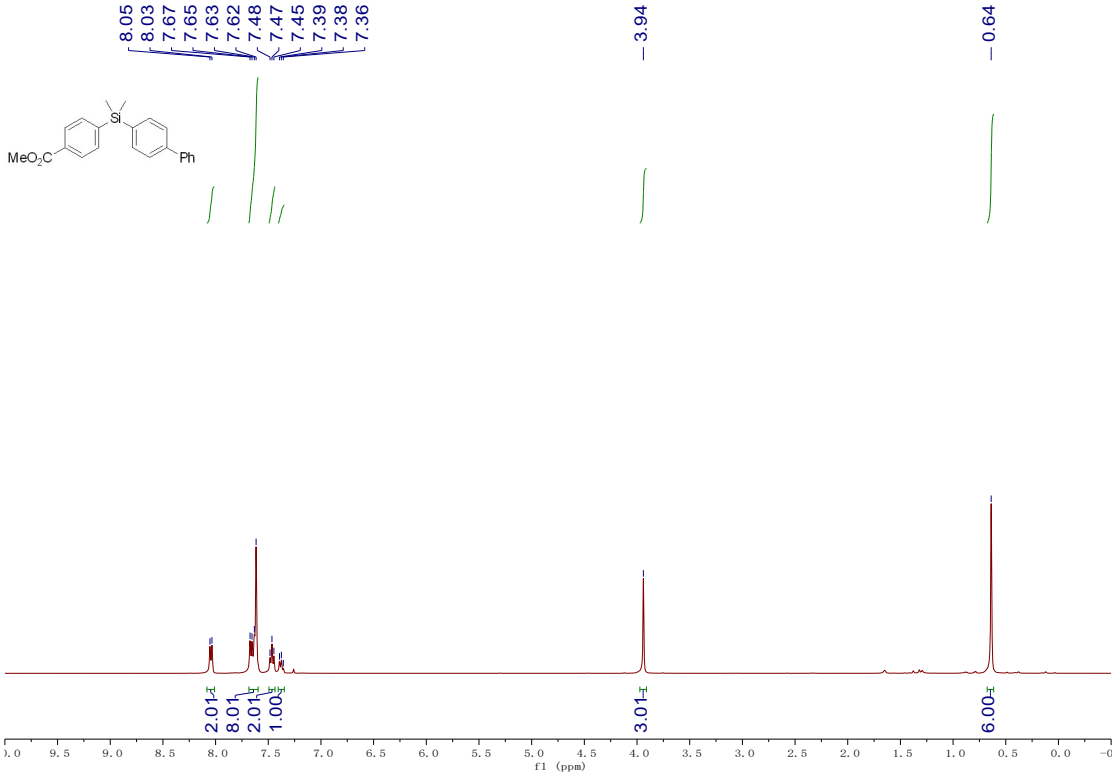


4l: Synthesized from **1m** by following general procedure A on a 0.2 mmol scale. 37.0 mg obtained, 55% isolated yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 28.9 Hz, 10H), 7.35 (s, 9H), 5.53 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.58,

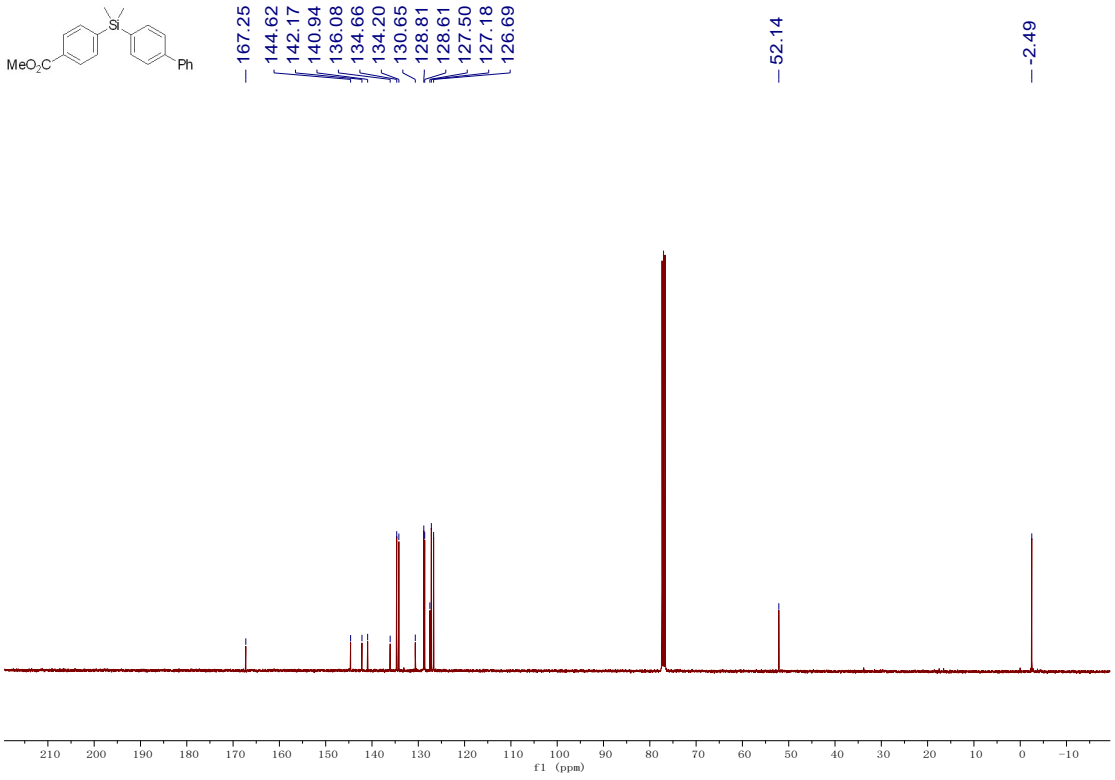
140.91, 136.33, 135.86, 133.34, 132.07, 129.90, 128.84, 128.13, 127.58, 127.21, 126.82. HRMS (EI) calcd. for $C_{24}H_{20}Si$ $[M]^+$: 336.1334, Found: 336.1321.

5. NMR Spectra

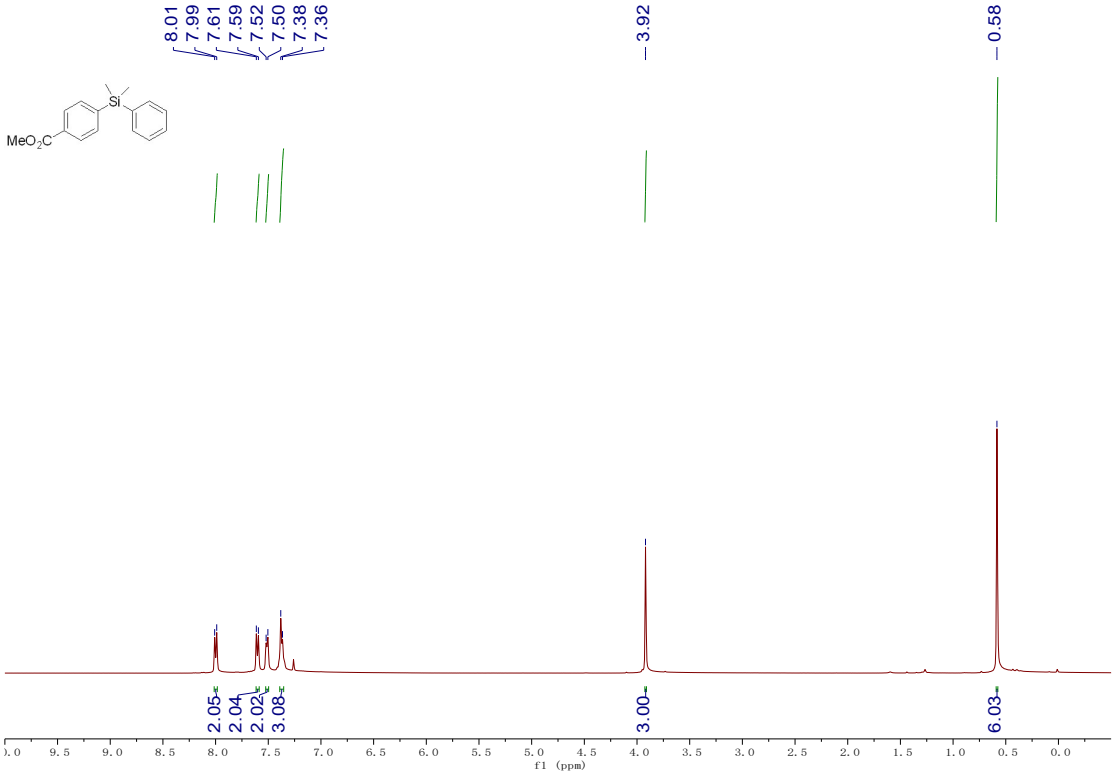
^{1}H NMR for **3a**



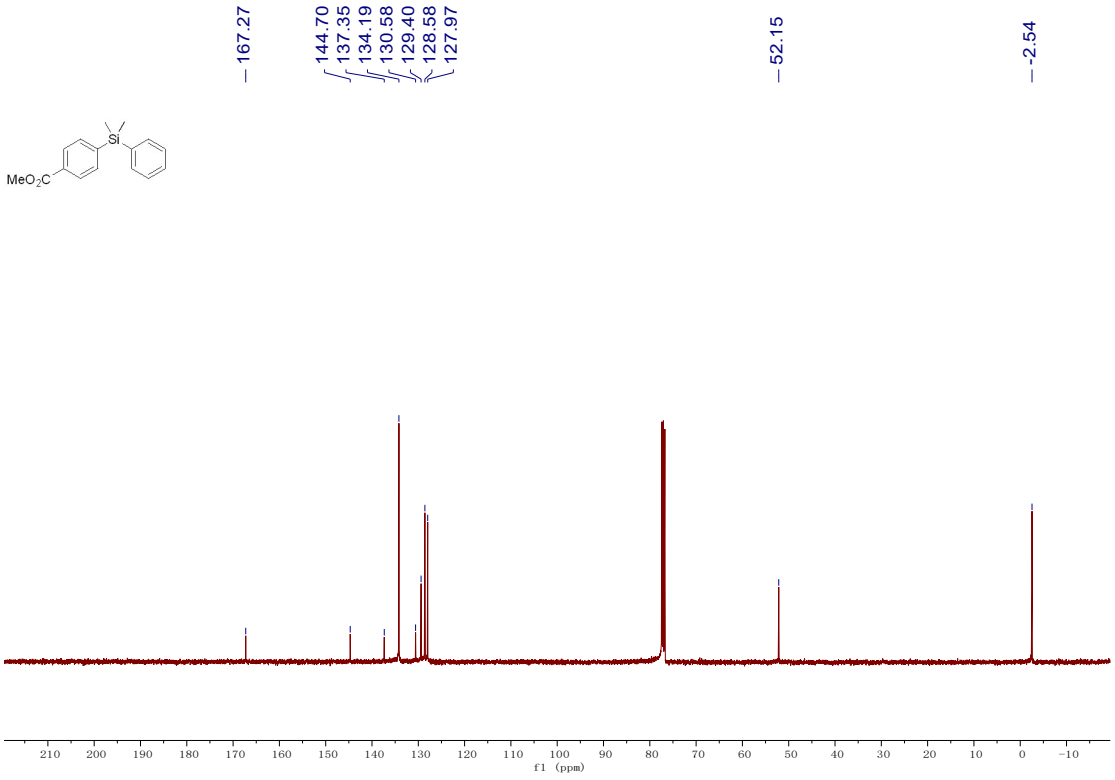
^{13}C NMR for **3a**



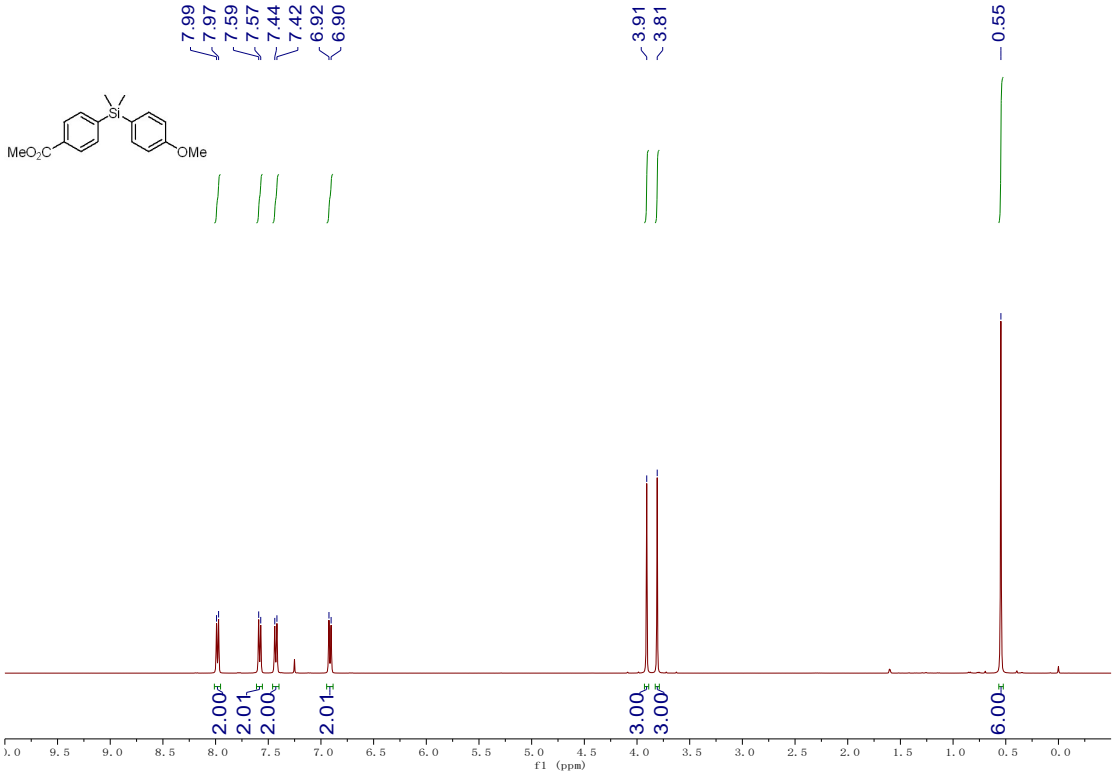
^{1}H NMR for **3b**



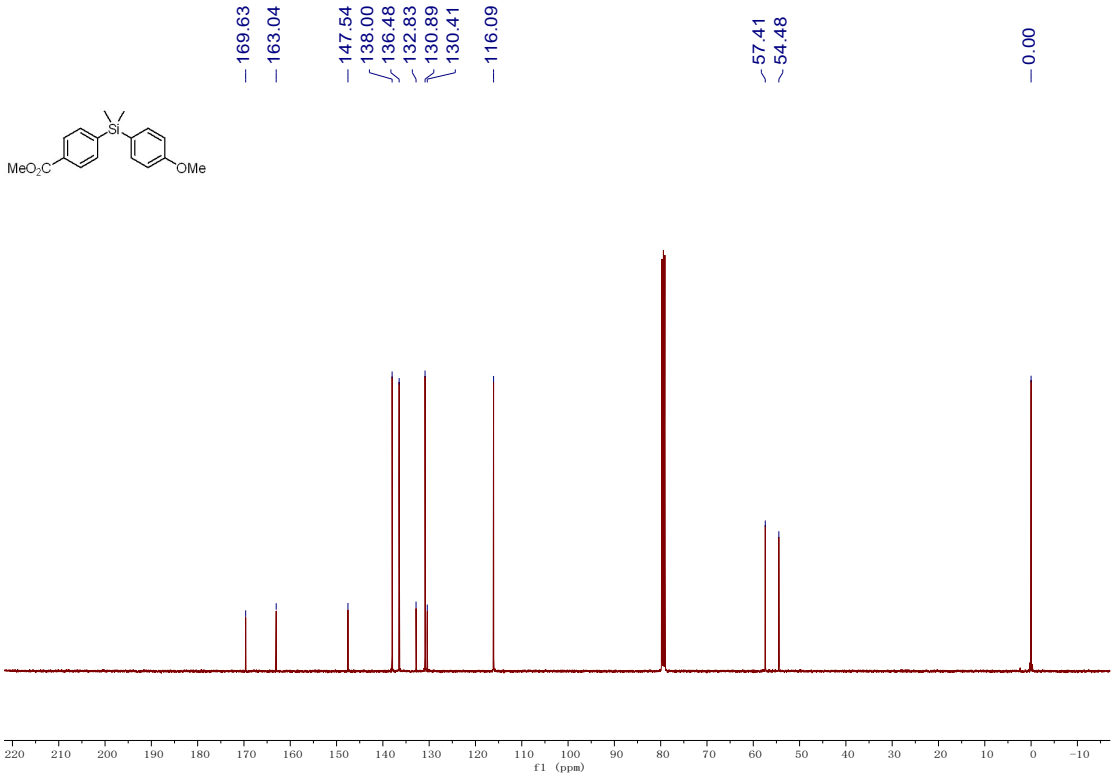
^{13}C NMR for **3b**



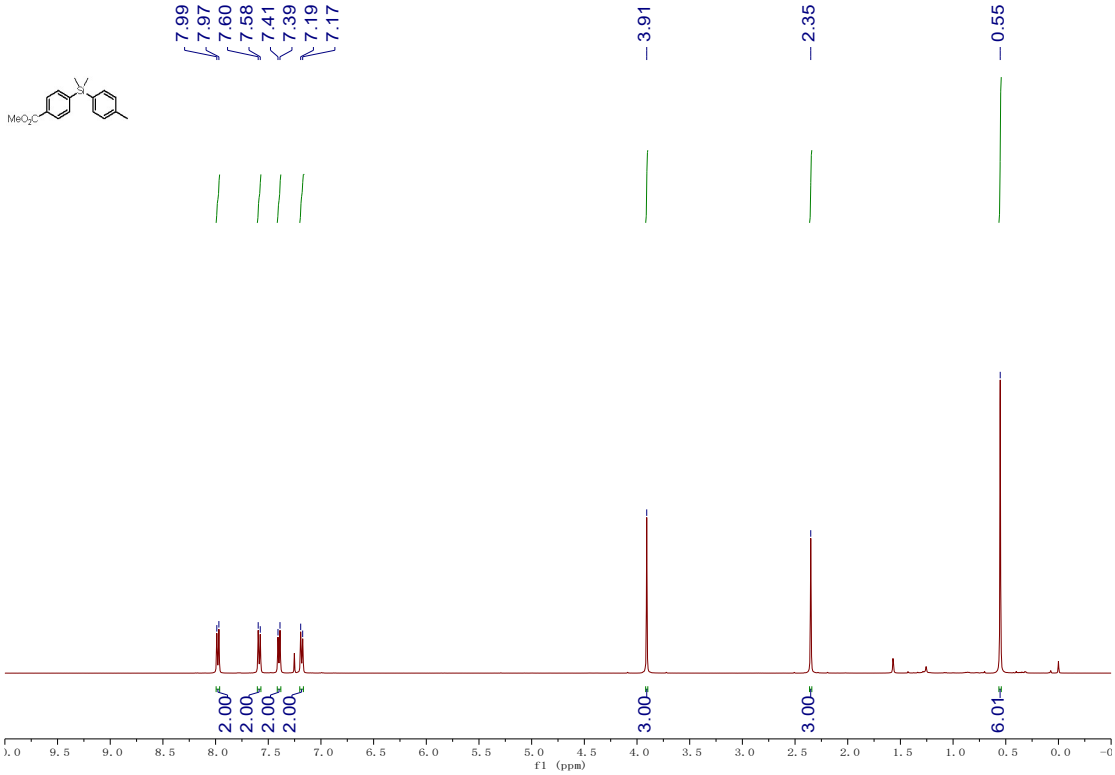
^{1}H NMR for **3c**



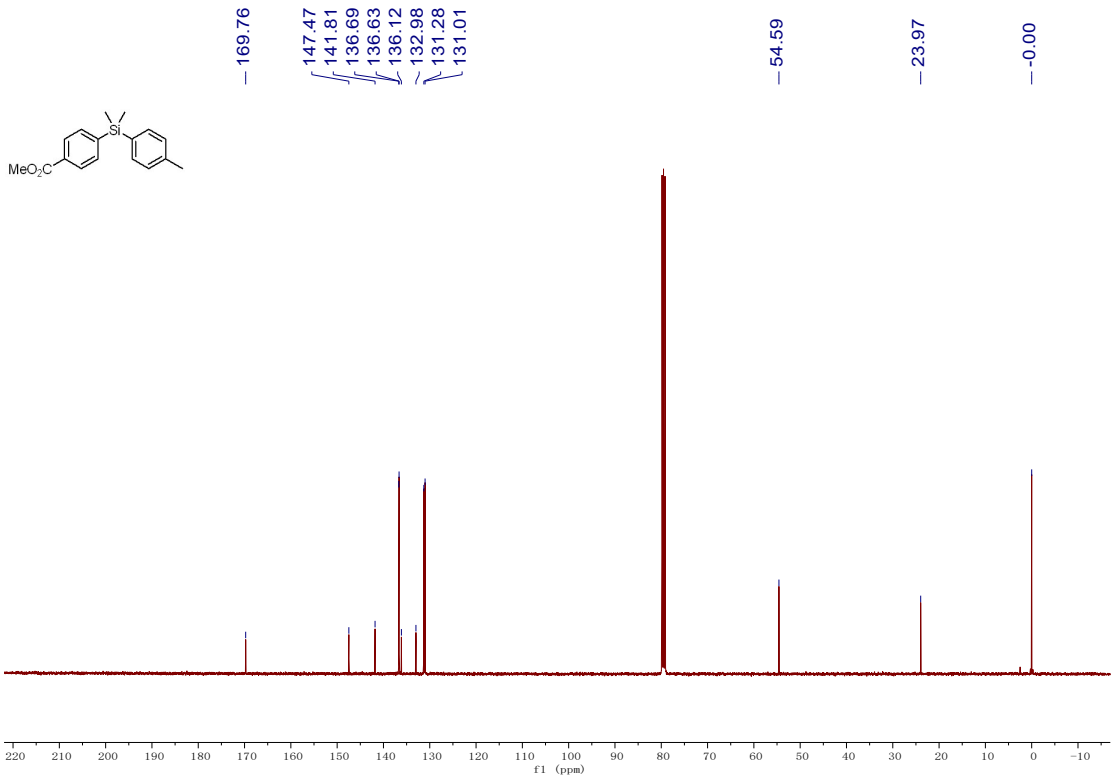
^{13}C NMR for **3c**



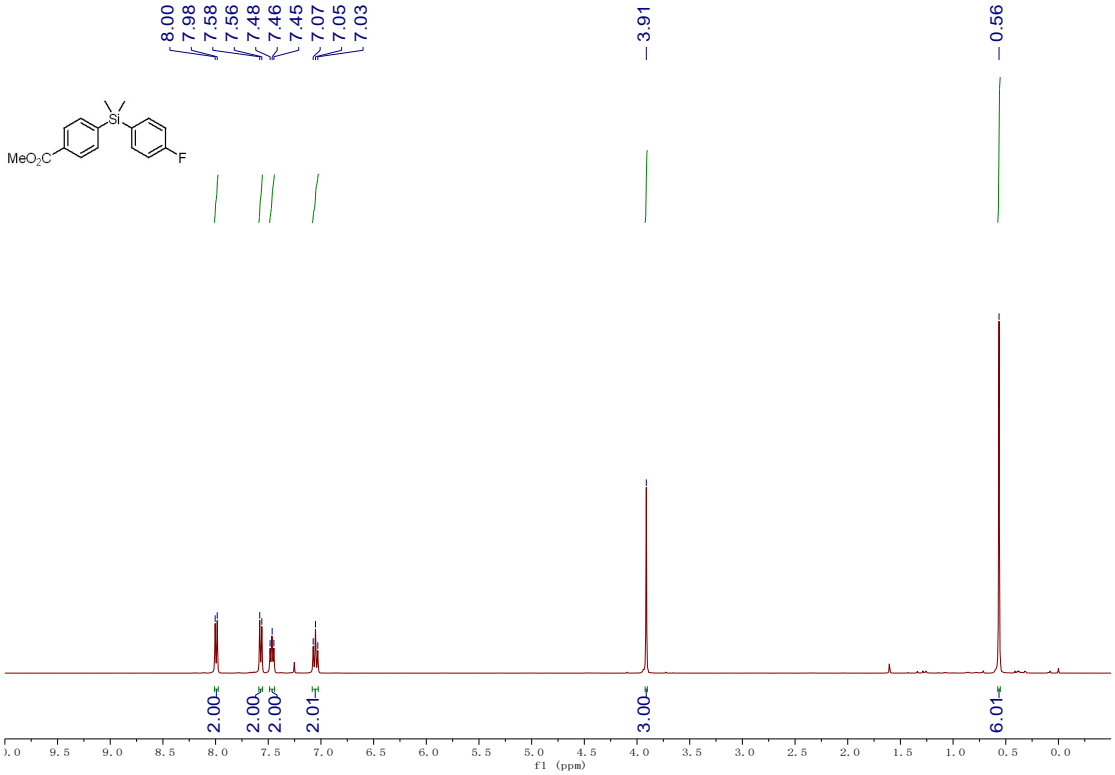
^{1}H NMR for **3d**



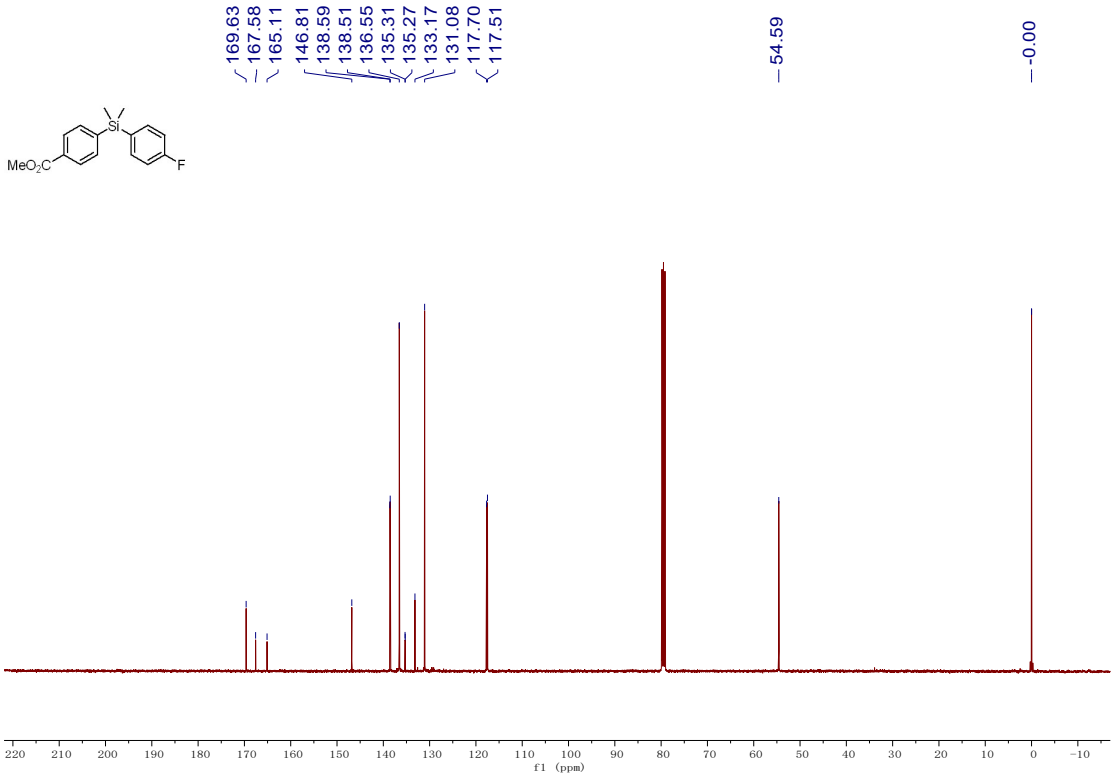
^{13}C NMR for **3d**



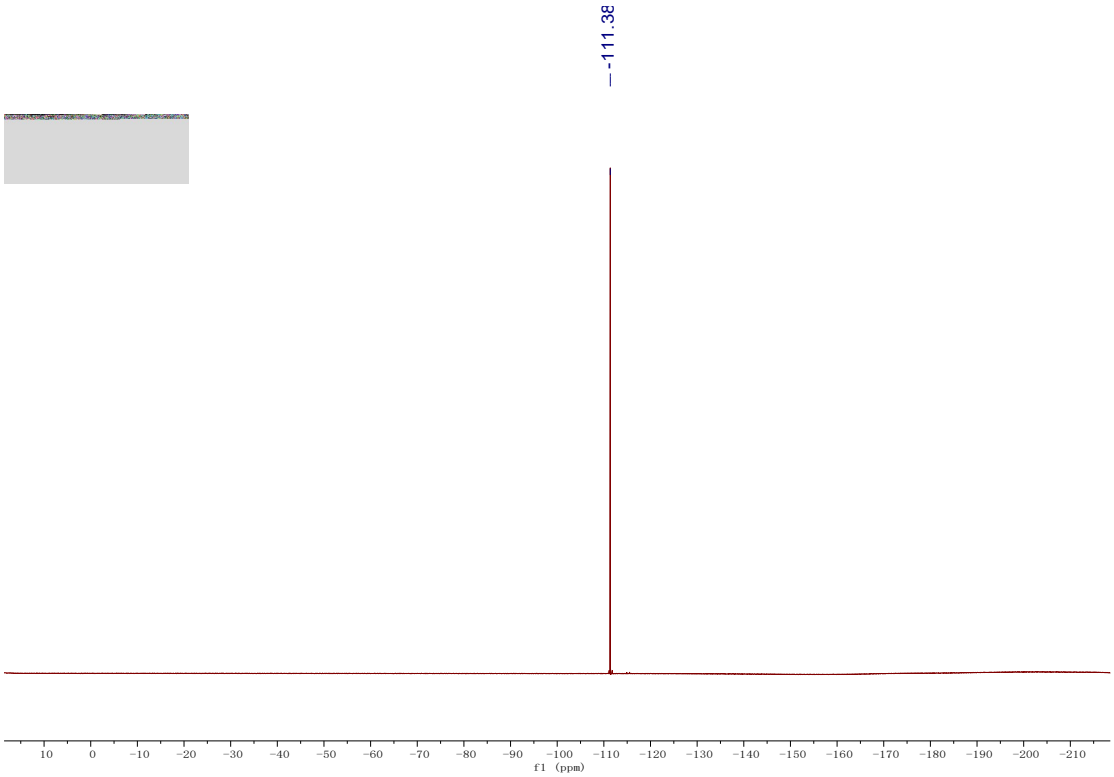
^{1}H NMR for **3e**



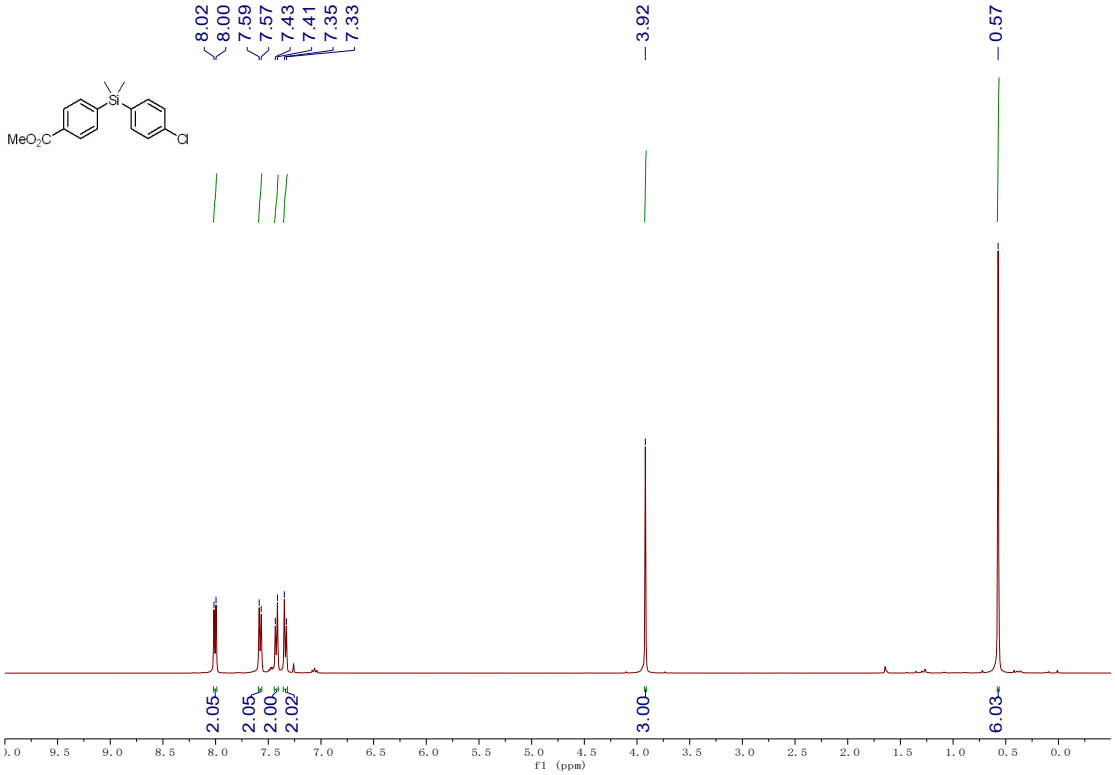
^{13}C NMR for **3e**



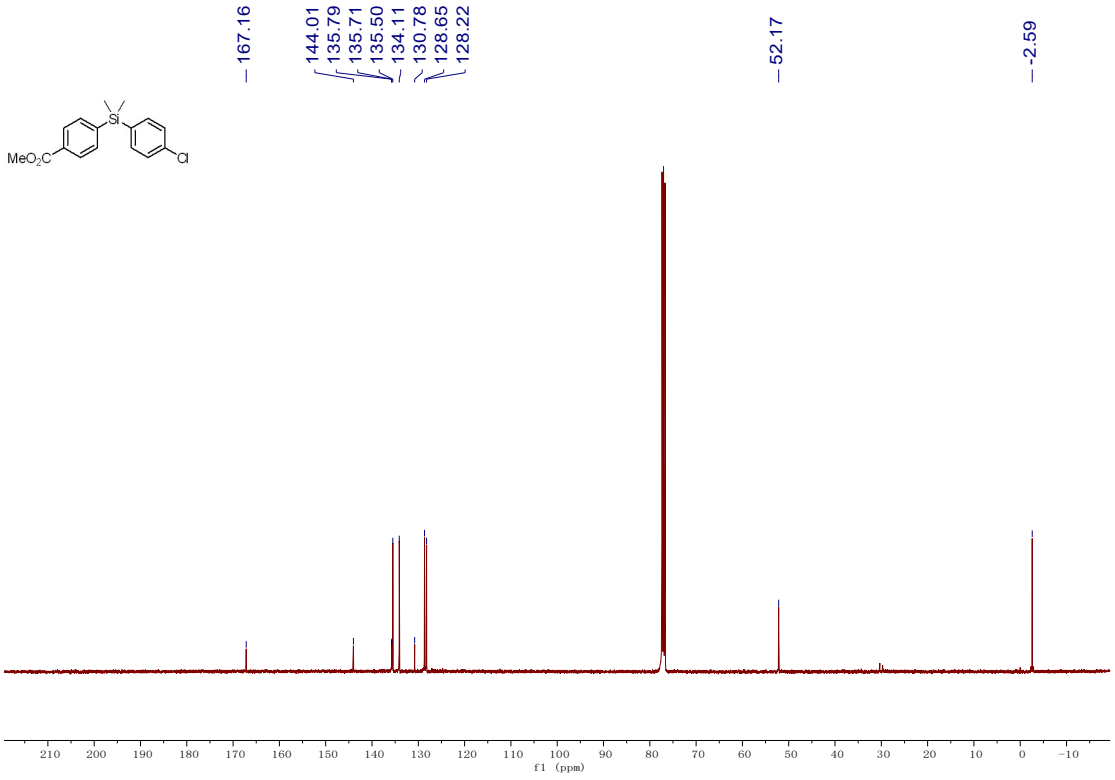
^{19}F NMR for **3e**



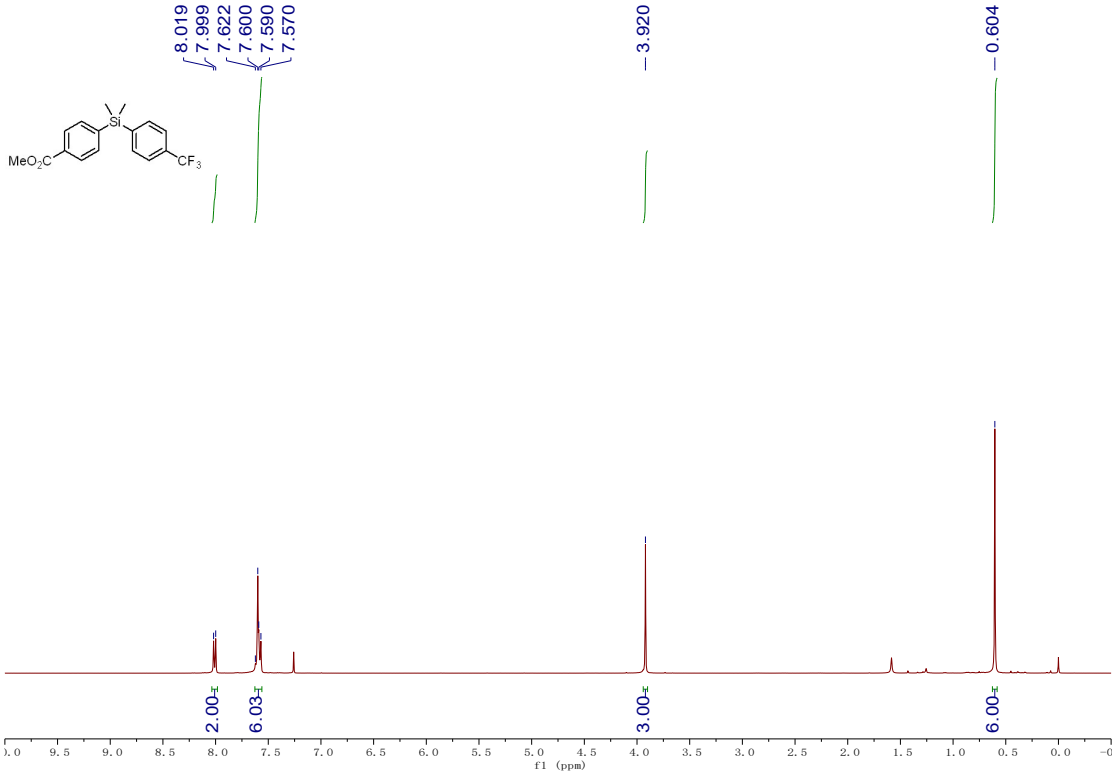
^{1}H NMR for **3f**



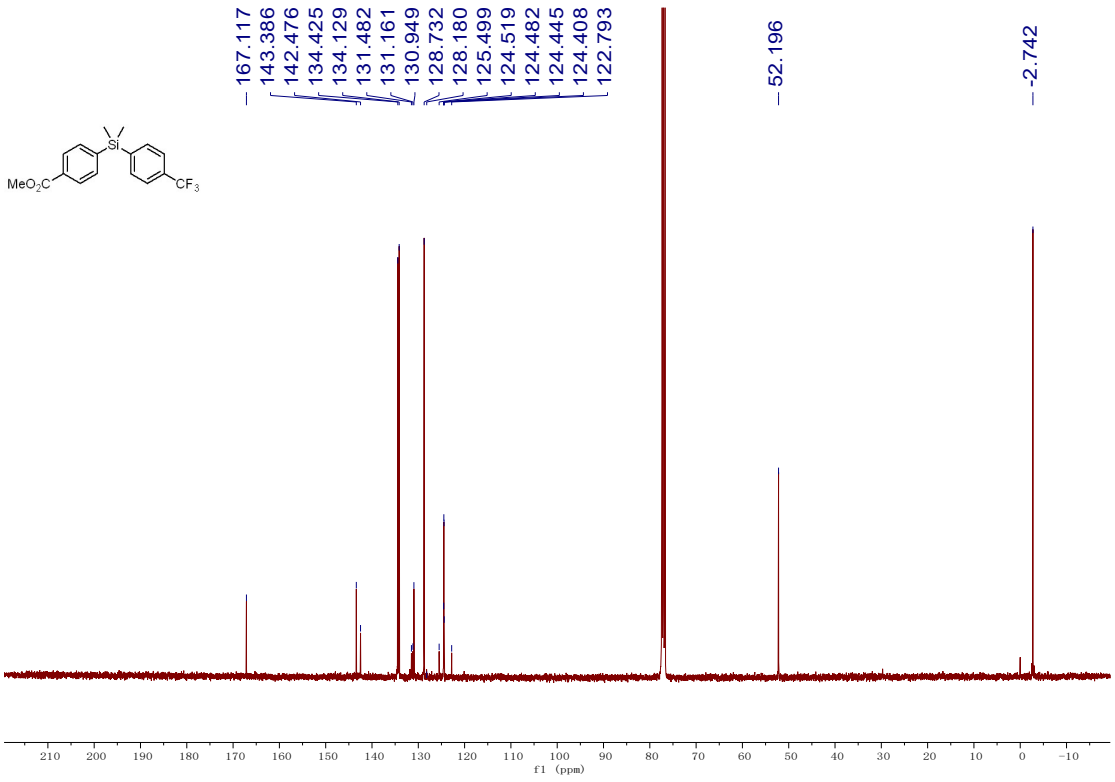
^{13}C NMR for **3f**



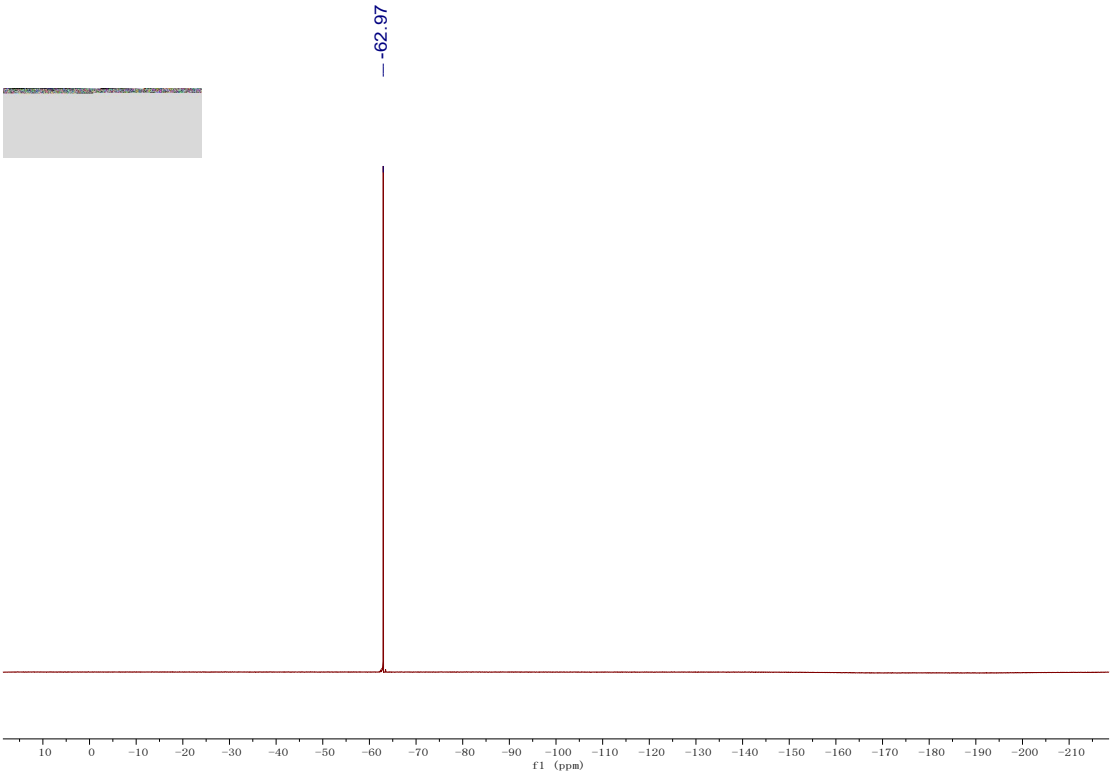
^{1}H NMR for **3g**



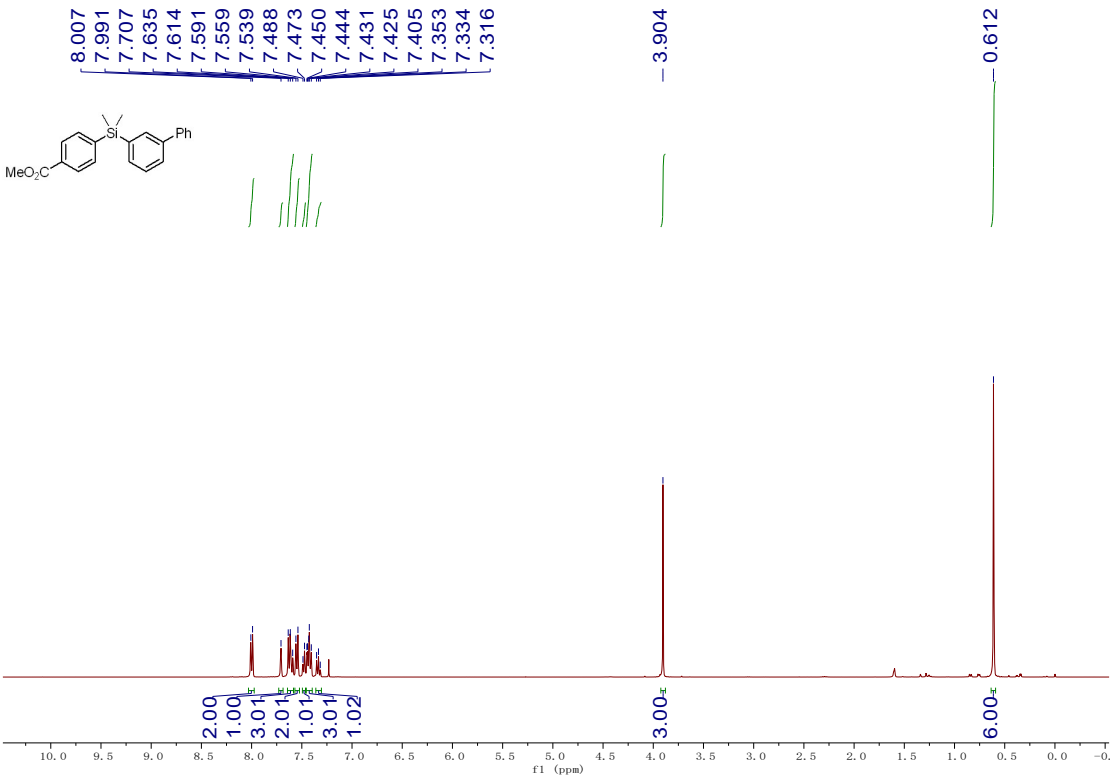
^{13}C NMR for **3g**



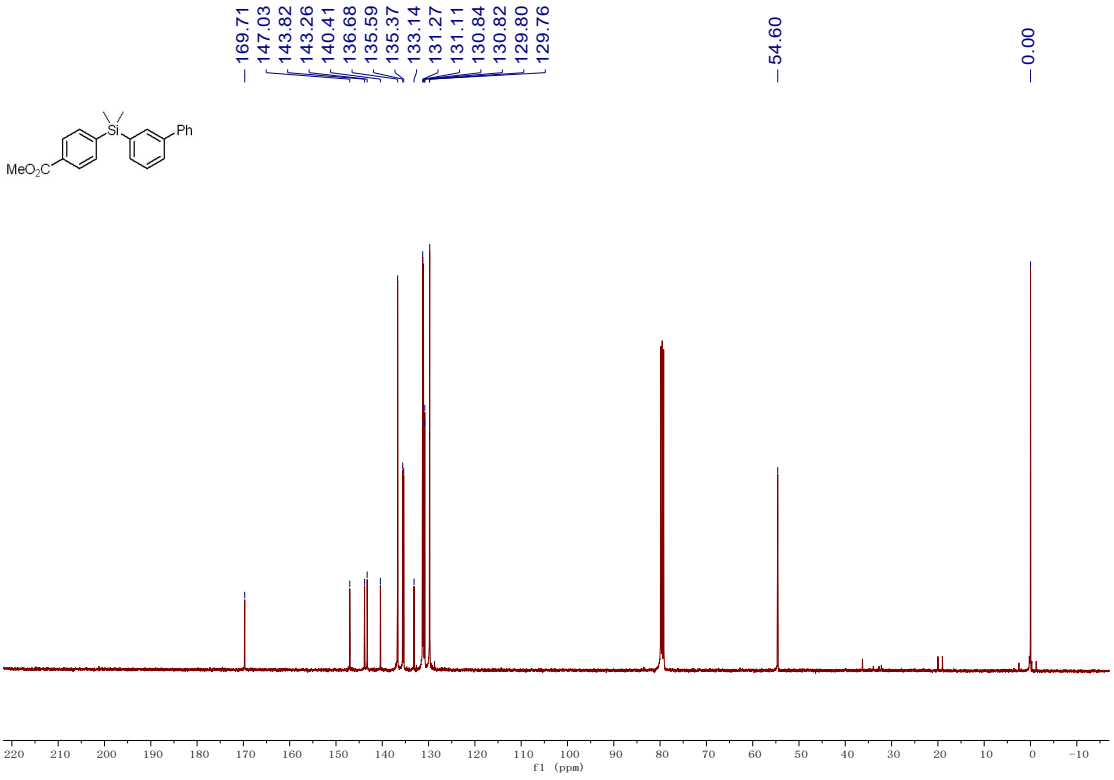
^{19}F NMR for **3g**



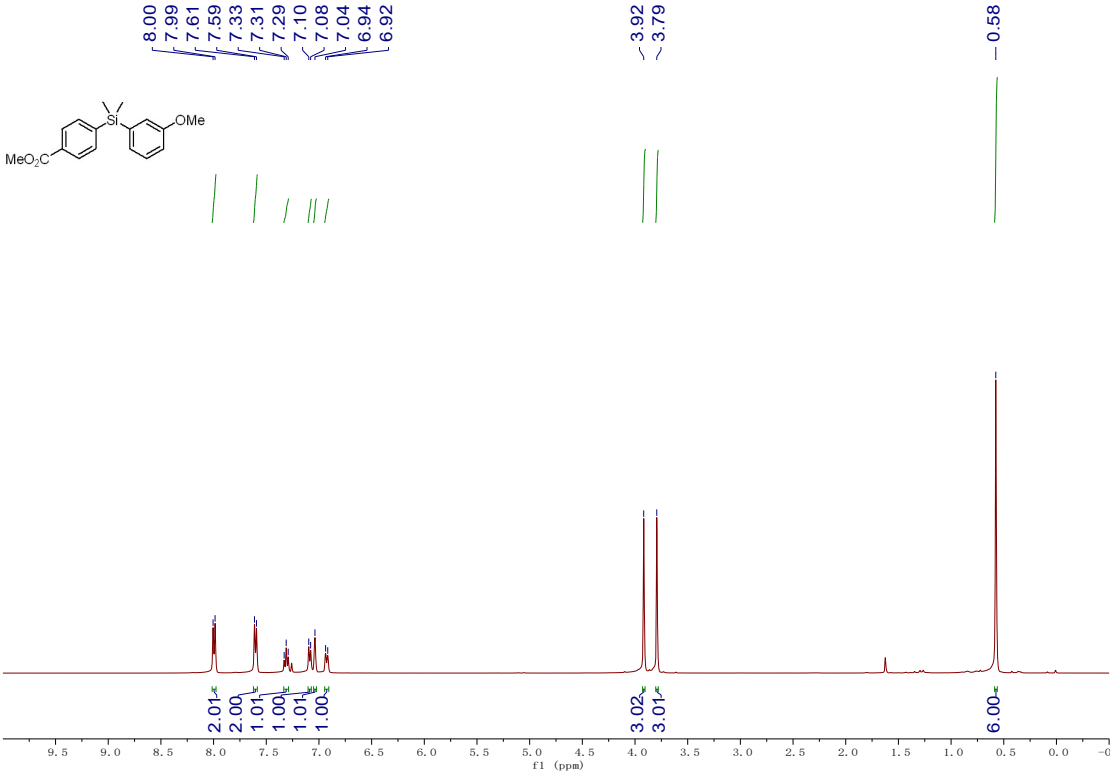
^{1}H NMR for **3h**



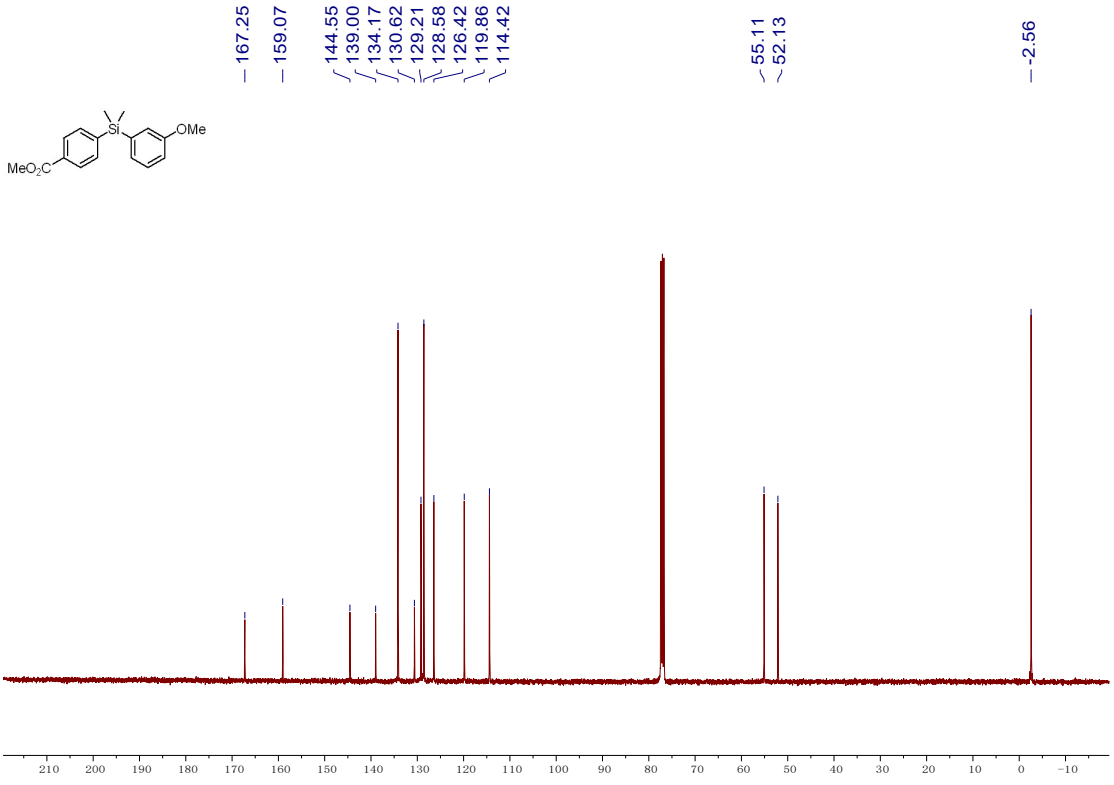
^{13}C NMR for **3h**



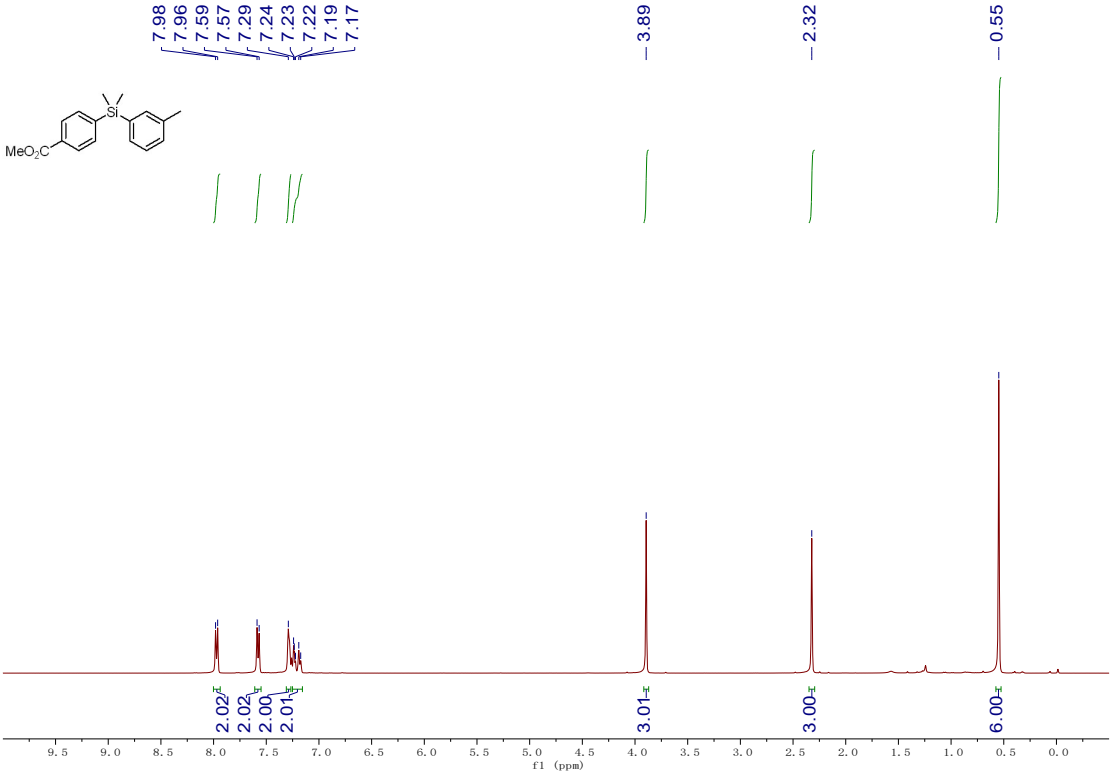
^{1}H NMR for **3i**



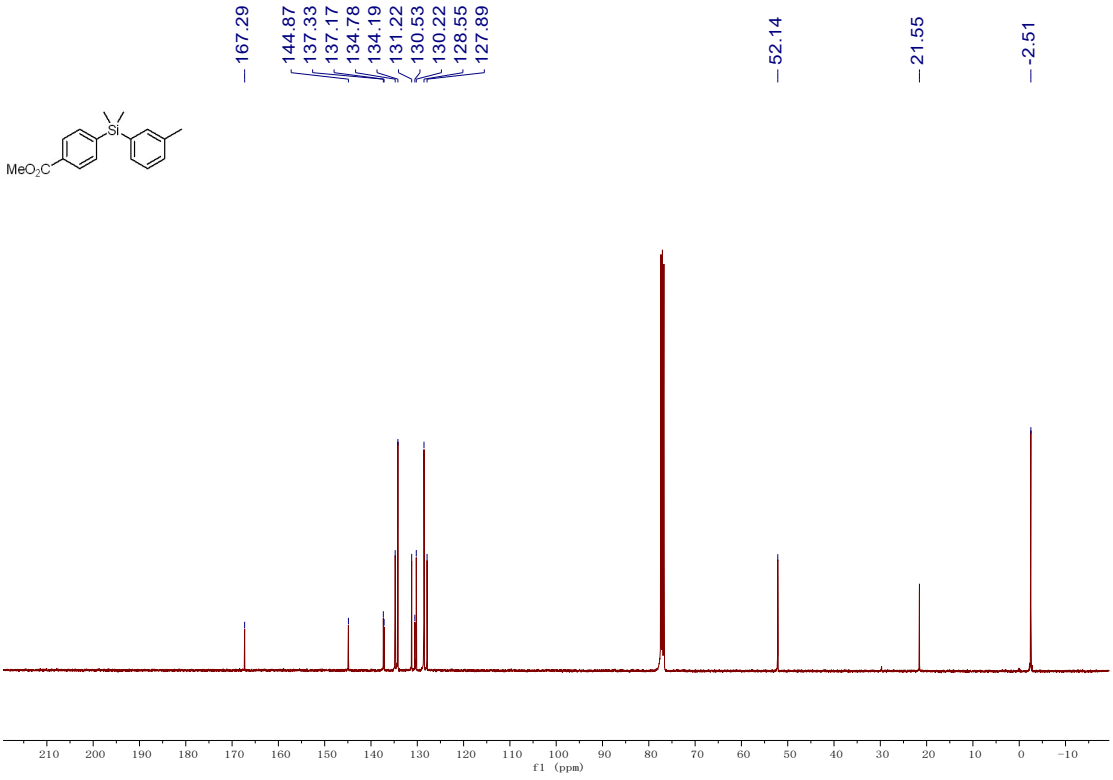
^{13}C NMR for **3i**



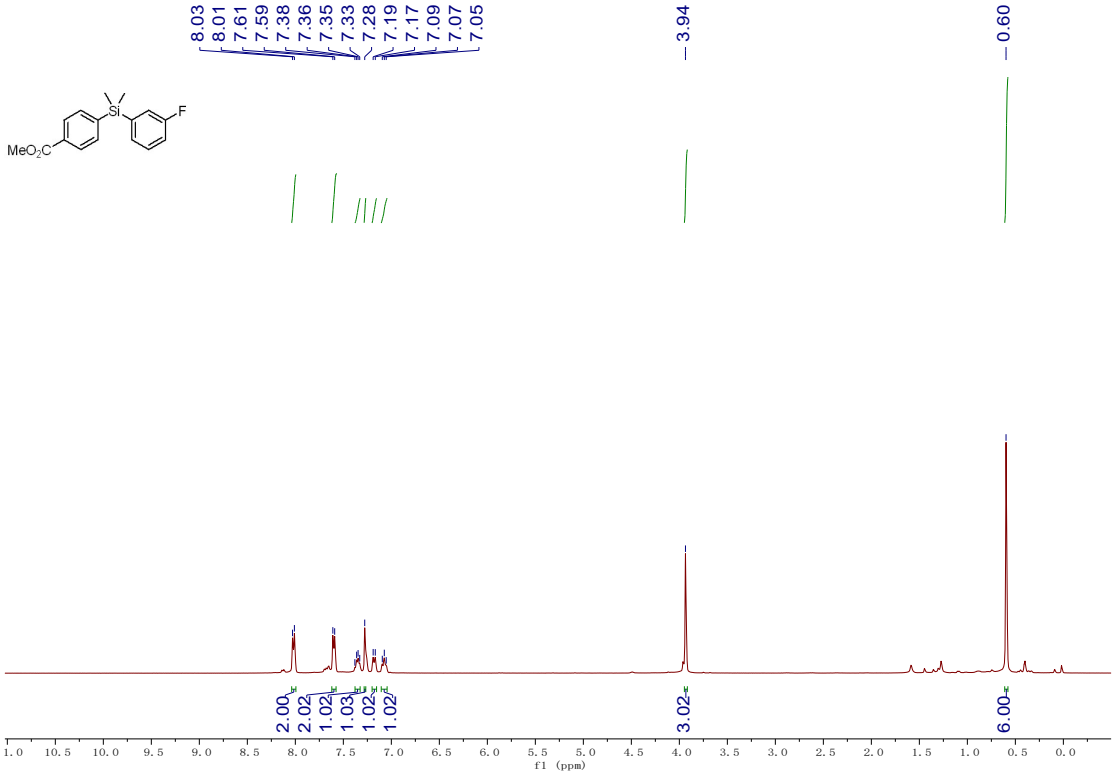
^{1}H NMR for **3j**



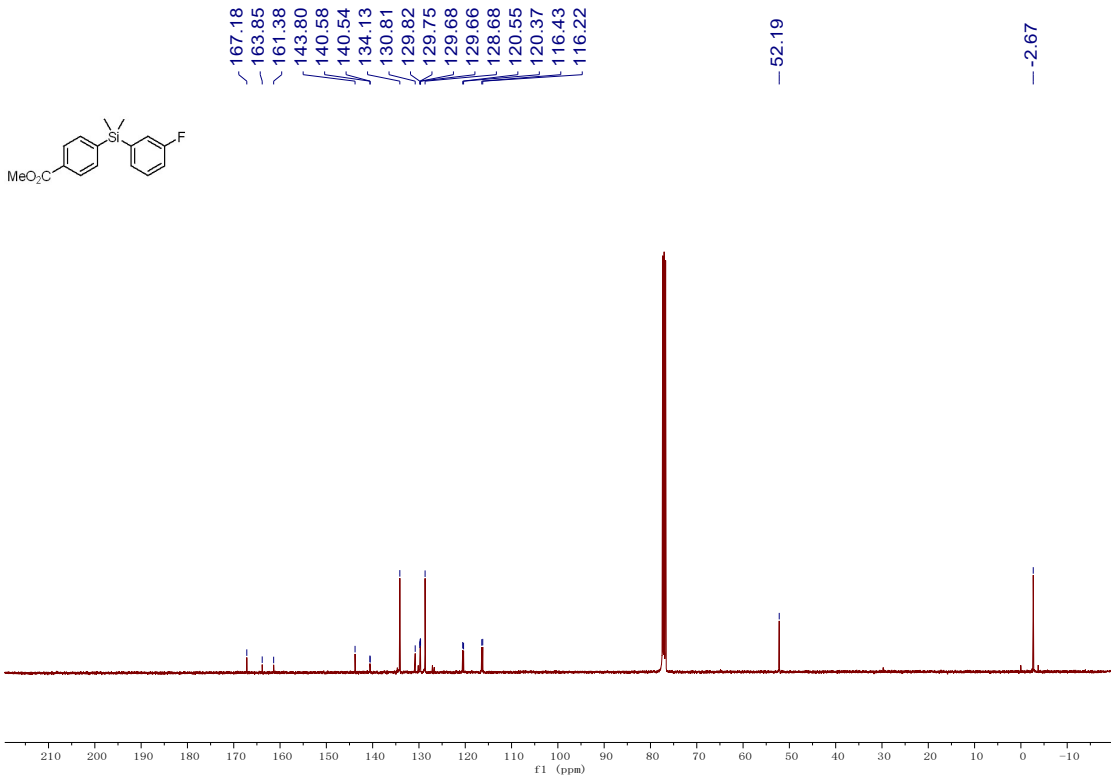
^{13}C NMR for **3j**



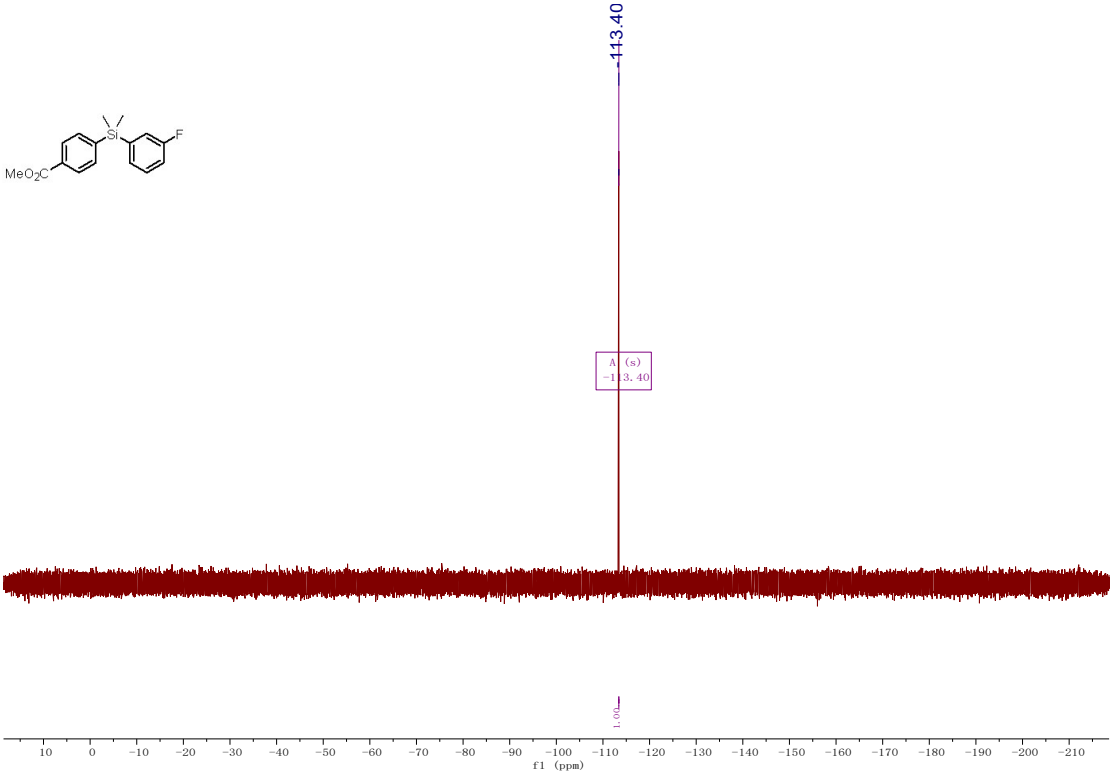
^{1}H NMR for **3k**



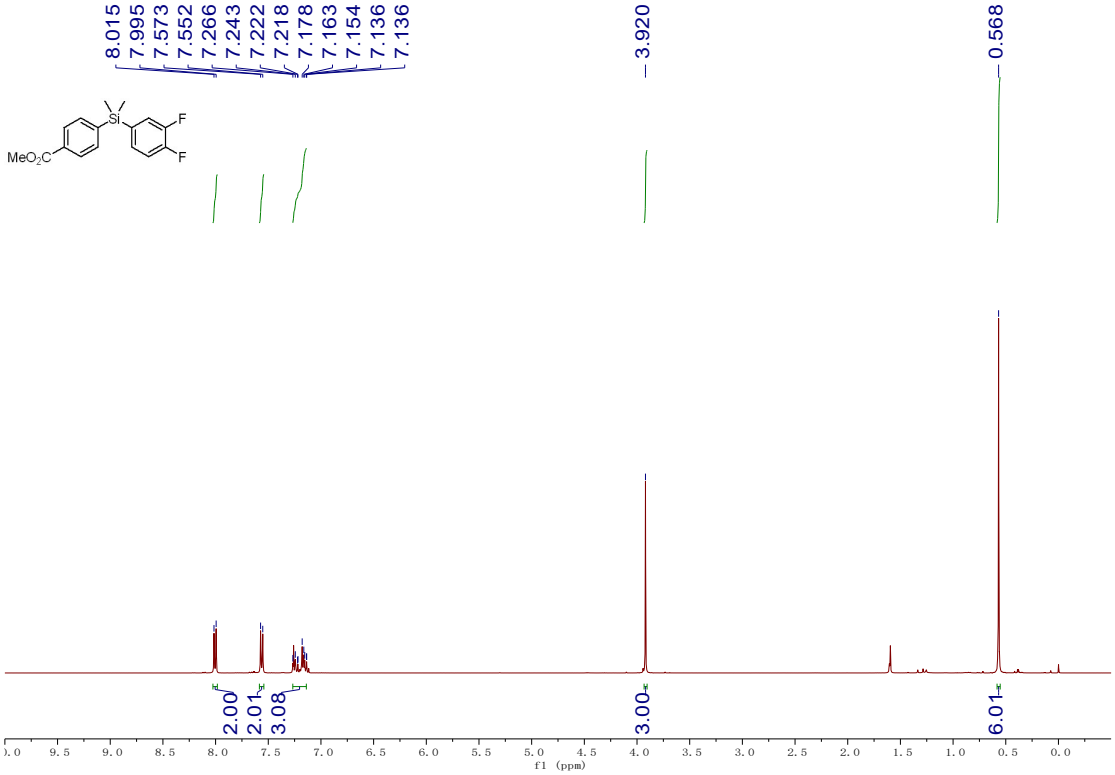
^{13}C NMR for **3k**



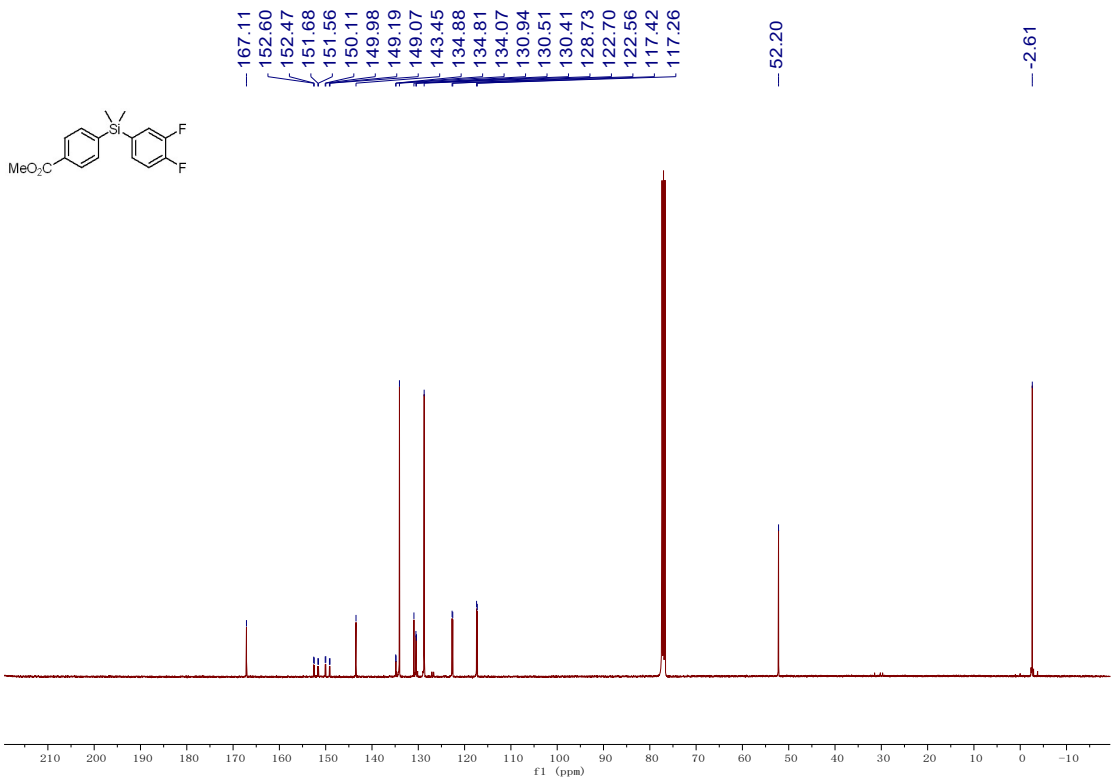
^{19}F NMR for **3k**



^{1}H NMR for **3l**



^{13}C NMR for **3l**



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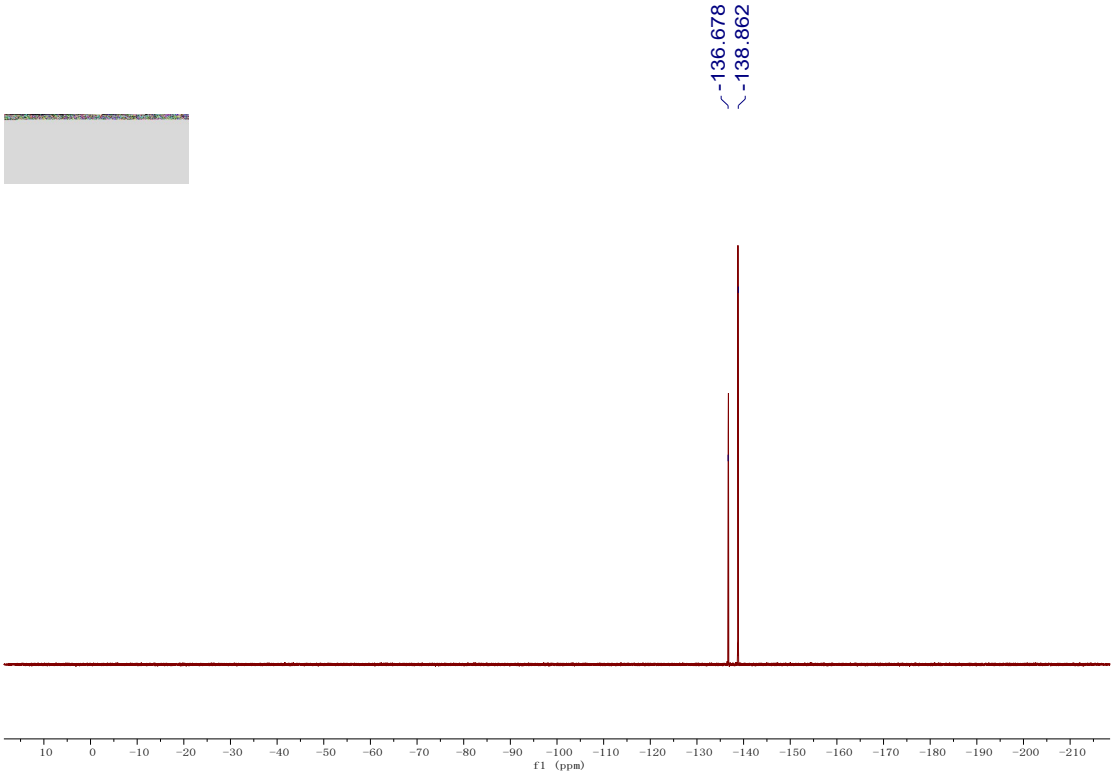
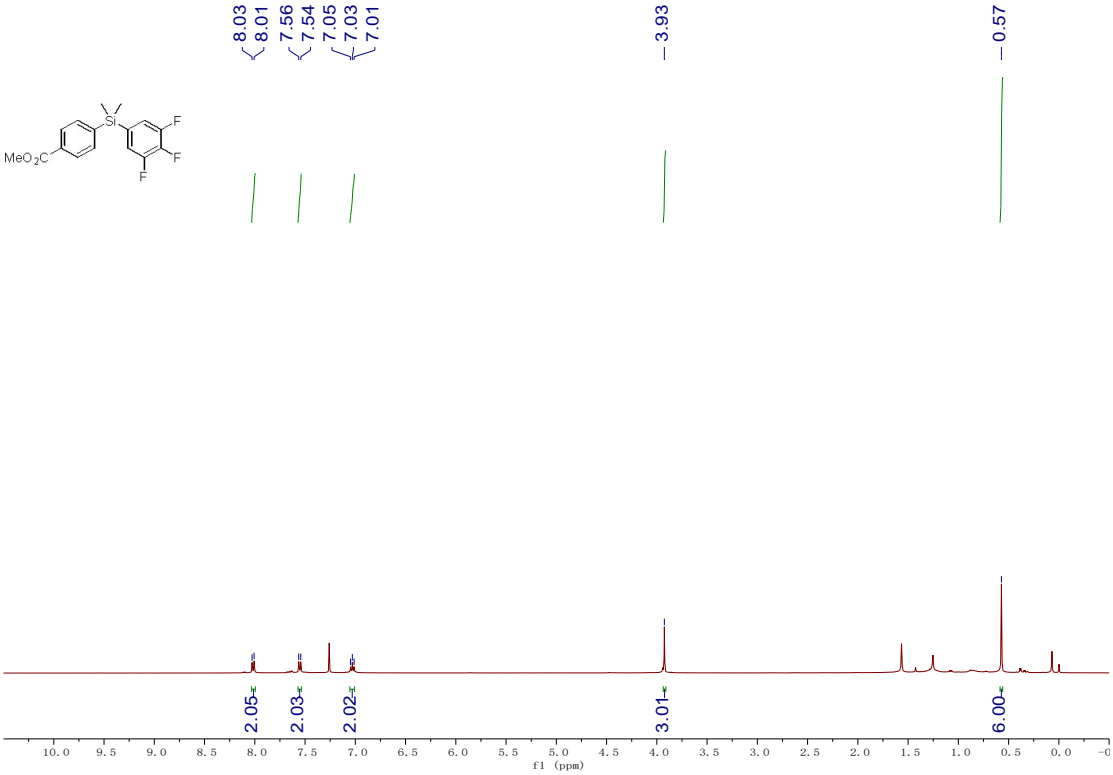
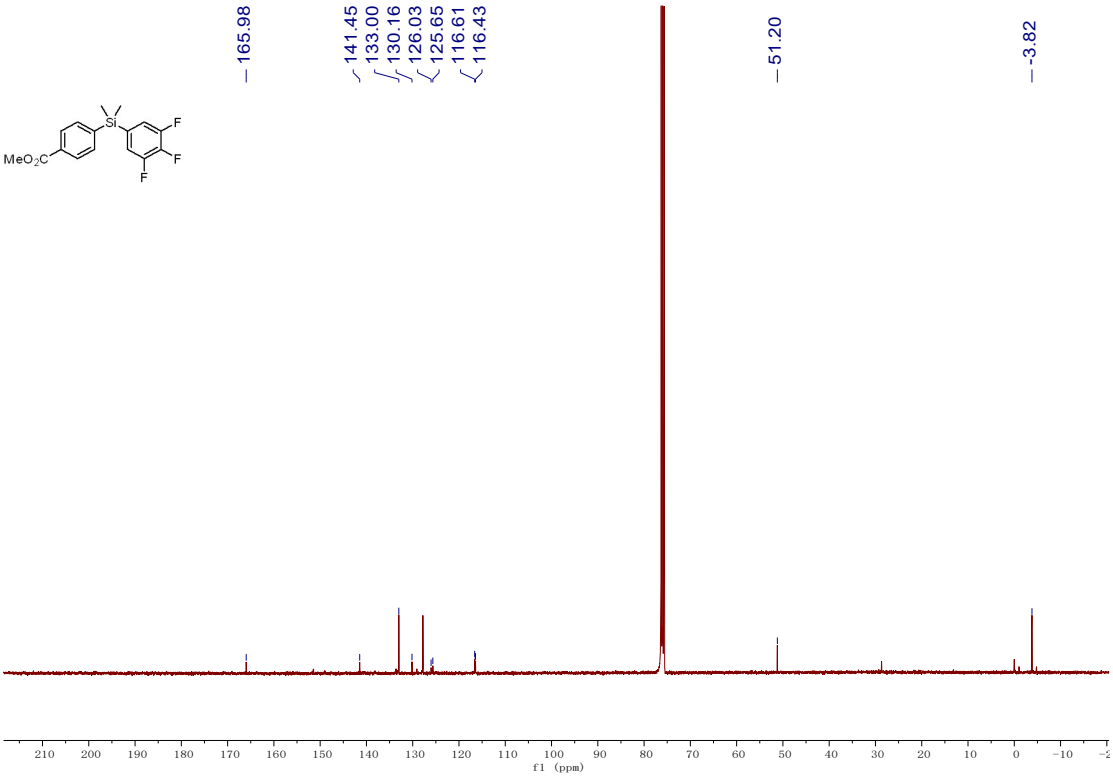


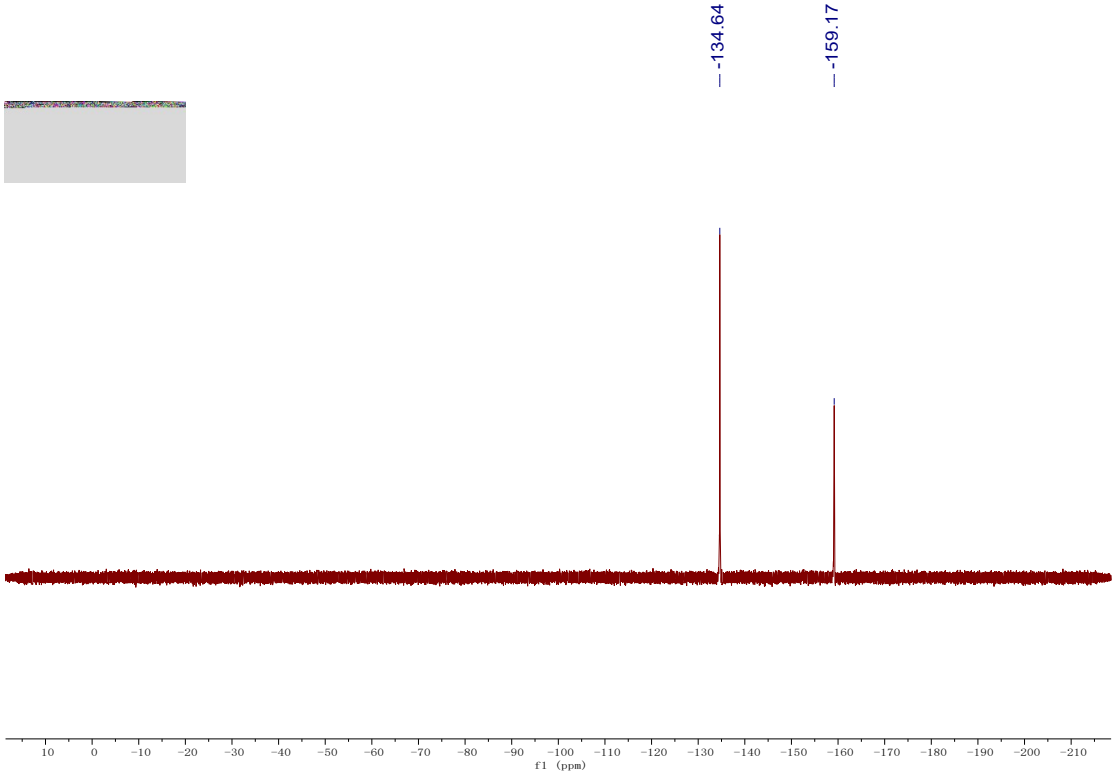
^{1}H NMR for **3m**



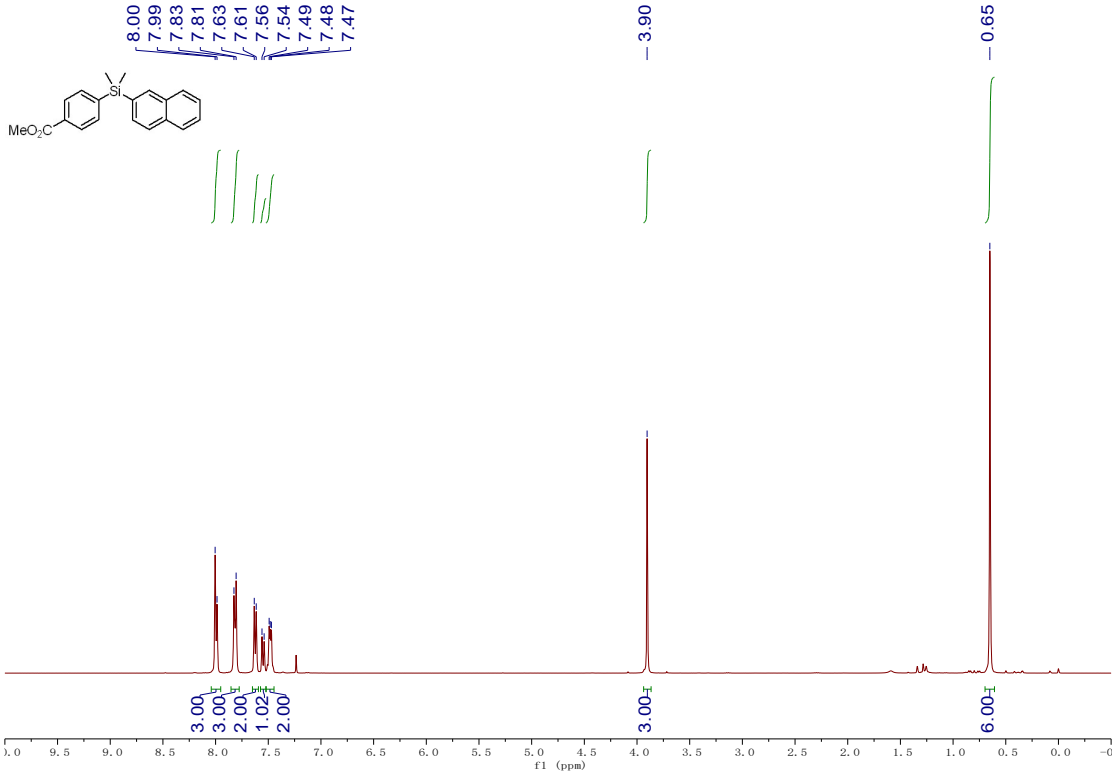
^{13}C NMR for **3m**



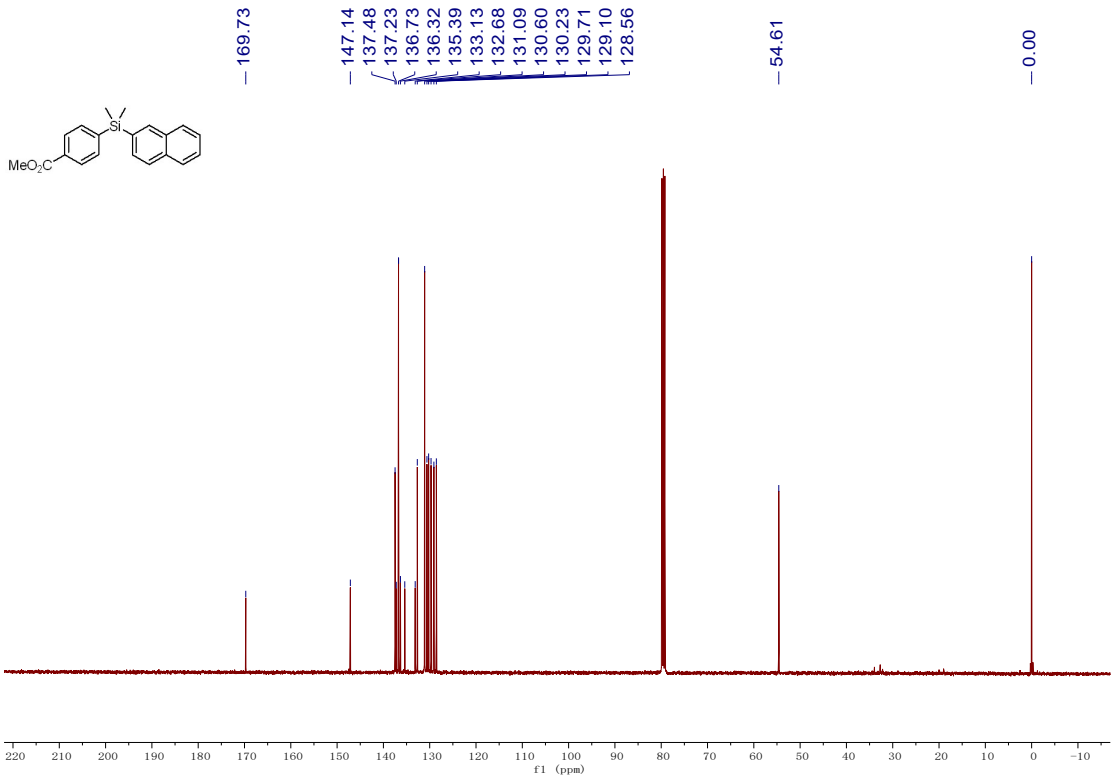
^{19}F NMR for **3m**



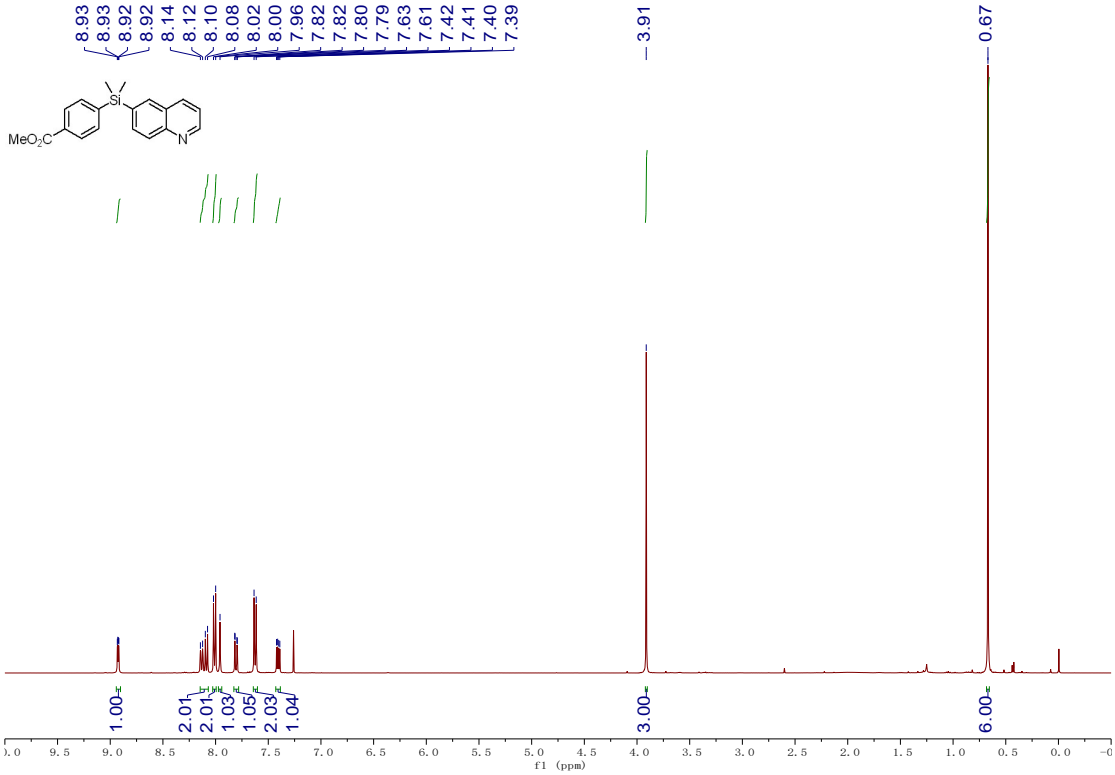
^{1}H NMR for **3n**



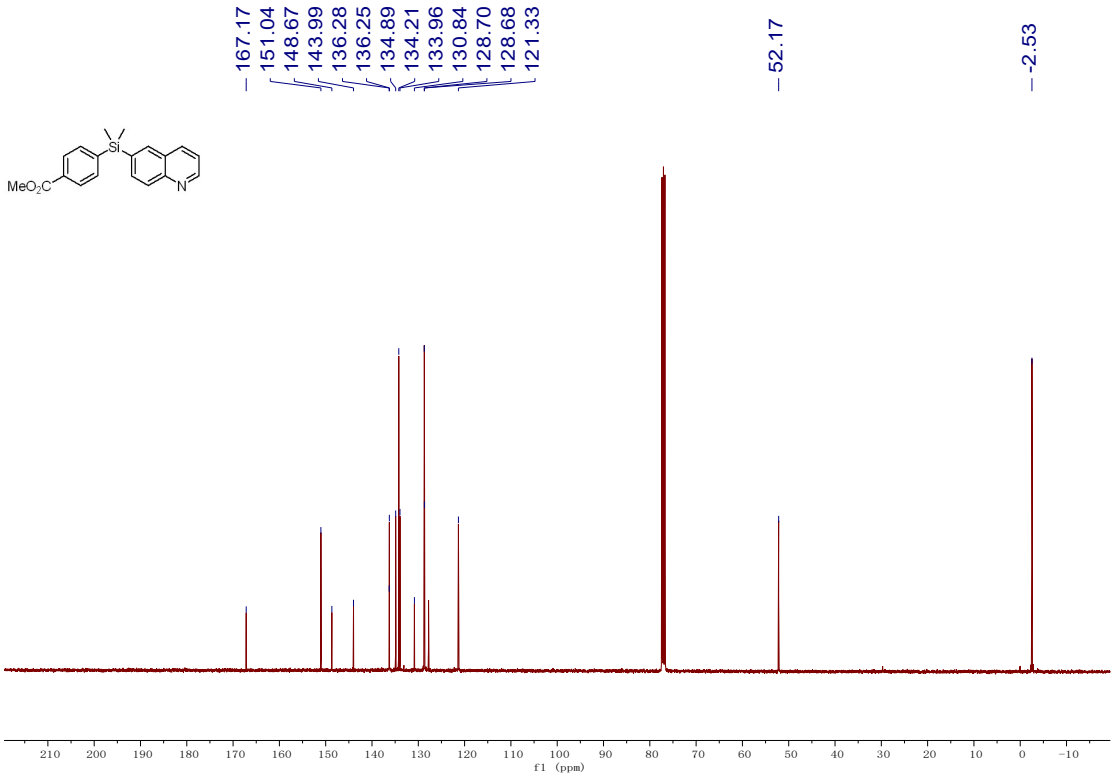
^{13}C NMR for **3n**



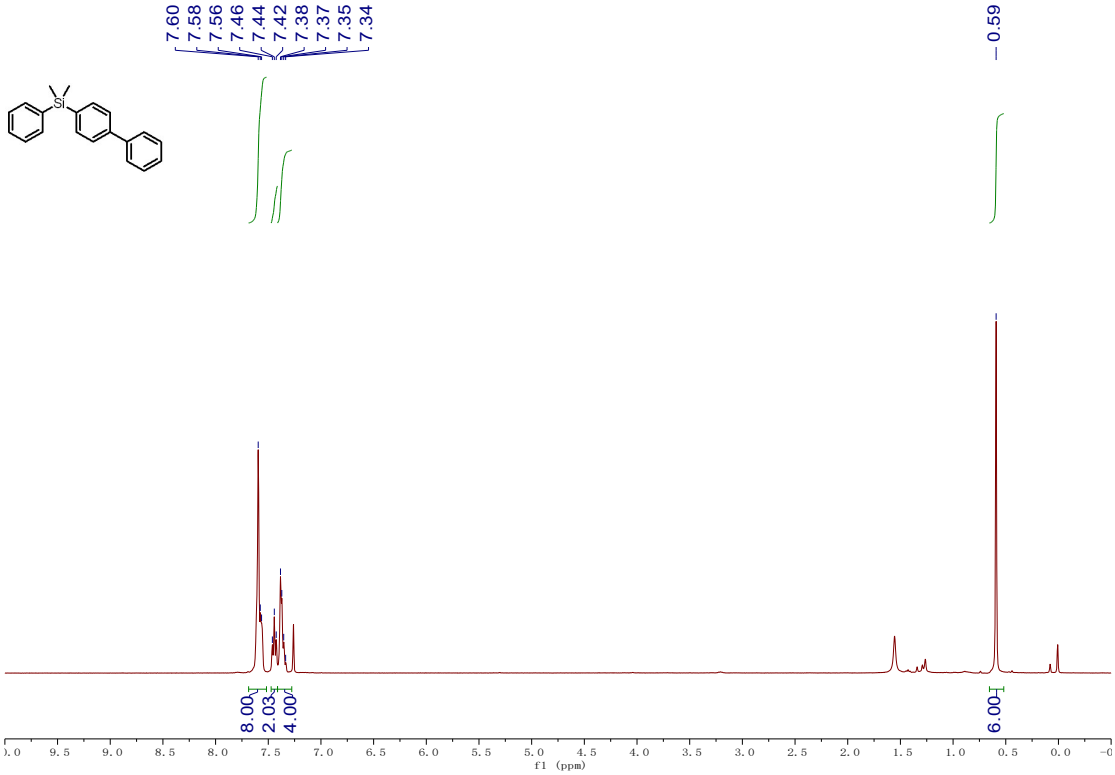
^{1}H NMR for **3o**



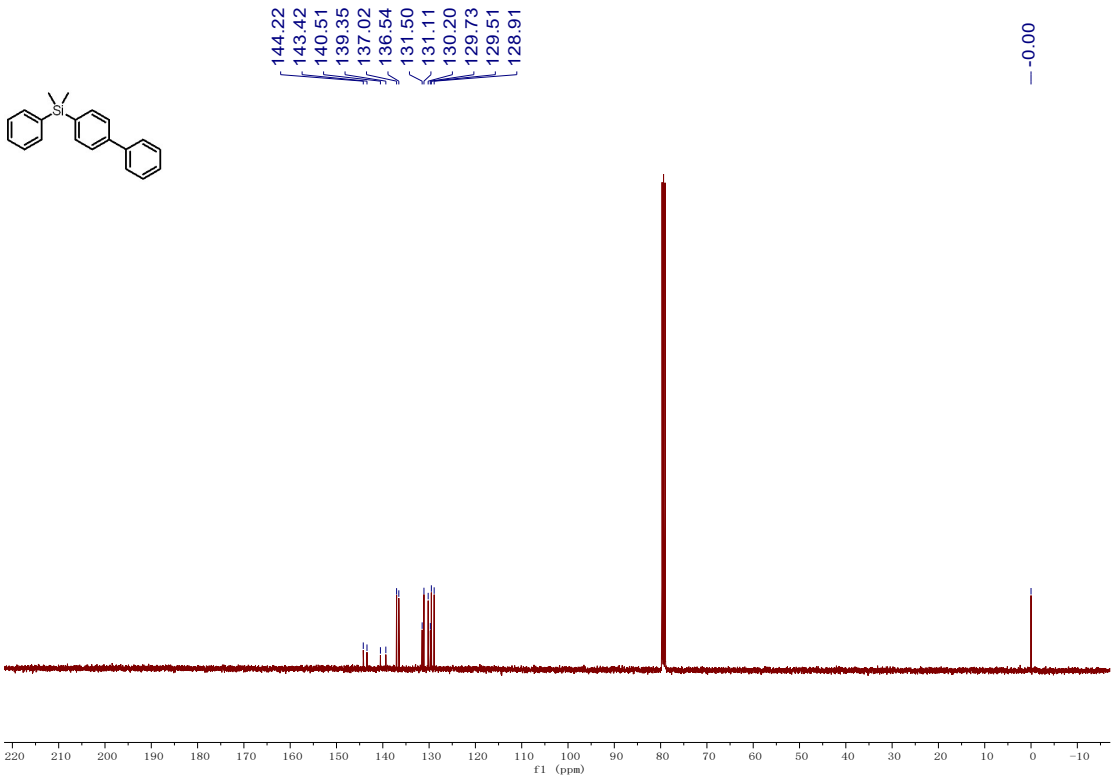
^{13}C NMR for **3o**



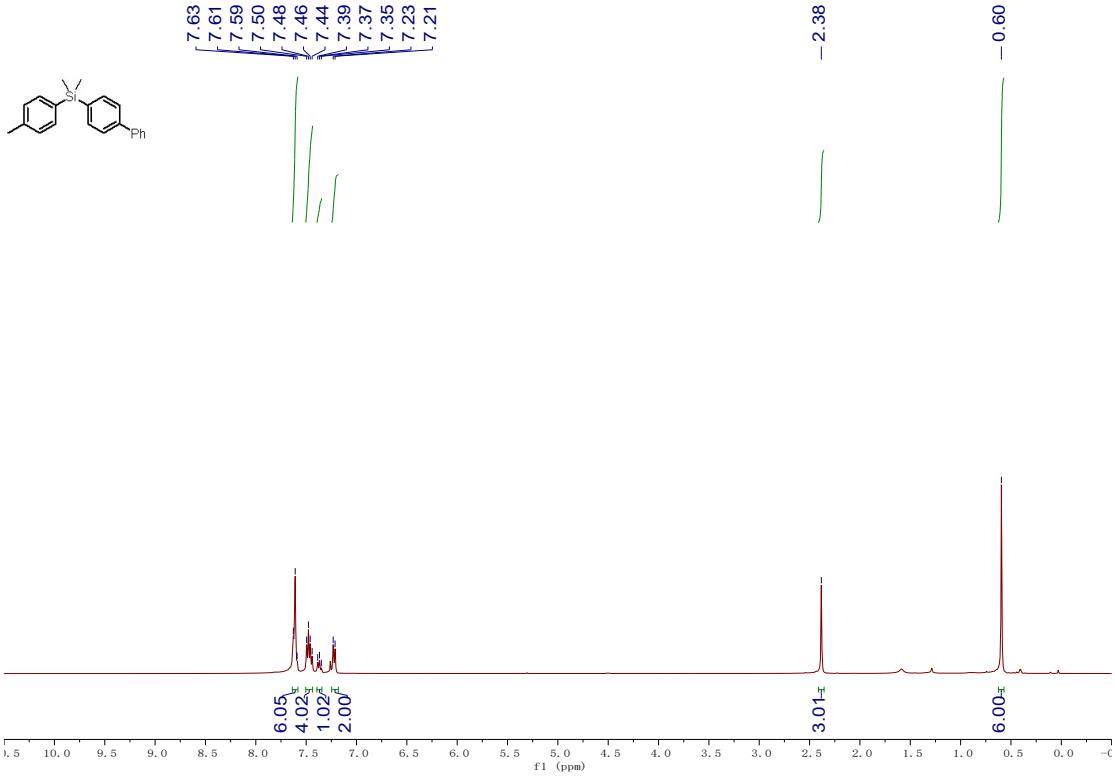
^{1}H NMR for **4a**



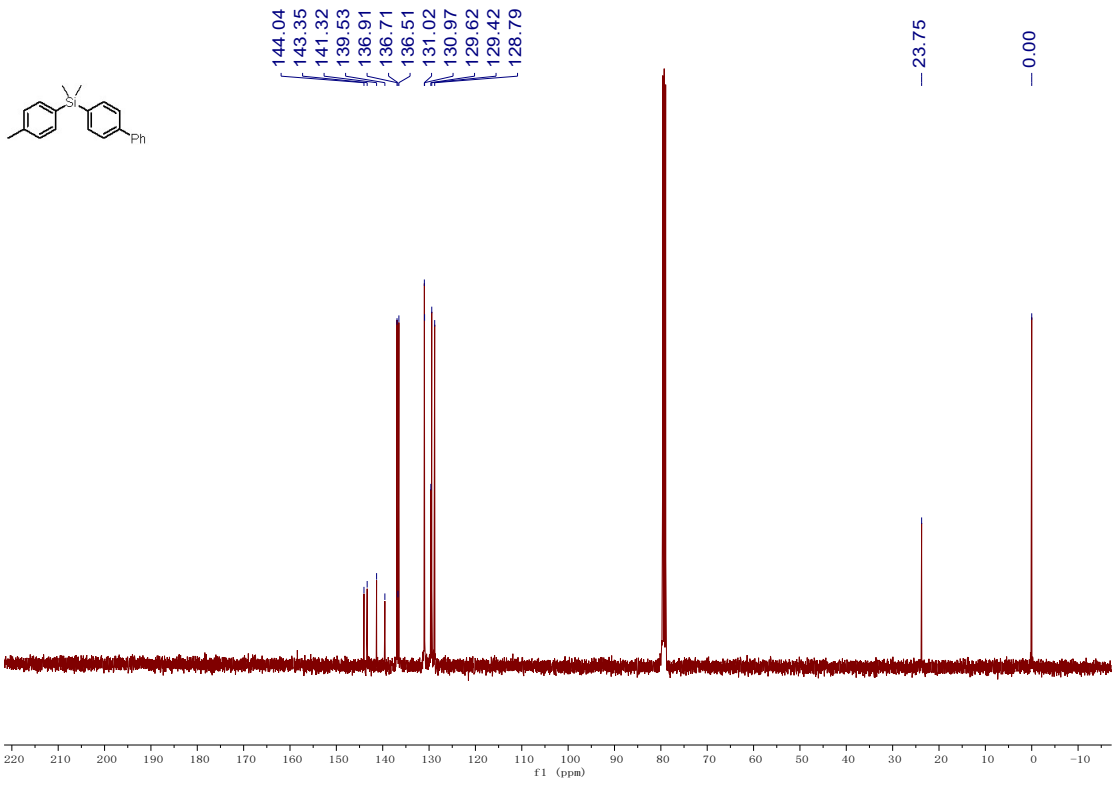
^{13}C NMR for **4a**



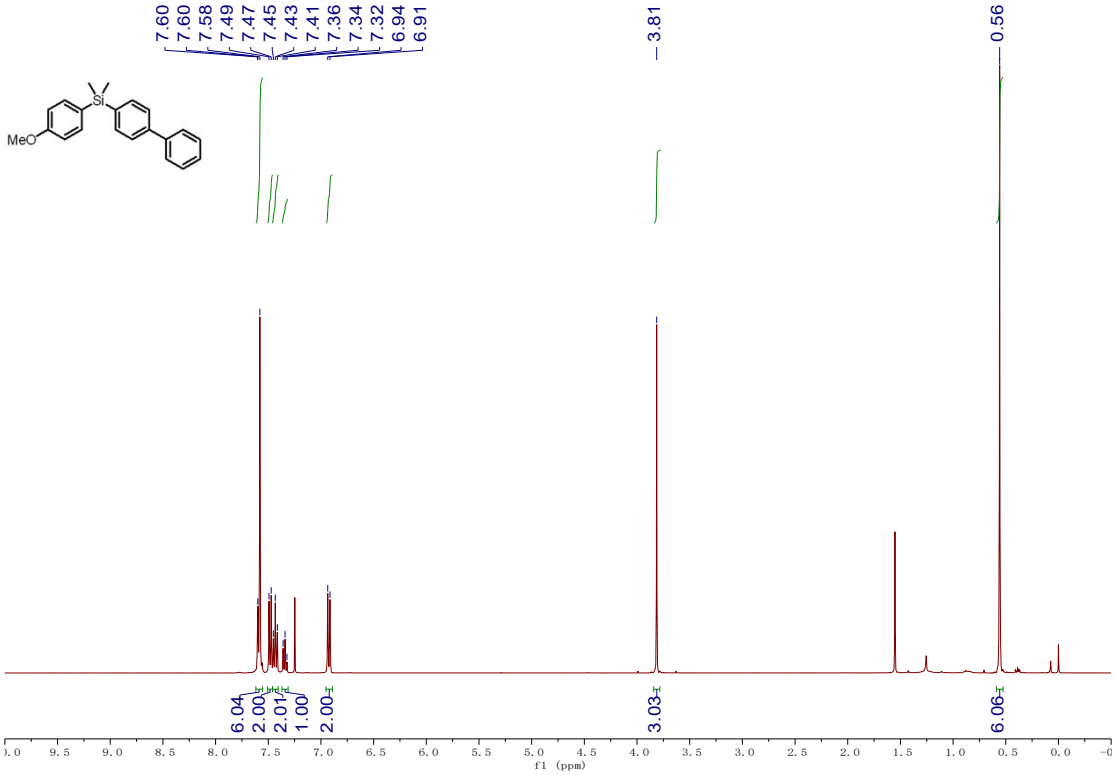
^{1}H NMR for **4b**



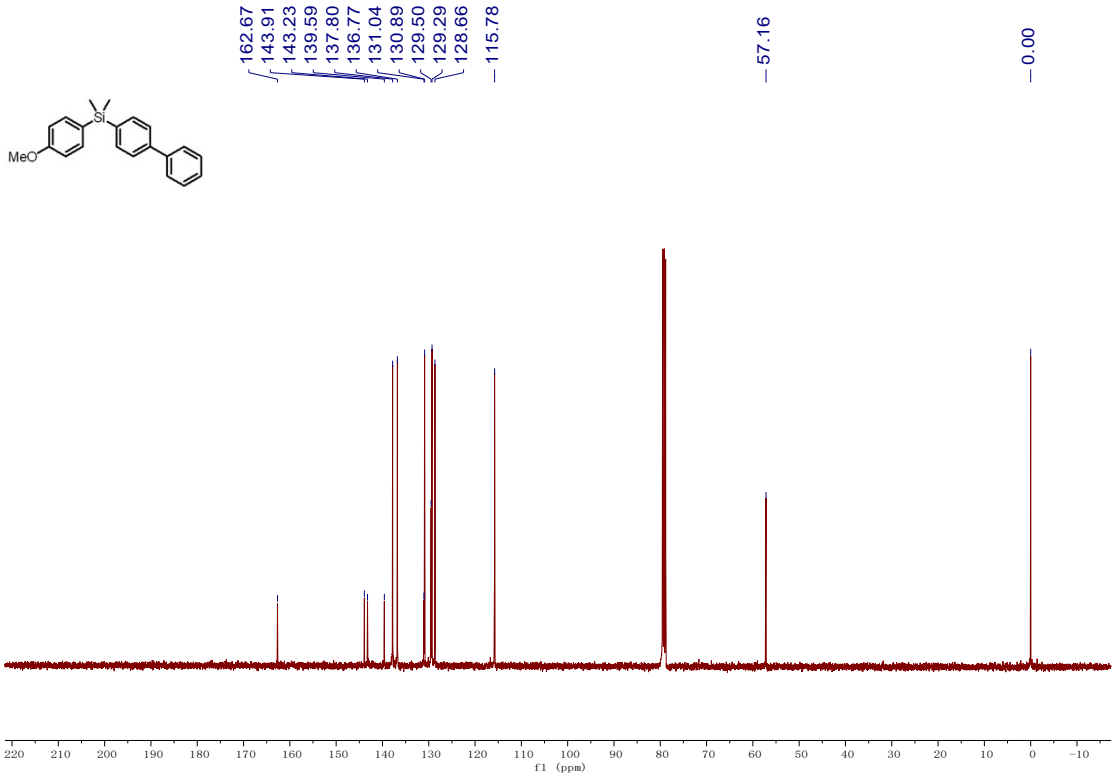
^{13}C NMR for **4b**



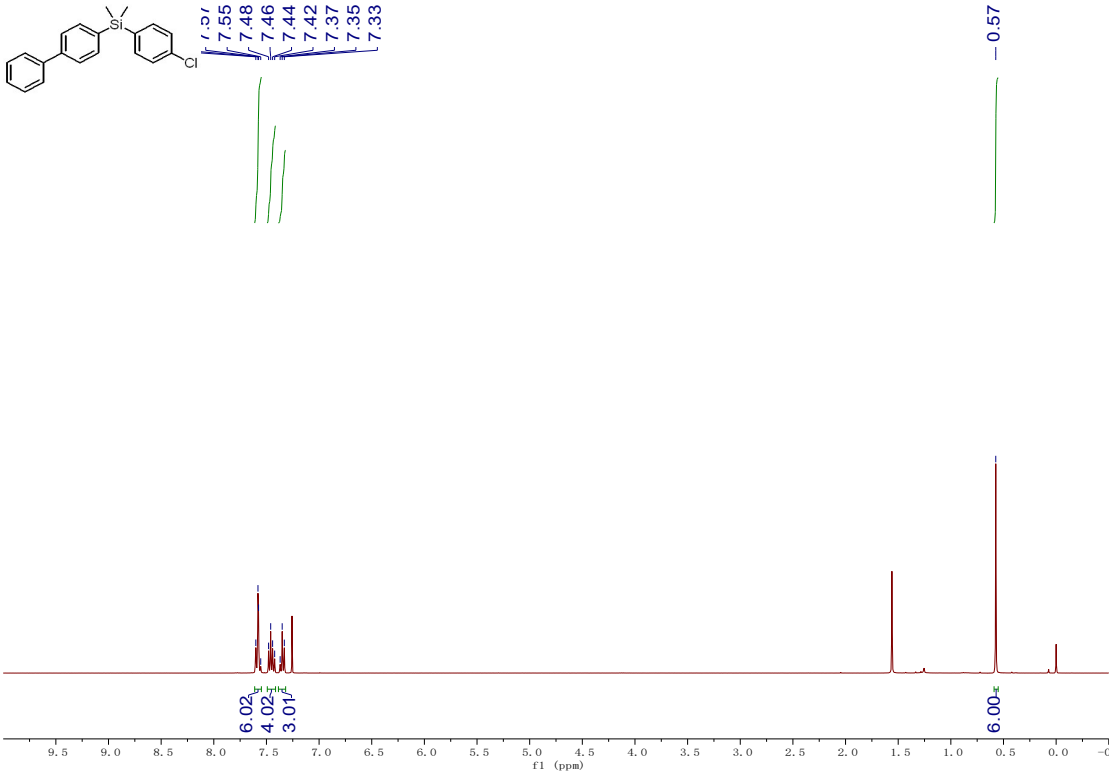
^{1}H NMR for **4c**



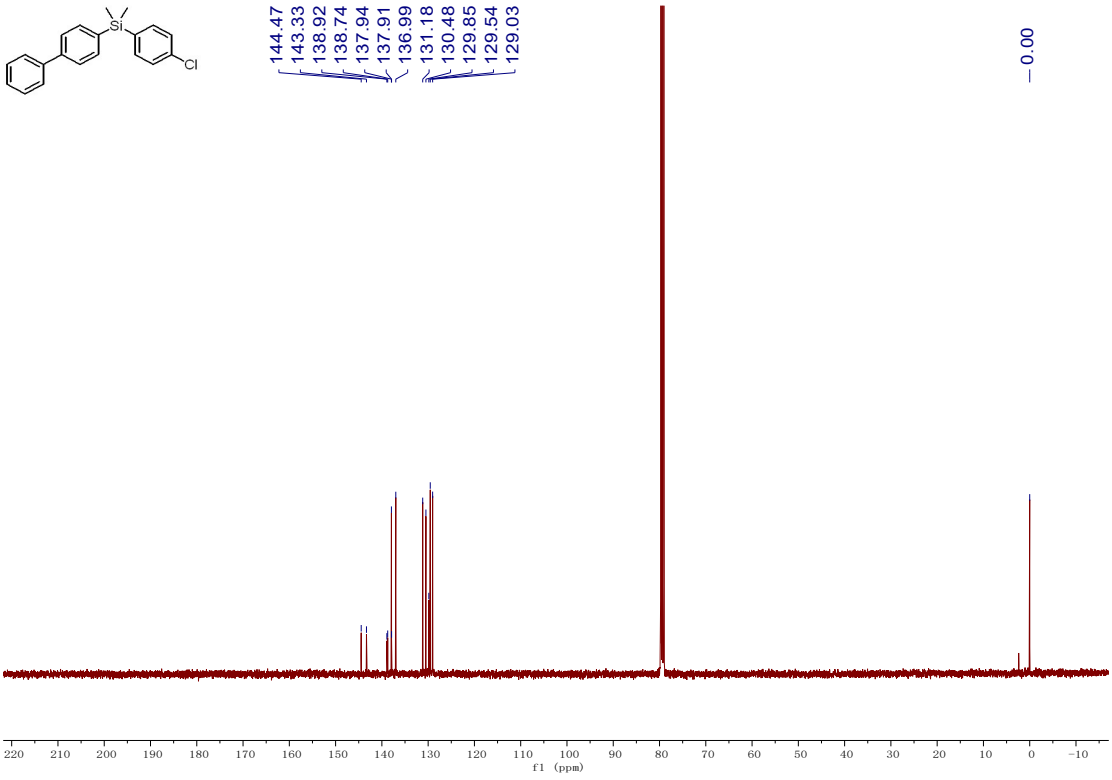
^{13}C NMR for **4c**



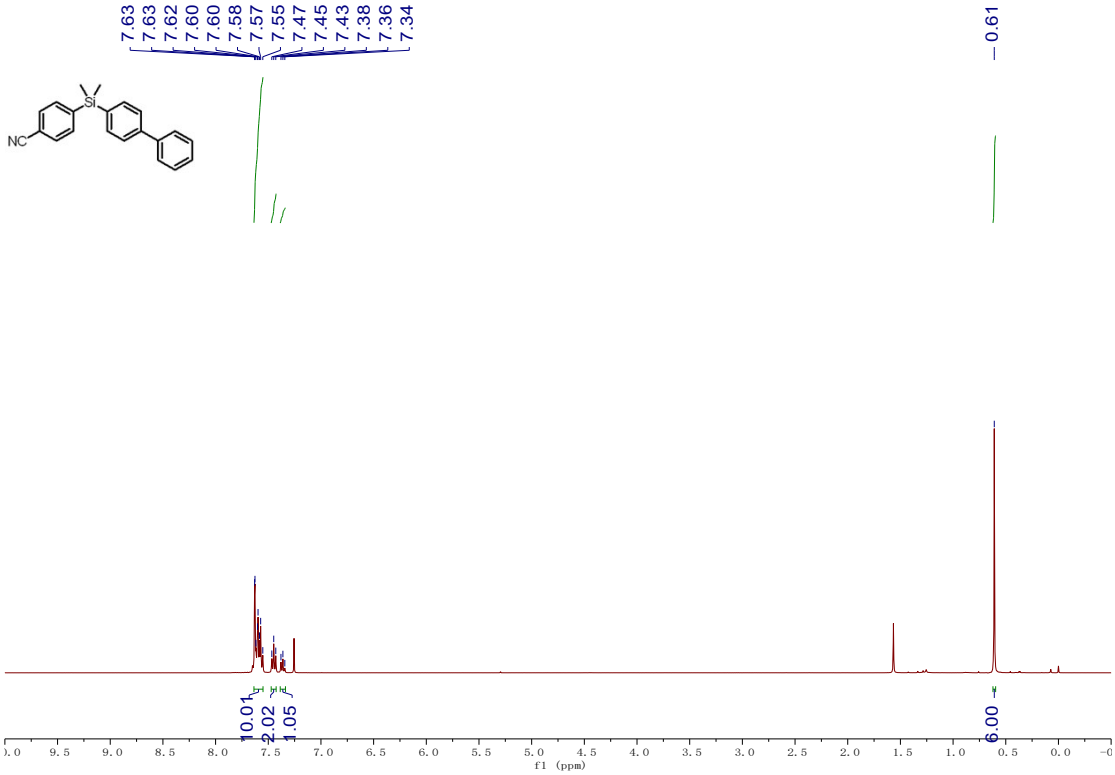
^{1}H NMR for **4d**



^{13}C NMR for **4d**



^{1}H NMR for **4e**



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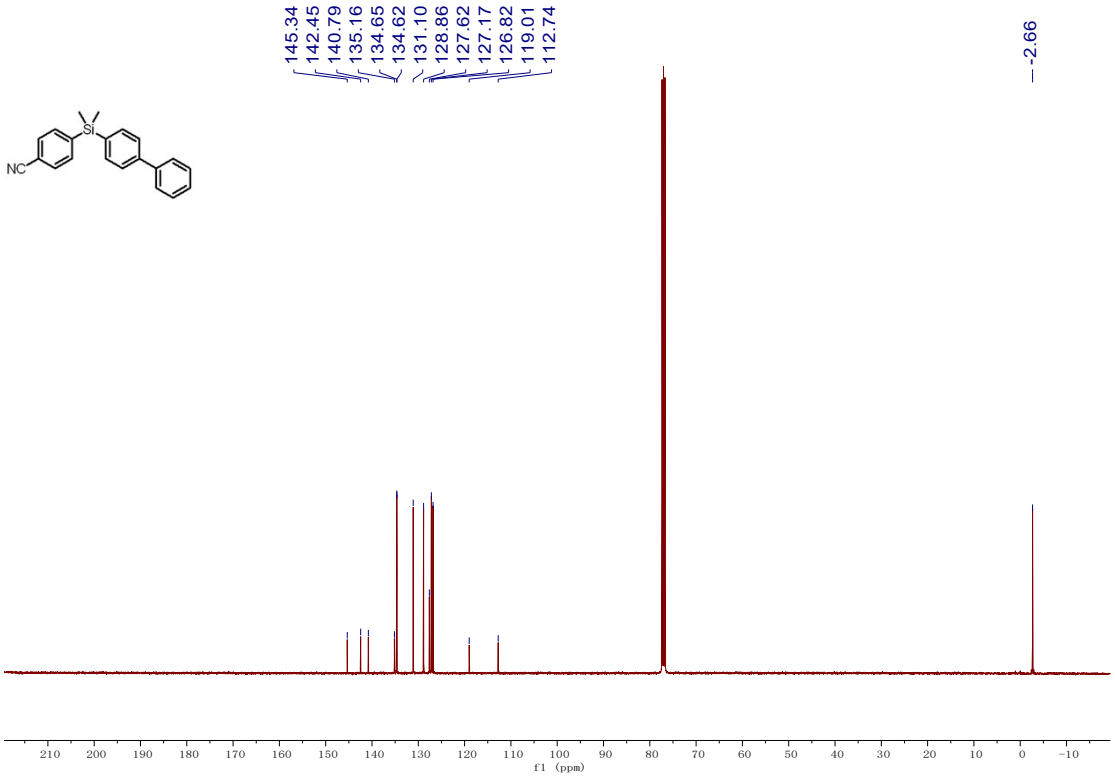
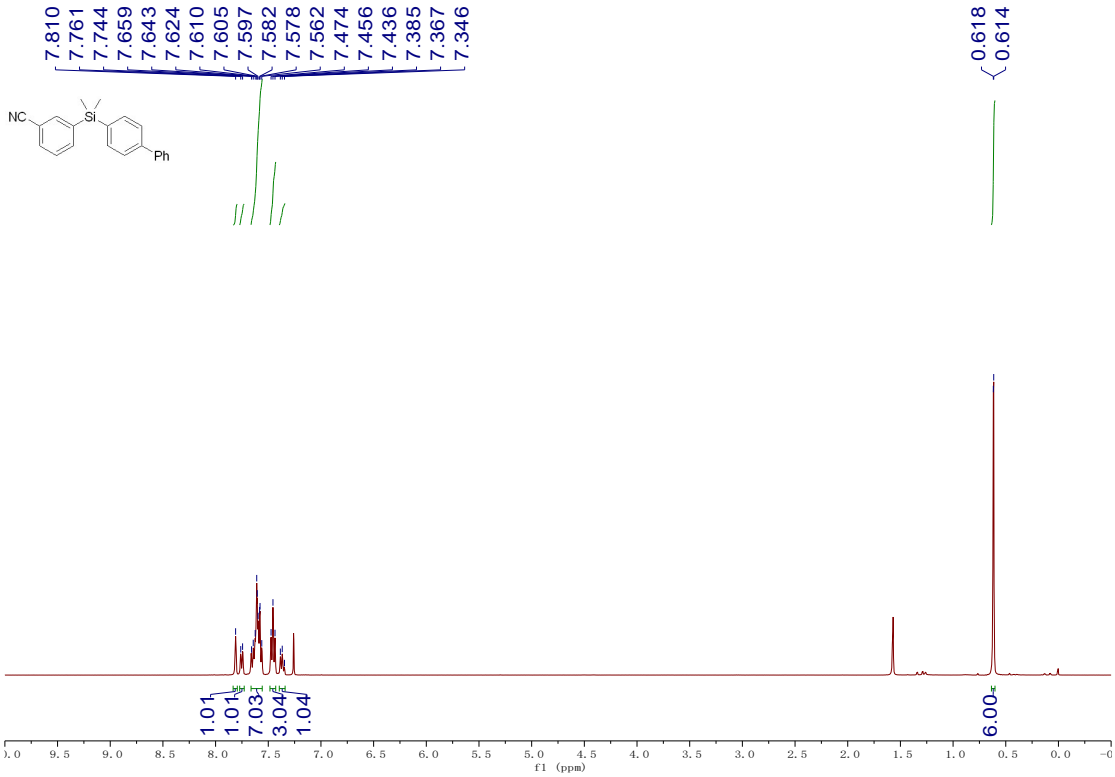


^{1}H NMR for **4f**



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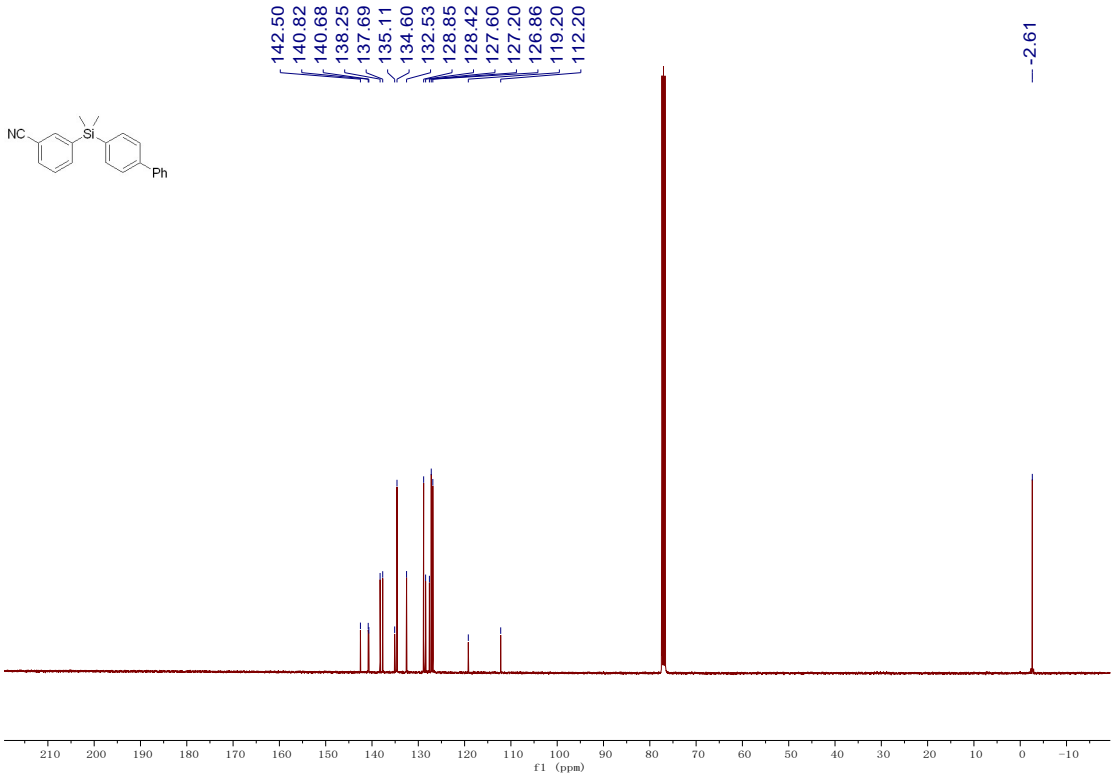
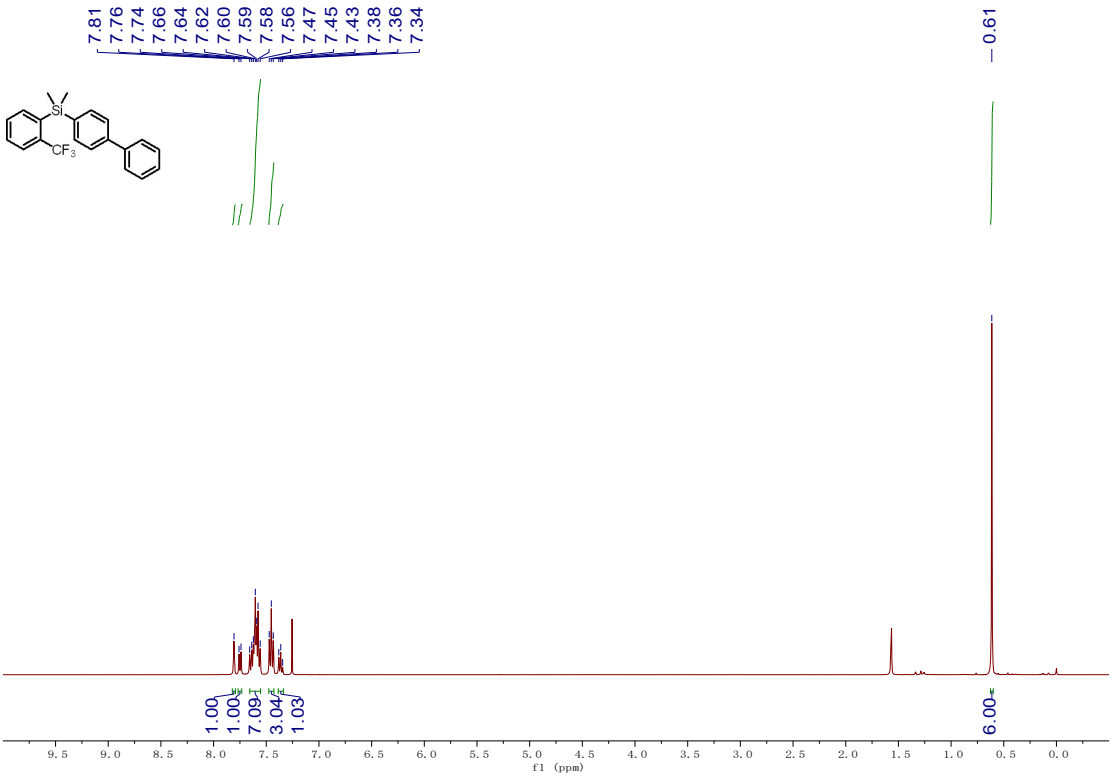
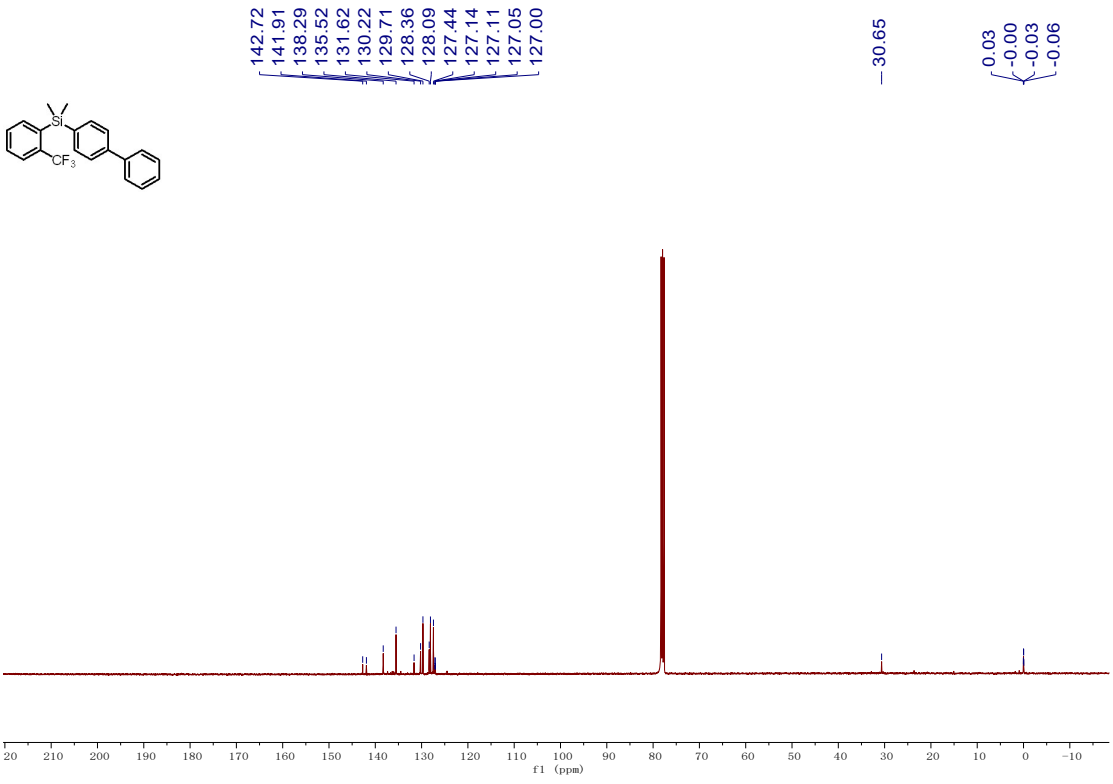


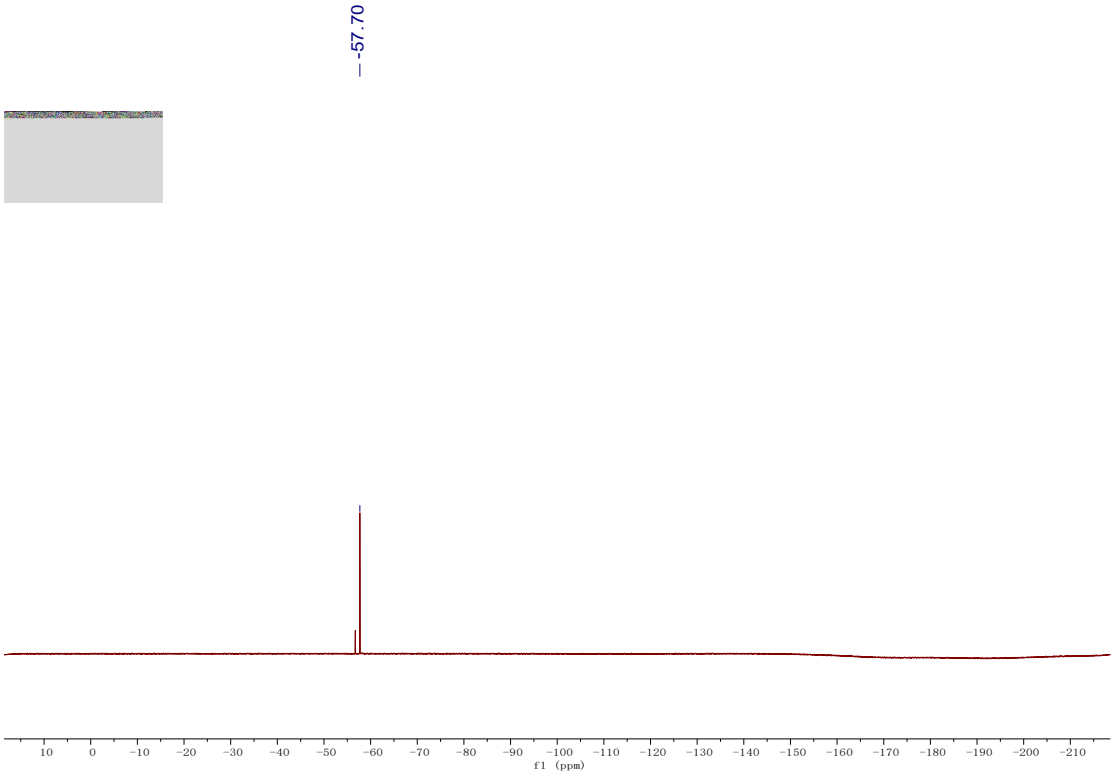
^{1}H NMR for **4g**



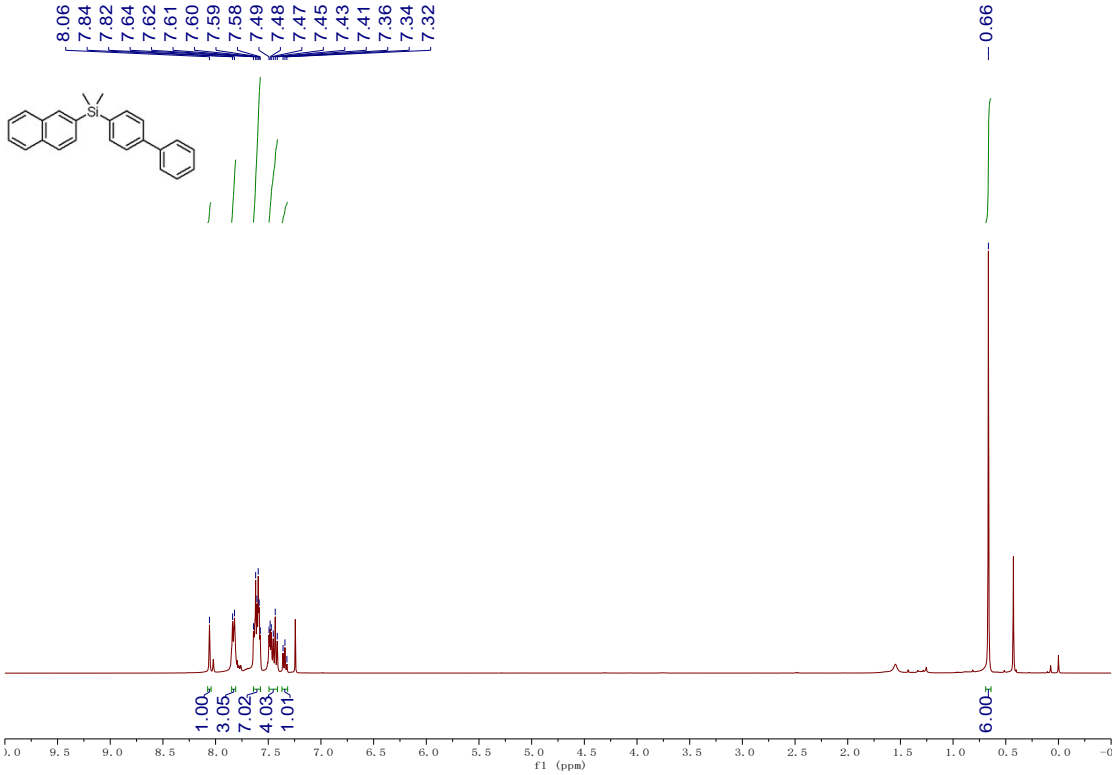
^{13}C NMR for **4g**



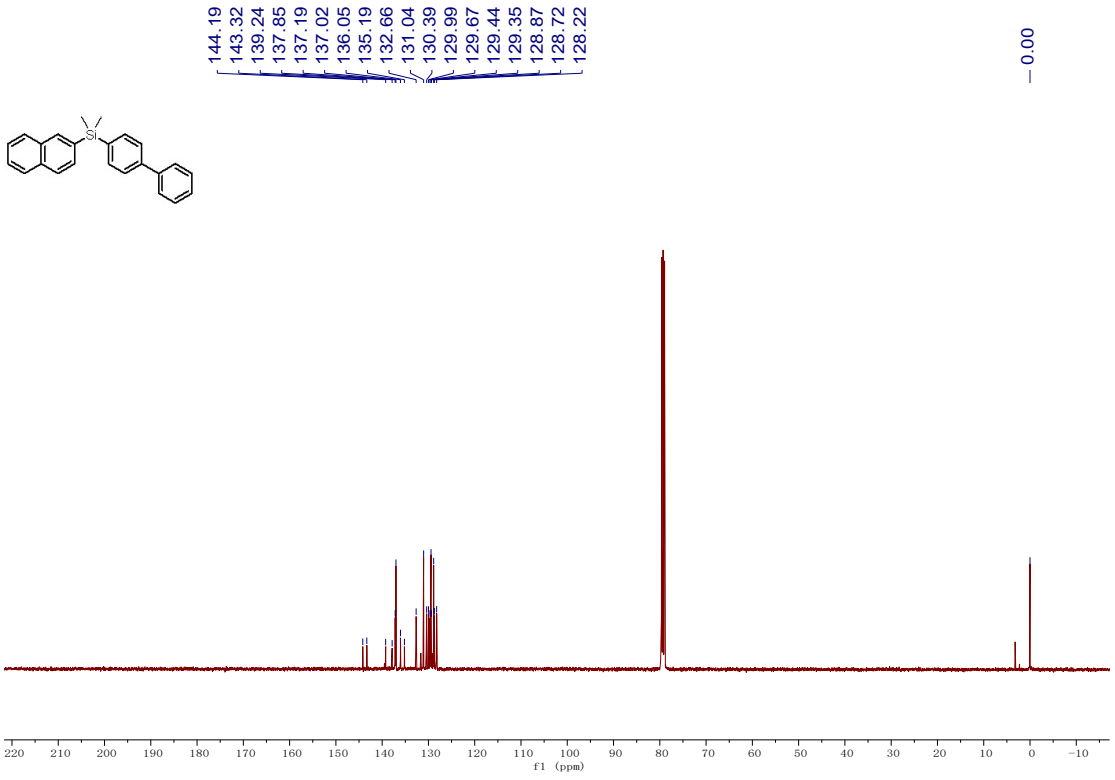
^{19}F NMR for **4g**



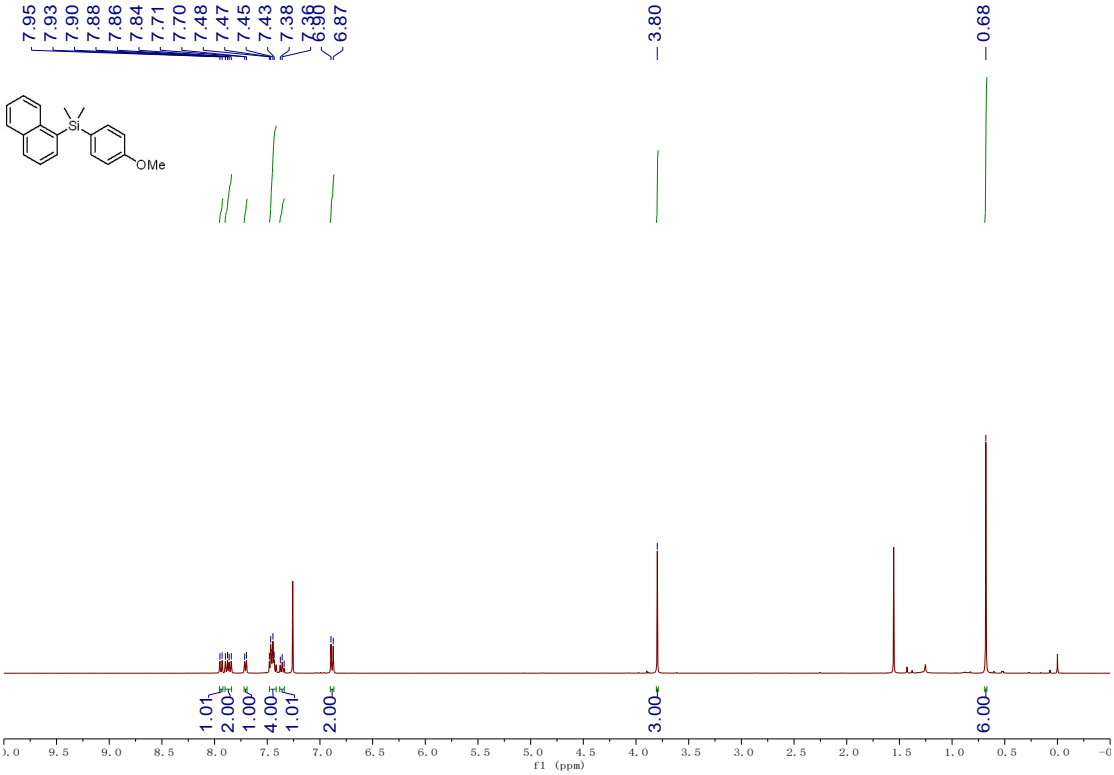
^{1}H NMR for **4h**



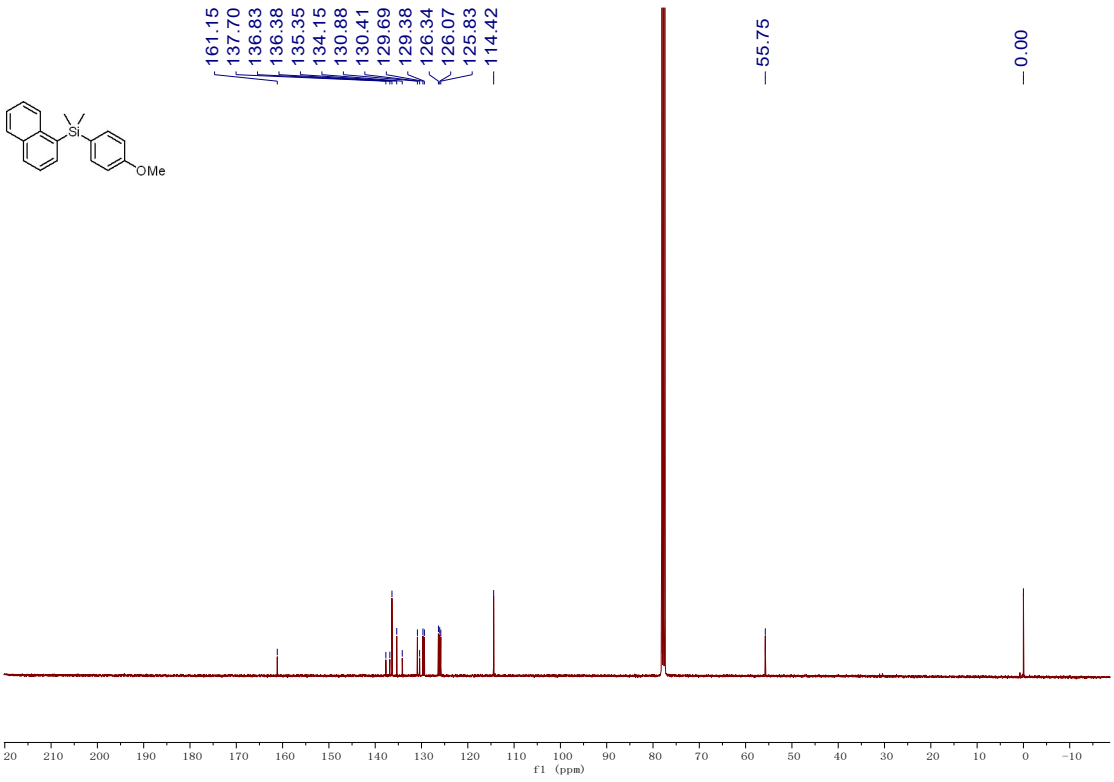
^{13}C NMR for **4h**



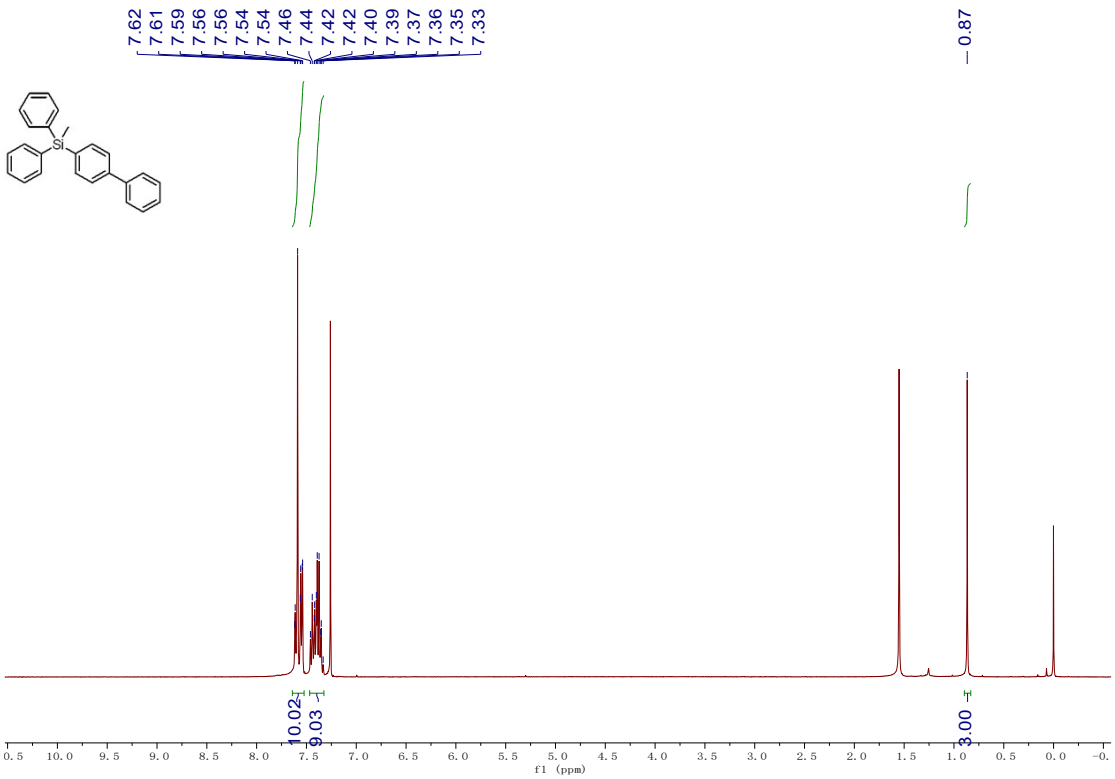
^{1}H NMR for **4i**



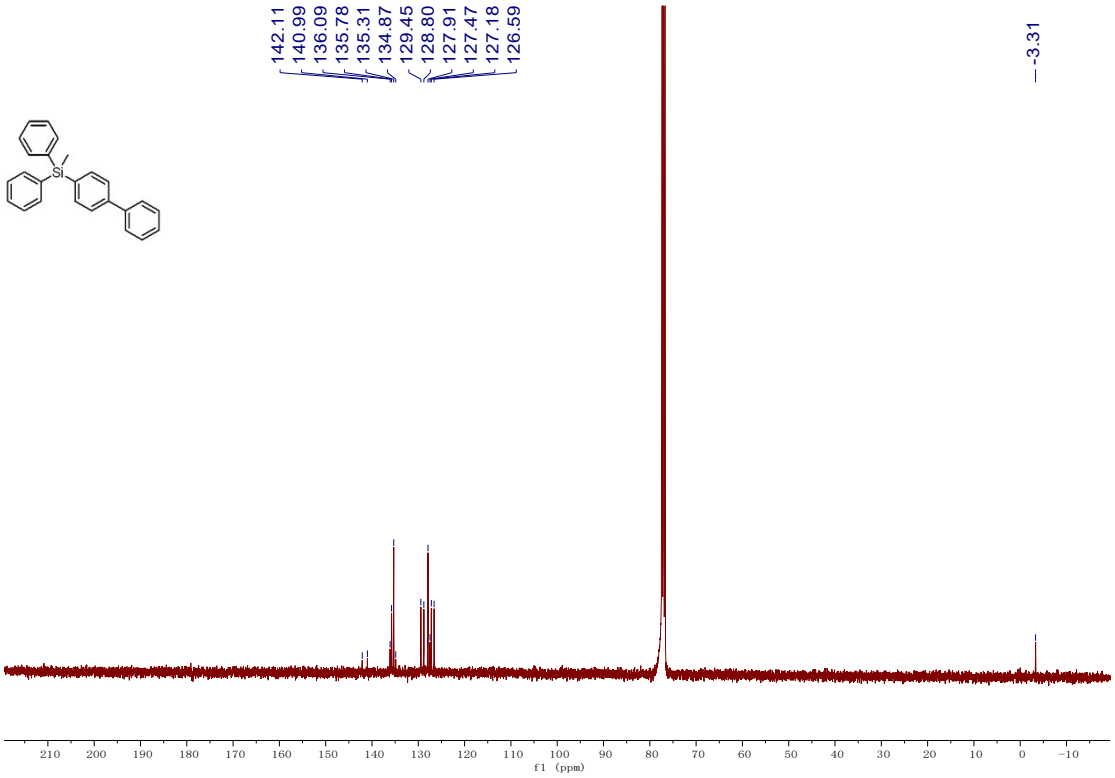
^{13}C NMR for **4i**



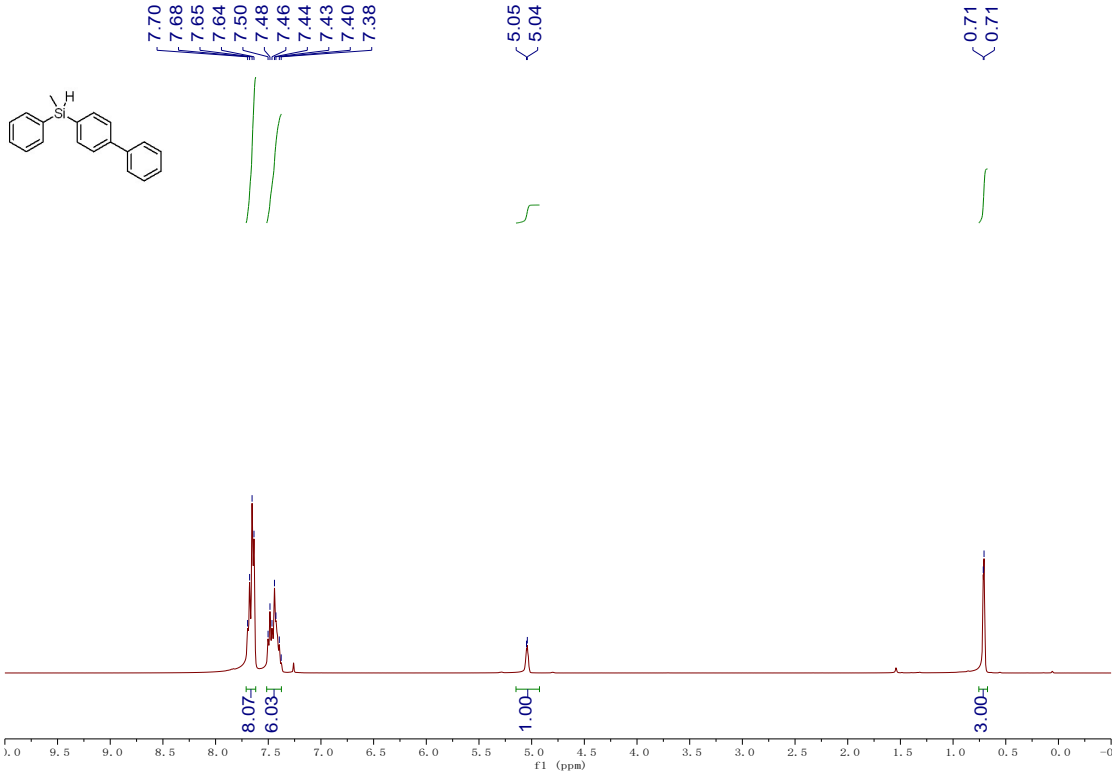
^{1}H NMR for **4j**



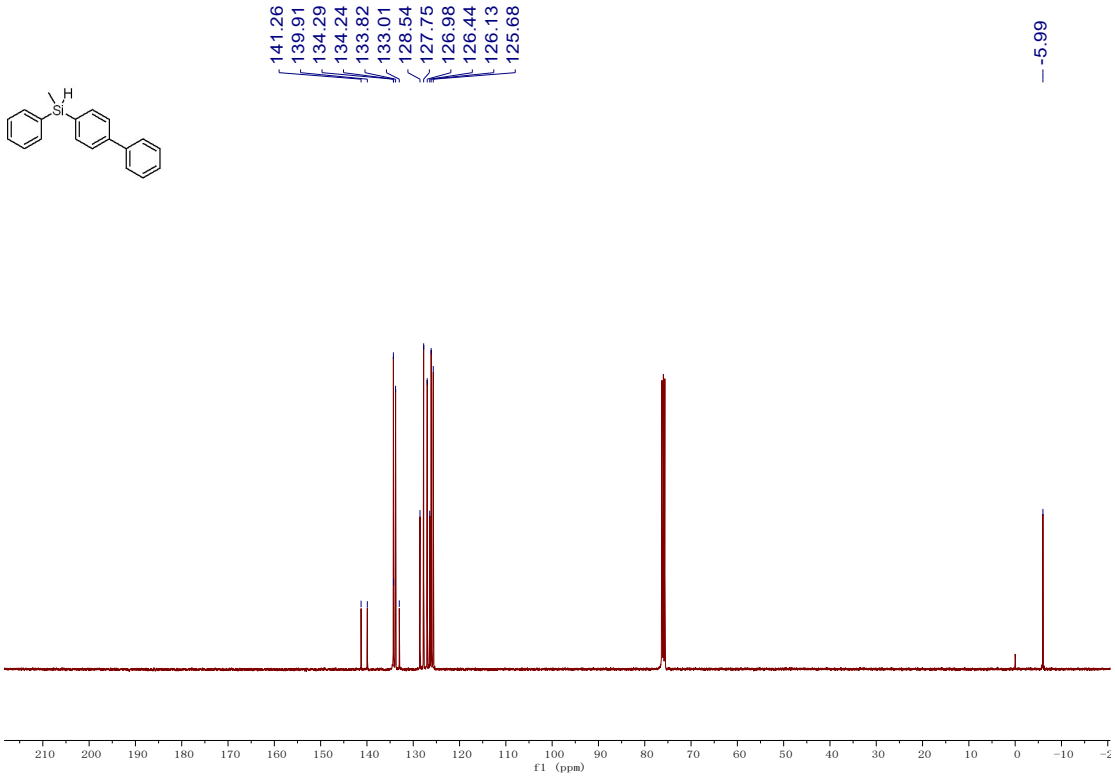
^{13}C NMR for **4j**



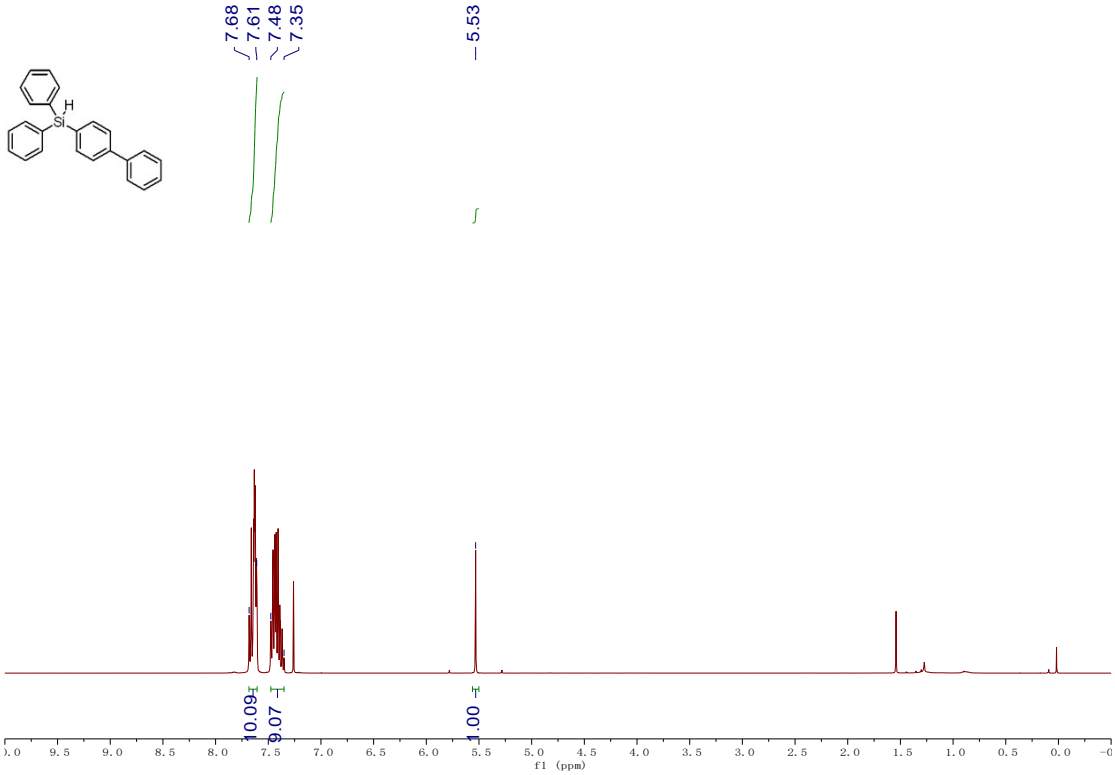
^{1}H NMR for **4k**



^{13}C NMR for **4k**



^{1}H NMR for **4l**



^{13}C NMR for **4l**