Supporting Information

Visible-light-driven hydrolytic oxidation of organosilanes to silanols with $FeCl_3$ as dual functional catalyst

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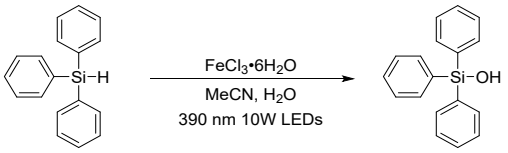
1 General information:

The solvents, reagents, and deuterated solvents were purchased from Energy, Aladdin, Adamas, Innochem and Sigma-Aldrich without further purification unless otherwise noted. Chemical shifts were denoted in ppm on the δ scale relative to residual solvent peaks as an internal standard: $CDCl_3$ (δ 7.28 for ^1H NMR), $CDCl_3$ (δ 77.0 for ^{13}C NMR), DMSO-*d6* (δ 2.50 for ^1H NMR), DMSO-*d6* (δ 39.5 for ^{13}C NMR). Signal patterns are indicated as s, singlet; d, doublet; t, triplet; m, multiplet; br, broaden peak. High resolution mass spectra (HRMS) were obtained from Analysis and Testing Center of Dalian University of Technology on Thermo Fisher Scientific Q Exactive Plus instrument. The material of the photoreaction vessels is regular borosilicate glass. Flash column chromatography was performed on silica gel (200-300 mesh). 10W blue light source from 390 nm LED. The melting points of solid substances were measured using an X-4 Precision Microscopic Melting Point Tester.

2 Experimental procedures

2.1 Table S1. Optimization of Reaction Conditions



1a **2a**

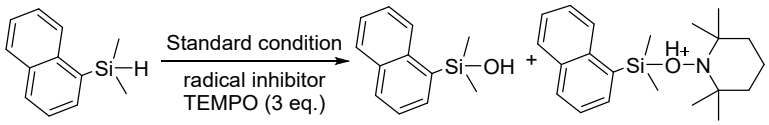
Entry	Catalyst	Solvent	H_2O	Yield[b]
1	$FeCl_2$	MeCN	200μL	96%
2	$CeCl_3$	MeCN	200μL	90%
3	**$FeCl_3·6H_2O$**	**MeCN**	**200μL**	**98%**
4	$Fe(NO_3)_3·9H_2O$	MeCN	200μL	60%
5	$FeSO_4·7H_2O$	MeCN	200μL	trace
6	NaCl	MeCN	200μL	trace
7	LiCl	MeCN	200μL	trace
8	**$FeCl_3·6H_2O$**	**Acetone**	**200μL**	**98%**
9	$FeCl_3·6H_2O$	CH_3NO_2	200μL	90%
10	$FeCl_3·6H_2O$	AcOEt	200μL	72%
11	$FeCl_3·6H_2O$	CH_3OH	200μL	31%
12	$FeCl_3·6H_2O$	DMSO	200μL	trace
13	$FeCl_3·6H_2O$	THF	200μL	trace

14	$FeCl_3·6H_2O$	DCE	200μL	trace	
15	$FeCl_3·6H_2O$	$(CF_3)_2CHOH$	200μL	trace	
16	$FeCl_3·6H_2O$	Benzene	200μL	trace	
17	$FeCl_3·6H_2O$ (0.1 eq.)	Acetone	200μL	92%	
18	$FeCl_3·6H_2O$ (0.05 eq.)	Acetone	200μL	97%	
19	$FeCl_3·6H_2O$ (0.025 eq.)	Acetone	200μL	96%	
20	**$FeCl_3·6H_2O$ (0.01 eq.)**	**Acetone**	**200μL**	**98%**	
21	$FeCl_3·6H_2O$ (0.01 eq.)	Acetone	100μL	67%	
22	$FeCl_3·6H_2O$ (0.01 eq.)	Acetone	50μL	97%	
23	$FeCl_3·6H_2O$ (0.01 eq.)	Acetone	25μL	95%	
24	**$FeCl_3·6H_2O$ (0.01 eq.)**	**Acetone**	**10μL**	**98(96%)[c]**	
25	-	Acetone	10μL	0%[d]	
26	$FeCl_3·6H_2O$ (0.01 eq.)	Acetone	10μL	0%	
27	$FeCl_3·6H_2O$ (0.01 eq.)	Acetone	-	80%	

[a]Standard conditions: **1a** (0.2 mmol), catalyst (0.2 eq.), solvent (2 mL), H_2O (0.2 mL) at room temperature for 2 h under 390 nm blue LEDs (10 W). [b] Yield determined by ^1H NMR analysis using 1,3,5-Trimethoxybenzene as the internal standard.[c] Isolated yield.[d] No illumination.

2.2 Mechanism study

2.2.1 Radical trapping experiment:



1v **2v**, N.D. **3**, detected by HRMS

In a 5 mL glass vessel, substrate **1v** (0.2 mmol, 1.0 equiv), $FeCl_3·6H_2O$ (0.01 equiv), TEMPO (0.6 mmol, 3.0 equiv), and H_2O (10 μL) were successively added. Then, acetone (2 mL) was added to dissolve the substrate. The resulting mixture was irradiated at room temperature with a 10 W, 390 nm blue LED for 2 hours. After the reaction, 0.1 mL of the reaction solution was taken for high-resolution mass spectrometry (HRMS) analysis (Figure S1). The results indicated the generation of a silyl radical during the photocatalytic process.

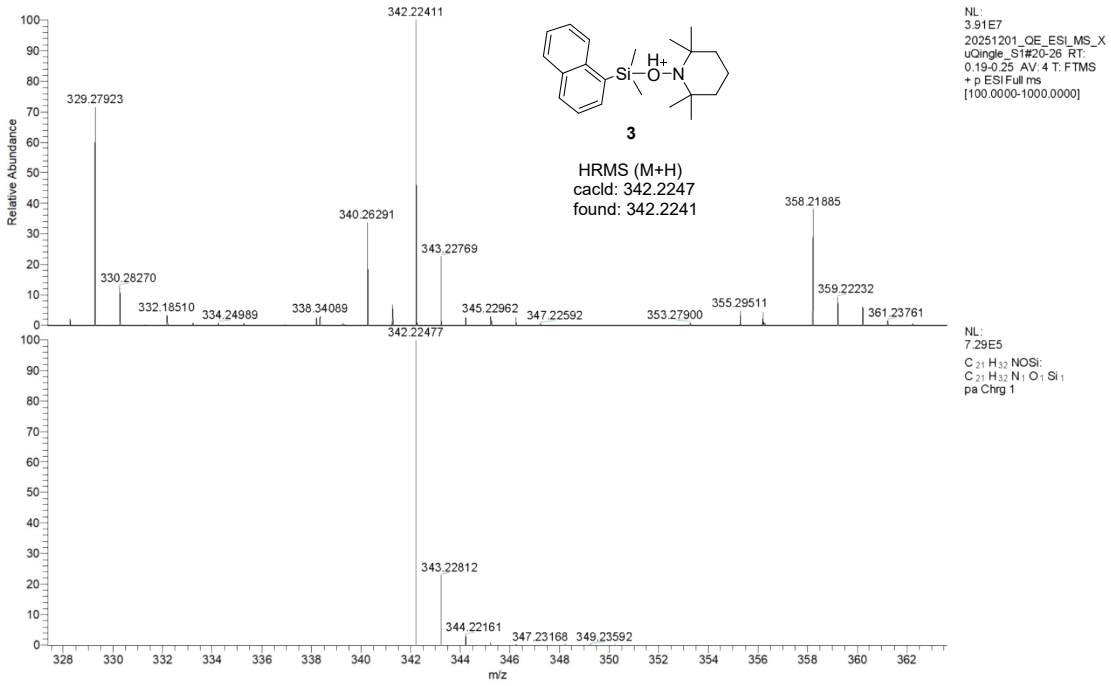


Figure S1. High-resolution mass spectrometry (HRMS) of **3**

2.2.2 The Light/Dark Experiments

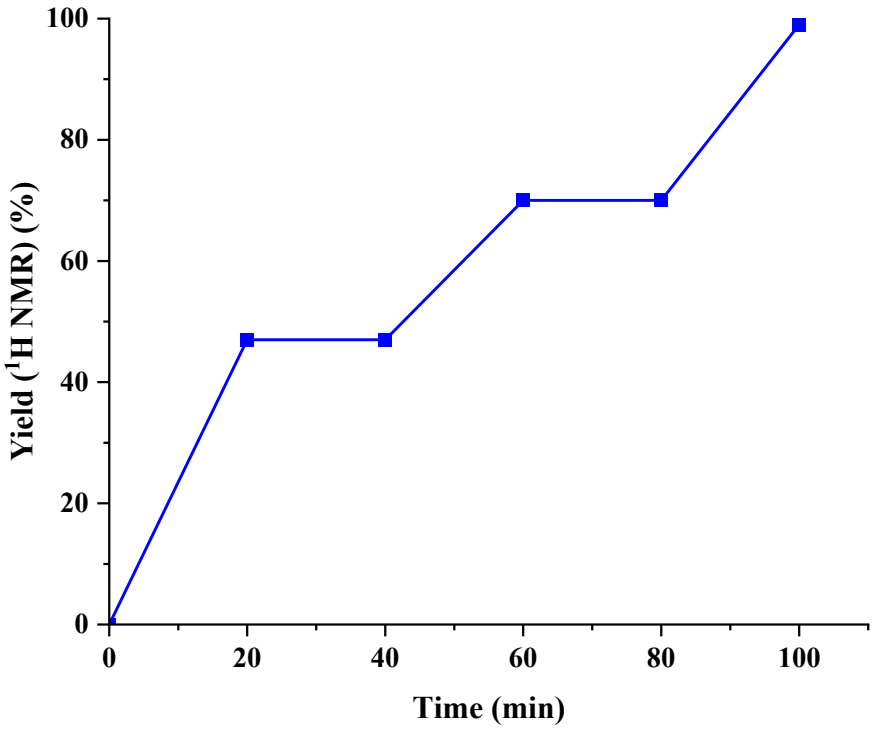
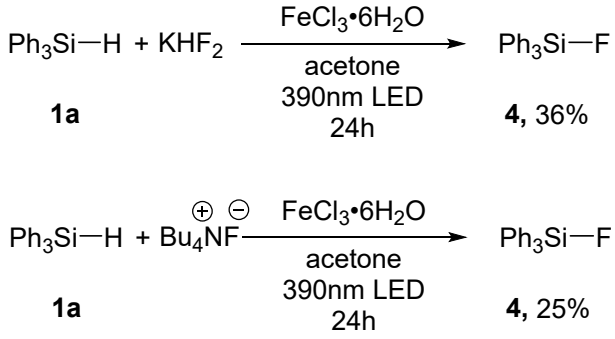


Figure S2. The Light/Dark Experiments of **2a**

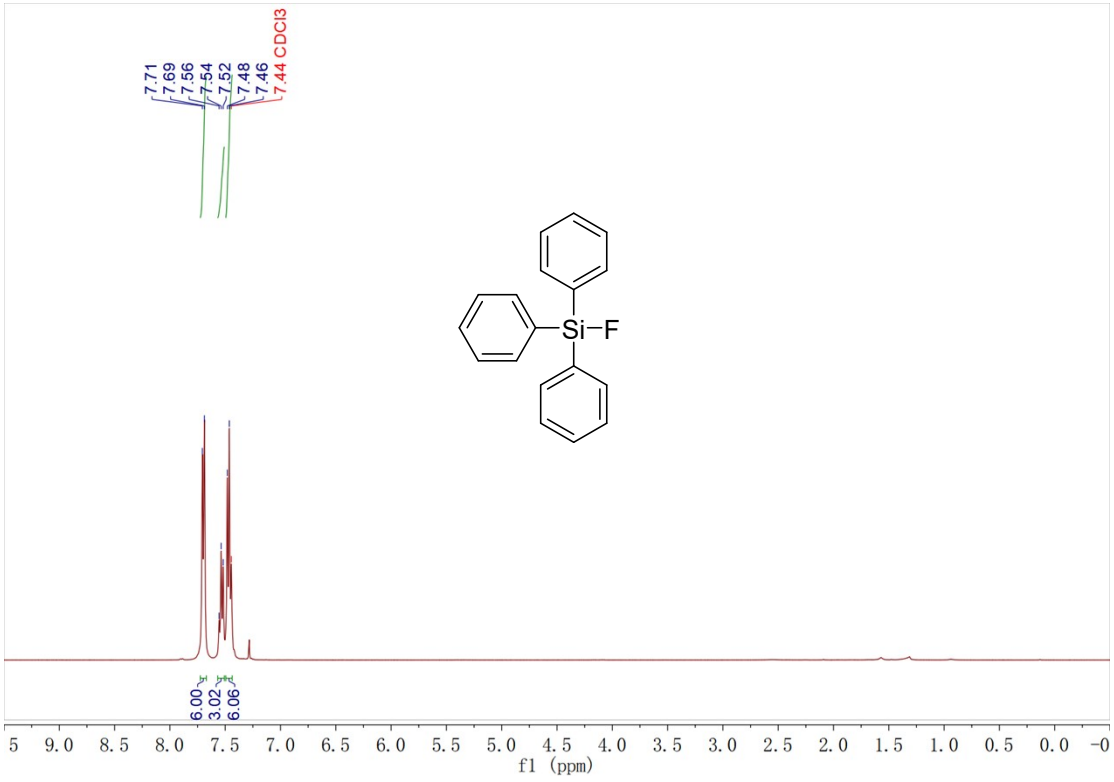
In a 10 mL glass reaction vessel, substrate 1a (0.4 mmol, 1.0 equiv), $FeCl_3 \cdot 6H_2O$ (0.01 equiv), and H_2O (20 μL) were successively added. Then, acetone (4 mL) was added to dissolve the substrate. The resulting mixture was irradiated at room temperature with a 10 W, 390 nm blue LED for 60

minutes. After the reaction, the light source was removed, and the reaction vial was completely wrapped in aluminum foil to shield from light during the subsequent time points as shown in Figure S2. At each specified time point, a 0.5 mL aliquot was taken. The solvent was removed under reduced pressure to obtain the crude product. The residue was diluted with $CDCl_3$ and analyzed by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

2.2.3 Silicon Cation Capture Experiment

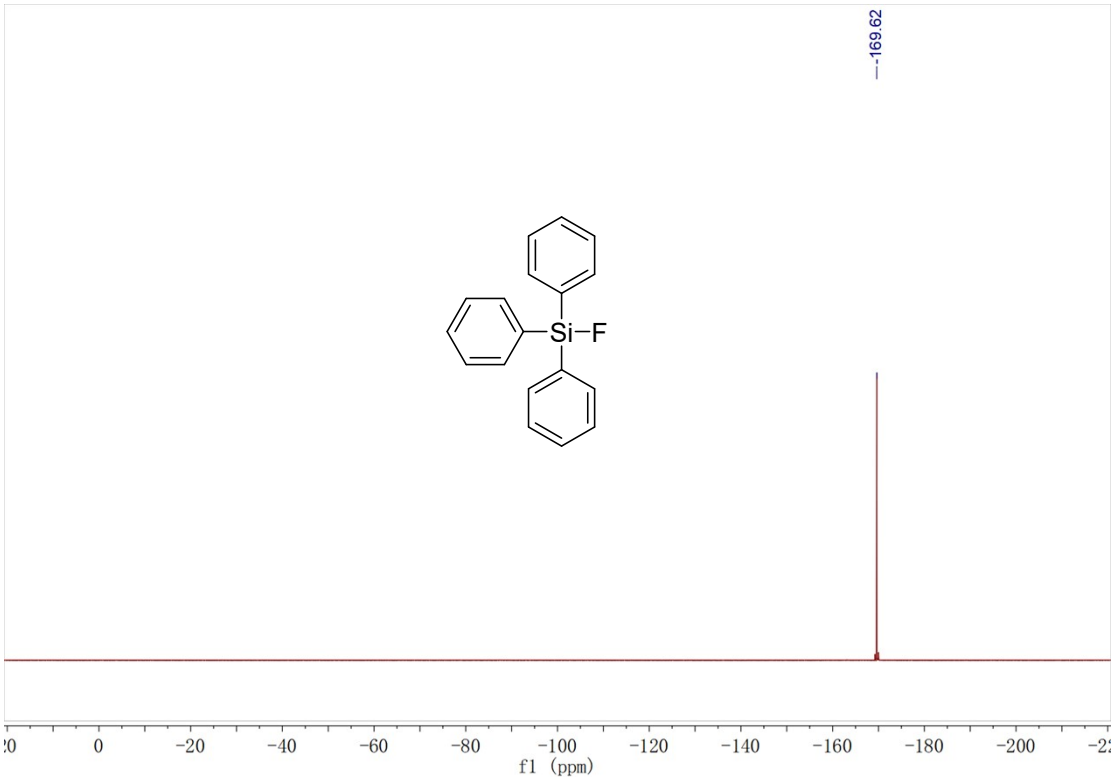


In two separate 5 mL glass vials, substrate **1a** (0.2 mmol, 1.0 equiv) and $FeCl_3 \cdot 6H_2O$ (0.01 equiv) were combined. To the first vial, KHF_2 (0.8 mmol, 4.0 equiv) was added, followed by acetone (2 mL) to dissolve the mixture. To the second vial, tetrabutylammonium fluoride (TBAF, 0.8 mmol, 4.0 equiv) was added, also followed by acetone (2 mL). The resulting mixtures in both vials were then irradiated at room temperature with a 10 W, 390 nm LED for 24 hours. After purification by column chromatography, the fluorosilane product was isolated in yields of 36% and 25%, respectively (see Figures S2 and S3). These results further confirm the photoinduced generation of a silyl cation intermediate.



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.3 Hz, 6H), 7.54 (t, *J* = 7.3 Hz, 3H), 7.47 (d, *J* = 7.3 Hz, 6H).

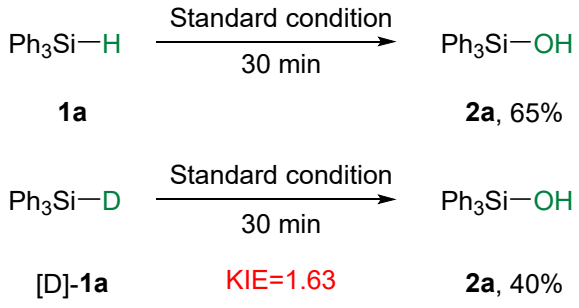
Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of **4**



^{19}F NMR (377 MHz, Chloroform-*d*) δ -169.6.

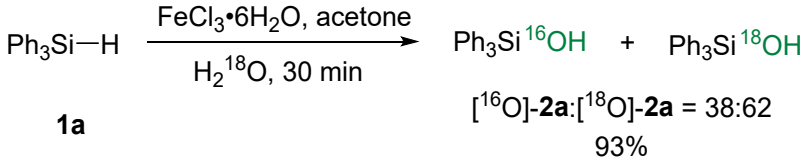
Figure S4. ^{19}F NMR (377 MHz, $CDCl_3$) of **4**

2.2.4 Parallel kinetic isotope effect experiment:



Two parallel reactions were conducted. In the first, substrate 1a (0.2 mmol, 1.0 equiv), $FeCl_3·6H_2O$ (0.01 equiv), and H_2O (10 μL) were placed in a 5 mL glass vial and dissolved in acetone (2 mL). In the second, deuterated substrate [D]-1a (0.2 mmol, 1.0 equiv), $FeCl_3·6H_2O$ (0.01 equiv), and H_2O (10 μL) were added to a separate 5 mL vial and likewise dissolved in acetone (2 mL). Both mixtures were irradiated simultaneously at room temperature using a 10 W, 390 nm LED for 30 min. After completion, each reaction mixture was purified by flash silica column chromatography (eluent: petroleum ether/ethyl acetate = 15:1), affording the corresponding products in 65% and 40% yield, respectively. The product ratio was determined to be 1.63:1, giving a kinetic isotope effect kH/kD = 1.63. This result indicates that cleavage of the Si–H bond is involved in the rate-determining step of the reaction.

2.2.5 Reaction with $H_2{}^{18}O$:



In a 5 mL glass reaction vial, substrate **1a** (0.2 mmol, 1.0 equiv), $FeCl_3 \cdot 6H_2O$ (0.01 equiv), and $H_2{}^{18}O$ (10 μL) were added successively. Acetone (2 mL) was then added to dissolve the mixture. The resulting solution was irradiated at room temperature for 30 minutes using a 10 W, 390 nm blue LED. After then, the solvent was removed under reduced pressure, and the residue was purified by flash silica column chromatography (petroleum ether/ethyl acetate = 15:1) to afford product **2a** (52 mg, 93% yield). High-resolution mass spectrometry (ESI-HRMS) of **2a** (Figure S5) revealed that the product consisted of 38% [^{16}O]-**2a** and 62% [^{18}O]-**2a**. Combined with the previous control experiment, in which the reaction did not proceed under a nitrogen atmosphere, these results indicate that the oxygen in the product originates not only from the added water but also from atmospheric oxygen.

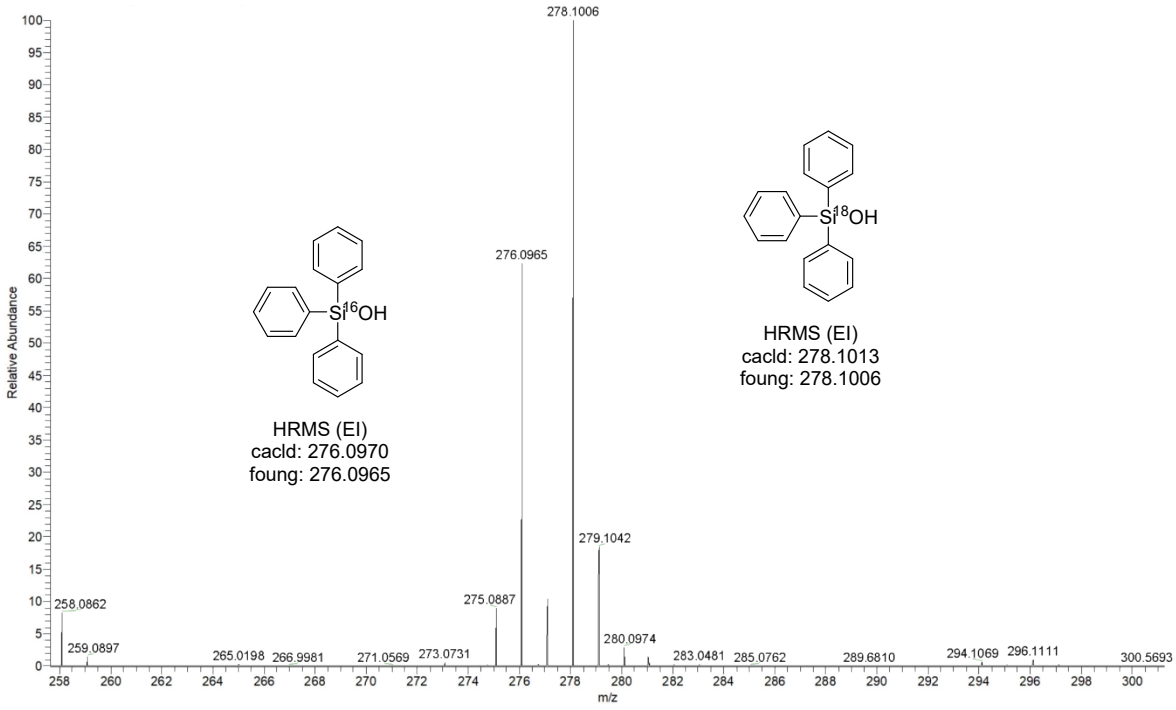


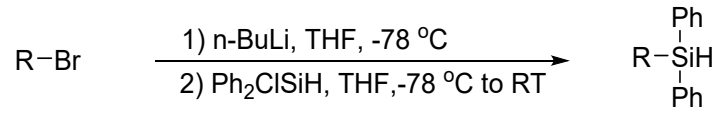
Figure S5. High-resolution mass spectrometry (HRMS) of [^{16}O]-**2a** and [^{18}O]-**2a**

2.2.6 Control Experiment for the Possible Formation of DMDO:

In a 5 mL glass reaction vial, $FeCl_3 \cdot 6H_2O$ (0.01 equiv) was added, followed by acetone (2 mL) and H_2O (10 μL). The mixture was stirred at room temperature for 30 minutes under air with irradiation using a 10 W, 390 nm blue LED (no silane substrate added). A piece of KI-starch test paper was then dipped into the reaction mixture. No color change was observed, indicating the absence of detectable peroxides (including DMDO). This result confirms that DMDO is not formed under our reaction conditions.

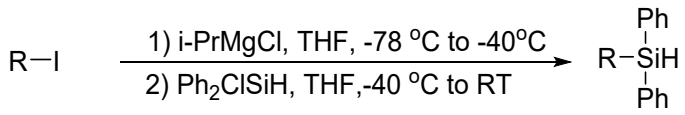
2.3 Synthesis of substrates

1) General procedure for the preparation of starting materials of **1a**-**1o**, **1u**, **1v**.[1]



In a 100 mL round-bottom flask, aryl bromide (5.0 mmol, 1.0 equiv) in THF (10 mL) was cooled to -78 °C. *n*-BuLi (3.2 mL,1.6 M in THF, 6.0 mmol, 1.2 equiv) was added dropwise slowly over 30 min. The resulting mixture was stirred at -78 °C for 2 h before the dropwise addition of chlorodiphenylsilane (6.0 mmol, 1.2 equiv). The reaction was allowed to warm to room temperature and stirred for 8 h. The reaction mixture was quenched with NH_4Cl (15 mL, saturated aqueous solution) and the mixture was extracted with Et_2O (3x15 mL). The combined organic layer was washed with water (20 mL), brine (20 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford the hydrosilane.

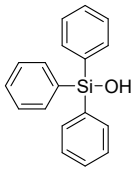
2) General procedure for the preparation of starting materials of **2aa, 2ab, 2ac**:[1]



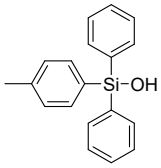
In a 100 mL round-bottom flask, aryl iodide (5.0 mmol, 1.0 equiv) in THF (10 mL) was cooled to -78 °C. *i*-PrMgCl (3 mL, 2.0 M in THF, 6.0 mmol, 1.2 equiv) was added dropwise slowly over 15 min. The resulting mixture was allowed to warm to -40 °C in 2 h and maintained at -40 °C for another 2 h before the dropwise addition of chlorodiphenylsilane (6.0 mmol, 1.2 equiv). The reaction was allowed to warm to room temperature and stirred for 8 h. The reaction mixture was quenched with NH_4Cl (15 mL, saturated aqueous solution) and the mixture was extracted with CH_2Cl_2 (3x15 mL). The combined organic layer was washed with water (20 mL), brine (20 mL), dried over anhydrous Na2SO4, and then concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford the hydrosilane.

2.4 General procedure for the dehydrogenative coupling of H_2O and Organosilanes

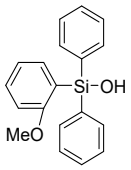
Triphenylsilanol (2a) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 54 mg, 98% yield, colorless oil, known compound[1]. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.68 (dt, *J* = 6.7, 1.5 Hz, 6H), 7.52 – 7.47 (m, 3H), 7.46 – 7.40 (m, 6H), 2.95 (s, 1H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 135.2, 135.0, 130.2, 128.0.



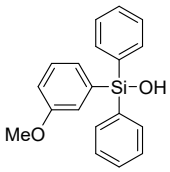
Diphenyl(*p*-tolyl)silanol (2b) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 44 mg, 76% yield, pale yellow oil, known compound[1]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.63 (m, 4H), 7.59 – 7.52 (m, 2H), 7.51 – 7.38 (m, 6H), 7.25 (d, *J* = 7.5 Hz, 2H), 2.66 (s, 1H), 2.41 (d, *J* = 1.7 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.2, 135.4, 135.1, 135.0, 131.5, 130.1, 128.8, 127.9, 21.7.



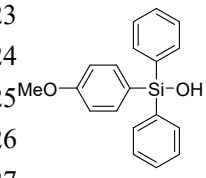
(2-methoxyphenyl)diphenylsilanol (2c) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 53 mg, 87% yield, pale yellow oil, known compound[7]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 – 7.61 (m, 4H), 7.48 – 7.37 (m, 7H), 7.25 (s, 1H), 7.01 – 6.93 (m, 2H), 3.77 (s, 3H), 3.17 (s, 1H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.4, 136.9, 135.6, 135.1, 132.0, 129.9, 127.8, 123.3, 121.0, 110.1, 55.4.



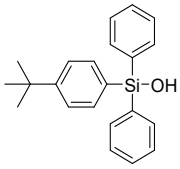
(3-methoxyphenyl)diphenylsilanol (2d) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 47 mg, 77% yield, pale yellow oil, known compound[2]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.61 (m, 4H), 7.50 – 7.36 (m, 7H), 7.28 – 7.19 (m, 2H), 7.01 (dd, *J* = 8.3, 2.7 Hz, 1H), 3.80 (s, 3H), 2.83 (s, 1H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.0, 136.7, 135.0, 135.0, 130.2, 129.3, 128.0, 127.4, 120.2, 115.7, 55.2.



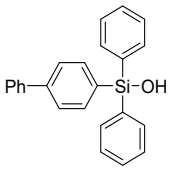
(4-methoxyphenyl)diphenylsilanol (2e) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 51 mg, 84% yield, pale yellow oil, known compound[1]. 1H NMR (500 MHz, Chloroform-*d*) δ 7.68 – 7.63 (m, 4H), 7.60 – 7.55 (m, 2H), 7.50 – 7.38 (m, 6H), 6.99 – 6.94 (m, 2H), 3.85 (s, 3H), 2.49 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 161.3, 136.7, 135.5, 135.0, 130.1, 128.0, 126.1, 113.7, 55.1.



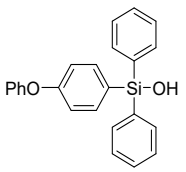
(4-(tert-butyl)phenyl)diphenylsilanol (2f) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 59 mg, 88% yield, colorless oil, known compound[1]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.66 (m, 4H), 7.63 – 7.58 (m, 2H), 7.48 – 7.39 (m, 8H), 2.65 (s, 1H), 1.36 (s, 9H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.2, 135.4, 135.0, 135.0, 131.6, 130.0, 128.0, 125.0, 34.8, 31.2.



[1,1'-biphenyl]-4-yldiphenylsilanol (2g) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 68 mg, 97% yield, white solid, mp: 104-106 °C, known compound[1]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.69 (m, 6H), 7.67 – 7.62 (m, 4H), 7.52 – 7.37 (m, 9H), 2.83 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.8, 140.9, 135.6, 135.2, 135.1, 133.9, 130.2, 128.9, 128.0, 127.7, 127.3, 126.7.

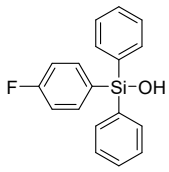


(4-phenoxyphenyl)diphenylsilanol (2h) was purified by flash column chromatography on silica

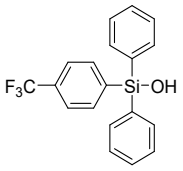


gel (petroleum ether/ethyl acetate = 10:1). 72 mg, 99% yield, colorless oil, known compound[3]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.63 (m, 4H), 7.64 – 7.58 (m, 2H), 7.51 – 7.36 (m, 8H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.13 – 6.99 (m, 4H), 2.79 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.4, 156.4, 136.8, 135.2, 135.0, 130.2, 129.9, 129.0, 128.0, 123.8, 119.6, 117.9.

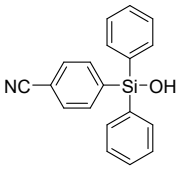
(4-fluorophenyl)diphenylsilanol (2i) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 54 mg, 92% yield, white solid, mp: 117-119 °C, known compound[4]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.60 (m, 6H), 7.51 – 7.46 (m, 2H), 7.42 (dd, *J* = 7.9, 6.5 Hz, 4H), 7.13 – 7.07 (m, 2H), 2.66 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.6, 163.1, 137.2, 137.1, 135.0, 134.9, 130.8, 130.3, 128.0, 115.3, 115.1.^{19}F NMR (377 MHz, Chloroform-*d*) δ -110.00.



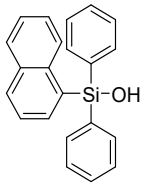
diphenyl(4-(trifluoromethyl)phenyl)silanol (2j) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 57 mg, 83% yield, pale yellow oil, known compound[1]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.67 – 7.59 (m, 6H), 7.53 – 7.47 (m, 2H), 7.46 – 7.39 (m, 4H), 3.07 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.1, 135.34, 135.31, 135.0, 134.98, 134.2, 130.6, 130.5, 128.18, 128.15, 124.52. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.9.



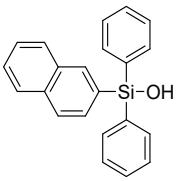
4-(hydroxydiphenylsilyl)benzonitrile (2k) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 48 mg, 80% yield, colorless oil, known compound[1]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.74 (m, 2H), 7.66 – 7.59 (m, 6H), 7.53 – 7.48 (m, 2H), 7.47 – 7.38 (m, 4H), 2.64 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.1, 135.4, 134.9, 133.8, 131.2, 130.7, 128.2, 118.9, 113.5.



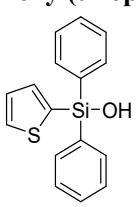
naphthalen-1-yldiphenylsilanol (2l) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 48 mg, 74% yield, pale yellow oil, known compound[1]. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.19 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.75 – 7.64 (m, 5H), 7.49 (m, 4H), 7.45 – 7.38 (m, 5H), 2.89 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.2, 136.6, 135.7, 135.1, 133.5, 133.0, 131.1, 130.2, 129.0, 128.9, 128.1, 126.2, 125.7, 125.1.



naphthalen-2-yldiphenylsilanol (2m) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 58 mg, 89% yield, white solid, mp: 52-54 °C, known compound[2]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.91 – 7.83 (m, 3H), 7.71 (m, 5H), 7.59 – 7.42 (m, 8H), 2.79 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.4, 135.1, 135.1, 134.3, 132.8, 132.6, 130.6, 130.3, 128.5, 128.1, 127.8, 127.3, 127.0, 126.1.

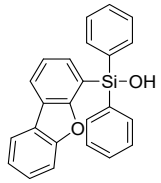


diphenyl(thiophen-2-yl)silanol (2n) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 45 mg, 80% yield, colorless oil, known

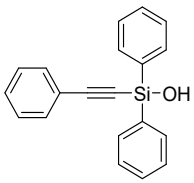


compound[1]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.67 (m, 5H), 7.54 – 7.41 (m, 7H), 7.29 – 7.25 (m, 1H), 2.54 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.7, 134.9, 134.8, 134.7, 132.6, 130.4, 128.4, 128.0.

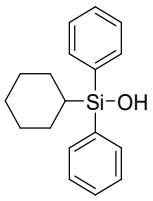
dibenzo[b,d]furan-4-yldiphenylsilanol (2o) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 72 mg, 99% yield, white solid, mp: 46-48 °C, known compound[1]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.6, 1.4 Hz, 1H), 8.00 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.73 (m, 4H), 7.55 – 7.35 (m, 12H), 3.29 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.9, 155.9, 135.1, 134.7, 134.3, 130.4, 128.0, 127.2, 124.0, 123.2, 122.9, 122.9, 122.8, 120.7, 118.2, 111.9.



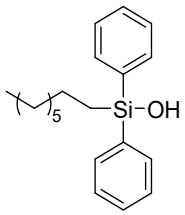
diphenyl(phenylethynyl)silanol (2p) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 20 mg, 33% yield, colorless oil, known compound[4]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86 (ddd, *J* = 7.9, 3.3, 1.6 Hz, 3H), 7.62 (dt, *J* = 8.3, 1.6 Hz, 2H), 7.56 – 7.30 (m, 10H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 134.6, 134.5, 132.4, 130.6, 129.4, 128.4, 128.1, 122.2, 108.0, 89.7.



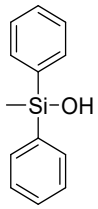
cyclohexyldiphenylsilanol (2q) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 22 mg, 40% yield, colourless solid, mp: 154-156 °C, known compound[2]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.70 – 7.62 (m, 4H), 7.49 – 7.38 (m, 6H), 1.90 – 1.83 (m, 2H), 1.77 (ddd, *J* = 7.4, 4.9, 2.4 Hz, 3H), 1.36 – 1.24 (m, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 135.4, 134.6, 129.8, 127.9, 27.9, 26.9, 26.8, 25.5.



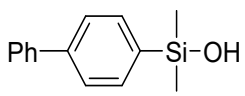
octyldiphenylsilanol (2r) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 45 mg, 73% yield, colourless oil, known compound[5]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.0 Hz, 4H), 7.48 – 7.34 (m, 6H), 2.46 (h, *J* = 12.3 Hz, 1H), 1.48 (d, *J* = 7.8 Hz, 2H), 1.40 – 1.25 (m, 11H), 1.18 (dd, *J* = 10.1, 6.3 Hz, 2H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.5, 134.2, 129.9, 127.9, 33.5, 31.9, 29.3, 29.2, 23.0, 22.7, 15.1, 14.2.



methyldiphenylsilanol (2s) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 42 mg, 99% yield, colourless oil, known compound[1]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.61 (m, 4H), 7.48 – 7.38 (m, 6H), 2.41 (s, 1H), 0.70 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.1, 134.0, 129.9, 128.0.

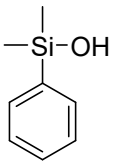


[1,1'-biphenyl]-4-yldimethylsilanol (2t) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 34 mg, 75% yield, white solid, mp: 77-79 °C, known

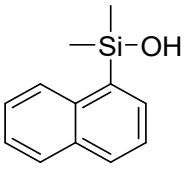


compound[6]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.58 (m, 6H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 0.43 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.0, 141.1, 138.5, 133.6, 128.8, 127.4, 127.2, 126.5, 1.0.

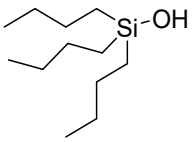
dimethyl(phenyl)silanol (2u) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 18 mg, 60% yield, colourless oil, known compound[4].^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.56 (m, 2H), 7.43 – 7.36 (m, 3H), 0.37 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.8, 133.0, 129.3, 127.7, 0.9.



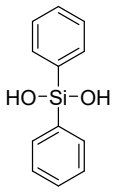
dimethyl(naphthalen-1-yl)silanol (2v) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 29 mg, 73% yield, colourless oil, known compound[4]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 – 8.27 (m, 1H), 7.94 – 7.88 (m, 2H), 7.80 (dd, *J* = 6.8, 1.4 Hz, 1H), 7.58 – 7.48 (m, 3H), 1.99 (s, 1H), 0.61 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.9, 136.6, 133.4, 133.3, 130.5, 129.1, 128.2, 126.1, 125.6, 125.1, 1.4.



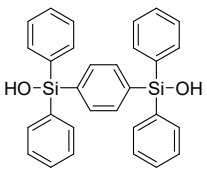
Tributylsilanol (2w) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). 30 mg, 70% yield, colorless oil, known compound[1].^{1}H NMR (500 MHz, Chloroform-*d*) δ 1.40 – 1.26 (m, 12H), 0.91 (t, *J* = 6.9 Hz, 9H), 0.64 – 0.43 (m, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 26.7, 25.5, 15.5, 13.8.



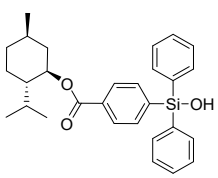
Diphenylsilanediol (2x) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1). 32 mg, 74% yield, white solid, mp: 142-144 °C, known compound[1]. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.66 – 7.57 (m, 4H), 7.41 – 7.31 (m, 6H), 6.97 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 138.3, 134.5, 129.8, 127.9.



1,4-phenylenebis(diphenylsilanol) (2y) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1). 82 mg, 86% yield, white solid, mp: 234-236 °C, known compound[1]. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.60 (s, 4H), 7.58 – 7.54 (m, 8H), 7.45 – 7.36 (m, 12H), 7.18 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 138.6, 136.8, 135.0, 134.2, 130.2, 128.3.

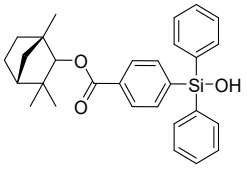


(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(hydroxydiphenylsilyl)benzoate (2aa) was purified by flash column chromatography on silica gel (petroleum ether/ethyl

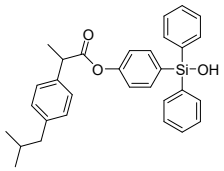


acetate = 5:1). 69 mg, 76% yield, colorless oil, known compound[1]. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.08 – 8.01 (m, 2H), 7.79 – 7.72 (m, 2H), 7.64 (dt, J = 8.0, 1.5 Hz, 4H), 7.51 – 7.38 (m, 6H), 4.97 (td, J = 10.9, 4.4 Hz, 1H), 3.16 (s, 1H), 2.19 – 2.11 (m, 1H), 1.99 (pd, J = 6.9, 2.7 Hz, 1H), 1.77 (dq, J = 14.9, 3.3 Hz, 2H), 1.63 – 1.54 (m, 2H), 1.19 – 1.10 (m, 2H), 0.97 (d, J = 4.9 Hz, 4H), 0.95 (d, J = 5.2 Hz, 3H), 0.82 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 141.3, 135.0, 135.0, 134.6, 132.0, 130.3, 128.7, 128.1, 75.1, 47.3, 40.9, 34.3, 31.5, 26.5, 23.6, 22.1, 20.9, 16.6.

(1S,4R)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 4-(hydroxydiphenylsilyl)benzoate (2ab) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1). 68 mg, 75% yield, pale yellow oil, known compound[3]. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.10 – 8.03 (m, 2H), 7.78 – 7.73 (m, 2H), 7.65 (dt, J = 6.6, 1.5 Hz, 4H), 7.51 – 7.46 (m, 2H), 7.45 – 7.38 (m, 4H), 4.64 (d, *J* = 1.9 Hz, 1H), 2.67 (s, 1H), 2.00 – 1.87 (m, 1H), 1.85 – 1.75 (m, 2H), 1.69 (dq, *J* = 10.4, 2.1 Hz, 1H), 1.54 (tdd, *J* = 12.5, 5.8, 4.1 Hz, 1H), 1.29 (d, *J* = 1.7 Hz, 1H), 1.21 (s, 5H), 1.13 (s, 3H), 0.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 135.01, 134.98, 134.5, 132.0, 130.4, 128.7, 128.1, 86.9, 48.7, 48.4, 41.5, 39.9, 29.8, 26.9, 25.9, 20.3, 19.5.



5-(hydroxydiphenylsilyl)phenyl 2-(4-isobutylphenyl)propanoate (2ac) was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1). 57 mg, 60% yield, colorless oil, known compound[1].1H NMR (500 MHz, Chloroform-d) δ 7.63 (td, J = 6.3, 3.2 Hz, 6H), 7.51 – 7.45 (m, 2H), 7.40 (t, J = 7.4 Hz, 4H), 7.36 (d, J = 7.8 Hz, 2H), 7.20 (s, 2H), 7.05 (d, J = 8.0 Hz, 2H), 4.00 (q, J = 7.1 Hz, 1H), 3.10 (s, 1H), 2.54 (d, J = 7.2 Hz, 2H), 1.94 (dq, J = 13.4, 6.7 Hz, 1H), 1.66 (d, J = 7.2 Hz, 3H), 0.98 (d, J = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.3, 152.6, 140.9, 137.2, 136.4, 135.0, 135.0, 132.7, 130.2, 129.6, 128.0, 127.3, 121.0, 45.4, 45.1, 30.3, 22.5, 18.6.



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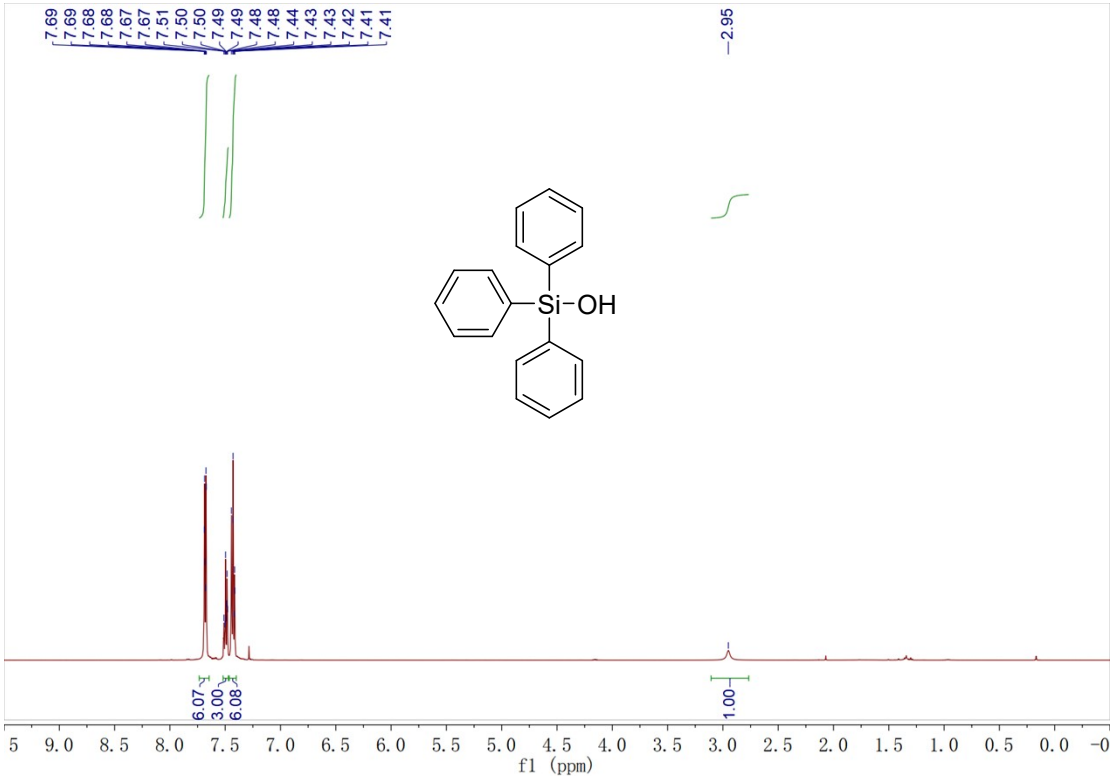
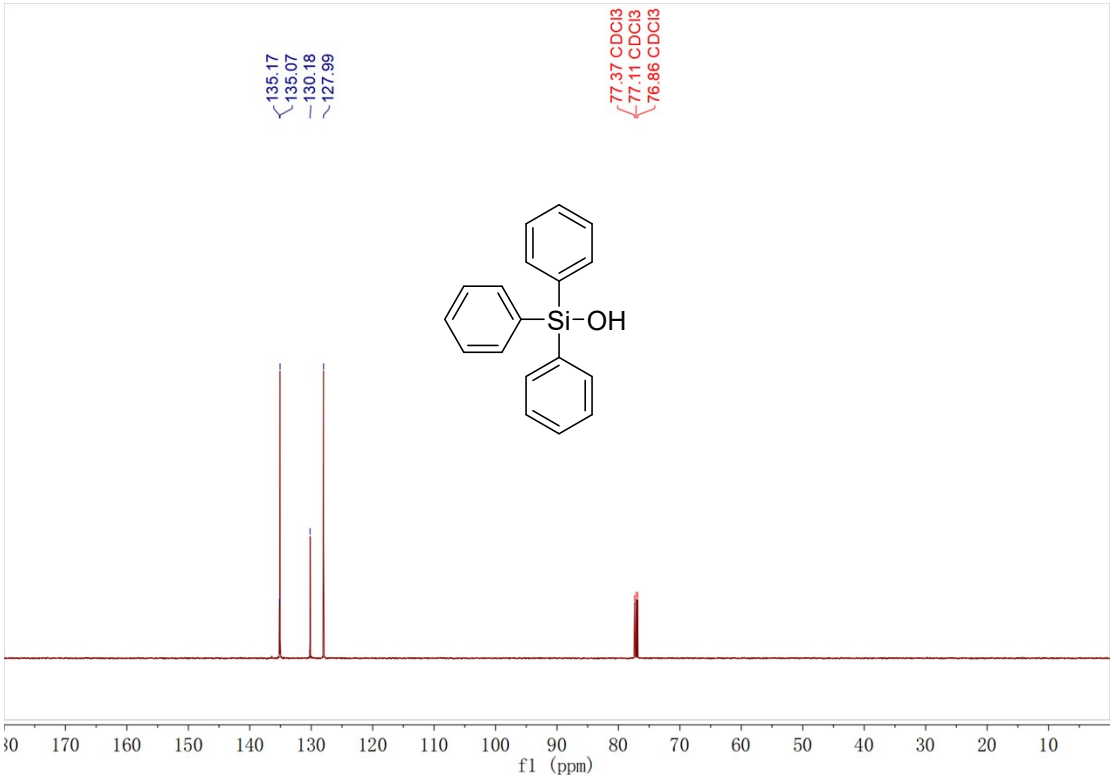
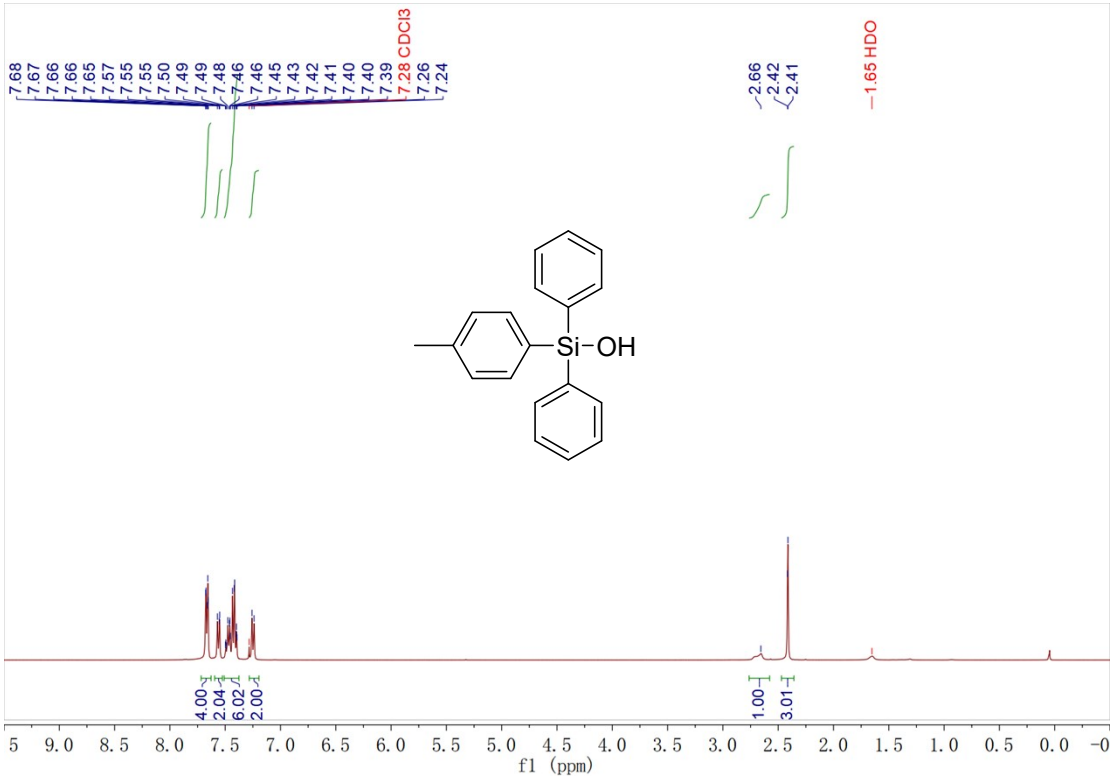
4 Copies of NMR for the Compounds



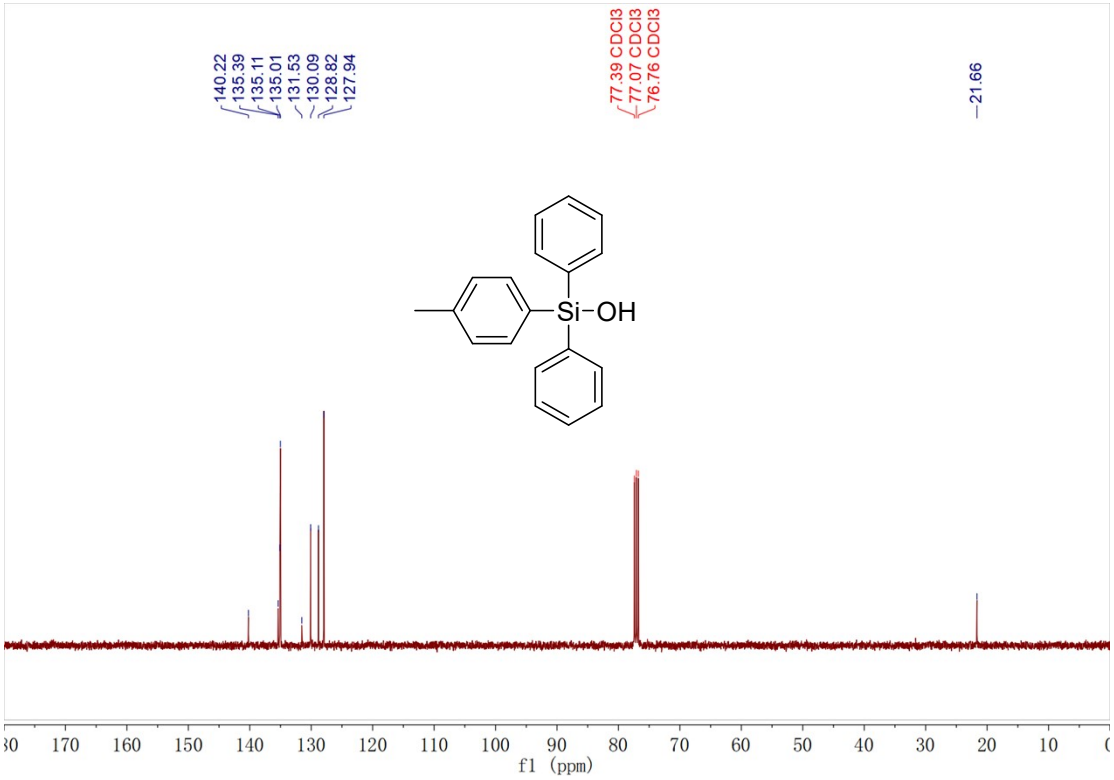
^{1}H NMR (500 MHz, $CDCl_3$) of **2a**



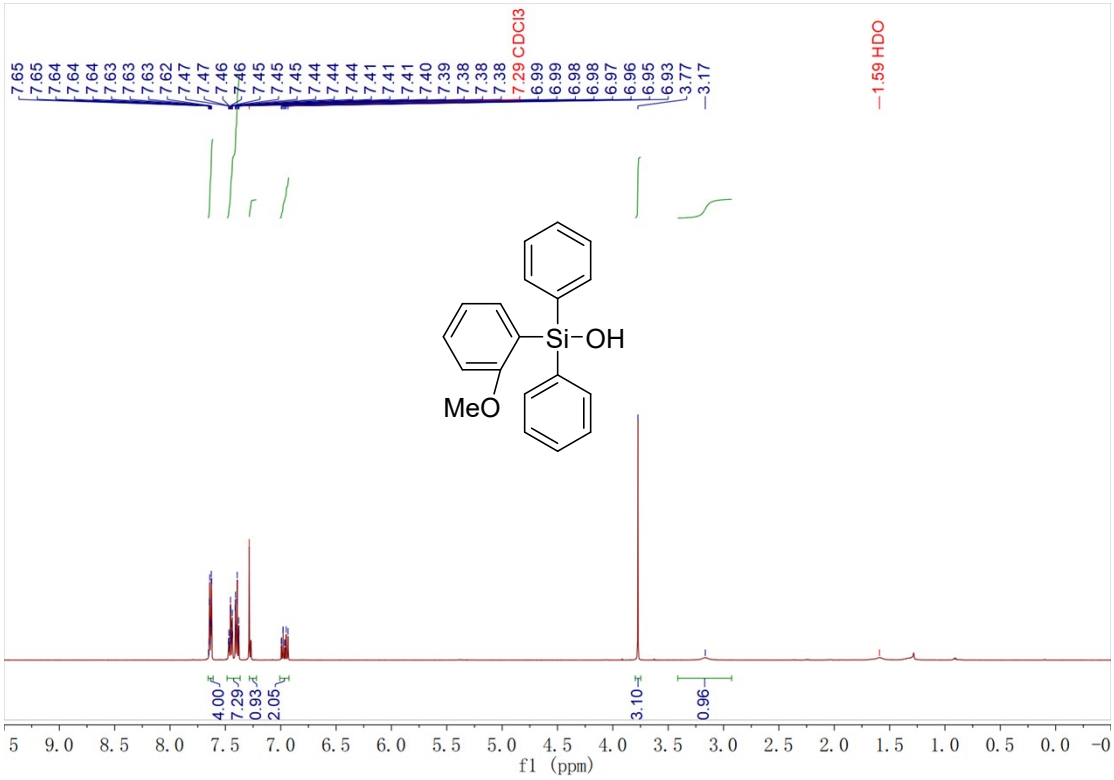
^{13}C NMR (126 MHz, $CDCl_3$) of **2a**



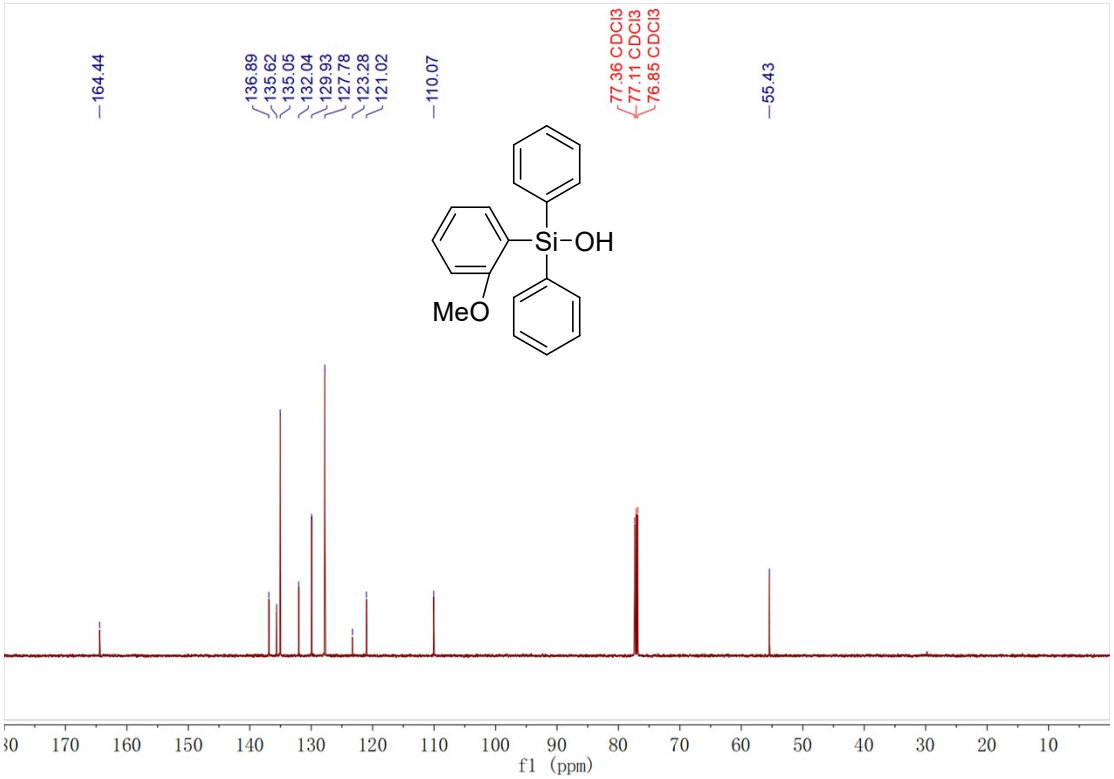
^{1}H NMR (400 MHz, $CDCl_3$) of **2b**



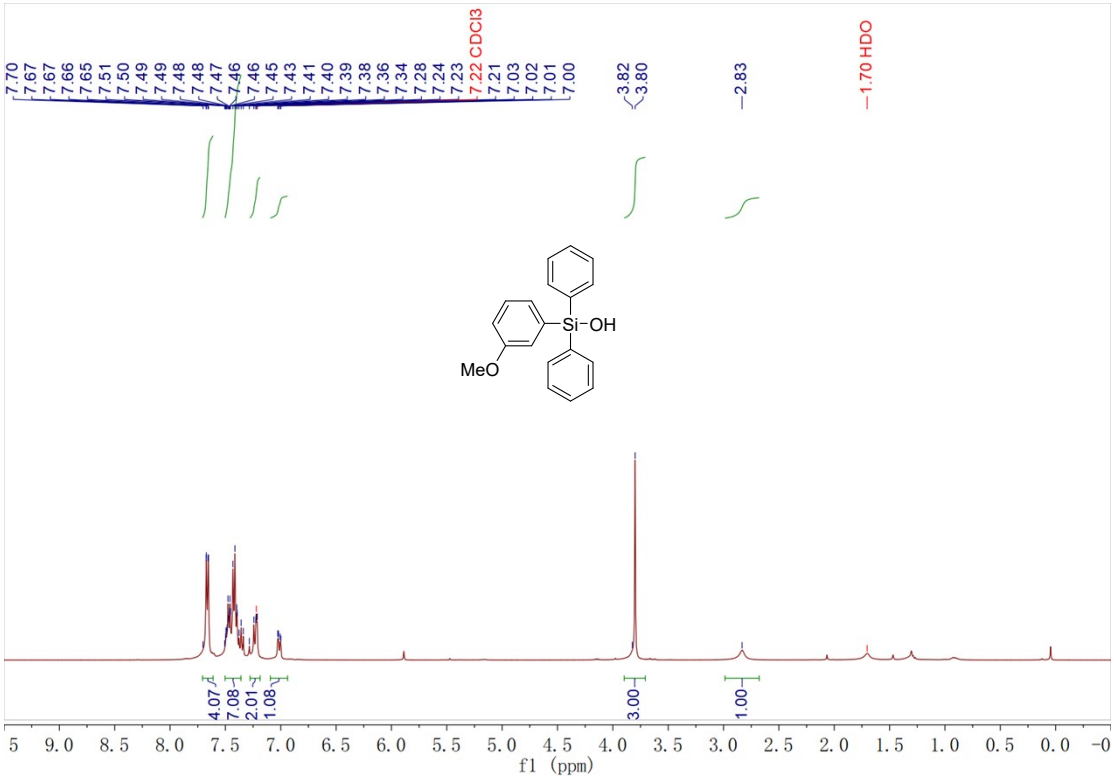
^{13}C NMR (100 MHz, $CDCl_3$) of **2b**



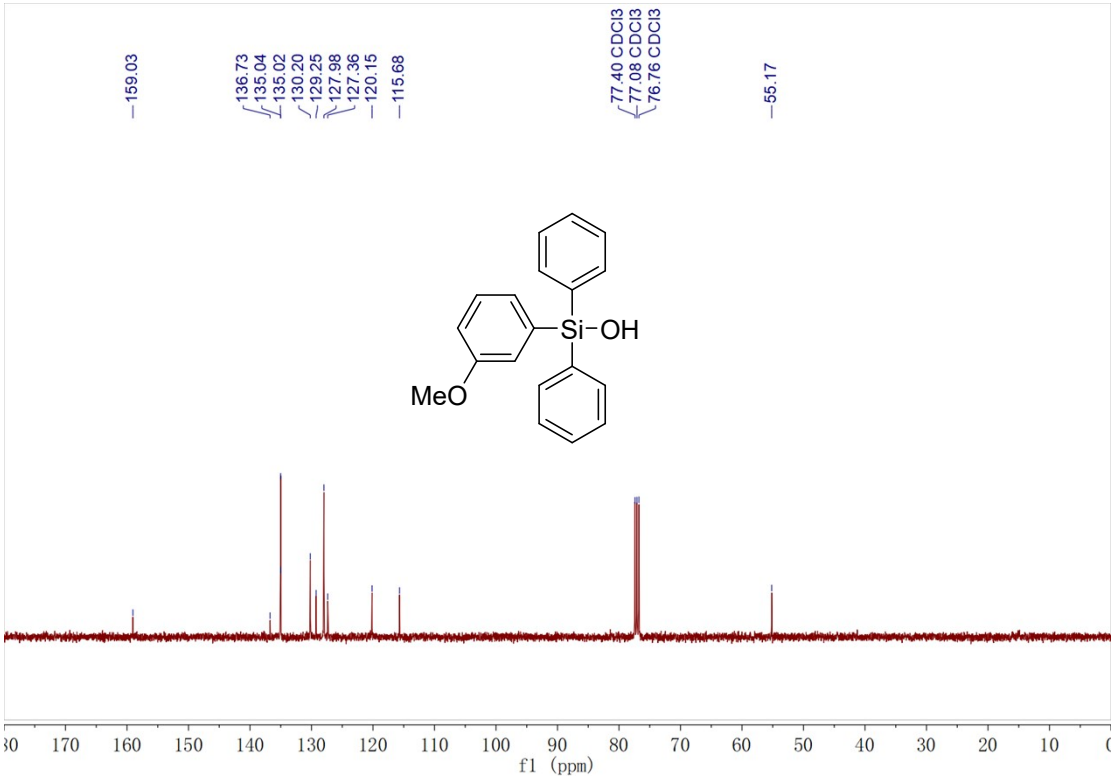
^{1}H NMR (500 MHz, $CDCl_3$) of **2c**



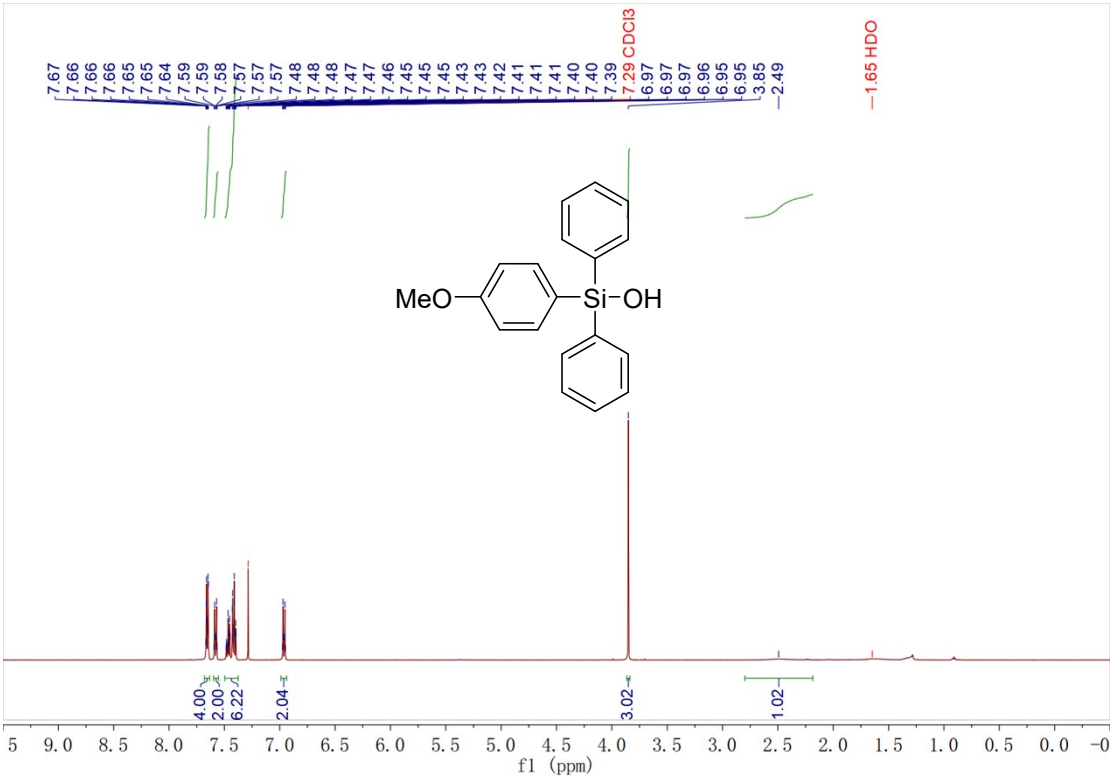
^{13}C NMR (126 MHz, $CDCl_3$) of **2c**



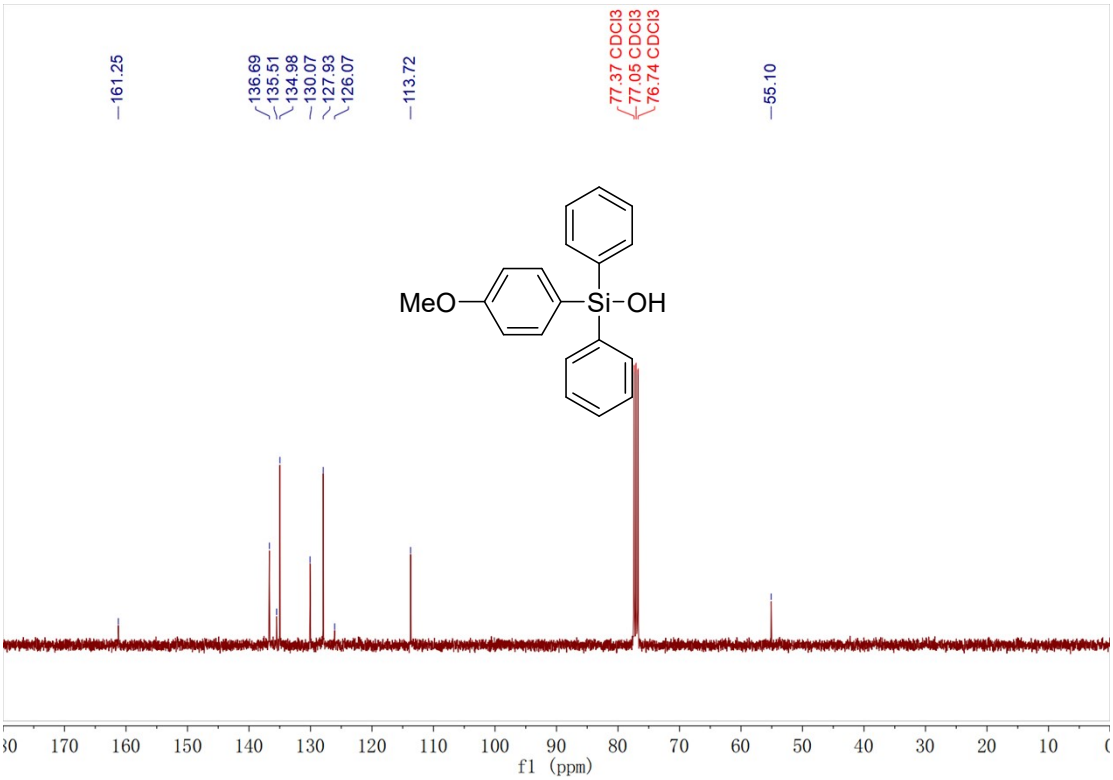
^{1}H NMR (400 MHz, $CDCl_3$) of **2d**



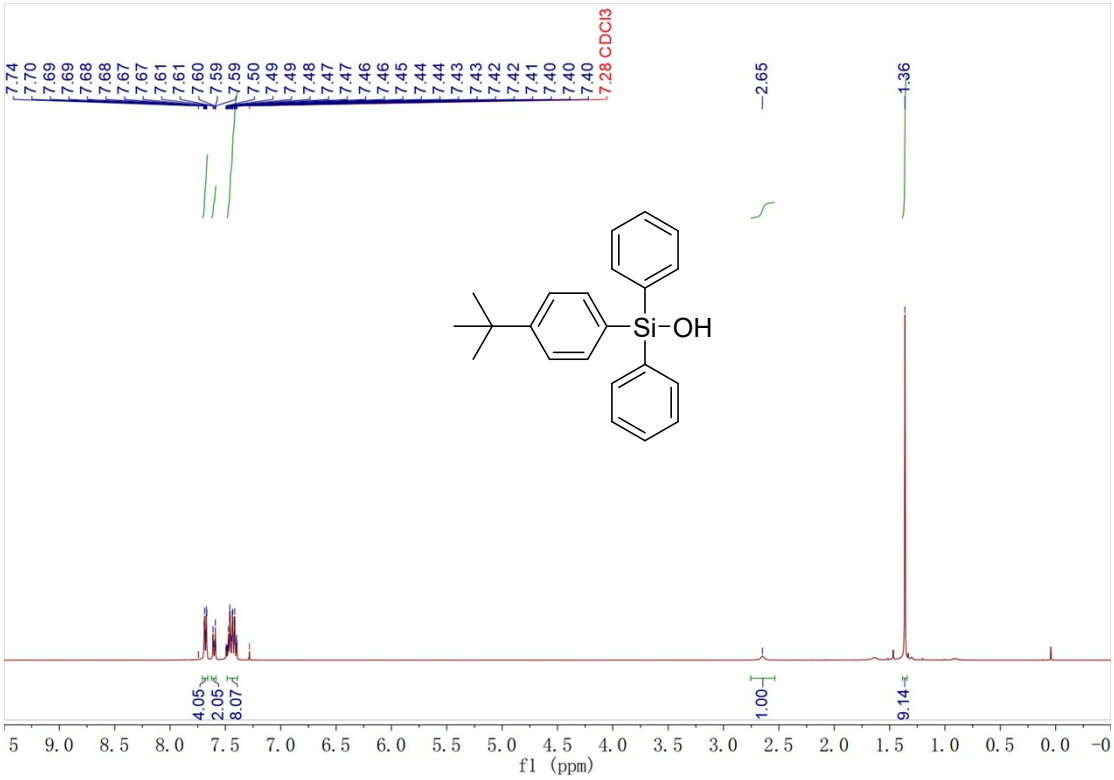
^{13}C NMR (100 MHz, $CDCl_3$) of **2d**



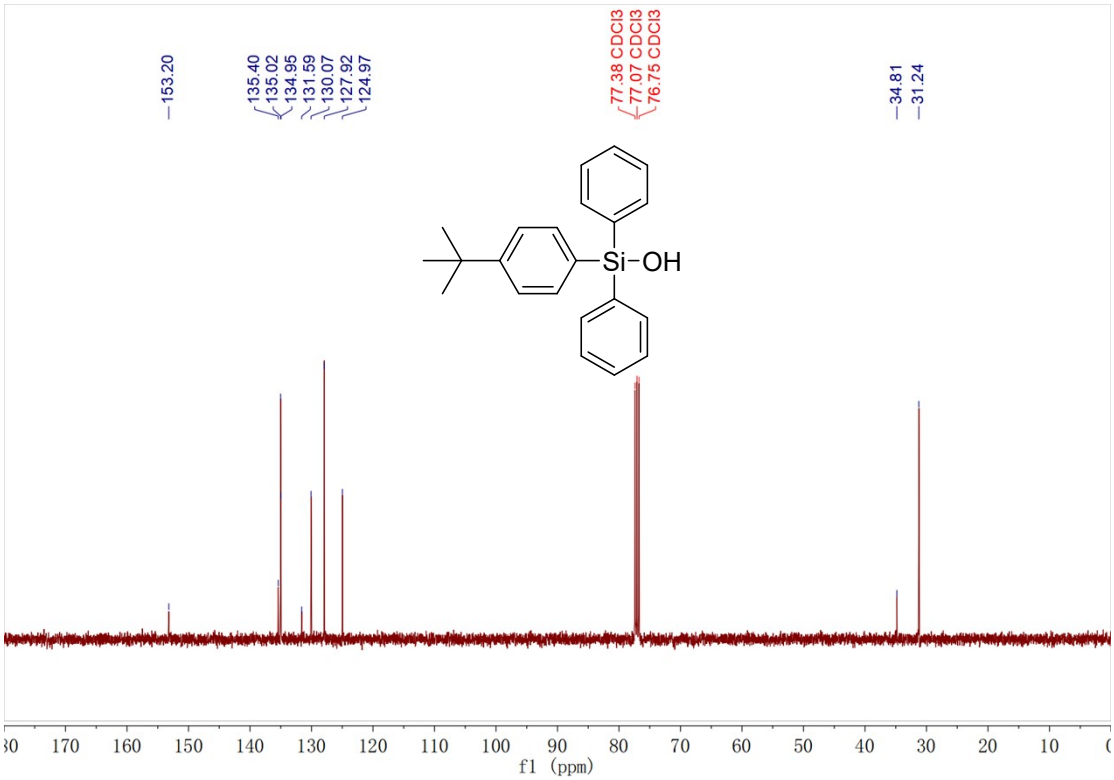
^{1}H NMR (400 MHz, $CDCl_3$) of **2e**



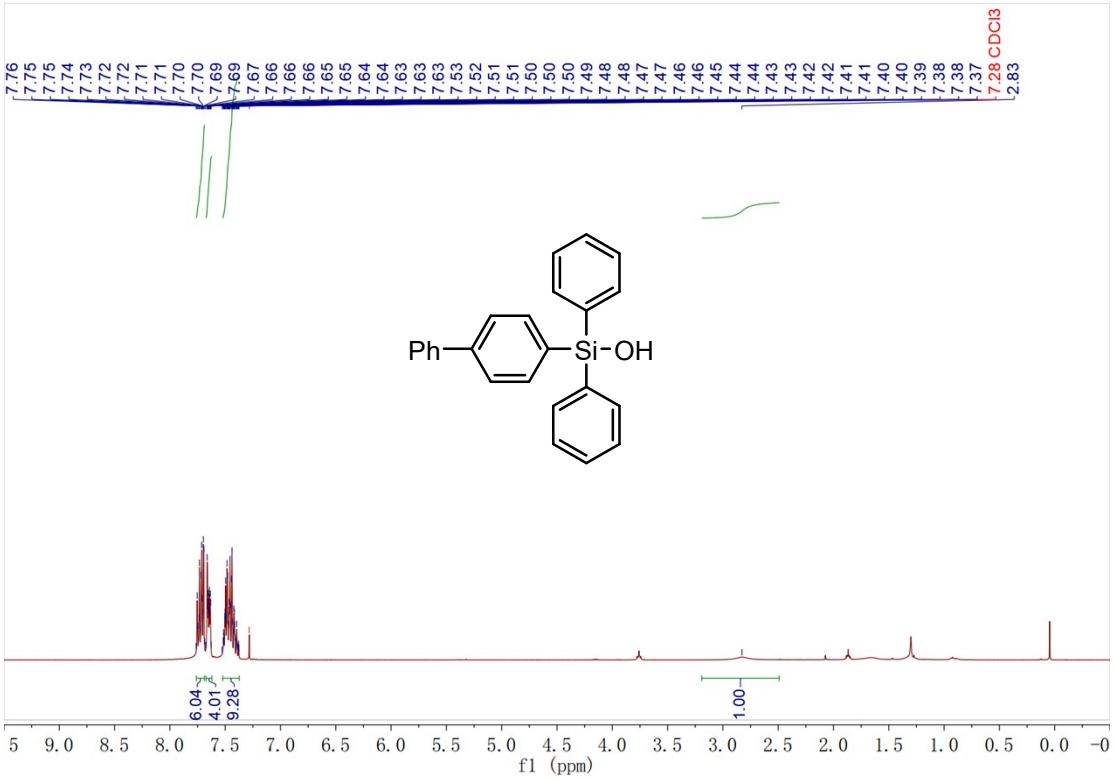
^{13}C NMR (100 MHz, $CDCl_3$) of **2e**



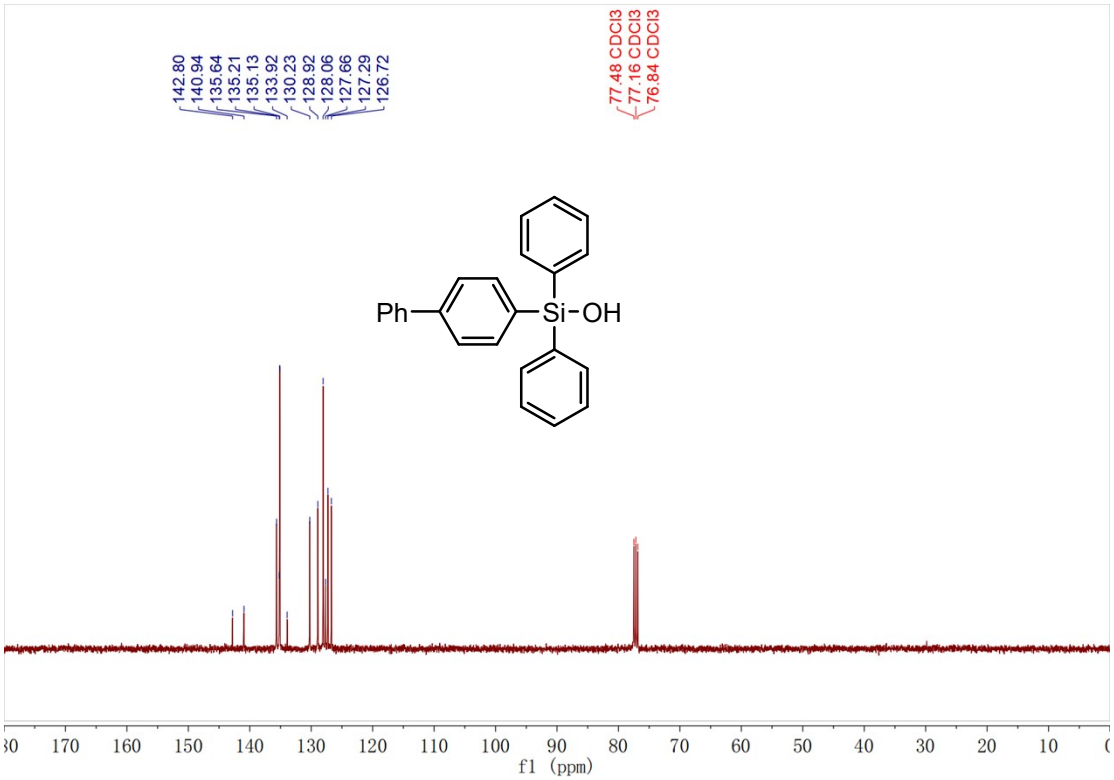
^{1}H NMR (400 MHz, $CDCl_3$) of **2f**



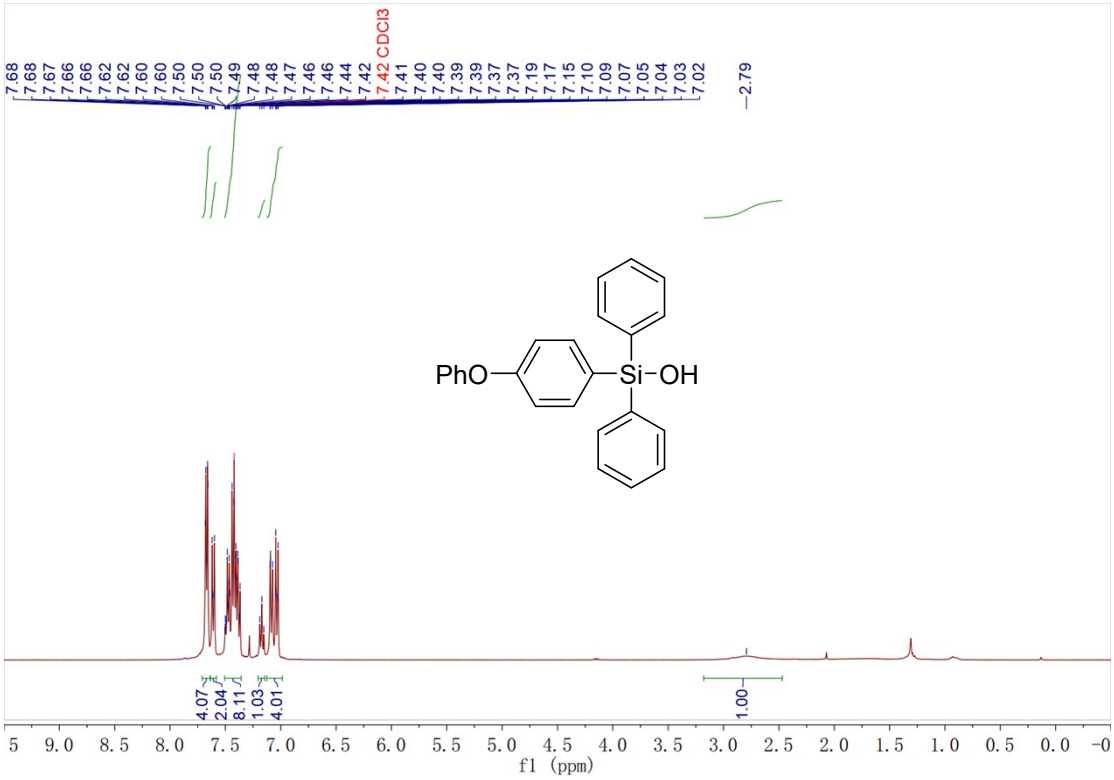
^{13}C NMR (100 MHz, $CDCl_3$) of **2f**



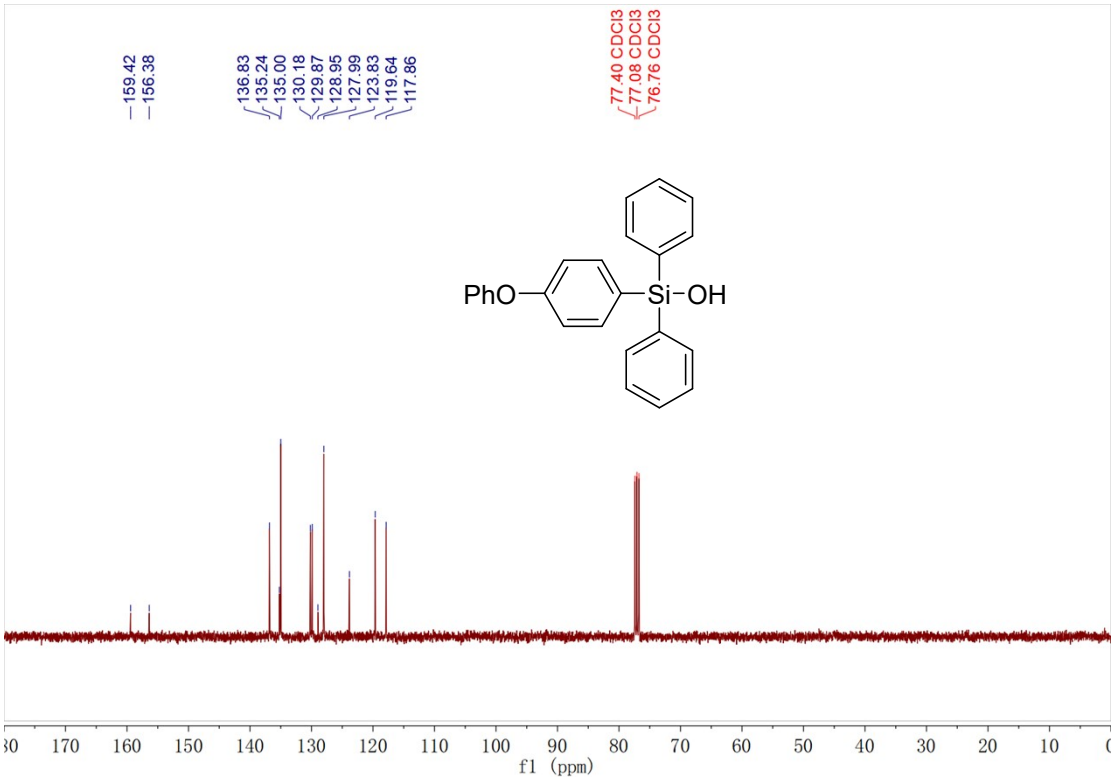
^{1}H NMR (400 MHz, $CDCl_3$) of **2g**



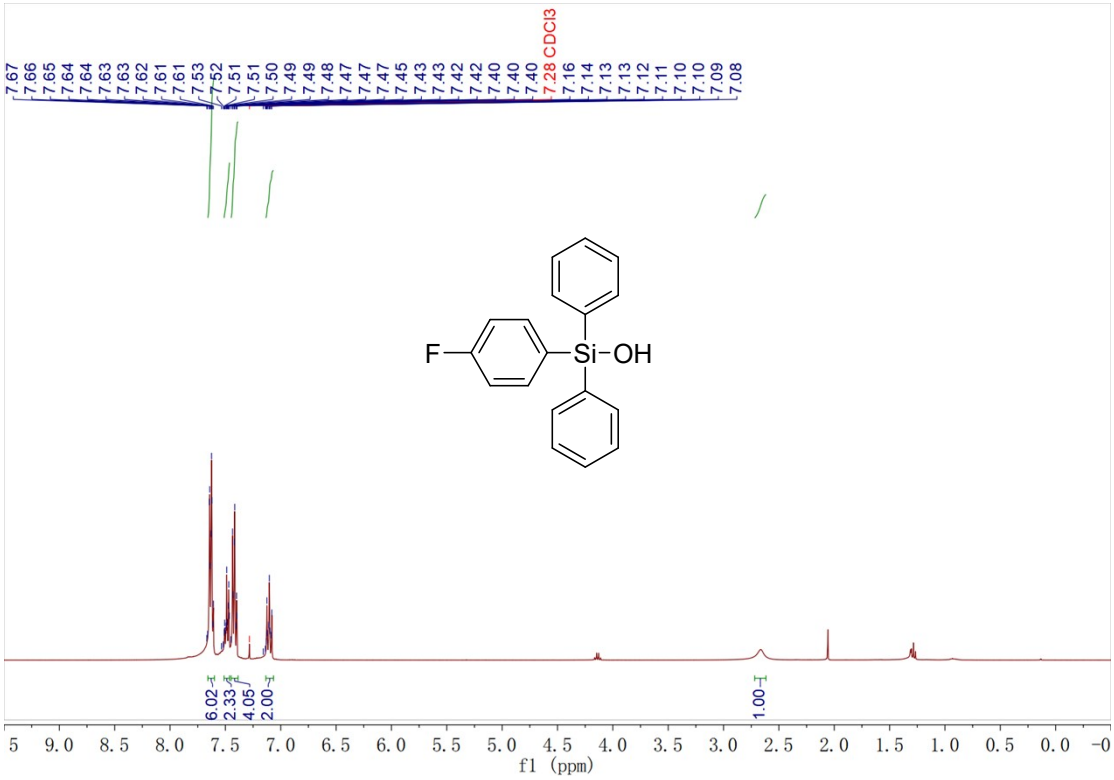
^{13}C NMR (100 MHz, $CDCl_3$) of **2g**



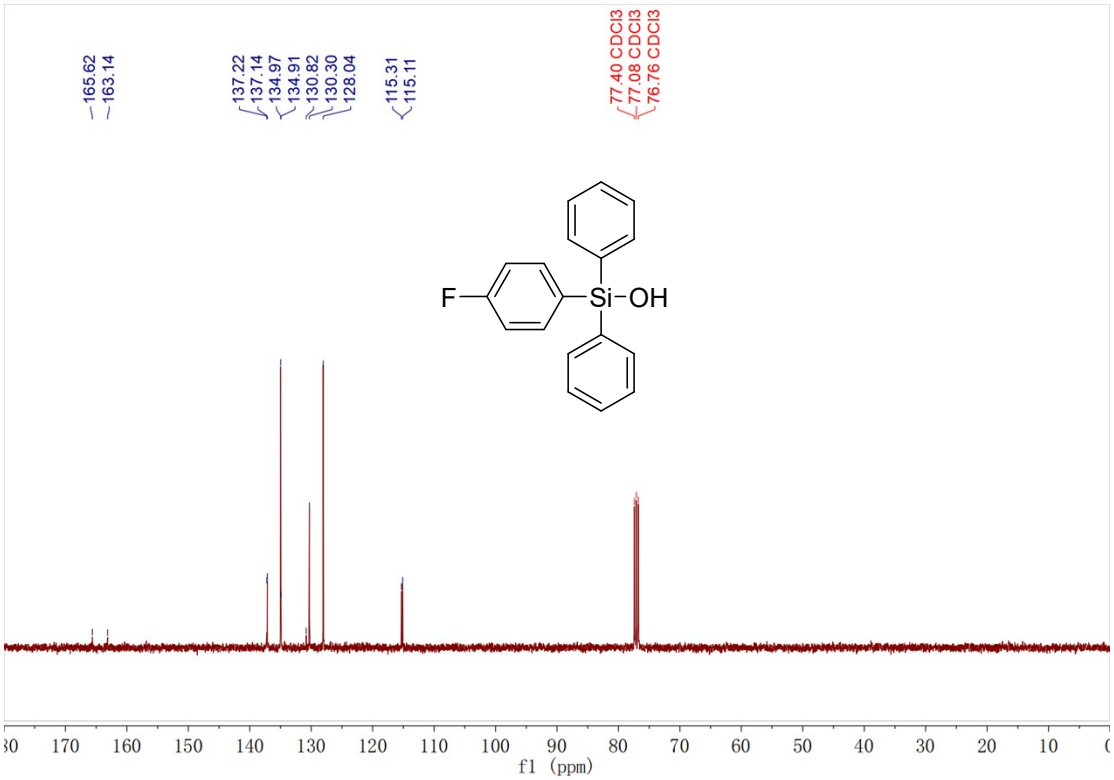
^{1}H NMR (400 MHz, $CDCl_3$) of **2h**



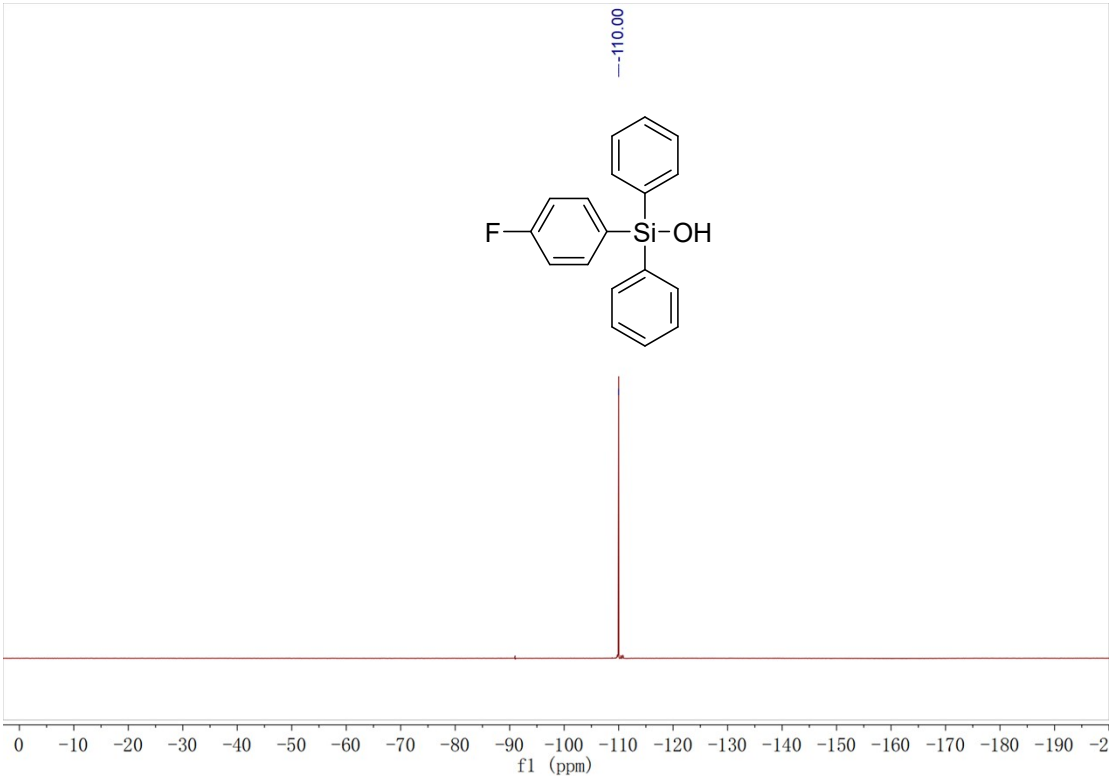
^{13}C NMR (100 MHz, $CDCl_3$) of **2h**



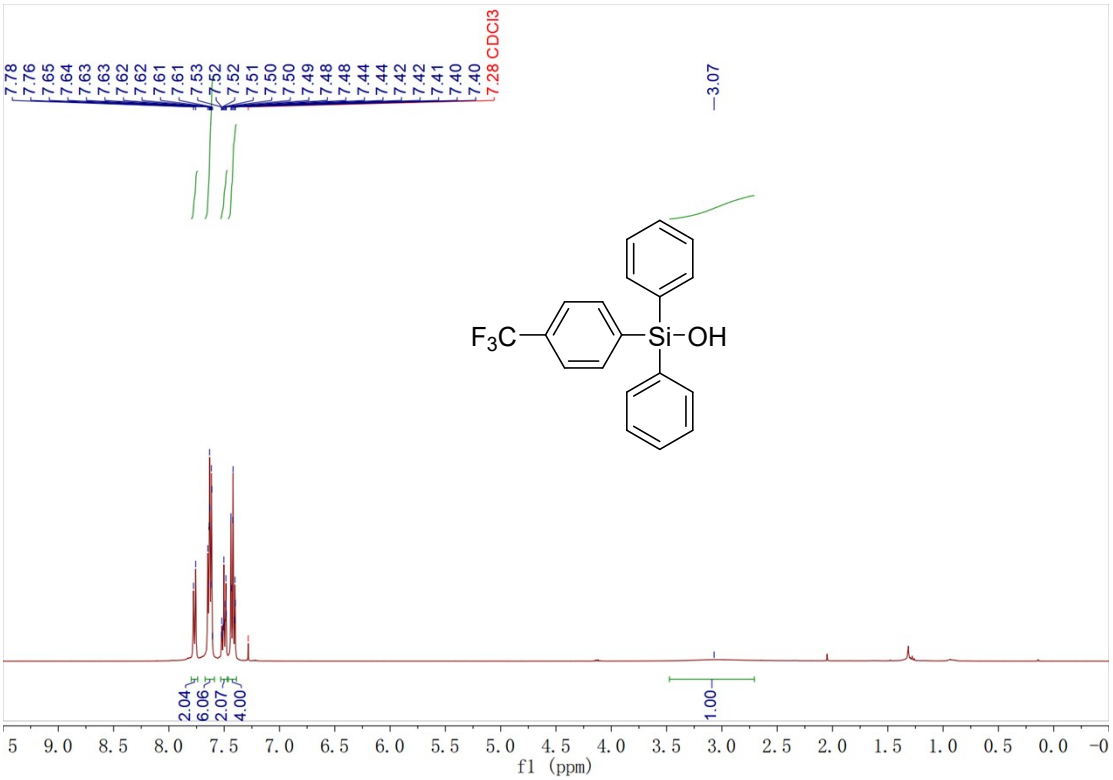
^{1}H NMR (400 MHz, $CDCl_3$) of **2i**



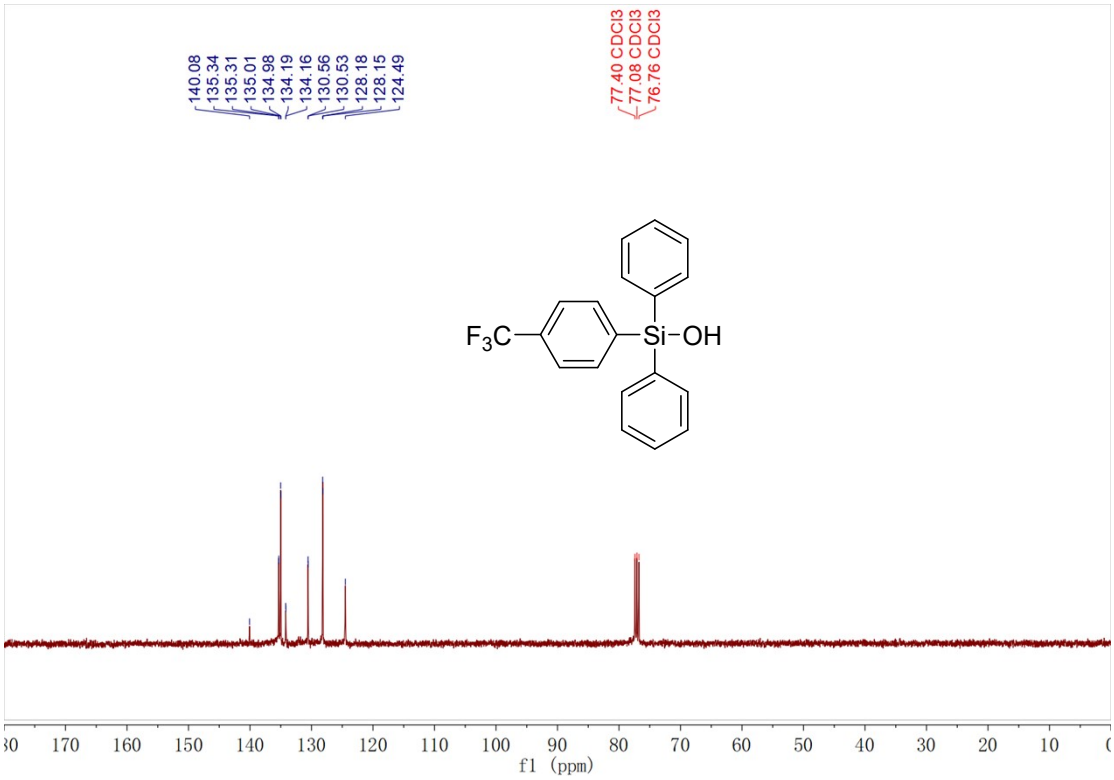
^{13}C NMR (100 MHz, $CDCl_3$) of **2i**



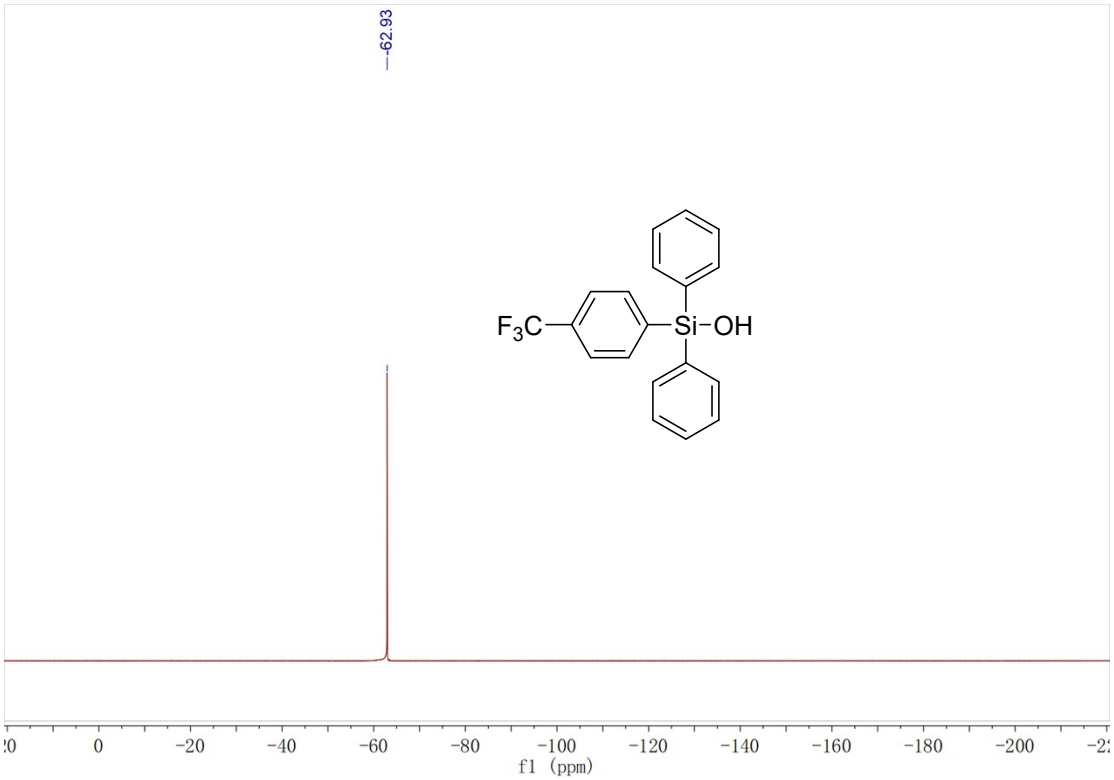
^{19}F NMR (377 MHz, $CDCl_3$) of **2i**



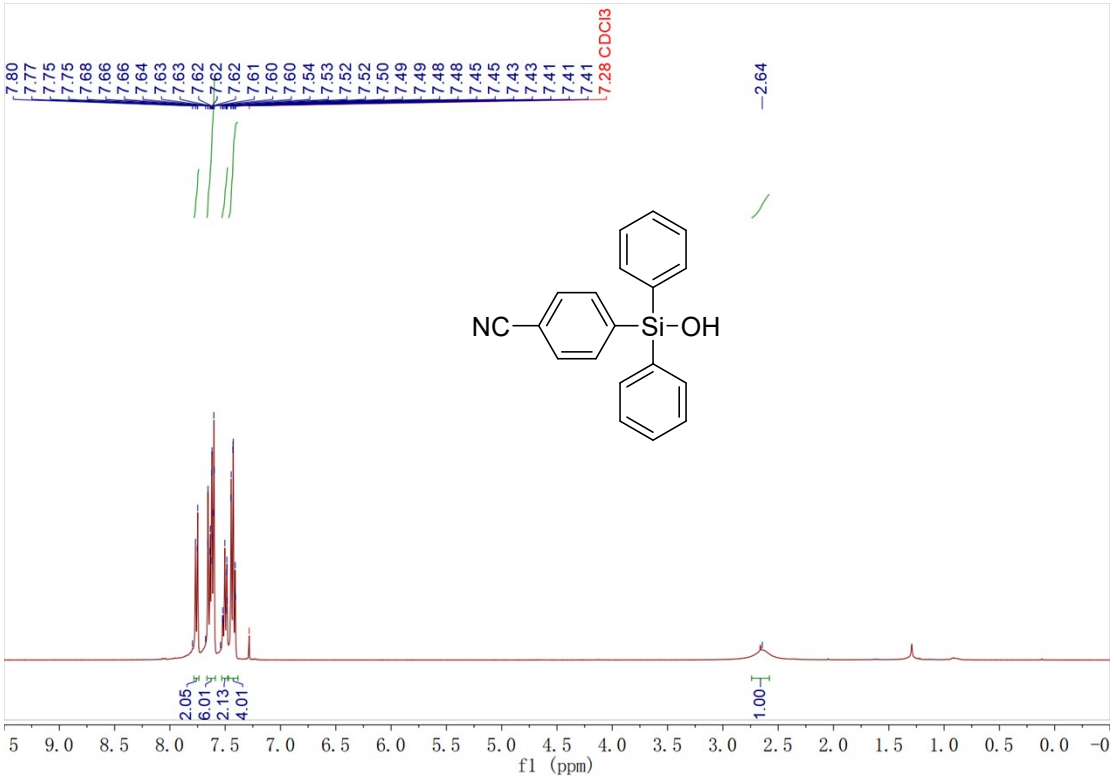
^{1}H NMR (400 MHz, $CDCl_3$) of **2j**



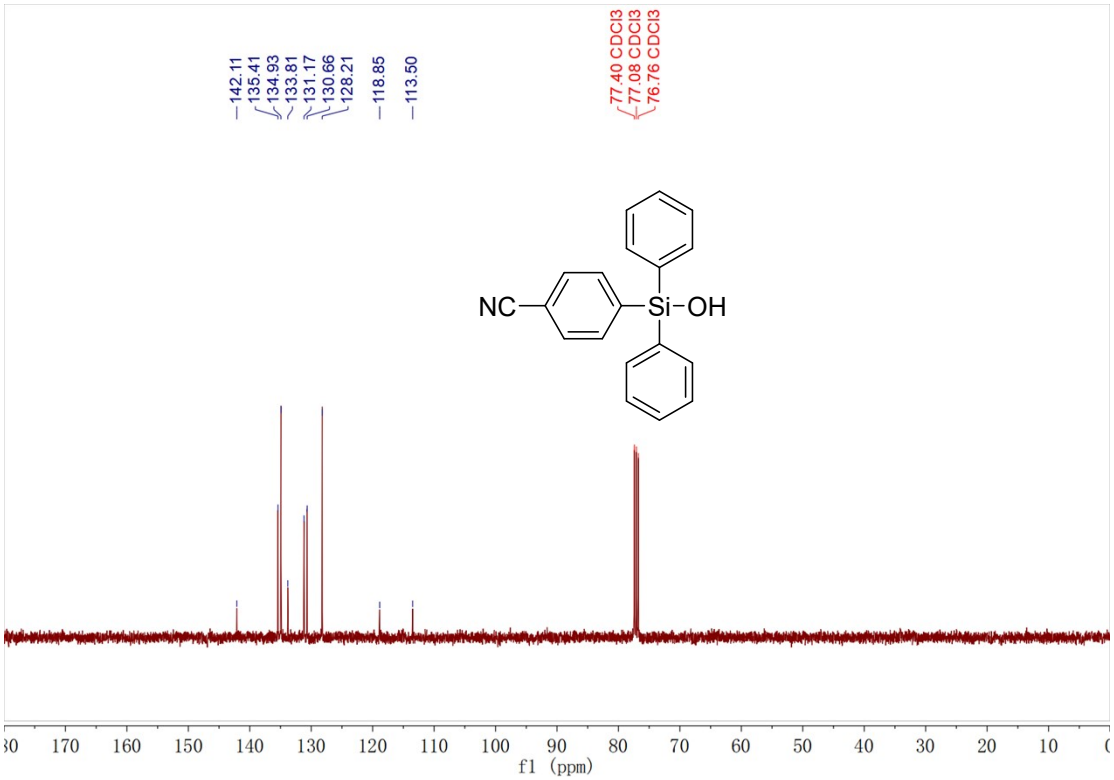
^{13}C NMR (100 MHz, $CDCl_3$) of **2j**



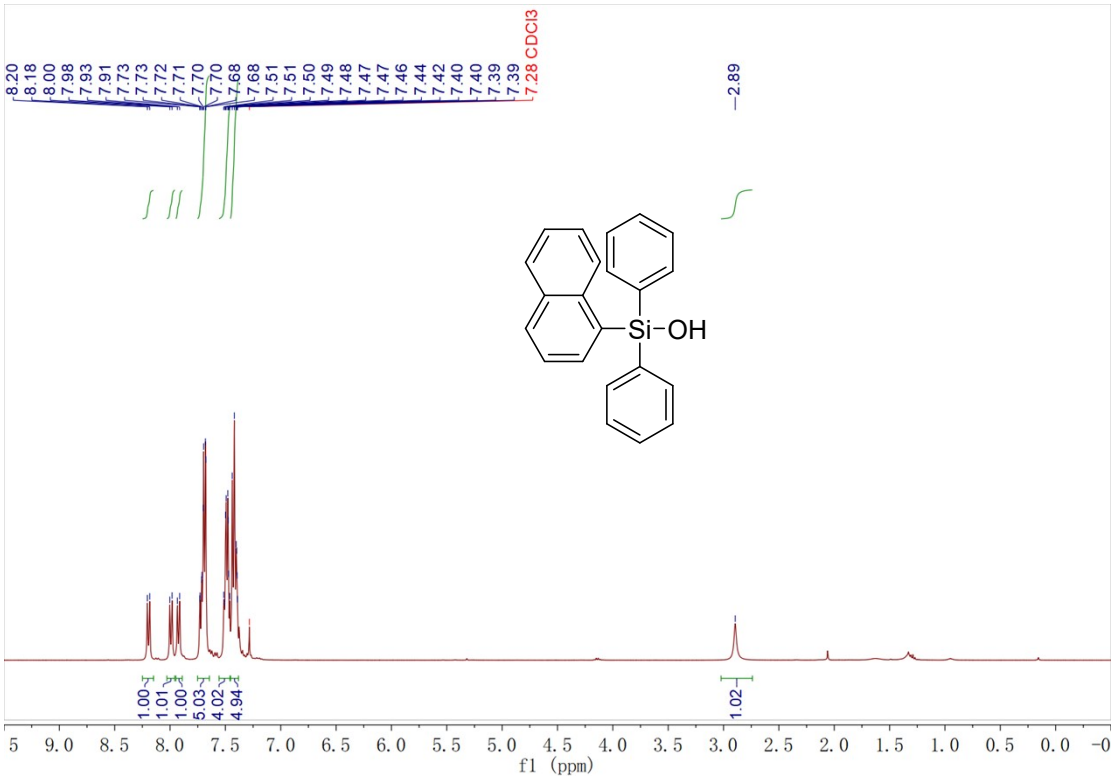
^{19}F NMR (377 MHz, $CDCl_3$) of **2j**



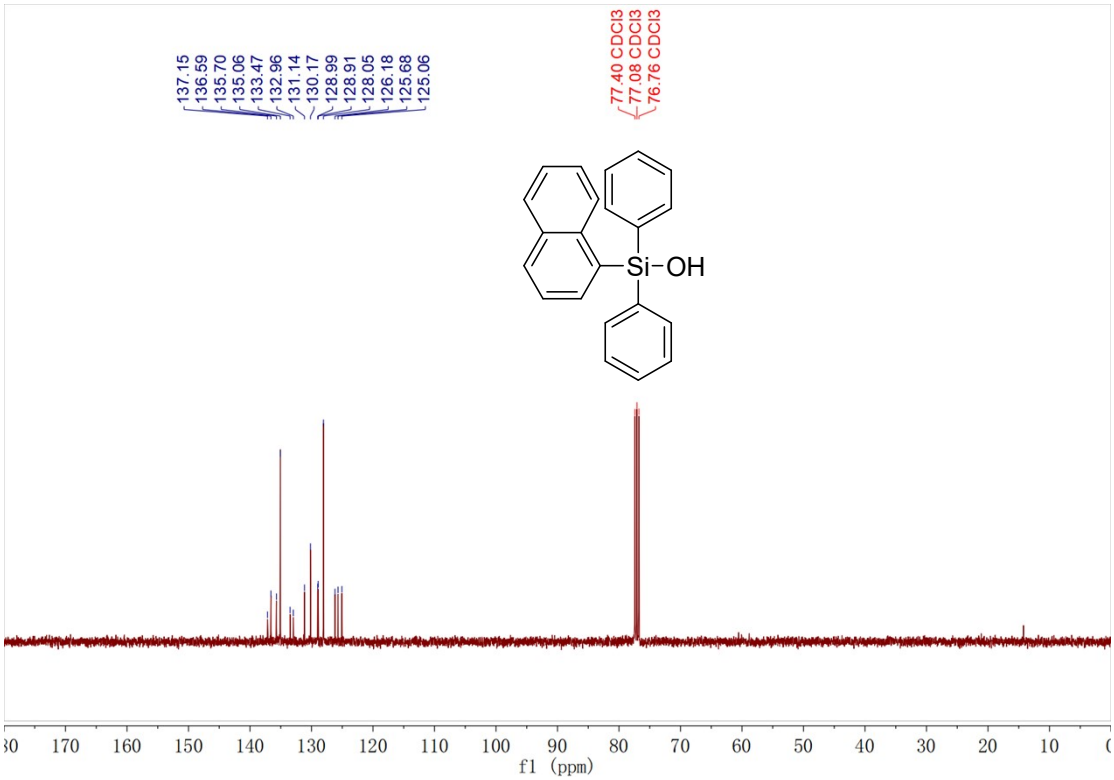
^{1}H NMR (400 MHz, $CDCl_3$) of **2k**



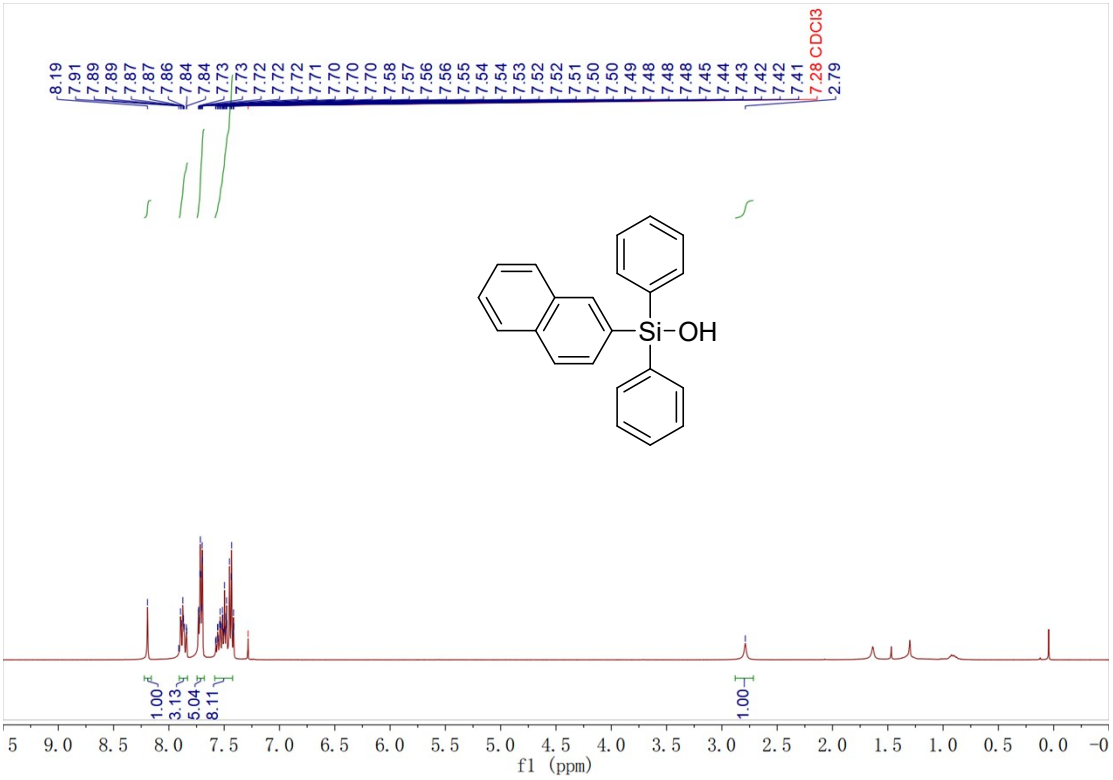
^{13}C NMR (100 MHz, $CDCl_3$) of **2k**



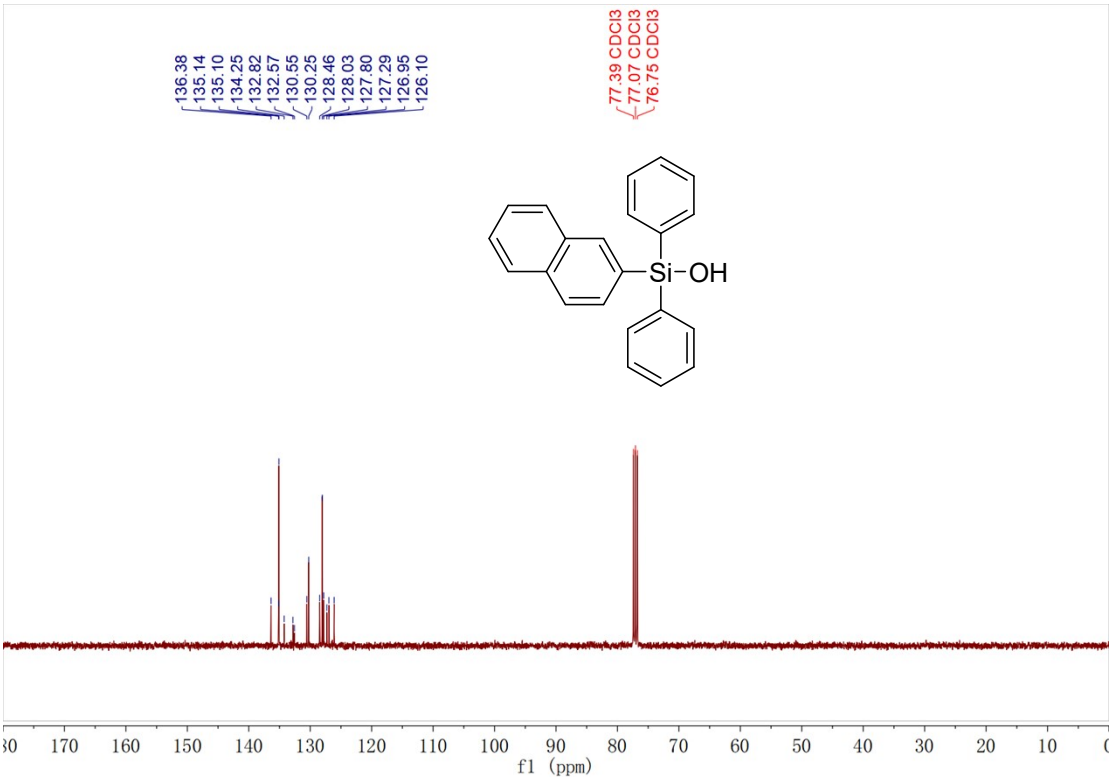
^{1}H NMR (400 MHz, $CDCl_3$) of **2l**



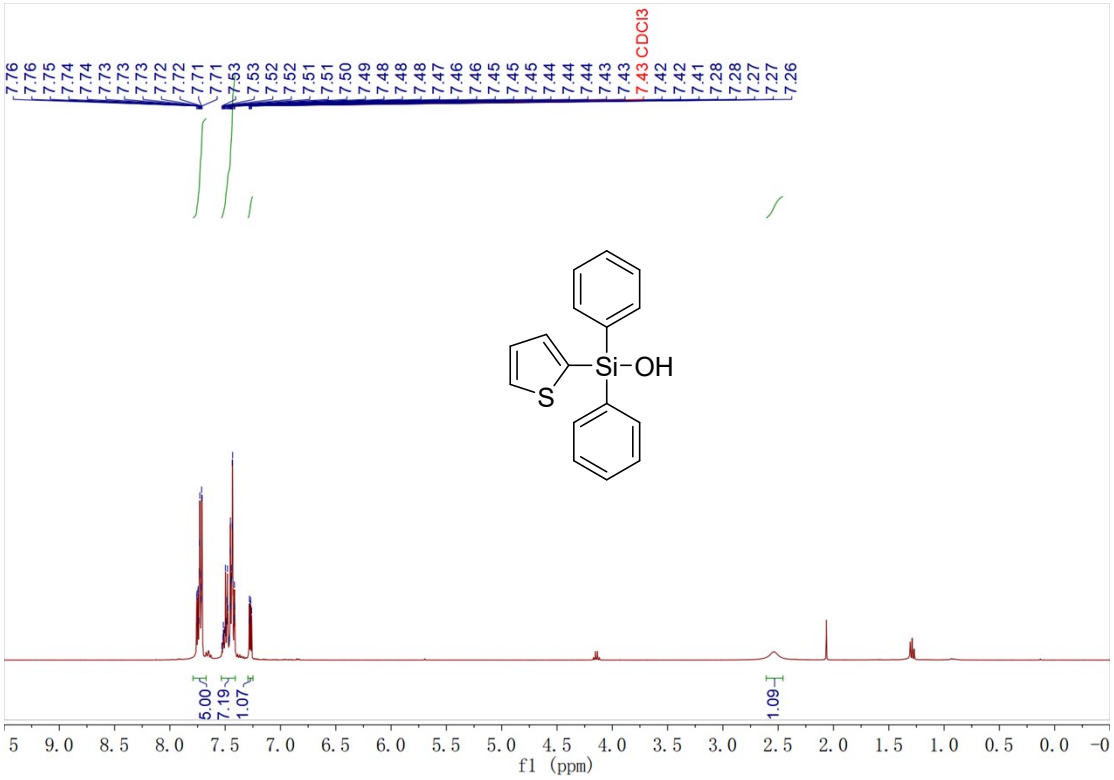
^{13}C NMR (100 MHz, $CDCl_3$) of **2l**



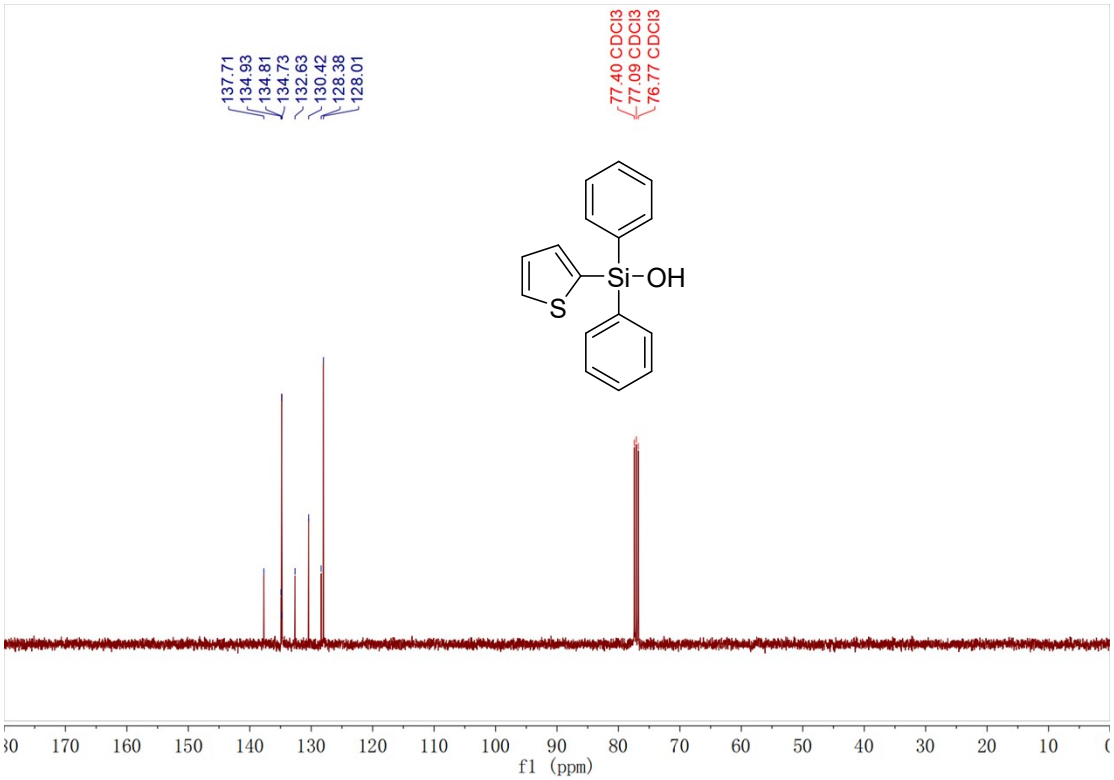
^{1}H NMR (400 MHz, $CDCl_3$) of **2m**



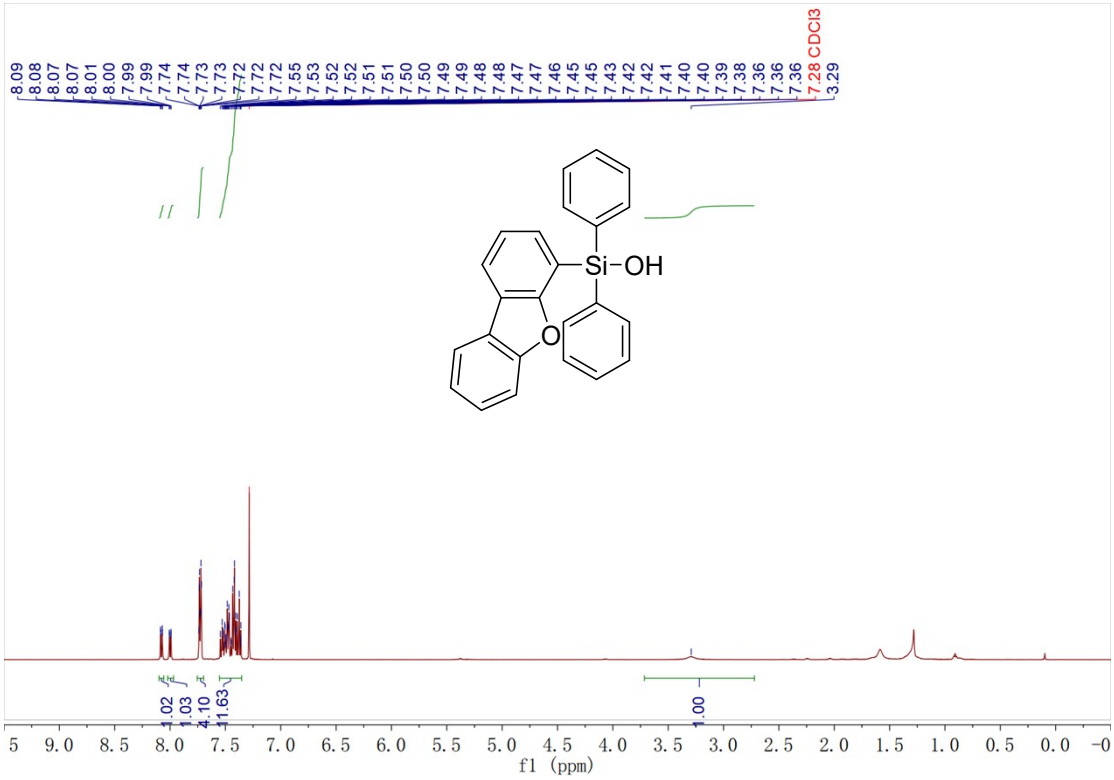
^{13}C NMR (100 MHz, $CDCl_3$) of **2m**



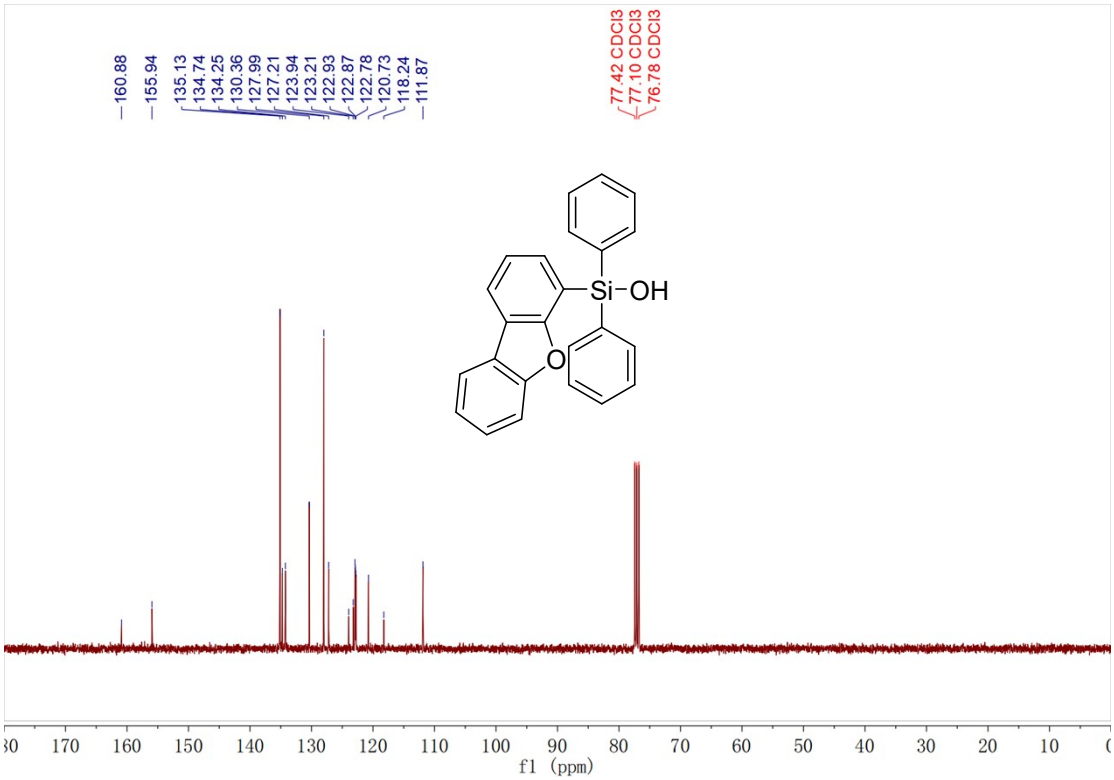
^{1}H NMR (400 MHz, $CDCl_3$) of **2n**



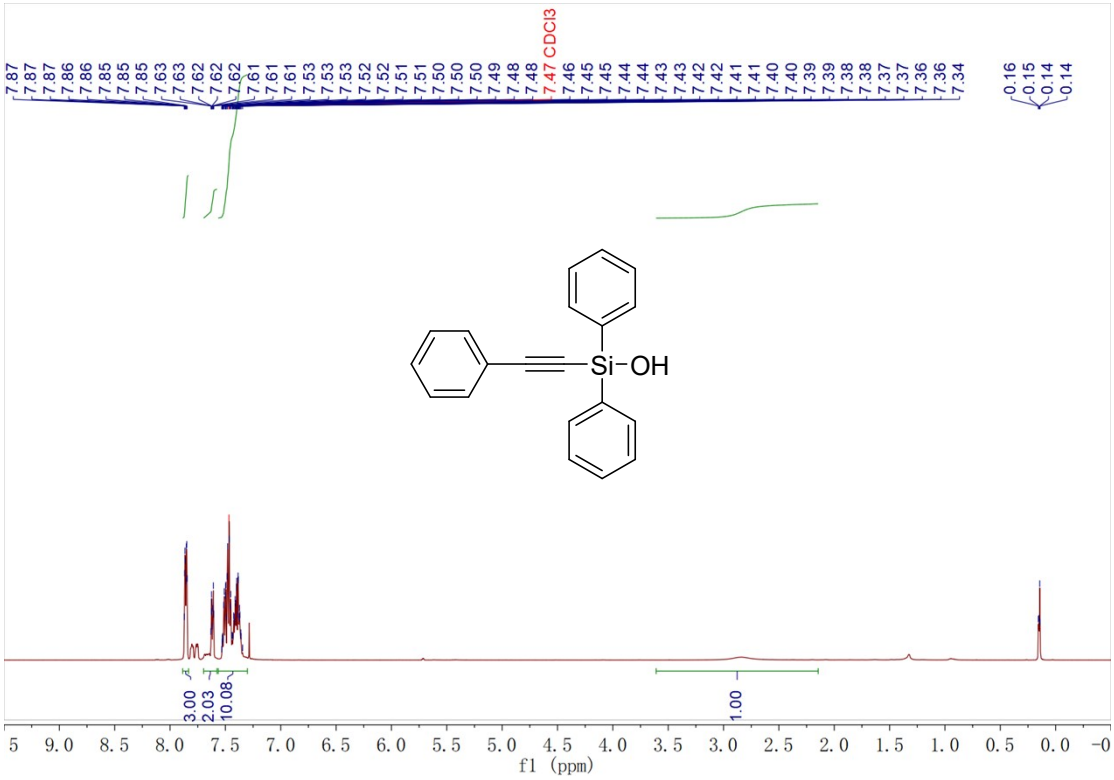
^{13}C NMR (100 MHz, $CDCl_3$) of **2n**



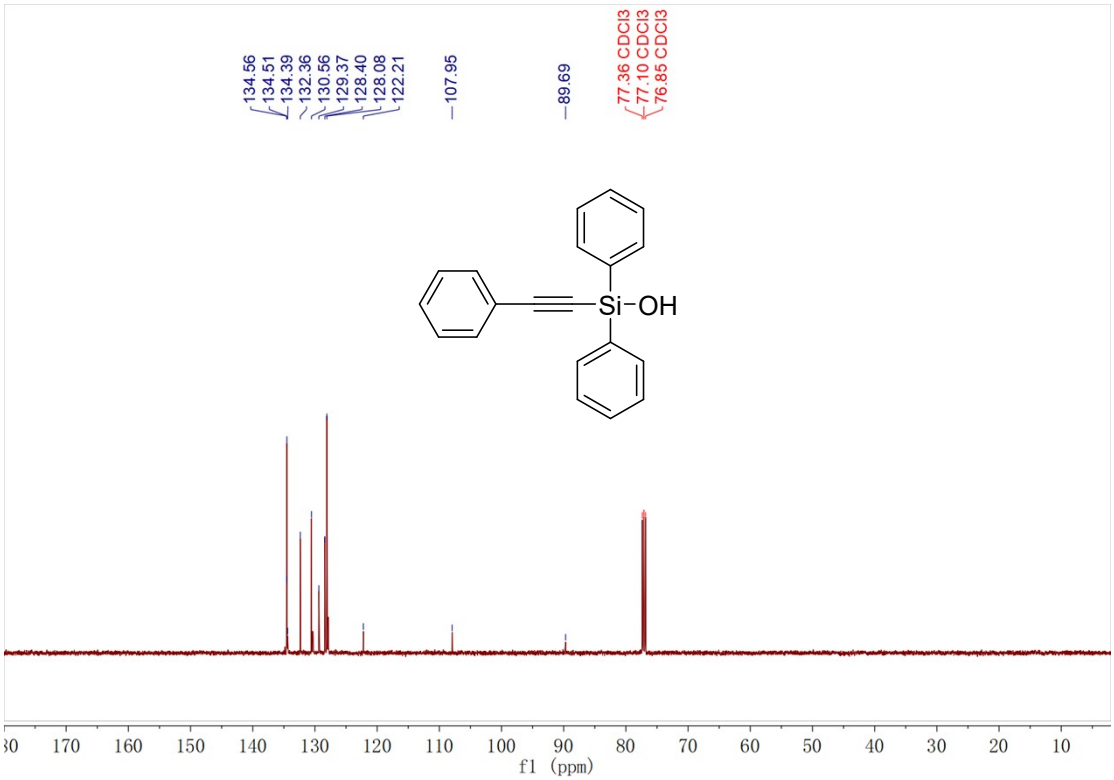
^{1}H NMR (500 MHz, $CDCl_3$) of **2o**



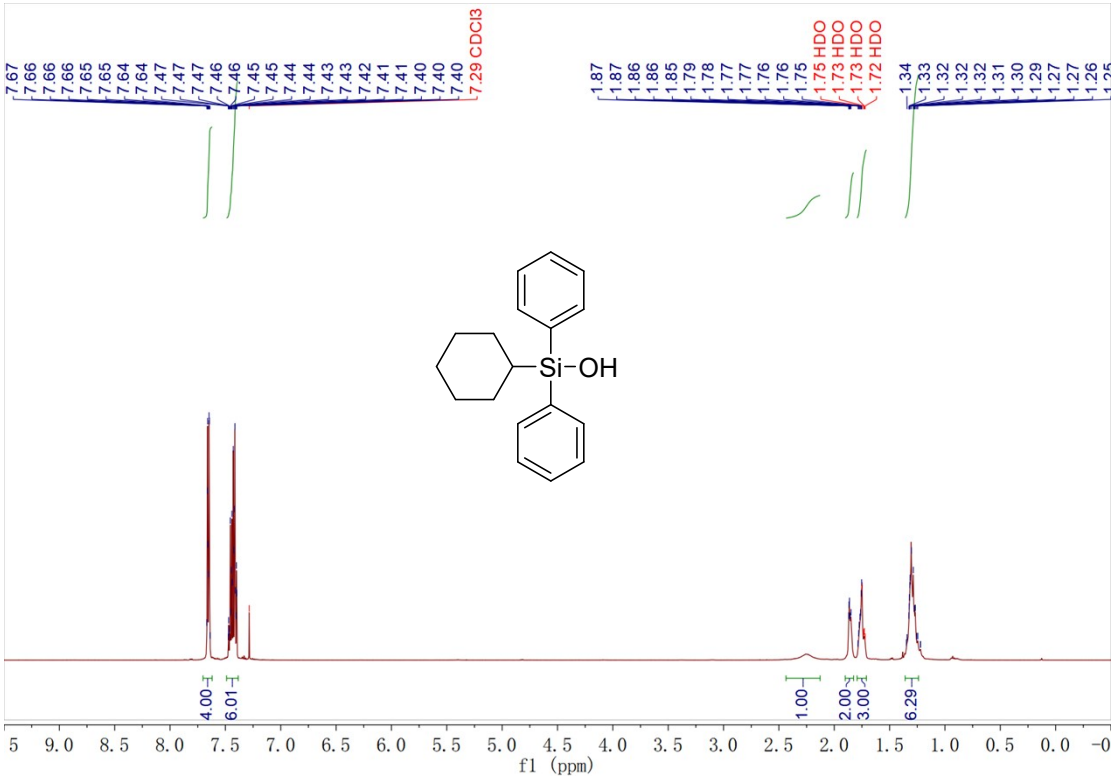
^{13}C NMR (100 MHz, $CDCl_3$) of **2o**



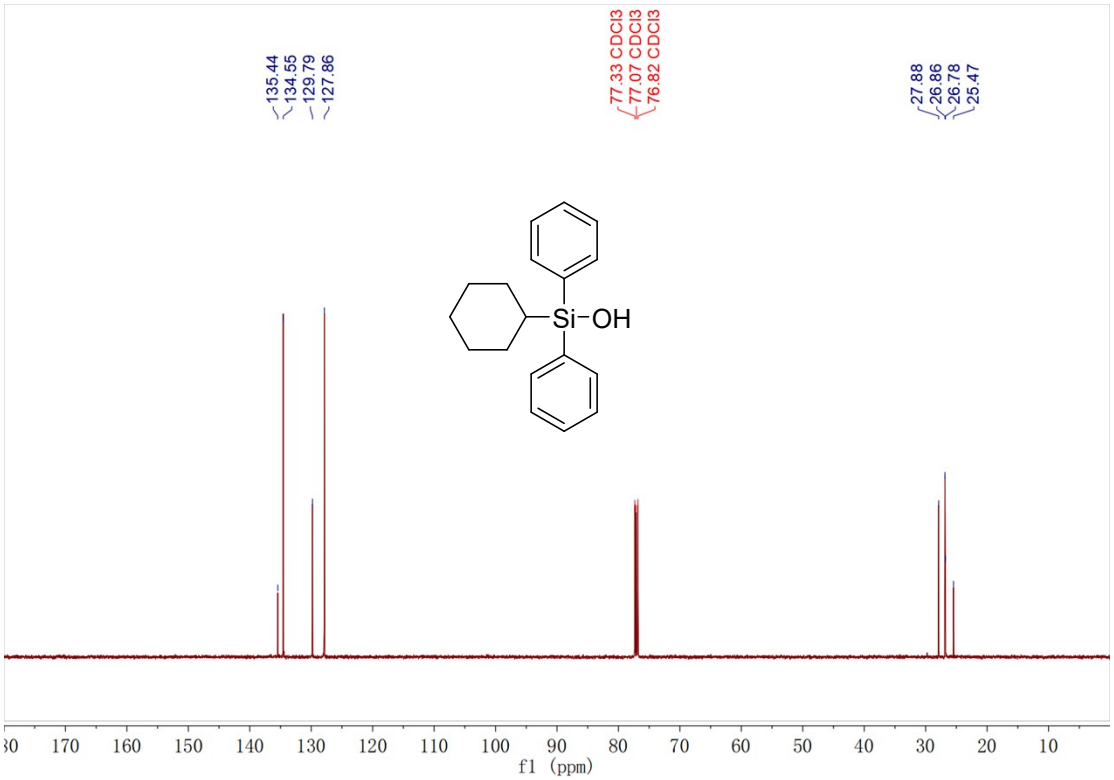
^{1}H NMR (500 MHz, $CDCl_3$) of **2p**



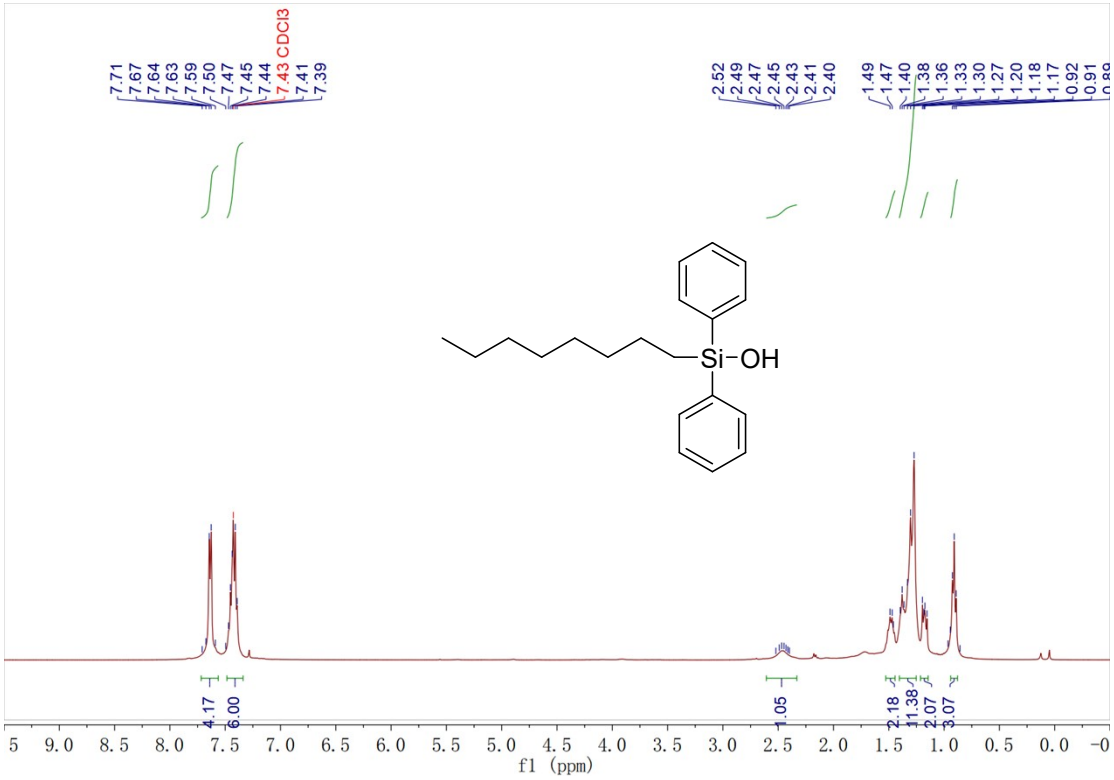
^{13}C NMR (126 MHz, $CDCl_3$) of **2p**



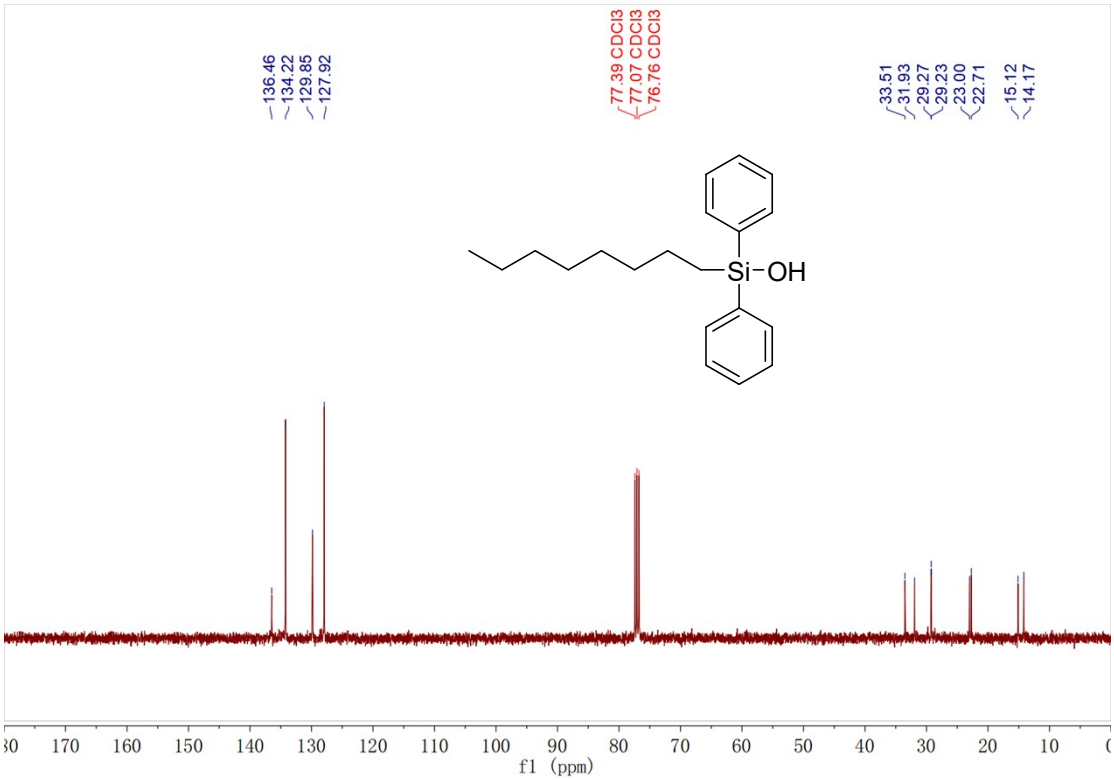
^{1}H NMR (500 MHz, $CDCl_3$) of **2q**



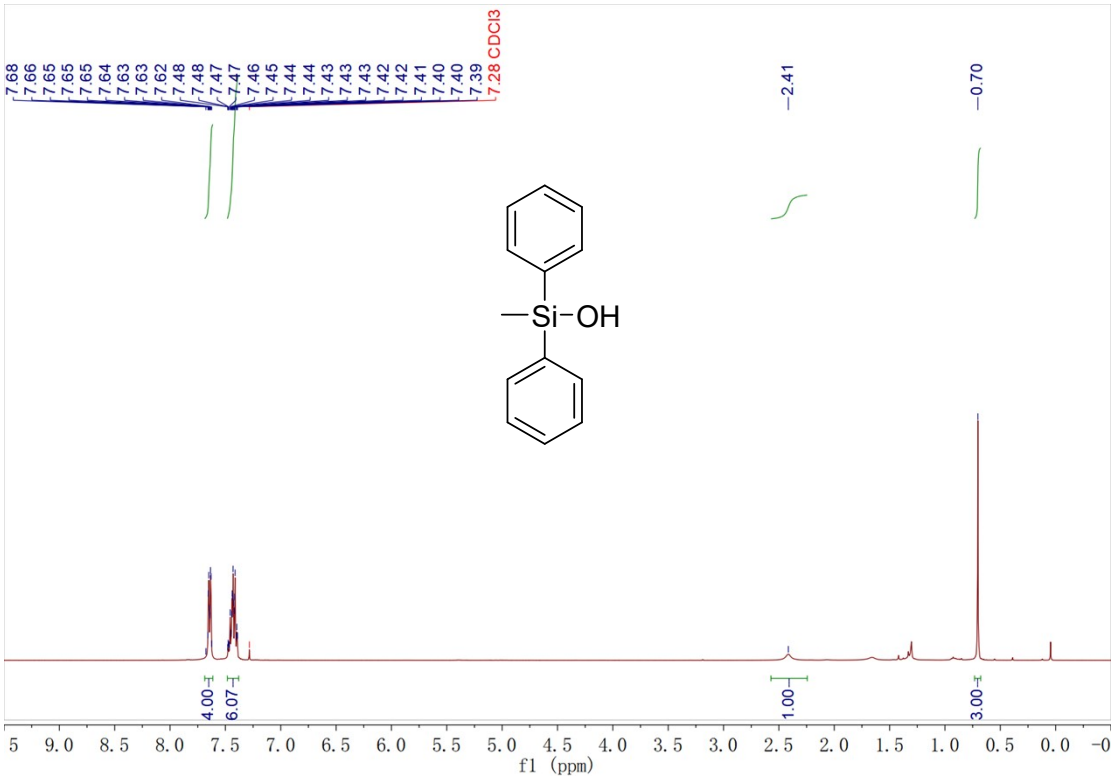
^{13}C NMR (126 MHz, $CDCl_3$) of **2q**



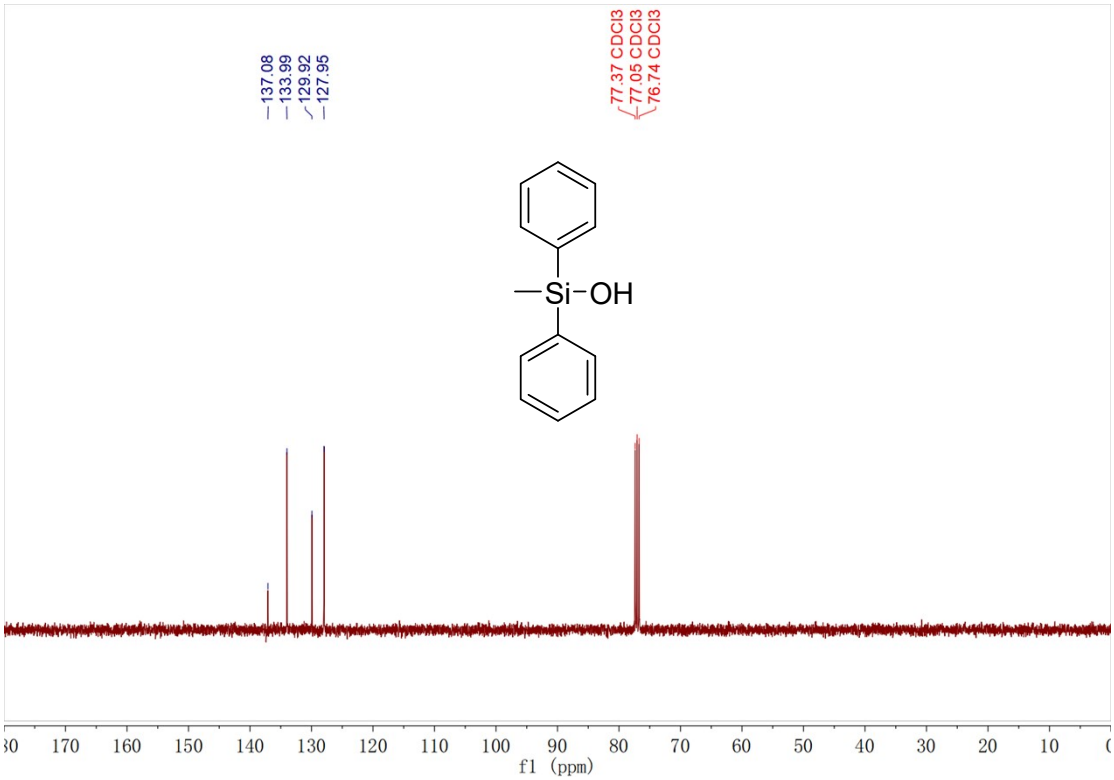
^{1}H NMR (400 MHz, $CDCl_3$) of **2r**



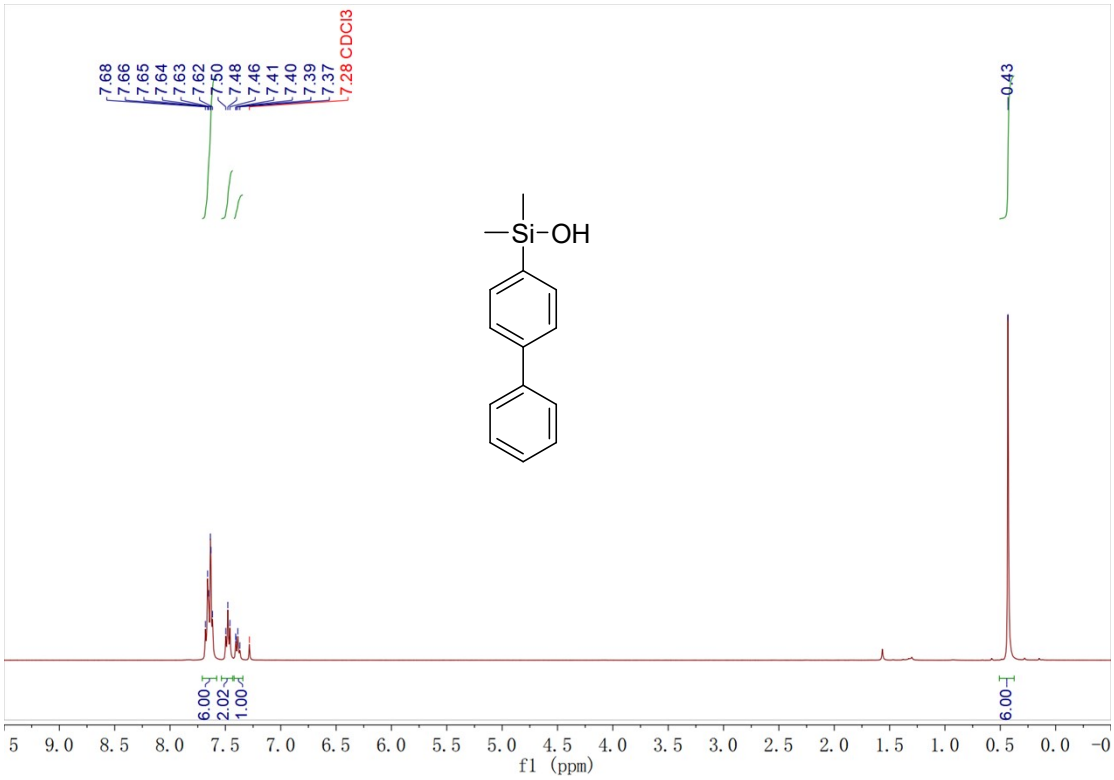
^{13}C NMR (100 MHz, $CDCl_3$) of **2r**



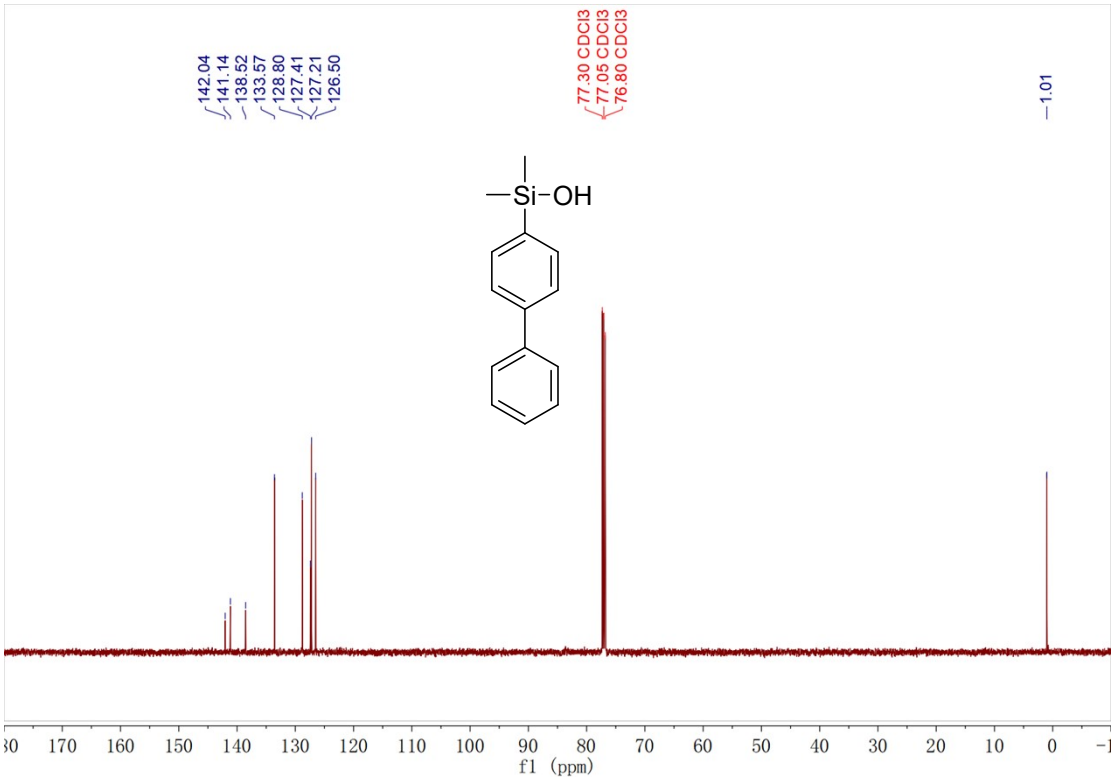
^{1}H NMR (400 MHz, $CDCl_3$) of **2s**



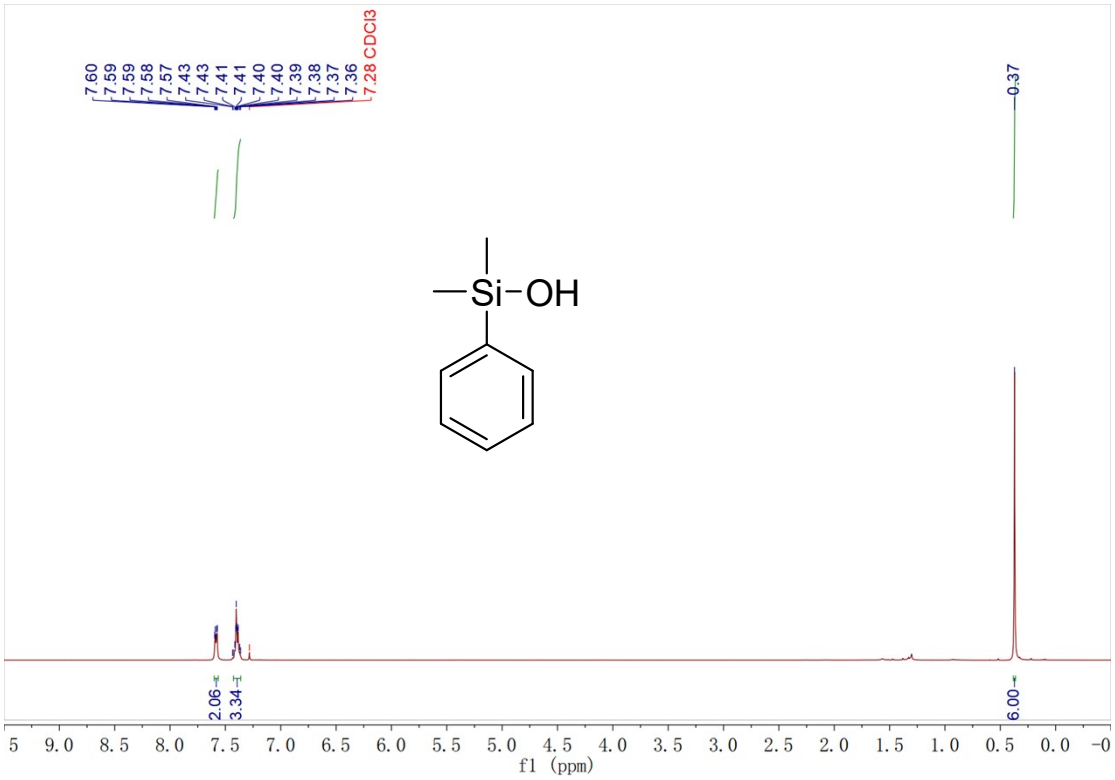
^{13}C NMR (100 MHz, $CDCl_3$) of **2s**



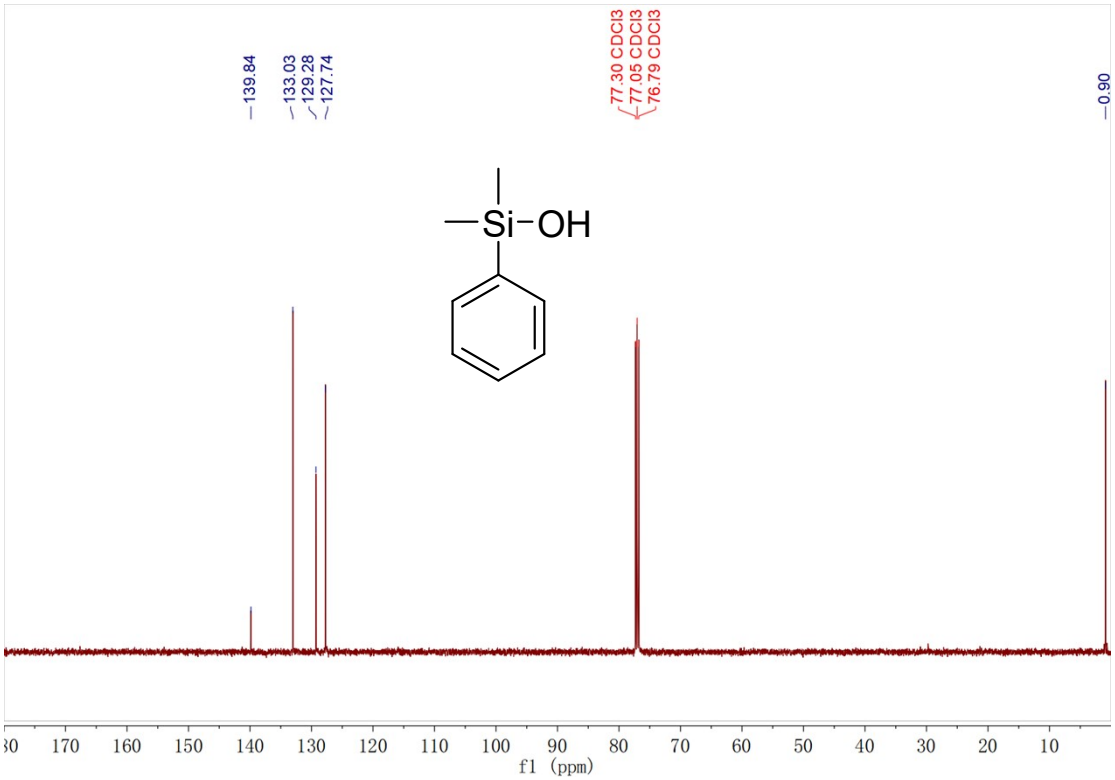
^{1}H NMR (400 MHz, $CDCl_3$) of **2t**



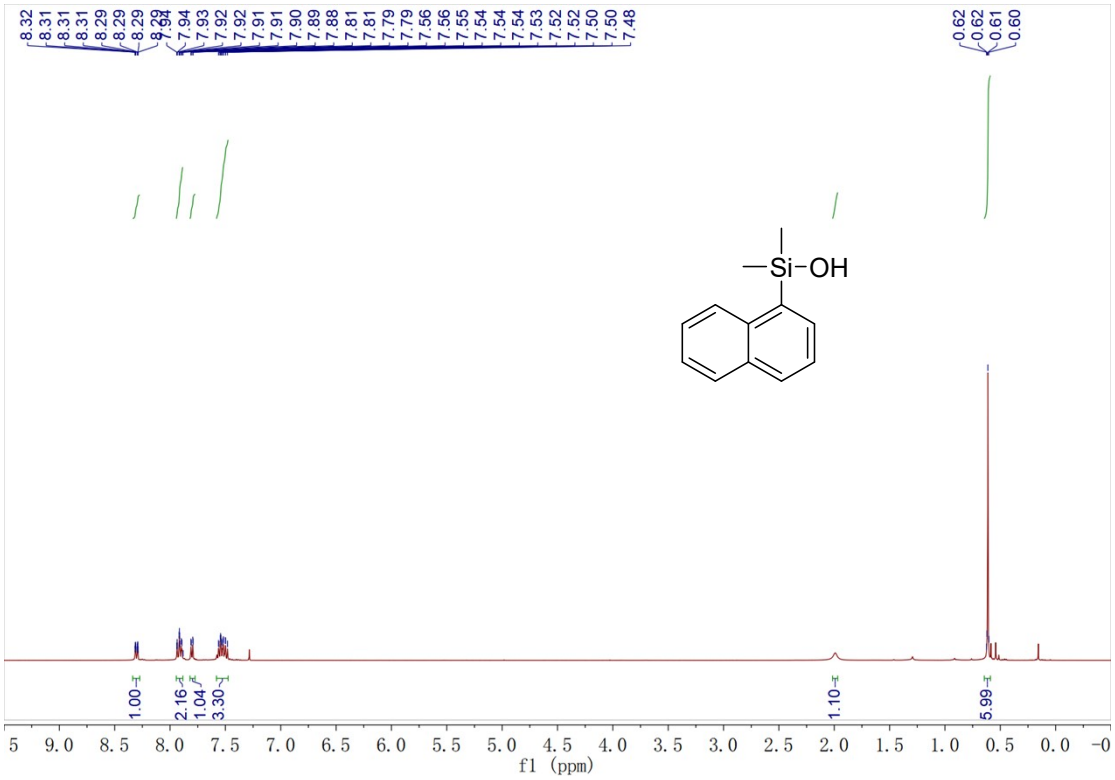
^{13}C NMR (126 MHz, $CDCl_3$) of **2t**



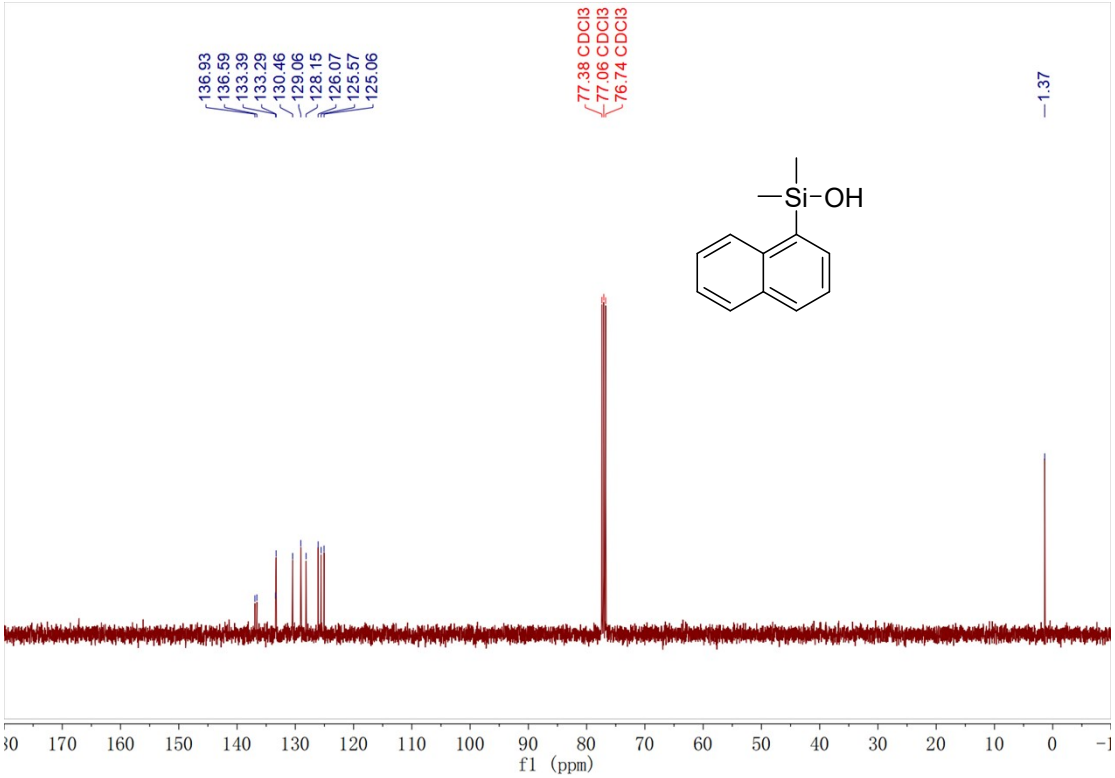
^{1}H NMR (400 MHz, $CDCl_3$) of **2u**



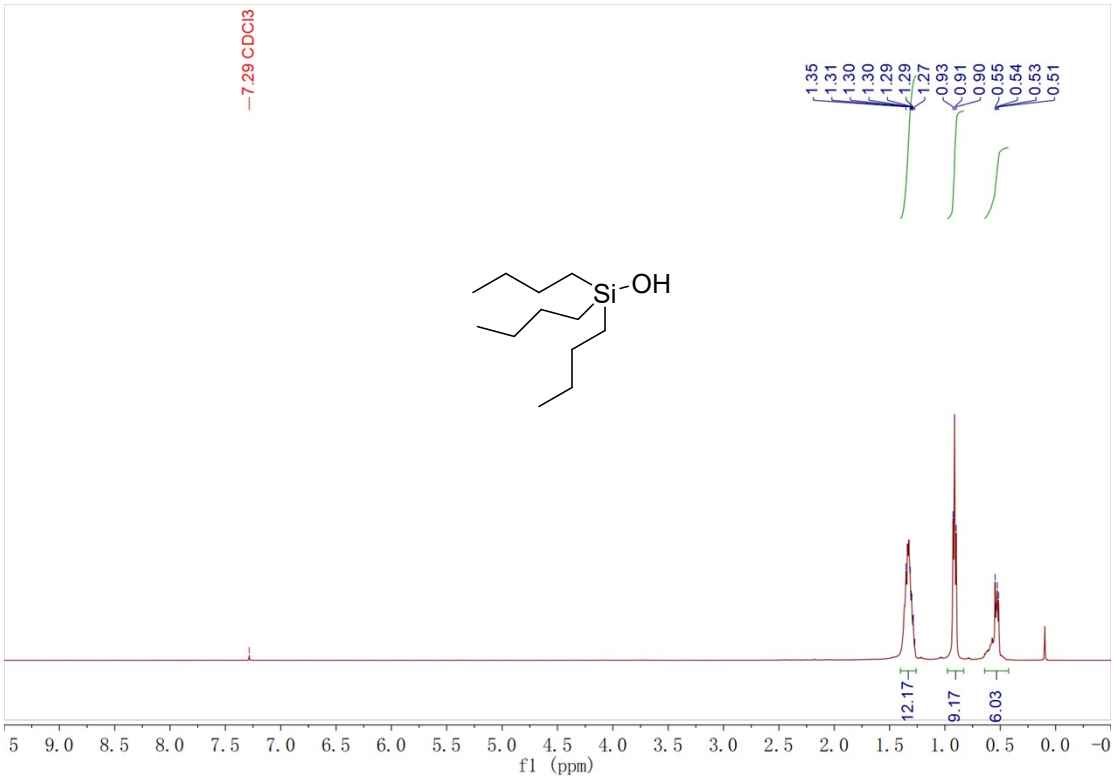
^{13}C NMR (126 MHz, $CDCl_3$) of **2u**



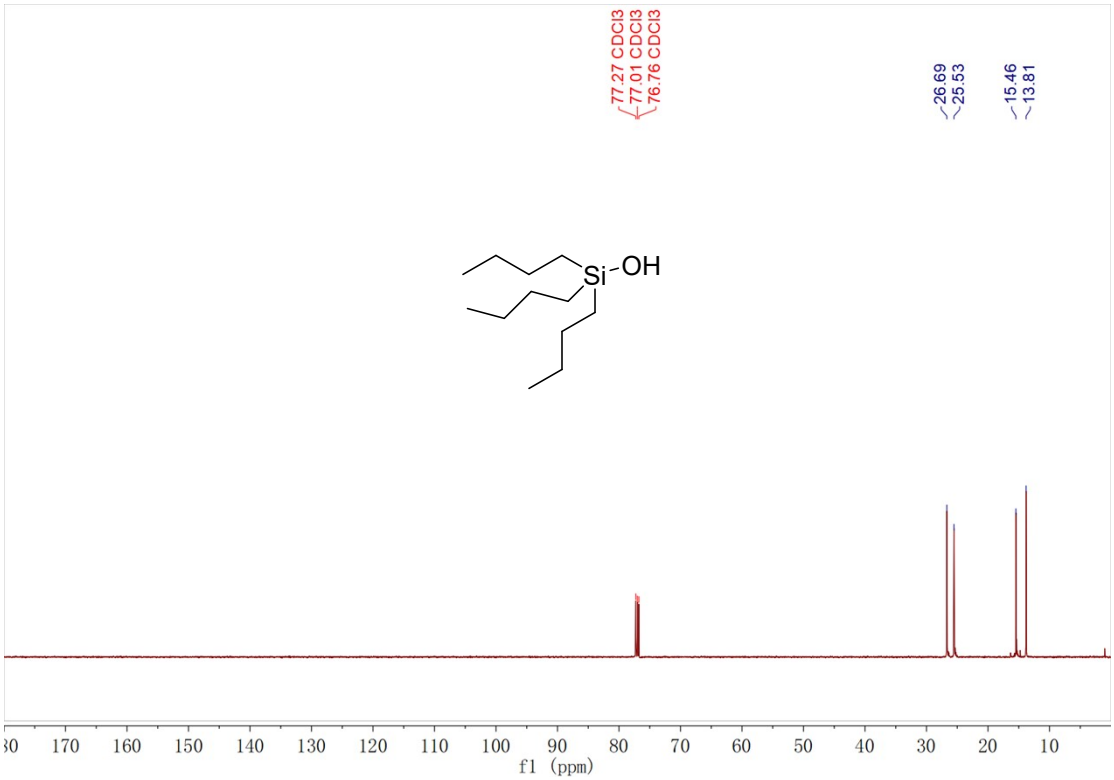
^{1}H NMR (400 MHz, $CDCl_3$) of **2v**



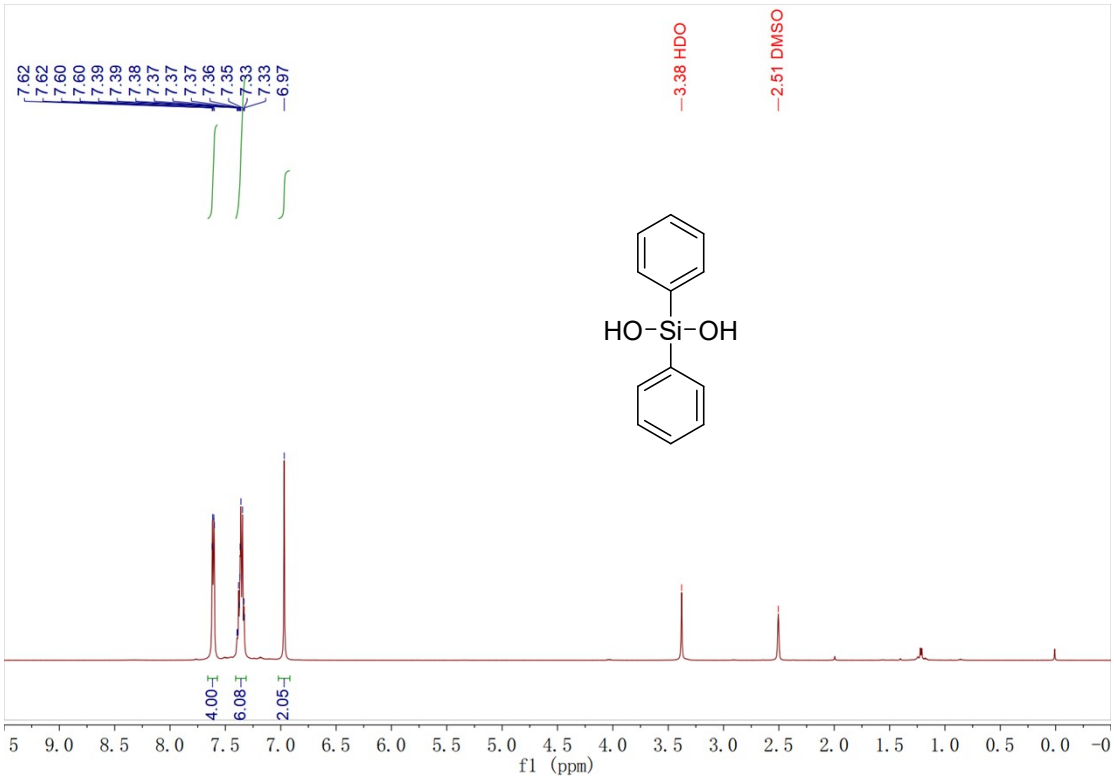
^{13}C NMR (100 MHz, $CDCl_3$) of **2v**



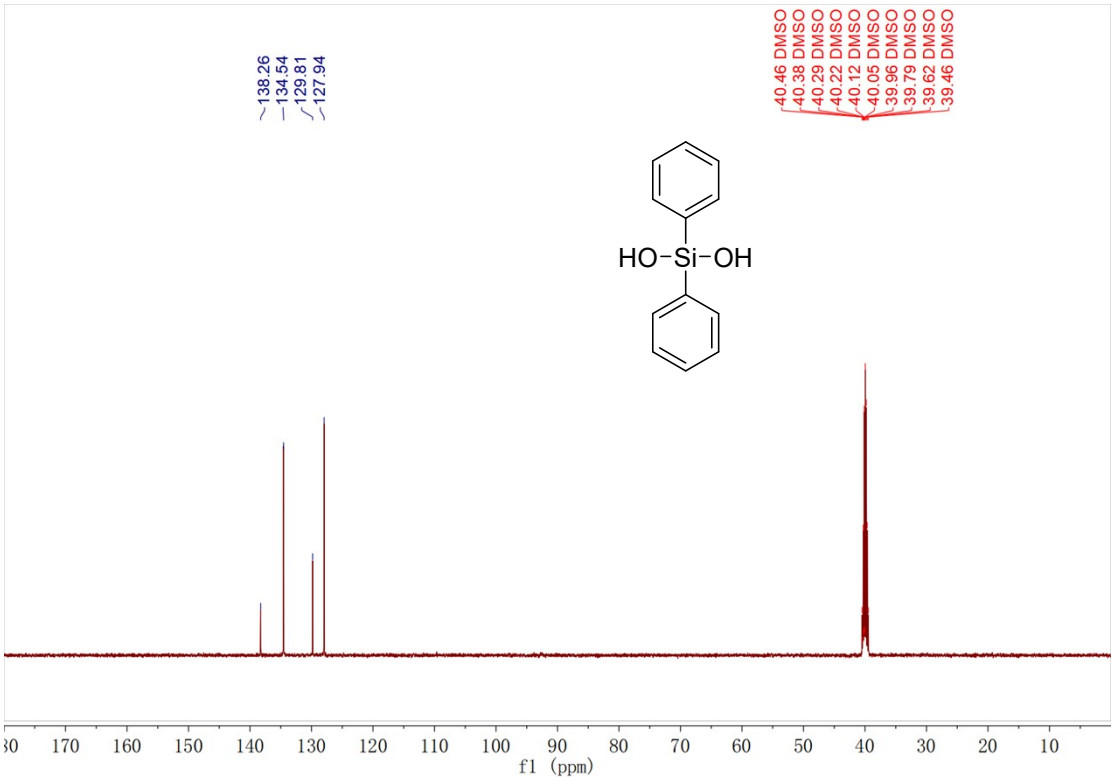
^{1}H NMR (500 MHz, $CDCl_3$) of **2w**



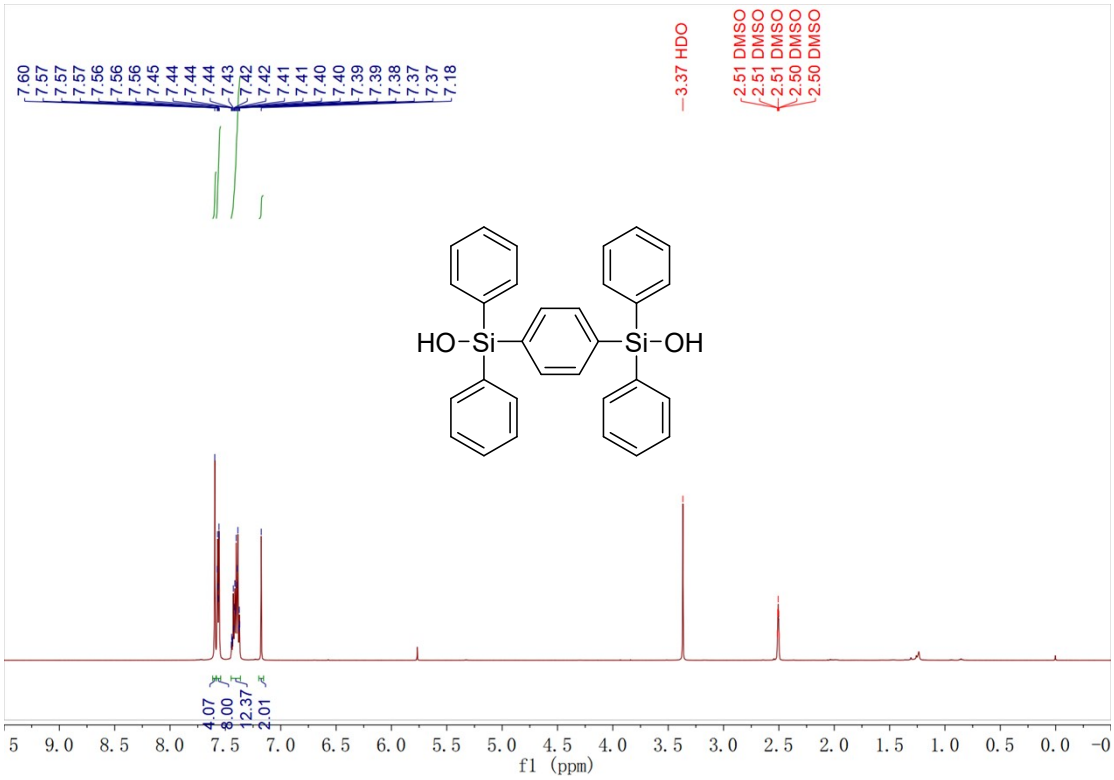
^{13}C NMR (126 MHz, $CDCl_3$) of **2w**



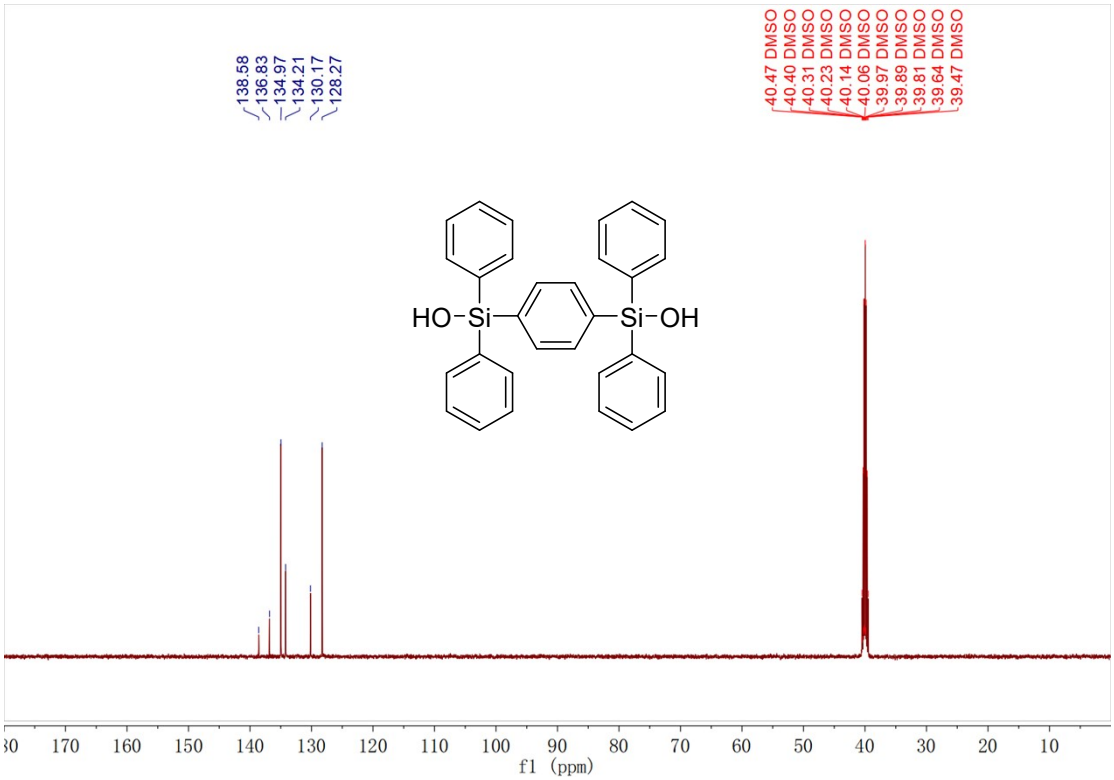
^{1}H NMR (500 MHz, DMSO-*d6*) of **2x**



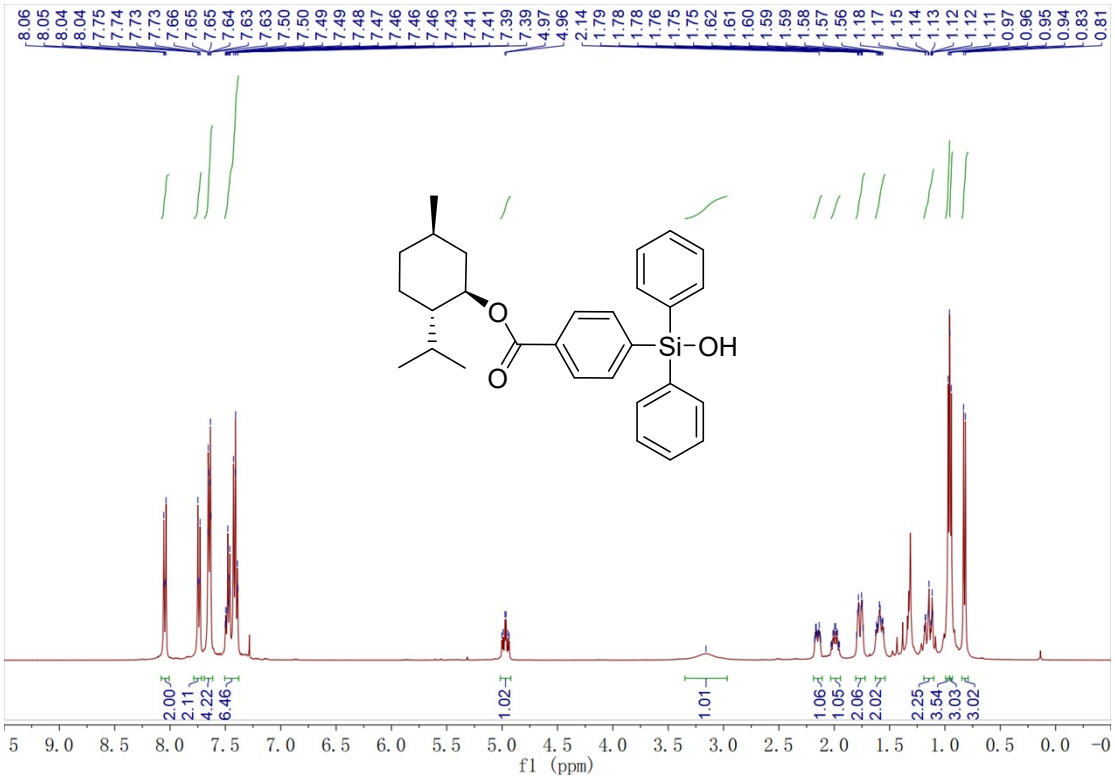
^{13}C NMR (126 MHz, DMSO-*d6*) of **2x**



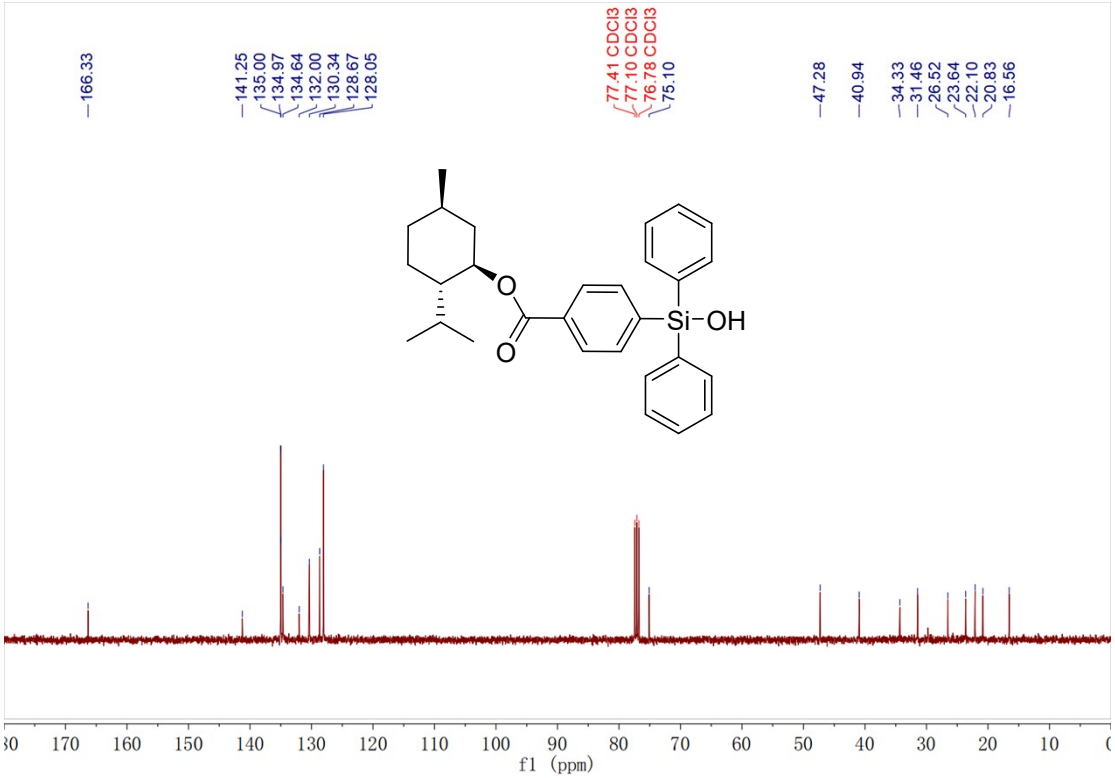
^{1}H NMR (500 MHz, DMSO-*d6*) of **2y**



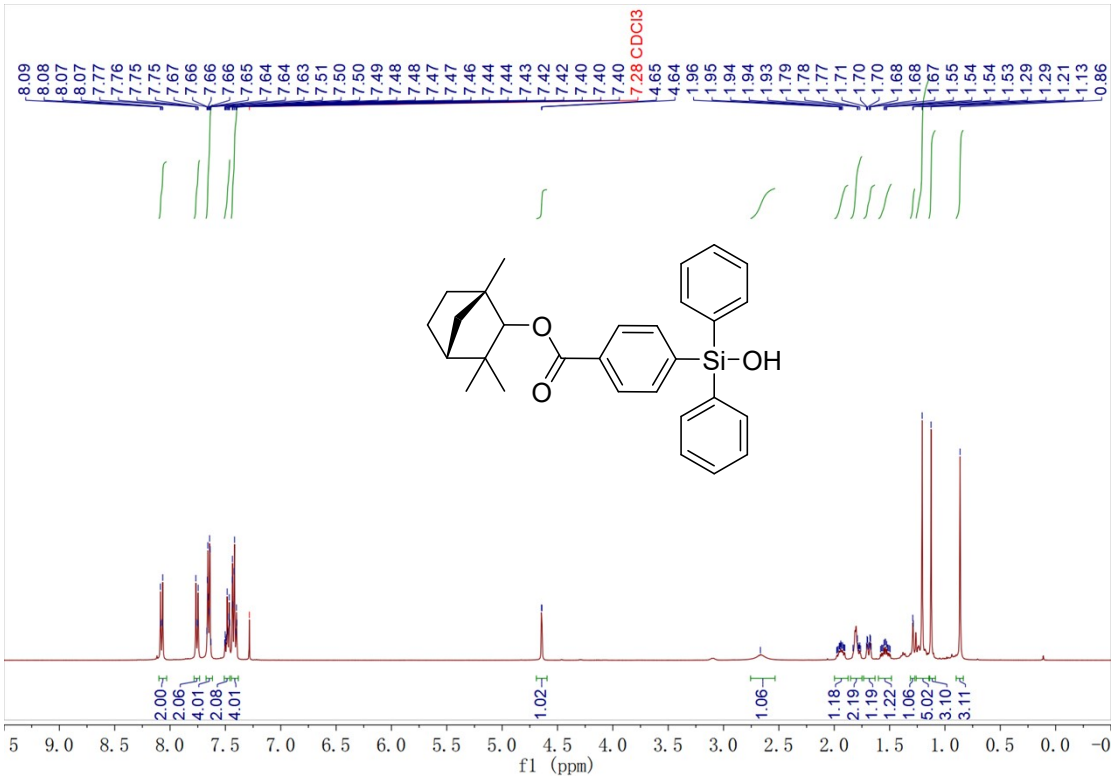
^{13}C NMR (126 MHz, DMSO-*d6*) of **2y**



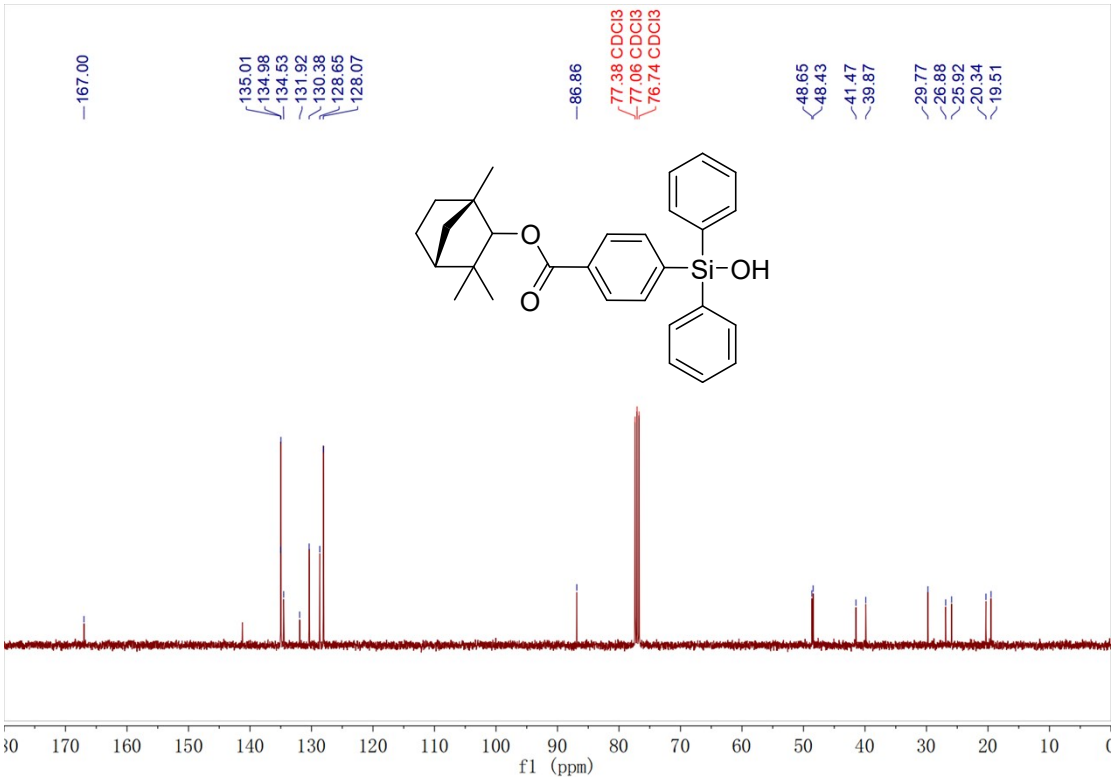
^{1}H NMR (400 MHz, $CDCl_3$) of **2aa**



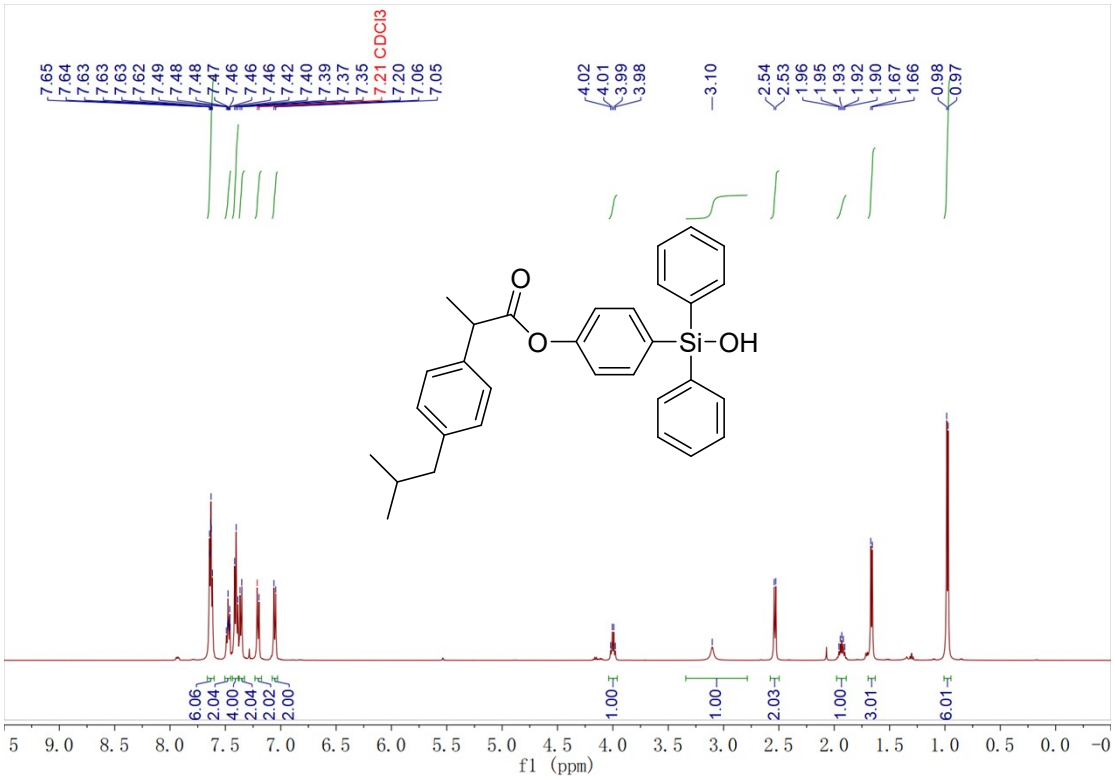
^{13}C NMR (100 MHz, $CDCl_3$) of **2aa**



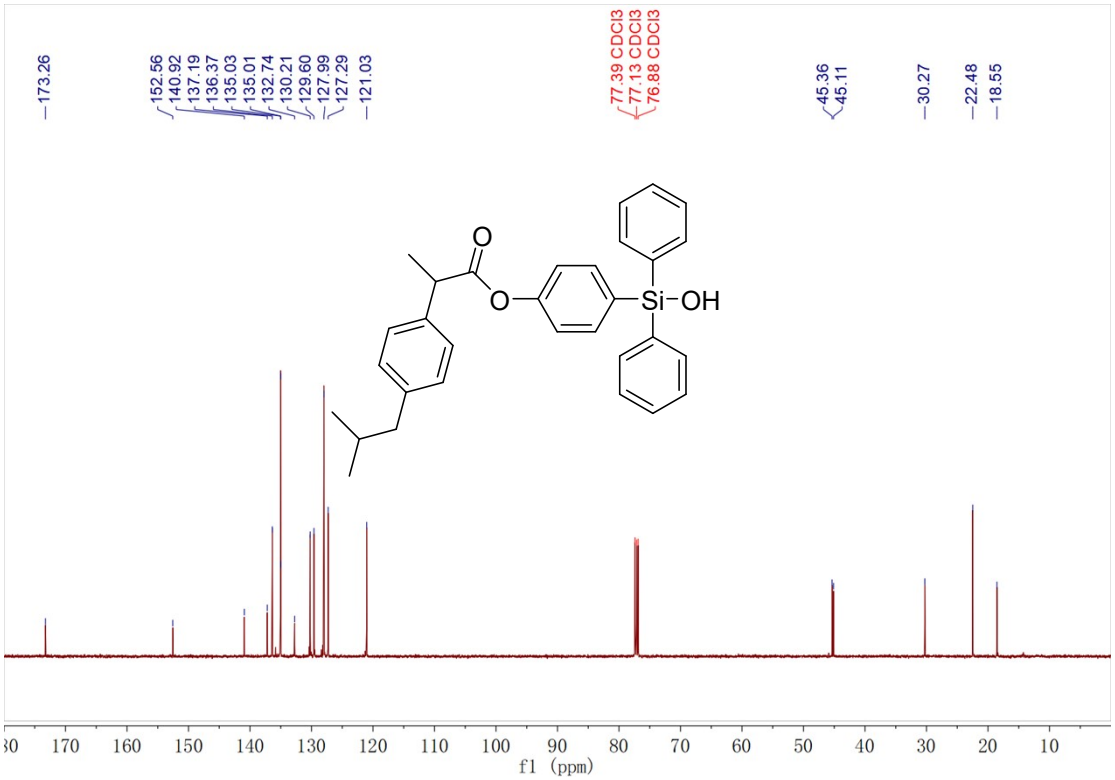
^{1}H NMR (400 MHz, $CDCl_3$) of **2ab**



^{13}C NMR (100 MHz, $CDCl_3$) of **2ab**



^{1}H NMR (500 MHz, $CDCl_3$) of **2ac**



^{13}C NMR (126 MHz, $CDCl_3$) of **2ac**