

Supporting information

**Visible-Light-Driven Oxidation of Organsilanes by
Charge-Transfer Complex**

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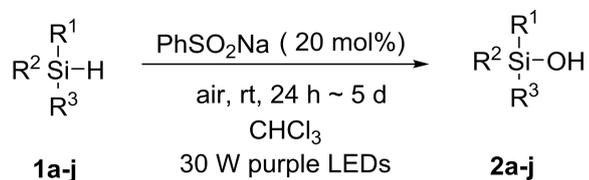
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1. General Information

All the reagents including silane and sodium sulfonates were purchased from commercial suppliers and used without further purification unless otherwise specified. ^1H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES+ mass spectrometer and acetonitrile was used to dissolve the sample. Column chromatography was carried out on silica gel (200-300 mesh).

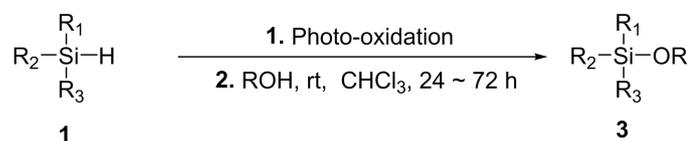
2. General Procedures

2.1. General procedure for the oxidation of silane



To a 15 mL reaction tube equipped with a magnetic stirring bar, silane **1a-j** (0.2 mmol, 1.0 equiv.), PhSO₂Na (20 mol%), CHCl₃ (2 mL) were added. The vessel was capped with a rubber stopper inserting a needle to connect to air. The tube was stirred at room temperature under irradiation of 30 W purple LEDs (distance app. 5 cm) for 24 h-5 d. The reaction was detected by TLC or ¹H NMR (CH₂Br₂ as an internal standard), and the solvent was removed under reduced pressure after the reaction was complete. The residue was purified by flash column chromatography (PE/EA, 100/3-100/4) or direct filtration to afford the desired product **2**.

2.2. General procedure for the synthesis of silicone ether



The silanol was prepared under the standard photo-oxidation conditions and used without purification. The one step reaction completed, adding supplementary solvent, solvent (CHCl₃) needed to be dried to move water. The corresponding primary, secondary or tertiary alcohols (0.4 mmol, 2 equiv.) were added in the reaction mixture. The reaction mixture was stirred at room temperature for 24-72 h and detected by TLC or ¹H NMR. Thereafter, the solvent was removed under reduced pressure and then the residue was purified by flash column chromatography (PE-PE/EA, 100-100/1) or direct filtration to afford the desired product **3**.

2.3 Experimental set-up (Figure S1-S2)

The light source used for illuminating the reaction vessel consists of purple LEDs ($\lambda_{\text{max}} = 405$ nm) purchased from Taobao (<https://gpiled.taobao.com/>).

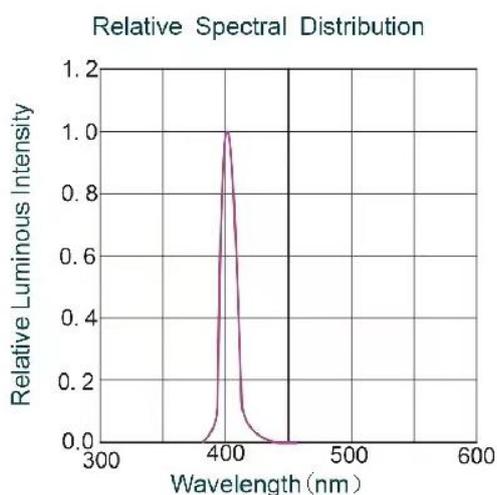


Figure S1. The emission spectra of the purple LEDs

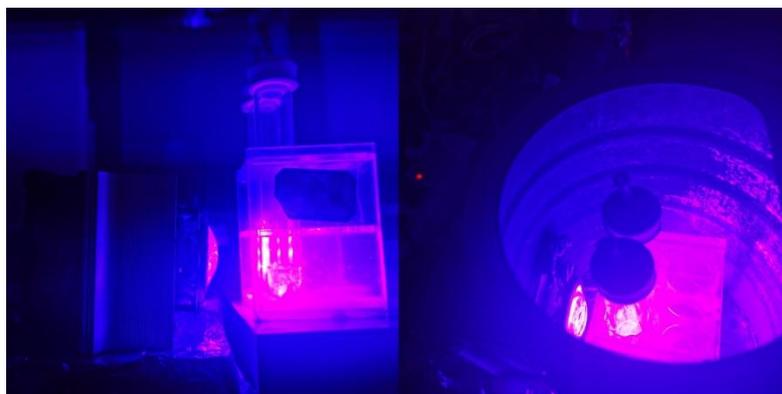
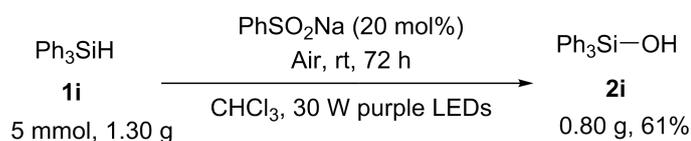
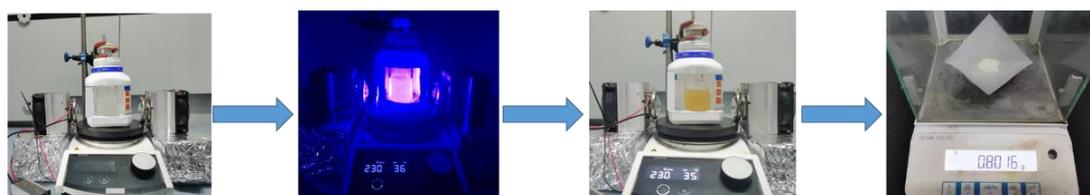


Figure S2. The set-up for the reaction (photographed by Juntao He)

2.4 Scale-up reaction



1i (5.0 mmol, 1.30 g), PhSO_2Na (1.0 mmol, 164 mg), and CHCl_3 (50.0 mL) were added to a 150 mL seal tube equipped with a stirring bar. The vessel was connected to the atmosphere by inserting a needle. The tube was stirred at room temperature under irradiation of purple LEDs (405nm)(30W \times 2, distance app. 5 cm) for 72 h. The solvent was removed under vacuum and the residue was purified by flash column chromatography (PE/ EA = 100/3 to 100/4) to afford the product **2i** (0.8 g, 61% yield).



Initial State (1l: 5mmol)

The reaction process (72 h)

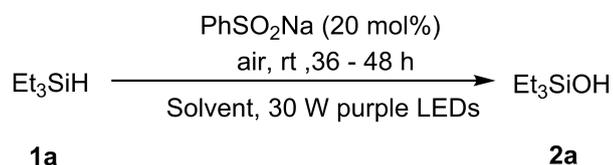
End State

2i: 0.8g (61%)

Figure S3. The scale-up reaction for synthesis of **2i** (photographed by Juntao He)

3. Detailed Optimization of Reaction Conditions

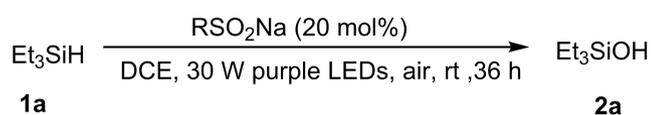
3.1. Optimization of reaction conditions I (Table S1)



Entry	Solvent	Time(h)	Atmosphere	Yield(%) ^b
1	DCE	48	O ₂	65
2	DMF	48	O ₂	22
3	EA	48	O ₂	trace
4	CHCl ₃	36	O ₂	87
5	DCM	48	O ₂	71
6	CH ₃ CN	48	O ₂	trace
7	C ₂ H ₅ OH	48	O ₂	trace
8	THF	48	O ₂	34
9	Acetone	48	O ₂	trace
10	n-hexane	48	O ₂	-
11	toluene	48	O ₂	-
12	CHCl ₃	36	air	95(84) ^c
13	CHCl ₃	48	air	86
14	CHCl ₃	48	Ar	trace
15 ^d	CHCl ₃	48	air	nr

^a Reaction conditions: **1a** (0.2 mmol), PhSO₂Na (20 mol%), solvent (2 mL), 30 W purple LEDs, O₂, rt, 36 h. ^b Yield were determined by analysis of the crude ¹H NMR using CH₂Br₂ as an internal standard, nr = no reaction. ^c Isolated yield. ^d No light

3.2. Optimization of the reaction conditions II (Table S2)



Entry	Lights	RSO ₂ Na	Yield(%) ^b
1	30 W purple LEDs	PhSO ₂ Na	95(84) ^c
2	30 W purple LEDs	<i>p</i> -CH ₃ -PhSO ₂ Na	70
3	30 W purple LEDs	<i>p</i> -F-PhSO ₂ Na	63
4	30 W purple LEDs	CH ₃ SO ₂ Na	49
5	30 W purple LEDs	CF ₃ SO ₂ Na	47
6	30 W purple LEDs	-	0
7	30 W green LEDs	PhSO ₂ Na	trace
8	30 W white LEDs	PhSO ₂ Na	trace
9	30 W blue LEDs	PhSO ₂ Na	62

^a Reaction conditions: **1a** (0.2 mmol), RSO₂Na (20 mol%), CHCl₃ (2 mL), 30 W purple LEDs, rt, air, 36 h; ^b Yield were determined by analysis of the crude ¹H NMR using CH₂Br₂ as an internal standard, nr = no reaction. ^c Isolated yield. Note : 30 W purple LEDs (400-405nm), 30 W green LEDs (550-555nm), 30 W white LEDs (6000-6500K), 30 W blue LEDs (450-455nm)

4. Mechanistic Investigations

4.1. Radical trapping experiments (Table S3)

Et_3SiH	Radical trapping reagent PhSO_2Na (20 mol%) CHCl_3 , 30 W purple LED, air, rt, 36 h	Et_3SiOH
1a		2a
Radical Trapping Reagent	Et ₃ SiOH (yield%) ^b	
BHT (1 equiv.)	Trace	
BHT (3 equiv.)	Trace	
TEMPO (1 equiv.)	Full inhibition	
<i>p</i> -Benzoquinone (1 equiv.)	26%	
<i>p</i> -Benzoquinone (3 equiv.)	9%	

^a Reaction conditions: **1a** (0.2 mmol), PhSO₂Na (20 mol%), solvent (2 mL), 30 W purple LEDs, O₂, rt, 36 h. ^b Yield were determined by analysis of the crude ¹H NMR using CH₂Br₂ as an internal standard

The resulting mass spectrum clearly shows a peak corresponding to the coupled product between BHT radical and the expected ·SO₂Ph, **BHT-1** HRMS (ESI): C₂₁H₂₈KO₃S⁺ [M+K]⁺ Calcd 399.1391, Found 399.1396; BHT radical and expected free radical intermediate **BHT-2** HRMS (ESI): C₂₁H₃₈NaO₃S⁺ [M+Na]⁺ Calcd 357.2585, Found 357.2584; TEMPO radical and the expected ·SO₂Ph, **TEMPO-1** HRMS (ESI): C₁₅H₂₄NO₃S⁺ [M+H]⁺ Calcd 298.1472, Found 298.1467; TEMPO radical and expected free radical intermediate **TEMPO-2** HRMS (ESI): C₁₅H₃₄NOSi⁺ [M+H]⁺ Calcd 272.2405, Found 272.2397. (Figure S5)

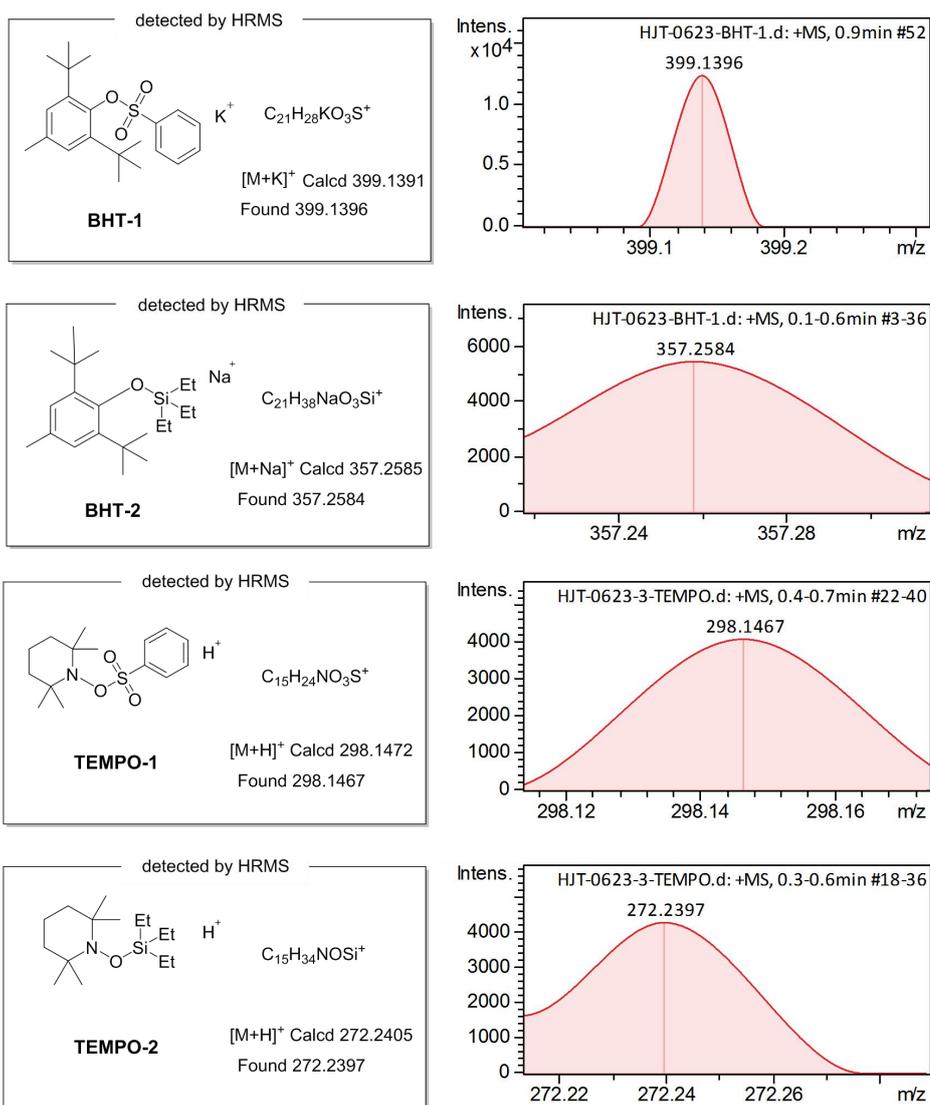


Figure S4. Radical trapping experiments

4.2. Detection of silicon peroxide as key intermediate

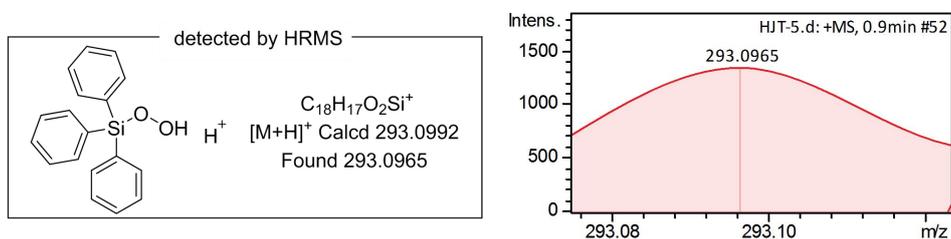


Figure S5. Intermediate trapping experiment

To a 15 mL reaction tube equipped with a magnetic stirring bar, triphenylsilane (0.2 mmol, 1.0 equiv.), PhSO_2Na (20 mol%), CHCl_3 (2 mL) were added. The vessel was capped with a rubber stopper inserting a needle to connect to air. The tube was stirred at room temperature under

irradiation of 30 W purple LEDs (distance app. 5 cm) for 24 h. The reaction was detected by HRMS.

4.3. Transformation of silanol to silyl ether



One-pot procedure: to a 15 mL reaction tube equipped with a magnetic stirring bar, triphenylsilanol (0.2 mmol, 1.0 equiv.), MeOH (2.0 eq.), PhSO₂Na (20 mol% or 0 mol%), dry CHCl₃ (2 mL) were added, stirring at room temperature for 24 hours. The reaction was detected by TLC or ¹H NMR.

Step by step procedure: Preparing four 15 mL reaction tubes in parallel equipped with magnetic stirring bars, triphenylsilane (0.2 mmol, 1.0 equiv.), PhSO₂Na (20 mol%), CHCl₃ (2 mL) were added. The vessel was capped with a rubber stopper inserting a needle to connect to air. The tube was stirred at room temperature under irradiation of 30 W purple LEDs (distance app. 5 cm). Methanol was added at 12 h, 18 h, 24 h and 36 h respectively, at the same time, adding supplementary solvent dry CHCl₃, stirring at room temperature, isolated and calculated reaction products.

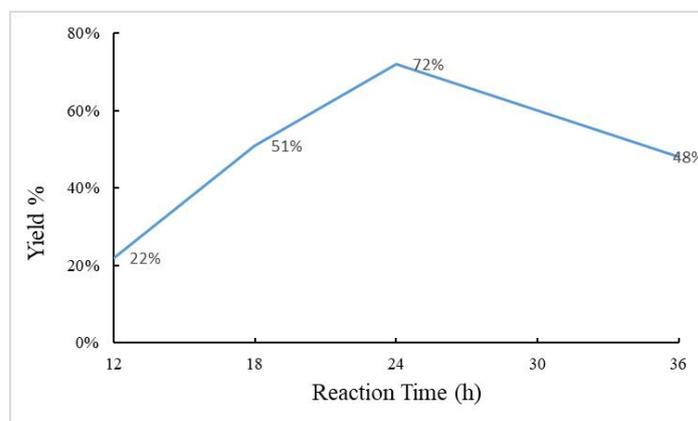


Figure S6. Screening methanol addition time

4.4. Time profile of the transformation with the light on/off over time

Reaction was set up parallel on a 0.4 mmol scale according to the general procedure, triethylsilicane as substrate and extra 0.5 equiv. of CH₂Br₂ was added as the internal standard.

After being irradiated for 3 h, an aliquot (50.0 μL) from the reaction mixture was transferred into a nuclear magnetic tube charged with 0.5 mL of CDCl_3-d_1 . The yield of product was determined by ^1H NMR. Then the reaction mixture was stirred for 3 h with light-off. All of the following yields were analyzed in the identical way after a 3 hour light on or off.

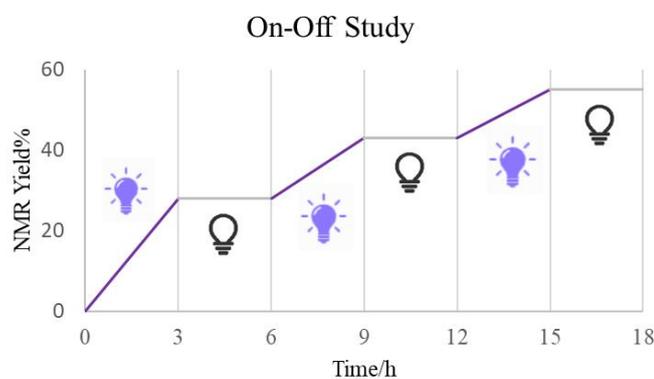


Figure S7. On-Off study

4.5. Calculation of quantum yield

The quantum yield was calculated by the method reported by Yoon group and modified appropriately.^{1, 2} First, standard ferrioxalate actinometry was used to calculate the intensity of LED light used in the experiment, and then the quantum yield of the reaction was calculated.

A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21g potassium ferrioxalate hydrate in 30 mL of 0.05M H_2SO_4 and stored in the dark. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5M H_2SO_4 and stored in the dark. 2 mL of 0.15M ferrioxalate solution were taken and put into a 15mL sealed tube under the protection of argon. After 90S irradiation by 405 nm LED lamp with an emission slit width at 10.0 nm, 0.35mL of the phenanthroline solution was added immediately, and the solution was stirred in the dark for 1h to achieve complete coordination. In addition, 0.35 mL phenanthroline solution was added to 2 mL 0.15M ferrioxalate solution and stirred in the dark for 1h to serve as blank control. 3 mL of distilled water was put into a colorimetric dish, and 30 μL of blank and experimental solution were added respectively. The absorption value at 510 nm was scanned with UV spectrophotometer and repeated measurement three times to find the average. The conversion was calculated as eq (1):

$$\text{mol Fe}^{2+} = \frac{V \cdot \Delta A \cdot 100}{l \cdot \epsilon} \quad (1)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ϵ is the molar absorptivity at 510 nm ($11,100 \text{ L mol}^{-1} \text{ cm}^{-1}$).³ The mol Fe^{2+} was calculated (average of three experiments) to be 3.52×10^{-6} . The photon flux can be calculated as eq (2).

$$\text{photo flux} = \frac{\text{mol Fe}^{2+}}{\phi \cdot t \cdot f} \quad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.14 at $\lambda = 405 \text{ nm}$),⁴ t is the time (90.0 s), and f is the fraction of light absorbed at $\lambda = 405 \text{ nm}$ ($\cong 1$). The photo flux was calculated to be $3.42 \times 10^{-8} \text{ einstein s}^{-1}$

The absorbance of the above ferrioxalate solution at 405 nm was > 3 . The fraction of light absorbed (f) by this solution was calculated using eq 3, where A is the measured absorbance at 405 nm. So the $f \cong 1$.

$$f = 1 - 10^{-A} \quad (3)$$

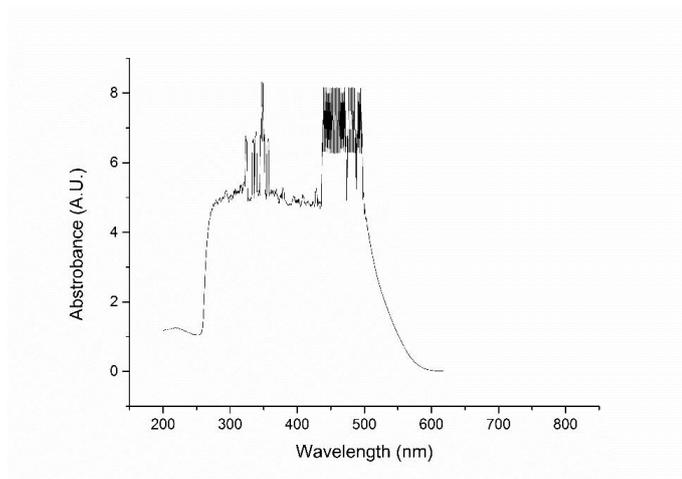


Figure S9. Absorbance of the ferrioxalate actinometer solution.

To a 10 mL reaction tube equipped with a magnetic stirring bar, **1a** (0.2 mmol, 1.0 equiv.), PhSO_2Na (20 mol%), CHCl_3 (2.0 mL) were added. The vessel was connected to the atmosphere by inserting a needle. The tube was stirred at room temperature under irradiation of 30 W purple LEDs ($\lambda = 405 \text{ nm}$, distance app. 5 cm) for 12 h. Then, the organic phase was removed by rotary evaporation under decompression condition. Finally, the target product was separated by rapid

column chromatography. This reaction was repeated three times, the yield was calculated as 26.2%, 24.8% and 29.1% respectively, and the final average yield was 26.7%. The quantum yield was determined using eq (4):

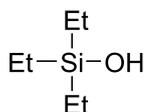
$$\phi = \frac{\text{moles of product formed}}{\text{photo flux} \cdot t \cdot f} \quad (4)$$

$$\phi = \frac{12 \times 10^{-5} \text{ mol}}{3.42 \times 10^{-8} \text{ einstein s}^{-1} \cdot 43200 \text{ s}} = 0.08 \quad (4)$$

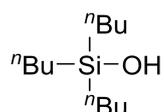
4.6. Controlled experiments of reaction with H₂¹⁸O and ¹⁶O₂

A mixture of Ph₃SiH **2i** (0.2 mmol), PhSO₂Na (20 mol%) was added into the a freshly dried Schlenk tube. The tube was evacuated and backfilled with ¹⁶O₂ (three times) via an oxygen balloon. Then dry CHCl₃ 2 mL and H₂¹⁸O (20 μL) was added into the system. The reaction mixture was evolved with oxygen balloon and stirred under the irradiation of a 30W purple LED at room temperature. We monitored the reaction at the reaction time was 12 h. At last, the solvent was removed under reduced pressure, the crude product was purified by column chromatography with petroleum ether/ethyl acetate (100:4) as eluent to give the product **2i**. The products were analyzed by ¹H NMR (see the NMR spectrum) and MS as follows. T

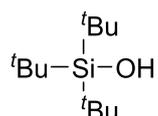
5. Characteristic Data of the Corresponding Products



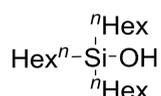
Triethylsilanol (2a), purification by suction filtration; 22.2 mg, 84%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 0.93 (t, $J = 7.9$ Hz, 9H), 0.52 (q, $J = 8.0$ Hz, 6H). Analytic data is in accordance with literature data.⁵



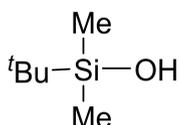
Tributylsilanol (2b), purification by suction filtration; 41.5 mg, 96%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 1.27 (s, 12H), 0.89 – 0.87 (m, 9H), 0.57 – 0.50 (m, 6H). Analytic data is in accordance with literature data.⁵



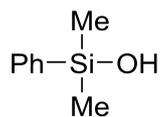
Triisopropylsilanol (2c), purification by suction filtration; 28.2 mg, 87%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 3.71 (s, 1H), 1.05 (s, 27H). Analytic data is in accordance with literature data.⁵



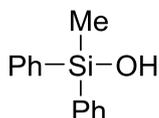
Trihexylsilanol (2d), purification by suction filtration; 37.9 mg, 63%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 1.32 – 1.28 (m, 24H), 0.90-0.87 (m, 9H), 0.60 – 0.55 (m, 6H). Analytic data is in accordance with literature data.⁵



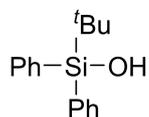
***tert*-Butyldimethylsilanol (2e)**, purification by suction filtration; 24.3 mg, 92%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 0.87 (s, 6H), 0.05 (s, 9H). Analytic data is in accordance with literature data.⁵



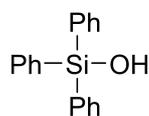
Dimethylphenylsilanol (2f), purification by flash chromatography (PE/EA, 100/4); 27.9 mg, 92%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.52 – 7.51 (m, 2H), 7.33 – 7.30 (m, 3H), 0.30 (s, 6H). Analytic data is in accordance with literature data.⁵



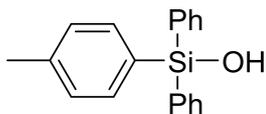
Methyldiphenylsilanol (2g), purification by flash chromatography (PE/EA, 100/4); 40.7 mg, 95%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.53 – 7.50 (m, 4H), 7.38 – 7.28 (m, 6H), 0.57 (s, 3H). Analytic data is in accordance with literature data.⁵



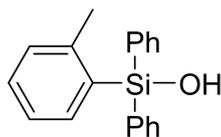
tert-Butyldiphenylsilanol (2h), purification by flash chromatography (PE/EA, 100/4); 23.1 mg, 45%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.72 – 7.70 (m, 4H), 7.43 – 7.35 (m, 6H), 1.07 (s, 9H). Analytic data is in accordance with literature data.⁵



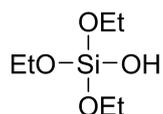
Triphenylsilanol (2i), purification by flash chromatography (PE/EA, 100/4); 49.1 mg, 89%, white solid. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.62 (d, $J = 7.6$ Hz, 6H), 7.45 – 7.35 (m, 9H), 2.48 (s, 1H). Analytic data is in accordance with literature data.⁵



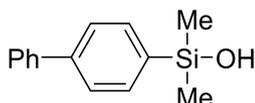
Diphenyl(p-tolyl)silanol (2j), purification by flash chromatography (PE/EA, 100/4); 36.6 mg, 63%, $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.64 – 7.61 (m, 4H), 7.52 (d, $J = 7.8$ Hz, 2H), 7.43 – 7.36 (m, 6H), 7.21 (d, $J = 7.5$ Hz, 2H), 2.37 (s, 3H). Analytic data is in accordance with literature data.¹¹



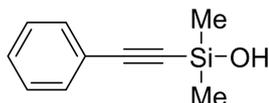
Diphenyl(o-tolyl)silanol (2k), purification by flash chromatography (PE/EA, 100/4); 41.8 mg, 72%, $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.61 – 7.58 (m, 4H), 7.44-7.35 (m, 8H), 7.20 – 7.15 (m, 2H), 2.32 (s, 3H). Analytic data is in accordance with literature data.¹¹



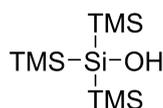
Triethoxysilanol (2l), purification by suction filtration; 36.6 mg, 90%, colorless oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 3.72 (q, $J = 7.0$ Hz, 6H), 1.24 (t, $J = 7.0$ Hz, 9H). Analytic data is in accordance with literature data.⁵



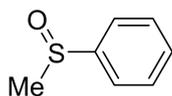
(1,1'-Biphenyl)-4-yl dimethylsilanol (2m), purification by suction filtration; 35.6 mg, 78%, white solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.60 (m, 6H), 7.45 (d, $J = 7.9$ Hz, 2H), 7.37 (d, $J = 7.4$ Hz, 1H), 0.42 (s, 1H). Analytic data is in accordance with literature data.¹²



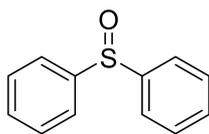
Dimethyl(phenylethynyl)silanol (2n), purification by suction filtration; 25.8 mg, 73%, colorless oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, $J = 5.6$ Hz, 2H), 7.32 – 7.26 (m, 3H), 0.39 (s, 1H). Analytic data is in accordance with literature data.¹²



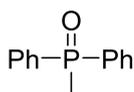
1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-ol (2o), purification by suction filtration; 48.9 mg, 93%, colorless oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 0.18 (s, 27H). Analytic data is in accordance with literature data.¹³



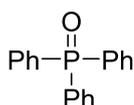
Methylphenylsulfoxide (2p), purification by flash chromatography (PE/EA, 100/60); 24.5 mg, 88%, colorless oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.67-7.64 (m, 2H), 7.56 – 7.50 (m, 3H), 2.73 (s, 3H). Analytic data is in accordance with literature data.¹⁴



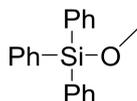
Diphenylsulfoxide (2q), purification by flash chromatography (PE/EA, 100/20); 33.4 mg, 83%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.59-7.56 (m, 4H), 7.41-7.36 (m, 6H). Analytic data is in accordance with literature data.¹⁵



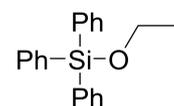
Methyldiphenylphosphineoxide (2r), purification by flash chromatography (PE/EA, 100/60); 40.1 mg, 95%, white solid. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.77-7.69 (m, 4H), 7.53-7.44 (m, 6H), 2.03 (s, 3H). $^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 29.87. Analytic data is in accordance with literature data.¹⁶



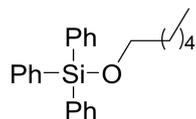
Triphenylphosphineoxide (2s), flash chromatography (PE/EA, 100/60); 52.3 mg, 95%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.70 – 7.65 (m, 6H), 7.56 – 7.52 (m, 3H), 7.48-7.44 (m, 6H). $^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 29.07. Analytic data is in accordance with literature data.¹⁶



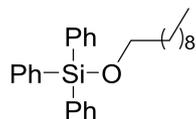
Methoxytriphenylsilane (3a), purification by flash chromatography (PE/EA, 100/2); 41.7 mg, 72%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.64 – 7.61 (m, 6H), 7.45 – 7.36 (m, 9H), 3.64 (s, 3H). Analytic data is in accordance with literature data.⁵



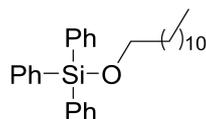
Ethoxytriphenylsilane (3b), purification by flash chromatography (PE/EA, 100/2); 39.5 mg, 65%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.64 – 7.61 (m, 6H), 7.45 – 7.35 (m, 9H), 3.87 (q, $J = 7.0$ Hz, 2H), 1.23 (t, $J = 7.0$ Hz, 3H). Analytic data is in accordance with literature data.⁵



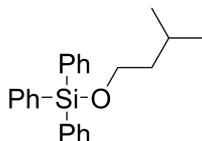
***n*-Hexethoxytriphenylsilane (3c)**, purification by flash chromatography (PE/EA, 100/2); 37.5 mg, 52%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.64 – 7.61 (m, 6H), 7.44 – 7.35 (m, 9H), 3.79 (t, J = 6.6 Hz, 2H), 1.62 – 1.55 (m, 2H), 1.34 – 1.21 (m, 6H), 0.85 (t, J = 6.9 Hz, 3H). Analytic data is in accordance with literature data.⁷



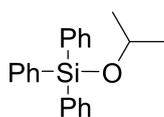
***n*-Decethoxytriphenylsilane (3d)**, purification by flash chromatography (PE/EA, 100/2); 26.7 mg, 32%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.63 – 7.61 (m, 6H), 7.45 – 7.35(m, 9H), 3.78 (t, J = 6.6 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.28 – 1.22(m, 14H), 0.88 (t, J = 6.9 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 135.4, 134.5, 129.9, 127.8, 64.0, 32.6, 31.9, 29.61, 29.56, 29.35, 29.33, 25.8, 22.7, 14.1; **HRMS (ESI)**: $\text{C}_{28}\text{H}_{37}\text{OSi}^+$ $[\text{M}+\text{H}]^+$ Calcd 417.2608, Found 417.2609.



Dodecethoxytriphenylsilane (3e), purification by flash chromatography (PE/EA, 100/2); 23.12mg, 26%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.63 – 7.61 (m, 6H), 7.45 – 7.35(m, 9H), 3.78 (t, J = 6.6 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.25 – 1.22 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 135.4, 134.5, 129.9, 127.8, 64.0, 32.5, 31.9, 29.68, 29.65, 29.6, 29.4, 25.8, 22.7, 14.1; **HRMS (ESI)**: $\text{C}_{30}\text{H}_{40}\text{KOSi}^+$ $[\text{M}+\text{K}]^+$ Calcd 483.2480, Found 483.2475.

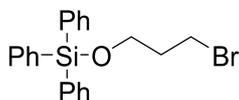


(Isopentyloxy)triphenylsilane (3f), purification by flash chromatography (PE/EA, 100/2); 34.7 mg, 50%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.63 – 7.62 (m, 6H), 7.42 – 7.35 (m, 9H), 3.82 (t, J = 6.7 Hz, 2H), 1.80 – 1.70 (m, 1H), 1.48 (q, J = 6.7 Hz, 2H), 0.83 (d, J = 6.6 Hz, 6H). Analytic data is in accordance with literature data.⁸

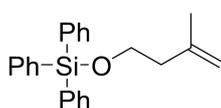


Isopropoxytriphenylsilane (3g), purification by flash chromatography (PE/EA, 100/2); 28.7

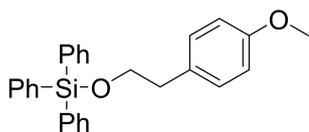
mg, 45%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.64 – 7.62 (m, 6H), 7.45 – 7.35 (m, 9H), 4.22 – 4.13 (m, 1H), 1.18 (d, $J = 6.0$ Hz, 6H). Analytic data is in accordance with literature data.⁸



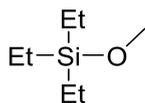
(3-Bromopropoxy)triphenylsilane (3h), purification by flash chromatography (PE/EA, 100/2); 41.3 mg, 52%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.55 – 7.53 (m, 6H), 7.38 – 7.28 (m, 9H), 3.84 (t, $J = 5.7$ Hz, 2H), 3.47 (t, $J = 6.6$ Hz, 2H), 2.04 – 1.98 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 135.4, 134.0, 130.1, 127.9, 61.5, 35.5, 30.4; **HRMS (ESI)**: $\text{C}_{42}\text{H}_{43}\text{BrOSi}^+ [2\text{M}+\text{H}]^+$ Calcd 795.1142, Found 795.1132.



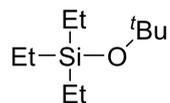
((3-Methylbut-3-en-1-yl)oxy)triphenylsilane (3i), purification by flash chromatography (PE/EA, 100/2); 43.4mg, 63%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.64 – 7.61 (m, 6H), 7.45 – 7.35 (m, 9H), 4.73 (s, 1H), 4.68 (s, 1H), 3.89 (t, $J = 7.0$ Hz, 2H), 2.30 (t, $J = 6.9$ Hz, 2H), 1.65 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 142.7, 135.4, 134.4, 130.0, 127.9, 111.9, 62.6, 40.8, 22.7; **HRMS (ESI)**: $\text{C}_{23}\text{H}_{25}\text{OSi}^+ [\text{M}+\text{H}]^+$ Calcd 345.1669, Found 345.1666.



(4-Methoxyphenethoxy)triphenylsilane (3j), purification by flash chromatography (PE/EA, 100/2); 54.1 mg, 66%, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.58 – 7.56 (m, 6H), 7.44 – 7.33 (m, 9H), 7.04 (d, $J = 8.6$ Hz, 2H), 6.78 (d, $J = 8.6$ Hz, 2H), 3.94 (t, $J = 7.1$ Hz, 2H), 3.76 (s, 3H), 2.82 (t, $J = 7.1$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 158.1, 135.4, 134.3, 130.9, 130.1, 130.0, 127.9, 113.7, 65.3, 55.3, 38.4; **HRMS (ESI)**: $\text{C}_{27}\text{H}_{26}\text{NaO}_2\text{Si}^+ [\text{M}+\text{Na}]^+$ Calcd 433.1594, Found 433.1592.



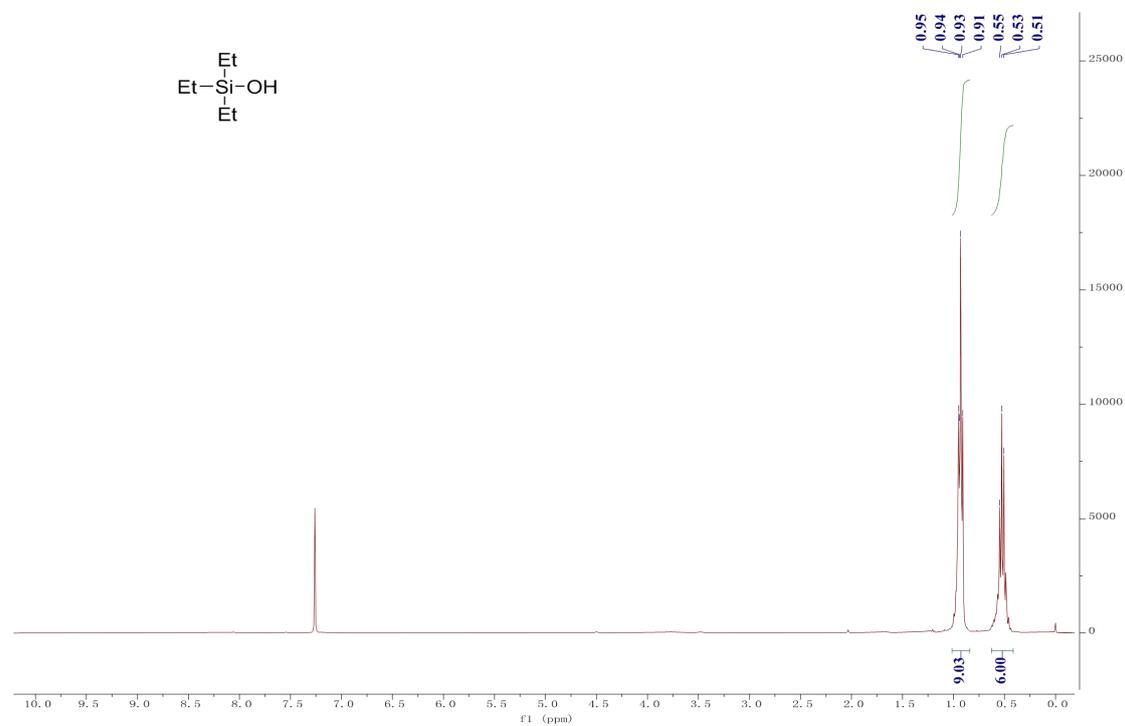
Methoxytriethylsilane (3k), purification by suction filtration; 22.2 mg, 76%, colorless oil. **¹H NMR** (400 MHz, Chloroform-*d*) δ 3.49 (s, 3H), 0.98 (t, $J = 8$ Hz, 9H), 0.59 (q, $J = 8$ Hz, 6H). Analytic data is in accordance with literature data.⁹



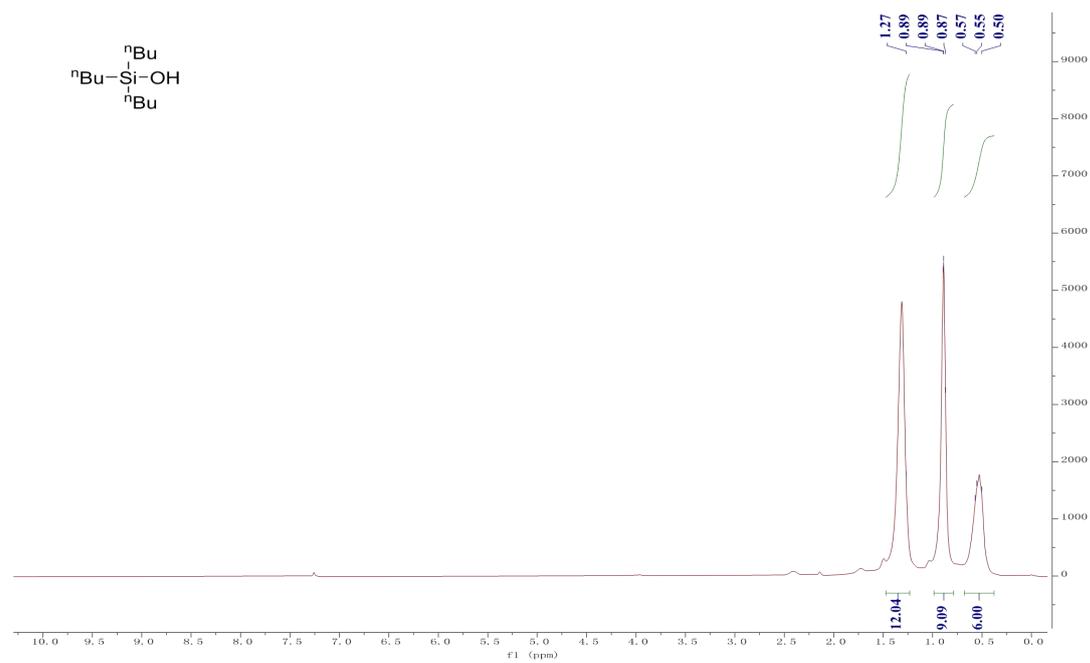
tert-Butylthoxy-triethyl-silane (3l), purification by suction filtration; 19.19 mg, 51%, colorless oil. **¹H NMR** (400 MHz, Chloroform-*d*) δ 1.28 (s, 9H), 0.94 (dt, $J = 11.5, 7.9$ Hz, 9H), 0.52 (d, $J = 8.0$ Hz, 6H). Analytic data is in accordance with literature data.¹⁰

6. Copies of the NMR Spectrum of the Corresponding

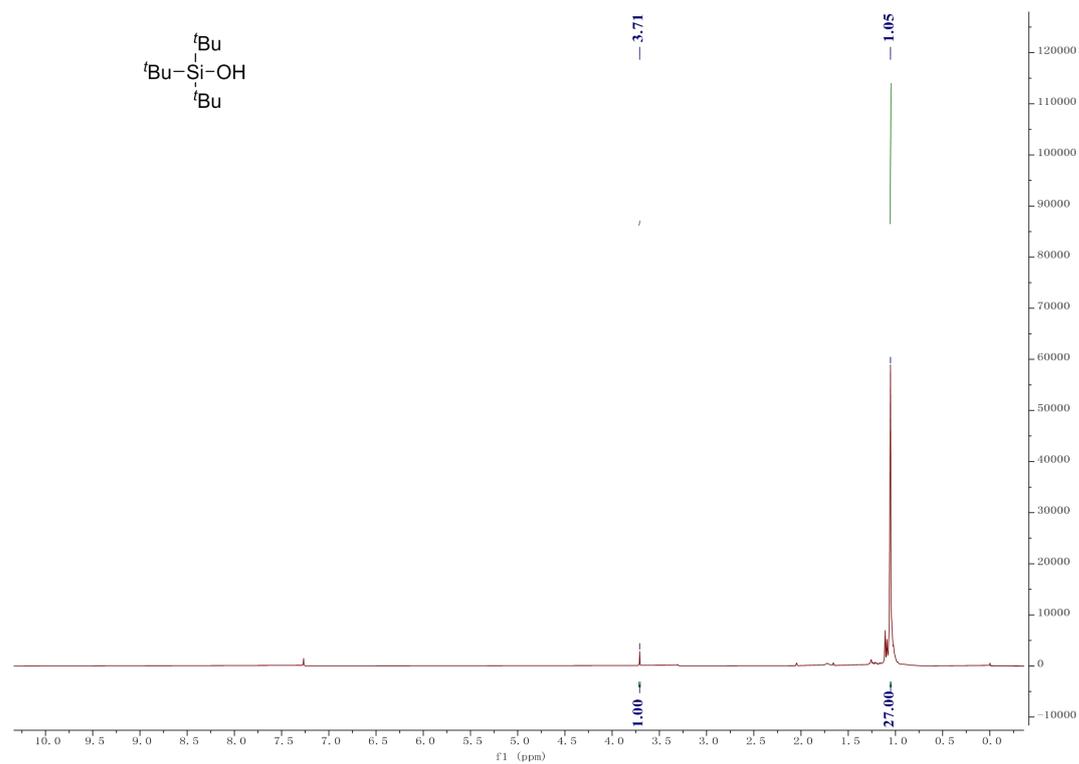
^1H NMR (400 MHz, CDCl_3) spectrum of product 2a



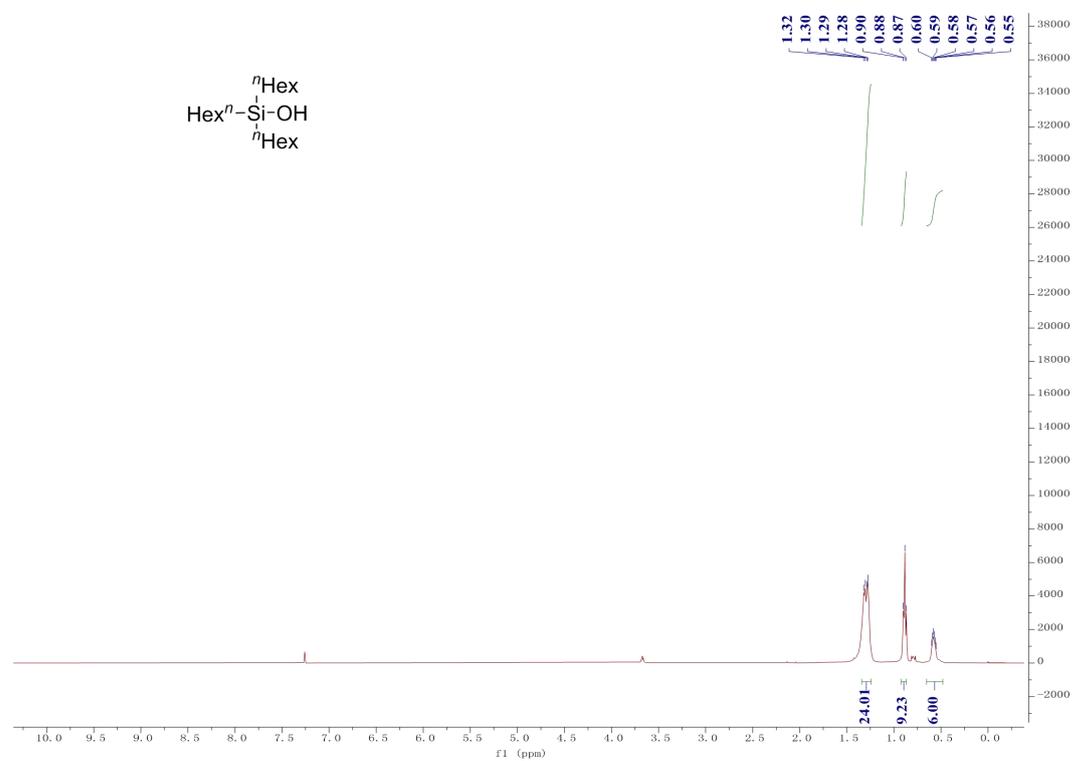
^1H NMR (400 MHz, CDCl_3) spectrum of product 2b



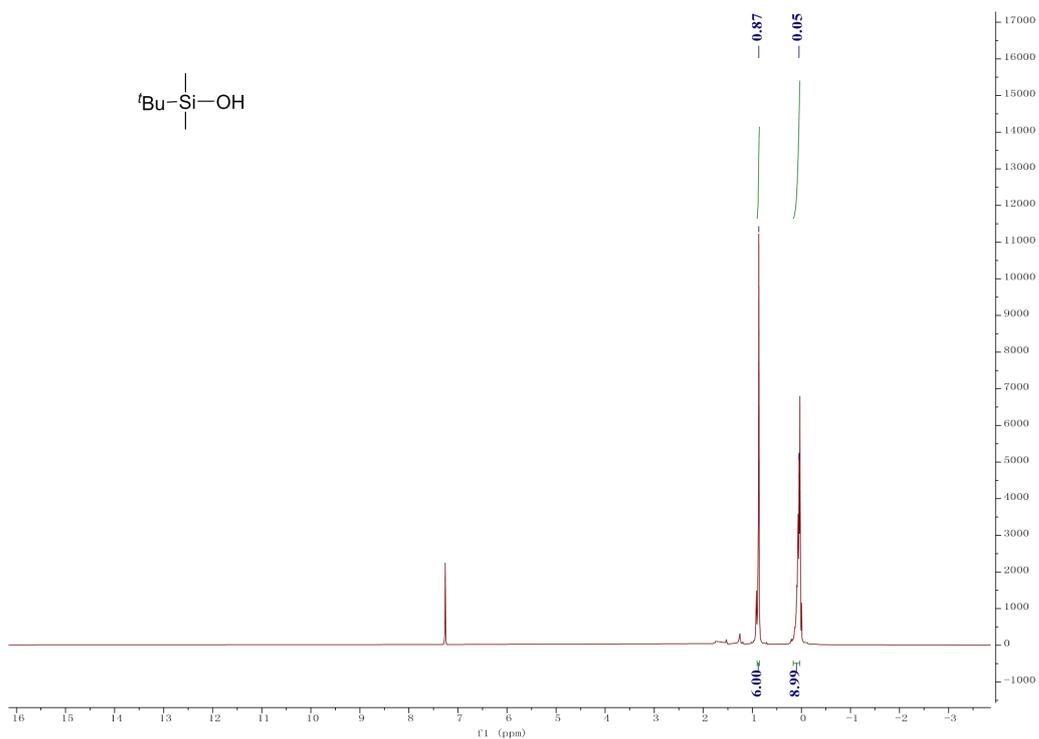
¹H NMR (400 MHz, CDCl₃) spectrum of product 2c



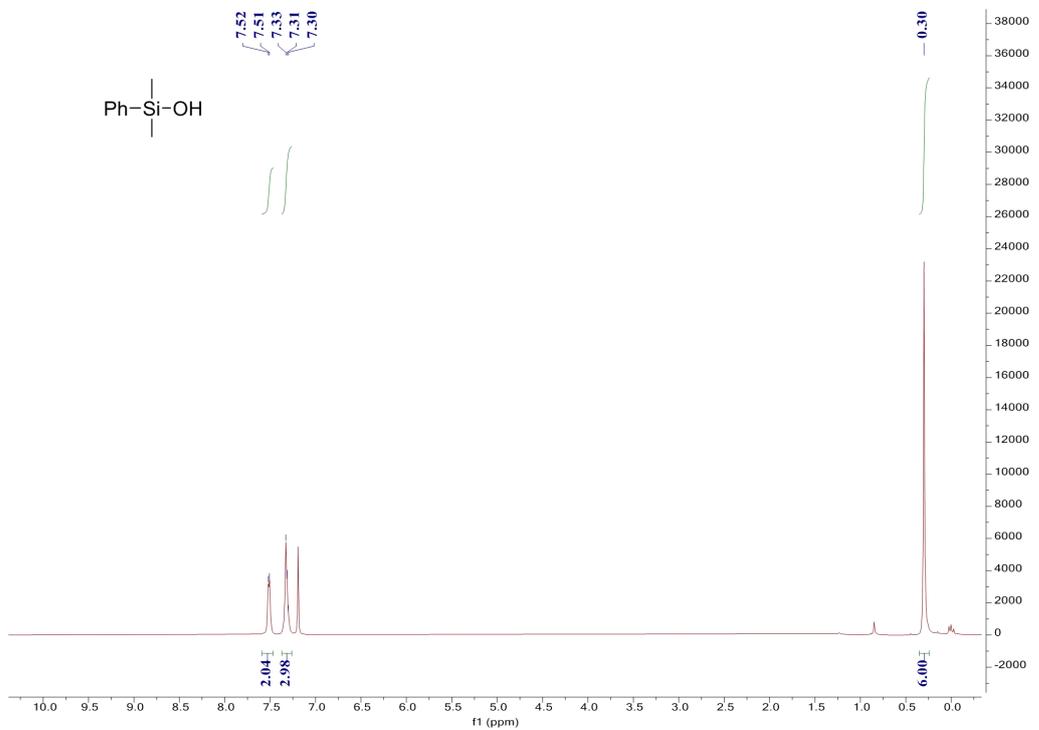
¹H NMR (400 MHz, CDCl₃) spectrum of product 2d



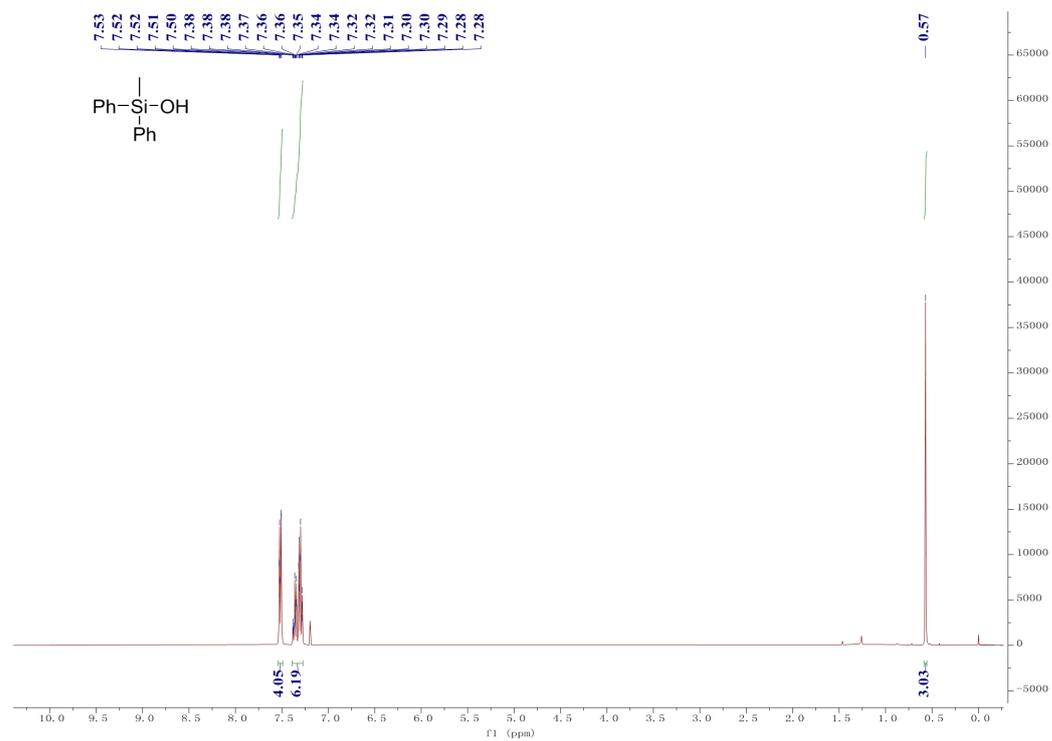
¹H NMR (400 MHz, CDCl₃) spectrum of product 2e



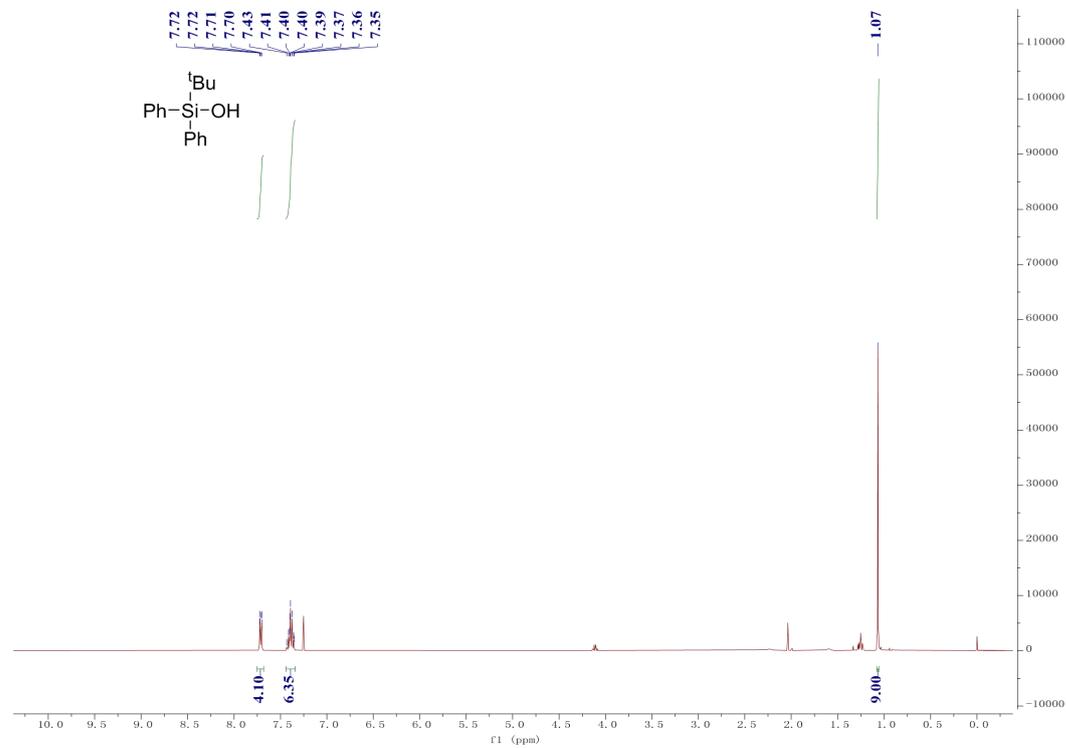
¹H NMR (400 MHz, CDCl₃) spectrum of product 2f



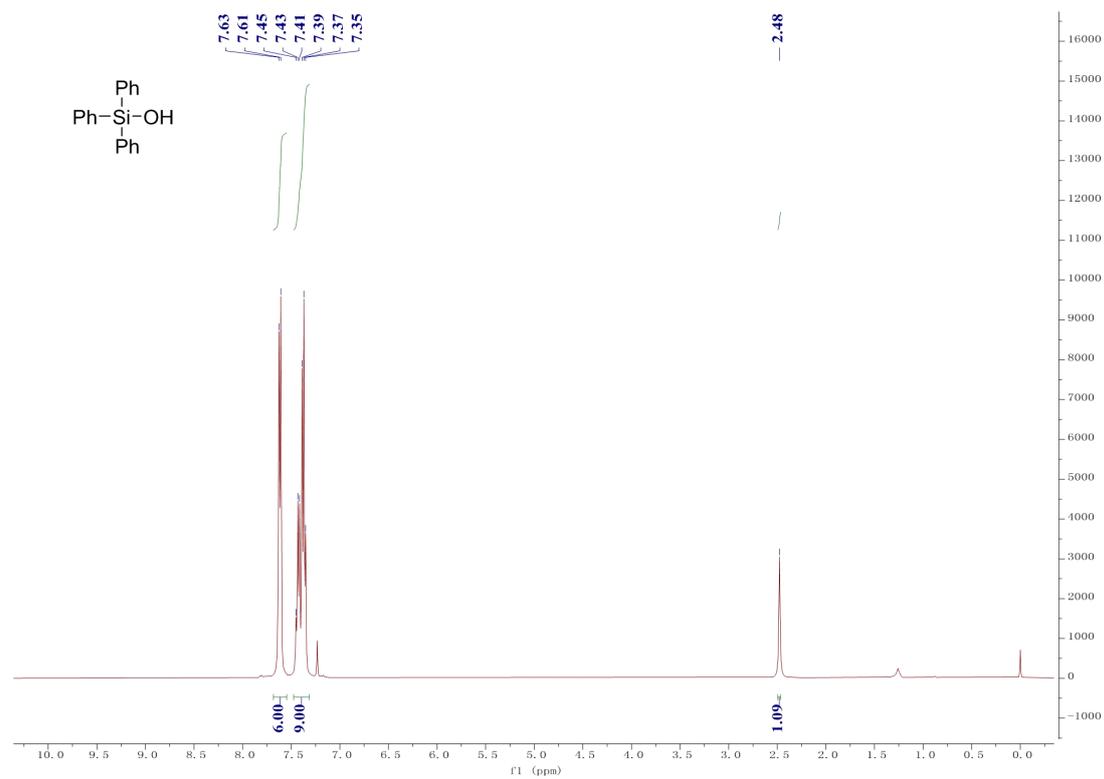
^1H NMR (400 MHz, CDCl_3) spectrum of product 2g



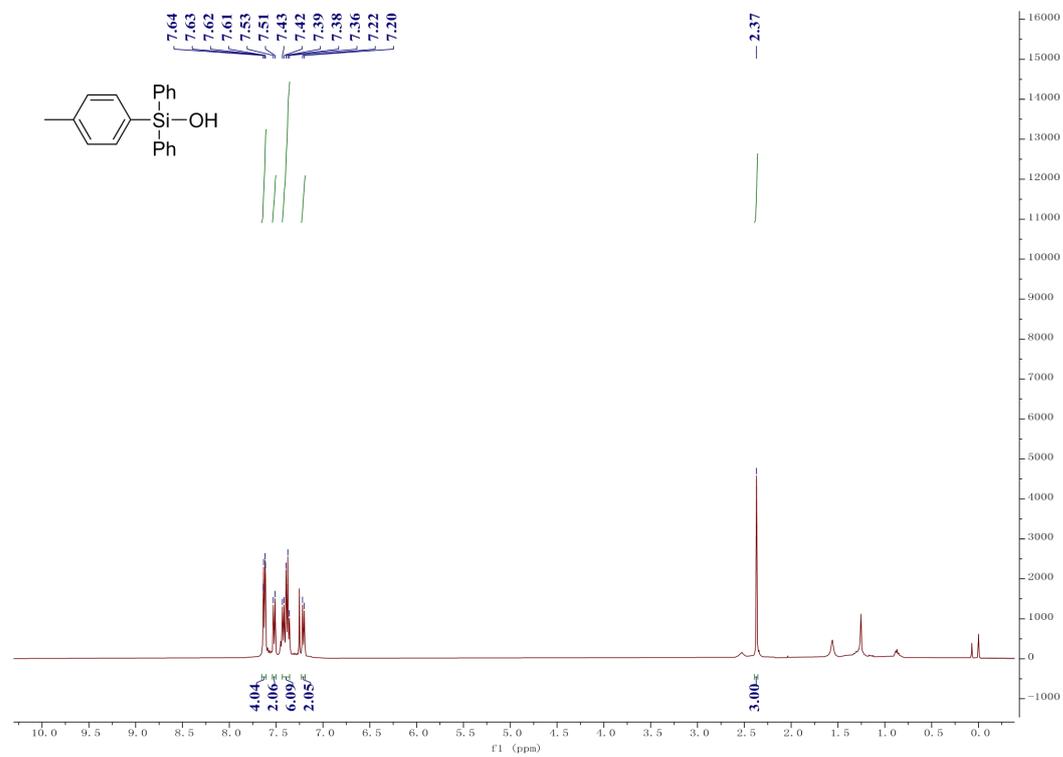
^1H NMR (400 MHz, CDCl_3) spectrum of product 2h



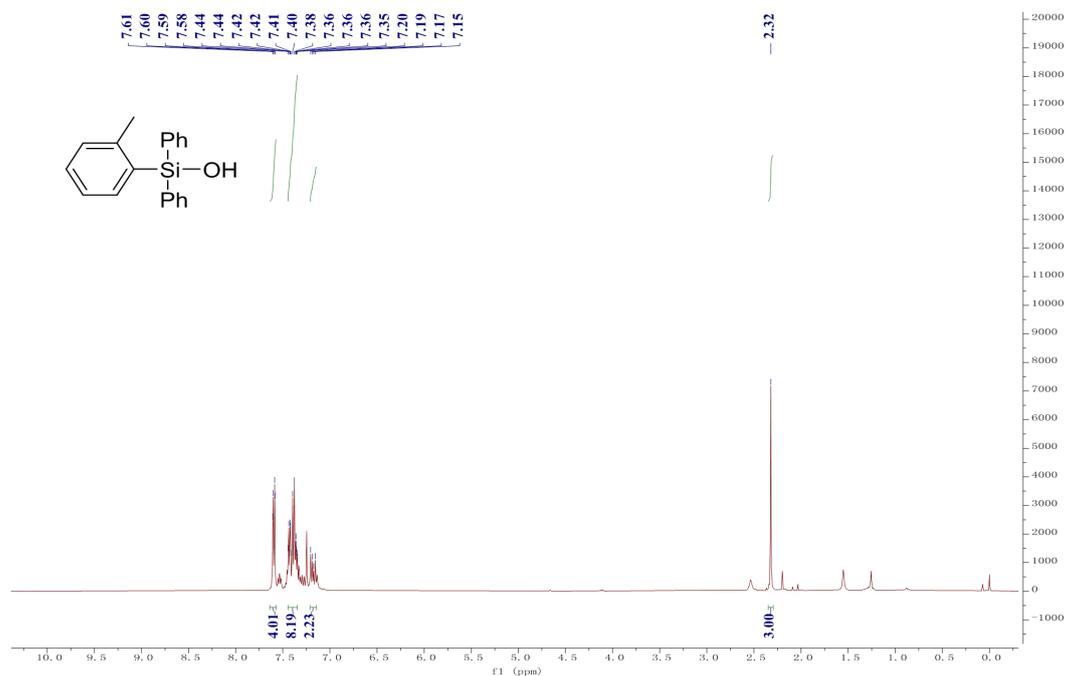
¹H NMR (400 MHz, CDCl₃) spectrum of product 2i



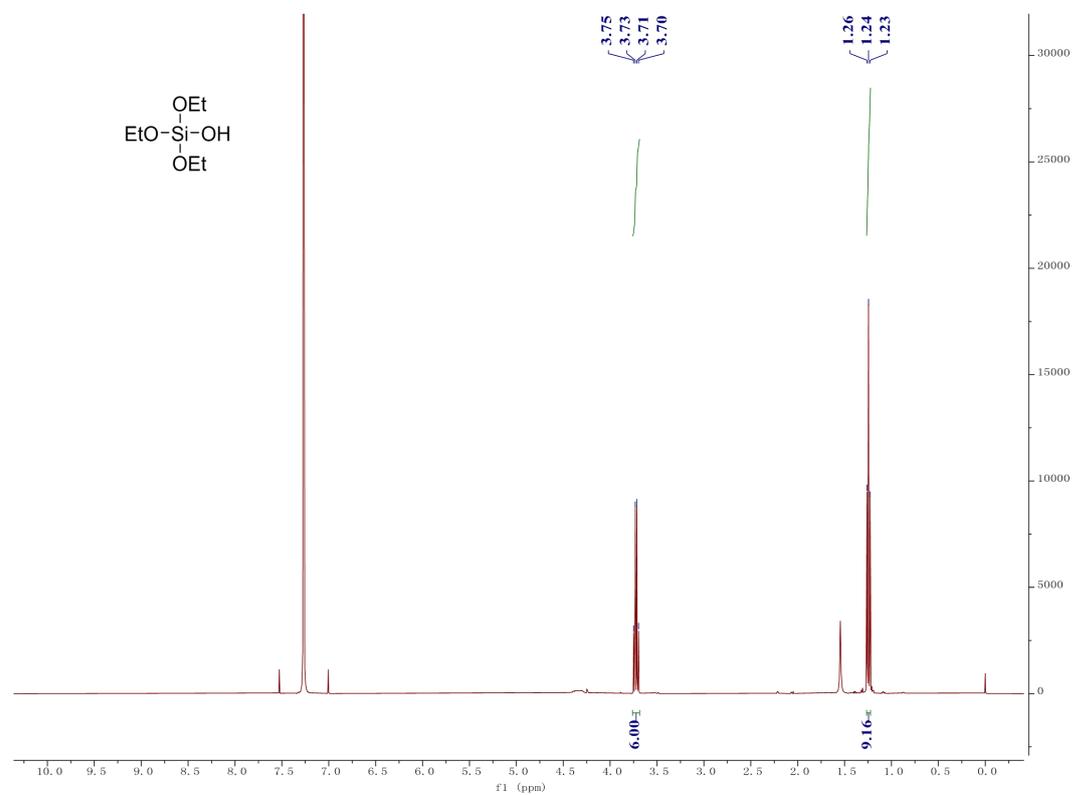
¹H NMR (400 MHz, CDCl₃) spectrum of product 2j



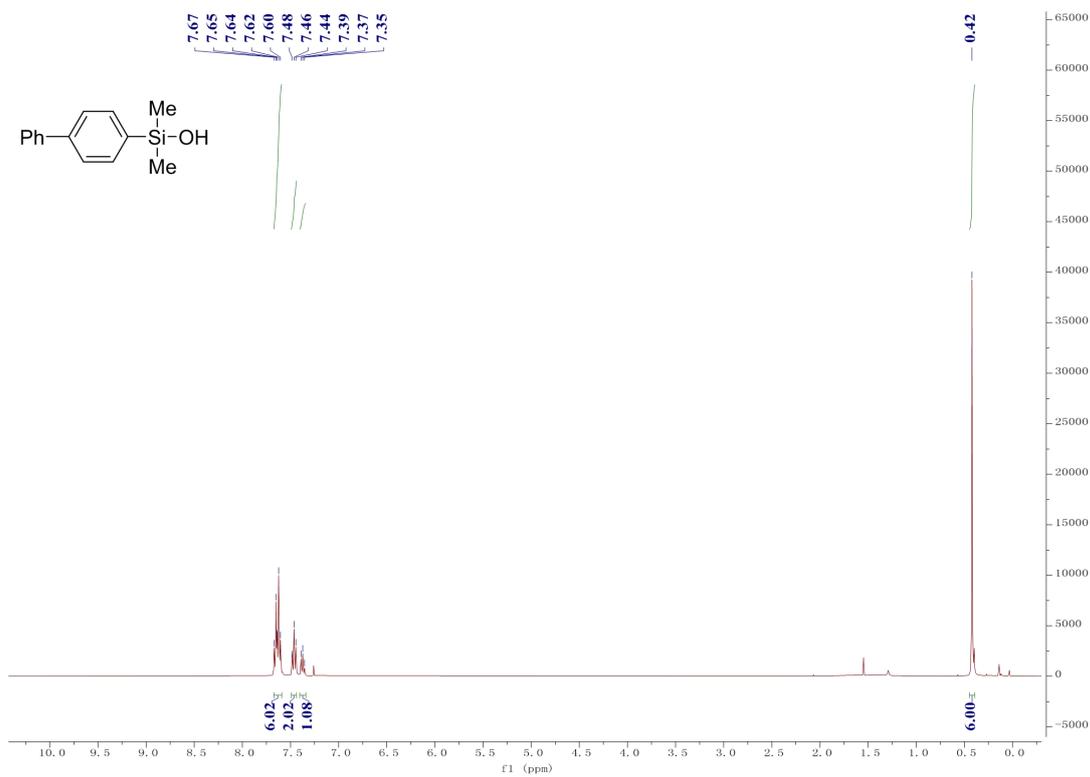
¹H NMR (400 MHz, CDCl₃) spectrum of product 2k



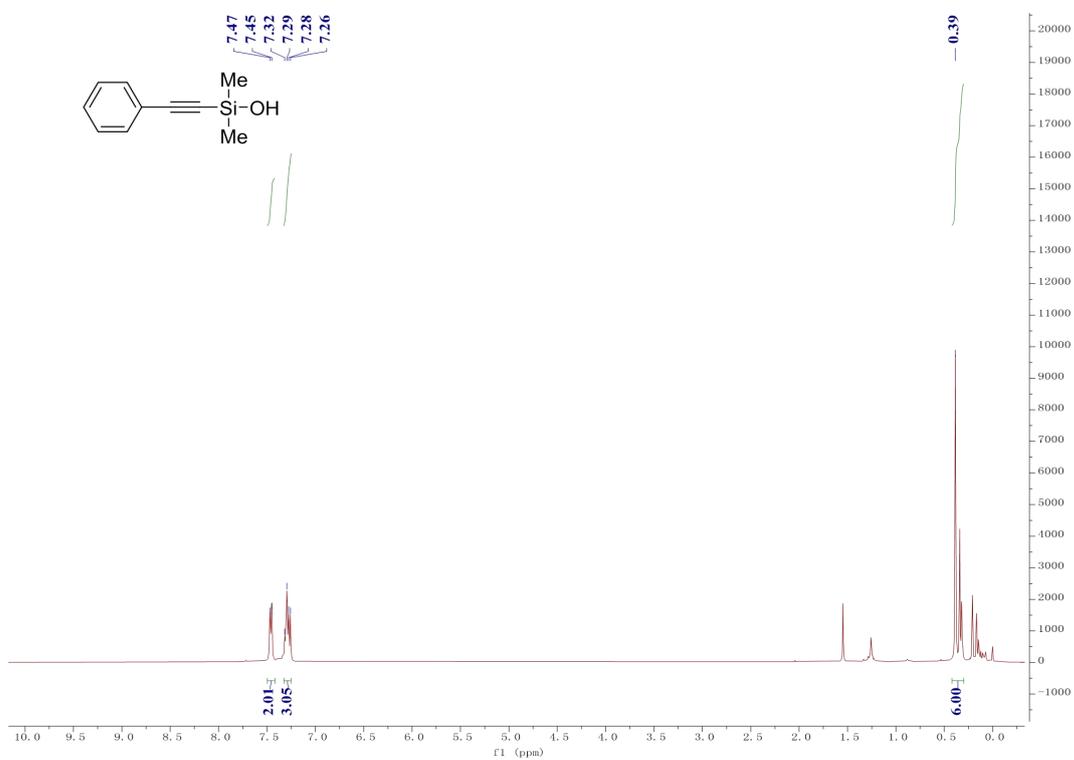
¹H NMR (400 MHz, CDCl₃) spectrum of product 2l



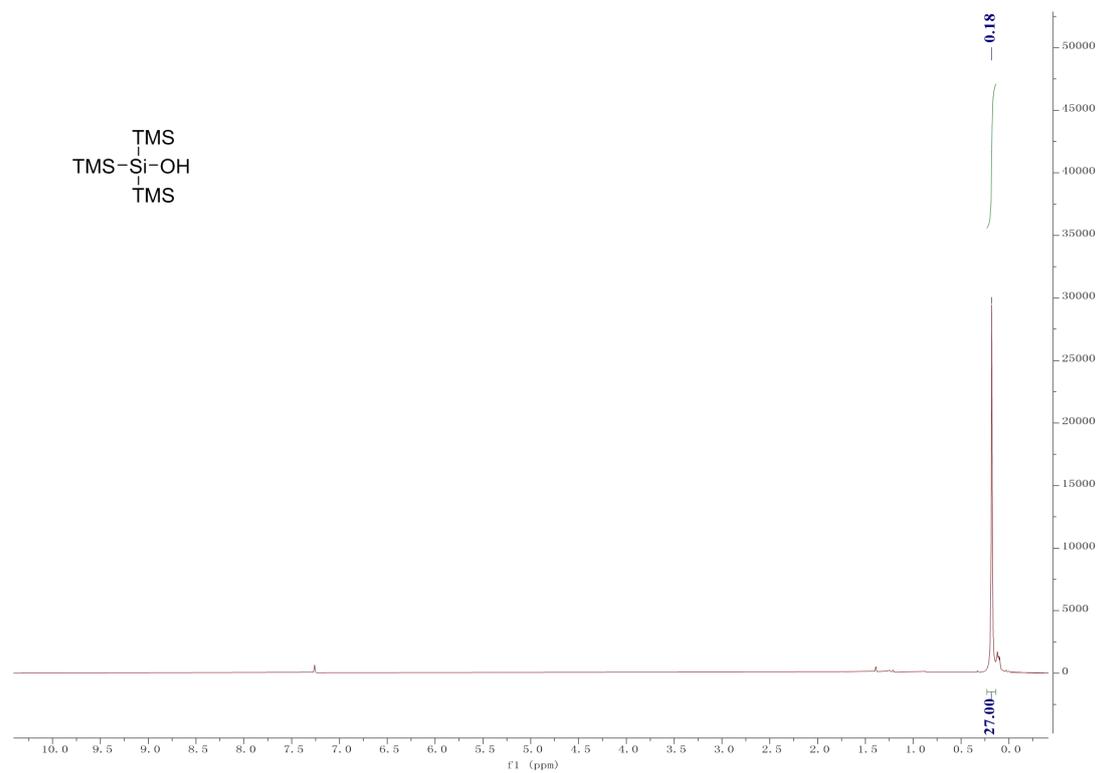
¹H NMR (400 MHz, CDCl₃) spectrum of product 2m



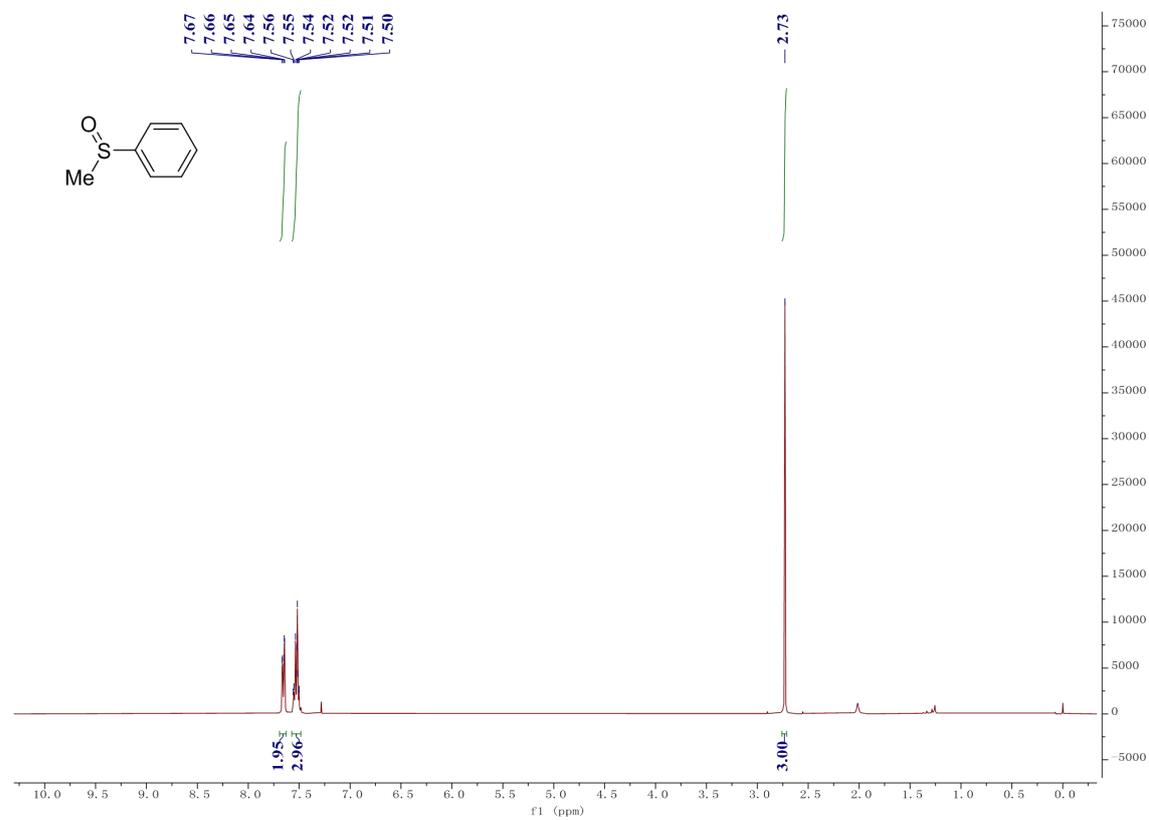
¹H NMR (400 MHz, CDCl₃) spectrum of product 2n



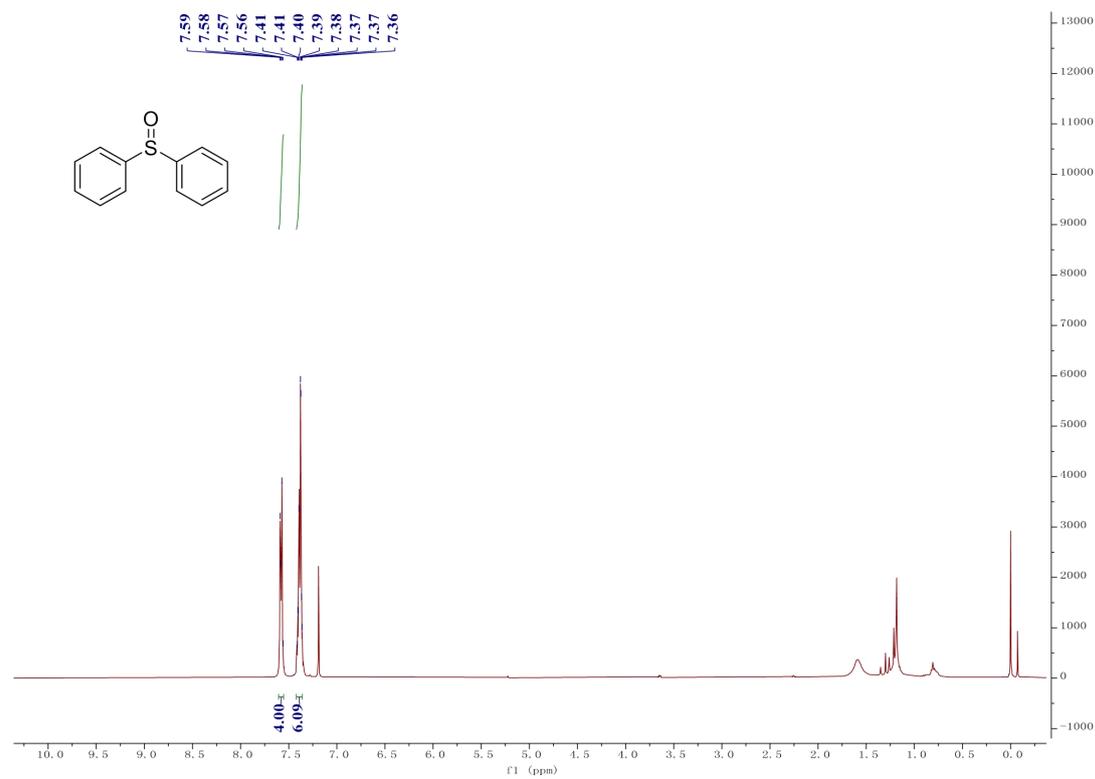
^1H NMR (400 MHz, CDCl_3) spectrum of product 2o



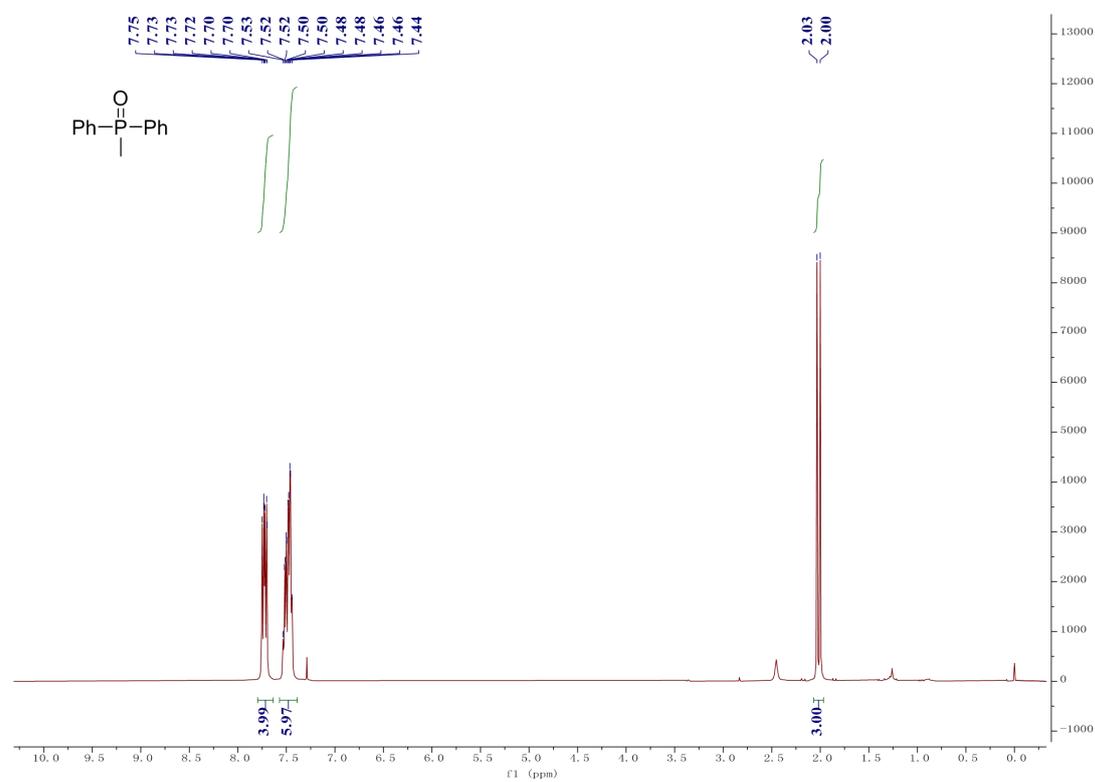
^1H NMR (400 MHz, CDCl_3) spectrum of product 2p



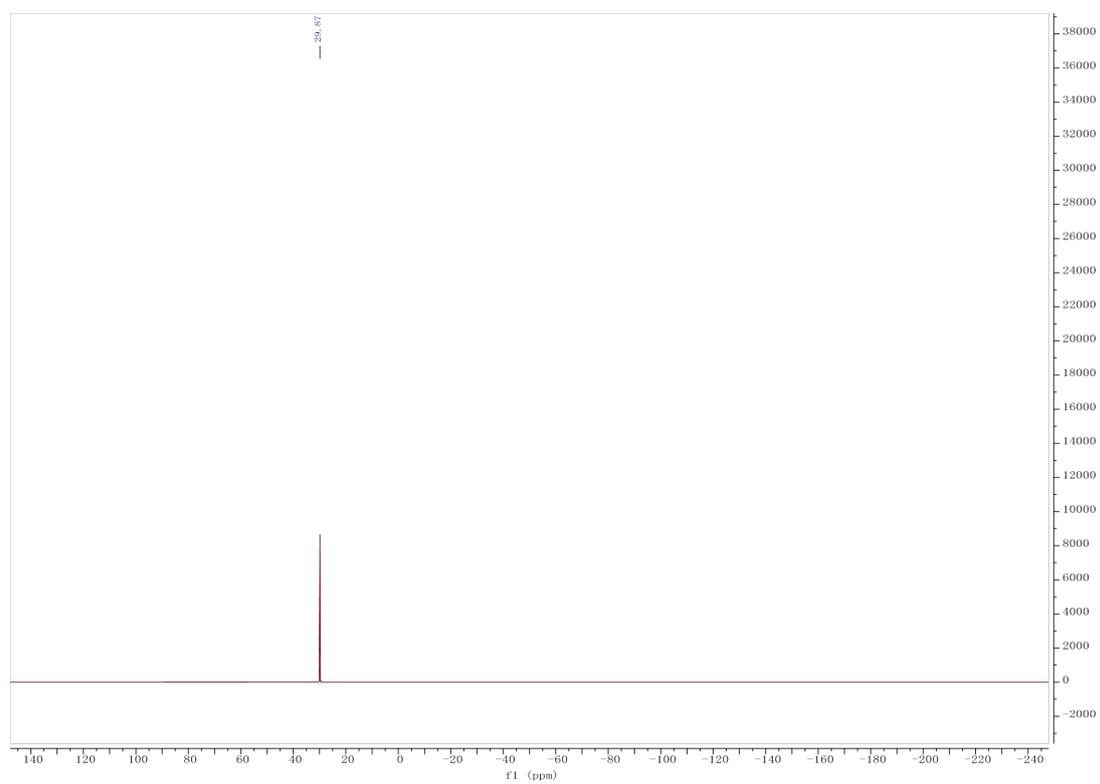
¹H NMR (400 MHz, CDCl₃) spectrum of product 2q



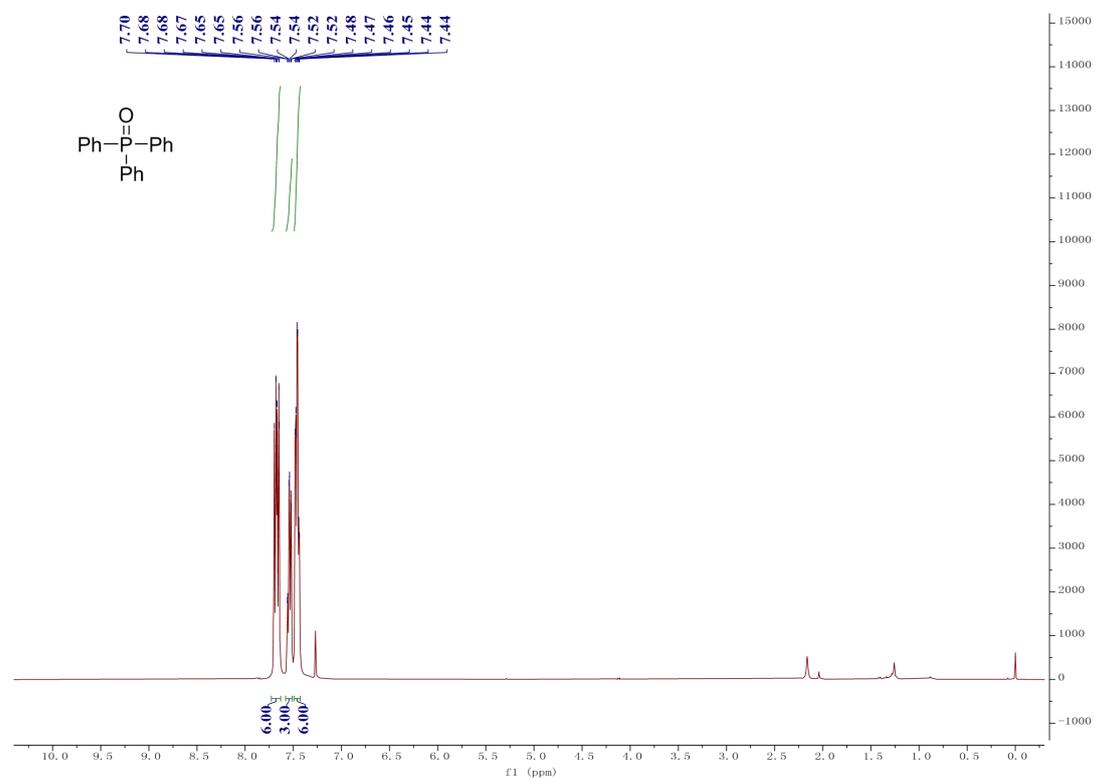
¹H NMR (400 MHz, CDCl₃) spectrum of product 2r



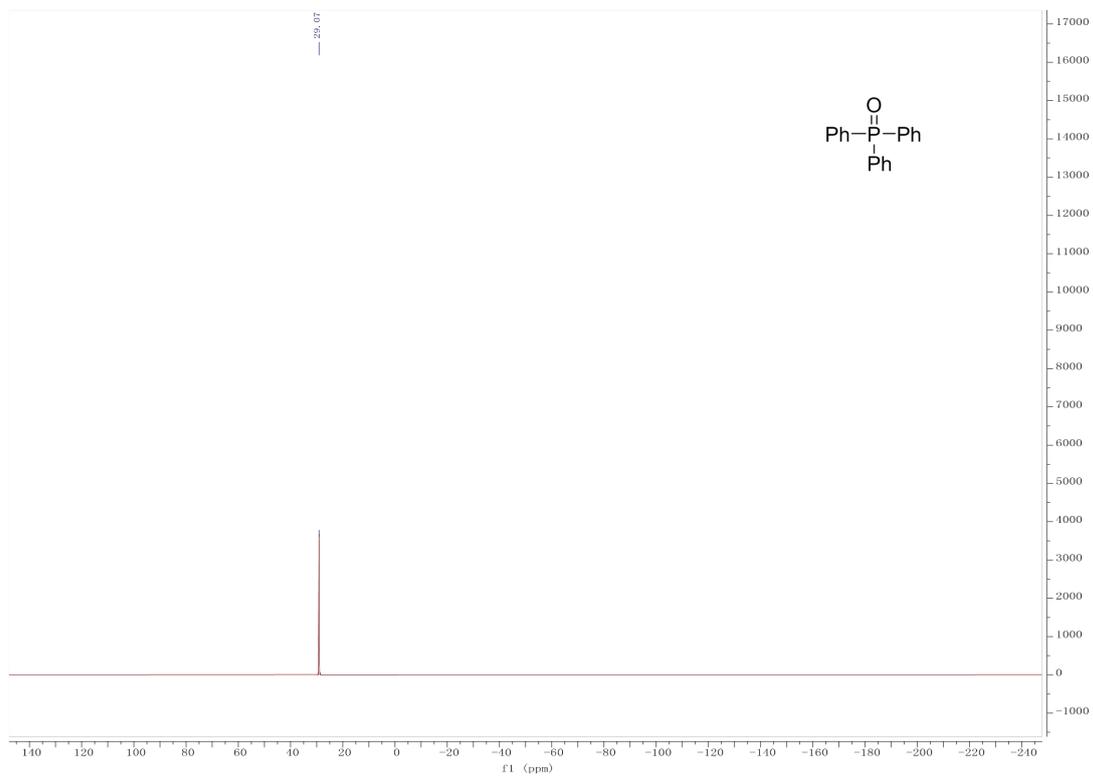
³¹P NMR (400 MHz, CDCl₃) spectrum of product 2r



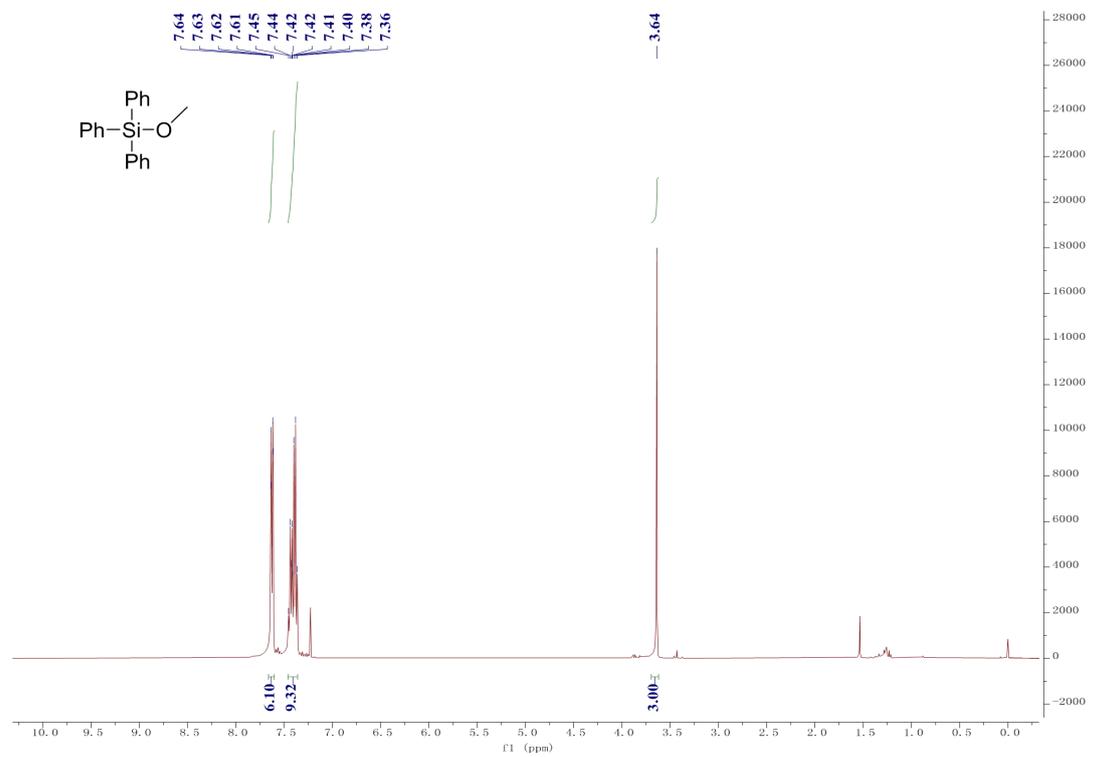
¹H NMR (400 MHz, CDCl₃) spectrum of product 2s



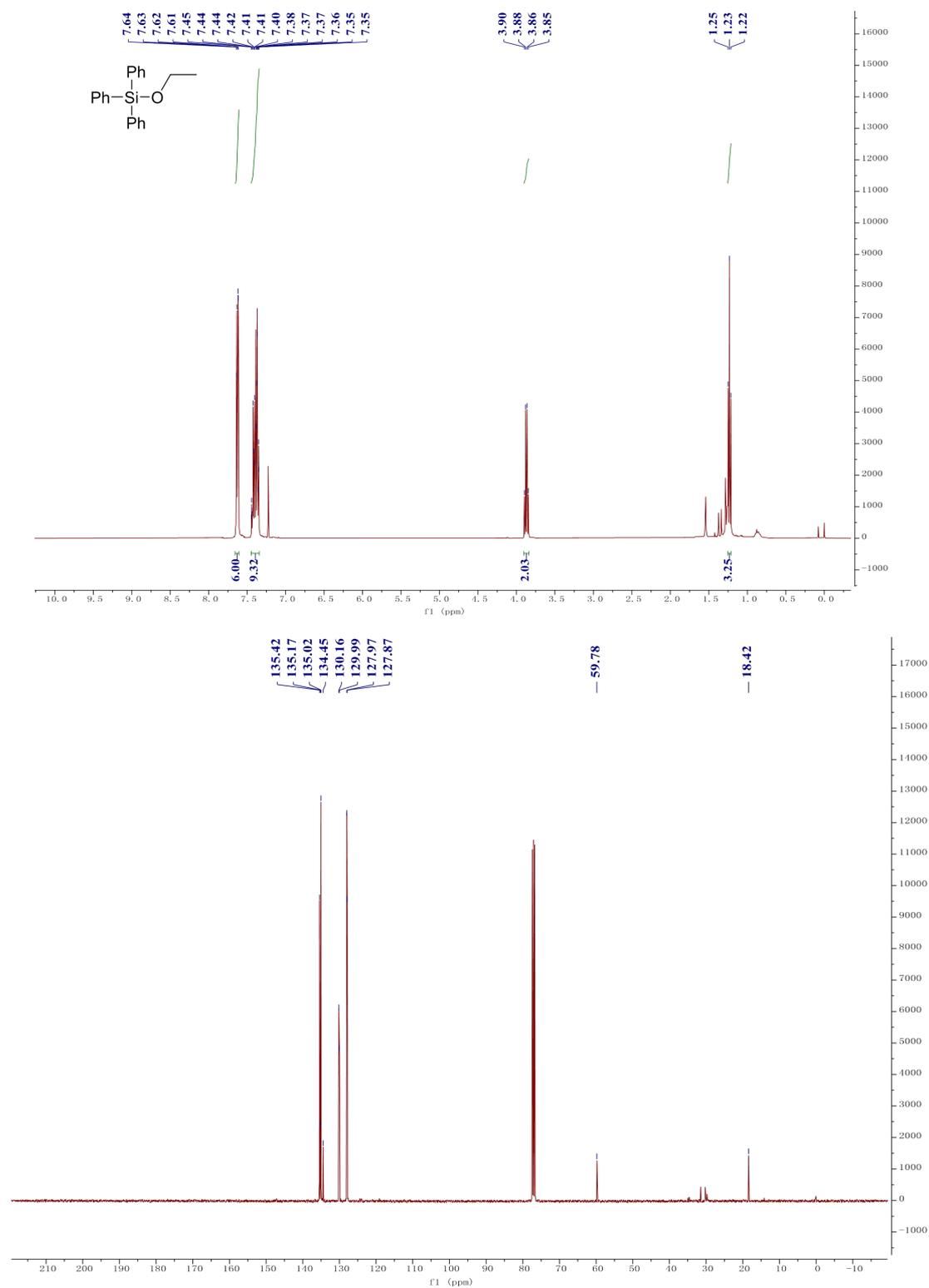
^{31}P NMR (400 MHz, CDCl_3) spectrum of product 2s



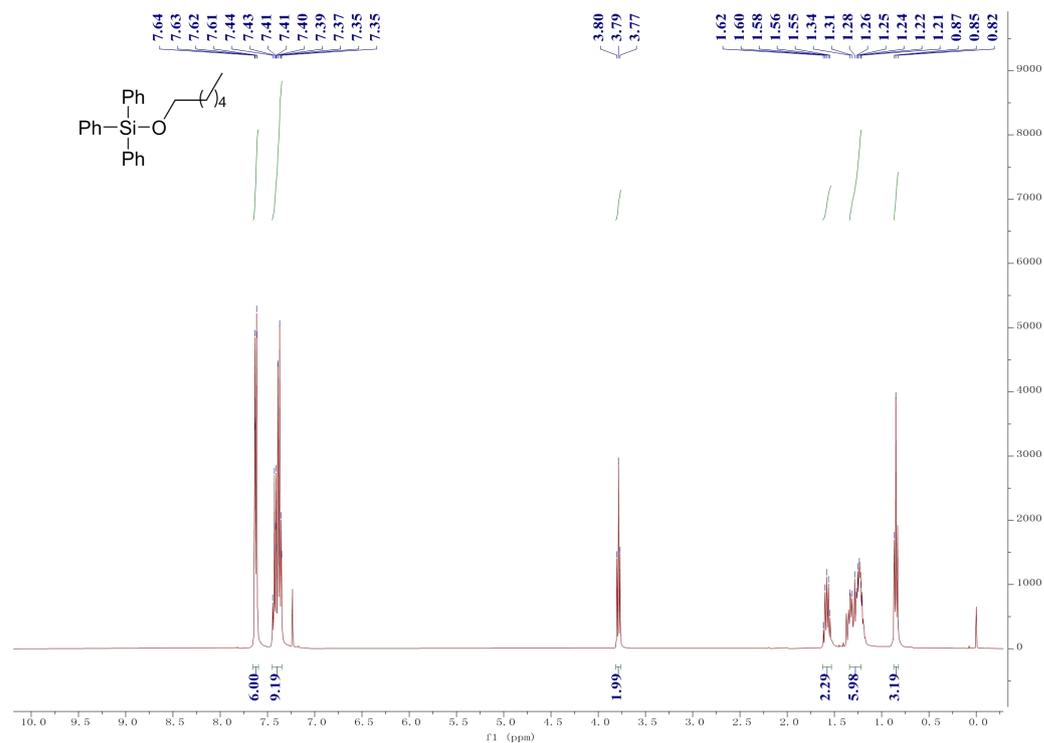
^1H NMR (400 MHz, CDCl_3) spectrum of product 3a



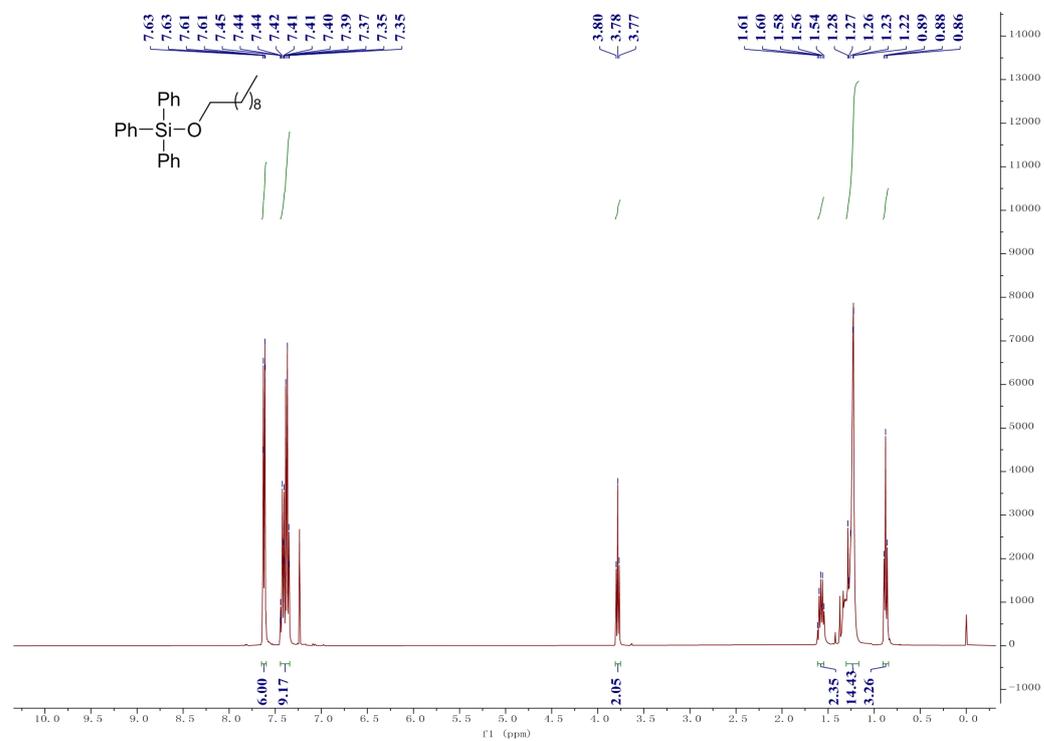
^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3) spectrum of product 3b

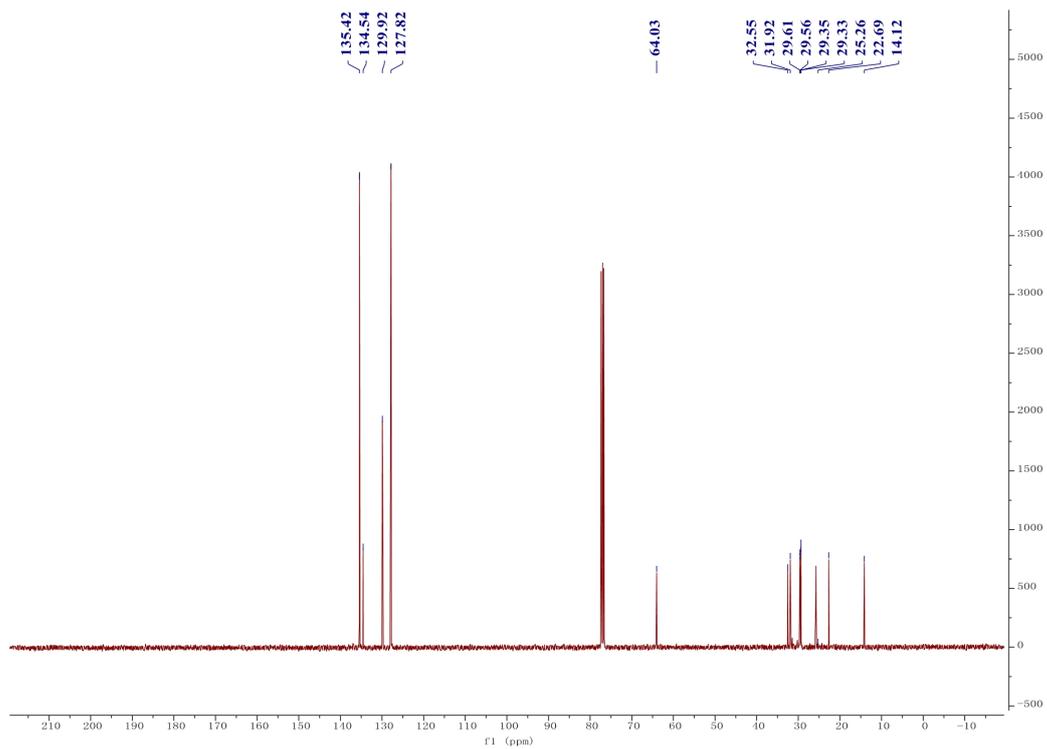


^1H NMR (400 MHz, CDCl_3) spectrum of product 3c

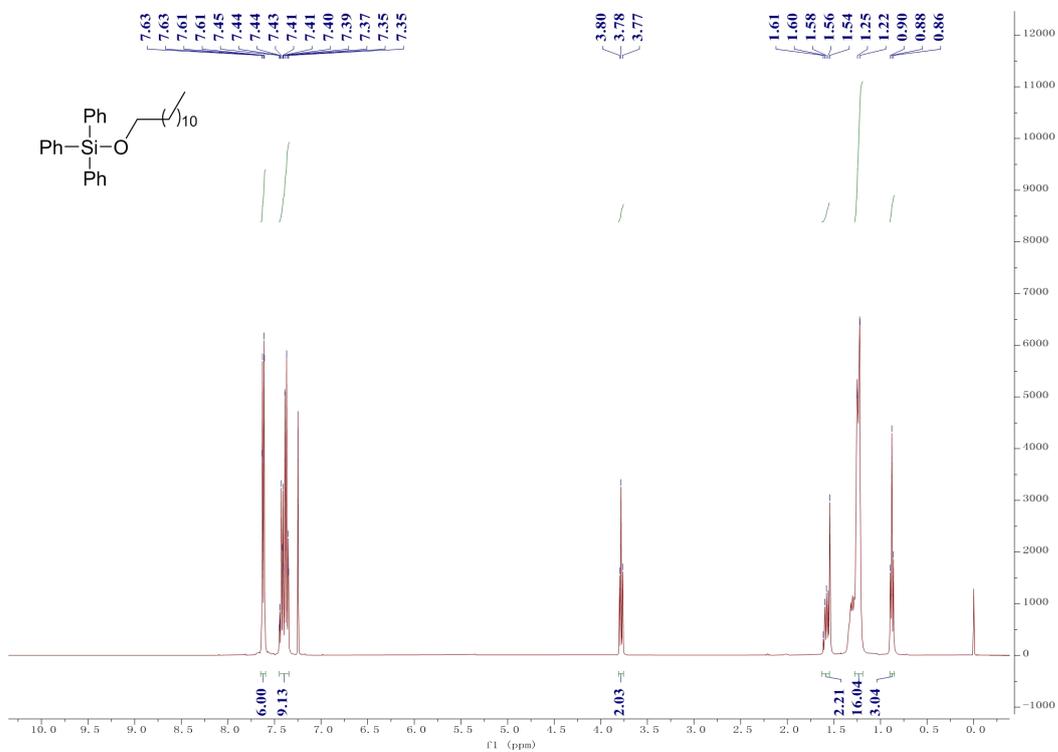


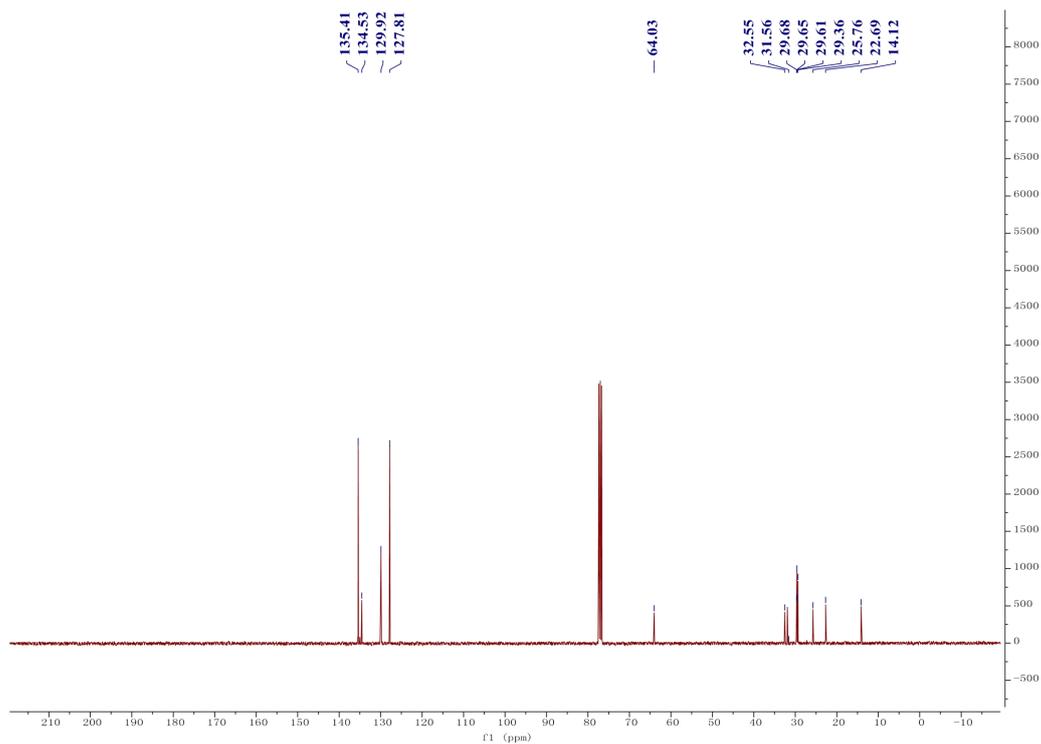
^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3) spectrum of product 3d



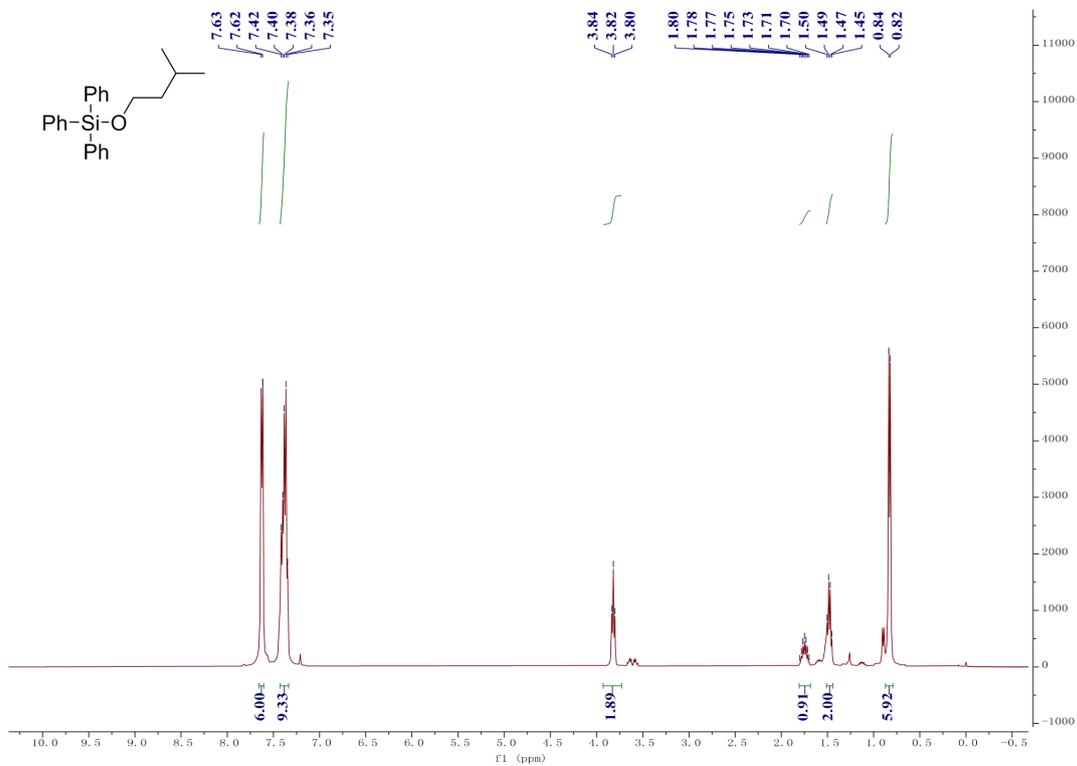


¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) spectrum of product 3e

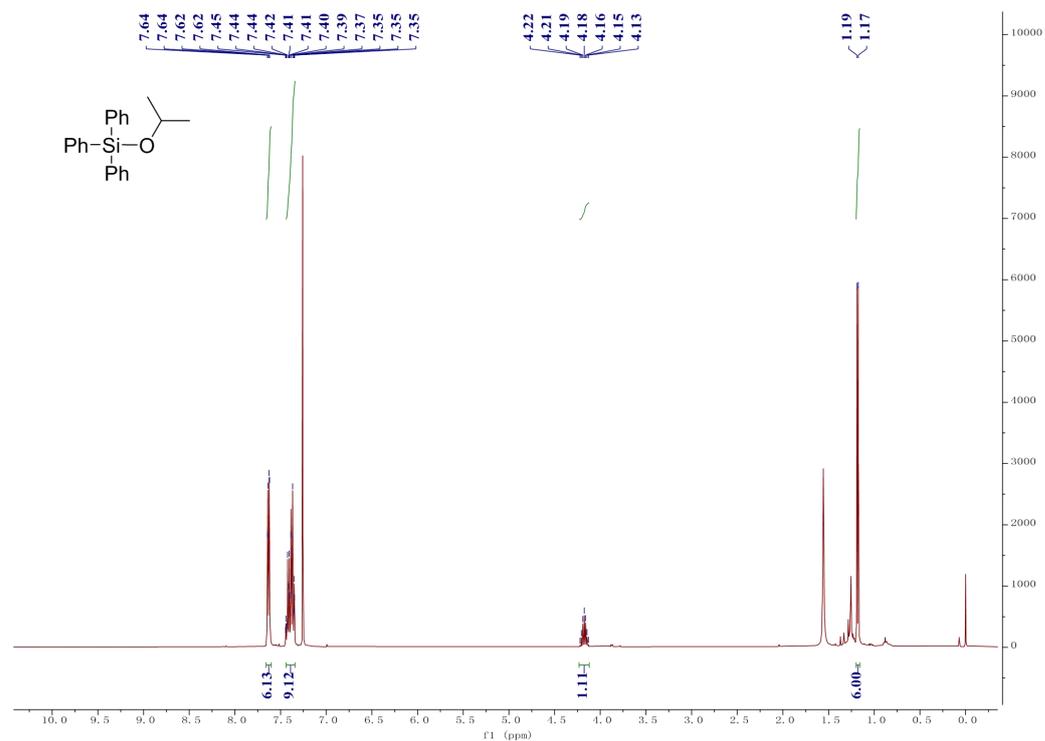




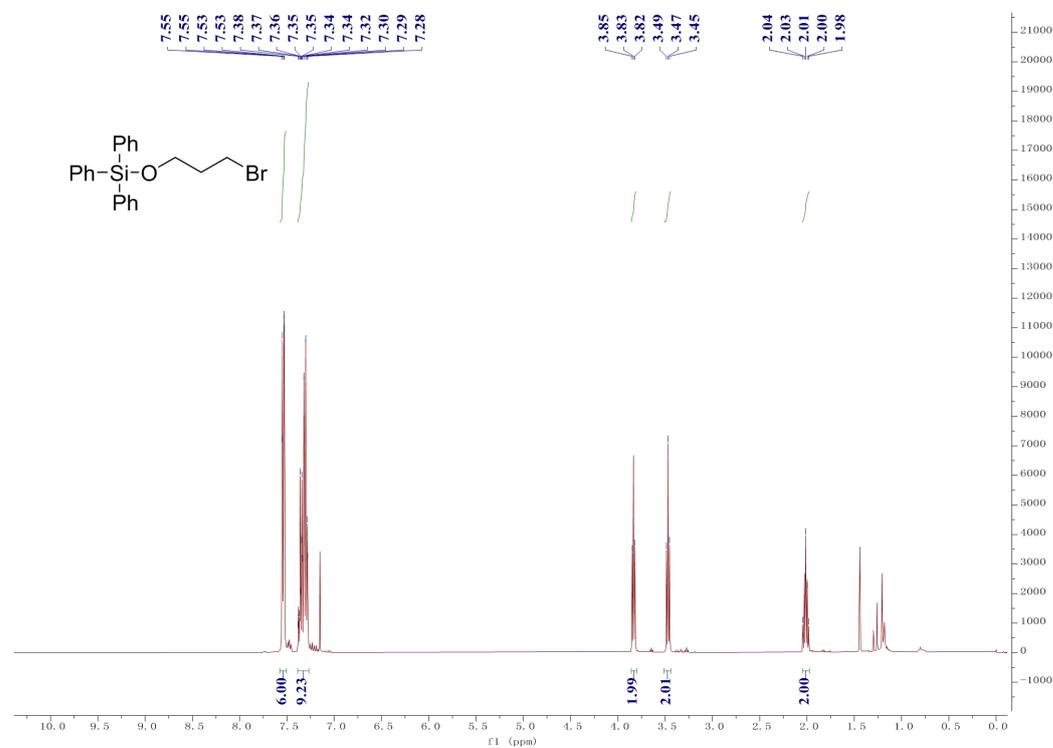
¹H NMR (400 MHz, CDCl₃) spectrum of product 3f

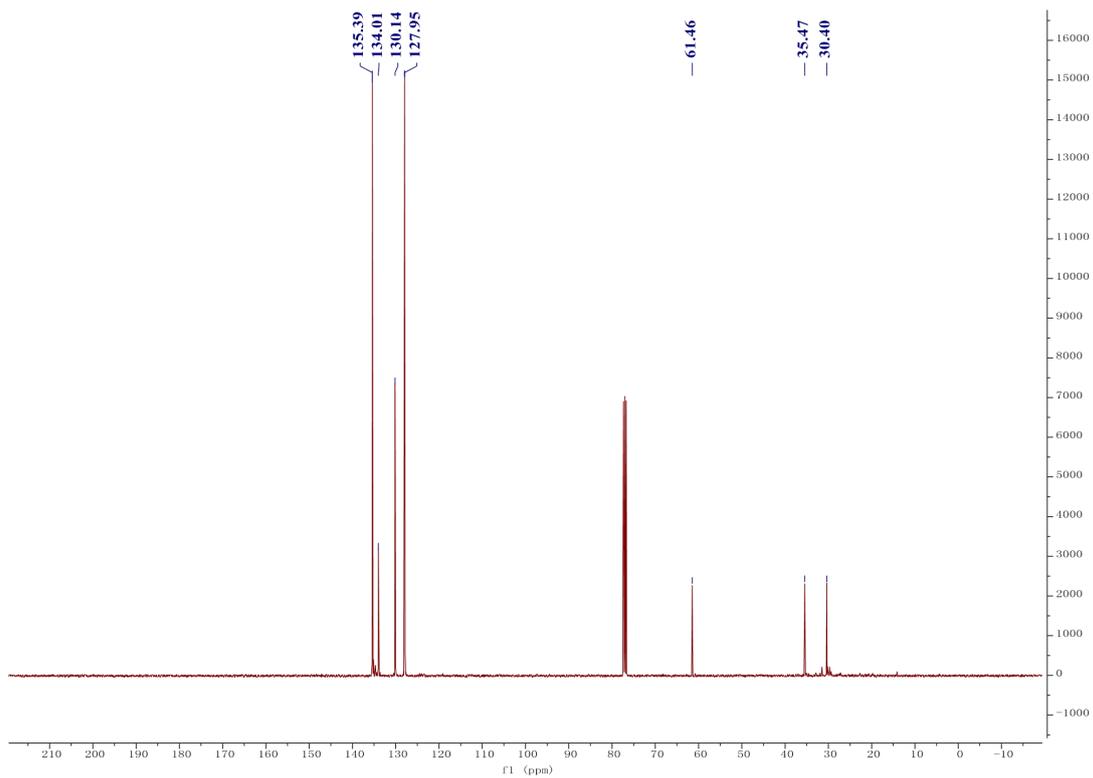


¹H NMR (400 MHz, CDCl₃) spectrum of product 3g

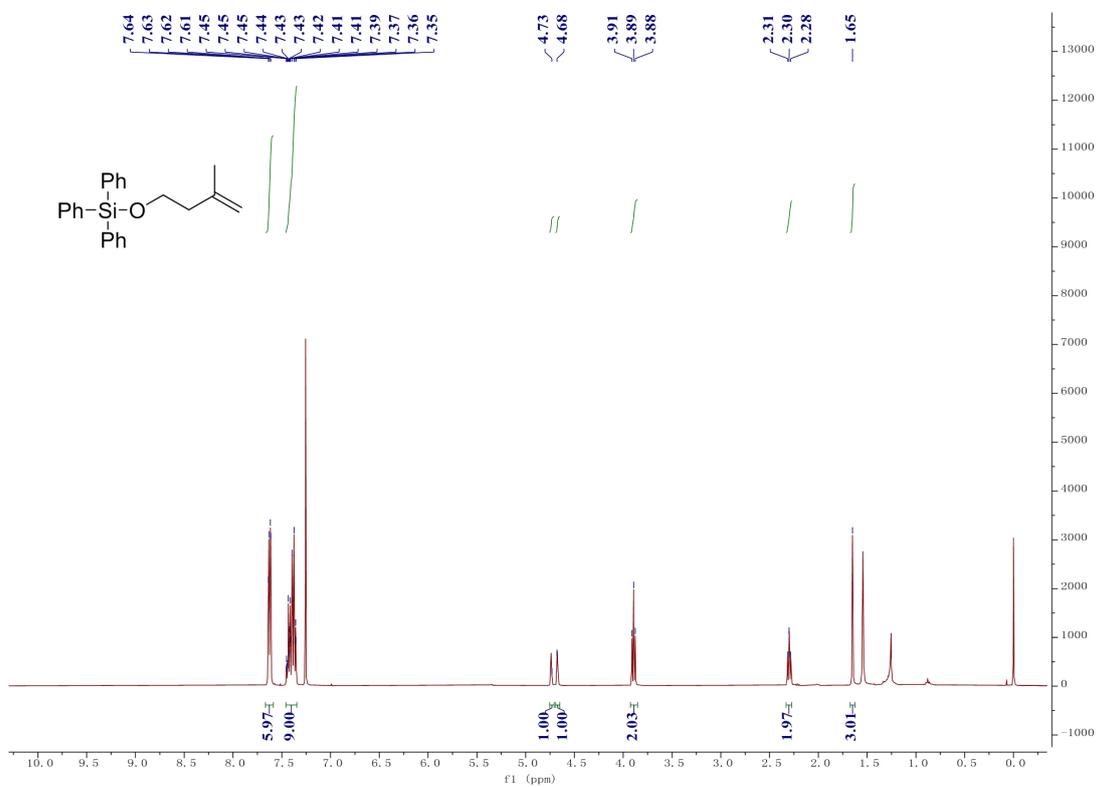


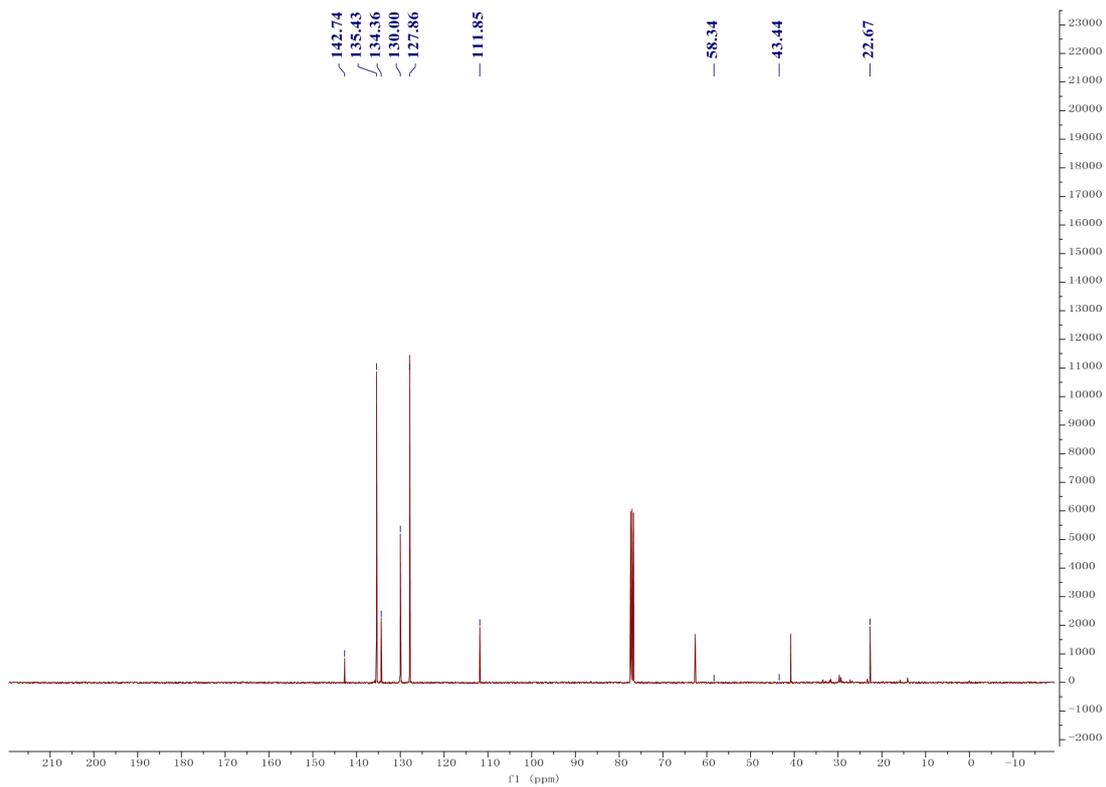
¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) spectrum of product 3h



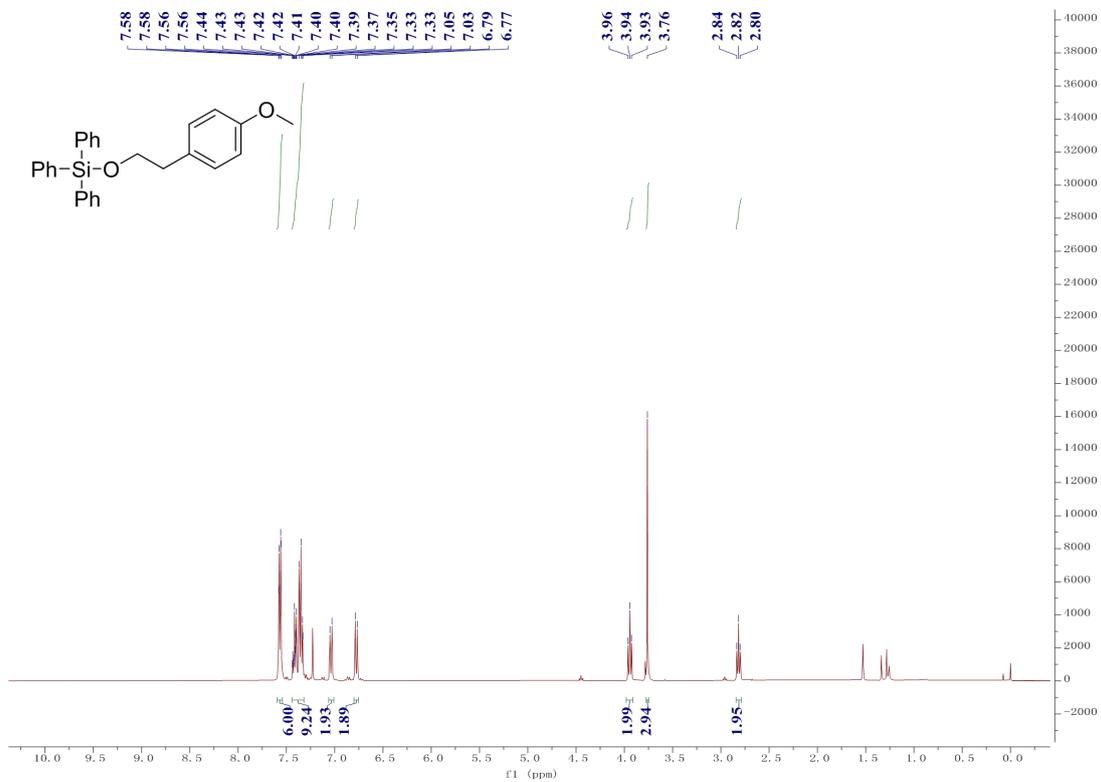


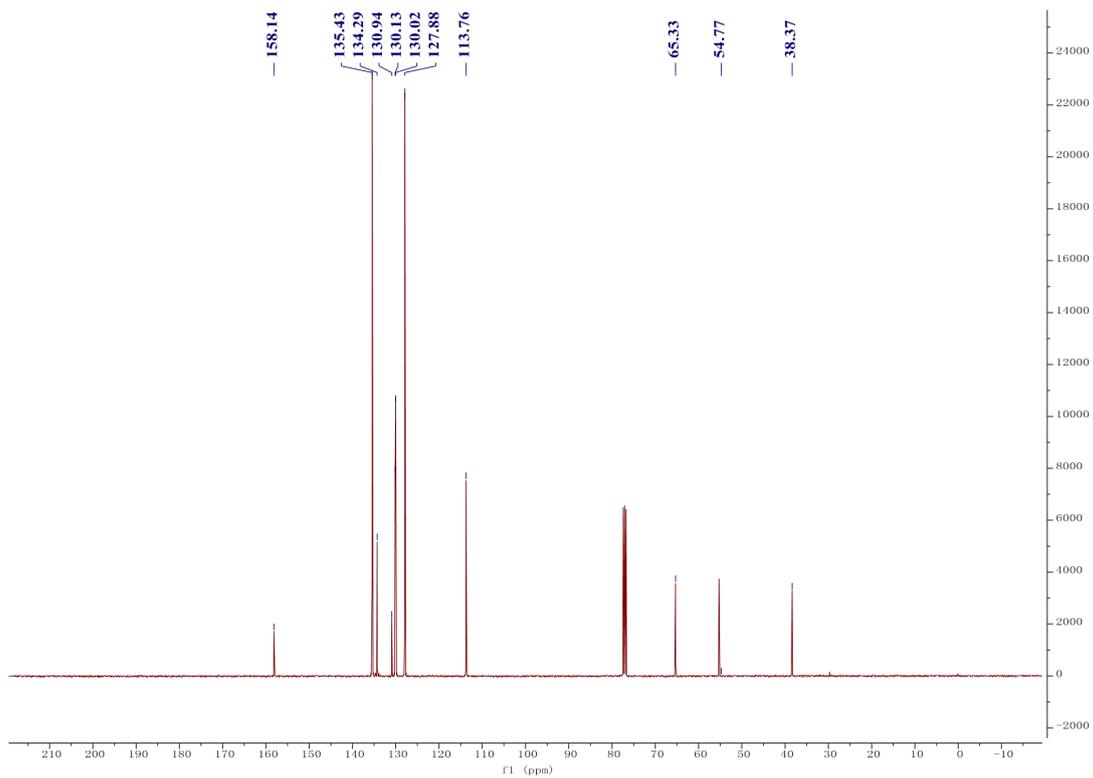
¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) spectrum of product 3i



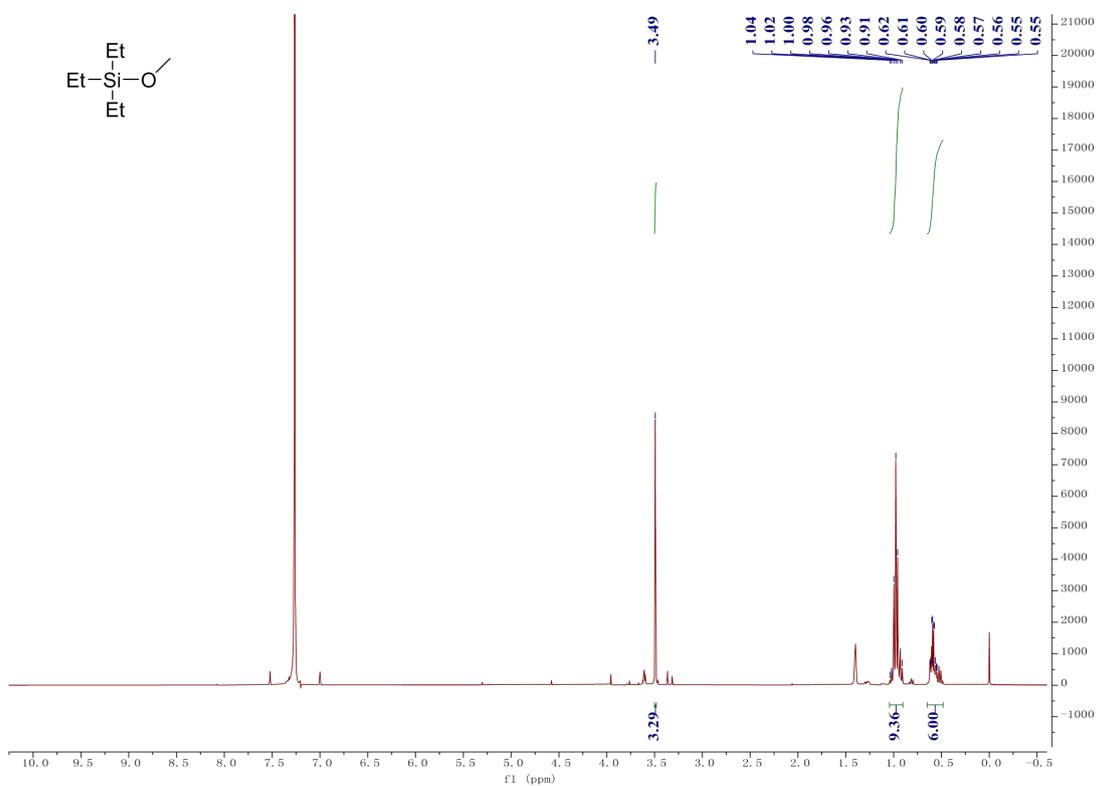


^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3) spectrum of product 3j

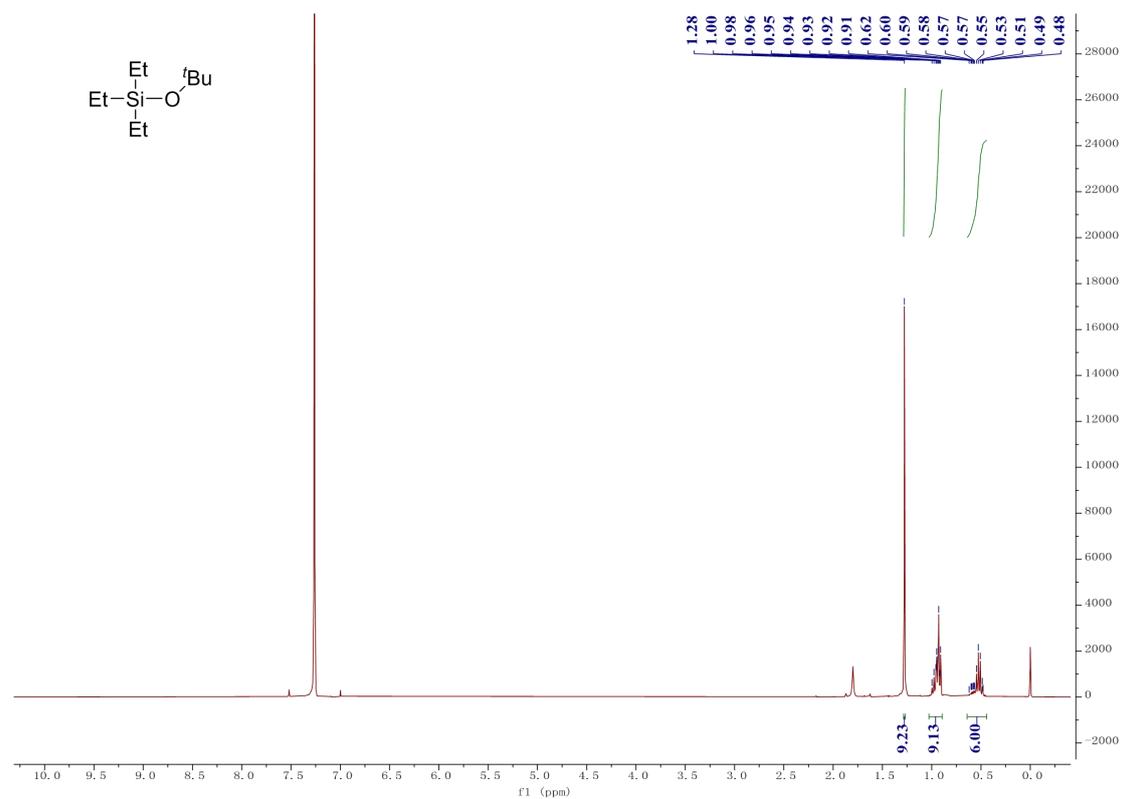




^1H NMR (400 MHz, CDCl_3) spectrum of product 3k



¹H NMR (400 MHz, CDCl₃) spectrum of product 3I



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