Electronic Supplementary Material (ESI) for ChemComm.


Supporting Information

# Hydrogenation of Silyl Formate: Sustainable Production of Silanol and Methanol from Silane and Carbon Dioxide

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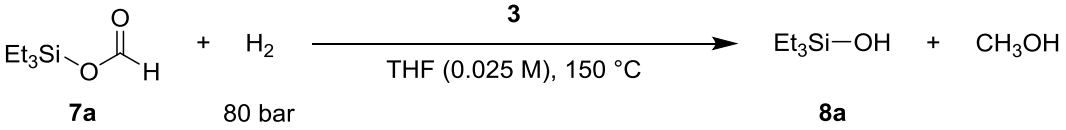
## 1. General Experimental Details

Unless otherwise stated, all reactions were carried out using a stainless-steel autoclave or in an argon-filled glove box. All anhydrous solvents were purchased from Aldrich and used without further purification. NMR spectroscopy experiments were conducted with a Varian 400 and 500 MHz or a Bruker 300 MHz system. NMR spectra were processed with ACD NMR Processor or MestReNova. Chemical shifts are reported in ppm and referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for $^1H$, 77.16 ppm for $^{13}C$; $C_6H_6$ in $C_6D_6$: 7.16 ppm for $^1H$, 128.06 ppm for $^{13}C$; $CH_3CN$ in $CD_3CN$: 1.94 ppm for $^1H$). Coupling constants are reported in Hertz. GC analyses were carried out with a 7980A GC system from Agilent Technologies, equipped with a DB-624UI column and FID detector, using *p*-xylene as an internal standard. Analytical TLC was performed on a Merck 60 F254 silica gel plate (0.25mm thickness). Column chromatography was performed on Merck 60 silica gel (230–400 mesh). Silyl formates were prepared in accordance with a literature procedure.[1-2] All starting materials and reagents were purchased from Acros, Aldrich, Alfa Aesar, TCI, and Strem Chemical Inc., and used without further purification unless otherwise stated. High-resolution mass spectrometry (HRMS) analysis was performed at Korea Basic Science Institute Daegu Center using EI method.

## 2. Turnover Number (TON) Test

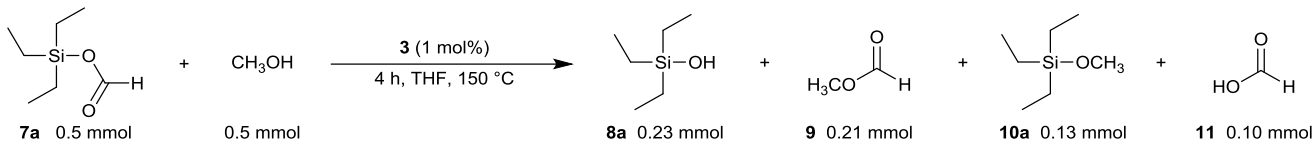
**Table S1**. Turnover number (TON) test with decreased loading of **3**.[a]




| entry | **3** (ppm) | Time (h) | yield[b] | | TON | |
|---|---|---|---|---|---|---|
| | | | **8a** | $CH_3OH$ | **8a** | $CH_3OH$ |
| 1 | 1000 | 12 | 92 | 96 | 920 | 960 |
| 2 | 500 | 24 | 84 | 95 | 1680 | 1900 |
| 3 | 500 | 48 | 99 | 37 | 1980 | 740 |
| 4 | 500 | 72 | 47 | 6 | 940 | 120 |
| 5 | 200 | 24 | 50 | 18 | 2500 | 900 |
| 6 | 200 | 48 | 40 | 12 | 2000 | 600 |

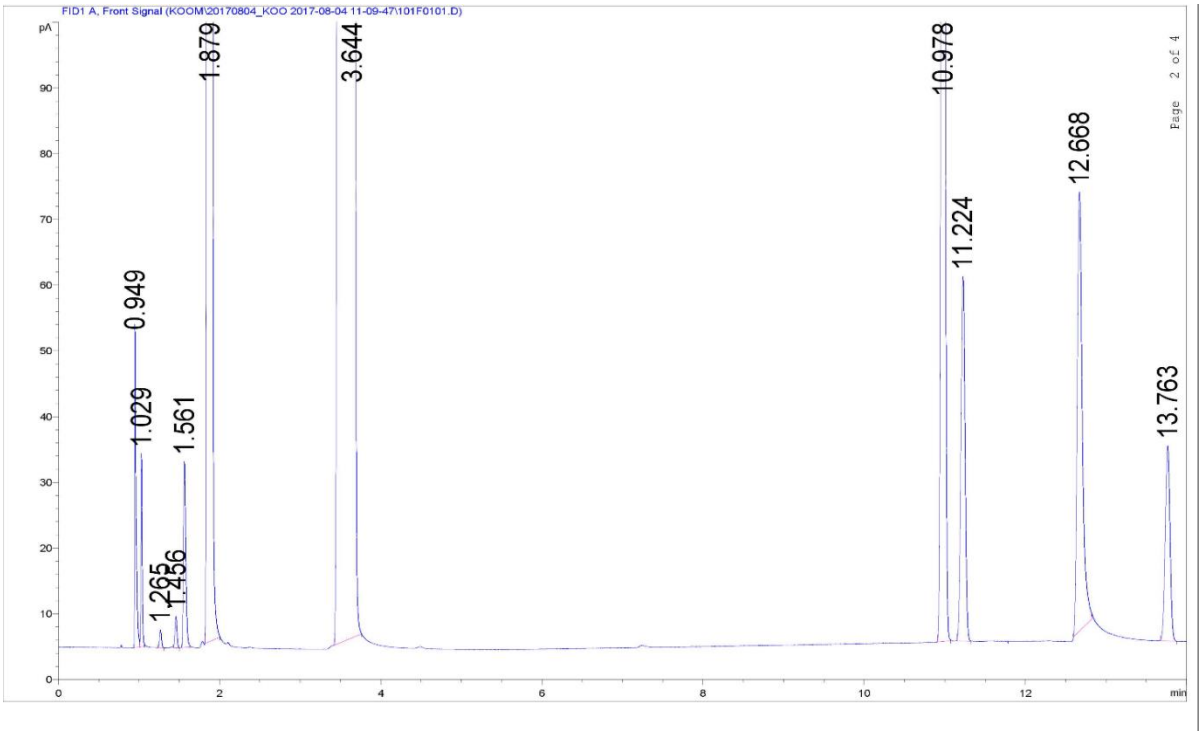
[a] Reaction conditions: **7a** (0.5 mmol, 1.0 equiv.), THF (20 mL), 150 °C, $H_2$ (80 bar). [b] Yields were determined by GC analysis using *p*-xylene as an internal standard.

## 3. Stoichiometric Reaction to Investigate the Mechanism




A 50 mL Schlenk flask containing a magnetic stirring bar was charged with **3** (1 mol%, 2.93 mg, 0.005 mmol) under Ar flow. Triethylsilyl formate **7a** (1.0 equiv, 0.5 mmol) was then added to the Schlenk flask as a solution in tetrahydrofuran (0.025 M, 20.0 mL), followed by the methanol (1.0 equiv, 0.5 mmol). The Schlenk flask was sealed, and heated to 150 °C for 4 h. Upon completion of the reaction, the mixture was cooled to 0 °C for 30 minutes. Triethyl silanol **8a**, methyl formate **9**, and triethylmethoxy silane **10a** were analyzed by GC using *p*-xylene (2.0 equiv, 123.3 µL, 1.0 mmol) as an internal standard. Formic acid **11** could not be detected by GC. Thus, qualitative and quantitative analyses of formic acid were performed by $^{1}$H NMR using *p*-xylene (2.0 equiv, 123.3 µL, 1.0 mmol) as an internal standard.

**Table S2**. Quntitataive analysis by GC




| retention time (min) | compound | area | yield (mmol) |
|---|---|---|---|
| 1.029 | methyl formate **9** | 37.5 | 0.210 |
| 10.978 | *p*-xylene | 936.4 | (internal standard) |
| 11.224 | triethylmethoxy silane **10a** | 195.6 | 0.126 |
| 12.668 | triethyl silanol **8a** | 294.4 | 0.231 |

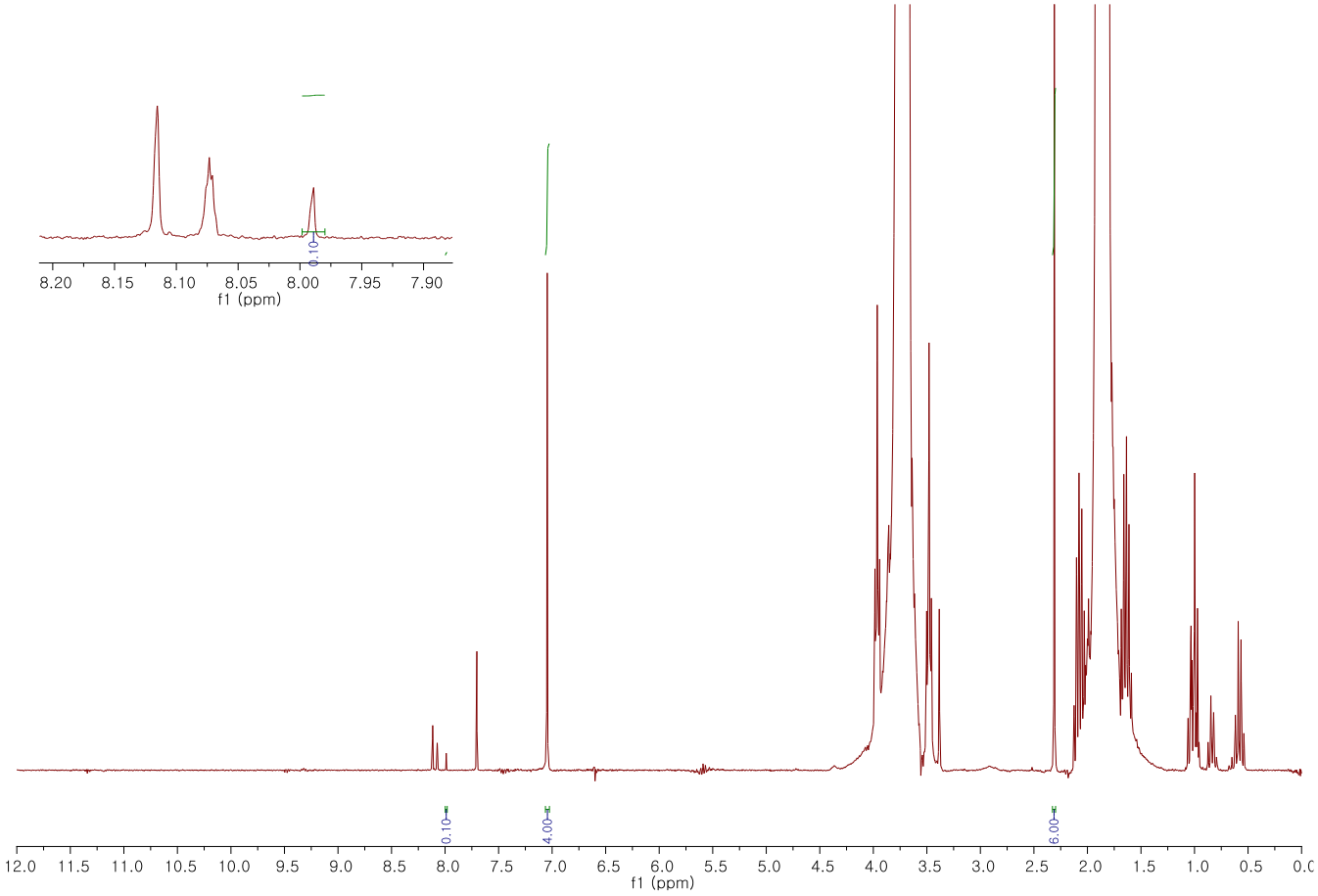
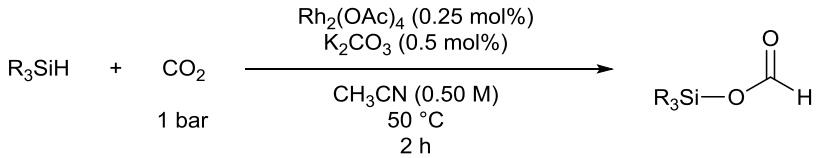



**Figure S1**. Formic acid **11** analysis by $^{1}$H NMR

## 4. Synthesis of Silyl Formates

General Procedure A: **7a**, **7c–7f**, **7h** and **7i**

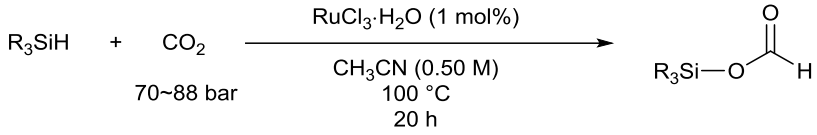



**Scheme S1**

The silyl formates were prepared according to a literature procedure.[1] $K_2CO_3$ was dried at 120 °C in an oven overnight. Inside a glove box, a 50 mL Schlenk flask containing a magnetic stirring bar was charged with $K_2CO_3$ (0.5 mol%, 3.5 mg, 0.025 mmol) and $Rh_2(OAc)_4$ (0.25 mol%, 5.5 mg, 0.0125 mmol). Hydrosilane (5.0 mmol) was then added to the Schlenk flask as a solution in acetonitrile (0.50 M, 10.0 mL). The Schlenk flask was sealed, replaced with 1 bar of $CO_2$, and heated to 50 °C for 2 h. Upon completion of the reaction, the mixture was cooled to room temperature. The solution was filtered by syringe filter, and the solvent was removed using a rotary evaporator. The product was purified by vacuum distillation. The purity of the product was determined by $^{1}$H NMR analysis. Silyl formates need

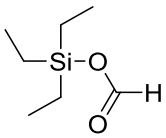
to be purified by vacuum distillation,[3-5] due to rapid hydrolysis by water in air.[6] The observed impurity was only siloxane (checked by GC-MS and $^1$H NMR). The purity of the reported compounds could not be improved even with multiple times (five or more) of vacuum distillations.

General Procedure B: **7b** and **7g**



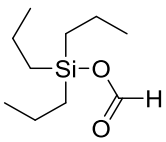

**Scheme S2**

The silyl formates were prepared according to a literature procedure.[2] Inside a glove box, a 67 mL stainless-steel autoclave containing a magnetic stirring bar was charged with $RuCl_3 \cdot H_2O$ (1 mol%, 10.4 mg, 0.05 mmol). Hydrosilane (5.0 mmol) was then added to the reactor as a solution in acetonitrile (0.50 M, 10.0 mL). The reactor was sealed, pressurized with 70~88 bar of $CO_2$, and heated to 100 °C for 20 h. Upon completion of the reaction, the mixture was cooled to room temperature. Unreacted $CO_2$ was carefully released in a fume hood. The solution was filtered by a syringe filter, and all the solvent was removed using a rotary evaporator. The product was purified by vacuum distillation. The purity of the product was determined by $^1$H NMR analysis. Silyl formates need to be purified by vacuum distillation,[3-5] due to rapid hydrolysis by water in air.[6] The observed impurity was only siloxane (checked by GC-MS and $^1$H NMR). The purity of the reported compounds could not be improved even with multiple times (five or more) of vacuum distillations.



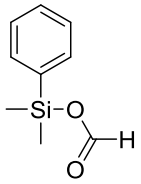

**Triethylsilyl formate (7a)**

Colorless liquid (99% purity was calculated by $^1$H NMR). Reaction was conducted at 70 °C for 12 h. $^1$H NMR (300 MHz, $C_6D_6$) δ = 7.74 (s, 1H), 0.91 (t, *J*=7.8, 9H), 0.68 (q, *J*=7.8, 6H). The identity of the compound was confirmed by comparison with reported data.[7]



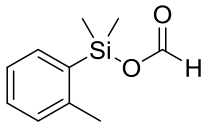

**Tri-n-propylsilyl formate (7b)**

Redish brown liquid (90% purity was calculated by $^1$H NMR). $^1$H NMR (300 MHz, $C_6D_6$) δ = 7.77 (s, 1H), 1.35 (dq, *J*=15.2, 7.7, 6H), 0.93 (t, *J*=7.2, 9H), 0.72 (t, 6H). $^{13}$C NMR (75 MHz, $C_6D_6$) δ = 160.41, 18.28, 16.80, 16.47. HRMS (EI): m/z $[M]^+$ calcd for $C_{10}H_{22}O_2Si$: 202.1384, found: 202.1386.



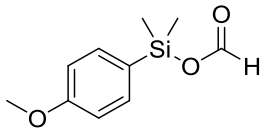

**Dimethylphenylsilyl formate (7c)**

Colorless liquid (94% purity was calculated by $^1$H NMR). $^1$H NMR (300 MHz, $C_6D_6$) δ = 7.71 (s, 1H), 7.52 – 7.54 (m, 2H), 7.20 – 7.18 (m, 3H), 0.43 (s, 6H). The identity of the compound was confirmed by comparison with reported data.[7]



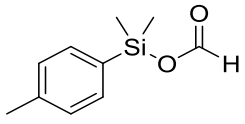

**Dimethyl(2-methylphenyl)silyl formate (7d)**

Colorless liquid (90% purity was calculated by $^1$H NMR). $^1$H NMR (300 MHz, $C_6D_6$) δ = 7.72 (s, 1H), 7.50 (dd, *J*=7.3, 1.5, 1H), 7.13 (d, *J*=1.6, 1H), 7.06 (td, *J*=7.4, 0.7, 1H), 7.00 – 6.97 (m, 1H), 2.26 (s, 3H), 0.46 (s, 6H). $^{13}$C NMR (75 MHz, $C_6D_6$) δ = 160.21, 143.41, 134.68, 134.02, 130.74, 130.38, 125.48, 22.74, -0.33. HRMS (EI): m/z $[M]^+$ calcd for $C_{10}H_{14}O_2Si$: 194.0758, found: 194.0760.



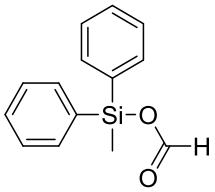

**Dimethyl(4-methoxyphenyl)silyl formate (7e)**

Yellow liquid (90% purity was calculated by $^1$H NMR). $^1$H NMR (300 MHz, $CD_3CN$) δ = 8.10 (s, 1H), 7.61 – 7.56 (m, 2H), 7.00 – 6.96 (m, 2H), 3.81 (s, 3H), 0.54 (s, 6H). The identity of the compound was confirmed by comparison with reported data.[1]



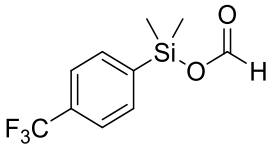

**Dimethyl(4-methylphenyl)silyl formate (7f)**

Colorless liquid (90% purity was calculated by $^1$H NMR). $^1$H NMR (300 MHz, $C_6D_6$) δ = 7.71 (s, 1H), 7.51 (d, *J*=7.9, 2H), 7.04 (d, *J*=7.5, 2H), 2.09 (s, 3H), 0.45 (s, 6H). $^{13}$C NMR (75 MHz, $C_6D_6$) δ = 160.48, 140.42, 134.06, 131.86, 129.09, 21.49, -1.53. HRMS (EI): m/z $[M]^+$ calcd for $C_{10}H_{14}O_2Si$: 194.0758, found: 194.0765.



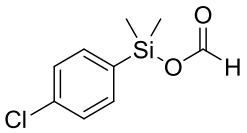
**Diphenylmethylsilyl formate (7g)**

Yellow liquid (94% purity was calculated by $^1$H NMR). $^1$H NMR (300 MHz, $CD_3CN$) δ = 8.22 (s, 1H), 7.66 – 7.63 (m, 4H), 7.49 – 7.40 (m, 6H), 0.87 (s, 3H). The identity of the compound was confirmed by comparison with reported data.[1]



**Dimethyl(4-trifluoromethylphenyl)silyl formate (7h)**

Colorless liquid (86% purity was calculated by $^1$H NMR). $^1$H NMR (300 MHz, $CD_3CN$) δ = 8.12 (s, 1H), 7.85 (d, *J*=8.2, 2H), 7.73 (d, *J*=8.1, 2H), 0.60 (s, 6H). The identity of the compound was confirmed by comparison with reported data.[1]



**Dimethyl(4-chlorophenyl)silyl formate (7i)**

Yellow liquid (86% purity was calculated by $^1$H NMR). $^1$H NMR (300 MHz, $CD_3CN$) δ = 8.10 (s, 1H), 7.66 – 7.62 (m, 2H), 7.46 – 7.42 (m, 2H), 0.56 (s, 6H). The identity of the compound was confirmed by comparison with reported data.[1]

## 5. GC-MS Spectra of Silyl Formates

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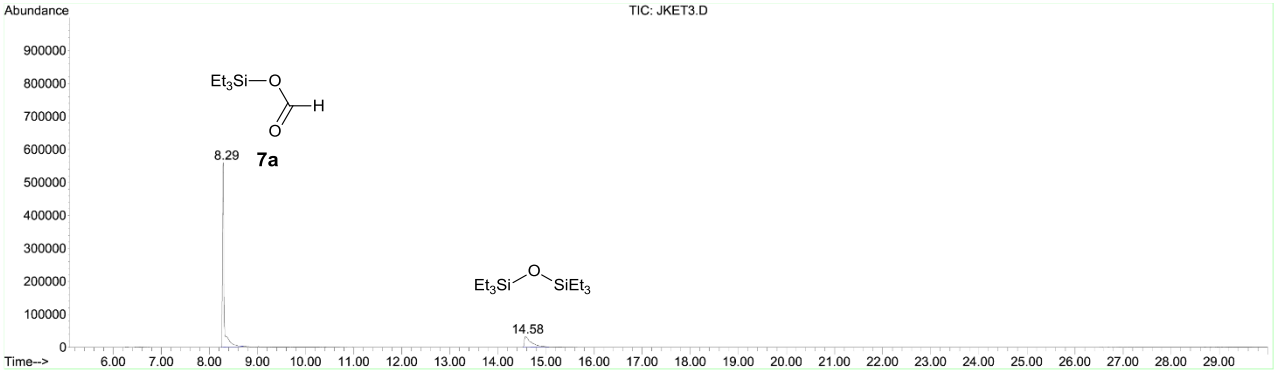


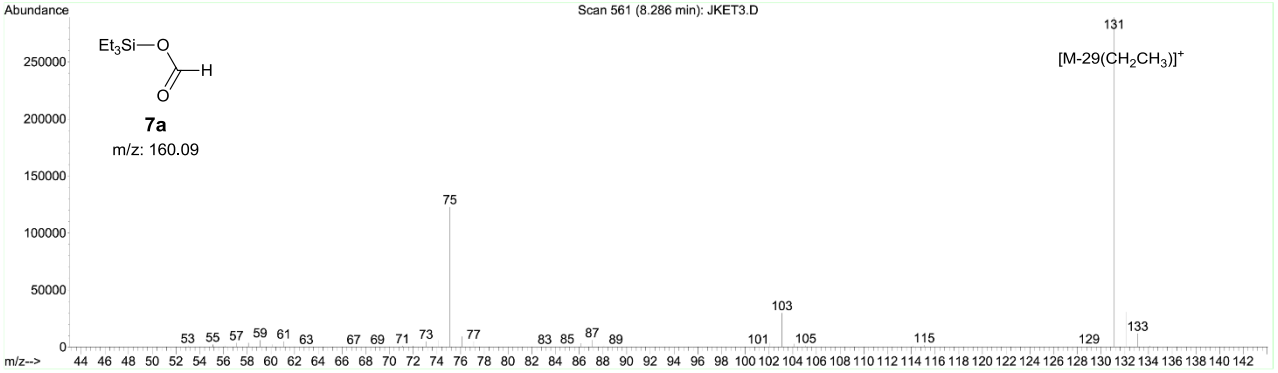


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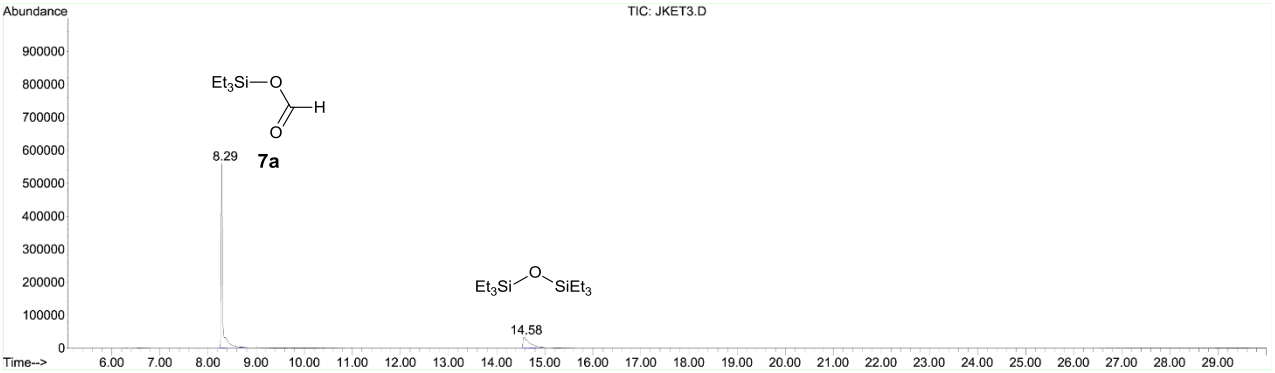


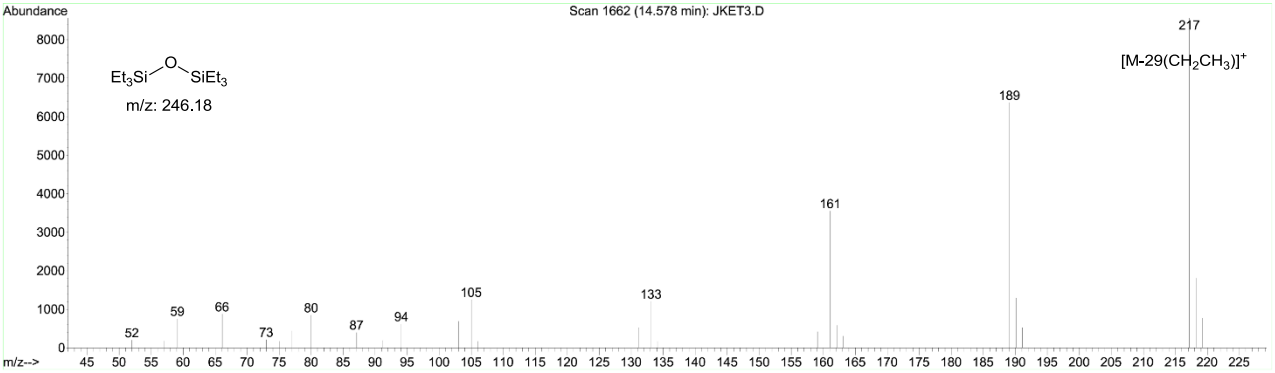

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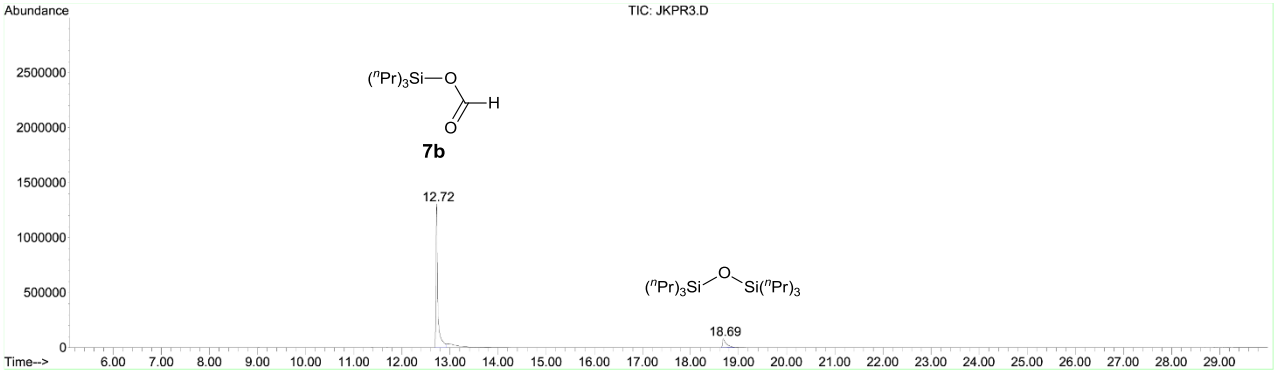


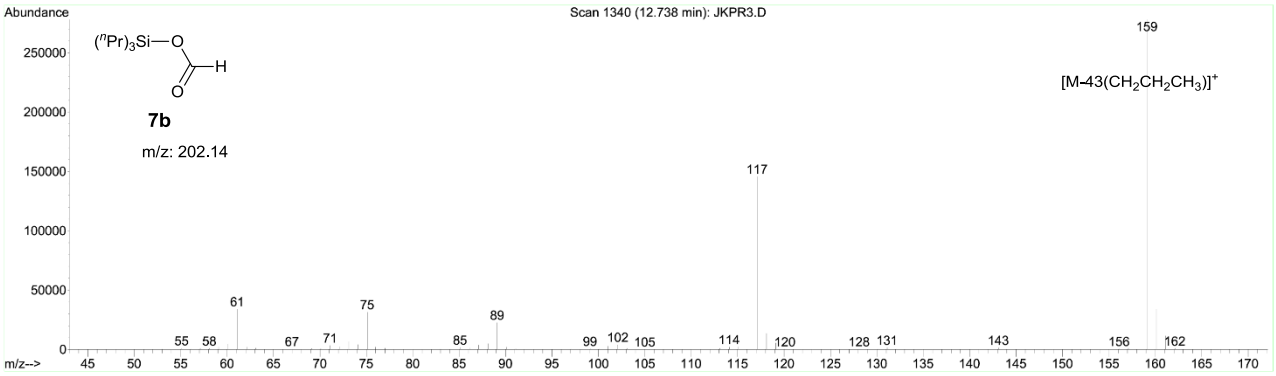



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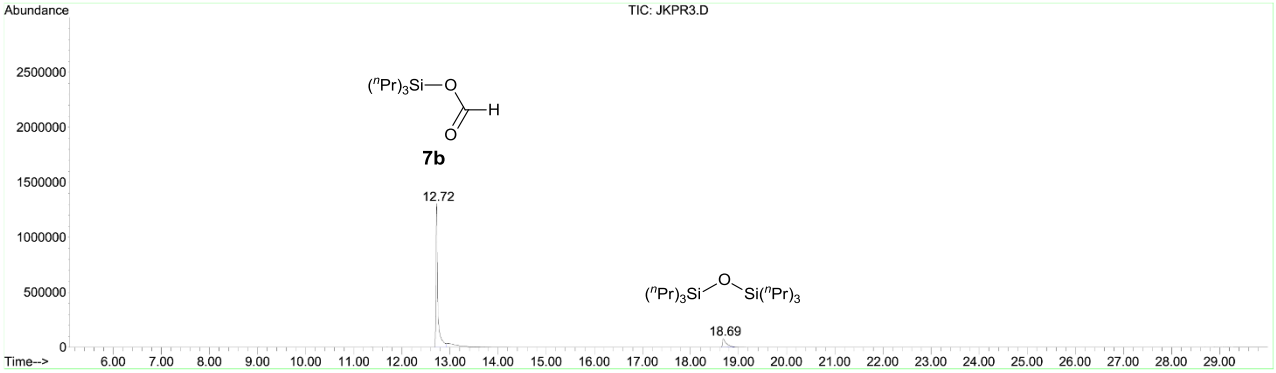


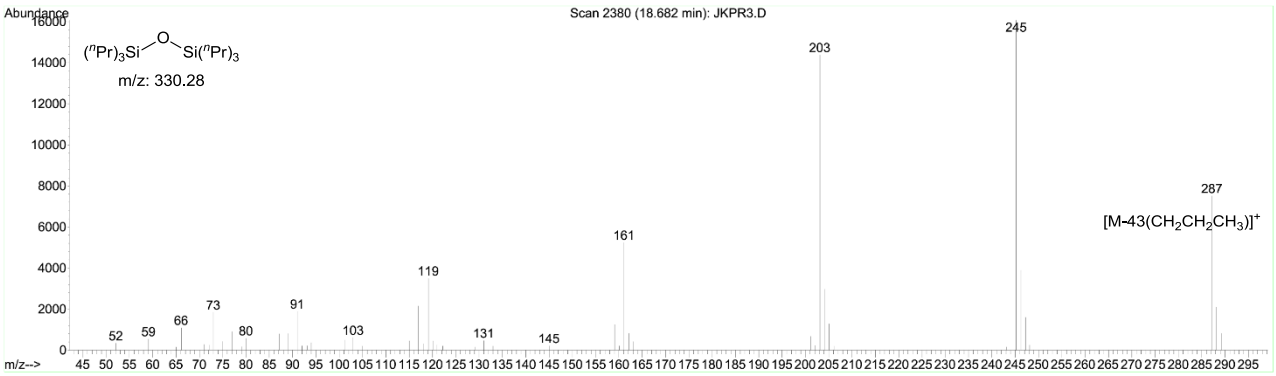

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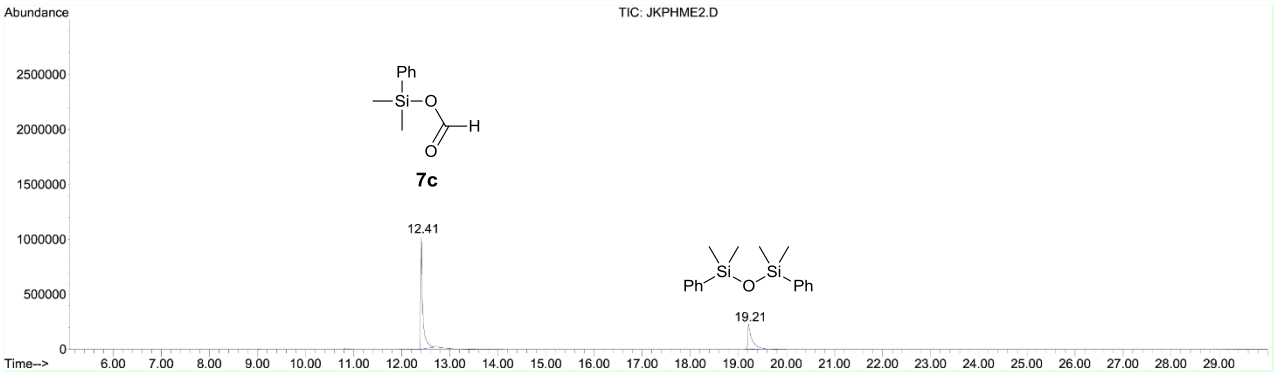


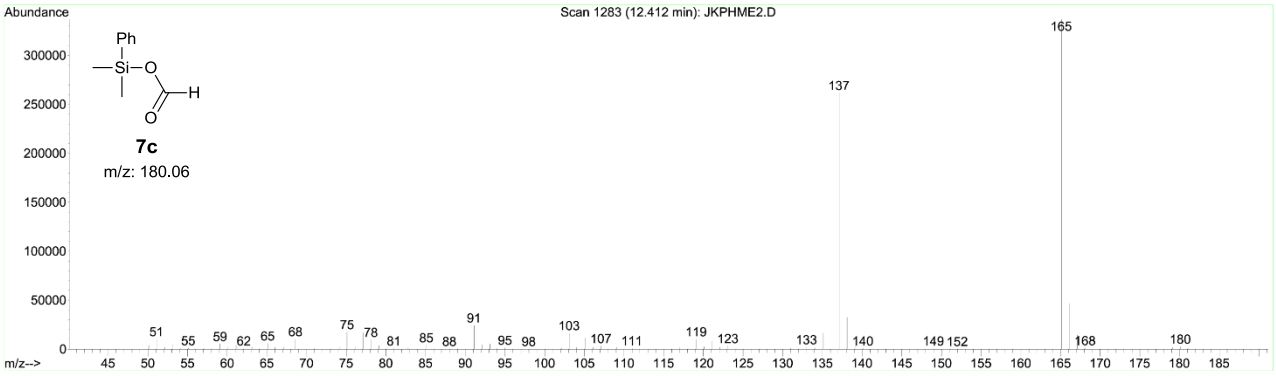



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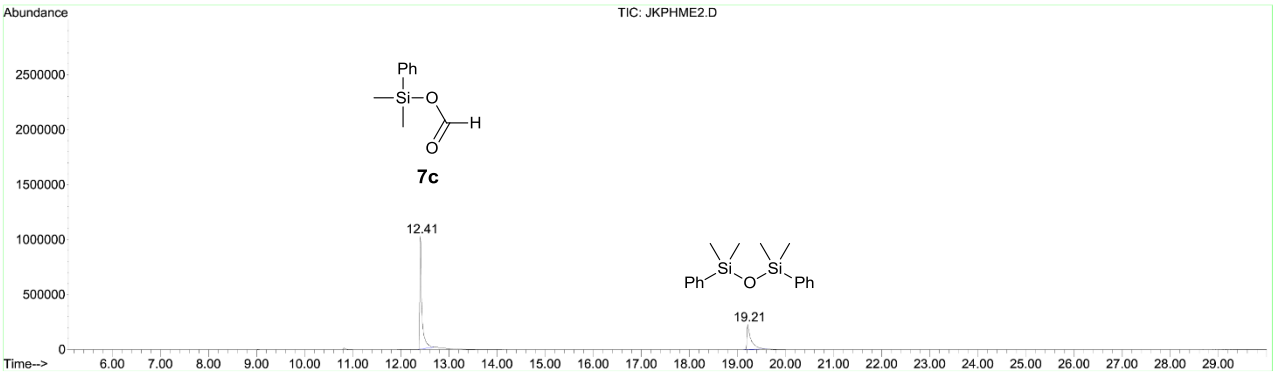


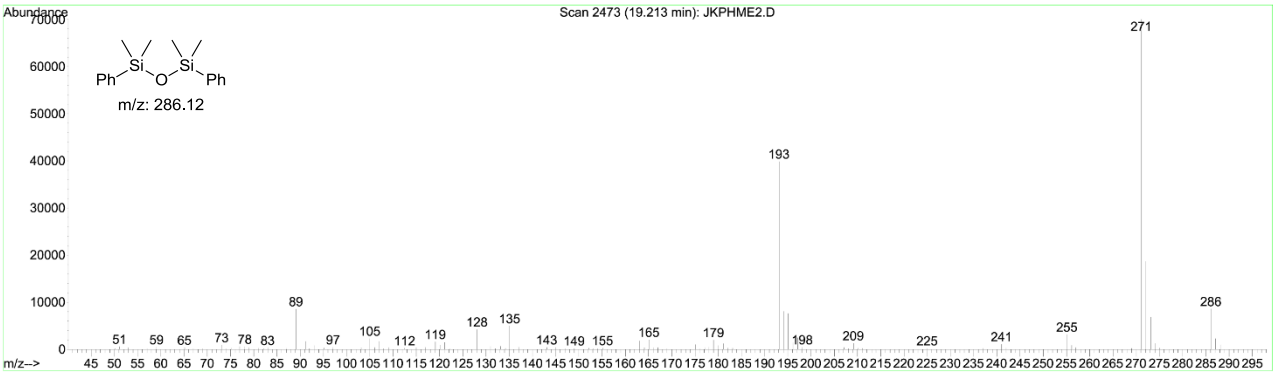

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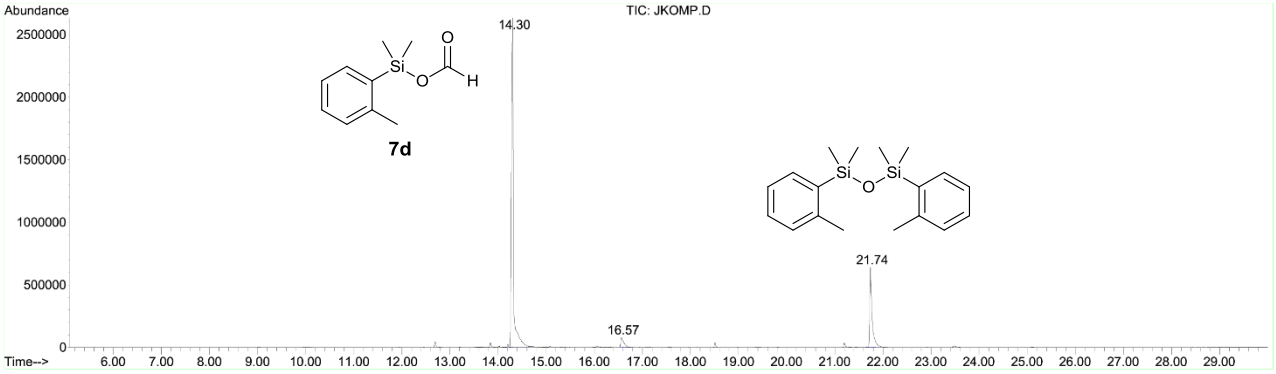


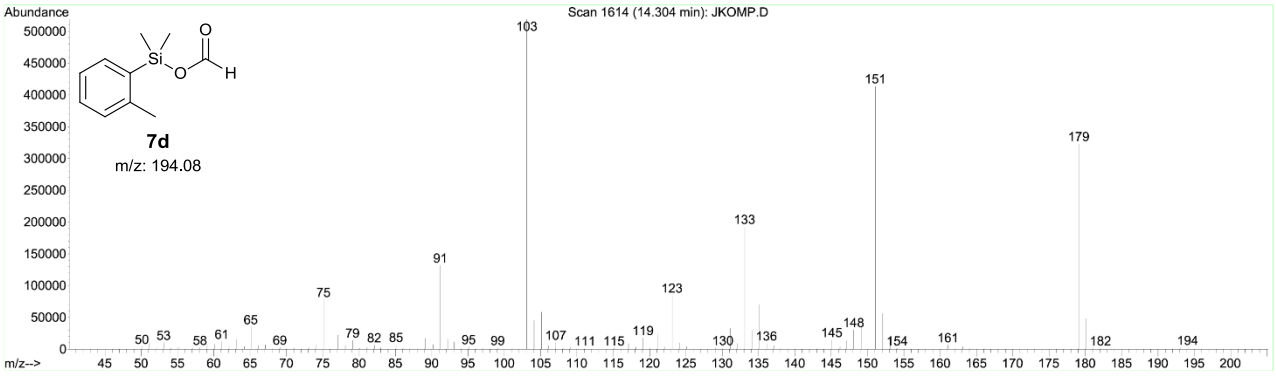



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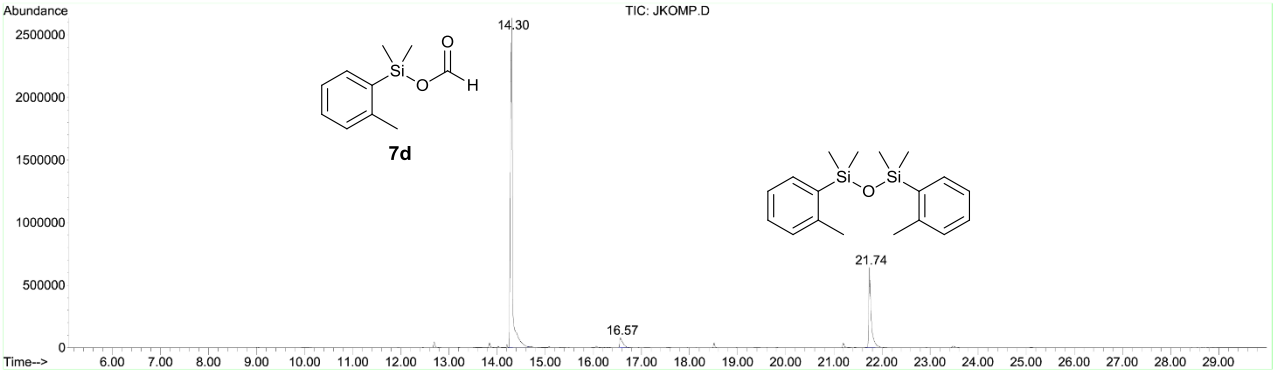


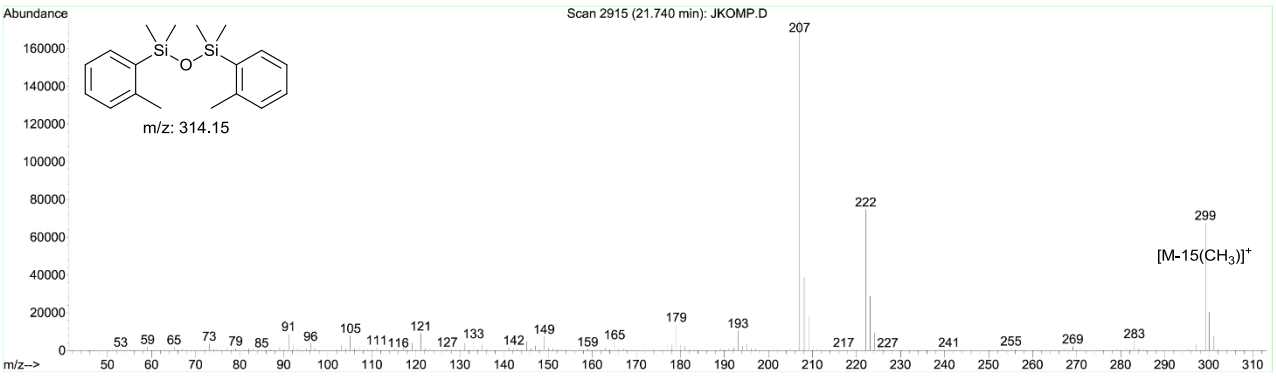

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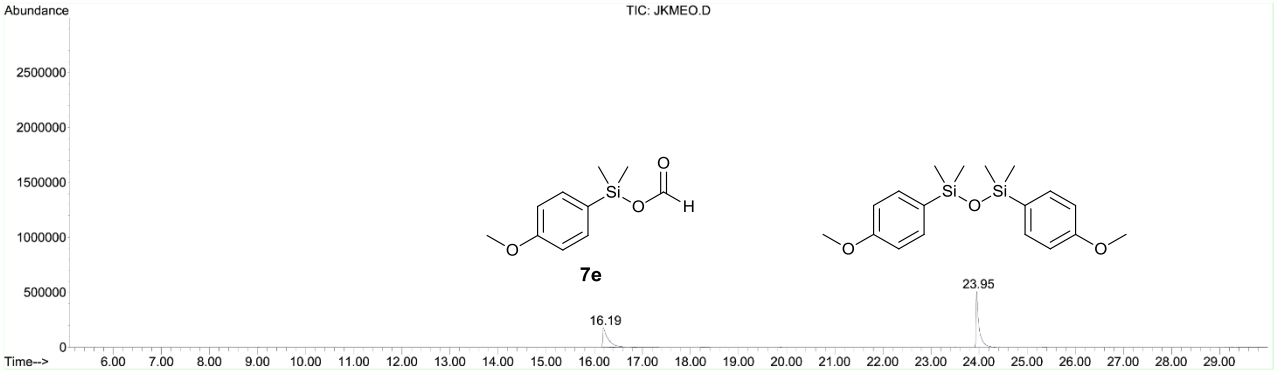


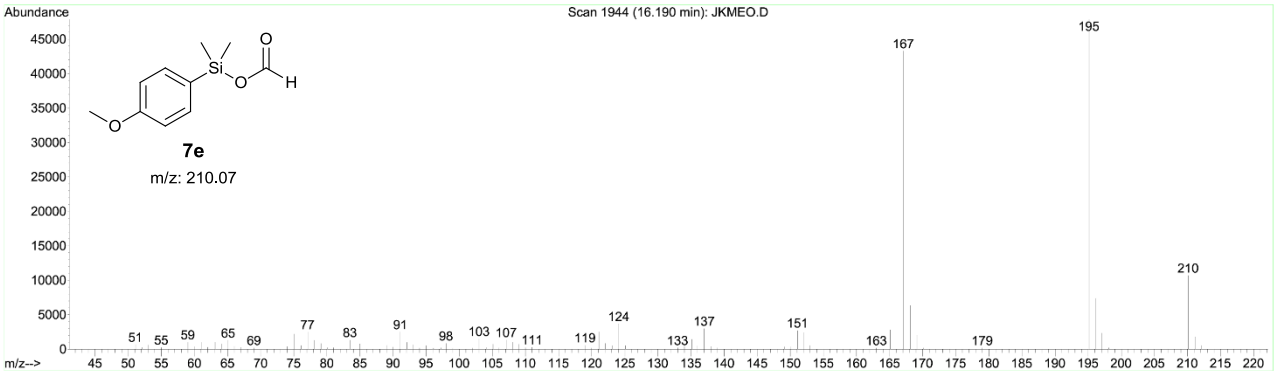



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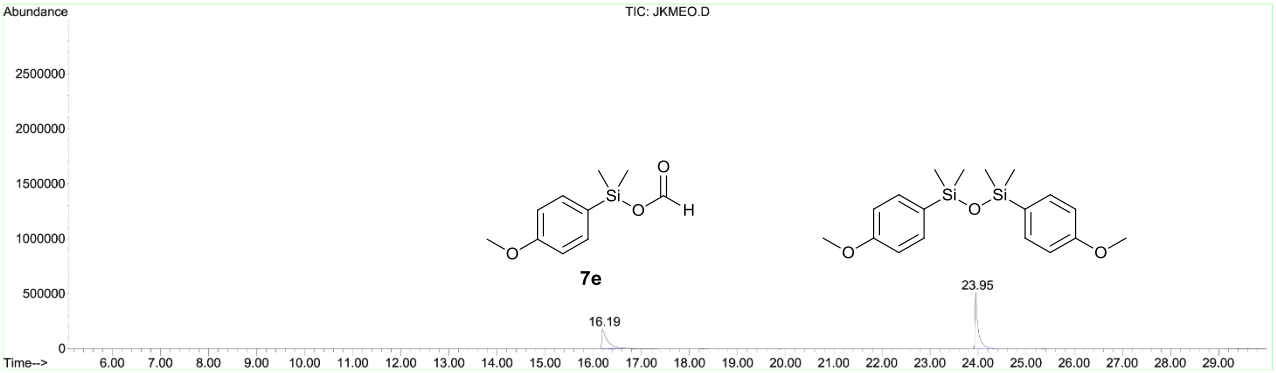


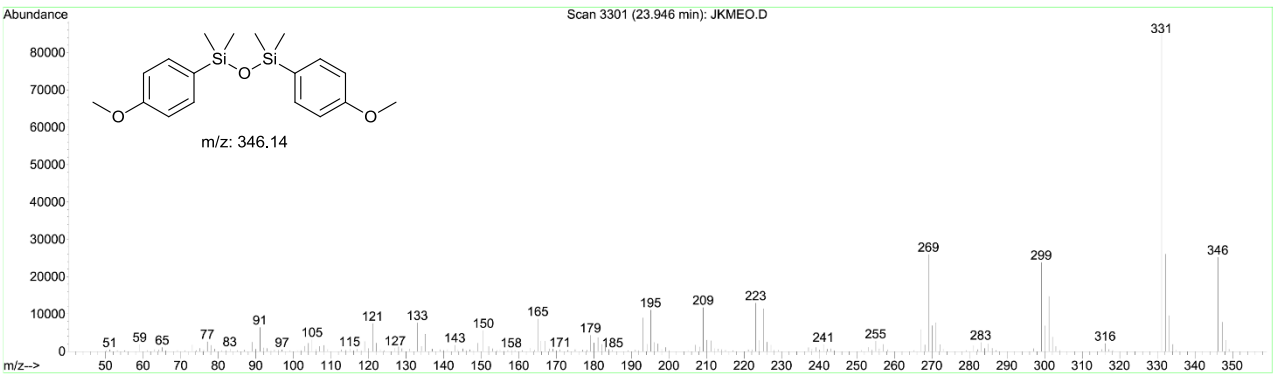

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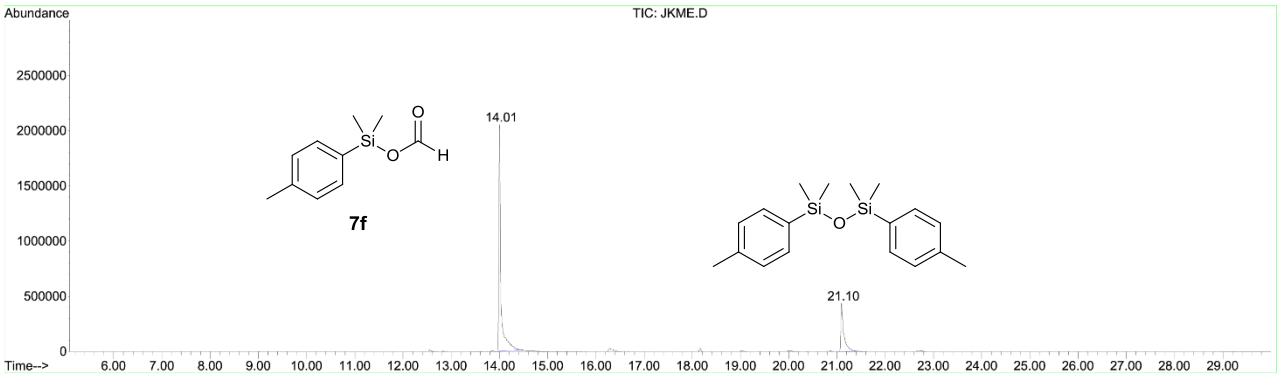


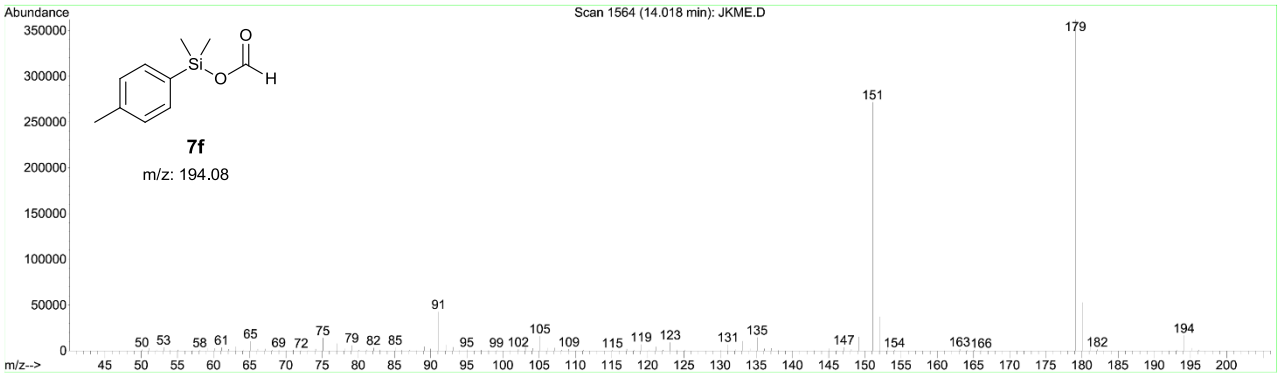



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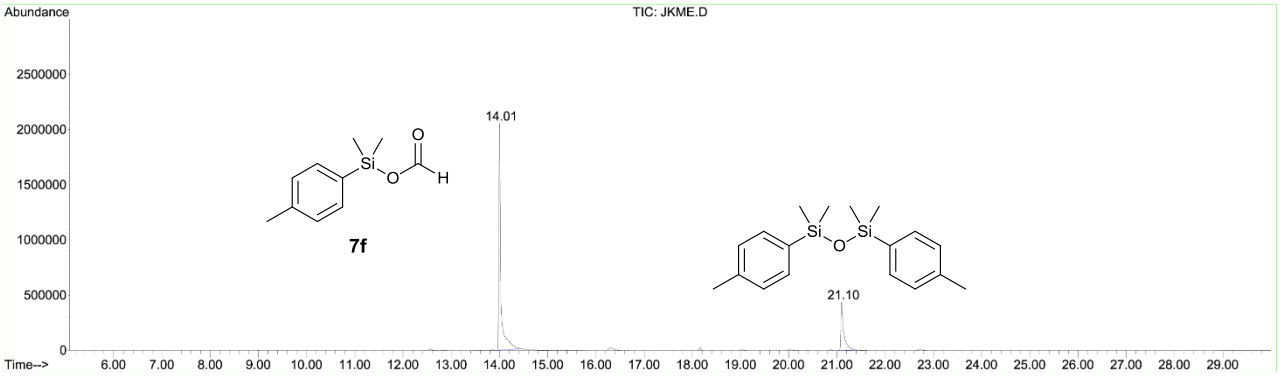


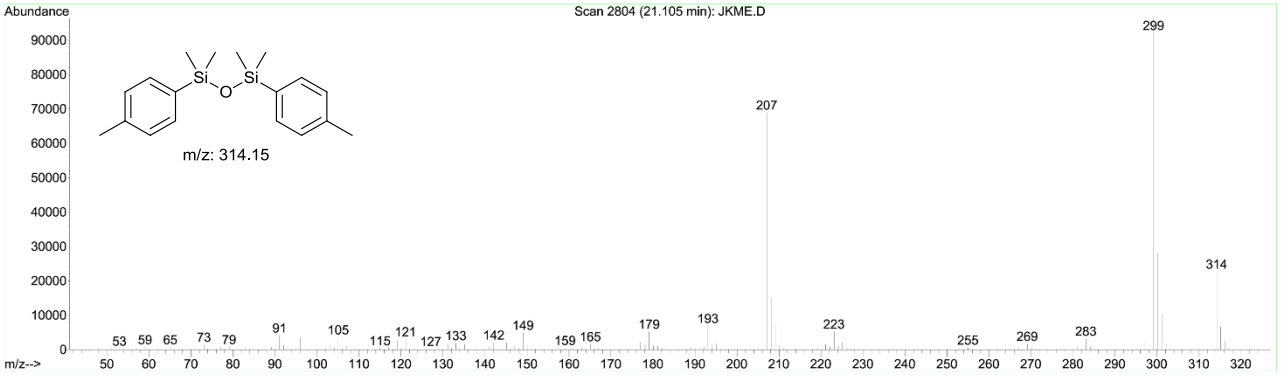

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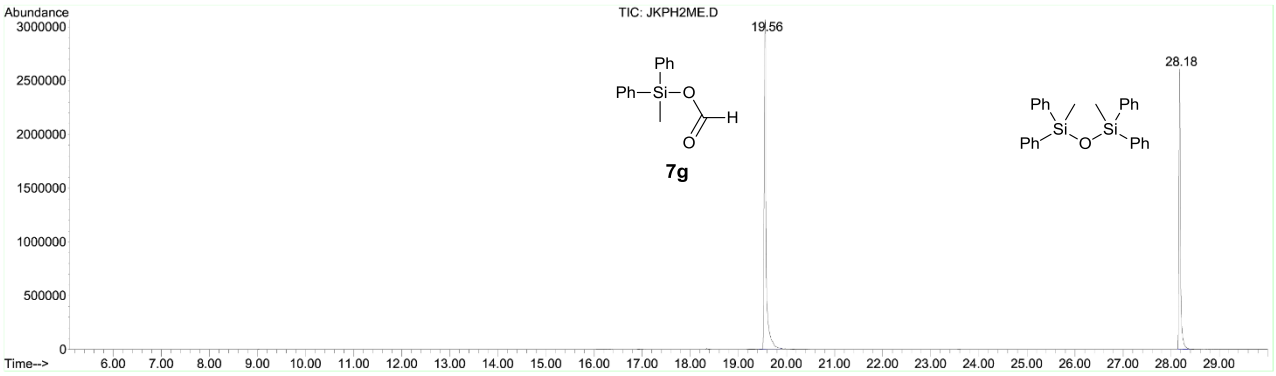


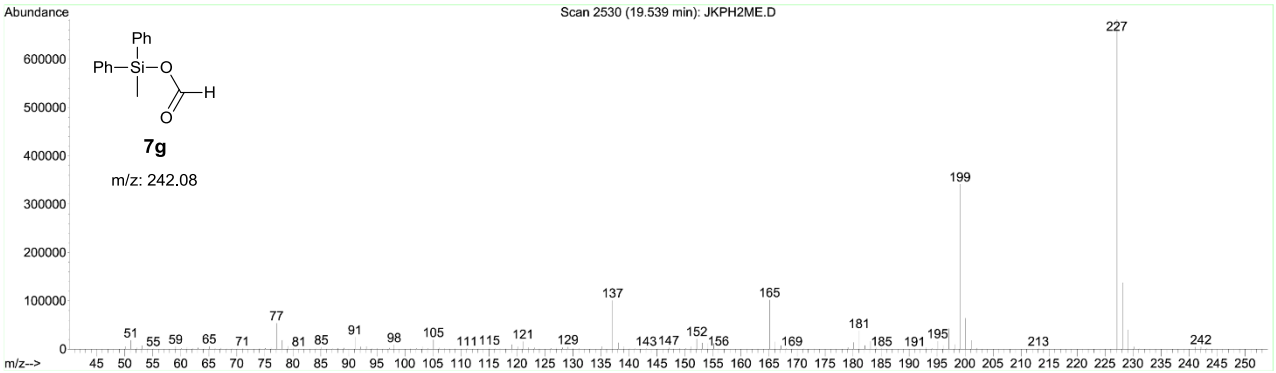



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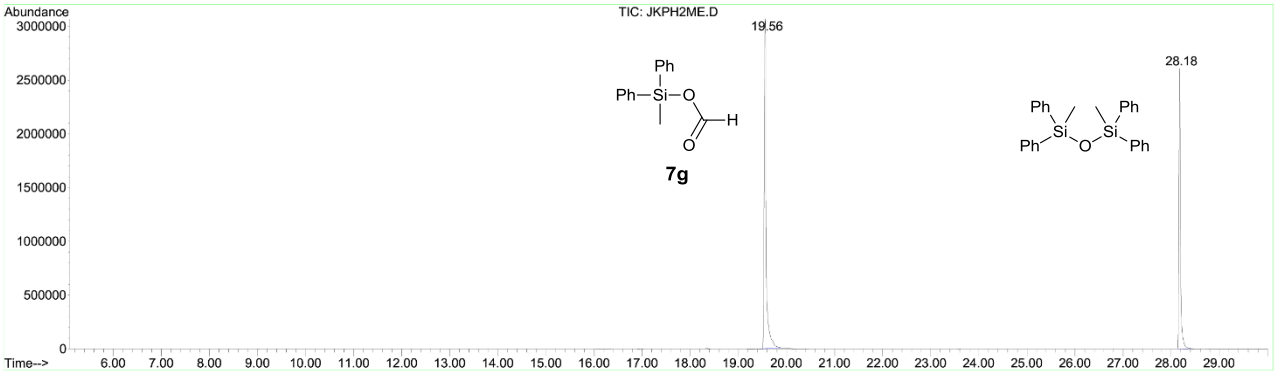


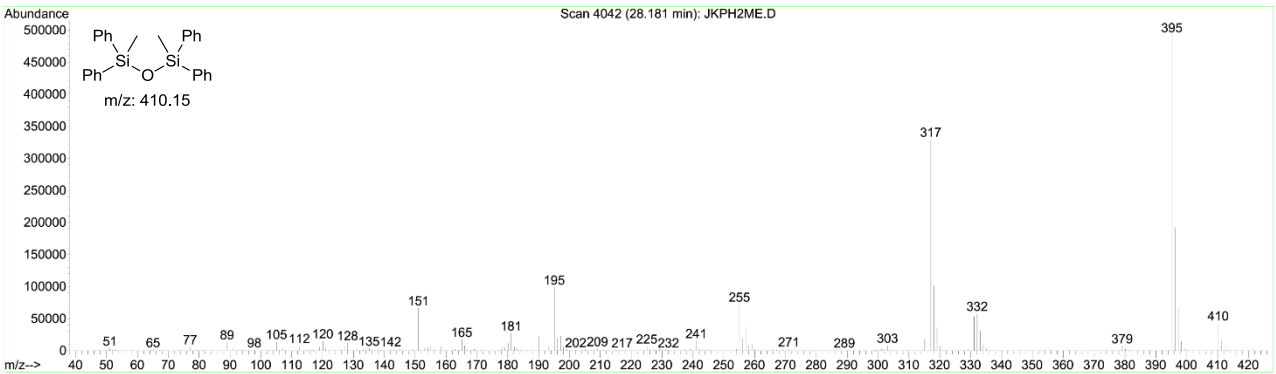

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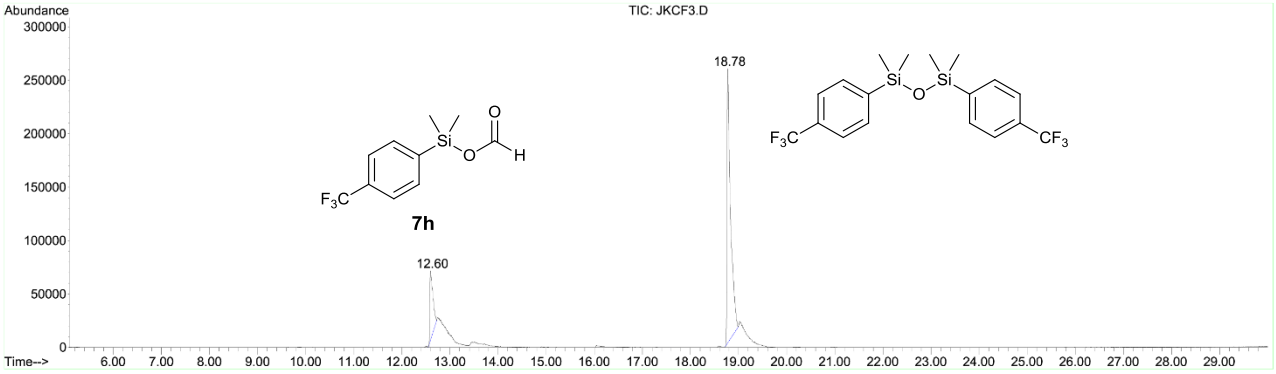


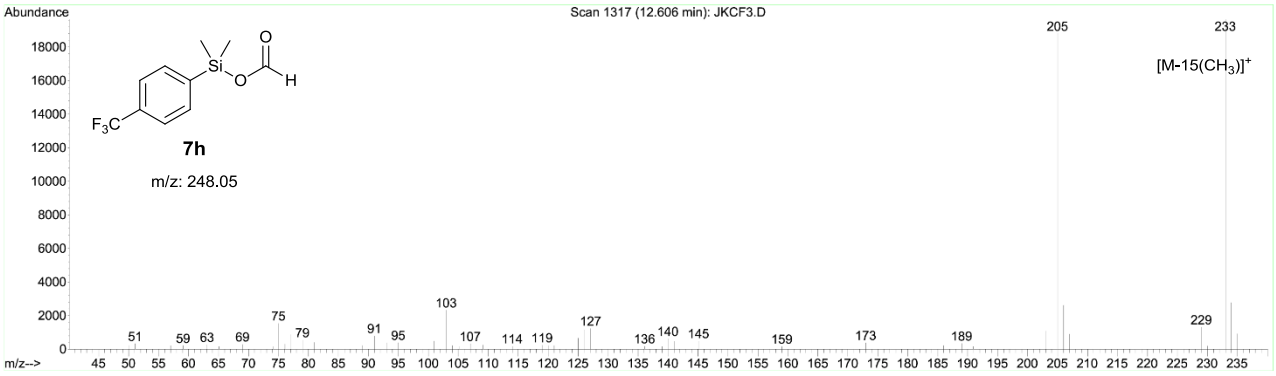


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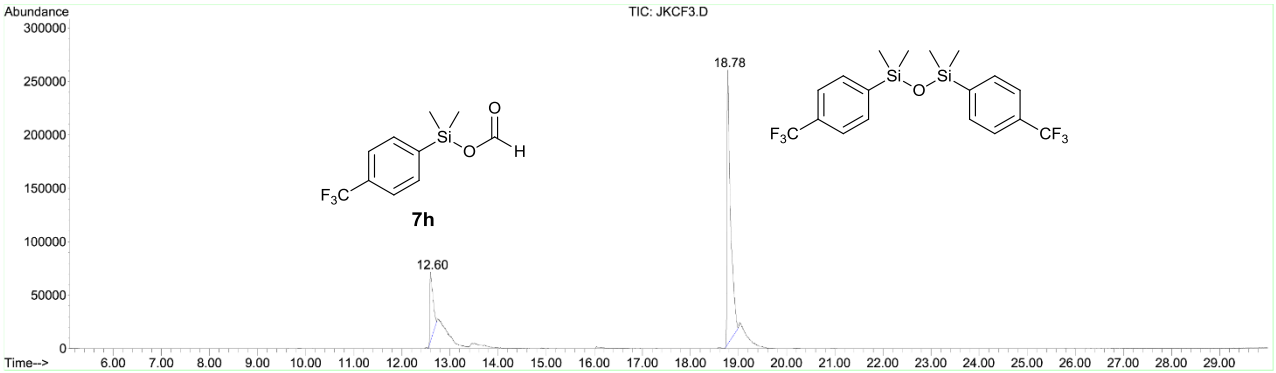


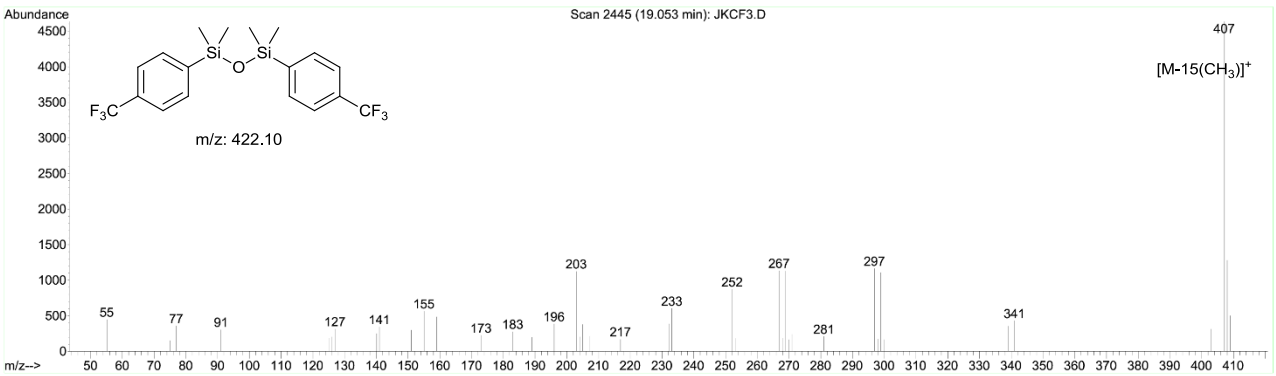

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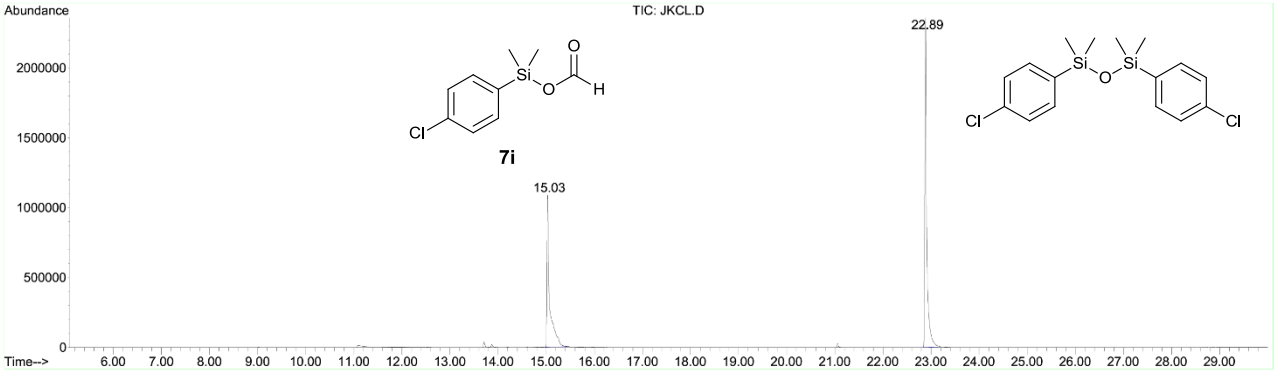


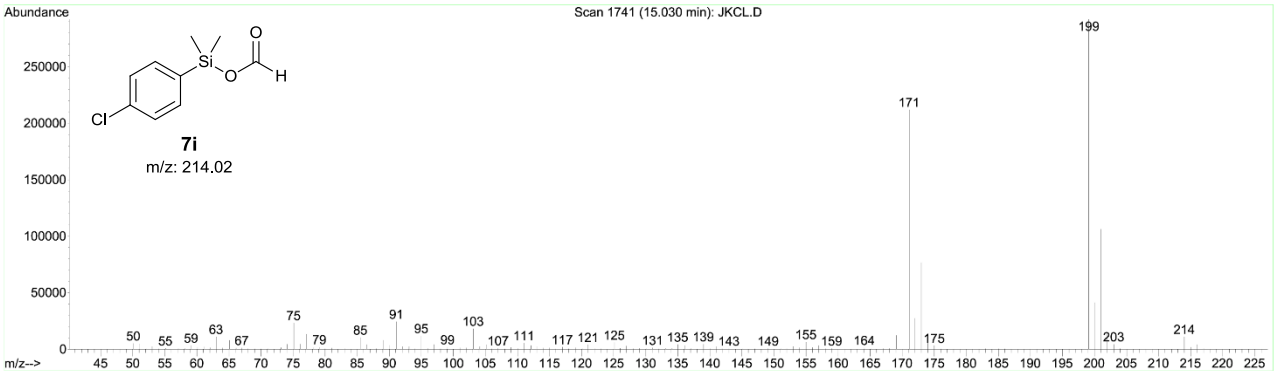


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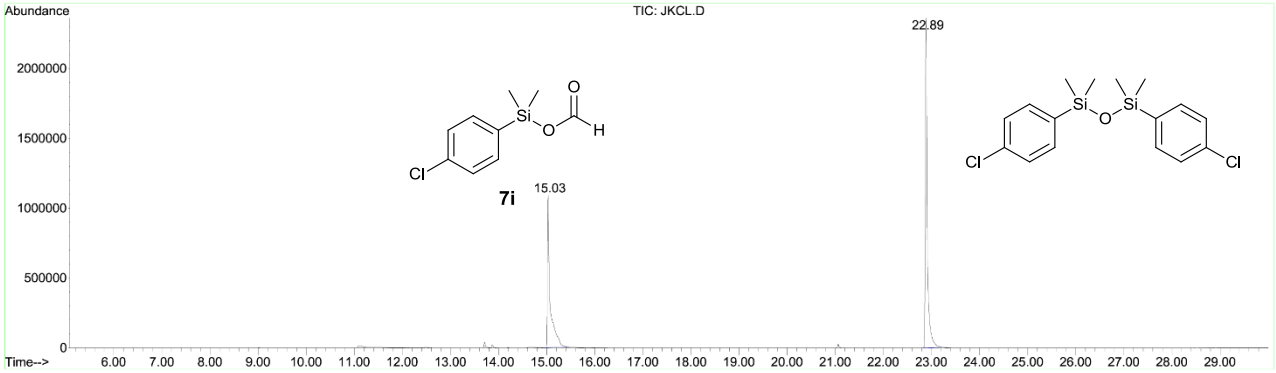
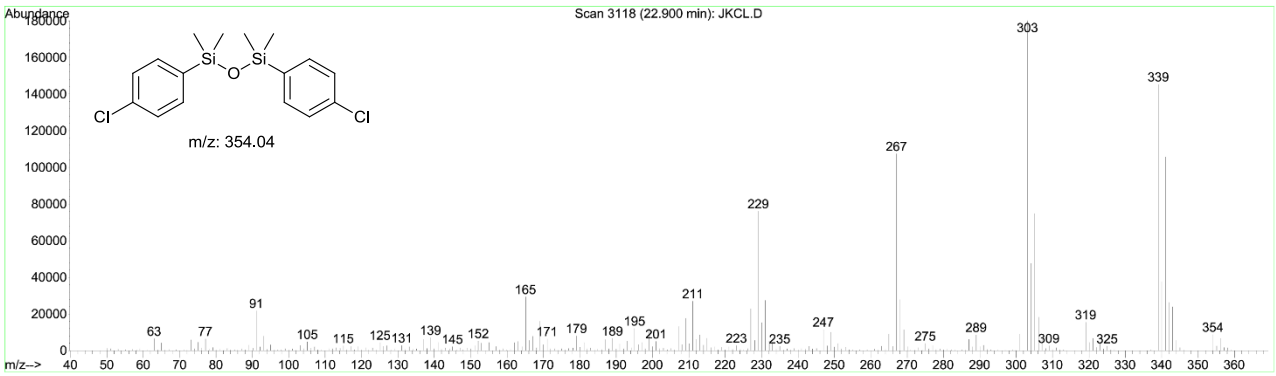
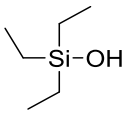


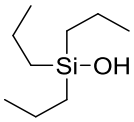
**6. Hydrogenation of Silyl Formates**

Inside a glove box, a 67mL stainless steel autoclave containing a magnetic stirring bar was charged with complex **3** (1 mol%, 2.93 mg, 0.005 mmol). Silyl formate 7 (1.0 equiv, 0.5 mmol) was then added to the reactor as a solution in tetrahydrofuran (0.025 M, 20.0 mL). The reactor was sealed, pressurized with $H_2$ (10 bar), and heated to 150 °C for 12 h. Upon completion of the reaction, the mixture was cooled to 0 °C for 30 minutes. Unreacted $H_2$ was carefully released in a fumehood. Methanol was analyzed by GC using *p*-xylene (1.0 equiv, 61.6 µL, 0.5 mmol) as an internal standard, and silanol was isolated by silica column chromatography with hexane/ethyl acetate (20:1).



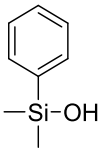

**Triethylsilanol (8a)**

Colorless liquid (60.8 mg, 0.460 mmol, 92%). Reaction was conducted with 0.1 mol% of **3**. $^1$H NMR (300 MHz, $CDCl_3$) δ = 1.40 (s, 1H), 0.97 (t, *J*=7.9, 9H), 0.60 (q, *J*=7.9, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ = 6.69, 5.89. The identity of the compound was confirmed by comparison with reported data.[8]



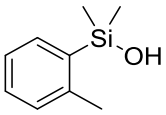

**Tri-n-propylsilanol (8b)**

Colorless liquid (80.2 mg, 0.460 mmol, 92%). Reaction was conducted with 2.0 mol% of **3**. $^1$H NMR (300 MHz, $CDCl_3$) δ = 2.89 (s, 1H), 1.45 – 1.33 (m, 6H), 0.97 (t, *J*=7.3, 9H), 0.61 – 0.55 (m, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ = 18.29, 17.80, 16.63. The identity of the compound was confirmed by comparison with reported data.[9]



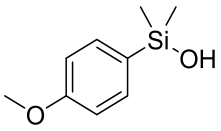

**Dimethylphenylsilanol (8c)**

Colorless liquid (70.0 mg, 0.460 mmol, 92%). $^1$H NMR (300 MHz, $CDCl_3$) δ = 7.62 – 7.59 (m, 2H), 7.41 – 7.36 (m, 3H), 2.70 (s, 1H), 0.40 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ = 139.23, 133.18, 129.71, 127.99, 0.06. The identity of the compound was confirmed by comparison with reported data.[8]



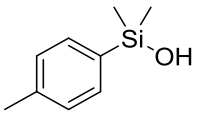
**Dimethyl(2-methylphenyl)silanol (8d)**

Colorless liquid (68.2 mg, 0.410 mmol, 82%). Reaction was conducted with 2 mol% of **3**. $^{1}$H NMR (300 MHz, $CDCl_3$) δ = 7.57 (d, *J*=7.1, 1H), 7.34 (t, *J*=7.4, 1H), 7.21 (t, *J*=7.1, 2H), 2.77 (s, 1H), 2.53 (s, 3H), 0.45 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ = 143.37, 137.47, 134.22, 129.98, 129.91, 125.03, 22.86, 1.10. The identity of the compound was confirmed by comparison with reported data.[10]



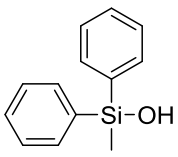
**Dimethyl(4-methoxyphenyl)silanol (8e)**

Colorless liquid (69.3 mg, 0.380 mmol, 76%). Reaction was conducted with 80 bar of $H_2$ pressure. $^{1}$H NMR (300 MHz, $CDCl_3$) δ = 7.53 (d, *J*=8.6, 2H), 6.93 (d, *J*=8.5, 2H), 3.82 (s, 3H), 2.12 (s, 1H), 0.39 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ = 160.93, 134.76, 130.33, 113.73, 55.17, 0.20. The identity of the compound was confirmed by comparison with reported data.[11]



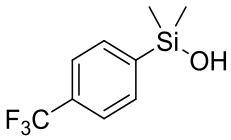
**Dimethyl(4-methylphenyl)silanol (8f)**

Colorless liquid (62.4 mg, 0.375 mmol, 75%). Reaction was conducted with 80 bar of $H_2$ pressure. $^{1}$H NMR (300 MHz, $CDCl_3$) δ = 7.51 (d, *J*=7.9, 2H), 7.22 (d, *J*=7.7, 2H), 2.38 (s, 3H), 2.16 (s, 1H), 0.40 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ = 139.70, 135.66, 133.25, 128.83, 21.63, 0.14. The identity of the compound was confirmed by comparison with reported data.[11]



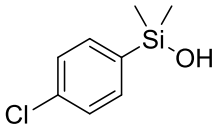
**Diphenylmethylsilanol (8g)**

Colorless liquid (30.0 mg, 0.140 mmol, 28%). $^{1}$H NMR (300 MHz, $CDCl_3$) δ = 7.65 (dd, *J*=7.8, 1.5, 4H), 7.51 – 7.39 (m, 6H), 3.43 (s, 1H), 0.67 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ = 137.12, 134.09, 129.90, 127.96, -1.25. The identity of the compound was confirmed by comparison with reported data.[8]



**Dimethyl(4-trifluoromethylphenyl)silanol (8h)**

Colorless liquid (74.9 mg, 0.340 mmol, 68%). $^{1}$H NMR (300 MHz, $CDCl_3$) δ = 7.71 (d, *J*=7.9, 2H), 7.62 (d, *J*=8.2, 2H), 1.97 (s, 1H), 0.43 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ = 143.97, 133.50, 132.29, 131.87, 131.44, 131.01, 129.70, 126.09, 124.65, 124.60, 124.55, 124.50, 122.49, 118.88, 0.13. The identity of the compound was confirmed by comparison with reported data.[10]

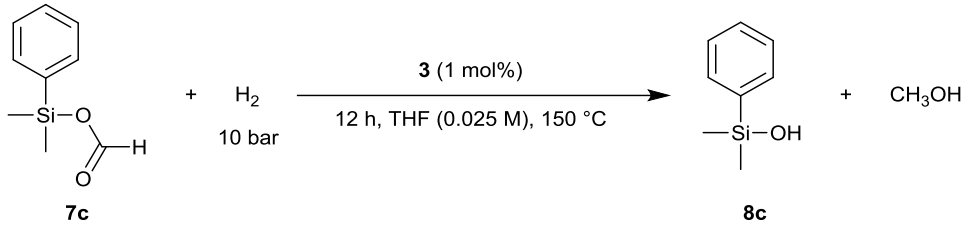


**Dimethyl(4-chlorophenyl)silanol (8i)**

Colorless liquid (49.5 mg, 0.265 mmol, 53%). $^{1}$H NMR (300 MHz, $CDCl_3$) δ = 7.48 (d, *J*=8.2, 2H), 7.34 (d, *J*=8.2, 2H), 2.84 (s, 1H), 0.36 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ = 137.42, 136.02, 134.58, 128.22, 0.10. The identity of the compound was confirmed by comparison with reported data.[12]

## 7. Effect of Siloxane Impurity on the Reaction.

**Table S3**. Effect of Siloxane Impurity on the Reaction.[a]




| entry | purity[b] | yield[c] | |
|---|---|---|---|
| | | **8c** | $CH_3OH$ |
| 1 | 94 | 92 | 99 |
| 2 | 87 | 91 | 99 |
| 3 | 75 | 92 | 99 |

[a] Reaction conditions: **7c** (0.5 mmol, 1.0 equiv.), **3** (1 mol%), THF (20 mL), 150 °C, $H_2$ (10 bar). [b] Purity was checked by $^{1}$H NMR. [c] Yields were determined by GC analysis using *p*-xylene as an internal standard.

**8. References**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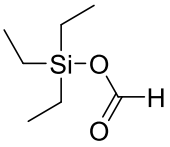
12. T. Mitsudome, S. Arita, H. Mori, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Angew. Chem. Int. Ed.*, 2008, **47**, 7938-7940.

## 9. NMR Spectra

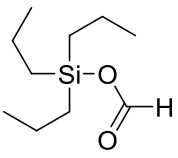
$^1$H NMR (**7a**) ($C_6D_6$)



(purity: 94%)

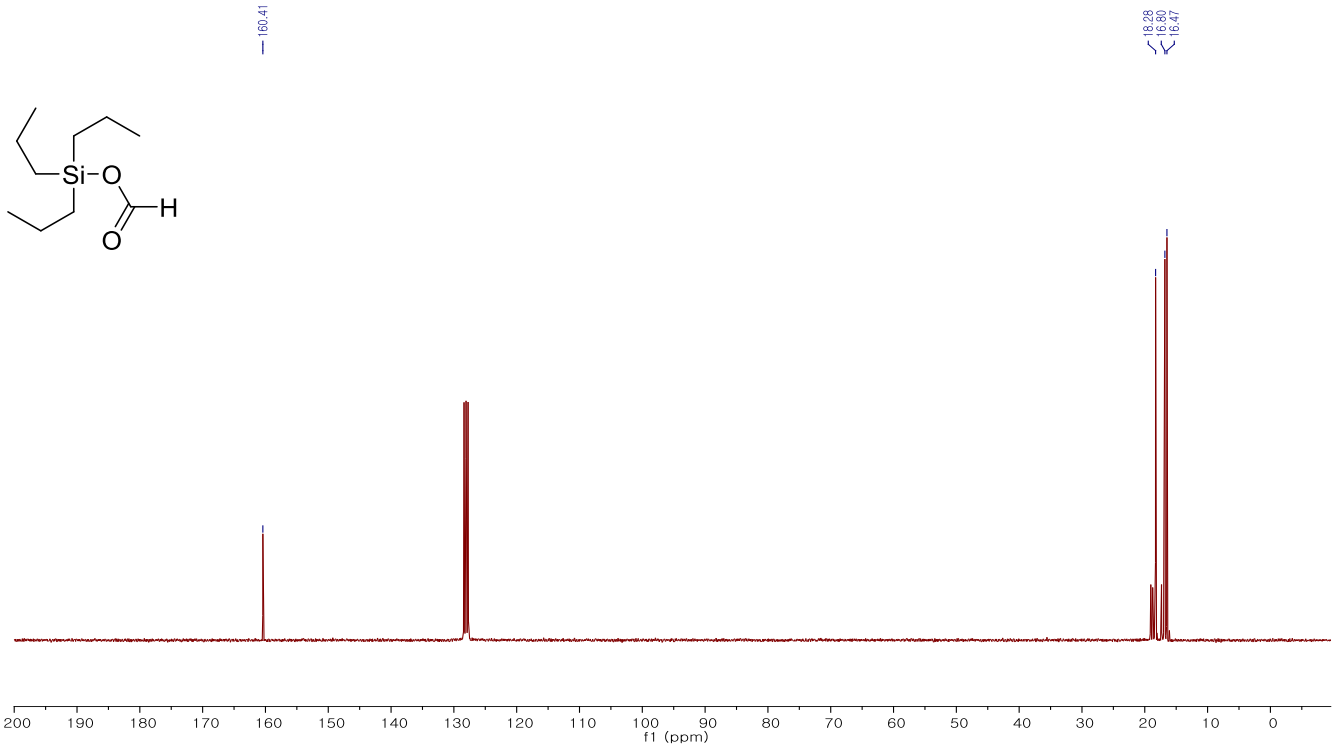



$^1$H NMR (**7b**) ($C_6D_6$)

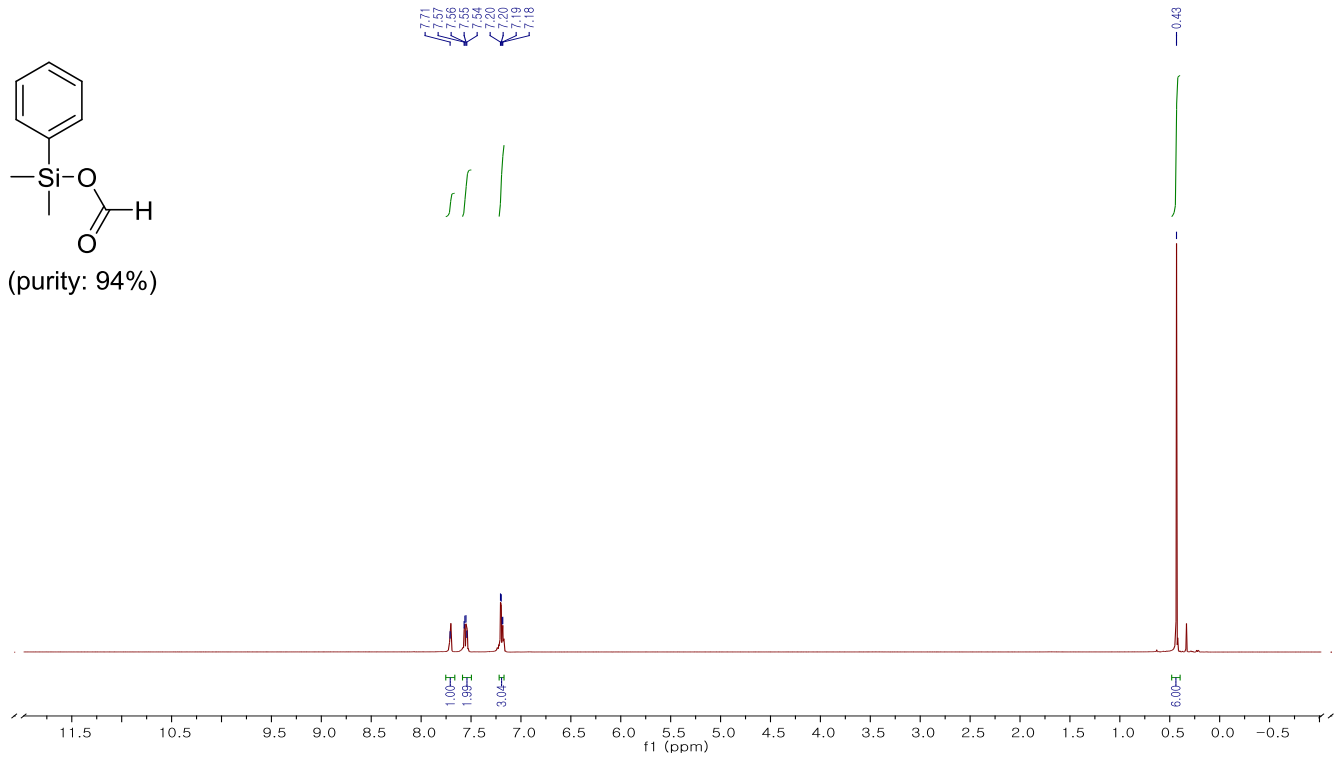


(purity: 90%)

$^{13}$C NMR (**7b**) ($C_6D_6$)

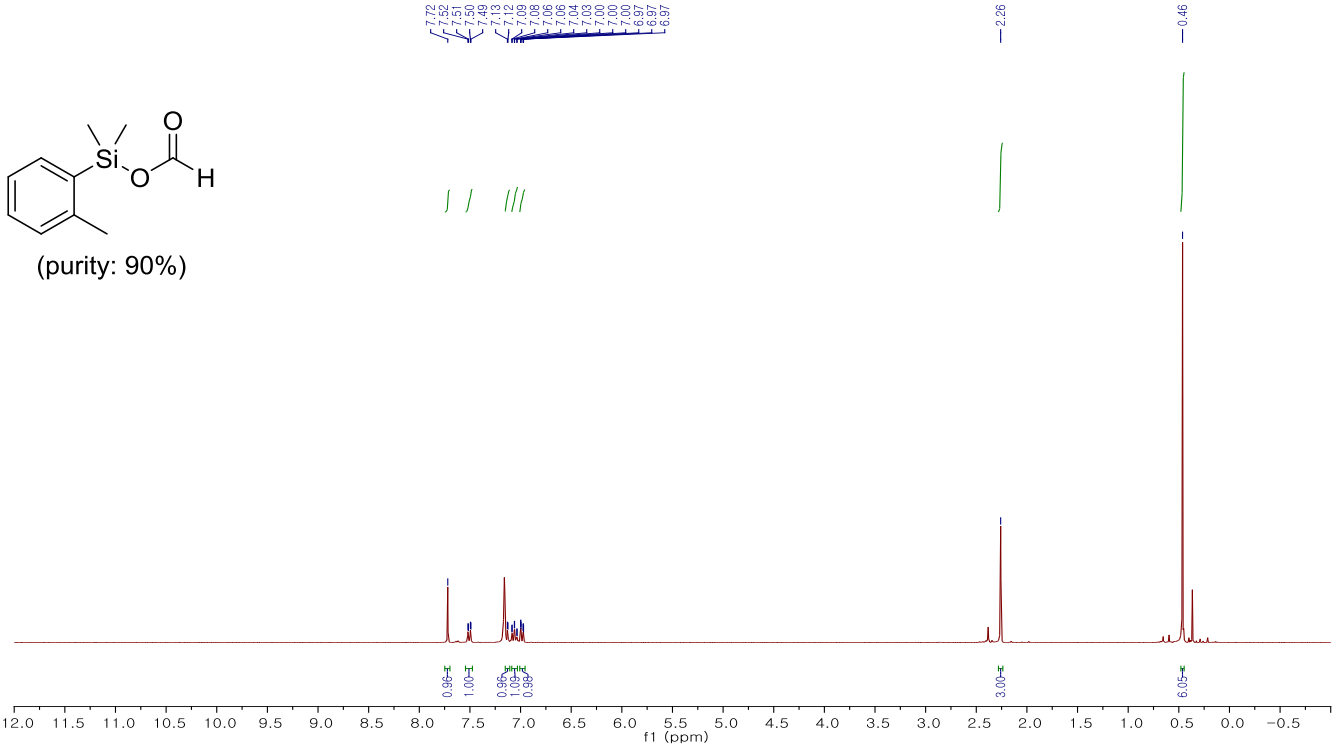



$^{1}$H NMR (**7c**) ($C_6D_6$)



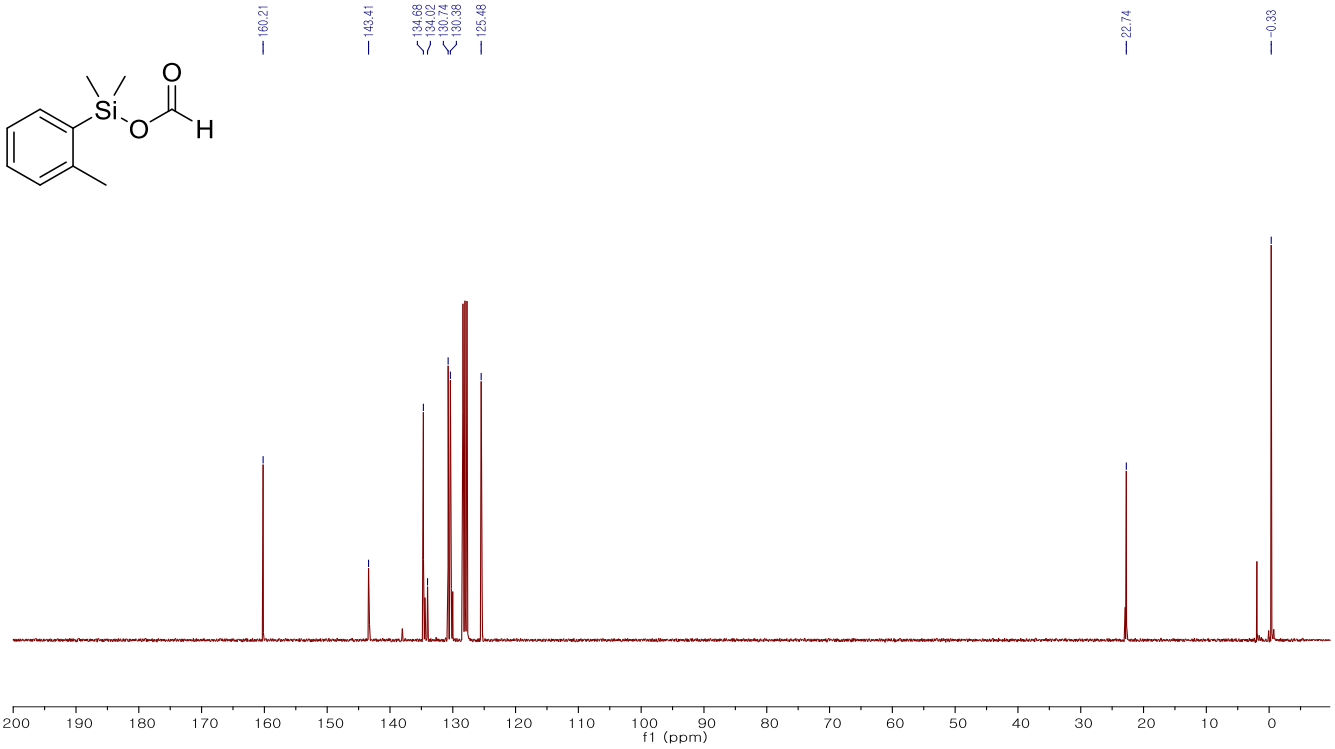

(purity: 94%)

$^{1}$H NMR (**7d**) ($C_6D_6$)

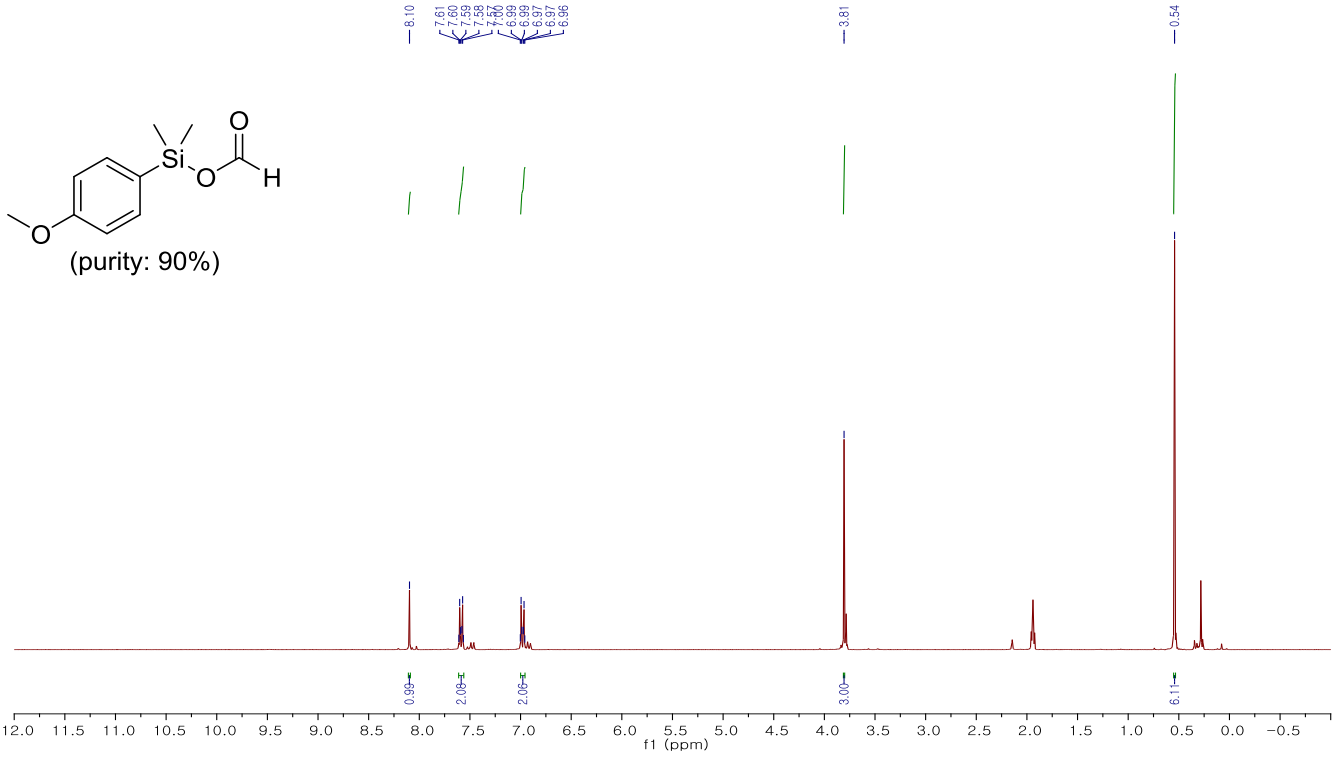



(purity: 90%)

$^{13}$C NMR (**7d**) ($C_6D_6$)

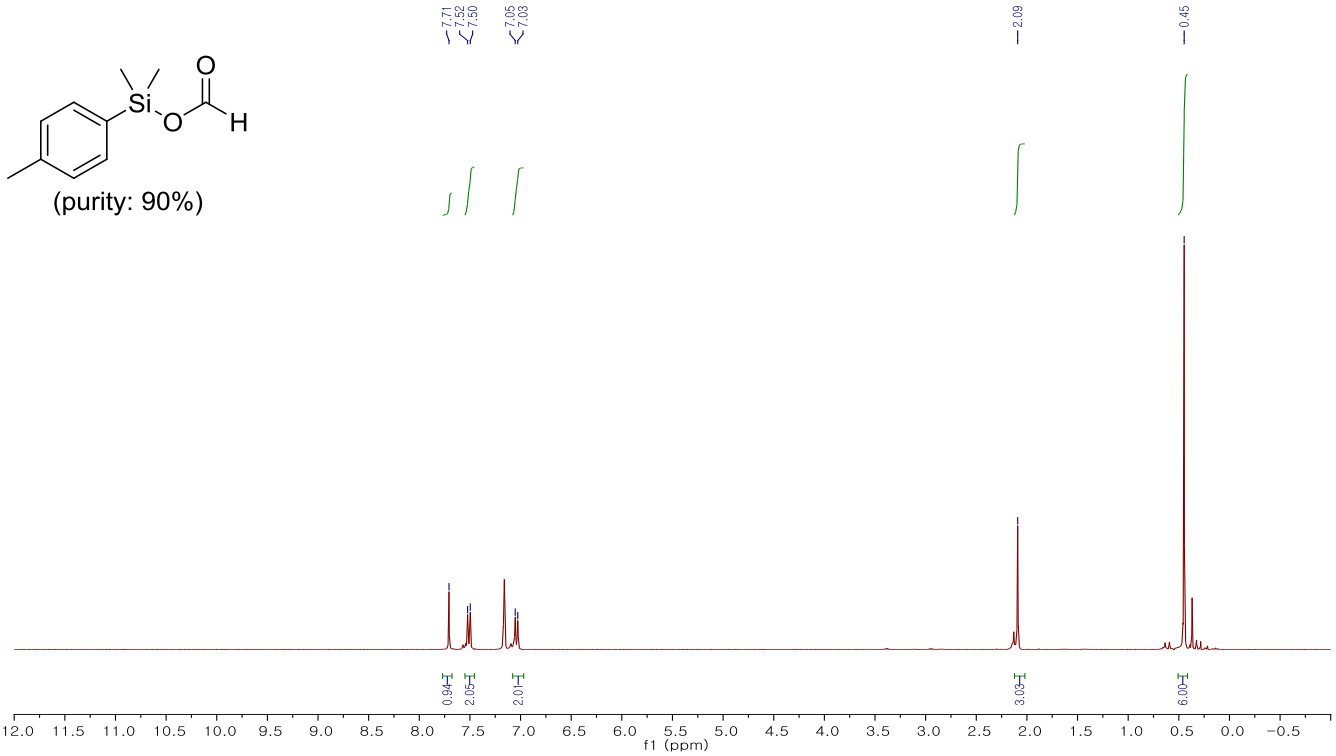


$^1$H NMR (**7e**) ($CD_3CN$)



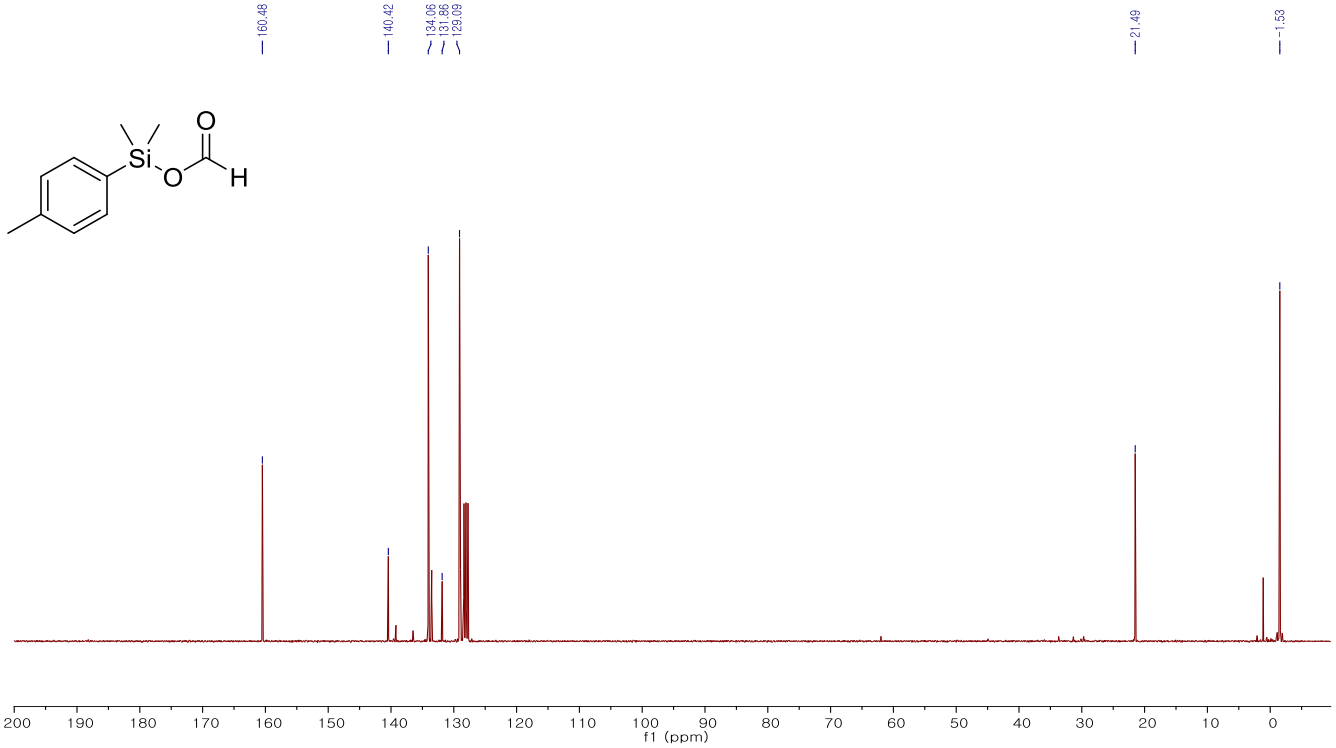

(purity: 90%)

$^1$H NMR (**7f**) ($C_6D_6$)

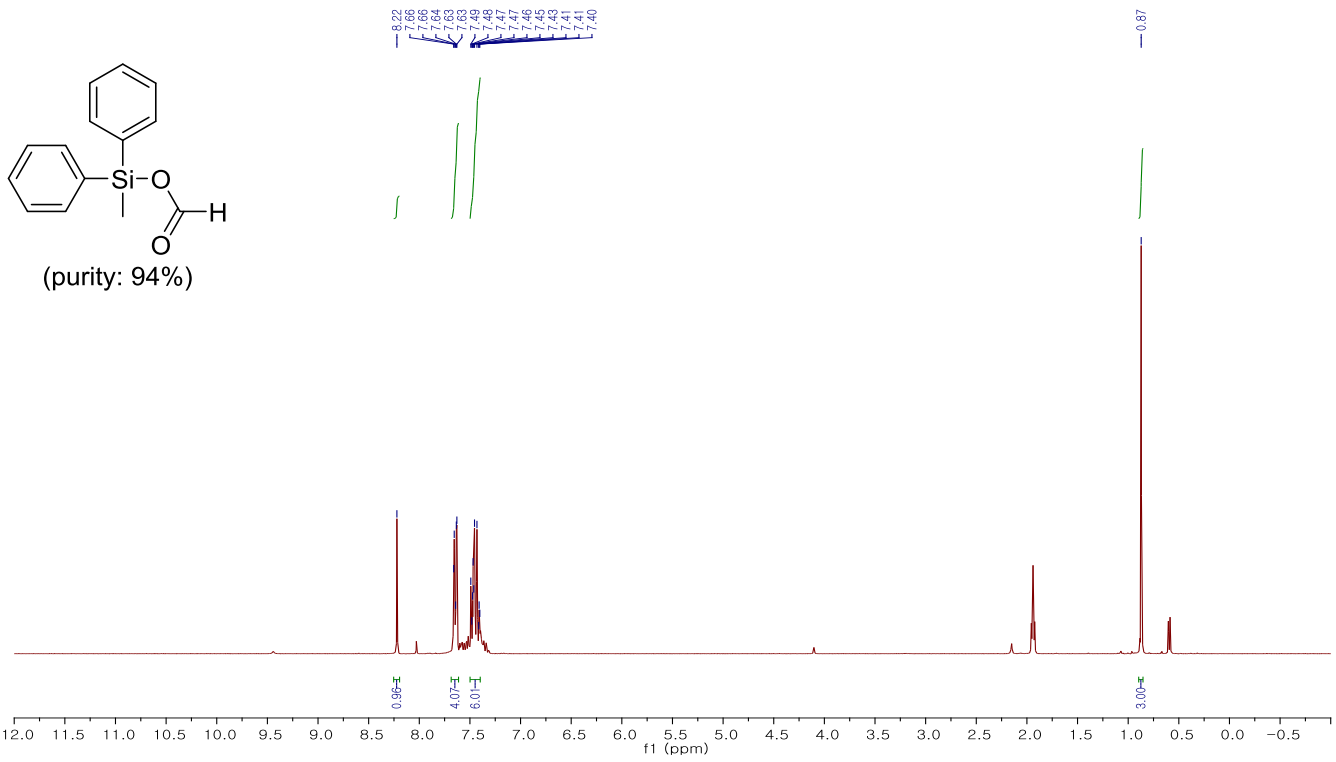



(purity: 90%)

$^{13}$C NMR (**7f**) ($C_6D_6$)

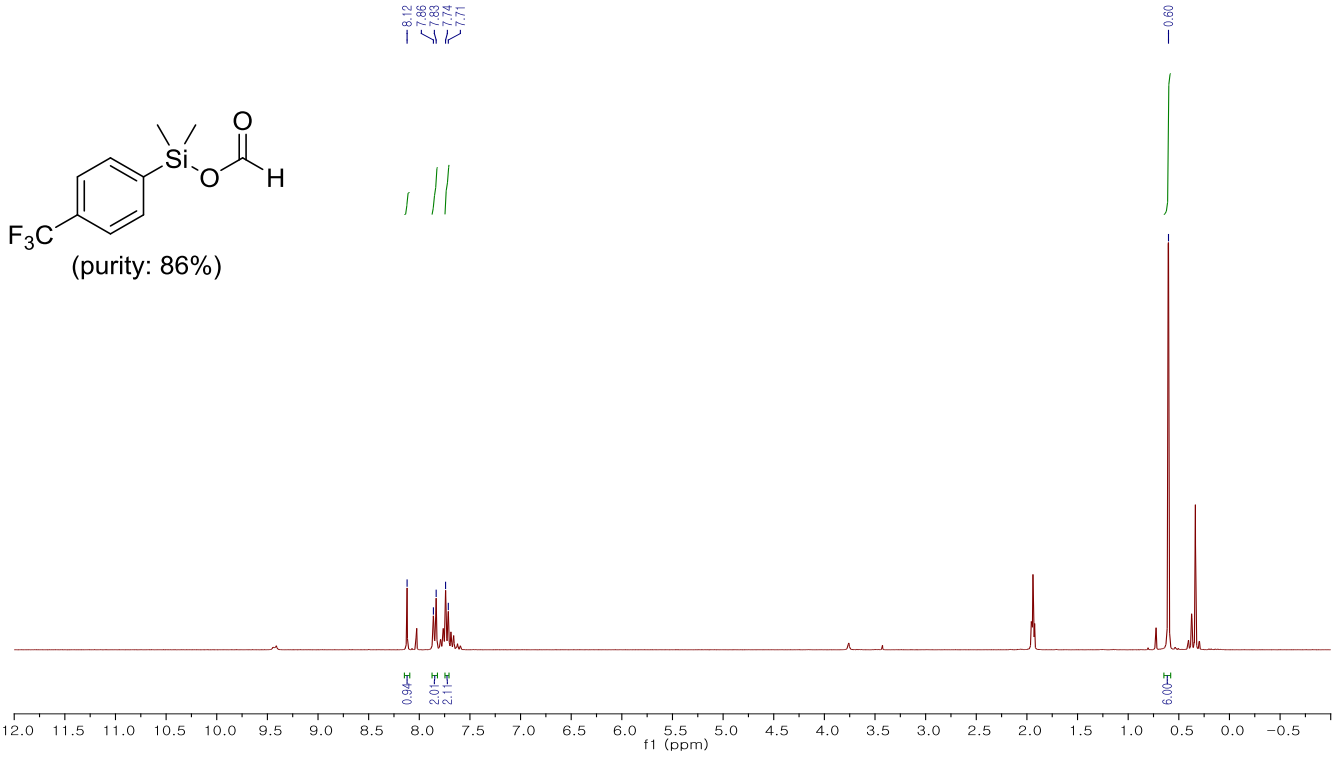



$^{1}$H NMR (**7g**) ($CD_3CN$)

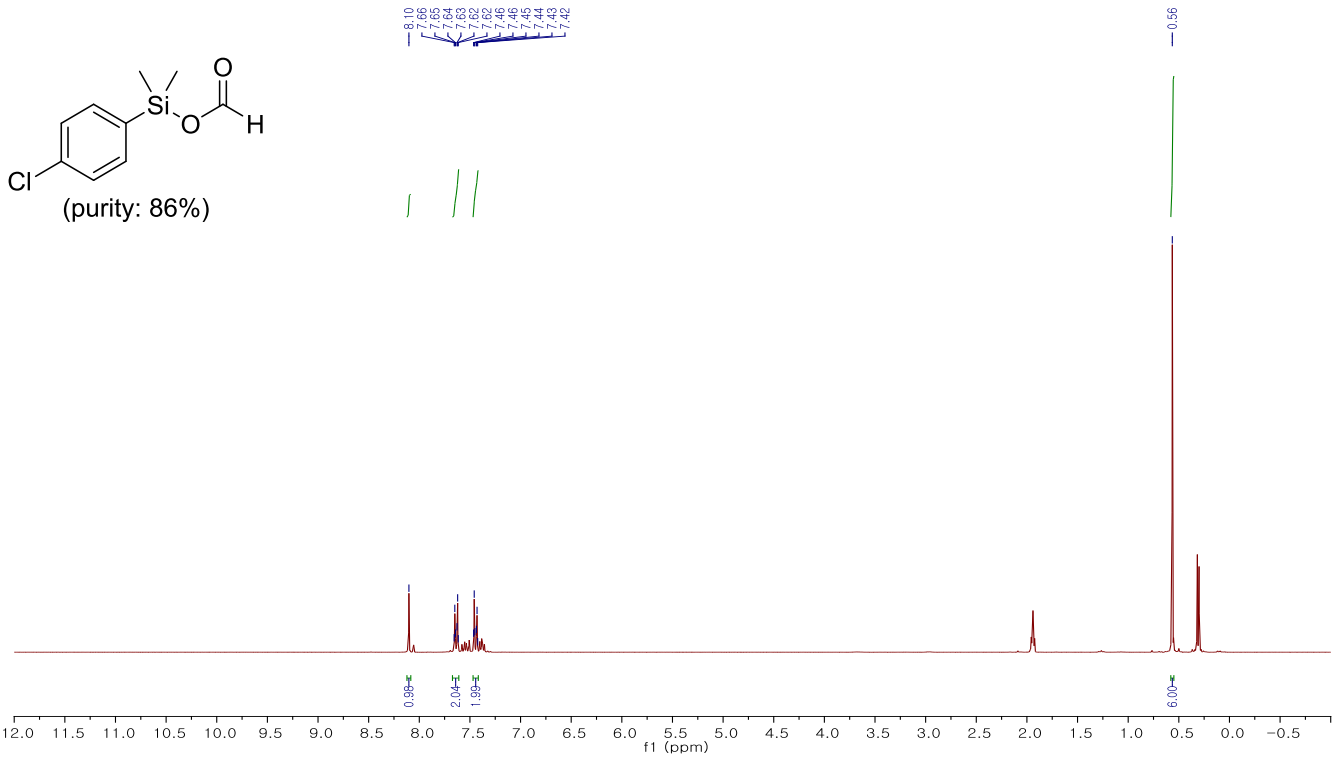



(purity: 94%)

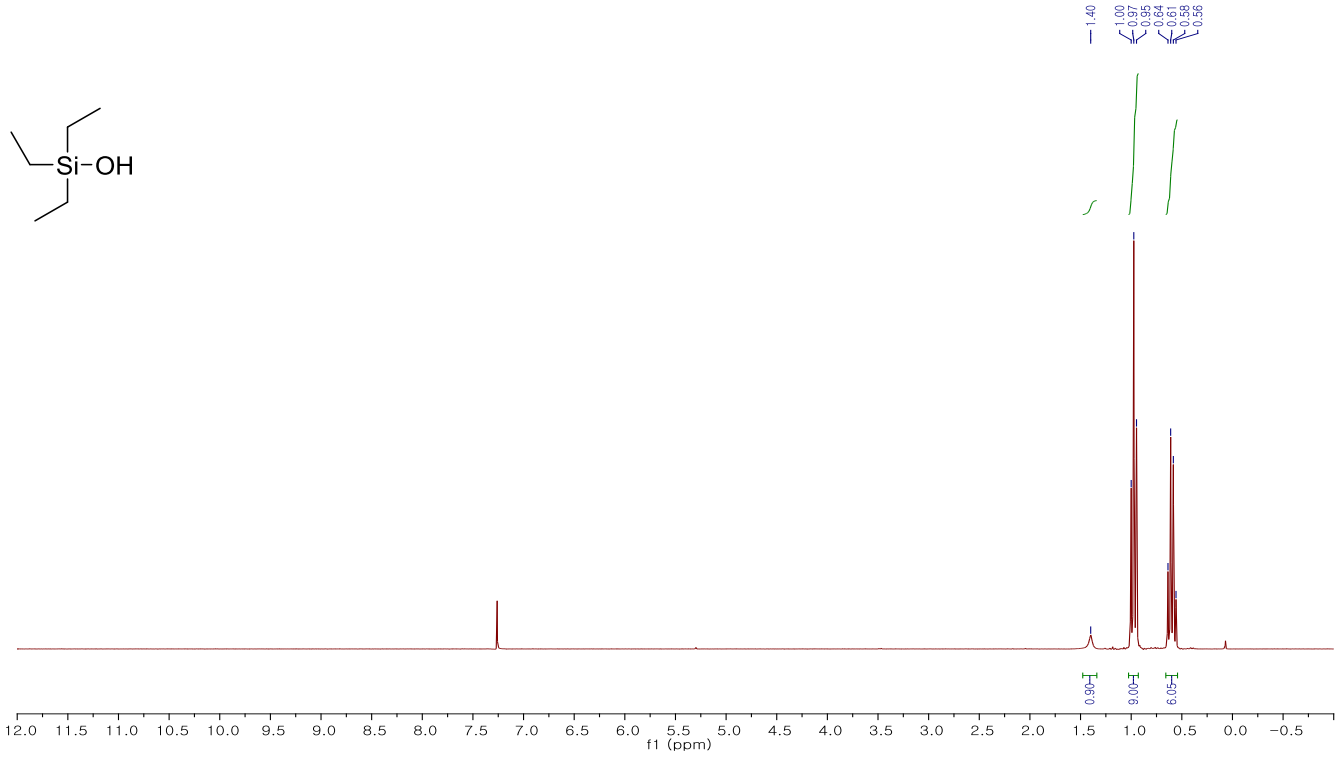
$^1$H NMR (**7h**) ($CD_3CN$)



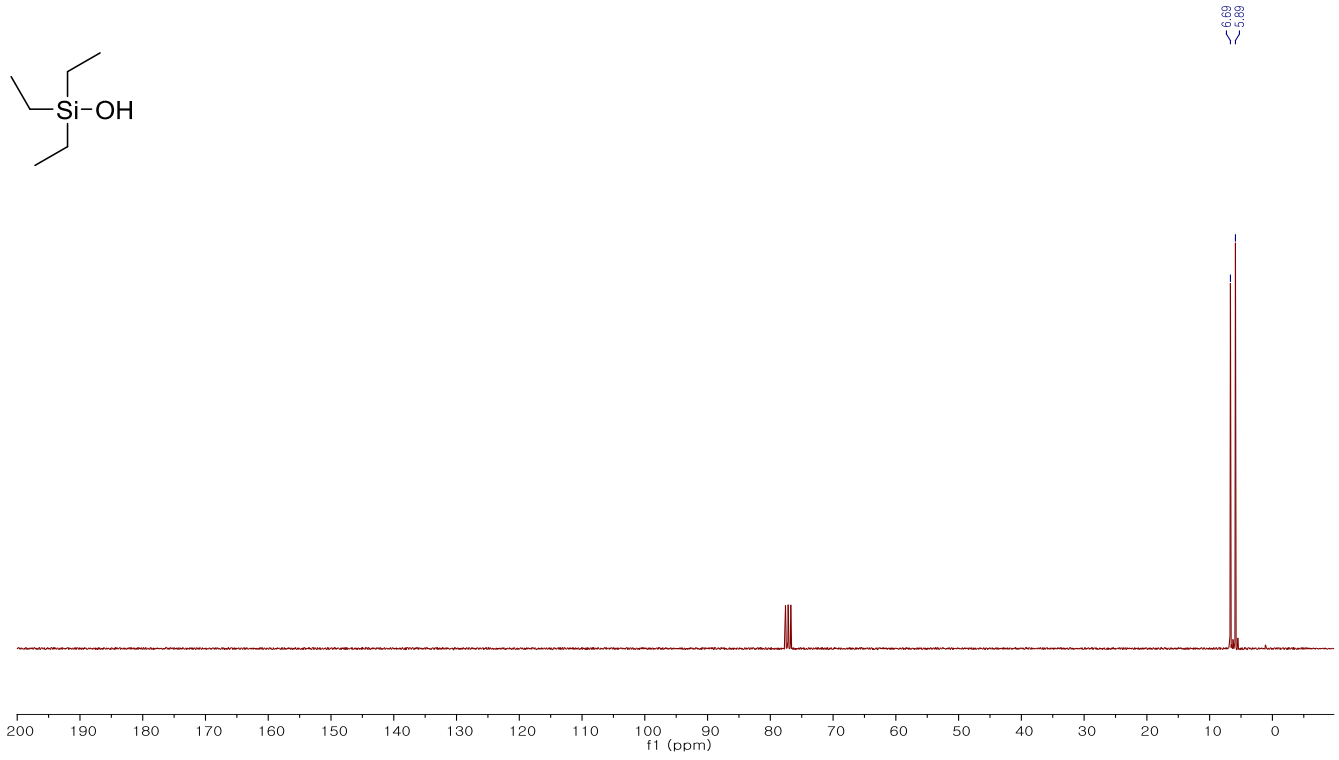

$^1$H NMR (**7i**) ($CD_3CN$)



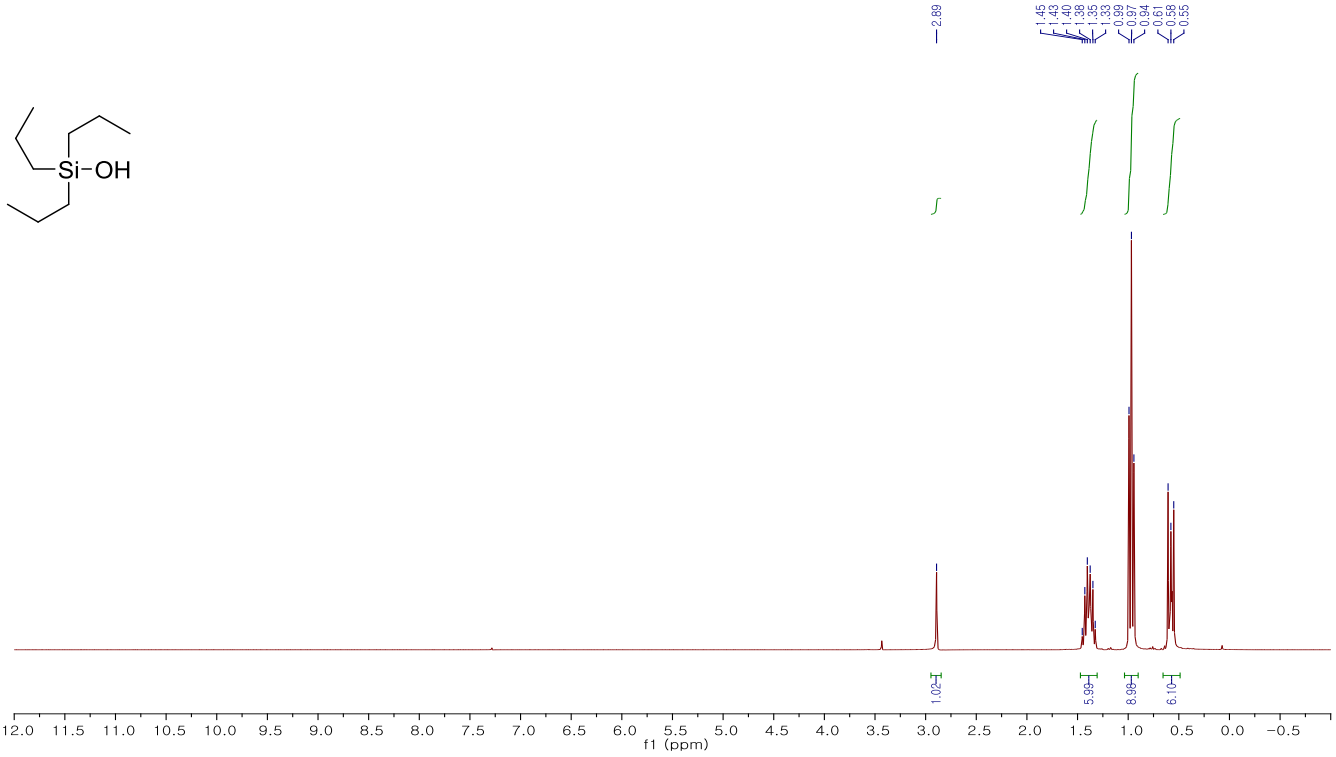
$^{1}$H NMR (**8a**) ($CDCl_3$)



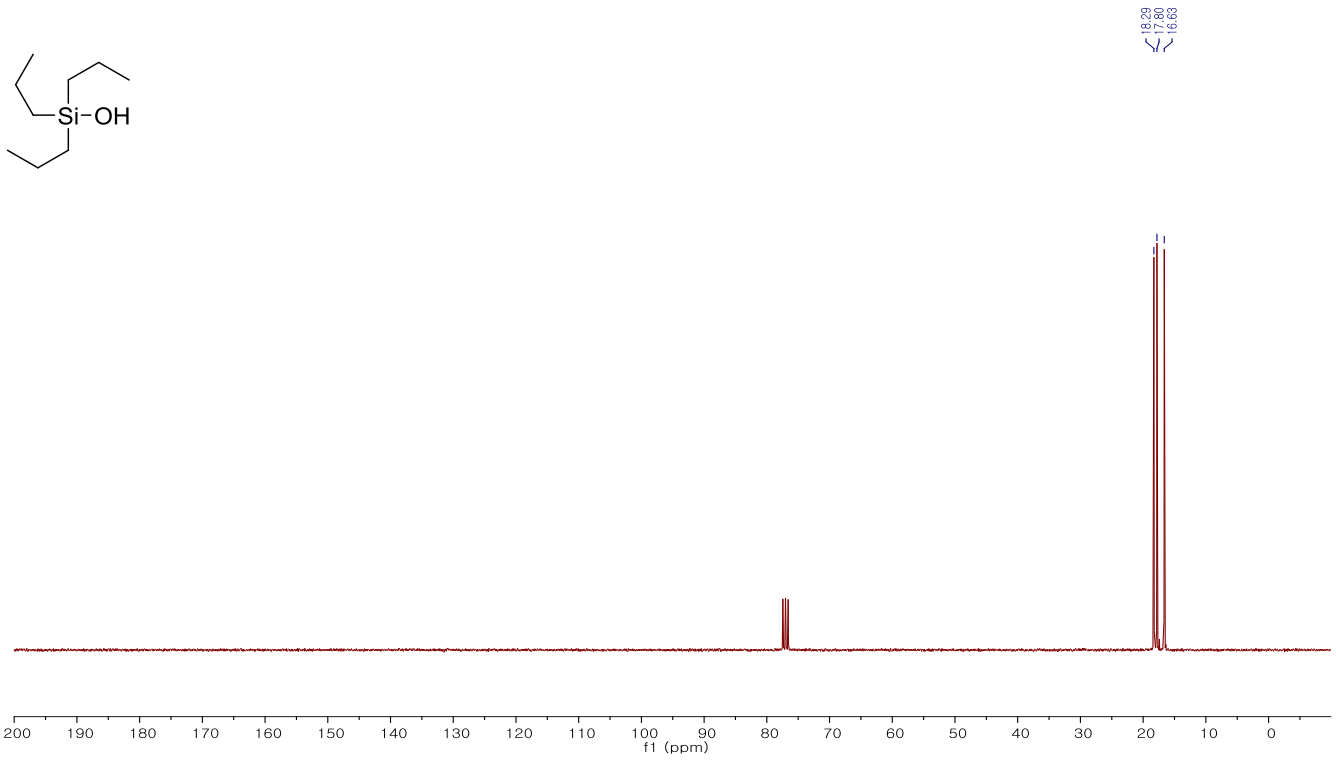

$^{13}$C NMR (**8a**) ($CDCl_3$)



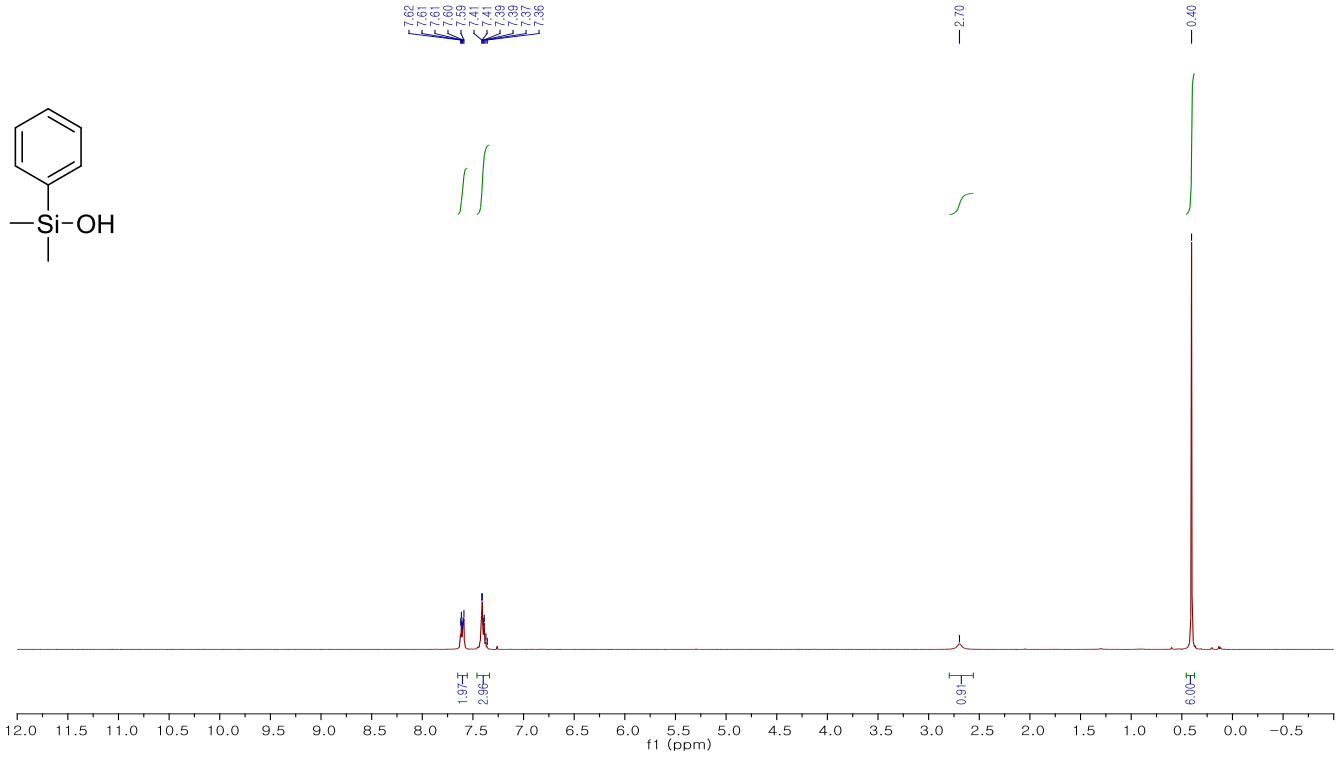
$^{1}$H NMR (**8b**) ($CDCl_3$)



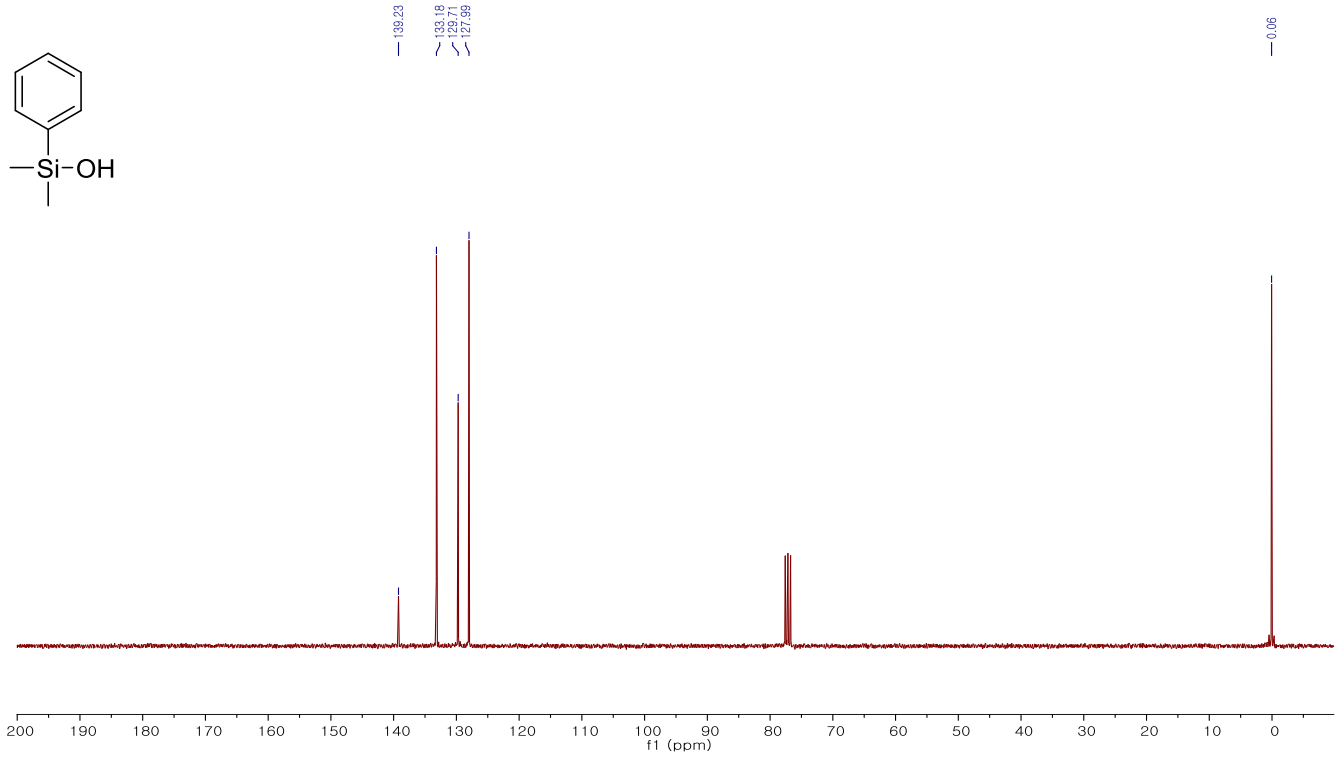

$^{13}$C NMR (**8b**) ($CDCl_3$)



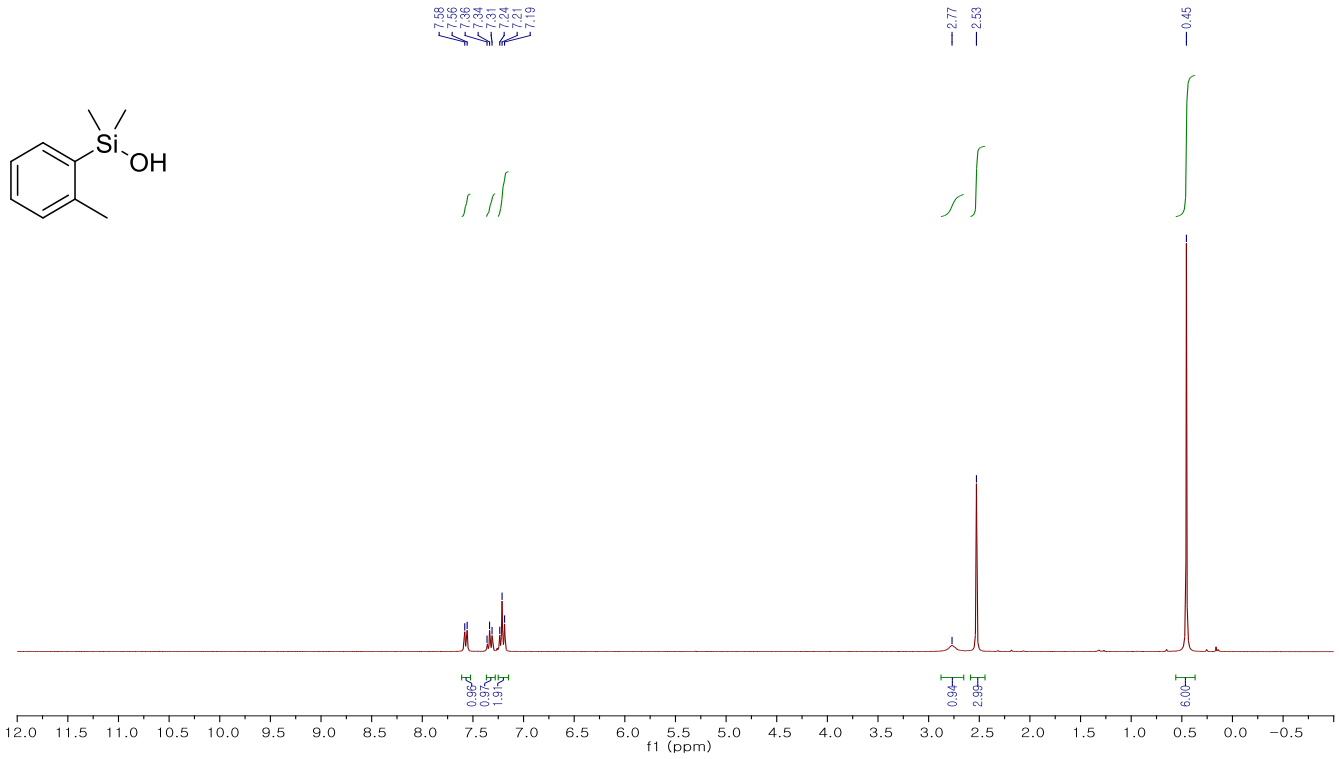
$^{1}$H NMR (**8c**) ($CDCl_3$)



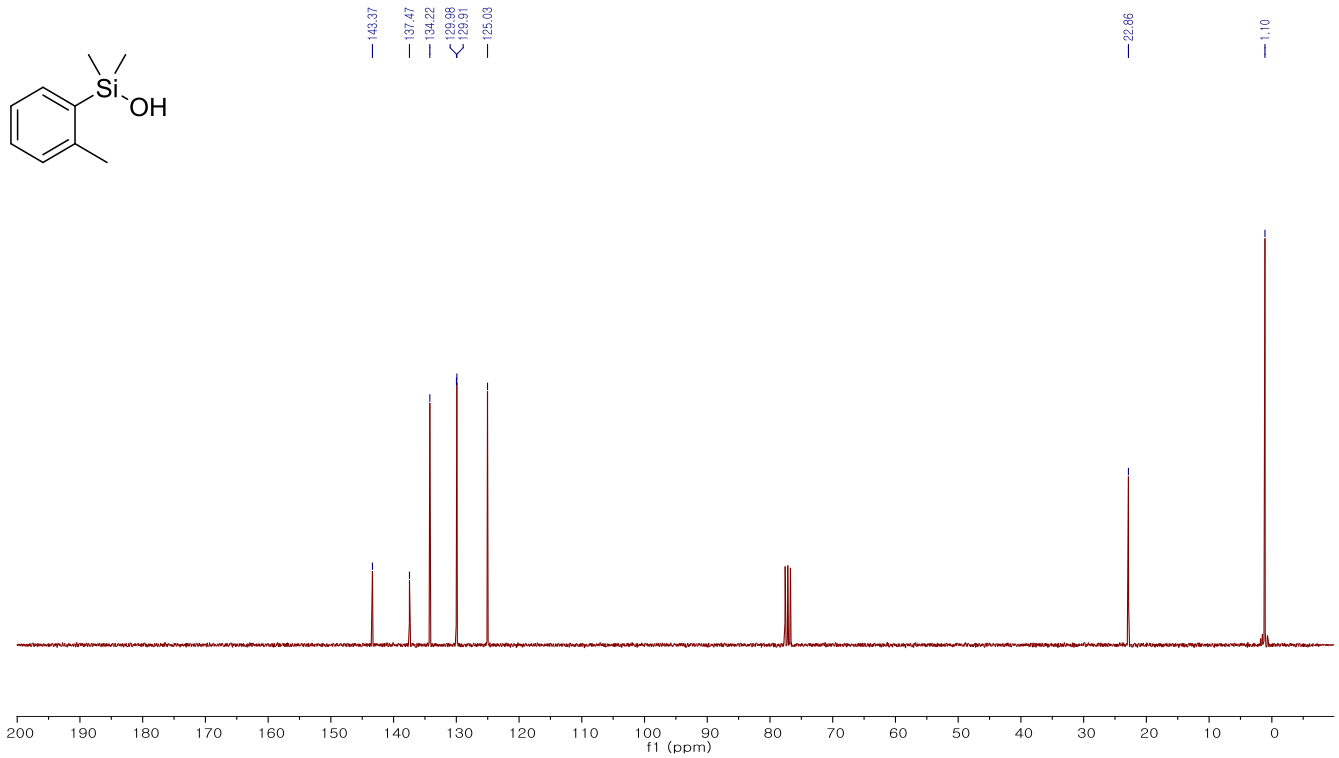

$^{13}$C NMR (**8c**) ($CDCl_3$)



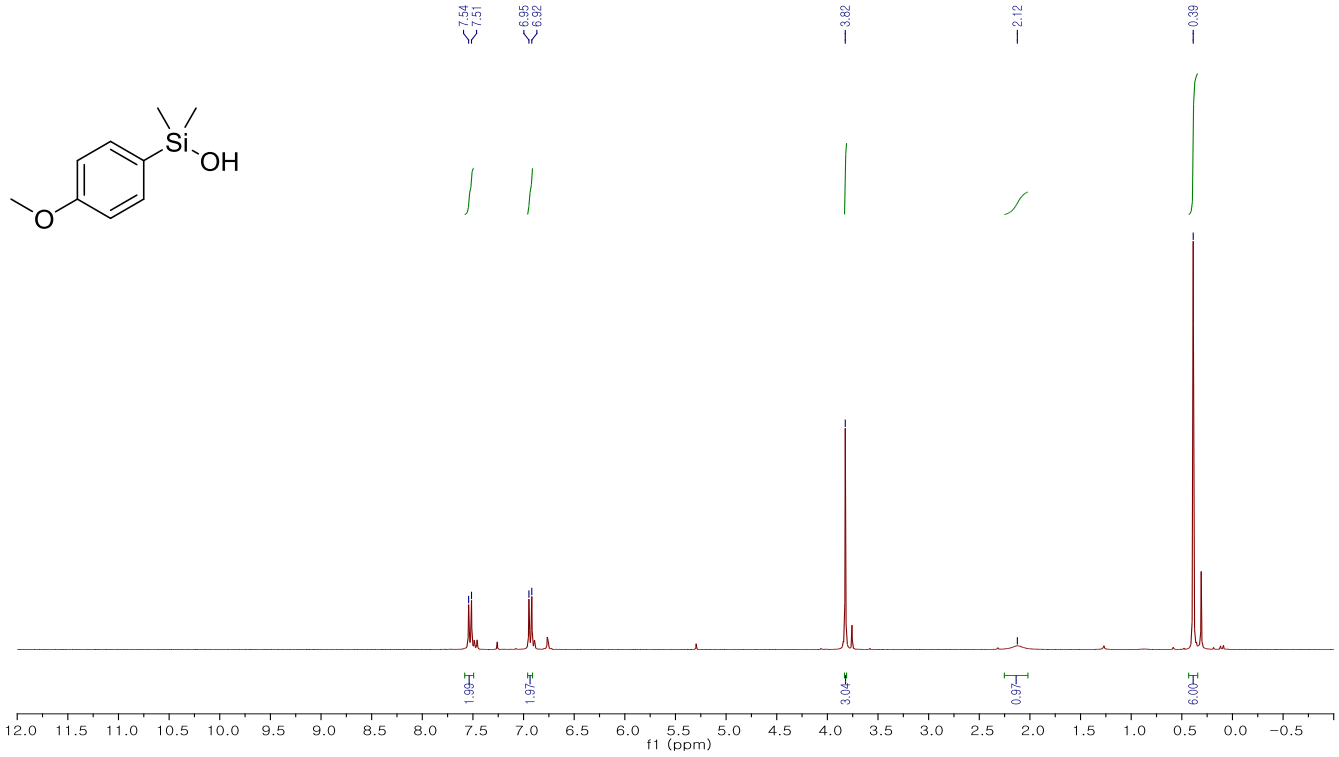
$^{1}$H NMR (**8d**) ($CDCl_3$)



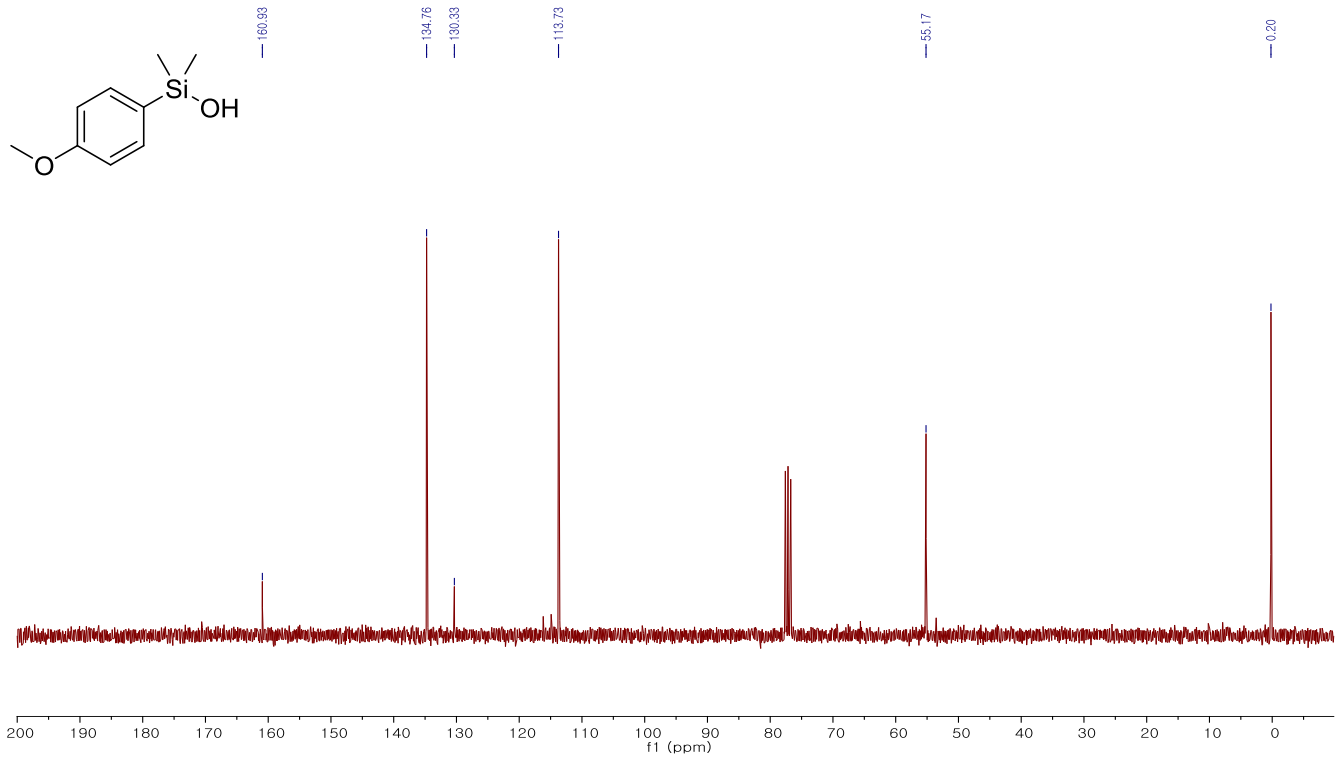

$^{13}$C NMR (**8d**) ($CDCl_3$)



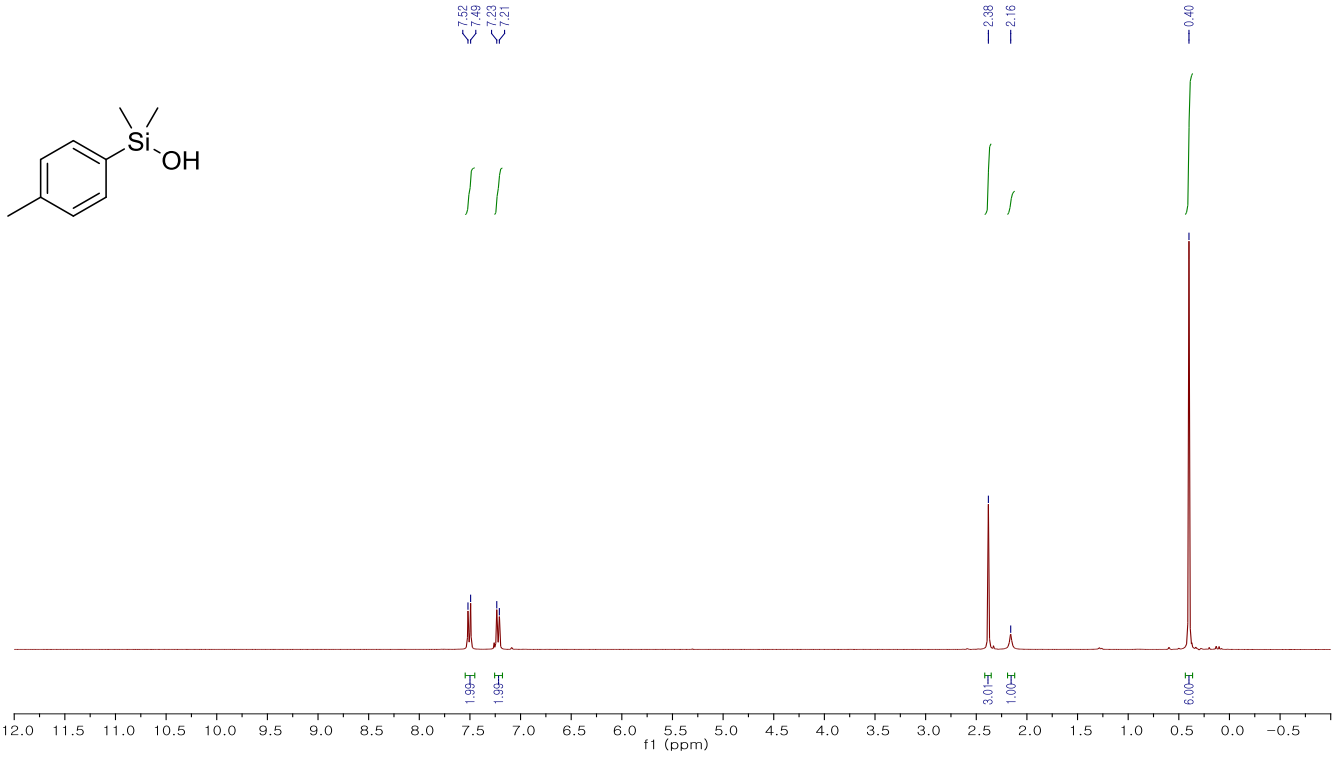
$^{1}$H NMR (**8e**) ($CDCl_3$)



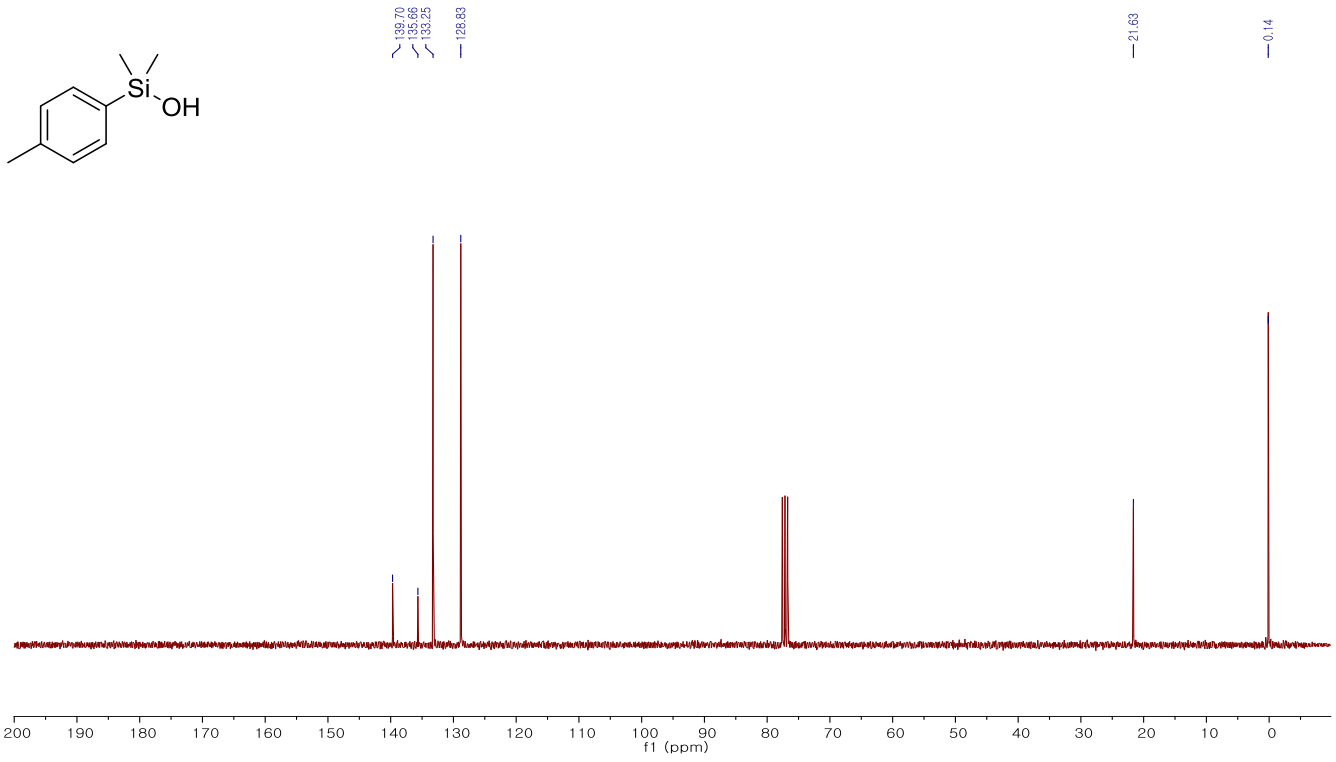

$^{13}$C NMR (**8e**) ($CDCl_3$)



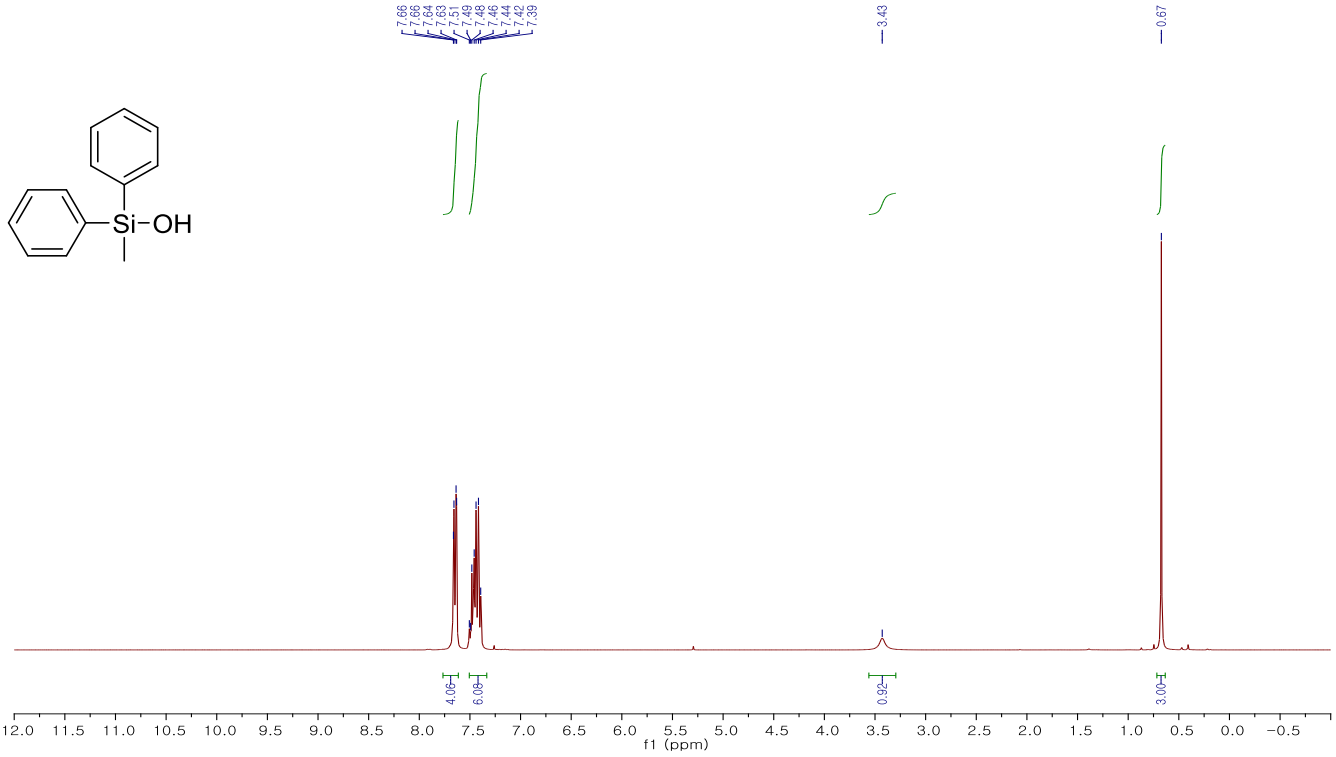
$^{1}$H NMR (**8f**) ($CDCl_3$)



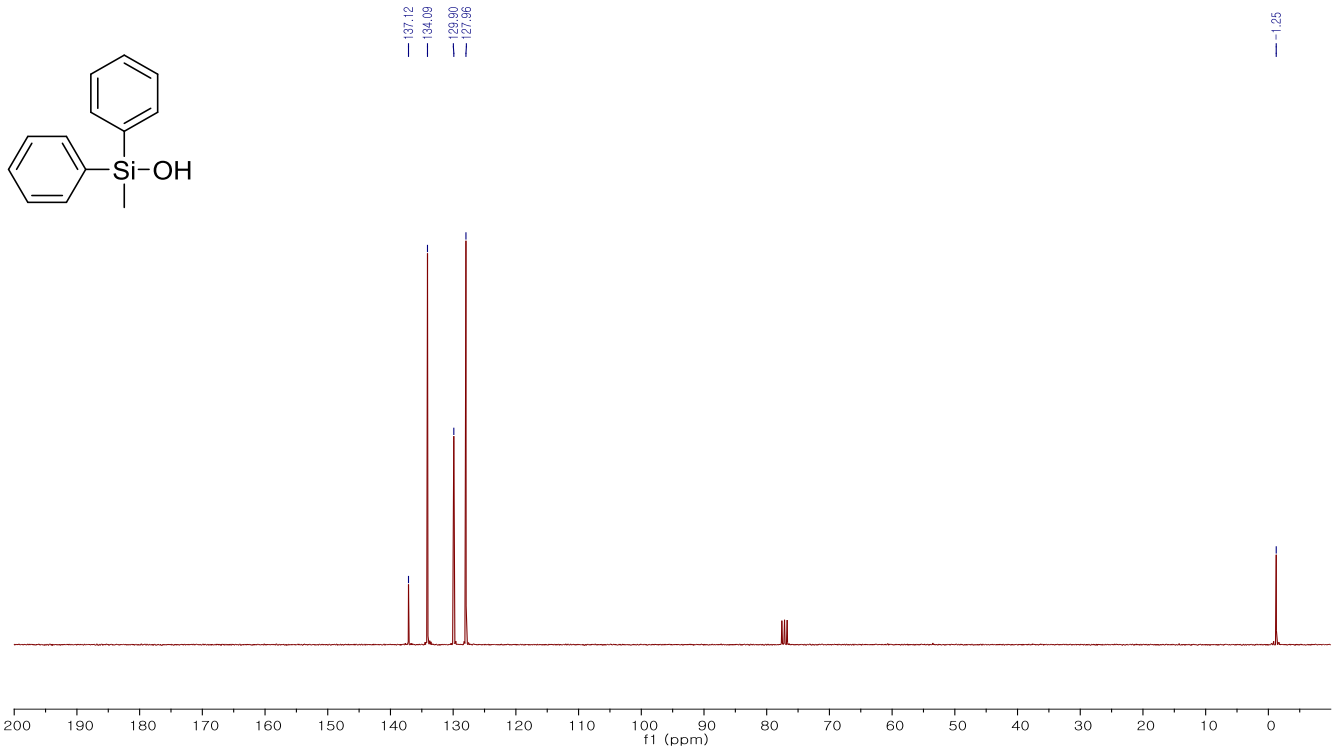

$^{13}$C NMR (**8f**) ($CDCl_3$)



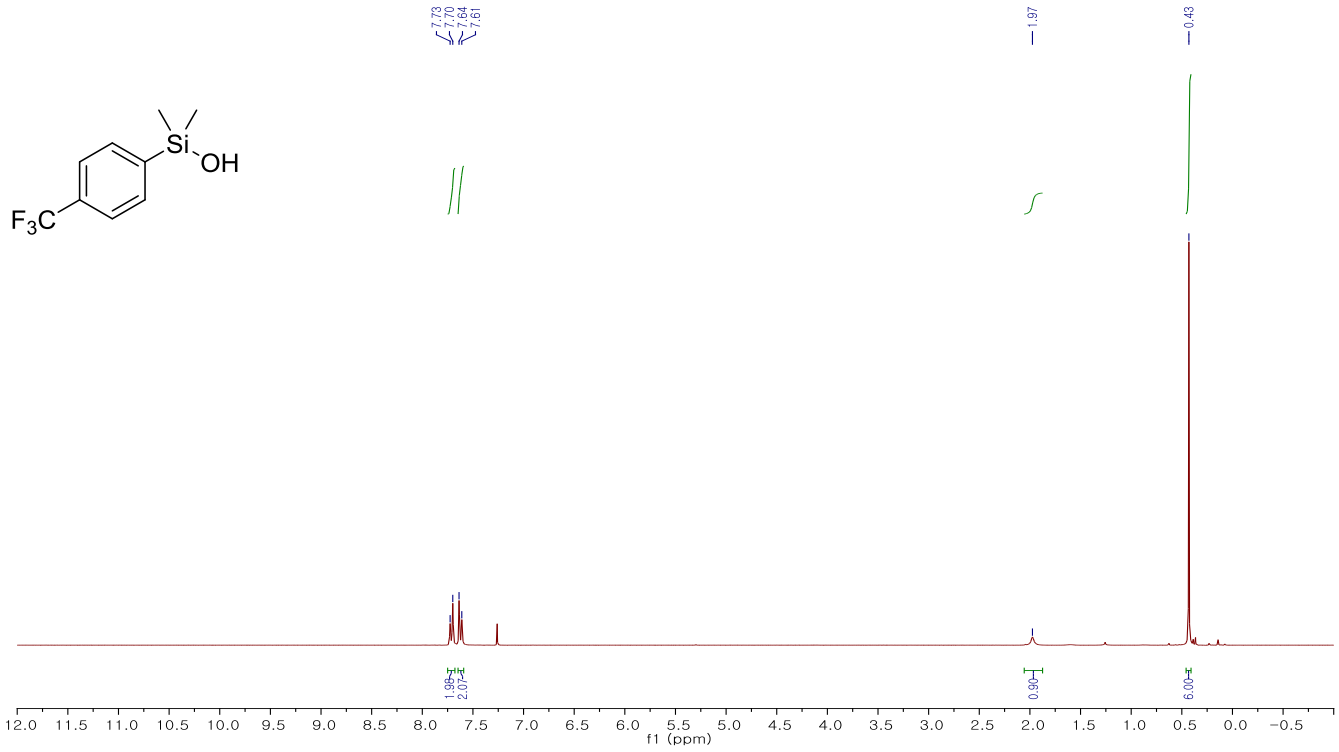
$^{1}$H NMR (**8g**) ($CDCl_3$)



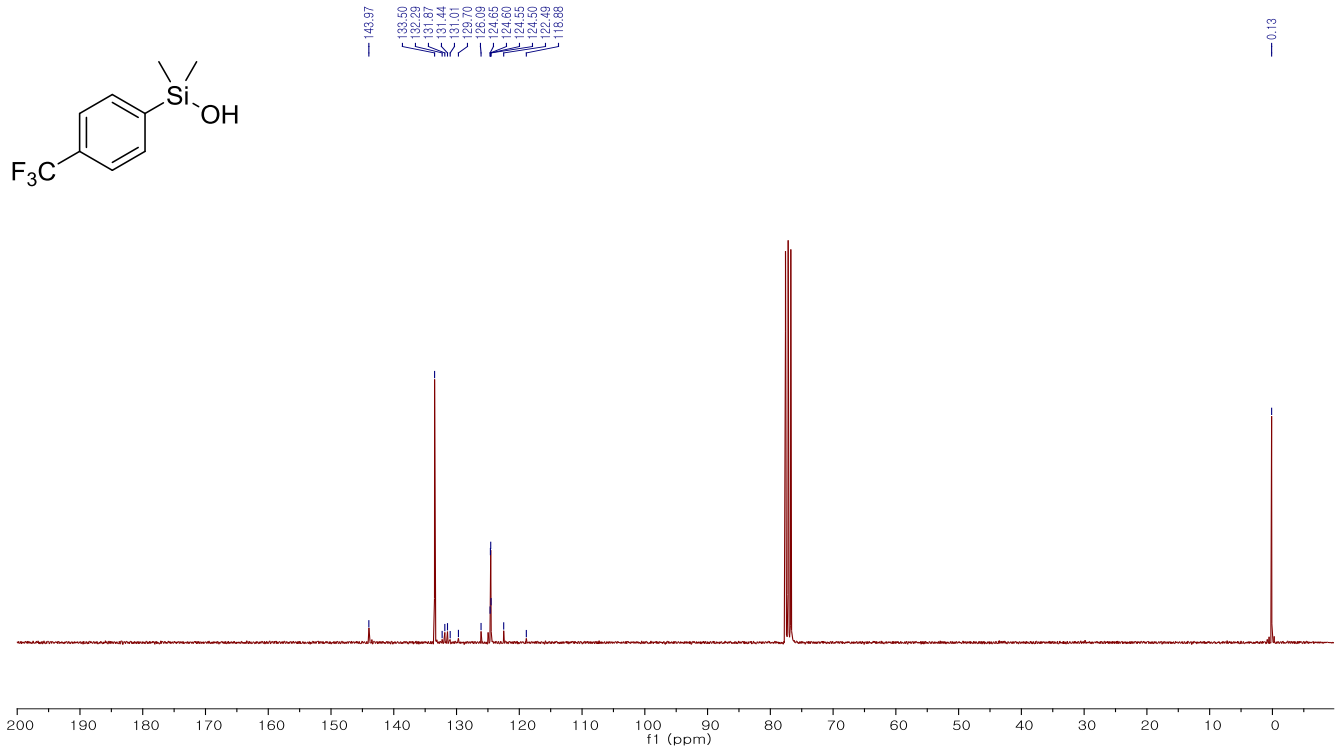

$^{13}$C NMR (**8g**) ($CDCl_3$)



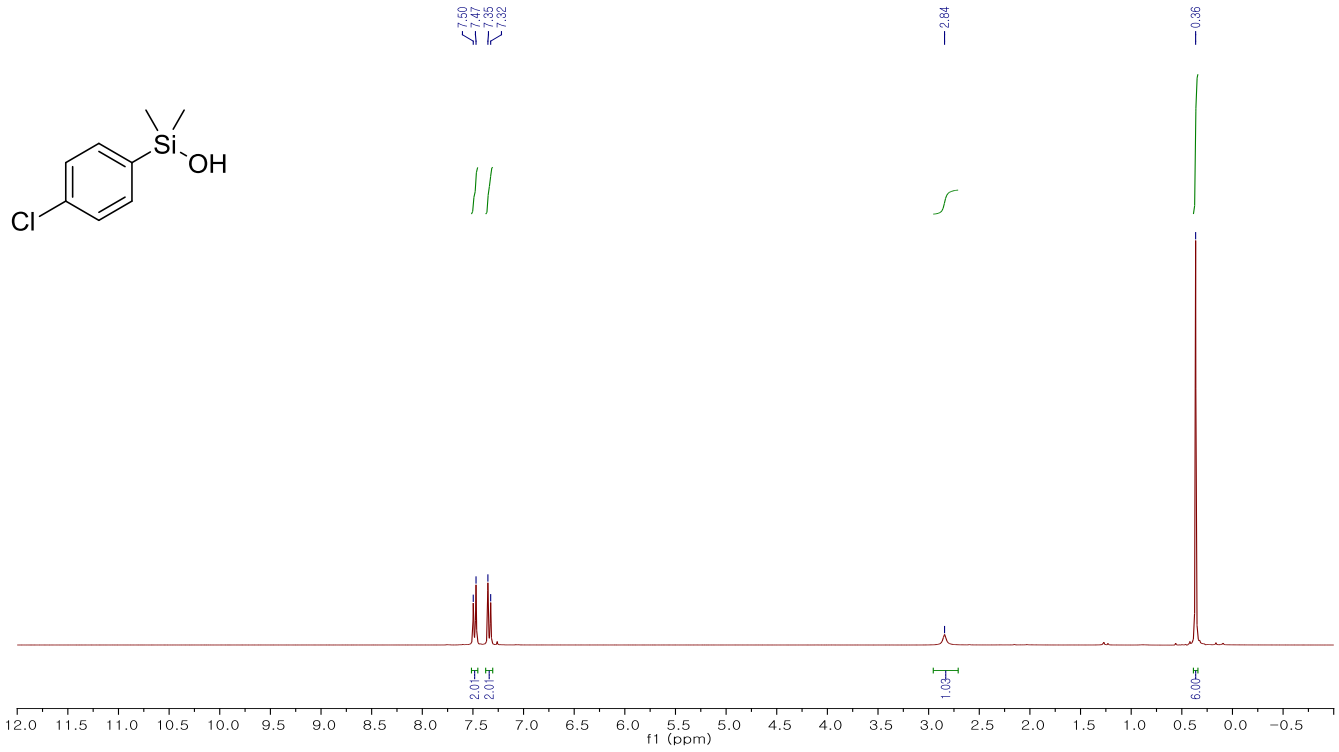
$^{1}$H NMR (**8h**) ($CDCl_3$)




$^{13}$C NMR (**8h**) ($CDCl_3$)



$^{1}$H NMR (**8i**) ($CDCl_3$)




$^{13}$C NMR (**8i**) ($CDCl_3$)