

## Supporting Information

### **Bentonite-Gold Nanohybrid as Heterogeneous Green Catalyst for Selective Oxidation of Silanes**

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## **1. Materials**

The bentonite clay used in the experiments was supplied by M/s Sigma Aldrich. The reagents and solvents were purchased from Alfa Aesar, Spectrochem and Merck and used without further purification. All reactions were carried out in oven dried glassware. Progress of the reactions was monitored by thin layer chromatography. Solvents were removed using Buchi E.L. rotary evaporator.

## **2. Experimental and Characterization Methods**

### **2.1. Syntheses of Au nanoparticles loaded organofunctionalized bentonites**

#### **2.1.1. Synthesis of acid activated bentonite (Ben-4h)**

Bentonite (10 g) was dispersed in 200 mL 4M hydrochloric acid and refluxed for 4 h. After cooling, the supernatant liquid was discarded and the activated bentonite was repeatedly dispersed in deionised water until the supernatant liquid was free from  $\text{Cl}^-$  ions. Then it was freeze dried using lyophilizer for overnight. All measurements were done at room temperature unless otherwise stated.

#### **2.1.2. Synthesis of organofunctionalized bentonite (Ben-MP)**

0.5 g of acid activated bentonite was mixed with (3-Mercaptopropyl)trimethoxysilane, MPTMS (0.525 g, 0.0027 moles) and phenyltriethoxysilane, PTES (0.502 g, 0.0021 moles) in toluene (15 mL) and stirred for 12 h at room temperature in argon atmosphere. Then the solvent was removed by filtration and the functionalized clay was washed with the same solvent followed by drying under vacuum.

#### **2.1.3. Synthesis of Au nanoparticle loaded organofunctionalised bentonite (Au-MPBen)**

0.5 g of organofunctionalized bentonite was impregnated with 30 mL aqueous solution of  $\text{HAuCl}_4$  (0.200 g, 0.005 moles) under vigorous stirring condition for 3 h. The filtrate was removed by centrifugation, resulted the formation of Au loaded organofunctionalized bentonite. Then it was dispersed in 10 mL water and reduced with  $\text{NaBH}_4$  (0.275 g in 20 mL distilled water, 0.007 moles) which was added slowly under vigorous stirring condition at room temperature for 3 h. Finally the product was centrifuged, washed several times with distilled water and dried at 60 °C for 12 h.

## 2.2. Characterization Techniques

NMR spectra were recorded on Bruker Avance 500 NMR spectrometer at 500 MHz ( $^1\text{H}$ ) and 125 MHz ( $^{13}\text{C}$ ). Chemical shifts are reported in  $\delta$  (ppm) relative to TMS as internal standard. Mass spectrum was recorded under ESI-HRMS using analyser type, orbitrap mass spectrometer (Thermo Exactive). IR spectra were recorded on Bruker Alpha-T FT-IR spectrometer and absorbances are reported in  $\text{cm}^{-1}$ . X-ray diffraction studies were carried out using a powder X-ray diffractometer (Philips X'Pert Pro) with  $\text{Cu K}\alpha$  radiation. Surface morphology was analysed using a FEI, TECNAI S Transmission Electron Microscopy (TEM). The electronic structure aspects of the sample were investigated using ESCA+ Omicron Nanotechnology apparatus with Al source by XPS (X-ray photoelectron spectroscopy). Elemental analysis was performed by ICP-MS (Inductively coupled plasma mass spectroscopy) using a Thermo Scientific ICAP Qc instrument.

## 2.3. Catalytic activity towards the oxidation of silanes

To a solution of dimethylphenylsilane (0.37 mmol, 0.050 g) in  $\text{THF:H}_2\text{O} / 7:3$  (1mL) under  $\text{O}_2$  atmosphere, the catalyst (1 mg, 52  $\mu\text{mol}$  %) was added. The reaction mixture was allowed to stir for 30 min at room temperature. The catalyst was removed by centrifugation, washed three times with ethylacetate, dried over  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum. The product (silanol) was obtained in 99 % yield without further purification.

## 3. Experimental Procedure for Mechanism Study

### a. Using $\text{D}_2\text{O}$

To a solution of dimethylphenylsilane (0.37 mmol, 0.050 g) in  $\text{THF:D}_2\text{O} / 7:3$  (1mL) under  $\text{O}_2$  atmosphere, the catalyst (1 mg, 52  $\mu\text{mol}$  %) was added. The reaction mixture was allowed to stir for overnight at room temperature. The catalyst was removed by centrifugation, washed three times with ethylacetate, dried over  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum to afford deuterium incorporated silanol in quantitative yield. This was confirmed by ESI-HRMS analysis which gave  $\text{M}^+$  ion peak at 153.

### b. Using $\text{CD}_3\text{OD}$

To a solution of dimethylphenylsilane (0.37 mmol, 0.050 g) in  $\text{THF:CD}_3\text{OD} / 7:3$  (1mL) under  $\text{O}_2$  atmosphere, the catalyst (1 mg, 52  $\mu\text{mol}$  %) was added. The reaction mixture was allowed to stir for overnight at room temperature. The catalyst was removed by centrifugation, washed three

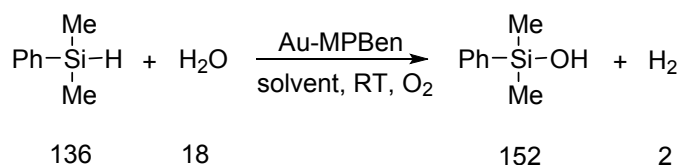
times with ethylacetate, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum to afford deuterium incorporated methoxydimethylphenylsilane in quantitative yield. This was confirmed by ESI-HRMS analysis which gave [M+H]<sup>+</sup> ion peak at 170.

#### 4. Calculation of Atom Economy

Atom economy of the reaction was calculated using the formula,

$$\text{Atom economy} = (\text{mass of product}/\text{mass of all product}) \times 100$$

For the oxidation of silane to silanol,



$$\text{Atom Economy} = (152 \times 100)/154 = 98.7\%$$

#### 5. Calculation of TON and TOF

TON and TOF values based on the total amount of gold were calculated as

$$\begin{aligned}
 \text{TON} &= \text{total amount of product (mol)}/\text{total amount of gold (mol)} \\
 &= 0.0073/3.67 \times 10^{-6} \\
 &= 1990
 \end{aligned}$$

$$\begin{aligned}
 \text{TOF} &= \text{TON}/\text{time ( h )} \\
 &= 1990/6 \\
 &= 332 \text{ h}^{-1}
 \end{aligned}$$

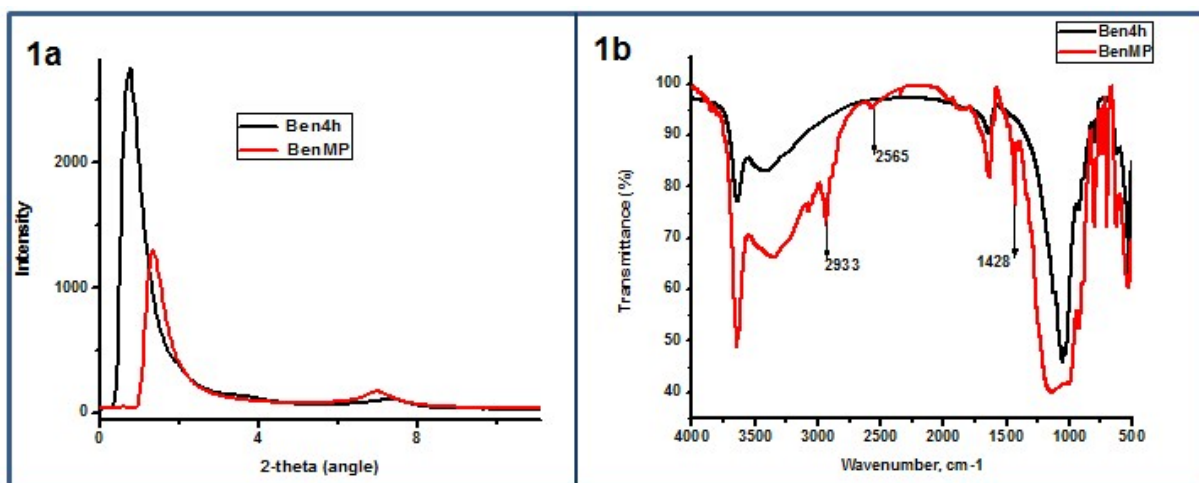
The fraction of gold atoms exposed to the surface of AuNP was calculated based on the work of Boudart and Djéga-Mariadassou.<sup>1</sup>The strength or percentage of gold nanoparticles that are exposed to substrate is approximately 0.9/d, where d is the spherical metal particle diameter in nm. Thus gold nanoparticles with a diameter of 4 nm have about 22.5% (0.9/4 nm) of their atoms lying at the surface of the AuNP. As a result, adjusted TON and TOF values adjusted TON and TOF values based on surface atoms are 8844 and 1475 h<sup>-1</sup>, respectively.

1. M. Boudart, G. Djéga-Mariadassou in *Kinetics of Heterogeneous Catalytic Reactions*, Princeton University Press, Princeton, N. J., 1984, pp 26.

## 6. Recycling Experiment

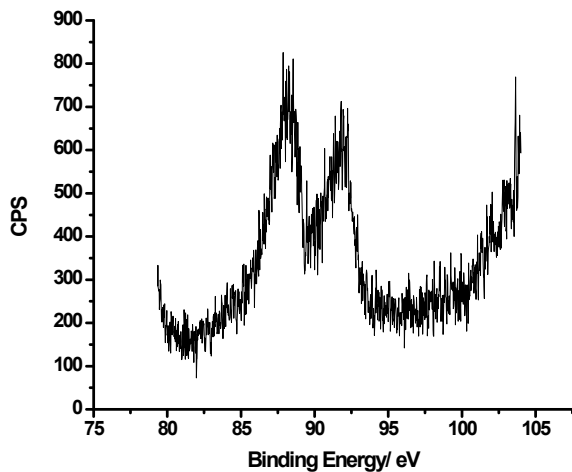
To a solution of dimethylphenylsilane (0.37 mmol, 0.050 g) in THF:H<sub>2</sub>O / 7:3 (1mL) under O<sub>2</sub> atmosphere, the catalyst (1 mg, 52 μmol %) was added. The reaction mixture was allowed to stir for 30 min at room temperature. The catalyst was removed by centrifugation, washed three times with ethylacetate, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The product (silanol) was obtained in 99 % yield without further purification. The catalyst was reused for the second reaction after washing with THF. The oxidation reaction was repeated for four more cycles by reusing the recycled catalyst from the previous reaction. After fifth run, TEM analysis was carried out to ensure the morphology of the catalyst.

## 7. XRD pattern and IR spectra of Ben-4h and Ben-MP



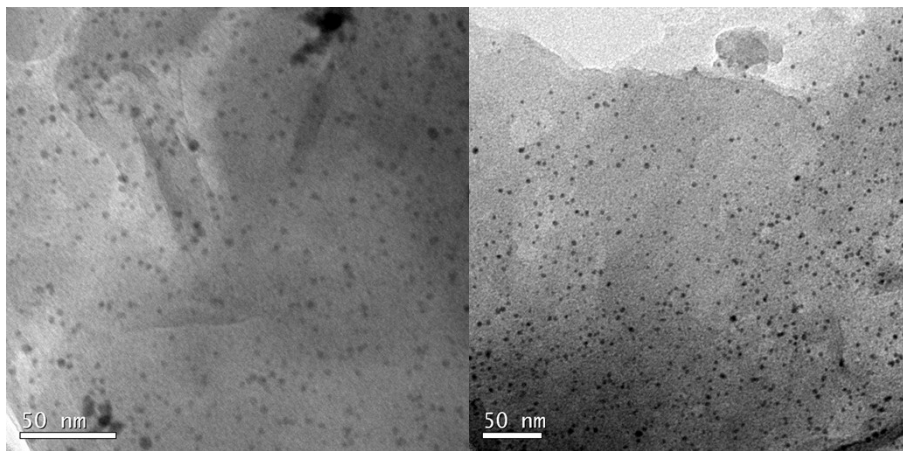
**SFig. 1a)** XRD pattern of acid activated bentonite (Ben-4h) and organofunctionalised bentonite (Ben-MP). **1b)** IR spectra of acid activated bentonite (Ben-4h) and organofunctionalised bentonite (Ben-MP).

## 8. XPS spectrum of the Catalyst (Au-MPBen)



SFig.2 XPS spectrum of Au-MPBen

## 9. TEM image of the Catalyst (Au-MPBen) after 1<sup>st</sup> and 5<sup>th</sup> use



SFig. 3 TEM images of Au-MPBen after 1<sup>st</sup> and 5<sup>th</sup> use (scale bar=50 nm).

## 10. Spectral Characterization

### Dimethylphenylsilanol

**<sup>1</sup>H NMR** (500 MHz; CDCl<sub>3</sub>) δ (ppm): 7.59-7.57 (m, 2H), 7.39-7.35 (m, 3H), 2.35 (brs, 1H), 0.39 (s, 6H). **<sup>13</sup>C NMR** (125 MHz; CDCl<sub>3</sub>) δ (ppm): 139.2, 133.2, 129.8, 128.0, 0.09. **MS** (ESI-HRMS, m/z): Calcd for C<sub>8</sub>H<sub>12</sub>OSi, [M-H]<sup>-</sup>: 151.0584, Found: 151.0570.

### Dimethylbenzylsilanol

**<sup>1</sup>H NMR** (500 MHz; CDCl<sub>3</sub>) δ (ppm): 7.25-7.21 (m, 2H), 7.10-7.05 (m, 3H), 2.17 (s, 2H), 1.89 (brs, 1H), 0.13 (s, 6H). **<sup>13</sup>C NMR** (125 MHz; CDCl<sub>3</sub>) δ (ppm): 139.2, 128.5, 128.3, 124.4, 28.2, -0.59. **MS** (ESI-HRMS, m/z): Calcd for C<sub>9</sub>H<sub>14</sub>OSi, [M-H]<sup>-</sup>: 165.0741, Found: 165.0739.

### Methyldiphenylsilanol

**<sup>1</sup>H NMR** (500 MHz; CDCl<sub>3</sub>) δ (ppm): 7.58-7.57 (m, 4H), 7.41-7.33 (m, 6H), 2.68 (s, 1H), 0.63 (s, 3H). **<sup>13</sup>C NMR** (125 MHz; CDCl<sub>3</sub>) δ (ppm): 137.2, 134.1, 130.0, 128.0, -1.16. **MS** (ESI-HRMS, m/z): Calcd for C<sub>13</sub>H<sub>14</sub>OSi, [M-H]<sup>-</sup>: 213.0741, Found: 213.0739.

### Diphenylsilanediol

**<sup>1</sup>H NMR** (500 MHz; acetone-d<sub>6</sub>) δ (ppm): 7.57-7.56 (m, 4H), 7.26-7.18 (m, 6H), 5.86 (s, 2H). **<sup>13</sup>C NMR** (125 MHz; acetone-d<sub>6</sub>) δ (ppm): 138.3, 135.2, 130.3, 128.3. **MS** (ESI-HRMS, m/z): Calcd for C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>Si, [M-H]<sup>-</sup>: 215.0534, Found: 215.0532.

### Triphenylsilanol

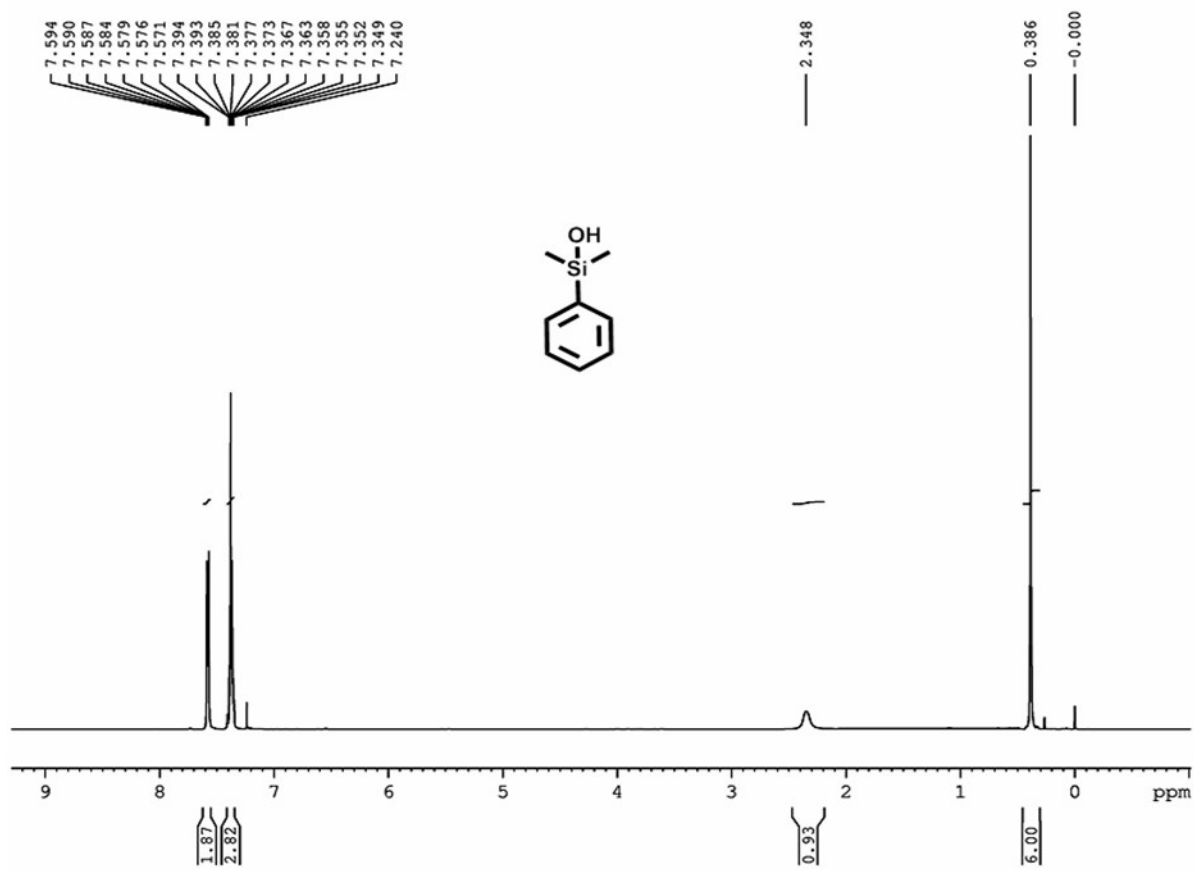
**<sup>1</sup>H NMR** (500 MHz; CDCl<sub>3</sub>) δ (ppm): 7.60 (d, 1H, 6H), 7.44-7.40 (m, 3H), 7.37-7.34 (m, 6H), 2.84 (brs, 1H). **<sup>13</sup>C NMR** (125 MHz; CDCl<sub>3</sub>) δ (ppm): 135.2, 135.0, 130.1, 128.0. **MS** (ESI-HRMS, m/z): Calcd for C<sub>18</sub>H<sub>16</sub>OSi, [M-H]<sup>-</sup>: 275.0897, Found: 275.0894.

### 1, 4-Bis(hydroxydimethylsilyl)benzene

**<sup>1</sup>H NMR** (500 MHz; DMSO-d<sub>6</sub>) δ (ppm): 7.53 (s, 4H), 5.88 (brs, 2H), 0.23 (s, 12H). **<sup>13</sup>C NMR** (125 MHz; DMSO-d<sub>6</sub>) δ (ppm): 141.3, 132.1, 0.57. **MS** (ESI-HRMS, m/z): Calcd for C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>Si<sub>2</sub>, [M-H]<sup>-</sup>: 225.0772, Found: 225.0771.

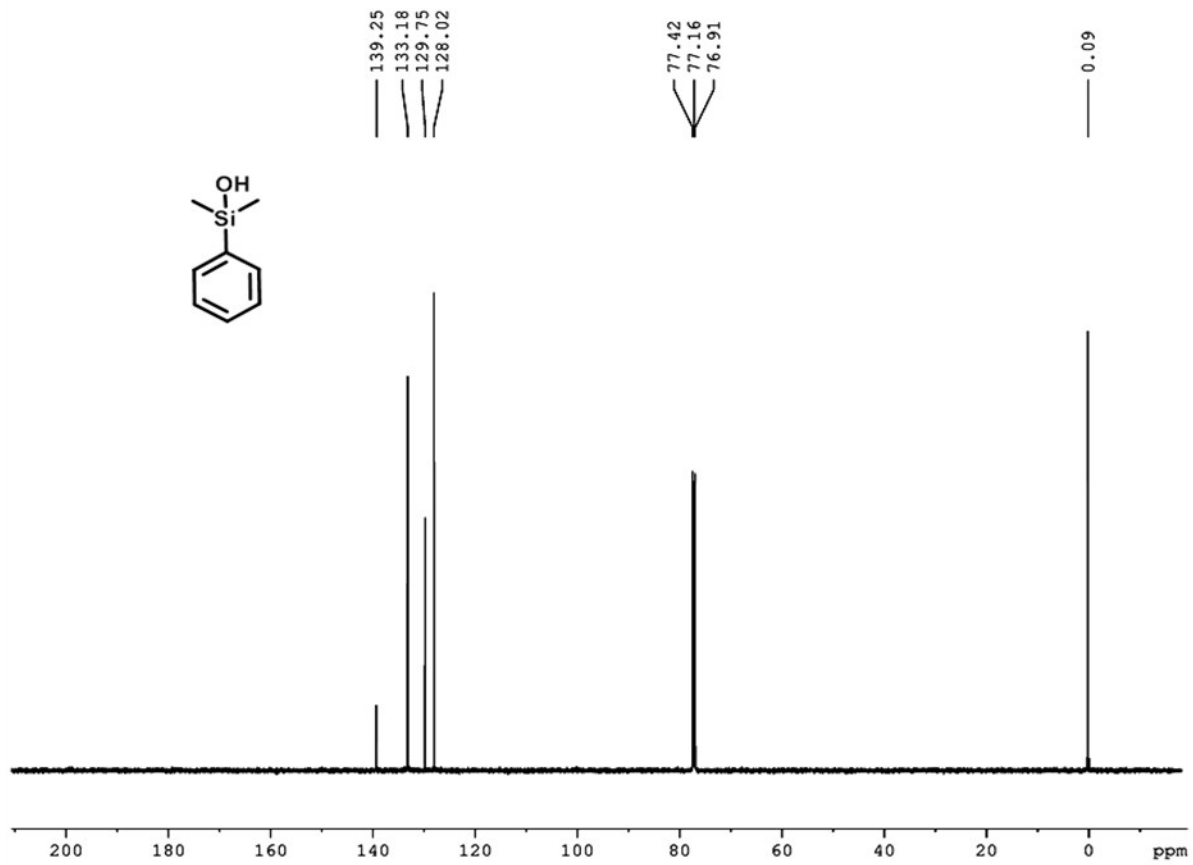
### Triisopropylsilanol

**<sup>1</sup>H NMR** (500 MHz; CDCl<sub>3</sub>) δ (ppm): 5.01 (s, 1H), 1.43 (s, 21H). **<sup>13</sup>C NMR** (125 MHz; CDCl<sub>3</sub>) δ (ppm): 30.3, 21.1. **MS** (ESI-HRMS, m/z): Calcd for C<sub>9</sub>H<sub>22</sub>OSi, [M-H]<sup>-</sup>: 173.1367, Found: 173.1364.

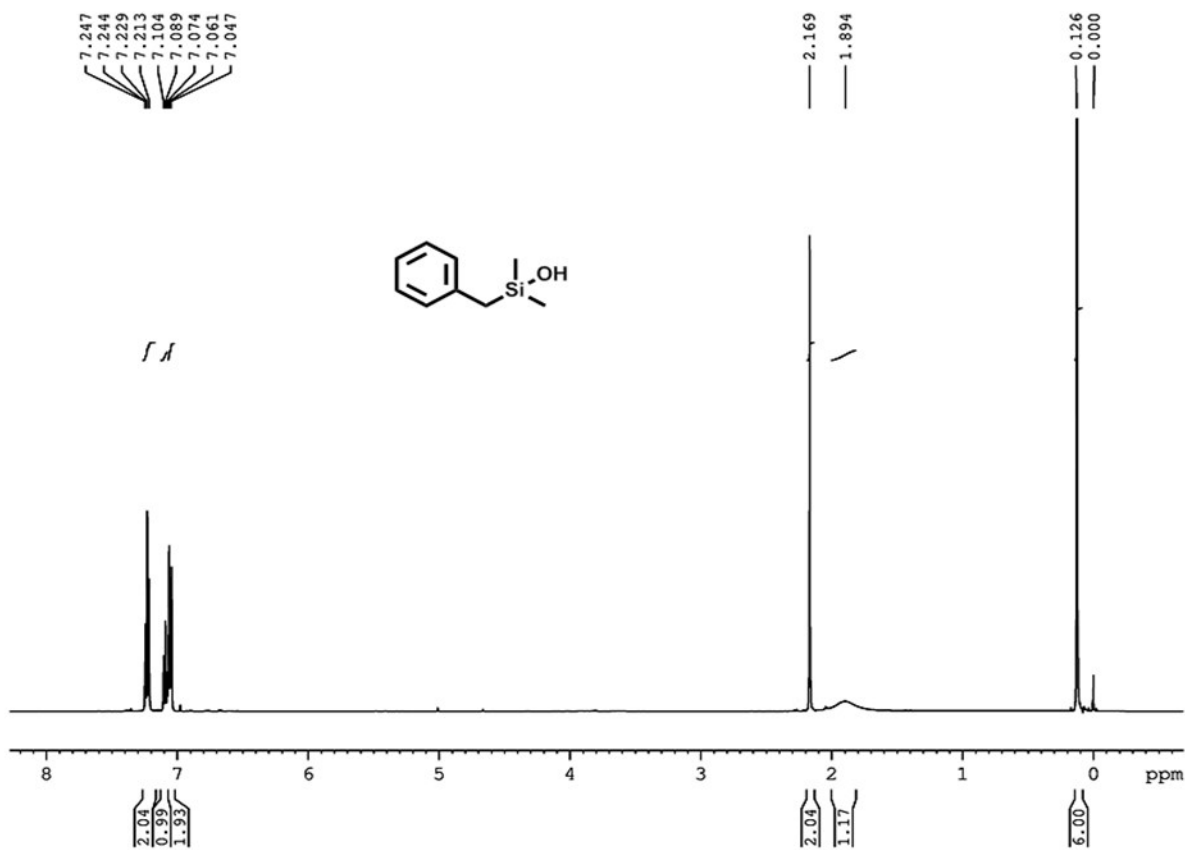


S1:  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ) of Dimethylphenylsilanol

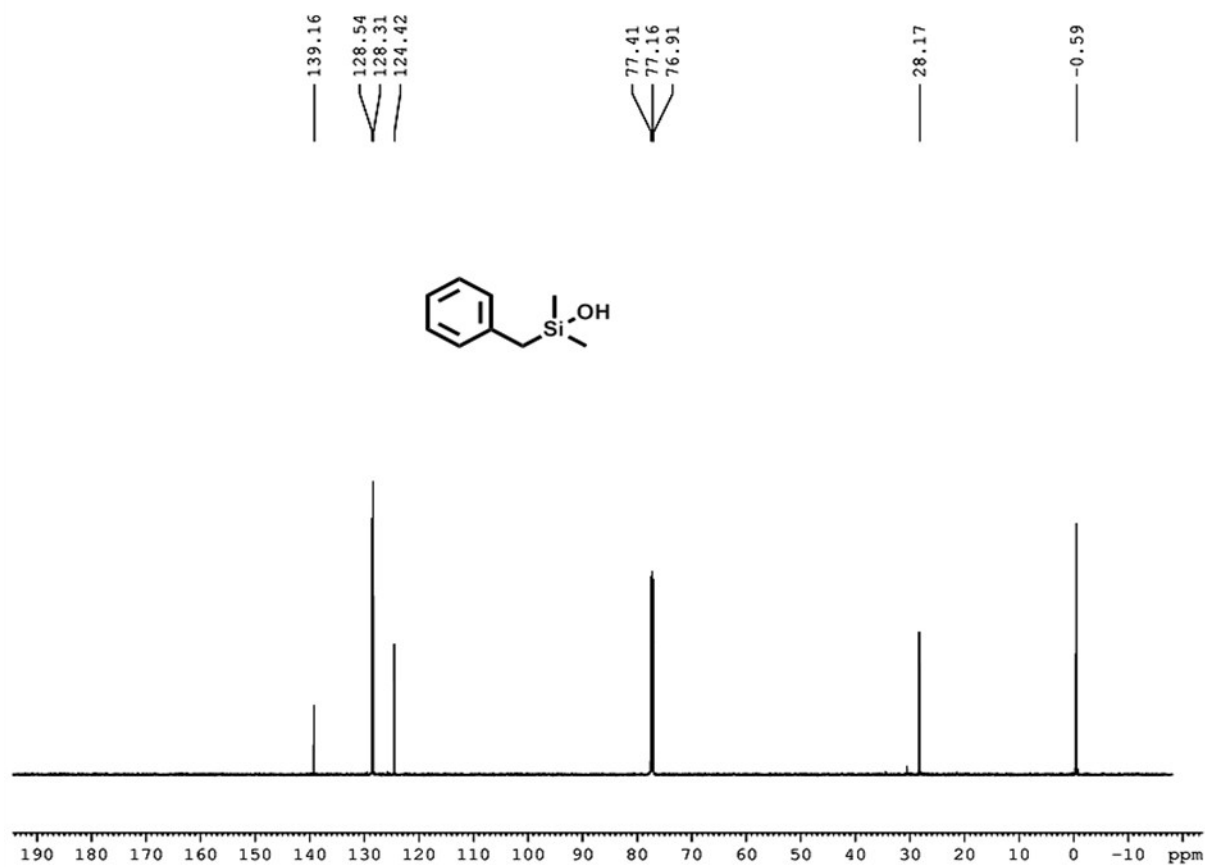




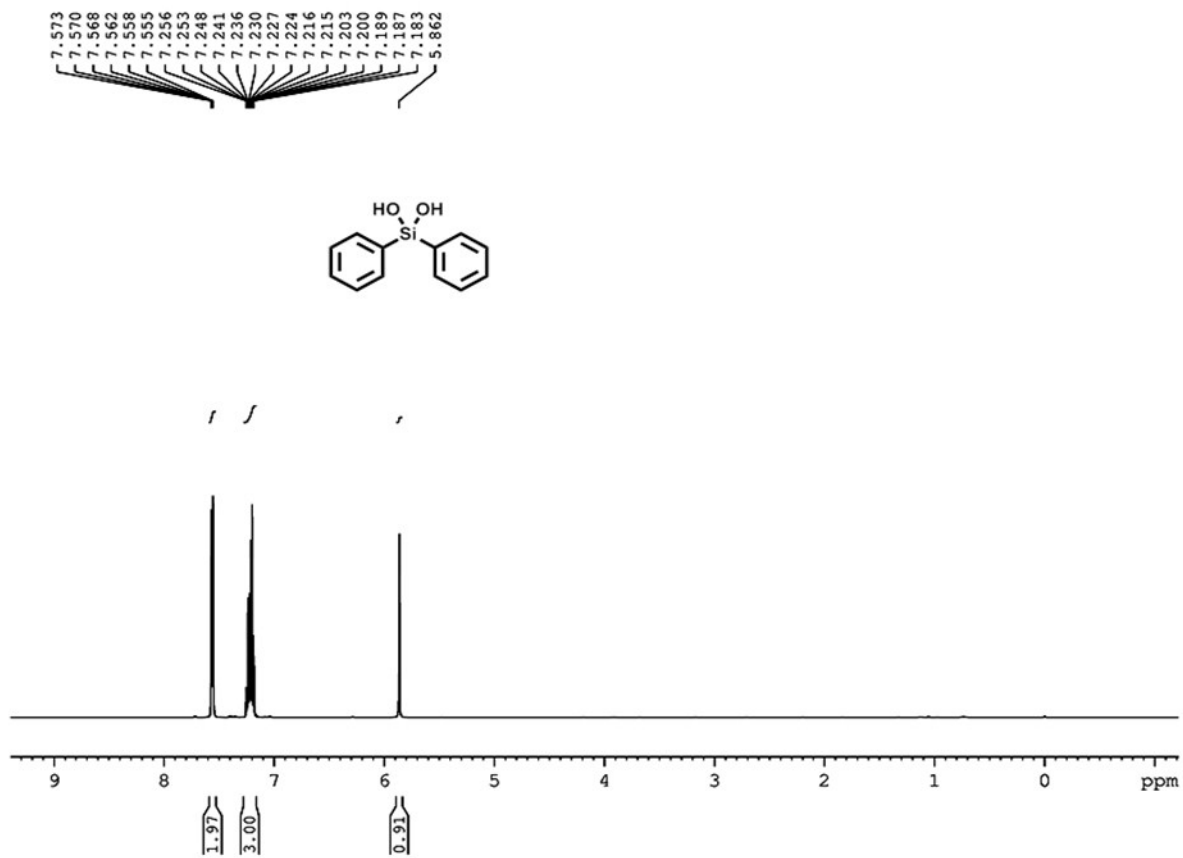
**S2:**  $^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ) of Dimethylphenylsilanol



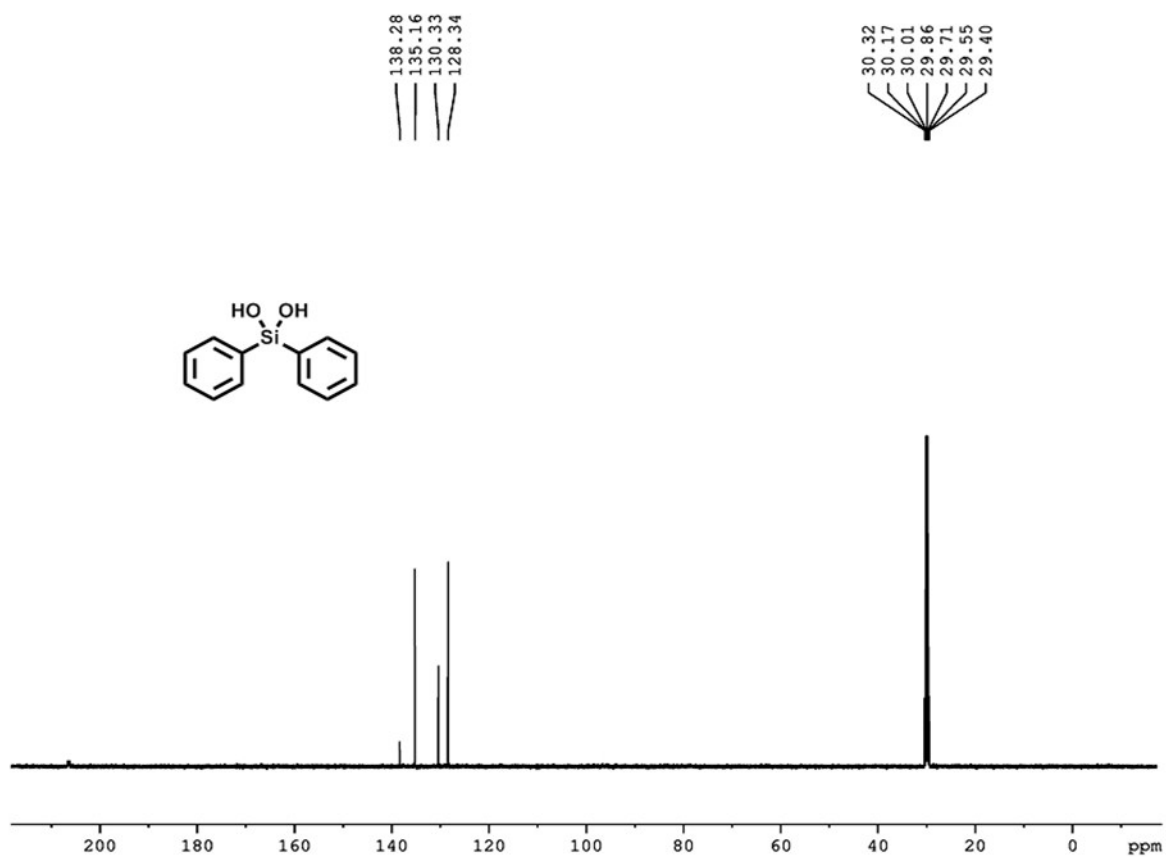
S3:  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ) of Dimethylbenzylsilanol



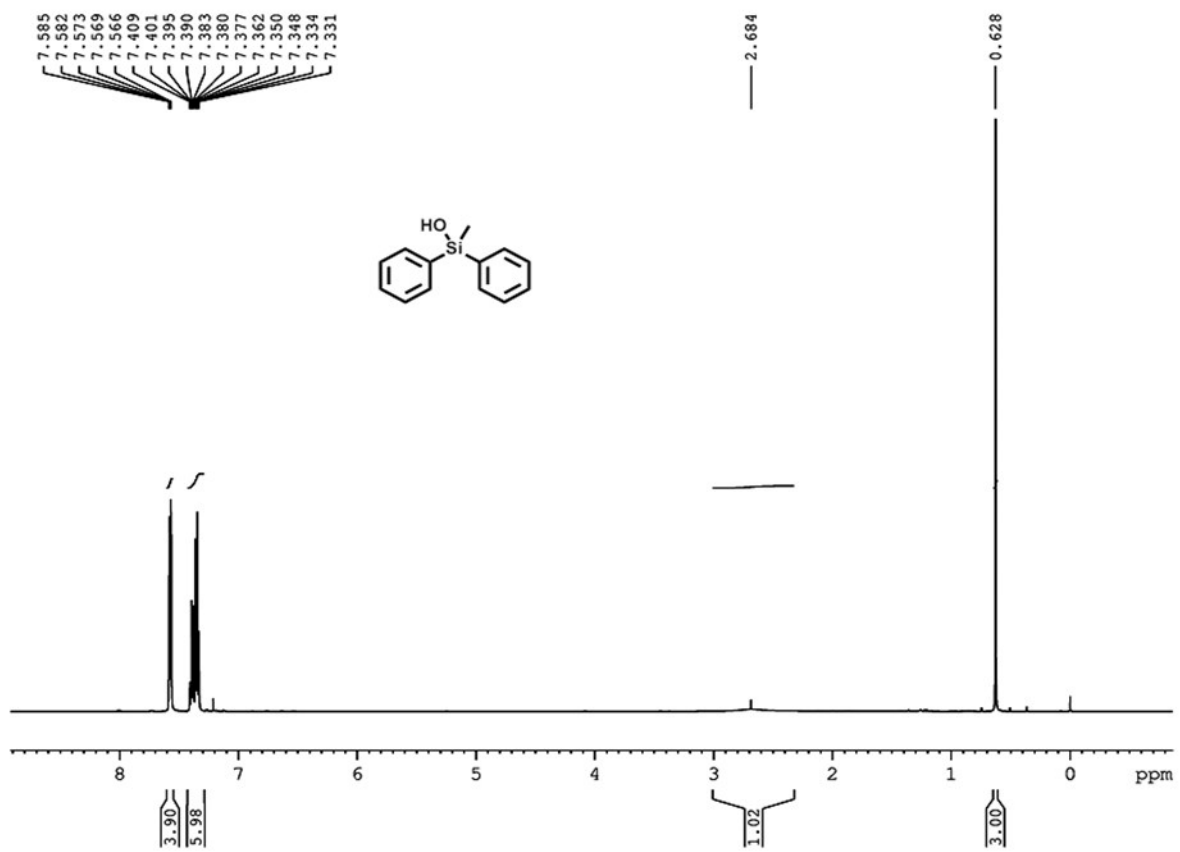
**S4:**  $^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ) of Dimethylbenzylsilanol



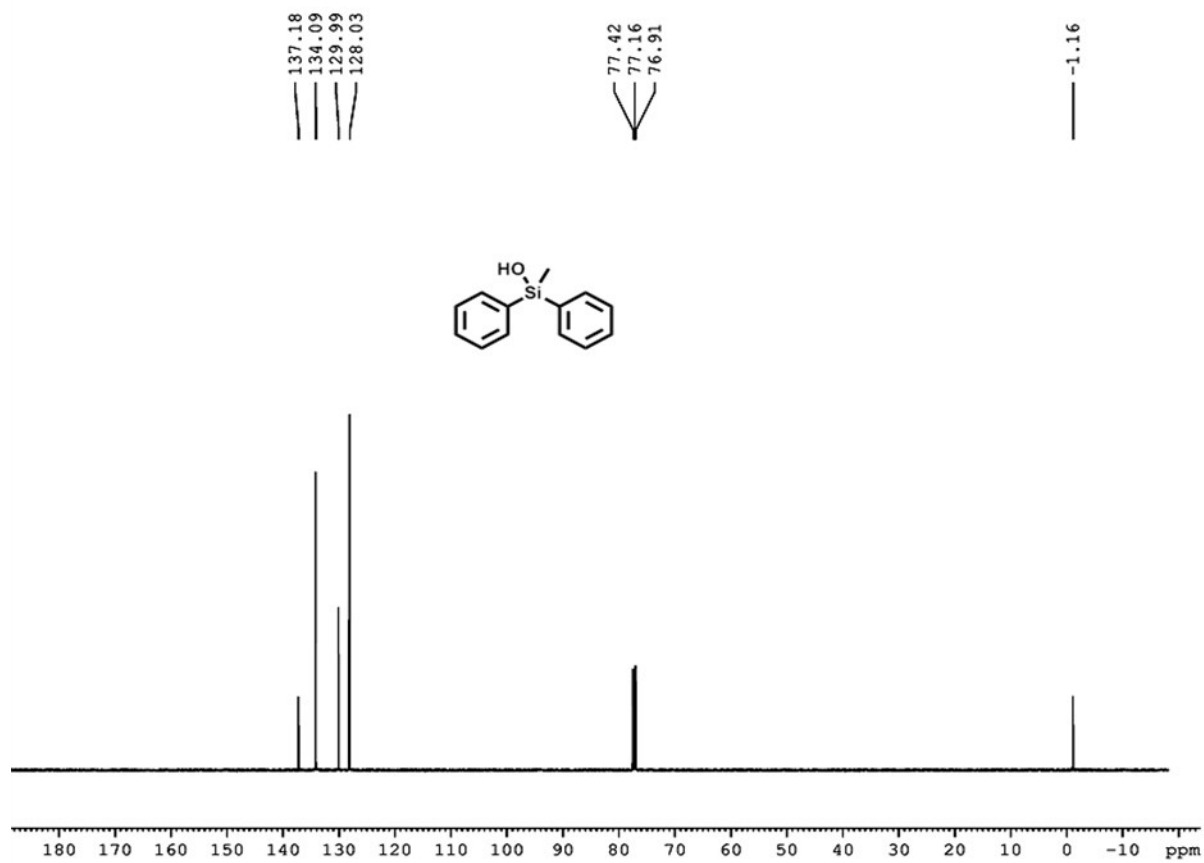
**S5:**  $^1\text{H}$  NMR (500 MHz; Acetone- $\text{d}_6$ ) of Diphenylsilanediol



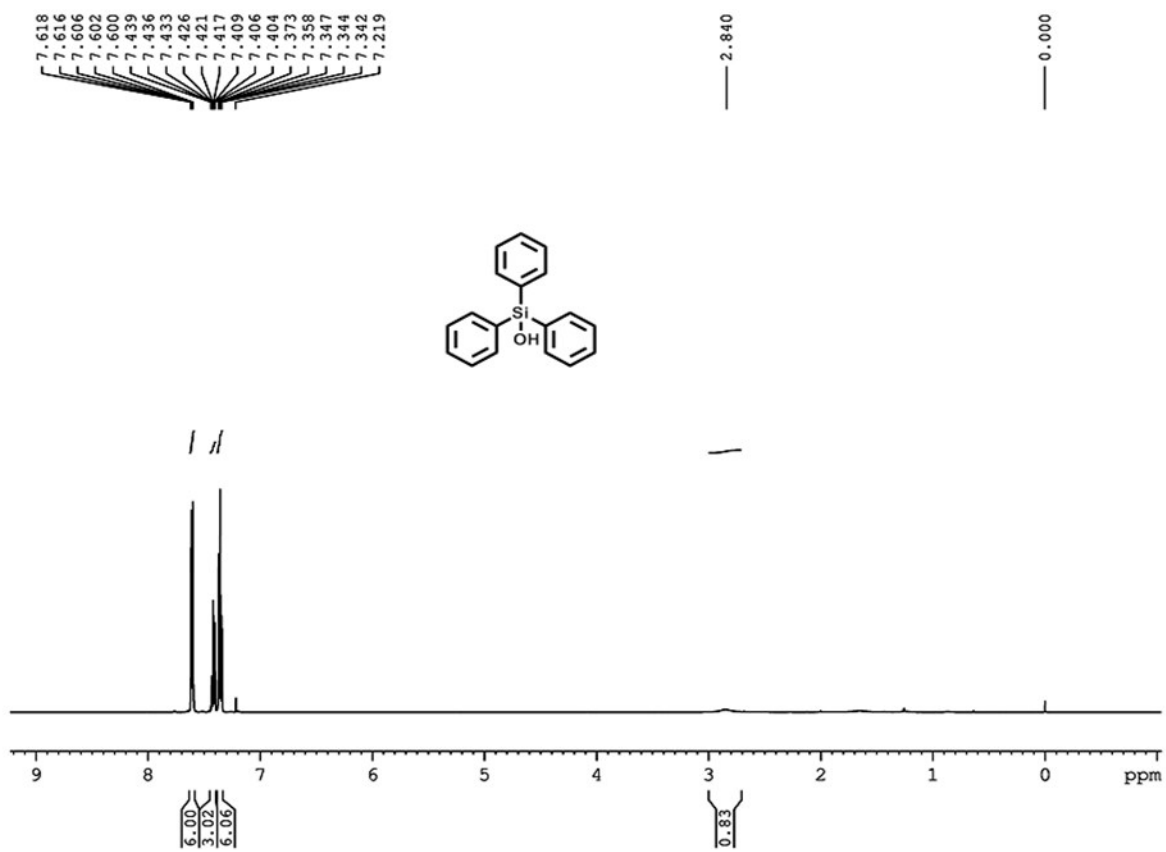
**S6:**  $^{13}\text{C}$  NMR (125 MHz; Acetone-  $\text{d}_6$ ) of Diphenylsilanediol



S7:  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ) of Methylphenylsilanol

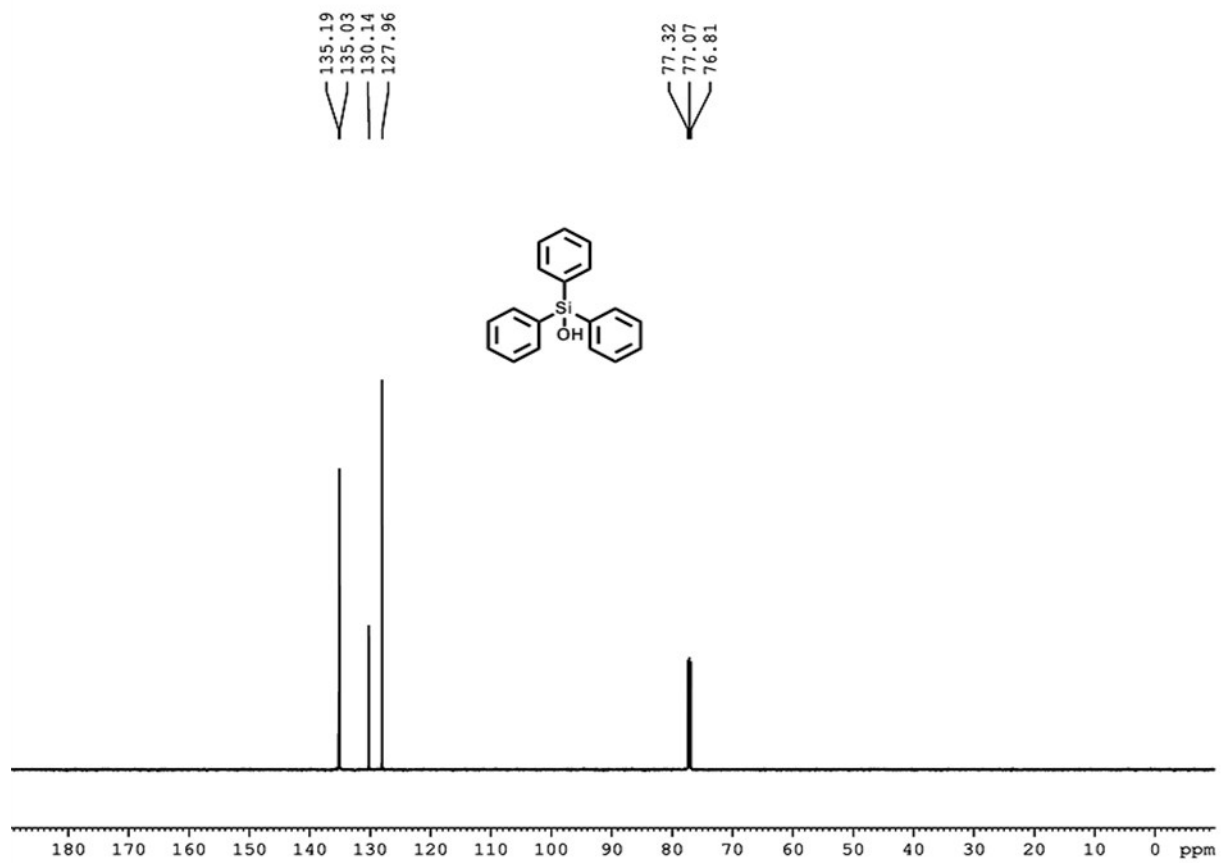


**S8:**  $^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ) of Methylphenylsilanol

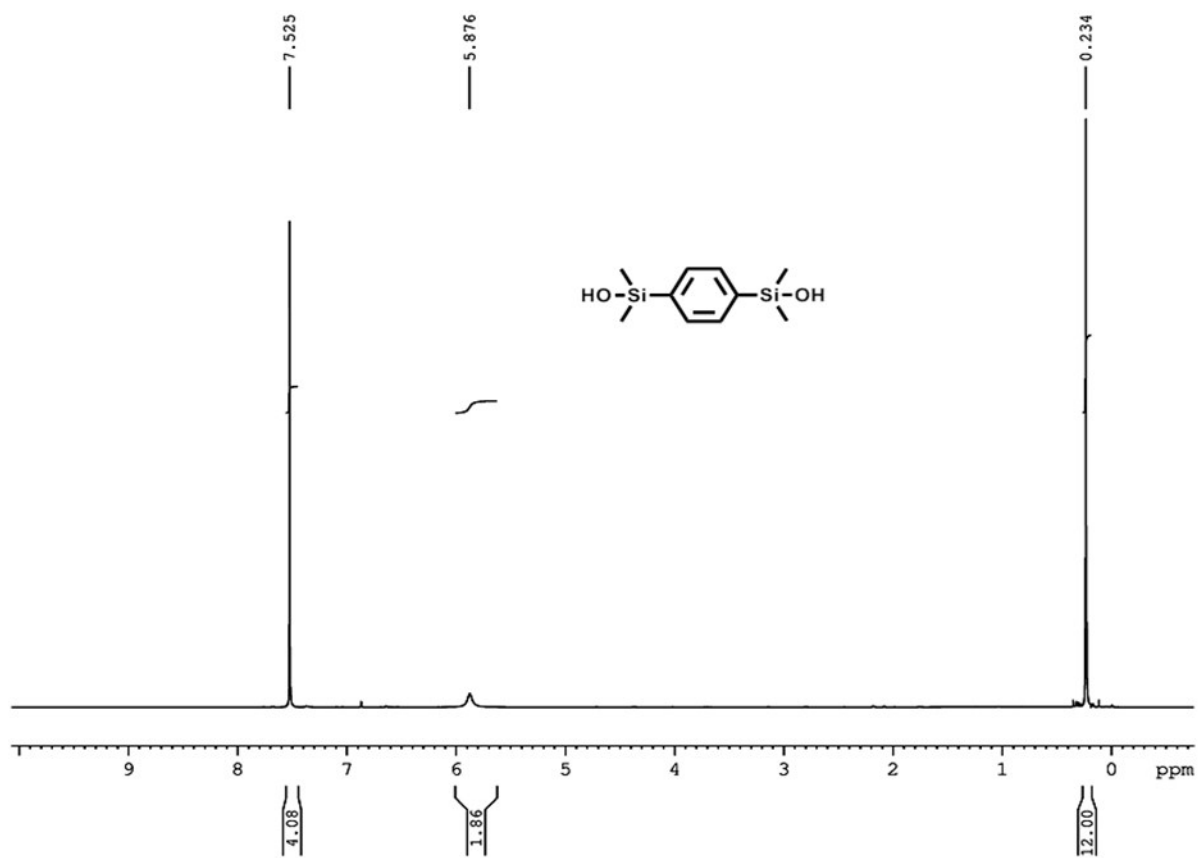


S9:  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ) of Triphenylsilanol

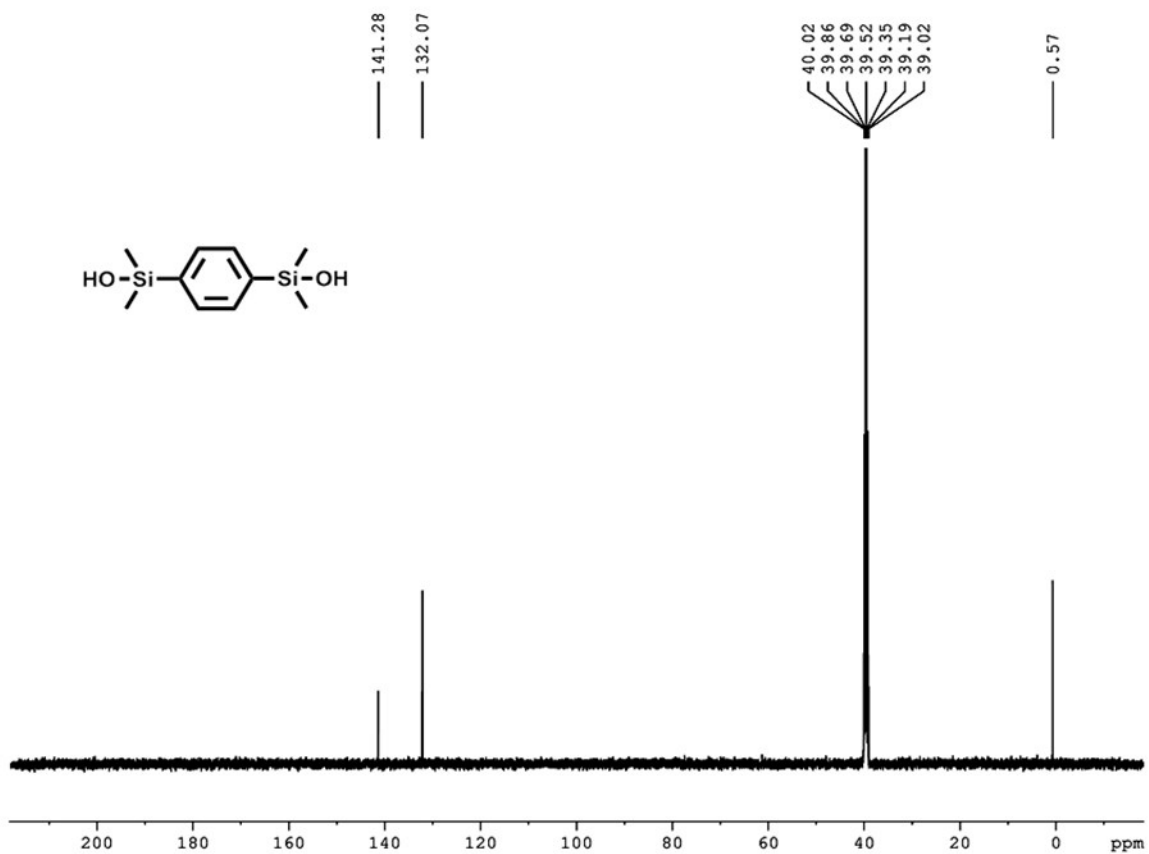




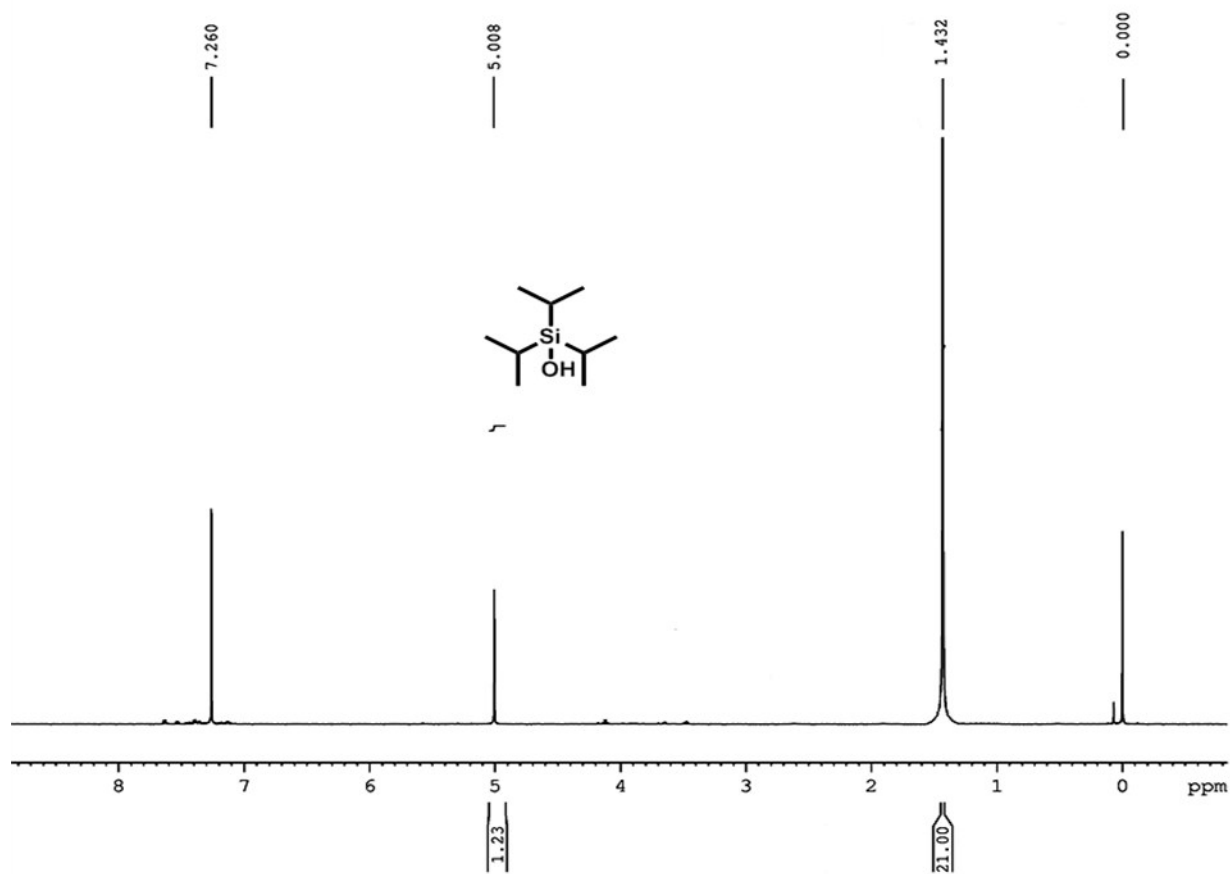
S10:  $^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ) of Triphenylsilanol



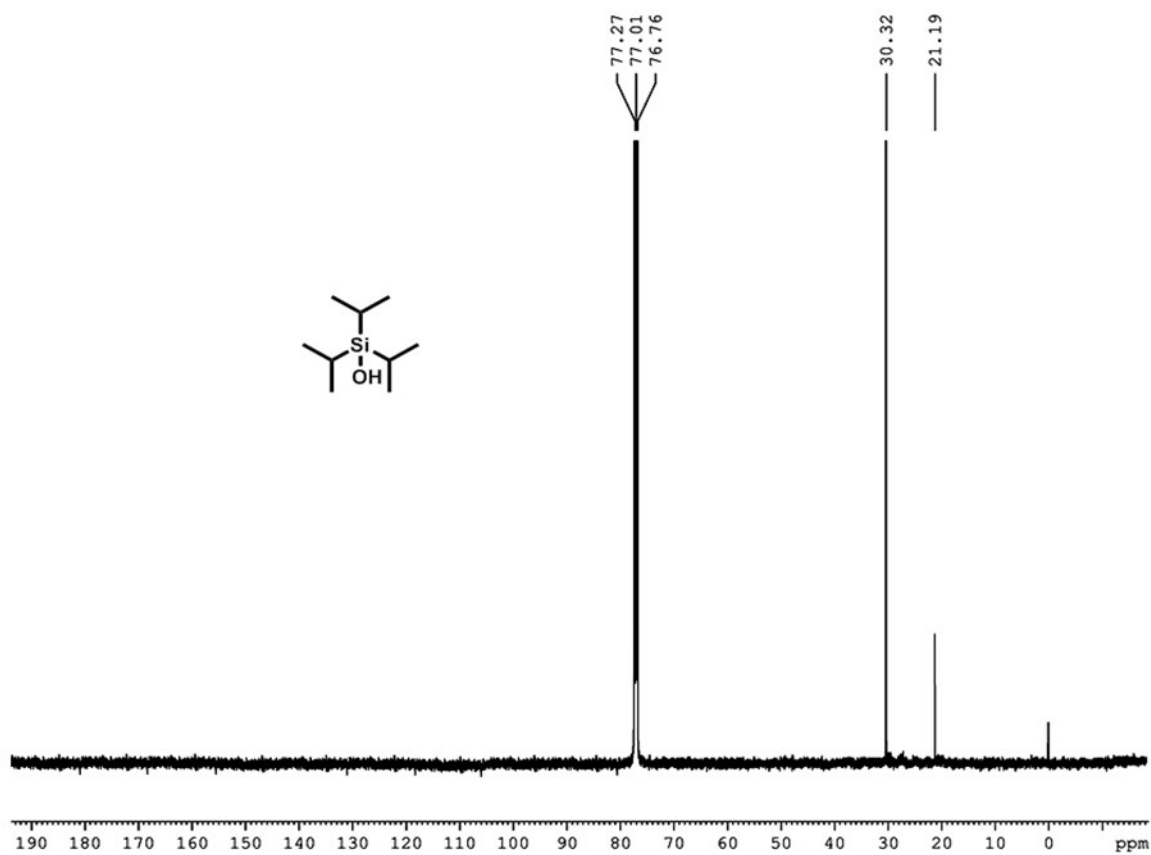
**S11:**  $^1\text{H}$  NMR (500 MHz; DMSO- $d_6$ ) of 1,4-Bis(hydroxydimethylsilyl)benzene



**S12:**  $^{13}\text{C}$  NMR (125 MHz; DMSO- $\text{d}_6$ ) of 1,4-Bis(hydroxydimethylsilyl)benzene



**S13:**  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ) of Triisopropylsilanol



**S14:**  $^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ) of Triisopropylsilanol