Silylation Reactions on Nanoporous Gold via Homolytic Si-H Activation of Silanes

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Supporting Information

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1. Preparation of the nanoporous gold (NPG):

High purity (> 99.99%) Ag and Au were melted at 1100 ºC in air to prepare Au/Ag alloy, which was cold-rolled down to thickness of 25 μm. Foil samples were cleaned in ethanol and pure water in a sonicator, and then 70% (wt.) nitric acid was used to achieve the nanoporous structure by leaching of silver for 18 hours at room temperature. Final samples were washed to neutral with pure water and dried in a desiccator at room temperature in air.

Reference: *Angew. Chem. Int. Ed.* **2010**, *49*, 10093-10095

An FEI Verios 460L field emission scanning electron microscope, equipped with an Oxford INCA x-sight Energy Dispersive X-ray Spectrometer (EDS) was used to acquire SEM images and chemical composition information.

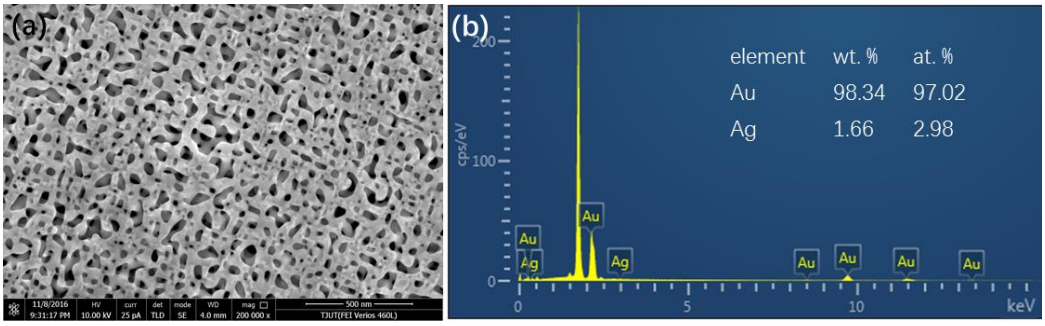


Figure S1. (a) Scanning electron microscopy (SEM) image and (b) EDS analyses of nanoporous gold foils.

2. The TON (turnover number) and the TOF (turnover frequency)

TON is defined as the ratio of product molecules per active site of catalyst [see the SI of *Science* **327**, 319 (2009)]. BET surface area = 4 m^2/g. It was assumed that every surface atom is an active site as an upper limit. The density of surface atoms for the energetically most stable Au (111) surface is 1.4×10^{19} atoms/m^2. Avogadro's constant = 6.02×10^{23} mol^{-1}.

Accordingly the TON of the model reaction can be estimated as:

$$\text{TON} = \frac{\text{Product Molecules}}{\text{Active Sites}} = \frac{1 \times 10^{-3}\ \text{mol} \times 6.022 \times 10^{23}\ \text{mol}^{-1}}{4\ \text{m}^2/\text{g} \times 2 \times 10^{-3}\ \text{g} \times 1.4 \times 10^{19}\ \text{atoms/m}^2} = 5377$$

$$\text{TOF} = \text{TON/Time} = 5377/2\text{h} = 2689\ \text{h}^{-1}$$

3. Catalytic reactions: general information, methods and data

General information

Components were visualized by UV and/or potassium permanganate staining. ^{1}H-, ^{13}C- and ^{29}Si-NMR were recorded on a Bruker Ascend^{TM} 400 spectrometers. Chemical shifts

(in ppm) were referenced to internal solvent peaks (^{1}H, ^{13}C) or an external TMS (10% in $CDCl_3$ or d_6-DMSO) reference (^{29}Si). Mass spectra were recorded using a Waters micromass GCT Mass Spectrometer or Bruker Esquire-LC Mass Spectrometer. GC-MS data were obtained on an SHIMADZU GCMS-QP2012 containing an Agilent DB-5ms capillary column (thickness 0.25 μm, length 30.0 m, diameter 0.25 mm).High resolution mass spectra (HRMS) were recorded on a Bruker Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (APEX IV) or a Waters micromass GCT Mass Spectrometer. Elemental analysis was run on a Elementar Vario MICRO CUBE. Unless otherwise noted, starting materials obtained from commercial suppliers were used without further purification. Solvents were purified by the solvent purification assembly (VAC 103991). EPR tests were run on a JEOL JES-FA200 ESR spectrometer.

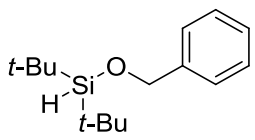
Preparation of reaction solution with 0.5 ppm Au (I) or Au (III):

1 mg AuCl (Me_2S) was dissolved in 670 mL ethanol to make a 1 μg/mL Au (I) solution. Then 0.5 mL of 1 μg/mL Au (I) solution was diluted with ethanol to 1 L, which gave Au (I) stock solution with 5×10^{-4} μg/mL. 5 μL of 5×10^{-4} μg/mL Au (I) stock solution was added to the reaction system (5 mL toluene, 1.0 mmol substrate, 2.1 mmol silane). The mixture was stirred for 2 h at 50 °C under argon balloon.

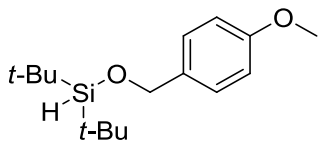
1 mg $AuCl_3 \cdot 4H_2O$ was dissolved in 470 mL H_2O to make a 1 μg/mL Au (III) solution. Then 0.5 mL of 1 μg/mL Au (III) solution was diluted with H_2O to 1 L, which gave Au (III) stock solution with 5×10^{-4} μg/mL. 5 μL of 5×10^{-4} μg/mL Au (III) stock solution was added to the reduction system (5 mL toluene, 1.0 mmol substrate, 2.1 mmol silane). The mixture was stirred for 2 h at 50 °C under argon balloon.

3.1 Mono alcoholysis of di-*tert*-butylsilane and diethylsilane

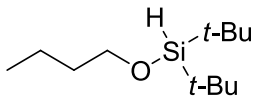
General procedure A for the silylation of alcohol catalyzed by the NPG: alcohol (1 mmol, 1 eq.) and NPG (0.01 mmol, 0.01 eq.) were added to the toluene (5 mL). Then silane (1.1 mmol, 1.1 eq) was added. The reaction was stirred at 50 ˚C for 2 h - 36 h under nitrogen balloon. The completion of the reaction was monitored by TLC, NMR or GC. Then the reaction was concentrated under reduced pressure and the product was purified by silica gel column chromatography.



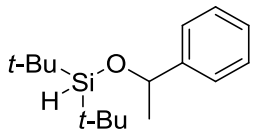
[2a]: Using procedure A: Reaction was performed with benzl alcohol **1a** (108 mg, 1.0 mmol) and di-*tert*-butylsilane (159 mg, 1.1 mmol). Both toluene and acetone are good solvent under our test, giving the same results. Product **2a** was obtained as colorless oil (233 mg, 93% yield) by column chromatography (PE: EA = 100: 0 to 100: 1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.37 – 7.32 (m, 4H), 7.27 – 7.23 (m, 1H), 4.87 (s, 2H), 4.12 (s, 1H), 1.03 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 141.16, 128.33, 127.13, 126.50, 69.01, 27.43, 20.38. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ 18.11. **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{26}NaOSi$ $[M+Na]^+$: 273.16451; found: 273.16453.



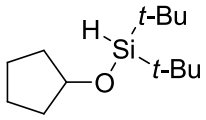
[2b]: Using procedure A: Reaction was performed with (4-methoxyphenyl) methanol (**1b**, 280 mg, 1.0 mmol) and di-*tert*-butylsilane (159 mg, 1.1 mmol). **2b** was obtained as colorless oil after column chromatography (PE, 264 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.27 (d, 2H, *J* = 8.8 Hz), 6.87 (d, 2H, *J* = 8.6 Hz), 4.79 (s, 2H), 4.09 (s, 1H), 3.81 (s, 3H), 1.01 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 158.89, 133.36, 128.12, 113.74, 68.77, 55.40, 27.43, 20.34. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ 17.64. **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{29}O_2Si$ $[M+H]^+$: 281.19313; found: 281.19297.



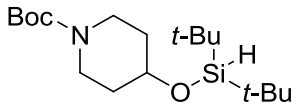
[2c]: Using procedure A: Reaction was performed with butan-1-ol (**1c**, 74 mg, 1.0 mmol) and di-*tert*-butylsilane (159 mg, 1.1 mmol). **2c** was obtained as colorless oil after column chromatography (PE, 195 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 3.96 (s, 1H), 3.73 (t, 2H, *J* = 6.4 Hz), 1.57 – 1.50 (m, 2H), 1.41 – 1.32 (m, 2H), 0.99 (s, 18H), 0.92 (t, 3H, *J* = 7.6 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 67.01, 34.97, 27.42, 20.24, 19.10, 14.04. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ 16.40. **HRMS** (EI, *m/z*): calcd for $C_{12}H_{28}OSi$ $[M]^+$: 216.1904; found: 216.1912.



[2d]: Using procedure A: Reaction was performed with 1-phenylethanol (**1d**, 122 mg, 1.0 mmol) and di-*tert*-butylsilane (159 mg, 1.1 mmol). **2d** was obtained as colorless oil (251 mg, 95% yield) after column chromatography (PE: EA = 100: 0 to 50: 1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.34 – 7.30 (m, 4H), 7.26 – 7.21 (m, 1H), 4.92 (t, 1H, *J* = 6.4 Hz), 1.46 (d, 3H, *J* = 6 Hz), 1.06 (s, 9H), 0.88 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 146.41, 128.22, 126.98, 125.63, 74.25, 27.56, 27.30, 26.74, 20.28, 19.93. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ 14.09. **MS** (EI, *m/z*): $[M\text{-}t\text{Bu}]^+$ 207. Anal.Calcd for $C_{16}H_{28}OSi$: C, 72.66; H, 10.67. Found: C, 72.59; H, 10.65.

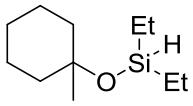


[2e]: Using procedure A: Reaction was performed with cyclopentanol (**1e**, 86 mg, 1.0 mmol) and di-*tert*-butylsilane (159 mg, 1.1 mmol). **2e** was obtained as a colorless oil after column chromatography (PE: EA = 100: 0 to 100: 1, 226 mg, 99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 4.33 – 4.31 (m, 1H), 3.99 (s, 1H), 1.75 – 1.51 (m, 7H), 0.98 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 77.97, 35.32, 27.47, 23.10, 20.03. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ 12.86. **HRMS** (EI, *m/z*): calcd for $C_{13}H_{28}OSi$ $[M]^+$: 228.1904; found: 228.1912.

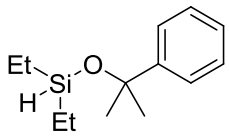


[2f]: Using procedure A: Reaction was performed with *tert*-butyl 4-hydroxypiperidine-1-carboxylate (**1f**, 201 mg, 1.0 mmol) and di-*tert*-butylsilane (159 mg, 1.1 mmol). **2f** was obtained as a colorless oil after column chromatography (PE: EA = 20:1, 326 mg, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 4.02 (s, 1H), 3.95-3.89 (m, 1H), 3.69-3.62 (m, 2H), 3.25-3.19 (m, 2H), 1.80-1.74 (m, 2H), 1.61-1.49 (m,

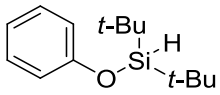
2H), 1.45 (s, 9H), 0.99 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 155.04, 79.45, 70.71, 40.86, 33.91, 28.60, 27.45, 20.04. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ 13.38. **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{37}NNaO_3Si$ $[M+Na]^+$: 366.2435; found: 366.2435.



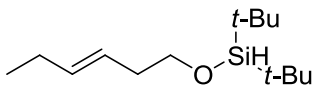
[2g]: Using procedure A: Reaction was performed with 1-methylcyclohexanol (**1g**, 114 mg, 1.0 mmol) and diethylsilane(132 mg, 1.5 mmol). **2g** was obtained as colorless oil after column chromatography (PE, 186 mg, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 4.54 (quint, 1H, *J* = 2.3 Hz), 1.65-1.54 (m, 4H), 1.48-1.32 (m, 4H), 1.27-1.25 (m, 1H), 1.23 (s, 3H), 0.98 (t, 3H, *J* = 8.0 Hz), 0.62 (q, 4H, *J* = 7.9 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 73.07, 39.92, 25.92, 22.77, 7.01. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ -2.86. Anal.Calcd for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07. Found: C, 65.89; H, 12.02.



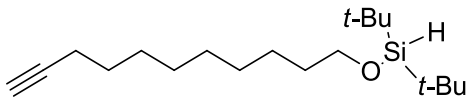
[2h]: Using procedure A: Reaction was performed with 2-phenylpropan-2-ol (**1h**, 136 mg, 1.0 mmol) and diethylsilane (132 mg, 1.5 mmol). **2h** was obtained as colorless oil after column chromatography (PE: EA = 100: 0 to 100: 1, 214 mg, 96% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.48 – 7.46 (m, 2H), 7.34 – 7.31 (m, 2H), 7.24 – 7.23 (m, 1H), 4.55 (t, 1H, *J* = 2.4 Hz), 1.62 (s, 6H), 0.99 (t, 6H, *J* = 8 Hz), 0.65 (q×d, 4H, *J* = 7.6 Hz, 2.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 149.69, 128.06, 126.52, 124.79, 75.19, 31.88, 6.96, 6.74. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ -0.17. Anal.Calcd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97. Found: C, 70.33; H, 10.01.



[2i]: Using procedure A: Reaction was performed with phenol (**1i**, 94 mg, 1.0 mmol) and di-*tert*-butylsilane (159 mg, 1.1 mmol). **2i** was obtained as colorless oil after column chromatography (PE, 199 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.25 – 7.22 (m, 2H), 6.96 – 6.92 (m, 3H), 4.45 (s, 1H), 1.06 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 157.32, 129.56, 121.10, 119.15, 27.44, 27.28, 20.34. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ 12.16. **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{25}OSi$ $[M+H]^+$: 237.16692; found: 237.16685.

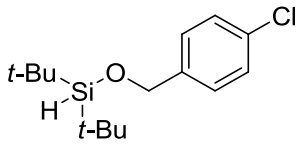


[2j]: Using procedure A: Reaction was performed with (*E*)-hex-3-en-1-ol (**1j**, 100 mg, 1.0 mmol) and di-*tert*-butylsilane (159 mg, 1.1 mmol). **2j** was obtained as a colorless oil after column chromatography (PE: EA = 100: 0 to 100: 1, 228 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 5.48 – 5.41(m, 1H), 5.38– 5.32(m, 1H), 3.98 (s, 1H), 3.73 (t, 2H, 6.8 Hz), 2.34 – 2.29 (m, 2H), 2.10 – 2.02 (m, 2H), 1.00 (s, 18H), 0.97 (t, 3H, *J* = 7.6 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 133.51, 124.97, 66.86, 30.79, 27.24, 20.64, 20.07, 14.31. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ 16.90. **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{30}NaOSi$ $[M+Na]^+$: 265.19581; found: 265.19540.

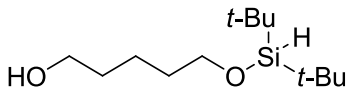


[2k]: Using procedure A: Reaction was performed with undec-10-yn-1-ol (**1k**, 168 mg, 1.0 mmol) and di-*tert*-butylsilane (159 mg, 1.1

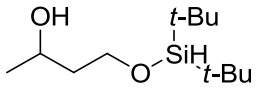
mmol). **2k** was obtained as a colorless oil after column chromatography (PE, 261 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 3.96 (s, 1H), 3.72 (t, 2H, *J* = 6.6 Hz), 2.17 (d×t, 2H, *J* = 2.6 Hz, 7.0 Hz), 1.93 (t, 1H, *J* = 2.6 Hz), 1.56 – 1.49 (m, 4H), 1.40 – 1.29 (m, 10H), 0.99 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 84.94, 68.18, 67.30, 32.82, 29.62, 29.50, 29.50, 29.20, 28.90, 28.65, 27.43, 25.89, 20.24, 18.55. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ 16.57. **HRMS** (ESI, *m/z*): calcd for $C_{19}H_{39}OSi$ $[M+H]^+$: 311.2765; found: 311.2762.



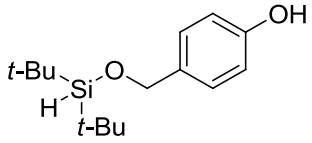
[2l]: Using procedure A: Reaction was performed with (4-chlorophenyl) methanol (**1l**, 143 mg, 1.0 mmol) and di-*tert*-butylsilane (159 mg, 1.1 mmol). **2l** was obtained as a colorless crystal after column chromatography (PE, 248 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.32-7.29 (m, 4H), 4.81 (s, 2H), 4.08 (s, 1H), 1.02 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 139.66, 132.83, 128.50, 127.87, 68.35, 27.40, 20.35. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ 18.59. **HRMS** (EI, *m/z*): calcd for $C_{15}H_{25}ClOSi$ $[M]^+$: 284.1358; found: 284.1367.



[2m]: Using procedure A: Reaction was performed with pentane-1, 5-diol (**1m**, 104 mg, 1.0 mmol) and di-*tert*-butylsilane (144 mg, 1 mmol). **2m** was obtained as a colorless oil after column chromatography (PE: EA = 100: 0 to 100: 10, 210 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 3.96 (s, 1H), 3.74 (t, 2H, *J* = 6.4 Hz), 3.65 (t, 2H, *J* = 6.4 Hz), 1.63 – 1.55 (m, 4H), 1.46 – 1.41 (m, 2H), 1.31 (s, 1H), 0.99 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 67.08, 63.13, 32.64, 32.51, 27.41, 22.11, 20.23. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ 16.74. **HRMS** (ESI, *m/z*): calcd for $C_{13}H_{30}NaO_2Si$ $[M+Na]^+$: 269.19073; found: 269.19116.



[2n]: Using procedure A: Reaction was performed with butane-1, 3-diol (**1n**, 90 mg, 1.0 mmol) and di-*tert*-butylsilane (144 mg, 1 mmol). **2n** was obtained as colorless oil after column chromatography (PE: EA = 100: 0 to 10: 1, 193 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 4.21 – 3.92 (m, 4H), 3.10 (s, 1H), 1.75 – 1.62 (m, 2H), 1.20 (d, 3H, *J* = 6.4 Hz), 0.99 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 67.99, 66.85, 40.42, 27.46, 27.32, 27.31, 27.06, 23.52, 20.24, 20.12. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ 19.27. **HRMS** (ESI, *m/z*): calcd for $C_{12}H_{28}NaO_2Si$ $[M+Na]^+$: 255.17508; found: 255.17510.



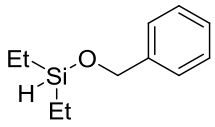
[2o]: Using procedure A: Reaction was performed with 4-(hydroxymethyl)phenol (**1o**, 124 mg, 1.0 mmol) and di-*tert*-butylsilane (144 mg, 1 mmol). **2o** was obtained as colorless oil after column chromatography (PE: EA = 100: 0 to 5: 1, 203 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.22 (d, 2H, *J* = 8.4 Hz), 6.79 (d, 2H, *J* = 8.4 Hz), 5.00 (s, 1H), 4.78 (s, 2H), 4.10 (s, 1H), 1.02 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 154.74, 133.45, 128.44, 115.21, 68.82, 27.42, 20.33. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ 18.03. **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{27}O_2Si$

$[M+H]^+$: 267.17748; found: 267.17221.

3.2 Synthesis of unstable hydridosilyl ethers(2p, 2q, 2r) with diethylsilane

Benzyloxydiethylsilane (2q):

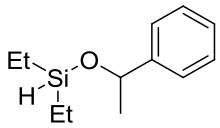
Benzyl alcohol (**1a**, 1.0 mmol, 1 eq.) and NPG (0.01 mmol, 0.01 eq.) were added to the $CDCl_3$ (5 mL). Then diethylsilane (1.5 mmol, 1.5 eq.) was added. The reaction was stirred at r.t. for 1h under nitrogen balloon. The completion of the reaction was monitored by ^1H NMR. The crude ^1H NMR (see the spectrum data below) showed **1a** was totally converted to **2q**. **2q** was not stable and can be degraded to **1a** when separated by silica or alumina column.



Crude ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.37 – 7.36 (m, 4H), 7.29 – 7.26 (m, 1H), 7.21 (m, 0.2 H), 4.79 (s, 2H), 4.53 (s, 1H), 1.02 (q, 9H, *J* = 8.0 Hz), 0.76-0.62 (m, 6H). **GCMS** of the reaction mixture when the reaction finished: m/z 194.1 (3.4%, $[M]^+$), 165.1 (100%, $[M-Et]^+$).

Diethyl(1-phenylethoxy)silane (2r):

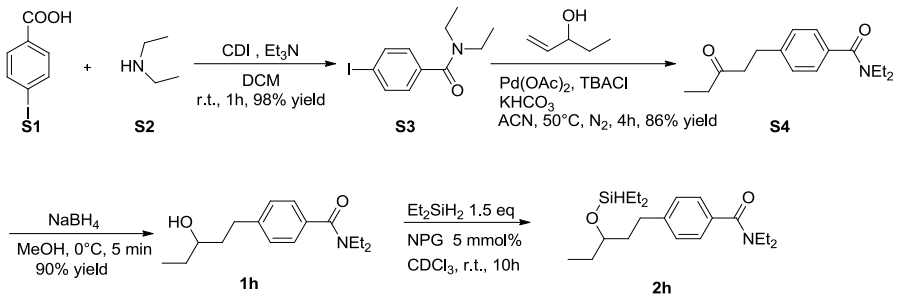
1-Phenylethanol (**1d**, 1.0 mmol, 1 eq.) and NPG (0.01 mmol, 0.01 eq.) were added to the $CDCl_3$ (5 mL). Then diethylsilane (1.5 mmol, 1.5 eq.) was added. The reaction was stirred at r.t. for 1 h under nitrogen balloon. The completion of the reaction was monitored by ^1H NMR. The crude ^1H NMR (see the spectrum data below) showed **1d** was totally converted to **2r**. Then the reaction was concentrated under reduced pressure and the product was purified by silica gel column chromatography (PE: EA = 50: 1 to 25: 1) to give **2r** as a colorless oil (114 mg, 55% yield). Low isolated yield is due to the instability of **2r**. 50 mg (0.41 mmol) **1d** was recovered from the column with PE: EA = 2: 1 as the eluent. Pure **2r** was not stable on silica or alumina column, but still much more stable than **2q**. Pure **2r** can kept intact after several days under nitrogen atmosphere.



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.35 – 7.31 (m, 4H), 7.29 – 7.21 (m, 1H), 4.87 (q, 4H, *J* = 6.4 Hz), 4.44 (s, 1H), 1.47 (d, 2H, *J* = 6.4 Hz), 0.99 (t, 3H, *J* = 7.9 Hz), 0.92 (t, 3H, *J* = 7.9 Hz), 0.70 – 0.59 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 146.11, 128.32, 127.13, 125.51, 72.60, 26.55, 6.83, 6.77, 5.63, 5.60. **^{29}Si NMR** (80 MHz, $CDCl_3$, ppm) δ 10.19. **GCMS** of the reaction mixture when the reaction finished: *m/z* 208.2 (1.6%, $[M]^+$), 193.2 (15.9%, $[M-Me]^+$), 179.1 (7.9%,$[M-Et]^+$), 103.1 (100.0%, $[OSi(H)Et_2]^+$). **HRMS** (EI, *m/z*): calcd. for $C_{10}H_{15}OSi$ $[M-Et]^+$: 179.0887; found: 179.0895. calcd. for $C_{11}H_{17}OSi$ $[M-Me]^+$: 193.1043; found: 193.1051.

When 1-phenylethanol (**1d**, 1.0 mmol, 2 eq.) was treated with 1 eq. Et_2SiH_2 in the presence of NPG (0.01 mmol, 0.01 eq.) in $CDCl_3$, *only* mono alcoholysis product was found according to the crude ^1H NMR (see spectrum data part).

4-(3-(Diethylsilyloxy)pentyl)-N,N-diethylbenzamide (2p)



The synthesis of **1p** employed the synthetic method of Eric M. Simmons & John F. Hartwig (*Nature,* 2012, **483,** 70). Crude HNMR and GC-MS showed TM was got. We did not get separated **2p**. **2p** is not stable on silica or alumina column and can be degraded into **1p**.

***N,N*-diethyl-4-iodobenzamide (S3):**

4-Iodobenzoic acid (**S1**, 3 g, 12 mmol) was dissolved in CH_2Cl_2 (30 mL). 1,1'-Carbonyldiimidazole (CDI, 2 g, 13 mmol) was added slowly (CO_2 evolution!). Then the mixture was stirred for 1h at r.t. Then Et_3N (5 mL, 36 mmol) and Et_2NH (3.7 mL, 36 mmol) were added sequentially. The resulting mixture was stirred for another 1h at r.t. After completion, the reaction mixture was washed with brine (30 mL ×5). Organic phase was dried over anhydrous magnesium sulphate and then filtrate a short SiO_2 plug. The filtration was concentrated to give *N,N*-diethyl-4-iodobenzamide (**S3**) as a white solid (2.96 g, 98% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 3.52 (br s,2H), 3.24 (br s, 2H), 1.21 (br s, 3H), 1.11 (br s, 3H).

***N,N*-diethyl-4-(3-oxopentyl)benzamide (S4):**

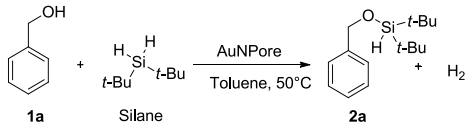
A 20 mL 3-necked bottle was charged with $Pd(OAc)_2$ (8.5 mmol, 5 mol %), $KHCO_3$ (4.3 mmol, 2.5 eq.), tetrabutylammonium chloride (1.7 mmol, 1.0 eq.), aryl iodide (1.7 mmol, 1.0 eq.), 1-penten-3-ol (3.4 mmol, 2.0 eq.) and MeCN (3.4 mL). A stir bar was added, and nitrogen was introduced into the bottle by several nitrogen balloons. Then the bottle was placed in a preheated oil bath at 50 °C and stirred for 4h under nitrogen balloon. After completion of the reaction (determined by TLC), the stir bar was removed and the mixture was concentrated under vacuum. The resulting residue was diluted with ethyl acetate (10 mL) and washed with water (10 mL×3). The organic layer was dried over anhydrous magnesium sulphate and then filtrate a short SiO_2 plug. The filtration was concentrated by rotary evaporation and then separated by column chromatography (PE: EA = 5: 1 to 2: 1). *N*, *N*-diethyl-4-(3-oxopentyl)benzamide (**S4**) was got as yellow oil (370 mg, 86& yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 3.51 (br s, 2H), 3.25 (br s, 2H), 2.90 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.39 (q, *J* = 7.4 Hz, 2H), 1.18 (br s, 3H), 1.12 (br s, 3H), 1.02 (t, *J* = 7.3 Hz, 3H).

***N,N*-diethyl-4-(3-hydroxypentyl)benzamide (1p):**

S4 (250mg, 0.96 mmol) in MeOH (5 mL) at 0 °C was treated with $NaBH_4$ (115 mg, 1.4 mmol). The resulting mixture was stirred for 5 min at 0 ºC in an ice-water bath. The reaction mixture was then concentrated to remove methanol by rotary evaporation. The crude was diluted with EA (15 mL) and then washed with water (2 x 15mL). The organic layer was dried over anhydrous magnesium sulfate and then filtered by a short SiO_2 plug. The filtration was concentrated by rotary evaporation and used to the next step without further purification. **1p** was got as a colorless oil (227 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 3.55-3.49 (m,3H), 3.27 (br s, 2H), 2.83-2.76 (m, 1H), 2.70-2.63 (m, 1H), 1.80-1.70 (m, 3H), 1.68-1.40 (m, 2H), 1.20-1.12 (2 × br s, 6H), 0.93 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, CDCl3) δ 171.58, 143.66, 134.89, 128.54, 126.64, 72.58, 38.50, 32.00, 30.48, 9.97.

4-(3-(diethylsilyloxy)pentyl)-*N*,*N*-diethylbenzamide (2p):
N,*N*-diethyl-4-(3-hydroxypentyl)benzamide (**S5**, 92 mg, 0.35 mmol) and NPG (3.4 mg, 5 mol%) were added to $CDCl_3$ (1.75 mL). Diethylsilane (0.53 mmol) was added. The mixture was then stirred for 10 h at r.t. under nitrogen. **Crude ^{1}H NMR** showed 4-(3-(diethylsilyloxy)pentyl)-*N*,*N*-diethylbenzamide (**2p**) was got. Crude **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, 2H, *J* = 7.7 Hz), 7.21 (d, 2H, *J* = 7.6 Hz), 4.49 (t, 0.3H, *J* = 2.4 Hz), 4.47 (quint, 1H, *J* = 2.4 Hz), 3.54-3.49 (m, 1H), 3.40 (brs, 4H), 2.79-2.70 (m, 1H), 2.68-2.63 (m, 1H), 2.02-1.98 (m, 2H), 1.74-1.45 (m, 2H), 1.17 (t, 6H, *J* = 6.6 Hz), 1.04 (q, 0.8 H, *J* = 7.6 Hz), 0.98-0.91 (m, 14H), 0.63-0.57 (m, 6H), 0.49 (q, 1H, *J* = 7.6 Hz). **GC-MS** of the reaction solution: *m/z* 348.3 (13%, $[M-H]^+$), 320.2 (11%, $[M-Et]^+$), 262.2 (100%, $[M-SiEt_2H]^+$), 173.1 (8%, $[CH_2CH_2(C_2H_5)CHOSi(H)Et_2]^+$).

3.3 Recycling of the NPG catalyst[a].

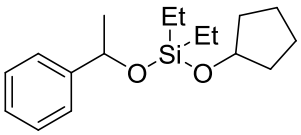


Entry	Catalyst	t (h)	Yield of **2a**[b]
1	fresh	2	90%
2	reuse 1	2.5	87%
3	reuse 2	5	94%
4	reuse 3	8	93%
5	reuse 4	8	91%
6	reuse 5	8	92%

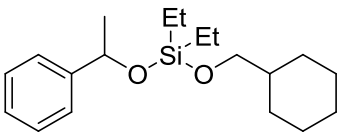
[a] Reactions were performed with 1a (1 mmol), silane (1.1 mmol) and catalyst (1 mol %) in toluene (5 ml) at 50˚C under nitrogen balloon. [b] Isolated yield.

4. One-pot synthesis of unsymmetrical silaketals

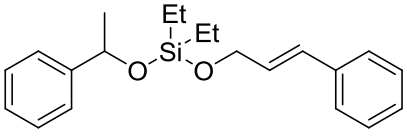
General procedure B for one-pot synthesis of unsymmetrical silaketals. The corresponding alcohol (1.5 mmol, 1.5 eq.) and the NPG (0.05 mmol, 0.05 eq.) were added to the anhydrous dichloromethane (2.5 mL). Then hydridosilyl ether (1.0 mmol, 1 eq., synthetized by general procedure A) in anhydrous dichloromethane (1.0 ml) was added. The reaction was stirred at 50 ℃ under nitrogen balloon. The completion of the reaction was monitored by TLC or GC. Then the reaction was concentrated under reduced pressure and the product was purified by silica gel column chromatography.



[6a]: Using procedure B: Reaction was performed with cyclopentanol (129 mg, 1.5 mmol) and diethyl(1-phenylethoxy)silane **2f** (general procedure A, 1.0 mmol). Product was obtained as yellow oil (190 mg, 65% yield) by column chromatography (PE: DCM = 9:1). **^{1}H NMR** (400M, $CDCl_3$, ppm) δ 7.40 - 7.32 (m, 4H), 7.28 - 7.23 (m, 1H), 5.04 (q, 1H, *J* = 6.4 Hz), 4.33 (m, 1H), 1.73 - 1.70 (m, 3H), 1.63 - 1.59 (m, 2H), 1.54 - 1.48 (m, 6H), 1.00 (t, 3H, *J* = 8.0 Hz), 0.92 (t, 3H, J = 8.0 Hz), 0.68 - 0.64 (m, 2H), 0.59 - 0.52 (m, 2H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 146.78, 128.21, 126.88, 125.40, 74.12, 70.30, 35.78, 35.69, 27.17, 23.33, 23.31, 6.74, 6.64, 4.84, 4.68. **HRMS** (EI, *m/z*): calcd for $C_{17}H_{28}O_2Si$ $[M]^+$: 292.1853. Found: 292.1853.



[6b]: Using procedure B: Reaction was performed with cyclohexylmethanol (171 mg, 1.5 mmol) and diethyl(1-phenylethoxy)silane **2f** (general procedure A, 1.0 mmol). Product **2m** was obtained as colorless oil (240mg, 75% yield) by column chromatography (PE: DCM = 9:1). **^{1}H NMR** (400M, $CDCl_3$, ppm) δ 7.36 - 7.29 (m, 4H), 7.37 - 7.20 (m, 1H), 5.00 (q, 1H, *J* = 6.4 Hz), 3.37 (ddt, 2H, J_1 = 6.8 Hz, J_2 = 9.6 Hz, J_3 = 10.0 Hz), 1.68 - 1.66 (m, 5H), 1.46 - 1.07 (m, 7H), 0.98 (t, 2H, *J* = 8.0 Hz), 0.89 (t, 2H, *J* = 8.0 Hz), 0.87 - 0.78 (m, 2H), 0.65 - 0.50 (m, 4H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 146.69, 128.24, 126.93, 125.41, 70.35, 68.35, 40.45, 29.85, 29.79, 27.18, 26.85, 26.06, 6.76, 6.67, 4.36, 4.25. **HRMS** (EI, *m/z*): calcd for $C_{19}H_{32}O_2Si$ $[M]^+$: 320.2166. Found: 320.2167.



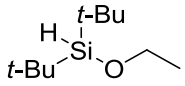
[6c]: Using procedure B: Reaction was performed with 3-phenylprop-2-en-1-ol (201 mg, 1.5 mmol) and diethyl(1-phenylethoxy)silane **2f** (general procedure A, 1.0 mmol). Product was obtained as yellow oil (221mg, 65% yield) by column chromatography (PE: DCM = 9:1).**^{1}H NMR** (400M, $CDCl_3$, ppm) δ 7.38 - 7.31(m, 8H), 7.26 - 7.23(m, 2H), 6.54 (d, 1H, J = 16.0 Hz), 6.21 (dt, 1H, J_1 = 5.2 Hz, J_2 = 16.0 Hz), 5.05 (q, 1H, J = 6.4 Hz), 4.32 (ddt, 1H, J_1 = 5.2 Hz, J_2 = J_3= 14.0 Hz), 1.48 (d, 3H, J = 6.4 Hz), 1.02 (t, 2H, J = 8.4 Hz), 0.94 (t, 2H, J = 7.6 Hz), 0.70 (q, 3H, J = 7.6 Hz), 0.64 (m, 3H);**^{13}C NMR** (101M, $CDCl_3$, ppm) δ 146.51, 137.18, 130.03, 128.74, 128.63, 128.33, 127.50, 127.07, 126.57, 125.42,

70.57, 63.35, 27.19, 6.74, 6.64, 4.45, 4.36;**HRMS** (EI, *m/z*): calcd for $C_{21}H_{28}O_2Si$ $[M]^+$: 340.18531. Found: 340.18561.

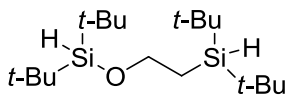
5. Ring-opening/silylation of cyclic ethers

5.1 General procedure C for the ring-opening/silylation of cyclic ethers catalyzed by the NPG: To a dry sealed tube charged with argon, cyclic ethers (3.0 mmol, 1.0 eq.), di-*tert*-butylsilane (6.6 mmol, 951mg) and NPG (0.09 mmol, 18 mg) was added. The reaction was stirred and heated for 0.5 - 36h. The crude product was then purified on silica gel.

Ring-opening/silylation of ethylene epoxide (**7a**):
Using modified procedure C: Reaction was performed with ethylene epoxide **7a** (132 mg, 3.0 mmol) and di-*tert*-butylsilane (951 mg, 6.6 mmol) at 0 ℃ at the beginning then heat to 50 ℃ for about 0.5 h. Products **8a** (85 mg, 15%) and **9a** (695 mg, 70%) were obtained as colorless oil by column chromatography (pure hexanes).

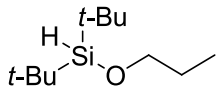


[8a]: ^{1}**H NMR** (400M, $CDCl_3$, ppm) δ 3.96 (s, 1H), 3.81 (q, *J* = 6.96 Hz, 2H), 1.20 (t, *J* = 6.96 Hz, 3H), 0.99 (s,18H). ^{13}**C NMR** (101M, $CDCl_3$, ppm) δ 62.82, 27.38, 20.11, 18.45. **HRMS** (EI, *m/z*): calcd for $C_{10}H_{24}OSi$ $[M]^+$: 188.1591; found: 188.1599.

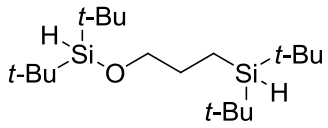


[9a]: ^{1}**H NMR** (400M, $CDCl_3$, ppm) δ 3.97 (s, 1H), 3.89 (t, *J* = 8.80 Hz, 2H), 3.24 (t, *J* = 2.52 Hz, 1H), 1.01-1.00 (m, 2H), 1.00 (d, 36H). ^{13}**C NMR** (101M, $CDCl_3$, ppm) δ 66.11, 28.82, 27.44, 20.14, 18.74, 14.65. ^{29}**Si NMR** (80M, $CDCl_3$, ppm) δ 16.43, 8.68. **HRMS** (EI, *m/z*): calcd for $C_{18}H_{42}OSi_2$ $[M]^+$: 330.2769; found: 330.2777.

Ring-opening/silylation of trimethylene oxide (**7b**):
Using procedure C: Reaction was performed with trimethylene epoxide **7b** (180 mg, 3.0 mmol), di-*tert*-butylsilane (951 mg, 6.6 mmol) and 3ml toluene as solvent at 50 ℃ for about 3 h. Products **8b** (61 mg, 10%) and **9b** (795 mg, 77%) were obtained as colorless oil by column chromatography (pure hexanes).

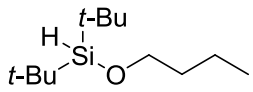


[8b]: ^{1}**H NMR** (400M, $CDCl_3$, ppm) δ 3.97 (s, 1H), 3.69 (t, *J* = 6.64 Hz, 2H), 1.61-1.53 (m, 2H) 0.99 (s, 18H) 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}**C NMR** (101M, $CDCl_3$, ppm) δ 68.98, 27.42, 26.00, 20.24, 10.45. **HRMS** (EI, *m/z*): calcd for $C_{11}H_{26}OSi$ $[M]^+$: 202.1747; found: 202.1757.

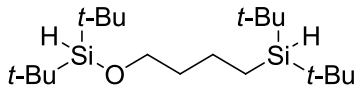


[9b]: ^{1}H NMR (400M, $CDCl_3$, ppm) δ 3.97 (s, 1H), 3.70 (t, *J* = 6.64 Hz, 2H), 3.32 (s, 1H), 1.74 - 1.66 (m, 2H), 1.00 (d, 36H), 0.66 - 0.61 (m, 2H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 69.93, 30.03, 28.94, 27.43, 20.24, 19.03, 4.80. **^{29}Si NMR** (80M, $CDCl_3$, ppm) 16.58, 14.39. **HRMS** (EI, *m/z*): calcd for $C_{19}H_{44}OSi_2$ $[M]^+$: 344.2925; found: 344.2931.

Ring-opening/silylation of tetrahydrofuran (**7c**):
Using procedure C: Reaction was performed with tetrahydrofuran **7c** (648 mg, 3.0mmol) and di-*tert*-butylsilane (951 mg, 6.6 mmol) at 90 ℃ for about 7 h. Products **8c** (39 mg, 6%) and **9c** (880 mg, 82%) were obtained as colorless oil by column chromatography (pure hexanes).

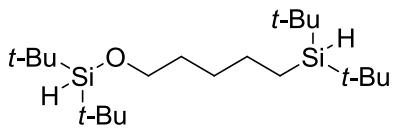


[8c]: ^{1}H NMR (400M, $CDCl_3$, ppm) δ 3.96 (s, 1H), 3.73(t, 2H, *J* = 6.56 Hz), 1.55 - 1.52 (m, 2H), 1.40 - 1.34 (m, 2H), 0.99 (s, 1H), 0.91 (t, 2H *J* = 7.36 Hz). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 67.01, 34.98, 27.42, 20.24, 19.11, 14.03. **HRMS** (EI, *m/z*): calcd for $C_{12}H_{28}OSi$ $[M]^+$: 216.1904; found: 216.1910.



[9c]: ^{1}H NMR (400M, $CDCl_3$, ppm) δ 3.97 (s, 1H), 3.74 (t, 2H, *J* = 6.24 Hz), 3.31 (s, 1H), 1.62 - 1.51 (m, 4H) 1.00 - 0.99 (d, 36H), 0.66 - 0.61 (m, 2H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 66.78, 36.77, 29.01, 27.45, 23.17, 20.25, 19.00, 8.97. **HRMS** (EI, *m/z*): calcd for $C_{20}H_{46}OSi_2$ $[M]^+$: 358.3082; found: 358.3091.

Ring-opening/silylation of tetrahydropyran (**7d**):
Using procedure C: Reaction was performed with tetrahydrofuran **7d** (258 mg, 3.0 mmol) and di-*tert*-butylsilane (951 mg, 6.6 mmol) at 90 ℃ for about 36 h. Product **9d** (915 mg, 82%) was obtained as colorless oil by column chromatography (pure hexanes).

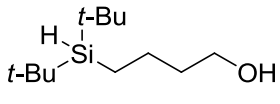


[9d]: ^{1}H NMR (400M, $CDCl_3$, ppm) δ 3.96(s, 1H), 3.73 (t, 2H, *J* = 6.6 Hz), 3.30(s, 1H), 1.60 - 1.36 (m, 6H), 1.00 - 0.99(d, 36H), 0.64 - 0.59 (m, 2H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 67.25, 32.49, 29.94, 28.98, 27.43, 26.80, 20.24, 18.99, 9.22.**^{29}Si NMR** (80M, $CDCl_3$, ppm) 16.51, 14.01. **HRMS** (EI, *m/z*): calcd for $C_{21}H_{48}OSi_2$ $[M]^+$: 372.3238; found: 372.3241.

Chemoselective O-Si cleavage of the bis-silicon 9c

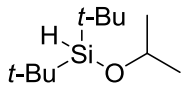
4-(di-*tert*-butylsilyl)butan-1-ol

Di-*tert*-butyl(4-(di-*tert*-butylsilyl)butoxy)silane **9c** (0.5 mmol, 180 mg) in 0.5 ml THF was added tetrabutylammonium fluoride solution (1.0 M in THF, 0.6ml). The reaction mixture was stirred at r.t. for about 1h till the completion of the reaction monitored by TLC. The resulting residue was diluted with ethyl acetate (10 mL) and washed with water (10 mL×2). The organic layer was dried over anhydrous magnesium sulphate and then filtrate a short SiO_2 plug. The filtration was concentrated by rotary evaporation and then separated by column chromatography (PE: EA = 5: 1). **10** was obtained 194mg, 90% yield.



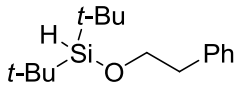
^{1}H NMR (400M, $CDCl_3$, ppm) δ 3.68 – 3.64(m, 2H), 3.31(s, 1H), 1.64 - 1.57(m, 2H), 1.55 - 1.51(m, 2H), 1.00(s, 1H), 0.64(m, 2H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 62.85, 36.80, 28.95, 23.19, 18.97, 8.96. **RMS** (ESI, *m/z*): calcd for $C_{12}H_{28}NaOSi$ $[M+Na]^+$: 239.1802; found: 239.1810.

Ring-opening/silylation of propylene oxide (**7e**):
Using procedure C: Reaction was performed with propylene oxide 7e (174 mg, 3.0 mmol) and di-tert-butylsilane (951 mg, 6.6 mmol) at 40℃ for 4 h. Product **8c** (422 mg, 70%) and **10e** (138 mg, 23%) were obtained as colorless oil by column chromatography (pure hexanes).

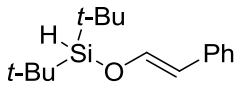


[10e]: ^{1}H NMR (400M, $CDCl_3$, ppm) δ 4.02 (q, 2H, *J* = 6.04 Hz), 4.00 (s, 1H), 1.18 (d, 6H, *J* = 6.04 Hz), 0.98 (s, 18H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 68.34, 27.49, 25.44, 19.97. **HRMS** (EI, *m/z*): calcd for $C_{11}H_{26}OSi$ $[M]^+$: 202.1747; found: 202.1750.

Ring-opening/silylation of styrene oxide (**7f**):
Using procedure C: Reaction was performed with styrene oxide **7f** (360 mg, 3.0 mmol) and di-*tert*-butylsilane (951 mg, 6.6 mmol) at 40℃ for 4 h. Product **8f** (435 mg, 55%) and **10f** (275 mg, 35%) were obtained by column chromatography (pure hexanes).

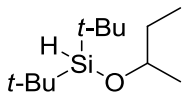


[8f]: **^{1}H NMR** (400M, $CDCl_3$, ppm) δ 7.30–7.18 (m, 5H), 3.98 (s, 1H), 3.94 (t, 2H, *J* = 7.32 Hz), 2.89 - 2.86(t, 2H, *J* = 7.32 Hz,), 0.97 (s, 18H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 139.07, 129.24, 128.39, 126.26, 68.39, 39.51, 27.35, 20.20. **HRMS** (EI, *m/z*): calcd for $C_{16}H_{28}OSi$ $[M]^+$: 264.1904; found: 264.1902.



[10f]: ^{1}H NMR (400M, $CDCl_3$, ppm) δ 7.66 - 7.64 (d, 2H, *J* = 7.52 Hz), 7.32 - 7.28(m, 2H), 7.17 - 7.13(t, 1H, *J* = 7.38 Hz), 6.46 (d, 2H, *J* = 6.56 Hz), 5.29(d, 2H, *J* = 6.56 Hz), 4.20(s, 1H), 1.08(s, 18H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ143.22, 136.39, 128.39, 128.26, 125.78, 108.25, 27.05, 20.03. **HRMS** (EI, *m/z*): calcd for $C_{16}H_{26}OSi$ $[M]^+$: 262.1747; found: 262.1746.

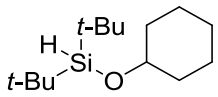
Ring-opening/silylation of 2-butene oxide (**7g**):
Using procedure C: Reaction was performed with 2-butene oxide **7g** (216 mg, 3.0 mmol) and di-*tert*-butylsilane (951 mg, 6.6 mmol) at 40℃ for 4 h. Product **8g** (530 mg, 82%) was obtained as colorless oil by column chromatography (pure hexanes).



[8g]: ^{1}H NMR (400M, $CDCl_3$, ppm) δ 4.02 (s, 1H), 3.83 (q, 1H, *J* = 6 Hz), 1.55 - 1.53 (m, 1H), 1.47 - 1.43(m, 1H), 1.15 (d, 3H) 0.98 (d, 18H), 0.89 (t, 3H, *J* = 7.48 Hz). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 9.82, 19.94, 20.28, 22.24, 27.55, 32.16, 72.81. **HRMS** (EI, *m/z*): calcd for $C_{12}H_{28}OSi$ $[M]^+$: 216.1904; found: 216.1910.

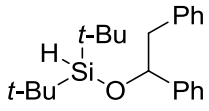
Ring-opening/silylation of cyclopentaneoxide (**7h**):
Using procedure C: Reaction was performed with cyclopentane oxide **7h** (252 mg, 3.0 mmol) and di-*tert*-butylsilane (951 mg, 6.6 mmol) at 40℃ for 4 h. Product **2e** (595 mg, 87%) was obtained as colorless oil by column chromatography (pure hexanes).

Ring-opening/silylation of cyclohexene oxide (**7i**):
Using procedure C: Reaction was performed with cyclohexene oxide **7i** (284 mg, 3.0 mmol) and di-*tert*-butylsilane (951 mg, 6.6 mmol) at 40℃ for 4 h. Product **8i** (618 mg, 85%) was obtained as colorless oil by column chromatography (pure hexanes).

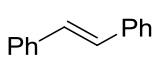


[8i]: ^{1}H NMR (400M, $CDCl_3$, ppm) δ 4.01 (s, 1H), 3.67 (m, 1H), 1.85 - 1.82 (m, 2H), 1.73 - 1.72 (m, 2H), 1.50 - 1.47 (m, 1H), 1.38 - 1.24 (m, 5H), 0.99 (s, 18H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 73.88, 35.45, 27.53, 25.89, 24.15, 20.03. **HRMS** (EI, *m/z*): calcd for $C_{14}H_{30}OSi$ $[M]^+$: 242.2060; found: 242.2074.

Ring-opening/silylation of trans-stilbene oxide (**7j**):
Using procedure C: Reaction was performed with trans-stilbene oxide **7j** (588 mg, 3.0 mmol) and di-*tert*-butylsilane (951 mg, 6.6 mmol) with 6ml toluene as solvent at 70℃ for 5 h. Product **8j** (448mg, 44%) and **10j** (226mg, 42%) were obtained as white soild by column chromatography (pure hexanes).



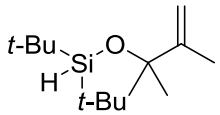
[8j]: ^{1}H NMR (400M, $CDCl_3$, ppm) δ 7.26 - 7.17 (m, 8H), 7.03 - 7.01(m, 2H), 4.92(t, 1H, *J* = 6.64 Hz), 3.92(s, 1H), 3.18 - 3.13(m, 2H), 2.96 - 2.91(m, 2H), 0.95(s, 9H), 0.85(s, 9H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 143.71, 138.29, 130.05, 128.06, 127.97, 127.33, 126.80, 126.22, 79.71, 47.31, 27.55, 27.39, 20.22, 20.02. **HRMS** (EI, *m/z*): calcd for $C_{22}H_{32}OSi$ $[M]^+$: 340.2217; found: 340.2224.



[10j]: ^{1}H NMR (400M, $CDCl_3$, ppm) δ 7.52 (d, 4H, *J* = 7.56), 7.36 (t,

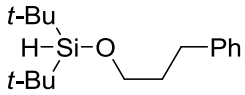
4H, *J* = 7.60 Hz), 7.28 – 7.24 (m, 4H), 7.12(s, 2H).

Ring-opening/silylation of tetramethylethylene oxide (**7k**):
Using procedure C: Reaction was performed with tetramethylethylene oxide **7k** (300 mg, 3.0 mmol) and di-*tert*-butylsilane (951 mg, 6.6 mmol) at 70℃ for 5 h. Product **8k** (435 mg, 60%) was obtained by column chromatography (pure hexanes).

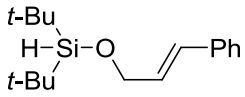


[8k]: ^{1}H NMR (400M, $CDCl_3$, ppm) δ 4.95 (s, 1H), 4.71(s, 1H), 4.17(s, 1H), 1.80(s, 3H), 1.39(s, 6H), 0.97(s, 18H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 108.43, 75.63, 29.34, 27.81, 19.84, 19.18. **HRMS** (EI, *m/z*): calcd for $C_{14}H_{30}OSi$ $[M]^+$: 242.2060; found: 242.2070.

Ring-opening/silylation of 2-phenyloxetane (**7l**)
Using procedure C: Reaction was performed with 2-phenyloxetane **7l** (402mg, 3.0 mmol) and di-*tert*-butylsilane (951 mg, 6.6 mmol) at 70℃ for 5 h. Product **8l** (670 mg, 80%) and 10**l** (83mg**,** 10%) was obtained by column chromatography (pure hexanes).

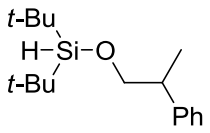


[8l]: ^{1}H NMR (400M, $CDCl_3$, ppm) δ 7.32 – 7.26 (m, 2H), 7.23 – 7.18(m, 3H), 4.02 (s, 1H), 3.79(t, 2H, *J* = 6.28), 2.72 (t, 2H, *J* = 7.64), 1.93 – 1.86 (m, 2H), 1.03 (s, 18H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 142.40, 128.63, 128.44, 125.83, 66.42, 34.55, 32.29, 27.44, 20.26. **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{31}OSi$ $[M+H]^+$: 279.2139; found: 279.2136.

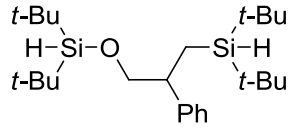


[8l]: ^{1}H NMR (400M, $CDCl_3$, ppm) δ 7.36 (d, 2H, J = 7.44), 7.33 – 7.29 (m, 2H), 7.22 (t, 1H), 7.22 (t, 1H, *J* = 7.16), 6.62 (d, 2H, J = 16.0), 6.30 (dt, 1H, J1 = 15.6, J2 = 5.2), 4.46 (d, 1H, J = 4.40), 4.05(s, 1H), 1.03(s, 18H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 137.25, 129.96, 128.88, 128.66, 127.50, 126.56, 67.88, 27.41, 20.32. **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{29}OSi$ $[M+H]^+$: 277.1982; found: 277.1980.

Ring-opening/silylation of 3-phenyloxetane (**7m**)
Using procedure C: Reaction was performed with 3-phenyloxetane **7m** (402 mg, 3.0 mmol) and di-*tert*-butylsilane (951 mg, 6.6 mmol) at 70℃ for 5 h. Product **8m** (100 mg, 12%) and 9**m** (972mg**,** 77%) was obtained by column chromatography (pure hexanes).

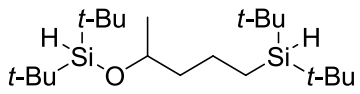


[8m]: ^{1}H NMR (400M, $CDCl_3$, ppm) δ 7.31 – 7.17(m, 5H), 3.96 (s, 1H), 3.81 (dd, 1H, J1 = 43, J2 = 6.0), 3.79 (dd, 1H, J1 =43, J2 = 6.0), 2.98 – 2.93(m, 1H), 0.97 (s, 9H), 0.93 (s, 9H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 144.61, 128.36, 127.70, 126.37, 73.08, 42.70, 27.42, 27.36, 20.41, 20.18, 17.99. **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{31}OSi$ $[M+H]^+$: 279.2139; found: 279.2142.



[9m]: **^{1}H NMR** (400M, $CDCl_3$, ppm) δ 7.29 – 7.15(m, 5H), 3.92 (s, 1H), 3.86 – 3.83 (m, 2H), 3.20 (s, 1H), 3.01 – 2.94 (m, 1H), 1.28 – 1.22(m, 1H), 1.02 (s, 9H), 0.97 (s, 9H), 0.88(s, 9H), 0.87(s, 9H), 0.85 – 0.79 (m, 1H) **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 144.67, 128.41, 128.13, 126.30, 73.67, 46.33, 28.98, 28.76, 27.45, 27.30, 20.38, 20.15, 19.17, 18.65, 12.30. **HRMS** (ESI, *m/z*): calcd for $C_{25}H_{49}OSi2$ $[M+H]^+$: 421.3316; found: 421.3312.

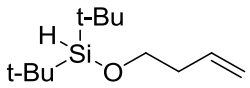
Ring-opening/silylation of 2-methyltetrahydrofuran (**7n**):
Using procedure C: Reaction was performed with tetrahydrofuran **7n** (258 mg, 3.0 mmol) and di-*tert*-butylsilane (951 mg, 6.6 mmol) at 90 ℃ for about 15 h. Product **9n** (870 mg, 78%) was obtained as colorless oil by column chromatography (pure hexanes).



[9n]: **^{1}H NMR** (400M, $CDCl_3$, ppm) δ4.02 (s, 1H), 3.91 - 3.87 (m, 1H), 3.31 (t, 1H, *J* = 2.4 Hz), 1.59 - 1.48 (m, 4H), 1.16 (d, 3H, *J* = 6.08 Hz), 1.00 (s, 18H) 0.99 - 0.98 (d, 18H), 0.63 - 0.61 (m, 2H). **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 71.36, 43.75, 28.99, 27.57, 27.54, 22.89, 22.77, 20.28 19.91, 18.98, 9.40. **^{29}Si NMR** (80M, $CDCl_3$, ppm) 13.84, 10.71. **HRMS** (EI, *m/z*): calcd for $C_{21}H_{48}OSi_2$ $[M]^+$: 372.3238; found: 372.3247.

Synthesis of (but-3-enyloxy) di-tert-butylsilane for mechanism study:

Using procedure A: Reaction was performed with 3-Buten-1-ol (321 mg, 1.5 mmol) and di-*tert*-butylsilane (231 mg, 1.6 mmol). Product **12** was obtained as colorless oil (296 mg, 93% yield) by column chromatography (PE: EA = 100: 1).

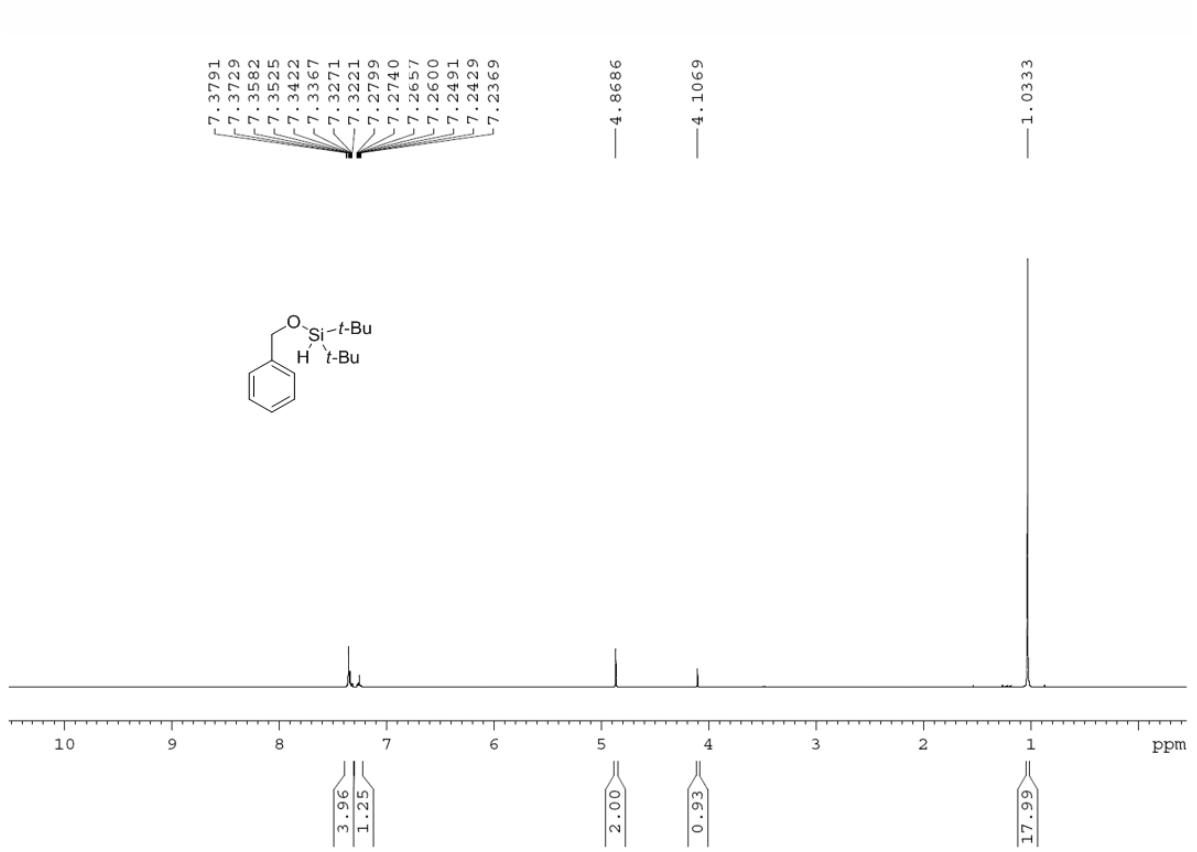


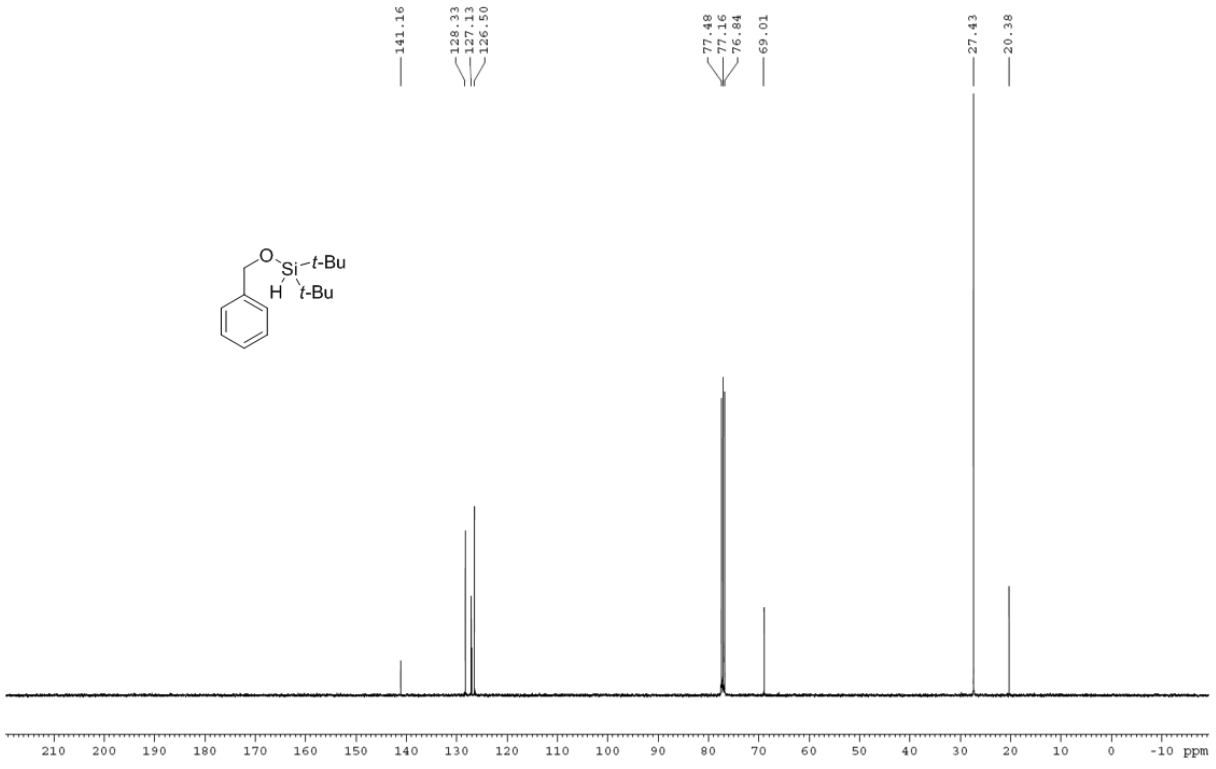
^{1}H NMR (400M, $CDCl_3$, ppm) δ 5.89 - 5.79(m, 1H), 5.10 (d, 1H, *J* = 1.2 Hz), 5.06 - 5.17 (m, 2H), 3.97(s, 1H), 3.79(t, 2H, *J* = 6.8Hz), 2.32(q, 2H, *J* = 6.8 Hz), 0.99(s, 18H); **^{13}C NMR** (101M, $CDCl_3$, ppm) δ 135.53, 116.49, 66.75, 37.39, 27.40, 20.24; **HRMS** (EI, *m/z*): calcd for $C_{12}H_{26}OSi$ $[M]^+$: 214.1747; found: 214.1756.

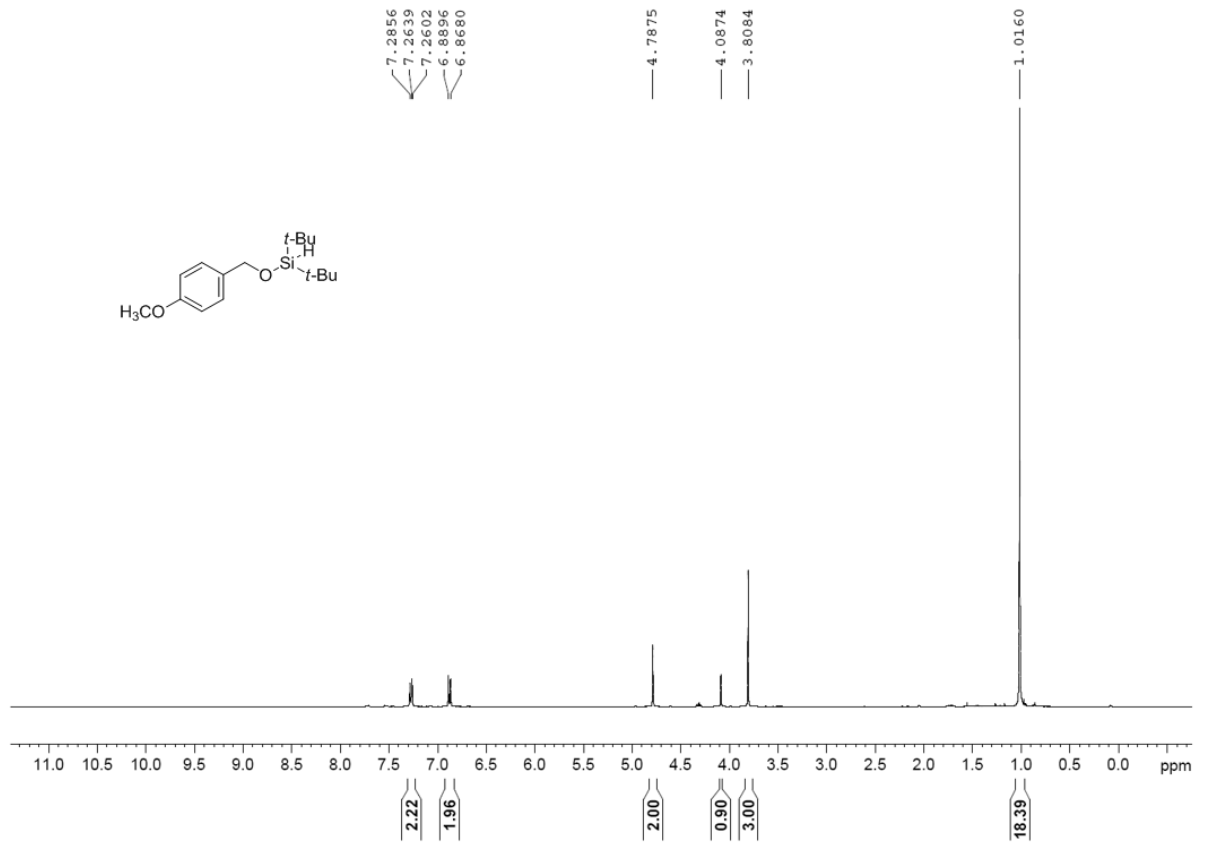
Mechanism study
Using procedure C: Reaction was performed with (but-3-enyloxy) di-*tert*-butylsilane (214mg, 1.0 mmol) and di-*tert*-butylsilane (158 mg, 1.1 mmol) at 70 ℃ for about 7 h. substrate (but-3-enyloxy) di-*tert*-butylsilane kept unconverted.

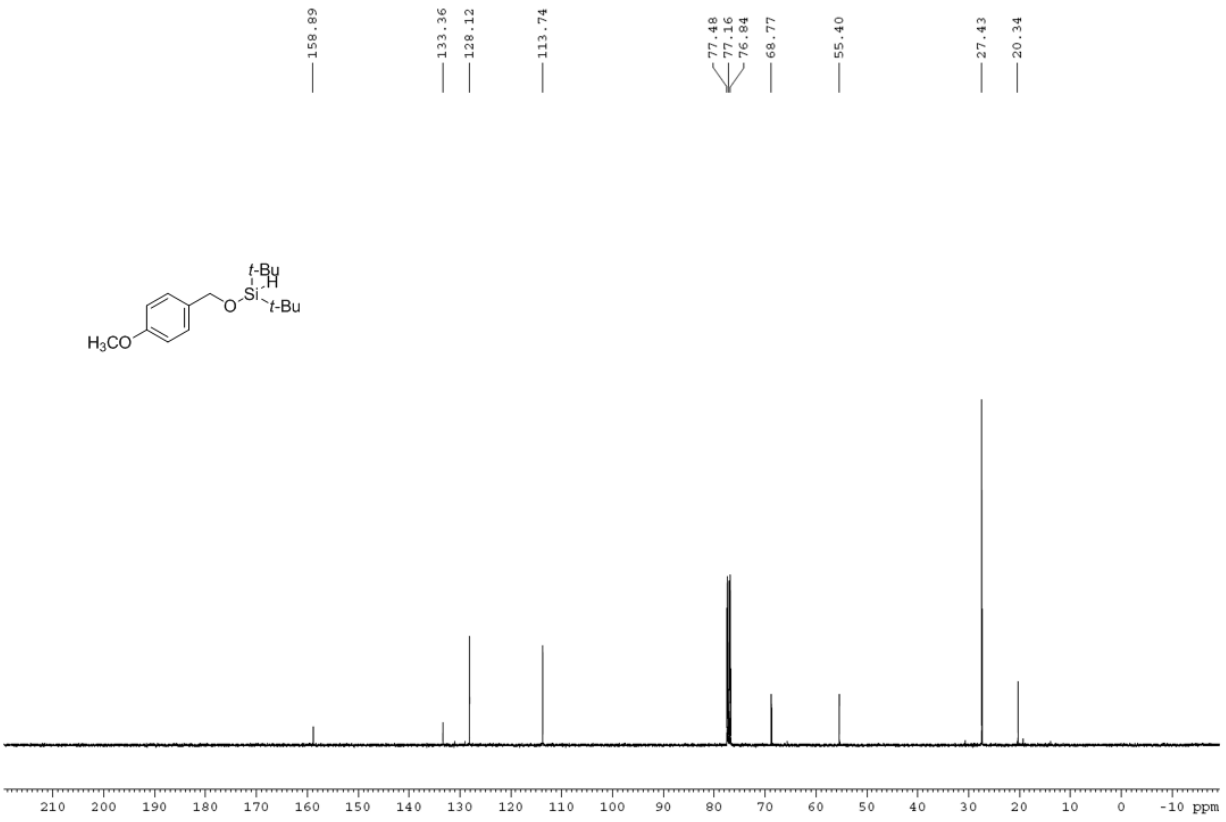
6. ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR spectra of related compounds

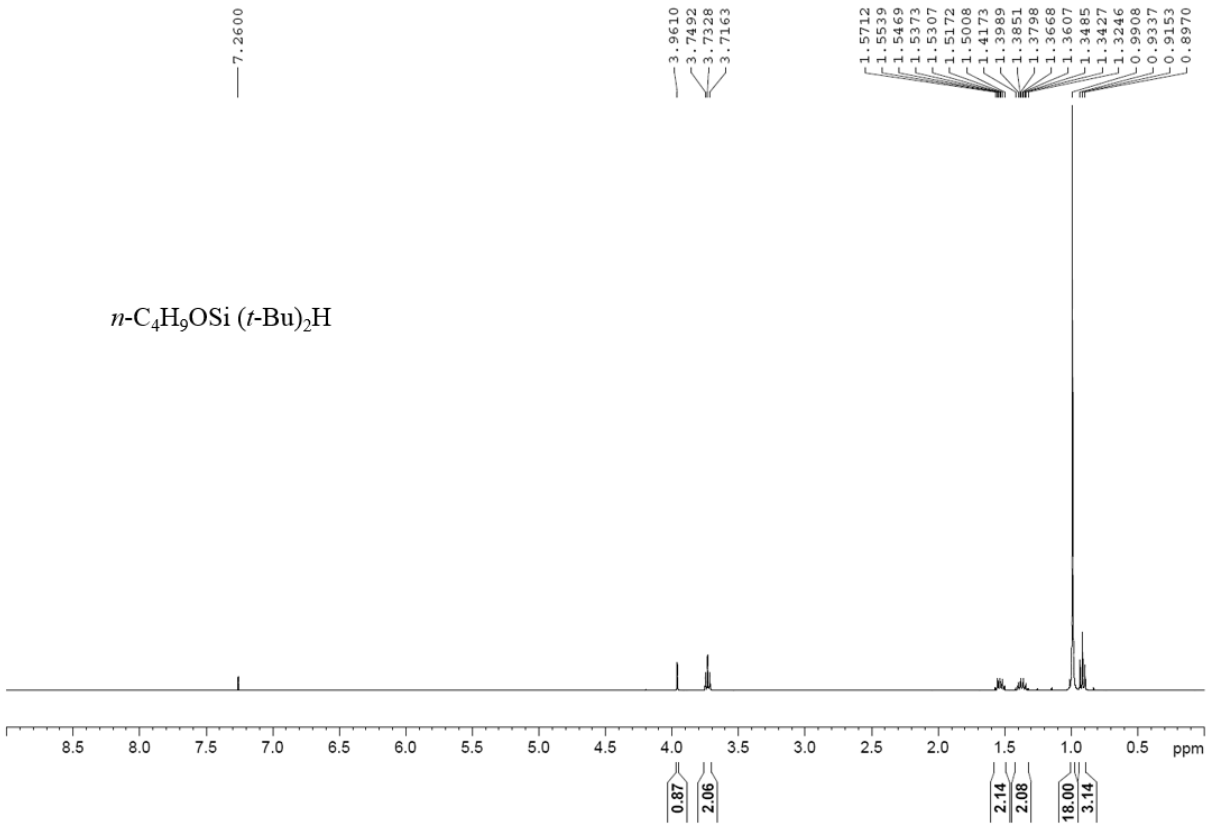
Mono alcoholysis of di-*tert*-butylsilane and diethylsilane (**2a** – **2o**)



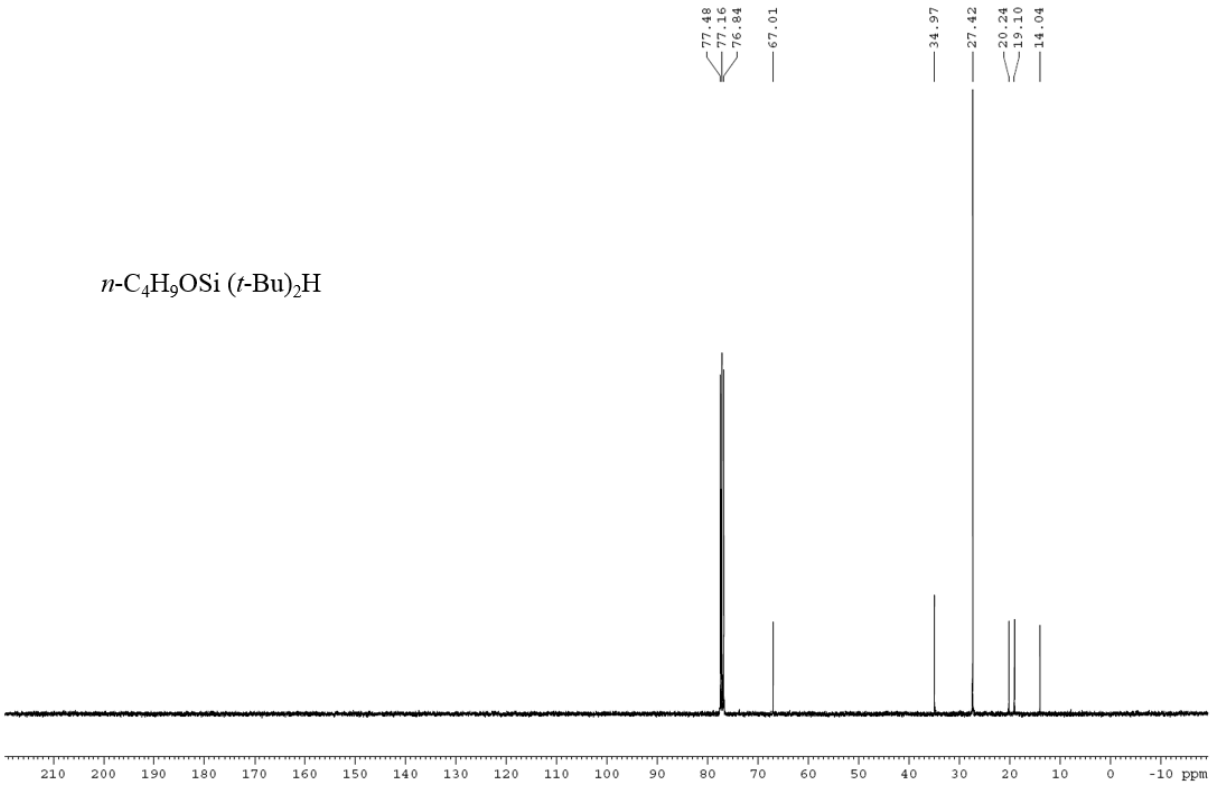



7.2856
7.2639
7.2602
6.8896
6.8680
4.7875
4.0874
3.8084
1.0160
t-Bu
H
Si
O
t-Bu
H3CO
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.22
1.96
2.00
0.90
3.00
18.39

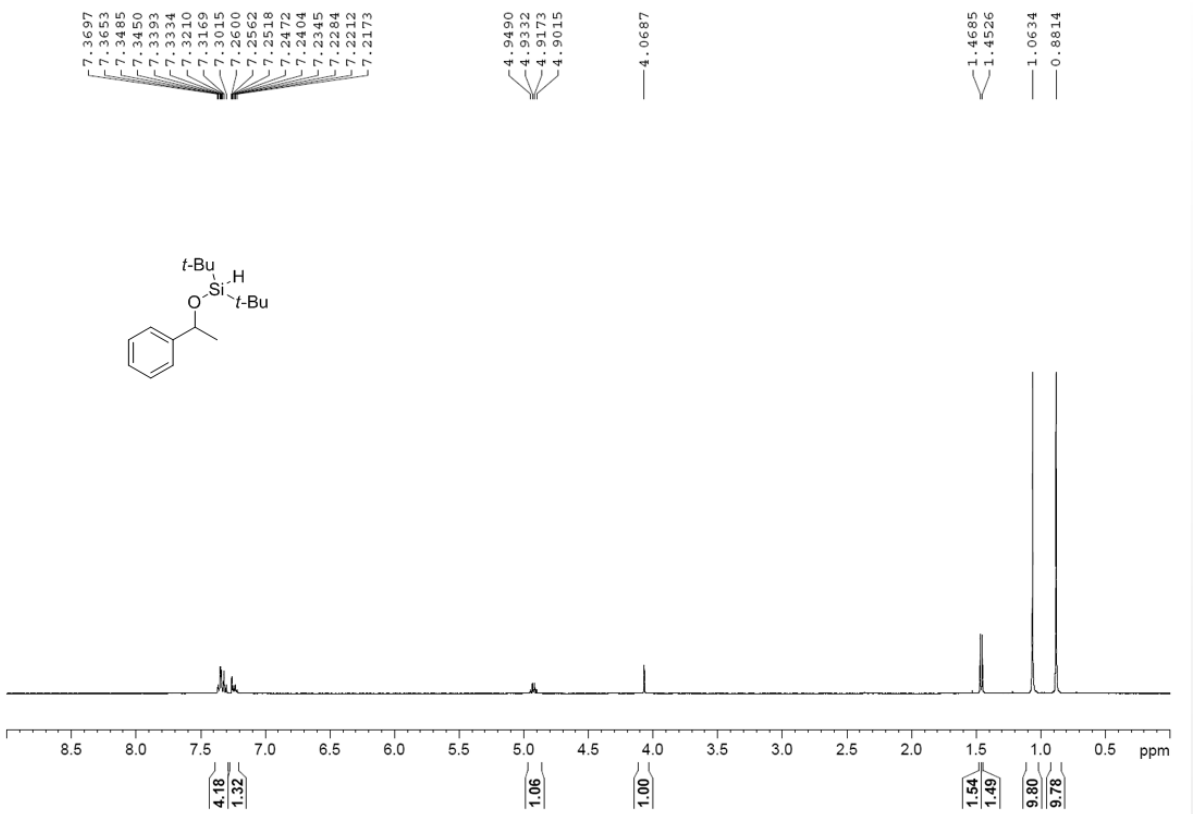

158.89
133.36
128.12
113.74
77.48
77.16
76.84
68.77
55.40
27.43
20.34
t-Bu
H
Si
O
t-Bu
H3CO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm



n-C_4H_9OSi (*t*-Bu)$_2$H



n-C_4H_9OSi (*t*-Bu)$_2$H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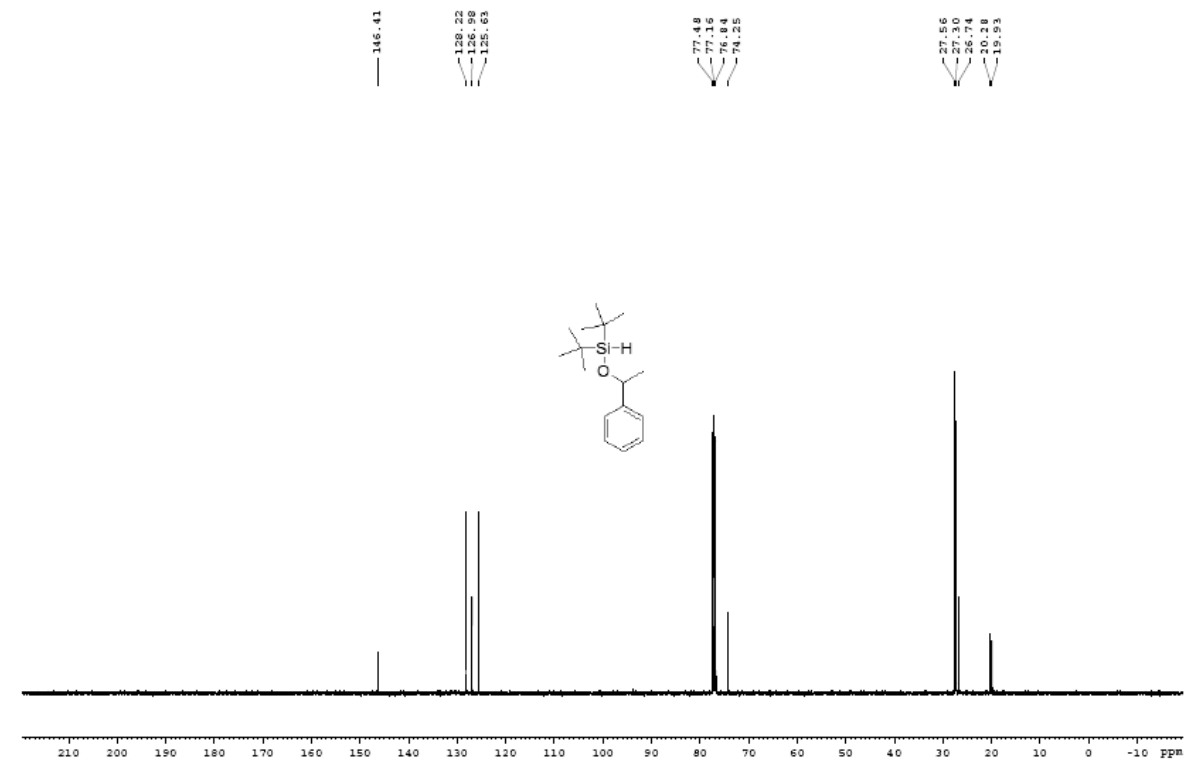
7.3485
7.3450
7.3393
7.3334
7.3210
7.3169
7.3015
7.2600
7.2562
7.2518
7.2472
7.2404
7.2345
7.2284
7.2212
7.2173
4.9490
4.9332
4.9173
4.9015
4.0687
1.4685
1.4526
1.0634
0.8814
t-Bu
Si
H
O
t-Bu
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.18
1.32
1.06
1.00
1.54
1.49
9.80
9.78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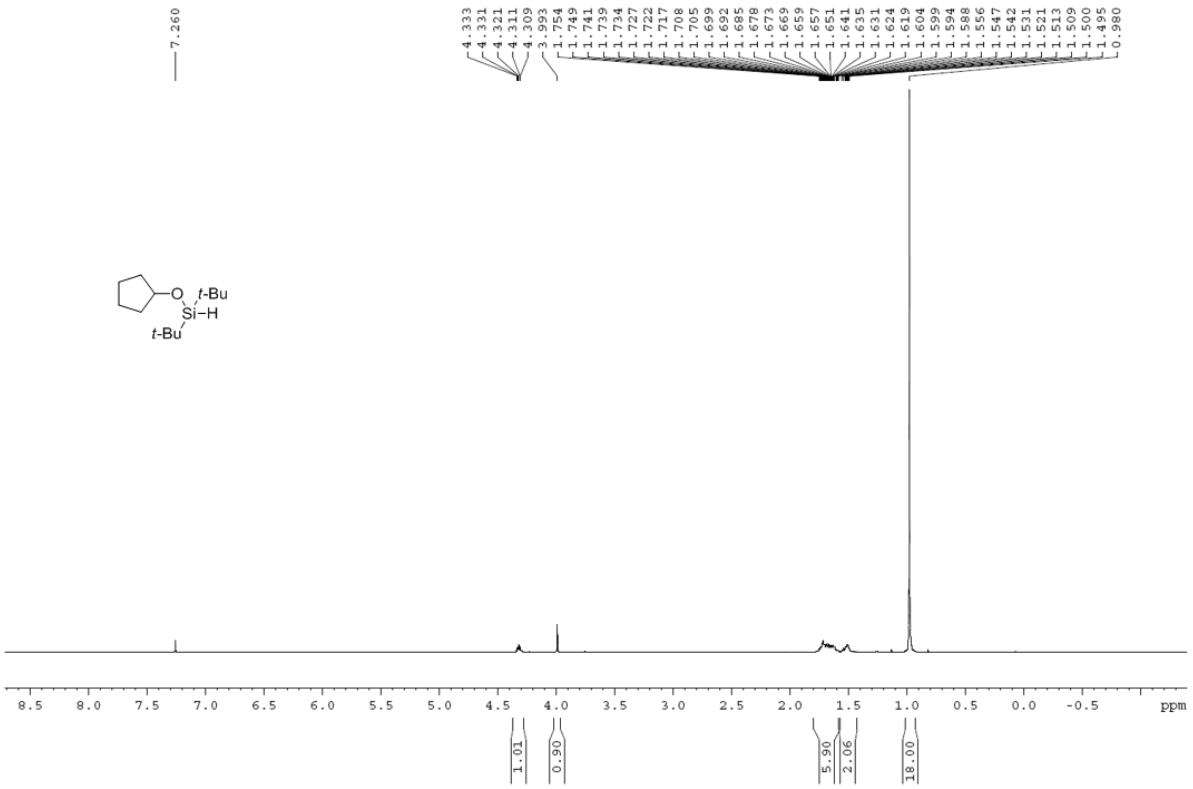
128.22
126.98
125.63
77.48
77.16
76.84
74.25
27.56
27.30
26.74
20.28
19.93
Si
H
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm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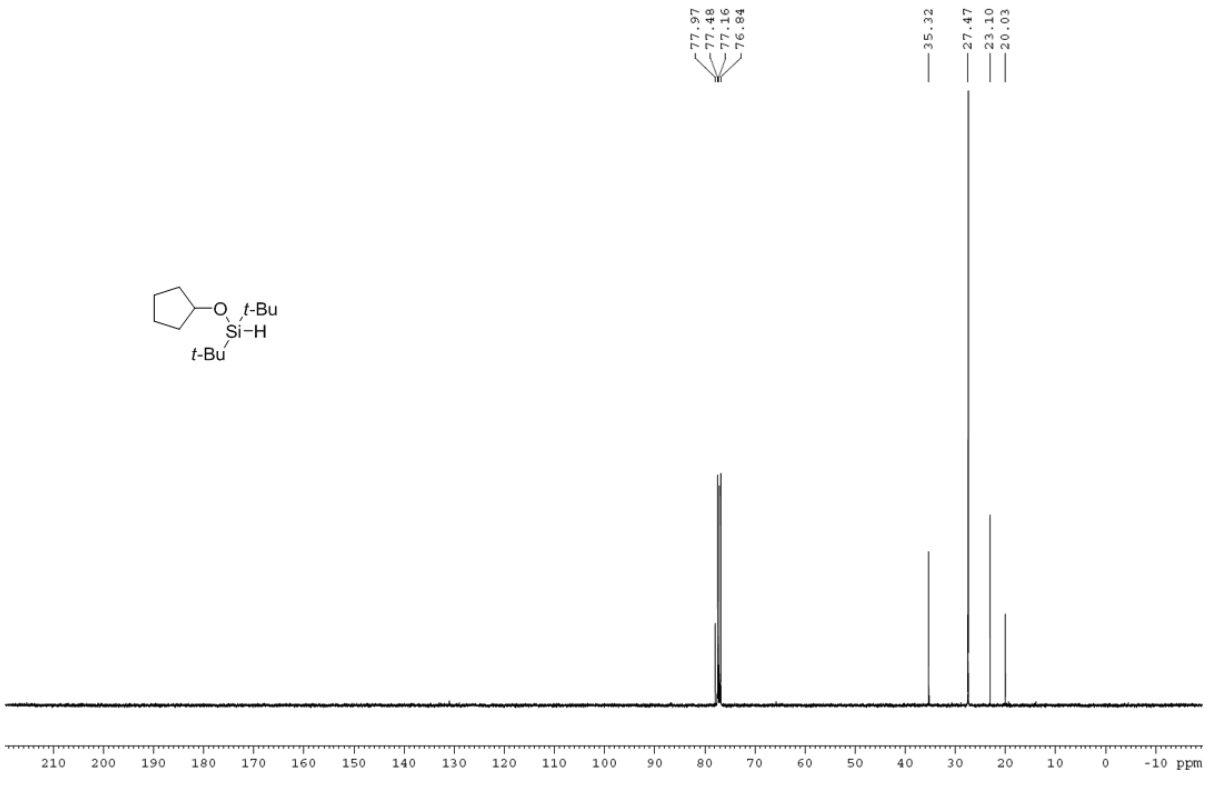
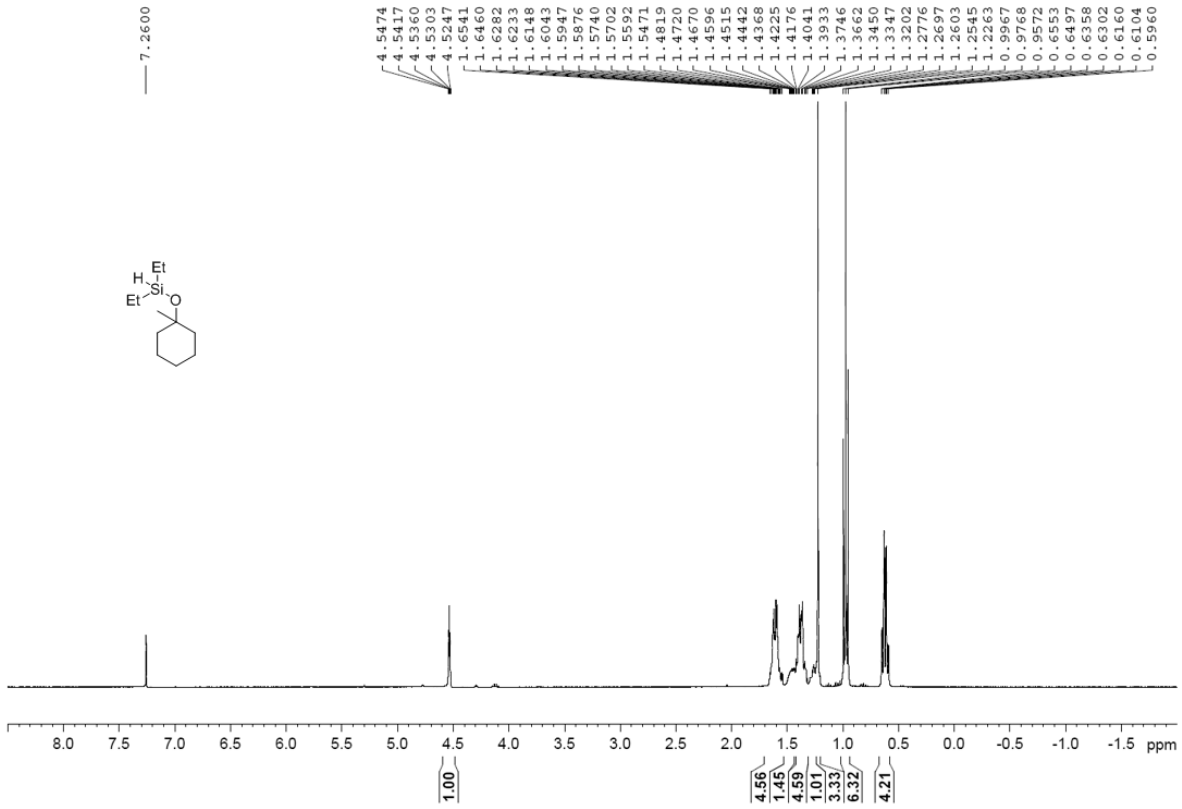
4.333
4.331
4.321
4.311
4.309
3.993
1.754
1.749
1.741
1.739
1.734
1.727
1.722
1.717
1.708
1.705
1.699
1.692
1.685
1.678
1.673
1.669
1.659
1.657
1.651
1.641
1.635
1.631
1.624
1.619
1.604
1.599
1.594
1.588
1.556
1.547
1.542
1.531
1.521
1.513
1.509
1.500
1.495
0.980
O
t-Bu
Si–H
t-Bu
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.01
0.90
5.90
2.06
18.00


77.97
77.48
77.16
76.84
35.32
27.47
23.10
20.03
O
t-Bu
Si–H
t-Bu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm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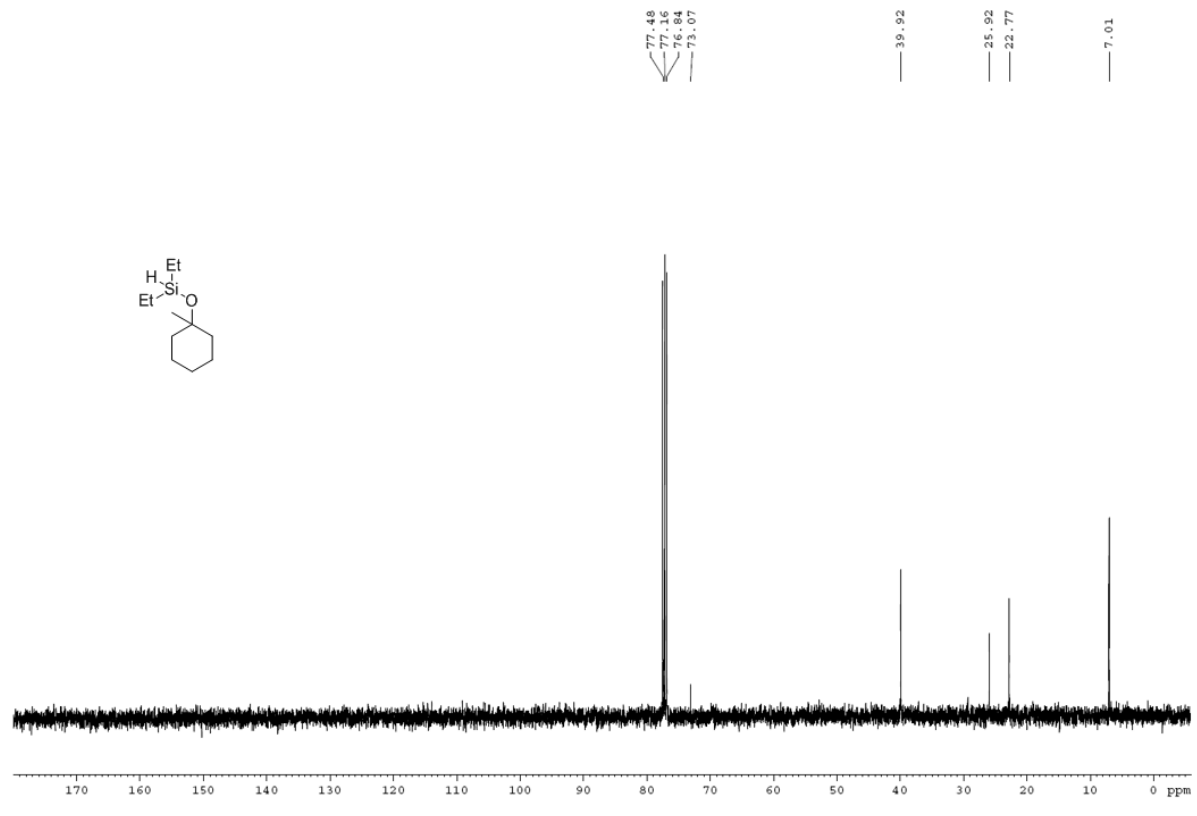
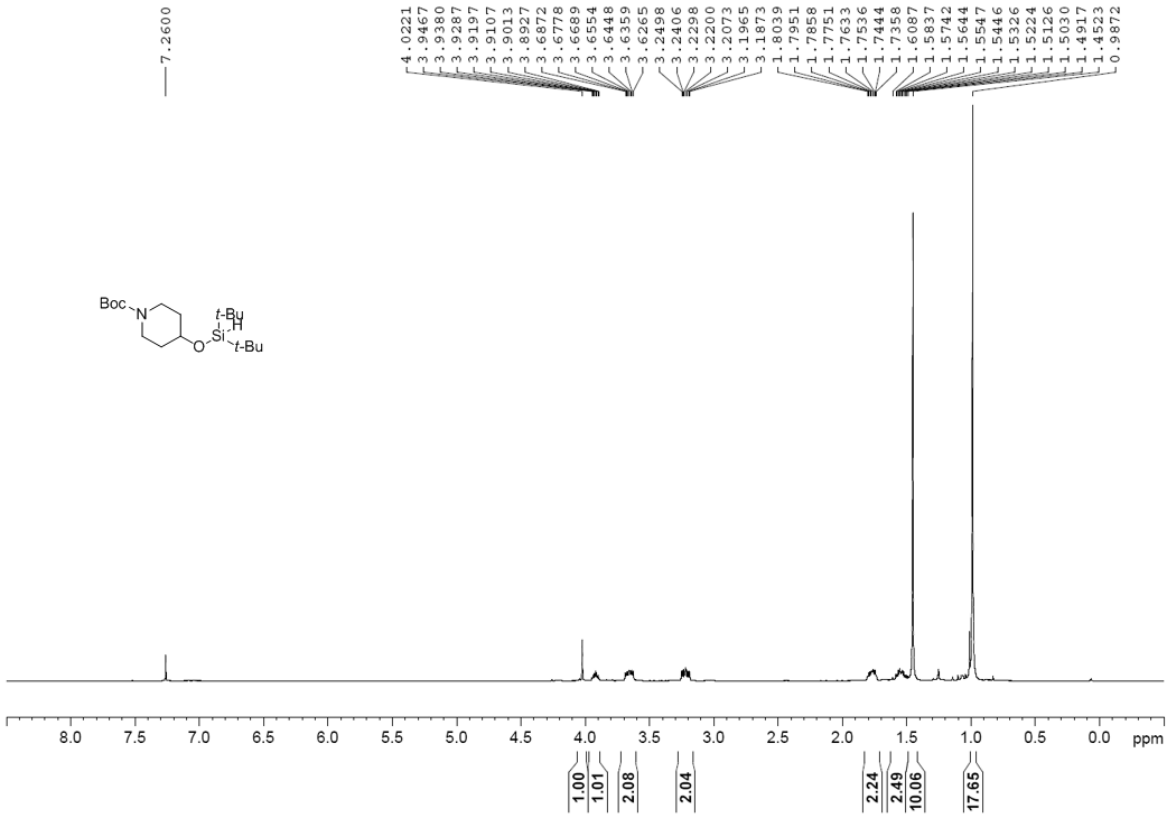
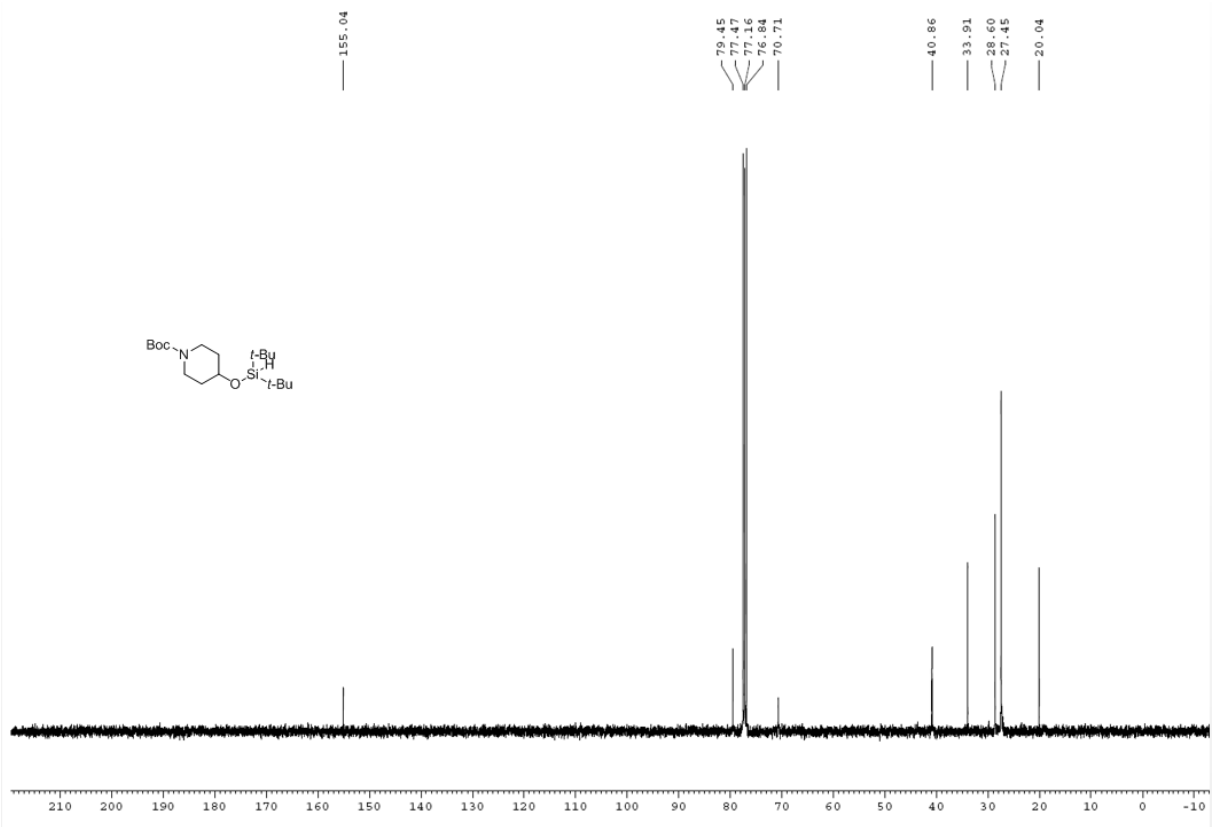
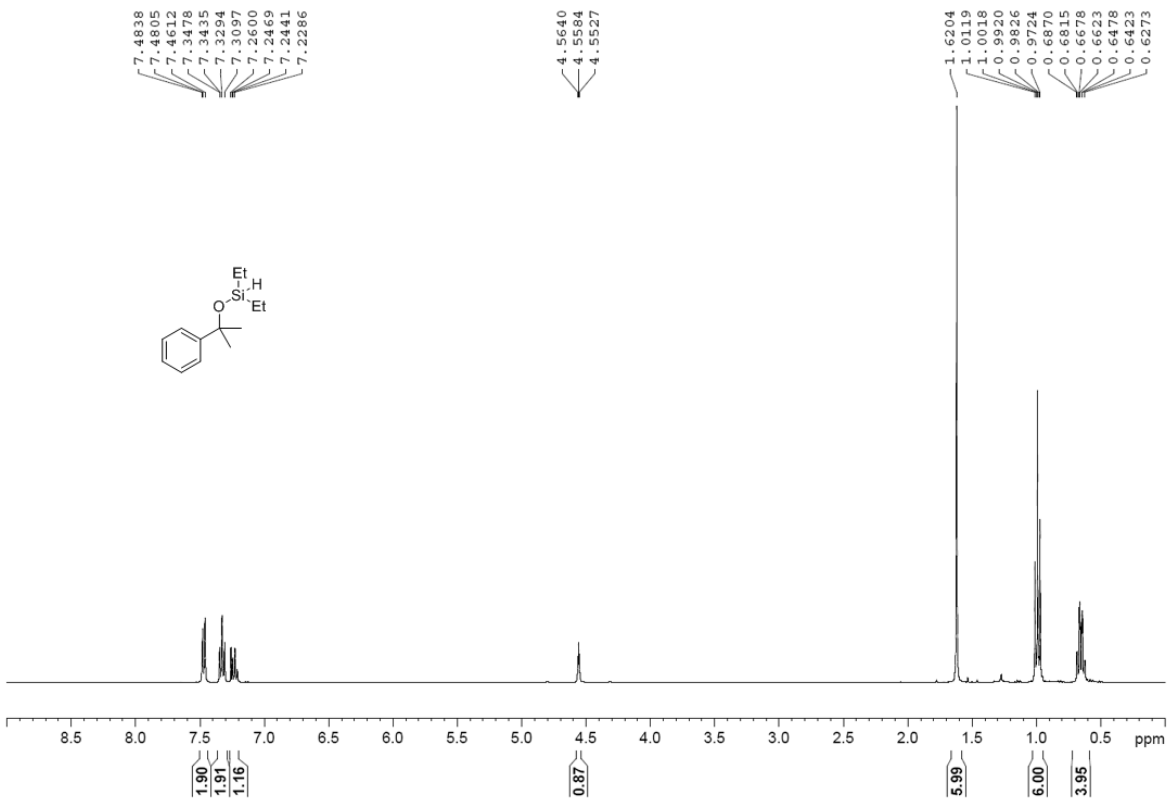
4.5474
4.5417
4.5360
4.5303
4.5247
1.6541
1.6460
1.6282
1.6233
1.6148
1.6043
1.5947
1.5876
1.5740
1.5702
1.5592
1.5471
1.4819
1.4720
1.4670
1.4596
1.4515
1.4442
1.4368
1.4225
1.4176
1.4041
1.3933
1.3746
1.3662
1.3450
1.3347
1.3202
1.2776
1.2697
1.2603
1.2545
1.2263
0.9967
0.9768
0.9572
0.6553
0.6497
0.6358
0.6302
0.6160
0.6104
0.5960
Et
H
Si
Et
O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 ppm
1.00
4.56
1.45
4.59
1.01
3.33
6.32
4.21


77.48
77.16
76.84
73.07
39.92
25.92
22.77
7.01
Et
H
Si
Et
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.2600
4.0221
3.9467
3.9380
3.9287
3.9197
3.9107
3.9013
3.8927
3.6872
3.6778
3.6689
3.6554
3.6448
3.6359
3.6265
3.2498
3.2406
3.2298
3.2200
3.2073
3.1965
3.1873
1.8039
1.7951
1.7858
1.7751
1.7633
1.7536
1.7444
1.7358
1.6087
1.5837
1.5742
1.5644
1.5547
1.5446
1.5326
1.5224
1.5126
1.5030
1.4917
1.4523
0.9872
Boc
N
O
Si
t-Bu
H
t-Bu
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.01
2.08
2.04
2.24
2.49
10.06
17.65


155.04
79.45
77.47
77.16
76.84
70.71
40.86
33.91
28.60
27.45
20.04
Boc
N
O
Si
t-Bu
H
t-Bu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10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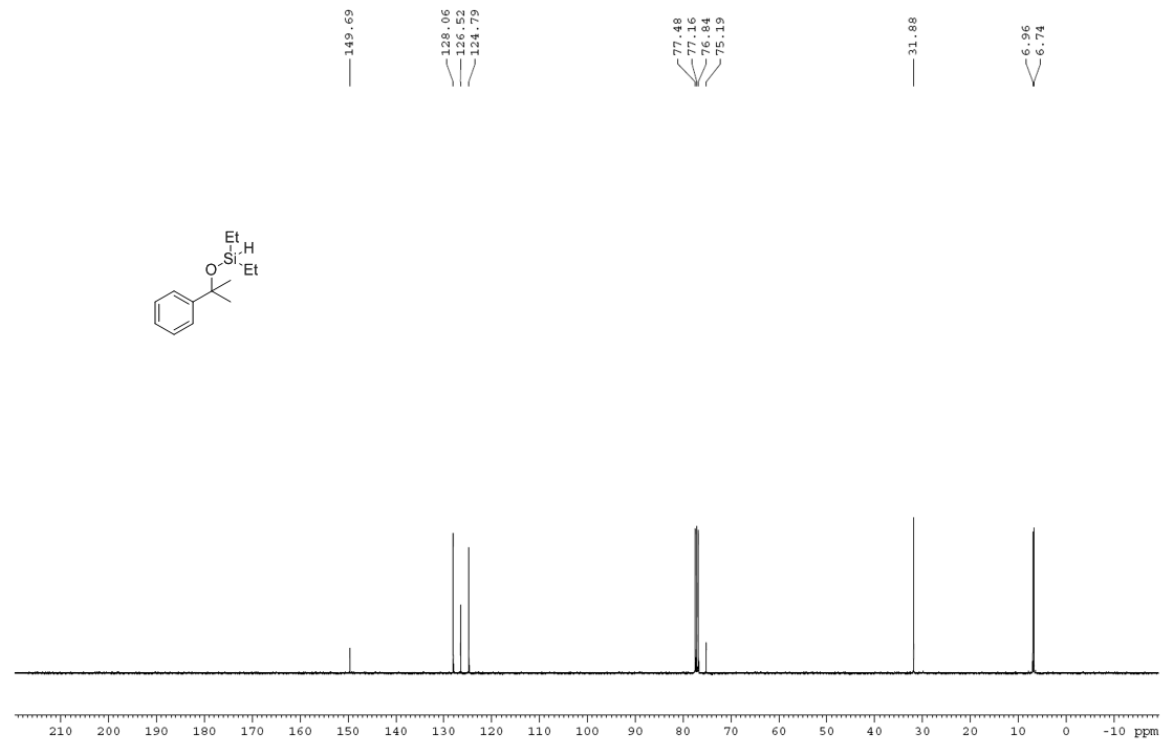
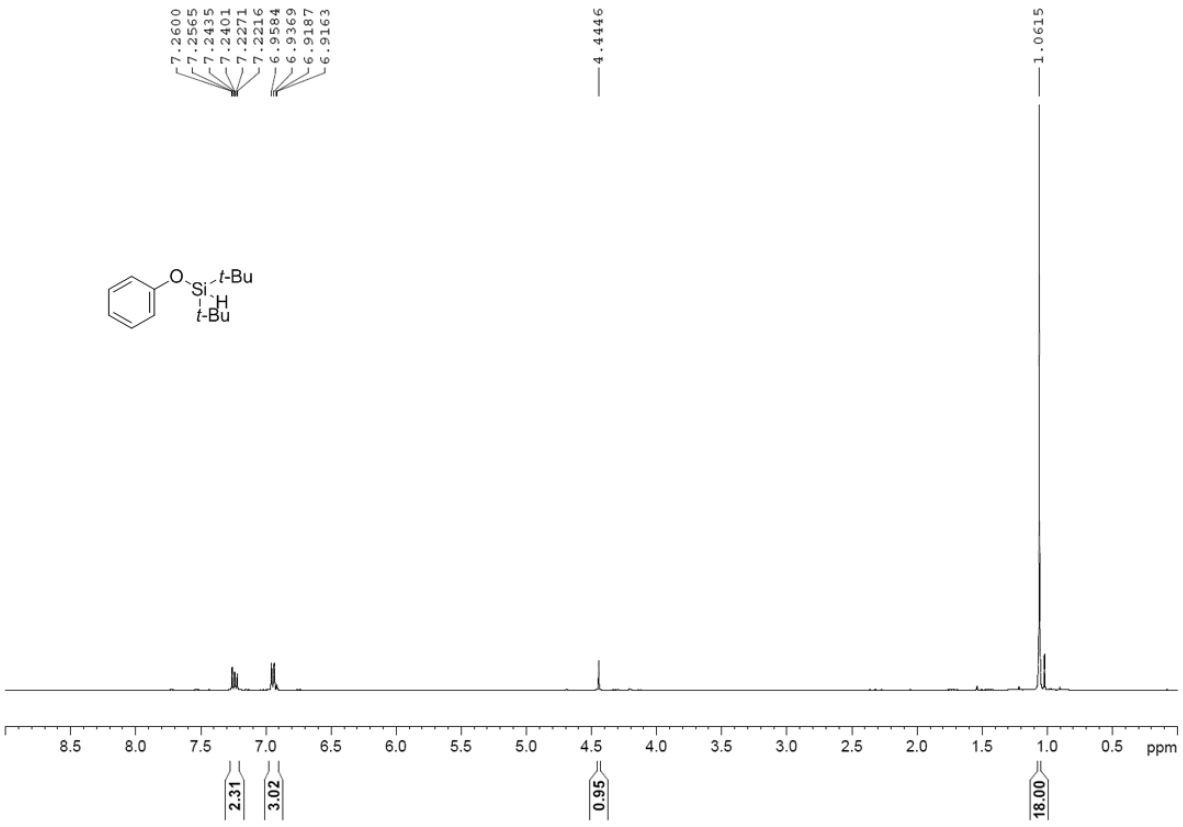
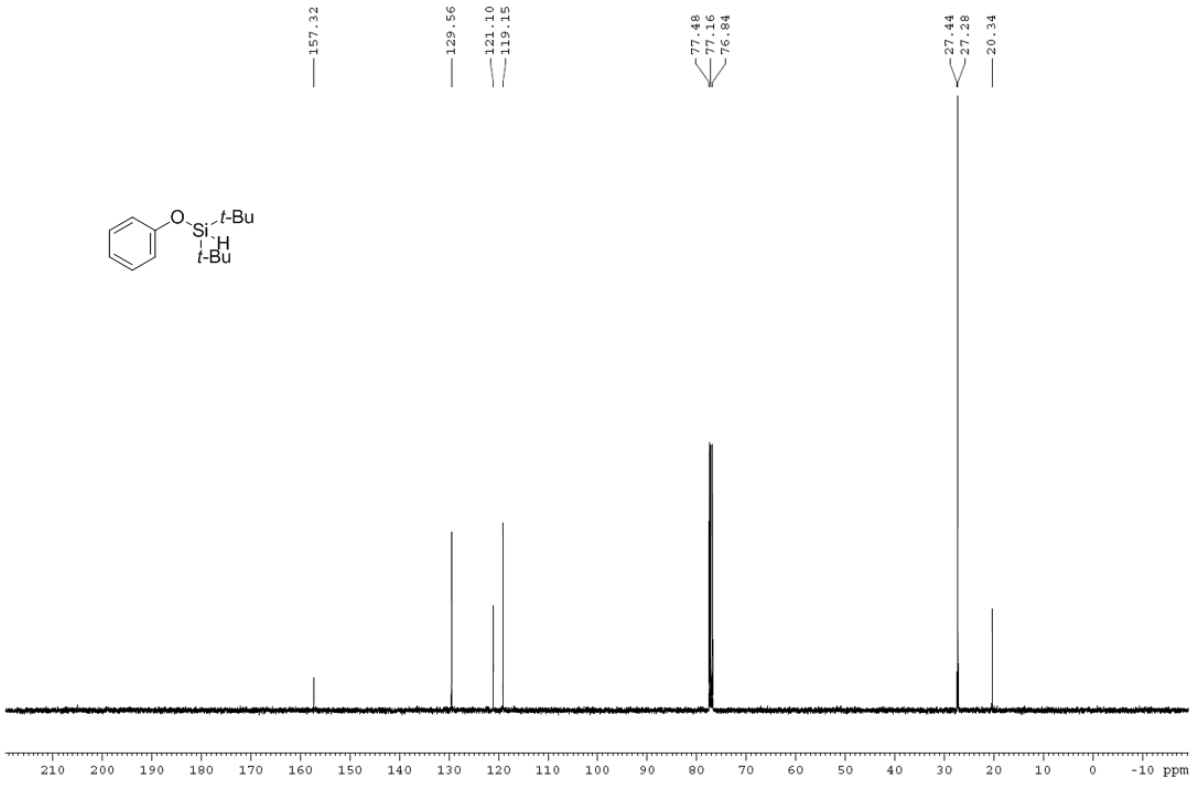
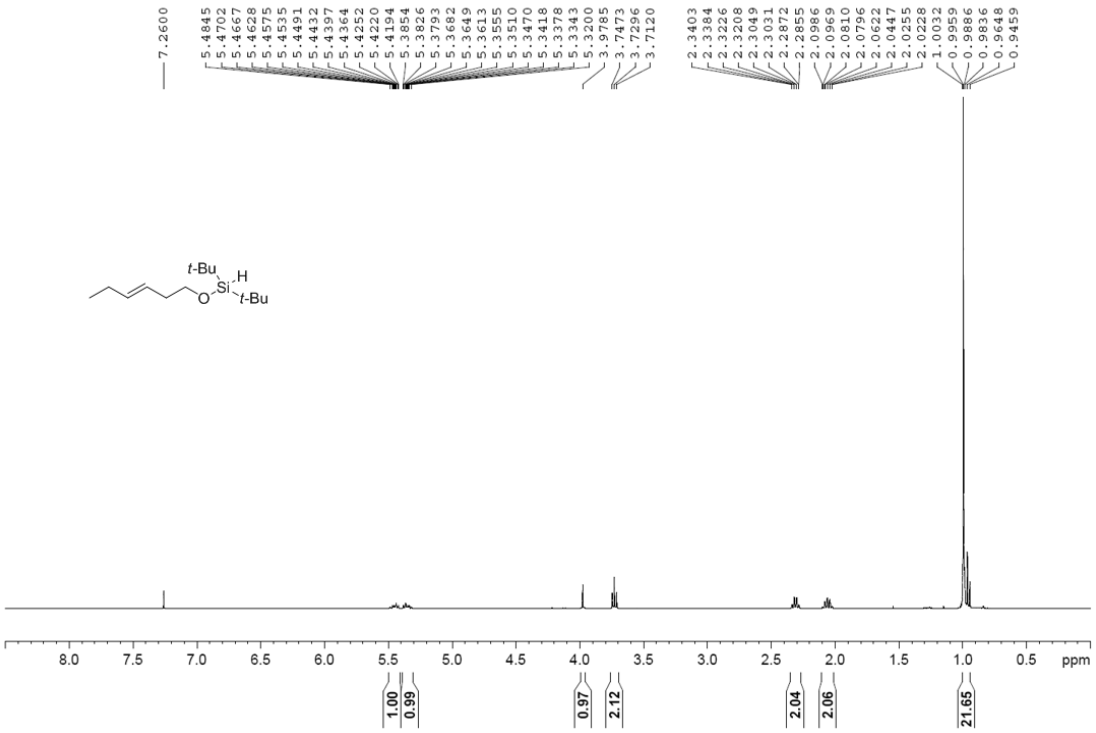
7.4805
7.4612
7.3478
7.3435
7.3294
7.3097
7.2600
7.2469
7.2441
7.2286
4.5640
4.5584
4.5527
1.6204
1.0119
1.0018
0.9920
0.9826
0.9724
0.6870
0.6815
0.6678
0.6623
0.6478
0.6423
0.6273
Et
Si
H
O
Et
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.90
1.91
1.16
0.87
5.99
6.00
3.95


149.69
128.06
126.52
124.79
77.48
77.16
76.84
75.19
31.88
6.96
6.74
Et
Si
H
O
Et
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


7.2600
7.2565
7.2435
7.2401
7.2271
7.2216
6.9584
6.9369
6.9187
6.9163
4.4446
1.0615
O
Si
t-Bu
H
t-Bu
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.31
3.02
0.95
18.00


157.32
129.56
121.10
119.15
77.48
77.16
76.84
27.44
27.28
20.34
O
Si
t-Bu
H
t-Bu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm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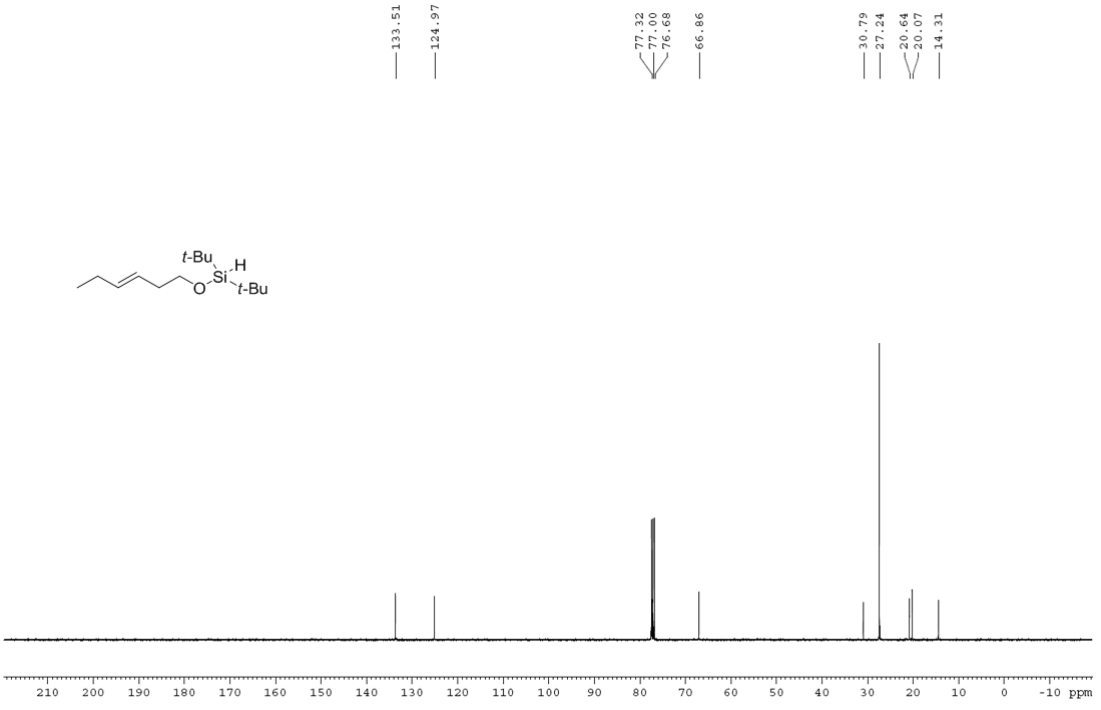
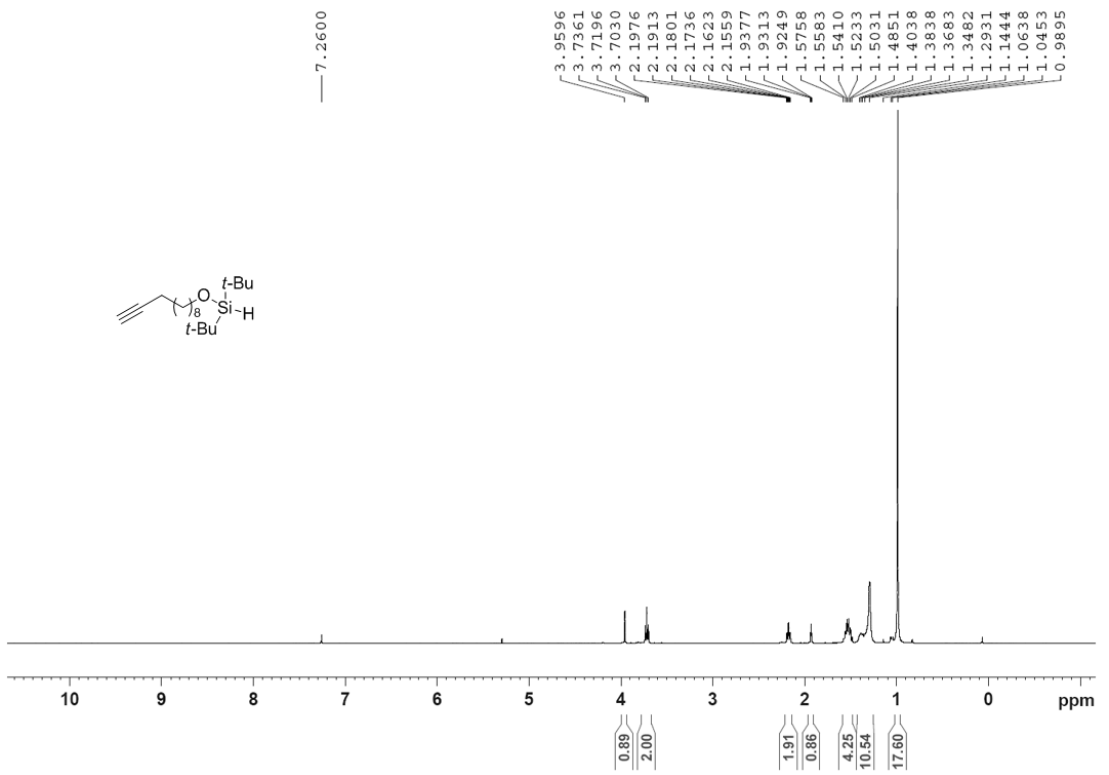
5.4845
5.4702
5.4667
5.4628
5.4575
5.4535
5.4491
5.4432
5.4397
5.4364
5.4252
5.4220
5.4194
5.3854
5.3826
5.3793
5.3682
5.3649
5.3613
5.3555
5.3510
5.3470
5.3418
5.3378
5.3343
5.3200
3.9785
3.7473
3.7296
3.7120
2.3403
2.3384
2.3226
2.3208
2.3049
2.3031
2.2872
2.2855
2.0986
2.0969
2.0810
2.0796
2.0622
2.0447
2.0255
2.0228
1.0032
0.9959
0.9886
0.9836
0.9648
0.9459
t-Bu
Si
H
O
t-Bu
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.99
0.97
2.12
2.04
2.06
21.65


133.51
124.97
77.32
77.00
76.68
66.86
30.79
27.24
20.64
20.07
14.31
t-Bu
Si
H
O
t-Bu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm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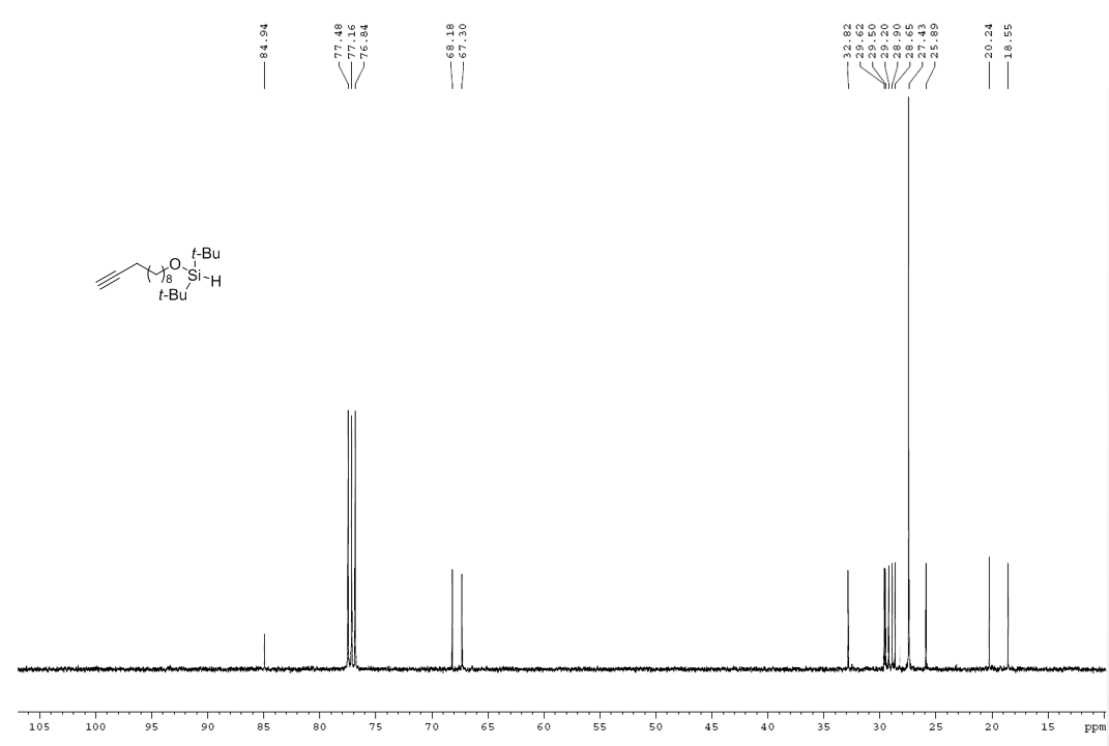
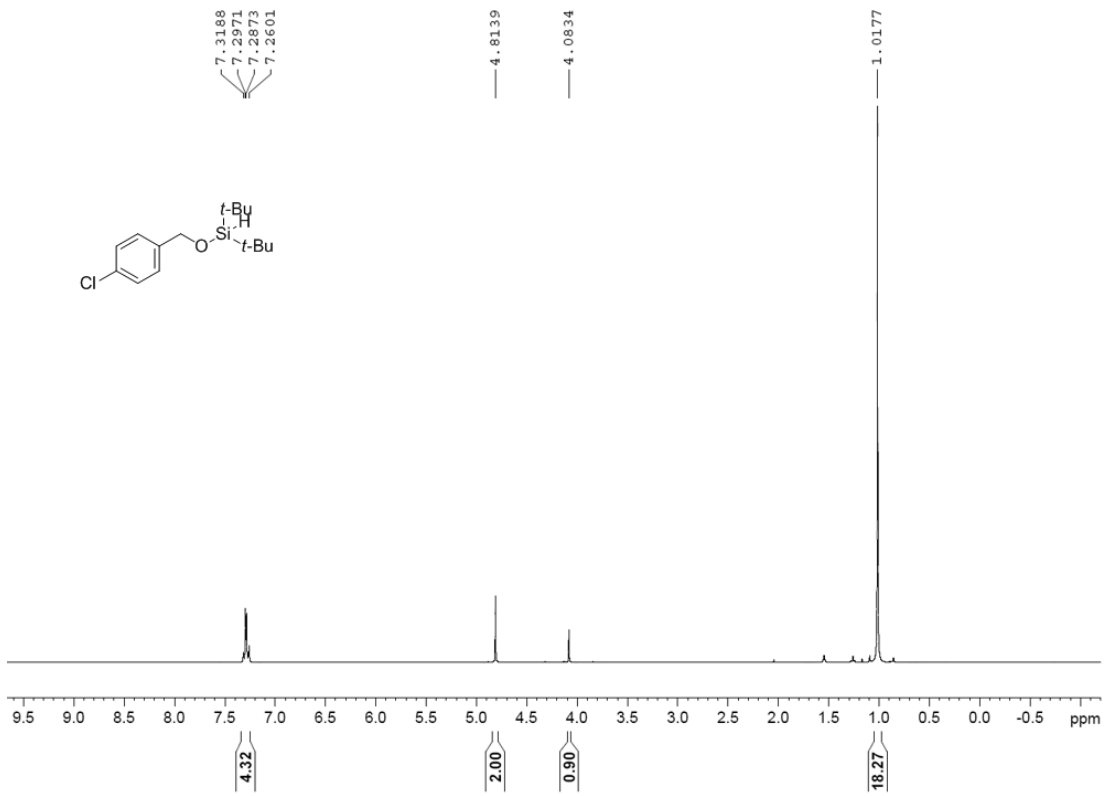
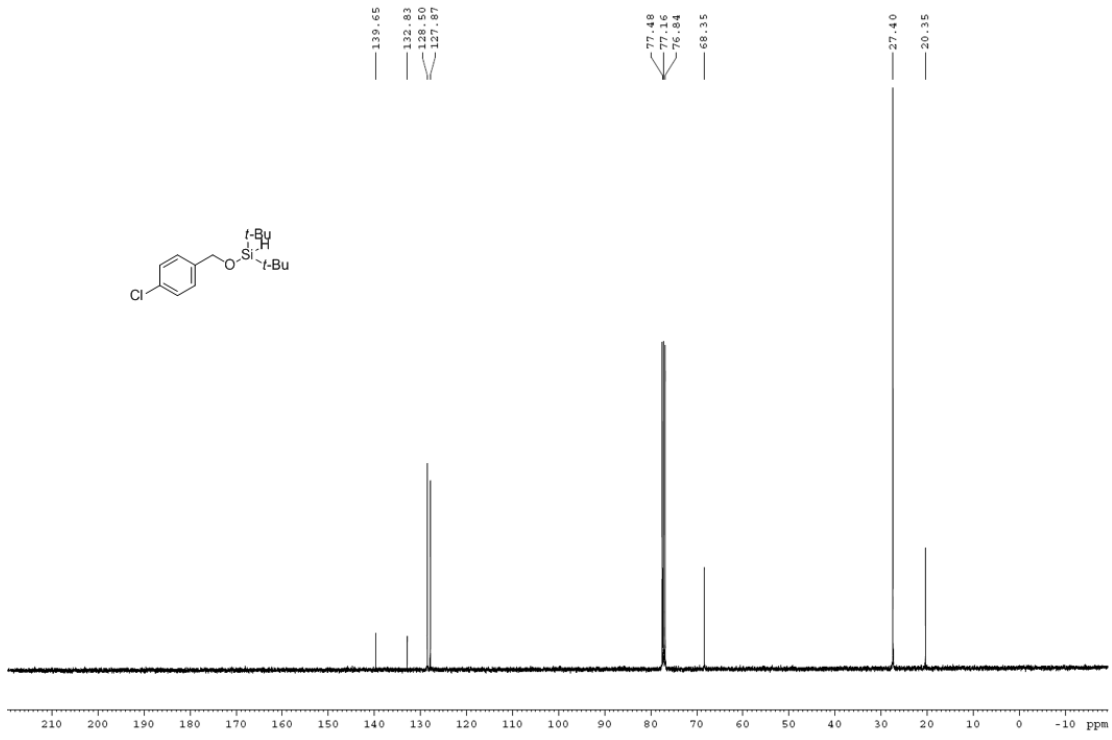
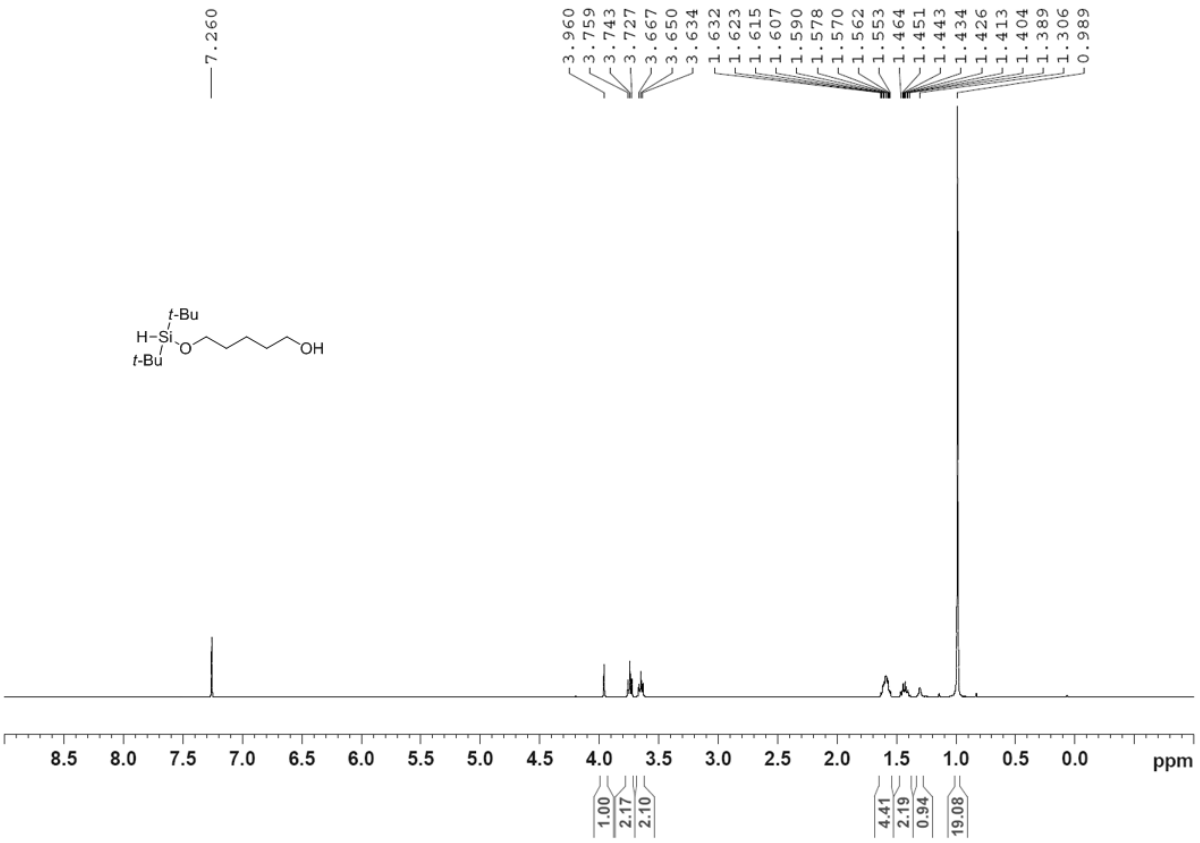
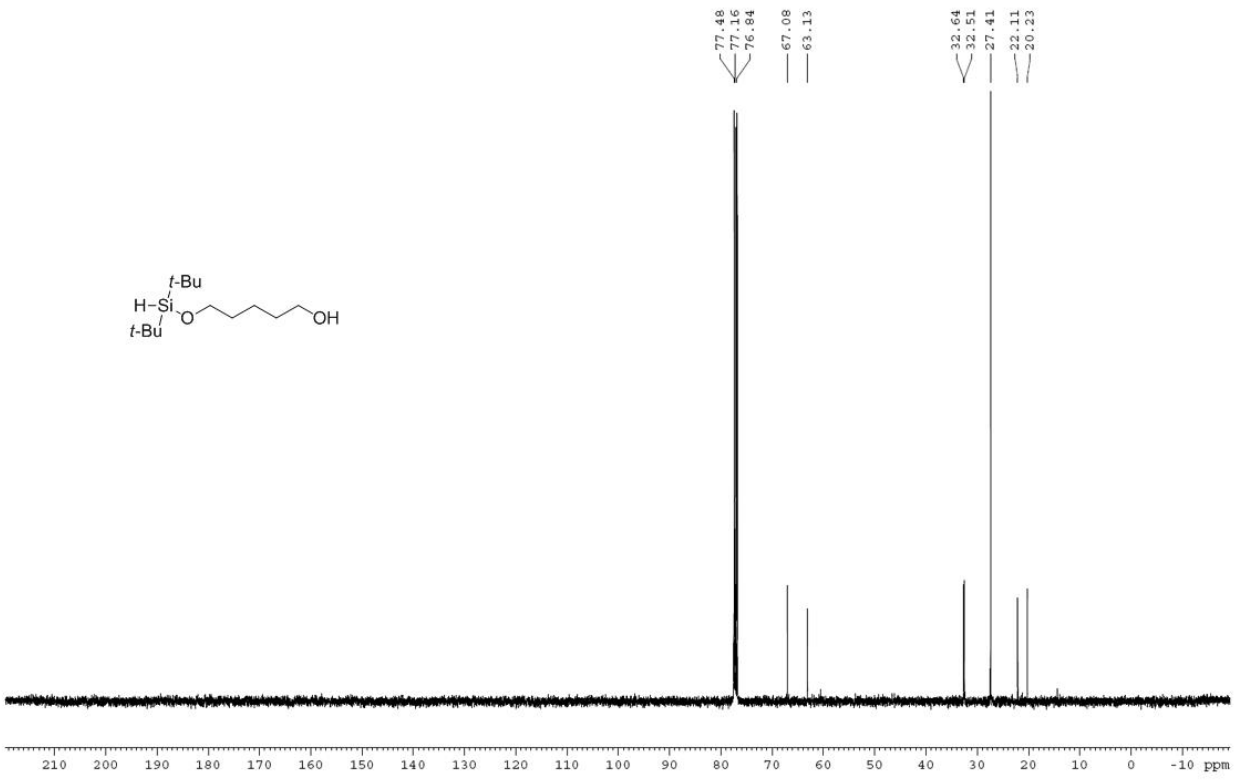
3.9596
3.7361
3.7196
3.7030
2.1976
2.1913
2.1801
2.1736
2.1623
2.1559
1.9377
1.9313
1.9249
1.5758
1.5583
1.5410
1.5233
1.5031
1.4851
1.4038
1.3838
1.3683
1.3482
1.2931
1.1444
1.0638
1.0453
0.9895
t-Bu
O
Si
H
t-Bu
10
9
8
7
6
5
4
3
2
1
0
ppm
0.89
2.00
1.91
0.86
4.25
10.54
17.60

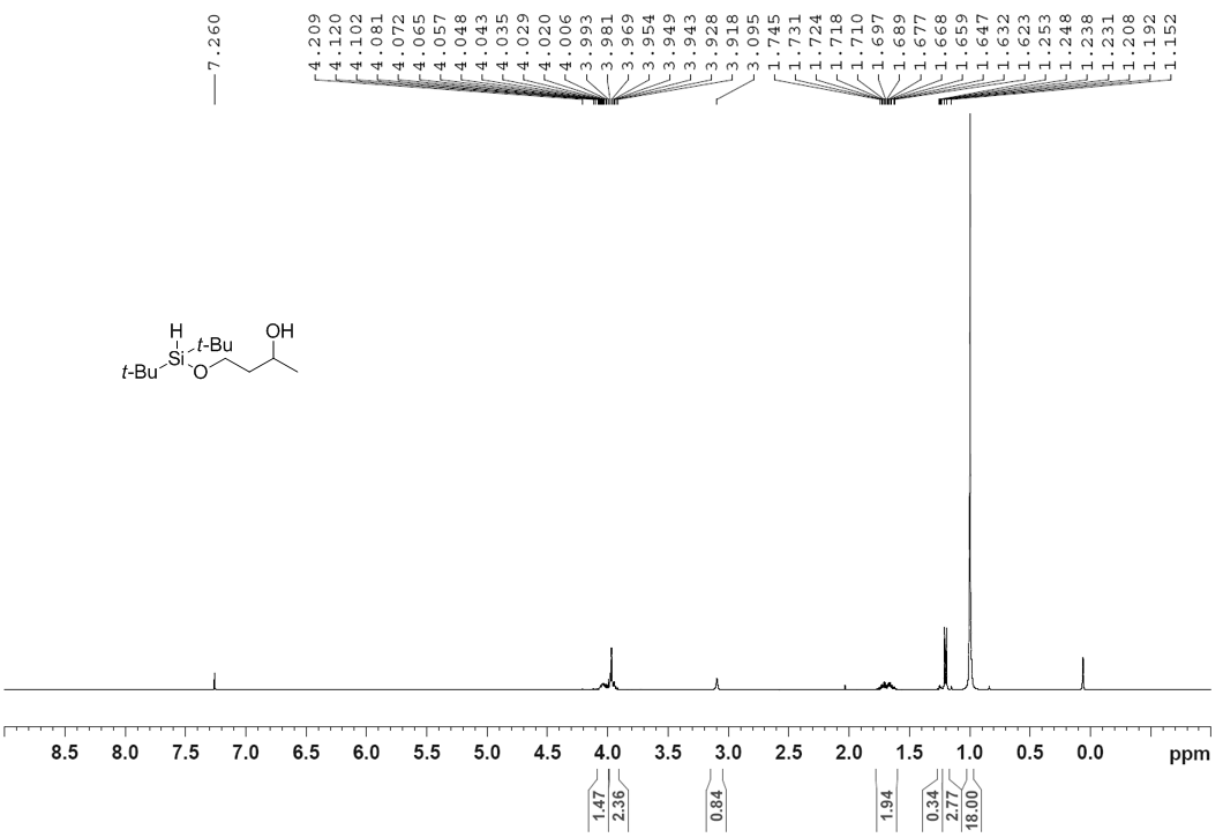

84.94
77.48
77.16
76.84
68.18
67.30
32.82
29.62
29.50
29.20
28.90
28.65
28.43
25.89
20.24
18.55
t-Bu
O
Si
H
t-Bu
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
ppm

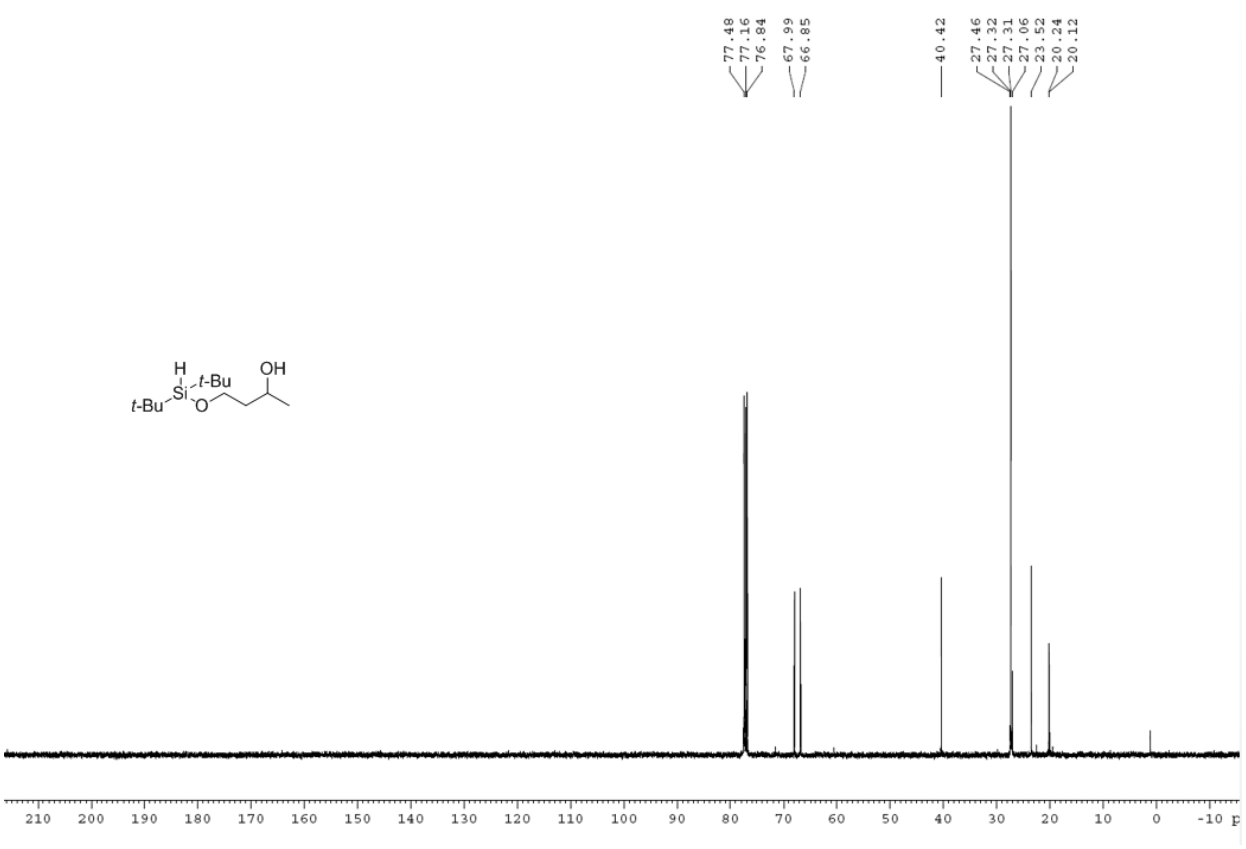

7.3188
7.2971
7.2873
7.2601
4.8139
4.0834
1.0177
t-Bu
H
Si
O
t-Bu
Cl
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
4.32
2.00
0.90
18.27

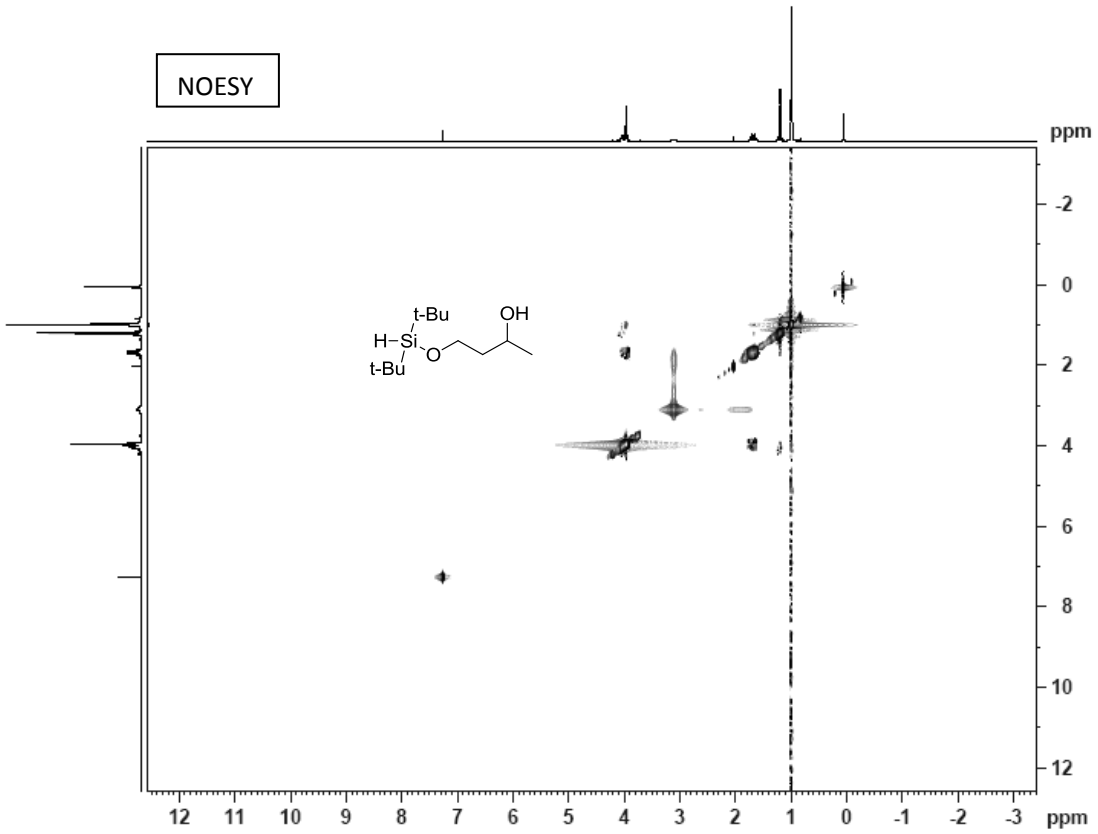

139.65
132.83
128.50
127.87
77.48
77.16
76.84
68.35
27.40
20.35
t-Bu
H
Si
O
t-Bu
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

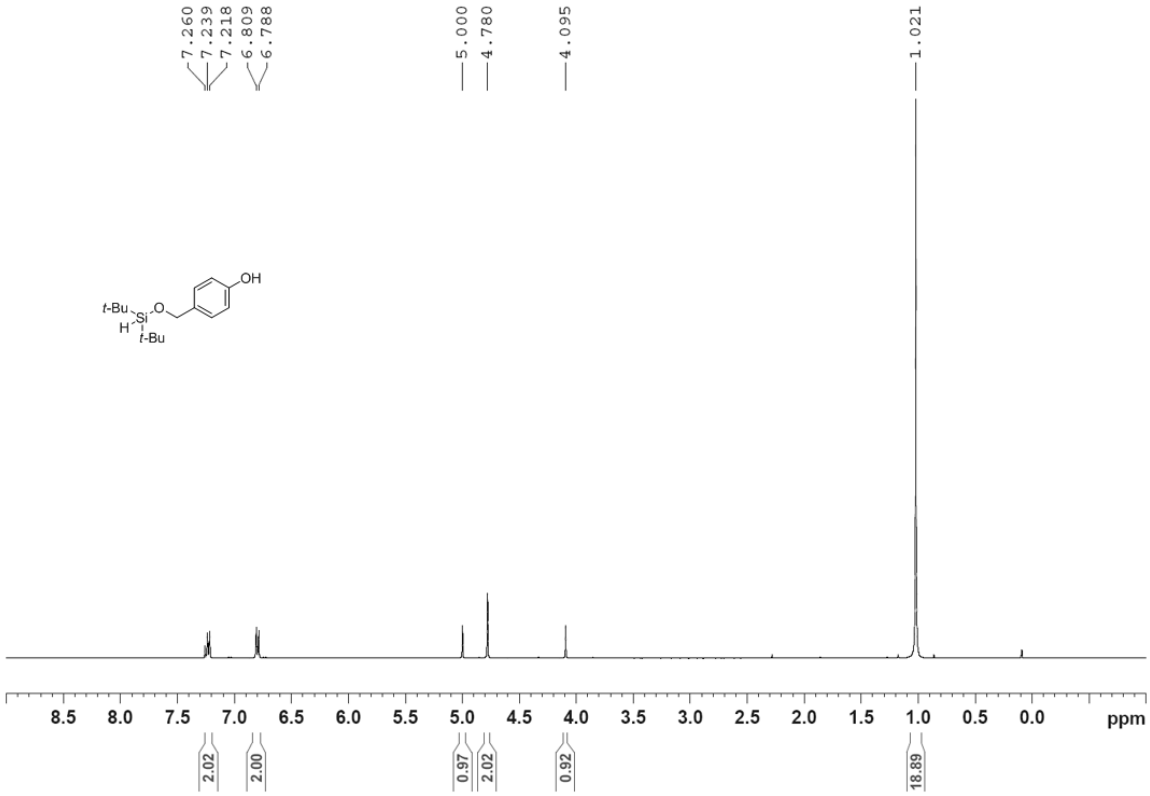

7.260
3.960
3.759
3.743
3.727
3.667
3.650
3.634
1.632
1.623
1.615
1.607
1.590
1.578
1.570
1.562
1.553
1.464
1.451
1.443
1.434
1.426
1.413
1.404
1.389
1.306
0.989
t-Bu
H–Si
O
t-Bu
OH
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.17
2.10
4.41
2.19
0.94
19.08

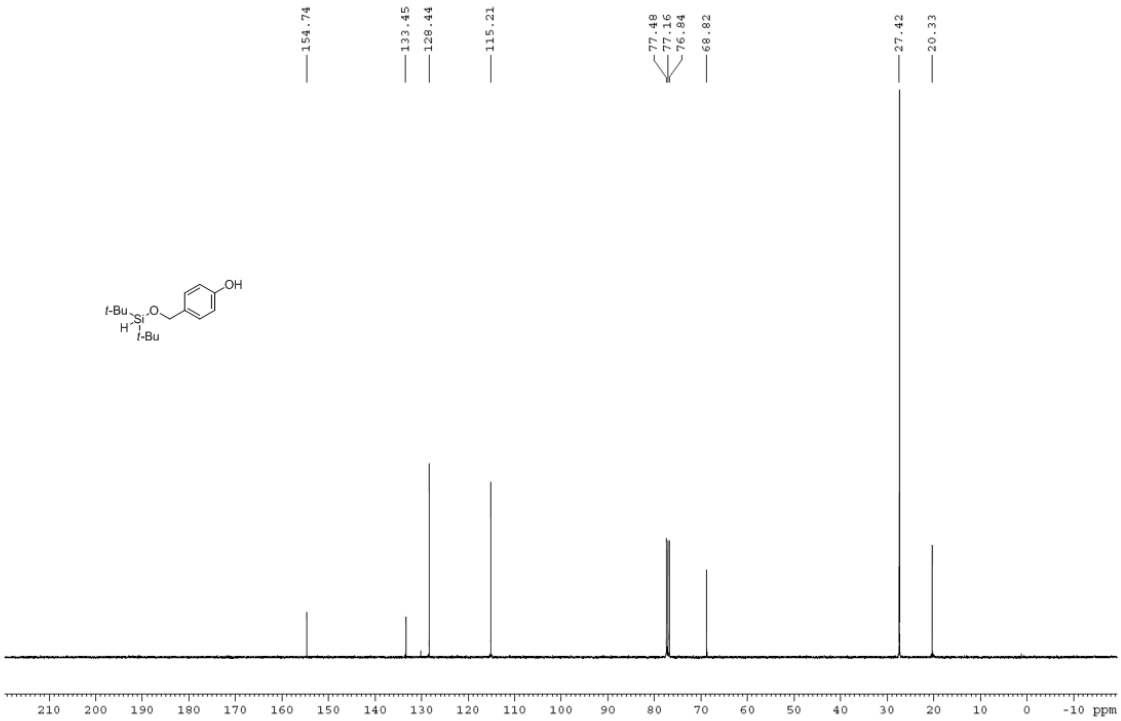

77.48
77.16
76.84
67.08
63.13
32.64
32.51
27.41
22.11
20.23
t-Bu
H–Si
O
t-Bu
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

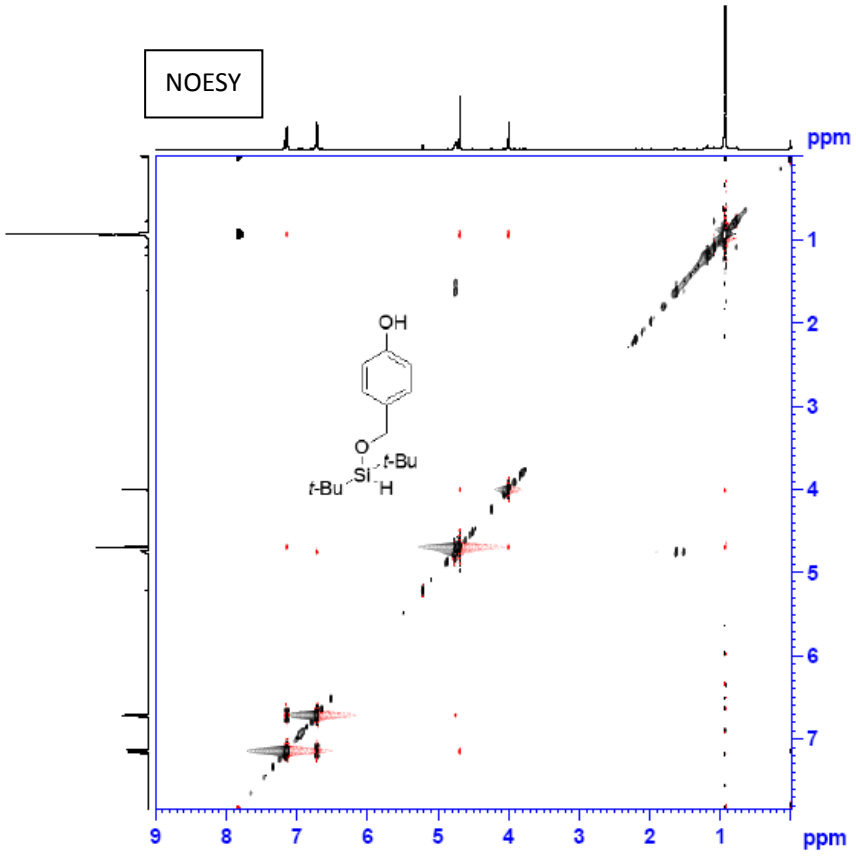

7.260
4.209
4.120
4.102
4.081
4.072
4.065
4.057
4.048
4.043
4.035
4.029
4.020
4.006
3.993
3.981
3.969
3.954
3.949
3.943
3.928
3.918
3.095
1.745
1.731
1.724
1.718
1.710
1.697
1.689
1.677
1.668
1.659
1.647
1.632
1.623
1.253
1.248
1.238
1.231
1.208
1.192
1.152
H
Si
t-Bu
t-Bu
O
OH
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.47
2.36
0.84
1.94
0.34
2.77
18.00


77.48
77.16
76.84
67.99
66.85
40.42
27.46
27.32
27.31
27.06
23.52
20.24
20.12
H
Si
t-Bu
t-Bu
O
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 p

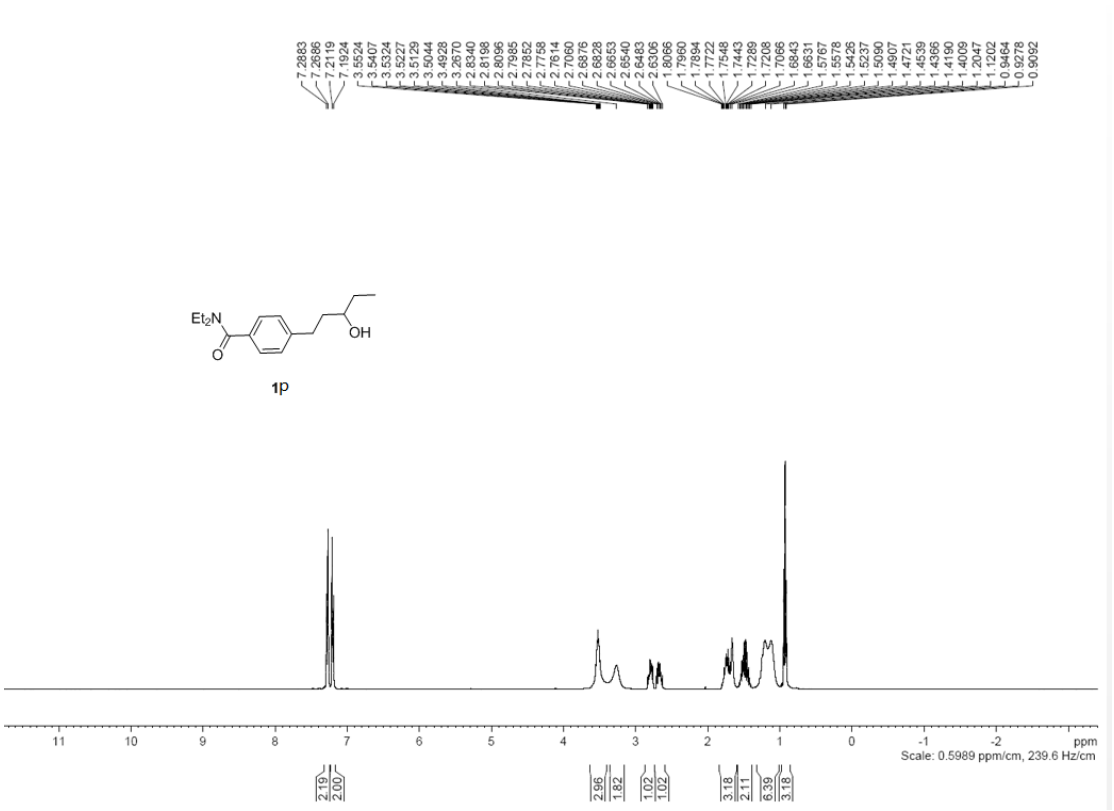

NOESY
t-Bu
OH
H–Si
O
t-Bu
ppm
-2
0
2
4
6
8
10
12
12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm

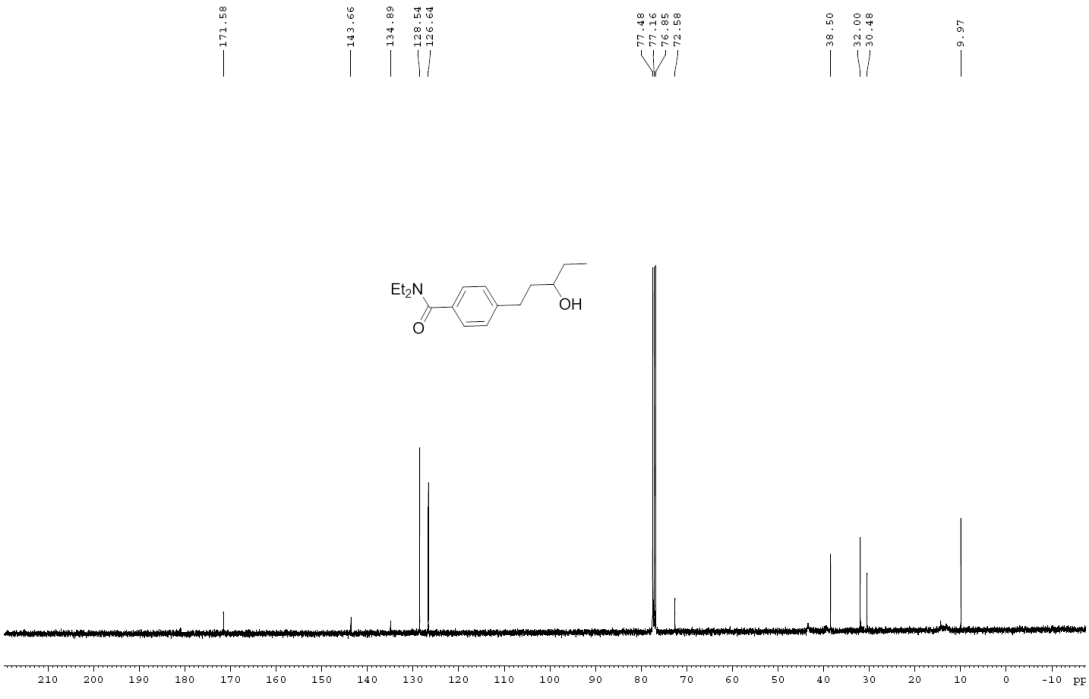

7.260
7.239
7.218
6.809
6.788
5.000
4.780
4.095
1.021
OH
t-Bu
Si
H
O
t-Bu
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.02
2.00
0.97
2.02
0.92
18.89

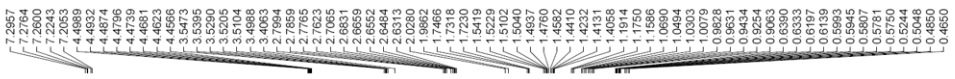

154.74
133.45
128.44
115.21
77.48
77.16
76.84
68.82
27.42
20.33
OH
t-Bu
Si
H
O
t-Bu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


NOESY
ppm
1
2
3
4
5
6
7
OH
O
t-Bu
Si
t-Bu
H
9 8 7 6 5 4 3 2 1
ppm

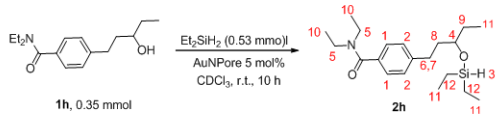
Unstable hydridosilyl ethers(2p, 2q, 2r) with diethylsilane

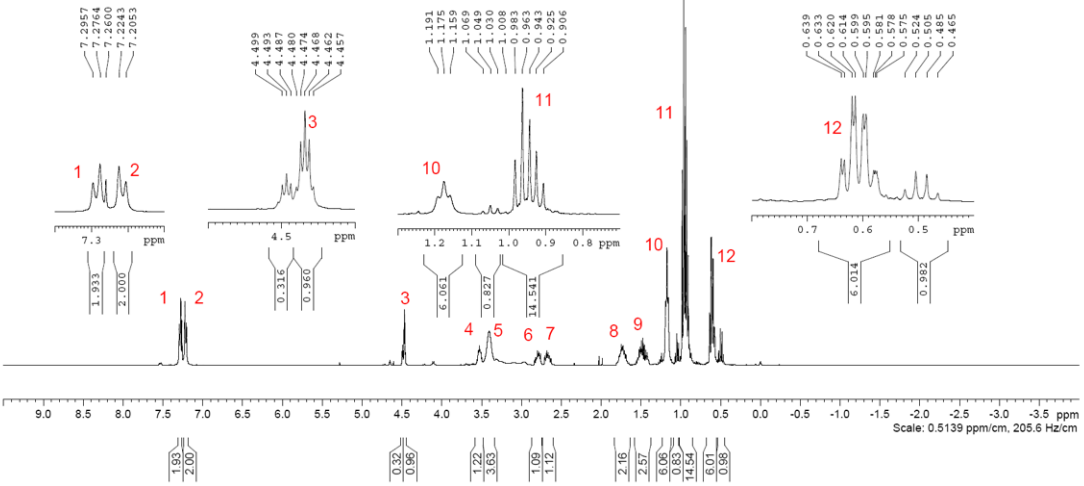


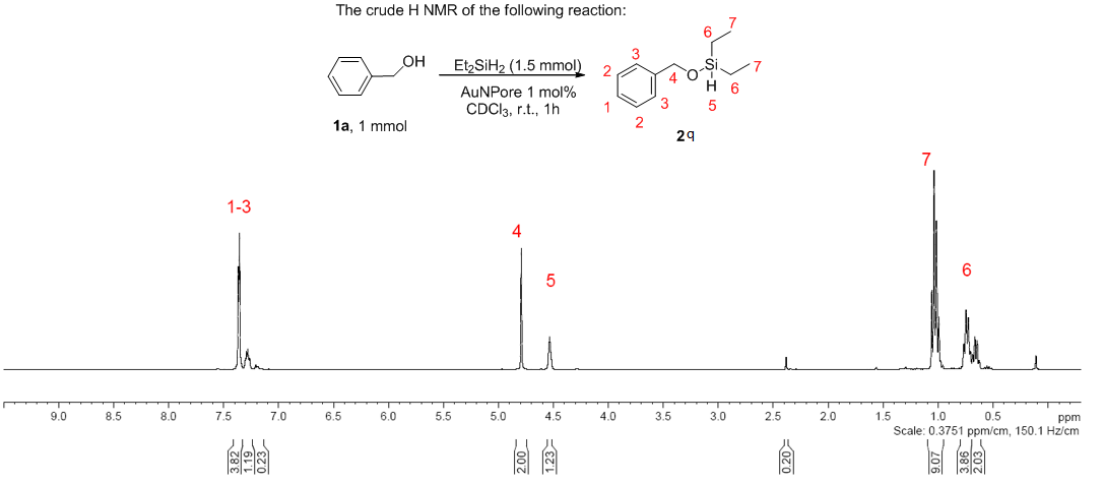




Crude H NMR of the following reaction:

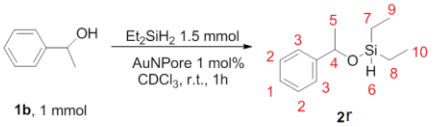


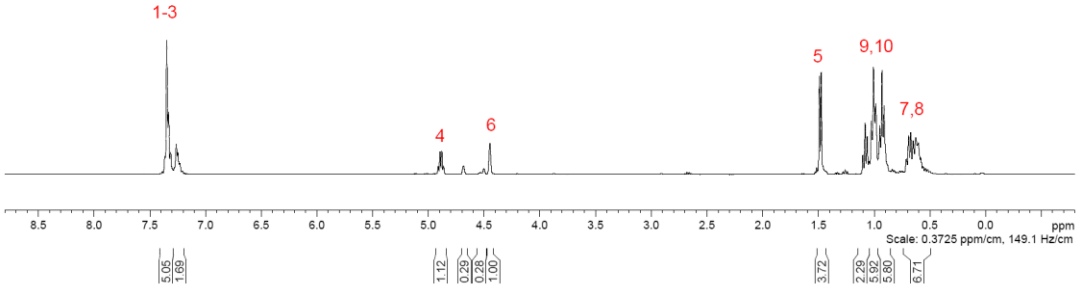


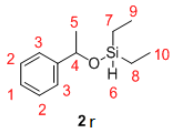


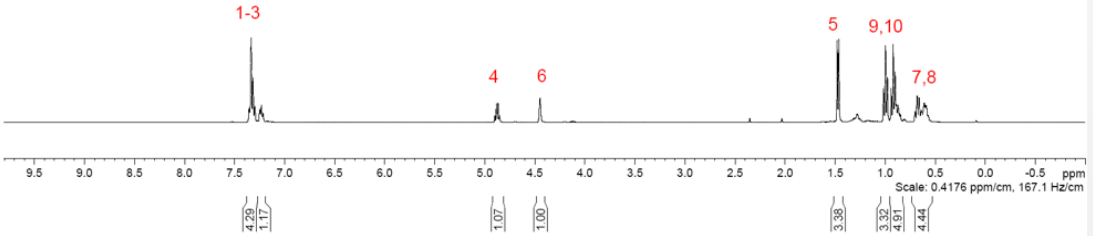
The crude H NMR of the following reaction:

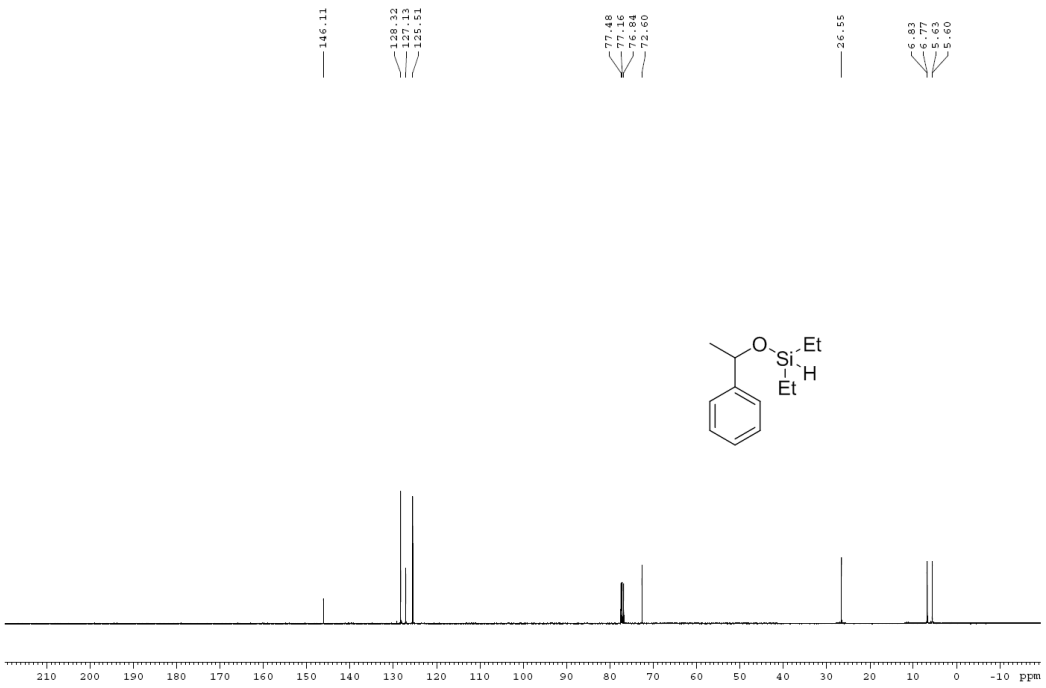
The crude H NMR of the following reaction:



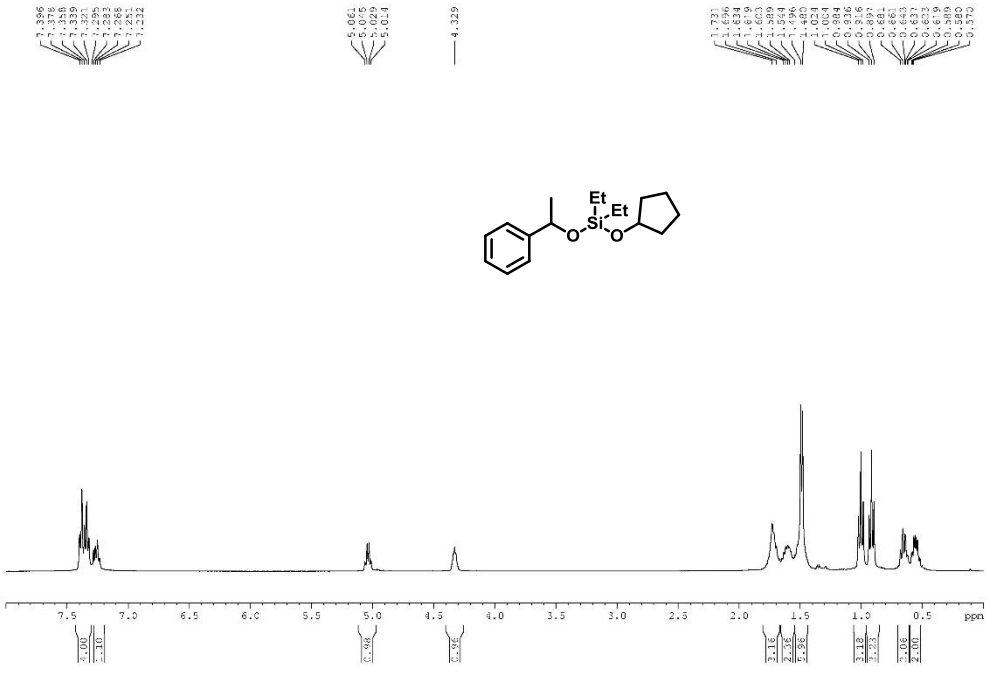


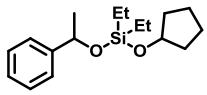


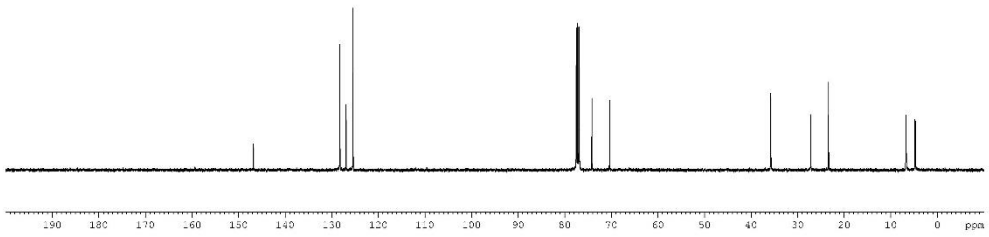


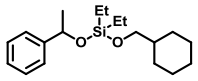


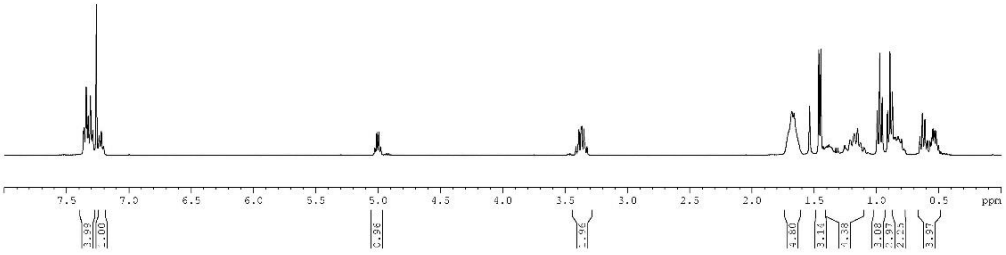
Unsymmetrical silaketals (**6a** – **6c**)



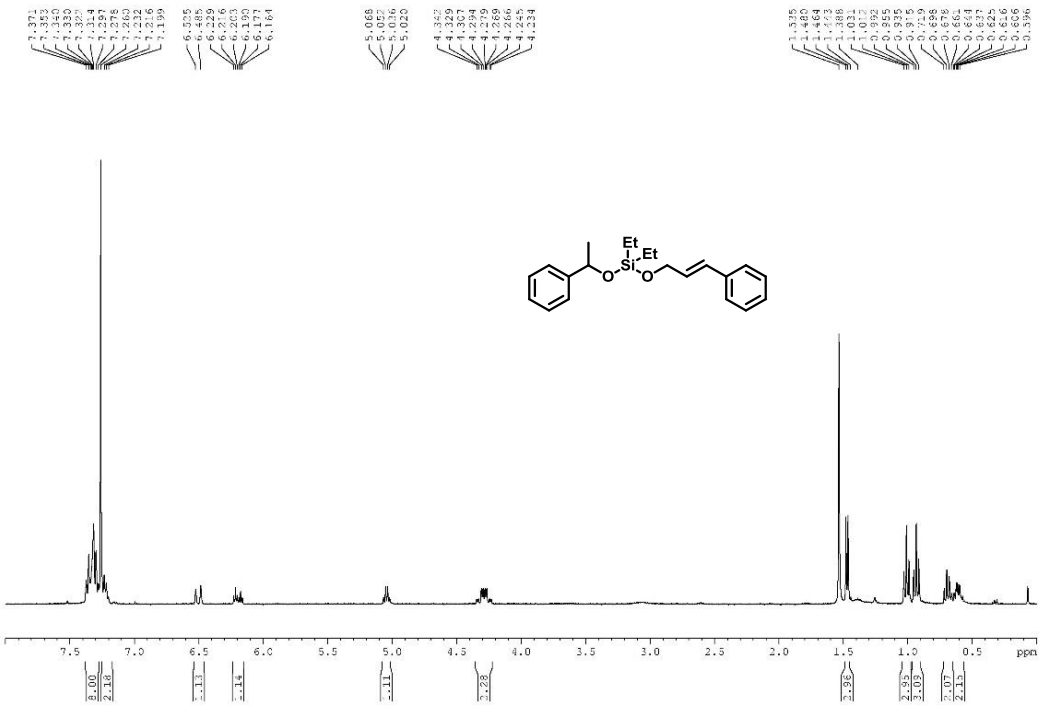


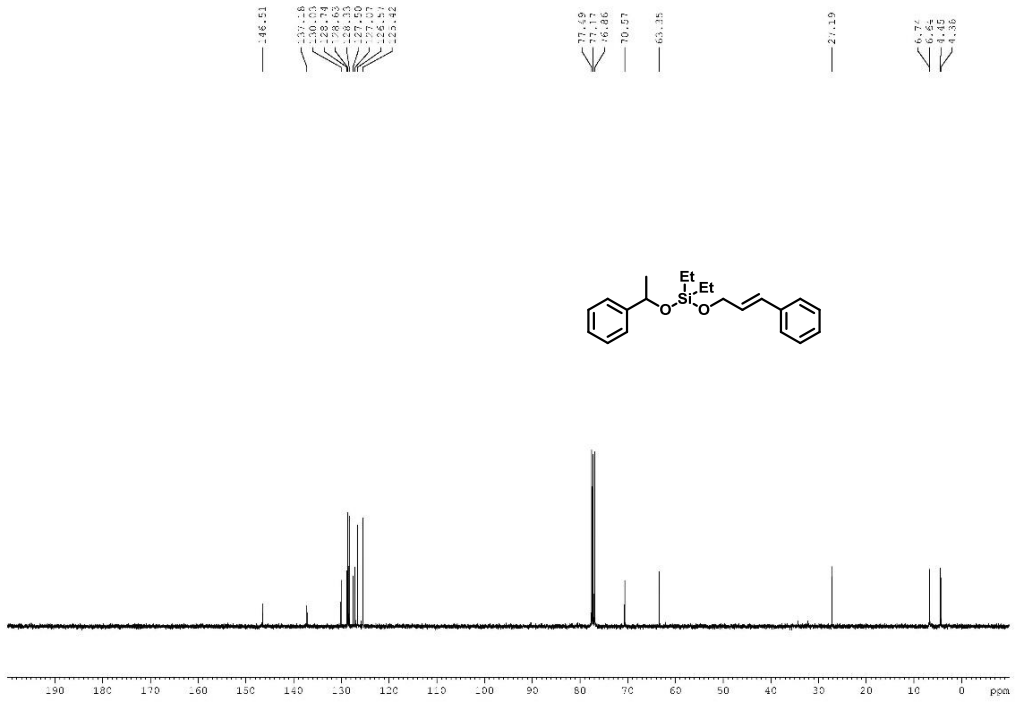




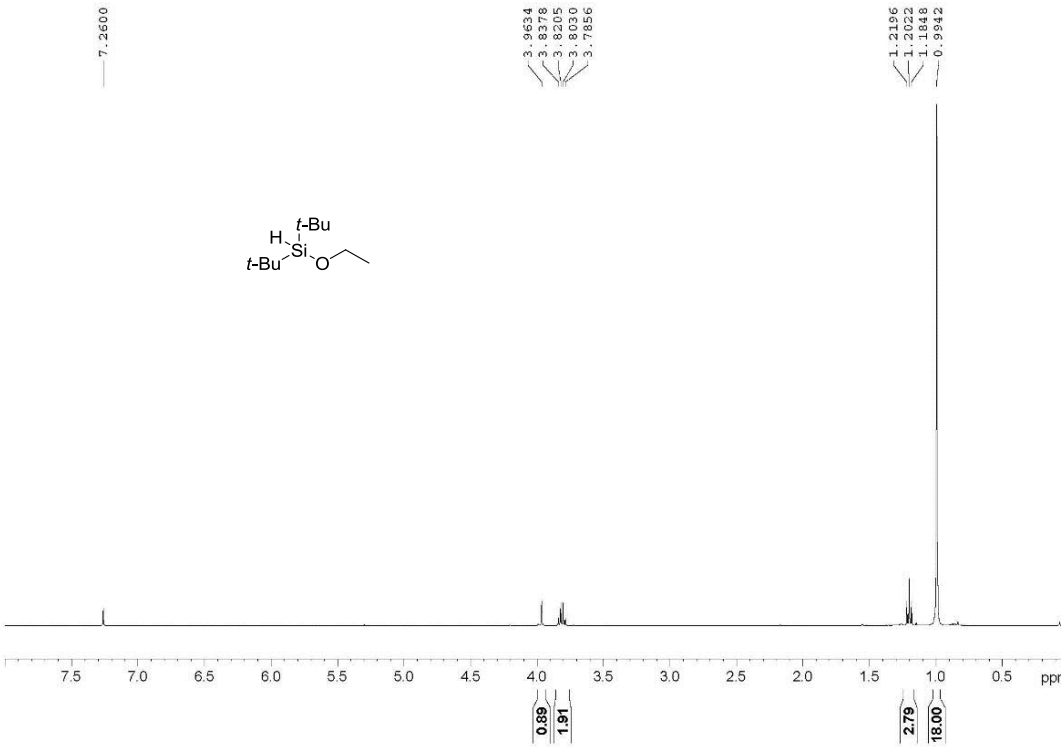


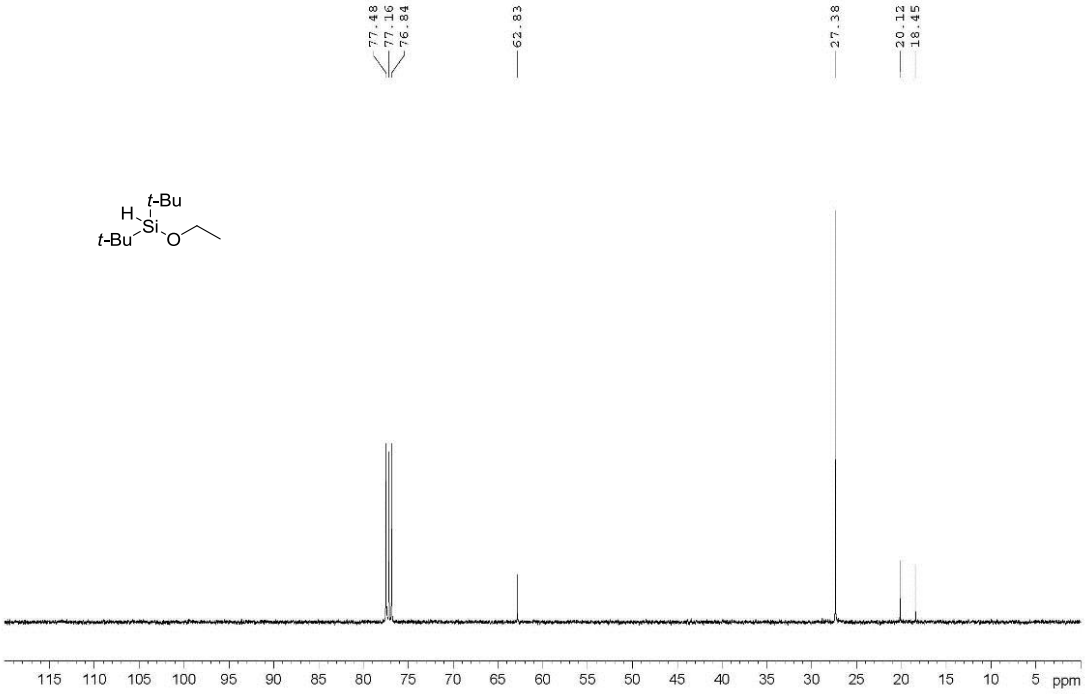

146.69
128.24
126.93
125.41
77.48
77.16
76.84
70.35
68.35
40.45
39.85
29.79
27.18
26.85
26.06
6.76
6.67
4.36
4.25
Et
Si
Et
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

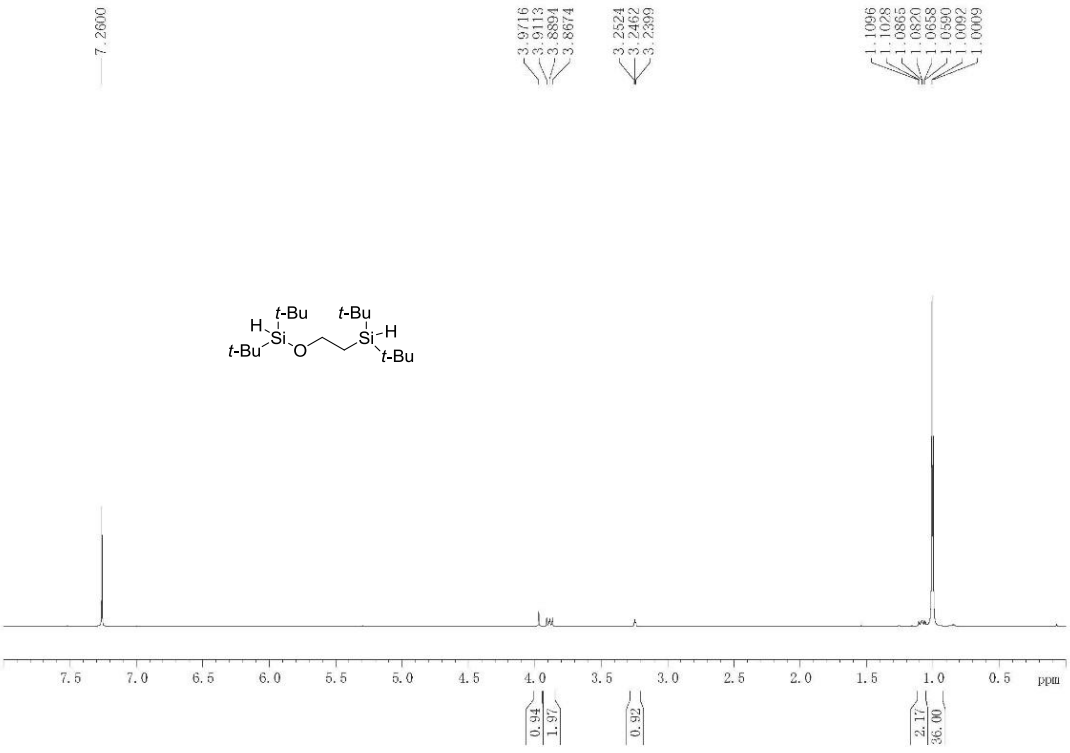

7.371
7.353
7.340
7.330
7.314
7.297
7.278
7.260
7.232
7.216
7.199
6.235
6.485
6.229
6.216
6.203
6.190
6.177
6.164
5.068
5.057
5.036
5.020
4.342
4.329
4.307
4.294
4.279
4.269
4.266
4.245
4.234
1.535
1.480
1.464
1.443
1.386
1.031
0.982
0.955
0.935
0.915
0.729
0.698
0.678
0.662
0.637
0.625
0.606
0.596
Et
Si
Et
O
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
8.00
2.18
1.13
1.14
1.11
3.28
3.98
2.99
3.09
2.07
2.11

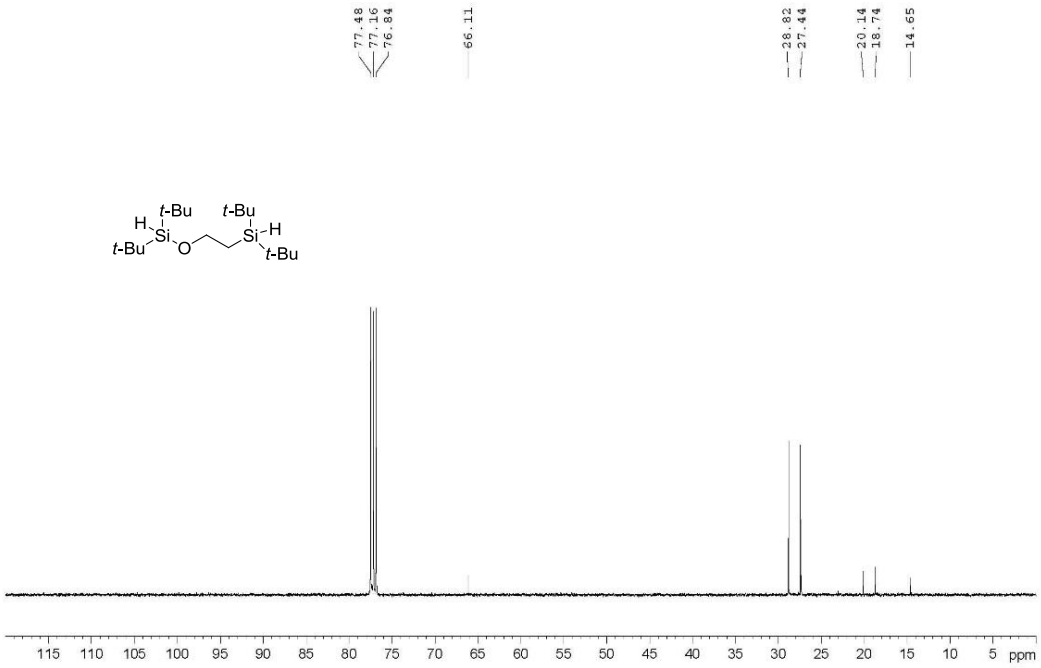


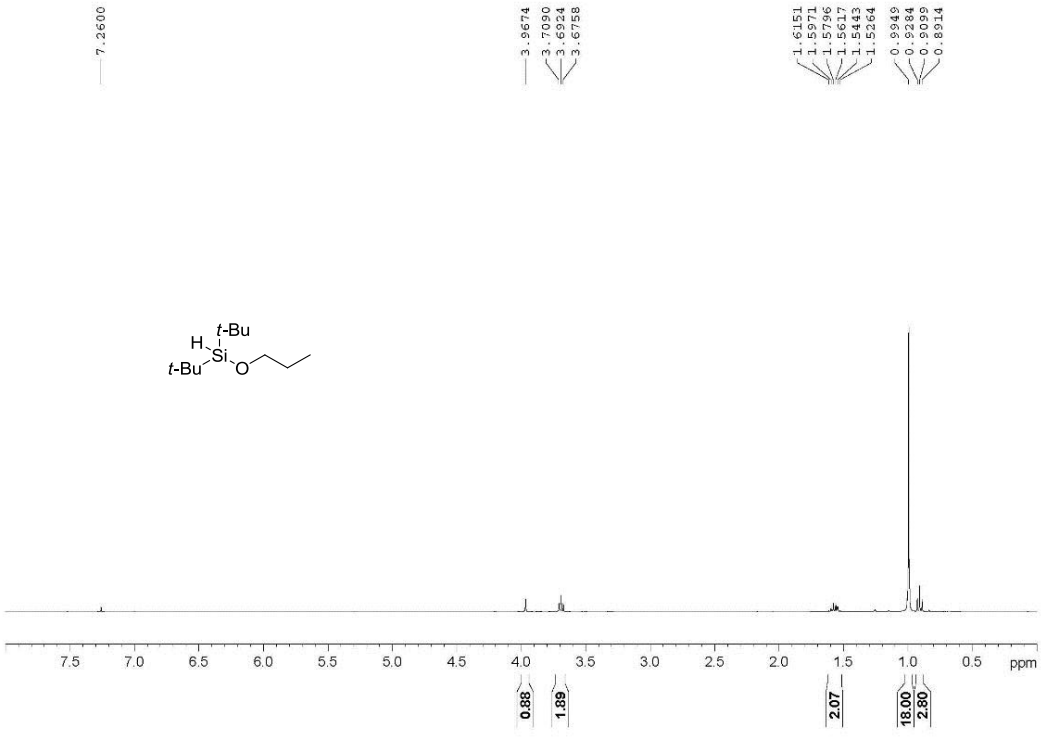
Ring-opening/silylation of cyclic ethers(**8, 9, 10**)

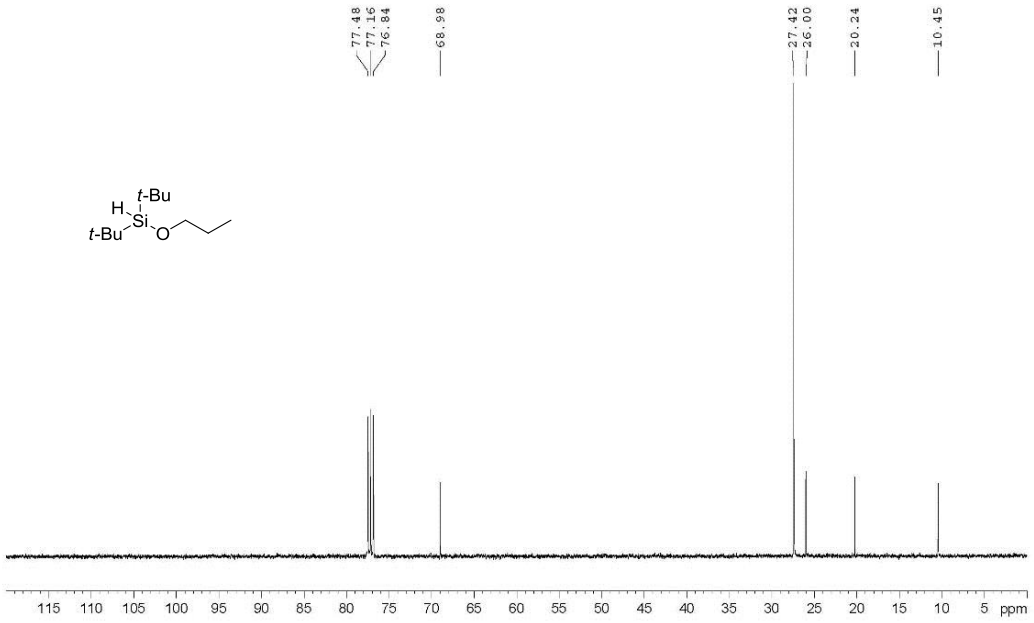


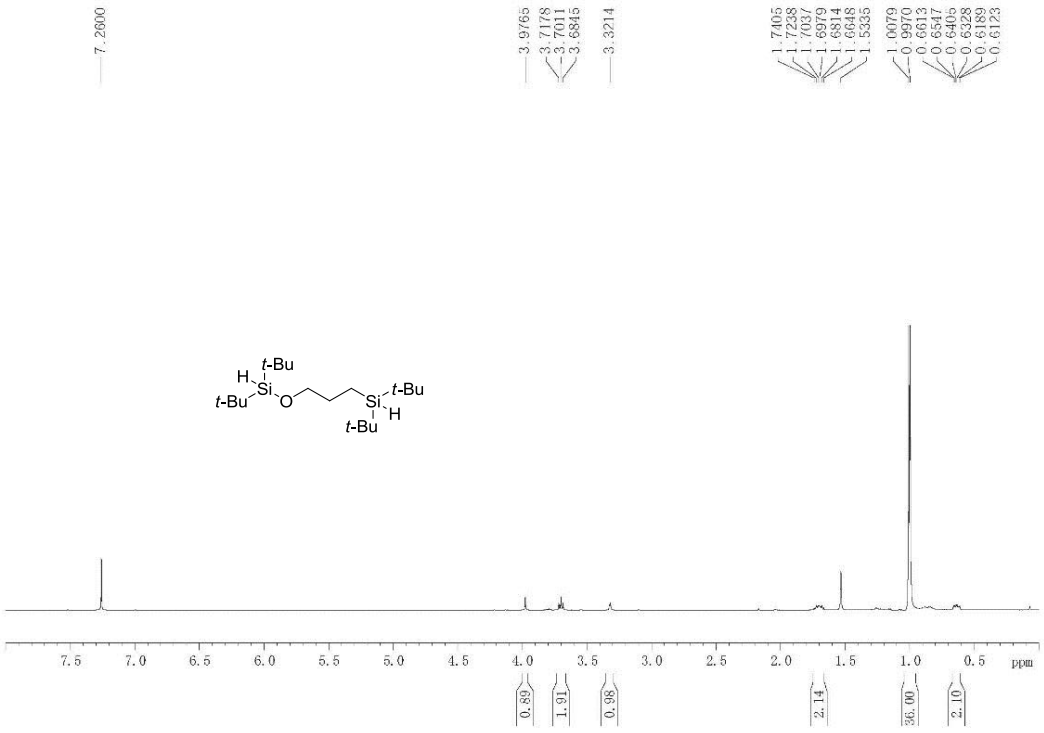

77.48
77.16
76.84
62.83
27.38
20.12
18.45
t-Bu
H
Si
t-Bu
O
115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

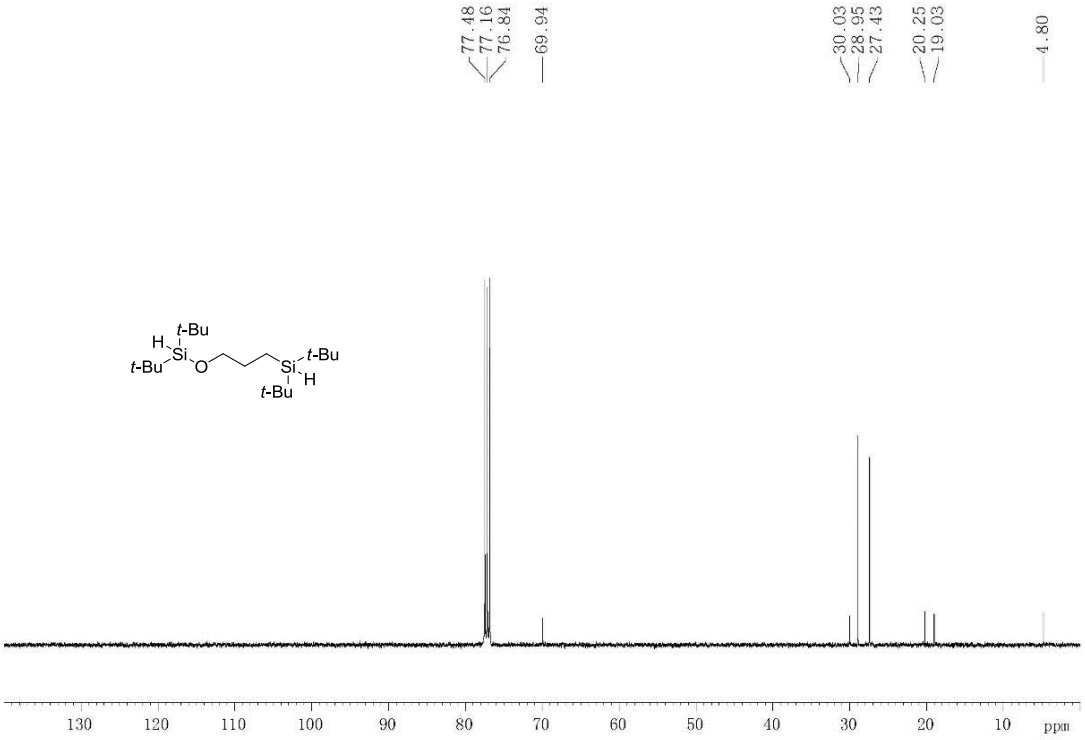

7.2600
3.9716
3.9113
3.8894
3.8674
3.2524
3.2462
3.2399
1.1096
1.1028
1.0885
1.0820
1.0658
1.0590
1.0092
1.0009
t-Bu
t-Bu
H
Si
O
Si
H
t-Bu
t-Bu
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.94
1.97
0.92
2.17
36.00

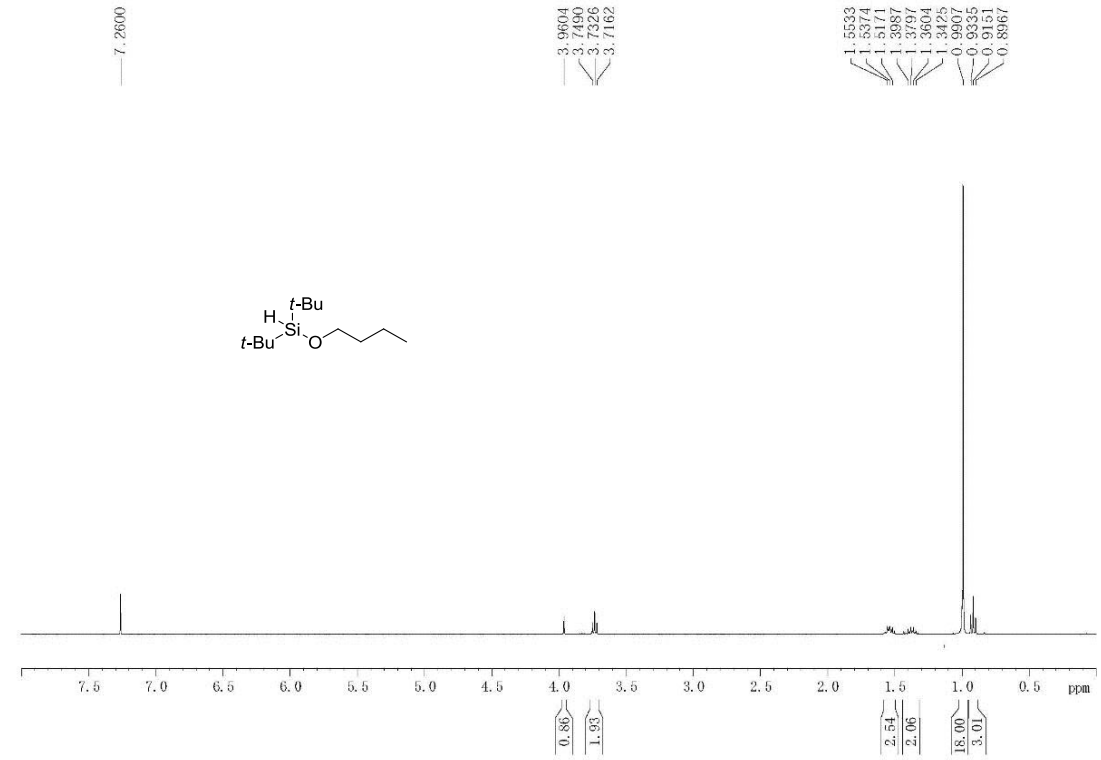

77.48
77.16
76.84
66.11
28.82
27.44
20.14
18.74
14.65
t-Bu
t-Bu
H
Si
O
Si
H
t-Bu
t-Bu
115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

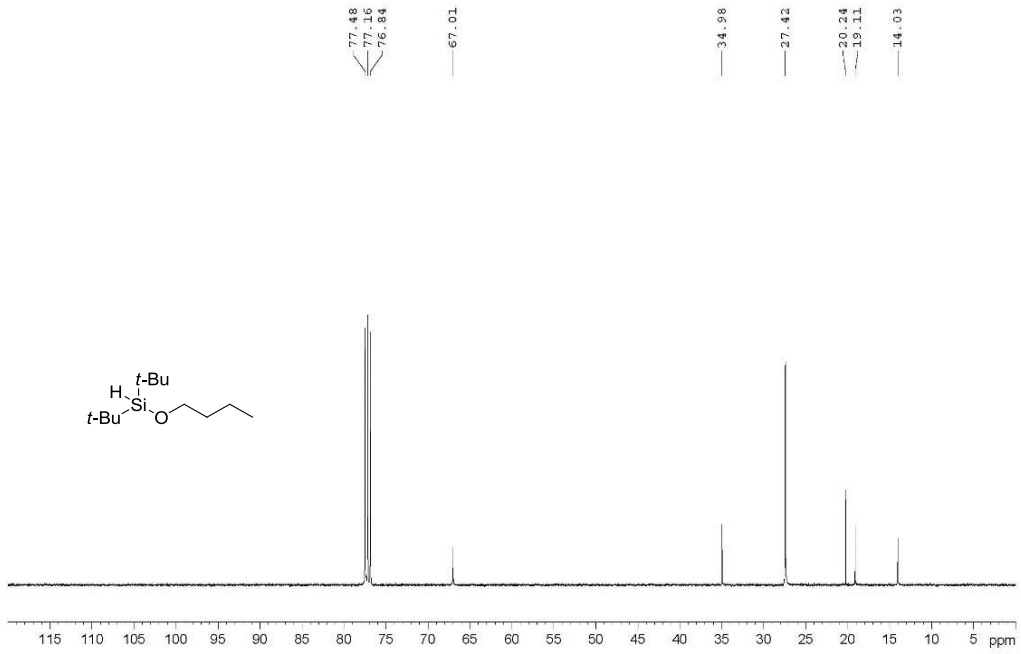

7.2600
3.9674
3.7090
3.6924
3.6758
1.6151
1.5971
1.5796
1.5617
1.5443
1.5264
0.9949
0.9284
0.9099
0.8914
t-Bu
H
Si
O
t-Bu
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.88
1.89
2.07
18.00
2.80

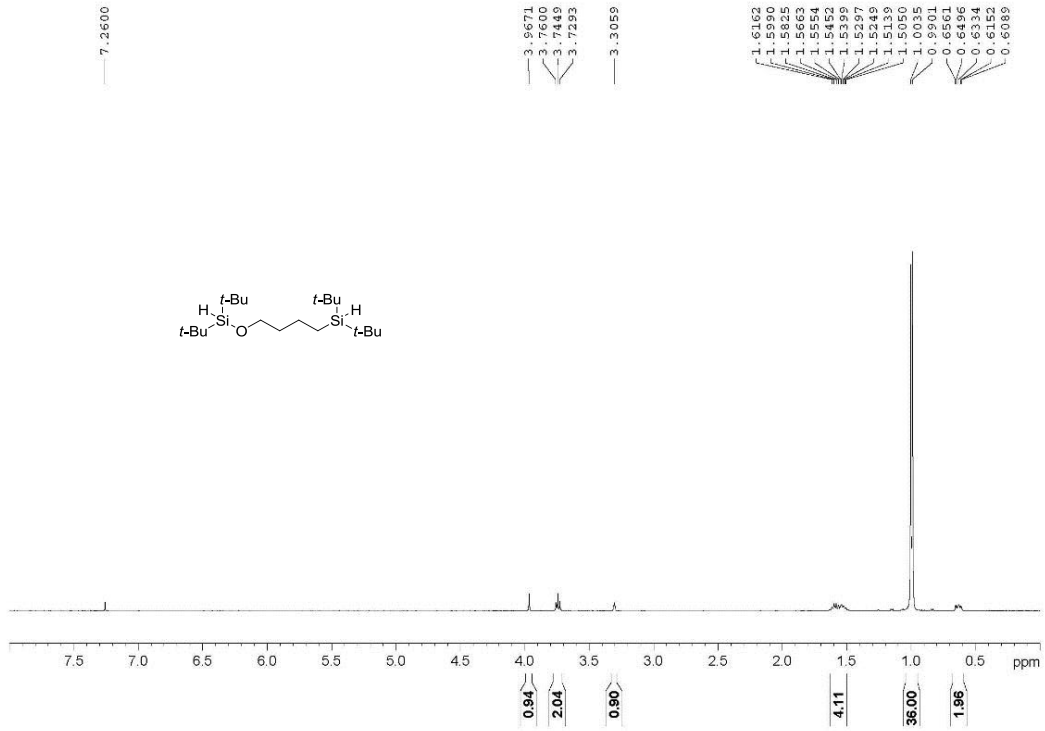

77.48
77.16
76.84
68.98
27.42
26.00
20.24
10.45
t-Bu
H
Si
t-Bu
O
115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

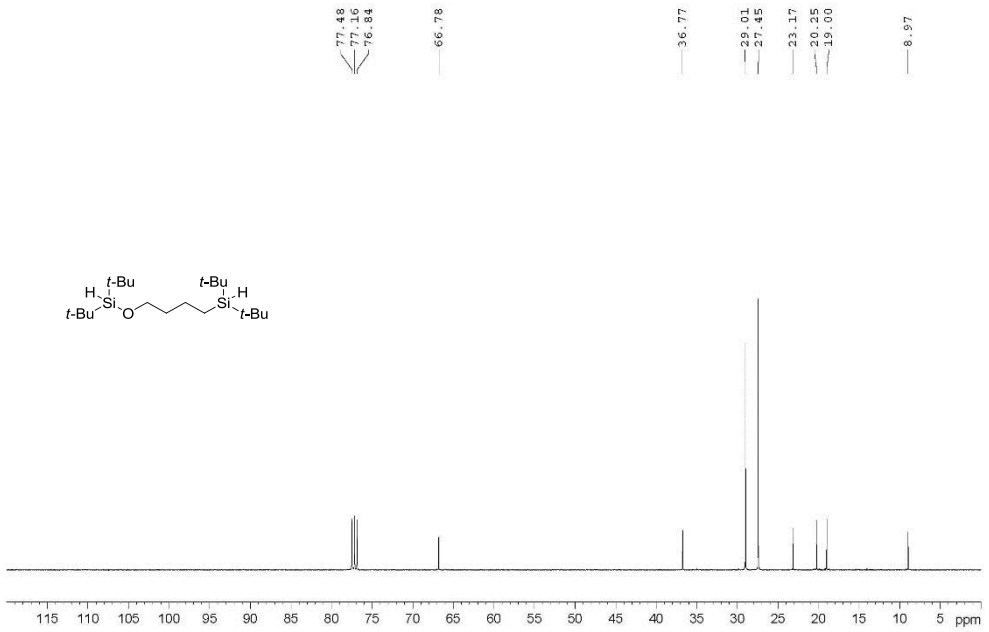

7.2600
3.9766
3.7178
3.7011
3.6845
3.3214
1.7405
1.7238
1.7037
1.6979
1.6814
1.6648
1.5335
1.0079
0.9970
0.6613
0.6547
0.6405
0.6328
0.6189
0.6123
t-Bu
H
Si
O
t-Bu
t-Bu
Si
H
t-Bu
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.89
1.91
0.98
2.14
36.00
2.10

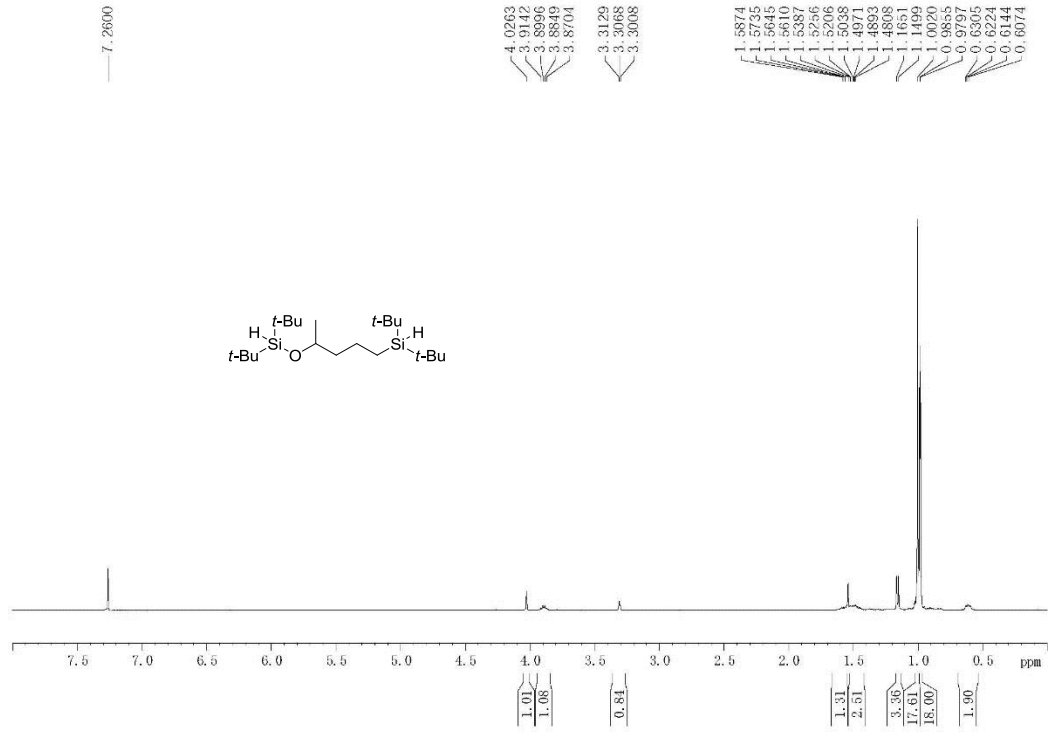

77.48
77.16
76.84
69.94
30.03
28.95
27.43
20.25
19.03
4.80
t-Bu
H
Si
O
t-Bu
t-Bu
Si
H
t-Bu
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

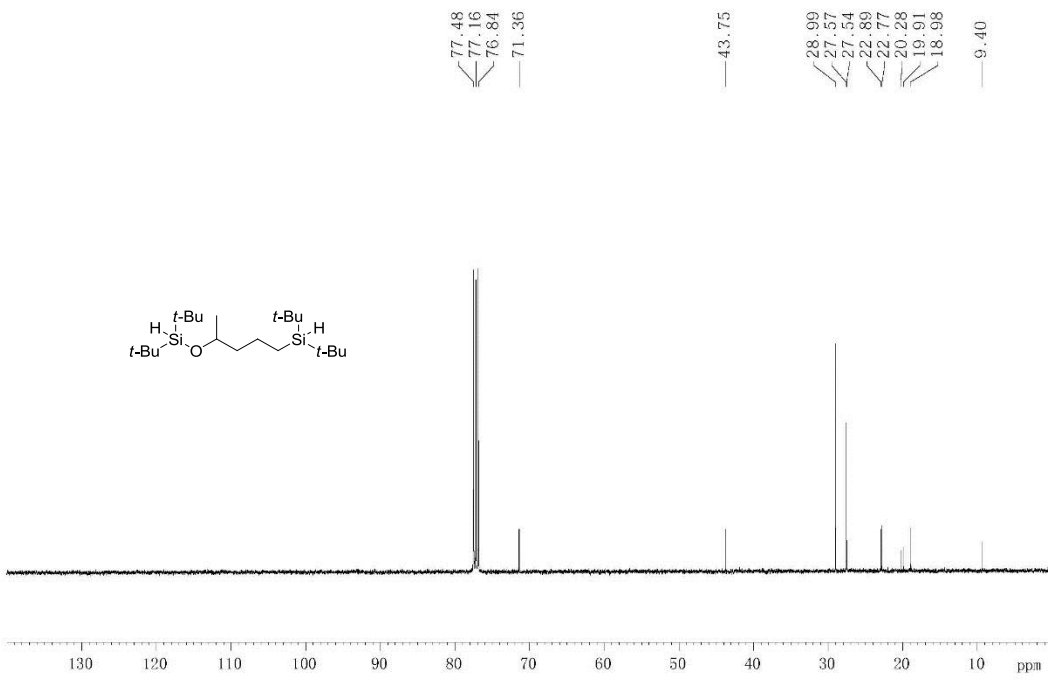

7.2600
3.9604
3.7490
3.7326
3.7162
1.5533
1.5374
1.5171
1.3987
1.3797
1.3604
1.3425
0.9907
0.9335
0.9151
0.8967
t-Bu
H
Si
O
t-Bu
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.86
1.93
2.54
2.06
18.00
3.01

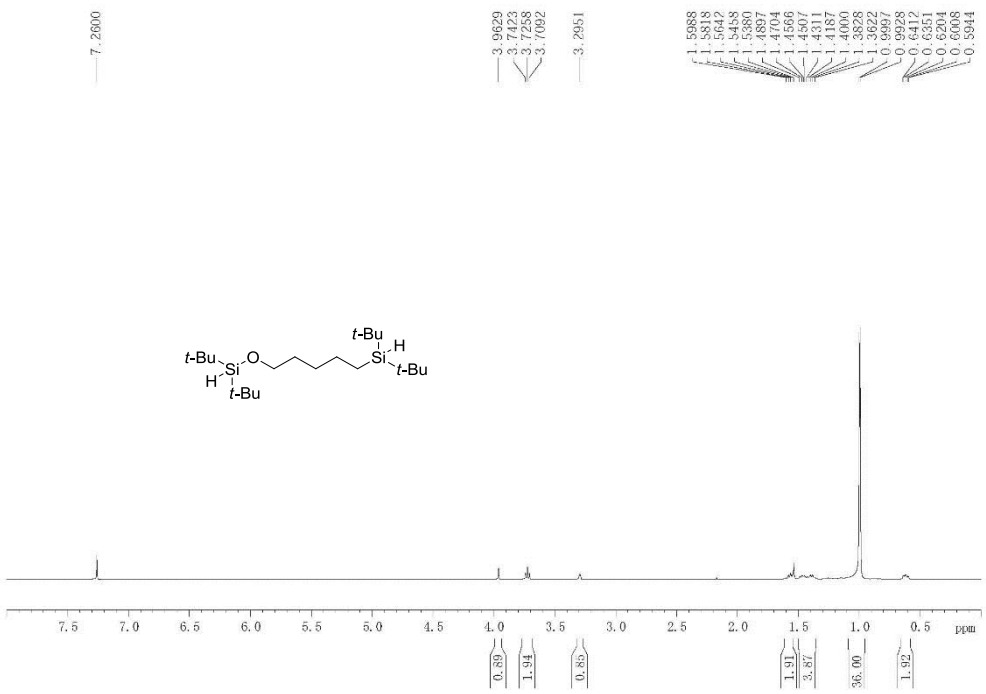

77.48
77.16
76.84
67.01
34.98
27.42
20.24
19.11
14.03
t-Bu
H
Si
t-Bu
O
115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

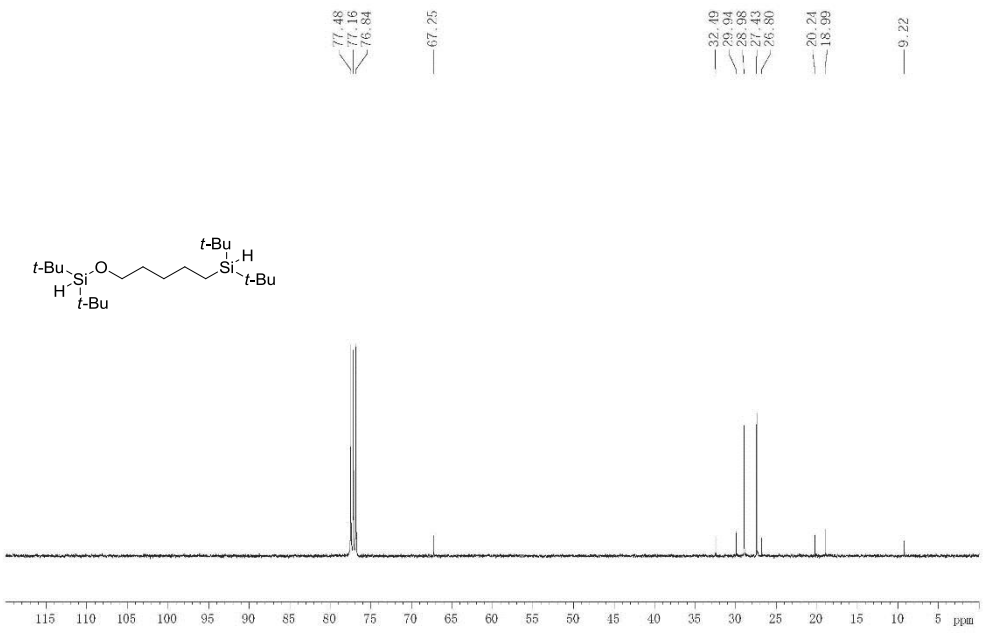

7.2600
3.9671
3.7600
3.7449
3.7293
3.3059
1.6162
1.5990
1.5825
1.5663
1.5554
1.5452
1.5399
1.5297
1.5249
1.5139
1.5050
1.0035
0.9901
0.6561
0.6496
0.6334
0.6152
0.6089
t-Bu
H
Si
t-Bu
O
t-Bu
Si
H
t-Bu
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.94
2.04
0.90
4.11
36.00
1.96

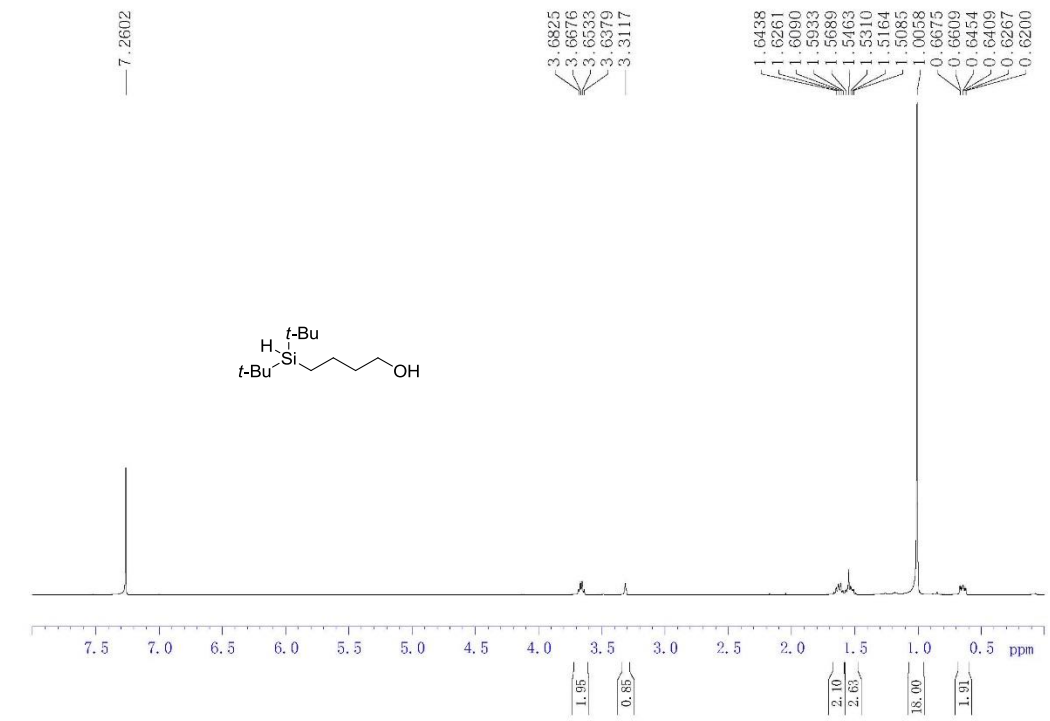

77.48
77.16
76.84
66.78
36.77
29.01
27.45
23.17
20.25
19.00
8.97
t-Bu
H
Si
t-Bu
O
t-Bu
Si
H
t-Bu
115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

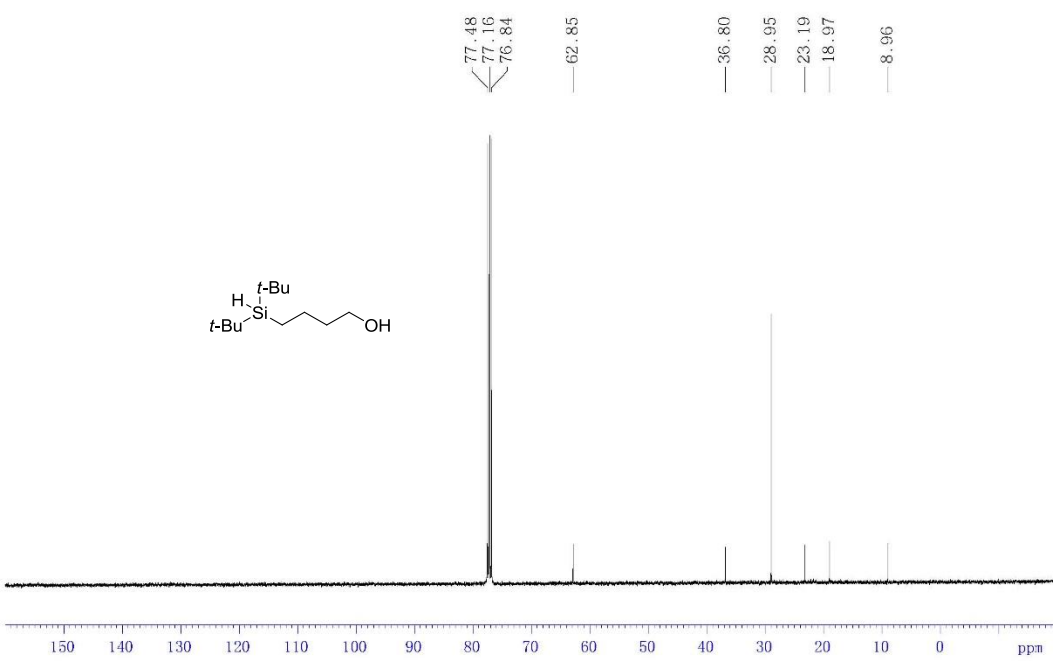

7.2600
4.0263
3.9142
3.8996
3.8849
3.8704
3.3129
3.3068
3.3008
1.5874
1.5735
1.5645
1.5610
1.5387
1.5256
1.5206
1.5038
1.4971
1.4893
1.4808
1.1651
1.1499
1.0020
0.9855
0.9797
0.6305
0.6224
0.6144
0.6074
t-Bu
H
Si
t-Bu
O
t-Bu
Si
H
t-Bu
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.01
1.08
0.84
1.31
2.51
3.36
17.61
18.00
1.90

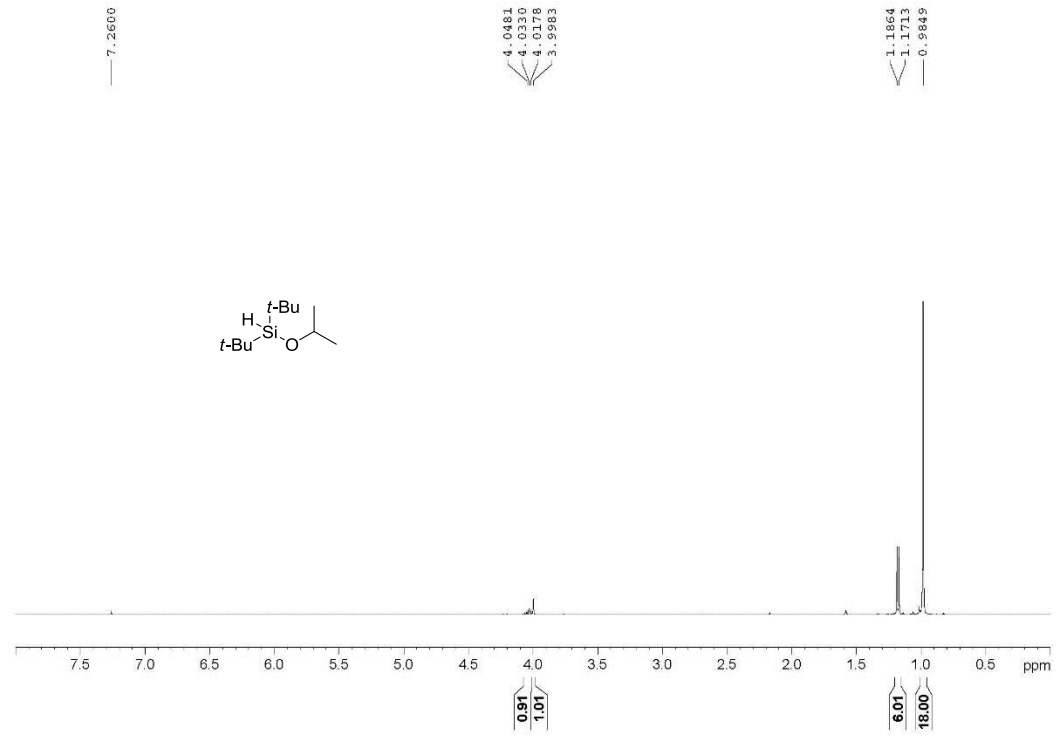

77.48
77.16
76.84
71.36
43.75
28.99
27.57
27.54
22.89
22.77
20.28
19.91
18.98
9.40
t-Bu
H
Si
O
t-Bu
t-Bu
Si
H
t-Bu
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

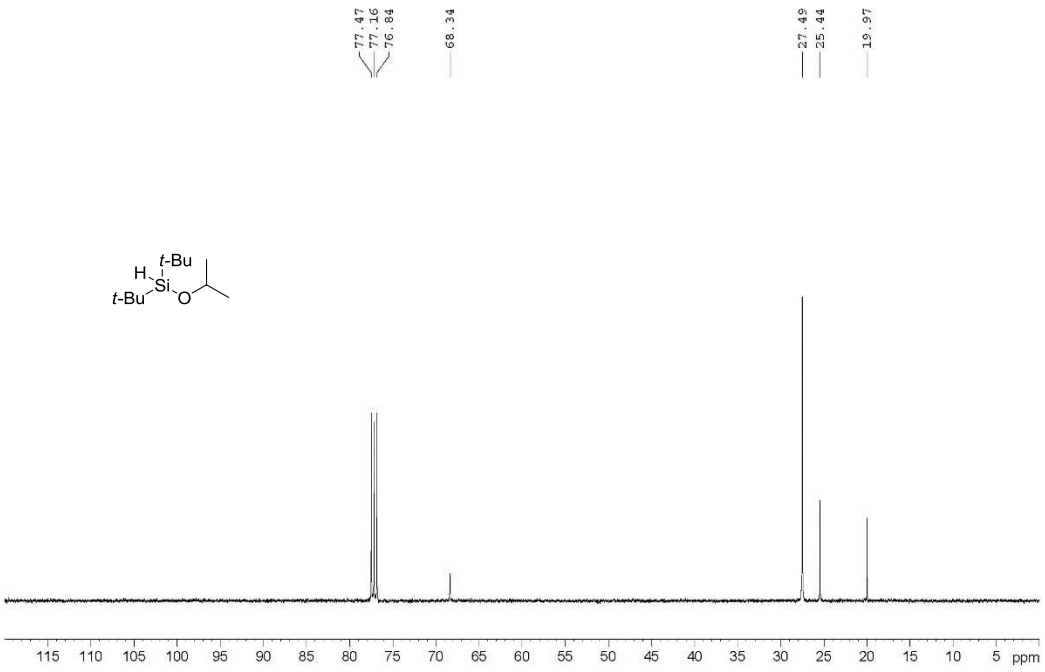

7.2600
3.9629
3.7423
3.7258
3.7092
3.2951
1.5988
1.5818
1.5642
1.5458
1.5380
1.4897
1.4704
1.4566
1.4507
1.4311
1.4187
1.4000
1.3828
1.3622
0.9997
0.9928
0.6412
0.6351
0.6204
0.6008
0.5944
t-Bu
t-Bu
Si
H
O
H
Si
t-Bu
t-Bu
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.89
1.94
0.83
1.91
3.87
36.00
1.92

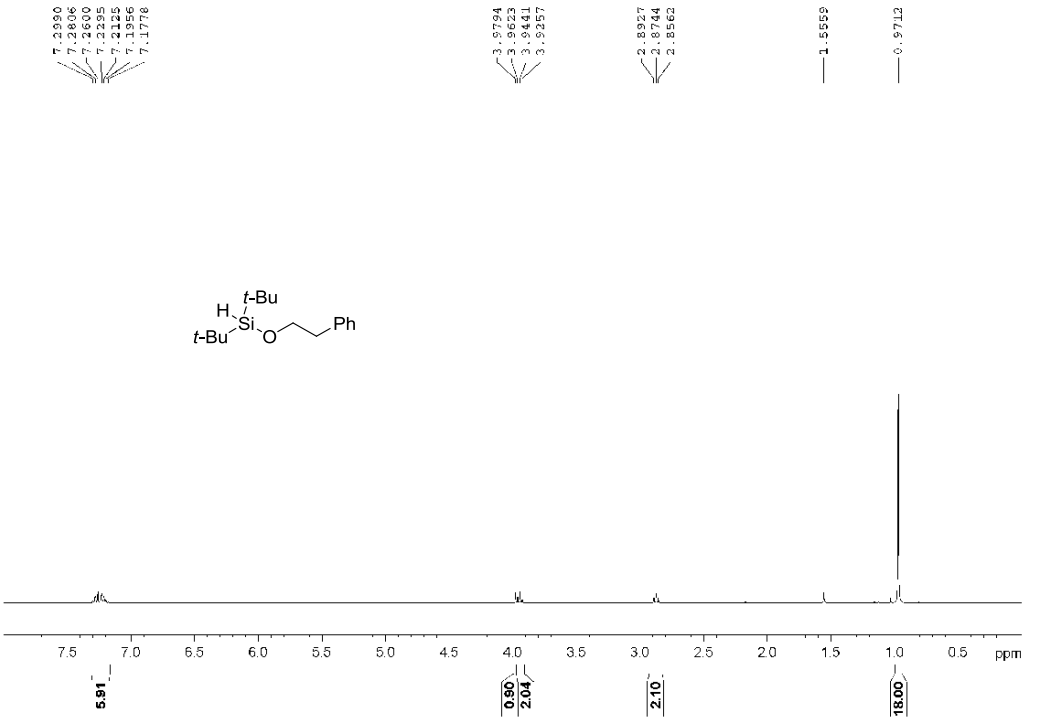

77.48
77.16
76.84
67.25
32.49
29.94
28.98
27.43
26.80
20.24
18.99
9.22
t-Bu
H
Si
O
t-Bu
t-Bu
H
Si
t-Bu
t-Bu
115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

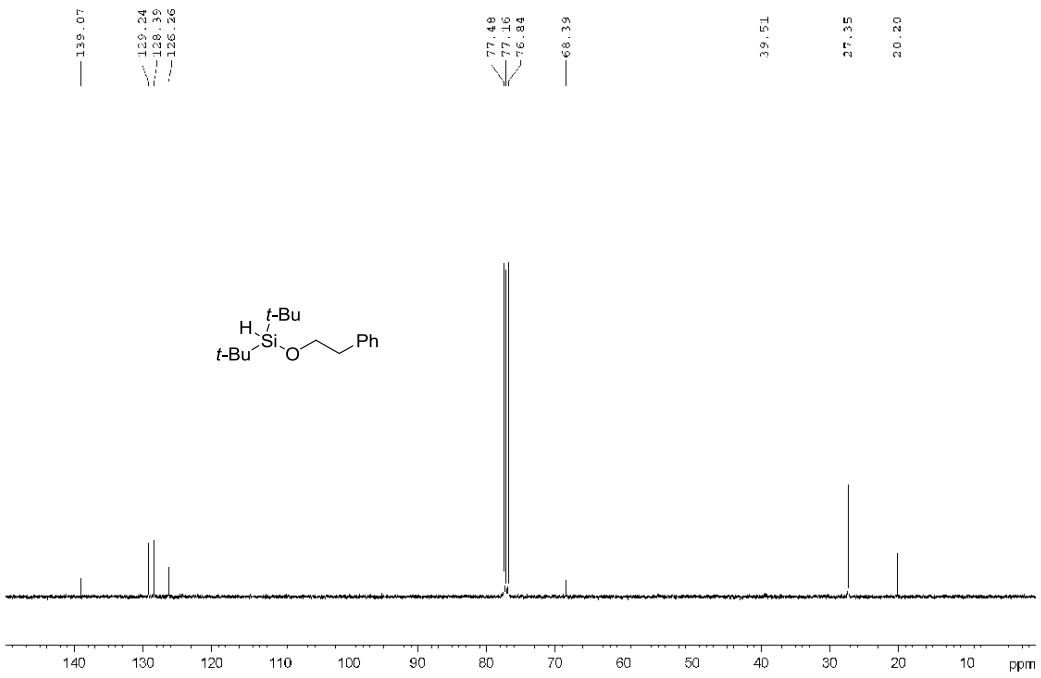

7.2602
3.6825
3.6676
3.6533
3.6379
3.3117
1.6438
1.6261
1.6090
1.5933
1.5689
1.5463
1.5310
1.5164
1.5085
1.0058
0.6675
0.6609
0.6454
0.6409
0.6267
0.6200
t-Bu
H
Si
t-Bu
OH
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.95
0.85
2.10
2.63
18.00
1.91

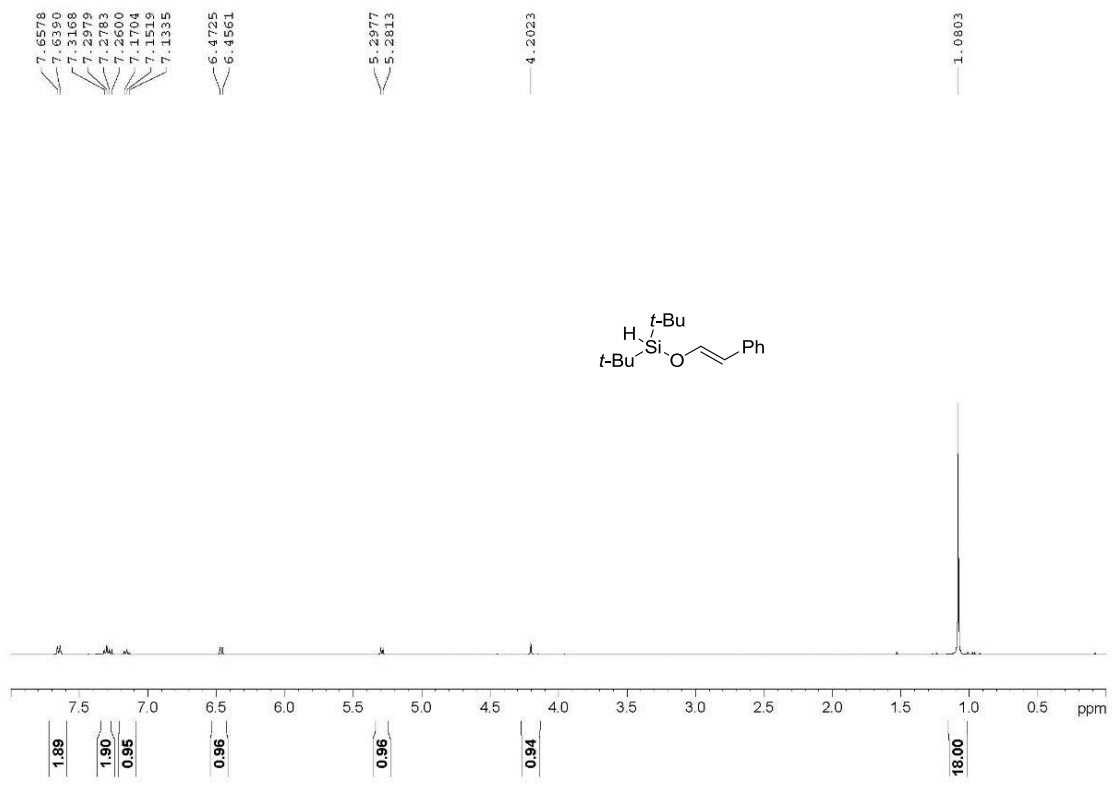

77.48
77.16
76.84
62.85
36.80
28.95
23.19
18.97
8.96
t-Bu
H
Si
t-Bu
OH
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

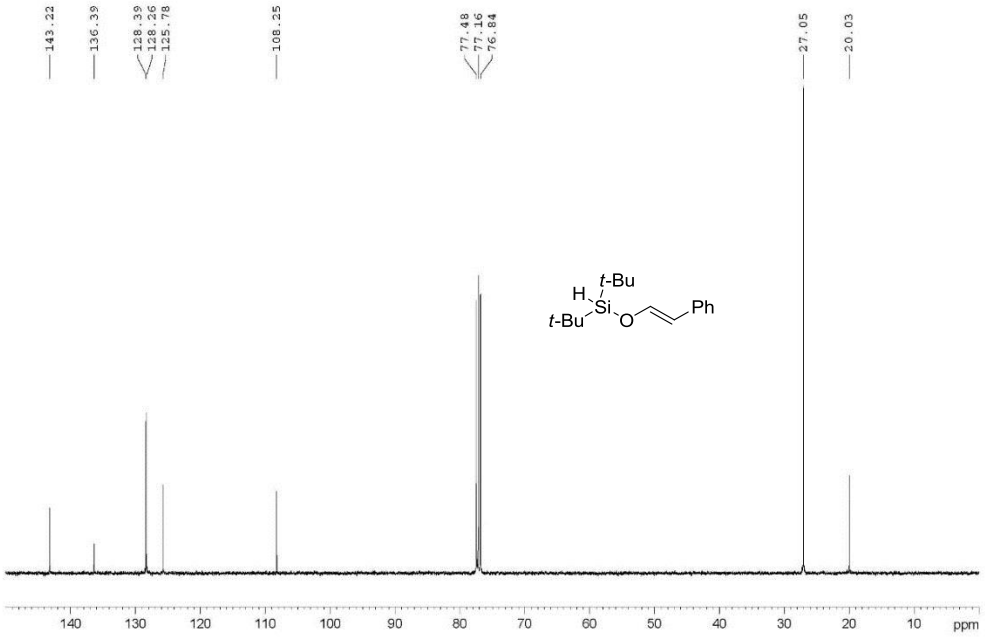

7.2600
4.0481
4.0330
4.0178
3.9983
1.1864
1.1713
0.9849
t-Bu
H
Si
t-Bu
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.91
1.01
6.01
18.00

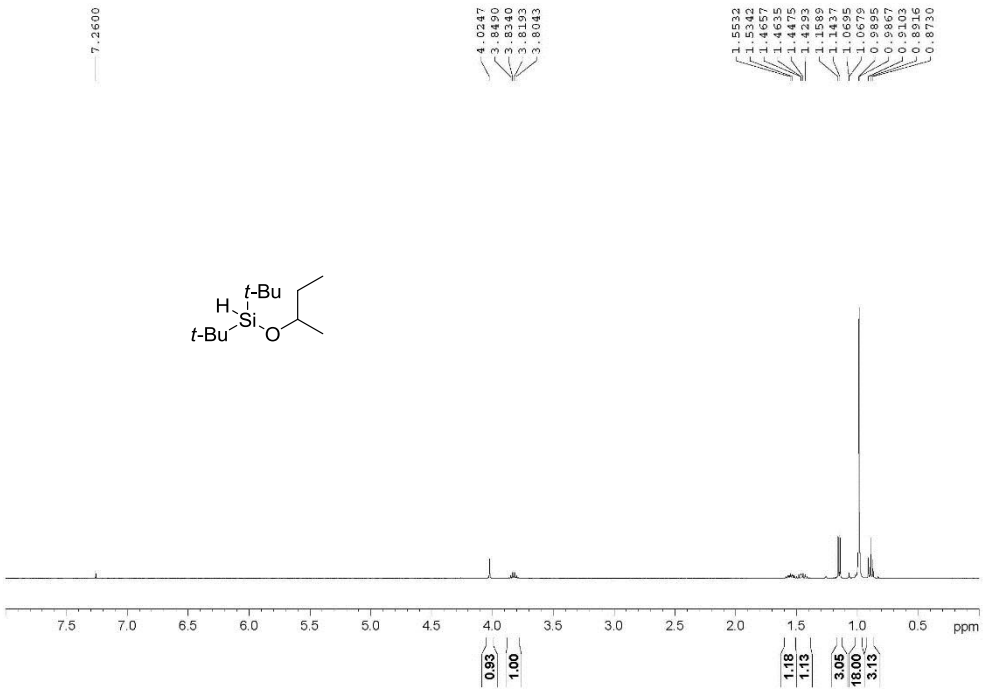

77.47
77.16
76.84
68.34
27.49
25.44
19.97
t-Bu
H
Si
t-Bu
O
115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

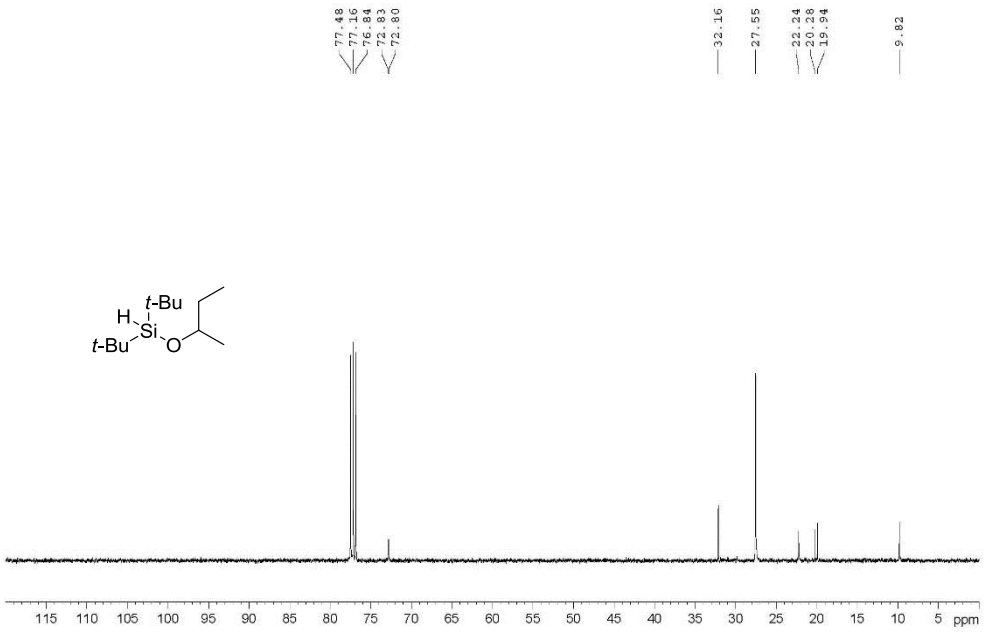

7.2990
7.2806
7.2600
7.2295
7.2225
7.1956
7.1778
3.9794
3.9623
3.9441
3.9257
2.8927
2.8744
2.8562
1.5559
0.9712
t-Bu
H
Si
t-Bu
O
Ph
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.91
0.90
2.04
2.10
18.00

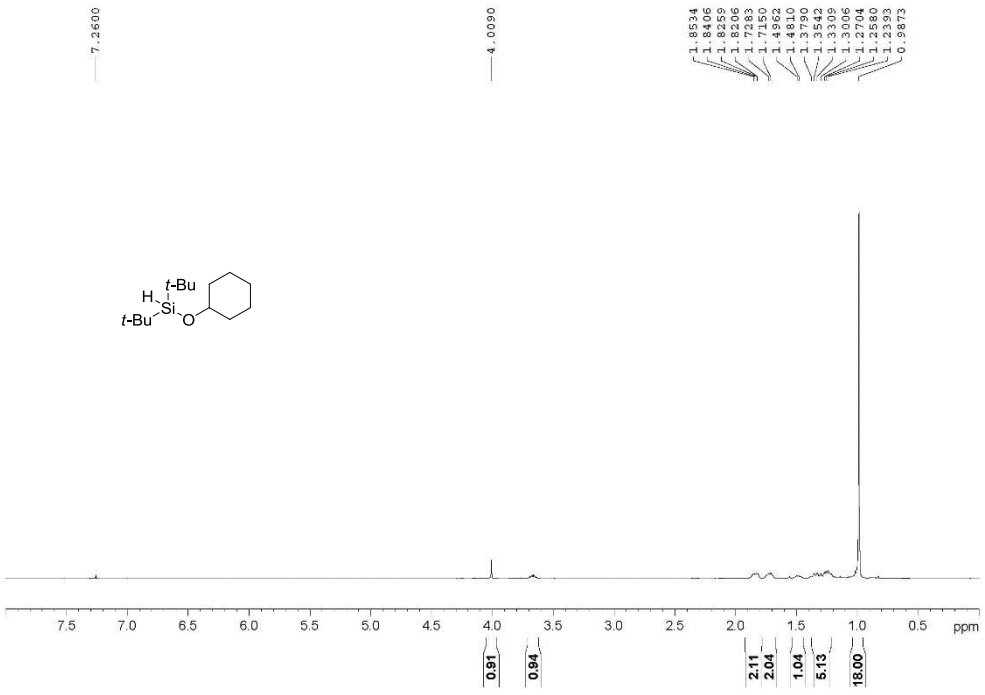

139.07
129.24
128.39
126.26
77.48
77.16
76.84
68.39
39.51
27.35
20.20
H
Si
O
t-Bu
t-Bu
Ph
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

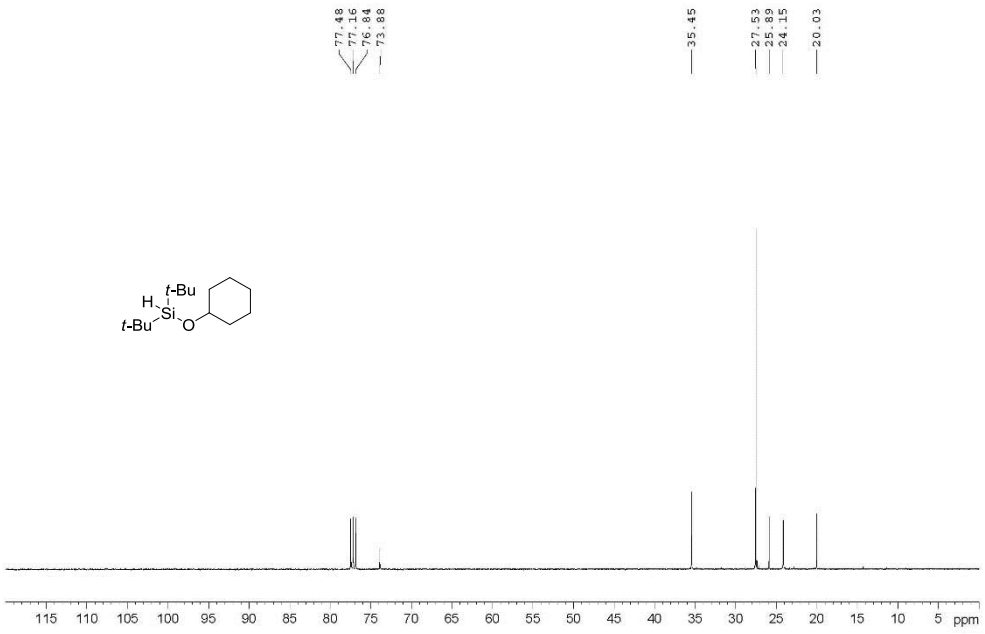

7.6578
7.6390
7.3168
7.2979
7.2783
7.2600
7.1704
7.1519
7.1335
6.4725
6.4561
5.2977
5.2813
4.2023
1.0803
H
Si
O
t-Bu
t-Bu
Ph
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.89
1.90
0.95
0.96
0.96
0.94
18.00

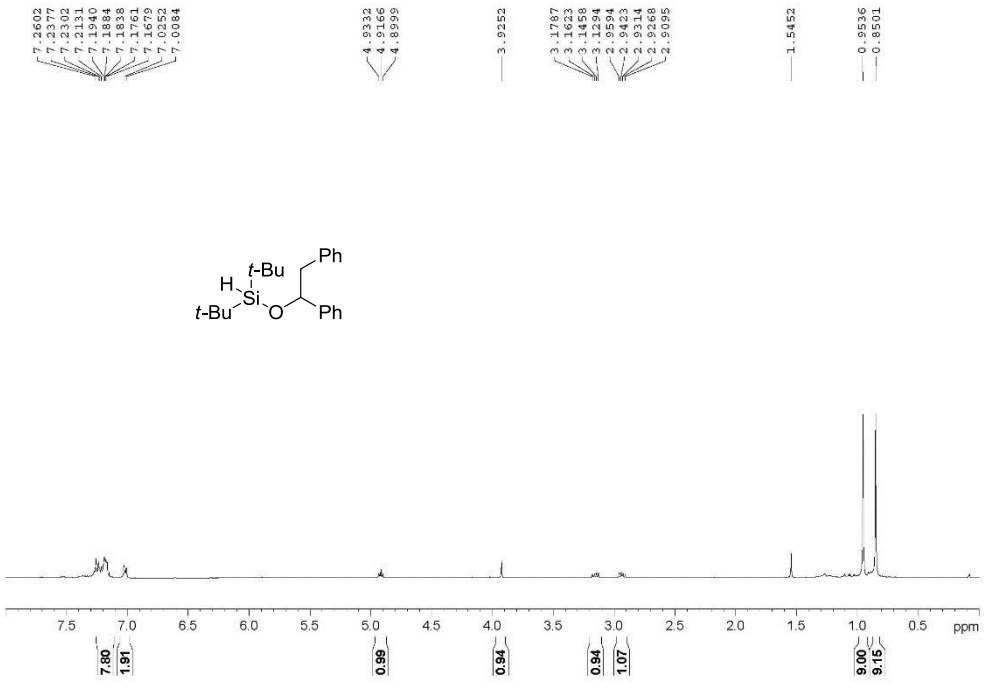

143.22
136.39
128.39
128.26
125.78
108.25
77.48
77.16
76.84
27.05
20.03
t-Bu
H
Si
t-Bu
O
Ph
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

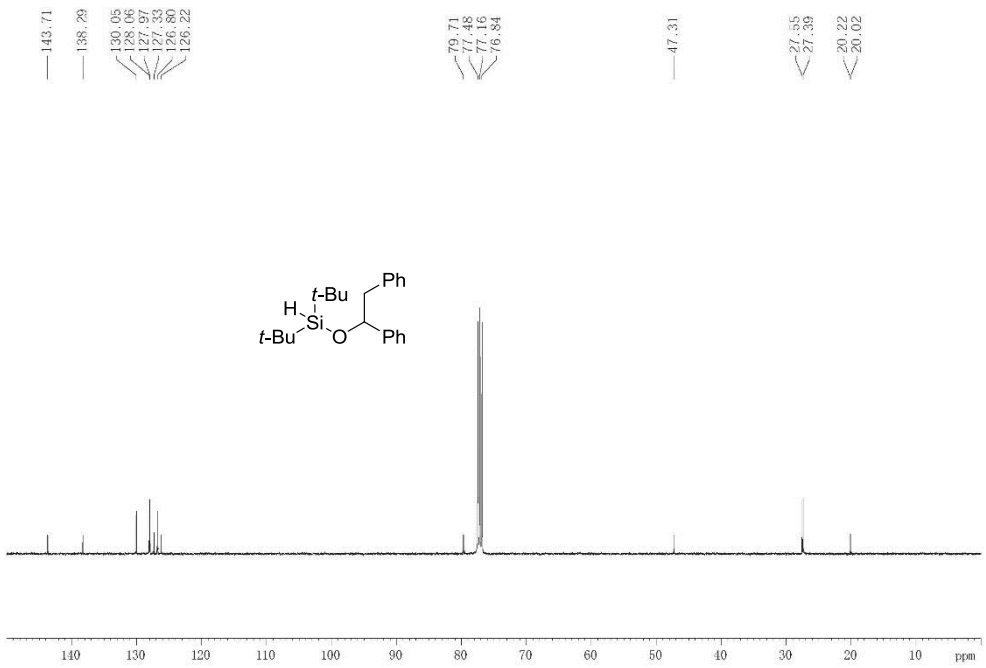

7.2600
4.0247
3.8490
3.8340
3.8193
3.8043
1.5532
1.5340
1.4657
1.4635
1.4475
1.4293
1.1589
1.1437
1.0695
1.0679
0.9895
0.9867
0.9103
0.8916
0.8730
t-Bu
H
Si
t-Bu
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.93
1.00
1.18
1.13
3.05
18.00
3.13

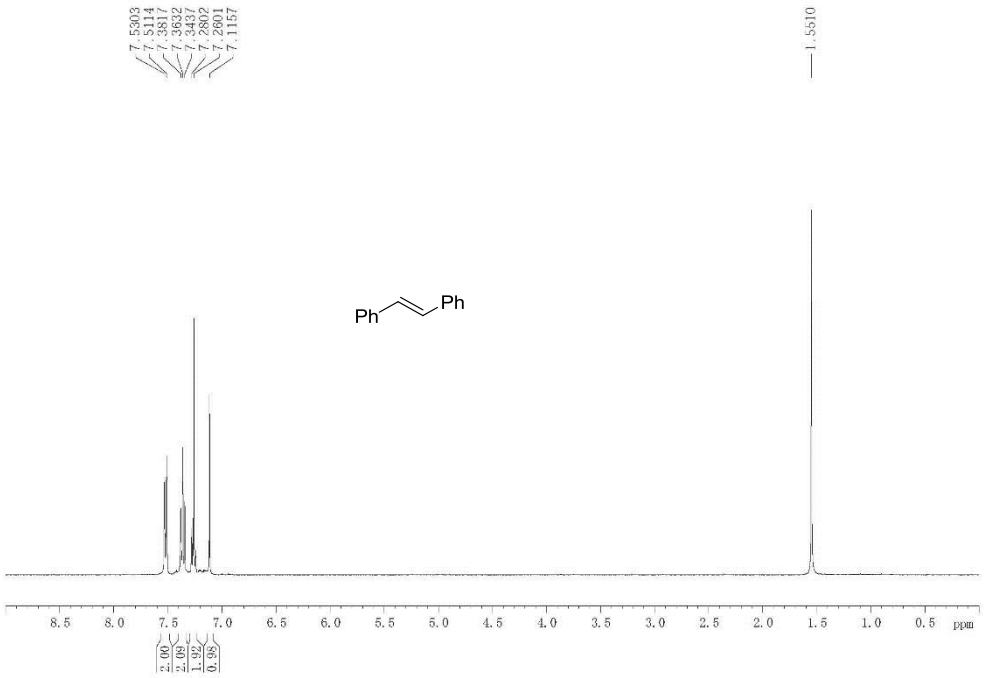

77.48
77.16
76.84
72.83
72.80
32.16
27.55
22.24
20.28
19.94
9.82
t-Bu
H
Si
t-Bu
O
115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

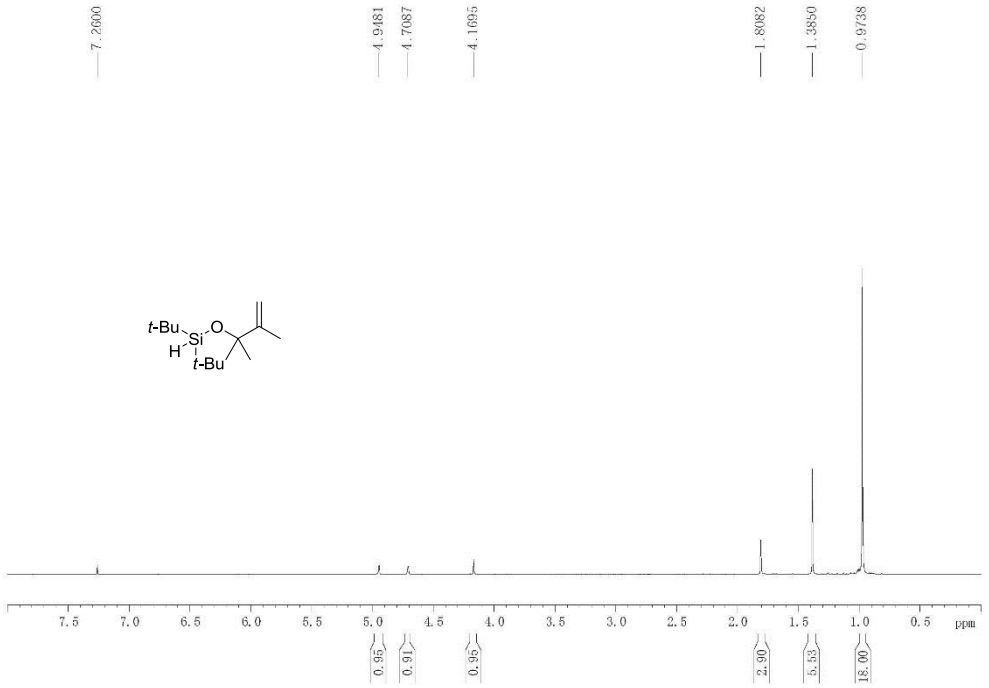

7.2600
4.0090
1.8534
1.8406
1.8259
1.8206
1.7283
1.7150
1.4962
1.4810
1.3790
1.3542
1.3309
1.3006
1.2704
1.2580
1.2393
0.9873
t-Bu
H
Si
t-Bu
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.91
0.94
2.11
2.04
1.04
5.13
18.00

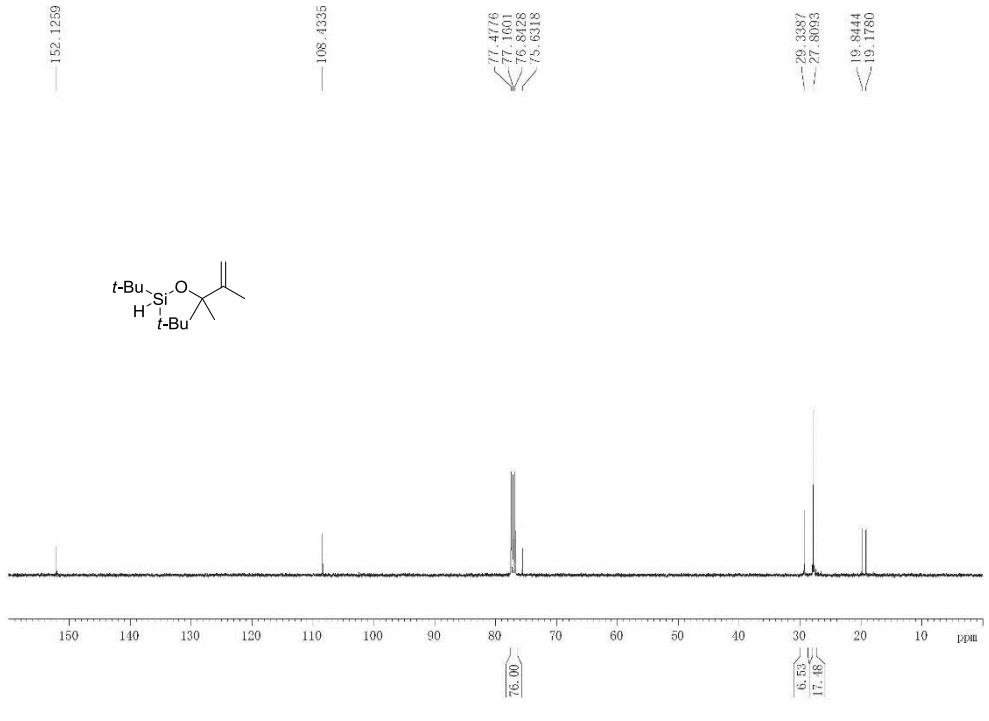

77.48
77.16
76.84
73.88
35.45
27.53
25.89
24.15
20.03
t-Bu
H
Si
O
t-Bu
115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

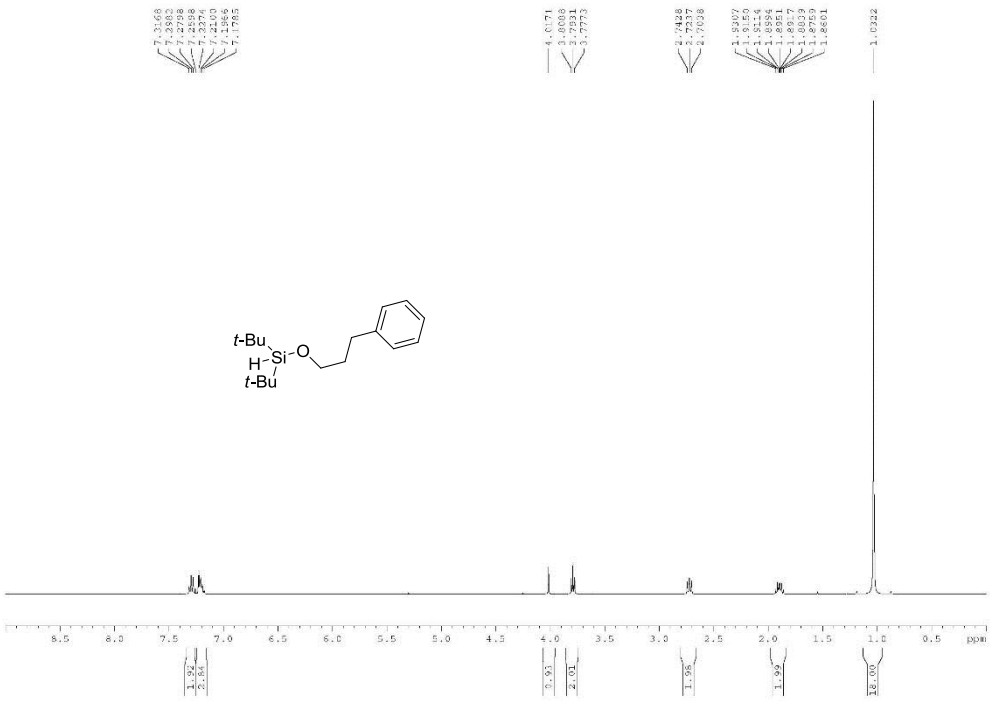

7.2602
7.2377
7.2302
7.2131
7.1940
7.1884
7.1838
7.1761
7.1679
7.0252
7.0084
4.9332
4.9166
4.8999
3.9252
3.1787
3.1623
3.1458
3.1294
2.9534
2.9423
2.9314
2.9188
2.9095
1.5452
0.9536
0.8501
Ph
t-Bu
H
Si
O
t-Bu
Ph
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
7.00
1.91
0.99
0.94
0.94
1.07
9.00
9.15

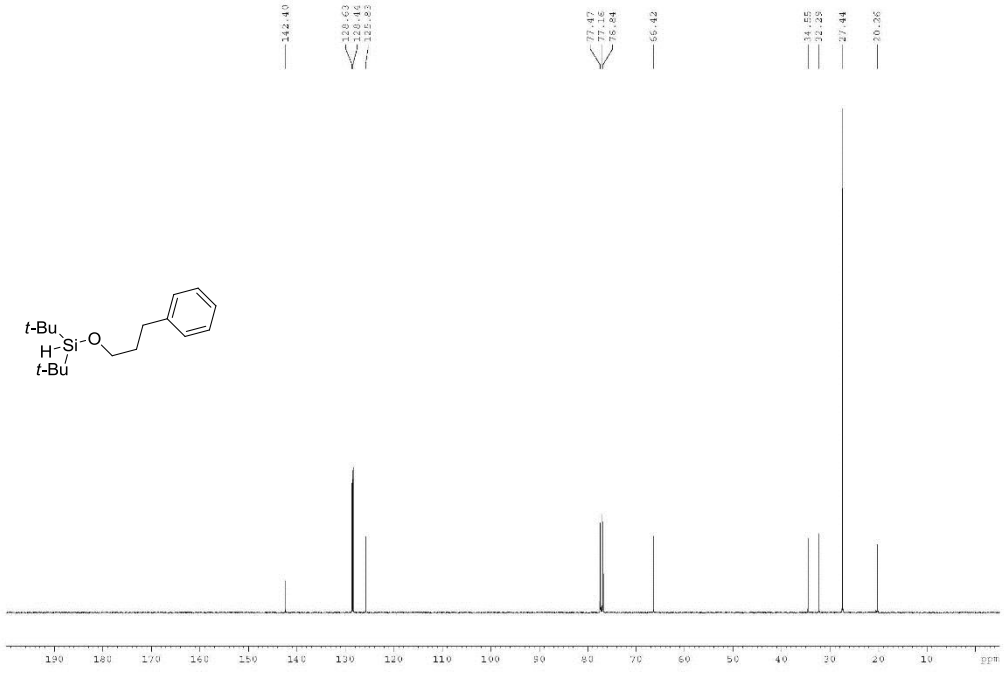

143.71
138.29
130.05
128.06
127.97
127.33
126.80
126.22
79.71
77.48
77.16
76.84
47.31
27.55
27.39
20.22
20.02
t-Bu
H
Si
O
t-Bu
Ph
Ph
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

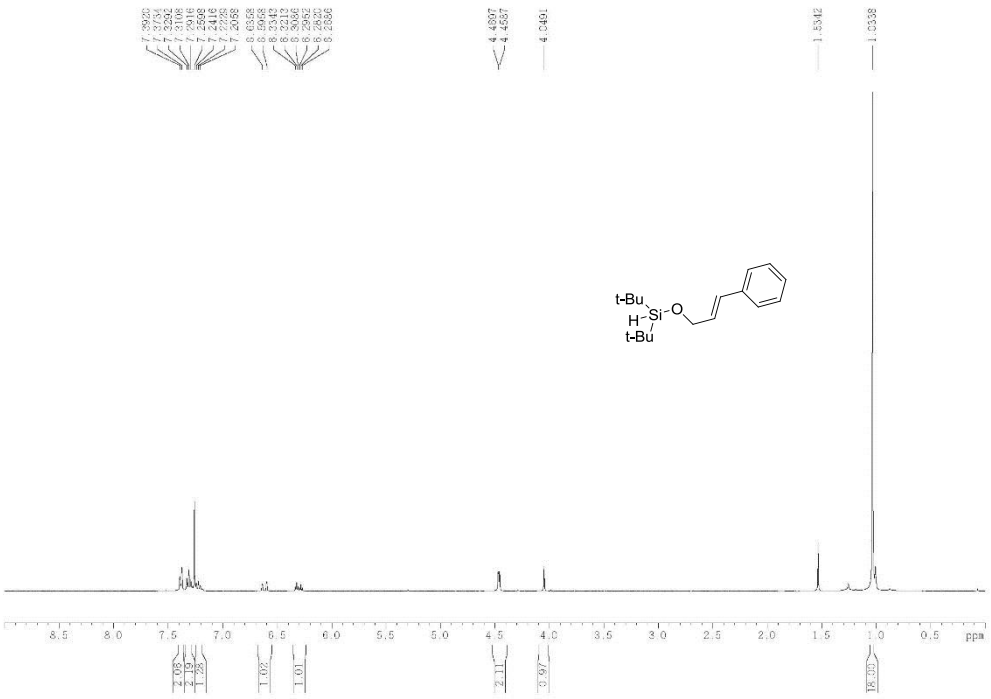

7.5303
7.5114
7.3817
7.3632
7.3437
7.2802
7.2601
7.1157
1.5510
Ph
Ph
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.09
1.92
0.98

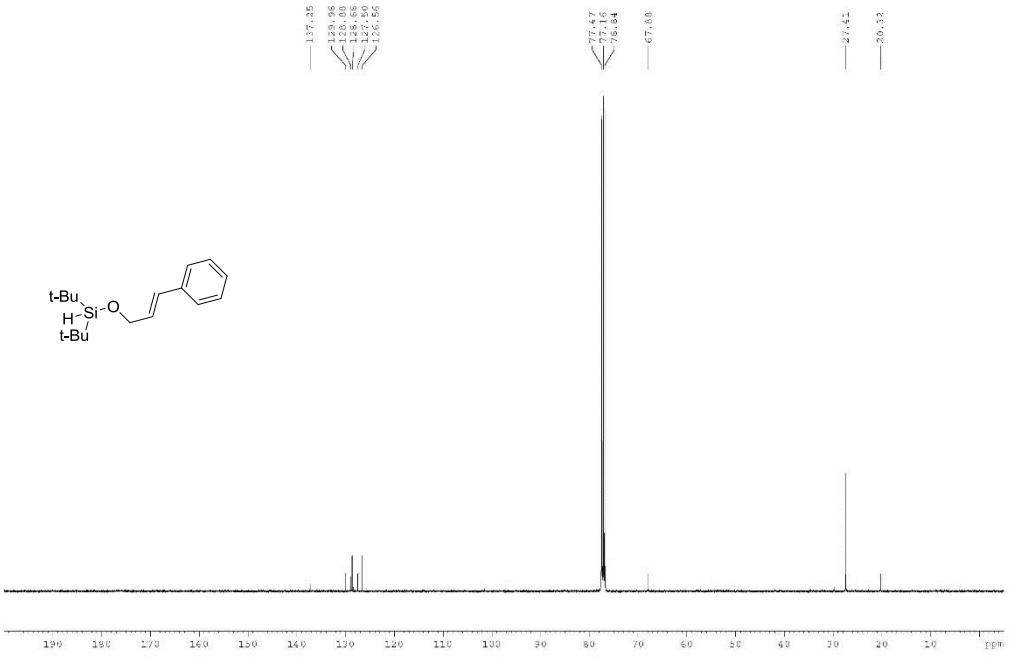

7.2600
4.9481
4.7087
4.1695
1.8082
1.3850
0.9738
t-Bu
Si
H
O
t-Bu
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.95
0.91
0.95
2.90
5.53
18.00

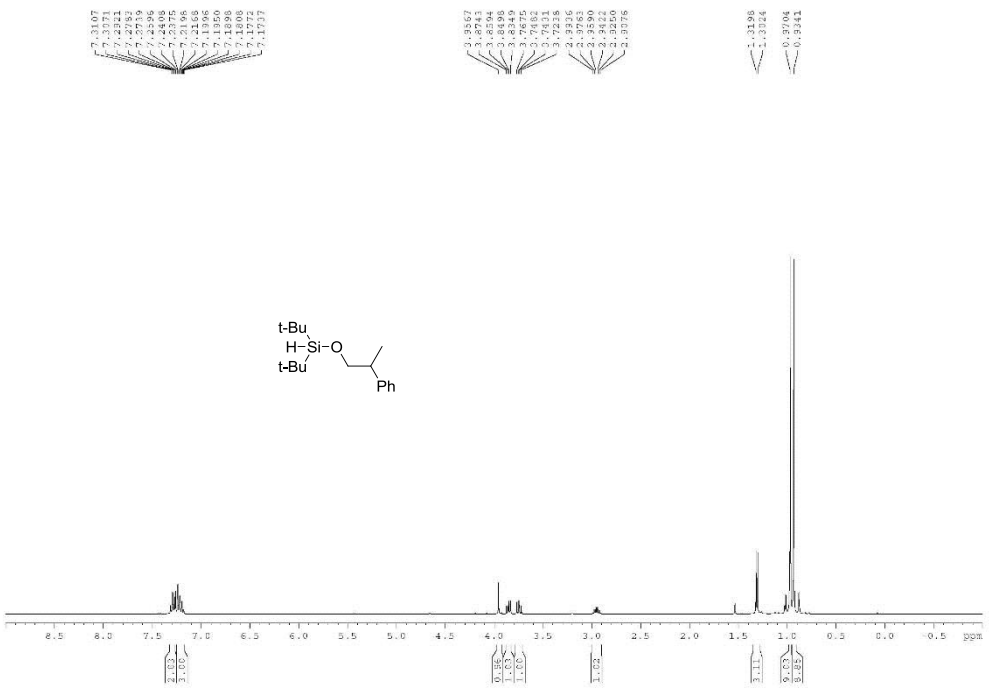

152.1259
108.4335
77.4776
77.1601
76.8428
75.6318
29.3387
27.8093
19.8444
19.1780
t-Bu
Si
H
O
t-Bu
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
76.00
6.53
17.48

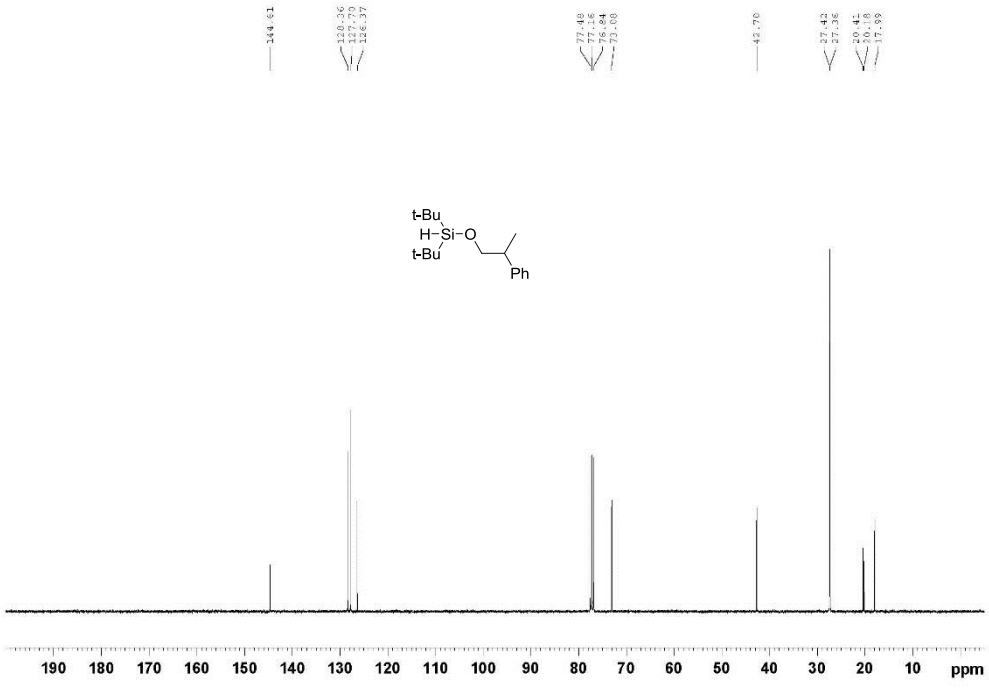

7.3168
7.3082
7.2798
7.2628
7.2576
7.2426
7.2400
7.1966
7.1785
4.0171
3.0008
3.7931
3.7773
2.7428
2.7337
2.7038
1.9307
1.9150
1.9114
1.8994
1.8851
1.8817
1.8039
1.8759
1.8601
1.0322
t-Bu
Si
O
H
t-Bu
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.92
2.84
0.93
2.01
1.96
1.92
18.00

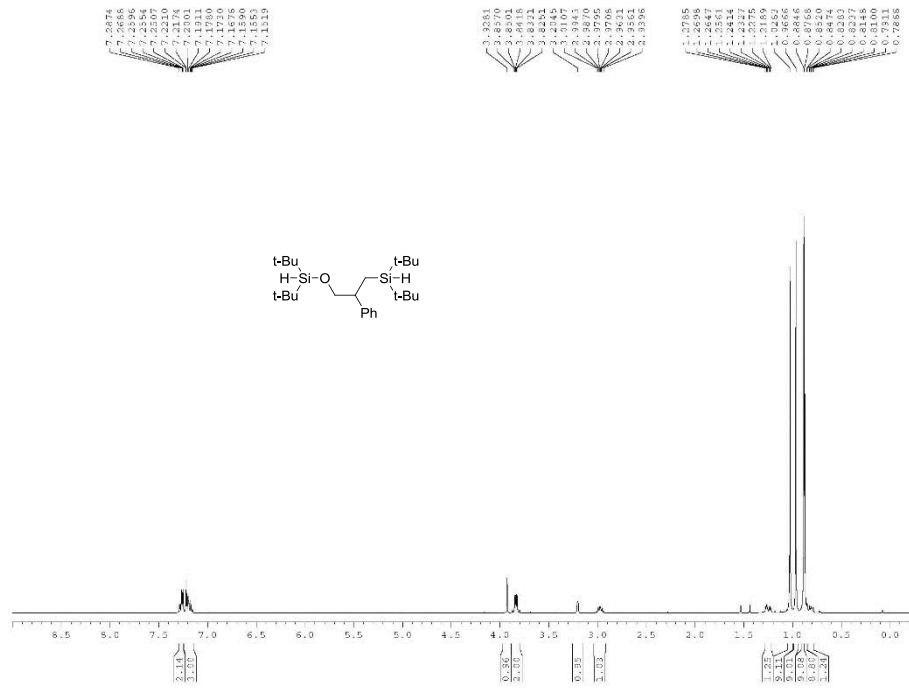

142.40
128.63
128.46
125.83
77.47
77.16
76.84
66.42
34.55
32.29
27.44
20.36
t-Bu
Si
O
H
t-Bu
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

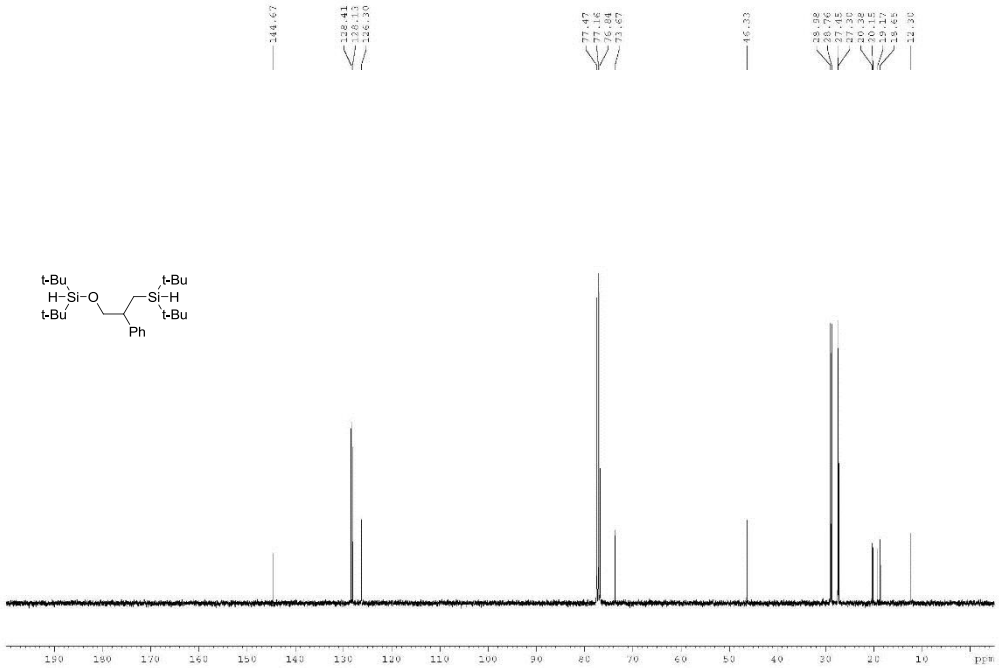

7.3920
7.3734
7.3592
7.3106
7.2916
7.2608
7.2416
7.2228
7.2068
6.6358
6.5908
6.5743
6.3213
6.3066
6.2952
6.2830
6.2680
6.2586
4.4897
4.4657
4.0491
1.5342
1.0338
t-Bu
H
Si
O
t-Bu
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.06
2.78
1.38
1.02
1.01
2.11
0.97
18.00

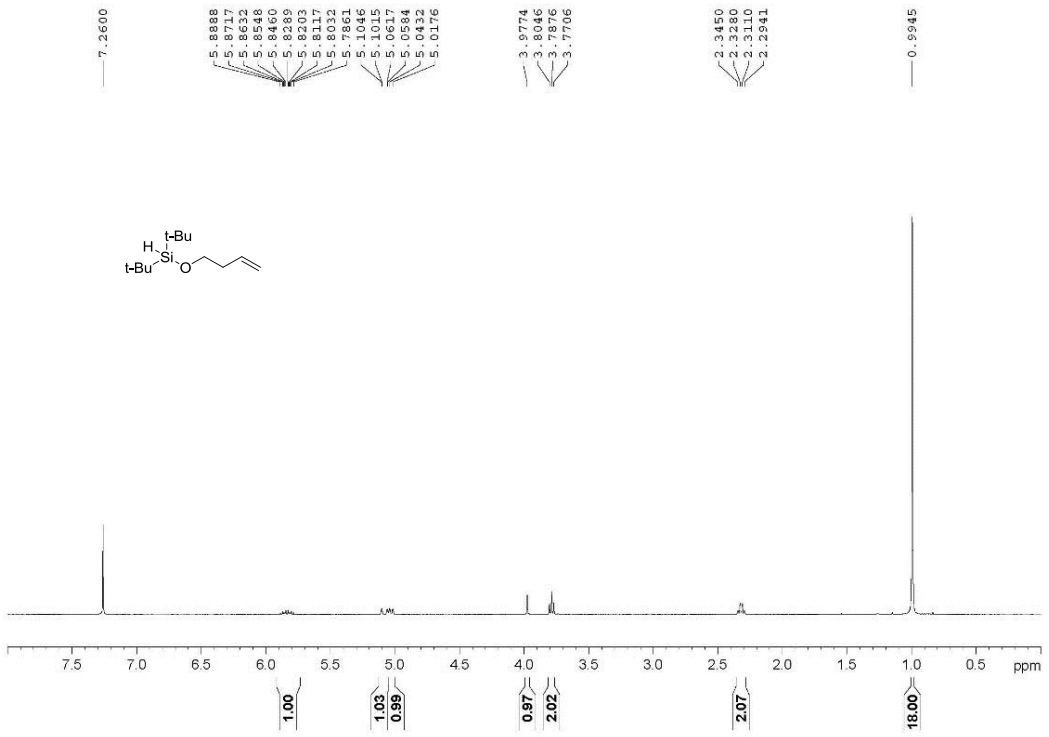

137.25
129.98
128.68
128.55
127.50
126.56
77.47
77.15
76.84
67.88
27.42
20.32
t-Bu
H
Si
O
t-Bu
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

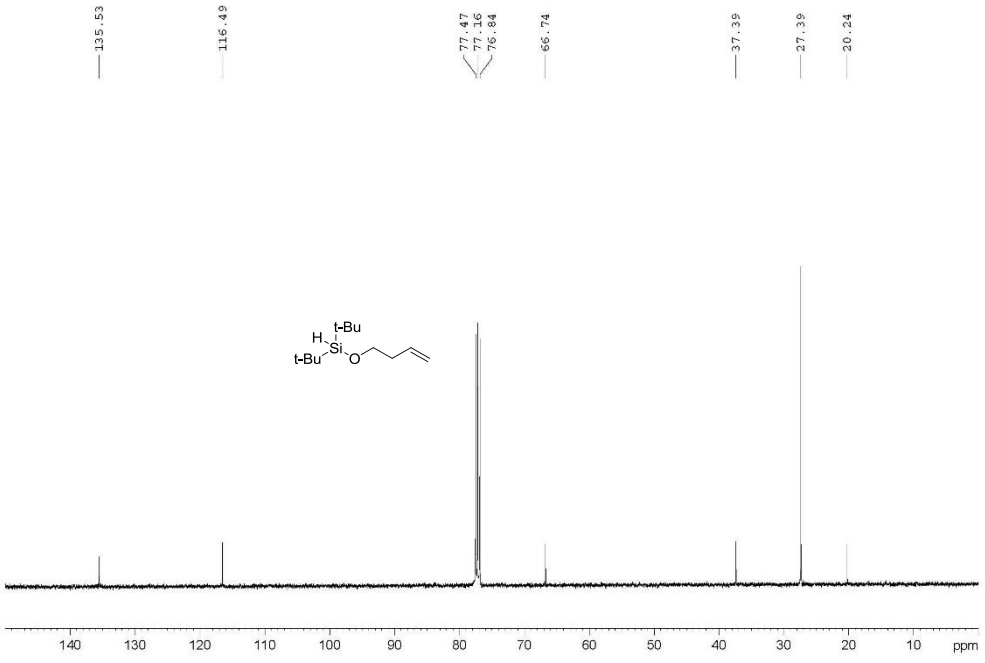

t-Bu
H–Si–O
t-Bu
Ph
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm


t-Bu
H–Si–O
t-Bu
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


t-Bu
H–Si–O
t-Bu
t-Bu
Si–H
t-Bu
Ph
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm


t-Bu
H–Si–O
t-Bu
t-Bu
Si–H
t-Bu
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.2600
5.8888
5.8717
5.8632
5.8548
5.8460
5.8289
5.8203
5.8117
5.8032
5.7861
5.1046
5.1015
5.0617
5.0584
5.0432
5.0176
3.9774
3.8046
3.7876
3.7706
2.3450
2.3280
2.3110
2.2941
0.9945
t-Bu
H
Si
t-Bu
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.03
0.99
0.97
2.02
2.07
18.00


135.53
116.49
77.47
77.16
76.84
66.74
37.39
27.39
20.24
t-Bu
H
Si
t-Bu
O
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm