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

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1. Preparation of the nanoporous gold (NPG):

High purity (> 99.99%) Ag and Au were melted at 1100 °C 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.


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.](image)

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 m²/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 $1.4 \times 10^{19}$ atoms/m². Avogadro’s constant $= 6.02 \times 10^{23}$ mol⁻¹. Accordingly the TON of the model reaction can be estimated as:

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

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

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™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 de-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$_2$S) 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 $5 \times 10^{-4}$ μg/mL. 5 μL of $5 \times 10^{-4}$ 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$_3$·4H$_2$O was dissolved in 470 mL H$_2$O to make a 1 μg/mL Au (III) solution. Then 0.5 mL of 1 μg/mL Au (III) solution was diluted with H$_2$O to 1 L, which gave Au (III) stock solution with $5 \times 10^{-4}$ μg/mL. 5 μL of $5 \times 10^{-4}$ 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 alcoholsysis 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 benzil 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$_{13}$H$_{26}$NaOSi [M+Na]$^+$: 273.16451; found: 273.16453.
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) \(\delta 7.27\) (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) \(\delta 158.89, 133.36, 128.12, 113.74, 68.77, 55.40, 27.43, 20.34\). \(^{29}\)Si NMR (80 MHz, CDCl\(_3\), ppm) \(\delta 17.64\). HRMS (ESI, \(m/z\)) calcd for C\(_{16}\)H\(_{29}\)O\(_2\)Si [M+H]\(^+\): 281.19313; found: 281.19297.

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) \(\delta 3.96\) (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) \(\delta 67.01, 34.97, 27.42, 20.24, 19.10, 14.04\). \(^{29}\)Si NMR (80 MHz, CDCl\(_3\), ppm) \(\delta 16.40\). MS (EI, \(m/z\)): \([M-\text{tBu}]^+\) 207. Anal. Calcd for C\(_{12}\)H\(_{28}\)OSi: C, 72.66; H, 10.67. Found: C, 72.59; H, 10.65.

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) \(\delta 7.34\) – \(7.30\) (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) \(\delta 146.41, 128.22, 126.98, 125.63, 74.25, 27.56, 27.30, 26.74, 20.28, 19.93\). \(^{29}\)Si NMR (80 MHz, CDCl\(_3\), ppm) \(\delta 14.09\). MS (EI, \(m/z\)): [M-\text{tBu}]^+ 207. Anal. Calcd for C\(_{16}\)H\(_{28}\)OSi [M+] 216.1904; found: 216.1912.

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) \(\delta 4.33\) – \(4.31\) (m, 1H), \(3.99\) (s, 1H), \(1.75\) – \(1.51\) (m, 7H), \(0.98\) (s, 18H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\), ppm) \(\delta 77.97, 35.32, 27.47, 23.10, 20.03\). \(^{29}\)Si NMR (80 MHz, CDCl\(_3\), ppm) \(\delta 12.86\). HRMS (EI, \(m/z\)): calcd for C\(_{13}\)H\(_{28}\)OSi [M+] 228.1904; found: 228.1912.

Using procedure A: Reaction was performed with tert-butyl 4-hydroxy piperidine-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) \(\delta 4.02\) (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), \(1.39\) (s, 18H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\), ppm) \(\delta 77.97, 35.32, 27.47, 23.10, 20.03\). \(^{29}\)Si NMR (80 MHz, CDCl\(_3\), ppm) \(\delta 12.86\). HRMS (EI, \(m/z\)): calcd for C\(_{15}\)H\(_{30}\)OSi [M+] 230.1904; found: 230.1905.
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 $\text{C}_{18}\text{H}_{37}\text{NaO}_3\text{Si}$ [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.

[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 (qxd, 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 -2.86. Anal.Calcd for $\text{C}_{11}\text{H}_{22}\text{OSi}$: C, 65.93; H, 12.07. Found: C, 65.89; H, 12.02.

[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 $\text{C}_{14}\text{H}_{25}\text{OSi}$ [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 $\text{C}_{14}\text{H}_{30}\text{NaO}_3\text{Si}$ [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
2k was obtained as a colorless oil after column chromatography (PE, 261 mg, 84% yield). ¹H NMR (400 MHz, CDCl₃, ppm) δ 3.96 (s, 1H), 3.72 (t, 2H, J = 6.6 Hz), 2.17 (dxt, 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). ¹³C NMR (101 MHz, CDCl₃, ppm) δ 84.94, 68.18, 67.30, 32.82, 29.62, 29.50, 29.20, 28.90, 28.65, 27.43, 25.89, 20.24, 18.55. ²⁹Si NMR (80 MHz, CDCl₃, ppm) δ 16.57. HRMS (ESI, m/z): calcd for C₁₉H₃₉OSi [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). ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.32 – 7.29 (m, 4H), 4.81 (s, 2H), 4.08 (s, 1H), 1.02 (s, 18H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ 139.66, 132.83, 128.50, 127.87, 68.35, 27.40, 20.35. ²⁹Si NMR (80 MHz, CDCl₃, ppm) δ 18.59. HRMS (EI, m/z): calcd for C₁₅H₂₅ClOSi [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 10: 1, 210 mg, 85% yield). ¹H NMR (400 MHz, CDCl₃, 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). ¹³C NMR (101 MHz, CDCl₃, ppm) δ 67.99, 66.85, 40.42, 27.46, 27.32, 27.31, 27.06, 23.52, 20.24, 20.12. ²⁹Si NMR (80 MHz, CDCl₃, ppm) δ 19.27. HRMS (ESI, m/z): calcd for C₁₂H₂₈NaO₂Si [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). ¹H NMR (400 MHz, CDCl₃, 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). ¹³C NMR (101 MHz, CDCl₃, ppm) δ 154.74, 133.45, 128.44, 115.21, 68.82, 27.42, 20.33. ²⁹Si NMR (80 MHz, CDCl₃, ppm) δ 18.03. HRMS (ESI, m/z): calcd for C₁₃H₂₇O₂Si [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). ¹H NMR (400 MHz, CDCl₃, 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). ¹³C NMR (101 MHz, CDCl₃, ppm) δ 154.74, 133.45, 128.44, 115.21, 68.82, 27.42, 20.33. ²⁹Si NMR (80 MHz, CDCl₃, ppm) δ 18.03. HRMS (ESI, m/z): calcd for C₁₃H₂₇O₂Si
3.2 Synthesis of unstable hydridosilyl ethers(2p, 2q, 2r) with diethylsilane

Benzylkoxydiethylsilane (2q):
Benzyl alcohol (1a, 1.0 mmol, 1 eq.) and NPG (0.01 mmol, 0.01 eq.) were added to the CDCl₃ (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 ¹H NMR (400 MHz, CDCl₃, 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 CDCl₃ (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.

¹H NMR (400 MHz, CDCl₃, 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). ¹³C NMR (101 MHz, CDCl₃, ppm) δ 146.11, 128.32, 127.13, 125.51, 72.60, 26.55, 6.83, 6.77, 5.63, 5.60. ²⁹Si NMR (80 MHz, CDCl₃, 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)Et₂]+). HRMS (EI, m/z): calcd. for C₁₀H₁₅OSi [M-Et]+: 179.0887; found: 179.0895. calcd. for C₁₁H₁₇OSi [M-Me]+: 193.1043; found: 193.1051.

When 1-phenylethanol (1d, 1.0 mmol, 2 eq.) was treated with 1 eq. Et₃SiH₂ in the presence of NPG (0.01 mmol, 0.01 eq.) in CDCl₃, only mono alcoholsysis product was found according to the crude ¹H NMR (see spectrum data part).
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-Iodobenoic acid (**S1**, 3 g, 12 mmol) was dissolved in CH$_2$Cl$_2$ (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$_3$N (5 mL, 36 mmol) and Et$_2$NH (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$_3$) $\delta$ 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$_3$) $\delta$ 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 (250 mg, 0.96 mmol) in MeOH (5 mL) at 0 °C was treated with NaBH₄ (115 mg, 1.4 mmol). The resulting mixture was stirred for 5 min at 0 °C 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 15 mL). The organic layer was dried over anhydrous magnesium sulfate and then filtered by a short SiO₂ 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).

1H NMR (400 MHz, CDCl₃) δ 7.27 (d, J = 7.9 Hz, 2H), 7.20 (d, J = 7.8 Hz, 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); 13C 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 CDCl₃ (1.75 mL). Diethyilsilane (0.53 mmol) was added. The mixture was then stirred for 10 h at r.t. under nitrogen. Crude 1H NMR showed 4-(3-(diethylsilyloxy)pentyl)-N,N-diethylbenzamide (2p) was got. Crude 1H NMR (400 MHz, CDCl₃) 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-SiEt₂H]⁺), 173.1 (8%, [CH₂CH₂(C₂H₅)CHOH(II)Et₂]⁺).

3.3 Recycling of the NPG catalyst[a].

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
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<th>Yield of 2a[b]</th>
</tr>
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<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>reuse 1</td>
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</tr>
<tr>
<td>6</td>
<td>reuse 5</td>
<td>8</td>
<td>92%</td>
</tr>
</tbody>
</table>

[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 silakets

**General procedure B** for one-pot synthesis of unsymmetrical silakets. 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., synthesized by general procedure A) in anhydrous dichloromethane (1.0 mL) was added. The reaction was stirred at 50 °C 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). ¹H NMR (400M, CDCl₃, 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).

¹³C NMR (101M, CDCl₃, 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 C₁₇H₂₈O₂Si [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 (240 mg, 75% yield) by column chromatography (PE: DCM = 9:1). ¹H NMR (400M, CDCl₃, 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, J₁ = 6.8 Hz, J₂ = 9.6 Hz, J₃ = 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). ¹³C NMR (101M, CDCl₃, ppm) δ 146.78, 128.24, 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 C₁₉H₃₂O₂Si [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 (221 mg, 65% yield) by column chromatography (PE: DCM = 9:1). ¹H NMR (400M, CDCl₃, 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, J₁ = 5.2 Hz, J₂ = 16.0 Hz), 5.05 (q, 1H, J = 6.4 Hz), 4.32 (ddt, 1H, J₁ = 5.2 Hz, J₂ = 9.6 Hz, J₃ = 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), ¹³C NMR (101M, CDCl₃, 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_{2}Si [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, 951 mg) and NPG (0.09 mmol, 18 mg) was added. The reaction was stirred and heated for 0.5 - 36 h. 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 °C at the beginning then heat to 50 °C 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]: ¹H NMR (400M, CDCl₃, 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). ¹³C NMR (101M, CDCl₃, ppm) δ 62.82, 27.38, 20.11, 18.45. HRMS (EI, m/z): calcd for C₁₀H₂₄OSi [M]^+ : 188.1591; found: 188.1599.

[9a]: ¹H NMR (400M, CDCl₃, 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). ¹³C NMR (101M, CDCl₃, ppm) δ 66.11, 28.82, 27.44, 20.14, 18.74, 14.65. ²⁹Si NMR (80M, CDCl₃, ppm) δ 16.43, 8.68. HRMS (EI, m/z): calcd for C₁₈H₄₂OSi₂ [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 °C 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]: ¹H NMR (400M, CDCl₃, 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). ¹³C NMR (101M, CDCl₃, ppm) δ 68.98, 27.42, 26.00, 20.24, 10.45. HRMS (EI, m/z): calcd for C₁₈H₄₂OSi₂ [M]^+ : 202.1747; found: 202.1757.
[9b]: \textit{^1}H NMR (400M, CDCl$_3$, ppm) $\delta$ 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). \textit{^13}C NMR (101M, CDCl$_3$, ppm) $\delta$ 69.93, 30.03, 28.94, 27.43, 20.24, 19.03, 4.80. \textit{^29}Si NMR (80M, CDCl$_3$, ppm) 16.58, 14.39. HRMS (EI, $m/z$): calcd for C$_{19}$H$_{44}$O$_2$Si [M]+: 344.29; found: 344.2931.

Ring-opening/silylation of tetrahydrofuran (7c):
Using procedure C: Reaction was performed with tetrahydrofuran 7c (648 mg, 3.0 mmol) and di-tert-butylsilane (951 mg, 6.6 mmol) at 90 °C 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]: \textit{^1}H NMR (400M, CDCl$_3$, ppm) $\delta$ 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). \textit{^13}C NMR (101M, CDCl$_3$, ppm) $\delta$ 67.01, 34.98, 27.42, 20.24, 19.11, 14.03. HRMS (EI, $m/z$): calcd for C$_{12}$H$_{28}$O$_2$Si [M]$^+$: 216.1904; found: 216.1910.

[9c]: \textit{^1}H NMR (400M, CDCl$_3$, ppm) $\delta$ 3.97 (s, 1H), 3.74 (t, 2H, $J = 6.24$ Hz), 3.30 (s, 1H), 1.60 - 1.36 (m, 6H), 1.00 - 0.99 (d, 36H), 0.66 - 0.61 (m, 2H). \textit{^13}C NMR (101M, CDCl$_3$, ppm) $\delta$ 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$_{46}$O$_2$Si [M]$^+$: 358.3082; found: 358.3091.

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

[9d]: \textit{^1}H NMR (400M, CDCl$_3$, ppm) $\delta$ 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). \textit{^13}C NMR (101M, CDCl$_3$, ppm) $\delta$ 67.25, 32.49, 29.94, 28.98, 27.43, 26.80, 20.24, 18.99, 9.22. \textit{^29}Si NMR (80M, CDCl$_3$, ppm) 16.51, 14.01. HRMS (EI, $m/z$): calcd for C$_{21}$H$_{46}$O$_2$Si [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 SiO₂ plug. The filtration was concentrated by rotary evaporation and then separated by column chromatography (PE: EA = 5: 1). 10 was obtained 194mg, 90% yield.

**1H NMR** (400M, CDCl₃, 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). **13C NMR** (101M, CDCl₃, ppm) δ 62.85, 36.80, 28.95, 23.19, 18.97, 8.96. **RMS** (ESI, m/z): calcd for C₁₂H₂₈NaOSi [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°C for 4 h. Product 8c (422 mg, 70%) and 10e (138 mg, 23%) were obtained as colorless oil by column chromatography (pure hexanes).

**[10e]**: **1H NMR** (400M, CDCl₃, 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). **13C NMR** (101M, CDCl₃, ppm) δ 68.34, 27.49, 25.44, 19.97. **HRMS** (EI, m/z): calcd for C₁₁H₂₆OSi [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°C for 4 h. Product 8f (435 mg, 55%) and 10f (275 mg, 35%) were obtained by column chromatography (pure hexanes).

**[8f]**: **1H NMR** (400M, CDCl₃, 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). **13C NMR** (101M, CDCl₃, ppm) δ 139.07, 129.24, 128.39, 126.26, 68.39, 39.51, 27.35, 20.20. **HRMS** (EI, m/z): calcd for C₁₆H₂₈OSi [M⁺]: 264.1904; found: 264.1902.

**[10f]**: **1H NMR** (400M, CDCl₃, 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). **13C NMR** (101M, CDCl₃, ppm) δ143.22, 136.39, 128.39, 128.26, 125.78, 108.25, 27.05, 20.03. **HRMS** (EI, m/z): calcd for C₁₆H₂₆OSi [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°C 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) \(\delta\) 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) \(\delta\) 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 cyclopentane oxide (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°C for 4 h. Product 2e (595 mg, 87%) was obtained as colorless oil by column chromatography (pure hexanes).

[8h]: \(^1\)H NMR (400M, CDCl\(_3\), ppm) \(\delta\) 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) \(\delta\) 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 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°C 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) \(\delta\) 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) \(\delta\) 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.

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°C 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) \(\delta\) 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) \(\delta\) 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) \(\delta\) 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-\textit{tert}-butylsilane (951 mg, 6.6 mmol) at 70°C for 5 h. Product 8k (435 mg, 60%) was obtained by column chromatography (pure hexanes).

\[
\text{[8k]: } ^1\text{H NMR (400M, CDCl}_3, \text{ppm) } \delta 4.95 (s, 1H), 4.71(s, 1H), 4.17(s, 1H), 1.80(s, 3H), 1.39(s, 6H), 0.97(s, 18H).}
\]  
\[
^13\text{C NMR (101M, CDCl}_3, \text{ppm) } \delta 108.43, 75.63, 29.34, 27.81, 19.84, 19.18.}
\]  

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

\[
\text{[8l]: } ^1\text{H NMR (400M, CDCl}_3, \text{ppm) } \delta 7.32 – 7.26 (m, 2H), 7.23 – 7.18(m, 3H), 4.02 (s, 1H), 3.79(t, 2H, } J = 6.28), 2.72 (t, 2H, } J = 7.64), 1.93 – 1.86 (m, 2H), 1.03 (s, 18H).}
\]  
\[
^13\text{C NMR (101M, CDCl}_3, \text{ppm) } \delta 142.40, 128.63, 128.44, 125.83, 66.42, 34.55, 32.29, 27.44, 20.26.}
\]  
\text{HRMS (ESI, m/z): calcd for C}_{17}\text{H}_{31}\text{OSi} [M+H]^+: 279.2139; found: 279.2136.

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

\[
\text{[8m]: } ^1\text{H NMR (400M, CDCl}_3, \text{ppm) } \delta 7.31 – 7.17(m, 5H), 3.96 (s, 1H), 3.81 (dd, 1H, J1 = 43, J2 = 6.0), 3.79 (dd, 1H, J1 =43, J2 = 6.0), 2.98 – 2.93(m, 1H), 0.97 (s, 9H), 0.93 (s, 9H).}
\]  
\[
^13\text{C NMR (101M, CDCl}_3, \text{ppm) } \delta 144.61, 128.36, 127.50, 126.56, 67.88, 27.41, 20.32.}
\]  
[9m]: \(^1\)H NMR (400M, CDCl\(_3\), ppm) \(\delta 7.29 - 7.15\) (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) \(\delta 144.67, 128.41, 128.13, 126.30, 73.67, 46.33, 28.98, 28.76, 27.45, 27.30, 20.38, 20.15, 19.17, 18.65, 12.30\).

HRMS (ESI, m/z): calcd for C\(_{25}\)H\(_{49}\)OSi\(_2\) [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-butyldiylsilane (951 mg, 6.6 mmol) at 90 \(^\circ\)C 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) \(\delta 4.02\) (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) \(\delta 71.36, 43.75, 28.99, 27.57, 27.54, 22.89, 22.77, 20.28, 19.91, 18.98, 9.40, 13.84, 10.71\). 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-butyldiylsilane for mechanism study:
Using procedure A: Reaction was performed with 3-Buten-1-ol (321 mg, 1.5 mmol) and di-tert-butyldiylsilane (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) \(\delta 5.89 - 5.79\) (m, 1H), 5.10 (d, 1H, \(J = 1.2\) Hz), 5.06 - 5.17 (m, 2H), 3.97 (s, 1H), 3.79 (t, 2H, \(J = 6.8\) Hz), 2.32 (q, 2H, \(J = 6.8\) Hz), 0.99 (s, 18H); \(^13\)C NMR (101M, CDCl\(_3\), ppm) \(\delta 135.53, 116.49, 66.75, 37.39, 27.40, 20.24\); 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-butyldiylsilane (214mg, 1.0 mmol) and di-tert-butyldiylsilane (158 mg, 1.1 mmol) at 70 \(^\circ\)C for about 7 h. substrate (but-3-enyloxy) di-tert-butyldiylsilane kept unconverted.
6. $^1$H NMR, $^{13}$C NMR, $^{29}$Si NMR spectra of related compounds

Mono alcoholsysis of di-tert-butyilsilane and diethylsilane (2a – 2o)
$n$-C$_3$H$_7$OSi (t-Bu)$_2$H

$\textit{n-C}_3\text{H}_7\text{OSi (t-Bu)}_2\text{H}$
Unstable hydridosilyl ethers(2p, 2q, 2r) with diethylsilane
The crude H NMR of the following reaction:

\[
\text{HO}
\]

\[
\text{Et$_2$Zn, 1.5 mmol}
\]

\[
\text{AchNPare 1 mol%}
\]

\[
\text{COC$_2$I, 1.5 mmol, 1h}
\]

1b: 1 mmol

\[
2r
\]

1-3

4 6

5

9, 10

7, 8

\[
\text{ppm}
\]
Unsymmetrical silaketals (6a – 6c)
Ring-opening/silylation of cyclic ethers(8, 9, 10)