Sodium hydroxide–catalyzed dehydrocoupling of alcohols with hydrosilanes

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General information.

Unless otherwise stated, reactions were performed in oven-dried brand-new Fisherbrand scintillation vials flushed with argon or in flame-dried Schlenk flasks under argon connected on a Schlenk line using dry, degassed solvents and brand-new stirring bars. Solvents were dried by passage through an activated alumina column under argon.\(^1\) Reaction progress was monitored by thin-layer chromatography (TLC), GC-MS, or GC-FID analyses. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, phosphomolybdic acid, or KMnO\(_4\) staining. Silicycle SiliaFlash P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography.\(^1\)H NMR spectra were recorded on a Varian Inova 500 MHz spectrometer in CDCl\(_3\), THF-\(d_8\), or Benzene-\(d_6\) and are reported relative to residual solvent peak at \(\delta\) 7.26 ppm, \(\delta\) 3.58 ppm, or \(\delta\) 7.16 ppm respectively. \(^1\)C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (126 MHz) in CDCl\(_3\), THF-\(d_8\), or Benzene-\(d_6\) and are reported relative to residual solvent peak at \(\delta\) 77.16 ppm, \(\delta\) 67.21 ppm, or \(\delta\) 128.06 ppm respectively. Data for \(^1\)H NMR are reported as follows: chemical shift (\(\delta\) ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septet, m = multiplet, br s = broad singlet, br d = broad doublet, app = apparent. Data for \(^1\)C NMR are reported in terms of chemical shifts (\(\delta\) ppm). IR spectra were obtained on a Perkin Elmer Spectrum BXII spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm\(^{-1}\)). GC-FID analyses were obtained on an Agilent 6890N gas chromatograph equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent). GC-MS analyses were obtained on an Agilent 6850 gas chromatograph equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent). High resolution mass spectra (HRMS) were acquired from the California Institute of Technology Mass Spectrometry Facility.

Silanes were purchased from Aldrich and distilled before use. NaOH was purchased from Aldrich (semiconductor grade, pellets, 99.99% trace metals basis) and was pulverized

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(mortar and pestle) and heated (150 °C) under vacuum prior to use. Powdered and vacuum-dried (as above) ACS grade ≥97% NaOH from Aldrich gives identical results. Alcohol and phenol substrates were purchased from Aldrich, TCI, or Acros.
Part I. General observations.
THF and DME proved to be suitable solvents. The addition of DMF to reaction mixtures enabled the silylation in challenging cases; several substrates failed to silylate without the addition of DMF. See characterization data (Part II) for a comprehensive view of all substrates that required addition of DMF. No product was observed in the absence of catalyst.

Part II. Experimental and analytics.

1. General procedure for cross-dehydrogenative O–H silylation and characterization data.

\[
\text{alcohol} \quad \text{NaOH (10 mol %)} \quad [\text{Si}] \quad \text{THF, } T, \text{ time} \quad \text{silyl ether}
\]

To a hot, oven-dried 2 dram scintillation vial equipped with a magnetic stirring bar, NaOH (0.05 mmol, 10 mol %) was added and the vial was purged with argon until cool. Alcohol (0.5 mmol, 1 equiv) was then added under a steady stream of argon, followed by solvent (0.5 mL) and silane (0.75 mmol, 1.5 equiv). The vial was then sealed and the mixture was stirred at the indicated temperature for the indicated time. After the reaction was complete, the reaction mixture was diluted with diethyl ether (2 mL), filtered through a short pad of silica gel, and concentrated under reduced pressure. Volatiles were removed under high vacuum and the resultant material was purified by silica gel flash chromatography if necessary to give the desired O–Si product. Note that since this silylation protocol produces stoichiometric H₂, the reaction – especially when performed on a reasonable scale as in the case of 11 (page 24) – should be conducted in a well vented system and under conditions that are appropriately suitable and safe. Reactions were carried out behind protective shielding when performed in closed vials. In cases where this was not possible, the reactions were carried out in septum-capped vials connected via a needle to an argon manifold and a bubbler if necessary.
(Benzyloxy)dimethyl(phenyl)silane 2a: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (54 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product 2a (113.9 mg, 94% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). Rf = 0.53 (5% EtOAc in hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.70 – 7.66 (m, 2H), 7.48 – 7.42 (m, 3H), 7.40 – 7.35 (m, 4H), 7.30 (dddd, J = 6.7, 6.2, 3.1, 1.7 Hz, 1H), 4.77 (s, 2H), 0.49 (s, 6H). This compound has been previously characterized.²

(Benzyloxy)triethylsilane 2b: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (54 mg, 0.5 mmol, 1.0 equiv), Et₃SiH (87 mg, 120 µL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 45 °C for 18 h. The desired product 2b (101.2 mg, 91% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). Rf = 0.27 (5% EtOAc in hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.31 (m, 4H), 7.27 – 7.23 (m, 1H), 4.75 (s, 2H), 1.00 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 7.9 Hz, 6H). This compound has been previously characterized.³

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(Benzyloxy)(methyl)diphenylsilane 2c: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (54 mg, 0.5 mmol, 1.0 equiv), Ph₂MeSiH (149 mg, 150 µL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product 2c (129.4 mg, 85% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). R_f = 0.50 (5% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl₃) δ 7.65 – 7.62 (m, 4H), 7.44 – 7.37 (m, 6H), 7.36 – 7.32 (m, 4H), 7.29 – 7.26 (m, 4H), 4.82 (d, J = 0.9 Hz, 2H), 0.68 (s, 3H). This compound has been previously characterized.^[4]

(Benzyloxy)(tert-butyl)dimethylsilane 2d: The general procedure was followed. The reaction was performed with NaOH (4.0 mg, 0.1 mmol, 20 mol %), benzyl alcohol (54 mg, 0.5 mmol, 1.0 equiv), (t-Bu)Me₂SiH (87 mg, 124 µL, 1.5 mmol, 3.0 equiv), 0.25 mL dimethylformamide (DMF) and 0.25 mL of tetrahydrofuran (THF) at 65 °C for 24 h. The desired product 2d (66.2 mg, 60% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). R_f = 0.42 (5% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl₃) δ 7.35 (d, J = 4.6 Hz, 4H), 7.28 – 7.24 (m, 1H), 4.78 (d, J = 0.6 Hz, 2H), 0.98 (s, 9H), 0.14 (s, 6H). This compound has been previously characterized.^[5]

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(Benzyloxy)di-tert-butylsilane 2e: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (54 mg, 0.5 mmol, 1.0 equiv), \((t\text{-Bu})_2\text{SiH}_2\) (108 mg, 148 µL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product 2e (120.2 mg, 96% yield) was obtained as a colorless oil after removal of volatiles under high vacuum (45 mtorr) for 2 hours. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.39 – 7.34 (m, 4H), 7.29 – 7.25 (m, 1H), 4.88 (d, \(J = 0.7\) Hz, 2H), 4.12 (s, 1H), 1.05 (s, 18H). This compound has been previously characterized.\(^6\)

(Benzyloxy)triisopropylsilane 2f: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (54 mg, 0.5 mmol, 1.0 equiv), \((i\text{-Pr})_3\text{SiH}\) (119 mg, 154 µL, 0.75 mmol, 1.5 equiv), 0.25 mL dimethylformamide (DMF), and 0.25 mL of tetrahydrofuran (THF) at 65 °C for 18 h. The desired product 2f (112.4 mg, 85% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). \(R_f = 0.52\) (5% EtOAc in hexanes); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.40 – 7.32 (m, 4H), 7.27 – 7.23 (m, 1H), 4.87 (d, \(J = 1.5\) Hz, 2H), 1.26 – 1.17 (m, 3H), 1.12 (d, \(J = 7.0\) Hz, 18H). This compound has been previously characterized.\(^7\)

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1-(Benzyloxy)-1,1,2,2,2-pentamethyldisilane 2g: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (54 mg, 0.5 mmol, 1.0 equiv), Me$_5$Si$_2$H (99 mg, 137 µL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 24 h. Concentration of the reaction mixture and purification of the resulting residue via Kugelrohr distillation (120 mTorr, 60 °C) gave 79.9 mg (67% yield) of 2g as a colorless oil. $^1$H NMR (500 MHz, THF-$d_8$) δ 7.31 – 7.24 (m, 4H), 7.21 – 7.15 (m, 1H), 4.68 (q, J = 0.7 Hz, 2H), 0.23 (s, 6H), 0.10 (s, 9H); $^{13}$C NMR (126 MHz, THF-$d_8$) δ 142.61, 128.96, 127.71, 127.01, 66.02, -0.52, -1.79. IR (Neat Film NaCl) 3363, 3088, 3065, 3030, 2952, 2893, 1595, 1495, 1453, 1376, 1259, 1246, 1207, 1091, 1067, 1026, 835, 803, 766, 729, 695, 655, 617 cm$^{-1}$; HRMS (EI+) calc’d for C$_{12}$H$_{23}$OSi$_2$ [M+H]: 239.1288, found 239.1295.

Bis(benzyloxy)diethylsilane 2h: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (108 mg, 1.0 mmol, 1.0 equiv), Et$_2$SiH$_2$ (49 mg, 71 µL, 0.55 mmol, 0.55 equiv), and 1.0 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product 2h (120.8 mg, 80% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). R$_f$ =0.43 (5% EtOAc in hexanes); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.35 (d, J = 4.4 Hz, 8H), 7.31 – 7.26
(m, 2H), 4.82 (s, 4H), 1.05 (t, J = 7.9 Hz, 6H), 0.76 (q, J = 8.0 Hz, 4H). This compound has been previously characterized.⁸

Bis(benzylxylo)(methyl)(phenyl)silane 2i: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (108 mg, 1.0 mmol, 1.0 equiv), MePhSiH₂ (67 mg, 76 µL, 0.55 mmol, 0.55 equiv), and 1.0 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product 2i (158.8 mg, 95% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). Rf = 0.44 (5% EtOAc in hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.76 (dd, J = 7.9, 1.5 Hz, 2H), 7.49 – 7.43 (m, 3H), 7.39 – 7.37 (m, 8H), 7.33 – 7.28 (m, 2H), 4.91 – 4.82 (m, 4H), 0.50 (s, 3H). This compound has been previously characterized.⁹

((4-Fluorobenzyl)oxy)dimethyl(phenyl)silane 4a: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 4-fluorobenzyl alcohol (63 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv),

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0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product 4a (146.0 mg, 79% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes).  

\[ R_f = 0.48 \ (5\% \text{ EtOAc in hexanes}) \]

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\] \delta \ 7.65 – 7.59 (m, 2H), 7.46 – 7.37 (m, 3H), 7.31 – 7.25 (m, 2H), 7.06 – 6.97 (m, 2H), 4.67 (q, J = 0.8 Hz, 2H), 0.45 (s, 6H); 

\[ ^{13}C \text{ NMR (126 MHz, CDCl}_3\] \delta \ 162.14 (d, J = 244.4 Hz), 137.50, 136.53 (d, J = 2.9 Hz), 133.64, 129.90, 128.37 (d, J = 8.3 Hz), 128.06, 115.19 (d, J = 21.1 Hz), 64.48, -1.60. IR (Neat Film NaCl) 3440, 3070, 3050, 3022, 2958, 2866, 1605, 1509, 1463, 1427, 1417, 1375, 1294, 1253, 1221, 1155, 1117, 1082, 826, 789, 741, 700, 645 cm\(^{-1}\); HRMS (EI+) calc’d for C\(_{15}\)H\(_{16}\)O\(_3\)SiF [(M+H)-H\(_2\)]: 259.0955, found 259.0951.

\[ ((4-\text{Bromobenzyl}oxy)\text{dimethyl(phenyl)silane 4b:} \]

The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 4-bromobenzyl alcohol (94 mg, 0.5 mmol, 1.0 equiv), PhMe\(_2\)SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), 0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 65 °C for 24 h. The desired product 4b (146.2 mg, 91% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes).  

\[ R_f = 0.48 \ (5\% \text{ EtOAc in hexanes}) \]

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\] \delta \ 7.61 (dd, J = 7.7, 1.8 Hz, 2H), 7.47 - 7.34 (m, 5H), 7.19 (dt, J = 8.7, 0.7 Hz, 2H), 4.66 (d, J = 0.8 Hz, 2H), 0.44 (s, 6H). This compound has been previously characterized.\(^\text{10}\)

**Dimethyl((4-nitrobenzyl)oxy)(phenyl)silane 4c:** The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 4-nitrobenzyl alcohol (77 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), 0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 65 °C for 18 h. The desired product 4c (102.2 mg, 71% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). R_f = 0.38 (5% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl₃) δ 8.21 – 8.15 (m, 2H), 7.60 (dd, J = 7.8, 1.7 Hz, 2H), 7.47 (dt, J = 8.8, 0.8 Hz, 2H), 7.44 – 7.38 (m, 3H), 4.79 (t, J = 0.8 Hz, 2H), 0.47 (s, 6H); ^13C NMR (126 MHz, CDCl₃) δ 148.51, 147.18, 136.92, 133.59, 130.13, 128.18, 126.77, 123.68, 64.03, -1.73. IR (Neat Film NaCl) 3423, 2958, 1641, 1608, 1519, 1527, 1253, 1117, 1094, 856, 830, 786, 735, 700 cm⁻¹; HRMS (EI+) calc’d for C₁₅H₁₈SiO₃N [M+H]: 288.1056, found 288.1058.

**Methyl 4-(((dimethyl(phenyl)silyl)oxy)methyl)benzoate 4d:** The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), methyl 4-(hydroxymethyl)benzoate (83 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 µL,
0.75 mmol, 1.5 equiv), 0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 65 °C for 24 h. The desired product 4d (100.6 mg, 67% yield) was obtained as a colorless oil by silica gel flash chromatography (gradient 15% EtOAc to 30% EtOAc in hexanes). R_f = 0.62 (15% EtOAc in hexanes); 1H NMR (500 MHz, CDCl_3) δ 8.01 (d, J = 8.3 Hz, 2H), 7.63 – 7.60 (m, 2H), 7.45 – 7.36 (m, 5H), 4.76 (d, J = 0.8 Hz, 2H), 3.92 (s, 3H), 0.46 (s, 6H). This compound has been previously characterized. 11

4-(Methoxycarbonyl)benzyl 4-(((dimethyl(phenyl)silyl)oxy)methyl)benzoate 4d-SI: Also isolated from the column was 4d-SI (36.9 mg, 34% silylation yield / 17% yield based on methyl 4-(hydroxymethyl)benzoate stoichiometry) as a colorless solid. R_f = 0.43 (15% EtOAc in hexanes); 1H NMR (500 MHz, CDCl_3) δ 8.08 – 8.03 (m, 4H), 7.62 – 7.58 (m, 2H), 7.51 (dt, J = 8.6, 0.7 Hz, 2H), 7.43 – 7.37 (m, 5H), 5.42 (s, 2H), 4.76 (d, J = 0.8 Hz, 2H), 3.93 (s, 3H), 0.44 (s, 6H); 13C NMR (126 MHz, CDCl_3) δ 166.88, 166.31, 146.62, 141.30, 137.26, 133.61, 130.02, 129.97, 129.90, 128.63, 128.09, 127.72, 126.27, 65.94, 64.53, 52.32, -1.64.

((4-Methoxybenzyl)oxy)dimethyl(phenyl)silane 4e: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 4-methoxybenzyl alcohol (69 mg, 0.5 mmol, 1.0 equiv), PhMe_2SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product 4e (117.9 mg, 87% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). R_f = 0.29 (5% EtOAc in hexanes); 1H NMR (500

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MHZ, CDCl$_3$) $\delta$ 7.62 (dd, $J = 7.5$, 2.0 Hz, 2H), 7.44 – 7.37 (m, 3H), 7.25 – 7.20 (m, 2H), 6.87 (d, $J = 8.6$ Hz, 2H), 4.64 (d, $J = 0.6$ Hz, 2H), 3.81 (s, 3H), 0.42 (s, 6H). This compound has been previously characterized.$^{12}$

3-((((Dimethyl(phenyl)silyloxy)methyl)pyridinesilane 4f: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), pyridin-3-ylmethanol (55 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product 4f (118.1 mg, 97% yield) was obtained as a colorless oil by removal of volatiles at 80 °C at 60mTorr. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.52 (dt, $J = 2.3$, 0.8 Hz, 1H), 8.49 (dd, $J = 4.8$, 1.6 Hz, 1H), 7.65 (dtd, $J = 7.8$, 1.7, 0.9 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.43 – 7.37 (m, 3H), 7.26 (ddd, $J = 7.9$, 4.8, 0.9 Hz, 1H), 4.70 (dt, $J = 0.6$ Hz, 2H), 0.44 (s, 6H). This compound has been previously characterized.$^{13}$

Dimethyl(phenyl)(thiophen-2-ylmethoxy)silane 4g: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), thiophen-2-ylmethanol (57 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product 4g (119.2 mg, 96% yield) was obtained as a colorless oil by removal of volatiles


at 80 °C at 60mTorr. $^1\text{H NMR (500 MHz, CDCl}_3\delta 7.63 - 7.58 (m, 2H), 7.44 - 7.37 (m, 3H), 7.28 (dd, J = 4.4, 1.9 Hz, 1H), 7.00 (d, J = 4.4 Hz, 2H), 4.76 (d, J = 0.8 Hz, 2H), 0.41 (s, 6H). This compound has been previously characterized.\textsuperscript{14}

(Furan-2-ylmethoxy)dimethyl(phenyl)silane $4h$: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), furfuryl alcohol (49 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 45 °C for 18 h. The desired product $4h$ (101.1 mg, 87% yield) was obtained as a colorless oil by removal of volatiles at 80 °C at 60mTorr. $^1\text{H NMR (500 MHz, CDCl}_3\delta 7.62 (ddd, J = 7.5, 2.4, 1.3 Hz, 2H), 7.46 - 7.33 (m, 4H), 6.32 (dt, J = 3.4, 1.8 Hz, 1H), 6.21 (t, J = 2.5 Hz, 1H), 4.62 (d, J = 2.0 Hz, 2H), 0.43 (d, J = 1.9 Hz, 6H). This compound has been previously characterized.\textsuperscript{15}

Dimethyl(phenyl)((2,4,6-trimethylbenzyl)oxy)silane $4i$: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), mesitylmethanol (75 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), 0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 65 °C for 18 h. Concentration of the reaction mixture and purification of the resulting residue


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via Kugelrohr distillation (100 mTorr, 210 °C) gave 118.7 mg (84% yield) of 4i as a colorless oil. (Note: the purified material obtained by Kugelrohr distillation was accompanied by ca. 5% unidentified by-products; however, further purification by chromatography was precluded by the instability of 4i on SiO₂ as well as its decomposition under prolonged heating). ¹H NMR (500 MHz, THF-d₈) δ 7.59 – 7.55 (m, 2H), 7.36 – 7.30 (m, 3H), 6.79 – 6.73 (m, 2H), 4.66 (s, 2H), 2.24 (t, J = 0.6 Hz, 6H), 2.20 (s, 3H), 0.35 (s, 6H); ¹³C NMR (126 MHz, THF-d₈) δ 139.02, 137.93, 137.61, 134.72, 134.46, 130.42, 129.65, 128.68, 59.98, 21.23, 19.79, -1.48. IR (Neat Film NaCl) 3421, 3069, 3048, 3008, 2957, 2918, 1614, 1583, 1427, 1373, 1253, 1147, 1118, 1046, 848, 829, 784, 740, 699, 644 cm⁻¹; HRMS (EI⁺) calc’d for C₁₆H₁₆FSi [(M+H)-H₂]: 283.1518, found 283.1526.

2-(2-((Dimethyl(phenyl)silyl)oxy)ethyl)isoindoline-1,3-dione 4j: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 2-(2-hydroxyethyl)isoindoline-1,3-dione (96 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), 0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 65 °C for 24 h. The desired product 4j (101.6 mg, 62% yield) was obtained as a colorless oil by silica gel flash chromatography (20% EtOAc in hexanes). R_f = 0.45 (20% EtOAc in hexanes); ¹H NMR (500 MHz, Benzene-d₆) δ 7.52 – 7.50 (m, 1H), 7.50 (dd, J = 2.4, 0.6 Hz, 1H), 7.43 (dd, J = 5.4, 3.0 Hz, 2H), 7.16 – 7.15 (m, 1H), 7.15 – 7.14 (m, 1H), 7.14 (d, J = 2.3 Hz, 1H), 6.87 (ddd, J = 5.5, 3.0, 0.5 Hz, 2H), 3.74 – 3.67 (m, 2H), 3.68 – 3.62 (m, 2H), 0.26 (s, 6H); ¹³C NMR (126 MHz, Benzene-d₆) δ 167.96, 137.77, 133.81, 133.39, 132.66, 129.84, 128.13, 122.95, 60.16, 40.23, -1.81. IR (Neat Film NaCl) 2956, 1773, 1713, 1615, 1467, 1427, 1392, 1362, 1319, 1252, 1189, 1116, 1022, 929, 859, 829, 788, 718, 700 cm⁻¹; HRMS (EI⁺) calc’d for C₁₈H₂₀O₃SiN [M+H]: 326.1213, found 326.1223.
Dimethyl(phenyl)((5-phenylpentyl)oxy)silane 4k: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 5-phenylpentanol (82 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 45 °C for 18 h. The desired product 4k (146.3 mg, 98% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). R_f = 0.46 (5% EtOAc in hexanes); {1}H NMR (500 MHz, CDCl₃) δ 7.63 (ddq, J = 6.2, 1.9, 0.9 Hz, 2H), 7.46 – 7.41 (m, 3H), 7.32 (tt, J = 7.5, 0.9 Hz, 2H), 7.22 (ddt, J = 9.9, 7.3, 1.3 Hz, 3H), 3.65 (td, J = 6.7, 1.1 Hz, 2H), 2.67 – 2.63 (m, 2H), 1.74 – 1.58 (m, 4H), 1.47 – 1.38 (m, 2H), 0.44 (t, J = 1.0 Hz, 6H); {13}C NMR (126 MHz, CDCl₃) δ 142.79, 138.10, 133.58, 129.66, 128.51, 128.34, 127.93, 125.71, 63.15, 36.04, 32.57, 31.41, 25.59, -1.65. IR (Neat Film NaCl) 3385, 3067, 3025, 2933, 2857, 1603, 1495, 1452, 1427, 1341, 1254, 1119, 1055, 831, 791, 726, 698 cm⁻¹; HRMS (EI+) calc’d for C₁₉H₂₇O₃Si [M+H]: 299.1831, found 299.1840.

Dimethyl((3-methylcyclohex-2-en-1-yl)oxy)(phenyl)silane 4l: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 3-methylcyclohex-2-en-1-ol (56 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 µL, 0.75
mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 45 °C for 48 h. The desired product 4l (113.4 mg, 92% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). R_f = 0.43 (5% EtOAc in hexanes); 1H NMR (500 MHz, CDCl_3) δ 7.64 – 7.56 (m, 2H), 7.38 (dd, J = 5.0, 1.9 Hz, 3H), 5.34 (dd, J = 3.1, 1.6 Hz, 1H), 4.20 (dt, J = 5.0, 1.6 Hz, 1H), 1.99 – 1.69 (m, 4H), 1.64 (tt, J = 1.6, 0.9 Hz, 3H), 1.55 – 1.42 (m, 2H), 0.40 (d, J = 1.1 Hz, 6H); 13C NMR (126 MHz, CDCl_3) δ 138.64, 137.78, 133.69, 129.59, 127.89, 125.14, 67.41, 32.13, 30.08, 23.80, 19.83, -0.80, -0.91. IR (Neat Film NaCl) 3423, 3069, 2935, 2862, 1645, 1427, 1251, 1074, 1024, 992, 894, 880, 828, 786, 738, 700 cm^{-1}; HRMS (EI+) calc’d for C_{15}H_{21}O Si [(M+H)-H_2]: 245.1362, found 245.1368.

(Hex-2-yn-1- yloxy)dimethyl(phenyl)silane 4m: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), hex-2-yn-1-ol (49 mg, 0.5 mmol, 1.0 equiv), PhMe_2SiH (102 mg, 115 μL, 0.75 mmol, 1.5 equiv), and 0.5 mL of 1 tetrahydrofuran (THF) at 45 °C for 18 h. The desired product 4m (99.9 mg, 86% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). R_f = 0.43 (5% EtOAc in hexanes); 1H NMR (500 MHz, CDCl_3) δ 7.62 – 7.59 (m, 2H), 7.42 – 7.36 (m, 3H), 4.27 (t, J = 2.2 Hz, 2H), 2.16 (tt, J = 7.1, 2.2 Hz, 2H), 1.51 (h, J = 7.3 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H), 0.45 (s, 6H); 13C NMR (126 MHz, CDCl_3) δ 137.36, 133.71, 129.84, 127.97, 85.99, 78.37, 51.93, 22.11, 20.92, 13.66, -1.46. Note: this product decomposes slowly in CDCl_3. IR (Neat Film NaCl) 3420, 2956, 1646, 1254, 1118, 1067, 1026, 830, 789, 726, 698 cm^{-1}; HRMS (EI+) calc’d for C_{14}H_{19}O Si [M+H]: 231.1205, found 231.1207.
(Cyclopropylmethoxy)dimethyl(phenyl)silane 4n: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), cyclopropanemethanol (36 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), 0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 65 °C for 18 h. Concentration of the reaction mixture and purification of the resulting residue via Kugelrohr distillation (120 mTorr, 65 °C) gave 65.4 mg (63% yield) of 4n as a colorless oil. Note: product is volatile under high vacuum. (Note: the purified material obtained by Kugelrohr distillation was accompanied by ca. 5% unidentified by-products; however, further purification by chromatography was precluded by the instability of 4n on SiO₂). ¹H NMR (500 MHz, Benzene-d₆) δ 7.63 – 7.58 (m, 2H), 7.27 – 7.19 (m, 3H), 3.40 (d, J = 6.4 Hz, 2H), 0.95 (ttt, J = 8.0, 6.4, 4.9 Hz, 1H), 0.34 (s, 6H), 0.32 – 0.28 (m, 2H), 0.12 – 0.05 (m, 2H); ¹³C NMR (126 MHz, Benzene-d₆) δ 138.63, 133.92, 129.80, 128.19, 67.54, 13.68, 3.23, -1.38. IR (Neat Film NaCl) 3070, 3006, 2958, 2862, 1470, 1427, 1403, 1251, 1177, 1116, 1073, 851, 826, 785, 740, 699 cm⁻¹; HRMS (EI+) calc’d for C₁₂H₁₈OSi [M+•]: 206.1127, found 206.1148.

Dimethyl(oxiran-2-ylmethoxy)(phenyl)silane 4o: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), glycidol (37 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product 4o (74.8 mg, 72% yield) was obtained as a colorless oil by silica gel flash chromatography (10% EtOAc in hexanes). R₇
= 0.60 (10% EtOAc in hexanes); $^1$H NMR (500 MHz, Benzene-$d_6$) δ 7.63 – 7.53 (m, 2H), 7.22 (dd, J = 5.5, 1.8 Hz, 3H), 3.58 (dd, J = 11.9, 2.9 Hz, 1H), 3.33 (dd, J = 11.9, 5.3 Hz, 1H), 2.78 (ddt, J = 5.4, 3.9, 2.7 Hz, 1H), 2.24 (dd, J = 5.3, 4.0 Hz, 1H), 2.16 (dd, J = 5.3, 2.6 Hz, 1H), 0.33 (s, 6H). This compound has been previously characterized.  

![Diagram](image_url)

**(((3s,5s,7s)-Adamantan-1-yl)oxy)dimethyl(phenyl)silane 4p:** The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 1-adamantol (76 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 65 °C for 18 h. The desired product 4p (66.2 mg, 60% yield) was obtained as a colorless oil by removal of volatiles at 80 °C at 60mTorr. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.68 – 7.62 (m, 2H), 7.40 – 7.38 (m, 3H), 2.13 – 2.08 (m, 3H), 1.80 (dt, J = 3.3, 0.8 Hz, 6H), 1.64 – 1.55 (m, 6H), 0.43 (s, 6H). This compound has been previously characterized.  

![Diagram](image_url)

**Dimethyl(octyloxy)(phenyl)silane 4q:** The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 1-octanol (65 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product 4q (111.1 mg, 84% yield) 

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was obtained as a colorless oil by silica gel flash chromatography (100% hexanes). $R_f = 0.49$ (100% hexanes); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.64 – 7.58 (m, 2H), 7.41 (dd, $J = 5.0$, 1.9 Hz, 3H), 3.62 (t, $J = 6.7$ Hz, 2H), 1.60 – 1.51 (m, 2H), 1.32 – 1.24 (m, 10H), 0.97 – 0.85 (m, 3H), 0.41 (s, 6H). This compound has been previously characterized.$^{18}$

**Dimethyl(phenyl)(3,3,3-trifluoropropoxy)silane 4r:** The general procedure was followed. The reaction was performed with 3,3,3-trifluoropropanol (114 mg, 1.00 mmol. 1.0 equiv), Me$_2$PhSiH (204 mg, 230 $\mu$L, 1.5 mmol, 1.5 equiv), NaOH (4.0 mg, 0.10 mmol, 10 mol%) and THF (1.0 mL). The reaction was heated to 60°C for 24 hours, then concentrated in vacuo and purified by silica gel column chromatography (5% EtOAc in hexanes) to afford 4r (220 mg, 89% yield) as a colorless oil. $R_f = 0.48$ (5% EtOAc in hexanes); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.76 – 7.55 (m, 2H), 7.55 – 7.41 (m, 3H), 3.91 (t, $J = 6.7$ Hz, 2H), 2.43 (qt, $J = 10.7$, 6.7 Hz, 2H), 0.49 (s, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 137.18, 133.54, 130.00, 128.11, 56.34 (q, $J = 3.9$ Hz), 36.96 (q, $J = 27.4$ Hz), -1.96; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -64.60 (t, $J = 10.7$ Hz). IR (Neat Film NaCl) 3051, 3070, 3022, 3012, 2959, 3002, 2892, 1591, 1410, 1382, 1347, 1255, 1152, 1137, 1119, 1094, 1050, 1025, 1006, 917, 830, 728, 699 cm$^{-1}$; HRMS (EI+) calc’d for C$_{15}$H$_{18}$O$_2$Si [M+] : 248.0844, found 248.0836.

**3-chloropropoxy)dimethyl(phenyl)silane 4s:** The general procedure was followed. The reaction was performed with 3-chloropropanol (94 mg, 1.00 mmol. 1.0 equiv), Me$_2$PhSiH

(204 mg, 230 µL, 1.5 mmol, 1.5 equiv), NaOH (4.0 mg, 0.10 mmol, 10 mol%) and THF (1.0 mL). The reaction was heated to 60°C for 24 hours, then concentrated in vacuo and purified by silica gel flash chromatography (5% EtOAc in hexanes) to afford 4s (178 mg, 78% yield) as a colorless oil. R_f = 0.43 (5% EtOAc in hexanes); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.80 – 7.60 (m, 2H), 7.57 – 7.38 (m, 3H), 3.84 (t, J = 5.8 Hz, 2H), 3.73 (q, J = 6.5 Hz, 2H), 3.58 (q, J = 7.0 Hz, 1H), 2.17 – 1.96 (m, 2H), 1.31 (t, J = 7.0 Hz, 1H), 0.50 (d, J = 4.3 Hz, 6H); \(^1\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 137.61, 133.47, 129.75, 127.96, 59.44, 41.71, 35.21, -1.87. Note the high volatility of the product, which prevents quantitative solvent removal by high vacuum (i.e., that some residual solvent signals remain). IR (Neat Film NaCl) 3069, 3050, 3011, 2958, 2874, 2361, 2343, 1427, 1253, 1118, 1097, 1068, 830, 788, 699 cm\(^{-1}\); HRMS (FAB+) calc’d for C\(_{11}\)H\(_{17}\)ClOSi [M+H]: 229.0816, found 229.0797.

(4-Methoxyphenoxy)dimethyl(phenyl)silane 4t: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 4-methoxyphenol (62 mg, 0.5 mmol, 1.0 equiv), PhMe\(_2\)SiH (102 mg, 115 µL, 0.75 mmol, 1.5 equiv), 0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 65 °C for 18 h. The desired product 4t (106.0 mg, 82% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). R_f = 0.45 (5% EtOAc in hexanes); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.63 (dd, J = 7.8, 1.7 Hz, 2H), 7.45 – 7.36 (m, 3H), 6.74 (s, 4H), 3.74 (s, 3H), 0.50 (s, 6H); \(^1\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 154.32, 148.85, 137.40, 133.61, 130.00, 128.06, 120.73, 114.57, 55.70, -1.11. IR (Neat Film NaCl) 3420, 2958, 2833,1638, 1505, 1465, 1441, 1427, 1253, 1233, 1118, 1037, 911, 831,787, 729, 700 cm\(^{-1}\); HRMS (EI+) calc’d for C\(_{15}\)H\(_{18}\)O\(_2\)Si [M+•]: 258.1076, found 258.1083.
2,2’-bis((dimethyl(phenyl)silyl)oxy)-1,1’-binaphthene 4u: The general procedure was followed. The reaction was performed with 2,2’-binaphthol (286 mg, 1.00 mmol, 1.0 equiv), Me₂PhSiH (408 mg, 460 µL, 3.0 mmol, 3.0 equiv), NaOH (4.0 mg, 0.10 mmol, 10 mol%) and DME (1.0 mL). The reaction was heated to 80°C for 24 hours, then concentrated in vacuo and purified by silica gel column chromatography (5% EtOAc in hexanes) to afford 4u (393 mg, 71% yield) as a colorless oil. R_f = 0.41 (5% EtOAc in hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.96 – 7.87 (m, 4H), 7.43 – 7.28 (m, 8H), 7.28 – 7.21 (m, 10H), 0.27 (s, 6H), 0.18 (s, 6H); ^13C NMR (101 MHz, CDCl_3) δ 151.11, 137.66, 134.54, 133.31, 129.52, 128.99, 127.72, 126.22, 126.03, 123.71, 122.48, 121.14, -0.63, -0.95. Note that some small impurity signals are present, which could not be removed with further purification. IR (Neat Film NaCl) 3067, 3052, 2958, 2921, 1955, 1889, 1620, 1591, 1503, 1473, 1459, 1355, 1338, 1264, 1249, 1120, 1004, 995, 842, 832, 745, 699 cm⁻¹; HRMS (FAB+) calc’d for C_{36}H_{34}O_{2}Si_{2} [M+] : 554.2090, found 554.2097.

Di-tert-butyl(phenoxy)silane 6: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), phenol (47 mg, 0.5 mmol, 1.0 equiv), (t-Bu)_2SiH (108 mg, 148 µL, 0.75 mmol, 1.5 equiv), 0.25 mL dimethylformamide (DMF) and 0.25 mL of tetrahydrofuran (THF) at 65 °C for 24 h. The desired product 6 (106.5 mg, 90% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). R_f = 0.77 (5% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl_3) δ
7.26 – 7.21 (m, 3H), 6.95 – 6.93 (m, 2H), 4.44 (s, 1H), 1.07 (s, 18H). This compound has been previously characterized.19

![Chemical structure](image1)

2,4,4,7,7-pentamethyl-2-phenyl-1,3,2-dioxasilepane 9: The general procedure was followed. The reaction was performed with 2,5-dimethyl-2,5-hexanediol (146 mg, 1.00 mmol, 1.0 equiv), MePhSiH₂ (183 mg, 205 µL, 1.50 mmol, 1.5 equiv), NaOH (4.0 mg, 0.10 mmol, 10 mol%) and THF (1.0 mL). The reaction was stirred at 60°C for 24 h, then concentrated in vacuo to afford the product 9 (235 mg, 89% yield) as a clear oil. ¹H NMR (500 MHz, CDCl₃) δ 7.84 – 7.70 (m, 2H), 7.46 – 7.40 (m, 3H), 1.94 – 1.86 (m, 4H), 1.42 (s, 6H), 1.31 (s, 6H), 0.42 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 138.65, 133.75, 129.33, 127.58, 74.92, 68.02, 38.06, 25.70, 0.78. IR (Neat Film NaCl) 3069, 3050, 3025, 2973, 2933, 2131, 1591, 1429, 1258, 1143, 1122, 1038, 1028, 1011, 998, 782, 724, 699 cm⁻¹; HRMS (EI⁺) calc’d for C₁₅H₁₈O₂Si [M++]: 264.1546, found 264.1536. This product is quite unstable hydrolytically.

![Chemical structure](image2)

2,2-diethyl-4,4,5,5-tetramethyl-1,3,2-dioxasilolane 10: The general procedure was followed. The reaction was performed with pinacol (118 mg, 1.0 mmol, 1.0 equiv), Et₂SiH₂ (132 mg, 194 µL, 1.5 mmol, 1.5 equiv), and 1.0 mL of tetrahydrofuran (THF), then NaOH (40.0 mg, 1.0 mmol, 10 mol %) was added and the mixture was stirred at 25 °C for 20 h. GC analyses showed full and clean conversion to product; however, concentration of the reaction mixture and attempts at purification of the resulting residue via Kugelrohr distillation or column chromatography on silica gel or silica gel treated with NEt₃ resulted in decomposition and the formation of siloxanes and recovery of pinacol.

![Chemical structure](image)

2,4,4,5,5-Pentamethyl-2-phenyl-1,3,2-dioxasilolane 11: A modified general procedure was followed to account for greater volumes of hydrogen evolution since this reaction is performed on a larger scale. The reaction is performed in a flame-dried 50 mL round bottom Schlenk flask equipped with a magnetic stirring bar that is allowed to cool to room temperature and which is connected to an argon manifold by means of a hose attached to the side arm of the flask. The side arm contains a lightly greased glass stopcock valve. The tap is opened subjecting the flask to a positive pressure of argon. The flask is charged with pinacol (1.18 g, 10.0 mmol, 1.0 equiv), MePhSiH₂ (1.22 g, 1.37 mL, 10.0 mmol, 1.0 equiv), and 10.0 mL of tetrahydrofuran (THF) (liquids are added through a rubber septum via a syringe). Next, the rubber septum is briefly removed while the flask is under a constant argon stream, and NaOH (40.0 mg, 1.0 mmol, 10 mol %) was added [Note: vigorous evolution of hydrogen occurs upon addition of NaOH]. Once vigorous hydrogen evolution is visibly completed, the rubber septum is replaced and a bubbler is installed by means of a needle through the flask’s septum connected to the bubbler by Tygon tubing, enabling the hydrogen to be safely vented as the reaction progresses. The mixture was stirred at 25 °C for 20 h. Concentration of the reaction mixture and purification of the resulting residue
via Kugelrohr distillation (150 mTorr, 120 °C) gave 2.19 g (93% yield) of 11 as a colorless oil. Note: product is volatile under high vacuum. $^1$H NMR (500 MHz, Benzene-$d_6$) δ 7.77 – 7.71 (m, 2H), 7.20 – 7.17 (m, 3H), 1.22 (s, 6H), 1.16 (s, 6H), 0.43 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 136.58, 134.03, 130.42, 128.21, 81.80, 26.03, -0.35. IR (Neat Film NaCl) 3441, 3071, 2980, 1643, 1464, 1428, 1366, 1260, 1161, 1121, 1026, 793, 736, 699 cm$^{-1}$; HRMS (EI+) calc’d for C$_{13}$H$_{20}$O$_2$Si [M+•]: 236.1233, found 236.1237.

2. Synthesis of 2,2,4,4,6,6-Hexaethyl-1,3,5,2,4,6-trioxatrisilinane 2j.

$\text{H}_2\text{O}$ \[ \xrightarrow{\text{NaOH (10 mol %)}} \] \[ \xrightarrow{\text{Et$_2$SiH$_2$ (1.0 equiv)}} \] $\text{THF, 25 °C}$ \[ \xrightarrow{18 \text{ h}} \] \[ \begin{array}{c} \text{Si} \text{O} \text{Si} \\ + \text{other ring sizes} \end{array} \]

2,2,4,4,6,6-Hexaethyl-1,3,5,2,4,6-trioxatrisilinane 2j: To a solution of diethylsilane (0.5 mL, 3.85 mmol, 1.0 equiv) in THF (2.0 mL) was added NaOH (15.4 mg, 0.39 mmol, 10 mol %) and H$_2$O (1.0 mL, 55 mmol, 15 equiv). The vial was then sealed and the mixture was stirred at 25 °C for 24 h. The reaction mixture was diluted with 2 mL Et$_2$O and analyzed by GC-MS, in which 2,2,4,4,6,6-hexaethyl-1,3,5,2,4,6-trioxatrisilinane was the major product observed (mass = 306.2). Several other larger ring sizes were observed in smaller amounts.

1-phenyl-1H-benzo[d]imidazole 13: To a mixture of the PhSiMe(pin) reagent 11 (freshly prepared, 71.0 mg, 0.3 mmol, 2.0 equiv), benzimidazole 12 (17.6 mg, 0.15 mmol, 1.0 equiv) and Cu(OAc)\(_2\) (30.0 mg, 0.165 mmol, 1.1 equiv) in DMF (1.5 mL) is added TBAF (0.3 mL, 1.0M solution in THF) dropwise at 25 °C. The mixture is allowed to stir for 36 h at 25°C, after which NaHCO\(_3\) saturated solution (2.0 mL) is carefully added and then the mixture is partitioned between EtOAc and hexanes (5.0 mL each). The aqueous layer is extracted with a 1:1 EtOAc:hexanes mixture (2x15 mL) then the combined organic layers are washed with H\(_2\)O (2x10 mL) and brine (1x10 mL), then dried over MgSO\(_4\). The mixture is then filtered, the solvent is removed, and the resulting residue is purified via silica gel flash chromatography (gradient 20% EtOAc in hexanes to 70% EtOAC in hexanes) to yield 13 as a colorless solid (21.2 mg, 71% yield). \(R_f = 0.25\) (20% EtOAc in hexanes). This compound has been previously characterized.\(^{20}\)

Part III. $^1$H NMR and $^{13}$C NMR spectra.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2b.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2c.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2d.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2e.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2f.
$^1$H NMR (500 MHz, THF-$d_8$) of compound 2g.
$^{13}$C NMR (126 MHz, THF-$d_8$) of compound 2g.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2h.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2i.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4a.
$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4a.
$^{1}H$ NMR (500 MHz, CDCl$_3$) of compound 4b.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4c.
$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4c.
**Supplementary Information for Toutov, Betz, Haibach, Romine, and Grubbs**

**SI-42**

$^1$H NMR (500 MHz, CDCl$_3$) of compound 4d.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4d-SI.
$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4d-SI.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4e.
$^1$H NMR (500 MHz, CDCl₃) of compound 4f.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4g.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4h.
$^1$H NMR (500 MHz, THF-$d_8$) of compound 4i.
$^{13}$C NMR (126 MHz, THF-$d_8$) of compound 4i.
$^1$H NMR (500 MHz, Benzene-$d_6$) of compound 4j.
$^{13}$C NMR (126 MHz, Benzene-$d_6$) of compound 4j.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4k.
$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4k.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4l.

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$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4l.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4m.
$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4m.
$^1$H NMR (500 MHz, Benzene-$d_6$) of compound 4n.
$^{13}$C NMR (126 MHz, Benzene-d$_6$) of compound 4n.
$^1$H NMR (500 MHz, Benzene-$d_6$) of compound 40.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4p.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4q.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4r.
$\text{F}_3\text{C} - \text{O} - \text{SiMe}_2\text{Ph}$

$\begin{align*}
\begin{array}{cccc}
137.18 & 133.54 & 130.00 & 128.11 \\
56.39 & 56.52 & 56.30 & 37.29 \\
36.85 & 36.63 & 36.96 & \\
\end{array}
\end{align*}$

$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4r.
$^{19}$F NMR (282 MHz, CDCl$_3$) of compound 4r.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4s.
\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) of compound 4s.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4t.
$^1$H C NMR (126 MHz, CDCl₃) of compound 4t.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4u.
$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4u.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 6.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 9.
$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 9.
\[^1\text{H}\text{ NMR (500 MHz, Benzene-}d_6\text{) of compound 11.}\]
$^{13}$C NMR (126 MHz, Benzene-$d_6$) of compound 11.

[Chemical structure image]