

**SUPPLEMENTARY MATERIAL**

**The Design, Synthesis and Validation of Recoverable and Readily Reusable Siloxane Transfer Agents for Pd-Catalyzed Cross-Coupling Reactions**

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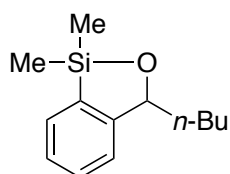
Experimental procedures and spectral data for all new compounds, including copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

**General.** All moisture-sensitive reactions were performed using syringe-septum cap techniques under an inert atmosphere of N<sub>2</sub>. All glassware was flame dried or dried in an oven (140 °C) for at least 4 h prior to use. Reactions were magnetically stirred unless otherwise stated. Tetrahydrofuran (THF), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and diethyl ether (Et<sub>2</sub>O) were dried by passage through alumina in a Pure Solve™ PS-400 solvent purification system. Unless otherwise stated, solvents and reagents were used as received. Analytical thin layer chromatography was performed on pre-coated silica gel 60 F-254 plates (particle size 40-55 micron, 230-400 mesh) and visualized by a uv lamp or by staining with PMA (2 g phosphomolybdic acid dissolved in 20 mL absolute ethanol), KMnO<sub>4</sub> (1.5 g of KMnO<sub>4</sub>, 10 g of K<sub>2</sub>CO<sub>3</sub> and 2.5 mL of 5% aq. NaOH in 150 mL H<sub>2</sub>O), or CAM (4.8 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O and 0.2 g of Ce(SO<sub>4</sub>)<sub>2</sub> in 100 mL of a 3.5 N H<sub>2</sub>SO<sub>4</sub> solution) stain. Column chromatography was performed using silica gel (40-63 micron particle size, 230-300 mesh) and compressed air pressure with commercial grade solvents. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. NMR spectra were recorded at 500 MHz/125 MHz (<sup>1</sup>H NMR/<sup>13</sup>C NMR) on a 500 MHz spectrometer at 300 K. Chemical shifts are reported in parts per million with the residual solvent peak as an internal standard. <sup>1</sup>H NMR spectra are tabulated as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, qn=quintet, dd=doublet of doublets, ddd= doublet of doublet of doublets, dddd= doublet of doublet of doublet of doublets, dt= doublet of triplets, m=multiplet, b=broad), coupling constant and integration. <sup>13</sup>C NMR spectra are tabulated by observed peak. Melting points were determined using a capillar melting point apparatus and are uncorrected. Infrared spectra were measured on a FT/IR 480 plus spectrometer. High-resolution mass spectra (HRMS) were obtained at the University of Pennsylvania on a Waters GCT Premier spectrometer. Single crystal X-ray structures were determined at the University of Pennsylvania. X-ray intensity data were collected on a Rigaku Mercury CCD or Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at a temperature of 143(1) K.

## Experimental Procedures.

Compounds **1e**,<sup>1</sup> **1f**,<sup>1,2</sup> **16b**<sup>3</sup>, Et<sub>2</sub>SiHCl<sup>4</sup> and the corresponding vinyl iodides of **13a**,<sup>3</sup> **13b**,<sup>5</sup> and **13c**<sup>6</sup> were prepared according to previously reported procedures.

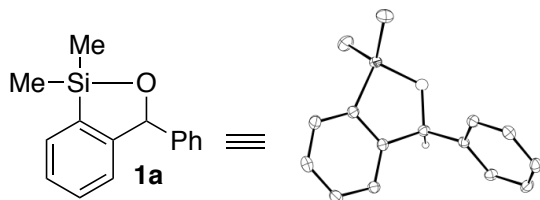
**Preparation of water-washed silica gel for column chromatography (where specified):** Silica gel was suspended in H<sub>2</sub>O and the slurry mixture was then packed into a prepared column. The obtained H<sub>2</sub>O-washed silica gel packed column was then rinsed with 2 column volumes of acetone, 1 column volume of EtOAc and 2 column volumes of hexanes, successively. The obtained column is then ready for use. Note: Water-washed silica gel proved optimal in minimizing the "streakage" of siloxanes **1**, **1a**, **1b**, **1c**, and **1d** leading to improved purification.



**3-Butyl-1,1-dimethyl-1,3-dihydrobenzo[c][1,2]oxasilole (1).** To a cooled solution of benzaldehyde **10** (21.0 g, 198 mmol, 1.00 equiv) in hexanes (733 mL, pre-dried over MgSO<sub>4</sub>) and Et<sub>2</sub>O (587 mL) at 0 °C was added *n*-BuLi (224 mL, 1.94 M in hexanes, 435 mmol, 2.20 equiv) dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 30 minutes. The flask was then fitted with a reflux condenser and the reaction mixture was heated to reflux (75 °C) for 16 h. A dark solution resulted and the reaction mixture was allowed to cool to room temperature. The reflux condenser was removed and the reaction mixture was cooled to -78 °C and Me<sub>2</sub>SiHCl (48.4 mL, 435 mmol, 2.20 equiv) was then added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 8 h. The resulting pale yellow slurry was then quenched with H<sub>2</sub>O (300 mL) and the aqueous phase extracted with Et<sub>2</sub>O (3 × 100 mL). The combined organic layers were washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure.

The resulting crude orange oil was taken up in THF (200 mL) at room temperature and 4 Å molecular sieves (3.00 g) and KO*t*-Bu (1.10 g, 9.90 mmol, 0.05 equiv) were added as a single portion and vigorous evolution of H<sub>2</sub> was observed. The reaction mixture was allowed to stir at room temperature for 5 h, quenched with H<sub>2</sub>O (50 mL) and the aqueous phase extracted with Et<sub>2</sub>O (3 × 100 mL). The combined organic layers were washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure. Flash chromatography on water-washed silica (100 % hexanes then 1% EtOAc in hexanes) followed by Kugelrohr distillation (85-95 °C, 0.05 mmHg) provided **1** (22.7 g, 103 mmol, 52% yield) as a colorless oil. Analytical data matches that which has been previously reported:<sup>7</sup> *R*<sub>f</sub> 0.35 (1% EtOAc in hexanes); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 7.0 Hz, 1H), 7.41 (td, *J* = 7.5, 1.0 Hz, 1H), 7.29 (t, *J* = 7.0 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H),

5.26 (dd,  $J = 7.5, 3.5$  Hz, 1H), 1.93 (m, 1H), 1.62 (m, 1H), 1.50-1.20 (m, 4H), 0.90 (t,  $J = 7.5$  Hz, 3H), 0.41 (s, 3H), 0.38 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  153.5, 135.8, 131.0, 129.7, 127.0, 122.4, 81.9, 38.9, 27.5, 23.0, 14.2, 1.5, 0.8; IR (neat) 3059 (s), 2958 (m), 2927 (m), 2858 (m), 1594 (s), 1443 (s), 1250 (s), 1080 (s), 919 (m), 865 (s), 830 (s), 789 (s), 744 (s)  $\text{cm}^{-1}$ ; HRMS (ES+)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{21}\text{OSi}$   $[\text{M}+\text{H}]^+$  221.1362, found 221.1367.

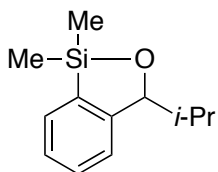


### 1,1-Dimethyl-3-phenyl-1,3-

**dihydrobenzo[*c*][1,2]oxasilole (1a):** Phenylmagnesium bromide (10.4 mL, 3.00 M in  $\text{Et}_2\text{O}$ , 31.3 mmol, 1.20 equiv) was added dropwise to a vigorously stirred solution of 2-bromobenzaldehyde (4.82 g, 26.1 mmol, 1.00 equiv) in  $\text{Et}_2\text{O}$  (75 mL) at  $0^\circ\text{C}$ . The reaction mixture was stirred at room temperature for 12 h, quenched with sat. aq.  $\text{NH}_4\text{Cl}$  (25 mL) and the aqueous phase extracted with  $\text{Et}_2\text{O}$  (2 x 25 mL). The combined organic layers were washed with brine, dried ( $\text{MgSO}_4$ ), and concentrated under reduced pressure. Flash chromatography on silica (1%  $\text{Et}_2\text{O}$  in hexanes then 10%  $\text{Et}_2\text{O}$  in hexanes) provided the desired (2-bromophenyl)(phenyl)methanol (**S1**) (6.44 g, 24.5 mmol, 94% yield) as a white solid. Analytical data matches that which has been previously reported:<sup>8</sup>  $R_f$  0.3 (10%  $\text{EtOAc}$  in hexanes);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61-7.52 (m, 2 H), 7.41 (d,  $J = 6.9$  Hz, 2 H), 7.37-7.31 (m, 3 H), 7.28 (t,  $J = 7.1$  Hz, 1 H), 7.15 (dt,  $J = 1.6, 7.6$  Hz, 1 H), 6.21 (d,  $J = 3.8$  Hz, 1 H), 2.34 (d,  $J = 4.0$  Hz, 1 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.6, 142.3, 133.0, 129.3, 128.6, 127.9, 127.8, 127.2, 126.7, 122.9, 74.9.

The resulting (2-bromophenyl)(phenyl)methanol (**S1**) (4.29 g, 16.3 mmol, 1.00 equiv) was dissolved in THF (50 mL) and *n*-BuLi (14.7 mL, 2.45 M in hexanes, 35.9 mmol, 2.20 equiv) was added dropwise at  $-78^\circ\text{C}$ . The reaction mixture was stirred for 1 h, followed by the addition of  $\text{Me}_2\text{SiHCl}$  (3.90 mL, 35.9 mmol, 2.20 equiv) at  $-78^\circ\text{C}$ . The resulting reaction mixture was allowed to warm to room temperature and stirred for 12 h. The reaction mixture was quenched by addition of *t*-BuOH (20 mL) and stirred for 5 h, followed by the addition of  $\text{H}_2\text{O}$  (20 mL) and stirred for another 2 h. The aqueous phase was then extracted with  $\text{Et}_2\text{O}$  (2 x 25 mL) and the combined organic layers were washed with brine, dried ( $\text{MgSO}_4$ ), and concentrated under reduced pressure. Flash chromatography on water-washed silica gel (100% hexanes then 1%  $\text{Et}_2\text{O}/\text{Hexanes}$ ) provided the desired siloxane **1a** (1.82 g, 26.8 mmol, 46% yield) as a white crystalline solid: **m.p.** 45.5 - 46.5  $^\circ\text{C}$ ;  $R_f$  0.3 (5%  $\text{Et}_2\text{O}$  in hexanes);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63-7.59 (m, 1 H), 7.36-7.26 (m, 7 H), 7.05-7.01 (m, 1 H), 6.17 (s, 1 H), 0.53 (s, 3 H), 0.45 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  152.6, 143.9, 135.3, 130.8, 129.9, 128.7, 127.9, 127.3, 127.3, 123.9, 84.2, 1.4, 0.7; IR ( $\text{CH}_2\text{Cl}_2$ ) 3057 (m), 2964 (m), 2874 (m), 1447 (m), 1265 (s), 1181 (m), 1136 (m), 1042 (s),

1016 (s), 862 (s), 822 (s), 793 (s), 740 (s), 702 (s), 656 (m)  $\text{cm}^{-1}$ ; **HRMS** ( $\text{CI}^+$ )  $m/z$  calculated for  $\text{C}_{15}\text{H}_{17}\text{SiO}$   $[\text{M}+\text{H}]^+$  241.1049, found 241.1034.

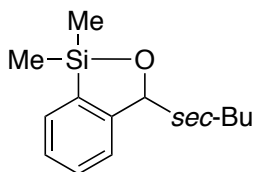


**3-Isopropyl-1,1-dimethyl-1,3-dihydrobenzo[c][1,2]oxasilole (1b):**

Phenylmagnesium bromide (11.7 mL, 3.00 M in  $\text{Et}_2\text{O}$ , 35.1 mmol, 1.20 equiv) was added dropwise to a vigorously stirred solution of isobutyraldehyde (2.11 g, 29.3 mmol, 1.00 equiv) in  $\text{Et}_2\text{O}$  (50 mL) at  $0^\circ\text{C}$ . The reaction mixture was warmed to room temperature and stirred for 12 h, then quenched with sat. aq.  $\text{NH}_4\text{Cl}$  (25 mL). The aqueous phase extracted with  $\text{Et}_2\text{O}$  (2 x 25 mL) and the combined organic layers were washed with brine, dried ( $\text{MgSO}_4$ ) and concentrated under reduced pressure. Flash chromatography on silica, (10%  $\text{Et}_2\text{O}$  in hexanes) provided the desired 2-methyl-1-phenylpropan-1-ol (**S2**) (4.09 g, 27.2 mmol, 93% yield) as a colorless oil. Analytical data matches that which has been previously reported:<sup>9</sup>  $R_f$  0.15 (10%  $\text{Et}_2\text{O}$  in hexanes);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.26 (m, 5 H), 4.37 (dd,  $J = 3.3, 6.8$  Hz, 1 H), 2.02-1.91 (m, 1 H), 1.82 (d,  $J = 3.4$  Hz, 1 H), 1.01 (d,  $J = 6.7$  Hz, 3 H), 0.81 (d,  $J = 6.7$  Hz, 3 H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 128.3, 127.6, 126.7, 80.2, 35.4, 19.2, 18.4.

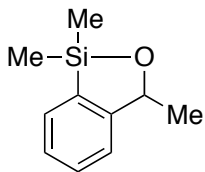
The resulting 2-methyl-1-phenylpropan-1-ol (**S2**) (2.76 g, 18.4 mmol, 1.00 equiv) was dissolved in hexanes (125 ml, pre-dried over  $\text{MgSO}_4$ ) and  $\text{Et}_2\text{O}$  (100 ml) at  $0^\circ\text{C}$  and  $n\text{-BuLi}$  (22.9 ml, 1.77 M in hexanes, 40.5 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 30 minutes. The flask was then fitted with a reflux condenser and the system was heated to reflux ( $75^\circ\text{C}$ ) for 16 h. A dark solution resulted and the reaction mixture was allowed to cool to room temperature. The reflux condenser was removed and the reaction mixture was cooled to  $-78^\circ\text{C}$ .  $\text{Me}_2\text{SiHCl}$  (4.40 ml, 40.5 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 12 h. The slurry was quenched by addition of  $t\text{-BuOH}$  (20 mL) and stirred for 5 h, followed by the addition of  $\text{H}_2\text{O}$  (20 ml) and stirred for another 2 h. The aqueous phase was extracted with  $\text{Et}_2\text{O}$  (2 x 25 mL) and the combined organic layers were washed with brine, dried ( $\text{MgSO}_4$ ), filtered and concentrated under reduced pressure. Flash chromatography on water-washed silica gel (100% hexanes then 1%  $\text{Et}_2\text{O}$ /Hexanes) followed by Kugelrohr distillation ( $75\text{-}80^\circ\text{C}$ , 0.025 mmHg) provided **1b** (1.48 g, 7.17 mmol, 39% yield) as a colorless oil:  $R_f$  0.5 (5%  $\text{Et}_2\text{O}$  in hexanes);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 7.1$  Hz, 1 H), 7.39 (dt,  $J = 1.0, 7.5$  Hz, 1 H), 7.29 (t,  $J = 7.2$  Hz, 1 H), 7.20 (d,  $J = 7.7$  Hz, 1 H), 5.17 (d,  $J = 2.2$  Hz, 1 H), 2.12 (dspt,  $J = 2.5, 6.8$  Hz, 1 H), 1.17 (d,  $J = 6.9$  Hz, 3 H), 0.60 (d,  $J = 6.7$  Hz, 3 H), 0.41 (s, 3 H), 0.36 (s, 3 H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  152.5, 136.4, 130.8, 129.7, 127.0, 122.4, 86.5, 34.6, 20.4, 15.0, 1.0, 0.8; **IR** (neat) 3060 (m), 2963 (s), 2873 (m), 1594 (m), 1469 (m), 1442 (m), 1383 (m), 1365 (m), 1251 (s), 1198 (m), 1137 (m), 1120 (m),

1102 (m), 1067 (s), 1014 (s), 953 (s), 874 (s), 830 (s), 788 (s), 744 (s), 704 (m), 651 (m)  $\text{cm}^{-1}$ ; **HRMS** ( $\text{CI}^+$ )  $m/z$  calculated for  $\text{C}_{11}\text{H}_{15}\text{SiO}$  [ $\text{M-Me}$ ] $^+$  191.0892, found 191.0893.

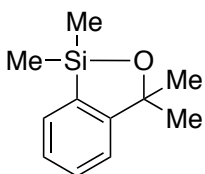


**3-(*sec*-Butyl)-1,1-dimethyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (1c):**

To a cooled solution of benzaldehyde **10** (3.25 g, 30.6 mmol, 1.00 equiv) in hexanes (125 mL, pre-dried over  $\text{MgSO}_4$ ) and  $\text{Et}_2\text{O}$  (100 mL) at 0 °C was added *sec*-BuLi (26.2 mL, 1.4 M in cyclohexane, 36.7 mmol, 1.20 equiv) dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 5 h, at which time *n*-BuLi (20.7 mL, 1.77 M in hexanes, 36.7 mmol, 1.20 equiv) was added dropwise. The flask was then fitted with a reflux condenser and the system was heated to reflux (75 °C) for 16 h. A dark solution resulted and the reaction mixture was allowed to cool to room temperature. The reflux condenser was removed and the reaction mixture was cooled to -78 °C and  $\text{Me}_2\text{SiHCl}$  (7.97 mL, 67.3 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 12 h. The slurry was quenched by addition of *t*-BuOH (20 mL) and stirred for 5 h, followed by the addition of  $\text{H}_2\text{O}$  (20 mL) and stirred for another 2 h. The aqueous phase was extracted with  $\text{Et}_2\text{O}$  (2 x 25 mL) and the combined organic layers were washed with brine, dried ( $\text{MgSO}_4$ ), filtered and concentrated under reduced pressure. Flash chromatography on water-washed silica gel (100% hexanes then 1%  $\text{Et}_2\text{O}$ /Hexanes) followed by Kugelrohr distillation (140-160 °C, 0.01 mmHg) provided **1c**, isolated as a 5:3 ratio of diastereomers by  $^1\text{H}$  NMR spectroscopy (2.02 g, 9.17 mmol, 30% yield) as a colorless oil:  $R_f$  0.55 (5%  $\text{Et}_2\text{O}$  in hexanes); *Major diastereoisomer*:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 7.1$  Hz, 1 H), 7.39 (t,  $J = 7.5$  Hz, 1 H), 7.29 (t,  $J = 7.1$  Hz, 1 H), 7.21 (d,  $J = 7.7$  Hz, 1 H), 5.20 (d,  $J = 2.2$  Hz, 1 H), 1.88-1.79 (m, 1 H), 1.13 (d,  $J = 6.9$  Hz, 3 H), 1.08-1.01 (m, 2 H), 0.79 (t,  $J = 7.4$  Hz, 3 H), 0.40 (s, 3 H), 0.36 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  152.3, 136.6, 130.9, 129.6, 126.9, 122.4, 86.7, 41.8, 22.5, 16.9, 12.5, 1.0, 0.8. *Minor diastereoisomer*:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 7.1$  Hz, 1 H), 7.39 (t,  $J = 7.5$  Hz, 1 H), 7.29 (t,  $J = 7.1$  Hz, 1 H), 7.19 (d,  $J = 7.7$  Hz, 1 H), 5.20 (d,  $J = 1.2$  Hz, 1 H), 1.88-1.79 (m, 1 H), 1.74-1.65 (m, 1 H), 1.53-1.43 (m, 1 H), 1.04 (t,  $J = 7.7$  Hz, 3 H), 0.55 (d,  $J = 6.7$  Hz, 3 H), 0.40 (s, 3 H), 0.36 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  152.7, 136.4, 130.8, 129.7, 126.9, 122.2, 84.62, 41.5, 31.9, 27.5, 12.5, 1.0, 0.7; **IR** (neat) 3060 (m), 2962 (s), 2875 (s), 1594 (m), 1443 (s), 1375 (m), 1323 (m), 1250 (s), 1197 (m), 1137 (m), 1107 (s), 1068 (s), 1040 (s), 1014 (s), 960 (s), 875 (s), 826 (s), 789 (s), 746 (s), 705 (m), 653 (m)  $\text{cm}^{-1}$ ; **HRMS** ( $\text{CI}^+$ )  $m/z$  calculated for  $\text{C}_{13}\text{H}_{19}\text{SiO}$  [ $\text{M-H}$ ] $^+$  221.1362, found 221.1368.



**1,1,3-Trimethyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (1d):** To a cooled solution of benzaldehyde **10** (2.63 g, 24.8 mmol, 1.00 equiv) in hexanes (125 ml, pre-dried over MgSO<sub>4</sub>) and Et<sub>2</sub>O (100 ml) at 0 °C was added MeLi (1.36 M in Et<sub>2</sub>O, 29.7 mmol, 1.20 equiv) dropwise. The resulting solution was allowed to warm to room temperature and stirred for 5 h, at which time *n*-BuLi (12.1 mL, 2.45 M in hexanes, 29.7 mmol, 1.20 equiv) was added dropwise. The flask was then fitted with a reflux condenser and the system was heated to reflux (75 °C) for 16 h. A dark solution resulted and the reaction mixture was allowed to cool to room temperature. The reflux condenser was removed and the reaction mixture was cooled to -78 °C and Me<sub>2</sub>SiHCl (5.20 ml, 54.6 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 12 h. The reaction mixture was quenched by addition of *t*-BuOH (20 mL) and stirred for 5 h, followed by the addition of H<sub>2</sub>O (20 ml) and stirred for another 2 h. The aqueous phase was extracted with Et<sub>2</sub>O (2 x 25 mL) and the combined organic layers were washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure. Flash chromatography on water-washed silica gel (100% hexanes then 1% Et<sub>2</sub>O/Hexanes) followed by Kugelrohr distillation (55 °C, 0.01 mmHg) provided **1d** (1.55 g, 8.69 mmol, 35 % yield) as a colorless oil: *R*<sub>f</sub> 0.45 (5% Et<sub>2</sub>O in hexanes); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 7.1 Hz, 1 H), 7.40 (dt, *J* = 0.8, 7.5 Hz, 1 H), 7.30 (t, *J* = 7.3 Hz, 1 H), 7.22 (d, *J* = 7.7 Hz, 1 H), 5.34 (q, *J* = 6.5 Hz, 1 H), 1.51 (d, *J* = 6.5 Hz, 3 H), 0.41 (s, 3 H), 0.37 (s, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 154.5, 135.2, 131.0, 129.8, 127.0, 122.3, 78.0, 25.4, 1.7, 0.6; IR (neat) 3060 (m), 2968 (s), 2924 (m), 2867 (m), 1595 (m), 1444 (s), 1368 (m), 1318 (s), 1251 (s), 1199 (m), 1137 (m), 1086 (s), 1028 (s), 929 (s), 855 (s), 828 (s), 793 (s), 759 (s), 742 (s), 696 (m), 653 (m) cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) *m/z* calculated for C<sub>9</sub>H<sub>11</sub>SiO [M-Me]<sup>+</sup> 163.0579, found 163.0578.



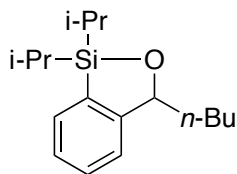
**1,1,3,3-Tetramethyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (1f):**<sup>1</sup> Following a previously reported procedure,<sup>1</sup> methyl 2-bromobenzoate (9.70 g, 45.0 mmol, 1.00 equiv) was dissolved in Et<sub>2</sub>O (100 ml) and cooled to 0 °C. Methylmagnesium bromide (99 mL, 1.0 M in Bu<sub>2</sub>O, 99.0 mmol, 2.20 equiv) was then added via cannula into the reaction mixture. The resulting solution was heated to reflux (40 °C) for 2 h then cooled to room temperature before being quenched with sat. aq. NH<sub>4</sub>Cl (75 mL). The aqueous phase extracted with Et<sub>2</sub>O (2 x 50 mL). The combined organic layers were washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure to afford 2-(2-

bromophenyl)propan-2-ol (**S3**) (8.30 g, ca. 38.8 mmol, 1.00 equiv), which was used without further purification.

To the crude alcohol was added conc. HCl (3 drops) and 3,4-dihydro-2H-pyran (**S3**) (4.07 g, 48.5 mmol, 1.20 equiv) and stirred neat at room temperature for 24 h. The mixture was diluted with Et<sub>2</sub>O (50 mL), and washed with a sat. aq. NaHCO<sub>3</sub> (25 mL). The aqueous layer was extracted with Et<sub>2</sub>O (2 x 50 mL) and the combined organic layers were washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure to afford 2-((2-(2-bromophenyl)propan-2-yl)oxy)tetrahydro-2H-pyran (**S4**) (8.30 g, ca. 38.8 mmol, 1.00 equiv) which was used without further purification.

The crude THP-protected product (**S4**) was dissolved in THF (50 mL) and *n*-BuLi (23.3 mL, 2.00 M in hexanes, 46.6 mmol, 1.20 equiv) was added dropwise at -78 °C. The reaction mixture was stirred for 1 h, followed by the addition of Me<sub>2</sub>SiHCl (6.30 mL, 58.2 mmol, 1.50 equiv) at -78 °C. The resulting reaction mixture was allowed to warm to room temperature and stirred for 12 h. The reaction mixture was quenched by addition of H<sub>2</sub>O (50 ml). The aqueous phase was then extracted with Et<sub>2</sub>O (2 x 30 mL) and the combined organic layers were washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure to afford dimethyl(2-(2-((tetrahydro-2H-pyran-2-yl)oxy)propan-2-yl)phenyl)silane (**S5**) (8.30 g, ca. 38.8 mmol, 1.00 equiv) which was used without further purification.

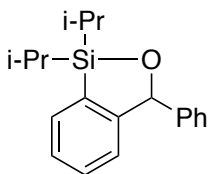
To this crude material (**S5**) was added MeOH (50 mL) and *p*-toluenesulfonic acid monohydrate (370 mg, 1.94 mmol, 0.05 equiv), and the mixture was stirred at room temperature for 12 h before concentration under reduced pressure. The residue was diluted with Et<sub>2</sub>O (25 mL), and washed with a sat. aq. NaHCO<sub>3</sub> (25 mL). The aqueous layer was extracted with Et<sub>2</sub>O (2 x 25 mL), and the combined organic layers were washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure. Kugelrohr distillation (60 °C, 0.01 mmHg) provided **1f** (3.27 g, 17.0 mmol, 38% yield from methyl 2-bromobenzoate) as a colorless oil. Analytical data matches that which has been previously reported:<sup>2</sup> **R<sub>f</sub>** 0.3 (1% Et<sub>2</sub>O in hexanes); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.52 (dt, *J* = 7.1, 0.9 Hz, 1 H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1 H), 7.30 (dt, *J* = 7.2, 0.9 Hz, 1 H), 7.22 (d, *J* = 7.7 Hz, 1 H), 1.55 (s, 6 H), 0.39 (s, 6 H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 157.6, 134.4, 130.6, 129.7, 126.6, 122.1, 83.5, 32.1, 1.37.



**3-Butyl-1,1-diisopropyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (2c):** To a cooled solution of benzaldehyde **10** (3.08 g, 29.0 mmol, 1.00 equiv) in hexanes (125 ml, pre-dried over MgSO<sub>4</sub>) and Et<sub>2</sub>O (100 ml) at 0 °C was added *n*-BuLi (27.8 mL, 2.3 M in



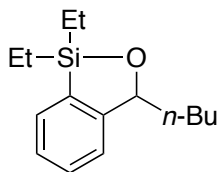
hexanes, 63.9 mmol, 2.20 equiv) dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 30 minutes. The flask was then fitted with a reflux condenser and the system was heated to reflux (75 °C) for 16 h. A dark solution resulted and was allowed to cool to room temperature, the reflux condenser was removed and the reaction mixture was cooled to -78 °C and *i*-Pr<sub>2</sub>SiHCl (10.9 ml, 63.8 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 12 h. The reaction mixture was quenched by addition of 3M HCl in MeOH (40 mL) at 0 °C and stirred for 12 h at room temperature. Water (100 mL) was added and stirred for another 2 h and the aqueous phase extracted with Et<sub>2</sub>O (2 x 50 mL). The combined organic layers were washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure. Flash chromatography on silica (1% Et<sub>2</sub>O/Hexanes) provided **2c** (5.94 g, 21.5 mmol, 74% yield) as a colorless oil: *R<sub>f</sub>* 0.70 (5% Et<sub>2</sub>O in hexanes); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.53 (d, *J* = 7.1 Hz, 1 H), 7.38 (t, *J* = 7.5 Hz, 1 H), 7.27 (t, *J* = 7.1 Hz, 1 H), 7.20 (d, *J* = 7.7 Hz, 1 H), 5.18-5.14 (m, 1 H), 1.94-1.86 (m, 1 H), 1.60-1.48 (m, 3 H), 1.45-1.30 (m, 2 H), 1.25-1.16 (m, 2 H), 1.06 (d, *J* = 6.7 Hz, 3 H), 1.05 (d, *J* = 7.1 Hz, 3 H), 1.00 (d, *J* = 7.5 Hz, 3 H), 0.93 (d, *J* = 7.3 Hz, 3 H), 0.92 (t, *J* = 7.3 Hz, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 154.7, 132.4, 132.2, 129.5, 126.7, 122.2, 82.3, 39.1, 28.1, 23.0, 17.6, 17.5, 17.2, 17.1, 14.2, 13.4, 12.9; IR (neat) 3059 (m), 3000 (m), 2941 (s), 2864 (s), 1595 (m), 1464 (s), 1443 (m), 1381 (m), 1261 (m), 1111 (m), 1080 (s), 1054 (m), 1012 (m), 988 (m), 973 (m), 917 (s), 880 (s), 846 (m), 831 (m), 816 (m), 749 (s), 716 (s), 668 (s), 648 (m), 612 (m) cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) *m/z* calculated for C<sub>14</sub>H<sub>21</sub>SiO [M-C<sub>3</sub>H<sub>7</sub>]<sup>+</sup> 233.1726, found 233.1726.



**1,1-Diisopropyl-3-phenyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (2d):** To the previously prepared (2-bromophenyl)(phenyl)methanol (**S1**) (5.18 g, 19.7 mmol, 1.00 equiv) dissolved in THF (50 mL) was added *n*-BuLi (19.0 mL, 2.28 M in hexanes, 43.3 mmol 2.20 equiv) dropwise at -78 °C. The reaction mixture was stirred for 1 h, followed by the addition of *i*-Pr<sub>2</sub>SiHCl (7.39 mL, 43.3 mmol, 2.20 equiv) at -78 °C. The resulting reaction mixture was allowed to warm to room temperature and stirred for 12 h. The slurry was quenched by addition of 3M HCl in MeOH (40 mL) at 0 °C and stirred for 4 h at room temperature. Water (100 mL) was added and stirred for another 2 h and the aqueous phase extracted with Et<sub>2</sub>O (2 x 50 mL). The combined organic layers were washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure. Flash chromatography on silica (1% Et<sub>2</sub>O/Hexanes) provided **2d** (4.12 g, 13.9 mmol, 71% yield) as a colorless oil: *R<sub>f</sub>* 0.45 (5% Et<sub>2</sub>O in hexanes); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.63-7.59 (m, 1 H), 7.37-7.27 (m, 7 H), 6.99 (d, *J* = 6.9 Hz, 1 H), 6.12 (s, 1 H), 1.39-1.24 (m, 2 H), 1.16 (d, *J* = 7.5 Hz, 3 H), 1.13 (d, *J* = 7.5 Hz, 3 H), 1.06 (d, *J* = 5.7 Hz, 3 H), 1.04 (d, *J* = 5.7 Hz, 3 H); <sup>13</sup>C NMR

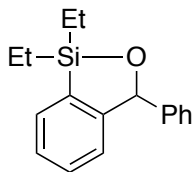
(125 MHz, CDCl<sub>3</sub>)  $\delta$  153.4, 143.8, 132.7, 131.9, 129.8, 128.6, 128.0, 127.8, 127.0, 123.9, 84.6, 17.7, 17.2, 13.6, 13.3; **IR** (neat) 3061 (m), 3031 (m), 3000 (m), 2942 (s), 2891 (m), 2864 (s), 1592 (m), 1494 (m), 1463 (s), 1442 (s), 1383 (m), 1263 (m), 1182 (m), 1133 (m), 1077 (m), 1065 (s), 1038 (s), 1014 (s), 988 (s), 919 (m), 881 (m), 815 (s), 747 (s), 732 (s), 713 (s), 698 (s), 669 (s), 633 (m) cm<sup>-1</sup>; **HRMS** (CI<sup>+</sup>) *m/z* calculated for C<sub>16</sub>H<sub>17</sub>SiO [M-C<sub>3</sub>H<sub>7</sub>]<sup>+</sup> 253.1049, found 253.1056.

**Preparation of Et<sub>2</sub>SiHCl from commercially available Et<sub>2</sub>SiH<sub>2</sub>:**<sup>4</sup> Anhydrous CuCl<sub>2</sub> (96.5 g, 714 mmol, 2.10 equiv) was dried under vacuum at 200 °C in a 2000 two-necked RBF for 12 hours with stirring. Upon cooling to room temperature, CuI (3.24 g, 17.0 mmol, 0.05 equiv), Et<sub>2</sub>O (680 mL ~ 0.5 M) and Et<sub>2</sub>SiH<sub>2</sub> (30.0 g, 340 mmol, 1.00 equiv) were successively added and the resulting slurry was stirred at room temperature for 43 hours. After 4 hours, it was noted that reaction went from an orange brown to light grey in color with black precipitate. After 43 hours, the reaction mixture was filtered under N<sub>2</sub> atmosphere and the flask rinsed with Et<sub>2</sub>O (2 x 50 mL). The Et<sub>2</sub>O was distilled (35 °C) and the reaction mixture transferred to a 100 mL flame-dried RBF via syringe, carefully leaving behind any remaining Cu salts. Kugelrohr distillation (95-100 °C) of this crude reaction mixture under N<sub>2</sub> provided Et<sub>2</sub>SiHCl (32.2 g, 263 mmol, 77% yield) whose analytical data matches that which has been previously reported.<sup>4</sup>

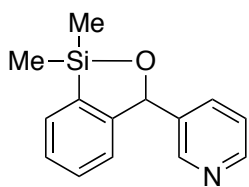


**3-Butyl-1,1-diethyl-1,3-dihydrobenzo[c][1,2]oxasilole (2a):** To a cooled solution of benzaldehyde **10** (10.0 g, 94.2 mmol, 1.00 equiv) in hexanes (500 mL, pre-dried over MgSO<sub>4</sub>) and Et<sub>2</sub>O (400 mL) at 0 °C was added *n*-BuLi (86.4 mL, 2.40 M in hexanes, 2.20 equiv) dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 30 minutes. The flask was then fitted with a reflux condenser and the system was heated to reflux (75 °C) for 16 h. A dark solution resulted and the reaction mixture was allowed to cool to room temperature. The reflux condenser was removed and the reaction mixture was cooled to -78 °C and Et<sub>2</sub>SiHCl (28.9 mL, 207 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 8 h. The resulting pale yellow slurry was then quenched with H<sub>2</sub>O (300 mL) with vigorous evolution of H<sub>2</sub> gas observed. The reaction mixture was allowed to stir for 5 h and the aqueous layer extracted with Et<sub>2</sub>O (3 x 100 mL). The combined organic layers were washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure. Flash chromatography on silica (100 % hexanes to 1% EtOAc in hexanes) provided **2a** (6.2 g, 25.0 mmol, 53% yield) as a colorless oil: *R<sub>f</sub>* 0.45 (1% EtOAc in hexanes); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 (d, *J* = 7.1 Hz, 1H), 7.39 (td, *J* = 7.5, 1.0 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 5.22 (dd, *J* = 8.0, 3.3 Hz, 1H), 1.92 (m, 1H), 1.59 (m, 1H), 1.52-1.30 (m, 4H), 0.99 (t, *J* = 7.7 Hz, 3H), 0.94-

0.88 (m, 6H), 0.88-0.78 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  154.2, 133.7, 131.6, 129.6, 126.8, 122.3, 82.12, 39.1, 27.8, 22.9, 14.2, 7.38, 7.16, 6.88, 6.60; IR (neat) 3058 (m), 2956 (s), 2932 (m), 2874 (m), 1459 (s), 1080 (s), 1013 (m), 916 (s), 741 (s)  $\text{cm}^{-1}$ ; HRMS ( $\text{Cl}^+$ )  $m/z$  calculated for  $\text{C}_{15}\text{H}_{24}\text{OSi}$   $[\text{M}]^+$  248.1596, found 248.1593.



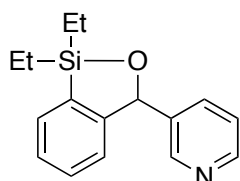
**1,1-Diethyl-3-phenyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (2b):** To the previously prepared (2-bromophenyl)(phenyl)methanol (**S1**) (4.16 g, 15.8 mmol, 1.00 equiv) dissolved in THF (120 mL) was added *n*-BuLi (14.6 mL, 2.39 M in hexanes, 34.8 mmol, 2.20 equiv) dropwise at  $-78^\circ\text{C}$ . The reaction mixture was stirred for 1 h, followed by the addition of  $\text{Et}_2\text{SiHCl}$  (4.84 mL, 34.8 mmol, 2.20 equiv) at  $-78^\circ\text{C}$ . The resulting pale yellow slurry was then quenched with  $\text{H}_2\text{O}$  (300 mL) with vigorous evolution of  $\text{H}_2$  gas observed. The reaction mixture was allowed to stir for 5 h and the aqueous phase was extracted with  $\text{Et}_2\text{O}$  (2 x 50 mL), the combined organic layers were washed with brine, dried ( $\text{MgSO}_4$ ), filtered and concentrated under reduced pressure. Flash chromatography on silica (100% hexanes to 5%  $\text{Et}_2\text{O}$  in hexanes) provided **2b** (1.74 g, 6.48 mmol, 41% yield) as a colorless oil:  $R_f$  0.45 (5%  $\text{Et}_2\text{O}$  in hexanes);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63-7.60 (m, 1 H), 7.36-7.27 (m, 7 H), 7.02 (d,  $J = 7.1$  Hz, 1 H), 6.16 (s, 1 H), 1.08 (t,  $J = 7.9$  Hz, 3 H), 1.02-0.95 (m, 5 H), 0.95-0.82 (m, 2 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  153.2, 143.9, 133.6, 131.4, 129.9, 128.6, 128.0, 127.5, 127.1, 123.9, 84.4, 7.4, 7.1, 7.0, 6.7; IR (neat) 3059 (m), 2999 (m), 2956 (s), 2878 (s), 1595 (m), 1486 (m), 1451 (s), 1412 (m), 1343 (w), 1265 (m), 1236 (m), 1182 (m), 1133 (m), 1012 (bs), 964 (m), 926 (m), 871 (m), 817 (s), 739 (bs), 661 (m), 629 (m)  $\text{cm}^{-1}$ ; HRMS ( $\text{Cl}^+$ )  $m/z$  calculated for  $\text{C}_{17}\text{H}_{21}\text{SiO}$   $[\text{M}+\text{H}]^+$  269.1362, found 269.1366.



**3-(1,1-Dimethyl-1,3-dihydrobenzo[*c*][1,2]oxasilol-3-yl)pyridine (3a):** To a cooled solution of  $\text{Et}_2\text{O}$  (420 mL) containing *n*-BuLi (48.7 mL, 2.00 M in hexanes, 1.30 equiv) at  $-78^\circ\text{C}$  was added 3-bromopyridine (20.0 g, 127 mmol, 1.20 equiv) dropwise. The resulting yellow slurry was allowed to stir at  $-78^\circ\text{C}$  for 30 min. 2-Bromobenzaldehyde (19.5 g, 106 mmol, 1.00 equiv) was added dropwise and the reaction mixture was allowed to stir for 5 h at  $-78^\circ\text{C}$ . The reaction was then warmed to  $0^\circ\text{C}$  and quenched with 3M aq. HCl (100 mL). The organic layer was washed with another portion of 3M aq. HCl (50 mL). The acidic aqueous layers were collected and neutralized to pH 8-9 with 1M aq. NaOH (350 mL), producing a white turbid mixture that was extracted with  $\text{Et}_2\text{O}$  (3 x 150 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ), filtered and

concentrated under reduced pressure. Flash chromatography on silica (0.5% to 1% to 5% MeOH in CH<sub>2</sub>Cl<sub>2</sub>) provided (2-bromophenyl)(pyridin-3-yl)methanol (**S6**) (23.6 g, 89.4 mmol, 85% yield) as an off-white crystalline solid: Analytical data matches that which has been previously reported:<sup>10</sup> **R<sub>f</sub>** 0.35 (5% MeOH in CH<sub>2</sub>Cl<sub>2</sub>); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.57 (d, *J* = 1.8 Hz, 1H), 8.41 (dd, *J* = 4.7, 1.1 Hz, 1H), 7.69 (td, *J* = 7.6, 1.6 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.53 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.23 (dd, *J* = 7.8, 4.8 Hz, 1H), 7.16 (td, *J* = 7.5, 1.5 Hz, 1H), 6.21 (s, 1H), 3.93 (s, 1H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 148.9, 148.7, 142.1, 138.2, 134.9, 133.1, 129.6, 128.5, 128.1, 123.6, 122.7, 72.7.

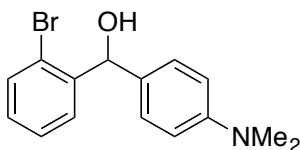
To a cooled solution of (2-bromophenyl)(pyridin-3-yl)methanol (**S6**) (7.00 g, 26.5 mmol, 1.00 equiv) in a mixture (1:1) of THF (100 mL) and Et<sub>2</sub>O (100 mL) at -78 °C was added *n*-BuLi (29.2 mL, 2.00 M in hexanes, 2.20 equiv) dropwise. The resulting dark yellow slurry was allowed to stir at -78 °C for 30 min and Me<sub>2</sub>SiHCl (6.50 mL, 58.3 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 12 h. The resulting orange slurry was then quenched with H<sub>2</sub>O (100 mL) with vigorous evolution of H<sub>2</sub> gas observed. The reaction mixture was allowed to stir for 5 h and extracted with Et<sub>2</sub>O (3 × 50 mL). The combined organic layers were collected and washed with 1M aq. HCl (3 × 50 mL). The acidic aqueous layers were collected and neutralized to pH 8-9 with 1M aq. NaOH (150 mL) producing a white turbid mixture that was extracted with Et<sub>2</sub>O (3 × 100 mL). The combined organic layers were dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure. Flash chromatography on silica (0.5% to 1% to 5% MeOH in CH<sub>2</sub>Cl<sub>2</sub>) followed by Kugelrohr distillation (135 - 150 °C, 0.01 mmHg) provided **3a** (3.14 g, 13.0 mmol, 49% yield) as an off-white amorphous solid: **R<sub>f</sub>** 0.2 (5% MeOH in CH<sub>2</sub>Cl<sub>2</sub>); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.61 (d, *J* = 1.7 Hz, 1H), 8.53 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.63 (m, 1H), 7.53 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.33 (m, 2H), 7.25 (m, 1H), 7.00 (m, 1H), 6.20 (s, 1H), 0.53 (s, 3H), 0.46 (s, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 151.4, 149.3, 148.8, 139.3, 135.2, 134.7, 131.0, 130.1, 127.6, 123.6, 123.5, 81.7, 1.23, 0.56; **IR** (neat) 3057 (m), 2959 (s), 1662 (m), 1579 (m), 1475 (s), 1427 (s), 1252 (s), 1181 (s), 1136 (s), 1051 (m), 860 (m), 822 (s), 791 (s), 750 (s), 713 (s) cm<sup>-1</sup>; **HRMS** (ES<sup>+</sup>) *m/z* calculated for C<sub>14</sub>H<sub>16</sub>NOSi [M+H]<sup>+</sup> 242.1001, found 242.0993.



**3-(1,1-Diethyl-1,3-dihydrobenzo[c][1,2]oxasilol-3-yl)pyridine (3b):**

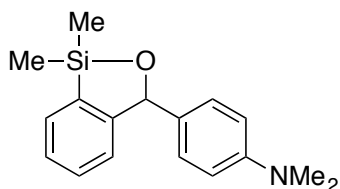
To a cooled solution of (2-bromophenyl)(pyridin-3-yl)methanol (**S6**) (7.00 g, 26.5 mmol, 1.00 equiv) in a mixture (1 : 1) of dry THF (100 mL) and dry Et<sub>2</sub>O (100 mL) at -78 °C was added *n*-BuLi (26.5 mL, 2.20 M in hexanes, 2.20 equiv) dropwise. The resulting dark yellow slurry was allowed to stir at -78 °C for 30 min and Et<sub>2</sub>SiHCl (8.15 mL, 58.3 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to

room temperature and stirred for 12 h. The resulting red-brown solution was then quenched with H<sub>2</sub>O (100 mL) with vigorous evolution of H<sub>2</sub> gas observed. The reaction mixture was allowed to stir for 5 h and extracted with Et<sub>2</sub>O (3 × 50 mL). The combined organic layers were collected and washed with 1M aq. HCl (3 × 50 mL). The acidic aqueous layers were collected and neutralized to pH 8-9 with 1M aq. NaOH (150 mL) producing a white turbid mixture that was extracted with Et<sub>2</sub>O (3 × 100 mL). The combined organic layers were dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure. Flash chromatography on silica (0.5% to 1% to 3% MeOH in CH<sub>2</sub>Cl<sub>2</sub>) provided **3b** (3.6 g, 13.4 mmol, 51% yield) as pale yellow oil: *R<sub>f</sub>* 0.45 (5% MeOH in CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.62 (d, *J* = 1.0 Hz, 1H), 8.53 (dd, *J* = 4.6, 1.2 Hz, 1H), 7.62 (m, 1 H), 7.53 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.33 (m, 2 H), 7.23 (m, 1 H), 6.99 (d, *J* = 6.6 Hz, 1H), 6.19 (s, 1 H), 1.05 (m, 3 H), 1.0-0.88 (m, 7 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 152.0, 149.4, 149.2, 139.3, 134.8, 133.6, 131.5, 130.1, 127.5, 123.7, 123.6, 81.9, 7.25, 7.00, 6.87, 6.51; IR (neat) 3057 (m), 2957 (m), 2876 (s), 2942 (s), 1580 (s), 1425 (m), 1235 (s), 1183 (s), 1134 (s), 1050 (m), 1017 (m), 817 (m), 744 (s) cm<sup>-1</sup>; HRMS (ES<sup>+</sup>) *m/z* calculated for C<sub>16</sub>H<sub>20</sub>NOSi [M+H]<sup>+</sup> 270.1314, found 270.1314.

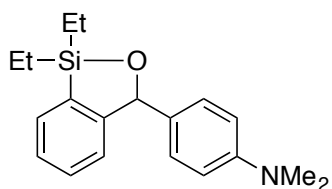


**(2-Bromophenyl)(4-(dimethylamino)phenyl)methanol (S9):** In a two-necked 500 mL round-bottom flask, Mg turnings (10.5 g, 432 mmol, 10.0 equiv) were flame-dried under vacuum. Upon cooling to room temperature, THF (72 mL), 4-bromo-*N,N*-dimethylaniline (12.9 g, 64.9 mmol, 1.50 equiv) as a solution in THF (72 mL) and a crystal of I<sub>2</sub> were added. The flask fitted with a reflux condenser and the solution vigorously stirred. Once the resulting exotherm had subsided, the reaction mixture was heated to reflux (70 °C) for 1 h. This Grignard reagent was then allowed to cool to room temperature and added to a cooled solution of 2-bromobenzaldehyde (8.00 g, 43.2 mmol, 1.00 equiv) in THF (87 mL) at 0°C via cannula over 10 min. The reaction was then allowed to reach room temperature and stirred for 12 h and quenched with sat. aq. NH<sub>4</sub>Cl (100 mL). The aqueous phase was then extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure. Flash chromatography on silica (3% to 10% EtOAc in hexanes) provided of the desired (2-bromophenyl)(4-(dimethylamino)phenyl)methanol (**S9**) (12.6 g, 41.2 mmol, 95% yield) as a blue crystalline solid: *R<sub>f</sub>* 0.2 (10% EtOAc in hexanes); <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 7.71 (dd, *J* = 7.7, 1.5 Hz, 1 H), 7.53 (dd, *J* = 7.9, 1.0 Hz, 1 H), 7.37 (td, *J* = 7.6, 1.0 Hz, 1 H), 7.24 (m, 2 H), 7.14 (td, *J* = 7.7, 1.5 Hz, 1 H), 6.69 (m, 2 H), 6.07 (s, 1 H), 2.94 (s, 6 H), 2.58 (bs, 1 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.3, 143.2, 132.9, 130.3, 128.8, 128.6, 128.4, 128.3, 127.7, 122.8, 112.8, 112.6, 112.3, 74.8, 40.7; IR (neat) 3387 (bs), 2887 (m), 2802 (s), 1613 (s), 1521 (s), 1352 (s), 1162 (s), 1017 (m), 810 (s), 758 (s),

741 (s)  $\text{cm}^{-1}$ ; **HRMS** ( $\text{ES}^+$ )  $m/z$  calculated for  $\text{C}_{15}\text{H}_{17}\text{NOBr}$   $[\text{M}+\text{H}]^+$  306.0494, found 306.0497.



**4-(1,1-Dimethyl-1,3-dihydrobenzo[c][1,2]oxasilol-3-yl)-N,N-dimethylaniline (3c):** (2-Bromophenyl)(4-(dimethylamino)phenyl)methanol (**S9**) (2.33 g, 7.61 mmol, 1.00 equiv) was dissolved in THF (25 mL) and *n*-BuLi (7.6 mL, 2.20 M in hexanes, 16.7 mmol, 2.20 equiv) was added dropwise at  $-78^\circ\text{C}$ . The reaction mixture was stirred for 45 min, followed by the addition of  $\text{Me}_2\text{SiHCl}$  (2.00 mL, 16.7 mmol, 2.20 equiv) at  $-78^\circ\text{C}$ . The resulting reaction mixture was allowed to warm to room temperature and stirred for 12 h. The slurry was quenched with  $\text{H}_2\text{O}$  (50 mL) with vigorous evolution of  $\text{H}_2$  gas observed. The reaction mixture was allowed to stir for 5 h and extracted with EtOAc ( $3 \times 25$  mL). The combined organic layers were collected and washed with 3M aq. HCl ( $3 \times 25$  mL). The acidic aqueous layers were collected and neutralized to pH 8-9 with 1M aq. NaOH producing a white turbid mixture that was extracted with  $\text{Et}_2\text{O}$  ( $3 \times 75$  mL). The combined organic layers were dried ( $\text{MgSO}_4$ ), filtered and concentrated under reduced pressure. Flash chromatography on silica (5%  $\text{Et}_2\text{O}$  in hexanes) provided **3c** (795 mg, 2.81 mmol, 37% yield) as an yellow crystalline solid:  $R_f$  0.1 (25% EtOAc in hexanes);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (dd,  $J = 6.0, 1.8$  Hz, 1 H), 7.33 (m, 2 H), 7.14 (m, 2 H), 7.06 (m, 1 H), 6.72 (m, 2 H), 6.14 (s, 1 H), 2.95 (s, 6 H), 0.52 (s, 3 H), 0.46 (s, 3 H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  153.3, 150.5, 135.5, 132.1, 130.6, 129.8, 128.5, 128.3, 127.1, 124.1, 112.7, 84.2, 40.8, 1.57, 0.66; **IR** (neat) 3419 (bs), 2921 (m), 1615 (s), 1523 (s), 1443 (s), 1348 (s), 1251 (s), 1163 (s), 1134 (s), 861 (s), 822 (s), 789 (s), 743 (s)  $\text{cm}^{-1}$ ; **HRMS** ( $\text{CI}^+$ )  $m/z$  calculated for  $\text{C}_{17}\text{H}_{22}\text{NOSi}$   $[\text{M}+\text{H}]^+$  284.1471, found 284.1459.



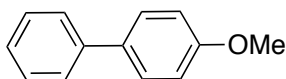
**4-(1,1-Diethyl-1,3-dihydrobenzo[c][1,2]oxasilol-3-yl)-N,N-dimethylaniline (3d):** (2-Bromophenyl)(4-(dimethylamino)phenyl)methanol (**S9**) (7.00 g, 22.9 mmol, 1.00 equiv) dissolved in THF (230 mL), *n*-BuLi (22.9 mL, 2.20 M in hexanes, 50.4 mmol, 2.20 equiv) was added dropwise at  $-78^\circ\text{C}$ . The reaction mixture was stirred for 45 min, followed by the addition of  $\text{Et}_2\text{SiHCl}$  (7.00 mL, 50.4 mmol, 2.20 equiv) at  $-78^\circ\text{C}$ . The resulting reaction mixture was allowed to warm to room temperature and stirred for 12 h. The slurry was quenched with  $\text{H}_2\text{O}$  (100 mL) with vigorous evolution of  $\text{H}_2$  gas observed. The reaction mixture was allowed to stir for 5 h and extracted with EtOAc ( $3 \times 50$  mL). The combined organic layers were collected and washed with 3M aq. HCl ( $3 \times 50$

mL). The acidic aqueous layers were collected and neutralized to pH 8-9 with 1M aq. NaOH (300 mL) producing a white turbid mixture that was extracted with Et<sub>2</sub>O (3 × 100 mL). The combined organic layers were dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure. Flash chromatography on silica (5% EtOAc in hexanes) provided **3d** (3.6 g, 11.6 mmol, 51% yield) as a yellow oil: *R<sub>f</sub>* 0.3 (15% EtOAc in hexanes); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.64 (dd, *J* = 6.0, 1.5 Hz, 1 H), 7.37-7.30 (m, 2 H), 7.17-7.15 (m, 2 H), 7.06 (m, 1 H), 6.74- 6.70 (m, 2 H), 6.15 (s, 1 H), 2.95 (s, 6 H), 1.08 (m, 3 H), 1.04-0.88 (m, 7 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 153.8, 150.4, 133.8, 132.0, 131.2, 129.7, 128.7, 126.8, 124.1, 112.5, 84.3, 40.7, 7.43, 7.11, 6.99, 6.65; IR (neat) 2955 (m), 2875 (m), 2800 (s), 1614 (s), 1523 (s), 1444 (m), 1348 (s), 1230 (s), 1162 (s), 1132 (s), 997 (m), 949 (s), 823 (m), 723 (m) cm<sup>-1</sup>; HRMS (ES<sup>+</sup>) *m/z* calculated for C<sub>19</sub>H<sub>26</sub>NOSi [M+H]<sup>+</sup> 312.1784, found 312.1783.

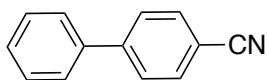
**General Procedure A:** To a cooled solution of siloxane (0.81 mmol, 1.8 equiv) in Et<sub>2</sub>O (1.2 mL) for siloxanes **3a-d** or THF (1.2 mL) for siloxanes **1**, **1a-f**, **2a-d**, at room temperature was added a solution of PhLi in Bu<sub>2</sub>O (0.68 mmol, 1.5 equiv) and allowed to stir for 2 h. After 1.5 h had elapsed following PhLi addition, in a separate flask were combined PdCl<sub>2</sub> (2.50 mg, 0.014 mmol, 0.03 equiv), CuI (8.60 mg, 0.045 mmol, 0.1 equiv) and dpca (6.7 mg, 0.018 mmol, 0.04 equiv) in THF (1 mL) at room temperature and stirred for 30 min. The aryl halide (0.45 mmol, 1.0 equiv) was added to the orange slurry, followed by addition of the siloxane/PhLi reaction mixture by cannula (flask rinsed with 0.5 mL of THF). After 2 h at room temperature, the reaction mixture was diluted with Et<sub>2</sub>O (2 mL) and quenched according to the siloxane used in the reaction; **1**, **1a-f**, **2a-d** quenched with sat. aq. NH<sub>4</sub>Cl (5 mL); **3a-b** quenched with 1M aq. HCl (5 mL); **3c-d** quenched with 3M aq. HCl (5 mL).

For siloxanes **1**, **1a-f**, **2a-d** the aqueous layer was extracted with Et<sub>2</sub>O (3 × 5 mL) and the combined organic layers were dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. Flash chromatography provided the cross-coupled product and the recovered siloxane (where possible as with siloxanes **2a-d**).

For siloxanes **3a-d**, the organic layer was washed with either 1M or 3M aq. HCl (3 × 5 mL) (according to siloxane, see above), and the acidic aqueous layers were collected. The organic layer was then washed with sat. aq. NaHCO<sub>3</sub> (5 mL), dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. Flash chromatography provided the cross-coupled product. The acidic aqueous layer was then basified to pH 8-9 with 1M aq. NaOH, producing a white turbid mixture that was then extracted with Et<sub>2</sub>O (3 × 50 mL). The combined organic layers were dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure to provide the recovered siloxane.



**4-Methoxy-1,1'-biphenyl (S10):** Following General Procedure A, the product was purified by chromatography on SiO<sub>2</sub> (1% EtOAc in hexanes) to afford **S10** (80.0 mg, 0.43 mmol, 96% with siloxane **2a**, 163 mg, 81% recovery; 81.0 mg, 0.44 mmol, 98% with siloxane **2b**, 185 mg, 85% recovery; 81.0 mg, 0.44 mmol, 98% with siloxane **3b**, 210 mg, 96% recovery; 81.0 mg, 0.44 mmol, 98% with siloxane **3d**, 242 mg, 96% recovery) as a colorless solid. Analytical data matches that which has been previously reported for **S10**:<sup>11</sup> *R<sub>f</sub>* 0.5 (1% EtOAc in hexanes); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.57-7.53 (m, 4 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 7.31 (t, *J* = 7.4 Hz, 1 H), 6.99 (d, *J* = 8.7 Hz, 2 H), 3.86 (s, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.3, 141.0, 133.9, 128.9, 128.3, 126.9, 126.8, 114.3, 55.5.



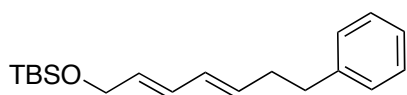
**[1,1'-Biphenyl]-4-carbonitrile (S11):** Following General Procedure A, the product was purified by chromatography on SiO<sub>2</sub> (1% EtOAc in hexanes) to afford **S11** (74.0 mg, 0.41 mmol, 92% with siloxane **2a**, 175 mg, 87% recovery; 73.0 mg, 0.40 mmol, 91% with siloxane **2b**, 193 mg, 89% recovery; 77.0 mg, 0.43 mmol, 96% with siloxane **3b**, 214 mg, 98% recovery; 75.0 mg, 0.42 mmol, 94% with siloxane **3d**, 242 mg, 96% recovery) as a colorless solid. Analytical data matches that which has been previously reported for **S11**:<sup>12</sup> *R<sub>f</sub>* 0.3 (1% EtOAc in hexanes); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.73 (d, *J* = 8.3 Hz, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.59 (d, *J* = 7.4 Hz, 2 H), 7.49 (t, *J* = 7.2 Hz, 2 H), 7.43 (t, *J* = 7.3 Hz, 1 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.8, 139.3, 132.8, 129.3, 128.8, 127.9, 127.4, 119.1, 111.1.

**General Procedure B:** To a solution of alkenyl iodide or aryl iodide (0.68 mmol, 1.50 equiv) in Et<sub>2</sub>O (1 mL) for siloxanes **3a-d** or THF (1 mL) for siloxanes **1**, **1a-f**, **2a-d**, at -78 °C was added *t*-BuLi in pentane (1.35 mmol, 3.00 equiv), and a white or yellow (depending on alkenyl iodide or aryl iodide) slurry developed. The reaction mixture was allowed to stir for 40 min at -78 °C and 20 min at room temperature, at which time a solution of siloxane (0.81 mmol, 1.80 equiv) in THF or Et<sub>2</sub>O, according to siloxane as noted above (0.5 mL + 0.2 mL rinse), was added and allowed to stir at room temperature for 2 h. After 1.5 h had elapsed following siloxane addition, in a separate flask were combined PdCl<sub>2</sub> (2.50 mg, 0.014 mmol, 0.03 equiv), CuI (8.60 mg, 0.045 mmol, 0.1 equiv) and dpca (6.7 mg, 0.018 mmol, 0.04 equiv) in THF (1 mL) at room temperature and stirred for 30 min. The alkenyl halide or aryl iodide (0.45 mmol, 1.00 equiv) was added as a solution in THF (0.3 mL) to the orange slurry, immediately followed by addition of the siloxane reaction mixture by cannula (flask rinsed with 0.5 mL of THF). After 2-12 h at room temperature, the reaction mixture was diluted with Et<sub>2</sub>O (2 mL) and quenched according to the siloxane used in the reaction; **1**, **1a-f**, **2a-d** quenched with sat. aq. NH<sub>4</sub>Cl (5 mL); **3a-b** quenched with 1M aq. HCl (5 mL); **3c-d** quenched with 3M aq. HCl (5 mL).

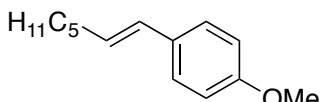


For siloxanes **1**, **1a-f**, **2a-d**, the aqueous layer was extracted with Et<sub>2</sub>O (3 × 5 mL) and the combined organic layers were dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. Flash chromatography provided the cross-coupled product and the recovered siloxane (where possible as with siloxanes **2a-d**).

For siloxanes **3a-d**, the organic layer was washed with either 1M or 3M aq. HCl (3 × 5 mL) (according to siloxane, see above), and the acidic aqueous layers were collected. The organic layer was then washed with sat. aq. NaHCO<sub>3</sub> (5 mL), dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. Flash chromatography provided the cross-coupled product. The acidic aqueous layer was then basified to pH 8-9 with 1M aq. NaOH, producing a white turbid mixture which was then extracted with Et<sub>2</sub>O (3 × 50 mL). The combined organic layers were dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure to provide the recovered siloxane.

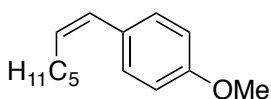


**tert-Butyldimethyl(((2E,4E)-7-phenylhepta-2,4-dien-1-yl)oxy)silane (S13):** Following General Procedure B, the product was purified by chromatography on SiO<sub>2</sub> (1% EtOAc in hexanes) to afford **S13** in >20:1 E/Z ratio as a colorless oil (125 mg, 0.41 mmol, 92% with siloxane **2a**, 171 mg, 85% recovery; 124 mg, 0.41 mmol, 91% with siloxane **2b**, 191 mg, 88% recovery; 131 mg, 0.43 mmol, 96% with siloxane **3b**, 214 mg, 98% recovery; 135 mg, 0.44 mmol, 99% with siloxane **3d**, 239 mg, 95% recovery): *R<sub>f</sub>* 0.3 (1% EtOAc in hexanes); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.31-7.25 (m, 2 H), 7.21-7.17 (m, 3 H), 6.19 (dd, *J* = 10.6, 15.0 Hz, 1 H), 6.08 (dd, *J* = 10.6, 15.0 Hz, 1 H), 5.75-5.62 (m, 2H), 4.21 (d, *J* = 5.5 Hz, 2 H), 2.72 (t, *J* = 7.5 Hz, 2 H), 2.41 (q, *J* = 7.5 Hz, 2 H), 0.93 (s, 9 H), 0.83 (s, 6 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 141.9, 133.4, 130.8, 130.4, 130.3, 128.6, 128.5, 126.0, 63.8, 35.9, 34.6, 26.1, 18.6, -5.01. IR (neat) 3026 (m), 2954 (m), 2930 (s), 2856 (s) 1468 (m), 1254 (s), 1109 (m), 1066 (bs), 988 (s), 837 (s), 776 (s) cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) *m/z* calculated for C<sub>15</sub>H<sub>21</sub>OSi [M-C<sub>4</sub>H<sub>9</sub>]<sup>+</sup> 245.1362, found 245.1368.



**(E)-1-(Hept-1-en-1-yl)-4-methoxybenzene (S14):** Following General Procedure B, the product was purified by chromatography on SiO<sub>2</sub> (1% EtOAc in hexanes) to afford **S14** in >20:1 E/Z ratio as a colorless oil (89.0 mg, 0.44 mmol, 97% with siloxane **2a**, 169 mg, 84% recovery; 88.0 mg, 0.43 mmol, 96% with siloxane **2b**, 195 mg, 90% recovery; 87.0 mg, 0.43 mmol, 95% with siloxane **3b**, 212 mg, 97% recovery; 87.0 mg, 0.42 mmol, 94% with siloxane **3d**, 237 mg, 94% recovery) as a colorless solid. Analytical data matches that which has been previously reported for **S14**:<sup>14</sup> *R<sub>f</sub>* 0.3 (1% EtOAc in hexanes); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.28 (dd, *J* = 2.0, 6.5 Hz, 2 H), 6.84 (dd, *J* = 2.1, 6.6 Hz, 2 H), 6.32 (d, *J* = 15.7 Hz, 1 H), 6.09 (dt, *J* = 7.2, 15.8 Hz, 1 H), 3.80 (s, 3 H), 2.18 (qd, *J* = 1.3, 7.3 Hz, 2 H), 1.46 (qn, *J* = 7.2 Hz, 2 H), 1.40-1.37 (m, 4 H), 0.90

(t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 131.2, 129.6, 129.5, 127.1, 114.2, 55.7, 33.5, 31.4, 29.5, 22.7, 14.1.



**(Z)-1-(Hept-1-en-1-yl)-4-methoxybenzene (S15):** Following General Procedure A, the product was purified by chromatography on  $\text{SiO}_2$  (1% EtOAc in hexanes) to afford **S15** in >20:1 Z/E ratio as a colorless oil (80.0 mg, 0.39 mmol, 87% with siloxane **2a**, 173 mg, 86% recovery; 82.0 mg, 0.40 mmol, 89 % with siloxane **2b**, 189 mg, 87% recovery; 88.0 mg, 0.43 mmol, 96% with siloxane **3b**, 212 mg, 97% recovery, 87.0 mg, 0.42 mmol, 94% with siloxane **3d**, 242 mg, 96% recovery). Analytical data matches that which has been previously reported for **S15**:<sup>14</sup>  $R_f$  0.3 (1% EtOAc in hexanes);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (d,  $J = 8.6$  Hz, 2 H), 6.87 (d,  $J = 8.8$  Hz, 2 H), 6.33 (d,  $J = 11.7$  Hz, 1 H), 5.55 (dt,  $J = 7.3, 11.6$  Hz, 1 H), 3.82 (s, 3 H), 2.29 (qd,  $J = 1.3, 7.3$  Hz, 2 H), 1.45 (qn,  $J = 7.6$  Hz, 2 H), 1.36-1.28 (m, 4 H), 0.90 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 131.7, 130.5, 130.1, 128.4, 113.5, 55.1, 31.4, 29.7, 28.9, 22.6, 14.2.

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