Intramolecular Hydrosilylation and Silicon Assisted Cross-Coupling: An Efficient Rout to Trisubstituted Homoallylic Alcohols

Scott E. Denmark*, Weitao Pan

Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801

SUPPORTING INFORMATION

General Experimental

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Unity 400 (400 MHz, ^{1}H; 100 MHz, ^{13}C), Unity 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C). Spectra are referenced to residual chloroform (δ 7.26 ppm, ^{1}H; δ 77.0 ppm, ^{13}C).

Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Mass spectroscopy was performed by the University of Illinois Mass Spectrometer Center. Electron impact (EI) spectra were performed on a Finnigan-MAT CH-5 spectrometer. Data are reported in the form of m/z (intensity relative to base peak = 100). Infrared spectra (IR) were recorded on a Mattson Galaxy 5020 spectrophotometer. Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%); w (weak, 0-33%). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

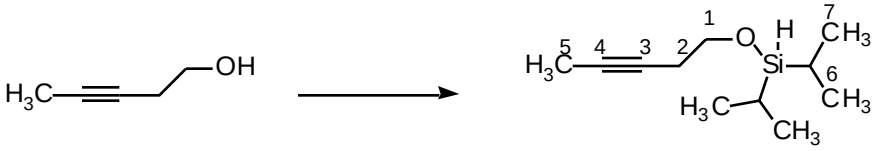
Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV light and/or Iodine. Diethyl ether was freshly distilled; other solvents for chromatography and filtration were technical grade and distilled from the indicated drying agents: pentane ($CaCl_2$). Column chromatography was performed using EM Science 230-400 mesh silica gel.

Analytical capillary gas chromatography (GC) was performed using the following gas chromatography fitted with a flame ionization detector (H_2 carrier gas, 1 mL/min): Hewlett Packard 5890 Series II. The following column was used: HP-5 50-m cross-linked 5%-Phenyl methyl silicone gum phase. The detector temperature was 300 °C. Retention times (t_R) and integrated ratios were obtained from Hewlett Packard 3393A integrators.

Gas chromatography-mass spectroscopy (GC-MS) was performed using the following gas chromatography (Hewlett Packard 5890 Series II.) fitted with HP-5970 series mass selective detector. The following column was used: HP-1 25-m 100%-Dimethyl polysiloxane gum phase.

Kugelrohr distillation were performed on a Büchi GKR-50 Kugelrohr; boiling points (bp) corresponding to uncorrected air-bath temperatures; melting points (mp) were performed in sealed tubes and were determined on a Thomas-Hoover capillary melting point apparatus and were uncorrected. Most commercial reagents were purified by distillation or recrystallization prior to use. All reactions were performed under an inert atmosphere of dry N_2 unless otherwise specified.

Preparation of Diisopropyl-(3-pentynyloxy)silane (1a).



1a

To a cold (0 °C) solution of 3-pentynol (5.880 g, 70.0 mmol, 1.0 equiv), 4-dimethylaminopyridine (DMAP) (840 mg, 7.00 mmol, 0.10 equiv), and triethylamine (TEA) (9.80 ml, 71.0 mmol, 1.01 equiv) in 100 mL of dry hexane was added dropwise chlorodiisopropylsilane (11.0 g, 71.0 mmol, 1.01 equiv) over 20 minutes. The resulting white suspension was allowed to warm to room temperature and was stirred overnight. The reaction mixture was filtered through a short silica pad (10 g) and the solvent was then evaporated *in vacuo* to give a colorless liquid. Fractional distillation of this liquid afforded 11.2 g (81%) of **1a** as a colorless liquid. An analytical sample (0.48 g) was obtained by redistillation of a 0.50 g sample by Kugelrohr distillation.

Data for **1a**:

bp: 62 °C (1.3 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

4.16 (t, J = 1.7 Hz, HSi, 1 H); 3.78 (t, J = 7.0 Hz, H_2C(1), 2 H); 2.39 (m, H_2C(2), 2 H); 1.78 (t, J = 2.6 Hz, H_3C(5), 3 H); 1.05 (m, H_3C(6), HC(7), 14 H).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

77.02 (C(3)), 76.08 (C(4)), 64.83 (C(1)), 23.06 (C(2)), 17.52 (C(7)), 17.43 (C(7)), 12.56 (C(5)), 3.64 (C(6)).

IR: (neat)

2943 (s), 2923 (s), 2866 (s), 2091 (m), 1463 (m), 1384 (m), 1102 (m), 842 (s), 800 (s).

MS: (EI, 70 eV)

155 (M^+- 43, 100), 127 (25), 113 (35), 83 (30).

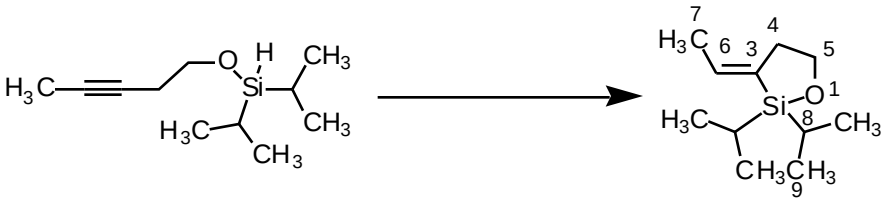
TLC: R_f 0.89 (pentane/ether, 7/3, SiO_2)

GC: t_R **1a** 5.42 min (98.5%), unknown impurities 5.00 min (0.5%), 5.33 min (0.4%), 5.71 min (0.6%) (HP-5, injector 225 °C, column 300 °C, 15 psi).

Analysis: $C_{11}H_{22}OSi$ (198.38)

Calculated	C, 66.60;	H, 11.18;	Si, 14.16%
Found	C, 66.58;	H, 11.14;	Si, 14.28%

Preparation of (*E*)-3-Ethyliden2,2-diisopropyl-1-oxa-2-silacyclopentane (2a).



1a **2a**

To a solution of silane **1a** (10.2 g, 51.5 mmol) in 200 mL of dry dichloromethane at room temperature was added $H_2PtCl_2 \cdot 6H_2O$ (0.90 mL of 0.2 M solution in isopropanol, 0.18 mmol, 0.35% equiv). A vigorous exotherm was noted and reaction mixture was cooled in a tap water bath, and stirring was continued for 70 min. The solvent was then evaporated *in vacuo* to give 10.7 g of an amber liquid. Fractional distillation of the liquid afforded 8.50 g of **2a** (83%) as a colorless liquid.

Data for **2a**:

bp: 57 °C (0.5 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

5.93 (m, HC(6), 1 H); 4.00 (t, J = 6.6 Hz, $H_2C(5)$, 2 H); 2.47 (m, $H_2C(4)$, 2 H); 1.77 (md, J = 6.6 Hz, $H_3C(7)$, 3 H); 1.01 (m, HC(8), $H_3C(9)$, 14 H).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

136.76 (C(3)), 133.46 (C(6)), 67.25 (C(5)), 32.50 (C(4)), 17.32/17.25 (C(9)/C(9')), 16.85(C(8)), 12.64 (C(7)).

IR: (neat)

2941 (s), 2865 (s), 1643 (s), 1463 (s), 1053 (s), 1022 (s)

MS: (EI, 70 eV)

198 (M^+, 10), 173 (15), 155 (100), 127 (60), 105 (26), 77 (45).

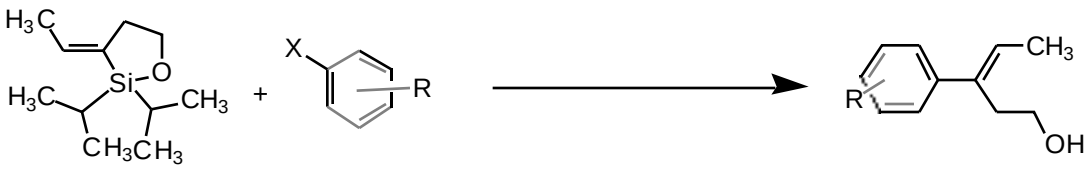
TLC: R_f 0.74 (pentane/ether, 4/1, SiO_2)

GC: t_R **2** 5.56 min (100%) (HP-5, injector 225 °C, column 300 °C, 15 psi).

Analysis: $C_{11}H_{22}OSi$ (198.38)

Calculated	C, 66.60;	H, 11.18;	Si, 14.16%
Found	C, 66.38;	H, 11.29;	Si, 14.28%

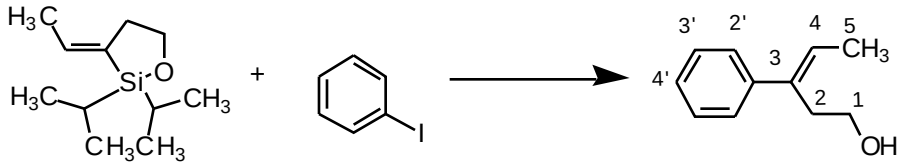
General Procedure for Coupling of Oxasilacyclopentanes



2a **3**

In a two-necked flask fitted with a rubber septum and gas inlet tube, the oxasilacyclopentane, **2a** (1.1 equiv) was dissolved in a solution of tetrabutylammonium fluoride (TBAF) (2.0 equiv), at ambient temperature under nitrogen. The electrophile (1.0 equiv) was added portionwise or in one portion as specified below. The palladium catalyst (5 mol% of Pd) was added in one portion to the mixture following the first portion of electrophile and the mixture was stirred at designated temperature for a designated period of time. The reaction mixture was purified with a specified amount of silica gel as indicated below by column chromatography. The products were further purified by Kugelrohr distillation and/or sublimation.

Reaction of Iodobenzene with Oxasilacyclopentane 2a. (*E*)-3-Phenyl-3-penten-1-ol (3a).



2a **3a**

Following the General Procedure, **2a** (432 mg, 2.18 mmol, 1.10 equiv), was dissolved in a solution of TBAF in THF (4.0 mL, 4.0 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. Iodobenzene (405 mg, 1.98 mmol, 1.0 equiv) was added in three portions over 20-min intervals and $Pd(dba)_2$ (56 mg, 0.098 mmol, 0.050 equiv) was added following the first portion of iodide. The mixture was stirred at rt for a total of 400 min and then was extracted with 50 ml of 1/1 ether-pentane three times. Removal of the solvents *in vacuo* afforded the crude product as a yellow oil. Purification of the oil by column chromatography (SiO_2, 63 g, pentane/ether, 9/1) and Kugelrohr distillation afforded 284 mg (88%) of **3a** as a colorless oil. Biphenyl (4.0 mg, ca 2%) was also isolated.

Data for **3a**:

bp: 82-83 °C air bath (0.2 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.34 (m, HC(2'), HC(3'), 4 H); 7.25 (tt, J = 1.5, 7.1 Hz, HC(4'), 1 H); 5.94 (q, J = 6.8 Hz, HC(4), 1 H); 3.66 (t, J = 6.9 Hz, H_2C(1), 2 H); 2.85 (q, J = 6.9, H_2C(2), 2H); 1.87 (d, J = 7.1 Hz, H_3C(5), 3 H); 1.52 (br s, OH, 1 H).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

142.90, 137.06, 128.60, 127.04, 126.48, 126.00, 61.42 (C(1)), 33.08 (C(2)), 14.59 (C(5)).

IR: ($CHCl_3$)

3620 (m), 3060 (m), 3012 (s), 2965 (s), 2924 (m), 2885 (m), 1599 (w), 1493 (m), 1444 (m), 1388 (w), 1234 (w), 1045 (s), 1030 (s), 860 (w).

MS: (EI, 70 eV)

162 (M^+, 60), 144 (35), 129 (87), 129 (87), 117 (72), 103 (27), 91(100), 78 (35).

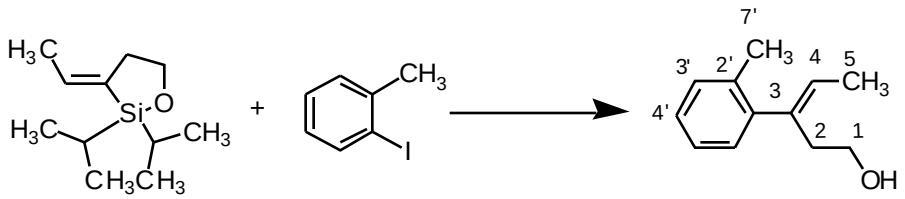
TLC: R_f 0.39 (pentane/ether, 2/3)

GC: t_R **3a** 4.53 min (100%) (HP-5, injector 225 °C, column 270 °C, 15 psi).

Analysis: $C_{11}H_{14}O$ (162.23)

Calculated	C, 81.44;	H, 8.70%
Found	C, 81.27;	H, 8.59%

Reaction of 2-Iodotoluene with Oxasilacyclopentane 2a. (*E*)-3-(2-Methylphenyl)-3-penten-1-ol (3b).



2a **3b**

Following the General Procedure, **2a** (254 mg, 1.28 mmol, 1.1 equiv), was dissolved in a solution of TBAF in THF (2.3 mL, 2.3 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 2-Iodotoluene (252 mg, 1.17 mmol, 1.0 equiv) was added in three portions over 30-min intervals and $Pd(dba)_2$ (34 mg, 0.058 mmol, 0.050 equiv) was added following the first portion of iodide. The mixture was stirred at rt for a total of 470 min. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO_2, 31 g, pentane/ether, 9/1). Removal of the solvent and Kugelrohr distillation of the resulting oil afforded 153 mg (74%) of **3b** as a colorless oil.

Data for **3b**:

bp: 135 °C air bath (0.1 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.19-7.13 (m, HC(4'), HC(5'), HC(6'/3'), 3 H); 7.50 (dd, *J* = 1.3, 6.4 Hz, HC(3'/6'), 1 H); 5.53 (q, *J* = 6.8 Hz, HC(4), 1 H); 3.59 (t, *J* = 6.8 Hz, H_2C (1), 2 H); 2.68 (t, H_2C(2), 2 H); 2.28 (s, H_3C(7'), 3 H); 1.85 (d, *J* =6.8 Hz, H_3C(5), 3 H); 1.40 (br s, OH, 1 H)

^{13}C NMR: (125.6 MHz, $CDCl_3$)

143.90, 137.74, 135.52, 130.37, 129.14, 126.97, 126.73, 125.74, 60.99 (C(1)), 34.86 (C(2)), 20.06 (C(7')), 14.06 (C(5)).

IR: ($CHCl_3$)

3620 (m), 3062 (w), 3011 (s), 2957 (s), 2926 (m), 2884 (m), 1600 (w), 1485 (m), 1454 (m), 1381 (m), 1042 (s), 1011 (m), 862 (m).

MS: (EI, 70 eV)

176 (M^+, 77), 161 (17), 143 (100), 129 (97), 115 (83), 105 (82), 92 (75), 77 (28)

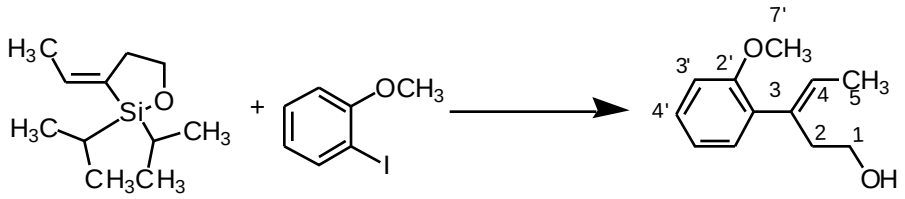
TLC: R_f 0.53 (pentane/ether, 2/3, SiO_2)

GC: t_R **3b** 4.53 min (100%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

Analysis: $C_{12}H_{16}O$ (176.26)

Calculated	C, 81.77;	H, 9.15%
Found	C, 81.81;	H, 9.20%

Reaction of 2-Iodoanisole with Oxasilacyclopentane 2a. (*E*)-3-(2-Methoxyphenyl)-3-penten-1-ol (3c).



2a **3c**

Following the General Procedure, **2a** (230 mg, 1.16 mmol, 1.1 equiv) was dissolved in a solution of TBAF in THF (2.1 mL, 2.1 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 2-Iodoanisole (247 mg, 1.056 mmol, 1.0 equiv) was added in three portions over 60-min intervals and $Pd(dba)_2$ (30 mg, 0.052 mmol, 0.050 equiv) was added following the first portion of iodide. The mixture was stirred at 35 °C for a total of 600 min. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO_2, 30 g, pentane/ether, 10/1). Removal of the solvent and Kugelrohr distillation of the resulting oil afforded 151 mg (74%) of **3c** as a colorless oil.

Data for **3c**:

bp: 150 °C air bath (0.1 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.26 (ddd, J = 1.7, 7.1, 7.5 Hz HC(4'/5'), 1 H); 7.09 (dd, J = 1.7, 7.3 Hz, HC(3'/6'), 1 H); 6.93 (dt, J = 1.2, 7.5 Hz, HC(5'/4'), 1 H), 6.89 (br d, J = 8.1 Hz, HC(6'/3'), 1 H), 5.65 (q, J = 6.8 Hz, HC(4), 1 H); 3.83 (s, H_3C(7'), 3 H), 3.56 (t, J = 6.8 Hz, H_2C(1), 2 H); 2.74 (t, J = 6.8 Hz, H_2C(2), 2 H); 1.84 (d, J =6.8 Hz, H_3C(5), 3 H); 1.80 (br s, OH, 1 H).

^{13}C NMR: (125.6 MHz, CDCl3)

156.79, 135.81, 133.22, 130.60, 128.38, 127.66, 120.96, 110.78, 61.00 (C(1)), 55.66 (C(7')), 34.21 (C(2)), 14.21 (C(5)).

IR: ($CHCl_3$)

3616 (w), 3012 (s), 2961 (m), 2884 (w), 2838 (w), 1597 (w), 1578 (w), 1489 (s), 1464 (s), 1435 (s), 1237 (s), 1047 (s), 1028 (s), 865 (w).

MS: (EI, 70 eV)

192 (M^+, 100), 174 (27), 159 (60), 147 (65), 131 (55), 91 (55), 77 (27).

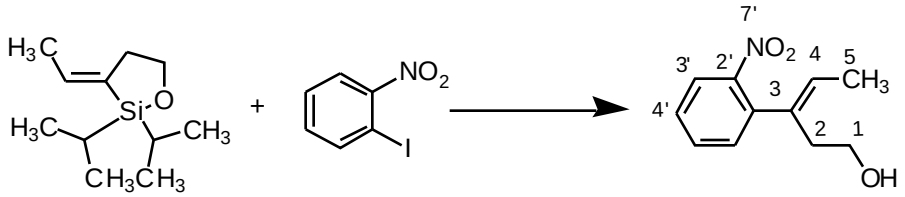
TLC: R_f 0.44 (pentane/ether, 2/3, SiO_2)

GC: t_R **3c** 4.76 min (100%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

Analysis: $C_{12}H_{16}O_2$ (192.26)

Calculated	C, 74.97;	H, 8.39%
Found	C, 74.70;	H, 8.15%

Reaction of 2-Iodonitrobenzene with Oxasilacyclopentane 2a. (*E*)-3-(2-Nitrophenyl)-3-penten-1-ol (3d).



2a **3d**

Following the General Procedure, **2a** (230 mg, 1.16 mmol, 1.1 equiv), was dissolved in a solution of TBAF in THF (2.1 mL, 2.1 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 2-Iodonitrobenzene (263 mg, 1.06 mmol, 1.0 equiv) was added in one portion and $Pd(dba)_2$ (30.0 mg, 0.053 mmol, 0.050 equiv) was then added. The mixture was stirred at 35 °C for a total of 23 h. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO_2, 32 g, pentane/ether, 17/3). Removal of the solvent and Kugelrohr distillation of the resulting oil afforded 124 mg (56%) of **3d** as a yellow oil.

Data for **3d**:

bp: 132 °C air bath (0.05 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.78 (dd, *J* = 1.1, 8.2 Hz, HC(3'), 1 H); 7.54 (dt, *J* = 1.1, 7.5 Hz, HC(5'), 1 H); 7.39 (dt, *J* = 1.3, 8.2 Hz, HC(4'), 1 H); 7.33 (dd, *J* = 1.3, 7.5 Hz, HC(6'), 1 H); 5.59 (q, *J* = 6.9 Hz, HC(4), 1 H); 3.68 (t, *J* = 6.2 Hz, H_2C(1), 2 H); 2.76 (t, *J* = 6.2 Hz , H_2C(2), 2 H); 1.89 (br s, OH, 1 H); 1.82 (d, *J* =6.9 Hz, H_3C(5), 3 H).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

149.76, 138.74, 134.14, 132.45, 130.94, 128.55, 127.84, 124.40 (C(4)), 61.00 (C(1)), 34.78 (C(2)), 14.50 (C(5)).

IR: ($CHCl_3$)

3608 (w), 3011 (w), 2960 (w), 2927 (w), 2883 (w), 1606 (w), 1528 (s), 1359 (m), 1051 (m), 856 (w).

MS: (EI, 70 eV)

207 (M^+, 3), 190 (4), 172 (8), 160 (15), 146 (33), 135 (37), 120 (100), 104 (40), 91 (47), 77 (53).

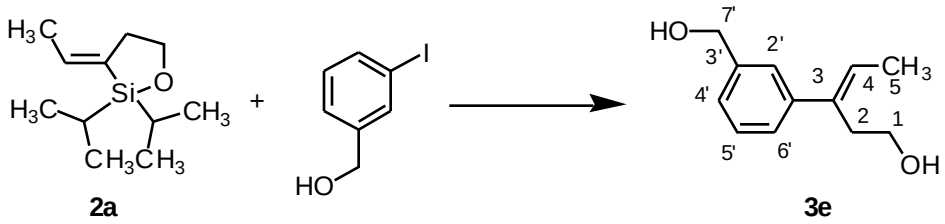
TLC: R_f 0.53 (ether, SiO_2)

GC: t_R **3d** 5.46 min (100%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

Analysis: $C_{11}H_{13}NO_3$ (207.23)

Calculated	C, 63.76;	H, 6.32;	N, 6.76%
Found	C, 63.57;	H, 6.54;	N, 6.73%

Reaction of 3-Iodobenzyl Alcohol with Oxasilacyclopentane 2a. (*E*)-3-(3-Hydroxymethylphenyl)-3-penten-1-ol (3e).



Following the General Procedure, **2a** (248 mg, 1.25 mmol, 1.1 equiv), was dissolved in a solution of TBAF in THF (2.3 mL, 2.3 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 2-Iodobenzyl alcohol (264 mg, 1.13 mmol, 1.0 equiv) was added in three portions over 25-min intervals and $Pd(dba)_2$ (32.4 mg, 0.0565 mmol, 0.050 equiv) was added following the first portion of iodide. The mixture was stirred at rt for a total of 300 min. The crude mixture was then loaded onto 2 g of silica gel and was purified by column

chromatography (SiO_2, 31 g, pentane/ether, 9/7 → 1/1). Removal of the solvent and Kugelrohr distillation of the resulting oil afforded 176 mg (81%) of **3e** as a colorless oil.

Data for **3e**:

bp: 220 °C air bath (0.08 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.36 (s, HC(2'), 1 H); 7.31-7.23 (m, HC(4'), HC(5'), HC(6'), 3 H); 5.94 (q, J = 6.9 Hz, HC(4), 1 H); 4.69 (s, $H_2C(7')$, 2 H); 3.64 (t, J = 6.9 Hz, $H_2C(1)$, 2 H); 2.84 (t, $H_2C(2)$, 2 H); 1.86 (d, J= 7.1 Hz, $H_3C(5)$, 3 H); 1.70 (br s, OH, 1 H).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

143.28, 141.16, 136.92, 128.82, 126.26, 125.80, 125.67, 125.13, 65.58 (C(7')), 61.41 (C(1)), 33.05 (C(2)), 14.58 (C(5)).

IR: ($CHCl_3$)

3611 (s), 3012 (s), 2961 (m), 2937 (m), 2884 (m), 1603 (w), 1401 (s), 1384 (m), 1233 (m), 1016 (s), 908 (m).

MS: (EI, 70 eV)

192 (M^+, 25), 174 (22), 156 (43), 143 (85), 129 (100), 117 (62), 103 (22), 91 (85), 77 (40).

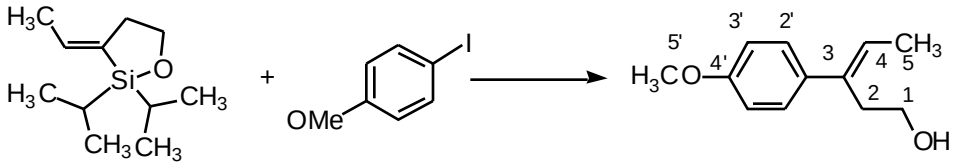
TLC: R_f 0.32 (ether, SiO_2)

GC: t_R **3e** 5.59 min (100%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

Analysis: $C_{12}H_{16}O_2$ (192.26)

Calculated	C, 74.97;	H, 8.39%
Found	C, 74.89;	H, 8.15%

Reaction of 4-Iodoanisole with Oxasilacyclopentane 2a. (*E*)-3-(4-Methoxyphenyl)-3-penten-1-ol (3f).



2a **3f**

Following the General Procedure, **2a** (238 mg, 1.2 mmol, 1.1 equiv), was dissolved in a solution of TBAF in THF (2.2 mL, 2.2 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 4-Iodoanisole (256 mg, 1.09 mmol, 1.0 equiv) was added in three portions over 30-min intervals and $Pd(dba)_2$ (31.4 mg, 0.055 mmol, 0.050 equiv) was added following the first portion of iodide. The mixture was stirred at 35 °C for a total of 390 min. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO_2, 29 g, pentane/ether, 10/1). Removal of the solvent and Kugelrohr distillation of the resulting oil afforded 150 mg (72%) of **3f** as a colorless oil[1].

Data for **3f**:

bp: 150 °C air bath (0.10 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.30 (d, *J* = 8.8 Hz HC(2'), 2 H); 6.87 (d, *J* = 8.8 Hz, HC(3'), 2 H); 5.87 (q, *J* = 6.9 Hz, HC(4), 1 H); 3.82 (s, H_3C(7'), 3 H); 3.66 (m, H_2C(1), 2 H); 2.81 (t, *J* = 6.6 Hz, H_2C(2), 2 H); 1.84 (d, *J*= 6.9 Hz, H_3C(5), 3 H); 1.36 (br s, OH, 1 H).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

158.84, 136.38, 135.35, 127.48, 124.58, 113.95, 61.47 (C(1)), 55.50 (C(5')), 33.07 (C(2)), 14.52 (C(5)).

IR: ($CHCl_3$)

3621 (m), 3010 (s), 2960 (s), 2938 (s), 2839 (m), 1608 (s), 1512 (s), 1464 (s), 1442 (m), 1288 (s), 1246 (s), 1109 (s), 1035 (s), 822 (s).

MS: (EI, 70 eV)

192 (M^+, 100), 147 (99), 135 (45), 121 (55), 91 (42), 77 (47).

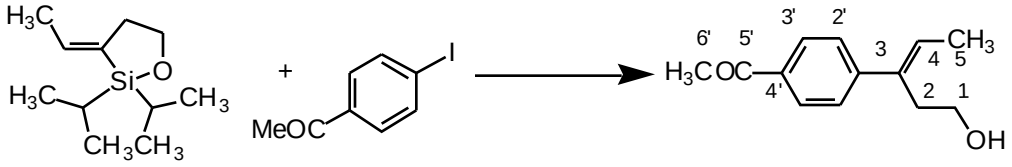
TLC: R_f 0.29 (pentane/ether, 2/3, SiO_2)

GC: t_R **3f** 5.31 min (100%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

Analysis: $C_{12}H_{16}O_2$ (192.26)

Calculated	C, 74.97;	H, 8.39%
Found	C, 74.66;	H, 8.26%

Reaction of 4-Iodoacetophenone with Oxasilacyclopentane 2a. 1-[(4-[1-(2-Hydroxyethyl)-(*E*)-1-propenyl)]phenyl]ethanone (3g).



2a **3g**

Following the General Procedure, **2a** (270 mg, 1.41 mmol, 1.1 equiv), was dissolved in a solution of TBAF in THF (2.6 mL, 2.6 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 4-Iodoacetonphenone (316 mg, 1.28 mmol, 1.0 equiv) was added in three portions over 25-min intervals and $Pd(dba)_2$ (32 mg, 0.056 mmol, 0.050 equiv) was added following the first portion of iodide. The mixture was stirred at rt for a total of 300 min. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO_2, 32.0 g, pentane/ether, 4/1). Removal of the solvent and Kugelrohr distillation of the resulting oil and subsequent sublimation (55 °C /0.1 mm Hg) afforded 185 mg (70%) of **3g** as a white solid.

Data for **3g**:

bp: 150 °C air bath (0.10 mm Hg)

mp: 36-38 °C

^{1}H NMR: (500 MHz, $CDCl_3$)

7.93 (br d, *J* = 8.6 Hz, HC(3'), 2 H); 7.45 (br d, *J* = 8.6 Hz HC(2'), 2 H); 6.06 (q, *J* = 7.1 Hz, HC(4), 1 H); 3.66 (m, H_2C(1), 2 H); 2.86 (t, *J* = 7.1 Hz, H_2C(2), 2 H); 2.60 (s, H_3C(6'), 3 H), 1.90 (d, *J*= 6.9 Hz, H_3C(5), 3 H); 1.36 (br t, *J* = 4.7 Hz, OH, 1 H).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

197.98 (C(5')), 147.72, 136.45, 135.72, 128.81, 128.21, 126.49, 61.86 (C(1)), 32.81 (C(2)), 26.78, (C(6')), 14.76 (C(5)).

IR: ($CHCl_3$)

3628 (w), 3024 (w), 3012 (m), 2963 (w), 1679 (s), 1602 (s), 1407 (w), 1360 (m), 1270 (s), 1045 (m), 956 (w), 820 (m).

MS: (EI, 70 eV)

204 (M^+, 100), 189 (87), 171 (53), 159 (42), 143 (75), 128 (40), 115 (45), 105 (17), 91 (23), 77 (17).

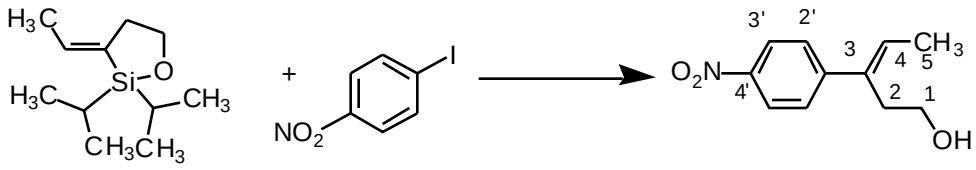
TLC: R_f 0.14 (pentane/ether 2/3, SiO_2)

GC: t_R **3g** 6.30 min (100%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

Analysis: $C_{13}H_{16}O_2$ (204.27)

Calculated	C, 76.44;	H, 7.96%
Found	C, 76.28;	H, 7.79%

Reaction of 4-Iodonitrobenzene with Oxasilacyclopentane 2a. (*E*)-3-(4-Nitrophenyl)-3-penten-1-ol (3h).



2a **3h**

Following the General Procedure, **2a** (311 mg, 1.57 mmol, 1.1 equiv), was dissolved in a solution of TBAF in THF (2.9 mL, 2.9 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 4-Iodonitrobenzene (356 mg, 1.43 mmol, 1.0 equiv) was added in three portions over 30-min intervals and $Pd(dba)_2$ (41 mg, 0.071 mmol, 0.050 equiv) was added following the first portion of iodide. The mixture was stirred at rt for a total of 375 min. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO_2, 33 g, pentane/ether, 25/4). Removal of the solvent and sublimation (60 °C /0.1 mm Hg) of the resulting product afforded 187 mg (63%) of **3h** as a yellow solid.

Data for **3h**:

mp: 55-56 °C

^{1}H NMR: (500 MHz, $CDCl_3$)

8.18 (d, *J* = 8.5 Hz, HC(3'), 2 H); 7.52 (br d, *J* = 8.5 Hz HC(2'), 2 H); 6.10 (q, *J* = 6.9 Hz, HC(4), 1 H); 3.68 (t, *J* = 6.9 Hz , H_2C(1), 2 H); 2.86 (t, *J* = 6.9 Hz, H_2C(2), 2 H); 1.90 (d, *J*= 6.9 Hz, H_3C(5), 3 H); 1.49 (br s, *J* = 4.7 Hz, OH, 1 H).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

149.66, 146.79, 135.91, 129.81, 127.05, 123.96, 61.26 (C(1)), 32.79 (C(2)), 14.88 (C(5)).

IR: ($CHCl_3$)

3614 (w), 3029 (w), 3015 (w), 1597 (m), 1518 (s), 1348 (s), 1229 (w), 1036 (w).

MS: (EI, 70 eV)

207 (M^+, 25), 189 (17), 172 (64), 142 (60), 130 (90), 115 (100), 107 (25), 91 (37), 77 (30).

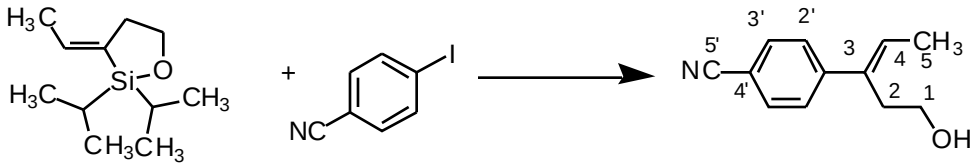
TLC: R_f 0.51 (ether, SiO_2)

GC: t_R **3h** 6.51 min (95.8%); a minor isomer of **3h** 5.92 min (4.2%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

Analysis: $C_{11}H_{13}NO_3$ (207.23)

Calculated	C, 63.76;	H, 6.32;	N, 6.76%
Found	C, 63.82;	H, 6.53;	N, 6.57%

Reaction of 4-Iodobenzonitrile with Oxasilacyclopentane 2a. 4-[1-(2-Hydroxyethyl)-(*E*)-1-propenyl)]benzonitrile (3i).



2a **3i**

Following the General Procedure, **2a** (221 mg, 1.12 mmol, 1.1 equiv), was dissolved in a solution of TBAF in THF (2.0 mL, 2.0 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 4-Iodobenzonitrile (232 mg, 1.01 mmol, 1.0 equiv) was added in one portion and $Pd(dba)_2$ (26 mg, 0.050 mmol, 0.050 equiv) was added. The mixture was stirred at 45 °C for a total of 900 min. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO_2, 33 g, pentane/ether, 3/1 → 3/2). Removal of the solvent and Kugelrohr distillation of the resulting product afforded 135 mg (70%) of

3i as a colorless oil. (1,1'-Biphenyl)-4,4'-dicarbonitrile, the homocoupling product of 4-iodobenzonitrile, was also isolated (6.0 mg, 3%).

Data for **3i**:

bp: 170 °C (0.1 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.61 (d, *J* = 8.1 Hz, HC(3'), 2 H); 7.46 (br d, *J* = 8.1 Hz HC(2'), 2 H); 6.04 (q, *J* = 6.8 Hz, HC(4), 1 H); 3.66 (t, *J* = 6.8 Hz , H_2C(1), 2 H); 2.84 (t, *J* = 6.8 Hz, H_2C(2), 2 H); 1.90 (d, *J*= 6.8 Hz, H_3C(5), 3 H); 1.47 (br s, *J* = 4.7 Hz, OH, 1 H).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

147.60, 136.08, 132.45, 129.10, 127.04, 119.25, 110.46 (-CN), 61.26 (C(1)), 32.70 (C(2)), 14.81 (C(5)).

IR: ($CHCl_3$)

3623 (w), 3024 (m), 3013 (s), 2962 (m), 2923 (w), 2229 (s), 1605 (m), 1503 (m), 1407 (w), 1231 (m), 1180 (w), 1042 (s), 853 (m), 822 (m).

MS: (EI, 70 eV)

187 (M^+, 55), 168 (72), 154 (100), 142 (57), 129 (37), 116 (58), 104 (11), 89 (17).

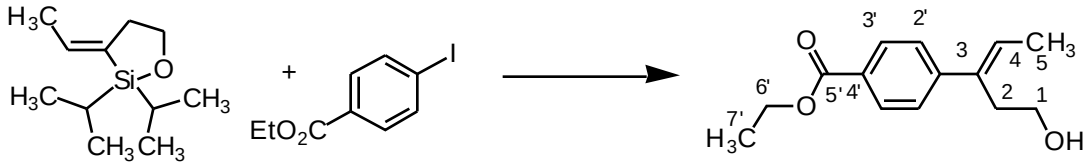
TLC: R_f 0.20 (pentane/ether, 2/3, SiO_2)

GC: t_R **3i** 5.83 min (100%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

Analysis: $C_{11}H_{13}NO_2$ (191.23)

Calculated	C, 76.98;	H, 7.00;	N, 7.48%
Found	C, 76.68;	H, 6.95;	N, 7.45%

Reaction of Ethyl 4-Iodobenzoate with Oxasilacyclopentane 2a. Ethyl 4-[1-(2-Hydroxyethyl)-(*E*)-1-propenyl)]benzoate (3j).



2a **3j**

Following the General Procedure, **2a** (275 mg, 1.39 mmol, 1.1 equiv), was dissolved in a solution of TBAF in THF (2.5 mL, 2.5 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. Ethyl 4-iodobenzoate (348 mg, 1.26 mmol, 1.0 equiv) was added in three portions over 30-min intervals and $Pd(dba)_2$ (36 mg, 0.063 mmol, 0.050 equiv) was added following the first portion of iodide. The mixture was stirred at 45 °C for a total of 15 h. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO_2, 31 g, pentane/ether, 7/1). Removal of the solvent and Kugelrohr distillation of the resulting product afforded 254 mg (86%) of **3j** as a colorless oil.

Data for **3j**:

bp: 195 °C (0.1 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.99 (dt, *J* =1.9, 8.2 Hz, HC(3'), 2 H); 7.42 (dt, *J* = 1.9, 8.1 Hz, HC(2'), 2 H); 6.03 (q, *J* = 7.1 Hz, HC(4), 1 H); 4.38 (t, *J* = 7.0 Hz, H_2C(6'), 2 H), 3.65 (t, *J* = 7.1 Hz , H_2C(1), 2 H); 2.86 (t, *J* = 7.1 Hz, H_2C(2), 2 H); 1.88 (d, *J*= 7.1 Hz, H_3C(5), 3 H); 1.70 (br s, OH, 1 H), 1.40 (t, *J*=7.0 Hz, H_3C(7'), 3 H).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

166.80 (C(5')), 147.42, 136.51, 129.91, 128.95 127.91, 126.28, 61.34 (C(1)), 61.11 (C(6')), 32.86 (C(2)), 14.72 (C(5)), 14.55 (C(7')).

IR: ($CHCl_3$)

3625 (w), 3425 (w), 3004 (s), 2935 (s), 2875 (s), 1710 (s), 1607 (m), 1446 (m), 1384 (s), 1279 (s), 1110 (s), 1043 (s), 1021 (s).

MS: (EI, 70 eV)

234 (M^+, 43), 189 (44), 159 (27), 143 (100), 128 (46), 115 (47), 91 (33), 77 (17).

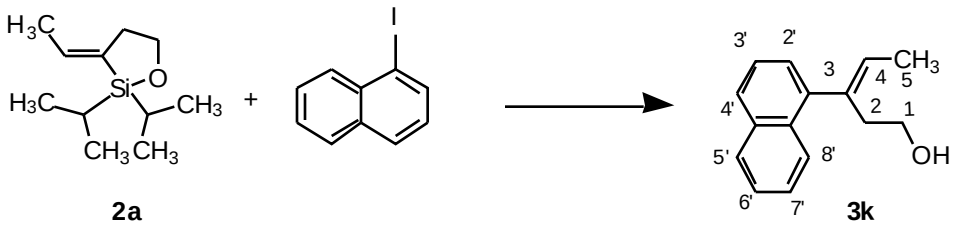
TLC: R_f 0.68 (ether, SiO_2)

GC: t_R **3j** 6.74 min (100%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

Analysis: $C_{14}H_{18}O_3$ (234.30)

Calculated	C, 71.78;	H, 7.74%
Found	C, 71.85;	H, 7.86%

Reaction of 1-Iodonaphthalene with Oxasilacyclopentane 2a. (*E*)-3-(1-Naphthyl)-3-penten-1-ol (3k).



2a **3k**

Following the General Procedure, **2a** (243 mg, 1.23 mmol, 1.1 equiv), was dissolved in a solution of TBAF in THF (2.2 mL, 2.2 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 1-Iodonaphthalene (283 mg, 1.12 mmol, 1.0 equiv) was added in three portions over 55-min intervals and $Pd(dba)_2$ (32 mg, 0.056 mmol, 0.050 equiv) was added following the first portion of iodide. The mixture was stirred at 35 °C for a total of 500 min. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO_2, 32 g, pentane/ether, 9/1). Removal of the solvent and subsequent sublimation (60 °C/0.1 mm Hg) of the resulting product afforded 180 mg (76%) of **3k** as a white solid.

Data for **3k**:

mp: 66-68 °C

^{1}H NMR: (500 MHz, $CDCl_3$)

7.98 (m, HC(5'/8'), 1 H); 7.87 (m, H(C8'/5'), 1 H); 7.78 (d, *J* = 8.2 Hz, H(C2'/4'), 1 H), 7.50 (m, HC(6'), HC(7'), 2 H), 7.45 (br t, *J* = 7.9 Hz, HC(3'), 1 H); 7.26 (d, *J* = 6.9 Hz, HC(4'/2'), 1 H), 5.76 (q, *J* = 6.9 Hz, HC(4), 1 H); 3.59 (t, *J* = 6.9 Hz , H_2C(1), 2 H); 2.863 (t, *J* = 6.9 Hz, H_2C(2), 2 H); 1.96 (d, *J*= 6.9 Hz, H_3C(5), 3 H); 1.95 (br s, OH, 1 H).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

142.21, 136.70, 134.04, 131.91, 128.61, 128.17, 127.39, 126.02, 125.95, 125.91, 125.89, 125.56, 61.25 (C(1)), 36.65 (C(2)), 14.25 (C(5)).

IR: ($CHCl_3$)

3619 (m), 3060 (m), 3043 (m), 3012 (s), 2956 (s), 2926 (s), 2885 (m), 2863 (m), 1591 (w), 1506 (w), 1453 (w), 1393 (m), 1243 (m), 1187 (w), 1049 (s), 1030 (s), 1041 (m), 802 (s).

MS: (EI, 70 eV)

212 (M^+, 55), 193 (15), 181 (70), 165 (100), 152 (50), 128 (25), 115 (13).

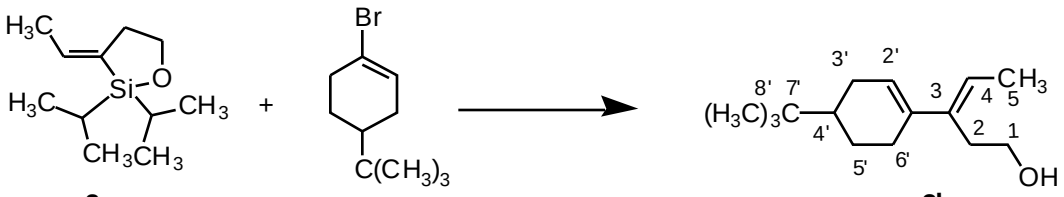
TLC: R_f 0.34 (pentane/ether, 1/1, SiO_2)

GC: t_R **3k** 6.36 min (96.2%), minor isomer of **3k** 7.12 min (3.8%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

Analysis: $C_{15}H_{16}O$ (212.29)

Calculated	C, 84.87;	H, 7.60%
Found	C, 84.77;	H, 7.78%

Reaction of 1-Bromo-4-*tert*-butyl-1-cyclohexene with Oxasilacyclopentane 2a. (*E*)-3-(4-*tert*-Butyl-1-cyclohexenyl)-3-penten-1-ol (3l).



2a **3l**

Following the General Procedure, **2a** (215 mg, 1.09 mmol, 1.04 equiv), was dissolved in a solution of TBAF in THF (2.1 mL, 2.0 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 1-Bromo-4-*tert*-butyl-1-cyclohexene[2] (227 mg, 1.04 mmol, 1.0 equiv) was added in one portion and $[allylPdCl]_2$ (9.5 mg, 0.028 mmol, 0.050 equiv of Pd) was then added. The mixture was stirred at 45 °C for a total of 46 h. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO_2, 33 g, pentane/ether, 9/1). Removal of solvent and sublimation (50 °C/0.1 mm Hg) of the resulting product afforded 103 mg (45%) of **3l** as a white solid.

Data for **3l**:

mp: 56-58 °C

^{1}H NMR: (500 MHz, $CDCl_3$)

5.83 (m, HC(2'), 1 H); 5.70 (q, J =6.8 Hz HC(4), 1 H); 3.66 (t, J = 6.9 Hz , H_2C(1), 2 H); 2.61 (t, J = 6.8 Hz, H_2C(2), 2 H); 2.31 (br d, 1 H), 2.13 (m, 2 H), 1.90 (m,

2 H), 1.76 (d, *J*= 6.8 Hz, $H_3C(5)$, 3 H); 1.39 (br s, OH, 1 H), 1.20 (m, 2 H), 0.89 (s, $H_3C(8')$, 9 H).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

136.96 (C(1'/3)), 136.71(C(3/1')), 123.30, 121.56, 62.14 (C(1)), 44.18, 32.35 (C(2)), 30.60, 27.97, 27.63, 27.38, 24.57, 14.28 (C(5)).

IR: ($CHCl_3$)

3618 (w), 3007 (s), 2974 (s), 2929 (s), 1602 (w), 1457 (m), 1384 (m), 1242 (m), 1111 (s), 1044 (m).

MS: (EI, 70 eV)

222 (M^+, 65), 165 (90), 147 (38), 121 (54), 105 (87), 116 (58), 91 (100), 79 (63).

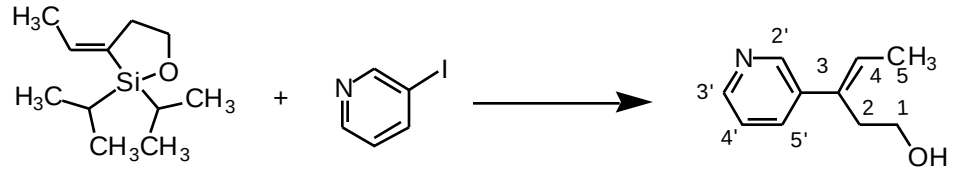
TLC: R_f 0.56 (pentane/Et_2O, 3/2, SiO_2)

GC: t_R **3i** 5.61 min (100%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

Analysis: $C_{15}H_{26}O$ (222.37)

Calculated	C, 81.02;	H, 11.79%
Found	C, 80.94;	H, 11.82%

Reaction of 3-Iodopyridine with Oxasilacyclopentane 2a. (*E*)-3-(3-Pyridyl)-3-penten-1-ol (3m).



2a **3m**

Following the General Procedure, **2a** (440 mg, 2.2 mmol, 1.1 equiv), was dissolved in a solution of TBAF in THF (4.0 mL, 4.0 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 3-Iodopyridine (412 mg, 2.0 mmol, 1.0 equiv) was added in one portion and $Pd(dba)_2$ (57 mg, 0.10 mmol, 0.050 equiv) was then added. The mixture was stirred at 45 °C for a total of 45 h. The crude mixture was then loaded onto 4 g of silica gel and was purified by column chromatography (SiO_2, 75 g, pentane/ether, 1/1). Removal of the solvent and Kugelrohr distillation of resulting product afforded 240 mg (74%) of **3m** as a colorless oil.

Data for **3m**:

bp: 150 °C (0.1 mm Hg)

^{1}H NMR: (400 MHz, $CDCl_3$)

8.57 (d, *J* =2.2 Hz, HC(2'), 1 H); 8.44 (dd, *J* = 4.9, 1.4 Hz, HC(4'), 1 H); 7.66 (ddd, *J* = 1.4 Hz, 2.2, 8.1 Hz, HC(6'), 1 H), 7.24 (dd, *J* = 4.9, 8.1 Hz, HC(5'), 1 H), 5.94 (q, *J* = 6.8 Hz, HC(4), 1 H); 3.66 (t, *J* = 6.8 Hz , H_2C(1), 2 H); 2.82 (t, *J* = 6.8 Hz, H_2C(2), 2 H); 2.10 (br s, OH, 1 H); 1.88 (d, *J*= 6.8 Hz, H_3C(5), 3 H).

^{13}C NMR: (100.5 MHz, $CDCl_3$)

147.97, 147.76, 138.52, 134.25, 133.84, 127.84, 123.42, 61.07 (C(1)), 32.92 (C(2)), 14.69 (C(5)).

IR: ($CHCl_3$)

3622 (w), 3011 (s), 2964 (m), 1568 (w), 1477 (w), 1235 (m), 1040 (m), 1026 (m), 802(m).

MS: (EI, 70 eV)

163 (100), 144 (87), 132 (85), 117 (98), 104 (20), 92 (25), 77 (23).

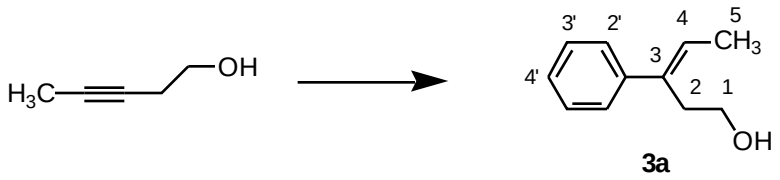
TLC: R_f 0.17 (ether, SiO_2)

GC: t_R **3m** 4.88 min (100%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

Analysis: $C_{10}H_{13}NO$ (163.22)

Calculated	C, 73.59;	H, 8.03;	N, 8.58%
Found	C, 73.33;	H, 8.11;	N, 8.31%

One-pot Arylation of 3-Pentyn-1-ol with Iodobenzene. (*E*)-3-Phenyl-3-penten-1-ol (3a).



3a

In a two-necked flask was placed 3-pentyn-1-ol (160 mg, 1.90 mmol, 1.3 equiv) and tetramethyldisilazane (0.26 mL, 1.50 mmol, 1.0 equiv) was added dropwise at rt. The mixture was stirred for 1 h, whereupon dry THF (3.0 mL) was added followed by platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (50 uL, in xylenes). The mixture was stirred at rt for 1 h (GC/MS monitoring indicated hydrosilylation was completed). To this mixture was added dropwise a solution of TBAF in THF (3.3 mL, 3.3 mmol, 2.2 equiv). Iodobenzene (306 mg, 1.50 mmol, 1.0 equiv) and $Pd(dba)_2$ (84 mg, 0.15 mmol, 0.10 equiv) were each added in one portion, successively to the mixture. The mixture was stirred at rt for 40 min. The reaction mixture was loaded onto 4 g of silica gel and was purified by column chromatography (SiO_2, 40 g, pentane/ether, 9/1) and Kugelrohr distillation afforded 206 mg (85%) of **3a** as a colorless oil. Biphenyl was neither detected nor isolated.

Data for **3a**:

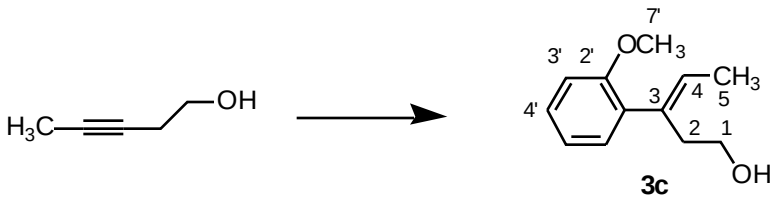
bp: 82-83 °C air bath (0.2 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.34 (m, HC(2'), HC(3'), 4 H); 7.25 (tt, J = 1.5, 7.1 Hz, HC(4'), 1 H); 5.94 (q, J = 6.8 Hz, HC(4), 1 H); 3.66 (t, J = 6.9 Hz, H_2C(1), 2 H); 2.85 (q, J = 6.9, H_2C(2), 2 H); 1.870 (d, J = 7.1 Hz, H_3C(5), 3 H); 1.52 (br s, OH, 1 H).

GC: t_R **3a** 4.53 min (96.6%), a minor isomer of **3a** 4.62 min (2.8%), an unknown impurity 4.34 min (0.4%) (HP-5, injector 225 °C, column 270 °C, 15 psi).

One-pot Arylation of 3-Pentyn-1-ol with 2-Iodoanisole. (*E*)-3-(2-Methoxyphenyl)-3-penten-1-ol (3c).



In a two-necked flask was placed 3-pentyn-1-ol (160 mg, 1.90 mmol, 1.3 equiv) and tetramethyldisilazane (0.27 mL, 1.56 mmol, 1.04 equiv) was added dropwise at rt. The mixture was stirred for 100 min, whereupon dry THF (3.0 mL) was added followed by platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (55 uL, in xylenes). The mixture was stirred at rt for 1 h (GC/MS monitoring indicated hydrosilylation was completed). To this mixture was added dropwise a solution of TBAF in THF (3.3 mL, 3.3 mmol, 2.2 equiv). 2-Iodoanisole (351 mg, 1.50 mmol, 1.0 equiv) and $Pd(dba)_2$ (84 mg, 0.15 mmol, 0.10 equiv) were added in one portion, successively to the mixture. The mixture was stirred at 35 °C for 480 min. The reaction mixture was loaded onto 4 g of silica gel and was purified by column chromatography (SiO_2, 41 g, pentane/ether, 9/1) and Kugelrohr distillation afforded 215 mg (75%) of **3c** as a colorless oil.

Data for **3c**:

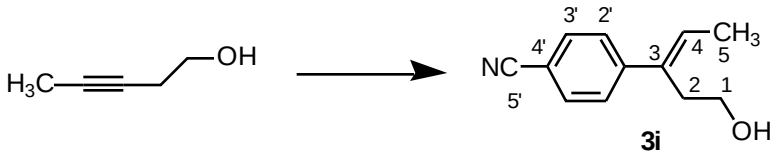
bp: 150 °C air bath (0.1 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.26 (ddd, *J* = 1.7, 7.1, 7.5 Hz HC(4'/5'), 1 H); 7.09 (dd, *J* = 1.7, 7.3 Hz, HC(3'/6'), 1 H); 6.93 (dt, *J* = 1.2, 7.5 Hz, HC(5'/4'), 1 H), 6.89 (br d, *J* = 8.1 Hz, HC(6'/3'), 1 H), 5.65 (q, *J* = 6.8 Hz, HC(4), 1 H); 3.83 (s, H_3C(7'), 3 H), 3.56 (t, *J* = 6.8 Hz, H_2C(1), 2 H); 2.74 (t, *J* = 6.8 Hz, H_2C(2), 2 H); 1.84 (d, *J* =6.8 Hz, H_3C(5), 3 H); 1.80 (br s, OH, 1 H).

GC: t_R **3c** 4.76 min (98.0%), a minor isomer of **3c** 4.86 min (1.7%), an unknown impurity 4.66 min (0.2%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

One-pot Arylation of 3-Pentyn-1-ol with 4-Iodobenzonitrile. (*E*)-3-(4-Cyanophenyl)-3-penten-1-ol (3i).



3i

In a two-necked flask was placed 3-pentyn-1-ol (126 mg, 1.50 mmol, 1.3 equiv) and tetramethyldisilazane (0.24 mL, 1.38 mmol, 1.2 equiv) was added dropwise at rt. The mixture was stirred for 1 h, whereupon dry THF (2.0 mL) was added followed by platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (35 uL, in xylenes). The mixture was stirred at rt for 1 h (GC/MS monitoring indicated hydrosilylation was completed). To this mixture was added dropwise a solution of TBAF in THF (3.3 mL, 3.3 mmol, 2.2 equiv). 4-Iodobenzonitrile (260 mg, 1.13 mmol, 1.0 equiv) and $Pd(dba)_2$ (63.0 mg, 0.15 mmol, 0.10 equiv) were added in one portion, successively to the mixture. The mixture was stirred at rt for 180 min. The reaction mixture was loaded onto 3 g of silica gel and was purified by column chromatography (SiO_2, 40 g, pentane/ether, 3/1) and Kugelrohr distillation afforded 160 mg (74%) of **3i** as a colorless oil. (1,1'-Biphenyl)-4,4'-dicarbonitrile (4.0 mg, 2%) was also isolated.

Data for **3i**:

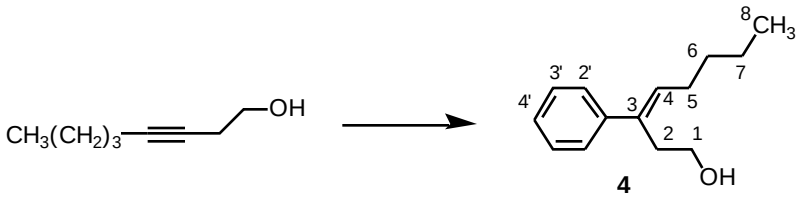
bp: 170 °C (0.2 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.61 (d, *J* = 8.1 Hz, HC(3'), 2 H); 7.46 (br d, *J* = 8.1 Hz HC(2'), 2 H); 6.04 (q, *J* = 6.8 Hz, HC(4), 1 H); 3.66 (t, *J* = 6.8 Hz , H_2C(1), 2 H); 2.84 (t, *J* = 6.8 Hz, H_2C(2), 2 H); 1.90 (d, *J*= 6.8 Hz, H_3C(5), 3 H); 1.47 (br s, *J* = 4.7 Hz, OH, 1 H).

GC: t_R **3i** 5.83 min (96.7%), a minor isomer of **3i** 6.06 min (3.3%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

One-pot Arylation of 3-Octyn-1-ol with 4-Iodobenzene with 10% $Pd(dba)_2$. (*E*)-3-Phenyl-3-octen-1-ol (4).



In a two-necked flask was placed 3-octyn-1-ol (246 mg, 1.95 mmol, 1.3 equiv) and tetramethyldisilazane (0.27 mL, 1.56 mmol, 1.04 equiv) was added dropwise at rt. The mixture was stirred for 1.5 h, then the reaction mixture was evacuated at rt for 10 m to remove TMDS. Dry THF (3.0 mL) was added followed by platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (70 uL, in xylenes). The mixture was stirred at rt for 1.5 h (GC/MS monitoring indicated hydrosilylation was completed). To this mixture was added dropwise a solution of TBAF in THF (3.3 mL, 3.3 mmol, 2.2 equiv). Iodobenzene (303 mg, 1.50 mmol, 1.0 equiv) and $Pd(dba)_2$ (84 mg, 0.15 mmol, 0.10 equiv) were added in one portion, successively to the mixture. The mixture was stirred at rt for 40 min. The reaction mixture was loaded onto 4 g of silica gel and was purified by column chromatography (SiO_2, 45 g, pentane/ether, 23/2) and Kugelrohr distillation afforded 257 mg (84%) of **4** as a colorless oil.

Data for **4**:

bp: 145 °C (0.2 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.39-7.32 (m, HC(2'), HC(3'), 4 H); 7.27 (m, HC(4'), 1 H); 5.85 (t, *J* =7.3 Hz, HC(4), 1 H); 3.64 (t, *J* = 6.9 Hz , H_2C(1), 2 H); 2.84 (t, *J* = 6.9 Hz, H_2C(2), 2 H); 2.25 (q, *J*= 7.5 Hz, H_2C(5), 2 H), 1.48-1.38 (m, H_2C(6), H_2C(7), OH, 5 H); 0.96 (t, *J* = 7.3 Hz, H_3C(8), 3 H).

^{13}C NMR: (125.6 MHz, $CDCl_3$)

142.91, 135.95, 132.43, 128.59, 127.05, 126.56, 61.58 (C(1)), 33.39, 32.29, 28.69, 22.70, 14.26 (C(8)).

IR: ($CHCl_3$)

3622 (w), 3012 (m), 2970 (s), 2930 (s), 2874 (m), 1599 (w), 1493 (m), 1466 (m), 1446 (m), 1381 (w), 1042 (s), 1030 (m).

MS: (EI, 70 eV)
204 (M^+, 37), 159 (42), 143 (100), 128 (45), 117 (72), 105 (65), 91 (65), 77 (42).

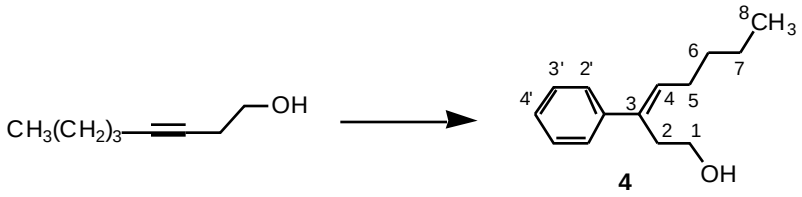
TLC: R_f 0.50 (pentane/Et_2O, 2/3, SiO_2)

GC: t_R **4** 10.68 min (97.3%), an isomer of **4** 10.46 (2.2%), an unknown impurity 6.73 (.52%), (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

Analysis: $C_{14}H_{20}O$ (204.31)

Calculated	C, 82.30;	H, 9.87%
Found	C, 82.08;	H, 9.47%

One-pot Arylation of 3-Octyn-1-ol with 4-Iodobenzene with 5% $Pd(dba)_2$. (*E*)-3-Phenyl-3-octen-1-ol (4).



4

In a two-necked flask was placed 3-octyn-1-ol (246 mg, 1.90 mmol, 1.3 equiv) and tetramethyldisilazane (0.27 mL, 1.56 mmol, 1.04 equiv) was added dropwise at rt. The mixture was stirred for 1 h, then the mixture was evacuated at rt for 10 m to remove TMDS. Dry THF (3.0 mL) was added followed by platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (50 uL, in xylenes). The mixture was stirred at rt for 1 h (GC/MS monitoring indicated hydrosilylation was completed). To this mixture was added dropwise a solution of TBAF in THF (3.3 mL, 3.3 mmol, 2.2 equiv). Iodobenzene (305 mg, 1.50 mmol, 1.0 equiv) and $Pd(dba)_2$ (42 mg, 0.15 mmol, 0.050 equiv) were added in one portion, successively to the mixture. The mixture was stirred at rt for 90 min. The reaction mixture was loaded onto 4 g of silica gel and was purified by column chromatography (SiO_2, 46 g, pentane/ether, 23/2) and Kugelrohr distillation afforded 257 mg (85%) of **4** as a colorless oil.

Data for **4**:

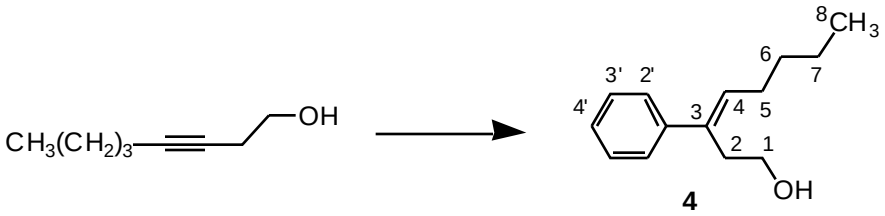
bp: 160 °C (0.2 mm Hg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.39-7.32 (m, HC(2'), HC(3'), 4 H); 7.27 (m, HC(4'), 1 H); 5.85 (t, J =7.3 Hz, HC(4), 1 H); 3.64 (t, J = 6.9 Hz , H_2C(1), 2 H); 2.837 (t, J = 6.9 Hz, H_2C(2), 2 H); 2.25 (q, J= 7.5 Hz, H_2C(5), 2 H), 1.48-1.38 (m, H_2C(6), H_2C(7), OH, 5 H); 0.96 (t, J = 7.3 Hz, H_3C(8), 3 H).

GC: t_R **4** 10.68 min (98.3%), an isomer of **4** 10.46 (1.7%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

One-pot Arylation of 3-Octyn-1-ol with 4-Iodobenzene with 5% Pd(dba)$_2$ and Lower Hydrosilylation Concentration. (*E*)-3-Phenyl-3-octen-1-ol (4).



In a two-necked flask was placed 3-octyn-1-ol (246 mg, 1.95 mmol, 1.3 equiv) and tetramethyldisilazane (0.27 mL, 1.56 mmol, 1.04 equiv) was added dropwise at rt. The mixture was stirred for 1 h, then the mixture was evacuated at rt for 10 m to remove TMDS. Dry THF (10.0 mL) was added followed by platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (30 uL, in xylenes). The mixture was stirred at rt for 2 h (GC/MS monitoring indicated hydrosilylation was completed), then was concentrated to 2.0 mL. To this mixture was added dropwise a solution of TBAF in THF (3.3 mL, 3.3 mmol, 2.2 equiv). Iodobenzene (303 mg, 1.50 mmol, 1.0 equiv) and Pd(dba)$_2$ (42 mg, 0.15 mmol, 0.050 equiv) were added in one portion, successively to the mixture. The mixture was stirred at rt for 90 min. The reaction mixture was loaded onto 4 g of silica gel and was purified by column chromatography (SiO_2, 56 g, pentane/ether, 9/1) afforded 275 mg of **4** as a yellow liquid. The NMR data matched those for the previous reaction, but the material was not pure. However, the isomeric ratio was not changed.

Data for **4**:

GC: t_R **4** 10.68 min (98.3%), an isomer of **4** 10.46 (1.7%) (HP-5, injector 225 °C, detector 300 °C, column 270 °C, 15 psi).

References

(1) Compound **3f** is known: Sakurai, H.; Tokumaru, K.; Itoh, H.; Terakawa, K.; Kikuchi, K.; Caldwell, R. A.; Hsu, C. C. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1049. However, no physical data was reported.

(2) Prepared according to the following: Napolitano, E.; Fiaschi, R.; Mastrorilli, E. *Synthesis* **1986**, 122.