Intramolecular Syn and Anti-Hydrosilylation and Silicon-Assisted Cross-Coupling: Highly Regio- and Stereoselective Synthesis of Trisubstituted Allylic Alcohols

Scott E. Denmark* and Weitao Pan

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

SUPPORTING INFORMATION

General Experimental

All reactions were performed in oven (150 °C) and/or flame-dried glassware under an inert atmosphere of dry argon. All the solvents used were reagent grade and distilled from the indicated drying agents: dichloromethane: P_2O_5 ; diethyl ether, dioxane and tetrahydrofuran: Na, benzophenone; toluene, hexane, dimethylformamide, and dimethoxyethane: CaH_2 ; methanol: $Mg(OMe)_2$; ethyl acetate: K_2CO_3 . “Brine” refers to a saturated solution of NaCl. Bulb-to-bulb distillations were performed on a Büchi GKR-50 Kugelrohr and boiling points (bp) correspond to the uncorrected recorded air bath temperatures (ABT). Melting points (mp) were recorded in sealed vacuum glass capillaries on a Thomas-Hoover melting point apparatus are corrected. All reaction temperatures correspond to internal temperatures measured by Teflon-coated thermocouples unless otherwise noted. All reactions were performed under an inert atmosphere of dry N_2 unless otherwise specified.

1H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Unity 400 (400 MHz, 1H ; 100 MHz, ^{13}C), Unity 500 (500 MHz, 1H ; 126 MHz, ^{13}C). Spectra are referenced to residual chloroform (7.26 ppm, 1H ; 77.0 ppm, ^{13}C). Chemical shifts are reported in ppm (); 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%-Dimethylpolysiloxane gum phase.

Most commercial reagents were purified by distillation or recrystallization prior to use. A 1.0 M solution of tetrabutylammonium fluoride in THF was prepared from solid tetrabutylammonium fluoride trihydrate ($\text{TBAF} \cdot 3\text{H}_2\text{O}$, Fluka) and distilled THF in a volumetric flask and was stored in a Schlenk bottle. Palladium bis(dibenzylideneacetone) ($\text{Pd}(\text{dba})_2$) was purchased from Jansen and used without purification. Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex $\text{Pt}(\text{DVDS})$, solution in xylene was purchased from Aldrich.

The following compounds were prepared by literature methods: Stryker's catalyst $[\text{CuH}(\text{PPh}_3)]_6$ ¹ and $[\text{RuCl}_2(\text{benzene})]_2$.²

Preparation of Dimethyl-(2'-butynyloxydimethylsiloxyl)silane

The Stryker catalyst $[\text{CuH}(\text{PPh}_3)]_6$ (70 mg, 0.036 mmol, 0.0012 equiv) was placed in a 250-mL flask in the dry box. The stopper was removed and a mixture of 2-butyne-1-ol (2.1 g, 30.0 mmol) and tetramethyldisiloxane (105 g, 783 mmol, 26.1 equiv) was added quickly. The mixture was stirred at ambient temperature for 11 h before another portion of Stryker catalyst (10 mg, 0.005 mmol, 0.00017 equiv) was added. The mixture was allowed to stir for another 9 h and then solvent was carefully removed at ambient temperature in vacuo (120 mmHg to 40 mmHg). Direct distillation of the residual brown suspension afforded 5.0 g of a colorless oil. This oil was placed

under vacuum at 20 mmHg at ambient temperature overnight and the residue (4.5 g) was redistilled (25 °C, 0.2 mmHg) to afford 4.35 g (72%) of **1** as a colorless liquid.

Data for 1:

bp: 25 °C (0.1 mmHg)

¹H NMR: (500 MHz, CDCl₃)

4.73 (hept, *J* = 2.8 Hz, 1 H, HSi); 4.32 (q, *J* = 2.4 Hz, 2 H, H₂C(1)); 1.85 (t, *J* = 2.4 Hz, 3 H, H₃C(8)); 0.22 (d, *J* = 2.8 Hz, 6 H, H₃C(2')); 0.15 (s, 6 H, H₃C('))

¹³C NMR: (125.6 MHz, CDCl₃)

81.31 (C(2)), 77.00 (C(3)), 51.05 (C(1)), 3.83 (C(4)), 0.84/-0.88 (C(1')/C(2'))

IR: (neat)

3012 (s), 2964 (s), 2924 (m), 2904 (m), 2868 (m), 2127 (s), 1458 (m), 1416 (m), 1373 (m), 1259 (s), 1220 (m), 1001 (s), 908 (s), 852 (s), 842 (s), 827 (s), 804 (s)

MS: (EI, 70 eV)

202 (M⁺, 29), 187 (37), 159 (5), 149 (10), 133 (100), 119 (7), 83 (10)

GC: *t_R* **1** 9.40 min (94.4%), 7.28 min (3.9 %), 4.02 (1.0%) and other small peaks (Ultra-2, injector 225 °C, column 100 °C, 15 psi)

HRMS: C₈H₁₈O₂Si₂ (202.40)

Calcd 201.0767 (for C₈H₁₇O₂Si₂, M⁺-1)

Found 201.0767

Preparation of (E)-5-Ethylidene-2,2,4,4-tetramethyl-1,3-dioxane-2,4-disilacyclohexane ((E)-2c).

To a solution of **1** (268 mg, 1.33 mmol) in acetonitrile/CH₂Cl₂ (24 mL, 1/1) in a 50-mL, round-bottom flask fitted with a nitrogen inlet, thermocouple, and magnetic stir bar, was added Hünig base (40 μL, 0.23 mmol, 0.17 equiv). The solution was cooled to 0 °C in an ice bath before a solution of Pt(DVDS) in xylenes (40 μL) was added and the mixture was stirred at 0 °C for 330 min. The solvents were carefully removed at ambient temperature by gentle application of vacuum (400 to 120 mmHg). Direct Kugelrohr distillation of the residue afforded 161 mg (60%) of (E)-**2c** as a colorless oil.

Data for (E)-2c:bp: 25 °C (0.1 mmHg, ABT)¹H NMR: (500 MHz, CDCl₃)5.80 (qt, *J* = 1.0, 6.8 Hz, 1 H, HC(7)); 4.70 (q, *J* = 1.0 Hz, 2 H, H₂C(6)); 1.68 (dt, *J* = 1.2, 6.8 Hz, 3 H, H₃C(8)); 0.26 (s, 6 H, H₃C(1'/2')); 0.20 (s, 6 H, H₃C(2'/1'))¹³C NMR: (125.6 MHz, CDCl₃)

141.81 (C(5)), 133.76 (C(7)), 63.97 (C(6)), 14.33 (C(8)), 1.10/-0.76 (C(1')/C(2'))

IR: (neat)

3010 (s), 2962 (s), 2925 (m), 2848 (m), 1622 (s), 1442 (m), 1408 (m), 1363 (m), 1257 (s), 1221 (m), 1157 (s), 1068 (s), 1034 (s), 968 (s), 858 (s), 831 (s), 806 (s)

MS: (EI, 70 eV)202 (M⁺, 29), 187 (37), 159 (5), 149 (10), 133 (100), 119 (7), 83 (10)TLC: *R_f* 0.74 (pentane/Et₂O, 4/1, SiO₂)GC: *t_R* **2c** 9.40 min (98.2%), 9.40 min (1.0%), 8.20 (0.8%) (HP-5, injector 225 °C, column 300 °C, 15 psi)HRMS: C₈H₁₈O₂Si₂ (202.40)

Calcd 202.0845

Found 202.0853

Preparation of (Z)-5-Ethyliden-2,2,4,4-tetramethyl-1,3-dioxasilacyclohexane ((Z)-2c)

A solution of [RuCl₂(C₆H₆)] (372 mg, 0.74 mmol, 0.063 equiv) in dry dichloromethane (150 mL) was placed into a 250-mL, round-bottom flask equipped with a condenser, which was connected with a two necked-connector fitted with a rubber septum and a gas inlet tube. The catalyst was heated to reflux for 10 min. To the solution was added a solution of silane **1** (2.44 g, 12.1 mmol) in dry dichloromethane (10 mL) by syringe pump under reflux over 90 min. The reaction mixture gradually turned red. The solvent was then evaporated *in vacuo* and pentane (50 mL) was added to precipitate the Ru catalyst which was filtered off. The flask and residue were rinsed with ether (10 mL) and the combined organic filtrates were filtered through activated charcoal. Evaporation of the solvent afforded 2.5 g of a yellow oil. After standing at rt overnight,

the residual volatile components were then removed under high vacuum (1 mmHg) for 30 min. The product (*Z*)-**2c** was obtained as an oligomeric residue that was used directly.

General Procedure for Coupling of Dioxadisilacyclohexanes (**2c**)

In a two-necked, round-bottom flask fitted with a rubber septum and gas inlet tube, the dioxadisilacyclohexane, **2c** was dissolved in a solution of tetrabutylammonium fluoride (TBAF, 1.0 M in dioxane), at ambient temperature under nitrogen. The electrophile (1.0 equiv) was added in one portion or portionwise as specified below. The palladium catalyst (5 mol% of Pd) was added in one portion to the solution 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 Dioxadisilacyclohexane (*E*)-**2c**. (*Z*)-2-Phenyl-2-buten-1-ol ((*Z*)-**3a**)

Following the General Procedure, (*E*)-**2c** (216 mg, 1.07 mmol, 1.07 equiv) was dissolved in a solution of TBAF in dioxane (2.0 mL, 2.0 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. Iodobenzene (205 mg, 1.0 mmol, 1.0 equiv) was added followed by $Pd(dba)_2$ (27.5 mg, 0.048 mmol, 0.048 equiv). The mixture was stirred at ambient temperature for 200 min and 35 °C for another 85 min. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO_2 , 10 g, pentane/ Et_2O , 1/0 → 10/1). Removal of the solvent and Kugelrohr distillation of the resulting oil afforded 118 mg (79%) of (*Z*)-**3a**³ as a colorless oil.

Data for (*Z*)-**3a**:

bp: 100 °C (0.2 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.47-7.45(m, 2 H); 7.38-7.35 (m, 2 H); 7.30-7.28 (m, 1 H); 6.06 (q $J = 7.0$ Hz, HC(3), 1 H); 4.61 (s, 2 H, H₂C(1)); 1.93 (d, $J = 7.0$ Hz, 3 H, H₃C(4)); 1.62 (br s, 1 H, -OH)

¹³C NMR: (125.6 MHz, CDCl₃)

141.32, 139.76, 128.76, 127.28, 126.98, 124.49, 56.69 (C(1)), 14.34 (C(4))

GC: t_R (Z)-**3a** 6.29 min (100%) (Ultra-2, injector 225 °C, detector 300 °C, column 180 °C, 15 psi)

Reaction of 2-Iodoanisole with Dioxadisilacyclohexane (*E*)-2c**. (Z)-2-(2-Methoxyphenyl)-2-buten-1-ol ((Z)-**3b**)**

Following the General Procedure, (*E*)-**2c** (218 mg, 1.08 mmol, 1.08 equiv) was dissolved in a solution of TBAF in dioxane (2.0 mL, 2.0 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 2-Iodoanisole (234 mg, 1.0 mmol, 1.0 equiv) was added in three portions (94 mg, 78 mg, 62 mg) over 25-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 ambient temperature for 13 h and then 40 °C for another 13 h. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO₂, 15 g, pentane to pentane/Et₂O, 10/1). Removal of the solvent and Kugelrohr distillation of the resulting oil afforded 144 mg (81%) of (Z)-**3b** as a colorless oil.

Data for (Z)-3b**:**

bp: 115 °C (0.1 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.28 (ddd, $J = 1.7, 7.3, 8.3$ Hz, HC(4'/5'), 1 H); 7.09 (dd, $J = 1.7, 7.3$ Hz, 1 H, HC(3'/6')); 6.97 (dt, $J = 1.2, 7.3$ Hz, HC(5'/4'), 1 H), 6.92 (br d, $J = 8.3$ Hz, 1 H, HC(6'/3')), 5.79 (q, $J = 7.1$ Hz, 1 H, HC(3)); 4.41 (d, $J = 6.3$ Hz, 2 H, H₂C(1)); 3.89 (s, 3 H, H₃C(7)); 2.43 (t, $J = 6.3$ Hz, 1 H, -OH); 1.92 (d, $J = 6.9$ Hz, 3 H, H₃C(4))

¹³C NMR: (125.6 MHz, CDCl₃)

156.49, 139.90, 132.53, 130.7, 129.41, 128.61, 121.45, 110.66, 61.02 (C(1)), 55.84 (C(7')), 14.13 (C(4))

IR: (CHCl₃)

3573 (w), 3010 (s), 2966 (m), 2945 (m), 2892 (m), 2840 (m), 1597 (m), 1579 (m), 1489 (s), 1466 (s), 1437 (s), 1396 (m), 1294 (m), 1261 (s), 1234 (s), 1178 (m), 1051 (m), 1022 (s), 972 (s)

MS: (EI, 70 eV)

178 (M⁺, 100), 163 (15), 145 (32), 131 (26), 121 (50), 115 (25), 108 (32), 91 (52), 77 (21)

TLC: *R_f* 0.48 (Et₂O, SiO₂)

GC: *t_R* (Z)-**3b** 5.39 min (100%) (Ultra-2, injector 225 °C, detector 300 °C, column 220 °C, 15 psi).

Analysis: C₁₁H₁₄O₂ (178.23)

Calcd C, 74.13; H, 7.92%

Found C, 73.92; H, 8.15%

Reaction of 3-Iodobenzyl Alcohol with Dioxadisilacyclohexane (E)-2c. (Z)-2-(3-Hydroxymethylphenyl)-2-buten-1-ol ((Z)-3c)

Following the General Procedure, **2a** (213 mg, 1.05 mmol, 1.05 equiv) was dissolved in a solution of TBAF in dioxane (2.0 mL, 2.0 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 2-Iodobenzyl alcohol (235 mg, 1.0 mmol, 1.0 equiv) was added in three portions (115 mg, 60 mg, 60 mg) over 20-min intervals and Pd(dba)₂ (27.5 mg, 0.048 mmol, 0.048 equiv) was added following the first portion of iodide. The mixture was stirred at rt for 5 h 25 min and then 40 °C for another 1 h 50 min. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO₂, 8.5 g, pentane to pentane/Et₂O, 9/1 to 2/1 to 1/1). Removal of the solvent and Kugelrohr distillation of the resulting oil afforded 145 mg (81%) of (Z)-**3c** as a colorless oil.

Data for (Z)-3c:

bp: 150 °C (0.003 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)
 7.46 (s, HC(2'), 1 H); 7.40-7.34 (m, 2 H); 7.29-7.27 (m, 1 H); 6.02 (q, *J* = 7.1 Hz, 1 H, HC(3)); 4.73 (s, 2 H, H₂C(7')); 4.63 (s, 2 H, H₂C(1)); 1.93 (d, 3 H, *J* = 7.1 Hz, H₃C(4)); 1.60 (br s, OH, 2 H)

¹³C NMR: (125.6 MHz, CDCl₃)
 1431.61, 141.30, 139.53, 128.95, 127.17, 125.92, 125.79, 125.14, 65.52 (C(7')), 59.54 (C(1)), 14.58 (C(4))

IR: (CHCl₃)
 3608 (s), 3029 (s), 3012 (s), 2940 (m), 2883 (m), 1606 (w), 1485 (m), 1437 (m), 1385 (m), 1232 (m), 1232 (m), 1186 (m), 1022 (s), 980 (s)

MS: (EI, 70 eV)
 178 (M⁺, 96), 160 (22), 145 (50), 130 (940), 117 (100), 105 (34), 91 (98), 77 (43)

TLC: *R_f* 0.16 (Et₂O, SiO₂)

GC: *t_R* (Z)-**3c** 10.50 min (100%) (Ultra-2, injector 225 °C, detector 300 °C, column 220 °C, 15 psi)

HRMS: C₁₂H₁₆O₂ (178.23)
 Calcd 178.0994
 Found 178.0998

Reaction of 4-Iodoanisole with Dioxadisilacyclohexane (*E*)-2c**. (Z)-2-(4-Methoxyphenyl)-2-buten-1-ol ((Z)-**3d**)**

Following the General Procedure, (*E*)-**2c** (210 mg, 1.04 mmol, 1.04 equiv), was dissolved in a solution of TBAF in dioxane (2.0 mL, 2.2 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 4-Iodoanisole (235 mg, 1.0 mmol, 1.0 equiv) was added followed by Pd(dba)₂ (27.5 mg, 0.048 mmol, 0.048 equiv). The mixture was stirred at rt for 3 h 15 min, and then at 35 °C for 2 h. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO₂, 10 g, pentane/Et₂O, 1/0 → 9/1). Removal of the solvent and sublimation of the resulting solid (48 °C /0.2 mmHg) afforded 127 mg (71%) of (Z)-**3d** as a white solid.⁴

Data for (Z)-3d:mp: 46 °C¹H NMR: (500 MHz, CDCl₃)7.39 (dt, *J* = 2.0, 8.8 Hz, 2 H, HC(2')); 6.91 (dd, *J* = 2.0, 8.8 Hz, 2 H, HC(3')); 5.91 (q, *J* = 7.1 Hz, 1 H, HC(3)); 4.59 (d, *J* = 7.1 Hz, 2 H, H₂C(1)); 3.83 (s, 3 H, H₃C(5')); 1.90 (d, *J* = 7.1 Hz, 3 H, H₃C(4)); 1.41 (t, *J* = 5.1 Hz, 1 H, OH)¹³C NMR: (125.6 MHz, CDCl₃)

159.02, 139.09, 133.68, 127.56, 125.35, 114.14, 59.73 (C(1)), 55.50 (C(5')), 14.25 (C(4))

IR: (CHCl₃)

3610 (m), 3024 (w), 3012 (m), 2958 (w), 2937 (s), 2910 (w), 1608 (m), 1511 (s), 1466 (w), 1290 (m), 1246 (s), 1180 (m), 1038 (m), 976 (m), 825 (m)

MS: (EI, 70 eV)178 (M⁺, 100), 160 (33), 135 (26), 121 (67), 115 (27), 108 (21), 91 (34), 77 (22)TLC: *R_f* 0.52 (Et₂O, SiO₂)GC: *t_R* (Z)-3d 6.39 min (100%) (Ultra-2, injector 225 °C, detector 300 °C, column 220 °C, 15 psi)Analysis: C₁₁H₁₄O₂ (178.23)

Calcd C, 74.13; H, 7.92%

Found C, 73.91; H, 7.62%

HRMS: C₁₁H₁₄O₂

Calcd 178.09938

Found 178.09923

Reaction of 4-Iodoacetophenone with Dioxadisilacyclohexane (E)-2c. 1-[(4-[1-(2-Hydroxymethyl)-(Z)-1-propenyl)]phenyl]ethanone ((Z)-3e)

Following the General Procedure, (E)-2c (220 mg, 1.09 mmol, 1.09 equiv), was dissolved in a solution of TBAF in dioxane (2.0 mL, 2.0 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol, 1.0 equiv) was added in three portions over 20-

min intervals and Pd(dba)₂ (27 mg, 0.047 mmol, 0.047 equiv) was added following the first portion of iodide. The mixture was stirred at rt for a total of 10 h and 5 min. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO₂, 11 g, pentane/Et₂O, 1/0 → 9/1 → 2/1). Removal of the solvent and sublimation of the resulting solid (60 °C /0.1 mmHg) afforded 156 mg (82%) of (Z)-**3e** as a white solid.

Data for (Z)-**3e**:

mp: 49 °C

¹H NMR: (500 MHz, CDCl₃)

7.93 (dd, *J* = 1.7, 6.9 Hz, 2 H, HC(3')); 7.54 (dd, *J* = 1.7, 6.9 Hz, 2 H, HC(2')); 6.13 (q, *J* = 7.1 Hz, 1 H, HC(3)); 4.63 (br s, 2 H, H₂C(1)); 2.60 (s, 3 H, H₃C(6')), 1.95 (d, *J* = 7.1 Hz, 3 H, H₃C(4)); 1.36 (br s, 1 H, -OH)

¹³C NMR: (125.6 MHz, CDCl₃)

198.11 (C(5')), 146.23, 138.99, 135.78, 129.34, 128.87, 126.47, 59.37 (C(1)), 26.84, (C(6')), 14.51 (C(5))

IR: (CHCl₃)

3610 (w), 3006 (w), 3012 (m), 1680 (s), 1603 (s), 1360 (m), 1269 (s), 1188 (w), 1020 (w), 978 (m), 958 (w), 908 (w)

MS: (EI, 70 eV)

190 (M⁺, 50), 175 (100), 157 (23), 147 (17), 129 (40), 115 (27), 105 (11), 91 (17), 77 (12)

TLC: *R_f* 0.32 (Et₂O, SiO₂)

GC: *t_R* (Z)-**3e** 9.18 min (98.3%), an unknown 7.81 (1.7%) (Ultra-2, injector 225 °C, detector 220 °C, column 220 °C, 15 psi)

Analysis: C₁₃H₁₆O₂ (190.24)

Calcd C, 75.76; H, 7.42%

Found C, 75.66; H, 7.37%

Reaction of Methyl 2-Iodobenzoate with Dioxadisilacyclohexane (*E*)-2c. 3,4-Dihydro-4-(*Z*)-ethylidene-1H-2-benzopyran-1-one ((*Z*)-3f)

Following the General Procedure, (*E*)-2c (220 mg, 1.09 mmol, 1.09 equiv) was dissolved in a solution of TBAF in dioxane (1.0 mL, 1.0 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. 2-Iodobenzoate (262 mg, 1.0 mmol, 1.0 equiv) was added followed by Pd(dba)₂ (27.0 mg, 0.047 mmol, 0.047 equiv). The mixture was stirred at rt for 16.3 h and 40 °C for 19 h, then Pd(dba)₂ (13 mg, 0.022 mmol, 0.022 equiv) was added. The reaction was continued at 40 °C for 5.5 h. The sample was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO₂, 11 g, pentane to pentane/Et₂O, 20/1). Removal of the solvent and Kugelrohr distillation of the resulting yellow oil afforded 99 mg (57%) of (*Z*)-3f as a colorless oil.

Data for (*Z*)-3f:

bp: 160 °C (0.2 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

8.12 (ddd, *J* = 0.85, 8.0 Hz, 1 H, HC(4'/5')); 7.60 (ddd, *J* = 0.6, 1.3, 7.1 Hz, 1 H, HC(3'/6')); 7.54 (distorted d, *J* = 7.2 Hz, 1 H, HC(5'/4')), 7.44 (ddd, *J* = 0.6, 7.1, 7.2 Hz, HC(6'/3')), 6.33 (qt, *J* = 7.1 Hz, 1 H, HC(5)); 5.10 (br s, 2 H, H₂C(3)); 1.95 (d, *J* = 7.3 Hz, 3 H, H₃C(6))

¹³C NMR: (125.6 MHz, CDCl₃)

165.25 (C(1)), 138.87, 134.14, 130.61, 125.48, 127.38, 125.78, 123.25, 122.87, 66.28 (C(3)), 14.04 (C(6))

IR: (CHCl₃)

3028 (w), 3012 (w), 1724 (s), 1710 (s), 1603 (w), 1462 (m), 1394 (w), 1269 (m), 1234 (m), 1122 (m), 987 (w)

MS: (EI, 70 eV)

174 (M⁺, 83), 145 (100), 131 (23), 117 (57)

TLC: *R_f* 0.31 (pentane/Et₂O, 7/3, SiO₂)

GC: *t_R* (*Z*)-3f 8.76 min (96.6%), 8.01 min (2.7%), 11.7 min (0.7%) (Ultra-2, injector 225 °C, detector 220 °C, column 220 °C, 15 psi)

HRMS:	$C_{12}H_{16}O_2$ (174.26)
Calcd	174.0681
Found	174.0682

Reaction of Iodobenzene with Dioxadisilacyclohexane (Z)-2c. (E)-2-Phenyl-2-buten-1-ol ((E)-3a)

Following the General Procedure, (Z)-**2c** (251 mg, 1.27 mmol, 1.07 equiv) was dissolved in a solution of TBAF in dioxane (1.0 mL, 1.0 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. Iodobenzene (220 mg, 1.08 mmol) was added followed by $\text{Pd}(\text{dba})_2$ (29 mg, 0.050 mmol, 0.048 equiv). The mixture was stirred at rt for 5 h then siloxane (10 mg) and TBAF (1.0 mL, 1.0 mmol) were added. Reaction was continued for another 18 h before more siloxane (50 mg) was added. The reaction was continued for another 12 h, then TBAF (0.50 mL) and $\text{Pd}(\text{dba})_2$ (5.5 mg) were added. After stirring the mixture for another 35 h at ambient temperature, the solvent was removed. The residue was loaded onto 2.0 g of SiO_2 and was purified by column chromatography (SiO_2 , 10 g, pentane to pentane/ Et_2O , 1/0 – 10/1). Removal of the solvent and Kugelrohr distillation of the resulting oil afforded 91 mg (57%) of (E)-**3a**⁵ as a colorless oil.

Data for (E)-3a:

bp: 90 °C (0.2 mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)
 7.40 (t, $J = 7.5$ Hz, 2 H, HC(3')); 7.31 (tt, $J = 1.3, 7.5$ Hz, 1 H, HC(4')); 7.26 (distorted d, 2 H, HC(2')); 5.86 (qt, $J = 1.2, 6.8$ Hz, 1 H, HC(3)); 4.36 (t, $J = 1.2$ Hz, 2 H, $\text{H}_2\text{C}(1)$); 1.67 (d, $J = 1.2$ Hz, 3 H, $\text{H}_3\text{C}(4)$); 1.52 (br s, 1 H, -OH)

^{13}C NMR: (125.6 MHz, CDCl_3)
 141.20, 138.49, 128.92, 128.62, 127.34, 123.75, 68.39 (C(1)), 14.62 (C(4))

GC: t_R (E)-**3a** 5.54 min (97.7%), 6.29 min (2.3%) (Ultra-2, injector 225 °C, detector 300 °C, column 180 °C, 15 psi)

Reaction of 2-Iodoanisole with Dioxadisilacyclohexane (Z)-2c. (E)-2-(2-Methoxyphenyl)-2-buten-1-ol ((E)-3b)

Following the General Procedure, (Z)-2c (282 mg, 1.16 mmol, 1.1 equiv) was dissolved in a solution of TBAF in dioxane (1.0 mL, 1.0 mmol, 1.0 equiv) and the mixture was stirred for 10 min at rt. 2-Iodoanisole (236 mg, 1.056 mmol, 1.0 equiv) was added followed by Pd(dba)₂ (30 mg, 0.052 mmol, 0.050 equiv). The mixture was stirred at ambient temperature for a 6 h before another portion TBAF (1.0 mL) was added. After stirring the mixture for another 13 h at ambient temperature, siloxane (50 mg) was added followed by TBAF solution (0.50 mL). A final portion of siloxane (40 mg) was added after stirring for another 25 h at ambient temperature. The mixture was stirred at ambient for another 23 h and 40 °C for 3 h before it was loaded onto 3 g of silica gel and was purified by column chromatography (SiO₂, 11 g, pentane/Et₂O, 1/0 – 10/1). Removal of the solvent and Kugelrohr distillation of the resulting yellow oil afforded 116 mg (65%) of (E)-3b as a colorless oil.

Data for (E)-3b:

bp: 100 °C (0.2 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)
 7.30 (ddd, *J* = 1.7, 7.3, 8.3 Hz, HC(4'/5'), 1 H); 7.09 (dd, *J* = 1.7, 7.3 Hz, 1 H, HC(3'/6')); 6.99 (t, *J* = 7.3 Hz, HC(5'/4'), 1 H), 6.95 (br d, *J* = 8.3 Hz, 1 H, HC(6'/3')), 5.93 (q, *J* = 6.8 Hz, 1 H, HC(3)); 4.29 (br s, 2 H, H₂C(1)); 3.84 (s, 3 H, H₃C(7')); 2.07 (br s, 1 H, -OH); 1.55 (d, *J* = 6.8 Hz, 3 H, H₃C(4))

¹³C NMR: (125.6 MHz, CDCl₃)
 157.02, 138.93, 131.28, 128.85, 127.56, 125.30, 120.98, 111.12, 67.93 (C(1)), 55.77 (C(7')), 14.73 (C(4))

IR: (CHCl₃)
 3606 (w), 3012 (m), 2985 (m), 2960 (w), 2941 (w), 1599 (w), 1579 (m), 1491 (s), 1464 (m), 1435 (m), 1244 (s), 1103 (w), 1047 (w), 1028 (m), 980 (m)

MS: (EI, 70 eV)
 178 (M⁺, 100), 160 (27), 145 (30), 121 (32), 108 (23), 91 (13)

TLC: *R_f* 0.57 (Et₂O, SiO₂)

GC: t_R (*E*)-**3b** 5.11 min (98.4%), 5.39 min (1.5%) (Ultra-2, injector 225 °C, detector 300 °C, column 220 °C, 15 psi)

HRMS: C₁₁H₁₄O₂ (178.23)
 Calcd 178.0994
 Found 178.0991

Reaction of 4-Iodoanisole with Dioxadisilacyclohexane (Z)-2c. (*E*)-2-(4-Methoxyphenyl)-2-buten-1-ol ((*E*)-3d)

Following the General Procedure, (*Z*)-**2c** (333 mg, 1.65 mmol, 1.65 equiv), was dissolved in a solution of TBAF in dioxane (1.0 mL, 1.0 mmol, 1.0 equiv) and the mixture was stirred for 10 min at rt. 4-Iodoanisole (235 mg, 1.0 mmol, 1.0 equiv) was added followed by Pd(dba)₂ (30.0 mg, 0.052 mmol, 0.052 equiv). The mixture was stirred at ambient temperature for 20 min before another portion of TBAF (1.0 mL, 1.0 mmol, 1.0 equiv) was added. The mixture was stirred at ambient temperature for a total of 20 h and at 40 °C for another 3.5 h. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO₂, 11 g, pentane/Et₂O, 1/0 9/1). Removal of the solvent and Kugelrohr distillation of the resulting oil afforded 90 mg (50%) of (*E*)-**3d** as a colorless oil.⁶

Data for (*E*)-3d:

bp: 105 °C (0.02 mmHg, ABT)

¹H NMR: (400 MHz, CDCl₃)
 7.19 (dt, *J* = 2.5, 8.8 Hz, 2 H, HC(2')); 6.93 (dd, *J* = 2.5, 8.8 Hz, 2 H, HC(3')); 5.81 (q, *J* = 6.8 Hz, 1 H, HC(3)); 4.32 (t, *J* = 1.2 Hz, 2 H, H₂C(1)); 3.84 (s, 3 H, H₃C(5')); 1.90 (dt, *J* = 1.0, 6.8 Hz, 3 H, H₃C(4)); 1.59 (broad, 1 H, OH)

¹³C NMR: (100 MHz, CDCl₃)
 158.85, 140.43, 130.61, 130.07.56, 123.34, 114.01, 68.48 (C(1)), 55.49 (C(5')), 14.68 (C(4))

GC: t_R (*E*)-**3d** 5.92 min (97.3%), 5.31 min (2.7%) (Ultra-2, injector 225 °C, detector 300 °C, column 220 °C, 15 psi)

Reaction of 4-Iodoacetophenone with Dioxadisilacyclohexane (Z)-2c. 1-[(4-[1-(2-Hydroxymethyl)-(Z)-1-propenyl)]phenyl]ethanone ((E)-3e)

Following the General Procedure, (Z)-2c (333 mg, 1.41 mmol, 1.1 equiv) was dissolved in a solution of TBAF in THF (1.0 mL, 1.0 mmol, 1.0 equiv) and the mixture was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol, 1.0 equiv) was added in two portions over 1-h intervals and Pd(dba)₂ (30 mg, 0.051 mmol, 0.050 equiv) was added following the first portion of iodide. The mixture was stirred at rt for a total of 5.5 h before another portion of TBAF (1.0 mL) was added. The stirring was continued at ambient temperature for another 17 h and at 40 °C for 10 h. The crude mixture was then loaded onto 3 g of silica gel and was purified by column chromatography (SiO₂, 15 g, pentane/Et₂O, 1/0 10/1 5/1 3/1 2/1). Removal of the solvent and Kugelrohr distillation of the resulting oil and subsequent distillation afforded 123 mg (64%) of (E)-3e as a colorless oil.

Data for (E)-3e:

bp: 135 °C (0.2 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.95 (d, *J* = 8.4 Hz, 2 H, HC(3'')); 7.34 (dd, *J* = 8.4 Hz, 2 H, HC(2'')); 5.90 (q, *J* = 7.1 Hz, 1 H, HC(3)); 4.34 (t, *J* = 1.1 Hz, 2 H, H₂C(1)); 2.60 (s, 3 H, H₃C(6'')); 2.58 (t, *J* = 2.1 Hz, 1 H, OH); 1.64 (dt, *J* = 1.1 Hz, 3 H, H₃C(4))

¹³C NMR: (125.6 MHz, CDCl₃)

198.28 (C(5'')), 144.06, 140.41, 135.95, 129.24, 128.63, 125.17, 67.91 (C(1)), 26.82, (C(6'')), 14.70 (C(5))

IR: (CHCl₃)

3606 (w), 3026 (w), 3012 (m), 2920 (w), 1680 (s), 1604 (m), 1402 (m), 1360 (m), 1269 (s), 1230 (m), 1184 (w), 1074 (w), 984 (m), 958 (w), 850 (w)

MS: (EI, 70 eV)

190 (M⁺, 82), 175 (100), 157 (8), 147 (20), 129 (18), 83 (27)

TLC: *R_f* 0.40 (Et₂O, SiO₂)

GC: t_R (*E*)-**3e** 7.88 min (98.0%), 9.18 min (1.4%), 8.44 min (0.4%), 5.27 min (0.2%)
(Ultra-2, injector 225 °C, detector 220 °C, column 220 °C, 15 psi)

HRMS: $C_{13}H_{16}O_2$ (190.24)
Calcd 190.0994
Found 190.0997

Reaction of Methyl 2-Iodobenzoate with Dioxadisilacyclohexane (*Z*)-2c**. 3,4-Dihydro-4-*(E)*-ethylidene-1H-2-benzopyran-1-one ((*E*)-**3f**)**

Following the General Procedure, (*Z*)-**2c** (340 mg, 1.68 mmol, 1.68 equiv), was dissolved in a solution of TBAF in dioxane (1.0 mL, 1.0 mmol, 2.0 equiv) and the mixture was stirred for 10 min at rt. Methyl 2-iodobenzoate (264 mg, 1.01 mmol, 1.0 equiv) was added followed by $Pd(dba)_2$ (43.0 mg, 0.075 mmol, 0.074 equiv) was then added. After stirring at ambient temperature for 1 h, to the mixture was added another portion of TBAF (1.0 mL, 1.0 mmol, 1.0 equiv). The mixture was stirred at ambient temperature for a total of 22 h and at 35 °C for 13 h, then more siloxane (30 mg, 0.15 mmol, 0.15 equiv) and $Pd(dba)_2$ (20 mg, 0.035 mmol, 0.035 equiv) were added. The mixture was stirred at 35 °C for 10 h before it was loaded onto 2 g of silica gel and was purified by column chromatography (SiO_2 , 14 g, pentane/ether, 1/0 20/1). Kugelrohr distillation of resulting yellow oil afforded 85 mg (49%) of (*E*)-**3f** as a colorless oil.

Data for (*E*)-3f**:**

bp: 135 °C (0.2 mmHg, ABT)

1H NMR: (400 MHz, $CDCl_3$)
8.11 (md, $J = 8.6$ Hz, 1 H, HC(4'/5')); 7.62-7.58 (m, 2H); 7.46 (ddd, $J = 2.0, 7.6.6, 7.8$ Hz, 1 H), 5.71 (d, $J = 1.0$ Hz, 1 H, $H_2C(3)$); 5.38 (d, $J = 1.5$ Hz, 1 H, $H_2C(3)$); 5.20 (qt, $J = 1.2, 6.6$ Hz, 1 H, HC(5)); 1.59 (d, $J = 6.6$ Hz, 3 H, $H_3C(6)$)

^{13}C NMR: (125.6 MHz, $CDCl_3$)
164.81 (C(1)), 140.11, 136.99, 134.30, 130.36, 129.44, 124.14, 123.81, 113.09, 77.49 (C(3)), 20.20 (C(6))

IR: ($CHCl_3$)

3039 (w), 3037 (w), 3035 (w), 3027 (w), 3012 (w), 2991 (w), 1718 (s), 1604 (w), 1461 (w), 1363 (w), 1338 (m), 1271 (s), 1234 (m), 1122 (s), 1074 (m), 916 (w)

MS: (EI, 70 eV)

(174, M⁺, 15), 159 (17), 132 (53), 103 (25), 84 (100), 77 (13)

TLC: R_f 0.25 (pentane/Et₂O, 7/3, SiO₂)

GC: t_R (E)-**3f**, 7.0 min (98.5%); 12.48 min (0.7%) (Ultra-2, injector 225 °C, detector 220 °C, column 220 °C, 15 psi)

HRMS: C₁₂H₁₆O₂ (174.26)

Calcd 174.0681

Found 174.0678

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