Sequential Ring-Closing Metathesis and Silicon-Assisted Cross-Coupling Reactions: Stereocontrolled Synthesis of Highly Substituted Unsaturated Alcohols

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SUPPORTING INFORMATION

General Experimental

All reactions were performed in oven-dried (140 °C) or flame-dried glassware under an inert atmosphere of dry Ar or N_2. The following reaction solvents were distilled from the indicated drying agents: diethyl ether (Na, benzophenone), THF (Na, benzophenone), CH_2Cl_2 (P_2O_5), benzene (Na), toluene (Na), methanol ($Mg(OMe)_2$), triethylamine (CaH_2). *n*-Butyllithium solutions were titrated following the method of Gilman[1]. Brine refers to a saturated aqueous solution of NaCl. Grignard solutions were titrated using 2,2'-phenanthroline as an indicator[2]. Kugelrohr distillations were performed on a Büchi GKR-50 Kugelrohr; boiling points (bp) corresponding to uncorrected air-bath temperatures (ABT). All reaction temperatures correspond to internal temperatures measured by Teflon-coated thermocouples unless otherwise noted.

^{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) and residual acetone (δ 2.04 ppm, ^{1}H; δ 29.8 ppm, ^{13}C).

Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), 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 or aluminum oxide, basic gel plates with QF-254 indicator. Visualization was accomplished with UV light and/or Iodide. Diethyl ether was of reagent grade and used as received; other solvents for chromatography and filtration were technical grade and distilled from the indicated drying agents: hexane and pentane ($CaCl_2$); CH_2Cl_2 ($CaCl_2$); ethyl acetate (K_2CO_3). Column chromatography was performed using EM Science 230-400-mesh silica gel or Aldrich 150-mesh aluminum oxide, activated, basic, Brockmann I.

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 or Ultra-2 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.

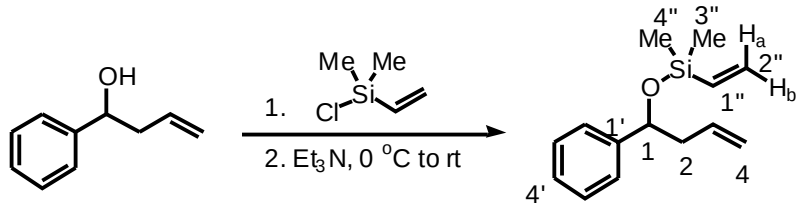
All commercial reagents were purified by distillation or recrystallization prior to use. A 1.0 M solution of tetrabutylammonium fluoride in THF was prepared from solid tetrabutylammonium fluoride trihydrate (TBAF•$3H_2O$, Fluka) and distilled THF in a volumetric flask and was stored in a Schlenk bottle. Palladium bis(dibenzylideneacetone) ($Pd(dba)_2$) was purchased from Jansen and used without purification. π-Allylpalladium chloride dimer $[allylPdCl]_2$ was purchased from ACROS and was recrystallized from benzene prior to use.

Literature Preparations

The following compounds were prepared by literature methods: 1-phenyl-3-buten-1-ol,[3] 1-phenyl-2-propen-1-ol,[4] 1-phenyl-4-penten-1-ol[5] Schrock's catalyst[6] (2,6-diisopropylphenyl-imidoneophylidenemolybdenum(VI) bis(hexafluoro-*t*-butoxide).

Experimental Procedures.

Preparation of Dimethyl[(1-phenyl-3-butenyl)oxy]vinylsilane (3).



3

In a 50-mL flask was placed 1-phenyl-3-buten-1-ol (3.19 g, 21.5 mmol) and Et_3N (4.48 mL, 32.25 mmol, 1.5 equiv) in CH_2Cl_2 (30 mL) under N_2 atmosphere at 0 °C (ice bath temperature). To the mixture was added dropwise with chlorodimethylvinylsilane (3.86 mL, 28.0 mmol, 1.2 equiv). The mixture was allowed to warm to room temperature and was stirred for 2 h. The mixture was then poured to ice water (30 mL) and was extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent was removed by rotary evaporation. The residue was distilled under reduced pressure to afford 4.59 g (92%) of **3** as a colorless liquid.

Analytical Data for **3**:

bp: 74-75 °C (0.1 mmHg)

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

7.38-7.26 (m, 5 H, 2 x HC(2'), 2 x HC(3'), HC(4')), 6.11 (dd, *J* = 19.8, 14.9, 1 H, HC(1")), 6.00 (dd, *J* = 14.9, 4.4, 1 H, H_bC(2")), 5.80-5.78 (m, 1 H, HC(3)), 5.77 (dd, *J* = 20.0, 4.4, 1 H, H_aC(2")), 5.11-5.05 (m, 2 H, H_2C(4)), 4.74 (dd, *J* = 7.6, 5.5, 1 H, HC(1)), 2.59-2.43 (m, 2 H, H_2C(2)), 0.18 (s, 3 H, CH_3), 0.13 (s, 3 H, CH_3).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

144.6 (C(1')), 137.7 (C(1")), 135.1 (C(3)), 133.0 (C(2")), 128.0 (2 C, C(3')), 127.0 (C(4')), 126.0 (2 C, C(2')), 116.9 (C(4)), 75.0 (C(1)), 45.0 (C(2)), -1.5, -1.7.

IR: (NaCl)

2960 (s), 1641 (m), 1407 (m), 1253 (s), 1087 (s), 1068 (s), 1009 (s), 916 (s), 836 (s), 785 (s).

MS: (CI, 130 eV)

233 (4, M^++1), 217 (34), 205 (35), 191 (100), 155 (23), 131 (37), 85 (19).

TLC: R_f 0.13 (silica gel, hexane, PMA)

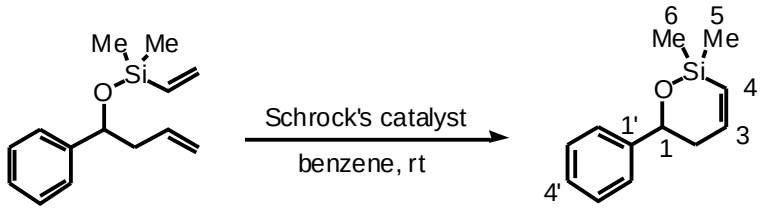
GC: t_R 11.43 min (U-2, 150 °C, 15 psi)

Analysis:	$C_{14}H_{20}OSi$	(232.40)	
	Calculated:	C: 72.36;	H: 8.67%
	Found:	C: 72.22;	H: 8.56%

General Procedure I. Molybdenum-Catalyzed Ring-Closing Metathesis of 3 or 7.

Into a flame-dried, 25-mL flask was placed freshly distilled benzene which was then moved into a dry box. Schrock's catalyst (0.05-0.08 equiv) and compound **3** or **7** (1.0 equiv) were added sequentially to the flask. The yellow-brown solution was stirred at room temperature in the dry box. The mixture was monitored by ^{1}H-NMR analysis. When the reaction was complete, the solvent was removed by rotary evaporation to give a brown residue, which was filtered through a short column of silica gel which was further eluted with hexane/EtOAc, 49/1. The filtrate was concentrated followed by Kugelrohr distillation to afford the product.

Ring-Closing Metathesis of 3. Preparation of 2,2-Dimethyl-6-phenyl-1-oxa-2-silacyclohex-3-ene (4).



3 **4**

Following General Procedure I, benzene (10 mL), Schrock's catalyst (38 mg, 0.05 mmol, 0.05 equiv), and **3** (232 mg, 1.0 mmol) were combined and the mixture was stirred at room temperature for 1 h in the dry box. After removal of the solvent by rotary evaporation, the residue was filtered through a short column of silica gel which was eluted with 100 mL of hexane/EtOAc, 49/1. The filtrate was concentrated followed by Kugelrohr distillation to afford 193 mg (95%) of **4** as a colorless liquid.

Analytical Data for **4**:

bp: 95-100 °C (0.4 mmHg ABT)

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

7.43 (dd, *J* = 8.8, 1.6, 2 H, 2 x HC(2')), 7.37 (td, *J* = 8.8, 1.6, 2 H, 2 x HC(3')), 7.28 (tt, *J* = 8.8, 1.6, 1 H, HC(4')), 6.86 (ddd, *J* = 14.0, 6.0, 2.4, 1 H, HC(3)), 5.88 (ddd, *J* = 14.0, 2.8, 0.8, 1 H, HC(4)), 5.01 (dd, *J* = 10.0, 3.6, 1 H, HC(1)), 2.43-2.38 (m, 2 H, H_2C(2)), 0.3 (s, 3 H, CH_3), 0.28 (s, 3 H, CH_3).

^{13}C NMR: (100.6 MHz, $CDCl_3$)
147.0 (C(3)), 144.4 (C(1')), 128.3 (2 C, C(3')), 127.4 (C(4)), 127.2 (C(4')), 125.6 (2 C, C(2')), 73.3 (C(3)), 39.0 (C(4)), -0.2, -0.6.

IR: (NaCl)
1587 (s), 1521 (s), 1064 (s), 957 (s), 837 (s), 789 (s).

MS: (EI, 70 eV)
204 (37, M^+), 189 (7), 130 (100), 98 (35), 83 (22).

TLC: R_f 0.15 (silica gel, hexane/EtOAc, 49/1, PMA)

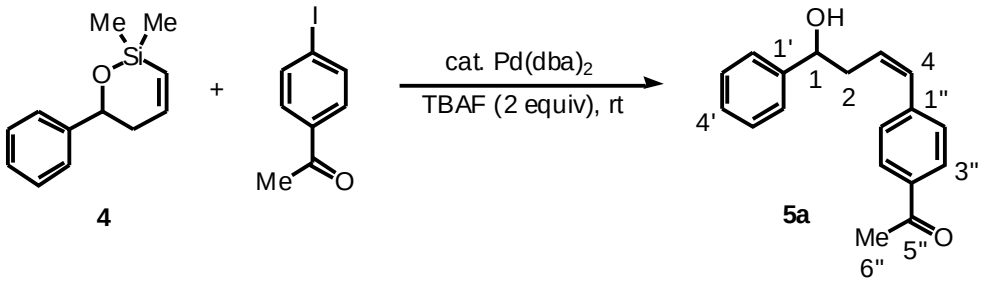
GC: t_R 15.20 min (HP-5, 150 °C, 15 psi)

Analysis: $C_{12}H_{16}OSi$ (204.35)
Calculated: C: 70.53; H: 7.89%
Found: C: 70.34; H: 7.96%

General Procedure II. Palladium-Catalyzed Cross-Coupling of 4 or 8 with Aryl or Alkenyl Halides.

Substrate **4** or **8** (1.1 equiv) was dissolved in a solution of TBAF (1.0 M in THF, 2.0 equiv) under an Ar atmosphere at ambient temperature. After 2 min, aryl or alkenyl halide (1.0 equiv) and the palladium catalyst (0.03-0.1 equiv) were then added sequentially. The reaction was monitored by TLC analysis. When the halide was consumed, 2 mL of EtOAc/hexane, 7/3 were added. The mixture was filtered through a short column of silica gel, which was then eluted with EtOAc/hexane, 7/3 (150-200 mL). The filtrate was concentrated by rotary evaporation to give a crude product, which was purified by silica gel chromatography.

Coupling Reaction of 4 with 4-Iodoacetophenone. Preparation of 1-{4-[(*Z*)-4-hydroxy-4-phenyl-1-butenyl]phenyl}ethanone (5a).



4

Following General Procedure II, **4** (225 mg, 1.1 mmol, 1.1 equiv), a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv), 4-iodoacetophenone (246 mg, 1.0 mmol) and

$Pd(dba)_2$ (28.7 mg, 0.05 mmol, 0.05 equiv) were combined. The mixture was stirred at room temperature for 10 min and then 2 mL of EtOAc/hexane, 7/3 were added. The mixture was filtered through a short column of silica gel which was eluted with 150 mL of EtOAc/hexane, 7/3. The filtrate was concentrated to give a crude product which was purified by chromatography (silica gel, hexane/EtOAc, 8/2 to 7/3) to afford 240 mg (90%) of **5a** as a pale yellow (non-distillable) oil.

Analytical Data for **5a**:

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

7.88 (d, *J* = 8.2, 2 H, 2 x HC(3")), 7.36-7.27 (m, 7 H, 2 x HC(2'), 2 x HC(3'), HC(4'), 2 x HC(2")), 6.58 (d, *J* = 12.0, 1 H, HC(4)), 5.86 (dt, *J* = 11.6, 7.2, 1 H, HC(3)), 4.82 (m, 1 H, HC(1)), 2.89-2.70 (m, 2 H, H_2C(2)), 2.58 (s, 3 H, H_3C(6")), 2.27 (s, 1 H, HO).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.8 (C(5")), 143.8 (C(1')), 142.0 (C(1")), 135.1 (C(4")), 130.4 ((3)), 130.3 (C(4)), 128.7 (2 C, C(2")), 128.4 (2 C, (C(3')), 128.2 (2 C, C(3")), 127.6 (C(4')), 125.7 (2 C, C(2')), 73.8 (C(1)), 38.2 (C(2)), 26.4 (C(6")).

IR: (NaCl)

3439 (s), 3025 (s), 1677 (s), 1602 (s), 1400 (s), 1358 (s), 1270 (s), 1182 (s), 1058 (s), 960 (m), 854 (s), 759 (s).

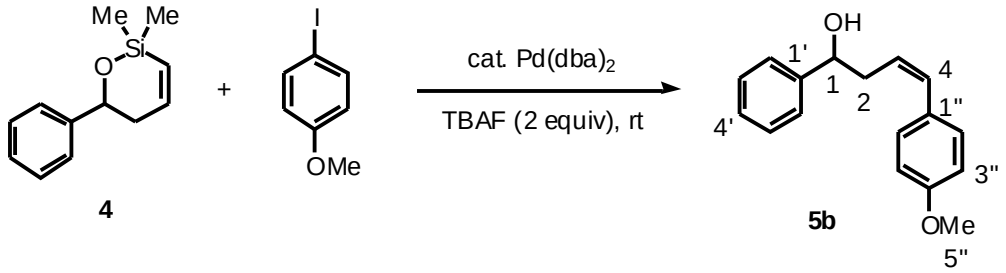
MS: (FAB)

267 (32, M^++1), 249 (74), 205 (24), 154 (100), 136 (80).

HRMS: calcd for $C_{18}H_{17}O_2$ (M^+-H): 265.1228; found: 265.1229

TLC: R_f 0.18 (silica gel, hexane/EtOAc, 4/1, PMA)

Coupling Reaction of 4 with 4-Iodoanisole. Preparation of (*Z*)-1-Phenyl-4-(4-methoxyphenyl)-3-buten-1-ol (5b).



4 **5b**

Following General Procedure II, **4** (225 mg, 1.1 mmol, 1.1 equiv), a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv), 4-iodoanisole (234 mg, 1.0 mmol) and $Pd(dba)_2$

(17.2 mg, 0.03 mmol, 0.03 equiv) were combined. The mixture was stirred at room temperature for 30 min and then 2 mL of EtOAc/hexane, 7/3 were added. The mixture was filtered through a short column of silica gel which was eluted with 150 mL of EtOAc/hexane, 7/3. The filtrate was concentrated to give a crude product which was purified by chromatography (silica gel, hexane/EtOAc, 9/1 to 4/1) to afford 234 mg (92%) of **5b** as a pale yellow (non-distillable) oil.

Analytical Data for **5b**:

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

7.39-7.28 (m, 5 H, 2 x HC(2'), 2 x HC(3'), HC(4')), 7.24 (dt, *J* = 8.4, 1.6, 2 H, 2 x HC(2")), 6.88 (dt, *J* = 8.8, 2.0, 2 H, 2 x HC(3")), 6.53 (d, *J* = 11.6, 1 H, HC(4)), 5.65 (dt, *J* = 11.6, 7.2, 1 H, HC(3)), 4.81 (t, *J* = 5.6, 1 H, HC(1)), 3.81 (s, 3 H, H_3C(5")), 2.87 (dtd, *J* = 15.2, 8.0, 1.6, 1 H, HC(2)), 2.75 (dddd, *J* = 15.2, 6.8, 5.2, 1.6, 1 H, HC(2)), 2.21 (s, 1 H, HO).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

158.3 (C(4")), 144.0 (C(1')), 131.0 (C(4)), 130.0 (2 C, C(2")), 129.7 (C(1")), 128.4 (2 C, C(3')), 127.6 (C(4')), 126.2 (C(3)), 125.8 (2 C, C(2')), 113.5 (2C, C(3")), 74.1 (C(1)), 55.2 (C(5")), 38.2 (C(2)).

IR: (NaCl)

3432 (s), 1607 (s), 1510 (s), 1249 (s), 1175 (s), 1034 (s), 841 (s), 701 (s).

MS: (FAB)

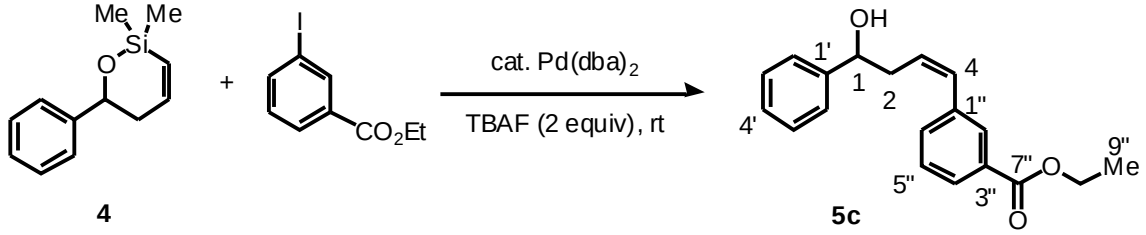
255 (9, M^++1), 254 (21, M^+), 237 (84), 148 (100), 107 (33).

TLC: R_f 0.17 (silica gel, hexane/EtOAc, 4/1, PMA)

Analysis: $C_{17}H_{18}O_2$ (254.33)

Calculated:	C: 80.28;	H: 7.13%
Found:	C: 80.20;	H: 7.26%

Coupling Reaction of 4 with Ethyl 3-Iodobenzoate. Preparation of Ethyl 3-[(*Z*)-4-hydroxy-4-phenyl-1-butenyl]benzoate (5c).



4 **5c**

Following General Procedure II, **4** (225 mg, 1.1 mmol, 1.1 equiv), a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv), ethyl 3-iodobenzoate (276 mg, 1.0 mmol) and $Pd(dba)_2$ (17.2 mg, 0.03 mmol, 0.03 equiv) were combined. The mixture was stirred at room temperature for 30 min and then 2 mL of EtOAc/hexane, 7/3 were added. The mixture was filtered through a short column of silica gel which was eluted with 150 mL of EtOAc/hexane, 7/3. The filtrate was concentrated to give a crude product which was purified by chromatography (silica gel, hexane/EtOAc, 9/1 to 4/1) to afford 276 mg (93%) of **5c** as a pale yellow (non-distillable) oil.

Analytical Data for **5c**:

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

7.96 (s, 1 H, HC(2")), 7.90 (dd, *J* = 7.6, 1.2, 1 H, HC(4")), 7.43 (d, *J* = 7.6, 1 H, HC(6")), 7.39-7.26 (m, 6 H), 6.58 (d, *J* = 11.6, 1 H, HC(4)), 5.80 (dt, *J* = 11.6, 7.2, 1 H, HC(3)), 4.82 (dd, *J* = 7.6, 5.6, 1 H, HC(1)), 4.37 (q, *J* = 7.2, 2 H, H_2C(8")), 2.83 (dtd, *J* = 15.2, 7.6, 1.6, 1 H, HC(2)), 2.76-2.69 (m, 1 H, HC(2)), 2.26 (br s, 1 H, HO), 1.39 (t, *J* = 7.2, 3 H, H_3C(9")).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

166.6 (C(7")), 143.8 (C(1')), 137.3 (C(1")), 132.9 (C(6")), 130.6 (C(4)), 130.3 (C(3")), 129.8 (C(2")), 129.0 (C(3), 128.4 (2 C, C(3')), 128.2 (C(5")), 127.8 (C(4")), 127.6 (C(4')), 125.8 (2 C, C(2')), 74.0 (C(1)), 61.0 (C(8")), 38.0 (C(2)), 14.3 (C(9")).

IR: (NaCl)

3465 (s), 1718 (s), 1602 (m), 1280 (s), 1188 (s), 1106 (s), 759 (s), 701 (s).

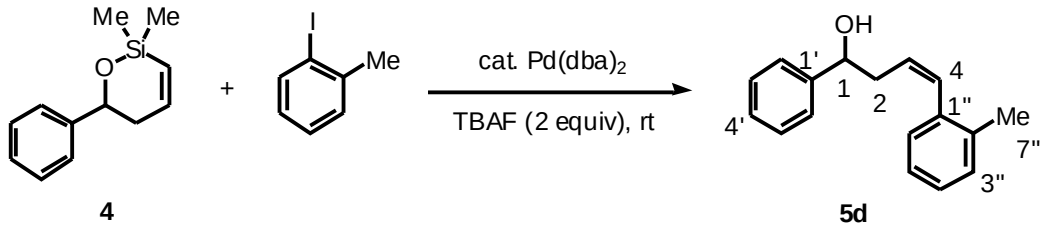
MS: (EI, 70 eV)

296 (0.2, M^+), 278 (2), 251 (5), 205 (3), 191 (100), 117 (54), 107 (39).

TLC: R_f 0.34 (silica gel, hexane/EtOAc, 3/1, PMA)

Analysis:	$C_{19}H_{20}O_3$	(296.37)	
	Calculated:	C: 76.99;	H: 6.81%
	Found:	C: 76.85;	H: 6.75%

Coupling Reaction of 4 with 2-Iodotoluene. Preparation of (*Z*)-1-Phenyl-4-(2-methylphenyl)-3-buten-1-ol (5d).



4 **5d**

Following General Procedure II, **3** (225 mg, 1.1 mmol, 1.1 equiv), a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv), 2-iodotoluene (218 mg, 1.0 mmol) and $Pd(dba)_2$ (17.2 mg, 0.03 mmol, 0.03 equiv) were combined. The mixture was stirred at room temperature for 30 min and then 2 mL of EtOAc/hexane, 7/3 were added. The mixture was filtered through a short column of silica gel which was eluted with 150 mL of EtOAc/hexane, 7/3. The filtrate was concentrated to give a crude product which was purified by chromatography (silica gel, hexane/EtOAc, 9/1 to 4/1) to afford 212 mg (89%) of **5d** as a pale yellow (non-distillable) oil.

Analytical Data for **5d**:

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

7.37-7.27 (m, 5 H), 7.19-7.13 (m, 4 H), 6.61 (d, *J* = 11.6, 1 H, HC(4)), 5.79 (dt, *J* = 11.6, 7.2, 1 H, HC(3)), 4.76 (dd, *J* = 7.2, 6.0, 1 H, HC(1)), 2.74-2.58 (m, 2 H, H_2C(2)), 2.22 (s, 3 H, H_3C(7")), 2.06 (br s, 1 H, HO).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

143.8 (C(1')), 136.22, 136.17, 130.9, 129.7, 128.9, 128.4 (2 C, C(3')), 127.6, 127.5, 127.0, 125.9 (2 C, C(2')), 125.3, 74.1 (C(1)), 37.9 (C(2)), 19.8 (C(7")).

IR: (NaCl)

3381 (s), 1601 (m), 1486 (m), 1454 (s), 1056 (s), 756 (s), 700 (s).

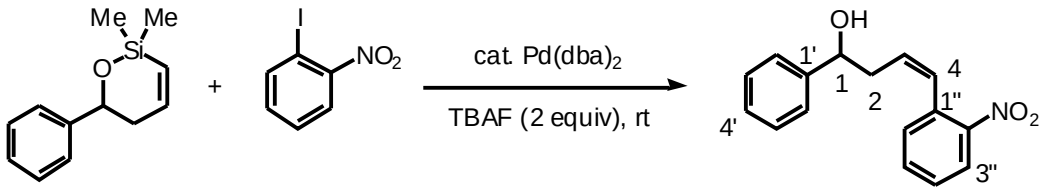
MS: (FAB)

239 (3, M^++1), 238 (4, M^+), 237 (14), 221 (100), 154 (59), 132 (46), 107 (90).

TLC: R_f 0.20 (silica gel, hexane/EtOAc, 17/3, PMA)

Analysis:	$C_{17}H_{18}O$	(238.33)	
	Calculated:	C: 85.67;	H: 7.61%
	Found:	C: 85.54;	H: 7.45%

Coupling Reaction of 4 with Ethyl 2-Iodo-1-nitrobenzene. Preparation of (*Z*)-1-Phenyl-4-(2-nitrophenyl)-3-buten-1-ol (5e).



4 **5e**

Following General Procedure II, **4** (225 mg, 1.1 mmol, 1.1 equiv), a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv), 2-iodo-1-nitrobenzene (249 mg, 1.0 mmol) and $Pd(dba)_2$ (17.2 mg, 0.03 mmol, 0.03 equiv) were combined. The mixture was stirred at room temperature for 90 min and then 2 mL of EtOAc/hexane, 7/3 were added. The mixture was filtered through a short column of silica gel which was eluted with 150 mL of EtOAc/hexane, 7/3. The filtrate was concentrated to give a crude product which was purified by chromatography (silica gel, hexane/EtOAc, 9/1 to 4/1) to afford 233 mg (86%) of **5e** as a pale yellow (non-distillable) oil.

Analytical Data for **5e**:

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

7.99 (d, *J* = 8.0, 1 H, HC(3")), 7.52 (t, *J* = 7.6, 1 H, HC(5")), 7.4 (t, *J* = 8.0, 1 H, HC(4")), 7.36-7.24 (m, 6 H), 6.82 (d, *J* = 11.6, 1 H, HC(4)), 5.87 (dt, *J* = 11.6, 8.0, 1 H, HC(3)), 4.74 (t, *J* = 7.2, 1 H, HC(1)), 2.63-2.47 (m, 2 H, H_2C(2)), 2.25 (br s, 1 H, HO).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

148.0 (C(2")), 143.5 (C(1')), 132.8 (C(5")), 132.4 (C(1")), 131.8 (C(6")), 129.3 (C(3)), 128.4 (2 C, C(3')), 128.3 (C(4)), 127.9 (C(4")), 127.6 (C(4')), 125.7 (2 C, C(2')), 124.5 (C(3")), 73.5 (C(1)), 38.0 (C(2)).

IR: (NaCl)

3551 (s), 3401 (s), 1607 (m), 1523 (s), 1345 (s), 1056 (m), 858 (m), 788 (m), 757 (s), 701 (s).

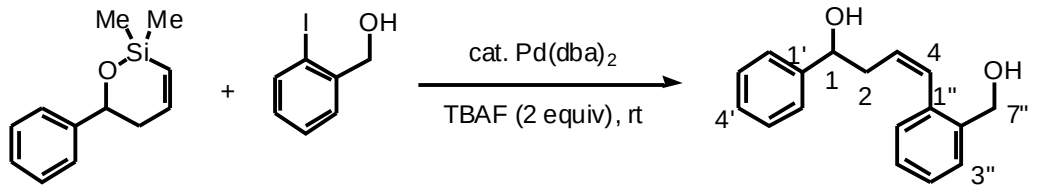
MS: (FAB)
270 (7, M^++1), 269 (7, M^+), 268 (16), 252 (62), 235 (30), 218 (27),206 (44), 162 (36), 145 (33), 117 (100), 107 (77).

TLC: R_f 0.19 (silica gel, hexane/EtOAc, 3/1, PMA)

Analysis: $C_{16}H_{15}NO_3$ (269.30)

Calculated:	C: 71.36	H: 5.61	N: 5.20%
Found:	C: 71.05;	H: 5.65	N: 5.20%

Coupling Reaction of 4 with Ethyl 2-Iodobenzyl Alcohol. Preparation of (*Z*)-1-Phenyl-4-(2-hydroxymethylphenyl)-3-buten-1-ol (5f).



4 **5f**

Following General Procedure II, **4** (225 mg, 1.1 mmol, 1.1 equiv), a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv), 2-iodobenzyl alcohol (234 mg, 1.0 mmol) and $Pd(dba)_2$ (28.7 mg, 0.05 mmol, 0.05 equiv) were combined. The mixture was stirred at room temperature for 180 min and then 2 mL of EtOAc/hexane, 7/3 were added. The mixture was filtered through a short column of silica gel which was eluted with 150 mL of EtOAc/hexane, 7/3. The filtrate was concentrated to give a crude product which was purified by chromatography (silica gel, hexane/EtOAc, 9/1 to 7/3) to afford 230 mg (90%) of **5f** as a colorless (non-distillable) oil.

Analytical Data for **5f**:

^{1}H NMR: (400 MHz, $CDCl_3$)
7.31-7.20 (m, 8 H), 7.10-7.08 (m, 1 H), 6.68 (d, *J* = 11.5, 1 H, HC(4)), 5.80 (ddd, *J* = 11.5, 8.0, 6.8, 1 H, HC(3)), 4.67 (dd, *J* = 7.6, 4.8, 1 H, HC(1)), 4.53 (d, *J* = 12.2, 1 H, HC(7")), 4.41 (d, *J* = 12.4, 1 H, HC(7")), 3.39 (br s, 2 H, HO), 2.59-2.44 (m, 2 H, H_2C(2)).

^{13}C NMR: (100.6 MHz, $CDCl_3$)
143.9 (C(1')), 138.5, 136.1, 129.8, 129.6, 129.4, 128.4, 128.2 (2 C, C(3')), 127.4 (C(4')), 127.21, 127.19, 125.6 (2 C, C(2')), 73.4 (C(1)), 62.9 (C(7")), 37.8 (C(2)).

IR: (NaCl)
3360 (s), 1602 (m), 1452 (m), 1041 (s), 1006 (s), 758 (s), 700 (s).

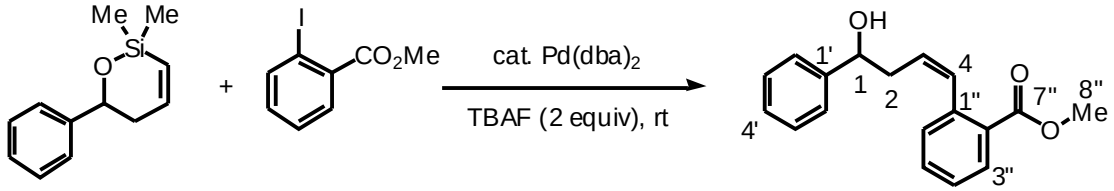
MS: (CI, 130 eV)
237 (9, M^++1−H_2O), 219 (22), 207 (54), 130 (42), 107 (15), 91 (100).

TLC: R_f 0.08 (silica gel, hexane/EtOAc, 7/3, PMA)

Analysis: $C_{17}H_{18}O_2$ (254.33)

Calculated:	C: 80.28;	H: 7.13%
Found:	C: 80.20;	H: 7.17%

Coupling Reaction of 4 with Methyl 2-Iodobenzoate. Preparation of Methyl 2-[(*Z*)-4-hydroxy-4-phenyl-1-butenyl]benzoate (5g).



4 **5g**

Siloxane **4** (225 mg, 1.1 mmol, 1.1 equiv) was dissolved in a solution of TBAF (1.0 M in THF, 2.0 mL, 2.0 mmol, 1.0 equiv) at ambient temperature. After 2 min, methyl 2-iodobenzoate (262 mg, 1.0 mmol) and $Pd(dba)_2$ (17.2 mg, 0.03 mmol, 0.03 equiv) were then added sequentially. The mixture was stirred at room temperature for 180 min and another portion of $Pd(dba)_2$ (11.5 mg, 0.02 mmol, 0.02 equiv) was added. The mixture was stirred for another 180 min at room temperature (total: 360 min) and then 2 mL of EtOAc/hexane, 7/3 were added. The mixture was filtered through a short column of silica gel which was eluted with 150 mL of EtOAc/hexane, 7/3. The filtrate was concentrated to give a crude product which was purified by chromatography (silica gel, hexane/EtOAc, 9/1 to 4/1) to afford 237 mg (84%) of **5g** as a pale yellow (non-distillable) oil.

Analytical Data for **5g**:

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

7.95 (dd, *J* = 8.0, 1.5, 1 H, HC(3")), 7.45 (td, *J* = 7.5, 1.5, 1 H, HC(5")), 7.34-7.23 (m, 6 H), 7.21 (d, *J* = 7.5, 1 H, HC(6")), 6.98 (d, *J* = 11.5, 1 H, HC(4)), 5.78 (ddd, *J* = 11.5, 8.5, 7.5, 1 H, HC(3)), 4.74 (dt, *J* = 8.0, 4.5, 1 H, HC(1)), 3.87 (s, 3 H, HC(8")), 2.72 (m, 1 H, OH), 2.61 (dtd, *J* = 14.0, 8.0, 1.5, 1 H, H_aC(2)), 2.55 (dddd, *J* = 14.0, 6.5, 4.5, 1.5, 1 H, H_bC(2)).

^{13}C NMR: (126 MHz, $CDCl_3$)

167.8 (C(7")), 143.8 (C(1')), 138.7 (C(1")), 132.7 (C(4)), 131.8 (C(5")), 130.7 (C(6")), 130.4 (C(3")), 129.0 (C(2")), 128.2 (2 C, C(3')), 127.3 (C(4')), 126.9 (C(3)), 126.8 (C(4")), 125.7 (2 C, C(2')), 73.4 (C(1)), 52.0 (C(8")), 38.0 (C(2)).

IR: (NaCl)

3475 (m), 1712 (s), 1450 (s), 1434 (s), 1295 (s), 1267 (s), 1079 (s), 757 (s), 701 (s).

MS: (FAB)

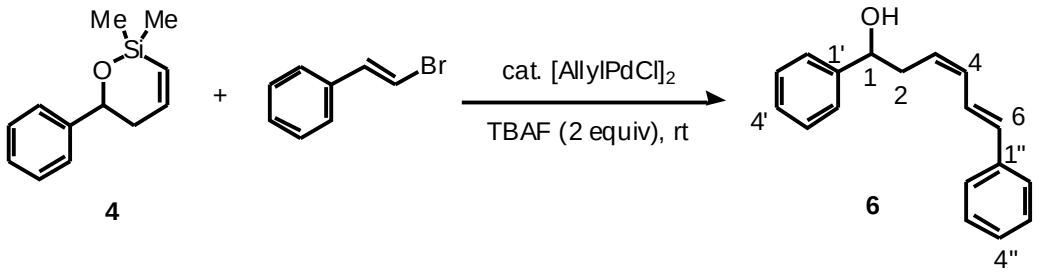
283 (15, M^++1), 282 (6, M^+), 265 (90), 133 (100), 215 (42), 176 (41), 154 (79), 136 (59).

TLC: R_f 0.18 (silica gel, hexane/EtOAc, 3/1, PMA)

Analysis: $C_{18}H_{18}O_3$ (282.34)

Calculated:	C: 76.57;	H: 6.43%
Found:	C: 76.63;	H: 6.40%

Coupling Reaction of 4 with (*E*)-2-Bromostyrene. Preparation of (3*Z*,5*E*)-1,6-Diphenyl-3,5-hexadien-1-ol (6).



4 **6**

Following General Procedure II, **4** (225 mg, 1.1 mmol, 1.1 equiv), a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv), (*E*)-2-bromostyrene (183 mg, 1.0 mmol) and $[allylPdCl]_2$ (9.2 mg, 0.025 mmol, 0.025 equiv) were combined. The mixture was stirred at room temperature for 5 h and then 2 mL of EtOAc/hexane, 7/3 were added. The mixture was filtered through a short column of silica gel which was eluted with 150 mL of EtOAc/hexane, 7/3. The filtrate was concentrated to give a crude product which was purified by chromatography (silica gel, hexane/EtOAc, 19/1 to 17/3) to afford 194 mg (78%) of **6** as a pale yellow (non-distillable) oil.

Analytical Data for **6**:

^{1}H NMR: (500 MHz, CD_3COCD_3)

7.47-7.42 (m, 4 H), 7.33-7.28 (m, 4 H), 7.22-7.19 (m, 2 H), 7.15 (dd, *J* = 15.5, 11.0, 1 H, HC(5)), 6.54 (d, *J* = 15.5, 1 H, HC(6)), 6.21 (t, *J* = 11.0, 1 H, HC(4)), 5.60 (dt, *J* = 10.5, 7.5, 1 H, HC(3)), 4.77 (q, *J* = 6.0, 1 H, HC(1)), 4.34 (dd, *J* = 4.0, 2.0, 1 H, HO), 2.82-2.70 (m, 2 H, H_2C(2)).

^{13}C NMR: (126 MHz, CD_3COCD_3)

146.6, 138.5, 133.2, 131.2, 129.8, 129.4 (2 C), 128.8 (2 C), 128.2, 127.7, 127.2 (2 C), 126.8 (2 C), 125.4, 74.0 (C(1)), 38.8 (C(2)).

IR: (NaCl)

3392 (m), 3027 (m), 1602 (w), 1492 (m), 1450 (m), 1407 (m), 1049 (m), 985 (m), 946 (m), 757 (m), 730 (s), 700 (s)

MS: (EI, 70eV)

250 (4, M^+), 232 (33), 141 (44), 128 (70), 115 (65), 107 (53), 91 (32), 77 (100).

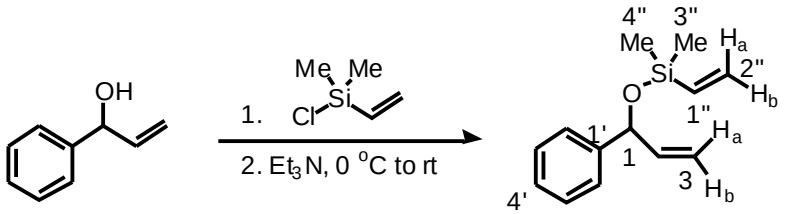
TLC: R_f 0.13 (silica gel, hexane/EtOAc, 9/1, PMA)

Analysis: $C_{18}H_{18}O$ (250.34)

Calculated: C: 86.36; H: 7.25%

Found: C: 86.12; H: 7.25%

Preparation of Dimethyl[(1-phenyl-2-propenyl)oxy]vinylsilane (7a).



7a

In a 25-mL flask was placed 1-phenyl-2-propen-1-ol (1.34 g, 10.0 mmol) and Et_3N (2.08 mL, 15.0 mmol, 1.5 equiv) in CH_2Cl_2 (10 mL) under N_2 atmosphere at 0 °C (internal). To the solution was added dropwise chlorodimethylvinylsilane (1.66 mL, 12.0 mmol, 1.2 equiv). The solution was allowed to warm to room temperature and was stirred for 1 h. The mixture was then poured to ice water (30 mL) and was extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent was removed by rotary evaporation. The residue was purified by chromatography (silica gel, hexane/EtOAc, 49/1) followed Kugelrohr distillation under reduced pressure to afford 1.96 g (90%) of **7a** as a colorless liquid.

Analytical Data for **7a**:

bp: 105-110 °C (1.0 mmHg ABT)

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

7.37-7.25 (m, 5 H, 2 x HC(2'), 2 x HC(3'), HC(4')), 6.14 (dd, *J* = 20.0, 14.8, 1 H, HC(1")), 6.02 (dd, *J* = 14.8, 4.0, 1 H, $H_bC(2")$), 5.98 (ddd, *J* = 16.8, 10.0, 6.0, 1 H, HC(2)), 5.79 (dd, *J* = 20.0, 4.0, 1 H, $H_aC(2")$), 5.29 (dt, *J* = 17.2, 1.6, 1 H, $H_aC(3)$), 5.20 (d, *J* = 6.0, 1 H, HC(1)), 5.13 (dt, *J* = 10.0, 1.6, 1 H, $H_bC(3)$), 0.23 (s, 3 H, CH_3), 0.19 (s, 3 H, CH_3).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

143.2 (C(1')), 141.1 (C(2)), 137.6 (C(1")), 133.2 (C(2")), 128.2 (2 C, C(3')), 127.2 (C(4')), 126.2 (2 C, C(2')), 114.1 (C(3)), 75.9 (C(1)), -1.4 , -1.5.

IR: (NaCl)

2961 (s), 1595 (m), 1452 (m), 1407 (s), 1254 (s), 1125 (s), 1086 (s), 1063 (s), 1030 (s), 869 (s), 837 (s), 785 (s).

MS: (EI, 70 eV)

218 (11, M^+), 217 (13), 203 (31), 191 (29), 117 (100).

TLC: R_f 0.34 (silica gel, hexane/EtOAc, 49/1, PMA)

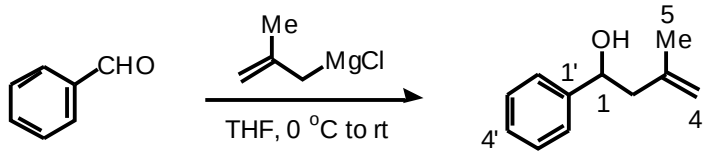
GC: t_R 10.96 min (HP-5, 150 °C, 15 psi)

Analysis: $C_{13}H_{18}OSi$ (218.37)

Calculated: C: 71.50; H: 8.31%

Found: C: 71.26; H: 8.31%

Preparation of 3-Methyl-1-phenyl-1-buten-1-ol.



To a solution of benzaldehyde (3.05 mL, 30 mmol) in THF (30 mL) was added 2-methylallylmagnesium chloride (0.8 M in THF, 45 mL, 36 mmol, 1.2 equiv) under N_2 at 0 °C (internal). The mixture was warmed to room temperature and was stirred for 1.5 h. The mixture was then poured into saturated aqueous NH_4Cl solution (30 mL) and was extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine (30 mL), then were dried (Na_2SO_4) and filtered. The solvent was removed by rotary evaporation and the residue was

purified by Kugelrohr distillation to afford 4.33 g (89%) of 3-methyl-1-phenyl-1-buten-1-ol as a colorless oil which gave spectroscopic data consistent with literature reported[7].

Analytical Data for **3-methyl-1-phenyl-1-buten-1-ol**:

bp: 85-90 °C (0.4 mmHg ABT)

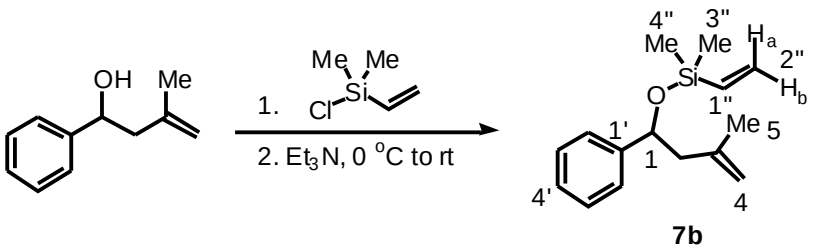
^{1}H NMR: (400 MHz, $CDCl_3$)

7.41-7.27 (m, 5 H, 2 x HC(2'), 2 x HC(3'), HC(4')), 4.94 (t, *J* = 1.6, 1 H, HC(4)), 4.87 (s, 1 H, HC(4)), 4.81 (dd, *J* = 7.2, 6.4, 1 H, HC(1)), 2.44 (d, *J* = 6.8, 2 H, H_2C(2)), 2.22 (d, *J* = 7.2, 1 H, HO), 1.81 (s, 3 H, H_3C(5)).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

144.0 (C(1')), 142.3 (C(3)), 128.3 (2 C, C(3')), 127.4 (C(4')), 125.7 (2 C, C(2')), 114.0 (C(4)), 71.3 (C(1)), 48.3 (C(2)), 22.3 (C(5)).

Preparation of Dimethyl[(1-phenyl-3-methyl-3-butenyl)oxy]vinylsilane (7b).



7b

In a 25-mL flask was placed 3-methyl-1-phenyl-3-buten-1-ol (2.43 g, 15.0 mmol) and Et_3N (3.13 mL, 22.5 mmol, 1.5 equiv) in CH_2Cl_2 (15 mL) under a N_2 atmosphere at 0 °C (internal). To the solution was added dropwise chlorodimethylvinylsilane (2.48 mL, 18.0 mmol, 1.2 equiv). The mixture was allowed to warm to room temperature and was stirred for 1 h. The mixture was then poured to ice water (30 mL) and the aqueous phase was extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent was removed by rotary evaporation. The residue was purified by chromatography (silica gel, hexane/EtOAc, 49/1) followed Kugelrohr distillation under reduced pressure to afford 3.32 g (90%) of **7b** as a colorless liquid.

Analytical Data for **7b**:

bp: 100-105 °C (0.8 mmHg ABT)

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

7.33-7.23 (m, 5 H, 2 x HC(2'), 2 x HC(3'), HC(4')), 6.07 (dd, *J* = 19.6, 14.8, 1 H, HC(1")), 5.97 (dd, *J* = 14.8, 4.4, 1 H, H_bC(2")), 5.73 (dd, *J* = 19.6, 4.4, 1 H, H_aC(2")), 4.81 (dd, *J* = 8.4, 5.2, 1 H, HC(1)), 4.79 (s, 1 H, HC(4)), 4.70 (d, *J* = 0.8, 1 H, HC(4), 2.49 (dd, *J* = 13.6, 8.0, 1 H, HC(2)), 2.34 (dd, *J* = 13.6, 5.2, HC(2)), 1.75 (s, 3 H, H_3C(5)), 0.13 (s, 3 H, CH_3), 0.08 (s, 3 H, CH_3).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

145.0 (C(1')), 142.4 (C(3)), 137.7 (C(1")), 132.9 (C(2")), 128.0 (2 C, (C(3')), 127.0 (C(4')), 126.0 (2 C, C(2')), 113.1 (C(4)), 74.2 (C(1)), 49.0 (C(2)), 23.0 (C(5)), -1.5, -1.7.

IR: (NaCl)

2964(s), 1649 (m), 1594 (m), 1453 (m), 1407 (m), 1253 (s), 1090 (s), 1070 (s), 1007 (m), 940 (s), 889 (s), 833 (s), 785 (s).

MS: (EI, 70 eV)

245 (1, M^+-1), 231 (14), 219 (11), 191 (100), 145 (20), 85 (10).

TLC: R_f 0.26 (silica gel, hexane/EtOAc, 49/1, PMA)

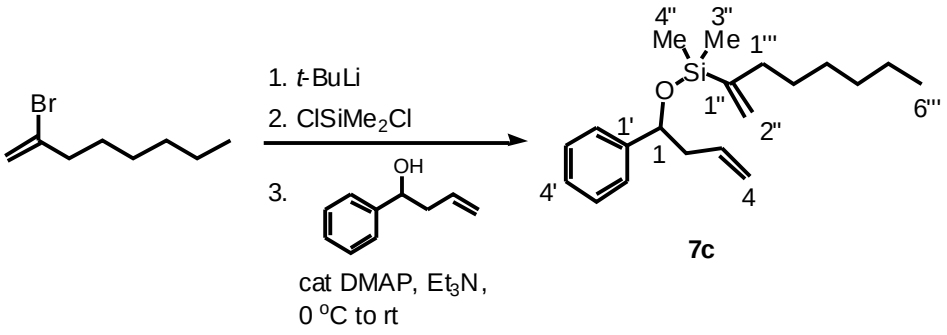
GC: t_R 16.72 min (HP-5, 150 °C, 15 psi)

Analysis: $C_{15}H_{22}OSi$ (246.43)

Calculated: C: 73.11; H: 9.00%

Found: C: 72.84; H: 9.05%

Preparation of (1-Phenyl-3-buten-1-yloxy)-(2-octenyl)dimethylsilane (7c).



To a solution of 2-bromo-1-octene (1.25 g, 6.6 mmol, 1.1 equiv) in Et_2O (7 mL) was added dropwise *t*-BuLi (1.5 M, 8.8 mL, 13.2 mmol, 2.2 equiv) under a N_2 atmosphere at –78 °C

(internal). The pale-yellow, cloudy mixture was stirred for 1 h at –78 °C (internal). The mixture was then added to a solution of dichlorodimethylsilane (1.82 mL, 15.0 mmol, 2.5 equiv) in Et_2O (10 mL) by cannula at –78 °C (internal). The mixture was allowed to warm to room temperature and was stirred for 2 h whereupon a white solid precipitated. After removal of solvent and excess dichlorodimethylsilane under reduced pressure, hexane (50 mL) was added and the solids were removed by Schlenk filtration. After removal of the solvent, the residue was dissolved in CH_2Cl_2 (5 mL). The solution was then added to a solution of 1-phenyl-3-buten-1-ol (888 mg, 6.0 mmol, 1.0 equiv), 4-dimethylaminopyridine (110 mg, 0.9 mmol, 0.15 equiv), and Et_3N (1.25 mL, 9.0 mmol, 1.5 equiv) in CH_2Cl_2 (10 mL) under N_2 atmosphere at 0 °C (internal). The mixture was allowed to warm to room temperature and was stirred for 2 h. The mixture was then poured to ice water (20 mL) and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent was removed by rotary evaporation. The residue was purified by chromatography (silica gel, hexane) followed Kugelrohr distillation under reduced pressure to afford 1.25 g (66%) of **7c** as a colorless liquid.

Analytical Data for **7c**:

bp: 125-130 °C (0.2 mmHg ABT)

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

7.33-7.21 (m, 5 H, 2 x HC(2'), 2 x HC(3'), HC(4')), 5.75 (ddt, *J* = 16.8, 10.0, 7.2, 1 H, HC(3)), 5.61 (dt, *J* = 2.8, 1.6, 1 H, HC(2")), 5.40 (d, *J* = 2.8, 1 H, HC(2")), 5.05-5.00 (m, 2 H, $H_2C(4)$), 4.67 (dd, *J* = 7.2, 5.6, 1 H, HC(1)), 2.51 (dt, *J* = 14.4, 7.2, 1 H, $H_aC(2)$), 2.41 (dtd, *J* = 13.6, 5.6, 1.2, 1 H, $H_bC(2)$), 2.08 (t, *J* = 7.4, 2 H, $H_2C(1'")$), 1.40-1.24 (m, 8 H, $H_2C(2'")$, $H_2C(3'")$, $H_2C(4'")$, $H_2C(5'")$), 0.90 (t, *J* = 6.4, 3 H, $H_3C(6'")$), 0.10 (s, 3 H, CH_3), 0.09 (s, 3 H, CH_3).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

150.7 (C(1")), 144.7 (C(1')), 135.1 (C(3)), 128.0 (2 C, C(3')), 127.0 (C(4')), 126.0 (2 C, C(2')), 125.5 (C(2")), 116.9 (C(4)), 75.0 (C(1)), 45.1 (C2)), 35.5 (C(1'")), 31.8, 29.9, 28.8, 22.7, 14.1 (C(6'")), -1.3, -1.6.

IR: (NaCl)

2957 (s), 2928 (s), 1641 (m), 1454 (m), 1252 (s), 1086 (s), 993 (m), 916 (s), 833 (s), 783 (s).

MS: (CI, 130 eV)

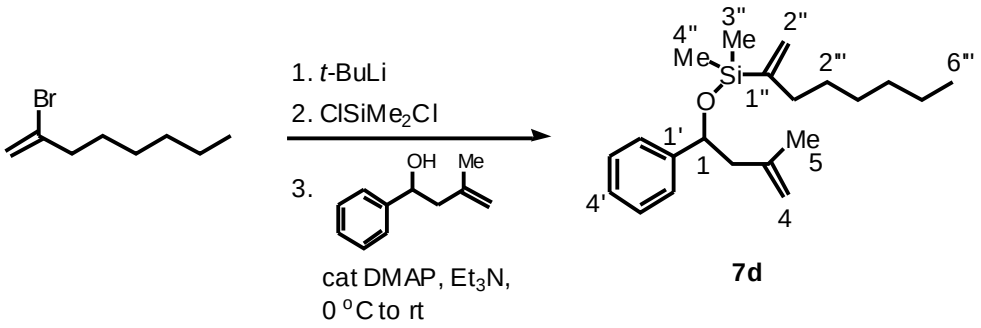
317 (4, M^++1), 315 (5), 301 (40), 275 (100), 239 (10), 205 (98), 131 (63), 75 (36).

TLC: R_f 0.22 (silica gel, hexane, PMA)

GC: t_R 19.36 min (HP-5, 200 °C, 15 psi)

Analysis:	$C_{20}H_{32}OSi$	(316.56)	
	Calculated:	C: 75.88;	H: 10.19%
	Found:	C: 75.91;	H: 10.26%

Preparation of Dimethyl-(2-octenyl)-[(1-phenyl-3-methyl-3-butenyl)oxy]silane (7d).



To a solution of 2-bromo-1-octene (2.85 g, 15.0 mmol, 1.2 equiv) in Et_2O (15 mL) was added dropwise with *t*-BuLi (1.5 M, 20.0 mL, 30.0 mmol, 2.4 equiv) under N_2 atmosphere at –78 °C (internal). The pale-yellow, cloudy mixture was stirred for 1 h at –78 °C (internal). The mixture was then added to a solution of dichlorodimethylsilane (3.8 mL, 31.25 mmol, 2.5 equiv) in Et_2O (15 mL) via cannula at –78 °C (internal). The mixture was allowed to warm to room temperature and was stirred for 2 h whereupon a white solid precipitated. After removal of solvent and excess dichlorodimethylsilane under reduced pressure, hexane (50 mL) was added and the solids were removed by Schlenk filtration. After removal of the solvent, the residue was dissolved in CH_2Cl_2 (5 mL). The solution was then added to a solution mixture of 1-phenyl-3-methyl-3-buten-1-ol (2.03 g, 12.5 mmol, 1.0 equiv), 4-dimethylaminopyridine (229 mg, 1.88 mmol, 0.15 equiv), and Et_3N (2.6 mL, 18.8 mmol, 1.5 equiv) in CH_2Cl_2 (10 mL) under N_2 atmosphere at 0 °C (internal). The mixture was allowed to warm to room temperature and was stirred for 2 h. The mixture was then poured to ice water (20 mL) and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent was removed by rotary evaporation. The residue was purified by chromatography (silica gel, hexane) followed Kugelrohr distillation under reduced pressure to afford 2.85 g (69%) of **7d** as a colorless liquid.

Analytical Data for **7d**:

bp: 140-145 °C (0.1 mmHg ABT)

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

7.33-7.23 (m, 5 H, 2 x HC(2'), 2 x HC(3'), HC(4')), 5.61 (dd, *J* = 1.6, 0.8, 1 H, $H_aC(2'')$), 5.40 (d, *J* = 2.8, 1 H, $H_bC(2'')$), 4.78 (dd, *J* = 7.6, 5.6, 1 H, HC(1)), 4.77 (s, 1 H, $H_aC(4)$), 4.67 (s, 1 H, $H_bC(4)$), 2.50 (dd, *J* = 13.6, 7.6, 1 H, $H_aC(2)$), 2.33 (dd, *J* = 13.6, 5.6, 1 H, $H_bC(2)$), 2.08 (t, *J* = 7.6, 2 H, $H_2C(1''')$), 1.73 (s, 3 H, $H_3C(5)$), 1.39-1.26 (m, 8 H, $H_2C(2''')$, $H_2C(3''')$, $H_2C(4''')$, $H_2C(5''')$), 0.91 (t, *J* = 6.8, 3 H, $H_3C(6''')$), 0.09 (s, 6 H, $H_3C(3'')$, $H_3C(4'')$).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

150.7 (C(1'')), 145.0 (C(1')), 142.3 (C(3)), 127.9 (2 C, C(3')), 127.0 (C(4')), 126.1 (2 C, C(2')), 125.4 (C(2'')), 113.3 (C(4)), 74.3 (C(1)), 49.2 (C(2)), 35.5 (C(1''')), 31.8, 29.3, 28.8, 23.1 (C(5)), 22.7, 14.1 (C(6''')), -1.4, -1.6.

IR: (NaCl)

2957 (s), 2927 (s), 1648 (m), 1602 (m), 1453 (m), 1373 (m), 1252 (s), 1088 (s), 1069 (s), 937 (m), 890 (m), 830 (s), 782 (s).

MS: (CI, 130 eV)

331 (2, M^++1), 329 (3), 315 (32), 275 (100), 219 (72), 145 (48).

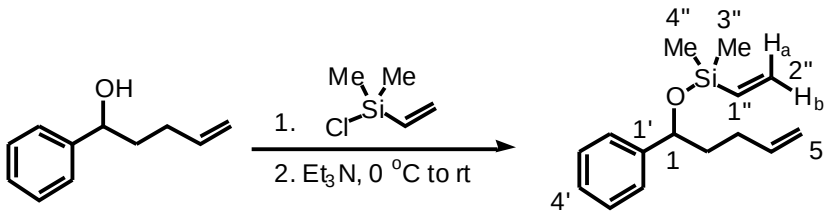
TLC: R_f 0.45 (silica gel, hexane/EtOAc, 49/1, PMA)

GC: t_R 23.29 min (HP-5, 200 °C, 15 psi)

Analysis: $C_{21}H_{34}OSi$ (330.59)

Calculated:	C: 76.31;	H: 10.38%
Found:	C: 76.16;	H: 10.61%

Preparation of Dimethyl[(1-phenyl-4-pentenyl)oxy]vinylsilane (7e).



7e

In a 50-mL flask was placed 1-phenyl-4-penten-1-ol (3.24 g, 20.0 mmol) and Et_3N (4.2 mL, 30.0 mmol, 1.5 equiv) in CH_2Cl_2 (20 mL) under a N_2 atmosphere at 0 °C (internal). To the mixture was added dropwise chlorodimethylvinylsilane (3.3 mL, 24.0 mmol, 1.2 equiv). The

mixture was allowed to warm to room temperature and was stirred for 0.5 h. The mixture was then poured to ice water (30 mL) and the aqueous phase was extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent was removed by rotary evaporation. The residue was purified by chromatography (silica gel, hexane/EtOAc, 49/1) followed Kugelrohr distillation under reduced pressure to afford 4.48 g (91%) of **7e** as a colorless liquid.

Analytical Data for **7e**:

bp: 80-85 °C (0.2 mmHg ABT)

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

7.35-7.23 (m, 5 H, 2 x HC(2'), 2 x HC(3'), HC(4')), 6.08 (dd, *J* = 20.0, 14.8, 1 H, HC(1")), 5.97 (dd, *J* = 14.8, 4.4, 1 H, H_bC(2")), 5.83 (ddt, *J* = 16.8, 10.0, 6.8, 1 H, HC(4)), 5.74 (dd, *J* = 20.0, 4.4, 1 H, H_aC(2")), 5.05-4.96 (m, 2 H, H_2C(5)), 4.68 (dd, *J* = 7.6, 4.8, 1 H, HC(1)), 2.18-2.20 (m, 2 H, H_2C(3)), 1.92-1.69 (m, 2 H, H_2C(2)), 0.14 (s, 3 H, CH_3), 0.09 (s, 3 H, CH_3).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

145.1 (C(1')), 138.4 (C(4)), 137.7 (C(1")), 132.9 (C(2")), 128.1 (2 C, C(3')), 127.0 (C(4')), 125.9 (2 C, C(2')), 114.6 (C(5)), 74.5 (C(1)), 39.6 (C(3)), 30.0 (C(2)), -1.5, -1.7.

IR: (NaCl)

2944 (s), 1641 (m), 1594 (m), 1493 (m), 1452 (m), 1407 (s), 1253 (s), 1089 (s), 1008 (s), 957 (s), 911 (s), 837 (s), 784 (s), 700 (s).

MS: (CI, 130 eV)

247 (18, M^++1), 245 (12), 231 (85), 219 (76), 191 (100), 145 (27).

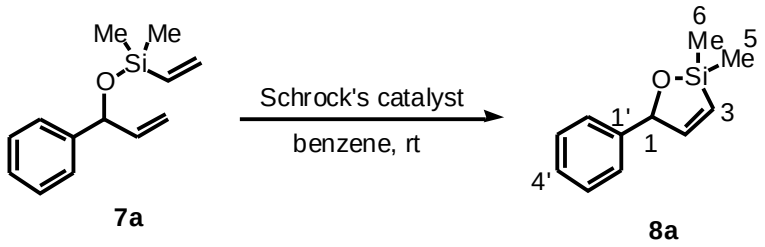
TLC: R_f 0.16 (silica gel, hexane/EtOAc, 99/1, PMA)

GC: t_R 18.68 min (HP-5, 150 °C, 15 psi)

Analysis: $C_{15}H_{22}OSi$ (246.43)

Calculated:	C: 73.11;	H: 9.00%
Found:	C: 73.12;	H: 9.36%

Ring-Closing Metathesis of 7a. Preparation of 2,2-Dimethyl-5-phenyl-1-oxa-2-silacyclopent-3-ene (8a).



7a **8a**

Following General Procedure I, benzene (10 mL), Schrock's catalyst (53.6 mg, 0.07 mmol, 0.07 equiv), and **7a** (218 mg, 1.0 mmol, 1.0 equiv) were combined and the mixture was stirred at room temperature for 3 h in the dry box. After removal of the solvent under reduced pressure, the residue was filtered through a short column of Celite which was then eluted with 100 mL of hexane/EtOAc, 49/1. The filtrate was concentrated followed by Kugelrohr distillation to afford 168 mg (89%) of **8a** as a colorless liquid.

Analytical Data for **8a**:

bp: 55-60 °C (0.1 mmHg ABT)

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

7.38-7.27 (m, 5 H, 2 x HC(2'), 2 x HC(3'), HC(4)), 6.91 (dd, *J* = 10.4, 1.6, 1 H, HC(2)), 6.14 (dd, *J* = 10.4, 2.4, 1 H, HC(3)), 5.72 (t, *J* = 1.6, 1 H, HC(1)), 0.40 (s, 3 H, CH_3), 0.35 (s, 3 H, CH_3).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

153.0 (C(2)), 142.0 (C(1')), 128.5 (2 C, C(3')), 127.5 (C(3)), 126.4 (C(4')), 126.0 (2 C, C(2')), 84.7 (C(1)), 1.3, 0.5.

IR: (NaCl)

3029 (m), 2964 (m), 1558 (m), 1492 (m), 1251 (s), 1120 (m), 1022 (s), 850 (s), 788 (s).

MS: (EI, 70 eV)

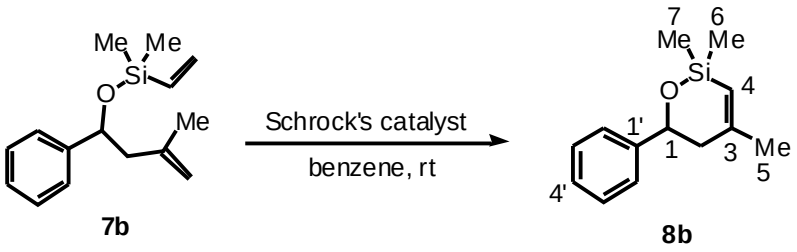
190 (57, M^+), 189 (100), 175 (23), 162 (19), 133 (41), 105 (30), 77 (28).

GC: t_R 7.11 min (HP-5, 180 °C, 15 psi)

Analysis: $C_{11}H_{14}OSi$ (190.32)

Calculated:	C: 69.42;	H: 7.41%
Found:	C: 69.25;	H: 7.45%

Ring-Closing Metathesis of 7b. Preparation of 2,2,4-Trimethyl-6-phenyl-1-oxa-2-silacyclohex-3-ene (8d).



7b **8b**

Following General Procedure I, benzene (10 mL), Schrock's catalyst (53.6 mg, 0.07 mmol, 0.07 equiv), and **7b** (246 mg, 1.0 mmol, 1.0 equiv) were combined and the mixture was stirred at room temperature for 12 h in the dry box. ^{1}H NMR analysis showed that the reaction was not complete (conversion: 90%). To the mixture was added another portion of catalyst (7.6 mg, 0.01 mmol, 0.01 equiv) and the mixture was stirred for another 3 h. After removal of the solvent under reduced pressure, the residue was filtered through a short column of silica gel which was eluted with 100 mL of hexane/EtOAc, 49/1. The filtrate was concentrated and the residue was purified by Kugelrohr distillation to afford 199 mg (91%) of **8b** as a colorless liquid.

Analytical Data for **8b**:

bp: 95-100 °C (0.2 mmHg ABT)

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

7.42 (d, J = 8.4, 2 H, 2 x HC(2')), 7.36 (t, J = 8.4, 2 H, 2 x HC(3')), 7.27 (tt, J = 7.6, 1.2, 1 H, HC(4')), 5.50 (dd, J = 2.4, 1.6, 1 H, HC(4)), 4.97 (dd, J = 10.8, 2.4, 1 H, HC(1)), 2.41 (dddd, J = 17.2, 10.8, 2.4, 1.2, 1 H, $H_aC(2)$), 2.19 (dd, J = 17.6, 2.4, 1 H, $H_bC(2)$), 1.90 (s, 3 H, $H_3C(5)$), 0.26 (s, 3 H, CH_3), 0.24 (s, 3 H, CH_3).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

155.7 (C(3)), 144.5 (C(1')), 128.3 (2 C, C(3')), 127.2 (C(4')), 125.6 (2 C, C(2')), 120.5 (C(4)), 73.4 (C(1)), 43.4 (C(2)), 28.3 (C(5)), -0.1, -0.4.

IR: (NaCl)

2964 (m), 1608 (s), 1496 (m), 1438 (s), 1369 (s), 1251 (s), 1216 (s), 1085 (s), 1068 (s), 1006 (s), 921 (s), 889 (s), 854 (s), 808 (s), 773 (s), 750 (s).

MS: (EI, 70 eV)

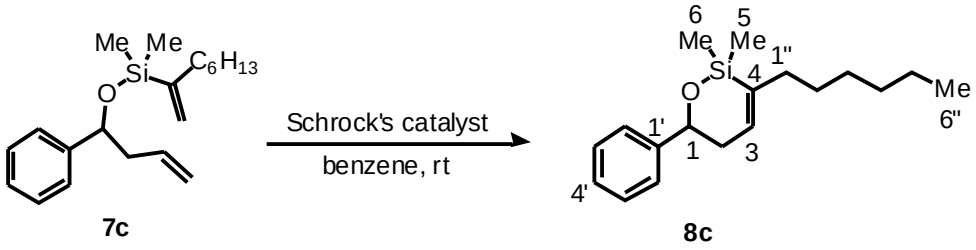
218 (40, M^+), 203 (79), 144 (83), 129 (57), 112 (52), 97 (100).

TLC: R_f 0.28 (silica gel, hexane/EtOAc, 49/1, PMA)

GC: t_R 9.96 min (HP-5, 180 °C, 15 psi)

Analysis: $C_{13}H_{18}OSi$ (218.37)
Calculated: C: 71.50; H: 8.31%
Found: C: 71.23; H: 8.47%

Ring-Closing Metathesis of 7c. Preparation of 2,2-Dimethyl-3-hexyl-6-phenyl-1-oxa-2-silacyclohex-3-ene (8c).



7c **8c**

Following General Procedure I, benzene (10 mL), Schrock's catalyst (53.6 mg, 0.07 mmol, 0.07 equiv), and **7c** (316 mg, 1.0 mmol, 1.0 equiv) were combined and the mixture was stirred at room temperature for 12 h in the dry box. After removal of the solvent under reduced pressure, the residue was filtered through a short column of silica gel which was eluted with 100 mL of hexane/EtOAc, 49/1. The filtrate was concentrated followed by Kugelrohr distillation to afford 259 mg (90%) of **8c** as a colorless liquid.

Analytical Data for **8c**:

bp: 130-135 °C (0.1 mmHg ABT)

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

7.39 (d, *J* = 6.8, 2 H, 2 x HC(2')), 7.34 (t, *J* = 7.2, 2 H, 2 x HC(3')), 7.25 (t, *J* = 6.8,1 H, HC(4')), 6.40 (dd, *J* = 5.2, 1.2, 1 H, HC(3)), 4.92 (dd, *J* = 10.0, 3.2, 1 H, HC(1)), 2.44-2.29 (m, 2 H, H_2C(2)), 2.11 (t, *J* = 6.8, 2 H, H_2C(1")), 1.41-1.30 (m, 8 H, H_2C(2"), H_2C(3"), H_2C(4"), H_2C(5")), 0.91 (t, *J* = 7.2, 3 H, H_3C(6")), 0.28 (s, 3 H, CH_3), 0.26 (s, 3 H, CH_3).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

144.5 (C(1')), 140.1 (C(4)), 138.9 (C(3)), 128.2 (2 C, C(3')), 127.1 (C(4')), 125.6 (2 C, C(2')), 73.5 (C(1)), 38.7 (C(2)), 35.3 (C(1'")), 31.7, 29.5, 29.2, 22.7, 14.1 (C(6")), -0.6, -0.7.

IR: (NaCl)

2956 (s), 2925 (s), 2856 (s), 1604 (m), 1454 (m), 1249 (s), 1068 (s), 1025 (s), 916 (s), 829 (s), 781 (s).

MS: (EI, 70 eV)
288 (46, M^+), 273 (28), 217 (41), 203 (97), 165 (45), 149 (43), 129 (100), 111 (68), 75 (92)).

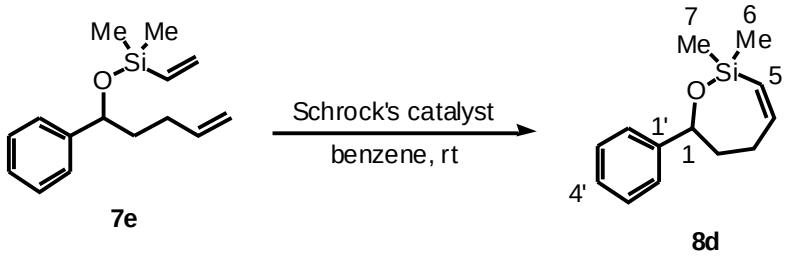
TLC: R_f 0.34 (silica gel, hexane/EtOAc, 49/1, PMA)

GC: t_R 25.25 min (HP-5, 200 °C, 15 psi)

Analysis: $C_{18}H_{28}OSi$ (288.51)

Calculated:	C: 74.94;	H: 9.78%
Found:	C: 75.17;	H: 9.93%

Ring-Closing Metathesis of 7e. Preparation of 2,2-Dimethyl-7-phenyl-1-oxa-2-silacyclohept-3-ene (8d).



7e **8d**

Following General Procedure II, benzene (10 mL), Schrock's catalyst (38.3 mg, 0.05 mmol, 0.05 equiv), **7e** (246 mg, 1.0 mmol, 1.0 equiv) were combined and the mixture was stirred at room temperature for 6 h in the dry box. ^{1}H NMR analysis showed that the reaction was not complete (conversion: 80%). To the mixture was added another portion of catalyst (15.3 mg, 0.02 mmol, 0.02 equiv) and the mixture was stirred for another 6 h (conversion: 91%). After removal of the solvent under reduced pressure, the residue was filtered through a short column of silica gel which was eluted with 100 mL of hexane/EtOAc, 49/1. The filtrate was concentrated and the residue was purified by chromatography (silica gel, hexane/CH_2Cl_2, 17/3) followed by Kugelrohr distillation to afford the product 176 mg (81%) of **8d** as a colorless oil.

Analytical Data for **8d**:

bp: 75-80 °C (0.1 mmHg ABT)

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

7.38-7.32 (m, 4 H, 2 x HC(2'), 2 x HC(3')), 7.26-7.22 (m, 1 H, HC(4')), 6.68 (dt, J = 14.4, 5.2, 1 H, HC(4)), 5.70 (dt, J = 14.4, 1.2, 1 H, HC(5)), 5.11 (dd, J = 7.2, 3.2, 1 H, HC(1)), 2.47-2.39 (m, 1 H, $H_aC(3)$), 2.35-2.18 (m, 2 H, $H_aC(2)$, $H_bC(3)$), 2.08-2.00 (m, 1 H, $H_bC(2)$), 0.32 (s, 3 H, CH_3), 0.28 (s, 3 H, CH_3).

^{13}C NMR: (100.6 MHz, $CDCl_3$)
148.4 (C(4)), 144.9 (C(1')), 129.4 (C(5)), 128.1 (2 C, C(3')), 126.7 (C(4')), 125.4 (2 C, C(2')), 75.4 (C(1)), 37.5 (C(3)), 29.3 (C(2)), 0.7, 0.2.

IR: (NaCl)
2962 (m), 1606 (m), 1494 (m), 1450 (m), 1118 (m), 1064 (m), 950 (m), 840 (s), 788 (s), 700 (s).

MS: (EI, 70 eV)
218 (24, M^+), 217 (100), 203 (6), 179 (28), 143 (46), 105 (61), 75 (96).

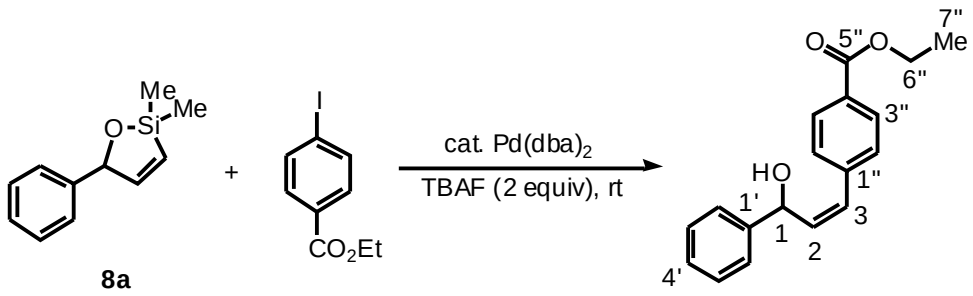
TLC: R_f 0.30 (silica gel, hexane/EtOAc, 49/1, PMA)

GC: t_R 11.42 min (HP-5, 180 °C, 15 psi)

Analysis: $C_{13}H_{18}OSi$ (218.37)

Calculated:	C: 71.50;	H: 8.31%
Found:	C: 71.43;	H: 8.33%

Coupling Reaction of 8a with Ethyl 4-Iodobenzoate. Preparation of Ethyl 4-[(*Z*)-3-hydroxy-3-phenyl-1-propenyl]benzoate (9a).



8a **9a**

Following General Procedure II, **8a** (209 mg, 1.1 mmol, 1.1 equiv), a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv), ethyl 4-iodobenzoate (276 mg, 1.0 mmol) and $Pd(dba)_2$ (17.2 mg, 0.03 mmol, 0.03 equiv) were combined. The mixture was stirred at room temperature for 30 min and then 2 mL of EtOAc/hexane, 7/3 were added. The mixture was filtered through a short column of silica gel which was eluted with 150 mL of EtOAc/hexane, 7/3. The filtrate was concentrated to give a crude product which was purified by chromatography (silica gel, hexane/EtOAc, 19/1 to 4/1) to afford 240 mg (85%) of **9a** as a pale yellow (non-distillable) oil.

Analytical Data for **9a**:

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

8.01 (d, *J* = 8.5, 2 H, 2 x HC(3")), 7.41 (d, *J* = 7.5, 2 H, 2 x HC(2')), 7.38 (d, *J* = 8.5, 2 H, 2 x HC(2")), 7.37 (t, *J* = 7.7, 2 H, 2 x HC(3')), 7.30 (t, J = 7.3, 1 H, HC(4')), 6.68 (d, *J* = 11.5, 1 H, HC(3)), 6.03 (dd, *J* = 11.5, 9.5, 1 H, HC(2)), 5.58 (dd, *J* = 9.5, 3.0, 1 H HC(1)), 4.37 (q, *J* = 7.0, 2 H, H_2C(6")), 2.39 (d, *J* = 3.5, 1 H, HO), 1.39 (t, *J* = 7.0, 3 H, H_3C(7")).

^{13}C NMR: (126 MHz, $CDCl_3$)

166.4 (C(5")), 142.9 (C(1')), 140.9 (C(1")), 135.0 (C(2)), 130.2 (C(3)), 129.5 (2 C, C(3")), 129.2 (C(4")), 128.72 (2 C, C(3')), 128.69 (2 C, C(2")), 127.9 (C(4')), 126.2 (2 C, C(2')), 70.0 (C(1)), 61.0 (C(6")), 14.2 (C(7")).

IR: (NaCl)

3424(s), 2983 (m), 1712 (s), 1608 (s), 1452 (m), 1396 (s), 1280 (s), 1178 (s), 1106 (s), 877 (m), 757 (s), 700 (s).

MS: (FAB)

283 (16, M^++1), 282 (13, M^+), 265 (100), 237 (20), 154 (29), 136 (24).

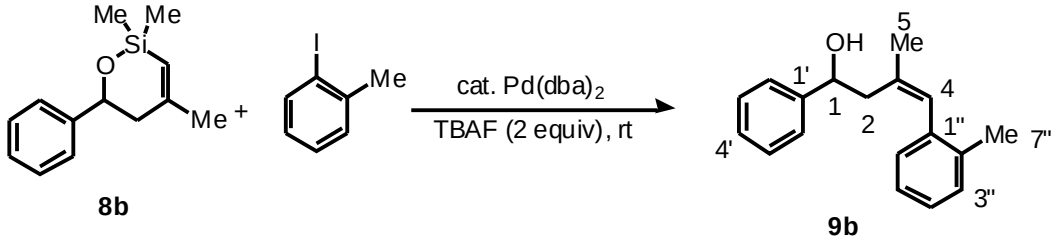
TLC: R_f 0.21 (silica gel, hexane/EtOAc, 4/1, PMA)

Analysis: $C_{18}H_{18}O_3$ (282.34)

Calculated: C: 76.56; H: 6.43%

Found: C: 76.70; H: 6.50%

Coupling Reaction of 8b with 2-Iodotoulene. Preparation of (*Z*)-1-Phenyl-3-methyl-4-(2-methylphenyl)-3-buten-1-ol (9b).



8b **9b**

Following General Procedure II, **8b** (240 mg, 1.1 mmol, 1.1 equiv), a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv), 2-iodotoluene (218 mg, 1.0 mmol) and $Pd(dba)_2$ (17.2 mg, 0.03 mmol, 0.03 equiv) were combined. The mixture was stirred at room temperature for 45 min and then 2 mL of EtOAc/hexane, 7/3 were added. The mixture was filtered through a short column of silica gel which was eluted with 150 mL of EtOAc/hexane, 7/3. The filtrate was

concentrated to give a crude product which was purified by chromatography (silica gel, hexane/EtOAc, 19/1 to 9/1) to afford (209 mg (83%) of **9b** as a pale yellow (non-distillable) oil.

Analytical Data for **9b**:

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

7.31-7.21 (m, 5 H), 7.16-7.12 (m, 4 H), 6.40 (s, 1 H, HC(4)), 4.87 (ddd, *J* = 8.4, 5.2, 2.8, 1 H, HC(1)), 2.70 (dd, *J* = 13.6, 8.8, 1 H, $H_aC(2)$), 2.46 (dd, *J* = 13.6, 5.4, 1 H, $H_bC(2)$), 2.15 (s, 3 H, $H_3C(7'')$), 1.99 (s, 3 H, $H_3C(5)$), 1.88 (s, 1 H, HO).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

144.0 (C(1')), 137.0, 136.4, 134.6 (C(3)), 129.6, 129.4, 128.3 (2 C, C(3')), 128.2, 127.5 (C(4')), 126.6, 125.8 (2 C, C(2')), 125.4, 72.4 (C(1)), 42.0 (C(2)), 23.6 (C(5)), 19.9 (C(7'')).

IR: (NaCl)

3399 (m), 2966 (m), 2913 (m), 1650 (m), 1454 (m), 1378 (m), 1216 (m), 1047 (m), 875 (m), 748 (s), 700 (s).

MS: (FAB)

252 (6, M^+) 251 (8), 235 (92), 154 (47), 146 (100), 136 (33).

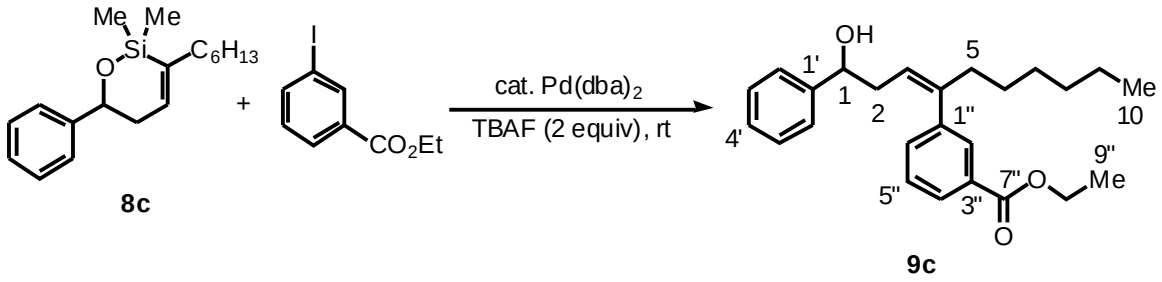
TLC: R_f 0.16 (silica gel, hexane/EtOAc, 9/1, PMA)

Analysis: $C_{18}H_{20}O$ (252.36)

Calculated: C: 85.67; H: 7.99%

Found: C: 85.86; H: 8.05%

Coupling Reaction of 8c with Ethyl 3-Iodobenzoate. Preparation of Ethyl 3-[(*Z*)-1-hexyl-4-hydroxy-4-phenyl-1-butenyl]benzoate (9c).



Siloxane **8c** (317 mg, 1.1 mmol, 1.1 equiv) was dissolved in a solution of TBAF (1.0 M in THF, 2.0 mL, 2.0 mmol, 1.0 equiv) under an Ar atmosphere at ambient temperature. After 2 min, ethyl 3-iodobenzoate (69 mg, 0.25 mmol, 0.25 equiv) and $Pd(dba)_2$ (14.3 mg, 0.025 mmol, 0.025 equiv) were then added sequentially. The mixture was stirred at room temperature for 3 h.

Additional portions of ethyl 3-iodobenzoate (69 mg, 0.25 mmol, 0.25 equiv) and $Pd(dba)_2$ (14.3 mg, 0.025 mmol, 0.025 equiv) were added 3 times at 3 h intervals. The mixture was stirred for 24 h at room temperature and then 2 mL of EtOAc/hexane, 7/3 were added. The mixture was filtered through a short column of silica gel which was eluted with 150 mL of EtOAc/hexane, 7/3. The filtrate was concentrated to give a crude product which was purified by chromatography (silica gel, hexane/EtOAc, 19/1 to 4/1) to afford 307 mg (81%) of **9c** as a pale yellow (non-distillable) oil.

Analytical Data for **9c**:

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

7.91 (dt, *J* = 8.0, 1.5, 1 H, HC(4")), 7.76 (t, *J* = 1.5, 1 H, HC(2")), 7.35 (t, *J* = 8.0, 1 H, HC(5")), 7.31-7.23 (m, 5 H, 2 x HC(2'), 2 x HC(3'), HC(4')), 7.16 (dt, *J* = 8.0, 1.5, 1 H, HC(6")), 5.53 (t, *J* = 7.3, 1 H, HC(3)), 4.68 (t, *J* = 6.0, 1 H, HC(1)), 4.37 (q, *J* = 7.0, 2 H, H_2C(8")), 2.41-2.32 (m, 4 H, H_2C(2), H_2C(5)), 2.12 (s, 1 H, HO), 1.40 (t, *J* = 7.0, 3 H, H_3C(9")), 1.28-1.22 (m 8 H, H_2C(6), H_2C(7), H_2C(8), H_2C(9)), 0.86 (t, *J* = 7.1, 3 H, H_3C(10)).

^{13}C NMR: (126 MHz, $CDCl_3$)

166.7 (C(7")), 144.0 (C(1')), 143.6 (C(4)), 141.2 (C(1")), 132.9 (C(6")), 130.3 (C(3")), 129.3 (C(2")), 128.3 (2 C, C(3')), 128.0 (C(5")), 127.7 (C(4')), 127.4 (C(4")), 125.8 (2 C, C(2')), 122.8 (C(3)), 74.2 (C(1)), 60.9 (C(8")), 39.2 (C(2)), 38.6 (C(5)), 31.5, 28.7, 27.8, 22.5, 14.3 (C(9")), 14.0 (C(10)).

IR: (NaCl)

3469 (m), 2929 (s), 1720 (s), 1602 (m), 1454 (m), 1367 (m), 1280 (s), 1106 (m), 1025 (m), 757 (s), 701 (s)).

MS: (FAB)

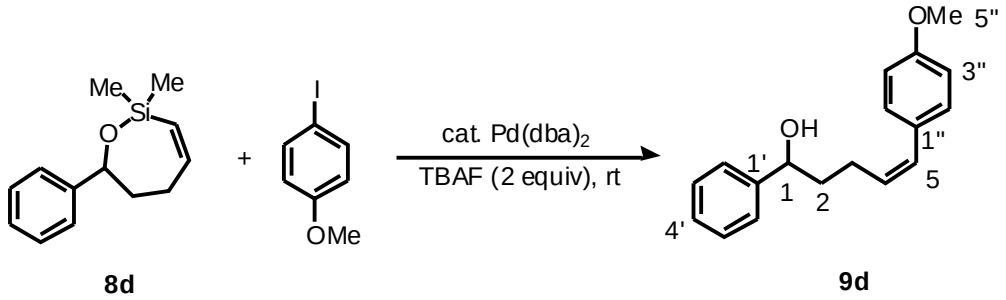
380 (8, M^+), 379 (15), 363 (100), 333 (20), 317 (18), 274 (41), 154 (48), 136 (46).

TLC: R_f 0.28 (silica gel, hexane/EtOAc, 4/1, PMA)

Analysis: $C_{25}H_{32}O_3$ (380.53)

Calculated:	C: 78.90;	H: 8.48%
Found:	C: 78.85;	H: 8.46%

Coupling Reaction of 8d with 4-Iodoanisole. Preparation of (*Z*)-1-Phenyl-5-(4-methoxyphenyl)-4-penten-1-ol (9d).



8d **9d**

Following General Procedure II, **8d** (240 mg, 1.1 mmol, 1.1 equiv), a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv), 4-iodoanisole (234 mg, 1.0 mmol, 1.0 equiv) and $Pd(dba)_2$ (17.2 mg, 0.03 mmol, 0.03 equiv) were combined. The mixture was stirred at room temperature for 30 min and then 2 mL of EtOAc/hexane, 7/3 were added. The mixture was filtered through a short column of silica gel which was eluted with 150 mL of EtOAc/hexane, 7/3. The filtrate was concentrated to give a crude product which was purified by chromatography (silica gel, hexane/EtOAc, 19/1 to 17/3) to afford 228 mg (85%) of **9d** as a pale yellow (non-distillable) oil.

Analytical Data for **9d**:

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

7.35-7.27 (m, 5 H, 2 x HC(2'), 2 x HC(3'), HC(4')), 7.19 (d, *J* = 8.5, 2 H, 2 x HC(2")), 6.85 (dt, *J* = 8.5, 1.2, 2 H, 2 x HC(3")), 6.39 (d, *J* = 11.5, 1 H, HC(5)), 5.60 (dt, *J* = 11.5, 7.5, 1 H, HC(4)), 4.70 (m 1 H, HC(1)), 3.81 (s, 3 H, H_3C(5")), 2.49-2.36 (m, 2 H, H_2C(3)), 1.99-1.93 (m, 2 H, HO, H_aC(2)), 1.89-1.82 (m, 1 H, H_bC(2)).

^{13}C NMR: (126 MHz, $CDCl_3$)

158.2 (C(4")), 144.5 (C(1')), 130.3 (C(5)), 130.1 (C(1")), 129.9 (2 C, C(2")), 128.9 (C(4)), 128.4 (2 C, C(3')), 127.5 (C(4')), 125.8 (2 C, C(2')), 113.5 (2 C, C(3")), 74.0 (C(1)), 55.2 (C(5")), 39.1 (C(3)), 24.9 (C(2)).

IR: (NaCl)

3401 (m), 3006 (m), 2933 (m), 1606 (s), 1509 (s), 1454 (m), 1245 (s), 1176 (s), 1033 (s), 840 (s), 757 (s), 701 (s).

MS: (FAB)

269 (14, M^++1), 268 (50, M^+), 251 (11), 154 (100), 147 (73), 136 (67).

HRMS: calcd for $C_{18}H_{20}O_2$: 268.1463; found: 268.1464

TLC: R_f 0.17 (silica gel, hexane/EtOAc, 4/1, PMA)

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