A Quantitative Examination of the Effects of Silicon Substituents on the Efficiency of Cross-Coupling Reactions

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SUPPORTING INFORMATION

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General Experimental

All reactions were performed in oven-dried (140 °C) or flame-dried glassware under an inert atmosphere of dry N_2. The following reaction solvents were distilled from the indicated drying agents: diethyl ether (sodium, benzophenone), toluene (Na), methanol ($Mg(OMe)_2$), triethylamine (CaH_2), *tert*-butyl alcohol was distilled over Na. *n*-Butyllithium solutions were titrated following the method of Gilman.[1] Brine refers to a sat. aq. solution of NaCl.

^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded on 500 MHz, ^{1}H; 470 MHz, ^{19}F; 126 MHz, ^{13}C spectrometers. Spectra were referenced to residual chloroform (7.26 ppm, ^{1}H; 77.00 ppm, ^{13}C). Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d

(doublet), t (triplet), q (quartet), qn (quintet), sept (septet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. ^{1}H and ^{13}C NMR assignments are corroborated by 2D experiments (HETCOR and COSY). Spectra are available on request from denmark@scs.uiuc.edu. Mass spectroscopy data (EI, CI, FAB) are reported in the form of (m/z). Infrared spectra (IR) were recorded in NaCl cells and peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%); w (weak, 0-33%).

Analytical thin-layer chromatography was performed on silica or aluminum oxide, basic gel plates with QF-254 indicator. Visualization was accomplished with $KMnO_4$, UV light and/or iodine. 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 ($CaCl_2$); ethyl acetate (K_2CO_3); dichloromethane ($CaCl_2$). Column chromatography was performed using 230-400-mesh silica.

Analytical capillary gas chromatography (GC) was performed using a gas chromatograph fitted with a flame ionization detector (H_2 carrier gas, 1 mL/min): 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 a reporting integrator. Retention times (HP 5, 250 °C, 15 psi): t_R naphthalene, 4.84 min; t_R **12**, 6.43 min; t_R **13**, 8.30 min; t_R **14**, 4.94 min; t_R **15**, 5.60 min; t_R **16**, 5.52 min; t_R **17**, 6.65 min. Retention times (HP 5, 200 °C, 15 psi): t_R naphthalene, 5.48 min; t_R **14**, 6.06 min; t_R **15**, 8.47 min.

Bulb-to-bulb distillations were performed on a Kugelrohr, boiling points (bp) corresponding to uncorrected air-bath temperatures (ABT). 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. A solution of THF containing TBAF (1.0 M) and naphthalene (0.25 M) was prepared from solid tetrabutylammonium fluoride trihydrate (TBAF•$3H_2O$, Fluka) or naphthalene and distilled THF in a volumetric flask and was stored in a Schlenk bottle. Palladium bis(dibenzylideneacetone) ($Pd(dba)_2$) and allylpalladium chloride dimer were used without purification. The *t*-Bu_3P-Pt(0)-DVDS complex was prepared by the literature procedure[2]: *t*-Bu_3P (32 mg, 0.158 mmol) was dissolved in platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylene (1.5 mL

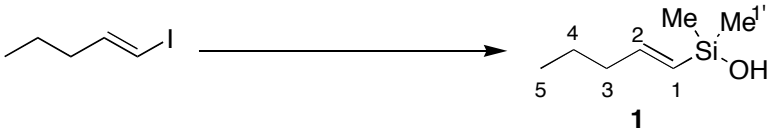
xylene solution). The mixture was stirred at 65 °C (oil bath) for 5 min and then was slowly cooled to room temperature. This solution could be stored under nitrogen in the freezer (-20 °C) indefinitely.

The following compounds were prepared by literature methods. (*E*)-1-iodo-1-heptene,[3] (*E*)-1-iodo-1-pentene,[4] (*E*)-dimethyl-(1-heptenyl)silanol[3] (**2**), (*E*)-diisopropyl-(1-heptenyl)-silanol[3] (**4**), (*E*)-1-[4-(1-heptenyl)phenyl]ethanone[3] (**13**), (*E*)-4-methoxy-2-(1-pentenyl)benzene[5] (**14**), (*E*)-1-(1-heptenyl)-4-methoxybenzene[3] (**15**), (*E*)-1-(1-heptenyl)-2-methylbenzene[3] (**17**), 4-(trimethylsilyl)ethynylbenzaldehyde[6] (**18**) and $(i\text{-Pr}_3\text{P})_2\text{RuHCl(CO)}$[7].

Experimental Procedures

Preparation of Alkenylsilane Precursors.

(*E*)-Dimethyl-(1-pentenyl)silanol (1)



1

To a solution of (*E*)-1-iodo-1-pentene (4.90 g, 25.0 mmol) in diethyl ether (50 mL) under dry N_2 at -78 °C, was added *n*-butyllithium (16.0 mL, 25.0 mmol, 1.55 M, 1.0 equiv) over 10 min and the reaction mixture was stirred at -78 °C for 30 min. A solution of hexamethylcyclotrisiloxane (1.854 g, 8.33 mmol, 0.33 equiv) in diethyl ether (30 mL) was then added over 5 min at -78 °C. The mixture was warmed to room temperature and was stirred for 24 h. The solution was then cooled to 0 °C and was quenched with water (15 mL). The aqueous phase was extracted with diethyl ether (3 × 20 mL) and the combined organic extracts were washed with water (1 × 20 mL) and brine (3 × 25 mL). The organic layer was dried ($MgSO_4$) and filtered. The solvent was then evaporated in vacuo to give an yellow oil which was purified by distillation to afford 3.06 g (85%) of **1** as a colorless oil. Repeated distillation provided analytically pure material.

Data for **1**:

bp: 113 °C (100 mmHg)

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

6.18 (dt, *J* = 18.9, 6.2, 1 H, HC(2)), 5.65 (dt, *J* = 18.9, 1.5, 1 H, HC(1)), 2.10 (qd, *J* = 7.0, 1.7, 2 H, H_2C(3)), 1.58 (s, OH, 1 H), 1.43 (sext, *J* = 7.3, 2 H, H_2C(4)),

0.90 (t, J = 7.3, 3 H, $H_3C(5)$), 0.19 (s, 6 H, $2H_3C(1')$)

^{13}C NMR: (101 MHz, $CDCl_3$)

149.2 (C(1)), 128.4 (C(2)), 38.6 (C(3)), 21.6 (C(4)), 13.7 (C(5)), 0.0 (C(1'))

IR: (NaCl)

3271 (s), 2960 (s), 2931 (s), 2875 (s), 1620 (s), 1252 (s), 991 (s), 866 (s), 843 (s)

MS: (EI, 70 eV)

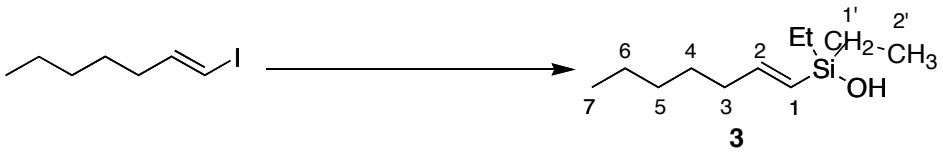
144 (M^+, 3.0), 129 (100), 116 (5), 101 (9), 75 (20), 61 (24)

TLC: R_f 0.14 (pentane/Et_2O, 9/1) [$KMnO_4$]

Analysis: $C_7H_{16}OSi$ (144.29)

Calc.:	C, 58.27;	H, 11.18%
Found:	C, 57.92;	H, 11.32%

(*E*)-Diethyl-(1-heptenyl)silanol (3)



3

To a solution of (*E*)-1-iodo-1-heptene (6.72 g, 30.0 mmol) in diethyl ether (60 mL) under dry N_2 at -78 °C, was added *n*-butyllithium (19.4 mL, 30.0 mmol, 1.55 M, 1.0 equiv) over 10 min and the reaction mixture was stirred at -78 °C for 30 min. A solution of hexaethylcyclotrisiloxane (3.07 g, 10 mmol, 0.33 equiv) in diethyl ether (15 mL) was then added over 5 min at -78 °C. The mixture was warmed to room temperature and was stirred for 24 h. The solution was then cooled to 0 °C and quenched with water (30 mL). The aqueous phase was extracted with diethyl ether (3 × 25 mL) and the combined organic extracts were washed with water (1 × 25 mL) and brine (2 × 30 mL). The organic layer was dried ($MgSO_4$) and filtered. The solvent was then evaporated in vacuo to give an yellow oil which was purified by distillation to afford 4.97 g (83%) of **3** as a colorless oil.

Data for **3**:

bp: 93 °C (0.8 mmHg)

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

6.20 (dt, J = 18.8, 6.3, 1 H, HC(2)), 5.59 (dt, J = 18.8, 1.5, 1 H, HC(1)), 2.13 (qd,

J = 7.1, 1.5, 2 H, HC(3)), 1.52 (brs, OH, 1 H), 1.40 (qn, J = 7.3, 2 H, $H_2C(4)$), 1.29 (m, 4 H, $H_2C(5)$ and $H_2C(6)$), 0.97 (t, J = 7.8, 6 H, $2H_3C(2')$), 0.88 (t, J = 7.1, 3 H, $H_3C(7)$), 0.63 (q, J = 8.1, 4 H, $2H_2C(1')$)

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

150.3 (C1), 125.6 (C(2)), 36.7 (C(3)), 31.4 (C(4)), 28.2 (C(5)), 22.5 (C(6)), 14.0 (C(7)), 6.5 (C(2')), 6.4 (C(2'))

IR: (NaCl)

3294 (s, br), 2927 (s), 2956 (s), 2875 (s), 1618 (s), 1618 (s), 1460 (s), 1238 (m), 995 (s), 837 (s)

MS: (EI, 70 eV)

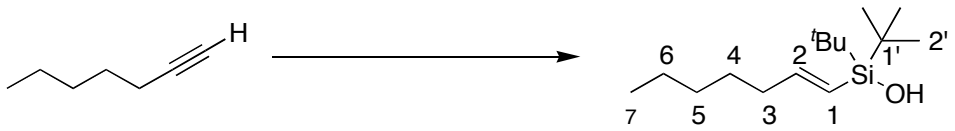
200 (M^+, 0.6), 171 (100), 143 (6), 115 (3), 95 (7), 75 (50), 61 (5)

TLC: R_f 0.16 (pentane/Et_2O, 9/1) [$KMnO_4$]

Analysis: $C_{11}H_{24}OSi$ (200.39)

Calc.:	C, 65.93;	H, 12.07;	Si, 14.02%
Found:	C, 65.63;	H, 12.26;	Si, 14.24%

(*E*)-Di-*tert*-butyl-(1-heptenyl)silanol (5)



5

Hexachloroplatinic acid (62 mg, 132 μmol, 0.01 equiv) was dissolved in 1 mL of 2-propanol and 10 mL of diethyl ether in a dry round-bottom flask equipped with a stir bar and a reflux condenser under an atmosphere of dry N_2. Chloro(di-*tert*-butyl)silane (3.4 mL, 16.5 mmol, 1.1 equiv) was then added and the mixture was heated to reflux for 1 h. A solution of 1-heptyne (1.44 g, 15 mmol) in 5 mL of dry ether was then added dropwise over 10 min. After the addition was complete, the mixture was heated in an oil bath to reflux for 24 h. After cooling to room temperature, the solvent was evaporated in vacuo and the residual oil was distilled (105 °C at 0.8 mmHg) to give 3.64 g (89%) of the chlorosilane as a colorless liquid.

The intermediate chlorosilane (3.64 g, 13.3 mmol) was dissolved in 50 mL of THF and a

sat. aq. solution of $NaHCO_3$ (30 mL) was added. The mixture was stirred at 50 °C overnight. The layers were separated and the aqueous phase was washed with diethyl ether (2 x 20 mL). Combined organic layers were washed with water (2 x 20 mL) and brine (2 x 20 mL) and dried ($MgSO_4$), filtered, and the solvents evaporated in vacuo. The resulting oil was purified by column chromatography (SiO_2, hexane/EtOAc, 9/1) and distilled to give 2.57 g (67%) of **5** as a colorless oil.

Data for **5**:

bp: 117 °C (0.8 mmHg)

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

6.22 (dt, *J* = 18.6, 6.3, 1 H, HC(2)), 5.63 (dt, *J* = 18.8, 1.5, 1 H, HC(1)), 2.18 (qd, *J* = 7.1, 1.2, 2 H, H_2C(3)), 1.44 (qn, *J* = 7.3, 2 H, H_2C(4)), 1.40 (s, OH, 1 H), 1.32 (m, 4 H, H_2C(5) and H_2C(6)), 1.02 (s, 18 H, 6H_3C(2')), 0.91 (t, *J* = 6.6, 3 H, H_3C(7))

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

150.1 (C(1)), 126.7 (C(2)), 36.8 (C(3)), 31.3 (C(4)), 28.4 (C(5)), 27.6 (C(2')), 22.5 (C(6)), 19.8 (C(1')), 14.0 (C(7))

IR: (NaCl)

3469 (s, br), 2966 (s), 2856 (s), 1616 (s), 1470 (s), 1363 (s), 823 (s)

MS: (EI, 70 eV)

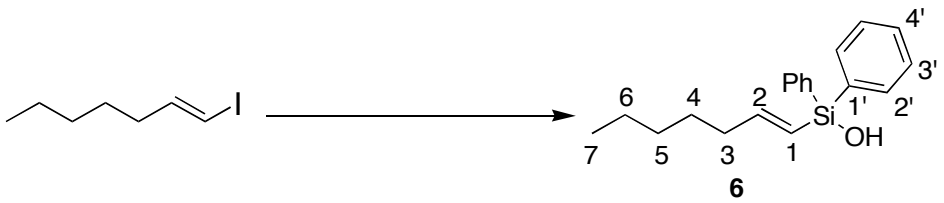
256 (M^+, 1.0), 199 (83), 181 (20), 157 (26), 129 (99), 115 (67), 75 (100), 61 (37)

TLC: R_f 0.32 (pentane/Et_2O, 9/1) [$KMnO_4$]

Analysis: $C_{15}H_{32}OSi$ (256.50)

Calc.:	C, 70.24;	H, 12.58%
Found:	C, 70.11;	H, 12.88%

(*E*)-Diphenyl-(1-heptenyl)silanol (6)



6

To a solution of (*E*)-1-iodo-1-heptene (2.29 g, 10.2 mmol) in diethyl ether (25 mL) under dry N_2 at -78 °C, was added *n*-butyllithium (6.6 mL, 10.2 mmol, 1.55 M, 1.0 equiv) over 10 min and the reaction mixture was stirred at -78 °C for 30 min. A solution of diphenylchlorosilane (2.0 mL, 10.2 mmol, 1.0 equiv) in diethyl ether (10 mL) was then added over 5 min at -78 °C. After stirring for 30 min at -78 °C, the mixture was warmed to room temperature and was stirred for 2 h, during which time a white precipitate formed. The solution was then cooled to 0 °C and was quenched (ice/sat. aq. ammonium chloride, 1/1, 40 mL). The aqueous phase was extracted with pentane (2 × 20 mL) and the combined organic extracts were washed with brine (2 × 20 mL). The organic layer was dried ($MgSO_4$) and filtered. The solvent was then evaporated in vacuo to give an yellow oil which was distilled (146 °C at 0.8 mmHg) to afford 2.28 g (79%) of the hydrosilane.

The intermediate silane (1.73 g, 6.16 mmol) was dissolved in 10 mL of diethyl ether and $Bu_4N^+OH^-$ in MeOH was slowly dropwise over 5 min, with vigorous gas evolution. After being stirred for 10 min the mixture was quenched in a mixture of ether and water (75 mL, 30 mL). The phases were separated and the aqueous layer was extracted with ether (2 x 25 mL). The combined organic extracts were washed with water (2 x 15 mL) and brine (2 x 15 mL) then were dried ($MgSO_4$), filtered, and the solvent was evaporated in vacuo. The resulting oil was purified by distillation to give 1.66 g (92%) of **6** as colorless oil.

Data for **6**:

bp: 165 °C (0.8 mmHg)

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

7.65 (dd, *J* = 7.7, 1.3, 4 H, HC(2')), 7.39 (m, 6 H, HC(3') and HC(4')), 6.33 (dt, *J* = 18.7, 2.9, 1 H, HC(2)), 5.99 (d, *J* = 18.7, 1 H, HC(1)), 2.22 (s, OH, 1 H), 2.21 (qd, *J* = 7.7, 1.5, 2 H, $H_2C(3)$), 1.44 (qn, *J* = 7.3, 2 H, $H_2C(4)$), 1.31 (m, 4 H, $H_2C(5)$ and $H_2C(6)$), 0.89 (t, *J* = 6.9, 3 H, $H_3C(7)$)

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

153.7 (C1), 136.0 (C(1')), 134.6 (C(2')), 129.9 (C(4')), 127.8 (C(3')), 124.0 (C(2)), 36.7 (C(3)), 31.4 (C(4)), 28.0 (C(5)), 22.5 (C(6)), 14.0 (C(7))

IR: (NaCl)

3278 (s, br), 3068 (s), 3049 (s), 2956 (s), 2927 (s), 2856 (s), 1616 (s), 1429 (s), 1118 (s), 997 (s), 849 (s), 878 (s)

MS: (EI, 70 eV)

296 (M^+, 16), 239 (17), 225 (65), 199 (100), 123 (59), 77 (17), 58 (9)

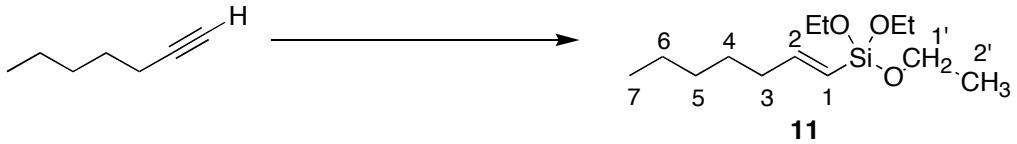
TLC: R_f 0.21 (pentane/Et_2O, 9/1) [$KMnO_4$ + UV]

CG: t_R 4.93 min (>99%) (HP5, injector 225 °C, column 200 °C, 15 psi)

Analysis: $C_{19}H_{20}O_1Si$ (172.34)

Calc.:	C, 76.97;	H, 8.16;	Si, 9.47%
Found	C, 76.75;	H, 8.16;	Si, 9.67%

(*E*)-(1-Heptenyl)triethoxysilane (11)



11

Triethoxysilane (970 μL 5.3 mmol, 1.05 equiv) was combined with a solution of platinum(0)-DVDS-*t*-Bu_3P (50 μL) in xylene. The solution was cooled to 0 °C and 1-heptyne (655 μL, 5.0 mmol) was added. The ice bath was then removed and the reaction was stirred for 4 h. All volatile materials were then removed by evaporation under high vacuum and the residual oil was Kugelrohr distilled at 150 °C (3 mmHg). The distillate was purified by radial chromatography (SiO_2, pentane/Et_2O, 19/1) and then was distilled on a Kugelrohr to give 690 mg (52%) of **11** as a colorless oil.

Data for **11**:

bp: 125 °C (0.4 mmHg, ABT)

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

6.42 (dt, *J* = 17.9, 6.3, 1 H, HC(2)), 5.40 (dt, *J* = 18.2, 1.6, 1 H, HC(1)), 3.81 (q, *J* = 7.1, 6 H, HC(1'), 2.13 (qd, *J* = 7.4, 1.5, 2 H, H_2C(3)), 1.41 (qn, *J* = 7.3, 2 H,

$H_2C(4)$), 1.29 (m, 4 H, $H_2C(5)$ and $H_2C(6)$), 1.22 (t, J = 7.1, 9 H, $3H_3C(2')$), 0.88 (t, J = 6.6, 3 H, $H_3C(7)$)

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

154.3 (C(1)), 118.9 (C(2)), 58.6 (C(1'), 36.7 (C(3)), 31.5 (C(4)), 28.1 (C(5)), 22.6 (C(6)), 18.4 (C(2')), 14.2 (C(7))

IR: (NaCl)

2973 (s), 2927 (s), 1619 (m), 1442 (w), 1390 (m), 1166 (s), 1105 (s), 958 (s)

MS: (EI, 70 eV)

260 (M^+, 2), 245 (5), 215 (16), 189 (9), 163 (100), 135 (10), 119 (25)

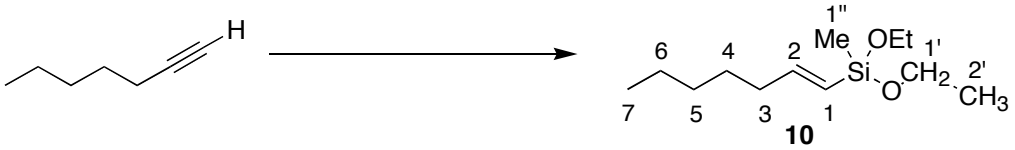
TLC: R_f 0.23 (pentane/Et_2O, 19/1) [$KMnO_4$]

CG: t_R 7.74 min (>99%) (HP5, injector 225 °C, column 180 °C, 15 psi)

Analysis: $C_{13}H_{28}O_3Si$ (260.18)

Calc.:	C, 59.96;	H, 10.85%
Found	C, 59.87;	H, 11.13%

(*E*)-Diethoxy-(1-heptenyl)methylsilane (10)



10

Diethoxymethylsilane (850 μL. 5.3 mmol, 1.05 equiv) was combined with a solution of platinum(0)-DVDS-*t*-Bu_3P (50 μL) in xylene. The reaction was cooled to 0 °C and 1-heptyne (655 μL, 5.0 mmol) was added. The ice bath was then removed and the reaction was stirred for 4 h. All volatile materials were then removed by evaporation under high vacuo and the residual oil was distilled. The resulting oil was purified by radial chromatography (SiO_2, pentane/Et_2O, 19/1) and then was distilled to give 563 mg (49%) of **10** as a colorless oil.

Data for **10**:

bp: 115 °C (0.4 mmHg, ABT)

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

6.29 (dt, J = 18.5, 6.2, 1 H, HC(2)), 5.52 (dt, J = 18.5, 1.7, 1 H, HC(1)), 3.76 (q, J = 7.1, 4 H, $2H_2C(1')$, 2.12 (qd, J = 7.5, 1.5, 2 H, $H_2C(3)$), 1.39 (qn, J = 7.2, 2 H,

$H_2C(4)$), 1.27 (m, 4 H, $H_2C(5)$ and $H_2C(6)$), 1.19 (t, J = 7.1, 6 H, $3H_2C(2')$), 0.87 (t, J = 7.0, 3 H, $H_3C(7)$), 0.16 (s, 3 H, $H_3C(1'')$)

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

152.3 (C(1)), 123.5 (C(2)), 58.3 (C(1'), 36.7 (C(3)), 31.5 (C(4)), 28.2 (C(5)), 22.7 (C(6)), 18.5 (C(2')), 14.2 (C(7)), -4.2 (C(1''))

IR: (NaCl)

2970 (s), 2927 (s), 2875 (s), 1620 (m), 1458 (w), 1390 (m), 1255 (m), 1105 (s), 1079 (s), 952 (s), 823 (s)

MS: (EI, 70 eV)

230 (M^+, 1), 215 (100), 185 (9), 171 (19), 133 (54), 89 (12), 77 (13)

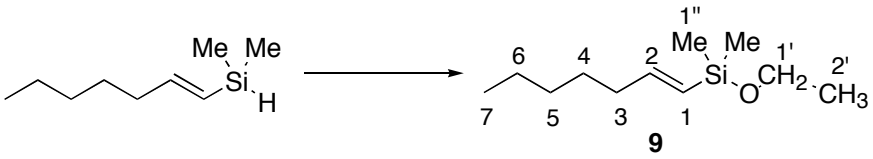
TLC: R_f 0.22 (pentane/Et_2O, 19/1) [$KMnO_4$]

CG: t_R 5.35 min (>99%) (HP5, injector 225 °C, column 180 °C, 15 psi)

Analysis: $C_{12}H_{26}O_2Si$ (230.17)

Calc.:	C, 62.56;	H, 11.38%
Found:	C, 62.37;	H, 11.33%

(*E*)-Dimethylethoxy-(1-heptenyl)silane (9)



9

Sodium (16 mg, 0.7 mmol, 0.01 equiv) was added to 10 mL of dry ethanol and the resulting solution was stirred for 30 min. The solution was cooled to -4 °C (internal temperature) and the silane (1.09 g, 7.0 mmol) was slowly added whereupon gas evolution was observed. After being stirred for 1 h at room temperature, the mixture was diluted with ether (50 mL) and then was filtered through a plug of Celite. The solvent was evaporated in vacuo and the resulting oil was distilled to give 952 mg (68%) of **9** as colorless oil.

Data for **9**:

bp: 120 °C (0.6 mmHg, ABT)

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

6.17 (dt, J = 18.5, 6.1, 1 H, HC(2)), 5.61 (dt, J = 18.5, 1.7, 1 H, HC(1)), 3.65 (q, J

= 7.1, 2 H, $H_2C(1')$, 2.12 (qd, *J* = 7.5, 1.5, 2 H, $H_2C(3)$), 1.40 (qn, *J* = 7.5, 2 H, HC(4)), 1.29 (m, 4 H, $H_2C(5)$ and $H_2C(6)$), 1.18 (t, *J* = 7.1, 3 H, $H_3C(2')$), 0.88 (t, *J* = 7.0, 3 H, $H_3C(7)$), 0.16 (s, 3 H, $H_3C(1'')$)

^{13}C NMR: (101 MHz, $CDCl_3$)

150.1 (C(1)), 127.2 (C(2)), 58.5 (C(1'), 36.8 (C(3)), 31.6 (C(4)), 28.4 (C(5)), 22.7 (C(6)), 18.7 (C(2')), 14.2 (C(7)), -1.5 (C(1''))

IR: (NaCl)

2969 (s), 2927 (s), 2873 (s), 1618 (m), 1460 (w), 1390 (w), 1250 (s),1109 (s), 1080 (s), 993 (s), 837 (s)

MS: (EI, 70 eV)

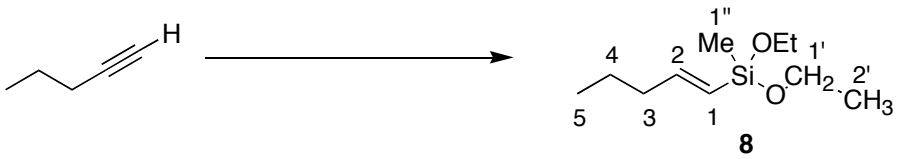
200 (M^+, >1%), 185 (100), 141 (10), 103 (26)

TLC: R_f 0.30 (hexane/EtOAc, 20/1) [$KMnO_4$]

CG: t_R 5.04 min (>99%) (HP5, injector 225 °C, column 170 °C, 15 psi)

HRMS: calcd for $C_{11}H_{24}O_1Si$: 200.1596; found: 200.1601

(*E*)-Diethoxy-(1-pentenyl)methylsilane (8)



8

Diethoxymethylsilane (850 μL. 5.3 mmol, 1.05 equiv) was combined with a solution of platinum(0)-DVDS-*t*-Bu_3P (50 μL) in xylene. The solution was cooled to 0 °C and 1-pentyne (492 μL. 5.0 mmol) was added. The ice bath was then removed and the reaction was stirred for 4 h. All volatile materials were then removed by evaporation under high vacuo and the residual oil was distilled. The resulting oil was purified by radial chromatography (SiO_2, pentane/Et_2O, 19/1) and distilled to give 450 mg (43%) of **8** as colorless oil.

Data for **8**:

bp: 95 °C (0.8 mmHg, ABT)

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

6.28 (dt, *J* = 18.7, 6.4, 1 H, HC(2)), 5.52 (dt, *J* = 19.0, 1.4, 1 H, HC(1)), 3.76 (q, *J* = 7.0, 4 H, $2H_2C(1')$, 2.11 (qd, *J* = 7.6, 1.5, 2 H, $H_2C(3)$), 1.43 (sext, *J* = 7.3, 2 H,

$H_2C(4)$), 1.21 (t, J = 7.0, 6 H, $2H_3C(2')$), 0.89 (t, J = 7.3, 3 H, $H_3C(5)$), 0.16 (s, 3 H, $H_3C(1'')$)

^{13}C NMR: (100 MHz, $CDCl_3$)

151.9 (C(1)), 123.8 (C(2)), 58.4 (C(1'), 38.8 (C(3)), 21.7 (C(4)), 18.5 (C(2')), 13.8 (C(5)), -4.2 (C(1''))

IR: (NaCl)

2969 (m), 2927 (m), 2875 (m), 1620 (w), 1390 (w), 1390 (m), 1255 (w), 1166 (s), 1105 (s), 1078 (s), 951 (s), 806 (s)

MS: (EI, 70 eV)

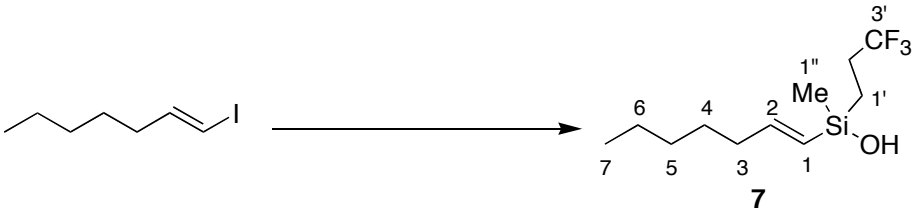
202 (M^+, 2.9), 187 (100), 143 (29.3), 133 (37.0), 89 (11.2), 77 (14.0)

TLC: R_f 0.22 (pentane/Et_2O, 19/1) [$KMnO_4$]

Analysis: $C_{10}H_{22}O_2Si$ (202.14)

Calc.:	C, 59.34;	H, 10.97%
Found	C, 59.10;	H, 11.33%

(*E*)-Trifluoropropylmethyl-(1-heptenyl)silanol (7)



7

To a solution of (*E*)-1-iodo-1-heptene (2.0 g, 8.9 mmol) in dry ether (15 mL) under dry N_2 at -78 °C was added a solution of *n*-butyllithium (5.76 mL, 8.9 mmol, 1.55 M in hexane, 1.0 equiv) dropwise over 10 min. The reaction mixture was stirred at -78 °C for 1 h. Then a solution of methyl(1,1,1-trifluoropropyl)cyclotrisiloxane (1.39 g, 2.9 mmol, 0.33 equiv) in dry ether (5 mL) was added over 5 min at -78 °C. The mixture was warmed to room temperature and was stirred for 12 h. The solution was then cooled to 0 °C and was quenched with water (20 mL). The aqueous phase was extracted with ether (3 × 25 mL) and the combined organic extracts were washed with water (1 × 25 mL) and brine (2 × 30 mL). The organic layer was dried with $MgSO_4$ (anhydrous) and was filtered. The solvent was then evaporated in vacuo to give a yellow residue, which was purified by distillation to afford 1.695 g (75%) of **7** as colorless oil.

Data for **7**:

bp: 105 °C (0.4 mmHg, ABT)

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

6.22 (dt, *J* = 18.6, 6.2, 1 H, HC(2)), 5.58 (dt, *J* = 18.6, 1.5, 1 H, HC(1)), 2.13 (qd, *J* = 7.3, 1.5, 2 H, H_2C(3)), 2.06 (m, 2 H, H_2C(2')) 1.40 (qn, *J* = 7.3, 2 H, H_2C(4)), 1.29 (m, 4 H, H_2C(5) and H_2C(6)), 0.89 (t, *J* = 7.1, 3 H, H_3C(7)), 0.85 (m, 2 H, H_2C(1')), 0.21 (s, 3 H, H_3C(1''))

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

151.6 (C(1)), 128.0 (q, *J* = 277, (C(3')), 125.8 (C(2)), 36.8 (C(3)), 31.5 (C(4)), 28.2 (q, *J* = 30 Hz, (C(2')), 28.2 (C(5)), 22.6 (C(6)), 14.1 (C(7)), 8.7 (d, *J* = 1.8 Hz. (C1')), -1.8 (C(1''))

IR: (NaCl)

3269 (s), 2960 (s), 2931 (s), 2859 (s), 1618 (s), 1446 (m), 1365 (m), 1315 (m), 1265 (s), 1209 (s), 1126 (s), 995 (m), 899 (s), 854 (s)

MS: (EI, 70 eV)

157 (M-97, $CH_2CH_2CF_3$, 100), 95 (12), 79 (24), 61 (41)

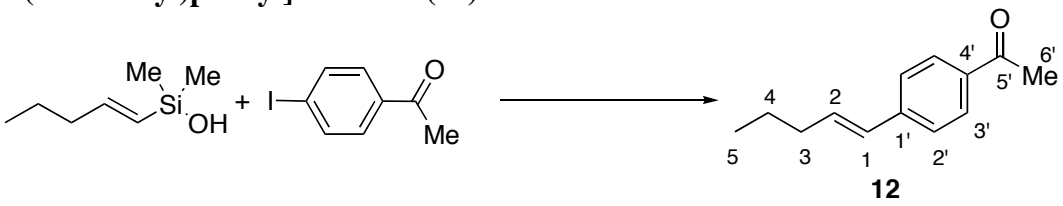
TLC: R_f 0.34 (hexane/EtOAc, 8/1) [$KMnO_4$]

CG: t_R 4.93 min (>99%) (HP5, injector 225 °C, column 200 °C, 15 psi)

Analysis: $C_{11}H_{21}O_1F_3$ Si (230.17)

Calc.:	C, 51.94;	H, 8.33%
Found	C, 52.02;	H, 8.67%

(*E*)-1-[4-(1-Pentenyl)phenyl]ethanone (12)



12

(*E*)-Dimethyl-(1-pentenyl)silanol ((*E*)-**1** (317 mg, 2.2 mmol, 1.1 equiv) was added to a solution of TBAF (4.0 mL, 1.0 M in THF, 2 equiv) and $Pd(dba)_2$ (58 mg. 0.1 mmol, 0.05 equiv). 4-Iodoacetophenone (493 mg, 2.0 mmol) was added and the mixture was stirred for 10 min at room temperature. The reaction mixture was then filtered through a short silica gel column (20 g). The plug was washed with hexane/EtOAc, 4/1 (200 mL) and the solvent was evaporated in vacuo. The residue was purified by column chromatography (Reverse Phase C18, MeOH/H_2O, 9/1) and distillation to afford 331 mg (88%) of **12** as colorless oil.

Data for **12**:

bp: 130 °C (0.8 mmHg, ABT)

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

7.89 (d, J = 8.5, 2 H, HC(3')), 7.41 (d, J = 8.3, 2 H, HC(2')), 6.39 (m, 2 H HC(1) and HC(2)), 2.58 (s, 3 H, H_3C(6')), 2.26 (q, J = 5.9, 2 H, H_2C(3)), 1.53 (sept, J = 7.3, 2 H, H_2C(4)), 0.97 (t, J = 7.3, 3 H, H_3C(5))

^{13}C NMR: (101 MHz, $CDCl_3$)

197.6 (C(5')), 142.6 (C(4')), 135.4 (C(1')), 134.3 (C(2)), 129.1 (C(1)), 128.7 (C(3')), 125.9 (C(2')), 35.2 (C(3)), 26.5 (C(6')), 22.3 (C(4)), 13.7 (C(5))

IR: (NaCl)

2960 (s), 2931 (s), 2872 (s), 1680 (s), 1603 (s), 1412 (s), 1358 (s), 1269 (s), 1180 (s), 966 (s), 850 (s)

MS: (EI, 70 eV)

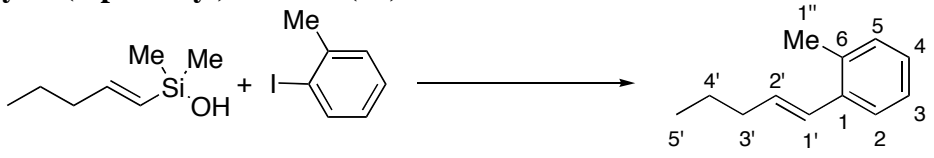
188 (M^+, 75), 173 (100), 159 (6), 145 (16), 131 (60), 115 (73), 103 (18), 91 (18), 77 (22), 63 (19)

TLC: R_f 0.45 (hexane/EtOAc, 4/1) [UV + $KMnO_4$]

Analysis: $C_{13}H_{16}O$ (188.27)

Calc.:	C, 82.94;	H, 8.57%
Found	C, 82.65;	H, 8.57%

(*E*)-1-Methyl-2-(1-pentenyl)benzene (16)



16

(*E*)-Dimethyl(1-pentenyl)silanol ((*E*)-**1** (158 mg, 1.1 mmol, 1.1 equiv) was added to a solution of TBAF (2.0 mL, 1 M in THF, 2.0 mmol, 2 equiv) and $Pd(dba)_2$ (58 mg. 0.1 mmol, 0.05 equiv). 2-Iodotoluene (127 μL, 1.0 mmol) was added and the mixture was stirred for 30 min at room temperature. The reaction mixture was then filtered through a short silica gel column (20 g). The plug was washed with hexane/EtOAc, 4/1 (200 mL) and the solvent was evaporated in vacuo. The residue was purified by column chromatography (Reverse Phase C18, MeOH/H_2O 9/1) and distillation to afford 128 mg (80%) of **16** as colorless oil.

Data for **16**:

bp: 100 °C (5.0 mmHg, ABT)

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

7.42 (d, J = 7.3, 1 H, HC(6)), 7.20 (m, 3 H HC(3), HC(4) and HC(5)), 6.57 (d, J = 15.6, 1 H, HC(1')), 6.09 (dt, J = 15.6, 6.9, 1 H, HC(2')), 2.33 (s, 3 H, H_3C(1")), 2.21 (qd, J = 7.1, 1.2, 2 H, H_2C(3')), 1.51 (sept, J = 7.2, 2 H, H_2C(4')), 0.96 (t, J = 7.2, 3 H, H_3C(5'))

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

137.0 (C(1)), 134.8 (C(2)), 132.3 (C(1')), 130.1 (C(3')), 127.7 (C(2')), 126.6 (C(4)), 125.9 (C(6)), 125.4 (C(5)), 35.3 (C(3')), 22.5 (C(4')), 16.7 (C(1")), 13.6 (C(5'))

IR: (NaCl)

3022 (m), 2958 (s), 2927 (s), 1602 (w), 1485 (m), 1461 (m), 1379 (w), 1259 (w), 1045 (m), 964 (s)

MS: (EI, 70 eV)

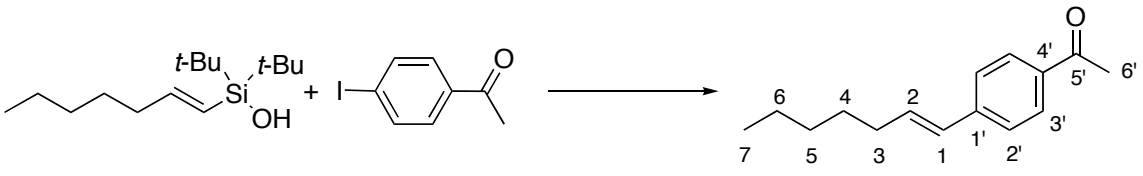
160 (M^+, 44), 131 (100), 115 (21), 91 (31)

TLC: R_f 0.87 (SiO_2 hexane) [UV + $KMnO_4$]

CG: t_R 6.32 min (96%) (HP5, injector 225 °C, column 200 °C, 15 psi)

HRMS: calcd for $C_{12}H_{16}$: 160.1252; found: 160.1254

(*E*)-1-[4-(1-Heptenyl)phenyl]ethanone (13)[3]



13

(*E*)-Di-*tert*-butyl(1-heptenyl)silanol **5** (307 mg, 1.2 mmol, 1.2 equiv) was added to a solution of TBAF (2.0 mL, 1 M in THF, 2.0 mmol, 2.0 equiv) and $Pd(dba)_2$ (28.7 mg. 0.05 mmol, 0.05 equiv). 4-Iodoacetophenone (246 mg, 1.0 mmol) was added to the mixture. The mixture was stirred at 50 °C for 19 h. The reaction mixture was then filtered through a short silica gel column (20 g). The plug was washed with hexane/EtOAc, 4/1 (50 mL) and the solvent was evaporated in vacuo. The residue was purified by column chromatography (SiO_2, hexane/EtOAc, 9/1 then hexane/EtOAc, 4/1) to afford product **13** and 29 mg (12%) of 1,1'-[1,1'-biphenyl]-4,4'-diyl-bisethanone (homocoupling product). Further purification by Kugelrohr distillation afforded 331 mg (59%) of **13** as colorless oil.[3]

Data for **13**:

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

7.89 (d, J = 8.5, 2 H, HC(3')), 7.41 (d, J = 8.3, 2 H, HC(2')), 6.39 (m, 2 H, HC(1) and HC(2)), 2.58 (s, 3 H, H_3C(6')), 2.26 (q, J = 5.9, 2 H, H_2C(3)), 1.53 (sept, J = 7.3, 2 H, H_2C(4)), 0.97 (t, J = 7.3, 3 H, H_3C(5))

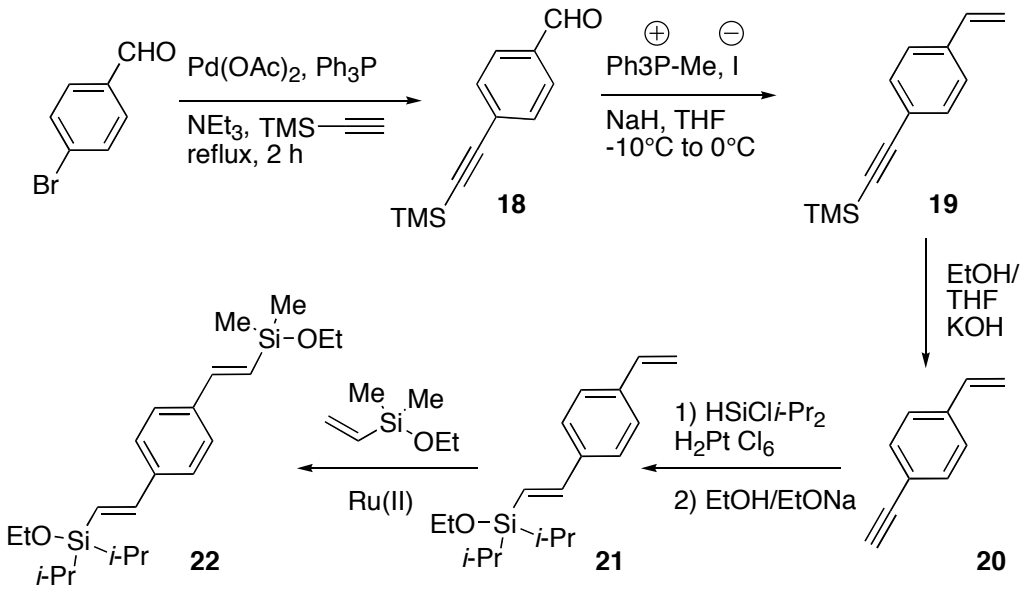
^{13}C NMR: (101 MHz, $CDCl_3$)

197.6 (C(5')), 142.6 (C(4')), 135.4 (C(1')), 134.3 (C(2)), 129.1 (C(1)), 128.7 (C(3')), 125.9 (C(2')), 35.2 (C(3)), 26.5 (C(6')), 22.3 (C(4)), 13.7 (C(5))

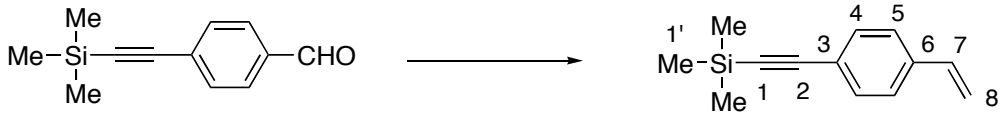
TLC: R_f 0.45 (hexane/EtOAc, 4/1) [UV + $KMnO_4$]

CG: t_R 8.30 min (>99%) (HP5, injector 225 °C, column 250 °C, 15 psi)

Preparation of Ethoxy(di-(1-methylethyl)) 2-[4-[(*E*)-2-(Ethoxydimethylsilyl)ethenyl]-phenyl]ethenylsilane



[(4-(Ethenylphenyl)ethynyl]trimethylsilane (19)[8]



To a suspension of triphenylphosphonium iodide (4.85 g, 12.0 mmol, 1.1 equiv) in 10 mL of THF at -20 °C, was added a solution of *n*-butyllithium (7.75 mL, 1.55 M in hexane, 12.0 mmol, 1.1 equiv). The reaction was stirred for 30 min at -10 °C, then for 1 h at room temperature. The mixture was cooled to -20 °C and a solution of aldehyde **18** (2.0 g, 10.0 mmol) in 5 mL of THF was slowly added. The reaction was allowed to warm to room temperature and was stirred for 1 h whereupon the reaction mixture was quenched with water (30 mL). The aqueous phase was extracted with ether (3 × 25 mL) and the combined organic extracts were washed with water (1 × 25 mL) and brine (2 × 30 mL). The organic layer was dried with $MgSO_4$ (anhydrous) and filtered. After evaporation of the solvent, the residue was purified by column chromatography (SiO_2, hexane) and distillation to afford 1.60 g (81%) of **19**[8] as colorless oil.

Data for **19**:

mp: 90 °C (0.4 mmHg, ABT)

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

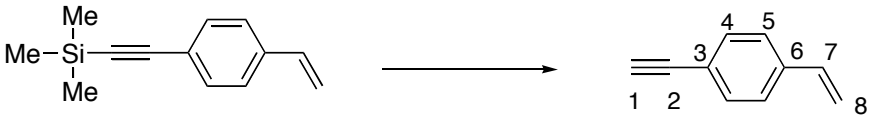
7.42 (d, *J* = 8.3, 2 H, HC(4)), 7.36 (d, *J* = 8.1, 2 H, HC(5)), 6.70 (dd, *J* = 17.1, 11.0, 1 H, HC(7), 5.78 (d, *J* = 17.1, 1 H, HC(8)), 5.31 (d, *J* = 11.0, 1 H, HC(8)), 3.12 (s, 1 H, HC(1))

^{13}C NMR: (101 MHz, $CDCl_3$)

137.8 (C(6)), 136.4 (C(7)), 132.3 (C(4), 126.2 (C(5)), 122.6 (C(3)), 115.0 (C(8)), 105.3 (C(2)), 95.0 (C(1)), 0.2 (C(1'))

TLC: R_f0.35 (hexane) [UV + $KMnO_4$]

4-Ethenyl-1-ethynylbenzene (20)[9]



19 **20**

To a solution of **19** (1.40 g, 7.0 mmol) in 10 mL of THF and 10 mL of ethanol, cooled to 0 °C (external ice bath) was added an aqueous solution of KOH (7.0 mL, 7.0 mmol, 1.0 M, 1.0 equiv). The reaction was warmed to room temperature and was stirred for 1 h whereupon the reaction was quenched with water (50 mL). The aqueous phase was extracted with ethyl acetate (3 × 35 mL) and the combined organic extracts were washed with water (1 × 30 mL) and brine (2 × 30 mL). The organic layer was dried with $MgSO_4$ (anhydrous) and filtered. After evaporation of the solvent, the residue was purified by column chromatography (SiO_2, hexane) and distillation to afford 786 mg (88%) of **20** as colorless oil.[9]

Data for **20**:

bp: 60 °C (0.4 mmHg, ABT)

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

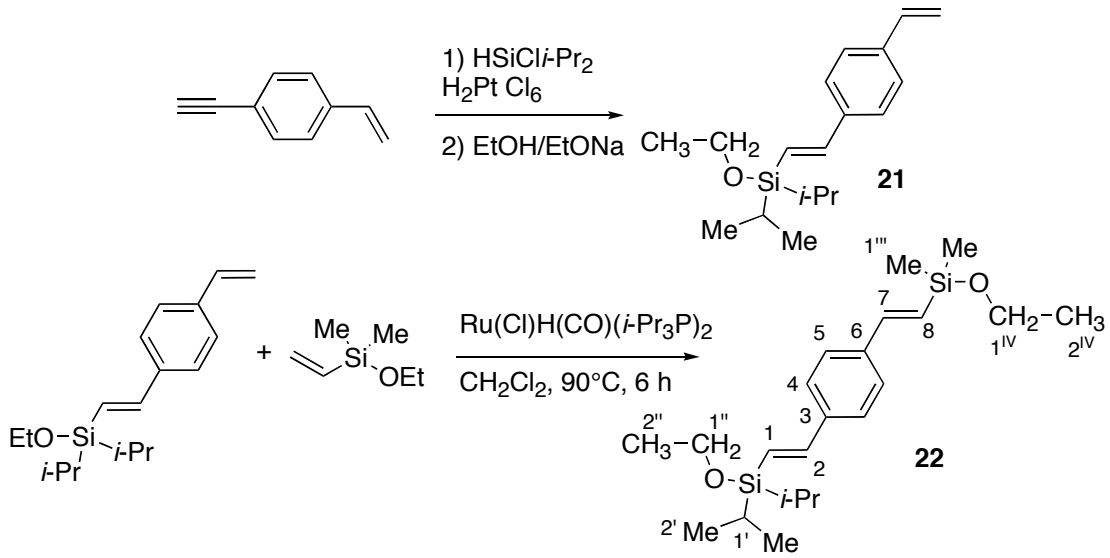
7.46 (d, *J* = 8.1, 2 H, HC(4)), 7.33 (d, *J* = 8.3, 2 H, HC(5)), 6.69 (dd, *J* = 17.5, 11.0, 1 H, HC(7), 5.76 (d, *J* = 17.5, 1 H, HC(8)), 5.29 (d, *J* = 11.0, 1 H, HC(8)), 0.26 (s, 9 H, $3H_3C$(1'))

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

138.2 (C(6)), 136.3 (C(7)), 132.5 (C(4), 126.3 (C(5)), 121.5 (C(3)), 115.3 (C(8)), 83.8(C(2)), 77.9 (C(1))

TLC: R_f 0.33 (hexane) [UV + $KMnO_4$]

Ethoxy(di-(1-methylethyl)) 2-[4-[(*E*)-2-(Ethoxydimethylsilyl)ethenyl]phenyl]ethenylsilane (22)



A mixture of **20** (740 mg, 5.7 mmol) and diisopropylchlorosilane (1.05 mL, 6.0 mmol, 1.05 equiv) and Pt(0)-DVDS solution (25 μL). The mixture was stirred for 2.5 h at room temperature and all volatile materials were removed under high vacuum. The residue was dissolved in 10 mL of hexane and 1.0 mL of ethanol (17 mmol, 3.0 equiv) and triethylamine (1.2 mL, 8.6 mmol, 1.5 equiv) was added. The reaction mixture was further stirred for 1 h and was filtered. The filtrate was evaporated in vacuo and the resulting oil was purified by column chromatography (SiO_2, hexane/CH_2Cl_2, 7/1) to afford (*E*)-**21** as colorless oil.

Compound **21** was placed in a Schlenk tube with 3 mL of dichloromethane, followed by ethoxydimethylvinylsilane (1.03 ml, 6.3 mmol, 1.2 equiv). The tube was placed in a dry-box and Ruthenium catalyst (13 mg, 0.026 mmol, 0.5% mol equiv) was added. The tube was sealed, removed from the dry-box and heated at 100 °C for 12 h. After being cooled to room temperature, the solvent was evaporated. The residue was purified by column chromatography (SiO_2, hexane/CH_2Cl_2 2/1) and distillation to afford 1.29 g (58%) of **22** as colorless oil.

Data for **22**:

bp: 190 °C (0.3 mmHg, ABT)

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

7.44 (s, 4 H, HC(4) and HC(5)), 7.03 (d, *J* = 19.5, 1 H, HC(2)), 6.97 (d, *J* = 19.3, 1 H, HC(7)), 6.43 (d, *J* = 19.3, 1 H, HC(8)), 6.36 (d, *J* = 19.5, 1 H, HC(1)), 3.81 (q, *J* = 7.1, 2 H, $H_2C(1^{IV})$), 3.72 (q, *J* = 7.1, 2 H, $H_2C(1")$, 1.23 (m, 6 H, $H_3C(2")$ and $H_3C(2^{IV})$), 1.07 (m, 14 H, $4H_3C(2')$ and 2HC(1')), 0.28 (s, 6 H, $2H_3C(1"')$)

^{13}C NMR: (101 MHz, $CDCl_3$)

146.3 (C(2)), 145.2 (C(7)), 138.4(C(3)), 138.0 (C(6)), 127.0 (C(4)), 126.9 (C(5)), 126.9 (C(8)), 122.9 (C(1)), 59.5 ($C(1^{IV})$), 58.7 (C(1")), 18.9 ($C(2^{IV})$), 18.7 (C(2")), 17.7/17.6 (C(2')), 12.7 (C(1)), -1.5 (C(1"'))

IR: (NaCl)

2960 (s), 2865 (s), 1605 (m), 1556 (w), 1506 (w), 1463 (m), 1390 (m), 1251 (s), 1081 (s), 989 (s), 843 (s)

MS: (EI, 70 eV)

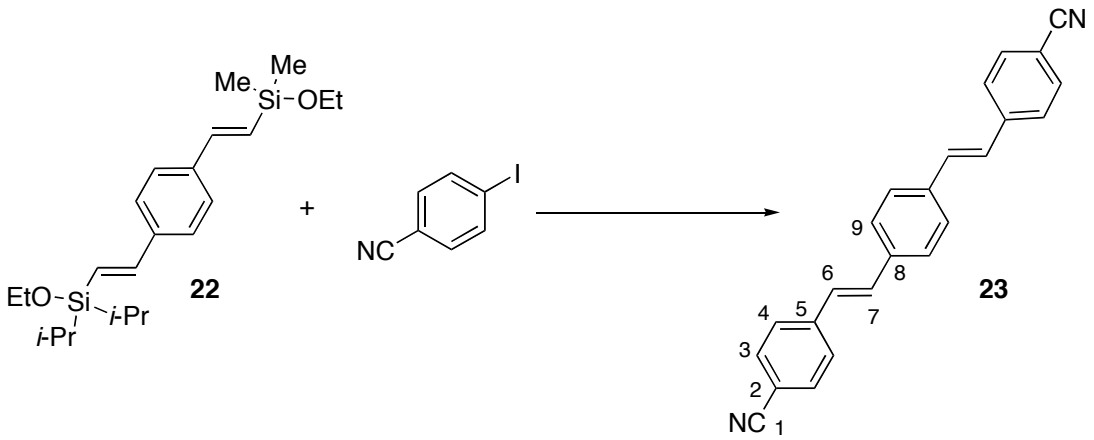
390 (M^+, 6), 375 (2), 347 (100), 103 (32), 75 (10)

TLC: R_f 0.26 (hexane/CH_2Cl_2, 2/1) [UV + $KMnO_4$]

CG: t_R 16.3 min (>99%) (HP5, injector 225 °C, column 250 °C, 15 psi)

HRMS: calc for $C_{22}H_{38}O_2Si_2$: 390.2410; found: 390.2410

(*E*,*E*)-4,4'-(1,4-Phenylenediethendiyl)bisbenzonitrile (23)[10]



Bis-silane **22** (390 mg, 1.0 mmol), 4-iodobenzonitrile (458 mg, 2.0 mmol, 2.0 equiv), and $(allylPdCl)_2$ (9.3 mg. 0.025 mmol, 0.025 equiv) were dissolved in a solution of TBAF (4.0 mL, 1.0 mmol, 1 M in THF, 4 equiv). The reaction mixture was stirred for 6 h at room temperature.

The solution was quenched with water (20 mL) and was extracted with EtOAc (5 × 20 mL) and the combined organic phases were washed with brine (20 mL). The organic layer was dried with $MgSO_4$ (anhydrous) and was filtered. The solvent was then evaporated in vacuo to give a solid which was purified by column chromatography (SiO_2, CH_2Cl_2/hexane, 2/1) to afford 262 mg (79%) of **23** as yellow solid.[10]

Data for **23**:

mp: 288 °C

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

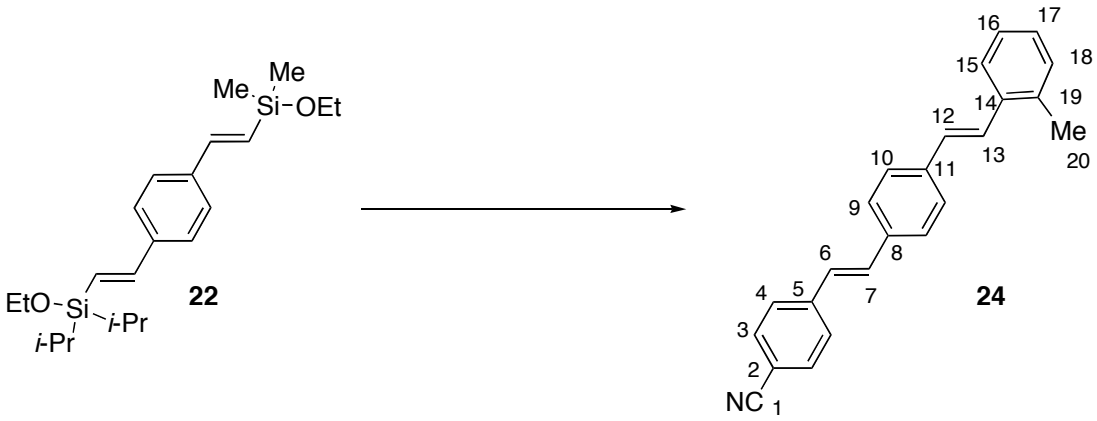
7.65 (d, J = 8.4, 4 H, HC(4)), 7.60 (d, J = 8.4, 4 H, HC(3)), 7.56 (s, 4 H, HC(9)), 7.21 (d, J = 16.3, 2 H, HC(6)), 7.13 (d, J = 16.3, 2 H, HC(7)),

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

141.8 (C(5)), 136.8 (C(8)), 132.7 (C(3)), 131.9 (C(6)), 127.6 (C(4)), 127.4 (C(7)), 127.1 (C(9)), 119.2 (C(1)), 110.9 (C(2))

TLC: R_f 0.26 (CH_2Cl_2/hexane, 2/1) [UV + $KMnO_4$]

4-[2-[4-[2-(2-Methylphenyl)ethenyl]phenyl]ethenyl]benzonitrile (24)



A solution of bis-silane **22** (390 mg, 1.0 mmol), 4-iodobenzonitrile (229 mg, 1.0 mmol, 1.0 equiv), and $(allylPdCl)_2$ (9.3 mg. 0.025 mmol, 0.025 equiv) in DME (4 mL) was stirred at room temperature for 5 min and then TMSOK (512 mg, 4.0 mmol, 4.0 equiv) was added. The reaction mixture was stirred at room temperature for 6 h whereupon EtOAc (20 mL) was added and the reaction was stirred for 10 min further. The reaction mixture was then filtered through a short silica gel column (20 g) and the plug was washed with EtOAc (100 mL) and the solvent was evaporated in vacuo. To the crude product was added 2-iodotoluene (128 μL, 1.0 mmol, 1.0

equiv), $(allylPdCl)_2$ (9.3 mg. 0.025 mmol, 0.025) and a solution of TBAF (3.0 mL, 1 M in THF, 3.0 mmol, 3.0 equiv). The reaction mixture was stirred for 4 h at room temperature, then EtOAc (25 mL) was added. After stirring 10 min further, the reaction was quenched with water (25 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic extracts were washed with water (1 × 30 mL) and brine (1 × 30 mL). The organic layer was dried over $MgSO_4$ (anhydrous) and was filtered. After evaporation of the solvent, the residue was purified by column chromatography (SiO_2, hexane/CH_2Cl_2, 2/1) and sublimed to afford 244 mg (76%) of **24** as yellow solid.

Data for **24**:

mp: 294 °C (subl.)

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

7.64 (d, J = 8.5, 2 H, HC(4)), 7.60 (m, 3 H, HC(3) and HC(15)), 7.54 (s, 4 H, HC(9) and HC(10)), 7.38 (d, J = 16.4, 1 H, HC(13)), 7.21 (m, 4 H, HC(6), HC(16), HC(17), and HC(18)), 7.11 (d, J = 16.3, 1 H, HC(7)), 7.01 (d, J = 16.1, 1 H, HC(12)), 2.45 (s, 3 H, HC20))

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

142.1 (C(5)), 138.3 (C(14)), 136.4 (C(8)), 136.1 (C(11)), 135.8(C(19)), 132.7 (C(3)), 132.2 (C(6)), 130.7 (C(18)), 129.5 (C(17)), 127.9 (C(15)), 127.5 (C(4)), 127.3 (C(7)), 127.2 (C(9)), 127.0 (C(10)), 126.7 (C(16)), 126.5 (C(12)), 125.5 (C(13)), 119.3 (C(1)), 110.7 (C(2)), 20.1 (C(20))

IR: ($CHCl_3$)

3021 (m), 2227 (s), 1600 (s), 1514 (w), 1460 (w), 1214 (w), 1174 (w), 964 (s)

MS: (EI, 70 eV)

321 (M^+, 100), 203 (13), 157 (16)

TLC: R_f 0.21 (hexane/CH_2Cl_2, 2/1) [UV + $KMnO_4$]

CG: t_R 31.24 min (100%) (HP5, injector 225 °C, column 275 °C, 15 psi)

HRMS: calc for $C_{24}H_{19}N_1$: 331.1518; found: 321.1517

Determination of Response Factors for 1-[(*E*)-4-(1-Pentenyl)phenyl]ethanone (12) and 1-[(*E*)-4-(1-Heptenyl)phenyl]ethanone (13) with Respect to Naphthalene.

Samples containing various amount of 1-[(*E*)-4-(1-pentenyl)phenyl]ethanone (**12**) or 1-[(*E*)-4-(1-heptenyl)phenyl]ethanone (**13**), and naphthalene were weighed (amounts given below) into small vials. The samples were diluted with 10 mL of dry THF and were then injected into the GC three times to give the areas indicated below. The response factor for every sample was calculated by

$$\text{response factor} = \frac{\text{mmol } \mathbf{12} \times \text{area naphthalene}}{\text{area } \mathbf{12} \times \text{mmol naphthalene}}$$

mg naphth	mmol naphth	area naphth	mg **12**	mmol **12**	area **12**	response factor
45.6	0.354	17650	80.5	0.428	27031	0.788
45.6	0.354	17642	80.5	0.428	26972	0.790
45.6	0.354	17621	80.5	0.428	26752	0.795
44.4	0.345	30424	62.9	0.334	36812	0.801
44.4	0.345	30041	62.9	0.334	36498	0.797
44.4	0.345	30478	62.9	0.334	36904	0.800
44.0	0.342	19642	59.1	0.314	23376	0.772
44.0	0.342	19695	59.1	0.314	23403	0.773
44.0	0.342	19727	59.1	0.314	23490	0.771
					average	0.787

$$\text{response factor} = \frac{\text{mmol } \mathbf{13} \text{ x area naphthalene}}{\text{area } \mathbf{13} \text{ x mmol naphthalene}}$$

mg naphth	mmol naphth	area naphth	mg **13**	mmol **13**	area **13**	response factor
48.0	0.373	28933	73.8	0.341	38879	0.681
48.0	0.373	29169	73.8	0.341	39474	0.676
48.0	0.373	28908	73.8	0.341	39126	0.676
45.6	0.354	17650	70.7	0.327	24499	0.665
45.6	0.354	17642	70.7	0.327	2444	0.666
45.6	0.354	17621	70.7	0.327	24403	0.666
44.4	0.345	30424	77.6	0.359	46491	0.681
44.4	0.345	30041	77.6	0.359	46519	0.672
44.4	0.345	30478	77.6	0.359	46953	0.675
					average	0.673

Determination of Response Factors for (*E*)-1-Methyl-2-(1-pentenyl)benzene (16) and (*E*)-1-Methyl-2-(1-heptenyl)benzene (17) with Respect to Naphthalene.

Samples containing various amount of (*E*)-1-methyl-2-(1-pentenyl)benzene (**16**), (*E*)-1-methyl-2-(1-heptenyl)benzene (**17**), and naphthalene were weighed (amounts given below) into small vials. The samples were diluted with 10 mL dry THF and were then injected into the GC three times to give the areas indicated below. The response factor for every sample was calculated by

$$\text{response factor} = \frac{\text{mmol } \mathbf{16} \text{ x area naphthalene}}{\text{area } \mathbf{16} \text{ x mmol naphthalene}}$$

mg naphth	mmol naphth	area naphth	mg **9**	mmol **9**	area **9**	response factor
40.5	0.315	30289	44.6	0.278	31003	0.864
40.5	0.315	29947	44.6	0.278	30419	0.871
40.5	0.315	28763	44.6	0.278	29302	0.868
40.3	0.313	32362	52.1	0.325	39808	0.844
40.3	0.313	41383	52.1	0.325	51256	0.838
40.3	0.313	49832	52.1	0.325	61671	0.839
40.3	0.313	30144	49.8	0.311	34553	0.866
40.3	0.313	44474	49.8	0.311	51428	0.858
40.3	0.313	39946	49.8	0.311	46094	0.860
					average	0.857

$$\text{response factor} = \frac{\text{mmol } \mathbf{17} \text{ x area naphthalene}}{\text{area } \mathbf{17} \text{ x mmol naphthalene}}$$

mg naphth	mmol naphth	area naphth	mg **17**	mmol **17**	area **17**	Response factor
41.9	0.325	36983	57.1	0.303	48111	0.716
41.9	0.325	39439	57.1	0.303	51425	0.715
41.9	0.325	40007	57.1	0.303	52262	0.713
40.5	0.315	32362	36.7	0.195	28947	0.693
40.5	0.315	41383	36.7	0.195	37631	0.681
40.5	0.315	49832	36.7	0.195	45294	0.682
40.3	0.313	30289	18.5	0.098	13049	0.728
40.3	0.313	29947	18.5	0.098	12827	0.733
40.3	0.313	28763	18.5	0.098	12351	0.731
					average	0.710

Determination of Response Factors for (*E*)-1-Methoxy-4-(1-pentenyl)benzene (14) and (*E*)-1-Methoxy-4-(1-heptenyl)benzene (15) with Respect to Naphthalene.

Samples containing various amount of (*E*)-1-methoxy-4-(1-pentenyl)benzene (**14**) or (*E*)-1-methoxy-4-(1-heptenyl)benzene (**15**), and naphthalene were weighed (amounts given below) into small vials. The samples were diluted with 10 mL dry THF and were then injected into the GC three times to give the areas indicated bellow. The response factor for every sample was calculated by

$$\text{response factor} = \frac{\text{mmol } \mathbf{14} \times \text{area naphthalene}}{\text{area } \mathbf{14} \times \text{mmol naphthalene}}$$

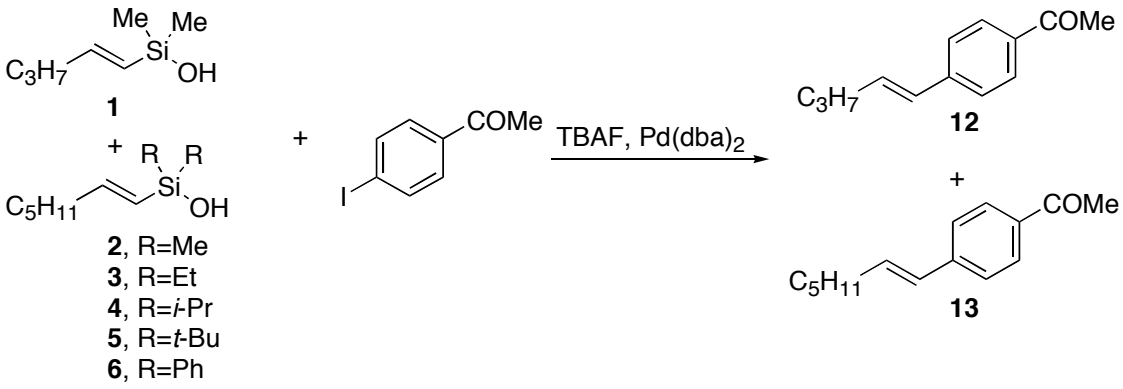
mg naphth	mmol naphth	area naphth	mg **14**	mmol **14**	area **14**	response factor
46.7	0.365	72420	53.5	0.304	62181	0.970
46.7	0.365	71762	53.5	0.304	61892	0.965
46.7	0.365	72116	53.5	0.304	62232	0.965
46.3	0.363	47337	42.9	0.244	33038	0.964
46.3	0.363	47327	42.9	0.244	33121	0.961
46.3	0.363	47095	42.9	0.244	32856	0.964
38.3	0.299	35469	59.1	0.314	26951	0.974
38.3	0.299	35430	59.1	0.314	27081	0.968
38.3	0.299	35546	59.1	0.314	26987	0.975
					average	0.967

$$\text{response factor} = \frac{\text{mmol } \mathbf{15} \text{ x area naphthalene}}{\text{area } \mathbf{15} \text{ x mmol naphthalene}}$$

mg naphth	mmol naphth	area naphth	mg **15**	mmol **15**	area **15**	response factor
52.5	0.410	60006	61.2	0.300	54756	0.801
52.5	0.410	60681	61.2	0.300	55506	0.799
52.5	0.410	60742	61.2	0.300	55982	0.794
46.7	0.365	72116	79.7	0. 390	97750	0.789
46.7	0.365	71762	79.7	0. 390	97148	0.790
46.7	0.365	72420	79.7	0. 390	97336	0.796
46.4	0.363	47095	56.0	0.363	44820	0.795
46.4	0.363	47327	56.0	0.363	45218	0.792
46.4	0.363	47337	56.0	0.363	45330	0.790
					average	0.794

Competition Experiments from Table 1 (Carbon Substituent Effects).

Competition Experiments with 4-Iodoacetophenone. General Procedure I.



(*E*)-Dimethyl-(1-pentenyl)silanol (**1**), together with one of the other 1-heptenylsilanols (**2**-**6**), naphthalene, and $Pd(dba)_2$ were dissolved in a TBAF solution (1.0 M in THF) in a flame-dried, 5-mL, 2-neck, round-bottomed flask under N_2. The 4-iodoacetophenone was then added slowly to maintain an internal temperature < 30 °C. After the reaction was complete, determined by TLC, 25-μL samples were taken via syringe. The sample aliquots were filtered through a plug of silica gel washing with hexane/ethyl acetate, 4/1 to achieve a total sample volume of ~2 mL. These samples were then subjected to GC analysis. The reaction mixture was filtered through a plug of silica gel (~15 g). The plug was washed with hexane/ethyl acetate, 4/1, (100 mL), and the solvent was evaporated in vacuo. The residue was purified by column chromatography (Reverse Phase C18, $MeOH/H_2O$, 9/1) to afford the **12**, and **13** which were further purified by Kugelrohr distillation.

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Dimethyl-(1 heptenyl)silanol (2) with 4-Iodoacetophenone

Following General Procedure I, **1** (83.9 mg, 0.58 mmol), **2** (97.1 mg, 0.56 mmol), naphthalene (67.7 mg, 0.53 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 4-iodoacetophenone (123.0 mg, 0.50 mmol) was stirred at room temperature for 10 min and then sample aliquots were taken and reaction was worked up to afford 48 mg (51%) of **12** and 47 mg (43%) of **13**. GC analysis of samples showed a **12**/**13** ratio of 52.2/47.8.

GC Data:

	area naphth	area **12**	area **13**	response factor **12/13**	ratio **12/13**x100
sample1	5546	4247	4396	0.78/0.67	53.1/46.9
sample2	6125	7688	8524	0.78/0.67	51.3/48.7
average	5836	5968	6460	0.78/0.67	52.2/47.8

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Dimethyl-(1-heptenyl)silanol (2) with 4-Iodoacetophenone

Following General Procedure I, **1** (71.8 mg, 0.50 mmol), **2** (85.9 mg, 0.50 mmol), naphthalene (65.3 mg, 0.51 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 4-iodoacetophenone (123.0 mg, 0.50 mmol) was stirred at room temperature for 10 min and then sample aliquots were taken and reaction was worked up to afford 43 mg (46%) of **12** and 48 mg (44%) of **13**. GC analysis of samples showed a **12/13** ratio of 50.1/49.9.

GC Data:

	area naphth	area **12**	area **13**	response factor **12/13**	ratio **12/13**x100
sample 1	15309	10206	11863	0.78/0.67	50.2/49.84

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Dimethyl-(1-heptenyl)silanol (2) with 4-Iodoacetophenone

Following General Procedure I, **1** (72.1 mg, 0.50 mmol), **2** (86.2 mg, 0.50 mmol), naphthalene (64.5 mg, 0.50 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 4-iodoacetophenone (123.0 mg, 0.50 mmol) was stirred at room temperature for 10 min and then sample aliquots were taken and reaction was worked up to afford 40 mg (43%) of **12** and 46 mg (43%) of **13**. GC analysis of samples showed a **12/13** ratio of 49.9/50.1.

GC Data:

	area naphth	area **12**	area **13**	response factor **12/13**	ratio **12/13**x100
sample 1	6207	3990	4598	0.78/0.67	50.4/49.6
sample 2	8196	4404	5257	0.78/0.67	49.5/50.1
average	7202	4197	4928	0.78/0.67	49.9/50.1

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Dimethyl-(1-heptenyl)silanol (2) with 4-Iodoacetophenone

Following General Procedure I, **1** (71.7 mg, 0.50 mmol), **2** (86.2 mg, 0.50 mmol), naphthalene (64.2 mg, 0.50 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.2 mg 0.025 mmol), and 4-iodoacetophenone (123.1 mg, 0.50 mmol) was stirred at room temperature for 10 min and then sample aliquots were taken and reaction was worked up to afford 41 mg (44%) of **12** and 47 mg (43%) of **13**. GC analysis of samples showed a **12**/**13** ratio of 50.9/49.1.

GC Data:

	area naphth	area **12**	area **13**	response factor **12**/**13**	ratio **12**/**13**x100
sample 1	7691	4788	5450	0.78/0.67	50.7/49.3
sample 2	7560	4886	5463	0.78/0.67	51.1/48.9
average	7626	4837	5457	0.78/0.67	50.9/49.1

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diethyl-(1-heptenyl)silanol (3) with 4-Iodoacetophenone

Following General Procedure I, **1** (71.4 mg, 0.50 mmol), **3** (100.4 mg, 0.50 mmol), naphthalene (64.3 mg, 0.50 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 4-iodoacetophenone (123.0 mg, 0.50 mmol) was stirred at room temperature for 10 min and then sample aliquots were taken and reaction was worked up to afford 49 mg (52%) of **12** and 40 mg (37%) of **13**. GC analysis of samples showed a **12**/**13** ratio of 56.7/43.3.

GC Data:

	area naphth	area **12**	area **13**	response factor **12**/**13**	ratio **12**/**13**x100
sample 1	14122	9596	8559	0.78/0.67	56.7/43.3
sample 2	18001	12673	11386	0.78/0.67	56.6/43.4
average	16062	11135	9973	0.78/0.67	56.7/43.3

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diethyl-(1-heptenyl)silanol (3) with 4-Iodoacetophenone

Following General Procedure I, **1** (71.9 mg, 0.50 mmol), **3** (100.4 mg, 0.50 mmol), naphthalene (64.6 mg, 0.50 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4

mg 0.025 mmol), and 4-iodoacetophenone (123.0 mg, 0.50 mmol) was stirred at room temperature for 10 min and then sample aliquots were taken and reaction was worked up to afford 49 mg (52%) of **12** and 44 mg (41%) of **13**. GC analysis of samples showed a **12**/**13** ratio of 56.6/43.4.

GC Data:

	area naphth	area **12**	area **13**	response factor **12**/**13**	ratio **12**/**13**x100
sample 1	12519	8940	8231	0.78/0.67	55.9/44.1
sample 2	8857	6408	5624	0.78/0.67	57.1/42.9
average	10688	7674	6928	0.78/0.67	56.6/43.4

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs. (*E*)-Di-isopropyl-(1-heptenyl)silanol (4) with 4-Iodoacetophenone

Following General Procedure I, **1** (71.3 mg, 0.49 mmol), **4** (115.1 mg, 0.50 mmol), naphthalene (65.3 mg, 0.51 mmol), TBAF (2.0 mL, 2.0 mmol, 1M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 4-iodoacetophenone (123.0 mg, 0.50 mmol) was stirred at room temperature for 10 min and then sample aliquots were taken and reaction was worked up to afford 51 mg (54%) of **12** and 41 mg (38%) of **13**. GC analysis of samples showed a **12**/**13** ratio of 59.8/40.2.

GC Data:

	area naphth	area **12**	area **13**	response factor **12**/**13**	ratio **12**/**13**x100
sample 1	8312	6852	5043	0.78/0.67	61.4/38.6
sample 2	17074	11744	9869	0.78/0.67	58.2/41.8
average	12693	9298	7456	0.78/0.67	59.8/40.2

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Di-(1-methylethyl)-(1-heptenyl)-silanol (4) with 4-Iodoacetophenone

Following General Procedure I, **1** (72.4 mg, 0.50 mmol), **4** (114.5 mg, 0.50 mmol), naphthalene (66.4 mg, 0.52 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 4-iodoacetophenone (123.0 mg, 0.50 mmol) was stirred at room temperature for 10 min and then sample aliquots were taken and reaction was worked up to afford 49 mg (52%) of **12** and 37 mg (34%) of **13**. GC analysis of samples showed a **12**/**13** ratio of 59.9/40.1.

GC Data:

	area naphth	area **12**	area **13**	response factor **12/13**	ratio **12/13**x100
sample 1	9300	6470	5213	0.78/0.67	59.2/40.8
sample 2	8435	6870	5238	0.78/0.67	60.5/39.5
average	8868	6670	5226	0.78/0.67	59.9/40.1

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Di-(1,1-dimethylethyl)-(1-heptenyl)silanol (5) with 4-Iodoacetophenone

Following General Procedure I, **1** (71.4 mg, 0.50 mmol), **5** (127.9 mg, 0.50 mmol), naphthalene (63.7 mg, 0.50 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 4-iodoacetophenone (123.0 mg, 0.50 mmol) was stirred at room temperature for 10 min and then sample aliquots were taken and reaction was worked up to afford 78.2 mg (83%) of **12**. GC analysis of samples showed a **12/13** ratio of 96.7/3.3.

GC Data:

	area naphth	area **12**	area **13**	response factor **12/13**	ratio **12/13**x100
sample 1	9077	10986	465	0.78/0.67	96.5/3.5
sample 2	12930	15354	581	0.78/0.67	96.8/3.2
average	11004	13170	523	0.78/0.67	96.7/3.3

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Di-(1,1-dimethylethyl)-(1-heptenyl)silanol (5) with 4-Iodoacetophenone

Following General Procedure I, **1** (72.0 mg, 0.50 mmol), **5** (130.6 mg, 0.51 mmol), naphthalene (65.0 mg, 0.51 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 4-iodoacetophenone (123.0 mg, 0.50 mmol) was stirred at room temperature for 10 min and then sample aliquots were taken and reaction was worked up to afford 77.9 mg (83%) of **12**. GC analysis of samples showed a **12/13** ratio of 96.1/3.9.

GC Data:

	area naphth	area **12**	area **13**	response factor **12/13**	ratio **12/13**x100
sample 1	12043	13323	727	0.78/0.67	95.5/4.5
sample 2	16246	18945	748	0.78/0.67	96.7/3.3
average	14145	16134	738	0.78/0.67	96.1/3.9

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoacetophenone

Following General Procedure I, **1** (72.7 mg, 0.50 mmol), **6** (148.5 mg, 0.50 mmol), naphthalene (64.0 mg, 0.50 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 4-iodoacetophenone (123.1 mg, 0.50 mmol) was stirred at room temperature for 10 min and then sample aliquots were taken and reaction was worked up to afford 42 mg (44%) of **12** and 47 mg (43%) of **13**. GC analysis of samples showed a **12**/**13** ratio of 50.0/50.0.

GC Data:

	area naphth	area **12**	area **13**	response factor **12**/**13**	ratio **12**/**13**x100
sample 1	6743	4314	5140	0.78/0.67	49.5/50.5
sample 2	11856	7302	7979	0.78/0.67	51.7/48.3
sample 3	13140	9921	12249	0.78/0.67	48.7/51.3
average	10580	7179	8456	0.78/0.67	50.0/50.0

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoacetophenone

Following General Procedure I, **1** (72.6 mg, 0.50 mmol), **6** (148.7 mg, 0.50 mmol), naphthalene (64.5 mg, 0.50 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 4-iodoacetophenone (123.2 mg, 0.50 mmol) was stirred at room temperature for 10 min and then sample aliquots were taken and reaction was worked up to afford 41 mg (44%) of **12** and 47 mg (43%) of **13**. GC analysis of samples showed a **12**/**13** ratio of 48.5/51.5.

GC Data:

	area naphth	area **12**	area **13**	response factor **12**/**13**	ratio **12**/**13**x100
sample 1	15024	10671	13154	0.78/0.67	48.7/51.3
sample 2	20718	15021	18537	0.78/0.67	48.7/51.3
sample 3	17660	12865	16263	0.78/0.67	48.0/51.9
average	17801	12852	15985	0.78/0.67	48.5/51.5

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoacetophenone

Following General Procedure I, **1** (86 μL, 0.50 mmol), **6** (148.4 mg, 0.50 mmol), naphthalene (65.9 mg, 0.51 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 4-iodoacetophenone (123.0 mg, 0.50 mmol) was stirred at room temperature for 10 min and then sample aliquots were taken and reaction was worked up to afford 43 mg (46%) of **12** and 48 mg (45%) of **13**. GC analysis of samples showed a **12**/**13** ratio of 48.4/51.6.

GC Data:

	area naphth	area **12**	area **13**	response factor **12**/**13**	ratio **12**/**13**x100
sample 1	8544	6339	7850	0.78/0.67	48.6/51.4
sample 2	9659	7489	8883	0.78/0.67	49.7/50.3
sample 3	8171	6224	8210	0.78/0.67	47.0/53.0
average	8791	6684	8314	0.78/0.67	48.4/51.6

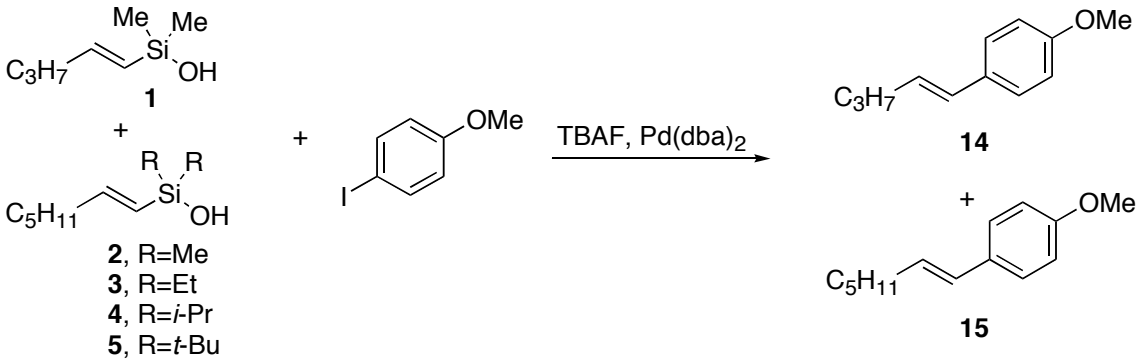
Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoacetophenone

Following General Procedure I, **1** (86 μL, 0.50 mmol), **6** (148.6 mg, 0.50 mmol), naphthalene (65.3 mg, 0.51 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 4-iodoacetophenone (123.0 mg, 0.50 mmol) was stirred at room temperature for 10 min and then sample aliquots were taken and reaction was worked up to afford 42 mg (45%) of **12** and 48 mg (44%) of **13**. GC analysis of samples showed a **12**/**13** ratio of 51.1/48.9.

GC Data:

	area naphth	area **12**	area **13**	response factor **12**/**13**	ratio **12**/**13**x100
sample 1	9901	9577	10105	0.78/0.67	52.6/47.4
sample 2	7927	7712	8825	0.78/0.67	50.5/49.5
sample 3	9563	6545	7641	0.78/0.67	50.0/50.0
average	9130	7945	8857	0.78/0.67	51.1/48.9

Competition Experiments with 4-Iodoanisole. General Procedure II.



A flame-dried, 5-mL, 2-neck, round-bottomed flask under N_2 was charged with (*E*)-dimethyl-(1-pentenyl)silanol (**1**), one of the 1-heptenylsilanols (**2-6**) and 4-iodoanisole. THF solutions of naphthalene (0.25 M) and TBAF (1.0 M) were added next followed by $Pd(dba)_2$. After 30 min two 25 μL samples were taken via syringe. The sample aliquots were filtered through a plug of silica gel washing with Et_2O to achieve a total sample volume of ~2 mL. These samples were then subjected to GC analysis. Reactions were performed in duplicate.

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Dimethyl-(1 heptenyl)silanol (2) with 4-Iodoanisole

Following General Procedure II, **1** (28.8 mg, 0.20 mmol), **2** (34.2 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) and $Pd(dba)_2$ (5.8 mg 0.01 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14**/**15** ratio of 50.6/49.4.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	17073	6579	7905	0.97/0.79	50.3/49.7
	15511	7350	9663	0.97/0.79	48.1/51.9
sample 2	17040	6385	7683	0.97/0.79	50.3/49.7
	15464	6638	7780	0.97/0.79	50.9/49.1
average	16272	6738	8258	0.97/0.79	49.9/50.1

reaction 2	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	15930	6665	7546	0.97/0.79	51.8/48.2
	15320	6589	7544	0.97/0.79	51.5/48.5
sample 2	18365	7931	8950	0.97/0.79	51.9/48.1
	19179	8006	9632	0.97/0.79	50.3/49.7
average	17199	7298	8418	0.97/0.79	51.4/48.6

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diethyl-(1 heptenyl)silanol (3) with 4-Iodoanisole

Following General Procedure II, **1** (28.8 mg, 0.20 mmol), **3** (40.0 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14**/**15** ratio of 53.3/46.7.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	52775	28507	30906	0.97/0.79	52.9/47.1
	52994	28515	31363	0.97/0.79	52.5/47.5
sample 2	53364	27642	28943	0.97/0.79	53.7/46.3
	55121	28645	29998	0.97/0.79	53.7/46.3
average	53564	28327	30303	0.97/0.79	53.2/46.8

reaction 2	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	63211	34126	37476	0.97/0.79	52.6/47.4
	62612	33889	37294	0.97/0.79	52.5/47.5
sample 2	62206	31979	33055	0.97/0.79	54.0/46.0
	60815	31267	32562	0.97/0.79	53.9/46.1
average	62211	32815	35097	0.97/0.79	53.3/46.7

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Di-(1-methylethyl)-(1 heptenyl)-silanol (4) with 4-Iodoanisole

Following General Procedure II, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 61.7/38.3.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	54347	26594	19788	0.97/0.79	62.1/37.9
	53748	26239	19719	0.97/0.79	61.8/38.2
sample 2	51248	25325	19255	0.97/0.79	61.6/38.4
	55214	26984	20228	0.97/0.79	61.9/38.1
average	53639	26286	19748	0.97/0.79	61.9/38.1

reaction 2	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	81797	47840	36408	0.97/0.79	61.6/38.4
	72884	43003	32741	0.97/0.79	61.6/38.4
sample 2	75205	43959	33739	0.97/0.79	61.3/38.7
	76017	45032	34276	0.97/0.79	61.6/38.4
average	76476	44959	34291	0.97/0.79	61.5/38.5

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Di-(1,1-dimethylethyl)-(1 heptenyl)silanol (5) with 4-Iodoanisole

Following General Procedure II, **1** (28.8 mg, 0.20 mmol), **5** (51.2 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 96.1/3.9.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	55450	47522	2288	0.97/0.79	96.1/3.9
	54932	47437	2288	0.97/0.79	96.2/3.8
sample 2	54793	48162	2439	0.97/0.79	96.0/4.0
	54829	48032	2455	0.97/0.79	96.0/4.0
average	55001	47788	2368	0.97/0.79	96.1/3.9

reaction 2	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample1	71951	62296	2900	0.97/0.79	96.3/3.7
	72755	62632	2910	0.97/0.79	96.3/3.7
sample2	42415	37516	1926	0.97/0.79	96.0/4.0
	43065	37744	1942	0.97/0.79	95.9/4.1
average	57547	50047	2420	0.97/0.79	96.1/3.9

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole

Following General Procedure II, **1** (28.8 mg, 0.20 mmol), **6** (59.2 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 56.3/43.7.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	32648	17120	16258	0.97/0.79	56.2/43.8
	34431	17747	17204	0.97/0.79	55.6/44.3
sample 2	37270	20655	19817	0.97/0.79	55.9/44.1
	39301	21202	20540	0.97/0.79	55.7/44.3
average	35913	19181	18455	0.97/0.79	55.9/44.1

reaction 2	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	40364	21219	19995	0.97/0.79	56.3/43.6
	42465	21045	19731	0.97/0.79	56.5/43.5
sample 2	49337	24853	22506	0.97/0.79	57.3/42.7
	46962	24173	22295	0.97/0.79	56.9/43.1
average	44782	22823	21132	0.97/0.79	56.8/43.2

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Trifluoropropyl-(1-heptenyl)-methylsilanol (7) with 4-Iodoanisole

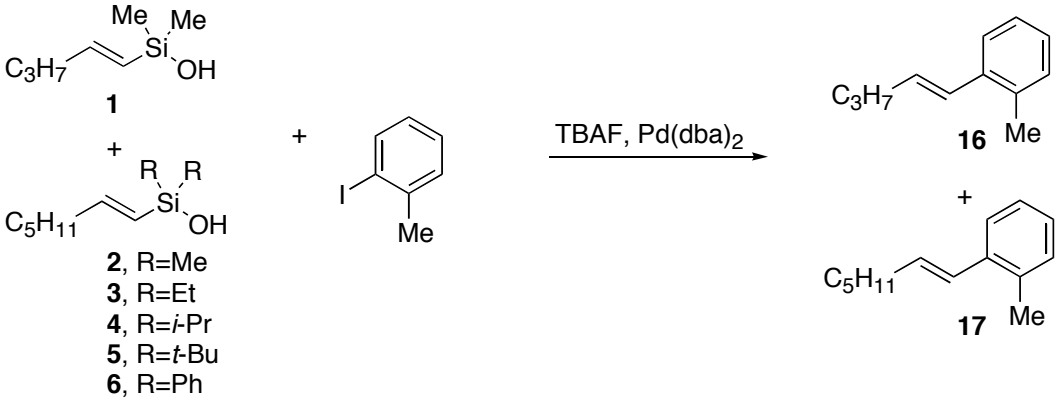
Following General Procedure V (see p 51), **1** (28.8 mg, 0.20 mmol), **7** (50.8 mg, 0.20 mmol), 4-iodotoluene (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) was stirred for 1 h and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14**/**15** ratio of 44.6/55.4.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	19529	7840	11073	0.96/0.79	46.3/53.7
	19238	7758	11028	0.96/0.79	46.2/53.8
sample 2	15705	6999	11244	0.96/0.79	43.1/56.9
	15460	6956	11174	0.96/0.79	43.1/56.9
average	17483	7388	11130	0.96/0.79	44.7/55.3

reaction 2	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	14099	5661	8606	0.96/0.79	44.5/55.5
	13931	6098	8592	0.96/0.79	46.4/53.6
sample 2	16252	7291	11442	0.96/0.79	43.7/56.3
	14740	6575	10250	0.96/0.79	43.8/56.2
average	14756	6406	9723	0.96/0.79	44.6/55.4

Competition Experiments with 2-Iodotoluene. General Procedure III.



(*E*)-Dimethyl-(1-pentenyl)silanol (**1**), together with one of the other 1-heptenylsilanols (**2-6**), naphthalene, and $Pd(dba)_2$ were dissolved in a TBAF solution (1.0 M in THF) in a flame-dried, 5-mL, 2-neck, round-bottomed flask under N_2. The 2-iodotoluene was then added slowly to maintain an internal temperature <30 °C. After 30 min 25-μL samples were taken via syringe. The sample aliquots were filtered through a plug of silica gel washing with pentane to achieve a total sample volume of ~2 mL. These samples were then subjected to GC analysis. The reaction mixture was filtered through a plug of silica gel (~15g). The plug was washed with hexane/ethyl acetate, 9/1, (100 mL), and the solvent was evaporated in vacuo. The residue was purified by column chromatography (Reverse Phase C18, MeOH/H_2O, 9/1) to afford the **16**, and **17** which were further purified by Kugelrohr distillation.

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Dimethyl-(1-heptenyl)silanol (2) with 2-Iodotoluene

Following General Procedure III, **1** (86 μL, 0.50 mmol), **2** (86.2 mg, 0.50 mmol), naphthalene (65.1 mg, 0.51 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 2-iodotoluene (63.6 μL, 0.50 mmol) was stirred at room temperature for 30 min and then sample aliquots were taken and reaction was worked up to afford 35 mg (44%) of **16** and 42 mg (45%) of **17**. GC analysis of samples showed a **16**/**17** ratio of 49.4/50.6.

GC Data:

	area naphth	area **16**	area **17**	response factor **16/17**	ratio **16/17** 100
sample 1	22228	13304	16519	0.85/0.71	49.3/50.7
sample 2	19390	11289	14030	0.85/0.71	49.3/50.7
sample 3	19452	11439	13917	0.85/0.71	49.8/50.2
average	20357	12011	14822	0.85/0.71	49.4/50.6

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Dimethyl-(1-heptenyl)silanol (2) with 2-Iodotoluene

Following General Procedure III, **1** (86 μL, 0.50 mmol), **2** (86.2 mg, 0.50 mmol), naphthalene (64.4 mg, 0.50 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 2-iodotoluene (63.6 μL, 0.50 mmol) was stirred at room temperature for 30 min and then sample aliquots were taken and reaction was worked up to afford 35 mg (44%) of **16** and 42 mg (45%) of **17**. GC analysis of samples showed a **16**/**17** ratio of 50.9/49.1.

GC Data:

	area naphth	area **16**	area **17**	response factor **16/17**	ratio **16/17**x100
sample 1	7524	3507	4071	0.85/0.71	50.9/49.1
	7675	3501	4117	0.85/0.71	50.7/49.3
sample 2	12969	5873	6829	0.85/0.71	50.9/49.1
	12933	5888	6848	0.85/0.71	50.9/49.1
sample 3	11107	5041	5868	0.85/0.71	50.9/49.1
	10846	5052	5896	0.85/0.71	50.9/49.1
average	10509	4810	5605	0.85/0.71	50.9/49.1

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diethyl-(1-heptenyl)silanol (3) with 2-Iodotoluene

Following General Procedure II, **1** (86 μL, 0.50 mmol), **3** (100.6 mg, 0.50 mmol), naphthalene (64.6 mg, 0.50 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 2-iodotoluene (63.6 μL, 0.50 mmol) was stirred at room temperature for 30 min and then sample aliquots were taken and reaction was worked up to afford 42 mg (52%) of **16** and 39 mg (42%) of **17**. GC analysis of samples showed a **16**/**17** ratio of 57.5/42.5.

GC Data:

	area naphth	area **16**	area **17**	response factor **16**/**17**	ratio **16**/**17**x100
sample 1	19186	14700	13093	0.85/0.71	57.5/42.5
sample 2	11585	8532	7937	0.85/0.71	56.5/43.5
sample 3	9163	6769	5760	0.85/0.71	58.6/41.4
average	13311	10000	8930	0.85/0.71	57.5/42.5

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diethyl-(1-heptenyl)silanol (3) with 2-Iodotoluene

Following General Procedure III, **1** (86 μL, 0.50 mmol), **3** (100.1 mg, 0.50 mmol), naphthalene (66.2 mg, 0.52 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 2-iodotoluene (63.6 μL, 0.50 mmol) was stirred at room temperature for 30 min and then sample aliquots were taken and reaction was worked up to afford 41 mg (51%) of **16** and 33 mg (35%) of **17**. GC analysis of samples showed a **16**/**17** ratio of 59.6/40.4.

GC Data:

	area naphth	area **16**	area **17**	response factor **16**/**17**	ratio **16**/**17**x100
sample 1	12814	7894	6425	0.85/0.71	59.7/40.3
	12655	7761	6326	0.85/0.71	59.7/40.3
sample 2	11794	7148	5773	0.85/0.71	59.9/40.1
	11860	7216	5768	0.85/0.71	60.1/39.9
sample 3	10871	6531	5507	0.85/0.71	58.9/41.1
	10639	6591	5438	0.85/0.71	59.4/40.6
average	11772	7190	5873	0.85/0.71	59.6/40.4

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Di-(1-methylethyl)-(1-heptenyl)-silanol (4) with 2-Iodotoluene

Following General Procedure III, **1** (86 μL, 0.50 mmol), **4** (114.7 mg, 0.50 mmol), naphthalene (64.2 mg, 0.50 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 2-iodotoluene (63.6 μL, 0.50 mmol) was stirred at room temperature for 30 min and then sample aliquots were taken and reaction was worked up to afford 42 mg (53%) of **16** and 36 mg (38%) of **17**. GC analysis of samples showed a **16**/**17** ratio of 59.8/40.2.

GC Data:

	area naphth	area **16**	area **17**	response factor **16**/**17**	ratio **16**/**17**x100
sample 1	74249	52466	41686	0.85/0.71	60.3/39.7
	74750	52972	42788	0.85/0.71	59.9/40.1
sample 2	23057	16155	13050	0.85/0.71	59.9/40.1
	23271	16273	13294	0.85/0.71	59.6/40.4
sample 3	27105	18791	15527	0.85/0.71	59.4/40.6
	27118	18732	15176	0.85/0.71	59.8/40.2
average	41592	29232	23587	0.85/0.71	59.8/40.2

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Di(1-methylethyl)-(1-heptenyl)-silanol (4) with 2-Iodotoluene

Following General Procedure III, **1** (86 μL, 0.50 mmol), **4** (114.7 mg, 0.50 mmol), naphthalene (66.7 mg, 0.52 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 2-iodotoluene (63.6 μL, 0.50 mmol) was stirred at room temperature for 30 min and then sample aliquots were taken and reaction was worked up to afford 43 mg (54%) of **16** and 32 mg (34%) of **17**. GC analysis of samples showed a **16**/**17** ratio of 61.1/38.9.

GC Data:

	area naphth	area **16**	area **17**	response factor **16**/**17**	ratio **16**/**17**x100
sample 1	9060	5548	4243	0.85/0.71	61.2/38.8
	9143	5568	4247	0.85/0.71	61.3/38/7
sample 2	9447	5773	4473	0.85/0.71	60.9/39.1
	9477	5797	4453	0.85/0.71	61.1/38.9
sample 3	12196	7549	5773	0.85/0.71	61.2/38.8
	12295	7597	5819	0.85/0.71	61.2/38.8
average	10270	6305	4835	0.85/0.71	61.1/38.9

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Di-(1,1-dimethylethyl)-(1-heptenyl)silanol (5) with 2-Iodotoluene

Following General Procedure III, **1** (86 μL, 0.50 mmol), **5** (129.7 mg, 0.51 mmol), naphthalene (64.8 mg, 0.51 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 2-iodotoluene (63.6 μL, 0.50 mmol) was stirred at room temperature for

30 min and then sample aliquots were taken and reaction was worked up to afford 67 mg (84%) of **16**. GC analysis of samples showed a **16**/**17** ratio of 100.0/0.0.

GC Data:

	area naphth	area **16**	area **17**	response factor **16**/**17**	ratio **16**/**17**x100
sample 1	10039	9771	0	0.85/0.71	100/0
	9995	9802	0	0.85/0.71	100/0
sample 2	7633	7435	0	0.85/0.71	100/0
	7644	7352	0	0.85/0.71	100/0
sample 3	8640	8404	0	0.85/0.71	100/0
	8633	8453	0	0.85/0.71	100/0
average	8764	8536	0	0.85/0.71	100.0/0.0

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Di-(1,1-dimethylethyl)-(1-heptenyl)silanol (5) with 2-Iodotoluene

Following General Procedure III, **1** (86 μL, 0.50 mmol), **5** (128.2 mg, 0.50 mmol), naphthalene (65.2 mg, 0.51 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 2-iodotoluene (63.6 μL, 0.50 mmol) was stirred at room temperature for 30 min and then sample aliquots were taken and reaction was worked up to afford 65 mg (82%) of **16**. GC analysis of samples showed a **16**/**17** ratio of 100.0/0.0.

GC Data:

	area naphth	area **16**	area **17**	response factor **16**/**17**	ratio **16**/**17**x100
sample 1	8955	7390	0	0.85/0.71	100/0
	8965	7397	0	0.85/0.71	100/0
sample 2	11055	9174	0	0.85/0.71	100/0
	11114	9165	0	0.85/0.71	100/0
sample 3	10557	8605	0	0.85/0.71	100/0
	10412	8650	0	0.85/0.71	100/0
average	10176	8397	0	0.85/0.71	100.0/0.0

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 2-Iodotoluene

Following General Procedure III, **1** (86 μL, 0.50 mmol), **6** (146.8 mg, 0.50 mmol), naphthalene (69.7 mg, 0.54 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 2-iodotoluene (63.6 μL, 0.50 mmol) was stirred at room temperature for 30 min and then sample aliquots were taken and reaction was worked up to afford 35 mg (44%) of **16** and 42 mg (45%) of **17**. GC analysis of samples showed a **16**/**17** ratio of 50.1/49.9.

GC Data:

	area naphth	area **16**	area **17**	response factor **16**/**17**	ratio **16**/**17**x100
sample 1	18494	9737	11707	0.85/0.71	50.1/49.9
	19365	10020	21041	0.85/0.71	50.1/49.9
sample 2	19794	10345	12443	0.85/0.71	50.1/49.9
	20137	10600	12710	0.85/0.71	50.1/49.9
sample 3	15928	8320	10035	0.85/0.71	50.5/50.0
	16400	8516	10157	0.85/0.71	50.3/49.7
average	18353	9590	13016	0.85/0.71	50.1/49.9

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 2-Iodotoluene

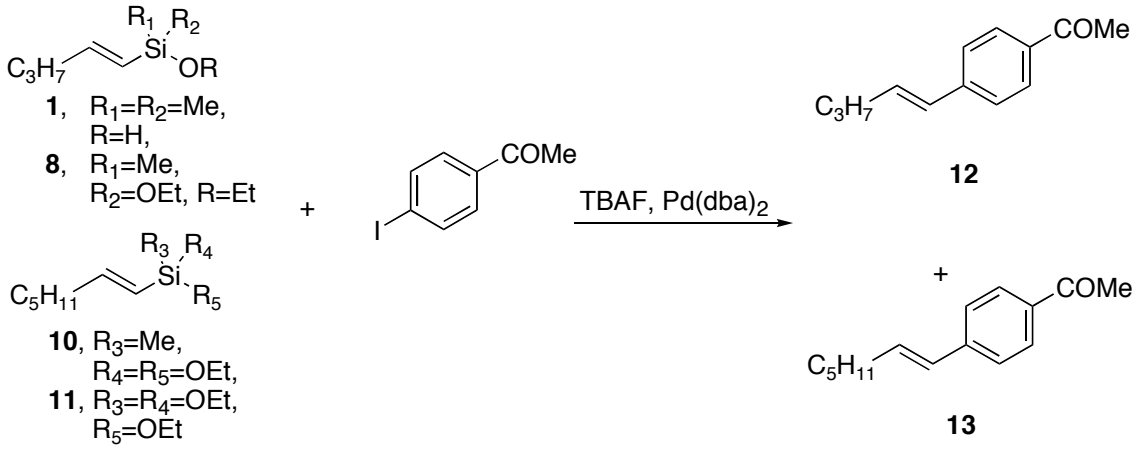
Following General Procedure III, **1** (86 μL, 0.50 mmol), **6** (149.3 mg, 0.50 mmol), naphthalene (70.3 mg, 0.55 mmol), TBAF (2.0 mL, 2.0 mmol, 1.0 M in THF), $Pd(dba)_2$ (14.4 mg 0.025 mmol), and 2-iodotoluene (63.6 μL, 0.50 mmol) was stirred at room temperature for 30 min and then sample aliquots were taken and reaction was worked up to afford 36 mg (45%) of **16** and 43 mg (45%) of **17**. GC analysis of samples showed a **16**/**17** ratio of 50.2/49.8.

GC Data:

	area naphth	area **16**	area **17**	response factor **16/17**	ratio **16/17**x100
sample 1	13621	7254	8332	0.85/0.71	51.2/48.8
	14192	7372	8437	0.85/0.71	51.3/48.7
sample 2	16065	8346	9522	0.85/0.71	51.4/48.6
	16195	8446	9711	0.85/0.71	51.2/48.8
sample 3	13461	6945	8040	0.85/0.71	51.0/49.0
	13655	7067	8222	0.85/0.71	50.9/49.1
average	14532	7572	8711	0.85/0.71	50.2/49.8

Competition Experiment from Table 2 (Heteroatom Substituent Effects).

Competition Experiments with 4-Iodoacetophenone. General Procedure IV.



A flame-dried, 5-mL, 2-neck, round-bottomed flask under N_2 was charged with (*E*)-dimethyl-(1-pentenyl)silanol (**1**) or (*E*)-diethoxy-(1-pentenyl)methylsilane (**8**), (*E*)-triethoxy-(1-heptenyl)silane (**10**) or (*E*)-diethoxy-(1-heptenyl)methylsilane (**11**), and 4-iodoacetophenone. THF solutions of naphthalene (0.25 M) and TBAF (1.0 M) were added next. The mixture was stirred at room temperature for 1 h and $Pd(dba)_2$ was added. After 30 min two 25-μL samples were taken via syringe. The sample aliquots were filtered through a plug of silica gel washing with Et_2O to achieve a total sample volume of ~2 mL. These samples were then subjected to GC analysis. Reactions were performed in duplicate.

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diethoxy-(1-heptenyl)methyl-silane (10) with 4-Iodoacetophenone

Following General Procedure IV, **1** (28.8 mg, 0.20 mmol), **15** (46.0 mg, 0.20 mmol), 4-iodoacetophenone (49.2 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) was stirred for 1 h and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **12**/**13** ratio of 49.2/50.8.

GC Data:

reaction 1	area naphth	area **12**	area **13**	response factor **12**/**13**	ratio **12**/**13**x100
sample 1	43234	22649	28321	0.78/0.67	48.4/51.6
	43001	20833	26167	0.78/0.67	48.3/51.7
sample 2	24316	15081	18853	0.78/0.67	48.4/51.6
	31582	15703	18656	0.78/0.67	49.7/50.3
average	35533	18567	22999	0.78/0.67	48.7/51.3

reaction 2	area naphth	area **12**	area **13**	response factor **12**/**13**	ratio **12**/**13**x100
sample 1	33537	16512	18458	0.78/0.67	51.2/48.8
	37849	18562	21433	0.78/0.67	50.4/49.6
sample 2	36630	16186	20262	0.78/0.67	48.4/51.6
	44103	19495	23721	0.78/0.67	49.0/51.0
average	38030	17689	20969	0.78/0.67	49.8/50.2

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Triethoxy-(1-heptenyl)silane (11) with 4-Iodoacetophenone

Following General Procedure IV, **1** (28.8 mg, 0.20 mmol), **11** (52 mg, 0.20 mmol), 4-iodoacetophenone (49.2 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) was stirred for 1 h and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **12**/**13** ratio of 73.9/26.1.

GC Data:

reaction 1	area naphth	area **12**	area **13**	response factor **12/13**	ratio **12/13**x100
sample 1	33285	19312	7574	0.78/0.67	74.9/25.1
	34349	20642	8491	0.78/0.67	74.0/26.0
sample 2	41452	24629	10241	0.78/0.67	73.8/26.2
	37199	23529	9387	0.78/0.67	74.6/25.4
average	36571	22028	8923	0.78/0.67	74.3/25.7

reaction 2	area naphth	area **12**	area **13**	response factor **12/13**	ratio **12/13**x100
sample 1	31830	23506	9484	0.78/0.67	74.4/25.6
	30942	22643	9222	0.78/0.67	74.2/25.8
sample 2	36959	23815	11330	0.78/0.67	71.1/28.8
	34267	21527	8693	0.78/0.67	74.4/25.6
average	33500	22873	9682	0.78/0.67	73.5/26.5

Competition of (*E*)- Diethoxy-(1-pentenyl)methylsilane (8) vs (*E*)-Triethoxy-(1-heptenyl)-silane (11) with 4-Iodoacetophenone

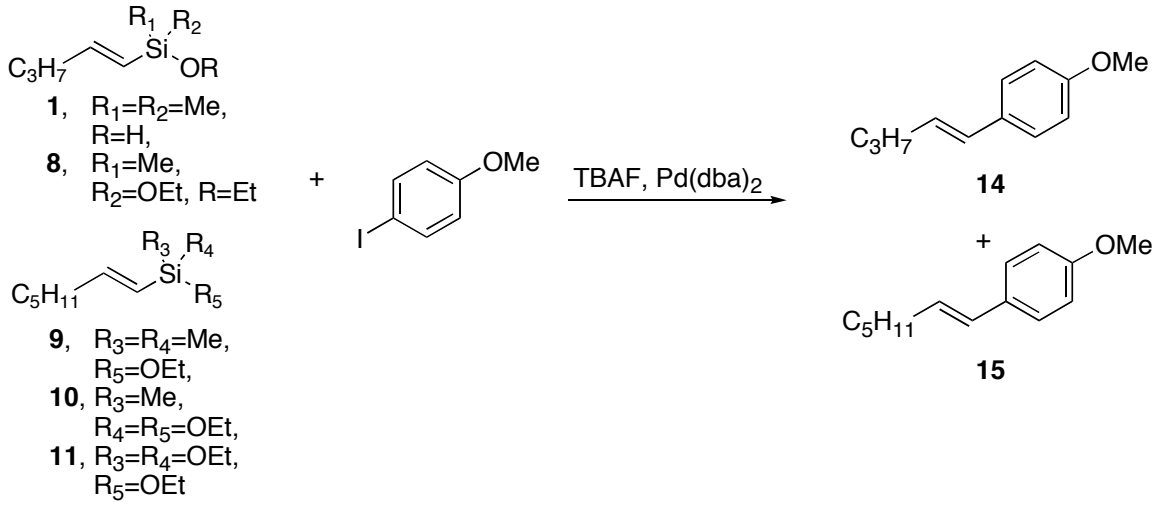
Following General Procedure IV, **8** (40.4 mg, 0.20 mmol), **14** (52.0 mg, 0.20 mmol), 4-iodoacetophenone (49.2 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) was stirred for 1 h and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **12/13** ratio of 73.1/26.9.

GC Data:

reaction 1	area naphth	area **12**	area **13**	response factor **12/13**	ratio **12/13**x100
sample 1	46263	19698	8310	0.78/0.67	73.5/26.5
	46379	21699	9886	0.78/0.67	72.0/28.0
sample 2	39019	18565	8469	0.78/0.67	72.0/28.0
	37506	18054	8248	0.78/0.67	72.0/28.0
average	42292	19504	8728	0.78/0.67	72.4/27.6

reaction 2	area naphth	area **12**	area **13**	response factor **12/13**	ratio **12/13**x100
sample 1	34306	20132	8667	0.78/0.67	73.1/26.9
	34281	20059	8871	0.78/0.67	72.6/27.4
sample 2	29777	17456	6818	0.78/0.67	75.0/25.0
	29877	17692	6950	0.78/0.67	74.9/25.1
average	32060	18835	7827	0.78/0.67	73.9/26.1

Competition Experiments with 4-Iodoanisole. General Procedure V.



A flame-dried, 5-mL, 2-neck, round-bottomed flask under N_2 was charged with (*E*)-dimethyl-(1-pentenyl)silanol (**1**) or (*E*)-diethoxy-(1-pentenyl)methylsilane (**8**), (*E*)-diethoxy-(1-heptenyl)methylsilane (**11**) or (*E*)-Triethoxy-(1-heptenyl)silane (**15**) or (*E*)-dimethylethoxy-(1-heptenyl)silane (**17**) and 4-iodoanisole. THF solutions of naphthalene (0.25 M) and TBAF (1.0 M) were added next. The mixture was stirred at room temperature for 1 h and $Pd(dba)_2$ was added. After 30 min two 25-μL samples were taken via syringe. The sample aliquots were filtered through a plug of silica gel washing with Et_2O to achieve a total sample volume of ~2 mL. These samples were then subjected to GC analysis. Reactions were performed in duplicate.

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diethoxy-(1-heptenyl)methylsilane (10) with 4-Iodoanisole

Following General Procedure V, **1** (28.8 mg, 0.20 mmol), **10** (46.0 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in

THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) was stirred for 1 h and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14**/**15** ratio of 56.6/43.4.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	33508	19836	19364	0.96/0.79	55.5/44.5
	35651	20941	19949	0.96/0.79	56.1/43.9
sample 2	39588	24024	21623	0.96/0.79	57.5/42.5
	40440	24611	22066	0.96/0.79	57.6/42.4
average	37297	22353	20751	0.96/0.79	56.7/43.3

reaction 2	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	36310	21747	19973	0.96/0.79	57.0/43.0
	35890	21662	19462	0.96/0.79	57.5/42.5
sample 2	59786	35099	33646	0.96/0.79	56.0/44.0
	59901	35132	33666	0.96/0.79	56.0/44.0
average	47972	28410	26687	0.96/0.79	56.6/43.4

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Triethoxy-(1-heptenyl)silane (11) with 4-Iodoanisole

Following General Procedure V, **1** (28.8 mg, 0.20 mmol), **11** (52.0 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) was stirred for 1 h and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14**/**15** ratio of 81.5/18.5.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	63425	43224	11789	0.96/0.79	81.7/18.3
	63784	43594	11822	0.96/0.79	81.8/18.2
sample 2	39579	27782	7613	0.96/0.79	81.6/18.4
	40022	28112	7527	0.96/0.79	81.9/18.1
average	51703	35678	9688	0.96/0.79	81.8/18.2

reaction 2	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	62306	48939	13656	0.96/0.79	81.4/18.6
	63805	49961	13845	0.96/0.79	81.5/18.5
sample 2	58500	46520	12973	0.96/0.79	81.4/18.6
	58898	46305	12986	0.96/0.79	81.3/18.7
average	60877	47931	13365	0.96/0.79	81.4/18.6

Competition of (*E*)- Diethoxy-(1-pentenyl)methylsilane (8) vs (*E*)-Triethoxy-(1-heptenyl)-silane (11) with 4-Iodoanisole

Following General Procedure V, **8** (40.4 mg, 0.20 mmol), **11** (52.0 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) was stirred for 1 h and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 76.4/23.6.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	49082	28098	10621	0.96/0.79	76.3/23.7
	46729	27132	10294	0.96/0.79	76.2/23.8
sample 2	48724	28213	10717	0.96/0.79	76.2/23.8
	47371	27367	10313	0.96/0.79	76.4/23.6
average	47977	27703	10486	0.96/0.79	76.3/23.7

reaction 2	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	48650	30306	11392	0.96/0.79	76.4/23.6
	49689	30847	11457	0.96/0.79	76.6/23.4
sample 2	49986	31218	11555	0.96/0.79	76.7/23.3
	49589	30895	11566	0.96/0.79	76.5/23.5
average	49479	30817	11493	0.96/0.79	76.6/23.4

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)- Dimethyl-(1-heptenyl)ethoxy-silane (9) with 4-Iodoanisole

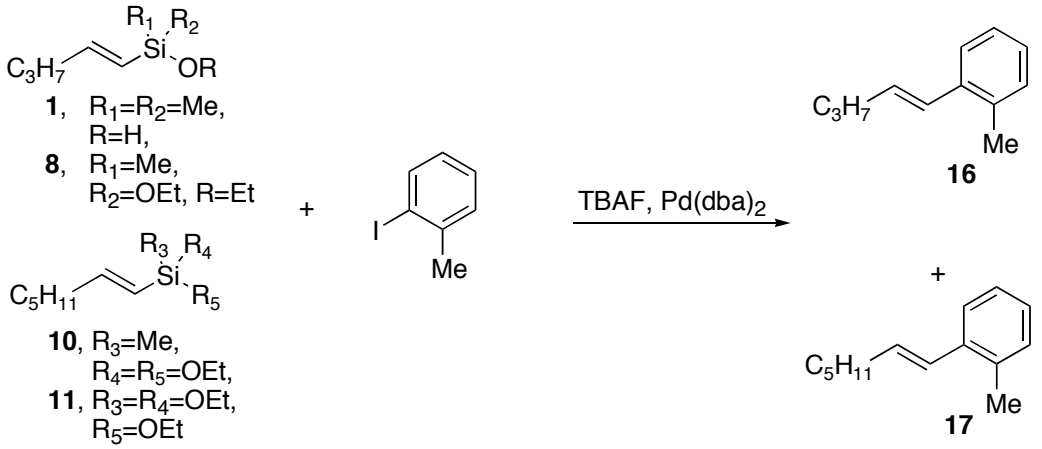
Following General Procedure V, **1** (28.8 mg, 0.20 mmol), **9** (40.0 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) was stirred for 1 h and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 49.4/50.6.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	55280	29310	33723	0.96/0.79	53.8/46.2
	51732	30201	40037	0.96/0.79	48.7/51.3
sample 2	136226	66353	78334	0.96/0.79	50.8/49.2
	103450	61348	79557	0.96/0.79	51.4/48.6
average	86672	46803	57913	0.96/0.79	51.2/48.8

reaction 2	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	36181	19548	25300	0.96/0.79	46.8/53.2
	33750	16723	22760	0.96/0.79	47.8/52.2
sample 2	51360	22762	23731	0.96/0.79	48.4/51.6
	33920	19852	27421	0.96/0.79	47.2/52.8
average	38803	19721	24803	0.96/0.79	47.6/52.4

Competition Experiments with 2-Iodotoluene. General Procedure VI.



A flame-dried, 5-mL, 2-neck, round-bottomed flask under N_2 was charged with (*E*)-dimethyl-(1-pentenyl)silanol (**1**) or (*E*)-diethoxy-(1-pentenyl)methylsilane (**8**), (*E*)-triethoxy-(1-heptenyl)silane (**10**) or (*E*)-diethoxy-(1-heptenyl)methylsilane (**11**), and 2-iodotoluene. THF solutions of naphthalene (0.25 M) and TBAF (1.0 M) were added next. The mixture was stirred at room temperature for 1 h and $Pd(dba)_2$ was added. After 30 min two 25-μL samples were taken via syringe. The sample aliquots were filtered through a plug of silica gel washing with Et_2O to achieve a total sample volume of ~2 mL. These samples were then subjected to GC analysis. Reactions were performed in duplicate.

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diethoxy-(1-heptenyl)methylsilane (10) with 2-Iodotoluene

Following General Procedure VI, **1** (28.8 mg, 0.20 mmol), **10** (46.0 mg, 0.20 mmol), 2-iodotoluene (25.6 μL, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) was stirred for 1 h and Pd(dba)2 (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **16**/**17** ratio of 51.4/48.6.

GC Data:

reaction 1	area naphth	area **16**	area **17**	response factor **16/17**	ratio **16/17**x100
sample 1	40099	23444	18578	0.86/0.71	51.1/48.9
	17578	10609	9030	0.86/0.71	49.3/50.7
sample 2	34377	20022	15754	0.86/0.71	51.3/48.7
	31432	18853	15953	0.86/0.71	49.5/50.5
average	30872	18232	14829	0.86/0.71	50.3/49.7

reaction 2	area naphth	area **16**	area **17**	response factor **16/17**	ratio **16/17**x100
sample 1	35409	19881	15110	0.86/0.71	52.1/47.9
	36556	23764	18105	0.86/0.71	52.1/47.9
sample 2	50075	27983	20912	0.86/0.71	52.6/47.4
	46599	26336	19575	0.86/0.71	52.7/47.3
average	42160	24491	18426	0.86/0.71	52.4/47.6

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Triethoxy-(1-heptenyl)silane (11) with 2-Iodotoluene

Following General Procedure VI, **1** (28.8 mg, 0.20 mmol), **14** (52.0 mg, 0.20 mmol), 2-iodotoluene (25.6 μL, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) was stirred for 1 h and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **16**/**17** ratio of 81.1/18.9

GC Data:

reaction 1	area naphth	area **16**	area **17**	response factor **16/17**	ratio **16/17**x100
sample 1	65559	41279	11396	0.86/0.71	81.4/18.6
	64535	40389	11127	0.86/0.71	81.4/18.6
sample 2	49213	30732	8575	0.86/0.71	81.2/18.8
	49089	30672	8514	0.86/0.71	81.3/18.7
average	57099	35768	9903	0.86/0.71	81.3/18.7

reaction 2	area naphth	area **16**	area **17**	response factor **16**/**17**	ratio **16**/**17**x100
sample 1	57551	41549	11813	0.86/0.71	80.9/19.1
	58493	42322	12015	0.86/0.71	80.9/19.1
sample 2	50523	36321	10311	0.86/0.71	80.9/19.1
	51554	37040	10517	0.86/0.71	81.0/19.0
average	54530	39308	11164	0.86/0.71	80.9/19.1

Competition of (*E*)- Diethoxy-(1-pentenyl)methylsilane (8) vs (*E*)-Triethoxy-(1-heptenyl)-silane (11) with 2-Iodotoluene

Following General Procedure VI, **8** (40.4 mg, 0.20 mmol), **11** (52.0 mg, 0.20 mmol), 2-iodotoluene (25.6 μL, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) was stirred for 1 h and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **16**/**17** ratio of 74.4/25.6.

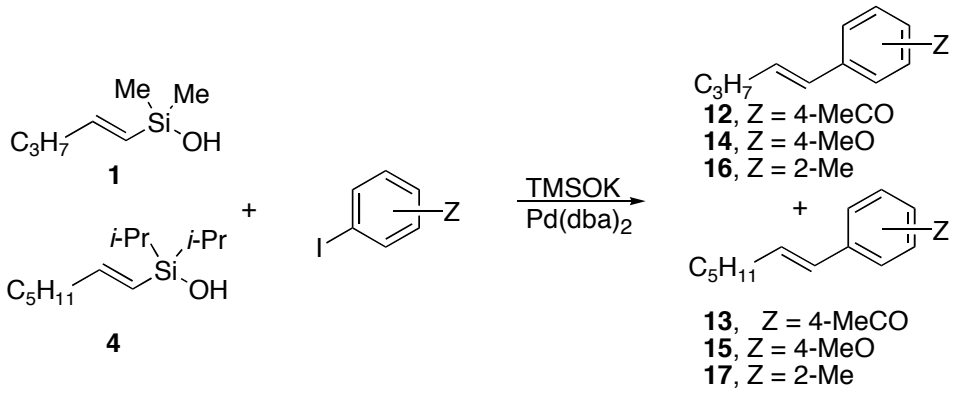
GC Data:

reaction 1	area naphth	area **16**	area **17**	response factor **16**/**17**	ratio **16**/**17**x100
sample 1	60499	46284	19176	0.86/0.71	74.4/25.6
	63396	48347	19938	0.86/0.71	74.2/25.8
sample 2	49896	33954	14214	0.86/0.71	74.2/25.8
	51629	34852	14214	0.86/0.71	74.7/25.3
average	56355	40859	16886	0.86/0.71	74.4/25.6

reaction 2	area naphth	area **16**	area **17**	response factor **16**/**17**	ratio **16**/**17**x100
sample 1	55396	37786	15739	0.86/0.71	74.3/25.7
	55300	37694	15739	0.86/0.71	74.3/25.7
sample 2	40863	31296	13097	0.86/0.71	74.2/25.8
	40115	30675	12811	0.86/0.71	74.3/25.7
average	47919	34363	14347	0.86/0.71	74.3/25.7

Competition Experiments with Potassium Trimethylsilanolate as Activator.

Competition Experiments with Carbon Substituents in the Presence of Potassium Trimethylsilanolate. General Procedure VII.



A flame-dried, 5-mL, 2-neck, round-bottomed flask under N_2 was charged with (*E*)-dimethyl-(1-pentenyl)silanol (**1**), di(1-methylethyl)-(1-heptenyl)silanol (**4**) and the aryl iodide. A THF solution of naphthalene (0.25 M) was added next followed by TMSOK and $Pd(dba)_2$. After an appropriate time, two 25-μL samples were taken via syringe. The sample aliquots were filtered through a plug of silica gel washing with Et_2O to achieve a total sample volume of ~2 mL. These samples were then subjected to GC analysis. Reactions were performed in duplicate.

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diisopropyl-(1-heptenyl)silanol (4) with 4-Iodoacetophenone

Following General Procedure VII, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoacetophenone (49.2 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in DME) and TMSOK (25.8 mg, 0.80 mmol) and $Pd(dba)_2$ (5.8 mg 0.01 mmol) were stirred at room temperature for 14 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **12**/**13** ratio of 100/0.

GC Data:

reaction 1	area naphth	area **12**	area **13**	response factor **12/13**	ratio **12/13**x100
sample 1	8109	7911	0	0.78/0.67	100/0
	7088	7579	0	0.78/0.67	100/0
sample 2	10186	9874	0	0.78/0.67	100/0
	9290	9418	0	0.78/0.67	100/0
average	8668	8696	0	0.78/0.67	100.0/0.0

reaction 2	area naphth	area **12**	area **13**	response factor **12/13**	ratio **12/13**x100
sample 1	9034	1325	0	0.78/0.67	100/0
	7985	10105	0	0.78/0.67	100/0
sample 2	9303	11746	0	0.78/0.67	100/0
	9312	11335	0	0.78/0.67	100/0
average	8909	8628	0	0.78/0.67	100.0/0.0

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Di(1-methylsethy)-(1 heptenyl)-silanol (4) with 2-Iodotoluene

Following General Procedure VII, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 2-iodotoluene (25.6 μL, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in DME) and TMSOK (25.8 mg, 0.80 mmol) and $Pd(dba)_2$ (5.8 mg 0.01 mmol) were stirred at room temperature for 4 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **16**/**17** ratio of 93.7/6.3.

GC Data:

reaction 1	area naphth	area **16**	area **17**	response factor **16/17**	ratio **16/17**x100
sample 1	16988	12745	947	0.78/0.67	94.2/5.8
	15051	10791	801	0.78/0.67	94.2/5.8
sample 2	13632	10101	962	0.78/0.67	92.7/7.3
	13838	10258	981	0.78/0.67	92.7/7.3
average	14877	10974	923	0.78/0.67	93.5/6.5

reaction 2	area naphth	area **16**	area **17**	response factor **16/17**	ratio **16/17**x100
sample 1	14763	13054	1042	0.78/0.67	93.8/6.8
	14012	12536	1002	0.78/0.67	93.7/6.3
sample 2	22285	19442	1322	0.78/0.67	94.7/5.4
	19526	17396	1371	0.78/0.67	93.9/6.1
average	17647	15607	1184	0.78/0.67	93.9/6.1

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Di-(1-methylethyl)-(1 heptenyl)-silanol (4) with 4-Iodoanisole

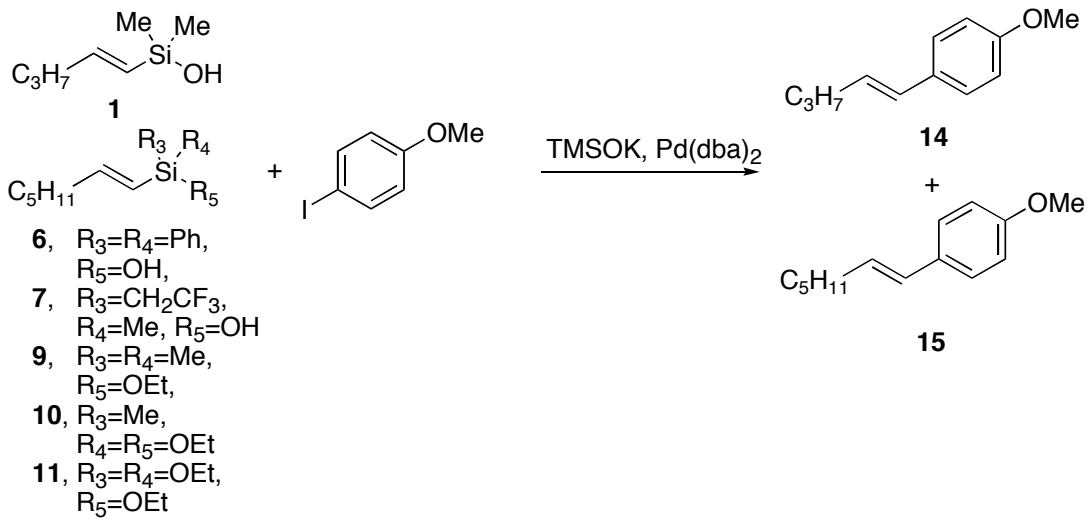
Following General Procedure VII, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in DME) and TMSOK (25.8 mg, 0.80 mmol) and $Pd(dba)_2$ (5.8 mg 0.01 mmol) were stirred at room temperature for 4 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 95.0/5.0.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	10177	8386	663	0.96/0.79	93.9/6.0
	11986	9371	642	0.96/0.79	94.7/5.3
sample 2	14510	10237	549	0.96/0.79	95.8/4.2
	13521	10010	545	0.96/0.79	95.7/4.3
average	12549	9501	600	0.96/0.79	95.0/5.0

reaction 2	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	12820	9712	609	0.96/0.79	95.1/4.9
	14275	10540	650	0.96/0.79	95.2/4.8
sample 2	15035	8525	498	0.96/0.79	95.4/4.6
	12941	7787	543	0.96/0.79	94.6/5.4
average	13768	9141	575	0.96/0.79	95.1/4.9

Competition Experiments with 4-Iodoanisole in the Presence of Potassium Trimethylsilanolate. General Procedure VIII.



A flame-dried, 5-mL, 2-neck, round-bottomed flask under N_2 was charged with (*E*)-dimethyl-(1-pentenyl)silanol (**1**), one of the (1-heptenyl)silanols (**6**-**11**) and 4-iodoanisole. A THF solution of naphthalene (0.25 M) was added next followed by TMSOK and $Pd(dba)_2$. After 4 h, two 25-μL samples were taken via syringe. The sample aliquots were filtered through a plug of silica gel washing with Et_2O to achieve a total sample volume of ~2 mL. These samples were then subjected to GC analysis. Reactions were performed in duplicate.

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diphenyl-(1 heptenyl)silanol (6) with 4-Iodoanisole

Following General Procedure VIII, **1** (28.8 mg, 0.20 mmol), **6** (59.2 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TMSOK (102 mg, 0.80 mmol) and $Pd(dba)_2$ (5.8 mg 0.01 mmol) were stirred at room temperature for 4 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14**/**15** ratio of 20.6/79.4.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	10920	2036	10383	0.96/0.79	19.3/80.7
	13224	2111	10117	0.96/0.79	20.3/79.7
sample 2	12746	2744	12088	0.96/0.79	21.6/78.4
	10889	2812	11887	0.96/0.79	22.4/77.6
average	11945	2426	11119	0.96/0.79	20.9/79.1

reaction 2	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	27002	5281	25181	0.96/0.79	20.3/79.7
	22444	4990	24059	0.96/0.79	20.2/79.8
sample 2	21416	4494	22861	0.96/0.79	19.3/80.7
	23732	5307	23967	0.96/0.79	21.2/78.8
average	23649	5018	24017	0.96/0.79	20.3/79.7

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Trifluoropropyl-(1-heptenyl)-methylsilanol (7) with 4-Iodoanisole

Following General Procedure VIII, **1** (28.8 mg, 0.20 mmol), **7** (50.8 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TMSOK (102 mg, 0.80 mmol) were stirred for 1 h and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 4 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 34.9/65.1.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	9213	3254	7782	0.96/0.79	33.7/66.3
	10920	3618	7965	0.96/0.79	35.6/64.4
sample 2	18740	5826	12499	0.96/0.79	36.2/63.8
	17974	5708	12352	0.96/0.79	36.0/64.0
average	14212	4602	10150	0.96/0.79	35.4/64.6

reaction 2	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	15913	4443	10072	0.96/0.79	34.9/65.1
	14890	4399	10118	0.96/0.79	34.6/65.4
sample 2	16420	4736	10709	0.96/0.79	35.0/65.0
	14129	4372	10713	0.96/0.79	33.1/66.9
average	15338	4488	10403	0.96/0.79	34.4/65.6

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)- Dimethyl-(1-heptenyl) ethoxysilane (9) with 4-Iodoanisole

Following General Procedure VIII, **1** (28.8 mg, 0.20 mmol), **9** (40.0 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TMSOK (102 mg, 0.80 mmol) were stirred for 1 h and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 4 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 48.1/51.9.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	7822	3398	4320	0.96/0.79	48.9/51.1
	5984	2763	4025	0.96/0.79	45.5/54.4
sample 2	5884	2883	4082	0.96/0.79	46.2/53.7
	6834	2846	3733	0.96/0.79	48.1/51.9
average	6631	2973	4040	0.96/0.79	47.2/52.8

reaction 2	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	14268	5150	6635	0.96/0.79	48.6/51.4
	12609	4823	6132	0.96/0.79	48.9/51.1
sample 2	11388	3972	4765	0.96/0.79	50.4/49.6
	8838	4555	5975	0.96/0.79	48.1/51.9
average	11776	4625	5877	0.96/0.79	49.0/51.0

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diethoxy-(1-heptenyl)methyl-silane (10) with 4-Iodoanisole

Following General Procedure VIII, **1** (28.8 mg, 0.20 mmol), **10** (46.0 mg, 0.20 mmol), 4-iodotoluene (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TMSOK (102 mg, 0.80 mmol, 4 equiv) was stirred for 1 h and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 4 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14**/**15** ratio of 45.2/54.8.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	12383	5015	6820	0.96/0.79	47.2/52.8
	14152	5473	7759	0.96/0.79	46.2/53.8
sample 2	14350	5591	7614	0.96/0.79	47.2/52.8
	12685	5158	7438	0.96/0.79	45.8/54.2
average	13393	5309	7408	0.96/0.79	46.6/53.4

reaction 2	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	10483	3694	5885	0.96/0.79	43.3/56.7
	10944	3532	5508	0.96/0.79	43.8/56.1
sample 2	13787	4374	6477	0.96/0.79	45.1/54.9
	11565	3684	5892	0.96/0.79	43.2/56.8
average	11695	3821	5941	0.96/0.79	43.9/56.1

Competition of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Triethoxy-(1-heptenyl)silane (11) with 4-Iodoanisole

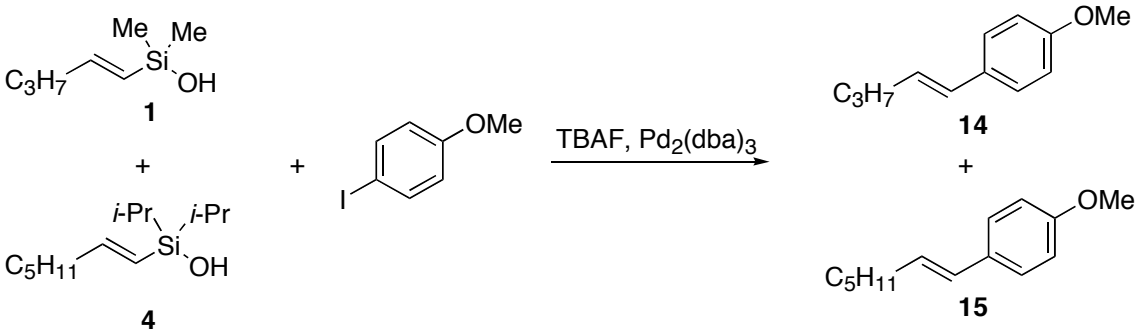
Following General Procedure VIII, **1** (28.8 mg, 0.20 mmol), **11** (52.0 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), a solution of naphthalene (0.8 mL, 0.20 mmol, 0.25 M in THF) and TMSOK (102 mg, 0.80 mmol, 4 equiv) were stirred for 1 h and $Pd(dba)_2$ (5.8 mg 0.01 mmol) was added. The reaction was stirred at room temperature for 4 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14**/**15** ratio of 51.6/48.4.

GC Data:

reaction 1	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	20487	8602	10147	0.96/0.79	50.8/49.2
	20825	11020	12209	0.96/0.79	52.4/47.6
sample 2	22197	9139	10343	0.96/0.79	51.8/48.2
	20003	8185	9599	0.96/0.79	50.9/49.1
average	20878	9237	10575	0.96/0.79	51.5/48.5

reaction 2	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	19421	6903	7745	0.96/0.79	52.0/48.0
	14983	6151	7832	0.96/0.79	48.9/51.1
sample 2	17814	7132	8018	0.96/0.79	52.0/48.0
	17462	6857	7118	0.96/0.79	53.8/46.2
average	17420	6761	7678	0.96/0.79	51.7/48.3

Competition Experiments of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole. General Procedure IX.



(*E*)-Dimethyl-(1-pentenyl)silanol (**1**), together with (*E*)-Di(1-methylethyl)-(1-heptenyl)-silanol (**4**), naphthalene, and 4-iodoanisole were dissolved in a TBAF solution (1.0 M in THF) in a flame-dried, 5-mL, 2-neck, round-bottomed flask under Ar. $Pd_2(dba)_3$ was added next and the resulting mixture stirred for 1 h. Two 25 μL samples were then taken via syringe. The sample aliquots were filtered through a plug of silica gel washing with EtOAc to achieve a total sample volume of ~2 mL. These samples were then subjected to GC analysis. Reactions were performed in duplicate.

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole and 1 equiv TBAF.

Following General Procedure IX, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (22.3 mg), TBAF (0.2 mL, 0.20 mmol, 1.0 M in THF) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 53.4/46.6.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	33357	14468	14037	0.87/0.79	53.1/46.9
sample 2	40130	16930	16170	0.87/0.79	53.6/46.4
average	36744	15699	15104	0.87/0.79	53.4/46.6

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole and 1 equiv TBAF.

Following General Procedure IX, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (11.6 mg), TBAF (0.2 mL, 0.20 mmol, 1.0 M in THF) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 55.7/44.3.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	18797	12336	10723	0.87/0.79	55.9/44.1
sample 2	30774	19873	17691	0.87/0.79	55.4/44.6
average	24745	16105	14207	0.87/0.79	55.7/44.3

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole and 2 equiv TBAF.

Following General Procedure IX, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (11.4 mg), TBAF (0.4 mL, 0.40 mmol, 1.0 M in THF) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two

sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 58.5/41.5.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	25030	25148	19628	0.87/0.79	58.5/41.5
sample 2	26012	26279	20708	0.87/0.79	58.4/41.6
average	25521	25714	20168	0.87/0.79	58.5/41.5

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole and 2 equiv TBAF.

Following General Procedure IX, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (22.2 mg), TBAF (0.4 mL, 0.40 mmol, 1.0 M in THF) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 58.5/41.5.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	29357	18201	14864	0.87/0.79	57.5/42.6
sample 2	26383	14283	10732	0.87/0.79	59.4/40.6
average	27870	16242	12798	0.87/0.79	58.5/41.6

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole and 4 equiv TBAF.

Following General Procedure IX, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (20.8 mg), TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 66.9/33.1.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	8147	4295	2282	0.87/0.79	67.5/32.5
sample 2	14041	7763	4282	0.87/0.79	66.8/33.4
average	11094	6029	3282	0.87/0.79	66.9/33.1

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole and 4 equiv TBAF.

Following General Procedure IX, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (14.1 mg), TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 65.0/34.0.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	10116	8167	4814	0.87/0.79	65.2/34.8
sample 2	10205	9091	5443	0.87/0.79	64.9/35.1
average	10161	8629	5129	0.87/0.79	65.1/34.9

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole and 8 equiv TBAF.

Following General Procedure IX, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (23.5 mg), TBAF (1.6 mL, 1.60 mmol, 1.0 M in THF) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 67.1/32.9.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	21870	12164	6563	0.87/0.79	67.1/32.9
sample 2	6474	3705	2023	0.87/0.79	67.1/32.9
average	14172	7935	4293	0.87/0.79	67.1/32.9

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole and 8 equiv TBAF.

Following General Procedure IX, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (14.5 mg), TBAF (1.6 mL, 1.60 mmol, 1.0 M in THF) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14**/**15** ratio of 66.1/33.9.

GC Data:

	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	7962	4936	2450	0.87/0.79	68.9/31.1
sample 2	14725	10608	6836	0.87/0.79	63.1/36.9
average	11344	7772	4643	0.87/0.79	66.1/33.9

Competition of 2 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 2 equiv (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole and 8 equiv TBAF.

Following General Procedure IX, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoanisole (23.4 mg, 0.10 mmol), naphthalene (10.3 mg), TBAF (0.8 mL, 0.8 mmol, 1.0 M in THF) and $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14**/**15** ratio of 68.0/32.0.

GC Data:

	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	15634	8491	4485	0.87/0.79	68.1/31.9
sample 2	16164	9183	4751	0.87/0.79	67.9/32.1
average	15899	8837	4618	0.87/0.79	68.0/32.0

Competition of 2 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 2 equiv (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole and 8 equiv TBAF.

Following General Procedure IX, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoanisole (23.4 mg, 0.10 mmol), naphthalene (11.0 mg), TBAF (0.8 mL, 0.8 mmol, 1.0 M in THF) and $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) were stirred at room temperature for 1 h and then

two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 66.0/34.0.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	12430	6762	3973	0.87/0.79	65.3/34.7
sample 2	11752	5981	3294	0.87/0.79	66.7/33.4
average	12091	6372	3634	0.87/0.79	66.0/34.0

Competition of 3 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 3 equiv (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole and 12 equiv TBAF.

Following General Procedure IX, **1** (43.2 mg, 0.30 mmol), **4** (68.5 mg, 0.30 mmol), 4-iodoanisole (23.4 mg, 0.10 mmol), naphthalene (8.7 mg), TBAF (1.2 mL, 1.2 mmol, 1.0 M in THF) and $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 68.8/31.2.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	7068	4567	2183	0.87/0.79	69.8/30.2
sample 2	12681	8735	4560	0.87/0.79	67.9/32.1
average	9875	6651	3372	0.87/0.79	68.8/31.2

Competition of 3 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 3 equiv (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole and 12 equiv TBAF.

Following General Procedure IX, **1** (43.2 mg, 0.30 mmol), **4** (68.5 mg, 0.30 mmol), 4-iodoanisole (23.4 mg, 0.10 mmol), naphthalene (10.3 mg), TBAF (1.2 mL, 1.2 mmol, 1.0 M in THF) and $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 69.9/30.1.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	8751	5424	2666	0.87/0.79	69.2/30.8
sample 2	11933	7329	3381	0.87/0.79	70.5/29.5
average	12091	6372	3634	0.87/0.79	69.9/30.1

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole and 1 equiv TMSOK.

Following General Procedure IX, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (20.5 mg), TMSOK (0.2 mL, 0.20 mmol, 1.0 M in THF) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 1.0/0.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	51446	13127	0	0.87/0.79	1.0/0
sample 2	44112	10900	0	0.87/0.79	1.0/0
average	47779	12014	0	0.87/0.79	1.0/0

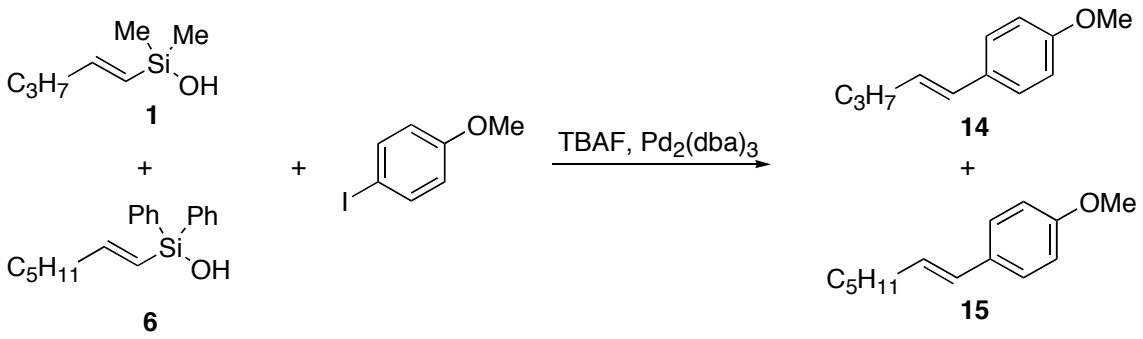
Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Di(1-methylethyl)-(1-heptenyl)silanol (4) with 4-Iodoanisole and 2 equiv TMSOK.

Following General Procedure IX, **1** (28.8 mg, 0.20 mmol), **4** (45.6 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (19.5 mg), TMSOK (0.4 mL, 0.40 mmol, 1.0 M in THF) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 1.0/0.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	42337	23484	0	0.87/0.79	1.0/0
sample 2	58993	33079	0	0.87/0.79	1.0/0
average	50665	28282	0	0.87/0.79	1.0/0

Competition Experiments of (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole. General Procedure X.



(*E*)-Dimethyl-(1-pentenyl)silanol (**1**), together with (*E*)-diphenyl-(1-heptenyl)silanol (**6**), naphthalene, and 4-iodoanisole were dissolved in a TBAF solution (1.0 M in THF) in a flame-dried, 5-mL, 2-neck, round-bottomed flask under Ar. $Pd_2(dba)_3$ was added next and the resulting mixture stirred for 1 h. Two 25 μL samples were then taken via syringe. The sample aliquots were filtered through a plug of silica gel washing with EtOAc to achieve a total sample volume of ~2 mL. These samples were then subjected to GC analysis. Reactions were performed in duplicate.

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 1 equiv TBAF.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (20.1 mg), TBAF (0.2 mL, 0.20 mmol, 1.0 M in THF), and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 42.3/57.7.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	22546	9143	14358	0.87/0.79	41.3/58.7
sample 2	33737	12703	18270	0.87/0.79	43.4/56.6
average	28141	10923	16314	0.87/0.79	42.3/57.7

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 1 equiv TBAF.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (15.9 mg), TBAF (0.2 mL, 0.20 mmol, 1.0 M in THF), and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14**/**15** ratio of 40.3/59.7.

GC Data:

	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	17268	8725	14173	0.87/0.79	40.5/59.5
sample 2	13180	6984	11599	0.87/0.79	40.0/60.0
average	15224	7854	12886	0.87/0.79	40.3/59.7

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 2 equiv TBAF.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (20.2 mg), TBAF (0.4 mL, 0.40 mmol, 1.0 M in THF), and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14**/**15** ratio of 50.2/49.8.

GC Data:

	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	20967	12601	13955	0.87/0.79	49.9/50.1
sample 2	25207	14023	15160	0.87/0.79	50.5/49.5
average	23087	13312	14557	0.87/0.79	50.2/49.8

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 2 equiv TBAF.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (15.9 mg), TBAF (0.4 mL, 0.40 mmol, 1.0 M in THF), and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two

sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 50.2/49.8.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	11532	7726	8375	0.87/0.79	50.5/49.5
sample 2	20061	13663	15283	0.87/0.79	49.7/50.3
average	15796	10694	11829	0.87/0.79	50.2/49.8

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 4 equiv TBAF.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (19.5 mg), TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF), and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 59.5/40.5.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	12345	7335	5487	0.87/0.79	59.6/40.4
sample 2	16274	10275	7769	0.87/0.79	59.4/40.6
average	14309	8805	6628	0.87/0.79	59.5/40.5

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 4 equiv TBAF.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (15.9 mg), TBAF (0.8 mL, 0.80 mmol, 1.0 M in THF), and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 59.8/40.2.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	23124	21653	16187	0.87/0.79	59.6/40.4
sample 2	27174	16805	12354	0.87/0.79	60.0/40.0
average	25149	19229	14270	0.87/0.79	59.8/40.2

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 8 equiv TBAF.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (25.4 mg), TBAF (1.6 mL, 1.60 mmol, 1.0 M in THF), and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 50.5/49.5.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	17080	6780	6930	0.87/0.79	51.9 /48.1
sample 2	13917	5536	6292	0.87/0.79	49.3/50.7
average	15498	6158	6611	0.87/0.79	50.5/49.5

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 8 equiv TBAF.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (15.9 mg), TBAF (1.6 mL, 1.60 mmol, 1.0 M in THF), and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 49.5/50.5.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	9853	6193	7086	0.87/0.79	49.1/50.9
sample 2	9333	6034	6722	0.87/0.79	49.8/50.2
average	9593	6113	6904	0.87/0.79	49.5/50.5

Competition of 2 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 2 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 8 equiv TBAF.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (23.4 mg, 0.10 mmol), naphthalene (10.8 mg), TBAF (0.8 mL, 0.8 mmol, 1.0 M in THF), and $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 59.4/40.6.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	11521	5999	4543	0.87/0.79	59.3/40.7
sample 2	13250	6885	5197	0.87/0.79	59.4/40.6
average	12385	6442	4847	0.87/0.79	59.4/40.6

Competition of 2 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 2 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 8 equiv TBAF.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (23.4 mg, 0.10 mmol), naphthalene (15.9 mg), TBAF (0.8 mL, 0.8 mmol, 1.0 M in THF), and $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 59.9/40.1.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	8203	8043	5865	0.87/0.79	60.2/39.8
sample 2	5103	4599	3444	0.87/0.79	59.6/40.4
average	6653	4821	4654	0.87/0.79	59.9/40.1

Competition of 3 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 3 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 12 equiv TBAF.

Following General Procedure X, **1** (43.3 mg, 0.30 mmol), **6** (88.9 mg, 0.30 mmol), 4-iodoanisole (23.4 mg, 0.10 mmol), naphthalene (15.9 mg), TBAF (1.2 mL, 1.2 mmol, 1.0 M in THF), and $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) were stirred at room temperature for 1 h and then

two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 58.8/41.2.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	9551	4979	3736	0.87/0.79	59.6/40.4
sample 2	7102	6100	4907	0.87/0.79	57.9/42.1
average	8326	5539	4321	0.87/0.79	58.8/41.2

Competition of 3 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 3 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 12 equiv TBAF.

Following General Procedure X, **1** (43.3 mg, 0.30 mmol), **6** (88.9 mg, 0.30 mmol), 4-iodoanisole (23.4 mg, 0.10 mmol), naphthalene (13.6 mg), TBAF (1.2 mL, 1.2 mmol, 1.0 M in THF), and $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 57.7/42.3.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	12218	5908	4766	0.87/0.79	57.8/42.2
sample 2	14495	6549	5322	0.87/0.79	57.6/42.4
average	13356	6228	5044	0.87/0.79	57.7/42.3

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 1 equiv TMSOK.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (18.1 mg), TMSOK (25.6 mg, 0.20 mmol), THF (0.4 mL) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 15.8/84.2.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	28110	1051	6006	0.87/0.79	16.2/83.8
sample 2	33532	1120	6827	0.87/0.79	15.3/84.7
average	30821	1085	6416	0.87/0.79	15.8/84.2

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 1 equiv TMSOK.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (15.9 mg), TMSOK (25.6 mg, 0.20 mmol), THF (0.4 mL) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 12.5/87.5.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	26560	992	7692	0.87/0.79	12.5/87.5
sample 2	14063	509	3952	0.87/0.79	12.5/87.5
average	20311	750	5822	0.87/0.79	12.5/87.5

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 2 equiv TMSOK.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (15.9 mg), TMSOK (51.2 mg, 0.40 mmol), THF (0.4 mL) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 15.7/84.3.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	27147	3535	20885	0.87/0.79	15.8/84.2
sample 2	37987	5169	30850	0.87/0.79	15.6/84.4
average	32567	4352	25867	0.87/0.79	15.7/84.3

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 2 equiv TMSOK.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (19.6 mg), TMSOK (51.2 mg, 0.40 mmol), THF (0.4 mL) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 16.3/83.7.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	37643	4556	25154	0.87/0.79	16.7/83.3
sample 2	30725	3506	20405	0.87/0.79	16.0/84.0
average	34184	4031	22779	0.87/0.79	16.3/83.7

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 4 equiv TMSOK.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (20.9 mg), TMSOK (103 mg, 0.80 mmol), THF (0.8 mL) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 40.2/59.8.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	20175	7329	12366	0.87/0.79	39.6/60.4
sample 2	19947	7353	11844	0.87/0.79	40.7/59.3
average	20061	7341	12105	0.87/0.79	40.2/59.8

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 4 equiv TMSOK.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (15.9 mg), TMSOK (103 mg, 0.80 mmol), THF (0.8 mL) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then

two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 31.4/68.6.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	14843	6020	14238	0.87/0.79	31.8/68.2
sample 2	16122	6836	16818	0.87/0.79	31.0/69.0
average	15482	6428	15528	0.87/0.79	31.4/68.6

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 4 equiv TMSOK.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (13.1 mg), TMSOK (103 mg, 0.80 mmol), THF (0.8 mL) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 35.2/64.8.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	16624	9111	16841	0.87/0.79	37.4/62.6
sample 2	18291	9833	22055	0.87/0.79	33.0/67.0
average	17457	9472	19448	0.87/0.79	35.2/64.8

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 8 equiv TMSOK.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (20.1 mg), TMSOK (205 mg, 1.60 mmol), THF (1.6 mL) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 61.2/38.8.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	9806	6231	4376	0.87/0.79	61.1/38.9
sample 2	7811	4701	3283	0.87/0.79	61.3/38.7
average	8808	5466	3829	0.87/0.79	61.2/38.8

Competition of 1 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 1 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 8 equiv TMSOK.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol), naphthalene (15.9 mg), TMSOK (205 mg, 1.60 mmol), THF (1.6 mL) and $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 56.4/43.6.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	6228	2407	1909	0.87/0.79	58.2/41.8
sample 2	5060	2138	1971	0.87/0.79	54.5/45.5
average	5644	2272	1940	0.87/0.79	56.4/43.6

Competition of 2 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 2 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 8 equiv TMSOK.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (23.4 mg, 0.10 mmol), naphthalene (11.9 mg), TMSOK (103 mg, 0.80 mmol), THF (0.8 mL) and $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 35.7/64.3.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	11054	3523	7644	0.87/0.79	33.7/66.3
sample 2	12260	4103	7514	0.87/0.79	37.6/62.4
average	11657	3813	7579	0.87/0.79	35.7/64.3

Competition of 2 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 2 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 8 equiv TMSOK.

Following General Procedure X, **1** (28.8 mg, 0.20 mmol), **6** (59.3 mg, 0.20 mmol), 4-iodoanisole (23.4 mg, 0.10 mmol), naphthalene (15.9 mg), TMSOK (103 mg, 0.80 mmol), THF (0.8 mL) and $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 33.5/66.5.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	6176	2685	5603	0.87/0.79	34.6/65.4
sample 2	5039	2091	4827	0.87/0.79	32.4/67.6
average	5607	2388	5215	0.87/0.79	33.5/66.5

Competition of 3 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 3 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 12 equiv TMSOK.

Following General Procedure X, **1** (43.3 mg, 0.30 mmol), **6** (88.9 mg, 0.20 mmol), 4-iodoanisole (23.4 mg, 0.10 mmol), naphthalene (14.0 mg), TMSOK (103 mg, 0.80 mmol), THF (0.8 mL) and $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) were stirred at room temperature for 1 h and then two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14/15** ratio of 39.6/60.4.

GC Data:

	area naphth	area **14**	area **15**	response factor **14/15**	ratio **14/15**x100
sample 1	7584	2232	3655	0.87/0.79	40.3/59.7
sample 2	8436	2222	3845	0.87/0.79	39.0/61.0
average	8010	2227	3750	0.87/0.79	39.6/60.4

Competition of 3 equiv (*E*)-Dimethyl-(1-pentenyl)silanol (1) vs 3 equiv (*E*)-Diphenyl-(1-heptenyl)silanol (6) with 4-Iodoanisole and 12 equiv TMSOK.

Following General Procedure X, **1** (43.3 mg, 0.30 mmol), **6** (88.9 mg, 0.20 mmol), 4-iodoanisole (23.4 mg, 0.10 mmol), naphthalene (15.9 mg), TMSOK (103 mg, 0.80 mmol), THF (0.8 mL) and $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) were stirred at room temperature for 1 h and then

two sample aliquots were taken and analyzed twice on GC. GC analysis of samples showed a **14**/**15** ratio of 36.2/63.8.

GC Data:

	area naphth	area **14**	area **15**	response factor **14**/**15**	ratio **14**/**15**x100
sample 1	4874	1863	3955	0.87/0.79	34.2/65.8
sample 2	4703	2188	3917	0.87/0.79	38.2/61.8
average	4788	2025	3936	0.87/0.79	36.2/63.8

References

(1) Gilman, H.; Cartledge, F. K.; Sin, S.-Y. *J. Organomet. Chem.* **1963**, *1*, 8.

(2) Chandra, G.; Lo, P. Y.; Hitencock, P. B.; Lappert, M. F. *Organometallics* **1987**, *6*, 191.

(3) Denmark, S. E.; Wehrli, D.; Choi, J. Y. *Org. Lett.* **2000**, *2*, 2491.

(4) Barrett, A. G. M.; Bennett, A. J.; Menzer, S.; Smith, M. L.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **1999**, *64*, 162.

(5) Le Bigot, Y.; Delmas, M.; Gaset, A. *Synth. Commun.* **1982**, *12*, 1115.

(6) Austin, W. B.; Bilow, N.; Kelleghan, J.; Lau, J. S. Y. *J. Org. Chem.* **1981**, *46*, 2280.

(7) Esteruelas M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221.

(8) Tsuda, K.; Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1993**, *26*, 6985.

(9) Meng, H.-H. B.; Dalton, L. R.; Wu, S.-T. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1994**, *250*, 303.

(10) Stammel, C.; Frohlich, R.; Wolf, C.; Wenck, H.; de Meijere, A.; Mattay, J. *Eur. J. Org. Chem.* **1999**, 1790.