Mild and General Cross-Coupling of (α-Alkoxyvinyl)-silanols and -silyl Hydrides

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SUPPORTING INFORMATION

General Experimental

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Unity 400 (400 MHz, ^{1}H; 100 MHz, ^{13}C; 376 MHz, ^{19}F), Unity 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C; 470 MHz, ^{19}F). Spectra are referenced to residual chloroform (δ 7.26 ppm, ^{1}H; δ 77.0 ppm, ^{13}C) and residual benzene (δ 7.16 ppm, ^{1}H; δ 128 ppm, ^{13}C).

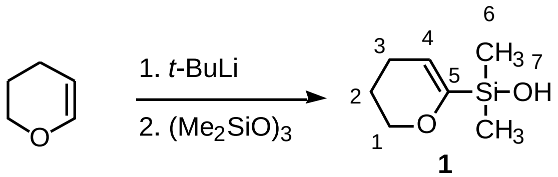
Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Mass spectroscopy was performed by the University of Illinois Mass Spectrometer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

Analytical thin-layer chromatography was performed on Merck silica or aluminum oxide, basic gel plates with QF-254 indicator. Visualization was accomplished with UV light and/or Iodide. Diethyl ether was of reagent grade and used as received; other solvents for chromatography and filtration were technical grade and distilled from the indicated drying agents: hexane and pentane ($CaCl_2$); ethyl acetate (K_2CO_3). Column chromatography was performed using EM Science 230-400-mesh silica gel or Aldrich 150-mesh aluminum oxide, activated, basic, Brockmann I.

Analytical capillary gas chromatography (GC) was performed using the following gas chromatography fitted with a flame ionization detector (H_2 carrier gas, 1 mL/min): Hewlett Packard 5890 Series II. The following column was used: HP-5 50-m cross-linked 5%-Phenyl methyl silicone gum phase or Ultra-2 50-m cross-linked 5%-Phenyl methyl silicone gum phase. The detector temperature was 300 °C. Retention times (t_R) and integrated ratios were obtained from Hewlett Packard 3393A integrators.

Kugelrohr distillations were performed on a Büchi GKR-50 Kugelrohr; boiling points (bp) corresponding to uncorrected air-bath temperatures. All commercial reagents were purified by distillation or recrystallization prior to use. A 1.0 M solution of tetrabutylammonium fluoride in THF was prepared from solid tetrabutylammonium fluoride trihydrate (TBAF•$3H_2O$, Fluka) and distilled THF in a volumetric flask and was stored in a Schlenk bottle. A 1.0 M solution of tetrabutylammonium hydroxide in MeOH (TBAOH) was purchased from Aldrich and used without purification. Palladium bis(dibenzylideneacetone) ($Pd(dba)_2$) was purchased from Jansen and used without purification. π-Allylpalladium chloride dimer $[allylPdCl]_2$ was purchased from ACROS and was recrystallized from benzene prior to use. All reactions were performed under an inert atmosphere of dry N_2.

Preparation of [2-(5,6-Dihydro-4H-pyranyl)]dimethylsilanol (1) [II-luc95FD].



1

To a solution of *t*-butyllithium (10.0 mL, 14 mmol, 1.4 M in heptane) under dry N_2 at –78 °C was added THF (1.15 mL, 1.4 mmol). The resulting yellow suspension was stirred at –78 °C for 10 min, then 3,4-dihydro-2H-pyran (1.30 mL, 14 mmol, 1.0 equiv) was added. The mixture was allowed to warm to 0 °C and was stirred for 1.5 h whereby a colorless solution was obtained.

After cooling the solution to –78 °C, a solution of hexamethylcyclotrisiloxane (1.04 g, 4.6 mmol, 0.33 equiv) in dry THF (2.0 mL) was added over 5 min at –78 °C. The mixture was allowed to warm to 0 °C and was stirred for at that temperature 1.5 h. The mixture was then allowed to warm to room temperature and was stirred for 1.5 h during which time a white suspension formed. The solution was then cooled to 0 °C and was quenched with water (20 mL). The aqueous phase was extracted with ethyl acetate (5 × 20 mL) and the combined organic phases were washed with water (1 × 20 mL) and brine (1 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate and were filtered. The filtrate was then evaporated *in vacuo* to give a yellow oil which was purified by column chromatography (silica gel, hexane/ethyl acetate, 7/1) and by distillation to afford 1.51g (68%) of **1** as a colorless oil.

Data for **1**:

bp: 53 °C (0.6 mmHg).

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

5.11 (dd, *J* = 3.6, 3.9 Hz, HC(4), 1 H); 3.95 (t, *J* = 5.1 Hz, HC(1), 2 H); 2.36 (br s, HC(7), 1 H); 2.00 (dt, *J* = 3.9, 6.3 Hz, HC(3), 2 H); 1.83 (tt, *J* = 5.1, 6.3 Hz, HC(2), 2 H); 0.21 (s, HC(6), 6 H).

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

159.0 (C(5)), 111.8 (C(4)), 65.8 (C(1)), 22.7 (C(3)), 20.6 (C(2)), -1.1 (C(6)).

IR: (NaCl)

3369 (s, br), 2960 (s), 2864 (m), 1619 (s), 1447 (w), 1252 (s), 1103 (m), 1047 (s), 874 (s); 782 (s).

MS: (EI, 70 eV)

158 (M^+, 35), 133 (30), 125 (12), 113 (12), 77 (49), 75 (100).

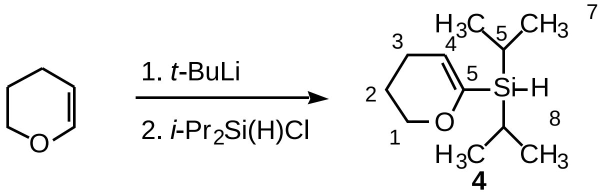
TLC: R_f 0.24 (SiO_2, hexane/EtOAc, 7/1).

GC: t_R **1**, 6.50 min (100%) (U2, injector 135 °C column 130 °C, 15 psi).

Analysis: $C_7H_{14}O_2Si$ (158.27)

Calculated:	C, 53.14;	H, 8.93%
Found:	C, 53.18;	H, 8.83%.

Preparation of [2-(5,6-Dihydro-4H-pyranyl)]diisopropylsilane (4) [III-luc5KFK].



4

To a solution of *t*-butyllithium (5.0 mL, 8.0 mmol, 1.6 M in heptane) under dry N_2 at –78 °C was added THF (0.65 mL, 8.0 mmol, 1.0 equiv). The resulting yellow suspension was stirred at –78 °C for 10 min, then 3,4-dihydro-2H-pyran (1.30 mL, 8.0 mmol, 1.0 equiv) was added. The mixture was allowed to warm to 0 °C and stirred for 1.5 h whereby a colorless solution was obtained.

After cooling the solution to –78 °C, chlorodiisopropylsilane (1.36 mL, 8.0 mmol, 1.0 equiv) was then added. The mixture was stirred for 1.5 h at –78 °C, then was allowed to warm to room temperature and was stirred for 1.5 h during which time a white suspension formed. After addition of heptane (10 mL), the suspension was filtered through a short plug of Celite. The solvent was then evaporated *in vacuo* to give a white suspension. After Kugelrohr distillation

(130 °C at 0.6 mmHg), the colorless oil obtained was purified by column chromatography (silica gel, hexane) and was distilled again to give 1.20 g (75%) of **4** as a colorless oil.

Data for **4**:

bp: 105 °C air bath (0.6 mmHg).

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

5.07 (t, *J* = 3.9 Hz, HC(4), 1 H); 3.91 (dd, *J* = 4.9, 5.3 Hz, HC(1), 2 H); 3.47 (br s, HC(8), 1 H); 2.02 (dt, *J* = 3.9, 6.3 Hz, HC(3), 2 H); 1.84 (dtt, *J* = 4.9, 5.3, 6.4 Hz, HC(2), 2 H); 1.06-1.00 (m, HC(6) and HC(7), 14 H).

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

156.0 (C(5)), 114.6 (C(4)), 65.7 (C(1)), 23.0 (C(3)), 21.1 (C(2)), 18.8/18.9 (C(7)/C(7')), 10.2 (C(6)).

IR: (NaCl)

2943 (s), 2864 (m), 2111 (s), 1615 (s), 1462 (m), 1273 (m), 1047 (m), 803 (s).

MS: (EI, 70 eV)

198 (M^+, 24), 197 (47), 156 (25), 141 (45), 125 (51), 113 (100), 99 (42), 85 (65), 77 (68).

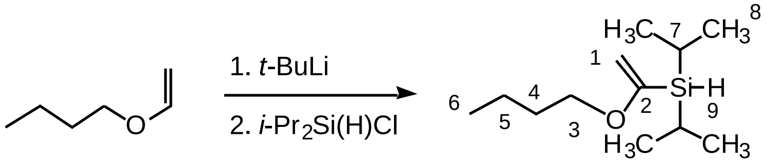
TLC: R_f 0.52 (SiO_2, hexane).

GC: t_R **4**, 13.10 min (98%) (U2, injector 135 °C, column 130 °C, 15 psi).

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

Calculated:	C, 66.62;	H, 11.19;	Si, 14.12%
Found:	C, 66.33;	H, 11.01;	Si, 14.18%.

Preparation of (1-Butoxyvinyl)diisopropylsilane (5) [III-luc9KFK].



5

To a solution of *t*-butyllithium (5.0 mL, 7.5 mmol, 1.5 M in heptane) under dry N_2 at –78 °C was added THF (0.60 mL, 7.5 mmol, 1.0 equiv). The resulting yellow suspension was stirred at –78 °C for 10 min, then *n*-butyl vinyl ether (0.97 mL, 7.5 mmol, 1.0 equiv) was added. The mixture was allowed to warm to 0 °C and was stirred for 1.5 h whereby a colorless solution was obtained.

After cooling the solution to –78 °C, chlorodiisopropylsilane (1.30 mL, 7.5 mmol, 1.0 equiv) was added. The mixture was stirred for 1.5 h at –78 °C, was allowed to warm to room temperature and was stirred for 1.5 h during which time a white suspension was formed. After addition of heptane (10 mL), the suspension was filtered through a short plug of Celite. The filtrate was then evaporated *in vacuo* to give a white suspension. After Kugelrohr distillation (120 °C at 0.6 mmHg), the colorless oil obtained was purified by column chromatography (silica gel, hexane) and was distilled again to give 1.16 g (72%) of **5** as a colorless oil.

Data for **5**:

bp: 54 °C (0.6 mmHg).

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

4.69 (d, J = 1.6 Hz, H_ZC(1), 1 H); 4.35 (d, J = 1.6 Hz, H_EC(1), 1 H); 3.64 (t, J = 6.4 Hz, HC(3), 2 H); 3.57 (t, J = 2.3 Hz, HC(9), 1 H); 1.63 (m, HC(4), 2 H); 1.41 (m, HC(5), 2 H); 1.05 (m, HC(7) and HC(8), 14 H); 0.93 (t, J = 7.3 Hz, HC(6), 3 H).

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

165.4 (C(2)), 97.0 (C(1)), 66.1 (C(3)), 31.1 (C(4)), 19.4 (C(5)), 18.4/18.5 (C(8)/C(8')), 13.8 (C(6)), 10.0 (C(7)).

IR: (NaCl)

2942 (s), 2866 (s), 2116 (s), 1582 (s), 1463 (s), 1216 (s), 1003 (m), 802 (s).

MS: (EI, 70 eV)

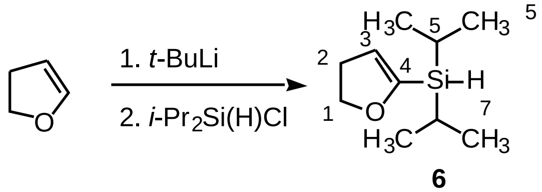
214 (M^+, 7), 187 (40), 157 (100), 145 (50), 129 (65), 115 (80), 87 (78), 73 (72).

TLC: R_f 0.89 (SiO_2, hexane).

GC: t_R **5**, 12.05 min (97%) (U2, injector 135 °C, column 130 °C, 15 psi).

HRMS: calcd for $C_{12}H_{26}OSi$: 214.1753; found: 214.1752.

Preparation of 2-(4,5-Dihydrofuranyl)diisopropylsilane (6) [III-luc7KFK].



6

To a solution of *t*-butyllithium (5.0 mL, 7.5 mmol, 1.5 M in heptane) under dry N_2 at –78 °C was added THF (0.60 mL, 7.5 mmol, 1.0 equiv). The resulting yellow suspension was stirred at –78 °C for 10 min, then 2,3-dihydrofuran (0.567 mL, 7.5 mmol, 1.0 equiv) was added. The mixture was warmed to 0 °C and was stirred for 1.5 h whereby a white suspension was obtained.

After cooling the suspension to –78 °C, chlorodiisopropylsilane (1.30 mL, 7.5 mmol, 1.0 equiv) was added. The mixture was stirred for 1.5 h at –78 °C, was allowed to warm to room temperature and was stirred for 1.5 h. After addition of heptane (10 mL), the suspension was filtered through a short plug of Celite. The filtrate was then evaporated *in vacuo* to give a white suspension. After Kugelrohr distillation (120 °C at 0.6 mmHg), the colorless oil obtained was purified by column chromatography (silica gel, hexane) and was distilled again to give 987 mg (71%) of **6** as a colorless oil.

Data for **6**:

bp: 95 °C air bath (0.6 mmHg)

^{1}H NMR: (500 MHz, CDCl$_3$)

5.32 (t, *J* = 2.6 Hz, HC(4), 1 H); 4.26 (t, *J* = 9.7 Hz, HC(3), 2 H); 3.66 (brs, HC(7), 1 H); 2.59 (dt, *J* = 2.6, 9.7 Hz, HC(2), 2 H); 1.06 (m, HC(5) and HC(6), 14 H).

^{13}C NMR: (125 MHz, CDCl$_3$)

157.0 (C(4)), 114.5 (C(3)), 71.2 (C(1)), 30.6 (C(2)), 18.5/18.6 (C(6)/C(6')), 10.0 (C(5)).

IR: (NaCl)

2943 (s), 2865 (m), 2117 (s), 1593 (m), 1462 (m), 1095 (m), 928 (m), 789 (s).

MS: (EI, 70 eV)

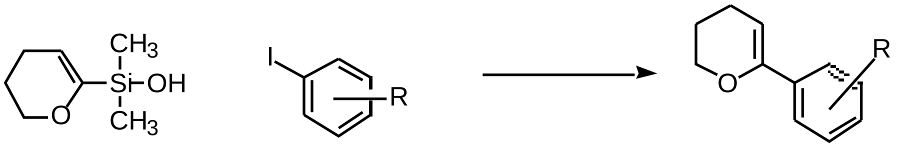
184 (M$^+$, 41), 173 (16), 156 (27), 142 (56), 113 (78), 99 (100), 83 (68), 77 (65).

TLC: R_f 0.48 (SiO$_2$, hexane).

GC: t_R **6**, 919 min (96%) (U2, injector 135 °C, column 130 °C, 15 psi).

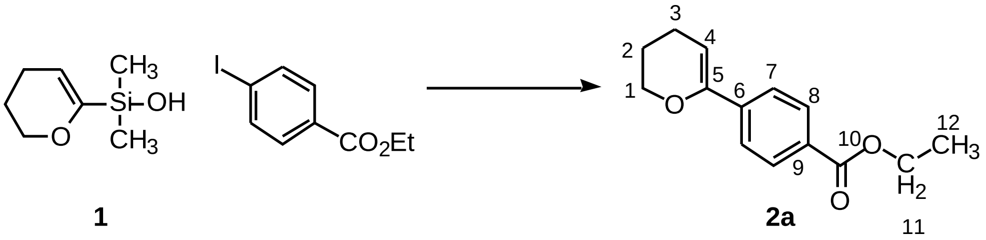
HRMS: calcd for C$_{10}$H$_{20}$OSi: 184.1283; found: 184.1287.

General Procedure for Coupling of Silanols.



To the organosilanol (1.2 mmol) was added a solution tetrabutylammonium fluoride (TBAF) in THF (1.0 M, 2.0 mL, 2.0 mmol). The aryl iodide or vinyl iodide (1.0 mmol, 1.0 equiv) was added to the mixture, followed by the palladium catalyst (5 mol% of Pd) and the mixture was stirred at room temperature for 10 min to 4 h. The mixture was then filtered through a short plug of silica gel or alumina (10 g). The plug was washed with diethyl ether (50 mL) and the solvent was evaporated *in vacuo*. Purification of the residue by column chromatography afforded the coupling product which was further purified by Kugelrohr distillation or crystallization.

Reaction of Ethyl 4-Iodobenzoate with Silanol 1 [II-luc38FX]. Ethyl 4-[2-(5,6-Dihydro-4H-pyranyl)]benzoate (2a).



Following the General Procedure, **1** (190 mg, 1.2 mmol, 1.2 equiv), was dissolved in a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv) and was stirred for 10 min at rt. Ethyl 4-iodobenzoate (0.166 mL, 1.0 mmol) and $[\text{allylPdCl}]_2$ (9 mg, 0.025 equiv) were added. The suspension was stirred at rt for 10 min and then was filtered through a short plug of SiO_2. Purification of the residue by column chromatography (SiO_2, hexane/EtOAc, 20/1) and recrystallization from hexane afforded 195 mg (84%) of **2a** as a colorless oil.

Data for **2a**:

mp: 76-78 °C (hexane).

^{1}H NMR: (500 MHz, benzene-*d*$_6$)

8.22 (d, *J* = 8.4 Hz, HC(8), 2 H); 7.65 (d, *J* = 8.4 Hz, HC(7), 2 H); 5.20 (dd, *J* = 4.0, 4.1 Hz, HC(4), 1 H); 4.13 (q, *J* = 7.1 Hz, HC(11), 2H); 3.78 (dd, *J* = 4.9, 5.1 Hz, HC(1), 2 H); 1.82 (dt, *J* = 4.1, 6.5 Hz, HC(3), 2 H); 1.42 (tt, *J* = 5.1, 6.5 Hz, HC(2), 2 H); 1.01 (t, *J* = 7.1 Hz, HC(12), 3 H).

^{13}C NMR: (125 MHz, benzene-*d*$_6$)

166.2 (C(10)), 150.3 (C(5)), 140.8 (C(6)), 129.9 (C(7)), 124.4(C(8)), 99.5 (C(4)), 66.3 (C(1)), 60.7 (C(11)), 22.3 (C(3)), 21.0 (C(2)), 14.3 (C(12)).

IR: (NaCl, $CHCl_3$)

2982 (w), 2935 (w), 1711 (s), 1609 (w), 1430 (w), 1258 (s), 1108 (m), 920 (w), 748 (m).

MS: (EI, 70 eV)

232 (M^+, 50), 177 (100), 159 (31), 149 (54), 77 (29).

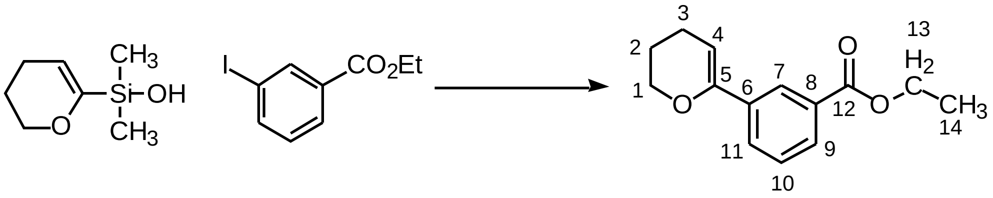
TLC: R_f 0.28 (SiO_2, hexane/EtOAc, 20/1).

GC: t_R **2a**, 5.55 min (100%) (HP5, injector 225 °C, column 225 °C, 15 psi).

Analysis: $C_{14}H_{16}O_3$ (232.10)

Calculated:	C, 72.38;	H, 6.95%
Found:	C, 72.21;	H, 6.92%.

Reaction of Ethyl 3-Iodobenzoate with Silanol 1 [II-luc28FK]. Ethyl 3-[2-(5,6-Dihydro-4H-pyranyl)]benzoate (2b).



1 **2b**

Following the General Procedure, **1** (190 mg, 1.2 mmol, 1.2 equiv), was dissolved in a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv) and was stirred for 10 min at rt. Ethyl 3-iodobenzoate (0.166 mL, 1.0 mmol) and $[\text{allylPdCl}]_2$ (9 mg, 0.025 equiv) were added. The suspension was stirred at rt for 10 min and then was filtered through a short plug of SiO_2. Purification of the residue by column chromatography (SiO_2, hexane/EtOAc, 20/1) and distillation afforded 200 mg (86%) of **2b** as a colorless oil.

Data for **2b**:

bp: 175 °C air bath (0.6 mmHg).

^{1}H NMR: (400 MHz, benzene-d_6)

8.10 (dd, J = 1.6, 7.8 Hz, HC(7), 1 H); 7.73 (dd, J = 1.7, 7.8 Hz, HC(11), 1 H); 7.10 (t, J = 7.6 Hz, HC(10), 1 H); 5.21 (t, J = 4.1 Hz, HC(4), 1 H); 4.12 (q, J = 7.1, HC(13)), 2H); 3.79 (t, J = 5.1 Hz, HC(1), 2 H); 1.81 (dt, J = 4.1, 6.3 Hz, HC(3), 2 H); 1.43 (tt, J = 5.1, 6.3 Hz, HC(2), 2 H); 0.99 (t, J = 7.1 Hz, HC(14), 3 H).

^{13}C NMR: (100.6 MHz, benzene-d_6)

166.4 (C(12)), 151.2 (C(5)), 137.1 (C(6)), 131.1 (C(11)), 128.3 (C(8)), 128.1(C(7)), 127.8 (C(10)), 125.9 (C(9)), 98.3 (C(4)), 66.4 (C(1)), 60.9 (C(13)), 22.4 (C(3)), 21.0 (C(2)), 14.3 (C(14)).

IR: (NaCl)

2933 (s), 2869 (s), 1719 (s), 1651 (s), 1447 (w), 1303 (s), 1213 (m), 1087 (s), 923 (w), 754 (s).

MS: (EI, 70 eV)

232 (M^+, 79), 177 (100), 159 (39), 149 (40), 77 (38).

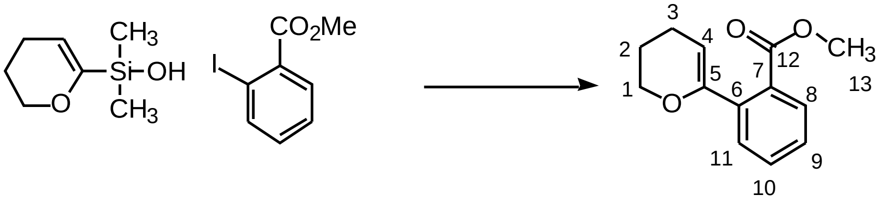
TLC: R_f 0.23 (SiO_2, hexane/EtOAc, 20/1).

GC: t_R **2b**, 9.25min (100%) (HP5, injector 200 °C, column 200 °C, 15 psi).

Analysis: $C_{14}H_{16}O_3$ (232.10)

Calculated:	C, 72.38;	H, 6.95%
Found:	C, 72.20;	H, 7.06%.

Reaction of Methyl 2-Iodobenzoate with Silanol 1 [II-luc49FK]. Methyl 2-[2-(5,6-Dihydro-4H-pyranyl)]benzoate (2c).



1 **2c**

Following the General Procedure, **1** (190 mg, 1.2 mmol, 1.2 equiv), was dissolved in a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv) and was stirred for 10 min at rt. Methyl 2-iodobenzoate (0.151 mL, 1.0 mmol) and $[allylPdCl]_2$ (9 mg, 0.025 equiv) were added. The suspension was stirred at rt for 4 hours and then was filtered through a short plug of SiO_2. Purification of the residue by column chromatography (SiO_2, hexane/EtOAc, 20/1) and distillation afforded 200 mg (92%) of **2c** as a colorless oil.

Data for **2c**:

bp: 170 °C air bath (0.4 mmHg).

^{1}H NMR: (400 MHz, benzene-d_6)

7.64 (dd, J = 1.4, 7.6 Hz, HC(11), 1 H); 7.32 (dd, J = 1.4, 7.6 Hz, HC(8), 1 H); 7.01 (ddd, J = 1.3, 7.6 Hz, HC(9), 1 H); 6.93 (ddd, J = 1.2, 7.6 Hz, HC(10), 1 H); 4.98 (t, J = 3.9 Hz, HC(4), 1 H); 3.86 (dd, J = 5.1, 5.2 Hz, HC(1), 2 H); 3.58 (s, HC(13), 1H); 1.91 (dt, J = 3.9, 6.4 Hz, HC(3), 2 H); 1.52 (tt, J = 5.4, 6.5 Hz, HC(2), 2 H).

^{13}C NMR: (100.6 MHz, benzene-d_6)

169.0 (C(12)), 153.8 (C(5)), 137.8 (C(10)), 131.9 (C(6)), 130.7 (C(11)), 129.4 (C(7)), 128.0 (benzene + C(9)), 128.9 (C(8)), 100.0 (C(4)), 66.6 (C(1)), 51.6 (C(13)), 22.4 (C(3)), 21.1 (C(2)).

IR: (NaCl)

2949 (m), 2876 (w), 1728 (s), 1658 (m), 1432 (m), 1291 (s), 1100 (m), 918 (m), 758 (m).

MS: (EI, 70 eV)

218 (M^+, 50), 186 (60), 163 (100), 158 (59), 129 (30), 77 (49).

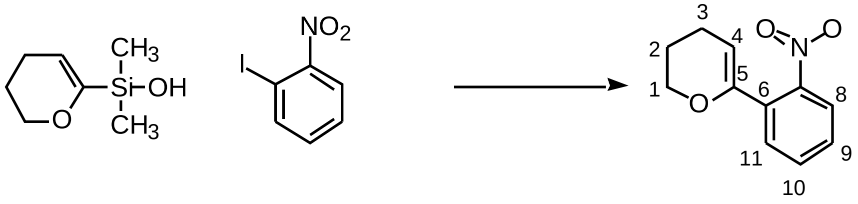
TLC: R_f 0.27 (SiO_2, hexane/EtOAc, 20/1).

GC: t_R **2c**, 12.21 min (100%) (HP5, injector 200 °C, column 200 °C, 15 psi).

Analysis: $C_{13}H_{14}O_3$ (218.09)

Calculated:	C, 71.53;	H, 6.48%
Found:	C, 71.34;	H, 6.45%.

Reaction of 2-Iodonitrobenzene with Silanol 1 [II-luc49FK]. 6-(2-Nitrophenyl)-3,4-dihydro-2H-pyran (2d).



1 **2d**

Following the General Procedure, **1** (190 mg, 1.2 mmol, 1.2 equiv), was dissolved in a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv) and was stirred for 10 min at rt. 2-Iodonitrobenzene (249 mg, 1.0 mmol) and $[allylPdCl]_2$ (9 mg, 0.025 equiv) were added. The suspension was stirred at rt for 10 min and then was filtered through a short plug of SiO_2. Purification of the residue by column chromatography (SiO_2, hexane/Et_2O, 20/1) and distillation afforded 174 mg (85%) of **2d** as a colorless oil.

Data for **2d**:

bp: 190 °C air bath (1.5 mmHg).

^{1}H NMR: (400 MHz, benzene-d_6)

7.25 (dd, J = 0.9, 8.06 Hz, HC(8), 1 H); 7.08 (dd, J = 1.3, 7.9 Hz, HC(11), 1 H); 6.80 (m, HC(10), 1 H); 6.33 (m, HC(9), 1 H); 4.91 (t, J = 3.9 Hz, HC(4), 1 H); 3.77 (dd, J = 5.1, 5.2 Hz, HC(1), 2 H); 1.81 (dt, J = 3.9, 6.4 Hz, HC(3), 2 H); 1.41 (tt, J = 5.4, 6.5 Hz, HC(2), 2 H).

^{13}C NMR: (100.6 MHz, benzene-d_6)

151.1 (C(5)), 149.4 (C(7)), 131.9 (C(10)), 131.4 (C(6)), 129.8 (C(11)), 128.7 (C(9)), 123.9 (C(8)), 101.9 (C(4)), 66.8 (C(1)), 22.0 (C(3)), 20.0 (C(2)).

IR: (NaCl)

2933 (s), 2877 (s), 1659 (s), 1530 (s), 1364 (s), 1299 (s), 1067 (m), 918 (m), 749 (s).

MS: (EI, 70 eV)

205 (M^+, 7), 173 (7), 135 (46), 104 (82), 79 (81), 71 (100).

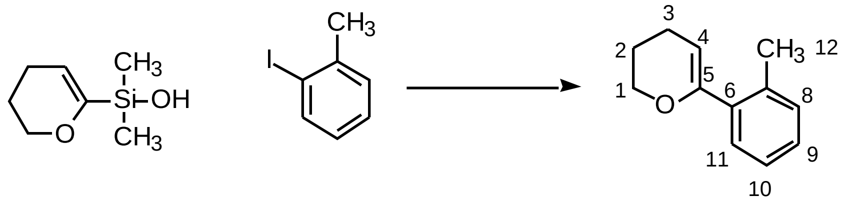
TLC: R_f 0.25 (SiO_2, hexane/Et_2O, 20/1).

GC: t_R **2d**, 8.35 min (100%) (HP5, injector 225 °C, column 225 °C, 15 psi).

Analysis: $C_{11}H_{11}NO_3$ (205.21)

Calculated:	C, 64.38;	H, 5.40;	N, 6.83%
Found:	C, 64.48;	H, 6.37;	N, 7.03%.

Reaction of 2-Iodotoluene with Silanol 1 [II-luc85FK]. 6-(2-Methylphenyl)-3,4-dihydro-2H-pyran (2e).



1 **2e**

Following the General Procedure, **1** (190 mg, 1.2 mmol, 1.2 equiv), was dissolved in a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv) and was stirred for 10 min at rt. 2-Iodotoluene (0.127 mL, 1.0 mmol) and [allylPdCl]$_2$ (9 mg, 0.025 equiv) were added. The suspension was stirred at rt for 10 min and then was filtered through a short plug of SiO_2. Purification of the residue by column chromatography (SiO_2, hexane/Et_2O, 50/1) and distillation afforded 140 mg (80%) of **2e** as a colorless oil.

Data for **2e**:

bp: 110 °C air bath (1.0 mmHg).

^{1}H NMR: (400 MHz, benzene-*d*$_6$)

7.43 (dd, *J* = 2.0, 7.8 Hz, HC(11), 1 H); 7.03-7.11(m, HC(8), HC (9), HC(10), 3H0; 4.81 (t, *J* = 3.8 Hz, HC(4), 1 H); 3.84 (dd, *J* = 5.1, 5.4 Hz, HC(1), 2 H); 2.42 (s, HC(12), 3H); 1.90 (dt, *J* = 3.9, 6.4 Hz, HC(3), 2 H); 1.52 (tt, *J* = 5.4, 6.4 Hz, HC(2), 2 H).

^{13}C NMR: (100.6 MHz, benzene-*d*$_6$)

154.8 (C(5)), 137.9 (C(6)), 136.5 (C(7)), 130.4 (C(9)), 129.2 (C(8)), 128.0 (benzene + C(11)), 125.6 (C(10)), 100.0 (C(4)), 65.9 (C(1)), 22.5 (C(3)), 20.8 (C(2)), 20.3 (C(12)).

IR: (NaCl)

2948(s), 2928 (s), 1659 (s), 1343 (s), 1295 (s), 1069 (s), 916(s), 756 (s).

MS: (EI, 70 eV)

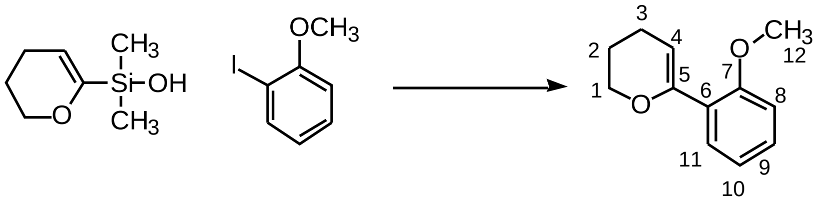
174 (M^+, 100), 145 (53), 131 (49), 119 (85), 91 (79), 77 (19).

TLC: R_f 0.33 (SiO_2, hexane/Et_2O, 30/1).

GC: t_R **2e**, 7.06 min (97%) (HP5, injector 200 °C, column 200 °C, 15 psi).

HRMS: calcd for $C_{12}H_{14}O$: 174.1044; found: 174.1042.

Reaction of 2-Iodoanisole with Silanol 1 [II-luc34FK+III-luc15FK]. 6-(2-Methoxyphenyl)-3,4-dihydro-2H-pyran (2f).



1 **2f**

Following the General Procedure, **1** (190 mg, 1.2 mmol, 1.2 equiv), was dissolved in a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv) and was stirred for 10 min at rt. 2-Iodoanisole (0.130 mL, 1.0 mmol) and [allylPdCl]$_2$ (9 mg, 0.025 equiv) were added. The suspension was stirred at rt for 20 min and then was filtered through a short plug of SiO$_2$. Purification of the residue by column chromatography (SiO$_2$, hexane/EtOAc, 40/1) and distillation afforded 142 mg (74%) of **2f** as a colorless oil.

Data for **2f**:

bp: 150 °C air bath (0.8 mmHg).

^{1}H NMR: (400 MHz, benzene-d_6)

7.85 (brd, J = 7.2 Hz, HC(11), 1 H); 7.07 (ddd, J = 1.7, 7.3, 8.2 Hz, HC(9), 1 H); 6.91 (dd, J = 7.4, 7.96 Hz, HC(10), 1 H); 6.57 (d, J = 8.2 Hz, HC(8), 1 H); 5.72 (t, J = 3.8 Hz, HC(4), 1 H); 3.94 (dd, J = 5.0, 5.1 Hz, HC(1), 2 H); 3.32 (s, HC(12), 1H); 2.03 (dt, J = 3.8, 6.6 Hz, HC(3), 2 H); 1.57 (m, HC(2), 2 H).

^{13}C NMR: (100.6 MHz, benzene-d_6)

157.5 (C(7)), 149.8 (C(5)), 129.0 (C(9)), 128.8 (C(11)), 126.5 (C(6)), 120.6 (C(10)), 111.5 (C(8)), 102.2 (C(4)), 66.4 (C(1)), 55.1 (C(12)), 22.8 (C(3)), 21.4 (C(2)).

IR: (NaCl)

2931 (s), 2870 (m), 2840 (m), 1643 (m), 1598 (m), 1492 (s), 1345 (m), 1253 (s), 1124 (w), 918 (m), 754 (s).

MS: (EI, 70 eV)

190 (M$^+$, 87), 175 (11), 161 (12), 147 (13), 135 (100), 121 (19), 105 (26), 92 (19), 77 (40).

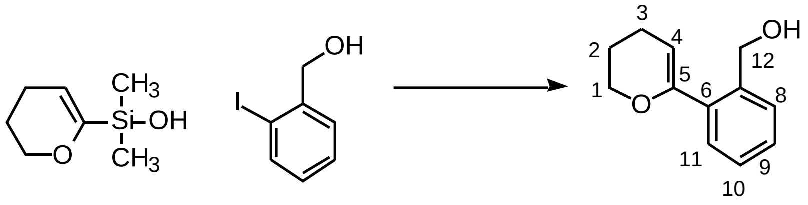
TLC: R_f 0.32 (SiO$_2$, hexane/EtOAc, 30/1).

GC: t_R **2f**, 8.72 min (100%) (U2, injector 200 °C, column 200 °C, 15 psi).

Analysis: $C_{12}H_{14}O_2$ (190.24)

Calculated:	C, 75.75;	H, 7.42%
Found:	C, 75.52;	H, 7.16%.

Reaction of 2-Iodobenzyl Alcohol with Silanol 1 [II-luc76FK]. 2-[2-(5,6-Dihydro-4H-pyranyl)]-phenylmethanol (2g).



1 **2g**

Following the General Procedure, **1** (190 mg, 1.2 mmol, 1.2 equiv), was dissolved in a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv) and was stirred for 10 min at rt. 2-Iodobenzyl alcohol (234 mg, 1.0 mmol) and Pd(dba)$_2$ (29 mg, 0.05 equiv) were added. The suspension was stirred at rt for 4 hours and then was filtered through a short plug of SiO$_2$. Purification of the residue by column chromatography (SiO$_2$, hexane/EtOAc, 7/1) and distillation afforded 168 mg (88%) of **2g** as a colorless oil. Despite repeated purification, an analytically pure sample could not be obtained.

Data for **2g**:

bp: 120 °C air bath (0.5 mmHg).

^{1}H NMR: (500 MHz, benzene-d_6)

7.39 (brd, J = 7.7 Hz, HC(8), 1 H); 7.35 (dd, J = 1.4, 7.5 Hz, HC(11), 1 H); 7.12 (ddd, J = 1.5, 7.5 Hz, HC(10), 1 H); 7.05 (ddd, J = 1.5, 7.5 Hz, HC(9), 1 H); 4.81 (t, J = 3.8 Hz, HC(4), 1 H); 4.69 (d, J = 6.7 Hz, HC(12), 1 H); 3.67 (dd, J = 4.8, 5.3 Hz, HC(1), 2 H); 2.42 (m, HO, 1 H); 1.8 (dt, J = 3.9, 6.5 Hz, HC(3), 2 H); 1.41 (m, HC(2), 2 H).

^{13}C NMR: (125 MHz, benzene-d_6)

154.3 (C(5)), 1340.2 (C(7)), 137.0 (C(10)), 129.1 (C(11)), 128.8 (C(9)), 127.5 (C(8)), 100.9 (C(4)), 66.2 (C(1)), 64.2 (C(12)), 22.2 (C(3)), 20.8 (C(2)).

IR: (NaCl)

3401 (brs), 2930 (m), 2874 (m), 1658 (s), 1344 (s), 1294 (s), 1067 (s), 916 (m), 759 (m).

MS: (EI, 70 eV)

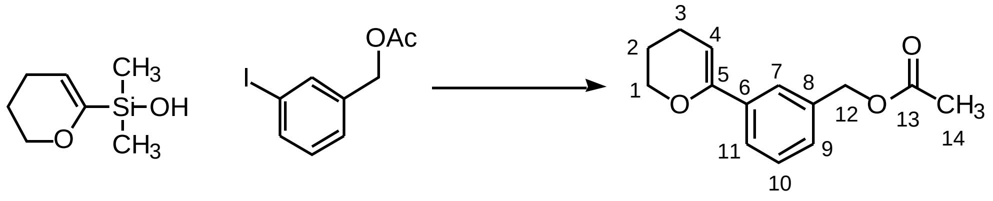
190 (M$^+$, 44), 161 (57), 133 (76), 117 (60), 105 (100), 77 (75).

TLC: R_f 0.24 (SiO$_2$, hexane/EtOAc, 7/1).

GC: t_R **2g**, 12.42 min (100%) (HP5, injector 190 °C, column 175 °C, 15 psi).

HRMS: calcd for $C_{12}H_{14}O_2$: 190.0993; found: 190.0994.

Reaction of 3-Iodobenzyl Acetate with Silanol 1 [II-luc77FK]. 3-[2-(5,6-Dihydro-4H-pyranyl)]benzyl Acetate (2h).



1 **2h**

Following the General Procedure, **1** (190 mg, 1.2 mmol, 1.2 equiv), was dissolved in a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv) and was stirred for 10 min at rt. 3-Iodobenzyl acetate (276 mg, 1.0 mmol) and $[allylPdCl]_2$ (9 mg, 0.025 equiv) were added. The suspension was stirred at rt for 10 min and then was filtered through a short plug of SiO_2. Purification of the residue by column chromatography (SiO_2, hexane/Et_2O, 15/1) and distillation afforded 201 mg (87%) of **2h** as a colorless oil.

Data for **2h**:

bp: 160 °C air bath (0.5 mmHg).

^{1}H NMR: (400 MHz, benzene-d_6)

7.77 (brs, HC(7), 1H); 7.60 (ddd, J = 1.7, 4.9 Hz, HC(10), 1 H); 7.11 (m, HC(9), HC(10), 2 H); 5.23 (t, J = 4.2 Hz, HC(4), 1 H); 4.98 (s, HC(12), 2H); 3.84 (dd, J = 4.8, 5.4 Hz, HC(1), 2 H); 1.87 (dt, J = 4.1, 6.5 Hz, HC(3), 2 H); 1.62 (s, HC(14), 3H); 1.47 (ddt, J = 5.0, 6.4 Hz, HC(2), 2 H).

^{13}C NMR: (100.6 MHz, benzene-d_6)

169.9 (C(13)), 151.9 (C(5)), 137.1 (C(6)), 136.6 (C(8)), 128.5 (C(10)), 128.0 (benzene + C(7)), 124.9 (C(11)), 124.5 (C(9)), 97.5 (C(4)), 66.3 (C(1)), 66.2 (C(12)), 22.5 (C(3)), 21.0 (C(2)), 20.4 (C(14)).

IR: (NaCl)

2932 (w), 2845 (w), 1739 (s), 1650 (m), 1462 (w), 1226 (s), 1082 (s), 922 (w), 722 (w).

MS: (EI, 70 eV)

232 (M^+, 26), 177 (100), 163 (20), 135 (48), 89 (68).

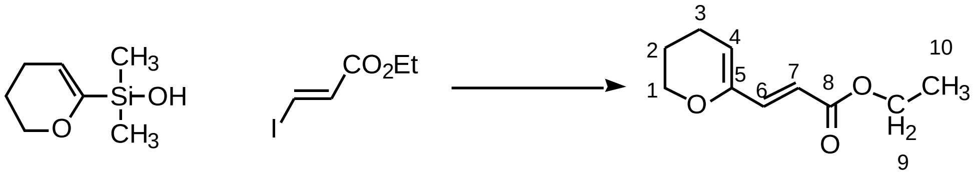
TLC: R_f 0.28 (SiO_2, hexane/Et_2O, 15/1).

GC: t_R **2h**, 15.99 min (100%) (U2, injector 200 °C, column 200 °C, 15 psi).

Analysis: $C_{14}H_{16}O_3$ (232.10)

Calculated:	C, 72.38;	H, 6.95%
Found:	C, 72.32;	H, 7.16%.

Reaction of Ethyl (*E*)-2-Iodopropenoate with Silanol 1 [III-luc11F]. Ethyl (*E*)-3-[2-(5,6-Dihydro-4H-pyranyl)]propenoate (3).



1 **3**

Following the General Procedure, **1** (190 mg, 1.2 mmol, 1.2 equiv), was dissolved in a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv) and was stirred for 10 min at rt. Ethyl (*E*)-2-iodopropenoate (226 mg, 1.0 mmol) and $[\text{allylPdCl}]_2$ (9 mg, 0.025 equiv) were added. The suspension was stirred at rt for 10 min and then was filtered through a short plug of SiO_2. Purification of the residue by column chromatography (Al_2O_3, hexane/Et_2O, 10/1) afforded 148 mg (81%) of **3** as a colorless oil.

Data for **3**:

^{1}H NMR: (500 MHz, benzene-d_6)

7.26 (d, J = 15.4 Hz, HC(6), 1 H); 6.59 (d, J = 15.4 Hz, HC(7), 1 H); 4.74 (t, J = 4.2 Hz, HC(4), 1 H); 4.04 (q, J = 7.1 Hz, HC(9), 2H); 3.58 (t, J = 4.9 Hz, HC(1), 2 H); 1.61 (dt, J = 5.1, 5.8 Hz, HC(3), 2 H); 1.24 (m, HC(2), 2H); 0.96 (t, J = 7.1 Hz, HC(10), 3 H).

^{13}C NMR: (125 MHz, benzene-d_6)

167.0 (C(8)), 150.6 (C(5)), 140.2 (C(6)), 117.3 (C(7)), 110.4 (C(4)), 68.5 (C(1)), 60.1 (C(9)), 21.8 (C(3)), 21.2 (C(2)), 14.2 (C(10)).

IR: (NaCl)

2979 (s), 2936 (s), 1719 (s), 1641 (s), 1466 (m), 1367 (m), 1267 (s), 1230 (s), 1061 (s), 973 (m), 776 (w).

MS: (EI, 70 eV)

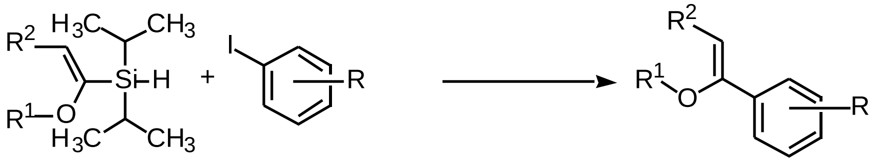
182 (M^+, 98), 153 (81), 137 (46), 127 (32), 109 (100), 99 (35), 81 (50).

TLC: R_f 0.22 (Al_2O_3, hexane/Et_2O, 10/1).

GC: t_R **3**, 5.78 min (>99%) (U2, injector 225 °C, column 225 °C, 15 psi).

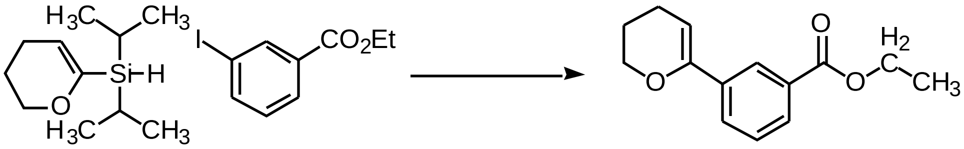
HRMS: calcd for $C_{10}H_{14}O_3$: 182.0942; found: 182.0945.

General Procedure for Coupling of Hydridosilanes.



To the hydridosilane (1.2 or 1.4 mmol) at 0 °C was added a solution of TBAF in THF (1.0 M, 2.0 mL or 2.8 mL, 2.0 or 2.8 equiv, (Fluka)) or a solution of tetrabutylammonium hydroxide (TBAOH) in MeOH (1.0 M, 3.0 mL, 3.0 equiv). The mixture was stirred 10 min at 0 °C and 10 min further at rt until no further gas evolution was observed. The aryl iodide (1.0 mmol, 1.0 equiv) was added to the mixture, followed by the palladium complex [allylPdCl]$_2$ (9 mg, 2.5 mol%). The mixture was stirred at rt for 10 min to 15 h and was then filtered through a short plug of silica gel or aluminum oxide (basic, activated, Brockmann I). The plug was washed with diethyl ether (50 mL) and the solvent was evaporated *in vacuo.* Purification of the residue by column chromatography affords the coupling product which was further purified by Kugelrohr distillation or crystallization.

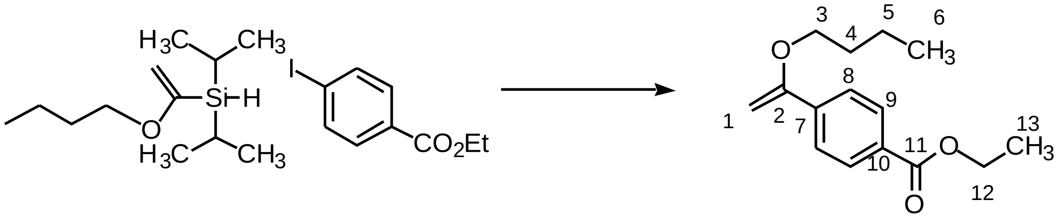
Reaction of Ethyl 3-Iodobenzoate with Silane 4 [II-luc84FK]. Ethyl 3-[2-(5,6-Dihydro-4H-pyranyl)]benzoate (2b).



4 **2b**

Following the General Procedure, **4** (238 mg, 1.2 mmol, 1.2 equiv), was dissolved in a solution of TBAF in THF (1.0 M, 2.0 mL, 2.0 mmol, 2.0 equiv) at 0 °C and was stirred for 10 min. The solution was allowed to warm to rt and was stirred for 10 min further. Ethyl 3-iodobenzoate (0.166 mL, 1.0 mmol) and [allylPdCl]$_2$ (9 mg, 0.025 equiv) were added. The suspension was stirred at rt for 10 min and then was filtered through a short plug of SiO$_2$. Purification of the residue by column chromatography (SiO$_2$, hexane/EtOAc, 20/1) and distillation afforded 200 mg (81%) of the previously described compound **2b**.

Reaction of Ethyl 4-Iodobenzoate with Silane 5 [III-luc10FK]. 4-(1-Butoxyethenyl)benzoate (7).



5 **7**

Following the General Procedure, **5** (300 mg, 1.4 mmol, 1.4 equiv), was dissolved in a solution of TBAF in THF (1.0 M, 2.8 mL, 2.8 mmol, 2.8 equiv) at 0 °C and was stirred for 10 min. The solution was allowed to warm to rt and was stirred for 10 min further. Ethyl 4-iodobenzoate (0.166 mL, 1.0 mmol) and $[allylPdCl]_2$ (9 mg, 0.025 equiv) were added. The suspension was stirred at rt for 10 min and then was filtered through a short plug of Al_2O_3. Purification of the residue by column chromatography (Al_2O_3, hexane/Et_2O, 30/1) and distillation afforded 221 mg (89%) of **7** as a colorless oil.

Data for 7:

bp: 150 °C air bath (0.5 mmHg).

^{1}H NMR: (500 MHz, benzene-d_6)

8.17 (d, J = 7.9 Hz, HC(7), 1 H); 7.70 (d, J = 7.9 Hz, HC(9), 1 H); 4.66 (d, J = 2.7 Hz, H_EC(1), 1 H); 4.13 (d, J = 2.7 Hz, H_ZC(1), 1 H); 4.12 (q, J = 7.3 Hz, HC(12)), 2H); 3.54 (t, J = 6.5 Hz, HC(3), 2 H); 1.52 (m, HC(4), 2H); 1.31 (m, HC(5), 2H); 1.01 (t, J = 7.3 Hz, HC(13), 3 H); 0.82 (t, J = 7.3 Hz, HC(6), 3 H).

^{13}C NMR: (125 MHz, benzene-d_6)

166.0 (C(11)), 159.4 (C(2)), 141.7 (C(7)), 130.9 (C(10)), 129.8 (C(8)), 125.5 (C(9)), 83.1 (C(1)), 67.6 (C(3)), 60.7 (C(12)), 31.4 (C(4)), 19.6 (C(5)), 14.2 (C(13)), 13.9 (C(6)).

IR: (NaCl)

2960 (s), 2935 (s), 1720 (s), 1610 (s), 1275 (s), 1128 (s), 1105 (s), 1021 (m), 778 (s).

MS: (EI, 70 eV)

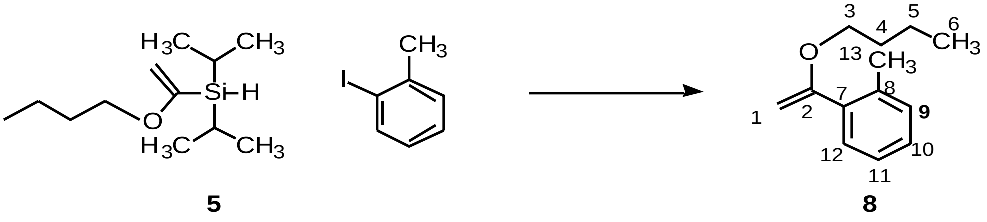
248 (M^+, 4), 233 (81), 203 (24), 193 (66), 177 (100), 164 (16), 147 (54).

TLC: R_f 0.31 (Al_2O_3, hexane/Et_2O, 20/1).

GC: t_R **7**, 12.60 min (100%) (HP5, injector 200 °C, column 200 °C, 15 psi).

HRMS: calcd for $C_{15}H_{20}O_3$; 248.1412; found: 248.1415.

Reaction of 2-Iodotoluene with Silane 5 [III-luc25FK]. 1-(1-Butoxyethenyl)-2-methylbenzene (8).



Following the General Procedure, **5** (300 mg, 1.4 mmol, 1.4 equiv), was dissolved in a solution of TBAF in THF (1.0 M, 2.8 mL, 2.8 mmol, 2.8 equiv) at 0 °C and was stirred for 10 min. The solution was allowed to warm to rt and was stirred for 10 min further. 2-Iodotoluene (0.127 mL, 1.0 mmol) and [allylPdCl]$_2$ (9 mg, 0.025 equiv) were added. The suspension was stirred at rt for 30 min and then was filtered through a short plug of Al_2O_3. Purification of the residue by column chromatography (Al_2O_3, hexane) and distillation afforded 158mg (83%) of **8** as a colorless oil.

Data for **8**:

bp: 110 °C air bath (0.3 mmHg).

^{1}H NMR: (400 MHz, benzene-d_6)

7.46 (dd, J = 1.9, 7.3 Hz, HC(12), 1 H); 7.08 (dt, J = 1.7, 7.1 Hz, HC(10), 1 H); 7.03 (m, HC(9)+HC(11), 2H), 6.62 (m, 1H, H11); 4.26 (d, J = 1.9 Hz, H_EC(1); 1 H); 4.25 (d, J = 1.9 Hz, H_ZC(1), 1 H); 3.58 (t, J = 6.4 Hz, HC(3)), 2H); 2.36 (s, HC(13), 3H), 1.51 (m, HC(4), 2H); 1.29 (m, HC(5), 2H); 0.79 (t, J = 7.3 Hz, HC(6), 3 H).

^{13}C NMR: (100 MHz, benzene-d_6)

163.1 (C(2)), 138.7 (C(7)), 136.4 (C(8)), 130.5 (C(10)), 129.5 (C(9)), 128.5 (C(12)), 125.7 (C(11)), 85.3 (C(1)), 67.4 (C(3)), 31.4 (C(4)), 20.2 (C(13)), 19.7 (C(5)), 13.9 (C(6)).

IR: (NaCl)

2960 (s), 2934 (s), 2873 (s), 1646 (s), 1601 (m), 1460 (m), 1307 (s), 1137 (m), 1098 (s), 941 (w), 806 (m), 766 (m).

MS: (EI, 70 eV)

190 (M$^+$, 6), 175 (26), 134 (16), 119 (100), 91 (25), 77 (5), 65 (9).

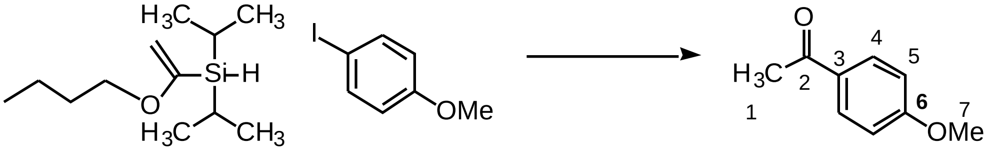
TLC: R_f 0.72 (Al_2O_3, hexane).

GC: t_R **8**, 8.22 min (>99%) (HP5, injector 175 °C, column 175 °C, 15 psi).

Analysis: $C_{13}H_{18}O$ (190.28)

Calculated:	C, 82.06;	H, 9.53%
Found:	C, 82.06;	H, 9.56%.

Reaction of 4-Iodoanisole with Silane 4 [III-luc21FK]. 4-Methoxyacetophenone (9).



5

9

Following the General Procedure, **5** (300 mg, 1.4 mmol, 1.4 equiv), was dissolved in a solution of TBAF in THF (1.0 M, 2.8 mL, 2.8 mmol, 2.8 equiv) at 0 °C and was stirred for 10 min. The solution was allowed to warm to rt and was stirred for 10 min further. 4-Iodoanisole (234 mg, 1.0 mmol) and $[allylPdCl]_2$ (9 mg, 0.025 equiv) were added. The suspension was stirred at rt for 10 min and then was filtered through a short plug of Al_2O_3. The residue was dissolved in 2.0 mL of Et_2O and was stirred with 2.0 mL of 1 M aqueous HCl for 5 min. The aqueous phase was extracted with Et_2O (3 × 5 mL) and the combined organic phases were washed with water (1 × 20 mL) and brine (1 × 20 mL). The organic layers were dried over anhydrous sodium sulfate and were filtered. The filtrate was then evaporated *in vacuo* to give a yellow solid which was purified by column chromatography (SiO_2, hexane/Et_2O, 8/1) and distillation to afford 142 mg, (94%) of **9** as a white solid. The data for **9** match those reported in the literature.[1]

Data for **9**:

mp: 35-37 °C.

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

7.93 (d, *J* = 9.0 Hz, HC(4), 2 H); 6.93 (d, *J* = 9.0 Hz, HC(5), 2 H); 3.87 (s, HC(7), 3H); 2.55 (s, HC(1), 3H).

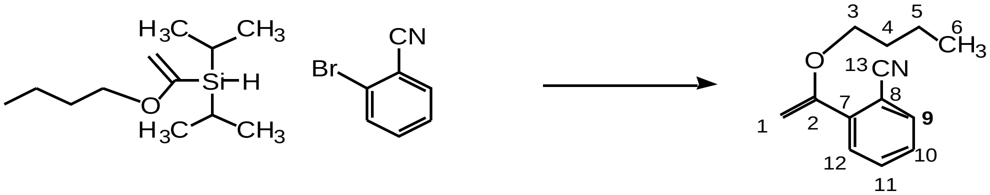
^{13}C NMR: (100.5 MHz, $CDCl_3$)

196.9 (C(2)), 163.7 (C(6)), 130.8 (C(4)), 130.6 (C(3)), 113.9 (C(5)), 55.6 (C(7)), 26.5 (C(1)).

TLC: R_f 0.24 (SiO_2, hexane/Et_2O, 8/1).

GC: t_R **9**, 6.99 min (100%) (U2, injector 200 °C, column 180 °C, 15 psi).

Reaction of 2-Bromobenzonitrile with Silane 5. 2-(1-Butoxyethynyl)benzonitrile (10).



5 **10**

Following the General Procedure, **5** (300 mg, 1.4 mmol, 1.4 equiv), was dissolved in a solution of TBAF in THF (1.0 M, 2.8 mL, 2.8 mmol, 2.8 equiv) at 0 °C and was stirred for 10 min. The solution was allowed to warm to rt and was stirred for 10 min further. 2-Bromobenzonitrile (182 mg, 1.0 mmol, 1.0 equiv) and [allylPdCl]$_2$ (9 mg, 0.025 equiv) were added. The suspension was stirred at rt for 15 h and then was filtered through a short plug of Al_2O_3. Purification of the residue by column chromatography (Al_2O_3, hexane/Et_2O, 15/1) and distillation afforded 149 mg (74%) of **10** as a colorless oil.

Data for **10**:

bp: 110 °C air bath (0.1 mmHg).

^{1}H NMR: (500 MHz, benzene-d_6)

7.29 (d, J = 7.9 Hz, HC(9), 1 H); 7.11 (d, J = 7.7 Hz, HC(12), 1 H); 6.85 (m, 1H, HC(10)), 6.62 (m, 1H, HC(11)); 4.57 (d, J = 3.0 Hz, H_EC(1); 1 H); 4.26 (d, J = 3.0 Hz, H_ZC(1), 1 H); 3.58 (t, J = 6.5 Hz, HC(3)), 2H); 1.64 (m, HC(4), 2H); 1.37 (m, HC(5), 2H); 0.83 (t, J = 7.3 Hz, HC(6), 3 H).

^{13}C NMR: (125 MHz, benzene-d_6)

158.8 (C(2)), 133.7 (C(11)), 131.8 (C(10)), 128.5 (C(9)), 128.4 (C(12)), 118.3 (C(13)), 111.5 (C(8)), 87.1 (C(1)), 68.3 (C(3)), 31.0 (C(4)), 19.6 (C(5)), 13.9 (C(6)).

IR: (NaCl)

2960 (s), 2937 (s), 2874 (m), 2227 (s), 1620 (s), 1466 (m), 1315 (s), 1262 (m), 1140 (s), 1090 (m), 942 (w), 818 (m), 769 (s).

MS: (EI, 70 eV)

201 (M^+, 9), 186 (53), 172 (16), 159 (23), 146 (84), 145 (100), 128 (35), 118 (31), 103 (23), 90 (19), 76 (19).

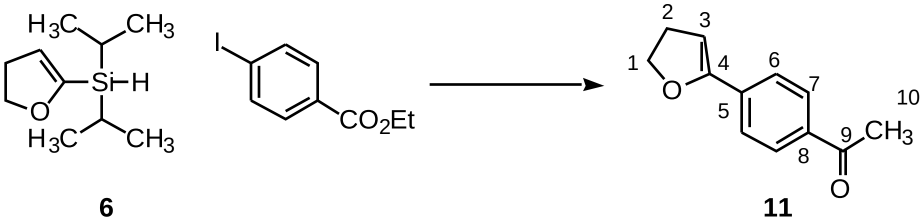
TLC: R_f 0.26 (Al_2O_3, hexane/Et_2O, 15/1).

GC: t_R **10**, 15.05 min (97%) (U2, injector 190 °C, column 190 °C, 15 psi).

Analysis: $C_{13}H_{15}ON$ (201.27)

Calculated:	C, 77.58;	H, 7.51;	N, 6.98%
Found:	C, 77.50;	H, 7.57;	N, 7.01%.

Reaction of 4-Iodoacetophenone with Silane 6 [III-luc14FX]. 1-[4-(4,5-Dihydrofuranyl)]ethanone (11).



6 **11**

Following the General Procedure, **6** (220 mg, 1.2 mmol, 1.2 equiv), was dissolved in a solution of TBAOH in MeOH (1.0 M, 3 mL, 3.0 mmol, 3.0 equiv) at 0 °C and was stirred for 10 min. The solution was allowed to warm to rt and was stirred for 10 min further. 4-Iodoacetophenone (246 mg, 1.0 mmol, 1.0 equiv) and $[allylPdCl]_2$ (9 mg, 0.025 equiv) were added. The suspension was stirred at rt for 10 min and then was filtered through a short plug of SiO_2. Purification of the residue by column chromatography (SiO_2, hexane/EtOAc, 8/1) and recrystallization from pentane afforded 133 mg (71%) of **11** as a white solid.

Data for **11**:

mp: 98-100 °C (pentane).

^{1}H NMR: (400 MHz, benzene-d_6)

7.77 (d, J = 8.3 Hz, HC(7), 2 H); 7.58 (d, J = 8.4 Hz, HC(6), 2 H); 5.16 (t, J = 2.7 Hz, HC(3), 1 H); 4.10 (t, J = 9.4 Hz, HC(1)), 2H); 2.32 (dt, J = 2.7, 9.4 Hz, HC(2), 2 H); 2.07 (s, HC(10), 3 H).

^{13}C NMR: (100 MHz, benzene-d_6)

195.9 (C(9)), 155.7 (C(4)), 137.0 (C(5)), 135.3 (C(8)), 128.6 (C(6)), 125.3 (C(7)), 98.0 (C(3)), 69.8 (C(1)), 30.9 (C(10)), 26.1 (C(2)).

IR: (NaCl, $CHCl_3$)

3021 (w), 2987 (w), 1681 (s), 1606 (m), 14310 (m), 1361 (m), 1271 (m), 1051 (m), 956 (w), 763 (m).

MS: (EI, 70 eV)

188 (M^+, 94), 173 (44), 147 (100), 115 (28), 104 (18), 77 (9).

TLC: R_f 0.23 (hexane/EtOAc, 8/1).

GC: t_R **11**, 13.41 min (100%) (U2, injector 200 °C, column 200 °C, 15 psi).

Analysis: $C_{12}H_{12}O_2$ (188.23)

Calculated:	C, 76.56;	H, 6.43%
Found:	C, 76.65;	H, 6.46%.

References

(1) (a) Buckingham, J. *Dictionary of Organic Compounds*, 5th ed.; Chapman Hall: New York, 1982; (b) Pouchet, C. J.; Behnke, J. *The Aldrich Library of ^{13}C and ^{1}H Ft NMR Spectra*, edition I, Aldrich Chem. Co., Inc.