SUPPORTING INFORMATION

Synthesis of Biaryls by Intramolecular Radical Aryl Migration from Silicon to Carbon

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General. TLC: *Merck* silica gel *60 F*$_{254}$ plates; detection with UV or dipping into a soln. of $KMnO_4$ (1.5 g in 333 mL 1M NaOH) or a soln. of $Ce(SO_4)_2 \cdot H_2O$ (10 g), phosphormolybdic acid hydrate (25 g), conc. H_2SO_4 (60 mL), and H_2O (940 mL), followed by heating. FC: *Fluka* silica gel *60* (40 - 63 μm); at *ca.* 0.3 bar. M.p.: *Büchi-510* apparatus; uncorrected. I.R. Spectra: *Perkin-Elmer-782* spectrophotometer (*s* = strong, *m* = medium, *w* = weak). NMR Spectra: *Bruker AMX 500* (^{1}H 500 MHz, ^{13}C 125 MHz), *AMX 400* (^{1}H 400 MHz, ^{13}C 100 MHz), *ARX 300* (^{1}H 300 MHz, ^{13}C 75 MHz), *Varian Gemini 300* (^{1}H 300 MHz, ^{13}C 75 MHz), or *Gemini 200* (^{1}H 200 MHz, ^{13}C 50 MHz); chemical shifts (δ) in ppm relative to $SiMe_4$ (= 0 ppm); Mass Spectra: *VG Tribrid* (EI) in *m/z* (% of basis peak). Elemental analyses were performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH-Zürich. Tetrahydrofuran (THF) and benzene (PhH) were freshly destilled from sodium/benzophenone.

General procedure (GP 1) for the silylation of secondary alcohols: The chlorosilane was dissolved under Ar in Et_2O, THF or CH_2Cl_2. The solution was cooled to 0 °C and NEt_3 was added. A solution of the alcohol in Et_2O, THF or CH_2Cl_2 was added over 3 min. DMAP was added and the suspension formed was allowed to warm to rt and stirred for 3-12 h. Addition of hexane or pentane and filtration of the solid gave after evaporation of the solvent the crude product which was purified either by distillation or flash chromatography.

General procedure (GP 2) for the silylation of secondary alcohols: The chlorosilane was dissolved under Ar in DMF. After addition of imidazole, the solution was cooled to 0 °C and a solution of the alcohol in DMF was added. The reaction mixture was allowed to warm to rt and stirred for 12 h. After addition of sat. NH_4Cl, the reaction mixture was extracted with Et_2O and the organic phase was washed with brine, dried ($MgSO_4$) and the solvent evaporated. The crude product was purified by flash chromatography.

1-(2-Bromophenyl)ethanol

Bromacetophenone (2.0 g, 10.1 mmol) was dissolved in ethanol (80 mL) and cooled to 0 °C. $NaBH_4$ (1.52 g, 40 mmol) was added in one portion. The suspension was stirred for 10 min at 0 °C, then allowed to warm to rt and stirred at that temp. for 12 h. After addition of sat. NH_4Cl, most of the ethanol was evaporated *in vacuo*. Et_2O was added to the remaining solution, which was subsequently washed with sat. NH_4Cl and brine. The organic phase was dried ($MgSO_4$) and evaporated. Purification by FC (Et_2O/pentane 1:5) afforded 1-(2-bromophenyl)ethanol: 2.0 g (9.95 mmol, 99%) as a colorless oil. The physical data are in agreement with the values reported in literature.[1]

[1-(2-Bromophenyl)ethoxy]diphenyl(trimethylsilyl)silane (1)

According to GP 1 with 1-(2-bromophenyl)ethanol (500 mg, 2.5 mmol), THF (10+2 mL), NEt_3 (0.38 mL, 2.75 mmol), diphenyl(trimethylsilyl)chlorosilane[2] (724 mg, 2.5 mmol) and DMAP (cat.). Purification by FC (pentane/Et_2O 200:1) afforded **1**: 1.037 g (92%). I.R. ($CHCl_3$): 3068*m*, 3007*w*, 2953*m*, 2894*m*, 1957*w*, 1887*w*, 1821*w*, 1588*m*, 1568*m*, 1484*w*, 1468*m*, 1440*m*, 1428*s*, 1370*s*, 1312*w*, 1264*m*, 1128*s*, 1088*s*, 1047*s*, 1022*s*, 998*w*, 952*s*, 856*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.76-7.73 (*m*, 1 aromat. H); 7.54-7.51 (*m*, 6 aromat. H); 7.43-7.29 (*m*, 11 aromat. H); 7.09-7.04 (*m*, 1 aromat. H); 5.23 (*q*, J = 6.2 Hz, 1 H, HCO); 1.38 (*d*, J = 6.2 Hz, 3 H, CH_3); 0.11 (*s*, 9 H, $Si(CH_3)_3$). ^{13}C-NMR (100 MHz, $CDCl_3$): 145.52 (C); 136.83 (C); 136.68 (C); 134.79 (CH); 134.59 (CH); 132.15 (CH); 129.52 (CH); 129.37 (CH); 128.28 (CH); 127.86 (CH); 127.79 (CH); 127.59 (CH); 127.54 (CH); 125.40 (CH); 120.83 (C); 71.32 (CH); 25.53 (CH_3); -1.40 (CH_3). EI-MS: 454.3 (<1, $[M]^+$), 383.1 (16), 381.1 (16), 287.2 (8), 272.2 (12), 271.2 (48), 200.1 (18), 199.1 (96), 193.1 (17), 88.0 (10), 86.0 (64), 84.0 (100), 51.0 (20), 49.0 (61), 47.0 (10), 18.0 (16). Anal. Calcd for $C_{23}H_{27}BrOSi_2$ (455.54): C 60.64, H 5.97; found: C 60.59, H 6.02.

([1-(2-Bromophenyl)ethoxy]diphenylsilyl)trimethylgermane (2)

According to GP 1 with 1-(2-bromophenyl)ethanol (323 mg, 1.6 mmol), THF (6+1 mL), NEt_3 (0.22 mL, 1.6 mmol), (chlorodiphenylsilyl)trimethylgermane[3] (489 mg, 1.5 mmol) and DMAP (cat.). Purification by FC (pentane/Et_2O 200:1) afforded **2**: 516 mg (71%). I.R. ($CHCl_3$): 3068*m*, 2974*m*, 2904*m*, 1957*w*, 1887*w*, 1821*w*, 1710*m*, 1568*w*, 1469*m*, 1428*s*, 1371*m*, 1094*s*, 1023*s*, 953*s*. ^{1}H-NMR (400 MHz, CDCl$_3$): 7.75-7.72 (*m*, 1 aromat. H); 7.57-7.53 (*m*, 2 aromat. H); 7.52-7.48 (*m*, 2 aromat. H); 7.47-7.28 (*m*, 8 aromat. H); 7.09-7.05 (*m*, 1 aromat. H); 5.25 (*q*, *J* = 6.2 Hz, 1 H, HCO); 1.41 (*d*, *J* = 6.2 Hz, 3 H, CH$_3$); 0.19 (*s*, 9 H, Ge(CH$_3$)$_3$). ^{13}C-NMR (100 MHz, CDCl$_3$): 145.23 (C); 136.39 (C); 136.35 (C); 134.61 (CH); 134.38 (CH); 132.18 (CH); 129.73 (CH); 129.55 (CH); 128.34 (CH); 127.94 (CH); 127.83 (CH); 127.62 (CH); 127.45 (CH); 120.83 (C); 71.52 (CH); 25.44 (CH$_3$); -1.85 (CH$_3$). EI-MS: 499.1 (<1, [M-H]$^+$), 485.0 (1), 383.0 (32), 381.0 (31), 287.1 (8), 200.1 (22), 199.1 (100), 137.0 (9). Anal. Calcd for $C_{23}H_{27}BrGeOSi$ (500.07): C 55.24, H 5.44; found: C 55.36, H 5.24.

([1-(2-Bromophenyl)ethoxy]diphenylsilyl)trimethylstannane (3)

According to GP 1 with 1-(2-bromophenyl)ethanol (300 mg, 1.5 mmol), THF (5+1 mL), NEt$_3$ (0.25 mL, 1.8 mmol), (chlorodiphenylsilyl)trimethylstannane[4] (683 mg, 1.8 mmol) and DMAP (cat.). Purification by FC (pentane/Et$_2$O 150:1) afforded **3**: 495 mg (60%). I.R. (CHCl$_3$): 3068*m*, 2977*m*, 2910*m*, 1468*m*, 1428*s*, 1371*m*, 1266*w*, 1088*s*, 1022*s*, 953*s*. ^{1}H-NMR (400 MHz, CDCl$_3$): 7.72-7.70 (*m*, 1 aromat. H); 7.58-7.53 (*m*, 2 aromat. H); 7.51-7.29 (*m*, 10 aromat. H); 7.11-7.06 (*m*, 1 aromat. H); 5.24 (*q*, *J* = 6.3 Hz, 1 H, HCO); 1.44 (*d*, *J* = 6.3 Hz, 3 H, CH$_3$); 0.06 (*s*, 9 H, Sn(CH$_3$)$_3$). ^{13}C-NMR (100 MHz, CDCl$_3$): 144.90 (C); 137.44 (C); 134.41 (CH); 134.12 (CH); 132.32 (CH); 129.84 (CH); 129.60 (CH); 128.47 (CH); 128.10 (CH); 127.95 (CH); 127.72 (CH); 127.43 (CH); 121.01 (C); 72.16 (CH); 25.35 (CH$_3$); -10.53 (CH$_3$). EI-MS: 545.1 (2, [M-H]$^+$), 531.0 (2), 383.0 (42), 381.0 (41), 317.1 (7), 287.1 (8), 199.1 (100). Anal. Calcd for $C_{23}H_{27}BrOSiSn$ (546.17): C 50.58, H 4.98; found: C 50.60, H 4.91.

([1-(2-Bromophenyl)ethoxy]*tert*-butyldiphenylsilane (4)

According to GP 1 with 1-(2-bromophenyl)ethanol (583 mg, 2.9 mmol), THF (10+2 mL), NEt$_3$ (0.40 mL, 2.9 mmol), *tert*-butyldiphenylchlorosilane (0.67 mL, 2.6 mmol) and DMAP (cat.). Purification by FC (pentane/Et$_2$O 300:1) afforded **4**: 849 mg (74%). I.R. (CHCl$_3$): 3071*m*, 2930*s*, 2858*s*, 1959*w*, 1892*w*, 1825*w*, 1589*w*, 1471*s*, 1428*s*, 1371*m*, 1266*w*, 1106*s*, 1022*s*, 955*s*. ^{1}H-NMR (400 MHz, CDCl$_3$): 7.80-7.77 (*m*, 1 aromat. H); 7.74-7.69 (*m*, 2 aromat. H); 7.52-7.48 (*m*, 2 aromat. H); 7.45-7.31 (*m*, 6 aromat. H); 7.28-7.24 (*m*, 2 aromat. H); 7.08-7.03 (*m*, 1 aromat. H); 5.19 (*q*, *J* = 6.2 Hz, 1 H, HCO); 1.31 (*d*, *J* = 6.2 Hz, 3 H, CH$_3$); 1.06 (*s*, 9 H, *t*-Bu). ^{13}C-NMR (100 MHz, CDCl$_3$): 145.52 (C); 135.75 (CH); 135.71 (CH); 134.17 (C); 133.40 (C); 132.09 (CH); 129.61 (CH); 129.51 (CH); 128.14 (CH); 127.55 (CH); 127.54 (CH); 127.53 (CH); 127.46 (CH); 120.78 (C); 70.78 (CH); 26.96 (CH$_3$); 25.34 (CH$_3$); 19.27 (C). EI-MS: 423.1 (<1, [M-CH$_3$]$^+$), 383.0 (31), 381.0 (29), 287.1 (4), 199.0 (100). Anal. Calcd for $C_{24}H_{27}BrOSi$ (439.47): C 65.59, H 6.19; found: C 65.78, H 6.13.

[1-(2-Bromophenyl)-ethoxy]diphenylmethylsilane (5)

According to GP 1 with 1-(2-bromophenyl)ethanol (363 mg, 1.8 mmol), THF (6+2 mL), NEt_3 (0.25 mL, 1.8 mmol), diphenylmethylchlorosilane (0.34 mL, 1.6 mmol) and DMAP (cat.). Purification by FC (pentane/Et_2O 100:1) afforded **5**: 546 mg (84%). I.R. ($CHCl_3$): 3070*m*, 3008*m*, 1958*w*, 1889*w*, 1823*w*, 1590*w*, 1568*w*, 1469*m*, 1428*s*, 1371*m*, 1090*s*, 1022*s*, 957*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.72 (*dxd*, J_1 = 7.8 Hz J_2 = 1.8 Hz, 1 aromat. H,); 7.58-7.50 (*m*, 4 aromat. H); 7.43-7.29 (*m*, 8 aromat. H); 7.10-7.05 (*m*, 1 aromat. H); 5.27 (*q*, *J* = 6.3 Hz, 1 H, HCO); 1.42 (*d*, *J* = 6.3 Hz, 3 H, CH_3); 0.56 (*s*, 3 H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): 145.24 (C); 136.15 (C); 136.09 (C); 134.36 (CH); 134.27 (CH); 132.20 (CH); 129.82 (CH); 129.76 (CH); 128.34 (CH); 127.83 (CH); 127.79 (CH); 127.63 (CH); 127.58 (CH); 120.86 (C); 70.49 (CH); 25.38 (CH_3); -2.67 (CH_3). EI-MS: 396.1 (<1, $[M]^+$), 383.0 (47), 381.0 (45), 199.1 (100), 197.1 (7), 181.1 (9), 165.1 (9), 137.1 (18). Anal. Calcd for $C_{21}H_{21}BrOSi$ (397.39): C 63.47, H 5.33; found: C 63.68, H 5.36.

[1-(2-Bromophenyl)-ethoxy]triphenylsilane (6)

According to GP 2 with 1-(2-bromophenyl)ethanol (300 mg, 1.5 mmol), DMF (2+1 mL), imidazole (152 mg, 2.24 mmol) and triphenylchlorosilane (440 mg, 1.5 mmol). Purification by FC (pentane/Et_2O 100:1) afforded **6**: 251 mg (37%). M.p. 66-68 °C. I.R. ($CHCl_3$): 3070*m*, 3008*m*, 1959*w*, 1892*w*, 1826*w*, 1590*w*, 1568*w*, 1484*w*, 1469*m*, 1429*s*, 1372*m*, 1117*s*, 1090*s*, 1048*m*, 1022*m*, 998*w*, 958*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.78-7.77 (*m*, 1 aromat. H); 7.60-7.57 (*m*, 6 aromat. H); 7.48-7.23 (*m*, 11 aromat. H); 7.05-7.01 (*m*, 1 aromat. H); 5.37 (*q*, *J* = 6.2 Hz, 1 H, HCO); 1.40 (*d*, *J* = 6.2 Hz, 3 H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): 145.04 (C); 135.46 (C); 135.39 (CH); 135.19 (CH); 134.23 (C); 132.10 (CH); 129.97 (CH); 129.79 (CH); 128.25 (CH); 127.80 (CH); 127.76 (C); 127.69 (CH); 127.58 (CH); 120.82 (C); 70.99 (CH); 25.35 (CH_3). EI-MS: 458.3 (2, $[M]^+$), 457.3 (5), 446.2 (7), 445.2 (23), 444.2 (7), 443.2 (22), 383.1 (11), 382.1 (16), 381.1 (15), 380.1 (17), 379.2 (11), 260.2 (26), 259.2 (100), 203.0 (8), 201.0 (12), 200.1 (15), 199.1 (76), 197.1 (10), 181.1 (19), 180.2 (11). Anal. Calcd for $C_{26}H_{23}BrOSi$ (459.46): C 67.97, H 5.05; found: C 68.17, H 5.24.

(2-Bromobenzyloxy)triphenylsilane (7)

2-Bromobenzylalcohol (500 mg, 2.7 mmol) was dissolved in pyridine (1.5 mL) and toluene (1.5 mL) at rt. Then triphenylchlorosilane (749 mg, 2.57 mmol) was added and stirring was continued for 14 h at rt. After addition of Et_2O, the reaction mixture was washed with sat. NH_4Cl and brine, dried ($MgSO_4$), and the solvent evaporated. Purification by FC (pentane/Et_2O 100:1) afforded **7**: 764 mg (64%). I.R. ($CHCl_3$): 3071*m*, 3008*m*, 1959*w*, 1908*w*, 1826*w*, 1590*w*, 1570*w*, 1468*w*, 1429*s*, 1378*m*, 1118*s*, 1092*s*, 1043*m*, 1026*m*, 998*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.72-7.65 (*m*, 7 aromat. H); 7.49-7.23 (*m*, 11 aromat. H); 7.13-7.09 (*m*, 1 aromat. H); 4.92 (*s*, 2 H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): 139.57 (C); 135.41 (CH); 135.19 (C); 133.73 (CH); 132.09 (CH); 130.22 (CH); 129.79 (CH); 128.35 (CH); 127.99 (CH); 127.90 (CH); 127.70 (CH); 127.37 (CH); 121.25 (C); 65.25 (CH_2). EI-MS: 444.1 (<1, $[M]^+$), 369.0 (54), 368.0 (44), 367.0 (61), 366.1 (32), 289.0 (24), 288.1 (27), 287.1 (47), 261.0 (10), 259.1 (53), 257.1 (37), 211.1 (45), 202.9 (99), 200.9 (100), 199.1 (39), 183.1 (57), 181.0 (38), 170.9 (52), 168.9 (55), 167.1 (45), 166.1 (99), 165.1 (55).

General Procedure (GP 3) for the aryl migration reaction: The silyl ether was dissolved in benzene under argon and heated to reflux. Slow addition of a solution of Bu_3SnH and AIBN in benzene over 7 h (syringe pump). After complete addition of the tin hydride solution, stirring was continued at that temperature for 30 min. The solution was then allowed to cool to rt and MeLi was added. After stirring for 12 h at rt, H_2O and Et_2O were slowly added. The reaction mixture was washed with sat. aq. NH_4Cl and brine. The organic phase was dried ($MgSO_4$) and evaporated to yield the crude product.

2-(1-Hydroxyethyl)diphenyl (8)

from **1**: According to GP 3 with silylether **1** (145 mg, 0.32 mmol), benzene (7 mL), Bu_3SnH (0.10 mL, 0.34 mmol), AIBN (7 mg, 0.03 mmol) in benzene (0.5 mL) and MeLi (1 mL, 0.65 mmol). Purification by FC (Et_2O/pentane 1:6) afforded a mixture of **8**: 35 mg (55%) and [2-(1-hydroxyethyl)phenyl]diphenylmethylsilane **10:** 27 mg (28%). The ratio was determined by ^{1}H-NMR-spectroscopy of the crude product. The physical data of **8** are in agreement with literature data[5]. [2-(1-hydroxyethyl)phenyl]diphenylmethylsilane **10**: I.R. ($CHCl_3$): 3602*w*, 3069*w*, 3008*m*, 2978*w*, 2928*w*, 1589*w*, 1487*w*, 1428*s*, 1379*m*, 1108*s*, 1069*m*, 1039*w*, 998*m*, 895*m*, 613*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.63-7.21 (*m*, 14 arom. H); 4.92 (*q*, J = 6.3 Hz, 1 H, HCO); 1.18 (*d*, J = 6.3 Hz, 3 H, CH_3); 0.89 (*s*, $SiCH_3$). ^{13}C-NMR (100 MHz, $CDCl_3$): 153.57 (C); 138.16 (C); 137.95 (CH); 137.93 (C); 136.49 (CH); 136.36 (CH); 134.34 (C); 132.06 (CH); 130.92 (CH); 129.49 (CH); 128.49 (CH); 127.21 (CH); 71.14 (CH); 25.60 (CH_3). EI-MS: 318.1 (<1, $[M]^+$), 239.1 (11), 226.1 (20), 225.1 (100), 207.1 (10). Anal. Calcd for: $C_{21}H_{22}OSi$ (318.49): C 79.20, H 6.96; found: C 79.12, H 7.07.

from **2**: According to GP 3 with silylether **2** (177 mg, 0.30 mmol), benzene (6 mL), Bu_3SnH (82 µL, 0.31 mmol), AIBN (15 mg, 0.09 mmol) in benzene (0.5 mL) and MeLi (2.9 mL, 4.4 mmol). Purification by FC (Et_2O/pentane 1:5) afforded a mixture of **8**: 30 mg (52%) and **10**: 37 mg (39%). The product ratio was determined by ^{1}H-NMR-spectroscopy.

from **3**: According to GP 3 with silylether **3** (161 mg, 0.30 mmol), benzene (6 mL), Bu_3SnH (82 μL, 0.31 mmol), AIBN (15 mg, 0.09 mmol) in benzene (0.5 mL) and MeLi (2.9 mL, 4.4 mmol). Purification by FC (Et_2O/pentane 1:6) afforded **10**: 79 mg (84%).

from **4**: According to GP 3 with silylether **4** (175 mg, 0.40 mmol), benzene (8 mL), Bu_3SnH (111 μL, 0.42 mmol), AIBN (20 mg, 0.12 mmol) in benzene (0.5 mL) and MeLi (3.9 mL, 6.0 mmol). Purification by FC (Et_2O/pentane 1:6) afforded **8**: 44 mg (56%).

from **5**: According to GP 3 with silylether **5** (131 mg, 0.33 mmol), benzene (7 mL), Bu_3SnH (92 μL, 0.35 mmol), AIBN (16 mg, 0.10 mmol) in benzene (0.5 mL) and MeLi (3.2 mL, 4.9 mmol). Purification by FC (Et_2O/pentane 1:5) afforded **8**: 34 mg (52%). An unidentified side product (4%) could not be separated from **8**..

from **6**: According to GP 3 with silylether **6** (150 mg, 0.33 mmol), benzene (7 mL), Bu_3SnH (92 μL, 0.35 mmol), AIBN (7 mg, 0.04 mmol) in benzene (0.5 mL) and MeLi (1 mL, 0.65 mmol). Purification by FC (Et_2O/pentane 1:6) afforded **8**: 46 mg (71%).

2-Hydroxymethyldiphenyl (9)

According to GP 3 with silylether **7** (150 mg, 0.33 mmol), benzene (7 mL), Bu_3SnH (96 μL, 0.36 mmol), AIBN (7 mg, 0.04 mmol) in benzene (0.5 mL) and MeLi (1 mL, 0.65 mmol). Purification by FC (Et_2O/pentane 1:6) afforded a mixture of **9**: 32 mg (52%) and benzyl alcohol: 6 mg (17%), which was removed by drying at 0.05 mbar for 12 h. The physical data of **9** are in agreement with the values reported in literature.[6]

General Procedure 4 (GP 4) for the preparation of the chlorodisilanes: The dichlorodiarylsilane was dissolved under Ar in THF and cooled to 0 °C. NEt_3 (1.2 equiv) and $HNEt_2$ (1 equiv) were added according to a literature procedure.[7] After stirring for 4 h at 0 °C, hexane was added and the suspension was filtered and distilled to afford the corresponding diethylaminochlorosilane. The diethylaminochlorosilane was then reacted with lithium dimethylphenylsilanide according to ref. 8 to afford the diethylaminodisilane. The aminodisilane was then converted to the chlorodisilane in CH_2Cl_2 with acetyl chloride at 0 °C according to ref. 4.

1-Chloro-2,2-dimethyl-1,1-di(4-fluoro-phenyl)-2-phenyl-disilane

According to GP 4 with di(4-fluoro-phenyl)dichlorosilane (18.8 g, 65 mmol), NEt_3 (10.4 mL, 75 mmol) and $HNEt_2$ (6.75 mL, 65 mmol) in THF (48 mL). Distillation (0.01 Torr, 80-95 °C) afforded (chlorodi(4-fluoro-phenyl)silanyl)diethyl amide (17.9 g, 84%). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.79-7.68 (*m*, 4 aromat. H); 7.22-7.06 (*m*, 4 aromat. H); 2.93 (*q*, J = 7.1 Hz, 4H, CH_2); 1.06 (*t*, J = 7.1 Hz, 6H, CH_3). Dimethylphenylchlorosilane (2.9 mL, 17.5 mmol) and

Li-wire (0.43 g, 62 mmol) were reacted in THF (35 mL) at 0 °C according to ref. 2. The Li-silanide solution thus formed was slowly added to a solution of (chlorodi(4-fluoro-phenyl)silanyl)diethyl amide (5.70 g, 17.5 mmol) in THF (13 mL) at 0 °C. After stirring for 1 h at 0 °C, hexane (90 mL) was added and the salts were filtered off under Ar. Distillation (0.02 Torr, 115-135 °C afforded di(4-fluoro-phenyl)-(*N*,*N*-diethylamino)-(dimethylphenylsilyl)silane (3.20 g, 43%). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.48-7.02 (*m*, 13 aromat. H); 2.95 (*q*, J = 13.6 Hz, 4H, CH_2); 0.93 (*t*, J = 13.6 Hz, 6H, CH_3); 0.43 (*s*, 6H, CH_3). Di(4-fluoro-phenyl)-(*N*,*N*-diethylamino)-(dimethylphenylsilyl)silane (3.20 g, 7.5 mmol) was dissolved in CH_2Cl_2 (7 mL) at 0 °C and acetyl chloride (0.54 mL, 7.5 mmol) was added. After 2 h, the solvent was removed and the residue distilled (0.02 Torr, 100-120 °C) to afford 1-chloro-2,2-dimethyl-1,1-di(4-fluoro-phenyl)-2-phenyl-disilane: 2.39 g (82%) in about 90% purity. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.47-7.02 (*m*, 13 aromat. H); 0.53 (*s*, 6H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 164.70 (*d*, $J_{C\text{-}F}$ = 251.4 Hz); 136.87 (*d*, $J_{C\text{-}F}$ = 7.3 Hz); 134.49 (CH); 129.72 (CH); 128.31 (CH); 116.23 (C); 115.72 (*d*, $J_{C\text{-}F}$ = 19.54 Hz, CH); -4.04 (CH_3).

1-Chloro-2,2-dimethyl-1,1-di(2-thienyl)-2-phenyl-disilane

According to GP 4 with di(2-thienyl)dichlorosilane (10.4 g, 39 mmol), NEt_3 (6.32 mL, 45 mmol) and $HNEt_2$ (4.1 mL, 39 mmol) in THF (25 mL). Distillation (0.04 Torr, 95-100 °C) afforded (chlorodi(2-thienyl)silanyl)diethyl amide (9.92 g, 76%) in about 90% purity. Dimethylphenylchlorosilane (7.4 mL, 44.4 mmol) and Li-wire (1.07 g, 155 mmol) were reacted in THF (80 mL) at 0 °C according to ref. 2. The Li-silanide solution formed was slowly added to a solution of (chlorodi(2-thienyl)silanyl)diethyl amide (9.92 g, 30 mmol) in THF (30 mL) at 0 °C. After stirring for 2 h at 0 °C and removal of 80% of the solvent, pentane (90 mL) was added and the salts were filtered off under Ar. Distillation (0.04 Torr, 130-140 °C afforded di(2-thienyl)-(*N*,*N*-diethylamino)-(dimethylphenylsilyl)silane (7.08 g, 60%) with 95% purity. Di(2-thienyl)-(*N*,*N*-diethylamino)-(dimethylphenylsilyl)silane (7.08 g, 18 mmol) was dissolved in CH_2Cl_2 (15 mL) at 0 °C and acetyl chloride (1.25 mL, 18 mmol) was added. After 2 h, the solvent was removed and the residue distilled (0.04 Torr, 120-130 °C) to afford 1-chloro-2,2-dimethyl-1,1-di(2-thienyl)-2-phenyl-disilane: 2.91 g (34%) in about 75% purity. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.72-7.19 (*m*, 11 aromat. H); 0.58 (*s*, 6H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$) 137.37; 134.42; 133.52; 133.21; 129.52; 128.52; 128.02; -4.21.

General Procedure 5 (GP 5) for the preparation of the chlorosilanes:[9] The dichlorodiarylsilane was dissolved under Ar in pentane or Et_2O. After addition of *tert*-butyllithium (1.6 M in pentane) or methyllithium (1.55 M in hexane), the reaction mixture was refluxed for 14 h. The suspension was filtered under Ar and the filtrate distilled to afford the corresponding alkyldiarylchlorosilane.

tert-Butyl-di(4-fluoro-phenyl)chlorosilane

According to GP 5 with di(4-fluoro-phenyl)dichlorosilane (6.98 g, 24 mmol), *t*-BuLi (18 mL, 29 mmol) in pentane (5 mL). *Bulb-to-bulb* distillation (0.04 Torr, 120-130 °C) afforded *tert*-butyl-di(4-fluoro-phenyl)chlorosilane (2.91 g, 39%). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.75-7.70 (*m*, 4 aromat. H); 7.15-7.09 (*m*, 4 aromat. H); 1.13 (*s*, 9H, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): 164.74 (*d*, $J_{C\text{-}F}$ = 251.5 Hz, C); 137.59 (*d*, $J_{C\text{-}F}$ = 8.5 Hz, CH); 128.89 (C); 115.53 (*d*, $J_{C\text{-}F}$ = 19.5 Hz, CH); 26.42 (CH_3); 20.71 (C).

tert-Butyl-di(2-thienyl)chlorosilane

According to GP 5 with di(2-thienyl)dichlorosilane (9.08 g, 34 mmol), *t*-BuLi (26 mL, 41 mmol) in pentane (7 mL). The reaction afforded a 1:1 mixture of *tert*-butyl-di(2-thienyl)chlorosilane (1.23 g, 13%) and di(2-thienyl)dichlorosilane (1.13 g), which could not be separated by distillation. ^{1}H-NMR (300 MHz, $CDCl_3$) 7.75-7.73 (*m*, 2 aromat. H); 7.57-7.56 (*m*, 2 aromat. H); 7.29-7.24 (*m*, 2 aromat. H); 1.16 (*s*, 9H, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$) 138.86 (CH); 134.78 (C); 132.99 (CH); 128.67 (CH); 25.65 (CH_3).

Di(4-methoxyphenyl)methylchlorosilane

According to GP 5 with di(4-methoxyphenyl)dichlorosilane (3.59 g, 11.4 mmol), MeLi (8.1 mL, 12.6 mmol) in Et_2O (15 mL) with refluxing for 1 hour.[10] *Bulb-to-bulb* distillation (0.05 Torr, 120-130 °C) afforded a 1:1 mixture of di(4-methoxy-phenyl)methylchlorosilane (1.38 g, 41%) and di(4-methoxy-phenyl)dimethylsilane (1.28 g, 41%) which could not be separated by distillation. ^{1}H-NMR (300 MHz, $CDCl_3$) 7.60-7.56 (*m*, 4 aromat. H); 6.99-6.91 (*m*, 4H, aromat. H); 3.82 (*s*, 3 H, OMe); 0.52 (*s*, 3 H, SiMe). ^{13}C-NMR (75 MHz, $CDCl_3$) 161.83 (C); 136.03 (CH); 126.09 (C); 114.07 (CH); 55.14 (CH_3); 1.31 (CH_3).

[1-(2-Bromophenyl)ethoxy]di(4-fluoro-phenyl)(dimethylphenylsilyl)silane (15):

According to GP 1 with 1-(2-bromophenyl)ethanol (281 mg, 1.4 mmol), THF (5+1 mL), NEt_3 (0.20 mL, 1.4 mmol), 1-chloro-2,2-dimethyl-1,1-di(4-fluoro-phenyl)-2-phenyl-disilane (494 mg, 1.3 mmol) and DMAP (cat.). Purification by FC (pentane/Et_2O 150:1) afforded **15**: 604 mg (86 %). Because of decompostition during FC, minor amounts of 1-(2-bromophenyl)ethanol (10 %) could not be removed. I.R. ($CHCl_3$): 3068*m*, 2975*m*, 1901*w*, 1587*s*, 1488*s*, 1469*m*, 1440*m*, 1371*m*, 1161*s*, 1100*s*, 1023*s*, 954*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.61-7.58 (*m*, 1 aromat. H); 7.41-7.22 (*m*, 11 aromat. H); 7.08-6.95 (*m*, 5 aromat. H); 5.16 (*q, J* = 6.2 Hz, 1 H, HCO); 1.30 (*d*, *J* = 6.2 Hz, 3 H, CH_3); 0.41 (*s*, 3 H, CH_3); 0.37 (*s*, 3 H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): 164.05 (*d*, $J_{C\text{-}F}$ = 249.5 Hz, C); 164.03 (*d*, $J_{C\text{-}F}$ = 249.0 Hz, C); 145.05 (C); 137.50 (C); 136.87 (*d*, $J_{C\text{-}F}$ = 7.6 Hz, CH); 136.74 (*d*, $J_{C\text{-}}$

$_F$ = 7.6 Hz, CH); 134.21 (CH); 132.17 (CH); 131.65 (*d*, $J_{C\text{-}F}$ = 3.7 Hz, C); 131.41 (*d*, $J_{C\text{-}F}$ = 3.8 Hz, C); 128.85 (CH); 128.37 (CH); 127.81 (CH); 127.58 (CH); 127.43 (CH); 120.79 (C); 115.12 (*d*, $J_{C\text{-}F}$ = 19.8 Hz, CH); 115.07 (*d*, $J_{C\text{-}F}$ = 19.7 Hz, CH); 71.42 (CH); 25.43 (CH_3); -3.12 (CH_3); -3.15 (CH_3). EI-MS: 419.0 (13, $[M\text{-}SiMe_2Ph]^+$), 369.1 (15), 323.1 (12), 273.1 (18), 235.0 (100), 85.9 (13), 83.9 (18).

[1-(2-Bromophenyl)ethoxy]di(2-thienyl)(dimethylphenylsilyl)silane (16):

According to GP 1 with 1-(2-bromophenyl)ethanol (305 mg, 1.5 mmol), THF (6+1 mL), NEt_3 (0.21 mL, 1.5 mmol), 1-chloro-2,2-dimethyl-1,1-di(2-thienyl)-2-phenyl-disilane (504 mg, 1.4 mmol) and DMAP (cat.). Purification by FC (pentane/Et_2O 200:1) afforded **16**: 623 mg (85 %). An unidentified side product could not be removed by FC. I.R. ($CHCl_3$): 3070*w*, 3008*w*, 1568*w*, 1469*w*, 1427*w*, 1403*m*, 1371*w*, 1325*w*, 1088*s*, 1022*m*, 954*m*, 838*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.70-7.63 (*m*, 3 aromat. H); 7.43-7.40 (*m*, 3 aromat. H); 7.35-7.24 (*m*, 7 aromat. H); 7.22-7.13 (*m*, 1 aromat. H); 7.12-7.04 (*m*, 1 aromat. H); 5.28 (*q*, *J* = 6.2 Hz, 1 H, HCO); 1.35 (*d*, *J* = 6.2 Hz, 3 H, CH_3); 0.48 (*s*, 3 H, CH_3); 0.45 (*s*, 3 H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): 145.09 (C); 136.82 (CH); 136.69 (CH); 135.38 (C); 134.90 (C); 134.39 (CH); 132.28 (CH); 132.21 (CH); 132.10 (CH); 128.93 (CH); 128.26 (CH); 128.20 (CH); 127.78 (CH); 127.73 (CH); 127.68 (C); 127.57 (CH); 127.52 (CH); 120.79 (C); 71.56 (CH); 25.38 (CH_3); -3.48 (CH_3). EI-MS: 530.1 (<1, $[M^+]$), 395.0 (12), 393.0 (11), 345.1 (97), 299.1 (13), 267.0 (17), 261.1 (65), 211.0 (100), 185.0 (18).

[1-(2-Bromophenyl)ethoxy]*tert*-butyldi(4-fluoro-phenyl)silane (17):

According to GP 2 with 1-(2-bromophenyl)ethanol (751 mg, 3.7 mmol), DMF (2+1 mL), imidazole (254 mg, 3.7 mmol) and *tert*-butyldi(4-fluoro-phenyl)chlorosilane (581 mg, 1.87 mmol). Purification by FC (pentane/Et_2O 400:1) afforded **17**: 583 mg (66%). I.R. ($CHCl_3$): 3066*w*, 2960*s*, 2931*s*, 2860*s*, 1905*w*, 1588*s*, 1499*s*, 1470*s*, 1371*m*, 1163*s*, 1103*s*, 1048*m*, 1022*m*, 956*m*, 647*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.72 (*dxd*, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1 aromat. H); 7.67-7.62 (*m*, 2 aromat. H); 7.47-7.42 (*m*, 2 aromat. H); 7.37 (*dxd*, J_1 = 8.0 Hz, J_2 = 1.1 Hz, 1 aromat. H); 7.34-7.29 (*m*, 1 aromat. H); 7.11-7.04 (*m*, 3 aromat. H); 6.99-6.93 (*m*, 2 aromat. H); 5.15 (*q*, *J* = 6.2 Hz, 1 H, HCO); 1.32 (*d*, *J* = 6.2 Hz, 3 H, CH_3); 1.05 (*s*, 9 H, *t*-Bu). ^{13}C-NMR (100 MHz, $CDCl_3$): 164.11 (*d*, $J_{C\text{-}F}$ = 249.6 Hz, C); 164.00 (*d*, $J_{C\text{-}F}$ = 249.6 Hz, C); 145.15 (C); 137.69 (*d*, $J_{C\text{-}F}$ = 7.5 Hz, CH); 137.65 (*d*, $J_{C\text{-}F}$ = 7.5 Hz, CH); 132.16 (CH); 129.41 (*d*, $J_{C\text{-}F}$ = 3.8 Hz, C); 128.81 (*d*, $J_{C\text{-}F}$ = 3.8 Hz, C); 128.31 (CH); 127.58 (CH); 127.48 (CH); 120.82 (C); 114.92 (*d*, $J_{C\text{-}F}$ = 19.6 Hz, CH); 114.80 (*d*, $J_{C\text{-}F}$ = 19.6 Hz, CH); 70.85 (CH); 26.85 (CH_3); 25.31 (CH_3); 19.19 (C). EI-MS: 459.1 (<1, $[M\text{-}CH_3]^+$), 419.0 (46), 417.0 (45), 323.1 (6), 313.0 (5), 235.0 (100), 183.0 (5), 104.0 (5). Anal. Calcd for: $C_{24}H_{25}BrF_2OSi$ (475.45): C 60.63, H 5.30; found: C 60.63, H 5.34.

[1-(2-Bromophenyl)ethoxy]*tert*-butyldi(2-thienyl)silane (18):

According to GP 2 with 1-(2-bromophenyl)ethanol (1.4 g, 7.0 mmol), DMF (2+1 mL), imidazole (500 mg, 7.0 mmol) and *tert*-butyldi(2-thienyl)chlorosilane (545 mg, 1.90 mmol). Purification by FC (pentane/Et_2O 400:1) afforded **18**: 451 mg (53%). I.R. ($CHCl_3$): 3068*w*, 2959*m*, 2931*s*, 2859*m*, 1807*w*, 1569*m*, 1470*s*, 1404*s*, 1371*m*, 1129*m*, 1090*s*, 1048*m*, 1022*m*, 957*m*, 617*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.81-7.75 (*m*, 2 aromat. H); 7.66-7.63 (*m*, 1 aromat. H); 7.57-7.55 (*m*, 1 aromat. H); 7.46-7.37 (*m*, 2 aromat. H); 7.34-7.29 (*m*, 2 aromat. H); 7.19-7.07 (*m*, 2 aromat. H); 5.31 (*q, J* = 6.2 Hz, 1 H, HCO); 1.40 (*d*, *J* = 6.2 Hz, 3 H, CH_3); 1.11 (*s*, 9 H, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): 145.22 (C); 137.95 (CH); 132.23 (CH); 132.15 (CH); 132.10 (CH); 131.58 (C); 128.28 (C); 128.10 (CH); 127.92 (CH); 127.58 (CH); 127.55 (CH); 120.84 (C); 71.13 (CH); 26.17 (CH_3); 25.34 (CH_3); 19.07 (C). EI-MS: 449.0 (<1, $[M(^{79}Br)-H]^+$), 436.9 (<1, $[M(^{81}Br)-CH_3]^+$), 395.0 (42), 393.0 (38), 299.0 (4), 211.0 (100), 185.0 (5), 143.0 (4). Anal. Calcd for: $C_{20}H_{23}BrOS_2Si$ (451.52): C 53.20, H 5.13; found: C 53.25, H 5.32.

[1-(2-Bromophenyl)ethoxy]di(4-methoxyphenyl)methylsilane (19):

According to GP 2 with 1-(2-bromophenyl)ethanol (1.0 g, 5.0 mmol), DMF (1+1 mL), imidazole (300 mg, 4.4 mmol) and *tert*-butyldi(4-methoxyphenyl)chlorosilane (514 mg, 1.76 mmol). Purification by FC (pentane/Et_2O 40:1) afforded **19**: 709 mg (88%). I.R. ($CHCl_3$): 3008*m*, 2974*w*, 2838*w*, 1594*s*, 1565*m*, 1503*s*, 1467*m*, 1279*s*, 1118*s*, 1030*m*, 956*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.72 (*dxd*, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1 aromat. H); 7.51-7.42 (*m*, 5 aromat. H); 7.34-7.29 (*m*, 1 aromat. H); 7.08 (*txd*, J_1 = 7.6 Hz, J_2 = 1.9 Hz, 1 aromat. H); 6.93-6.87 (*m*, 4 aromat. H); 5.25 (*q, J* = 6.2 Hz, 1 H, HCO); 3.82 (*s*, 3 H, CH_3); 3.81 (*s*, 3 H, CH_3); 1.40 (*d*, *J*=6.2 Hz, 3H, CH_3); 0.51 (*s*, 3 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.94 (C); 145.43 (C); 135.95 (CH); 135.87 (CH); 132.18 (CH); 128.28 (CH); 127.62 (CH); 127.37 (C); 120.89 (C); 70.30 (CH); 55.05 (CH_3); 25.39 (CH_3); -2.33 (CH_3). EI-MS: 456.3 (1, $[M(^{79}Br)]^+$), 443.3 (11, $[M(^{81}Br)-CH_3]^+$), 350.1 (21), 335.1 (9), 273.1 (27), 259.1 (100), 243.1 (10), 210.1 (10), 167.0 (9). Anal. Calcd for: $C_{23}H_{25}BrO_3Si$ (457.44): C 60.39, H 5.51; found: C 60.55, H 5.43.

4-Fluoro-2‘-(1-hydroxyethyl)biphenyl (20)

from **15**: According to GP 3 with silylether **15** (193 mg, 0.35 mmol), benzene (7 mL), Bu_3SnH (97 µL, 0.37 mmol), AIBN (17 mg, 0.10 mmol) in benzene (0.5 mL) and MeLi (3.4 mL, 5.2 mmol). Purification by FC (Et_2O/pentane 1:5) afforded **20**: 37 mg (49%). M.p. 108 °C. I.R. ($CHCl_3$): 3606*w*, 3008*w*, 2977*w*, 1607*w*, 1513*s*, 1481*m*, 1447*w*, 1377*w*, 1158*m*, 1077*m*, 1048*w*, 997*w*, 892*w*, 840*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.67 (*dxd*, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1 aromat. H); 7.43 (*txd*, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1 aromat. H); 7.34-7.24 (*m*, 3 aromat. H); 7.20-7.08 (*m*, 3 aromat. H); 4.94 (*qxd*, J_1 = 6.2 Hz, J_2 = 2.2 Hz, 1 H, HCO); 1.68 (*d*, *J* = 2.5 Hz, 1 H, OH); 1.41 (*d*, *J* = 6.2 Hz, 3 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 162.12 (*d*, $J_{C\text{-}F}$ = 246.6 Hz, C); 143.10 (C); 136.79 (C); 130.83 (*d*, $J_{C\text{-}F}$ = 8.6 Hz, CH); 130.04 (CH); 128.18 (CH); 127.23 (CH); 125.40 (CH); 115.09 (*d*, $J_{C\text{-}F}$ = 22.0 Hz, CH); 66.47 (CH); 24.91 (CH_3). EI-MS: 215.8 (8, $[M]^+$), 200.8 (17), 197.8 (34), 182.8 (100), 169.8 (36), 151.8 (22). Anal. Calcd for: $C_{14}H_{13}FO$ (216.25): C 77.76, H 6.06; found: C 77.66, H 6.18.

from **17**: According to GP 3 with silylether **17** (143 mg, 0.30 mmol), benzene (6 mL), Bu_3SnH (84 µL, 0.31 mmol), AIBN (15 mg, 0.09 mmol) in benzene (0.5 mL) and MeLi (2.9 mL, 4.4 mmol). Purification by FC (Et_2O/pentane 1:5) afforded **20**: 23 mg (35%).

4-Methoxy-2'-(1-hydroxyethyl)biphenyl (22)

According to GP 3 with silylether **19** (203 mg, 0.44 mmol), benzene (9 mL), Bu_3SnH (124 µL, 0.466 mmol), AIBN (22 mg, 0.133 mmol) in benzene (0.5 mL) and MeLi (4.3 mL, 6.7 mmol). Purification by FC (Et_2O/pentane 1:3) afforded **22**: 78 mg (77%). I.R. ($CHCl_3$): 3605*m*, 3008*s*, 2934*m*, 2838*m*, 1611*s*, 1516*s*, 1481*s*, 1442*m*, 1378*w*, 1293*m*, 1076*m*, 1037*m*, 998*m*, 892*m*, 638*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.67 (*dxd*, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1 aromat. H); 7.41 (*txd*, J_1 = 7.1 Hz, J_2 = 1.7 Hz, 1 aromat. H); 7.37-7.18 (*m*, 4 aromat. H); 7.00-6.93 (*m*, 2 aromat. H); 5.02 (*q*, *J* = 6.2 Hz, 1 H, HCO); 3.87 (*s*, 3 H, CH_3); 1.76 (*s*, 1 H, OH); 1.42 (*d*, *J* = 6.2 Hz, 3 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 158.77 (C); 143.26 (C); 140.02 (C); 133.26 (C); 130.35 (CH); 130.19 (CH); 127.76 (CH); 127.13 (CH); 125.35 (CH); 113.62 (CH); 66.50 (CH); 55.32 (CH_3); 24.88 (CH_3). EI-MS: 228.1 (53, $[M]^+$), 213.1 (10), 210.1 (63), 195.1 (100), 185.1 (12), 179.1 (20), 165.0 (19), 152.0 (21).

3-Brom-1-phenylbut-3-en-1-ol

To a suspension of tin powder (178 mg, 1.5 mmol) and 2,3-dibromopropene (0.29 mL, 0.30 mmol) in 1:1 mixture of Et_2O and water (2 mL) 2 drops of HBr (48% in H_2O) were added. After addition of benzaldehyde (0.10 mL, 1.0 mmol), the reaction mixture was stirred for 6 h at rt. After quenching with H_2O (10 mL), the reaction mixture was extracted three times with Et_2O. The combined organic phase was dried ($MgSO_4$) and the solvent evaporated. Purification by FC (pentane/Et_2O 5:1) afforded 3-bromo-1-phenylbut-3-en-1-ol: 210 mg (96%). The physical data are in agreement with the values reported in literature.[11]

(3-Bromo-1-phenylbut-3-enyloxy)triphenylsilane (23)

3-Bromo-1-phenylbut-3-en-1-ol (200 mg, 0.88 mmol) was dissolved in DMF (2 mL). Imidazole (90 mg, 1.32 mmol) and triphenylchlorosilane (286 mg, 0.97 mmol) were added.

The reaction mixture was stirred for 14 h at rt. After addition of Et_2O, the reaction mixture was washed with NH_4Cl and brine, dried ($MgSO_4$) and the solvent evaporated. Purification by FC (pentane/Et_2O 100:1) afforded **23**: 255 mg (60%). I.R. ($CHCl_3$): 3070*m*, 3008*m*, 2912*w*, 1959*w*, 1892*w*, 1826*w*, 1632*m*, 1590*w*, 1486*w*, 1454*w*, 1428*s*, 1366*w*, 1308*w*, 1116*s*, 1082*s*, 1069*s*, 1024*m*, 998*w*, 947*m*, 894*m*, 635*w*, 622*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.55-7.51 (*m*, 6 aromat. H); 7.41-7.40 (*m*, 3 aromat. H); 7.40-7.29 (*m*, 6 aromat. H); 7.24-7.18 (*m*, 5 aromat. H); 5.40 (*dxdxd*, $J_1 = J_2 = 1.0$ Hz, $J_3 = 1.7$ Hz, 1 H, CH_2=C); 5.29 (*d*, $J = 1.6$ Hz, 1 H, CH_2=C); 5.12 (*t*, $J = 6.3$ Hz, 1 H, HCO); 2.97 (*dxdxd*, $J_1 = 14.1$ Hz, $J_2 = 6.8$ Hz, $J_3 = 0.9$ Hz, 1 H, CH_2); 2.71 (*dxdxd*, $J_1 = 14.1$ Hz, $J_2 = 6.2$ Hz, $J_3 = 0.9$ Hz, 1 H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): 142.78 (C); 135.58 (CH); 134.11 (C); 129.92 (CH); 129.80 (C); 128.02 (CH); 127.69 (CH); 127.48 (CH); 126.47 (CH); 119.76 (CH_2); 74.05 (CH); 52.26 (CH_2). EI-MS: 365.1 (83), 260.0 (55), 259.0 (100), 181.0 (31), 167.0 (29). Anal. Calcd for $C_{28}H_{25}BrOSi$ (485.49): C 69.27 H 5.19; found: C 69.46 H 5.27.

(3-Bromo-1-phenylbut-3-enyloxy)diphenyl(trimethylsilyl)silane (24)

According to GP 1 with 3-bromo-1-phenylbut-3-en-1-ol (200 mg, 0.9 mmol), THF (10+2 mL), NEt_3 (0.15 mL, 1.1 mmol), diphenyl(trimethylsilyl)chlorosilane[2] (307 mg, 1.1 mmol) and DMAP (cat.). Purification by FC (pentane/Et_2O 100:1) afforded **24**: 408 mg (96%). I.R. ($CHCl_3$): 3068*w*, 3008*w*, 2952*w*, 2894*w*, 1954*w*, 1887*w*, 1826*w*, 1632*m*, 1588*w*, 1494*w*, 1454*w*, 1428*m*, 1364*m*, 1307*w*, 1107*s*, 1082*s*, 1066*s*, 1024*m*, 998*w*, 944*w*, 893*m*, 857*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.55-7.19 (*m*, 15 aromat. H); 5.39 (*dxdxd*, $J_1 = 1.6$ Hz, $J_2 = J_3 = 0.9$ Hz, 1 H, C=CH_2); 5.29 (*d*, $J = 1.6$ Hz, 1 H; C=CH_2); 5.02 (*t*, $J = 6.17$ Hz, 1 H, HCO); 2.92 (*dxdxd*, $J_1 = 14.1$ Hz, $J_2 = 6.9$ Hz, $J_3 = 0.9$ Hz, 1 H, CH_2); 2.66 (*dxdxd*, $J_1 = 14.0$ Hz, $J_2 = 6.0$ Hz, $J_3 = 0.9$ Hz, 1 H, CH_2); 0.07 (*s*, 9 H; $(CH_3)_3Si$). ^{13}C-NMR (100 MHz, $CDCl_3$): 143.34 (C); 136.60 (C); 136.40 (C); 135.10 (CH); 134.86 (CH); 129.86 (C); 129.45 (CH); 129.32 (CH); 128.01 (CH); 127.70 (CH); 127.66 (CH); 127.44 (CH); 126.34 (CH); 119.59 (CH_2); 74.09 (CH); 52.77 (CH_2); -1.45 (CH_3). EI-MS: 407.1 (7, $[M(^{79}Br)\text{-}SiMe_3]^+$), 367.0 (23), 271.1 (100), 263.0 (52), 261.0 (52), 255.1 (27), 199.1 (25), 197.1 (30), 193.1 (52), 181.1 (30), 167.1 (65), 135.1 (31), 84.0 (50), 49.0 (22). Anal. Calcd for $C_{25}H_{29}OSi_2Br$ (481.58): C 62.35, H 6.07; found: C 62.46, H 6.16.

(2-Bromophenoxy)diphenyl(trimethylsilyl)silane (25)

According to GP 1 with 2-bromophenol (200 mg, 1.2 mmol), THF (10+2 mL), NEt_3 (0.19 mL, 1.4 mmol), diphenyl(trimethylsilyl)chlorosilane[2] (404 mg, 1.4 mmol) and DMAP (cat.). Purification by FC (pentane/Et_2O 100:1) afforded **25**: 413 mg (84%). I.R. ($CHCl_3$): 3070*w*, 3008*w*, 2953*w*, 2892*w*, 1476*s*, 1440*m*, 1428*m*, 1281*s*, 1108*s*, 1047*m*, 1029*m*, 913*s*, 839*s*, 648*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.76-7.65 (*m*, 4 aromat. H); 7.58-7.49 (*m*, 1 aromat. H); 7.45-7.28 (*m*, 6 aromat. H); 7.02-6.97 (*m*, 1 aromat. H); 6.80-6.72 (*m*, 1 aromat. H); 6.71-

6.69 (*m*, 1 aromat. H); 0.13 (*s*, 9 H, $(CH_3)_3Si$). ^{13}C-NMR (100 MHz, $CDCl_3$): 153.07 (C); 135.73 (C); 134.63 (CH); 134.35 (CH); 134.14 (CH); 133.27 (CH); 130.44 (CH); 129.87 (CH); 129.63 (CH); 129.34 (CH); 128.33 (CH); 128.09 (CH); 127.87 (CH); 127.82 (CH); 127.57 (CH); 122.51 (CH); 120.00 (CH); 115.16 (C); -1.39 (CH_3). EI-MS: 426.1 (<1, $[M(^{79}Br)]^+$), 411.0 (7, $[M(^{79}Br)\text{-}CH_3]^+$), 355.0 (94), 353.0 (100, $[M(^{79}Br)\text{-}SiMe_3]^+$), (24), 274.0 (47), 273.0 (88), 263.0 (25), 261.0 (27), 197.1 (43), 181.1 (25), 135.1 (22), 86.0 (28), 84.0 (44), 49.0 (20). Anal. Calcd for $C_{21}H_{23}BrOSi_2$ (427.49): C 59.00, H 5.42; found: C 59.15, H 5.42.

(2-Bromophenoxy)triphenylsilane (26)

Under Ar, 2-bromophenol (300 mg, 1.7 mmol) was dissolved in CH_2Cl_2 (6 mL). Then NEt_3 (0.48 mL, 3.4 mmol) and triphenylchlorosilane (511 mg, 1.7 mmol) were added. After stirring for 45 min at rt, the reaction mixture was diluted with Et_2O and washed with sat. NH_4Cl and brine. The organic phase was dried ($MgSO_4$) and the solvent evaporated. Purification by FC (pentane/Et_2O 100:1) afforded **26**: 613 mg (82%). M.. p. 74-75 °C. I.R. ($CHCl_3$): 3072*m*, 3008*m*, 1959*w*, 1892*w*, 1826*w*, 1780*w*, 1579*m*, 1477*s*, 1441*m*, 1429*s*, 1118*s*, 1106*m*, 1048*m*, 1030*m*, 997*w*, 927*s*, 646*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.74-7.73 (*m*, 6 aromat. H); 7.50-7.36 (*m*, 10 aromat. H); 6.99-6.95 (*m*, 1 aromat. H); 6.79-6.74 (*m*, 2 aromat. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 152.04 (C); 135.55 (CH); 133.34 (CH); 133.10 (C); 130.44 (CH); 128.10 (CH); 127.99 (CH); 122.72 (CH); 120.23 (CH); 115.27 (CH). EI-MS: 430.0 (25, $[M(^{79}Br)]^+$), 354.9 (33, $[M(^{81}Br)\text{-}Ph]^+$), 353.0 (32), 273.0 (59), 261.0 (21), 260.0 (25), 259.0 (100), 230.1 (32). Anal. Calcd for $C_{24}H_{19}BrOSi$ (431.40): C 66.82, H 4.44; found: C 66.67, H 4.55.

(2-Bromophenoxy)diphenylmethylsilane (27)

According to GP 1 with 2-bromophenol (0.31 mL, 2.9 mmol), THF (15+2 mL), NEt_3 (0.48 mL, 3.5 mmol), diphenylmethylchlorosilane (0.73 mL, 3.5 mmol) and DMAP (cat.). Purification by FC (pentane/Et_2O 100:1) afforded **27**: 975 mg (91%). I.R. ($CHCl_3$): 3071*m*, 3008*m*, 1959*w*, 1902*w*, 1823*w*, 1590*m*, 1477*s*, 1428*s*, 1282*s*, 1120*s*, 1047*m*, 1030*m*, 924*s*, 643*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.79-7.75 (*m*, 4 aromat. H); 7.58-7.26 (*m*, 7 aromat. H); 7.06 (*txd*, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1 aromat. H); 6.83 (*txd*, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1 aromat. H); 6.78 (*dxd*, J_1 = 8.1 Hz, J_2 = 1.6 Hz, 1 aromat. H); 0.83 (*s*, 3 H, SiMe). ^{13}C-NMR (75 MHz, $CDCl_3$): 152.16 (C); 135.04 (C); 134.54 (CH); 133.41 (CH); 130.32 (CH); 128.26 (CH); 128.05 (CH); 122.83 (CH); 120.39 (CH); 115.43 (C); -2.48 (CH_3). EI-MS: 370.1 (35, $[M(^{81}Br)]^+$), 355.0 (100, $[M(^{81}Br)\text{-}CH_3]^+$), 293.0 (12), 273.1 (52), 263.0 (13), 211.0 (23), 197.1 (40).

Biphenyl-2-ol (28) und 2-(trimethylsilyl)phenol (29)

According to GP 3 with silylether **25** (250 mg, 0.58 mmol), benzene (13 mL), Bu_3SnH (169 µL, 0.63 mmol), AIBN (12 mg, 0.07 mmol) in benzene (0.5 mL) and MeLi (1 mL, 0.65 mmol). Purification by FC (Et_2O/pentane 1 : 10) afforded **28**: 38 mg (38 %) and **29**: 49 mg (50%). The physical data are in agreement with the values reported in literature.[12,13]

Crystal Structure of (2-Bromophenoxy)triphenylsilane (26)

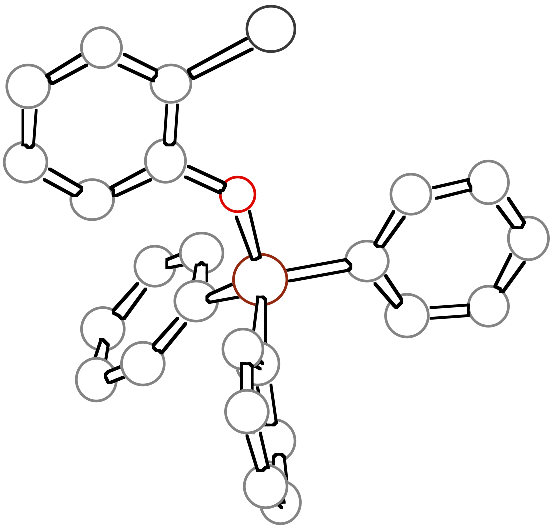

Table 1. Crystal data and structure refinement for **26**.

Empirical formula	C24 H19 Br O Si
Formula weight	431.39
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 10.189(7) A alpha = 90 deg. b = 11.553(6) A beta = 104.83(6) deg. c = 18.272(14) A gamma = 90 deg.
Volume	2079(2) A^3
Z	4
Density (calculated)	1.378 Mg/m^3
Absorption coefficient	2.045 mm^-1

F(000)	880
Crystal size	0.5 x 0.3 x 0.2 mm
Theta range for data collection	2.09 to 20.04 deg.
Index ranges	-9<=h<=9, 0<=k<=11, 0<=l<=17
Reflections collected	2016
Independent reflections	1939 [R(int) = 0.0245]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1939 / 0 / 244
Goodness-of-fit on F^2	0.844
Final R indices [I>2sigma(I)]	R1 = 0.0323, wR2 = 0.0706
R indices (all data)	R1 = 0.0484, wR2 = 0.0724
Largest diff. peak and hole	0.385 and -0.234 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **26.** U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br	1521(1)	1355(1)	4260(1)	63(1)
Si	4292(1)	3136(1)	3056(1)	42(1)
O	3008(3)	2827(3)	3415(2)	53(1)
C(1)	1920(5)	3422(5)	3519(3)	39(1)
C(2)	1110(5)	2865(4)	3913(3)	42(1)
C(3)	14(6)	3437(6)	4038(3)	67(2)
C(4)	-269(6)	4550(6)	3781(4)	83(2)
C(5)	526(7)	5080(5)	3398(3)	72(2)
C(6)	1608(6)	4533(5)	3260(3)	54(2)
C(7)	3703(5)	3187(4)	2013(3)	38(1)
C(8)	2379(6)	2896(5)	1641(4)	63(2)
C(9)	1952(6)	2849(6)	863(4)	83(2)
C(10)	2868(8)	3077(5)	448(3)	73(2)
C(11)	4157(7)	3365(5)	796(3)	59(2)
C(12)	4552(5)	3423(4)	1569(3)	53(2)
C(13)	5430(5)	1884(4)	3353(3)	39(1)
C(14)	5047(5)	895(6)	3678(3)	61(2)
C(15)	5837(7)	-41(5)	3854(4)	77(2)
C(16)	7093(7)	-50(6)	3718(4)	72(2)
C(17)	7538(6)	885(7)	3393(3)	70(2)
C(18)	6709(6)	1854(5)	3224(3)	56(2)
C(20)	5883(6)	4543(5)	4181(4)	66(2)
C(19)	5160(5)	4501(5)	3431(3)	43(1)
C(21)	6567(6)	5534(7)	4485(4)	82(2)
C(22)	6559(6)	6474(6)	4049(5)	76(2)
C(23)	5839(6)	6466(6)	3305(4)	70(2)
C(24)	5157(5)	5479(5)	3015(3)	53(2)

Table 3. Bond lengths [A] and angles [deg] for **26.**

Br-C(2)	1.867(5)
Si-O	1.645(4)
Si-C(7)	1.846(5)
Si-C(13)	1.847(5)
Si-C(19)	1.851(5)
O-C(1)	1.358(5)
C(1)-C(6)	1.376(6)
C(1)-C(2)	1.386(6)
C(2)-C(3)	1.366(6)
C(3)-C(4)	1.373(7)
C(4)-C(5)	1.346(7)
C(5)-C(6)	1.350(7)
C(7)-C(12)	1.357(6)
C(7)-C(8)	1.388(6)
C(8)-C(9)	1.377(8)
C(9)-C(10)	1.371(8)
C(10)-C(11)	1.347(7)
C(11)-C(12)	1.367(7)
C(13)-C(18)	1.383(6)
C(13)-C(14)	1.389(7)

C(14)-C(15)	1.337(7)
C(15)-C(16)	1.365(8)
C(16)-C(17)	1.365(7)
C(17)-C(18)	1.389(7)
C(20)-C(21)	1.380(8)
C(20)-C(19)	1.381(7)
C(19)-C(24)	1.361(7)
C(21)-C(22)	1.347(8)
C(22)-C(23)	1.369(8)
C(23)-C(24)	1.369(7)

O-Si-C(7)	109.7(2)
O-Si-C(13)	102.5(2)
C(7)-Si-C(13)	110.0(2)
O-Si-C(19)	113.0(2)
C(7)-Si-C(19)	110.7(2)
C(13)-Si-C(19)	110.7(2)
C(1)-O-Si	134.9(3)
O-C(1)-C(6)	123.3(5)
O-C(1)-C(2)	117.0(5)
C(6)-C(1)-C(2)	119.7(5)
C(3)-C(2)-C(1)	118.9(5)
C(3)-C(2)-Br	121.2(4)
C(1)-C(2)-Br	119.9(4)
C(2)-C(3)-C(4)	120.4(5)
C(5)-C(4)-C(3)	120.1(5)
C(4)-C(5)-C(6)	120.9(6)
C(5)-C(6)-C(1)	120.0(5)
C(12)-C(7)-C(8)	116.3(5)
C(12)-C(7)-Si	122.4(4)
C(8)-C(7)-Si	121.1(4)
C(9)-C(8)-C(7)	121.8(5)
C(10)-C(9)-C(8)	118.9(6)
C(11)-C(10)-C(9)	120.4(6)
C(10)-C(11)-C(12)	119.6(6)
C(7)-C(12)-C(11)	123.0(5)
C(18)-C(13)-C(14)	115.7(5)
C(18)-C(13)-Si	121.1(4)
C(14)-C(13)-Si	123.1(4)
C(15)-C(14)-C(13)	123.3(5)
C(14)-C(15)-C(16)	119.9(6)
C(15)-C(16)-C(17)	120.3(6)
C(16)-C(17)-C(18)	118.9(5)
C(13)-C(18)-C(17)	121.9(5)
C(21)-C(20)-C(19)	121.0(6)
C(24)-C(19)-C(20)	116.7(5)
C(24)-C(19)-Si	124.6(5)
C(20)-C(19)-Si	118.7(5)
C(22)-C(21)-C(20)	120.3(6)
C(21)-C(22)-C(23)	120.2(6)
C(24)-C(23)-C(22)	118.7(6)
C(19)-C(24)-C(23)	123.1(6)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **26.**
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br	67(1)	53(1)	80(1)	11(1)	36(1)	-2(1)
Si	38(1)	50(1)	42(1)	3(1)	14(1)	-2(1)
O	48(2)	54(2)	63(3)	16(2)	28(2)	9(2)
C(1)	33(3)	48(4)	33(3)	-4(3)	7(3)	12(3)
C(2)	40(4)	42(3)	45(4)	0(3)	15(3)	-8(3)
C(3)	46(4)	73(5)	94(5)	7(4)	43(4)	2(4)
C(4)	65(5)	70(5)	131(6)	17(5)	53(5)	31(4)
C(5)	71(5)	55(4)	100(6)	29(4)	41(4)	21(4)
C(6)	49(4)	59(5)	64(4)	19(4)	30(3)	11(4)
C(7)	35(3)	38(3)	39(3)	-3(3)	8(3)	-8(3)
C(8)	53(5)	88(5)	50(5)	-11(4)	18(4)	-2(4)
C(9)	49(4)	136(6)	58(5)	-38(5)	0(4)	7(4)
C(10)	87(5)	90(5)	37(4)	-12(4)	9(5)	12(4)
C(11)	70(5)	68(5)	43(5)	-7(3)	22(4)	-18(4)
C(12)	53(4)	68(4)	38(4)	-6(3)	11(3)	-20(3)
C(13)	38(4)	39(4)	39(4)	5(3)	9(3)	-1(3)
C(14)	37(4)	67(5)	77(5)	0(4)	12(3)	19(4)
C(15)	50(4)	68(5)	117(6)	26(4)	32(4)	11(4)
C(16)	76(6)	59(5)	78(5)	16(4)	12(4)	24(4)
C(17)	42(4)	95(6)	73(5)	0(4)	16(4)	18(4)
C(18)	43(4)	69(5)	59(4)	11(3)	19(3)	2(4)
C(20)	79(5)	59(5)	61(5)	4(4)	19(4)	-1(4)
C(19)	43(4)	54(4)	31(4)	2(3)	10(3)	1(3)
C(21)	84(5)	86(6)	67(6)	-28(5)	0(4)	-5(5)
C(22)	66(5)	60(5)	103(7)	-33(5)	25(5)	-13(4)
C(23)	71(5)	68(6)	71(5)	-4(4)	21(4)	-5(4)
C(24)	55(4)	49(4)	50(4)	-8(4)	7(3)	-7(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic
displacement parameters (A^2 x 10^3) for **26.**

	x	y	z	U(eq)
H(3A)	-562(6)	3060(6)	4306(3)	93
H(4A)	-1036(6)	4950(6)	3875(4)	117
H(5A)	320(7)	5857(5)	3221(3)	100
H(6A)	2160(6)	4919(5)	2981(3)	76
H(8A)	1743(6)	2722(5)	1933(4)	88
H(9A)	1027(6)	2660(6)	615(4)	117
H(10A)	2589(8)	3030(5)	-95(3)	102
H(11A)	4795(7)	3529(5)	504(3)	82
H(12A)	5471(5)	3639(4)	1808(3)	74
H(14A)	4170(5)	883(6)	3783(3)	85
H(15A)	5521(7)	-705(5)	4074(4)	107
H(16A)	7666(7)	-717(6)	3852(4)	101
H(17A)	8410(6)	873(7)	3283(3)	98
H(18A)	7033(6)	2522(5)	3011(3)	78
H(20A)	5911(6)	3874(5)	4496(4)	93

H(21A)	7051(6)	5552(7)	5010(4)	115
H(22A)	7057(6)	7153(6)	4260(5)	106
H(23A)	5814(6)	7138(6)	2993(4)	97
H(24B)	4652(5)	5477(5)	2493(3)	74

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