Supporting Information for:

Alkenyl- and Aryl[2-(hydroxymethyl)phenyl]dimethylsilanes: A New Entry to Tetraorganosilicon Reagents for the Silicon-Based Cross-Coupling Reaction

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General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Flush column chromatography was performed using Merck silica gel 60 (40–63 μm), Kanto Chemical silica gel (spherical, 40–50 μm), or aluminium oxide 90 neutral (20–63 μm). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F₂₅₄ (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline KMnO₄ solution followed by heating.

Apparatus. Proton and carbon nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded on a Varian Mercury 400 (¹H NMR, 400 MHz; ¹³C NMR, 101 MHz) spectrometer with solvent resonance as the internal standard (¹H NMR, CHCl₃ at 7.26 ppm or C₆H₆ at 7.15 ppm; ¹³C NMR, CDCl₃ at 77.0 ppm or C₆D₆ at 128.0 ppm). ¹H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Melting points were determined using a YANAKO MP-500D. Mass spectra were obtained with a JEOL JMS-700 (EI and CI) or JEOL JMS-HX110A (FAB+) spectrometer.

Chemicals. Unless otherwise noted, commercially available reagents were used without purification. Diethyl ether, THF, and hexane were distilled from sodium/benzophenone ketyl. Anhydrous DMSO was purchased from Aldrich and used without further purification. *N*-(2-Diphenylphosphinobenzylidene)cyclohexylamine (**4**) was prepared according to the reported procedure.¹

(A) Preparation of silicon reagents

Preparation of dimethyl[2-(2-tetrahydro-2H-pyranoxymethyl)phenyl]silane.

To a mixture of 2-bromophenylmethanol (34 g, 0.18 mol) and 3,4-dihydro-2H-pyran (18 g, 0.22 mol) were added 10 drops of concentrated hydrochloric acid, and the resulting mixture was stirred at rt overnight. The mixture was diluted with diethyl ether, neutralized with a saturated NaHCO_3 aqueous solution, dried over anhydrous MgSO_4 , and concentrated in vacuo to give 2-(2-tetrahydro-2H-pyranoxymethyl)bromobenzene, which was dissolved in THF (450 mL). The solution was added a 1.6 M *n*-BuLi solution in hexane (124 mL, 0.20 mol) over 40 min at -78°C , and the resulting solution was stirred for 50 min before the addition of chlorodimethylsilane (20 g, 0.22 mol) at -78°C . The mixture was warmed gradually at rt overnight and quenched with H_2O . After evaporation of THF, the residue was extracted with diethyl ether, and the combined organic layers were washed with brine and dried over anhydrous MgSO_4 . Distillation under vacuum gave the title compound (38 g, 83%) as a colorless oil, bp 135°C (1.0 mmHg). ^1H NMR (400 MHz, CDCl_3) δ 7.54 (dd, $J = 7.2, 1.4$ Hz, 1H), 7.44 (dd, $J = 7.5, 0.5$ Hz, 1H), 7.37, (td, $J = 7.5, 1.5$ Hz, 1H), 7.29 (td, $J = 7.3, 1.3$ Hz, 1H), 4.86 (d, $J = 11.9$ Hz, 1H), 4.73 (t, $J = 3.6$ Hz, 1H), 4.59 (d, $J = 11.7$ Hz, 1H), 4.56–4.51 (m, 1H), 3.98–3.89 (m, 1H), 3.60–3.52 (m, 1H), 1.94–1.45 (m, 6H), 0.364 (d, $J = 3.7$ Hz, 3H), 0.360 (d, $J = 3.7$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 143.6, 136.5, 134.7, 129.4, 128.3, 127.0, 98.1, 69.1, 62.1, 30.6, 25.5, 19.3, $-3.0, -3.1$; IR (neat) 2943, 2124, 1250, 1202, 1119, 1080, 1055, 1026, 974, 885, 837, 752 cm^{-1} ; MS (EI, 70 eV) m/z (%) 250 (M^+ , 0.1), 164 (12), 163 (14), 150 (17), 149 (100), 85 (22); Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_2\text{Si}$; C, 67.15; H, 8.86. Found: C, 67.44; H, 8.91.

Preparation of oxasilacyclopentane **3** from dimethyl[2-(2-tetrahydro-2H-pyranoxymethyl)phenyl]silane.

Dimethyl[2-(2-tetrahydro-2H-pyranoxymethyl)phenyl]silane (75 g, 0.30 mol) was treated with *p*-toluenesulfonic acid monohydrate (1.1 g, 6.0 mmol) in MeOH (500 mL) at rt for 16 h. After evaporation of MeOH, the residue was distilled to give **3** (41 g, 83%) as a colorless oil, bp 45°C (2.0 mmHg). ^1H NMR (400 MHz, CDCl_3) δ 7.59 (dd, $J = 7.1, 0.4$ Hz, 1H), 7.42–7.37 (m, 1H), 7.33–7.28, (m, 1H), 7.23 (dd, $J = 7.5, 0.7$ Hz, 1H), 5.16 (s, 2H), 0.40 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.7, 135.0, 131.0, 129.5, 126.8, 121.6, 71.5, 0.6; IR (neat) 3360, 3057, 2953, 2897, 2860, 1701, 1593, 1445, 1350, 1252, 1200, 1134, 1067, 1051, 1024, 858, 829, 791, 748, 692, 652 cm^{-1} ; MS (EI, 70 eV) m/z (%) 165 (M^+ , 9), 164 (58), 163 (26), 151 (13), 150 (45), 149 (100), 105 (15); Anal. Calcd for $\text{C}_9\text{H}_{12}\text{OSi}$; C, 65.80; H, 7.36. Found: C, 65.60; H, 7.34.

Preparation of dimethyl[2-(2-acetoxymethyl)phenyl]silane (**5**).

To a suspension of LiAlH_4 (0.38 g, 10 mmol) in diethyl ether (30 mL) was added **3** (1.64 g, 10 mmol) at 0 °C, and the resulting mixture was stirred at rt for 100 min before the addition of acetyl chloride (7.1 mL, 100 mmol) at 0 °C. Stirring was continued at rt overnight, and the mixture was filtered through a Florisil and then a silica gel pad. The residue was purified by flash chromatography on silica gel to give **5** (1.4g, 67%) as a colorless oil, R_f 0.30 (hexane–ethyl acetate = 20:1). ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, J = 7.0 Hz, 1H), 7.42–7.32 (m, 3H), 5.20 (s, 2H), 4.58–4.51 (m, 1H), 2.10 (s, 3H), 0.37 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.8, 140.9, 137.2, 135.0, 129.6, 129.1, 127.8, 66.6, 21.1, –3.1; IR (neat) 2959, 2127, 1742, 1437, 1379, 1362, 1236, 1130, 1080, 1026, 966, 887, 839, 756 cm^{-1} ; MS (EI, 70 eV) m/z (%) 208 (M^+ , 6), 207 (37), 194 (14), 193 (81), 165 (59), 163 (24), 152 (25), 151 (98), 150 (29), 149 (100), 148 (24), 147 (27), 145 (12), 135 (27), 134 (12), 133 (55), 131 (11), 123 (14), 121 (14), 119 (13), 117 (38), 105 (20), 91 (34), 75 (46); Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2\text{Si}$; C, 63.42; H, 7.74. Found: C, 63.48; H, 7.74.

Preparation of (*E*)-[2-(hydroxymethyl)phenyl]dimethyl(1-octenyl)silane (**1a**) by platinum-catalyzed hydrosilylation.

To a solution of dimethyl[2-(2-tetrahydro-2H-pyranoxymethyl)phenyl]silane (10 g, 40 mmol) and 1-octyne (4.4 g, 40 mmol) in hexane (4 mL) were added a 10% hexane solution of *t*-Bu₃P (80 mg, 40 μmol) and a 0.01 M hexane solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (4.0 mL, 40 μmol) at 0 °C. The resulting mixture was stirred at rt for 2 h, filtered through a Celite pad, and concentrated in vacuo. The residue was dissolved in MeOH (140 mL) and treated with *p*-toluenesulfonic acid monohydrate (152 mg, 0.80 mmol) at rt for 4 h. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel to give the title compound (9.0 g, 81%) as a colorless oil, R_f 0.25 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.55 (dd, J = 7.3, 1.3 Hz, 1H), 7.46 (dd, J = 7.5, 0.7 Hz, 1H), 7.40 (td, J = 7.5, 1.5 Hz, 1H), 7.28 (td, J = 7.3, 1.3 Hz, 1H), 6.15 (dt, J = 18.7, 6.4 Hz, 1H), 5.83 (dt, J = 18.7, 1.5 Hz, 1H), 4.74 (s, 2H), 2.17–2.12 (m, 2H), 1.42–1.25 (m, 8H), 0.90–0.83 (m, 3H), 0.39 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.7, 146.4, 137.1, 135.1, 130.0, 128.2, 128.0, 127.0, 65.4, 36.8, 31.7, 28.9, 28.5, 22.6, 14.1, –1.2; IR (neat) 3329, 2957, 2926, 2855, 1614, 1466, 1435, 1248, 1126, 1078, 991, 841, 783, 746, 687 cm^{-1} ; MS (EI, 70 eV) m/z (%) 276 (M^+ , 0.1), 261 (32), 243 (14), 199 (12), 177 (13), 173 (11), 166 (27), 165 (66), 164 (51), 163 (44), 160 (11), 159 (42), 151 (25), 150 (30), 149 (100), 148 (27), 147 (50), 146 (16), 145 (51), 137 (12), 135 (31), 133 (14), 131 (22), 129 (18), 105 (16), 91 (18), 75 (32), 61 (39), 59

(13), 55 (11); Anal. Calcd for C₁₇H₂₈OSi; C, 73.85; H, 10.21. Found: C, 73.86; H, 10.42.

(E)-[2-(Hydroxymethyl)phenyl]dimethyl(5-cyano-1-pentenyl)silane

(1b). Following the procedure for **1a**, the reaction using the silane (1.3 g, 5.0 mmol) and 5-hexynenitrile (0.46 g, 5.0 mmol) gave the title compound (1.1 g, 84%) as a colorless oil, *R_f* 0.30 (hexane–ethyl acetate =

4:1). ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.40 (td, *J* = 7.4, 1.2 Hz, 1H), 7.29 (td, *J* = 7.4, 1.2 Hz, 1H), 6.06 (dt, *J* = 18.5, 6.0 Hz, 1H), 5.95 (d, *J* = 18.4 Hz, 1H), 4.73 (s, 2H), 2.36–2.29 (m, 4H), 1.82–1.75 (m, 2H), 0.40 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 146.4, 145.6, 136.2, 135.0, 131.2, 129.7, 127.7, 126.9, 119.5, 65.1, 35.2, 24.0, 16.4, –1.3; IR (neat) 3443, 2953, 2249, 1618, 1433, 1250, 1124, 1078, 991, 910, 827, 733 cm^{–1}; MS (EI, 70 eV) *m/z* (%) 259 (M⁺, 0.3), 244 (33), 242 (18), 226 (24), 165 (39), 164 (44), 163 (22), 150 (15), 149 (100), 147 (25), 145 (20), 135 (11); Anal. Calcd for C₁₅H₂₁NOSi; C, 69.45; H, 8.16. Found: C, 69.68; H, 8.15.

(E)-[2-(Hydroxymethyl)phenyl]dimethyl(2-phenylethenyl)silane **(1c).**

Following the procedure for **1a**, the reaction using the silane (0.55 g, 2.2 mmol) and phenylacetylene (0.20 g, 2.0 mmol) gave the title compound (0.45 g, 84%) as a colorless oil, *R_f* 0.20 (hexane–ethyl acetate = 10:1). ¹H NMR (400 MHz,

CDCl₃) δ 7.62 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.51–7.41 (m, 4H), 7.37–7.27 (m, 4H), 6.97 (d, *J* = 19.2 Hz, 1H), 6.67 (d, *J* = 19.2 Hz, 1H), 4.79 (s, 2H), 0.52 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 146.5, 145.2, 138.0, 136.4, 135.3, 130.0, 128.6, 128.3, 127.9, 127.8, 127.1, 126.5, 65.4, –1.2; IR (neat) 3444, 3055, 2955, 2359, 1605, 1572, 1495, 1447, 1435, 1248, 1198, 1124, 1076, 1028, 991, 847, 831, 812, 777, 748, 691 cm^{–1}; MS (EI, 70 eV) *m/z* (%) 268 (M⁺, 0.5), 253 (11), 235 (15), 165 (14), 164 (29), 163 (19), 150 (15), 149 (100), 147 (13), 137 (35), 135 (10), 105 (11), 104 (25), 103 (12), 91 (24); Anal. Calcd for C₁₇H₂₀OSi; C, 76.07; H, 7.51. Found: C, 75.73; H, 7.55.

(E)-[2-(Hydroxymethyl)phenyl]dimethyl(4-octen-4-yl)silane **(1g).**

Following the procedure for **1a**, the reaction using the silane (0.55 g, 2.2 mmol) and 4-octyne (0.22 g, 2.0 mmol) gave the title compound (0.45 g, 81%) as a colorless oil, *R_f* 0.25 (hexane–ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.54 (dd, *J* =

7.2, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.40 (td, *J* = 7.3, 1.4 Hz, 1H), 7.30–7.26 (m, 1H), 5.80 (t, *J* = 7.2 Hz, 1H), 4.70 (s, 2H), 2.12–2.06 (m, 4H), 1.38 (m, 2H), 1.28–1.18 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.83 (t, *J* = 7.2 Hz, 3H), 0.40 (s, 6H); ¹³C NMR (101 MHz, CDCl₃)

δ 146.6, 142.8, 140.2, 136.7, 135.3, 129.6, 128.0, 126.9, 65.2, 32.1, 30.8, 23.4, 22.6, 14.5, 14.0, -1.2; IR (neat) 3319, 2957, 2930, 2870, 1611, 1466, 1435, 1377, 1248, 1124, 1078, 1015, 833, 816, 770, 750, 687 cm^{-1} ; MS (EI, 70 eV) m/z (%) 276 (M^+ , 0.1), 261 (19), 166 (15), 165 (100), 164 (15), 163 (24), 151 (22), 150 (12), 149 (79), 148 (13), 147 (61), 145 (30), 135 (19), 91 (11), 75 (14), 61 (19), 59 (10), 55 (10); Anal. Calcd for $\text{C}_{17}\text{H}_{28}\text{OSi}$; C, 73.85; H, 10.21. Found: C, 73.67; H, 10.06.

Preparation of 1a by the platinum-catalyzed hydrosilylation of 1-octyne using 5. A 1.0 M solution of 1-octyne in hexane (0.50 mL, 0.50 mmol) was added dropwise to a mixture of **5** (104 mg, 0.50 mmol), *t*-Bu₃P (10% hexane solution, 10 mg, 5.0 μmol), and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (0.01 M hexane solution, 0.50 mL, 5.0 μmol) at 0 °C. The resulting mixture was stirred at rt for 4 h, filtered through a Florisil pad, and concentrated in vacuo. The residue was dissolved in MeOH (2.5 mL) and water (2.5 mL) and treated with K_2CO_3 (1.4 g, 10 mmol) at 50 °C for 24 h. The mixture was extracted with diethyl ether, and the combined organic layers were washed with water and brine and dried over anhydrous MgSO_4 ; the residue was purified by flash chromatography on silica gel to give **1a** (113 mg, 82%).

Preparation of [2-(hydroxymethyl)phenyl]dimethyl(propen-1-yl)silane [1d, (Z):(E) = 94:6]. A solution of (Z)-propen-1-ylmagnesium bromide in THF (70 mL) [prepared from (Z)-1-bromo-1-propene (6.0 g, 50 mmol) and Mg (1.71 g, 50 mmol)]² was added to a THF (20 mL) solution of **3** (5.8 g, 35 mmol) at 0 °C, and the resulting mixture was stirred at rt overnight. The mixture was diluted with diethyl ether and

filtered to remove unreacted magnesium; the filtrate was washed with a saturated NH_4Cl aqueous solution, water, and brine and dried over anhydrous MgSO_4 . After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel to give the title compound [6.8 g, 94%, (Z):(E) = 94:6 as estimated by GC analysis] as a colorless oil, R_f 0.26 (hexane–ethyl acetate = 7:1). [Spectra of (Z)-isomer] ^1H NMR (400 MHz, CDCl_3) δ 7.59 (dd, J = 7.3, 1.5 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.41 (td, J = 7.5, 1.5 Hz, 1H), 7.29 (td, J = 7.3, 1.3 Hz, 1H), 6.52 (dq, J = 13.9, 7.0 Hz, 1H), 5.76 (dq, J = 13.9, 1.5 Hz, 1H), 4.72 (s, 2H), 1.64 (dd, J = 6.8, 1.6 Hz, 3 H), 0.45 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 146.3, 145.1, 137.5, 134.7, 129.7, 129.3, 128.2, 127.0, 65.4, 19.1, -0.2; IR (neat) 3319, 3055, 2961, 2910, 1609, 1435, 1248, 1200, 1124, 1078, 1034, 826, 777, 746, 696, 658 cm^{-1} ; MS (EI, 70 eV) m/z (%) 206 (M^+ , 0.1), 191 (12), 173 (29), 166 (10), 165 (62), 164 (37), 163 (18), 150 (15), 149 (100), 148 (11), 147 (39), 145 (48), 135 (16), 131 (14), 105 (11), 91 (11), 75 (43), 61 (19); Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{OSi}$; C, 69.84; H, 8.79. Found: C, 69.82; H, 8.81.

Preparation of [2-(hydroxymethyl)phenyl]dimethyl(propen-2-yl)silane (1e). To a solution of **3** (7.5 g, 46 mmol) in THF (50 mL) was added a 0.5 M solution of 2-propenylmagnesium bromide in THF (100 mL, 50 mmol) at 0 °C, and the resulting mixture was stirred at rt for 9 h. The mixture was diluted with diethyl ether, washed with a saturated NH₄Cl aqueous solution, water, and brine, and dried over anhydrous

MgSO₄. After removal of the solvents in vacuo, the residue was distilled under vacuum to give the title compound (8.4 g, 89%) as a colorless oil, bp 75 °C (0.4 mmHg). ¹H NMR (400 MHz, CDCl₃) δ 7.55 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.48 (ddd, *J* = 7.7, 1.3, 0.5 Hz, 1H), 7.42 (td, *J* = 7.5, 1.5 Hz, 1H), 7.30 (td, *J* = 7.3, 1.5 Hz, 1H), 5.71 (dq, *J* = 3.1, 1.6 Hz, 1H), 5.37 (dq, *J* = 3.1, 1.3 Hz, 1H), 4.72 (s, 2H), 1.92 (br s, 1H), 1.82 (dd, *J* = 1.6, 1.3 Hz, 3 H), 0.44 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 147.3, 146.6, 135.4, 135.3, 129.7, 126.9, 126.6, 65.1, 22.5, -2.1; IR (neat) 3329, 2951, 1435, 1248, 1126, 1078, 1034, 924, 835, 818, 775, 754, 696, 662 cm⁻¹; MS (EI, 70 eV) *m/z* (%) 206 (M⁺, 0.3), 191 (26), 189 (14), 173 (39), 166 (17), 165 (100), 164 (17), 163 (23), 150 (13), 149 (75), 148 (17), 147 (78), 146 (12), 145 (61), 135 (18), 131 (14), 105 (10), 75 (30); Anal. Calcd for C₁₂H₁₈OSi; C, 69.84; H, 8.79. Found: C, 69.82; H, 8.56.

Preparation of [2-(hydroxymethyl)phenyl]dimethyl(1-phenylethenyl)silane (1f).

To a solution of 1-phenylethenylmagnesium bromide in THF (16 mL) [prepared from α-bromostyrene (3.7 g, 20 mmol) and Mg (0.50 g, 21 mmol)]³ was added a THF (9 mL) solution of **3** (3.0 g, 19 mmol) at rt, and the resulting mixture was stirred at rt for 2 h and then at 50 °C for 2 h. The mixture was diluted with diethyl ether and filtered

to remove unreacted magnesium; the filtrate was washed with a saturated NH₄Cl aqueous solution, water, and brine and dried over anhydrous MgSO₄. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel to give the title compound (1.5 g, 30%) as a colorless oil, R_f 0.28 (hexane–ethyl acetate = 5:1). ¹H NMR (400 MHz, CDCl₃) δ 7.61 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.48 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.43 (td, *J* = 7.4, 1.3 Hz, 1H), 7.31 (td, *J* = 7.3, 1.5 Hz, 1H), 7.25–7.15 (m, 3H), 7.13–7.08 (m, 2H), 6.04 (d, *J* = 1.4 Hz, 1H), 5.71 (d, *J* = 1.4 Hz, 1H), 4.73 (s, 2H), 1.55 (br s, 1H), 0.48 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 152.0, 146.5, 143.6, 135.8, 135.3, 129.9, 128.8, 128.2, 128.1, 127.1, 126.72, 126.65, 65.2, -0.8; IR (neat) 3339, 3055, 2955, 1597, 1489, 1439, 1408, 1250, 1200, 1124, 1078, 1028, 934, 831, 812, 781, 754, 708, 633 cm⁻¹; MS (EI, 70 eV) *m/z* (%) 268 (M⁺, 0.2), 253 (6), 235 (25), 209 (10), 166 (15), 165 (100), 163 (22), 149 (32), 148 (11), 147 (60), 145 (23), 137 (22), 135 (12), 104 (20); Anal. Calcd for C₁₇H₂₀OSi; C, 76.07; H, 7.51. Found: C, 76.31; H, 7.48.

Preparation of [2-(hydroxymethyl)phenyl]dimethyl(2-methyl-1-propenyl)silane (1h).

A 0.5 M THF solution of 2-methyl-1-propenylmagnesium bromide (100 mL, 50 mmol) was added to a solution of **3** (7.5 g, 46 mmol) in THF (50 mL) at 0 °C, and the resulting mixture was stirred at rt overnight before dilution with diethyl ether. The mixture was washed with a saturated NH₄Cl aqueous solution, water, and brine and dried over anhydrous MgSO₄. After removal of the solvents in vacuo, flash chromatography on neutral aluminum oxide (activity grade III) gave the title compound (7.1 g, 71%) as a colorless oil, *R*_f 0.26 (hexane–ethyl acetate = 5:1). ¹H NMR (400 MHz, C₆D₆) δ 7.57 (d, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 5.41 (s, 1H), 4.63 (d, *J* = 5.9 Hz, 2H), 1.78 (t, *J* = 5.9 Hz, 1H), 1.66 (s, 3H), 1.46 (s, 3H), 0.37 (s, 6H); ¹³C NMR (101 MHz, C₆D₆) δ 153.4, 147.3, 137.5, 134.9, 129.7, 128.0, 127.0, 123.8, 65.3, 29.3, 23.2, 0.0; IR (neat) 3238, 2953, 2907, 1620, 1437, 1371, 1246, 1123, 1076, 1036, 858, 833, 816, 800, 773, 745, 700, 644, 459 cm⁻¹; MS (EI, 70 eV) *m/z* (%) 220 (M⁺, 0.04), 205 (10), 165 (28), 164 (32), 163 (17), 150 (14), 149 (100), 148 (10), 147 (25), 145 (30), 135 (10), 105 (10), 75 (27), 61 (16); Anal. Calcd for C₁₃H₂₀OSi; C, 70.85; H, 9.15. Found: C, 70.83; H, 9.23.

Preparation of [2-(hydroxymethyl)phenyl]dimethyl(phenyl)silane (2a).

A 1.0 M solution of phenylmagnesium bromide (65 mL, 65 mmol) in THF was added over 15 min to a solution of **3** (9.9 g, 60 mmol) in diethyl ether (250 mL) at –78 °C, and the mixture was stirred at –78 °C for 2 h and then at rt overnight. The reaction was quenched with a saturated NH₄Cl aqueous solution (40 mL) at 0 °C. The aqueous layer was extracted with diethyl ether (2 x 60 mL), and the combined organic layers were washed with water (2 x 75 mL) and brine (50 mL) and dried over anhydrous MgSO₄. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford **2a** (13.8 g, 95%) as a colorless solid (mp 53–54 °C), *R*_f 0.39 (hexane–ethyl acetate = 4:1). ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.54–7.41 (m, 4H), 7.41–7.29 (m, 4H), 4.54 (s, 2H), 1.38–1.22 (br s, 1H), 0.62 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 146.5, 139.0, 135.8, 135.5, 133.8, 130.0, 129.2, 128.1, 128.0, 127.0, 65.3, –1.1; IR (KBr) 3298, 2953, 1427, 1250, 1111, 1076, 1018, 826, 777, 739, 702, 640, 482, 419 cm⁻¹; MS (EI, 70 eV) *m/z* (%) 243 (M⁺, 0.1), 227 (39), 211 (12), 210 (21), 209 (100), 165 (47), 164 (11), 149 (28), 147 (18), 135 (11), 105 (12); Anal. Calcd for C₁₅H₁₈OSi; C, 74.33; H, 7.49. Found: C, 74.18; H, 7.52.

Preparation of [2-(hydroxymethyl)phenyl]dimethyl(4-fluorophenyl)silane

(2b). Following the procedure for **2a**, the reaction using a 2.0 M Et₂O solution of 4-fluorophenylmagnesium bromide (17 mL, 33 mmol) and **3** (4.9 g, 30 mmol) gave the title compound (6.8 g, 86%) as a colorless oil, *R*_f 0.17 (hexane–ethyl acetate = 4:1). ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 7.7 Hz, 1H),

7.51–7.41 (m, 4H), 7.32 (td, *J* = 7.0, 1.8 Hz, 1H), 7.08–7.01 (m, 2H), 4.54 (s, 2H), 1.44 (br s, 1H), 0.61 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 163.7 (d, *J* = 248.4 Hz), 146.5, 135.8 (d, *J* = 7.6 Hz), 135.5, 134.4 (d, *J* = 3.8 Hz), 130.1, 128.0, 127.1, 115.2 (d, *J* = 19.9 Hz), 65.2, –0.9; IR (neat) 3331, 2955, 1587, 1499, 1261, 1250, 1231, 1163, 1103, 1078, 826, 812, 775, 756, 517 cm^{–1}; MS (EI, 70 eV) *m/z* (%) 245 (M⁺–Me, 87), 243 (14), 229 (14), 228 (22), 227 (100), 183 (10), 149 (24), 147 (12), 79 (11); Anal. Calcd for C₁₅H₁₇FOSi; C, 69.19; H, 6.58. Found: C, 69.19; H, 6.58.

Preparation of [2-(hydroxymethyl)phenyl]dimethyl(2-methylphenyl)silane (2c).

Following the procedure for **2a**, the reaction using **3** (4.9 g, 30 mmol) and a 2.0 M solution of 2-methylphenylmagnesium bromide in THF (17 mL, 33 mmol) gave the title compound (7.6 g, 99%) as a colorless oil, *R*_f 0.36 (hexane–ethyl acetate = 5:1).

¹H NMR (400 MHz, CDCl₃) δ 7.64–7.55 (m, 2H), 7.45–7.39 (m, 2H), 7.35–7.30 (m, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 4.46 (s, 2H), 2.17 (s, 3H), 1.34 (br s, 1H), 0.64 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 146.3, 143.8, 137.0, 136.7, 135.0, 134.6, 130.1, 129.8, 128.3, 127.2, 125.5, 65.2, 22.8, –0.6; IR (neat) 3339, 3055, 2955, 1589, 1437, 1258, 1128, 1078, 1032, 835, 818, 773, 745, 691, 642 cm^{–1}; MS (EI, 70 eV) *m/z* (%) 256 (M⁺, 0.03), 242 (11), 241 (51), 225 (10), 224 (21), 223 (100), 179 (11), 178 (10), 166 (10), 165 (44), 164 (16), 163 (13), 149 (57), 147 (26), 145 (10), 105 (13), 92 (14), 91 (26); Anal. Calcd for C₁₆H₂₀OSi; C, 74.95; H, 7.86. Found: C, 75.24; H, 7.94.

Preparation of [2-(hydroxymethyl)phenyl]dimethyl(2-thienyl)silane (2d).

A solution of 2-thienylmagnesium bromide in THF (23 mL) [prepared from 2-bromothiophene (5.4 g, 33 mmol) and Mg (0.82 g, 34 mmol)]⁴ was added to **3** (4.9 g, 30 mmol) in THF (10 mL) at 0 °C, and the resulting mixture was stirred at rt for 22

h. The mixture was diluted with diethyl ether, washed with a saturated NH₄Cl aqueous solution, water, and brine, and dried over anhydrous MgSO₄. After removal of the solvent in vacuo, flash chromatography on silica gel gave the title compound (5.9 g, 79%) as a colorless oil, *R*_f 0.21 (hexane–ethyl acetate = 5:1). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, *J* = 4.6, 0.9 Hz, 1H), 7.57 (dd, *J* = 7.4, 0.7 Hz, 1H), 7.50–7.41 (m, 2H), 7.34–7.28 (m, 2H), 7.20 (dd, *J* = 4.6, 3.4 Hz, 1H), 4.64 (s,

2H), 1.47 (s, 1H), 0.68 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 146.5, 138.5, 135.6, 135.3, 131.3, 130.2, 128.4, 128.2, 127.1, 65.3, 0.2; IR (neat) 3337, 2955, 1435, 1406, 1252, 1213, 1126, 1080, 991, 833, 812, 777, 754, 710, 654 cm^{-1} ; MS (EI, 70 eV) m/z (%) 233 ($\text{M}^+ - \text{Me}$, 42), 231 (15), 217 (14), 216 (19), 215 (100), 164 (19), 163 (12), 150 (10), 149 (73); Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{OSSi}$; C, 62.85; H, 6.49. Found: C, 62.96; H, 6.49.

(B) Cross-coupling reaction

Cross-coupling of 1a–1h with aryl iodides. A general procedure. To a mixture of K_2CO_3 (304 mg, 2.2 mmol), tri(2-furyl)phosphine (4.6 mg, 20 μmol), and PdCl_2 (1.8 mg, 10 μmol) in DMSO (2.5 mL) were added an alkenylsilane (1.1 mmol) and an aryl iodide (1.0 mmol) sequentially, and the resulting mixture was stirred at 35 $^\circ\text{C}$. After the time specified in Table 1, the mixture was diluted with diethyl ether, washed with water and brine, and dried over anhydrous MgSO_4 . Concentration in vacuo followed by flash chromatography on silica gel afforded the corresponding coupling product in a yield listed in Table 1.

(E)-1-(4-Cyanophenyl)-1-octene (entry 1). A colorless oil, R_f 0.31 (hexane–ethyl acetate = 20:1). ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 6.38–6.35 (m, 2H), 2.24–2.20 (m, 2H), 1.50–1.42 (m, 2H), 1.40–1.25 (m, 6H), 0.92–0.86 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 142.4, 135.5, 132.2, 128.3, 126.3, 119.1, 109.8, 33.1, 31.6, 28.9, 28.8, 22.5, 14.0; IR (neat) 2955, 2928, 2855, 2226, 1649, 1605, 1502, 1466, 1412, 1175, 966, 856, 733, 552 cm^{-1} ; MS (EI, 70 eV) m/z (%) 213 (M^+ , 18), 143 (11), 142 (34), 130 (19), 129 (100), 116 (14), 115 (11); Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{N}$; C, 84.46; H, 8.98. Found: C, 84.37; H, 8.96.

(E)-1-(4-Ethoxycarbonylphenyl)-1-octene (entry 2). A colorless oil, R_f 0.40 (hexane–ethyl acetate = 20:1). ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, J = 7.0 Hz, 2H), 7.38 (d, J = 7.0 Hz, 2H), 6.45–6.32 (m, 2H), 4.37 (q, J = 7.2 Hz, 2H), 2.23 (q, J = 7.2 Hz, 2H), 1.53–1.28 (m, 11H), 0.94–0.86 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.5, 142.4, 134.2, 129.8, 129.0, 128.5, 125.7, 60.8, 33.2, 31.7, 29.1, 28.9, 22.6, 14.3, 14.1; IR (neat) 2957, 2928, 2855, 1715, 1607, 1466, 1412, 1366, 1275, 1177, 1107, 1020, 968, 957, 864, 762, 696 cm^{-1} ; MS (EI, 70 eV) m/z (%) 261 ($\text{M}^+ + 1$, 14), 260 (M^+ , 76), 215 (37), 177 (16), 176 (100), 161 (11), 148 (45), 145 (23), 132 (10), 131 (55), 129 (16), 128 (13), 118 (10), 117 (86), 116 (23), 115 (49), 91 (18); Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2$; C, 78.42; H, 9.29. Found: C, 78.45; H, 9.41.

(E)-1-(4-Acetylphenyl)-1-octene (entry 3). A colorless oil, R_f 0.30 (hexane–ethyl acetate = 20:1). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 6.43–6.33 (m, 2H), 2.57 (s, 3H), 2.23 (q, J = 6.4 Hz, 2H), 1.52–1.42 (m, 2H), 1.40–1.25 (m, 6H), 0.92–0.86 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 197.5, 142.6, 135.3, 134.5, 128.8, 128.7, 125.8, 33.1, 31.7, 29.1, 28.9, 26.5, 22.6, 14.0; IR (neat) 2957, 2926, 2855, 1682, 1603, 1410, 1358, 1267, 1180, 966, 592 cm^{-1} ; MS (EI, 70 eV) m/z (%) 231 ($\text{M}^+ + 1$, 12), 230 (M^+ , 73), 216 (11), 215 (72), 148 (10), 147 (15), 146 (56), 145 (11), 134 (11), 131 (100), 128 (11), 117 (19), 116 (12), 115 (36); Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}$; C, 83.43; H, 9.63. Found: C, 83.72; H, 9.74.

(E)-1-(4-Formylphenyl)-1-octene (entry 4). A colorless oil, R_f 0.30 (hexane–ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3) δ 9.96 (s, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 6.64–6.42 (m, 2H), 2.28–2.22 (m, 2H), 1.53–1.44 (m, 2H), 1.40–1.25 (m, 6H), 0.92–0.86 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.7, 144.1, 135.4, 134.8, 130.1, 128.9, 126.3, 33.2, 31.7, 29.0, 28.9, 22.6, 14.1; IR (neat) 2955, 2926, 2855, 1697, 1603, 1568, 1304, 1213, 1167, 966, 851, 802 cm^{-1} ; MS (EI, 70 eV) m/z (%) 216 (M^+ , 43), 133 (14), 132 (100), 131 (39), 117 (62), 116 (11), 115 (29), 91 (19); Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}$; C, 83.28; H, 9.32. Found: C, 83.40; H, 9.37.

(E)-1-(4-Nitrophenyl)-1-octene (entry 5). A colorless oil, R_f 0.17 (hexane–ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 6.46–6.42 (m, 2H), 2.30–2.20 (m, 2H), 1.54–1.42 (m, 2H), 1.40–1.24 (m, 6H), 0.93–0.87 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 146.3, 144.4, 136.7, 128.0, 126.3, 123.9, 33.2, 31.6, 28.91, 28.87, 22.6, 14.0; IR (neat) 2955, 2928, 2855, 1649, 1597, 1518, 1466, 1342, 1109, 968, 955, 860, 824, 745, 689 cm^{-1} ; MS (EI, 70 eV) m/z (%) 234 ($\text{M}^+ + 1$, 11), 233 (M^+ , 67), 151 (12), 150 (40), 149 (100), 137 (29), 129 (13), 128 (17), 119 (22), 117 (19), 116 (79), 115 (70), 103 (13), 91 (11), 55 (11); HRMS (FAB+) Calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_2$: $[\text{M} + \text{H}]^+$, 234.1494. Found: m/z 234.1497.

(E)-1-(4-Chlorophenyl)-1-octene (entry 6). A colorless oil, R_f 0.60 (hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.26 (s, 4H), 6.33 (dt, J = 15.5, 1.2 Hz, 1H), 6.21 (dt, J = 15.5, 6.8 Hz, 1H), 2.20 (q, J = 6.8 Hz, 2H), 1.52–1.42 (m, 2H), 1.40–1.23 (m, 6H), 0.94–0.88 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 136.4, 132.2, 132.0, 128.54,

128.49, 127.1, 33.0, 31.7, 29.2, 28.9, 22.6, 14.1; IR (neat) 2957, 2926, 2855, 1709, 1491, 1466, 1404, 1092, 1013, 964, 845, 820, 802, 735 cm^{-1} ; MS (EI, 70 eV) m/z (%) 224 ($\text{M}^+ + 2$, 15), 222 (M^+ , 44), 153 (29), 152 (12), 151 (88), 140 (31), 139 (10), 138 (100), 129 (10), 125 (17), 117 (11), 116 (36), 115 (46); HRMS (EI, 70 eV) Calcd for $\text{C}_{14}\text{H}_{19}\text{Cl}$: M^+ , 222.1175. Found: m/z 222.1172.

(*E*)-1-(4-Methoxyphenyl)-1-octene (entry 7). A colorless oil, R_f 0.36 (hexane–ethyl acetate = 50:1). ^1H NMR (400 MHz, CDCl_3) δ 7.28 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 6.33 (d, J = 15.7 Hz, 1H), 6.09 (dt, J = 15.7, 7.0 Hz, 1H), 3.81 (s, 3H), 2.19 (q, J = 7.5 Hz, 2H), 1.50–1.42 (m, 2H), 1.40–1.26 (m, 6H), 0.93–0.88 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.6, 130.8, 129.1, 129.0, 126.9, 113.9, 55.2, 33.0, 31.8, 29.5, 28.9, 22.6, 14.1; IR (neat) 2955, 2926, 2855, 1609, 1510, 1466, 1248, 1175, 1038, 964, 841 cm^{-1} ; MS (EI, 70 eV) m/z (%) 218 (M^+ , 39), 148 (12), 147 (100), 134 (14), 121 (15), 91 (10); Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}$: C, 82.52; H, 10.16. Found: C, 82.52; H, 9.98.

(*E*)-1-[3-(*tert*-Butyldimethylsilyloxymethyl)phenyl]-1-octene

(entry 8). A colorless oil, R_f 0.35 (hexane–ethyl acetate = 50:1).

^1H NMR (400 MHz, CDCl_3) δ 7.30 (s, 1H), 7.25–7.13 (m, 3H), 6.37 (d, J = 15.7 Hz, 1H), 6.22 (dt, J = 15.7, 6.9 Hz, 1H), 4.72 (s, 2H), 2.20 (q, J = 7.7 Hz, 2H), 1.50–1.42 (m, 2H), 1.38–1.26 (m, 6H), 0.95 (s, 9H), 0.39 (t, J = 6.9 Hz, 3H), 0.10 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 141.5, 137.8, 131.2, 129.7, 128.3, 124.49, 124.47, 123.5, 64.9, 33.0, 31.7, 29.3, 28.9, 26.0, 22.6, 18.4, 14.1, –5.2; IR (neat) 2955, 2928, 2856, 1462, 1256, 1105, 1080, 962, 837, 777 cm^{-1} ; MS (EI, 70 eV) m/z (%) 332 (M^+ , 2), 276 (27), 275 (100), 245 (16), 201 (34); Anal. Calcd for $\text{C}_{21}\text{H}_{36}\text{OSi}$: C, 75.84; H, 10.91. Found: C, 75.97; H, 11.13.

(*E*)-1-[3-(Hydroxymethyl)phenyl]-1-octene (entry 9). A colorless oil, R_f

0.30 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.36 (s,

1H), 7.32–7.27 (m, 2H), 7.21–7.18 (m, 1H), 6.38 (d, J = 15.6 Hz, 1H), 6.26 (dt, J = 16.0, 6.8 Hz, 1H), 4.68 (s, 2H), 2.21 (q, J = 7.2 Hz, 2H), 1.51–1.42 (m, 2H), 1.40–1.26 (m, 6H), 0.93–0.87 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 141.0, 138.3, 131.7, 129.4, 128.7, 125.35, 125.32, 124.4, 65.4, 33.0, 31.7, 29.3, 28.9, 22.6, 14.1; IR (neat) 3329, 2955, 2926, 2855, 1466, 1433, 1020, 962, 775, 733, 696 cm^{-1} ; MS (EI, 70 eV) m/z (%) 218 (M^+ , 36), 134 (42), 132 (16), 131 (16), 129 (24), 128 (12), 118 (14), 117 (100), 115 (22), 105 (10), 91 (20); Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}$: C, 82.52; H, 10.16. Found: C, 82.63; H, 10.40.

(E)-1-(2-Methylphenyl)-1-octene (entry 10). A colorless oil, R_f 0.71 (hexane).

^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 7.2$ Hz, 1H), 7.19–7.10 (m, 3H), 6.57 (d, $J = 15.6$ Hz, 1H), 6.10 (dt, $J = 15.6, 6.8$ Hz, 1H), 2.34 (s, 3H), 2.23 (q, $J = 7.2$ Hz, 2H), 1.54–1.42 (m, 2H), 1.40–1.26 (m, 6H), 0.92–0.88 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 137.1, 134.8, 132.6, 130.1, 127.5, 126.7, 126.0, 125.4, 33.3, 31.7, 29.4, 28.9, 22.6, 19.8, 14.1; IR (neat) 3020, 2957, 2926, 2855, 1485, 1460, 1377, 962, 745 cm^{-1} ; MS (EI, 70 eV) m/z (%) 202 (M^+ , 42), 132 (13), 131 (100), 129 (12), 118 (51), 117 (18), 116 (17), 115 (18), 105 (16), 91 (15); Anal. Calcd for $\text{C}_{15}\text{H}_{22}$; C, 89.04; H, 10.96. Found: C, 88.97; H, 11.18.

(E)-1-(1-Naphthyl)-1-octene (entry 11). A colorless oil, R_f 0.50 (hexane).

^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 7.6$ Hz, 1H), 7.84 (d, $J = 7.2$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.58–7.40 (m, 4H), 7.11 (d, $J = 15.2$ Hz, 1H), 6.24 (dt, $J = 16.0, 7.2$ Hz, 1H), 2.33 (q, $J = 7.6$ Hz, 2H), 1.60–1.52 (m, 2H), 1.46–1.32 (m, 6H), 0.94–0.88 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 135.8, 134.6, 133.6, 131.1, 128.4, 127.1, 126.8, 125.74, 125.65, 125.58, 124.0, 123.5, 33.5, 31.8, 29.4, 29.0, 22.7, 14.1; IR (neat) 3059, 3044, 2955, 2926, 2855, 1591, 1508, 1466, 1394, 964, 775, 727 cm^{-1} ; MS (EI, 70 eV) m/z (%) 238 (M^+ , 44), 168 (17), 167 (100), 166 (15), 165 (35), 154 (21), 153 (24), 152 (22), 141 (13); Anal. Calcd for $\text{C}_{18}\text{H}_{22}$; C, 90.70; H, 9.30. Found: C, 90.61; H, 9.32.

(E)-1-(3-Pyridyl)-1-octene (entry 12). A colorless oil, R_f 0.35 (hexane–ethyl acetate = 5:1).

^1H NMR (400 MHz, CDCl_3) δ 8.56 (br s, 1H), 8.42 (br d, $J = 3.7$ Hz, 1H), 7.65 (d, $J = 7.9$ Hz, 1H), 7.22 (dd, $J = 7.8, 4.8$ Hz, 1H), 6.38–6.26 (m, 2H), 2.26–2.20 (m, 2H), 1.52–1.43 (m, 2H), 1.40–1.26 (m, 6H), 0.92–0.86 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 147.8, 147.7, 133.8, 133.5, 132.5, 126.1, 123.4, 33.1, 31.7, 29.1, 28.9, 22.6, 14.1; IR (neat) 3024, 2955, 2926, 2855, 2359, 2341, 1653, 1568, 1466, 1414, 1022, 964, 708 cm^{-1} ; MS (EI, 70 eV) m/z (%) 189 (M^+ , 46), 146 (10), 132 (10), 130 (10), 119 (14), 118 (87), 117 (37), 106 (27), 105 (100), 93 (14), 91 (15); Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{N}$; C, 82.48; H, 10.12. Found: C, 82.20; H, 10.06.

(E)-1-(2-Thienyl)-1-octene (entry 13). A colorless oil, R_f 0.70 (hexane).

^1H NMR (400 MHz, CDCl_3) δ 7.08 (d, $J = 5.2$ Hz, 1H), 6.95–6.91 (m, 1H), 6.86 (d, $J = 3.2$ Hz, 1H), 6.50 (d, $J = 15.6$ Hz, 1H), 6.07 (dt, $J = 15.6, 6.8$ Hz, 1H), 2.17 (q, $J = 7.2$ Hz, 2H), 1.52–1.41 (m, 2H), 1.40–1.24 (m, 6H), 0.94–0.86 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 131.3, 127.2, 124.1, 123.0, 122.9, 108.2, 32.9, 31.7, 29.2, 28.9, 22.6, 14.1; IR (neat) 2955, 2926,

2855, 1724, 1686, 1676, 1466, 1437, 1420, 1377, 1211, 1042, 953, 853, 723, 692 cm^{-1} ; MS (EI, 70 eV) m/z (%) 194 (M^+ , 41), 147 (10), 124 (12), 123 (100), 110 (46), 97 (14), 73 (18); HRMS (EI, 70 eV) Calcd for $\text{C}_{12}\text{H}_{18}\text{S}$: M^+ , 194.1129. Found: m/z 194.1126.

(E)-6-(4-Ethoxycarbonylphenyl)-5-hexenenitrile (entry 14).

A colorless oil, R_f 0.30 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, J = 6.4 Hz, 2H), 7.39 (d, J = 6.8 Hz, 2H), 6.50 (d, J = 16.0 Hz, 1H), 6.31–6.22 (m, 1H), 4.36 (q, J = 7.2 Hz, 2H), 2.44–2.38 (m, 4H), 1.86 (m, 4H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.4, 141.4, 131.2, 130.4, 129.9, 129.1, 125.9, 119.4, 60.9, 31.7, 24.8, 16.5, 14.3; IR (neat) 2984, 2937, 2907, 2243, 1711, 1607, 1458, 1437, 1414, 1366, 1271, 1180, 1126, 1109, 1092, 1024, 968, 955, 768, 750, 694 cm^{-1} ; MS (EI, 70 eV) m/z (%) 244 ($\text{M}^+ + 1$, 14), 243 (M^+ , 81), 199 (15), 198 (100), 197 (16), 196 (19), 170 (12), 157 (14), 145 (15), 130 (14), 129 (43), 128 (22), 117 (57), 116 (16), 115 (40); HRMS (EI, 70 eV) Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2$: M^+ , 243.1259. Found: m/z 243.1259.

(E)-4-Ethoxycarbonylstilbene (entry 15).

A colorless solid (mp 106.0–106.5 $^{\circ}\text{C}$), R_f 0.30 (hexane–ethyl acetate = 20:1). ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 8.4 Hz, 2H), 7.58–7.52 (m, 4H), 7.41–7.36 (m, 2H), 7.32–7.27 (m, 1H), 7.22 (d, J = 16.4 Hz, 1H), 7.13 (d, J = 16.4 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.4, 141.7, 136.7, 131.1, 130.0, 129.2, 128.8, 128.2, 127.6, 126.8, 126.3, 60.9, 14.4; IR (KBr) 2976, 1705, 1607, 1367, 1283, 1180, 1130, 1109, 1024, 976, 770, 696, 527 cm^{-1} ; MS (EI, 70 eV) m/z (%) 253 ($\text{M}^+ + 1$, 20), 252 (M^+ , 100), 208 (12), 207 (65), 180 (10), 179 (54), 178 (57); Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2$: C, 80.93; H, 6.39. Found: C, 81.18; H, 6.27.

Ethyl 4-(propen-1-yl)benzoate [(Z):(E) = 94:6] (entry 16).

A colorless oil, R_f 0.33 (hexane–ethyl acetate = 20:1). [Spectra of (Z)-isomer] ^1H NMR (400 MHz, CDCl_3) δ 8.01 (dd, J = 8.4 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 6.46 (dd, J = 11.8, 1.8 Hz, 1H), 5.90 (dq, J = 11.8, 7.2 Hz, 1H), 4.38 (q, J = 7.2 Hz, 2H), 1.91 (dd, J = 7.2, 1.8 Hz, 3H), 1.40 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.5, 142.2, 129.4, 129.1, 129.0, 128.7, 128.3, 60.8, 14.8, 14.3; IR (neat) 2980, 1715, 1609, 1367, 1310, 1277, 1178, 1105, 1020, 866, 773, 733, 721, 700 cm^{-1} ; MS (EI, 70 eV) m/z (%) 190 (M^+ , 50), 162 (12), 146 (13), 145 (100), 117 (20), 115 (25), 91 (10); Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$: C, 75.76; H, 7.42. Found: C, 75.90; H, 7.44.

Ethyl 4-(propen-2-yl)benzoate (entry 17). A colorless oil, R_f 0.40 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.00 (dd, J = 8.0 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 5.47 (dq, J = 1.3, 0.7 Hz, 1H), 5.19 (qd, J = 1.5, 1.3 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 2.17 (dd, J = 1.5, 0.7 Hz, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.7, 145.8, 142.7, 129.8, 129.5, 125.6, 114.7, 61.1, 21.9, 14.6; IR (neat) 2980, 2359, 2341, 1715, 1609, 1367, 1275, 1184, 1123, 1103, 1020, 899, 860, 783, 719 cm^{-1} ; MS (EI, 70 eV) m/z (%) 190 (M^+ , 42), 162 (19), 146 (13), 145 (100), 115 (20); HRMS (FAB+) Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$: M^+ , 190.0994. Found: m/z 190.0993.

1-(4-Ethoxycarbonylphenyl)-1-phenylethene (entry 18). A colorless solid (mp 46.7–47.3 °C), R_f 0.33 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.36–7.30 (m, 5H), 5.55 (d, J = 1.1 Hz, 1H), 5.54 (d, J = 1.1 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.4, 149.3, 145.9, 140.8, 129.7, 129.5, 128.3, 128.2, 128.0, 115.8, 60.9, 14.3; IR (KBr) 1717, 1279, 1105, 775, 702 cm^{-1} ; MS (EI, 70 eV) m/z (%) 253 (M^+ +1, 18), 252 (M^+ , 97), 224 (14), 208 (18), 207 (100), 179 (44), 178 (68), 177 (11), 176 (11); Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2$: C, 80.93; H, 6.39. Found: C, 81.01; H, 6.47.

1-(4-Methoxyphenyl)-1-phenylethene (entry 19). A colorless solid (mp 75.3–76.8 °C), R_f 0.39 (hexane–ethyl acetate = 15:1). ^1H NMR (400 MHz, CDCl_3) δ 7.38–7.31 (m, 5H), 7.28 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.41 (d, J = 1.4 Hz, 1H), 5.36 (d, J = 1.4 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.6, 149.7, 142.0, 134.2, 129.6, 128.6, 128.4, 127.9, 113.7, 113.2, 55.5; IR (KBr) 3005, 2951, 2835, 1908, 1811, 1605, 1572, 1508, 1491, 1456, 1441, 1290, 1250, 1180, 1028, 901, 843, 785, 708, 581, 552 cm^{-1} ; MS (EI, 70 eV) m/z (%) 253 (M^+ +1, 18), 252 (M^+ , 97), 224 (14), 208 (18), 207 (100), 179 (44), 178 (68), 177 (11), 176 (11); Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{O}$: C, 85.68; H, 6.71. Found: C, 85.67; H, 6.73.

(E)-4-(4-Ethoxycarbonylphenyl)-4-octene (entry 20). A colorless oil, R_f 0.40 (hexane–ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 8.6 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 5.76 (t, J = 7.3 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 2.49 (t, J = 7.5 Hz, 2H), 2.19 (q, J = 7.3 Hz, 2H), 1.53–1.42 (m, 2H), 1.41–1.32 (m, 5H), 0.97 (t, J = 7.3 Hz, 3H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz,

CDCl₃) δ 166.6, 148.0, 139.4, 131.1, 129.5, 128.4, 126.2, 60.8, 31.4, 30.7, 22.9, 21.8, 14.4, 14.0, 13.9; IR (neat) 2959, 2932, 2872, 1720, 1607, 1462, 1408, 1366, 1273, 1180, 1107, 1020, 858, 772, 706 cm⁻¹; MS (EI, 70 eV) m/z (%) 261 (M⁺+1, 15), 260 (M⁺, 79), 231 (16), 217 (44), 215 (31), 190 (21), 189 (15), 187 (51), 173 (30), 159 (16), 157 (13), 146 (13), 145 (100), 143 (17), 131 (35), 130 (15), 129 (46), 128 (32), 127 (10), 117 (63), 116 (11), 115 (31), 91 (19); Anal. Calcd for C₁₇H₂₄O₂; C, 78.42; H, 9.29. Found: C, 78.28; H, 9.14.

1-(4-Ethoxycarbonylphenyl)-2-methylpropene (entry 21). A colorless oil, R_f 0.38 (hexane–ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 6.29 (s, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.93 (s, 3H), 1.88 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.6, 143.3, 137.9, 129.3, 128.5, 127.7, 124.6, 60.8, 27.1, 19.6, 14.3; IR (neat) 2980, 1715, 1607, 1410, 1366, 1275, 1178, 1103, 1020, 878, 760, 706 cm⁻¹; MS (EI, 70 eV) m/z (%) 205 (M⁺+1, 11), 204 (M⁺, 78), 160 (14), 159 (100), 131 (32), 116 (12), 115 (19), 91 (16); Anal. Calcd for C₁₃H₁₆O₂; C, 76.44; H, 7.90. Found: C, 76.24; H, 7.99.

(5E,7E)-Tetradeca-5,7-dienitrile (entry 22). A colorless oil, R_f 0.42 (hexane–ethyl acetate = 5:1). ¹H NMR (400 MHz, CDCl₃) δ 6.11–5.94 (m, 2H), 5.63 (dt, J = 14.6, 7.0 Hz, 1H), 5.46 (dt, J = 14.8, 7.0 Hz, 1H), 2.34 (t, J = 7.1 Hz, 2H), 2.22 (q, J = 7.1 Hz, 2H), 2.06 (dt, J = 7.1, 7.0 Hz, 2H), 1.80–1.71 (m, 2H), 1.45–1.20 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 134.1, 132.6, 129.6, 128.5, 119.6, 32.6, 31.7, 31.2, 29.2, 28.9, 25.0, 22.6, 16.3, 14.1; IR (neat) 3017, 2957, 2926, 2855, 2247, 1456, 1437, 989, 733 cm⁻¹; MS (EI, 70 eV) m/z (%) 206 (M⁺+1, 10), 205 (M⁺, 59), 204 (M⁺–1, 13), 177 (37), 176 (34), 162 (13), 148 (36), 135 (16), 134 (100), 121 (29), 120 (60), 107 (15), 106 (16), 95 (15), 94 (26), 93 (52), 91 (25), 83 (21), 82 (10), 81 (67), 80 (45), 79 (39), 77 (22), 67 (45), 55 (15); Anal. Calcd for C₁₄H₂₃N; C, 81.89; H, 11.29. Found: C, 82.18; H, 11.56.

(5E,7Z)-Tetradeca-5,7-dienitrile (entry 23). A colorless oil, R_f 0.36 (hexane–ethyl acetate = 7:1). ¹H NMR (400 MHz, CDCl₃) δ 6.37 (ddq, J = 15.1, 10.9, 1.3 Hz, 1H), 5.94 (t, J = 10.9 Hz, 1H), 5.55 (dt, J = 15.0, 7.6 Hz, 1H), 5.37 (dt, J = 10.9, 7.6 Hz, 1H), 2.35 (t, J = 7.1 Hz, 2H), 2.27 (m, 2H), 2.16 (m, 2H), 1.77 (m, 2H), 1.41–1.21 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 131.7, 130.8, 127.84, 127.81, 119.6, 31.7, 31.5, 29.6, 28.9, 27.7, 25.0, 22.6, 16.4, 14.1; IR (neat) 3020, 2957, 2928, 2855,

2247, 1456, 984, 949, 735 cm^{-1} ; MS (EI, 70 eV) m/z (%) 205 (M^+ , 43), 204 (M^+-1 , 11), 177 (51), 176 (40), 162 (14), 148 (40), 135 (15), 134 (100), 121 (30), 120 (70), 107 (16), 106 (19), 95 (16), 94 (29), 93 (50), 91 (26), 83 (31), 82 (12), 81 (79), 80 (53), 79 (44), 77 (25), 67 (53), 55 (19), 54 (10); Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{N}$; C, 81.89; H, 11.29. Found: C, 82.19; H, 11.18.

Gram-scale cross-coupling reaction. To a mixture of K_2CO_3 (9.1 g, 66 mmol), tri(2-furyl)phosphine (138 mg, 0.60 mmol), and PdCl_2 (54 mg, 0.30 mmol) in DMSO (75 mL) were added **1a** (9.1 g, 33 mmol) and ethyl 4-iodobenzoate (8.3 g, 30 mmol) sequentially, and the resulting mixture was stirred at 35 °C for 21 h. The mixture was diluted with diethyl ether, washed with water and brine, and dried over anhydrous MgSO_4 . Concentration in vacuo followed distillation under vacuum (1.0 mmHg) gave cyclic silyl ether **3** (3.1 g, 62%); the residue was further purified by flash chromatography on silica gel to give (*E*)-1-(4-ethoxycarbonylphenyl)-1-octene (7.6 g, 97%)

Cross-coupling of 2a–2d with aryl iodides. A general procedure. To a mixture of an arylsilane (0.81 mmol), K_2CO_3 (194 mg, 1.4 mmol), *N*-(2-diphenylphosphinobenzylidene)cyclohexylamine (**4**) (10.4 mg, 28 μmol), and PdCl_2 (3.7 mg, 21 μmol) in DMSO (4.0 mL) were added an aryl iodide (0.7 mmol) and water (25 mg, 1.4 mmol) sequentially, and the resulting mixture was stirred at 50 °C. After the time specified in Table 2, the mixture was diluted with diethyl ether, washed with water and brine, and dried over anhydrous MgSO_4 . Concentration in vacuo followed by flash chromatography on silica gel afforded the corresponding coupling product in a yield listed in Table 2. The spectra of the biaryls shown in entries 1–5 agreed well with those reported by us recently.⁵

4-Fluoro-4'-ethoxycarbonylbiphenyl (entry 6). A colorless solid (mp 64.6–65.4 °C), R_f 0.33 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, J = 8.5 Hz, 2H), 7.64–7.55 (m, 4H), 7.16 (t, J = 8.8 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.4, 162.9 (d, J = 247.7 Hz), 144.5, 136.2, 130.1, 129.2, 128.9 (d, J = 8.4 Hz), 126.8, 115.8 (d, J = 22.2 Hz), 61.0, 14.3; IR (KBr) 2990, 1717, 1599, 1528, 1495, 1367, 1279, 1238, 1190, 1113, 1026, 833, 772 cm^{-1} ; MS (EI, 70 eV) m/z (%) 245 (M^++1 , 10), 244 (M^+ , 60), 216 (23), 200 (17), 199 (100); Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{FO}_2$; C, 73.76; H, 5.36. Found: C, 73.49; H, 5.34.

4-Ethoxycarbonyl-2'-methylbiphenyl (entry 7). A colorless oil, R_f 0.19 (hexane–ethyl acetate = 20:1). ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.31–7.21 (m, 4H), 4.41 (q, J = 7.1 Hz, 2H), 2.27 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.6, 146.6, 140.9, 135.2, 130.5, 129.5, 129.4, 129.2, 128.9, 127.8, 125.9, 61.0, 20.4, 14.4; IR (neat) 2980, 1715, 1611, 1481, 1400, 1367, 1277, 1178, 1101, 1026, 1007, 858, 779, 754, 727, 708 cm^{-1} ; MS (EI, 70 eV) m/z (%) 241 ($\text{M}^+ + 1$, 14), 240 (M^+ , 77), 212 (15), 196 (18), 195 (100), 167 (30), 166 (16), 165 (39), 152 (25); Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2$; C, 79.97; H, 6.71. Found: C, 79.83; H, 6.76.

2-(4-Ethoxycarbonylphenyl)thiophene (entry 8). A colorless solid (mp 66.3–67.3 °C), R_f 0.36 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, J = 8.6 Hz, 2H), 7.67 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 3.7 Hz, 1H), 7.36 (d, J = 5.1 Hz, 1H), 7.12 (dd, J = 5.1, 3.7 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.3, 143.1, 138.5, 130.2, 129.1, 128.3, 126.2, 125.5, 124.4, 61.0, 14.3; IR (KBr) 3094, 3067, 2999, 2976, 2359, 1697, 1605, 1462, 1425, 1412, 1366, 1317, 1277, 1263, 1184, 1169, 1111, 1016, 862, 773, 727, 710, 698 cm^{-1} ; MS (EI, 70 eV) m/z (%) 233 ($\text{M}^+ + 1$, 10), 232 (M^+ , 84), 204 (25), 188 (15), 187 (100), 159 (13); Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}$; C, 67.21; H, 5.21. Found: C, 67.01; H, 5.25.

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CCCCC/C=C/c1ccc([N+](=O)[O-])cc1

entry 5 of Table 1

¹³C NMR (101 MHz)

4929-59-04-074

Pulse Sequence: s2pul

entry 5 of Table 1

¹H NMR (400 MHz)

entry 6 of Table 1

Pulse Sequence: s2pul

4929-59-04-076

¹³C NMR (101 MHz)

entry 6 of Table 1

¹H NMR (400 MHz)

entry 13 of Table 1

4930-59-04-092c fr.5-9

Pulse Sequence: s2pul

¹³C NMR (101 MHz)

4930-59-04-092c fr. 5-9

Pulse Sequence: s2pul

entry 13 of Table 1

^1H NMR (400 MHz)

entry 14 of Table 1

¹³C NMR (101 MHz)

4y11-59-04-152

Pulse Sequence: s2pul

entry 14 of Table 1

¹H NMR (400 MHz)

entry 17 of Table 1

¹³C NMR (101 MHz)

entry 17 of Table 1