Nickel Catalyzed Dealkoxylating $\text{C}_{\text{sp2}}$-$\text{C}_{\text{sp3}}$ Cross Coupling Reactions - Stereospecific Synthesis of Allylsilanes from Enol Ethers

Supporting Information

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**General:** Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were technical grade and distilled prior to use. Toluene used in reactions was analytical grade and distilled from benzophenone/Na. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel (Macherey Nagel, particle size 0.040-0.063 mm). Solvent mixtures are understood as volume/volume. 

$^1$H-NMR and $^{13}$C-NMR were recorded on a Varian AV300, AV400 or AV600 spectrometer in CDCl$_3$ and are reported relative to the solvents residual $^1$H-signal (CHCl$_3$, δ(H) 7.26). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm$^{-1}$).

**General procedure for dealkoxylating cross coupling reactions:**

An oven-dried reaction tube containing a stirring bar was charged with enol ether substrate (if solid; 0.25 mmol), yellow Ni(COD)$_2$ (3.4 mg, 5 mol%) and NHC ligand (if needed; 5 mol%) under argon. The tube was immediately sealed and again flushed with argon. Subsequently, freshly distilled toluene (1.5 mL), enol ether (if liquid) and a LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL) were added under argon atmosphere by a syringe and the reaction mixture was stirred at the corresponding temperature for the indicated time. Upon purification via column chromatography (elution with hexane:EtOAc = 40:1) the pure product was obtained after solvent removal.

*(E)-Trimethyl(3-(naphthalen-2-yl)allyl)silane (3a)*

Prepared according to the general procedure using *(E)-2-(2-methoxyvinyl)naphthalene (46.1 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a white solid, mp = 62.0 – 63.0 °C. Analytical data were in accordance with those reported in literature.$^1$

$^1$H NMR (400 MHz, CDCl$_3$): δ = 7.80 – 7.74 (m, 3H), 7.64 (s, 1H), 7.57 (dd, J = 8.5, 1.3 Hz, 1H), 7.47 – 7.37 (m, 2H), 6.45 – 6.35 (m, 2H), 1.77 – 1.73 (m, 2H), 0.10 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 136.0, 133.9, 132.5, 128.5, 128.5, 128.0, 127.8, 127.7, 126.2, 125.2, 124.6, 123.6, 24.3, 1.7; IR (ATR): $\tilde{\nu}$ = 2952, 1627, 1403, 1242, 1144, 962, 837, 749, 690 cm$^{-1}$; EI-MS: m/z = 240.1 (M$^+$, 20), 165.1 (10), 73.2 (TMS$^+$, 100).
(3,4-Dihyronaphthalen-1-yl)methyltrimethylsilane (3b)

Prepared according to the general procedure using 4-methoxy-1,2-dihyronaphthalene (40.1 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil. Analytical data were in accordance with those reported in literature.$^2$

$^1$H NMR (600 MHz, CDCl$_3$): δ = 7.23 - 7.17 (m, 2H), 7.14 - 7.12 (m, 2H), 5.70 (t, $J$ = 4.6 Hz, 1H), 2.75 - 2.72 (m, 2H), 2.26 - 2.21 (m, 2H), 1.94 (s, 2H), 0.01 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ = 136.9, 135.9, 134.3, 127.4, 126.5, 126.0, 123.5, 122.9, 29.0, 23.3, 22.4, -1.0; IR (ATR): $\tilde{\nu}$ = 2941, 1738, 1424, 1366, 1244, 844, 752 cm$^{-1}$; EI-MS: m/z = 216.2 (M$^+$, 7), 129.1 (40), 128.1 (33), 115.1 (40), 73.2 (TMS$^+$, 100).

((6,7-Dihydro-5H-benzo[7]annulen-9-yl)methyl)trimethylsilane (3c)

Prepared according to the general procedure using 9-methoxy-6,7-dihydro-5H-benzo[7]annulene (43.6 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$): δ = 7.28 - 7.09 (m, 4H), 5.76 (t, $J$ = 7.2 Hz, 1H), 2.54 (t, $J$ = 7.0 Hz, 2H), 2.09 - 1.99 (m, 2H), 1.94 (s, 2H), 1.76 (q, $J$ = 7.2 Hz, 2H), -0.17 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 142.4, 140.8, 139.1, 128.8, 126.6, 126.4, 125.9, 123.6, 34.9, 32.7, 27.2, 24.8, -1.3; IR (ATR): $\tilde{\nu}$ = 2926, 2854, 1444, 1247, 845, 752, 692 cm$^{-1}$; EI-MS: m/z = 229.2 (M$^+$, 4), 73.2 (TMS$^+$, 100), 57.3 (56).

(Z)-Trimethyl(3-(naphthalen-2-yl)allyl)silane (3d)

Prepared according to the general procedure using (Z)-2-(2-methoxyvinyl)naphthalene (46.1 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$): 7.83 - 7.76 (m, 4H), 7.51 - 7.41 (m, 3H), 6.50 (d, $J$ = 11.7 Hz, 1H), 5.83 (dt, $J$ = 11.7, 9.1 Hz, 1H), 1.94 (dd, $J$ = 9.1, 1.5 Hz, 2H), 0.08 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 135.9, 133.5, 132.1, 129.7, 127.9, 127.7, 127.6, 127.4, 127.1, 126.9, 126.0, 125.5, 20.0, -1.4; IR (ATR): $\tilde{\nu}$ = 2953, 1719, 1487, 1368, 1248, 1149, 845, 735 cm$^{-1}$; EI-MS: m/z = 240.1 (M$^+$, 73), 73.1 (TMS$^+$, 100).
(3,3-Diphenylallyl)trimethylsilane (3e)

Prepared according to the general procedure using (2-methoxyethene-1,1-diyl) dibenzene (52.6 mg, 0.25 mmol), Ni(COD)_2 (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH_2SiMe_3 solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil.

^1H NMR (400 MHz, CDCl_3): δ = 7.42 – 7.35 (m, 2H), 7.34 – 7.15 (m, 8H), 6.18 (t, J = 8.8 Hz, 1H), 1.65 (d, J = 8.8 Hz, 2H), 0.02 (s, 9H); ^13C NMR (100 MHz, CDCl_3): δ = 143.4, 140.6, 139.7, 130.4, 128.3, 128.1, 127.0, 126.7, 126.5, 126.4, 21.1, -1.4; IR (ATR): ν = 3023, 2953, 1740, 1246, 842, 759, 696 cm⁻¹; EI-MS: m/z = 266.1 (M⁺, 93), 251.1 (40), 73.2 (TMS⁺, 100).

(2-(9H-Fluoren-9-ylidene)ethyl)trimethylsilane (3f)

Prepared according to the general procedure using 9-(methoxymethylene)-9H-fluorene (59.1 mg, 0.25 mmol), Ni(COD)_2 (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH_2SiMe_3 solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 0.5 h at room temperature. Isolated as a yellow oil.

^1H NMR (400 MHz, CDCl_3): 7.91 (d, J = 7.2 Hz, 1H), 7.82 – 7.62 (m, 3H), 7.39 – 7.26 (m, 4H), 6.93 (t, J = 9.9 Hz, 1H), 2.42 (d, J = 9.9 Hz, 2H), 0.13 (s, 9H); ^13C NMR (100 MHz, CDCl_3): δ = 140.5, 139.9, 138.0, 137.8, 132.8, 129.5, 127.0, 126.7, 126.6, 124.5, 119.8, 119.5, 119.2, 22.9, -1.1; IR (ATR): ν = 3023, 2953, 1717, 1635, 1443, 1248, 841, 730 cm⁻¹; EI-MS: m/z = 264.1 (M⁺, 25), 189.0 (13), 73.2 (TMS⁺, 100).

(2-(9H-Xanthen-9-ylidene)ethyl)trimethylsilane (3g)

Prepared according to the general procedure using 9-(methoxymethylene)-9H-xanthen (56.1 mg, 0.25 mmol), Ni(COD)_2 (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH_2SiMe_3 solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a yellow oil.

^1H NMR (300 MHz, CDCl_3): 7.47 (dd, J = 7.8, 1.6 Hz, 1H), 7.32 (dd, J = 8.0, 1.5 Hz, 1H), 7.15 – 6.93 (m, 6H), 5.85 (t, J = 9.5 Hz, 1H), 1.96 (d, J = 9.5 Hz, 2H), 0.00 (s, 9H); ^13C NMR (75 MHz, CDCl_3): δ = 153.1, 151.4, 134.9, 128.0, 127.6, 127.1, 126.8, 124.5, 124.4, 123.7, 123.4, 122.6, 116.8, 116.3, 20.7, -1.2; IR (ATR): ν = 2953, 1733, 1604, 1452, 1243, 1030, 844, 753 cm⁻¹; EI-MS: m/z = 280.4 (M⁺, 33), 207 (98), 198.3 (51), 197.3 (100), 73.3 (TMS⁺, 100).

(3-Butylhept-2-en-1-yl)trimethylsilane (3h)

Prepared according to the general procedure using 5-(methoxymethylene)nonane (42.6 mg, 0.25 mmol), Ni(COD)_2 (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH_2SiMe_3 solution (1.0 M in
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de, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil.

**1H NMR** (300 MHz, CDCl₃): δ = 5.13 (t, J = 8.5 Hz, 1H), 2.00 – 1.93 (m, 4H), 1.44 – 1.22 (m, 10H), 0.95 – 0.86 (m, 6H), -0.01 (s, 9H); **13C NMR** (75 MHz, CDCl₃): δ = 137.5, 119.8, 36.8, 30.9, 30.6, 29.3, 23.1, 22.6, 18.3, 14.2, 14.1, -1.6; **IR** (ATR): ν = 2948, 2866, 1739, 1455, 1369, 1243, 844, 754, 693 cm⁻¹; **EI-MS**: m/z = 225.5 (M⁺, 17), 75.3 (19), 73.3 (TMS⁺, 100).

(2-((Dihydro-2H-thiopyran-4(3H)-ylidene)ethyl)trimethylsilane (3i)

Prepared according to the general procedure using 4-((methoxymethylene)tetrahydro-2H-thiopyran (36.1 mg, 0.25 mmol), Ni(COD)₂ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH₂SiMe₃ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil.

**1H NMR** (300 MHz, CDCl₃): δ = 5.21 (t, J = 8.6 Hz, 1H), 2.66 – 2.56 (m, 4H), 2.48 – 2.39 (m, 4H), 1.40 (d, J = 8.6 Hz, 2H), -0.01 (s, 9H); **13C NMR** (75 MHz, CDCl₃): δ = 133.6, 120.5, 39.1, 31.3, 30.3, 30.1, 17.8, -1.6; **IR** (ATR): ν = 2947, 1739, 1366, 1219, 845 cm⁻¹; **EI-MS**: m/z = 200.4 (M⁺, 20), 85.3 (47), 83 (50), 73.4 (TMS⁺, 100), 57.4 (66).

1-Benzyl-4-((2-(trimethylsilyl)ethylidene)piperidine (3j)

Prepared according to the general procedure using 1-benzyl-4-((methoxymethylene)piperidine (54.3 mg, 0.25 mmol), Ni(COD)₂ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH₂SiMe₃ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a light yellow oil.

**1H NMR** (400 MHz, CDCl₃): δ = 7.36 – 7.21 (m, 5H), 5.15 (t, J = 8.6 Hz, 1H), 3.50 (s, 2H), 2.43 – 2.37 (m, 4H), 2.23 – 2.18 (m, 4H), 1.39 (d, J = 8.6 Hz, 2H), -0.02 (s, 9H); **13C NMR** (100 MHz, CDCl₃): δ = 138.7, 133.4, 129.2, 128.2, 127.0, 118.2, 63.3, 55.7, 54.6, 36.2, 28.0, 17.9 -1.7; **IR** (ATR): ν = 2950, 1697, 1484, 1363, 1248, 1152, 845, 739, 694 cm⁻¹; **EI-MS**: m/z = 273.1 (M⁺, 100), 272.1 (57), 200.1 (92), 91.1 (57), 73.1 (TMS⁺, 35).

(2-Cyclohexylideneethyl)trimethylsilane (3k)

Prepared according to the general procedure using (methoxymethylene)cyclohexane (31.5 mg, 0.25 mmol), Ni(COD)₂ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH₂SiMe₃ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil. Analytical data were in accordance with those reported in literature.³

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**1H NMR** (400 MHz, CDCl₃): δ = 5.07 (t, J = 8.5 Hz, 1H), 2.09 – 2.02 (m, 4H), 1.58 – 1.42 (m, 6H), 1.37 (d, J = 8.5 Hz, 2H), -0.03 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 137.0, 116.8, 37.4, 29.0, 28.5, 27.7, 27.2, 17.8, -1.7; IR (ATR): ν = 2927, 2854, 1443, 1246, 1152, 843, 692 cm⁻¹; EI-MS: m/z = 182.1 (M⁺, 6), 181.1 (21), 99.1 (85), 73.1 (TMS⁺, 100).

**Trimethyl(2-cycloheptylideneethyl)trimethylsilane (3l)**

Prepared according to the general procedure using (methoxymethylene)cycloheptane (35.1 mg, 0.25 mmol), Ni(COD)₂ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH₂SiMe₃ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil.

**1H NMR** (400 MHz, CDCl₃): δ = 5.16 (t, J = 8.5 Hz, 1H), 2.23 – 2.13 (m, 4H), 1.60 – 1.44 (m, 8H), 1.35 (d, J = 8.5 Hz, 2H), -0.02 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 138.8, 120.4, 38.1, 30.2, 30.13, 30.08, 29.6, 27.0, 18.3, -1.5; IR (ATR): ν = 2920, 2855, 1446, 1247, 1152, 840, 759, 692 cm⁻¹; EI-MS: m/z = 196.1 (M⁺, 50), 84.9 (88), 82.9 (100), 73.1 (TMS⁺, 55).

**Trimethyl(2-(naphthalen-2-yl)allyl)silane (3m)**

Prepared according to the general procedure using trimethyl(1-(naphthalen-2-yl)vinyl)oxy)silane (60.6 mg, 0.25 mmol), Ni(COD)₂ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH₂SiMe₃ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a light yellow oil. Analytical data were in accordance with those reported in literature.²

**1H NMR** (600 MHz, CDCl₃): 7.87 – 7.79 (m, 4H), 7.63 (dd, J = 8.6, 1.7 Hz, 1H), 7.51 – 7.45 (m, 2H), 5.33 (d, J = 1.1 Hz, 1H), 5.01 (d, J = 1.1 Hz, 1H), 2.18 (s, 2H), -0.04 (s, 9H); ¹³C NMR (150 MHz, CDCl₃): δ = 146.4, 140.0, 133.4, 132.8, 128.2, 127.7, 127.6, 126.1, 125.8, 125.0, 124.98, 110.8, 26.1, -1.2; IR (ATR): ν = 2953, 2106, 1610, 1416, 1248, 1155, 846, 749 cm⁻¹; EI-MS: m/z = 240.2 (M⁺, 74), 225.1 (44), 73.2 (TMS⁺, 100).

**Trimethyl(2-(naphthalen-1-yl)allyl)silane (3n)**

Prepared according to the general procedure using trimethyl(1-(naphthalen-1-yl)vinyl)oxy)silane (60.6 mg, 0.25 mmol), Ni(COD)₂ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH₂SiMe₃ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a light yellow oil. Analytical data were in accordance with those reported in literature.⁴

**1H NMR** (600 MHz, CDCl₃): 8.19 – 8.15 (m, 1H), 7.87 – 7.84 (m, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.35 (dd, J = 7.0, 0.9 Hz, 1H), 5.23 (d, J = 1.0 Hz, 1H), 5.03 (d, J = 1.0 Hz, 1H), 2.15 (s, 2H), -0.10 (s, 9H); ¹³C NMR (150 MHz, CDCl₃): δ = 146.7, 142.9, 133.9,
130.9, 128.4, 127.3, 126.2, 125.6, 125.6, 125.3, 125.1, 113.7, 29.8, -1.3; IR (ATR): $\tilde{\nu}$ = 2953, 1739, 1371, 1245, 845, 779 cm$^{-1}$; EI-MS: m/z = 241.5 (M$^+$, 11), 165.3 (15), 73.3 (TMS$^+$, 100).

(Z)-(2,3-Diphenylallyl)trimethylsilane (3o)

Prepared according to the general procedure using (Z)-(1,2-diphenylvinyl)oxy)trimethylsilane (67.1 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil. Analytical data were in accordance with those reported in literature.$^5$

$^1$H NMR (600 MHz, CDCl$_3$): 7.47 (d, $J$ = 7.4 Hz, 2H), 7.39 – 7.36 (m, 6H), 7.31 – 7.24 (m, 2H), 6.58 (s, 1H), 2.36 (s, 2H), -0.12 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 145.2, 141.7, 139.0, 128.8, 128.28, 128.27, 127.2, 127.0, 126.2, 125.6, 21.6, -0.71; IR (ATR): $\tilde{\nu}$ = 2952, 2323, 1599, 1493, 1249, 1154, 847, 756, 694 cm$^{-1}$; EI-MS: m/z = 266.2 (M$^+$, 44), 73.2 (TMS$^+$, 100).

(Z)-Trimethyl(2-phenylbut-2-en-1-yl)silane (3p)

Prepared according to the general procedure using (Z)-trimethyl(1-phenylprop-1-en-1-yl)oxy)silane (51.6 mg, 0.25 mmol), Ni(COD)$_2$ (6.8 mg, 10 mol%), SiPrHCl (10.8 mg, 10 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil. Analytical data were in accordance with those reported in literature.$^2$

$^1$H NMR (400 MHz, CDCl$_3$): 7.35 – 7.22 (m, 4H), 7.22 – 7.15 (m, 1H), 5.60 (q, $J$ = 6.8 Hz, 1H), 1.99 (s, 2H), 1.73 (d, $J$ = 6.8 Hz, 3H), -0.14 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 145.1, 139.0, 128.1, 126.6, 126.4, 119.6, 20.7, 14.9, -0.9; IR (ATR): $\tilde{\nu}$ = 2962, 1494, 1444, 1249, 1157, 893, 846, 772, 697 cm$^{-1}$; EI-MS: m/z = 204.3 (M$^+$, 9), 83.3 (30), 73.2 (TMS$^+$, 100), 57.4 (53).

Trimethyl(3-methyl-2-phenylbut-2-en-1-yl)silane (3q)

Prepared according to the general procedure using trimethyl(2-methyl-1-phenylprop-1-en-1-yl)oxy)silane (55.1 mg, 0.25 mmol), Ni(COD)$_2$ (6.8 mg, 10 mol%), SiPrHCl (10.8 mg, 10 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 100 °C. Isolated as a colorless oil. Analytical data were in accordance with those reported in literature.$^5$

$^1$H NMR (400 MHz, CDCl$_3$): 7.28 – 7.24 (m, 2H), 7.17 – 7.10 (m, 3H), 1.88 (s, 2H), 1.75 (s, 3H), 1.59 (s, 3H), -0.18 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 145.2, 132.5, 129.3, 127.8, 125.8, 123.9, 25.8, 22.2, 21.2, -0.8; IR (ATR): $\tilde{\nu}$ = 3385, 2920, 2324, 2106, 1248, 1163, 841, 768, 697 cm$^{-1}$; EI-MS: m/z = 218.2 (M$^+$, 5), 73.2 (TMS$^+$, 100).
(E)-Trimethyl(2-methylene-4-phenylbut-3-en-1-yl)silane (3r)

Prepared according to the general procedure using (E)-trimethyl(4-phenylbuta-1,3-dien-2-yl)oxy)silane (54.6 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil. Analytical data were in accordance with those reported in literature.$^6$

$^1$H NMR (400 MHz, CDCl$_3$): 7.45 – 7.38 (m, 2H), 7.36 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 6.81 (d, $J$ = 16.2 Hz, 1H), 6.47 (d, $J$ = 16.2 Hz, 1H), 5.04 (s, 1H), 4.88 (s, 1H), 1.85 (s, 2H), 0.06 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 144.0, 137.6, 132.2, 128.8, 128.7, 127.4, 114.9, 22.3, -1.0; IR (ATR): $\bar{\nu}$ = 2949, 1684, 1609, 1450, 1252, 1039, 973, 844, 748, 694 cm$^{-1}$; EI-MS: m/z = 216.1 (M$^*$, 4), 105.0 (40), 91.1 (38), 73.2 (TMS$^+$, 100).

((1H-Inden-3-yl)methyl)trimethylsilane (3s)

Prepared according to the general procedure using ((1H-inden-3-yl)oxy)trimethylsilane (51.1 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a yellow oil. Analytical data were in accordance with those reported in literature.$^7$

$^1$H NMR (400 MHz, CDCl$_3$): 7.44 (d, $J$ = 7.3 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.21 – 7.15 (m, 1H), 6.01 (s, 1H), 3.33 (d, $J$ = 1.4 Hz, 2H), 2.03 (d, $J$ = 1.3 Hz, 2H), 0.03 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 146.3, 144.5, 141.6, 125.9, 125.8, 124.2, 123.5, 119.3, 37.8, 17.6, -1.2; IR (ATR): $\bar{\nu}$ = 2922, 1731, 1454, 1381, 1245, 846, 763, 716 cm$^{-1}$; EI-MS: m/z = 202.2 (M$^*$, 5), 115.1 (30), 73.2 (TMS$^+$, 100).

((3,4-Dihyronaphthalen-1-yl)methyl)trimethylsilane (3t)

Prepared according to the general procedure using ((3,4-dihyronaphthalen-1-yl)oxy)trimethylsilane (54.6 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil. Analytical data were in accordance with those reported in literature.$^2$

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.23 – 7.17 (m, 2H), 7.14 – 7.12 (m, 2H), 5.70 (t, $J$ = 4.6 Hz, 1H), 2.75 – 2.72 (m, 2H), 2.26 – 2.21 (m, 2H), 1.94 (s, 2H), 0.01 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 136.9, 135.9, 134.3, 127.4, 126.5, 126.0, 123.5, 122.9, 29.0, 23.3, 22.4, -1.0; IR (ATR): $\bar{\nu}$ = 2941, 1738, 1424, 1366, 1244, 844, 752 cm$^{-1}$; EI-MS: m/z = 216.2 (M$^*$, 7), 129.1 (40), 128.1 (33), 115.1 (40), 73.2 (TMS$^+$, 100).
1-Methyl-2-(3-(trimethylsilyl)prop-1-en-2-yl)-1H-pyrrole (3u)

Prepared according to the general procedure using 1-methyl-2-((trimethylsilyl)oxy)vinyl)-1H-pyrrole (48.8 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$): 6.58 (t, $J = 2.1$ Hz, 1H), 6.11 – 6.07 (m, 2H), 4.93 (d, $J = 1.5$ Hz, 1H), 4.81 (d, $J = 1.5$ Hz, 1H), 3.66 (s, 3H), 1.90 (s, 2H), -0.09 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 138.2, 135.5, 123.7, 110.1, 108.7, 107.0, 35.6, 28.4, -1.5; IR (ATR): $\tilde{\nu}$ = 2931, 1738, 1366, 1215, 1090, 704 cm$^{-1}$; EI-MS: m/z = 193.1 (M$^+$, 7), 122.2 (100), 73.2 (TMS$^+$, 44).

(2-(Furan-2-yl)allyl)trimethylsilane (3v)

Prepared according to the general procedure using ((1-(furan-2-yl)vinyl)oxy)trimethylsilane (45.6 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$): 7.33 (d, $J = 1.6$ Hz, 1H), 6.36 (dd, $J = 3.3$, 1.6 Hz, 1H), 6.25 (d, $J = 3.3$ Hz, 1H), 5.39 (d, $J = 1.0$ Hz, 1H), 4.74 (d, $J = 1.0$ Hz, 1H), 1.84 (s, 2H), 0.01 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 155.5, 141.7, 135.1, 111.1, 107.2, 106.4, 23.5, -1.4; IR (ATR): $\tilde{\nu}$ = 2920, 2857, 1716, 1456, 1368, 846, 731 cm$^{-1}$; EI-MS: m/z = 180.3 (M$^+$, 4), 73.2 (TMS$^+$, 100).

Trimethyl(2-phenylallyl)silane (3w)

Prepared according to the general procedure using trimethyl(1-(phenylvinyl)oxy)silane (48.1 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil. Analytical data were in accordance with those reported in literature.$^2$

$^1$H NMR (600 MHz, CDCl$_3$): 7.43 – 7.39 (m, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.23 (m, 1H), 5.14 (d, $J = 1.2$ Hz, 1H), 4.88 (d, $J = 1.2$ Hz, 1H), 2.03 (s, 2H), -0.09 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 146.7, 142.9, 128.1, 127.3, 126.4, 110.1, 26.2, -1.33; IR (ATR): $\tilde{\nu}$ = 2953, 1741, 1247, 845, 772, 697 cm$^{-1}$; EI-MS: m/z = 190.3 (M$^+$, 11), 73.3 (TMS$^+$, 100), 57.3 (29), 55.3 (30).

Trimethyl(2-(o-tolyl)allyl)silane (3x)

Prepared according to the general procedure using trimethyl(1-(o-tolyl)vinyl)oxy)silane (51.6 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil.
$^1$H NMR (600 MHz, CDCl$_3$): 7.17 – 7.11 (m, 4H), 5.02 (s, 1H), 4.78 (s, 1H), 2.36 (s, 3H), 1.92 (s, 2H), -0.08 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 147.8, 144.4, 134.5, 130.3, 128.5, 126.7, 125.4, 112.5, 28.8, 20.2, -1.3; IR (ATR): $\tilde{\nu}$ = 2953, 1742, 1248, 1161, 846, 764 cm$^{-1}$; EI-MS: $m/z$ = 204.1 (M$^+$, 10), 73.2 (TMS$^+$, 100), 57.3 (10).

Trimethyl(2-($m$-tolyl)allyl)silane (3y)

Prepared according to the general procedure using trimethyl((1-($m$-tolyl)vinyl)oxy)silane (51.6 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 ºC. Isolated as a colorless oil. Analytical data were in accordance with those reported in literature.$^2$

$^1$H NMR (600 MHz, CDCl$_3$): 7.23 – 7.18 (m, 3H), 7.09 – 7.05 (m, 1H), 5.13 (s, 1H), 4.86 (s, 1H), 2.36 (s, 3H), 2.02 (s, 2H), -0.08 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 146.8, 142.8, 137.6, 128.01, 127.99, 127.1, 123.5, 109.9, 26.2, 21.6, -1.3; IR (ATR): $\tilde{\nu}$ = 2951, 1741, 1246, 848, 788, 703 cm$^{-1}$; EI-MS: $m/z$ = 205.1 (M$^+$, 20), 191.1 (46), 97.2 (51), 73.2 (TMS$^+$, 57), 71.2 (53), 69.2 (61), 57.3 (100).

Trimethyl(2-($p$-tolyl)allyl)silane (3z)

Prepared according to the general procedure using trimethyl((1-($p$-tolyl)vinyl)oxy)silane (51.6 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 ºC. Isolated as a colorless oil. Analytical data were in accordance with those reported in literature.$^8$

$^1$H NMR (600 MHz, CDCl$_3$): 7.31 (d, $J$ = 8.0 Hz, 2H), 7.12 (d, $J$ = 8.0 Hz, 2H), 5.12 (s, 1H), 4.83 (s, 1H), 2.35 (s, 3H), 2.02 (s, 2H), -0.08 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 146.4, 139.9, 136.9, 128.8, 126.2, 109.4, 26.1, 21.2, -1.3; IR (ATR): $\tilde{\nu}$ = 2951, 1742, 1248, 844, 694 cm$^{-1}$; EI-MS: $m/z$ = 205.2 (M$^+$, 22), 191.1 (75), 97.2 (54), 73.2 (TMS$^+$, 100), 57.3 (97).

(2-(3,4-Dimethylphenyl)allyl)trimethylsilane (3aa)

Prepared according to the general procedure using ((1-(3,4-dimethylphenyl)vinyl)oxy)trimethylsilane (55.1 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 ºC. Isolated as a colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$): 7.19 (s, 1H), 7.14 (dd, $J$ = 7.8, 1.7 Hz, 1H), 7.06 (d, $J$ = 7.8 Hz, 1H), 5.11 (d, $J$ = 1.5 Hz, 1H), 4.81 (d, $J$ = 1.5 Hz, 1H), 2.27 (s, 3H), 2.25 (s, 3H), 2.00 (s, 2H), -0.08 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 146.5, 140.3, 136.1, 135.6, 129.4, 127.6, 123.8, 109.2, 26.1, 20.0,
19.5, -1.3; IR (ATR): $\tilde{\nu} = 2948, 1741, 1446, 1247, 846, 695$ cm$^{-1}$; EI-MS: m/z = 218.2 (M$^+$, 7), 205.1 (56), 71.3 (56), 69.3 (60), 57.3 (100).

**Trimethyl(2-(4-(trifluoromethyl)phenyl)allyl)silane (3bb)**

Prepared according to the general procedure using trimethyl((1-(4-(trifluoromethyl)phenyl)vinyl)oxy)silane (65.1 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_3$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a colorless oil. Analytical data were in accordance with those reported in literature.$^9$

$^1$H NMR (400 MHz, CDCl$_3$): 7.57 – 7.49 (m, 4H), 5.19 (s, 1H), 4.97 (s, 1H), 2.03 (s, 2H), -0.09 (s, 9H); $^1$C NMR (100 MHz, CDCl$_3$): $\delta$ = 146.8, 145.5, 129.2 (q, $J = 32.1$ Hz), 126.5, 125.1 (q, $J = 3.7$ Hz), 124.2 (q, $J = 270.1$ Hz), 112.0, 26.0, -1.5; $^{19}$F NMR (564 MHz, CDCl$_3$): $\delta$ = -62.4 (s, CF$_3$); IR (ATR): $\tilde{\nu} = 2955, 1739, 1323, 1122, 840, 694$ cm$^{-1}$; EI-MS: m/z = 259.2 (M$^+$, 6), 97.2 (32), 75.2 (39), 73.2 (TMS$^+$, 100).

**Z-(Z)-2-(3-(Trimethylsilyl)prop-1-en-1-yl)phenol (5a)**

Prepared according to the general procedure using benzo[b]furan (29.5 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), SIPrHCl (5.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_3$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 16 h at -10 °C. Isolated as a light yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$): 7.20 – 7.15 (m, 1H), 7.09 (d, $J = 7.5$ Hz, 1H), 6.94 – 6.87 (m, 2H), 6.25 (d, $J = 11.0$ Hz, 1H), 5.99 (dt, $J = 11.0$, 8.8 Hz, 1H), 5.19 (s, 1H), 1.59 (dd, $J = 8.8$, 1.3 Hz, 2H), -0.01 (s, 9H); $^1$C NMR (150 MHz, CDCl$_3$): $\delta$ = 152.4, 133.9, 129.8, 128.4, 123.8, 120.8, 120.2, 115.0, 20.3, -1.7; IR (ATR): $\tilde{\nu} = 3450, 2953, 1582, 1484, 1453, 1244, 1211, 1150, 845, 750$ cm$^{-1}$; EI-MS: m/z = 206.1 (M$^+$, 19), 73.1 (TMS$^+$, 100).

**Z-(Z)-3-(3-(Trimethylsilyl)prop-1-en-1-yl)-(1,1'-biphenyl)-4-ol (5b)**

Prepared according to the general procedure using 5-phenylbenzo[b]furan (48.6 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), SIPrHCl (5.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_3$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 16 h at -10 °C. Isolated as a light yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$): 7.57 – 7.55 (m, 2H), 7.44 – 7.41 (m, 3H), 7.36 – 7.29 (m, 2H), 7.00 (d, $J = 8.4$ Hz, 1H), 6.31 (d, $J = 11.1$ Hz, 1H), 6.05 (dt, $J = 11.1$, 8.8 Hz, 1H), 5.24 (s, 1H), 1.64 (dd, $J = 8.8$, 1.0 Hz, 2H), 0.01 (s, 9H); $^1$C NMR (150 MHz, CDCl$_3$): $\delta$ = 152.0, 141.0, 134.2, 133.4, 128.8, 128.4, 127.2, 126.8, 126.7, 124.1, 120.7, 115.4, 20.5, -1.7; IR (ATR): $\tilde{\nu} = 3516, 2952, 1602, 1481, 1248,
1194, 1152, 846, 758, 697 \text{ cm}^{-1}; \textbf{EI-MS}: m/z = 282.1 (M^+, 100), 267.1 (75), 239.1 (59), 73.1 (TMS^+, 96).

(Z)-4-(3-(Trimethylsilyl)prop-1-en-1-yl)-[1,1'-biphenyl]-3-ol (5c)

Prepared according to the general procedure using 6-phenylbenzofuran (48.6 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), SIPrHCl (5.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 16 h at -10 °C. Isolated as a light yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): 7.65 – 7.60 (m, 2H), 7.47 – 7.41 (m, 2H), 7.38 – 7.32 (m, 1H), 7.19 – 7.16 (m, 3H), 6.29 (d, $J = 11.1$, 1H), 6.02 (dt, $J = 11.1$, 8.8 Hz, 1H), 5.25 (s, 1H), 1.65 (dd, $J = 8.8$, 1.4 Hz, 2H), 0.02 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 152.7, 141.4, 140.7, 134.0, 130.2, 128.8, 127.4, 127.0, 122.9, 120.6, 119.0, 113.6, 20.5, -1.7; IR (ATR): $\tilde{\nu}$ = 3329, 2953, 1648, 1611, 1409, 1246, 844, 755, 696 \text{ cm}^{-1}; \textbf{EI-MS}: m/z = 282.1 (M^+, 79), 267.1 (27), 223.1 (58), 207.1 (31), 165.0 (36), 73.2 (TMS^+, 100).

(Z)-4-((Trimethylsilyl)methyl)-2-(3-(trimethylsilyl)prop-1-en-1-yl)phenol (5d)

Prepared according to the general procedure using 5-bromobenzofuran (49.2 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), SIPrHCl (5.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 2.5 equiv., 0.625 mL). The reaction mixture was stirred for 16 h at -10 °C. Isolated as a light yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): 6.78 – 6.73 (m, 3H), 6.22 (d, $J = 11.1$ Hz, 1H), 5.93 (dt, $J = 11.1$, 8.7 Hz, 1H), 4.90 (s, 1H), 1.98 (s, 2H), 1.61 (dd, $J = 8.7$, 1.4 Hz, 2H), -0.01 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 149.3, 133.1, 131.8, 129.0, 127.9, 123.5, 121.3, 114.8, 25.9, 20.2, -1.7, -1.8; IR (ATR): $\tilde{\nu}$ = 3451, 2953, 1491, 1245, 1161, 843, 696 \text{ cm}^{-1}; \textbf{EI-MS}: m/z = 292.2 (M^+, 60), 219.1 (27), 189.0 (33), 73.1 (TMS^+, 100).

(Z)-2-(2-Methyl-3-(trimethylsilyl)prop-1-en-1-yl)phenol (5e)

Prepared according to the general procedure using 2-methylbenzofuran (33.0 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), SIPrHCl (5.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): 7.17 – 7.10 (m, 1H), 7.03 (d, $J = 7.4$ Hz, 1H), 6.92 – 6.83 (m, 2H), 5.97 (s, 1H), 5.19 (s, 1H), 1.92 (s, 3H), 1.63 (s, 2H), -0.05 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 152.5, 143.5, 130.1, 128.1, 125.1, 120.1, 115.7, 114.8, 26.3, 24.7, -0.6; IR (ATR): $\tilde{\nu}$ = 3355, 2954, 1737,
1667, 1477, 1245, 842, 750 cm$^{-1}$; **EI-MS**: $m/z = 220.2$ (M$^+$, 5), 219.3 (11), 145.1 (100), 73.2 (TMS$^+$, 76).

**(Z)-2-(2-((Trimethylsilyl)methyl)hex-1-en-1-yl)phenol (5f)**

Prepared according to the general procedure using 2-butylbenzofuran (43.6 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), SIPrHCl (5.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): 7.18 – 7.10 (m, 1H), 7.06 – 7.00 (m, 1H), 6.92 – 6.83 (m, 2H), 5.97 (s, 1H), 5.17 (s, 1H), 2.21 – 2.14 (m, 2H), 1.63 (s, 2H), 1.59 – 1.50 (m, 2H), 1.43 – 1.34 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H), -0.07 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 152.5, 147.9, 130.2, 128.1, 125.1, 120.1, 114.8, 114.7, 39.0, 30.7, 22.7, 22.7, 14.1, -0.6; IR (ATR): $\tilde{\nu} = 3382, 2950, 1666, 1608, 1460, 1241, 843, 751$ cm$^{-1}$; **EI-MS**: $m/z = 262.1$ (M$^+$, 16), 261.1 (17), 187.1 (100), 73.2 (TMS$^+$, 89).

**(Z)-2-(2-((Trimethylsilyl)methyl)undec-1-en-1-yl)phenol (5g)**

Prepared according to the general procedure using 2-nonylbenzofuran (61.1 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), SIPrHCl (5.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): 7.16 – 7.11 (m, 1H), 7.03 (d, $J = 7.1$ Hz, 1H), 6.91 – 6.83 (m, 2H), 5.96 (s, 1H), 5.16 (s, 1H), 2.19 – 2.13 (m, 2H), 1.62 (s, 2H), 1.58 – 1.50 (m, 2H), 1.34 – 1.29 (m, 12H), 0.89 (t, $J = 6.8$ Hz, 3H), -0.08 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 152.5, 147.9, 130.2, 128.1, 125.1, 120.1, 114.8, 114.7, 39.3, 32.0, 29.7, 29.64, 29.64, 29.60, 29.4, 28.6, 22.8, 14.2, -0.6; IR (ATR): $\tilde{\nu} = 3386, 2924, 2856, 1726, 1668, 1608, 1458, 1240, 843, 751$ cm$^{-1}$; **EI-MS**: $m/z = 332.3$ (M$^+$, 5), 257.2 (67), 147.0 (33), 145.1 (26), 131.1 (23), 107.1 (24), 73.2 (TMS$^+$, 100).

**(Z)-2-(2-Phenyl-3-((trimethylsilyl)prop-1-en-1-yl)phenol (5h)**

Prepared according to the general procedure using 2-phenylbenzofuran (48.6 mg, 0.25 mmol), Ni(COD)$_2$ (6.8 mg, 10 mol%), SIPrHCl (10.8 mg, 10 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 80 °C. Isolated as a yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$): 7.51 – 7.47 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.30 (m, 1H), 7.20 (t, $J = 8.1$ Hz, 1H), 7.17 (d, $J = 7.5$ Hz, 1H), 6.97 – 6.92 (m, 2H), 6.44 (s, 1H), 5.18 (s, 1H), 2.11 (s, 2H), -0.21 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 152.7, 146.5, 143.4, 129.8, 128.5, 128.4, 127.8, 126.8, 124.9, 120.3, 118.2, 115.1, 22.2, -0.8; IR (ATR): $\tilde{\nu} = 3368, 2952, 1662, 1599, 1484, 1241, 846, 753, 697$ cm$^{-1}$; **EI-MS**: $m/z = 282.3$ (M$^+$, 11), 281.2 (10), 208.2 (18), 207.1 (100), 178.1 (13), 73.2 (TMS$^+$, 71).
(Z)-2-(4-(Trimethylsilyl)but-2-en-2-yl)phenol (5i)

Prepared according to the general procedure using 3-methylbenzofuran (33.0 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), SIPrHCl (5.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 2 h at 60 °C. Isolated as a yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$): 7.19 – 7.15 (m, 1H), 7.02 (dd, $J = 7.5, 1.6$ Hz, 1H), 6.95 – 6.88 (m, 2H), 5.76 (td, $J = 8.5, 1.3$ Hz, 1H), 5.33 (s, 1H), 1.99 (d, $J = 1.3$ Hz, 3H), 1.31 (dd, $J = 8.5, 0.9$ Hz, 2H), -0.06 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 151.3$, 129.0, 128.9, 128.3, 127.7, 127.5, 120.4, 114.8, 25.4, 20.1, -1.7; IR (ATR): $\tilde{\nu} = 3438$, 2952, 1704, 1639, 1483, 1449, 1240, 845, 752 cm$^{-1}$; EI-MS: m/z = 220.1 (M$^+$, 8), 145.0 (61), 103.1 (62), 73.1 (TMS$^+$, 100).

(Z)-6-(Trimethylsilyl)hex-4-en-1-ol (5j)

Prepared according to the general procedure using 3,4-dihydro-2H-pyran (21.0 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), SIPrHCl (5.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 16 h at -10 °C. Isolated as a colorless oil. Analytical data were in accordance with those reported in literature.10

$^1$H NMR (400 MHz, CDCl$_3$): 5.50 – 5.36 (m, 1H), 5.35 – 5.20 (m, 1H), 3.66 (t, $J = 6.5$ Hz, 2H), 2.11 – 2.04 (m, 2H), 1.68 – 1.59 (m, 2H), 1.48 (dd, $J = 8.6, 0.4$ Hz, 2H), 1.46 (bs, 1H), 0.00 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 126.7$, 126.4, 62.9, 32.8, 23.5, 18.6, -1.7; IR (ATR): $\tilde{\nu} = 3336$, 2944, 1739, 1374, 1245, 1054, 845, 704 cm$^{-1}$; EI-MS: m/z = 171.3 (M$^+$, 9), 81.2 (11), 73.2 (TMS$^+$, 100).

(Z)-1-Phenyl-5-(trimethylsilyl)pent-3-en-1-ol (5k)

Prepared according to the general procedure using 2-phenyl-2,3-dihydrofuran (36.5 mg, 0.25 mmol), Ni(COD)$_2$ (3.4 mg, 5 mol%), SIPrHCl (5.4 mg, 5 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution in pentane (1 M, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 16 h at -10 °C. Isolated as a light yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): 7.40 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 5.65 – 5.55 (m, 1H), 5.34 – 5.25 (m, 1H), 4.68 (dd, $J = 8.1, 5.2$ Hz, 1H), 2.57 – 2.35 (m, 2H), 2.04 (bs, 1H), 1.57 – 1.42 (m, 2H), -0.01 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 144.3$, 129.6, 128.5, 127.5, 125.9, 122.4, 74.1, 37.2, 18.9, -1.7; IR (ATR): $\tilde{\nu} = 3401$, 2952, 2896, 1737, 1376, 1246, 1040, 845, 698 cm$^{-1}$; EI-MS: m/z = 234.3 (M$^+$, 4), 105.1 (48), 73.2 (TMS$^+$, 100).
(Z)-1-((Tert-butyldiphenylsilyloxy)-7-(trimethylsilyl)hept-5-en-2-ol (5l)

Prepared according to the general procedure using tert-butyl((3,4-dihydro-2H-pyran-2-yl)methoxy)diphenylsilane (88.1 mg, 0.25 mmol), Ni(COD)$_2$ (6.8 mg, 10 mol%), SIPr.HCl (10.8 mg, 10 mol%), freshly distilled toluene (1.5 mL), and LiCH$_2$SiMe$_3$ solution in pentane (1 M, 1.3 equiv., 0.325 mL). The reaction mixture was stirred for 16 h at -10 °C. Isolated as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.70 – 7.66 (m, 4H), 7.46 – 7.36 (m, 6H), 5.47 – 5.35 (m, 1H), 5.27 – 5.20 (m, 1H), 3.79 – 3.71 (m, 1H), 3.68 (dd, J = 10.1, 3.5 Hz, 1H), 3.51 (dd, J = 10.1, 7.3 Hz, 1H), 2.50 (d, J = 3.5 Hz, 1H), 2.16 – 1.99 (m, 2H), 1.58 – 1.37 (m, 4H), 1.08 (s, 9H), 0.00 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 135.63, 135.61, 133.28, 133.26, 129.9, 127.8, 126.8, 126.2, 71.7, 68.1, 32.9, 26.9, 23.2, 19.3, 18.5, -1.7; IR (ATR): $\bar{\nu}$ = 3460, 2941, 2863, 1739, 1427, 1374, 1246, 1106, 846, 699 cm$^{-1}$; EI-MS: m/z = 383.1 (73), 271.0 (100), 73.1 (TMS$^+$, 71).

Starting material synthesis

Synthesis of 2-(2-Methoxyvinyl)naphthalene (1a & 1d)

Preparation according to literature.$^{[1]}$ E and Z isomers were separated by chromatography. (E)-2-(2-methoxyvinyl)naphthalene (1a): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.81 – 7.72 (m, 3H), 7.61 (s, 1H), 7.48 – 7.36 (m, 3H), 7.20 (d, $J$ = 13.0 Hz, 1H), 5.99 (d, $J$ = 13.0 Hz, 1H), 3.75 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 149.4, 134.0, 133.9, 132.1, 128.2, 127.7, 127.5, 126.2, 125.1, 123.8, 123.4, 105.4, 56.7. (Z)-2-(2-methoxyvinyl)naphthalene (1d): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.02 (s, 1H), 7.83 – 7.71 (m, 4H), 7.47 – 7.36 (m, 2H), 6.23 (d, $J$ = 7.0 Hz, 1H), 5.39 (d, $J$ = 7.0 Hz, 1H), 3.85 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 148.5, 133.8, 133.6, 131.9, 128.0, 127.6, 127.1, 126.5, 125.9, 125.2, 105.8, 60.9.
References


Spectra

3a

[Chemical structures and spectra images]

3a
\[\text{SiMe}_3\]

3t

\[\text{SiMe}_3\]

3t