Supporting Information

Titanocene-Catalyzed Regioselective Carbomagnesation of Alkenes and Dienes

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2,2-Dimethyl-4,4-diphenylbutane (3): To a mixture of 1,1-diphenylethane (173.6 mg, 0.96 mmol), *tert*-butyl chloride (187 mg, 2.02 mmol) and *n*-BuMgCl (0.90 M in THF, 3.4 mL, 3.1 mmol), was added Cp₂TiCl₂ (12 mg, 0.05 mmol) at 0 °C under nitrogen. After stirring for 2 h, H₂O was added to the solution at 0 °C, and the mixture was again warmed to 20 °C. A saturated aqueous NH₄Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over MgSO₄, and evaporated to give a yellow crude product (94% NMR yield). Purification by HPLC with CHCl₃ as an eluent afforded 185 mg (82%) of **3** as a colorless oil. IR (NaCl) 3025, 2953, 2864, 1493, 1474, 1450, 1364, 743, 701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.21 (m, 8H), 7.13-7.09 (m, 2H), 4.05 (t, *J* = 6.65 Hz, 1H), 2.09 (d, *J* = 6.65 Hz, 2H), 0.82 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 146.3, 128.0, 127.4, 125.5, 49.3, 48.3, 31.4, 30.1; MS (EI) *m/z* (relative intensity, %) 238 (M⁺, 24), 168 (19), 167 (100), 165 (14), 152 (7); HRMS calcd for C₁₈H₂₂ 238.1721, found 238.1719. Anal. Calcd for C₁₈H₂₂: C, 90.70; H, 9.30. Found: C, 90.79; H, 9.21.

6,6-Dimethyl-4,4-diphenyl-1-heptene (4): To a mixture of 1,1-diphenylethane (347 mg, 1.92 mmol), *tert*-butyl chloride (207 mg, 2.23 mmol) and *n*-BuMgCl (0.90 M in THF, 4.9 mL, 4.4 mmol), was added Cp₂TiCl₂ (25 mg, 0.1 mmol) at 0 °C under nitrogen. After stirring for 2 h, allyl bromide was added to the solution at 0 °C, and the mixture was again warmed to 20 °C. A saturated aqueous NH₄Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over MgSO₄, and evaporated to give a yellow crude product (66% NMR yield). Purification by HPLC with CHCl₃ as an eluent afforded 288 mg (54%) of **4** as a colorless oil. IR (NaCl) 2980, 2952, 2908, 1495, 1479, 1444, 913, 757, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.11 (m, 10H), 5.43-5.33 (m, 1H), 4.94-4.90 (m, 2H), 3.06 (d, *J*=7.08 Hz, 2H), 2.20 (s, 2H), 0.69 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 149.2, 135.0, 128.1, 127.4, 125.2, 117.2, 49.4, 48.7, 43.1, 32.3, 31.7; MS (EI) *m/z* (relative intensity, %) 237 (M⁺-C₃H₅, 84), 181 (90), 165 (13), 129 (56), 91 (39), 57 (100), 41 (39); HRMS calcd for C₂₁H₂₆: 279.2112, found 279.2116; Anal. Calcd for C₂₁H₂₆: C, 90.59; H, 9.41. Found: C, 90.42; H, 9.32.

1-Cyclohexyl-2-triethylsilylethane (7): To a mixture of triethylvinylsilane (141 mg, 1.00 mmol), cyclohexyl bromide (319 mg, 1.94 mmol) and *n*-BuMgCl (0.90 M in THF, 3.4 mL, 3.1 mmol), was added Cp₂TiCl₂ (12 mg, 0.05 mmol) at 0 °C under nitrogen. After stirring for 2 h, H₂O was added to the solution at 0 °C, and the mixture was again warmed to 20 °C. A saturated aqueous NH₄Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over MgSO₄, and evaporated to give a yellow crude product (84% NMR yield). Purification by HPLC with CHCl₃ as an eluent afforded 288 mg (71%) of **6** as a colorless oil. IR (NaCl) 2918, 2851, 1448, 1416, 1238, 1015, 842, 790, 780, 756, 728 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.75-1.62 (m, 5H), 1.25-1.07 (m, 6H), 0.91 (t, *J*=7.93 Hz, 9H), 0.87-0.81 (m, 2H), 0.54-0.46 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 40.9, 32.9, 31.2, 26.8, 26.4, 8.1, 7.5, 3.3; MS (EI) *m/z* (relative intensity, %) 197 (M⁺-C₂H₅, 100), 167 (20), 115 (36), 87 (62), 59 (22); HRMS calcd for C₁₂H₂₅Si (M-C₂H₅): 197.1726, found 197.1729; Anal. Calcd for C₁₄H₃₀Si: C, 74.25; H, 13.35. Found: C, 74.13; H, 13.29.

3-Deuterio-2,3,5,5-tetramethyl-1-heptene (10a) and 1-Deuterio-2,3,5,5-tetramethyl-2-heptene (10b): To a mixture of 2,3-dimethyl-1,3-butadiene (155 mg, 1.88 mmol), *tert*-amyl chloride (410 mg, 3.85 mmol) and *n*-BuMgCl (0.90 M in THF, 6.9 mL, 6.2 mmol), was added Cp₂TiCl₂ (24 mg, 0.10 mmol) at 0 °C under nitrogen. After stirring for 2 h, D₂O was added to the solution at 0 °C, and the mixture was again warmed to 20 °C. A saturated aqueous NH₄Cl solution (50 mL) was added, and the

product was extracted with ether (50 mL), dried over MgSO_4 , and evaporated to give a yellow crude product (94% NMR yield). Purification by HPLC with CHCl_3 as an eluent afforded 82 mg (30%) of **10** as a colorless oil. mixture IR (NaCl): 2964, 2880, 1465, 1376, 1363, 886 cm^{-1} ; MS (EI) m/z (relative intensity, %): 155 (M^+ , 31); HRMS calcd for $\text{C}_{11}\text{H}_{21}\text{D}$: 155.1783, found 155.1786. **10a**: ^1H NMR (400 MHz, CDCl_3): δ 4.70 (s, 1H), 4.60 (s, 1H), 1.67-1.64 (m, 3H), 1.42 (d, $J = 14.2$ Hz, 1H), 1.29-1.20 (m, 2H), 1.09 (d, $J = 14.2$ Hz, 1H), 1.00 (s, 3H), 0.87-0.79 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 126.6, 125.9, 46.2, 35.9, 30.3, 26.7, 21.4, 21.2, 20.6 (t, 1 C), 8.6; **10b**: ^1H NMR (400 MHz, CDCl_3): δ 2.00 (s, 2H), 1.67-1.64 (m, 8H), 1.29-1.20 (m, 2H), 0.87-0.79 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 151.8, 108.6, 36.9 (t, 1 C), 34.7, 33.6, 27.2, 27.0, 22.9, 18.7, 8.5.

2,3,5,5-Tetramethyl-1-tributylstannyl-2-heptene (11): To a mixture of 2,3-dimethyl-1,3-butadiene (81 mg, 0.99 mmol), *tert*-amyl chloride (214 mg, 2.02 mmol) and *n*-BuMgCl (0.90 M in THF, 3.4 mL, 3.1 mmol), was added Cp_2TiCl_2 (12 mg, 0.05 mmol) at 0 $^\circ\text{C}$ under nitrogen. After stirring for 2 h, tributylstannyl chloride (490 mg, 1.5 mmol) was added to the solution at 0 $^\circ\text{C}$, and the mixture was again warmed to 20 $^\circ\text{C}$. A saturated aqueous NH_4Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over MgSO_4 , and evaporated to give a yellow crude product (78% NMR yield). Purification by HPLC with CHCl_3 as an eluent afforded 320 mg (72%, $E/Z = 80/20$) of **11** as a colorless oil. (E isomer) IR (NaCl) 2958, 2924, 2871, 2853, 1463, 1376 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.98 (s, $^2J_{\text{Sn}} = 6.1$ Hz, 2H), 1.72 (s, 2H), 1.64 (s, 3H), 1.62 (s, 3H), 1.52-1.44 (m, 6H), 1.34-1.22 (m, 8H), 0.91-0.81 (m, 24H); NOE difference measurement: irradiation of methylene protons at δ 1.98 ($-\text{CH}_2-\text{Sn}^n\text{Bu}_3$) caused enhancement of the methyl protons at δ 1.64 (5.3%) and 1.62 (8.5%), while no enhancement was observed for methylene protons at δ 1.72 ($-\text{CH}_2-\text{Amyl}$); ^{13}C NMR (100 MHz, CDCl_3): δ 130.6, 121.0, 46.5, 36.2, 35.6, 29.2, 27.4, 26.8, 22.2, 21.7, 19.4, 13.7, 9.8, 8.7; MS (EI) m/z (relative intensity, %) 444 (12), 387 (7), 291 (100), 235 (80), 179 (51), 71 (18), 43 (13); HRMS calcd for $\text{C}_{23}\text{H}_{48}\text{Sn}$: 444.2784, found 444.2776. Anal. Calcd for $\text{C}_{23}\text{H}_{48}\text{Sn}$: C, 62.31; H, 10.91. Found: C, 62.03; H, 10.86. (Z isomer) ^1H NMR (400 MHz, CDCl_3) δ 1.91 (s, $^2J_{\text{Sn}} = 6.1$ Hz, 2H), 1.76 (s, 2H), 1.55 (s, 6H), 1.52-1.44 (m, 6H), 1.34-1.22 (m, 8H), 0.91-0.81 (m, 24H)

3-Benzyl-2,3,6,6-tetramethyl-1-heptene (12): To a mixture of 2,3-dimethyl-1,3-butadiene (81 mg, 0.99 mmol), neopentyl bromide (298 mg, 1.97 mmol) and *n*-BuMgCl (0.90 M in THF, 3.4 mL, 3.1 mmol), was added Cp_2TiCl_2 (12 mg, 0.05 mmol) at 0 $^\circ\text{C}$ under nitrogen. After stirring for 2 h, benzyl bromide (291 mg, 1.7 mmol) was added to the solution at 0 $^\circ\text{C}$, and the mixture was again warmed to 20 $^\circ\text{C}$. A saturated aqueous NH_4Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over MgSO_4 , and evaporated to give a yellow crude product. Purification by HPLC with CHCl_3 as an eluent afforded 320 mg (70%) of **12** as a colorless oil. IR (NaCl) 2953, 2865, 1453, 1376, 1364, 893, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.23-7.07 (m, 5H), 4.82 (s, 1H), 4.53 (s, 1H), 2.76 (d, $J = 13.3$ Hz, 1H), 2.57 (d, $J = 13.3$ Hz, 1H), 1.78 (s, 3H), 1.55-1.48 (m, 1H), 1.23-1.16 (m, 1H), 1.08-1.01 (m, 2H), 0.91 (s, 3H), 0.86 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.0, 138.7, 130.1, 127.1, 125.4, 112.0, 46.5, 42.9, 37.7, 33.9, 30.0, 29.4, 22.5, 19.7; MS (EI) m/z (relative intensity, %) 244 (M^+ , 47), 153 (28), 97 (65), 91 (35), 83 (100), 69 (45), 57 (80), 41 (18); HRMS calcd for $\text{C}_{18}\text{H}_{28}$: 244.2191, found 244.2203; Anal. Calcd for $\text{C}_{18}\text{H}_{28}$: C, 88.45; H, 11.55. Found: C, 88.30; H, 11.56.

3-Benzoyl-4-cyclohexyl-2,3-dibenzyl-1-butene (13): To a mixture of 2,3-dibenzyl-1,3-butadiene (226

mg, 0.97 mmol), cyclohexyl bromide (341 mg, 2.09 mmol) and *n*-BuMgCl (0.90 M in THF, 3.4 mL, 3.1 mmol), was added Cp₂TiCl₂ (12 mg, 0.05 mmol) at 0 °C under nitrogen. After stirring for 2 h, benzoyl chloride (212 mg, 1.5 mmol) was added to the solution at 0 °C, and the mixture was again warmed to 20 °C. A saturated aqueous NH₄Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over MgSO₄, and evaporated to give a yellow crude product (73% NMR yield). Purification by HPLC with CHCl₃ as an eluent afforded 297 mg (73%) of **13** as a yellow oil. IR (NaCl): 2975, 2925, 2852, 1675, 1447, 1120, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.13 (d, *J* = 7.33 Hz, 2H), 7.50 (t, *J* = 7.45 Hz, 1H), 7.39 (t, *J* = 7.69 Hz, 2H), 7.24-7.14 (m, 6H), 7.09 (d, *J* = 7.81 Hz, 2H), 6.86 (d, *J* = 8.30 Hz, 2H), 5.04 (s, 1H), 4.61 (s, 1H), 3.43 (d, *J* = 14.2 Hz, 1H), 3.32 (d, *J* = 14.2 Hz, 1H), 3.28 (d, *J* = 17.0 Hz, 1H), 2.98 (d, *J* = 17.0 Hz, 1H), 1.94-1.84 (m, 2H), 1.80-1.77 (m, 1H), 1.68-1.65 (m, 1H), 1.57-1.47 (m, 3H), 1.36-1.33 (m, 1H), 1.31-1.21 (m, 1H), 1.15-0.97 (m, 3H), 0.68-0.59 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 202.1, 150.9, 137.9, 137.3, 137.2, 132.0, 130.6, 129.6, 129.1, 127.9, 127.8, 127.3, 126.0, 125.9, 114.4, 60.5, 40.5, 39.9, 39.6, 35.3, 34.4, 33.7, 26.6, 26.3, 26.1; MS (EI) *m/z* (relative intensity, %): 422 (M⁺, 21), 331 (69), 302 (34), 211 (37), 105 (100), 91 (53); HRMS calcd for C₃₁H₃₄(¹⁸O): 422.2610, found 422.2611.

6,6-Dimethyl-1,3,4-triphenyl-3-octene (14): To a mixture of 2,3-diphenyl-1,3-butadiene (208 mg, 1.01 mmol), *tert*-Amyl chloride (216 mg, 2.03 mmol) and *n*-BuMgCl (0.90 M in THF, 3.4 mL, 3.1 mmol), was added Cp₂TiCl₂ (12 mg, 0.05 mmol) at 0 °C under nitrogen. After stirring for 2 h, benzyl bromide (280 mg, 1.6 mmol) was added to the solution at 0 °C, and the mixture was again warmed to 20 °C. A saturated aqueous NH₄Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over MgSO₄, and evaporated to give a yellow crude product. Purification by HPLC with CHCl₃ as an eluent afforded 319 mg (86%, *E/Z* = 4/96) of **14** as a colorless oil. (*Z* isomer) IR (NaCl) 3023, 2960, 1490, 1441, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.28-6.89 (m, 15H), 2.89 (t, *J* = 8.0 Hz, 2H), 2.52 (t, *J* = 8.0 Hz, 2H), 2.42 (s, 2H), 1.14 (q, *J* = 7.52 Hz, 2H), 0.70 (t, *J* = 7.52 Hz, 3H), 0.68 (s, 6H) ; NOE difference measurement: irradiation of methylene protons at δ 2.42 (-CH₂-*t*Amyl) caused enhancement of the methylene protons at δ 2.89 (-CH₂-Ph, 12%); ¹³C NMR (100 MHz, CDCl₃) δ 144.3, 142.8, 141.8, 139.2, 136.6, 129.9, 129.7, 128.2, 127.9, 127.1, 126.8, 125.4, 125.2, 124.9, 44.2, 37.2, 35.8, 35.4, 34.0, 26.9, 8.4; MS (EI) *m/z* (relative intensity, %): 368 (M⁺, 100), 298 (37), 207 (72), 193 (61), 91 (78); HRMS calcd for C₂₈H₃₂: 368.2504, found 358.2502; Anal. Calcd for C₂₈H₃₂: C, 91.25; H, 8.75. Found: C, 91.15; H, 8.48.

3-Benzyl-4-*tert*-butyl-cyclohexene (15): To a mixture of 1,3-cyclohexadiene (93 mg, 1.12 mmol), *tert*-butyl chloride (186 mg, 2.00 mmol) and *n*-BuMgCl (0.90 M in THF, 3.4 mL, 3.1 mmol), was added Cp₂TiCl₂ (12 mg, 0.05 mmol) at 0 °C under nitrogen. After stirring for 2 h, benzyl bromide (284 mg, 1.6 mmol) was added to the solution at 0 °C, and the mixture was again warmed to 20 °C. A saturated aqueous NH₄Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over MgSO₄, and evaporated to give a yellow crude product (73% NMR yield). Purification by HPLC with CHCl₃ as an eluent afforded 102 mg (40%) of **15** as a colorless oil. IR (NaCl) 3024, 2956, 2866, 1453, 1364, 717, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.24 (m, 2H), 7.18-7.15 (m, 3H), 5.72-5.69 (m, 1H), 5.66-5.56 (m, 1H), 2.64 (d, *J* = 7.32 Hz, 2H), 2.30 (brs, 1H), 2.01-1.86 (m, 2H), 1.75-1.62 (m, 2H), 1.30-1.28 (m, 1H), 0.81 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 140.9, 131.3, 128.9, 127.7, 126.6, 125.4, 44.5, 43.8, 37.2, 33.6, 28.7, 23.0, 20.9; MS (EI) *m/z* (relative intensity, %): 228

(M⁺, 7), 172 (20), 137 (34), 91 (31), 81 (35), 67 (27), 57 (100); HRMS calcd for C₁₇H₂₄: 228.1878, found 228.1875; Anal. Calcd for C₁₇H₂₄: C, 89.41; H, 10.59. Found: C, 89.36; H, 10.51.

3-Deuterio-2,3-dimethyl-4-naphtyl-1-butene (16a) and 1-Deuterio-2,3-dimethyl-4-naphtyl-2-butene (16b): To a mixture of 2,3-dimethyl-1,3-butadiene (1580 mg, 19.2 mmol), 2-bromonaphthalene (400.4 mg, 1.93 mmol) and *n*-BuMgCl (0.50 M in THF, 10 mL, 5.0 mmol), was added Cp₂TiCl₂ (25 mg, 0.10 mmol) at 0 °C under nitrogen. After stirring for 2 h, 1-Iodo-octane D₂O was added to the solution at 0 °C, and the mixture was again warmed to 20 °C. A saturated aqueous NH₄Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over MgSO₄, and evaporated to give a yellow crude product (81% NMR yield). Purification by HPLC with CHCl₃ as an eluent afforded 300.1 mg (74%) of **16a** and **16b** as a colorless oil. IR (NaCl) 2964, 1642, 1508, 1452, 1372, 889, 810, 742 cm⁻¹; **16a**: ¹H NMR (400 MHz, CDCl₃) δ 7.80-7.72 (m, 3H), 7.57-7.55 (m, 1H), 7.45-7.37 (m, 2H), 7.31-7.28 (m, 1H), 4.69 (s, 2H), 2.93 (d, *J* = 13.55 Hz, 1H), 2.64 (d, *J* = 13.55 Hz, 1H), 1.76 (s, 3H), 1.02 (s, 3H); **16b**: ¹H NMR (400 MHz, CDCl₃) δ 7.80-7.72 (m, 3H), 7.57-7.55 (m, 1H), 7.45-7.37 (m, 2H), 7.31-7.28 (m, 1H), 3.54 (s, 2H), 1.84 (s, 3H), 1.76 (s, 2H), 1.62 (s, 3H); **16a**: ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 138.6, 133.3, 131.8, 127.6, 127.4, 127.3, 127.2, 127.0, 125.6, 124.9, 109.5, 42.3 (t), 42.0, 20.0, 19.0; MS (EI) *m/z* (relative intensity, %) 211 (16), 141 (100), 115 (13); HRMS calcd for C₁₆H₁₇D 211.1470, found 211.1474; Anal. Calcd for C₁₆H₁₇D: C, 90.94; H, 8.11; D, 0.95. Found: C, 90.67; H, 8.07; D, 0.92.

3-Benzoyl-2,3,5-trimethyl-1,5-hexadiene (17): To a mixture of 2,3-dimethyl-1,3-butadiene (1631 mg, 19.8 mmol), 2-bromo-1-propene (242 mg, 2.00 mmol) and *n*-BuMgCl (0.90 M in THF, 4.7 mL, 4.2 mmol), was added Cp₂TiCl₂ (25 mg, 0.10 mmol) at 0 °C under nitrogen. After stirring for 2 h, 1-benzoyl chloride (424 mg, 3.0 mmol) was added to the solution at 0 °C, and the mixture was again warmed to 20 °C. A saturated aqueous NH₄Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over MgSO₄, and evaporated to give a yellow crude product (54% NMR yield). Purification by HPLC with CHCl₃ as an eluent afforded 235 mg (52%) of **17** as a yellow oil. IR (neat): 2972, 2947, 1678, 1446, 965, 895, 711, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 7.32 Hz, 2H), 7.46 (t, *J* = 7.32 Hz, 1H), 7.36 (t, *J* = 7.56 Hz, 2H), 5.12 (s, 1H), 5.10 (s, 1H), 4.81 (s, 1H), 4.58 (s, 1H), 2.78 (d, *J* = 13.79 Hz, 1H), 2.60 (d, *J* = 13.79 Hz, 1H), 1.78 (s, 3H), 1.62 (s, 3H), 1.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 203.2, 147.8, 141.9, 137.3, 131.5, 128.5, 127.7, 114.9, 112.1, 55.8, 44.5, 24.4, 22.6, 20.8; MS (EI) *m/z* (relative intensity, %): 228 (M⁺, 3), 185 (11), 123 (21), 105 (100), 77 (27); HRMS calcd for C₁₆H₂₀O: 228.1514, found 228.1527; Anal. Calcd for C₁₆H₂₀O: C, 84.16; H, 8.83. Found: C, 84.07; H, 8.83.

3-Methyl-1-(trimethylsilyl)-1-(4-methylphenyl)-3-butene (18): To a mixture of *p*-methylstyrene (1111 mg, 9.4 mmol), 2-bromo-1-propene (353 mg, 2.9 mmol), Me₃SiCl (116 mg, 1.07 mmol) and *n*-BuMgCl (0.90 M in THF, 4.4 mL, 4.0 mmol) was added Cp₂TiCl₂ (12 mg, 0.05 mmol) at 0 °C under nitrogen. After stirring for 2 h, similar workup gave an orange crude product (80% NMR yield). Purification by HPLC with CHCl₃ as an eluent afforded 183 mg (74%) of **18** as a colorless oil. IR (NaCl) 2954, 1510, 1248, 885, 862, 840 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.02 (d, *J* = 8.05 Hz, 2H), 6.89 (d, *J* = 8.05 Hz, 2H), 4.62 (d, *J* = 5.62 Hz, 2H), 2.56-2.42 (m, 2H), 2.29-2.23 (m, 1H), 2.28 (s, 3H), 1.61 (s, 3H), -0.05 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 144.6, 139.5, 133.1, 128.2, 127.2, 110.9, 37.1, 34.0, 22.0, 20.9, -2.9; MS (EI) *m/z* (relative intensity, %) 232 (M⁺, 32), 158 (28), 143 (29),

73 (100); HRMS calcd for $C_{15}H_{24}Si$ 232.1647, found 232.1647; Anal. Calcd for $C_{15}H_{24}Si$: C, 77.51; H, 10.41. Found: C, 77.41; H, 10.63.

1-(4-Methylphenyl)-2-(2-naphthyl)-1-(triethylsilyl)ethane (19): To a mixture of *p*-methylstyrene (1060 mg, 9.0 mmol), 2-chloronaphthalene (442 mg, 2.7 mmol), Et_3SiCl (134 mg, 0.89 mmol) and *n*-BuMgCl (0.90 M in THF, 4.4 mL, 4.0 mmol) was added Cp_2TiCl_2 (12 mg, 0.05 mmol) at 0 °C under nitrogen. After stirring for 2 h, similar workup gave an orange crude product (70% NMR yield). Purification by HPLC with $CHCl_3$ as an eluent afforded 193 mg (60%) of **19** as a colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.71-7.60 (m, 3H), 7.44 (s, 1H), 7.38-7.31 (m, 2H), 7.18-7.16 (m, 1H), 6.93-6.91 (m, 4H), 3.22 (d, $J = 7.69$ Hz, 2H), 2.58 (t, $J = 7.69$ Hz, 1H), 2.22 (s, 3H), 0.94 (t, $J = 7.93$ Hz, 9H), 0.58 (q, $J = 7.97$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 139.4, 133.4, 133.2, 131.6, 128.5, 127.8, 127.3, 127.2, 127.1, 126.3, 125.3, 124.6, 36.4, 35.4, 21.0, 7.79, 2.7; MS (EI) m/z (relative intensity, %) 360 (M^+ , 50), 244 (100), 115 (69), 87 (51), 59 (20); HRMS calcd for $C_{25}H_{32}Si$ 360.2273, found 360.2267

3-[Phenyl-(dimethylphenylsilyl)-methyl]-2,3-dihydrobenzofuran (23): To a mixture of *O*-cinamyl-2-bromophenol **22** (285 mg, 0.98 mmol), $PhMe_2SiCl$ (349 mg, 2.0 mmol) and *n*-BuMgCl (0.90 M in THF, 3.3 mL, 3.0 mmol) was added Cp_2TiCl_2 (12 mg, 0.05 mmol) at 0 °C under nitrogen. After stirring for 2 h, similar workup gave an orange crude product (76% NMR yield). Purification by HPLC with $CHCl_3$ as an eluent afforded 238 mg (70%) of **23** as a white solid. IR (NaCl) 3020, 2960, 2901, 1591, 1461, 1450, 1429, 1251, 1229, 1113, 971, 836, 810, 785, 753, 739, 704, 508 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.44 (m, 2H), 7.37-7.32 (m, 2H), 7.27-7.23 (m, 3H), 7.19-7.15 (m, 1H), 7.04-7.02 (m, 2H), 6.99-6.95 (m, 1H), 6.67 (d, $J = 7.81$ Hz, 1H), 6.49 (t, $J = 7.56$, 1H), 6.17 (d, $J = 7.32$ Hz, 1H), 4.49-4.44 (m, 1H), 4.04-3.99 (m, 2H), 2.61-2.59 (m, 1H), 0.33 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 141.6, 137.3, 133.6, 130.9, 129.0, 128.5, 128.0, 127.6, 127.5, 125.0, 124.9, 119.5, 109.0, 75.9, 43.8, 41.8, -1.9, -4.4; MS (EI) m/z (relative intensity, %) 344 (M^+ , 27), 266 (55), 251 (38), 226 (26), 135 (100), 119 (68), 91 (29); HRMS calcd for $C_{23}H_{24}OSi$ 344.1596, found 344.1596; Anal. Calcd for $C_{23}H_{24}OSi$: C, 80.18; H, 7.02. Found: C, 79.89; H, 7.09.

1-(4-Chlorophenyl)-3-[3-(2,3-dihydrobenzofuranyl)]-3-methyl-1-(trimethylsilyl)-butane (29): To a mixture of *p*-chlorostyrene (270 mg, 1.95 mmol), *O*-(3-methyl-2-butenyl)-2-bromophenol **28** (941 mg, 3.9 mmol), Me_3SiCl (421 mg, 3.9 mmol) and *n*-BuMgCl (0.90 M in THF, 6.7 mL, 6.0 mmol) was added Cp_2TiCl_2 (25 mg, 0.10 mmol) at 0 °C under nitrogen. After stirring for 2 h, similar workup gave an orange crude product (75% NMR yield). Purification by HPLC with $CHCl_3$ as an eluent afforded 532 mg (73%) of **29** as a colorless oil. the following spectra and analytical data were obtained from 1.2:1 mixture of diastereomers: IR (NaCl) 2957, 2896, 1484, 1458, 1260, 1249, 1230, 1096, 841, 752 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) major: δ 7.25-7.07 (m, 4H), 6.98-6.93 (m, 2H), 6.82-6.70 (m, 2H), 4.26 (dd, $J = 3.66, 9.52$ Hz, 1H), 3.83 (t, $J = 9.28$ Hz, 1H), 3.07 (dd, $J = 3.66, 9.03$ Hz, 1H), 2.13-2.09 (m, 1H), 2.00-1.94 (m, 1H), 1.79-1.77 (m, 1H), 0.84 (s, 3H), 0.75 (s, 3H), 0.00 (s, 9H); minor: δ 7.25-7.07 (m, 4H), 6.98-6.93 (m, 2H), 6.82-6.70 (m, 2H), 4.50-4.40 (m, 2H), 3.20 (dd, $J = 4.15, 8.79$ Hz, 1H), 2.13-2.09 (m, 1H), 1.79-1.77 (m, 1H), 1.62-1.58 (m, 1H), 0.82 (s, 3H), 0.57 (s, 3H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) mixture of major and minor; δ (160.4, 160.3), (143.48, 143.43), (129.4, 129.3), (128.4, 128.3), (128.0, 127.9), 127.6 (1 C), (126.0, 125.9), (119.4, 119.3), (109.1, 109.0), (73.0, 72.9), (51.8, 50.5), 39.6 (1 C), (38.65, 38.61), 38.1 (1 C), (25.2, 24.7), (24.2, 23.7), -3.1 (3 C); MS (EI)

m/z (relative intensity, %) 372 (M^+ , 13), 315 (11), 264 (28), 179 (19), 131 (58), 119 (28), 73 (100); HRMS calcd for $C_{22}H_{29}ClOSi$ 372.1676, found 372.1677; Anal. Calcd for $C_{22}H_{29}ClOSi$: C, 70.84; H, 7.84. Found: C, 70.85; H, 7.78.