SUPPORTING INFORMATION

Nickel-Catalyzed Cross-Coupling of Neopentyl Arenesulfonates with Methyl and Primary Alkylmagnesium Bromides

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Experimental Section

Solvents were distilled from an appropriate drying agent prior to use: THF and DME from sodium-benzophenone ketyl. Et₂O and toluene were distilled from calcium hydride. Pyridine was dried over CaH₂ and distilled. Commercially available reagents were used without further purification unless otherwise stated. ¹H NMR (300 or 500 MHz) and ¹³C NMR (75 or 125 MHz) were registered in CDCl₃ or acetone-*d*₆ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in δ units (ppm) by assigning TMS resonance in the ¹H spectrum as 0.00 ppm and CDCl₃ resonance in the ¹³C spectrum as 77.2 ppm. All coupling constants, *J*, are reported in hertz (Hz). Column chromatography was performed on silica gel 60, 70-230 mesh. GC analysis was performed on a bonded 5% phenylpolysiloxane BPX 5 capillary column (SGE, 30 m, 0.32 mm i.d.). Electron impact (EI, 70 eV) was used as the ionization method for the mass spectrometry.

General Procedure for the Preparation of Arenesulfonates (1a-1c).

To 2,2-dimethyl-3-phenyl-1-propanol (5.52 mmol) in chloroform (12 mL) at 0 °C were added pyridine (0.85 mL, 10.5 mmol) dropwise over a period of 20 min and sulfonyl chloride (5.25 mmol) in small portions. This reaction mixture was stirred at room temperature for 12 h and diluted with Et₂O and then 0.1% aqueous HCl. The separated organic layer was washed with 0.1% aqueous HCl, water, and saturated aqueous NaCl; dried over MgSO₄; and concentrated in vacuo. The crude sulfonates **1** were purified by either column chromatography or recrystallization.

2,2-Dimethyl-3-phenyl-1-propyl *p*-tert-butylbenzenesulfonate (1a) was prepared by the reaction of 2,2-dimethyl-3-phenyl-1-propanol (0.91 g, 5.52 mmol) with 4-*tert*-butylbenzenesulfonyl chloride (1.22 g, 5.25 mmol). The crude compound was purified by recrystallization from cyclohexane to give **1a** (1.70 g, 90%) as a white crystalline solid: mp 103-103.5 °C (uncorrected); TLC R_f 0.46 (EtOAc:*n*-hexane = 1:4); ^1H NMR (300 MHz, CDCl_3) δ 0.88 (s, 6H), 1.37 (s, 9H), 2.55 (s, 2H), 3.67 (s, 2H), 6.99-7.03 (m, 2H), 7.14-7.21 (m, 3H), 7.57 (d, $J = 8.73$ Hz, 2H), 7.85 (d, $J = 8.73$ Hz, 2H); ^{13}C NMR (75 MHz, acetone- d_6) δ 24.2 ($\times 2$), 31.3 ($\times 3$), 35.8, 35.9, 44.8, 77.8, 127.2, 127.5 ($\times 2$), 128.8 ($\times 2$), 128.9 ($\times 2$), 131.4 ($\times 2$), 134.4, 138.6, 158.8; HRMS (EI, 70 eV) calcd for $\text{C}_{21}\text{H}_{28}\text{O}_3\text{S}$ (M^+) 360.1759, found 360.1432.

2,2-Dimethyl-3-phenyl-1-propyl 2-naphthylsulfonate (1b) was prepared by the reaction of 2,2-dimethyl-3-phenyl-1-propanol (0.91 g, 5.52 mmol) with 2-naphthalenesulfonyl chloride (1.19 g, 5.25 mmol). The crude compound was purified by recrystallization from cyclohexane to give **1b** (1.69 g, 91%) as a white crystalline solid: mp 86-87 °C (uncorrected); TLC R_f 0.36 (EtOAc:*n*-hexane = 1:4); ^1H NMR (300 MHz, CDCl_3) δ 0.87 (s, 6H), 2.55 (s, 2H), 3.71 (s, 2H), 6.98-7.01 (m, 2H), 7.11-7.14 (m, 3H), 7.64-7.75 (m, 2H), 7.89-8.05 (m, 4H), 8.52 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.9 ($\times 2$), 35.2, 44.2, 77.4, 122.7, 126.4, 127.9, 128.0 ($\times 2$), 128.1, 129.5, 129.5, 129.8, 129.9, 130.5 ($\times 2$), 132.1, 132.9, 135.4, 137.4; HRMS (EI, 70 eV) calcd for $\text{C}_{21}\text{H}_{22}\text{O}_3\text{S}$ (M^+) 354.1290, found 354.1275. Anal. calcd for $\text{C}_{21}\text{H}_{22}\text{O}_3\text{S}$: C, 71.16; H, 6.26; S, 9.05. found: C, 71.11; H, 6.19; S, 8.97.

Dineopentyl 4,4'-biphenyldisulfonate (1d) was prepared by the reaction of neopentyl alcohol (0.63 g, 7.13 mmol) with sulfonyl chloride (1.0 g, 2.85 mmol). The crude compound was purified by recrystallization from *n*-hexane to give **1d** (1.08 g, 83%) as a white solid: TLC R_f 0.74 (EtOAc); mp 193-194 °C (uncorrected); ^1H NMR (300 MHz, CDCl_3) δ 0.93 (s, 18H), 3.75 (s, 4H), 7.79 (d, J = 8.56 Hz, 4H), 8.03 (d, J = 8.56 Hz, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 26.1 ($\times 6$), 31.8 ($\times 2$), 80.1 ($\times 2$), 128.4 ($\times 4$), 128.9 ($\times 4$), 136.3 ($\times 2$), 144.6 ($\times 2$); HRMS (EI, 70 eV) calcd for $\text{C}_{22}\text{H}_{30}\text{O}_6\text{S}_2$ (M^+) 454.1484, found 454.1480. Anal. calcd for $\text{C}_{22}\text{H}_{30}\text{O}_6\text{S}_2$: C, 58.12; H, 6.65; S, 14.11. found: C, 58.16; H, 6.32; S, 14.03.

2,2-Dimethyl-3-phenyl-1-propyl 5-dimethylamino-1-naphthalenesulfonate (1c) was prepared by the reaction of 2,2-dimethyl-3-phenyl-1-propanol (0.64 g, 3.91 mmol) with dansyl chloride (1.00 g, 3.70 mmol). The crude compound was purified by column chromatography (EtOAc:*n*-hexane = 1:10) to give **1c** (1.23 g, 84%) as a fluorescent yellowish oil: TLC R_f 0.36 (EtOAc:*n*-hexane = 1:4); ^1H NMR (300 MHz, CDCl_3) δ 0.82 (s, 6H), 2.52 (s, 2H), 2.89 (s, 6H), 3.62 (s, 2H), 6.94-6.97 (m, 2H), 7.10-7.15 (m, 3H), 7.22 (dd, J = 7.56, 0.67 Hz, 1H), 7.54 (dd, J = 8.56, 7.38 Hz, 1H), 7.62 (dd, J = 8.73, 7.56 Hz, 1H), 8.27 (dd, J = 7.38, 1.17 Hz, 1H), 8.38 (dt, J = 8.73, 0.67 Hz, 1H), 8.62 (dt, J = 8.56, 1.17 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 24.1 ($\times 2$), 35.3, 44.3, 45.5 ($\times 2$), 77.6, 115.8, 119.9, 123.3, 126.1, 126.4, 128.1 ($\times 2$), 128.9, 130.1, 130.6 ($\times 2$), 131.6, 137.6, 139.0, 152.1; HRMS (EI, 70 eV) calcd for $\text{C}_{23}\text{H}_{27}\text{NO}_3\text{S}$ (M^+) 397.1712, found 397.1298.

General Procedure for the Preparation of Biphenylsulfonates (1e-1j).

To the solution of 2,2-dimethyl-3-phenyl-1-propyl 4-bromobenzenesulfonate (5.22 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.181 g, 0.157 mmol) in toluene (12 mL) was added 2.0 M aqueous Na_2CO_3 (6.0 mL) under an Ar atmosphere. To the resulting mixture was added arylboronic acid (5.74 mmol), which was

dissolved in ethanol (3 mL). The reaction mixture was heated at reflux for 6 h with vigorous stirring. To the resulting mixture was added 30% hydrogen peroxide (0.3 mL) to oxidize the residual boronic acid. The mixture was stirred at room temperature for 1 h and diluted with EtOAc. The organic layer was washed with water and brine; dried over MgSO_4 ; filtered through a small pad of silica gel in a sintered glass filter; and concentrated in vacuo. *p*-Tolyl-, *p*-*tert*-butylphenyl-, *p*-anisole-, *p*-vinylphenyl-, and biphenylboronic acid were prepared according to a literature procedure.¹ Phenylboronic acid was used as obtained commercially.

2,2-Dimethyl-3-phenyl-1-propyl 1',1''-biphenyl-4'-sulfonate (1e) was prepared by the reaction of 2,2-dimethyl-3-phenyl-1-propyl 4-bromobenzenesulfonate (2.00 g, 5.22 mmol) with phenylboronic acid (0.70 g, 5.74 mmol) in the presence of $\text{Pd}(\text{PPh}_3)_4$ (0.181 g, 0.157 mmol) and 2 M aq. Na_2CO_3 (6.0 mL) by using toluene (12.0 mL) as solvent. The crude product was purified by recrystallization from *n*-hexane to give **1e** (1.41 g, 71%) as a white solid: TLC R_f 0.43 (Et_2O :*n*-hexane = 1:4); mp 74-75 °C (uncorrected); ^1H NMR (300 MHz, CDCl_3) δ 0.89 (s, 6H), 2.57 (s, 2H), 3.72 (s, 2H), 7.00-7.05 (m, 2H), 7.15-7.21 (m, 3H), 7.42-7.53 (m, 3H), 7.63 (d, J = 6.72 Hz, 2H), 7.76 (d, J = 8.73 Hz, 2H), 7.99 (d, J = 8.73 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 24.1 ($\times 2$), 35.4, 44.3, 77.4, 126.5, 127.6 ($\times 2$), 128.1 ($\times 2$), 128.2 ($\times 2$), 128.7 ($\times 2$), 129.0, 129.4 ($\times 2$), 130.7 ($\times 2$), 134.7, 137.6, 139.3, 147.0; HRMS (EI, 70 eV) calcd for $\text{C}_{23}\text{H}_{24}\text{O}_3\text{S}$ (M^+) 380.1446, found 380.1403. Anal. calcd for $\text{C}_{23}\text{H}_{24}\text{O}_3\text{S}$: C, 72.60; H, 6.36; S, 8.43. found: C, 72.73; H, 6.30; S, 8.35.

2,2-Dimethyl-3-phenyl-1-propyl 4''-methyl-1',1''-biphenyl-4'-sulfonate (1f) was prepared by the reaction of 2,2-dimethyl-3-phenyl-1-propyl 4-bromobenzenesulfonate (2.00 g, 5.22 mmol) with *p*-tolylboronic acid (0.78 g, 5.74 mmol) in the presence of Pd(PPh₃)₄ (0.181 g, 0.157 mmol) and 2 M aq. Na₂CO₃ (6.0 mL) by using toluene (12.0 mL) as solvent. The crude product was purified by recrystallization from *n*-hexane to give **1f** (1.50 g, 73%) as a fluffy white solid: TLC *R_f* 0.45 (Et₂O:*n*-hexane = 1:4); mp 89-91 °C (uncorrected); ¹H NMR (300 MHz, CDCl₃) δ 0.89 (s, 6H), 2.42 (s, 3H), 2.56 (s, 2H), 3.71 (s, 2H), 7.00-7.03 (m, 2H), 7.15-7.19 (m, 3H), 7.31 (d, *J* = 8.06 Hz, 2H), 7.53 (d, *J* = 8.06 Hz, 2H), 7.75 (d, *J* = 8.39 Hz, 2H), 7.97 (d, *J* = 8.39 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 21.3, 24.1 (×2), 35.4, 44.4, 77.4, 126.5, 127.5 (×2), 127.8 (×2), 128.2 (×2), 128.7 (×2), 130.1 (×2), 130.7 (×2), 134.4, 136.4, 137.7, 139.1, 146.9; HRMS (EI, 70 eV) calcd for C₂₄H₂₆O₃S (M⁺) 394.1603, found 394.1567. Anal. calcd for C₂₄H₂₆O₃S: C, 73.06; H, 6.64; S, 8.13. found: C, 73.00; H, 6.56; S, 7.73.

2,2-Dimethyl-3-phenyl-1-propyl 4''-tert-butyl-1',1''-biphenyl-4'-sulfonate (1g) was prepared by the reaction of 2,2-dimethyl-3-phenyl-1-propyl 4-bromobenzenesulfonate (2.00 g, 5.22 mmol) with *p*-tert-butylphenylboronic acid (1.02 g, 5.74 mmol) in the presence of Pd(PPh₃)₄ (0.181 g, 0.157 mmol) and 2 M aq. Na₂CO₃ (6.0 mL) by using toluene (12.0 mL) as solvent. The crude product was purified by recrystallization from *n*-hexane to give **1g** (1.78 g, 78%) as a fluffy white solid: TLC *R_f* 0.44 (Et₂O:*n*-hexane = 1:4); mp 76-77 °C (uncorrected); ¹H NMR (300 MHz, CDCl₃) δ 0.90 (s, 6H), 1.38 (s, 9H), 2.57 (s, 2H), 3.71 (s, 2H), 6.98-7.04 (m, 2H), 7.15-7.23 (m, 3H), 7.53 (d, *J* = 8.56 Hz, 2H), 7.59 (d, *J* = 8.56 Hz, 2H), 7.81 (d, *J* = 8.73 Hz, 2H), 7.98 (d, *J* = 8.73 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 24.2 (×2), 31.5 (×3), 34.9, 35.5, 44.4, 77.5, 126.3 (×2), 126.5, 127.2 (×2), 127.8 (×2), 128.1 (×2), 128.6 (×2), 130.6 (×2), 134.3, 136.3, 137.6, 146.7, 152.2; HRMS (EI, 70 eV) calcd for C₂₇H₃₂O₃S (M⁺) 436.2072, found 436.2071. Anal. calcd for C₂₇H₃₂O₃S: C, 74.27; H, 7.39; S, 7.34. found: C, 74.26; H, 7.24; S, 7.73.

2,2-Dimethyl-3-phenyl-1-propyl 4''-methoxy-1',1''-biphenyl-4'-sulfonate (1h) was prepared by the reaction of 2,2-dimethyl-3-phenyl-1-propyl 4-bromobenzenesulfonate (2.00 g, 5.22 mmol) with *p*-methoxyphenylboronic acid (0.87 g, 5.74 mmol) in the presence of Pd(PPh₃)₄ (0.181 g, 0.157 mmol) and 2 M aq. Na₂CO₃ (6.0 mL) by using toluene (12.0 mL) as solvent. The crude product was purified by recrystallization from *n*-hexane to give **1h** (1.59 g, 74%) as a white solid: TLC *R_f* 0.33 (Et₂O:*n*-hexane = 1:4); mp 84-85 °C (uncorrected); ¹H NMR (300 MHz, CDCl₃) δ 0.89 (s, 6H), 2.57 (s, 2H), 3.71 (s, 2H), 3.88 (s, 3H), 7.00-7.05 (m, 2H), 7.03 (d, *J* = 9.07 Hz, 2H), 7.16-7.21 (m, 3H), 7.59 (d, *J* = 9.07 Hz, 2H), 7.73 (d, *J* = 8.72 Hz, 2H), 7.96 (d, *J* = 8.72 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 24.1 (×2), 35.4, 44.3, 55.5, 77.3, 114.8 (×2), 126.5, 127.4 (×2), 128.2 (×2), 128.7 (×2), 128.8 (×2), 130.7(×2), 131.6, 134.0, 137.6, 146.5, 160.6; HRMS (EI, 70 eV) calcd for C₂₄H₂₆O₄S (M⁺) 410.1552, found 410.1597. Anal. calcd for C₂₄H₂₆O₄S: C, 70.22; H, 6.38; S, 7.81. found: C, 70.3; H, 6.31; S, 7.86.

2,2-Dimethyl-3-phenyl-1-propyl 4''-vinyl-1',1''-biphenyl-4'-sulfonate (1i) was prepared by the reaction of 2,2-dimethyl-3-phenyl-1-propyl 4-bromobenzenesulfonate (2.00 g, 5.22 mmol) with *p*-vinylphenylboronic acid (0.85 g, 5.74 mmol) in the presence of Pd(PPh₃)₄ (0.181 g, 0.157 mmol) and 2 M aq. Na₂CO₃ (6.0 mL) by using toluene (12.0 mL) as solvent. The crude product was purified by recrystallization from *n*-hexane to give **1i** (1.61 g, 76%) as a slightly yellowish solid: TLC *R_f* 0.53 (Et₂O:*n*-hexane = 1:4); mp 90-91 °C (uncorrected); ¹H NMR (300 MHz, CDCl₃) δ 0.90 (s, 6H), 2.57 (s, 2H), 3.71 (s, 2H), 5.35 (d, *J* = 10.93 Hz, 1H), 5.85 (d, *J* = 17.60 Hz, 1H), 6.78 (dd, *J* = 17.60, 10.93 Hz, 1H), 7.00-7.03 (m, 2H), 7.15-7.20 (m, 3H), 7.54 (d, *J* = 8.39 Hz, 2H), 7.61 (d, *J* = 8.39 Hz, 2H), 7.78 (d,

$J = 8.56$ Hz, 2H), 7.99 (d, $J = 8.56$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 24.1 ($\times 2$), 35.4, 44.4, 77.4, 115.3, 126.6, 127.2 ($\times 2$), 127.8 ($\times 2$), 127.9 ($\times 2$), 128.2 ($\times 2$), 128.8 ($\times 2$), 130.7 ($\times 2$), 134.8, 136.3, 137.7, 138.4, 138.6, 146.5; HRMS (EI, 70 eV) calcd for $\text{C}_{25}\text{H}_{26}\text{O}_3\text{S}$ (M^+) 406.1603, found 406.1440.

2,2-Dimethyl-3-phenyl-1-propyl 1',1'',1'''-terphenyl-4'-sulfonate (1j) was prepared by the reaction of 2,2-dimethyl-3-phenyl-1-propyl 4-bromobenzenesulfonate (2.00 g, 5.22 mmol) with biphenylboronic acid (1.14 g, 5.74 mmol) in the presence of $\text{Pd}(\text{PPh}_3)_4$ (0.18 g, 0.157 mmol) and 2 M aq. Na_2CO_3 (6.0 mL) by using toluene (12.0 mL) as solvent. The crude product was purified by recrystallization from *n*-hexane to give **1j** (1.62 g, 68%) as a fluffy white solid: TLC R_f 0.50 (UV 254 nm blue tailing spot, $\text{Et}_2\text{O}:\text{n-hexane} = 1:1$); mp 161-162 °C (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ 0.90 (s, 6H), 2.57 (s, 2H), 3.72 (s, 2H), 7.01-7.03 (m, 2H), 7.15-7.21 (m, 3H), 7.39 (t, $J = 7.35$ Hz, 1H), 7.48 (dd, $J = 7.80$, 7.35 Hz, 2H), 7.65 (d, $J = 7.80$ Hz, 2H), 7.71 (d, $J = 8.70$ Hz, 2H), 7.73 (d, $J = 8.70$ Hz, 2H), 7.82 (d, $J = 8.25$ Hz, 2H), 8.00 (d, $J = 8.25$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 24.2 ($\times 2$), 35.5, 44.4, 77.5, 126.5, 127.3 ($\times 2$), 127.6, 127.8 ($\times 2$), 127.9 ($\times 2$), 128.0 ($\times 2$), 128.1 ($\times 2$), 128.7 ($\times 2$), 129.1 ($\times 2$), 130.6 ($\times 2$), 134.7, 137.5, 138.0, 140.4, 141.8, 146.4; HRMS (EI, 70 eV) calcd for $\text{C}_{29}\text{H}_{28}\text{O}_3\text{S}$ (M^+) 456.1756, found 456.1766. Anal. calcd for $\text{C}_{29}\text{H}_{28}\text{O}_3\text{S}$: C, 76.28; H, 6.18; S, 7.02. found: C, 76.32; H, 6.06; S, 6.31.

General Procedure for the Cross-Coupling Reactions of **1** with **2**.

To a stirred solution of sulfonate **1** (0.30 mmol) and dppeNiCl_2 (0.015 mmol) in THF (10 mL) was slowly added Grignard reagents **2** (0.90 mmol) at room temperature. The reaction mixture was heated at reflux for 6 h, cooled to room temperature, and an additional 0.60 mmol of **2** was added to the solution. The resulting mixture was heated at reflux for 6 h, cooled to room temperature, and diluted with Et_2O .

The organic layer was washed with a 1% aqueous HCl, water, and brine; dried over MgSO₄; and concentrated in vacuo.

***N,N*-Dimethyl-5-methyl-1-naphthalenamine (3c)** was prepared by the reaction of **1c** (119 mg, 0.30 mmol) with methylmagnesium bromide **2a** (3.0 M in Et₂O, 0.30 mL, 0.90 mmol + 0.20 mL, 0.60 mmol) in the presence of dppeNiCl₂. The crude compound was purified by column chromatography (EtOAc:*n*-hexane = 1:10) to give **3c** (43.9 mg, 79%) as a yellow oil: TLC *R_f* 0.53 (Et₂O:*n*-hexane = 1:4); ¹H NMR (300 MHz, CDCl₃) δ 2.68 (s, 3H), 2.89 (s, 6H), 7.10 (d, *J* = 7.22 Hz, 1H), 7.28-7.45 (m, 3H), 7.69 (d, *J* = 8.39 Hz, 1H), 8.14 (d, *J* = 8.39 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 19.9, 45.4 (×2), 114.1, 119.3, 122.7, 125.0, 125.8, 126.8, 129.2, 134.2, 134.8, 151.6; HRMS (EI, 70 eV) calcd for C₁₃H₁₅N (M⁺), 185.1204, found 185.1286.

4,4'-Dimethylbiphenyl (3d) was prepared by the reaction of **1d** (136 mg, 0.30 mmol) with methylmagnesium bromide **2a** (3.0 M in Et₂O, 0.60 mL, 1.8 mmol + 0.40 mL, 1.2 mmol) in the presence of dppeNiCl₂. The crude compound was purified by column chromatography (EtOAc:*n*-hexane = 1:10) to give **3d** (45.93 mg, 84%) as a white solid: mp 119-120 °C (an authentic sample² mp 118-120 °C).

4,4'-Dimethylbiphenyl (3d) was also prepared by the reaction of **1f** (118 mg, 0.30 mmol) with methylmagnesium bromide **2a** (3.0 M in Et₂O, 0.30 mL, 0.90 mmol + 0.20 mL, 0.60 mmol) in the presence of dppeNiCl₂. The crude compound was purified by column chromatography (EtOAc:*n*-hexane = 1:4) to give **3d** (45.38 mg, 83%) as a white solid.

4-Methylbiphenyl (3e) was prepared by the reaction of **1e** (114 mg, 0.30 mmol) with methylmagnesium bromide **2a** (3.0 M in Et₂O, 0.30 mL, 0.90 mmol + 0.20 mL, 0.60 mmol) in the presence of dppeNiCl₂. The crude compound was purified by column chromatography (EtOAc:*n*-hexane = 1:4) to give **3e** (42.39 mg, 84%) as a white solid: mp 45-48 °C (an authentic sample³ mp 44-47 °C).

4-Methyl-4'-tert-butylbiphenyl (3f) was prepared by the reaction of **1g** (131 mg, 0.30 mmol) with methylmagnesium bromide **2a** (3.0 M in Et₂O, 0.30 mL, 0.90 mmol + 0.20 mL, 0.60 mmol) in the presence of dppeNiCl₂. The crude compound was purified by column chromatography (EtOAc:*n*-hexane = 1:10) to give **3f** (56.53 mg, 84%) as a white solid: mp 75-76 °C (uncorrected); TLC *R*_f 0.66 (Et₂O:*n*-hexane = 1:4); ¹H NMR (300 MHz, CDCl₃) δ 1.36 (s, 9H), 2.39 (s, 3H), 7.24 (d, *J* = 8.48 Hz, 2H), 7.45 (d, *J* = 8.73 Hz, 2H), 7.49 (d, *J* = 8.48 Hz, 2H), 7.53 (d, *J* = 8.73 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 21.2, 31.5 (×3), 34.6, 125.9 (×2), 126.9 (×2), 127.1 (×2), 129.7 (×2), 137.0, 138.5, 138.6, 150.2; HRMS (EI, 70 eV) calcd for C₁₇H₂₀ (M⁺), 224.1565, found 224.1546. Anal. calcd for C₁₇H₂₀: C, 91.01; H, 8.99. found: C, 91.23; H, 8.87.

4-Methyl-4'-methoxybiphenyl (3g) was prepared by the reaction of **1h** (123 mg, 0.30 mmol) with methylmagnesium bromide **2a** (3.0 M in Et₂O, 0.30 mL, 0.90 mmol + 0.20 mL, 0.60 mmol) in the presence of dppeNiCl₂. The crude compound was purified by column chromatography (Et₂O:*n*-hexane = 1:4) to give **3g** (47.58 mg, 80%) as a white solid: mp 102-104 °C (uncorrected); TLC *R*_f 0.49 (Et₂O:*n*-hexane = 1:4); ¹H NMR (300 MHz, CDCl₃) δ 2.38 (s, 3H), 3.84 (s, 3H), 6.96 (d, *J* = 8.90 Hz, 2H), 7.22 (d, *J* = 8.40 Hz, 2H), 7.45 (d, *J* = 8.40 Hz, 2H), 7.51 (d, *J* = 8.90 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ

21.1, 55.435, 114.4 (×2), 126.8 (×2), 128.2 (×2), 129.7 (×2), 134.0, 136.6, 138.3, 159.3; HRMS (EI, 70 eV) calcd for C₁₄H₁₄O (M⁺), 198.1045, found 198.1024. Anal. calcd for C₁₄H₁₄O: C, 84.81; H, 7.12; S, 8.07. found: C, 84.88; H, 7.01; S, 7.99.

4-Methyl-*p*-terphenyl (3i) was prepared by the reaction of **1j** (137 mg, 0.30 mmol) with methylmagnesium bromide **2a** (3.0 M in Et₂O, 0.30 mL, 0.90 mmol + 0.20 mL, 0.60 mmol) in the presence of dppeNiCl₂. The crude compound was purified by column chromatography (Et₂O:*n*-hexane = 1:10) to give **3i** (63.04 mg, 86%) as a white solid: TLC *R_f* 0.66 (Et₂O:*n*-hexane = 1:4); mp 209-210 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ 2.41 (s, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.66 (s, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 21.2, 127.2 (×2), 127.3 (×2), 127.6 (×2), 127.6, 127.7 (×2), 129.1 (×2), 129.8 (×2), 137.4, 138.1, 140.1, 140.4, 141.1; HRMS (EI, 70 eV) calcd for C₁₉H₁₆ (M⁺): 244.1252. found 244.1249.

4-Neopentylbiphenyl (3j) was prepared by the reaction of **1e** (114 mg, 0.30 mmol) with neopentylmagnesium bromide **2b** (0.5 M in THF, 1.80 mL, 0.90 mmol + 1.20 mL, 0.60 mmol) in the presence of dppeNiCl₂. The crude compound was purified by column chromatography (EtOAc:*n*-hexane = 1:10) to give **3j** (49.13 mg, 73%) as a white solid: TLC *R_f* 0.76 (EtOAc:*n*-hexane = 1:4); mp 62-63 °C (uncorrected); ¹H NMR (300 MHz, CDCl₃) δ 0.94 (s, 9H), 2.53 (s, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.43 (dd, *J* = 7.3, 7.5 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 7.3 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 29.5 (×3), 32.0, 50.0, 126.6 (×2), 127.2 (×3), 129.0 (×2), 131.2 (×2), 138.9, 139.2, 141.4; Anal. calcd for C₁₇H₂₀: C, 91.01; H, 8.99. found: C, 90.75; H, 8.92.

4-Methyl-4'-neopentylbiphenyl (3k) was prepared by the reaction of **1f** (136 mg, 0.30 mmol) with neopentylmagnesium bromide **2b** (0.5 M in THF, 1.80 mL, 0.90 mmol + 1.20 mL, 0.60 mmol) in the presence of dppeNiCl₂. The crude compound was purified by column chromatography (EtOAc:*n*-hexane = 1:10) to give **3k** (55.78 mg, 78%) as a white solid: TLC *R_f* 0.74 (EtOAc:*n*-hexane = 1:4); mp 69-70 °C (uncorrected); ¹H NMR (300 MHz, CDCl₃) δ 0.94 (s, 9H), 2.39 (s, 3H), 2.53 (s, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 21.1, 29.4 (×3), 31.8, 49.8, 126.1 (×2), 126.8 (×3), 129.4 (×2), 130.8 (×2), 136.7, 138.5, 138.6; Anal. calcd for C₁₈H₂₂: C, 90.70; H, 9.30. found: C, 90.53; H, 9.21.

2-(2-Methyl-2-phenylpropyl)naphthalene (3l) was prepared by the reaction of **1b** (106 mg, 0.30 mmol) with 2-methyl-2-phenylpropylmagnesium chloride **2c** (0.5 M in Et₂O, 1.8 mL, 0.90 mmol + 1.2 mL, 0.60 mmol) in the presence of dppeNiCl₂. The crude compound was purified by preparative TLC in *n*-hexane to afford **3l** (58.58 mg, 75%) as a white solid: TLC *R_f* 0.72 (EtOAc:*n*-hexane = 1:4); mp 68-69 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ 1.37 (s, 6H), 3.03 (s, 2H), 6.88 (dd, *J* = 8.40, 1.61 Hz, 1H), 7.18-7.23 (m, 1H), 7.27-7.34 (m, 5H), 7.37-7.43 (m, 2H), 7.58 (d, *J* = 8.40 Hz, 1H), 7.66 (dd, *J* = 6.66, 2.42 Hz, 1H), 7.75 (dd, *J* = 6.66, 2.42 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 28.4 (×2), 39.1, 51.4, 125.4, 125.8, 126.0, 126.5, 126.9 (×2), 127.7, 127.8, 128.2 (×2), 129.1, 129.4, 132.3, 133.4, 136.8, 149.2; HRMS (EI, 70 eV) calcd for C₂₀H₂₀ (M⁺): 260.1565. found 260.1554. Anal. calcd for C₂₀H₂₀: C, 92.26; H, 7.74. found: C, 91.98; H, 7.72.

4-(2-Methyl-2-phenylpropyl)biphenyl (3m) was prepared by the reaction of **1e** (114 mg, 0.30 mmol) with 2-methyl-2-phenylpropylmagnesium chloride **2c** (0.5 M in Et₂O, 1.8 mL, 0.90 mmol + 1.2 mL, 0.60 mmol) in the presence of dppeNiCl₂. The crude compound was purified by recrystallization in ethanol to afford **3m** (52.41 mg, 61%) as a white solid: TLC *R_f* 0.72 (EtOAc:*n*-hexane = 1:4); mp 94-95 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ 1.35 (s, 6H), 2.91 (s, 2H), 6.87 (d, *J* = 8.11 Hz, 2H), 7.18-7.22 (m, 1H), 7.28-7.34 (m, 5H), 7.36-7.42 (m, 4H), 7.55 (d, *J* = 7.24 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 28.4 (×2), 39.0 (×2), 50.9, 125.9, 126.4 (×2), 126.5 (×2), 127.2 (×2), 127.2, 128.2 (×2), 129.0 (×2), 131.1 (×2), 138.3, 139.0, 141.3, 149.3; HRMS (EI, 70 eV) calcd for C₂₂H₂₂ (M⁺): 286.1721. found: 286.1726. Anal. calcd for C₂₂H₂₂: C, 92.26; H, 7.74. found: C, 92.18; H, 7.65.

4-Methoxy-4'-(2-methyl-2-phenylpropyl)biphenyl (3n) was prepared by the reaction of **1h** (123 mg, 0.30 mmol) with 2-methyl-2-phenylpropylmagnesium chloride **2c** (0.5 M in Et₂O, 1.8 mL, 0.90 mmol + 1.2 mL, 0.60 mmol) in the presence of dppeNiCl₂. The crude compound was purified by recrystallization in ethanol to afford **3n** (62.66 mg, 66%) as a white solid: TLC *R_f* 0.54 (EtOAc:*n*-hexane = 1:4); mp 112-113 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ 1.35 (s, 6H), 2.90 (s, 2H), 3.84 (s, 3H), 6.85 (d, *J* = 8.16 Hz, 2H), 6.94 (d, *J* = 8.77 Hz, 2H), 7.18-7.22 (m, 1H), 7.28-7.34 (m, 6H), 7.48 (d, *J* = 8.77 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 28.3 (×2), 39.0 (×2), 50.9, 55.5, 114.4 (×2), 125.9, 125.7 (×2), 126.5 (×2), 128.2 (×2), 128.2 (×2), 131.1 (×2), 133.9, 137.7, 138.6, 149.3, 159.3; HRMS (EI, 70 eV) calcd for C₂₃H₂₄O (M⁺): 316.1827. found 316.1811. Anal. calcd for C₂₃H₂₄O: C, 87.30; H, 7.64. found: C, 86.94; H, 7.52.

2-Benzyl-naphthalene (3o) was prepared by the reaction of **1b** (106 mg, 0.30 mmol) with benzylmagnesium bromide **2d** (1.0 M in THF, 0.90 mL, 0.90 mmol + 0.60 mL, 0.60 mmol) in the presence of dppeNiCl₂. The crude compound was purified by preparative TLC in n-hexane to afford **3m** (22.92 mg, 35%) as a white solid; TLC R_f 0.70 (EtOAc:n-hexane = 1:4); mp 35-36 °C (lit.^{4a} mp 35.5 °C, lit.^{4b} mp 34-37 °C); ¹H NMR (300 MHz, CDCl₃) δ 4.12 (s, 2H), 7.15-7.33 (m, 6H), 7.39-7.44 (m, 2H), 7.62 (s, 1H), 7.71-7.81 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 42.2, 125.6, 126.2, 126.4, 127.4, 127.8, 127.9 (×2), 128.4, 128.8 (×2), 129.3 (×2), 132.4, 133.9, 138.9, 141.3.

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Figure S2. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **1b**

Figure S3. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **1c**

Figure S4. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **1d**

Figure S5. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **1e**

Figure S6. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **1f**

Figure S7. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (125 MHz, CDCl_3) spectrum of **1g**

Figure S8. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **1h**

Figure S9. ¹H NMR (300 MHz, CDCl₃) & ¹³C NMR (75 MHz, CDCl₃) spectrum of **1i**

Figure S10. ^1H NMR (500 MHz, CDCl_3) & ^{13}C NMR (125 MHz, CDCl_3) spectrum of **1j**

Figure S11. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **3c**

Figure S12. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **3f**

Figure S13. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **3g**

Figure S14. ^1H NMR (500 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **3i**

Figure S15. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **3j**

Figure S16. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **3k**

Figure S17. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **3I**

Figure S18. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **3m**

Figure S19. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **3n**

Figure S20. ^1H NMR (300 MHz, CDCl_3) & ^{13}C NMR (75 MHz, CDCl_3) spectrum of **3o**