Supporting Information

Palladium-Catalyzed Arylation of α,α -Disubstituted Arylmethanols to Give Biaryls via Cleavage of C-C or C-H Bond

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Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, for CDCl_3 or $\text{DMSO}-d_6$ solutions. MS analysis was made by EI. GC analysis was carried out using a Silicon OV-17 glass column (i.d. 2.6 mm x 1.5 m) or a CBP-1 capillary column (i.d. 0.25 mm x 25 m). Aryldiphenylmethanols, 2-aryl-2-propanols, and 1-(biphenyl-2-yl)-1-cyclohexanol (**1c**) were prepared by the reactions of the corresponding arylmagnesium bromides with benzophenone, acetone, and cyclohexanone, respectively, except the following substrates. Alcohols **1d** and **15c** were obtained by the reactions of methyl 2-(1-naphthyl)benzoate with MeMgI and of ketone **17a** with PhMgBr , respectively, in ether. **1d**: mp 91-93 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.29 (s, 3H), 1.41 (s, 3H), 1.64 (s, 1H), 7.09 (dd, 1H, $J = 1.4$, 7.3 Hz), 7.28 (dt, 1H, $J = 1.1$, 7.3 Hz), 7.34-7.50 (m, 6H), 7.73 (dd, 1H, $J = 1.4$, 8.0 Hz), 7.84-7.87 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 32.16, 32.32, 74.03, 124.75, 125.84, 125.98, 126.13, 126.23, 126.97, 126.98, 127.65, 127.68, 128.05, 132.64, 133.05, 133.46, 137.33, 141.09, 147.24; MS m/z 262 (M^+). Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{O}$: C, 86.99; H, 6.99. Found: C, 86.70; H, 6.79. **15c**: mp 217-219 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.02 (s, 1H), 6.37 (dd, 1H, $J = 1.1$, 7.7 Hz), 6.70-6.73 (m, 1H), 6.78-6.81 (m, 1H), 6.94 (dt, 1H, $J = 1.5$, 7.7 Hz), 6.97-7.12 (m, 4H), 7.16-7.37 (m, 12H), 7.44-7.48 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 83.88, 125.82, 126.30, 126.51, 127.18, 127.27, 127.65, 127.67, 127.67, 127.72, 127.92, 128.01, 128.42, 129.83, 130.01, 130.67, 130.75, 133.36, 139.05, 140.31, 141.15, 141.23, 144.68, 147.71, 148.26; MS m/z 412 (M^+). Anal. Calcd for $\text{C}_{31}\text{H}_{24}\text{O}$: C, 90.26; H, 5.86. Found: C, 90.18; H, 5.78. 2-(2,6-Dimethylphenyl)-2-propanol was prepared from 2,6-dimethylphenyl lithium and acetone in THF.¹ The following experimental details may be regarded as typical in scale and methodology.

Reaction of 2-(biphenyl-2-yl)-2-propanol (1b) with 2-bromotoluene (2b) (Table 1, entry 1): In a 100 cm³ two-necked flask was placed Cs₂CO₃ (1.5 mmol, 489 mg), which was then dried at 150 °C in vacuo for 2 h. Then, Pd(OAc)₂ (0.025 mmol, 5.6 mg), PPh₃ (0.15 mmol, 39 mg), **1b** (0.5 mmol, 106 mg), **2b** (1.5 mmol, 256 mg), 1-methylnaphthalene (ca. 100 mg) as internal standard, and *o*-xylene (5 mL) were added. The resulting mixture was stirred under N₂ (balloon) at 160 °C (bath temperature) for 24 h. After cooling the reaction mixture was poured into water, extracted with diethyl ether, and dried over sodium sulfate. The solvent was removed in vacuo. The residue was purified by column chromatography on silica gel using hexane-diethyl ether (99:1) as eluent to afford compound **7** (108 mg, 55%): mp 155-156 °C; ¹H NMR (400 MHz, DMSO-*d*₆, 150 °C) δ 1.11 (s, 6H), 2.20 (s, 6H), 3.06 (s, 1H), 6.75-6.86 (m, 6H), 6.92-6.96 (m, 2H), 7.04-7.12 (m, 6H), 7.31 (t, 1H, *J* = 7.5 Hz); ¹³C NMR (100 MHz, DMSO-*d*₆, 150 °C) δ 19.62, 32.30, 73.01, 122.89, 123.39, 124.25, 125.59, 125.65, 126.07, 128.17, 128.94, 130.35, 132.32, 134.66, 134.85, 139.46, 141.06, 142.83, 146.10; MS *m/z* 392 (M⁺). Anal. Calcd for C₂₉H₂₈O: C, 88.73; H, 7.18. Found: C, 88.62; H, 7.31. The methyl peaks of ¹H NMR at rt, 100 °C, and 150 °C are shown in Figure 1. The sample for X-ray analysis was obtained by recrystallization from hexane. Its ORTEP drawing is shown in Figure 2.

FIGURE 1. Methyl peaks of compound **7** in ^1H NMR for $\text{DMSO}-d_6$ solution at different temperatures.

FIGURE 2. ORTEP drawing of compound **7**.
Crystal data: $\text{C}_{29}\text{H}_{28}\text{O}$, Mw = 392.54, triclinic, space group P-1 (#2), T = 293 K, a = 10.222(10), b = 10.812(9), c = 12.050(9), $\alpha = 66.96(4)^\circ$, $\beta = 68.77(5)^\circ$, $\gamma = 83.88(6)^\circ$, V = 1141(1) $\text{\AA}^3$, Z = 2, 3128 reflections measured, R = 0.079, Rw = 0.186.

Reaction of 2-(2-methoxy-1-naphthyl)-2-propanol with 2-chloroanisole (Table 9, entries 4-6): In a 100 cm^3 two-necked flask was placed Cs_2CO_3 (1 mmol, 326 mg), which was then dried at 150 $^\circ\text{C}$ in vacuo for 2 h. Then, $\text{Pd}(\text{OAc})_2$ (0.025 mmol, 5.6 mg), PCy_3 (0.05 mmol, 14 mg), the alcohol (0.5 mmol, 93 mg), and *o*-xylene (2.5 mL) were added. The resulting mixture was stirred under N_2 at rt for 0.5 h, and then, the chloride (1 mmol, 142 mg), 1-methylnaphthalene (ca. 100 mg) as internal standard, and *o*-xylene (2.5 mL) were added to the flask. The resulting mixture was stirred under N_2 (balloon) at 160 $^\circ\text{C}$ (bath temperature) for 4 h. After cooling the reaction mixture was filtered with diethyl ether and the solvents were removed in vacuo. The residue was purified by column chromatography on silica gel using hexane-ethyl acetate

(95:5) as eluent to give 2-methoxy-1-(2-methoxyphenyl)naphthalene² (117 mg, 89%): mp 91-92 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.68 (s, 3H), 3.82 (s, 3H), 7.06 (d, 1H, *J* = 8.4 Hz), 7.08 (dt, 1H, *J* = 1.1, 7.3 Hz), 7.21 (dd, 1H, *J* = 1.8, 7.3 Hz), 7.28-7.33 (m, 2H), 7.35-7.37 (m, 1H), 7.37 (d, 1H, *J* = 8.8 Hz), 7.42 (ddd, 1H, *J* = 1.5, 7.7, 8.1 Hz), 7.79-7.82 (m, 1H), 7.87 (d, 1H, *J* = 8.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 55.70, 56.95, 111.30, 114.16, 120.54, 122.10, 123.39, 125.23, 125.35, 126.09, 127.82, 128.83, 129.05, 129.06, 132.40, 133.63, 154.24, 157.72; MS *m/z* 264 (M⁺). The product (611 mg, 93%) was also isolated by treatment of the alcohol (2.5 mmol) and the chloride (3 mmol) under the same conditions. The reaction of the alcohol (0.5 mmol) and the chloride (1 mmol) in the presence of [PhPd(OH)PCy₃]₂³ (5.6 mg, 0.0058 mmol) in place of Pd(OAc)₂-PCy₃ for 6 h afforded 94% GC yield.

Products: Mono-substituted biaryls other than 2- and 4-trifluoromethyl-1,1'-biphenyls, 1-phenylnaphthalene, and 2-phenylthiophene were identified and quantified using the corresponding commercially available samples. An authentic sample of 4-trifluoromethylbiphenyl (mp 68-69 °C) was prepared by the Suzuki-Miyaura reaction.⁴ The characterization data of other products are given below. Compounds **7-11**, **14c**, **17c**, 9-(2-methoxyphenyl)phenanthrene, and methyl 2-(2,6-dimethylphenyl)benzoate are new. The ee value of 2-methoxy-1,1'-binaphthyl was determined by optical rotation in THF.⁵

Compound 5:⁶ oil; ¹H NMR (400 MHz, CDCl₃) δ 1.28 (s, 3H), 1.37 (s, 3H), 1.61 (s, 1H), 7.00 (d, 1H, *J* = 7.7 Hz), 7.08-7.24 (m, 7H), 7.30-7.44 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 31.72, 33.70, 74.50, 125.52, 126.52, 126.70, 126.76, 127.08, 127.63, 127.71, 129.82, 130.03, 130.25, 133.13, 137.97, 140.47, 141.27, 142.44, 146.15; HRMS calcd for C₂₁H₂₀O 288.1514, found 288.1513.

Compound 6:⁶ mp 99.5-100.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.01 (s,

6H), 1.55 (s, 1H), 6.91-6.97 (m, 3H), 7.03-7.07 (m, 1H), 7.12-7.19 (m, 10H), 7.41 (d, 2H, $J = 7.2$ Hz), 7.47 (t, 1H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 32.09, 74.96, 124.74, 126.45, 126.76, 127.27, 127.30, 127.56, 129.44, 130.02, 134.79, 135.00, 140.82, 141.49, 141.88, 146.29; MS m/z 364 (M^+). Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{O}$: C, 88.97; H, 6.63. Found: C, 88.69; H, 6.79.

Compound 8: mp 148-149 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 150 °C) δ 1.13 (s, 6H), 2.01 (s, 6H), 2.14 (s, 6H), 3.05 (s, 1H), 6.75-6.93 (m, 10H), 7.08 (d, 2H, $J = 7.3$ Hz), 7.30 (t, 1H, $J = 7.3$ Hz); ^{13}C NMR (400 MHz, $\text{DMSO}-d_6$, 150 °C) δ 19.13, 19.40, 32.27, 73.02, 122.69, 124.19, 125.52, 126.00, 126.32, 128.04, 128.80, 130.99, 131.64, 132.21, 132.36, 134.78, 139.48, 140.87, 142.72, 146.15; MS m/z 420 (M^+). Anal. Calcd for $\text{C}_{31}\text{H}_{32}\text{O}$: C, 88.52; H, 7.66. Found: C, 88.43; H, 7.72.

Compound 9: mp 184-185 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$, mixture of rotamers) δ 0.12-1.31 (6H, 4 peaks at 0.12, 0.27, 1.23, and 1.31 in ratio of ca. 3:1:3:2; Me), 3.56-4.47 (1H, 3 peaks at 3.56, 3.98, and 4.47 in ratio of ca. 0.15:1:0.3; OH), 6.07-8.13 (m, 21H). Anal. Calcd for $\text{C}_{35}\text{H}_{28}\text{O}$: C, 90.48; H, 6.07. Found: C, 90.13; H, 6.48.

Compound 10: mp 146-147 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 150 °C) (Figure 3) δ 1.10-1.34 (m, 7H), 1.51-1.62 (m, 3H), 2.21 (s, 6H), 2.41 (s, 1H), 6.76-6.80 (m, 3H), 6.86-7.06 (m, 9H), 7.15 (d, 2H, $J = 7.3$ Hz), 7.34 (t, 1H, $J = 7.3$ Hz); HRMS m/z (M^+) calcd for $\text{C}_{32}\text{H}_{32}\text{O}$ 432.2453, found: 432.2450.

Compound 11: mp 158-160 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 150 °C) (Figure 4) δ 1.21 (s, 6H), 2.15 (s, 3H), 3.17 (s, 1H), 6.85-7.34 (m, 10H), 7.40-7.43 (m, 2H), 7.82-7.89 (m, 2H); HRMS m/z (M^+) calcd for $\text{C}_{26}\text{H}_{24}\text{O}$ 352.1827, found: 352.1833.

FIGURE 3. ^1H NMR of Compound **10** in $\text{DMSO-}d_6$ at $150\text{ }^\circ\text{C}$.

FIGURE 4. ^1H NMR of Compound **11** in $\text{DMSO-}d_6$ at $150\text{ }^\circ\text{C}$.

Compound 12:⁷ oil; ^1H NMR (400 MHz, CDCl_3) δ 1.63 (s, 6H), 6.94 (dd, 1H, $J = 1.1, 8.1\text{ Hz}$), 6.99-7.03 (m, 1H), 7.19-7.35 (m, 4H), 7.71-7.73 (m,

2H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.55, 77.50, 118.03, 121.48, 122.19, 122.45, 122.83, 123.16, 127.65, 127.91, 128.58, 129.38, 139.50, 152.74; MS m/z 210 (M^+).

Compound 14a:⁸ mp 203-204 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.61-7.65 (m, 6H), 8.61-8.65 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 123.26, 127.18, 129.76; MS m/z 228 (M^+).

Compound 14b:⁹ mp 158-160 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.50 (s, 6H), 7.58-7.64 (m, 4H), 8.37 (s, 2H), 8.59-8.63 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.29, 123.02, 123.22, 123.84, 126.60, 127.00, 127.88, 129.49, 129.75, 136.17; MS m/z 256 (M^+). Anal. Calcd for $\text{C}_{20}\text{H}_{16}$: C, 93.70; H, 6.29. Found: C, 93.45; H, 6.48.

Compound 14c: mp 178-179 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.62-7.69 (m, 4H), 8.30 (t, 2H, $J = 10.3$ Hz), 8.36-8.39 (m, 2H), 8.59-8.63 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 111.25 (dd, $J_{\text{C-F}} = 7.3, 11.9$ Hz), 123.29, 123.42, 127.11 (t, $J_{\text{C-F}} = 5.6$ Hz), 127.48, 127.59, 128.48, 129.68, 150.10 (dd, $J_{\text{C-F}} = 15.6, 250.0$ Hz). Anal. Calcd for $\text{C}_{18}\text{H}_{10}\text{F}_2$: C, 81.81; H, 3.81. Found: C, 81.52; H, 3.66.

Compound 17a:⁶ mp 119-120 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.03-7.09 (m, 5H), 7.25-7.39 (m, 11H), 7.42-7.47 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 125.97, 126.42, 127.15, 127.74, 127.80, 127.84, 129.35, 130.02, 130.07, 130.19, 130.26, 130.59, 132.15, 132.36, 137.23, 138.48, 139.22, 140.41, 140.94, 142.32, 196.59; MS m/z 334 (M^+). Anal. Calcd for $\text{C}_{25}\text{H}_{18}\text{O}$: C, 89.79; H, 5.43. Found: C, 89.56; H, 5.51.

Compound 17b: oil; ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 100 °C)(Figure 5) δ 1.91 (s, 3H), 6.82-6.85 (m, 2H), 6.92 (d, 1H, $J = 8.4$ Hz), 6.97-7.01 (m, 1H), 7.12 (dd, 1H, $J = 1.8, 7.3$ Hz), 7.18-7.32 (m, 6H), 7.36-7.40 (m, 5H), 7.54-7.58 (m, 1H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 100 °C) δ 19.28, 124.39, 125.72,

126.33, 126.42, 126.48, 127.73, 128.24, 129.22, 129.39, 129.59, 129.98, 130.22, 130.22, 131.38, 132.31, 135.15, 136.84, 137.72, 139.08, 139.17, 139.73, 140.75, 195.30; HRMS m/z (M^+) calcd for $C_{26}H_{20}O$ 348.1514, found: 348.1510.

FIGURE 5. 1H NMR of Compound **17b** in $DMSO-d_6$ at 100 °C.

Compound 18:⁶ mp 178-179 °C; 1H NMR (400 MHz, $CDCl_3$) δ 6.97-7.03 (m, 6H), 7.06-7.11 (m, 9H), 7.16-7.20 (m, 3H), 7.35 (d, 2H, $J = 7.7$ Hz), 7.41 (t, 1H, $J = 7.3$ Hz), 7.45 (t, 1H, $J = 7.7$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.29, 126.14, 127.47, 127.55, 127.62, 129.51, 129.87, 129.92, 130.03, 130.12, 131.97, 133.91, 136.88, 137.87, 138.24, 141.16, 141.43, 141.86, 195.96; MS m/z 410 (M^+). Anal. Calcd for $C_{31}H_{22}O$: C, 90.70; H, 5.40. Found: C, 90.35; H, 5.58.

2-Phenylfuran (eq 8):¹⁰ oil; 1H NMR (400 MHz, $CDCl_3$) δ 6.47 (dd, 1H, $J = 1.8, 3.3$ Hz), 6.64 (d, 1H, $J = 3.3$ Hz), 7.21-7.43 (m, 4H), 7.65-7.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.93, 111.60, 123.78, 127.30, 128.64, 129.57, 142.03, 154.04; MS m/z 144 (M^+).

9-(2-Methoxyphenyl)anthracene (eq 9):¹¹ mp 177-179 °C; 1H NMR (400 MHz, $CDCl_3$) δ 3.60 (s, 3H), 7.14 (d, 1H, $J = 8.1$ Hz), 7.15 (dt, 1H, $J = 1.1, 7.3$ Hz), 7.26 (dd, 1H, $J = 1.8, 7.3$ Hz), 7.32 (ddd, 2H, $J = 1.5, 6.6, 8.8$ Hz),

7.41-7.45 (m, 2H), 7.52 (ddd, 1H, $J = 1.8, 7.3, 8.1$ Hz), 7.60 (dd, 2H, $J = 1.5, 8.8$ Hz), 8.02 (d, 2H, $J = 8.4$ Hz), 8.47 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.67, 111.30, 120.67, 124.97, 125.17, 126.51, 126.74, 127.32, 128.39, 129.28, 130.35, 131.43, 132.84, 133.74, 158.02; MS m/z 284 (M^+).

9-(2-Methoxyphenyl)phenanthrene (eq 10): mp 100-102 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.68 (s, 3H), 7.05 (d, 1H, $J = 7.7$ Hz), 7.10 (dt, 1H, $J = 1.1, 7.3$ Hz), 7.35 (dd, 1H, $J = 1.8, 7.3$ Hz), 7.43-7.50 (m, 2H), 7.56-7.66 (m, 4H), 7.67 (s, 1H), 7.87 (dd, 1H, $J = 1.5, 7.7$ Hz), 8.71 (d, 1H, $J = 8.1$ Hz), 8.74 (d, 1H, $J = 8.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 55.55, 110.94, 120.69, 122.55, 122.67, 126.20, 126.25, 126.42, 126.58, 127.16, 127.78, 128.64, 129.13, 129.62, 130.15, 130.22, 131.44, 131.74, 131.84, 135.84, 157.46; MS m/z 284 (M^+). Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{O}$: C, 88.70; H, 5.67. Found: C, 88.45; H, 5.64.

2-(Trifluoromethyl)-1,1'-biphenyl (Table 5, entries 7 and 8; Table 7, entry 8):¹² oil; ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.42 (m, 6H), 7.44 (t, 1H, $J = 7.7$ Hz), 7.55 (dd, 1H, $J = 7.7, 8.4$ Hz), 7.74 (d, 1H, $J = 7.7$ Hz); MS m/z 222 (M^+).

2,6-Dimethyl-1,1'-biphenyl (Table 6, entry 1):¹³ oil; ^1H NMR (400 MHz, CDCl_3) δ 2.03 (s, 6H), 7.09-7.17 (m, 5H), 7.32 (t, 1H, $J = 7.3$ Hz), 7.41 (t, 2H, $J = 7.7$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.82, 126.58, 127.00, 127.26, 128.39, 129.00, 136.02, 141.08, 141.85; MS m/z 182 (M^+).

2-Methoxy-2',6'-dimethyl-1,1'-biphenyl (Table 6, entry 3; Table 7, entry 5):¹⁴ oil; ^1H NMR (400 MHz, CDCl_3) δ 2.00 (s, 6H), 3.72 (s, 3H), 6.97 (d, 1H, $J = 8.1$ Hz), 7.00-7.04 (m, 2H), 7.10 (d, 2H, $J = 7.3$ Hz), 7.16 (dd, 1H, $J = 6.2, 8.8$ Hz), 7.31-7.35 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.43, 55.38, 110.83, 120.64, 126.99, 127.04, 128.34, 129.49, 130.63, 136.56, 138.18, 156.49; MS m/z 212 (M^+).

Methyl 2-(2,6-dimethylphenyl)benzoate (Table 6, entry 4; Table 7,

entry 6): mp 39-40 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.93 (s, 6H), 3.61 (s, 3H), 7.07 (d, 2H, *J* = 7.3 Hz), 7.13-7.17 (m, 2H), 7.43 (ddd, 1H, *J* = 1.5, 7.3, 7.9 Hz), 7.57 (ddd, 1H, *J* = 1.5, 7.3, 7.7 Hz), 8.01 (dd, 1H, *J* = 1.5, 7.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 20.55, 51.85, 126.86, 126.93, 127.03, 130.11, 130.27, 130.57, 132.17, 135.18, 141.03, 142.22, 167.43; MS *m/z* 240 (M⁺). Anal. Calcd for C₁₆H₁₆O₂: C, 79.97; H, 6.71. Found: C, 79.74; H, 6.65.

1-(2-Methoxyphenyl)naphthalene (Table 6, entry 7):¹⁵ mp 98-99 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.68 (s, 3H), 7.03-7.09 (m, 2H), 7.28 (dd, 1H, *J* = 1.8, 7.3 Hz), 7.35-7.47 (m, 4H), 7.52 (dd, 1H, *J* = 7.0, 8.1 Hz), 7.57 (d, 1H, *J* = 7.7 Hz), 7.85 (d, 1H, *J* = 9.5 Hz), 7.87 (d, 1H, *J* = 8.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 55.53, 110.98, 120.53, 125.33, 125.52, 125.61, 126.41, 127.26, 127.62, 128.10, 128.96, 129.53, 131.92, 132.13, 133.45, 136.95, 157.23; MS *m/z* 234 (M⁺).

Methyl 2-(1-naphthyl)benzoate (Table 6, entry 8; Table 8, entry 5):¹⁶ mp 91-92 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.36 (s, 3H), 7.30-7.52 (m, 7H), 7.60 (dt, 1H, *J* = 1.2, 7.4 Hz), 7.85 (d, 1H, *J* = 8.3 Hz), 7.88 (d, 1H, *J* = 8.0 Hz), 8.02 (d, 1H, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 51.70, 125.07, 125.48, 125.56, 125.88, 125.94, 127.52, 127.53, 128.16, 130.03, 131.50, 131.54, 131.84, 132.00, 133.21, 139.59, 141.33, 167.87; MS *m/z* 262 (M⁺).

4-Methoxy-2'-methyl-1,1'-biphenyl (Table 7, entry 2):¹⁷ oil; ¹H NMR (400 MHz, CDCl₃) δ 2.27 (s, 3H), 3.84 (s, 3H), 6.93-6.98 (m, 2H), 7.20-7.26 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 20.51, 55.26, 113.48, 125.72, 126.94, 129.88, 130.22, 130.26, 134.37, 135.46, 141.54, 158.50; MS *m/z* 198 (M⁺).

Ethyl 4-(2-methylphenyl)benzoate (Table 7, entry 3):¹⁸ oil; ¹H NMR (400 MHz, CDCl₃) δ 1.42 (t, 3H, *J* = 7.3 Hz), 2.26 (s, 3H), 4.40 (q, 2H, *J* = 7.3 Hz), 7.20-7.29 (m, 4H), 7.39 (d, 2H, *J* = 8.4 Hz), 8.09 (d, 2H, *J* = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.36, 20.35, 60.93, 125.87, 127.79, 128.94, 129.20,

129.36, 129.50, 130.46, 135.16, 140.90, 146.62, 166.56; MS m/z 240 (M^+).

2,6,2'-Trimethyl-1,1'-biphenyl (Table 7, entry 4):¹⁷ oil; ^1H NMR (400 MHz, CDCl_3) δ 1.94 (s, 6H), 1.97 (s, 3H), 7.00-7.09 (m, 1H), 7.10 (d, 2H, J = 8.1 Hz), 7.15-7.18 (m, 1H), 7.23-7.27 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 19.38, 20.31, 126.02, 126.89, 126.97, 127.19, 127.25, 128.83, 129.94, 135.85, 140.52, 141.07; MS m/z 196 (M^+).

1-(4-Methylphenyl)naphthalene (Table 8, entry 3):¹⁹ mp 48-50 °C; ^1H -NMR (400 MHz, CDCl_3) δ 2.45 (s, 3H), 7.29 (d, 2H, J = 8.4 Hz) 7.37-7.43 (m, 4H), 7.45-7.52 (m, 2H), 7.83 (d, 1H, J = 8.1 Hz), 7.89 (d, 1H, J = 8.4 Hz), 7.91 (d, 1H, J = 9.1 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 21.22, 125.37, 125.68, 125.89, 126.08, 126.85, 127.41, 128.22, 128.94, 129.93, 131.70, 133.80, 136.89, 137.80, 140.23; MS m/z 218 (M^+).

2-Methoxy-1,1'-binaphthyl (Table 8, entry 6):⁵ mp 106-107 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.75 (s, 3H), 7.14 (d, 1H, J = 8.8 Hz), 7.21 (dd, 1H, J = 1.1, 5.5 Hz), 7.27 (dd, 1H, J = 1.1, 5.5 Hz), 7.30-7.33 (m, 2H), 7.42-7.47 (m, 3H), 7.61 (t, 1H, J = 7.7 Hz), 7.86 (d, 1H, J = 8.0 Hz), 7.93 (d, 1H, J = 8.0 Hz), 7.94 (d, 1H, J = 8.0 Hz), 7.97 (d, 1H, J = 8.8 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 56.77, 113.84, 123.24, 123.55, 125.49, 125.55, 125.66, 125.83, 126.16, 126.36, 127.72, 127.78, 128.21, 128.42, 129.01, 129.45, 132.93, 133.68, 134.25, 134.52, 154.60; MS m/z 284 (M^+).

1-(2,6-Dimethylphenyl)naphthalene (Table 8, entry 7):²⁰ mp 74-75 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.90 (s, 6H), 7.17 (d, 2H, J = 7.3 Hz), 7.24 (d, 1H, J = 8.1 Hz), 7.26 (d, 1H, J = 7.0 Hz), 7.32-7.37 (m, 2H), 7.44-7.49 (m, 1H), 7.54 (dd, 1H, J = 7.0, 8.1 Hz), 7.86 (d, 1H, J = 8.1 Hz), 7.90 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.36, 125.37, 125.68, 125.76, 126.04, 126.43, 127.17, 127.25, 127.30, 128.27, 131.74, 133.74, 136.99, 138.74, 139.63; MS m/z 232 (M^+).

1-(2-Methyl-6-nitrophenyl)naphthalene (Table 8, entry 8):²¹ mp 111-112 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.98 (s, 3H), 7.24 (dd, 1H, *J* = 1.1, 7.0 Hz), 7.33 (d, 1H, *J* = 9.4 Hz), 7.40 (ddd, 1H, *J* = 1.1, 6.8, 7.5 Hz), 7.46-7.52 (m, 3H), 7.56 (d, 1H, *J* = 7.3 Hz), 7.82 (d, 1H, *J* = 8.1 Hz), 7.88-7.92 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 20.23, 121.40, 124.87, 125.39, 125.92, 126.04, 126.59, 128.21, 128.46, 128.52, 131.57, 133.50, 133.88, 133.91, 133.96, 140.30, 150.75; MS *m/z* 263 (M⁺). Anal. Calcd for C₁₇H₁₃NO₂: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.30; H, 4.92; N, 5.29.

2-Methoxy-1-phenylnaphthalene (Table 9, entry 1):²² mp 70-71 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.73 (s, 3H), 7.17-7.34 (m, 6H), 7.38-7.42 (m, 3H), 7.71-7.73 (m, 1H), 7.77 (d, 1H, *J* = 9.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 56.76, 113.84, 123.49, 125.24, 126.27, 127.04, 127.81, 128.12, 129.02, 129.05, 130.94, 130.95, 133.59, 136.41, 153.71; MS *m/z* 234 (M⁺).

2-Methoxy-1-(2-methylphenyl)naphthalene (Table 9, entry 3):²³ mp 95-96 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.99 (s, 3H), 3.84 (s, 3H), 7.18 (d, 1H, *J* = 7.0 Hz), 7.24-7.38 (m, 7H), 7.81-7.84 (m, 1H), 7.89 (d, 1H, *J* = 9.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 19.71, 56.56, 113.59, 123.45, 124.49, 125.03, 125.58, 126.30, 127.47, 127.82, 128.97, 128.98, 129.81, 130.82, 133.44, 136.10, 137.61, 153.65; MS *m/z* 248 (M⁺).

Methyl 2-(2-methoxy-1-naphthyl)benzoate (Table 9, entry 7):²⁴ mp 83-84 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.46 (s, 3H), 3.80 (s, 3H), 7.29-7.35 (m, 5H), 7.49 (dt, 1H, *J* = 1.5, 7.6 Hz), 7.61 (dt, 1H, *J* = 1.5, 7.6 Hz), 7.80-7.82 (m, 1H), 7.87 (d, 1H, *J* = 8.7 Hz), 8.08 (dd, 1H, *J* = 1.5, 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 51.60, 56.58, 113.34, 123.33, 124.67, 124.73, 126.26, 127.34, 127.89, 128.93, 128.98, 130.22, 131.68, 131.81, 132.49, 133.19, 137.50, 153.14, 167.57; MS *m/z* 292 (M⁺).

1-(2,6-Dimethylphenyl)-2-methoxynaphthalene (Table 9, entry 8):²⁵

mp 104-105 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.88 (s, 6H), 3.84 (s, 3H), 7.14 (d, 1H, *J* = 8.8 Hz), 7.18 (d, 2H, *J* = 7.3 Hz), 7.24 (d, 1H, *J* = 5.9 Hz), 7.27-7.34 (m, 2H), 7.38 (d, 1H, *J* = 8.8 Hz), 7.83 (d, 1H, *J* = 7.3 Hz), 7.89 (d, 1H, *J* = 9.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 20.09, 56.38, 113.52, 123.27, 123.49, 124.37, 126.50, 127.16, 127.31, 127.95, 128.86, 129.11, 132.83, 135.70, 137.38, 153.42; MS *m/z* 262 (M⁺).

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