

Supporting Information

Cross-Coupling of Triallyl(aryl)silanes with Aryl Bromides and Chlorides: An Alternative Convenient Biaryl Synthesis

Akhila K. Sahoo, Takuro Oda, Yoshiaki Nakao, Tamejiro Hiyama*

Experimental Section

General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with the standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^1H , 270 MHz; ^{13}C , 67.8 MHz), Varian Mercury 200 (^1H , 200 MHz; ^{13}C , 50.3 MHz; ^{19}F , 188 MHz), Varian Gemini 2000 (^1H , 300 MHz; ^{13}C , 75.5 MHz), or Varian INOVA 500 (^{13}C , 126 MHz) spectrometer using tetramethylsilane (^1H and ^{13}C) and fluorotrichloromethane (^{19}F) as an internal standard. Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC-908 equipped with JAIGEL-1H and -2H (chloroform as an eluent). High-resolution mass spectra (HRMS) were obtained with a JEOL JMS-HX110A (FAB+) spectrometer. GC-MS and HRMS analyses were obtained with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. Melting points were determined using a YANAKO MP-500D. Unless otherwise noted, reagents were commercially available and used without further purification. Anhydrous DMSO was purchased from Aldrich. THF, ether, and toluene were distilled from sodium/benzophenone ketyl before use. All the temperatures are uncorrected.

4-Trifluoromethylbiphenyl (Table 2, entry 1; Table 8, entry1): Colorless solid, mp 64–65 °C (lit.^[1] mp 64–66 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.69 (bs, 4H), 7.62–7.56 (m, 2H), 7.54–7.38 (m, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 144.7, 139.7, 129.2 (d, *J* = 32 Hz), 129.0, 128.2, 127.4, 127.2, 125.7 (q, *J* = 3.8 Hz), 124.4 (d, *J* = 271 Hz); ¹⁹F NMR (188 MHz, CDCl₃): δ = – 62.85 (s).

3-Trifluoromethylbiphenyl (Table 2, entry 2): Colorless oil;^[1b] ¹H NMR (200 MHz, CDCl₃): δ = 7.87–7.72 (m, 2H), 7.65–7.34 (m, 7H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 142.0, 139.7, 131.1 (d, *J* = 32 Hz), 130.4, 129.2, 129.0, 128.0, 127.2, 124.2 (d, *J* = 272 Hz), 123.8 (q, *J* = 3.8 Hz); ¹⁹F NMR (188 MHz, CDCl₃): δ = – 63.01 (s).

4-Fluorobiphenyl (Table 2, entry 3; Table 8, entry 2): Colorless solid, mp 74–75 °C (Ald.^[1b, 2] mp 75–79 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.61–7.28 (m, 7H), 7.18–7.05 (m, 2H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 162.4 (d, *J* = 247 Hz), 140.2, 137.2, 128.8, 128.6 (d, *J* = 8.0 Hz), 127.2, 127.0, 115.6 (d, *J* = 21 Hz); ¹⁹F NMR (188 MHz, CDCl₃): δ = – (116.31–116.16) (m).

4-(Ethoxycarbonyl)biphenyl (Table 2, entry 4; Table 8, entry 4; Table 11, entry 2; Table 13, entry 2): Colorless solid, mp 47–48 °C (lit.^[3] mp 48–49 °C); ¹H NMR (200 MHz, CDCl₃): δ = 8.12 (dt, *J* = 8.6, 2.0 Hz, 2H), 7.75–7.59 (m, 4H), 7.53–7.31 (m, 3H), 4.41 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (67.8 MHz, CDCl₃): δ = 166.3, 145.3, 139.8, 129.9, 129.1, 128.8, 127.9, 127.1, 126.8, 60.9, 14.4.

4-Cyanobiphenyl (Table 2, entry 5; Table 8, entry 5; Table 12, entry 2): Colorless solid, mp 85–86 °C (lit.^[4] mp 86–87 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.75–7.63 (m, 4H), 7.62–7.54 (m, 2H), 7.53–7.36 (m, 3H); ¹³C NMR (67.8 MHz, CDCl₃): δ = 145.4, 138.9, 132.4, 128.9, 128.5, 127.5, 127.0, 118.8, 110.7.

4-Acetylbiphenyl (Table 2, entry 6; Table 8, entry 6): Colorless solid, mp 118–120 °C (lit.^[5] mp 119–119.5 °C); ¹H NMR (200 MHz, CDCl₃): δ = 8.08–7.98 (m, 2H), 7.73–7.59 (m, 4H), 7.53–7.37 (m, 3H), 2.62 (s, 3H); ¹³C NMR (67.8 MHz, CDCl₃): δ = 197.4, 145.5, 139.6, 135.6, 128.8, 128.7, 128.1, 127.1, 127.0, 26.7.

4-Nitrobiphenyl (Table 2, entry 7): Yellow solid, mp 104–105 °C (lit.^[4] mp 102–103 °C); ¹H NMR (200 MHz, CDCl₃): δ = 8.37–8.27 (m, 2H), 7.79–7.71 (m, 2H), 7.68–7.59 (m, 2H), 7.57–7.41 (m, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 147.4, 146.9, 138.6, 129.0, 128.8, 127.6, 127.2, 123.9.

4-Formylbiphenyl (Table 2, entry 8): Colorless solid, mp 57–58 °C (lit.^[6] mp 59–60 °C); ¹H NMR (200 MHz, CDCl₃): δ = 10.05 (s, 1H), 8.05–7.89 (m, 2H), 7.82–7.71 (m, 2H), 7.69–7.56 (m, 2H), 7.54–7.35 (m, 3H); ¹³C NMR (67.8 MHz, CDCl₃): δ = 191.7, 147.0, 139.5, 135.0, 130.1, 128.9, 128.3, 127.6, 127.2.

4-Chlorobiphenyl (11) (Table 2, entry 9): Colorless solid, mp 76–77 °C (lit.^[7] mp 76–78 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.58–7.32 (m, 9H); ¹³C NMR (50.3 MHz, CDCl₃) δ 139.7, 139.4, 133.2, 128.73, 128.71, 128.2, 127.4, 126.8.

4-Methoxybiphenyl (Table 3, entry 1; Table 8, entry 7; Table 11, entry 1; Table 12, entry 1; Table 13, entry 1): Colorless solid, mp 86–87 °C (lit.^[8, 9, 10] mp 87 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.59–7.48 (m, 4H), 7.46–7.19 (m, 3H), 7.05–6.92 (m, 2H), 3.82 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 159.0, 140.6, 133.5, 128.6, 127.9, 126.54, 126.48, 114.0, 55.1.

4-Methylbiphenyl (Table 3, entry 2; Table 8, entry 9): Colorless solid mp 44–45 °C (lit.^[9] mp 44–46 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.42–7.19 (m, 9H), 2.41 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 140.9, 138.1, 136.7, 129.3, 128.5, 126.8, 20.9.

4-*tert*-Butylbiphenyl (Table 3, entry 3): Glassy solid, mp 47–48 °C (lit.^[4] mp 47–49 °C); ¹H NMR (300 MHz, CDCl₃): δ = 7.71–7.58 (m, 4H), 7.58–7.44 (m, 4H), 7.43–7.33 (m, 1H), 1.45 (s, 9H); ¹³C NMR (75.5 MHz, CDCl₃): δ = 150.0, 140.9, 138.2, 128.6, 126.88, 126.86, 126.7, 125.6, 34.5, 31.4.

3,4-Dimethoxybiphenyl (Table 3, entry 4): Colorless solid, mp 69–70 °C (lit.^[11] mp 68–69 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.61–7.52 (m, 2H), 7.49–7.27 (m, 3H), 7.22–7.09 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H); ¹³C NMR (67.8 MHz, CDCl₃): δ = 148.8, 148.2, 140.6, 133.7, 128.4, 126.5, 119.0, 111.1, 109.9, 55.51, 55.49.

3,4-Methylenedioxybiphenyl (Table 3, entry 5; Table 8, entry 12): Colorless viscous oil,^[12] ¹H NMR (200 MHz, CDCl₃): δ = 7.59–7.27 (m, 5H), 7.12–7.01 (m, 2H), 6.93–6.84 (m, 1H), 6.02 (s, 2H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 148.0, 147.0, 140.8, 135.5, 128.7, 126.8, 120.5, 108.5, 107.6, 101.0.

3-(1,3-Dioxolan-2-yl)biphenyl (Table 3, entry 6): Colorless oil; IR (neat): ν = 2885, 1479, 1379, 1199, 1084, 760, 700 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 7.74–7.71 (m, 1H), 7.66–7.57 (m, 3H), 7.52–7.41 (m, 4H), 7.39–7.32 (m, 1H), 5.89 (s, 1H), 4.32–4.01 (m, 4H); ¹³C NMR (75.5 MHz, CDCl₃): δ = 141.1, 140.7, 138.3, 128.6, 128.5, 127.7, 127.2, 127.0, 125.2, 125.0, 103.5, 65.2; MS *m/z* (rel. intensity %) 226 (M⁺, 81), 225

(100), 181 (44), 165 (25), 154 (98), 73 (22); HRMS (EI⁺): Calcd for C₁₅H₁₄O₂: M⁺ 226.0994. Found: *m/z* 226.0986.

4-*N,N*-Diethylaminobiphenyl (Table 3, entry 7): Colorless solid mp 69–70 °C;^[13] ¹H NMR (200 MHz, CDCl₃): δ = 7.61–7.33 (m, 6H), 7.29–7.21 (m, 1H), 6.75 (dt, *J* = 7.0, 2.0 Hz, 2H), 3.38 (q, *J* = 7.0 Hz, 4H), 1.19 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 147.0, 141.2, 128.5, 127.8, 126.0, 125.7, 111.8, 44.3, 12.5.

4-Aminobiphenyl (Table 3, entry 8): Colorless solid, mp 49–50 °C (lit.^[14] mp 51 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.54–7.36 (m, 7H), 6.77 (d, *J* = 8.6 Hz, 2H), 3.69 (bs, 2H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 145.9, 141.2, 131.6, 128.7, 128.1, 126.4, 126.3, 115.4.

4-Biphenylmethanol (Table 3, entry 9): Colorless solid, mp 99–100 °C (Ald.^[15] mp 99–100 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.65–7.54 (m, 3H), 7.51–7.28 (m, 6H), 4.75 (d, *J* = 5.4 Hz, 2H), 1.69 (bs, 1H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 140.6, 140.2, 139.8, 128.6, 127.3, 127.2, 127.0, 126.9, 64.6.

2-Chlorobiphenyl (Table 4, entry 1): Colorless oil (lit.^[7b] mp 27 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.48–7.38 (m, 5H), 7.37–7.11 (m, 4H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 140.4, 139.3, 132.4, 131.3, 129.9, 129.4, 128.5, 128.0, 127.5, 126.8.

***o*-Terphenyl (Table 4, entry 2):** Colorless solid, mp 57–58 °C (Ald.^[16] mp 58–59 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.46–7.41 (bs, 4H), 7.24–7.09 (m, 10H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 141.4, 140.4, 130.5, 129.8, 127.8, 127.4, 126.4.

2-Methylbiphenyl (Table 4, entry 3; Table 9, entry 4; Table 11, entry 3): Colorless oil;^[17] ¹H NMR (200 MHz, CDCl₃): δ = 7.51–7.19 (m, 9H), 2.27 (s, 3H); ¹³C NMR (67.8

MHz, CDCl₃): δ = 141.8, 135.2, 130.2, 129.7, 129.1, 128.6, 127.9, 127.1, 126.6, 125.6, 20.5.

1-Phenylnaphthalene (Table 4, entry 4; Table 9, entry 7): Colorless oil;^[18] ¹H NMR (200 MHz, CDCl₃): δ = 7.94–7.82 (m, 3H), 7.58–7.36 (m, 9H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 140.7, 140.2, 133.7, 131.5, 130.0, 128.2, 127.6, 127.2, 126.9, 126.0, 125.7, 125.3.

2,6-Dimethylbiphenyl (Table 4, entry 5; Table 9, entry 8; Table 11, entry 4; Table 12, entry 5): Colorless oil;^[4] ¹H NMR (200 MHz, CDCl₃): δ = 7.47–7.28 (m, 3H), 7.22–7.04 (m, 5H), 2.03 (s, 6H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 141.7, 140.9, 135.9, 128.8, 128.3, 127.1, 126.9, 126.4, 20.7.

2,4,6-Trimethylbiphenyl (Table 4, entry 6): Colorless oil;^[19] ¹H NMR (300 MHz, CDCl₃): δ = 7.47–7.37 (m, 2H), 7.36–7.29 (m, 1H), 7.17–7.11 (m, 2H), 6.95 (bs, 2H), 2.34 (s, 3H), 2.01 (s, 6H); ¹³C NMR (75.5 MHz, CDCl₃): δ = 141.0, 138.9, 136.3, 135.8, 129.1, 128.2, 127.9, 126.4, 21.1, 20.8.

2-Methyl-1-phenylnaphthalene (Table 4, entry 7): Colorless viscous oil;^[20] ¹H NMR (300 MHz, CDCl₃): δ = 7.84–7.74 (m, 2H), 7.52–7.21 (m, 9H), 2.23 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃): δ = 139.7, 138.0, 132.9, 132.8, 131.8, 130.0, 128.5, 128.2, 127.6, 127.1, 126.8, 126.0, 125.7, 124.6, 20.9.

2-Phenylpyridine (Table 5, entry 1): Colorless oil;^[21] ¹H NMR (200 MHz, CDCl₃): δ = 8.71 (dt, J = 1.4, 4.8 Hz, 1H), 8.04–7.93 (m, 2H), 7.78–7.72 (m, 2H), 7.54–7.39 (m, 3H), 7.28–7.19 (m, 1H); ¹³C NMR (67.8 MHz, CDCl₃): δ = 157.2, 149.5, 139.2, 136.6, 128.8, 128.6, 126.7, 121.9, 120.4.

3-Phenylbenzothiophene (Table 5, entry 2): Colorless oil;^[22] ¹H NMR (200 MHz, CDCl₃): δ = 8.02–7.85 (m, 2H), 7.65–7.54 (m, 2H), 7.54–7.26 (m, 6H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 140.6, 137.9, 137.7, 135.8, 128.6, 127.4, 124.3, 124.2, 123.3, 122.8.

3-Phenylquinoline (Table 5, entry 3): Pale yellow viscous oil;^[23] ¹H NMR (200 MHz, CDCl₃): δ = 9.18 (d, J = 2.4 Hz, 1H), 8.27 (d, J = 2.4 Hz, 1H), 8.14 (dd, J = 0.6, 7.8 Hz, 1H), 7.85 (dd, J = 0.6, 7.8 Hz, 1H), 7.77–7.64 (m, 3H), 7.61–7.37 (m, 4H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 149.6, 147.0, 137.4, 133.4, 132.8, 129.1, 128.9, 128.8, 127.8, 127.7, 127.6, 127.1, 126.6.

2-Chloro-5-phenylpyridine (Table 5, entry 4): Colorless solid, mp 60–61 °C (lit.^[24] mp 62–63 °C); ¹H NMR (200 MHz, CDCl₃): δ = 8.59 (d, J = 2.8 Hz, 1H), 7.83 (dd, J = 2.8, 8.8 Hz, 1H), 7.59–7.35 (m, 6H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 149.9, 147.5, 136.8, 136.0, 135.2, 128.9, 128.1, 126.6, 123.9.

4-Phenyl-3,5-dimethylisoxazole (Table 5, entry 5): Colorless oil;^[25] ¹H NMR (300 MHz, CDCl₃): δ = 7.48–7.40 (m, 2H), 7.39–7.32 (m, 1H), 7.29–7.23 (m, 2H), 2.41 (s, 3H), 2.28 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 164.8, 158.3, 130.2, 128.8, 128.5, 127.2, 116.4, 11.5, 10.7.

4-Methoxy-4'-methylbiphenyl (Table 6, entry 1; Table 10, entry 2; Table 10, entry 7): Colorless solid, mp 108–109 °C (lit.^[17, 26] mp 108 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.51 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 2.38 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 158.7, 137.8, 136.1, 133.5, 129.3, 127.8, 126.4, 114.0, 55.1, 20.9.

2-Methoxy-4'-methylbiphenyl (Table 6, entry 2; Table 10, entry 3): Colorless solid, mp 76–77 °C (lit.^[4] mp 74–75 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.42 (d, J = 8.2 Hz,

1H), 7.39–7.19 (m, 5H), 7.08–6.91 (m, 2H), 3.78 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3): δ = 156.3, 136.4, 135.4, 130.6, 130.5, 129.2, 128.6, 128.2, 120.6, 110.9, 55.3, 21.0.

4-Fluoro-4'-methoxybiphenyl (Table 6, entry 3): Colorless solid, mp 89–90 °C (lit.^[27] mp 86–88 °C); ^1H NMR (300 MHz, CDCl_3): δ = 7.54–7.43 (m, 4H), 7.14–7.04 (m, 2H), 6.96 (d, J = 9.0 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3): δ = 161.9 (d, J = 244 Hz), 158.9, 136.7 (d, J = 3.4 Hz), 132.5, 128.0 (d, J = 8.0 Hz), 127.8, 115.3 (d, J = 21 Hz), 114.1, 55.2; ^{19}F NMR (188 MHz, CDCl_3): δ = – (117.25–117.09) (m).

4-Methoxy-4'-tert-butylbiphenyl (Table 6, entry 4): Colorless solid, mp 129–130 °C (lit.^[28] mp 127–128 °C); ^1H NMR (300 MHz, CDCl_3): δ = 7.56–7.41 (m, 6H), 6.96 (dd, J = 2.4, 9.0 Hz, 2H), 3.83 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (75.5 MHz, CDCl_3): δ = 158.7, 149.3, 137.7, 133.4, 127.8, 126.2, 125.5, 114.0, 55.2, 34.5, 31.4.

4-Methoxy-3',4'-methylenedioxybiphenyl (Table 6, entry 5; Table 10, entry 8): Colorless solid, mp 95–96 °C (lit.^[12] mp 95–96 °C); ^1H NMR (300 MHz, CDCl_3): δ = 7.46 (dt, J = 2.1, 8.7 Hz, 2H), 7.04–6.97 (m, 2H), 6.94 (dt, J = 2.1, 8.7 Hz, 2H), 6.85 (d, J = 7.8 Hz, 1H), 5.98 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3): δ = 158.6, 147.8, 146.3, 135.0, 133.3, 127.6, 119.8, 113.9, 108.3, 107.1, 100.9, 55.2.

3-(4-Methoxyphenyl)quinoline (Table 6, entry 6): Colorless solid, mp 69–70 °C (lit.^[23a] mp 78–79 °C); ^1H NMR (300 MHz, CDCl_3): δ = 9.15 (d, J = 2.1 Hz, 1H), 8.23 (d, J = 2.1 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.73–7.61 (m, 3H), 7.59–7.51 (m, 1H), 7.09–7.02 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3): δ =

159.4, 149.4, 146.6, 133.0, 131.9, 129.8, 128.8, 128.7, 128.1, 127.7, 127.5, 126.5, 114.3, 55.1.

3-(4-Methoxyphenyl)-benzothiophene (Table 6, entry 7): Colorless viscous oil; IR (neat): $\nu = 2833, 1529, 1495, 1286, 1248, 1178, 1034, 762 \text{ cm}^{-1}$; ^1H NMR (300 MHz, CDCl_3): $\delta = 7.91\text{--}7.84$ (m, 2H), 7.49 (dd, $J = 1.4, 4.4 \text{ Hz}$, 2H), 7.39–7.33 (m, 2H), 7.29 (bs, 1H), 6.99 (dd, $J = 1.4, 4.4 \text{ Hz}$, 2H), 3.85 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 158.9, 140.5, 137.9, 137.5, 129.6, 128.3, 124.2, 124.1, 122.8, 122.4, 114.0, 55.3$; MS m/z (rel. intensity %) 240 (M^+ , 100), 225 (53), 197 (16), 165 (5), 152 (6); HRMS (EI^+): Calcd for $\text{C}_{15}\text{H}_{12}\text{OS}$: M^+ 240.0609. Found: m/z 240.0606.

4-Methoxy-2',4',6'-trimethylbiphenyl (Table 6, entry 8): Colorless solid, mp 69–70 °C (lit.^[29] mp 71–73 °C); ^1H NMR (300 MHz, CDCl_3): $\delta = 7.04$ (dt, $J = 2.1, 8.7 \text{ Hz}$, 2H), 6.97–6.91 (m, 4H), 3.84 (s, 3H), 2.32 (s, 3H), 2.0 (s, 6H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 158.0, 138.5, 136.2, 133.1, 130.1, 127.9, 113.6, 55.0, 21.0, 20.8$.

4-Fluoro-2'-methylbiphenyl (Table 6, entry 9): Colorless oil;^[29b] ^1H NMR (300 MHz, CDCl_3): $\delta = 7.31\text{--}7.16$ (m, 6H), 7.14–7.04 (m, 2H), 2.25 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 161.7$ (d, $J = 246$), 140.8, 137.8 (d, $J = 3.4 \text{ Hz}$), 135.2, 130.5 (d, $J = 7.6 \text{ Hz}$), 130.2, 129.7, 127.3, 125.7, 114.8 (d, $J = 21 \text{ Hz}$), 20.5; ^{19}F NMR (188 MHz, CDCl_3): $\delta = - (116.67\text{--}116.52)$ (m).

2-Methyl-3',4'-methylenedioxybiphenyl (Table 6, entry 10): Colorless thick oil;^[30] ^1H NMR (300 MHz, CDCl_3): $\delta = 7.26\text{--}7.18$ (m, 4H), 6.88–6.83 (m, 1H), 6.81–6.79 (m, 1H), 6.78–6.74 (m, 1H), 5.99 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 147.1, 146.2, 141.4, 135.7, 135.2, 130.1, 129.7, 127.0, 125.6, 122.3, 109.7, 107.9, 100.8, 20.5$.

3-(2-Methylphenyl)quinoline (Table 6, entry 11): Colorless oil;^[23b] ¹H NMR (200 MHz, CDCl₃): δ = 8.93 (d, J = 2.0 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 2.0 Hz, 1H), 7.85 (dd, J = 1.4, 8.2 Hz, 1H), 7.79–7.68 (m, 1H), 7.63–7.53 (m, 1H), 7.39–7.28 (m, 4H), 2.34 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 151.3, 146.8, 137.9, 135.6, 135.1, 134.6, 130.5, 130.0, 129.2, 129.1, 128.0, 127.7, 127.5, 126.7, 126.0, 20.3.

1-(2-Methylphenyl)naphthalene (Table 6, entry 12): Colorless solid, mp 66–67 °C (lit.^[31] mp 67–68 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.94–7.83 (m, 2H), 7.58–7.21 (m, 9H), 2.02 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 140.2, 139.7, 136.7, 133.5, 131.9, 130.3, 129.8, 128.2, 127.5, 127.4, 126.5, 126.0, 125.9, 125.6, 125.5, 125.3, 20.0.

4-Cyano-4'-fluorobiphenyl (Table 6, entry 13, Table 10, entry 16): Colorless floppy solid, mp 76–77 °C;^[29a] ¹H NMR (200 MHz, CDCl₃): δ = 7.78–7.51 (m, 6H), 7.25–7.11 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ = 163.0 (d, J = 248 Hz), 144.6, 135.3 (d, J = 3.4 Hz), 132.6, 128.9 (d, J = 8.0 Hz), 127.6, 118.8, 116.0 (d, J = 21 Hz), 110.9; ¹⁹F NMR (188 MHz, CDCl₃): δ = – (113.66–113.52) (m).

4-Fluoro-4'-tert-butylbiphenyl (Table 6, entry 14): Colorless solid, mp 65–67 °C; IR (KBr): ν = 2966, 1499, 1219, 847, 818. ¹H NMR (200 MHz, CDCl₃): δ = 7.57–7.44 (m, 6H), 7.15–7.03 (m, 2H), 1.35 (s, 9H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 162.3 (d, J = 246 Hz), 150.2, 137.3, 128.5 (d, J = 8.0 Hz), 126.6, 125.8, 115.8 (d, J = 7.2 Hz), 115.4 (d, J = 6.8 Hz), 34.5, 31.3; MS m/z (rel. intensity %) 228 (M⁺, 38), 213 (100), 185 (22), 170 (8), 153 (5), 93 (6); HRMS (EI⁺): Calcd for C₁₆H₁₇F: M⁺ 228.1314. Found: m/z 228.1301; ¹⁹F NMR (188 MHz, CDCl₃): δ = – (116.75–116.63) (m).

3,4-Difluorobiphenyl (Table 8, entry 3): Colorless solid, mp 39–40 °C (lit.^[32] mp 41 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.58–7.12 (m, 8H); ¹³C NMR (50.3 MHz,

CDCl₃): δ = 151.5 (d, J = 247 Hz), 150.3 (d, J = 247 Hz), 139.1, 138.1 (q, J = 3.4 Hz), 128.9, 127.8, 126.9, 122.8 (q, J = 3.4 Hz), 117.4 (d, J = 17.5 Hz), 115.9 (d, J = 17.5 Hz); ¹⁹F NMR (188 MHz, CDCl₃): δ = – (140.85–140.62) (m), – (138.09–137.89) (m).

3-Methoxybiphenyl (Table 8, entry 8): Colorless oil;^[10] ¹H NMR (200 MHz, CDCl₃): δ = 7.63–7.54 (m, 2H), 7.49–7.29 (m, 4H), 7.22–7.11 (m, 2H), 6.94–6.86 (m, 1H), 3.83 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 159.8, 142.6, 140.9, 129.6, 128.6, 127.2, 127.0, 119.5, 112.7, 112.5, 55.0.

4-(Dimethoxymethyl)biphenyl (Table 8, entry 10): Colorless oil;^[6] ¹H NMR (200 MHz, CDCl₃): δ = 7.64–7.56 (m, 4H), 7.56–7.51 (m, 2H), 7.51–7.29 (m, 3H), 5.43 (s, 1H), 3.39 (s, 6H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 141.1, 140.5, 136.9, 128.6, 127.1, 126.94, 126.90, 126.7, 102.7, 52.4.

3,5-Dimethoxybiphenyl (Table 8, entry 11): Colorless solid, mp 62–63 °C (lit.^[33] mp 62 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.62–7.53 (m, 2H), 7.49–7.29 (m, 3H), 6.73 (d, J = 2.4 Hz, 2H), 6.47 (t, J = 2.4 Hz, 1H), 3.85 (s, 6H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 160.9, 143.3, 141.0, 128.5, 127.4, 127.0, 105.3, 99.1, 55.2.

3-Fluoro-4-methoxybiphenyl (Table 8, entry 13): Colorless solid, mp 78–79 °C (lit.^[34] mp 76–77 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.57–7.26 (m, 7H), 7.07–6.96 (m, 1H), 3.92 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 152.4 (d, J = 246 Hz), 146.9 (d, J = 11.1 Hz), 139.5, 134.2 (d, J = 6.5 Hz), 128.7, 127.1, 126.5, 122.5 (d, J = 3.4 Hz), 114.6 (d, J = 19.1 Hz), 113.4 (d, J = 2.3 Hz), 56.1; ¹⁹F NMR (188 MHz, CDCl₃): δ = – (135.61–135.49) (m).

2-Phenylthioxanthone (Table 8, entry 14): Yellow solid, mp 128–129 °C; IR (KBr): ν = 3055, 1634, 1591, 1466, 1325, 822, 747 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ = 8.87–8.84 (m, 1H), 8.68–8.62 (m, 1H), 7.91–7.84 (m, 1H), 7.75–7.58 (m, 4H), 7.56–7.36 (m, 5H); ^{13}C NMR (50.3 MHz, CDCl_3): δ = 179.2, 145.4, 138.9, 138.5, 136.7, 135.6, 131.7, 130.3, 129.4, 128.8, 128.6, 127.5, 127.1, 126.6, 126.0, 125.8, 125.6; HRMS (EI^+): Calcd for $\text{C}_{19}\text{H}_{12}\text{OS}$: M^+ 288.0609. Found: m/z 288.0612.

2-Trifluoromethylbiphenyl (Table 9, entry 1): Colorless oil;^[35] ^1H NMR (200 MHz, CDCl_3): δ = 7.78–7.71 (m, 1H), 7.61–7.27 (m, 8H); ^{13}C NMR (50.3 MHz, CDCl_3): δ = 141.4, 139.8, 132.0, 131.3, 128.9 (d, J = 1.1 Hz), 128.4 (d, J = 30.1 Hz), 127.7, 127.6, 127.3, 126.0 (d, J = 5.3 Hz), 124.2 (d, J = 274 Hz); ^{19}F NMR (188 MHz, CDCl_3): δ = –57.28 (s).

2-Fluorobiphenyl (Table 9, entry 2): Colorless solid, mp 73–74 °C (Ald.^[36] mp 73–74 °C); ^1H NMR (200 MHz, CDCl_3): δ = 7.59–7.09 (m, 9H); ^{13}C NMR (50.3 MHz, CDCl_3): δ = 159.8 (d, J = 248.1 Hz), 135.8, 130.7 (d, J = 3.4 Hz), 129.0, 128.9, 128.8, 128.4, 127.6, 124.3 (d, J = 3.8 Hz), 116.1 (d, J = 22.5 Hz); ^{19}F NMR (188 MHz, CDCl_3): δ = –(118.58–118.44) (m).

2-Methoxybiphenyl (Table 9, entry 3; Table 12, entry 3): Colorless oil;^[10] ^1H NMR (200 MHz, CDCl_3): δ = 7.57–7.22 (m, 7H), 7.08–6.95 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3): δ = 156.2, 138.3, 130.6, 130.5, 129.3, 128.4, 127.8, 126.7, 120.6, 111.0, 55.2.

2,5-Dimethylbiphenyl (Table 9, entry 5): Colorless oil;^[4] ^1H NMR (200 MHz, CDCl_3): δ = 7.45–7.26 (m, 5H), 7.19–7.03 (m, 3H), 2.35 (s, 3H), 2.23 (s, 3H); ^{13}C NMR

(50.3 MHz, CDCl₃): δ = 141.9, 141.6, 135.0, 132.0, 130.4, 130.1, 129.0, 127.9, 127.8, 126.5, 20.8, 19.8.

2-Phenyl-4-nitroanisole (Table 9, entry 6): Brown solid, mp 92–93 °C (lit.^[37] mp 93–94 °C); IR (KBr): ν = 2945, 1606, 1583, 1498, 1446, 1339, 1265, 1105, 1016, 822, 772, 700 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ = 8.29–8.18 (m, 2H), 7.57–7.34 (m, 5H), 7.08–6.98 (m, 1H), 3.93 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 161.2, 141.1, 135.9, 131.0, 129.1, 128.0, 127.7, 126.0, 124.5, 110.5, 56.0.

3-Phenylpyridine (Table 9, entry 9; Table 11, entry 5; Table 12, entry 4): Pale yellow oil,^[38] ¹H NMR (200 MHz, CDCl₃): δ = 8.85 (dd, J = 1.0, 2.4 Hz, 1H), 8.59 (dd, J = 1.6, 4.8 Hz, 1H), 7.92–7.84 (m, 1H), 7.64–7.32 (m, 6H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 148.0, 147.9, 137.4, 136.2, 133.9, 128.7, 127.7, 126.7, 123.2.

3-Phenylthiophene (Table 9, entry 10): Colorless solid, mp 88–89 °C (lit.^[38] mp 90–92 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.64–7.56 (m, 2H), 7.47–7.23 (m, 6H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 142.2, 135.7, 128.6, 127.0, 126.3, 126.2, 126.0, 120.1.

6-Phenylquinoline (Table 9, entry 11; Table 13, entry 3): Pale yellow solid, mp 109–110 °C (lit.^[39] mp 109–110 °C); ¹H NMR (200 MHz, CDCl₃): δ = 8.92 (dd, J = 1.8, 4.2 Hz, 1H), 8.25–8.15 (m, 2H), 8.03–7.94 (m, 2H), 7.77–7.69 (m, 2H), 7.56–7.36 (m, 4H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 150.0, 147.3, 139.9, 138.9, 135.9, 129.6, 128.9, 128.6, 128.1, 127.4, 127.1, 125.1, 121.1.

5-Phenyl-2-methylbenzoxazole (Table 9, entry 12): Colorless solid, mp 60–61 °C (Ald.^[40] mp 62–64 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.84 (t, J = 1.5 Hz, 1H), 7.65–7.56 (m, 2H), 7.52 (d, J = 1.5 Hz, 2H), 7.51–7.31 (m, 3H), 2.63 (s, 3H); ¹³C NMR

(50.3 MHz, CDCl₃): δ = 164.2, 150.3, 141.9, 140.9, 137.8, 128.6, 127.2, 126.9, 123.8, 117.7, 110.0, 14.4.

5-Phenyl-2-methylbenzothiazole (Table 9, entry 13): Colorless solid, mp 90–92 °C; ¹H NMR (200 MHz, CDCl₃): δ = 8.17 (d, J = 1.6 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 1.6 Hz, 1H), 7.65 (t, J = 1.6 Hz, 1H), 7.61 (dd, J = 4.0, 12.4 Hz, 1H), 7.54–7.33 (m, 3H), 2.86 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 167.4, 153.8, 140.5, 139.2, 134.3, 128.6, 127.2, 127.1, 123.9, 121.3, 120.4, 19.9; MS m/z (rel. intensity %) 225 (M⁺, 100), 207 (5), 184 (19), 152 (8), 139 (10), 113 (3); HRMS (EI⁺): Calcd for C₁₄H₁₁OS: M⁺ 225.0612. Found: m/z 225.0610.

4-Methyl-4'-(trifluoromethyl)biphenyl (Table 10, entry 1): Colorless solid, mp 119–120 °C (lit.^[41] mp 120 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.66 (t, J = 10.0 Hz, 4H), 7.53–7.45 (m, 2H), 7.27 (dd, J = 7.8, 0.7 Hz, 2H), 2.4 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 144.7, 138.2, 136.9, 129.7, 129.1 (d, J = 32.4 Hz), 127.2, 127.1, 125.7 (q, J = 3.8 Hz), 124.4 (d, J = 272 Hz), 21.1; ¹⁹F NMR (188 MHz, CDCl₃): δ = – 62.78 (s).

2,6,4'-Trimethylbiphenyl (Table 10, entry 4): Colorless oil (lit.^[42] mp 31–33 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.26–7.17 (m, 2H), 7.16–7.07 (m, 3H), 7.07–6.99 (m, 2H), 2.4 (s, 3H), 2.03 (s, 6H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 141.7, 137.9, 136.1, 135.9, 129.0, 128.7, 127.1, 126.8, 21.1, 20.8.

6-(4-Methylphenyl)quinoline (Table 10, entry 5): Colorless solid, mp 106–107 °C; IR (KBr): ν = 3016, 1591, 1495, 1122, 844, 822 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ = 8.9 (dd, J = 1.6, 4.2 Hz, 1H), 8.24–8.12 (m, 2H), 8.05–7.91 (m, 2H), 7.62 (dt, J = 8.2, 2.0 Hz, 2H), 7.41 (dd, J = 8.2, 4.2 Hz, 1H), 7.31 (brd, J = 7.8 Hz, 2H), 2.42 (s, 3H); ¹³C

NMR (50.3 MHz, CDCl₃): δ = 150.0, 147.4, 139.0, 137.4, 137.2, 136.0, 129.6, 129.5, 129.0, 128.3, 127.1, 124.9, 121.2, 21.0; MS m/z (rel. intensity %) 219 (M^+ , 100), 218 (69), 189 (9), 176 (3), 165 (3), 151 (3), 109 (7); HRMS (EI⁺): Calcd for C₁₆H₁₃N: M^+ 219.1048. Found: m/z 219.1070.

4-Methoxy-4'-(trifluoromethyl)biphenyl (Table 10, entry 6): Colorless solid, mp 121–122 °C (lit.^[43] mp 124–125 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.65 (bs, 4H), 7.59–7.51 (m, 2H), 7.0 (d, J = 8.6 Hz, 2H), 3.87 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 159.8, 144.2, 132.0, 128.4 (d, J = 32 Hz), 128.3, 126.8, 125.6 (q, J = 3.8 Hz), 124.4 (d, J = 271 Hz), 114.4, 55.2; ¹⁹F NMR (188 MHz, CDCl₃): δ = – 62.76 (s).

4-Methoxy-2'-methylbiphenyl (Table 10, entry 9; Table 10, entry 13): Colorless oil,^[10, 44] ¹H NMR (200 MHz, CDCl₃): δ = 7.43–7.19 (m, 6H), 7.05–6.93 (m, 2H), 3.85 (s, 3H), 2.28 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 158.3, 141.4, 135.2, 134.2, 130.13, 130.06, 129.7, 126.8, 125.6, 113.3, 55.0, 20.4.

4-Methoxy-2',6'-dimethylbiphenyl (Table 10, entry 10): Colorless solid mp 48–49 °C (lit.^[29a, 45] mp 50–51 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.21–6.85 (m, 7H), 3.84 (s, 3H), 2.04 (s, 6H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 158.1, 141.3, 136.3, 133.1, 129.9, 127.1, 126.7, 113.6, 54.9, 20.7.

3-(4-Methoxyphenyl)pyridine (Table 10, entry 11): Colorless solid, mp 61–62 °C (lit.^[46] mp 60–61 °C); ¹H NMR (200 MHz, CDCl₃): δ = 8.81 (dd, J = 0.8, 2.4 Hz, 1H), 8.53 (dd, J = 1.8, 5.0 Hz, 1H), 7.83–7.75 (m, 1H), 7.58–7.43 (m, 2H), 7.37–7.24 (m, 1H), 7.06–6.93 (m, 2H), 3.83 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 159.4, 147.6, 147.5, 135.8, 133.4, 129.8, 127.8, 123.1, 114.2, 54.9.

2-Methyl-4'-(trifluoromethyl)biphenyl (Table 10, entry 12): Colorless oil;^[47] ¹H NMR (200 MHz, CDCl₃): δ = 7.67 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.33–7.17 (m, 4H), 2.26 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 145.6, 140.5, 135.2, 130.5, 129.5, 128.3 (d, J = 37.4 Hz), 127.9, 126.0, 125.0 (d, J = 3.8 Hz), 124.3 (d, J = 271.6 Hz), 20.3; ¹⁹F NMR (188 MHz, CDCl₃): δ = – 62.85 (s).

2,6,2'-Trimethylbiphenyl (Table 10, entry 14): Colorless oil;^[4] ¹H NMR (200 MHz, CDCl₃): δ = 7.35–6.92 (m, 7H), 1.97 (s, 3H), 1.94 (s, 6H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 140.9, 140.4, 135.7, 135.4, 129.8, 128.7, 127.1, 126.9, 126.8, 125.9, 20.2, 19.3.

6-(2-Methylphenyl)quinoline (Table 10, entry 15): Colorless viscous oil; IR (KBr): ν = 3016, 2927, 1593, 1487, 1121, 841, 754 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ = 8.94 (dd, J = 1.8, 4.2 Hz, 1H), 8.23–8.12 (m, 2H), 7.77–7.68 (m, 2H), 7.43 (dd, J = 4.4, 8.4 Hz, 1H), 7.37–7.28 (m, 4H), 2.32 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 150.1, 147.0, 140.7, 140.0, 135.8, 135.1, 131.1, 130.2, 129.7, 128.7, 127.8, 127.4, 127.3, 125.7, 121.1, 20.2; HRMS (EI⁺): Calcd for C₁₆H₁₃N: M⁺ 219.1048. Found: m/z 219.1048.

4-Fluoro-4'-methylbiphenyl (Table 10, entry 17): Colorless solid, mp 75–76 °C (lit.^[29b, 44] mp 77–78 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.57–7.39 (m, 4H), 7.29–7.21 (m, 2H), 7.17–7.04 (m, 2H), 2.39 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 162.3 (d, J = 246 Hz), 137.3, 137.2 (d, J = 4.5 Hz), 137.0, 129.5, 128.4 (d, J = 7.9 Hz), 126.8, 115.5 (d, J = 21.4 Hz), 21.0; ¹⁹F NMR (188 MHz, CDCl₃): δ = – (116.81–116.68) (m).

4-Fluoro-2'-methoxybiphenyl (Table 10, entry 18): Yield of the product was estimated by ¹H NMR (200 MHz, CDCl₃) using 2,6-dimethylchlorobenzene as an internal standard.

4-Fluoro-2',6'-methylbiphenyl (Table 10, entry 19): Yield of the product was estimated by ^1H NMR (200 MHz, CDCl_3) using 2-chloroanisole as an internal standard.

6-(4-Fluorophenyl)quinoline (Table 10, entry 20): Colorless solid, mp 97–99 °C; IR (KBr): $\nu = 2934, 1518, 1493, 1246, 1161, 889, 831 \text{ cm}^{-1}$; ^1H NMR (200 MHz, CDCl_3): $\delta = 8.93$ (dd, $J = 1.8, 4.2 \text{ Hz}$, 1H), 8.27–8.14 (m, 2H), 7.98–7.89 (m, 2H), 7.75–7.62 (m, 2H), 7.43 (dd, $J = 4.2, 8.2 \text{ Hz}$, 1H), 7.25–7.12 (m, 2H); ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 162.6$ (d, $J = 247 \text{ Hz}$), 150.3, 147.4, 138.2, 136.3 (d, $J = 3.4 \text{ Hz}$), 136.1, 129.9, 128.9 (d, $J = 4.9 \text{ Hz}$), 128.8, 128.3, 125.2, 121.5, 115.8 (d, $J = 21.4 \text{ Hz}$); MS m/z (rel. intensity %) 223 (M^+ , 100), 222 (77), 194 (16), 175 (7), 169 (6), 111 (17), 85 (13); HRMS (EI^+): Calcd for $\text{C}_{15}\text{H}_{10}\text{FN}$: M^+ 223.0797. Found: m/z 223.0786; ^{19}F NMR (188 MHz, CDCl_3): $\delta = - (109.15\text{--}109.0)$ (m).

4-Methoxy-*p*-terphenyl (12): Following the general procedure D, 4-chlorobiphenyl (75 mg, 0.40 mmol) and triallyl(4-methoxyphenyl)silane (0.124 g, 0.48 mmol) were allowed to react for 8 h. Purification by GPC afforded **12** (91 mg, 87% yield) as a colorless solid, mp 194–197 °C.^[48] ^1H NMR (200 MHz, CDCl_3): $\delta = 7.71\text{--}7.28$ (m, 11H), 7.0 (d, $J = 8.8 \text{ Hz}$, 2H), 3.86 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): $\delta = 159.2, 140.8, 139.7, 139.5, 133.2, 128.8, 128.0, 127.4, 127.2, 127.03, 126.98, 114.3, 55.3$; MS m/z (rel. intensity %) 260 (M^+ , 100), 245 (92), 217 (76), 202 (35), 189 (24), 130 (30), 115 (14); HRMS (EI^+): Calcd for $\text{C}_{19}\text{H}_{16}\text{O}$: M^+ 260.1201. Found: m/z 260.1151.

3-Chlorobiphenyl (13): General procedure C was applied to the coupling of 3-bromochlorobenzene (0.192 g, 1.00 mmol) with triallyl(phenyl)silane (0.252 g, 1.10 mmol) for 12 h. Purification of the crude product by flash column chromatography on silica gel eluting with hexane/ethyl acetate (95 : 5) afforded the title compound (0.175 g,

93% yield) as a colorless oil.^[7b, 49] ¹H NMR (200 MHz, CDCl₃): δ = 7.61–7.51 (m, 3H), 7.51–7.24 (m, 6H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 143.0, 139.7, 134.6, 129.9, 128.8, 127.8, 127.2, 127.0, 125.2.

4-Methyl-*m*-terphenyl (14): General procedure C was applied to the coupling of 3-chlorobiphenyl (75 mg, 0.40 mmol) with triallyl(4-methylphenyl)silane (0.116 g, 0.48 mmol) for 8 h. Purification of the crude product by preparative GPC gave the title compound (79 mg, 81% yield) as a colorless semi solid. ¹H NMR (200 MHz, CDCl₃): δ = 7.81–7.76 (m, 1H), 7.67–7.59 (m, 2H), 7.58–7.21 (m, 10H), 2.39 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃): δ = 141.6, 141.5, 141.1, 138.1, 137.0, 129.4, 129.0, 128.6, 127.2, 127.1, 126.9, 125.8, 125.7, 21.0; MS *m/z* (rel. intensity %) 244 (M⁺, 100), 228 (81), 202 (55), 165 (68), 152 (47), 122 (51), 91 (29), 77 (15); HRMS (EI⁺): Calcd for C₁₉H₁₆: M⁺ 244.1251. Found: *m/z* 244.1211.

References

- [1] a) D. P. Matthews, J. P. Whitten, J. R. McCarthy, *Tetrahedron Lett.* **1986**, 27, 4861;
b) A. Zapf, M. Beller, *Chem. Eur. J.* **2000**, 6, 1830.
- [2] Aldrich Catalog No. 55,363-8.
- [3] M. Rottländer, P. Knochel, *J. Org. Chem.* **1998**, 63, 203.
- [4] J. P. Wolfe, R. A. Singer, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, 121, 9550.
- [5] M. E. Mowery, P. DeShong, *J. Org. Chem.* **1999**, 64, 1684.
- [6] I. Barba, R. Chinchilla, C. Gómez, *Tetrahedron* **1990**, 46, 7813.

- [7] a) I. Klement, M. Rottlander, C. E. Tucker, T. N. Majid, P. Knochel, P. Venegas, G. Cahiez, *Tetrahedron* **1996**, 52, 7201; b) H.-J. Lehmler, L. W. Robertson, *Chemosphere* **2001**, 45, 137.
- [8] J.-M. Becht, A. Gissot, A. Wagner, C. Mioskowski, *Chem. Eur. J.* **2003**, 9, 3209.
- [9] D. W. Old, J. P. Wolfe, S. L. Buchwald, *J. Am. Chem. Soc.* **1998**, 120, 9722.
- [10] B. H. Lipshutz, K. Siegmann, E. Garcia, F. Kayser, *J. Am. Chem. Soc.* **1993**, 115, 9276.
- [11] a) H. Hart, *J. Org. Chem.* **1985**, 50, 3104; b) D. A. Widdowson, Y.-Z. Zhang, *Tetrahedron* **1986**, 42, 2111.
- [12] S. Schneider, W. Bannwarth, *Helv. Chim. Acta.* **2001**, 84, 735.
- [13] K. Selvakumar, A. Zapf, A. Spannenberg, M. Beller, *Chem. Eur. J.* **2002**, 8, 3901.
- [14] C. Nájera, J. Gil-Moltó, S. Karlström, L. R. Falvello, *Org. Lett.* **2003**, 5, 1451; b) Aldrich Catalog No. A4,242-5.
- [15] Aldrich Catalog No. 12,383-8.
- [16] Aldrich Catalog No. T280-0.
- [17] A. F. Littke, C. Dai, G. C. Fu, *J. Am. Chem. Soc.* **2000**, 122, 4020.
- [18] S. Riggleman, P. DeShong, *J. Org. Chem.* **2003**, 68, 8106.
- [19] J. C. Anderson, H. Namli, C. A. Roberts, *Tetrahedron* **1997**, 53, 15123.
- [20] G. W. Kabalka, Y. Ju, Z. Wu, *J. Org. Chem.* **2003**, 68, 7915.
- [21] J. W. Tilley, S. Zawoiski, *J. Org. Chem.* **1988**, 53, 386.
- [22] I. D. Kersey, C. W. G. Fishwick, J. B. C. Findlay, P. Ward, *Tetrahedron* **1995**, 51, 6819.

- [23] a) S. Cacchi, G. Fabrizi, F. Marinelli, L. Moro, P. Pace, *Tetrahedron* **1996**, 52, 10225; b) M. Feuerstein, H. Doucet, M. Santelli, *J. Organomet. Chem.* **2003**, 687, 327.
- [24] a) H. Yamanaka, T. Araki, T. Sakamoto, *Chem. Pharm. Bull.* **1988**, 36, 2244; b) A. Lutzen, M. Hapke, *Eur. J. Org. Chem.* **2002**, 2292.
- [25] S. S. Labadie, *Synth. Commun.* **1994**, 24, 709.
- [26] a) K. Hirabayashi, J. Kawashima, Y. Nishihara, A. Mori, T. Hiyama, *Org. Lett.* **1999**, 1, 299; b) Y. Tamura, M.-W. Chun, K. Inoue, J. Minamikawa, *Synthesis* **1978**, 11, 822.
- [27] L. R. Moore, K. H. Shaughnessy, *Org. Lett.* **2004**, 6, 225.
- [28] a) M. B. Andrus, C. Song, *Org. Lett.* **2001**, 3, 3761; b) C. -H. Cho, H. -S. Yun, K. Park, *J. Org. Chem.* **2003**, 68, 3017.
- [29] a) G. A. Molander, B. Biolatto, *J. Org. Chem.* **2003**, 68, 4302; b) H. C. Bell, J. R. Kalman, G. L. May, J. T. Pinhey, S. Sternhell, *Aust. J. Chem.* **1979**, 32, 1531; c) S.-K. Kang, H.-W. Lee, S.-B. Jang, P.-S. Ho, *J. Org. Chem.* **1996**, 61, 4720.
- [30] N. Kataoka, Q. Shelby, J. P. Stambuli, J. F. Hartwig, *J. Org. Chem.* **2002**, 67, 5553.
- [31] Y. Terao, H. Wakui, T. Satoh, M. Miura, M. Nomura, *J. Am. Chem. Soc.* **2001**, 123, 10407.
- [32] E. Anklam, K.-D. Asmus, *J. Fluorine Chem.* **1988**, 38, 209.
- [33] G. C. Dol, P. C. J. Kamer, P. W. N. M. Van Leeuwen, *Eur. J. Org. Chem.* **1998**, 359.
- [34] R. J. Edsall, Jr., H. A. Harris, E. S. Manas, R. E. Mewshaw, *Bioorg. Med. Chem.* **2003**, 11, 3457.

- [35] D. Badone, M. Baroni, R. Cardamone, A. Ielmini, U. Guzzi, *J. Org. Chem.* **1997**, *62*, 7170.
- [36] Aldrich Catalog No. 10,274-1.
- [37] Y. Ahmad, M. I. Qureshi, M. I. Baig, *Can. J. Chem.* **1967**, *45*, 1539.
- [38] M. E. Mowery, P. DeShong, *Org. Lett.* **1999**, *1*, 2137.
- [39] C. E. Kaslow, M. Hayek, *J. Am. Chem. Soc.* **1951**, *73*, 4986.
- [40] Aldrich Catalog No. 22,225-9.
- [41] K.-i. Gouda, E. Hagiwara, Y. Hatanaka, T. Hiyama, *J. Org. Chem.* **1996**, *61*, 7232.
- [42] G. Altenhoff, R. Goddard, C. W. Lehmann, F. Glorius, *Angew. Chem. Int. Ed.* **2003**, *42*, 3690.
- [43] a) G. W. Gray, A. Mosley, *J. Chem. Soc., Perkin Trans. 2* **1976**, 97; c) S. E. Denmark, M. H. Ober, *Org. Lett.* **2003**, *5*, 1357.
- [44] A. H. Roy, J. F. Hartwig, *J. Am. Chem. Soc.* **2003**, *125*, 8704.
- [45] K. H. Shaughnessy, R. S. Booth, *Org. Lett.* **2001**, *3*, 2757.
- [46] a) G. Riggio, W. H. Hopff, A. A. Hofmann, P. G. Waser, *Helv. Chim. Acta* **1983**, *66*, 1039; b) F. Mongin, L. Mojovic, B. Guillaumet, F. Trécourt, G. Quéguiner, *J. Org. Chem.* **2002**, *67*, 8991; c) M. Ishikura, M. Kumada, M. Terashima, *Heterocycles* **1984**, *22*, 265.
- [47] H. Shiratani, T. Shintaku, N. Itaya, *Jpn. Kokai Tokkyo Koho* JP 2001213816 A2 20010807, **2001**.
- [48] S. Yamada, S. Tanabe, *Jpn. Kokai Tokkyo Koho* JP 07101900 A2 19950418, **1995**.
- [49] S. F. Nielsen, D. Peters, O. Axelsson, *Synth. Commun.* **2000**, *30*, 3501.