Synthesis of Fused Polycyclic Aromatics by the Palladium-Catalyzed Annulation of Arynes Using 2-Halobiaryls

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Supporting Information

General. The ^1H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz or 400 and 100 MHz respectively. All melting points are uncorrected. High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. All reagents were used directly as obtained commercially unless otherwise noted. All yields reported represent an average of two independent runs. The silylaryl triflate **2a**, CsF, P(*o*-tolyl) $_3$ and acetonitrile were purchased from Sigma-Aldrich Co. Pd(dba) $_2$ was purchased from Acros Organics. The substituted silylaryl triflates **2b**, **2c** and **2d** were prepared according to a literature procedure.¹

Preparation of the starting materials. All 2-halobiaryls were either commercially available (**1d**, **1e**, **1i**) or easily prepared from commercially available materials according to literature procedures (**1a**,² **1b**,² **1c**,³ **1g**⁴).

3-(2-Iodophenyl)-1-methylindole (1f). To a suspension of 30 mg of NaH (0.75 mmol, 60% in mineral oil) in DMF (4 mL) was added dropwise a solution of 3-(2-iodophenyl)indole⁵ (0.16 g, 0.5 mmol) in DMF (5 mL) at 0 °C. The resulting brown solution was stirred at 0 °C for 1 h and a solution of MeI (0.142 g, 1.0 mmol) in DMF (2 mL) was added dropwise at 0 °C. The resulting mixture was stirred at 0 °C for another 12 h. The reaction mixture was diluted with Et $_2$ O (30 mL), washed with brine (30 mL),

dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (20:1 Hexane/EtOAc) to afford 0.133 g of the indicated compound **1f** (80% yield) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 3.85 (s, 3H), 7.00 (td, *J* = 7.8, 1.8 Hz, 1H), 7.14 (td, *J* = 7.2, 0.9 Hz, 1H), 7.24-7.29 (m, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.44 (td, *J* = 7.5, 1.8 Hz, 1H), 8.00 (dd, *J* = 8.1, 1.2 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 140.3, 140.1, 136.7, 131.7, 128.5, 128.3, 128.2, 127.2, 122.1, 120.5, 119.9, 118.7, 109.7, 100.9, 33.2; IR (CDCl₃, cm⁻¹) 3051, 3007, 2918, 2849, 1477; HRMS *m/z* 333.0018 (calcd C₁₅H₁₂IN, 333.0014).

3-Iodo-2-phenylchromone (1h). To a solution of 1-(2-hydroxyphenyl)-3-phenyl-2-propyn-1-one⁶ (1.0 mmol), NaHCO₃ (2.0 mmol) in MeCN (10 mL) was added dropwise ICl (2.0 mmol) in 3 mL of MeCN. The reaction mixture was stirred at room temperature for 5 min. The reaction mixture was diluted with Et₂O (30 mL), and washed with satd aq Na₂S₂O₃ (30 mL). The organic layer was separated and the aqueous layer was extracted with another 25 mL of Et₂O. The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (20:1 Hexane/EtOAc) to afford 0.323 g of the indicated compound **1h** (93% yield) as a yellow solid: mp 127-129 °C (lit.⁷ 128 °C). The ¹H NMR spectrum matched the literature data.⁷

General procedure for the palladium-catalyzed annulation of arynes using 2-halobiaryls. To a solution of the 2-halobiaryl (0.3 mmol), Pd(dba)₂ (0.015 mmol), P(*o*-tolyl)₃ (0.015 mmol) and silylaryl triflate (0.6 mmol) in a mixed solvent (4 mL) consisting of acetonitrile and toluene was added CsF (0.9 mmol). The solution was allowed to stir at 110 °C for 24 h. The resulting solution was washed with brine (20 mL) and extracted with diethyl ether (20 mL). The combined ether fractions were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

2-Methyltriphenylene (3a). The indicated compound was obtained in a 92% yield (66.8 mg) as a white solid: mp 100-102 °C (lit.⁸ 101-103 °C); ¹H NMR (300 MHz, CDCl₃) δ 2.56 (s, 3H), 7.42 (dd, J = 8.4, 1.5 Hz, 1H), 7.57-7.44 (m, 4H), 8.39 (s, 1H), 8.47 (d, J = 8.4 Hz, 1H), 8.54-8.62 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 137.1, 130.1, 130.0, 129.9, 129.6, 128.9, 127.7, 127.4, 127.3 (2C), 127.0, 123.6, 123.5 (2C), 123.4, 123.3, 22.1; IR (CDCl₃, cm⁻¹) 3081, 3026, 2923, 2854, 1742, 1437; HRMS m/z 242.1098 (calcd C₁₉H₁₄, 242.1095).

2-Methoxytriphenylene (3b). The indicated compound was obtained in an 83% yield (64 mg) as a white solid: mp 100-101 °C; ¹H NMR (300 MHz, CDCl₃) δ 3.99 (s, 3H), 7.24 (dd, J = 9.0, 2.7 Hz, 1H), 7.57-7.65 (m, 4H), 8.01 (d, J = 2.7 Hz, 1H), 8.50-8.64 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 159.1, 131.5, 130.4, 130.1, 129.7, 129.0, 127.5, 127.4, 127.3, 126.5, 125.2, 124.0, 123.6, 123.5 (2C), 123.0, 116.0, 106.0, 55.7; IR (CDCl₃, cm⁻¹) 3074, 3006, 2959, 2938, 2837, 1615; HRMS m/z 258.1048 (calcd C₁₉H₁₄O, 258.1044).

2-Methyl-10-methoxytriphenylene (3c) and 2-methyl-11-methoxytriphenylene (3d). The indicated compounds were obtained as a white solid in an 86% yield (70 mg) as a 1:1 mixture. ^1H NMR (400 MHz, CDCl_3) δ 2.57 (s, 3H), 2.58 (s, 3H), 3.99 (s, 3H), 4.00 (s, 3H), 7.21-7.24 (m, 2H), 7.39 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.44 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.54-7.62 (m, 4H), 7.99-8.00 (m, 2H), 8.30 (s, 2H), 8.45-8.59 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.0 (2C), 137.1, 136.9, 131.5, 131.4, 130.5, 130.1, 129.7, 129.6, 129.3, 129.1, 129.0, 128.1, 127.9, 127.5, 127.0, 126.8, 126.7, 126.4, 125.2, 125.1, 124.1, 123.9, 123.6, 123.5, 123.4 (2C), 123.3, 123.0, 122.9, 115.9, 105.9 (2C), 55.8, 55.7, 22.1 (2C); IR (CDCl_3 , cm^{-1}) 3068, 3007, 2937, 2830, 1613; HRMS m/z 272.1205 (calcd $\text{C}_{20}\text{H}_{16}\text{O}$, 272.1201).

2-Nitrotriphenylene (3e). The indicated compound was obtained in a 75% yield (62 mg) as a yellow solid: mp 159-160 °C (lit.⁹ 162-163 °C); ^1H NMR (400 MHz, CDCl_3) δ 7.70-7.80 (m, 4H), 8.40 (dd, $J = 9.2, 2.4$ Hz, 1H), 8.62-8.73 (m, 5H), 9.48 (d, $J = 2.4$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 146.3, 134.1, 130.9, 130.1, 129.8, 129.2, 128.6, 128.5, 128.0, 127.9, 127.8, 124.3, 124.2, 123.5 (2C), 123.4, 120.8, 119.0; IR (CDCl_3 , cm^{-1}) 3064, 2919, 2848, 1515; HRMS m/z 273.0794 (calcd $\text{C}_{18}\text{H}_{11}\text{NO}_2$, 273.0789).

2,3-Dimethoxytriphenylene (3f). The indicated compound was obtained in a 94% yield (81 mg) as a white solid: mp 164-165 °C (lit.¹⁰ 164-165 °C). The ^1H NMR spectrum matched the literature data.¹¹ ^{13}C NMR (100 MHz, CDCl_3) δ 149.4, 129.6, 129.2, 127.1, 126.4, 124.2, 123.5, 122.9, 104.4, 56.1; IR (CDCl_3 , cm^{-1}) 3088, 3068, 2998, 2962, 2841, 1611; HRMS m/z 288.1154 (calcd $\text{C}_{20}\text{H}_{16}\text{O}_2$, 288.1150).

6,7,9-Trimethyldibenzo[*a,c*]carbazole (3g). The indicated compound was obtained in a 95% yield (88 mg) as a light yellow solid: mp 154-156 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.44 (s, 3H), 2.49 (s, 3H), 4.24 (s, 3H), 7.34-7.55 (m, 4H), 7.69 (td, $J = 7.5, 1.2$ Hz, 1H), 8.27 (s, 1H), 8.49 (s, 1H), 8.56 (d, $J = 7.8$ Hz, 1H), 8.68 (d, $J = 8.1$ Hz, 1H), 8.81 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 140.8, 135.4, 135.0, 129.9, 129.5, 126.9, 124.7, 123.8, 123.7, 123.6, 123.5, 123.4, 122.4, 121.8, 120.3, 112.9, 109.6, 34.6, 20.8, 20.7; IR (CDCl_3 , cm^{-1}) 3069, 2956, 2918, 2850; HRMS m/z 309.1522 (calcd $\text{C}_{23}\text{H}_{19}\text{N}$, 309.1517).

6,7-Dimethylbenzo[*b*]phenanthro[9,10-*d*]furan (3h). The indicated compound was obtained in a 75% yield (67 mg) as a white solid: mp 174-176 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.48 (s, 3H), 2.50 (s, 3H), 7.43-7.46 (m, 2H), 7.59 (td, $J = 8.4, 1.5$ Hz, 1H), 7.66-7.73 (m, 2H), 8.16 (s, 1H), 8.30-8.34 (m, 1H), 8.40 (s, 1H), 8.56 (dd, $J = 8.1, 0.9$ Hz, 1H), 8.67 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 155.8, 151.4, 136.8, 136.6, 129.2, 128.5, 128.1, 127.0, 126.0, 125.2, 125.0, 124.2, 124.0, 123.7, 123.4, 121.9, 120.6, 113.7, 112.0, 21.0, 20.3; IR (CDCl_3 , cm^{-1}) 3069, 2958, 2915; HRMS m/z 296.1205 (calcd $\text{C}_{22}\text{H}_{16}\text{O}$, 296.1201).

2,3-Dimethyldibenzo[*a,c*]xanthen-14-one (3i). The indicated compound was obtained in an 81% yield (79 mg) as a white solid: mp 180-181 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.43 (s, 3H), 2.45 (s, 3H), 7.41 (t, $J = 7.8$ Hz, 1H), 7.52-7.72 (m, 4H), 8.18 (s, 1H), 8.36 (dd, $J = 7.8, 1.2$ Hz, 1H), 8.44 (d, $J = 8.1$ Hz, 1H), 8.52 (d, $J = 8.1$ Hz, 1H), 9.77 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 178.3, 154.7, 154.4, 137.9, 135.7, 133.7, 133.6, 130.3, 127.9, 127.1, 126.7, 125.8, 124.6, 124.0, 123.5, 122.8, 122.6, 117.6, 112.5, 20.6, 20.5; IR (CDCl_3 , cm^{-1}) 3088, 2999, 2943, 1630, 1467; HRMS m/z 324.1154 (calcd $\text{C}_{23}\text{H}_{16}\text{O}_2$, 324.1150).

2,3-Dimethoxy-9,10-diphenylphenanthrene (3j). The indicated compound was obtained in a 92% yield (108 mg) as a white solid: mp 228-229 °C; ^1H NMR (300 MHz, CDCl_3) δ 3.71 (s, 3H), 4.14 (s, 3H), 6.92 (s, 1H), 7.13-7.25 (m, 10H), 7.42 (t, $J = 7.2$ Hz, 1H), 7.55 (d, $J = 7.8$ Hz, 1H), 7.62 (t, $J = 8.1$ Hz, 1H), 8.12 (s, 1H), 8.64 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.4, 149.3, 140.1, 140.0, 136.7, 135.8, 131.5, 131.4, 131.2, 129.6, 128.2, 127.9, 127.7, 127.2, 126.7, 126.6, 126.2, 125.9, 125.0, 122.2, 108.3, 103.4, 56.3, 55.8; IR (CDCl_3 , cm^{-1}) 3055, 3021, 2957, 2934, 2828, 1503; HRMS m/z 390.1624 (calcd $\text{C}_{28}\text{H}_{22}\text{O}_2$, 390.1619).

2,3-Dimethoxy-6-methyltriphenylene (3k). The indicated compound was obtained in a 24% yield (22 mg) as a white solid: mp 172-173 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.61 (s, 3H), 4.09 (s, 3H), 4.11 (s, 3H), 7.41 (d, $J = 8.4$ Hz, 1H), 7.58-7.62 (m, 2H), 7.91 (d, $J = 5.4$ Hz, 2H), 8.20 (s, 1H), 8.42-8.45 (m, 1H), 8.50 (d, $J = 8.4$ Hz, 1H), 8.57-8.60 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.5, 149.4, 136.8, 129.6, 129.4, 129.3, 127.9, 127.0, 126.7, 126.4, 124.4, 124.2, 123.5, 123.3, 122.9, 122.8, 104.6 (2C), 56.2, 56.1, 22.1;

IR (CDCl₃, cm⁻¹) 3020, 2960, 2936, 2914, 2834, 1613, 1513; HRMS m/z 302.1311 (calcd C₂₁H₁₈O₂, 302.1306).

Ethyl 6,7,10,11-tetramethyltriphenylene-2-carboxylate (3l). The indicated compound was obtained in a 50% yield (54 mg) as a light yellow solid: mp 148-150 °C; ¹H NMR (300 MHz, CDCl₃) δ 1.48 (t, *J* = 7.2 Hz, 3H), 2.41 (s, 3H), 2.42 (s, 3H), 2.43 (s, 3H), 2.45 (s, 3H), 4.48 (q, *J* = 7.2 Hz, 2H), 8.08-8.18 (m, 4H), 8.29 (s, 1H), 8.46 (d, *J* = 8.7 Hz, 1H), 9.17 (d, *J* = 1.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 167.3, 137.3, 136.6, 136.0, 135.8, 133.0, 129.2, 128.8, 128.1, 128.0, 127.4, 126.9, 126.6, 125.2, 124.5, 124.1, 123.7, 123.6, 123.1, 61.3, 20.6, 20.5, 20.4 (2C), 14.7; IR (CDCl₃, cm⁻¹) 3019, 2874, 2918, 1710, 1612; HRMS m/z 356.1781 (calcd C₂₅H₂₄O₂, 356.1776).

2,3,6,7,10,11-Hexamethyltriphenylene (3m). The indicated compound was obtained in a 22% yield (23 mg) as a white solid: mp 272-275 °C; ¹H NMR (300 MHz, CDCl₃) δ 2.50 (s, 18 H), 8.32 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 135.6, 127.8, 123.8, 20.5; IR (CDCl₃, cm⁻¹) 3041, 2915, 2850, 1455; HRMS m/z 312.1878 (calcd C₂₄H₂₄, 312.1884).

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indolec/vxr300/xxzhang

allu95/300/7/3/5

allu36/300/5/12/5

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1.266

allin08/3007/21/5