1,4-Palladium Migration Via C-H Activation, Followed by Arylation: Synthesis of Fused Polycycles

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General procedures. All ^1H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz or 400 and 100 MHz respectively. Thin-layer chromatography was performed using commercially prepared 60-mesh silica gel plates (Whatman K6F), and visualization was effected with short wavelength UV light (254 nm) and a basic KMnO_4 solution [3 g of KMnO_4 + 20 g of K_2CO_3 + 5 mL of NaOH (5 %) + 300 mL of H_2O]. 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. Compound **7** has been previously reported.¹

3'-Benzyl-2-iodobiphenyl (1). This biphenyl was prepared from 3'-bromomethyl-2-iodobiphenyl (**16**)¹ by following a procedure from the literature.² To a suspension of AgClO_4 (0.28 g, 1.4 mmol) in benzene (4.0 mL) was added compound **16** (0.261 g, 0.7 mmol) in benzene (4.0 mL) and the resulting mixture was stirred overnight at room temperature in the dark. The reaction mixture was diluted with diethyl ether (50 mL), filtered and washed with brine (25 mL). The organic layer was dried (Na_2SO_4), filtered and the solvent evaporated under reduced pressure. The residue was purified by silica gel column chromatography using 50:1 hexane/EtOAc to afford 0.187 g (72 %) of the indicated compound **1** as a colorless oil: ^1H NMR (CDCl_3) δ 4.03 (s, 3H), 6.97-7.01 (m, 1H), 7.15-7.34 (m, 11H), 7.92 (dd, J = 1.0, 8.0 Hz, 1H); ^{13}C NMR (CDCl_3) δ 42.0, 98.8,

126.2, 127.1, 128.2, 128.2, 128.3, 128.6, 128.8, 129.1, 130.1, 130.2, 139.6, 140.8, 141.0, 144.3, 146.6; IR (CH₂Cl₂) 3056, 3025, 2917, 1601, 1583, 1494, 1461 cm⁻¹; HRMS *m/z* 370.0224 (calcd for C₁₉H₁₅I, 370.0218).

2-Iodo-3'-methoxybiphenyl (17). Compound **17** was prepared by a procedure reported by Hart *et al.*³ A solution of 2-bromoiodobenzene (1.415 g, 5.0 mmol) in THF (10 mL) was added slowly (90 min) to a solution of 3-methoxyphenylmagnesium bromide [prepared from 3-bromoanisole (1.87 g, 10 mmol) and Mg (0.246 g, 10 mmol) in THF (30 mL)], and the mixture was stirred under Ar for an additional 14 h at room temperature. The reaction was quenched by adding I₂ (3.8 g, 15 mmol), and the mixture was stirred for an additional 30 min at room temperature. The excess I₂ was destroyed by adding 10 % aq NaHSO₃ (35 mL) and the organic layer was separated and rewashed with brine (20 mL). Finally, the organic layer was dried (MgSO₄), filtered, and the solvent removed under reduced pressure. The residue was chromatographed using 30:1 hexane/EtOAc to afford 0.620 g (40 %) of the desired compound **17** as a clear oil: ¹H NMR (CDCl₃) δ 3.84 (s, 3H), 6.88-6.95 (m, 3H), 7.01-7.05 (m, 1H), 7.29-7.38 (m, 3H), 7.95 (dd, *J* = 1.2, 8.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 55.4, 98.5, 113.4, 115.0, 121.8, 128.1, 128.9, 129.1, 130.1, 139.6, 145.5, 146.5, 159.1; HRMS *m/z* 309.9859 (calcd for C₁₃H₁₁IO, 309.9855).

2-Iodo-3'-phenoxybiphenyl (3). This biphenyl was prepared in two steps from 2-iodo-3-methoxybiphenyl (**17**). To a solution of compound **17** (0.97 g, 3.14 mmol) in CH₂Cl₂ (20 mL) at -78 °C was added 1.0 M BBr₃ in CH₂Cl₂ (4.1 mL, 4.1 mmol). The resulting solution was allowed to warm to room temperature and stirred for 2 h. The mixture was worked up with ice (15 g) and extracted with diethyl ether (75 mL). The organic layer was dried (Na₂SO₄), filtered and the solvent evaporated under reduced pressure. The residue was purified by silica gel column chromatography using 3:1

hexane/EtOAc to afford 0.91 g (98 %) of 3-(2-iodophenyl)phenol as a clear oil: ^1H NMR (CDCl_3) δ 5.04 (br s, 1H), 6.80-6.81 (m, 1H), 6.85-6.90 (m, 2H), 7.00-7.05 (m, 1H), 7.25-7.31 (m, 2H), 7.37 (dt, $J = 0.8, 7.6$ Hz, 1H), 7.94 (dd, $J = 0.8, 8.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 98.4, 114.7, 116.4, 122.0, 128.1, 128.9, 129.3, 130.0, 139.5, 145.8, 146.2, 155.0. 3-(2-Iodophenyl)phenol was phenylated by a literature procedure.⁴ A suspension of 3-(2-iodophenyl)phenol (0.222 g, 0.75 mmol), phenylboronic acid (0.183 g, 1.5 mmol), $\text{Cu}(\text{OAc})_2$ (0.163 g, 0.90 mmol), Et_3N (0.38 g, 3.75 mmol), 5 Angstrom molecular sieves (0.2 g) in CH_2Cl_2 (6.0 mL) was stirred under O_2 (1 atm) for 2 d at room temperature. The reaction mixture was diluted with diethyl ether (50 mL), filtered, and the solvent evaporated under reduced pressure. The residue was purified by silica gel column chromatography using 15:1 hexane/EtOAc to afford 0.129 g (46 %) of the indicated compound **3** as a clear oil: ^1H NMR (CDCl_3) δ 7.00-7.12 (m, 7H), 7.25-7.40 (m, 5H), 7.92 (dd, $J = 1.2, 8.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 98.4, 118.2, 119.1, 119.8, 123.4, 124.2, 128.2, 129.0, 129.4, 129.8, 130.0, 139.6, 145.9, 146.0, 156.8, 157.1; IR (CH_2Cl_2) 3058, 1578, 1488, 1460, 1222, cm^{-1} ; HRMS m/z 372.0020 (calcd for $\text{C}_{18}\text{H}_{13}\text{IO}$, 372.0011).

2-Iodo-1-phenylnaphthalene (5). To a solution of 3,4-dihydro-1-phenylnaphthalene (1.30 g, 6.3 mmol) and I_2 (2.24 g, 8.8 mmol) in anhydrous CH_3CN (15 mL) was added dropwise AgOTf (1.75 g, 6.8 mmol) in anhydrous CH_3CN (20 mL). The resulting mixture was stirred at room temperature in the dark for 1 h. The reaction was diluted with diethyl ether (70 mL) and washed with satd aq $\text{Na}_2\text{S}_2\text{O}_3$ (25 mL). The organic layer was dried (Na_2SO_4), filtered and the solvent removed under reduced pressure. The residue was dissolved in benzene (25 mL). To this solution was added DDQ (2.86 g, 12.6 mmol) and the reaction was heated at 65°C for 2 d. The resulting mixture was filtered and washed with 10 % aq Na_2CO_3 (25 mL). The organic layer was filtered, dried (Na_2SO_4) and the solvent removed under reduced pressure. The residue was purified by

silica gel column chromatography using 50:1 hexane/EtOAc to afford 1.47 g (70 %) of the indicated compound **5** as a clear oil: ^1H NMR (CDCl_3) δ 7.22-7.26 (m, 2H), 7.32-7.34 (m, 1H), 7.38-7.56 (m, 6H), 7.80-7.83 (m, 1H), 7.95 (d, J = 8.7 Hz, 1H); ^{13}C NMR (CDCl_3) δ 98.7, 126.5, 127.0, 127.4, 128.1, 128.1, 128.7, 129.3, 130.2, 133.1, 133.6, 135.8, 143.5, 144.7; IR (CH_2Cl_2) 3053, 1577, 1502, 1442, 1382, 1306 cm^{-1} ; HRMS m/z 329.9910 (calcd for $\text{C}_{16}\text{H}_{11}\text{I}$, 329.9906).

9-Iodo-10-(3-methylphenyl)phenanthrene (9). To a solution of 3-iodotoluene (1.0 mmol) and 2-ethynylbiphenyl⁵ (1.2 mmol, 1.2 equiv) in Et_3N (4.0 mL) were added $\text{PdCl}_2(\text{PPh}_3)_2$ (1.4 mg, 2 mol %) and CuI (2.0 mg, 1 mol %). The resulting mixture was then heated under a N_2 atmosphere at $55\text{ }^\circ\text{C}$ for 3 h. The mixture was allowed to cool to room temperature, and the ammonium salt was removed by filtration. The solvent was removed under reduced pressure and the residue was purified by column chromatography (40:1 hexane/EtOAc) on silica gel to afford 0.26 g of compound **18** in 97 % yield as a clear liquid: ^1H NMR (CDCl_3) δ 2.34 (s, 3H), 7.12-7.22 (m, 4H), 7.33-7.53 (m, 6H), 7.67-7.74 (m, 3H); ^{13}C NMR (CDCl_3) δ 21.5, 89.3, 92.7, 122.0, 123.5, 127.3, 127.7, 128.2, 128.4, 128.7, 128.7, 129.3, 129.7, 129.7, 132.2, 133.1, 138.2, 140.9, 144.1. To a solution of compound **18** (0.30 mmol) in CH_2Cl_2 (3 mL) under N_2 was added ICl (1.2 equiv) in CH_2Cl_2 (0.5 mL) at $-78\text{ }^\circ\text{C}$. The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h, diluted with diethyl ether (50 mL), washed with 25 mL of satd aq $\text{Na}_2\text{S}_2\text{O}_3$, dried (MgSO_4), and filtered. The solvent was evaporated under reduced pressure and the product was purified by chromatography (30:1 hexane/EtOAc) on a silica gel column to afford 0.117 g (99 %) of the indicated compound **9** as a white solid: mp $134\text{--}135\text{ }^\circ\text{C}$; ^1H NMR (CDCl_3) δ 2.44 (s, 3H), 7.07-7.09 (m, 2H), 7.30-7.32 (m, 1H), 7.41-7.45 (m, 3H), 7.63-7.70 (m, 3H), 8.45-8.48 (m, 1H), 8.67-8.73 (m, 2H); ^{13}C NMR (CDCl_3) δ 21.7, 106.5, 122.6, 122.7, 127.1, 127.1, 127.5, 128.1, 128.4, 128.5, 128.8, 130.3, 130.6, 130.6,

132.5, 132.5, 134.7, 138.1, 145.4, 145.5 (one sp^2 carbon missing due to overlap); IR (CH_2Cl_2) 3067, 2971, 2921, 1602, 1563 cm^{-1} ; HRMS m/z 394.0226 (calcd for $C_{21}H_{15}I$, 394.0219).

1-Benzyl-3-(2-iodophenyl)indole (11). To a solution of (2-iodophenyl)acetaldehyde⁶ (0.738 g, 3.0 mmol) in 15 mL of absolute ethanol was added 0.356 g of PhNHNH₂ (3.3 mmol) and 57.6 mg of CH₃SO₃H (0.6 mmol). The resulting yellow solution was then stirred at room temperature for 1 h. Another 0.519 g of CH₃SO₃H (5.4 mmol) was then added to the reaction mixture and the reaction was stirred at 85 °C. After 2 days, the reaction was complete and was allowed to cool to room temperature. The ethanol was removed under reduced pressure and the residue was diluted with Et₂O (30 mL), washed with brine (30 mL), dried over Na₂SO₄, filtered and concentrated. The residue was purified by flash chromatography (5:1 hexane/EtOAc) to afford 0.41 g of compound **19** (43 % yield) as a yellow oil: ¹H NMR (CDCl₃) δ 7.01-7.05 (m, 1H), 7.14-7.18 (m, 1H), 7.23-7.27 (m, 1H), 7.38-7.49 (m, 4H), 7.54 (d, *J* = 8.0 Hz, 1H), 8.01 (dd, *J* = 1.2, 8.0 Hz, 1H), 8.27 (br s, 1H); ¹³C NMR (CDCl₃) δ 101.0, 111.5, 120.3, 120.4, 122.6, 123.8, 126.8, 128.2, 128.5, 131.6, 135.8, 140.0, 140.1 (one sp^2 carbon missing due to overlap). To a suspension of 30 mg of NaH (0.75 mmol, 60 % in mineral oil) in DMF (2 mL) was added dropwise a solution of compound **19** (0.16 g, 0.5 mmol) in DMF (4 mL) at 0 °C. A lot of bubbles were generated. The resulting brown solution was stirred at 0 °C for 45 min and a solution of PhCH₂Cl (0.127 g, 1.0 mmol) in DMF (1 mL) was added dropwise at 0 °C. The resulting mixture was stirred at 0 °C for 12 h. The reaction mixture was diluted with Et₂O (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 0.155 g of the indicated compound **11** (76 % yield) as a colorless oil: ¹H NMR (CDCl₃) δ 5.38 (s, 2H), 6.98-7.02 (m, 1H), 7.12-7.16 (m, 1H), 7.18-7.33 (m, 8H), 7.37-7.41 (m, 1H), 7.49 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.54-7.56 (m, 1H), 7.99 (dd, *J* = 1.2, 8.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 50.4, 101.1, 110.1,

119.2, 120.1, 120.4, 122.3, 127.1, 127.5, 127.9, 128.1, 128.2, 128.4, 129.0, 131.6, 136.3, 137.5, 140.0, 140.1; IR (neat) 3055, 3029, 2921, 1613, 1585 cm^{-1} ; HRMS m/z 409.0335 (calcd for $\text{C}_{21}\text{H}_{16}\text{IN}$, 409.0328).

1-(5-Phenyl-4-pentynyl)-3-(2-iodophenyl)indole (13). To a suspension of NaH (45.7 mg, 1.14 mmol, 60 % in mineral oil) in DMF (3 mL) was added dropwise a solution of compound **19** (0.243 g, 0.76 mmol) in DMF (5 mL) at 0 °C. A lot of bubbles were generated. The resulting brown solution was stirred at 0 °C for 45 min and a solution of 5-bromo-1-phenyl-1-pentyne (0.34 g, 1.52 mmol) in DMF (2 mL) was added dropwise at 0 °C. The resulting mixture was stirred at 0 °C for 12 h, diluted with Et_2O (30 mL), washed with brine (30 mL), dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (20:1 hexane/EtOAc) to afford 0.30 g of the indicated compound **13** (85 % yield) as a yellow oil: ^1H NMR (CDCl_3) δ 2.13-2.22 (m, 2H), 2.45 (t, J = 8.8 Hz, 2H), 4.41 (t, J = 8.8 Hz, 2H), 6.98-7.03 (m, 1H), 7.12-7.23 (m, 1H), 7.23-7.33 (m, 4H), 7.37-7.50 (m, 6H), 7.54-7.56 (m, 1H), 8.00 (dd, J = 1.6, 10.8 Hz, 1H); ^{13}C NMR (CDCl_3) δ 17.0, 29.1, 45.1, 82.3, 88.6, 101.1, 109.8, 118.7, 120.0, 120.4, 122.1, 123.8, 127.5, 128.0, 128.1, 128.2, 128.3, 128.5, 131.5, 131.8, 135.9, 140.1 (one sp^2 carbon missing due to overlap); IR (CH_2Cl_2) 3053, 2985, 1613, 1596, 1548 cm^{-1} ; HRMS m/z 461.0647 (calcd for $\text{C}_{25}\text{H}_{20}\text{IN}$, 461.0641).

***N*-(4-Phenoxyphenyl) *t*-butanamide.** To a solution of 4-phenoxyaniline (3.33 g, 18.0 mmol) in 70 mL of dried THF was added (Boc)₂O (4.71 g, 21.6 mmol) and the resulting yellow solution was refluxed at 80 °C for 6 h. The solvent was removed under reduced pressure and the reddish residue was recrystallized using hexane and EtOAc to afford 4.84 g of the indicated compound (85 % yield) as white needles: mp 109-111 °C; ¹H NMR (CDCl₃) δ 1.52 (s, 9H), 6.43 (br s, 1H), 6.95-6.98 (m, 4H), 7.06 (t, *J* = 3.6 Hz, 1H), 7.29-7.34 (m, 4H); ¹³C NMR (CDCl₃) δ 28.6, 80.7, 118.3, 120.2, 120.5, 123.0, 129.9, 134.2, 152.6, 153.2, 158.1.

***N*-(2-Iodo-4-phenoxyphenyl) *t*-butanamide.** To a solution of *N*-(4-phenoxyphenyl) *t*-butanamide (2.57 g, 9.02 mmol) in 20 mL of dry diethyl ether was added dropwise 10.6 mL of *t*-BuLi (1.7 M in pentane, 18.04 mmol) at -78 °C under Ar. The pale orange solution turned a pale yellow color when half of the *t*-BuLi solution had been added and eventually to yellow when all of the *t*-BuLi solution was added. The resulting yellow solution was then stirred at -78 °C for 30 min. A solution of ICH₂CH₂I (2.81 g, 9.92 mmol, recrystallized from diethyl ether) in 20 mL of dry ether was added dropwise to the reaction mixture and the resulting orange solution was stirred at -78 °C for another 30 min. The reaction mixture was allowed to warm up to room temperature and quenched by 50 mL of water. The organic layer was separated and dried over Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography (15:1 hexane/EtOAc) to afford 2.3 g of the desired compound (62 % yield) as a colorless oil: ¹H NMR (CDCl₃) δ 1.53 (s, 9H), 6.68 (br s, 1H), 6.96-6.98 (m, 2H), 7.02 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.08-7.12 (m, 1H), 7.30-7.35 (m, 2H), 7.42 (d, *J* = 2.8 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H); ¹³C NMR (CDCl₃) δ 28.5, 81.3, 89.5, 118.6, 120.2, 121.6, 123.6, 129.3, 130.0, 134.9, 153.0, 153.0, 157.4.

2-Iodo-4-phenoxyaniline. To a solution of *N*-(2-iodo-4-phenoxyphenyl) *t*-butanamide (0.82 g, 2.0 mmol) in 10 mL of CH₂Cl₂ was added dropwise 2.0 mL of TFA at 0 °C and the reaction was allowed to warm up to room temperature. The resulting colorless mixture was stirred at room temperature for 16 h, diluted with 20 mL of CH₂Cl₂, washed with brine (30 mL), dried over Na₂SO₄, filtered and concentrated. The residue was purified by flash chromatography (5:1 hexane/EtOAc) to afford 0.56 g of the indicated compound (91 % yield) as a pale orange solid: mp 54-56 °C; ¹H NMR (CDCl₃) δ 4.00 (s, 2H), 6.74 (d, *J* = 8.7 Hz, 1H), 6.88-6.91 (m, 2H), 6.93-6.95 (m, 1H), 7.01-7.07 (m, 1H), 7.26-7.32 (m, 2H), 7.36 (d, *J* = 2.7 Hz, 1H); ¹³C NMR (CDCl₃) δ 83.8, 115.2, 117.6, 121.6, 122.8, 129.9, 130.3, 143.5, 148.8, 158.6.

4-Phenoxy-2-phenylaniline. To a 50 mL round-bottom flask was added PdCl₂(PPh₃)₂ (0.103 g, 0.147 mmol), PhB(OH)₂ (0.358 g, 2.94 mmol), K₂CO₃ (0.406 g, 2.94 mmol), 2-iodo-4-phenoxyaniline (0.457 g, 1.47 mmol), 15 mL of DMF and 3 mL of H₂O. The whole mixture was then stirred at room temperature for 5 min, flushed with Ar and heated to 70 °C for 3 h. The reaction was allowed to cool to room temperature, diluted with diethyl ether (30 mL), washed with brine (50 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (5:1 hexane/EtOAc) to afford 0.342 g of the indicated compound (88 % yield) as a yellow oil: ¹H NMR (CDCl₃) δ 3.71 (br s, 2H), 6.75-6.77 (m, 1H), 6.87-6.90 (m, 2H), 6.97-7.03 (m, 3H), 7.25-7.35 (m, 3H), 7.41-7.60 (m, 4H); ¹³C NMR (CDCl₃) δ 116.9, 117.5, 120.4, 122.2, 122.3, 127.6, 129.0, 129.1, 129.2, 129.7, 139.1, 139.9, 148.9, 159.0.

2-Iodo-5-phenoxybiphenyl (15). To a solution of 4-phenoxy-2-phenylaniline (0.383 g, 1.47 mmol) in DME (4 mL) was added dropwise 3 mL of water containing 0.6 mL of conc H₂SO₄ (95 %). The resulting yellow mixture was cooled to 0 °C and a solution of NaNO₂ (0.152 g, 2.21 mmol) in water (1 mL) was added over 10 min. The the yellow reaction mixture was stirred at 0 °C for 20 min and a solution of NaI (1.10 g, 7.35 mmol) in water (3 mL) was added dropwise at 0 °C. The reaction mixture turned black when the NaI solution was added. After 10 min, the reaction was diluted with Et₂O (30 mL), and washed by satd Na₂S₂O₃ (30 mL), water (30 mL), and brine (30 mL). The organic layer was collected, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (30:1 hexane/EtOAc) to afford 0.44 g of

the indicated compound **15** (81 % yield) as a yellow solid: mp 68-70 °C; ¹H NMR (CDCl₃) δ 6.73 (dd, *J* = 3.0, 8.8 Hz, 1H), 6.97 (d, *J* = 2.8 Hz, 1H), 7.04-7.06 (m, 2H), 7.11-7.15 (m, 1H), 7.31-7.43 (m, 7H), 7.85 (d, *J* = 8.8 Hz, 1H); ¹³C NMR (CDCl₃) δ 90.4, 119.4, 119.5, 120.5, 124.1, 128.0, 128.2, 129.4, 130.1, 140.6, 143.9, 148.2, 156.6, 158.0; IR (CH₂Cl₂) 3056, 2981, 1583, 1561, 1490, cm⁻¹; HRMS *m/z* 372.0019 (calcd for C₁₈H₁₃IO, 372.0011)

Representative procedure for the palladium-catalyzed migration reactions. The appropriate aryl iodide (0.25 mmol), Pd(OAc)₂ (2.8 mg, 0.0125 mmol), 1,1-bis(diphenylphosphino)methane (dppm) (4.8 mg, 0.0125 mmol) and CsO₂CCMe₃ (CsPiv) (0.117 g, 0.5 mmol) in DMF (4 mL) were stirred under Ar at 100 °C for the specified length of time. The reaction mixture was allowed to cool to room temperature, diluted with diethyl ether (35 mL) and washed with brine (30 mL). The aqueous layer was reextracted with diethyl ether (15 mL). The organic layers were combined, dried (MgSO₄), filtered, and the solvent removed under reduced pressure. The residue was purified by flash chromatography on silica gel.

1-Phenyl-9H-fluorene (2). Compound **1** (92.5 mg, 0.25 mmol) was allowed to react under our standard reaction conditions at 110 °C for 3 d. The reaction mixture was chromatographed using 30:1 hexane/EtOAc to afford 24.2 mg (40 %) of the indicated compound **2** as a colorless oil: ¹H NMR (CDCl₃) δ 3.95 (s, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.19-7.22 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.45-7.55 (m, 7H); ¹³C NMR (CDCl₃) δ 37.0, 122.9, 124.0, 124.8, 126.3, 126.4, 127.5, 128.5, 128.8, 129.2, 137.9, 138.7, 141.3, 141.6, 143.7, 143.9 (one sp² carbon missing due to overlap); IR (CH₂Cl₂) 3056, 3025, 1454, 1417, 1478 cm⁻¹; HRMS *m/z* 242.1101 (calcd for C₁₉H₁₄, 242.1096).

1-Phenyldibenzofuran (4). Compound **3** (93.0 mg, 0.25 mmol) or compound **15** (93.0 mg, 0.25 mmol) was allowed to react under our standard reaction conditions for 1 d. The reaction mixtures were chromatographed using 30:1 hexane/EtOAc to afford 54.4 mg (89 %) (entry 2, Table 1) or 54.0 mg (88 %) (entry 8, Table 1) of the indicated compound **4**, respectively, as a white solid: mp 62-63 °C (lit⁷ mp 63-64 °C); ¹H NMR (CDCl₃) δ 7.10-7.14 (m, 1H), 7.24-7.26 (m, 1H), 7.37-7.42 (m, 1H), 7.46-7.64 (m, 9H); ¹³C NMR (CDCl₃) δ 110.5, 111.6, 121.8, 122.3, 122.5, 123.9, 124.0, 127.1, 127.1, 127.9, 128.6, 129.0, 138.0, 140.0, 156.4, 156.5. The other spectral properties were identical to those previously reported.⁷

Fluoranthene (6). Compound **5** (82.5 mg, 0.25 mmol) was allowed to react under our standard reaction conditions at 110 °C for 1 d. The reaction mixture was chromatographed using 50:1 hexane/EtOAc to afford 41.0 mg (81 %) of the indicated compound **6** as a white solid: mp 107-108 °C (lit⁸ mp 106-108 °C). The other spectral properties were identical to those previously reported.⁹

Benzo[e]acephenanthrylene (8). Compound **7**¹ (95.0 mg, 0.25 mmol) was allowed to react under our standard reaction conditions at 110 °C for 2 d. The reaction mixture was chromatographed using 50:1 hexane/EtOAc to afford 49.2 mg (78 %) of the

indicated compound **8** as a white solid: mp 166-167 °C (lit¹⁰ mp 165-166 °C). The other spectral properties were identical to those previously reported.¹¹

6-Methylbenzo[e]acephenanthrylene (10). Compound **9** (98.5 mg, 0.25 mmol) was allowed to react under our standard reaction conditions at 110 °C for 2 d. The reaction mixture was chromatographed using 50:1 hexane/EtOAc to afford 37.2 mg (56 %) of the indicated compound **10** as a white solid: mp 149-151 °C; ¹H NMR (CDCl₃) δ 2.50 (s, 3H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.59-7.80 (m, 5H), 7.91 (d, *J* = 7.2 Hz, 1H), 8.01-8.02 (m, 1H), 8.17 (s, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (CDCl₃) δ 21.9, 119.2, 121.2, 121.3, 121.3, 122.8, 123.2, 126.8, 127.0, 127.6, 128.3, 129.0, 130.2, 130.8, 132.4, 134.1, 135.3, 137.2, 137.5, 138.2, 138.9; IR (CH₂Cl₂) 2921, 2852, 1460, 1600, 1374 cm⁻¹; HRMS *m/z* 266.1099 (calcd for C₂₁H₁₄, 266.1096).

11-Phenyl-6H-isoindolo[2,1-a]indole (12). Compound **11** (103 mg, 0.25 mmol) was allowed to react under our standard reaction conditions for 1 d and afforded a 92 % yield of the indicated compound **12**, which is unstable on silica gel, as determined by ¹H NMR spectroscopy. To obtain pure compound **12**, the crude product was recrystallized (hexane/EtOAc) to afford a pale purple solid: mp 148-151 °C; ¹H NMR (DMSO-*d*₆) δ 5.27 (s, 2H), 7.09-7.13 (m, 1H), 7.21-7.25 (m, 1H), 7.36-7.39 (m, 3H), 7.51-7.58 (m, 3H), 7.63-7.65 (m, 1H), 7.68-7.70 (m, 3H), 7.74-7.76 (m, 1H); ¹³C NMR (DMSO-*d*₆) δ 48.2, 108.0, 110.2, 119.5, 120.0, 120.2, 122.0, 124.2, 126.2, 127.6, 128.0, 128.7, 128.9, 130.4, 131.9, 133.5, 134.4, 139.3, 142.7; IR (CH₂Cl₂) 3053, 2985, 1616, 1603, 1497 cm⁻¹; HRMS *m/z* 281.1209 (calcd for C₂₁H₁₅N, 281.1205).

9-Phenyl-7,8-dihydro-6H-benzo[c]pyrido[1,2,3-*lm*]carbazole (14). Compound **13** (116 mg, 0.25 mmol) was allowed to react under our standard reaction conditions for 12 h. The reaction mixture was chromatographed using 20:1 hexane/EtOAc to afford 54 mg (65 %) of the indicated compound **14** as a yellow solid: mp 239-241 °C; ^1H NMR (CDCl_3) δ 2.21-2.29 (m, 2H), 2.87 (t, $J = 6.0$ Hz, 2H), 4.31 (t, $J = 5.7$ Hz, 2H), 7.28-7.34 (m, 1H), 7.35-7.55 (m, 8H), 7.61-7.65 (m, 2H), 8.58 (d, $J = 7.8$ Hz, 1H), 8.74-8.77 (m, 1H); ^{13}C NMR (CDCl_3) δ 22.8, 24.8, 41.3, 109.1, 112.5, 119.9, 121.1, 122.3, 122.6, 123.2, 123.7, 123.9, 125.9, 127.4, 127.9, 128.5, 129.1, 129.2, 130.8, 135.3, 135.7, 139.1, 139.2; IR (CH_2Cl_2) 3053, 2986, 1421, 1265 cm^{-1} ; HRMS m/z 333.1523 (calcd for $\text{C}_{25}\text{H}_{19}\text{N}$, 333.1518). Anal. Calcd for $\text{C}_{25}\text{H}_{19}\text{N}$: C, 90.06; H, 5.74; N, 4.20. Found: C, 90.27; H, 5.44; N, 4.17.

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