SUPPORTING INFORMATION

A Flexible Synthesis of Phenanthrenes by a PtCl_2 Catalyzed Cycloisomerization Reaction

Alois Fürstner, and Victor Mamane*

Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany

fuerstner@mpi-muelheim.mpg.de

General. All reactions were carried out under Ar. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O , DME (Mg-anthracene), CH_2Cl_2 (P_4O_{10}), MeCN, Et_3N , pyridine, DMF (CaH_2), MeOH, EtOH (Mg), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a DPX 300, AV 400 or DMX 600 spectrometer (Bruker) in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1} . MS (EI): Finnigan MAT 8200 (70 eV), HRMS: Finnigan MAT 95. Melting points: Büchi melting point apparatus (uncorrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Lancaster, Fluka, Aldrich) were used as received.

Preparation of the Starting Materials

Scheme S-1.

Table S-1. Preparation of *ortho*-formyl biphenyl derivatives **1** by Suzuki coupling reactions according to Scheme S-1.

Entry	Product	Method	Yield
1	 1a	A	77%
2		B	79%
3	 1b	B	76%
4		B	54%
	 1f		

5		A	94%
6		B	90%
7		A	94%
8		A	92%
9		B	71%
10		A	85%

Representative Procedure for Method A. Synthesis of 2-(3,5-Dimethylphenyl)-4,5-methylenedioxy-benzaldehyde (1j). To a solution of 2-bromo-4,5-methylenedioxy-benzaldehyde (3.44 g, 15.0 mmol) and Pd(PPh₃)₄ (520 mg, 0.45 mmol) in DME (60 mL) is added a degassed solution of 3,4-dimethylphenzeneboronic acid (2.80 g, 18.5 mmol) in EtOH (14 mL) followed by a degassed solution of Na₂CO₃ (3.18 g, 30 mmol) in H₂O (14 mL). The resulting heterogeneous mixture is refluxed overnight before it is diluted with *tert*-butyl methyl ether. The organic layer is separated, washed with brine, dried over Na₂SO₄, and evaporated. Flash chromatography of the crude product (hexanes/EtOAc, 9/1) affords the title aldehyde **1j** as a white solid (3.50 g, 92%). Mp = 80-81°C; ¹H NMR (400 MHz, CDCl₃) δ

2.34 (s, 6H), 6.03 (s, 2H), 6.79 (s, 1H), 6.91 (s, 2H), 7.03 (s, 1H), 7.42 (s, 2H), 9.74 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.9, 101.7, 105.7, 109.8, 127.7, 128.1, 129.3, 137.1, 137.6, 143.6, 147.2, 151.6, 190.4. MS (EI) m/z 254 ($[\text{M}^+]$, 90), 239 (100), 226 (21), 152 (23). IR (KBr) 3080, 3008, 2915, 2871, 2786, 1675, 1615, 1501, 1480, 1249, 1035, 933, 870, 843 cm^{-1} . Anal. *calcd.* for $\text{C}_{16}\text{H}_{14}\text{O}_3$ (254.29): C, 75.58; H, 5.55; *found* C, 75.43; H 5.61.

Representative Procedure for Method B. Synthesis of 2-(3-Methoxyphenyl)benzaldehyde

(1h). To a degassed solution containing 3-bromoanisole (380 μL , 3.0 mmol), 2-formylbenzeneboronic acid (500 mg, 3.34 mmol) and CsF (1.27 g, 8.35 mmol) in DME (15 mL) is added $\text{Pd}(\text{PPh}_3)_4$ (135 mg, 0.12 mmol) and the resulting mixture is refluxed overnight. For work-up, EtOAc and water are added, the aqueous layer is repeatedly extracted with EtOAc, the combined organic layers are dried over Na_2SO_4 and evaporated. Flash chromatography of the residue (hexanes/EtOAc, 9/1) affords compound **1h** as a colorless syrup (570 mg, 90%). ^1H NMR (400 MHz, CDCl_3) δ 3.88 (s, 3H), 6.98 (m, 3H), 7.38 (t, J = 7.8 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.52 (d, J = 0.7 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 8.05 (d, J = 0.9 Hz, 1H), 10.02 (d, J = 0.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.0, 113.3, 115.3, 122.4, 127.1, 127.5, 128.1, 129.0, 129.7, 130.2, 133.1, 133.5, 138.8, 145.5, 159.2, 192.0. MS (EI) m/z 212 ($[\text{M}^+]$, 100), 184 (78), 154 (33), 141 (34), 115 (24). IR (KAP) 3062, 3002, 2938, 2837, 2752, 1693, 1597, 1581, 1567, 1494, 1473, 1220, 1213, 823, 764, 703 cm^{-1} . Anal. *calcd.* for $\text{C}_{12}\text{H}_{12}\text{O}_2$ (212.25): C, 79.23; H, 5.70; *found* C, 79.15; H, 5.63.

The other aldehydes shown in Table S-1 were prepared analogously. Their analytical and spectroscopic data are compiled below:

2-(3,5-Dimethoxyphenyl)benzaldehyde (1a). ^1H NMR (400 MHz, CDCl_3) δ 3.84 (s, 6H), 6.53 (d, J = 2.2 Hz, 2H), 6.56 (t, J = 2.2 Hz, 1H), 7.46 (dt, J = 7.5, 0.8 Hz, 1H), 7.52 (dd, J = 7.5, 0.9 Hz, 1H), 7.64 (dt, J = 7.5, 1.4 Hz, 1H), 8.05 (dd, J = 7.7, 1.2 Hz, 1H), 10.03 (d, J = 0.7 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.1, 99.7, 108.1, 127.0, 127.5, 130.0, 132.0, 133.1, 133.5, 139.5, 145.6, 160.3, 192.0. MS (EI) m/z 242 ($[\text{M}^+]$, 95), 214 (100), 185 (32), 139 (20), 128 (25). IR (KAP) 3063, 3001, 2960, 2938, 2839, 2759, 1693, 1593, 1568, 1458, 1420, 1217, 1205, 1156, 838, 822, 767 cm^{-1} . Anal. *calcd.* for $\text{C}_{15}\text{H}_{14}\text{O}_3$ (242.28): C, 74.36; H, 5.82; *found* C, 74.18; H, 5.90.

2-(3,5-Dimethylphenyl)benzaldehyde (1b). Mp 55-56°C. ^1H NMR (400 MHz, CDCl_3) δ 2.41 (s, 6H), 7.02 (s, 2H), 7.48 (m, 2H), 7.64 (dt, J = 7.5, 1.3 Hz, 1H), 8.04 (dd, J = 7.8, 1.2 Hz, 1H), 10.02 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.9, 127.0, 127.2, 127.7, 129.3, 130.3, 133.0, 133.4, 137.3, 137.6, 146.0, 192.3. MS (EI) m/z 210 ($[\text{M}^+]$, 85), 195 (100), 182

(31), 167 (60), 152 (22). IR (KBr) 3060, 3030, 2916, 2855, 2753, 1689, 1596, 1457, 1392, 1376, 848, 768 cm^{-1} . Anal. *calcd.* for $\text{C}_{15}\text{H}_{14}\text{O}$ (210.28): C, 85.68; H, 6.71; *found* C, 85.72; H, 6.68.

2-(2-Methoxyphenyl)benzaldehyde (1i). ^1H NMR (300 MHz, CDCl_3) δ 3.73 (s, 3H), 6.97 (d, $J = 8.2$ Hz, 1H), 7.08 (t, $J = 7.5$ Hz, 1H), 7.26 (dd, $J = 7.3, 1.6$ Hz, 1H), 7.40 (m, 4H), 7.63 (t, $J = 7.6$ Hz, 1H), 7.99 (dd, $J = 7.7, 0.9$ Hz, 1H), 9.71 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 55.8, 111.0, 121.4, 121.7, 127.0, 128.1, 130.4, 131.6, 131.8, 134.1, 134.4, 142.2, 156.7, 193.0. MS (EI) m/z 212 ($[\text{M}^+]$, 55), 181 (100), 169 (15), 139 (16), 115 (17). IR (KBr) 3060, 3017, 2963, 2934, 2837, 2750, 1693, 1593, 1496, 1477, 1461, 1453, 1431, 1230, 762 cm^{-1} . Anal. *calcd.* for $\text{C}_{12}\text{H}_{12}\text{O}_2$ (212.25): C, 79.23; H, 5.70; *found* C, 79.15; H, 5.81.

2-Naphtylbenzaldehyde (1f). Prepared as described in ref.¹

2-(2-Thienyl)benzaldehyde (1k).² ^1H NMR (300 MHz, CDCl_3) δ 7.00 (dd, $J = 3.6, 1.1$ Hz, 1H), 7.08 (dd, $J = 5, 3.5$ Hz, 1H), 7.35-7.60 (m, 3H), 7.93 (dd, $J = 7.6, 1$ Hz, 1H), 10.12 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 127.7, 128.1, 128.2, 128.6, 130.0, 131.7, 133.9, 134.6, 138.4, 139.2, 192.5.

2-(2-Formyl-phenyl)-pyrrole-1-carboxylic acid tert-butyl ester (1l). ^1H NMR (300 MHz, CD_2Cl_2) δ 1.30 (s, 9H), 6.27 (dd, $J = 3, 1.8$ Hz, 1H), 6.34 (t, $J = 3$ Hz, 1H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.48 (dd, $J = 3.1, 1.7$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.62 (dd, $J = 7.5, 1.4$ Hz, 1H), 7.95 (d, $J = 7.7$ Hz, 1H), 9.92 (s, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 28.0, 84.8, 111.3, 117.3, 123.3, 127.9, 128.9, 130.6, 132.3, 133.7, 136.2, 138.5, 149.7, 192.5. MS (EI) m/z 271 ($[\text{M}^+]$, 15), 215 (20), 171 (38), 143 (86), 115 (23), 57 (100). IR (KAP) 3153, 3064, 2981, 2934, 2832, 2746, 1744, 1698, 1600, 1576, 1497, 1477, 1459, 1338, 1313, 1149, 770, 733 cm^{-1} . Anal. *calcd.* for $\text{C}_{16}\text{H}_{17}\text{NO}_3$ (271.32): C, 70.83; H, 6.32; N, 5.16; *found* C, 70.93; H, 6.39; N, 5.22.

Scheme S-2

¹ Kumar, S. *Synthesis* **2001**, 841-844.

² O'Shea, D. F.; Sharp, J. T. *J. Chem. Soc., Perkin Trans. I* **1996**, 515-518.

1-Phenyl-3,4-dihydro-naphthalene-2-carbaldehyde (1g).³ A suspension of 1-chloro-3,4-dihydro-naphthalene-2-carbaldehyde (920 mg, 4.78 mmol),⁴ phenyl boronic acid (640 mg, 5.26 mmol), tetrabutylammonium bromide (1.54 g, 4.78 mmol), Pd(OAc)₂ (21.5 mg, 0.096 mmol) and potassium carbonate (1.2 g, 11.95 mmol) in degassed water (10 mL) is vigorously stirred for 3h at 45°C. After cooling, the mixture is diluted with water (30 mL), the aqueous phase is repeatedly extracted with ethyl acetate, the combined organic layers are dried over Na₂SO₄ and evaporated, and the crude product is purified by flash chromatography (SiO₂, CH₂Cl₂) to give product **1g** as a yellow solid (1.0 g, 90%). ¹H NMR (400 MHz, CDCl₃) δ 2.62 (t, J = 7.5 Hz, 2H), 2.85 (t, J = 7.5 Hz, 2H), 6.78 (d, J = 7.8 Hz, 1H), 7.06 (dt, J = 8.7, 1.7 Hz, 1H), 7.21 (m, 4H), 7.40 (m, 3H), 9.50 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 19.9, 27.3, 126.3, 127.5, 127.9, 128.1, 129.8, 130.1, 130.8, 134.0, 134.8, 134.9, 138.3, 154.0, 193.0.

Scheme S-3

³ Hesse, S. ; Kirch, G. *Synthesis* **2001**, 755-758.

⁴ Bussenius, J. ; Laber, N. ; Müller, T. ; Eberbach, W. *Chem. Ber.* **1994**, 127, 247-259.

Table S-2. Preparation of *ortho*-alkynylated biphenyl derivatives according to Scheme S-3.

Entry	Substrate	Method	X ⁺	Product	Yield
1	1a	B	H ₂ O	2a	69%
2	1b	A	H ₂ O	2b	81% ^a
3		B	H ₂ O		70%
4	1b	A	MeI	2c	80% ^a
5	1b	A	ClCOOMe	2d	83% ^a
6	1f	B	H ₂ O	2f	71%
7	1g	B	H ₂ O	2g	84%

8	1h	A	H ₂ O	2h	73% ^a
9	1i	B	H ₂ O	2i	95%
10	1j	A	Me ₂ SO ₄	2j	73%
11	1k	B	H ₂ O	2k	44%
12	1m	B	H ₂ O	2l	36% ^b
13	1m	A	Me ₂ SO ₄	2m	35% ^b

^a Refers to isolated yield over both steps. ^b Refers to the overall yield for alkyne formation/trapping and subsequent N-deprotection with NaOMe in THF.

Representative Procedure for Method A. Synthesis of 2-Ethynyl-3',5'-dimethylbiphenyl (2b). CBr₄ (3.30 g, 10 mmol) is added to a solution of PPh₃ (4.50 g, 20.0 mmol) in CH₂Cl₂ (60 mL) and the resulting yellow mixture is stirred for 10 min at 0°C. A solution of aldehyde **1b** (840 mg, 4.0 mmol) in CH₂Cl₂ (40 mL) is slowly introduced and stirring is continued for

1h at that temperature. The reaction is then quenched with brine, the aqueous layer is repeatedly extracted with CH₂Cl₂, the combined organic phases are dried (Na₂SO₄) and evaporated, and the residue is purified by flash chromatography (hexanes/EtOAc, 95/5) to give 2'-(2,2-dibromo-vinyl)-3,5-dimethyl-biphenyl as a yellow syrup (1.40 g, quant.) which exhibits the following spectroscopic properties: ¹H NMR (400 MHz, CDCl₃) δ 2.39 (s, 6H), 6.96 (s, 2H), 7.03 (s, 1H), 7.24 (s, 1H), 7.38 (m, 3H), 7.69 (dd, J = 5.2, 2.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.0, 90.0, 126.5, 127.0, 128.2, 128.7, 128.8, 129.4, 133.4, 137.4, 139.7, 141.0. MS (EI) *m/z* 366 ([M⁺], 1), 285 (10), 206 (100), 191 (20). IR (KAP) 3060, 3023, 2946, 2916, 2858, 1602, 1469, 1447, 851, 758.

n-BuLi (1.6 M in THF, 2.35 mL, 3.75 mmol) is added to a solution of the dibromide described above (531 mg, 1.50 mmol) in THF (8 mL) at –78°C and stirring is continued at that temperature for 5h. The cold mixture is then quenched with water, the aqueous phase is repeatedly extracted with *tert*-butyl methyl ether, the combined organic layers are dried over Na₂SO₄ and evaporated, and the crude product is purified by flash chromatography (hexanes/EtOAc, 98/2) to give alkyne **2b** as a colorless syrup (250 mg, 81%). ¹H NMR (400 MHz, CDCl₃) δ 2.39 (s, 6H), 3.05 (s, 1H), 7.03 (s, 1H), 7.22 (s, 2H), 7.29 (m, 1H), 7.38 (m, 2H), 7.61 (d, 1H, J = 7.3 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 20.9, 79.6, 82.6, 120.0, 126.4, 126.7, 128.5, 128.8, 129.2, 133.4, 137.0, 139.8, 144.3. MS (EI) *m/z* 206 ([M⁺], 100), 191 (95), 165 (14). IR (KAP) 3284, 3060, 3026, 2917, 2859, 2105, 1602, 1482, 1470, 1443, 1376, 851, 760, 649, 600 cm^{–1}. Anal. *calcd.* for C₁₆H₁₄ (206.29): C, 93.16; H, 6.84; *found* C, 92.97; H, 6.90.

Representative Procedure for Method B. Synthesis of 2-Ethynyl-3',5'-dimethoxybiphenyl (2a). *n*-BuLi (1.6 M in THF, 3.1 mL, 5.0 mmol) is added to a solution of diisopropylamine (753 μL, 5.37 mmol) at 0°C. After stirring for 10 min, the resulting solution of LDA is cooled to –78°C before a solution of Me₃SiCHN₂ (2 M in hexane, 2.5 mL, 5.0 mmol) is added dropwise and stirring is continued for 30 min at that temperature. A solution of aldehyde **1a** (1.00 g, 4.13 mmol) in THF (5 mL) is then slowly added and the resulting mixture is allowed to warm to ambient temperature over a period of 3 h. Quenching of the reaction with water, repeated extraction of the aqueous phase with *tert*-butyl methyl ether, drying of the combined organic phases over Na₂SO₄, evaporation of the solvent and flash chromatography of the residue (hexanes/EtOAc, 95/5) affords alkyne **2a** as a colorless syrup (680 mg, 69%). ¹H NMR (400 MHz, CDCl₃) δ 3.09 (s, 1H), 3.84 (s, 6H), 6.40 (t, J = 2.3 Hz, 1H), 6.76 (d, J = 2.3 Hz, 2H), 7.32 (m, 1H), 7.40 (m, 2H), 7.62 (d, J = 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 55.0, 80.1, 82.7, 99.6, 107.1, 120.0, 126.8, 128.5, 129.1, 133.6, 141.8,

144.0, 160.0. MS (EI) m/z 238 ($[M^+]$, 100), 223 (49), 207 (16), 195 (39), 180 (29), 165 (54), 152 (55). IR (KAP) 3280, 3063, 3001, 2958, 2937, 2836, 2104, 1594, 1457, 1418, 1204, 1154, 838, 761, 652, 629 cm^{-1} . Anal. *calcd.* for $\text{C}_{16}\text{H}_{14}\text{O}_2$ (238.29): C, 80.65; H, 5.92; *found* C, 80.48; H, 5.97.

All other alkynes shown in Table S-2 were prepared analogously. Their analytical and spectroscopic data are compiled below:

3,5-Dimethyl-2'-prop-1-ynyl-biphenyl (2c). ^1H NMR (400 MHz, CDCl_3) δ 1.96 (s, 3H), 2.39 (s, 6H), 7.01 (s, 1H), 7.20-7.28 (m, 3H), 7.30-7.37 (m, 1H), 7.50 (dd, $J = 7.5, 0.9$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 3.6, 20.6, 78.6, 87.9, 121.4, 126.3, 126.7, 127.3, 128.5, 129.0, 132.7, 139.8, 142.8. MS (EI) m/z 220 ($[M^+]$, 70), 205 (100), 189 (21), 179 (20). IR (KAP) 3059, 3025, 2951, 2915, 2856, 2731, 2229, 1603, 1563, 1485, 1470, 1443, 1376, 850, 759, 702 cm^{-1} . Anal. *calcd.* for $\text{C}_{17}\text{H}_{16}$ (220.31): C, 92.68; H, 7.32; *found* C, 92.56; H, 7.38.

3',5'-Dimethyl-biphen-2-yl-propionic acid methyl ester (2d). ^1H NMR (400 MHz, CDCl_3) δ 2.40 (s, 6H), 3.78 (s, 3H), 7.05 (s, 1H), 7.23 (s, 2H), 7.34 (dt, $J = 7.5, 1.5$ Hz, 1H), 7.48 (m, 2H), 7.66 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.5, 51.5, 82.9, 85.7, 116.9, 125.9, 126.0, 128.6, 128.65, 129.7, 133.5, 136.7, 138.1, 144.9, 153.4. MS (EI) m/z 264 ($[M^+]$, 67), 249 (32), 233 (73), 219 (25), 205 (100), 178 (23), 101 (20). IR (KBr) 3057, 3013, 2956, 2916, 2861, 2222, 1711, 1602, 1559, 1472, 1435, 1380, 1298, 1207, 1199, 856, 765, 702 cm^{-1} . Anal. *calcd.* for $\text{C}_{18}\text{H}_{16}\text{O}_2$ (264.32): C, 81.79; H, 6.10; *found* C, 81.89; H, 6.02.

1-Ethynyl-2-(1-naphtyl)-benzene (2f). ^1H NMR (300 MHz, CDCl_3) δ 2.78 (s, 1H), 7.35-7.75 (m; 9H), 7.91 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 80.7, 83.0, 122.8, 125.5, 126.1, 126.3, 126.5, 127.7, 127.9, 128.3, 128.5, 128.6, 128.9, 131.2, 132.3, 133.5, 138.8, 143.9. MS (EI) m/z 228 ($[M^+]$, 100), 202 (6), 113 (15), 101 (7). IR (KAP) 3287, 3060, 2106, 1590, 1505, 1481, 1439, 1393, 803, 782, 763, 644, 631 cm^{-1} . Anal. *calcd.* for $\text{C}_{18}\text{H}_{12}$ (228.30): C, 94.70; H, 5.30; *found* C, 94.58; H, 5.39.

3-Ethynyl-4-phenyl-1,2-dihydro-naphtalene (2g). ^1H NMR (400 MHz, CD_2Cl_2) δ 2.58 (t, $J = 7.5$ Hz, 2H), 2.90 (t, $J = 7.5$ Hz, 2H), 3.09 (s, 1H), 6.71 (d, $J = 7.8$ Hz, 1H), 7.04 (dt, $J = 8.7, 1.7$ Hz, 1H), 7.15 (m, 2H), 7.30-7.50 (m, 5H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 28.7, 29.8, 83.0, 85.4, 118.2, 127.0, 127.3, 128.1, 128.3, 128.5, 128.8, 130.7, 136.1, 137.1, 139.6, 146.0. MS (EI) m/z 230 ($[M^+]$, 100), 215 (52), 202 (15), 191 (11). IR (KBr) 3277, 3058, 3019, 2950, 2891, 2832, 2083, 1636, 1594, 1482, 1448, 1432, 1421, 783, 769, 754, 730, 701, 649, 621, 613 cm^{-1} . Anal. *calcd.* for $\text{C}_{18}\text{H}_{14}$ (230.31): C, 93.87; H, 6.13; *found* 93.69; H, 6.25.

2-Ethynyl-3'-methoxybiphenyl (2h). ^1H NMR (300 MHz, CDCl_3) δ 2.98 (s, 1H), 3.77 (s, 3H), 6.94 (dd, $J = 7.5, 1.1$ Hz, 1H), 7.17 (m, 2H), 7.33 (m, 2H), 7.40 (m, 2H), 7.63 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 55.7, 80.7, 83.5, 113.8, 115.2, 120.1, 123.1, 127.5, 129.4, 129.9, 134.3, 142.0, 144.6, 159.5. MS (EI) m/z 208 ($[\text{M}^+]$, 73), 193 (29), 178 (10), 165 (100), 139 (8). IR (KAP) 3283, 3062, 3000, 2956, 2935, 2834, 2104, 1604, 1581, 1471, 1421, 1218, 760, 652, 624 cm^{-1} . Anal. *calcd.* for $\text{C}_{15}\text{H}_{12}\text{O}$ (208.26): C, 86.51; H, 5.81; *found* C, 86.56; H, 5.75.

2-Ethynyl-2'-methoxybiphenyl (2i). ^1H NMR (400 MHz, CDCl_3) δ 2.92 (s, 1H), 3.78 (s, 3H), 7.01 (m, 2H), 7.25-7.45 (m, 5H), 7.59 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.6, 79.1, 83.1, 111.1, 120.3, 122.1, 126.9, 128.4, 129.1, 129.7, 130.3, 131.2, 133.0, 141.7, 156.8. MS (EI) m/z 208 ($[\text{M}^+]$, 100), 193 (23), 179 (22), 165 (90), 139 (12). IR (KAP) 3269, 3063, 3007, 2957, 2834, 2105, 1601, 1580, 1500, 1472, 1463, 1430, 1266, 1251, 1233, 760, 634 cm^{-1} . Anal. *calcd.* for $\text{C}_{15}\text{H}_{12}\text{O}$ (208.26): C, 86.51; H, 5.81; *found* C, 86.41; H, 5.79.

5-(3,5-Dimethyl-phenyl)-6-prop-1-ynyl-benzo[1,3]dioxole (2j). ^1H NMR (400 MHz, CDCl_3) δ 1.82 (s, 3H), 2.28 (s, 6H), 5.89 (s, 2H), 6.74 (s, 1H), 6.85 (s, 1H), 6.89 (s, 1H), 7.09 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 4.0, 21.0, 78.9, 86.5, 101.0, 109.2, 112.0, 115.0, 126.8, 128.3, 136.8, 138.4, 140.1, 145.9, 147.1. MS (EI) m/z 264 ($[\text{M}^+]$, 100), 249 (50), 234 (13), 219 (39), 189 (25). IR (KBr) 3008, 2915, 2229, 1596, 1505, 1486, 1415, 1381, 1365, 1238, 1035, 928, 882, 856 cm^{-1} . Anal. *calcd.* for $\text{C}_{18}\text{H}_{16}\text{O}_2$ (264.33): C, 81.79; H, 6.10; *found* C, 81.85; H, 6.03.

2-(2-Ethynyl-phenyl)-thiophene (2k).⁵ ^1H NMR (300 MHz, CDCl_3) δ 3.09 (s, 1H), 6.95 (dd, $J = 5.1, 3.7$ Hz, 1H), 7.09 (dt, $J = 7.5, 1.3$ Hz, 1H), 7.20 (m, 2H), 7.37 (dd, $J = 7.5, 1$ Hz, 1H), 7.46 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 82.0, 83.6, 120.0, 126.2, 127.4, 127.45, 127.7, 129.5, 129.6, 135.0, 136.9, 142.1.

2-(2-Ethynyl-phenyl)-1H-pyrrole (2l). ^1H NMR (400 MHz, CD_2Cl_2) δ 3.39 (s, 1H), 6.18 (dd, $J = 2.7, 1$ Hz, 1H), 6.59 (t, $J = 2.5$ Hz, 1H), 6.81 (dd, $J = 2.6, 1$ Hz, 1H), 7.07 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.27 (dt, $J = 7.6, 1.3$ Hz, 1H), 7.44 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.54 (dd, $J = 7.6, 1.2$ Hz, 1H), 9.75 (bs, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 83.5, 86.6, 110.7, 111.7, 117.8, 121.2, 127.9, 128.7, 131.8, 132.7, 136.5, 137.1. MS (EI) m/z 167 ($[\text{M}^+]$, 100), 139 (45). IR (KAP) 3433, 3280, 3105, 3062, 2960, 2924, 2098, 1596, 1483, 1463, 1449, 757, 726, 666, 621 cm^{-1} . Anal. *calcd.* for $\text{C}_{12}\text{H}_9\text{N}$ (167.21) C 86.20, H 5.42; *found* C 86.25, H 5.49.

⁵ Maeyama, K.; Iwasawa, N. *J. Org. Chem.* **1999**, *64*, 1344-1346.

2-(2-Prop-1-ynyl-phenyl)-1H-pyrrole (2m). ^1H NMR (300 MHz, CD_2Cl_2) δ 2.06 (s, 3H), 6.18 (dd, $J = 2.7$, 1 Hz, 1H), 6.55 (dd, $J = 2.7$, 1.2 Hz, 1H), 6.80 (dd, $J = 2.6$, 1.1 Hz, 1H), 7.02 (dt, $J = 7.6$, 1.2 Hz, 1H), 7.19 (dt, $J = 7.6$, 1.3 Hz, 1H), 7.34 (dd, $J = 7.7$, 1.1 Hz, 1H), 7.50 (dd, $J = 8$, 1 Hz, 1H), 9.82 (bs, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 5.1, 80.2, 90.8, 108.4, 110.0, 118.2, 119.2, 126.2, 126.9, 129.0, 133.9, 134.9. MS (EI) m/z 181 ($[\text{M}^+]$, 100), 152 (20), 77 (12). IR (KBr) 3425, 3102, 3060, 2960, 2913, 2849, 2239, 1596, 1565, 1484, 1463, 1450, 1407, 757, 723 cm^{-1} . Anal. *calcd.* for $\text{C}_{13}\text{H}_{11}\text{N}$ (181.24): C, 86.15; H, 6.12; N, 7.73; *found* C, 85.95; H, 6.20; N, 7.83.

Scheme S-4

2'-(4-Methoxy-phenylethynyl)-3,5-dimethyl-3,5-dimethyl-biphenyl (2e). CuI (9.25 mg, 0.049 mmol) is added to a solution of alkyne **2b** (250 mg, 1.214 mmol), *p*-iodoanisole (284 mg, 1.214 mmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (17 mg, 0.024 mmol) in $\text{Et}_3\text{N}/\text{DMF}$ (4/1, 2.5 mL) and the resulting mixture is heated at 45°C for 4 h. After cooling to room temperature, the reaction is quenched with a sat. aq. NH_4Cl , the aqueous layer is extracted with *tert*-butyl methyl ether, the combined organic phases are dried over Na_2SO_4 and evaporated, and the residue is purified by flash chromatography (hexanes/ EtOAc , 9/1) to give alkyne **2e** as a yellow syrup (240 mg, 63%). ^1H NMR (300 MHz, CDCl_3) δ 2.32 (s, 6H), 3.73 (s, 3H), 6.75 (d, $J = 7$ Hz, 2H), 6.96 (s, 1H), 7.20-7.40 (m, 7H), 7.53 (dd, $J = 7.2$, 1.5 Hz, 1H); MS (EI) m/z 312 ($[\text{M}^+]$, 100), 297 (67), 281 (27), 265 (24), 253 (24), 239 (20). IR (KAP) 3057, 3003, 2955, 2916, 2858, 2836, 2214, 1604, 1569, 1512, 1485, 1465, 1441, 1376, 1288, 1248, 851, 831, 759, 702 cm^{-1} . Anal. *calcd.* for $\text{C}_{23}\text{H}_{20}\text{O}$ (312.42): C, 88.43; H, 6.45; *found* C, 88.34; H, 6.57.

Scheme S-5

1-(2-Ethynyl-phenyl)-pyrrole (2n). A solution of 1-(2-bromophenyl)-pyrrole (444 mg, 2 mmol),⁶ trimethylsilylacetylene (420 μ L, 3 mmol), PdCl₂(PPh₃)₂ (70.2 mg, 0.1 mmol) and CuI (4.6 mg, 0.024 mmol) in Et₃N (10 mL) is refluxed for 16h. The mixture is allowed to cool to room temperature before it is filtered through a pad of silica, the filtrate is evaporated and the residue is chromatographed (hexanes) to give a yellow oil. To a solution of this oil in MeOH (30 mL) is added K₂CO₃ (1.4 g) and the mixture is stirred at ambient temperature for 1h. After evaporation of the solvent, the crude product is extracted with *tert*-butyl methyl ether, the combined ether phases are evaporated and the residue is purified by flash chromatography (hexanes) to give product **2n** as a yellow oil (150 mg, 45% over both steps). ¹H NMR (300 MHz, CDCl₃) δ 3.10 (s, 1H), 6.25 (t, J = 2.2 Hz, 2H), 7.03 (t, J = 2.2 Hz, 2H), 7.21 (m, 2H), 7.33 (dt, J = 7.3, 1.6 Hz, 1H), 7.53 (dd, J = 7.7 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 80.8, 82.4, 109.8, 117.3, 122.0, 125.5, 126.7, 130.2, 135.0, 143.0. MS (EI) *m/z* 167 ([M⁺], 100), 139 (22). IR (KAP) 3287, 3135, 3103, 3069, 2108, 1598, 1572, 1500, 1476, 1447, 761, 726 cm⁻¹. HRMS: *calcd.* 167.073499; *found* 167.073422; Anal. *calcd.* for C₁₂H₉N (167.21) C 86.20, H 5.42; *found* C 86.14, H 5.50.

1-(2-Oct-1-ynyl-phenyl)-pyrrole (2o). A solution of 1-(2-bromophenyl)-pyrrole (2.22 g, 5 mmol),⁶ 1-octyne (885 μ L, 6 mmol), PdCl₂(PPh₃)₂ (70 mg, 0.1 mmol) and CuI (9.5 mg, 0.5 mmol) in Et₃N (20 mL) is refluxed for 16h. The mixture is allowed to cool to ambient temperature before it is filtered through a pad of silica, the filtrate is evaporated and the residue is chromatographed (hexanes) to give product **2o** as a yellow oil (650 mg, 54%). ¹H NMR (400 MHz, CDCl₃) δ 0.82 (t, J = 6.8 Hz, 3H), 1.25 (m, 6H), 1.43 (m, 2H), 2.26 (t, J = 7 Hz), 6.21 (t, J = 2.2 Hz, 2H), 7.01 (t, J = 2.2 Hz), 7.12 (dt, J = 7.5, 1.6 Hz, 1H), 7.19 (m, 2H), 7.42 (dd, J = 7.7, 1.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.7, 19.2, 22.2, 28.0, 28.2, 31.0, 77.0, 95.1, 108.6, 118.5, 121.2, 124.5, 125.7, 128.0, 133.5, 141.6. MS (EI) *m/z* 251 ([M⁺], 21), 208 (11), 194 (27), 181 (100), 167 (12), 154 (12). IR (KAP) 2955, 2926, 2854, 2229, 1501, 1447, 1380, 758, 724 cm⁻¹. Anal. *calcd.* for C₁₈H₂₁N (251.37) C 86.01, H 8.42; *found* C 86.20, H 8.31.

⁶ Cheeseman, G. W.H.; Greenberg, S. G. *J. Organomet. Chem* **1979**, 166, 139-152.

Spectroscopic and Analytical Data of the Phenanthrenes and Heterocyclic Congeners

1,3-Dimethoxy-phenanthrene (3a).⁷ ¹H NMR (400 MHz, CDCl₃) δ 3.94 (s, 3H), 3.96 (s, 3H), 6.60 (d, J = 2.1 Hz, 1H), 7.45-7.60 (m, 4H), 7.80 (dd, J = 9.2, 1.9 Hz, 1H), 8.06 (d, J = 9 Hz, 1H), 8.50 (d, J = 7.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 55.9, 56.1, 95.7, 98.1, 118.9, 120.7, 123.5, 124.0, 126.3, 127.0, 129.0, 130.0, 132.6, 133.2, 157.5, 159.4. MS (EI) *m/z* 238 ([M⁺], 100), 223 (8), 195 (24), 180 (14), 163 (6), 152 (22). IR (KBr) 3050, 3000, 2958, 2936, 2834, 1619, 1601, 1579, 1521, 1505, 1466, 1454, 1424, 1403, 1269, 1153, 815, 750 cm⁻¹.

3,5-Dimethylphenanthrene (3b).⁸ ¹H NMR (400 MHz, CDCl₃) δ 2.66 (s, 3H), 2.79 (s, 3H), 7.36 (s, 1H), 7.60-7.75 (m, 2H), 7.78 (d, J = 9.1 Hz, 1H), 7.96 (m, 2H), 8.45 (s, 1H), 8.76 (d, J = 8.3 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 19.5, 21.7, 120.3, 122.4, 122.6, 125.4, 125.9, 126.0, 128.1, 128.5, 129.3, 130.1, 131.6, 134.3, 135.1, 135.4. MS (EI) *m/z* 206 ([M⁺], 100), 223 (18), 191 (42). IR (KBr) 3047, 3007, 2962, 2918, 2853, 1616, 1604, 1504, 1462, 1425, 1377, 858, 817, 754 cm⁻¹.

1,3,10-Trimethylphenanthrene (3c). ¹H NMR (400 MHz, CDCl₃) δ 2.58 (s, 3H), 2.99 (s, 6H), 7.27 (s, 1H), 7.48 (s, 1H), 7.56 (m, 2H), 7.76 (dd, J = 7.8, 1.5 Hz, 1H), 8.45 (s, 1H), 8.63 (dd, J = 7.8, 1.5 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 21.1, 25.7, 26.3, 114.0, 121.2, 122.5, 125.2, 126.0, 126.9, 128.1, 129.5, 131.4, 131.4, 132.3, 133.3, 134.7, 135.4. MS (EI) *m/z* 220 ([M⁺], 100), 205 (40), 189 (11). IR (KBr) 3042, 2970, 2911, 2855, 1613, 1600, 1571, 1494, 1462, 1450, 1439, 876, 751 cm⁻¹. Anal. *calcd.* for C₁₇H₁₆ (220.32): C, 92.68; H, 7.32; *found* C, 92.47; H, 7.28.

Benzo[c]phenanthrene (3f).⁹ ¹H NMR (400 MHz, CDCl₃) δ 7.52 (dt, J = 7, 1 Hz, 2H), 7.59 (dt, J = 6.9, 1.5 Hz, 2H), 7.72 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 7.92 (dd, J = 7.9, 1.4 Hz, 2H), 9.04 (d, J = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 125.5, 125.8, 126.5,

⁷ Ramana, M. M. V.; Potnis, P. V. *Synthesis* **1996**, 1090-1092.

⁸ (a) Regnault, A.; Canonne, P. *Tetrahedron* **1969**, 25, 2349-2365. (b) Shahidi, F.; Farrell, P. G.; Edward, J. T.; Canonne, P. *J. Org. Chem.* **1979**, 44, 950-953.

⁹ Sayer, J. M.; van Bladeren, P. J.; Yeh, H. J. C.; Jerina, D. M. *J. Org. Chem.* **1986**, 51, 452-456.

127.1, 127.6, 128.2, 131.8, 132.4, 135.0. MS (EI) m/z 228 ($[M^+]$, 100), 113 (25). IR (KBr) 3049, 3008, 1600, 1519, 1495, 833, 746 cm^{-1} .

5,6-Dihydro-benzo[c]phenanthrene (3g).¹⁰ ^1H NMR (300 MHz, CDCl_3) δ 2.74 (m, 2H), 2.82 (m, 2H), 7.19 (t, $J = 7.3$ Hz, 1H), 7.25 (m, 2H), 7.37 (m, 2H), 7.64 (d, $J = 8.2$ Hz, 1H), 7.78 (d, $J = 7.8$ Hz, 1H), 7.85 (d, $J = 7.8$ Hz, 1H), 8.46 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 29.1, 30.2, 124.5, 125.2, 125.6, 125.7, 126.1, 126.5, 127.2, 127.4, 128.25, 128.3, 129.7, 131.3, 133.5, 133.8, 136.8, 139.3. MS (EI) m/z 230 (M^+ , 100), 215 (18), 202 (8). IR (KAP) 3050, 2937, 2892, 2834, 1619, 1594, 1510, 1485, 1448, 1428, 1381, 813, 791, 757, 737 cm^{-1} .

3-Methoxyphenanthrene (para-3h).^{7,11,12} ^1H NMR (400 MHz, CDCl_3) δ 3.95 (s, 3H), 7.18 (dd, $J = 8.6, 2.1$ Hz, 1H), 7.45-7.60 (m, 3H), 7.61 (d, $J = 8.8$ Hz, 1H), 7.73 (d, $J = 8.7$ Hz, 1H), 7.80 (dd, $J = 9.2, 7.7$ Hz, 1H), 7.99 (d, $J = 2.4$ Hz, 1H), 8.53 (d, $J = 7.6$, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.1, 103.7, 116.3, 122.3, 124.2, 125.7, 126.2, 126.25, 126.4, 128.2, 129.6, 131.3, 132.1, 133.2, 158.1. MS (EI) m/z 208 ($[M^+]$, 100), 193 (24), 165 (60). IR (KBr) 3070, 3008, 2964, 2929, 2831, 1619, 1602, 1507, 1455, 1438, 1425, 1224, 843, 745 cm^{-1} .

1-Methoxyphenanthrene (ortho-3h).¹² ^1H NMR (400 MHz, CDCl_3) δ 3.97 (s, 3H), 6.94 (d, $J = 7.8$ Hz, 1H), 7.45-7.60 (m, 3H), 7.67 (d, $J = 9.1$ Hz, 1H), 7.82 (dd, $J = 7.6, 1.4$ Hz, 1H), 8.16 (d, $J = 9.2$ Hz, 1H), 8.20 (d, $J = 8.5$ Hz, 1H), 8.59 (d, $J = 8.2$, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 56.1, 106.2, 115.4, 120.7, 123.5, 123.6, 126.4, 126.7, 126.9, 127.0, 128.9, 130.4, 131.9, 132.6, 156.3. MS (EI) m/z 208 ($[M^+]$, 100), 193 (39), 165 (64). IR (KBr) 3051, 3001, 2956, 2935, 2831, 1620, 1608, 1597, 1522, 1463, 1434, 1253, 803, 754 cm^{-1} .

4-Methoxyphenanthrene (3i).¹³ ^1H NMR (400 MHz, CDCl_3) δ 4.07 (s, 3H), 7.09 (d, $J = 9.1$, 1H), 7.40-7.70 (m, 6H), 7.80 (dd, $J = 7.7, 1.6$ Hz), 9.59 (dd, $J = 8.6, 0.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 55.4, 108.0, 120.5, 121.2, 125.5, 126.0, 126.1, 126.7, 127.6, 127.9, 128.2, 130.0, 132.4, 134.3, 158.5. MS (EI) m/z 208 ($[M^+]$, 100), 193 (27), 165 (55). IR (KBr) 3138,

¹⁰ Lapouyade, R. ; Veyres, A. ; Hanafi, N. ; Couture, A. ; Lablache-Combier, A. *J. Org. Chem.* **1982**, 47, 1361-1364.

¹¹ Eirín, A.; Fernández, F.; González, C.; López, C. *Org. Prep. Proced. Int.* **1992**, 24, 509-516.

¹² Brown, C.; Sikkell, B. J.; Carvalho, C. F.; Sargent, M. V. *J. Chem. Soc., Perkin Trans. I* **1982**, 3007-3010.

¹³ (a) Mallory, F. B.; Rudolph, M. J.; Oh, S. M. *J. Org. Chem.* **1989**, 54, 4619-4626. (b) Fu, J.; Snieckus, V. *Can. J. Chem.* **2000**, 78, 905-919.

3048, 2995, 2962, 2939, 2835, 1609, 1598, 1569, 1449, 1431, 1417, 1245, 823, 739, 713 cm^{-1} .

Naphtho[1,2-*b*]thiophene (3k).⁵ ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, J = 5.3 Hz, 1H), 7.50 (dt, J = 4.1, 1.3 Hz, 2H), 7.55 (dd, J = 8, 1.2 Hz, 1H), 7.72 (d, J = 8.6 Hz, 1H), 7.92 (dd, J = 8.5, 1 Hz, 1H), 8.13 (dd, J = 8.1, 7.6 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 122.0, 123.6, 125.0, 125.1, 125.3, 125.6, 126.6, 128.8, 129.1, 130.8, 137.39, 137.42.

1-*H*-Benzo[*g*]indole (3l).¹⁴ ^1H NMR (400 MHz, CD_2Cl_2) δ 6.60 (dd, J = 3, 2 Hz, 1H), 7.22 (t, J = 2.8 Hz, 1H), 7.35 (dt, J = 7, 1.2 Hz, 1H), 7.44 (m, 2H), 7.83 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 8.93 (bs, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 104.9, 120.1, 121.3, 121.5, 122.5, 123.1, 124.6, 126.2, 126.4, 129.5, 131.1, 131.2. MS (EI) m/z 167 ($[\text{M}^+]$, 100), 139 (22). IR (KBr) 3414, 3428, 3065, 3045, 2960, 2925, 2852, 1623, 1594, 1568, 1528, 1494, 1469, 1450, 811, 721, 688 cm^{-1} .

4-Methyl-1*H*-benzo[*g*]indole (3m). ^1H NMR (400 MHz, CD_2Cl_2) δ 2.56 (s, 3H), 6.34 (dd, J = 3, 2.2 Hz, 1H), 7.20 (s, 1H), 7.23 (t, J = 2.8 Hz, 1H), 7.31 (dt, J = 6.9, 1.2 Hz, 1H), 7.39 (dt, J = 7, 1.3 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 8.95 (bs, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 19.7, 103.3, 120.0, 120.1, 121.4, 122.8, 124.6, 125.3, 125.5, 128.8, 131.0, 131.7. MS (EI) m/z 181 ($[\text{M}^+]$, 100), 152 (15), 90 (10), 77 (10). IR (KBr) 3418, 3048, 2982, 2935, 2912, 2850, 1570, 1531, 1497, 1433, 1382, 744, 729, 699 cm^{-1} . Anal. *calcd.* for $\text{C}_{13}\text{H}_{11}\text{N}$ (181.24): C, 86.15; H, 6.12; N, 7.73; *found* C, 86.07; H, 6.11; N, 7.63.

Pyrrolo[1,2-*a*]quinoline (3n).¹⁵ ^1H NMR (400 MHz, CD_2Cl_2) δ 6.41 (dd, J = 3.7, 1.3 Hz, 1H), 6.67 (dd, J = 3.6, 3 Hz, 1H), 6.88 (d, J = 9.3 Hz, 1H), 7.22 (dt, J = 7.9, 1 Hz, 2H), 7.40 (dt, 8.5, 1.5 Hz, 1H), 7.54 (dd, J = 7.8, 1.3 Hz, 1H), 7.75 (d, J = 1.5 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 103.5, 112.7, 113.4, 114.9, 119.3, 119.6, 124.3, 124.6, 128.5, 129.3, 131.8, 134.2. MS (EI) m/z 167 (M^+ , 100), 139 (12). IR (KBr) 3146, 3104, 3052, 2956, 2925, 2853, 1605, 1551, 1508, 1486, 1448, 1421, 801, 751, 702 cm^{-1} .

4-Hexyl-pyrrolo[1,2-*a*]quinoline (3o). ^1H NMR (400 MHz, CDCl_3) δ 0.84 (t, J = 6.8 Hz, 3H), 1.28 (m, 4H), 1.39 (m, 2H), 1.70 (m, 2H), 2.71 (t, J = 7.4 Hz, 2H), 6.48 (bs, 1H), 6.71 (s, 1H), 6.74 (s, 1H), 7.20 (dd, J = 7.9, 1 Hz, 1H), 7.36 (dt, J = 7.2, 1.4 Hz, 1H), 7.52 (dd, J = 7.8, 1.4 Hz), 7.77 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 22.3, 28.4, 29.0, 31.4,

¹⁴ Baudin, J.-B.; Julia, S. A.; Ruel, O. *Tetrahedron* **1987**, *43*, 881-889.

¹⁵ (a) Heffernan, M. L.; Irvine, G. M. *Aust. J. Chem.* **1976**, *29*, 799-814. (b) Jones, A. J.; Hanisch, P.; Heffernan, M. L.; Irvine, G. M. *Aust. J. Chem.* **1980**, *33*, 499-508.

32.1, 100.6, 111.7, 111.9, 113.6, 116.0, 123.0, 124.0, 126.4, 127.6, 131.1, 132.1. MS (EI) m/z 251 [M^+], 65), 208 (9), 194 (20), 181 (100). IR (KAP) 3142, 3101, 2955, 2923, 2852, 1540, 1487, 1455, 1422, 1385, 835, 753, 736, 700 cm^{-1} . Anal. *calcd.* for $\text{C}_{18}\text{H}_{21}\text{N}$ (251.37) C 86.01, H 8.42, N 5.57; *found* C 85.91, H 8.36, N 5.53.