Direct Intramolecular Arylation of Aldehydes Promoted by Reaction with IPy$_2$BF$_4$/HBF$_4$: Synthesis of Benzocyclic Ketones

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Experimental procedures and spectral and analytical data for all products.

**General:** All reactions were carried out under an atmosphere of dry N$_2$ using oven-dried glassware and syringes. Dichloromethane was dried by refluxing over P$_2$O$_5$ and distilled under a nitrogen atmosphere. Hexane and EtOAc were obtained from commercial suppliers. IPy$_2$BF$_4$ is commercially available (see Galchimia, NovaBiochem or Aldrich catalogues). TLC was performed on aluminum-backed plates coated with silica gel 60 with F$_{254}$ indicator (Scharlau). Flash column chromatography was carried out on silica gel 60, 230-240 mesh. $^1$H NMR (200, 300, 400 MHz) and $^{13}$C NMR (50.5, 75.5, 100 MHz) spectra were measured at room temperature on Bruker AC-200, AV-300 and AMX-400 instruments, respectively, with tetramethylsilane ($\delta = 0.0$, $^1$H NMR) or CDCl$_3$ ($\delta = 77.00$, $^{13}$C NMR) as internal standard. Carbon multiplicities were assigned by DEPT techniques. Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV on a HP 5987 A, and the intensities are reported as a percentage relative to the base peak after the corresponding m/z value. High-resolution mass spectra (HRMS) were determined on a Finnigan MAT 95 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 2400 and Carlo Erba 1108 microanalyzers.

**Starting Materials:**

**Scheme S1.** Preparation of orto-formyl biaryl derivatives by Suzuki coupling reactions

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\begin{align*}
\text{R} + \text{Br} & \xrightarrow{3 \text{ mol} \% \text{Pd(PPh}_3)_4, \text{Na}_2\text{CO}_3 (2 \text{ equiv}, \text{DME/} \text{EtOH/H}_2\text{O, reflujo)}} ^2 \text{R} + \text{CHO} \\
\text{R} + \text{Br} & \xrightarrow{4 \text{ mol} \% \text{Pd(PPh}_3)_4, \text{CsF, K}_3\text{PO}_4 (2 \text{ equiv}, \text{DME, reflujo)}} ^2 \text{R} + \text{CHO}
\end{align*}
$$

**method A**

**method B**
2-Formyl derivatives 6, 7 and 10 were prepared by the palladium-catalyzed reaction of 2-bromobenzaldehydes with boronic acids. The substrates 1, 3, 5, 6, 8, 12, 13, 14, 15 and 28 were accessible from the parent aryl bromide, iodine or triflate and 2-formylbenzeneboronic acid.

Representative Procedure for Method A. Synthesis of 2-(naphthalene-1-yl)thiophen-3-carboxaldehyde (7) [Chart 1]: To a solution of 2-bromothiophene-3-carboxaldehyde (955 mg, 5.0 mmol, 1.0 equiv) and Pd(PPh₃)₄ (173 mg, 0.15 mmol, 0.03 equiv) in DME (20mL) is added a degassed solution of naphthalen-1-ylboronic acid (1.06 g, 6.16 mmol, 1.2 equiv) in EtOH (5 mL), followed by a degassed solution of Na₂CO₃ (1.1g, 10 mmol, 2 equiv) in H₂O (5 mL). The resulting heterogeneous mixture is refluxed 15h, before it is diluted with diethyl ether (30 ml). The organic layer is separated, washed with brine, dried over Na₂SO₄, and evaporated. Chromatographic purification of the crude product (hexanes/ethyl acetate, 10/1) affords the aldehyde 7 as a white solid (0.97 g, 82%).

Representative Procedure for Method B. Synthesis of 2-(1,2-dihydroacenaphthylen-5-yl)benzaldehyde (12) [Chart 1]: To a degassed solution containing 5-bromo-1,2-dihydroacenaphthylene (699 mg, 3 mmol, 1.0 equiv), 2-formylbenzeneboronic acid (500 mg, 3.34 mmol, 1.1 equiv) and CsF (1.27g, 8.35 mmol) in DME (20 mL), is added Pd(PPh₃)₄ (135 mg, 0.12 mmol) and the resulting mixture is refluxed overnight. For work-up, EtOAc (20 ml) and water (20 ml) are added; the aqueous layer is extracted with EtOAc (3 x 50 mL). The combined organic layers are dried over Na₂SO₄ and evaporated. Chromatographic purification of the product (hexanes/ethyl acetate, 10/1) affords the aldehyde 12 as a white solid (573 mg, 74%).

Preparation of 2,2’-(naphthalene-1,4-diyl) dibenzaldehyde (14). A mixture of 1,4-diiodonaphtalene (570 mg, 1.5 mmol), 2-formylbenzeneboronic acid (500 mg, 3.34 mmol), CsF (1.27g, 8.35 mmol) and Pd(PPh₃)₄ (135 mg, 0.12 mmol) in DME (20 mL) is stirred at reflux overnight. The resulting yellow solution is worked-up as described in Procedure for Method B, afforded 379 mg of 14 as a white solid (75%).

Preparation of 2,2’-(naphthalene-1,5-diyl) dibenzaldehyde (15). To a solution of naphthalene-1,5-diyl bis(trifluoromethanesulfonate) (1.41g, 3.34 mmol) and 2-formylbenzeneboronic acid (1.0 g, 6.68) in DME (30 mL) is added Pd(PPh₃)₄ (381 mg, 0.33 mmol) and K₃PO₄ (3.54 g, 16.7 mmol). The suspension is stirred at 80°C for 48h. The reaction mixture is concentrated in vacuo and chromatographic purification of the product with hexanes/ethyl acetate, 10/1 affords the aldehyde 15 as a pale solid (530 mg, 47%).

Preparation of 2-phenylbenzaldehyde (9). To a solution of 2-bromobiphenyl (4.66g, 20 mmol) in THF (50mL) at -80°C is added n-BuLi (12.5 mL of a 1.6M solution in hexane, 20 mmol). The resulting yellow solution is stirred at -80°C for 30 min. DMF (15 mL) is then slowly added and the mixture is stirred for 1h at -80°C, allowed to warm to rt and stirring is continued for another 30 min. The resulting solution is diluted with CH₂Cl₂ and washed with a saturated aqueous solution of NH₄Cl, dried and concentrated in vacuo. Chromatographic purification eluting with 5:1 hexane/EtOAc affords 1.75 g (96%) of 9 as a yellow oil.

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1 The preparation of 1 is described in reference 9b
2 Preparation of 1,4-diodonaphtalene was carried out by diiodination of naphthalene with 2.1 equiv of IPy₂BF₄ and 4 equiv of triflic acid at rt for 15h. The reaction affords 1,4-diodonaphtalene with 69% yield. (J. Barluenga, J. M. González, M. A. García Martín, P. J. Campos Tetrahedron Lett. 1993, 34, 3893)
**General Procedure for the Synthesis of Compounds 2, 4, 16-27, 29 and 30 [Schemes 1, 2 and Chart 2]**: 

IPy$_2$BF$_4$ (0.74 g, 2 mmol, 2 equiv) was dissolved in dry CH$_2$Cl$_2$ (10 mL) and stirred for 5 min at rt. The solution was cooled down at -80°C, then tetrafluoroboric acid (542 µL, 54% solution in diethyl ether, 4 mmol, 4 equiv) was added. After 10 min., the mixture is filtered and the filtrate is maintained at -60°C in a cryocool apparatus until the aldehyde is added. The resulting mixture is stirred until disappearance of the starting material or no evolution of the reaction (reaction times are given in Table 1, Chart 2 and Schemes 1 and 2). The reaction mixture was poured into 100 g of crushed ice and vigorously stirred, allowing the temperature to rise up to rt. The organic layer was washed with a 5% aqueous solution of Na$_2$S$_2$O$_3$ (50 mL), dried over sodium sulfate, and concentrated. The products were purified by column chromatography (silica gel, hexane/EtOAc) to give the ketone. Yields are listed in Table 1, Chart 2 and Schemes 1 and 2.

**11-iodo-10-p-tolylyphalenol[9,1,2-cde]chromen-6(1H)-one (2)**. Yellow solid. $R_f = 0.47$ (Hexane: EtOAc, 10:1). M.p. 192-194 °C. $^1$H NMR (300 MHz, DCCl$_3$): $\delta = 8.66$ (d, $J = 8.0$ Hz, 1H), 8.07 (dd, $J = 8.2$, 1.6 Hz, 1H), 7.87 (d, $J = 8.1$ Hz, 2H), 7.68 (td, $J = 8.4$, 1.4 Hz, 1H), 7.61 (td, $J = 8.1$, 1.2 Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.24 (dd, $J = 8.1$, 1.5 Hz, 1H), 7.24 (dd, $J = 8.6$, 1.3 Hz, 1H), 5.31 (s, 2H), 2.51 (s, 3H) ppm. $^{13}$C NMR (75 MHz, DCCl$_3$): $\delta = 196.2$ (C), 156.8 (C), 144.1 (C), 134.9 (C), 133.1 (C), 132.4 (C), 132.3 (C), 130.5 (2 x CH), 130.0 (C), 129.7 (CH), 129.2 (CH), 129.1 (CH), 128.6 (C), 128.1 (CH), 126.5 (C), 126.3 (CH), 126.1 (C), 125.3 (CH), 123.6 (C), 121.6 (CH), 117.4 (CH), 84.1 (C), 67.9 (CH$_2$), 21.6 (CH$_3$) ppm. IR: $\nu$(KBr)/cm$^{-1}$: 3021, 2915, 1664, 1550, 1499, 815. MS (70 eV, EI): $m/z$ (%) = 474 ($M^+$, 8), 458 (10), 364 (18), 335 (100). HRMS (EI): calcd for C$_{25}$H$_{15}$IO$_2$: 474.0111; found: 474.0099.

**7H-Benzof[de]anthracen-7-one (4)**. Yellow solid. $R_f = 0.42$ (Hexane: EtOAc, 3:1). M.p. 143-144 °C. $^1$H NMR (300 MHz, DCCl$_3$): $\delta = 8.76$ (dd, $J = 7.3$, 1.2 Hz, 1H), 8.50 (dd, $J = 7.9$, 1.6 Hz, 1H), 8.40 (d, $J = 7.4$ Hz, 1H), 8.31 (dd, $J = 8.1$, 0.5 Hz, 1H), 8.19 (dd, $J = 8.1$, 1.3 Hz, 1H), 7.98 (d, $J = 8.2$ Hz, 1H), 7.77 (t, $J = 7.9$ Hz, 1H), 7.74 (td, $J = 7.4$, 1.6 Hz, 1H), 7.65 (t, $J = 7.6$ Hz, 1H), 7.56 (td, $J = 8.3$, 1.0 Hz) ppm. $^{13}$C NMR (75 MHz, DCCl$_3$): $\delta = 183.7$ (CO), 136.0 (C), 134.9 (CH), 133.2 (CH), 132.8 (C), 130.9 (C), 130.0 (CH), 129.6 (CH), 128.3 (C), 128.1 (CH), 127.9 (CH), 127.7 (C), 126.6 (C), 126.4 (2 x CH), 124.0 (CH), 122.9 (CH) ppm IR: $\nu$(KBr)/cm$^{-1}$: 1644, 1598, 1450, 754. MS (70 eV, EI): $m/z$ (%) = 230 (100), 202 (43), 101 (26), 69 (18). HRMS (EI): calcd for C$_{17}$H$_{10}$O: 230.0732; found: 230.0735. Elemental analisis (%) calcd: C 88.67, H 4.38; found: C 88.50, H 4.39.

**8-fluoro-7H-benzo[de]anthracen-7-one (16)**. Yellow oil. $R_f = 0.40$ (Hexane: EtOAc, 3:1). $^1$H-RMN (300 MHz, CDCl$_3$): $\delta = 8.96$ (d, $J = 8.1$ Hz, 1H), 8.69 (d, $J = 7.5$ Hz, 1H), 8.49 (d, $J = 8.1$ Hz, 1H), 7.95 (d, $J = 7.5$ Hz, 1H), 7.86 (d, $J = 9.7$ Hz, 1H), 7.77-7.70 (m, 1H), 7.41-7.38 (m, 2H), 6.83 (d, $J = 9.7$ Hz, 1H) ppm. $^{13}$C (75 MHz, CDCl$_3$): $\delta = 190$ (CO), 161.4 (C, d, $J_{CF} = 235$ Hz), 135.9 (C, d, $J_{CF} = 8$ Hz), 135.6 (CH, d, $J_{CF} = 8$ Hz) 134.3 (CH), 133.3 (CH), 133.0 (C), 131.6 (C), 130.8 (CH), 130.6 (CH), 128.9 (CH, d, $J_{CF} = 4$ Hz), 128.7 (C), 127.8 (CH), 127.4
9,10-dimethoxy-7H-benzo[de]anthracen-7-one (17). Yellow solid. $R_f = 0.39$ (Hexane: EtOAc, 3:1). M.p. 160-162 °C. $^1$H-RMN (300 MHz, CDCl$_3$): $\delta$ = 8.67 (d, $J$ = 7.4 Hz, 1H), 8.36 (d, $J$ = 7.4 Hz, 1H), 8.12 (d, $J$ = 8.0 Hz, 1H), 7.90 (d, $J$ = 8.2 Hz, 1H), 7.67 (td, $J$ = 8.0, 2.8 Hz, 1H), 7.47 (td, $J$ = 8.8, 1.7 Hz, 1H), 7.16 (s, 1H), 6.97 (s, 1H) ppm.

13C (75 MHz, CDCl$_3$): $\delta$ = 180.0 (CO), 151.4 (C), 140.5 (C), 132.9 (CH), 130.3 (C), 127.7 (CH), 127.0 (C), 126.6 (CH), 126.2 (C), 125.6 (C), 125.2 (C), 124.8 (C), 123.7 (CH), 123.3 (CH), 120.6 (CH), 113.2 (CH), 110.1 (CH), 56.3 (CH$_3$), 56.2 (CH$_3$) ppm. IR $\nu$ (KBr, cm$^{-1}$): 1699, 1380, 760. HRMS (EI): calcd for C$_{17}$H$_9$FO: 248.0637; found: 248.0639.

7H-phenaleno[1,2-b]thiophen-7-one (18). Yellow solid. $R_f = 0.35$ (Hexane: EtOAc, 3:1). M.p. 152-154 °C. $^1$H-RMN (300 MHz, CDCl$_3$): $\delta$ = 8.71 (d, $J$ = 7.4 Hz, 1H), 8.11 (dd, $J$ = 7.8, 1.6 Hz, 1H), 7.70-7.54 (m, 5H), 7.39 (d, $J$ = 5.1 Hz, 1H) ppm. 13C (75 MHz, CDCl$_3$): $\delta$ = 179.9 (C), 149.3 (C), 139.0 (C), 133.5 (CH), 132.7 (C), 132.1 (CH), 131.7 (CH), 130.9 (C), 129.4 (CH), 128.6 (CH), 127.8 (CH), 127.5 (C), 127.1 (CH), 125.6 (C), 120.4 (CH) ppm. HRMS (EI): calcd for C$_{15}$H$_8$OS: 236.0296; found: 236.0303.

9-bromo-5H-dibenzo[b,e]phenalen-5-one (19). Yellow solid. $R_f = 0.36$ (Hexane: EtOAc, 3:1). M.p. 191-192 °C. $^1$H-RMN (300 MHz, CDCl$_3$): $\delta$ = 8.48 (d, $J$ = 7.1 Hz, 1H), 8.35 (d, $J$ = 8.2 Hz, 1H), 8.27 (d, $J$ = 7.7 Hz, 1H), 8.14 (d, $J$ = 7.9 Hz, 1H), 8.01-7.97 (m, 2H), 7.64 (d, $J$ = 8.3 Hz, 1H), 7.43-7.29 (m, 4H) ppm. 13C (75 MHz, CDCl$_3$): $\delta$ = 185.2 (CO), 142.3 (C), 138.4 (C), 134.9 (C), 134.1 (CH), 133.5 (C), 133.3 (C), 133.1 (CH), 132.7 (C), 130.6 (CH), 129.9 (CH), 129.3 (C), 128.4 (CH), 127.8 (CH), 127.4 (CH), 126.9 (C), 126.8 (CH), 126.5 (CH), 126.4 (CH), 123.1 (C) ppm. HRMS (EI): calcd for C$_{21}$H$_{11}$BrO: 357.9993; found: 357.9984.

9H-fluoren-9-one (20). Yellow solid. $R_f = 0.53$ (Hexane: EtOAc, 10:1). $^1$H-RMN (300 MHz, CDCl$_3$): $\delta$ = 7.65 (dd, $J$ = 7.4, 0.8 Hz, 1H), 7.53-7.45 (m, 2H), 7.32-7.26 (m, 1H) ppm. 13C (75 MHz, CDCl$_3$): $\delta$ = 193.6 (CO), 144.2 (C), 134.5 (CH), 133.9 (C), 128.9 (CH), 124.0 (CH), 120.2 (CH) ppm. IR $\nu$(KBr, cm$^{-1}$): 3080, 1726, 1690, 1613, 1430, 1019. HRMS (EI): calcd for C$_{13}$H$_8$O: 180.0575; found: 180.0577.

10H-benzo[b]indeno[2,1-d]thiophen-10-one (21). Yellow solid. $R_f = 0.43$ (Hexane: EtOAc, 3:1). M.p. 204-206 °C. $^1$H-RMN (300 MHz, CDCl$_3$): $\delta$ = 8.13 (dd, $J$ = 7.8, 1.5 Hz, 1H), 7.86-7.63 (m, 4H), 7.60-7.43 (m, 3H) ppm. 13C (75 MHz,
CDCl$_3$; $\delta$ = 187.4 (CO), 162.4 (C), 144.2 (C), 138.8 (C), 137.1 (C), 135.0 (C), 133.8 (CH), 132.6 (CH), 129.7 (CH), 126.8 (CH), 125.5 (CH), 123.7 (CH), 123.3 (CH), 123.1 (CH), 120.4 (C) ppm. IR $\nu$(KBr, cm$^{-1}$): 1720, 1697, 1610. HRMS (EI): calcd for C$_{16}$H$_8$OS: 236.0296; found: 236.0300.

$^{1}$-methylindeno[2,1-b]indol-2(1H)-one (22). Yellow solid. $R_t = 0.62$ (Hexane: EtOAc, 3:1). M.p. 147-149ºC. $^1$H-RMN (300 MHz, CDCl$_3$): $\delta$ = 7.65 (dd, $J$ = 8.9, 1.1 Hz, 1H), 7.36-7.23 (m, 4H), 7.20-7.17 (m, 1H), 7.10-7.08 (m, 1H), 6.99-6.96 (m, 1H), 3.85 (s, 3H) ppm. $^{13}$C (75 MHz, CDCl$_3$): $\delta$ = 185.0 (CO), 147.2 (C), 144.1 (C), 140.6 (C), 137.4 (C), 134.1 (CH), 133.7 (C), 126.6 (CH), 126.2 (CH), 123.7 (CH), 122.1 (CH), 121.9 (CH), 121.4 (C), 119.2 (CH), 111.7 (CH), 30.8 (CH$_3$) ppm. IR $\nu$(KBr, cm$^{-1}$): 3054, 1704.

7-oxo-7H-benzo[de]anthracen-4-yl trifluoromethanesulfonate (24). Yellow solid. $R_t = 0.36$ (Hexane: EtOAc, 3:1). M.p. 212-214ºC. $^1$H-RMN (300 MHz, CDCl$_3$): $\delta$ = 8.83 (d, $J$ = 8.2 Hz, 1H), 8.59-8.55 (m, 2H), 7.84-7.61 (m, 5H), 6.72 (d, $J$ = 9.6 Hz, 1H) ppm. $^{13}$C (75 MHz, CDCl$_3$): $\delta$ = 182.2 (CO), 149.9 (C), 135.2 (C), 134.0 (C), 130.4 (CH), 127.7 (2 x C), 126.5 (CH), 126.1 (C), 125.7 (CH), 125.3 (CH), 124.7 (CH), 124.6 (CH), 124.0 (CH), 123.8 (CH), 123.5 (C), 122.1 (C, c, $J$ = 180 Hz, CF$_3$), 119.3 (CH) ppm. HRMS (EI): calcd for C$_{18}$H$_9$F$_3$O$_4$S: 378.0174; found: 378.0183.

3-(2-Formylphenyl)-7H-benzo[de]anthracen-7-one (25). Yellow solid. $R_t = 0.34$ (Hexane: EtOAc, 3:1). M.p. 161-163 ºC. $^1$H-RMN (300 MHz, CDCl$_3$): $\delta$ = 9.62 (s, 1H), 8.81 (d, $J$ = 7.4 Hz, 1H), 8.52 (d, $J$ = 9.1 Hz, 1H), 8.48 (d, $J$ = 7.6 Hz, 1H), 8.36 (d, $J$ = 8.2 Hz, 1H), 8.13 (dd, $J$ = 8.2, 1.4 Hz, 1H), 7.79-7.71 (m, 3H), 7.64-7.60 (m, 3H), 7.55 (dd, $J$ = 8.2, 1.1 Hz, 1H), 7.46 (dd, $J$ = 7.4, 1.1 Hz, 1H) ppm. $^{13}$C (75 MHz, CDCl$_3$): $\delta$ = 191.1 (CHO), 183.6 (CO), 140.4 (C), 139.3 (C), 136.3 (C), 136.0 (CH), 135.0 (C), 134.6 (CH), 134.3 (C), 133.7 (CH), 132.8 (CH), 131.6 (C), 131.4 (C), 130.9 (CH), 130.3 (CH), 129.9 (CH), 128.5 (CH), 128.1 (CH), 127.9 (C), 127.7 (CH), 127.5 (C), 127.2 (CH), 127.1 (CH), 126.6 (CH) ppm. IR $\nu$ (KBr, cm$^{-1}$): 3391, 1693, 1649, 1597, 1316. HRMS (EI): calcd for C$_{25}$H$_{12}$O$_2$: 334.0994; found: 334.0986.
4-(2-Formylphenyl)-7H-benzo[de]anthracen-7-one (26). Yellow solid. \( R_f = 0.35 \) (Hexane: EtOAc, 3:1). M.p. 163-165 °C. \(^1\)H-RMN (300 MHz, CDCl\(_3\)): \( \delta = 9.65 \) (s, 1H), 8.83 (d, \( J = 7.4 \) Hz, 1H), 8.54 (dd, \( J = 8.0, 1.4 \) Hz, 1H), 8.52-8.49 (m, 1H), 8.38 (d, \( J = 8.2 \) Hz, 1H), 8.15 (dd, \( J = 8.0, 1.4 \) Hz, 1H), 7.80 (dd, \( J = 7.1, 1.4 \) Hz, 1H), 7.76-7.73 (m, 2H), 7.69-7.57 (m, 4H), 7.49 (dd, \( J = 7.4, 1.1 \) Hz, 1H) ppm. \(^{13}\)C (75 MHz, CDCl\(_3\)): \( \delta = 191.1 \) (CHO), 183.6 (CO), 140.3 (C), 137.9 (C), 133.9 (C), 136.7 (CH), 133.5 (CH), 132.5 (C), 132.0 (C), 131.4 (CH), 129.6 (C), 129.5 (C), 128.9 (CH), 128.7 (CH), 128.6 (CH), 128.1 (CH), 127.7 (CH), 127.2 (CH), 126.0 (C), 125.7 (CH), 125.3 (CH), 124.9 (CH), 124.3 (CH), 123.8 (CH) ppm. HRMS (EI): calcd for C\(_{24}\)H\(_{14}\)O\(_2\): 334.0994; found: 334.0990.

7,14-dihydrodibenzo[b,i]pyren-7,14-dione (27). Yellow solid. \( R_f = 0.23 \) (Hexane: EtOAc, 3:1). M.p. 225-227 °C. \(^1\)H-RMN (300 MHz, CDCl\(_3\)): \( \delta = 9.69-9.65 \) (m, 1H), 8.56-8.51 (m, 1H), 7.75 (d, \( J = 7.1 \) Hz, 1H), 7.65 (d, \( J = 7.1 \) Hz, 1H), 7.59-7.50 (m, 2H) ppm. \(^{13}\)C (75 MHz, CDCl\(_3\)): \( \delta = 183.5 \) (CO), 136.3 (C), 143.8 (C), 134.6 (C), 134.3 (CH), 132.4 (CH), 130.8 (CH), 130.6 (CH), 130.4 (C), 129.8 (C), 127.6 (CH), 127.2 (CH) ppm. IR (KBr, cm\(^{-1}\)): 3001, 1640, 1593, 1458. HRMS (EI): calcd for C\(_{24}\)H\(_{12}\)O\(_2\): 332.0837; found: 332.0811. Elemental analysis (%) calcd C 86.73, H 3.64; found: C 86.64, H 3.65.

8H-benzo[gh]tetraphen-8-one (29). Yellow solid. \( R_f = 0.25 \) (Hexane: EtOAc, 10:1). M.p. 182-184 °C. \(^1\)H-RMN (300 MHz, CDCl\(_3\)): \( \delta = 8.69-8.61 \) (m, 3H), 8.64 (s, 1H), 8.47 (dd, \( J = 7.7, 1.1 \) Hz, 1H), 8.15 (d, \( J = 7.4 \) Hz, 1H), 7.72-7.50 (m, 5H), 7.43 (td, \( J = 7.6, 1.1 \) Hz, 1H) ppm. \(^{13}\)C (75 MHz, CDCl\(_3\)): \( \delta = 182.5 \) (CO), 134.2 (C), 133.9 (C), 132.4 (CH), 131.3 (C), 130.3 (C), 129.1 (CH), 128.6 (C), 128.5 (C), 127.9 (C), 127.7 (CH), 127.1 (CH), 126.8 (CH), 126.7 (CH), 126.4 (CH), 125.9 (C), 125.5 (CH), 125.3 (CH), 124.8 (CH), 122.4 (CH), 122.3 (CH) ppm. HRMS (EI): calcd for C\(_{21}\)H\(_{12}\)O: 280.0888; found: 280.0894.

9H-indeno[2,1-]phenanthren-9-one (30). Yellow solid. \( R_f = 0.33 \) (Hexane: EtOAc, 3:1). M.p. 185-187 °C. \(^1\)H-RMN (300 MHz, CDCl\(_3\)): \( \delta = 9.24 \) (dd, \( J = 7.1, 1.2 \) Hz, 1H), 8.73 (dd, \( J = 8.2, 1.6 \) Hz, 1H), 8.69-8.60 (m, 2H), 8.06 (d, \( J = 7.4 \) Hz, 1H), 7.81-7.61 (m, 5H), 7.51 (td, \( J = 7.4, 1.6 \) Hz, 1H), 7.33 (td, \( J = 7.8, 0.6 \) Hz, 1H) ppm. \(^{13}\)C (75 MHz, CDCl\(_3\)): \( \delta = 196.5 \) (CO), 144.8 (C), 144.0 (C), 134.8 (C), 134.5 (C), 134.1 (CH), 131.2 (CH), 129.4 (C), 129.0 (C), 128.6 (C), 127.8 (C), 127.7 (CH), 127.5 (CH), 127.4 (CH), 126.2 (CH), 125.9 (CH), 125.5 (CH), 124.0 (CH), 123.7 (CH), 123.5 (CH), 122.8 (CH) ppm. IR (KBr, cm\(^{-1}\)): 1696, 1644. HRMS (EI): calcd for C\(_{21}\)H\(_{12}\)O: 280.0888; found: 280.0881.
Copies of representative NMR-spectra: