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The synthesis of angularly fused polyaromatic compounds by using a light-assisted, base-mediated cyclization reaction

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The synthesis of substituted polyaromatic compounds that contain at least four benzene rings fused together in an angular fashion is described. Suzuki coupling of 1-bromo-3,4-dihydronaphthalene-2-carbaldehyde with a number of aromatic boronic acids affords products such as 1-(1,4-dimethoxy-3-methyl-2-naphthyl)-3,4-dihydronaphthalene-2-carbaldehyde. Exposure of these dihydronaphthalenes to potassium *tert*-butoxide and DMF at 80 °C yields polyaromatic compounds such as 9,14-dimethoxynaphtho[1,2-*a*]anthracene.

Introduction

The Polycyclic Aromatic Hydrocarbons (PAHs) form a large class of compounds found mainly in petrochemical sources. Their activity as carcinogens was first recognized more than eighty years ago; indeed, they were the first organic compounds (as distinct from microorganisms) to be demonstrably effective in causing disease.[1] More recently, this class of compounds has been studied extensively for other reasons. For example, since the discovery of fullerenes, the synthesis of PAHs has witnessed a major renaissance.[2] However of interest to our research group is the large number of polyaromatic and aromatic compounds being used as ligands in transition metal-catalysed reactions. The prototypical, and still most frequently used, chiral phosphine-containing polyaromatic ligand is BINAP **1** (Fig. 1), which gained prominence as a result of the work of Noyori.[3,4] Another well-known binaphthyl ligand is binaphthol **2**, derivatives of which are also widely used in asymmetric synthesis, either as ligands in their own right or as chiral auxiliaries.[5–8] However, these ligands are not limited to polyaromatic compounds containing a naphthalene backbone, as illustrated, for example, by the polycyclic aromatic ligands **3a**[9] and **3b**,[10,11] as well as the phenanthrene complex **3c**.[12] Therefore new methods for the synthesis of substituted aromatic and polyaromatic compounds with the potential to be converted into ligands for metal-catalyzed reactions are important.

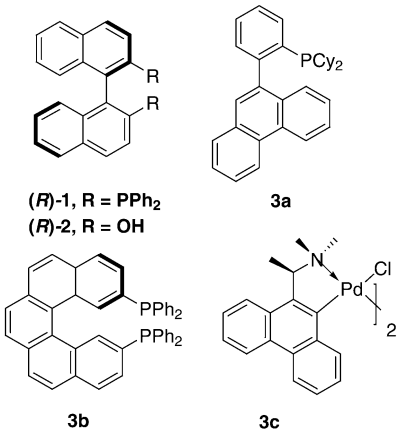
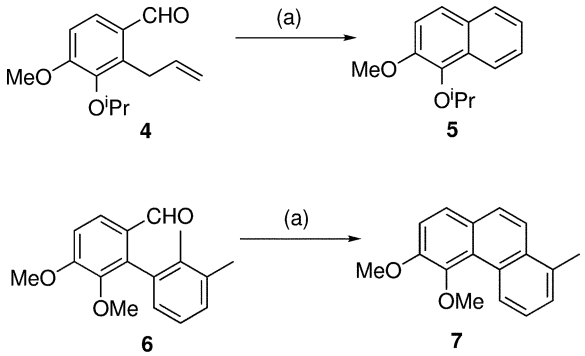


Fig. 1 Representative aromatic ligands.

In 1997 we reported that treatment of *o*-allyl benzaldehydes and analogous aryl ketones with potassium *tert*-butoxide and simultaneous irradiation from a high-pressure mercury lamp resulted in the formation of naphthalenes, such as shown in the conversion of **4** → **5**.[13] Since that time we have extended the use of this methodology to the synthesis of polyaromatic compounds such as phenanthrenes (*e.g.* **6** → **7**)[14] (Scheme 1). In addition, benzo- and pyrido-fused carbazoles have been synthesized using this methodology.[15,16] In this paper we wish to disclose the extension of this methodology for the synthesis of substituted polyaromatic compounds that contain at least four benzene rings fused together in an angular fashion.



Scheme 1 Synthesis of naphthalenes and phenanthrenes. *Reagents and conditions*: (a) KOBu^t, DMF, 80 °C, *hν*; **5**, 81%; **7**, 70%.[14]

Results and discussion

Treatment of 1-bromo-3,4-dihydronaphthalene-2-carbaldehyde **8**[17,18] with a variety of aromatic boronic acids **9a–d** under typical Suzuki coupling conditions resulted in the formation of the desired 3,4-dihydronaphthalenes **10a–d** in acceptable to good yields (Scheme 2, Table 1). With these products in hand, the stage was now set to attempt our novel reaction to produce the desired polyaromatic compounds. We believed that under the reaction conditions not only would ring formation occur but also aromatization of the 3,4-dihydronaphthalene was to be expected.

Subjecting substrate **10a** to our normal reaction conditions (4 eq. KOBu^t, DMF, 80 °C and *hν*) resulted in the formation of the desired product **11a**[19,20] in good yield. Benzo[*c*]phenanthrene (BcP) **11a**, is known to be a relatively weak carcinogen.[19]

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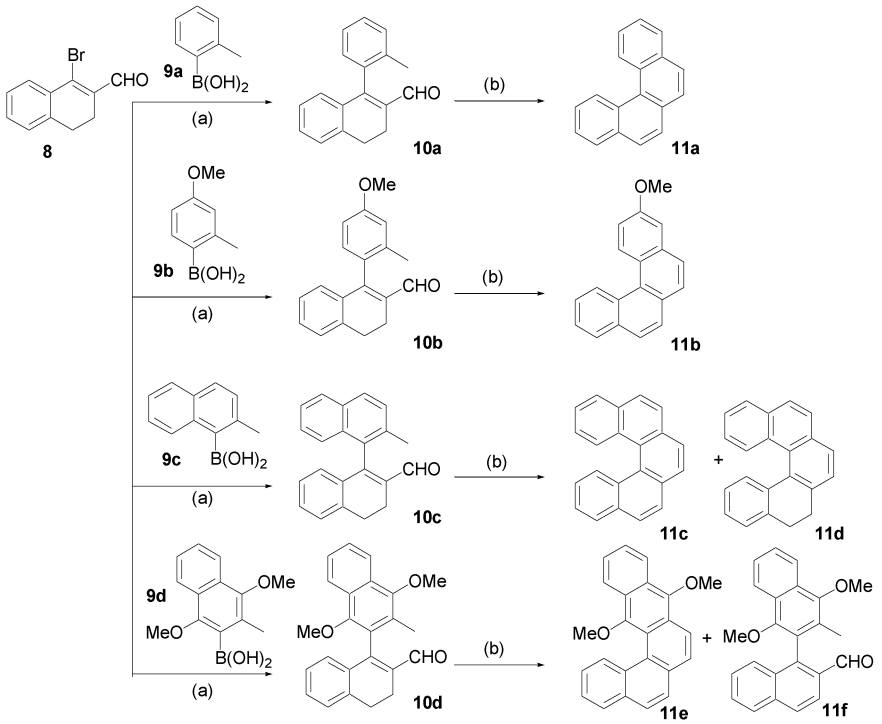


Scheme 2 Synthesis of polyaromatic compounds. *Reagents and conditions*: (a) 10 mol% $Pd(PPh_3)_4$, 2 M aq. Na_2CO_3, DME–EtOH; (b) $KOBu^t$, DMF, 80 °C, *hv*. For yields see Table 1.

Table 1 Yields of polyaromatic compounds **10** and **11** (see Scheme 2)

10; Yield (%)	**11**; Yield (%)	No *hv*
10a; 88	**11a**; 78[a]	
10b; 100	**11b**; 93[b]	
10c; 58	**11c**; 70, **11d**; 14	
	11c; 82, **11d**; 0[b]	
10d; 72	**11e**; 18, **11f**; 70[a]	**11e**; 79, **11f**; 0[b]

[a] 4 eq $KOBu^t$. [b] 8 eq $KOBu^t$.

However, attempting the same ring closing reaction on the remaining three substrates **10b–d** proved to be more problematic. For substrates **10c** and **10d** presumably this is because the portion of the molecule derived from the boronic acid contains substituents other than hydrogen in all positions *ortho* to the stereogenic axis, causing out-of-plane twisting such that steric hindrance to rotation makes the ring-closing reaction more difficult.

Treatment of substrates **10b** and **10c** under our standard ring closing reaction conditions (4 eq. $KOBu^t$, DMF, 80 °C and *hv*) gave the desired products **11b** and **11c** but the reactions were not clean. In the case of **11c** it was clear that another unstable product **11d** was also formed in low yield if only 4 equivalents of potassium *tert*-butoxide was used. Examination of the ^1H NMR spectrum of this product showed clearly that ring closure had taken place as the signals arising from aromatic methyl and aldehyde substituents were absent, but that aromatization of the dehydronaphthalene had not yet taken place as there was a complex set of signals between δ 2.72 and 3.13. Further evidence to support the identity of this product was provided by a high-resolution mass spectrum (expected for $C_{22}H_{16}$ 280.1252; found 280.1255), which suggested that product **11d** was also formed under the reaction conditions. As the yield of **11d** was low and the product appeared to be unstable we were unable to fully characterize the product. However, exposure of **10b** and **10c** to the same reaction conditions but this time doubling the amount of base to 8 equivalents of potassium *tert*-butoxide afforded the desired products, **11b** and pentahelicine **11c**, in good yields (93% and 82% respectively). Finally, 9,14-dimethoxynaphtho[1,2-*a*]anthracene **11e** was obtained from **10d**. In this case the formation of the desired product was best achieved by treating the substrate **10d** with 8 equivalents of potassium *tert*-butoxide in the *absence* of the light source; this afforded the pentacyclic product **11e** in 79% yield. Using the light source, **11e** was obtained in poor yield (18%) with the major product being **11f**, the product of aromatization of the dihydronaphthalene **10d**.

We have speculated about the mechanism of this reaction resulting in the formation of substituted polyaromatic compounds in a previous paper.[14] It is possible that an anionic mechanism is in operation as the protons in the benzylic position are acidic and can therefore, under basic conditions, react with the carbonyl-containing substituent on the conjoined aromatic ring (see structure **12**, Fig. 2). It is interesting to note that the light source often speeds up the reaction, and therefore it is also possible that the reaction may proceed through an anionic photoenolisation process. In our work it has been found that the reaction is facilitated *specifically* by *tert*-butoxide bases.[14] Therefore intermediates such as **13** may be formed in the reaction. These bases can also act as single electron transfer reagents which may also aid the photoenolisation.[14]

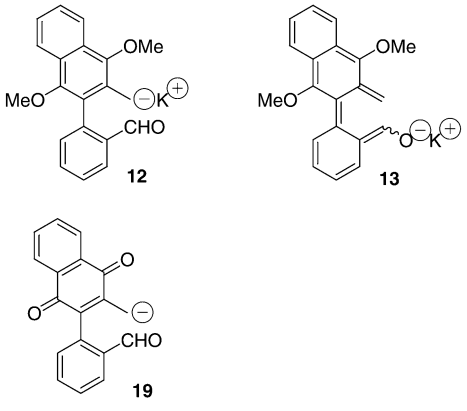


Fig. 2 Possible intermediates in the reaction.

However, it is also of interest that the formation of **11e** proceeded better in the *absence* of the light source. This may be as a result of the aromatisation of the dihydronaphthalene of **10d** proceeding more rapidly in the presence of the light source and oxygen, which was not rigorously excluded to afford predominantly **11f**. The product **11f** is then unable to undergo the required ring closure reaction as torsion about the biaryl axis probably positions the two reacting groups (the methyl substituent and the carbonyl) almost perpendicular to each other, irrespective of the actual mechanism involved.

An X-ray crystal structure of 9,14-dimethoxynaphtho[1,2-*a*]anthracene **11e** clearly showed the non-planar nature of the product, as expected (Fig. 3). The torsion angle C(14a)–C(14b)–C(14c)–C(1) showed clear deviation from planarity (28.2°), thereby highlighting the steric congestion in the bay region. These findings also vindicate our concerns regarding steric hindrance in the formation of the product. The deformations due to steric interaction also seem to result in increased olefinic character of some of the aromatic bonds. This is particularly clear for the bond between carbon atoms C14b and C14c, where the bond distance is 1.480 Å. Examination of the literature[21] indicates that even a simple polycyclic compound such as **11a** will show deviation from planarity. We believe that **11e** will display highly carcinogenic properties, as these are often associated with nonplanarity of polycyclic hydrocarbons.[21]

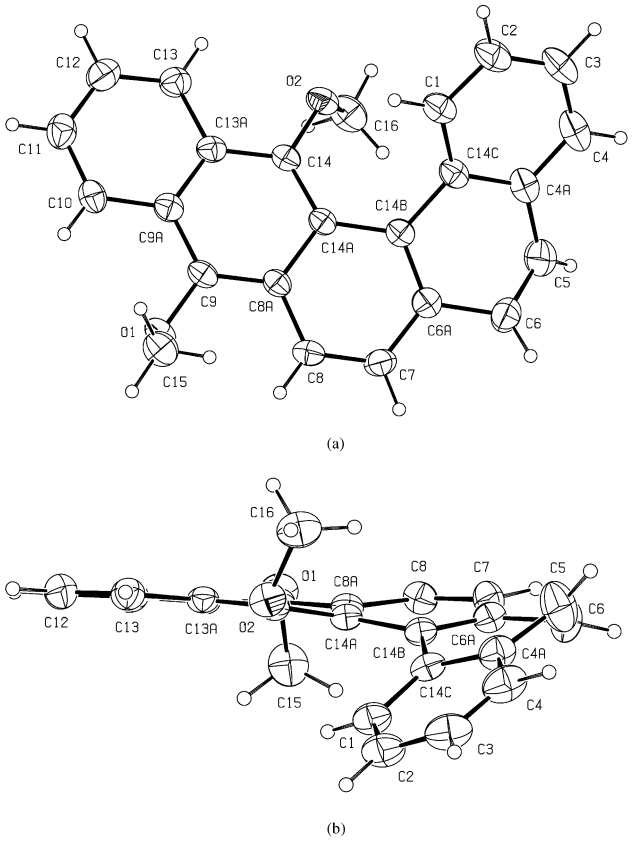
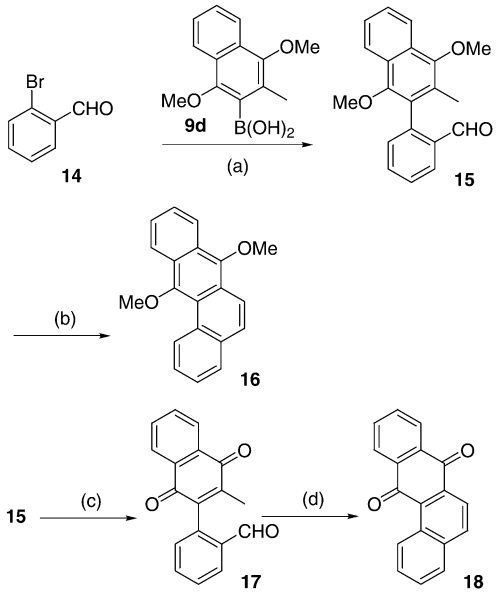


Fig. 3 ORTEP diagrams of the X-ray crystal structure of 9,14-dimethoxynaphtho[1,2-*a*]anthracene **11e** (ellipsoids at 50% probability). (a) Top view; (b) side view.

In an extension of the above investigation, 2-bromobenzaldehyde **14** was treated with 1,4-dimethoxy-3-methyl-2-naphthylboronic acid **9d** under Suzuki coupling conditions to afford the arylnaphthalene **15** in good yield (Scheme 3). Ring closure on **15** proceeded uneventfully to provide **16** in an excellent yield. Additionally, **15** was converted into the quinone **17**, exposure of which to potassium *tert*-butoxide in DMF under identical conditions gave the known quinone **18**.

Aromatic ring formation leading to **18** from a quinone precursor such as **17** has not been observed previously. While



Scheme 3 The synthesis of benzo[*a*]anthracene-7,12-dione. *Reagents and conditions:* (a) 10 mol% $Pd(PPh_3)_4$, 2 M aq. Na_2CO_3, DME–EtOH, 100%; (b) $KOBu^t$, DMF, 80 °C, *hv*, 87%; (c) CAN, H_2O–MeCN, 82%; (d) $KOBu^t$, DMF, 80 °C, *hv*, 82%.

detailed studies have not yet been conducted into the reaction mechanism of this process we believe that the reaction probably proceeds through the stabilized anionic intermediate **19** (Fig. 2), which is effectively a vinylogous enolate.

In conclusion, we have been able to demonstrate that our methodology for the synthesis of aromatic systems can be extended to the synthesis of strained polycyclic aromatic systems containing four or five benzene rings fused together in an angular fashion. The method provides a novel and simple procedure to access the desired products. It is also relatively versatile and could provide a range of products that are not accessible by traditional methods. At present we are working on using the developed methodology to include the synthesis of aromatic substrates that may have potential as ligands for transition metal-catalyzed reactions. In addition, the products **11a**, **11b**, **11c**, **11e** and **16** will be sent for biological evaluation as possible carcinogens.

Experimental

^1H NMR and ^{13}C NMR spectra were recorded either on a Bruker Ultrashield 300 or on a Bruker DRX-400 spectrometer at the frequency indicated. *J*-Values are given in Hz. Infra-red spectra were recorded on either a Bruker IFS 25 Fourier Transform spectrometer, or on a Bruker Vector 22 Fourier Transform spectrometer. Mass spectra were recorded on a Kratos MS 9/50, VG 70E MS or a VG 70 SEQ mass spectrometer. Macherey-Nagel Kieselgel 60 (particle size 0.063–0.200 mm) was used for conventional silica gel chromatography, and Macherey-Nagel Kieselgel 60 (particle size 0.040–0.063 mm) was used for preparative flash chromatography. All solvents used for reactions and chromatography were distilled prior to use.

1-Bromo-3,4-dihydronaphthalene-2-carbaldehyde 8

PBr_3 (3.3 cm^3, 34 mmol) was added dropwise to a solution of dry DMF (3.2 cm^3, 41 mmol) in dry CH_2Cl_2 (60 cm^3) cooled at 0 °C. The mixture was stirred for 1 h at 0 °C and a pale yellow suspension was formed. To this was added a solution of α-tetralone (1.8 cm^3, 14 mmol) in dry CH_2Cl_2 (50 cm^3), and the solution was heated at reflux for 1 h. After cooling the mixture to 0 °C, aqueous $NaHCO_3$ (80 cm^3) was added slowly until the effervescence had subsided. The mixture was extracted with CH_2Cl_2 (2 × 30 cm^3) and the organic phase was

then dried ($MgSO_4$) to give a yellow oil. The crude product was then purified by column chromatography (20% EtOAc–hexane) to afford a yellow solid, 1-bromo-3,4-dihydronaphthalene-2-carbaldehyde **8** (2.21 g, 76%): m.p. 42–43 °C (from EtOH; lit.,[17,18] 42–44 °C); ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) 2.62 (2H, t, *J* 8.0, CH_2), 2.83 (2H, t, *J* 8.0, CH_2), 7.19 (1H, dd, *J* 8.1 and 1.4, ArH), 7.26–7.38 (2H, m, 2 × ArH), 7.89 (1H, dd, *J* 8.6, 1.9, ArH) and 10.25 (1H, s, CHO); MS *m/z* 237 (M^+, 25%), 236 (26), 157 (13), 129 (76), 128 (100) and 127 (17).

Representative procedure for the preparation of the boronic acids

Toluene-2-boronic acid 9a. nBuLi (1.6 M, 2.1 cm^3, 3.3 mmol) was added dropwise to a solution of 2-bromotoluene (0.55 g, 3.2 mmol) in THF (15 cm^3) at −78 °C, resulting in a white suspension. The reaction mixture was stirred for 30 min at −78 °C, then $B(OMe)_3$ (0.92 cm^3, 8.2 mmol) was added. The resulting mixture was stirred at −78 °C for a further 30 min and then allowed to warm to rt. The reaction mixture was acidified with 10% aq. HCl solution and extracted with Et_2O (3 × 30 cm^3). The organic layer was then dried ($MgSO_4$) and concentrated under vacuum to afford an off-white crystalline material, toluene-2-boronic acid **9a** (0.40 g, 92%) that was used without further purification or characterization.

4-Methoxy-2-methylphenylboronic acid **9b**, 2-methyl-1-naphthylboronic acid **9c**, and 1,4-dimethoxy-3-methyl-2-naphthylboronic acid **9d** were prepared in a similar manner from 4-bromo-2-methylanisole,[22] 1-bromo-2-methylnaphthalene[23] and 2-bromo-1,4-dimethoxy-3-methylnaphthalene,[24] respectively.

Representative procedure for the Suzuki coupling reactions

1-(2-Methylphenyl)-3,4-dihydronaphthalene-2-carbaldehyde 10a. A solution of 1-bromo-3,4-dihydronaphthalene-2-carbaldehyde **8** (0.050 g, 0.21 mmol) in DME (1 cm^3) was deoxygenated by passing N_2 through the mixture for 5 min. The solution was then added to $Pd(PPh_3)_4$ (10 mol%, 0.024 g, 0.021 mmol) and stirred under an atmosphere of N_2 for 10 min at rt. A solution of 2-methylphenylboronic acid **9a** (0.043 g, 0.32 mmol) in EtOH (0.4 cm^3) was deoxygenated and added to the reaction mixture. The mixture was stirred for a further 10 min. A deoxygenated 2 M aqueous Na_2CO_3 solution (0.92 cm^3, 1.8 mmol) was then added to the reaction mixture that was stirred at rt for a further 5 min before being heated at reflux for 46 h. The mixture was cooled to rt and quenched with H_2O (20 cm^3) after which the organic material was extracted with CH_2Cl_2 (3 × 30 cm^3), dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The crude product was subjected to column chromatography (5–10% EtOAc–hexane) to afford the known product, 1-(2-methylphenyl)-3,4-dihydronaphthalene-2-carbaldehyde **10a** as a yellow solid (0.046 g, 88%). The spectroscopic data were in agreement with those reported by Kirsch.[25] m.p. 43–45 °C (lit. m.p. 54 °C[25]); ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) 2.08 (3H, s, $ArCH_3$), 2.55–2.66 (1H, m, CH), 2.73–2.83 (1H, m, CH), 2.91–2.96 (2H, m, CH_2), 6.74 (1H, d, *J* 7.7, ArH), 7.07–7.18 (2H, m, 2 × ArH), 7.25–7.38 (5H, m, 5 × ArH) and 9.48 (1H, s, CHO); ^{13}C NMR (75 MHz; $CDCl_3$) 19.6 (CH_2), 19.8 (CH_2), 27.6 ($ArCH_3$), 125.7 (CH), 126.8 (CH), 127.5 (CH), 127.8 (CH), 128.5 (CH), 129.5 (CH), 130.2 (CH), 130.5 (CH), 134.3 (C), 134.4 (C), 134.8 (C), 136.8 (C), 138.4 (C), 154.3 (C) and 193.1 (CHO); MS *m/z* 248 (M^+, 30%) and 233 (100).

The following compounds were prepared in a similar manner.

1-(4-Methoxy-2-methylphenyl)-3,4-dihydronaphthalene-2-carbaldehyde 10b. The product **10b** was isolated as a yellow oil (0.117 g, 100%): IR ν_{max} (film)/cm^{-1} 1735, 1659, 1611, 1561, 1498, 1455, 1364, 1306, 1241, 1201, 1185 and 1159; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) 2.05 (3H, s, $ArCH_3$), 2.56–2.64 (1H, m, CH), 2.72–2.82 (1H, m, CH), 2.89–2.94 (1H, m, CH_2), 3.86 (3H, s, OCH_3), 6.77–6.84 (3H, m, 3 × ArH), 7.06–7.13 (2H, m, 2 × ArH), 7.22–7.28 (2H, m, 2 × ArH) and 9.51 (1H, s, CHO); ^{13}C NMR (100MHz; $CDCl_3$) 20.0 (2 × CH_2), 27.6 ($ArCH_3$), 55.2 (OCH_3), 111.0 (CH), 115.8 (CH), 126.8 (CH), 127.0 (C), 127.5 (CH), 127.8 (CH), 128.1 (C), 130.2 (CH), 131.7 (CH), 134.7 (C), 138.3 (C), 138.4 (C), 154.1 (C), 159.6 (C) and 193.3 (CHO); MS *m/z* 278 (79%), 263 (M^+, 100), 247 (12) and 202 (13); HRMS calcd for $C_{19}H_{18}O_2$: 278.1307, found: 278.1313.

1-(2-Methyl-1-naphthyl)-3,4-dihydronaphthalene-2-carbaldehyde 10c. The product **10c** was isolated as a yellow solid (0.219 g, 58%) together with recovered starting material, 1-bromo-3,4-dihydronaphthalene-2-carbaldehyde **8** (0.080 g): m.p. 112–115 °C; IR ν_{max} (solid)/cm^{-1} 2842, 1665, 1607, 1562, 1506, 1428, 1360, 1336, 1286, 1260, 1237, 1189 and 1158; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) 2.27 (3H, s, $ArCH_3$), 2.79–2.83 (2H, m, CH_2), 3.02–3.09 (2H, m, CH_2), 6.58 (1H, d, *J* 7.7, ArH), 6.94–6.99 (1H, m, ArH), 7.23–7.45 (5H, m, 5 × ArH) 7.52 (1H, d, *J* 8.3, ArH), 7.86 (2H, d, *J* 8.3, 2 × ArH) and 9.27 (1H, s, CHO); ^{13}C NMR (75 MHz; $CDCl_3$) 19.8, 20.2 (2 × CH_2), 27.6 ($ArCH_3$), 125.4 (CH), 125.4 (CH), 126.8 (CH), 127.0 (CH), 127.2 (CH), 128.0 (CH), 128.0 (CH), 128.3 (CH), 128.4 (CH), 130.4 (CH), 130.8 (C), 131.8 (C), 133.0 (C), 134.1 (C), 134.5 (C), 135.4 (C), 138.5 (C), 152.6 (C) and 193.0 (CHO); MS *m/z* 299 (25%), 298 (M^+, 100), 297 (16), 284 (15), 283 (69), 281 (23), 279 (17), 269 (26), 255 (20), 254 (21), 253 (38), 252 (35) and 239 (19); HRMS calcd for $C_{22}H_{18}O$: 298.1358, found 298.1364.

1-(1,4-Dimethoxy-3-methyl-2-naphthyl)-3,4-dihydronaphthalene-2-carbaldehyde 10d. The product **10d** was isolated as a yellow solid (0.216 g, 72%): m.p. 96–97 °C; IR ν_{max} (solid)/cm^{-1} 2937, 2840, 1662, 1603, 1561, 1450, 1350, 1289, 1262, 1183, 1092, 1068, 964, 816 and 771; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) 2.15 (3H, s, $ArCH_3$), 2.73–2.80 (2H, m, CH_2), 2.97–3.03 (2H, m, CH_2), 3.67 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 6.80 (1H, d, *J* 7.8, ArH), 7.04–7.09 (1H, m, ArH), 7.24–7.30 (2H, m, 2 × ArH), 7.50–7.61 (2H, m, 2 × ArH), 8.08–8.11 (1H, m, ArH), 8.16 (1H, d, *J* 8.1, ArH) and 9.56 (1H, s, CHO); ^{13}C NMR (75 MHz; $CDCl_3$) 13.2 (CH_2), 19.9 (CH_2), 27.5 ($ArCH_3$), 61.5 (OCH_3), 61.9 (OCH_3), 122.3 (CH), 122.8 (CH), 125.8 (C), 125.9 (C), 126.0 (CH), 126.8 (CH), 126.8 (CH), 126.9 (CH), 127.2 (C), 128.0 (CH), 129.0 (C), 130.3 (CH), 134.3 (C), 134.8 (C), 138.5 (C), 149.8 (C), 150.2 (C), 150.4 (C) and 192.9 (CHO); MS *m/z* 359 (26%), 358 (M^+, 100), 328 (20), 327 (74) and 283 (20); HRMS calcd for $C_{24}H_{22}O_3$: 358.1569, found 358.1567.

Representative procedure for the ring-forming reactions

Benzo[*c*]phenanthrene 11a. $KOBu^t$ (0.090 g, 0.81 mmol), was added to 1-(2-methylphenyl)-3,4-dihydronaphthalene-2-carbaldehyde **10a** (0.050 g, 0.20 mmol) dissolved in dry DMF (6 cm^3), and the reaction mixture was heated under N_2 at 80 °C while being irradiated with a high-pressure Hg lamp through a quartz filter for 10 min. The reaction mixture was quenched by the addition of H_2O (50 cm^3), and the organic product was extracted with Et_2O (3 × 50 cm^3). The organic layers were dried ($MgSO_4$) and filtered. The resultant organic phase was then evaporated under reduced pressure and the residue subjected to column chromatography (5–20% EtOAc–hexane) to afford the product benzo[*c*]phenanthrene **11a** (0.036 g, 78%) as a white solid: m.p. 65–67 °C (lit. m.p. 66.5–67.5 °C[19]); ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) 7.63–7.81 (2H, m, 2 × ArH), 7.83 (1H, d, *J* 8.5, ArH), 7.91 (1H, d, *J* 8.6, ArH), 8.03 (1H, d, *J* 7.8, ArH) and 9.15 (1H, d, *J* 8.2, ArH);[20] ^{13}C NMR (75 MHz; $CDCl_3$) 125.8 (CH), 126.0 (C), 126.1 (CH), 126.8 (CH), 127.5 (CH), 127.9 (CH), 128.5 (CH), 130.3 (C), 131.0 (C) and 133.5 (C); MS *m/z* 229 (20%), 228 (M^+, 100), 227 (33), 226 (40) and 113 (23); HRMS calcd for $C_{18}H_{12}$: 228.0939, found: 228.0939.

3-Methoxybenzo[*c*]phenanthrene 11b. $KOBu^t$ (0.198 g, 1.76 mmol) was added to 1-(4-methoxy-2-methylphenyl)-3,4-dihydronaphthalene-2-carbaldehyde **10b** (0.060 g, 0.22 mmol) in dry DMF (6 cm^3), and the reaction mixture was heated at 80 °C under N_2 for 20 min. After the normal work-up procedure

3-methoxybenzo[*c*]phenanthrene **11b** (0.053 g, 93%) was obtained as a yellow solid: m.p. 75–76 °C; IR ν_{max} (solid)/cm^{-1} 1612, 1503, 1463, 1428, 1358, 1258, 1298, 1265, 1228, 1029, 923, 867, 832, 797 and 750; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) 4.01 (3H, s, OCH_3), 7.31–7.38 (2H, m, ArH), 7.59–7.69 (2H, m, 2 × ArH), 7.78–7.86 (4H, m, 4 × ArH), 8.00 (1H, d, *J* 7.6, ArH) and 9.03–9.08 (2H, m, 2 × ArH); ^{13}C NMR (75 MHz; $CDCl_3$) 55.4 (OCH_3), 108.0 (CH), 117.1 (CH), 125.1 (C), 125.8 (CH), 126.0 (CH), 126.5 (CH), 126.8 (CH), 126.9 (CH), 127.5 (CH), 127.9 (CH), 128.5 (CH), 129.5 (CH), 129.8 (C), 130.1 (C), 133.6 (C), 135.1 (C) and 157.5 (C); MS *m*/*z* 259 (27%), 258 (M$^+$, 100), 216 (12), 215 (57), 213 (17) and 189 (13); HRMS calcd for $C_{19}H_{14}O$: 258.1044, found: 258.1043.

Pentahelicene 11c and 5,6-Dihydropentahelicene 11d. (a) KOBu^t (0.114 g, 1.02 mmol) was added to **10c** (0.076 g, 0.25 mmol) dissolved in dry DMF (9 cm^3) and after subjecting the reaction mixture to the normal reaction conditions and column chromatography (5–20% EtOAc–hexane), two compounds were isolated. The major product was pentahelicene **11c** (0.049 g, 70%): m.p. 135–137 °C (not recrystallised); (lit. m.p. 145 °C[26]); ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) 7.30–7.33 (2H, m, 2 × ArH), 7.54–7.58 (2H, m, 2 × ArH), 7.91–8.03 (8H, m, 8 × ArH) and 8.56 (1H, d, *J* 8.5, ArH);[27] ^{13}C NMR (75 MHz; $CDCl_3$) 124.3 (CH), 126.2 (CH), 126.3 (CH), 127.0 (C), 127.2 (CH), 127.5 (CH), 127.8 (CH), 129.0 (CH), 130.8 (C), 132.3 (C) and 132.6 (C); MS *m*/*z* 278 (74%), 277 (M$^+$, 100), 276 (95), 274 (19) and 238 (13); HRMS calcd for $C_{22}H_{14}$: 278.1095 Found 278.1088. 5,6-Dihydropentahelicene **11d** was obtained as the minor product (0.010 g, 14%): ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) 2.72–3.13 (4H, m, 4 × ArH), 6.98–7.05 (1H, m, ArH), 7.10–7.22 (2H, m, ArH), 7.33–7.48 (3H, m, 3 × ArH), 7.50–7.56 (1H, m, ArH), 7.65–7.73 (3H, m, 3 × ArH), 7.80 (1H, d, *J* 8.5, ArH) and 8.45 (1H, d, *J* 8.5, ArH); HRMS calcd for $C_{22}H_{14}$: 280.1255, found: 279.1183.

(b) Repeating the reaction but using 8 equivalents of KOBu^t (0.241 g, 2.15 mmol) and **10c** (0.080 g, 0.27 mmol) led to the isolation of pentahelicene **11c** in good yield (0.062 g, 82%).

9,14-Dimethoxynaphtho[1,2-*a*]anthracene 11e and 1-(3-methyl-1,4-dimethoxy-2-naphthyl)-2-naphthaldehyde 11f. KOBu^t (0.075 g, 0.67 mmol) was added to **10d** (0.060 g, 0.17 mmol) dissolved in dry DMF (9 cm^3) and after subjecting the reaction mixture to the normal reaction conditions and column chromatography (5–20% EtOAc–hexane), two compounds were isolated, 9,14-dimethoxynaphtho[1,2-*a*]anthracene **11e** and 1-(3-methyl-1,4-dimethoxy-2-naphthyl)-2-naphthaldehyde **11f**. The minor product was **11e** (0.010 g, 18%): IR ν_{max} (film)/cm^{-1} 3050, 3005, 2932, 2837, 1731, 1617, 1591, 1559, 1504, 1473, 1451, 1412, 1363, 1289, 1113, 1096, 1060, 977, 834 and 752; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) 3.00, 4.20 (each 3H, s, OMe), 7.55–7.69 (5H, m, 5 × ArH), 7.83 (1H, d, *J* 8.4, ArH), 7.95–7.97 (1H, m, ArH), 8.01 (1H, d, *J* 8.4, ArH), 8.26 (1H, d, *J* 8.9, ArH), 8.32–8.41 (2H, m, 2 × ArH) and 8.56–8.59 (1H, m, ArH); ^{13}C NMR (75 MHz; $CDCl_3$) 60.2 (OCH_3), 63.6 (OCH_3), 118.5 (C), 121.8 (CH), 122.2 (CH), 123.4 (CH), 124.6 (CH), 125.0 (C), 125.5 (C), 125.6 (CH), 125.6 (CH) 125.9 (C), 125.9 (CH), 126.0 (CH), 126.7 (CH), 126.8 (C), 127.0 (CH), 128.5 (CH), 129.4 (C), 130.3 (CH), 131.3 (C), 132.7 (C), 147.8 (C) and 150.2 (C); MS *m*/*z* 338 (M$^+$, 100%), 323 (92), 292 (32), 279 (25), 250 (13), 219 (36), 167 (38), 154 (31), 149 (97), 139 (30), 125 (16), 83 (22) and 71 (24); HRMS calcd for $C_{24}H_{18}O_2$: 338.1307, found: 338.1321. The second product was 1-(3-methyl-1,4-dimethoxy-2-naphthyl)-2-naphthaldehyde **11f** (0.042 g, 70%): IR ν_{max} (film)/cm^{-1} 2955, 2927, 2854, 1727, 1590, 1454, 1352, 1283, 1095, 1061, 836, 797, 772 and 750; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) 1.96 (3H, s, $ArCH_3$), 3.37, 3.96 (each 3H, s, OMe), 7.42–7.45 (1H, m, ArH), 7.49–7.66 (4H, m, 4 × ArH), 7.96 (1H, brd, *J* 8.2, 1H), 8.01 (1H, brd, *J* 8.7, 1H), 8.11–8.16 (2H, m, 2 × ArH), 8.21–8.24 (1H, m, ArH) and 9.90 (1H, d, *J* 0.8, CHO); ^{13}C NMR (75 MHz; $CDCl_3$) 13.6 ($ArCH_3$), 61.6 (2×OCH_3), 122.3 (CH), 122.4 (CH), 122.9 (CH), 125.8 (C), 126.1 (CH), 126.6 (C), 126.7 (CH), 126.9 (CH), 127.2 (CH), 127.3 (C), 128.5 (CH), 128.7 (CH), 128. 9 (CH), 129.2 (C), 131.4 (C), 132.4 (C), 136.3 (C), 142.0 (C), 150.4 (C), 150.7 (C) and 192.5 (CHO); MS *m*/*z* 356 (M$^+$, 100%), 340 (41), 326 (79), 311 (46), 281 (44), 307 (54), 297 (40), 276 (66), 269 (37), 252 (36), 239 (38) and 150 (34); HRMS calcd for $C_{24}H_{20}O_3$: 356.1412, found: 356.1416.

KOBu^t (0.213 g, 1.90 mmol) was added to **10d** (0.085 g, 0.24 mmol) dissolved in dry DMF (20 cm^3) and after subjecting the reaction mixture to the normal reaction conditions but without exposure to the light source followed by chromatography (5–20% EtOAc–hexane), led to the isolation of only one product 9,14-dimethoxynaphtho[1,2-*a*]anthracene **11e** (0.063 g, 79%).

Single crystals of compound **11e** suitable for X-ray diffraction were selected directly from the analytical samples.

Crystal structure determination of compound 11e: crystal data. $C_{24}H_{18}O_2$, M = 338.38, orthorhombic, a =7.7959(9), b = 20.639(3), c = 11.0953(14) Å, U = 1785.2(4) Å^3, T = 293(2) K, space group $Pca2_1$ (No. 29), Z = 4, μ(Mo-Kα) = 0.079 mm^{-1}, 10163 reflections measured, 1858 unique (R_{int} = 0.044) which were used in all calculations. Final R indices [$I > 2\sigma(I)$], R_1 = 0.0464, $wR(F^2)$ = 0.1268. CCDC reference number 248479. See http://www.rsc.org/suppdata/ob/b4/b412932f/ for crystallographic data in .cif or other electronic format.

2-Bromo-1,4-dimethoxy-3-methylnaphthalene

A solution of $SnCl_2{\cdot}2H_2O$ (39.5 g, 0.175 mol) in concentrated HCl (33 cm^3) was added to a warm solution of 2-bromo-3-methylnaphthoquinone (13.24 g, 0.05273 mol) in EtOH (96%, 160 cm^3). H_2O was then added and the precipitate was filtered and recrystallized (H_2O) to afford the desired intermediate, 2-bromo-3-methyl naphthohydroquinone as white needles (13.08 g, 98%); m.p. 253–254°C (water) (lit. >250 °C[24]); ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) 2.52 (3H, s, $ArCH_3$), 5.31 (2H, brs, 2 × ArOH), 7.42–7.52 (2H, m, 2 × ArH) and 8.12–8.16 (2H, m, 2 × ArH); ^{13}C NMR (100 MHz; $CDCl_3$) 15.8 ($ArCH_3$), 108.0 (C), 117.3 (CH), 121.1 (CH), 121.5 (C), 123.0 (C), 124.5 (C), 126.1 (CH), 126.3 (CH), 142.1 (C) and 142.5 (C).

An aqueous solution of KOH (50%, 22 cm^3) was added to the intermediate naphthohydroquinone (0.502 g, 1.98 mmol) and dimethyl sulfate (6.85 cm^3). After heating at reflux for 1 h the reaction mixture was extracted with CH_2Cl_2 (2 × 30 cm^3), washed with aqueous 25% NH_3 (3 × 20 cm^3), dried ($MgSO_4$) and evaporated. Recrystallisation (MeOH) gave the desired 2-bromo-1,4-dimethoxy-3-methylnaphthalene as white plates (0.491 g, 88%): m.p. 84–85 °C (MeOH) (lit. 84–85 °C[24,28,29]); ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) 2.55 (3H, s, $ArCH_3$), 3.88, 3.97 (each 3H, s, $ArOCH_3$), 7.41–7.56 (2H, m, 2 × ArH) and 8.01–8.08 (2H, m, 2 × ArH).

2-(1,4-Dimethoxy-3-methyl-2-naphthyl)benzaldehyde 15

A solution of *ortho*-bromobenzaldehyde **14** (0.169 g, 0.913 mmol) in DME (8.0 cm^3) was deoxygenated by passing N_2 through the mixture for 10 min. The deoxygenated mixture was added to $Pd(PPh_3)_4$ (12 mol%, 0.122 g, 0.106 mmol) and stirred under N_2 for 10 min. A deoxygenated solution of arylboronic acid **9d** (synthesized in the same manner as indicated earlier, 0.400 g, 1.63 mmol) in DME (3 cm^3) was added to the mixture. After 10 min a deoxygenated aqueous Na_2CO_3 solution (2 M, 4.5 cm^3) was added to the reaction mixture that was stirred at rt for 10 min before being heated under reflux for 42 h. The cooled solution was quenched with H_2O (40 cm^3), extracted with CH_2Cl_2 (4 × 30 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the biaryl compound **15** as an orange oil (0.230 g, 82%) and recovered 1,4-dimethoxy-2-methylnaphthalene (0.028 g): IR ν_{max} (film)/cm^{-1} 3483, 3379, 3070$_{[el]}$, 3014, 2933, 2841, 2746, 1717, 1625, 1596, 1570, 1482, 1455, 1348, 1252 and 1266; ^{1}H NMR

(400 MHz; $CDCl_3$; Me_4Si) 2.13 (3H, s, $ArCH_3$), 3.46, 3.92 (each 3H, s, OCH_3), 7.37 (1H, d, *J* 7.6, ArH), 7.49–7.59 (3H, m, 3 × ArH), 7.66–7.72 (1H, m, ArH), 8.09–8.16 (3H, m, 3 × ArH) and 9.79 (1H, s, CHO); ^{13}C NMR (100 MHz; $CDCl_3$) 14.1 ($ArCH_3$), 61.1 (OCH_3), 61.3 (OCH_3), 122.2 (CH), 122.7 (CH), 125.7 (C), 125.9 (CH), 126.7 (CH), 127.1 (C), 127.3 (CH), 128.0 (CH), 128.2 (C), 128.8 (C), 131.5 (CH), 133.6 (CH), 134.1 (C), 140.8 (C), 149.7 (C), 150.3 (C) and 192.1 (CHO); MS *m*/*z* 307 (24%), 306 (M^+, 100), 291 (21), 276 (23), 260 (17), 259 (22), 232 (27), 231 (32), 203 (21) and 202 (20); HRMS calcd for $C_{20}H_{18}O_3$: 306.1256, found 306.1256.

7,12-Dimethoxybenzo[*a*]anthracene 16

KOBu^t (0.227 g, 2.02 mmol) was added to a solution of biaryl compound **15** (0.155 g, 0.506 mmol) in DMF (15 cm^3). The reaction mixture was treated in the normal manner to afford a residue that was purified by crystallization (EtOH–CH_2Cl_2–hexane) to give the desired product **16** as white plates (0.129 g, 88%): m.p. 135–137 °C (EtOH–CH_2Cl_2–hexane) (lit. m.p. 136–137 °C[30]); IR ν_{max} (solid)/cm^{-1} 3001, 2935, 2835, 1944, 1730, 1622, 1603, 1567, 1449, 1409, 1360, 1252, 1214, 1189, 1165, 1121 and 1103; ^1H NMR (400 MHz; $CDCl_3$; Me_4Si) 3.96, 4.10 (each 3H, s, OCH_3), 7.57–7.71 (5H, m, 5 × ArH), 7.82 (1H, dd, *J* 7.6, 1.6, ArH), 8.12 (1H, d, *J* 9.3, ArH), 8.32–8.35 (1H, m, ArH), 8.44–8.47 (1H, m, ArH) and 9.67 (1H, d, *J* 8.2, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) 60.9 (OCH_3), 63.1 (OCH_3), 120.7 (C), 121.0 (CH), 122.3 (CH), 123.2 (CH), 124.2 (C), 125.9 (CH), 126.0 (CH), 127.0 (CH), 127.3 (CH), 127.3 (C), 127.6 (CH), 128.2 (CH), 128.4 (CH), 130.0 (C), 132.6 (C), 148.6 (C) and 151.1 (C); MS *m*/*z* 289 (13%), 288 (M^+, 59), 274 (22), 273 (100), 258 (16), 257 (10), 230 (15), 202 (25) and 201 (9); HRMS calcd for $C_{20}H_{16}O_2$: 288.1150, found 288.1157.

2-(3-Methyl-1,4-dioxo-1,4-dihydro-2-naphthalenyl)-benzaldehyde 17

A solution of CAN (0.641 g, 1.17 mmol) in H_2O (1.0 cm^3) was added dropwise to a solution of biaryl compound **15** (0.119 g, 0.390 mmol) in MeCN (5.0 cm^3). After stirring for 5 min at rt the reaction mixture was extracted with CH_2Cl_2 (3 × 10 cm^3), dried ($MgSO_4$) and concentrated *in vacuo* to afford the desired naphthoquinone **17** (0.087 mg, 81%) as a yellow oil: IR ν_{max} (film)/cm^{-1} 3069, 3020, 2958, 2928, 2857, 2743, 1775, 1726, 1699, 1595, 1572, 1482, 1459, 1377, 1291, 1198, 1160 and 1121; ^1H NMR (400 MHz; $CDCl_3$; Me_4Si) 1.98 (3H, s, $ArCH_3$), 7.26 (1H, d, *J* 8.0, ArH), 7.61–7.78 (4H, m, 4 × ArH), 7.97 (1H, dd, *J* 7.5, 1.4, ArH), 8.06–8.09 (1H, m, ArH), 8.15–8.18 (1H, m, ArH) and 9.94 (1H, s, ArCHO); ^{13}C NMR (100 MHz; $CDCl_3$) 14.4 (ArMe), 126.4 (CH), 126.9 (CH), 129.2 (CH), 130.3 (CH), 132.2 (C), 132.2 (C), 132.5 (CH), 133.6 (CH), 133.6 (CH), 133.8 (CH), 134.3 (C), 135.2 (C), 143.3 (C), 145.9 (C), 183.6 (CO), 185.1 (CO) and 191.3 (CHO); MS *m*/*z* 276 (M^+, 28%), 261 (19), 248 (39), 247 (63), 234 (20), 233 (100), 219 (35), 191 (22), 189 (21), 104 (20) and 76 (18); HRMS calcd for $C_{18}H_{12}O_3$: 276.0786, found 276.0774.

Benzo[*a*]anthracene-7,12-dione 18

KOBu^t (0.097 g, 0.86 mmol) was added to a solution of biaryl naphthoquinone **17** (0.060 g, 0.22 mmol) in DMF (5 cm^3). The reaction mixture was stirred at 80 °C with simultaneous irradiation with a high-pressure Hg lamp through a quartz filter for 10 min. The reaction mixture was acidified with aqueous HCl, extracted with CH_2Cl_2 (3 × 40 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by crystallisation (EtOH–hexane) to afford the desired product **18** as yellow plates (0.046 g, 82%): m.p. 170–172°C (EtOH–hexane) (lit. m.p. 169 °C[31]); IR ν_{max} (film)/cm^{-1} 3018, 2924, 2853, 1724, 1666, 1590, 1506, 1459, 1429, 1378, 1326, 1307 and 1277; ^1H NMR (400 MHz; $CDCl_3$; Me_4Si) 7.65–7.85 (4H, m, 3 × ArH), 7.94 (1H, d, *J* 8.0, ArH), 8.21–8.34 (3H, m, 3 × ArH), 8.41 (1H, d, *J* 8.6, ArH) and 9.73 (1H, d, *J* 8.8, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) 122.5 (CH), 126.5 (CH), 127.2 (CH), 128.7 (CH), 128.8 (2×CH), 128.8 (C), 129.9 (CH), 130.5 (C), 132.2 (C), 133.5 (CH), 134.0 (C), 134.2 (CH), 135.1 (C), 135.3 (CH), 136.7 (C), 184.0 (CO) and 186.2 (CO).

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