Arylation of chloroanthraquinones by surprisingly facile Suzuki–Miyaura cross-coupling reactions

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Chloroanthraquinones were found to undergo facile Suzuki–cross coupling with substituted phenyl boronic acids using a commercial catalyst $Pd(PPh_3)_4$ and with $Pd(PPh_3)_4$ prepared *in situ* from $Pd(PPh_3)_2Cl_2$ and PPh_3.

Keywords: chloroarenes, anthraquinones, Suzuki–Miyaura cross-coupling, tetrakis(triphenylphosphino)palladium

The Suzuki–Miyaura cross coupling reaction of aryl- and alkylboronic acids with bromo- and iodoarenes is a well established reaction. As bromo- and iodoarenes are expensive in comparison to chloroarenes, the recent focus has been on the development of new catalysts and reaction protocols for the Suzuki reaction with chloroarenes. A number of catalysts had been proposed by Fu,[1] Buchwald[2] and others[3-8] in the last 20 years, in which the triphenylphosphine ligand of the original tetrakis[triphenylphosphino]palladium (0) was replaced by other ligands such as tris(*tert*-butyl)phosphine. With the advent of ligandless catalysts for Suzuki–Miyaura reactions, a number of highly reactive nanopalladium catalysts[9] have been developed for the coupling of chloroarenes. It has also been found that ligandless palladium catalysts can be used with aryl tetrafluoroborates in coupling reactions with aryl halides.[10] However, in the synthesis of arylated anthraquinones, as part of our search for highly conjugated π-systems, we have found that the use of specially prepared palladium catalysts are not always necessary in the reaction of chloroarenes. Thus, chloroanthraquinones easily undergo Suzuki cross coupling reactions with arylboronic acids in the presence of the original, commercially available $Pd(PPh_3)_4$.

Arylated anthraquinones **1** (Fig. 1) have attracted attention because of their interesting physical organic properties,[11,12] due to the interaction of the attached aryl groups with the π-system of the anthraquinone core as revealed by the UV and luminescence[13,14] spectra, the redox behaviour of the molecules,[12,15] and in the NMR shift values. Specifically, the interaction of the substituents with the C=O function of the anthraquinones has been subjected to investigation.[11] In practical applications, arylated anthraquinones have also been used as stabilisers of light-modulating fluids such as those containing liquid polybenzyltoluenes.[16] Our interest in these molecules lies in the study of their electrochemical behaviour. Having prepared a number of arylated anthraquinones from bromo substituted anthraquinones by Suzuki–Miyaura coupling reactions,[17] we pursued the question of whether it was possible to carry out the transformation with the respective chloro substituted anthraquinones.

Results and discussion

First, we had to synthesise chlorinated anthraquinones for which a number of synthetic procedures are known. Thus, 1,4-dichloroanthraquinone (**1a**) can be synthesised from

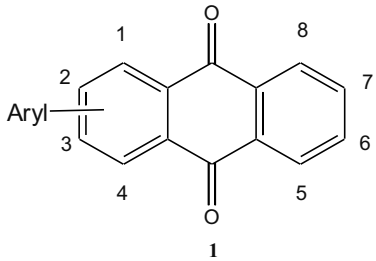

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Figure 1

1-hydroxyanthraquinone by chlorination and subsequent treatment of the 1-chloro-4-hydroxyanthraquinone with PCl_5.[18] 1,4-Dichloroanthraquinone (**1a**) can also be prepared by acylation of 1,4-dichlorobenzene (**3**) with phthaloyl chloride (**2**) and subsequent heating of the 2-(2,5-dichlorobenzoyl) benzoic acid intermediate with H_2SO_4 (Scheme 1),[19] or by treatment of 9,10-dihydroxy-2,3-dihydro-1,4-anthraquinone with PCl_5.[20,21]

In the present work, we chose to prepare chloroanthraquinones from 2,5-dichlorothiophene (**4a**). This was oxidised by *m*-CPBA to 2,5-dichlorothiophene-*S*-oxide and reacted *in situ* with naphthoquinones (Scheme 2). The use of thiophene *S*-oxides *in situ* as dienes in Diels Alder reactions has been found to be an efficientroute to multifunctionalised arenes.[22-24] This is especially true for thiophenes with electron donating substitutents. Thiophenes with electron-withdrawing substituents[23,25,26] such as chloro- or bromothiophenes **4** are much more difficult to oxidise. Nevertheless, at elevated temperatures it was possible to isolate chloroanthraquinones when chlorothiophenes were reacted with *m*-CPBA in the presence of naphthoquinones. Even in cases where the halothiophene *S*-oxides were oxidised further to halothiophene *S*,*S*-dioxides prior to undergoing a Diels Alder reaction, cycloaddition reactions were expected to proceed with the halothiophene *S*,*S*-dioxides equally well. Electron poor thiophene *S*,*S*-dioxides have been found to undergo cycloaddition reactions readily.[27,28] Thus, under the present conditions, halothiophene *S*,*S*-dioxides may also make a contribution to the reaction.

The resultant chloroanthraquinones **1a**–**e** were subjected to Suzuki–Miyaura cross coupling reactions with a number of different arylboronic acids. Tetrakis(triphenylphosphine) palladium(0) [$Pd(PPh_3)_4$] was used as catalyst and the reactions were run in a biphasic system of 1,2-dimethoxyethane (DME) and an aqueous sodium carbonate solution. The arylated anthraquinones were isolated in good yield. In case of

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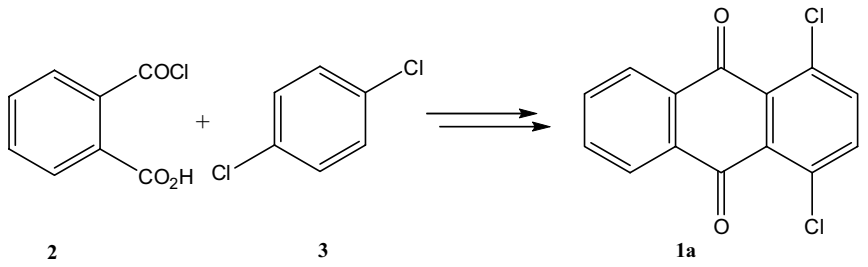
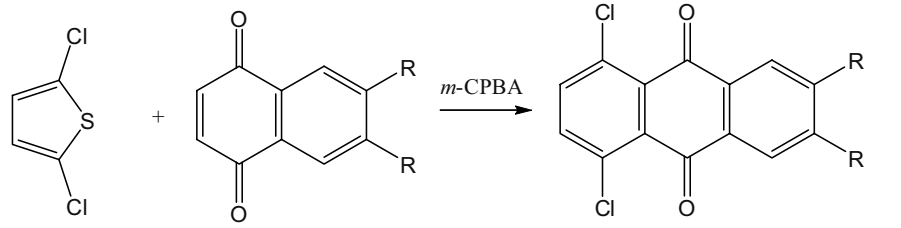
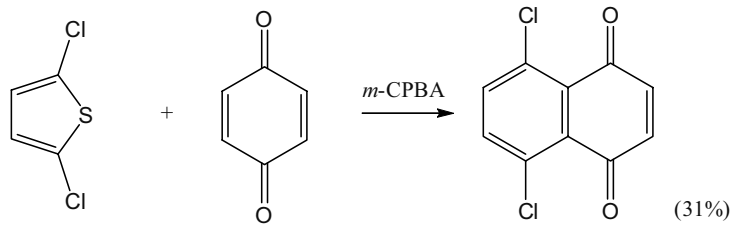


2 **3** **1a**

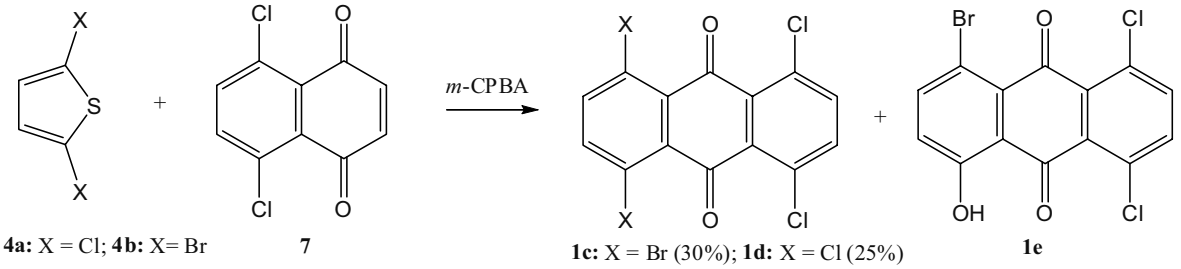
Scheme 1



4a **5a**: R = H; **5b**: R = CH_3 **1a**: R = H (37%); **1b**: R = CH_3 (38%)



4a **6** **7**



4a: X = Cl; **4b:** X= Br **7** **1c:** X = Br (30%); **1d:** X = Cl (25%) **1e**

Scheme 2

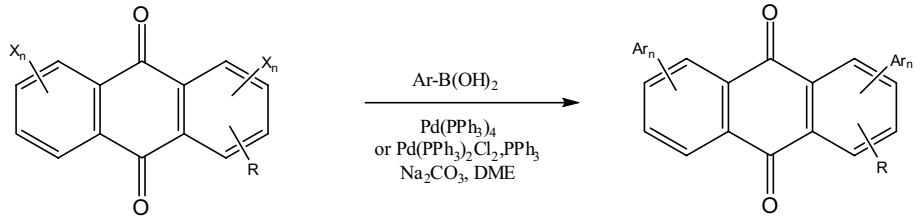
1,4-dibromo-5,8-dichloroanthraquinone (**1c**), all of the halo-groups exchanged with equal ease, so that a 5,8-diaryl-1,4-dichloroanthraquinone intermediate could not be isolated. Also, 1-bromo-5,8-dichloro-4-hydroxyanthraquinone (**1e**), which is a side-product in the oxidative cycloaddition of 2,5-dibromothiophene (**4b**) to 1,4-dichlorobenzoquinone (**7**), was transformed easily to 1-hydroxy-4,5,8-tris(4-methoxyphenyl)anthraquinone (**9k**) by a Suzuki–Miyaura cross-coupling reaction with 4-methoxyphenylboronic acid (**8a**). The use of $Pd(PPh_3)_4$, prepared *in situ* from $Pd(PPh_3)_2Cl_2$ and PPh_3, worked equally well.

In conclusion, we have shown that chloroanthraquinones undergo Suzuki–Miyaura coupling with the commercially available tetrakis(triphenylphosphine)palladium(0)[$Pd(PPh_3)_4$] and with the combination of $Pd(PPh_3)_2Cl_2$ and triphenylphosphine.

Experimental

CAUTION: Working with meta chloroperoxybenzoic acid at elevated temperatures is hazardous. The reactions should be carried out in a well-ventilated hood. Protection against an explosion should be set up. (The authors have not experienced any difficulties with these reactions. These measures are precautions.)

IR spectra were measured with JASCO IR-700, JASCO FTIR-6300 and Nippon Denshi JIR-AQ2OM machines. ^1H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer (^1H at 270 MHz and ^{13}C at 67.8 MHz). The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2 spectrometer [electron impact mode (EI), 70 eV or fast atom bombardment (FAB)]. Column chromatography was carried out on Wakogel C-300.

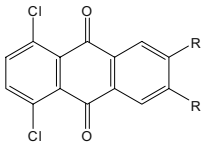
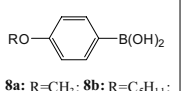
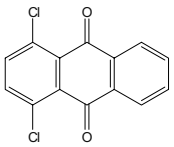
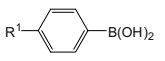
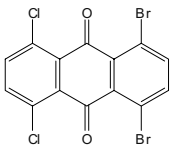
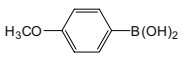
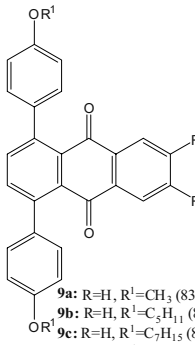
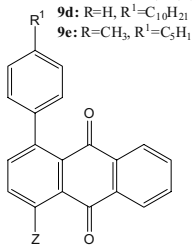
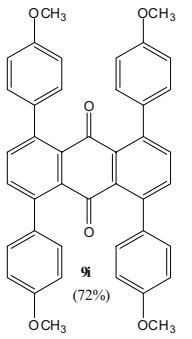


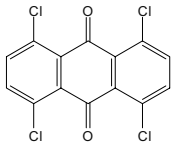
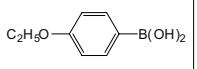
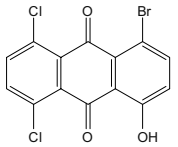
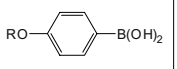
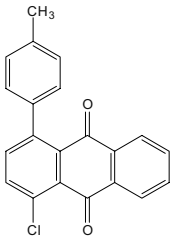
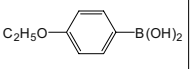
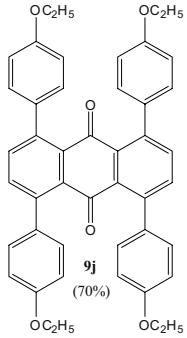
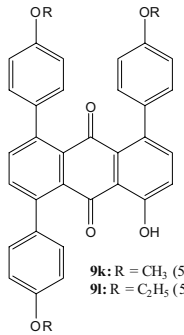
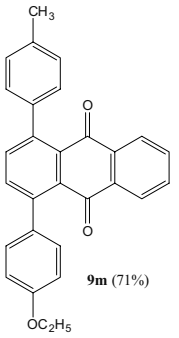
R = H, CH_3, X = Cl, Br; n = 0-2

Ar = aryl; R = H, CH_3; n = 0-2

Scheme 3

Table 1

Starting Material	Product
 **1a:** R = H; **1b:** R = CH_3	 **8a:** R=CH_3; **8b:** R=C_5H_{11}; **8c:** R=C_7H_{15}; **8d:** R=$C_{10}H_{21}$
 **1a**	 **8e:** R=CHO; **8f:** R=CH_3 **8g:** R=H
 **1d**	 **8a**
 **9a:** R=H, R^1=CH_3 (83%) **9b:** R=H, R^1=C_5H_{11} (85%) **9c:** R=H, R^1=C_7H_{15} (81%) **9d:** R=H, R^1=$C_{10}H_{21}$ (80%) **9e:** R=CH_3, R^1=C_5H_{11} (78%)	
 **9f:** R^1 = CHO; Z = *p*-C_6H_4-CHO (45%) **9g:** R^1 = CH_3; Z = Cl (53%) **9h:** R^1 = H; Z = C_6H_5 (68%)	
 **9i** (72%)	

Starting Material	Product
 **1e**	 **8e**
 **1f**	 **8a:** R = CH_3; **8e:** R = C_2H_5
 **9g**	 **8a**
 **9j** (70%)	
 **9k:** R = CH_3 (56%) **9l:** R = C_2H_5 (59%)	
 **9m** (71%)	

2,3-Dimethyl-5,8-naphthoquinone (**5b**) was prepared by the cycloaddition of 2,3-dimethylbuta-1,3-diene to *p*-benzoquinone under $EuCl_3$ catalysis (96 h, $ClCH_2CH_2Cl$, rt):[29] This reaction has been reported to proceed under $YbCl_3$ catalysis and we have found that it also proceeds in the presence of $EuCl_3$.With subsequent base catalysed enolisation[30] of the 4a,5,8,8a-tetrahydro-6,7-dimethyl-1,4-naphthoquinone which was formed and oxidation of the 6,7-dimethyl-5,8-dihydronaphthalene-1,4-diol (Ag_2O, Na_2SO_4, benzene)[31] to 6,7-dimethyl-5,8-dihydro-1,4-naphthoquinone, which in the last step was dehydrogenated (DDQ, benzene, reflux). [Here, we have used a biphasic system of 4N aq. NaOH and ether under ultrasonication. The enolisation has been reported to also go very well in the presence of triethylamine (Et_3N) or in the presence of acids such as HCl]. We used Ag2O in benzene as the oxidation agent as described for the oxidation of other hydroquinones to quinones. The reaction gives quantitative yields of 6,7-dimethyl-5,8-dihydro-1,4-naphthoquinone, when carried out at rt. Specifically for the transformation of 6,7-dimethyl-5,8-dihydronaphthalene-1,4-diol to 6,7-dimethyl-5,8-dihydro-1,4-naphthoquinone, the use of MnO_2 in acetone has been described.[31] *p*-Methoxyphenylboronic acid (**8a**) (TCI), *p*-formylphenylboronic acid (**8e**) (TCI), phenylboronic acid (**8g**) (TCI) and *p*-tolylboronic acid (**8f**) (Aldrich) were acquired commercially. *p*-Ethoxy-phenylboronic acids, **8c** and the homologous *p*-alkoxyphenylboronic acids **8b**–**d** were prepared from the corresponding *p*-alkoxy-bromobenzenes (a. *n*-BuLi, $B(OR)_3$, THF; b. HCl).[32]

1,4-Dichloroanthraquinone (**1a**);[18] *general procedure A:* A stirred solution of 2,5-dichlorothiophene (**4a**) (640 mg, 4.16 mmol) and 1,4-naphthoquinone (517 mg, 3.47 mmol) in $CHCl_3$ (20 mL) at 75 °C was treated with *m*-CPBA (70 w%, 4,76 g) in small portions. After 48 h, the mixture was cooled and poured into an aq. sat. Na_2CO_3 solution. After the mixture had been stirred for 15 min. at rt, it was extracted with chloroform (3 × 25 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (hexane/ether/

$CHCl_3$) to give **1a** (425 mg, 37%) as yellow needles, m.p. 187 °C; (Found: M^+, 275.9748. $C_{14}H_6O_2{}^{35}Cl_2$ requires M^+, 275.9745). δ_H (270 MHz, $CDCl_3$) 7.68 (2H, s), 7.77–7.81 (2H, m), 8.17–8.21 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 126.9 (2C, CH), 132.1 (2C, C_{quat}), 133.6 (2C, C_{quat}), 134.0 (2C, C_{quat}), 134.2 (2C, CH), 137.2 (2C, CH), 181.6 (2C, C_{quat}, CO). MS (EI, 70 eV) *m/z* (%) = 276 (M^+) (100).

1,4-Dichloro-6,7-dimethylanthraquinone (**1b**); *general procedure A:* Pale yellow needles, m.p. 194 °C; (Found: M^+, 304.0060. $C_{16}H_{10}O_2{}^{35}Cl_2$ requires M^+, 304.0058). δ_H (270 MHz, $CDCl_3$) 2.42 (6H, s, 2 CH_3), 7.64 (2H, s), 7.92 (2H, s); δ_C (67.8 MHz, $CDCl_3$) 20.3 (2C, CH_3), 127.7 (2C, CH), 129.6 (2C, C_{quat}), 131.6 (2C, C_{quat}), 133.8 (2C, C_{quat}), 140.0 (2C, CH), 144.3 (2C, C_{quat}), 181.7 (2C, C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) = 304 (M^+) (100).

1,4-Dibromo-5,8-dichloroanthraquinone (**1c**); *general procedure A*: Colourless solid, m.p. 210 °C; (Found: M^+, 433.7930. $C_{14}H_4O_2{}^{35}Cl^{37}Cl^{79}Br_2$ requires M^+, 433.7933). δ_H (270 MHz, $CDCl_3$) 7.60 (2H, s), 7.72 (2H, s); MS (EI, 70 eV) *m/z* (%) = 438 (3.3), 436 (9.2), 434 (9.6), 432 (3.9), 149 (34), 58 (100).

1,4-Bis(4-methoxyphenyl)anthraquinone (**9a**): *general procedure B*: A solution of **1a** (245 mg, 0.89 mmol), 4-methoxyphenylboronic acid (430 mg, 2.83 mmol), $Pd(PPh_3)_4$ (46 mg, $4.0 \cdot 10^{-5}$ mol) [or $Pd(PPh_3)_2Cl_2$ (30 mg, $4 \cdot 10^{-5}$ mol) and triphenylphosphine (30 mg, 0.11 mmol)] in a solvent mixture of DME (10 mL) and aq. Na_2CO_3 (2.32 g Na_2CO_3 in 15 mL H_2O, 6 mL) was kept at 70 °C for 18 h in an inert atmosphere. The solution was then cooled and poured into water (25 mL) and extracted with chloroform (3 × 15 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography of the residue on silica gel (hexane/$CHCl_3$/ether 3 : 1 : 1) gave **9a** (310 mg, 83%) as orange needles; m.p. 231 °C; (Found: M^+, 420.1367. $C_{28}H_{20}O_4$ requires M^+, 420.1362). ν_{max} (KBr/cm^{-1}) 2950, 2867, 1671, 1604, 1279, 1242, 1204, 1023, 971, 857, 830; δ_H (270 MHz, $CDCl_3$) 3.89 (6H, s, 2 OCH_3), 7.00 (4H, d, ^3J = 8.6 Hz), 7.26 (4H, d, ^3J = 8.6 Hz), 7.53 (2H, s), 7.68–7.72 (2H, m), 8.06–8.09 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 55.2 (2C, OCH_3), 113.7 (4C, CH), 126.7 (2C, CH), 129.3 (4C, CH), 133.7 (2C, CH), 132.9 (2C, C_{quat}), 134.1 (2C, C_{quat}), 134.5 (2C, C_{quat}), 136.6 (2C, CH), 143.6 (2C, C_{quat}), 158.9 (2C, C_{quat}), 184.3 (2C, C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 420 (M^+) (100), 389 (32), 333 (18), 313 (13), 276 (17). UV-Vis (CH3CN, nm) λmax 253 (59610), 271 (sh, 23890), 313 (13280).

1,4-Bis(4-pentoxyphenyl)anthraquinone (**9b**); general procedure B: Rose-coloured solid; m.p. 202 °C; (Found: MH^+, 533.2697. $C_{36}H_{37}O_4$ requires MH^+, 533.2692 [FAB]). ν_{max} (KBr/cm^{-1}) 2953, 2869, 1604, 1515, 1385, 1375, 1320, 1281, 859, 828; δ_H (270 MHz, $CDCl_3$) 0.96 (6H, t, ^3J = 7.0 Hz), 1.46 (8H, m), 1.84 (4H, m), 4.04 (4H, t, ^3J = 6.5 Hz), 6.99 (4H, d, ^3J = 8.6 Hz), 7.24 (4H, d, ^3J = 8.6 Hz), 7.53 (2H, s), 7.67–7.71 (2H, m), 8.06–8.09 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 14.1 (2C, CH_3), 22.5 (2C, CH_2), 28.3 (2C, CH_2), 29.1 (2C, CH_2), 67.9 (2C, OCH_2), 114.2 (4C, CH), 126.7 (2C, C_{quat}), 129.2 (4C, CH), 132.9 (2C, C_{quat}), 133.6 (2C, CH), 134.2 (2C, C_{quat}), 136.6 (2C, CH), 143.6 (2C, C_{quat}), 158.5 (2C, C_{quat}), 184.3 (2C, C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 533 (MH^+) (100), 391 (36). Calcd for $C_{36}H_{36}O_4$: C, 81.17; H, 6.81. Found: C, 80.79; H, 6.77%.

1,4-Bis(4-heptoxyphenyl)anthraquinone (**9c**); *general procedure B*: Rose-coloured solid, m.p. 205 °C; (Found: MH^+, 589.3313. $C_{40}H_{45}O_4$ requires MH^+, 589.3318 [FAB]). ν_{max} (KBr/cm^{-1}) 2950, 2867, 1673, 1604, 1515, 1318, 1280, 1244, 1206, 1023, 970, 858, 828; δ_H (270 MHz, $CDCl_3$) 0.92 (6H, t, ^3J = 6.8 Hz, 2 CH_3), 1.34–1.56 (16H, m), 1.83 (4H, m), 4.03 (4H, t, ^3J = 6.7 Hz, 2 OCH_2), 6.98 (4H, d, ^3J = 8.6 Hz), 7.24 (4H, d, ^3J = 8.6 Hz), 7.53 (2H, s), 7.67–7.70 (2H, m), 8.06–8.09 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 14.1 (2C, CH_3), 22.6 (2C, CH_2), 26.1 (2C, CH_2), 29.1 (2C, CH_2), 29.4 (2C, CH_2), 31.8 (2C, CH_2), 67.9 (2C, OCH_2), 114.1 (4C, CH), 126.7 (2C, C_{quat}), 129.2 (4C, CH), 132.9 (2C, C_{quat}), 133.6 (2C, CH), 134.2 (2C, CH), 134.3 (2C, C_{quat}), 136.6 (2C, CH), 143.6 (2C, C_{quat}), 158.5 (2C, C_{quat}), 184.3 (2C, C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 589 (MH^+) (30).

1,4-Bis(4-decyloxyphenyl)anthraquinone (**9d**); *general procedure B*: Orange-yellow solid, m.p. 197 °C; (Found: MH^+, 673.4277. $C_{46}H_{57}O_4$ requires MH^+, 673.4275 [FAB]). ν_{max} (KBr/cm^{-1}) 2950, 2867, 1673, 1604, 1515, 1280, 1243, 1204, 1023, 971, 857, 828; δ_H (270 MHz, $CDCl_3$) 0.89 (6H, t, ^3J = 7.0 Hz, 2 CH_3), 1.29–1.55 (28H, m), 1.78 – 1.86 (4H, m), 4.03 (4H, t, ^3J 6.5 Hz, 2 OCH_2), 6.98 (4H, d, ^3J = 8.6 Hz), 7.24 (4H, d, ^3J = 8.6 Hz), 7.53 (2H, s), 7.67–7.71 (2H, m), 8.06–8.09 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 14.1 (2C, CH_3), 22.7 (2C, CH_2), 26.1 (2C, CH_2), 29.3 (2C, CH_2), 29.4 (2C, CH_2), 29.5 (2C, CH_2), 29.6 (2C, CH_2), 29.7 (2C, CH_2), 31.9 (2C, CH_2), 67.9 (2C, OCH_2), 114.2 (4C, CH), 126.7 (2C, C_{quat}), 129.2 (4C, CH), 132.9 (2C, C_{quat}), 133.6 (2C,CH), 134.2 (2C, CH), 134.3 (2C, C_{quat}), 136.6 (2C, CH), 143.6 (2C, C_{quat}), 158.5 (2C, C_{quat}), 184.3 (2C, C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 673 (MH^+) (8), 672 (M^+) (10).

1,4-Bis(4-pentoxyphenyl)-6,7-dimethylanthraquinone (**9e**); *general procedure B*: Pale orange needles, m.p. 215 °C; (Found: MH^+, 561.3006. $C_{38}H_{41}O_4$ requires MH^+, 561.3005 [FAB]). ν_{max} (KBr/cm^{-1}) 2950, 2867, 1673, 1604, 1515, 1458, 1389, 1373, 1320, 1279, 1242, 1204, 1023, 971, 857, 828; δ_H (270 MHz, $CDCl_3$) 0.96 (6H, t, ^3J = 7.0 Hz, 2 CH_3), 1.81–1.86 (4H, m), 1.41–1.54 (8H, m), 2.35 (6H, s, 2 CH_3), 4.03 (4H, t, ^3J = 6.5 Hz), 6.98 (4H, d, ^3J = 8.6 Hz), 7.24 (4H, d, ^3J = 8.6 Hz), 7.51 (2H, s), 7.83 (2H, s); δ_C (67.8 MHz, $CDCl_3$) 14.1 (2C), 20.2 (2C), 22.5 (2C), 28.3 (2C), 29.1 (2C), 67.9 (2C), 114.1 (4C), 127.6 (2C), 129.2 (4C), 132.1 (2C), 133.0 (2C), 134.4 (2C), 136.4 (2C), 143.4 (2C), 143.6 (2C), 158.4 (2C), 184.5 (2C); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 561 (MH^+) (28), 419 (7.4), 326 (10). Calcd for $C_{38}H_{40}O_4$: C, 81.40; H, 7.19. Found: C, 80.87; H, 7.14%.

1,4-Bis(4-formylphenyl)anthraquinone (**9f**); *general procedure B*: Yellow solid; m.p. 243 °C; (Found: M^+, 417.1130. $C_{28}H_{17}O_4$ requires M^+, 417.1127). ν_{max} (KBr/cm^{-1}) 3068, 1687, 1677, 1602, 1380, 1319, 1259, 1211, 1168, 1091, 958, 827, 730; δ_H (270 MHz, $CDCl_3$) 7.51 (4H, d, ^3J = 8.1 Hz), 7.60 (2H, s), 7.73–7.76 (2H, m), 8.02 (4H, d, ^3J = 8.1 Hz), 8.06–8.09 (2H, m), 10.1 (2H, s, 2 CHO); δ_C (67.8 MHz, $CDCl_3$) 127.0 (2C, CH), 128.5 (4C, CH), 129.7 (4C, CH), 132.6 (2C, C_{quat}), 133.5 (2C, C_{quat}), 134.2 (2C, CH), 135.2 (2C, C_{quat}), 135.9 (2C, CH), 143.3 (2C, C_{quat}), 148.6 (2C, C_{quat}), 183.5 (2C, CO), 191.92 (2C, CHO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 417 (MH^+) (3.4).

1-Chloro-4-(4-methylphenyl)anthraquinone (**9g**); *general procedure B*: Yellow solid; m.p. 224 °C; (Found: 333.0685. $C_{21}H_{14}O_2{}^{35}Cl$ requires M^+, 333.0682). ν_{max} (KBr/cm^{-1}) 3001, 1672; δ_H (270 MHz, $CDCl_3$) 2.45 (3H, s, CH_3), 7.15 (2H, d, ^3J = 8.4 Hz), 7.27 (2H, d, ^3J = 8.4 Hz), 7.46 (1H, d, ^3J = 8.1 Hz), 7.69–7.80 (2H, m), 7.75 (1H, d, ^3J = 8.1 Hz), 8.03–8.06 (1H, m), 8.22–8.26 (1H, m); δ_C (67.8 MHz, $CDCl_3$) 21.3 (CH_3), 126.7 (CH), 126.9 (CH), 127.7 (2C, CH), 127.9 (C_{quat}), 129.0 (2C, CH), 131.2 (C_{quat}), 133.7 (C_{quat}), 133.9 (CH), 134.0 (CH), 134.1 (C_{quat}), 134.3 (C_{quat}), 136.4 (CH), 137.1 (C_{quat}), 137.3 (CH), 138.5 (C_{quat}), 143.8 (C_{quat}), 182.6 (C_{quat}, CO), 183.3 (C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 333 (MH^+) (4.4). Calcd for $C_{21}H_{14}O_2Cl$: C, 75.79; H, 3.94. Found: C, 75.86; H, 3.99%.

1,*4-Diphenylanthraquinone* (**9h**);[12,33] *general procedure B*: Yellow solid; (Found: MH^+, 361.1232. $C_{26}H_{17}O_2$ requires MH^+, 361.1229 [FAB]). ν_{max} (KBr/cm^{-1}) 3002, 1673, 758; δ_H (270 MHz, $CDCl_3$) 7.29–7.35 (4H, m), 7.43–7.48 (6H, m), 7.56 (2H, s), 7.66–7.71 (2H, m), 8.05–8.08 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 126.8 (2C, CH), 127.2 (2C, CH), 127.9 (4C, CH), 128.2 (4C, CH), 132.7 (2C, C_{quat}), 133.7 (2C, CH), 134.0 (2C, C_{quat}), 136.4 (2C, CH), 142.3 (2C, C_{quat}), 144.1 (2C, C_{quat}), 184.0 (2C, C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 361 (MH^+) (5.6). UV-Vis (CH3CN, nm) λmax 253 (36370), 269 (sh, 19190), 288 (sh, 7320).

1,4,5,8-Tetrakis(4-methoxyphenyl)anthraquinone (**9i**); *general procedure B*: Using 4-methoxyphenylboronic acid (860 mg, 5.66 mmol) and $Pd(PPh_3)_4$ (60 mg, 5.2×10^{-5} mol) [or $Pd(PPh_3)_2Cl_2$ (40 mg, $5.2 \cdot 10^{-5}$ mol) and triphenylphosphine (37 mg, 0.14 mmol)], in DME (15 mL) and aq. Na_2CO_3 (9 mL): pale orange solid; m.p. 251 °C; (Found: MH^+, 633.2286. $C_{42}H_{33}O_6$ requires MH^+, 633.2277 [FAB]). ν_{max} (KBr/cm^{-1}) 1671, 1608, 1575, 1514, 1460, 1328, 1291, 1247, 1029, 831; δ_H (270 MHz, $CDCl_3$) 3.84 (12H, s, 4 OCH_3), 6.85 (8H, d, ^3J = 8.4 Hz), 7.21 (8H, d, ^3J = 8.4 Hz), 7.48 (4H, s); δ_C (67.8 MHz, $CDCl_3$) 55.2 (4C, OCH_3), 113.4 (8C, CH), 130.3 (8C, CH), 131.9 (4C, C_{quat}), 134.5 (4C, CH), 135.5 (4C, C_{quat}), 140.3 (4C, C_{quat}), 159.0 (4C, C_{quat}), 188.4 (2C, C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 633 (MH^+) (1.0).

1,4,5,8-Tetrakis(4-ethoxyphenyl)anthraquinone (**9j**); *general procedure*: Analogous to the synthesis of **9i**: yellow orange solid; m.p. 307 °C; (Found: MH^+, 689.2910. $C_{46}H_{41}O_6$ requires MH^+, 689.2903 [FAB]). ν_{max} (KBr/cm^{-1}) 3002, 1673, 1245, 1205, 831; δ_H (270 MHz, $CDCl_3$) 1.42 (12H, t, ^3J = 7.0 Hz, 4 CH_3), 4.06 (8H, q, ^3J = 7.0 Hz, 4 OCH_2), 6.82 (8H, d, ^3J = 8.6 Hz), 7.19 (8H, d, ^3J = 8.6 Hz), 7.47 (4H, s); δ_C (67.8 MHz, $CDCl_3$) 14.9 (4C, CH_3), 63.4 (4C, OCH_2), 113.9 (8C, CH), 130.3 (8C, CH), 131.7 (4C, C_{quat}), 134.4 (4C, CH), 135.6 (4C, C_{quat}), 140.3 (4C, C_{quat}), 158.4 (4C, C_{quat}), 188.5 (2C, C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 689 (MH^+) (27).

1-Hydroxy-4,5,8-tris(4-methoxyphenyl)anthraquinone (**9k**); *general procedure B*: Analogous to the synthesis of **9i**: reddish solid; m.p. 238 °C; (Found: MH^+, 543.1805. $C_{35}H_{27}O_6$ requires MH^+, 543.1808 [FAB]). ν_{max} (KBr/cm^{-1}) 3430 (bs, OH), 3054, 3002, 1673, 1515, 1461, 1295, 1243, 1205, 1179, 1031, 827, 754; δ_H (270 MHz, $CDCl_3$) 3.82 (3H, s, OCH_3), 3.83 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 6.84 (2H, d, ^3J = 8.6 Hz), 6.87 (2H, d, ^3J = 8.6 Hz), 7.00 (2H, d, ^3J = 8.6 Hz), 7.14–7.29 (7H, m), 7.46 (1H, d, ^3J = 7.8 Hz), 7.47 (1H, d, ^3J = 8.4 Hz), 7.56 (1H, d, ^3J = 7.8 Hz), 12.21 (s, 1H, OH); δ_C (67.8 MHz, $CDCl_3$) 55.2 (2C, OCH_3), 55.3 (OCH_3), 113.6 (6C,

CH), 117.1 (C_{quat}), 122.1 (CH), 129.4 (2C, CH), 129.9 (2C, CH), 130.2 (2C, CH), 131.0 (C_{quat}), 132.2 (C_{quat}), 132.5 (C_{quat}), 134.0 (C_{quat}), 134.1 (C_{quat}), 134.2 (C_{quat}), 136.0 (CH), 136.4 (CH), 136.8 (C_{quat}), 139.5 (CH), 142.0 (C_{quat}), 142.9 (C_{quat}), 158.8 (C_{quat}), 159.0 (2C, C_{quat}), 161.0 (C_{quat}), 188.0 (C_{quat}, CO), 189.5 (C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 543 (MH^+) (1.4).

1-Hydroxy-4,5,8-tris(4-ethoxyphenyl)anthraquinone (**9l**); *general procedure B*: Analogous to the synthesis of **9i**: red-orange needles; m.p. 259 °C; (Found: M^+, 585.2270. $C_{38}H_{33}O_6$ requires M^+, 585.2277). ν_{max} (KBr/cm^{-1}) 3430 (bs, OH), 3054, 3002, 1671, 1513, 1460, 1295, 1243, 1205, 1178, 1030, 825, 752; δ_H (270 MHz, $CDCl_3$) 1.44 (6H, t, ^3J = 7.0 Hz, 2 CH_3), 1.48 (3H, t, ^3J = 7.0 Hz, CH_3), 4.05 (2H, q, ^3J = 7.0 Hz, OCH_2), 4.06 (2H, q, ^3J = 7.0 Hz, OCH_2), 4.13 (2H, q, ^3J = 7.0 Hz, OCH_2), 6.83 (2H, d, ^3J = 8.6 Hz), 6.85 (2H, d, ^3J = 8.6 Hz), 6.99 (2H, d, ^3J = 8.6 Hz), 7.14–7.29 (7H, m), 7.46 (1H, d, ^3J = 7.8 Hz), 7.47 (1H, d, ^3J = 8.4 Hz), 7.56 (1H, d, ^3J = 7.8 Hz), 12.20 (s, 1H, OH); δ_C (67.8 MHz, $CDCl_3$) 14.8 (2C, CH_3), 14.9 (CH_3), 63.3 (OCH_2), 63.4 (2C, OCH_2), 114.1 (6C, CH), 117.1 (C_{quat}), 122.1 (CH), 129.4 (2C, CH), 129.9 (2C, CH), 130.2 (2C, CH), 131.0 (C_{quat}), 132.2 (C_{quat}), 132.5 (C_{quat}), 134.0 (C_{quat}), 134.1 (C_{quat}), 134.2 (C_{quat}), 136.0 (CH), 136.4 (CH), 136.8 (C_{quat}), 139.5 (CH), 142.0 (C_{quat}), 142.9 (C_{quat}), 158.2 (C_{quat}), 159.0 (2C, C_{quat}), 161.0 (C_{quat}), 188.0 (C_{quat}, CO), 189.5 (C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 585 (MH^+) (14), 539 (3.5).

1-(4-Ethoxyphenyl)-4(4-methylphenyl)anthraquinone (**9m**); *general procedure B*: Yellow-orange solid, m.p. 247 °C; (Found: MH^+, 419.1651. $C_{29}H_{23}O_3$ requires MH^+, 419.1647). δ_H (270 MHz, $CDCl_3$) 1.47 (3H, t, ^3J = 7.0 Hz, CH_3), 2.46 (3H, s, CH_3), 4.12 (2H, q, ^3J = 7.0 Hz, OCH_2), 6.99 (2H, d, ^3J = 8.6 Hz), 7.21 (2H, d, ^3J = 7.6 Hz), 7.27 (2H, d, ^3J = 8.6 Hz), 7.28 (2H, d, ^3J = 7.6 Hz), 7.51 (1H, d, ^3J = 8.1 Hz), 7.55 (1H, d, ^3J = 8.1 Hz), 7.67–7.70 (2H, m), 8.06–8.09 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 14.9 (CH_3), 21.4 (CH_3), 63,4 (OCH_2), 114.1 (2C, CH), 127.8 (2C, CH), 128.9 (2C, CH), 129.2 (2C, CH), 132.8 (C_{quat}), 132.9 (C_{quat}), 133.6 (2C, CH), 134.1 (C_{quat}), 134.2 (C_{quat}), 134.3 (C_{quat}), 136.4 (CH), 136.6 (CH), 136.8 (C_{quat}), 139.4 (C_{quat}), 143.7 (C_{quat}), 143.8 (C_{quat}), 158.3 (C_{quat}), 184.2 (C_{quat}, CO), 184.3 (C_{quat}, CO); FAB, 3-nitrobenzyl alcohol) *m/z* (%) 419 (MH^+) (100). Calcd for $C_{29}H_{22}O_3$: C, 83.23; H, 5.30. Found: C, 83.15; H, 5.27%.

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