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Article

Brominated Thiophenes as Precursors in the Preparation of Brominated and Arylated Anthraquinones

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Abstract: Brominated anthraquinones can be synthesized directly from bromothiophenes when these are reacted with 1,4-naphthoquinones in the presence of *meta*-chloroperoxybenzoic acid. The bromoanthraquinones are versatile building blocks in the preparation of arylated anthraquinones and of extended π -systems with interspersed anthraquinone units.

Keywords: Anthraquinone; Oxidative cycloaddition; Suzuki cross coupling; UV spectroscopy.

1. Introduction

Arylated anthraquinones **1** (Figure 1) have elicited interest in Physical Organic Chemistry [1,2] due to the interaction of the attached aryl groups with the π -system of the anthraquinone core, as evidenced in the corresponding UV and luminescence spectra [4,5], in the redox behavior of the molecules [2,3], and their NMR shift values. Specifically, the interaction of the substituents on the anthraquinone C=O function has been subjected to investigation [1]. In practical applications, arylated anthraquinones have

also been used as stabilizers of light-modulating fluids such as of fluids comprised of liquid polybenzyltoluenes [6]. Our interest in these molecules is in the study of their electrochemical behavior. In the following, a new direct preparation of arylated anthraquinones from bromothiophenes is presented.

Figure 1. General Structure of arylated Anthraquinones.



A number of synthetic routes to arylated anthraquinones are known. It has been shown by Bergmann *et al.* [7,8] that [4+2]-cycloaddition reactions of phenylbutadienes **2** with either 1,4-naphthoquinone (**3a**) or with *p*-benzoquinone give 1-phenylanthraquinone (**4a**) and 1,4-diphenylanthraquinone (**4b**) (from 1,4-naphthoquinone) and 1,5-diphenylanthraquinone and 1,4,5,8-tetraphenylanthraquinone (from *p*-benzoquinone), respectively (Scheme 1). The Diels-Alder approach has also been used for the synthesis of arenoanthraquinones such as of benz[a]anthracene-7,12-diones [9]. For the preparation of 1,4-diarylanthraquinones, Gautrot *et al.* [2] started from 1,4-dihydroxy-9,10-anthraquinone, which was transformed into its bistriflate **5**[3] and subsequently subjected to coupling reaction with arylboronic acids (Scheme 2) [2].

Scheme 1. Aryl substituted anthraquinones by [4+2]-cycloaddition reaction [7,8].



Coupling reactions have also been carried out with 1-diazoanthraquinone, which was prepared from the corresponding 1-aminoanthraquinone [10]. In order to have a versatile strategy to prepare aryl substituted anthraquinones in hand, we wanted to use haloanthraquinones as key intermediates, which we could subsequently transform into the target compounds by Suzuki cross coupling reactions. Again, preparative routes to haloanthraquinones are known. Thus, Battegay and Claudin prepared a number of dibromoanthraquinones from the corresponding diaminoanthraquinones by Sandmeyer reactions [11] and sulfonic acid functionalities could also be transformed to bromo substituents at elevated temperatures [11].

Scheme 2. 1,4-Diphenylanthraquinone by Suzuki-type coupling with aryl triflates [2].



Scheme 3. Bromination of an anthraquinone-disulfonic acid to a dibromoanthraquinone [11].



Based on our good experience in using thiophene *S*-oxides, either *in situ* [12-14] or in purified form [15-17], as dienes in the preparation of multi-functionalised arenes [18,19], we decided to utilize halogenated thiophene *S*-oxides as transient intermediates to prepare bromoanthraquinones. While most thiophenes themselves are unreactive or react sluggishly [20-22] and thiophene *S*,*S*-dioxides [23] often necessitate high temperatures to participate in [4+2]-cycloaddition reactions, thiophene *S*-oxides have been found to be reactive dienes in Diels-Alder type reactions. While a number of thiophene *S*-oxides [15-17,24-28], especially those with electron donating substituents have been isolated, thiophene *S*-oxides can be reacted *in situ* [12-14]. Thiophene *S*-oxides undergo cycloaddition reactions, when thiophenes are oxidized in the presence of a dienophile.



Scheme 4. In situ preparation and cycloaddition of a dibrominated thiophene S-oxide [30].

From our understanding, in halogenated thiophenes, the sulfur is more difficult to oxidize with peracids or with hydrogen peroxide than in the corresponding donor substituted thiophenes. On the other hand, oxidized halothiophenes – halothiophene *S*-oxides and halothiophene *S*,*S*-dioxides – should be more reactive dienes than their electron-donor substituted counterparts. Therefore, in all likelihood, halothiophene *S*-oxides would have to be used *in situ*. In fact, Torssell has reported on one example of a successful oxidative cycloaddition of a monobrominated thiophene with 1,4-naphthoquinone (**3a**), where the cycloadduct was produced in poor yield [29]. Our own work [30] on the oxidative cycloaddition of brominated and chlorinated thiophenes (eg, **8a**) to maleimides (eg, to **9**) indicated that halothiophene *S*-oxides can be produced *in situ* and can be reacted with electron poor dienophiles (Scheme 4).

2. Results and Discussion

In the present case, a variety of brominated thiophenes **8** were submitted to oxidative cycloaddition reactions with 1,4-naphthoquinones **3**. Heated solutions of thiophene **8** and 1,4-naphthoquinone (**3a**) were treated with *meta*-chloroperbenzoic acid in small portions over 48 h. Under these conditions, cycloaddition between intermediately formed thiophene *S*-oxides and 1,4-naphthoquinone **3** takes place, where the formulated, primary sulfoxy-bridged cycloadduct **11** loses the SO-bridge with concomitant aromatization (Scheme 5). The bromoanthraquinones **7** can be obtained, albeit in very moderate yield (Table 1). A number of more polar side products formed, depending on the substrate. One important type of side product are hydroxyanthraquinones **12** (Figure 2). That bromothiophene *S*-oxides are involved here, has been shown in the reaction under analogous conditions of 2,5-dibromothiophene (**8a**), 2,3,4,5-tetrabromothiophene (**8e**) and 2,5-dichlorothiophene with *N*-phenylmaleimide (**9**), where halogenated 7-thiabicyclo[2.2.1]heptene *S*-oxides are oxidized further to halothiophene *S*,*S*-dioxides, cycloaddition reactions may be expected to proceed as electron poor thiophene *S*,*S*-dioxides have been found to undergo cycloaddition reactions readily [31-33], so that under the present conditions, halothiophene *S*,*S*-dioxides can also contribute to the reaction.



Scheme 5. Preparation of bromoanthraquinones by oxidative cycloaddition of thiophenes to quinines.

Table 1. Preparation of bromoanthraquinones by oxidative cycloaddition of thiophenes to quinines.



Figure 2. Hydroxyanthraquinones as side products in the oxidative cycloaddition reactions of thiophenes to quinines.



The brominated anthraquinones obtained were subjected to Suzuki-Miyaura cross coupling reactions with a variety of arylboronic acids. Either $Pd(PPh_3)_4/PPh_3$ or $Pd(PPh_3)_2Cl_2/PPh_3$ was used as catalyst in a biphasic reaction medium of DME and aq. Na₂CO₃. The corresponding arylated anthraquinones were obtained in good yield. In the case of the 1-aryl-2,4-dibromoanthraquinones, the first aryl group enters selectively into the 4-position, *ie.*, away from the aryl function already present in the anthraquinone system (Figure 3). Prolonged reaction times and an excess of arylboronic acid make the 2-position accessible, also. In this manner it is possible to provide anthraquinones with three different aryl substituents in positions 1, 2 and 4.

Figure 3. Order of entry of further aryl substituents by Suzuki-Miyaura cross-coupling reaction.



Equally interesting is the fact that chlorinated anthraquinones exchange the chloro-substituent readily, and thus they undergo Suzuki-Miyaura cross coupling reactions with ease, too, even when using a common catalyst such as $Pd(PPh_3)_4$. Thus, 1,4-dibromo-5,8-dichloroanthraquinone (**7c**) can be converted to the 1,4,5,8-tetra-arylanthraquinone **4t** (see continued Table 2), using $Pd(PPh_3)_4$ as a catalyst, as can be 1-bromo-5,8-dichloro-4-hydroxyanthraquinone (**12b**) to **13** (Scheme 7).



Table 2. Arylated anthraquinones by Suzuki-Miyaura coupling of dibromoanthraquinones.



4n (Ar=Ph-*p*-Me, Ar¹=Ph-*p*-OMe) **4s** (Ar = Ph, Ar¹=Ph-*p*-OMe, **4o** (Ar=Ph, Ar¹=Ph-*p*-OPr) Ar² = Ph-*p*-OPr) (63%)





The anthraquinones obtained show spectral data typical for this species of compounds. Thus, in the mass spectra, many of the anthraquinones prepared above have $[M^+-CO]$ and $[M^+-2CO]$ fragmentation peaks that are typical for anthraquinones [34,35]. In their carbon NMR spectra, the carbonyl functions resonate at 184 – 185 ppm. In 1,2-aryl-substituted anthraquinones, the influence of the proximity of the π -system of one aryl group on the protons of the other can be noted by a high-field shift.

The UV-VIS spectra of most of the solutions of the arylated anthraquinones in acetonitrile show at least three distinct bands, usually associated with π - π^* transitions [36,37]. The strongest band, normally called a 'benzoid band' [37], is located at around $\lambda = 250$ nm for most of the compounds, which is in accordance to data gathered from other substituted anthraquinones. It could be shown that the substitution pattern of the aryl substituent in the anthraquinone has little influence on the wavelength of this absorption band. Methylation of the C6/C7 positions in the anthraquinone core leads to a shift of $\Delta \lambda = 10$ nm, where $\lambda_{max} = 263$ nm. A longer-wave $\pi - \pi^*$ -transition (often called a 'quinoid band' [37]) can be found as a shoulder at $\lambda = 265 - 270$ nm for the 1,4-diarylated anthraquinones. Again, there is very little influence of the substitution pattern of the aryl groups at C1 and C4 on the wavelength of this band. Also, 1,2,4-triarylated anthraquinones show this band within the same wavelength region. Where identifiable, this transition is shifted to lower energy for 6,7methylated anthraquinones (eg., for 4k, $\lambda = 279$ nm). A shift to higher wavelength is also found for the β -bromo substituted anthraquinone **4n** ($\lambda = 275$ nm). Two further π - π^* transitions can be noted, although they cannot be identified for all compounds measured. The first is found at around $\lambda = 300$ nm. The π - π^* transition with the longest wavelength can be noted at $\lambda = 350 - 380$ nm for the compounds measured. Substituent dependence of this transition has been reported for monosubstituted anthraquinones [36,37], and also in our case a substituent-dependence can be noted.

3. Experimental Section

Warning: Working with meta-chloroperoxybenzoic acid at elevated temperatures is hazardous. The reactions should be carried out in a well-ventilated hood. Protections against an explosion should be set up. (The authors themselves have not experienced any difficulties with these reactions. The above measures may be seen as protective precautions).

General

Melting points were measured on a Yanaco microscopic hot stage and are uncorrected. IR spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM machines. ¹H- and ¹³C-NMR spectra were recorded with a JEOL EX-270 (¹H at 270 MHz and ¹³C at 67.8 MHz) and JEOL Lambda 400 spectrometer (¹H at 395 MHz and ¹³C at 99.45 MHz). The chemical shifts are relative to TMS (solvent CDCl₃, 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 300.

The oxidative cycloaddition reactions were carried out with commercially available metachloroperbenzoic acid (m-CPBA, 70-75 w%, Acros), which was used without further purification. Pd(PPh₃)₄ (TCI), Pd(PPh₃)₂Cl₂ (TCI), 2,5-dibromothiophene (8a) (Aldrich), 2-methylthiophene (TCI), 2-bromothiophene (Aldrich), thiophene (Wako) and 2,5-dichlorothiophene (Aldrich) were acquired commercially. 2,3,4,5-Tetrabromothiophene (8e) (thiophene, Br₂, CHCl₃) [38], 2-bromo-5-methylthiophene (8f) (2-methylthiophene, NBS, CHCl₃, AcOH), 2-bromo-5-phenylthiophene (8b) and 2bromo-5-(p-tolyl)thiophene (a. 2-bromothiophene, Aryl-B(OH)₂, Pd(PPh₃)₄, DME, aq. Na₂CO₃; b. N-bromosuccinimide [NBS], CHCl₃, AcOH) [39] were prepared analogous to known procedures. 2,4-Dibromo-5-arylthiophenes, 8c and 8d, were synthesized by brominating 2-arylthiophenes using an excess [40] of NBS. 5,8-Dichloro-1,4-naphthoquinone (3c) was prepared by oxidative cycloaddition of 2,5-dichlorothiophene to p-benzoquinone [29]. 2,3-Dimethyl-5,8-naphthoquinone (3b) was prepared by cycloaddition of 2,3-dimethylbuta-1,3-diene to p-benzoquinone under EuCl₃ catalysis (96 h, ClCH₂CH₂Cl, rt) [41] with subsequent base catalysed enolisation [42,43] of the 4a,5,8,8a-tetrahydro-6,7-dimethyl-1,4-naphthoquinone formed and oxidation of the 6,7-dimethyl-5,8-dihydronaphthalene-1,4-diol (Ag₂O, Na₂SO₄, benzene) [44] to 6,7-dimethyl-5,8-dihydro-1,4-naphthoquinone, which in a last step was dehydrogenated (DDQ, benzene, reflux). p-Methoxyphenylboronic acid (TCI), omethoxyphenylboronic acid (TCI), phenylboronic acid (TCI), and p-tolylboronic acid (Aldrich) were acquired commercially. p-Ethoxy- and p-proposyphenylboronic acids were prepared from the corresponding *p*-alkoxy-bromobenzenes (a. *n*-BuLi, B(OEt)₃, THF; b. HCl) [45].

1,4-Dibromoanthraquinone (**7a**) [11,46]. To a stirred solution of dibromothiophene (**8a**, 1.00 g, 4.16 mmol) and 1,4-naphthoquinone (**3a**, 517 mg, 3.47 mmol) in CHCl₃ (20 mL) at 75 °C was added *m*-CPBA (70w%, 4.76 g) in small portions. After 48 h, the mixture was cooled and poured into an aq. sat. Na₂CO₃ solution. After the mixture was stirred for 15 min. at rt, it was extracted with chloroform (3 X 25 mL). The organic phase was dried over anhydrous MgSO₄ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (hexane/ether/CHCl₃ 8:1:1) to give **7a** (370 mg, 29%); $\delta_{\rm H}$ (270 MHz, CDCl₃) 7.78 – 7.81 (2H, m), 7.81 (2H, s), 8.20 – 8.23 (2H, m); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 122.1 (2C, C_{quat}), 126.9 (2C, CH), 133.5 (2C, C_{quat}), 133.6 (2C, C_{quat}), 134.2 (2C, CH), 140.6 (2C, CH), 181.6 (2C, C_{quat}, CO); MS (EI, 70 eV) m/z (%) 368 ([⁸¹Br₂]M⁺) (50), 366 ([⁸¹Br⁷⁹Br]M⁺) (100), 364 ([⁷⁹Br₂]M⁺) (51), 340 ([⁸¹Br₂]M⁺-CO) (15), 338 ([⁸¹Br⁷⁹Br]M⁺-CO) (30), 336 ([⁷⁹Br₂]M⁺ - CO) (15), 312 ([⁸¹Br₂]M⁺-2CO) (10), 310 ([⁸¹Br⁷⁹Br]M⁺-2CO) (21), 308 ([⁷⁹Br₂]M⁺-2CO) (11), 287 (11), 285 (11), 231 (15), 229 (15), 150 (73). HRMS Found: 365.8716. Calcd. for C₁₄H₆O₂⁷⁹Br⁸¹Br: 365.8715.

Selected data of other bromoanthraquinones

1,4-Dibromo-6,7-dimethylanthraquinone (**7b**). Yellow solid; $\delta_{\rm H}$ (270 MHz, CDCl₃) 2.42 (6H, s, 2 CH₃), 7.77 (s, 2H), 7.94 (s, 2H); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 20.3 (2C, CH₃), 122.1 (2C, C_{quat}), 127.8 (2C, CH), 131.5 (2C, C_{quat}), 133.7 (2C, C_{quat}), 140.4 (2C, CH), 144.5 (2C, C_{quat}), 181.8 (2C, C_{quat}, CO); MS (EI, 70 eV) m/z (%) 396 ([⁸¹Br₂]M⁺, 50), 394 ([⁸¹Br⁷⁹Br]M⁺, 100), 392 ([⁷⁹Br₂]M⁺, 50), 368 ([⁸¹Br₂]M⁺-CO, 12), 366 ([⁸¹Br⁷⁹Br]M⁺ - CO, 25), 364 ([⁷⁹Br₂]M⁺ - CO, 13). HRMS Found: 393.9033. Calcd. for C₁₆H₁₀O₂⁷⁹Br⁸¹Br: 393.9028.

1,4-Dibromo-5,8-dichloroanthraquinone (**7c**). Colorless solid; $\delta_{\rm H}$ (270 MHz, CDCl₃) 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). HRMS Found: 433.7930. Calcd. for C₁₄H₄O₂³⁵Cl³⁷Cl⁷⁹Br₂: 433.7933.

2,4-*Dibromo-1*-(4-*methylphenyl*)*anthraquinone* (**7f**). Yellow solid, mp. 183 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 2.47 (3H, s, CH₃), 7.01 (2H, d, ${}^{3}J$ = 8.1 Hz), 7.31 (2H, d, ${}^{3}J$ = 8.1 Hz), 7.50 – 7.80 (2H, m), 7.96 – 8.00 (1H, m), 8.20 – 8.23 (1H, m), 8.38 (1H, s); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 21.6, 122.1, 126.9, 127.6 (2C), 128.0, 129.0, 129.2 (2C), 131.3, 133.2, 133.4, 133.5, 134.0, 134.1, 137.3, 137.4, 143.6, 143.9, 182.1, 182.2; MS (EI, 70 eV) *m/z* (%) 456 ([${}^{81}{\rm Br}^{79}{\rm Br}$]M⁺) (18), 299 (100). HRMS Found: 455.9188. Calcd. for C₂₁H₁₂O₂⁸¹Br⁷⁹Br: 455.9185.

1,2,3,4-Tetrabromoanthraquinone (**7g**) [47]. Orange solid; mp. 200 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 7.76 – 7.79 (2H, m), 8.11 – 8.14 (2H, m); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 125.0 (2C, C_{quat}), 126.8 (2C, CH), 133.6 (2C, C_{quat}), 134.3 (2C, CH), 139.0 (2C, C_{quat}), 181.8 (2C, C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 527 ([⁸¹Br₃⁷⁹Br]MH⁺) (0.2), 526 ([⁸¹Br₃⁷⁹Br]M⁺) (0.1), 525 ([⁸¹Br₂⁷⁹Br₂]MH⁺) (0.3), 524 ([⁸¹Br₂⁷⁹Br₂]M⁺) (0.2), 523 ([⁸¹Br⁷⁹Br₃]MH⁺) (0.2). HRMS Found: 524.6993. Calcd. for C₁₄H₅O₂⁷⁹Br₂⁸¹Br₂: 524.6983 (MH⁺, FAB).

1,2,3,4-Tetrabromo-6,7-dimethylanthraquinone (**7h**). Slowly solidifying yellow oil; $\delta_{\rm H}$ (270 MHz, CDCl₃) 2.42 (6H, s, 2 CH₃), 7.86 (2H, s); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 20.3 (2C, CH₃), 127.7 (2C), 131.5 (2C), 134.5 (2C), 135.4 (2C), 138.7 (2C), 144.5 (2C), 181.8 (2C, CO); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 552 ([⁸¹Br₂⁷⁹Br₂]M⁺) (0.2)

1-Bromo-4-methylanthraquinone (**7i**) [48]. Beige colored solid; $\delta_{\rm H}$ (270 MHz, CDCl₃) 2.79 (3H, s, CH₃), 7.36 (1H, d, ${}^{3}J$ = 8.4 Hz), 7.74 – 7.78 (2H, m), 7.87 (1H, d, ${}^{3}J$ = 8.4 Hz), 8.15 – 8.24 (2H, m); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 23.6 (CH₃), 120.2 (C_{quat}), 126.6 (CH), 126.9 (CH), 127.8 (C_{quat}), 132.9 (C_{quat}), 133.8 (2C, CH), 134.4 (C_{quat}), 137.9 (CH), 140.2 (CH), 140.4 (C_{quat}), 141.9 (C_{quat}), 182.9 (C_{quat}, CO), 184.5 (C_{quat}, CO); MS (EI, 70 eV) *m*/*z* (%) 302 ([⁸¹Br]M⁺, 97), 300 ([⁷⁹Br]M⁺, 100), 274 ([⁸¹Br]M⁺-CO, 15), 272 ([⁷⁹Br]M⁺-CO, 15), 193 (59), 165 (90). HRMS Found: 301.9764. Calcd. for C₁₅H₉O₂⁸¹Br: 301.9767. Found: 299.9789. Calcd. for C₁₅H₉O₂⁷⁹Br: 299.9786.

1-Bromo-4,6,7-trimethylanthraquinone (**7j**). Yellow solid, mp. 194 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 2.42 (6H, s, 2 CH₃), 2.73 (3H, s, CH₃), 7.33 (1H, d, ³*J* = 8.4 Hz), 7.82 (1H, d, ³*J* = 8.4 Hz), 7.91 (1H, s),

7.95 (1H, s); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 20.2 (2C, CH₃), 20.7 (CH₃), 120.0 (C_{quat}), 127.4 (CH), 127.8 (CH), 131.7 (C_{quat}), 131.8 (C_{quat}), 132.6 (C_{quat}), 134.1 (C_{quat}), 137.7 (CH), 140.0 (CH), 141.8 (C_{quat}), 143.8 (C_{quat}, 2C), 183.2 (C_{quat}, CO), 184.8 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 330 ([⁸¹Br]M⁺) (100), 328 ([⁷⁹Br]M⁺) (100), 315 ([⁸¹Br]M⁺-CH₃) (38), 313 ([⁷⁹Br]M⁺-CH₃) (39), 302 ([⁸¹Br]M⁺-CO) (26), 300 ([⁸¹Br]M⁺-CO) (28), 287 ([⁸¹Br]M⁺-CH₃-CO) (26), 285 ([⁷⁹Br]M⁺-CO-CH₃) (26), 221 (55), 178 (83). HRMS Found: 328.0097. Calcd. for C₁₇H₁₃O₂⁷⁹Br: 328.0099.

1,4-Bis(*4-methylphenyl*)*anthraquinone* (**4c**) [49]. Under an inert atmosphere, a solution of **7a** (324 mg, 0.89 mmol), 4-methylphenylboronic acid (385 mg, 2.83 mmol), Pd(PPh₃)₂Cl₂ (30 mg, 4.0^{-10⁻⁵} mol) and triphenylphosphine (30 mg, 0.11 mmol) in a solvent mixture of DME (10 mL) and aq. Na₂CO₃ (2.32 g Na₂CO₃ in 15 mL H₂O, 6 mL) was kept at 65 °C for 18h. Thereafter the cooled solution was poured into water (25 mL) and extracted with chloroform (3 x 15 mL). The combined organic phase was dried over anhydrous MgSO₄ and was concentrated *in vacuo*. Column chromatography of the residue on silica gel (hexane/CHCl₃/ether 3:1:1) gave **4c** (293 mg, 85%) as an orange solid; mp. 265 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 2.45 (6H, s, 2 CH₃), 7.18 (4H, d, ³*J* = 7.6 Hz), 7.27 (4H, d, ³*J* = 7.6 Hz), 7.53 (2H, s), 7.65 – 7.70 (2H, m), 8.05 - 8.09 (2H, m); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 21.3 (2C, CH₃), 126.7 (2C, CH), 127.9 (4C, CH), 128.9 (4C, CH), 132.8 (2C, C_{quat}), 133.7 (2C, CH), 134.1 (2C, C_{quat}), 136.5 (2C, CH), 136.8 (2C, C_{quat}), 139.4 (2C, C_{quat}), 143.9 (2C, C_{quat}), 184.2 (2C, CO); MS (EI, 70 eV) *m/z* (%) = 388 (M⁺) (83), 373 (M⁺-CH₃) (100), 179 (40). HRMS Found: 388.1469. Calcd. for C₂₈H₂₀O₂: 388.1463. Found: C, 84.36; H, 5.12%. Calcd. for C₂₈H₂₀O₂:H₂O₂: C, 84.61; H, 5.33%. UV-Vis spectrum (CH₃CN, nm) λ_{max} 253 (44700), 268 (sh, 21310), 298 (9350), 358 (2470).

Selected data for other arylated anthraquinones

1,4-Diphenylanthraquinone (**4b**) [2,50] Yellow solid; $\delta_{\rm H}$ (270 MHz, CDCl₃) 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); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 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). HRMS Found: 361.1232. Calcd. for C₂₆H₁₇O₂: 361.1229 (MH⁺, FAB); UV-Vis spectrum (CH₃CN, nm) λ_{max} 253 (36370), 269 (sh, 19190), 288 (sh, 7320).

1,4-Bis(4-methoxyphenyl)anthraquinone (**4e**). Orange needles; mp. 231 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 3.89 (6H, s, 2 OCH₃), 7.00 (4H, d, ${}^{3}J$ = 8.6 Hz), 7.26 (4H, d, ${}^{3}J$ = 8.6 Hz), 7.53 (2H, s), 7.68 – 7.72 (2H, m), 8.06 – 8.09 (2H, m); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 55.2 (2C, OCH₃), 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). HRMS Found: 420.1367. Calcd. for C₂₈H₂₀O₄: 420.1362; UV-Vis spectrum (CH₃CN, nm) $\lambda_{\rm max}$ 253 (59610), 271 (sh, 23890), 313 (13280).

1,4-Bis(*4-ethoxyphenyl*)*anthraquinone* (**4f**). Orange needles; mp. 239 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 1.47 (3H, t, CH₃, ${}^{3}J$ = 7.0 Hz), 4.12 (2H, q, OCH₂, ${}^{3}J$ = 7.0 Hz), 6.98 (4H, d, ${}^{3}J$ = 8.4 Hz), 7.24 (4H, d, ${}^{3}J$ =

8.4 Hz), 7.53 (2H, s), 7.67 – 7.70 (2H, m), 8.05 – 8.09 (2H, m); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 14.9 (2C, CH₃), 63.4 (2C, OCH₂), 114.2 (4C, CH), 126.7 (2C, CH), 129.3 (4C, CH), 132.9 (2C, C_{quat}), 133.6 (2C, CH), 134.2 (2C, C_{quat}), 134.3 (2C, C_{quat}), 136.6 (2C, CH), 143.6 (2C, C_{quat}), 158.3 (2C, C_{quat}), 184.3 (2C, C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* (%) 449 (MH⁺) (7.5). HRMS Found: 449.1749. Calcd. for C₃₀H₂₅O₄: 449.1753. Found: C, 79.57; H, 5.47%. Calcd. for C₃₀H₂₄O₄·0.2H₂O: C, 79.70; H, 5.44%; UV-Vis spectrum (CH₃CN, nm) λ_{max} 253 (49430), 269 (sh, 21220), 314 (10910).

1,4-Diphenyl-6,7-dimethylanthraquinone (**4g**). Yellow needles, mp. 232 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 2.34 (6H, s, 2 CH₃), 7.30 – 7.34 (4H, m), 7.43 – 7.50 (6H, m), 7.53 (2H, s), 7.82 (2H, s); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 20.1 (2C, CH₃), 127.0 (2C, CH), 127.7 (2C, CH), 127.9 (4C, CH), 128.1 (4C, CH), 132.0 (2C, C_{quat}), 132.9 (2C, C_{quat}), 136.1 (2C, CH), 142.5 (2C, C_{quat}), 143.7 (2C, C_{quat}), 143.9 (2C, C_{quat}), 184.1 (2C, C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 389 (MH⁺) (5.3). HRMS Found: 389.1539. Calcd. for C₂₈H₂₁O₂: 389.1542 (FAB). Found: C, 85.80; H, 5.18%. Calcd. for C₂₈H₂₀O₂·0.2H₂O: C, 85.78; H, 5.24%; UV-Vis spectrum (CH₃CN, nm) λ_{max} 263 (41490), 338 (4480).

1,4-Bis(*4-heptoxyphenyl*)-6,7-*dimethylanthraquinone* (**4h**). Beige solid; mp. 181 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 0.92 (6H, t, ${}^{3}J$ = 6.2 Hz, 2 CH₃), 1.34 – 1.60 (16H, m), 1.78 – 1.86 (4H, m), 2.35 (6H, s, 2 CH₃), 4.03 (4H, t, ${}^{3}J$ = 6.5 Hz), 6.98 (4H, d, ${}^{3}J$ = 8.6 Hz), 7.23 (4H, d, ${}^{3}J$ = 8.6 Hz), 7.50 (2H, s), 7.83 (2H, s); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 14.1 (2C, CH₃), 20.2 (2C, CH₂), 22.7 (2C, CH₂), 26.1 (2C, CH₂), 29.1 (2C, CH₂), 29.4 (2C, CH₂), 31.8 (2C, CH₂), 67.9 (2C, OCH₂), 114.1 (4C, CH), 127.7 (2C, CH), 129.2 (4C, CH), 132.1 (2C, C_{quat}), 133.0 (2C, C_{quat}), 134.4 (2C, C_{quat}), 136.4 (2C, C_{quat}), 143.5 (2C, C_{quat}), 158.4 (2C, C_{quat}), 184.5 (2C, C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 617 (MH⁺) (0.5). HRMS Found: 617.3629. Calcd. for C₄₂H₄₉O₄: 617.3631 (MH⁺, FAB)

1,4-Bis(*4-nonyloxyphenyl*)-6,7-*dimethylanthraquinone* (**4i**). Yellow-orange solid; mp. 176 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 0.88 (6H, t, ${}^{3}J$ = 4.3 Hz, 2 CH₃), 1.30 (20H, m), 1.44 – 1.49 (4H, m), 1.78 – 1.85 (4H, m), 2.35 (6H, s, 2 CH₃), 4.03 (4H, t, ${}^{3}J$ = 6.5 Hz), 6.98 (4H, d, ${}^{3}J$ = 8.6 Hz), 7.23 (4H, d, ${}^{3}J$ = 8.6 Hz), 7.50 (2H, s), 7.83 (2H, s); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 14.1 (2C, CH₃), 20.2 (2C, CH₂), 22.7 (2C, CH₂), 26.1 (2C, CH₂), 29.3 (2C, CH₂), 29.4 (2C, CH₂), 29.5 (2C, CH₂), 29.6 (2C, CH₂), 31.9 (2C, CH₂), 67.9 (2C, OCH₂), 114.1 (4C, CH), 127.6 (2C, CH), 129.2 (4C, CH), 132.1 (2C, C_{quat}), 133.0 (2C, C_{quat}), 134.4 (2C, C_{quat}), 136.4 (2C, C_{quat}), 143.5 (2C, C_{quat}), 158.4 (2C, C_{quat}), 184.5 (2C, C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* (%) 673 (MH⁺) (100). HRMS Found: 673.4254. Calcd. for C₄₆H₅₇O₄: 673.4257 (MH₊, FAB).

1-(4-Methoxyphenyl)-4,6,7-trimethylanthraquinone (**4j**). Solid; $\delta_{\rm H}$ (270 MHz, CDCl₃) 2.30 (3H, s, CH₃), 2.40 (3H, s, CH₃), 2.86 (3H, s, CH₃), 3.87 (3H, s, OCH₃), 6.96 (2H, d, ${}^{3}J$ = 8.6 Hz), 7.19 (2H, d, ${}^{3}J$ = 8.6 Hz), 7.40 (1H, d, ${}^{3}J$ = 7.8 Hz), 7.50 (1H, d, ${}^{3}J$ = 7.8 Hz), 7.80 (1H, s), 7.94 (1H, s); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 20.1 (CH₃), 20.2 (CH₃), 23.8 (CH₃), 55.2 (OCH₃), 113.5 (2C, CH), 127.4 (CH), 127.5 (CH), 129.1 (2C, CH), 132.1 (C_{quat}), 132.2 (C_{quat}), 132.9 (C_{quat}), 133.0 (C_{quat}), 135.1 (C_{quat}), 136.7 (CH), 136.8 (CH), 141.1 (C_{quat}), 142.5 (C_{quat}), 143.3 (C_{quat}), 143.4 (C_{quat}), 158.6 (C_{quat}), 184.7 (C_{quat}, CO), 185.9 (C_{quat}, CO); MS (EI, 70 eV) m/z (%) 356 (M⁺) (84), 355 (100), 325 (32), 312 (14). HRMS

Found: 356.1413. Calcd. for C₂₄H₂₀O₃: 356.1412; UV-Vis spectrum (CH₃CN, nm) λ_{max} 263 (49630), 278 (sh, 19470), 339 (4880).

1-(4-Propoxyphenyl)-4,6,7-trimethylanthraquinone (**4k**). Yellow solid; mp. 215 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 1.07 (3H, t, ${}^{3}J$ = 7.6 Hz, CH₃), 1.56 (3H, s, CH₃), 1.85 (2H, dt, ${}^{3}J$ = 7.6 Hz, ${}^{3}J$ = 6.5 Hz), 2.35 (3H, s, CH₃), 2.41 (3H, s, CH₃), 3.99 (2H, t, ${}^{3}J$ = 6.5 Hz, OCH₂), 6.95 (2H, d, ${}^{3}J$ = 8.6 Hz), 7.17 (2H, d, ${}^{3}J$ = 8.6 Hz), 7.41 (1H, d, ${}^{3}J$ = 7.8 Hz), 7.50 (1H, d, ${}^{3}J$ = 7.8 Hz), 7.81 (1H, s), 7.94 (1H, s); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 10.6 (CH₃), 20.1 (CH₃), 20.2 (CH₃), 22.7 (CH₂), 23.8 (CH₃), 69.4 (OCH₂), 114.1 (2C, CH), 127.5 (CH), 127.6 (CH), 129.1 (2C, CH), 132.1 (C_{quat}), 132.2 (C_{quat}), 132.8 (C_{quat}), 133.0 (C_{quat}), 134.8 (C_{quat}), 136.7 (CH), 136.8 (CH), 141.1 (C_{quat}), 142.6 (C_{quat}), 143.3 (C_{quat}), 143.4 (C_{quat}), 158.2 (C_{quat}), 184.7 (C_{quat}, CO), 185.9 (C_{quat}, CO); MS (EI, 70 eV) m/z (%) 384 (M⁺) (68), 341 (M⁺-(CH₂)₂CH₃) (100). HRMs Found: 384.1718. Calcd. for C₂₆H₂₄O₃: 384.1725 UV-Vis spectrum (CH₃CN, nm) λ_{max} 263 (57850), 279 (sh, 20490), 330 (5580, ill-defined).

1-(4-Methoxyphenyl)-4-methylanthraquinone (**4l**) [50]. Yellow-orange needles; mp. 221 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 2.88 (3H, s, CH₃), 3.88 (3H, s, OCH₃), 6.97 (2H, d, ${}^{3}J$ = 8.6 Hz), 7.20 (2H, d, ${}^{3}J$ = 8.6 Hz), 7.44 (1H, d, ${}^{3}J$ = 8.1 Hz), 7.53 (1H, d, ${}^{3}J$ = 8.1 Hz), 7.67 – 7.75 (2H, m), 8.04 – 8.07 (1H, m), 8.19 – 8.23 (1H, m); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 23.8 (CH₃), 55.2 (OCH₃), 113.6 (2C, CH), 126.6 (CH), 129.2 (2C, CH), 132.8 (C_{quat}), 132.9 (C_{quat}), 133.5 (CH), 133.6 (CH), 134.1 (C_{quat}), 134.2 (C_{quat}), 134.8 (C_{quat}), 137.0 (CH, 3C), 141.3 (C_{quat}), 142.6 (C_{quat}), 158.7 (C_{quat}), 184.6 (C_{quat}, CO), 184.7 (C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 329 (MH⁺) (14). HRMS Found: 329.1183. Calcd. for C₂₂H₁₇O₃: 329.1178 (MH⁺, FAB). Found: C, 79.89; H, 4.73%. Calcd. for C₂₂H₁₆O₃ 0.1H₂O: C, 80.03; H, 4.91%; UV-Vis spectrum (CH₃CN, nm) λ_{max} 253 (38343), 269 (sh, 15440), 302 (5400), 354 (2505).

1-(4-Methoxyphenyl)-4-phenylanthraquinone (**4m**). Beige solid; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 391 (MH⁺) (7.6). HRMS Found: 391.1340. Calcd. for C₂₇H₁₉O₃: 391.1334 (MH⁺, FAB); UV-Vis spectrum (CH₃CN, nm) λ_{max} 253 (38520), 271 (sh, 18390), 306 (7980).

2-Bromo-1-(4-methylphenyl)-4-(4-methoxyphenyl)anthraquinone (**4n**). Orange needles; mp. 208 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 2.49 (3H, s, CH₃), 3.89 (3H, s, OCH₃), 7.01 (2H, d, ${}^{3}J$ = 8.9 Hz), 7.08 (2H, d, ${}^{3}J$ = 8.1 Hz), 7.27 (2H, d, ${}^{3}J$ = 8.9 Hz), 7.33 (2H, d, ${}^{3}J$ = 8.1 Hz), 7.66 – 7.70 (2H, m), 7.92 (1H, s), 8.00 – 8.07 (2H, m); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 485 ([81 BrM]H⁺) (7.2), 484 (81 BrM⁺) (8.0), 483 ([79 BrM]H⁺, 8.9), 482 (79 BrM⁺) (6.0). HRMS Found: 483.0595. Calcd. for C₂₈H₂₀O₃⁷⁹Br (MH⁺, FAB); UV-Vis spectrum (CH₃CN, nm) λ_{max} 258 (37150), 275 (sh, 16870), 309 (8100).

2-Bromo-1-phenyl-4-(4-propoxyphenyl)anthraquinone (**4o**). Yellow solid; mp. 183 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 1.08 (3H, t, ${}^{3}J = 7.3$ Hz, CH₃), 1.86 (2H, dt, ${}^{3}J = 7.3$ Hz, ${}^{3}J = 6.5$ Hz), 4.01 (2H, t, ${}^{3}J = 6.5$ Hz, OCH₂), 7.00 (2H, d, ${}^{3}J = 8.4$ Hz), 7.17 – 7.21 (2H, m), 7.25 (2H, d, ${}^{3}J = 8.4$ Hz), 7.48 – 7.54 (3H, m), 7.66 – 7.70 (2H, m), 7.93 (1H, s), 7.98 – 8.02 (1H, m), 8.04 – 8.07 (1H, m); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 10.6 (CH₃), 22.7 (CH₂), 69.5 (OCH₂), 114.3 (2C, CH), 126.7 (CH), 126.9 (CH), 127.4 (CH), 127.9 (2C, CH), 128.3 (2C, CH), 129.2 (2C, CH), 131.7 (C_{quat}), 132.3 (C_{quat}), 132.9 (C_{quat}), 133.6 (C_{quat}), 133.8 (CH), 133.9 (CH), 134.3 (C_{quat}), 141.0 (CH), 141.2 (C_{quat}), 142.9 (C_{quat}), 145.1 (C_{quat}), 155.8 (C_{quat}), 183.1 (C_{quat}, CO), 183.7 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 498 ([⁸¹Br]M⁺) (100), 496

 $([^{79}Br]M^{+})$ (98), 455 $([^{81}Br]M^{+}-(CH_{2})_{2}CH_{3})$ (84), 453 $([^{79}Br]M^{+}-(CH_{2})_{2}CH_{3})$ (81). HRMS Found: 496.0677. Calcd. for $C_{29}H_{21}O_{3}^{-79}Br$: 496.0674.

I-(4-Methylphenyl)-2,4-bis(4-ethoxyphenyl)anthraquinone (**4q**). Yellow needles, mp. 230 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 1.37 (3H, t, ${}^{3}J = 7.0$ Hz, CH₃), 1.46 (3H, t, ${}^{3}J = 7.0$ Hz, CH₃), 2.36 (3H, s, CH₃), 3.97 (2H, d, ${}^{3}J = 7.0$ Hz, OCH₂), 4.11 (2H, d, ${}^{3}J = 7.0$ Hz, OCH₂), 6.67 (2H, d, ${}^{3}J = 8.9$ Hz), 6.91 – 6.99 (6H, m), 7.08 (2H, d, ${}^{3}J = 7.8$ Hz), 7.29 (2H, d, ${}^{3}J = 8.9$ Hz), 7.57 (1H, s), 8.00 – 8.04 (2H, m), 8.06 – 8.09 (2H, m); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 14.7 (CH₃), 14.9 (CH₃), 21.4 (CH₃), 63.3 (OCH₂), 63.4 (OCH₂), 113.7 (2C, CH), 114.1 (2C, CH), 126.5 (CH), 126.7 (CH), 128.6 (2C, CH), 129.2 (2C, CH), 129.4 (2C, CH), 130.7 (2C, CH), 131.3 (Cquat), 132.0 (Cquat), 133.4 (CH), 133.5 (CH), 134.1 (Cquat), 134.2 (Cquat), 134.3 (Cquat), 134.5 (Cquat), 135.9 (Cquat), 137.0 (Cquat), 138.9 (CH), 141.6 (Cquat), 143.4 (Cquat), 147.4 (Cquat), 158.0 (Cquat), 158.3 (Cquat), 184.1 (Cquat, CO), 184.9 (Cquat, CO); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 539 (MH⁺) (31). HRMS Found: 539.2219. Calcd. for C₃₇H₃₁O₄: 539.2222. Found: C, 82.26; H, 5.62%. Calcd. for C₃₇H₃₀O₄: C, 82.50; H, 5.61%; UV-Vis spectrum (CH₃CN, nm) λ_{max} 250 (57030), 268 (sh, 31850), 298 (sh, 19440), 359 (6340).

1-(4-Methylphenyl)-2,4-bis(4-methoxyphenyl)anthraquinone (**4r**). Orange solid; mp. 230 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 2.36 (3H, s, CH₃), 3.75 (3H, s, OCH₃), 3.88 (3H, s, OCH₃), 6.69 (2H, d, ${}^{3}J$ = 8.6 Hz), 6.93 – 6.96 (4H, m), 6.99 (2H, d, ${}^{3}J$ = 8.6 Hz), 7.08 (2H, d, ${}^{3}J$ = 8.6 Hz), 7.31 (2H, d, ${}^{3}J$ = 8.6 Hz), 7.57 (1H, s), 7.65 – 7.69 (2H, m), 8.00 – 8.11 (2H, m); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 21.4 (CH₃), 55.1 (OCH₃), 55.2 (OCH₃), 113.1 (2C, CH), 113.6 (2C, CH), 126.5 (CH), 126.7 (CH), 128.6 (2C, CH), 129.2 (2C, CH), 129.4 (2C, CH), 130.7 (2C, CH), 131.4 (C_{quat}), 132.2 (C_{quat}), 133.5 (CH), 133.6 (CH), 134.1 (C_{quat}), 134.3 (C_{quat}), 134.5 (C_{quat}), 134.6 (C_{quat}), 135.9 (C_{quat}), 137.0 (C_{quat}), 138.9 (CH), 141.6 (C_{quat}), 143.4 (C_{quat}), 147.4(C_{quat}), 158.6 (C_{quat}), 158.9 (C_{quat}), 184.1 (C_{quat}, CO), 184.9 (C_{quat}, CO). MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 511 (MH⁺) (13). HRMS Found: 511.1905. Calcd. for C₃₅H₂₇O₄: 511.1909 (MH⁺, FAB); UV-Vis spectrum (CH₃CN, nm) λ_{max} 250 (50 085), 269 (sh, 26790), 300 (sh, 15980), 365 (4960).

2-(4-Methoxyphenyl)-1-phenyl-4-(4-propoxyphenyl)anthraquinone (**4s**). Light yellow needles; mp. 233 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 1.08 (3H, t, ${}^{3}J$ = 7.6 Hz, CH₃), 1.86 (2H, tt, ${}^{3}J$ = 7.6 Hz, ${}^{3}J$ = 6.2 Hz), 3.74 (3H, s, OCH₃), 4.00 (t, 2H, ${}^{3}J$ = 6.2 Hz, OCH₂), 6.68 (2H, d, ${}^{3}J$ = 8.6 Hz), 6.94 (2H, d, ${}^{3}J$ = 8.6 Hz), 6.99 (2H, d, ${}^{3}J$ = 8.6 Hz), 7.27 – 7.30 (3H, m), 7.04 – 7.08 (2H, m), 7.30 (2H, d, ${}^{3}J$ = 8.6 Hz), 7.59 (1H, s), 7.65 – 7.71 (2H, m), 8.00 – 8.03 (1H, m), 8.07 – 8.10 (1H, m); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 10.6 (CH₃), 22.7 (CH₂), 55.1 (OCH₃), 69.4 (OCH₂), 113.2 (CH, 2C), 114.2 (CH, 2C), 126.5 (CH), 126.6 (CH), 126.7 (CH), 127.7 (CH, 2C), 129.4 (CH, 4C), 130.7 (CH, 2C), 131.4 (C_{quat}), 132.6 (C_{quat}), 133.5 (CH), 133.6 (CH), 134.1 (C_{quat}), 134.2 (C_{quat}), 134.4 (C_{quat}), 138.9 (C_{quat}), 140.2 (C_{quat}), 141.5 (C_{quat}), 143.7 (C_{quat}), 147.3 (C_{quat}), 158.6 (C_{quat}), 158.7 (C_{quat}), 184.1 (C_{quat}, CO), 184.8 (C_{quat}, CO). MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 525 (MH⁺) (9), 524 (M⁺) (11). HRMS Found: 524.1990. Calcd. For C₃₆H₂₈O₄: 524.1988. UV-Vis spectrum (CH₃CN, nm) λ_{max} 249 (22370), 268 (sh, 12560), 298 (sh, 7490), 382 (2320).

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1,4,5,8-Tetrakis(4-methoxyphenyl)anthraquinone (**4t**). Pale orange solid; mp. 251 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 3.84 (12H, s, 4 OCH₃), 6.85 (8H, d, ³J = 8.4 Hz), 7.21 (8H, d, ³J = 8.4 Hz), 7.48 (4H, s); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 55.2 (4C, OCH₃), 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). HRMS Found: 633.2286. Calcd. for C₄₂H₃₃O₆: 633.2277 (MH⁺, FAB).

1,2,3,4-Tetrakis(*4-heptoxyphenyl*)*anthraquinone* (**4u**). Slowly crystallizing orange oil; $\delta_{\rm H}$ (270 MHz, CDCl₃) 0.88 (12H, t, ${}^{3}J = 7.0$ Hz, 4 CH₃), 1.28 – 1.31 (32H, m), 1.66 (4H, m), 1.72 (4H, m), 2.32 (6H, s, 2 CH₃), 3.74 (4H, t, ${}^{3}J = 6.5$ Hz), 3.90 (4H, t, ${}^{3}J = 6.5$ Hz), 6.39 (4H, d, ${}^{3}J = 8.6$ Hz), 6.52 (4H, d, ${}^{3}J = 8.6$ Hz), 6.70 (4H, d, ${}^{3}J = 8.6$ Hz), 6.86 (4H, d, ${}^{3}J = 8.6$ Hz), 7.78 (2H, s); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 14.0 (2C, CH₃), 14.1 (2C, CH₃), 20.1 (2C), 22.5 (2C), 22.6 (2C), 25.9 (2C), 26.1 (2C), 29.0 (2C), 29.1 (2C), 29.2 (2C), 29.4 (2C), 31.7 (2C), 31.8 (2C), 67.7 (4C, OCH₂), 112.9 (4C), 113.5 (4C), 128.5 (2C), 130.2 (4C), 131.2 (2C), 131.6 (4C), 132.4 (2C), 132.8 (2C), 133.2 (2C), 142.6 (2C), 143.2 (2C), 148.3 (2C), 157.2 (2C), 156.7 (2C), 184.8 (2C, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 997 (MH⁺) (100). HRMS Found: 997.6355. Calcd. for C₆₈H₈₅O₅: 997.6346.

1-Hydroxy-4,5,8-tris(*4-methoxyphenyl*)*anthraquinone* (**13**). Reddish solid; mp. 238 °C; $\delta_{\rm H}$ (270 MHz, CDCl₃) 3.82 (3H, s, OCH₃), 3.83 (3H, s, OCH₃), 3.90 (3H, s, OCH₃), 6.84 (2H, d, ³*J* = 8.6 Hz), 6.87 (2H, d, ³*J* = 8.6 Hz), 7.00 (2H, d, ³*J* = 8.6 Hz), 7.14 – 7.29 (7H, m), 7.46 (1H, d, ³*J* = 7.8 Hz), 7.47 (1H, d, ³*J* = 8.4 Hz), 7.56 (1H, d, ³*J* = 7.8 Hz), 12.21 (s, 1H, OH); $\delta_{\rm C}$ (67.8 MHz, CDCl₃) 55.2 (2C, OCH₃), 55.3 (OCH₃), 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). HRMS Found: 543.1805. Calcd. for C₃₅H₂₇O₆: 543.1808 (MH⁺, FAB).

4. Conclusions

Bromoanthraquinones can be synthesized by an oxidative cycloaddition to suitably substituted naphthoquinones. Bromoanthraquinones can be reacted further to arylated anthraquinones via Suzuki-Miyaura coupling. Initial results show that also chloro substituted anthraquinones undergo Suzuki reactions in presence of the commercially available Pd(PPh₃)₄. The UV-VIS spectra of most of the solutions of the arylated anthraquinones in acetonitrile show at least three distinct bands associated with π - π * transitions. Substituent dependence of the longest wavelength transition of the three bands can be noted.

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