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[A0024]

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

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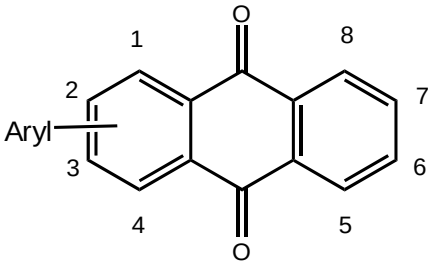
Abstract: Halogenated anthraquinones can be synthesized directly from halogenated thiophenes, when these are reacted with 1,4-naphthoquinones in the presence of *meta* chloroperoxybenzoic acid. The halogenated anthraquinones are versatile building blocks in the preparation of arylated anthraquinones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

INTRODUCTION

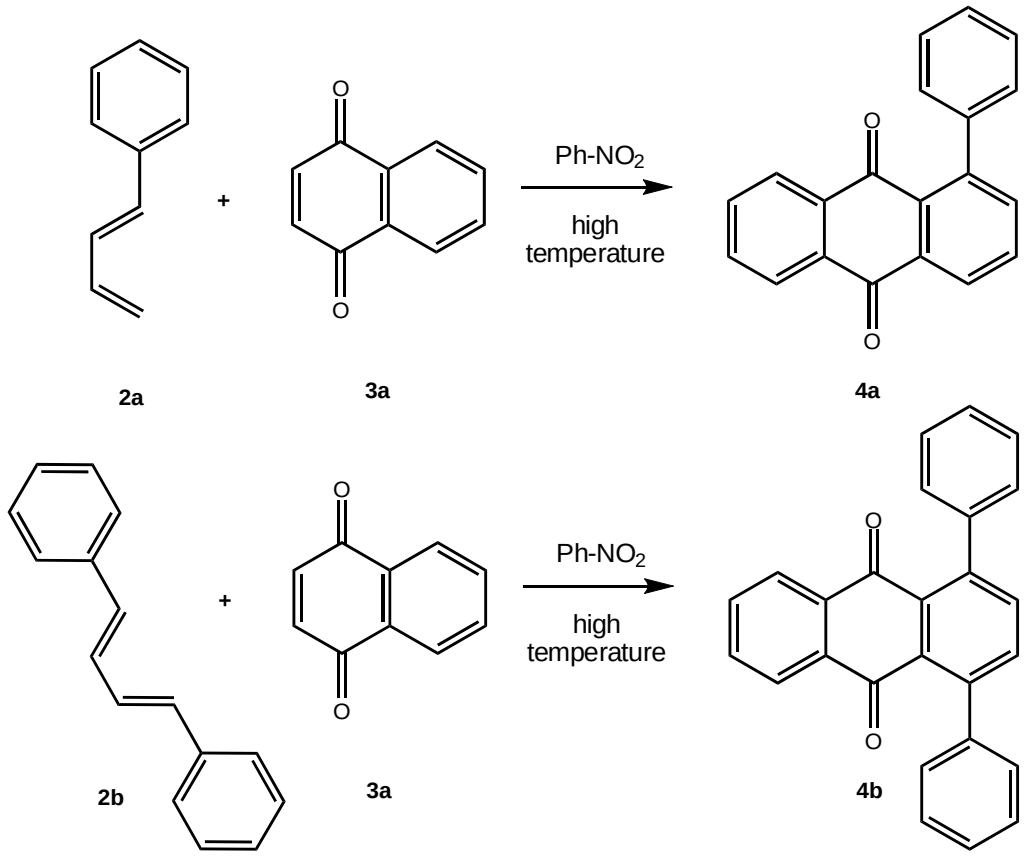
Arylated anthraquinones **1** (Fig. 1) have elicited interest in physical organic chemistry[1,2a] due to the interaction of the attached aryl groups with the π-system of the anthraquinone core as evidenced in the UV and luminescence[3,4] spectra, in the redox behavior of the molecules,[2] and the NMR shift values. Specifically, the interaction of the substituents on the C=O function of the anthraquinones 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.[5] Our interest in the molecules is in the study of the electrochemical behavior of these substances. In the following, a new direct preparation of arylated anthraquinones from halogenated thiophenes is presented.



1

Figure 1

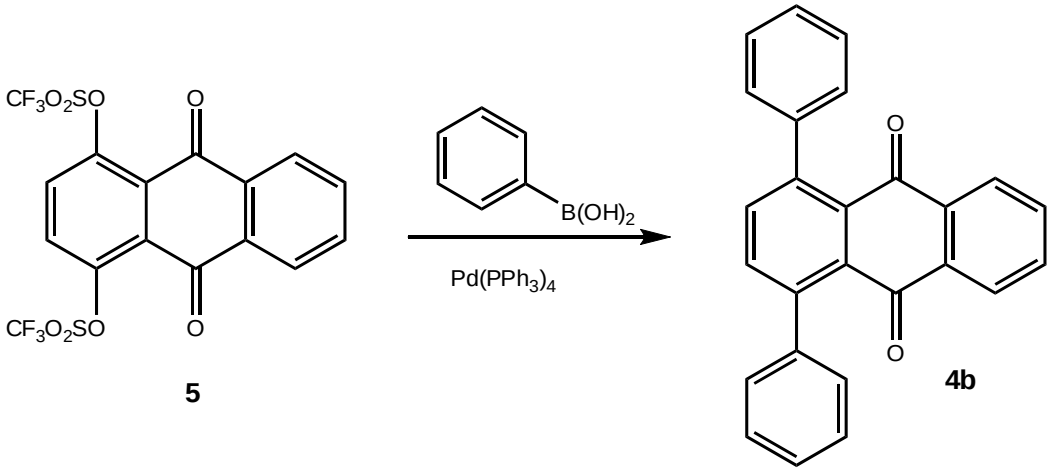
A number of synthetic routes to arylated anthraquinones are known. It has been shown by E. Bergmann et al.[6,7] that [4+2]-cycloaddition reactions of phenylbutadienes **2** with either 1,4-naphthoquinone (**3a**) or with *p*-benzoquinone (**3b**) give 1-phenylanthraquinone (**4a**) and 1,4-phenylanthraquinone (**4b**) (from 1,4-naphthoquinone) and 1,5-diphenylanthraquinone and 1,4,5,8-anthraquinone (from *p*-benzoquinone), respectively (Scheme 1). J. E. Gautrot et al[2a] started from 1,4-dihydroxy-9,10-anthraquinone, which was transformed into its bistriflate **5**[2b] and subsequently subjected to coupling reaction with arylboronic acids (Scheme 2).[2a]



E. Bergmann [ref. 6,7] **Scheme 1**

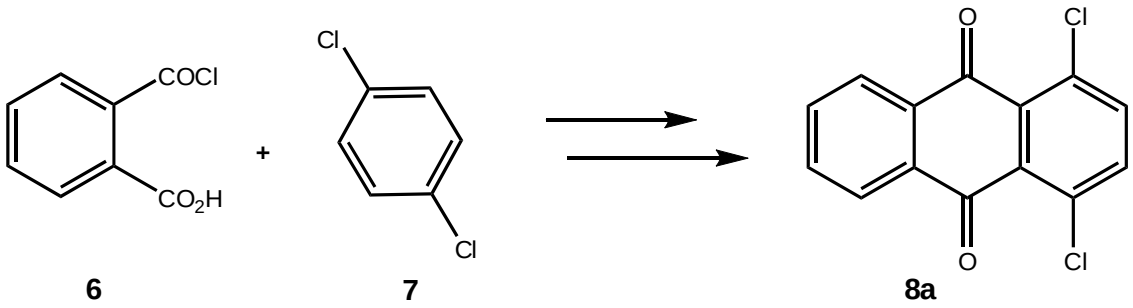
Coupling reactions have also been carried out with 1-diazoanthraquinone, which were prepared from the corresponding 1-aminoanthraquinone.[8] In order to have a versatile strategy to aryl substituted anthraquinones in hand, we wanted to use haloanthraquinones as key intermediates, which we could subsequently transform into the target compounds by Suzuki cross coupling reaction. Again, preparative routes to haloanthraquinones are known. Thus, M. Battegay and J. Claudin prepared a number of dibromoanthraquinone from the corresponding diaminoanthraquinones by Sandmeyer reaction.[9] For chlorinated anthraquinones, a larger number of synthetic procedures are known. Thus, 1,4-dichloroanthraquinone can be synthesized from

1-hydroxyanthraquinone by chlorination with subsequent treatment of the 1-chloro-4-hydroxyanthraquinone with PCl_5.[10] Also, 1,4-dichloroanthraquinone (**8a**) can be prepared by acylation of 1,4-dichlorobenzene (**7**) with phthaloyl chloride (**6**) and subsequent heating of the 2-(2,5-dichlorobenzoyl)benzoic acid intermediate with H_2SO_4 (Scheme 3),[11] or by treatment of 9,10-dihydroxy-2,3-dihydro-1,4-anthraquinone with PCl_5.[12,13]



J. E. Gautrot, P. Hodge et al. 2006 (ref. 2a)

Scheme 2

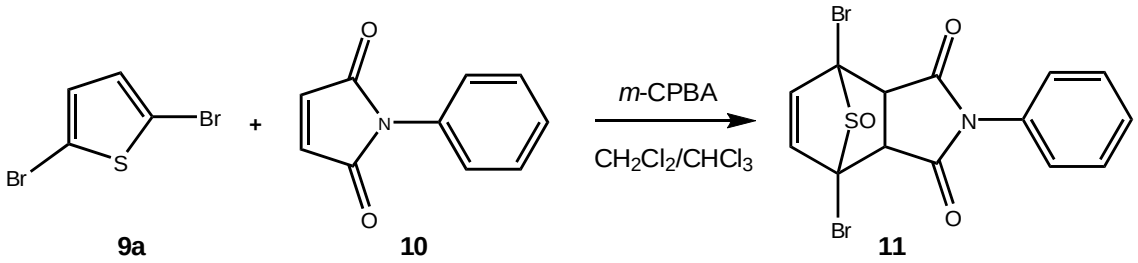


DE 3513981 (ref. 11)

Scheme 3

Based on our good experience in using thiophene *S*-oxides, either *in situ*[14] or in purified form,[15] as dienes in the preparation of multi-functionalised arenes,[16] we decided to utilize halogenated thiophene *S*-oxides as transient intermediates to prepare haloanthraquinones. While most thiophenes themselves are unreactive or react sluggishly[17] and thiophene *S*,*S*-dioxides[18] often necessitate high temperatures 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,[15,19,20] especially

those with electron donating substituents have been isolated, thiophene *S*-oxides can be reacted *in situ*.[14] Thus, thiophene *S*-oxides undergo cycloaddition reactions, when thiophenes are oxidized in the presence of a dienophile.



9a **10** **11**

T. Thiemann et al. (ref. 22)

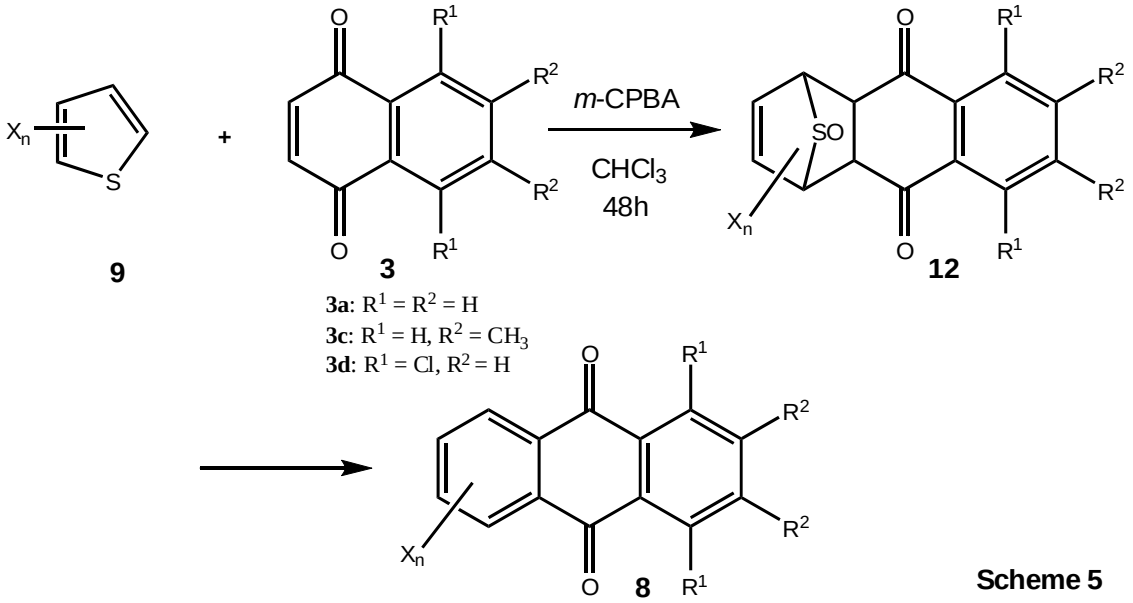
Scheme 4

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. It is for these two reasons that in all likelihood, halothiophene *S*-oxides would have to be used *in situ*. In fact, K. Torssell has reported on one example of a successful oxidative cycloaddition of a mono brominated thiophene with 1,4-naphthoquinone (**3a**), where the cycloadduct was produced in poor yield.[21] Our own work[22] on the oxidative cycloaddition of brominated and chlorinated thiophenes (eg., **9a**) to maleimides (eg., to **10**) indicated that halothiophene *S*-oxides can be produced *in situ* and can be reacted with electron poor dienophiles (Scheme 4).

RESULTS AND DISCUSSION

In the present case, a variety of brominated and chlorinated thiophenes **9** were submitted to oxidative cycloaddition reactions with 1,4-naphthoquinones **3**. Heated solutions of thiophene **9** and 1,4-naphthoquinone **3** were treated with *meta* chloroperbenzoic acid in small portions over 48h. Under these conditions, cycloaddition between intermediately formed thiophene *S*-oxides and 1,4-naphthoquinone **3** takes place, where the formulated, primary sulfoxy-bridged cycloadduct **12** loses the SO-bridge under concomitant aromatization (Scheme 5). The haloanthraquinones **8** can be obtained, albeit in very moderate yield (Table 1). A number of more polar side products form, depending on the substrate. One important type of side product are hydroxyanthraquinones **13** (Figure 2). That halothiophene *S*-oxides are involved here, has been shown in the reaction under analogous conditions of 2,5-dibromothiophene (**9a**), 2,3,4,5-tetrabromothiophene (**9e**) and 2,5-dichlorothiophene (**9g**) with *N*-phenylmaleimide (**10**), where halogenated

7-thiabicyclo[2.2.1]heptene *S*-oxides **11** could be isolated (Scheme 4).[22] Nevertheless, even in cases where halothiophene *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,[23] so that under the present conditions, halothiophene *S*,*S*-dioxides can also make a contribution to the reaction.



Scheme 5

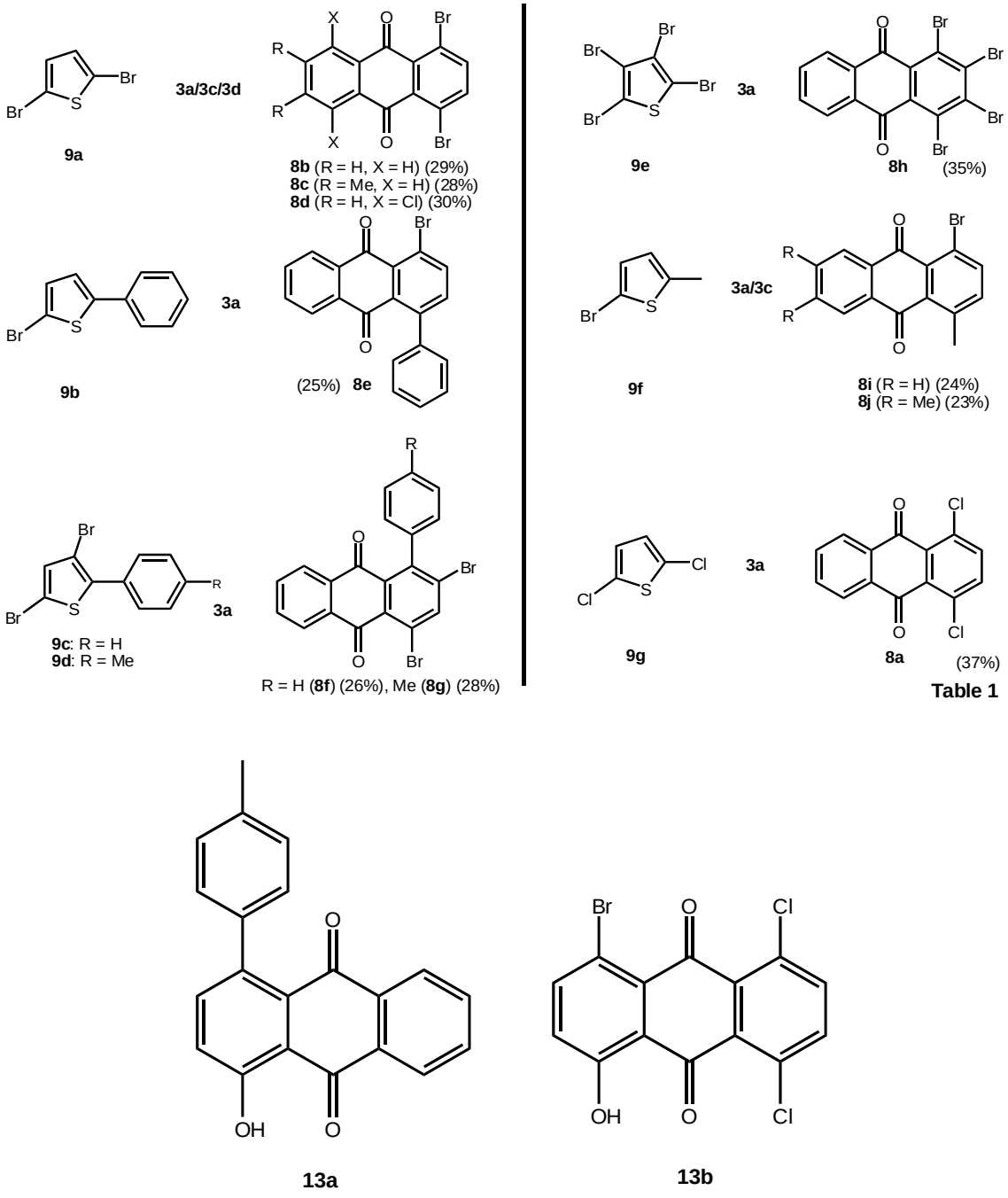


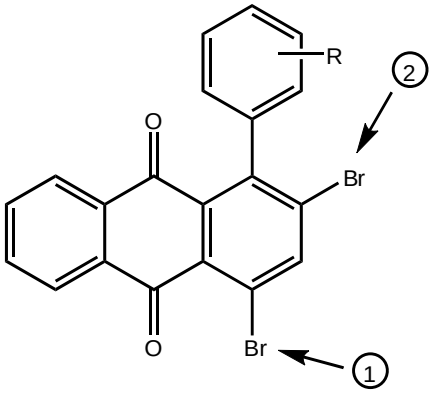
Table 1

13a **13b**

Figure 2

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. Na_2CO_3. 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.

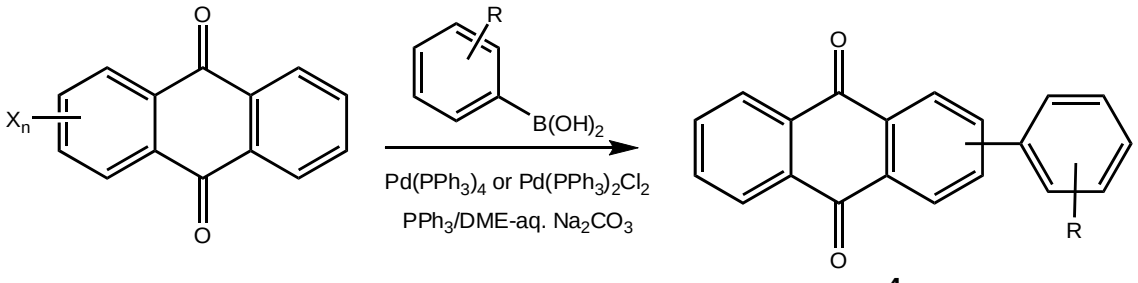


A

Order of entry of further aryl substituents
by Suzuki-Miyaura coupling cross-coupling

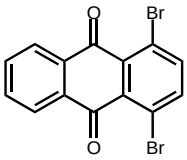
Figure 3

Equally interesting is the fact that chlorinated anthraquinones such as 1,4-dichloroanthraquinone (**8a**) 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 (**8d**) can be converted to the 1,4,5,8-tetra-arylanthraquinone **4r** (see continued Table 2), using $Pd(PPh_3)_4$ as a catalyst, as can be 1-bromo-5,8-dichloro-4-hydroxyanthraquinone (**13**) to **14** (Scheme 7).

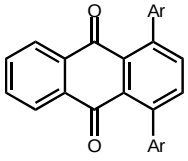


8 **4**

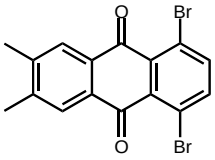
Scheme 6



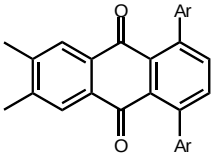
8b



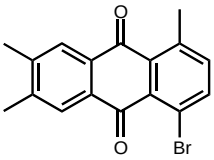
4b(Ar = Ph) (89%)
4c (Ar = Ph-*p*-Me) (85%)
4d (Ar = Ph-*o*-Me) (83%)
4e (Ar = Ph-*p*-OMe) (93%)
4f (Ar = Ph-p-OEt) (91%)



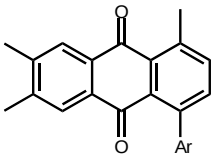
8c



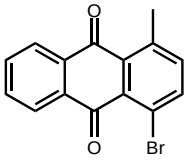
4g (Ar = Ph) (88%)



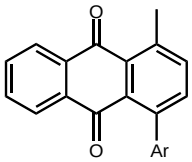
8i



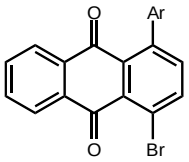
4h (Ar = Ph-*p*-OMe) (79%)
4i (Ar = Ph-p-OPr) (85%)



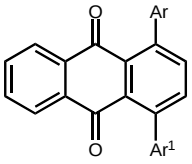
8h



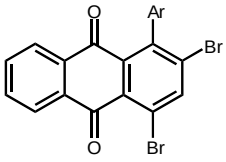
4j (Ar = Ph-*p*-OMe) (72%)



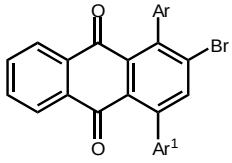
8e (Ar = Ph)



4k (Ar = Ph, Ar^1= Ph-*p*-OMe) (75%)



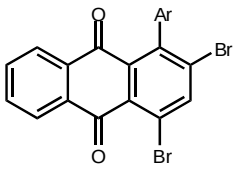
8f (Ar = Ph)
8g (Ar = Ph-*p*-Me)



4l (Ar=Ph-*p*-Me, Ar^1=Ph-*p*-OMe, 68%)
4m (Ar=Ph, Ar^1=Ph-*p*-OPr, 68%)

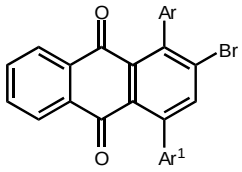
Table 2

The anthraquinones obtained show spectral data typical for this species of compounds. Thus, in the mass spectra, many of the anthraquinones prepared above have fragmentation peaks of $[M^+-CO]$ and $[M^+-2CO]$ that are typical for anthraquinones.[24] In carbon NMR, the carbonyl functions resonate at δ 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.

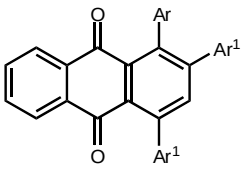


8f (Ar = Ph)
8g (Ar = Ph-*p*-Me)

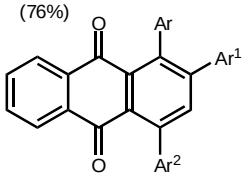
or



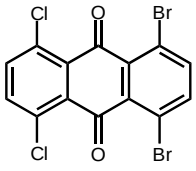
4l (Ar=Ph-*p*-Me, Ar^1=Ph-*p*-OMe)
4m (Ar=Ph, Ar^1=Ph-*p*-OPr)



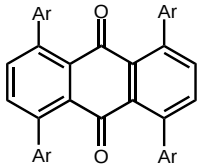
4n(Ar = Ph, Ar^1=Ph-*p*-OPr) (75%)
4o (Ar = Ph-*p*-Me, Ar^1=Ph-*p*-OEt) (74%)
4p (Ar = Ph-*p*-Me, Ar^1=Ph-*p*-OMe) (76%)



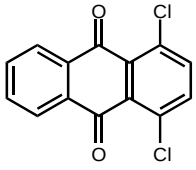
4q (Ar = Ph, Ar^1=Ph-*p*-OMe, Ar^2 = Ph-*p*-OPr) (63%)



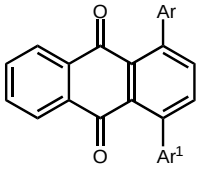
8d



4r (Ar = Ph-*p*-OMe) (72%)

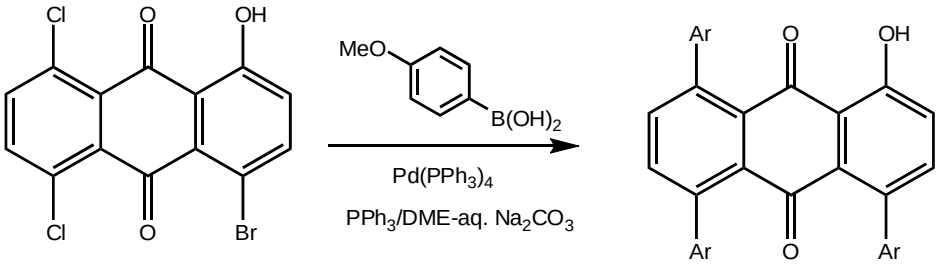


8a



4b (Ar = Ph) (68%)

Table 2 (continued)



13b **14** (56%)

Ar = MeO-*p*-Ph

Scheme 7

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.[25] The strongest band, normally called a 'benzoid band',[25b] is located at around λ = 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 λ_{max} = 263 nm. A longer-wave π-π*-transition (often called a 'quinoid band'[25b]) can be found as a shoulder at λ = 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 6,7-methylated anthraquinones (eg., for **4i**, λ = 279 nm). A shift to higher wavelength is also found for the β-bromo substituted anthraquinone **4l** (λ = 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 λ = 300 nm. The π-π* transition with the longest wavelength can be noted at λ = 350 – 380 nm for the compounds measured. Substituent dependence of this transition has been reported for mono-substituted anthraquinones,[25] and also in our case a substituent-dependence can be noted.

EXPERIMENTAL

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 hotstage and are uncorrected. IR spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM machines. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL EX-270 (^{1}H at 270 MHz and ^{13}C at 67.8 MHz) and JEOL Lambda 400 spectrometer (^{1}H at 395 MHz and ^{13}C at 99.45 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 300.
The oxidative cycloaddition reactions were carried out with commercially available *meta*-chloroperbenzoic acid (*m*-CPBA, 70-75 w%, Acros). *m*-CPBA was used without further purification. $Pd(PPh_3)_4$ (TCI), $Pd(PPh_3)_2Cl_2$ (TCI), 2,5-dibromothiophene (**9a**) (Aldrich), 2-methylthiophene (TCI), 2-bromothiophene (Aldrich), thiophene (Wako) and 2,5-dichlorothiophene (**9g**) (Aldrich) were acquired commercially. 2,3,4,5-Tetrabromothiophene (**9e**) (thiophene, Br_2, $CHCl_3$),[26] 2-bromo-5-methylthiophene (**9f**) (2-methylthiophene, NBS, $CHCl_3$, AcOH), 2-bromo-5-phenylthiophene (**9b**) and 2-bromo-5-(*p*-tolyl)thiophene (a. 2-bromothiophene, Aryl-$B(OH)_2$, $Pd(PPh_3)_4$, DME, aq. Na_2CO_3; b. N-bromosuccinimide [NBS], $CHCl_3$, AcOH)[27] were prepared analogous to known procedures. 2,4-Dibromo-5-arylthiophenes, **9c** and **9d**, were synthesized by brominating 2-arylthiophenes using an excess[28] of NBS. 5,8-Dichloro-1,4-naphthoquinone (**3d**) was prepared by oxidative cycloaddition of 2,5-dichlorothiophene (**9g**) to *p*-benzoquinone.[21] 2,3-Dimethyl-5,8-naphthoquinone (**3c**) was prepared by cycloaddition of 2,3-dimethylbuta-1,3-diene to *p*-benzoquinone under $EuCl_3$ catalysis (96h, $ClCH_2CH_2Cl$, rt)[29] with subsequent base catalysed enolisation[30] 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 (Ag_2O, Na_2SO_4, benzene)[31] to 6,7-dimethyl-5,8-dihydro-1,4-naphthoquinone, which in a last step was dehydrogenated (DDQ, benzene, reflux). *p*-Methoxyphenylboronic acid (TCI), *o*-methoxyphenylboronic acid (TCI), phenylboronic acid (TCI), and *p*-tolylboronic acid (Aldrich) were acquired commercially. *p*-Ethoxy- and *p*-propoxyphenylboronic acids were prepared from the corresponding *p*-alkoxy-bromobenzenes (a. *n*-BuLi, $B(OEt)_3$, THF; b. HCl).[32]

1,4-Dibromoanthraquinone (**8b**).[9,33] – To a stirred solution of dibromothiophene (**9a**, 1.00 g, 4.16 mmol) and 1,4-naphthoquinone (517 mg, 3.47 mmol) in $CHCl_3$ (20 mL) at

75 ºC was added *m*-CPBA (70w%, 4.76 g) in small portions. After 48h, the mixture was cooled and poured into an aq. sat. Na_2CO_3 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 $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (hexane/ether/$CHCl_3$ 8:1:1) to give **8b** (370 mg, 29%); δ_H (270 MHz, $CDCl_3$) 7.78 – 7.81 (2H, m), 7.81 (2H, s), 8.20 – 8.23 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 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 ($[^{81}Br_2]M^+$) (50), 366 ($[^{81}Br^{79}Br]M^+$) (100), 364 ($[^{79}Br_2]M^+$) (51), 340 ($[^{81}Br_2]M^+$-CO) (15), 338 ($[^{81}Br^{79}Br]M^+$-CO) (30), 336 ($[^{79}Br_2]M^+$ - CO) (15), 312 ($[^{81}Br_2]M^+$-2CO) (10), 310 ($[^{81}Br^{79}Br]M^+$-2CO) (21), 308 ($[^{79}Br_2]M^+$-2CO) (11), 287 (11), 285 (11), 231 (15), 229 (15), 150 (73). HRMS Found: 365.8716. Calcd. for $C_{14}H_6O_2{}^{79}Br^{81}Br$: 365.8715.

Selected data of other haloanthraquinones:

1,4-Dichlorobenzoquinone (**8a**).[10] – yellow needles; 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).

1,4-Dibromo-6,7-dimethylanthraquinone (**8c**). – yellow solid; δ_H (270 MHz, $CDCl_3$) 2.42 (6H, s, 2 CH_3), 7.77 (s, 2H), 7.94 (s, 2H); δ_C (67.8 MHz, $CDCl_3$) 20.3 (2C, CH_3), 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 ($[^{81}Br_2]M^+$, 50), 394 ($[^{81}Br^{79}Br]M^+$, 100), 392 ($[^{79}Br_2]M^+$, 50), 368 ($[^{81}Br_2]M^+$-CO, 12), 366 ($[^{81}Br^{79}Br]M^+$ - CO, 25), 364 ($[^{79}Br_2]M^+$ - CO, 13). HRMS Found: 393.9033. Calcd. for $C_{16}H_{10}O_2{}^{79}Br^{81}Br$: 393.9028.

1,4-Dibromo-5,8-dichloroanthraquinone (**8d**). – colorless solid; 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). HRMS Found: 433.7930. Calcd. for $C_{14}H_4O_2{}^{35}Cl^{37}Cl^{79}Br_2$: 433.7933.

2,4-Dibromo-1-(4-methylphenyl)anthraquinone (**8g**). – yellow solid, mp. 183 ºC; δ_H (270 MHz, $CDCl_3$) 2.47 (3H, s, CH_3), 7.01 (2H, d, ^3J = 8.1 Hz), 7.31 (2H, d, ^3J = 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); δ_C (67.8 MHz, $CDCl_3$) 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 ($[^{81}Br^{79}Br]M^+$) (18), 299 (100). HRMS Found: 455.9188. Calcd. for $C_{21}H_{12}O_2{}^{81}Br^{79}Br$: 455.9185.

1,2,3,4-Tetrabromoanthraquinone (**8h**).[34] - orange solid; mp. 200 ºC; δ_H (270 MHz, $CDCl_3$) 7.76 – 7.79 (2H, m), 8.11 – 8.14 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 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 ($[^{81}Br_3{}^{79}Br]MH^+$) (0.2), 526 ($[^{81}Br_3{}^{79}Br]M^+$) (0.1), 525 ($[^{81}Br_2{}^{79}Br_2]MH^+$) (0.3), 524 ($[^{81}Br_2{}^{79}Br_2]M^+$) (0.2), 523 ($[^{81}Br^{79}Br_3]MH^+$) (0.2). HRMS Found: 524.6993. Calcd. for $C_{14}H_5O_2{}^{79}Br_2{}^{81}Br_2$: 524.6983 ($MH^+$, FAB).

1-Bromo-4-methylanthraquinone (**8i**).[35] - beige colored solid; δ_H (270 MHz, $CDCl_3$) 2.79 (3H, s, CH_3), 7.36 (1H, d, ^3J = 8.4 Hz), 7.74 – 7.78 (2H, m), 7.87 (1H, d, ^3J = 8.4 Hz), 8.15 – 8.24 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 23.6 (CH_3), 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 ($[^{81}Br]M^+$, 97), 300 ($[^{79}Br]M^+$, 100), 274 ($[^{81}Br]M^+$-CO, 15), 272 ($[^{79}Br]M^+$-CO, 15), 193 (59), 165 (90). HRMS Found: 301.9764. Calcd. for $C_{15}H_9O_2{}^{81}Br$: 301.9767. Found: 299.9789. Calcd. for $C_{15}H_9O_2{}^{79}Br$: 299.9786.

1-Bromo-4,6,7-trimethylanthraquinone (**8j**). – yellow solid, mp. 194 ºC; δ_H (270 MHz, $CDCl_3$) 2.42 (6H, s, 2 CH_3), 2.73 (3H, s, CH_3), 7.33 (1H, d, ^3J = 8.4 Hz), 7.82 (1H, d, ^3J = 8.4 Hz), 7.91 (1H, s), 7.95 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 20.2 (2C, CH_3), 20.7 (CH_3), 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 ($[^{81}Br]M^+$) (100), 328 ($[^{79}Br]M^+$) (100), 315 ($[^{81}Br]M^+$-CH_3) (38), 313 ($[^{79}Br]M^+$-CH_3) (39), 302 ($[^{81}Br]M^+$-CO) (26), 300 ($[^{81}Br]M^+$-CO) (28), 287 ($[^{81}Br]M^+$-CH_3-CO) (26), 285 ($[^{79}Br]M^+$-CO-CH_3) (26), 221 (55), 178 (83). HRMS Found: 328.0097. Calcd. for $C_{17}H_{13}O_2{}^{79}Br$: 328.0099.

1,4-Bis(4-methylphenyl)anthraquinone (**4c**).[36] – In an inert atmosphere, a solution of **8b** (324 mg, 0.89 mmol), 4-methylphenylboronic acid (385 mg, 2.83 mmol), $Pd(PPh_3)_2Cl_2$ (30 mg, $4.0 \cdot 10^{-5}$ 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 65 ºC 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 $MgSO_4$ and was concentrated *in vacuo*. Column chromatography of the residue on silica gel (hexane/$CHCl_3$/ether 3:1:1) gave **4c** (293 mg, 85%) as an orange solid; mp. 265 ºC; δ_H (270 MHz, $CDCl_3$) 2.45 (6H, s, 2 CH_3), 7.18 (4H, d, ^3J = 7.6 Hz), 7.27 (4H, d, ^3J = 7.6 Hz), 7.53 (2H, s), 7.65 – 7.70 (2H, m), 8.05 - 8.09 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 21.3 (2C, CH_3), 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^+-CH_3) (100), 179 (40). HRMS Found: 388.1469. Calcd. for $C_{28}H_{20}O_2$: 388.1463. Found: C, 84.36; H, 5.12%. Calcd. for $C_{28}H_{20}O_2 \cdot H_2O$: C, 84.61; H, 5.33%. UV-Vis spectrum (CH_3CN, nm) λ_{max} 253 (44700), 268 (sh, 21310), 298 (9350), 358 (2470).

S*elected data for other arylated anthraquinones*:

1,4-Diphenylanthraquinone (**4b**).[2a,37] – yellow solid; 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). HRMS Found: 361.1232. Calcd. for $C_{26}H_{17}O_2$: 361.1229 (MH^+, FAB); UV-Vis spectrum (CH_3CN, nm) λ_{max} 253 (36370), 269 (sh, 19190), 288 (sh, 7320).

1,4-Bis(4-methoxyphenyl)anthraquinone (**4e**). – orange needles; mp. 231 ºC; 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). HRMS Found: 420.1367. Calcd. for $C_{28}H_{20}O_4$: 420.1362; UV-Vis spectrum (CH_3CN, nm) λ_{max} 253 (59610), 271 (sh, 23890), 313 (13280).

1,4-Bis(4-ethoxyphenyl)anthraquinone (**4f**). – orange needles; mp. 239 ºC; δ_H (270 MHz, $CDCl_3$) 1.47 (3H, t, CH_3, ^3J = 7.0 Hz), 4.12 (2H, q, OCH_2, ^3J = 7.0 Hz), 6.98 (4H, d, ^3J = 8.4 Hz), 7.24 (4H, d, ^3J = 8.4 Hz), 7.53 (2H, s), 7.67 – 7.70 (2H, m), 8.05 – 8.09 (2H,

m); δ_C (67.8 MHz, $CDCl_3$) 14.9 (2C, CH_3), 63.4 (2C, OCH_2), 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 $C_{30}H_{25}O_4$: 449.1753. Found: C, 79.57; H, 5.47%. Calcd. for $C_{30}H_{24}O_4 \cdot 0.2H_2O$: C, 79.70; H, 5.44%; UV-Vis spectrum (CH_3CN, nm) λ_{max} 253 (49430), 269 (sh, 21220), 314 (10910).

1,4-Diphenyl-6,7-dimethylanthraquinone (**4g**). – yellow needles, mp. 232 ºC; δ_H (270 MHz, $CDCl_3$) 2.34 (6H, s, 2 CH_3), 7.30 – 7.34 (4H, m), 7.43 – 7.50 (6H, m), 7.53 (2H, s), 7.82 (2H, s); δ_C (67.8 MHz, $CDCl_3$) 20.1 (2C, CH_3), 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 $C_{28}H_{21}O_2$: 389.1542 (FAB). Found: C, 85.80; H, 5.18%. Calcd. for $C_{28}H_{20}O_2 \cdot 0.2H_2O$: C, 85.78; H, 5.24%; UV-Vis spectrum (CH_3CN, nm) λ_{max} 263 (41490), 338 (4480).

1-(4-Methoxyphenyl)-4,6,7-trimethylanthraquinone (**4h**). – solid; δ_H (270 MHz, $CDCl_3$) 2.30 (3H, s, CH_3), 2.40 (3H, s, CH_3), 2.86 (3H, s, CH_3), 3.87 (3H, s, OCH_3), 6.96 (2H, d, ^3J = 8.6 Hz), 7.19 (2H, d, ^3J = 8.6 Hz), 7.40 (1H, d, ^3J = 7.8 Hz), 7.50 (1H, d, ^3J = 7.8 Hz), 7.80 (1H, s), 7.94 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 20.1 (CH_3), 20.2 (CH_3), 23.8 (CH_3), 55.2 (OCH_3), 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 $C_{24}H_{20}O_3$: 356.1412; UV-Vis spectrum (CH_3CN, nm) λ_{max} 263 (49630), 278 (sh, 19470), 339 (4880).

1-(4-Propoxyphenyl)-4,6,7-trimethylanthraquinone (**4i**). – yellow solid; mp. 215 ºC; δ_H (270 MHz, $CDCl_3$) 1.07 (3H, t, ^3J = 7.6 Hz, CH_3), 1.56 (3H, s, CH_3), 1.85 (2H, dt, ^3J = 7.6 Hz, ^3J = 6.5 Hz), 2.35 (3H, s, CH_3), 2.41 (3H, s, CH_3), 3.99 (2H, t, ^3J = 6.5 Hz, OCH_2), 6.95 (2H, d, ^3J = 8.6 Hz), 7.17 (2H, d, ^3J = 8.6 Hz), 7.41 (1H, d, ^3J = 7.8 Hz), 7.50 (1H, d, ^3J = 7.8 Hz), 7.81 (1H, s), 7.94 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 10.6 (CH_3), 20.1 (CH_3), 20.2 (CH_3), 22.7 (CH_2), 23.8 (CH_3), 69.4 (OCH_2), 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^+-$(CH_2)_2CH_3$) (100). HRMs Found: 384.1718. Calcd. for $C_{26}H_{24}O_3$: 384.1725 UV-Vis spectrum (CH_3CN, nm) λ_{max} 263 (57850), 279 (sh, 20490), 330 (5580, ill-defined).

1-(4-Methoxyphenyl)-4-methylanthraquinone (**4j**).[37] – yellow-orange needles; mp. 221 ºC; δ_H (270 MHz, $CDCl_3$) 2.88 (3H, s, CH_3), 3.88 (3H, s, OCH_3), 6.97 (2H, d, ^3J = 8.6 Hz), 7.20 (2H, d, ^3J = 8.6 Hz), 7.44 (1H, d, ^3J = 8.1 Hz), 7.53 (1H, d, ^3J = 8.1 Hz), 7.67 – 7.75 (2H, m), 8.04 – 8.07 (1H, m), 8.19 – 8.23 (1H, m); δ_C (67.8 MHz, $CDCl_3$) 23.8 (CH_3), 55.2 (OCH_3), 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 $C_{22}H_{17}O_3$: 329.1178 (MH^+, FAB). Found: C, 79.89; H, 4.73%. Calcd. for $C_{22}H_{16}O_3 \cdot 0.1H_2O$: C, 80.03; H, 4.91%; UV-Vis spectrum (CH_3CN, nm) λ_{max} 253 (38343), 269 (sh, 15440), 302 (5400), 354 (2505).

1-(4-Methoxyphenyl)-4-phenylanthraquinone (**4k**). – beige solid; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 391 (MH^+) (7.6). HRMS Found: 391.1340. Calcd. for $C_{27}H_{19}O_3$: 391.1334 (MH^+, FAB); UV-Vis spectrum (CH_3CN, nm) λ_{max} 253 (38520), 271 (sh, 18390), 306 (7980).

2-Bromo-1-(4-methylphenyl)-4-(4-methoxyphenyl)anthraquinone (**4l**). – orange needles; mp. 208 ºC; δ_H (270 MHz, $CDCl_3$) 2.49 (3H, s, CH_3), 3.89 (3H, s, OCH_3), 7.01 (2H, d, ^3J = 8.9 Hz), 7.08 (2H, d, ^3J = 8.1 Hz), 7.27 (2H, d, ^3J = 8.9 Hz), 7.33 (2H, d, ^3J = 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 $C_{28}H_{20}O_3{}^{79}Br$ (MH^+, FAB); UV-Vis spectrum (CH_3CN, nm) λ_{max} 258 (37150), 275 (sh, 16870), 309 (8100).

2-Bromo-1-phenyl-4-(4-propoxyphenyl)anthraquinone (**4m**). – yellow solid; mp. 183 ºC; δ_H (270 MHz, $CDCl_3$) 1.08 (3H, t, ^3J = 7.3 Hz, CH_3), 1.86 (2H, dt, ^3J = 7.3 Hz, ^3J = 6.5 Hz), 4.01 (2H, t, ^3J = 6.5 Hz, OCH_2), 7.00 (2H, d, ^3J = 8.4 Hz), 7.17 – 7.21 (2H, m), 7.25 (2H, d, ^3J = 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); δ_C (67.8 MHz, $CDCl_3$) 10.6 (CH_3), 22.7 (CH_2), 69.5

(OCH_2), 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 ([^{81}Br]M^+) (100), 496 ([^{79}Br]M^+) (98), 455 ([^{81}Br]M^+-$(CH_2)_2CH_3$) (84), 453 ([^{79}Br]M^+-$(CH_2)_2CH_3$) (81). HRMS Found: 496.0677. Calcd. for $C_{29}H_{21}O_3{}^{79}Br$: 496.0674.

1-(4-Methylphenyl)-2,4-bis(4-methoxyphenyl)anthraquinone (**4p**). – orange solid; mp. 230 ºC; δ_H (270 MHz, $CDCl_3$) 2.36 (3H, s, CH_3), 3.75 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 6.69 (2H, d, ^3J = 8.6 Hz), 6.93 – 6.96 (4H, m), 6.99 (2H, d, ^3J = 8.6 Hz), 7.08 (2H, d, ^3J = 8.6 Hz), 7.31 (2H, d, ^3J = 8.6 Hz), 7.57 (1H, s), 7.65 – 7.69 (2H, m), 8.00 – 8.11 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 21.4 (CH_3), 55.1 (OCH_3), 55.2 (OCH_3), 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 $C_{35}H_{27}O_4$: 511.1909 (MH^+, FAB); UV-Vis spectrum (CH_3CN, nm) λ_{max} 250 (50 085), 269 (sh, 26790), 300 (sh, 15980), 365 (4960).

2-(4-Methoxyphenyl)-1-phenyl-4-(4-propoxyphenyl)anthraquinone (**4q**). – light yellow needles; mp. 233 ºC; δ_H (270 MHz, $CDCl_3$) 1.08 (3H, t, ^3J = 7.6 Hz, CH_3), 1.86 (2H, tt, ^3J = 7.6 Hz, ^3J = 6.2 Hz), 3.74 (3H, s, OCH_3), 4.00 (t, 2H, ^3J 6.2 Hz, OCH_2), 6.68 (2H, d, ^3J = 8.6 Hz), 6.94 (2H, d, ^3J = 8.6 Hz), 6.99 (2H, d, ^3J = 8.6 Hz), 7.27 – 7.30 (3H, m), 7.04 – 7.08 (2H, m), 7.30 (2H, d, ^3J = 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); δ_C (67.8 MHz, $CDCl_3$) 10.6 (CH_3), 22.7 (CH_2), 55.1 (OCH_3), 69.4 (OCH_2), 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) UV-Vis spectrum (CH_3CN, nm) λ_{max} 249 (22370), 268 (sh, 12560), 298 (sh, 7490), 382 (2320).

1-(4-Methylphenyl)-2,4-bis(4-ethoxyphenyl)anthraquinone (**4o**). – yellow needles, mp. 230 ºC; δ_H (270 MHz, $CDCl_3$) 1.37 (3H, t, ^3J = 7.0 Hz, CH_3), 1.46 (3H, t, ^3J = 7.0 Hz,

CH_3), 2.36 (3H, s, CH_3), 3.97 (2H, d, ^3J = 7.0 Hz, OCH_2), 4.11 (2H, d, ^3J = 7.0 Hz, OCH_2), 6.67 (2H, d, ^3J = 8.9 Hz), 6.91 – 6.99 (6H, m), 7.08 (2H, d, ^3J = 7.8 Hz), 7.29 (2H, d, ^3J = 8.9 Hz), 7.57 (1H, s), 8.00 – 8.04 (2H, m), 8.06 – 8.09 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 14.7 (CH_3), 14.9 (CH_3), 21.4 (CH_3), 63.3 (OCH_2), 63.4 (OCH_2), 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 (C_{quat}), 132.0 (C_{quat}), 133.4 (CH), 133.5 (CH), 134.1 (C_{quat}), 134.2 (C_{quat}), 134.3 (C_{quat}), 134.5 (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}), 158.0 (C_{quat}), 158.3 (C_{quat}), 184.1 (C_{quat}, CO), 184.9 (C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 539 (MH^+) (31). HRMS Found: 539.2219. Calcd. for $C_{37}H_{31}O_4$: 539.2222. Found: C, 82.26; H, 5.62%. Calcd. for $C_{37}H_{30}O_4$: C, 82.50; H, 5.61%; UV-Vis spectrum (CH_3CN, nm) λ_{max} 250 (57030), 268 (sh, 31850), 298 (sh, 19440), 359 (6340).

1,4,5,8-Tetrakis(4-methoxyphenyl)anthraquinone (**4r**). – pale orange solid; mp. 251 ˚C; 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}t), 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 $C_{42}H_{33}O_6$: 633.2277 (MH^+, FAB).

1-Hydroxy-4,5,8-tris(4-methoxyphenyl)anthraquinone (**14**). – reddish solid; mp. 238 ˚C; 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). HRMS Found: 543.1805. Calcd. for $C_{35}H_{27}O_6$: 543.1808 (MH^+, FAB).

REFERENCES

1 J. M. Josien and N. Fuson, *Bull. Soc. Chim. Fr.*, 1952, 389.

2 a) J. E. Gautrot, P. Hodge, D. Cupertino, and M. Helliwell, *New J. Chem.*, 2006,

30, 1801; b) H. D. H. Showalter, E. M. Berman, J. L. Johnson, and W. E. Hunter, *Tetrahedron Lett.*, 1985, **26**, 157.

3 N. A. Shcheglova, D. N. Shigorin, and N. S. Dokunikhin, *Zh. Fiz. Khim.*, 1966, **40**, 1048; *Chem. Abstr.*, 1966, **65**, 9958b.

4 N. A. Shcheglova, D. N. Shigorin, and N. S. Dokunikhin, *Zh. Fiz. Khim.*, 1965, **39**, 3039; *Chem. Abstr.*, 1965, **64**, 12058f.

5 D. A. Orser (General Electric Company, Schenectady, N.Y., USA) US Pat. 3764549 (Oct. 9, 1973); *Chem. Abstr.*, 1973, **79**, 141431j.

6 C. Weizmann, E. Bergmann and L. Haskelberg, *J. Chem. Soc.*, 1939, 391.

7 E. Bergmann, L. Haskelberg, and F. Bergmann, *J. Org. Chem.*, 1942, **7**, 303.

8 V. A. Puchkov, *Zh. Vsesoy. Khim. Obshch. im. D. I. Mendeleeva*, 1961, **6**, 238; *Chem. Abstr.*, 1961, **55**, 19877g.

9 M. Battegay and J. Claudin, *Bull. Soc. Chim.*, 1921, **29**, 1017.

10 V. V. Kozlov, *Zh. Obshch. Khim.*, 1947, **17**, 289; *Chem. Abstr.*, **42**, 2581.

11 H. Schoenhagen and R. Schmitz (Bayer AG), DE 3513981 (Oct. 30, 1986); *Chem. Abstr.*, 1987, **106**, 20008.

12 P. A. Krapcho and Z. Getahun, *Synth. Commun.*, 1985, **15**, 907.

13 F. Ihlan, D. S. Tyson, and M. A. Meador, *Org. Lett.*, 2006, **8**, 577.

14 a) Y. Q. Li, T. Thiemann, T. Sawada, and M. Tashiro, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2323; b) T. Thiemann, Y. Q. Li, S. Mataka, and M. Tashiro, *J. Chem. Res.* (*S*), 1995, 384, (*M*), 1995, 2364; c) T. Thiemann, Y. Q. Li, C. Thiemann, T. Sawada, D. Ohira, M. Tashiro, and S. Mataka, *Heterocycles*, 2000, 1215.

15 a) Y. Q. Li, M. Matsuda, T. Thiemann, T. Sawada, and S. Mataka, *Synlett*, 1996, 461; b) Y. Q. Li, T. Thiemann, T. Sawada, S. Mataka, and M. Tashiro, *J. Org. Chem.*, 1997, **62**, 7926; c) Y. Q. Li, T. Thiemann, K. Mimura, T. Sawada, S. Mataka, and M. Tashiro, *Eur. J. Org. Chem.*, 1998, 1841.

16 for reviews, see: a) T. Thiemann and K. Gopal Dongol, *J. Chem. Res.* (*S*), 2002, 303; (M), 2002, 701; b) T. Thiemann, D. J. Walton, A. O. Brett, J. Iniesta, F. Marken, and Y. Q. Li, *ARKIVOC*, 2009, Vol. **ix**, 96.

17 Exceptions are strained thiophenes: a) J. Nakayama and J. Kuroda, *J. Am. Chem. Soc.*, 1993, **115**, 4612; or thiophenes with very effective electron-donor substituents: b) J. M. Barker, P. R. Huddleston, and S. W. Shutler, *J. Chem. Soc., Perkin Trans. 1*, 1975, 2483; c) D. N. Reinhoudt, H. C. Volger, and M. C. G. Kouwenhouven, *Tetrahedron Lett.*, 1972, 3647.

18 This is underscored by theoretical calculations, see, *cf.*: B. S. Jursic and D.

Coupe, *J. Heterocycl. Chem.*, 1995, **32**, 1455.

19 a) N. Furukawa, S. Zhang, S. Sato, and M. Higaki, *Heterocycles*, 1997, **44**, 61; b) J. Nakayama, H. Nagasawa, Y. Sugihara, and A. Ishii, *J. Am. Chem. Soc.*, 1997, **119**, 9077; c) N. Furukawa, S.-Z. Zhang, E. Horn, S. Takahashi, S. Sato, M. Yokoyama, and K. Yamaguchi, *Heterocycles*, 1998, **47**, 793.

20 a) P. Pouzet, I. Erdelmeier, D. Ginderow, J.-P. Mornon, P. M. Dansette, and D. Mansuy, *J. Heterocycl. Chem.* 1997, **34**, 1567; b) P. Pouzet, I. Erdelmeier, P. Ginderow, J. P. Mornon, P. M. Dansette, and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1995, 473.

21 K. Torssell, *Acta Chem. Scand., Ser. B*, 1976, **30**, 353.

22 T. Thiemann, M. L. Sa e Melo, A. S. Campos Neves, Y. Li, S. Mataka, M. Tashiro, U. Geiβler, and D. Walton, *J. Chem. Res.* (*S*), 1998, 346.

23 a) M. S. Raasch, *J. Org. Chem.*, 1980, **45**, 856; b) M. S. Raasch, *J. Org. Chem.*, 1980, **45**, 867; c) D. P. G. Hamon and P. R. Spurr, *J. Chem. Soc., Chem. Commun.*, 1982, 373.

24 a) M. Hesse, H. Meier, and B. Zeeh, *Spectroscopic Methods in Organic Chemistry*, Georg Thieme Verlag, Stuttgart, 1997, p. 246; b) E. S. Wraight, *Some Newer Phys. Methods Struct. Chem., Proc. Symp.*, 1967, 67; *Chem. Abstr.*, 1969, **70**, 62337u.

25 a) Z. Yoshida and F. Takabayashi, *Tetrahedron*, 1968, **24**, 933; b) R. H. Peters and H. H. Sumners, *J. Chem. Soc.*, 1953, 2101.

26 *cf.*, E. Ertas and T. Ozturk, *Tetrahedron Lett.*, 2004, **45**, 3405.

27 see also: Y. Goldberg and H. Alper, *J. Mol. Cat.*, 1994, **88**, 377.

28 N. Gjoes and S. Gronowitz, *Acta Chem. Scand.*, 1972, **26**, 1851.

29 This reaction has been reported to proceed under $YbCl_3$ catalysis: X. Fang, B. P. Warner, and J. G. Watkin, *Synth. Commun.*, 2000, **30**, 2669. We have found that it proceeds also in the presence of $EuCl_3$.

30 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: a) M. P. Fernandez, B. Gonzalez, M. Pardo, and J. L. Soto, *Anal. Quim.*, 1994, **90**, 477 (for Et_3N); b) S. Kotha and E. Manivannan, *Ind. J. Chem., Sect. B*, 2002, **41B**, 808 (for HCl).

31 We used Ag_2O 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, also: ref. 30b.

32 *cf.*, K. Fuchibe and T. Akiyama, *J. Am. Chem. Soc.*, 2006, **128**, 1434.

33 M. Kondo, M. Murata, H. Nishihara, E. Nishibori, S. Aoyagi, M. Yoshida, Y. Kinoshita, and M. Sakata, *Angew. Chem. Int. Ed. Engl.*, 2006, **45**, 5461.

34 A. Hofmann, *Monatsh. Chem.*, 1915, **36**, 805.

35 R. N. Castle, H. Kudo, and M. L. Lee, *Coll. Czech Chem. Commun.*, 1991, **56**, 2269.

36 H. Mizuno, S. Kubota (Seiko Epson Corp.), JP Pat. 04011214 (1992); *Chem. Abstr.*, 1992, **116**, 221636.

37 N. I. Ganushchak, A. V. Dombrovskii, and O. A. Vislobitskaya, *Zh. Obshch. Khim.*, 1963, **33**, 2532.