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TETRAHEDRON

A Novel Acid-Catalyzed Rearrangement of 9,10-Diaryl-9,10-dihydroanthracene-9,10-diols Affording 10,10'-Diaryl-9-anthrones.#

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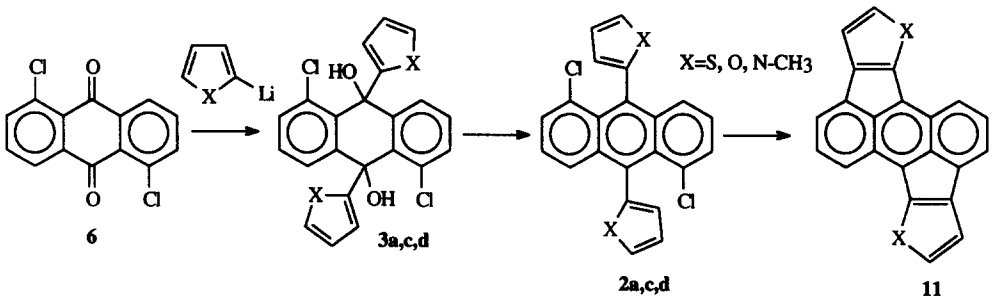
Abstract: Usually, 9,10-diarylanthracenes can be obtained by reduction of the corresponding 9,10-diaryl-9,10-dihydroanthracene-9,10-diols with KI/NaH_2PO_2 in acetic acid. In contrast, we found that in case of heteroaromatic aryl substituents and when *peri* substituents are present on the anthracene residue, high amounts of anthrones are formed. These anthrones can be considered to result from a vinylogous pinacol rearrangement of the initial diol. To the best of our knowledge, this type of rearrangement is rarely observed, and the 10,10'-diaryl-9-anthrones obtained in this way, are difficult to prepare otherwise. We prepared a number of such compounds and studied the mechanism of the transformation involved. The results are in agreement with a bridged transition state **10**.

INTRODUCTION

Recently we have used the highly fluorescing and photostable rubicene as a core in dendrimer chemistry[1]. A new approach towards disubstituted rubicenes was devised[2]. In order to obtain the so far unknown heterocyclic analogues of rubicene **11**, which are of potential use as organic donors[3], we tried to adapt our method[2] for the synthesis of symmetrically disubstituted rubicenes. By adding heteroaryllithium derivatives to 1,5-dichloroanthraquinone **6**, the corresponding diols **3a,c,d** were obtained (Scheme 1). It is well known[4] that 9,10-diaryl-9,10-dihydroanthracene-9,10-diols are normally transformed into the corresponding 9,10-diarylanthracenes by the reduction of the former compounds using KI and NaH_2PO_2 in refluxing acetic acid. However, we found that this reaction failed to yield the 1,5-dichloro-9,10-diheteroarylanthracenes **2a,c,d** of interest.



Scheme 1

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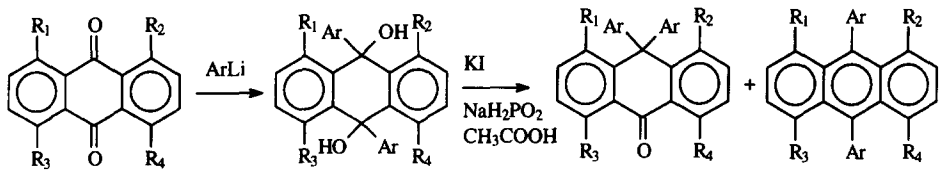
RESULTS AND DISCUSSION

Initially, we prepared the diols **3a**, **3c** and **3d** in order to transform them into the rubicene analogues **11** as mentioned above (Scheme 1). We generated the lithiated heterocycles by literature procedures[5] and then reacted them with the appropriate anthraquinone. The desired diols are mainly in the *trans* configuration, although in some cases, a minor fraction of the *cis* isomer was present and could be separated by column chromatography. All experiments were carried out with the *trans* isomers, contaminated by small percentages of the respective *cis* isomer (0-5%). In the cases where a significant amount of *cis* isomer was present in the reaction substrate, we did not find any difference in the results.



3a,c,f,g,h,i,l,o,q **1a,c,i** **2a,c,f,g,h,i,l,o,q**

Scheme 2

Table 1: Yields of anthrones **1a-q** and anthracenes **2a-q**

	R1	R2	R3	R4	Ar	yield (%) **1a-q**	yield (%) **2a-q**
3a	Cl	H	H	Cl	thien-2-yl	71	12
3b	Cl	H	H	Cl	5-methylthien-2-yl	°	°
3c	Cl	H	H	Cl	fur-2-yl	41	5
3d	Cl	H	H	Cl	1-methylpyrrol-2-yl	°	°
3e	Cl	H	H	Cl	1-methylindol-2-yl	°	°
3f	Cl	H	H	Cl	phenyl	-	93
3g	Cl	H	H	Cl	4-methoxyphenyl	-	91
3h	Cl	H	H	Cl	3-methoxyphenyl	-	89
3i	Cl	H	H	H	thien-2-yl	69[b]	12[c]
3j	H	H	Cl	Cl	thien-2-yl	°	°
3k	OBu	H	OBu	H	thien-2-yl	°	°
3l	OBu	H	H	OBu	thien-2-yl	5	83
3m	OBu	OBu	H	H	thien-2-yl	°	°
3n	SPh	H	H	SPh	thien-2-yl	°	°
3o	H	H	H	H	thien-2-yl	-	90
3p	H	H	H	H	1-methylpyrrol-2-yl	°	°
3q	H	H	H	H	4-methoxyphenyl	-	93

(a) treatment of diols **3a-q** with KI/NaH_2PO_2 in boiling acetic acid during 1h. (b) Mixture of isomers **1i/1i'** in a ratio of 2/1 (**1i**: $R_1=R_2=R_3=H, R_4=Cl$; **1i'**: $R_1=Cl$, $R_2=R_3=R_4=H$) (c) Not fully characterized MS (EI) *m/z* 376 (M^+) - (°)Experiment not carried out

We found that when the anthracenediols **3a** and **3c** were reacted following the literature conditions[6], the expected anthracenes **2a** and **2c** were present only in small amounts in the reaction mixture (Table 1). The main products are the anthrones **1a** and **1c**, apparently formed by migration of one of the aryl substituents (Scheme 2).

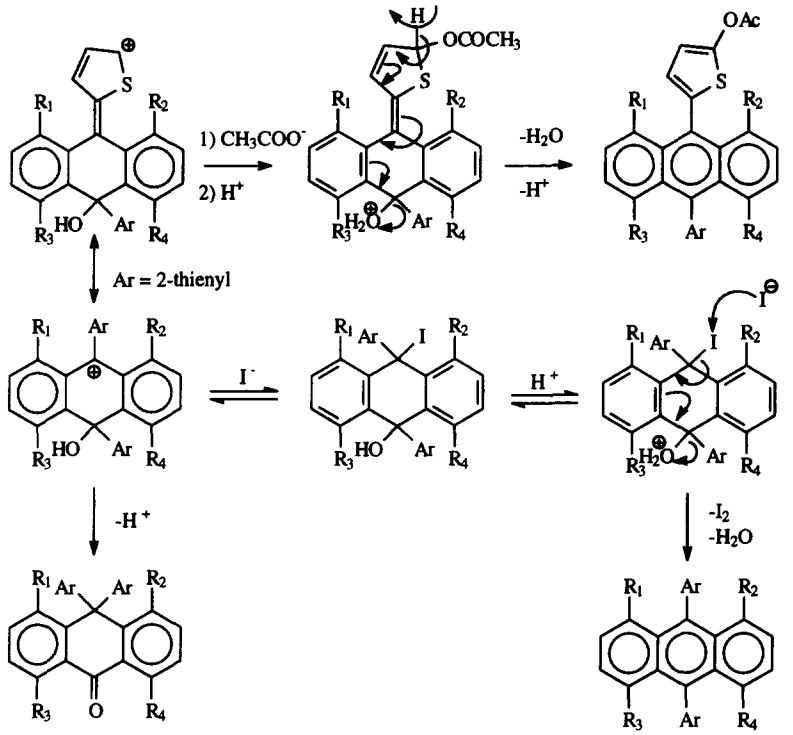
As clearly shown by the behaviour of compounds **3b** and **3e**, the migration occurs on the *ipso* position (Table 2). It has been observed that the analogous compound **3o**, lacking chlorine substituents at the 1- and 5-positions, was readily transformed into the anthracene **2o** under the same reaction conditions[7]. When we repeated this experiment, we found it to be reproducible (Table 1). This indicates the importance of the *peri* substituents in determining the reaction pathway.

Table 2: Yields of anthrones **1a-q**, acylated compounds **4a-q** and anthracenes **5a-q** upon heating of diols **3a-q** in acetic acid during 30 min.

substrate	yield (%) **1a-q**	yield (%) **4a-q**	yield (%) **5a-q**
3a	74	-	-
3b	63	-	-
3c	46	-	-
3d	94	-	-
3e	48	-	-
3f	-	88[d]	-
3g	-	86[d]	-
3i	73[a]	-	-
3j	87	-	-
3k	73	-	traces[b]
3l	46	-	traces[b]
3m	traces[c]	-	67
3n	53	-	-
3o	-	-	83
3q	-	91[d]	-

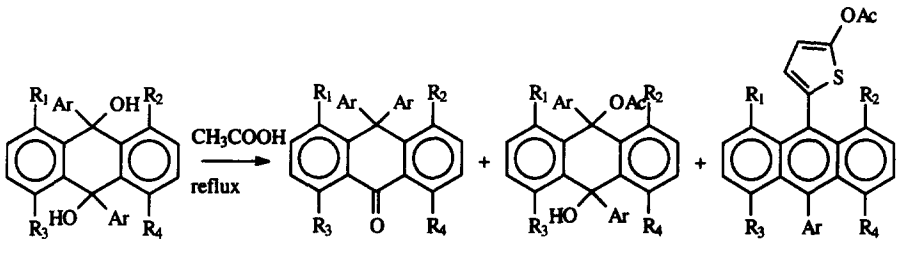
(a) See footnote (a) table 1 (b) Detected by TLC (characteristic yellowish fluorescence), not characterized (c) Detected by TLC, not characterized (d) As these compounds were of no importance for our further investigations, they were not fully characterized. Absence of fluorescence and C=O stretch at ~1710 cm^{-1} distinguished compounds of type **4** from type **5**.

In both cases, we can assume that a carbocation is formed on the 9-position by loss of water from the protonated compound (Scheme 3).



Scheme 3

In the process leading to an anthracene, this cation is captured by a iodide anion and the iodo alcohol thus formed is further reduced to afford the anthracene. *Peri* chlorosubstituents hinder the formation of a planar carbocationic centre by steric interactions with the *meso* aryl substituent. Stabilization of the system can then only be achieved by migration of the aryl substituent from the 10-position, resulting in the formation of the title anthrones. As could be expected, the yield of anthrones **1** was increased (Table 2), by omitting the KI and NaH_2PO_2 from the reaction mixture (Scheme 4).



Scheme 4

However, reflux of the *peri* unsubstituted diol **3o** in acetic acid, did not give a rearranged product and the anthracene **5o** was isolated in excellent yield (Table 2). Probably, this compound is formed by addition of acetic acid as a nucleophile on the 5-position of the thienyl substituent, which is electron poor due to delocalization of the carbocation created (Scheme 3). Elimination of water gives then rise to the formation of

the anthracene **5o**. This observation demonstrates again the effect of the chloro *peri* substituents, as in the presence of the latter, attack on the thienyl substituent was not observed. Treatment of the monochloro-substituted diol **3i**, turned out to yield a mixture of the two possible rearrangement products **1i** and **1i'** in a ratio of 2/1. In this case, the initial formation of a carbocation will most favorably proceed on the 10-position which is as far as possible from the electron withdrawing chlorine. However, the selectivity is not very pronounced. In contrast, total selectivity was observed in formation of dichloroanthrone **1j** (from diol **3j**) having its carbonyl function between two chlorine substituents. Such anthrones are very difficult to prepare by other strategies. A more important conclusion, which could be drawn from the behaviour of diol **3i**, is the fact that stabilization of a carbocation formed on the 10-position is also hindered by a substituent on the 1-position. This follows from the fact that on reflux of **3i** in acetic acid, no attack of acetate on the 10-thienylgroup, nor significantly more anthracene formation than in the case of compound **3a** (in the presence of KI and NaH_2PO_2) occurred (Table 1). Thus, formation of a planar carbocation on the 10-position is also unfavoured by the presence of the 1-substituent, as the latter one has to pass one of the two 9-substituents when the initial boat conformation of the central ring is turning into a planar system.

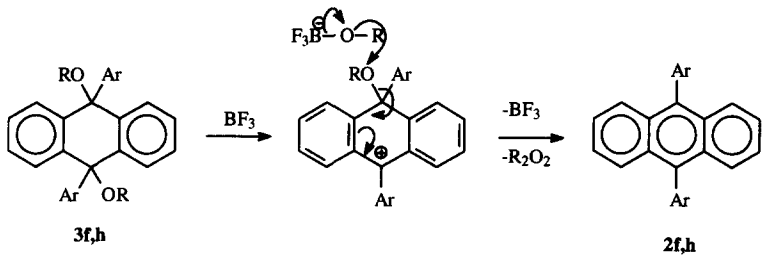
On the basis of the above findings can be predicted that the electronic properties of the *peri* substituents should not have a dramatic influence on this reaction. This was shown clearly by the moderate to good yields of anthrones **1k-l** and **1n** obtained using the diols **3k-l** and **3n**, possessing electron donating substituents on the anthracene ring, as the substrates (Table 2). However, as could be expected from their carbocation stabilizing properties, and from the fact that the steric effect of the alkoxy substituents is less important, it is still possible to obtain the anthracene **2l**, by means of the reductive procedure[5], without significant interference of the rearrangement (Table 1). Formation of the anthracene **5m** causes the yield of anthrone **1m** to drop dramatically. The stabilization of the intermediate carbocation is sufficient to prevent the rearrangement. In this case the electron donating alkoxy groups induce total regioselectivity for anthracene formation by addition of acetate.

As $BF_3.Et_2O$ is known to be an excellent promotor of pinacol rearrangements[8] we treated the substrates mentioned in Table 3 with this strong Lewis acid. These reactions were carried out at room temperature in dichloromethane, generally resulting in the expected rearrangement. The yields of the anthrones were usually higher than those obtained by reflux in acetic acid, except for **3l**, probably due to parasitic complexation of the alkoxy substituents, inducing decomposition, and for **3d**, probably due to the acid sensitive pyrrole residues. More important however is that even when *peri* substituents are absent, good yields of the anthrones can be achieved because anthracene formation following the alternative pathway, *i.e.* attack of acetate as described in scheme 3, is excluded.

In contrast with the bis(heteroaryl) substituted compounds, the analogous rearrangement of the diols **3f-g** and **3q** was not observed upon reflux in acetic acid which resulted in acylation of one of the hydroxyl functions. Treatment of compounds **3f-h** and **3q** with $BF_3.Et_2O$, however, resulted in migration in case of the 4-methoxyphenyl substituted derivatives, yielding the anthrones **1g** and **1q** as the main products. However, in case of diols **3f** and **3h**, only a trace of the rearrangement products could be detected by TLC and the anthracenes **2f** and **2h** were obtained in high yields (Table 3). Although we did not investigate the mechanism of the latter transformation, we propose a probable one, involving the formation of peroxide, in Scheme 5. However, we have found no trace of these peroxides in the reaction mixtures.

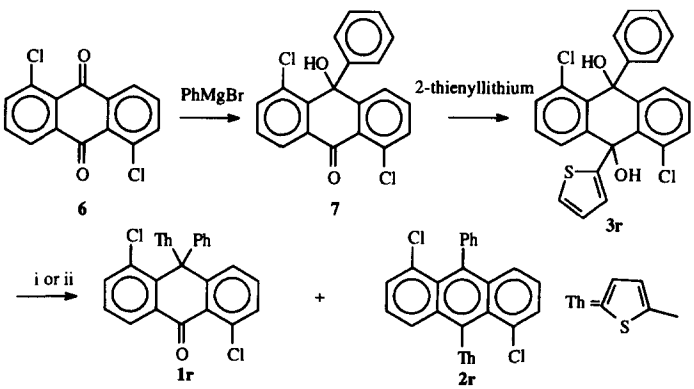
Table 3: Yields of anthrones **1a-q** and anthracenes **2a-q** upon treatment of diols **3a-q** with $BF_3.Et_2O$ in dichloromethane at room temperature during 30 min.

substrate	yield (%) **1a-q**	yield (%) **2a-q**
3a	84	traces[b]
3b	72	traces[a]
3c	71	traces[b]
3d	24	traces[a]
3e	85	traces[a]
3f	traces[a]	86
3g	86	9
3h	traces	83
3j	91	traces
3l	traces	-
3m	traces	-
3o	56	traces
3q	69	traces



3f,h **2f,h**

Scheme 5



6 **7** **3r**

1r **2r**

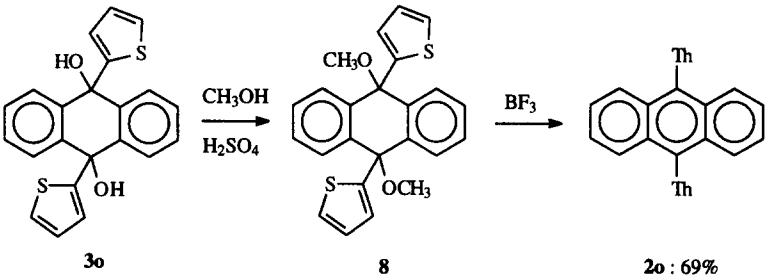
i : KI, NaH_2PO_2, CH_3COOH, reflux; yield **1r** = 69, **2r** = 13%
ii : CH_3COOH, reflux; yield **1r** = 78%, **2r** not found

Scheme 6

The asymmetric diol **3r** readily rearranged in the reaction conditions indicated in scheme 6, yielding again the anthrone **1r** in good yield with only a minor fraction of anthracene **2r**. This clearly demonstrates new interesting possibilities for the synthesis of 10,10'-diarylanthrones. We assumed the thienyl group of **3r** to have migrated although this was not strictly experimentally verified. Synthesis of the asymmetrically substituted diol **3r** (Scheme 6) was found to be most easily achieved by dropwise addition of phenylmagnesium bromide to a suspension of 1,5-dichloroanthraquinone **6** in THF. The monoadduct **7** was isolated and treated with an excess of 2-thienyllithium, yielding diol **3r** in good overall yield.

From the above results, it is clear that diols substituted with electron rich aromatic rings gave higher yields of anthrones. This is most spectacularly revealed by the observation that a single washing with diluted hydrochloric acid of a solution of the *peri* unsubstituted dipyrrolyl derivative **3p** is sufficient to induce total rearrangement yielding **1p**. Obviously, there is some steric assistance of the 1-methyl substituents on the pyrrole residues. This fact suggests a high dependance of the migratory aptitude on the π-electron density of the migrating aryl group.

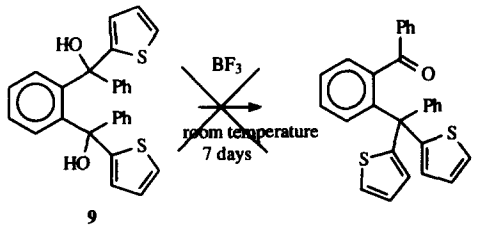
In order to elucidate the mechanism of this transformation we did a number of additional experiments. Firstly, diol **3o** was treated with warm methanol in the presence of a catalytic amount of sulfuric acid, yielding the dimethoxy derivative **8** (Scheme 7). Diols **3a** and **3j**, however, did not yield any methoxy derivatives under the same circumstances. Instead, the respective anthrones were formed. This observation again reveals the difference in tendency to rearrange between **3a** and **3j**, and **3o** respectively, due to the effects of the *peri* substituents. The dimethoxy derivative **8** was treated with $BF_3.Et_2O$ in order to promote its rearrangement. However, only a small amount of the expected anthrone **1o** was isolated and the anthracene **2o** turned out to be the main product. The latter compound probably results from a reaction pathway similar to that followed in the formation of **2f** and **2h** (Scheme 5).



3o **8** **2o** : 69%

Scheme 7

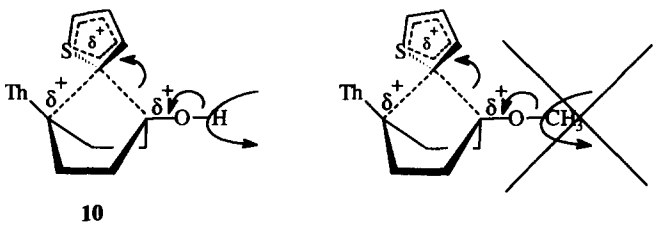
Furthermore, we synthesized the open-chain diol **9** (Scheme 8), which has structural similarity to diol **3o**. Although this diol was treated with $BF_3.Et_2O$ during seven days, no traces of any rearrangement product could be detected, and the substrate was recovered quantitatively. This result strongly suggests the interference of a highly organized transition state in the rearrangement. This transition state is not readily reached from a compound, as diol **9**, which has significantly more degrees of freedom than its analogue **3o**.



9

Scheme 8

On the basis of these observations, we propose a transition state **10** as shown in figure 1, which can be seen as formed by nucleophilic attack of the migrating aryl substituent onto the initially formed carbocation. This assumption readily explains the strong dependance of the rearrangement on π-electron density of the migrating aryl group. Moreover, as it is necessary to 'freeze' more or less the initial boat conformation of the central six membered ring, the role of the *peri* substituents, which prevent breakdown of this boat conformation, can be readily understood. The formation of this transition state is unfavored, starting from a compound such as diol **9**, which has too many degrees of freedom.



10

Figure 1

This transition state **10** can also explain the behaviour of **3o** and **8** when treated with $BF_3.Et_2O$. It is clear that, starting from **10**, concerted removal of a proton (Figure 1) is easier than that of a methyl group.

CONCLUSION

We have clearly demonstrated that the classical reduction of 9,10-diaryl-9,10-dihydroxy-9,10-dihydro-anthracenes, *i.e.* using KI/NaH_2PO_2 in refluxing acetic acid, fails totally when one or more voluminous *peri* substituents are present and at least one aryl substituent is a 2-thienyl, 2-furyl, 2-pyrrolyl or 2-indolyl group. In this case, anthrone formation occurs by migration of one of the aryl substituents. Using neat acetic acid or $BF_3.Et_2O$, depending on the nature of the substrate, we have found it to be possible to synthesize, in good yields, 10,10'-diarylanthrones, even without *peri* substituents, when at least one aryl group is electron rich. These compounds are obviously difficult to obtain by other methods. The strong dependency of this migration on 1) the π-electron density of the migrating aryl substituent, 2) the presence of *peri* substituents and 3) the necessity of incorporation of the rearranging 1,2-bis(hydroxymethyl)benzene system in a dihydroanthracene framework, as well as 4) the different behaviour of dimethoxy derivative **8**, strongly suggests that the observed transformation occurs via a transition state **10** as mentioned in figure 1. In further work, we will look for alternative ways of converting the diols **3a-d** into the corresponding anthracenes **2a-d** and into heterocyclic rubicene analogues.

EXPERIMENTAL

General

All starting compounds were obtained from ACROS Organics and were used without further purification. THF and diethyl ether were dried using standard methods. TMEDA was dried by distillation over $LiAlH_4$. Description of ^1H, ^{13}C NMR, IR and mass spectrometry, as well as the preparation and characterization of compounds **3f,g,h** and **2f,g,h** have previously been published[2].

General procedure for the preparation of 9,10-diaryl-9,10-dihydroanthracene-9,10-diols. To a solution of the appropriate aryllithium (15mmol), prepared by literature procedures[4], in diethyl ether (150mL) was added the appropriate anthraquinone (5mmol). This suspension was stirred for 15 hours, usually resulting in a clear solution. Water (100mL) was added carefully and the layers separated. The organic layer was dried over magnesium sulfate and the solvent was evaporated in vacuum. To the pasty residue, methanol (180mL) was added and the mixture left for 45 min. The fine white precipitate was filtered and washed with methanol (2x20mL) and diethyl ether (2x20mL) and dried in vacuum. As the diols, obtained in this way, usually contain a small fraction of the *cis* isomer which is not completely removed by recrystallization, melting points of these mixtures are not reported. If unspecified, the spectral data listed below, belong to the *trans* isomers.

1,5-Dichloro-9,10-dihydroanthracene-9,10-dithienyl-9,10-diol **3a** was obtained following the general procedure as a *cis/trans* mixture (0.3/1) in 82% yield. The isomers were readily separated by column chromatography (SiO_2) with dichloromethane as the eluent.

cis derivative Mp 293°C. ^1H NMR (400MHz, DMSO) δ (ppm) 6.54(dd, $J_{3,4}$ = 3.5Hz, $J_{3,5}$ = 1.0Hz, 2H; 3-H thiophene), 6.77(dd, $J_{4,5}$ = 5.0Hz, $J_{3,4}$ = 3.5Hz, 2H; 4-H thiophene), 6.95(s, 2H; OH), 7.22(dd, J_o = 8.0Hz, J_m = 1.3Hz, 2H; 2,6-H dihydroanthracene), 7.28(t, J = 8.0Hz, 2H; 3,7-H dihydroanthracenediol), 7.32(dd, $J_{4,5}$ = 5.0Hz, $J_{3,5}$ = 1.0Hz, 2H; 5-H thiophene), 7.73(dd, J_o = 8.0Hz, J_m = 1.3Hz, 2H; 4,8-H dihydroanthracenediol). ^{13}C NMR (100MHz, DMSO) δ (ppm) 71.5, 123.8, 124.5, 126.3, 127.9, 128.8, 130.2, 133.5, 134.2, 144.3, 154.7. MS (EI) *m/z* 444 (M^+).

trans derivative Mp 215°C. ^1H NMR (400MHz, DMSO) δ (ppm) 6.40(dd, $J_{3,4}$ = 3.6Hz, $J_{3,5}$ = 1.2Hz, 2H; 3-H thiophene), 6.67(s, 2H; OH), 6.75(dd, $J_{4,5}$ = 5.1Hz, $J_{3,4}$ = 3.6Hz, 2H; 4-H thiophene), 7.32(dd, J_o = 8.1Hz, J_m = 1.5Hz, 2H; 2,6-H dihydroanthracene), 7.34(dd, $J_{4,5}$ = 5.1Hz, $J_{3,5}$ = 1.2Hz, 2H; 5-H thiophene), 7.39(t, J = 8.1Hz, 2H; 3,7-H dihydroanthracenediol), 7.96(dd, J_o = 8.1Hz, J_m = 1.5Hz, 2H; 4,8-H dihydroanthracenediol). ^{13}C NMR (100MHz, DMSO) δ (ppm) 71.2, 123.8, 124.9, 125.9, 127.2, 129.0, 130.6, 133.3, 133.9, 143.8, 152.7. MS (CI) *m/z* 445 (MH^+).

1,5-Dichloro-9,10-dihydroanthracene-9,10-bis(5-methylthienyl)-9,10-diol **3b** was obtained following the general procedure as a *cis/trans* mixture (1/15) in 76% yield. This mixture was used without further purification. ^1H NMR (400MHz, DMSO) δ (ppm) 2.33(s, 6H; CH_3), 6.08(d, $J_{3,4}$ = 3.5Hz, 2H; 3-H thiophene), 6.40(dbr, $J_{3,4}$ = 3.5Hz, 2H; 4-H thiophene), 6.55(s, 2H; OH), 7.32(dd, J_o = 8.0Hz, J_m = 1.5Hz, 2H; 2,6-H dihydroanthracenediol), 7.38(t, J = 8.0Hz, 2H; 3,7-H dihydroanthracenediol), 7.94(dd, J_o = 8.0Hz, J_m = 1.5Hz, 2H; 4,8-H dihydroanthracenediol). ^{13}C NMR (100MHz, DMSO) δ (ppm) 14.8, 71.2, 123.7, 124.0, 127.1, 128.9, 130.5, 133.3, 133.8, 138.2, 144.1, 149.8. MS (CI) *m/z* 473 (MH^+).

1,5-Dichloro-9,10-dihydroanthracene-9,10-difuryl-9,10-diol **3c** was obtained following the general procedure as a *cis/trans* mixture (1/4) in 79% yield. This mixture was used without further purification. ^1H NMR (400MHz, DMSO) δ (ppm) 6.10(d, $J_{3,4}$ = 3.2Hz, 2H; 3-H furan), 6.29(dd, $J_{3,4}$ = 3.2Hz, $J_{4,5}$ = 1.7Hz, 2H; 4-H furan), 6.60(s, 2H; OH), 7.35(m, 6H; 5-H furan and 2,3,6,7-H dihydroanthracene), 7.87(dd, J_o = 7.7Hz, J_m = 1.9Hz, 2H; 4,8-H dihydroanthracene). ^{13}C NMR (100MHz, DMSO) δ (ppm) 69.7, 106.3, 110.4, 127.3, 128.9, 130.6, 132.6, 133.2, 141.5, 142.7, 157.3. MS (CI) *m/z* 413 (MH^+).

1,5-Dichloro-9,10-dihydroanthracene-9,10-bis(1-methylpyrrol-2-yl)-9,10-diol **3d** was obtained as a viscous oil after column chromatography (SiO_2/CH_2Cl_2) of the evaporated organic layer (see general procedure) in 65% yield. ^1H NMR (250MHz, 50°C, $CDCl_3$) δ (ppm) 3.31(s, 6H; CH_3), 3.83(sbr, 2H; OH), 5.92(tbr, 2H; 3-H pyrrole), 5.99(t, J = 3.3Hz, 2H; 4-H pyrrole), 6.46(t, J = 2.1Hz, 2H; 5-H pyrrole), 7.19(t, J = 8Hz, 2H; 3,7-H dihydroanthracene), 7.28(dd, J_o = 8Hz, J_m = 1Hz, 2H; 2,6-H dihydroanthracene), 7.43(dbr, J = 8Hz, 2H; 4,8-H dihydroanthracene). MS (CI) *m/z* 439 (MH^+).

1,5-Dichloro-9,10-dihydroanthracene-9,10-bis(1-methylindol-2-yl)-9,10-diol **3e** was obtained as a viscous oil after column chromatography (SiO_2/CH_2Cl_2) of the evaporated organic layer (see general procedure) in 54% yield. The oil was used without further purification. MS (EI) *m/z* 538 (M^+).

1-Chloro-9,10-dihydroanthracene-9,10-dithienyl-9,10-diol **3i** was obtained following the general procedure as a *cis/trans* mixture (2/5) in 84% yield. ^1H NMR (400MHz, $CDCl_3$) δ (ppm) 2.86(s, 1H; 10-OH), 4.82(s, 1H; 9-OH), 6.79-6.84(3xdd, 3H; thiophene), 6.92(dd, J_o = 5.1Hz, J_m = 2.9Hz, 1H; thiophene), 7.16(dd, J_o = 5Hz, J_m = 1.3Hz, 1H; thiophene), 7.19-7.24(m, 2H), 7.28(t, J = 7.9Hz, 1H; dihydroanthracene), 7.31-7.37(m, 3H), 7.54(dd, J_o = 7.9Hz, J_m = 1.4Hz, 1H; 4-H dihydroanthracene), 7.95(ddbr, J_o = 8.0Hz, J_m = 0.9Hz, 1H; 5-H or 8-H dihydroanthracene). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 73.2, 73.8, 124.3, 124.6, 124.8, 125.4, 126.6, 126.9, 127.9, 128.0, 128.27, 128.33, 129.0, 129.7, 131.6, 133.5, 136.0, 136.7, 139.0, 143.0, 153.1, 153.5. MS (EI) *m/z* 410 (M^+).

1,8-Dichloro-9,10-dihydroanthracene-9,10-dithienyl-9,10-diol **3j** was obtained following the general procedure as a *cis/trans* mixture (1/2) in 86% yield. This mixture was readily separated by column chromatography (SiO_2) with dichloromethane as the eluent.

cis derivative ^1H NMR (250MHz, DMSO) δ (ppm) 6.67(dd, $J_{3,4}$ = 3.6Hz, $J_{3,5}$ = 1.1Hz, 1H; 3-H thiophene), 6.74(dd, $J_{4,5}$ = 5.1Hz, $J_{3,4}$ = 3.6Hz, 1H; 4-H thiophene), 6.84(s, 1H; OH), 6.84(dd, $J_{3,4}$ = 3.6Hz, $J_{3,5}$ = 1.1Hz, 1H; 3-H thiophene), 6.89(dd, $J_{4,5}$ = 5.1Hz, $J_{3,4}$ = 3.6Hz, 1H; 4-H thiophene), 7.10(s, 1H; OH), 7.17-7.23(m, 4H; 2,3,6,7-H dihydroanthracene), 7.27(dd, $J_{3,5}$ = 1.1Hz, $J_{4,5}$ = 5.1Hz, 1H; 5-H thiophene), 7.33(dd, $J_{3,5}$ = 1.1Hz, $J_{4,5}$ = 5.1Hz, 1H; 5-H thiophene), 7.43(dd, J_o = 7.2Hz, J_m = 2.1Hz, 2H; 4,5-H dihydroanthracene). ^{13}C NMR (62MHz, DMSO) δ (ppm) 72.2, 72.8, 123.9, 124.5, 125.2, 126.9, 127.6, 128.12, 128.14, 128.4, 131.6, 132.9, 137.7, 141.1, 149.1, 156.6. MS (CI) *m/z* 445 (MH^+).

trans derivative ^1H NMR (250MHz, DMSO) δ (ppm) 6.19(dd, $J_{3,4}$ = 3.6Hz, $J_{3,5}$ = 1.1Hz, 1H; 3-H thiophene), 6.29(dd, $J_{3,4}$ = 3.6Hz, $J_{3,5}$ = 1.1Hz, 1H; 3-H thiophene), 6.57(dd, $J_{4,5}$ = 5.1Hz, $J_{3,4}$ = 3.6Hz, 1H; 4-H thiophene), 6.61(s, 1H; OH),6.76(dd, $J_{4,5}$ = 5.1Hz, $J_{3,4}$ = 3.6Hz, 1H; 4-H thiophene), 7.07(s, 1H; OH), 7.1827(dd, $J_{3,5}$ = 1.1Hz, $J_{4,5}$ = 5.1Hz, 1H; 5-H thiophene), 7.37-7.46(m, 5H; 5-H thiophene and 2,3,6,7-H dihydroanthracene), 8.01(dd, J_o = 7.5Hz, J_m = 2.1Hz, 2H; 4,5-H dihydroanthracene). ^{13}C NMR (62MHz, DMSO) δ (ppm) 70.7, 72.5, 124.39, 124.40, 125.7, 126.0, 126.4, 126.5, 126.7, 128.4, 132.0, 133.3, 137.7, 140.9, 147.1, 153.6. MS (CI) *m/z* 445 (MH^+).

1,4-Dibutoxy-9,10-dihydroanthracene-9,10-dithienyl-9,10-diol **3k** was obtained as the almost pure *trans* isomer (<3% of *cis* isomer present) in 85% yield. ^1H NMR (250MHz, DMSO) δ (ppm) 0.88(t, 6H; CH_3), 1.20-1.35(m, 4H; CH_3CH_2), 1.43-1.55(m, 4H; $-OCH_2CH_2$), 3.55(dt, ^1J = 9Hz, ^3J = 7Hz, 2H; OCH_2), 3.98(dt, ^1J = 9Hz, ^3J = 7Hz, 2H; OCH_2), 5.84(s, 2H; OH), 6.61(d, $J_{3,4}$ = 2.8Hz, 2H; 3-H thiophene), 6.77(dd, $J_{4,5}$ = 5.1Hz, $J_{3,4}$ = 2.8Hz, 2H; 4-H thiophene), 7.00(s, 2H; 3,4-H dihydroanthracene), 7.11-7.14(m, 2H; 6,7-H dihydroanthracene), 7.18(d, $J_{4,5}$ = 5.1Hz, 2H; 5-H thiophene), 7.58-7.62(m, 2H; 5,8-H dihydroanthracene). MS (EI) *m/z* 520 (M^+).

1,5-Dibutoxy-9,10-dihydroanthracene-9,10-dithienyl-9,10-diol **3l** was obtained as the almost pure *trans* isomer (<2% of *cis* isomer present) in 88% yield. ^1H NMR (400MHz, DMSO) δ (ppm) 0.79(t, 6H; CH_3), 1.11-1.14(m, 4H; CH_3CH_2), 1.42-1.45(m, 4H; $-OCH_2CH_2$), 3.73(dt, ^1J = 9Hz, ^3J = 6Hz, 2H; OCH_2), 4.04(dt, ^1J = 9Hz, ^3J = 6Hz, 2H; OCH_2), 6.05(s, 2H; OH), 6.28(dd, $J_{3,4}$ = 3.6Hz, $J_{3,5}$ = 1.2Hz, 2H; 3-H thiophene), 6.69(dd, $J_{4,5}$ = 5.1Hz, $J_{3,4}$ = 3.6Hz, 2H; 4-H thiophene), 6.98(d, J = 8.2Hz, 2H; 2,6-H dihydroanthracene), 7.29(dd, $J_{4,5}$ = 5.1Hz, $J_{3,5}$ = 1.2Hz, 2H; 5-H thiophene), 7.38(t, J = 8.2Hz, 2H; 3,7-H dihydroanthracene), 7.61(d, J = 8.2Hz, 2H; 4,8-H dihydroanthracene). ^{13}C NMR (100MHz, DMSO) δ (ppm) 13.6, 18.4, 30.4, 68.1, 71.0, 111.3, 119.8, 123.1, 124.3, 125.6, 125.8, 128.9, 140.4, 154.9, 155.8. MS (EI) *m/z* 520 (M^+).

1,8-Dibutoxy-9,10-dihydroanthracene-9,10-dithienyl-9,10-diol **3m** was obtained following the general procedure as a *cis/trans* mixture (1/2) in 82% yield. This mixture was readily separated by column chromatography (SiO_2) with dichloromethane as the eluent.

trans derivative ^1H NMR (250MHz, DMSO) δ (ppm) 0.90(t, 6H; CH_3), 1.29-1.43(m, 4H; CH_3CH_2), 1.55-1.66(m, 4H; OCH_2CH_2), 3.81(dt, ^1J = 9Hz, ^3J = 6Hz, 2H; OCH_2), 3.93(dt, ^1J = 9Hz, ^3J = 6Hz, 2H; OCH_2), 5.73(s, 1H; OH), 6.24(dd, $J_{3,4}$ = 3.6Hz, $J_{3,5}$ = 1.3Hz, 1H; 3-H thiophene), 6.28(dd, $J_{3,4}$ = 3.6Hz, $J_{3,5}$ = 1.3Hz, 1H; 3-H thiophene), 6.58(dd, $J_{4,5}$ = 5.1Hz, $J_{3,4}$ = 3.6Hz, 1H; 4-H thiophene), 6.71(dd, $J_{4,5}$ = 5.1Hz, $J_{3,4}$ = 3.6Hz, 1H; 4-H thiophene), 6.73(s, 1H; OH), 6.96(dd, J_o = 8Hz, J_m = 1Hz, 2H; 2,6-H dihydroanthracene), 7.16(dd, $J_{4,5}$ = 5.1Hz, $J_{3,5}$ = 1.3Hz, 1H; 5-H thiophene),

7.32(dd, $J_{4,5}$ = 5.1Hz, $J_{3,5}$ = 1.3Hz, 1H; 5-H thiophene), 7.34(t, J = 8Hz, 2H; 3,7-H dihydroanthracene), 7.48(dd, J_o = 8Hz, J_m = 1Hz, 2H; 4,8-H dihydroanthracene). ^{13}C NMR (62MHz, $CDCl_3$) δ (ppm) 13.9, 19.2, 31.0, 68.9, 72.4, 73.0, 112.6, 119.8, 123.0, 124.68, 124.73, 125.2, 126.0, 126.2, 128.1, 128.8, 139.7, 152.0, 153.1, 156.3. MS (EI) *m/z* 520 (M^+).

cis derivative ^{1}H NMR (250MHz, DMSO) δ (ppm) 0.92(t, 6H; CH_3), 1.29-1.43(m, 4H; CH_3CH_2), 1.55-1.66(m, 4H; OCH_2CH_2), 3.81(dt, ^{1}J = 9Hz, ^{3}J = 6Hz, 2H; OCH_2), 3.93(dt, ^{1}J = 9Hz, ^{3}J = 6Hz, 2H; OCH_2), 5.58(s, 1H; OH), 6.51(dd, $J_{3,4}$ = 3.6Hz,$J_{3,5}$ = 1.3Hz, 1H; 3-H thiophene), 6.6124(dd, $J_{3,4}$ = 3.6Hz,$J_{3,5}$ = 1.3Hz, 1H; 3-H thiophene), 6.68(dd, $J_{4,5}$ = 5.1Hz, $J_{3,4}$ = 3.6Hz, 1H; 4-H thiophene), 6.75-6.80(m, 4H, OH + 4-H thiophene + 2,6-H dihydroanthracene), 7.09(dd, J_o = 8Hz, J_m = 1Hz, 2H; 2,6-H dihydroanthracene), 7.13-7.16(m, 4H; 3,4,7,8-H dihydroanthracene), 7.18(dd, $J_{4,5}$ = 5.1Hz, $J_{3,5}$ = 1.3Hz, 1H; 5-H thiophene), 7.23(dd, $J_{4,5}$ = 5.1Hz, $J_{3,5}$ = 1.3Hz, 1H; 5-H thiophene). ^{13}C NMR (62MHz, DMSO) δ (ppm) 157.0, 156.1, 154.5, 140.5, 128.3, 128.2, 126.2, 124.7, 124.2, 123.7, 123.6, 122.2, 120.4, 111.2, 72.5, 72.1, 67.9, 30.4, 18.8, 13.8. MS (EI) *m/z* 520 (M^+).

1,5-Bis(phenylsulfanyl)-9,10-dihydroanthracene-9,10-dithienyl-9,10-diol **3n** was obtained as the almost pure *trans* isomer (<2% of *cis* isomer present) in 81% yield. ^{1}H NMR (400MHz, DMSO) δ (ppm) 6.22(dd, $J_{3,4}$ = 3.6Hz, $J_{3,5}$ = 1.2Hz, 2H; 3-H thiophene), 6.66(dd, $J_{4,5}$ = 5.1Hz, $J_{3,4}$ = 3.6Hz, 2H; 4-H thiophene), 6.89(dd, J_o = 7.9Hz, J_m = 1.1Hz, 2H; 2,6-H dihydroanthracene), 7.07(s, 2H; OH), 7.20-7.30(m, 14H; phenyl + 5-H thiophene + 3,7-H dihydroanthracene), 7.92(dd, J_o = 7.9Hz, J_m = 1.1Hz, 2H; 4,8-H dihydroanthracene). ^{13}C NMR (100MHz, DMSO) δ (ppm) 72.1, 124.6, 124.7, 125.26, 125.34, 127.8, 128.0, 129.4, 130.2, 133.2, 136.2, 136.9, 139.3, 142.6, 151.7. MS (CI) *m/z* 593 (MH^+).

9,10-Dihydroanthracene-9,10-bis(1-methylpyrrol-2-yl)-9,10-diol **3p** was obtained following the general procedure as a *cis/trans* mixture (1/2) in 79% yield. The isomers were readily separated by column chromatography (SiO_2) with dichloromethane as the eluent.

cis derivative ^{1}H NMR (400MHz, DMSO) δ (ppm) 2.81(s, 6H; CH_3), 5.85(s, 2H; OH), 5.95(dd, $J_{3,4}$ = 3.4Hz, $J_{3,5}$ = 2.7Hz, 2H; 3-H pyrrole), 6.45($J_{4,5}$ = 2.5Hz, $J_{3,4}$ = 3.4Hz, 2H; 4-H pyrrole), 6.48(dd, $J_{4,5}$ = 2.5Hz, $J_{3,5}$ = 2.7Hz, 2H, 5-H pyrrole), 7.24-7.29(m, 4H; 2,3,6,7-H dihydroanthracene), 7.32-7.33(m, 4H; 1,4,5,8-H dihydroanthracene). ^{13}C NMR (100MHz, DMSO) δ (ppm) 34.8, 70.4, 105.3, 107.8, 123.2, 127.4, 128.2, 138.7, 139.0. MS (CI) *m/z* 371 (MH^+).

trans derivative ^{1}H NMR (400MHz, DMSO) δ (ppm) 2.67(s, 6H; CH_3), 5.75(s, 2H; OH), 6.09(dd, $J_{3,4}$ = 3.4Hz, $J_{3,5}$ = 2.7Hz, 2H; 3-H pyrrole), 6.49($J_{4,5}$ = 2.5Hz, $J_{3,4}$ = 3.4Hz, 2H; 4-H pyrrole), 6.72(dd, $J_{4,5}$ = 2.5Hz, $J_{3,5}$ = 2.7Hz, 2H, 5-H pyrrole), 6.95-6.97(m, 4H; 2,3,6,7-H dihydroanthracene), 7.29-7.31(m, 4H; 1,4,5,8-H dihydroanthracene). ^{13}C NMR (100MHz, DMSO) δ (ppm) 34.6, 72.0, 105.8, 109.9, 123.5, 127.4, 128.1, 135.1, 140.8. MS (CI) *m/z* 371 (MH^+).

1,5-Dichloro-10-hydroxy-10'-phenyl(10H)anthracen-9-one **7**. To a suspension of 1,5-dichloroanthraquinone (7g; 25mmol) in dry THF (140mL), was added dropwise, during 45 minutes, a solution of phenylmagnesium bromide (27mmol) in THF (30mL). After the addition was complete, the resulting clear solution was stirred for 12h at room temperature. Water was added (100mL) and after vigorous shaking, the organic layer was separated. The water layer was extracted with dichloromethane (2x80ml). The combined organic layers were dried over magnesium sulfate and evaporated in vacuum. To the pasty residue, toluene (150mL) was added and the resulting suspension was refluxed for 15 minutes. The hot solution was filtered and the precipitate purified by column chromatography (SiO_2) with dichloromethane/petroleum ether (8/2) as the eluent. The title compound was obtained as a white solid in 42% yield. Mp 227°C. ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) 4.54(s, 1H; OH), 7.18(t, J = 7.2Hz, 1H; 4-H phenyl), 7.24(t, J = 7.2Hz, 3,5-H phenyl), 7.31(d, J = 7.2Hz, 2H; 2,6-H phenyl), 7.39(dd, J_o = 7.8Hz, J_m = 1.4Hz, 1H; 2-H anthrone), 7.41(t, J = 7.8Hz, 1H; 3-H anthrone), 7.48(t, J = 7.8Hz, 1H; 7-H anthrone), 7.57(dd, J_o = 7.8Hz, J_m = 1.4Hz, 1H; 2-H anthrone), 7.78(dd, J_o = 7.8Hz, J_m = 1.4Hz, 1H; 4-H anthrone), 8.30(dd, J_o = 7.8Hz, J_m = 1.4Hz, 1H; 8-H anthrone). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 74.1, 124.9, 125.2, 126.8, 127.3, 127.5, 128.5, 129.7, 131.5, 132.4, 133.8, 134.1, 134.2, 136.2, 140.6, 144.5, 150.1, 181.9. MS (EI) *m/z* 354 (M^+).

1,5-Dichloro-9,10-dihydroanthracene-9-phenyl-10-thienyl-9,10-diol **3r**. Compound **7** (1g; 2.8mmol) was added to a solution of 2-thienyllithium (10 mmol) in diethyl ether (30mL) under argon. The resulting suspension was stirred for another 15 hours. Water (20mL) was added and after vigorous shaking the organic layer was separated, dried over magnesium sulfate and evaporated in vacuum. The pasty residue was crystallized from methanol. The compound obtained in this way contains about 7% of the *cis* isomer. Yield: 72%. ^{1}H NMR (400MHz, DMSO) δ (ppm) 6.25(s, 1H; OH),

6.48(s, 1H; OH), 6.59(dd, $J_{3,4}$ = 3.6Hz, $J_{3,5}$ = 1.2Hz, 1H; 3-H thiophene), 6.85(dd, $J_{4,5}$ = 5.0Hz, $J_{3,4}$ = 3.6Hz, 1H; 4-H thiophene), 7.14(t, J = 7.2Hz, 1H; 4-H phenyl), 7.20-7.38(m, 8H, 2,3,6,7-H dihydroanthracene + 2,3,5,6-H phenyl), 7.40(dd, $J_{4,5}$ = 5.0Hz, $J_{3,5}$ = 1.2Hz, 1H; 5-H thiophene), 7.59(dd, J_o = 7.9Hz, J_m = 1.2Hz, 1H; 4- or 8-H dihydroanthracene), 7.93(dd, J_o = 7.9Hz, J_m = 1.2Hz, 1H; 4- or 8-H dihydroanthracene). ^{13}C NMR (100MHz, DMSO) δ (ppm) 71.4, 72.5, 124.1, 124.6, 125.0, 125.9, 126.0, 126.2, 127.6, 128.3, 128.8, 129.0, 130.2, 130.5, 133.0, 133.4, 133.8, 134.7, 143.7, 144.2, 147.6, 153.3. MS (EI) *m/z* 438 (M^+).

Preparation of the anthrones **1**

The two main strategies for preparation of the anthrones give different yields as mentioned in table 2 (rearrangement induced by acetic acid) and table 3 (rearrangement induced by boron trifluoride) respectively. If an anthrone was prepared by each of these procedures, it will be mentioned with the one that gives the highest yield.

General procedure (A) the synthesis of anthrones **1d,i,j,k,l,m,n**

The appropriate diol **3d,i,j,k,l,m,n** (2 mmol) was suspended in acetic acid (18 mL) and this mixture heated for 90 minutes. After cooling to room temperature, the precipitate was washed with methanol and dried under vacuum (for compounds **1d**, **1i/1i'** and **1j**. If no precipitate was formed, the solvent was evaporated in vacuum and the compound was purified by column chromatography (SiO_2) with dichloromethane as the eluent (for compounds **1k**, **1l**, **1m** and **1n**).

1,5-Dichloro-10,10'-bis(1-methylpyrrol-2-yl)(10H)anthracen-9-one **1d** Mp 197°C. ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) 3.09(s, 6H; CH_3), 5.28(dd, $J_{3,4}$ = 3.7Hz, $J_{3,5}$ = 2.1Hz, 2H; 3-H pyrrole), 5.97(dd, $J_{3,4}$ = 3.7Hz, $J_{4,5}$ = 2.8Hz, 2H; 4-H pyrrole), 6.54 (dd, $J_{3,5}$ = 2.1Hz, $J_{4,5}$ = 2.8Hz, 2H; 5-H pyrrole), 6.88(dd, J_o = 8.0Hz, J_m = 1.1Hz, 1H; 8-H), 7.33(t, J = 8Hz, 1H; 7-H), 7.39(t, J = 8Hz, 1H; 3-H), 7.47(dd, J_o = 8Hz, J_m = 1.1Hz, 1H; 6-H), 7.53(dd, J_o = 8Hz, J_m = 1.5Hz, 1H; 2-H), 7.99(dd, J_o = 8.0Hz, J_m 1.5Hz, 1H; 4-H). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 36.0, 50.1, 106.8, 112.8, 124.4, 127.2, 127.8, 128.8, 130.6, 131.1, 131.6, 133.2, 133.3, 133.8,135.7, 139.0, 140.0, 148.9, 184.0. IR (KBr) νCO 1681 cm^{-1}. MS (EI) *m/z* 420 (M^+).

Following the general procedure, an unseparable mixture of 1-chloro-10,10'-bis(thien-2-yl)(10H)anthracen-9-one 1i and *4-chloro-10,10'-bis(thien-2-yl)(10H)anthracen-9-one* **1i'** was obtained. IR (KBr) νCO 1668 cm^{-1}. MS (EI) *m/z* 392 (M^+). From ^{1}H NMR, it was obvious that the ratio **1i/1i'** was 2/1, although the spectrum of the mixture was too complex to be able to derive the separated spectra of the single compounds.

1,8-Dichloro-10,10'-bis(thien-2-yl)(10H)anthracen-9-one **1j** Mp 334°C. ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) 6.56(dd, $J_{3,4}$ = 3.6Hz, $J_{3,5}$ = 1.2Hz, 2H; 3-H thiophene), 6.89(dd, $J_{4,5}$ = 5.2Hz, $J_{3,4}$ = 3.6Hz, 2H; 4-H thiophene), 7.19(dd, J_o = 8.0Hz, J_m = 1.1Hz, 2H; 4,5-H anthrone), 7.26(dd, $J_{4,5}$ = 5.2Hz, $J_{3,5}$ = 1.2Hz, 2H; 5-H thiophene),7.37(t, J = 8.0Hz, 2H; 2,6-H anthrone), 7.48(dd, J_o = 8.0Hz, J_m = 1.1Hz, 2H; 2,7-H anthrone). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 51.2, 126.3, 126.6, 127.3, 129.1, 131.0, 131.8, 131.9, 133.0, 148.6, 150.0, 182.9. IR (KBr) νCO 1681 cm^{-1}. MS (EI) *m/z* 420 (M^+). EA (%C, %H, %S) Calculated: 61.8, 2.8, 15.0, Found: 62.3, 2.9, 15.2.

1,4-Dibutoxy-10,10'-bis(thien-2-yl)(10H)anthracen-9-one **1k** Mp 111°C. ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) 0.84(t, 3H; CH_3), 1.01(t, 3H; CH_3), 1.18(m, 2H; CH_2CH_3), 1.29(m, 2H; CH_2CH_3), 1.57(m, 2H; OCH_2CH_2), 1.88(m, 2H; OCH_2CH_2), 3.65(t, 2H; 1-OCH_2), 4.06(t, 2H; 4-OCH_2), 6.81(m, 4H; 3,4-H thiophene), 7.01-7.03(m, 2H; 2,3-H anthrone), 7.09-7.10(m, 2H; 5-H thiophene), 7.19-7.26(m, 1H; 8-H anthrone), 7.37-7.41(m, 2H; 6,7-H anthrone), 8.14-8.17(m, 1H; 5-H anthrone). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 13.8, 14.0, 19.1, 19.3, 30.8, 31.5, 50.0, 68.6, 69.9, 114.5, 118.4, 122.4, 124.1, 125.6, 126.5, 126.6, 127.3, 129.4, 132.1, 132.2, 136.8, 147.3, 150.1, 151.4, 153.3, 184.2. IR (KBr) νCO 1652 cm^{-1}. MS (CI) *m/z* 503 (MH^+). EA (%C, %H, %S) Calculated: 71.7, 6.0, 12.8, Found: 71.8, 6.1, 13.2.

1,5-Dibutoxy-10,10'-bis(thien-2-yl)(10H)anthracen-9-one **1l** was obtained as an amorphous solid. ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) 0.84(t, 3H; CH_3), 1.00(t, 3H; CH_3), 1.17(m, 2H; CH_2CH_3), 1.32(m, 2H; CH_2CH_3), 1.59(m, 2H; CH_2CH_2O), 1.91(m, 2H; CH_2CH_2O), 3.72(t, 2H; 5-OCH_2CH_2), 4.10(t, 2H; 1-OCH_2CH_2), 6.81(dd, $J_{4,5}$ = 5.1Hz, $J_{3,4}$ = 3.6Hz, 2H; 4-H thiophene), 6.84(dd, $J_{3,4}$ = 3.6Hz, $J_{3,5}$ = 1.3Hz, 2H; 3-H thiophene), 6.89-6.92(m, 2H; 2,4-H anthrone), 7.03(dd, J_o = 8.0Hz, J_m = 1.2Hz, 1H; 6-H anthrone), 7.09(dd, $J_{4,5}$ = 5.1Hz, $J_{3,5}$ = 1.3Hz, 2H; 5-H thiophene), 7.34(t, J = 8.2Hz, 1H; 3-H anthrone),7.39(t, J = 8Hz, 1H; 7-H anthrone), 7.84 (dd, J_o = 8Hz, J_m = 1.2Hz, 1H; 8-H anthrone). ^{13}C

NMR (100MHz, $CDCl_3$) δ (ppm) 13.8, 13.9, 19.1, 19.3, 30.7, 31.3, 50.0, 68.2, 69.0, 11.4, 116.3, 119.3, 120.0, 122.4, 124.2, 125.6, 126.7, 128.8, 133.2, 133.7, 134.7, 151.3, 151.5, 152.0, 159.2, 183.5). MS (EI) *m/z* 502 (M^+).

1,5-Bis(phenylsulfanyl)-10,10'-bis(thien-2-yl)(10H)anthracen-9-one **1n** Mp 220°C. ^1H NMR (400MHz, $CDCl_3$) δ (ppm) 6.69(dd, J_o = 7.4Hz, J_m = 1.5Hz, 1H; 6-H anthrone), 6.88(dd, $J_{4,5}$= 5.1Hz, $J_{3,4}$= 3.6Hz, 2H; 4-H thiophene),7.08(dd, $J_{3,4}$ = 3.6Hz, $J_{3,5}$ = 3.6Hz, 2H; 3-H thiophene),7.12-7.20(m, 5H), 7.21(dd, $J_{4,5}$ = 5.1Hz, $J_{3,5}$ = 1.1Hz, 2H; 5-H thiophene), 7.31(t, J = 7.7Hz, 1H; 3-H anthrone), 7.37(dd, J_o = 7.7Hz, J_m= 1.5Hz, 1H; 2-H anthrone),7.42(m, 3H),7.61(m, 2H), 8.29(dd, J_o = 7.7Hz, J_m = 1.5Hz,1H; 4-H anthrone). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 52.3, 124.4, 125.3, 125.7, 125.8, 126.4, 127.5, 128.4, 129.1, 129.3, 129.7, 132.2, 132.8, 132.9, 136.0, 138.1, 140.1, 144.8, 145.0, 149.6, 151.5. IR (KBr) νCO 1649 cm^{-1}. MS (EI) *m/z* 575 (M^+). EA (%C, %H, %S) Calculated: 71.0, 3.9, 22.3, Found: 70.7, 4.1, 22.3.

General procedure (B) for the synthesis of anthrones **1a,b,c,e,g,o,q**

The appropriate diol **3a,b,c,e,g,o,q** (2 mmol) was suspended in dichloromethane (25 mL). Through a septum, boron trifluoride etherate (10 mmol) was added by a syringe. The mixture, which immediately turned dark green to blue, was then stirred for 30 minutes. The reaction was quenched by addition of a solution (10mL / 1M) of sodium hydroxyde and the layers were separated. The organic layer was dried over magnesium sulfate and the solvent was evaporated in vacuum. The residue was taken up in warm methanol, from which the anthrones readily crystallized. The precipitate was filtered and washed with methanol.

1,5-Dichloro-10,10'-bis(thien-2-yl)(10H)anthracen-9-one **1a** Mp 234°C. ^1H NMR (400MHz, DMSO) δ (ppm) 6.98(dd, $J_{4,5}$ = 5.1Hz, $J_{3,4}$ = 3.7Hz, 2H; 4-H thiophene), 7.05(dd, $J_{3,4}$ = 3.7Hz, $J_{3,5}$ = 1.2Hz, 2H; 3-H thiophene), 7.39(dd, J_o = 7.5Hz, J_m = 1.7Hz, 1H; 2- or 4-H anthrone), 7.48(dd, $J_{4,5}$ = 5.1Hz, $J_{3,5}$ = 1.2Hz, 2H, 5-H thiophene), 7.56(dd, J_o = 7.5Hz, J_m = 1.7Hz, 1H; 2- or 4-H anthrone), 7.60(t, J = 7.5Hz, 1H; 3-H anthrone), 7.64(t, J = 7.8Hz, 1H; 7-H anthrone), 7.77(dd, J_o = 7.8Hz, J_m = 1.5Hz, 1H; 6-H anthrone), 8.12(dd, J_o = 7.8Hz, J_m = 1.5Hz, 1H; 8-H anthrone). ^{13}C NMR (100MHz, DMSO) δ (ppm) 51.0, 125.2, 126.4, 126.6, 126.8, 128.0, 129.1, 130.0, 131.0, 132.2, 133.9, 134.1, 134.8, 137.0, 141.8, 148.1, 151.6, 181.7. IR (KBr) νCO 1670 cm^{-1}. MS (EI) *m/z* 426 (M^+). EA (%C, %H, %S) Calculated: 61.8, 2.8, 15.0, Found: 61.7, 3.1, 15.4.

1,5-Dichloro-10,10'-bis(5-methylthien-2-yl)(10H)anthracen-9-one **1b** Mp 206°C. ^1H NMR (400MHz, $CHCl_3$) δ (ppm) 2.37(s, 6H; CH_3), 6.52(dq, $J_{3,4}$ = 3.6Hz, ^4J = 1.1Hz, 2H; 4-H thiophene), 6.70(d, $J_{3,4}$ = 3.6Hz, 2H; 3-H thiophene), 7.36(t, J = 7.8Hz, 1H; 7-H anthrone), 7.40-7.45(m, 3H; 3,6,8-H anthrone), 7.43(dd, J_o = 7.8Hz, J_m = 1.5Hz, 1H; 2-H anthrone), 8.19(dd, J_o = 7.8Hz, J_m = 1.5Hz, 1H; 4-H anthrone). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 15.2, 51.9, 124.3, 126.4, 126.9, 128.0, 129.0, 129.1, 130.9, 132.7, 133.6, 135.0, 135.6, 136.8, 140.4, 142.3, 146.0, 152.0, 182.7. IR (KBr) νCO 1672 cm^{-1}. MS (EI) *m/z* 454 (M^+).

1,5-Dichloro-10,10'-bis(fur-2-yl)(10H)anthracen-9-one **1c** Mp 199°C. ^1H NMR (400MHz, DMSO) δ (ppm) 6.47(m, 4H; 3,4-H furan), 7.36(dd, J_o = 7.1Hz, J_m = 2.2Hz, 1H; 4-H anthrone), 7.56-7.61(m,4H; 5-H furan and 2,3-H anthrone), 7.64(t, J = 7.9Hz, 1H; 7-H anthrone), 7.75(dd, J_o = 7.9Hz, J_m = 1.5Hz, 1H; 6-H anthrone), 8.17(dd, J_o = 7.9Hz, J_m = 1.5Hz, 1H; 8-H anthrone). ^{13}C NMR (100MHz, DMSO) δ (ppm) 54.8, 109.6, 110.8, 125.6, 126.5, 128.3, 129.9, 131.3, 132.7, 133.6, 134.0, 134.8, 136.4, 137.5, 142.9, 146.5, 152.4,181.4. IR (KBr) νCO 1661 cm^{-1}. MS (EI) *m/z* 394 (M^+).

1,5-Dichloro-10,10'-bis(1-methylindol-2-yl)(10H)anthracen-9-one **1e** Mp >335°C. ^1H NMR (400MHz, $CHCl_3$) δ (ppm) 3.36(s, 6H; CH_3), 5.75(s, 2H; 3-H indole), 6.89(dd, J_o = 8.0Hz, J_m = 1.5Hz, 1H; 4-H anthrone), 7.09(m, 2H; indole), 7.21-7.29(m, 4H; indole), 7.31(t, J = 8.0Hz, 1H; 3-H anthrone), 7.45(m, 2H; indole), 7.46(t, J = 8Hz, 1H; 7-H anthrone), 7.53(dd, J_o = 8Hz, J_m = 1.5Hz, 1H; 2-H anthrone), 7.56(dd, J_o = 8Hz, J_m = 1.5Hz, 1H; 6-H anthrone), 8.03(dd, J_o = 8.0Hz, J_m = 1.5Hz, 1H; 8-H anthrone). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 30.9, 51.1, 106.5, 109.2, 119.9, 121.0, 122.3, 126.7, 127.5, 127.9, 129.4, 130.7, 131.6, 131.8, 133.5, 133.6, 136.0, 138.4, 139.1, 139.2, 140.8, 147.3, 183.5. IR (KBr) νCO 1686 cm^{-1}. MS (EI) *m/z* 520 (M^+).

1,5-Dichloro-10,10'-bis(4-methoxyphenyl)(10H)anthracen-9-one **1g** Mp 223°C. ^1H NMR (400MHz, $CHCl_3$) δ (ppm) 3.77(s, 6H; CH_3), 6.75(d, J = 9Hz, 4H; 3,5-H phenyl), 6.95(d, J= 8.0Hz, 4H; 2,6-H phenyl), 7.28(t, J = 8Hz, 1H, 3-H anthrone), 7.38(m, 1H; 2-H anthrone),7.41(t, J = 8.0Hz, 1H; 7-H anthrone), 7.54(dd, J_o = 8Hz, J_m = 1.5Hz, 1H;6-H anthrone), 8.11(dd, J_o = 8Hz, J_m = 1.5Hz, 1H; 8-H anthrone). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 55.2, 57.3, 113.5,

126.9, 128.56, 128.61, 130.2, 130.3, 130.9, 131.9, 133.4, 134.7, 136.2, 136.5, 137.6, 143.4, 153.5, 158.4, 184.0. IR (KBr) νCO cm^{-1}. MS (EI) *m/z* 462 (M^+).

10,10'-Bis(thien-2-yl)(10H)anthracen-9-one **1o** Mp 197°C. ^1H NMR (400MHz, $CDCl_3$) δ (ppm) 6.71(dd, $J_{3,4}$ = 3.6Hz, $J_{3,5}$ = 1.2Hz, 2H; 3-H thiophene), 6.86(dd, $J_{4,5}$ = 5.2Hz, $J_{3,4}$ = 3.6Hz, 2H; 4-H thiophene), 7.20(dd, $J_{4,5}$ = 5.2Hz, $J_{3,5}$ = 1.2Hz, 2H; 5-H thiophene), 7.44(d br, J = 7.8Hz, 2H; 4.5-H anthrone), 7.48(td, J_o = 7.8Hz, J_m = 1.2Hz, 2H; 3,6-H anthrone), 7.56(td, J_o = 7.8Hz, J_m = 1.2Hz, 2H; 2,7-H anthrone), 8.30(dd, J_o = 7.8Hz, J_m = 1.2Hz, 2H; 1,8-H anthrone). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 52.0, 126.0, 126.1, 127.4, 128.0, 128.5, 129.8, 130.9, 132.9, 148.1, 151.2, 183.6. IR (KBr) νCO cm^{-1}. MS (EI) *m/z* 358 (M^+).

10,10'-Bis(4-methoxyphenyl)(10H)anthracen-9-one **1q** Mp 209°C. ^1H NMR (400MHz, $CHCl_3$) δ (ppm) 3.75(s, 6H; CH_3), 6.74(d, J = 9Hz, 4H; 3,5-H phenyl), 6.90(d, J = 9Hz, 4H; 2,6-H phenyl), 7.17(m, 2H; 4,5-H anthrone), 7.43(m, 4H; 2,3,6,7-H anthrone), 8.27(m, 2H; 1,8-H anthrone). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 55.2, 57.0, 113.3, 127.0, 127.3, 130.5, 131.1, 132.2, 132.5, 138.6, 149.9, 158.2, 184.6. IR (KBr) νCO cm^{-1}. MS (EI) *m/z* 394 (M^+). EA (%C, %H) Calculated: 82.7, 5.5, Found: 82.4, 5.8.

10,10'-Bis(1-methylpyrrol-2-yl)(10H)anthracen-9-one **1p** . The crude solution of diol **3p** in diethyl ether was washed twice with a 2M solution of hydrochloric acid (50mL). The organic layer was separated and dried over magnesium sulfate. The solvent was evaporated in vacuum and the residue crystallized from methanol. The anthrone **1p** was obtained as dark crystals in 78% overall yield (calculated from the starting anthraquinone). Mp 208°C. ^1H NMR (400MHz, $CDCl_3$) δ (ppm) 3.08 (s, 6H; CH_3), 5.33(dd, $J_{3,5}$ = 2.0Hz, $J_{3,4}$ = 3.7Hz, 2H; 3-H pyrrole),5.96(dd, $J_{3,4}$ = 3.7Hz, $J_{4,5}$ = 2.8Hz, 2H; 4-H pyrrole), 6.54(dd, $J_{4,5}$ = 2.8Hz, $J_{3,5}$ = 2.0Hz, 2H; 5-H pyrrole), 7.14-7.16(m, 2H; 4,5-H anthrone), 7.45-7.48(m, 4H; 2,3,6,7-H anthrone), 8.20-8.22(m, 2H; 1,8-H anthrone). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 36.8, 50.3, 106.2, 112.7, 124.6, 127.6, 127.7, 128.8, 131.9, 133.2, 134.6, 146.2, 184.9. IR (KBr) νCO 1667cm^{-1}. MS (EI) *m/z* 324 (M^+).

1,5-Dichloro-10-phenyl-10'-thienyl(10H)anthracen-9-one **1r** Mp 222°C. ^1H NMR (400MHz, $CHCl_3$) δ (ppm) 6.69(dd, $J_{3,4}$ = 3.7Hz, $J_{3,5}$ = 1.1Hz, 1H; 3-H thiophene), 6.85(dd, $J_{4,5}$ = 5.1Hz, $J_{3,4}$ = 3.7Hz, 1H; 4-H thiophene), 7.00(dd, J_o = 8.0Hz, J_m = 1.2Hz, 1H; 4-H anthrone), 7.18(dd, $J_{4,5}$ = 5.1Hz, $J_{3,5}$ = 1.1Hz, 1H; 5-H thiophene), 7.20-7.22(m, 2H; 2,6-H phenyl), 7.28-7.29(m, 3H; 3,4,5-H anthrone), 7.30(t, J = 8.0Hz, 1H; 3-H anthrone), 7.42(dd, J_o = 8.0Hz, J_m = 1.2Hz, 1H; 2-H anthrone), 7.44(t, J = 7.8Hz, 1H; 7-H anthrone), 7.57(dd, J_o = 7.8Hz, J_m = 1.5Hz, 1H; 6-H anthrone), 8.19(dd, J_o = 7.8Hz, J_m = 1.5Hz, 1H; 8-H anthrone). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 55.0, 126.0, 126.5, 127.06, 127.11, 127.6, 128.3, 128.5, 129.0, 129.3, 130.1, 130.9, 132.4, 133.7, 134.2, 136.6, 136.9, 143.1, 145.7, 147.2, 152.5, 183.2. IR (KBr) νCO 1670cm^{-1}. MS (CI) *m/z* 421 (MH^+). EA (%C, %H, %S) Calculated: 68.4, 3.3, 7.6, Found: 68.9, 3.5, 7.2.

General procedure for the preparation of anthracenes **5m,o** *and the acetic esters* **4f,g** *and* **4q** A suspension of the appropriate diol (2mmol) in acetic acid (17mL) was refluxed for 2 hours. After cooling, the solvent was evaporated in vacuum and the residue purified by column chromatography (SiO_2) with dichloromethane as the eluent.

9-(5-Acetoxythien-2-yl)-10-thienylanthracene **5o** was obtained as an amorphous solid. ^1H NMR (400MHz, $CHCl_3$) δ (ppm) 2.34(s, 3H, CH_3), 6.91-6.94(dd (AB-system), 2H, 3,4-H acetoxythienyl), 7.21(dd, $J_{3,4}$ = 3.4Hz, $J_{3,5}$ = 1.2Hz, 1H, 3-H 10-thienyl), 7.31(dd, $J_{4,5}$ = 5.2Hz, $J_{3,4}$ = 3.4Hz, 1H, 4-H 10-thienyl), 7.38-7.44(m, 4H, 2,3,6,7-H anthracene), 7.62(dd, $J_{4,5}$ = 5.2Hz, $J_{3,5}$ = 1.2Hz, 1H, 5-H 10-thienyl), 7.85-7.87 and 7.96-7.99(2xm, 4H 1,4,5,8-H anthracene). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 20.8, 113.3, 125.6, 125.7, 125.8, 126.6, 126.7, 126.8, 127.2, 129.5, 129.7, 130.5, 131.1, 131.5, 131.7, 138.9, 152.6, 167.3. IR (KBr) νCO 1750cm^{-1}. MS (EI) *m/z* 400 (M^+).

1,8-Dibutoxy-9-(5-acetoxythien-2-yl)-10-thienylanthracene **5m** was obtained as an amorphous solid. ^1H NMR (400MHz, $CHCl_3$) δ (ppm) 0.87(t, 6H, CH_3), 1.29(m, 4H, CH_3CH_2-), 1.48(m, 4H, CH_2CH_2O-), 3.79(t, 4H, -OCH_2), 6.53 and 6.64(2xd, J = 3.8Hz, 2H, 3,4-H acetoxythienyl), 6.69(dd, $J_{2,3}$ = $J_{6,7}$ 7.4Hz, $J_{2,4}$ = $J_{5,7}$ = 1.2Hz, 2H, 2,7-H anthracene), 7.12(dd, $J_{3,4}$ = 3.4Hz, $J_{1,2}$ = 1.2Hz, 1H, 3-H 10-thienyl), 7.23(dd, $J_{3,4}$ = $J_{5,6}$ = 8.8Hz, $J_{2,3}$ = $J_{6,7}$ = 7.4Hz, 2H, 3,6-H anthracene), 7.26(dd, $J_{4,5}$ = 5.2Hz, $J_{3,4}$ = 3.4Hz, 1H, 4-H 10-thienyl), 7.29(dd, $J_{3,4}$ = $J_{5,6}$ = 8.8Hz, $J_{2,4}$ = $J_{5,7}$ = 1.2Hz, 2H, 4,5-H anthracene), 7.57(dd, $J_{4,5}$ = 5.2Hz, $J_{3,5}$ = 1.2Hz, 1H, 5-H 10-thienyl). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 13.9, 19.8, 20.8, 30.7, 68.5, 105.2, 111.6, 119.0, 121.3, 125.4, 125.8, 126.5, 127.0, 127.8, 129.2, 130.0, 133.5, 139.8, 140.8, 150.9, 157.0, 167.3. IR (KBr) νCO 1750cm^{-1}. MS (EI) *m/z* 544 (M^+).

1,5-Dibutoxy-9,10-dithienylanthracene **2l** A suspension of diol **3l** (1.04g; 2mmol), KI (3g; 18mmol), and NaH_2PO_2 (3g; 34mmol) in acetic acid (23 mL) was refluxed for 2 hours. After cooling to room temperature, the greenish precipitate was filtered and washed with water (2x10mL) and methanol (2x10mL). Anthracene **2l** was obtained as a greenish, amorphous solid in 83% yield. ^{1}H NMR (400MHz, $CHCl_3$) δ (ppm) 0.87(s, 6H, CH_3), 1.21-1.29(m, 8H, $CH_2CH_2CH_2O$-), 3.74(t, 4H, CH_2O-), 6.67(dd, $J_{2,3} = J_{6,7} = 7.4$Hz, $J_{2,4} = J_{6,8} = 1.1$Hz, 2H, 2,6-H anthracene), 6.97(dd, $J_{3,4} = 3.3$Hz, $J_{3,5} = 1.2$Hz, 2H, 3-H thiophene), 7.14(dd, $J_{4,5} = 5.1$Hz, $J_{3,4} = 3.3$Hz, 2H, 4-H thiophene), 7.19(dd, $J_{3,4} = J_{7,8} = 9.0$Hz, $J_{2,3} = J_{6,7} = 7.4$Hz, 2H, 3,7-H anthracene), 7.28(dd, $J_{3,4} = J_{7,8} = 9.0$Hz, $J_{2,4} = J_{6,8} = 1.1$Hz, 2H, 4,8-H anthracene), 7.44(dd, $J_{4,5} = 5.1$Hz, $J_{3,5} = 1.2$Hz, 2H, 5-H thiophene). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 13.9, 19.8, 30.7, 68.1, 104.9, 119.4, 124.4, 124.5, 125.1, 125.9, 127.1, 128.4, 134.4, 144.9, 155.9. MS (EI) *m/z* 486 (M^+).

9,10-Dithienylanthracene **2o** was obtained following the literature procedure[6] in 90% yield. Mp 244°C (Lit[6] : 244°C). ^{1}H NMR (250MHz, $CHCl_3$) δ (ppm) 7.21(dd, $J_{3,4} = 3.6$Hz, $J_{3,5} = 1.2$Hz, 2H, 3-H thiophene), 7.32(dd, $J_{4,5} = 5.1$Hz, $J_{3,4} = 3.6$Hz, 2H, 4-H thiophene), 7.37-7.42(m, 4H, 2,3,56,7-H anthracene), 7.62(dd, $J_{4,5} = 5.1$Hz, $J_{3,5} = 1.2$Hz, 2H, 5-H thiophene), 7.84-7.89(m, 4H, 1,4,5,8-H anthracene).

1,5-Dichloro-9,10-dithienylanthracene **2a** was obtained as a byproduct of the procedure described for compound **2l**. In this case the work-up was slightly different. The rearrangement product was filtered off and the filtrate evaporated in vacuum. To the residue, dichloromethane (20mL) and water (10mL) were added and the mixture was shaken vigorously. The layers were separated and the organic layer was dried over magnesium sulfate and evaporated in vacuum. The residue was separated by column chromatography (SiO_2) with dichloromethane/petroleum ether (1/1) as the eluent. The anthracene **2a** was obtained as yellow crystals. Mp 232 °C. ^{1}H NMR (400MHz, $CHCl_3$) δ (ppm) 7.13(dd, $J_{3,4} = 3.5$Hz, $J_{3,5} = 1.2$Hz, 2H, 3-H thiophene), 7.22(dd, $J_{4,5} = 5.1$Hz, $J_{3,4} = 3.5$Hz, 2H, 4-H thiophene), 7.24(dd, $J_{3,4} = J_{7,8} = 9.0$Hz, $J_{2,3} = J_{6,7} = 7.1$Hz, 2H, 3,7-H anthracene), 7.55(dd, $J_{2,3} = J_{6,7} = 7.1$Hz, $J_{2,4} = J_{6,8} = 1.2$Hz, 2H, 2,6-H anthracene), 7.60(dd, $J_{4,5} = 5.1$Hz, $J_{3,5} = 1.2$Hz, 2H, 5-H thiophene), 7.87(dd, $J_{3,4} = J_{7,8} = 9.0$Hz, $J_{2,4} = J_{6,8} = 1.2$Hz, 2H, 4,8-H anthracene). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 125.2, 126.8, 127.1, 127.2, 128.2, 130.3, 130.4, 130.7, 131.3, 134.0, 140.8. MS (EI) *m/z* 410 (M^+).

1,5-Dichloro-9,10-difurylanthracene **2c** was obtained analogously to **2a**, as yellowish green crystals. Mp 189 °C. ^{1}H NMR (400MHz, $CHCl_3$) δ (ppm) 6.49(dd, $J_{4,5} = 3.2$Hz, $J_{3,5} = 0.8$Hz, 2H; 5-H furan), 6.65(dd, $J_{4,5} = 3.2$Hz, $J_{3,4} = 1.9$Hz, 2H; 4-H furan), 7.28(dd, $J_{3,4} = J_{7,8} = 9.0$Hz, $J_{2,3} = J_{6,7} = 7.2$Hz, 2H; 3,7-H anthracene), 7.58(dd, $J_{2,3} = J_{6,7} = 7.2$Hz, $J_{2,4} = J_{6,8} = 1.1$Hz, 2H; 2,5-H anthracene), 7.72(dd, $J_{3,4} = 1.9$Hz, $J_{3,5} = 0.8$Hz, 2H; 3-H furan), 7.75(dd, $J_{3,4} = J_{7,8} = 9.0$Hz, $J_{2,4} = J_{6,8} = 1.1$Hz, 2H; 4,8-H anthracene). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 111.6, 113.5, 125.7, 126.3, 127.6, 128.6, 130.0, 131.0, 135.3, 142.1, 149.1. MS (EI) *m/z* 378 (M^+).

1,5-Dichloro-9-phenyl-10-thienylanthracene **2r** was obtained analogously to **2a** as yellow crystals. Mp 188 °C. ^{1}H NMR (400MHz, $CHCl_3$) δ (ppm) 7.14-7.18(m, 2H), 7.20-7.25(m, 2H), 7.35-7.37(m, 2H), 7.47-7.50(m, 4H), 7.7.54(dd, $J_o = 6.7$Hz, $J_m = 1.1$Hz, 2H), 7.59(s, br, 1H), 7.60(dd, $J_o = 3.1$Hz, $J_m = 1.1$Hz, 1H), 7.87(dd, $J_o = 9.0$Hz, $J_m = 1.1$Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 124.6, 125.2, 126.7, 127.0, 127.1, 127.6, 127.7, 128.2, 128.8, 129.8, 130.2, 130.7, 131.31, 131.34, 131.44, 133.5, 135.2, 138.7, 140.7, 141.1. MS (CI) *m/z* 405 (MH^+).

9,10-Dimethoxy-9,10-dithienyl-9,10-dihydroanthracene **8**. To a suspension of diol **3o** (0.5g; 1.3mmol) in methanol (10 mL) was added concentrated sulfuric acid (0.3 mL), in a dropwise manner, under vigorous stirring. The suspension was then gently warmed, resulting in a clear solution withing a few minutes, followed by the formation of a white precipitate after 15 min. The suspension was then cooled to room temperature and filtered. The precipitate was washed with cold methanol (2x5mL) and diethyl ether (2x5mL) affording the title compound as a white solid as a *cis/trans* mixture (1/6) in 94% yield. *cis derivative* ^{1}H NMR (250MHz, $CDCl_3$) δ (ppm) 2.98(s, 6H; OCH_3), 6.18(dd, $J_{3,4} = 3.5$Hz, $J_{3,5} = 1.2$Hz, 2H, 3-H thiophene), 6.63(dd, $J_{4,5} = 5.1$Hz, $J_{3,4} = 3.5$Hz, 2H, 4-H thiophene), 7.13(dd, $J_{4,5} = 5.1$Hz, $J_{3,5} = 1.2$Hz, 2H, 5-H thiophene), 7.39-7.43(m, 4H; 2,3,6,7-H dihydroanthracene), 7.75-7.79(m, 4H; 1,4,5,8-H dihydroanthracene). *trans derivative* ^{1}H NMR (250MHz, $CDCl_3$) δ (ppm) 3.08(s, 6H; OCH_3), 6.58(dd, $J_{3,4} = 3.5$Hz, $J_{3,5} = 1.2$Hz, 2H, 3-H thiophene), 6.81(dd, $J_{4,5} = 5.1$Hz, $J_{3,4} = 3.5$Hz, 2H, 4-H thiophene), 7.16(dd, $J_{4,5} = 5.1$Hz, $J_{3,5} = 1.2$Hz, 2H, 5-H thiophene), 7.27-7.32(m, 4H; 2,3,6,7-H dihydroanthracene), 7.54-7.59(m, 4H; 1,4,5,8-H dihydroanthracene). IR (KBr) (cm^{-1}) 3096, 3066 (sp_2C-H), 2986, 2943, 2891, 2815 (sp^2C-H), 1603 (C=C).

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