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GENERAL SYNTHESES OF NOVEL ANTHRACENE-9,10-DIONE DERIVATIVES: THE 2-(1-ARYL-2-NITROETHYL)-1,4-DIHYDROXYANTHRACENE-9,10-DIONES, 2-(1-ARYLETHENYL)-1,4-DIHYDROXYANTHRACENE-9,10-DIONES AND 2-(1-ARYLETHYL)-1,4-DIHYDROXYANTHRACENE-9,10-DIONES

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Abstract: In an attempt to explore a possible approach to 3-aryl-5-hydroxyanthra[1,2-b]furan-6,11-diones **4** *via* the nitro-derivatives **3**, we have unexpectedly obtained, starting from leucoquinizarin **1** and various (2-chloro-2-nitroethenyl)benzenes **2**, the hitherto unknown title anthracene-9,10-diones **5**, **6** or **7** depending on the reaction conditions employed.

Molecules exhibiting an anthraquinonoid structure constitute an important class of chemicals. In particular, anthracene-9,10-dione derivatives have received considerable attention due to their industrial applications (*e.g.* textile dyestuffs,[1] pulping additives,[2] pigments for reprography,[3] organic dyes for liquid-crystal display devices,[4] materials for optical data storage,[5]...) or their biological properties and the ensuing pharmaceutical potentialities. In this connection, the 9,10-anthraquinone molecular skeleton has given rise to numerous products which have been successfully evaluated in various fields (*e.g.* for their antibacterial,[6] antifungal,[7] antimalarial,[8] laxative,[9] spasmolytic,[10] or anti-HIV[11] properties). However, most efforts have been directed towards syntheses of anthracene-9,10-dione-based antitumor antibiotics,[12] and several anticancer drugs belonging to this series are widely used in the treatment of neoplastic diseases.[12g,13]

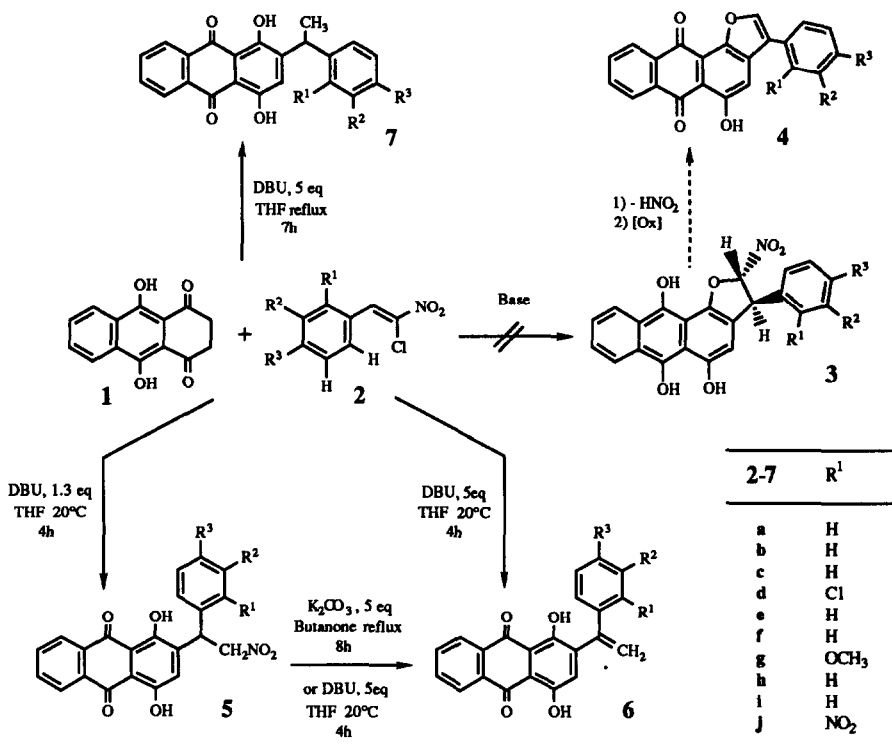
In this context, and in the course of our continued interest in the utilization of (2-chloro-2-nitroethenyl)benzenes **2** as building blocks in synthesis,[14] we have investigated the reaction of these β-chloro-β-nitrostyrenes **2** with 2,3-dihydro-9,10-dihydroxyanthracene-1,4-dione (leucoquinizarin) **1**. This work was undertaken with the aim of performing a novel approach to 3-aryl-5-hydroxyanthra[1,2-b]furan-6,11-diones **4**. The devised route involved the preliminary formation of 3-aryl-2,3-dihydro-2-nitro-5,6,11-trihydroxyanthra[1,2-*b*]furans **3**, the further denitration of which, followed by oxidation, would have given the anticipated furoanthraquinones **4**. Unexpectedly, however, the attempted base-promoted reactions between the above-mentioned reagents failed to yield any heterocyclic compound, but gave the so far unknown 2-substituted-anthracene-9,10-diones **5**, **6** or **7**

depending on the reaction conditions and relative amounts of base involved. Thus, as depicted in scheme 1, under inert atmosphere, using anhydrous and previously swept free of air tetrahydrofuran as solvent, we have found that :

1) In the presence of a slight excess of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), at room temperature, the reaction of *Z*-(2-chloro-2-nitroethenyl)benzenes **2a-g** provides the 2-(1-aryl-2-nitroethyl)-1,4-dihydroxy-anthracene-9,10-diones **5a-g** (table 1), whereas the treatment of the β-chloro-β-nitrostyrenes **2h-j** (bearing a nitro group on the aromatic ring) gives mainly the methylidene derivatives **6h-j**. Nevertheless, the use of potassium fluoride (instead of DBU) enabled us to obtain the pure dinitro compound **5j** although, in the cases of **5h** and **5i**, the products remain contaminated with variable quantities of unreacted leucoquinizarin in spite of repeated chromatographies.

2) For all the considered examples, the use of a larger amount of DBU results in the formation of the denitrated 2-(1-arylethenyl)-1,4-dihydroxyanthracene-9,10-diones **6a-j** when the reaction is performed at 20°C (Table 2).

3) In the presence of a same excess of DBU, a prolonged refluxing of the reaction medium affords the 2-(1-arylethyl)-1,4-dihydroxyanthracene-9,10-diones **7a-g** if the condensation is carried out starting from the β-chloro-β-nitrostyrenes **2a-g** (table 3), but produces complex and untractable mixtures when the dinitro compounds **2h-j** are involved. In these last instances, only quinizarin could be isolated in the reaction residues, and characterized.



2-7	R^1	R^2	R^3
a	H	H	H
b	H	H	Cl
c	H	Cl	H
d	Cl	H	H
e	H	H	OCH_3
f	H	OCH_3	H
g	OCH_3	H	H
h	H	H	NO_2
i	H	NO_2	H
j	NO_2	H	H

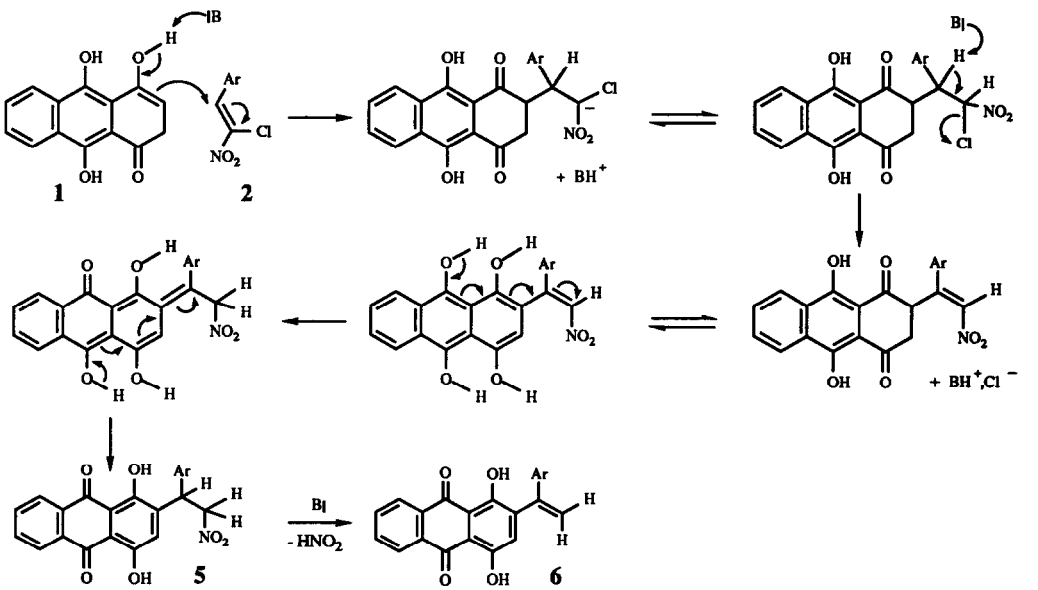
Scheme 1

Furthermore, we have checked, in the case of **5b** selected as a representative of its class of products, that the conversion of the nitro-derivatives **5** into the arylethyl products **6** is achievable by treatment with potassium carbonate in boiling butanone or with an excess of DBU in tetrahydrofuran at room temperature. Such base-catalysed eliminations of a nitro group are greatly facilitated by the lability of the benzylic proton.[15]

We have also established that, under argon atmosphere, when treated with an equimolecular amount of DBU in dry, oxygen-free tetrahydrofuran, at room temperature, the leucoquinizarin **1** is completely converted, after four hours, to give 49% of pure isolated 1,4-dihydroxyanthracene-9,10-dione (quinizarin) and uncharacterized very polar material. Such a side-reaction could be responsible for the rather low yields obtained, even if (as practised in the present work) the syntheses are carried out with an excess of leucoquinizarin **1**.

DBU has been selected to promote these reactions after we had ascertained that other bases such as triethylamine, pyridine, 2,6-lutidine, sodium amide, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or 1,4-diazabicyclo[2.2.2]octane (DABCO) lead to lower yields or no reaction at all under various conditions.

A proposed mechanism to account for the formation of the anthraquinone derivatives **5** and **6** is reported in scheme 2. With regard to the methyl compounds **7**, Their obtaining is all the more difficult to explain since we have checked that neither the nitro derivatives **5**, nor the methylidene derivatives **6** give products **7** when treated with DBU in refluxing THF. However, hypotheses involving a disproportionation process (the yields in compounds **7** never overstep 50%) or a single electron transfer mechanism implicating one of the reaction intermediates (such a possibility could be related to previous works devoted to replacement of nitro groups by hydrogen[16]) cannot be completely discarded.



Scheme 2

The reactions described herein are related to the Marschalk alkylation.[17] In particular, enolate reactions of leucoquinizarin with Michael type acceptors have been reported.[18]

The spectral data for compounds **5**, **6** and **7** are reported in tables 4, 5 and 6, respectively. Such substituted 1,4-anthracene-9,10-diones can be regarded as novel intermediates to provide access to biologically attractive derivatives related to anthracyclines, and several encouraging attempts in this field are currently in progress.

Table1: Compounds **5a-g** and **5j** prepared.[a]

Compound	Yield (%)[b]	melting point (°C) (recrystallization solvent)	Molecular formula (molecular weight)	Analysis (%) Calculated / (found) C	H	N
5a	55	209-210	$C_{22}H_{15}NO_6$	67.87	3.88	3.60
		(2-propanol/benzene)	(389.4)	(67.98)	(3.87)	(3.45)
5b	50	179-180	$C_{22}H_{14}ClNO_6$	62.35	3.33	3.30
		(2-propanol/benzene)	(423.8)	(62.34)	(3.32)	(3.15)
5c	45	180-183[c]	$C_{22}H_{14}ClNO_6$	62.35	3.33	3.30
		(2-propanol/benzene)	(423.8)	(62.47)	(3.43)	(3.31)
5d	33	211-212[d]	$C_{22}H_{14}ClNO_6$	62.35	3.33	3.30
		(2-propanol/benzene)	(423.8)	(62.29)	(3.57)	(3.23)
5e	50	178-180	$C_{23}H_{17}NO_7$	65.87	4.09	3.34
		(2-propanol/benzene)	(419.4)	(65.92)	(4.07)	(3.29)
5f	41	206-208	$C_{23}H_{17}NO_7$	65.87	4.09	3.34
		(2-propanol/benzene)	(419.4)	(65.63)	(3.96)	(3.05)
5g	60	221-222[e]	$C_{23}H_{17}NO_7$	65.87	4.09	3.34
		(2-propanol/benzene)	(419.4)	(66.05)	(4.15)	(3.31)
5j	41	241-243	$C_{22}H_{14}N_2O_8$	60.83	3.25	6.45
		(2-propanol/benzene)	(434.4)	(61.01)	(3.28)	(6.27)

[a] With regard to dinitro derivatives **5i** and **5j**, pure products have not been isolated because they were always contaminated with unreacted leucoquinizarin.

[b] Yield of analytically pure product based on **2**.

[c] Allotropic change at 170-175°C.

[d] Allotropic change at 172-176°C.

[e] Allotropic change at 214-218°C.

Table2: Compounds **6a-j** prepared.

Compound	Yield (%)[a]	melting point (°C) (recrystallization solvent)	Molecular formula (molecular weight)	Analysis (%) Calculated / (found) C	H	N
6a	35	149-150	$C_{22}H_{14}O_4$	77.18	4.12	-
		(2-propanol/benzene)	(342.4)	(77.07)	(4.27)	-
6b	38	178-182	$C_{22}H_{13}ClO_4$	70.13	3.48	-
		(cyclohexane/benzene)	(376.8)	(70.40)	(3.67)	-
6c	36	149-151	$C_{22}H_{13}ClO_4$	70.13	3.48	-
		(hexane/benzene)	(376.8)	(70.06)	(3.58)	-
6d	33	137-140	$C_{22}H_{13}ClO_4$	70.13	3.48	-
		(2-propanol)	(376.8)	(70.09)	(3.46)	-
6e	26	168-170	$C_{23}H_{16}O_5$	74.19	4.33	-
		(cyclohexane/benzene)	(372.4)	(73.93)	(4.33)	-
6f	40	128-130	$C_{23}H_{16}O_5$	74.19	4.33	-
		(cyclohexane/benzene)	(372.4)	(73.99)	(4.32)	-
6g	32	142-143	$C_{23}H_{16}O_5$	74.19	4.33	-
		(cyclohexane/benzene)	(372.4)	(74.23)	(4.19)	-
6h	22	250-251	$C_{22}H_{13}NO_6$	68.22	3.38	3.62
		(cyclohexane/benzene)	(387.4)	(68.39)	(3.37)	(3.83)
6i	26	204-205	$C_{22}H_{13}NO_6$	68.22	3.38	3.62
		(cyclohexane/benzene)	(387.4)	(68.26)	(3.50)	(3.40)
6j	29	186-188	$C_{22}H_{13}NO_6$	68.22	3.38	3.62
		(cyclohexane/benzene)	(387.4)	(68.20)	(3.41)	(3.65)

[a] Yield of analytically pure product based on **2**.

Table3: Compounds**7a-g** prepared.[a]

Compound	Yield (%)[b]	melting point (°C) (recrystallization solvent)	Molecular formula (molecular weight)	Analysis (%) Calculated / (found) C	H
7a	37	178-179	$C_{22}H_{16}O_4$	76.83	4.68
		(hexane)	(344.4)	(76.53)	(4.66)
7b	40	171-173	$C_{22}H_{15}ClO_4$	69.76	3.99
		(2-propanol/benzene)	(378.8)	(70.03)	(4.00)
7c	39	200-201	$C_{22}H_{15}ClO_4$	69.76	3.99
		(hexane/benzene)	(378.8)	(69.53)	(4.03)
7d	37	157-159	$C_{22}H_{15}ClO_4$	69.76	3.99
		(hexane)	(378.8)	(69.98)	(3.93)
7e	41	166-167	$C_{23}H_{18}O_5$	73.79	4.85
		(hexane/cyclohexane)	(374.4)	(74.01)	(4.74)
7f	33	134-136	$C_{23}H_{18}O_5$	73.79	4.85
		(hexane)	(374.4)	(73.51)	(4.92)
7g	30	166-167	$C_{23}H_{18}O_5$	73.79	4.85
		(hexane)	(374.4)	(73.58)	(4.78)

[a] Starting from **2h-j**, the reactions lead to complex mixtures and the corresponding products **7h-j** have never been isolated.

[b] Yield of analytically pure product based on **2**.

Table 4: Spectral data of compound **5a-g** and **5j**

Compound	IR $\nu_{C=O}$ (cm^{-1})	MS[a] *m/z*	^{1}H-NMR δ, J (Hz)
5a	1627	389 ($M^{+\cdot}$), 373,355, 343, 342, 341, 340, 325, 324, 297,240, 239, 85, 83 (base peak), 77, 43	4.78-5.48 (m, 3H); 7.15 (s, 1H); 7.22-7.47 (m, 5H); 7.68-7.93 (m, 2H); 8.16-8.43 (m, 2H); 12.80 (s, 1H, exchangeable with D_2O); 13.57 (s, 1H, exchangeable with D_2O)
5b	1627	425 and 423 (base peak, $M^{+\cdot}$), 379, 378, 377, 376, 360, 358, 341, 327, 324, 240, 239, 226, 102, 85, 83, 77	4.77-5.47 (m, 3H); 7.12 (s, 1H); 7.18-7.43 (m, 4H); 7.68-7.95 (m, 2H); 8.18-8.45 (m, 2H); 12.80 (s, 1H, exchangeable with D_2O); 13.58 (s, 1H, exchangeable with D_2O)
5c	1628	425 and 423 ($M^{+\cdot}$), 407, 379, 378 377, 376, 360, 358, 341, 313, 240, 239, 102, 85, 83 (base peak), 77, 43	4.82-5.47 (m, 3H); 7.13 (s, 1H); 7.12-7.45 (m, 4H); 7.67-7.95 (m, 2H); 8.18-8.77 (m, 2H); 12.82 (s, 1H, exchangeable with D_2O); 13.57 (s, 1H, exchangeable with D_2O)
5d	1627	425 and 423 ($M^{+\cdot}$), 378, 376, 341, 239, 226, 213, 152, 128, 113, 105, 102,101, 77(base peak), 43	4.83-5.30 (m, 2H); 5.82 (t, 1H, J = 7); 7.03 (s, 1H); 7.22-7.60 (m, 4H); 7.70-7.98 (m, 2H); 8.22-8.53 (m, 2H); 12.81 (s, 1H, exchangeable with D_2O); 13.62 (s, 1H, exchangeable with D_2O)
5e	1626	437 ($M + NH_4^+$), 420 (MH^+), 388, 373, 240, 197, 165, 150 (base peak), 135	3.78 (s, 3H); 4.78-5.47 (m, 3H); 7.15 (s, 1H); 6.75-7.43 (m, 4H); 7.68-8.00 (m, 2H); 8.20-8.48 (m, 2H); 12.78 (s, 1H, exchangeable with D_2O); 13.54 (s, 1H, exchangeable with D_2O)
5f	1627	419 ($M^{+\cdot}$), 373, 358, 356, 355, 213 178, 149, 129, 105, 91, 85, 83, 77, 43 (base peak)	3.82 (s, 3H); 4.83-5.52 (m, 3H); 6.78-7.48 (m, 5H); 7.70-7.98 (m, 2H); 8.23-8.55 (m, 2H); 12.83 (s, 1H, exchangeable with D_2O); 13.60 (s, 1H, exchangeable with D_2O)
5g	1626	419 ($M^{+\cdot}$), 373, 372, 355, 342, 341, 327, 253, 213, 179, 105, 91, 87, 85, 83 (base peak), 77	3.85 (s, 3H); 4.88-5.37 (m, 2H); 5.63 (t, 1H, J = 7) 6.83-7.47 (m,5H); 7.72-8.00 (m, 2H); 8.27-8.53 (m, 2H); 12.84 (s, 1H, exchangeable with D_2O); 13.60 (s, 1H, exchangeable with D_2O)
5J	1627	434 ($M^{+\cdot}$), 388, 370, 356, 342, 328, 300, 242, 226, 91, 77, 43 (base peak)	5.27-5.97 (m, 3H); 7.43-8.37 (m, 9H); 12.77 (br.s, 1H, exchangeable with D_2O); 13.26 (br. s, 1H, exchangeable with D_2O)[b]

[a] Electron impact (70eV), except for **5e** (chemical ionization / NH_3).
[b] Performed in DMSO-d_6

Table 5: Spectral data of compound **6a-j**

Compound	IR $\nu_{C=O}$ (cm^{-1})	MS[a] *m/z*	^{1}H-NMR δ, J (Hz)
6a	1625	342 ($M^{+\cdot}$), 324 (base peak), 297, 239, 225, 152, 128, 115, 105,102, 101, 85, 83, 77	5.53 (d, 1H, J = 0.9); 5.83 (d, 1H, J = 0.9); 7.17-7.58 (m, 6H); 7.70-7.97 (m, 2H); 8.23-8.50 (m, 2H); 12.95 (s, 1H, exchangeable with D_2O); 13.33 (s, 1H, exchangeable with D_2O)
6b	1625	378 and 376 (base peak, $M^{+\cdot}$), 361, 360, 359, 358, 341, 323, 295, 267, 253, 239, 151, 127,101, 83, 77	5.55 (br. s, 1H); 5.82 (br. s, 1H); 7.15-7.48 (m, 5H); 7.65-7.97 (m, 2H); 8.23-8.53 (m, 2H); 12.90 (s, 1H, exchangeable with D_2O); 13.30 (s, 1H, exchangeable with D_2O)
6c	1625	378 and 376 (base peak, $M^{+\cdot}$), 360, 358, 341, 323, 295, 284, 267, 239, 226, 113, 102,101, 77	5.60 (s, 1H); 5.85 (s, 1H); 7.17-7.48 (m, 5H); 7.72-8.00 (m, 2H); 8.22-8.52 (m, 2H); 12.88 (s, 1H, exchangeable with D_2O); 13.31 (s,1H, exchangeable with D_2O)
6d	1629	378 and 376 ($M^{+\cdot}$), 341, 313, 255, 239, 226, 126, 113, 105, 102, 101, 77 (base peak)	5.70 (d, 1H, J = 1.2); 6.15 (d, 1H, J = 1.2); 7.08 (s, 1H); 7.17-7.48 (m, 4H); 7.72-7.92 (m, 2H); 8.25-8.47 (m, 2H); 12.83 (s, 1H, exchangeable with D_2O); 13.70 (s, 1H, exchangeable with D_2O)
6e	1624	372 ($M^{+\cdot}$, base peak), 357, 354, 341, 339, 311, 283, 255, 240, 226, 215, 158, 152, 115, 105, 102, 83, 77	3.82 (s, 3H); 5.42 (s, 1H); 5.72 (s, 1H); 6.77-7.00 (m,2H); 7.12-7.48 (m, 3H); 7.67-7.97 (m, 2H); 8.17-8.45 (m, 2H); 13.01 (s, 1H, exchangeable with D_2O); 13.48 (s, 1H, exchangeable with D_2O)
6f	1624	372 ($M^{+\cdot}$), 357, 355, 354 (base peak), 341, 339, 311, 283, 255, 240, 226, 215, 158, 152, 127, 115,102, 83, 77	3.75 (s, 3H); 5.52 (s, 1H); 5.82 (s, 1H); 6.73-7.02 (m,3H); 7.10-7.43 (m, 2H); 7.63-7.93 (m, 2H); 8.18-8.47 (m, 2H); 12.87 (s, 1H, exchangeable with D_2O); 13.30 (s, 1H, exchangeable with D_2O)
6g	1625	372 ($M^{+\cdot}$, base peak), 357, 354, 341, 339, 311, 283, 255, 240, 239, 226, 139, 128, 115, 105, 102, 101, 77	3.65 (s, 3H); 5.77 (d, 1H, J = 1.5); 5.93 (d, 1H, J = 1.5); 6.75-7.10 (m,2H); 7.22-7.47 (m, 3H); 7.63-7.93 (m, 2H); 8.17-8.45 (m, 2H); 12.83 (s, 1H, exchangeable with D_2O); 13.63 (s, 1H, exchangeable with D_2O)
6h	1626	387 ($M^{+\cdot}$), 369, 340, 323, 295, 268, 239, 226, 208, 152, 126, 105, 102, 101,77 (base peak)	5.73 (d, 1H, J = 2); 5.97 (d, 1H, J = 2); 7.36 (s, 1H); 7.44-7.53 (m, 2H); 7.80-7.92 (m,2H); 8.13-8.25 (m, 2H); 8.30-8.44 (m, 2H); 12.91 (s, 1H, exchangeable with D_2O); 13.25 (s, 1H, exchangeable with D_2O)
6i	1626	387 ($M^{+\cdot}$, base peak), 370, 369, 341, 340, 323, 283, 255, 239, 226,152, 102,101, 83, 77, 43	5.70 (s, 1H); 5.93 (s, 1H); 7.25-7.72 (m, 3H); 7.80-8.00 (m, 2H); 8.10-8.29 (m, 2H); 8.30-8.52 (m, 2H); 13.20 (s, 1H, exchangeable with D_2O); 13.53 (s, 1H, exchangeable with D_2O)
6J	1625	387 ($M^{+\cdot}$), 370 (base peak), 358, 342, 341, 326, 255, 237, 226, 149, 127, 105, 102, 101, 85, 83, 77	5.73 (br. s, 1H); 6.18 (br. s, 1H); 7.10 (S, 1H); 7.42-8.10 (m, 4H); 7.72-7.90 (m, 2H); 8.23-8.50 (m, 2H); 13.07 (s, 1H, exchangeable with D_2O); 13.97 (s, 1H, exchangeable with D_2O);

[a] Electron impact (70eV).

Table 6: Spectral data of compound **7a-g**

Compound	IR $\nu_{C=O}$ (cm^{-1})	MS[a] *m/z*	^{1}H-NMR δ, J (Hz)
7a	1623	344 ($M^{+\cdot}$, base peak), 329,327,326, 253, 239, 226, 215,158, 127,115, 105, 102, 101, 91, 77	1.63 (d, 3H, J = 7.5); 4.67 (q, 1H, J = 7.5); 7.17 (s, 1H); 7.20-7.40 (m, 5H); 7.67-7.93 (m, 2H); 8.23-8.48 (m, 2H); 12.87 (s, 1H, exchangeable with D_2O); 13.47 (s, 1H, exchangeable with D_2O)
7b	1624	380 and 378 (base peak, $M^{+\cdot}$), 363, 362, 361, 360, 343, 328,253, 239 226, 215, 139, 105, 102, 101, 77	1.62 (d, 3H, J = 7.5); 4.63 (q, 1H, J = 7.5); 7.18 (s, 1H); 7.17-7.37 (m, 4H); 7.67-7.93 (m, 2H); 8.22-8.47 (m, 2H); 12.85 (s, 1H, exchangeable with D_2O); 13.40 (s, 1H, exchangeable with D_2O)
7c	1624	380 and 378 (base peak, $M^{+\cdot}$), 363, 362, 361, 360, 343, 328, 253, 225, 139, 105, 102, 101, 85, 83, 77	1.63 (d, 3H, J = 7.5); 4.67 (q, 1H, J = 7.5); 7.13-7.33 (m, 5H); 7.72-7.93 (m, 2H); 8.22-8.45 (m, 2H); 12.93 (s, 1H, exchangeable with D_2O); 13.48 (s, 1H, exchangeable with D_2O)
7d	1624	380 and 378 ($M^{+\cdot}$), 344, 343, 328, 327, 239, 226, 149, 139, 128, 125, 105,102,101, 77 (base peak),43	1.60 (d, 3H, J = 7.5); 5.02 (q, 1H, J = 7.5); 7.00 (s, 1H); 7.10-7.52 (m, 4H); 7.67-7.93 (m, 2H); 8.20-8.47 (m, 2H); 12.95 (s, 1H, exchangeable with D_2O); 13.50 (s, 1H, exchangeable with D_2O)
7e	1624	374 ($M^{+\cdot}$, base peak), 359, 357, 356, 343, 341, 187, 164, 158, 145, 115, 105, 103, 102, 101, 91, 77	1.62 (d, 3H, J = 7.5); 3.78 (s, 3H); 4.65 (q, 1H, J = 7.5); 6.76-6.97 (m, 2H); 7.10-7.37 (m, 2H); 7.15 (s, 1H); 7.68-7.93 (m, 2H); 8.20-8.47 (m, 2H); 12.93 (s, 1H, exchangeable with D_2O); 13.53 (s, 1H, exchangeable with D_2O)
7f	1624	374 ($M^{+\cdot}$), 359, 357, 356, 343,341, 226, 213, 158, 129,127, 115, 105, 103,102, 101, 91, 77 (base peak)	1.62 (d, 3H, J = 7.5); 3.73 (s, 3H); 4.63 (q, 1H, J = 7.5); 6.67-6.97 (m, 3H); 7.12-7.37 (m, 1H); 7.15 (s, 1H); 7.67-7.94 (m, 2H); 8.23-8.43 (m, 2H); 12.92 (s, 1H, exchangeable with D_2O); 13.51 (s, 1H, exchangeable with D_2O)
7g	1623	374 ($M^{+\cdot}$), 359, 356, 343,327, 253, 226, 158,128, 121, 115, 105, 103, 102, 101, 91, 77 (base peak)	1.57 (d, 3H, J = 7.5); 3.75 (s, 3H); 4.97 (q, 1H, J = 7.5); 6.80-7.40 (m, 4H); 7.05 (s, 1H); 7.66-7.97 (m, 2H); 8.25-8.58 (m, 2H); 12.97 (s, 1H, exchangeable with D_2O); 13.53 (s, 1H, exchangeable with D_2O)

[a] Electron impact (70eV).

EXPERIMENTAL

Melting points were measured on a Köfler hot stage apparatus and are uncorrected. Mass spectra were obtained with a Nermag-Ribermag R10-10C spectrometer either under electron impact conditions (70 eV) or using chemical ionization method (NH_3). Infrared spectra were recorded on a Perkin-Elmer 1710 spectrophotometer as chloroform solutions. ^1H NMR spectra were determined either at 90 MHz with a Varian EM 390 spectrometer or, in the case of difficultly soluble products, at 270 MHz using a Bruker HX 270 apparatus for deuteriochloroform solutions (unless otherwise stated) with tetramethylsilane as internal reference. Microanalyses were carried out by the "Service d'Analyse du C.N.R.S., Vernaison". Silica gel Merck (230-400 Mesh ASTM) was used for column chromatography. Anhydrous tetrahydrofuran was obtained by distillation from benzophenone/sodium, then saturated, prior to use, by bubbling with dry Argon in order to remove dissolved oxygen and avoid interfering oxidations. Starting *Z*-(2-chloro-2-nitroethenyl)benzenes **2a-j** were synthesized according to a previously described procedure.[14c] Commercially available reagents (Janssen Chimica) were used without further purification.

Preparation of 2-(1-aryl-2-nitroethyl)-1,4-dihydroxyanthracene-9,10-diones:

-*Compounds* 5a-g:

A mixture of the appropriate (2-chloro-2-nitroethenyl)benzene (**2a-g**, 5 mmol), leucoquinizarin (**1**, 1.45 g, 6 mmol) and anhydrous, oxygen-free tetrahydrofuran (25 mL) was placed, under inert atmosphere, in a dried, two-necked, 50 mL round-bottomed flask fitted with a septum inlet. This mixture was vigorously stirred with a magnetic bar till the starting materials were completely dissolved, and DBU (0.99 g, 0.97 mL, 6.5mmol) was added with a syringe. A slight heating occured whilst a change in the colour took place. The stirring was continued, at room temperature, for four additional hours before the solvent was removed under reduced pressure. The residue was taken up with dichloromethane (150 mL) and normal hydrochloric acid (100 mL). The organic layer was separated, then the aqueous phase extracted with dichloromethane (3 x 40 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, filtered, then evaporated *in vacuo* to leave a crude material which was chromatographed on a silica gel column (120 g, eluent chloroform/cyclohexane 2:1, then pure chloroform). Removal of the solvents under reduced pressure provided satisfactorily pure **5a-g** (Table 1) which were subsequently recrystallized.

-*Compounds* 5h-j:

As described above, starting from β-chloro–β-nitrostyrenes **2h-j**, but replacing DBU by potassium fluoride (0.58 g, 10 mmol) and maintaining the stirring for six days at room temperature, pure **5j** was obtained after silica gel chromatography (150 g, eluent dichloromethane) followed by recristallization (benzene/2-propanol). Unfortunately, under the same conditions, **5h** and **5i** remained contaminated with starting unreacted leucoquinizarin, even after repeated chromatographies and recrystallizations.

Preparation of 2-(1-arylethenyl)-1,4-dihydroxyanthracene-9,10-diones 6a-j:

A mixture of the appropriate (2-chloro-2-nitroethenyl)benzene (**2a-j**, 5 mmol), leucoquinizarin (**1**, 1.45 g, 6mmol) and anhydrous, oxygen-free tetrahydrofuran (25 mL) was placed, under inert atmosphere, in a dried two-necked, 50 mL round-bottomed flask equipped with a septum inlet. The mixture was efficiently stirred with a magnetic bar. When the reagents were completely dissolved, DBU (3.81 g, 3.73 mL, 25 mmol) was added with a syringe. The reaction was moderately exothermic and a modification of the colour occured. The reaction mixture was stirred at 20°C for four additional hours. The solvent was removed under diminished pressure to leave a crude material which was taken up with dichloromethane (150 mL in the cases of **6a-g**, 400 mL in the cases of **6h-j**) and normal hydrochlorid acid (100 mL). The organic phase was separated. The aqueous layer was extracted with dichloromethane (3 x 60 mL). The combined dichloromethane extracts were dried (Magnesium sulfate), filtered, then evaporated under reduced pressure to give a residue which was flash-chromatographed on a silica gel column (200 g, eluent chloroform). Removal of the solvent *in vacuo* gave pure **6a-j** which were further recrystallized under appropriate conditions (Table 2).

With regard to the starting dinitro compounds **2h-j**, it is noteworthy that the above-described method for the preparation of **5a-g**, which involves only a slight excess of DBU (1.2 eq.), proved efficient to afford the methylidene derivatives **6h-j** in yields similar to those obtained using a larger excess of base (5 eq.).

Preparation of the 2-(1-arylethyl)-1,4-dihydroxyanthracene-9,10-diones 7a-g:

A mixture of the appropriate (2-chloro-2-nitroethenyl)benzenes (**2a-g**, 5 mmol), leucoquinizarin (**1**, 1.45 g, 6 mmol) and anhydrous, oxygen-free tetrahydrofuran (25 mL) was placed, under inert atmosphere, in a dried, two-necked, 50 mL round-bottomed flask provided with a septum inlet and a water condenser. This mixture was magnetically stirred until the starting materials were completely dissolved, then gently refluxed using a

thermostated oil bath. DBU (3.80 g, 3.73 mL, 25 mmol) was carefully added with a syringe maintaining a moderate boiling. Seven hours later, the reaction mixture was allowed to cool to room temperature, placed in a 500-mL erlenmeyer flask, then dissolved in dichloromethane (150 mL). To this stirred solution, 3N hydrochloric acid (50 mL) was added. Ten minutes later, the organic layer was separated, and the aqueous phase extracted with dichloromethane (3 x 60 mL). The combined organic extracts were dried over magnesium sulfate, filtered, then concentrated under reduced pressure to leave a crude product which was chromatographed on a silica gel column (200 g, eluent chloroform). Evaporation of the solvent *in vacuo* gave pure **7a-g** (Table 3) which were subsequently recrystallized.

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