Synthesis and electrochemistry of annoquinone-A, cypripedin methyl ether, denbinobin and related 1,4-phenanthrenequinones

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(received 25 Oct 00; accepted 08 Nov 01; published on the web 16 Nov 01)

Abstract

The natural product annoquinone-A (**1**), the 1,4-phenanthrenequinones **41**–**75** and the 9,10-dihydro-1,4-phenanthrenequinones **76**–**81** were prepared by Diels-Alder reaction of the styrenes **23**–**37** with the benzoquinones **38**–**40**. The sterically hindered 5-methoxy compounds, which adopt a twisted conformation as shown by X-ray analysis, are only formed in trace amounts or as the less hindered 9,10-dihydro-1,4-phenanthrenequinones **76**–**81**. The twisted conformation also leads to characteristic changes in the NMR spectra and the redox potential. Reaction of methoxybenzoquinone with styrenes preferentially affords the 3-methoxy-1,4-phenanthrenequinones. Selective ether cleavage of the 5-methoxy group in **60** leads to the natural product denbinobine (**3**). Small amounts of C-9 hydroxylated compounds (**57**, **66**, **68**, **73**, and **75**) were also formed in the Diels-Alder reactions. In an alternative synthesis, using the photocylization of the stilbenes **84**–**87** followed by CAN oxidation, the 1,4-phenanthrenequinones **45**, **51**, **59** [methyl ether of cyprepidine (**2**)], **92** and the 1,2-phenanthrenequinone **93** were prepared. The Thiele-Winter reaction of **41**, **55**, and **56** yields

mixtures of ca. 1:1 oxygenation at C-2 and C-3, thus complementing the Diels-Alder reaction in the preparation of 2-methoxy-1,4-phenanthrenequinones. The 1,4-phenanthrenequinones **46**, **54**, **67** are easily epoxidized with alkaline hydroperoxide to **102**–**104** in analogy to 1,4-naphthoquinones.

Keywords: 1,4-Phenanthrenquinones, Diels-Alder reaction, photocylization of stilbenes, CAN oxidation, Thiele-Winter reaction, epoxidation

Introduction

Phenanthrenequinones of non-terpenoide origin occur relatively rarely in the plant kingdom,[1-5] whereas highly oxygenated phenanthrenes such as orchinol or hircinol from orchids[6-12] playing an important role as phytoalexins (review[13]), are more widely distributed. Other hydroxy- or methoxyphenanthrenes have been used in traditional medicine and were isolated from *Tannus communis*,[14] *Combretum* species (termite resistant,[5,15,16] tropical hardwood[17]), or more recently from *Eulophia nuda*.[18,19] Some of the phenanthrenequinones isolated from various sources may be derived from the hydroxylated phenanthrenes by oxidation.

Three major groups of 1,4-phenanthrenequinones may be distinguished according to their structure and biosynthesis. Representatives of the first group are hydroxy- and methoxy-substituted compounds such as annoquinone-A (**1**),[1] cypripedine (**2**),[3,20] denbinobine (**3**)[21] and combrestatin C-1 (**4**).[5] An example for a phenylated 1,4-phenanthrenequinone is latinone (**5**), isolated from east Indian rosewood (*Dalbergia latifolia* Roxb.).[4] The third and largest group comprises diterpene derived alkylated 1,4-phenanthrenequinones related to the abietanes; plectranthone A (**6**) isolated by Eugster, Rüedi et al. from *Plectranthus sp.* is just one example.[22,23] The group of the tanshinones is probably also derived from diterpenes. They comprise mostly furan-fused 1,2- and 1,4-phenanthrenequinones and are constituents of the chinese drug Dan Shen.[24] Antimicrobial and cytostatic properties have been described for annoquinone-A (**1**)[1] and combrestatin C-1(**5**).[5]

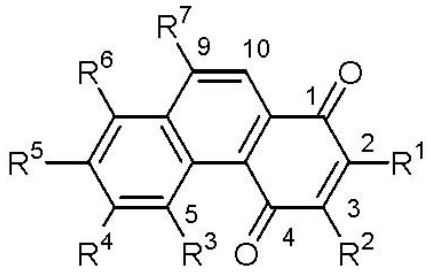


Figure 1. Structures of diverse naturally occurring 1,4-phenanthrenequinones.

	R^1	R^2	R^3	R^4	R^5	R^6	R^7
Annoquinone-A (1)[1]	H	OMe	H	H	H	H	H
Cypripedin (2)[3]	OMe	H	H	H	OH	OMe	H
Denbinobine (3)[21]	H	OMe	OH	H	OMe	H	H
Combretastatin C-1 (4)[5]	OMe	OMe	H	OMe	OH	H	H
Latinone (5)[25]	OMe	H	H	OMe	OH	H	H
Plectranthone A (6)[11]	allyl	OH	Me	H	Me	Me	H

Unfortunately, 1,2- and 1,4-phenanthrenequinones also exhibit allergenic properties. Contact dermatitis of the hands and the face were described by botanists collecting field-grown lady's slippers as early as 1875[26] and 1894.[27] Recently, the first allergenic 1,4-phenanthrenequinone cypripedine (**2**) was isolated from *Cypripedium calceolus*[3] and the east Indian rosewood (*Dalbergia latifolia*) containing latinone (**4**)[4] is also known for allergy-inducing properties.[15]

In order to learn more about the relationship of structure and sensitizing properties,[28] and to study the chemistry and electrochemistry a number of known and new 1,4-phenanthrenequinones belonging to the first group were synthesized. Two methods were applied in the synthesis of 1,4-phenanthrenequinones. A direct method is the Diels-Alder reaction of styrenes and benzoquinones[1,4, 29-35] that leads to the substituted phenanthrenequinones or the corresponding dihydo compounds as depicted in Scheme 1. Recently, this synthesis has been used in connection with the preparation of the carcinogenic benz[*a*]anthracenes.[36,31]

In the second method, oxygenated phenanthrenes are oxidized to the corresponding quinones. The presence of hydroxy or methoxy groups in ring A is necessary to avoid the easily occurring oxidation to 9,10-phenanthrenequinones. The photocyclization of stilbenes was used to prepare the required phenanthrenes. This approach gives complementary results to the Diels-Alder reaction with respect to the substitution pattern of the phenanthrene skeleton[5,7,37,38] (for reviews see,[39,40] for an alternative Lewis acid-mediated cyclization-dehydration sequence see[41]).

The alkoxylated styrenes **23**–**37** (Scheme 1) used in the Diels-Alder reaction with the benzoquinones **38**–**40** were prepared in 92–98 % yield from the benzaldehydes **7**–**21** in a Wittig reaction employing the procedure of Boden[42] (see experimental part, general procedure II). The aldehydes **7**–**18** are commercially available and the benzyl ethers **19** and **21** were prepared by benzylation of the corresponding phenols[43] (see experimental part, general procedure I). The unknown benzyl ether **20**, required for the synthesis of cyprepidine, was obtained by selective acetylation of 2,3-dihydroxybenzaldehyde to 3-acetoxy-2-hydroxybenzaldehyde,[44] methylation to 3-acetoxy-2-methoxybenzaldehyde **22**, followed by benzylation with simultaneous acetate cleavage to afford the mixed benzylmethyl ether **23** in 60 % overall yield.

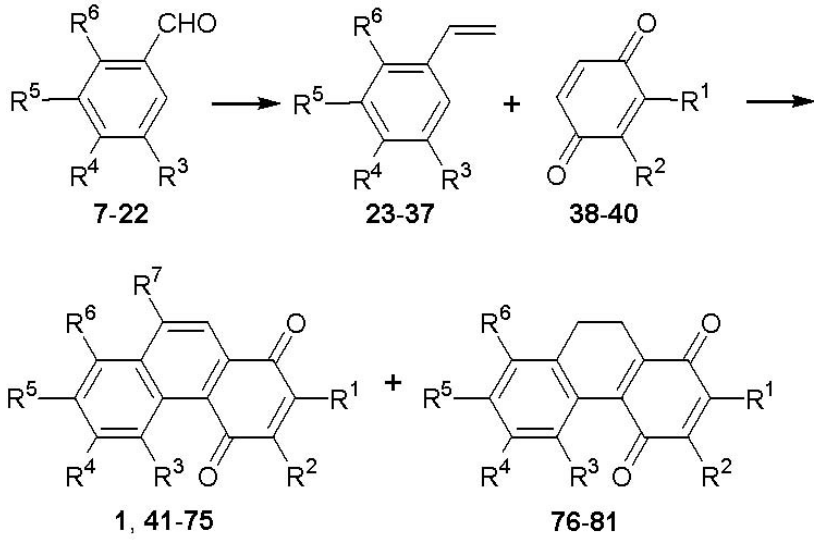
Diels-Alder reactions

Diels-Alder reactions with stilbenes, in which the double bond of the aromatic system is part of the diene, were first reported by Hudson and Robinson[45] and by Buckner[46] (for reviews see ref.[47,48]). In the reactions of **23**–**37** a fivefold excess of the benzoquinones **38**–**40** was used to afford the 1,4-phenanthrenequinones **1** and **41**–**75** in addition to the 1,4-dihydrophenanthrenequinones **76**–**81** (see experimental part, general procedure III). The excess of benzoquinones was necessary for dehydrogenation of the intermediate dihydro-1,4-phenanthrenequinones resulting from tautomerisation of the direct Diels-Alder adducts (for discussion of the intermediates see[47]). The reaction was catalyzed by small amounts of trichloroacetic acid[29] and the catalytic activity may in part be attributed to acceleration of the isomerization processes. Reaction times, yields and melting points of the and 9,10-dihydro-1,4-phenanthrenequinones are summarized in Table 1.

The 9,10-dihydro-1,4-phenanthrenequinones **76**, **78**, **79**, and **81** were isolated in four cases together with the corresponding unsaturated 1,4-phenanthrenequinones **44**, **51**, **54**, and **69**. In

two reactions, the dihydro compounds **77** and **80** were the only products isolated in the Diels-Alder reactions. Dehydrogenation of the 9,10-dihydro-phenanthrenequinones **79** and **80** to **54** and **60** could be achieved by treatment with palladium-charcoal at 184 ^{o}C in good yield (see experimental part, general procedure IV).

The ^{1}H-NMR spectral data of the six monomethoxy-1,4-phenanthrenequinones (**1**, **42**–**46**) served to calculate increment values for the chemical shift differences to the unsubstituted 1,4-phenanthrenequinone **41** listed in Table 2. These data served to unambiguously assign the regioisomers formed in the Diels-Alder reaction of styrenes with methoxybenzoquinone **39** (see below). Comparison of calculated and measured values (see experimental part) showed excellent additivity of these increments in all 1,4-phenanthrenequinones with exception of those with neighboring methoxy groups. Minor deviations from this linear effect were only seen in *ortho*-disubstituted 1,4-phenanthrenequinones.



Scheme 1. Diels-Alder reaction of styrenes and benzoquinones leading to 1,4-phenanthrenequinones and 9,10-dihydro-1,4-phenanthrenequinones

ArCHO	R^3	R^4	R^5	R^6	$ArCH=CH_2$
7	H	H	H	H	23
8	H	H	H	OMe	24
9	H	H	OMe	H	25
10	H	OMe	H	H	26
11	H	H	OMe	OMe	27
12	H	OMe	H	OMe	28
13	OMe	H	H	OMe	29
14	H	OMe	OMe	H	30
15	OMe	H	OMe	H	31
16	H	OMe	OMe	OMe	32
17	OMe	OMe	H	OMe	33
18	OMe	OMe	OMe	H	34
19	H	H	OMe	OBzl	35
20	H	H	OBzl	OMe	36
21	H	OMe	OBzl	H	37
22	H	H	OAc	OMe	-

Table 1. Reaction times, yields, and melting points of 1,4-phenanthrenequinones (**1**, **41–75**) and of 8,9-dihydro-1,4-phenanthrenequinones (**76–81**)

PQ	R^1	R^2	R^3	R^4	R^5	R^6	R^7	Time [d]	Yield [%]	m.p. [°C]	Ref. m.p. °C[29]	PQ H_2	Yield [%]	m.p. [°C]
41	H	H	H	H	H	H	H	6	14	143	145	-		
42	OMe	H	H	H	H	H	H	17	1	135		-		
1	H	OMe	H	H	H	H	H	17	14	170	170–172[1]	-		
43	H	H	OMe	H	H	H	H	18	2	111	106.5–108.5	-		
44	H	H	H	OMe	H	H	H	3	28	203	202–203			

Table 1. Continued

45	H	H	H	H	OMe	H	H	18	15	153	153	**76**	5	150
46	H	H	H	H	H	OMe	H	4	30	208	208–209	-		
47	H	OMe	H	OMe	H	H	H	3	10	215		-		
48	H	OMe	H	H	OMe	H	H	14	6	205		-		
49	H	OMe	H	H	H	OMe	H	11	19	246–247		-		
-	H	H	OMe	H	OMe	H	H					**77**	38	110
50	H	H	OMe	H	H	OMe	H	4	18	176	173–175	-		
51	H	H	H	OMe	OMe	H	H	3	12	236	23631	**78**	3	174
52	H	H	H	OMe	H	OMe	H	4	11	252		-		
53	H	H	H	OBzl	OMe	H	H	3	66	153		-		
54	H	H	H	H	OMe	OMe	H	6	9	198	196–198	**79**	17	143
55	H	H	H	H	OMe	OBzl	H	21	29	156		-		
56	H	H	H	H	OBzl	OMe	H	21	34	158		-		
57	H	H	H	H	H	OMe	OH	4	0.6	238		-		
58	OMe	H	H	OMe	H	OMe	H	3	2	253		-		
59	OMe	H	H	H	OMe	OMe	H	8	1	166		-		
60	H	OMe	OMe	H	OMe	H	H	-	0	167		**80**	37	189
61	H	OMe	OMe	H	H	OMe	H	5	15	219		-		
62	H	OMe	H	OMe	OMe	H	H	4	12	250		-		
63	H	OMe	H	OMe	H	OMe	H	3	34	228				
64	H	OMe	H	H	OMe	OMe	H	8	23	227		-		
65	H	H	OMe	OMe	OMe	H	H	7	15	139		-		
66	H	H	OMe	H	H	OMe	OH	4	3	169		-		
67	H	H	H	OMe	OMe	OMe	H	4	48	139		-		
68	H	H	H	H	OMe	OMe	OH	6	0.2	204		-		
69	OMe	OMe	H	H	OMe	OMe	H	11	24	157		**81**	12	125
70	OMe	H	H	OMe	OMe	OMe	H	3	4	217		-		
71	H	OMe	OMe	OMe	OMe	H	H	8	17	187		-		
72	H	OMe	OMe	OMe	H	OMe	H	6	9	200-201		-		

Table 1. Continued

73	H	OMe	OMe	H	H	OMe	OH	5	2	231	-
74	H	OMe	H	OMe	OMe	OMe	H	3	46	195	-
75	H	H	H	OMe	OMe	OMe	OH	3	2	217	-

Table 2. Shift increments [Δ ppm] of the proton signals in the ^{1}H NMR spectra of the monosubstitued 1,4-phenanthrenequinones 1, **42–46** compared with the unsubstituted 1,4-phenanthrenequinone (**41**)

Position of H	42	1	43	44	45	46
2-H	–	–0.83	–0.11	0	–0.02	–0.03
3-H	–0.80	–	0.11	0	0	.0.06
5-H	0.06	–0.05	–	–0.48	–0.05	–048
6-H	–0.02	–0.04	–0.67	–	–0.32	–0.13
7-H	–0.01	–0.05	–0.06	–0.34	–	–0.71
8-H	0	–0.03	–0.42	–0.09	–0.68	–
9-H	0.04	–0.03	–0.10	–0.05	0	0.49
10-H	–0.03	–0.01	–0.15	–0.11	–0.08	–0.07

The formation of two different regioisomers was possible in the reaction of the styrenes **25**, **30** and **32** with benzoquinone **38**. The structures were assigned based on the increments shown in Table 2. Only in the reaction of **25**, a 1,4-phenanthrenequinone **43** with a sterically hindered methoxy group at C-5 was formed in low yield (2 %) in addition to the major 7-methoxy compound **45** (15 %). The sterically favored regioisomers **51** and **53** were the only products detected in the other cases. A sterically hindered methoxy group at C-5 was present in the products that furnished exclusively the 9,10-dihydro-1,4-phenanthrenequinones **77** and **80**. Evidently, in the twisted dihydro compounds, there is less steric compression introduced by a 5-methoxy group than in the corresponding dehydrogenated 1,4-phenanthrenequinones.[49,50] The release of strain is also seen in the upfield shift of 5-H resonance in the ^{1}H NMR spectra of the 9,10-dihydro compounds by almost 1 ppm compared

to the 1,4-phenanthrenequinones. A deviation from a totally flattened conformation is also adopted by the 1,4-phenanthrenequinone **61** as shown by X-ray structure determination.[51] This is related to the skeletal deformation of related 4,5-disubstituted phenanthrenes and 9,10-dihydro phenanthrenes.[49] The possibility of forming 9,10-dihydro compounds by Diels-Alder reaction allows the synthesis of C-5 substituted 1,4-phenanthrenequinones by subsequent palladium catalyzed dehydrogenation. This is in contrast to the photocyclization of stilbenes where C-5 methoxylated phenanthrenes are not formed (see below).

The chromatographic analysis of the Diels-Alder reactions revealed the presence of polar hydroxylated 1,4-phenanthrenequinones in five cases. The position of the hydroxy group could not unambiguously be deduced from the spectral data alone. Therefore, an X-ray analysis was undertaken that proved the structure of **66**.[51] The phenolic groups in the other compounds were also located at C-9 as shown by comparison of their NMR spectra with **66** and the structures had to be represented as **57**, **66**, **68**, **73**, and **75**, respectively. The origin of the oxygen atom introduced during the Diels-Alder reactions probably arises from air oxygen but the mechanistic pathway remains unclear at the present time.

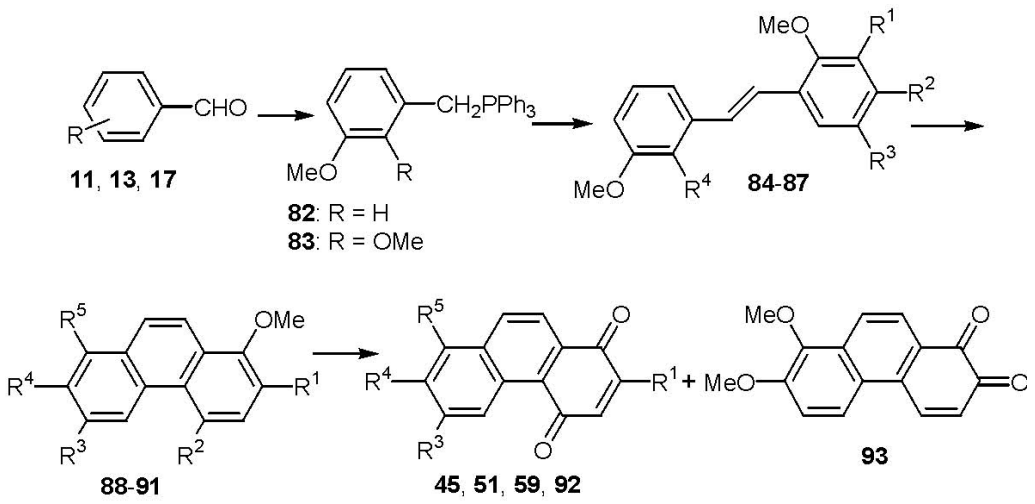
Several regioisomers can theoretically be formed in the reaction of methoxybenzoquinone (**39**) with the styrenes **23**–**37**. In practice, the number is reduced to two isomers because the addition occurs only at the non-substituted ethylene linkage of the benzoquinone, probably for steric as well as electronic reasons.[30,47] However, two regioisomers result depending on the relative orientation of the styrene and the methoxybenzoquinone. There is a controversy in the literature concerning this stereochemical question. Kashisawa et al.[30] state that 3-methoxy-1,4-phenanthrenequinone (**1**) is formed in the reaction of styrene **7** with **39** in contrast to Lora-Tomaya[47] who deduced the C-2 position based on chemical degradation. The chemical shifts in the ^{1}H-NMR spectra for the quinoide protons at C-2 or C-3 are too small to be significant (Δ = 0.06 ppm for **1** and **42**) but the ^{13}C-NMR chemical shifts differ significantly and an assignment would be possible if the location of the methoxy group in compounds with a related structure would be know. The structures of two major products **49** and **64** from the reaction of the styrenes **23** and **26** with **39** were determined by X-ray analysis showing that the methoxy group was located at C-3.[52] Comparison of the ^{13}C-NMR spectra showed that all major regioisomers (**1**, **63**, **64**, and **74**) had a methoxy group at C-3 and the minor isomers **42**, **58**, **59**, and **70** had a methoxy group at C-2. In seven other cases (**47**–**49**, **61**, **62**, **71**, and **72**) the 3-methoxy-1,4-phenanthrenequinones were the **only** products that could be isolated in

addition to the dihydro compound **77**. The physical and spectral properties of the major reaction product **1** were identical to those reported for the natural product annoquinone-A, the antimicrobial and cytotoxic compound isolated from *Annona montana.*[1]

Photocyclization

The photocyclization of stilbenes to phenanthrenes is probably one of the most often used photochemical reactions.[39,40] The multistep conversion comprises isomerization of *E*-stilbenes to *Z*-stilbenes, followed by cyclization of intermediate radicals to dihydrophenanthrenes that are irreversibly dehydrogenated to phenanthrenes in the presence of oxidants.[37] The stilbenes **84**–**87** required for our investigation were prepared by Wittig reaction using the procedure of Boden[42] starting form the aldehydes **11**, **13** and **17** and the phosphonium salts **82** and **83**. Upon irradiation of the stilbenes **84**, **85**, and **86**, the photocyclization products 1,4,7-trimethoxyphenanthrene **88**, 1,2,7,8-tetramethoxyphenanthrene **89**, and 1,4,7,8-tetramethoxyphenanthrene **90** were formed without loss of methoxy groups. As expected, only the sterically less hindered 7-methoxy compound **88** resulted from the photolysis of **84**. The preferential formation of the less hindered regioisomer has also been observed in hydroxylated precursors.[7] A methoxy group was eliminated during the irradiation of **87** yielding the 1,2,6,7-tetramethoxyphenanthrene **91**.

The subsequent oxidation to 1,4-phenanthrenequinones can be effected by ether cleavage followed by air oxidation[31] or in one step using ceric ammonium nitrate (CAN).[53,54] In the clean oxidation, the reagent preferentially cleaved the *para*-methoxy groups of the tri- and tetramethoxyphenanthrenes **88** and **90** to afford the 1,4-phenanthrenequinones **45** and **51**. A separable mixture of the *ortho*-quinone **93** and the *para*-quinone **59** was isolated in the oxidation of **87**. The 1,4-phenanthrenequinone **59** was identical with a methylated sample of the natural product cypripedine (**2**). A 1,4-phenanthrenequinone **92** of isomeric structure was obtained by CAN treatment of **89**. The results demonstrate that 2-methoxy-1,4-phenanthrenequinones and 1,2-phenanthrenequinones that are not easily accessible by Diels-Alder reactions, but can be prepared efficiently by CAN oxidation from photochemically generated phenanthrenes (general procedure VIII). On the other hand, sterically hindered 4,5-disubstituted phenanthrenes and thus their putative oxidation products, the 5-methoxy-1,4-phenanthrenequinones, cannot be obtained by this route.



Scheme 2. Photocyclization of stilbenes (ST 84–87) to the phenanthrenes (PH 88–91) and CAN-oxidation to 1,4- and 1,2-phenanthrenequinones

ST	R^1	R^2	R^3	R^4
84	H	H	H	OMe
85	OMe	OMe	H	H
86	OMe	H	H	OMe
87	H	OMe	OMe	OMe

PH	R^1	R^2	R^3	R^4	R^5	PQ
88	H	OMe	H	OMe	H	**45**
89	OMe	H	OMe	OMe	H	**92**
90	H	OMe	H	OMe	OMe	**51**
91	OMe	H	H	OMe	OMe	**59**

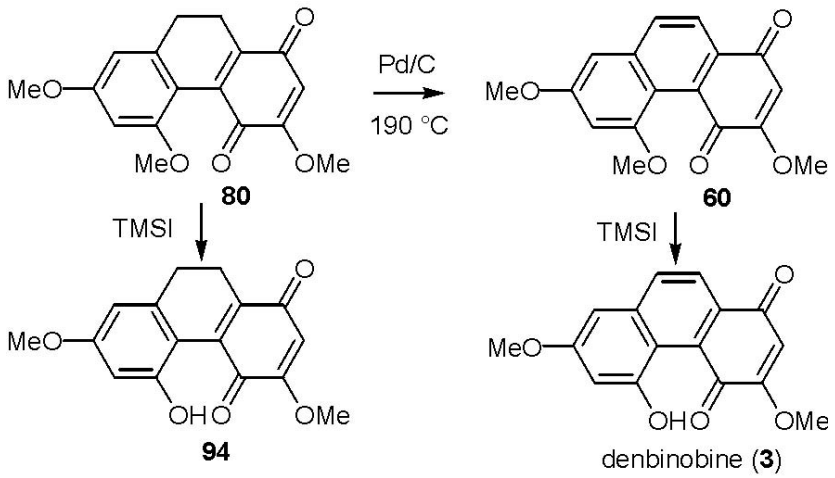
Chemical reactions with 1,4-phenanthrenequinones

1. Synthesis of denbinobine (3) and isocypripedine (97)

A 1,4-phenanthrenequinone named denbinobine was isolated by Talapatra et al.[21] from

Dendrobium nobile Lindl. Structure **3** was assigned to the natural product, but the position of the methoxy group at C-3 was merely based on the assumption that the molecule is of acetogenin origin. However, as recently pointed out by Thomson,[4] phenylalanine is incorporated into two rings of the very common oxygenated phenanthrenes in orchids such as hircinol.

In the synthesis of **3**, we started from the 9,10-dihydro 1,4-phenanthrenequinone **80** which could be dehydrogenated with palladium/charcoal to **60** in 95 % yield. The crucial step was the selective demethylation of the trimethyl ethers **80** and **60** that could be effected by treatment with one equivalent of trimethlysilyl iodide[55] to afford **94** and **3** in 72 and 62 % yields, respectively. This remarkable selectivity in the cleavage of the sterically hindered methyl ether even in preference of the vinylogous ester (OMe at C-3) is a characteristic feature of the angular arrangement of 1,4-phenanthrenequinones.



Scheme 3. Synthesis of denbinobine (**3**) by dehydrogenation of **80** and selective demethylation of **60**

Structure **3** was confirmed by X-ray structure determination and Fig. 2 shows the ORTEP-plot with numbering scheme and bond distances (e. s. d.'s are 0.001 Å for C- and O-atoms, and 0.01 Å for H-atoms). The smaller hydroxy group at C-5 causes less twisting of the molecule as compared to similar 5-methoxy compounds **60** and **65.**[51]

Comparison of the data of **3** with published values for the natural product[21] shows identity of the melting point (215 ^{o}C) and good agreement of the ^{1}H-NMR spectra and the

fragmentation pattern in the mass spectrum. However, deviations are seen in the intensities of the peaks of the mass spectrum. Unfortunately, no sample of the natural product was available for direct comparison with **3**. 1,4-Phenanthrenequinones could not be extracted from *Dentrobium nobile* cultivated at various places in Europe.

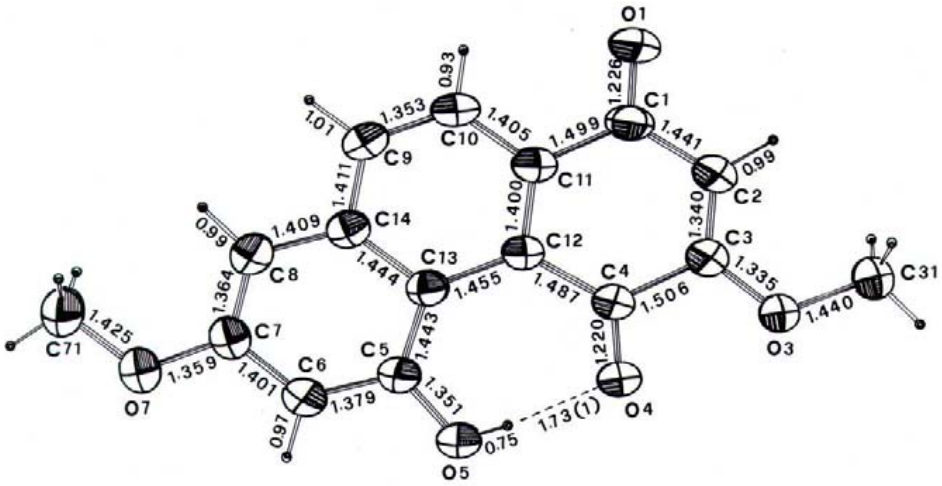


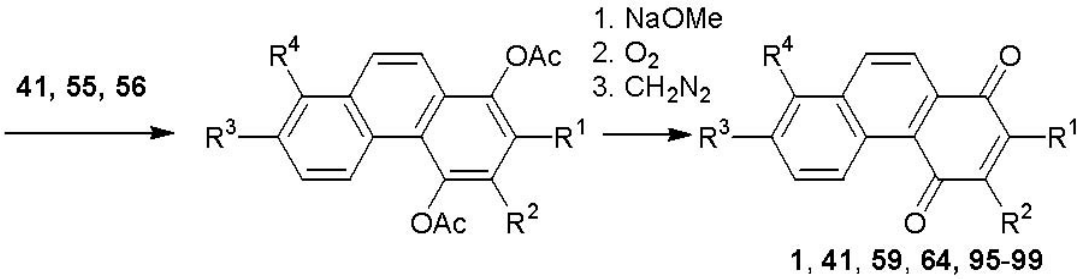
Figure 2. ORTEP-Plot of denbinobin (**3**) with numbering scheme and bond distances (Å)

The Thiele-Winter reaction

In the Diels-Alder reaction of styrenes with methoxybenzoquinone (**38**), only traces of the corresponding 2-methoxy-1,4-phenanthrenequinones could be isolated. We have investigated the possibility to prepare these compounds in connection with a synthesis of cypripedine by introducing an additional oxygen atom at C-2 and/or C-3 into the quinone part using the Thiele-Winter reaction.[56,57] The 1,4-phenanthrenequinones **41**, **55,** and **56** were treated with acetic anhydride and catalytic amounts of perchloric acid. The benzyl ether was cleaved under these acidic conditions. The triacetoxylated phenanthrenes resulting from the Thiele-Winter reaction were not isolated but directly subjected to saponification, air oxidation, diazomethane treatment and chromatographic separation to afford the 1,4-phenanthrenequinones **1**, **41**, **59**, **64** and **95**–**99** (general procedure VI). The first four products **1**, **41**, **59**, and **64** could be identified by comparison with the previously prepared Diels-Alder adducts (see above). The C-3 methoxylated products **1**, **64**, **96**, and **97** were formed with a slight preference over their C-2 counterparts **41**, **59**, and **95** thus complementing the regiochemical outcome of the Diels-

Alder reaction of styrenes with methoxybenzoquinone **39** (yields and m. p. see Scheme 4).

In an attempt to synthesize cypripedine (**2**) by selective methylation, the three saponified Thiele-Winter products, resulting from the benzyl ether **56**, were treated with equivalent amounts of diazomethane to yield the monophenol **97** in addition to an inseparable mixture of the hydroxy-1,4-phenanthrenequinones **98** and **99**. Structure **97** is isomeric (OMe on C-3 instead of C-2) to cypripedine **(2**). For structural proof, the inseparable mixture of phenols **98** and **99** were methylated and identified as the separable trimethoxy-1,4-phenanthrenequinones **59** and **64**.

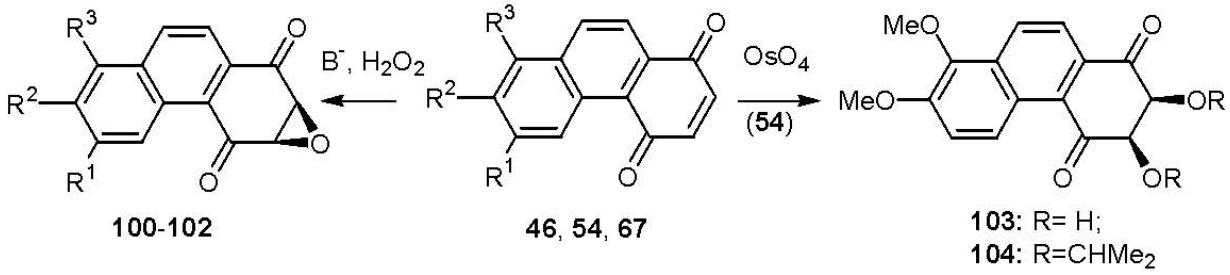


Scheme 4. Thiele-Winter reaction of 1,4-phenanthrenequinones **41**, **55**, **56** to afford the 2- and 3-methoxy-1,4-phenanthrenequinones **1**, **41**, **59**, **64**, **95-99**

PQ	R^1	R^2	R^3	R^4	Yield [%]	m.p. [°C]
41	OMe	H	H	H	31	135
1	H	OMe	H	H	38	138
59	OMe	H	OMe	OMe	11	166
64	H	OMe	OMe	OMe	18	227
95	OMe	H	OMe	OH	9	249
96	H	OMe	OMe	OH	1	286
97	H	OMe	OH	OMe	9	251
98	OH	H	OMe	OMe	7	262
99	H		OH	OMe		OMe

Finally, the reactivity of the quinoid double bond of 1,4-phenanthrenequinones was

studied in hydroxylation and epoxidation reactions. The *cis*-dihydroxylation of 7,8-dimethoxy-1,4-phenanthrenequinone **54** proceeded smoothly upon treatment with catalytic amounts of osmium tetroxide and sodium perchlorate to give the diol **103** that was also characterized as acetonide **104**. Epoxidation with hydrogen peroxide in basic solution converted **46**, **54**, and **67** in good yield into the epoxides **100**–**102** (general procedure VII). Therefor, in the epoxidation[58] and *cis*-dihydroxylation[59] reactions, the 1,4-phenanthrenequinones show similar reactivity to the 1,4-naphthoquinones and 1,4-benzoquinones.



Scheme 5. Epoxidation and cis-hydroxylation of the 1,4-phenanthrenequinones **46**, **54**, and **74**

PQE	R^1	R^2	R^3	Yield [%]	m.p. [°C]
100	H	H	OMe	79	218
101	H	OMe	OMe	81	165
102	OMe	OMe	OMe	60	133

Electrochemistry

Cyclic voltammograms of ten different 1,4-phenanthrenequinones **(1, 41-46, 54, 64, 70, 74)** were measured to determine redox potentials for possible correlation with their allergenic and sensitizing properties.[28] The voltammetric measurements were performed in highly purified acetonitrile[60] under rigorous exclusion of water.[61] Under these conditions, the resulting anions and most dianions are quite persistent. Figure 3 shows the cyclic voltammogram of **45** with two successive one-electron transfers. The electrochemical data determined with a home-built computer-controlled apparatus are collected in Table 3 (for definition of values see legend of Figure 3).

It is interesting to observe that methoxy-substitution on the distant ring C (positions 5–8, **41, 44-46, 54**) of the 1,4-phenanthrenequinones has only a small influence on the redox potential compared to the parent 1,4-phenanthrenequinone **41**. Not surprisingly, direct methoxy substitution on the quinoid double bond as in **1**, **64, 70,** and **74** increases the absolute value of the potential by 108–143 mV. A remarkable deviation is seen in the potential of the sterically hindered 5-methoxy compound **43** in which the value is increased by –118 mV approaching the value of naphthoquinone (–1018 mV). We rationalize this behavior by the twisted conformation of the **43** resulting in decreased conjugation of the quinoide part of the molecule with ring C.

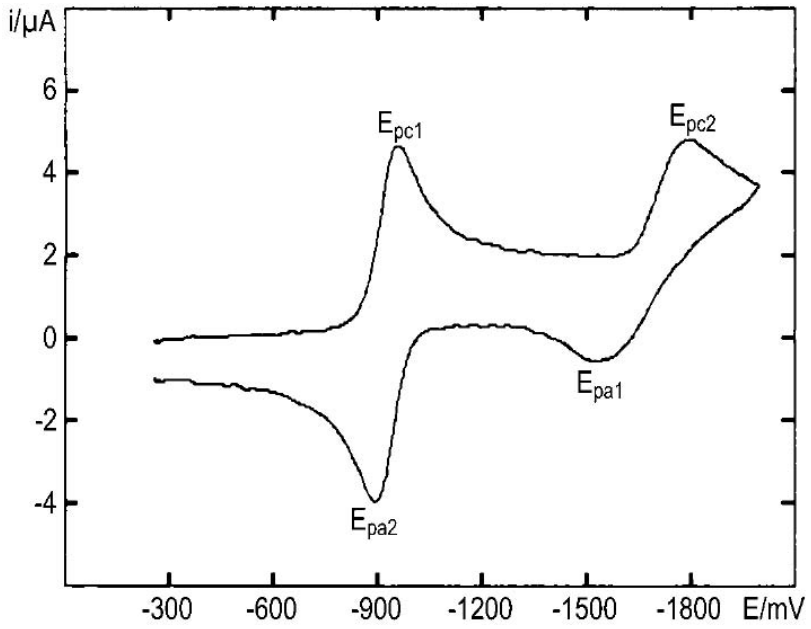


Figure 3. Cyclic voltammogram for 45 with two successive one-electron transfers. (E_{pc1}: cathodic peak potential 1. ET, E_{pc2}: cathodic peak potential 2. ET, E_{pa1}: anodic peak potential 1. ET, E_{pa2}: anodic peak potential 2. ET); ET = electron transfer

Table 3. Electrochemical data of the 1,4-phenanthrenequinones

	1	**41**	**43**	**44**	**45**	**46**	**54**	**64**	**70**	**74**
E_{pc1}	–1050	–940	–1058	–956	–956	–940	–934	–1048	–1073	–1083
E_{pc2}	–1942	–1821	–1850	–1884	–1799	–1675	–1783	–1934	–1877	–1917
ΔE_{p1} = Epa1 – Epc1	80	56	82	75	67	63	63	64	76	76
i_{pa1}/i_{pc1}	0.84	8.86	0.82	0.79	0.84	0.89	0.81	0.87	0.88	0.81

Finally, we have investigated the redox potential of 1,4-phenanthrenequinone **41** with respect to the other mono- bi- and tricyclic quinones benzoquinone (**105**), 1,4-napthoquinone (**106**, 9,10-phenanthrenequinone **107** and 9,10-anthraquinone **108**. In Figure 4, the redox potential E_{pc}[62] of the quinones is correlated with their LUMO energies (absolute values). A relatively linear correlation is observed.

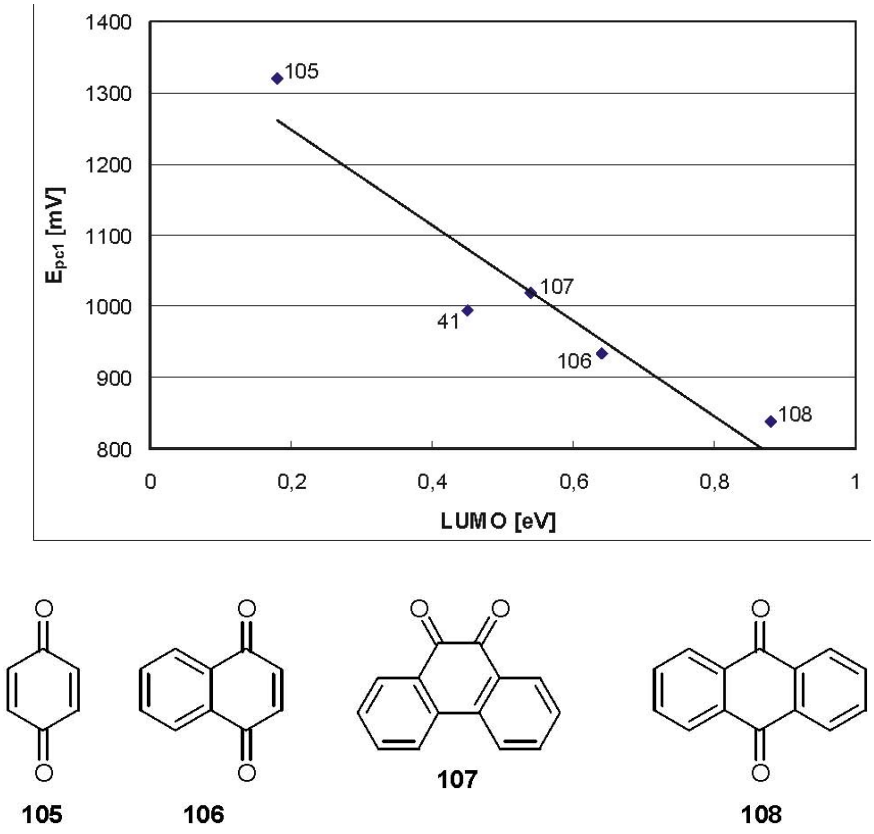


Figure 4. Redox potential E_{pc} of the quinones **41**, **105**, **106**, **107**, and **108** correlated with their LUMO energy (absolute values)

Experimental Section

Crystal data for denbinobin. $C_{16}H_{12}O_5$, M_r = 284.27, triclinic, space group P-1$^-$ with unit cell dimensions a = 8.560(1), b = 8.657(1), c = 9.184(1) Å, α = 110.04(1), β = 94.47(1), γ = 98.14(1)°, V = 631.0(3) Å^3, Z = 2, D_x = 1.496 Mg m^{-3}, Cu-K$_\alpha$ radiation, λ = 1.5418 Å, μ = 0.899 mm^{-1}, F(000) = 296, T = 296 K, final R = 0.050 for 2292 observed reflections.

Experimental part of the X-ray structure determination

Small amounts of denbinobin were recrystallized from dichloromethane. A dark-red plate shaped crystal with dimensions 0.25x0.24x0.65 mm was used for the measurements. Cell parameters were obtained by least-squares refinement from the angular settings of 25 reflections in the range 25° < θ < 76°. Enraf-Nonius CAD-4 diffractometer with graphite monochromatized CuK$_\alpha$ radiation was applied. The intensities of 2850 reflections with 2°<θ<75° (-10 ≤ h ≤ 0, -10 ≤ k ≤ 10, -11 ≤ l ≤ 11) were measured on the diffractometer by the θ-2θ scan technique at a variable scan rate 0.3° to 20° min^{-1}. 2292 unique reflections were observed above background with I>3 σ (I), σ (I) based on counting statistics; 288 reflections were unobserved by this criterion.

Data reduction, Lorentz-polarization correction, absorption correction (ψ -scan technique), solution, and refinement of the structure were carried out with the CAD-4 structure determination package.[63] A superstructure effect was observed in the normalized structure factors of the eight parity groups: reflections with 1 = 2n showed values of about 1.20, those with 1 = 2n+1 only of about 0.65. In addition, hypercentricity was noticed in the data statistics. For this reason the structure had to be solved in the space group P 1, in combination of MULTAN82 and Fourier calculations. The centre of symmetry was determined by two similar molecular fragments. The psotional and anisotropic temperature parameters of the C and O atoms were refined with unit weight. All H atoms were localized in the subsequent difference Fourier map. In the final cycle of full matrix least-squares refinement positional parameters of all atoms and anisotropic temperature factor coefficients for the C and O atoms were varied. The temperature parameters of the H atoms were refined isotropically. The final R was 4.96 %, 238 parameter refined, number of reflections 2292. The max. height in the final difference Fourier synthesis was 0.27 eA^{-3}. Tables of thermal parameters, bond distances and angles have been deposited.[64]

3-Acetyloxy-2-methoxybenzaldehyde (22). A solution of 3-acetyloxy-2-hydroxybenzaldehyd (2.50 g, 14 mmol) in methyl iodide (50 mL) was treated under nitrogen with Ag_2O (9.30 g). The suspension was stirred for 4 h (TLC monitoring), filtered, the filtrate evaporated under reduced pressure, and the residue purified by flash chromatography on silica gel (dichloromethane) to yield **22** (2.21 g) (81%); mp 55 °C. IR (CCl_4): ν = 1780 cm^{-1} (Ac), 1700 (C=O), 1480, 1255, 1195; UV: λ_{max} (lgε) = 212 nm (4.126), 250 (3.883), 301 (3.264); ^{1}H NMR (400 MHz): δ = 2.38 (s, 3H, CH_3), 3.96 (s, 3H, OCH_3), 7.22 (dd, $J_{4,5}$ = 8 Hz, $J_{5,6}$ = 8 Hz, 1H, 5-H), 7.34 (dd, $J_{4,5}$ = 8 Hz, $J_{4,6}$ = 2 Hz, 1H, 4-H), 7.74 (dd, $J_{5,6}$ = 8 Hz, $J_{4,6}$ = 2 Hz, 1H, 6-H), 10.38 (s, 1H, CHO); Ms: *m/z* (%) = 194 (9, M^+), 152 (100), 137 (24), 134 (24), 109 (20), 106 (32). Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.56; H, 5.29.

General procedure 1. Benzylation of phenols

To a solution of NaOH (416 mg, 1.0 mmol) in (7.4 mL) was added the phenolic benzaldehyde (6.6 mmol) in dimethyl sulfoxide (2 mL) and benzyl chloride (1.2 mL, 10.4 mmol). The mixture was stirred for 4–8 h at 20 °C under nitrogen (TLC monitoring) and then quenched by addition of ice-water. The mixture was extracted with diethyl ether (50 mL), the organic phase washed three times with water (50 mL), dried (Na_2SO_4), and concentrated at reduced pressure. The residue was purified by column chromatography on silica gel to afford the respective benzyl ethers.

2-Benzyloxy-3-methoxybenzaldehyde (19). According to procedure I, 2-hydroxy-3-methoxybenzaldehyde (1.00 g, 6.6 mmol) was converted to **19**; yield: 1.51 g (95%); mp 45 °C (ref.[43]: 45°C). ^{1}H NMR (400 MHz): δ = 3.91 (s, 3H, OCH_3), 5.16 (s, 2H, CH_2), 7.18 (m_c, 3H, Ar-H), 7.34 (m_c, 5H, C_6H_5), 10.22 (s, 1H, CHO).

3-Benzyloxy-2-methoxybenzaldehyde (20). According to procedure I, 3-Acetoxy-2-methoxybenzaldehyde (1.28 g, 6.6 mmol) was benzylated to give **20**, yield 1.459 g (91%). IR: ν = 1695 cm^{-1} (C=O), 1585, 1275, 1250, 1225, 1005; UV: $_{max}$ (lg) = 214 nm (4.478), 254 (4.038), 320 (3.640); ^{1}H NMR (300 MHz): δ = 4.03 (s, 3H, OCH_3), 5.16 (s, 2H, CH_2), 7.10 (m_c, 1H, 5-H), 7.20 (dd, $J_{4,5}$ = 8 Hz, 1H, 4-H), 7.41 (m_c, 6H, 6-H, C_6H_5), 10.45 (s, 1H, CHO); MS (30°C): *m/z* (%) = 242 (11, M^+), 92 (8), 91 (100), 65 (11). Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.20; H, 5.59.

3-Benzyloxy-4-methoxybenzaldehyde (21). According to procedure I, 3-Hydroxy-4-methoxybenzaldehyde (1.00 g, 6.6 mmol) was converted to **21**; yield: 1.50 g (94%). ^{1}H NMR (300 MHz): δ = 3.97 (s, 3H, OCH_3), 5.20 (s, 2H, CH_2), 7.00 (d, J = 8 Hz, 1H, 5-H), 7.32 - 7.49 (m, 7H, 2-H, 6-H, C_6H_5).

General procedure 2. Synthesis of styrols by Wittig reaction

A solution of the benzaldehyde (10 mmol), methyltriphenylphosphonium bromide (4.286 g, 12 mmol), K_2CO_3 (6.63 g, 48 mmol) and 18-crown-6 (30 mg) in dry THF (30 mL) was stirred under nitrogen at 60 °C (3-6 h, TLC monitoring).[42] The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether) to afford the styrols. Known stryrols are only characterized by their ^{1}H NMR spectra.

2-Benzyloxy-3-methoxystyrol (35). Yield: 2.367 g (98%). ^{1}H NMR (300 MHz): δ = 3.87 (s, 3H, OCH_3), 4.97 (s, 2H, CH_2), 5.24 (dd, J_{cis} = 11 Hz, J_{gem} = 1 Hz, 1H, β-H), 5.72 (dd, J_{trans} = 18 Hz, J_{gem} = 1 Hz, 1H, α-H), 6.85 (dd, $J_{4,5}$ = 8 Hz, $J_{4,6}$ = 1 Hz, 1H, 4-H), 7.08 (m_c, 2H, 5-H, à-H), 7.30 (m_c, 5H, C_6H_5), 7.48 (dd, $J_{5,6}$ = 8 Hz, $J_{4,6}$ = 1 Hz, 1H, 6-H).

3-Benzyloxy-2-methoxystyrol (36). Yield: 2.423 g (10 mmol). IR: ν = 1580 cm^{-1} (C=C), 1475, 1405, 1275, 1010; UV: $_{max}$ (lg) = 221 nm (4.507), 251 (4.033), 295 (3.240); ^{1}H NMR (400 MHz): δ = 3.85 (s, 3H, OCH_3), 5.12 (s, 2H, CH_2), 5.30 (dd, J_{cis} = 11 Hz, J_{gem} = 1 Hz, 1H, β-H), 5.76 (dd, J_{trans} = 18 Hz, J_{gem} = 1 Hz, 1H, α-H), 6.87 (dd, $J_{4,5}$ = 8 Hz, $J_{4,6}$ = 1 Hz, 1H, 4-H), 6.98 (dd, $J_{4,5}$ = 8 Hz, $J_{5,6}$ = 8 Hz, 1H, 5-H), 7.04 (dd, J_{cis} = 11 Hz, J_{trans} = 18 Hz, 1H à-H), 7.13 (dd, $J_{5,6}$ = 8 Hz, $J_{4,6}$ = 1 Hz, 1H, 6-H), 7.39 (m_c, 5H, C_6H_5); Ms: *m/z* (%) = 240 (2, M^+), 121 (7), 91 (100), 78 (20), 65 (31), 51 (23). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.10; H, 6.84.

3-Benzyloxy-4-methoxystyrol (37). Yield: 2.282 g (95%). ^{1}H NMR (400 MHz): δ = 3.83 (s, 3H, OCH_3), 5.06 (dd, J_{cis} = 11 Hz, J_{gem} = 1 Hz, 1H , β-H), 5.11 (s, 2H, CH_2), 5.48 (dd, J_{trans} = 18 Hz, J_{gem} = 1 Hz, 1H, β-H), 6.60 (dd, J_{cis} = 11 Hz, J_{trans} = 18 Hz, 1H, α-H), 6.84 (d, J = 9 Hz, 1H, 5-H), 6.95 (dd, $J_{5,6}$ = 9 Hz, $J_{2,6}$ = 3 Hz, 1H, 6-H), 7.00 (d, J = 3 Hz, 1H, 2-H), 7.37 (m_c, 5H, C_6H_5).

2,4-Dimethoxystyrol (28). Yield: 1.512 g (92%). ^{1}H NMR (400 MHz): δ = 3.75 (s, 3H,

OCH_3), 3.76 (s, 3H, OCH_3), 5.09 (dd, J_{cis} = 11 Hz, J_{gem} =2 Hz, 1H, β-H), 5.58 (dd, J_{trans} = 18 Hz, J_{gem} = 2 Hz, 1H, β-H), 6.39 (d, J = 2 Hz, 1H, 3-H), 6.42 (dd, $J_{5,6}$ = 8 Hz, $J_{3,5}$ = 2 Hz, 1H, 5-H), 6.92 (dd, J_{cis} = 11 Hz, J_{trans} = 18 Hz, 1H, α-H), 7.34 (d, J = 8 Hz, 1H, 6-H).

3,5-Dimethoxystyrol (31). Yield: 1.624 (99%). ^{1}H NMR (400 MHz): δ = 3.76 (s, 6H, OCH_3), 5.23 (dd, J_{cis} = 11 Hz, J_{gem} = 1 Hz, 1H, β-H), 5.71 (dd, J_{trans} = 18 Hz, J_{gem} = 1 Hz, 1H, β-H), 6.37 (d, J = 2 Hz, 4-H), 6.55 (d, J = 2 Hz, 2H, 2-H, 6-H), 6.62 (dd, J_{cis} = 11 Hz, J_{trans} = 18 Hz, 1H, -H).

2,3,4-Trimethoxystyrol (32). Yield: 1.806 g (93%). ^{1}H NMR (400 MHz): δ = 3.85 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 5.18 (dd, J_{cis} = 11 Hz, J_{gem} = 1H, β-H), 5.64 (dd, J_{trans} = 18 Hz, J_{gem} = 1 Hz, 1H, β-H), 6.65 (d, J = 9 Hz, 1H, 5-H), 6.92 (dd, J_{cis} = 11 Hz, J_{trans} = 18 Hz, α-H), 7.19 (d, J = 9 Hz, 1H, 6-H).

3,4,5-Trimethoxystyrol (34). Yield: 1.832 g (94%). ^{1}H NMR (400 MHz): δ = 3.85 (s, 3H, OCH_3), 3.87 (s, 6H, OCH_3), 5.21 (dd, J_{cis} = 11 Hz, J_{gem} = 1 Hz, 1H, β-H), 5.65 (dd, J_{trans} = 18 Hz, J_{gem} =1 Hz, 1H, β-H), 6.63 (dd, J_{cis} = 11 Hz, J_{trans} = 18 Hz, 1H, α-H), 6.63 (s, 2H, 2-H, 6-H).

General procedure 3. Synthesis of 1,4-phenanthenequinones by Diels-Alder reaction

A solution of the styrene (3.4 mmol), 1,4-benzoquinone (17 mmol), 2-methoxy-1,4-benzoquinone or 2,3-dimethoxy-1,4-benzoquinone (each 17 mmol) and trichloroacetic acid (34 mg) were heated to 100 °C in toluene for the times indicated in Table 1. The crude product was chromatographed on neutral alumina (dichloromethane). The solvent was removed under reduced pressure and the residue sublimed to remove the benzoquinone. The residue was chromatographed on silica gel (CH_2Cl_2) and the pure fractions crystallized from petroleum ether. For yields, melting points and reaction times see Table 1.

1,4-Phenanthrenequinone (41). ^{1}H NMR: δ = 6.94 (d, J = 10 Hz, 1H, 2-H), 6.97 (d, J = 10 Hz, 1H, 3-H), 7.65 (ddd, $J_{7,8}$ = 8 Hz, $J_{6,7}$ = 7 Hz, $J_{5,7}$ = 1 Hz, 1H, 7-H), 7.74 (ddd, $J_{5,6}$ = 9 Hz, $J_{6,7}$ = 7 Hz, $J_{6,8}$ = 2 Hz, 1H, 6-H), 7.89 (ddd, $J_{7,8}$ = 8 Hz, $J_{6,8}$ =2 Hz, $J_{5,8}$ = 1 Hz, 1H, 8-H), 8.16 (d, J = 9 Hz, 1H, 10-H), 8.17 (d, J = 9 Hz, 1H, 9- H), 9.55 (ddd, $J_{5,6}$ = 9 Hz, $J_{5,7}$ = 1 Hz, $J_{5,8}$ = 1 Hz, 1H, 5-H). ^{13}C NMR: δ = 121.78 (C-10), 127.08 (C-10a), 127.84 (C-5), 128.62 (C-

8), 129.83 (C-8a), 130.04 (C-6), 130.73 (C-4b), 132.16 (C-4a), 135.04 (C-9), 135.73 (C-2), 140.42 (C-3), 185.63 (C-4), 187.94 (C-1).

6-Methoxy-1,4-phenanthrenequinone (44). IR: ν = 1650 cm^{-1} (C=0), 1615 (C=C), 1590, 1460, 1305, 1275, 1220, 1080, 840; UV: λ_{max} (lg ε) = 234 nm (4.606), 269 (4.144), 283 sh (4.048), 372 (3.517), 450 (3.422); ^{1}H NMR (300 MHz): δ = 4.03 (s, 3H, OCH_3), 6.94 (d, *J* = 10 Hz, 1H, 2-H), 6.97 (d, *J* = 10 Hz, 1H, 3-H), 7.31 (dd, $J_{7,8}$ = 9 Hz , $J_{5,7}$ = 3 Hz, 1H, 7-H), 7.80 (d, *J* = 9 Hz, 1H, 8-H), 8.05 (d, *J* = 8 Hz, 1H, 10-H), 8.12 (d, *J* = 8 Hz, 1H, 9-H), 9.07 (d, *J* = 3 Hz, 1H, 5-H); ^{13}C NMR: δ = 55.53 (OCH_3), 105.59 (C-5), 119.88 (C-10), 121.66 (C-7), 125.35 (C-10a), 129.98 (C-8), 131.82 (C-8a), 132.43 (C-4b), 132.69 (C-4a), 134.72 (C-9), 135.68 (C-2), 140.58 (C-3), 161.46 (C-6), 185.83 (C-4), 188.07 (C-1).

7-Methoxy-1,4-phenanthrenequinone (45); 5-methoxy-1,4-phenanthrenequinone (43) and 9,10-dihydro-7-methoxy-1,4-phenanthrenequinone (76)

Data for 45. Mp 153°C (ref.[29]: 153°C). IR: ν = 1650 cm^{-1} (C=O), 1610 (C=C), 1240, 1080, 850; UV: λ_{max} (lg ε) = 233 nm (4.622), 250 sh (4.265), 291 (4.010), 301 (4.106), 390 3.684); ^{1}H NMR (250 MHz): δ = 4.01 (s, 3H, OCH_3), 6.96 (d, *J* = 10 Hz, 1H, 2-H), 6.97 (d, *J* = 10 Hz, 1H, 3-H), 7.21 (d, *J* = 3 Hz, 1H, 8-H), 7.42 (dd, $J_{5,6}$ = 10 Hz, $J_{6,8}$ = 3 Hz, 1H, 6-H), 8.08 (d, *J* = 9 Hz, 1H, 10-H), 8.17 (d, *J* = 9 Hz, 1H, 9-H), 9.50 (d, *J* = 10 Hz, 1H, 5-H). ^{13}C NMR: δ = 55.39 (OCH_3), 106.62 (C-8), 122.63 (C-6), 122.63 (C-10), 125.09 (C-10a), 127.24 (C-8a), 129.51 (C-5), 130.24 (C-4b), 133.43 (C-9), 135.95 (C-2), 138.67 (C-4a), 140.16 (C-3), 159.44 (C-7), 185.61 (C-4), 188.27 (C-1).

Data for 43. Mp 111°C (ref.[18]: 106.5–108.5°C). IR: ν = 1665 cm^{-1} (C=O), 1610 (C=C), 1455, 1295, 1265, 1095, 825; UV: λ_{max} (lg ε) = 227 nm (4.444), 261 (4.063), 299 (4.150), 368 (3.210), 433 (3.145); ^{1}H NMR (300 MHz): δ = 3.97 (s, 3H, OCH_3), 6.83 (d, *J* = 10 Hz, 1H, 2-H), 7.07 (d, *J* = 8 Hz, 1H, 6-H), 7.08 (d, *J* = 10 Hz, 1H, 3-H), 7.47 (d, *J* = 8 Hz, 1H, 8-H), 7.59 (dd, $J_{6,7}$ = 8 Hz, $J_{7,8}$ = 8 Hz, 1H, 7-H), 8.01 (d, *J* = 9 Hz, 1H, 10-H), 8.07 (d, *J* = 9 Hz, 1H, 9-H).

Data for 76. Mp 150°C. IR: ν = 1643 cm^{-1} (C=O), 1607 (C=C), 1552, 1433, 1285, 1252, 1134, 1123, 1066, 1028, 840; UV: λ_{max} (lg ε) = 215 nm (4.310), 255 (4.283), 460 (3.550); ^{1}H NMR (400 MHz): δ = 2.74 (m, 4H, 9-, 10-H), 3.85 (s, 3H, OCH_3), 6.75 (d, *J* = 10 Hz, 1H, 2-

H), 6.77 (d, *J* = 3 Hz, 1H, 8-H), 6.78 (d, *J* = 10 Hz, 1H, 3-H), 6.84 (dd, $J_{5,6}$ = 9 Hz, $J_{6,8}$ = 3 Hz, 1H, 6-H), 8.04 (d, *J* = 9 Hz, 1H, 5-H). MS (70°C *m/z* (%) = 240 (100, M^+), 197 (31), 169 (17), 158 (18), 115 (24). Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.25; H, 5.14.

8-Methoxy-1,4-phenanthrenequinone (46) and 9-hydroxy-8-methoxy-1,4-phenanthrenequinone (57)

Data for 46. Mp 208°C (ref.[18]: 208-209°C). IR: ν = 1655 cm^{-1} (C=O), 1610 (C=C), 1580, 1470, 1305, 1270, 1240, 1120, 840; UV: λ_{max} (lg ε) = 224 nm (4.519), 257 (4.059), 299 (4.231) 367 (3.270), 450 (3.187); ^{1}H NMR: δ = 4.02 (s, 3H, OCH_3), 6.91 (s, 2H, 2-, 3-H), 6.94 (d, *J* = 9 Hz, 1H, 7-H), 7.61 (t, *J* = 9 Hz, 1H, 6-H), 8.09 (d, *J* = 9 Hz, 1H, 10-H), 8.66 (d, *J* = 9 Hz, 1H, 9-H), 9.07 (d, *J* = 9 Hz, 1H, 5-H); ^{13}C NMR: δ = 55.75 (OCH_3), 106.52 (C-7), 119.65 (C-5), 121.04 (C-10), 126.65 (C-10a), 128.94 (C-8a), 129.10 (C-9), 130.33 (C-6), 130.98 (C-4b), 132.53 (C-4a), 135.61 (C-2), 140.63 (C-3), 155.33 (C-8), 185.82 (C-4), 187.88 (C-1).

Data for 57. Mp 238°C. IR: ν = 3260 cm^{-1} (OH), 1660 (C=0), 1650, 1600 (C=C), 1565, 1310, 1215, 1130, 1105, 1005, 845; UV: λ_{max} (lg ε) = 218 nm (4.458), 256 (4.032), 297 sh (4.210), 307 (4.271), 329 (3.430), 480 (3.372); ^{1}H NMR: δ = 4.12 (s, 3H, OCH_3), 6.86 (s, 2H, 2-, 3-H), 6.98 (d, *J* = 9 Hz, 1H, 7-H), 7.47 (s, 1H, 10-H), 7.59 (t, *J* = 9 Hz, 1H, 6-H), 9.31 (d, *J* = 9 Hz, 1H, 5-H), 10.34 (s, 1H, OH); MS (120°C): *m/z* (%) = 254 (100, M^+), 239 (82), 226 (59), 211 (84), 183 (83), 172 (55), 155 (73). Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.87; H, 3.96. Found: C, 70.60; H, 4.35.

5,8-Dimethoxy-1,4-phenanthrenequinone (50) and 9-hydroxy-5,8-dimethoxy-1,4-phenanthrenequinone (66)

Data for 50. Mp 176°C (ref.[18]: 173-175°C). IR: ν = 1660 cm^{-1} (C=O), 1605 (C=C), 1590, 1460, 1300, 1260, 1100, 1020, 815; UV: λ_{max} (lg ε) = 220 nm (4.464), 227 (4.467), 260 sh (3.994), 295 sh (4.025), 313 (4.135), 350 sh (3.443), 399 (3.031), 495 (2.906); ^{1}H NMR: δ = 3.89 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 6.76 (d, *J* = 10 Hz; 1H, 2-H), 6.86 (d, *J* = 8 Hz, 1H, 7 -H), 6.93 (d, *J* = 8 Hz, 2H, 6-H), 7.04 (d, *J* = 10 Hz, 1H, 3-H), 8.01 (d, *J* = 9 Hz, 1H, 10-H), 8.44 (d, *J* = 9 Hz, 1H, 9-H); ^{13}H NMR: δ = 56.14 (OC_3), 56.27 (OCH_3), 107.65 (C-6), 109.46

(C-7), 121.19 (C-10), 121.82 (C-10a), 127.22 (C-9), 129.65 (C-8a), 132.56 (C-4b), 133.27 (C-4a), 134.76 (C-2), 140.58 (C-3), 149.61 (C-8), 150.95 (C-5), 184.80 (C-4), 186.13 (C-1).

Data for 66. Mp 169°C. IR: ν = 3205 cm^{-1} (OH), 1665 (C=O), 1655, 1610 (C=C), 1510 , 1450, 1395, 1295, 1110, 820; UV: λ_{max} (lg ε) = 210 nm (4.268), 225 (4.245), 261 (4.276), 298 (3.921), 350 (3.761), 392 (3.551), 500 (2.780); ^{1}H NMR: δ = 3.90 (s, 3H, OCH3), 4.06 (s, 3H, OCH_3), 6.66 (d, *J* = 10 Hz, 1H, 2-H), 6.92 (s, 2H, 6-, 7-H), 6.93 (d, *J* = 10 Hz, 1H, 3-H), 7.38 (s, 1H, 10-H), 10.18 (s, 1H, OH); MS (170°C): *m/z* (%) = 284 (100, M^+), 269 (48), 241 (47). Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.25. Found: C, 67.33; H, 4.29.

6,7-Dimethoxy-1,4-phenanthrenequinone (51) and 9,10-dihydro-6,7-dimethoxy-1,4-phenanthrenequinone (78)

Data for 51. Mp 236°C (ref.[18]: 236°C). IR: ν = 1660 cm^{-1} (C=O), 1610 (C=C), 1585, 1285, 1310, 1260, 1075, 1020, 845; UV: λ_{max} (lg ε) = 145 nm (4.639), 285 sh (3.973), 297 sh (3.843), 425 (3.783); ^{1}H NMR: δ = 4.02 (s, 3H, OCH_3), 4.09 (s, 3H, OCH_3), 6.87 (s, 2H, 2-, 3-H), 7.07 (s, 1H, 8-H), 7.97 (s, 2H, 9-, 10-H), 9.02 (s, 1H, 5-H); ^{13}C NMR: δ = 55.90 (OCH_3), 56.11 (OCH_3), 106.17 (C-5), 106.68 (C-8), 120.85 (C-10), 125.27 (C-10a), 126.40 (C-8a), 130.72 (C-4b), 132.87 (C-9), 133.87 (C-4a), 135.99 (C-2), 140.34 (C-3), 151.35 (C-7), 153.22 (C-6), 185.69 (C-4), 188.39 (C-1).

Data for 78. Mp 174°C. IR: ν = 1645 cm^{-1} (C=O), 1600 (C=C), 1550, 1510, 1260, 1060; UV: λ_{max} (lg ε) = 219 nm (4.375), 257 (4.121), 287 (4.057), 498 (3.467); ^{1}H NMR (400 MHz): δ = 2.73 (m, 4H, 9-, 10-H), 3.93 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 6.74 (d, *J* = 10 Hz, 1H, 2-H), 6.75 (s, 1H, 8-H), 6.79 (d, *J* = 10 Hz, 1H, 3-H), 7.77 (s, 1H, 5-H); MS (100°C): *m/z* (%) = 270 (100, M^+), 255 (7), 227 (16), 184 (8). Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.01; H, 5.19.

6,8-Dimethoxy-1,4-phenanthrenequinone (52). Mp 252°C. IR: ν = 1655 cm^{-1} (C=O), 1645, 1615 (C=C), 1610, 1580, 1405, 1305, 1260, 1155, 850; UV: λ_{max} (lg ε) = 230 nm (4.578), 253 sh (4.024), 299 (4.175), 307 (4.214), 378 (3.429), 503 (3.334); ^{1}H NMR (250 MHz): δ = 4.00 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 6.63 (d, *J* = 2 Hz, 1H, 7-H), 6.93 (d, *J* = 9 Hz, 1H, 2-H), 6.95 (d, *J* = 9 Hz, 1H, 3-H), 8.01 (d, *J* = 9 Hz, 1H, 10-H), 8.60 (dd, $J_{9,10}$ = 9 Hz, $J_{5,9}$ = 1 Hz, 1H, 9-H), 8.68 (dd, $J_{5,8}$ = 2 Hz, $J_{5,9}$ = 1 Hz, 1H, 5-H); ^{13}C NMR: δ = 55.61 (OCH_3), 55.78

(OCH_3), 97.46 (C-5), 100.07 (C-7), 119.15 (C-10), 124.84 (C-10a), 125.64 (C-8a), 129.10 (C-9), 132.50 (C-4b), 133.20 (C-4a), 135.57 (C-2), 140.88 (C-3), 156.36 (C-8), 162.35 (C-6), 186.20 (C-1); MS (110°C): *m/z* (%) = 268 (100, M^+), 225 (59), 195 (58), 182 (47), 169 (40), 154 (44), 141 (42), 126 (45). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.69; H, 4.30.

7,8-Dimethoxy-1,4-phenanthrenequinone (54), 9,10-dihydro-7,8-dimethoxy-1,4-phenanthrenequinone (79) and 9-hydroxy-7,8-dimethoxy-1,4-phenanthrenequinone (68)

Data for 54. Mp 198°C (ref.[18]: 196-198°C). IR: ν = 1650 cm^{-1} (C=O), 1600 (C=C), 1585, 1475, 1305, 1275, 1075, 1000, 840; UV: λ_{max} (lg ε) = 233 nm (4.574), 252 sh (4.153), 306 (4.156), 387 (3.985), 450 (3.178); ^{1}H NMR: δ = 4.00 (s, 3H, OCH_3), 4.04 (s, 3H, OCH_3), 6.90 (s, 2H, 2-, 3-H), 7.48 (d, *J* = 10 Hz, 1H, 6-H), 8.09 (d, *J* = 9 Hz, 1H, 10-H), 8.49 (d, *J* = 9 Hz, 1H, 9-H), 9.30 (d, *J* = 10 Hz, 1H, 5-H); ^{13}C NMR: δ = 56.53 (OCH_3), 61.31 (OCH_3), 118.31 (C-6), 121.98 (C-10), 124.79 (C-5), 125.09 (C-10a), 127.17 (C-8a), 128.07 (C-9), 130.60 (C-4b), 132.54 (C-4a), 135.81 (C-2), 140.14 (C-3), 142.56 (C-8), 150,31 (C-7), 185.61 (C-4), 188.18 (C-1).

Data for 79. Mp 143°C. IR: ν = 1655 cm^{-1} (C=O), 1645 (C=O), 1595 (C=C), 1490, 1275, 1065, 850; UV: λ_{max} (lg ε) = 216 nm (4.358), 252 (4.283), 308 (3.681), 459 (3.536); ^{1}H NMR: δ = 2.75 (m_c, 4H, 9-, 10-H), 3.79 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.74 (s, 2H, 2-,3-H), 6.83 (d, *J* = 8 Hz, 1H, 5-H); MS (100°C): *m/z* (%) = 270 (100, M^+), 255 (25), 239 (21), 227 (20), 212 (17). Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.96, H 5.11.

Data for 68. Mp 204°C. IR: ν = 3225 cm^{-1} (OH), 1665 (C=O), 1650, 1610 (C=C), 1605, 1555, 1510, 1470, 1300, 1280, 1100, 1065, 850; UV: λ_{max} (lg ε) = 226 nm (4.446), 250 (4.339), 316 (4.275), 386 (3.315), 490 (3.320); ^{1}H NMR (300 MHz): δ = 4.05 (s, 3H, OCH_3), 4.12 (s, 3H, OCH_3), 6.85 (s, 2H, 2-, 3-H), 7.46 (s, 1H, 10-H), 7.49 (d, *J* = 10 Hz, 1H, 6H), 9.50 (d, *J* = 10 Hz, 1H, 5H), 10.76 (s, 1H, OH); MS (120°C): *m/z* (%) = 284 (100, M^+), 269 (65), 241 (47), 213 (-14). Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.25. Found: C, 67.54; H, 4.69.

5,6,7-Trimethoxy-1,4-phenanthrenequinone (65). mp 139°C. IR: ν = 1675 cm^{-1} (C=O), 1665 (C=O), 1470, 1420, 1275, 1085, 835; UV: λ_{max} (lg ε) = 210 nm sh (4.127), 241 (4.529),

286 (4.074), 301 (4.055), 392 (3.674); ^{1}H NMR: δ = 3.96 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 6.79 (d, *J* = 10 Hz, 1H, 2-H), 6.94 (s, 1H, 8-H), 7.04 (d, *J* = 10 Hz, 1H, 3-H), 7.85 (d, *J* = 9 Hz, 1H, 10-H), 7.95 (d, *J* = 9 Hz, 2H, 9-H); ^{13}C NMR: δ = 56.08 (OCH_3), 60.87 (OCH_3), 61.13 (OCH_3), 102.73 (C-8), 120.10 (C-10a), 121.36 (C-10), 130.72 (C-8a), 131.68 (C-9), 133.27 (C-4b), 134.64 (C-4a), 135.09 (C-2), 140.23 (C-3), 143.72 (C-7), 150.23 (C-6), 155.62 (C-5), 184.61 (C-4), 186.48 (C-1); MS (100°C): *m/z* (%) = 298 (100, M^+), 283 (47), 255 (87), 225 (80), 212 (49), 184 (41), 169 (80), 141 (49). Anal. Calcd for $C_{17}H_{14}O_5$: + 0.2 $CHCl_3$ C, 65.12; H, 4.44. Found: C, 65.35; H, 4.44.

6,7,8-Trimethoxy-1,4-phenanthrenequinone (67) and 9-hydroxy-6,7,8-trimethoxy-1,4-phenanthrenequinone (75)

Data for 62. Mp 139°C. IR: ν = 1665 cm^{-1} (C=O), 1650, 1610 (C=C), 1585, 1410, 1310, 1265, 1110, 1075, 1040, 855; UV: λ_{max} (lg ε) = 239 nm (6.616), 290 (4.055), 301 (4.046), 401 (3.608); ^{1}H NMR: δ = 4.03 (s, 3H, OCH_3), 4.06 (s, 3H, OCH_3), 4.09 (s, 3H, OCH_3), 6.91 (s, 2H, 2-, 3-H), 7.97 (d, *J* = 9 Hz, 1H, 10-H), 8.39 (d, *J* = 9 Hz, 1H, 9-H), 8.89 (s, 1H, 5-H); ^{13}C NMR: δ = 56.05 (OCH_3), 61.09 (OCH_3), 61.65 (OCH_3), 102.40 (C-5), 120.04 (C-10), 125.08 (C-10a), 127.66 (C-8a), 128.42 (C-9), 128.75 (C-4b), 131.98 (C-4a), 135.76 (C-2), 140.49. (C-3), 142.63 (C-8), 147.43 (C-7), 156.68 (C-6), 185.81 (C-4), 188.23 (C-1); MS (50°C): *m/z* (%) = 198 (100, M^+), 289 (82), 255 (82), 240 (77), 223 (44), 212 (59), 197 (42), 184 (47), 169 (69). Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.29; H, 4.56.

Data for 97. Mp 217°C. IR: ν = 1660 cm^{-1} (C=O), 1645, 1610 (C=C), 1590, 1480, 1305, 1270, 1110. UV: λ_{max} (lg ε) = 225 nm (4.399), 246 (4.571), 301 sh (4.185), 311 (4.232), 390 (3.497), 486 (3.378); ^{1}H NMR: δ = 4.00 (s, 3H, OCH_3), 4.07 (s, 3H, OCH_3), 4.17 (s, 3H, OCH_3), 6.82 (s, 2H, 2-, 3-H), 7.35 (s, 1H, 10-H), 9.08 (s, 1H, 5-H), 10.51 (s, 1H, OH); MS (120°C): *m/z* (%) = 314 (100, M^+), 299 (47), 271 (36), 256 (16), 185 (19). Anal. Calcd for $C_{17}H_{14}O_{26}$: C, 64.97; H, 4.49. Found: C, 64.76; H, 4.46.

6-Benzyloxy-7-methoxy-1,4-phenanthrenequinone (53). Yield 772 mg (66%). mp 153°C. IR: ν = 1655 cm^{-1} (C=O), 1615, (C=C), 1510, 1485, 1070, 840; UV: λ_{max} (lg ε) = 215 nm sh (4.248), 246 (4.689), 273 sh (4.12-3), 285 (4.040), 301 sh (3.875), 430 (3.738); ^{1}H NMR: δ = 4.11 (s, 3H, OCH_3), 5.32 (s, 2H, CH_2), 6.91 (d, *J* = 10 Hz, 1H, 2-H), 6.92 (d, *J* = 10 Hz, 1H, 3-H), 7.17 (s, 1H, 8-H), 7.42 (m_c, 5H, C_6H_5), 7.94 (d, *J* = 8 Hz, 1H, 10-H), 8.02 (d, *J* = 8 Hz,

1H, 9-H), 9.10 (s, 1H, 5-H); MS (35°C): *m/z* (%) = 344 (15, M^+), 242 (16), 91 (100, Bzl). Anal. Calcd for $C_{22}H_{16}O_4$ + 2 H_2O: C, 69.47; H, 5.30. Found: C, 69.95; H, 5.12.

7-Benzyloxy-8-methoxy-1,4-phenanthrenequinone (56). Yield: 397 mg (34%); mp 168°C. IR: ν = 1650 cm^{-1} (C=O), 1609 (C=C), 1587, 1479, 1311, 1272, 1232, 1114, 1040; UV: λ_{max} (lg ε) = 234 nm (4.642), 255 sh (4.162), 304 (4.204), 387 (3.531), 460 (3.210); ^{1}H NMR (400 MHz): δ = 4.04 (s, 3H, OCH_3), 5.33 (s, 2H, CH_2), 6.93 (s, 2H, 2-, 3-H), 7.41 (m_c, 5H, C_6H_5), 7.53 (d, *J* = 10 Hz, 1H, 6-H), 8.15 (d, *J* = 9 Hz, 1H, 10-H), 8.54 (d, *J* = 9 Hz, 1H, 9-H), 9.28 (d, *J* = 10 Hz, 1H, 5-H); MS (120°C): *m/z* (%) = 344 (30, M^+), 253 (16, M - Bzl), 225 (17), 91 (100, Bzl). Anal. Calcd for $C_{22}H_{16}O_4$:C, 76.73; H, 4.68. Found: C,76.63; H, 4.51.

8-Benzyloxy-7-methoxy-1,4-phenanthrenequinone (55). Yield: 337 mg (29%), mp 156°C. IR: ν = 1650 cm^{-1} (C=O), 1605 (C=C), 1590, 1475, 1305, 1270, 1220, 1110, 1080, 980, 840; UV: λ_{max} (lg ε) = 234 nm (4.625), 255 sh (4.154), 305 (4.199), 390 (3.545), 434 (3.236); ^{1}H NMR (300 MHz): δ = 4.07 (s, 3H, OCH_3), 5.18 (s, 2H, CH_2), 6.91 (d, *J* = 10 Hz, 1H, 2-H), 6.93 (d, *J* = 10 Hz, 1H, 3-H), 7.42 (m_c, 5H, C_6H_5), 7.54 (d, *J* = 10 Hz, 1H, 6-H), 8.06 (d, *J* = 9 Hz, 1H, 10-H), 8.47 (dd, $J_{9,10}$ = 9 Hz, $J_{5,9}$ = 1 Hz, 1H, 9-H) 9.35 (dd, $J_{5,6}$ = 10 Hz, $J_{5,9}$ = 1Hz, 1H, 5-H); MS(70°C): *m/z* (%) = 344 (19, M^+), 253 (28, M - Bzl), 225 (14), 91 (100, Bzl), 84 (28). Anal. Calcd for $C_{22}H_{16}O_4$ (344.37) Ber. C 76.73 H 4.68. Found: C, 76.55; H, 4.47.

9,10-Dihydro-5,7-dimethoxy-1,4-phenanthrenequinone (77). Yield: 348 mg (38%), mp 110°C. IR: ν = 1645 cm^{-1} (C=O), 1602 (C=C), 1558, 1352, 1303, 1281, 1231, 1155, 1102; UV: λ_{max} (lg ε) = 221 nm (4.390), 249 (4.132), 287 (3.990), 423 (3.519); ^{1}H NMR (400 MHz): δ = 2.63 (m, 4H, 9-, 10-H), 3.78 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.41 (d, *J* = 2 Hz, 1H, 8-H), 6.43 (d, *J* = 2 Hz, 1H, 6-H), 6.70 (d, *J* = 10 Hz, 1H, 2-H), 6.80 (d, *J* = 10 Hz, 1H, 3-H); MS (75°C): *m/z* (%) = 270 (100, M^+), 153 (17), 227 (21), 188 (23). Anal. Calcd for $C_{16}H_{14}O_6$ (270.29) C 71.10 H 5.22. Found: C 71.62 H 5.23.

3-Methoxy-1,4-phenanthrenequinone (1) and 2-methoxy-1,4-phenanthrenequinone (42)

Data for 1. Mp 170°C (ref.[1)]: 170-172 °C). IR: ν = 1671 cm^{-1} (C=O), 1647 (C=O), 1624 (C=C), 1457, 1334, 1320, 1250, 1240, 1195, 1179 1102, 834; UV: λ_{max} (lg ε) = 227 nm (4.539), 275 sh (4.322), 281 (4.353), 313 (3.846), 369 (3.534); ^{1}H NMR (250 MHz): δ = 3.92 (s, 3H, OCH_3), 6.11 (s, 1H, 2H), 7.60 (ddd, $J_{6,7}$ = 7 Hz, $J_{7,8}$ = 8 Hz, $J_{5,7}$ = 1 Hz, 1H, 7-H), 7.70

(ddd, $J_{5,6}$ = 9 Hz, $J_{6,7}$ = 7 Hz, $J_{6,8}$ = 2 Hz, 1H, 6-H), 7.86 (ddd, $J_{7,8}$ = 8 Hz, $J_{6,8}$ = 2 Hz, $J_{5,8}$ = 1 Hz, 1H, 8-H), 8.14 (d, J =9 Hz, 1H, 9-H), 8.15 (d, J = 9 Hz, 1H, 10-H), 9.50 (ddd, $J_{5,6}$ = 9 Hz, $J_{5,7}$ = 1Hz, $J_{5,8}$ = 1 Hz, 1H, 5-H); ^{13}C NMR: δ = 56.58 (OCH_3), 107.10 (C-2), 121.73 (C-10), 125.96 (C-10a), 127.49 (C-5), 128.34 (C-7), 128.71 (C-6), 129.90 (C-8a), 130.23 (C-8), 132.50 (C-4b), 135.57 (C-9), 136.14 (C-4a), 160.70 (C-3), 182.26 (C-4), 185 14 (C-1); MS (80°C): *m/z* (%) = 238 (100, M^+), 223 (40), 209 (14), 181 (15), 167 (14), 152 (26), 139 (91), 126 (25). Anal. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.62; H, 4.23.

Data for 42. Mp 135°C. IR: ν = 1680 cm^{-1} (C=O), 1645 (C=O), 1620 (C=C), 1235, 1065, 775; UV: λ_{max} (lg ε) = 223 nm (4.598), 281 (4.450), 312 (3.873), 372 (3.345), 396 sh (3.183); ^{1}H NMR (400 MHz): δ = 3.92 (s, 3H, OCH_3), 6.17 (s, 1H, 3-H), 7.64 (ddd, $J_{6,7}$ = 8 Hz, $J_{7,8}$ =8 Hz, $J_{5,7}$ = 1 Hz, 1H, 7-H), 7.72 (ddd, $J_{5,6}$ = 9 Hz, $J_{6,7}$ = 8 Hz, $J_{6,8}$ = 2 Hz, 1H, 6-H), 7.89 (ddd, $J_{7,8}$ =8 Hz, $J_{5,8}$ = 1 Hz, $J_{6,8}$ = 2 Hz, 1H, 8-H), 8.13 (d, J = 9 Hz, 1H, 10-H), 8.21 (d, J = 9 Hz, 1H, 9-H), 9.61 (ddd, $J_{5,6}$ = 9 Hz, $J_{5,7}$ = 1 Hz, $J_{5,8}$ = 1 Hz, 1H, 5-H); ^{13}C NMR: δ = 56.28 (OCH_3), 111.40 (C-3), 121.80 (C-10), 127.17 (C-10a), 128.36 (C-5), 128.50 (C-7), 128.62 (C-6), 128.70 (C-8a), 129.88 (C-8), 131.14 (C-4b), 134.31 (C-9), 136.84 (C-4a), 158.15 (C-2), 181.00 (C-4), 188.12 (C-1); MS (100°C): *m/z* (%) = 238 (100, M^+), 210 (24), 152 (25), 139 (67), 126 (26). Anal. Calcd for $C_{15}H_{10}O_3$: + 0.03 CCl_4 C, 74.33; H, 4.15. Found: C, 74.29; H, 4.20.

3,6-Dimethoxy-1,4-phenanthrenequinone (47). Yield: 91 mg (10%), mp 215 °C. IR: ν = 1670 cm^{-1} (C=O), 1645 (C=O), 1520 (C=C), 1590, 1460, 1240, 1220, 1090, 1025, 840; UV: λ_{max} (lg ε) = 237 nm (4.584), 286 (4.236), 307 sh (3.801), 392 (3.467), 452 (3.424); ^{1}H NMR: δ = 3.93 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 6.12 (s, 1H, 2-H), 7.26 (dd, $J_{7,8}$ = 10 Hz, $J_{5,7}$ = 2 Hz, 1H, 7-H), 7.77 (d, J = 10 Hz, 1H, 8-H), 8.06 (s, 2H, 9-, 10-H), 9.03 (d, J = 2 Hz, 1H, 5-H); ^{13}H NMR: δ = 55.49 (OCH_3), 56.49 (OCH_3), 105.38 (C-5), 107.22 (C-2), 119.87 (C-10), 121.52 (C-7), 124.36 (C-10a), 130.14 (C-8), 132.06 (C-8a), 132.18 (C-4b), 133.17 (C-4a), 135.30 (C-9), 160.85 (C-3), 161.68 (C-6), 182.46 (C-4), 185.29 (C-1); MS (90°C): *m/z* (%) = 268 (100, M^+), 253 (32), 238 (12), 197 (32), 169 (76), 139 (30), 126 (51). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.08; H, 4.16.

3,7-Dimethoxy-1,4-phenanthrenequinone (48). mp 205°C. IR: ν = 1670 cm^{-1} (C=O), 1645 (C=O), 1615 (C=C), 1485, 1250, 1240, 1200, 1005, 840; UV: λ_{max} (lg ε) = 236 nm (4.606),

252 sh (4.184), 298 (4.288), 315 (3.787), 386 (3.661); ^{1}H NMR: δ = 3.94 (s, 1H, OCH_3), 3.94 (s, 1H, OCH_3), 6.09 (s, 1H, 2-H), 7.13 (d, *J* = 3 Hz, 1H, 8-H), 7.35 (dd, $J_{5,6}$ = 10 Hz, $J_{6,8}$ = 3 Hz, 1H, 6-H), 7.99 (d, *J* = 9 Hz, 1H, 10-H), 8.14 (d, *J* = 9 Hz, 1H, 9-H), 9.41 (d, *J* = 10 Hz, 1H, 5-H); ^{13}C NMR: δ = 55.46 (OCH_3), 56.54 (OCH_3), 106.86 (C-8), 107.24 (C-2), 122.58 (C-6), 122.78 (C-10), 125.30 (C-10a), 126.29 (C-8a), 129.26 (C-5), 130.65 (C-4b), 133.98 (C-9), 138.39 (C-4a), 159.27 (C-7), 160.70 (C-3), 182.55 (C-4), 185.24 (C-1); MS (170°C): *m/z* (%) = 268 (100, M^+), 253 (24), 238 (15), 197 (33), 169 (63), 139 (15), 126 (31).

3,8-Dimethoxy-1,4-phenanthrenequinone (49). Yield: 172 mg (19%). mp 240-241°C. IR: ν = 1670 cm^{-1} (C=O), 1645 (C=O), 1620 (C=C), 1585, 1460, 1260, 1220, 1180, 1015, 855; UV: λ_{max} (lg ε) = 224 nm (4.536), 292 (4.398), 320 sh (3.613), 373 (3.359), 460 (3.136); ^{1}H NMR: δ = 3.94 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 6.13 (s, 1H, 2-H), 6.94 (d, *J* = 8 Hz, 1H, 7-H), 7.62 (t, *J* = 8 Hz, 1H, 6-H), 8.15 (d, *J* = 9 Hz, 1H, 10-H), 8.69 (d, *J* = 9 Hz, 1H, 9-H), 9.08 (d, *J* = 8 Hz, 1H, 5-H); ^{13}C NMR: δ = 55.75 (OCH_3), 56.49 (OCH_3), 106.29 (C-7), 107.14 (C-2), 119.43 (C-5), 121.03 (C-10), 125.66 (C-10a), 128.72 (C-8a), 129.63 (C-9), 130.56 (C-6), 131.15 (C-4b), 132.98 (C-4a), 155.44 (C-8), 161.01 (C-3), 182.21 (C-4), 185.27 (C-1); MS (100°C): *m/z* (%) = 168 (100, M^+), 253 (57), 238 (45), 197 (49), 169 (67), 139 (51), 126 (52). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.73; H, 4.49.

3,5,8-Trimethoxy-1,4-phenanthrenequinone (61) and 9-hydroxy-3,5,8-trimethoxy-1,4-phenanthrenequinone (73)

Data for 61. Mp 219°C. IR: ν = 1670 cm^{-1} (C=O), 1645 (C=O), 1610 (C=C), 1590, 1465, 1260, 1230, 1180, 1095, 1020, 845; UV: λ_{max} (lg ε) = 215 nm (4.513), 235 sh (4.358), 277 (4.198), 308 (4.246), 351 sh (3.507), 490 (2.967); ^{1}H NMR: δ = 3.91 (s, 3H, OCH_3), 3.93 (OCH_3), 3.96 (s, 3H, OCH_3), 6.01 (s, 1H, 2-H), 6.89 (d, *J* = 9 Hz, 1H, 7-H), 6.96 (d, *J* = 9 Hz, 1H, 6-H), 8.06 (d, *J* = 9 Hz, 1H, 9-H), 8.48 (d, *J* = 9 Hz, 1H, 10-H); ^{13}C NMR: δ = 56.00 (OCH_3), 56.16 (OCH_3), 56.48 (OCH_3), 106.17 (C-2), 107.15 (C-6), 109.39 (C-7), 121.14 (C-10), 121.68 (C-10a), 127.73 (C-9), 129.29 (C-8a), 131.89 (C-4b), 132.93 (C-4a), 149.57 (C-8), 150.61 (C-5), 163.18 (C-3), 181.38 (C-4), 184.47 (C-1); MS (100°C): *m/z* (%) = 298 (100, M^+), 283 (96), 255 (60), 225 (45), 199 (36), 169 (38), 141 (38). Anal. Calcd for $C_{17}H_{14}O6$: C, 68.45; H, 4.73. Found: C, 68.38; H, 4.70.

Data for 73. Mp 231°C. IR: ν = 1670 cm^{-1} (C=O), 1645 (C=O), 1615 (C=C), 1510, 1400,

1260, 1195, 1175; UV: λ_{max} (lg ε) = 216 nm (4.433), 265 sh (4.057), 287 (4.338), 315 (4.206), 345 sh (3.670), 366 (3636), 487 (3.200); ^{1}H NMR: δ = 3.91 (s, 6H, OCH_3), 4.05 (s, 3H, OCH_3), 5.97 (s, 1H, 2-H), 6.92 (s, 2H, 6-, 7-H), 7.42 (s, 1H, 10-H), 10.22 (s, 1H, OH); MS (120°C): *m/z* (%) = 314 (100, M^+), 299 (58), 297 (24), 271 (30), 243 (24). Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.97; H, 4.49. Found: C, 64.75; H, 4.46.

3,6,7-Trimethoxy-1,4-phenanthrenequinone (72). Yield: 119 mg (12%). mp 250°C. IR: ν = 1670 cm^{-1} (C=O), 1640 (C=O), 1620 (C=C), 1485, 1260, 1235, 1090, 1010, 835; UV: λ_{max} (lg ε) = 244 nm (4.372), 262 sh (4.038), 287 (3.929), 295 (3.898), 320 (3.556), 424 (3.639); ^{1}H NMR: δ = 3.93 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 6.09 (s, 1H, 2-H), 7.10 (s, 1H, 8-H), 8.00 (s, 2H, 9-, 10-H), 9.06 (s, 1H, 5-H); ^{13}C NMR: δ = 55.87 (OCH_3), 56.04 (OCH_3), 56.43 (OCH_3), 106.03 (C-5), 106.75 (C-8), 107.32 (C-2), 120.72 (C-10), 124.18 (C-10a), 126.60 (C-8a), 131.04 (C-4b), 133.39 (C-9), 133.45 (C-4a), 151.08 (C-7), 153.34 (C-6), 160.65 (C-3), 182.71 (C-4), 185.24 (C-1); MS (120°C): *m/z* (%) = 298 (100, M^+), 283 (34), 255 (25), 227 (58), 199 (68), 169 (20), 155 (27). Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.42; H, 4.45.

3,6,8-Trimethoxy-1,4-phenanthrenequinone (63) and 2,6,8-trimethoxy-1,4-phenanthrenequinone (58)

Data for 63. Mp 228°C. IR: ν = 1660 cm^{-1} (C=O), 1645 (C=O), 1625 (C=C), 1255, 1240, 1230, 1205, 1180, 845; UV: λ_{max} (lg ε) = 231 nm (4.609), 294 (4.308), 388 (3.388), 495 (3.408); ^{1}H NMR (250 MHz): δ = 3.94 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 6.13 (s, 1H, 2-H), 6.61 (d, *J* = 2 Hz, 1H, 7-H), 8.03 (d, *J* = 9 Hz, 1H, 10-H), 8.58 (d, *J* = 9 Hz, 1H, 9-H), 8.67 (d, *J* = 2 Hz, 1H, 5-H); ^{13}C NMR: δ = 55.55 (OCH_3), 55.77 (OCH_3), 56.49 (OCH_3), 97.38 (C-5), 99.86 (C-7), 107.14 (C-2), 119.11 (C-10), 123.80 (C-10a), 125.40 (C-8a), 129.72 (C-9), 132.72 (C-4b), 133.66 (C-4a), 156.53 (C-8), 160.96 (C-3), 162.60 (C-6), 182.38 (C-4), 185.47 (C-1); MS (100°C): *m/z* (%) = 298 (100, M^+), 283 (17), 255 (14), 227 (25), 199 (37). Anal. Calcd for $C_{17}H_{14}O_5$ + 0.5 H_2O C, 66.45; H, 4.92. Found: C, 66.55; H, 4.53.

Data for 58. Mp 253°C. IR: ν = 1665 cm^{-1} (C=O), 1645 (C=O), 1630 (C=C), 1260, 1235, 1210; UV: λ_{max} (lg ε) = 229 nm (4.348), 299 (4.166), 385 (2.958), 520 (3.113), 630 (2.812); ^{1}H NMR (250 MHz): δ = 3.91 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 6.12

(s, 1H, 3-H), 6.61 (d, *J* = 2 Hz, 1H, 7-H), 8.04 (d, *J* = 9 Hz, 1H, 10-H), 8.52 (d, *J* = 9 Hz, 1H, 9-H), 8.70 (d, *J* = 2 Hz, 1H, 5-H); ^{13}C NMR: δ = 55.61 (OCH_3), 55.75 (OCH_3), 56.18 (OCH_3), 97.86 (C-5), 100.15 (C-7), 111.81 (C-3), 119.30 (C-10), 124.89 (C-10), 126.10 (C-8a), 128.33 (C-9), 132.31 (C-4b), 132.49 (C-4a), 156.25 (C-8), 158.10 (C-2), 161.96 (C-6), 180.98 (C-4), 188.36. (C-1); MS: *m/z* (%) = 298 (100, M^+), 227 (50), 199 (62), 152 (32), 141 (46), 126 (32), 113 (42), 69 (42). Anal. Calcd for $C_{17}H_{14}O_5$:C, 68.45; H, 4.73. Found: C, 67.98 H 4.56.

3,7,8-Trimethoxy-1,4-phenanthrenequinone (64) and 2,7,8-trimethoxy-1,4-phenanthrenequinone (59)

Data for 79. Mp 227°C. IR: ν = 1670 cm^{-1} (C=O), 1645 (C=O), 1620 (C=C), 1605, 1475, 1275, 1215, 1175, 1090, 840; UV: λ_{max} (lg ε) = 231 nm (4.577), 272 sh (4.129), 301 (4.312), 330 sh (3.692), 382 (3.530), 450 nm (3.053); ^{1}H NMR: δ = 3.92 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 6.09 (s, 1H, 2-H), 7.49 (d, *J* = 10 Hz, 1H, 6-H), 8.12 (d, *J* = 8 Hz, 1H, 10-H), 8.48 (d, *J* = 8 Hz, 1H, 9-H), 9.27 (d, *J* = 10 Hz, 1H, 5-H); ^{13}C NMR: δ = 56.40 (OCH_3), 56.46 (OCH_3), 61.32 (OCH_3), 107.13 (C-2), 118.48 (C-6), 121.98 (C-8), 124.43 (C-5), 125.24 (C-10a), 126.14 (C-8a), 128.64 (C-9), 131.02 (C-4b), 132.33 (C-4a), 142.59 (C-8), 150.06 (C-7), 160.60 (C-3), 182.55 (C-4), 185.24 (C-1); MS (120°C): *m/z* (%) = 298 (100, M^+), 283 (79), 255 (70), 227 (45), 199 (27), 171 (48), 141 (43). Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.35; H, 4.53.

Data for 80. Mp 166°C. IR: ν = 1650 cm^{-1} (C=O), 1640, 1630 (C=C), 1600, 1480, 1280, 1240, 1120, 1075; UV: λ_{max} (lg ε) = 232 nm (4.442), 250 sh (4.141), 292 sh (4.144), 303 (4.189), 328 sh (3.671), 385 (3.342), 453 (2.974); ^{1}H NMR: δ = 3.90 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 4.04 (s, 3H, OCH_3), 6.10 (s, 1H, 3-H), 7.46 (d, *J* = 9 Hz, 1-H, 6-H), 8.14 (d, *J* = 9 Hz, 1H, 10-H), 8.44 (d, *J* = 9 Hz, 1H, 9-H), 9.36 (d, *J* = 9 Hz, 1H, 5-H); ^{13}C NMR: δ = 56.23 (OCH_3), 56.48 (OCH_3), 61.32 (OCH_3), 111.12 (C-3), 117.97 (C-6), 122.05 (C-10), 125.19 (C-10a), 125.47 (C-5), 127.27 (C-9), 127.40 (C-8a), 129.56 (C-4b), 132.91 (C-4a), 142.37 (C-8), 150.37 (C-7), 158.31 (C-2), 180.88 (C-4), 188.38 (C-1); MS: *m/z* (%) = 298 (5, M^+), 196 (56), 138 (100), 110 (55), 108 (68), 69 (84). Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.29; H, 4.70.

3,5,6,7-Tetramethoxy-1,4-phenanthrenequinone (71). Yield: 187 mg (17%), mp 175°C. IR: ν = 1680 cm^{-1} (C=O), 1640 (C=O), 1615 (C=C), 1605, 1470, 1425, 1275, 1200, 1165, 1125,

1090; UV: λ_{max} (lg ε) = 244 nm (4.624), 300 (4.324), 391 (3.590); ^{1}H NMR: δ = 3.93 (s, 6H, OCH_3), 4.00 (s, 3H, OCH_3), 4.07 (s, 3H, OCH_3), 6.01 (s, 1H, 2-H), 6.94 (s, 1H, 8-H), 7.89 (d, *J* = 9 Hz, 1H, 10-H), 8.03 (d, *J* = 9 Hz, 1H, 9-H); ^{13}C NMR: δ = 56.10 (OCH_3), 56.55 (OCH_3), 60.82 (OCH_3), 61.05 (OCH_3), 102.75 (C-8), 106.27 (C-2), 120.23 (C-10a), 121.35 (C-10), 131.19 (C-8a), 132.10 (C-9), 134.31 (C-4b), 143.78 (C-4a), 150.04 (C-5), 155.36 (C-8), 162.93 (C-3, C-7), 181.80 (C-4), 184.41 (C-1); MS (130°C): *m/z* (%) = 328 (100, M^+), 313 (67), 285 (78), 270 (29), 255 (65), 199 (58). Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 65.26; H 4.85.

3,5,6,8-Tetramethoxy-1,4-phenanthrenequinone (72). Yield: 103 mg (9%). mp 200-201°C. IR: ν = 1675 cm^{-1} (C=O), 1650 (C=O), 1620 (C=C), 1605, 1465, 1260, 1210, 1175, 1085, 1010, 835; UV: λ_{max} (lg ε) = 234 nm (4.523), 303 (4.259), 370 sh (3.161), 505 (3.167); ^{1}H NMR: δ = 3.94 (s, 6H, OCH_3), 4.00 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 6.02 (s, 1H, 2-H), 6.77 (s, 1H, 7-H), 7.91 (d, *J* = 8 Hz, 1H, 10-H), 8.43 (d, *J* = 8 Hz, 1H, 9-H); ^{13}C NMR: δ = 56.16 (OCH_3), 56.56 (OCH_3), 57.25 (OCH_3), 60.53 (OCH_3), 98.45 (C-7), 106.16 (C-2), 118.81 (C-10), 124.26 (C-10a), 125.12 (C-8a), 127.96 (C-9), 130.78 (C-4b), 133.95 (C-4a), 138.87 (C-8), 152.04 (C-5), 152.36 (C-6), 163.28 (C-3), 181.34 (C-4), 184.64 (C-1). MS (125°C): *m/z* (%) = 328 (100, M+), 313 (99), 285 (96), 255 (47), 225 (27), 199 (26), 184 (19). Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 65.00; H, 4.82.

3,6,7,8-Tetramethoxy-1,4-phenanthrenequinone (74) and 2,6,7,8-tetramethoxy-1,4-phenanthrenequinone (70)

Yields: **74** 509 mg (46%); **70** 42 mg (4%).

Data for 74. mp 195°C. IR: ν = 1665 cm^{-1} (C=O), 1645 (C=O), 1620 (C=C), 1480, 1360, 1260, 1245, 1230, 1120, 1080; UV: λ_{max} (lg ε) = 212 nm sh (4.394), 240 (4.698), 289 (4.235), 297 (4.242), 322 (3.663); ^{1}H NMR: δ = 3.94 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 4.07 (s, 6H, OCH_3), 6.11 (s, 1H, 2-H), 8.01 (d, *J* = 9 Hz, 1H, 10-H), 8.45 (d, *J* = 9 Hz, 1H, 9-H), 8.88 (s, 1H, 5H); ^{13}C NMR: δ = 55.99 (OCH_3), 56.48 (OCH_3), 61.07 (OCH_3), 61.66 (OCH_3), 102.21 (C-5), 107.21 (C-2), 119.98 (C-10), 124.01 (C-10a), 127.87 (C-8a), 128.44 (C-4b), 129.04 (C-9), 132.46 (C-4a), 142.33 (C-8), 147.53 (C-7), 156.86 (C-6), 160.67 (C-3), 182.59 (C-4), 185.28 (C-1); MS (130°C): *m/z* (%) = 328 (100, M^+), 313 (76), 297 (13), 285 (76), 270 (62), 255 (38), 242 (41), 227 (42), 199 (56). Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 64.93; H, 4.65.

Data for 82. Mp 217°C. IR: ν = 1675 cm^{-1} (C=O), 1635 (C=O), 1620 (C=C), 1480, 1240, 1130, 1075; UV: λ_{max} (lg ε) = 238 nm (4.584), 298 (4.289), 320 sh (3.717), 405 (3.543). ^{1}H NMR: δ = 3.91 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 4.04 (s, 3H, OCH_3), 4.08 (s, 3H, OCH_3), 6.09 (s, 1H, 3-H), 8.05 (d, *J* = 9 Hz, 1H, 10-H), 8.38 (d, *J* = 9 Hz, 1H, 9-H), 8.93 (s, 1H, 5-H); ^{13}C NMR: δ = 56.01 (OCH_3), 56.15 (OCH_3), 61.04 (OCH_3), 61.88 (OCH_3), 102.82 (C-5), 111.39 (C-3), 120.12 (C-10), 125.22 (C-10a), 126.96 (C-8a), 127.55 (C-9), 129.28 (C-4b), 131.16 (C-4a), 142.29 (C-8), 147.39 (C-7), 156.38 (C-6), 158.41 (C-2), 186.44 (C-4), 189.89 (C-1); MS (100°C): *m/z* (%) = 313 (45), 285 (31), 270 (19), 199 (12). Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 65.43; H, 5.34.

9,10-Dihydro-3,5,7-trimethoxy-1,4-phenanthrenequinone (80). Yield: 377 mg (37%), mp 189°C. IR: ν = 1680 cm^{-1} (C=O), 1630 (C=C), 1600, 1560, 1285, 1230, 1195, 1135; UV: λ_{max} (lg ε) = 219 nm (4.389), 262 (4.191), 272 sh (4.121), 287 sh (4.012), 326 (3.655), 475 (3.443); ^{1}H NMR: δ = 2.62 (s, 4H, 9-, 10-H), 3.79 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 5.86 (s, 1H, 2-H), 6.64 (s, 2H, 6-, 8-H); ^{13}C NMR: δ = 20.50 (C-10), 28.90 (C-9), 55.44 (OCH_3), 55.87 (OCH_3), 56.22 (OCH_3), 97.71 (C-8), 105.80 (C-6), 105.81 (C-2), 112.20 (C-10a), 139.01 (C-8a), 140.55 (C-4b), 142.44 (C-4a), 158.52 (C-5), 159.87 (C-7), 162.22 (C-3), 180.33 (C-4), 185.83 (C-1); MS (100°C): *m/z* = 300 (100 %, M^+), 285 (35), 257 (99), 242 (59), 215 (63), 128 (71), 115 (93); Anal. Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37. Found: C, 68.07; H, 5.40.

2,3,7,8-Tetramethoxy-1,4-phenanthrenequinone (69) and 9,10-dihydro-2,3,7,8-tetramethoxy-1,4-phenanthrenequinone (81)

Yields: **69**, 263 mg (24%); **81**, 140 mg (12%).

Data for 87. Mp 157 °C. IR: ν = 1663 cm^{-1} (C=O),1632 (C=C), 1610, 1480, 1282, 1229, 1214, 1202, 1080, 1047, 1020; UV: λ_{max} (lg ε) = 231 nm (4.624), 256 sh (4.126), 305 (4.385), 354 (3.748); ^{1}H NMR (400 MHz): δ = 3.99 (s, 3H, OCH_3), 4.05 (s, 3H, OCH_3), 4.11 (s, 3H, OCH_3), 4.14 (s, 3H, OCH_3), 7.50 (d, *J* = 10 Hz, 1H, 6-H), 8.14 (d, *J* = 9 Hz, 1H, 10-H), 8.46 (d, *J* = 9 Hz, 1H, 9-H), 9.29 (d, *J* = 10 Hz, 1H, 5-H); MS (110°C): *m/z* (%) = 328 (100, M^+), 313 (44), 285 (19), 171 (15). Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 65.93; H, 4.65.

Data for 81. Mp 125°C. IR: ν = 1669 cm^{-1} (C=O), 1638 (C=C). 1592, 1490, 1275, 1228, 1149, 1071, 1040, 1004; UV: λ_{max} (lg ε) = 214 nm (4.449), 259 (4.267), 350 (3.831), 494 (3.336); ^{1}H NMR (400 MHz): δ = 2.74 (m_c, 4H, 9-, 10-H), 4.04 (s, 3H, OCH_3), 4.06 (s, 3H, OCH_3), 6.85 (d, *J* = 9 Hz, 1H, 6-H), 7.81 (d, *J* = 9 Hz, 1H, 5-H); MS (100°C): *m/z* (%) = 330 (100, M^+), 315 (42), 299 (27), 259 (16); Anal. Calcd for $C_{18}H_{18}O_6$: C, 65.45; H, 5.49. Found: C, 65.43; H, 5.34.

General procedure 4. Aromatization of 9,10-dihydro-1,4-phenanthrenchinones to 1,4-phenanthrenchinones

A mixture of the 9,10-dihydro-1,4-phenanthrenequinone (0,77 mmol) and palladium on charcoal (5 %, 43 mg) was heated to 180–190 °C for 2–3 h (TLC monitoring). The melt was dissolved in dichloromethane, filtered, purified by flash chromatography on silica gel and crystallized from dichloromethane/petroleum ether.

3,5,7-Trimethoxy-1,4-phenanthrenequinone (60). Yield from 230 mg (0.77 mmol) of **80**, 218 mg (95%). mp 167°C. IR: ν = 1685 cm^{-1} (C=O), 1645 (C=O), 1615 (C=C), 1280, 1245, 1210, 1165, 1095; UV: λ_{max} (lg ε) = 228 nm sh (4.392), 237 (4.415), 302 (4.308), 377 (3.368); ^{1}H NMR (300 MHz): δ = 3.93 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 6.01 (s, 1H, 2-H), 6.71 (d, *J* = 2 Hz, 1H, 6-H), 6.78 (d, *J* = 2 Hz, 1H, 8-H), 7.89 (d, *J* = 8 Hz, 1H, 10-H), 8.06 (d, *J* = 8 Hz, 1H, 9-H); ^{13}C NMR: δ = 55.59 (OCH_3), 55.98 (OCH_3), 56.47 (OCH_3), 99.32 (C-6), 102.07 (C-9), 106.29 (C-3), 117.04 (C-10a), 122.64 (C-10), 130.91 (C-8a), 132.26 (C-9), 132.91 (C-4b), 139.04 (C-4a), 158.29 (C-5), 160.93 (C-7), 163.01 (C-3), 181.76 (C-4), 184.56 (C-1); MS (100°C): *m/z* (%) = 298 (100, M^+), 283 (31), 227 (24), 199 (28). Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.29; H, 4.56.

7,8-Dimethoxy-1,4-phenanthrenequinone (54). Yield form 208 mg (0.77 mmol) of **90** (29 mg recovered): 167 mg (94%). Data see above.

5-Hydroxy-3,7-dimethoxy-1,4-phenanthrenequinone (3) (Denbinobin)

A solution of 3,5,7-trimethoxy-1,4-phenanthrenequinone **(60)** (50 mg, 0 17 mmol) in dichloromethane (1 mL) was treated with iodotrimethylsilane (0.4 mL). The mixture was stirred for 15 min (TLC monitoring) and quenched by addition of methanol (1 mL). The and the solvent removed under reduced pressure and the residue redissolved in diethyl ether (10

mL). The solution was washed with water (3 mL) and brine (3 mL), dried ($CaCl_2$), filtered and the solvent removed under reduced pressure. The residue was purified by preparative TLC chromatography on silica gel (1 mm, dichloromethane) and the phenolic product crystallized from dichloromethane/petroleum ether to yield denbinobin (**3**) 35 mg (72%), mp 215 °C (ref.[21] m.p. 215 °C). IR: ν = 1645 cm^{-1} (C=O), 1630 (C=O), 1615 (C=C), 1335, 1245, 1175, 1085; UV: λ_{max} (lg ε) = 237 nm (4.527), 310 (4.328), 401 (3.407); UV (Ethanol): λ_{max} (lg ε) = 240 nm (4.512), 312 (4.329), 403 (3.407); ^{1}H NMR (300 MHz): δ = 3.94 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 6.17 (s, 1H, 2-H), 6.83 (d, *J* = 3 Hz, 1H, 8-H), 6.94 (d, *J* = 3 Hz, 1H, 6-H), 8.08 (d, *J* = 9 Hz, 1H, 10-H), 8.14 (d, *J* = 9 Hz, 1H, 9-H), 11.00 (s, 1H, OH), MS (120°C): *m/z* (%) = 284 (100, M^+), 213 (63), 185 (34).

9,10-Dihydro-5-hydroxy-3,7-dimethoxy-1,4-phenanthrenequinone (94). 9,10-Dihydro-3,5,7-trimethoxy-1,4-phenanthrenequinone (**80**) (51 mg, 0.17 mmol) were treated with iodotrimethylsilane as described for **3** to yield the phenolic dihydro-1,4-phenanthrenequinone **94** (30 mg, 62%), mp 172°C. IR: ν = 1645 cm^{-1} (C=O), 1615 (C=C), 1555, 1430, 1310, 1240, 1220, 1205, 1130; UV: λ_{max} (lg ε) = 221 nm (4.380), 259 (4.140), 269 sh (4.089), 283 sh (4.016), 314 (3.822), 476 (3.363); ^{1}H NMR (400 MHz): δ = 2.67 (s, 4H, 9-, 10-H), 3.81 (s, 3H, OCH_3), 5.99 (s, 1H, 2-H), 6.41 (d, *J* = 3 Hz, 1H, 8-H), 6.46 (d, *J* = 3 Hz, 1H, 6-H), 8.85 (s, 1H, OH); MS (120°C): *m/z* (%) = 286 (100, M^+), 271 (41), 243 (49). Anal. Calcd for $C_{16}H_{14}O_5$ (286.29) + 0.5 H_2O C, 65.08; H, 5.12. Found: C, 65.31; H, 4.84.

Thiele-Winter reaction with 1,4-phenanthrenequinones, saponification and methylation, General procedure 4

A solution of 1,4-phenanthrenequinone (0.15 mmol) in acetic anhydride (4 mL) was treated with perchloric acid (0.15 mL). The reaction was quenched after 15 min by addition of ice-water (30 g). The mixture was stirred for 1 h to hydrolyze the anhydride and then extracted with dichloromethane (10 mL). The organic phase was washed with water (5 mL) and brine (5 mL), dried ($CaCl_2$), filtered and the solvent removed under reduced pressure. The residue was dissolved in methanol (1 mL) and saponified by addition of 1N NaOMe (0.6 mL). After 15 min the solution was acidified by addition of 1N HCl (1 mL). The suspension was extracted with dichloromethane, the organic phase was dried ($CaCl_2$), filtered and the solvent removed under reduced pressure. The residue was purified by preparative TLC

chromatography on silica gel and the products crystallized from dichloromethane /petroleum ether. Yields and mp see Scheme 4.

2-Methoxy-1,4-phenanthrenequinone (41) and 3-methoxy-1,4-phenanthrenequinone (1). 1,4-Phenanthreneqionone (36 mg, 0.15 mmol) was converted to the methoxy-1,4-phenanthreneqionones 41 and 1 in (31%) (39%) yield, respectively.

2,7,8-Trimethoxy-1,4-phenanthrenequinone (59) and 3,7,8-Trimethoxy-1,4-phenanthrenequinone (64). According to the general procedure VI, 8-benzyloxy-7-methoxy-1,4-phenanthrenequinone (**55**) (52 mg, 0.15 mmol) was converted to the quinones **59** and **64** in 11% and 18% yield, respectively. With one equivalent of diazomethane solution the monophenols **95** and **96** were isolated (9 and 16 % yield, respectively)

8-Hydroxy-2,7-dimethoxy-1,4-phenanthrenequinone (95). Mp 249°C. IR: ν = 3530 cm^{-1} (OH), 1665 (C=O), 1625 (C=C), 1585, 1480, 1260, 1240, 1115, 1065; UV: λ_{max} (lg ε) = 222 nm sh (4.435), 235 (4.475), 274 (4.021), 314 (4.312), 395 (3.272), 512 (2.989).
^{1}H NMR (400 MHz): δ = 3.91 (s, 3H, OCH_3), 4.06 (s, 3H, OCH_3), 6.04 (s, 1H, OH), 6.12 (s, 1H, 3-H), 7.44 (d, *J* = 10 Hz, 1H, 6-H), 8.15 (d, *J* = 9 Hz, 1H, 10-H), 8.50 (dd, $J_{9,10}$ = 9 Hz, $J_{5,9}$ = 1 Hz, 1H, 9-H), 9.19 (dd; $J_{5,6}$ = 10 Hz, $J_{5,9}$ = 1 Hz, 1H, 5-H); Ms: *m/z* (%) = 284 (100, M^+), 269 (51), 241 (53), 213 (17), 185 (16), 170 (17). Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.25. Found: C, 67.55; H, 4.12.

8-Hydroxy-3,7-dimethoxy-1,4-phenanthrenequinone (96). Mp 286°C. IR: ν = 3480 cm^{-1} (OH), 1670, 1655 (C=O), 1620 (C=C), 1485, 1290, 820; UV: λ_{max} (lg ε) = 231 nm (4.487), 273 (4.078), 311 (4.257), 391 (3.359), 516 (2.908); ^{1}H NMR (400 MHz): δ = 3.93 (s, 3H, OCH_3), 4.06 (s, 3H, OCH_3), 6.07 (s, 1H, OH), 6.12 (s, 1H, 2-H), 7.49 (d, *J* = 10 Hz, 1H, 6-H), 8.15 (d, *J* = 9 Hz, 1H, 10-H), 8.58 (dd, $J_{9,10}$ = 9 Hz, $J_{5,9}$ = 1 Hz, 1H, 9-H), 9.13 (dd, $J_{5,6}$ = 10 Hz, $J_{5,9}$ = 1Hz, 1H, 5-H); MS: *m/z* (%) = 284 (100, M^+), 269 (50), 241 **(41),** 213 (12), 185 (14), 170 (15). Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60, H, 4.25. Found: C, 66.95; H, 4.18.

7-Hydroxy-3,8-dimethoxy-1,4-phenanthrenequinone (97), 2-hydroxy-7,8-dimethoxy-1,4-phenanthrenequinone (98) and 3-hydroxy-7,8-dimethoxy-1,4-phenanthrene-quinone (99). 52 mg (0.15 mmol) of 7-benzyloxy-8-methoxy-1,4-phenanthrenequinone **(56)** was

converted according to general procedure VI. The crude product was separated by preparative TLC to give two fractions: Quinone 97 (4 mg, 9%) and a mixture of quinones **98** and **99** (3 mg, 7%).

Data for 97. Mp: 250-251°C. IR: ν = 3480 cm^{-1} (OH), 1640 (C=O), 1620 (C=C), 1480, 1250, 1180, 1140; UV: λ_{max} (lg ε) = 207 nm sh (4.172), 233 (4.526), 266 (4.127), 305 (4.237), 390 (3.475); ^{1}H NMR (400 MHz): δ = 3.93 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 5.98 (s, 1H, OH), 6.14 (s, 1H, 2-H), 7.47 (d, *J* = 10 Hz, 1H, 6-H), 8.22 (d, *J* = 10 Hz, 1H, 10-H), 8.34 (dd, $J_{9,10}$ = 10 Hz, $J_{5,9}$ = 1 Hz, 1H, 9-H), 9.29 (dd, $J_{5,6}$ = 10 Hz, $J_{5,9}$ = 1 Hz, 1H, 5-H); Ms (130°C): *m/z* (%) = 284 (76, M^+), 269 (77), 241 (37), 192 (24), 123 (24), 84 (100). Anal. Calcd for $C_{16}H_{12}O_5$; C, 67.60; H, 4.25. Found: C, 66.73; H, 4.20.

Data for 98 and 99. Mp 262°C. ^{1}H NMR (400 MHz): δ = 3.93 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 6.13 (s, 1H, 2- o. 3-H), 6.15 (s, 1H, 2- o. 3-H), 7.44 (d, *J* = 9 Hz, 1H, 6-H), 7.47 (d, *J* = 9 Hz, 1H, 6-H), 8.22 (d, *J* = 9 Hz, 1H, 10-H), 8.26 (d, *J* = 9 Hz, 1H, 9-H), 8.34 (d, *J* = 9 Hz, 1H, 5-H). Ms (125°C): *m/z* (%) = 284 (97,M^+), 269 **(100)**, 241 **(46)**, 84 (67).

Epoxidation of 1,4-phenanthrenchinones. General procedure 7

A solution of the 1,4-phenanthrenchinone (0.19 mmol) in ethanol (5 mL) was treated at 45°C with 0.53 mL of 30% H_2O_2 and 0.53 mL of saturated Na_2CO_3 solution. After 5 min, the mixture was poured into ice-water (30 g) and extracted with extracted five times with dichloromethane (20 mL). The combined organic phases were dried ($CaCl_2$), filtered, and the solvent removed under reduced pressure. The products were crystallized from dichloromethane / petroleum ether.

2,3-Epoxy-2,3-dihydro-8-methoxy-1,4-phenanthrenequinone (100). 45 mg (0.19 mmol) of 8-methoxy-1,4-phenanthrenequinone (46) was converted to the epoxide 100. Yield 38 mg (79%). Mp 218°C (decomp.). IR: ν = 1695 cm^{-1} (C=O), 1575, 1315, 1295, 1270, 1245 (Epoxid), 750; UV: λ_{max} (lg ε) = 221 nm (4.361), 283 (4.403), 328 (3.312), 392 (3.332); ^{1}H NMR (300 MHz): δ = 4.03 (s, 3H, OCH_3), 4.10 (d, *J* = 4 Hz, 1H, 2-H), 4.15 (d, *J* = 4Hz, 1H, 3-H), 7.00 (d, *J* = 8 Hz, 1H, 7-H), 7.62 (dd, $J_{5,6}$ = 8 Hz, $J_{6,7}$ = 8 Hz, 1H, 6-H), 7.94 (d, *J* = 9 Hz, 1H, 10-H), 8.45 (d, *J* = 9 Hz, 1H, 9-H), 8.67 (d, *J* = 8 Hz, 1H, 5-H); MS(100°C): *m/z* (%):

254 (100, M^+), 226 (16), 211 (16), 183 (37), 127 (22), 113 (15). Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.87; H, 3.96. Found: C, 70.37, H, 4.02.

2,3-Epoxy-2,3-dihydro-7,8-dimethoxy-1,4-phenanthrenequinone (101). 51 mg (0.19 mmol) of 7,8-dimethoxy-1,4-phenanthrenequinone (**54**) was converted to the epoxide **101**. Yield: 44 mg (81%). mp 165°C. IR: ν = 1695 cm^{-1} (C=O), 1480, 1280 (epoxide); UV: λ_{max} (lg ε) = 219 nm (4.354), 288 (4.503), 373 (3.548); ^{1}H NMR: δ = 3.96 (s, 3H, OCH_3), 4.07 (s, 3H, OCH_3), 4.05 (d, *J* = 5 Hz, 1H, 2H), 4.12 (d, *J* = 5 Hz, 1H, 3-H), 7.43 (d, *J* = 10 Hz, 1H, 6-H), 7.87 (d, *J* = 9 Hz, 1H, 10-H), 8.44 (d, *J* = 9 Hz, 1H, 9-H), 8.63 (d, *J* = 10 Hz, 1H, 5-H); MS (120°C): *m/z* (%) = 284 (100, M^+), 269 (63), 149 (50), 97 (58), 83 (61), 69 (94), 57 (78), 43 (87). Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.25. Found: C, 67.76; H, 4.34.

2,3-Epoxy-2,3-dihydro-6,7,8-trimethoxyphenanthren-1,4-dion (102). 57 mg (0.19 mmol) 6,7,8-trimethoxy-1,4-phenanthrenequinone (**67**) was converted to the epoxide **102**. Yield 36 mg (60%). mp 133°C. IR: ν = 1690 cm^{-1} (C=O), 1680, 1475, 1410, 1270 (Epoxid), 1245, 1130, 1120, 1035; UV: λ_{max} (lg ε) = 216 nm (4.458), 237 (4.374), 292 (4.405), 356 (3.650); ^{1}H NMR (300 MHz): δ = 4.03 (s, 3H, OCH_3), 4.05 (s, 3H, OCH_3), 4.09 (d, *J* = 4 Hz, 1H, 2-H), 4.12 (d, *J* = 4 Hz, 1H, 3-H), 7.85 (d, *J* = 9 Hz, 1H, 10-H), 8.22 (s, 1H, 5-H), 8.43 (d, *J* = 9 Hz, 1H, 9-H); MS (70°C): *m/z* (%): 314 (100, M^+), 299 (34), 271 (31), 256 (17). Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.97, H, 4.49. C, 64.70; H, 4.50.

cis-Hydroxylation of 54. 2,3-dihydro-2,3-dihydroxy-7,8-dimethoxyphenanthrene-1,4-dione (103)

A solution of 7,8-dimethoyxy-1,4-phenanthrenequinone (**54**) in THF (2 mL) was treated at 20 °C with an aqueous solution of osmium tetroxide (2 %, 1.4 mL) and sodium chlorate (61 mg). The mixture was stirred for 3 h. Part of the diol 103 precipitated and was filtered of. Another crop was obtained by extraction with dichloromethane and usual workup. Yield 150 mg (89 %); mp 185 °C. IR: 1690 (CO), 1680 (C=O), 1605 (C=C), 1590, 1480, 1275, 1085, 1035, 815; UV: λ_{max} (1gε) = 223 (4.354), 284 (4.583), 365 (3.637); ^{1}H-NMR: δ = 3.90 (s; 3H,OCH_3), 4.01 (s; 3H, OCH_3), 4.46 (s; 2H, 2-u.3-H), 7.73 (d, J = 10Hz; 1H, 6-H), 7.98 (d, J = 9Hz; 1H, 10-H), 8.42 (d, J = 9Hz; 1H, 9-H), 8.86 (d, J = 10Hz; 1H, 5-H); MS (160°C): *m/e* = 302 (100%, M^+), 286 (33), 256 (39), 241 (44), 186 (51), 171 (44), 115 (63).

2,3-Dihydro-7,8-dimethoxy-2,3-cis-isopropylidendioxyphenanthren-1,4-dion (104)

A solution of diol **103** (20 mg, 0.07 mmol), 0.03 mL of orthoformic methyl ester, and 4 mg of *p*-toluenesulfonic acid in dry acetone (0.5 mL) was refluxed for 30 min. The solvent was removed under reduced pressure, the residue redissolved in dichloromethane, washed with water, dried ($CaCl_2$), and the solvent removed under reduced pressure. The residue was purified by preparative TLC on silica gel to afford 15 mg of acetonide **104** (63 %), mp 161 °C. IR: 1715 (C=0), 1690 (C=0), 1605 (C=C), 1480, 1280, 1215, 1085, 985, 825; UV: λ_{max} (1gε) = 220 (4.400), 239 (4.458), 254 sh (4.271), 291 (4.115), 332 sh (3.609), 351 (3.525); ^{1}H-NMR: δ = 1.46 (s; 3H, CH_3), 1.49 (s; 3H, CH_3), 3.97 (s; 3H, OCH_3), 4.02 (s; 3H, OCH_3), 5.01 (s; 2H, 2-u.3-H), 7.47 (d, J = 10Hz; 1H, 6-H), 8.00 (d, J = 9Hz; 1H, 10-H), 8.46 (d, J = 9Hz; 1H, 9-H), 8.70 (d, J = 10Hz; 1H, 5-H); MS (140°C): *m/e* = 342 (100%, M^+), 256 (65), 241 (66), 213 (31), 171 (24), 84 (94).

Stilbene-cyclizations. General procedure 5

The stilbenes **84**–**87** were prepared by Wittig reaction of the aldehydes **11**, **13**, and **17** with the phosphonium salts **82** and **83** according to the General Procedure I (modification of Boden.[42]). A solution of the stilbene (1.3 mmol) in freshly distilled cyclohexene (130 mL) and 0.07 mol of iodine was irradiated in a water-cooled photoreactor with 360 nm light until the starting material was consumed (TLC control). The intermediate phenanthrenes were purified by flash chromatography on silica gel (dichloromethane), crystallized and directly subjected to the oxidative CAN demethylation.

Oxidative CAN demethylations. General procedure 8

A solution of the phenanthrene (0.4 mmol) in a mixture of water (0.6 mL) and acetonitrile (1.4 mL) was treated with 0.2 g of pyridine-2,6-dicarboxylic acid N-oxide[53] and a solution of ceriumammonium nitrate (CAN, 0.5 g) in 2 mL of acetonitrile/water (1:1). The mixture was stirred for 30 min at 0 °C (TLC control) and quenched with water after conversion of the starting material. The product was extracted with dichloromethane, purified by flash chromatography on silica gel and crystallized.

7-Methoxy-1,4-phenanthrenquinone (45). Yield 97 %. mp 154 °C (ref.[29]: 153 °C).

7,8-Dimethoxy-1,4-phenanthrenquinone (51). Yield 91 %. mp 190 °C (ref.[29] : 196-198 °C).

2,7,8-Trimethoxy-1,4-phenanthrenquinone (59). Yield: 10 %; mp 184-186 °C.

2,6,7-Trimethoxy-1,4-Phenanthrenquinone (92). Yield 14 %; mp above 250 °C (decomp.). ^{1}H NMR (90 MHz, $CDCl_3$): δ = 3.96; 4.09; 4.15; (3 s, 3 H, OCH_3); 6.13 (s, 1H, Ar-H); 7.1 (s, 1H, Ar-H); AB-signal (δ_A=7.75; δ_B =8.24; *J* = 9 Hz; Ar-H); 9.69 (s, 3H, Ar-H); UV (methanol): λ_{max} (lg ε) = 243 nm (4.43); 278 (3.93); 285 (3.91); 298 (3.88); 318 (3.60); 425 (3.52). Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.82; H, 4.66.

7,8-Dimethoxy-1,2-phenanthrenquinone (93). mp 185-186 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.0 (s, 3H, OCH_3); 4.06 (s, 3H, OCH_3); AX-signal (δ_A = 6.53; δ_X =8.22; *J* = 11 Hz; Ar-H); AX-signal (δ_A = 7.45; δ_X =8.23; *J* = 9 Hz, Ar-H); AB-signal (δ_A = 8.01; δ_B = 8.09; *J* = 10 Hz, Ar-H); IR (KBr): 1665 cm^{-1} (C=O), 1600 (C=C), 1480, 1280, 1080, 1030, 850, 790, 750. Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 72.04; H, 4.43.

Cyclic voltammograms

A 0.1 m solution of tetrabutylammonium (TBAP) perchlorate in acetonitrile[60] was used as electrolyte. The solution was dried with N super alumina (Woelm) inside the electrochemical cell as described.[61] The cell was equipped with following electrodes: Working electrode: 1 mm diameter platinum disk; auxiliary electrode: platinum spiral; Reference electrode: Ag/Ag+/TBAP-MeCN. Electrochemical data was determined with a home built computer controlled apparatus. For data of cyclic voltammograms from ten different 1,4-phenanthrenequinones **(1, 41-46, 54, 64, 70, 74)** see Table 3.

References

1. Wu, T.; Jong, T.-T.; Tien, H.-J.; Kuoh, C.-S.; Furukawa, H.; Lee, K.-H. *Phytochem.* **1987**, *26*, 1623.
2. Reisch, J.; Báthory, B.; Navák, J.; Szendrei, K.; Minker, E. *Herba Hungarica* **1972**, *11*, 61.
3. Schmalle, H. W.; Hausen, B. M. *Naturwissenschaften* **1979**, *66*, 527.
4. Criodian, T. O.; O'Sullivan, M.; Meegan, M. J.; Donnelly, D. M. X. *Phytochem.* **1981**, *20*, 1089.

5. Singh, S. B.; Petit, G. R. *J. Am. Chem. Soc.* **1989**, *111*, 4105.
6. Fisch, M. H.; Flick, B. H.; Arditti, J. *Phytochemistry* **1973**, *12*, 437.
7. Letcher, R. M.; Nhamo, L. R. M. *J. Chem. Soc.* **1973**, 1263.
8. Hardegger, E.; Schellenbaum, M.; Corrodi, H. *Helv. Chim. Acta* **1963**, *46*, 1171.
9. Steiner, K.; Egli, C.; Rigassi, N.; Helali, S. E.; Hyrdegger, E. *Helv. Chim. Acta* **1974**, *57*, 1137.
10. Schmalle, H. W.; Jarchow, O. H.; Hausen, B. M.; Schulz, K.-H. *Funkt. Biol. Med.* **1983**, *2*, 9.
11. Hardegger, E.; Biland, H. R.; Corrodi, H. *Helv. Chim. Acta* **1963**, *46*, 1354.
12. Stermitz, F. R.; Suess, T. R.; Schauer, C. K.; Anderson, O. P. *J. Natur. Prod.* **1983**, *46*, 417.
13. Griesebach, H.; Ebel, J. *Angew. Chem.* **1978**, *90*, 668; *Angew. Chem. Int. Ed.* **1978**, *17*, 635.
14. Reisch, J.; Báthory, M.; Novák, I.; Szendrei, K. *Herba Hung.* **1970**, *9*, 43.
15. Hausen, B. M. *Woods Injurious to Human Health*; de Gruyter.
16. Letcher, R. M.; Nhamo, L. R. M. *J. Chem. Soc. C* **1971**, 3070.
17. Hausen, B. M. *Toxic and Sensitizing Orchids* In *Orchid Biology*; Arditti, J., Ed.; Cornell Press, 1984; Vol. 3, p. 262.
18. Bhandari, S. R.; Kapadi, A. H. *Phytochem.* **1983**, *22*, 747.
19. Tuchinda, P.; Udchachon, J.; Khumtaveeporn, K.; Taylor, W. C.; Engelhardt, L. M.; White, A. *Phytochem.* **1988**, *27*, 3267.
20. Bartsch, H.-H.; Schmalle, H. W.; Jarchow, O. H.; Hausen, B. M.; Schulz, K. H. *Acta. Cryst.* **1986**, *C42*, 322.
21. Talapatra, B.; Mukhopadhyay, P.; Chaudhurry, P.; Talapatra, S. K. *Indian J. Chem.* **1982**, *21B*, 386.
22. Alder, A. C.; Rüedi, P.; Eugster, C. H. *Helv. Chim. Acta* **1984**, *67*, 1003.
23. Alder, A. C.; Rüedi, P.; Prewo, R.; Bieri, J. H.; Eugster, C. H. *Helv. Chim. Acta* **1986**, *69*, 1395.
24. Chang, H. M.; Cheng, K. P.; Choang, T. F.; Chow, H. F.; Chui, K. Y.; Hon, P. M.; Tan, F. W. L.; Yang, Y. *J. Org. Chem.* **1990**, *55*, 3537.
25. Thomson, R. H. *Naturally Occurring Quinones III. Recent Advances*; Chapman and Hall, 1987.

26. Babock, H. H. *Pharmacist* **1875**, *8*, 1.
27. MacDouglas, D. T. *Minnesota Bot. Stud.* **1894**, *1*, 32.
28. Hausen, B. M. *unpublished results*.
29. Manning, W. B.; Kelly, T. P.; Muschik, G. M. *J. Org. Chem.* **1980**, *45*, 2535.
30. Inouye, Y.; Kakisawa, H. *Bull. Soc. Chim. Jpn.* **1971**, *44*, 563.
31. Rosen, B. I.; Weber, W. P. *J. Org. Chem.* **1977**, *42*, 3463.
32. Engler, T. E.; Sampath, U.; Naganathan, S.; Vander Velde, D.; Takusagawa, F.; Yohannes, D. *J. Org. Chem.* **1989**, *54*, 5712.
33. Engler, T. A.; Letavic, M. A.; Reddy, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 5068.
34. Blatter, K.; Schlüter, A.; Wegner, G *J. Org. Chem.* **1989**, *54*, 2396.
35. Carreno, M. C.; Mahugo, J.; Urbano, A. *Tetrahedron Lett.* **1977**, *38*, 3047.
36. Manning, W. B.; Tomaszewski, J. E.; Muschik, G. M.; Sato, R. I. *J. Org. Chem.* **1977**, *42*, 3465.
37. Mallory, F. B.; Wood, C. S.; Gordon, J. T. *J. Am. Chem. Soc.* **1964**, *86*, 3094.
38. Kelly, T. R.; Jagoe, C. T.; Li, Q. *J. Org. Chem.* **1989**, *111*, 4522.
39. Blackburn, E. V.; Timmons, C. J. *Q. Rev., Chem. Soc.* **1969**, *23*, 482.
40. Laarhoven, W. H.; Prinsen, W. J. *Top. Curr. Chem.* **1984**, *125*, 63.
41. Kraus, G. A.; Melekhov:, A. *J. Org. Chem.* **1999**, *64*, 1720.
42. Boden, R. M. *Synthesis* **1976**, 784.
43. Merz, H.; Fink, G. *Arch. Pharm. Ber. dtsch. Pharm. Ges.* **1956**, *289*, 347.
44. Kemp, Weiz oder.
45. Hudson, B. J. F.; Robinson, R. *J. Chem. Soc.* **1941**, 715.
46. Bruckner, V. *Ber.* **1942**, *75*, 2034.
47. Lora-Tamayo, M. *Tetrahedron* **1958**, *4*, 17.
48. Wagner-Jauregg, T. *Synthesis* **1980**, 769.
49. Cosmo, R.; Hambley, T. W.; Sternhell, S. *J. Org. Chem.* **1987**, *52*, 3119.
50. Mannschreck, A.; Gmahl, E.; Burgemeister, T.; Kastner, F.; Sinnwell, V. *Angew. Chem.* **1988**, *100*, 299; *Angew. Chem. Int. Ed.* **1988**, *27*, 270.
51. Schmalle, H. W.; Jarchow, O. H.; Hausen, B. M.; Schulz, K.-H.; Krohn, K.; Loock, U. *Actra. Cryst.* **1987**, *C43*, 109.
52. Schmalle, H. W.; Jarchow, O. H.; Hausen, B. M.; Schulz, K.-H.; Krohn, K.; Loock, U. *Acta. Cryst.* **1986**, *C42*, 1039.

53. Syper, L.; Kloc, K.; Mlochowski, J.; Szulc, Z. *Synthesis* **1979**, 521.
54. Jacob, P.; III; Callery, P. S.; Shulgin, A. T.; Castagnoli Jr., N. *J. Org. Chem.* **1976**, *41*, 3627.
55. Jung, M. E.; Syster, M. A. *J. Org. Chem.* **1977**, *42*, 3761.
56. McOmie, J. F. W.; Blatchly, M. J. *Org. React.* **1972**, *19*, 2007.
57. Thiele, J. *Ber.* **1898**, *31*, 1247.
58. Rashid, A.; Read, G. *J. Chem. Soc. (C)* **1967**, 1223.
59. Mondon, A.; Krohn, K. *Chem. Ber.* **1972**, *105*, 3726.
60. Kiesele, H. *Anal. Chem.* **1980**, *52*, 2230.
61. Kiesele, H. *Anal. Chem.* **1981**, *53*, 1952.
62. The first cathodic peak potentials (Epc1, see Figure 3) are ca. 28.5 to 50 mV (according to kinetics) more negative than E0. The peak potentials are used for the correlation with the LUMO energies.
63. Frenz, B. A. SDP, Enraf-Nonius Structure Determination; Package. SDP User's Guide, Version 1982; Enraf- Nonius: Delft, The Netherlands.
64. Additional material to this paper can be ordered referring to the No. CSD 52795, names of the authors and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein - Leopoldshafen 2, FRG.