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Benzannulation of Axial Chiral Biscarbene Complexes of Chromium: An Approach to Novel C_2-Symmetrical Redox-Active Bi(phenanthrenequinones)**

Philipp Tomuschat,[a] Lars Kröner,[a] Eberhard Steckhan,[a] Martin Nieger,[b] and Karl Heinz Dötz*[a]

Dedicated to Professor Ernst Otto Fischer on the occasion of his 80th birthday

Abstract: The biscarbene chromium complex **1** (derived from binaphthol) undergoes benzannulation upon reaction with 1- and 3-hexyne to give the biphenanthrenes **2**–**5**. Subsequent column chromatography and recrystallisation yield two diastereomeric $Cr(CO)_3$ complexes **3a** and **3b**, which bear elements of both axial and planar chirality. The annulation products have been characterized by CD spectroscopy. Oxidative workup of the primary annulation product **2** affords the C_2-symmetrical axial chiral bi(phenanthrenequinones) **4** and **5**. Deprotection of **4** with boron tribromide or aluminium trichloride gives the binaphthol-related skeletons **6** and **8**, whereas reaction of **4** with trimethylsilyl iodide (TMSI) results in the unexpected formation of the helicene **7**. X-ray structure analysis of **7** indicates π stacking of the arene and quinone rings, as well as a unit cell in which two molecules of the helicene and two molecules of chloroform are connected by C–H ··· O hydrogen bonding. Comparative cyclovoltammetric studies on **4**, **5**, **7**, and the 'monomer' **9** show that the angular quinone moieties are electrochemically independent.

Keywords: biaryls · carbene complexes · chirality · chromium · circular dichroism · cyclic voltammetry

Introduction

Recently we have reported the organometallic functionalization of 1,1′-binaphthol to axial chiral biscarbene complexes of chromium.[1] Under the appropriate conditions, these compounds may be exploited in benzannulation reactions to provide a straightforward route to planar chiral tricarbonylchromium complexes and to enantiomerically pure C_2-symmetrical quinones, which are difficult to obtain by other methods. The few examples of diastereoselective benzannulation reactions that are currently known are based either on carbene complexes with a chiral center in the alkoxy carbene side chain,[2] in the unsaturated carbene side chain,[3] or on the incorporation of α-chiral propargylic ethers.[4] We became interested in tricarbonylchromium complexes as they combine elements of both axial and planar chirality. We started from the axial chiral 1,1′-binaphthol precursor which is readily available as both enantiomers. Over the last two decades, the 1,1′-binaphthyl skeleton has attracted increasing attention in stereoselective synthesis and asymmetric catalysis.[5] Several binaphthyl-based, chiral metal complexes have been used in asymmetric hydrogenations,[6] and in Diels–Alder,[7] aldol,[8] Michael,[9] and carbonyl–ene reactions.[10]

Results and Discussion

Synthesis of biphenanthrene $Cr(CO)_3$ complexes with axial and planar chirality: Upon reaction with 3-hexyne in boiling THF the biscarbene complex (*R*)-**1** (derived from binaphthol) underwent benzannulation to give the angular product (*R*)-**2**; (*S*)-**2** is accessible by the same method. In accordance with previous reports, no linear annulation resulting in the formation of the bianthracene skeleton was observed.[11]

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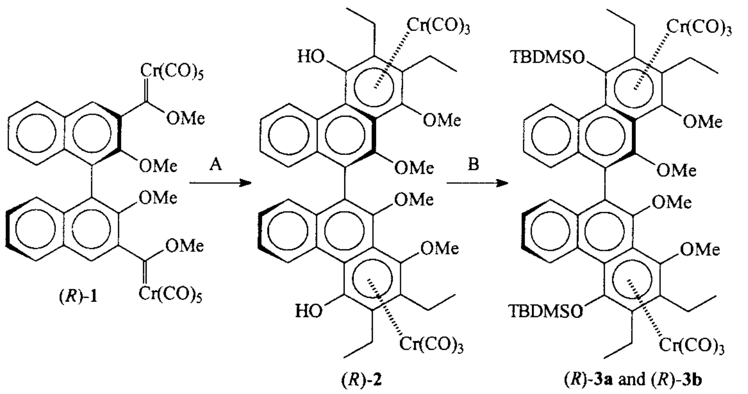


Scheme 1. Benzannulation of the biscarbene complex (R)-**1**. A) 3-Hexyne, THF, 66 °C, 2 h; B) TBDMSCl/NEt$_3$, 20 °C, 2 h.

Since monoprotected hydroquinone Cr(CO)$_3$ complexes are notoriously sensitive to oxidation, the biphenanthrenol **2** was protected in situ with *tert*-butyldimethylchlorosilane and triethylamine to form the bisether hydroquinone complex **3**, as outlined for the *R* series in Scheme 1.

Based on the C_2 symmetry of the enantiomerically pure complex **1**, two new elements of planar chirality arose from the annulation reaction. Therefore, four diastereomers of **3** are predicted in the *R* or the *S* series, respectively, and two of each were isolated in diastereomerically pure form as the major products after column chromatography and recrystallization from *n*-hexane (Figure 1).

Both diastereomers differ in their number of ^{1}H and ^{13}C NMR signals. One isomer produces only a half set of signals to indicate C_2 symmetry, whereas the other isomer gives rise to the expected set of signals suggestive of C_1 symmetry. This is illustrated by the ^{13}C NMR signals of the aromatic carbon atoms as shown in Figure 2.

Optical properties of bi(phenanthrenehydroquinone) complexes: The dinuclear biphenanthrene complexes **3** combine the inherent axial chirality from the binaphthol precursor with two additional planes of chirality from the benzannulation reaction. We speculated whether the CD spectra of the diastereomerically pure biphenanthrene complexes are dominated by the planar or by the axial elements of chirality. Simple tricarbonylchromium complexes display only a weak CD effect in the region of the π → π* electronic transition, and

Abstract in German: *Über die Benzanellierung des Biscarbenkomplexes **1** mit 1- und 3-Hexin lassen sich die Biphenanthrene **2**–**5** aufbauen. Nach säulenchromatographischer Reinigung und Umkristallisation wurden die beiden diastereomeren Cr(CO)$_3$-Komplexe **3a** und **3b** erhalten, die Elemente planarer und axialer Chiralität aufweisen. Oxidative Aufarbeitung der Anellierungsprodukte **2** lieferte die C_2-symmetrischen Bi(phenanthrenchinone) **4** und **5**. Durch Spaltung des Aryl-Methylethers mit Bortribromid oder Aluminiumtrichlorid wurden die Binaphthol-ähnlichen Gerüste **6** und **8** erhalten. Überraschenderweise ergab die Reaktion von **4** mit Trimethylsilyliodid (TMSI) das Helicen **7**. Dessen Elementarzelle enthält zwei Moleküle des Helicens, die über charge-transfer Wechselwirkungen zwischen den Chinon- und den angularen Aren-Ringen miteinander verbunden sind, sowie zwei Moleküle Chloroform, die ihrerseits via C–H···O Wasserstoffbrücken an die Helicene gebunden sind. Nach vergleichenden cyclovoltammetrischen Untersuchungen von **4**, **5**, **7** und dem ‘Monomer’ **9** sind die Chinoneinheiten elektrochemisch voneinander unabhängig.*

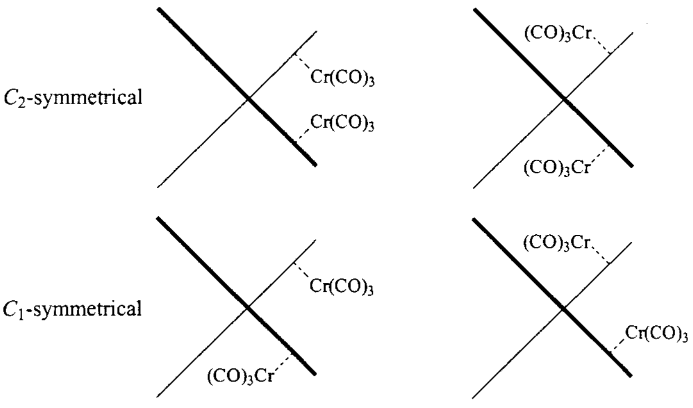
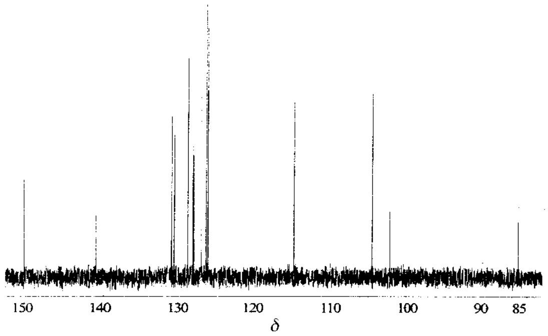
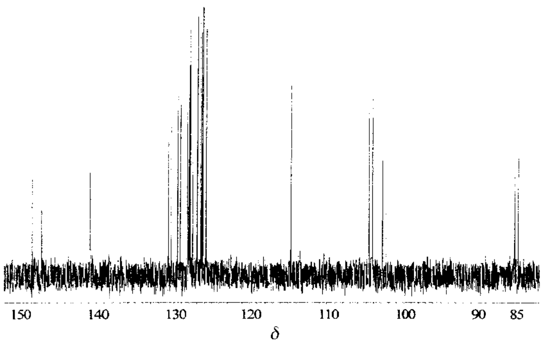


Figure 1. Diastereomers predicted from the benzannulation of (R)-**1**.



C_2-symmetrical (R)-**3a**



C_1-symmetrical (R)-**3b**

Figure 2. Selected ^{13}C NMR spectra of the major diastereomers (R)-**3a** and (R)-**3b**.

an additional effect of the same order of magnitude in the region of the metal-to-ligand charge transfer (MLCT) transitions.[12] On the other hand, a very strong CD effect is observed for binaphthyl and other related systems in the range of the $\pi \rightarrow \pi^*$ (^1B) electronic transition. The shape and intensity of this CD effect correlate directly with the dihedral angle defined by the two aromatic systems.[13] Thus, the CD spectra of **3** were expected to provide information about the dihedral angle.

In order to locate the position of the ^1B electronic transition of the phenanthrenequinone chromophore, we recorded UV/Vis spectra of the C_2-symmetrical tricarbonylchromium complexes (*R*)- and (*S*)-**3a**, and of the C_1-symmetrical complexes (*R*)- and (*S*)-**3b**. We found absorption maxima at $\lambda = 225$ (**3a**) and 227 nm (**3b**). The absorption maxima for the MLCT transitions were observed at 402 nm (**3a**) and 397 nm (**3b**), respectively (Figure 3).

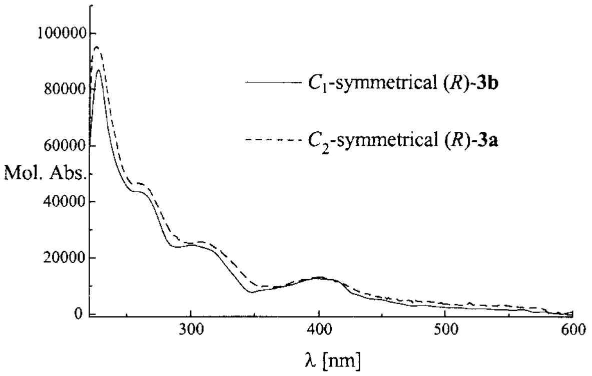


Figure 3. UV/Vis spectra of (*R*)-**3a** and (*R*)-**3b** in $CHCl_3$.

We also recorded the CD spectra of the diastereomerically pure annulation products derived from the pure biscarbene complexes (*R*)-**1** and (*S*)-**1**. As predicted, the CD spectra of the C_2-symmetrical complexes (*R*)-**3a** and (*S*)-**3a**, as well as those of the C_1-symmetrical (*R*)-**3b** and (*S*)-**3b**, are accurate mirror images in shape and intensity. However, the CD spectra for the (*R*)-**3a**/(*R*)-**3b** and (*S*)-**3a**/(*S*)-**3b** pairs are clearly different and vary significantly in the shape and intensity of the bands that originate from both the $\pi \rightarrow \pi^*$ and the MLCT transitions. For (*R*)- and (*S*)-**3a**, strong CD effects are observed in the region of the $\pi \rightarrow \pi^*$ transition (233 nm, $\Delta\varepsilon = 157$), accompanied by a complex structure and an unusually high $\Delta\varepsilon$ value of 24 at 415 nm in the region of the MLCT transition (Figure 4). In contrast, (*R*)- and (*S*)-**3b** display only a weak CD effect for the $\pi \rightarrow \pi^*$ transitions, which overlap with a structure of three maxima at 242, 264, and 294 nm. For the MLCT transition, a $\Delta\varepsilon$ value of 4 is detected at 417 nm as expected (Figure 5).

The intensity and shape of the CD signal caused by the $\pi \rightarrow \pi^*$ transition of the biaryl system depend on the dihedral angle defined by the two aromatic systems. Between 100 and 110° the form of the CD signal turns from a positive to a negative couplet. For values between these two angles the detected CD signal can be very weak. Thus, the weak CD signal observed for the C_1-symmetrical (*R*)- and (S)-**3b** may be rationalized in terms of a dihedral angle of between 100 and 110°.

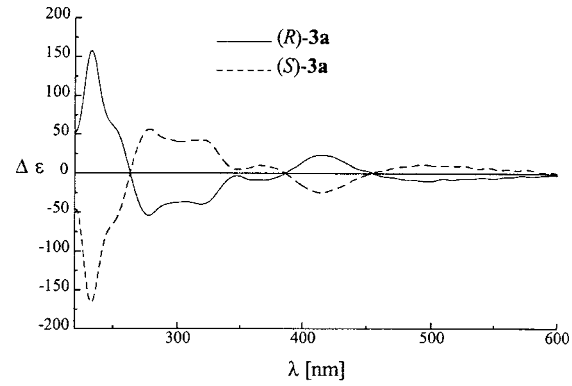


Figure 4. CD spectra of the C_2-symmetrical tricarbonylchromium complexes **3a** in $CHCl_3$.

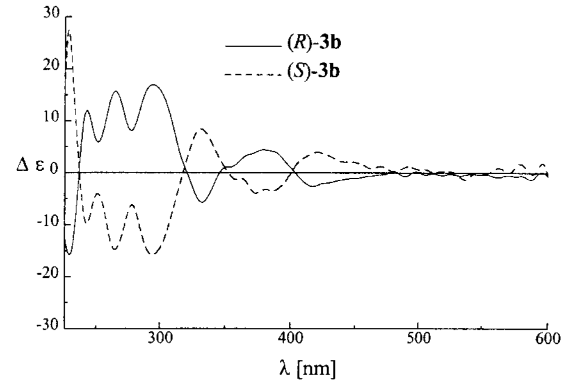
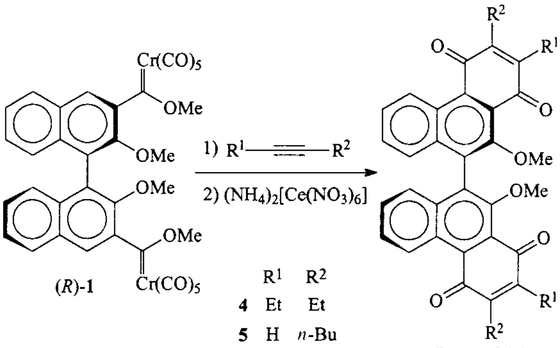


Figure 5. CD spectra of the C_1-symmetrical tricarbonylchromium complexes **3b** in $CHCl_3$.

Axial chiral bi(phenanthrenequinones): Oxidation of the annulation products afforded the corresponding quinones. In situ oxidation of the bischromium phenanthrene complexes (generated by reaction of racemic and (*R*)-biscarbene complexes with 1- and 3-hexyne) with $(NH_4)_2[Ce(NO_3)_6]$ gave the dimethoxy bi(phenanthrenequinones) **4** and **5**, which were isolated by column chromatography in moderate yields as yellow solids (56% and 36%, respectively) (Scheme 2).

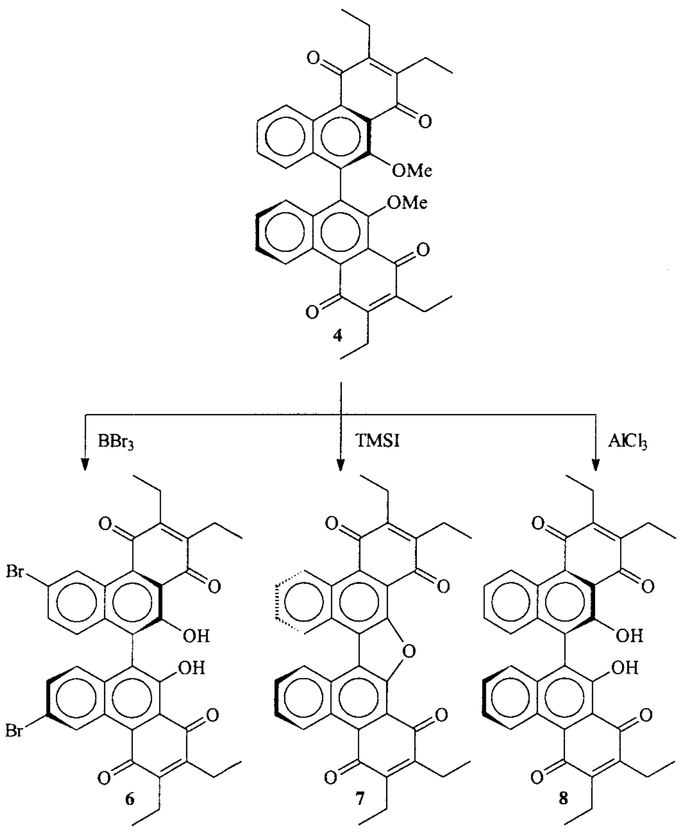


Scheme 2. Synthesis of biphenanthrenediquinones **4** and **5**.

Since chiral biaryl diols are efficient ligands for enantioselective catalysis, we aimed to deprotect **4** in order to generate biphenanthrenols suitable for the chelation of a metal center. However, the demethylation of the dimethoxy bi(phenanthrenequinone) **4** was not trivial. Boron tribromide has previously proved effective in the demethylation of 1,1′-dimethoxybinaphthyl in excellent yields.[14] To account for the presence of additional basic oxygen atoms,[15] we used six equivalents of boron tribromide for the demethylation, and subsequently obtained the deprotected bi(phenanthrenequinone) **6** with additional bromine substituents in the positions 6 and 6′. We suppose that molecular bromine is formed during the reaction as a result of competing oxidation of bromide by the quinone moiety. The dibromine then effects the electrophilic bromination assisted by the excess of boron tribromide. A similar bromination has been described in the literature for 1,1′-bi-2-naphthols, which were used in the synthesis of macromolecules[16] and polymeric 1,1′-bi-2-naphthols.[17]

In order to avoid concomitant bromination we employed TMSI to cleave the aryl methyl ether.[18] However, instead of the expected diol, we obtained the helicene **7** in 36 % yield. Presumably, the use of excess TMSI (10 equiv) cleaves both aryl methyl ether bonds which is followed by monodesilylation to give a monosilyl diol intermediate. Subsequent intramolecular nucleophilic substitution of the silyloxy group by the phenol results in the formation of the central furan ring.

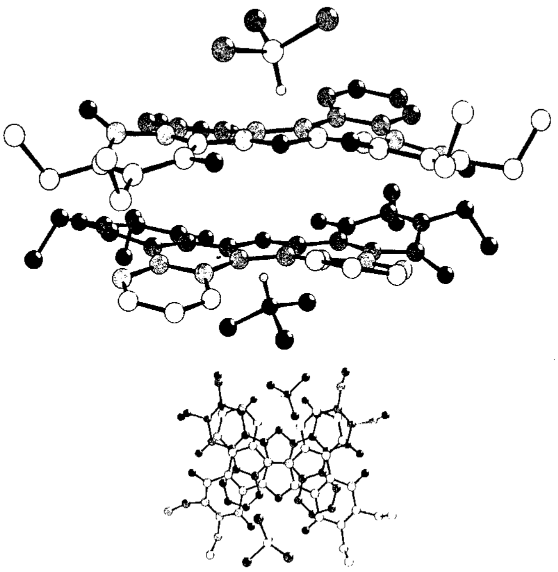
Finally, clean deprotection of **4** was effected by aluminium chloride (10 equiv).[19] The reaction worked well in the presence of a carbonyl group near the aryl methyl ether. After acidic workup and column chromatography, the dihydroxy bi(phenanthrenequinone) **8** was isolated in excellent yield as a deep purple solid (Scheme 3).

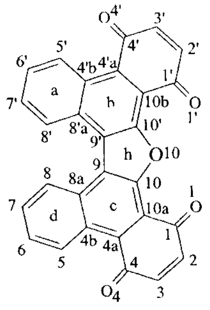


Scheme 3. Ether cleavage of **4** by Lewis acids.

Molecular structure of helicene 7: Recrystallization of **7** from CH_2Cl_2, which also contained small amounts of $CHCl_3$, afforded bright red crystals suitable for X-ray analysis.

The structure of dinaphtho[2,1-b:1′,2′-d]-annulated five-membered aromatic heterocycles[20] reflects the *peri* interactions of the hydrogen atoms H8 and H8′, which impose a helical configuration. The helicity can be quantified by the dihedral angles defined by the least square planes of adjacent rings. The central heterocycle in **7** is essentially planar, as indicated by the small torsion angle C10, C9, C9′, C10 a′. The helical distortion is less pronounced than in the [2,1-b:1′,2′-d]pyrrole analogue[20] (Figure 6). The torsion angles between





	helicene 7	pyrrole
C8a, C9, C9′, C8a′[a]	-10.1(3)°	24.5°
C7, C9, C9′, C7′[a]	-16.3(3)°	33.8°
C10, C9, C9′, C10a′[a]	-3.1(3)°	5.4°
b ^ h[b]	4.2(3)°	6.8°
c ^ h[b]	6.3(3)°	7.5°
a ^ h[b]	13.3(3)°	17.7°
d ^ h[b]	14.6(3)°	19.2°
C8, C8′[c]	3.221(4) Å	3.3 Å
C8, O10, C8′[d]	39.5(7)°	40.7°

Figure 6. Molecular structure and selected molecular dimensions of helicene **7**, a) torsion angle [°], b) dihedral angle defined by least-square planes [°], c) distance [Å], d) angle [°].

Table 1. Redox potentials of compounds **4**, **5**, **7** and **9**.

Potential [V]/compound	4	5	7	9
first redox pair:				
reduction	– 1.141	– 1.048	– 0.885	– 1.080
oxidation	– 1.008	– 0.934	– 0.795	– 0.982
second redox pair:				
reduction	– 1435	– 1.372	– 1.408	– 1.500
oxidation	– 1.289	– 1.272	– 1.311	– 1.378

the carbon atoms C8a, C9, C9′, C8a′ and C7, C9, C9′, C7′ are distinctly smaller, reflecting a reduced twisting of the two naphthyl rings. The distance between the two *peri* carbon atoms C8 and C8′ (3.221(4) Å) together with the angle C8, O10, C8′ (39.5(7)°) characterize the influence of the heterocycle *h* on the distance between the *a* and the *d* rings .

The unit cell contains the *P* and *M* enantiomers of **7**, along with two molecules of $CHCl_3$. The two enantiomers are tilted towards each other by 180° at a distance which varies between 3.2 and 4.2 Å. The shortest distance is found between the atoms C1 and C7 (3.2455(3) Å), which permits a typical charge transfer interaction[21] between the angular aromatic ring and the quinone system. This type of π stacking occurs selectively on one side of the helicene dimer.

The $CHCl_3$ molecules are located unsymmetrically with respect to the three oxygen atoms O1′, O10, O1, but somewhat twisted towards oxygen atom O1. The distance between the hydrogen atom of the $CHCl_3$ molecule and the atoms O1′ (2.6334(3) Å) and O10 (2.7273(3) Å) is within the limits of van der Waals distances, whereas its distance to atom O1 is reduced to 2.336 Å which is characteristic of $C{-}H\cdots O$ hydrogen bonding.[22]

Redox properties of 4, 5, 7, and 9: The bi(phenanthrenequinones) **4** and **5** represent rare examples that combine axial chirality with the redox-active quinone/hydroquinone system.[23] In order to elucidate their potential in stereoselective redox reactions we characterized **4** and **5** by cyclic voltammetry. For comparison, we also included in our study the helicene **7** (a bridged form of **4**) and the monoquinone 2,3-diethylphenanthrene-1,4-dione (**9**). Apart from the redox potentials, we were interested in whether the redox systems of **4** and **5** are reversible, and whether the two quinone units in **4**, **5**, and **7** display any electronic interaction.

The cyclic voltammogram of **9** (Figure 7) shows two redox pairs. The first one is characterized by a cathodic peak potential of – 1080 mV and an anodic peak potential of – 982 mV, and is both chemically and electrochemically reversible. The reverse anodic peak of the second redox pair at – 1500 and – 1378 mV is broadened, as is often observed with quinones and is commonly attributed to a slower heterogeneous electron-transfer rate constant.[24] The two reductions represent one-electron steps as determined by quantification with equal amounts of ferrocene. The first step is considered to correspond to the formation of the semiquinone anion radical, which subsequently undergoes further reduction to the hydroquinone dianion.

The cyclic voltammograms of biquinones **4**, **5**, and **7** (Figure 8) resemble that recorded for the monoquinone **9**. They differ, however, in the reversibility of the anodic peak for the second redox pair, and also in the tendency towards peak-splitting of the first redox pair (observed for **4** and **5**, but not for **7**). Based on quantification with ferrocene, the peak intensities of both reduction steps correspond to the uptake of two electrons. Compared with **9**, the two quinone subunits in **4**, **5**, and **7** have to be considered as individual electronically non-coupled systems. Thus, in the first reduction step two electrons (one for each quinone subunit) are transferred independently at the same potential to generate the bi(semiquinone radical anion). Similarly, in the second step another pair of electrons is transferred independently to both subunits to form the bi(hydroquinone dianion). This is easily explained for compounds **4** and **5** by an almost orthogonal twist of the biaryl system, but was unexpected for the helicene **7**. Semi-empirical calculations at the PM3 and AM1 levels suggested a dihedral angle along the central carbon–carbon bond of 88(±1)° for **4**, and 87(±1)° for **5**, respectively. Because of the reduced twisting of the biaryl system in **7**, electronic coupling of both quinone units seemed possible. This behavior would result in the peak-splitting of both cyclovoltammetric waves. However, only two reversible systems are observed, which indicates two independent redox pairs. In contrast, for compounds **4** and **5**, the first redox pair shows peak-broadening with a tendency towards splitting. Our explanation takes into account that the two quinone systems are strongly twisted against each other. For the heterogeneous electron transfer from the electrode to the biquinone, the orientation of the two quinone subunits with respect to the electrode surface is quite different. Therefore, it can be assumed that the heterogeneous electron-transfer rate to both quinone systems should also differ significantly, which, in turn, suggests a peak-splitting even if the second electron transfer is thermodynamically favored.[25] This explanation is supported by the fact that peak-broadening is reduced when the potential scan rate is lowered from 100 to 10 mV s^{-1}. For helicene **7**, the orientation of the two quinone subunits with respect to the electrode surface is very similar and therefore no peak-broadening is detected.

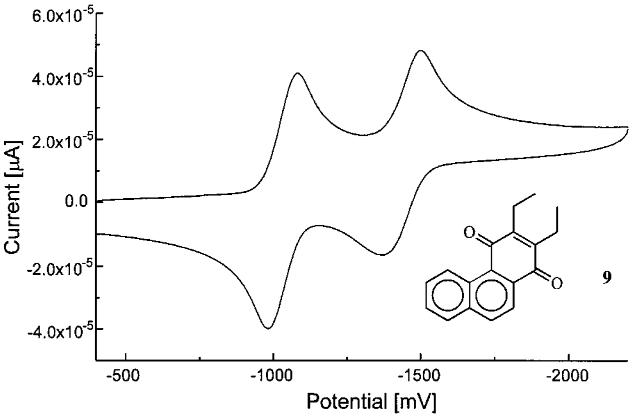


Figure 7. Cyclic voltammogram of monoquinone **9** in DMF/$LiClO_4$ (0.1 M) at 100 mV s^{-1}.

The first reduction of **7** proceeds much more easily (– 0.890 V) than is observed for the bi(phenanthrenequinones) **4** (– 1.141 V) and **5** (– 1.046 V). However, the

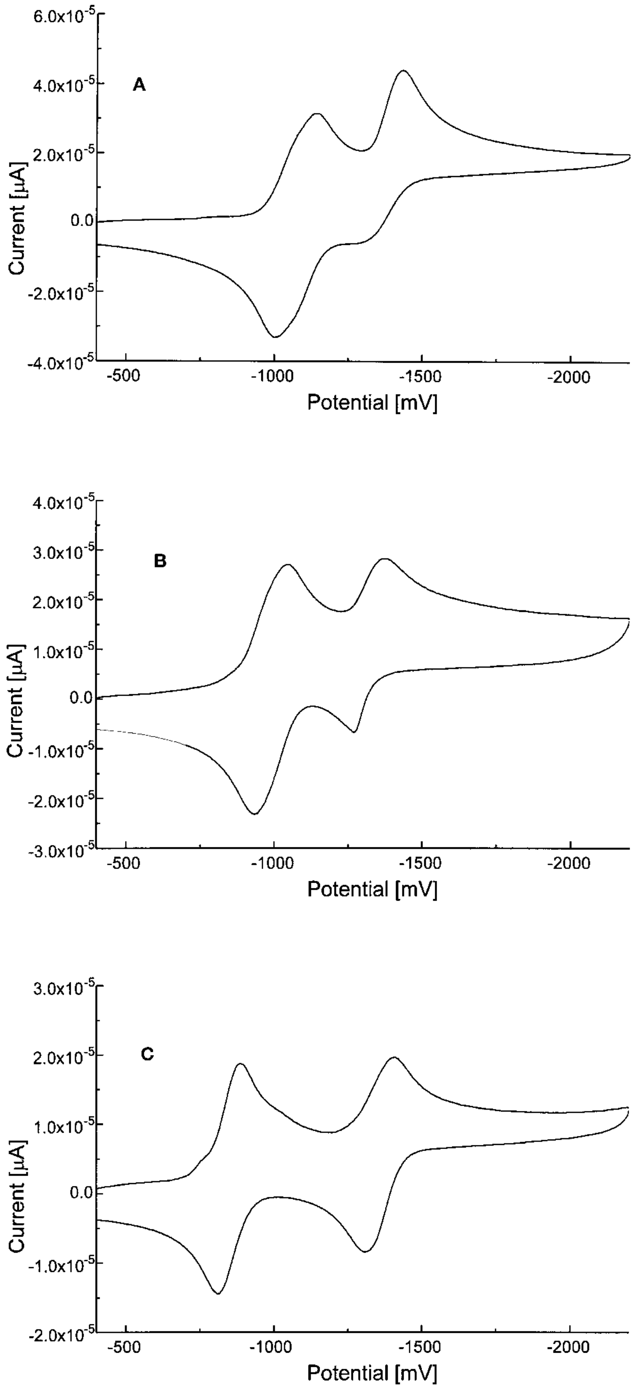


Figure 8. Cyclic voltammograms of **4** (A), **5** (B), and **7** (C) in DMF/$LiClO_4$ at 100 $mV s^{-1}$.

potentials of the second reduction are comparable for all three compounds. This results in an increase in the potential difference between the first and second reductions for **7** (0.520 V) compared with quinones **4** (0.294 V) and **5** (0.324 V) which can be understood by the stabilization of the bi(semiquinone anion) of **7** through the extended aromatic system. The reduction of **5** occurs at a less negative potential (−1.046 V) than that of **4** (−1.141 V). This difference reflects the more efficient overall electron donation by the two ethyl groups in **4** compared with that of the *n*-alkyl and hydrogen substituents in **5**.

The fact that the anodic peak of the second redox pair is generally lower than the corresponding cathodic peak can be rationalized by a subsequent chemical reaction (presumably protonation of the strongly basic dianion) and/or by a slower heterogeneous electron-transfer rate for the oxidation of the bi(hydroquinone dianion).

Conclusion

We have developed a straightforward route to the enantiomerically pure axial chiral bi(phenanthrenequinones) **3** and **4** in four steps from readily available enantiopure binaphthols via carbene complexes. These compounds may be used as mediators in palladium-[26] or copper-catalyzed[27] stereoselective oxidation reactions. We characterized the quinones **4** and **5** by cyclic voltammetry with the aim of applying these compounds to electrochemically induced oxidation reactions[28] and we demonstrated that the two quinone units of **4**, **5**, and **7** are electrochemically independent. Diols **6** and **8** with unprotected hydroxy groups are potential catalysts for the well-established binaphthol chemistry which employs Lewis acids. Furthermore, their O–H acidity may be relevant to asymmetric protonations.[29]

Experimental Section

All operations were performed under argon. Solvents were dried by distillation over sodium–potassium alloy or sodium hydride. The petroleum ether mixture used was 40–60 °C. ^1H and ^{13}C NMR: Bruker DRX 500. Chemical shifts refer to those of the residual solvent signal based on $\delta_{TMS} = 0.00$. FT-IR: Nicolet Magna 550. MS: Kratos 1H Concept. Elemental analyses: Heraeus CHN-O-Rapid. CD and UV/Vis: 0.02 cm path length cell, Jasco J-720 spectropolarimeter. CV: Electrochemical Analyzer BAS 100 B/W, Bioanalytical Systems Inc., West Lafayette, IN, USA. All cyclic voltammograms were recorded with a potential scan rate of 100 $mV s^{-1}$, unless indicated otherwise. The experiments were performed in a conventional three-electrode cell with a glassy carbon working electrode (3 mm diameter), a platinum wire counter electrode, and a Ag/$AgNO_3$ reference electrode (separated from the solution by a Vycor plug). $LiClO_4$ in DMF (0.1 M) was used as the supporting electrolyte.

Arene–Cr(CO)$_3$ complexes (*R*)-3a and (*R*)-3b: 3-Hexyne (1.15 mL, 10 mmol) was added to a solution of the biscarbene complex (*R*)-**1** (0.78 g, 1 mmol) in THF (10 mL). The solution was stirred under reflux for 2 h. The mixture was cooled to room temperature and then added to a solution of *tert*-butyldimethylchlorosilane (0.75 g, 5 mmol) in triethylamine (1.40 mL, 10 mmol). The resulting solution was stirred for 2 h at 20 °C and filtered through silica gel. Chromatographic separation (silica gel, 10 °C; petroleum ether/diethyl ether 10:1) of the red residue yielded first the C_2-symmetrical tricarbonylchromium complex (*R*)-**3a** ($R_f = 0.52$), and next the C_1-symmetrical complex (*R*)-**3b** ($R_f = 0.44$). The pure diastereomers (*R*)-**3a** and (*R*)-**3b** were obtained as red crystals after recrystallization from *n*-hexane.

C_2-symmetrical (*R*)-**3a**: Yield = 0.19 g (0.17 mmol, 17%); ^1H NMR (500.13 MHz, $CDCl_3$, 25 °C): $\delta = -0.31$ (s, 6H; Si-CH_3); 0.12 (s, 6H; Si-CH_3); 1.07 (s, 18H; Si-$C(CH_3)_3$), 1.28 (t, $^3J(H,H) = 7.35$ Hz, 6H; CH_3), 1.41 (t, $^3J(H,H) = 7.30$ Hz, 6H; CH_3), 2.31 (dq, $^2J(H,H) = 14$ Hz, $^3J(H,H) = 7$ Hz, 2H; CH_2), 2.65 (m, 4H; CH_2), 3.01 (dq, $^2J(H,H) = 14$ Hz, $^3J(H,H) = 7$ Hz, 2H; CH_2), 3.38 (s, 6H; 1,1′-OCH_3), 3.87 (s, 6H, 10,10′-OCH_3), 7.01 (d, $^3J(H,H) = 7.95$ Hz, 2H; 8,8′-H), 7.13 ('t', $^3J(H,H) = 7.95$ Hz, 2H; 7,7′-H), 7.39 ('t', $^3J(H,H) = 8.35$ Hz, 2H; 6,6′-H), 9.06 (d, $^3J(H,H) = 8.40$ Hz, 2H; 5,5′-H); ^{13}C NMR (125.76 MHz, $CDCl_3$, 25 °C): $\delta = -3.33$ (Si-CH_3), −2.83 (Si-CH_3), 14.72 (CH_3), 18.84 (CH_3), 18.62 (CH_2), 19.57 (CH_2), 21.95 (Si-$C(CH_3)_3$), 25.87 (Si-$C(CH_3)_3$), 61.72 (1-OCH_3), 68.82 (10-OCH_3), 85.18, 102.16, 104.43, 114.50 (C_{aryl} ($Cr(CO)_3$)), 125.76, 125.98, 126.64, 127.67, 127.76, 128.40, 130.18, 130.56, 140.32 (C_{aryl}), 149.57 (C-10), 233.66 ($Cr(CO)_3$); IR (PE): $\tilde{\nu} = 1958$ (vs, C=O, A_1^1), 1895, 1885 cm^{-1} (s, C=O, E); MS (FAB): m/z (%): 1119.3 ($[M+H]^+$, 27), 1034.3 ($[M-3CO]^+$, 27), 1006.3 ($[M-4CO]^+$, 62), 982.3 ($[M-Cr(CO)_3]^+$, 18), 950.3 ($[M-6CO]^+$, 40), 898.3 ($[M-Cr(CO)_3-3CO]^+$, 100), 846.3 ($[M-2Cr(CO)_3]^+$, 53); $C_{58}H_{70}O_{12}Cr_2Si_2$ (1119.35): calcd C 62.24, H 6.30; found C 61.95 H 6.39.

C_1-symmetrical (*R*)-**3b**: Yield = 0.13 g (0.12 mmol, 12%), ^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): $\delta = -0.40$ (s, 3H; Si-CH_3), -0.34 (s, 3H; Si-CH_3), 0.09 (s, 3H; Si-CH_3), 0.11 (s, 3H; Si-CH_3), 1.05 (s, 9H; Si-*C*(CH_3)$_3$), 1.09 (s, 9H; Si-*C*(CH_3)$_3$), 1.28 (m, 6H; CH_3), 1.41 (m, 6H; CH_3), 2.28 (dq, ^2J(H,H) = 14 Hz, ^3J(H,H) = 7 Hz, 2H; CH_2), 2.68 (m, 4H; CH_2), 2.98 (m, 2H; CH_2), 3.36 (s, 3H; 1-OCH_3), 3.81 (s, 3H; OCH_3), 3.82 (s, 3H; OCH_3), 3.83 (s, 3H; OCH_3), 6.93 (d, ^3J(H,H) = 7.85 Hz, 1H), 7.12 ('t', ^3J(H,H) = 7.40 Hz, 1H), 7.26 ('t', ^3J(H,H) = 7.55 Hz, 1H), 7.40 ('t', ^3J(H,H) = 7.60 Hz, 1H), 7.46 ('t', ^3J(H,H) = 7.60 Hz, 1H), 7.54 (d, ^3J(H,H) = 8.15 Hz, 1H), 9.04 (d, ^3J(H,H) = 8.45 Hz, 1H), 9.08 (d, ^3J(H,H) = 8.45 Hz, 1H); ^{13}C NMR (125.76 MHz, $CDCl_3$, 25 °C): $\delta = -3.60$ (Si-CH_3), -3.22 (Si-CH_3), -3.13 (Si-CH_3), -2.96 (Si-CH_3), 14.73 (br, 2CH_3), 18.51 (CH_2), 18.64 (CH_2), 18.81 (CH_3), 19.03 (CH_3), 19.47 (CH_2), 19.54 (CH_2), 21.85 (Si-*C*(CH_3)$_3$), 21.97 (Si-*C*(CH_3)$_3$), 25.83 (Si-C(*C*H_3)$_3$), 25.86 (Si-C(*C*H_3)$_3$), 61.49, 62.41 (1- and 1′-OCH_3), 68.65, 69.09 (10- and 10′-OCH_3), 84.81, 85.29, 102.38, 102.80, 104.12, 104.58, 113.96, 114.62 (C_{aryl} ($Cr(CO)_3$)), 125.74, 126.21, 126.37, 126.50, 126.90, 126.99, 127.50, 127.84, 127.98, 128.19, 128.22, 129.13, 129.46, 130.33, 130.64, 130.67, 140.74, 140.77 (C_{aryl}), 147.00, 148.23 (C-10 and C-10′), 233.50, 233.90 ($Cr(CO)_3$); IR (PE): $\tilde{\nu} = 1958$ (vs, C=O, A_1^1), 1896, 1885 cm^{-1} (s, C=O, E); MS (FAB): m/z (%): 1119.3 ($[M+H]^+$, 41), 1034.3 ($[M-3CO]^+$, 81), 1006.3 ($[M-4CO]^+$, 48), 950.3 ($[M-6CO]^+$, 57), 898.5 ($[M-Cr(CO)_3-3CO]^+$, 100), 846.3 ($[M-2Cr(CO)_3]^+$, 30), $C_{58}H_{70}O_{12}Cr_2Si_2$ (1119.35): calcd C 62.24, H 6.30; found C 62.00, H 6.44.

The enantiomerically pure complexes (*S*)-**3a** and (*S*)-**3b** were prepared from the biscarbene complex (*S*)-**1** by the same procedure.

(*R*,*S*)-2,2′-3,3′-Tetraethyl-10,10′-dimethoxy-9,9′-bi(phenanthrene-1,4-dione) (4) and **(*R*,*S*)-3,3′-di-*n*-butyl-10,10′-dimethoxy-9,9′-bi(phenanthrene-1,4-dione) (5)**: 3-Hexyne (1-hexyne) (1.14 mL, 10 mmol) was added to a solution of the biscarbene complex (*R*,*S*)-**1** (0.78 g, 1 mmol) in THF (10 mL). The solution was stirred under reflux for 2 h and was subsequently cooled to room temperature. A solution of $(NH_4)_2[Ce(NO_3)_6]$ (7.67 g, 14 mmol) in nitric acid (28 mL, 0.1M) was then added, and the mixture was stirred for 2 h. After addition of diethyl ether (30 mL), the organic layer was separated, washed with saturated aqueous $NaHCO_3$ (10 mL) and water, dried over $MgSO_4$, and finally filtered. The solvent was evaporated and the residue was purified by column chromatography on silica gel.

(*R*,*S*)-**4**: Yellow foam; $R_f = 0.56$ (petroleum ether/diethyl ether, 3:1), yield = 0.33 g (0.56 mmol, 56%); ^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): $\delta = 1.18$ (t, ^3J(H,H) = 7.50 Hz, 6H; CH_3), 1.25 (t, ^3J(H,H) = 7.55 Hz, 6H; CH_3), 2.69 (m, 8H; CH_2), 3.51 (s, 6H; OCH_3), 7.12 (ddd, ^3J(H,H) = 8.50 Hz, ^4J(H,H) = 1.2 Hz, ^5J(H,H) = 0.6 Hz, 2H; 8,8′-H), 7.34 (ddd, ^3J(H,H) = 8.50 Hz, ^3J(H,H) = 6.75 Hz, ^4J(H,H) = 1.25 Hz, 2H; 7,7′-H), 7.58 (ddd, ^3J(H,H) = 8.90 Hz, ^3J(H,H) = 6.75 Hz, ^4J(H,H) = 1.35 Hz, 2H; 6,6′-H), 9.36 (ddd, ^3J(H,H) = 8.95 Hz, ^4J(H,H) = 1.1 Hz, ^5J(H,H) = 0.7 Hz, 2H; 5,5′-H); ^{13}C NMR (125.76 MHz, $CDCl_3$, 25 °C): $\delta = 13.91$ (CH_3), 13.97 (CH_3), 20.01 (CH_2), 20.28 (CH_2), 62.14 (OCH_3), 125.80, 126.80, 127.13, 128.37, 128.42, 128.91, 131.85, 133.73, 136.35 (C_{aryl}), 146.82 (C=C), 147.58 (C=C), 153.11 (C-10, C-10′), 185.43 (C=O), 188.82 (C=O); IR (CH_2Cl_2): $\tilde{\nu} = 1657$ cm^{-1} (vs, C=O); MS (70 eV, EI): m/z (%): 586.2 ($[M]^+$, 91), 571.1 ($[M-CH_3]^+$, 20), 555.1 ($[M-OCH_3]^+$, 100); HRMS (70 eV, EI): calcd for $C_{38}H_{34}O_6$ 586.2355; found 586.2367.

(*R*,*S*)-**5**: Orange foam; $R_f = 0.42$ (petroleum ether/diethyl ether, 3:1), yield = 0.21 g (0.36 mmol, 36%); ^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): $\delta = 0.97$ (t, ^3J(H,H) = 7.35 Hz, 6H; CH_3), 1.46 ('sex', ^3J(H,H) = 7.39 Hz, 4H; CH_2), 1.62 ('quin', ^3J(H,H) = 7.60 Hz, 4H; CH_2), 2.64 (td, ^3J(H,H) = 7.65 Hz, ^4J(H,H) = 1.09 Hz, 4H; CH_2), 3.50 (s, 6H; OCH_3), 6.71 (t, ^4J(H,H) = 1.19 Hz, 2H; 2,2′-H), 7.13 (br, d, ^3J(H,H) = 8.24 Hz, 2H; 8,8′-H), 7.35 (ddd, ^3J(H,H) = 8.34 Hz, ^3J(H,H) = 6.95 Hz, ^4J(H,H) = 1.24 Hz, 2H; 6,6′-H), 7.59 (ddd, ^3J(H,H) = 8.84 Hz, ^3J(H,H) = 6.80 Hz, ^4J(H,H) = 1.34 Hz, 2H; 7,7′-H), 9.37 (br, d, ^3J(H,H) = 8.85 Hz, 2H; 5,5′-H); ^{13}C NMR (125.76 MHz, $CDCl_3$, 25 °C): $\delta = 13.80$ (CH_3), 22.47 (CH_2), 29.02 (CH_2), 29.89 (CH_2), 62.10 (OCH_3), 125.73, 126.10, 127.37, 128.15, 128.60, 129.05, 131.88, 133.68, 134.20, 136.37 (C_{aryl}), 151.48, 153.06 (C-2, C-3), 185.01, 188.88 (C-1, C-4); IR (CH_2Cl_2): $\tilde{\nu} = 1659$ cm^{-1} (vs, C=O); MS (70 eV, EI): $m/z = 586.1$ (M^+, 58), 555.1 ($[M^+-OCH_3]^+$, 100), 513.1 ($[M-OCH_3-C_3H_6]^+$, 35); HRMS (70 eV, EI): calcd for $C_{38}H_{34}O_6$ 586.2355; found 586.2355.

(*R*,*S*)-6,6′-Dibromo-2,2′-3,3′-tetraethyl-10,10′-dihydroxy-9,9′-bi(phenanthrene-1,4-dione) (6): Boron tribromide (0.57 mL, 6 mmol) was added to a solution of bi(phenanthrenequinone) (*R*,*S*)-**4** (0.58 g, 1 mmol) in CH_2Cl_2 (10 mL) at −78 °C. The solution was stirred for 2 h at this temperature and for an additional 4 h at 25 °C. Water was added (20 mL) and the mixture was stirred vigorously for 2 h. After addition of CH_2Cl_2 (100 mL) the organic layer was separated, washed with water, dried over $MgSO_4$, and filtered. The solvent was evaporated and the residue was purified by column chromatography (silica gel, CH_2Cl_2, $R_f = 0.95$) to give a deep purple solid. Yield 0.22 g (0.31 mmol, 31%); ^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): $\delta = 1.19$ (t, ^3J(H,H) = 7.45 Hz, 6H; CH_3), 1.24 (t, ^3J(H,H) = 7.45 Hz, 6H; CH_3), 2.66 (m, 4H; CH_2), 2.74 (m, 4H; CH_2), 6.97 (d, ^3J(H,H) = 9.15 Hz, 2H; 8,8′-H), 7.40 (dd, ^3J(H,H) = 9.15 Hz, ^4J(H,H) = 1.90 Hz, 2H; 7,7′-H), 9.70 (d, ^4J(H,H) = 1.95 Hz, 2H; 5,5′-H), 12.50 (s, 2H; OH); ^{13}C NMR (125.76 MHz, $CDCl_3$, 25 °C): $\delta = 13.89$ (CH_3), 14.08 (CH_3), 19.53 (CH_2), 20.69 (CH_2), 118.20, 122.82, 125.00, 126.15, 126.26, 127.76, 130.60, 133.01, 136.05 (C_{aryl}), 145.56, 151.28 (C-2, C-3), 154.06 (C10), 187.06, 191.96 (C-1, C-4); IR (CH_2Cl_2): $\tilde{\nu} = 3212$ (s, O−H), 1653 (s, C=O), 1638 [vs, C=O), 1620 cm^{-1} (s, C=C); MS (FAB): m/z (%) 718.0 ($[M+2H]^+$, 100), 638 ($[M+2H-Br]^+$, 44%); $C_{36}H_{28}Br_2O_6$ (716.42): calcd C 60.35, H 3.94; found C 60.42, H 4.19.

6,7,11,12-Tetraethyl-5,8,10,13-tetrahydrodiphenanthro[9,10-b:9,10-d]furan-5,8,10,13-tetraone (7): TMSI (0.95 mL, 7 mmol) was added to a solution of bi(phenanthrenequinone) (*R*,*S*)-**4** (0.58 g, 1 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred at 25 °C for 48 h. Methanol (20 mL) was then added and the solution was stirred for an additional 5 h. The solvent was evaporated and the residue was dissolved in THF (20 mL). A solution of $(NH_4)_2[Ce(NO_3)_6]$ (16.3 g, 30 mmol) in nitric acid (60 mL, 0.1M) was added and the mixture was stirred for 2 h. After addition of diethyl ether (30 mL) a red solid formed at the phase boundary and was extracted to give pure product. The organic layer was separated, washed twice with water, dried over $MgSO_4$, and filtered. The solvent was then evaporated and the residue was purified by column chromatography (silica gel, CH_2Cl_2, $R_f = 0.66$) to give a bright red solid. Yield 0.195 g (0.36 mmol, 36%); ^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): $\delta = 1.26$ (m, 12H; CH_3), 2.77, 2.75 ('q', ^3J(H,H) = 7.55 Hz, 8H; CH_2), 7.78 (m, 4H; 1,17-H, 2,16-H), 8.94 (dd, ^3J(H,H) = 8.30 Hz, ^4J(H,H) = 1.09 Hz, 2H; 3,15-H), 9.49 (dd, ^3J(H,H) = 8.45 Hz, ^4J(H,H) = 1.39 Hz, 2H; 4,14-H); ^{13}C NMR (125.76 MHz, $CDCl_3$, 25 °C): $\delta = 14.12$ (CH_3), 14.14 (CH_3), 19.84 (CH_2), 20.63 (CH_2), 119.79, 124.31, 125.12, 127.77, 128.16, 128.52, 129.48, 129.88, 130.86 (C_{aryl}), 146.05, 148.82 (C=C), 152.47 (C-9a), 184.27, 187.85 (C=O), IR (CH_2Cl_2): $\tilde{\nu} = 1658$ cm^{-1} (s, C=O); MS (70 eV, EI): m/z (%): 540.2 ($[M]^+$, 100), 525.1 ($[M-CH_3]^+$, 3), 512.1 ($[M-C_2H_4]^+$, 9), 497.2 ($[M-C_2H_4-CH_3]^+$, 22), 469.1 ($[M-2C_2H_4-CH_3]^+$, 1); HRMS (70 eV, EI): calcd for $C_{36}H_{28}O_5$: 540.1937; found 540.1936.

2,2′-3,3′-Tetraethyl-10,10′-dihydroxy-9,9′-bi(phenanthrene-1,4-dione) (8): Dry aluminium trichloride (1.33 g, 10 mmol) was added to a solution of bi(phenanthrenquinone) (*R*,*S*)-**4** (0.58 g, 1 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred for 4 h at 25 °C, and then hydrochloric acid (40 mL, 1.0M) was added to the solution. The mixture was stirred vigorously overnight. After addition of diethyl ether the organic layer was separated, washed with saturated aqueous $NaHCO_3$ and water, dried over $MgSO_4$, and filtered. The solvent was evaporated and the residue was purified by column chromatography (silica gel, CH_2Cl_2, $R_f = 0.9$) to give a purple-black solid. Yield = 0.48 g (0.86 mmol, 86%); ^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): $\delta = 1.19$ (t, ^3J(H,H) = 7.56 Hz, 6H; CH_3), 1.24 (t, ^3J(H,H) = 7.55 Hz, 6H; CH_3), 2.62–2.80 (m, 8H; CH_2), 7.13 (br, d, ^3J(H,H) = 8.55 Hz, 2H; 8,8′-H), 7.33 (ddd, ^3J(H,H) = 8.58 Hz, ^3J(H,H) = 6.68 Hz, ^4J(H,H) = 1.26 Hz, 2H; 7,7′-H), 7.50 (ddd, ^3J(H,H) = 9.00 Hz, ^3J(H,H) = 6.71 Hz, ^4J(H,H) = 1.37 Hz, 2H; 6,6′-H), 9.40 (br, d, ^3J(H,H) = 8.95 Hz, 2H; 5,5′-H), 12.47 (s, 2H; OH); ^{13}C NMR (125.76 MHz, $CDCl_3$, 25 °C): $\delta = 13.90$ (CH_3), 14.06 (CH_3), 19.44 (CH_2), 20.63 (CH_2), 117.73, 124.89, 125.21, 125.49, 127.70, 128.51, 128.89, 129.51, 137.76 (C_{aryl}), 145.22, 151.09 (C-2, C-3), 153.68 (C-10), 187.62, 192.08 (C-1, C-4); IR (CH_2Cl_2): $\tilde{\nu} = 3213$ (s, O−H), 1652 (s, C=O), 1637 (vs, C=O), 1618 cm^{-1} (s, C=C); MS (FAB): m/z (%): 560.2 ($[M+2H]^+$, 61), 559.2 ($[M+H]^+$, 100), 558.2 ($[M]^+$, 71). The enantiomerically pure quinones (R)-**4**, (R)-**5**, (R)-**6**, and (R)-**8** were prepared from the biscarbene complex (R)-**1** by the same procedure.

X-ray structural analysis of 7:[29] $C_{36}H_{28}O_5 \cdot CHCl_3$, $M_r = 659.95\,g\,mol^{-1}$, triclinic space group $P\bar{1}$ (no. 2), red plates, crystal size $0.35 \times 0.18 \times 0.08$ mm, $Z = 2$, $a = 10.540(1)$, $b = 11.623(1)$, $c = 12.663(1)$ Å, $V = 1511.6(2)$ Å^3, $\alpha = 89.47(1)^\circ$, $\beta = 78.66(1)^\circ$, $\gamma = 83.67(1)^\circ$, $\rho_{calcd} = 1.450\,g\,cm^{-3}$, $\mu(Cu_{K\alpha}) = 3.121\,mm^{-1}$, $T = 200(2)$ K, 6130 reflections were collected, of which the 5682 symmetry-independent reflections were used for structure solution (direct methods)[30] and refinement (full-matrix least-squares on F^2, 461 parameters, 275 restraints),[31] non-hydrogen atoms were refined anisotropically. H atoms were located by difference electron density and treated as riding atoms ($wR_2 = 0.221$, $R_1 = 0.074$ for $I > 2.0\sigma(I)$). One quinone ring is partly disordered. An empirical absorption correction was made on the basis of Ψ-scans. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102614. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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