Enantioselective Approach to Both Enantiomers of Helical Bisquinones

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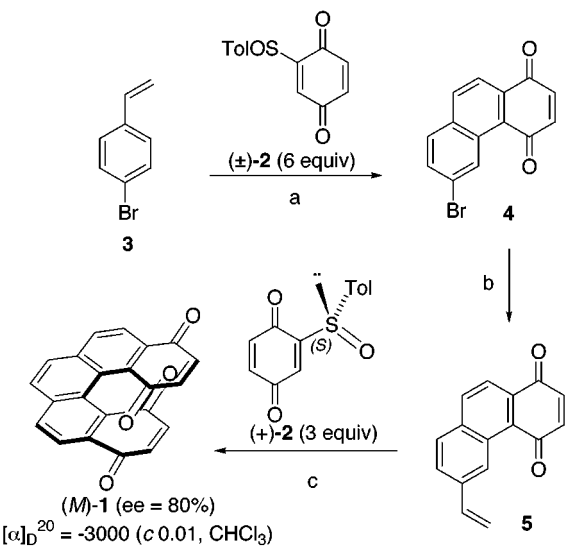
Molecular self-organization of helicoidal structures is a topic of increasing interest due to the exceptional properties that result in the associated species.[1] Molecules such as helicenebisquinones, which are organized spontaneously into columnar aggregates when the parent quinones are nonracemic,[1c−e] show enormous specific rotations. The circular dichroisms of absorptions associated with helical polymers synthesized from helicene bis(salicylaldehydes) and 1,2-phenylenediamine bound by a transition-metal salt are also very large.[2] The starting materials for such polymers are also homochiral helicenebisquinones.

The synthetic asymmetric approaches reported up to date to optically active helicenes are based on diastereoselective photocyclizations using chiral auxiliaries[3] and asymmetric metal-mediated coupling reactions.[4] These methods but one example[3a] suffer from low asymmetric induction. Classical,[5] chromatographic,[6] and enzymatic[7] resolutions have also been employed to prepare nonracemic helicenes.

The strategy described by Katz, based on a double Diels−Alder cycloaddition between 1,4-quinones and 1,4-divinylarenes, allows for the rapid and efficient construction of racemic helicenebisquinones.[5h,j,7a,8] As a part of our research program involving Diels−Alder reactions of enantiomerically pure sulfinylquinones, we have developed the tandem [4+2] cycloaddition/pyrolytic sulfoxide elimination as a general one pot strategy to enantiomerically enriched polycyclic dihydroquinones.[9] Our results showed a high ability of the sulfoxide to control the regiochemistry and π-facial diastereoselectivity of the process, being the quinone moiety responsible for the complete *endo* selectivity achieved. The tandem sequence could be applied to the synthesis of optically active helicenebisquinones such as **1** (Scheme 1), provided that vinylarenes reacted in a diastereoselective manner with homochiral (*SS*)-(2-*p*-tolylsulfinyl)-1,4-benzoquinone (**2**). Our approach shows an additional advantage over those previously reported because the spontaneous elimination of the sulfoxide in the initially formed adduct facilitates further aromatization that can be completed by an excess of sulfinylquinone. In this paper, we report the first enantioselective approach to helical bisquinones utilizing the asymmetric Diels−Alder reaction as the key step to achieve the proper absolute sterochemistry.

Scheme 1[a]



[a] (a) 12 Kbar, CH_2Cl_2, 2 d, 53%; (b) CH_2=$CHSnBu_3$, $Pd(PPh_3)_4$, toluene, 110 °C, 5 h, 40%; (c) 4 Kbar, CH_2Cl_2, 7 d, 22%.

Results and Discussion

Initially, we attempted a one-pot strategy to **1** based on a double cycloaddition between (*SS*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone (**2**)[10] and *p*-divinylbenzene. Unfortunately, the expected helical quinone **1** was not detected

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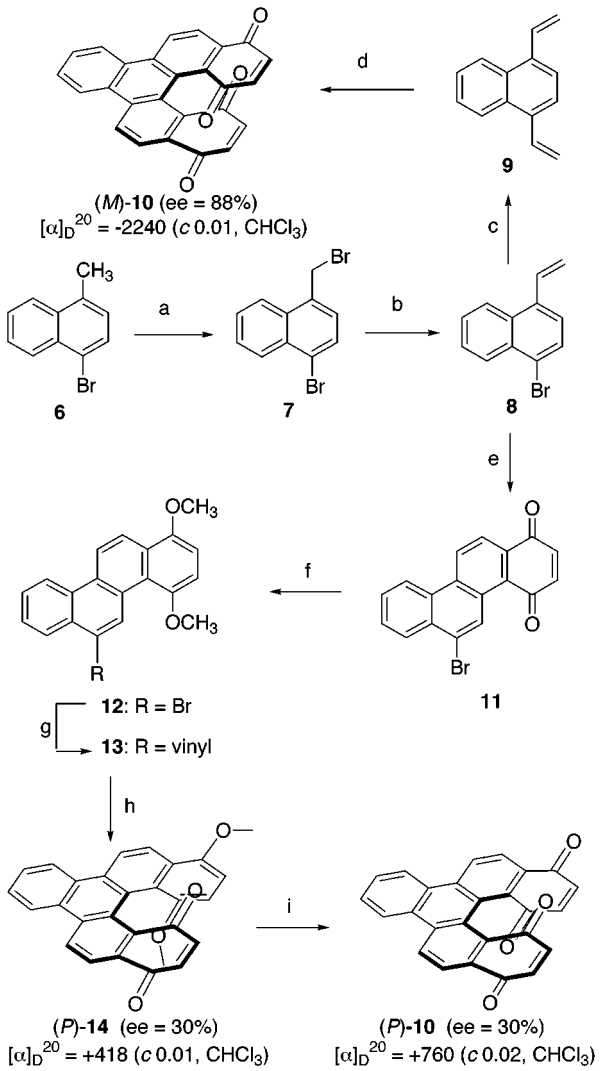
either under reflux of high boiling solvents or high pressures or in the presence of different Lewis acid calalysts. This disappointing result prompted us to develop a stepwise and more versatile route to optically active **1** (Scheme 1).

Thus, the cycloaddition of commercially available *p*-bromostyrene (**3**) with an excess[11] of racemic sulfinylquinone **2**[10] under high-pressure conditions afforded 6-bromo-1,4-phenanthrenequinone (**4**).[12] Neither the initial Diels−Alder adduct nor the pyrolyzed (-TolSOH) intermediate was detected. The presence of the sulfoxide in **2** was essential to increase the reactivity of the dienophile, because no reaction occurred when compound **3** was treated with 1,4-benzoquinone as dienophile under the same conditions. Compound **4** was transformed into 6-vinyl-1,4-phenanthrenequinone (**5**) after Stille coupling[13] with vinyltributyltin. Diels−Alder cycloaddition of **5** with enantiomerically pure **2** under high-pressure conditions, gave helicenebisquinone *(M)*-**1**[14,15] in optically active form {$[\alpha]^{20}_D = -3000$ (*c* 0.01, $CHCl_3$), 80% ee}. The absolute configuration of (−)-**1** was assigned as *(M)* according to the well-established stereochemical outcome of these cycloadditions and by comparison with the sign of the optical rotation of other helicenes.[16]

To extend these good results, we thought of using 1,4-divinylnaphthalene (**9**) as the diene partner. As depicted in Scheme 2, compound **9** was obtained from commercially available 1-bromo-4-methylnaphthalene (**6**) after benzylic bromination, Wittig reaction, and Stille coupling with vinyltributyltin. Thus, 1,4-divinylnaphthalene (**9**) could be synthesized in three steps and 49% overall yield from compound **6**. Cycloaddition of sulfinylquinone (+)-**2** and **9** under high-pressure conditions provided helicenebisquinone (*M*)-**10** {$[\alpha]^{20}_D = -2240$ (*c* 0.01, $CHCl_3$)}. The ee of (−)-**10** could not be evaluated at this stage due to its low solubility in all tested solvents.[17]

As outlined in Scheme 2, this methodology was extended to a differently substituted helicenequinone. Thus, 1-bromo-4-methylnaphthalene (**8**) reacted with racemic sulfinylquinone **2**[18] under thermal conditions to afford 6-bromo-1,4-chrysenequinone (**11**), which after reduction and methylation was transformed into 6-bromo-1,4-dimethoxychrysene (**12**). Further treatment of **12** with vinyltributyltin under the Stille coupling conditions gave rise to 6-vinyl-1,4-dimethoxychrysene (**13**). Diels−Alder reaction of **13** with (+)-**2** yielded optically active helicenequinone (*P*)-**14** {$[\alpha]^{20}_D = +418$ (*c* 0.01, $CHCl_3$)}. Interestingly, the sign of the optical rotation for (+)-**14** was opposite to that obtained for derivatives (−)-**1** and (−)-**10**. This new helicenequinone **14** shows a proximal disposition between a donor and an acceptor moiety, enabling an intra- and intermolecular stacking between the electron-rich and electron-poor rings.[19] Compound **14** was soluble in many solvents[17] and a 30% ee could be measured from a ^{1}H NMR study using $Pr(hfc)_3$ as chiral lanthanide shift reagent.[20] The transformation of (+)-**14** into the helicenebisquinone (*P*)-**10** {$[\alpha]^{20}_D = +760$ (*c* 0.01, $CHCl_3$), 30% ee} was achieved from CAN oxidation. Assuming that no racemization occurred during the oxidation step, an 88% ee could be calculated for the helicenebisquinone (*M*)-**10** previously obtained from 1,4-divinylnaphthalene (**9**).

Scheme 2[a]



[a] (a) NBS, benzoyl peroxide, CCl_4, 80 °C, 3 h, 85%; (b) i. PPh_3, acetone, 60 °C, 4 h; ii. CH_2O, NaOH, rt, 3 h, 89%; (c) CH_2=$CHSnBu_3$, $Pd(PPh_3)_4$, toluene, 110 °C, 2 h, 65%; (d) (+)-**2** (6 equiv), 4 Kbar, CH_2Cl_2, 4 d, 12%. (e) (±)-**2** (3 equiv), toluene, 110 °C, 2 h, 84%; (f) i. $Na_2S_2O_4$, Et_2O, rt; ii. Me_2SO_4, K_2CO_3, acetone, 60 °C, 24 h, 45%; (g) CH_2=$CHSnBu_3$, $Pd(PPh_3)_4$, toluene, 110 °C, 4 h, 63%; (h) (+)-**2** (3 equiv), 12 Kbar, CH_2Cl_2, 48 h, 41%; (i) CAN, CH_3CN/H_2O, rt, 2 h, 59%.

(11) An excess (3 or 6 equiv) of the sulfinylquinone was always necessary to dehydrogenate the corresponding dihydroquinonic intermediates into the aromatic systems.

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(14) The ee of (−)-**1** was determined from its optical rotation in CH_3CN, {$[\alpha]^{20}_D = -2680$ (*c* 0.01)}, if compared with that calculated by Katz, {$[\alpha]^{20}_D = +3358$ (*c* 0.01, CH_3CN)}, for enantiomerically pure (+)-**1** in ref 7a.

(15) The half-life for racemization of nonracemic **1** is ca. 1 h at 75 °C (see ref 5h).

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(17) Low solubility of unsubstituted helicenebisquinones is a frequent handicap for their further application in polymer synthesis.

(18) When the same reaction was carried out with 6 equiv of 1,4-benzoquinone (CH_3CN, 80 °C, 48 h) the yield was lower (69%).

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(20) The racemic helicene **14** necessary for such evaluation was prepared from racemic sulfinylquinone **2**.

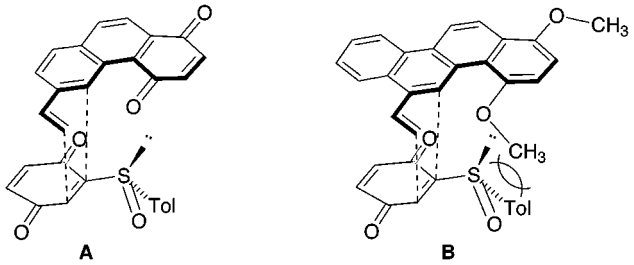

Figure 1. *Endo* approaches of vinylarenes on the *s-cis* conformation of sulfinylquinone (+)-**2**.

According to the model proposed for (S*S*)-*p*-tolylsulfinylquinone cycloadditions,[9b−d,g] the (*M*) absolute configuration of helicenes (−)-**1** and (−)-**10** must result from the *endo* approach of the vinylarene toward the less encumbered face of the quinone, which bears the lone electron pair at sulfur in the *s-cis* conformation of (+)-**2** (**A** in Figure 1). Although the formation of helicene (+)-**14** with (*P*) configuration is not easy to rationalize, an inspection of molecular models revealed an unfavorable interaction between the OMe group at C-4 of approaching **13** and the sulfinylic oxygen of (+)-**2** (**B** in Figure 1), which could be responsible for the inversion of the π-facial diastereoselectivity observed. A likely evolution of an *s-trans* conformation of (+)-**2** from the less sterically demanding face could be the origin of this result.

In summary, a direct and easy access to enantioenriched helicenebisquinones *(M)*-**1** and antipodal *(M)*- and *(P)*-**10** is reported. Our synthesis features their preparation using sulfinylquinone (+)-**2** to effect the asymmetric Diels−Alder reactions with vinylarenes in a highly stereoselective manner.

Experimental Section

Melting points were obtained in open capillary tubes and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz, respectively. All reactions were monitored by thin-layer chromatography that was performed on precoated sheets of silica gel 60, and flash column chromatography was done with silica gel 60 (230−400 mesh) from Macherey-Nagel. Eluting solvents are indicated in the text. The apparatus for inert atmosphere experiments was dried by flaming in a stream of dry argon. CH_2Cl_2 was dried over P_2O_5. For routine workup, hydrolysis was carried out with water, extractions with CH_2Cl_2, and solvent drying with Na_2SO_4. High-pressure reactions were performed in a Unipress Equipment 101LV 30/16 in polyethylene vials.

General Procedure for High-Pressure Diels−Alder Reactions, Method A. A mixture of excess of (*SS*)-(2-*p*-tolylsulfinyl)-1,4-benzoquinone (**2**) and the corresponding vinylarene (0.1 mmol) in dry CH_2Cl_2 (1 mL) was submitted to high-pressure conditions. After the time required in each case and evaporation of the solvent, the crude product was obtained.

General Procedure for Stille Cross-Coupling Reactions, Method B. A mixture of the corresponding bromoarene (0.5 mmol), tributylvinylstannane (1 mmol), $Pd(PPh_3)_4$ (0.02 mmol), and one crystal of 4-*tert*-butylcatechol in 10 mL of toluene was refluxed for 2−5 h under argon in the dark. The mixture was treated with saturated aqueous KF solution and extracted with EtOAc. After workup, the crude product was obtained.

6-Bromo-1,4-phenanthrenequinone (4). Compound **4** was obtained from commercially available 1-bromo-4-vinylbenzene (**3**) and 6 equiv of (±)-**2** following method A at 4 Kbar for 2 d, after flash chromatography (eluent, CH_2Cl_2/hexane 50:50), in 53% yield: mp 179−180 °C (MeOH); ^{1}H NMR δ 9.79 (m, 1H), 8.18 (d, 1H, J = 8.6 Hz), 8.13 (dd, 1H, J = 0.6 and 8.6 Hz), 7.78 (dd, 1H, J = 1.1 and 8.8 Hz), 7.73 (dd, 1H, J = 1.7 and 8.8 Hz), 7.01 and 6.96 (AB system, 2H, J = 10.2 Hz); ^{13}C NMR δ 187.45, 185.36, 140.40, 135.79, 134.91, 134.72, 132.54, 132.10, 130.53, 130.01, 129.90, 125.82, 125.27, 122.26.

6-Vinyl-1,4-phenanthrenequinone (5). Compound **5** was obtained from **4** following method B for 5 h, after flash chromatography (eluent, CH_2Cl_2/hexane 50:50), in 40% yield: ^{1}H NMR δ 9.48 (broad s, 1H, H_5), 8.18 (s, 2H, H_9 and H_{10}), 7.81 (m, 2H, H_7 and H_8), 6.97 (dd, 1H, J = 11.0 and 18.0 Hz), 6.95 (m, 2H), 5.98 (d, 1H, J = 18.0 Hz), 5.46 (d, 1H, J = 11.0 Hz).

Helicenebisquinone (*M*)-1. Compound (*M*)-**1** was obtained from **5** and 3 equiv of (+)-**2** following method A at 4 Kbar for 7 d, after flash chromatography (eluent, CH_2Cl_2), in 22% yield: mp >300 °C; ^{1}H NMR δ 8.27 (d, 2H, J = 8.3 Hz), 8.09 (d, 2H, J = 8.3 Hz), 7.84 (s, 2H), 6.98 (d, 2H, J = 10.1 Hz), 6.87 (d, 2H, J = 10.1 Hz); EI-MS *m*/*z* (%) 338 (M^+, 100), 282 (48), 256 (75), 200 (38), 100 (26); HRMS (EI) calcd for $C_{22}H_{10}O_4$ 338.05791, found 338.05859.

1-Bromo-4-bromomethylnaphthalene (7). A mixture of commercially available 1-bromo-4-methylnaphthalene (**6**) (1 g, 4.5 mmol), *N*-bromosuccinimide (966 mg, 5.4 mmol), and benzoyl peroxide (73 mg, 0.3 mmol) in CCl_4 (15 mL) was refluxed for 3 h. After workup and crystallization (hexane), compound **7** was obtained in 85% yield: mp 102−104 °C; ^{1}H NMR δ 8.32 and 8.15 (2m, 2H), 7.70 (m, 2H), 7.66 and 7.39 (AB system, 2H, J = 7.5 Hz), 4.92 (s, 2H); ^{13}C NMR δ 133.24, 132.31, 132.05, 129.47, 127.95, 127.79, 127.50, 127.36, 124.41, 124.12, 30.93. Anal. Calcd for $C_{11}H_8Br_2$: C, 44.31; H, 2.71; Br, 47.02. Found: C, 44.58; H, 2.56; Br, 46.98.

1-Bromo-4-vinylnaphthalene (8). A solution of **7** (1.14 g, 3.8 mmol) and PPh_3 (1 g, 3.8 mmol) in 50 mL of acetone was refluxed for 4 h. After evaporation of the solvent, the crude phosphonium bromide was obtained. To a mixture of 17.9 mL of formaldehyde (37% aqueous solution) and 3.8 mmol of the above obtained phosphonium bromide in H_2O (10 mL) was slowly added a solution of 1.43 g of NaOH in H_2O (7 mL). After 3 h, the mixture was extracted with CH_2Cl_2. After workup and flash chromatography (eluent, hexane), compound **8** was obtained as a colorless liquid in 89% yield: ^{1}H NMR δ 8.29 and 8.12 (2m, 2H), 7.58 (m, 2H), 7.78 and 7.45 (AB system, 2H, J = 8.0 Hz), 7.58 (dd, 1H, J = 11.3 and 17.2 Hz), 5.80 (dd, 1H, J = 1.6 and 17.2 Hz), 5.54 (dd, 1H, J = 1.6 and 11.3 Hz); ^{13}C NMR δ 135.14, 133.24, 131.75, 131.47, 129.45, 127.29, 126.70, 126.36, 123.71, 123.52, 122.43, 117.36.

1,4-Divinylnaphthalene (9). Compound **9** was obtained from **8** following method B for 2 h, after flash chromatography (eluent, hexane), in 65% yield: ^{1}H NMR δ 8.19 (dd, 2H, J = 3.2 and 6.4 Hz), 7.66 (s, 2H), 7.57 (dd, 2H, J = 3.2 and 6.4 Hz), 7.53 (dd, 2H, J = 11.0 and 17.2 Hz), 5.84 (dd, 2H, J = 1.6 and 17.2 Hz), 5.52 (dd, 2H, J = 1.6 and 11.0 Hz); ^{13}C NMR δ 135.51, 134.34, 131.10, 125.86, 124.21, 123.48, 116.99.

Helicenebisquinone (*M*)-10. Compound (*M*)-**10** was obtained from **9** and 6 equiv of (+)-**2** following method A at 4 Kbar for 4 d, after flash chromatography (eluent, CH_2Cl_2), in 12% yield: mp >300 °C; ^{1}H NMR δ 8.84 (d, 2H, J = 8.6 Hz), 8.60 (m, 2H), 8.34 (d, 2H, J = 8.6 Hz), 7.80 (m, 2H), 6.98 (d, 2H, J = 10.1 Hz), 6.84 (d, 2H, J = 10.1 Hz); EI-MS *m*/*z* (%) 388 (M^+, 19), 306 (12), 254 (43), 248 (49), 149 (100), 77 (61). Anal. Calcd for $C_{26}H_{12}O_4$: C, 80.40; H, 3.11. Found: C, 80.17; H, 3.30.

6-Bromo-1,4-chrysenequinone (11). A solution of **8** (783 mg, 3.4 mmol) and (±)-**2** (2.46 g, 10 mmol) in toluene (20 mL) was refluxed for 2 h. After evaporation of the solvent and precipitation in MeOH, pure **11** was obtained in 84% yield: mp 240−245 °C (MeOH); ^{1}H NMR δ 9.93 (d, 1H, J = 0.8 Hz), 9.05 (d, 1H, J = 8.8 Hz), 8.72 (m, 1H), 8.42 (m, 1H), 8.37 (d, 1H, J = 8.8 Hz), 7.80 (m, 2H), 7.04 and 6.99 (AB system, 2H, J = 10.1 Hz); ^{13}C NMR δ 187.73, 185.26, 140.99, 136.14, 134.16, 132.26, 131.00, 130.05, 129.74, 129.39, 128.84, 128.35, 128.32, 128.08, 127.75, 126.06, 123.71, 123.47; EI-MS *m*/*z* (%) 338 (M^+ + 2, 96), 336 (M^+, 95), 257 (100), 254 (22), 200 (35), 175 (24), 149 (19), 128 (21). Anal. Calcd for $C_{18}H_9BrO_2$: C, 64.29; H, 2.70; Br, 23.49. Found: C, 64.05; H, 2.91; Br, 23.60.

6-Bromo-1,4-dimetoxychrysene (12). A mixture of compound **11** (760 mg, 2.25 mmol) in 150 mL of ethyl ether and sodium dithionite (3.82 g, 22.5 mmol) in 150 mL of H_2O was vigorously shaken in a separatory funnel for 10 min. After separation of the organic layer and workup, the corresponding crude hydroquinone was obtained and used without further

purification. To a suspension of the above obtained hydroquinone (763 mg, 2.25 mmol) in 50 mL of acetone were added Me_2SO_4 (0.85 mL, 9.0 mmol) and K_2CO_3 (4.6 g, 33.7 mmol). After refluxing for 24 h, the mixture was diluted with water and extracted with CH_2Cl_2. After workup and flash chromatography (eluent, CH_2Cl_2/hexane 40:60), compound **12** was obtained in 45% yield: ^{1}H NMR δ 10.18 (s, 1H), 8.81 and 8.42 (2m, 2H), 8.72 and 8.50 (AB system, 2H, J = 9.4 Hz), 7.73 (m, 2H), 7.08 and 6.95 (AB system, 2H, J = 8.6 Hz), 4.11 and 4.03 (2s, 6H); ^{13}C NMR δ 152.30, 149.70, 130.88, 130.77, 130.09, 128.82, 128.65, 127.48, 127.24, 126.78, 125.51, 123.52, 121.42, 121.37, 120.90, 108.17, 105.45, 56.20, 55.92; EI-MS m/z (%) 368 (M^+ + 2, 99), 336 (M^+, 100), 353 (34), 351 (34), 272 (36), 257 (75), 136 (23), 77 (29); HRMS (EI) calcd for $C_{20}H_{15}BrO_2$ 366.02554, found 366.02588.

6-Vinyl-1,4-dimetoxychrysene (13). Compound **13** was obtained from **12** following method B for 4 h, after flash chromatography (eluent, CH_2Cl_2/hexane 40:60), in 63% yield: ^{1}H NMR δ 9.90 (s, 1H, H_5), 8.86 and 8.26 (2m, 2H), 8.76 and 8.47 (AB system, 2H, J = 9.3 Hz), 7.69 (m, 2H), 7.63 (dd, 1H, J = 11.0 and 17.3 Hz), 7.10 and 6.97 (AB system, 2H, J = 8.6 Hz), 6.02 (dd, 1H, J = 1.8 and 17.3 Hz), 5.57 (d, 1H, J = 1.8 and 11.0 Hz), 4.11 and 4.04 (2s, 6H); ^{13}C NMR δ 152.73, 150.03, 135.76, 133.42, 130.18, 129.87, 129.25, 128.26, 126.36, 125.99, 125.57, 124.63, 123.98, 123.80, 122.56, 121.16, 120.87, 116.80, 108.75, 105.28, 56.57, 56.01; EI-MS m/z (%) 388 (M^+, 19), 306 (12), 254 (43), 248 (49), 149 (100), 77 (61); HRMS (EI) calcd for $C_{22}H_{18}O_2$ 314.13068, found 314.13022.

Helicenequinone (*P*)-14. Compound (*P*)-**14** was obtained from **13** and 3 equiv of (+)-**2** following method A at 12 Kbar for 2 d, after flash chromatography (eluent, CH_2Cl_2), in 41% yield: mp >300 °C; ^{1}H NMR δ 8.89 and 8.34 (AB system, 2H, J = 8.6 Hz), 8.72−8.60 (m, 4H), 7.75 (m, 2H), 6.93 and 6.75 (AB system, 2H, J = 10.2 Hz), 6.91 and 6.82 (AB system, 2H, J = 8.6 Hz), 4.05 and 3.51 (2s, 6H); ^{13}C NMR δ 185.70, 183.66, 150.37, 148.66, 140.10, 135.87, 135.72, 134.06, 131.95, 130.98, 128.77, 128.73, 127.69, 127.59, 126.53, 125.27, 124.58, 124.44, 123.78, 123.75, 123.55, 123.01, 122.78, 119.78, 106.77, 104.67, 55.82, 55.40; EI-MS m/z (%) 314 (M^+, 100), 299 (40), 284 (15), 255 (13), 226 (11), 202 (10), 149 (59), 84 (75); HRMS (EI) calcd for $C_{28}H_{18}O_4$ 418.12051, found 418.12076.

Helicenebisquinone (*P*)-10. To a solution of (*P*)-**14** (12.5 mg, 0.03 mmol) in CH_3CN (1 mL) was added CAN (40 mg, 0.075 mmol) in H_2O (1 mL). The mixture was stirred for 2 h, and after workup and flash chromatography (eluent, CH_2Cl_2), compound (*P*)-**10** was obtained in 59% yield.

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Supporting Information Available: Copies of ^{1}H NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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