SUPPORTING INFORMATION FOR


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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 which was performed on precoated sheets of silica gel 60, and flash column chromatography was done with silica gel 60 (230-400 mesh) unless specified. Eluting solvents are indicated in the text. The apparatus for inert atmosphere experiments was dried by flaming in a stream of dry argon. CH$_2$Cl$_2$, toluene and THF were dried with 4 A molecular sieves previously activated by calefaction in a microwave oven. All other reagent quality solvents were used without purification. For routine workup, hydrolysis was carried out with water, extractions with CH$_2$Cl$_2$, and solvent drying with MgSO$_4$.

6-Methoxy-3,3(ethylenedioxy)-1,2,3,4,9,10-hexahydrophenanthrene (5)
A 2.3 g (10 mmol) sample of 3-keto-6-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (4) was treated with 1.8 mL (32.22 mmol) of ethylene glycol in 20 mL of refluxing toluene containing 12 mg of p-toluenesulfonic acid for 2 d until formation of water (Dean-Stark trap) ceased. The toluene layer was washed with water and, after workup, compound 5 was obtained as a red oil (2.9 g, quantitative yield), which was used in the next step without further purification: $^1$H NMR $\delta$ 7.11 (d, $J = 8.1$ Hz, 1H), 6.82 (d, $J = 2.8$ Hz, 1H), 6.75 (dd, $J = 8.1$ and 2.7 Hz, 1H), 4.15-4.05 (m, 4H), 3.87 (s, 3H), 2.82 (t, $J = 8.1$ Hz, 2H), 2.74 (s, 2H), 2.53-2.49 (m, 2H), 2.33-2.27 (m, 2H), 1.97-1.93 (m, 2H); $^{13}$C NMR $\delta$ 158.2, 136.7, 133.5, 128.0, 127.4, 127.1, 110.2, 108.5, 107.8, 64.2 (2C), 54.9, 35.4, 30.9, 29.8, 28.6, 27.0; MS (EI): m/z (%) 272 (M$^+$, 79), 257 (16), 227 (8), 211 (18), 199 (5), 186 (100), 171 (33), 165 (8), 155 (20), 141 (13), 128 (21), 115 (16), 99 (5), 86 (16); HRMS (EI) calcd for C$_{17}$H$_{20}$O$_3$ (M$^+$) 272.14059, found 272.14124.

6-Methoxy-3,3(ethylenedioxy)-1,2,3,4-tetrahydrophenanthrene (6)

DDQ (5.1 g, 22 mmol) in CH$_2$Cl$_2$ (100 ml) was added to a solution of 5 (5.1 g, 18 mmol) in CH$_2$Cl$_2$ (100 ml). The mixture was stirred at room temperature for 15 min, diluted with CH$_2$Cl$_2$, and washed several times with NaHCO$_3$. After several extractions with CH$_2$Cl$_2$, elimination of the solvent and flash chromatography (hexane/CH$_2$Cl$_2$ 1:5), compound 6 (4.1 g, 85% yield) was obtained as a white solid: mp 80–81 ºC; $^1$H NMR $\delta$ 7.76 (d, $J = 9.3$ Hz, 1H), 7.63 (d, $J = 8.5$ Hz, 1H), 7.21-7.16 (m, 3H), 4.16-4.04 (m, 4H), 3.95 (s, 3H), 3.35 (s, 2H), 3.20-3.16 (m, 2H), 2.12-

2.07 (m, 2H); $^{13}$C NMR $\delta$ 157.6, 133.2, 132.9, 129.6, 127.5, 127.1, 125.7, 124.7, 116.7, 108.4, 101.3, 64.2 (2C), 54.9, 36.3, 31.1, 28.6; MS (EI): m/z (%) 270 (M+, 51), 198 (7), 184 (100), 165 (14), 141 (14), 115 (9); HRMS (EI) calcd for C$_{17}$H$_{18}$O$_{3}$ (M$^+$) 270.12543, found 270.12559.

1,2,4,5,7,8-Hexahydrophenanthrene-3,6-dione (7)

![Chemical Structure 7](image)

Sodium was added in small portions, under vigorous stirring, to a solution of 6 (560 mg, 2.1 mmol) in 25 ml of EtOH (HPLC grade) heated at 90 ºC. The addition rate must be adapted to achieve that several pieces of sodium of middle size must be always present in the reaction mixture. The reaction was monitored by TLC until complete extinction of the starting material. After 90 min, EtOH was added and the mixture was stirred until the consumption of all sodium. The mixture was cooled to room temperature and the flask was introduced in a ice bath. HCl was added to bring pH acid and, after 5 min at 0 ºC, the reaction mixture was warmed to room temperature and stirred for 15 min. After several extractions with CH$_2$Cl$_2$, the organic phases were neutralized with saturated aqueous NaHCO$_3$. After workup and flash chromatography (CH$_2$Cl$_2$/EtOAc 9:1), compound 7 was obtained as a pale-brown solid, in 90% yield: mp 140–141 ºC; $^1$H NMR $\delta$ 7.15 (s, 2H), 3.49 (s, 4H), 3.13-3.04 (m, 4H), 2.64-2.59 (m, 4H); $^{13}$C NMR $\delta$ 210.2, 135.6, 131.9, 126.9, 41.8, 39.0, 29.4; MS (EI): m/z (%) 214 (M$^+$, 73), 172 (100), 144 (18), 130 (59), 115 (24), 97 (5), 84 (22), 71 (14); HRMS (EI) calcd for C$_{14}$H$_{14}$O$_{2}$ (M$^+$) 214.09943, found 214.09938.
3,6-Bis[(trifluoromethanesulfonyl)oxy]-1,2,7,8-tetrahydrophenanthrene (8)

![Chemical structure of 8]

A solution of 0.5M KHMDS in toluene (3.42 mL, 1.71 mmol) was added to a solution of 7 (183 mg, 0.8 mmol) and N-phenyl-bis-trifluoromethanesulfonylmide (611 mg, 1.71 mmol) in dry THF (14 mL) at –78 ºC under argon. The mixture was stirred for 2 h and quenched with H₂O. After workup and flash chromatography (hexane/EtOAc 9:1), compound 8 (249 mg, 65%) was obtained as a white solid: mp 56–57 ºC; ¹H NMR δ 7.01 (s, 2H), 6.65 (s, 2H), 3.05-2.97 (m, 4H), 2.70-2.62 (m, 4H); ¹³C NMR δ 151.3, 132.2, 127.6, 127.2, 114.0, 28.9, 26.3; MS (EI): m/z (%) 478 (M⁺, 27), 345 (88), 317 (5), 212 (100), 184 (45), 155 (27), 69 (47); HRMS (EI) calcd for C₁₆H₁₂O₆F₆S₂ (M⁺) 477.99570, found 477.99795.

3,6-Divinyl-1,2,7,8-tetrahydrophenanthrene (2a)

![Chemical structure of 2a]

To a stirred solution of compound 8 (339 mg, 0.71 mmol) in dry THF (15 mL), containing LiCl (300 mg, 7.08 mmol) and [Pd(PPh₃)₄] (65 mg, 0.05 mmol), vinyltributylstannane (0.41 mL, 1.42 mmol) was added under argon. The mixture was refluxed for 4.5 h, diluted with hexane (50 mL) and washed with 10% aqueous NH₄OH solution, water and brine. After workup and flash chromatography (hexane), compound 2a was obtained as a white solid, in 86% yield: mp 78–79 ºC; ¹H NMR δ 6.97 (s, 2H), 6.89 (s, 2H), 6.72 (dd, J = 18 and 10.5 Hz, 2H), 5.43 (d, J = 18 Hz, 2H), 5.23 (d, J = 10.5 Hz, 2H), 2.89–2.84 (m, 4H), 2.52–2.47 (m, 4H); ¹³C NMR δ 138.9, 138.6,
134.5, 129.8, 125.7, 123.9, 112.7, 28.3, 22.1; MS (EI): m/z (%): 234 (M+, 100), 205 (7), 193 (26), 178 (16), 165 (18), 152 (8), 84 (16), 71 (5); HRMS (EI) calcd for C_{18}H_{18} (M+) 234.13982, found 234.14085.

3,6-Bis(1-ethoxyvinyl)-1,2,7,8-tetrahydrophenanthrene (2b)

![Structure 2b]

To a stirred solution of compound 8 (206 mg, 0.43 mmol) in dry THF (9 mL), containing LiCl (233 mg, 5.47 mmol) and [Pd(PPh_{3})_{4}] (45 mg, 0.04 mmol), (1-ethoxyvinyl)tributylstannane (0.33 mL, 0.86 mmol) was added under argon. The mixture was refluxed for 5.5 h, diluted with hexane (30 mL) and washed with 10% aqueous NH_{4}OH solution, water and brine. After workup and flash chromatography (hexane) using alumina deactivated with 10% water as the stationary phase, compound 2b was obtained as a very unstable white solid, in 35% yield: {^1}H NMR δ 7.52 (s, 2H), 6.92 (s, 2H), 4.45 (d, J = 2.1 Hz, 2H), 4.24 (d, J = 2.1 Hz, 2H), 3.89 (q, J = 7.0 Hz, 4H), 2.85-2.77 (m, 4H), 2.49-2.41 (m, 4H), 1.45 (t, J = 7.0 Hz, 6H).

3,6-Bis(1-oxoethyl)-1,2,7,8-tetrahydrophenanthrene (9)

![Structure 9]

To a stirred solution of compound 8 (159 mg, 0.31 mmol) in dry THF (8 mL), containing LiCl (138 mg, 3.15 mmol) and [Pd(PPh_{3})_{4}] (31 mg, 0.02 mmol), (1-ethoxyvinyl)tributylstannane (0.20 mL, 0.64 mmol) was added under argon. The mixture was refluxed for 5.5 h. After elimination of the solvent and flash chromatography (CH_{2}Cl_{2}, then CH_{2}Cl_{2}/EtOAc 1:1), compound 9 (60 mg,
75%) was obtained as a white solid: mp 130-132 °C; $^1$H NMR δ 7.94 (s, 2H), 7.40 (s, 2H), 2.97–2.90 (m, 4H), 2.74-2.68 (m, 4H), 2.64 (s, 6H); $^{13}$C NMR δ 198.5, 139.9, 136.6, 131.5, 130.13, 129.0, 28.1, 25.7, 21.0; MS (EI): m/z (%) 266 (M$^+$, 100), 251 (45), 233 (78), 179 (66), 165 (32), 149 (24), 97 (11), 69 (30); HRMS (EI) calcd for C$_{18}$H$_{18}$O$_2$ (M$^+$) 266.13089, found 266.13068.

3,6-Bis[1-(tert-butylidimethylsiloxy)vinyl]-1,2,7,8-tetrahydrophenanthrene (2c)

![Structure of 2c]

To a stirred solution of bis-ketone 9 (36 mg, 0.14 mmol) in dry THF (2.4 mL) at -78 °C was added under argon a solution of 0.5 M KHMDS in toluene (0.58 mL, 0.29 mmol), followed by tert-butylidimethylsilyl trifluoromethanesulfonate (0.07 mL, 0.28 mmol). After 1 h, hexane (1.5 mL) was added and the mixture was washed with NaOH 1M. After workup, compound 2c (71 mg, 93%) was obtained as a yellow solid and used in the next step without further purification: $^1$H NMR δ 7.28 (s, 2H); 6.92 (s, 2H), 4.67 (s, 2H), 4.41 (s, 2H), 2.82-2.72 (m, 4H), 2.48-2.38 (m, 4H), 1.01 (s, 18H), 0.22 (s, 12H); MS (EI): m/z (%) 494 (M$^+$, 73), 438 (38), 382 (27), 308 (38), 231 (13), 190 (18), 147 (13); HRMS (EI) calcd for C$_{30}$H$_{46}$O$_2$Si$_2$ (M$^+$) 494.30380, found 494.303638.

5,6b,7,8,11b,12b,14-Octahydro-[7]-helicenebisquinone (10a)

![Structure of 10a]
To a solution of *bis*-diene 2a (110 mg, 0.47 mmol) in CH$_2$Cl$_2$ (5 mL), a solution of (SS)-1$^2$ (232 mg, 0.94 mmol) in CH$_2$Cl$_2$ (5 mL) was added at -20 ºC under argon. After 4 and 8 days, two new portions of (SS)-1 (58 mg, 0.23 mmol) in CH$_2$Cl$_2$ (1 mL) were added. The mixture was then stirred for 3 days and the solvent eliminated under reduced pressure. After flash chromatography (CH$_2$Cl$_2$), compound 10a was obtained as an orange solid, in 50% yield: mp > 160 ºC; $[\alpha]_{D}^{20}$ = −686 (c 0.04, CHCl$_3$); $^1$H NMR δ 7.11-7.05 (m, 2H), 6.67-6.37 (m, 4H), 5.75-5.45 (m, 2H), 4.68-4.46 (m, 2H), 3.67-3.61 (m, 2H), 3.07-2.03 (m, 8H); HRMS (EI) calcd for C$_{30}$H$_{22}$O$_4$ (M$^+$) 446.15240, found 446.15181.

((M)-7,8,11,12-Tetrahydro-[7]-helicenebisquinone (3a)

![Diagram of (M)-3a]

A solution of (-)-10a (21 mg, 0.05 mmol) and DDQ (42 mg, 0.18 mmol) in CH$_2$Cl$_2$ (1.2 mL) was stirred at 5 ºC for 20 h. The mixture was then washed several times with NaHCO$_3$. After workup and flash chromatography (hexane/acetone 2:1), compound (M)-3a was obtained as an orange solid, in 90% yield: mp > 160 ºC; $([\alpha]_{D}^{20}$ = −5825 (c 0.01, CHCl$_3$), 96% ee); $^1$H NMR δ 7.82 (d, $J$ = 7.7 Hz, 2H), 7.56 (d, $J$ = 7.7 Hz, 2H), 7.26 (s, 2H), 6.45 (d, $J$ = 10.1 Hz, 2H), 6.04 (d, $J$ = 10.1 Hz, 2H), 2.91–2.35 (m, 8H); $^{13}$C NMR δ 185.4, 183.9, 150.3, 139.9, 138.7, 135.8, 134.5, 131.9, 131.5, 131.2, 130.6, 127.8, 125.4, 30.7, 30.0; MS (EI): m/z (%) 442 (M$^+$, 100), 423 (7), 300 (13), 276 (10), 149 (19), 91 (7); HRMS (EI) calcd for C$_{30}$H$_{18}$O$_4$ (M$^+$) 442.12039, found 442.12051.

The ee was determined by chiral HPLC (Chiralcel OD, hexane/2-propanol 70:30, 0.5 mL/min, $R_t$ = 33.5 min (M-enantiomer) and 41.4 min (P-enantiomer).

(M)-6,13-Diethoxy-7,8,11,12-tetrahydro[7]helicenebisquinone (3b)

![Chemical Structure Image]

From diene 2b. To a stirred solution of 2b (14 mg, 0.045 mmol) in dry CH₂Cl₂ (0.5 mL) at −20 ºC under argon, a solution of (SS)-1 (22 mg, 0.086 mmol) in CH₂Cl₂ (0.6 mL) was added. After 19 h at −20 ºC, a new portion of (SS)-1 (58 mg, 0.23 mmol) in CH₂Cl₂ (0.6 mL) was added. After 7 d, the solvent was evaporated and the residue purified by flash chromatography (CH₂Cl₂), to give (M)-3b as a red solid, in 47% yield: \([\alpha]_{20}^{D} = -2938 \ (c \ 0.06, \ CHCl₃), \ 96\% \ ee\}; \ ^1H\ NMR \ \delta 7.30 \ (s, \ 2H), \ 7.25 \ (s, \ 2H), \ 6.42 \ (d, \ J = 10.2 \ Hz, \ 2H), \ 6.03 \ (d, \ J = 10.2 \ Hz, \ 2H), \ 4.35-4.05 \ (m, \ 4H), \ 3.40-3.30 \ (m, \ 2H), \ 2.88-2.17 \ (m, \ 6H), \ 1.54-1.48 \ (t, \ J = 7 \ Hz, \ 6H); \ ^13C\ NMR \ \delta 184.4, \ 184.2, \ 158.8, \ 140.2, \ 139.0, \ 138.4, \ 136.7, \ 135.1, \ 132.0, \ 127.4, \ 106.6, \ 64.6, \ 29.7, \ 22.3, \ 14.7; \ MS \ (EI): \ m/z \ (\%) \ 530 \ (M^+, \ 100), \ 501 \ (15), \ 473 \ (7), \ 287 \ (6); \ HRMS \ (EI) \ calcd \ for \ C_{34}H_{26}O_{6} \ (M^+) \ 530.17194, \ found \ 530.17294.

From tetrahydro[7]helicene (M)-3c. To a vigorously stirred suspension of CsF (45.6 mg, 0.30 mmol) and EtI (0.23 mL, 3 mmol) in DMF (3 mL), a solution of enantiomerically pure helicene (M)-3c (21.4 mg, 0.03 mmol) in DMF (3 mL) was added via cannula under argon. The mixture was stirred for 1 h, quenched with water and extracted several times with Et₂O. After workup and flash chromatography (CH₂Cl₂), compound (M)-3b was obtained in 82% yield: \([\alpha]^{20}_{D} = -3180 \ (c \ 0.05, \ CHCl₃), \ >99\% \ ee\}. The ee for (M)-3b was determined by chiral HPLC (Chiralcel OD, hexane/2-propanol 70:30, 0.5 mL/min, Rₚ = 27.4 min (P-enantiomer) and 76.9 min (M-enantiomer).
(M)-6,13-Diethoxy[7]helicenebisquinone (11)

A solution of enantiopure (M)-3b (11 mg, 0.02 mmol) and DDQ (56 mg, 0.25 mmol) in toluene (4 mL) was heated at 160-165 °C in a sealed tube. After 6 days, the residue was purified by flash chromatography (hexane/aceton 4:1) to give compound (M)-11 as a red solid, in 83% yield: mp 136-137 °C; {[α]_D^20 = -825 (c 0.08, CHCl_3), >99% ee}; ^1H NMR δ 8.42 (d, J = 8.9 Hz, 2H), 8.02 (d, J = 8.9 Hz, 2H), 7.39 (s, 2H), 6.48 (d, J = 10.1 Hz, 2H), 5.95 (d, J = 10.1 Hz, 2H), 4.48-4.33 (m, 4H), 1.64 (t, J = 7.3 Hz, 6H); MS (EI): m/z (%) 256 (M^+, 100), 501 (15), 473 (7), 287 (6); HRMS (EI) calcd for C_34H_22O_6 (M^+) 526.14240, found 526.14164.

The ee for (M)-11 was determined by chiral HPLC (Chiralcel OD, hexane/2-propanol 70:30, 0.5 mL/min, R_t = 94.8 min.

(M)-6,13-Bis[tert-butyldimethylsilyloxy]-7,8,11,12-tetrahydro[7]helicenebisquinone (3c)

To a solution of bis-diene 2c (60 mg, 0.12 mmol) in CH_2Cl_2 (2.5 ml) at -45 °C, (SS)-1 (59 mg, 0.24 mmol) in CH_2Cl_2 (1.5 mL) was added. After 1 h, DDQ (218 mg, 0.96 mmol) was added and the mixture warmed to -25 °C. After 2 d, the solvent was evaporated and the residue was purified by flash chromatography (CH_2Cl_2), to give compound (M)-3c as a red solid, in 25% yield: {[α]_D^20 = -1990 (c 0.02, CHCl_3), >99% ee}; ^1H NMR δ 7.29 (s, 2H), 7.28 (s, 2H), 6.48 (d, J =
10.5 Hz, 2H), 6.10 (d, J = 10.5 Hz, 2H), 3.34-2.30 (m, 8H), 1.11 (s, 18H), 0.39 (s, 6H), 0.37 (s, 6H); $^{13}$C NMR δ 184.1 (2C), 156.1, 141.4, 140.1, 138.4, 137.4, 135.3, 132.2, 131.8, 127.5, 125.2, 114.4, 29.8, 25.7, 23.1, 18.3; MS (EI): m/z (%) 645 (M$^+$, 100), 125 (5), 97 (16), 73 (70); HRMS (EI) calcd for C$_{42}$H$_{46}$O$_6$Si$_2$ (M$^+$) 702.28125, found 702.28330.

The ee for (M)-3c was determined by chiral HPLC (Chiralcel OD, hexane/2-propanol 95:5, 0.5 mL/min, $R_t = 10.0$ min (P-enantiomer) and 12.5 min (M-enantiomer).