SUPPLEMENTARY INFORMATION FOR


Alfonso Latorre, Antonio Urbano,* M. Carmen Carreño*
antonio.urbano@uam.es, carmen.carrenno@uam.es

Synthesis of dienes (rac)-1a,b, (rac)-5 and (rac)-7

10a,b → 11a,b → 12a,b

i. Na, EtOH  
ii. HCO₂Et, Et₂O  
0 °C to rt

84% for 11a  
76% for 11b

11a,b → 13a,b

i. O, Et₂N, MeOH  
ii. KOH, H₂O, rt

80% for 12a  
78% for 12b

13a,b → 14a,b

Pd(PPh₃)₄, Cs₂CO₃  
toluene, EtOH, H₂O, 95 °C

81% for 13a  
65% for 13b

14a,b → 15, 16

Pd(PPh₃)₄, LiCl, 90 °C

56%

12b → 15, 16

DBMP, Tf₂O, rt, 90%

63% for 1a  
42% for 1b

80% for 14b

84% for 11a  
76% for 11b

81% for 13a  
65% for 13b

80% for 12a  
78% for 12b
Synthesis of diene \((rac)-7\)

\[
\begin{array}{c}
\text{Ph} \\ \text{17} \quad \text{Tf}_2\text{NPh, KHDMs} \\ \text{THF, \(-78\ ^\circ\text{C}\)} \\
\text{98\%} \\ \text{Ph} \\ \text{18} \quad \text{O Tf} \\ \text{Ph} \\ \text{19} \\
\text{Ph} \\ \text{18} \quad \text{O Et} \\ \text{SnBu}_3 \quad \text{Pd(PPPh}_3)_4 \quad \text{LiCl, 90\^\circ\text{C}} \\
\text{ii. Flash chromatography} \\
\text{62\%} \\
\text{Ph} \\ \text{19} \\
\text{Ph} \\ \text{18} \quad \text{O TbDMS} \\ \text{THF, \(-78\ ^\circ\text{C}\) to rt} \\
\text{85\%} \\
\text{Ph} \\ \text{18} \quad \text{O TbDMS} \\ \text{THF, \(-78\ ^\circ\text{C}\) to rt} \\
\text{85\%} \\
\text{(rac)-7} \\
\end{array}
\]

**Experimental Procedures**

Melting points were obtained in open capillary tubes and are uncorrected. \(^1\text{H}\) and \(^{13}\text{C}\) 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) of Merck. Eluting solvents are indicated in the text. The apparatus for inert atmosphere experiments was dried by flaming in a stream of dry argon. Ethyl ether, CH\(_2\)Cl\(_2\), THF and CH\(_3\)CN were dried over 4Å molecular sieves. 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\(_4\).

**8-Bromo-5-methoxy-3,4-dihydronaphthalen-1(2H)-one (10b)**

To a vigorously stirred solution of commercially available 5-methoxy-1-tetralone (3.4 g, 18.9 mmol) in CH\(_3\)CN (105 mL), NBS (4.1 g, 22.6 mmol) was added. After 48 h, the solvent was evaporated and the residue purified by flash chromatography (eluent CH\(_2\)Cl\(_2\)) to give \(10\) as a yellow solid, in 96% yield: m.p. 52-53 °C; \(^1\text{H}\) NMR \(\delta\) 2.07-2.16 (m, 2H), 2.70 (dd, \(J = 6.7\) and 6.8 Hz, 1H), 2.93 (dd, \(J = 6.2\) and 6.3 Hz, 1H), 3.88 (s, 3H), 6.85 (d, \(J = 8.7\) Hz, 1H), 7.53 (d, \(J = 8.7\) Hz, 1H); \(^{13}\text{C}\) NMR \(\delta\) 22.0, 23.6, 39.9, 55.9, 111.3, 114.5, 131.4, 133.4, 136.0, 156.0, 197.2; MS (EI): \(m/z\) (%) 76 (37), 198 (48), 226 (51), 254 (M\(^+\), 100), 256 (M\(^+\) + 2, 96); HRMS (EI) calcd for C\(_{11}\)H\(_{11}\)O\(_2\)Br (M\(^+\)) 253.9942 found 253.9932.
General procedure for the α-formylation of 1-tetralones. Method A.

To a solution of the corresponding 1-tetralone 10a,b (3.2 g, 12.6 mmol) in dry Et$_2$O (12.6 mL) under argon, an excess of sodium metal (6 or 7 pieces of ca. 0.5 cm), ethyl formate (1.46 mL, 18.9 mmol) and EtOH (0.15 mL) were added at 0 °C. After stirring for 30 min at 0 °C and overnight at rt, the mixture was treated with water at 0 °C and stirred 30 min. The organic phase was washed with water, and the combined aqueous extracts treated with HCl until acidity. The solution was extracted with Et$_2$O and washed with sodium bicarbonate. After workup and flash chromatography, pure α-formyl derivatives 11a,b were obtained.

8-Bromo-2-(hydroxymethylene)-7-methoxy-3,4-dihyronaphthalen-1(2H)-one (11a)

Compound 11a was obtained from 1-tetralone 10a\(^\text{1}\) following method A (eluent hexane/EtOAc 3:1) as a yellow solid, in 84% yield: m.p. 84-86 °C; \(^1\)H NMR δ 2.44 (dd, \(J = 6.9 \) and 5.6 Hz, 2H), 2.81 (dd, \(J = 6.9 \) and 8.6 Hz, 2H), 3.92 (s, 3H), 6.98 (d, \(J = 8.7 \) Hz, 1H), 7.18 (d, \(J = 8.7 \) Hz, 1H), 7.79 (d, 9.2 Hz, 1H); \(^13\)C NMR δ 23.9, 30.0, 56.8, 110.6, 112.1, 115.5, 127.9, 132.0, 137.1, 155.8, 170.0, 187.1; MS (EI): \(m/z\) (%) 115 (85), 131 (85), 174 (95), 255 (47), 281 (\(M^+\), 100), 283 (\(M^+ + 2\), 88); HRMS (EI) calcd for C$_{12}$H$_{11}$O$_3$Br (M$^+$) 281.9892, found 281.9897.

8-Bromo-2-(hydroxymethylene)-5-methoxy-3,4-dihyronaphthalen-1(2H)-one (11b)

Compound 11b was obtained from 1-tetralone 10b\(^\text{1}\) following method A (eluent hexane/EtOAc 1:1) as a yellow solid, in 76% yield: m.p. 90-91 °C; \(^1\)H NMR δ 2.43 (dd, \(J = 6.5 \) and 7.1 Hz, 2H), 2.87 (dd, \(J = 6.5 \) and 7.1 Hz, 2H), 3.86 (s, 3H), 6.85 (d, \(J = 8.9 \) Hz, 1H), 7.52 (d, \(J = 8.9 \) Hz, 1H), 7.78 (d, \(J = 9.0 \) Hz, 1H); \(^13\)C NMR δ 22.5, 22.9, 55.9, 110.1, 111.7, 114.9, 131.2, 133.7, 134.5, 155.5, 169.8, 186.6; MS (EI): \(m/z\) (%) 115 (51), 139 (59), 174 (84), 253 (82), 282 (\(M^+\), 100), 284 (\(M^+ + 2\), 96); HRMS (EI) calcd for C$_{12}$H$_{11}$O$_3$Br (M$^+$) 281.9891, found 281.9881.

General procedure for the Robinson Annulation. Method B.

To a stirred mixture of the corresponding α-formyl 1-tetralone 11a,b (2.18 g, 7.73 mmol) in anhydrous methanol (31 mL) at 0 °C, Et₃N (2.1 mL) was added dropwise. After complete dissolution, methyl vinyl ketone (0.76 mL, 9.27 mmol) was added at 0 °C and the reaction mixture stirred at room temperature for 20 h. After neutralization with acetic acid (0.92 mL), the solvents were evaporated and the residue redissolved in dioxane (17.5 mL). After addition of a solution of KOH (1.4 g) in water (16 mL), the mixture was vigorously stirred for 3.5 h at room temperature. Then, the solution was diluted with water, saturated with NaCl, and extracted with CH₂Cl₂. After workup and flash chromatography, pure tetrahydrophenanthrenones 12a,b were obtained.

5-Bromo-6-methoxy-1,2,10,10a-tetrahydrophenanthren-3(9H)-one (12a)

![Image of 12a structure]

Compound 12a was obtained from α-formyl-1-tetralone 11a following method B (eluent hexane/EtOAc 3:1) as a white solid, in 80% yield: m.p. 89-90 °C; ¹H NMR δ 1.69-2.03 (m, 3H), 2.14 (m, 1H), 2.39-2.70 (m, 3H), 2.80 (m, 1H), 3.88 (s, 3H), 6.51 (d, J = 2.6 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H); ¹³C NMR δ 27.8, 28.8, 30.2, 34.8, 37.7, 56.6, 110.6, 112.3, 126.5, 129.1, 135.3, 137.1, 155.1, 157.7, 199.4; MS (EI): m/z (%) 128 (28), 171 (48), 199 (100), 306 (M⁺, 46), 308 (M⁺ + 2, 88); HRMS (EI) calcd for C₁₅H₁₅O₂Br (M⁺) 306.0255, found 306.0261.

5-Bromo-6-methoxy-1,2,10,10a-tetrahydrophenanthren-3(9H)-one (12b)

![Image of 12b structure]

Compound 12b was obtained from α-formyl-1-tetralone 11b following method B (eluent hexane/EtOAc 2:1) as a white solid, in 78% yield: m.p. 108-110 °C; ¹H NMR δ 1.72-1.99 (m, 3H), 2.15-2.24 (m, 1H), 2.27-2.37 (m, 1H), 2.43-2.58 (m, 2H), 2.69-2.78 (m, 1H), 3.04 (dt, J = 5.5, 16.2 Hz, 1H), 3.8 (s, 3H), 6.57 (d, J = 2.1 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 7.46 (d, J = 8.8 Hz, 1H); ¹³C NMR δ 21.2, 28.5, 29.6, 34.8, 36.9, 55.8, 111.2, 111.8, 128.6, 131.6, 132.2, 136.1, 155.2, 158.0, 199.6; MS (EI): m/z (%) 115 (20), 128 (33), 171 (50), 199 (100), 306 (M⁺, 40), 307 (M⁺ + 2, 39); HRMS (EI) calcd for C₁₅H₁₅O₂Br (M⁺) 306.0255, found 306.0245.
General procedure for the Suzuki Coupling. Method C.

To a mixture of bromo derivatives 12a,b (635 mg, 2.06 mmol), naphtyl boronic acid (1.23 g, 7.20 mmol), CsCO$_3$ (1.55 g, 4.73 mmol) and Pd(PPh$_3$)$_4$ (190 mg, 8% mol) under argon, toluene (10 mL), EtOH (10 mL) and H$_2$O (6 mL) were added. The reaction mixture was heated to 100 ºC for 12 h, filtered with celite and washed with water. After workup and flash chromatography, pure biaryls 13a,b were obtained.

6αMethoxyα5α(1αnaphthyl)α1,2,10,10aαtetrahydrophenanthrenα3(9H)αone (13a)

Compound 13a was obtained, as a 70:30 mixture of diastereomers, from bromo derivative 12a following method C (eluent hexane/EtOAc/CH$_2$Cl$_2$ 6:1:2), as a yellow solid, in 81% yield: $^1$H NMR $\delta$ 1.72-2.09 (m, 8H), 2.14-2.35 (m, 4H), 2.56-2.85 (m, 6H), 3.58 (s, 3H), 3.65 (s, 3H), 5.08 (d, $J$ = 2.0 Hz, 1H), 5.42 (d, $J$ = 2.1 Hz, 1H), 6.97 (d, $J$ = 8.3 Hz, 1H), 7.03 (d, $J$ = 8.4 Hz, 1H), 7.04 (dd, $J$ = 1.1 and 7.0 Hz, 1H), 7.22-7.27 (m, 4H), 7.34-7.47 (m, 5H), 7.51-7.58 (m, 2H), 7.79 (d, $J$ = 8.4 Hz, 1H), 7.78-7.81 (m, 1H), 7.85 (d, $J$ = 8.1 Hz, 1H); $^{13}$C NMR $\delta$ 28.0, 29.5, 29.6, 29.9, 30.1, 34.9, 36.1, 37.0, 37.4, 56.0, 56.2, 111.7, 112.7, 124.6, 125.2, 125.3, 125.5, 125.6, 125.7, 126.1, 126.4, 126.7, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.5, 128.6, 129.9, 131.8, 133.3, 133.4, 133.7, 133.9, 134.0, 135.6, 136.8, 136.9, 156.4, 156.5, 158.7, 158.8, 199.1, 199.2; MS (EI): m/z (%) 239 (34), 265 (46), 298 (34), 336 (44), 354 (M$^+$, 100); HRMS (EI) calcd for C$_{25}$H$_{22}$O$_2$ (M$^+$) 354.1620, found 354.1614.

8αMethoxyα5α(1αnaphthyl)α1,2,10,10aαtetrahydrophenanthrenα3(9H)αone (13b).
Compound 13b was obtained, as a 70:30 mixture of diastereomers, from bromo derivative 12b following method C (eluent hexane/EtOAc/CH₂Cl₂ 6:1:2), as a yellow solid, in 65% yield: $^1$H NMR $\delta$ 1.70-1.86 (m, 3H), 1.90-1.97 (m, 1H), 2.01-2.23 (m, 6H), 2.28-2.39 (m, 1H), 2.65-2.83 (m, 5H), 3.03-3.18 (m, 2H), 3.96 (s, 6H), 5.31 (d, $J = 2.0$ Hz, 1H), 5.48 (d, $J = 2.0$ Hz, 1H), 6.97 (d, $J = 8.4$ Hz, 1H), 7.03 (d, $J = 8.4$ Hz, 1H), 7.13 (dd, $J = 1.1$ and 7.0 Hz, 1H), 7.17-7.19 (m, 1H), 7.23 (d, $J = 8.3$ Hz, 1H), 7.26-7.29 (m, 2H), 7.31-7.35 (m, 1H), 7.39-7.45 (m, 3H), 7.47-7.53 (m, 1H), 7.55-7.59 (m, 2H), 7.82-7.85 (m, 3H), 7.93 (d, $J = 8.3$ Hz, 1H); $^{13}$C NMR $\delta$ 20.5, 20.8, 27.6, 28.0 (2C), 28.1, 33.6, 34.5, 34.8, 35.2, 54.2, (2C), 108.6, 109.4, 123.7, 123.9, 124.1, 124.2, 124.4 (2C), 124.5, 124.8, 125.6, 125.8, 126.1, 126.3, 126.4, 127.1, 127.2, 127.3, 128.4, 129.0, 129.6, 129.7, 129.9, 130.0, 130.6, 132.1, 132.6, 134.5, 138.1, 138.3, 154.2, 154.5, 157.4, 197.6 (2C); MS (EI): m/z (%) 239 (28), 252 (31), 298 (26), 336(30), 354 (M$^+$, 100); HRMS (EI) calcd for C$_{25}$H$_{22}$O$_2$ (M$^+$) 354.1620, found 354.1615.

General procedure for the enol triflate formation. Method D.

To a solution of the corresponding tetrahydrophenanthrene (0.42 mmol) and di-tert-butylmethylpyridine (75 mg, 0.42 mmol) in CH$_2$Cl$_2$ (5.3 mL) at 0 ºC, triflic anhydride (74 µL, 0.42 mmol) was slowly added, under argon. After stirring for 30 minutes at rt, the solution was cooled to 0 ºC and hexane was added. After 10 minutes, the solution was filtered with celite, the solvent evaporated, and the resulting enol triflates were used in the next step without further purification.

6-Methoxy-5-(1-naphthyl)-1,2,9,10-tetrahydrophenanthren-3-yl trifluoromethanesulfonate (14a).

![Diagram of compound 14a]

Compound 14a was obtained from tetrahydrophenanthrene 13a (148 mg) following method D as a yellow oil, in 92% yield: $^1$H NMR $\delta$ 2.04-2.13 (m, 1H), 2.20-2.52 (m, 5H), 2.72 (t, $J = 6.7$ Hz, 2H), 3.63 (s, 3H), 4.92 (s, 1H), 6.87 (d, $J = 8.9$ Hz, 1H), 7.24-7.28 (m, 2H), 7.37 (t, $J = 7.0$ Hz, 1H), 7.43-7.51 (m, 3H), 7.85-7.90 (m, 2H); $^{13}$C NMR $\delta$ 25.2, 28.6, 29.1, 29.9, 55.9, 108.9, 117.0, 118 (q, $J = 322$ Hz, 1C), 124.9, 125.0, 125.2, 125.5, 125.7, 125.8, 125.9, 127.2, 128.1, 128.3, 129.6, 132.6, 133.5, 134.6, 135.4, 137.5, 144.4, 156.6; MS (EI): m/z (%) 303 (26), 320 (17), 335 (100), 352 (19), 486 (M$^+$, 48); HRMS (EI) calcd for C$_{26}$H$_{21}$O$_4$F$_3$S (M$^+$) 486.1112, found 486.1103.
8-Methoxy-5-(1-naphthyl)-1,2,9,10-tetrahydrophenanthren-3-yl trifluoromethanesulfonate (14b)

Compound 14b was obtained from tetrahydrophenanthrenone 13b (148 mg) following method D as a yellow oil, in 80% yield: \(^1\)H NMR \(\delta\) 2.03-2.07 (m, 4H), 2.45-2.59 (m, 2H), 2.71-2.93 (m, 2H), 3.92 (s, 3H), 5.10 (s, 1H), 6.91 (d, \(J = 8.5\) Hz, 1H), 7.19 (d, \(J = 8.5\) Hz, 1H), 7.32-7.38 (m, 2H), 7.41-7.49 (m, 2H), 7.59 (d, \(J = 8.8\) Hz, 1H), 7.81-7.89 (m, 2H); \(^13\)C NMR \(\delta\) 21.2, 25.2, 27.7, 28.9, 55.7, 109.2, 117.0, 125.3, 125.4, 125.7, 125.8, 125.9, 126.0, 127.5, 127.9, 128.4, 128.8, 130.7, 132.2, 133.8, 134.4, 136.9, 139.8, 144.8, 155.5; MS (FAB): \(m/z\) (%) 335 (100), 486 (M\(^+\), 60); HRMS (EI) calcd for C\(_{26}\)H\(_{21}\)O\(_4\)F\(_3\)S (M\(^+\)) 486.1113, found 486.1104.

**General procedure for the Stille coupling: synthesis of dienes. Method E.**

To a mixture of the corresponding enol triflate (0.267 mmol), LiCl (56 mg, 1.3 mmol) and Pd(PPh\(_3\))\(_4\) (15 mg, 5% mol) in dry THF (2.6 mL), under argon, vinyltributylstannane (84 mg, 0.267 mmol) was added dropwise. The reaction mixture was refluxed for the time indicated in each case, filtered with celite and washed with water. After workup and flash chromatography, pure 3-vinyl tetrahydrophenanthrenes were obtained.

6-Methoxy-5-(1-naphthyl)-3-vinyl-1,2,9,10-tetrahydrophenanthrene (1a).

Compound 1a was obtained from enol triflate 14a (129 mg) following method E (90 min, eluent hexane/CH\(_2\)Cl\(_2\) 1:3) as a colourless oil, in 63% yield \(^1\)H NMR \(\delta\) 1.87-1.93 (m, 2H), 2.19-2.25 (m, 3H), 2.32-2.43 (m, 1H), 2.68-2.73 (m, 2H), 3.61 (s, 3H), 4.58 (d, \(J = 10.6\) Hz, 1H), 4.76 (d, \(J = 17.3\) Hz, 1H), 4.84 (s, 1H), 5.28 (dd, \(J = 10.6\) and 17.3 Hz, 1H), 6.83 (d, \(J = 8.2\) Hz, 1H), 7.21 (m, 1H), 7.23 (m, 1H), 7.31-7.44 (m, 3H), 7.54 (d, \(J = 8.4\) Hz, 1H), 7.76 (d, \(J = 8.4\) Hz, 1H), 7.83 (d, \(J = 8.2\) Hz, 1H); \(^13\)C NMR \(\delta\) 20.6, 29.1, 29.2, 29.3, 55.9, 108.3, 109.3, 125.0, 125.1, 125.2, 125.5, 126.4, 127.0, 127.5, 128.0, 128.4, 128.8, 130.2, 131.1, 133.0, 133.3, 135.9, 136.3, 138.2, 139.3, 156.5; MS (EI): \(m/z\) (%) 165 (6), 239 (6), 289 (12), 364 (M\(^+\), 100); HRMS (EI) calcd for C\(_{27}\)H\(_{24}\)O\(_1\) (M\(^+\)) 364.1827, found 364.1815.
8-Methoxy-5-(1-naphthyl)-3-vinyl-1,2,9,10-tetrahydrophenanthrene (1b).

Compound 1b was obtained from enol triflate 14b (129 mg) following method E (90 min, eluent hexane/CH₂Cl₂ 15:1 in Al₂O₃) as a colourless oil, in 42% yield: ¹H NMR δ 1.83 (ddd, J = 6.3, 9.7 and 16.2 Hz, 1H), 1.99 (ddd, J = 7.5, 8.4 and 16.2 Hz, 1H), 2.23-2.36 (m, 4H), 2.76 (ddd, J = 7.7, 8.0 and 15.5 Hz, 1H), 2.86 (ddd, J = 7.6, 7.9 and 7.5 Hz, 1H), 3.92 (s, 3H), 4.59 (d, J = 10.7 Hz, 1H), 5.02 (s, 1H), 5.39 (dd, J = 10.7 and 17.3 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.31-7.45 (m, 4H), 7.65 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H); ¹³C NMR δ 20.7, 21.3, 28.2, 29.1, 55.7, 108.6, 109.5, 125.1, 125.4, 125.5, 125.6, 126.3, 127.2, 127.5, 127.6, 128.0, 127.7, 128.9, 130.4, 131.4, 132.4, 133.5, 135.6, 138.2, 138.6, 140.7, 155.3; MS (EI): m/z (%) 144 (11), 165 (11), 289 (22), 335 (22), 364 (M⁺, 100); HRMS (EI) calcd for C₂₇H₂₄O₁ (M⁺) 364.1827, found 364.1840.

General procedure for the synthesis of 14-aryl-[5]helicenequinones. Method F.

To a mixture of the corresponding 3-vinyltetrahydrophenanthrene (0.11 mmol) and (S,S)-5-methyl-2-(p-tolylsulfinyl)-1,4-benzoquinone (2)² (54 mg, 0.22 mmol) at –27 ºC, CH₂Cl₂ (5.5 mL) was rapidly added, under argon. The reaction mixture was stirred at the temperature and for the time indicated in each case. After elimination of the solvent and flash chromatography, the corresponding pure 14-aryl-[5]helicenequinones were obtained.

(P,aS)-13-Methoxy-3-methyl-14-(1-naphtyl)-7,8,9,10-tetrahydro-[5]-helicenequinone (3a) and (P,aR)-13-methoxy-3-methyl-14-(1-naphtyl)-7,8,9,10-tetrahydro-[5]-helicenequinone (4a).

---

Compounds \((P,aS)-3a\) and \((P,aR)-4a\) were obtained, as a 50:50 mixture, from 3-vinyltetrahydrophenanthrene \(1a\) (40 mg) following method F (12 h at –27 °C and 3 h at room temperature, eluent CH\(_2\)Cl\(_2\)) as a red solid, in 68% overall yield. Analytic amounts of both diastereoisomers could be obtained after preparative HPLC (Column C18, 250 x 4.6 mm, 5 µm; H\(_2\)O/CH\(_3\)CN 20/80; \(R_t\) \((P,aS)-3a\): 14.93 min, \(R_t\) \((P,aR)-4a\): 16.96 min):

Diastereoisomer \((P,aS)-3a\): m.p. 220–221 °C; \([\alpha]_D^{20} = +936 (c = 0.012 \text{ in CHCl}_3)\), 99% ee (Chiral HPLC: Daicel Chiralpak OD, hexane/2-propanol 98:2; 1.0 mL min\(^{-1}\), 254 nm, \(R_t = 33.0 \text{ min, } T = 25 °C\)); \(^1\)H NMR \(\delta\) 1.77 (d, \(J = 1.3\) Hz, 3H), 2.27–2.40 (m, 3H), 2.50–2.63 (m, 3H), 2.87 (dd, \(J = 4.6\) and 13.4 Hz, 1H), 3.02 (ddd, \(J = 5.5, 14.2\) and 14.6 Hz, 1H), 3.53 (s, 3H), 6.06 (q, \(J = 1.3\) Hz, 1H), 6.74 (d, \(J = 7.0\) Hz, 1H), 6.81–6.87 (m, 2H), 7.09 (d, \(J = 7.6\), 1H), 7.18–7.28 (m, 3H), 7.34 (d, \(J = 7.6\) Hz, 1H), 7.40 (d, \(J = 7.9\) Hz, 1H), 7.54 (d, \(J = 8.2\) Hz, 1H); \(^{13}\)C NMR \(\delta\) 15.7, 29.4, 29.8, 29.9, 30.2, 55.5, 107.3, 122.0, 124.0, 125.1, 125.4, 125.5, 126.5, 126.7, 127.2, 127.4, 128.2, 128.5, 129.8, 130.7, 130.8, 131.2, 132.5, 133.0, 135.9, 136.0, 136.6, 137.4, 142.9, 144.8, 148.8, 155.8, 184.5, 185.3; MS (EI): \(m/z\) (%) 241 (5), 451 (6), 482 (M\(^+\), 100); HRMS (EI) calcd for C\(_{34}\)H\(_{26}\)O\(_3\) (M\(^+\)) 482.1881, found 482.1881.

Diastereoisomer \((P,aR)-4a\): m.p. 203–205°C; \([\alpha]_D^{20} = +977 (c = 0.009 \text{ in CHCl}_3)\), 98% ee (Chiral HPLC: Daicel Chiralpak OD, hexane/2-propanol 95:5; 0.8 mL min\(^{-1}\), 254 nm, \(R_t = 20.8 \text{ min, } T = 25 °C\)); \(^1\)H NMR \(\delta\) 2.11 (d, \(J = 1.5\) Hz, 3H), 2.14–2.26 (m, 4H), 2.35 (dd, \(J = 5.6\) and 17.2 Hz, 1H), 2.60 (dd, \(J = 5.0\), 16.3 and 16.5 Hz, 1H), 2.86 (dd, \(J = 1.7, 4.9\) and 13.8 Hz, 1H), 3.00 (ddd, \(J = 5.5, 13.9\) and 14.6 Hz, 1H), 3.59 (s, 3H), 6.53 (q, \(J = 1.5\) Hz, 1H), 6.66 (d, \(J = 7.8\) Hz, 1H), 6.90 (d, \(J = 8.3\) Hz, 1H), 6.96 (dd, \(J = 7.1\) and 8.1 Hz), 7.08–7.13 (m, 2H), 7.17–7.22 (m, 1H), 7.25–7.28 (m, 3H), 7.39 (d, \(J = 8.2\) Hz, 1H), 7.45 (d, \(J = 8.2\) Hz, 1H); \(^{13}\)C NMR \(\delta\) 15.9, 28.4, 29.1, 29.6, 30.4, 55.9, 108.5, 122.2, 123.3, 123.5, 125.2, 125.8, 125.9, 126.7, 127.1, 128.0, 128.3, 128.6, 129.5, 130.1, 130.2, 131.0, 132.2, 133.3, 133.7, 135.4 (2C), 136.4, 144.6, 144.8, 148.3, 155.9, 184.4, 186.0; MS (EI): \(m/z\) (%) 175 (5), 241 (5), 451 (6), 482 (M\(^+\), 100); HRMS (EI) calcd for C\(_{34}\)H\(_{26}\)O\(_3\) (M\(^+\)) 482.1881, found 482.1881.

\((P,aR)-11\text{-methoxy-3-methyl-14-(1-naphtyl)-7,8,9,10-tetrahydro-[5]-helicenequinone (3b) and (P,aS)-11-Methoxy-3-methyl-14-(1-naphthyl)-7,8,9,10-tetrahydro-[5]-helicenequinone (4b)}\)
Compounds \((P,aR)-\text{3b}\) and \((P,aS)-\text{4b}\) were obtained, as an unseparable 20:80 mixture, from 3-vinyltetrahydrophenanthrene \(\text{1b}\) (40 mg) following method F (12 h at \(-27 \, ^\circ\text{C}\) and 3 h at \(-10 \, ^\circ\text{C}\), eluent hexane/CH\(_2\)Cl\(_2\) 3:1) as a red solid, in 74% overall yield: m.p. 220-221 \, ^\circ\text{C}; [\alpha]_{D}^{20} = +1434 (c = 0.009 in CHCl\(_3\)); MS (EI): \(m/z\) (%): 391 (12), 482 (M\(^+\), 100); HRMS (EI) calcd for C\(_{34}\)H\(_{26}\)O\(_3\) (M\(^+\)) 482.1881, found 482.1875.

The following data correspond to the major diastereoisomer \((P,aS)-\text{4b}\) and were obtained from the mixture: 93\% ee (Chiral HPLC: Daicel Chiralpak IB, hexane/2-propanol 95:5; 0.6 mL min\(^{-1}\), 254 nm, \(R_{t} = 19.1\) min, \(T = 25 \, ^\circ\text{C}\)); \(^1\)H NMR \(\delta\): 2.10 (d, \(J = 1.4\) Hz, 3H), 2.17-2.25 (m, 3H), 2.37-2.51 (m, 3H), 2.55-2.62 (m, 2H), 3.51 (dd, \(J = 4.2\) and 10.2 Hz, 1H), 3.96 (s, 3H), 6.47 (q, \(J = 1.4\) Hz, 1H), 6.64 (d, \(J = 7.6\) Hz, 1H), 6.92 (d, \(J = 8.4\) Hz, 1H), 6.95-7.07 (m, 3H), 7.14 (d, \(J = 7.3\) Hz, 1H), 7.21-7.29 (m, 4H), 7.44 (d, \(J = 8.4\) Hz, 1H); \(^{13}\)C NMR \(\delta\): 124.0, 125.3, 125.5, 125.8 (2C), 126.5, 127.0, 127.4, 127.8, 128.2, 128.7, 129.9, 130.4, 130.8, 131.9, 132.8, 133.7, 135.2, 136.3, 142.0, 144.8, 144.9, 147.5, 155.4, 184.2, 186.0.

5-Bromo-1,2,9,10-tetrahydro-8-methoxyphenanthren-3-yl-trifluoromethanesulfonate (15).

![Chemical Structure](image)

Compound 15 was obtained from tetrahydrophenanthreneone 12b (128 mg) following method D as a pale yellow oil, in 90\% yield: \(^1\)H NMR \(\delta\): 2.16 (dd, \(J = 6.1\) and 7.0 Hz, 2H), 2.62 (br s, 4H), 2.68 (dd, \(J = 6.1\) and 7.0 Hz, 2H), 3.80 (s, 3H), 6.65 (d, \(J = 8.7\) Hz, 1H), 6.73 (s, 1H), 7.37 (d, \(J = 8.7\) Hz, 1H); \(^{13}\)C NMR \(\delta\): 21.6, 25.5, 27.3, 30.3, 55.7, 110.2, 111.0, 117.6, 118.6 (q, \(J = 320\) Hz), 125.1, 128.2, 132.3, 134.4, 139.4, 144.2, 155.2; MS (EI): \(m/z\) (%): 196 (100), 224 (78), 436 (M\(^+\) – 2, 89), 438 [(M\(^+\) – 2) + 2, 89]; HRMS (EI) calcd for C\(_{16}\)H\(_{14}\)O\(_4\)BrF\(_3\)S (M\(^+\) – 2) 435.9592, found 435.9574.

5-Bromo-8-methoxy-3-vinyl-1,2,9,10-tetrahydrophenanthrene (16).

![Chemical Structure](image)

Compound 16 was obtained from enol triflate 15 (116 mg) following method E (50 min, eluent hexane in neutral Al\(_2\)O\(_3\) deactivated with 10\% of water) as a colourless oil, in 56\% yield: \(^1\)H NMR \(\delta\)
2.20 (dd, J = 7.4 and 7.7 Hz, 2H), 2.40-2.41 (m, 4H), 2.67 (dd, J = 7.4 and 7.7 Hz, 2H), 3.81, (s, 3H), 5.04 (d, J = 10.8 Hz, 1H), 5.23 (d, J = 17.4 Hz, 1H), 6.58 (dd, J = 10.8 and 17.4 Hz, 1H), 6.61-6.64 (m, 2H), 7.38 (d, J = 8.9 Hz, 1H); \(^{13}\)C NMR δ 21.0, 21.7, 27.9, 29.5, 55.8, 110.5, 110.6 (2C), 127.5, 128.2, 128.5, 131.1, 132.1, 135.6, 138.8, 140.8, 155.1. MS (EI): m/z (%) 165 (87), 194 (95), 316 (M\(^+\), 100), 318 (M\(^+\) + 2, 85).

5-(2-Biphenyl)-8-methoxy-3-vinyl-1,2,9,10-tetrahydrophenanthrene (5)

\[
\text{OMe} \quad \text{5}
\]

A mixture of bromo tetrahydrophenanthrene 16 (46 mg, 0.14 mmol), 2-biphenyl boronic acid (70 mg, 0.33 mmol), Ba(OH)\(_2\)·8H\(_2\)O (102 mg, 0.32 mmol) and Pd(PPh\(_3\))\(_4\) (13 mg, 8% mol) in DME (3.5 mL), under argon, was heated at 90 °C for 1 h. The reaction mixture was filtered with celite and washed with water. After workup and flash chromatography (hexane/CH\(_2\)Cl\(_2\) 10:1 in Al\(_2\)O\(_3\) deactivated with 10% of water), pure compound 5 was obtained as a colourless oil, in 62% yield: \(^1\)H NMR δ 1.55-1.66 (m, 1H), 1.80 (ddd, J = 4.7, 5.0 and 16.1 Hz, 1H), 2.04-2.27 (m, 5H), 2.82 (ddd, J = 4.2, 4.3 and 15.7 Hz, 1H), 3.85 (s, 3H), 4.80 (d, J = 10.6 Hz, 1H), 4.97 (d, J = 17.2 Hz, 1H), 5.27 (s, 1H), 5.81 (dd, J = 10.6 and 17.2 Hz, 1H), 6.80 (d, J = 8.6 Hz, 1H), 6.84-6.88 (m, 2H), 7.07-7.09 (m, 3H), 7.13 (d, J = 8.6 Hz, 1H), 7.27-7.29 (m, 1H), 7.34-7.37 (m, 2H), 7.42-7.45 (m, 1H); \(^{13}\)C NMR δ 20.8, 20.9, 27.9, 28.8, 55.6, 108.6, 109.6, 125.5, 125.9, 127.1, 127.4, 127.5, 127.8 (2C), 129.7 (2C), 130.1, 130.3, 130.6, 131.1, 135.0, 138.3, 139.1, 141.3, 141.4 (2C), 155.0; MS (EI): m/z (%) 165 (13), 239 (7), 315 (6), 359 (7), 390 (M\(^+\), 100); HRMS (EI) calcd for C\(_{29}\)H\(_{26}\)O (M\(^+\)) 390.1983, found 390.1985.

(P,aS)-14-(2-Biphenyl)-11-methoxy-3-methyl-7,8,9,10-tetrahydro-[5]-helicenequinone (6)
Compound \((P,aS)-6\) was obtained from 3-vinyltetrahydrophenanthrene \(5\) (43 mg) following method F (12 h at \(-27 °C, 5 \text{ h at } -10 °C\); eluent hexane/\(\text{CH}_2\text{Cl}_2/\text{EtOAc} 6:2:1\)) as a red solid, in 75% yield: m.p. 229-230 °C; \([\alpha]_D^{20} = +1970\) (c = 0.01 in CHCl\(_3\)), 95% ee (Chiral HPLC: Daicel Chiralpak IA, hexane/2-propanol 90:10; 0.8 mL min\(^{-1}\), 254 nm, \(R_e = 9.6 \text{ min, } T = 25 °C\)); \(^1\)H NMR \(\delta 1.82\) (m, 2H), 2.02 (dd, \(J = 5.0 \text{ and } 16.8 \text{ Hz, } 1\text{H})\), 2.11 (d, \(J = 1.4 \text{ Hz, } 1\text{H})\), 2.17-2.41 (m, 4H), 3.25 (ddd, \(J = 1.5, 5.1 \text{ and } 15.2 \text{ Hz, } 1\text{H})\), 3.95 (s, 3H), 6.48 (q, \(J = 1.4 \text{ Hz, } 1\text{H})\), 6.77-6.80 (m, 2H), 6.88-7.00 (m, 4H), 7.05-7.07 (m, 3H), 7.19 (d, \(J = 7.6 \text{ Hz, } 1\text{H})\), 7.55 (d, \(J = 7.6 \text{ Hz, } 1\text{H})\); \(^{13}\)C NMR \(\delta 15.9, 20.9, 28.4, 28.7, 29.0, 55.4, 108.6, 123.9, 125.9, 126.1, 126.2, 127.4, 127.6, 128.6, 128.7, 129.5, 129.6, 130.1, 130.5, 130.6, 130.7, 133.4, 134.5, 134.8, 136.4, 138.3, 139.6, 142.0, 144.7, 145.7, 147.6, 155.0, 184.6, 186.1); MS (EI): \(m/z\) (%) 165 (13), 189 (6), 239 (6), 477 (6), 508 \((\text{M}^+, 100)\); HRMS (EI) calcd for C\(_{36}\)H\(_{28}\)O\(_3\) \((\text{M}^+)\) 508.2038, found 508.2016.

8α(2αBiphenyl)α3,4αdihydronaphtalenα2αtrifluoromethanesulfonate (18).

To a solution of 8α(2αbiphenyl)α3,4αdihydronaphtalenα2αtrifluoromethanesulfonate (17) \(^3\) (64 mg, 0.21 mmol) and N-phenyl-bis(trifluoromethanesulfonimide) (82 g, 0.23 mmol) in dry THF (2.1 mL) was slowly added a solution of KHMDS 0.5M in THF (0.46 mL, 0.23 mmol) at \(-78 \text{ °C}, \) under argon. The mixture was stirred for 80 min and quenched with H\(_2\)O at \(-78 \text{ °C}. \) After warming to room temperature, workup and flash chromatography (eluent EtOAc/hexane 1:5), compound 18 was obtained as a colorless oil, in 98% yield; \(^1\)H NMR \(\delta 2.46\) (ddd, \(J = 7.9, 9.1 \text{ and } 16.9 \text{ Hz, } 1\text{H})\), 2.53 (ddd, \(J = 7.3, 8.2 \text{ and } 16.9 \text{ Hz, } 1\text{H})\), 2.96 (m, 2H), 6.19 (s, 1H), 6.97-7.17 (m, 8H), 7.26-7.29 (m, 1H), 7.38-7.48 (m 3H), \(^{13}\)C NMR \(\delta 26.1, 29.1, 117.0, 126.3, 126.5, 127.3, 127.3, 128.2, 128.5, 129.4, 129.5, 130.2, 131.0, 132.0, 133.2, 135.6, 138.0, 139.7, 141.0, 141.5, 149.9; MS (EI): \(m/z\) (%) 239 (37), 279 (100), 297 (79), 430 \((\text{M}^+, 36)\); HRMS (EI) calcd for C\(_{23}\)H\(_{17}\)O\(_3\)F\(_3\)S \((\text{M}^+)\) 430.0850, found 430.0850.

2-Acetyl-8α(2αbiphenyl)α3,4αdihydronaphthalene (19)

To a mixture of enol triflate 18 (255 mg, 0.59 mmol), LiCl (123 mg, 2.9 mmol) and Pd(PPh3)4 (34 mg, 5% mol) in THF (5.9 mL), under argon, (1-ethoxyvinyl)-tributylstannane (166 µL, 0.65 mmol) was added. The reaction mixture was heated at 90 ºC for 1.5 h, filtered with celite and washed with water. The solvent was evaporated and the residue was charged in a flash column chromatography for 1 h to provoke the hydrolysis of the vinyl ether. Then, the residue was eluted with a mixture of EtOAc/hexane 1:6, to obtain pure compound 19 as a white solid, in 62% yield: m.p. 140-141 ºC; 1H NMR δ 2.03-2.16 (m, 1H), 2.16 (s, 3H), 2.40-2.50 (m, 1H), 2.68 (dd, J = 6.1 and 7.4 Hz, 2H), 7.01-7.06 (m, 3H), 7.07-7.13 (m, 5H), 7.21 (d, J = 7.3 Hz, 1H), 7.35-7.38 (m, 1H), 7.42-7.50 (m, 3H); 13C NMR δ 20.4, 25.2, 28.1, 126.7, 127.4, 127.8, 128.3, 129.1, 129.4, 129.5, 130.0, 130.5, 131.2, 135.5, 137.9 (2C), 138.3, 140.8, 140.9, 141.6, 198.5; MS (EI): m/z (%) 203 (25), 252 (31), 265 (50), 281 (82), 324 (M+, 100); HRMS (EI) calcd. for C24H20O (M+) 324.1514, found 324.1519.

8α(2αBiphenyl)α2α[1α(tert-butlydimethylsilyloxy)vinyl]α3,4αdihydronaphthalene (7)

To a solution of methyl ketone 19 (35 mg, 0.1 mmol) in THF (2.1 mL) was slowly added a solution of KHMDS 0.5M in THF (0.24 mL, 0.12 mmol) at –78 ºC, under argon, and the mixture stirred for 10 min. Then, TBDMSOTf (0.26 mL, 0.12 mmol) was added and the mixture was stirred for 1.5 h and quenched with H2O at –78 ºC. After warming to room temperature, workup and flash chromatography (hexane in Al2O3 deactivated with 10% of water), compound 7 was obtained as a colorless oil, in 85% yield: 1H NMR δ 0.05 (s, 3H), 0.07 (s, 3H), 0.73 (s, 9H), 2.22 (ddd, J = 8.0, 8.2 and 15.2 Hz, 1H), 2.37 (ddd, J = 7.7, 8.0 and 15.2 Hz, 1H), 2.78 (m, 2H), 4.33 (d, J = 0.9 Hz, 1H), 4.54 (d, J = 0.9 Hz, 1H), 6.75 (s, 1H), 6.83 (ddd, J = 1.7 and 7.2 Hz, 1H), 6.92-6.98 (m, 2H), 7.03-7.06 (m, 2H), 7.08-7.12 (m, 3H), 7.27-7.30 (m, 1H), 7.32-7.37 (m, 1H), 7.38-7.41 (m, 2H); 13C NMR δ –4.8, –4.7, 18.0, 23.5, 25.7, 28.7, 92.1, 122.6, 125.8, 126.1, 126.2, 127.0, 127.4, 127.5, 128.5, 128.9, 129.5, 130.0, 131.1, 132.0, 132.6, 134.8, 135.7, 139.3, 141.4, 156.0; MS (EI): m/z (%) 371 (100), 382 (53), 397 (64), 415 (75), 438 (M+, 59); HRMS (EI) calcd. for C30H34O (M+) 438.2378, found 438.2371.

(P,aS)-12-(2-Biphenyl)-6-(tert-butlydimethylsilyloxy)-7,8-dihydro-[4]-helicenequinone (9a)
Compound (P,aS)-9a was obtained following method F (18 h, −27 °C, eluent hexane/CH₂Cl₂ 1:3) from diene 7 and (SS)-2-(p-tolylsulfanyl)-1,4-benzoquinone (8)² (0.18 mmol, 44 mg, 2 equiv) as an orange solid, in 76% yield: m.p. 183-184 °C; [α]D²⁰ = +748 (c = 0.033 in CHCl₃), 85% ee (Chiral HPLC: Daicel Chiralpak IA, hexane/2-propanol 90:10; 0.8 mL min⁻¹, 254 nm, R₁ = 7.9 min, T = 25 °C); ¹H NMR (500 MHz) δ 0.27 (s, 3H), 0.43 (s, 3H), 1.03 (s, 3H), 1.22 (dd, J = 4.6 and 15.4 Hz, 1H), 2.73 (td, J = 4.41 and 15.8 Hz, 1H), 6.28 and 6.39 (AB system, J = 5.1 and 15.5 Hz, 2H), 6.31-6.33 (m, 2H), 6.84-6.87 (m, 2H), 6.96-7.00 (m, 2H), 7.12 (s, 1H), 7.22-7.24 (m, 2H), 7.30 (d, J = 7.6 Hz, 1H), 7.36-7.41 (m, 3H); ¹³C NMR δ −4.4, −3.8, 18.3, 22.3, 25.6, 29.4, 112.4, 125.9, 126.6, 127.0, 127.3, 127.4, 127.5, 128.3, 128.4, 129.6, 130.9, 131.4, 132.4, 134.9, 135.1, 135.6, 139.6, 139.7, 140.3 (2C), 140.5, 140.9, 155.4, 185.0, 185.9; MS (EI): m/z (%) 136 (68), 137 (12), 139 (100), 145 (39), 154 (100), 154 (100), 307 (19), 429 (M⁺ + 1, 8); HRMS (FAB) calcd for C₃₀H₃₄O₃Si (M⁺) 542.2277, found 542.2254.

(P,aS)-12-(2-Biphenyl)-6-hydroxy-7,8-dihydro-[4]-helicenequinone (9b)

To a solution of OTBDMS derivative (P,aS)-9a (13.5 mg, 0.025 mmol) in THF (2 mL), a solution of TBAF 1M in THF (0.05 mL, 0.05 mmol) was added at 0 °C. The reaction was stirred 1 h and quenched with NH₄Cl. After workup and flash chromatography (CH₂Cl₂), compound (P,aS)-9b was obtained as an orange solid, in 75% yield: m.p. 226-228 °C; [α]D²⁰ = +1034 (c = 0.014 in CHCl₃); ¹H NMR δ 1.25 (dd, J = 5.1 and 15.5 Hz, 1H), 2.26 (dd, J = 4.6 and 15.5 Hz, 1H), 2.58-2.71 (m, 2H), 5.85 (s, 1H), 6.30 and 6.41 (AB system, J = 10.1 Hz, 2H), 6.31-6.33 (m, 1H), 6.87-6.92 (m, 2H), 6.97-7.04 (m, 2H), 7.20-7.26 (m, 2H), 7.21 (s, 1H), 7.30-7.32 (m, 1H), 7.37 (dd, J = 7.1 and 7.6 Hz, 1H), 7.37 (d, J = 7.3 Hz, 1H), 7.41-7.44 (m, 1H); ¹³C NMR δ 21.6, 29.2, 110.5, 126.0, 126.5, 126.9, 127.3, 127.4, 127.5, 128.4, 128.5, 129.5, 131.0, 131.6, 132.0, 134.8, 135.0, 135.4, 137.3, 139.4, 140.2, 140.3, 140.5, 140.6, 140.9, 155.6, 185.2, 185.7; MS (FAB): m/z (%) 136 (68), 154 (100), 307 (19), 429 (M⁺ + 1, 8); HRMS (FAB) calcd for C₃₀H₂₁O₃ (M⁺ + 1) 429.1491, found 429.1481.

General synthesis of bis-(–)-camphanates. Method G.

Et₃N (195 µL) and CH₂Cl₂ (3 mL) were added to a mixture of the corresponding helicenequinone (0.066 mmol), activated Zn (56 mg, 0.85 mmol), (–)-camphanoyl chloride (72 mg, 0.33 mmol) and
DMAP (3.8 mg, 0.033 mmol), under argon. The mixture was refluxed for the time indicated in each case. Filtration through celite, aided by several ethyl acetate washes, removed remaining Zn. The organic solution was washed with saturated aqueous NaHCO₃, 2% HCl and water. After workup and flash chromatography, the corresponding pure bis(−)-camphanate was obtained.

(PₐS)-14-(2-Biphenyl)-11-methoxy-7,8,9,10-tetrahydro-[5]-helicene-bis(−)-camphanoyl-hydroquinone (20).

\[
\text{MeO} \quad \text{R}^* = \quad \text{O} \quad \text{Me} \\
\text{OR}^* \quad \text{(PₐS)-20}
\]

Compound (PₐS)-20 was obtained from helicenequinone (PₐS)-6 (16 mg) following method G (45 min, eluent hexane/EtOAc 2:1) as a pale brown solid, in 78% yield; m.p. 200-202 °C; \([\alpha]_{D}^{20} = +355 \text{ (c = 0.12 in CHCl₃)}; \) \(^1H\) NMR (500 MHz) \(\delta \) 0.80 (s, 3H), 1.00 (3H), 1.05 (3H), 1.23 (3H), 1.26 (s, 3H), 1.59-1.68 (m, 2H), 1.74 (m, 5H), 2.03-2.12 (m, 3H), 2.16-2.39 (m, 3H), 2.26 (s, 3H), 2.58 (dt, \(J = 5.5 \text{ and 15.6 Hz, 1H}), 2.67 (ddd, \(J = 4.2, 10.7 \text{ and 15.0 Hz, 1H}), 3.06 (dd, \(J = 5.3 \text{ and 15.0 Hz, 1H}), 3.88 \text{ (s, 3H)}, 6.59-6.60 \text{ (m, 4H)}, 6.73-6.77 \text{ (m, 3H)}, 6.79 \text{ (d, } J = 8.5 \text{ Hz, 1H}), 6.97 \text{ (d, } J = 8.5 \text{ Hz, 1H}, 7.01 \text{ (m, 3H)}, 7.06-7.08 \text{ (m, 2H)}; \) \(^13C\) NMR \(\delta \) 9.8, 9.9, 16.7, 16.9, 17.0, 17.1, 17.2, 20.2, 28.6, 28.7, 28.8, 28.9, 29.0, 31.6, 54.4, 54.8, 55.1, 55.2, 56.2, 90.9, 91.2, 108.0, 118.3, 119.2, 123.6, 123.8, 125.6, 127.7, 126.8, 127.2, 127.3, 128.5, 129.1, 129.3, 129.5, 129.6, 130.5, 132.3, 135.9, 136.8, 138.0, 140.1, 140.6, 141.7, 143.1, 145.3, 154.8, 165.0, 178.1, 178.2; MS (MALDI): \(m/z\) (%)

673 (100), 870 (M⁺, 34); HRMS (MALDI) calcd for C₅₆H₅₄O₃ (M⁺) 870.3815, found 870.3762.

(PₐS)-12-(2-Biphenyl)-6-[[tert-butyldimethylsilyl]oxy]-7,8-dihydro-[4]-helicene-bis(−)-camphanoyl-hydroquinone (21)

\[
\text{OTBDMS} \quad \text{OR}^* = \quad \text{O} \\
\text{OR}^* \quad \text{(PₐS)-21}
\]
Compound (P,aS)-21 was obtained from helicenequinone (P,aS)-9a (59 mg) following method G (50 min, eluent hex/EtOAc 3:1) as a yellow solid, in 72% yield: m.p. 194-195°C; [α]D20 = +252 (c = 0.16 in CHCl3); 1H NMR (500 MHz) δ 0.23 (s, 3H), 0.44 (s, 3H), 0.65 (s, 3H), 1.03 (s, 9H), 1.06 (s, 3H), 1.22 (s, 6H), 1.23 (s, 3H), 1.34 (dt, J = 4.4 and 16.0 Hz, 1H), 1.46 (ddd, J = 4.2, 9.3 and 13.7 Hz, 1H), 1.60 (ddd, J = 3.9, 9.1 and 13.2 Hz, 1H), 1.83-1.88 (m, 2H), 2.03-2.09 (m, 2H), 2.32 (ddd, J = 4.6, 9.3 and 13.4 Hz, 1H), 2.39 (dt, J = 4.2 and 14.3 Hz, 1H), 2.56-2.72 (m, 3H), 6.13-6.15 (m, 2H), 6.26 (d, J = 8.0 Hz, 1H), 6.70 (d, J = 7.6 Hz, 1H), 6.78-6.82 (m, 3H), 6.87 (s, 1H), 7.03, (dd, J = 7.6 and 7.7 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.24-7.27 (m, 1H), 7.36 (dd, J = 7.4 and 7.6 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H); 13C NMR δ –4.7, –3.7, 9.6, 9.8, 16.5, 17.0, 17.1, 17.2, 18.2, 23.1, 25.6, 29.1, 29.2, 29.6, 29.8, 31.3, 54.1, 54.5, 54.6, 54.9, 90.7, 90.9, 105.2, 114.6, 116.0, 122.2, 125.5, 125.7, 126.7, 127.1, 127.2, 127.5, 128.1, 129.3, 130.9, 131.0, 133.4, 137.6, 139.5, 139.7, 140.0 (2C), 141.1, 142.6, 143.1, 151.7, 165.0, 166.0, 177.7, 177.8; MS (EI): m/z (%) 904 (M+, 100), 905 (M+ + 1, 65); HRMS (MALDI) calcd for C36H60O9Si (M+) 904.4038, found 904.4001.

**X-Ray Crystallography**

**Crystal data for (P,aR)-4a:** C34H26O3, M = 482.55, triclinic, a = 10.1039(6), b = 11.6511(7), c = 11.8095(7) Å, α = 116.0420(10), β = 90.402(3), γ = 95.849(4)°, U = 1240.50(13) Å³, T = 100(2) K, space group P1, Z = 2, 22716 measured and 22716 independent reflections (Rint = 0.000), R1 = 0.0584, wR2 = 0.1639, Flack x parameter = –0.5(6).

**Crystal data for (P,aS)-6:** C36H28O3, M = 508.58, orthorhombic, a = 7.6471(4), b = 15.5793(9), c = 21.7870(13) Å, U = 2595.60(3) Å³, T = 100(2) K, space group P212121, Z = 4, 106248 measured and 5503 independent reflections (Rint = 0.0507), R1 = 0.0308, wR2 = 0.0854, Flack x parameter = –0.1(9).
13a (70:30)
(P,αS)-3a
(P,aR)-3b + (P,aS)-4b (20:80)
\[(P,aR)-3b + (P,aS)-4b\]
R* = \( \text{(P,aS)-20} \)
$R^* = \text{structure image}$

$(P,aS)-20$
(P,aS)-9a
$R^* = \text{OTBDMS}$

$\text{(P,aS)-21}$
(P,aS)-9b