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Total Synthesis of Heliophenanthrone

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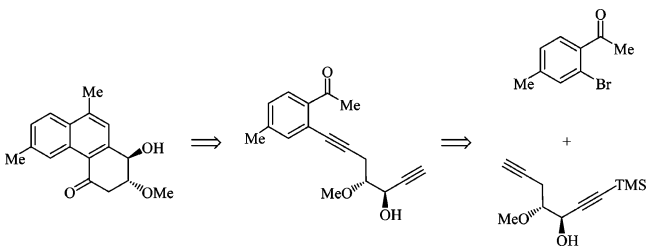
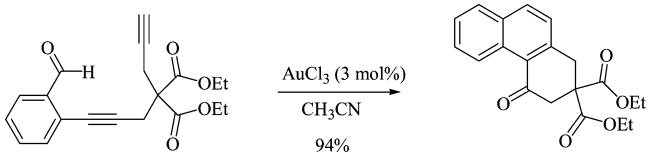


The total synthesis of *rac*-heliophenanthrone (**3a**) was achieved by a convergent approach, making use of a transition-metal-catalyzed domino process with an intramolecular Diels−Alder reaction at an isobenzopyrylium cation as key step.

Heliophenanthrone (**3a**) is a dihydrophenanthrene derivative which was isolated from *Heliotropium ovalifolium* by Hostettmann et al.[1] This herbaceous plant is infamous for its toxicity for cattle and sheep, but has also delivered some lead compounds for antibacterial and antifungal benzoquinones.[2]

We became interested in the synthesis of this natural product during our studies on gold-catalyzed domino processes.[3] Gold and platinum salts as catalysts are a focus of current interest: as rather soft and carbophilic Lewis acids they have demonstrated high activity in various reactions,[4] such as in alkylations of arenes and β-ketoesters, nucleophilic additions to alkenes and alkynes, as well as in isomerizations of enynes.[5] Gold, platinum, and copper salts are known for inducing the cyclization of *o*-alkynylbenzaldehydes and *o*-alkynylaryl ketones to isobenzopyrylium salts, which are interesting reactive intermediates for subsequent transformations, such as cycloaddition processes to polycyclic ring systems.[6] We envisioned that the tricyclic heliophenanthrone (**3a**) would be a suitable target for such a domino process.

SCHEME 1. Cyclization to Model Phenanthrone 2



The successful transformation of model compound **1**[7] to phenanthrone **2** via an intramolecular Diels−Alder reaction confirmed the applicability of this method for the construction of the target framework (Scheme 1). In analogy, our retrosynthetic analysis of heliophenanthrone (**3a**) suggested the substituted acetophenone **5** and the heptadiyne diastereoisomer **6a** as building blocks for a convergent total synthesis (Scheme 2).

Coupling component **5** is conveniently synthesized in just one step from 3-bromotoluene following the procedure of Yu et al.[8] For the synthesis of bisalkyne **6a** the glyoxylate **7** was chosen as starting material (Scheme 3). The first ethynyl group was introduced by a Reformatsky-type reaction with an organozinc reagent generated in situ.[9] Supported by sonication, this reaction took less than 5 min. After distillation of the crude product, the pentynoic ester **8** was obtained in 67% yield. The three-step sequence of methylation at the hydroxyl function,[10] reduction of the ester with $LiAlH_4$,[11] and subsequent Swern oxidation[12] gave the corresponding aldehyde **10**

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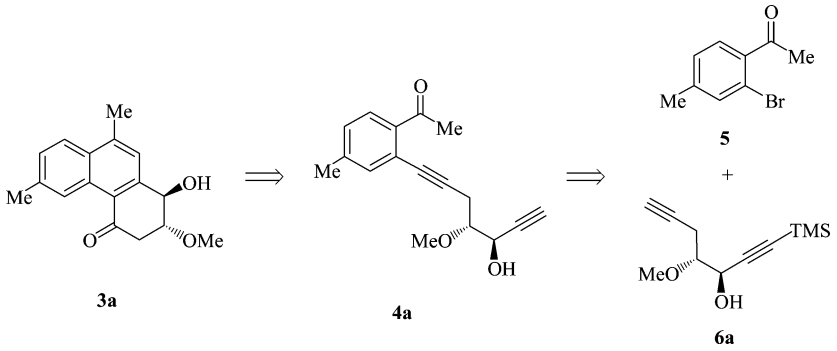
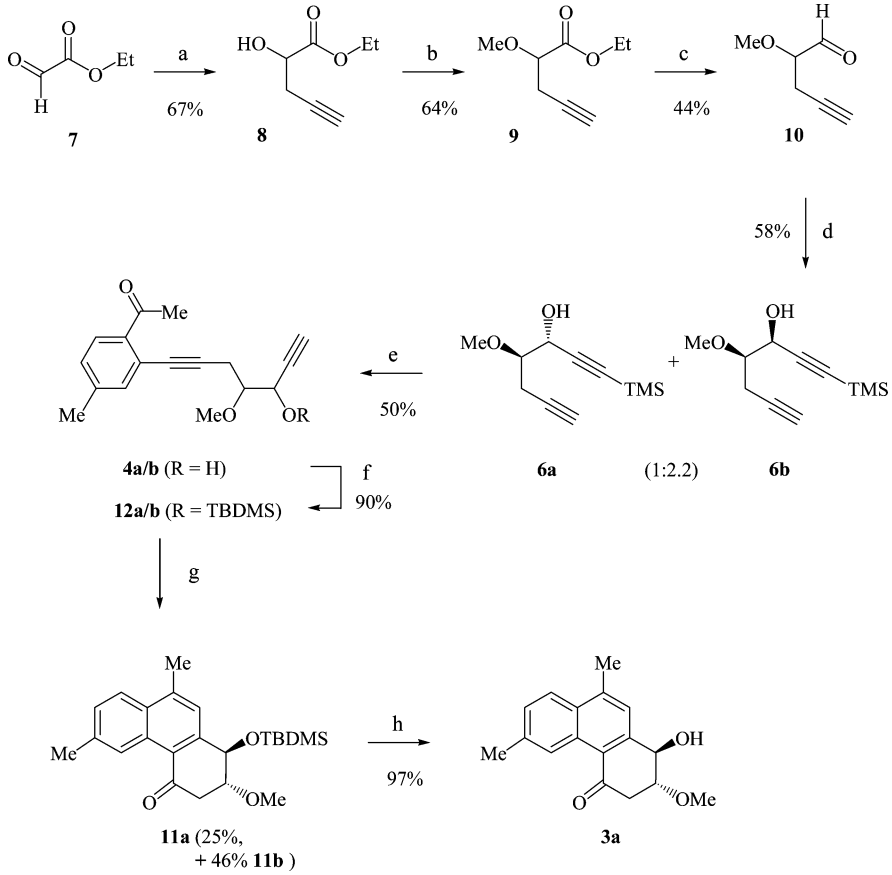
SCHEME 2. Retrosynthetic Analysis of Heliophenanthrone (3a)



SCHEME 3. Total Synthesis of *Rac*-Heliophenanthrone (3a)[a]



[a] Key: (a) Zn, Propargyl bromide, dioxane, sonication, 5 min; (b) NaH, MeI, THF; (c) (1) $LiAlH_4$, THF, (2) Swern oxidation; (d) TMS-acetylene, *n*-BuLi, THF; (e) (1) + aryl bromide **5**, Sonogashira coupling reaction, (2) *n*-Bu_4NF, THF; (f) TBDMSCl, imidazole, DMF; (g) $PtCl_2$, dioxane, 120 °C, 3 h; (h) HF, CH_3CN, 2 h.

in acceptable overall yield. Finally, lithiated trimethylsilyl acetylene was classically added to the aldehyde functionality.[13] The resulting mixture of diastereoisomers **6a** and **6b** in the ratio 1:2.2 was directly coupled with aryl bromide **5** in a Sonogashira reaction,[14] followed by the cleavage of the TMS group with *n*-Bu_4NF solution in THF:[15] the mixture of diastereomeric ketones **4a** and **4b** was obtained by flash chromatography in 50% yield. As it turned out, the hydroxyl group had to be protected for the gold-catalyzed step; otherwise, the reaction completely failed. Silylation with TBDMS chloride was chosen for protection to give **12a/b** in 90% yield.[15] The gold(III) chloride catalyzed cyclization of these dialkynyl ketones to the TBDMS-protected heliophenanthrone **11a** and its diastereomer **11b** gave only a moderate 35% overall yield. By changing to platinum(II) chloride as

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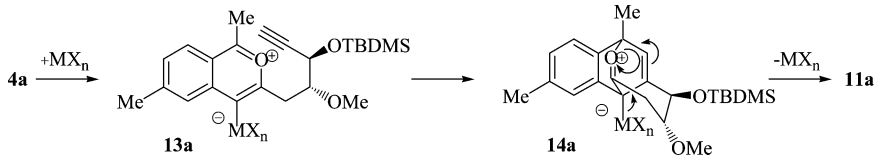
SCHEME 4. Mechanistic Rationale



catalyst in dioxane at 120 °C the overall yield of **11a/b** was raised to 71%. The mechanistic rationale (Scheme 4) for this domino process includes isobenzopyrylium cation **13a** and the Diels−Alder product **14a** as reactive intermediates.[3,6,16]

The two diastereoisomers **11a** and **11b** were easily separated by flash chromatography, as anticipated with the minor isomer **11a** as the protected natural product. Desilylation had to be performed under very mild conditions to prevent dehydratization and subsequent aromatization. With aqueous HF in acetonitrile[17] this final step in the synthesis of heliophenanthrone succeeded with almost quantitative yield, and the spectroscopic data (^{1}H NMR, MS) of the product proved to be identical with reported data.[1]

The transition-metal-catalyzed formation of isobenzopyrylium salts with a subsequent Diels−Alder reaction was proven to be a very valuable method for the construction of highly functionalized carbocyclic ring systems, with heliophenanthrone (**3a**) as a representative example. A high degree of complexity is achieved in just one preparative step, thus demonstrating the synthetic potential of this domino process.[18]

Experimental Section

4-Oxo-3,4-dihydro-1*H*-phenanthrene-2,2-dicarboxylic Acid Diethyl Ester (2). In a screw-capped flask, 170 mg (0.50 mmol) of **1** and 4.5 mg (15 μmol) of $AuCl_3$ were dissolved in 10 mL of acetonitrile. The mixture was stirred at 80 °C for 3 h, and after cooling to room temperature it was filtered through a short silica pad (eluent: ethyl acetate). Evaporation of the solvents and flash chromatography of the residue (SiO_2, petroleum ether/MTBE (4:1) $R_f = 0.27$) gave product **2** (160 mg, 0.47 mmol) in a yield of 94% as colorless crystals (mp 83 °C). IR (KBr): $\tilde{\nu}$ = 3055 (m), 2988 (s), 2904 (m), 2877 (m), 1755 (vs), 1729 (vs), 1673 (s), 1594 (s), 1511 (s), 1442 (m), 1434 (s), 1384 (m), 1371 (s), 1330 (s), 1306 (vs), 1253 (vs), 1209 (vs), 1188 (vs), 1162 (s), 1151 (s), 1139 (s), 1125 (s), 1092 (m), 1078 (s), 1053 (s), 1039 (s), 1012 (s), 819 (s), 752 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.16 (t, J = 7.0 Hz, 6H), 3.26 (s, 2H), 3.67 (s, 2H), 4.15 (q, J = 7.0 Hz, 4H), 7.35 (d, J = 8.0 Hz, 1H), 7.51 (td, J = 7.5, 1.0 Hz, 1H), 7.64 (td, J = 7.8, 1.5 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.5 Hz, 1H), 9.44 (d, J = 9.0 Hz, 1H). ^{13}C NMR {^{1}H} ($CDCl_3$, 100 MHz): δ = 14.2 36.9, 45.4, 55.1, 62.2, 126.37, 126.42, 126.88, 126.92, 128.5, 129.4, 131.3, 133.3, 135.4, 142.2, 169.9, 195.6. MS (70 eV, EI): m/z = 340 [M$^+$] (48), 295 (7), 267 (100), 239 (16), 221 (16), 195 (52), 177 (14), 165 (46), 140 (12). Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.19; H, 5.73.

2-Methoxypent-4-ynal (10). In a 250 mL, three-neck flask equipped with a mechanical stirrer and two dropping funnels was added with stirring a mixture of 2.30 mL (25.1 mmol) of oxalyl chloride and 60 mL of CH_2Cl_2 at −70 °C. A 3.90 mL (50.2 mmol) portion of DMSO in 10 mL of CH_2Cl_2 was added dropwise. After 2 min, 2.60 g (22.8 mmol) of 2-methoxy-pent-4-yn-1-ol in 20 mL of CH_2Cl_2 was added dropwise within 5 min and the mixture stirred an additional 15 min. A 16.0 mL (114 mmol) portion of triethylamine was added, and after 5 min the reaction was allowed to warm to room temperature. Water was added, and the aqueous phase was extracted 3 times with CH_2Cl_2. The organic extract was washed with brine and dried over sodium sulfate. The solvent was removed by distillation under normal pressure, and the aldehyde **10** was distilled under vacuum (∼30 mbar, 70 °C). The product **10** (1.57 g, 14.0 mmol, 61%) is a colorless liquid. IR (NaCl): $\tilde{\nu}$ = 3289 (vs), 2993 (w), 2937 (s), 2832 (s), 2735 (w), 2121 (w), 1736 (vs), 1189 (s), 1115 (vs), 1042 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.05 (t, J = 2.5 Hz, 1H), 2.61 (m, 2H), 3.53 (s, 3H), 3.72 (td, J = 6.0, 1.5 Hz, 1H), 9.71 (d, J = 1.5 Hz, 1H); ^{13}C NMR {^{1}H} ($CDCl_3$, 100 MHz): δ = 20.2 58.7, 71.1, 78.6, 83.2, 201.7. MS (70 eV, EI): m/z = 112 [M$^+$] (0.6), 83 (100), 68 (18), 55 (15), 53 (32), 51 (13), 45 (13). Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.16. Found: C, 64.63; H, 7.24.

4-Methoxy-1-trimethylsilanylhepta-1,6-diyn-3-ol (6a/b). To a solution of 1.65 g (16.8 mmol) of trimethylsilylacetylene in 20 mL of THF was dropped 10.7 mL (16.9 mmol) of *n*-butyllithium (1.6 M in hexane) at −78 °C. The mixture was stirred for 1 h, and then 1.57 g (14 mmol) of **10** in 10 mL of THF was added. The reaction was warmed to room temperature, and 50 mL of water was added. The aqueous layer was extracted three times with 20 mL portions of MTBE. The organic extract was washed with brine and dried over sodium sulfate. The solvents were evaporated, and the crude product was distilled in a vacuum (1 mbar, 95−102 °C). The diastereoisomers **6a** and **6b** (1.71 g, 8.12 mmol, 58%) were obtained in the ratio 1/2.2 as a colorless liquid. IR (NaCl): $\tilde{\nu}$ = 3431 (s), 3299 (s), 2959(s), 2900 (s), 2832 (m), 2174 (m), 2122 (w), 1251 (s), 1114 (s), 1071 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.18 (s, 9H), 2.02 ("t", 1H), 2.58 (m, 2H), 3.44−3.49 (m, 1H), 3.53 and 3.57 (s, 3H), 4.45 and 4.58 (d, J = 5.0 and 4.5 Hz, 1H). ^{13}C NMR {^{1}H} ($CDCl_3$, 100 MHz): δ = −0.09 and −0.06, 20.2 and 20.6, 59.0 and 59.4, 64.1 and 64.3, 70.2 and 70.6, 80.3 and 80.9, 82.0 and 82.2, 91.9, 102.8 and 103.7. MS (70 eV, EI): m/z = 210 (M$^+$, 0.4), 164 (5), 99 (10), 89 (10), 83 (100), 78 (7), 73 (73). Anal. Calcd for $C_{11}H_{18}O_2Si$: C, 62.81; H, 8.63. Found: C, 62.60; H, 8.59.

1-[2-(5-Hydroxy-4-methoxyhepta-1,6-diynyl)-4-methylphenyl]ethanone (4a/b). In a screw-capped flask 480 mg (2.25 mmol) of acetophenone **5**, 521 mg (2.48 mmol) of dialkyne **6a** and **6b**, 47.0 mg (0.07 mmol, 3 mol %) of $PdCl_2(PPh_3)_2$, and 6.00 mg (0.03 mmol, 1.5 mol %) of CuI were suspended in 20 mL of triethylamine. The mixture was heated under stirring at 80 °C for 5 h. The suspension was filtered through a short silica pad with ethyl acetate as eluent. After evaporation of the solvents, the residue was dissolved in 2 mL of THF. Five milliliters of a 1 M *n*-Bu_4NF solution in THF was added, and the solution was stirred for 2.5 h at room temperature. Brine was added, and the aqueous layer was extracted with MTBE. The organic extract was washed with an aqueous 5% HCl solution and dried over sodium sulfate. Evaporation of the solvents and flash chromatography of the residue (SiO_2, petroleum ether/ethyl acetate (2:1) $R_f = 0.26$) gave product **4a/b** (304 mg, 1.13 mmol, 50%) as yellow oil. IR (NaCl): $\tilde{\nu}$ = 3425 (vs, br), 3289 (vs), 2926 (m), 2831 (s), 2328 (m), 2227 (w), 2116 (w), 1677 (vs), 1600 (s), 1357 (s), 1280 (s), 1249 (s), 1112 (s), 1064 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.35 (s, 3H), 2.52 ("t", 1H), 2.67 (s, 3H), 2.76−2.96 ("dd" and "dd", 2H), 3.49−3.65 (m, 1H), 3.57 and 3.59 (s, 3H), 4.61 and 4.71 (dd, J = 4.8, 2.0 Hz and 4.3, 2.0 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.32 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H). ^{13}C NMR {^{1}H} ($CDCl_3$, 100 MHz): δ = 21.3 21.4 and 21.5, 29.6 and 29.7, 58.9 and 59.1, 63.9 and 64.0, 74.4 and 74.7, 81.6, 82.0 and 82.1, 82.2, 91.0 and 91.1, 122.09 and 122.13, 128.90 and 128.92, 129.20 and 129.24,

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135.0 and 135.1, 137.89 and 137.93, 142.1, 199.7. MS (70 eV, EI): m/z = 269 [M^+] (0.8), 255 (6), 221 (10), 215 (40), 196 (100), 185 (18), 172 (44), 146 (13), 128 (36), 115 (15). Anal. Calcd $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.46; H, 6.70.

1-{2-[5-(*tert*-Butyldimethylsilanyloxy)-4-methoxyhepta-1,6-diynyl]-4-methyl-phenyl}ethanone (12a/b). To a solution of 288 mg (1.07 mmol) of **4a/b** in 10 mL of DMF 241 mg (1.60 mmol) of *tert*-butyldimethylsilyl chloride and 254 mg (3.73 mmol) of imidazole were successively added. After being stirred overnight, the mixture was diluted with 20 mL of brine and extracted with MTBE (5 × 10 mL). The organic layer was washed with a cooled aqueous 5% HCl solution and with brine and dried over sodium sulfate. Evaporation of the solvents and flash chromatography of the residue (SiO_2, petroleum ether/ethyl acetate (10:1) R_f = 0.16) gave product **12a/b** (369 mg, 0.96 mmol, 90%) as yellow oil. IR (NaCl): $\tilde{\nu}$ = 3305 (s), 2953 (vs), 2928 (vs), 2889 (s), 2856 (vs), 2229 (w), 2115 (w), 1680 (vs), 1602 (s), 1358 (s), 1278 (s), 1253 (vs), 1118 (vs), 838 (vs), 781 (vs), 671 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.14 and 0.15 (s, 3H), 0.17 (s, 3H), 0.92 and 0.93 (s, 9H), 2.34 (s, 3H), 2.45 ("t", 1H), 2.71 and 2.72 (s, 3H), 2.74−2.94 (m, 2H), 3.46−3.54 (m, 1H), 3.56 and 3.58 (s, 3H), 4.58−4.59 ("dd", 1H), 7.14 (d, J = 8.0 Hz, 1H), 7.31 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H). ^{13}C NMR {^1H} ($CDCl_3$, 100 MHz): δ = −5.0, −4.9, −4.6 , −4.5, 18.3 and 18.4, 21.3, 21.8 and 21.9, 25.9, 30.1 and 30.2, 59.3 and 59.6, 64.5 and 64.7, 73.8 and 74.4, 81.1 and 81.5, 82.5 and 82.9, 83.0 and 83.2, 92.7 and 93.3, 122.4, 128.8, 128.9, 134.8, 138.3, 141.9, 200.2 and 200.3. MS (70 eV, EI): m/z = 384 [M^+] (2), 353 (8), 327 (43), 295 (5), 215 (25), 196 (41), 185 (7), 171 (50), 157 (5), 141 (5), 128 (16), 115 (8), 89 (100). HRMS (ESI) calcd for $C_{23}H_{33}O_3Si$ (M^+ + H) 385.2193, found 385.2205.

1-(*tert*-Butyldimethylsilanyloxy)-2-methoxy-6,9-dimethyl-2,3-dihydro-1*H*-phenanthren-4-one (11a) and (11b). In a screw-capped flask 107 mg (0.28 mmol) of **12a/b** and 4.0 mg (14 μmol) of $PtCl_2$ were dissolved in 20 mL of dioxane. The mixture was stirred at 120 °C for 3 h, and after being cooled to room temperature it was filtered through a short silica pad (eluent: ethyl acetate). Evaporation of the solvents and flash chromatography of the residue (SiO_2, petroleum ether/ethyl acetate (16:1), R_f = 0.30, 0.23) gave product **11a** (fraction 1, 27.0 mg, 0.07 mmol, 25%) and product **11b** (fraction 2, 49.0 mg 0.13 mmol, 46%) in an overall yield of 71% as yellow resin (**11a**, mp 104−105 °C; **11b**, mp 89−90 °C). **11a**. IR (KBr): $\tilde{\nu}$ = 2962 (s), 2927 (s), 2895 (s), 2855 (s), 1663 (s), 1259 (s), 1242 (s), 1142 (s), 1106 (s), 1095 (s), 778 (m), 676 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.15 (s, 3H), 0.23 (s, 3H), 0.94 (s, 9H), 2.55 (s, 3H), 2.72 (s, 3H), 2.77 and 3.29 (dd and dd, J = 16.6, 7.0 Hz and 16.6, 4.0 Hz, 2H), 3.42 (s, 3H), 3.78 ("ddd", J = 6.5, 4.0 Hz, 1H), 4.90 (d, J = 6.0 Hz, 1H), 7.39 (dd, J = 8.5, 1.5 Hz, 1H), 7.41 (s, 1H), 7.90 (d, J = 8.6 Hz, 1H), 9.25 (s, 1H).; ^{13}C NMR {^1H} ($CDCl_3$, 100 MHz): δ = −4.3, −4.1, 18.4, 20.5, 22.3, 26.1, 42.2, 57.0, 72.7, 80.5, 124.0, 124.8, 126.1, 126.7, 128.5, 131.0, 131.3, 138.7, 142.0, 144.6, 197.7. MS (70 eV, EI): m/z = 384 [M^+] (1.5), 327 (100), 295 (9), 209 (5), 179 (5), 149 (5). **11b**. IR (KBr): $\tilde{\nu}$ = 2928 (s), 2854 (s), 1664 (vs), 1140 (s), 1112 (s), 1075 (s), 986 (s), 838 (vs), 776 (s), 676 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.10 (s, 3H), 0.21 (s, 3H), 0.90 (s, 9H), 2.56 (s, 3H), 2.73 (s, 3H), 2.87 and 3.17 (dd and dd, J = 17.0, 4.5 Hz and 17.0, 8.5 Hz, 2H), 3.45 (s, 3H), 3.86 (ddd, J = 8.5, 4.5, 2.5 Hz, 1H), 5.09 (d, J = 2.5 Hz, 1H), 7.35 (s, 1H), 7.39 (dd, J = 8.8, 1.5 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 9.25 (s, 1H).; ^{13}C NMR {^1H} ($CDCl_3$, 100 MHz): δ = −4.4, −4.2, 18.5, 20.5, 22.3, 25.9, 41.6, 56.9, 71.6, 78.5, 124.1, 124.9, 125.8, 126.5, 128.5, 131.1, 131.4, 139.8, 142.1, 144.4, 198.3. MS (70 eV, EI): m/z = 384 [M^+] (1), 327 (65), 221 (6), 179 (5), 89 (100). Anal. Calcd $C_{23}H_{32}O_3Si$: C, 71.83; H, 8.39. Found: C, 71.68; H, 8.51.

***rac*-Heliophenanthrone (3a).** In a 25 mL flask,30 mg (77 μm) of **11a** was dissolved in 2 mL of 5% of a 40% aqueous solution of HF in acetonitrile. After 2 h of stirring at room temperature, 10 mL of chloroform and 10 mL of water were added. The organic phase was removed, and the aqueous layer was extracted once again with 10 mL of chloroform. Evaporation of the solvents and flash chromatography of the residue (SiO_2, petroleum ether/ethyl acetate (1:2) R_f = 0.23) gave product **3a** (21 mg, 73 μm, 93%) as colorless crystals (mp 157−158 °C). IR (KBr): $\tilde{\nu}$ = 3330 (br, s), 2924 (s), 1662 (vs), 1595 (s), 1243 (m), 1177 (m), 1145 (m), 1113 (s), 1079 (m), 1051 (m), 833 (m), 815 (m), 750 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.57 (s, 3H), 2.65 and 3.31 (dd and dd, J = 16.3, 10.6 Hz and 16.3, 4.5 Hz, 2H), 2.76 (s, 3H), 3.52 (s, 3H), 3.71 (ddd, J = 10.6, 8.5, 4.5 Hz, 1H), 4.91 (d, J = 8.5 Hz, 1H), 7.41 (dd, J = 8.5, 1.5 Hz, 1H), 7.70 (s, 1H), 7.93 (d, J = 8.5 Hz, 1H), 9.28 (s, 1H). ^{13}C NMR {^1H} ($CDCl_3$, 100 MHz): δ = 20.6, 22.4, 43.3, 57.0, 72.7, 80.7, 123.6, 123.7, 124.2, 126.4, 128.7, 130.9, 131.2, 139.1, 143.0, 144.2, 196.9.; MS (70 eV, EI): m/z = 270 [M^+] (51), 212 (100), 184 (36), 169 (17), 155 (23), 141 (8), 128 (5), 115 (5).

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Supporting Information Available: Characterization data and spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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