Highly Stereoselective Synthesis of Perhydro-8a-(hydroxymethyl)-phenanthrene-1,2,4,5,7,8-hexol and Derivatives

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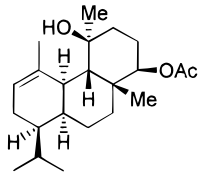
Diterpenes of the type tetradecahydrophenanthrene with *cis,trans,cis* ring junctions are very rare natural compounds. The compounds α-dictalediol monoacetate (**1**)[1] and *β*-dictalediol monoacetate (**2**)[2] were isolated from a brown algae of the genus *Dictyota*, the extracts of which exhibit cytotoxic, antibacterial, and antiviral activities.[1] We wish to disclose here a highly convergent synthetic approach to *cis,trans,cis*-perhydrophenanthrene ring systems bearing up to six alcoholic moieties (with three different kinds of protective groups) and one angular oxymethyl substituent,[3] making them analogues of **1** and **2**.[4] The method is based on the stereoselective Diels−Alder cyclodimerization of 2-vinyl-7-oxabicyclo[2.2.1]hept-2-ene derivatives[5] and subsequent chemoselective ethereal ring opening of the two 7-oxabicyclo[2.2.1]heptane moieties.



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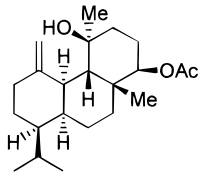

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The bromoalkenol **4**, derived from 7-oxabicyclo[2.2.1]-hept-5-en-2-one (**3**) in three steps,[6] underwent a Sonogashira coupling[7] with ethynyltrimethylsilane ([Pd(PPh$_3$)$_4$]/CuI as catalyst) in DMF (50 °C, 4 h), giving **5** (79%). Reduction of **5** with zinc activated by KCN[8] afforded diene **6** (88%). When heated to 55 °C (120 h), a 37% solution of **6** in CH_3CN furnished one single cyclodimer **7** isolated in 61% yield. The structure of **7** was assigned from 2D ^{1}H NMR spectra (COSY, NOESY). It was further confirmed by oxidation (Dess−Martin periodinane) into the known diketone **8**.[5] Acetylation (Ac_2O/pyridine/DMAP) of diol **7** provided the diacetate **9** (98%), the vinyl group of which could be oxidized chemoselectively with $NaIO_4/OsO_4$ in aqueous dioxane,[9] giving the aldehyde **10** (57%). Reduction of **10** with $NaBH_4$ in $MeOH/CH_2Cl_2$ followed by esterification with Ac_2O/pyridine furnished **11** (77%).

With the goal of carrying out chemoselective oxa-bridge openings, we treated **11** under various acidic conditions with the hope of quenching intermediate allylic cations derived from the 2-methylidene-7-oxabicyclo[2.2.1]heptane moiety. Unfortunately, we did not find conditions under which aromatization was avoided. With $BF_3{\cdot}Et_2O$, a mixture was obtained from which the styrene derivative **12** was isolated in 36% yield. Using Me_3SiOTf, the same compound was obtained in 75% yield. Hydrogenation (H_2/Pd−C, AcOEt) of **12** afforded **13**, which underwent a smooth S_N2-type heterolysis of the ethereal bridge on heating with HBr/AcOH (55 °C, 18 h), giving bromide **14** (80%). In this case, the less hindered bridgehead center of the 7-oxabicyclo[2.2.1]heptane system is attacked by the bromide anion.[10] Interestingly, treatment of **13** with BBr_3 (CH_2Cl_2, −20 °C) resulted in oxa-ring opening without incorporation of bromine. Workup with water gave instead the diacetate **16** (69%), suggesting that the ether cleavage is assisted by the *endo* acetoxy moiety with formation of an intermediate of type **15**. Intermediate **15** subsequently reacts with water and gives **16** selectively.[11] The diacetate **16** was deprotected by methanolysis ($MeOH/NH_3$, 20 °C), affording the tetrol **17**. The relative configurations of **14**, **16**, and **17** were determined by their ^{1}H NMR spectra and double irradiation experiments.

In order to avoid aromatization during the ethereal bridge cleavage, we reduced triacetate **11** with H_2/Pd−C, providing **18** (99%). All of our attempts to open one of the two ethereal bridges of **18** gave complicated mixtures, probably due to the inefficient participation ability of the two *endo* acetoxy substituents. We thus exchanged the acetates of **18** for three *p*-methoxybenzoates (anisoates) as in **19**, which proved to be a low-yielding process (saponification, followed by esterification). Thus, the dienediol **7** was benzylated[12] to provide **20** (95%), which was then oxidized with $NaIO_4/OsO_4$ to give aldehyde **21** (76%). Reduction of **21** with $NaBH_4$

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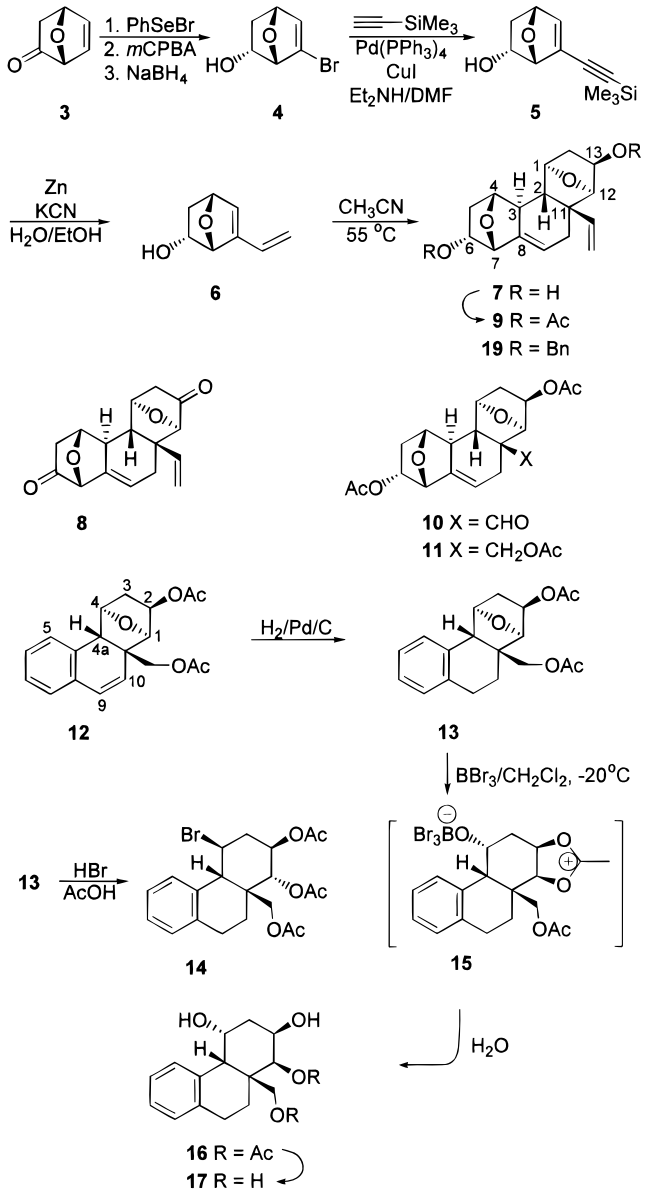

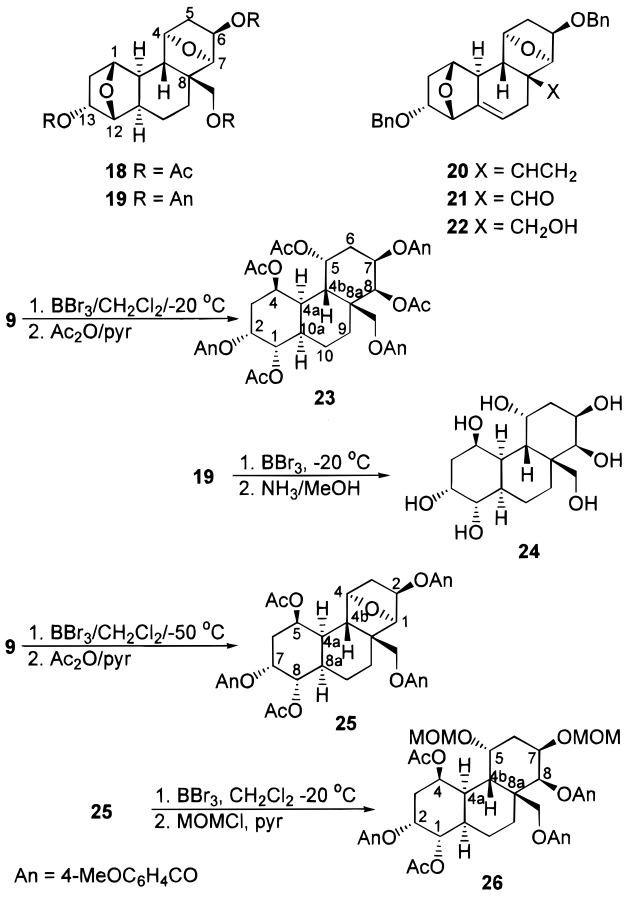

gave **22** (89%), which was hydrogenated, hydrogenolyzed (H_2/Pd−C), and then esterified with *p*-$MeOC_6H_4COCl$/pyridine/4-(dimethylamino)pyridine to provide **19** (94%).

Treatment of triester **19** with BBr_3 in CH_2Cl_2 at −20 °C gave a major compound that was insoluble in most organic solvents. Acetylation (Ac_2O/pyridine, DMAP, 20 °C) provided the tetraacetate **23**, the ^{1}H- and ^{13}C NMR spectra of which showed broad signals even at 100 °C (toluene). The structure of **23** was determined by single-crystal X-ray diffraction (see the Supporting Information).[13] In contrast to the preparation of **16**, in which migration of the *endo* acetoxy group resulted from its participation in the reaction, no migration of the (*p*-methoxybenzoyl)oxy substituents occurred during the BBr_3-induced heterolysis of the two 7-oxabicyclo[2.2.1]-heptane ethereal bridges of **19** and quenching of the cationic intermediates with water.

When the treatment of **19** with BBr_3 at −20 °C was followed by methanolysis (MeOH/NH_3, 50 °C), the heptol **24** (51%) was obtained, the structure of which was confirmed from spectral data and an elemental analysis. On treating **19** with BBr_3 in CH_2Cl_2 at −50 °C (instead of −20 °C), a regioselective oxa-bridge opening was observed leading to the diacetate **25** (75%), after acetylation of the intermediate diol. The ^{1}H and ^{13}C NMR spectra of **25** showed broad signals at 25 °C that coalesced above 60 °C (benzene). Typical vicinal coupling constants between proton pairs H-C(4a)/H-C(4b) (9.9 Hz), H-C(8)/H-C(8a) (8.0 Hz), H-C(5)/H-C(4b) (4.2 Hz), and H_{endo}-C(4)/H-C(4a) (0 Hz)[14] proved that the oxa bridge at C(1), C(12) of **19** had been opened and not that at C(4), C(7). The reasons for the observed regioselectivity are not obvious. For the moment we must admit that the participation of the *endo* (*p*-methoxybenzoyl)oxy group of **19** at C(6) is impeded by the *endo* [(*p*-methoxybenzoyl)oxy]methyl substituent at C(8) perhaps for steric, conformational, or/and solvation reasons.

Treatment of **25** with BBr_3 in CH_2Cl_2 at −20 °C gave a major diol intermediate that was converted into **26** (47%) on treatment with CH_3OCH_2Cl/(*i*-Pr)$_2$EtN. Methanolysis of this diol provided the heptol **24**, as expected, thus proving the structure of **25** and **26**. This reaction also afforded a small amount (25%) of the regioisomeric diol in which no migration of the (*p*-methoxybenzoyl)oxy substituent occurred. This compound was converted into **23** upon acetylation.

This note discloses a very efficient synthetic approach to polyfunctional perhydrophenanthrene systems with *cis*,*trans*,*cis* ring junctions. The discovery of regioselec-

(13) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-101. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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tive BBr_3-induced ethereal bridge openings of the 1,4:5,8-bis(epoxy)phenanthrene intermediates makes the method extremely versatile. Since the starting 7-oxabicyclo[2.2.1]hept-5-en-2-one (**3**) can be obtained readily in both enantiomeric forms ("naked sugars of the first generation"[15]), the new perhydropolyhydroxyphenanthrene derivatives presented here can, in principle, be prepared in their two enantiomerically pure forms since the cyclodimerization of the semicyclic dienes such as **6** requires homochiral matching.[5]

Experimental Section

General Methods. See ref 16.

(±)-6-[(Trimethylsilyl)ethynyl]-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol (5). (±)-6-Bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol (3.03 g, 15.9 mmol),[6] ethynyltrimethylsilane (4.4 mL, 32 mmol), anhydrous DMF (15 mL), Et_2NH (4 mL), CuI (121 mg, 0.64 mmol), and $Pd(Ph_3P)_4$ (368 mg, 0.32 mmol) were introduced successively into a Schlenk vessel. After degassing (two freeze/thaw cycles, vacuum line), the mixture was stirred at 50 °C for 4 h. The solvent was removed by distillation *in vacuo* and the residue taken up with EtOAc (20 mL). The solution was filtered through a pad of silica gel (3 cm), rinsing with EtOAc (400 mL). After solvent evaporation, the brownish oil was purified by flash chromatography (silica gel, EtOAc/CH_2Cl_2/light petroleum 1:1:3), yielding 2.59 g (79%) of a yellow oil that crystallized from CH_2Cl_2/hexane at −20 °C: mp 77−78 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.75 (1 H, d, J = 1.9 Hz), 4.97 (1 H, dd, J = 5.0, 1.9 Hz), 4.86 (1 H, d, J = 4.3 Hz), 4.53 (1 H, br dddd, J = 8.1, 7.5, 4.3, 2.4 Hz), 2.33 (1 H, ddd, J = 12.1, 8.1, 5.0 Hz), 1.65 (OH, br d, J = 7.5 Hz), 1.10 (1 H, dd, J = 12.1, J = 2.4 Hz), 0.20 (9 H, s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 142.0, 127.3, 102.4, 98.2, 82.4, 80.3, 68.8, 35.4, −0.2.

(±)-6-Vinyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol (6). A suspension of **5** (1.20 g, 6.24 mmol), 5:4 EtOH/H_2O (15 mL), KCN (4.10 g, 62.4 mmol), and Zn (powder, 5 g) was stirred vigourously in the dark at 20 °C for 50 min. The solid was removed via filtration through Celite, rinsing with EtOH, the solution was concentrated to 40 mL by solvent evaporation, and NaCl was added until saturation. The mixture was extracted with CH_2Cl_2 (10 mL, 10 times). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated, giving 786 mg (88%) of a colorless oil that polymerizes quickly at 20 °C: ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.59 (1 H, dd, J = 17.5, 10.7 Hz), 6.39 (1 H, d, J = 1.7 Hz), 5.37 (1 H, d, J = 17.5 Hz), 5.24 (1 H, d, J = 10.7 Hz), 5.10 (1 H, d, J = 4.6 Hz), 4.92 (1 H, dd, J = 4.8, 1.7 Hz), 4.54 (1 H, dddd, J = 8.3, 8.1, 4.6, 2.3 Hz), 2.32 (1 H, ddd, J = 12.0, 8.1, 4.8 Hz), 1.58 (1 H, br d, J = 8.3 Hz), 1.06 (1 H, dd, J = 12.0, 2.3 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.4, 133.5, 130.6, 116.9, 80.0, 79.4, 68.6, 35.6.

(1*RS*,2*SR*,3*SR*,4*RS*,6*RS*,7*RS*,11*SR*,12*RS*,13*RS*)-11-Vinyl-15,16-dioxapentacyclo[10.2.1.1^{4,7}.0^{3,8}.0^{2,11}]hexadec-8-ene-6,13-diol (7). A mixture of crude **6** (1.05 g, 7.60 mmol), CH_3CN (3 mL), and BHT (2,6-di-*tert*-butyl-*p*-cresol, 120 mg) was heated in the dark at 55 °C for 120 h. The mixture was filtered through a pad of silica gel (boiling EtOAc, 200 mL), and the solution was concentrated by evaporation to 5 mL. After cooling to −20 °C, 667 mg of colorless crystals were collected. The mother liquor was purified by flash chromatography (silica gel, EtOAc), giving 60 mg of crystalline **7**: yield 727 mg (69%); mp 152−153 °C (EtOAc); ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.20 (1 H, dd, J = 17.5, 10.8 Hz), 5.78 (1 H, m), 5.06 (1 H, d, J = 10.8 Hz), 5.01 (1 H, d, J = 17.5 Hz), 4.68 (1 H, d, J = 5.0 Hz), 4.67−4.26 (2 H, m), 4.41 (1 H, d, J = 5.6 Hz), 4.33 (1 H, d, J = 6.2 Hz), 3.97 (1 H, d, J = 4.5 Hz), 2.45 (1 H, ddd, J = 12.7, 10.6, 6.2 Hz), 2.34 (1 H, ddd, J = 12.8, 9.6, 5.6 Hz), 2.30−2.16 (2 H, m), 2.06 (1 H, br d, J = 8.4 Hz), 1.99 (2 H, br s), 1.70 (1 H, br d, J = 8.4 Hz), 1.26 (1 H, dd, J = 12.8, 2.7 Hz), 1.17 (1 H, dd, J = 12.7, 4.9 Hz); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 141.4, 142.2, 121.0, 114.9, 84.6, 84.5, 81.3, 75.5, 70.7, 54.9, 51.8, 48.4, 40.1, 39.4, 34.8.

(1*RS*,2*SR*,3*SR*,4*RS*,7*RS*,11*SR*,12*RS*)-11-Vinyl-15,16-dioxapentacyclo[10.2.1.1^{4,7}.0^{3,8}.0^{2,11}]hexadec-8-ene-6,13-dione (8). A mixture of **7** (250 mg, 0.905 mmol), Dess−Martin periodinane (1.15 g, 2.72 mmol), and CH_2Cl_2 (30 mL) was stirred at 20 °C for 2 h. The mixture was diluted with CH_2Cl_2 (50 mL) and washed with a 10% aqueous solution of $Na_2S_2O_3$ (50 mL, twice), each aqueous phase being extracted with CH_2Cl_2 (10 mL, twice). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was filtered through a pad of silica gel, rinsing with CH_2Cl_2/EtOAc (13:1), and crystallized from EtOAc/light petroleum, yielding 207 mg (84%) of colorless needles, mp 142−143 °C (EtOAc/light petroleum). Spectral characteristics were identical to those already reported.[5]

(1*RS*,2*SR*,3*SR*,4*RS*,6*RS*,7*RS*,11*SR*,12*RS*,13*RS*)-11-Vinyl-15,16-dioxapentacyclo[10.2.1.1^{4,7}.0^{2,11}.0^{3,8}]hexadec-8-ene-6,13-diyl Diacetate (9). A mixture of **8** (0.3 g, 1.09 mmol), anhydrous pyridine (2 mL), Ac_2O (2 mL), and DMAP (4-(dimethylamino)pyridine, 10 mg) was stirred at 20 °C for 16 h. After solvent evaporation, the residue was purified by flash chromatography (silica gel, EtOAc/light petroleum 1:2), yielding 387 mg (99%) of a colorless oil that crystallized from a minimum of hexane: colorless prisms; mp 108−110 °C (hexane); ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.85 (1 H, dd, J = 17.3, 10.9 Hz), 5.60 (1 H, ddd, J = 6.8, 3.9, 3.2 Hz), 4.98−4.90 (3 H, m), 4.86 (1 H, d, J = 10.9 Hz), 4.81 (1 H, d, J = 17.3 Hz), 4.40, 4.35 (2 H, 2 d, J = 5.5, 6.1 Hz), 4.27 (1 H, d, J = 4.4 Hz), 2.42 (1 H, ddd, J = 12.7, 10.8, 6.1 Hz), 2.34 (1 H, ddd, J = 13.0, 9.7, 5.5 Hz), 2.27 (1 H, dd, J = 13.5, 6.8 Hz), 2.08 (1 H, dd, J = 13.5, 3.9 Hz), 1.99, 1.97 (6 H, 2 s), 1.96 (1 H, dd, J = 9.3, 3.2 Hz), 1.84 (1 H, d, J = 9.3 Hz), 1.51 (1 H, dd, J = 12.7, 2.4 Hz), 1.48 (1 H, dd, J = 13.0, 4.8 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.9, 170.8, 141.8, 140.9, 118.2, 112.0, 84.4, 83.5, 80.7, 79.6, 75.0, 73.5, 54.5, 53.4, 47.3, 36.7, 37.3, 33.1, 21.0, 20.9.

(1*RS*,2*SR*,3*SR*,4*RS*,6*RS*,7*RS*,11*SR*,12*RS*,13*RS*)-11-Formyl-15,16-dioxapentacyclo[10.2.1.1^{4,7}.0^{2,11}.0^{3,8}]hexadec-8-ene-6,13-diyl Diacetate (10). A mixture of **9** (372 mg, 1.03 mmol), 9:5 dioxane/H_2O (14 mL), $NaIO_4$ (442 mg, 2.06 mmol), and a 0.1 M CCl_4 solution of OsO_4 (1.03 mL, 0.103 mmol) was stirred at 20 °C for 8 h. After solvent evaporation to half volume, NaCl was added until saturation and the solution was extracted with CH_2Cl_2 (10 mL, five times). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by flash chromatography (silica gel, EtOAc/light petroleum 1:1), giving 214 mg (57%) of a colorless powder that was recrystallized from CH_2Cl_2/hexane: mp 185−188 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.51 (1 H, s), 5.58 (1 H, ddd, J = 7.2, 3.7, 1.4 Hz), 5.01 (1 H, ddd, J = 10.4, 4.6, 4.1 Hz), 4.93−4.89 (2 H, m), 4.47 (1 H, d, J = 6.2 Hz), 4.45 (1 H, d, J = 5.8 Hz), 4.42 (1 H, d, J = 4.6 Hz), 2.82 (1 H, dd, J = 14.1, 7.2 Hz), 2.49 (1 H, ddd, J = 13.2, 10.4, 6.2 Hz), 2.38 (1 H, d, J = 9.2 Hz), 2.38−2.31 (1 H, m), 2.06 (1 H, dd, J = 14.1, 3.7 Hz), 2.03 (1 H, dd, J = 9.2, 1.4 Hz), 2.00, 1.96 (6 H, 2 s), 1.50 (1 H, J = 11.9, 2.4 Hz), 1.46 (1 H, dd, J = 13.2, 4.1 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 199.1, 170.5, 169.8, 143.1, 116.2, 84.1, 83.4, 79.9, 79.3, 73.5, 73.1, 63.7, 50.6, 46.5, 36.4, 35.5, 28.8, 20.7, 20.5.

(1*RS*,2*SR*,3*SR*,4*RS*,6*RS*,7*RS*,11*RS*,12*RS*,13*RS*)-11-(Acetoxymethyl)-15,16-dioxapentacyclo[10.2.1.1^{4,7}.0^{2,11}.0^{3,8}]-hexadec-8-ene-6,13-diyl Diacetate (11). $NaBH_4$ (40 mg) was added to a stirred solution of **10** (172 mg, 0.47 mmol) in 4:3 MeOH/CH_2Cl_2 (7 mL) cooled to 0 °C. After being stirred at 0 °C for 15 min, 10% aqueous HCl was added to pH 4. The solution was concentrated to a quarter of the volume by solvent evaporation, and NaCl was added until saturation. The mixture was extracted with CH_2Cl_2 (10 mL, eight times). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was taken with anhydrous pyridine (3 mL), and Ac_2O (3 mL) and DMAP (5 mg) were added. After the mixture was stirred at 20 °C for 2 days, the solvent was evaporated *in vacuo* and the residue filtered through a pad of silica gel (EtOAc/light petroleum 1:1), yielding 148 mg (77%) of a colorless solid

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that was recrystallized from EtOAc/hexane to give colorless needles; mp 182−182.5 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.66 (1 H, ddd, J = 7.3, 3.5, 1.5 Hz), 5.02 (1 H, ddd, J = 10.9, 5.4, 4.5 Hz), 4.95 (1 H, d, J = 4.8 Hz), 4.89 (1 H, ddd, J = 9.6, 4.8, 2.4 Hz), 4.32 (2 H, 2 d, J = 6.2, 5.5 Hz), 4.24 (1 H, d, J = 4.5 Hz), 4.04 (2 H, br s), 2.47 (1 H, ddd, J = 12.8, 10.9, 6.2 Hz), 2.35 (1 H, ddd, J = 14.1, 7.3 Hz), 2.30 (1 H, ddd, J = 12.9, 9.6, 5.5 Hz), 2.03, 1.96, 1.94 (9 H, 3 s), 1.97 (1 H, dd, J = 9.4, 1.5 Hz), 1.88 (1 H, dd, J = 14.1, 3.5 Hz), 1.47 (1 H, dd, J = 12.9, 2.4 Hz), 1.46 (1 H, dd, J = 12.8, 5.4 Hz), 1.29 (1 H, d, J = 9.4 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.6, 170.5, 170.3, 141.6, 117.6, 83.6, 82.3, 79.9, 79.4, 74.7, 73.2, 66.9, 53.2, 51.6, 46.8, 36.4, 34.8, 30.0, 20.7, 20.6, 20.5.

(1*RS*,2*RS*,4*RS*,4a*RS*,10a*RS*)-10a-(Acetoxymethyl)-1,2,3,4,-4a,10a-hexahydro-1,4-epoxyphenanthren-2-yl Acetate (12). $Me_3SiOSO_2CF_3$ (98 μL, 120 mg, 0.44 mmol) was added to a stirred solution of **11** (73 mg, 0.128 mmol) in anhydrous CH_2Cl_2 (3 mL) and Ac_2O (0.4 mL) cooled to 0 °C. After the solution was stirred at 0 °C for 2 h, a saturated aqueous solution of $NaHCO_3$ (15 mL) was added, and the mixture was stirred vigorously at 0 °C for 15 min. The organic phase was collected, and the aqueous layer was extracted with CH_2Cl_2 (10 mL, three times). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by flash chromatography (silica gel, EtOAc/light petroleum 1:3), yielding 44 mg (75%) of a solid that was recrystallized from CH_2Cl_2/hexane: mp 159−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.13, 7.07−7.05, 7.01−6.99 (4 H, 3 m), 6.41 (1 H, d, J = 9.8 Hz), 5.76 (1 H, d, J = 9.8 Hz), 5.18 (1 H, ddd, J = 11.0, 4.6, 4.5 Hz), 4.53 (1 H, d, J = 5.7 Hz), 4.51, 4.46 (2 H, 2 d, J = 11.0 Hz), 4.46 (1 H, d, J = 4.5 Hz), 3.11 (1 H, s), 2.57 (1 H, ddd, J = 12.9, 11.0, 5.7 Hz), 2.07, 2.02 (6 H, 2 s), 1.77 (1 H, dd, 12.9, J = 4.6 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.6, 170.4, 133.7, 130.9, 128.4, 128.3, 128.1, 127.4, 127.2, 127.1, 89.6, 83.0, 75.1, 69.1, 52.1, 51.6, 37.6, 20.8, 20.7.

(1*RS*,2*RS*,4*RS*,4a*RS*,10a*RS*)-10a-(Acetoxymethyl)-1,2,3,4,-4a,9,10,10a-octahydro-1,4-epoxyphenanthren-2-yl Acetate (13). A mixture of **12** (30 mg, 91 μmol), 10% Pd on charcoal (20 mg), and EtOAc (8 mL) was degassed and pressurized with H_2 (1 atm). After being stirred at 20 °C for 3 h, the mixture was filtered through Celite and the solvent was evaporated, yielding 30 mg (100%) of a colorless solid that was recrystallized from $CHCl_3$/hexane: mp 148−149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.09 (4 H, m), 5.14 (1 H, ddd, J = 11.0, 4.9, 4.6 Hz), 4.60 (1 H, d, J = 5.9 Hz), 4.46 (2 H, s), 4.39 (1 H, d, J = 4.6 Hz), 2.79 (1 H, ddd, J = 16.0, 6.4, 4.4 Hz), 2.69 (1 H, s), 2.63 (1 H, ddd, J = 16.0, 6.5, 4.3 Hz), 2.58 (1 H, ddd, J = 12.8, 11.0, 5.9 Hz), 2.09, 2.04 (6 H, 2 s), 1.97 (1 H, ddd, J = 13.3, 6.4, 4.3 Hz), 1.85 (1 H, ddd, J = 13.3, 6.5, 4.3 Hz), 1.67 (1 H, dd, J = 12.8, 4.9 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 171.0, 170.5, 137.8, 136.7, 128.7, 128.4, 126.4, 126.1, 86.7, 83.2, 74.6, 66.9, 51.6, 49.0, 36.4, 30.1, 25.7, 20.8.

(1*RS*,2*RS*,4*SR*,4a*RS*,10a*RS*)-10a-(Acetoxymethyl)-4-bromo-1,2,3,4,4a,9,10, 10a-octahydrophenanthrene-1,2-diyl Diacetate (14). A mixture of **13** (11 mg) in 33% HBr in AcOH (1.5 mL) was heated to 55 °C for 18 h. After solvent evaporation, the residue was purified by flash chromatography (silica gel, EtOAc/light petroleum 1:2), yielding 12 mg (80%) of a colorless viscous oil: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.30−7.09 (4 H, m), 5.38 (1 H, d, J = 10.2 Hz), 5.16 (1 H, ddd, J = 11.7, 10.2, 4.9 Hz), 4.08 (1 H, J = 12.6, 11.2, 4.3 Hz), 3.89, 3.39 (2 H, 2 d, J = 11.5 Hz), 3.11 (1 H, d, J = 11.2 Hz), 3.00 (1 H, ddd, J = 13.4, 9.2, 4.0 Hz), 2.83 (1 H, ddd, J = 12.7, 4.9, 4.3 Hz), 2.82−2.73, 2.19−2.10, 1.74−1.67 (3 H, 3 m), 2.20 (1 H, ddd, J = 12.7, 12.6, 11.7 Hz), 2.06, 2.05 (6 H, 3 H, 2 s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.7, 170.3, 169.9, 134.2, 134.1, 132.4, 128.7, 127.9, 125.3, 72.6, 69.9, 64.2, 49.7, 49.5, 42.7, 40.8, 24.4, 20.9, 20.9, 20.8, 20.7.

(1*RS*,2*SR*,4*SR*,4a*SR*,10a*SR*)-10a-(Acetoxymethyl)-1,2,3,4,-4a,9,10,10a-octahydro-2,4-dihydroxyphenanthren-1-yl Acetate (16). A 1 M solution of BBr_3 in CH_2Cl_2 (160 μL) was added to a stirred solution of **13** (26 mg, 79 μmol) in CH_2Cl_2 (2.5 mL) cooled to −18 °C. After the solution was stirred at −18 °C for 50 min, a saturated aqueous solution of $NaHCO_3$ (15 mL) was added, and the mixture was stirred vigorously at 0 °C for 15 min. The aqueous layer was extracted with CH_2Cl_2 (5 mL, five times). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated, yielding 27 mg (98%) of a colorless solid that was recrystallized from $CHCl_3$/hexane: mp 155−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19−7.10 (4 H, m), 5.28 (1 H, d, J = 1.9 Hz), 4.47 (1 H, ddd, J = 11.8, 4.8, 1.9 Hz), 4.21 (1 H, ddd, J = 3.1, 2.9, 2.5 Hz), 4.07, 3.65 (2 H, 2 d, J = 11.4 Hz), 2.95−2.80 (2 H, m), 2.63 (1 H, d, J = 2.5 Hz), 2.46−2.38, 1.87−1.82 (2 H, 2 m), 2.13, 2.02 (6 H, 2 s), 2.12−2.01 (2 H, m), 2.00, 1.25 (2 H, 2 br s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 171.6, 171.1, 136.7, 133.9, 129.4, 129.2, 127.1, 126.7, 74.5, 72.7, 63.8, 63.7, 42.5, 40.2, 33.9, 25.0, 23.4, 21.0, 20.7.

(1*RS*,2*SR*,4*SR*,4a*SR*,10a*SR*)-1,2,3,4,4a,9,10,10a-Octahydro-10a-(hydroxymethyl)phenanthrene-1,2,4-triol (17). A solution of **16** (13 mg, 37 μmol) in MeOH saturated with NH_3 (2 mL) was stirred for 24 h at 20 °C. After solvent evaporation, the residue was purified by column chromatography (Florisil, MeOH/CH_2Cl_2 1:15), yielding 6 mg (61%) of a colorless solid recrystallized from MeOH/AcOEt/light petroleum: colorless prisms; mp 197−199 °C. ^{1}H NMR (400 MHz, CD_3OD) δ 7.16−7.13 (4 H, m), 4.47 (1 H, ddd, J = 12.2, 4.1, 1.9 Hz), 4.26 (1 H, ddd, J = 3.8, 3.2, 3.1 Hz), 3.86 (1 H, d, J = 1.9 Hz), 3.65, 3.29 (2 H, 2 d, J = 11.1 Hz), 2.91−2.87 (2 H, m), 2.66 (1 H, dd, J = 3.8, 1.4 Hz), 2.41−2.33 (1 H, m), 2.19 (1 H, ddd, J = 12.9, 12.2, 3.1 Hz), 1.90 (1 H, ddd, J = 12.9, 4.1, 3.2 Hz), 1.69 (1 H, m); ^{13}C NMR (100.6 MHz, CD_3OD) δ 138.7, 137.7, 130.5, 129.8, 127.1, 126.8, 75.6, 74.0, 65.8, 64.8, 42.6, 42.4, 35.8, 26.2, 24.2.

(1*RS*,2*SR*,3*SR*,4*SR*,6*SR*,7*RS*,8*SR*,11*SR*,12*RS*,13*RS*)-8-(Acetoxymethyl)-15,16-dioxapentacyclo[10.2.1.1^{4,7}.0^{2,11}.0^{3,8}]-hexadeca-6,13-diyl Diacetate (18). A mixture of **11** (77 mg, 0.19 mmol), 10% Pd on charcoal (65 mg), and EtOAc (20 mL) was degassed and pressurized with H_2 (1 atm). After being stirred at 20 °C for 24 h, the mixture was filtered through Celite, and the solvent was evaporated, yielding 76 mg (99%) of a colorless solid: mp 170−171 °C (EtOAc); ^{1}H NMR (360 MHz, $CDCl_3$) δ 4.98 (1 H, ddd, J = 10.9, 6.0, 5.0 Hz), 4.85 (1 H, ddd, J =10.2, 4.7, 3.7 Hz), 4.51, 4.14 (2 H, 2 d, J = 11.5 Hz), 4.20 (1 H, d, J = 4.7 Hz), 4.17 (1 H, d, J = 6.5 Hz), 4.17 (1 H, d, J = 5.0 Hz), 4.10 (1 H, d, J = 5.8 Hz), 2.52 (1 H, ddd, J = 8.6, 8.5, 8.4 Hz), 2.43 (1 H, ddd, J = 12.9, 10.9, 6.5 Hz), 2.27 (1 H, ddd, J = 13.0, 10.2, 5.8 Hz), 2.05, 2.04, 1.96 (9 H, 3 s), 1.84 (1 H, dd, J = 8.6, 8.1 Hz), 1.77−1.72, 1.67−1.60, 1.20−1.10 (4 H, 3 m), 1.43 (1 H, dd, J = 12.9, 6.0 Hz), 1.32 (1 H, d, J = 8.1 Hz), 1.25 (1 H, dd, J = 13.0, 3.7 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 170.7, 170.4, 85.8, 84.2, 82.9, 81.7, 74.9, 73.3, 65.0, 50.8, 47.7, 46.6, 36.4, 35.6, 33.4, 27.0, 20.9, 20.7, 20.7.

(1*RS*,2*RS*,3*SR*,4*RS*,6*RS*,7*RS*,8*RS*,11*RS*,12*SR*,13*RS*)-8-[[(4′-Methoxybenzoyl)oxy]methyl]-15,16-dioxapentacyclo-[10.2.1.1^{4,7}.0^{2,11}.0^{3,8}]hexadeca-6,13-diyl Bis(4′-methoxybenzoate) (19). A mixture of **22** (90 mg, 0.19 mmol), 10% Pd on charcoal (50 mg), and 1:1 EtOAc/MeOH (12 mL) was degassed and pressurized with H_2 (1 atm). After being stirred at 20 °C for 15 h, the mixture was filtered through Celite and the solvent evaporated. The residue was taken up with anhydrous pyridine (4 mL), and anisoyl chloride (4-$MeOC_6H_4COCl$, 0.3 g, 1.76 mmol) and DMAP (5 mg) were added. After the mixture was stirred at 20 °C for 24 h, H_2O (5 mL) was added and the mixture stirred at 20 °C for 2 h. After addition of 2 N aqueous H_2SO_4 (50 mL), the mixture was extracted with CH_2Cl_2 (20 mL, three times). The combined organic extracts were washed with a saturated aqueous solution of $NaHCO_3$ (20 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL, three times). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by flash chromatography (silica gel, EtOAc/light petroleum 1:1), yielding 124 mg (93%), colorless oil that crystallized from EtOAc/light petroleum: mp 201−202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.96, 7.59−7.57 (6 H, 2m), 6.96−6.93, 6.75−6.73, 6.56−6.53 (6 H, 3 m), 5.27 (1 H, ddd, J = 10.9, 6.2, 4.1 Hz), 5.12 (1 H, ddd, J = 13.1, 4.3, 3.6 Hz), 4.75, 4.37 (2 H, 2 d, J = 11.5 Hz), 4.52 (1 H, d, J = 4.1 Hz), 4.36 (1 H, d, J = 4.3 Hz), 4.30 (1 H, d, J = 6.2 Hz), 4.24 (1 H, d, J = 5.7 Hz), 3.88, 3.83, 3.75 (9 H, 3 s), 2.71−2.64 (1 H, m), 2.55 (1 H, ddd, J = 12.8, 10.9, 6.2 Hz), 2.42 (1 H, ddd, J = 13.1, 10.2, 5.7 Hz), 1.99 (1 H, dd, J = 9.4, 8.2 Hz), 1.91−1.87 (1 H, m), 1.75 (1 H, dd, J = 12.8, 6.2 Hz), 1.65−1.59 (1 H, m), 1.52 (1 H, d, J = 8.2 Hz), 1.46 (1 H, dd, J = 13.1, 3.6 Hz), 1.48−1.15 (2 H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 165.9, 165.8, 165.6, 163.5, 163.0, 162.9, 131.6, 131.3, 131.2, 122.0, 121.9, 121.3, 113.6, 113.0, 112.9, 85.6, 84.3, 83.2, 82.0, 75.6, 73.5, 65.2, 55.4, 55.3, 55.2, 51.3, 47.7, 46.7, 36.7, 35.8, 33.0, 27.1, 20.8.

(1*RS*,2*SR*,3*SR*,4*RS*,6*RS*,7*RS*,11*SR*,12*RS*,13*RS*)-6,13-Bis-(benzyloxy)-11-vinyl-15,16-dioxapentacyclo[10.2.1.-

$1^{4,7}.0^{2,11}.0^{3,8}$]hexadec-8-ene (20). NaH (55% in oil, 300 mg) was added to a solution of **7** (0.4 g, 1.44 mmol) in anhydrous THF (12 mL) cooled to 0 °C. After the solution was stirred at 0 °C for 10 min, $PhCH_2Br$ (0.38 mL, 3.18 mmol) and Bu_4NI (53 mg, 144 μmol) were added. The mixture was stirred at 20 °C for 20 h. A saturated aqueous solution of NH_4Cl (10 mL) and then H_2O (10 mL) were added. The solution was saturated with NaCl and extracted with CH_2Cl_2 (10 mL, six times). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by flash chromatography (silica gel, EtOAc/light petroleum 1:3), yielding 627 mg (95%) of a colorless oil: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.38−7.28 (m, 10 H), 6.25 (1 H, dd, J = 17.3, 10.7 Hz), 5.76 (1 H, dd, J = 7.2, 3.8, 2.3 Hz), 4.91 (1 H, dd, J = 17.3, 0.8 Hz), 4.89 (1 H, dd, J = 10.7, 0.8 Hz), 4.75 (1 H, d, J = 4.8 Hz), 4.54, 4.51, 4.46, 4.43 (4 H, 4 d, J = 11.6 Hz), 4.38 (1 H, d, J = 5.6 Hz), 4.35 (1 H, d, J = 6.2 Hz), 4.15 (1 H, ddd, J = 9.6, 4.8, 3.1 Hz), 4.15 (1 H, ddd, J = 10.4, 5.6, 4.2 Hz), 4.07 (1 H, d, J = 4.2 Hz), 2.42 (1 H, dd, J = 13.7, 7.2 Hz), 2.36 (1 H, ddd, J = 12.2, 10.4, 6.2 Hz), 2.26 (1 H, ddd, J = 12.5, 9.6, 5.6 Hz), 2.17 (1 H, dd, J = 13.7, 3.8 Hz), 2.10 (1 H, dd, J = 9.5, 2.3 Hz), 1.83 (1 H, d, J = 9.5 Hz), 1.45 (1 H, dd, J = 12.2, 5.6 Hz), 1.44 (1 H, dd, J = 12.5, 3.1 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.0, 141.5, 137.9, 137.8, 128.1, 128.0, 127.6, 127.5, 127.3, 127.2, 118.0, 110.9, 84.4, 84.2, 81.2, 80.9, 80.0, 78.0, 72.0, 71.5, 54.6, 47.7, 54.4, 37.3, 32.5, 32.5.

(1*RS*,2*SR*,3*SR*,4*RS*,6*RS*,7*RS*,8*SR*,12*RS*,13*RS*)-6,13-Bis(benzyloxy)-15,16-dioxapentacyclo[10.2.1.$1^{4,7}$.$0^{2,11}$.$0^{3,8}$]hexadec-10-ene-8-carbaldehyde (21). A mixture of **20** (676 mg, 1.48 mmol), 9:5 dioxane /H_2O (28 mL), $NaIO_4$ (633 mg, 2.96 mmol), and a 0.1 M solution of OsO_4 in CCl_4 (1.48 mL, 0.148 mmol) was stirred at 20 °C for 19 h. After solvent evaporation to reduce the volume by half, the mixture was extracted with CH_2Cl_2 (10 mL, seven times). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by flash chromatography (silica gel, EtOAc/light petroleum 1:2), yielding 518 mg (76%), colorless viscous oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.58 (1 H, s), 7.39−7.26 (10 H, m), 5.70 (1 H, ddd, J = 7.3, 3.8, 2.3 Hz), 4.70 (1 H, d, J = 4.6), 4.47, 4.49 (2 H, 2 d, J = 11.6 Hz), 4.44, 4.42 (2 H, 2 d, J = 5.0, 5.1 Hz), 4.39 (2 H, s), 4.33 (1 H, d, J = 4.4 Hz), 4.17−4.06 (2 H, m), 2.91 (1 H, dd, J = 14.0, 7.3 Hz), 2.36 (1 H, d, J = 9.7 Hz), 2.35−2.22 (2 H, m), 2.13 (1 H, dd, J = 9.7, 2.3 Hz), 2.09 (1 H, dd, J = 14.0, 3.8 Hz), 1.48 (1 H, dd, J = 12.6, 4.0 Hz), 1.43 (1 H, dd, J = 12.4, 2.8 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 200.2, 143.8, 137.8, 137.1, 128.3, 128.2, 127.7, 127.5, 116.8, 85.6, 84.3, 80.5, 80.1, 79.5, 78.1, 72.2, 71.8, 63.3, 51.9, 47.2, 37.4, 36.0, 29.1.

[(1*RS*,2*RS*,3*SR*,4*RS*,6*RS*,7*RS*,8*RS*,12*RS*,13*RS*)-6,13-Bis(benzyloxy)-15,16-dioxapentacyclo[10.2.1.$1^{4,7}$.$0^{2,11}$.$0^{3,8}$]hexadec-10-en-8-yl]methanol (22). $NaBH_4$ (50 mg) was added to a stirred solution of **21** (200 mg, 0.436 mmol) in 2:1 MeOH/CH_2Cl_2 (9 mL) cooled to 0 °C. After being stirred at 20 °C for 20 min, the mixture was acidified with 10% aqueous HCl (pH 4). Solvent was evaporated to half volume, and NaCl was added until saturation. The mixture was extracted with CH_2Cl_2 (10 mL, 7 times). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated, yielding 179 mg (89%) of a colorless oil that crystallized from EtOAc/hexane: mp 144−145 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.40−7.28 (10 H, m), 5.83 (1 H, ddd, J = 7.4, 3.0, 2.9 Hz), 4.74 (1 H, d, J = 4.6 Hz), 4.62, 4.53 (2 H, 2 d, J = 11.6 Hz), 4.51, 4.44 (2 H, 2 d, J = 11.5 Hz), 4.31, 4.30 (2 H, 2 d, J = 7.8, 6.0 Hz), 4.21−4.11 (2 H, m), 4.04 (1 H, d, J = 4.4 Hz), 3.67 (1 H, br d, J = 11.8 Hz), 3.37 (1 H, br dd, J = 11.8, 9.1 Hz), 3.26 (1 H, br d, J = 9.1 Hz), 2.59 (1 H, dd, J = 14.0, 7.4 Hz), 2.32−2.20 (2 H, m), 2.05 (1 H, br d, J = 9.6 Hz), 1.91 (1 H, br d, J = 14.0 Hz), 1.41 (1 H, dd, J = 12.4, 2.8 Hz), 1.40 (1 H, dd, J = 10.5, 5.4 Hz), 1.31 (1 H, d, J = 9.6 Hz); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 142.7, 138.0, 136.9, 128.6, 128.3, 128.2, 127.8, 127.7, 118.2, 84.3, 84.2, 81.3, 80.7, 80.3, 78.2, 73.4, 71.8, 67.0, 54.7, 53.3, 47.5, 37.5, 34.7, 30.6.

(1*RS*,2*SR*,4*SR*,4a*SR*,4b*RS*,5*SR*,7*SR*,8*RS*,8a*SR*,10a*SR*)-1,4,5,8-Tetraacetoxyperhydro-8a-[((4′-methoxybenzoyl)oxy]methyl]phenanthrene-2,7-diyl Bis(4′-methoxybenzoate) (23). A 1 M solution of BBr_3 in CH_2Cl_2 (116 μL, 116 μmol) was added to a stirred solution of **19** (20 mg, 29 μmol) in CH_2Cl_2 (3 mL) cooled to −18 °C. After the solution was stirred at −18 °C for 45 min, a saturated aqueous solution of $NaHCO_3$ (10 mL) was added, and the mixture was stirred vigorously at 0 °C for 5 min. The aqueous layer was extracted with EtOAc (5 mL, five times). The combined organic phases were dried ($MgSO_4$), the solvent was evaporated, and the residue was purified by flash chromatography (silica gel, EtOAc/light petroleum 2:1 and then EtOAc). The product was taken up with anhydrous pyridine (1 mL). Ac_2O (1 mL) and DMAP (2 mg) were added, and the mixture was stirred at 20 °C for 13 h. The solvent was evaporated, and the residue was purified by flash chromatography (silica gel, EtOAc/light petroleum 1:1), yielding 13 mg (50%) of a colorless solid that was recrystallized from EtOAc/light petroleum: mp 231−232 °C; ^{1}H NMR (400 MHz, toluene-d_8, 100 °C) δ 8.34, 8.30, 8.21 (6 H, 3 d, $J \cong$ 8.6 Hz), 6.95−6.93 (6 H, m), 5.94−5.76 (4 H, m), 5.69, 4.35 (2 H, 2 br d, J = 11.4 Hz), 5.61, 5.45 (2 H, 2 br s), 3.57, 3.53 (9 H, 2 s), 2.75−2.71 (1 H, m), 2.56−2.54 (1 H, m), 2.43−1.91 (9 H, m), 2.04, 1.98 (12 H, 2 s).

(1*RS*,2*SR*,4*SR*,4a*SR*,4b*RS*,5*SR*,7*SR*,8*RS*,8a*SR*,10a*SR*)-Perhydro-8a-(hydroxymethyl)phenanthrene-1,2,4,5,7,8-hexol (24). The same procedure as for the preparation of **23** was employed until the first flash chromatography, when 60 mg (87 μmol) of **19** and 348 μmol of a 1 M solution of BBr_3 in CH_2Cl_2 were used. The product was dissolved in MeOH saturated with NH_3 (15 mL) and stirred at 50 °C for 70 h. After solvent evaporation, the residue was purified by column chromatography (Florisil, MeOH/CH_2Cl_2 1:2), yielding 14 mg (51%) of a colorless solid recrystallized from MeOH/Et_2O: colorless prisms; mp 262−264 °C; ^{1}H NMR (400 MHz, D_2O) δ 4.35 (1 H, br d, J = 13.0 Hz), 4.18 (1 H, br s), 4.12−4.07 (3 H, m), 4.10, 3.66 (2 H, 2 d, J = 11.7 Hz), 3.96 (1 H, dd, J = 11.7, 3.4 Hz), 2.41 (2 H, br s), 2.12−1.98 (3 H, m), 1.82−1.59 (6 H, m); ^{13}C NMR (100.6 MHz, D_2O) δ 71.1, 70.3, 69.3, 68.6, 67.3, 66.6, 64.3, 45.0, 38.5, 37.9, 37.2, 34.8, 34.6, 24.4, 20.8.

(1*RS*,2*RS*,4*RS*,4a*RS*,4b*RS*,5*RS*,7*RS*,8*SR*,8a*RS*,10a*RS*)-5,8-Diacetoxyperhydro-10a-[[(4′-methoxybenzoyl)oxy]methyl]-1,4-epoxyphenanthrene-2,7-diyl Bis(4′-methoxybenzoate) (25). A 1 M solution of BBr_3 in CH_2Cl_2 (468 μL, 468 μmol) was added to a stirred solution of **19** (80 mg, 117 μmol) in CH_2Cl_2 (8 mL) cooled to −78 °C. After the solution was stirred at −50 °C for 15 min, a saturated aqueous solution of $NaHCO_3$ (20 mL) was added, and the mixture was stirred vigorously at 0 °C for 5 min. The organic layer was collected, and the aqueous layer was extracted with EtOAc (5 mL, four times). The combined organic extracts were dried ($MgSO_4$), the solvent was evaporated, and the residue was taken up with anhydrous pyridine (3 mL). After addition of Ac_2O (2 mL) and DMAP (5 mg), the mixture was stirred at 20 °C for 13 h. The solvent was evaporated and the residue purified by flash chromatography (silica gel, EtOAc/light petroleum 1:2, then 2:3, and finally 1:1), yielding 77 mg (84%) of a colorless oil that crystallized from EtOAc/light petroleum: colorless prisms; mp 211−212 °C; ^{1}H NMR (400 MHz, C_6D_6, 70 °C) δ 8.22−8.18, 8.03−7.96 (6 H, 2 m), 6.77−6.69, 6.63−6.59 (6 H, 2 m), 5.77 (1 H, ddd, J = 7.3, 3.6, 2.3 Hz), 5.62 (1 H, ddd, J = 10.9, 4.9, 4.5 Hz), 5.36 (1 H, dd, J = 8.0, 2.3 Hz), 5.33 (1 H, ddd, J = 8.3, 4.2, 3.8 Hz), 5.21, 4.57 (2 H, 2 d, J = 11.2 Hz), 4.54 (1 H, d, J = 4.5 Hz), 4.42 (1 H, d, J = 5.3 Hz), 3.33, 3.32, 3.25 (9 H, 3 s), 2.40 (1 H, ddd, J = 12.7, 10.9, 5.2 Hz), 2.37−2.29 (2 H, m), 2.15 (1 H, ddd, J = 13.7, 7.3, 3.8 Hz), 2.00 (1 H, ddd, J = 13.7, 8.3, 3.6 Hz), 1.97, 1.87 (6 H, 2 s), 1.93−1.87 (1 H, m), 1.79−1.67 (2 H, m), 1.73 (1 H, d, J = 9.9 Hz), 1.55 (1 H, dd, J = 12.7, 4.9 Hz), 1.54−1.50 (1 H, m); ^{13}C NMR (100.6 MHz, C_6D_6, 70 °C) δ 170.2, 170.1, 166.6, 166.4, 165.9, 164.6, 164.4, 164.3, 132.6, 132.5, 132.4, 124.1, 123.8, 123.4, 114.7, 114.5, 114.4, 85.7, 84.2, 75.8, 73.5, 73.4, 68.8, 67.1, 55.5, 55.4, 55.3, 50.0, 37.9, 35.5, 37.6, 31.1, 28.9, 20.8, 21.4, 21.0.

(1*RS*,2*SR*,4*SR*,4a*RS*,4b*SR*,5*SR*,7*SR*,8*RS*,8a*SR*,10a*SR*)-5,8-Diacetoxyperhydro-10a-[[(4′-methoxybenzoyl)oxy]methyl]-2,4-bis(methoxymethoxy)phenanthrene-1,7-diyl Bis(4′-methoxybenzoate) (26). A 1 M solution of BBr_3 in CH_2Cl_2 (437 μL, 437 μmol) was added to a stirred solution of **25** (77 mg, 109 μmol) in CH_2Cl_2 (8 mL) cooled to −18 °C. After the solution was stirred at −18 °C for 30 min, a saturated aqueous solution of $NaHCO_3$ (25 mL) was added, and the mixture was stirred vigorously at 0 °C for 5 min. The aqueous layer was extracted with CH_2Cl_2 (10 mL, four times). The combined organic phases were dried ($MgSO_4$), the solvent was evaporated, and the residue was dissolved in anhydrous CH_2Cl_2 (5 mL). After the residue was cooled to 0 °C, (i-Pr)$_2$NEt (556 μL, 3.2 mmol) and CH_3OCH_2Cl (97 μL, 1.28 mmol) were added. The mixture was stirred at 20 °C for 15 h. MeOH (1 mL) was added, and

after 5 min, CH_2Cl_2 (10 mL). The solution was washed with 1 N aqueous HCl (15 mL, twice) and then with a saturated aqueous solution of $NaHCO_3$ (15 mL, twice). Each aqueous phase was extracted with CH_2Cl_2 (10 mL, twice). The combined organic extracts were dried ($MgSO_4$), the solvent was evaporated, and the residue was purified by flash chromatography (silica gel, EtOAc/CH_2Cl_2 1:15), yielding 46 mg (47%) of a colorless viscous oil: ^{1}H NMR (400 MHz, C_6D_6, 70 °C) δ 8.23−8.19, 8.15−8.12 (6 H, 2 m), 6.83−6.81, 6.76−6.70 (6 H, 2 m), 5.77−5.76 (1 H, m), 5.74 (1 H, d, J = 3.7 Hz), 5.66−5.62 (2 H, m), 5.57, 4.77 (2 H, 2 d, J = 11.7 Hz), 4.71, 4.65 (2 H, 2 d, J = 6.5 Hz), 4.64−4.58 (1 H, m), 4.59, 4.58 (2 H, 2 d, J = 6.7 Hz), 4.36−4.34 (1 H, m), 3.33, 3.32, 3.31, 3.30, 3.23 (15 H, 5 s), 2.79−2.77 (2 H, m), 2.67−2.65 (1 H, m), 2.43−2.27 (3 H, m), 2.04−1.80 (5 H, m), 1.87, 1.79 (6 H, 2 s); ^{13}C NMR (100.6 MHz, C_6D_6, 70 °C) δ 170.1, 169.3, 166.3, 165.6, 165.3, 164.1, 164.0, 163.0, 132.1, 132.0, 123.8, 123.3, 114.3, 114.2, 114.1, 96.7, 95.9, 74.9, 74.0, 73.6, 73.4, 67.2, 66.9, 55.5, 55.4, 55.0, 54.9, 43.1, 39.8, 37.3, 33.3, 32.3, 31.8, 26.9, 22.3, 21.1, 20.6.

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Supporting Information Available: Further spectral data and elemental analyses for all of the compounds described in the Experimental Section. X-ray radiocrystallographic data on the crystal and molecular structure of compound **23** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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