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SUPPLEMENTARY MATERIAL

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

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(±)-6-[(Trimethylsilyl)ethynyl]-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol (5). UV (MeCN): λ_{max} = 251 nm (ε = 7200), 240 (7600). IR (film) ν 3400, 3000, 2940, 2890, 2140, 1580, 1440, 1400, 1300, 1240, 1210, 1210, 1170, 1130, 1130, 1070, 1020, 980, 930, 910, 850, 800, 750, 690, 620 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 6.75 (*d*, ^3J = 1.9, H-C(5)); 4.97 (*dd*, ^3J = 5.0, 1.9, H-C(4)); 4.86 (*d*, ^3J = 4.3, H-C(1)); 4.53 (br *dddd*, ^3J = 8.1, 7.5, 4.3, 2.4, H-C(2)); 2.33 (*ddd*, ^2J = 12.1, ^3J = 8.1, 5.0, H_{exo}-C(3)); 1.65 (br *d*, ^3J = 7.5, OH); 1.10 (*dd*, ^2J = 12.1, ^3J = 2.4, H_{endo}-C(3)); 0.20 (*s*, TMS). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 142.0 (*d*, ^1J(C,H) = 177, C(5)); 127.3 (*s*, C(6)); 102.4 (*s*, C(β)); 98.2 (*s*, C(α)); 82.4 (*d*, ^1J(C,H) = 167, C(1)); 80.3 (*d*, ^1J(C,H) = 166, C(4)); 68.8 (*d*, ^1J(C,H) = 156, C(2)); 35.4 (*t*, ^1J(C,H) = 136, C(3)); -0.2 (*q*, ^1J(C,H) = 120, TMS). CI-MS (NH_3) m/z: 208 (1, M^+), 166 (4), 165 (11), 164 (64), 150 (13), 149 (100). Anal. calc. for $C_{11}H_{16}O_2Si$ (208.03): C 63.42, H 7.74, Si 13.48; found: C 63.49, H 7.77, Si 13.49.

(±)-6-Vinyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol (6). UV (MeCN): 237 (9100). IR (film) ν 3400, 3080, 2980, 2940, 1620, 1570, 1440, 1410, 1340, 1300, 1210, 1170, 1130, 1070, 1020, 990, 970, 900, 850, 820, 790, 720 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 6.59 (*dd*, ^3J = 17.5, 10.7, H-C(α)); 6.39 (*d*, ^3J = 1.7, 1H, H-C(5)); 5.37 (*d*, ^3J = 17.5, H_Z-C(β)); 5.24 (*d*, ^3J = 10.7, H_E-C(β)); 5.10 (*d*, ^3J = 4.6, H-C(1)); 4.92 (*dd*, ^3J = 4.8, 1.7, H-C(4)); 4.54 (*dddd*, ^3J = 8.3, 8.1, 4.6, 2.3, H-C(2)); 2.32 (*ddd*, ^2J = 12.0, ^3J = 8.1, 4.8, H_{exo}-C(3)); 1.58 (br *d*, ^3J = 8.3, OH); 1.06 (*dd*, ^2J =

12.0, ^3J = 2.3, H_{endo}-C(3)). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.4 (*s*, C(6)); 133.5 (*d*, ^1J(C,H) = 172, C(5)); 130.6 (*d*, ^1J(C,H) = 156, C(α)); 116.9 (*dd*, ^1J(C,H) = 161, 156, C(β)); 80.0 (*d*, ^1J(C,H) = 165, C(4)); 79.4 (*d*, ^1J(C,H) = 163, C(1)); 68.6 (*d*, ^1J(C,H) = 155, C(2)); 35.6 (*t*, ^1J(C,H) = 135, C(3)). CI-MS (NH_3) m/z 139 (0.3, $M + H^+$), 138 (0.4, M^+), 120 (1), 110 (1), 95 (8), 94 (100), 93 (5), 91 (3).

(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-en-6,13-diol (7). IR (KBr) ν 3400, 3060, 2960, 2940, 2880, 1630, 1420, 1330, 1260, 1160, 1150, 1090, 1070, 1020, 980, 970, 930, 900, 880, 850, 810, 800, 780, 660 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$) δ 6.20 (*dd*, ^3J = 17.5, 10.8, H-C(α)); 5.78 (*m*, H-C(9)); 5.06 (*d*, ^3J = 10.8, H_E-C(β)); 5.01 (*d*, ^3J = 17.5, H_Z-C(β)); 4.68 (*d*, ^3J = 5.0, H-C(7)); 4.67-4.26 (*m*, H-C(6), H-C(13)); 4.41 (*d*, ^3J = 5.6, H-C(4)); 4.33 (*d*, ^3J = 6.2, H-C(1)); 3.97 (*d*, ^3J = 4.5, H-C(12)); 2.45 (*ddd*, ^2J = 12.7, ^3J = 10.6, 6.2, H_{exo}-C(14)); 2.34 (*ddd*, ^2J = 12.8, ^3J = 9.6, 5.6, H_{exo}-C(5)); 2.30-2.16 (*m*, 2H, H-C(10)); 2.06 (br *d*, ^3J = 8.4, HO-C(13)); 1.99 (br *s*, H-C(2), H-C(3)); 1.70 (br *d*, ^3J = 8.4, HO-C(6)); 1.26 (*dd*, ^2J = 12.8, ^3J = 2.7, H_{endo}-C(5)); 1.17 (*dd*, ^2J = 12.7, ^3J = 4.9, H_{endo}-C(14)). ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 141.4 (*s*, C(8)); 142.2 (*d*, ^1J(C,H) = 149, C(9)); 121.0 (*d*, ^1J(C,H) = 164, C(α)); 114.9 (*t*, ^1J(C,H) = 157, C(β)); 84.6, 84.5, 81.3, 75.5, 70.7 (5*d*, ^1J(C,H) = 157, 158, 159, 153, 154, C(1), C(4), C(6), C(7), C(12), C(13)); 54.9 (*s*, C(11)); 51.8, 48.4 (2*d*, ^1J(C,H) = 135, 136, C(2), C(3)); 40.1, 39.4 (2*t*, ^1J(C,H) = 133, 134, C(5), C(14)); 34.8 (*t*, ^1J(C,H) = 132, C(10)). CI-MS (NH_3) m/z 277 (26, $M + H^+$), 233 (13), 232 (100), 185 (11), 159 (14), 145 (10), 131 (12), 117 (15), 115 (10), 94 (34), 91 (16). Anal. calc. for $C_{16}H_{20}O_4$ (276.33): C 69.55, H 7.30; found: C 69.65, H 7.22.

(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). Colorless prisms, mp 142-143°C (AcOEt/light petroleum). IR (KBr): 3010, 1760, 1406, 1288, 1240, 1156, 1004, 987, 965, 926, 902, 855, 784, 583, 541, 448 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 5.95 (*dd*, ^3J = 7.1, 4.0, ^4J = 2.5, H-C(9)); 5.68 (*dd*, ^3J = 17.2, 10.8, H-C(α)); 5.00 (*d*, ^3J = 10.8, H_E-C(β)); 4.91 (*d*, ^3J = 17.2, H_Z-C(β)); 4.79 (*d*, ^3J = 5.9, H-C(1)); 4.70 (*d*, ^3J = 6.0, H-C(4)); 4.57 (*s*, H-C(12)); 3.94 (*s*, H-C(7)); 2.61 (*dd*, ^2J = 17.3, ^3J = 5.9, H_{exo}-C(14)); 2.50 (*dd*, ^2J = 17.6, ^3J = 6.0, H_{exo}-C(5)), 2.36 (*dd*, ^2J = 13.9, ^3J = 7.3, H_{eq}-

C(10)); 2.18 (*dd*, ^3J = 9.7, ^4J = 2.5, H-C(3)); 2.13 (*dd*, ^2J = 13.9, ^3J = 4.0, H_{ax}-C(10)); 2.11 (*d*, ^2J = 17.3, H_{endo}-C(14)); 2.02 (*d*, ^2J = 17.6, H_{endo}-C(5)); 1.99 (*d*, ^3J = 9.7, H-C(2)). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 208.7, 207.6 (2*s*, C(6), C(13)); 139.4 (*d*, ^1J(C,H) = 154, C(9)); 136.9 (*s*, C(8)); 121.9 (*d*, ^1J(C,H) = 167, C(α)); 116.1 (*dd*, ^1J(C,H) = 160, 155, C(β)); 87.4, 82.5, 81.9, 79.1 (4*d*, ^1J(C,H) = 165, 170, 169, 162, C(1), C(4), C(7), C(12)); 52.7 (*s*, C(11)); 51.2, 46.5 (2*d*, ^1J(C,H) = 135, 136, C(2), C(3)); 42.9, 42.8 (2*t*, ^1J(C,H) = 135, C(5), C(14)); 33.4 (*t*, ^1J(C,H) = 132, C(10)). CI-MS (NH_3) m/z: 271 (1, M^+), 244 (100), 187 (29), 159 (38), 133 (60), 131 (30), 129 (34), 128 (35), 117 (62), 115 (50), 108 (40), 94 (48), 91 (76). Anal. calcd. for $C_{16}H_{16}O_4$ (272.30): C 70.57, H 5.87; found: C 70.67, H 5.87.

(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-en-6,13-diyl Diacetate (9). IR (KBr) ν 2982, 1737, 1376, 1248, 1065, 914, 835, 603 cm^{-1}. ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.85 (*dd*, ^3J = 17.3, 10.9, H-C(α)); 5.60 (*ddd*, ^3J = 6.8, 3.9, ^4J = 3.2, H-C(9)); 4.98-4.90 (*m*, H-C(6), H-C(7), H-C(13)); 4.86 (*d*, ^3J = 10.9, H_E-C(β)); 4.81 (*d*, ^3J = 17.3, H_Z-C(β)); 4.40, 4.35 (2*d*, ^3J = 5.5, 6.1, H-C(1), H-C(4)); 4.27 (*d*, ^3J = 4.4, H-C(12)); 2.42, 2.34 (2*ddd*, ^2J = 12.7, 13.0, ^3J(CHOAc) = 10.8, 9.7, ^3J = 6.1, 5.5, H_{exo}-C(5), H_{exo}-C(14)); 2.27 (*dd*, ^2J = 13.5, ^3J = 6.8, H_{eq}-C(10)); 2.08 (*dd*, ^2J = 13.5, ^3J = 3.9, H_{ax}-C(10)); 1.99, 1.97 (2*s*, Ac); 1.96 (*dd*, ^3J = 9.3, ^4J = 3.2, H-C(3)); 1.84 (*d*, ^3J = 9.3, H-C(2)); 1.51, 1.48 (2*dd*, ^2J = 12.7, 13.0, ^3J = 2.4, 4.8, H_{endo}-C(5), H_{endo}-C(14)). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.9, 170.8 (2*s*, Ac); 141.8 (*d*, ^1J(C,H) = 155, C(9)); 140.9 (*s*, C(8)); 118.2 (*d*, ^1J(C,H) = 165, C(α)); 112.0 (*t*, ^1J(C,H) = 156, C(β)); 84.4, 83.5, 80.7, 79.6 (4*d*, ^1J(C,H) = 152, 160, 158, 165, C(1), C(4), C(7), C(12)); 75.0, 73.5 (2*d*, ^1J(C,H) = 156, 158, C(6), C(13)); 54.5 (*s*, C(11)); 53.4, 47.3 (2*d*, ^1J(C,H) = 136, 139, C(2), C(3)); 36.7, 37.3, 33.1 (3*t*, ^1J(C,H) = 136, 137, 130, C(5), C(10), C(14)); 21.0, 20.9 (2*q*, ^1J(C,H) = 130, Ac). CI-MS (NH_3) m/z 361 (16, $M + H^+$), 318 (36), 317 (100), 301 (19), 274 (7), 257 (11), 240 (18), 167 (21), 137 (35), 128 (23), 115 (22), 95 (27), 94 (52), 91 (31). Anal. calc. for $C_{20}H_{24}O_6$ (360.41): C 66.65, H 6.71; found: C 66.48, H 6.61.

(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-en-6,13-diyl Diacetate (10). IR (KBr) ν 2982,

1733, 1375, 1254, 1235, 1217, 1066, 1049, 1032, 913, 835, 823, 602 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 9.51 (*s*, CHO); 5.58 (*ddd*, ^3J = 7.2, 3.7, ^4J = 1.4, H-C(9)); 5.01 (*ddd*, ^3J = 10.4, 4.6, 4.1, H-C(13)); 4.93-4.89 (*m*, H-C(6), H-C(7)); 4.47 (*d*, ^3J = 6.2, H-C(1)); 4.45 (*d*, ^3J = 5.8, H-C(4)); 4.42 (*d*, ^3J = 4.6, H-C(12)); 2.82 (*dd*, ^2J = 14.1, ^3J = 7.2, H_{eq}-C(10)); 2.49 (*ddd*, ^2J = 13.2, ^3J = 10.4, 6.2, H_{exo}-C(14)); 2.38 (*d*, ^3J = 9.2, H-C(2)); 2.38-2.31 (m, H_{exo}-C(5)); 2.06 (*dd*, ^2J = 14.1, ^3J = 3.7, H_{ax}-C(10)); 2.03 (*dd*, ^3J = 9.2, ^4J = 1.4, H-C(3)); 2.00, 1.96 (2*s*, Ac); 1.50 (*dd*, ^2J = 11.9, ^3J = 2.4, H_{endo}-C(5)); 1.46 (*dd*, ^2J = 13.2, ^3J = 4.1, H_{endo}-C(14)). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 199.1 (*d*, ^1J(C,H) = 179, CHO); 170.5, 169.8 (2*s*, Ac); 143.1 (*s*, C(8)); 116.2 (*d*, ^1J(C,H) = 166, C(9)); 84.1, 83.4, 79.9, 79.3 (4*d*, ^1J(C,H) = 157, 164, 159, 166, C(1), C(4), C(7), C(12)); 73.5, 73.1 (2*d*, ^1J(C,H) = 160, C(6), C(13)); 63.7 (*d*, ^2J(C,H) = 21, C(11)); 50.6, 46.5 (2*d*, ^1J(C,H) = 136, 134, C(2), C(3)); 36.4, 35.5 (2*t*, ^1J(C,H) = 135, 136, C(5), C(14)); 28.8 (*t*, ^1J(C,H) = 133, C(10)); 20.7, 20.5 (2*q*, ^1J(C,H) = 130, Ac). CI-MS (NH_3) m/z 380 (45, $M + NH_4^+$), 363 (12, $M + H^+$), 362 (11, M^+), 320 (34), 319 (100), 303 (25), 260 (27), 259 (45), 147 (39), 137 (29), 91 (25). Anal. calc. for $C_{19}H_{22}O_7$ (362.38): C 62.98, H 6.12; found: C 62.92, H 6.22.

(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-en-6,13-diyl Diacetate (11). IR (KBr) ν 2990, 1736, 1379, 1362, 1257, 1063, 1038, 994, 838, 610, 580 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$) δ 5.66 (*ddd*, ^3J = 7.3, 3.5, ^4J = 1.5, H-C(9)); 5.02 (*ddd*, ^3J = 10.9, 5.4, 4.5, H-C(13)); 4.95 (*d*, ^3J = 4.8, H-C(7)); 4.89 (*ddd*, ^3J = 9.6, 4.8, 2.4, H-C(6)); 4.32 (2*d*, ^3J = 6.2, 5.5, H-C(1), H-C(4)); 4.24 (*d*, ^3J = 4.5, H-C(12)); 4.04 (br *s*, CH_2OAc); 2.47 (*ddd*, ^2J = 12.8, ^3J = 10.9, 6.2, H_{exo}-C(14)); 2.35 (*dd*, ^2J = 14.1, ^3J = 7.3, H_{eq}-C(10)); 2.30 (*ddd*, ^2J = 12.9, ^3J = 9.6, 5.5, H_{exo}-C(5)); 2.03, 1.96, 1.94 (3*s*, Ac); 1.97 (*dd*, ^2J = 9.4, ^4J = 1.5, H-C(3)); 1.88 (*dd*, ^2J = 14.1, ^3J = 3.5, H_{ax}-C(10)); 1.47 (*dd*, ^2J = 12.9, ^3J = 2.4, H_{endo}-C(5)); 1.46 (*dd*, ^2J = 12.8, ^3J = 5.4, H_{endo}-C(14)); 1.29 (*d*, ^3J = 9.4, H-C(2)). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.6, 170.5, 170.3 (3*s*, Ac); 141.6 (*s*, C(8)); 117.6 (*d*, ^1J(C,H) = 164, C(9)); 83.6, 82.3, 79.9, 79.4 (4*d*, ^1J(C,H) = 157, 161, 159, 166, C(1), C(4), C(7), C(12)); 74.7, 73.2 (2*d*, ^1J(C,H) = 153, 154, C(6), C(13)); 66.9 (*t*, ^1J(C,H) = 150, CH_2OAc); 53.2, 46.8 (2*d*, ^1J(C,H) = 135, 132, C(2), C(3)); 51.6 (*s*, C(11)); 36.4, 34.8 (2*t*, ^1J(C,H) = 135, 134, C(5), C(14)); 30.0 (*t*, ^1J(C,H) = 134, C(10)); 20.7, 20.6, 20.5 (3*q*, ^1J(C,H) = 130, 129, 130, Ac). CI-

MS (NH_3) m/z 406 (2, M^+), 364 (10), 363 (28), 304 (12), 129 (16), 123 (17), 91 (30), 85 (74), 83 (100). Anal. calc. for $C_{21}H_{26}O_8$ (406.43): C 62.06, H 6.45; found: C 62.17, H 6.46.

(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). UV (MeCN): 266 (7800), 259 (7600), 225 (18000), 219 (18300). IR (KBr) ν 3003, 1740, 1380, 1359, 1260, 1064, 1041, 995, 919, 805, 732, 567 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.21-7.13, 7.07-7.05, 7.01-6.99 (3*m*, H-C(5), H-C(6), H-C(7), H-C(8)); 6.41 (*d*, ^3J = 9.8, H-C(9)); 5.76 (*d*, ^3J = 9.8, H-C(10)); 5.18 (*ddd*, ^3J = 11.0, 4.6, 4.5, H-C(2)); 4.53 (*d*, ^3J = 5.7, H-C(4)); 4.51, 4.46 (2*d*, ^2J = 11.0, CH_2OAc); 4.46 (*d*, ^3J = 4.5, H-C(1)); 3.11 (*s*, H-C(4a)); 2.57 (*ddd*, ^2J = 12.9, ^3J = 11.0, 5.7, H_{exo}-C(3)); 2.07, 2.02 (2*s*, Ac); 1.77 (*dd*, ^2J = 12.9, ^3J = 4.6, H_{endo}-C(3)). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.6, 170.4 (2*s*, Ac); 133.7, 130.9 (2*s*, C(4b), C(8a)); 128.4, 128.3, 128.1, 127.4, 127.2, 127.1 (6*d*, ^1J(C,H) = 159-164, C(5), C(6), C(7), C(8), C(9), C(10)); 89.6, 83.0, 75.1 (3*d*, ^1J(C,H) = 161, 162, 158, C(1), C(2), C(4)); 69.1 (*t*, ^1J(C,H) = 150, CH_2OAc); 52.1 (*d*, ^1J(C,H) = 131, C(4a)); 51.6 (*s*, C(10a)); 37.6 (*t*, ^1J(C,H) = 133, C(3)); 20.8, 20.7 (2*q*, ^1J(C,H) = 130, Ac). CI-MS (NH_3) m/z 346 (14, $M + NH_4^+$), 329 (17, $M + H^+$), 328 (13, M^+), 268 (39), 213 (85), 209 (30), 208 (30), 179 (40), 167 (32), 158 (41), 142 (30), 141 (100), 128 (35), 127 (39), 115 (34). Anal. calc. for $C_{19}H_{20}O_5$ (328.36): C 69.50, H 6.14; found: C 69.62, H 6.12.

(1*RS*,2*RS*,4*RS*,4a*RS*,10a*RS*)-10a-(Acetoxymethyl)-1,2,3,4,4a,9,10,10a-octa-hydro-1,4-epoxyphenanthren-2-yl Acetate (13). UV (MeCN): 272 (870), 265 (890), 212 (8100), 200 (11300). IR (KBr) ν 3000, 2937, 1741, 1386, 1364, 1257, 1231, 1063, 1040, 990, 922, 840, 762, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.22-7.09 (*m*, H-C(5), H-C(6), H-C(7), H-C(8)); 5.14 (*ddd*, ^3J = 11.0, 4.9, 4.6, H-C(2)); 4.60 (*d*, ^3J = 5.9, H-C(4)); 4.46 (*s*, CH_2OAc); 4.39 (*d*, ^3J = 4.6, H-C(1)); 2.79 (*ddd*, ^2J = 16.0, ^3J = 6.4, 4.4, H-C(9)); 2.69 (*s*, H-C(4a)); 2.63 (*ddd*, ^2J = 16.0, ^3J = 6.5, 4.3, H-C(9)); 2.58 (*ddd*, ^2J = 12.8, ^3J = 11.0, 5.9, H_{exo}-C(3)); 2.09, 2.04 (2*s*, Ac); 1.97 (*ddd*, ^2J = 13.3, ^3J = 6.4, 4.3, H-C(10)); 1.85 (*ddd*, ^2J = 13.3, ^3J = 6.5, 4.3, H-C(10)); 1.67 (*dd*, ^2J = 12.8, ^3J = 4.9, H_{endo}-C(3)). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 171.0, 170.5 (2*s*, Ac); 137.8, 136.7 (2*s*, C(4b), C(8a)); 128.7, 128.4, 126.4, 126.1 (4*d*, ^1J(C,H) = 158-

160, C(5), C(6), C(7), C(8)); 86.7, 83.2, 74.6 (3*d*, ^1J(C,H) = 160, 161, 153, C(1), C(2), C(4)); 66.9 (*t*, ^1J(C,H) = 148, CH_2OAc); 51.6 (*d*, ^1J(C,H) = 129, C(4a)); 49.0 (*s*, C(10a)); 36.4 (*t*, ^1J(C,H) = 135, C(3)); 30.1, 25.7 (2*t*, ^1J(C,H) = 130, 128, C(9), C(10)); 20.8 (2*q*, ^1J(C,H) = 130, Ac). CI-MS (NH_3) m/z 348 (9, $M + NH_4^+$), 331 (6, $M + H^+$), 330 (6, M^+), 271 (31), 228 (17), 210 (29), 197 (19), 181 (19), 155 (17), 143 (44), 142 (100), 141 (40), 129 (36), 128 (43), 115 (30). Anal. calc. for $C_{19}H_{22}O_5$ (330.38): C 69.07, H 6.71; found: C 69.09, H 6.67.

(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). UV (MeCN): 271 (880), 254 (1100), 199 (18200). IR (KBr) ν 2957, 1742, 1369, 1245, 1045, 760, 746 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$) δ 7.30-7.09 (*m*, H-C(5), H-C(6), H-C(7), H-C(8)); 5.38 (*d*, ^3J = 10.2, H-C(1)); 5.16 (*ddd*, ^3J = 11.7, 10.2, 4.9, H-C(2)); 4.08 (*d*, ^3J = 12.6, 11.2, 4.3, H-C(4)); 3.89, 3.39 (2*d*, ^2J = 11.5, CH_2OAc); 3.11 (*d*, ^3J = 11.2, H-C(4a)); 3.00 (*ddd*, ^2J = 13.4, ^3J = 9.2, 4.0, H-C(9)); 2.83 (*ddd*, ^2J = 12.7, ^3J = 4.9, 4.3, H_{eq}-C(3)); 2.82-2.73, 2.19-2.10, 1.74-1.67 (3*m*, H-C(9), H_2-C(10)); 2.20 (*ddd*, ^2J = 12.7, ^3J = 12.6, 11.7, H_{ax}-C(3)); 2.06, 2.05 (2*s*, 9H, Ac). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.7, 170.3, 169.9 (3*s*, Ac); 134.2, 134.1 (2*s*, C(4b), C(8a)); 132.4, 128.7, 127.9, 125.3 (4*d*, ^1J(C,H) = 158-160, C(5), C(6), C(7), C(8)); 72.6, 69.9 (2*d*, ^1J(C,H) = 147, 149, C(1), C(2)); 64.2 (*t*, ^1J(C,H) = 148, CH_2OAc); 49.7 (*d*, ^1J(C,H) = 151, C(4)); 49.5 (*d*, ^1J(C,H) = 128, C(4a)); 42.7 (*s*, C(10a)); 40,8 (*t*, ^1J(C,H) = 135, C(3)); 24.4 (*t*, ^1J(C,H) = 128, C(9)); 20.9 (*t*, ^1J(C,H) = 129, C(10)); 20.9, 20.8, 20.7 (3*q*, ^1J(C,H) = 130, Ac). CI-MS (NH_3) m/z 470 [472] (10, $M + NH_4^+$), 453 [455] (3, $M + H^+$), 452 [454] (2, M^+), 393 [395] (13), 392 [394] (15), 313 (14), 272 [274] (24), 193 (100), 181 (50), 179 (71), 141 (66). Anal. calc. for $C_{21}H_{25}O_6Br$ (453.33): C 55.74, H 5.57; found: C 55.85, H 5.67.

(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). UV (MeCN): 272 (1100), 265 (1100), 260 (1000), 210 (8600), 199 (15400). IR (KBr) ν 3437, 2936, 1717, 1381, 1250, 1078, 1035, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.19-7.10 (*m*, H-C(5), H-C(6), H-C(7), H-C(8)); 5.28 (*d*, ^3J = 1.9, H-C(1)); 4.47 (*ddd*, ^3J = 11.8, 4.8, 1.9, H-C(2)); 4.21 (*ddd*, ^3J = 3.1, 2.9, 2.5, H-C(4)); 4.07, 3.65 (2*d*, ^2J = 11.4, CH_2OAc); 2.95-

2.80 (*m*, H_2-C(9)); 2.63 (*d*, ^3J = 2.5, H-C(4a)); 2.46-2.38, 1.87-1.82 (2*m*, H_2-C(10)); 2.13, 2.02 (2*s*, Ac); 2.12-2.01 (*m*, H_2-C(3)); 2.00, 1.25 (2 br *s*, OH). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 171.6, 171.1 (2*s*, Ac); 136.7, 133.9 (2*s*, C(4b), C(8a)); 129.4, 129.2, 127.1, 126.7 (4*d*, ^1J(C,H) = 158-160, C(5), C(6), C(7), C(8)); 74.5, 72.7, 63.8 (3*d*, ^1J(C,H) = 152, 147, 144, C(1), C(2), C(4)); 63.7 (*t*, ^1J(C,H) = 148, CH_2OAc); 42.5 (*d*, ^1J(C,H) = 127, C(4a)); 40.2 (*s*, C(10a)); 33.9 (*t*, ^1J(C,H) = 128, C(9)); 25.0, 23.4 (*t*, ^1J(C,H) = 129, 130, C(3), C(10)); 21.0, 20.7 (2*q*, ^1J(C,H) = 130, Ac). CI-MS (NH_3) ν 349 (1, $M + H^+$), 348 (2, M^+), 288 (31), 270 (12), 228 (38), 215 (40), 210 (50), 197 (53), 179 (29), 143 (46), 142 (61), 141 (48), 129 (51), 128 (63), 91 (27), 83 (100). Anal. calc. for $C_{19}H_{24}O_6$ (348.40): C 65.50, H 6.94; found: C 65.40, H 5.94.

(1*RS*,2*SR*,4*SR*,4a*SR*,10a*SR*)-1,2,3,4,4a,10,10a-octahydro-10a-(hydroxymethyl)phenanthrene-1,2,4-triol (17). UV (MeCN): 272 (1100), 265 (1100), 259 (1000), 200 (15000). IR (KBr) ν 3444, 2937, 2876, 1451, 1331, 1277, 1179, 1078, 1037, 992, 957, 932, 800, 744, 662 cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD) δ 7.16-7.13 (*m*, H-C(5), H-C(6), H-C(7), H-C(8)); 4.47 (*ddd*, ^3J = 12.2, 4.1, 1.9, H-C (2)); 4.26 (*ddd*, ^3J = 3.8, 3.2, 3.1, H-C(4)); 3.86 (*d*, ^3J = 1.9, H-C(1)); 3.65, 3.29 (2*d*, ^2J = 11.1, CH_2OH); 2.91-2.87 (*m*, H_2-C(9)); 2.66 (*dd*, ^3J = 3.8, ^4J = 1.4, H-C(4a)); 2.41-2.33 (*m*, H_{ax}-C(10)); 2.19 (*ddd*, ^2J = 12.9, ^3J = 12.2, 3.1, H_{ax}-C(3)); 1.90.(*ddd*, ^2J = 12.9, ^3J = 4.1, 3.2, H_{eq}-C(3)); 1.69 (*m*, H_{eq}-C(10)). ^{13}C NMR (100.6 MHz, CD_3OD) δ 138.7, 137.7 (2*s*, C(4b), C(8a)); 130.5, 129.8, 127.1, 126.8 (4*d*, ^1J(C,H) = 154-163, C(5), C(6), C(7), C(8)); 75.6, 74.0, 65.8 (3*d*, ^1J(C,H) = 148, 141, 146, C(1), C(2), C(4)); 64.8 (*t*, ^1J(C,H) = 145, CH_2OH); 42.6 (*d*, ^1J(C,H) = 123, C(4a)); 42.4 (*s*, C(10a)); 35.8 (*t*, ^1J(C,H) = 129, C(9)); 26.2, 24.2 (*t*, ^1J(C,H) = 127, 134, C(3), C(10)). CI-MS (NH_3) m/z 265 (8, $M + H^+$), 246 (19, M^+ - H_2O), 229 (26), 228 (34, M^+ - 2 H_2O), 215 (27), 198 (79), 141 (68), 129 (84), 128 (100), 115 (58), 91 (76). Anal. calc. for $C_{15}H_{20}O_4$ (264.32): C 68.16, H 7.63; found: C 68.33 H 7.69.

(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). IR (KBr) ν 2987, 2962, 1737, 1377, 1362, 1260, 1230, 1063, 1039, 1002, 914, 859, 788, 612, 540 cm^{-1}. ^{1}H NMR (360 MHz, $CDCl_3$) δ 4.98 (*ddd*, ^3J = 10.9, 6.0, 5.0, H-C(6)); 4.85 (*ddd*, ^3J = 10.2, 4.7, 3.7, H-C(13)); 4.51, 4.14 (2*d*, ^2J = 11.5, CH_2OAc); 4.20 (*d*, ^3J =

4.7, H-C(12)); 4.17 (*d*, ^3J = 6.5, H-C(4)); 4.17 (*d*, ^3J = 5.0, H-C(7)); 4.10 (*d*, ^3J = 5.8, H-C(1)); 2.52 (*ddd*, ^3J = 8.6, 8.5, 8.4, H-C(11)); 2.43 (*ddd*, ^2J = 12.9, ^3J = 10.9, 6.5, H_{exo}-C(5)); 2.27 (*ddd*, ^2J = 13.0, ^3J = 10.2, 5.8, H_{exo}-C(14)); 2.05, 2.04, 1.96 (3*s*, Ac); 1.84 (*dd*, ^3J = 8.6, 8.1, H-C(2)); 1.77-1.72, 1.67-1.60, 1.20-1.10 (3*m*, H_2-C(9), H_2-C(10)); 1.43 (*dd*, ^2J = 12.9, ^3J = 6.0, H_{endo}-C(5)); 1.32 (*d*, ^3J = 8.1, H-C(3)); 1.25 (*dd*, ^2J = 13.0, ^3J = 3.7, H_{endo}-C(14)). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 170.7, 170.4 (2*s*, Ac); 85.8, 84.2, 82.9, 81.7 (4*d*, ^1J(C,H) = 157, 157, 161, 158, C(1), C(4), C(7), C(12)); 74.9, 73.3 (2*d*, ^1J(C,H) = 157, 158, C(6), C(13)); 65.0 (*t*, ^1J(C,H) = 148, CH_2OAc); 50.8, 46.6, 36.4 (3*d*, ^1J(C,H) = 131, 135, 129, C(2), C(3), C(11)); 47.7 (*s*, C(8)); 35.6, 33.4, 27.0, 20.7 (4*t*, ^1J(C,H) = 127, 135, 129, 128, C(5), C(9), C(10), C(14)); 20.9, 20.7 (2*q*, ^1J(C,H) = 129, Ac). CI-MS (NH_3) m/z 426 (73, $M + NH_4^+$), 409 (100, $M + H^+$), 349 (29), 288 (35), 129 (26), 91 (30). Anal. calc. for $C_{21}H_{28}O_8$ (408.45): C 61.75, H 6.91; found: C 61.80, H 6.97.

(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). UV (MeCN): 255 (59000), 200 (59000). IR (KBr) ν 2946, 1710, 1607, 1511, 1279, 1256, 1168, 1125, 1103, 1030, 843, 768, 695 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.96, 7.59-7.57 (2*m*, 2H, 4H, H-C(2'), H-C(6')); 6.96-6.93, 6.75-6.73, 6.56-6.53 (3*m*, H-C(3'), H-C(5')); 5.27 (*ddd*, ^3J = 10.9, 6.2, 4.1, H-C(6)); 5.12 (*ddd*, ^3J = 13.1, 4.3, 3.6, H-C(13)); 4.75, 4.37 (2*d*, ^2J = 11.5, CH_2OAn); 4.52 (*d*, ^3J = 4.1, H-C(7)); 4.36 (*d*, ^3J = 4.3, H-C(12)); 4.30 (*d*, ^3J = 6.2, H-C(4)); 4.24 (*d*, ^3J = 5.7, H-C(1)); 3.88, 3.83, 3.75 (3*s*, OMe); 2.71-2.64 (*m*, H-C(11)); 2.55 (*ddd*, ^2J = 12.8, ^3J = 10.9, 6.2, H_{exo}-C(5)); 2.42 (*ddd*, ^2J = 13.1, ^3J = 10.2, 5.7, H_{exo}-C(14)); 1.99 (*dd*, ^3J = 9.4, 8.2, H-C(2)); 1.91-1.87 (*m*, H-C(9)); 1.75 (*dd*, ^2J = 12.8, ^3J = 6.2, H_{endo}-C(5)); 1.65-1.59 (*m*, H-C(10)); 1.52 (*d*, ^3J = 8.2, H-C(3)); 1.46 (*dd*, ^2J = 13.1, ^3J = 3.6, H_{endo}-C(14)); 1.48-1.15 (*m*, 2H, H-C(9), H-C(10)). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 165.9, 165.8, 165.6 (3*s*, COO); 163.5, 163.0, 162.9 (3*s*, C(4')); 131.6, 131.3, 131.2 (3*d*, ^1J(C,H) = 163, 163, 156, C(2'), C(6')); 122.0, 121.9, 121.3 (3*s*, C(1')); 113.6, 113.0, 112.9 (3*d*, ^1J(C,H) = 162, 161, 161, C(3'), C(5')); 85.6 (*d*, ^1J(C,H) = 156, C(4)); 84.3 (*d*, ^1J(C,H) = 157, C(1)); 83.2 (*d*, ^1J(C,H) = 161, C(7)); 82.0 (*d*, ^1J(C,H) = 166, C(12)); 75.6, (*d*, ^1J(C,H) = 161, C(6)); 73.5, (*d*, ^1J(C,H) = 166, C(13)); 65.2 (*t*, ^1J(C,H) = 149, CH_2OAn); 55.4, 55.3, 55.2 (3*q*, ^1J(C,H) = 145, MeO); 51.3 (*d*, ^1J(C,H)

= 130, C(3)); 47.7 (*s*, C(8)); 46.7 (*d*, ^1J(C,H) = 134, C(2)); 36.7 (*d*, ^1J(C,H) = 131, C(11)); 35.8 (*t*, ^1J(C,H) = 135, C(14)); 33.0 (*t*, ^1J(C,H) = 133, C(5)); 27.1 (*t*, ^1J(C,H) = 129, C(9)); 20.8 (*t*, ^1J(C,H) = 127, C(10)). CI-MS (NH_3) m/z 685 (1, M^+), 549 (2), 533 (1), 136 (10), 135 (100). Anal. calc. for $C_{39}H_{41}O_{11}$ (685.75): C 68.31, H 6.03; found: C 68.10, H 5.76.

(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). UV (MeCN): 212 (9200). IR (film) ν 3050, 2960, 2860, 1630, 1490, 1440, 1410, 1390, 1350, 1260, 1210, 1170, 1150, 1090, 1040, 1020, 990, 930, 900, 830, 800, 780, 740, 690, 660 cm^{-1}.^{1}H NMR (360 MHz, $CDCl_3$) δ 7.38-7.28 (m, Ph); 6.25 (*dd*, ^3J = 17.3, ^3J = 10.7, H-C(α)); 5.76 (*ddd*, ^3J = 7.2, 3.8, ^4J = 2.3, H-C(9)); 4.91 (*dd*, ^3J = 17.3, ^2J = 0.8, H_Z-C(β)); 4.89 (*dd*, ^3J = 10.7, ^2J = 0.8, H_E-C(β)); 4.75 (*d*, ^3J = 4.8, H-C(7)); 4.54, 4.51, 4.46, 4.43 (4*d*, ^2J = 11.6, $C\underline{H}_2$Ph); 4.38 (*d*, ^3J = 5.6, H-C(4)); 4.35 (*d*, ^3J = 6.2, H-C(1)); 4.15 (*ddd*, ^3J = 9.6, 4.8, 3.1, H-C(6); 4.15 (*ddd*, ^3J = 10.4, 5.6, 4.2, H-C(13); 4.07 (*d*, ^3J = 4.2, H-C(12)); 2.42 (*dd*, ^2J = 13.7, ^3J = 7.2, H_{eq}-C(10)); 2.36 (*ddd*, ^2J = 12.2, ^3J = 10.4, 6.2, H_{exo}-C(14)); 2.26 (*ddd*, ^2J = 12.5, ^3J = 9.6, 5.6, H_{exo}-C(5)); 2.17 (*dd*, ^2J = 13.7, ^3J = 3.8, H_{ax}-C(10)); 2.10 (*dd*, ^3J = 9.5, ^4J = 2.3, H-C(3)); 1.83 (*d*, ^3J = 9.5, H-C(2)); 1.45 (*dd*, ^2J = 12.2, ^3J = 5.6, H_{endo}-C(14)); 1.44 (*dd*, ^2J = 12.5, ^3J = 3.1, H_{endo}-C(5)). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.0 (*d*, ^1J(C,H) = 156, C(9)); 141.5 (*s*, C(8)); 137,9, 137.8 (2*s*, Ph); 128.1, 128.0, 127.6, 127.5, 127.3, 127.2, (6*d*, ^1J(C,H) = 161, 160, 159, 159, 162, 164, Ph); 118.0 (*d*, ^1J(C,H) = 163, C(α)); 110.9 (*t*, ^1J(C,H) = 156, C(β)); 84.4, 84.2, 81.2, 80.0 (4*d*, ^1J(C,H) = 156, 156, 156, 160, C(1), C(4), C(7), C(12)); 80,9, 78,0 (2*d*, ^1J(C,H) = 147, 149, C(6), C(13)); 72,0, 71.5 (2*t*, ^1J(C,H) = 141, CH_2Ph); 54.6, 47.7 (2*d*, ^1J(C,H) = 133, 135, C(2), C(3)); 54.4 (*s*, C(11)); 37.3, 32.5 (2*t*, ^1J(C,H) = 133, C(5), C(14)); 32.5 (*t*, ^1J(C,H) = 131, C(10)). CI-MS (NH_3) m/z 457 (1, $M + H^+$), 366 (20), 365 (80), 275 (9), 259 (6), 231 (7), 215 (6), 137 (12), 105 (9), 91 (100), 83 (11).

(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). UV (MeCN): 263 (400), 257 (500), 251 (450), 212 (9200). IR (CCl_4) ν 3020, 2960, 2850, 2730, 1710, 1440, 1390, 1340, 1310, 1250, 1200, 1170, 1090, 1040, 1030, 990, 940,

900, 690 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 9.58 (*s*, CHO); 7.39-7.26 (m, Ph); 5.70 (*ddd*, ^3J = 7.3, ^3J = 3.8, ^4J = 2.3, H-C(10)); 4.70 (*d*, ^3J = 4.6, H-C(12)); 4.47, 4.49 (2*d*, ^2J = 11.6, CH_2Ph); 4.44, 4.42 (2*d*, ^3J = 5.0, 5.1, H-C(1,4)); 4.39 (*s*, CH_2Ph); 4.33 (*d*, ^3J = 4.4, H-C(7)); 4.17-4.06 (m, H-C(6), H-C(13)); 2.91 (*dd*, ^2J = 14.0, ^3J = 7.3, H_{eq}-C(9)); 2.36 (*d*, ^3J = 9.7, H-C(3)); 2.35-2.22 (m, H_{exo}-C(5), H_{exo}-C(14)); 2.13 (*dd*, ^3J = 9.7, ^4J = 2.3, H-C(2)); 2.09 (*dd*, ^2J = 14.0, ^3J = 3.8, H_{ax}-C(9)); 1.48 (*dd*, ^2J = 12.6, ^3J = 4.0, H_{endo}-C(5)); 1.43 (*dd*, ^2J = 12.4, ^3J = 2.8, H_{endo}-C(14)). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 200.2 (*d*, ^1J(C,H) = 180, CHO); 143.8 (*s*, C(11)); 137.8, 137.1 (2*s*, Ph); 128.3, 128.2, 127.7, 127.5 (4*d*, ^1J(C,H) = 160, Ph); 116.8 (*d*, ^1J(C,H) = 164, C(10)); 85.6, 84.3, 80.5, 80.1 (4*d*, ^1J(C,H) = 159, 157, 163, 161, C(1), C(4), C(7), C(12)); 79.5, 78.1 (2*d*, ^1J(C,H) = 151, 148, C(6), C(13)); 72.2, 71.8 (2*t*, ^1J(C,H) = 142, CH_2Ph); 63.3 (*d*, ^2J(C,H) = 20, C(8)); 51.9, 47.2 (2*d*, ^1J(C,H) = 137, 136, C(2), C(3)); 37.4, 36.0 (2*t*, ^1J(C,H) = 133, 134, C(5), C(14)); 29.1 (*t*, ^1J(C,H) = 133, C(9)). CI-MS (NH_3) ν 367 (6, M^+ - Bn), 323 (2), 277 (2), 259 (24), 147 (4), 92 (11), 91 (100).

(1*RS*,2*RS*,3*SR*,4*RS*,6*RS*,7*RS*,8*RS*,12*RS*,13*RS*)-6,13-Bis(benzyloxy)-15,16-dioxa-pentacyclo[10.2.1.1^{4,7}.0^{2,11}.0^{3,8}]hexadec-10-en-8-yl Methanol (22). IR (KBr) ν 3504, 2944, 1718, 1654, 1497, 1454, 1354, 1207, 1175, 1092, 993, 943, 842, 740, 698, 658, 589 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$) δ 7.40-7.28 (*m*, Ph); 5.83 (*ddd*, ^3J = 7.4, 3.0, ^4J = 2.9, H-C(10)); 4.74 (*d*, ^3J = 4.6, H-C(12)); 4.62, 4.53 (2*d*, ^2J = 11,6, CH_2Ph); 4.51, 4.44 (2*d*, ^2J = 11.5, CH_2Ph); 4.31, 4.30 (2*d*, ^3J = 7.8, 6.0, H-C(1), H-C(4)); 4.21-4.11 (*m*, H-C(6), H-C(13)); 4.04 (*d*, ^3J = 4.4, H-C(7)); 3.67 (br *d*, ^2J = 11.8, CH_2OH); 3.37 (br *dd*, ^2J = 11.8, ^3J = 9.1, CH_2OH); 3.26 (br *d*, ^3J = 9.1, OH); 2.59 (*dd*, ^2J = 14.0, ^3J = 7.4, H_{eq}-C(9)); 2.32-2.20 (*m*, H_{exo}-C(5), H_{exo}-C(14)); 2.05 (br *d*, ^3J = 9.6, H-C(2)); 1.91 (br *d*, ^2J = 14.0, H_{ax}-C(10)); 1.41, 1.40 (2*dd*, ^2J = 12.4, 10.5, ^3J = 2.8, 5.4, H_{endo}-C(5), H_{endo}-C(14)); 1.31 (*d*, ^3J = 9.6, H-C(3)). ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 142.7 (*s*, C(11)); 138.0, 136.9 (2*s*, Ph); 128.6, 128.3, 128.2, 127.8, 127.7 (5*d*, ^1J(C,H) = 158-160, Ph); 118.2 (*d*, ^1J(C,H) = 162, C(10)); 84.3, 81.3, 80.7, 80.3 (4*d*, ^1J(C,H) = 157, 160, 160, 160, C(1), C(4), C(7), C(12)); 84.2. 78.2 (2*d*, ^1J(C,H) = 150, C(6), C(13)); 73.4, 71.8 (2*t*, ^1J(C,H) = 144, 143, CH_2Ph); 67.0 (t, ^1J(C,H) = 143, CH_2OH); 54.7 (*s*, C(8)); 53.3, 47.5 (2*d*, ^1J(C,H) = 134, 135, C(2), C(3)); 37.5, 34.7 (2*t*, ^1J(C,H) = 133, 133, C(5), C(14)); 30.6 (*t*, ^1J(C,H) = 130, C(9)). CI-MS (NH_3) m/z

478 (100, $M + NH_4^+$), 461 (10, $M + H^+$), 370 (6), 369 (5), 108 (21), 106 (21), 91 (36). Anal. calc. for $C_{29}H_{32}O_5$ (460.57): C 75.63, H 7.00; found: C 75.59, H 7.05.

(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'-methoxybenzoyloxy)methyl]phenanthrene-2,7-diyl Bis(4'-methoxybenzoate) (23). IR (KBr) ν 2938, 1741, 1716, 1607, 1512, 1458, 1420, 1372, 1258, 1127, 1168, 1101, 1026, 939, 769, 697, 613 cm^{-1}. ^1H NMR (400 MHz, toluene-d_8, 100°C) δ 8.34, 8.30, 8.21 (3*d*, ^3J = 8.7, 8.5, 8.7, H-C(2'), H-C(6')); 6.95-6.93 (*m*, H-C(3'), H-C(5')); 5.94-5.76 (br *m*, H-C(1), H-C(2), H-C(7), H-C(8)); 5.69, 4.35 (2 br *d*, ^2J = 11.4, CH_2OAn); 5.61, 5.45 (2 br *s*, H-C(4), H-C(5)); 3.57, 3.53 (2*s*, MeO); 2.75-2.71 (br *m*, H-C(4a)); 2.56-2.54 (br *m*, H-C(4b)); 2.43-1.91 (br *m*., H-C(3), H-C(6), H-C(9), H-C(10), H-C(10a)); 2.04, 1.98 (2*s*, Ac). CI-MS (NH_3) m/z 889 (1, $M + H^+$), 677 (10), 271 (19), 253 (24), 252 (50), 211 (37), 210 (100), 197 (40), 192 (83), 180 (74). Anal. calc. for $C_{47}H_{52}O_{17}$ (888.92): C 63.51, H 5.90; found: C 63.39, H 6.05.

(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). IR (KBr) ν 3424, 3312, 2948, 2936, 2925, 1407, 1362, 1301, 1241, 1222, 1121, 1075, 1060, 1040, 1022, 957, 860, 835, 653, 623, 533 cm^{-1}. ^1H NMR (400 MHz, D_2O) δ 4.35 (br *d*, ^3J = 13.0, H-C(5)), 4.18 (br *s*, H-C(7)); 4.12-4.07 (*m*, H-C(2), H-C(8), H-C(9)); 4.10, 3.66 (2*d*, ^2J = 11.7, CH_2OH); 3.96 (*dd*, ^3J = 11.7, 3.4, H-C(1)); 2.41 (br *s*, H-C(4a), H-C(4b)); 2.12-1.98 (*m*, 3H, H-C(3), H-C(6), H-C(10a)); 1.82-1.59 (*m*, 6H, H-C(3), H-C(6), H-C(9), H-C(10)). ^{13}C NMR (100.6 MHz, D_2O) δ 71.1, 70.3, 69.3, 68.6, 67.3, 64.3 (6*d*, ^1J(C,H) = 149, 149, 149, 135, 135, 150, C(1), C(2), C(4), C(5), C(7), C(8)); 66.6 (*t*, ^1J(C,H) = 143, CH_2OH); 45.0 (*s*, C(8a)); 38.5, 37.9, 37.2 (3*d*, ^1J(C,H) = 136, 131, 127, C(4a), C(4b), C(10a)); 34.8, 34.6 (*t*, ^1J(C,H) = 127, 128, C(3), C(6)); 24.4, 20.8 (*t*, ^1J(C,H) = 126, 129, C(9), C(10)). CI-MS (NH_3) m/z 300 (3, $M^+ - H_2O$), 283 (5), 282 (7, $M^+ - 2H_2O$), 265 (23), 264 (31, $M^+ - 3H_2O$), 252 (41), 247 (41), 246 (23, $M^+ - 4H_2O$), 229 (14), 228 (23, $M^+ - 5H_2O$), 131 (34), 129 (40), 115 (31), 105 (42), 91 (100). Anal. calc. for $C_{15}H_{26}O_7$ (318.37): C 56.59, H 8.23; found: C 56.59, H 8.26.

(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'-methoxybenzoyloxy)methyl]-1,4-epoxyphenanthrene-2,7-diyl Bis(4'-methoxybenzoate) (25). IR (KBr) ν 2954, 1715, 1606, 1511, 1269, 1169, 1102, 1027, 847, 789 cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 70°C) δ 8.22-8.18, 8.03-7.96 (2*m*, 2H, 4H, H-C(2'), H-C(6')); 6.77-6.69, 6.63-6.59 (2*m*, 4H, 2H, H-C(3'), H-C(5')); 5.77 (*ddd*, ^3J = 7.3, 3.6, 2.3, H-C(7)); 5.62 (*ddd*, ^3J = 10.9, 4.9, 4.5, H-C(2)); 5.36 (*dd*, ^3J = 8.0, 2.3, H-C(8)); 5.33 (*ddd*, ^3J = 8.3, 4.2, 3.8, H-C(5)); 5.21, 4.57 (2*d*, ^2J = 11.2, CH_2OAn); 4.54 (*d*, ^3J = 4.5, H-C(1)); 4.42 (*d*, ^3J = 5.3, H-C(4)); 3.33, 3.32, 3.25 (3*s*, OMe); 2.40 (*ddd*, ^2J = 12.7, ^3J = 10.9, 5.2, H_{exo}-C(3)); 2.37-2.29 (*m*, H-C(4b), H-C(10a)); 2.15 (*ddd*, ^2J = 13.7, ^3J = 7.3, 3.8, H_{eq}-C(6)); 2.00 (*ddd*, ^2J = 13.7, ^3J = 8.3, 3.6, H_{ax}-C(6)); 1.97, 1.87 (2*s*, Ac); 1.93-1.87 (*m*, 1H, H-C(10)); 1.79-1.67 (*m*, 2H, H-C(9), H-C(10)); 1.73 (*d*, ^3J = 9.9, H-C(4a)); 1.55 (*dd*, ^2J = 12.7, ^3J = 4.9, H_{endo}-C(3)); 1.54-1.50 (*m*, 1H, H-C(10)). ^{13}C NMR (100.6 MHz, C_6D_6, 70°C) δ 170.2, 170.1 (2*s*, Ac); 166.6, 166.4, 165.9 (3*s*, ArCOO); 164.6, 164.4, 164.3 (3*s*, C(4')); 132.6, 132.5, 132.4 (3*d*, ^1J(C,H) = 163-167, C(2'), C(6')); 124.1, 123.8, 123.4 (3*s*, C(1')); 114.7, 114.5, 114.4 (3*d*, ^1J(C,H) = 161, C(3'), C(5')); 85.7 (*d*, ^1J(C,H) = 160, C(4)); 84.2 (*d*, ^1J(C,H) = 160, C(1)); 75.8 (*d*, ^1J(C,H) = 154, C(2)); 73.5, 73.4 (2*d*, ^1J(C,H) = 146, C(5), C(8)); 68.8, (*d*, ^1J(C,H) = 151, C(7)); 67.1 (*t*, ^1J(C,H) = 148, CH_2OAn); 55.5, 55.4, 55.3 (3*q*, ^1J(C,H) = 144, MeO); 50.0 (*s*, C(10a)); 48.5 (*d*, ^1J(C,H) = 129, C(4b)); 37.9 (*d*, ^1J(C,H) = 128, C(4a)); 35.5 (*d*, ^1J(C,H) = 131, C(8a)); 37.6 (*t*, ^1J(C,H) = 136, C(3)); 31.1 (*t*, ^1J(C,H) = 131, C(6)); 28.9 (*t*, ^1J(C,H) = 122, C(10)); 20.8 (*t*, ^1J(C,H) = 132, C(9)); 21.4, 21.0 (2*q*, ^1J(C,H) = 130, 129, Ac). CI-MS (NH_3) m/z 727 (1, M^+ - AcOH), 651 (2, M^+ - An), 455 (1), 210 (1), 210 (1), 152 (3), 136 (10), 135 (100). Anal. calc. for $C_{43}H_{46}O_{14}$ (787.84): C 65.64, H 5.89; found: C 65.40, H 6.04.

(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'-methoxybenzoyloxy)methyl]-2,4-bis(methoxymethoxy)phenanthrene-1,7-diyl Bis(4'-methoxybenzoate) (26). IR (KBr) ν 2939, 1739, 1715, 1606, 1512, 1372, 1259, 1225, 1168, 1100, 1029, 848, 770, 696, 613 cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 70°C) δ 8.23-8.19, 8.15-8.12 (2*m*, H-C(2'), H-C(6')); 6.83-6.81, 6.76-6.70 (*m*, H-C(3'), H-C(5')); 5.77-5.76 (*m*, H-C(7)); 5.74 (*d*, ^3J = 3.7, H-C(1)); 5.66-5.62 (*m*, H-C(5), H-C(8)); 5.57, 4.77 (2*d*, ^2J = 11.7, CH_2OAn); 4.71, 4.65 (2*d*, ^2J = 6.5, CH_2OMe); 4.64-4.58 (*m*, H-C(4)); 4.59, 4.58 (2*d*, ^2J = 6.7, CH_2OMe); 4.36-4.34 (*m*,

H-C(2)); 3.33, 3.32, 3.31, 3.30, 3.23 (5*s*, MeO); 2.79-2.77 (*m*, H-C(4b), H-C(8a)); 2.67-2.65 (*m*, H-C(4a)); 2.43-2.27 (*m*, H_2-C(3), H-C(6)); 2.04-1.80 (*m*, H_2-C(9), H_2-C(10), H-C(3)); 1.87, 1.79 (2*s*, Ac). ^{13}C NMR (100.6 MHz, C_6D_6, 70°C) δ 170.1, 169.3 (2*s*, Ac); 166.3, 165.6, 165.5 (3*s*, ArCOO); 164.1, 164.0, 163.0 (3*s*, C(4')); 132.1, 132.0 (2*d*, ^1J(C,H) = 163, C(2'), C(6')); 123.8, 123.3 (2*s*, C(1')); 114.3, 114.2, 114.1 (3*d*, ^1J(C,H) = 161, C(3'), C(5')); 96.7, 95.9 (2*t*, ^1J(C,H) = 162, 162, O$\underline{C}H_2$OMe); 74.9, 74.0, 73.6, 73.4, 67.2 (5*d*, ^1J(C,H) = 143-149, C(1), C(2), C(4), C(5), C(7), C(8)); 66.9 (*t*, ^1J(C,H) = 145, CH_2OAn); 55.5, 55.4, 55.0, 54.9 (4*q*, ^1J(C,H) = 141-144, MeO); 43.1 (*s*, C(10a)); 39.8, 37.3, 33.3 (3*d*, ^1J(C,H) = 126, 129, 125, C(4a), C(4b), C(8a)); 32.3, 31.8, (2*t*, ^1J(C,H) = 129, 132, C(3), C(6)); 26.9, 22.3 (2*t*, ^1J(C,H) = 124, 128, C(9), C(10)); 21.1, 20.6 (2*q*, ^1J(C,H) = 129, Ac). CI-MS (NH_3) m/z 893 (1, $M + H^+$), 662 (1, M^+ - MeO), 848 (1, M^+ - MOM), 575 (1), 469 (1), 281 (3), 210 (1), 152 (2), 136 (9), 135 (74, An^+). Anal. calc. for $C_{47}H_{56}O_{17}$ (892.95): C 63.22, H 6.32; found: C 63.12, H 6.35.

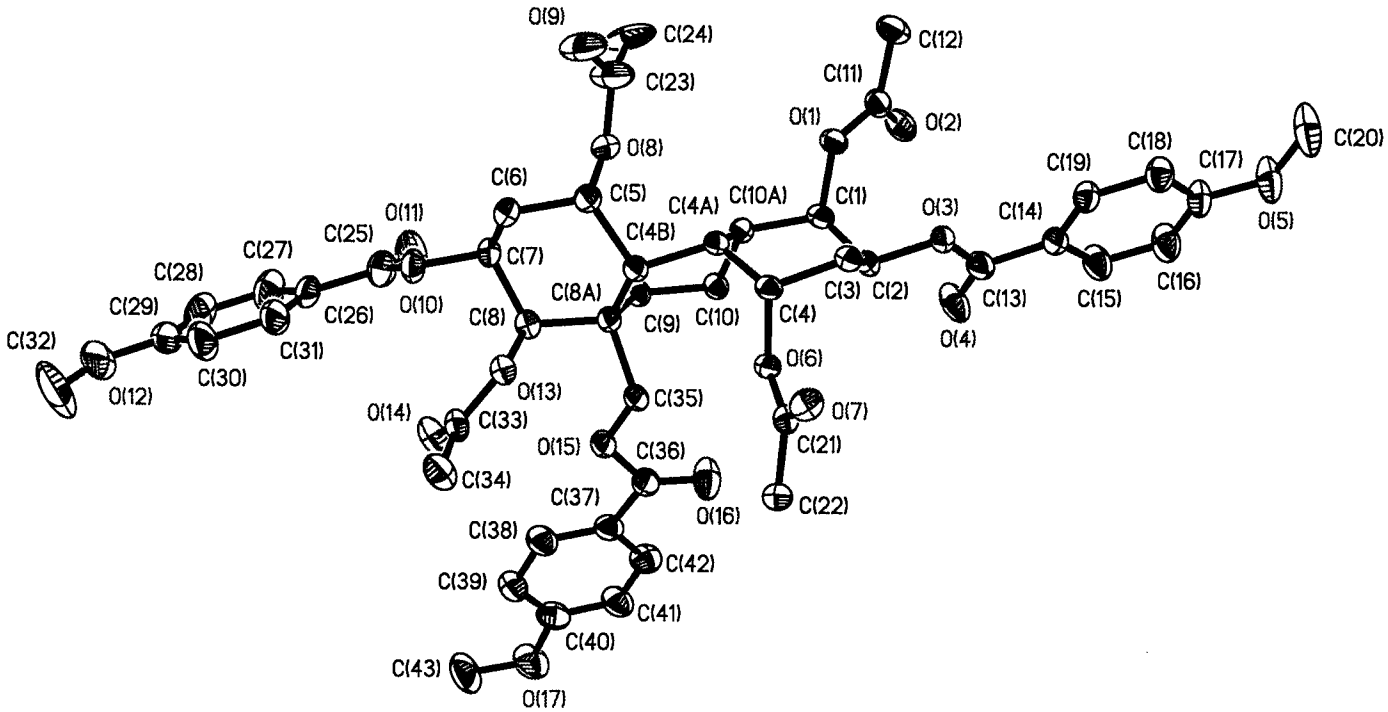

Figure : ORTEP representation of **23**.

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