

Supporting Information.

(4-Bromobenzyloxy)-triisopropylsilane (7) : Triisopropylsilyl chloride (12.37 g, 0.06 mol) and imidazole (9 g, 0.132 mol) in dry DMF (28 mL) was added at room temperature (21 °C), *via* cannula, to a stirred solution of DMF (50 mL) containing 4-bromobenzylalcohol (10 g, 0.053 mol). The reaction mixture was stirred for 1 h, Et₂O (100 mL) was added, followed by water (3x50 mL). The ether extract was dried (MgSO₄) and concentrated. The product was purified by flash chromatography (20:1 to 10:1, petroleum ether/ether) to afford 16.8 g (91%) of **7** as a colorless oil. ¹H NMR (CDCl₃, 500 MHz) δ 1.06-1.23 (m, 21H), 4.78 (s, 2H), 7.21-7.24 (m, 2H), 7.43-7.46 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 12.0, 18.0, 64.4, 120.4, 127.4, 131.2, 140.6. IR (neat, cm⁻¹) 1486, 1069, 1011, 882. MS (EI) 299 (M⁺ – iPr). HRMS (EI) m/z (M⁺ – iPr): calcd 299.0467, found 299.0481.

N,N-Diethyl-4-triisopropylsilyloxymethylbenzamide (8) : *sec*-BuLi (18.2 mL, 16 mmol, 0.88 M in THF) was added dropwise to a dry, stirred THF solution (50 mL, –78 °C) of (4-bromobenzyloxy)-triisopropylsilane **7** (5 g, 14.6 mmol). The reaction mixture was stirred at –78 °C for 30 min then diethylcarbamoyl chloride (4.62 mL, 36.4 mmol, 2.5 eq.) was added dropwise. The mixture was stirred at –78 °C for 25 min, then quenched with a saturated aqueous solution of NH₄Cl, allowed to warm to 21 °C, and extracted with Et₂O. The organic extract was dried (MgSO₄) and concentrated. The product was chromatographed (20:1 to 10:1, petroleum ether/ether) to give 3.6 g (68%) of **8** as white solid. mp = 40-42 °C. ¹H NMR (CDCl₃, 500 MHz) δ 1.06-1.23 (m, 21H), 4.78 (s, 2H), 7.21-7.24 (m, 2H), 7.43-7.46 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 12.0, 17.9, 64.6, 125.5, 126.2, 135.7, 142.7, 171.3. IR (neat, cm⁻¹) 1486, 1069, 1011, 882. MS (EI) 299 (M⁺ – iPr). HRMS (EI) m/z (M⁺ – iPr): calcd 299.0467, found 299.0481. Anal. Calcd for C₂₁H₃₇NO₂Si: C, 69.37; H, 10.26. Found: C, 69.50; H, 10.42.

N,N-Diethyl-2-formyl-4-triisopropylsilyloxymethylbenzamide (9) : A THF solution of *sec*-BuLi (19.53 mL, 21.5 mmol, 1.1M) was added to a stirred –78 °C solution of dry THF (65 mL) and TMEDA (3.245 mL, 21.5 mmol). A THF solution (65 mL) of amide **8** (6.5 g, 17.9 mmol) was added dropwise (the temperature should not exceed –70 °C during the addition). The reaction mixture was stirred at –78 °C for 15 min, then DMF (2.8 mL, 35.8 mmol) was added dropwise. The mixture was stirred for an additional 15 min, then quenched with a saturated aqueous solution of NH₄Cl, allowed to warm to 21 °C, and extracted with Et₂O. The organic extract was dried and concentrated. The product was chromatographed (20:1 to 10:1, petroleum ether/ether) to afford 6.16 g (88%) of **9** as a colourless oil. ¹H NMR (CDCl₃, 500 MHz) δ 0.95 (t, 3H, *J*=7.1 Hz), 1.07 (d, 18H, *J*=7 Hz), 1.13-1.21 (m, 3H), 1.28 (t, 3H, *J*=7.1 Hz), 3.10 (q, 2H, *J*=7.1 Hz), 3.59 (q, 2H, *J*=7.1 Hz), 4.88 (s, 2H), 7.31 (d, 1H, *J*=7.8 Hz), 7.63 (m, 1H), 7.87 (s, 1H), 10.03 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 12.0, 12.6, 13.9, 18.0, 39.1, 42.9, 64.4, 126.8, 126.9, 131.2, 132.5, 138.1, 143.1, 168.8, 190.6. IR (neat, cm⁻¹) 1700, 1486, 1104, 882. MS (EI) 391 (M⁺), 348, 275. HRMS (EI) m/z (M⁺): calcd 391.2544, found 391.2550. Anal. Calcd for C₂₂H₃₇NO₃Si: C, 67.48; H, 9.53; N, 3.58. Found: C, 67.21; H, 9.68; N, 3.46.

N,N-Diethyl-2-[1-hydroxy-3-(4-methoxy-benzyloxymethyl)-penta-2,4-dienyl]-4-triisopropylsilyloxymethylbenzamide (11) : A solution of *sec*-BuLi (30.7 mL, 0.04 mol, 1.3M) was added to a stirred solution of dry THF (150 mL) maintained at –78 °C. After 10 min, a solution of iododiene **10** (6.6 g, 0.02 mol) in dry THF (7 mL) was added quickly (20 sec), causing the solution to turn red. After 3 min, a solution of aldehyde (6 g, 0.015 mol) in dry THF (7 mL) was added quickly (20 sec). The reaction mixture was stirred at –78 °C for 15 min and the solution became lighter in colour. The cold bath was removed and the reaction was quenched with water when the temperature reached 0 °C. The mixture was extracted with Et₂O. The organic extract was dried and concentrated. The product was chromatographed (20:1 to 10:1, petroleum ether/ether) to give 7.8 g (85%) of **11** as a pale yellow oil. ¹H NMR (CDCl₃, 500 MHz) δ 0.95 (t, 3H, *J*=7.1 Hz), 1.07 (m, 18H), 1.10-1.20 (m, 6H), 3.05 (m, 2H), 3.4 (bs, 1H), 3.55 (bs, 1H), 3.75 (s, 3H), 4.11 (s, 2H), 4.28 (q, 2H, *J*=11.3), 4.80 (s, 2H), 5.06 (d, 1H, *J*=10.7 Hz), 5.31 (d, 1H, *J*=17.5 Hz), 5.5 (bs, 1H), 6.03 (s, 1H), 6.28 (bs, 1H), 6.80 (d, 2H, *J*=8.3 Hz), 7.12 (m, 3H), 7.29 (d, 2H, *J*=7.8 Hz). ¹³C NMR (CDCl₃, 125 MHz) δ 12(3), 13.7, 15.2, 18.0(6), 39.1, 43.3, 55.2, 64.1,

64.5, 71.7, 113.6(2), 113.9, 124.3(2), 128.5, 129.3(2), 130.1, 133.7, 138.1(2), 143.2, 159.1. IR (neat, cm^{-1}) 3385, 2943, 1513, 1462, 1104, 882. MS (EI) 595 (M^+), 406, 333, 205. Anal. Calcd for $\text{C}_{35}\text{H}_{53}\text{NO}_5\text{Si}$: C, 70.54; H, 8.97; N, 2.35. Found: C, 70.46; H, 8.95; N, 2.12.

3-[2-(4-Methoxy-benzyloxymethyl)-buta-1,3-dienyl]-5-triisopropylsilanyloxymethyl-3H-isobenzofuran-1-one (12) : *Para*-toluenesulfonic acid (9.73 g, 0.051 mol) was added to a solution of the amide **11** (5.95 g, 0.01 mol) in dry THF (200 mL) at 10-15 $^{\circ}\text{C}$. The reaction mixture was stirred for 3 h and quenched with saturated aqueous sodium bicarbonate (50 mL). The reaction mixture turned dark cherry red. It was extracted with Et_2O , and the organic extract was dried and concentrated. The product was chromatographed (20:1 to 10:1, petroleum ether/ether) to give 3.5 g (70%) of **12** as a pale yellow oil. ^1H NMR (CDCl_3 , 500 MHz) δ 1.05-1.20 (m, 21H), 3.76 (s, 3H), 4.35 (m, 2H), 4.54(m, 2H), 4.84 (d, 2H, $J=3.5$ Hz), 5.17 (d, 1H, $J=11$ Hz), 5.39 (d, 1H, $J=17.5$ Hz), 5.46 (d, 1H, $J=9.2$ Hz), 6.29 (dd, 1H, $J=17.5$ Hz, $J=9.2$ Hz), 6.30 (d, 1H, $J=11$ Hz), 6.84 (d, 2H, $J=8.7$ Hz), 7.26 (d, 2H, $J=8.7$ Hz), 7.37 (s, 1H), 7.51 (d, 1H, $J=7.9$ Hz), 7.82 (d, 1H, $J=7.9$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz) δ 11.9(3), 17.9(6), 55.2, 64.2, 64.6, 72.4, 77.6, 113.9(2), 115.8, 119.9, 124.4, 125.3, 126.6, 129.6(3), 137.3, 139.5, 149.1, 149.4, 159.4, 170.4. IR (neat, cm^{-1}) 1769, 1613, 1513, 1463, 1088, 882. MS (EI) 333.

3-[2-(4-Methoxy-benzyloxymethyl)-buta-1,3-dienyl]-5-triisopropylsilanyloxymethyl-1,3-dihydro-isobenzofuran-1-ol (13) : A solution of DIBAL-H (2.87 mL, 2.87 mmol, 1M) was added to a stirred solution of the lactone **12** (1 g, 1.91 mmol) in dry toluene (30 mL) maintained at -78°C . The reaction mixture was stirred at -78°C for 3 h and isopropanol (2 mL) was added. After 15 min, the cold bath was removed and the reaction was quenched with water when the temperature reached 0°C . The mixture was extracted with Et_2O , dried and concentrated. The product was chromatographed (20:1 to 10:1, petroleum ether/ether) to give 0.93 g (93%) of **13** as a pale yellow oil. ^1H NMR of the mixture of the 2 isomers (CDCl_3 , 500 MHz) δ 1.05-1.20 (m, 42H), 3.41 (d, 1H, $J=7.6$ Hz, OH), 3.54 (d, 1H, $J=8.2$ Hz, OH), 3.76 (s, 6H), 4.35 (m, 4H), 4.49(m, 4H), 4.79 (s, 4H), 5.12 (dd, 2H, $J=11$ Hz, $J=4.6$ Hz), 5.41 (dd, 2H, $J=17.5$ Hz, $J=8.5$ Hz), 5.57 (d, 1H, $J=9.1$ Hz), 5.74 (d, 1H, $J=9.1$ Hz), 5.94 (d, 1H, $J=9.1$ Hz), 6.19 (d, 1H, $J=9.1$ Hz), 6.29 (m, 2H), 6.41 (d, 1H, $J=8.2$ Hz), 6.50 (dd, 1H, $J=7.5$ Hz, $J=1.4$ Hz), 6.84 (d, 4H, $J=8.5$ Hz), 7.17 (m, 2H), 7.26 (m, 4H), 7.37 (s, 4H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 11.9, 17.9, 55.2, 63.6, 63.8, 64.7, 71.9, 72.0, 78.8, 79.2, 100.8, 101.1, 113.8, 114.9, 115.0, 119.5, 122.6, 122.7, 125.8, 125.9, 129.6, 129.7, 130.0, 130.1, 134.1, 135.7, 136.4, 137.5, 137.8, 137.8, 137.9, 138.0, 141.6, 143.6, 143.7, 159.2. IR (neat, cm^{-1}) 3386, 2943, 1613, 1513, 1463, 1093, 882. MS (FAB) 525 (M^++1), 524 (M^+), 387, 369, 327. Anal. Calcd for $\text{C}_{31}\text{H}_{44}\text{O}_5\text{Si}$: C, 70.95; H, 8.45. Found: C, 70.85; H, 8.48.

1-[2-(1-Hydroxy-2-methylallyl)-5-triisopropylsilanyloxymethylphenyl]-3-(4-methoxy-benzyloxymethyl)-penta-2,4-dien-1-ol (14) : A solution of isopropenylmagnesium bromide (83 mL, 33 mmol, 0.4M) was added at 0°C to a stirred solution of the lactol **13** (5.8 g, 11 mmol) in 150 mL of dry THF. The reaction mixture was stirred at 0°C for 1 h then quenched with a saturated aqueous solution of NH_4Cl and allowed to warm to 21°C . The mixture was extracted with Et_2O , and the organic extract dried and concentrated. The product was chromatographed (20:1 to 10:1, petroleum ether/ether) to give 5.48 g (88%) of **14** as a pale yellow oil consisting of 2 diastereoisomers. First diastereoisomer : ^1H NMR (CDCl_3 , 500 MHz) δ 1.05-1.20 (m, 21H), 1.58 (s, 3H), 3.24 (bs, 1H), 3.26 (bs, 1H), 3.77 (s, 3H), 4.19 (s, 2H), 4.37 (s, 2H), 4.80 (s, 2H), 5.02 (m, 1H), 5.09 (d, 1H, $J=11$ Hz), 5.25 (m, 3H), 5.89 (d, 1H, $J=7.9$ Hz), 6.03 (d, 1H, $J=7.9$ Hz), 6.31(dd, 1H, $J=11$ Hz, $J=17.5$ Hz), 6.83(m, 2H), 7.25 (m, 4H), 7.42 (d, 1H, $J=1.22$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.0(3), 18.0(6), 19.9, 55.2, 64.1, 64.6, 67.5, 72.1, 74.4, 111.0, 113.7, 113.8, 114.4, 124.7, 125.3, 128.4, 129.6(2), 136.3, 137.3, 137.6, 138.2, 140.8, 141.6, 146.0, 159.4. Second diastereoisomer : ^1H NMR (CDCl_3 , 500 MHz) δ 1.05-1.20 (m, 21H), 1.54 (s, 3H), 3.30 (bs, 1H), 3.33 (bs, 1H), 3.76 (s, 3H), 4.16 (s, 2H), 4.35 (m, 2H), 4.80 (m, 2H), 5.04 (s, 1H), 5.10 (d, 1H, $J=11$ Hz), 5.23 (d, 1H, $J=11.5$ Hz), 5.24 (s, 1H), 5.32 (d, 1H, $J=17.5$ Hz), 5.91 (d, 1H, $J=8$ Hz), 6.04 (d, 1H, $J=8$ Hz), 6.34 (dd, 1H, $J=11$ Hz, $J=17.5$ Hz), 6.82 (d, 2H, $J=8.5$ Hz), 7.16 (d, 2H, $J=8.5$ Hz), 7.23 (m, 2H), 7.45 (s, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.0(3), 18.0(6), 20.0, 55.2, 63.9, 64.6, 66.9, 71.9, 73.1, 111.0, 113.8(2), 114.4, 124.4, 125.3, 129.5, 129.7, 136.2, 137.1, 137.6, 138.2, 141.2, 141.7, 145.9, 159.3. IR (neat, cm^{-1}) 3386, 2943, 1612, 1513, 1463, 1038, 882. Anal. Calcd for $\text{C}_{34}\text{H}_{50}\text{O}_5\text{Si}$: C, 72.04; H, 8.89. Found: C, 71.86; H, 8.86.

4-(4-Methoxybenzyloxymethyl)-9a-methyl-6-triisopropylsilanyloxymethyl-1,2,4a,9a-tetrahydro-anthraquinone (16) : IBX (15.4 g, 55 mmol) was dissolved in DMSO (40 mL). A solution of diol **14** (6.22 g, 11 mmol) in DMSO (40 mL) was added at 21 °C. The reaction mixture was stirred at 21 °C overnight. Water was added and the solution was filtered. The filtrate was extracted with Et₂O, and the organic extract was dried and concentrated. The product was chromatographed (20:1 to 10:1, petroleum ether/ether) to give 3.33 g (54%) of **16** as a pale yellow oil. ¹H NMR (CDCl₃, 500 MHz) δ 1.05-1.15 (m, 21H), 1.25 (s, 3H), 1.35 (s, 1H), 2.22 (m, 1H), 2.31 (m, 2H), 3.55 (s, 1H), 3.76 (s, 3H), 3.81 (d, 2H, *J*=12 Hz), 4.15 (m, 2H), 4.78 (m, 2H), 5.82 (s, 1H), 6.82 (d, 2H, *J*=8.5 Hz), 7.16 (d, 2H, *J*=8.5 Hz), 7.72 (m, 2H), 8.03 (m, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 11.9(3), 18.0(6), 22.7, 25.2, 30.5, 48.1, 55.1, 58.7, 64.4, 71.4, 72.3, 113.5(2), 123.1, 127.2, 128.8, 129.3(2), 130.0, 131.2, 131.4, 131.9, 134.6, 148.8, 159.0, 198.8, 199.7. IR (neat, cm⁻¹) 1769, 1690, 1463, 1038, 882.

10-Hydroxy-4-(4-methoxybenzyloxymethyl)-9a-methyl-6-triisopropylsilanyloxymethyl-1,4a,9a,10-tetrahydro-2H-anthracen-9-one (17) : Aluminum tri-*tert*-butoxide (0.61 g, 2.49 mmol) was added to a stirred solution of the diketone **16** (0.7 g, 1.24 mmol) in a mixture of dry benzene (2.6 mL) and 2-methyl-2-propanol (13.4 mL). The reaction mixture was heated at reflux for 2.5 h, cooled to 21 °C, and a saturated aqueous solution of NH₄Cl was added. The mixture was extracted with Et₂O, and the organic extract was dried and concentrated. The product was chromatographed (20:1 to 10:1, petroleum ether/ether) to give 0.5 g (71%) of **17** as a pale yellow oil. ¹H NMR (CDCl₃, 500 MHz) δ 1.05-1.18 (m, 21H), 1.26 (s, 3H), 1.43 (m, 1H), 2.09 (m, 3H), 2.96 (s, 1H), 3.77 (s, 3H), 4.15 (d, 1H, *J*=12 Hz), 4.41 (d, 1H, *J*=8.6 Hz), 4.50 (m, 2H), 4.83 (s, 2H), 4.86 (s, 1H), 5.79 (d, 1H, *J*=3.2 Hz), 6.84 (m, 2H), 7.26 (m, 2H), 7.65 (m, 2H), 7.87 (d, 1H, *J*=1 Hz). ¹³C NMR (CDCl₃, 125 MHz) δ 12.0(3), 18.0(6), 21.8, 21.9, 22.0, 40.8, 52.6, 55.2, 64.5, 71.6, 74.7, 75.7, 113.8, 113.9, 124.1, 125.0, 125.7, 129.2(2), 130.1, 130.8, 131.8, 133.1, 141.3, 141.9, 159.1, 197.6. IR (neat, cm⁻¹) 3448, 2943, 1676, 1611, 1513, 1463, 882. MS (EI) 521 (M⁺-iPr), 443 (M⁺-PMB), 383, 341, 251, 121.

3-Methoxybenzoic acid 1-(4-methoxybenzyloxymethyl)-4a-methyl-10-oxo-7-triisopropylsilanyloxymethyl-3,4,4a,9,9a,10-hexahydro-anthracen-9-yl ester (18) : Triethylamine (0.6 mL, 4.25 mmol), *m*-anisoylchloride (0.6 mL, 4.25 mmol) and DMAP (0.16 g, 1.45 mmol) were added to a solution of alcohol **17** (0.8 g, 1.42 mmol) in dry CH₂Cl₂ (20 mL). The reaction mixture was stirred overnight. Two more equivalents of DMAP were added and after 1.5 h no starting material was detected by TLC. A saturated aqueous solution of NH₄Cl was then added. The mixture was extracted with Et₂O, and the organic extract was dried and concentrated. The product was chromatographed (20:1 to 10:1, petroleum ether/ether) to give 0.9 g (90%) of **18** as a pale yellow oil. ¹H NMR (CDCl₃, 200 MHz) δ 1.00-1.25 (m, 24 H), 1.50-1.75 (m, 2H), 2.11 (m, 1H), 3.15 (s, 1H), 3.75 (s, 3H), 3.85 (s, 3H), 4.10-4.60 (m, 4H), 4.80 (s, 2H), 5.80 (s, 1H), 6.55 (s, 1H), 6.85 (m, 2H), 7.10-7.95 (m, 9H). ¹³C NMR (CDCl₃, 50 MHz) δ 11.9(3), 18.0(6), 21.6, 21.7, 23.1, 40.3, 52.3, 55.1, 55.4, 64.3, 71.6, 74.6, 76.8, 113.7(2), 114.6, 114.8, 119.6, 120.9, 122.2, 122.8, 124.4, 124.8, 125.2, 129.7, 129.8, 129.9, 130.2, 130.6, 130.8, 131.5, 132.8, 138.1, 141.7, 159.0, 159.7, 159.8, 166.2, 196.8. MS (FAB) 699 (M⁺+1), 698 (M⁺), 561, 409, 121. IR (neat, cm⁻¹) 1722, 1681, 1612, 1586.

3-Methoxybenzoic acid 1-hydroxymethyl-4a-methyl-10-oxo-7-triisopropylsilanyloxymethyl-3,4,4a,9,9a,10-hexahydro-anthracen-9-yl ester (19) : DDQ (0.32 g, 1.42 mmol) was added to a solution of ketone **18** (0.9 g, 1.29 mmol) in CH₂Cl₂ (9 mL) containing H₂O (0.5 mL). The reaction mixture turned green and was stirred at 21 °C for 1.5 h (until the mixture was completely orange-pink). The solution was filtered through a pad of MgSO₄ and concentrated. The product was chromatographed (20:1 to 10:1, petroleum ether/ether) to give 0.54 g (72%) of **19** as a solid. ¹H NMR (CDCl₃, 200 MHz) δ 1.05-1.18 (m, 21H), 1.26 (s, 3H), 1.55 (m, 1H), 1.70 (m, 1H), 2.09 (m, 2H), 3.15 (s, 1H), 3.74 (s, 1H, OH), 3.87 (s, 3H), 4.20 (d, 1H, *J*=12 Hz), 4.33 (d, 1H, *J*=12 Hz), 4.84 (s, 2H), 5.83 (s, 1H), 6.56 (s, 1H), 7.20 (m, 2H), 7.51 (m, 1H), 7.63 (s, 1H), 8.18 (d, 2H, *J*=7.2 Hz). ¹³C NMR (CDCl₃, 50 MHz) δ 11.9(3), 18.0(6), 21.6, 21.9, 23.0, 40.6, 54.8, 55.4, 55.9, 64.3, 68.2, 76.7, 114.7, 119.8, 122.2, 124.8, 125.4, 125.9, 129.7(2), 130.7, 132.2, 133.9, 138.5, 141.9, 159.7, 166.2, 198.9. MS (FAB) 579 (M⁺+1), 427, 277, 185, 93.

3-Methoxybenzoic acid 9b-hydroxymethyl-3a-methyl-4-oxo-7-triisopropylsilanyloxymethyl-1a,2,3,3a,4,9,9a,9b-octahydro-1-oxa-cyclopropa[a]anthracen-9-yl ester (20) : NaHCO₃ (0.13 g, 1.54

mmol) was added to a solution of allylic alcohol **19** (0.445 g, 0.77 mmol) in dry CH₂Cl₂ (30 mL). The reaction mixture was cooled to 0 °C and *m*-chloroperoxybenzoic acid 50 % (0.53 g, 1.54 mmol) was added. The solution was stored overnight in the refrigerator. A saturated aqueous solution of NH₄Cl was then added. The mixture was extracted with Et₂O, and the organic extract was dried and concentrated. The product was chromatographed (20:1 to 10:1, petroleum ether/ether) to give 0.38 g (83%) of **20** as an unstable white solid which was used directly in the next reaction.

3-Methoxybenzoic acid 9b-acetoxymethyl-3a-methyl-4-oxo-7-triisopropylsilanyloxymethyl-1a,2,3,3a,4,9,9a,9b-octahydro-1-oxa-cyclopropa[a]anthracen-9-yl ester (21): Et₃N (133 µl, 0.96 mmol), acetic anhydride (91 µl, 0.96 mmol) and DMAP (6 mg, 8% mol) were added to a solution of epoxide **20** (0.38 g, 0.64 mmol) in dry CH₂Cl₂ (15 mL). The reaction mixture was stirred at 21 °C for 2 h. A saturated aqueous solution of NH₄Cl was then added. The mixture was extracted with Et₂O, and the organic extract was dried and concentrated. The product was chromatographed (20:1 to 10:1, petroleum ether/ether) to afford 0.36 g (90%) of **21**. ¹H NMR (CDCl₃, 500 MHz) δ 1.05-1.18 (m, 21H), 1.15 (s, 3H), 1.27 (m, 1H), 1.41 (m, 1H), 1.85 (m, 1H), 1.97 (m, 1H), 2.08 (s, 3H), 2.92 (s, 1H), 3.29 (s, 1H), 3.90 (s, 3H), 4.17 (d, 1H, *J*=11.4 Hz), 4.76 (d, 1H, *J*=11.4 Hz), 4.83 (s, 2H), 6.40 (s, 1H), 7.15 (d, 1H, *J*=8 Hz), 7.56 (m, 4H), 7.93 (s, 1H), 8.18 (d, 2H, *J*=8 Hz). ¹³C NMR (CDCl₃, 125 MHz) δ 11.9(3), 18.0(6), 19.6, 20.1, 20.8, 22.4, 38.2, 50.8, 57.6, 58.9, 64.2, 68.2, 75.9, 124.2, 124.3, 128.7, 129.3(2), 129.9, 130.2, 130.4, 130.9, 131.5, 133.6, 137.5, 141.8, 166.0, 170.4, 194.7.

Benzoic acid 9b-acetoxymethyl-3a,7-dimethyl-4-oxo-1a,2,3,3a,4,9,9a,9b-octahydro-1-oxa-cyclopropa[a]anthracen-9-y. ester (22): Following the procedures described above for compounds **19** to **21**, compound **2** was converted to the primary alcohol (DDQ), acetylated (Ac₂O), and epoxidized (m-CIPBA) to compound **22**. ¹H NMR (CDCl₃, 500 MHz) δ 1.27 (s, 3H), 1.40 (m, 1H), 1.75 (m, 1H), 2.01 (s, 3H), 2.05 (m, 1H), 2.15 (m, 1H), 2.31 (s, 3H), 2.78 (d, 1H, *J*=9.5 Hz), 3.23 (s, 1H), 3.79 (d, 1H, *J*=11.6 Hz), 4.52 (d, 1H, *J*=11.6 Hz), 6.64 (d, 1H, *J*=9.5 Hz), 7.00 (s, 1H), 7.20 (d, 1H, *J*=8.0 Hz), 7.49 (dd, 2H, *J*=7.8, 7.6 Hz), 7.60 (dd, 1H, *J*=7.8, 7.6 Hz), 7.92 (d, 1H, *J*=8.0 Hz), 8.18 (d, 1H, *J*=8.4 Hz). ¹³C NMR (CDCl₃, 125 MHz) δ 20.2, 20.7, 21.9, 22.7, 24.7, 43.1, 45.2, 56.9, 58.4, 67.3, 69.2, 125.9, 127.6, 128.2, 128.4, 128.7, 129.5, 129.9, 130.0, 133.4, 133.6, 140.4, 145.1, 165.7, 170.3, 199.7. X-ray structure analyses: Empirical formula C₂₆H₂₆O₆, Crystal size 0.10 x 0.08 x 0.05 mm, Crystal system orthorhombic, Space group *Pbca*, Unit cell dimensions *a*=19.716(3) Å, *b*=18.713(3) Å, *c*=23.882(3) Å, α=90°, β=90°, γ=90°, Volume=8811(2) Å³, Z=4, Calculated density=1.310 g cm⁻³, absorption coefficient 0.093 mm⁻¹, F(000) 3680, Theta range for data collection 1.71 to 26.37°, Reflections collected / unique 69041 / 9004 R1=0.0513, wR2=0.1167, Temperature 203(2) K.

Benzoic acid 1-acetoxy-2-hydroxy-1-hydroxymethyl-4a,7-dimethyl-10-oxo-1,2,3,4,4a,9,9a,10-octahydroanthracen-9-yl ester (24): Freshly distilled BF₃·OEt₂ (9 µl, 0.07 mmol) was added to a solution of epoxide **22** (0.027 g, 0.06 mmol) in dry CH₂Cl₂ (1 mL) maintained at -5 °C. The solution was stirred 1 h at -5 °C. A 10% aqueous solution of NaOAc was added. The mixture was extracted with Et₂O. The organic extract was dried and concentrated. The product was chromatographed (20:1 to 10:1, petroleum ether/ether) to give 0.012 g (42%) of **24**. ¹H NMR (CDCl₃, 200 MHz) δ 1.45 (s, 3H), 1.47 (m, 1H), 1.60 (m, 1H), 2.05 (m, 1H), 2.11 (s, 3H), 2.32 (m, 1H), 2.37 (m, 4H), 3.60 (d, 1H, *J*=11.5 Hz), 4.10 (d, 1H, *J*=11.5 Hz), 4.90 (m, 1H), 6.55 (s, 1H), 7.15 (s, 1H), 7.25 (m, 1H), 7.45 (m, 2H), 7.57 (m, 1H), 7.98 (m, 3H).

Benzoic acid 1-acetoxy-2-hydroxy-1-methanesulfonyloxymethyl-4a,7-dimethyl-10-oxo-1,2,3,4,4a,9,9a,10-octahydroanthracen-9-yl ester (25): Et₃N (9 µl, 0.064 mmol), methanesulfonylchloride (2.5 µl, 0.032 mmol) and a catalytic amount of DMAP were added to a solution of diol **24** (0.012 g, 0.026 mmol) in dry CH₂Cl₂ (2 mL). The reaction mixture was stirred at 21 °C for 3 h. Water was added and the mixture was extracted with CH₂Cl₂. The organic extract was dried and concentrated. The product was chromatographed (20:1 to 10:1, petroleum ether/ether) to give 0.01 g (62%) of **25**. ¹H NMR (CDCl₃, 500 MHz) δ 1.35 (m, 1H), 1.40 (s, 3H), 1.68 (m, 1H), 2.02 (m, 1H), 2.07 (s, 3H), 2.32 (m, 1H), 2.37 (s, 3H), 2.49 (s, 1H), 3.03 (s, 3H), 4.57 (d, 1H, *J*=11.3 Hz), 4.89 (d, 1H, *J*=11.3 Hz), 4.93 (t, 1H, *J*=2.6 Hz), 6.35 (s, 1H), 7.13 (s, 1H), 7.25 (m, 1H), 7.45 (m, 2H), 7.57 (m, 1H), 7.94 (d, 1H),

8.02 (m, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 21.2, 21.6, 22.0, 27.4, 29.6, 31.5, 37.6, 43.0, 49.3, 68.9, 70.5, 71.8, 73.9, 126.6(2), 128.6, 128.9, 129.7, 129.8(2), 130.1, 130.2, 130.6, 133.5, 137.6, 144.2, 166.1, 169.6, 199.1.

Benzoic acid 10b-acetoxy-4a,8-dimethyl-5-oxo-2a,3,4,4a,5,10,10a,10b-octahydro-1H-2-oxa-cyclobuta[a]anthracen-10-yl ester (26) : DBU (2.5 μl , 0.017 mmol) was added to a solution of mesylalcohol **25** (10 mg, 0.016 mmol) in dry toluene (1 mL). The reaction mixture was heated at 105 $^\circ\text{C}$ for 1.5 h. The toluene was evaporated and product was chromatographed to afford 5 mg (61%) of **26** as a white solid. Mp = 184-190 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 500 MHz) δ , 1.50 (s, 3H), 1.64 (m, 1H), 1.82 (m, 1H), 2.02 (s, 3H), 2.10 (m, 1H), 2.27 (m, 1H), 2.34 (s, 3H), 2.64 (d, 1H, $J=5.5$ Hz), 2.80 (d, 1H, $J=4.2$ Hz), 2.90 (d, 1H, $J=4.2$ Hz), 4.91 (bs, 1H), 6.50 (d, 1H, $J=5.5$ Hz), 7.09 (s, 1H), 7.22 (s, 1H), 7.44 (m, 2H), 7.57 (m, 1H), 7.96 (d, 1H, $J=8$ Hz), 8.08 (d, 2H, $J=8$ Hz, $J=1$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz) δ 21.1, 21.8, 25.7, 25.9, 28.9, 46.4, 47.8, 49.5, 57.6, 71.0, 73.9, 127.7, 128.0, 128.1, 128.5, 128.7, 129.9, 133.3, 133.7, 139.1, 145.1, 166.2, 169.6, 199.0. MS (FAB) 435 (M^++1). MS (EI) 434 (M^+), 419, 172, 105. HRMS (EI) m/z (M^+): calcd 434.17298, found 434.17047.