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TETRAHEDRON

Total Synthesis of Angucyclines, 10[1].
Oxygenation of Diels-Alder Products to Non-Aromatic Angucyclinones of the SF-2315 and Tetrangomycin Types

Karsten Krohn* and Jörg Micheel

Universität-GH-Paderborn, FB 13 Chemie und Chemietechnik,
Warburger Str. 100, 33098 Paderborn, Germany

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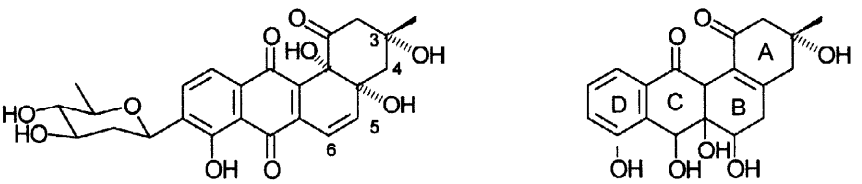
Abstract: The oxygenation of the Diels-Alder derivatives **5**, **6**, **16**, and **21** was investigated with MCPBA, dimethyldioxirane, osmium or ruthenium tetroxide, and molecular oxygen to yield the angucycline analogues **8**, **10**, **12**, **17**, **19**, **23**, and **24** with different oxygenation patterns.

The angucycline antibiotics have recently attracted much attention due to their wide range of biological activity and their interesting chemical structures [2,3]. Especially compounds with a hydroaromatic ring B like aquayamycin (**1**) (SS-228Y-type) or elmycin A (**2**) (tetrangomycin-type) are challenging synthetic targets [2]. So far, no synthesis of an angucyclinone with two hydroxy groups at C-4a and C-12b, the fusion points of ring A and ring B, has been achieved.



aquayamycin (**1**) elmycin A (**2**)

Figure 1. Structures of aquayamycin (**1**) (SS-228Y-type) and elmycin A (**2**) (tetrangomycin-type) [2]

The Diels-Alder reaction of a naphthoquinone and a vinylcyclohexene has proved to be a rapid approach to the construction of the angularly condensed tetracyclic skeleton of the angucyclinones [4–8]. *rac*-Rabelomycin [5] and *rac*-tetrangomycin [6] with an aromatic ring B were synthesized by our group using this

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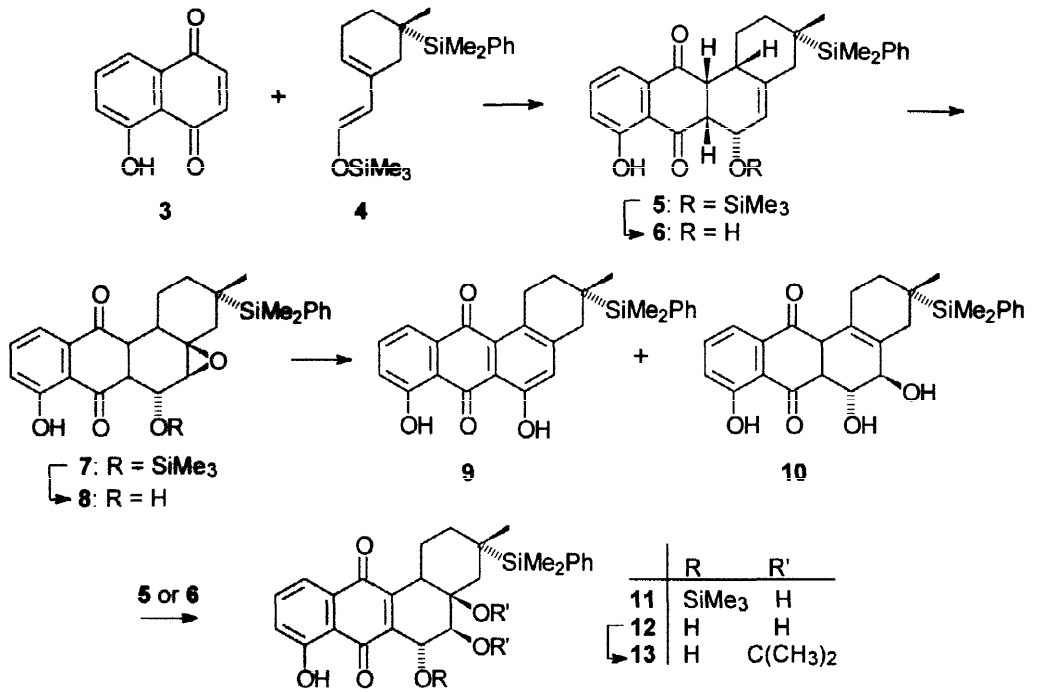
method and the problem of introducing the labile tertiary hydroxy group at C-3 (ring A) was solved by employing silylated dienes like **4** [9]. More recently, we focussed our attention on the carefully directed functionalization of ring B of hydroaromatic angucyclinones. In this communication we describe exploratory oxygenation reactions of primary Diels-Alder adducts such as **5** giving access to a number of hydroaromatic natural product analogues with different numbers of oxygen atoms attached to ring B.

RESULTS AND DISCUSSION

As outlined in a preceding communication [10], the primary Diels-Alder adduct **5** was prepared from juglone (**3**) [11] and the siloxydiene **4** [10] (Scheme 1). The crystal structure of a closely related cycloadduct [12] suggested that attack of an oxidizing agent would occur from the outer face of **5** *anti* to the siloxy group at C-6. In fact, treatment of the Diels-Alder adduct **5** with *meta*-chloroperbenzoic acid (MCPBA) gave an epoxide as one single diastereomer (72%) which was assigned structure **7**. The silyl ether of epoxide **7** was cleaved by treatment with a catalytic amount of hydrochloric acid to afford the epoxy alcohol **8**. We hoped that oxidation of epoxyalcohol **8** and subsequent aromatization would lead to an aromatic angucyclinone with two hydroxy groups at C-5 and C-6 related to fridamycin C, but treatment with various oxidizing agents gave only the usual aromatized rabelomycin derivative **9**. However, prolonged HCl treatment of the silyl ether **7** rather unexpectedly led to the formation of a very interesting hydroaromatic product in 29% yield alongside with epoxyalcohol **8** and the aromatization product **9**. The surprisingly stable new compound was identified as the diol **10**, formed by an epoxide-allylacohol rearrangement from epoxyalcohol **8**. The diol **10** is the first synthetic angucyclinone derivative with an isolated double bond between rings A and B which is structurally related to natural products such as elmycin A (**2**). In addition, the double bond on this position offers a possibility to introduce the two angular hydroxy groups of the SS-228Y type angucyclinones by means of a catalytic *cis*-dihydroxylation.

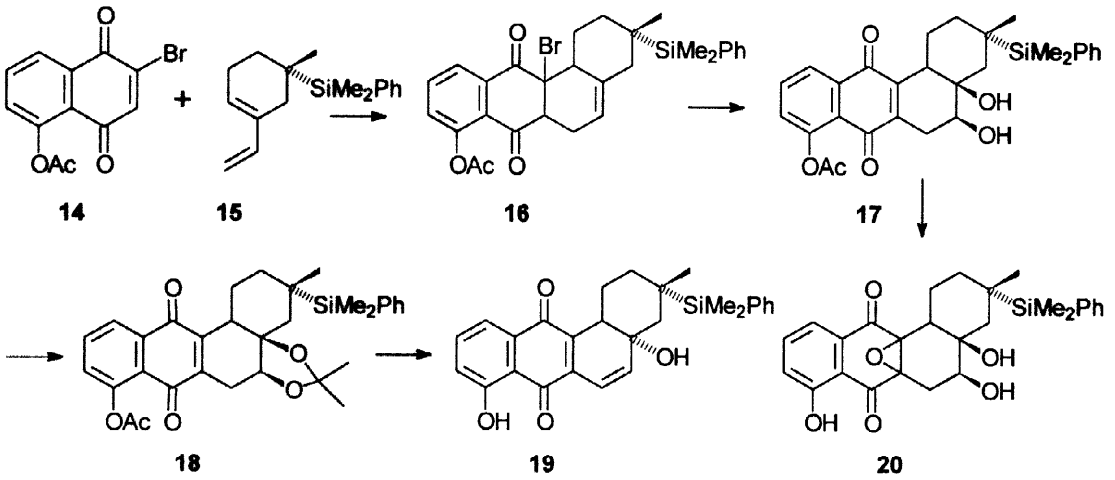
cis-Dihydroxylation of the tertiary double bond of primary Diels-Alder adduct **5** with a catalytic amount of osmium tetroxide in the presence of *N*-methylmorpholine-*N*-oxide (NMO) proceeded only very sluggishly, probably due to severe steric hinderance. The diol **11**, which had been oxidized to the quinone under the conditions of the osmylation, was isolated in very low yield together with aromatization product **9**. Aromatization probably occurred by base-catalyzed double β-elimination with *N*-methylmorpholine formed during the reaction by deoxygenation of NMO. A better result was obtained by employing the "flash" dihydroxylation procedure developed by Shing et al. [13]. The silyl ether at C-6 of the Diels-Alder adduct **5** was first cleaved by a catalytic amount of hydrochloric acid to yield the allylic alcohol **6** followed by treatment with a mixture of sodium periodate and ruthenium(III) chloride to afford the tetraol **12** (32%). The relative stereochemistry of **12** was confirmed by conversion to the acetonide **13** by treatment with a large excess of

dimethoxypropane (DMP). The acetonide **13** was formed as a single isomer in 86% yield from the crude triol **12** and the ^{1}H NMR coupling constant of $J_{5,6}$ = 2.6 Hz was in perfect agreement with a *trans*-relationship of the two oxygen atoms at C-5 and C-6.



Scheme 1.

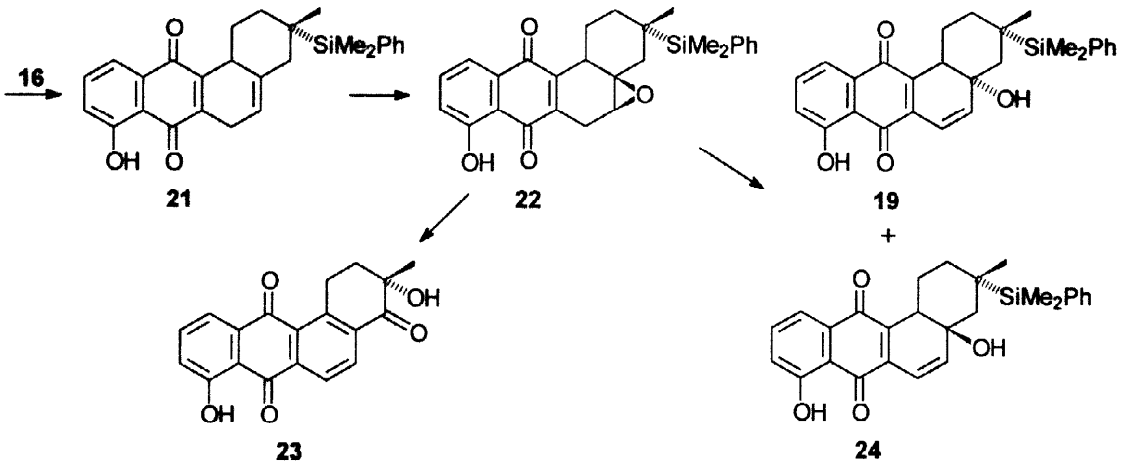
We started from the diol **17**, described in a preceding communication [12], to obtain new hydroaromatic angucyclinones **without** oxygen functionality at C-6. Thus, bromonaphthoquinone **14** was treated with the vinyldiene **15** [6,14] to afford the primary Diels-Alder adduct **16** which was *cis*-dihydroxylated using osmium tetroxide/NMO to yield diol **17** (Scheme 2). Elimination of hydrogen bromide occurred rapidly under the osmylation conditions. Our synthetic scheme anticipated the exploitation of the highly acidic protons at C-6 of the quinoid system **17** for the introducion of a new oxygen functionality in ring B. In fact, treatment of quinone **17** with tetrabutylammonium hydroxide (TBAH) as a mild base under an atmosphere of pure oxygen produced the epoxide **20** (42%) as a single diastereomer but of unknown relative stereochemistry. Mechanistically, the formation of the epoxide would comprise deprotonation of diol **17** at C-6, formation of a semiquinone methide, and addition of molecular oxygen as the principal steps, similar as proposed by Sulikowski et al. [15]. The diol **17** was transformed to the acetonide **18** by treatment with excess (DMP) (88%). Deprotonation at C-6 of this acetonide followed by elimination of acetone yielded the allylic alcohol **19** (43%), a possible starting material for the synthesis of SF-2315 type angucyclinones.



Scheme 2.

A better leaving group was needed to improve the yield of this interesting allylic alcohol **19**. Treatment of the primary Diels-Alder adduct **16** with a mild base afforded the quinone **21** (95%) and subsequent oxygenation with the strong oxidizing agent dimethyldioxirane [16] led to the epoxide **22** (97%) (Scheme 3). Once again, in accordance with results obtained by Sulikowski [8] and Larsen [17], the tetracyclic angucyclinone skeleton was attacked from the less hindered face. Finally, the epoxy group was opened with TBAH to afford the desired allylic alcohol **19** in 73% yield. Reversing the oxidation and the elimination steps of this reaction sequence gave rise to an interesting result. Oxygenation of the Diels-Alder adduct **16** with dimethyldioxirane followed by TBAH treatment furnished an inseparable mixture (1:1) of the two epimeric allylic alcohols **19** and **24**. This deviation of stereoselectivity in the epoxidation step is attributed to the strong electronic repulsion between the dipolar dioxirane molecule and the bromo substituent. The observation is of great importance for the synthesis of aquayamycin-type angucyclines with a hydroxyl group at C-3 *syn* to the two angular hydroxyl groups at C-4a and C-12b. The α-ketol **23**, an isomer of the natural product tetrangomycin [18], was prepared by treatment of the epoxide **22** with tetrabutylammonium fluoride (TBAF) under an air atmosphere in 46% yield.

The fluoride anion has different functions in this reaction sequence. Ring B of the epoxide **22** is aromatized under the influence of the mild base and the newly generated benzylic position at C-4 subsequently deprotonated. In addition, the fluoride anion initiates the cleavage of the carbon-silicon bond at C-3 by nucleophilic attack on the silicon atom. The α-ketol moiety is then formed by air oxidation of the anions produced by deprotonation at C-4 and by cleavage of the carbon-silicon bond at C-3 [19].



Scheme 3.

EXPERIMENTAL

For instrumentation and general methods see ref. [20].

(3R,6R*,6aS*,12aS*,12bR*)-3-(Dimethylphenylsilanyl)-6,8-dihydroxy-3-methyl-1,2,3,4,6,6a,12a,12b-octahydrobenzo[a]anthracene-7,12-dione* (**6**): Two drops of 1 N HCl were added at 0 °C to a solution of the Diels-Alder adduct **5** (200 mg, 0.386 mmol) in MeOH (4 ml) and CH_2Cl_2 (2 ml). The mixture was stirred for approximately 0.5 h at 0 °C and then extracted with CH_2Cl_2 (50 ml). The organic phase was washed twice with cold water (2 × 20 ml), dried (Na_2SO_4) and the solvent was removed at reduced pressure to afford the allylic alcohol **6** (153 mg, 89%) as an unstable yellow oil containing some aromatized product. The crude product was used for the next steps without further purification. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.68 (s; 6 H, $SiMe_2$), 1.08 (s; 3 H, Me), 1.19–1.65 (m; 2 H, 2-H), 1.91 (m; 1 H, 12b-H), 2.05 (d, J_{gem} = 14.3 Hz; 1 H, 4-H_a), 2.24–2.58 (m; 2 H, 1-H), 2.80 (d, J_{gem} = 14.3 Hz; 1 H, 4-H_e), 3.25 (br. s; 1 H, OH), 3.45 (m; 1 H, 6a-H), 3.61 (m; 1 H, 12a-H), 5.05 (m; 1 H, 6-H), 5.81 (br. s; 1 H, 5-H), 7.22–7.68 (m; 8H, 2'-H, 4'-H, 6'-H, 3'-H, 5'-H, 9-H, 10-H, 11-H), 12.01 (s; 1 H, OH).

(3R,4aS*,5R*,6S*,6aS*,12aS*,12bR*)-3-(Dimethylphenylsilanyl)-4a,5-epoxy-8-hydroxy-3-methyl-6-(trimethylsiloxy)-1,2,3,4,4a,5,6,6a,12a,12b-decahydrobenzo[a]anthracene-7,12-dione* (**7**): A solution of the Diels-Alder adduct **5** (80 mg, 0.154 mmol) in CH_2Cl_2 (8 ml) was treated with a solution of MCPBA (40 mg, 0.257 mmol) in CH_2Cl_2 (2 ml) and the mixture was stirred at room temp. for 0.5 h. The solution was dried (Na_2SO_4) and concentrated at reduced pressure. The residue was separated by TLC (silica gel, CH_2Cl_2) to afford epoxide **7** (59 mg, 72%), yellow oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.24 (s; 9H, $OSiMe_3$), 0.41 (s; 6 H,

$SiMe_2$), 0.90 (t, J_{gem} = 14.3 Hz; 2 H, 4-H), 1.17 (s; 3 H, Me), 1.33–1.52 (m; 2H), 1.82–1.93 (m; 2H), 2.72 (m; 2 H, 5-H, 12b-H), 3.10 (t, $J_{6a,12a}$ = 4.5 Hz; 1 H, 6a-H), 3.16 (t, $J_{12a,6a}$ = 4.5 Hz; 1 H, 12a-H), 4.56 (m; 1 H, 6-H), 7.17–7.68 (m; 8H, 2'-H, 4'-H, 6'-H, 3'-H, 5'-H, 9-H, 10-H, 11-H), 12.04 (s; 1 H, OH). –^{13}C NMR (75 MHz, $CDCl_3$): δ = –6.18 (q, SiMe), –5.99 (q, SiMe), –0.53 (q, $OSiMe_3$), 18.85 (s, C-3), 24.33 (t, C-2), 26.39 (q, Me), 33.00 (t), 36.43 (t), 40.26 (d, C-12b), 47.53 (d, C-12a), 54.26 (d, C-6a), 58.40 (d, C-5), 62.08 (d, C-4a), 68.18 (d, C-6), 116.71 (d, C-9), 119.37 (s), 122.53 (d, C-11), 128.02 (2 × d, C-3', C-5'), 129.45 (d, C-4'), 135.06 (2 × d, C-2', C-6'), 137.04 (d, C-10), 137.26 (s, C-1'), 139.60 (s), 161.68 (s, C-8), 196.86 (s, C-12), 205.82 (s, C-7). –MS (EI, 70 eV), *m/z* (%): 534 (3) [M^+], 259 (17), 147 (36), 135 (100) [$SiMe_2Ph^+$]. –$C_{30}H_{38}O_5Si_2$: Calcd. 534.2258; found. 534.2258 ± 3ppm (MS).

(3R,4aS*,5R*,6S*,6aS*,12aS*,12bR*)-3-(Dimethylphenylsilanyl)-4a,5-epoxy-6,8-dihydroxy-3-methyl-1,2,3,4,4a,5,6,6a,12a,12b-decahydrobenzo[a]anthracene-7,12-dione* (**8**): One drop of 1 N HCl was added to a solution of epoxide **7** (200 mg, 0.375 mmol) in MeOH (4 ml) and CH_2Cl_2 (2 ml) at 0 °C. The mixture was stirred for approximately 0.5 h at 0 °C and then extracted with CH_2Cl_2 (50 ml). The organic phase was washed twice with ice-cold water (2 × 20 ml), dried (Na_2SO_4) and the solvent was removed at reduced pressure to afford epoxyalcohol **8** (156 mg, 90%) as an unstable yellow oil containing some aromatization product **9** (5 %). The crude product was used for the next steps without further purification. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.37 (s; 6 H, $SiMe_2$), 1.03 (s; 3 H, Me), 1.21–1.94 (m; 3H), 2.12–2.24 (m; 1H), 2.45–2.53 (m; 2H), 2.81 (m; 1 H, 12b-H), 3.19 (br. s; 1 H, OH), 3.69 (m; 2 H, 6a-H, 12a-H), 4.09 (m; 1 H, 5-H), 4.95 (m; 1 H, 6-H), 7.23–7.67 (m; 8H, 2'-H, 4'-H, 6'-H, 3'-H, 5'-H, 9-H, 10-H, 11-H), 11.97 (s; 1 H, OH).

(3R,5S*,6S*,6aS*,12aR*)-3-(Dimethylphenylsilanyl)-5,6,8-trihydroxy-3-methyl-1,2,3,4,5,6,6a,12a-octahydrobenzo[a]anthracene-7,12-dione* (**10**): Two drops of 1 N HCl were added to a solution of epoxide **7** (200 mg, 0.375 mmol) in MeOH (4 ml) and CH_2Cl_2 (2 ml) at 0 °C. The mixture was stirred for approximately 1.5 h at 0 °C and then extracted with CH_2Cl_2 (50 ml). The organic phase was washed twice with ice-cold water (2 × 20 ml), dried (Na_2SO_4) and the solvent was removed at reduced pressure. The residue was purified by flash chromatography (CH_2Cl_2/Et_2O, 9:1) to afford from the polar fraction diol **10** (49 mg, 29%), yellow oil. – IR (KBr): $\tilde{\nu}$ = 3451 cm^{-1} (OH), 1698 (C=O), 1636 (C=O), 1455, 1346, 1234, 1160. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.28 (s; 6 H, $SiMe_2$), 0.89 (s; 3 H; Me), 1.42–2.37 (m; 6 H, 1-H, 2-H, 4-H), 3.39 (m; 2 H, 6a-H, 12a-H), 3.80 (m; 1 H, 6-H), 4.17 (m; 1 H, 5-H), 7.20 (d, $J_{9,10}$ = 8.1 Hz; 1 H, 9-H), 7.31–7.39 (m; 3 H, 2'-H, 4'-H, 6'-H), 7.45–7.53 (m; 3 H, 3'-H, 5'-H, 11-H), 7.63 (t, $J_{10,9} = J_{10,11}$ = 8.1 Hz; 1 H, 10-H), 12.20 (s; 1 H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –6.72 (q, SiMe), –6.52 (q, SiMe), 18.18 (s, C-3), 18.90 (q, Me), 24.93 (t, C-2), 27.82 (t, C-4), 33.95 (t, C-1), 49.15 (d), 49.60 (d), 71.16 (d, C-6), 73.84 (d, C-5), 117.62 (d, C-9), 118.25 (s), 122.67 (d, C-11), 127.38 (2 × d, C-3', C-5'), 128.66 (s), 128.75 (s), 128.78 (d, C-4'), 134.42 (2 × d, C-2', C-6'),

136.67 (s, C-1'), 136.72 (s), 137.16 (d, C-10), 161.46 (s, C-8), 195.90 (s, C-12), 205.51 (s, C-7). – MS (EI, 70 eV), *m/z* (%): 462 (1) [M^+], 426 (58) [$M^+ - 2 \times H_2O$], 348 (43) [$M^+ - 2 \times H_2O - C_6H_6$], 290 (44) [$M^+ - H - SiMe_2Ph$], 135 (100) [$SiMe_2Ph^+$]. – $C_{27}H_{30}O_5Si$: Calcd. 462.1863; found. 462.1863 ± 3 ppm (MS).

(3R,4aS*,5R*,6S*,12bR*)-3-(Dimethylphenylsilanyl)-3-methyl-4a,5,8-trihydroxy-6-(trimethylsiloxy)-1,2,3,4,4a,5,6,12b-octahydrobenzo[a]anthracene-7,12-dione* (**11**): A solution of Diels-Alder adduct **5** (200 mg, 0.386 mmol) in acetone (6 ml) and water (1 ml) was treated with a solution of OsO_4 in *tert*-butanol (2 ml, 2 × 10^{-2} M, 0.040 mmol, 10 mol%) and with NMO-monohydrate (183 mg, 1.351 mmol). The mixture was stirred for 2 d at 25 °C. A satd. solution of sodium hydrogen sulfite in water (1 ml) was added to the mixture which was stirred for 45 min and subsequently filtered. The filtrate was carefully neutralized with 1 N sulfuric acid, the acetone was removed at reduced pressure and the residue was extracted with CH_2Cl_2 (50 ml). The organic phase was washed twice with water (2 × 20 ml), dried (Na_2SO_4), and concentrated at reduced pressure. The residue was purified by flash chromatography (CH_2Cl_2/Et_2O, 9:1) to afford diol **11** from the fraction of maximum polarity; (38 mg, 18%), yellow oil. – IR (KBr): $\tilde{\nu}$ = 3441 cm^{-1}, 1674 (C=O), 1636 (C=O), 1611 (C=C), 1450, 1279, 1248. – UV (CH_2Cl_2): λ_{max} (lg ε) = 277 nm (3.84), 423 (1.75). – ^1H NMR (200 MHz, $CDCl_3$): δ = 0.27 (s; 3 H, SiMe), 0.30 (s; 3 H, SiMe), 0.34 (s; 9H, $OSiMe_3$), 1.09 (d, J_{gem} = 15.1 Hz; 1 H, 4-H_a), 1.24 (s; 3 H, Me), 1.95–2.02 (m; 2 H, 2-H), 2.10–2.27 (m; 2 H, 1-H), 2.58 (d, J_{gem} = 15.1 Hz; 1 H, 4-H_e), 2.99 (m; 1 H, 12b-H), 3.65 (d, $J_{5,6}$ = 2.8 Hz; 1 H, 5-H), 4.85 (d, $J_{6,5}$ = 2.8 Hz; 1 H, 6-H), 7.22–7.66 (m; 8H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H, 9-H, 10-H, 11-H), 11.96 (s; 1 H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = –5.30 (q, $SiMe_2$), 1.02 (q, $OSiMe_3$), 20.67 (s, C-3), 21.90 (t, C-2), 24.62 (q, Me), 30.89 (t, C-1), 38.89 (t, C-4), 39.67 (d, C-12b), 69.23 (d, C-5), 73.91 (s, C-4a), 76.70 (d, C-6), 119.01 (d, C-9), 123.97 (d, C-11), 127.82 (2 × d, C-3', C-5'), 128.31 (s), 129.37 (d, C-4'), 133.52 (s), 134.93 (2 × d, C-2', C-6'), 136.19 (d, C-10), 137.28 (s, C-1'), 142.18 (s), 148.27 (s), 161.27 (s, C-8), 185.52 (s, C-12), 189.24 (s, C-7). – MS (EI, 70 eV), *m/z* (%): 550 (2) [M^+], 460 (6) [$M^+ - OSiMe_3$], 414 (7) [$M^+ - H - SiMe_2Ph$], 324 (16) [$M^+ - 2 \times H - OSiMe_3 - SiMe_2Ph$], 135 (100) [$SiMe_2Ph^+$]. – $C_{30}H_{38}O_6Si_2$ (550.22): Calcd. C 65.43, H 6.96; found C 65.26, H 6.85

(3R,4aS*,5R*,6S*,12bR*)-3-(Dimethylphenylsilanyl)-4a,5,6,8-tetrahydroxy-3-methyl-1,2,3,4,4a,5,6,-12b-octahydrobenzo[a]anthracene-7,12-dione* (**12**): A vigorously stirred solution of allylic alcohol **6** (100 mg, 0.224 mmol) in EtOAc/MeCN (2 ml each) was treated with a solution of $RuCl_3$ trihydrate (8 mg, 0.031 mmol) and $NaIO_4$ (143 mg, 0.672 mmol) in water (0.7 ml) at 0 °C. The mixture was stirred for 5 min whereupon a satd. solution of sodium hydrogen sulfite (5 ml) was added. The mixture was extracted twice with EtOAc (2 × 10 ml). The combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was separated by flash chromatography (CH_2Cl_2/Et_2O, 8:2) to afford triol **12** (34 mg, 32%), yellow oil. – IR (KBr): $\tilde{\nu}$ = 3436 cm^{-1} (OH), 1642 (C=O), 1631 (C=O), 1618 (C=C), 1455, 1284, 1243. – UV (CH_2Cl_2):

λ_{max} (lg ε) = 275 nm (3.76), 425 (1.48). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.57 (s; 3 H, SiMe), 0.61 (s; 3 H, SiMe), 1.40 (s; 3 H, Me), 1.45 (d, J_{gem} = 14.6 Hz; 1 H, 4-H_a), 1.51–1.72 (m; 2 H, 2-H), 2.07–2.29 (m; 2 H, 1-H), 2.70 (d, J_{gem} = 14.6 Hz; 1 H, 4-H_e), 3.19 (m; 1 H, 12b-H), 3.95 (d, $J_{5,6}$ = 6.1 Hz; 1 H, 5-H), 4.99 (d, $J_{6,5}$ = 6.1 Hz; 1 H, 6-H), 7.46–7.86 (m; 8H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H, 9-H, 10-H, 11-H), 12.06 (br. s; 1 H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.15 (q, SiMe), –4.64 (q, SiMe), 20.03 (s, C-3), 21.38 (t, C-2), 27.89 (q, Me), 32.76 (t, C-1), 41.08 (t, C-4), 41.93 (d, C-12b), 70.52 (d, C-5), 72.66 (s, C-4a), 73.29 (d, C-6), 119.11 (d, C-9), 123.67 (d, C-11), 127.35 (2 × d, C-3', C-5'), 127.46 (s), 128.85 (d, C-4'), 132.28 (s), 134.25 (2 × d, C-2', C-6'), 136.40 (d, C-10), 137.82 (s, C-1'), 140.17 (s), 147.51 (s), 161.25 (s, C-8), 187.51 (s, C-12), 191.11 (s, C-7). – MS (EI, 70 eV), *m/z* (%): 478 (2) [M^+], 460 (7) [$M^+ - H_2O$], 442 (8) [$M^+ - 2 \times H_2O$], 426 (8), 307 (14) [$M^+ - 2 \times H_2O - SiMe_2Ph$], 280 (19), 135 (100) [$SiMe_2Ph^+$]. – $C_{27}H_{30}O_6Si$: Calcd. 478.1812; found. 478.1812 ± 3 ppm (MS).

(3R,4aS*,5R*,6S*,12bR*)--3-(Dimethylphenylsilanyl)-6,8-dihydroxy-4a,5-(dihydroxyacetonide)-3-methyl-1,2,3,4,4a,5,6,12b-octahydrobenzo[a]anthracene-7,12-dione* (**13**): Camphor sulphonic acid (approx. 1 mg) was added to a solution of triol **12** (30 mg, 0.063 mmol) in DMP (1 ml) and CH_2Cl_2 (1 ml). The solution was stirred at room temp. for 15 h. The solvent was removed at reduced pressure and the residue was filtered through a short column of silica gel (CH_2Cl_2) to afford acetonide **13** (28 mg, 86%), yellow oil. – IR (KBr): $\tilde{\nu}$ = 3441 cm^{-1} (OH), 1656 (C=O), 1633 (C=O), 1614 (C=C), 1455, 1367, 1294, 1248. – UV (CH_2Cl_2): λ_{max} (lg ε) = 275 nm (3.85), 422 (1.41). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.32 (s; 6 H, $SiMe_2$), 1.19 (s; 3 H, 3-Me), 1.27 (s; 3 H, acetonide-Me), 1.34 (s; 3 H, acetonide-Me), 1.47 (d, J_{gem} = 14.5 Hz; 1 H, 4-H_a), 1.76–2.36 (m; 4 H, 1-H, 2-H), 2.22 (d, J_{gem} = 14.5 Hz; 1 H, 4-H_e), 3.24 (m; 1 H, 12b-H), 4.14 (d, $J_{5,6}$ = 2.6 Hz; 1 H, 5-H), 5.31 (m; 1 H, 6-H), 7.20–7.37 (m; 4 H, 9-H, 2'-H, 4'-H, 6'-H), 7.53–7.64 (m; 4 H, 3'-H, 5'-H, 11-H, 10-H), 12.01 (s; 1 H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = –6.06 (q, $SiMe_2$), 18.12 (s, C-3), 26.42 (q, Me), 27.25 (q, acetonide-Me), 28.33 (q, acetonide-Me), 28.70 (t, C-2), 32.59 (t, C-1), 41.17 (t, C-4), 42.36 (d, C-12b), 62.56 (d, C-5), 77.64 (s, C-4a), 81.46 (d, C-6), 82.18 (s, acetonide), 115.22 (s), 119.72 (d, C-9), 124.65 (d, C-11), 127.88 (2 × d, C-3', C-5'), 129.33 (d, C-4'), 132.81 (s), 135.04 (2 × d, C-2', C-6'), 136.68 (d, C-10), 137.46 (s, C-1'), 140.19 (s), 150.24 (s), 161.71 (s, C-8), 184.17 (s, C-12), 190.05 (s, C-7). – MS (EI, 70 eV), *m/z* (%): 518 (12) [M^+], 460 (7) [$M^+ - COMe_2$], 442 (10) [$M^+ - COMe_2 - H_2O$], 364 (12), 308 (37) [$M^+ - COMe_2 - H_2O - SiMe_2Ph$], 280 (14), 265 (15), 240 (21), 135 (100) [$SiMe_2Ph^+$]. – $C_{30}H_{34}O_6Si$: Calcd. 518.2125; found. 518.2125 ± 3 ppm (MS).

rac-3-(Dimethylphenylsilanyl)-6a,12a-epoxy-4a,5,8-trihydroxy-3-methyl-1,2,3,4,4a,5,6,6a,12a,12b-decahydrobenzo[a]anthracene-7,12-dione (**20**): A solution of diol **17** (80 mg, 0.159 mmol) in THF (15 ml) was treated with a 1.5 M solution of TBAH in water (0.40 ml, 0.600 mmol) under an atmosphere of pure oxygen at 0 °C. The solution was stirred at 0 °C for 10 min and neutralized with a satd. solution of ammonium chloride. The

mixture was concentrated at reduced pressure and the residue was extracted with CH_2Cl_2/MeOH (5 ml). Petroleum ether was added to the organic phase whereupon the epoxidized compound **18** (32 mg, 42%) crystallized over night as yellow solid, m.p. 234–236 °C. – IR (KBr): $\tilde{\nu}$ = 3441 cm^{-1}, 1631 (C=O), 1605 (C=C), 1455, 1289. – UV (CH_2Cl_2): λ_{max} (lg ε) = 277 nm (3.81), 420 (1.45). – ^1H NMR (200 MHz, $CDCl_3$): δ = 0.34 (s; 6 H, $SiMe_2$), 1.09 (s; 3 H, Me), 0.85–1.51 (m; 3 H, 2-H, 4-H_a), 1.68–1.95 (m; 2 H, 1-H), 2.20 (d, J_{gem} = 13.6 Hz; 1 H, 4-H_e), 2.54 (m; 1 H, 6-H_a), 2.83 (m; 1 H, 12b-H), 3.11 (m; 1 H, 6-H_e), 4.17 (m; 1 H, 5-H), 7.30–7.39 (m; 4 H, 2'-H, 4'-H, 6'-H, 9-H), 7.51–7.60 (m; 4 H, 3'-H, 5'-H, 10-H, 11-H), 12.09 (s; 1 H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = –6.17 (q, $SiMe_2$), 19.51 (q, Me), 21.70 (s, C-3), 26.88 (t, C-2), 29.72 (t, C-1), 31.53 (t, C-4), 39.35 (t, C-6), 45.01 (d, C-12b), 61.02 (s), 65.35 (s), 68.09 (d, C-5), 72.09 (s, C-4a), 119.45 (d, C-9), 124.14 (d, C-11), 128.00 (2 × d, C-3', C-5'), 129.45 (d, C-4'), 135.20 (2 × d, C-2', C-6'), 136.40 (d, C-10), 136.94 (s, C-1'), 142.34 (s), 147.03 (s), 161.26 (s, C-8), 183.98 (2 × s, C-7, C-12). – MS (EI, 70 eV), *m/z* (%): 487 (2) [M^+], 462 (4) [M^+ – O], 444 (8) [M^+ – O –H_2O], 426 (10) [M^+ – O – 2 × H_2O], 310 (60) [M^+ – O – H_2O – $SiMe_2Ph$], 292 (37) [M^+ – O – 2 × H_2O – $SiMe_2Ph$], 135 (100) [$SiMe_2Ph^+$]. – $C_{27}H_{30}O_6Si$: Calcd. 478.1812; found. 478.1812 ± 3 ppm (MS).

(3R,4aS*,5R*,12bR*)-8-Acetoxy-4a,5-(dihydroxyacetonide)-3-(dimethylphenylsilanyl)-3-methyl-1,2,3,4,4a,5,6,12b-octahydrobenzo[a]anthracene-7,12-dione* (**18**): Camphor sulphonic acid (approx. 1 mg) was added to a solution of diol **17** (50 mg, 0.099 mmol) in DMP (1 ml) and CH_2Cl_2 (1 ml). The solution was stirred at room temp. for 15 h. The solvent was removed at reduced pressure and the residue was filtered through a short column of silica gel (CH_2Cl_2) to afford acetonide **18** (47 mg, 88%), yellow solid, m.p. 65 °C. – IR (KBr): $\tilde{\nu}$ = 1765 cm^{-1} (C=O), 1656 (C=O), 1643 (C=O), 1605 (C=C), 1400, 1286, 1270, 1188. – UV (CH_2Cl_2): λ_{max} (lg ε) = 273 nm (4.22), 330 (1.30). – ^1H NMR (200 MHz, $CDCl_3$): δ = 0.33 (s; 3 H, SiMe), 0.34 (s; 3 H, SiMe), 1.18 (s; 3 H, 3-Me), 1.28 (s; 3 H, acetonide-Me), 1.36 (s; 3 H, acetonide-Me), 1.37–1.57 (m; 2 H, 2-H), 1.42 (d, J_{gem} = 14.3 Hz; 1 H, 4-H_a), 1.93 (d, J_{gem} = 14.3 Hz; 1 H, 4-H_e), 2.00–2.20 (m; 3 H, 1-H, 6-H_a), 2.49 (s; 3 H, Ac), 3.17–3.36 (m; 2 H, 6-H_e, 12b-H), 4.15 (m; 1 H, 5-H), 7.30–7.42 (m; 4 H, 2'-H, 4'-H, 6'-H, 9-H), 7.52–7.57 (m; 2 H, 3'-H, 5'-H), 7.73 (t, $J_{10,9} = J_{10,11}$ = 7.9 Hz; 1 H, 10-H), 8.07 (dd, $J_{11,10}$ = 7.9 Hz, $J_{11,9}$ = 1.0 Hz; 1 H, 11-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = –5.93 (q, SiMe), –5.71 (q, SiMe), 18.54 (s, C-3), 21.55 (q, $COCH_3$), 24.15 (t, C-2), 25.60 (t, C-1), 26.43 (q, 3-Me), 27.55 (q, acetonide-Me), 28.24 (q, acetonide-Me), 32.06 (t, C-4), 40.00 (t, C-6), 40.77 (d, C-12b), 78.84 (d, C-5), 82.37 (s, C-4a), 108.90 (s, acetonide), 123.71 (s), 125.37 (d), 128.04 (2 × d, C-3', C-5'), 129.55 (d), 129.66 (d, C-4'), 134.52 (s), 134.67 (d, C-10), 134.91 (2 × d, C-2', C-6'), 137.43 (s, C-1'), 141.96 (s), 146.50 (s), 149.72 (s, C-8), 170.01 (s, $COCH_3$), 183.00 (s, C-7), 183.28 (s, C-12). – MS (EI, 70 eV), *m/z* (%): 544 (22) [M^+], 486 (15) [M^+ – $COMe_2$], 444 (33) [M^+ – $COMe_2$ – Ac], 297 (23), 135 (100) [$SiMe_2Ph^+$], 43 (17) [Ac^+]. – $C_{32}H_{36}O_6Si$: Calcd. 544.2281; found. 544.2281 ± 3 ppm (MS).

(3R,12bS*)-3-(Dimethylphenylsilanyl)-8-hydroxy-3-methyl-1,2,3,4,6,12b-hexahydrobenz[a]anthracen-7,12-dione* (**21**): At 0 °C solution of Diels-Alder adduct **16** (400 mg, 0.725 mmol) in THF (8 ml) was treated with a 1.5 M solution of TBAH in water (2.0 ml, 3.0 mmol). The solution was stirred at 0 °C for 10 min and neutralized with a solution of satd. ammonium chloride. The mixture was extracted twice with CH_2Cl_2 (2 × 50 ml). The combined organic phases were washed twice with ice-cold water (2 × 40 ml), dried (Na_2SO_4) and the solvent was removed at reduced pressure to afford quinone **21** (295 mg, 95%), yellow solid, m.p. 145–147 °C. – IR (KBr): $\tilde{\nu}$ = 3439 cm^{-1}, 1663 (C=O), 1634 (C=O), 1624 (C=C), 1455, 1281, 1237. – UV (CH_2Cl_2): λ_{max} (lg ε) = 273 nm (3.88), 414 (1.68). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.37 (s; 3 H, SiMe), 0.39 (s; 3 H, SiMe), 0.96 (s; 3 H, Me), 1.19–1.64 (m; 2 H, 2-H), 1.87 (d, J_{gem} = 13.5 Hz; 1 H, 4-H_a), 2.03–2.32 (m; 2 H, 1-H), 2.57 (d, J_{gem} = 13.5 Hz; 1 H, 4-H_e), 3.18–3.32 (m; 3 H, 6-H, 12b-H), 5.55 (s; 1 H, 5-H), 7.22–7.43 (m; 4 H, 2'-H, 4'-H, 6'-H, 9-H), 7.52–7.75 (m; 4 H, 3'-H, 5'-H, 10-H, 11-H), 12.11 (s; 1 H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –2.30 (q, $SiMe_2$), 25.17 (t, C-2), 26.30 (s, C-3), 28.89 (q, Me), 32.41 (t, C-1), 38.16 (t, C-4), 38.26 (d, C-12b), 46.13 (t, C-6), 114.64 (d, C-5), 115.25 (s), 119.31 (d, C-9), 124.16 (d, C-11), 127.89 (2 × d, C-3', C-5'), 129.29 (d, C-4'), 132.88 (s), 135.01 (2 × d, C-2', C-6'), 136.42 (d, C-10), 136.93 (s, C-1'), 138.97 (s; C-4a), 141.72 (s), 146.23 (s), 161.55 (s, C-8), 184.05 (s, C-12), 190.45 (s, C-7). – MS (EI, 70 eV), *m/z* (%): 428 (52) [M^+], 350 (71) [M^+ – C_6H_6], 292 (54) [M^+ – $SiMe_2Ph$], 135 (100) [$SiMe_2Ph^+$]. – $C_{27}H_{28}O_3Si$: Calcd. 428.1808; found. 428.1808 ± 3 ppm (MS).

(3R,4aS*,5R*,12bR*)-3-(Dimethylphenylsilanyl)-4a,5-epoxy-8-hydroxy-3-methyl-1,2,3,4,4a,5,6,12b-octahydrobenzo[a]anthracene-7,12-dione* (**22**): A solution of quinone **21** (300 mg, 0.701 mmol) in CH_2Cl_2 (50 ml) was treated with a 0.08 M solution of dimethyldioxirane [21] in acetone (25 ml, 2 mmol) at 0 °C. The solution was stirred for 1 h, dried ($MgSO_4$) and the solvent was removed at reduced pressure. The residue was filtered through a short column of silica gel (CH_2Cl_2) to afford epoxide **22** (302 mg, 97%), orange needles, m.p. 224 °C. – IR (KBr): $\tilde{\nu}$ = 3436 cm^{-1}, 1636 (C=O), 1615 (C=C), 1455, 1284, 1284, 1253. – UV (CH_2Cl_2): λ_{max} (lg ε) = 276 nm (3.86), 410 (1.62), 420 (1.78). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.36 (s; 3 H, SiMe), 0.39 (s; 3 H, SiMe), 1.04 (s; 3 H, Me), 1.33–1.46 (m; 2 H, 2-H), 1.68 (d, J_{gem} = 13.9 Hz; 1 H, 4-H_a), 1.83 (d, J_{gem} = 13.9 Hz; 1 H, 4-H_e), 1.97–2.19 (m; 3 H, 1-H, 6-H_a), 3.16–3.23 (m; 3 H, 5-H, 6-H_e, 12b-H), 7.20 (dd, $J_{9,10}$ = 6.8 Hz, $J_{9,11}$ = 2.8 Hz; 1 H, 9-H), 7.33–7.42 (m; 3 H, 2'-H, 4'-H, 6'-H), 7.51–7.59 (m; 4 H, 3'-H, 5'-H, 10-H, 11-H), 11.99 (s; 1 H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.58 (q, SiMe), –3.52 (q, SiMe), 23.35 (t, C-2), 25.45 (s, C-3), 29.03 (q, Me), 30.22 (t, C-1), 36.30 (t, C-4), 37.05 (d, C-12b), 43.50 (t, C-6), 59.20 (d, C-5), 59.95 (s, C-4a), 114.54 (s), 118.82 (d, C-9), 123.72 (d, C-11), 127.64 (2 × d, C-3', C-5'), 129.09 (d, C-4'), 131.93 (s), 134.51 (2 × d, C-2', C-6'), 135.85 (d, C-10), 137.95 (s, C-1'), 138.07 (s), 145.22 (s), 160.95 (s, C-8), 182.70 (s,

C-12), 189.51 (s, C-7). – MS (EI, 70 eV), *m/z* (%): 444 (44) [M^+], 366 (17) [$M^+ - C_6H_6$], 135 (100) [$SiMe_2Ph^+$]. – $C_{27}H_{28}O_4Si$: Calcd. 444.1757; found. 444.1757 ± 3 ppm (MS).

(3R,4aR*,12bR*)-3-(Dimethylphenylsilanyl)-4a,8-Dihydroxy-3-methyl-1,2,3,4,4a,12b-hexahydro-benzo[a]anthracene-7,12-dione* (**19**): A solution of epoxide **22** (200 mg, 0.450 mmol) in THF (20 ml) was treated with a 1.5 M solution of TBAH in water (1.2 ml, 1.8 mmol) at 0 °C. The ice bath was removed from the reaction flask and the solution was stirred for 45 min. The mixture was neutralized with a satd. solution of ammonium chloride and extracted twice with ether (2 × 30 ml). The combined organic phases were washed twice with water (2 × 30 ml), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was separated by flash chromatography (CH_2Cl_2/MeOH, 99:01) to afford the allylic alcohol **23** (146 mg, 73%), yellow solid, m.p. 85 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3498 cm^{-1}, 1638 (C=O), 1455, 1289, 1253, 1217. – UV (CH_2Cl_2): λ_{max} (lg ε) = 268 nm (4.21), 303 (3.22), 409 (2.31). – ^1H NMR (300 MHz, $CDCl_3$): δ = 0.27 (s; 3 H, SiMe), 0.30 (s; 3 H, SiMe), 0.98 (s; 3 H, Me), 1.07–1.26 (m; 2 H, 2-H), 1.38 (d, J_{gem} = 13.9 Hz; 1 H, 4-H_a), 1.69–1.88 (m; 2 H, 1-H), 2.06 (d, J_{gem} = 13.9 Hz; 1 H, 4-H_e), 3.06–3.11 (m; 1 H, 12b-H), 6.21 (d, $J_{6,5}$ = 9.5 Hz; 1 H, 6-H), 6.74 (d, $J_{5,6}$ = 9.5 Hz; 1 H, 5-H), 7.14 (dd, $J_{9,10}$ = 7.2 Hz, $J_{9,11}$ = 2.3 Hz; 1 H, 9-H), 7.22–7.31 (m; 3 H, 2'-H, 4'-H, 6'-H), 7.41–7.44 (m; 2 H, 3'-H, 5'-H), 7.48–7.54 (m; 2 H, 10-H, 11-H), 11.97 (s; 1 H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.19 (q, SiMe), –2.56 (q, SiMe), 23.12 (s, C-3), 26.88 (t, C-2), 29.82 (q, Me), 33.65 (t, C-1), 40.97 (d, C-12b), 47.45 (t, C-4), 69.14 (s, C-4a), 114.35 (s), 118.84 (d, C-6), 119.06 (d, C-9), 123.87 (d, C-11), 127.44 (2 × d, C-3', C-5'), 128.85 (d, C-4'), 132.45 (s), 134.33 (2 × d, C-2', C-6'), 134.73 (s), 136.09 (d, C-10), 138.01 (s, C-1'), 140.32 (d, C-5), 144.21 (s), 161.29 (s, C-8), 183.03 (s, C-12), 187.88 (s, C-7). – MS (EI, 70 eV), *m/z* (%): 444 (2) [M^+], 426 (29) [$M^+ - H_2O$], 348 (25) [$M^+ - H_2O - C_6H_6$], 333 (18) [$M^+ - H_2O - C_6H_6$ – Me], 297 (18), 290 (21) [$M^+ - H_2O$ – $SiMe_2Ph^+$], 135 (100) [$SiMe_2Ph^+$]. – $C_{27}H_{28}O_4Si$ (444.18): Calcd. C 72.94, H 6.35; found C 72.72, H 6.25.

rac-3,8-Dihydroxy-3-methyl-1,2-dihydro-3H-benzo[a]anthracene-4,7,12-trione (**23**): TBAF × 3 H_2O (88 mg, 0.337 mmol) was added to a solution of epoxide **22** (50 mg, 0.113 mmol) in dry THF (5 ml). The solution was stirred at room temp. for 15 h under an air atmosphere. The mixture was poured into water (30 ml) and extracted twice with ether (2 × 25 ml). The combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was separated by flash chromatography (CH_2Cl_2/MeOH, 99:01) to afford from the polar fraction α-ketol **24** (17 mg, 46%), yellow solid, m.p. 195–198 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3472 cm^{-1}, 1683 (C=O), 1667 (C=O), 1634 (C=O), 1580 (C=C), 1460, 1259. – UV (CH_2Cl_2): λ_{max} (lg ε) = 272 nm (4.44), 343 (1.12), 414 (1.55). – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.46 (s; 3 H, Me), 2.19 (m; 1 H, 2-H_a), 2.42 (m; 1 H, 2-H_e), 3.53 (m; 1 H, 1-H_a), 3.93 (m; 1 H, 1-H_e), 7.32 (d, $J_{9,10}$ = 8.2 Hz; 1 H, 9-H), 7.72 (t, $J_{10,9} = J_{10,11}$ = 8.2 Hz; 1 H, 10-H), 7.80 (d, $J_{11,10}$ = 8.2 Hz, 1 H, 11-H), 8.42 (d, $J_{6,5}$ = 8.2 Hz; 1 H, 6-H), 8.50 (d, $J_{5,6}$ = 8.2 Hz; 1

H, 5-H), 12.33 (s; 1 H, OH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.81 (q, Me), 27.42 (t, C-2), 35.50 (t, C-1), 73.63 (s, C-3), 115.95 (s), 120.23 (d, C-9), 124.27 (d, C-11), 126.303 (d, C-6), 132.05 (s), 133.54 (d, C-5), 135.07 (s), 135.94 (s), 137.78 (d, C-10), 138.55 (s), 147.19 (s), 162.61 (s, C-8), 184.35 (s, C-12), 188.15 (s, C-7), 201.33 (s, C-4). – MS (EI, 70 eV), *m/z* (%): 322 (51) [M^+], 294 (24) [M^+ – CO], 279 (100) [M^+ – CO – Me], 264 (56) [M^+ – CO – 2 × Me], 251 (42) [M^+ – CO – C_3H_7], 236 (43), 152 (29). – $C_{19}H_{14}O_5$: Calcd. 322.0841; found. 322.0841 ± 3 ppm (MS).

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