2,3,6,7-Tetrasubstituted Perhydroanthracenes: Stereoselective Synthesis and Biconformationality Studies

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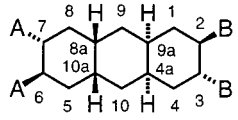
2,3,6,7-Tetrasubstituted perhydroanthracenes with the relative configuration 2β,3α,4aα,6β,7α,8aβ,9aα,10aβ have been synthesized stereoselectively. The biconformationality of these compounds has been investigated in solution by NMR and in the solid state by X-ray crystallography. A triple-ring flip **2** → **3** was realized for the first time by the covalently induced transition **29** → **30**.

Biconformational molecules have two low-energy conformations.[1] Besides well-known examples like cyclohexane and *cis*-decalin, *cis-anti-cis*-perhydroanthracene displays biconformationality.[2,3] The barrier for the triple-ring flip of the unsubstituted *cis-anti-cis*-perhydroanthracene has been determined to be 14 kcal/mol.[3]

Tetrasubstituted *cis-anti-cis*-perhydroanthracenes of type **1** (see Figure 1) are interesting candidates for switchable building blocks in the context of conformational control of molecular functions. The relative configuration 2β, 3α, 4aα, 6β, 7α, 8aβ, 9aα, 10aβ should − under the assumption that the *all*-chair ground-state conformation of the *cis-anti-cis*-perhydroanthracene will not be significantly changed by the tetrasubstitution − lead to the following biconformational system: In conformer **2** the A substituents are axial and the B substituents are equatorial. In conformer **3** the A substituents have changed place to equatorial positions and the B substituents are now at axial sites. Here we report the stereoselective synthesis of tetrasubstituted perhydroanthracenes with the relative configuration mentioned above. We answer the question whether the predicted equatorial-axial pattern can be observed in actual molecules, or whether the tetrasubstitution enforces a significant disturbance of the perhydroanthracene skeleton resulting in twist and/or boat conformations.

Compound **4** was chosen as a target structure for the following reasons: The hydroxy functions bear the option for further attachments. The division into secondary and primary alcohols should allow the A and B substituents to be selectively addressed in the course of these attachments.

In addressing the stereoselective synthesis of a biconformational system, it is advisable to fix the molecule in one of the two conformations. Otherwise a predictable stereochemical control by different shielding of half spaces (e.g. convex versus concave) will be very difficult. We choose sterically demanding *tert*-butyldiphenylsilyl (TBDPS) ethers at the B side as conformational anchors. This should lead in **5** to a fixation of the B substituents in equatorial positions, forcing the A substituents into axial places.



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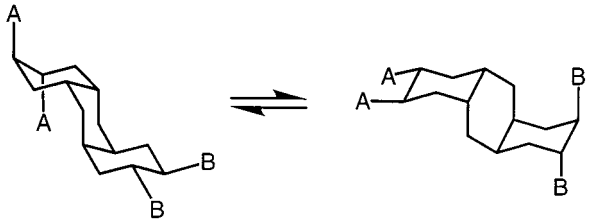
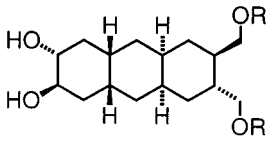


2 **3**

Figure 1. Biconformational 2β,3α,4aα,6β,7α,8aβ,9aα,10aβ-tetrasubstituted perhydroanthracene **1** with the two *all*-chair conformations **2** and **3**



4 R = H

5 R = TBDPS

Starting point of the synthesis of **5** was the Diels−Alder reaction (see Scheme 1) of 1-trimethylsiloxy-1,3-butadiene **6** and diethyl fumarate **7** to give the cyclohexene **8**.[4] Reduction of the ester groups and simultaneous cleavage of the trimethylsilyl ether gave a triol **9**, whose primary OH groups were protected as TBDPS ethers (**9** → **10**). After manganese dioxide oxidation of the allylic alcohol the cyclohexenone **11** was obtained. The second ring of the perhydroanthracene system was built up by a Lewis acid-cata-

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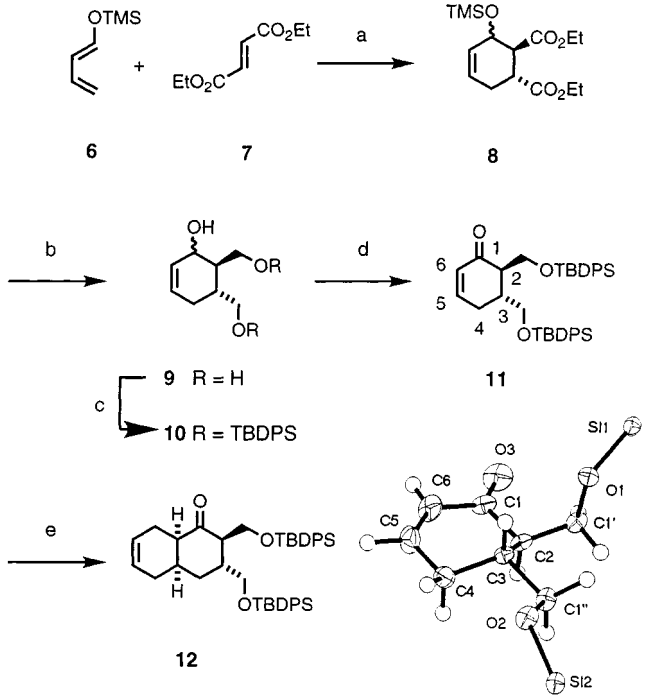
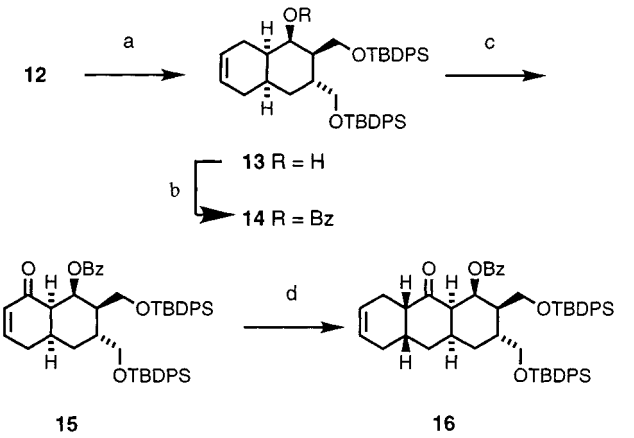
lyzed Diels–Alder reaction of the enone **11** with 1,3-butadiene leading to the cycloadduct **12**.[5] Only one stereoisomer was observed in this cycloaddition. The stereochemical outcome of the cyloaddition can be understood by inspection of the X-ray crystal structure of the enone **11**: In an *endo* transition state, the axial hydrogen at C-4 shields effectively the α side of the dienophile resulting in a preferred β attack.



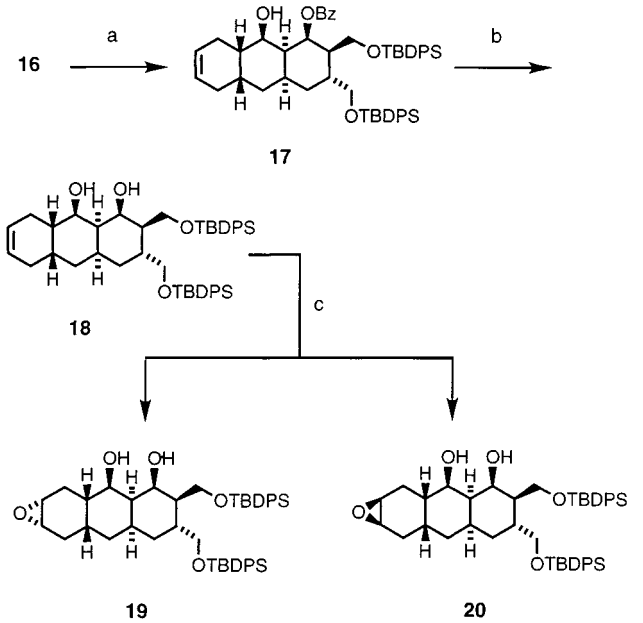
Scheme 1. Synthesis of the first two six-membered rings of the *cis-anti-cis*-perhydroanthracene skeleton. a) toluene, reflux, 12 h, 98%; b) $LiAlH_4$, THF, reflux, 3 h, 98%; c) TBDPSCl, imidazole, CH_2Cl_2/DMF, room temp., 12 h, 81%; d) MnO_2, CH_2Cl_2, reflux, 1 h; 99%; e) 1,3-butadiene, cat. $AlCl_3$/$AlCl_2Me$, toluene, −78°C -> room temp., 32 h, 80%; TBDPSCl: *tert*-butyldiphenylsilyl chloride

Next (see Scheme 2), the ketone functionality of **12** was reduced and the resulting alcohol was protected as its benzoate (**12** → **13** → **14**). The subsequent regioselective allylic oxidation of **14** provided the enone **15**. A possible explanation for the remarkable regioselectivity in this step may be a directing effect of the benzoate group on the selenium dioxide reagent. The Lewis acid-catalyzed Diels–Alder reaction of **15** with 1,3-butadiene resulting in the cycloadduct **16** finished the construction of the perhydroanthracene with the relative configuration *cis-anti-cis*. The stereochemical outcome of this cycloaddition was predicted by a diene attack from the convex side of the dienophile.

After stereoselective $NaBH_4$ reduction of ketone **16** the alcohol **17** was obtained. The X-ray crystal structure of **17** (Figure 2A) confirms the relative configuration of the substituents at positions 2 and 3 and of the *cis-anti-cis*-perhydroanthracene framework. Two assumptions about the preferred conformation of **17** could be verified: 1) the sterically demanding $CH_2OTBDPS$ groups play their role as conformational anchors and occupy equatorial positions; 2) both cyclohexane rings have chair conformations, the cyclohexene ring exists as a half chair.



Scheme 2. Completion of the synthesis of the *cis-anti-cis*-perhydroanthracene skeleton. a) 1. $NaBH_4$, MeOH/CH_2Cl_2, 0°C, 1 h, 99%; b). *n*BuLi, BzCl, THF, 0°C, 3 h, 99%; c) 1. SeO_2, dioxane/H_2O/Py, 450/10/1, 100°C, 7 h, 82%; 2. MnO_2, CH_2Cl_2, reflux, 1 h, 98%; d) 1,3-butadiene, 2.7 equiv. $AlBr_3$, toluene, −78 → −40°C, 10 min, 86%

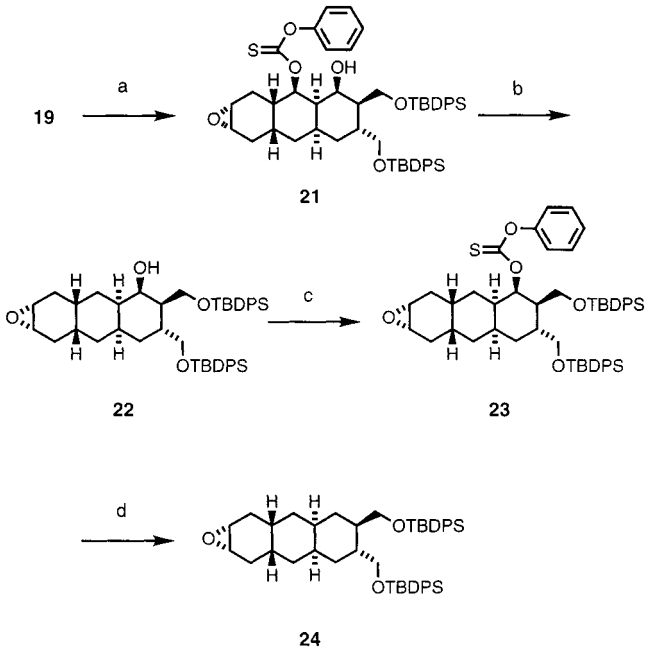


Scheme 3. Reduction, debenzoylation and 6,7-epoxidation. a) $NaBH_4$, MeOH/$CHCl_3$, 0°C → room temp., 60 min, 98%; b) 1. *n*BuMgCl, THF, 10°C, 4 h, 91%; c) MCPBA, CH_2Cl_2, 0°C, 3 h, 85%; MCPBA: *meta*-chloroperbenzoic acid

Cleavage of the sterically hindered benzoate was achieved (see Scheme 3) with butyl magnesium chloride (**17** → **18**). Epoxidation of the double bond in **18** resulted in a 2:1 mixture of the α-epoxide **19** and the β-epoxide **20**. Both epoxides could be separated by chromatography.

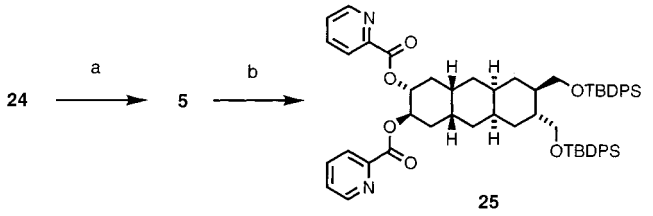
The Barton–McCombie[6] deoxygenation of the two secondary alcohol functions was adressed next. A simultaneous deoxygenation of both OH groups could not be achieved. Therefore, a stepwise route was chosen (see Scheme 4). The diol **19** was first transformed into the monothiocarbonate **21**. Reaction of **21** with tributyltin hydride cleanly afforded the monoalcohol **22**. The latter was al-

lowed to react to the thiocarbonate **23**, which could be deoxygenated to the desired product **24**.



Scheme 4. Barton–McCombie deoxygenation. a) PhOCSCl, Py, CH_2Cl_2, −15°C, 3 d, 75%; b) Bu_3SnH, AIBN, toluene, 90°C, 15 min, 99%; c) *n*BuLi, PhOCSCl, THF, −78 → 0°C, 3 h, 76%; d) Bu_3SnH, AIBN, toluene, 90°C, 15 min, 97%; AIBN: azobisisobutyronitrile

A stereopredictable opening of the epoxide functionality[7] to the *trans*-diaxial diol **5** concluded the synthesis of the perhydroanthracene target structure with all 8 stereocenters in place as shown in Scheme 5.



Scheme 5. Epoxide opening **24** → **5** and formation of the dipicolate **25**. a) $HClO_4$, acetone/H_2O, 0°C, 2 h, 76%; b) picolinic acid, EDC, DMAP, CH_2Cl_2, 25°C, 1.5 h, 91%; EDC: *N*-ethyl-*N*′-(dimethylamino)propylcarbodiimide; DMAP: 4-(dimethylamino)pyridine

NMR-ROESY studies of the bispicolyl ester **25** (relative to **5**, compound **25** showed fewer superpositions in the ^{1}H-NMR spectrum) indicate a solution conformation **26** (Figure 2B).[8] The CH_2OTBDPS groups in positions 2 and 3 are in agreement with the X-ray crystal structure of **17** equatorial, both *O*-substituents in positions 6 and 7 are axial. The two protons at C(6) and C(7) show a vicinal coupling constant of 3 Hz, a typical value for equatorial protons.

To demonstrate the triple-ring flip **2** → **3**, the conformational anchor in **5** had to be lifted, and instead the two secondary OH groups had to be equatorially fixed. Using acidic conditions the simultaneous cleavage of the TBDPS groups and the introduction of a 6,7-bisacetal functionality

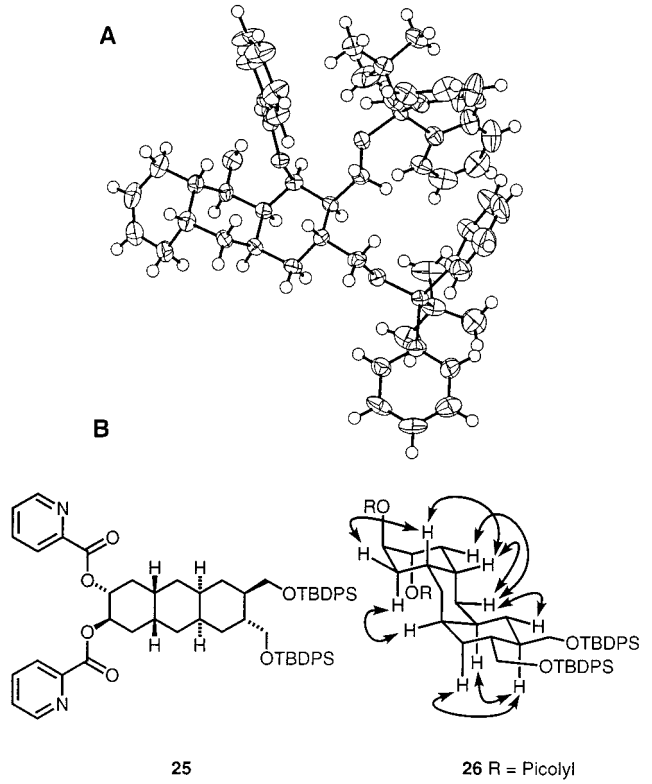
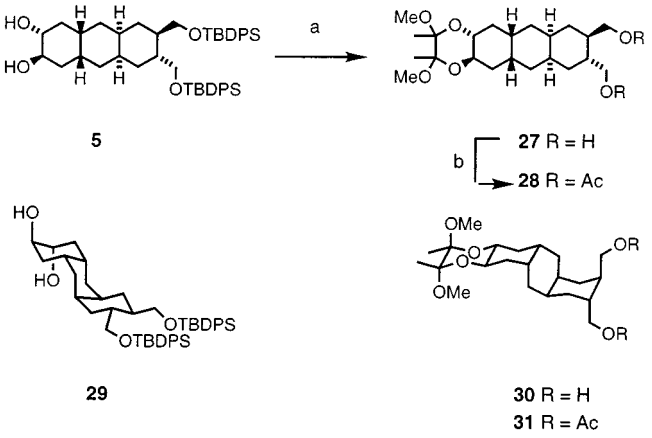


Figure 2. A: X-ray crystal structure of **17**; B: preferred conformation **26** of the bispicolyl ester **25** in solution ([D_8]toluene) based on ROESY data. Selected ROESY cross signals are marked by double arrows

could be achieved by formation of compound **27**[9] as given in Scheme 6.



Scheme 6. Covalently induced triple-ring flip **29** → **30** by conversion of **5** into **27**. a) 2,2′,3,3′-tetramethoxybutane, camphorsulfonic acid, MeOH, 60°C, 12 h, 60%; b) Et_3N, AcCl, CH_2Cl_2, 0°C, 1 h, 90%

The covalent clamp of the bisacetal should now anchor the *O*-substituents at positions 6 and 7 equatorially, with the consequence of triple-ring flip induction (**29** → **30**) and a diaxial arrangement of the CH_2OH groups at positions 2 and 3. The X-ray crystal structure of **27** (Figure 3A) shows indeed the predicted conformation **30**. The expansion of the $C_1-C_2-CH_2OH$ angle to on an average 113.5° demon-

strates clearly the 1,3-diaxial repulsive interaction (9a ↔ 2) located in the right chair of **30**.

To study the solution conformation of the perhydroanthracene system after the triple-ring flip, the diol **27** was converted into the diacetate **28**, which showed fewer superpositions in the ^{1}H-NMR spectrum. Inspection of the NOESY spectrum of **28** revealed the solution conformation **31** (Figure 3B).[8]

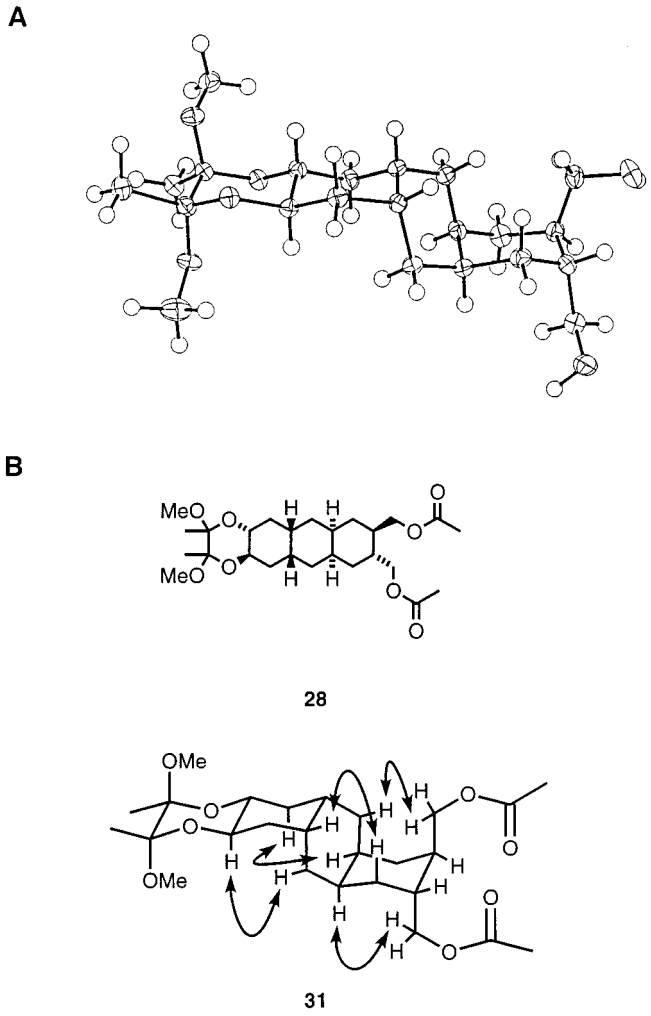


Figure 3. A: X-ray crystal structure of **27**; B: preferred conformation **31** of the diacetate **28** in solution ($CDCl_3$) based on NOESY data. Selected NOESY cross signals are marked by double arrows

In summary two objectives have been achieved: First, a stereoselective route to tetrasubstituted perhydroanthracenes of type **4** has been developed. Second, a triple-ring flip **2** → **3** was realized for the first time by the covalently induced transition **29** → **30**. This opens firm ground for further investigations using noncovalent ways of inducing this kind of triple-ring flip.

Experimental Section

General: All b.p.'s and m.p.'s are uncorrected values. − IR: Bruker IFS 88. − NMR: Bruker AC-300, DPX-300, AMX-500 and AMX-600. For ^{1}H NMR, $CDCl_3$ as solvent δ_H = 7.25, [D_6]DMSO as solvent δ_H = 2.50, [D_4]MeOH as solvent δ_H = 4.78; for ^{13}C NMR, $CDCl_3$ as solvent δ_C = 77.0, [D_6]DMSO as solvent δ_C = 39.5, [D_4]MeOH as solvent δ_C = 49.0. − Elemental analysis: CHN Rapid (Heraeus), CHNS-932 Analyzer (Leco). − HRMS: Finnigan MAT 95. − All reactions were performed under an inert atmosphere of argon in oven- or flame-dried glassware. Dry solvents: THF, benzene, and toluene were distilled from sodium benzophenone, CH_2Cl_2 was distilled from calcium hydride. All commercially available reagents were used without purification unless otherwise noted. All reactions were monitored by thin-layer chromatography (TLC) carried out on Merck F-254 silica glass plates visualized with UV light and/or heat-gun treatment with 5% phosphomolybdic acid in ethanol. Column chromatography (CC) was performed with Merck silica gel 60 (70−200 mesh and 230−400 mesh). PE: light petroleum ether, b.p. 40−60°C. MTBE: methyl *tert*-butyl ether.

(1*RS*,2*R,3*R**)-2,3-Dihydroxymethylcyclohex-5-en-1-ol (9). − 1. Diels−Alder Reaction:** A degassed solution of 1-trimethylsiloxybutadiene (**7**, 25.8 mL, 157 mmol), diethyl fumarate (**6**, 51.9 mL, 295 mmol), and hydroquinone (0.6 g, 5.45 mmol) in toluene (120 mL) was heated to 80°C for 15 h. The excess of trimethylsiloxybutadiene was removed in vacuo and the residue purified by CC on silica gel (400 g SiO_2; PE/ethyl acetate 10:1 → 4:1) to give 48.8 g (154 mmol, 98%) of the cyclohexene diester **8** as a colorless oil. R_f = 0.26 (PE/ethyl acetate 10:1). − IR (neat): $\tilde{\nu}$ = 3034 cm^{-1} (C=CH), 2981, 2959 (CH), 1737 (C=O), 1392, 1252, 1158 (CO), 1039, 844. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.01 [s, 9 H, $Si(CH_3)_3$], 1.15−1.22 (m, 6 H, CH_3, ethyl), 1.99 (dd, *J* = 16.6 and 8.7 Hz, 1 H, 4-H), 2.41 (dd, *J* = 13.6 and 3.9 Hz, 1 H, 4-H), 2.78 (dd, *J* = 12.2 and 3.9 Hz, 1 H, 2-H), 3.03 (dt, *J* = 12.2 and 8.7 Hz, 1 H, 3-H), 4.01−4.13 (m, 4 H, CH_2, ethyl), 4.46 (t, *J* = 3.9 Hz, 1 H, 1-H), 5.51−5.73 (m, 2 H, 5,6-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.1 [$Si(CH_3)_3$], 14.0 (CH_3, ethyl), 29.0 (C-4), 36.1 (C-3), 48.3 (C-2), 60.5 (CH_2, ethyl), 64.6 (C-1), 127.7, 127.8 (C-5,6), 171.1 175.6 (C-1′,2′). − **2. $LiAlH_4$ Reduction:** To a suspension of $LiAlH_4$ (10.0 g, 264 mmol) in THF (200 mL) was added dropwise at 0°C a solution of the diester **8** (26.0 g, 82.7 mmol) in THF (150 mL). The reaction mixture was heated to reflux for 3 h and then stirred for 16 h at room temp. After cooling to 0°C H_2O, NaOH (3 M) and again H_2O was added dropwise (15 mL each, **CAUTION!**). After completion of the addition, the reaction mixture was heated to reflux for 1 h and filtered through a pad of Celite. The filter pad was washed thoroughly with THF (3 × 100 mL) and the filtrate was concentrated in vacuo. The residue was distilled to afford 12.8 g of the triol **9** (81.0 mmol, 98%) as a colorless oil. B.p. 150°C/1 Torr; R_f = 0.31 (SiO_2, $CHCl_3$/MeOH, 8:1) − IR (neat): $\tilde{\nu}$ = 3337 cm^{-1} (OH), 3026 (C=CH), 2896 (CH), 1656 (C=C), 1434, 1174, 1063, 1035 (CO), 838. − ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 1.20−2.27 (m, 4 H, 2,3,4-H), 3.27−4.40 (m, 5 H, 1,1′,2′-H), 5.27−5.44 (m, 2 H, 5,6-H). − ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 28.0 (C-4), 33.2 (C-3), 42.9 (C-2), 60.4, 62.9, 63.7 (C-1,1′,2′), 128.2, 129.5 (C-5,6); additional signals of the minor epimer 28.1, 38.6, 45.4, 58.7, 62.9, 66,1, 126,3, 132.0. − $C_8H_{14}O_3$ (158.20): calcd. C 60.74, H 8.92; found C 60.99, H. 8.75.

(1*RS*,2*R,3*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)cyclohex-5-en-1-ol (10):** To a solution of the triol **9** (3.00 g, 19.0 mmol) and imidazole (3.20 g, 47.0 mmol) in CH_2Cl_2 (50 mL) was added dropwise at 0°C a solution of TBDPSCl (10.0 mL, 39.0 mmol) in CH_2Cl_2 (40 mL). The reaction mixture was stirred for 12 h at room temp., then saturated NH_4Cl solution (20 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), the combined organic layers were washed with saturated NaCl solution (100 mL), dried with $MgSO_4$ and concentrated in vacuo. The resi-

due was chromatographed on silica (100 g, PE/ethyl acetate, 10:1) to give 10.9 g of the allylic alcohol **10** (17.2 mmol, 90%) as a colorless oil. R_f = 0.38 (SiO_2, PE/ethyl acetate 10:1). − IR (neat): $\tilde{\nu}$ = 3438 cm^{-1} (OH), 3039 (C=CH), 2930 (CH), 1112 (CO). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.99 [s, 9 H, TBDPS, $(CH_3)_3$], 1.07 [s, 9 H, TBDPS, $(CH_3)_3$], 1.93−2.01 (m, 4 H, 2,3,4-H), 2.57 (br. s, 1 H, OH), 3.44−3.58 (m, 2 H) and 3.89−4.18 (m, 2 H) [1′,2′-H], 4.53 (br. s, 1 H, 1-H), 4.86 (br. s, 2 H, 5,6-H), 7.32−7.67 (m, 20 H, TBDPS, phenyl). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 [TBDPS, $C(CH_3)_3$], 27.0 [TBDPS, $C(CH_3)_3$], 28.9 (C-4), 33.7, 42.6 (C-2,3), 64.1 (C-2′), 65.4 (C-1′), 71.1 (C-1), 127.7, 127.8, 128.9, 129.6, 133.4, 133.7, 134.9, 135.6 (aromatic C and C=C). − $C_{40}H_{50}O_3Si_2$ (635.00): calcd. C 75.65, H 7.93; found C 75.46, H 8.06.

(2*R,3*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)cyclohex-5-en-1-one (11):** A mixture of the allylic alcohol **10** (7.34 g, 11.5 mmol) and MnO_2 (7.50 g, 86.5 mmol) in CH_2Cl_2 (150 mL) was heated to reflux for 2 h. After cooling to room temp., another 7.50 g of MnO_2 was added and the mixture was heated to reflux for 2 h. The reaction mixture was allowed to cool to room temp. and filtered through a pad of Celite. The filter pad was washed with CH_2Cl_2 (3 × 50 mL). After concentration in vacuo the residue was purified by CC on silica gel (100 g, PE/ethyl acetate, 10:1) to afford 7.21 g of the enone **11** (11.4 mmol, 99%) as a colorless oil, which crystallized upon storage at 0°C. − M.p. 74°C; R_f = 0.40 (SiO_2, PE/ethyl acetate 10:1). − IR (KBr): $\tilde{\nu}$ = 3099 cm^{-1} (C=CH), 2930 (CH), 1679 (C=O), 1427, 1116 (CO), 823, 703 (C=C). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.95 [s, 9 H, TBDPS, $(CH_3)_3$], 0.99 [s, 9 H, TBDPS, $(CH_3)_3$], 2.43 (m, 3 H, 3,4-H), 2.55 (m, 1 H, 2-H), 3.59 (m, 3 H, 1′,2′-H), 4.16 (dd, *J* = 10.1 and 4.1 Hz, 1 H, 1′-H), 6.00 (d, *J* = 10.2 Hz, 1 H, 6-H), 6.82 (dt, *J* = 4.3 and 10.3 Hz, 1 H, 5-H), 7.11−7.56 (m, 20 H, TBDPS, phenyl). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.7 [TBDPS, $C(CH_3)_3$], 27.3 [TBDPS, $C(CH_3)_3$], 28.1 (C-4), 37.8 (C-3), 50.1 (C-2), 60.4 (C-1′), 65.2 (C-2′), 125.7, 127.6, 129.5, 135.4, 135.6 (aromatic C and C-6), 148.6 (C-5), 199.4 (C-1). − $C_{40}H_{48}O_3Si_2$ (632.99): calcd. C 75.90, H 7.74; found C 75.84, H 7.64. − Crystal data of **11**: 0.45 × 0.40 × 0.16 mm, triclinic, $P\bar{1}$, *a* = 905.5 (2), *b* = 1342.4 (2), *c* = 1569.9 (3) pm, α = 75.51(2), β = 78.26(2), γ = 85.15(2)°, *V* = 1808 (1) 10^{-30} m^3, ρ_{ber} = 1.163 Mg/m^3, $2\Theta_{max}$ = 50.50°, Mo-K_α, 71.073 pm, φ-oscillation, 200 K, reflections: measured 12090, independent 6154, LP correction, no absorption correction, μ = 0.134 mm^{-1}, structure solution by direct methods [SHELXS-97 (Sheldrick, 1997)], structure refinement by full-matrix least squares with 6154 F^2 data [SHELXL-97 (Sheldrick, 1997)], 599 free parameters, all H atoms found in difference Fourier maps and refined freely in least-squares cycles, R_1 = 0.0458 [4141 reflections with $I > 2\sigma(I)$], wR_2 = 0.1041 (all reflections), residual electron density: −0.260 to 0.359 10^{30} e m^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103116. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

(2*R,3*R**,4a*R**,8a*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-1,2,3,4,4a,5,8,8a-octahydro-naphthalen-1-one (12):** $AlCl_3$ (752 mg, 5.65 mmol) and Me_3Al (50 μL 2 M in toluene, 0.10 mmol) were dissolved in toluene (20 mL) in a Schlenk tube. At 0°C a solution of the enone **11** (13.9 g, 21.9 mmol) in toluene (20 mL) was added and the reaction mixture was stirred for 0.5 h. The mixture was cooled to −60°C and 1,3-butadiene (15 mL, 172 mmol) was added. Then the vessel was sealed and the reaction mixture allowed to reach room temp.. After stirring for 32 h, the reaction mixture was poured into saturated $NaHCO_3$ solution (200 mL). A saturated NH_4Cl solution (200 mL) was added and the mixture filtered through a pad of Celite. The filter pad was washed thoroughly with diethyl ether (150 mL) and then the aqueous layer was extracted with diethyl ether (3 × 75 mL). The combined organic layers were washed with a saturated NaCl solution (100 mL), dried with $MgSO_4$ and concentrated in vacuo. CC of the residue on silica gel (200 g, PE/ethyl acetate, 10:1) gave 12.8 g of the cycloadduct **12** (17.5 mmol, 80%) as a colorless oil. − R_f = 0.63 (SiO_2, PE/ethyl acetate 10:1). − IR (neat): $\tilde{\nu}$ = 3070 cm^{-1} (C=CH), 2957 (CH), 1714 (C=O), 1427, 1112 (CO), 823, 701. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.92 [s, 9 H, TBDPS, $(CH_3)_3$], 1.01 [s, 9 H, TBDPS, $(CH_3)_3$], 1.74−2.09 (m, 4 H, 4,5,8-H), 2.20 (m_c, 1 H, 4-H), 2.32−2.45 (m, 3 H, 2,3,4a-H), 2.60−2.72 (m, 2 H, 8,8a-H), 3.45 (m_c, 1 H, 1′-H), 3.66 (m_c, 2 H, 2′-H), 4.09 (d, *J* = 9.9 Hz, 1 H, 1′-H), 5.61 (m_c, 2 H, 6,7-H), 7.18−7.39 (m, 12 H), 7.49−7.61 (m, 6 H), 7.64 (dd, *J* = 7.5 and 1.8 Hz, 2 H) [TBDPS, phenyl]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 [TBDPS, $C(CH_3)_3$], 19.4 [TBDPS, $C(CH_3)_3$], 24.1, 26.6 (C-5,8), 26.8 [TBDPS, $C(CH_3)_3$], 27.0 [TBDPS, $C(CH_3)_3$], 32.9 (C-4), 34.4 (C-4a), 37.8 (C-3), 47.6 (C-8a), 51.9 (C-2), 58.9 (C-1′), 65.2 (C-2′), 124.9, 125.0, 127.5, 127.6, 133.5, 133.6, 133.9, 135.5, 135.8, 135.9 (aromatic C and C-6,7), 209.5 (C-1). − $C_{44}H_{54}O_3Si_2$ (687.08): calcd. C 76.92, H 7.92; found C 76.57, H 7.87.

(1*R,2*R**,3*R**,4a*R**,8a*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-1,2,3,4,4a,5,8,8a-octahydronaphthalen-1-ol (13):** To a solution of ketone **12** (12.0 g, 17.5 mmol) in a 1:1 mixture of CH_2Cl_2 and methanol (100 mL) was added portionwise $NaBH_4$ (669 mg, 17.7 mmol) at 0°C. The mixture was stirred at 0°C for 3 h, quenched with saturated NH_4Cl solution (50 mL) and then concentrated in vacuo. The residue was partitioned between CH_2Cl_2 (50 mL) and a saturated NH_4Cl solution (100 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL) and the combined extracts were washed with saturated NaCl solution (100 mL), dried with $MgSO_4$ and concentrated in vacuo. CC of the residue on silica gel (100 g, PE/ethyl acetate, 10:1) afforded 12.0 g of alcohol **13** (17.4 mmol, 99%) as a colorless oil. − R_f = 0.44 (SiO_2, PE/ethyl acetate 10:1). − IR (neat): $\tilde{\nu}$ = 3586 cm^{-1} (OH), 3071, 3049 (C=CH), 1471, 1427, 1114 (CO), 821, 703. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.02 [s, 9 H, TBDPS, $(CH_3)_3$], 1.08 [s, 9 H, TBDPS, $(CH_3)_3$], 1.49−2.56 (m, 11 H, 2,3,4,4a,5,8,8a-H, OH), 3.50 (dd, *J* = 10.2 and 5.1 Hz, 1 H, 2′-H), 3.58 (dd, *J* = 10.2 and 3.4 Hz, 1 H, 2′-H), 3.81 (dd, *J* = 10.1 and 7.5 Hz, 1 H, 1′-H), 3.93 (dd, *J* = 10.1 and 4.5 Hz, 1 H, 1′-H), 4.29 (br. s, 1 H, 1-H), 5.81 (m_c, 2 H, 6,7-H), 7.22−7.42 (m, 12 H), 7.54−7.68 (m, 8 H) [TBDPS, phenyl]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 [TBDPS, $C(CH_3)_3$], 19.4 [TBDPS, $C(CH_3)_3$], 27.0 [TBDPS, $C(CH_3)_3$], 29.3, 29.7, 30.4, 31.1, 35.0, 37.3 (C-3,4,4a,5,8,8a), 46.3 (C-2), 64.3 (C-1′), 66.4 (C-2′), 74.9 (C-1), 125.4, 125.9, 127.6, 127.7, 128.3, 128.4, 129.0, 129.5, 129.6, 129.7, 133.5, 133.7, 133.9, 135.6, 135.6, 135.7 (aromatic C and C-6,7). − $C_{44}H_{56}O_3Si_2$ (689.10): calcd. C 76.69, H 8.19; found C 76.50, H 8.34.

(1*R,2*R**,3*R**,4a*R**,8a*R**)-1-Benzoyloxy-2,3-bis(*tert*-butyldiphenylsiloxymethyl)-1,2,3,4,4a,5,8,8a-octahydronaphthalene (14):** To a solution of alcohol **13** (30.4 g, 44.2 mmol) in THF (100 mL) was added dropwise at 0°C a 1.90 M solution of *n*BuLi in hexane (23.2 mL, 44.2 mmol). The mixture was stirred at 0°C for 0.5 h, then benzoyl chloride (6.20 mL, 53.0 mmol) was added in one portion. The reaction mixture was stirred for an additional 4 h at the same temperature and quenched with saturated $NaHCO_3$ solution (200 mL). The aqueous layer was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (50 mL), saturated NaCl solution (50 mL), dried

with $MgSO_4$ and concentrated in vacuo. The residue was subjected to CC on silica gel (300 g, PE/ethyl acetate, 10:1) to give 35.1 g of benzoate **14** (44.1 mmol, 99%) as a colorless solid which was recrystallized from MTBE. − M.p. 101°C; R_f = 0.48 (SiO_2, PE/ethyl acetate 10:1). − IR (KBr): $\tilde{\nu}$ = 2926 cm^{-1} (CH), 1720 (C=O), 1427, 1278, 1112 (CO), 1084, 1068, 998, 820, 705. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.05 [s, 9 H, TBDPS, $(CH_3)_3$], 1.07 [s, 9 H, TBDPS, $(CH_3)_3$], 1.74−1.82 (m, 2 H, 4-H), 1.95−2.00 (m, 2 H, 3,5-H), 2.02−2.20 (m, 3 H, 2,4a,8a-H), 2.34−2.42 (m, 2 H, 5,8-H), 2.58 (m_c, 1 H, 8-H), 3.44−3.58 (m, 3 H, 1′,2′-H), 3.87 (dd, *J* = 10.0 and 4.3 Hz, 1 H, 1′-H), 5.48 (m_c, 2 H, 6,7-H), 6.09 (br. s, 1 H, 1-H), 7.05 (t, *J* = 7.6 Hz, 2 H, benzoate), 7.25−7.70 (m, 21 H, TBDPS, phenyl, benzoate), 7.99 (d, *J* = 7.7 Hz, 2 H, benzoate). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.0 [TBDPS, *C*$(CH_3)_3$], 19.2 [TBDPS, *C*$(CH_3)_3$], 26.7 [TBDPS, C(*C*$H_3)_3$], 26.9 [TBDPS, C(*C*$H_3)_3$], 28.7, 29.0 (C-5,8), 30.4 (C-4a), 32.9 (C-3), 34.7 (C-4), 37.0, 45.8 (C-2,8a), 62.3 (C-1′), 66.3 (C-2′), 74.0 (C-1), 125.1, 126.3, 127.3, 127.5, 127.6, 128.1, 128.4, 129.2, 129.4, 129.5, 129.6, 131.4, 131.5, 132.2, 133.3, 135.5, 135.6, 135.7 (aromatic C and C-6,7), 165.9 (C=O). − $C_{51}H_{60}O_4Si_2$ (793.20): calcd. C 77.23, H 7.62; found C 76.92, H 7.89.

(4a*R,6*R**,7*R**,8*S**,8a*R**)-8-Benzoyloxy-6,7-bis(*tert*-butyldiphenylsiloxymethyl)-1,4,4a,5,6,7,8,8a-octahydronaphthalen-1-one (15). − 1. SeO_2 Oxidation:** A solution of benzoate **14** (4.50 g, 5.67 mmol) in a mixture of dioxane/H_2O/pyridine 450:10:1 (300 mL) was heated to reflux. To the boiling reaction mixture was added dropwise a solution of SeO_2 in dioxane/H_2O/pyridine 450:10:1 (150 mL). The reaction mixture was stirred for 6 h at 100°C. After cooling to room temp., H_2O (100 mL) was added and the solvent was removed in vacuo. The residue was partitioned between H_2O (100 mL) and ethyl acetate (100 mL). The aqueous layer was extracted with ethyl acetate (3 × 50 mL), the combined organic layers were washed with saturated NaCl solution (100 mL), dried with $MgSO_4$ and concentrated in vacuo. CC of the residue on silica gel (100 g, PE/ethyl acetate, 2:1) gave 3.76 g of the corresponding allylic alcohol (4.65 mmol, 82%) as a pale yellow oil. Analytical data for *(1S*,2R*,3R*,4aR*,8RS,8aS*)-1-Benzoyloxy-2,3-bis(tert-butyldiphenylsiloxymethyl)-1,2,3,4,4a,5,8,8a-octahydronaphthalen-8-ol*: R_f = 0.60 (SiO_2, PE/ethyl acetate, 2:1). − IR (neat): $\tilde{\nu}$ = 3446 cm^{-1} (OH), 2957, 2929, 1720 (C=O), 1472, 1427, 1274, 1112 (CO), 1083, 702. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.01 [s, 9 H, TBDPS, $(CH_3)_3$], 1.04 [s, 9 H, TBDPS, $(CH_3)_3$], 1.69−2.40 (m, 9 H, 2,3,4,4a,5,8a-H, OH), 3.41 (t, *J* = 10.0 Hz, 1 H), 3.49 (m_c, 2 H), 3.87 (dd, *J* = 10.1 and 5.2 Hz, 1 H) [1′,2′-H], 4.62 (br. s, 1 H, 8-H), 5.70 (m_c, 2 H, 6,7-H), 6.12 (br. s, 1 H, 1-H), 6.98 (t, *J* = 7.2 Hz, 2 H, benzoate), 7.20−7.66 (m, 21 H, TBDPS, phenyl and benzoate), 7.78 (d, *J* = 7.2 Hz, 2 H, benzoate). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 [TBDPS, *C*$(CH_3)_3$], 19.4 [TBDPS, *C*$(CH_3)_3$], 26.0 (C-5), 26.9 [TBDPS, C(*C*$H_3)_3$], 27.0 [TBDPS, C(*C*$H_3)_3$], 29.4 (C-4), 33.3, 34.2 (C-3,4a), 45.5, 46.0 (C-2,8a), 62.2, 66.3 (C-1′,2′), 66.9, 71.8 (C-1,8), 127.2, 127.5, 129.5, 129.6, 129.7, 132.6, 133.7, 135.6, 135.7, 135.8 (aromatic C and C-6,7), 165.9 (C=O). − **2. MnO_2 Oxidation:** A mixture of the allylic alcohol (5.20 g, 6.42 mmol) and MnO_2 (5.20 g, 60.0 mmol) in CH_2Cl_2 (250 mL) was heated to reflux for 2 h. After cooling to room temp. another 5.20 g of MnO_2 was added and the mixture was again heated to reflux for 2 h. Then the reaction mixture was allowed to cool to room temp. and filtered through a pad of Celite. The filter pad was washed with CH_2Cl_2 (3 × 50 mL). After concentration in vacuo the residue was purified by CC on silica gel (80 g, PE/ethyl acetate, 4:1) to afford 5.08 g of the enone **15** (6.29 mmol, 98%) as a colorless solid. Mp. 64°C (CH_2Cl_2). − R_f = 0.31 (SiO_2, PE/ethyl acetate 4:1). − IR (KBr): $\tilde{\nu}$ = 3071 cm^{-1} (C=CH), 2953 (CH), 1727 (C=O), 1677 (C=O), 1427, 1272, 1112 (CO), 1078, 703. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 [s, 9 H, TBDPS, $(CH_3)_3$], 1.02 [s, 9 H, TBDPS, $(CH_3)_3$], 1.76−1.80 (m, 2 H, 5-H), 1.83−2.04 (m, 1 H, 6-H), 2.04−2.12 (m, 1 H, 7-H), 2.12−2.24 (dt, *J* = 18.1 and 4.6 Hz, 1 H, 4-H), 2.59−2.80 (m, 3 H, 4,4a,8a-H), 3.42−3.62 (m, 3 H, 1′,2′-H), 3.90 (dd, *J* = 10.2 and 4.9 Hz, 1 H, 2′-H), 5.98 (d, *J* = 10.2 Hz, 1 H, 2-H), 6.20 (br. s, 1 H, 8-H), 6.75 (m, 1 H, 3-H), 7.00 (t, *J* = 6.5 Hz, 2 H, benzoate), 7.18−7.66 (m, 21 H, TBDPS, phenyl and benzoate), 7.63 (d, *J* = 7.1 Hz, 2 H, benzoate). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9 [TBDPS, *C*$(CH_3)_3$], 19.2 [TBDPS, *C*$(CH_3)_3$], 26.6 [TBDPS, C(*C*$H_3)_3$], 26.9 [TBDPS, C(*C*$H_3)_3$], 30.1 (C-5), 32.1, 32.8, 33.0 (C-4,6,7), 44.5 (C-4a), 51.2 (C-8a), 62.1, 65.8 (C-1′,2′), 70.8 (C-8), 127.3, 127.6, 128.4, 129.6, 130.2, 132.7, 133.0, 133.4, 135.5, 135.6 (aromatic C and C-2), 150.0 (C-3), 164.8 (C=O), 199.6 (C=O). − $C_{51}H_{58}O_5Si_2$ (807.17): calcd. C 75.89, H 7.24; found C 75.81, H 7.02.

(1S*,2R*,3R*,4aR*,8aS*,9aR*,10aS*)-1-Benzoyloxy-2,3-bis(*tert*-butyldiphenylsiloxymethyl)-1,2,3,4,4a,5,8,8a,9,9a,10,10a-dodecahydroanthracen-9-one (16): To a solution of the enone **15** (4.70 g, 5.82 mmol) in toluene (50 mL) at −78°C $AlBr_3$ (4.19 g, 15.7 mmol) dissolved in toluene (100 mL) was added and stirring was continued for an additional 15 min. An excess of 1,3-butadiene (5.25 mL, 3.15 g, 58.2 mmol) was added at this temperature. Then the vessel was sealed and the reaction mixture was allowed to warm to −40°C when the color of the mixture turned from yellow to red brown. After 10 min of stirring, the reaction mixture was quenched by adding Rochelle salt (150 mL; 1 M solution in H_2O). The aqueous layer was extracted with MTBE (3 × 150 mL); the combined organic layers were washed with saturated $NaHCO_3$ solution (100 mL), saturated NaCl solution (100 mL), dried with $MgSO_4$ and concentrated in vacuo. CC (150 g silica, PE/ethyl acetate 10:1) of the residue gave 4.32 g of **16** (86%) as a colorless oil. R_f = 0.23 (SiO_2, hexane/ethyl acetate 10:1). − IR (neat): $\tilde{\nu}$ = 3071 cm^{-1} (C=CH), 2957 (CH), 1727 (C=O), 1629 (C=C), 1428, 1390, 1362, 1270 (CO), 1112 (CO), 1070, 824, 703. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.92 [s, 9 H, TBDPS, $(CH_3)_3$], 0.95 [s, 9 H, TBDPS, $(CH_3)_3$], 1.47 (d, *J* = 13.2 Hz, 1 H, 10α-H), 1.64 (d, *J* = 13.8 Hz, 1 H, 4-H), 1.68−1.75 (m, 2 H, 4,8α-H), 1.83 (d, *J* = 16.8 Hz, 1 H, 5β-H), 1.84−2.02 (m, 3 H, 2,3,5α-H), 2.29 (td, *J* = 13,2 and 4.2 Hz, 1 H, 10β-H), 2.32 (br. s, 1 H, 10a-H), 2.43 (t, *J* = 6.0 Hz, 1 H, 8a-H), 2.53 (br. s, 1 H, 4a-H), 2.63 (d, *J* = 18 Hz, 1 H, 8β-H), 2.72 (br. s, 1 H, 9a-H), 3.38−3.47 (m, 3 H, 1′,2′-H), 3.78 (dd, *J* = 10.2 and 5.3 Hz, 1 H, 1′-H), 5.57 (br. s, 2 H, 6,7-H), 5.92 (t, *J* = 2.6 Hz, 1 H, 1-H), 6.99 (t, *J* = 7.7 Hz, 2 H, Bz-H), 7.23−7.54 (m, 21 H, phenyl, TBDPS, Bz, H), 7.55 (d, *J* = 7.2 Hz, 2 H, Bz, H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9 [TBDPS, *C*$(CH_3)_3$], 19.2 [TBDPS, *C*$(CH_3)_3$], 23.1 (C-8), 26.3 (C-5), 26.6 [TBDPS, $(CH_3)_3$], 26.9 [TBDPS, $(CH_3)_3$], 31.3 (C-4a), 32.6 (C-3), 33.4, 33.5 (C-4,10), 34.0 (C-10a), 45.4 (C-2), 47.5 (C-8a), 54.6 (C-9a), 62.2 (C-1′), 65.9 (C-2′), 69.8 (C-1), 124.8, 125.0 (C-6,7), 127.4, 127.6, 128.7, 129.3, 129.5, 129.6, 129.7, 133.1, 133.4, 133.5, 133.6, 135.5, 135.6, 135.7 (C aromatic). − $C_{55}H_{64}O_5Si_2$ (861.28): calcd. C 76.70, H 7.49; found C 76.53, H 7.41.

(1S*,2R*,3R*,4aR*,8aS*,9R*,9aS*,10aS*)-1-Benzoyloxy-2,3-bis(*tert*-butyldiphenylsiloxymethyl)-1,2,3,4,4a,5,8,8a,9,9a,10,10a-dodecahydroanthracen-9-ol (17): To a solution of the ketone **16** (2.07 g, 2.40 mmol) in a 1:1 mixture of CH_2Cl_2 and methanol (50 mL) was added portionwise $NaBH_4$ (118 mg, 3.12 mmol) at 0°C. The mixture was stirred at 0°C for 3 h, quenched with a saturated NH_4Cl solution (20 mL) and concentrated in vacuo. The residue was partitioned between 50 mL of CH_2Cl_2 and 50 mL of a saturated NH_4Cl solution. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL) and the combined extracts were washed with

a saturated NaCl solution (100 mL), dried with $MgSO_4$ and concentrated in vacuo. CC of the residue on silica gel (30 g, PE/ethyl acetate, 10:1) afforded 2.03 g of the alcohol **17** (2.35 mmol, 98%) as a colorless solid. − M.p. 211°C ($CHCl_3$/MeOH). R_f = 0.48 (SiO_2, PE/ethyl acetate, 10:1). − IR (KBr): $\tilde{\nu}$ = 3477 cm^{-1} (OH), 2925, 2856 (CH), 1699 (C=O), 1427, 1238, 1112 , 1071 (CO), 702. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 [s, 18 H, TBDPS, $(CH_3)_3$], 1.20 (m_c, 1 H, 4-H), 1.52−1.90 (m, 5 H, 5,8,8a-H, OH), 2.10−2.36 (m, 3 H, 4a,9a,10a-H), 2.58 (m_c, 1 H, 5-H), 3.46 (m_c, 2 H, 2′-H), 3.74 (dt, *J* = 12.2 and 6.0 Hz, 1 H, 9-H), 3.89 (m_c, 2 H, 1′-H), 5.42 (m_c, 2 H, 6,7-H), 6.16 (br. s, 1 H, 1-H), 6.89 (t, *J* = 7.6 Hz, 2 H, benzoate), 7.26−7.43 (m, 12 H), 7.51 (m_c, 6 H), 7.59 (d, *J* = 6.9 Hz, 2 H) [TBDPS, phenyl, benzoate], 7.62 (t, *J* = 7.7 Hz, 1 H), 8.00 (d, *J* = 7.3 Hz, 2 H, benzoate). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.2 [TBDPS, *C*$(CH_3)_3$], 19.9 [TBDPS, *C*$(CH_3)_3$], 25.1, 25.5 (C-5,8), 26.6 [TBDPS, C(*C*$H_3)_3$], 26.8 [TBDPS, C(*C*$H_3)_3$], 29.2, 31.6, 33.2 (C-3,4a,10a), 33.6, 34.9 (C-4,10), 36.1 (C-8a), 45.2 (C-9a), 46.0 (C-2), 62.3 (C-1′), 66.0 (C-2′), 69.5 (C-9), 70.4 (C-1), 124.7, 125.0 (C-6,7), 127.3, 127.5, 127.6, 128.7, 129.2, 129.5, 129.5, 129.6, 129.9, 130.4, 133.1, 133.3, 133.4, 133.6, 135.4, 135.5, 135.6 (aromatic C), 168.3 (C=O). − $C_{55}H_{66}O_5Si_2$ (863.29): calcd. C 76.52, H 7.71; found C 76.17, H 7.87. − Crystal data of **17**: 0.30 × 0.20 × 0.10 mm, monoclinic, $P2_1/n$, *Z* = 4, *a* = 1019.7 (2), *b* = 3571.3(4), *c* = 1351.0(3) pm, β = 98.48(1)°, *V* = 4866.1(15)·10^{-30} m^3, ρ_{ber} = 1.178 Mg/m^3, 2 Θ_{max} = 119.8°, Cu-K_α, (154.178 pm), ω/2 θ scans, 293(2) K. 7657 measured reflections, 7203 independent (R_{int} = 0.105), LP correction, no absorption correction, μ = 1.023 mm^{-1}, solution with direct methods [SHELXS-96 (Sheldrick, 1996)], refinement with F^2 values [SHELXL-96 (Sheldrick, 1996)], 568 parameters, H-atoms calculated and not refined, *wR* = *0*.2677 (F^2, all data), conventional *R* value: 0.0875 [4571 reflections with $I > 2\sigma(I)$], residual electron density: −0.399 to 0.422 e 10^{30} m^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102230. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223−336−033; e-mail: deposit@ccdc.cam.ac.uk].

(1*S,2*R**,3*R**,4a*R**,8a*S**,9*R**,9a*S**,10a*S**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-1,2,3,4,4a,5,8,8a,9,9a,10,10a-dodecahydroanthracene-1,9-diol (18):** To a solution of the benzoate **17** (2.80 g, 3.24 mmol) in THF (150 mL) was added at 0°C *n*BuMgCl (15 mL of a 2 M solution in THF, 30 mmol). The reaction mixture was stirred at 0°C for 4 h. Saturated NH_4Cl solution (100 mL) was added dropwise. The aqueous layer was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (100 mL), saturated NaCl solution (100 mL), dried with $MgSO_4$ and concentrated in vacuo. CC of the residue on silica (100 g, PE/ethyl acetate 8:1) gave the diol **18** (2.34 g, 2.94 mmol, 91%) as a white solid. − R_f = 0.17 (SiO_2, hexane/ethyl acetate 10:1). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 [s, 9 H, TBDPS, $(CH_3)_3$], 0.96 [s, 9 H, TBDPS, $(CH_3)_3$], 1.38−1.83 (m, 7 H, 2,5-H, 4,8-H_2, OH), 1.92−2.20 (m, 6 H, 3,4a,9a,10a-H, 10-H_2), 2.40 (m, 1 H, 5-H), 2.58 (m, 1 H, 8a-H), 3.16 (br. s, 1 H, OH), 3.40−3.52 (m, 2 H, 2′-H), 3.63−3.72 (m, 1 H, 9-H), 3.76 (dd, *J* = 10.6 and 5.1 Hz, 1 H, 1′-H), 3.89 (dd, *J* = 10.6 and 2.9 Hz, 1 H, 1′-H), 4.59 (br. s, 1 H, 1-H), 5.60 (m, 2 H, 6,7-H), 7.17−7.39 (m, 12 H) and 7.42−7.68 (m, 8 H) [TBDPS, phenyl]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 [TBDPS, *C*$(CH_3)_3$], 19.3 [TBDPS, *C*$(CH_3)_3$], 25.7, 25.9, (C-5,8), 26.9 [TBDPS, $(CH_3)_3$], 27.0 [TBDPS, $(CH_3)_3$], 29.1, 30.2, 31.7, (C-4a,10,10a), 33.8 (C-3), 35.2 (C-4), 36.6, (C-8a), 44.6(C-2), 45.2 (C-9a), 65.5 (C-1′), 65.9 (C-2′), 70.4, 70.4 (C-1,9), 124.7, 125.9, 127.5, 127.8, 129.5, 129.8, 129.9, 132.7, 132.8, 133.8, 133.9, 135.5 (C aromatic, 6,7). − $C_{48}H_{62}O_4Si_2$ (759.19): calcd. C 75.94, H 8.23; found C 75.70, H 8.48.

(1*S,2*R**,3*R**,4a*R**,6*S**,7*R**,8a*S**,9*R**,9a*S**,10a*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-6,7-epoxyperhydroanthracene-1,9-diol (19) and (1*S**,2*R**,3*R**,4a*R**,6*R**,7*S**,8a*S**,9*R**,9a*S**,10a*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-6,7-epoxyperhydroanthracene-1,9-diol (20):** To a solution of alkene **18** (1.00 g, 1.32 mmol) in CH_2Cl_2 (30 mL) was added at 0°C a solution of *meta*-chloroperbenzoic acid (756 mg, 2.63 mmol) in CH_2Cl_2 (20 mL). After stirring for 2 h at 0°C the reaction mixture was quenched with a saturated Na_2SO_3 solution (20 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (30 mL), with saturated NaCl solution (30 mL) and dried with $MgSO_4$. After concentration in vacuo the residue was subjected to CC on silica gel (50 g, hexane/isopropanol, 10:1) to afford 870 mg of a 2.3:1 (HPLC, hexane/isopropanol, 7:1) mixture of epoxides **19** and **20** (1.12 mmol, 85%) as a colorless oil. Both epoxides were separated by further CC on silica gel. − α-Epoxide **19**: R_f = 0.24 (SiO_2, hexane/isopropanol, 7:1). −^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 [s, 9 H, TBDPS, $(CH_3)_3$], 0.94 [s, 9 H, TBDPS, $(CH_3)_3$], 1.34−2.10 (m, 12 H, 2,3,4,4a,5,8α,9a,10,10a-H), 2.25 (ddd, *J* = 11.3, 7.5 and 3.8 Hz, 1 H, 8a-H), 2.41 (dd, *J* = 16.2 and 4.9 Hz, 1 H, 8β-H), 3.03 (dd, *J* = 4.5 and 4.5 Hz, 1 H, 7-H), 3.15 (s, 1 H, OH), 3.18 (d, *J* = 3.8 Hz, 1 H, 6-H), 3.41 (dd, *J* = 10.2 and 4.5 Hz, 1 H, 1′′-H), 3.46 (dd, *J* = 10.2 and 3.4 Hz, 1 H, 1′′-H), 3.57 (ddd, *J* = 11.3, 9.4 and 6.4 Hz, 1 H, 9-H), 3.74 (dd, *J* = 10.4 and 5.3 Hz, 1 H, 1′-H), 3.87 (dd, *J* = 10.4 and 2.8 Hz, 1 H, 1′-H), 4.51 (br. s, 1 H, 1-H), 7.13−7.33 (m, 12 H, aromatic H), 7.39−7.53 (m, 8 H, aromatic H). −^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1 [TBDPS, *C*$(CH_3)_3$], 19.3 [TBDPS, *C*$(CH_3)_3$], 23.9 (C-8), 24.9 (C-5), 26.9 [TBDPS, $(CH_3)_3$], 26.9 [TBDPS, $(CH_3)_3$], 27.7, 29.3, 29.9 (C-3,4a,10a), 33.3 (C-10), 34.8 (C-8a), 35.2 (C-4), 44.2 (C-2), 45.1 (C-9a), 50.0 (C-7), 53.5 (C-6), 65.5, 65.7 (C-1′,1′′), 70.5 (C-1), 70.9 (C-9), 127.5, 127.8, 129.5, 129.8, 129.9, 132.4, 132.6, 133.8, 135.5, 135.5, 135.6 (C aromatic). − β-Epoxide **20**: R_f = 0.35 (SiO_2, hexane/isopropanol, 7:1). −^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 [s, 9 H, TBDPS, $(CH_3)_3$], 0.94 [s, 9 H, TBDPS, $(CH_3)_3$], 1.33−2.22 (m, 11 H, 2,3,4,5,8α,9a,10a-H), 2.37 (ddd, *J* = 11.5, 5.7 and 5.7 Hz, 1 H, 8a-H), 2.57 (d, *J* = 15.8 Hz, 1 H, 8β-H), 3.07−3.12 (m, 2 H, 7-H, OH), 3.15 (dd, *J* = 4.5 and 4.5 Hz, 1 H, 6-H), 3.39 (dd, *J* = 10.0 and 4.9 Hz, 1 H, 1′′-H), 3.45 (dd, *J* = 10.0 and 2.8 Hz, 1 H, 1′′-H), 3.72 (dd, *J* = 10.5 and 4.9 Hz, 1 H, 1′-H), 3.86 (dd, *J* = 10.5 and 3.0 Hz, 1 H, 1′-H), 3.99 (ddd, *J* = 11.7, 6.4 and 6.4 Hz, 1 H, 9-H), 4.53 (br. s, 1 H, 1-H), 7.13−7.34 (m, 12 H, aromatic), 7.38−7.52 (m, 8 H, aromatic). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1 [TBDPS, *C*$(CH_3)_3$], 19.3 [TBDPS, *C*$(CH_3)_3$], 23.7 (C-8), 24.9 (C-5), 26.9 [TBDPS, $(CH_3)_3$], 26.9 [TBDPS, $(CH_3)_3$], 29.0, 30.1, 30.4 (C-3,4a,10a), 33.2 (C-10), 35.3 (C-4), 35.8 (C-8a), 44.5 (C-2), 45.0 (C-9a), 52.1 (C-6), 52.6 (C-7), 65.5 (C-1′), 65.8 (C-1′′), 70.5 (C-1), 71.4 (C-9), 127.5, 127.7, 129.4, 129.4, 129.8, 129.9, 132.6, 132.7, 133.7, 133.8, 135.5, 135.6 (C aromatic). − $C_{48}H_{62}O_5Si_2$ (775.19): calcd. C 74.37, H 8.06; found C 74.11, H 7.88.

(1*S,2*R**,3*R**,4a*R**,6*S**,7*R**,8a*S**,9*R**,9a*R**,10a*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-6,7-epoxy-9-(*O*-phenylthiocarbonyloxy)perhydroanthracen-1-ol (21):** To a solution of the diol **19** (1.30 g, 1.68 mmol) in CH_2Cl_2 (100 mL) was added at 0°C pyridine (1.36 mL, 1.30 g, 16.8 mmol) and *O*-phenylchlorothionoformate (1.16 mL, 1.45 g, 8.39 mmol). After 4 h of stirring at 0°C, the reaction was quenched by adding a saturated NH_4Cl solution (40 mL). The aqueous layer was extracted with CH_2Cl_2 (4 × 50 mL), and the combined organic layers were washed with 0.1 M HCl, saturated

$NaHCO_3$ aqueous solution and saturated NaCl aqueous solution (50 mL each), and dried with $MgSO_4$. The solvent was removed in vacuo. CC (25 g SiO_2, PE/ethyl acetate 6:1) gave 1.15 g (1.26 mmol, 75%) of the thiocarbonate **21** as colorless, viscous oil. R_f = 0.43 (SiO_2, hexane/ethyl acetate 4:1). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 [s, 9 H, TBDPS, $(CH_3)_3$], 1.12 [s, 9 H, TBDPS, $(CH_3)_3$], 1.13 (m, 1 H, 10α-H), 1.55−1.63 (m, 2 H, 4β,2-H), 1.65−1.93 (m, 2 H, 4α,5β-H), 1.95−2.23 (m, 4 H, 3,5α,8-H), 2.26−2.34 (m, 4 H, 4a,9a,10a,10β-H), 2.52 (d, *J* = 2.6 Hz, 1 H, OH), 2.92 (m, 1 H, 8a-H), 3.09 (dd, *J* = 4.3 and 4.3 Hz, 1 H, 7-H), 3.31 (d, *J* = 3.8 Hz, 6-H), 3.47 (m, 2 H, 2′-H), 3.73 (dd, *J* = 10.2 and 6.8 Hz, 1 H, 1′-H), 3.97 (dd, *J* = 10.0 and 3.6 Hz, 1 H, 1′-H), 4.49 (br. s, 1 H, 1-H), 5.49 (dd, *J* = 12.1 and 5.7 Hz, 1 H, 9 H), 7.12 (d, *J* = 8.5 Hz, 2 H, aromatic), 7.30−7.65 (m, 23 H, aromatic). −^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 [TBDPS, *C*$(CH_3)_3$], 19.3 [TBDPS, *C*$(CH_3)_3$], 24.3 (C-8), 24.8 (C-5), 26.9 [TBDPS, $(CH_3)_3$], 27.0 [TBDPS, $(CH_3)_3$], 27.9, 29.2, 30.3 (C-3,4a,10a), 31.0 (C-8a), 32.8 (C-10), 34.8 (C-4), 41.3 (C-9a), 44.8 (C-2), 49.5 (C-7), 53.3 (C-6), 64.3 (C-1′), 65.7 (C-2′), 68.8 (C-1), 85.5 (C-9), 120.9, 121.8, 122.0, 126.2, 126.5, 126.8, 127.5, 127.8, 127.8, 129.5, 129.5, 129.6, 129.8, 129.9, 133.0, 133.6, 135.5, 135.6 (aromatic), 153.4 (C-OPh), 195.6 (C=S). − $C_{55}H_{66}O_6Si_2S$ (911.36): calcd. C 72.48, H 7.30; found C 72.28, H 7.17.

(1*R,2*R**,3*R**,4a*R**,6*S**,7*R**,8a*S**,9a*R**,10a*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-6,7-epoxyperhydroanthracen-1-ol (22):** The thiocarbonate **21** (170 mg, 187 μmol) was dissolved in toluene (8 mL). Oxygen was removed under reduced pressure at −78°C. The solution was heated to 90°C when *n*Bu_3SnH (0.22 mL, 0.82 mmol) and AIBN were added. The reaction mixture was stirred at 90°C for 30 min. The solvent was evaporated in vacuo. The resulting crude product was purified by CC on silica (15 g, PE/ethyl acetate 4:1) to yield 141 mg (186 μmol, 99%) of the monoalcohol **22** as a colorless oil. R_f = 0.43 (SiO_2, hexane/ethyl acetate 4:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 [s, 9 H, TBDPS, $(CH_3)_3$], 1.05 [s, 9 H, TBDPS, $(CH_3)_3$], 1.48−1.73 (m, 8 H), 1.83 (m, 1 H) 1.90−2.11 (m, 6 H) [2,3,4a,5,5a,8a,10a-H, 4,8,9,10-H_2], 2.36 (m, 1 H, 5-H), 3.01 (br. s, 1 H, OH), 3.10 (m, 1 H), 3.23 (m, 1 H) [6,7-H], 3.53 (m, 2 H, 2′-H), 3.80 (m, 1 H, 1′-H), 3.94 (dd, *J* = 10.2 and 3.6 Hz, 1 H, 1′-H), 4.20 (m, 1 H, 1-H), 7.27−7.63 (m, 20 H, phenyl). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.1 [TBDPS, *C*$(CH_3)_3$], 19.3 [TBDPS, *C*$(CH_3)_3$], 23.4, 24.6 (C-5,8), 26.8 [TBDPS, $(CH_3)_3$], 26.9 [TBDPS, $(CH_3)_3$], 28.4 (C-9), 28.5 (C-10), 29.2 (C-4a), 31.0 (C-10a), 32.3 (C-8a) 34.0, 34.4, 39.0, 44.3 (C-2,3,4,9a), 50.7 (C-7), 53.4 (C-6), 65.6 (C-1′), 65.8 (C-2′), 76.2 (C-1), 115.7, 121.1, 127.9, 128.1, 128.2, 129.8, 129.9, 129.9, 130.1, 130.2, 133.3, 134.2, 134.2, 134.3, 135.9, 136.0 (phenyl).

(1*R,2*R**,3*R**,4a*R**,6S*,7*R**,8a*S**,9a*R**,10a*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-6,7-epoxy-1-(*O*-phenylthiocarbonyloxy)-perhydroanthracene (23):** The monoalcohol **22** (629 mg, 0.83 mmol) was dissolved in THF (25 mL) and *n*BuLi (0.34 mL, 0.84 mmol, 2.45 M in hexane) was added dropwise at −78°C. The reaction mixture turned to yellow and was stirred for 20 min. at the same temperature. *O*-phenylchlorothionoformate (0.15 mL, 1.08 mmol) was added. The cooling bath was removed, the reaction mixture was stirred for 3 h at 0°C and then quenched by adding 30 mL of a saturated $NaHCO_3$ aqueous solution and 30 mL of ethyl acetate. The aqueous layer was extracted with ethyl acetate (4 × 30 mL), the combined organic layers were washed with saturated NaCl aqueous solution (50 mL) and dried with $MgSO_4$. After removal of the solvent in vacuo the remaining crude product was purified by CC on silica (20 g, PE/ethyl acetate, 4:1) to yield 565 mg (0.63 mmol, 76%) of the thiocarbonate **23** as a colorless oil. − R_f = 0.22 (SiO_2, CH_2Cl_2/hexane 2:1). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95 [s, 9 H, TBDPS, $(CH_3)_3$], 1.01 [s, 9 H, TBDPS, $(CH_3)_3$], 1.40−2.08 (m, 16 H, 2,3,4a,8a,9a,10a-H, 4,5,8,9,10-H_2), 3.07 (t, *J* = 3.9 Hz, 1 H) and 3.09 (m, 1 H) [6,7-H], 3.38 (dd, *J* = 10.2 and 5.8 Hz, 1 H), 3.43−3.62 (m, 2 H), and 3.79 (dd, *J* = 10.2 and 6.0 Hz, 1 H) [1′,2′-H_2], 6.03 (br. s, 1 H, 1-H), 6.80 (d, *J* = 9.3 Hz, 2 H, OPh-H), 7.20−7.42 (m, 15 H), 7.51−7.68 (m, 8 H) [aromatic]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1 [TBDPS, *C*$(CH_3)_3$], 19.2 [TBDPS, *C*$(CH_3)_3$], 25.4, 26.6 (C-5,8), 26.8 [TBDPS, $(CH_3)_3$], 26.9 [TBDPS, $(CH_3)_3$], 26.7, 28.0, 28.2, 28.6, 29.9, 33.3, 34.0, 37.4 (C-3,4,4a,5a,8a,9,10,10a), 46.0, (C-2), 50.7, 52.5 (C-6,7), 62.3 (C-1′), 66.4 (C-2′), 85.5 (C-1), 121.9, 126.3, 129.4, 129.6, 153.2 (aromatic), 194.0 (C=S). −$C_{55}H_{66}O_5SSi_2$ (895.36): calcd. C 73.78, H 7.42; found C 73.96, H 7.43.

(2*R,3*R**,4a*R**,6*S**,7*R**,8a*S**,9a*S**,10a*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-6,7-epoxyperhydroanthracene (24):** The thiocarbonate **23** (280 mg, 312 μmol) was dissolved in toluene (25 mL). Oxygen was removed under reduced pressure at −78°C. The solution was heated to 90°C when *n*Bu_3SnH (0.60 mL, 2.23 mmol) and AIBN were added. The reaction mixture was stirred at 90°C for 30 min. The solvent was evaporated in vacuo. The resulting crude product was purified by CC (10 g SiO_2, PE/ethyl acetate 10:1) to yield 225 mg (303 μmol, 97%) of the alkane **24** as a colorless oil. − R_f = 0.43 (SiO_2, hexane/ethyl acetate 10:1). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 [s, 9 H, TBDPS, $(CH_3)_3$], 1.02 [s, 9 H, TBDPS, $(CH_3)_3$], 1.42−1.81 (m, 14 H) and 1.90−2.20 (m, 4 H) [2,3,4a,8a,9a,10a-H, 1,4,5,8,9,10-H_2], 3.08 (t, *J* = 4.3 Hz, 1 H) and 3.25 (m, 1 H) [6,7-H], 3.35 (m, 2 H) and 3.54 (m, 2 H) [1′,2′-H], 7.28−7.43 (m, 12 H) and 7.56−7.64 (m, 8 H) [phenyl]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.4 [TBDPS, *C*$(CH_3)_3$], 24.0, 25.7 (C-5,8), 26.9 [TBDPS, $(CH_3)_3$], 27.0 [TBDPS, $(CH_3)_3$], 27.8, 28.9, 29.5, 30.2, 30.7, 34.1, 35.2, 35.5, 39.9, 41.8 (C-1,2,3,4,4a,8a,9,9a,10,10a), 50.0, 53.6 (C-6,7), 66.4, 66.5 (C-1′,2′), 127.6, 129.5, 134.1, 135.6, 135.7 (phenyl). − $C_{48}H_{62}O_3Si_2$ (743.19): calcd. C 77.57, H 8.41; found C 77.26, H 8.67.

(2*R,3*R**,4a*R**,6*R**,7*R**,8a*S**,9a*S**,10a*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)perhydroanthracene-6,7-diol (5):** The epoxide **24** (325 mg, 0.437 mmol) was dissolved in acetone (75 mL). $HClO_4$ (0.3 mL of a 0.3 M aqueous solution) was added. The reaction mixture was stirred at 0°C for 3 h. Solid Na_2CO_3 (100 mg) was added. The solvent was removed in vacuo and the residue was purified by CC (7 g, SiO_2, PE/ethyl acetate 1:1) to yield 293 mg (0.385 mmol, 88%) of the diol **5** as colorless oil. R_f = 0.23 (SiO_2, hexane/ethyl acetate 1:1). − ^{1}H NMR (500 MHz, CD_3CN): δ = 0.94 [s, 9 H, TBDPS, $(CH_3)_3$], 0.97 [s, 9 H, TBDPS, $(CH_3)_3$], 1.12−2.04 (m, 19 H) and 2.16 (m, 1 H) [2,3,4a,8a,9a,10a-H, 1,4,5,8,9,10-H_2, 2-OH], 2.70 (d, *J* = 11.4 and 3.5 Hz, 1 H), 3.50 (m, 2 H), 3.62 (m, 1 H), 3.66 (dd, *J* = 10.1 and 4.4 Hz, 2 H) [6,7-H, 1′,2′-H_2], 7.39 (m, 7 H), 7.36−7.40 (m, 5 H), 7.60−7.66 (m, 8 H) [TBDPS, phenyl]. − ^{13}C NMR (125 MHz, CD_3CN): δ = 19.9 [TBDPS, *C*$(CH_3)_3$], 27.3 [TBDPS, $(CH_3)_3$], 29.9, 30.1, 30.5, 31.1, 32.6, 33.5, 34.8, 36.8 (C-1,2,3,4,5,8,8a,9,9a,10,10a), 67.4, 67.8, 71.6, (C-1′,2′,6,7), 128.7, 130.6, 134.9, 136.3, 136.4, 136.5 (C aromatic). − $C_{48}H_{64}O_4Si_2$ (761.20): calcd. C 75.74, H 8.47; found C 75.45, H 8.66.

(2*R,3*R**,4a*R**,6*R**,7*R**,8a*S**,9a*S**,10a*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-6,7-dipicolyloxyperhydroanthracene (25):** A solution of 60 mg (79 μmol) of **5** in CH_2Cl_2 (2 mL) was cooled to 0°C. DMAP (144 mg, 1.18 mmol), EDC (154 mg, 0.79 mmol) and picolinic acid (97 mg, 0.79 mmol) were added. The temperature was allowed to rise to 25°C. The color of the reaction mixture turned from yellow to violet. After additional 1.5 h the reaction was quenched with saturated NaCl aqueous solution (10 mL). CH_2Cl_2 (10 mL) was added. The aqueous layer was extracted with

CH_2Cl_2 (4 × 10 mL) and ethyl acetate (2 × 10 mL). Evaporation of the solvent in vacuo and purification of the residue by CC (12 g SiO_2, PE/ethyl acetate 1:1) yielded 70 mg (72 μmol, 91%) of the diester **25** as a colorless oil. R_f = 0.18 (SiO_2, hexane/ethyl acetate, 1:1). − ^{1}H NMR (600 MHz, 60°C, [D$_8$]toluene): δ = 1.04 (ddd, *J* = 12.9, 2.9 and 2.7 Hz, 1 H, 4β-H), 1.12 [s, 9 H, TBDPS, $(CH_3)_3$], 1.14 [s, 9 H, TBDPS, $(CH_3)_3$], 1.21 (ddd, *J* = 13.7, 2.9 and 2.8 Hz, 1 H, 9β-H), 1.34 (ddd, *J* = 12.2, 3.1 and 3.1 Hz, 1 H, 1α-H), 1.48−1.73 (m, 7 H, 10,2,1β,5β,3,9a-H), 1.80 (ddd, *J* = 13.0 Hz, 13.0 and 4.6 Hz, 1 H, 4α-H), 1.84−1.91 (m, 3 H, 4a,8a,8α-H), 2.29 (ddd, *J* = 14.8, 5.1 and 4.3 Hz, 1 H, 8β-H), 2.34 (bd, *J* = 12.1 Hz, 1 H, 10a-H), 2.47 (ddd, *J* = 13.9, 13.2 Hz and 2.2 Hz, 1 H, 5α-H), 2.55 (bdd, *J* = 12.0 and 10.8 Hz, 1 H, 9α-H), 5.52 (ddd, *J* = 2.9, 2.9 and 2.9 Hz, 1 H, 7-H), 5.64 (ddd, *J* = 3.0, 3.0 and 3.0 Hz, 1 H, 6-H) 6.72−6.75 (m, 2 H, pic-5-H), 7.09−7.13 (m, 2 H, pic-4-H), 7.20−7.23 (m, 12 H, phenyl, TBDPS), 7.70−7.72 (m, 8 H, phenyl, TBDPS), 7.91 (d, *J* = 7.7 Hz, 1 H, pic-3-H), 7.94 (d, *J* = 7.8 Hz, 1 H, pic-3-H), 8.43 (m, 2 H, pic-6-H). − ^{13}C NMR (75 MHz, 70°C, [D$_6$]DMSO): δ = 18.4 [TBDPS, *C*$(CH_3)_3$], 26.1 (C-5), 26.3, 26.4 [TBDPS, $(CH_3)_3$], 27.6, 28.4 (C-8a,4a), 28.1 (C-1), 28.7 (C-10a), 30.1 (C-8), 30.3 (C-4), 32.3 (C-9), 33.4 (C-10), 34.4 (C-9a), 34.9 (C-3), 40.7 (C-2), 66.0, 66.1 (C-1′,2′), 69.8 (C-7), 70.7 (C-6), 124.4, 124.5, 126.8, 127.2, 129.2, 133.1, 133.1, 134.6, 134.6, 134.7, 136.9, 137.0, 147.4, 147.4, 149.5, 149.5, 163.2 (C aromatic). − HRMS (M^+ + Na): calcd. 993.4670; found 993.4688.

(2*R,3*R**,4a*R**,6*R**,7*R**,8a*S**,9a*S**,10a*R**)-2,3-Dihydroxymethyl-6,7-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)perhydroanthracene (27):** To a solution of diol **5** (95 mg, 125 μmol) in methanol (3 mL) was added 2,2′,3,3′-tetramethoxybutane (27 mg, 150 μmol), trimethylorthoformate (53 mg, 500 μmol) and camphorsulfonic acid (2 mg, 9 μmol). The mixture was stirred at 50°C for 20 h. After cooling to room temp. the reaction was quenched with powdered $NaHCO_3$ (20 mg) and the solvent was removed in vacuo. CC of the residue on silica (5 g, PE/ethyl acetate, 1:1) afforded 30 mg of bisacetal **27** (76 μmol, 60%) as a white solid which was recrystallized from methanol. − M.p. 176°C. − R_f = 0.09 (SiO_2, PE/ethyl acetate 1:1). − ^{1}H NMR (600 MHz, [D$_4$]MeOH, 50°C): δ = 1.21−1.25 (m, 3 H, 1α,9β,10β-H), 1.23 (CH_3), 1.24 (CH_3), 1.30−1.34 (m, 1 H, 4α-H), 1.39−1.41 (m, 1 H, 8β-H), 1.53−1.55 (m, 2 H, 5α,5β-H), 1.59−1.63 (m, 1 H, 4β-H), 1.69−1.76 (m, 2 H, 1β,8α-H), 1.80−2.00 (m, 8 H, 2,3,4a,8a,9a,9α,10a,10α-H), 3.20 (s, 3 H, OCH_3), 3.21 (s, 3 H, OCH_3), 3.44−3.47 (m, 2 H, CH_2O, 7-H), 3.56−3.86 (m, 4 H, CH_2O, 6-H). − ^{13}C NMR (75 MHz, [D$_4$]MeOH, 50°C): δ = 18.45, 18.45, 25.58, 30.64, 31.04, 31.42, 31.54, 31.55, 33.44, 35.64, 35.76, 36.40, 38.76, 39.34, 48.31, 48.31, 65.83, 68.08, 69.20, 73.77, 101.15, 101.28. − HRMS ($C_{22}H_{38}O_6$ + Na^+) calcd. 421.2566; found 421.2604. − Crystal data of **27**: 0.60 × 0.25 × 0.07 mm, triclinic, $P\bar{1}$, *a* = 1089.2 (3), *b* = 1445.7 (4), *c* = 2901.5 (8) pm, α = 100.29 (3), β = 96.06 (3), γ = 90.11 (3)°, *V* = 4469 (2) 10^{-30} m^3, ρ_{ber} = 1.211 Mg/m^3, $2\Theta_{max}$ = 48.66°, Mo-K_α, 71.073 pm, φ rotation, 180 K, reflections: measured 23294, independent 13398, LP-correction, no absorption correction, μ = 0.087 mm^{-1}, structure solution by direct methods [SHELXS-97 (Sheldrick, 1997)], structure refinement by full-matrix least squares with 13398 F^2-data [SHELXL-97 (Sheldrick, 1997)], 1063 free parameters, H atoms geometrically generated and simultaneously refined with the corresponding C atoms (riding model), R_1 = 0.0593 [6001 reflections with $I > 2\sigma(I)$], wR_2 = 0.1293 (all reflections), residual electron density: −0.233 to 0.299·10^{30} e·m^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102288. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

(2*R,3*R**,4a*R**,6*R**,7*R**,8a*S**,9a*S**,10a*R**)-2,3-Diacetoxymethyl-6,7-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)perhydroanthracene (28):** To a solution of diol **27** (23 mg, 58 μmol) in CH_2Cl_2 (3 mL) was added at 0°C triethylamine (58 mg, 576 μmol). The mixture was stirred at 0°C for 10 min and then 23 mg (288 μmol) of acetyl chloride was added. After 1 h at 0°C the reaction was quenched with saturated NH_4Cl solution (3 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL), washed with a saturated NaCl solution (5 mL) and dried with Na_2SO_4. After concentration in vacuo the residue was purified by CC on silica (5 g, PE/ethyl acetate, 4:1) to give 25 mg of bisacetate **28** (52 μmol, 90%) as a colorless oil. − R_f = 0.23 (SiO_2, PE/ethyl acetate 4:1). − ^{1}H NMR (600 MHz, $CDCl_3$, 50°C): δ = 1.15 (ddd, *J* = 13.2 Hz, *J* = 2.8 Hz, *J* = 2.8 Hz, 1 H, 1α-H); 1.17−1.23 (m, 2 H, 9β,10β-H); 1.26 (s, 3 H, CH_3); 1.27 (s, 3 H, CH_3); 1.31 (ddd, *J* = 13.3 Hz, *J* = 3.5 Hz, *J* = 3.5 Hz, 1 H, 4α-H); 1.43 (ddd, *J* = 12.3 Hz, *J* = 4.2 Hz, *J* = 4.2 Hz, 1 H, 8β-H); 1.55−1.60 (m, 2 H, 5α,5β-H); 1.64 (ddd, *J* = 12.9 Hz, *J* = 12.9 Hz, *J* = 5.0 Hz, 1 H, 4β-H); 1.71 (ddd, *J* = 12.2 Hz, *J* = 12.3 Hz, *J* = 12.3 Hz, 1 H, 8α-H); 1.77−1.89 (m, 7 H, 1β,2,4a,8a,9a,9α,10α-H); 1.90−1.98 (m, 2 H, 3,10a-H); 2.03 (s, 6 H, 2 × CH_3, acetate); 3.22 (s, 3 H, OCH_3 α); 3.23 (s, 3 H, OCH_3 β); 3.50 (ddd, *J* = 11.6 Hz, *J* = 9.8 Hz, *J* = 4.6 Hz, 1 H, 7-H); 3.68 (ddd, *J* = 10.7 Hz, *J* = 9.9 Hz, *J* = 6.0 Hz, 1 H, 6-H); 3.93 (dd, *J* = 10.8 Hz, *J* = 5.9 Hz, 1 H, CH_2O); 4.04−4.11 (m, 2 H, CH_2O); 4.15 (dd, *J* = 10.9 Hz, *J* = 7.8 Hz, 1 H, CH_2O). − ^{13}C NMR (75 MHz, $CDCl_3$, 50°C): δ = 17.9 (2 × CH_3); 20.8 (2 × CH_3 acetate); 24.4 (C-1); 28.4 (C-9a); 28.8 (C-4a); 29.7 (C-3); 29.8 (C-8); 31.9 (C-10); 34.1 (C-4); 34.2 (C-5); 34.3 (C-10a); 34.5 (C-2); 34.5 (C-9); 34.6 (C-8a); 47.7 (2 × OCH_3); 66.3 (*C*H_2-C3); 67.5 (C-6); 68.2 (*C*H_2-C2); 71.9 (C-7); 99.4 (acetal); 99.5 (acetal); 171.0 (C=O); 171.1 (C=O). − HRMS ($C_{26}H_{42}O_8$) calcd. for M − 1: 481.2801; found 481.2806.

Acknowledgments

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[1] R. W. Hoffmann, M. Stahl, U. Schopfer, G. Frenking, *Chem. Eur. J.* **1998**, *4*, 559−566. The term biconformational refers to molecules with two low-energy conformers. If these conformers are populated to > 80%, the compound is called biconformational. In the case of the unsubstituted perhydroanthracene the two conformers have the same energy and are equally populated. In the case of the tetrasubstituted perhydroanthracene with different substituents A, B, the two conformers do not necessarily have the same energy and are differently populated. As long as the substituted perhydroanthracene systems display two distinct chair-chair-chair low-energy conformations, we consider it as reasonable to call them biconformational. One has to keep in mind that it is often the environment (e.g. solvent, membrane) that has a major influence on conformational preferences.

[2] E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds* Wiley, New York, **1994**, p. 686 ff.

[3] P. Vanhee, B. van de Graaf, D. Tavernier, J. M.A. Baas, *J. Org. Chem.* **1983**, *48*, 648−652; P. Vanhee, B. van de Graaf, J. M. A. Baas, D. Tavernier, *Tetrahedron Lett.* **1982**, *23*, 3837−3838; D. Tavernier, M. J. O. Anteunis, *Org. Magn. Res.* **1982**, *18*, 109−111.

[4] The cycloadduct is produced in the racemic form. The synthesis of the tetrasubstituted perhydroanthracene is described for the racemic series here. For the use of chiral fumarates as an potential approach to enantiomerically enriched cyclohexenones see: J. Jurczak, T. Bauer, C. Chapuis in *Methods Org. Chem. − E 21 Stereoselective Synthesis*, (Eds. G. Helmchen, R. W. Hoffmann, J. Mulzer, E. Schaumann), vol. 5, p. 2735, Thieme, Stuttgart, **1996**.
[5] F. Frinquelli, L. Minuti, F. Pizzo, A. Taticchi, *Acta Chem. Scand.* **1993**, *47*, 255−263.
[6] D. H. R. Barton, S. W. McCombie, *J. Chem. Soc., Perkin Trans. 1,* **1975**, 1574−1585.
[7] A. Fürst, P. A. Plattner, *Helv. Chim. Acta* **1949**, *32*, 275−283.
[8] A quantitative analysis on the different populations of the *all*-chair conformers is not yet possible with the existing data.
[9] S. V. Ley, H. W. M. Priepke, S. L. Warriner, *Angew. Chem.* **1994**, *106*, 2410−2412; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2290−2292; J.-L. Montchamp, F. Tian, M. E. Hart, J. W. Frost, *J. Org. Chem.* **1996**, *61*, 3897−3899.

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