Asymmetric Synthesis of Complicated Bicyclic and Tricyclic Polypropanoates *via* the Double *Diels-Alder* Addition of 2,2′-Ethylidenebis[3,5-dimethylfuran]

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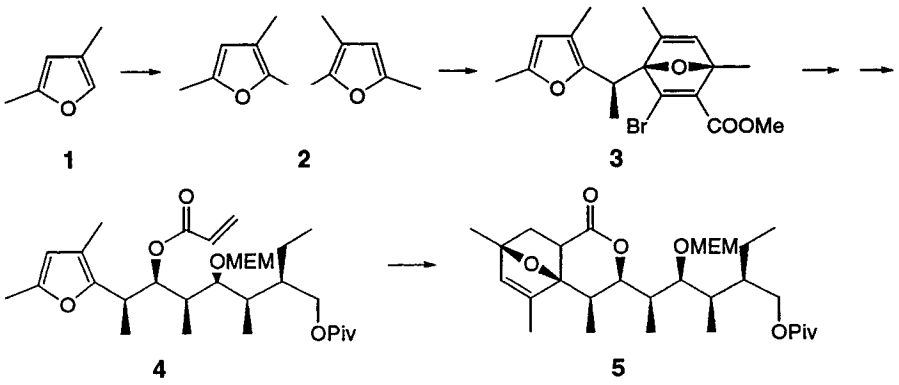
A new, non-iterative method for the asymmetric synthesis of long-chain and polycyclic polypropanoate fragments starting from 2,2′-ethylidenebis[3,5-dimethylfuran] (**2**) has been developed. Diethyl (2*E*,5*E*)-4-oxohepta-2,5-dienoate (**6**) added to **2** to give a single *meso*-adduct **7** containing nine stereogenic centers. Its desymmetrization was realized by hydroboration with (+)-IpcBH$_2$ (isopinocampheylborane), leading to diethyl (1*S*,2*R*,3*S*,4*S*,4a*S*,7*R*,8*R*,8a*R*,9a*S*,10*R*,10a*R*)-1,3,4,7,8,8a,9,9a-octahydro-3-hydroxy-2,4,5,7,10-pentamethyl-9-oxo-2*H*,10*H*-2,4a:7,10a-diepoxyanthracene-1,8-dicarboxylate ((+)-**8**; 78% e.e.). Alternatively, **7** was converted to *meso*-(1*R*,2*R*,4*R*,4a*R*,5*S*,7*S*,8*S*,8a*R*,9a*S*,10*s*,10a*S*)-1,8-bis(acetoxymethyl)-1,8,8a,9a-tetrahydro-2,4,5,7,10-pentamethyl-2*H*-10*H*-2,4a:7,10a-diepoxyanthracene-3,6,9(4*H*,5*H*,7*H*)-trione (**32**) that was reduced enantioselectively by BH_3 catalyzed by methyloxazaborolidine **19** derived from L-diphenylprolinol giving (1*S*,2*S*,4*S*,4a*S*,5*S*,6*R*,7*R*,8*R*,8a*S*,9a*R*,10*R*,10a*S*)-1,8-bis(acetoxymethyl)-1,8,8a,9a-tetrahydro-6-hydroxy-2,4,5,7,10-pentamethyl-2*H*,10*H*-2,4a:7,10a-diepoxyanthracene-3,9(4*H*,7*H*)-dione ((−)-**33**; 90% e.e.). Chemistry was explored to carry out chemoselective 7-oxabicyclo[2.2.1]heptanone oxa-ring openings and intra-ring C−C bond cleavage. Polycyclic polypropanoates such as (1*R*,2*S*,3*R*,4*R*,4a*R*,5*S*,6*R*,7*S*,8*R*,9*R*,10*R*,11*S*,12a*R*)-1-(ethoxycarbonyl)-1,3,4,7,8,9,10,11,12,12a-decahydro-3,11-dihydroxy-2,4,5,7,9-pentamethyl-12-oxo-2*H*,5*H*-2,4a:6,9:6,11-triepoxybenzocyclodecene-10,8-carbolactone (**51**), (1*S*,2*R*,3*R*,4*R*,4a*S*,5*S*,7*S*,8*R*,9*R*,10*R*,12*S*,12a*S*)-1,10-bis(acetoxymethyl)tetradecahydro-8-(methoxymethoxy)-2,4,5,7,9-pentamethyl-3,9-bis{[2-(trimethylsilyl)ethoxy]methoxy}-6,11-epoxycyclodecene-4a,6,11,12-tetrol ((+)-**83**), and (1*R*,2*R*,3*R*,4a*R*,4b*R*,5*S*,6*R*, 7*R*,8*R*,8a*S*,9*S*,10a*R*)-3,5-bis(acetoxymethyl)-4a,8a-dihydroxy-1-(methoxymethoxy)-2,6,8,9,10a-pentamethyl-2,7-bis{[2-(trimethylsilyl)-ethoxy]methoxy}dodecahydrophenanthrene-4,10-dione (**85**) were obtained in few synthetic steps.

Introduction. – The polypropanoates (= polypropionates) represent an important class of natural products associated with a broad spectrum of biological activity and whose structures encompass a large diversity of molecular architecture [1]. Their name stems from their biosynthetic pathway that implies the iterative condensation of propanoate units [2]. Biosynthetic approaches to the generation of polyketide (and polypropanoate) diversity by combinatorial reconstruction of existing natural pathways are currently well under way [3]. On their side, synthetic chemists have developed several ingenious methodologies to provide access to these systems, which possess a large number of stereogenic centers (see ref. 4–16 in [4] and ref. 3–24 in [5]). Among the lastest proposals, impressive successes have been realized by iterative, one-directional, boron-mediated [6][7], tin-mediated [8], or titanium-mediated [8][9] aldol chain elongation, and by crotylborane [10], crotylsilane [11], allenylstannane [12], and allenylzinc [13] additions to aldehydes. Very attractive strategies involve the simultaneous two-direction chain elongation followed by kinetic or chiral desymmetrization [14]. Others rely on bicyclic precursors that allow predictable diastereoselectivity for the installation of the various functions [15]. On our side, we have shown

that 2,4-dimethylfuran (**1**) adds to 1-cyanovinyl camphanates, giving diastereoisomerically pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl esters ('naked sugars of the second generation' [16]) that can be converted to enantiomerically pure propanoates containing up to eleven contiguous stereogenic centers and tertiary alcohols [17–19]. We have found also that 2,4-dimethylfuran (**1**) reacts with acetaldehyde under acidic conditions to give 2,2′-ethylidenebis[3,5-dimethylfuran] (**2**). Cycloaddition of **2** with methyl bromopropynoate gives a monoadduct **3** that has been converted into various racemic polypropanoate fragments such as **4** and **5** (*Scheme 1*) [20].

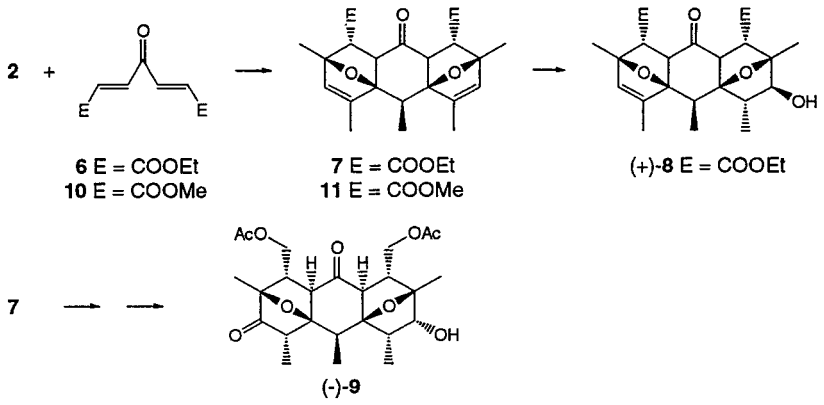
Scheme 1



1 **2** **3** **4** **5**

In a preliminary communication [21], we disclosed that **2** adds to diethyl (2*E*,5*E*)-4-oxohepta-2,5-dienedioate (**6**) to give a single adduct **7** in 95% yield that could be desymmetrized by asymmetric hydroboration leading to hydroxy derivative (+)-**8** with 78% enantiomeric excess (e.e.) (*Scheme 2*). Thus, in two steps, two 'flat' reagents **2** and **6** can be converted to an enantiomerically enriched polycyclic system containing eleven stereogenic centers! In a second preliminary communication [22], we showed that

Scheme 2



6 E = COOEt
10 E = COOMe

7 E = COOEt
11 E = COOMe

(+)-**8** E = COOEt

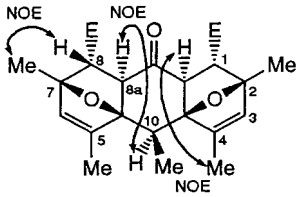
7

(-)-**9**

adduct **7** could be converted to hydroxy derivative (−)-**9** with 90% e.e. We describe here the details of these procedures and present methods for the chemical differentiation of the two 7-oxabicyclo[2.2.1]heptane moieties of these compounds and routes for their ring openings. This leads to tricyclic and bicyclic systems that have in common with long-chain polypropanoates their C-skeletons with alternating Me and OH or =O groups.

Results and Discussion. – *Double* Diels-Alder *Additions.* Various solvents and temperatures were tested for the cycloadditions of 2,2′-ethylidenebis[3,5-dimethylfuran] (**2**) to (2*E*,5*E*)-diethyl (**6**) and dimethyl (2*E*,5*E*)-4-oxohepta-2,5-dienedioate (**10**). The best yield (45%) in adduct **11** was obtained when reacting **2** with 1 equiv. of **10** in $CHCl_3$ at 25°, under atmospheric pressure. This yield could be improved to 55% applying a pressure of 5 kbar at 25°. Better results were obtained with the reaction **2** + **6** → **7**. Under atmospheric pressure, a 1:1 mixture of **2** and **6** in Et_2O left at 25° for 5 days, provided adduct **7** as a crystalline precipitate in 75% yield[1]). This adduct was isolated in 96% yield after pressuring **2**/**6** 1:1 in $CHCl_3$ (20°/5 kbar, 5 h). Attempts to obtain other diastereoisomeric adducts with **2** + **6** and **2** + **10** in the presence of *Lewis*-acid promoters such as $BF_3 \cdot Et_2O$ and $Yb(OTf)_3$ ($Tf = CF_3SO_3$) led to intractable mixtures.

The structures of adducts **7** and **11** were established by their spectral data, in particular by their ^{1}H-NMR spectra and with the help of NOE measurements (*Fig. 1*).



7 E = COOEt
11 E = COOMe

	δ(H) [ppm]	
	7	**11**
H–C(10)	2.88	2.88
H–C(8a)	2.99	2.99
H–C(8)	3.67	3.71
Me–C(5)	1.88	1.89
Me–C(7)	1.71	1.71

Fig. 1. *Selected* ^{1}*H-NMR Data of* **7** *and* **11**

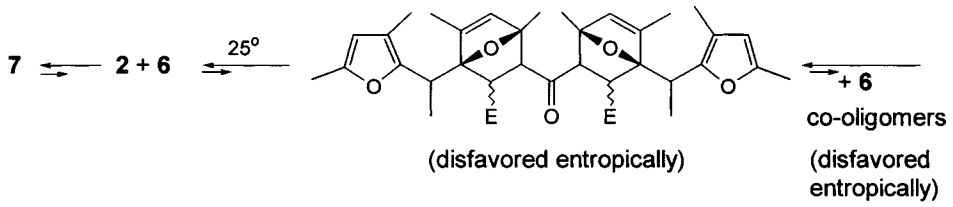
That of **7** was confirmed by single-crystal X-ray radiocrystallography of two derivatives, see below.

We attribute the high diastereoselectivity of the double *Diels-Alder* additions **2** + **6** → **7** and **2** + **10** → **11** to a thermodynamic control, as it is the case for most *Diels-Alder* additions of furan and substituted derivatives to alkenes at room temperature or above [23]. Steric factors make any other diastereoisomeric adducts less stable than **7** and **11**. Because of more negative entropy of condensation, the co-oligomerization (*Scheme 3*)

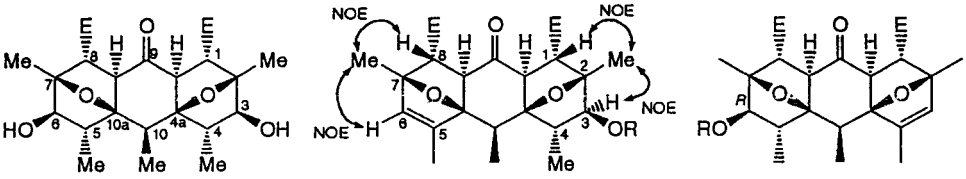
[1]) Experiment run by Miss *Anne Brunelle*, undergraduate student, University of Lausanne, 1997.

of bis-furan **2** with bis-dienophiles **6** and **10** are disfavored relative to the reactions **2** + **6** = **7** and **2** + **10** = **11**.

Scheme 3



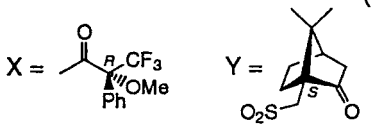
Desymmetrization. Along with the problem of introducing OH groups in **7** (or **11**) by hydroboration, we thought that the keto moiety had to be protected as an acetal. However, all our attempts to generate the dimethyl or ethylidene acetal of **11** [24] failed, or led to cycloreversion of the adduct on heating. We attribute this failure to the high steric hindrance about the oxo group at C(9) as confirmed by the fact that it was not reduced during the double hydroboration of **7** and **11** that provided diols **12** and **13**, respectively, in high yield. The selective '*exo*'-face hydroboration and regioselectivity of these double hydroborations were expected for steric reasons [17][20][23]. The structures of **12** and **13** were given by their spectral data and confirmed by 2D-NOESY ^{1}H-NMR spectra.



12 E = COOEt
13 E = COOMe

(+)-**8** E = COOEt, R = H
14 E = COOEt, R = X
(+)-**17** E = COOEt, R = Y

(-)-**15** E = COOMe, R = H
16 E = COOMe, R = X



Precedents from the literature suggested that dilongifolylborane (Lgf_2BH) is the reagent of choice for asymmetric hydroboration of trisubstituted alkenes [25]. Unfortunately, diene diesters **7** and **11** refused to react with this reagent. Thus, we turned to (−)-$IpcBH_2$ (isopinocampheylborane derived from (+)-α-pinene) and to (+)-$IpcBH_2$ [26]. With 1.1 equiv. of (+)-$IpcBH_2$ in THF and at −25°, **7** was hydroborated and oxidized ($NaBO_3 \cdot 4\ H_2O$) to give hydroxy-ene diester (+)-**8** in 58% yield with 78% e.e. (determined by ^{19}F-NMR of *Mosher*'s ester **14** obtained with (*S*)-α-methoxy-α-(trifluoromethyl)benzeneacetyl chloride [27]). Due to the lower solubility of diene diester **11** compared with **7**, its hydroboration could not be run in THF at −25°. With (−)-$IpcBH_2$, the monohydroboration of **11** (THF, 0°) gave (−)-**15**

in 55% yield and 70 ± 5% e.e. (determined by ^{1}H-NMR in the presence of [Eu(hfc)$_3$] (hfc = 3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato) [28]. When run in THP (tetrahydropyran) at −25°, the hydroboration with IpcBH$_2$ (oxidation with NaBO$_3$ · 4 H$_2$O) afforded (−)-**15** in 53% yield and with 82% e.e. (determined with *Mosher*'s ester **16** [27]). Lowering the reaction temperature to −40° did not improve the enantioselectivity. Enantiomerically pure (−)-**15** (> 98% e.e.) was obtained upon crystallization from CH$_2$Cl$_2$/Et$_2$O. We also tried the asymmetric hydroboration of **7** with Ipc$_2$BH formed *in situ* from (−)-α-pinene [29]. No reaction was observed in THF below 0°. At 20°, a low conversion rate and unsatisfactory enantioselectivity (64% e.e.) were observed.

Applying *Mosher*'s method [30] (^{1}H-NMR of (*R*)-esters **14**)[2]), the absolute configuration shown for (+)-**8** was established (*Fig. 2*). The relative configuration of **14** was confirmed by the measurement of significant NOEs between the pairs of resonance attributed to H−C(1)/Me−C(2)/H−C(3) and H−C(6)/Me−C(7)/H−C(8) (see structures (+)-**8** and **14**). Finally, we prepared the camphorsulfonate (+)-**17** by treatment of (+)-**8** with an excess of (1*S*)-camphorsulfonyl chloride and Et$_3$N (CH$_2$Cl$_2$, *N*,*N*-dimethylpyridin-4-amine (DMAP) as catalyst). Purification by flash chromatography and crystallization provided pure (+)-**17** in 80% yield, the structure of which has been established unambiguously by single-crystal X-ray-diffraction studies [21]. This confirmed the relative and absolute configuration of all the products presented above.

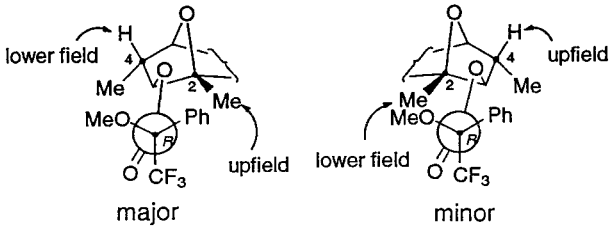


Fig. 2. Mosher's *^{1}H-NMR method for the determination of the absolute configuration of* **14**[2])

With the hope to improve the enantioselectivity and the yield of the desymmetrization of adduct **7**, we explored the possibility to run the enantioselective monoreduction of *meso*-triketone **18** obtained in 97% yield by oxidation of dihydroxy ketone **12** with PCC (pyridinium chlorochromate) in CH$_2$Cl$_2$ (*Scheme 4*). In the presence of 0.2 equiv. of enantiomerically pure CBS catalyst **19** [31], the reduction of **18** with BH$_3$ in THF followed by acidic workup (HCl/MeOH) furnished lactone (−)-**20** with a maximum yield of 52%. Lower yield in (−)-**20** was obtained when applying **19′** as catalyst [31], and bis-lactone **21** was isolated as a secondary product.

The enantiomer excess of (−)-**20** could not be evaluated from its ^{1}H-NMR spectrum in the presence of [Eu(hfc)$_3$] [28], nor by HPLC on chiral stationary phases. Attempts to generate diastereoisomeric aminals by *Alexakis*'s method [32] or sulfoximides by

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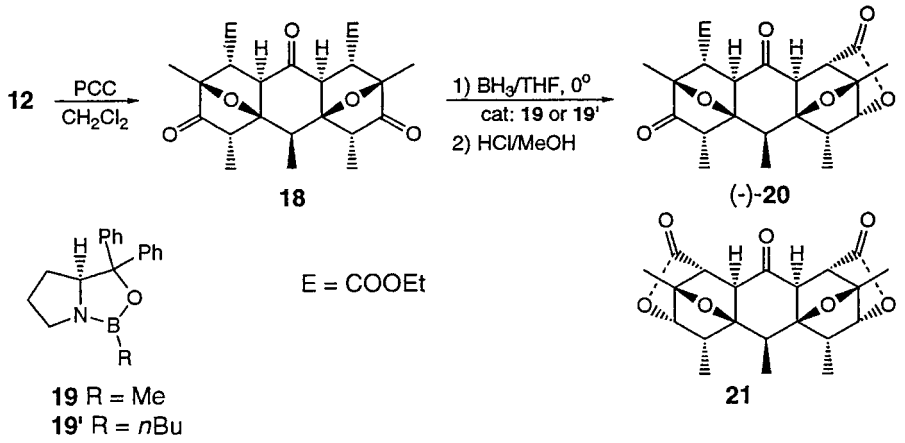
[2]) ^{1}H-NMR Data of (*R*)-esters **14** (anthracene numbering): *qd* of H−C(4) at δ 2.26 (major) and 2.16 (minor); *s* of Me−C(2) at δ 1.48 (major) and 1.60 (minor).

Scheme 4



Johnson's method [33] failed also. Lactone (−)-**20** was correlated with enantiomerically enriched (+)-**8** (78% e.e.) in the following way (*Scheme 5*). Oxidation of (+)-**8** with PCC in the presence of 3-Å molecular sieves (MS) gave (+)-**22** that was reduced ($NaBH_3CN$) and lactonized (MeOH/AcOH) into (−)-**23**. Hydroboration of (−)-**23** followed by oxidative workup with $NaBO_3 \cdot 4\ H_2O$ provided a mixture of (−)-**24** and (−)-**25** that could be separated by flash chromatography (silica gel). Enone (−)-**25** resulted from the base-induced, chemoselective 7-oxabicyclo[2.2.1]heptene oxa-bridge opening of (−)-**24**. Oxidation of (−)-**24** with PCC gave oxo-lactone (−)-**20** with $[\alpha]_D^{20} = -57.5$ ($c = 0.4$, $CHCl_3$; ≥78% e.e.) to be compared with $[\alpha]_D^{20} = -50$ ($c = 1.25$, $CHCl_3$) for (−)-**20** obtained by the asymmetric reduction of triketone **17** (*Scheme 4*). Direct reduction and hydroboration of (+)-**22** with $BH_3 \cdot Me_2S$ in THF, followed by oxidative workup with $NaBO_3 \cdot 4\ H_2O$ led to a mixture of products from which (−)-**25** could be isolated in 31% yield together with diketone **26** (by-product) (*Scheme 5*).

The chemoselective isomerization (−)-**24** → (−)-**25** gives us means to differentiate the chemistry of the two 7-oxabicyclo[2.2.1]heptane moieties of our polycyclic polypropanoates. This isomerization might be controlled thermodynamically, the tricyclic unit (with the '*endo*'-lactone moiety) being more strained than the bicyclic moiety. Treatment of (−)-**25** with pivaloyl chloride (Et_3N, CH_2Cl_2, DMAP) and then with $PhCO_2SO_2CF_3$ [34] provided **27** (31%), the circular dichroism spectrum of which showed the expected exciton-split *Cotton* effects [35] (UV: λ_{max} 238 nm, $\varepsilon = 13000$; $\Delta\varepsilon_{247} = 14.7$, $\Delta\varepsilon_{213} = -5.5$, in MeCN), in accordance with the configuration established by X-ray diffraction studies of derivative (+)-**17**. This double *Cotton* effect arises from the coupling of the main electric-transition ($\pi \rightarrow \pi^*$) moments of the enone and benzoate moieties, the two chromophores adopting a positive helical arrangement (*Fig. 3*).

To circumvent the formation of butyrolactones during the reductions of ketones derived from **7** (see *Schemes 4* and *5*), we reduced the latter with $LiAlH_4$ in THF at 20° (*Scheme 6*). Under these conditions, triol **28** with the (9*r*) configuration was the unique

Scheme 5

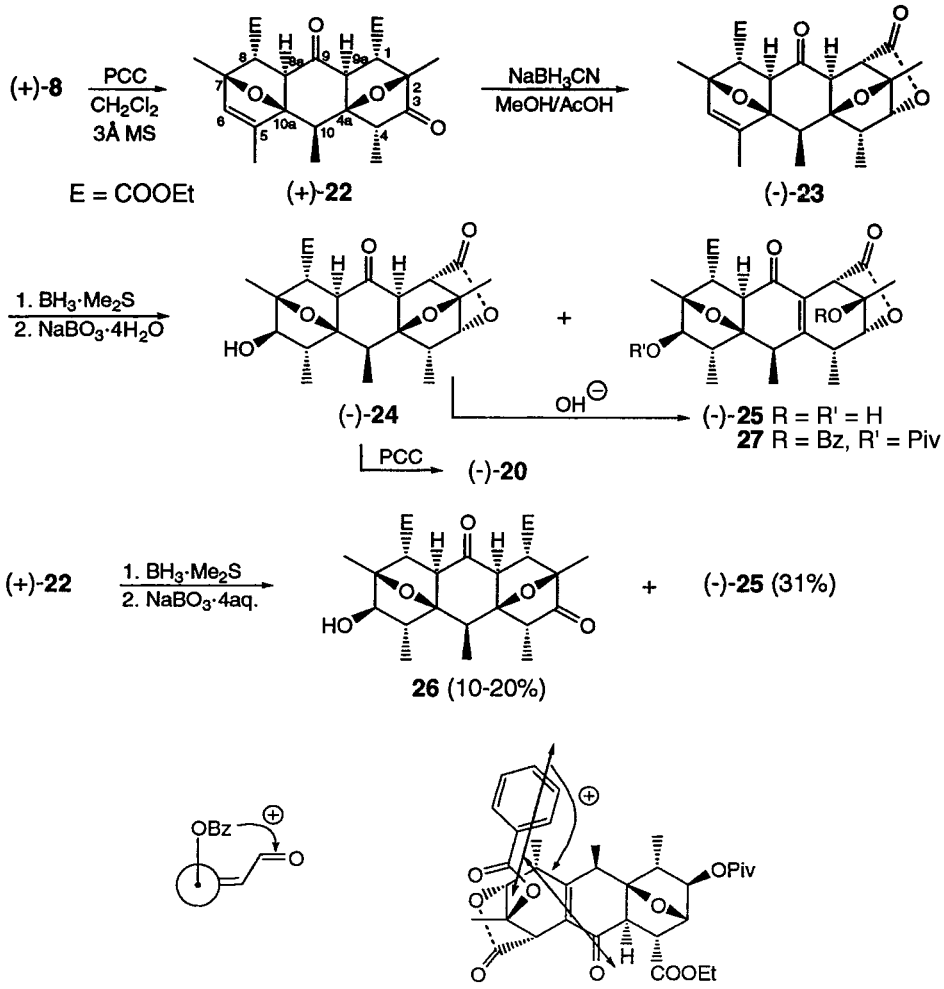
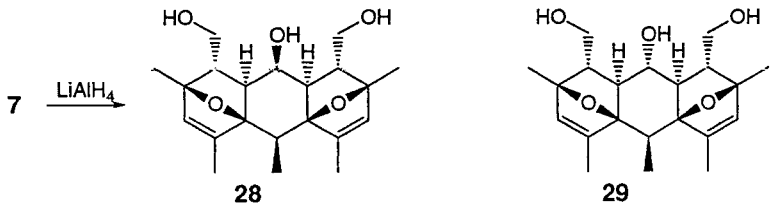


Fig. 3. *Circular dichroism of* **27** *in MeCN*

product, isolated nearly quantitatively. At the reflux temperature of THF, a 1.5:1 mixture of the (9*r*)- and (9*s*)-triols **28** and **29**, respectively, was formed. We first envisioned to protect triol **28** as tribenzyl or tris(triisopropylsilyl) ethers. The etherifications led to mixtures of products, the secondary alcohol reacting reluctantly. The further problems were encountered due to decomposition in the subsequent hydroboration and oxidation steps. We thus protected **28** as its diacetate **30** (98% yield) (*Scheme 7*). Steric hindrance rendered the secondary alcohol at C(9) unreactive in the esterification. The crude acetylation mixture from **28** was treated with $BH_3 \cdot Me_2S$ in THF. After oxidative workup ($NaBO_3 \cdot 4\ H_2O$) and flash chromatography, triol **31** (72% yield from **7**) was obtained pure after recrystallization. Oxidation of **31** with hydrated *N*-methylmorpholine *N*-oxide (NMO) in the presence of powdered 4-Å

molecular sieves and tetrapropylammonium perruthenate (TPAP) [36] as catalyst furnished triketone **32** in 69% yield. Enantioselective reduction of **32** with $BH_3 \cdot Me_2S$/CH_2Cl_2 and 0.2 equiv. of CBS catalyst **19** [31] provided, after acidic workup, monohydroxy derivative (−)-**33** (47%) and unreacted starting material that could be recovered in 30% yield. The enantiomer excess of (−)-**33** (90% e.e.) was measured by ^{1}H-NMR in the presence of [Eu(hfc)$_3$] [28]. The technique using *Mosher*'s esters [27] or *Johnson*'s sulfoximides [33] were judged unreliable because of incomplete and enantioselective reactions. Protection of hydroxy derivative (−)-**33** as a methoxymethyl (MOM) ether afforded (−)-**34** in 99% yield. Regioselective methanolysis of the diacetate was observed on treating (−)-**34** in MeOH with 4 equiv. of $Mg(OMe)_2$: the '*endo*'-(acetoxymethyl) group at C(1) reacted faster than the '*endo*'-(acetoxymethyl) group at C(8), leading to the selective formation of hemiacetal (−)-**35** (52% yield, recovery of 12% of (−)-**34**).

Scheme 6



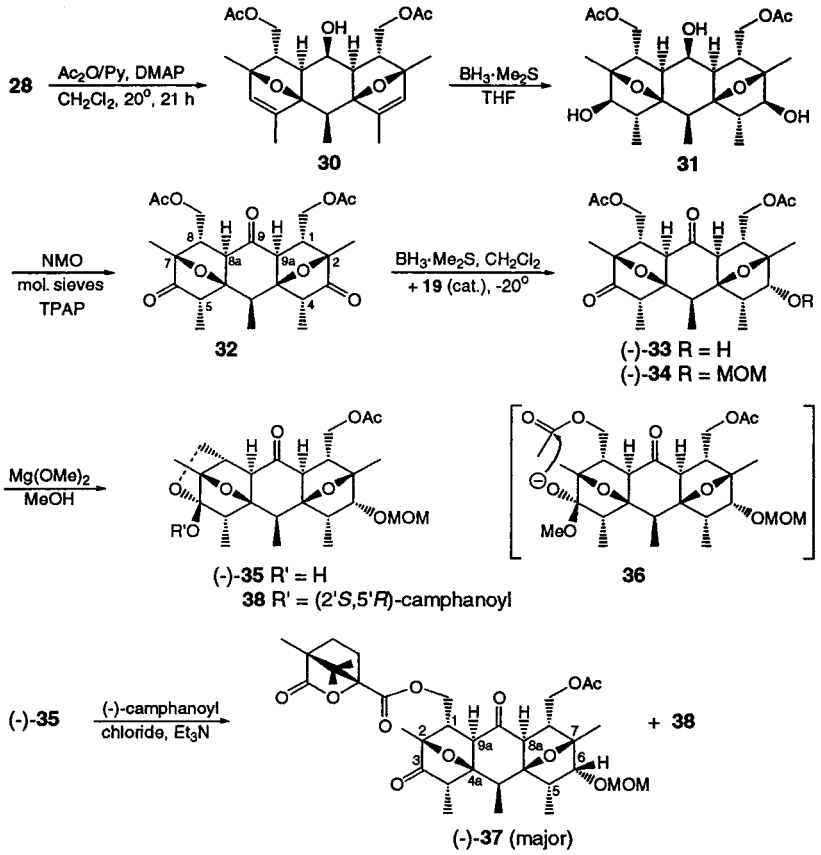
The regioselectivity of the methanolysis (−)-**34** → (−)-**35** can be attributed to a difference in steric effects, the '*endo*'-(acetoxymethyl) group at C(8) being in *gauche* interaction with the '*endo*'-(methoxymethoxy) moiety at C(6). The '*endo*'-(acetoxymethyl) group at C(1) resides in a less crowded environment (carbonyl at C(3)). Alternatively, one can invoke the addition of the MeO^- ion to the 3-keto moiety with formation of an '*endo*'-alcoholate intermediate **36** that adds to the acetate of the '*endo*'-(acetoxymethyl) group at C(1), and thus accelerates its methanolysis (*Scheme 7*).

Esterification of (−)-**35** with (−)-camphanoyl chloride gave a mixture of camphanates (−)-**37** and **38** that were separated by column chromatography on silica gel (66 and 22% yield, resp.). The crystal structure of (−)-**37** established unambiguously the structure and absolute configuration of (−)-**35** and of its precursors [22].

Cleavage of the Intraring C−C Bonds. The selective isomerization (−)-**24** → (−)-**25** (*Scheme 5*) offered a first possible path to the oxidative intraring C−C bond cleavage of our polycyclic systems. Thus, alcohol (−)-**25** was protected as its (*tert*-butyl)dimethylsilyl ether **39** in 95% yield (*Scheme 8*). Under *Luche*'s conditions [36], **39** was reduced to a mixture of alcohols **40** and **41**, separated and isolated in 85 and 4% yield, respectively. Structures **40** and **41** were deduced from their ^{1}H-NMR spectra (^3J(9,9a) = 8.4 Hz (axial/axial) in **40**, 5.8 Hz in **41**).

Attempts to cleave the C=C bond of **40** by ozonolysis or to oxidize it with OsO_4/Me_3NO,$KMnO_4$/[18]crown-6, $RuCl_3$/$NaIO_4$ [37], or by photo-oxidation all failed. We thus decided to protect diol **40** as a MOM polyether. Treatment of **40** with $MeOCH_2Cl$ and (i-Pr)$_2$NEt in CH_2Cl_2 led to mixtures of **42**–**44** (*Scheme 8*). We thus attempted to oxidize enone **39** directly with $RuCl_3$ (catalyst) and $NaIO_4$ (4 equiv.) in CCl_4/MeCN/

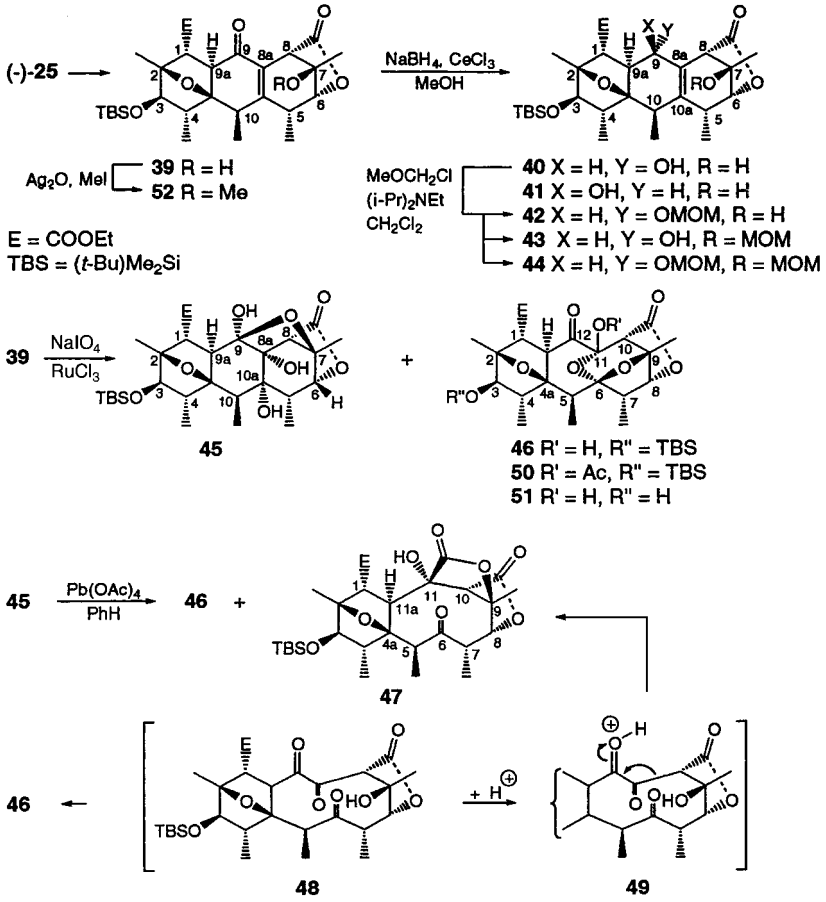
Scheme 7



MOM=$MeOCH_2$

H_2O. We were pleased to obtain a mixture of hemiacetals **45** and **46** that could be isolated in 30–42 and *ca.* 20% yield, respectively. This result indicates that the tertiary-alcohol moiety at C(7) of **39** does not control the '*syn*' dihydroxylation of the alkene. Molecular models suggest that the face of the alkene '*anti*' with respect to the tertiary alcohol at C(7) is more accessible, and thus explain the formation of 8a,10a-diol **45**. The *Malaprade* type of oxidation of **45** generates **46**. Treatment of pure **45** with $Pb(OAc)_4$ in anhydrous benzene furnished **46** (28%) and **47** (51%), the latter resulting from the regioselective benzil-benzilic acid rearrangement of intermediate α-diketone **48** *via* its conjugate acid **49** (*Scheme 8*). Treatment of the crude reaction mixture resulting from the $RuCl_3/NaIO_4$ oxidation of **39** with $Pb(OAc)_4$ provided a mixture from which pure **46** and **47** were isolated in 12 and 39% yield (2 steps), respectively. The structures of **45**–**47** were deduced from their spectral data (*Exper. Part*) and mode of formation. Product **45** was further characterized as its acetate **50** obtained in 73% yield under standard conditions. Attempts to induce *Baeyer-Villiger* lactonizations of **46** and **50** failed as both compounds did not react with *m*CPBA (*meta*-chloroperbenzoic acid).

Scheme 8



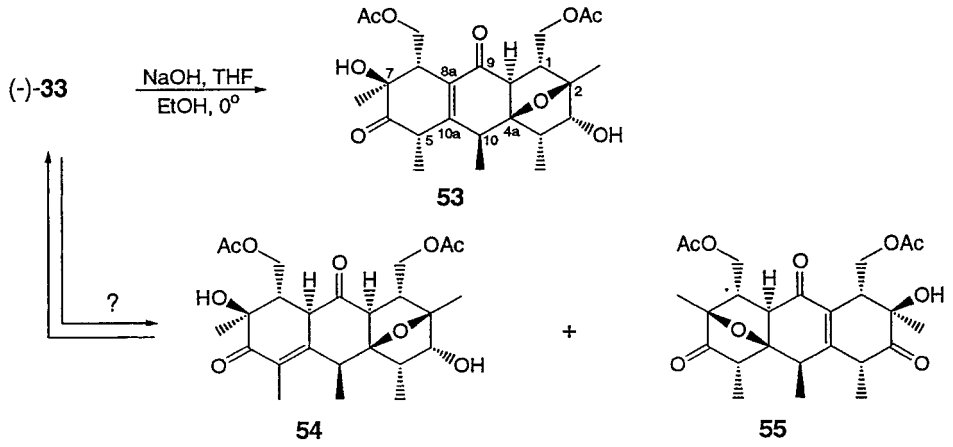
With CF_3CO_3H in CH_2Cl_2, **46** was desilylated at 0° (→ **51**) and decomposed on heating to 25°.

With the hope to have a better-behaved alkene moiety for intraring oxidative coupling, we protected **39** as methyl ether (MeI, Ag_2O, MeCN) **52** (82% yield) (*Scheme 8*). Unfortunately, treatment of **52** with $RuCl_3/NaIO_4$, followed by further treatment with $Pb(OAc)_4$ led to intractable mixtures of products.

The selective $Mg(OMe)_2$ induced methanolysis (−)-**34** → (−)-**35** (*Scheme 7*) allows, in principle, differentiation of the chemistry of the two 7-oxabicyclo[2.2.1]heptane moieties of our polycyclic systems. Alternatively, this can be done directly with (−)-**33** in the following way. Both carbonyl groups of (−)-**33** were expected [23] to allow the base-induced isomerization to give concurrently enones **53**–**55** (*Scheme 9*). To our surprise, we found that the treatment of (−)-**33** with NaOH in THF/EtOH 2:1 at 0° (30 min) led to a mixture composed mostly of **53**, (−)-**33**, and products of saponification. Pure **53** was isolated (36%) by flash chromatography (silica gel),

together with some starting material (−)-**33** (32%). Among the various explanations that could be proposed to explain the regioselective isomerization (−)-**33** → **53**, one needs to consider a possible thermodynamic control, **53** being more stable than the other isomeric enones **54** and **55** (differences in strain). The structure of **53** was deduced from its ^{1}H-NMR spectrum and by its 2D-COSY and HETCOR data.

Scheme 9

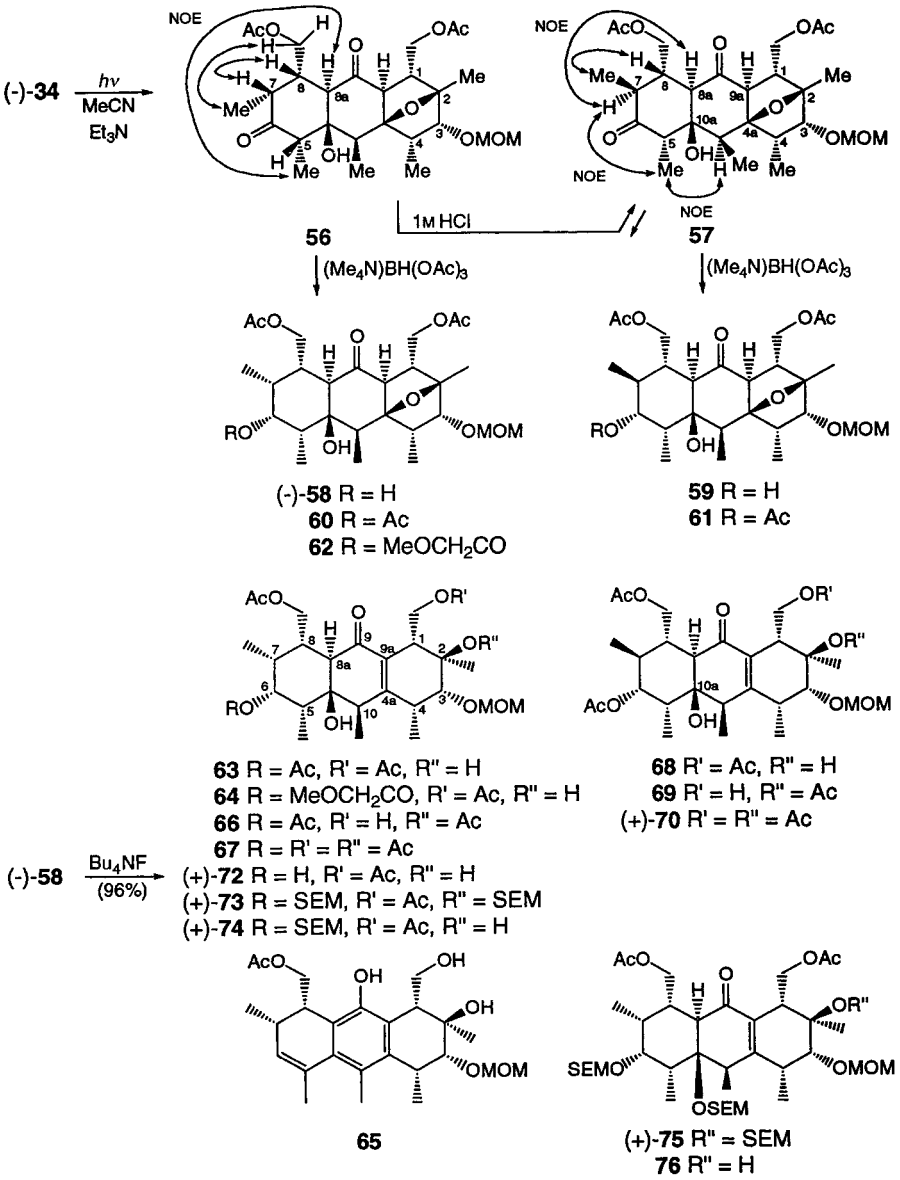


Another chemoselective 7-oxabicyclo[2.2.1]heptanone oxa-bridge cleavage was found applying *Cossy*'s photoreductive method [38]. Irradiation (low-pressure Hg lamp) of a 0.0123M solution of (−)-**34** (*Scheme 7*) in MeCN containing 5 equiv. of Et_3N (quartz vessel) led to the exclusive formation of β-hydroxycyclohexanone derivative **56** (*Scheme 10*). The irradiation was stopped after 60% conversion as further irradiation induced the decomposition of **56**. Pure **56** was isolated (60%) by flash chromatography at 0°. At 20°, silica gel catalyzed the epimerization of **56** into **57**. The latter isomerization was rapid and complete in the presence of 1M aq. HCl. The structures of **56** and **57** were established by their spectral data, in particular by their 2D-NOESY data, which displayed typical cross-peaks for signals of proton pairs (see *Scheme 10*).

The (7*R*) configuration of **56** was indicated by the NOE observed for signals of one proton of AcOCH_2−C(8) (δ(H) 4.17) and Me−C(7) (*d*, δ(H) 1.05), as well as by the absence of NOE between the latter signal and that of H−C(5) (*q*, δ(H) 2.48). No epimerization had occurred at C(5) in **56** as indicated by the strong NOE observed between the signals of Me−C(5) (*d*, δ(H) 1.28) and H−C(8a) (*d*, δ(H) 2.09). As expected for **57**, strong NOEs were observed between the signals of H−C(8) (*dddd*, δ(H) 2.47) and Me−C(7) (*d*, δ(H) 1.10), and between H−C(7) (*m*) and H−C(8a) (*d*, δ(H) 2.98). A vicinal coupling constant $^3J(7,8) =$ 10.8 Hz (axial/axial) observed in the ^{1}H-NMR spectrum of **57** confirmed a chair or nearly chair conformation for its cyclohexanone moiety.

Chemo- and stereoselective reduction of ketones **56** and **57** with $Me_4NBH(AcO)_3$ [39] furnished diols (−)-**58** (89%) and **59** (84%), respectively (*Scheme 10*). Their structures were given by their spectral data and those of the corresponding acetates **60** and **61** (quant.), respectively, obtained under standard conditions (AcCl, pyridine, CH_2Cl_2, DMAP (cat.)). For steric reasons, the tertiary-alcohol moiety at C(10a) was

Scheme 10



MOM=$MeOCH_2$, SEM=$Me_3SiCH_2CH_2OCH_2$

not esterified. We also prepared the methoxyacetate **62** (80%) by treating **58** with $MeOCH_2COCl$ and pyridine in CH_2Cl_2.

Heating **60** and **62** in DMF containing CsF (100°), a mixture of cyclohexenones **63** and **64**, respectively, with phenol derivative **65** were formed (*Scheme 10*). The best yield in cyclohexenone was observed with **60** → **63** (50% isolated **63**). Treatment of **60**

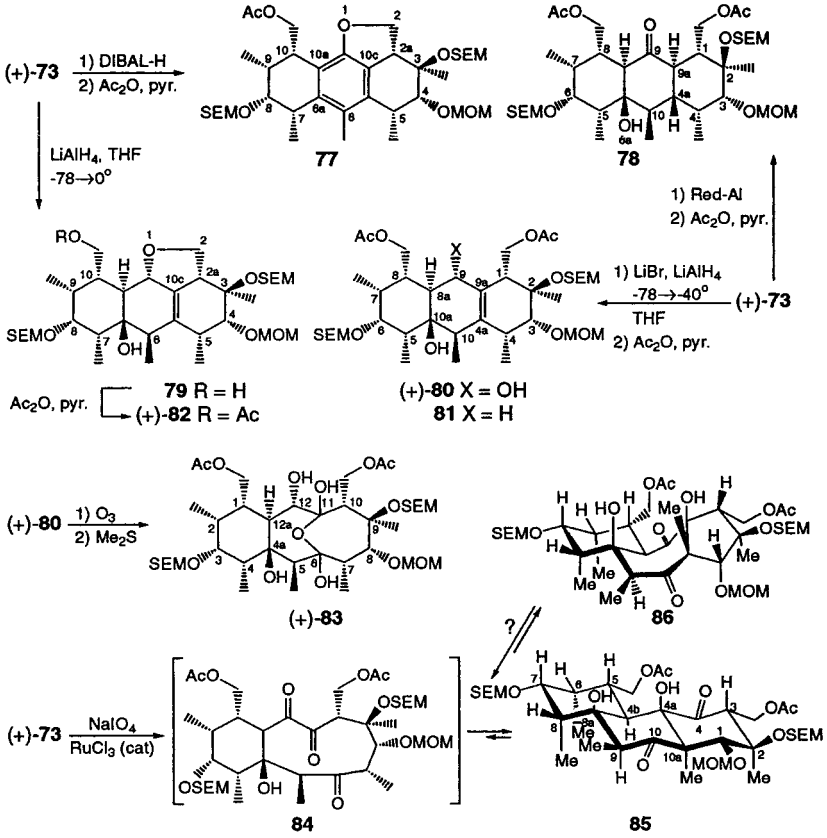
with Bu_4NF in THF at 20° led to a smoother 7-oxabicyclo[2.2.1]heptane → cyclohexenol isomerization, giving **63** and a second compound that is probably the product of acetate migration **66**. Acetylation of this mixture (Ac_2O, pyridine, DMAP (cat.)) provided tetraacetate **67** in 93% yield. Similarly, **61** was isomerized with Bu_4NF in THF to **68**/**69**, which were acetylated to (+)-**70** in 75% yield. Treatment of dihydroxy ketone (−)-**58** with Bu_4NF/THF was a very clean reaction delivering trihydroxy ketone (+)-**72** in 96% yield. Etherification of (+)-**72** with SEMCl ([2-(trimethylsilyl)ethoxy]methyl chloride) and *Hünig*'s base ((i-Pr)$_2$NEt) in CH_2Cl_2 gave a mixture from which (+)-**73**, (+)-**74**, (+)-**75**, and **76** could be isolated in 65, 16, 4, and 3% yield, respectively.

Reduction of the major enone (+)-**73** with (i-Bu)$_2$AlH (DIBAL-H) in CH_2Cl_2, followed by acetylation (Ac_2O/pyridine), gave the aromatic compound **77** in 42% yield (*Scheme 11*). *Red-Al* in toluene ((MeOCH$_2$CH$_2$O)$_2$AlH$_2$Na) led to the reduction of the alkene moiety of (+)-**73** providing cyclohexanone **78** in mediocre yield (25%). With $LiAlH_4$ in THF (− 78 to 0°), a low yield (31%) of the tetracyclic furan derivative **79** was obtained. When LiBr was used together with $LiAlH_4$ in anhydrous THF (− 78 to − 40°), **79** was a minor product, and cyclohexenol (+)-**80** was the major product isolated in 41% yield after acetylation and column chromatography (silica gel). The chromatography afforded a second product **81** resulting from allylic reduction. Ozonolysis of (+)-**80** (workup with Me_2S) generated the bis-hemiacetal (+)-**83**, which was isolated in 66% yield. The relative configurations at C(6) and C(11) could not be determined. Oxidative cleavage of the alkene moiety of cyclohexenone (+)-**73** with $NaIO_4$ and a catalytical amount of $RuCl_3 \cdot H_2O$ in CCl_4/MeCN/H_2O [39] provided the tricyclic system **85** together with an isomeric compound the structure of which could not be established. Diketone **85** arises probably by intramolecular aldol condensation of intermediate triketone **84** (*Scheme 11*).

The structures of products **77** to (+)-**83** and **85** were deduced form their mode of formation and confirmed by their spectral data, in particular with the help of their 2D-NOESY data. Product **77** arises probably by H_2O elimination from hydroxycyclohexenone (+)-**73**, that generates a phenolate intermediate which displaces one of its adjacent acetoxymethyl group. Because of the low yield of **77**, one cannot comment this apparent regioselectivity. The *trans-cisoid-trans-cisoid* configuration at the fusion sites of cyclohexanone **78** corresponds to the most stable diastereoisomer which is obtained under equilibrating conditions. Tricyclic diketone **85** is probably the most stable isomeric aldol that can be equilibrated with triketone **84** because of ring strain. The alternative isomer **86** is expected to be more strained than **85**.

For **78**, the H−C(4a)/H−C(9a) *trans* relationship is suggested by the observation of ^3J(4a,9a) = 11.7 Hz (axial/axial in the ^{1}H-NMR spectrum). The H−C(4a)/H−C(10) *trans* and H−C(4)/H−C(4a) *cis* relationships are established by ^3J(4a,10) = 11.7 Hz and ^3J(4,4a) = 4.3 Hz, respectively. The *trans* relationship between H−C(8a) and H−C(9) of (+)-**80** is suggested by ^3J(8a,9) = 7.0 Hz and between H−C(8) and H−C(8a) by ^3J(8,8a) = 11.0 Hz. The H−C(1) of **85** (δ(H) 4.78, *s*) showed ^{1}H,^{1}H-NOEs with H−C(3) (δ(H) 4.27, *dd*, ^3J = 10.3, 2.0 Hz) and OH−C(4a) (δ(H) 4.36, *s*) in the 2D-NOESY. Significant NOEs were also observed for H−C(4b) (δ(H) 2.94, *d*, ^3J(4b,5) = 11.0 Hz, axial H) with H−C(9) (δ(H) 3.35, *q*, ^3J = 6.6 Hz), with Me−C(6) (δ(H) 1.01, *d*), Me−C(8) (δ(H) 1.07 and Me−C(10a) (δ(H) 1.14, *s*). The signal assigned to OH−C(8a) (δ(H) 4.36, *s*) showed cross-peaks with the signals of H−C(5) (δ(H) 2.56), H−C(8) (δ(H) 2.04), and OH−C(4a) (δ(H) 2.45). The relatively large chemical shift of H−C(3) (4.27 ppm) is due to the proximity of the 4-oxo and *gauche*-positioned OH−C(4a) groups (compare with H−C(4b) (δ(H) 2.94) and H−C(5) (δ(H) 2.56). This feature is inconsistent with the alternative structure **86**.

Scheme 11



MOM=$MeOCH_2$, SEM=$Me_3SiCH_2CH_2OCH_2$

Conclusion. – Diesters **6** and **10** of (2*E*,5*E*)-4-oxohepta-2,5-diene dioic acid add to 2,2′-ethylidenebis[3,5-dimethylfuran] (**2**) to generate single *meso*-adducts containing nine stereogenic centers (*Scheme 2*). Two methods have been found for their desymmetrization: one of them relies on the asymmetric hydroboration of the two 7-oxabicyclo[2.2.1]heptene moieties of the adducts, the second one converts first the *meso*-adducts into a *meso*-triketone (see **32**, *i.e.*, (1*R*,2*R*,4*R*,4a*R*,5*S*,7*S*,8*S*,8a*R*,9a*S*,10*s*,10a*S*)-1,8-bis(acetoxymethyl)-1,8,8a,9a-tetrahydro-2,4,5,7,10-pentamethyl-2*H*,10*H*-2,4a:7,10a-diepoxyanthracene-3:6,9(4*H*,5*H*,7*H*)-trione) that undergoes a CBS-catalyzed (CBS = **19**) monohydroboration with 90% e.e. (*Scheme 7*). Several processes have been discovered that allow the differentiation of the chemistry of the two 7-oxabicyclo[2.2.1]heptane units of the enantiomerically enriched products thus obtained. In a few steps, they can be converted to tri- and bicyclic polypropanoates containing up to twelve stereogenic centers, including tertiary-alcohol centers.

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Experimental Part

General. See [40]. ^{1}H-NMR: signal assignments confirmed by 2D COSY and NOESY ^{1}H-NMR experiments. FC = flash chromatography on silica gel.

*Diethyl (2*E*,5*E*)-4-Oxohepta-2,5-dienoate* (**6**). To a soln. of diethyl 4-oxo-pimelate (= diethyl 4-oxoheptanedioate) [41] (50 ml, 54 g, 0.24 mol) in anh. CH_2Cl_2 (150 ml), a soln. of Br_2 (25 ml, 79 g, 0.49 mol) in anh. CH_2Cl_2 (50 ml) was added dropwise at 20°. At the end of the addition, the solvent was evaporated and the crude product treated with petroleum ether and filtered to give 69 g (76%) of diethyl 3,5-dibromo-4-oxopimelate as a white solid (m.p. 48–49°), pure enough to be used in the next step. To a soln. of diethyl 3,5-dibromo-4-oxopimelate (69 g) in CH_2Cl_2 (400 ml), anh. Et_3N (52 ml, 38 g, 0.37 mol) was added dropwise while cooling (H_2O bath). A yellow precipitate formed. After 30 min from the end of the addition, H_2O (100 ml, 2 ×) was added, the org. layer washed with H_2O (100 ml, twice), dried ($MgSO_4$), and evaporated, and the crude product recrystallized from EtOH: 32 g (79%) of **6**. Yellow solid. M.p. 50–51°. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.33 (*d*, ^3J = 16.0, H–C(2)); 6.81 (*d*, ^3J = 16.0, H–C(3)); 4.30 (*w*, ^3J = 7.5, MeCH_2O); 1.35 (*t*, ^3J = 7.5, *Me*CH$_2$O). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 188.2 (*s*, C(4)); 165.1 (*s*, C(1)); 137.5, 133.2 (2*d*, ^1J = 163, ^1J = 167, C(2), C(3)); 61.6 (*t*, ^1J = 148, MeCH$_2$O); 14.1 (*q*, ^1J = 127, *Me*CH$_2$O).

*Dimethyl (2*E*,5*E*)-4-Oxohepta-2,5-dienoate* (**10**). To a suspension of (2*E*,5*E*)-4-oxohepta-2,5-dienoic acid [42] (1.18 g, 6.9 mmol) in anh. DMF (7 ml), Cs_2CO_3 (3.4 g, 10.4 mmol) and then MeI (2.6 ml, 41.7 mmol) were added, and the mixture was stirred under N_2 at 20° for 1 day. The mixture was then poured into H_2O (50 ml), the precipitate filtered and dried *in vacuo*, and the crude product recrystallized from AcOEt: 720 mg (52%) of **10**. Yellow solid. M.p. 170–171°, see [43]. IR (KBr): 3070, 2960, 1730, 1680, 1620, 1435, 1325, 1300, 1280, 1210, 1100, 1000, 880, 775, 710, 640, 540. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.35 (*d*, ^3J = 16.0, H–C(2)); 6.83 (*d*, ^3J = 16.0, H–C(3)); 3.85 (*s*, MeO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 188.0 (*s*, C(4)); 165.5 (*s*, C(1)); 137.6, 132.7 (2*d*, ^1J(C,H) = 163, ^1J(C,H) = 167, C(2), C(3)); 52.5 (*q*, ^1J(C,H) = 148, MeO).

Diethyl meso-*(1*R*,2*R*,4a*R*,7*S*,8*S*,8a*S*,9a*R*,10*r*,10a*S*)-1,7,8,8a,9,9a-Hexahydro-2,4,5,7,10-pentamethyl-9-oxo-2*H*,10*H*-2,4a:7,10a-diepoxyanthracene-1,8-dicarboxylate* (**7**). To a mixture of 2,2′-ethylidenebis[3,5-dimethylfuran] (**2**) [20] (1.00 g, 4.6 mmol) and **6** (1.04 g, 4.6 mmol) in a 6.6-ml *Teflon* flask, $CHCl_3$ was added to fill the flask. After 5 h at 20°/5 kbar, the solvent was evaporated. Crystallization from Et_2O and chromatography (silica gel) of the mother-liquor residue (CH_2Cl_2/petroleum ether/Et_2O 14:6:1) afforded 1.97 g (96%) of **7**. White solid. M.p. 130–131°. IR (KBr): 1730, 1700, 1280, 1180. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.83 (*q*, ^4J = 1.7, H–C(3), H–C(6)); 4.09 (*m*, 2 MeCH_2O); 3.67 (*d*, ^3J = 3.0, H–C(1), H–C(8)); 2.99 (*d*, ^3J = 3.0, H–C(9a), H–C(8a)); 2.88 (*q*, ^3J = 7.3, H–C(10)); 1.88 (*d*, ^4J = 1.7, Me–C(4), Me–C(5)); 1.71 (*s*, Me–C(2), Me–C(7)); 1.24 (*t*, ^3J = 7.0, 2 *Me*CH$_2$O); 1.10 (*d*, ^3J = 7.3, Me–C(10)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 203.8 (*s*, C(9)); 171.6 (*s*, *C*O–C(1), *C*O–C(8)); 147.0 (*s*, C(4), C(5)); 133.8 (*d*, ^1J(C,H) = 172, C(3), C(6)); 94.5, 87.0 (2*s*, C(2), C(7), C(4a), C(10a)); 60.6 (*t*, ^1J(C,H) = 147, 2 MeCH_2O); 55.7, 55.0 (2*d*, ^1J(C,H) = 134, 138, C(1), C(8), C(8a), C(9a)); 29.5 (*d*, ^1J(C,H) = 119, C(10)); 18.6 (*q*, ^1J(C,H) = 127, *Me*–C(4), *Me*–C(5)); 14.1 (*q*, ^1J(C,H) = 127, 2 *Me*CH$_2$O); 12.1 (*q*, ^1J(C,H) = 127, *Me*–C(2), *Me*–C(7)); 11.4 (*q*, ^1J(C,H) = 129, *Me*–C(10)). CI-MS (NH_3): 444 (0.1, M^+), 399 (0.5, [M – EtO]$^+$), 317 (1), 271 (1), 218 (28), 217 (48), 203 (100), 123 (52), 99 (19). Anal. calc. for $C_{25}H_{32}O_7$ (444.52): C 67.55, H 7.26; found: C 67.63, H 7.33.

Dimethyl meso-*(1*R*,2*R*,4a*R*,7*S*,8*S*,8a*S*,9a*R*,10*r*,10a*S*)-1,7,8,8a,9,9a-Hexahydro-2,4,5,7,10-pentamethyl-9-oxo-2*H*,10*H*-2,4a:7,10a-diepoxyanthracene-1,8-dicarboxylate* (**11**). *a*) A mixture of **2** (1.35 g, 6.2 mmol) and **10** (1.23 g, 6.2 mmol) in $CHCl_3$ (8 ml) in the presence of a catalytic amount of hydroquinone was heated to 60–70° for 5 h. The solvent was evaporated and the residue purified by FC (CH_2Cl_2/petroleum ether/Et_2O 14:6:1) with concomitant recovery of the unreacted starting materials: 1.16 g (45%) of **11** as white crystals.

b) In a *Teflon* flask, **2** (50 mg, 0.227 mmol) and **10** (45 mg, 0.227 mmol) were mixed in $CHCl_3$ (2.5 ml) and kept for 5 h at 20°/5 kbar. After evaporation, the residue was purified by FC (CH_2Cl_2/petroleum ether/Et_2O 14:6:0.5): 52 mg (55%) of **11**. White solid. M.p. 124–126°. IR (KBr). 1745, 1730, 1700, 1435, 1385, 1355, 1330, 1290, 1210, 1135, 1100, 1045, 970, 925, 880, 840, 805, 770, 680. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.86 (*q*, ^4J = 1.6, H–C(3), H–C(6)); 3.71 (*d*, ^3J = 3.0, H–C(1), H–C(8)); 3.66 (*s*, 2 MeO); 2.99 (*d*, ^3J = 3.0, H–C(9a), H–C(8a)); 2.88 (*q*, ^3J = 7.2, H–C(10)); 1.89 (*d*, ^4J = 1.6, Me–C(4), Me–C(5)); 1.71 (*s*, Me–C(2), Me–C(7)); 1.12 (*d*, ^3J = 7.2, Me–C(10)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 203.7 (*s*, C(9)); 172.2 (*s*, *C*O–C(1), *C*O–C(8)); 147.1 (*s*, C(4), C(5)); 133.9 (*d*, ^1J(C,H) = 172, C(3), C(6)); 94.4, 86.9 (2*s*, C(2), C(7), C(4a), C(10a)); 55.9, 54.9 (2*d*, ^1J(C,H) = 133, 138, C(1), C(8), C(8a), C(9a)); 51.8 (*q*, ^1J(C,H) = 146, MeO); 29.5 (*d*, ^1J(C,H) = 118, C(10)); 18.5 (*q*, ^1J(C,H) = 128, *Me*–C(4), *Me*–C(5)); 12.1 (*q*, ^1J(C,H) = 128, *Me*–C(2), *Me*–C(7)); 11.4 (*q*, ^1J(C,H) = 119, *Me*–C(10)). CI-MS (NH_3): 434 (0.1, [M + NH_4]$^+$), 416 (0.2, M^+), 385 (0.5), 303 (2), 285

(0.4), 271 (1), 218 (28), 217 (62), 204 (15), 203 (100), 213 (50). Anal. calc. for $C_{23}H_{28}O_7$ (416.47): C 66.33, H 6.78; found: C 66.47, H 6.86.

Diethyl (1S,2R,3S,4S,4aS,7R,8R,8aR,9aS,10R,10aR)-1,3,4,7,8,8a,9,9a-Octahydro-3-hydroxy-2,4,5,7,10-pentamethyl-9-oxo-2H,10H-2,4a:7,10a-diepoxyanthracene-1,8-dicarboxylate ((+)-**8**) *and Diethyl* meso-*(1R,2S,3R,4R,4aR,5S,6S,7R,8S,8aS,9aR,10r,10aS)-1,3,4,5,6,7,8,8a,9,9a-Decahydro-3,6-dihydroxy-2,4,5,7,10-pentamethyl-9-oxo-2H,10H-2,4a:7,10a-diepoxyanthracene-1,8-dicarboxylate* (**12**). The complex [(+)-$IpcBH_2$]·TMEDA (*Aldrich* ($IpcBH_2$ = isopinocampheylborane, TMEDA = *N,N,N′,N′*-tetramethylethylenediamine); 5 g, 12 mmol) was introduced into a *Schlenk* tube equipped with a glass frit to perform a filtration under N_2 (thoroughly dried glassware, assembled under N_2). The complex was dissolved in anh. THF (20 ml), $BF_3 \cdot Et_2O$ (3.0 ml, 24 mmol) was added, and the mixture was stirred at 20° under N_2 for 2 h. The resulting TMEDA·$2BF_3$ complex was filtered, and a soln. of (+)-$IpcBH_2$ in THF was obtained and stored at 0°. This soln. was analyzed by hydrolysis with EtOH/THF 1:1 and found to be *ca.* 0.69M. To a soln. of **7** (3 g, 6.76 mmol) in anh. THF (15 ml) cooled to −25° under N_2, 0.69M (+)-$IpcBH_2$ (10.7 ml, 7.43 mmol, 1.1 equiv.) in THF was added. After 22 h stirring at −25°, H_2O (10 ml) and $NaBO_3 \cdot 4\ H_2O$ (3.1 g, 20 mmol, 3 equiv.) were added, and the mixture was stirred at 20° for 5 h. The aq. layer was extracted with CH_2Cl_2 (20 ml, 3 ×), the combined org. extract washed with brine (10 ml, 2 ×), dried ($MgSO_4$), and evaporated and the residue purified by FC (20 → 90% AcOEt/petroleum ether): 1.85 g (59%) of (+)-**8** as white solid (78% e.e., see **14**), some starting material mixed with isopinocampheol, and *ca.* 20% of **12**.

*Data of (+)-***8**: M.p. 55–56°. $[\alpha]_{589}^{20} = +5$, $[\alpha]_{577}^{20} = +26$, $[\alpha]_{546}^{20} = +29$, $[\alpha]_{435}^{20} = +47$, $[\alpha]_{405}^{20} = +55$ ($c = 0.6$, $CHCl_3$; e.e. 78%). IR (KBr): 3510, 1730, 1280. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.80 (*q*, $^4J = 1.5$, H–C(6)); 4.16, 4.08 (*q*, *m*, 2 MeCH_2O); 3.70 (*d*, $^3J = 4.3$, H–C(1)); 3.67 (*d*, $^3J = 3.0$, H–C(8)); 3.35 (*d*, $^3J = 3.5$, H–C(3)); 3.29 (*dd*, $^3J = 4.3$, $^4J = 0.8$, H–C(9a)); 2.92 (*dd*, $^3J = 3.0$, $^4J = 0.8$, H–C(8a)); 2.55 (*q*, $^3J = 7.3$, H–C(10)); 2.07 (*qd*, $^3J = 7.6$, 3.5, H–C(4)); 1.82 (*d*, $^4J = 1.5$, Me–C(5)); 1.70 (*s*, Me–C(7)); 1.57 (*s*, Me–C(2)); 1.28, 1.24 (2*t*, $^3J = 7.4$, 7.5, 2 *Me*CH_2O); 1.25 (*d*, $^3J = 7.6$, Me–C(4)); 1.14 (*d*, $^3J = 7.3$, Me–C(10)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 204.8 (*s*, C(9)); 171.5, 171.0 (2*s*, *C*O–C(1), *C*O–C(8)); 147.2 (*s*, C(5)); 133.6 (*d*, ^1J(C,H) = 172, C(6)); 95.2, 92.3, 87.9, 86.8 (4*s*, C(2), C(4a), C(7), C(10a)); 78.8 (*d*, ^1J(C,H) = 148, C(3)); 61.2, 60.7 (2*t*, ^1J(C,H) = 148, 148, 2 Me*C*H_2O); 55.1, 55.0, 52.4, 51.8, 51.4 (5*d*, ^1J(C,H) = 138, 134, 131, 136, 131, C(1), C(4), C(8), C(8a), C(9a)); 29.6 (*d*, ^1J(C,H) = 120, C(10)); 18.5 (*q*, ^1J(C,H) = 129, *Me*–C(5)); 16.7 (*q*, ^1J(C,H) = 128, *Me*–C(4)); 14.1 (2*q*, ^1J(C,H) = 127, 2 *Me*CH_2O); 12.7, 12.1 (2*q*, ^1J(C,H) = 126, 127, *Me*–C(2), *Me*–C(7)); 10.3 (*q*, ^1J(C,H) = 129, *Me*–C(10)). CI-MS (NH_3): 462 (17, M^+), 444 (1, $[M - H_2O]^+$), 417 (8, $[M - EtO]^+$), 373 (1), 335 (11), 271 (8), 217 (15), 189 (4), 123 (100). Anal. calc. for $C_{25}H_{34}O_8$ (462.54): C 64.92, H 7.41; found: C 64.92, H 7.53.

Data of **12**: White solid. M.p. 157–159°. IR (KBr): 3500, 1720, 1285, 1055. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.17 (*q*, $^3J = 7.1$, 2 MeCH_2O); 3.74 (*d*, $^3J = 3.8$, H–C(1), H–C(8)); 3.34 (*m*, H–C(3), H–C(6)); 3.26 (*d*, $^3J = 3.8$, H–C(9a), H–C(8a)); 2.24 (*q*, $^3J = 7.1$, H–C(10)); 2.03 (*dq*, $^3J = 2.5$, 7.3, H–C(4), H–C(5)); 1.68 (*m*, 2 OH); 1.58 (*s*, Me–C(2), Me–C(7)); 1.29 (*t*, $^3J = 7.1$, 2 *Me*CH_2O); 1.22 (*d*, $^3J = 7.3$, Me–C(4), Me–C(5)); 1.21 (*d*, $^3J = 7.1$, Me–C(10)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 205.5 (*s*, C(9)); 170.9 (*s*, *C*O–C(1), *C*O–C(8)); 93.4, 87.7 (2*s*, C(2), C(7), C(4a), C(10a)); 78.8 (*d*, ^1J(C,H) = 140, C(3), C(6)); 61.2 (*t*, ^1J(C,H) = 148, 2 Me*C*H_2O); 51.9, 51.7, 51.3 (3*d*, ^1J(C,H) = 132, 132, 134, C(1), C(8), C(4), C(5), C(8a), C(9a)); 30.0 (*d*, ^1J(C,H) = 124, C(10)); 16.7 (*q*, ^1J(C,H) = 128, *Me*–C(4), *Me*–C(5)); 14.2 (*q*, ^1J(C,H) = 127, 2 *Me*CH_2O); 12.9 (*q*, ^1J(C,H) = 128, *Me*–C(2), *Me*–C(7)); 9.1 (*q*, ^1J(C,H) = 127, *Me*–C(10)). CI-MS (NH_3): 480 (1, M^+), 462 (11, $[M - H_2O]^+$), 435 (11, $[M - EtO]^+$), 421 (15), 375 (8), 351 (100), 303 (25),259 (20), 231 (10), 171 (21), 125 (27), 109 (25), 85 (16). Anal. calc. for $C_{25}H_{36}O_9$ (480.55): C 62.49, H 7.55; found: C 62.34, H 7.53.

Dimethyl meso-*(1R,2S,3R,4R,4aR,5S,6S,7R,8S,8aS,9aR,10r,10aS)-1,3,4,5,6,7,8,8a,9,9a-Decahydro-3,6-dihydroxy-2,4,5,7,10-pentamethyl-9-oxo-2H,10H-2,4a:7,10a-diepoxyanthracene-1,8-dicarboxylate* (**13**). To a soln. of **11** (17 mg, 0.04 mmol) in anh. THF (1 ml) at −78°, $BH_3 \cdot Me_2S$ (*ca.* 10M in Me_2S) was added (4 µl, 0.04 mmol). The cooling bath was removed and the mixture stirred under N_2 at 20° for 2 h. Then H_2O (0.5 ml) was added, followed by $NaBO_3 \cdot 4\ H_2O$ (20 mg, 0.123 mmol), and the oxidation was carried out overnight at 20°. After addition of H_2O (3 ml), the mixture was extracted with CH_2Cl_2 (5 ml, 3 times), the org. layer washed with brine (5 ml, twice), dried ($MgSO_4$), and evaporated, and the crude purified by FC (50 → 90% AcOEt/petroleum ether): 17 mg (92%) of **13**. White solid. M.p. >250° (dec.). IR (KBr): 3550, 1715, 1285, 1220, 1050. ^{1}H-NMR (250 MHz, $CDCl_3$): 3.76 (*d*, $^3J = 4.0$, H–C(1), H–C(8)); 3.73 (*s*, 2 MeO); 3.35 (*m*, H–C(3), H–C(6)); 3.27 (*d*, $^3J = 4.0$, H–C(9a), H–C(8a)); 2.25 (*q*, $^3J = 7.1$, H–C(10)); 2.04 (*dq*, $^3J = 2.6$, 7.1, H–C(4), H–C(5)); 1.58 (*s*, Me–C(2), Me–C(7)); 1.22 (2*d*, $^3J = 7.1$, Me–C(4), Me–C(5), Me–C(10)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 205.4 (*s*, C(9)); 171.5 (*s*, *C*O–C(1), *C*O–C(8)); 93.4, 87.6 (2*s*, C(2), C(7), C(4a), C(10a)); 78.9 (*d*, ^1J(C,H) = 146, C(3), C(6)); 52.2 (*q*, ^1J(C,H) = 147, 2 MeO); 51.9, 51.7, 51.26 (3*d*, ^1J(C,H) = 132, 130, 136, C(1), C(8), C(4),

C(5), C(8a), C(9a)); 29.7 (*d*, ^1J(C,H) = 117, C(10)); 16.6 (*q*, ^1J(C,H) = 128, *Me*–C(4), *Me*–C(5)); 12.9 (*q*, ^1J(C,H) = 126, *Me*–C(2), *Me*–C(7)); 9.1 (*q*, ^1J(C,H) = 129, *Me*–C(10)). CI-MS (NH_3): 470 (0.2, $[M+NH_4]^+$), 452 (0.3, M^+), 434 (8, $[M-H_2O]^+$), 421 (7, $[M-MeO]^+$), 403 (5), 393 (16, $[M-COOMe]^+$), 337 (100), 303 (25), 259 (18), 166 (39), 109 (32). Anal. calc. for $C_{23}H_{32}O_9$ (452.50): C 61.05, H 7.13; found: C 61.07, H 7.06.

Diethyl (1S,2R,3S,4S,4aS,7R,8R,8aR,9aS,10R,10aR)-1,3,4,7,8,8a,9,9a-Octahydro-2,4,5,7,10-pentamethyl-9-oxo-3-[(2R)-3,3,3-trifluoro-2-methoxy-1-oxo-2-phenylpropoxy]-2H,10H-2,4a:7,10a-diepoxyanthracene-1,8-dicarboxylate (**14**). A mixture of (*R*)-(+)-MTPA (=(+)-(*R*)-α-methoxy α-(trifluoromethyl)benzeneacetic acid) (25 mg, 0.11 mmol), anh. hexane (0.5 ml), anh. DMF (2 µl), and freshly distilled $(COCl)_2$ (41 µl, 0.48 mmol) was stirred 1 h under N_2 at 20°. The precipitate was filtered off and the solvent evaporated. A soln. of (+)-**8** (15 mg, 0.032 mmol), anh. Et_3N (14 µl), and catalytic *N*,*N*-dimethylpyridin-4-amine (DMAP) in anh. CH_2Cl_2 (400 µl) was added, and the mixture was stirred at 20°. After 2 h, the mixture was diluted with CH_2Cl_2 (6 ml), washed with 1M aq. HCl (2 ml, 2 ×), 5% aq. Na_2CO_3 soln. (2 ml, twice), and brine (2 ml). The org. layer was then dried ($MgSO_4$) and the solvent evaporated, affording a mixture of the two diastereoisomers (d.r. 78%) in quantitative yield as a colorless oil.

Data of **14** (major): ^{1}H-NMR (400 MHz, $CDCl_3$): 7.60–7.55, 7.40–7.35 (2*m*, Ph); 5.82 (*q*, ^4J = 1.7, H–C(6)); 4.60 (*d*, ^3J = 2.6, H–C(3)); 4.30–4.05 (*m*, 2 MeCH_2O); 3.76 (*d*, ^3J = 4.2, H–C(1)); 3.67 (*d*, ^3J = 2.9, H–C(8)); 3.57 (*s*, MeO); 3.34 (*dd*, ^3J = 4.2, ^4J = 0.8, H–C(9a)); 2.95 (*dd*, ^3J = 2.9, ^4J = 0.8, H–C(8a)); 2.56 (*q*, ^3J = 7.1, H–C(10)); 2.26 (*qd*, ^3J = 7.3, 2.6, H–C(4)); 1.82 (*d*, ^4J = 1.7, Me–C(5)); 1.71 (*s*, Me–C(7)); 1.48 (*s*, Me–C(2)); 1.35 (*d*, ^3J = 7.3, Me–C(4)); 1.31, 1.25 (2*t*, ^3J = 7.1, 7.1, 2 *Me*CH_2O); 1.13 (*d*, ^3J = 7.3, Me–C(10)). ^{19}F-NMR (376.7 MHz, $CDCl_3 + CCl_3F$): −71.73 (rel. to CCl_3F). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 204.4 (*s*, C(9)); 171.5, 170.5 (2*s*, *C*O–C(1), *C*O–C(8)); 166.4 (*s*, *C*OO–C(3)); 147.0 (*s*, C(5)); 133.7 (*d*, ^1J(C,H) = 172, C(6)); 131.9 (*s*, arom. C); 129.6, 128.4, 127.2 (3*d*, ^1J(C,H) = 161, 167, 163, 5 arom. CH)); 123.3 (*q*, ^1J(C,F) = 289, CF_3); 95.0, 92.6, 86.9, 86.8 (4*s*, C(2), C(4a), C(7), C(10a)); 83.2 (*d*, ^1J(C,H) = 162, C(3)); 61.5, 60.8 (2*t*, ^1J(C,H) = 148, 148, 2 Me*C*H_2O); 55.4 (*q*, ^1J(C,H) = 144, MeO); 55.2, 55.0, 52.6, 52.2, 48.7 (5*d*, ^1J(C,H) = 139, 135, 131, 137, 134, C(1), C(4), C(8), C(8a), C(9a)); 29.6 (*d*, ^1J(C,H) = 120, C(10)); 18.5, 16.8, 14.2, 14.1, 12.7, 12.1, 10.2 (7*q*, ^1J(C,H) = 127, 128, 127, 127, 127, 127, 129, *Me*–C(5), *Me*–C(4), *Me*–C(2), *Me*–C(7), *Me*–C(10), 2 *Me*CH_2O); CF_3–*C* missing.

Data of Diethyl (1R,2S,3R,4R,4aR,7S,8S,8aS,9aR,10S,10aS)-1,3,4,7,8,8a,9,9a-Octahydro-2,4,5,7,10-pentamethyl-9-oxo-3-[(2R)-3,3,3-trifluoro-2-methoxy-1-oxo-2-phenylpropoxy]-2H,10H-2,4a:7,10a-diepoxyanthracene-1,8-dicarboxylate (**14′**; minor): ^{1}H-NMR (400 MHz, $CDCl_3$, selected signals): 7.53–7.49, 7.42–7.38 (2*m*, Ph); 5.82 (*q*, ^4J = 1.7, H–C(6)); 4.63 (*d*, ^3J = 2.6, H–C(3)); 2.52 (*q*, ^3J = 7.1, H–C(10)); 2.17 (*qd*, ^3J = 7.4, ^3J(3,4) = 2.6, H–C(4)); 1.69 (*s*, Me–C(2)); 1.52 (*s*, Me–C(7)); 0.99 (*d*, ^3J = 7.1, Me–C(10)). ^{19}F-NMR (376.7 MHz, $CDCl_3 + CCl_3F$): −71.96 (rel. to CCl_3F).

Dimethyl (1R,2S,3R,4R,4aR,7S,8S,8aS,9aR,10S,10aS)-1,3,4,7,8,8a,9,9a-Octahydro-3-hydroxy-2,4,5,7,10-pentamethyl-9-oxo-2H,10H-2,4a:7,10a-diepoxyanthracene-1,8-dicarboxylate ((−)-**15**). As described for (+)-**18** and **12**, with $[(-)\text{-IpcBH}_2]\cdot$TMEDA (244 mg, 0.586 mmol), THF (1 ml), and $BF_3\cdot Et_2O$ (0.147 ml, 1.172 mmol) (→ 0.23M (−)-$IpcBH_2$ in THF, by hydrolysis with Et_2O/THF 1:1). Then with **11** (27 mg, 0.065 mmol), THF (1 ml), and 1 equiv. of (−)-$IpcBH_2$ (18 h at −25°), and H_2O (1 ml) and $NaBO_3\cdot 4\,H_2O$ (31 mg, 0.201 mmol, 3.1 equiv.; 7 h at 20°). Workup with CH_2Cl_2 (3 ml, 3 ×) and brine (3 ml, 2 ×). FC (20% → 90% AcOEt/petroleum ether) gave 15 mg (53%) of (−)-**15** (82% ee, see **16**), 11% of **11**, and 10% of **19**. Recrystallization of a sample of (−)-**15** (140 mg) from CH_2Cl_2/Et_2O afforded (−)-**15** with >98% e.e. (28 mg, 20%). M.p. (>98% e.e.) 210–211° (m.p. of (±)-**15** 166–168°). $[\alpha]_{589}^{20} = -32$, $[\alpha]_{578}^{20} = -33$, $[\alpha]_{546}^{20} = -39$, $[\alpha]_{436}^{20} = -63$, $[\alpha]_{365}^{20} = -80$ (*c* = 0.9, $CHCl_3$). IR (KBr): 3515, 1725, 1705, 1460, 1435, 1280. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.82 (*q*, ^4J = 1.5, H–C(6)); 3.75 (*d*, ^3J = 4.0, H–C(1)); 3.73 (*s*, MeOOC–C(1)); 3.70 (*d*, ^3J = 3.0, H–C(8)); 3.65 (*s*, MeOOC–C(8)); 3.36 (*m*, H–C(3)); 3.31 (*dd*, ^3J = 4.0, ^4J = 1.0, H–C(9a)); 2.93 (*dd*, ^3J = 3.0, ^4J = 1.0, H–C(8a)); 2.57 (*q*, ^3J = 7.0, H–C(10)); 2.08 (*qd*, ^3J = 7.5, 2.5, H–C(4)); 1.84 (*d*, ^4J = 1.5, Me–C(5)); 1.71 (*s*, Me–C(7)); 1.58 (*s*, Me–C(2)); 1.27 (*d*, ^3J = 7.5, Me–C(4)); 1.17 (*d*, ^3J = 7.0, Me–C(10)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 204.7 (*s*, C(9)); 172.1, 171.5 (2*s*, *C*O–C(1), *C*O–C(8)); 147.2 (*s*, C(5)); 133.8 (*d*, ^1J(C,H) = 173, C(6)); 95.2, 92.3, 87.9, 86.8 (4*s*, C(2), C(4a), C(7), C(10a)); 78.9 (*d*, ^1J(C,H) = 140, C(3)); 55.2, 55.1, 52.6, 51.7, 51.6 (5*d*, ^1J(C,H) = 135, 140, 131, 136, 132, C(1), C(4), C(8), C(8a), C(9a)); 52.2, 51.9 (2*q*, ^1J(C,H) = 147, 147, 2 *Me*OOC); 29.6 (*d*, ^1J(C,H) = 119, C(10)); 18.5 (*q*, ^1J(C,H) = 127, *Me*–C(5)); 16.7 (*q*, ^1J(C,H) = 127, Me–C(4)); 12.7, 12.1 (2*q*, ^1J(C,H) = 126, ^1J(C,H) = 127, *Me*–C(2), *Me*–C(7)); 10.3 (*q*, ^1J(C,H) = 129, *Me*–C(10)). CI-MS (NH_3): 452 (0.1, $[M+H_2O]^+$), 434 (26, M^+), 403 (8, $[M-MeO]^+$), 321 (19), 271 (10), 217 (16), 166 (14), 123 (100), 85 (18). Anal. calc. for $C_{23}H_{30}O_8$ (434.49): C 63.58, H 6.96; found: C 63.68, H 6.85.

*Dimethyl (1*R*,2*S*,3*R*,4*aR*,7*S*,8*S*,8a*S*,9a*R*,10*S*,10a*S*)-1,3,4,7,8,8a,9,9a-Octahydro-2,4,5,7,10-pentamethyl-9-oxo-3-[(2*R*)-3,3,3-trifluoro-2-methoxy-1-oxo-2-phenylpropoxy]-2*H,*10*H-*2,4a:7,10a-diepoxyanthracene-1,8-dicarboxylate* (**16**). As described for **14**. A mixture of the two diastereoisomers (d.r. 82%) was obtained in quantitative yield. The pure major distereoisomer was obtained starting from enantiomerically pure (−)-**15** (obtained by crystallization as described above).

Data of **16** (major): ^{1}H-NMR (400 MHz, $CDCl_3$): 7.53–7.49, 7.42–7.38 (2*m*, Ph); 5.82 (*q*, ^4J = 1.7, H−C(6)); 4.60 (*d*, ^3J = 2.6, H−C(3)); 3.79, 3.65 (2*s*, 2 MeOOC); 3.77 (*d*, ^3J = 4.1, H−C(1)); 3.68 (*d*, ^3J = 3.0, H−C(8)); 3.52 (*s*, MeO−C(2′)); 3.33 (*dd*, ^3J = 4.1, ^4J = 0.8, H−C(9a)); 2.93 (*dd*, ^3J = 3.0, ^4J = 0.8, H−C(8a)); 2.51 (*q*, ^3J = 7.1, H−C(10)); 2.15 (*qd*, ^3J = 7.4, 2.6, H−C(4)); 1.81 (*d*, ^4J = 1.7, Me−C(5)); 1.69 (*s*, Me−C(7)); 1.52 (*s*, Me−C(2)); 1.33 (*d*, ^3J = 7.4, Me−C(4)); 0.98 (*d*, ^3J = 7.1, Me−C(10)). ^{19}F-NMR (376.7 MHz, $CDCl_3$ + CCl_3F): −71.93 (rel. to CCl_3F). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 204.3 (*s*, C(9)); 172.0, 171.1 (2*s*, *C*O−C(1), *C*O−C(8)); 166.4 (*s*, *C*OO−C(3)); 147.0 (*s*, C(5)); 133.8 (*d*, ^1J(C,H) = 171, C(6)); 131.7 (*s*, arom. C. quat.); 129.7, 128.5, 127.3 (3*d*, ^1J(C,H) = 161, 165, 160, 5 arom. CH); 123.3 (*q*, ^1J(C,H) = 289, CF_3); 95.0, 92.6, 86.9, 86.6 (4*s*, C(2), C(4a), C(7), C(10a)); 83.0 (*d*, ^1J(C,H) = 155, C(3)); 55.3 (*q*, ^1J(C,H) = 144, *Me*O−C(2′)); 52.5, 51.9 (2*q*, ^1J(C,H) = 147, 147, 2 *Me*OOC); 55.2, 55.1, 52.7, 52.2, 48.6 (5*d*, ^1J(C,H) = 139, 135, 131, 136, 131, C(1), C(4), C(8), C(8a), C(9a)); 29.5 (*d*, ^1J(C,H) = 119, C(10)); 18.5, 17.0, 12.8, 12.1, 9.9 (5*q*, ^1J(C,H) = 128, 128, 127, 130, 129, *Me*−C(5), *Me*−C(4), *Me*−C(2), *Me*−C(7), *Me*−C(10)); CF_3−*C*.

*Data of Dimethyl (1*S*,2*R*,3*S*,4*S*,4a*S*,7*R*,8*R*,8a*R*,9a*S*,10*R*,10a*R*)-1,3,4,7,8,8a,9,9a-Octahydro-2,4,5,7,10-pentamethyl-9-oxo-3-[(2*R*)-3,3,3-trifluoro-2-methoxy-1-oxo-2-phenylpropoxy]-2*H,*10*H-*2,4a:7,10a-diepoxyanthracene-1,8-dicarboxylate* (**16′**; minor): ^{1}H-NMR (400 MHz, $CDCl_3$, selected signals): 7.6, 7.43–7.35 (2*m*, Ph); 5.83 (*q*, ^4J = 1.7, H−C(6)); 4.58 (*d*, ^3J = 2.6, H−C(3)); 3.78, 3.65 (2*s*, 2 MeOOC); 3.57 (*s*, MeO−C(2′)); 2.95 (*dd*, ^3J = 8a,8) = 3.0, ^4J(8a,9a) = 0.9, H−C(8a)); 2.56 (*q*, ^3J = 7.2, H−C(10)); 2.27 (*qd*, ^3J = 7.3, ^3J(3,4) = 2.6, H−C(4)); 1.70 (*s*, Me−C(7)); 1.49 (*s*, Me−C(2)); 1.13 (*d*, ^3J = 7.2, Me−C(10)). ^{19}F-NMR (376.7 MHz, $CDCl_3$ + CCl_3F): −71.64 (rel. to CCl_3F).

*Diethyl (1*S*,2*R*,3*S*,4*S*,4a*S*,7*R*,8*R*,8a*R*,9a*S*,10*R*,10a*R*)-3-{{{[(1′*S*,4′*R*)-7,7-Dimethyl-2-oxobicyclo[2.2.1]hept-1-yl]methyl}sulfonyl}oxy}-1,3,4,7,8,8a,9,9a-octahydro-2,4,5,7,10-pentamethyl-9-oxo-2*H,*10*H-*2,4a:7,10a-diepoxyanthracene-1,8-dicarboxylate* ((+)-**17**). A mixture of (+)-**8** (103 mg, 0.22 mmol), anh. CH_2Cl_2 (2.5 ml), Et_3N (93 µl, 0.67 mmol), DMAP (2 mg), and camphorsulfonyl chloride (168 mg, 0.67 mmol) was stirred at 20° for 30 min. After dilution with CH_2Cl_2 (20 ml), the soln. was washed with 1M aq. HCl (4 ml, 4 ×), 5% aq. Na_2CO_3 soln. (4 ml, 4 ×), and brine (4 ml, 2 ×), dried ($MgSO_4$), and evaporated. FC (petroleum ether/AcOEt 4:1) gave 120 mg (80%) of crude (+)-**17** which was crystallized from Et_2O/pentane: white crystals. M.p. 158–160°. $[\alpha]_{589}^{20}$ = +44, $[\alpha]_{577}^{20}$ = +46, $[\alpha]_{546}^{20}$ = +53, $[\alpha]_{435}^{20}$ = +97, $[\alpha]_{405}^{20}$ = +122 (*c* = 1.3, $CHCl_3$). IR (KBr): 1725, 1365, 1290, 1205. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.82 (*q*, ^4J = 1.7, H−C(6)); 4.41 (*d*, ^3J = 2.8, H−C(3)); 4.30–4.20, 4.15–4.05 (2*m*, 2 Me*C*H_2O); 3.77 (*d*, ^3J = 4.2, H−C(1)); 3.68 (*d*, ^3J = 2.8, H−C(8)); 3.61 (*d*, ^2J = 15.0, 1 H, CH_2SO_2); 3.33 (*dd*, ^3J = 4.2, ^4J = 0.7, H−C(9a)); 3.04 (*d*, ^2J = 15.0, 1 H, CH_2SO_2); 2.94 (*dd*, ^3J = 2.8, ^4J = 0.7, H−C(8a)); 2.58–2.30 (*m*, H−C(4), H−C(10), H−C(4′), H_{exo}−C(3′)); 2.20–2.00 (*m*, 2 H−C(6′)); 1.95 (*d*, ^2J = 18.0, H_{endo}−C(3′)); 1.83 (*d*, ^4J = 1.7, Me−C(5)); 1.71, 1.63 (2*s*, Me−C(2), Me−C(7)); 1.65, 1.44 (2*m*, 2 H−C(5′)); 1.33 (*d*, ^3J = 7.3, Me−C(4)); 1.31, 1.25 (2*t*, ^3J = 7.1, ^3J = 7.1, 2 *Me*CH_2O); 1.17 (*d*, ^3J = 7.1, Me−C(10)); 1.13, 0.89 (2*s*, 2 Me−C(7′)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 214.0, 204.2 (2*s*, C(9), C(2′)); 171.4, 170.5 (2*s*, *C*O−C(1), *C*O−C(8)); 147.0 (*s*, C(5)); 133.7 (*d*, ^1J(C,H) = 172, C(6)); 95.1, 92.7, 86.94, 86.88 (4*s*, C(2), C(4a), C(7), C(10a)); 86.1 (*d*, ^1J(C,H) = 159, C(3)); 61.6, 60.7 (2*t*, ^1J(C,H) = 148, ^1J(C,H) = 148, 2 Me*C*H_2O); 58.0, 47.8 (2*s*, C(1′), C(7′)); 55.1, 55.0, 52.4, 52.2, 48.7, 42.7 (6*d*, ^1J(C,H) = 135, 135, 131, 133, 129, 145, C(1), C(4), C(8), C(8a), C(9a), C(4′)); 48.2, 42.4, 26.8, 24.9 (4*t*, ^1J(C,H) = 136, 135, 133, 130, C(3′), C(5′), C(6′), CH_2SO_2); 29.6 (*d*, ^1J(C,H) = 120, *Me*−C(10)); 19.8, 19.6, 18.5, 17.3, 14.2, 14.1, 12.1, 12.0, 10.3 (9*q*, ^1J(C,H) = 126, 126, 129, 128, 127, 127, 127, 127, 128, *Me*−C(5), *Me*−C(4), 2 *Me*CH_2O, *Me*−C(2), *Me*−C(7), *Me*−C(10), 2 *Me*−C(7′)). CI-MS (NH_3): 677 (6, $[M+H]^+$), 676 (9, M^+), 631 (2, $[M-EtO]^+$), 549 (2), 461 (3), 445 (8), 415 (2), 299 (18), 217 (44), 123 (100). Anal. calc. for $C_{35}H_{48}O_{11}S$ (676.82): C 62.11, H 7.15; found: C 62.07, H 7.01.

Diethyl meso-*(1*R*,2*S*,4*S*,4a*S*,5*R*,7*R*,8*S*,8a*S*,9a*R*,10*s*,10a*R*)-1,3,4,5,6,7,8,8a,9,9a-Decahydro-2,4,5,7,10-pentamethyl-3,6,9-trioxo-2*H,*10*H-*2,4a:7,10a-diepoxyanthracene-1,8-dicarboxylate* (**18**). To a soln. of **12** (1.32 g, 2.74 mmol) in anh. CH_2Cl_2 (10 ml), pyridinium chlorochromate (2.37 g, 10.97 mmol, 4 equiv.) was added followed by finely powdered activated 3-Å molecular sieves (600 mg). The mixture was stirred at 20° under N_2 overnight, then diluted with Et_2O (20 ml), and filtered over silica gel. The filtrate was evaporated: 1.26 g (97%) of pure **18**. White solid. M.p. 200–202°. IR (KBr): 1765, 1735, 1710. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.20–4.00 (*m*, 2 Me*C*H_2O); 3.80 (*d*, ^3J = 4.2, H−C(1), H−C(8)); 3.45 (*d*, ^3J = 4.2, H−C(9a), H−C(8a)); 2.65 (*q*, ^3J = 7.3, H−C(4), H−C(5)); 2.51 (*q*, ^3J = 7.1, H−C(10)); 1.60 (*s*, Me−C(2), Me−C(7)); 1.29 (*t*, ^3J = 7.3, 2 *Me*CH_2O); 1.27 (*d*, ^3J = 7.1, Me−C(10)); 1.25 (*d*, ^3J = 7.3, Me−C(4), Me−C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 210.7

(*s*, C(3), C(6)); 204.3 (*s*, C(9)); 169.3 (*s*, *C*O–C(1), *C*O–C(8)); 91.9, 88.6 (*s*, C(2), C(7), C(4a), C(10a)); 61.8 (*t*, ^1J(C,H) = 148, 2 Me*C*H$_2$O); 52.5, 52.2, 49.1 (3*d*, ^1J(C,H) = 141, 132, 128, C(1), C(8), C(8a), C(9a), C(4), C(5)); 31.1 (*d*, ^1J(C,H) = 117, C(10)); 14.4, 14.1, 9.7 (3*q*, ^1J(C,H) = 129, 127, 129, *Me*–C(2), *Me*–C(7), *Me*–C(4), *Me*–C(5), 2 *Me*CH$_2$O); 9.3 (*q*, ^1J(C,H) = 129, *Me*–C(10)). CI-MS (NH_3): 476 (4, M^+), 448 (42), 402 (25), 359 (14), 287 (78), 329 (100), 244 (30), 202 (26), 109 (31), 91 (25). Anal. calc. for $C_{25}H_{32}O_9$ (476.52): C 63.01, H 6.77; found: C 63.10, H 6.77.

*(1*S*,2*R*,3*S*,4*S*,4a*S*,5*S*,7*S*,8*R*,8a*R*,9a*S*,10*R*,10a*S*)-8-(Ethoxycarbonyl)-1,3,4,5,6,7,8,8a,9,9a-decahydro-2,4,5,7,10-pentamethyl-6,9-dioxo-2*H*,10*H-2,4 : 7,10a-diepoxyanthracene-1,3-carbolactone* ((–)-**20**) *and* meso-*(1*R*,2*S*,3*S*,4*R*,4a*R*,5*S*,6*R*,7*R*,8*S*,8a*S*,9a*R*,10*r*,10a*S*)-1,3,4,5,6,7,8,8a,9,9a-Decahydro-2,4,5,7,10-pentamethyl-9-oxo-2*H*,10*H-2,4a : 7,10a-diepoxyanthracene-1,3 : 8,6-biscarbolactone* (**21**). The chiral oxazaborolidine **19** (or **19′**, resp.) was prepared starting from L-diphenylprolinol (200 mg, 0.774 mmol) and methylboronic acid (or butylboronic acid, resp.) (1.5 equiv.) in refluxing toluene (15 ml) in a *Dean-Stark* apparatus. After 3 h, the solvent was distilled and the residue dissolved in degassed anh. toluene to give a 0.1M soln. of **19** (or **19′**, resp.). A 0.1M soln. of **19** (0.42 ml, 0.042 mmol, 0.2 equiv.) was added under N_2 to **18** (100 mg, 0.208 mmol, 1 equiv.), and the solvent was evaporated. Then, anh. CH_2Cl_2 (1 ml) was added and the mixture cooled to $-10°$. A 10M soln. of $BH_3 \cdot Me_2S$ (21 µl, 0.21 mmol, 1 equiv.) was added, and the mixture was stirred at $-10°$ under N_2 overnight. Methanolic 1M HCl (1 ml) was then added, the flask allowed to warm to 20°, and the mixture stirred for 10 min. AcOEt was added (10 ml), the mixture washed with sat. aq. $NaHCO_3$ soln. (3 ml, 2 ×) and brine (3 ml, 2 ×), dried ($MgSO_4$), and evaporated, and the residue purified by FC (petroleum ether/AcOEt 75 : 25): 43 mg (48%) of (–)-**20**, besides **21** in variable amounts depending on the reaction conditions.

Data of (–)-**20**). Colorless foam. $[\alpha]_{589}^{20} = -50$ ($c = 1.3$, $CHCl_3$; e.e. unknown). IR (KBr): 1785, 1720, 1280, 1270, 1160, 995. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.32 (*dd*, $^3J = 8.3$, $^4J = 1.0$, H–C(3)); 4.12 (*m*, Me*C*H_2O); 3.77 (*d*, $^3J = 4.3$, H–C(8)); 3.52 (*dd*, $^4J = 1.0$, $^3J = 1.0$, H–C(1)); 3.41 (*d*, $^3J = 4.3$, H–C(8a)); 3.11 (*d*, $^3J = 1.0$, H–C(9a)); 2.64 (*q*, $^3J = 7.3$, H–C(5)); 2.42 (*q*, $^3J = 7.1$, H–C(10)); 2.40 (*dq*, $^3J = 8.3$, 8.3, H–C(4)); 1.65, 1.59 (2*s*, Me–C(2), Me–C(7)); 1.27 (*t*, $^3J = 7.2$, *Me*CH$_2$O); 1.25 (*d*, $^3J = 7.1$, Me–C(10)); 1.24 (*d*, $^3J = 7.3$, Me–C(5)); 1.06 (*d*, $^3J = 8.3$, Me–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 210.8 (*s*, C(6)); 200.9 (*s*, C(9)); 176.1, 169.2 (2*s*, *C*O–C(1), *C*O–C(8)); 93.3, 92.3, 90.4, 88.3 (4*s*, C(2), C(4a), C(7), C(10a)); 83.4 (*d*, ^1J(C,H) = 167, C(3)); 61.8 (*t*, ^1J(C,H) = 144, Me*C*H$_2$O); 54.4 (*d*, ^1J(C,H) = 133, C(9a)); 52.2 (2*d*, ^1J(C,H) = 132, 132, C(1), C(8)); 49.0 (*d*, ^1J(C,H) = 126, C(5)); 46.3 (*d*, ^1J(C,H) = 152, C(8a)); 42.4 (*d*, ^1J(C,H) = 132, C(4)); 30.7 (*d*, ^1J(C,H) = 120, C(10)); 16.5, 14.3 (2*q*, ^1J(C,H) = 128, 129, *Me*–C(2), *Me*–C(7)); 14.0 (*q*, ^1J(C,H) = 127, *Me*CH$_2$O); 9.7 (*q*, ^1J(C,H) = 128, *Me*–C(5)); 9.5 (*q*, ^1J(C,H) = 127, *Me*–C(4)); 9.0 (*q*, ^1J(C,H) = 129, *Me*–C(10)). CI-MS (NH_3): 432 (11, M^+), 404 (56), 386 (43), 362 (53), 358 (67), 340 (56), 316 (82), 275 (100), 109 (70). Anal. calc. for $C_{23}H_{28}O_8$ (432.48): C 63.88, H 6.53; found: C 63.79, H 6.64.

Data of **21**: Colorless foam. IR (KBr): 1790, 1720, 990. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.32 (*dd*, $^3J = 8.2$, $^4J =$ 1.0, H–C(3), H–C(6)); 3.48 (*dd*, $^3J = 1.5$, $^4J = 1.0$, H–C(1), H–C(8)); 3.08 (*d*, $^3J = 1.5$, H–C(9a), H–C(8a)); 2.38 (*dq*, $^3J = 8.2$, 7.5, H–C(4), H–C(5)); 2.32 (*q*, $^3J = 7.0$, H–C(10)); 1.65 (*s*, Me–C(2), Me–C(7)); 1.20 (*d*, $^3J = 7.0$, Me–C(10)); 1.05 (*d*, $^3J = 7.5$, Me–C(4), Me–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 198.0 (*s*, C(9)); 176.0 (*s*, *C*O–C(1), *C*O–C(8)); 94.0, 90.2 (*s*, C(2), C(7), C(4a), C(10a)); 83.5 (*d*, ^1J(C,H) = 167, C(3), C(6)); 54.2, 46.2, 42.4 (3*d*, ^1J(C,H) = 133, 132, 132, C(1), C(8), C(8a), C(9a), C(4), C(5)); 30.3 (*d*, ^1J(C,H) = 121, C(10)); 16.5, 9.4 (2*q*, ^1J(C,H) = 128, 127, *Me*–C(2), *Me*–C(7), *Me*–C(4), *Me*–C(5)); 8.6 (*q*, ^1J(C,H) = 129, *Me*–C(10)). CI-MS (NH_3): 388 (36, M^+), 370 (20, $[M - H_2O]^+$), 344 (35), 331 (59), 315 (23), 304 (41), 125 (58), 109 (100), 79 (27).

*Diethyl (1*S*,2*R*,4*R*,4a*R*,7*R*,8*R*,8a*R*,9a*S*,10*R*,10a*R*)-1,3,4,7,8,8a,9,9a-Octahydro-2,4,5,7,10-pentamethyl-3,9-dioxo-2*H*,10*H-2,4a : 7,10a-diepoxyanthracene-1,8-dicarboxylate* ((+)-**22**). To a soln. of (+)-**8** (1.23 g, 2.7 mmol) in anh. CH_2Cl_2 (5 ml), pyridinium chlorochromate (0.86 g, 4.0 mmol, 1.5 equiv.) and activated 3-Å molecular sieves (600 mg) were added, and the mixture was stirred at 20° under N_2 overnight. Et_2O (20 ml) was added and the mixture filtered through silica gel, washing thoroughly with Et_2O. Evaporation gave 1.12 g (91%) of pure (+)-**22**, as white solid. An anal. pure sample was obtained by FC (petroleum ether/AcOEt 8 : 2). Colorless crystals. M.p. 166–168°. $[\alpha]_{589}^{20} = +30$, $[\alpha]_{577}^{20} = +30$, $[\alpha]_{546}^{20} = +33$, $[\alpha]_{435}^{20} = +44$, $[\alpha]_{405}^{20} = +43.0$ ($c = 0.6$, $CHCl_3$; e.e. *ca.* 78%). IR (KBr): 2985, 2940, 1750, 1730, 1700, 1460, 1370, 1280, 1220, 1190, 1155,1135, 1085, 1055, 975, 935, 880, 850, 820, 705, 640. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.84 (*q*, $^4J = 1.7$, H–C(6)); 4.18–4.05 (*m*, 2 Me*C*H_2O); 3.76 (*d*, $^3J = 4.4$, H–C(1)); 3.68 (*d*, $^3J = 2.8$, H–C(8)); 3.42 (*dd*, $^3J = 4.4$, $^4J = 0.9$, H–C(9a)); 2.97 (*dd*, $^3J = 2.8$, $^4J = 0.9$, H–C(8a)); 2.68, 2.65 (2*q*, $^3J = 7.0$, 7.2, H–C(4), H–C(10)); 1.85 (*d*, $^4J = 1.7$, Me–C(5)); 1.72, 1.58 (2*s*, Me–C(2), Me–C(7)); 1.27, 1.25 (2*t*, $^3J = 7.0$, 2 *Me*CH$_2$O); 1.27, 1.20 (2*d*, $^3J = 7.2$, 7.0, Me–C(4), Me–C(10)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 211.4 (*s*, C(3)); 204.1 (*s*, C(9)); 171.3, 169.6 (2*s*, *C*O–C(1), *C*O–C(8)); 146.8 (*s*, C(5)); 133.9 (*d*, ^1J(C,H) = 172, C(6)); 94.7, 91.4, 88.6, 87.1 (4*s*, C(2), C(4a), C(7), C(10a)); 61.6, 60.8

(2*t*, ^1J(C,H) = 148, 148, 2 Me*C*H$_2$O); 55.5, 55.1, 52.8, 52.7, 48.8 (5*d*, ^1J(C,H) = 138, 135, 127, 137, 129, C(1), C(4), C(8), C(8a), C(9a)); 30.2 (*d*, ^1J(C,H) = 120, C(10)); 18.5 (*q*, ^1J(C,H) = 127, *Me*–C(5)); 14.4 (*q*, ^1J(C,H) = 129, *Me*–C(2)); 14.1, 14.0 (2*q*, ^1J(C,H) = 127, 127, 2 *Me*CH$_2$O); 12.1 (*q*, ^1J(C,H) = 127, *Me*–C(7)); 10.3, 9.6 (2*q*, ^1J(C,H) = 129, 129, *Me*–C(4), *Me*–C(10)). CI-MS (NH_3): 460 (25, M^+), 415 (12, $[M - EtO]^+$), 368 (3), 333 (22), 305 (15), 263 (11), 233 (20), 191 (10), 123 (100), 99 (15). Anal. calc. for $C_{25}H_{32}O_8$ (460.52): C 65.20, H 7.00; found: C 65.09, H 6.90.

*(1*S*,2*R*,3*R*,4*S*,4a*S*,7*R*,8*R*,8a*R*,9a*S*,10*R*,10a*R*)-8-(Ethoxycarbonyl)-1,3,4,7,8,8a,9,9a-octahydro-2,4,5,7,10-pentamethyl-9-oxo-2*H*,10*H*,2,4a:7,10a-diepoxyanthracene-1,3-carbolactone* ((−)-**23**). To a suspension of (+)-**22** (471 mg, 1.02 mmol) in anh. MeOH (0.3 ml), AcOH (1 ml) was added followed by $NaBH_3CN$ (257 mg, 4.10 mmol, 4 equiv.). The soln. was stirred at 20° for 5 h. H_2O (20 ml) was added and the mixture extracted with CH_2Cl_2 (20 ml, 3 ×). The org. layer was washed with sat. aq. $NaHCO_3$ soln. (10 ml, 2 ×) and then dried ($MgSO_4$). Evaporation and FC of the residue (petroleum ether/AcOEt 5:2) gave 274 mg (64%) of (−)-**23**, besides a 2nd fraction (50 mg, 12%) of the product of 9-keto reduction, see below.

Data of (−)-**23**: Colorless solid. M.p. 163–165°. $[\alpha]_{589}^{20} = -37$, $[\alpha]_{577}^{20} = -39$, $[\alpha]_{546}^{20} = -47$, $[\alpha]_{435}^{20} = -97$, $[\alpha]_{405}^{20} = -130$ (*c* = 1.5, $CHCl_3$; e.e. *ca.* 78%). IR (KBr): 2985, 1785, 1720, 1460, 1390, 1350, 1255, 1225, 1190, 1155, 1095, 1050, 990, 960, 925, 885, 735. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.83 (*q*, ^4J = 1.7, H–C(6)); 4.31 (*d*, ^3J = 8.2, ^4J = 1.0, H–C(3)); 4.10 (*q*, ^3J = 7.0, MeC*H*$_2$O); 3.69 (*d*, ^3J = 3.0, H–C(8)); 3.52 (*dd*, ^3J = 1.0, ^4J = 1.0, H–C(1)); 3.10 (*dd*, ^3J = 1.0, ^4J = 0.7, H–C(9a)); 2.95 (*dd*, ^3J = 3.0, ^4J = 0.7, H–C(8a)); 2.60 (*q*, ^3J = 7.1, H–C(10)); 2.38 (*qd*, ^3J = 7.5, 8.2, H–C(4)); 1.82 (*d*, ^4J = 1.7, Me–C(5)); 1.72, 1.64 (2*s*, Me–C(2), Me–C(7)); 1.25 (*t*, ^3J = 7.0, *Me*CH$_2$O); 1.14 (*d*, ^3J = 7.1, Me–C(10)); 1.08 (*d*, ^3J = 7.5, Me–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 200.7 (*s*, C(9)); 176.3, 170.9 (2*s*, *C*O–C(1), *C*O–C(8)); 146.7 (*s*, C(5)); 133.3 (*d*, ^1J(C,H) = 172, C(6)); 95.0, 92.8, 90.0, 86.5 (4*s*, C(2), C(4a), C(7), C(10a)); 83.4 (*d*, ^1J(C,H) = 166, C(3)); 60.4 (*t*, ^1J(C,H) = 147, MeC*H*$_2$O); 55.0, 54.7, 54.5, 45.9, 41.9 (5*d*, ^1J(C,H) = 135, 133, 138, 152, 133, C(1), C(4), C(8), C(8a), C(9a)); 29.4 (*d*, ^1J(C,H) = 120, C(10)); 18.2, 16.3, 13.8, 11.7, 9.7, 9.0 (6*q*, ^1J(C,H) = 127, 128, 127, 127, 129, 127, *Me*–C(2), *Me*–C(4), *Me*–C(5), *Me*–C(7), *Me*–C(10), *Me*CH$_2$O). CI-MS (NH_3): 416 (40, M^+), 371 (10, $[M - EtO]^+$), 289 (100), 147 (6), 123 (52), 71 (11). Anal. calc. for $C_{23}H_{28}O_7$ (416.47): C 66.33, H 6.78; found: C 66.45, H 6.92.

*Data of (1*S*,2*R*,3*R*,4*S*,4a*S*,7*R*,8*R*,8a*S*,9*S*,9a*R*,10*R*,10a*R*)-8-(Ethoxycarbonyl)-1,3,4,7,8,8a,9,9a-octahydro-9-hydroxy-2,4a,5,7,10-pentamethyl-2*H*,10*H*-2,4:7,10a-diepoxyanthracene-1,3-carbolactone* (2nd fraction): White solid. M.p. 198–200° (dec.). IR (KBr): 3500, 1780, 1720. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.93 (*q*, ^4J = 1.5, H–C(6)); 4.32 (*dd*, ^3J = 8.1, ^4J = 0.8, H–C(3)); 4.12–4.05 (*m*, MeC*H*$_2$O); 3.82 (*ddd*, ^3J = 12.5, 4.0, 4.0, H–C(9), OH); 3.45 (*d*, ^3J = 2.8, H–C(8)); 2.93 (*dd*, ^3J = 1.6, ^4J = 0.8, H–C(1)); 2.87 (*d*, ^3J = 12.5, OH); 2.41 (*dd*, ^3J = 1.6, 4.0, H–C(9a)); 2.26 (*q*, ^3J = 7.2, H–C(10)); 2.26 (*dq*, ^3J = 8.1, 7.2, H–C(4)); 2.20 (*dd*, ^3J = 2.8, 4.0, H–C(8a)); 1.74 (*d*, ^4J = 1.5, Me–C(5)); 1.73, 1.65 (2*s*, Me–C(2), Me–C(7)); 1.25 (*t*, ^3J = 7.1, *Me*CH$_2$O); 1.10 (*d*, ^3J = 7.2, Me–C(10)); 0.96 (*d*, ^3J = 7.2, Me–C(4)). ^{13}C-NMR (69.9 MHz, $CDCl_3$): 177.8, 171.9 (2*s*, 2 COO); 146.8 (*s*, C(5)); 134.5 (*d*, ^1J(C,H) = 167, C(6)); 90.4, 90.2, 88.4, 86.3 (4*s*, C(2), C(4a), C(7), C(10a)); 84.1 (*d*, ^1J(C,H) = 166, C(3)); 69.2 (*d*, ^1J(C,H) = 146, C(9)); 60.5 (*t*, ^1J(C,H) = 147, MeC*H*$_2$O); 56.0, 50.2, 46.5, 44.6, 42.1 (5*d*, ^1J(C,H) = 136, 150, 135, 135, 134, C(1), C(4), C(8), C(8a), C(9a)); 29.6 (*d*, ^1J(C,H) = 119, C(10)); 18.3, 16.1, 12.0, 9.7, 8.9 (5*q*, ^1J(C,H) = 127, 127, 127, 128, 127, *Me*–C(2), *Me*–C(4), *Me*–C(5), *Me*–C(7), *Me*–C(10)); 14.2 (*q*, ^1J(C,H) = 127, *Me*CH$_2$O). CI-MS (NH_3): 418 (9, M^+), 400 (10, $[M - H_2O]^+$), 372 (8), 355 (14), 327 (7), 289 (72), 276 (11), 249 (4), 196 (5), 123 (100). Anal. calc. for $C_{23}H_{30}O_7$ (418.49): C 66.01, H 7.23; found: C 65.91, H 7.28.

*(1*S*,2*R*,3*R*,4*S*,4a*S*,5*R*,6*R*,7*S*,8*R*,8a*R*,9a*S*,10*S*,10a*R*)-8-(Ethoxycarbonyl)-1,3,4,5,6,7,8,8a,9,9a-decahydro-6-hydroxy-2,4,5,7,10-pentamethyl-9-oxo-2*H*,10*H*-2,4a:7,10a-diepoxyanthracene-1,3-carbolactone* ((−)-**24**), *(1*R*,2*S*,3*R*,4*R*,4a*S*,5*R*,6*R*,7*R*,8*S*,9a*R*,10*R*)-1-(Ethoxycarbonyl)-1,3,4,5,6,7,8,9,9a,10-decahydro-3,7-dihydroxy-2,4,5,7,10-pentamethyl-9-oxo-2*H*-2,4a-epoxyanthracene-8,6-carbolactone* ((−)-**25**), *and Diethyl (1*S*,2*R*,4*R*,4a*R*,5*R*,6*R*,7*S*,8*R*,8a*R*,9a*S*,10*S*,10a*R*)-1,3,4,5,6,7,8,8a,9,9a-Decahydro-6-hydroxy-2,4,5,7,10-pentamethyl-3,9-dioxo-2*H*,10*H*-2,4a:7,10a-diepoxyanthracene-1,8-dicarboxylate* (**26**). *a*) To a cooled (−78°) soln. of (+)-**22** (27 mg, 0.059 mmol) in anh. THF (0.5 ml), 10M $BH_3 \cdot Me_2S$ (18 µl) was added. The mixture was allowed to react at 20° for 2 h. H_2O (1 ml) was added, together with THF (0.5 ml) and $NaBO_3 \cdot 4\,H_2O$ (30 mg, 0.19 mmol), and the mixture was stirred at 20° for 20 h. After extraction with AcOEt (3 ml, 5 ×), washing with brine (2 ml, 2 ×), and evaporation, FC (AcOEt/petroleum ether 2:1) gave 8 mg (31%) of (−)-**25**, and **26** as a by-product which sometimes prevailed.

b) To a soln. of (−)-**23** (25 mg, 0.06 mmol) in anh. THF (1 ml), 10M $BH_3 \cdot Me_2S$ (12 µl) was added. The mixture was stirred at 20° for 6.5 h under N_2. H_2O (0.5 ml) was added, together with $NaBO_3 \cdot 4\,H_2O$ (55 mg, 0.36 mmol, 6 equiv.), and the mixture was stirred overnight. Extraction with AcOEt (3 ml, 5 ×), washing with

brine (2 ml, 2 ×), evaporation and FC (AcOEt/petroleum ether 2:1) yielded 16 mg (57%) of (−)-**25**, besides variable amounts of (−)-**24** depending on the reaction conditions.

*Data of (−)-***24**: White solid. M.p. 208–210° (dec.). $[\alpha]_{589}^{20} = -42$ ($c = 1.2$, $CHCl_3$; e.e. *ca.* 78%). IR (KBr): 3500, 1770, 1720. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.29 (*dd*, $^3J = 8.1$, $^4J = 0.8$, H–C(3)); 4.17 (*q*, $^3J = 7.1$, Me*CH*$_2$O); 3.72 (*d*, $^3J = 4.2$, H–C(8)); 3.49 (*dd*, $^4J = 0.8$, $^3J = 1.0$, H–C(1)); 3.35 (*d*, $^3J = 2.5$, H–C(6)); 3.27 (*d*, $^3J = 4.2$, H–C(8a)); 3.07 (*d*, $^3J = 1.0$, H–C(9a)); 2.36 (*dq*, $^3J = 8.1$, 7.6, H–C(4)); 2.27 (*q*, $^3J = 6.9$, H–C(10)); 2.06 (*qd*, $^3J = 7.4$, $^3J = 2.5$, H–C(5)); 1.63, 1.59 (2*s*, Me–C(2), Me–C(7)); 1.28 (*t*, $^3J = 7.1$, *Me*CH$_2$O); 1.24 (*d*, $^3J = 7.4$, Me–C(5)); 1.22 (*d*, $^3J = 6.9$, Me–C(10)); 1.04 (*d*, $^3J = 7.6$, Me–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 201.7 (*s*, C(9)); 176.4, 170.6 (2*s*, *C*O–C(1), *C*O–C(8)); 93.9, 93.2, 90.2, 87.6 (4*s*, C(2), C(4a), C(7), C(10a)); 83.6 (*d*, ^1J(C,H) = 166, C(3)); 78.7 (*d*, ^1J(C,H) = 154, C(6)); 61.3 (*t*, ^1J(C,H) = 148, Me*C*H$_2$O); 54.4, 51.9, 51.7, 51.4, 46.2, 42.4 (6*d*, ^1J(C,H) = 133, 132, 130, 137, 152, 131, C(1), C(4), C(5), C(8), C(8a), C(9a)); 30.1 (*d*, ^1J(C,H) = 121, C(10)); 16.6, 16.5, 12.8, 9.5, 8.9 (5*q*, ^1J(C,H) = 128, 128, 126, 127, 129, *Me*–C(2), *Me*–C(4), *Me*–C(5), *Me*–C(7), *Me*–C(10)); 14.1 (*q*, ^1J(C,H) = 127, *Me*CH$_2$O). CI-MS (NH_3): 434 (2, M^+), 416 (13, $[M - H_2O]^+$), 389 (15, $[M - EtO]^+$), 343 (20), 303 (100), 277 (21), 171 (33), 130 (76), 85 (27). Anal. calc. for $C_{23}H_{30}O_8$ (434.48): C 63.58, H 6.96; found: C 63.54, H 6.91.

*Data of (−)-***25**:White solid. M.p. 204–205°. $[\alpha]_{589}^{20} = -18$, $[\alpha]_{577}^{20} = -18$, $[\alpha]_{546}^{20} = -21$, $[\alpha]_{435}^{20} = -41$, $[\alpha]_{405}^{20} = -59$ ($c = 1.2$, $CHCl_3$; e.e. *ca.* 78%). UV (MeCN): 248 (7000), 193 (4300). IR (KBr): 3445, 2925, 1785, 1725, 1665, 1620, 1460, 1380, 1340, 1240, 1185, 1060, 965, 890. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.20 (*m*, Me*CH*$_2$O); 4.15 (*dd*, $^3J = 2.7$, $^4J = 1.4$, H–C(6)); 3.91 (*d*, $^4J = 1.4$, H–C(8)); 3.40 (*d*, $^3J = 2.6$, H–C(3)); 3.33 (*d*, $^3J = 4.1$, H–C(1)); 3.23 (*d*, $^3J = 4.1$, H–C(9a)); 3.02 (*qd*, $^3J = 7.5$, $^3J = 2.7$, H–C(5)); 2.75 (*q*, $^3J = 7.4$, H–C(10)); 1.99 (*qd*, $^3J = 7.4$, $^3J = 2.6$, H–C(4)); 1.55, 1.53 (2*s*, Me–C(2), Me–C(7)); 1.32 (*d*, $^3J = 7.4$, Me–C(10)); 1.30 (*t*, $^3J = 7.0$, *Me*CH$_2$O); 1.29 (*d*, $^3J = 7.5$, Me–C(5)); 1.17 (*d*, $^3J = 7.4$, Me–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 195.1 (*s*, C(9)); 173.2, 170.5 (2*s*, *C*O–C(1), *C*O–C(8)); 159.5 (*s*, C(10a)); 124.7 (*s*, C(8a)); 88.4, 87.3 (2*s*, C(2), C(4a)); 84.8 (*d*, ^1J(C,H) = 157, C(6)); 78.7 (*d*, ^1J(C,H) = 147, C(3)); 72.3 (*s*, C(7)); 61.4 (*t*, ^1J(C,H) = 148, Me*C*H$_2$O); 54.7, 51.1, 49.0, 45.9 (4*d*, ^1J(C,H) = 137, 131, 133, 152, C(1), C(4), C(8), C(9a)); 34.5, 31.8 (2*d*, ^1J(C,H) = 125, 124, C(5), C(10)); 24.1, 16.5, 14.2, 12.59, 12.58, 12.57 (6*q*, ^1J(C,H) = 127, 124, 127, 127, 127, 127, *Me*–C(2), *Me*–C(4), *Me*–C(5), *Me*–C(7), *Me*–C(10), *Me*CH$_2$O). CI-MS (NH_3): 435 (15, M^+), 389 (13), 375 (9), 359 (8), 329 (9), 305 (100), 159 (45), 231 (28), 186 (11), 125 (14), 71 (25). Anal. calc. for $C_{23}H_{30}O_8$ (434.48): C 63.58, H 6.96; found: C 63.66, H 7.12.

Data of **26**: Colorless foam. IR (KBr): 3500, 1765, 1725, 1450, 1370, 1265, 1050. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.20–4.10 (*m*, 2 Me*CH*$_2$O); 3.80 (*d*, $^3J = 4.2$, H–C(1)); 3.75 (*d*, $^3J = 4.2$, H–C(8)); 3.40 (*dd*, $^3J = 4.2$, $^4J = 0.7$, H–C(9a)); 3.37 (*d*, $^3J = 2.5$, H–C(6)); 3.31 (*dd*, $^3J = 4.2$, $^4J = 0.7$, H–C(8a)); 2.62 (*q*, $^3J = 7.3$, H–C(4)); 2.38 (*q*, $^3J = 7.1$, H–C(10)); 2.08 (*dq*, $^3J = 2.5$, 7.3, H–C(5)); 1.61, 1.59 (2*s*, Me–C(2), Me–C(7)); 1.30 (*d*, $^3J = 7.2$, 2 *Me*CH$_2$O); 1.26 (*d*, $^3J = 7.1$, Me–C(10)); 1.24 (2*d*, $^3J = 7.3$, 7.3, Me–C(4), Me–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 211.3 (*s*, C(3)); 204.8 (*s*, C(9)); 170.7, 169.5 (2*s*, *C*O–C(1), *C*O–C(8)); 92.8, 92.5, 88.4, 87.9 (4*s*, C(2), C(4a), C(7), C(10a)); 78.7 (*d*, ^1J(C,H) = 147, C(6)); 61.7, 61.3 (2*t*, ^1J(C,H) = 148, 148, 2 Me*C*H$_2$O); 52.1, 52.0, 51.9, 51.8, 51.5, 49.1 (6*d*, ^1J(C,H) = 132, 132, 132, 132, 136, 127, C(1), C(4), C(5), C(8), C(8a), C(9a)); 30.6 (*d*, ^1J(C,H) = 120, C(10)); 16.6, 14.4, 14.2, 14.0, 12.8, 9.7, 9.2 (7*q*, ^1J(C,H) = 127, 126, 127, 127, 126, 129, 129, *Me*–C(5), *Me*–C(2), *Me*–C(7), *Me*–C(4), *Me*–C(10), 2 *Me*CH$_2$O). CI-MS (NH_3): 496 (49, $[M + H_2O]^+$), 479 (47, $[M + H]^+$), 478 (18, M^+), 461 (100, $[M - OH]^+$), 450 (65), 433 (55, $[M - EtO]^+$), 408 (71), 387 (25), 359 (30), 321 (47), 275 (35), 109 (46).

*(1*R*,2*S*,3*R*,4*R*,4a*S*,5*R*,6*R*,7*R*,8*S*,9a*R*,10*R*)-7-(Benzoyloxy)-1-(ethoxycarbonyl)-1,3,4,5,6,7,8,9,9a,10-decahydro-2,4,5,7,10-pentamethyl-9-oxo-3-(2,2-dimethyl-1-oxopropoxy)-2*H*-2,4a-epoxyanthracene-8,6-carbolactone* (**27**). To a soln. of (−)-**25** (50 mg, 0.12 mmol) in anh. CH_2Cl_2 (1.5 ml), anh. Et_3N (36 µl, 0.26 mmol) was added, together with a cat. amount of DMAP and *t*-BuCOCl (16 µl). The mixture was stirred at 20° overnight, then diluted with CH_2Cl_2 (15 ml), and washed with 1M aq. HCl (4 ml, 2 ×), 5% aq. Na_2CO_3 soln. (4 ml, 2 ×), and brine (4 ml, 2 ×). The org. layer was dried ($MgSO_4$) and evaporated. FC (petroleum ether/AcOEt 7:3) afforded 35 mg (59%) of the product with a protected secondary-alcohol and a free tertiary-alcohol moiety, which was not characterized. This product was dissolved in anh. CH_2Cl_2 (1 ml), pyridine (33 µl, 0.41 mmol) was added and the soln. cooled to −78° before the addition of $PhCOOSO_2CF_3$ (46 µl, 0.27 mmol) (which was previously prepared from PhCOCl and CF_3SO_3H). The mixture was allowed to react at −78° for 30 min and then at 20° for 1.5 h. H_2O (6 ml) was added and the mixture extracted with AcOEt (6 ml, 3 ×). The org. layer was washed with sat. aq. $NaHCO_3$ soln. (3 ml, 2 ×) and brine (3 ml, 2 ×), dried ($MgSO_4$), and evaporated. FC (petroleum ether/AcOEt 4:1): 13 mg (31%) of **27**. Colorless oil. UV (MeCN): 238 (13000), 199 (9800). CD (MeCN): $\Delta\varepsilon_{247} = +14.7$, $\Delta\varepsilon_{213} = -5.5$. IR (KBr): 1805, 1730, 1670, 1285, 1160. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.85 (*dd*, $^3J = 27.5$, $^4J = 1.2$, 2 H_o); 7.56 (*tt*, $^3J = 7.5$, $^4J = 1.2$, H_p); 7.37 (*dd*, $^3J = 7.5$, 2 H_m); 4.91 (*dd*, $^3J = 2.8$, $^4J = 1.2$,

H–C(6)); 4.41 (*d*, ^3J = 2.7, H–C(3)); 4.37 (*d*, ^4J = 1.2, H–C(8)); 4.23 (*q*, ^3J = 7.1, MeCH_2O); 3.33, 3.29 (2*d*, ^3J = 4.0, 4.0, H–C(1), H–C(9a)); 2.81 (*qd*, ^3J = 7.3, 2.8, H–C(5)); 2.66 (*q*, ^3J = 7.3, H–C(10)); 1.95 (*qd*, ^3J = 7.4, 2.7, H–C(4)); 1.83 (*s*, Me–C(7)); 1.46 (*s*, Me–C(2)); 1.31 (*t*, ^3J = 7.1, *Me*CH$_2$O); 1.28 (*d*, ^3J = 7.3, Me–C(5)); 1.18 (*d*, ^3J = 7.4, Me–C(4)); 1.16 (*s*, *t*-Bu); 0.95 (*d*, ^3J = 7.3, Me–C(10)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 194.6 (*s*, C(9)); 177.8, 171.5, 170.2, 165.3 (4*s*, *C*O–C(1), *C*O–C(8), *C*O(Piv), *C*O(Bz)); 159.0 (*s*, C(10a)); 133.7 (*d*, ^1J(C,H) = 163, C_p); 129.8, 128.4 (2*d*, ^1J(C,H) = 164, 163, 2 C_m, 2 C_o); 128.9 (*s*, arom. C); 124.5 (*s*, C(8a)); 88.3, 86.1 (2*s*, C(2), C(4a)); 83.2, 79.8 (2*d*, ^1J(C,H) = 167, 147, C(3), C(6)); 79.1 (*s*, C(7)); 61.5 (*t*, ^1J(C,H) = 148, Me*C*H$_2$O); 55.7, 49.1, 48.5, 45.1, 34.7, 31.4 (6*d*, ^1J(C,H) = 138, 133, 134, 159, 128, 125, C(1), C(4), C(5), C(8), C(9a), C(10)); 38.7 (*s*, Me$_3$*C*); 27.0 (*q*, ^1J(C,H) = 127, *Me*$_3$C); 20.1, 16.5, 14.2, 12.6, 12.5, 12.3 (6*q*, ^1J(C,H) = 129, 128, 127, 127, 127, 129, *Me*–C(2), *Me*–C(4), *Me*–C(5), *Me*–C(7), *Me*–C(10), *Me*CH$_2$O). CI-MS (NH_3): 623 (4, M^+), 537 (4), 479 (5), 355 (2), 297 (6), 166 (6), 105 (100), 77 (28). Anal. calc. for $C_{35}H_{42}O_{10}$ (622.71): C 67.51, H 6.80; found: C 67.45, H 6.87.

meso-*(1*R,*2*S,*4a*R,*7*R,*8*S,*8a*S,*9*r,*9a*R,*10*s,*10a*S*)-1,7,8,8a,9,9a-Hexahydro-9-hydroxy-2,4,5,7,10-pentamethyl-2*H,*10*H-*2,4a:7,10a-diepoxyanthracene-1,8-dimethanol* (**28**) *and* meso-*(1*R,*2*S,*4a*R,*7*R,*8*S,*8a*S,*9*s,*9a*R,*10*s,*10a*S*)-1,7,8,8a,9,9a-Hexahydro-9-hydroxy-2,4,5,7,10-pentamethyl-2*H,*10*H-*2,4a:7,10a-diepoxyanthracene-1,8-dimethanol* (**29**). To a soln. of **7** (7.5 g, 16.87 mmol) in anh. THF (300 ml), 1M $LiAlH_4$ in THF (25.4 ml, 25.4 mmol, 1.5 equiv.) was added dropwise under N_2. The mixture was stirred at 25°. After 3 h, 2 ml of 1M $LiAlH_4$ in THF were added. After 1 more hour, 2 more ml of 1M $LiAlH_4$ in THF were added. After 5 h from the beginning, the mixture was cooled to 0°, and H_2O (1.16 ml) was added dropwise (→ gel). Then 15% aq. NaOH soln. (1.16 ml) was added dropwise under vigorous stirring, and the gel dissolved. H_2O (3.35 ml) was then added and the mixture allowed to warm to 20°. After 1 h stirring, the suspension was filtered into an extractor and the precipitate continuously extracted with THF overnight. The extract was evaporated and the residue (6.7 g) employed without any purification in the following step. An anal. sample was obtained by crystallization from MeOH/Et_2O. When the reaction was run in THF under reflux, a mixture of the two diastereoisomers **28** and **29** in a 1.5:1 ratio was obtained.

Data of **28**: White solid. M.p. 232–234°. IR (KBr): 3295, 1440, 1375, 1140, 1095, 1015. ^{1}H-NMR (400 MHz, CD_3OD): 6.03 (*q*, ^4J = 1.7, H–C(3), H–C(6)); 3.89 (*t*, ^3J = 3.7, H–C(9)); 3.40 (*m*, 2 CH_2OH); 2.71 (*dt*, ^3J = 3.0, 7.9, H–C(1), H–C(8)); 2.66 (*q*, ^3J = 7.4, H–C(10)); 1.85 (*d*, ^4J = 1.7, Me–C(4), Me–C(5)); 1.58 (*s*, Me–C(2), Me–C(7)); 1.42 (*dd*, ^3J = 3.0, 3.0, H–C(8a), H–C(9a)); 1.02 (*d*, ^3J = 7.4, Me–C(10)). ^{13}C-NMR (100.6 MHz, CD_3OD): 147.8 (*s*, C(4), C(5)); 135.3 (*d*, ^1J(C,H) = 170, C(3), C(6)); 91.0, 87.7 (2*s*, C(2), C(7), C(4a), C(10a)); 70.3 (*d*, ^1J(C,H) = 149, C(9)); 65.5 (*t*, ^1J(C,H) = 140, CH_2–C(1), CH_2–C(8)); 55.0, 46.8 (2*d*, ^1J(C,H) = 134, ^1J(C,H) = 132, C(1), C(8), C(9a), C(8a)); 30.4 (*d*, ^1J(C,H) = 119, C(10)); 19.0 (*q*, ^1J(C,H) = 128, *Me*–C(4), *Me*–C(5)); 12.2 (*q*, ^1J(C,H) = 124, *Me*–C(2), *Me*–C(7)); 11.6 (*q*, ^1J(C,H) = 128, *Me*–C(10)). CI-MS (NH_3): 380 (3.2, $[M + H_2O]^+$), 363 (100, $[M + H]^+$), 362 (70, M^+), 345 (7, $[M - OH]^+$), 344 (7, $[M - H_2O]^+$), 123 (16). Anal. calc. for $C_{21}H_{30}O_5$ (362.46): C 69.59, H 8.34; found: C 69.55, H 8.31.

Data of **29**: ^{1}H-NMR (400 MHz, CD_3OD): 5.95 (*q*, ^4J = 1.5, H–C(3), H–C(6)); 3.52 (*dd*, ^2J = 11.4, ^3J = 6.7, 2 H, 2 CH_2O); 3.44 (*t*, ^3J = 10.0, H–C(9)); 3.29 (*dd*, ^2J = 11.4, ^3J = 9.0, 2 H, 2 CH_2O); 2.50 (*q*, ^3J = 7.4, H–C(10)); 2.07 (*m*, H–C(1), H–C(8)); 1.85 (*d*, ^4J = 1.5, Me–C(4), Me–C(5)); 1.59 (*s*, Me–C(2), Me–C(7)); 1.05–1.00 (*m*, Me–C(10), H–C(8a), H–C(9a)).

meso-*(1*R,*2*S,*4a*R,*7*R,*8*S,*8a*S,*9*r,*9a*R,*10*s,*10a*S*)-1,7,8,8a,9,9a-Hexahydro-9-hydroxy-2,4,5,7,10-pentamethyl-2*H,*10*H-*2,4a:7,10a-diepoxyanthracene-1,8-dimethanol 1,8-Diacetate* (**30**). To a soln. of unpurified **28** (6.7 g, obtained from 7.5 g of **7**) in anh. CH_2Cl_2 (250 ml), anh. pyridine (8.1 ml, 101 mmol, 6 equiv.) and Ac_2O (3.2 ml, 34 mmol, 2 equiv.) were added, followed by DMAP (20 mg). The mixture was stirred at 20° overnight. Ac_2O (0.9 ml in 3 portions) and DMAP (10 mg, 2×) were added. After 21 h from the beginning, no more monoacetylated product could be detected by TLC. The mixture was diluted with CH_2Cl_2 (100 ml) and washed with 0.5M aq. HCl (80 ml, 3×) and brine (80 ml, 3×). The org. phase was dried ($MgSO_4$) and evaporated: 7.88 g of **30**, which was reacted further without any purification. An anal. pure sample was obtained by FC (petroleum ether/AcOEt 7:3). White solid. M.p. 171–172°. IR (KBr): 3520, 3060, 2995, 2945, 2880, 2360, 1640, 1340. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.97 (*q*, ^4J = 1.5, H–C(3), H–C(6)); 3.93–3.82 (*m*, 2 CH_2OAc, H–C(9)); 2.98 (*d*, ^3J = 12.0, OH); 2.93 (*dt*, ^3J = 7.8, 3.0, H–C(1), H–C(8)); 2.51 (*q*, ^3J = 7.4, H–C(10)); 2.05 (*s*, 2 MeCO); 1.79 (*d*, ^4J = 1.5, Me–C(4), Me–C(5)); 1.57 (*s*, Me–C(2), Me–C(7)); 1.36 (*dd*, ^3J = 3.7, 3.0, H–C(8a), H–C(9a)); 1.05 (*d*, ^3J = 7.4, Me–C(10)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.0 (*s*, 2 CO); 146.7 (*s*, C(4), C(5)); 134.2 (*d*, ^1J(C,H) = 170, C(3), C(6)); 89.3, 86.1 (2*s*, C(2), C(7), C(4a), C(10a)); 68.0 (*d*, ^1J(C,H) = 147, C(9)); 66.7 (*t*, ^1J(C,H) = 147, 2 *C*H$_2$OAc); 49.8 (*d*, ^1J(C,H) = 137, C(1), C(8)); 46.0 (*d*, ^1J(C,H) = 130, C(9a), C(8a)); 29.1 (*d*, ^1J(C,H) = 114, C(10)); 20.9 (*q*, ^1J(C,H) = 129, 2 *Me*CO); 18.3 (*q*, ^1J(C,H) = 126, *Me*–C(2), *Me*–C(7)); 12.2 (*q*, ^1J(C,H) = 124, *Me*–C(4), *Me*–C(5)); 11.2 (*q*, ^1J(C,H) = 124, *Me*–C(10)). CI-MS (NH_3): 447 (13,

$[M+H]^+$), 429 (11), 241 (12), 203 (10), 124 (16), 123 (100). Anal. calc. for $C_{25}H_{34}O_7$ (446.54): C 67.24, H 7.67; found: C 67.13, H 7.65.

meso-*(1*R*,2*R*,3*S*,4*S*,4a*R*,5*R*,6*R*,7*S*,8*S*,8a*S*,9*r*,9a*R*,10*s*,10a*S*)-1,8-Bis(acetoxymethyl)-1,3,4,5,6,7,8,8a,9,9a-decahydro-2,4,5,7,10-pentamethyl-2*H,*10*H-2,4a:7,10a-diepoxyanthracene-3,6,9-triol* (**31**). $BH_3 \cdot Me_2S$ (3.4 ml, 33.7 mmol) was added to a soln. of **30** (7.88 g, obtained from 7.5 g of **7**) in anh. THF (350 ml) stirred at $-78°$. The mixture was allowed to warm to 20°. After 4.5 h, the mixture was cooled to 0°, and H_2O (300 ml) was added dropwise under stirring, followed by $NaBO_3 \cdot 4\ H_2O$ (15.6 g, 101 mmol, 6 equiv.). The mixture was stirred at 20° overnight. The excess of $NaBO_3 \cdot 4\ H_2O$ was filtered off and washed with AcOEt. The aq. phase was continuously extracted with AcOEt. Evaporation and FC (AcOEt → AcOEt/MeOH 1:1, column 70 × 150 mm, 80-ml fractions) gave 5.9 g of **31** (72% from **7** (3 steps)). Purification by recrystallization from MeOH gave a white solid. M.p. 211–213°. IR (KBr): 3415, 1740, 1245, 1035. ^{1}H-NMR (400 MHz, CD_3OD): 4.27 (*dd*, ^2J = 11.3, ^3J = 8.6, 2 H, 2 CH_2OAc); 4.17 (*dd*, ^2J = 11.3, ^3J = 7.5, 2 H, 2 CH_2OAc); 3.54 (*d*, ^3J = 3.0, H–C(3), H–C(6)); 3.49 (*t*, ^3J = 3.4, H–C(9)); 2.71 (*dt*, ^3J = 8.6, 7.5, 4.2, H–C(1), H–C(8)); 2.09 (*s*, 2 MeCO); 2.00–1.90 (*m*, H–C(10), H–C(4), H–C(5)); 1.83 (*t*, ^3J = 4.2, H–C(9a), H–C(8a)); 1.44 (*s*, Me–C(2), Me–C(7)); 1.25 (*d*, ^3J = 7.3, Me–C(10)); 1.12 (*d*, ^3J = 7.4, Me–C(4), Me–C(5)). ^{13}C-NMR (100.6 MHz, CD_3OD): 172.5 (*s*, 2 CO); 88.4, 88.2 (2*s*, C(2), C(7), C(4a), C(10a)); 78.4 (*d*, ^1J(C,H) = 145, C(3), C(6)); 71.5 (*d*, ^1J(C,H) = 148, C(9)); 64.6 (*t*, ^1J(C,H) = 146, 2 *C*H_2OAc); 53.3 (*d*, ^1J(C,H) = 130, C(1), C(8)); 49.1 (*d*, ^1J(C,H) = 129, C(4), C(5)); 44.9 (*d*, ^1J(C,H) = 130, C(8a), C(9a)); 32.6 (*d*, ^1J(C,H) = 120, C(10)); 20.8 (*q*, ^1J(C,H) = 130, 2 *Me*CO); 16.6 (*q*, ^1J(C,H) = 127, *Me*–C(2), *Me*–C(7)); 12.8 (*q*, ^1J(C,H) = 126, *Me*–C(4), *Me*–C(5)); 8.8 (*q*, ^1J(C,H) = 129, *Me*–C(10)). CI-MS (NH_3): 483 (10, $[M+H]^+$), 482 (6, M^+), 422 (100), 404 (25), 364 (72), 346 (30), 311 (19), 123 (49). Anal. calc. for $C_{25}H_{38}O_9$ (482.57): C 62.22, H 7.94; found: C 62.14, H 7.91.

meso-*(1*R*,2*R*,4*R*,4a*R*,5*S*,7*S*,8*S*,8a*R*,9a*S*,10*S*,10a*S*)-1,8-Bis(acetoxymethyl)-1,8,8a,9a-tetrahydro-2,4,5,7,10-pentamethyl-2*H,*10*H-2,4a:7,10a-diepoxyanthracene-3,6,9(4*H,*5*H,*7*H)-trione* (**32**). Hydrated *N*-methylmorpholine oxide (6.6 g, 49 mmol) and activated powdered 4-Å molecular sieves (10 g) were added successively to a stirred suspension of **31** (3.7 g, 7.7 mmol) in anh. CH_2Cl_2 (35 ml) and MeCN (4 ml). After cooling to 0°, tetrapropylammonium perruthenate (TPAP; 344 mg, 0.98 mmol, 0.13 equiv.) was added portionwise. The mixture was stirred at 0° for 15 min, then at 20° for 15 h (TLC monitoring (i-Pr)$_2$O/MeOH 2:1). R_f 0.27 (**31**), 0.33 (**32**)). Evaporation, dissolution in CH_2Cl_2 (30 ml), filtration through a pad of silica gel (rinsing with AcOEt), evaporation, and crystallization from CH_2Cl_2/hexane afforded 2.53 g (69%) of colorless crystals. A second fraction of **32** was obtained after FC (petroleum ether/AcOEt 3:1). M.p. 210–212°. IR (KBr): 1760, 1745, 1730, 1710, 1235. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.09 (*dd*, ^2J = 11.8, ^3J = 6.7, 2 H, 2 CH_2OAc); 3.90 (*dd*, ^2J = 11.8, ^3J = 6.2, 2 H, 2 CH_2OAc); 2.96 (*ddd*, ^3J = 6.7, 6.2, 6.2, H–C(1), H–C(8)); 2.74 (*d*, ^3J = 6.2, H–C(9a), H–C(8a)); 2.67 (*q*, ^3J = 7.3, H–C(4), H–C(5)); 2.42 (*q*, ^3J = 7.1, H–C(10)); 2.03 (*s*, 2 MeCO); 1.47 (*s*, Me–C(2), Me–C(7)); 1.33 (*d*, ^3J = 7.1, Me–C(10)); 1.21 (*d*, ^3J = 7.3, Me–C(4), Me–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 212.2 (*s*, C(3), C(6)); 207.1 (*s*, C(9)); 170.4 (*s*, 2 Me*C*O); 90.2, 87.8 (2*s*, C(2), C(7), C(4a), C(10a)); 61.6 (*t*, ^1J(C,H) = 151, 2 CH_2O); 51.5, 49.2, 47.4 (3*d*, ^1J(C,H) = 121, 131, 141, C(1), C(8), C(4), C(5), C(8a), C(9a)); 31.0 (*d*, ^1J(C,H) = 111, C(10)); 20.6 (*q*, ^1J(C,H) = 131, 2 *Me*CO); 13.9, 10.0 (2*q*, ^1J(C,H) = 131, 131, *Me*–C(2), *Me*–C(7), *Me*–C(4), *Me*–C(5)); 9.0 (*q*, ^1J(C,H) = 131, *Me*–C(10)). CI-MS (NH_3): 494 (14, $[M+H_2O]^+$), 477 (3, $[M+H]^+$), 448 (62), 418 (11), 399 (24), 388 (73), 342 (100), 310 (19), 267 (34), 187 (23), 71 (43). Anal. calc. for $C_{25}H_{32}O_9$ (476.52): C 63.01, H 6.77; found: C 62.96, H 6.87.

*(1*S*,2*S*,4*S*,4a*S*,5*S*,6*R*,7*R*,8*R*,8a*S*,9a*R*,10*R*,10a*S*)-1,8-Bis(acetoxymethyl)-1,6,7,8,8a,9a-hexahydro-6-hydroxy-2,4,5,7,10-pentamethyl-2*H,*10*H-2,4a:7,10a-diepoxyanthracene-3,9(4*H,*5*H)-dione* ((−)-**33**). To a soln. of **32** (3.1 g, 6.5 mmol) in anh. CH_2Cl_2 (65 ml) at −20°, 10M $BH_3 \cdot Me_2S$ in Me_2S (0.65 ml, 6.5 mmol, 1 equiv.) was added under N_2, followed by methyloxazaborolidine **19** derived from L-diphenylprolinol and complexed with BH_3 (380 mg, 1.3 mmol, 0.2 equiv.). The mixture was stirred at −20° under N_2 for 20 h, then quenched with methanolic 1M HCl (6 ml), allowed to warm to 20°, then diluted with CH_2Cl_2 (50 ml), and washed with sat. aq. $NaHCO_3$ soln. (30 ml, 2 ×) and brine (20 ml). The aq. phase was extracted with CH_2Cl_2 (30 ml, 4 ×), the combined org. phase dried ($MgSO_4$) and evaporated, and the residue purified by FC (CH_2Cl_2/AcOEt 4:1, column 70 × 150 mm, 100-ml fractions): 1.46 g (47%) of (−)-**33** (R_f 0.24 in CH_2Cl_2/AcOEt 4:1; 90% e.e. by ^{1}H-NMR with [Eu(hfc)$_3$]) and 958 mg (31%) of **32**.

*Data of (−)-*__33__: White solid. M.p. 180–182°. $[\alpha]_{589}^{20} = -14$ (c = 1.2, $CHCl_3$; e.e. 90%). IR (KBr): 3500, 1740, 1455, 1370, 1240, 1035. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.55 (*dd*, ^2J = 11.6, ^3J = 9.5, 1 H, CH_2–C(8)); 4.35 (*dd*, ^2J = 11.6, ^3J = 4.7, 1 H, CH_2–C(8)); 4.04 (*dd*, ^2J = 11.8, ^3J = 6.4, 1 H, CH_2–C(1)); 3.87 (*dd*, ^2J = 11.8, ^3J = 6.5, 1 H, CH_2–C(1)); 3.87 (*m*, H–C(6)); 3.00 (*ddd*, ^3J = 6.5, 6.4, 5.0, H–C(1)); 2.84 (*dddd*, ^3J = 9.5, 5.3, 4.7, ^4J = 1.5, H–C(8)); 2.75 (*d*, ^3J = 5.3, H–C(8a)); 2.64 (*d*, ^3J = 5.0, H–C(9a)); 2.60 (*q*, ^3J = 7.3, H–C(4)); 2.48 (*dq*, ^3J = 5,6) = 10.5, ^3J = 7.4, H–C(5)); 2.29 (*q*, ^3J = 7.1, H–C(10)); 2.02 (*s*, *Me*COOCH$_2$C(1)); 2.01 (*s*, *Me*-

$COOCH_2C(8)$); 1.49 (*s*, Me−C(7)); 1.43 (*s*, Me−C(2)); 1.24 (*d*, $^3J = 7.1$, Me−C(10)); 1.18 (*d*, $^3J = 7.3$, Me−C(4)); 1.04 (*d*, $^3J = 7.4$, Me−C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 212.9, 207.6 (2*s*, C(3), C(9)); 171.3, 170.5 (2*s*, 2 Me*C*O); 92.9, 90.9, 87.6, 85.9 (4*s*, C(7), C(10a), C(2), C(4a)); 76.7 (*d*, ^1J(C,H) = 163, C(6)); 63.8 (*t*, ^1J(C,H) = 148, CH_2−C(8)); 61.8 (*t*, ^1J(C,H) = 148, CH_2−C(1)); 53.1 (*d*, ^1J(C,H) = 127, C(8a)); 51.3 (*d*, ^1J(C,H) = 129, C(9a)); 49.4 (*d*, ^1J(C,H) = 128, C(4)); 49.0 (*d*, ^1J(C,H) = 137, C(8)); 46.7 (*d*, ^1J(C,H) = 140, C(1)); 41.1 (*d*, ^1J(C,H) = 130, C(5)); 31.8 (*d*, ^1J(C,H) = 120, C(10)); 21.1 (*q*, ^1J(C,H) = 129, *Me*$COOCH_2$C(1)); 20.6 (*q*, ^1J(C,H) = 130, *Me*$COOCH_2$C(8)); 19.7 (*q*, ^1J(C,H) = 126, *Me*−C(7)); 14.0 (*q*, ^1J(C,H) = 131, *Me*−C(2)); 10.6 (*q*, ^1J(C,H) = 126, *Me*−C(5)); 10.1 (*q*, ^1J(C,H) = 123, *Me*−C(4)); 9.2 (*q*, ^1J(C,H) = 128, *Me*−C(10)). CI-MS (NH_3): 496 (10, $[M + H_2O]^+$), 479 (4, $[M + H]^+$), 478 (0.6, M^+), 450 (61), 419 (16, $[M$ − AcO]), 390 (100), 346 (38), 330 (69), 288 (29), 85 (85). Anal. calc. for $C_{25}H_{34}O_9$ (478.53): C 62.75, H 7.16; found: C 62.67, H 7.26.

*(1*S*,2*S*,4*S*,4a*S*,5*S*,6*R*,7*R*,8*R*,8a*S*,9a*R*,10*R*,10a*S*)-1,8-Bis(acetoxymethyl)-1,6,7,8,8a,9a-hexahydro-6-(methoxymethoxy)-2,4,5,7,10-pentamethyl-2*H*,10*H*-2,4a:7,10a-diepoxyanthracene-3,9(4*H*,5*H*)-dione* ((−)-**34**). P_4O_{10} (13.5 g, 95 mmol) was added to a stirred soln. of (−)-**32** (2.68 g, 0.37 mmol) in anh. $CH_2Cl_2/CH_2(OMe)_2$ 1:1 (128 ml). After stirring for 5 min at 20°, the excess P_2O_5 was filtered off and the filtrate collected in aq. $NaHCO_3$ soln. (150 ml). The org. phase was washed with sat. aq. $NaHCO_3$ soln. (30 ml, 3 ×) and brine (30 ml, 2 ×), dried ($MgSO_4$), and evaporated and the residue purified by FC (CH_2Cl_2/AcOEt 85:15, column 70 × 150 mm, 100-ml fractions): 2.9 g (99%) of (−)-**34**. Colorless foam. $[\alpha]_{589}^{20} = -29$, $[\alpha]_{577}^{20} = -29$, $[\alpha]_{546}^{20} = -33$, $[\alpha]_{435}^{20} = -48$, $[\alpha]_{405}^{20} = -51$ ($c = 1.4$, $CHCl_3$; e.e. ≈90%). IR (KBr): 1740, 1370, 1235, 1135, 1030. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.60–4.55 (*m*, MeOCH_2); 4.52 (*dd*, $^2J = 11.5$, $^3J = 10.0$, 1 H, CH_2−C(8)); 4.29 (*dd*, $^2J = 11.5$, $^3J = 4.7$, 1 H, CH_2−C(8)); 4.03 (*dd*, $^2J = 11.7$, $^3J = 6.4$, 1 H, CH_2−C(1)); 3.86 (*dd*, $^2J = 11.7$, $^3J = 6.4$, 1 H, CH_2−C(1)); 3.77 (*d*, $^3J = 10.6$, H−C(6)); 3.37 (*s*, *Me*OCH_2); 2.98 (*ddd*, $^3J = 6.4$, 6.4, 5.1, H−C(1)); 2.84 (*m*, H−C(8)); 2.73 (*d*, $^3J = 5.0$, H−C(8a)); 2.63 (*d*, $^3J = 5.1$, H−C(9a)); 2.59 (*q*, $^3J = 7.3$, H−C(4)); 2.53 (*dq*, $^3J = 10.6$, 7.3, H−C(5)); 2.27 (*q*, $^3J = 7.1$, H−C(10)); 2.00, 1.99 (2*s*, 2 MeCOO); 1.48 (*s*, Me−C(7)); 1.42 (*s*, Me−C(2)); 1.23 (*d*, $^3J = 7.1$, Me−C(10)); 1.17 (*d*, $^3J = 7.3$, Me−C(4)); 1.02 (*d*, $^3J = 7.3$, Me−C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 212.8, 207.6 (2*s*, C(3), C(9)); 171.3, 170.4 (2*s*, 2 Me*C*O); 96.8 (*t*, ^1J(C,H) = 163, MeOCH_2); 92.9, 90.8, 87.6, 85.2 (4*s*, C(2), C(4a), C(7), C(10a)); 82.2 (*d*, ^1J(C,H) = 149, C(6)); 63.7, 61.8 (2*t*, ^1J(C,H) = 151, ^1J(C,H) = 148, 2 AcOCH_2); 55.9 (*q*, ^1J(C,H) = 143, MeO); 53.1 (*d*, ^1J(C,H) = 130, C(8a)); 51.2 (*d*, ^1J(C,H) = 128, C(9a)); 49.3 (*d*, ^1J(C,H) = 125, C(4)); 49.0 (*d*, ^1J(C,H) = 135, C(8)); 46.7 (*d*, ^1J(C,H) = 137, C(1)); 40.1 (*d*, ^1J(C,H) = 131, C(5)); 31.7 (*d*, ^1J(C,H) = 123, C(10)); 21.0, 20.6 (2*q*, ^1J(C,H) = 130, ^1J(C,H) = 130, 2 *Me*CO); 19.9 (*q*, ^1J(C,H) = 127, *Me*−C(7)); 14.0 (*q*, ^1J(C,H) = 128, *Me*−C(2)); 11.2 (*q*, ^1J(C,H) = 127, *Me*−C(5)); 10.1 (*q*, ^1J(C,H) = 125, *Me*−C(4)); 9.2 (*q*, ^1J(C,H) = 130, *Me*−C(10)). CI-MS (NH_3): 540 (13, $[M + H_2O]^+$), 522 (1, M^+), 494 (73), 463 (21, $[M - OAc]^+$), 434 (100), 390 (74), 332 (54), 243 (46), 109 (85). Anal. calc. for $C_{27}H_{38}O_{10}$ (522.59): C 62.06, H 7.33; found: C 62.01, H 7.32.

*(1*S*,4*S*,5*S*,5a*S*,6*R*,6a*S*,7*S*,8*R*,9*R*,10*R*,10a*S*,11a*R*,14*S*)-10-(Acetoxymethyl)-1,4,5,8,9,10,10a,11a-octahydro-4-hydroxy-8-(methoxymethoxy)-5,6,7,9,14-pentamethyl-6*H*,7*H*-6a,9-epoxy-5a,1,4-(epoxymetheno)naphth[2,3-d]oxepin-11(2*H*)-one* ((−)-**35**). A 0.7M soln. of $Mg(OMe)_2$ in MeOH (1.5 ml, 1.04 mmol) was added dropwise to a stirred suspension of (−)-**34** (136 mg, 0.26 mmol) in anh. MeOH (3.5 ml). After stirring at 20° for 8 min, 0.2M aq. HCl was added until the pH was 5 (disappearance of the yellow color). After the addition of H_2O (3 ml) and AcOEt (7 ml), the aq. phase was extracted with AcOEt (3 ml, 4 ×), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue submitted to FC (petroleum ether/AcOEt 3:2 → 1:1, column 18 × 150 mm, 10-ml fractions): 65 mg (52%) of (−)-**35** and 16 mg (12%) of (−)-**34**. (−)-**35**: Colorless foam. $[\alpha]_{589}^{20} = -6.3$, $[\alpha]_{577}^{20} = -6.6$, $[\alpha]_{546}^{20} = -9.6$, $[\alpha]_{435}^{20} = -20$, $[\alpha]_{405}^{20} = -27$ ($c = 1.0$, $CHCl_3$; e.e. ≈90%). IR (film): 3415, 1715, 1250, 1030. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.60, 4.57 (*AB*, $^2J = 6.6$, 6.6, OCH_2O); 4.49 (*dd*, $^2J = 11.6$, $^3J = 9.9$, 1 H, CH_2−C(10)); 4.30 (*dd*, $^2J = 11.6$, $^3J = 4.8$, 1 H, CH_2−C(10)); 4.09 (*dd*, $^2J = 9.2$, $^3J = 5.4$, H_a−C(2)); 3.77 (*dd*, $^3J = 10.6$, $^4J = 1.7$, H−C(8)); 3.61 (*d*, $^2J = 9.2$, H_b−C(2)); 3.39 (*s*, MeO); 3.20 (*dd*, $^3J = 5.4$, ^3J(1, 11a) = 1.9, H−C(1)); 2.87 (*dddd*, $^3J = 9.9$, 4.9, 4.8, $^4J = 1.7$, H−C(10)); 2.69 (*d*, $^3J = 4.9$, H−C(10a)); 2.55 (br. *s*, H−C(11a)); 2.51 (*dq*, $^3J = 10.6$, 7.3, H−C(7)); 2.23 (*q*, $^3J = 7.1$, H−C(5)); 2.19 (*q*, $^3J = 7.1$, H−C(6)); 2.02 (*s*, MeCO); 1.49 (*s*, Me−C(9)); 1.38 (*s*, Me−C(14)); 1.20 (*d*, $^3J = 7.1$, Me−C(6)); 1.02 (*d*, $^3J = 7.3$, Me−C(7)); 1.00 (*d*, $^3J = 7.1$, Me−C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 206.5 (*s*, C(11)); 171.3 (*s*, Me*C*O); 109.0 (*s*, C(4)); 96.7 (*t*, ^1J(C,H) = 163, OCH_2O); 93.7, 91.1, 87.7, 84.9 (4*s*, C(5a), C(6a), C(9), C(14)); 82.4 (*d*, ^1J(C,H) = 148, C(8)); 67.3 (*t*, ^1J(C,H) = 150, C(2)); 63.9 (*t*, ^1J(C,H) = 149, CH_2−C(10)); 57.1 (*d*, ^1J(C,H) = 126, C(11a)); 55.8 (*q*, ^1J(C,H) = 141, MeO); 53.2 (*d*, ^1J(C,H) = 128, C(10a)); 49.2 (*d*, ^1J(C,H) = 132, C(5)); 48.2 (*d*, ^1J(C,H) = 134, C(10)); 44.9 (*d*, ^1J(C,H) = 145, C(1)); 40.1 (*d*, ^1J(C,H) = 133, C(7)); 30.9 (*d*, ^1J(C,H) = 122, C(6)); 21.0 (*q*, ^1J(C,H) = 129, *Me*CO); 19.9 (*q*, ^1J(C,H) = 127, *Me*−C(9)); 12.6 (*q*, ^1J(C,H) = 127, *Me*−C(14)); 11.1 (*q*, ^1J(C,H) = 126, *Me*−C(7)); 9.2 (*q*, ^1J(C,H) = 129, *Me*−C(6)); 9.0 (*q*, ^1J(C,H) = 127, *Me*−C(5)). CI-MS

(NH_3): 498 (21, $[M+H_2O]^+$), 480 (4, M^+), 452 (5), 435 (6); 421 (37, $[M-OAc]^+$), 389 (29), 375 (36), 358 (31), 351 (100), 331 (35), 319 (45), 71 (66). Anal. calc. for $C_{25}H_{36}O_9$ (480.55): C 62.49, H 7.55; found: C 62.48, H 7.55.

*(1*S*,2*S*,4*S*,4a*S*,5*S*,6*R*,7*R*,8*R*,8a*S*,9a*R*,10*R*,10a*S*)-8-(Acetoxymethyl)-1-{[(2′*S*,5′*R*)-camphanoyloxy]methyl}-1,6,7,8,8a,9a-hexahydro-6-(methoxymethoxy)-2,4,5,7,10-pentamethyl-2*H,*10*H*-2,4a:7,10a-diepoxyanthracene-3,9(4*H,*5*H*)-dione* ((−)-**37**) *and (1*S*,4*R*,5*S*,5a*S*,6*R*,6a*S*,7*S*,8*R*,9*R*,10*R*,10a*S*,11a*R*,14*S*)-10-(Acetoxymethyl)-1,4,5,8,9,10,10a,11a-octahydro-4-[(2′*S*,5′*R*)-camphanoyloxy]-8-(methoxymethoxy)-5,6,7,9,14-pentamethyl-6*H,*7*H-6a,9-epoxy-5a,1,4-(epoxymetheno)naphth[2,3-*d*]oxepin-11(2*H*)-one* (**38**). Anh. Et_3N (36 µl, 0.258 mmol), then (−)-camphanoyl chloride (42 mg, 0.194 mmol) and DMAP (3 mg) were added to a soln. of (−)-**35** (62 mg, 0.129 mmol) in anh. CH_2Cl_2 (3 ml). The mixture was stirred at 20° for 1.5 h, then diluted with CH_2Cl_2 (15 ml), and washed with 1M aq. HCl (3 ml, 2 ×), 5% aq. Na_2CO_3 soln. (3 ml, 2 ×), and brine (3 ml). FC (petroleum ether/AcOEt 3:2, column 10 × 150 mm, 5 ml-fractions) gave 56 mg (66%) of (−)-**37** (diastereoisomerically pure), 19 mg (22%) of **38** contaminated by (−)-**37**, and another product derived from **37**.

*Data of (−)-***37**: Crystals suitable for X-ray diffraction studies were obtained from CH_2Cl_2/Et_2O by slow solvent evaporation. White crystals. M.p. 192–194°. $[\alpha]_{589}^{20}=-41$, $[\alpha]_{577}^{20}=-40$, $[\alpha]_{546}^{20}=-49$, $[\alpha]_{435}^{20}=-78$, $[\alpha]_{405}^{20}=-87$ ($c=0.5$, $CHCl_3$). IR (KBr): 1790, 1740, 1435, 1380, 1265, 1030. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.62–4.55 (*AB*, OCH_2O); 4.44 (*dd*, $^2J=11.5$, $^3J=10.0$, 1 H, $CH_2-C(8)$); 4.34 (*dd*, $^2J=11.5$, $^3J=5.2$, 1 H, $CH_2-C(8)$); 4.07 (*dd*, $^2J=11.8$, $^3J=7.6$, 1 H, $CH_2-C(1)$); 4.01 (*dd*, $^2J=11.8$, $^3J=6.9$, 1 H, $CH_2-C(1)$); 3.77 (*dd*, $^3J=10.6$, $^4J=1.5$, H−C(6)); 3.39 (*s*, MeO); 3.07 (*ddd*, $^3J=7.6$, 7.1, $^3J(1,9a)=4.8$, H−C(1)); 2.84 (*dddd*, $^3J=10.0$, 5.2, 5.0, $^4J=1.5$, H−C(8)); 2.70 (*d*, $^3J=5.0$, H−C(8a)); 2.67 (*d*, $^3J=4.8$, H−C(9a)); 2.62 (*q*, $^3J=7.3$, H−C(4)); 2.54 (*dq*, $^3J(5,6)=10.6$, $^3J=7.4$, H−C(5)); 2.49–2.40, 2.08–2.00, 1.95–1.87, 1.70–1.60 (4*m*, 2 H−C(3′), 2 H−C(4′)); 2.28 (*q*, $^3J=7.1$, H−C(10)); 2.00 (*s*, MeCOO); 1.48, 1.46 (2*s*, Me−C(2), Me−C(7)); 1.24 (*d*, $^3J=7.1$, Me−C(10)); 1.18 (*d*, $^3J=7.3$, Me−C(4)); 1.10, 1.06, 0.95 (3*s*, 2 Me−C(7′), Me−C(5′)); 1.01 (*d*, $^3J=7.4$, Me−C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 212.8, 207.2 (2*s*, C(3), C(9)); 177.9, 171.1, 167.3 (3*s*, Me*C*O, C(1′), C(6′)); 96.7 (*t*, ^1J(C,H) = 162, OCH_2O); 92.8, 91.0, 90.0, 87.6, 85.1 (5*s*, C(2), C(4a), C(7), C(10a), C(2′)); 82.1 (*d*, ^1J(C,H) = 150, C(6)); 63.6 (*t*, ^1J(C,H) = 147, *C*H_2−C(8)); 63.2 (*t*, ^1J(C,H) = 148, *C*H_2−C(1)); 55.8 (*q*, ^1J(C,H) = 142, MeO); 54.7, 54.2 (2*s*, C(5′), C(7′)); 53.0 (*d*, ^1J(C,H) = 135, C(8a)); 51.7 (*d*, ^1J(C,H) = 129, C(9a)); 49.3 (*d*, ^1J(C,H) = 130, C(4)); 48.6 (*d*, ^1J(C,H) = 133, C(8)); 46.2 (*d*, ^1J(C,H) = 140, C(1)); 39.9 (*d*, ^1J(C,H) = 133, C(5)); 31.6 (*d*, ^1J(C,H) = 117, C(10)); 30.8, 28.9 (2*t*, ^1J(C,H) = 144, ^1J(C,H) = 139, C(3′), C(4′)); 21.0 (*q*, ^1J(C,H) = 130, *Me*COO); 19.9, 14.0 (2*q*, ^1J(C,H) = 127, ^1J(C,H) = 129, *Me*−C(2), *Me*−C(7)); 16.7, 16.6, 9.6 (3*q*, ^1J(C,H) = 127, 127, 129, 2 *Me*−C(7′), *Me*−C(5′)); 11.2 (*q*, ^1J(C,H) = 119, *Me*−C(5)); 10.0 (*q*, ^1J(C,H) = 128, *Me*−C(4)); 9.2 (*q*, ^1J(C,H) = 129, *Me*−C(10)). CI-MS (NH_3): 678 (27, $[M+H_2O]^+$), 660 (0.7, M^+), 601 (16), 539 (21), 531 (26), 510 (26), 392 (16), 109 (89), 71 (100). Anal. calc. for $C_{35}H_{48}O_{12}$ (660.75): C 63.62, H 7.32; found: C 63.66, H 7.27.

Data of **38**: Colorless oil. IR (film): 1790, 1765, 1735, 1265, 1105, 735. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.60, 4.57 (*AB*, $^2J=6.6$, OCH_2O); 4.48 (*dd*, $^2J=11.6$, $^3J=9.9$, 1 H, $CH_2-C(10)$); 4.29 (*dd*, $^2J=11.6$, $^3J=4.7$, 1 H, $CH_2-C(10)$); 4.26 (*dd*, $^2J=9.3$, $^3J=5.4$, $H_a-C(2)$); 3.80 (*d*, $^2J=9.3$, $H_b-C(2)$); 3.77 (*d*, $^3J=10.5$, H−C(8)); 3.38 (*s*, MeO); 3.23 (*dd*, $^3J=5.4$, 1.6, H−C(1)); 2.87 (*m*, H−C(10)); 2.72 (*d*, $^3J=5.1$, H−C(10a)); 2.64 (br. *s*, H−C(11a)); 2.50 (*dq*, $^3J=10.5$, 7.4, H−C(7)); 2.41, 2.06, 1.92, 1.69 (4*m*, 2 H−C(3′), 2 H−C(4′)); 2.27, 2.23 (2*q*, $^3J=7.0$, 7.1, H−C(5), H−C(6)); 2.01 (*s*, MeCOO); 1.49, 1.48 (2*s*, Me−C(9), Me−C(14)); 1.26, 1.17 (2*d*, $^3J=7.0$, 7.1, Me−C(5), Me−C(6)); 1.11, 1.05, 0.97 (3*s*, 2 Me−C(7′), Me−C(5′)); 1.02 (*d*, $^3J=7.4$, Me−C(7)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 206.0 (*s*, C(11)); 177.9 (3*s*, Me*C*O, C(1′), C(6′)); 112.0 (*s*, C(4)); 96.8 (*t*, ^1J(C,H) = 163, OCH_2O); 93.6, 92.2, 90.9, 90.8, 85.0 (5*s*, C(9), C(6a), C(14), C(5a), C(2′)); 82.2 (*d*, ^1J(C,H) = 151, C(8)); 70.0 (*t*, ^1J(C,H) = 149, C(2)); 63.8 (*t*, ^1J(C,H) = 148, *C*H_2−C(10)); 56.7 (*d*, ^1J(C,H) = 131, C(11a)); 55.9 (*q*, ^1J(C,H) = 142, MeO); 54.9, 54.4 (2*s*, C(5′), C(7′)); 53.3 (*d*, ^1J(C,H) = 126, C(10a)); 50.3 (*d*, ^1J(C,H) = 133, C(5)); 48.3 (*d*, ^1J(C,H) = 134, C(10)); 44.2 (*d*, ^1J(C,H) = 148, C(1)); 40.2 (*d*, ^1J(C,H) = 135, C(7)); 30.8 (*d*, ^1J(C,H) = 117, C(6)); 30.4, 29.0 (2*t*, ^1J(C,H) = 138, ^1J(C,H) = 136, C(3′), C(4′)); 21.1 (*q*, ^1J(C,H) = 129, *Me*COO); 19.9, 13.9 (2*q*, ^1J(C,H) = 127, 128, *Me*−C(9), *Me*−C(14)); 16.9, 16.8, 9.6 (3*q*, ^1J(C,H) = 123, 127, 128, 2 *Me*−C(7′), *Me*−C(5′)); 11.2 (*q*, ^1J(C,H) = 126, *Me*−C(7)); 10.7, 9.3 (2*q*, ^1J(C,H) = 127, 129, *Me*−C(5), *Me*−C(6)). CI-MS (NH_3): 678 (100, $[M+H_2O]^+$), 601 (42), 569 (26), 555 (34), 463 (28), 289 (37).

*(1*R*,2*S*,3*R*,4*R*,4a*S*,5*R*,6*R*,7*R*,8*S*,9a*R*,10*R*)-3-{[(*tert*-Butyl)dimethylsilyl]oxy}-1-(ethoxycarbonyl)-1,3,4,5,6,7,8,9,9a,10-decahydro-7-hydroxy-2,4,5,7,10-pentamethyl-9-oxo-2*H*-2,4a-epoxyanthracene-8,6-carbolactone* (**39**). (*t*-Bu)$Me_2SiOSO_2CF_3$ (0.42 ml, 2.39 mmol) was added to a stirred soln. of (−)-**25** (1.04 g, 2.39 mmol) and 2,6-lutidine (=2,6-dimethylpyridine; 1.38 ml, 12.0 mmol) in anh. CH_2Cl_2 (20 ml) cooled to −78°. After 2 h stirring at 0°, (*t*-Bu)$Me_2SiOSO_2CF_3$ (0.6 ml) was added and the stirring continued for 1 h. Then a sat. aq. $NaHCO_3$ soln. (5 ml) was added, the mixture extracted with CH_2Cl_2 (10 ml, 3 ×), the combined org. extract washed with 0.3M aq. HCl (5 ml, 2 ×) and brine (5 ml, 2 ×), dried ($MgSO_4$), and evaporated, and the residue

submitted to FC (petroleum ether/AcOEt 7:3): 1.26 g (95%) of **39**. White solid. M.p. 194–196°. UV (MeCN): 248 (15000), 195 (7900). IR (KBr): 3500, 1795, 1730, 1670, 1180, 1095, 1085. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.25–4.15 (*m*, MeCH_2O); 4.15 (*dd*, ^3J = 2.1, ^4J = 1.3, H–C(6)); 3.91 (*d*, ^4J = 1.3, H–C(8)); 3.37 (*d*, ^3J = 2.7, H–C(3)); 3.27 (*d*, ^3J = 4.0, H–C(1)); 3.21 (*d*, ^3J = 4.0, H–C(9a)); 3.02 (*qd*, ^3J = 7.5, 2.1, H–C(5)); 2.72 (*q*, ^3J = 7.4, H–C(10)); 2.01 (*qd*, ^3J = 7.4, 2.7, H–C(4)); 1.55, 1.47 (2*s*, Me–C(2), Me–C(7)); 1.31 (*d*, ^3J = 7.4, Me–C(10)); 1.30 (*t*, ^3J = 7.2, *Me*CH_2O); 1.29 (*d*, ^3J = 7.5, Me–C(5)); 1.12 (*d*, ^3J = 7.4, Me–C(4)); 0.89 (*s*, *t*-Bu); 0.04, 0.03 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 195.4 (*s*, C(9)); 173.3, 170.8 (2*s*, *C*O–C(1), *C*O–C(8)); 159.8 (*s*, C(10a)); 124.5 (*s*, C(8a)); 88.1, 87.6 (2*s*, C(2), C(4a)); 84.8 (*d*, ^1J(C,H) = 160, C(6)); 78.9 (*d*, ^1J(C,H) = 144, C(3)); 72.3 (*s*, C(7)); 61.3 (*t*, ^1J(C,H) = 148, Me*C*H_2O); 55.0, 50.9, 49.1, 45.8 (4*d*, ^1J(C,H) = 136, 132, 128, 152, C(1), C(4), C(8), C(9a)); 34.5, 31.7 (2*d*, ^1J(C,H) = 129, 124, C(5), C(10)); 25.7 (*q*, ^1J(C,H) = 125, *Me*$_3$C–Si); 17.9 (*s*, Me$_3$*C*–Si); 24.0, 16.9, 14.2, 12.7, 12.6, 12.5 (6*q*, ^1J(C,H) = 127, 128, 127, 129, 129, 129, *Me*–C(2), *Me*–C(4), *Me*–C(5), *Me*–C(7), *Me*–C(10), *Me*CH_2O); –4.5, –4.9 (2*q*, ^1J(C,H) = 119, 119, 2 Me–Si). CI-MS (NH_3): 549 (10, $[M+H]^+$), 548 (1, M^+), 503 (7, $[M-EtO]^+$), 491 (100, $[M-(t\text{-Bu})]^+$), 445 (69), 417 (16), 361 (14), 157 (11), 115 (22), 73 (72). Anal. calc. for $C_{29}H_{44}O_8Si$ (548.74): C 63.48, H 8.08, Si 5.12; found: C 63.53, H 7.99, Si 5.16.

*(1*R*,2*S*,3*R*,4*R*,4a*S*,5*R*,6*R*,7*R*,8*S*,9*S*,9a*S*,10*R*)- and (1*R*,2*S*,3*R*,4*R*,4a*S*,5*R*,6*R*,7*R*,8*S*,9*R*,9a*S*,10*R*)-3-[[(*tert-Butyl)dimethylsilyl]oxy}-1-(ethoxycarbonyl)-1,3,4,5,6,7,8,9,9a,10-decahydro-7,9-dihydroxy-2,4,5,7,10-pentamethyl-2*H*-2,4a-epoxyanthracene-8,6-carbolactone* (**40** and **41**, resp.). To a soln. of **39** (300 mg, 0.547 mmol) in anh. MeOH (7 ml), anh. $CeCl_3$ (135 mg, 0.547 mmol, 1 equiv.) and $NaBH_4$ (21 mg, 0.547, 1 equiv.) were added, and the mixture was stirred at 20° under N_2. After 1 h and the addition of 2 more equiv. of $NaBH_4$, 1M aq. HCl was added to neutrality, the soln. diluted with H_2O (10 ml) and extracted with Et_2O (10 ml, 3 ×), the org. layer dried and evaporated, and the residue submitted to FC (petroleum ether/AcOEt 3:2 → 1:1): 257 mg (85%) of **40** and 13 mg (4%) of **41**.

Data of **40**: Colorless oil. IR (KBr): 3440, 1780, 1725, 1380, 1265, 1070. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.18 (*m*, MeCH_2O); 4.10 (*dd*, ^3J = 2.2, ^4J = 1.0, H–C(6)); 3.85 (*m*, H–C(9)); 3.51 (*d*, ^4J = 1.0, H–C(8)); 3.38 (*d*, ^3J = 2.5, H–C(3)); 2.79 (*d*, ^3J = 3.0, H–C(1)); 2.78 (*qd*, ^3J = 6.8, 2.2, H–C(5)); 2.46 (*q*, ^3J = 7.0, H–C(10)); 2.35 (*s*, OH–C(7)); 2.23 (*dd*, ^3J = 3.0, 8.4, H–C(9a)); 1.88 (*qd*, ^3J = 6.8, 2.5, H–C(4)); 1.80 (*d*, ^3J = 9.7, OH–C(9)); 1.53, 1.51 (2*s*, Me–C(2), Me–C(7)); 1.31 (*t*, ^3J = 6.5, *Me*CH_2O); 1.19 (*d*, ^3J = 6.8, Me–C(5)); 1.15 (*d*, ^3J = 7.0, Me–C(10)); 1.01 (*d*, ^3J = 6.8, Me–C(4)); 0.9 (*s*, *t*-Bu); 0.04 (2*s*, 2 Me–Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 174.6, 171.4 (2*s*, *C*O–C(1), *C*O–C(8)); 139.1, 127.2 (2*s*, C(10a), C(8a)); 88.1, 87.1 (2*s*, C(2), C(4a)); 85.8 (*d*, ^1J(C,H) = 153, C(6)); 79.3 (*d*, ^1J(C,H) = 149, C(3)); 73.7 (*d*, ^1J(C,H) = 146, C(9)); 73.0 (*s*, C(7)); 61.1 (*t*, ^1J(C,H) = 148, Me*C*H_2O); 57.9, 53.0, 48.4, 47.8 (4*d*, ^1J(C,H) = 132, 133, 150, 136, C(1), C(4), C(8), C(9a)); 33.0, 32.5 (2*d*, ^1J(C,H) = 126, 124, C(5), C(10)); 25.8 (*q*, ^1J(C,H) = 125, *Me*$_3$C–Si); 18.0 (*s*, Me$_3$*C*–Si); 23.1, 17.4, 14.2, 13.5, 13.0, 11.7 (6*q*, ^1J(C,H) = 127, 124, 127, 129, 124, 126, *Me*–C(2), *Me*–C(4), *Me*–C(5), *Me*–C(7), *Me*–C(10), *Me*CH_2O); –4.4, –4.8 (2*q*, ^1J(C,H) = 120, 120, 2 Me–Si). CI-MS (NH_3): 550 (1, M^+), 515 (5); 505 (3, $[M-EtO]^+$), 493 (48), 475 (15), 429 (18), 401 (24), 419 (4), 363 (11), 327 (16), 283 (23), 249 (33), 237 (17), 73 (100). Anal. calc. for $C_{29}H_{46}O_8Si$ (550.76): C 63.24, H 8.42; found: C 63.35, H 8.57.

Data of **41**: Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.25–4.13 (*m*, MeCH_2O); 4.11 (*dd*, ^3J = 3.0, ^4J(6,8) = 1.0, H–C(6)); 3.83 (*dd*, ^3J(9,OH) = 9.8, ^3J = 5.8, H–C(9)); 3.44 (*m*, H–C(8), H–C(3)); 2.97 (*d*, ^3J = 3.0, H–C(1)); 2.78 (*qd*, ^3J = 7.1, ^3J(6, 5) = 3.0, H–C(5)); 2.71 (*dd*, ^3J = 3.0, 5.8, H–C(9a)); 2.65 (*d*, ^3J = 9.8, OH–C(9)); 2.55 (br. *s*, OH–C(7)); 2.43 (*q*, ^3J = 7.0, H–C(10)); 1.83 (*qd*, ^3J = 7.1, 2.8, H–C(4)); 1.52, 1.51 (2*s*, Me–C(2), Me–C(7)); 1.30 (*t*, ^3J = 7.2, *Me*CH_2O); 1.20, 1.18 (2*d*, ^3J = 7.1, 7.0, Me–C(5), Me–C(10)); 1.01 (*d*, ^3J = 7.1, Me–C(4)); 0.9 (*s*, *t*-Bu); 0.04 (2*s*, 2 Me–Si).

*(1*R*,2*S*,3*R*,4*R*,4a*S*,5*R*,6*R*,7*R*,8*S*,9*S*,9a*S*,10*R*)-3-[[(*tert-Butyl)dimethylsilyl]oxy}-1-(ethoxycarbonyl)-1,3,4,5,6,7,8,9,9a,10-decahydro-7-hydroxy-9-(methoxymethoxy)-2,4,5,7,10-pentamethyl-2*H*-2,4a-epoxyanthracene-8,6-carbolactone* (**42**), *(1*R*,2*S*,3*R*,4*R*,4a*R*,5*S*,6*R*,7*R*,8*S*,9*S*,9a*S*,10*R*)-1-[[(*tert-Butyl)dimethylsilyl]oxy}-1-(ethoxycarbonyl)-1,3,4,5,6,7,8,9,9a,10-decahydro-9-hydroxy-7-(methoxymethoxy)-2,4,5,7,10-pentamethyl-2*H*-2,4a:7,9-diepoxyanthracene-8,6-carbolactone* (**43**), *and (1*R*,2*S*,3*R*,4*R*,4a*S*,5*R*,6*R*,7*R*,8*S*,9*S*,9a*S*,10*R*)-3-[[(*tert-Butyl)dimethylsilyl]oxy}-1-(ethoxycarbonyl)-1,3,4,5,6,7,8,9,9a,10-decahydro-7,9-bis(methoxymethoxy)-2,4,5,7,10-pentamethyl-2*H*-2,4a-epoxyanthracene-8,6-carbolactone* (**44**). To a soln. of **40** (78 mg, 0.142 mmol) in anh. CH_2Cl_2 (1 ml), MeOCH_2Cl (0.108 ml, 1.42 mmol, 10 equiv.) was added at –20°, together with (i-Pr)$_2$NEt (0.486 ml, 2.83 mmol, 20 equiv.). The mixture was allowed to warm to 20°. More MeOCH_2Cl and (i-Pr)$_2$NEt were added in many portions (25 equiv.). After 3 h, MeOH (1 ml) was added, and the mixture was stirred for 1 h, then poured into 10 ml of ice-cold 1M aq. HCl, and extracted with CH_2Cl_2 (5 ml, 4 ×). Drying ($MgSO_4$), evaporation, and FC (petroleum ether/AcOEt 7:3 → 1:1) yielded 48 mg (47%) of **42**, 11 mg (13%) of **43**, and 14 mg (15%) of **44**.

Data of **42**. White solid. M.p. 62–65°. IR (KBr): 3500, 1785, 1730, 1465, 1380, 1100. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.73, 4.67 (2*d*, ^2J = 7.0, OCH_2O); 4.16 (*q*, ^3J = 7.1, Me*C*H_2O); 4.05 (*dd*, ^3J = 2.5, ^4J = 0.8, H–C(6)); 3.81 (*dd*, ^3J = 6.5, ^5J(9, 5) = 1.0, H–C(9)); 3.41 (*d*, ^3J = 3.1, H–C(3)); 3.35 (*s*, MeO); 2.94 (*d*, ^4J = 0.8, H–C(8)); 2.73 (*qdd*, ^3J = 7.0, 2.5, ^5J(9, 5) = 1.0, H–C(5)); 2.70 (*d*, ^3J = 4.3, H–C(1)); 2.62 (*dd*, ^3J = 4.3, 6.5, H–C(9a)); 2.56 (*q*, ^3J = 7.3, H–C(10)); 1.93 (*qd*, ^3J = 7.3, 3.1, H–C(4)); 1.48, 1.47 (2*s*, Me–C(2), Me–C(7)); 1.29 (*t*, ^3J = 7.1, *Me*CH_2O);1.19 (*d*, ^3J = 7.0, Me–C(5)); 1.18 (*d*, ^3J = 7.3, Me–C(10)); 1.08 (*d*, ^3J = 7.3, Me–C(4)); 0.88 (*s*, *t*-Bu); 0.02, 0.01 (2*s*, 2 Me–Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 173.4, 171.1 (2*s*, *C*O–C(1), *C*O–C(8)); 140.9, 125.5 (2*s*, C(10a), C(8a)); 97.2 (*t*, ^1J(C,H) = 162, OCH_2O); 88.7, 87.6 (2*s*, C(2), C(4a)); 85.2 (*d*, ^1J(C,H) = 158, C(6)); 81.3 (*d*, ^1J(C,H) = 149, C(9)); 79.3 (*d*, ^1J(C,H) = 145, C(3)); 73.6 (*s*, C(7)); 60.8 (*t*, ^1J(C,H) = 148, Me*C*H_2O); 56.0 (*q*, ^1J(C,H) = 142, MeO); 58.7, 51.8, 50.8, 45.1 (4*d*, ^1J(C,H) = 134, 132, 148, 141, C(1), C(4), C(8), C(9a)); 33.3, 32.0 (2*d*, ^1J(C,H) = 127, 128, C(5), C(10)); 25.7 (*q*, ^1J(C,H) = 125, *Me*$_3$C–Si); 18.0 (*s*, Me$_3$*C*–Si); 22.9, 17.0, 14.3, 13.2, 12.6, 11.4 (6*q*, ^1J(C,H) = 128, 127, 127, 128, 127, 126, *Me*–C(2), *Me*–C(4), *Me*–C(5), *Me*–C(7), *Me*–C(10), *Me*CH_2O); −4.4, −4.8 (2*q*, ^1J(C,H) = 119, 118, 2 Me–Si). CI-MS (NH_3): 612 (16, $[M+H]^+$), 594 (3, M^+), 549 (5, $[M-EtO]^+$), 537 (49, $[M-(t\text{-Bu})]^+$), 533 (17), 515 (19), 475 (52), 429 (19), 419 (12), 401 (32), 72 (100). Anal. calc. for $C_{31}H_{50}O_9Si$ (594.81): C 62.60, H 8.47, Si 4.72; found: C 62.50, H 8.41, Si 4.74.

Data of **43**: Colorless foam. IR (KBr): 3480, 1785, 1720, 1460, 1380, 1230, 1150, 1095, 1070. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.68, 4.51 (2*d*, ^2J = 7.2, OCH_2O); 4.17 (*m*, Me*C*H_2O); 4.13 (*dd*, ^3J = 2.5, ^4J = 1.1, H–C(6)); 3.83 (*m*, H–C(9)); 3.63 (*d*, ^4J = 1.1, H–C(8)); 3.37 (*d*, ^3J = 2.9, H–C(3)); 3.33 (*s*, MeO); 2.82 (*m*, H–C(5)); 2.79 (*d*, ^3J = 3.3, H–C(1)); 2.41 (*q*, ^3J = 7.3, H–C(10)); 2.18 (*dd*, ^3J = 9.1, 3.3, H–C(9a)); 1.86 (*qd*, ^3J = 7.3, 2.9, H–C(4)); 1.52 (2*s*, Me–C(2), Me–C(7)); 1.30 (*t*, ^3J = 7.2, *Me*CH_2O); 1.16 (*d*, ^3J = 7.5, Me–C(5)); 1.11 (*d*, ^3J = 7.3, Me–C(10)); 1.00 (*d*, ^3J = 7.3, Me–C(4)); 0.90 (*s*, *t*-Bu); 0.03 (*s*, 2 Me–Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 175.3, 171.6 (2*s*, *C*O–C(1), *C*O–C(8)); 137.8, 126.1 (2*s*, C(10a), C(8a)); 93.2 (*t*, ^1J(C,H) = 163, OCH_2O); 87.9, 87.2 (2*s*, C(2), C(4a)); 86.1 (*d*, ^1J(C,H) = 155, C(6)); 79.3 (*d*, ^1J(C,H) = 145, C(3)); (C(7) missing, probably hidden by $CHCl_3$) 73.7 (*d*, ^1J(C,H) = 147, C(9)); 61.0 (*t*, ^1J(C,H) = 148, Me*C*H_2O); 56.5 (*q*, ^1J(C,H) = 148, MeO); 57.9, 53.1, 47.9, 46.8 (4*d*, ^1J(C,H) = 133, 130, 135, 152, C(1), C(4), C(8), C(9a)); 33.1, 32.5 (2*d*, ^1J(C,H) = 125, 125, C(5), C(10)); 25.8 (*q*, ^1J(C,H) = 125, *Me*$_3$C–Si); 18.0 (*s*, Me$_3$*C*–Si); 21.3, 17.4, 14.2, 13.1, 13.0, 11.7 (6*q*, ^1J(C,H) = 128, 127, 127, 126, 126, 126, *Me*–C(2), *Me*–C(4), *Me*–C(5), *Me*–C(7), *Me*–C(10), *Me*CH_2O); −4.4, −4.8 (2*q*, ^1J(C,H) = 118, 118, 2 Me–Si). CI-MS (NH_3): 612 (12, $[M+H_2O]^+$), 594 (12, M^+), 577 (11, $[M-OH]^+$), 576 (12, $[M-H_2O]^+$), 562 (23), 549 (26, $[M-EtO]^+$), 537 (24, $[M-(t\text{-Bu})]^+$), 530 (11), 515 (11), 475 (8), 416 (33), 73 (100). Anal. calc. for $C_{31}H_{50}O_9Si$ (594.81): C 62.60, H 8.47; found: C 62.75, H 8.41.

Data of **44**: White solid. M.p. 50–51°. IR (KBr): 1800, 1730, 1465, 1380, 1150, 1100, 1035. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.78, 4.73 (2*d*, ^2J = 7.1, CH_2O–C(9)); 4.74, 4.48 (2*d*, ^2J = 7.4, CH_2O–C(7)); 4.17 (*m*, Me*C*H_2O); 4.10 (*dd*, ^3J = 2.5, ^4J = 1.2,H–C(6)); 3.80 (*ddd*, ^3J = 8.7, ^5J(9, 5) = ^5J(9, 10) = 2.0, H–C(9)); 3.37 (*d*, ^3J = 2.8, H–C(3)); 3.35, 3.32 (2*s*, 2 MeO); 3.16 (*d*, ^4J = 1.2, H–C(8)); 2.86 (*d*, ^3J = 3.4, H–C(1)); 2.79 (*qdd*, ^3J = 7.4, 2.5, ^5J(9, 5) = 2.0, H–C(5)); 2.53 (*dd*, ^3J = 8.7, 3.4, H–C(9a)); 2.41 (*qd*, ^3J = 7.3, ^5J(9, 10) = 2.0, H–C(10)); 1.88 (*qd*, ^3J = 7.4, 2.8, H–C(4)); 1.50 (2*s*, Me–C(2), Me–C(7)); 1.29 (*t*, ^3J = 7.1, *Me*CH_2O); 1.15 (*d*, ^3J = 7.4, Me–C(5)); 1.12 (*d*, ^3J = 7.3, Me–C(10)); 1.07 (*d*, ^3J = 7.4, Me–C(4)); 0.89 (*s*, *t*-Bu); 0.02, 0.01 (2*s*, 2 Me–Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 174.0, 171.5 (2*s*, *C*O–C(1), *C*O–C(8)); 137.5, 124.8 (2*s*, C(10a), C(8a)); 98.1, 93.0 (2*t*, ^1J(C,H) = 167, 167, 2 OCH_2O); 87.8, 87.7 (2*s*, C(2), C(4a)); 85.4 (*d*, ^1J(C,H) = 156, C(6)); 82.5 (*d*, ^1J(C,H) = 144, C(9)); 79.1 (*d*, ^1J(C,H) = 155, C(3)); 77.1 (*s*, C(7)); 60.6 (*t*, ^1J(C,H) = 148, Me*C*H_2O); 56.8, 56.1 (2*q*, ^1J(C,H) = 143, 142, 2 MeO); 58.5, 53.1, 48.0, 45.2 (4*d*, ^1J(C,H) = 132, 133, 152, 139, C(1), C(4), C(8), C(9a)); 33.1, 32.2 (2*d*, ^1J(C,H) = 125, 125, C(5), C(10)); 25.8 (*q*, ^1J(C,H) = 125, *Me*$_3$C–Si); 18.0 (*s*, Me$_3$*C*–Si); 21.2, 17.4, 14.3, 13.1, 12.9, 11.4 (6*q*, ^1J(C,H) = 127, 127, 128, 128, 128, 125, *Me*–C(2), *Me*–C(4), *Me*–C(5), *Me*–C(7), *Me*–C(10), *Me*CH_2O); −4.4, −4.8 (2*q*, ^1J(C,H) = 119, 118, 2 Me–Si). CI-MS (NH_3): 656 (4, $[M+H_2O]^+$), 538 (1, M^+), 593 (21, $[M-EtO]^+$), 581 (13, $[M-(t\text{-Bu})]^+$), 547 (17), 515 (8), 475 (17), 415 (8), 75 (100). Anal. calc. for $C_{33}H_{54}O_{10}Si$ (638.87): C 62.04, H 8.52, Si 4.40; found: C 61.93, H 8.35, Si 4.45.

*(1*R*,2*S*,3*R*,4*R*,4a*R*,5*S*,6*R*,7*R*,8*R*,8a*R*,9*R*,9a*R*,10*R*,10a*R*)-3-[[*(tert-*Butyl)dimethylsilyl]oxy]-1-(ethoxycarbonyl)-1,3,4,5,6,7,8,8a,9,9a,10,10a-dodecahydro-8a,9,10a-trihydroxy-2,4,5,7,10-pentamethyl-*2H*-2,4a:7,9-diepoxyanthracene-8,6-carbolactone* (**45**), *(1*R*,2*S*,3*R*,4*R*,4a*R*,5*S*,6*R*,7*S*,8 R,9*R*,10*R*,11*S*,12a*R*)-3-[[*(tert-*Butyl)dimethylsilyl]oxy]-1-(ethoxycarbonyl)-1,3,4,7,8,9,10,11,12,12a-decahydro-11-hydroxy-2,4,5,7,9-pentamethyl-12-oxo-2*H*,5*H*-2,4a:6,9:6,11-triepoxybenzocyclodecene-10,8-carbolactone* (**46**), *and (1*R*,2*S*,3*R*,4*R*,4a*S*,5*S*,7*S*,8*R*,9*R*,10*S*,11*S*,11a*S*)-[[*(tert-*Butyl)dimethylsilyl]oxy]-1-(ethoxycarbonyl)-1,2,3,4,5,6,7,8,9,10,11,11a-dodecahydro-11-hydroxy-2,4,5,7,9-pentamethyl-6-oxo-3-2,4a-epoxy-4a*H*-benzocyclononene-10,8:11,9-dicarbolactone* (**47**). To a soln. of **39** (463 mg, 0.844 mmol) in CCl_4/MeCN 1:1 (3.4 ml) and H_2O (2.6 ml), $NaIO_4$ (379 mg, 1.77 mmol, 2.1 equiv.) was added, followed by $RuCl_3 \cdot n\ H_2O$ (4 mg). The biphasic mixture was stirred for 22 h. During this period, more $NaIO_4$ (200 mg) and $RuCl_3 \cdot n\ H_2O$ (4 mg) were added. The mixture was diluted with CH_2Cl_2

(20 ml), the aq. phase extracted with CH_2Cl_2 (3 ml, 5 ×), the extract dried ($MgSO_4$) and evaporated, the residue suspended in Et_2O and filtered over *Celite*, and the filtrate evaporated, FC (petroleum ether/AcOEt 7:3 → 1:1) gave 205 mg (42%) of **45** and two other fractions containing **46** and **47** (less than 20%).

The latter two were also formed on addition of $Pb(OAc)_4$ (90 mg, 0.2 mmol, 1.2 equiv.) to a stirred soln. of **45** (100 mg, 0.172 mmol) in anh. benzene (3 ml). After stirring at 20° for 45 min, the mixture was diluted with Et_2O (10 ml) and filtered over silica gel. The filtrate was washed with sat. aq., $NaHCO_3$ soln. (5 ml, 3 ×), dried ($MgSO_4$), and evaporated. FC (petroleum ether/EtOAc 3:1) afforded 28 mg (28%) of **46** and 51 mg (51%) of **47**.

Data of **45**: White solid. M.p. 104–106°. IR (KBr): 3480, 1770, 1730, 1255, 1100. ^{1}H-NMR (400 MHz, $CDCl_3 + D_2O$): 4.23 (*m*, MeC*H*$_2$O); 4.03 (*dd*, ^3J = 2.4, ^4J = 0.7, H–C(6)); 3.37 (*d*, ^3J = 3.7, H–C(3)); 3.33 (*d*, ^3J = 6.8, H–C(1)); 3.15 (*d*, ^4J = 0.7, H–C(8)); 2.96 (*qd*, ^3J = 7.0, 2.4, H–C(5)); 2.41 (*d*, ^3J = 6.8, H–C(9a)); 2.25 (*q*, ^3J = 7.4, H–C(10)); 1.99 (*qd*, ^3J = 7.2, 3.7, H–C(4)); 1.52, 1.49 (2*s*, Me–C(2), Me–C(7)); 1.34 (*t*, ^3J = 7.2, *Me*CH$_2$O); 1.24 (*d*, ^3J = 7.0, Me–C(5)); 1.20 (*d*, ^3J = 7.4, Me–C(10)); 0.97 (*d*, ^3J = 7.2, Me–C(4)); 0.90 (*s*, *t*-Bu); 0.05, 0.04 (2*s*, 2 Me–Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 174.5, 173.0 (2*s*, *C*O–C(1), *C*O–C(8)); 103.7 (*s*, C(9)); 90.6 (*d*, ^1J(C,H) = 154, C(6)); 79.5 (*d*, ^1J(C,H) = 143, C(3)); 87.3, 87.1, 84.8, 82.7, 76.0 (5*s*, C(2), C(4a), C(7), C(8a), C(10a)); 61.8 (*t*, ^1J(C,H) = 149, Me*C*H$_2$O); 55.2, 52.5, 50.9, 44.8, 36.6, 34.0 (6*d*, ^1J(C,H) = 151, 133, 132, 131, 123, 130, C(1), C(4), C(5), C(8), C(9a), C(10)); 25.7 (*q*, ^1J(C,H) = 125, Me$_3$C–Si); 17.9 (*s*, Me$_3$*C*–Si); 21.6, 16.7, 14.1, 13.0, 11.7, 9.0 (6*q*, ^1J(C,H) = 128, 127, 127, 127, 130, 123, *Me*–C(2), *Me*–C(4), *Me*–C(5), *Me*–C(7), *Me*–C(10), *Me*CH$_2$O); –4.4, –4.7 (2*q*, ^1J(C,H) = 119, 118, 2 Me–Si). CI-MS (NH_3): 564 (13, [*M* – H_2O]$^+$), 525 (86, [*M* – (*t*-Bu)]$^+$), 507 (17), 489 (26), 433 (37), 415 (34), 75 (100). Anal. calc. for $C_{29}H_{46}O_{10}Si$ (582.76): C 59.77, H 7.96, Si 4.82; found: C 59.83, H 7.87, Si 4.80.

Data of **46**: Colorless foam. IR (KBr): 3475, 1760, 1725, 1460, 1390, 1245, 1185, 1090. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.58 (*d*, ^3J = 7.3, H–C(8)); 4.15 (*m*, MeC*H*$_2$O); 3.78 (*d*, ^3J = 5.4, H–C(1)); 3.75 (*d*, ^3J = 5.4, H–C(12a)); 3.53 (*s*, H–C(10)); 3.39 (*d*, ^3J = 2.6, H–C(3)); 2.28 (*qd*, ^3J = 7.5, 7.3, H–C(7)); 2.26 (*q*, ^3J = 7.3, H–C(5)); 1.91 (*qd*, ^3J = 7.1, 2.6, H–C(4)); 1.57 (*s*, Me–C(9), Me–C(2)); 1.28 (*t*, ^3J = 7.1, *Me*CH$_2$O); 1.23 (*d*, ^3J = 7.5, Me–C(7)); 1.13 (*d*, ^3J = 7.1, Me–C(4)); 1.05 (*d*, ^3J = 7.3, Me–C(5)); 0.89 (*s*, *t*-Bu); 0.04 (*s*, 2 Me–Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 200.2 (*s*, C(12)); 175.6, 170.9 (2*s*, *C*O–C(10), *C*O–C(1)); 111.3 (*s*, C(11)); 94.7, 92.6, 87.1, 84.8 (4*s*, C(9), C(6), C(2), C(4a)); 87.4 (*d*, ^1J(C,H) = 164, C(8)); 78.5 (*d*, ^1J(C,H) = 143, C(3)); 61.0 (*t*, ^1J(C,H) = 147, Me*C*H$_2$O); 55.6 (*d*, ^1J(C,H) = 147, C(10)); 54.3 (*d*, ^1J(C,H) = 131, C(4)); 52.8 (*d*, ^1J(C,H) = 132, C(12a)); 51.1 (*d*, ^1J(C,H) = 135, C(1)); 43.7 (*d*, ^1J(C,H) = 130, C(7)); 40.1 (*d*, ^1J(C,H) = 126, C(5)); 25.7 (*q*, ^1J(C,H) = 127, Me$_3$C–Si); 17.9 (*s*, Me$_3$*C*–Si); 22.4, 17.1 (2*q*, ^1J(C,H) = 129, 128, *Me*–C(9), *Me*–C(2)); 14.2 (*q*, ^1J(C,H) = 127, *Me*CH$_2$O); 12.3 (*q*, ^1J(C,H) = 126, *Me*–C(7)); 10.0 (*q*, ^1J(C,H) = 129, *Me*–C(5); 7.1 (*q*, ^1J(C,H) = 128, *Me*–C(4)); –4.4, –4.9 (2*q*, ^1J(C,H) = 118, 118, 2 Me–Si). CI-MS (NH_3): 598 (0.7, [*M* + H_2O]$^+$), 523 (100, [*M* – (*t*-Bu)]$^+$), 505 (8.8), 477 (16), 449 (11), 357 (10), 313 (11).

Data of **47**: Colorless foam. IR (KBr): 3430, 1795, 1750, 1730, 1160, 1090. ^{1}H-NMR (400 MHz, C_6D_6, 70°): 4.15 (*d*, ^3J = 3.9, H–C(8)); 3.91 (*m*, MeC*H*$_2$O); 3.78 (*s*, H–C(10)); 3.58–3.54 (2*d*, H–C(3), H–C(1)); 3.29 (*d*, ^3J = 5.8, H–C(11a)); 3.07 (*qd*, ^3J = 7.0, ^3J = 3.9, H–C(7)); 2.72 (*q*, ^3J = 7.2, H–C(5)); 2.28 (*qd*, ^3J = 7.6, ^3J = 3.0, H–C(4)); 1.66 (*s*, Me–C(9)); 1.31 (*s*, Me–C(2)); 1.29 (*d*, ^3J = 7.2, Me–C(5)); 1.19 (*d*, ^3J = 7.0, Me–C(7)); 1.15 (*d*, ^3J = 7.6, Me–C(4)); 0.96 (*s*, *t*-Bu); 0.95 (*t*, ^3J = 7.0, *Me*CCH$_2$O); 0.05 (*s*, 2 Me–Si). ^{13}C-NMR (100.6 MHz, C_6D_6, 70°): 198.2 (C(6)); 172.9, 170.2, 166.4 (*C*O–C(1), *C*O–C(11), *C*O–C(10)); 94.1 (C(11)); 87.8, 84.8, 79.0 (C(2), C(4a), C(9)); 87.6 (C(8)); 79.5 (C(3)); 61.8 (Me*C*H$_2$O); 63.1 (C(10)); 57.1 (C(11a)); 55.5 (C(4)); 50.8 (C(1)); 44.1 (C(5)); 36.8 (C(7)); 26.4 (*Me*$_3$C–Si); 18.6 (Me$_3$*C*–Si); 21.6 (*Me*–C(2)); 17.5 (*Me*–C(9)); 14.5 (*Me*CH$_2$O); 13.2 (*Me*–C(7); 12.8 (*Me*–C(4)); 11.5 (*Me*–C(5); –3.8, –4.2 (2 Me–Si). CI-MS (NH_3): 599 (0.52, [*M* + H_2O]$^+$), 598 (0.52), 581 (2, [*M* + H]$^+$), 580 (0.8, *M*$^+$), 523 (45, [*M* – (*t*-Bu)]$^+$), 495 (17), 477 (26), 449 (16), 433 (9), 403 (11), 251 (17), 97 (68), 73 (100). Anal. calc. for $C_{29}H_{44}O_{10}Si$ (580.74): C 59.98, H 7.64; found: C 59.91, H 7.58.

*(1*R*,2*S*,3*R*,4*R*,4a*R*,5*S*,6*R*,7*S*,8*R*,9*R*,10*R*,11*R*,12a*R*)-11-Acetoxy-3-{[(*tert*-Butyl)dimethylsilyl]oxy}-1-(ethoxycarbonyl)-1,3,4,7,8,9,10,11,12,12a-decahydro-2,4,5,7,9-pentamethyl-12-oxo-2*H*,5*H*-2,4a:6,9:6,11-triepoxybenzocyclodecene-10,8-carbolactone* (**50**). A mixture of **46** (32 mg, 0.055 mmol), anh. pyridine (0.5 ml), and Ac_2O (0.3 ml) was stirred at 20° for 1.5 h. Solvent evaporation at 20°/10^{-2} Torr and FC (petroleum ether/AcOEt 3:1) gave 25 mg (73%) of **50**. White solid. M.p. 90–92°. IR (KBr): 1775, 1730, 1210, 1050. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.51 (*d*, ^3J = 7.4, H–C(8)); 4.37 (*s*, H–C(10)); 4.14 (*q*, ^3J = 7.0, MeC*H*$_2$O); 3.86 (*d*, ^3J = 5.3, H–C(1)); 3.78 (*d*, ^3J = 5.3, H–C(12a)); 3.36 (*d*, ^3J = 2.6, H–C(3)); 2.33–2.23 (2*m*, H–C(7), H–C(5)); 2.13 (*s*, MeCO); 1.91 (*qd*, ^3J = 7.3, 2.6, H–C(4)); 1.60, 1.57 (2*s*, Me–C(9), Me–C(2)); 1.28 (*t*, ^3J = 7.0, *Me*CH$_2$O); 1.22 (*d*, ^3J = 7.3, Me–C(4)); 1.16, 1.06 (2*d*, ^3J = 7.0, 7.3, Me–C(7), Me–C(5)); 0.89 (*s*, *t*-Bu); 0.03 (*s*, 2 Me–Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 197.0 (*s*, C(12)); 172.2, 170.9, 167.0 (3*s*, *C O*–C(10), *C*O–C(1), COMe); 112.1 (*s*, C(11));

97.9 (*s*, C(6)); 92.7, 87.2, 85.0 (3*s*, C(9), C(2), C(4a)); 85.9 (*d*, ^1J(C,H) = 165, C(8)); 78.5 (*d*, ^1J(C,H) = 147, C(3)); 61.0 (*t*, ^1J(C,H) = 147, Me*C*H$_2$O); 54.4 (*d*, ^1J(C,H) = 130, C(4)); 52.9 (*d*, ^1J(C,H) = 133, C(12a)); 52.1 (*d*, ^1J(C,H) = 146, C(10)); 51.3 (*d*, ^1J(C,H) = 137, C(1)); 43.7 (*d*, ^1J(C,H) = 130, C(7)); 39.8 (*d*, ^1J(C,H) = 127, C(5)); 25.7 (*q*, ^1J(C,H) = 125, *Me*$_3$C–Si); 21.4 (*q*, ^1J(C,H) = 131, *Me*CO); 17.9 (*s*, Me$_3$*C*–Si); 22.6, 17.1 (2*q*, ^1J(C,H) = 129, 131, *Me*–C(9), *Me*–C(2)); 14.2 (*q*, ^1J(C,H) = 127, *Me*CH$_2$O); 12.3 (*q*, ^1J(C,H) = 126, Me–C(7)); 9.9 (*q*, ^1J(C,H) = 129, *Me*–C(5)); 7.1 (*q*, ^1J(C,H) = 129, *Me*–C(4)); –4.4, –4.9 (2*q*, ^1J(C,H) = 119, 118, 2 Me–Si). CI-MS (NH_3): 640 (6, $[M+H_2O]^+$), 622 (1, M^+), 583 (1), 565 (100), 563 (19, $[M-(t\text{-Bu})]^+$), 505 (10), 491 (7), 477 (8), 459 (6), 431 (6), 73 (43). Anal. calc. for $C_{31}H_{46}O_{11}Si$ (622.78): C 59.79, H 7.44, Si 4.51; found: C 59.65, H 7.40, Si 4.41.

*(1*R*,2*S*,3*R*,4*R*,4a*R*,5*S*,6*R*,7*S*,8*R*,9*R*,10*R*,11*S*,12a*R*)-1-(Ethoxycarbonyl)-1,3,4,7,8,9,10,11,12,12a-decahydro-3,11-dihydroxy-2,4,5,7,9-pentamethyl-12-oxo-2*H,5H*-2,4a:6,9:6,11-triepoxybenzocyclodecene-10,8-carbolactone* (**51**). CF_3CO_3H was generated *in situ* from 35% H_2O_2 (90 µl, 1.052 mmol) in 0.75 ml of CH_2Cl_2 and $(CF_3CO)_2O$ (0.67 ml, 4.81 mmol) at 0°. A soln. of **46** (21 mg, 0.036 mmol) in CH_2Cl_2 (0.5 ml) was then added. After 1.5 h at 0°, the mixture was allowed to warm to 20° and was then poured into 6 ml of 2% aq. K_2CO_3 soln. The mixture was extracted with CH_2Cl_2 (4 ml, 4 ×) and the combined org. layer washed with H_2O (2 ml, 2 ×), dried ($MgSO_4$), and evaporated. FC (petroleum ether/AcOEt 7:3 → pure AcOEt column 10 × 150 mm, 5-ml fractions) gave 4 mg (24%) of **51**. Colorless oil. IR (film): 3475, 1780, 1725, 1460, 1385, 1185, 1055. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.57 (*d*, ^3J = 7.3, H–C(8)); 4.18 (*m*, MeC*H*$_2$O); 3.83 (*d*, ^3J = 5.5, H–C(1)); 3.77 (*d*, ^3J = 5.5, H–C(12a)); 3.53 (*s*, H–C(10)); 3.46 (*m*, H–C(3)); 2.28 (2*m*, H–C(7), H–C(5)); 1.88 (*dq*, ^3J = 2.8, 7.2, H–C(4)); 1.64, 1.58 (2*s*, Me–C(9), Me–C(2)); 1.29 (*d*, ^3J = 7.2, Me–C(4)); 1.28 (*t*, ^3J = 7.1, *Me*CH$_2$O); 1.14, 1.06 (2*d*, ^3J = 7.1, 7.3, Me–C(7), Me–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 200.0 (*s*, C(12)); 175.5, 170.6 (2*s*, *C*O–C(10), *C*O–C(1)); 111.2 (*s*, C(11)); 94.6, 92.7, 86.7, 84.9 (4*s*, C(9), C(6), C(2), C(4a)); 87.3 (*d*, ^1J(C,H) = 163, C(8)); 78.4 (*d*, ^1J(C,H) = 144, C(3)); 61.2 (*t*, ^1J(C,H) = 148, Me*C*H$_2$O); 55.5 (*d*, ^1J(C,H) = 147, C(10)); 54.6 (*d*, ^1J(C,H) = 130, C(4)); 52.6 (*d*, ^1J(C,H) = 133, C(12a)); 51.0 (*d*, ^1J(C,H) = 135, C(1)); 43.7 (*d*, ^1J(C,H) = 130, C(7)); 40.1 (*d*, ^1J(C,H) = 127, C(5)); 22.4, 16.6 (2*q*, ^1J(C,H) = 129, 127, *Me*–C(9), *Me*–C(2)); 14.1 (*q*, ^1J(C,H) = 127, *Me*CH$_2$O); 12.4 (*q*, ^1J(C,H) = 126, *Me*–C(7)); 10.1 (*q*, ^1J(C,H) = 128, *Me*–C(5)); 7.0 (*q*, ^1J(C,H) = 128, *Me*–C(4)). CI-MS (NH_3): 484 (2, $[M+H_2O]^+$), 466 (3, M^+), 449 (7, $[M-OH]^+$), 448 (3, $[M-H_2O]^+$), 403 (6), 336 (36), 319 (50), 123 (100).

*(1*R*,2*S*,3*R*,4*R*,4a*S*,5*R*,6*R*,7*R*,8*S*,9a*R*,10*R*)-3-{[(*tert*-Butyl)dimethylsilyl]oxy}-1-(ethoxycarbonyl)-1,3,4,5,6,7,8,9,9a,10-decahydro-7-methoxy-2,4,5,7,10-pentamethyl-9-oxo-2*H*-2,4a-epoxyanthracene-8,6-carbolactone* (**52**). Ag_2O (80 mg, 0.35 mmol) and MeI (1 ml) were added to a stirred soln. of **39** (109 mg, 0.199 mmol) in MeCN (2 ml). The mixture was heated under reflux for 4 h, then diluted with Et_2O (15 ml), filtered through a *Celite* pad, and evaporated. FC (petroleum ether/AcOEt 4:1, column 25 × 150 mm, 10-ml fractions) gave 92 mg (82%) of **52**. Colorless foam. UV (MeCN): 247 (8600), 194 (6200). IR (KBr): 1790, 1275, 1660, 1620, 1195, 1095, 835, 775. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.20 (*m*, MeC*H*$_2$O); 4.15 (*dd*, ^3J = 2.8, ^4J = 1.1, H–C(6)); 4.02 (*d*, ^4J = 1.1, H–C(8)); 3.37 (*d*, ^3J = 2.6, H–C(3)); 3.32 (*d*, ^3J = 4.0, H–C(1)); 3.20 (*d*, ^3J = 4.0, H–C(9a)); 3.03 (*s*, MeO); 3.01 (*dq*, ^3J = 2.8, 7.5, H–C(5)); 2.70 (*q*, ^3J = 7.2, H–C(10)); 2.00 (*dq*, ^3J = 2.6, 7.4, H–C(4)); 1.49, 1.48 (2*s*, Me–C(2), Me–C(7)); 1.30 (*t*, ^3J = 7.0, *Me*CH$_2$O); 1.29 (*d*, ^3J = 7.2, Me–C(10)); 1.25 (*d*, ^3J = 7.5, Me–C(5)); 1.12 (*d*, ^3J = 7.4, Me–C(4)); 0.89 (*s*, *t*-Bu); 0.04, 0.03 (2*s*, 2 Me–Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 195.3 (*s*, C(9)); 173.3, 171.0 (2*s*, *C*O–C(1), *C*O–C(8)); 160.1 (*s*, C(10a)); 123.7 (*s*, C(8a)); 88.2, 87.5 (2*s*, C(2), C(4a)); 84.8 (*d*, ^1J(C,H) = 155, C(6)); 78.9 (*d*, ^1J(C,H) = 145, C(3)); 77.3 (*s*, C(7)); 61.1 (*t*, ^1J(C,H) = 147, Me*C*H$_2$O); 52.4 (*q*, ^1J(C,H) = 135, MeO); 54.5, 51.2, 49.2, 43.5 (4*d*, ^1J(C,H) = 135, 125, 127, 151, C(1), C(4), C(8), C(9a)); 34.5, 31.8 (2*d*, ^1J(C,H) = 129, 124, C(5), C(10)); 25.7 (*q*, ^1J(C,H) = 125, *Me*$_3$C–Si); 18.0 (*s*, Me$_3$*C*–Si); 18.7, 16.9, 14.2, 12.7, 12.6, 12.5 (6*q*, ^1J(C,H) = 127, 130, 127, 128, 128, 127, *Me*–C(2), *Me*–C(4), *Me*–C(5), *Me*–C(7), *Me*–C(10), *Me*CH$_2$O); –4.4, –4.8 (2*q*, ^1J(C,H) = 118, 118, 2 Me–Si). CI-MS (NH_3): 563 (46, $[M+H]^+$), 517 (13, $[M-OEt]^+$), 505 (100, $[M-(t\text{-Bu}]^+$), 459 (61), 431 (23), 375 (13), 73 (72). Anal. calc. for $C_{30}H_{46}O_8Si$ (562.77): C 64.03, H 8.24, Si 4.99; found: C 63.89, H 8.14, Si 4.92.

*(1*R*,2*R*,3*R*,4*S*,4a*R*,5*S*,7*S*,8*S*,9a*S*,10*S*)-1,8-Bis(acetoxymethyl)1,3,4,8,9a,10-hexahydro-3,7-dihydroxy-2,4,5,7,10-pentamethyl-2*H*-2,4a-epoxyanthracene-6,9-(5*H*,7*H*)-dione* (**53**). At 0°, 2M aq. NaOH (13 µl, 0.026 mmol, 0.5 equiv.) was added to a stirred soln. of (–)-**33** (25 mg, 0.052 mmol) in THF (1.9 ml) and EtOH (0.9 ml). After stirring at 0° for 30 min, H_2O (1 ml) was added, the mixture neutralized with 0.2N aq. HCl and diluted with Et_2O (6 ml), the aq. layer extracted with Et_2O (2 ml, 5 ×), and the org. phase washed with brine (3 ml, 2 ×), dried ($MgSO_4$), and evaporated. FC (CH_2Cl_2/MeOH 98:2, column 10 × 150 mm, 5-ml fractions) gave 9 mg (36%) of **53** and 8 mg (32%) of (–)-**33**. **53**: Colorless oil. UV (MeCN): 239 (8700), 193 (3300). IR (film): 3465, 1730, 1660, 1455, 1380, 1240. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.61 (*dd*, ^2J = 11.6, ^3J = 9.0, 1 H, CH_2–C(1)); 4.46 (*dd*, ^2J = 11.6, ^3J = 5.7, 1 H, CH_2–C(1)); 4.21 (*dd*, ^2J = 11.9, ^3J = 3.4, 1 H, CH_2–C(8)); 3.94 (*d*, ^3J = 10.2, H–C(3)); 3.84

(*dd*, ^2J = 11.9, ^3J = 2.8, 1 H, CH_2–C(8)); 3.49–3.43 (*m*, H–C(8), H–C(5)); 2.74 (*q*, ^3J = 7.3, H–C(10)); 2.69 (*d*, ^3J = 5.0, H–C(9a)); 2.61–2.57 (*m*, H–C(1)); 2.41 (*dq*, ^3J = 10.2, 7.5, H–C(4)); 2.10, 1.90 (2*s*, 2 MeCO); 1.47, 1.39 (2*s*, Me–C(2), Me–C(7)); 1.40 (*d*, ^3J = 8.0, Me–C(5)); 1.31 (*d*, ^3J = 7.3, Me–C(10)); 1.01 (*d*, ^3J = 7.5, Me–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 207.3, 198.2 (2*s*, C(6), C(9)); 171.4, 170.3 (2*s*, 2 Me*C*O); 158.1 (*s*, C(10a)); 127.3 (*s*, C(8a)); 89.6, 85.3 (2*s*, C(2), C(4a)); 77.2 (*d*, ^1J(C,H) = 131, C(3)); 73.4 (*s*, C(7)); 63.7, 62.7 (2*t*, ^1J(C,H) = 150, 150, 2 CH_2O); 51.7 (*d*, ^1J(C,H) = 132, C(1)); 49.7 (*d*, ^1J(C,H) = 126, C(9a)); 46.1, 40.9 (2*d*, ^1J(C,H) = 133, ^1J(C,H) = 125, C(8), C(5)); 40.9 (*d*, ^1J(C,H) = 125, C(4)); 33.3 (*d*, ^1J(C,H) = 123, C(10)); 21.2, 20.5 (2*q*, ^1J(C,H) = 129, 129, 2 *Me*CO); 19.8, 19.7 (2*q*, ^1J(C,H) = 128, ^1J(C,H) = 126, *Me*–C(2), *Me*–C(7)); 13.8 (*q*, ^1J(C,H) = 130, *Me*–C(5)); 12.7 (*q*, ^1J(C,H) = 130, *Me*–C(10)); 10.4 (*q*, ^1J(C,H) = 126, *Me*–C(4)). CI-MS (NH_3): 479 (9, $[M+H]^+$), 478 (2, M^+), 418 (24), 375 (32), 359 (61), 315 (32), 289 (41), 169 (53), 83 (100).

*(1*R*,2*R*,3*R*,4*S*,4a*S*,5S,7*R*,8*S*,8a*R*,9a*S*,10S,10a*S*)-* and *(1*R*,2*R*,3*R*,4*S*,4a*S*,5S,7S,8S,8a*R*,9a*S*,10S,10a*S*)-1,8-Bis(acetoxymethyl)-1,3,4,8,8a,9a,10,10a-octahydro-10a-hydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethyl-2*H*-2,4a-epoxyanthracene-6,9(5*H*,7*H*)-dione* (**56** and **57**, resp.). Et_3N (0.4 ml, 2.8 mmol) was added to 0.012M (–)-**34** (290 mg, 0.555 mmol) in MeCN (45 ml) in a quartz tube. Ar was bubbled through the soln. for 15 min, then the mixture was irradiated with low-pressure Hg lamps at 254 nm in a *Gräntzel*-type apparatus at 20° for 20 min (→ pale yellow soln.). The reaction was repeated 10 × with the same quantities (total: 2.9 g (5.55 mmol) of (–)-**34**). The combined reaction mixtures were evaporated to yield (–)-**34**/**56** 1:1, which was reduced without purification (see below). An anal. pure sample of **56** was obtained by FC (petroleum ether/AcOEt 7:3). On FC, also **57** was also isolated; the quantity of **57** increased if the crude was treated with 1M aq. HCl. The absence of **57** in the crude product was established by ^{13}C-NMR and by HPLC (petroleum ether/AcOEt 3:2; t_R 7.5 (–)-**34**), 9.9 (**56**), 13.2 min (**57**).

Data of **56**: Colorless foam. IR (film): 3485, 1740, 1710, 1455, 1385, 1240, 1130, 1035. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.64–4.57 (*AB*, MeOCH_2); 4.54 (*dd*, ^2J = 11.3, ^3J = 7.8, 1 H, CH_2–C(1)); 4.35 (*dd*, ^2J = 11.3, ^3J = 4.7, 1 H, CH_2–C(1)); 4.17 (*dd*, ^2J = 11.5, ^3J = 4.4, 1 H, CH_2–C(8)); 3.79 (*dd*, ^3J = 10.5, ^4J = 1.4, H–C(3)); 3.75 (*dd*, ^2J = 11.5, ^3J = 2.6, 1 H, CH_2–C(8)); 3.49–3.45 (*m*, H–C(8)); 3.40 (*s*, MeO); 3.40–3.36 (*m*, H–C(7)); 3.19 (*s*, OH); 2.80 (*dddd*, ^3J = 7.8, 4.7, 4.7, ^4J = 1.4, H–C(1)); 2.77 (*d*, ^3J = 4.7, H–C(9a)); 2.69 (*d*, ^3J = 5.0, H–C(8a)); 2.65 (*dq*, ^3J = 10.5, 7.4, H–C(4)); 2.48 (*q*, ^3J = 7.6, H–C(5)); 2.23 (*q*, ^3J = 6.8, H–C(10)); 2.06, 1.95 (2*s*, 2 MeCO); 1.49 (*s*, Me–C(2)); 1.28 (*d*, ^3J = 7.6, Me–C(5)); 1.16 (*d*, ^3J = 6.8, Me–C(10)); 1.05 (*d*, ^3J = 7.0, Me–C(7)); 1.03 (*d*, ^3J = 7.4, Me–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 214.3, 207.5 (2*s*, C(6), C(9)); 171.3, 170.7 (2*s*, 2 Me*C*O); 96.8 (*t*, ^1J(C,H) = 162, MeO*C*H_2); 93.9, 85.7, 80.6 (3*s*, C(2), C(4a), C(10a)); 81.9 (*d*, ^1J(C,H) = 135, C(3)); 64.9 (*t*, ^1J(C,H) = 149, *C*H_2–C(8)); 63.5 (*t*, ^1J(C,H) = 149, *C*H_2–C(1)); 56.0 (*q*, ^1J(C,H) = 149, MeO); 54.5 (*d*, ^1J(C,H) = 130, C(9a)); 53.3 (*d*, ^1J(C,H) = 117, C(8a)); 50.4 (*d*, ^1J(C,H) = 128, C(5)); 49.7 (*d*, ^1J(C,H) = 134, C(1)); 40.0 (*d*, ^1J(C,H) = 133, C(7)); 38.4 (*d*, ^1J(C,H) = 134, C(4)); 37.5 (*d*, ^1J(C,H) = 123, C(10)); 33.1 (*d*, ^1J(C,H) = 129, C(8)); 21.1, 20.7 (2*q*, ^1J(C,H) = 129, ^1J(C,H) = 130, 2 *Me*CO); 19.8 (*q*, ^1J(C,H) = 129, *Me*–C(2)); 14.5 (*q*, ^1J(C,H) = 128, *Me*–C(5)); 10.8, 10.6 (2*q*, ^1J(C,H) = 129, ^1J(C,H) = 123, *Me*–C(7), *Me*–C(4)); 7.8 (*q*, ^1J(C,H) = 128, *Me*–C(10)). CI-MS (NH_3): 542 (13, $[M+H_2O]^+$), 525 (1.5, $[M+H]^+$), 524 (1.2, M^+), 465 (8, $[M-OAc]^+$), 403 (13), 343 (14), 291 (26), 273 (17), 259 (26), 219 (38), 111 (62), 83 (100). Anal. calc. for $C_{27}H_{40}O_{10}$ (524.60): C 61.82, H 7.69; found: C 61.81, H 7.79.

Data of **57**: Colorless foam. IR (KBr): 3500, 1735, 1715, 1240, 1035. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.59–4.45 (*AB*, OCH_2O); 4.45 (*dd*, ^2J = 11.4, ^3J = 9.7, 1 H, CH_2–C(1)); 4.33–4.28 (*m*, 2 H, CH_2–C(1), CH_2–C(8)); 4.15 (*dd*, ^2J = 12.0, ^3J = 1.9, 1 H, CH_2–C(8)); 3.75 (*dd*, ^3J = 10.5, ^4J = 1.6, H–C(3)); 3.37 (*s*, MeO); 2.98 (*d*, ^3J = 10.8, H–C(8a)); 2.86 (*dddd*, ^3J = 9.7, 5.3, 5.3, ^4J = 1.6, H–C(1)); 2.74 (*d*, ^3J = 5.3, H–C(9a)); 2.68 (*q*, ^3J = 7.4, H–C(5)); 2.64–2.57 (*m*, H–C(7), H–C(4)); 2.47 (*dddd*, ^3J(8,8a) = 10.8, ^3J(8,7) = 10.8, ^3J = 1.9, 1.9, H–C(8)); 2.24 (*q*, ^3J = 7.0, H–C(10); 2.10, 2.01 (2*s*, 2 MeCO); 1.43 (*s*, Me–C(2)); 1.18 (*d*, ^3J = 7.4, Me–C(5)); 1.10 (*d*, ^3J = 6.3, Me–C(7)); 1.07 (*d*, ^3J = 7.0, Me–C(10)); 1.04 (*d*, ^3J = 7.3, Me–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 212.7, 207.4 (2*s*, C(6), C(9)); 171.2, 170.9 (2*s*, 2 Me*C*O); 96.8 (*t*, ^1J(C,H) = 163, OCH_2O); 94.4, 85.7, 83.2 (3*s*, C(2), C(4a), C(10a)); 81.9 (*d*, ^1J(C,H) = 152, C(3)); 64.0 (*t*, ^1J(C,H) = 150, *C*H_2–C(8)); 63.4 (*t*, ^1J(C,H) = 150, *C*H_2–C(1)); 55.9 (*q*, ^1J(C,H) = 142, MeO); 55.3 (*d*, ^1J(C,H) = 130, C(9a)); 52.3 (*d*, ^1J(C,H) = 136, C(5)); 51.5 (*d*, ^1J(C,H) = 124, C(8a)); 47.8 (*d*, ^1J(C,H) = 133, C(1)); 39.6 (*d*, ^1J(C,H) = 126, C(8)); 38.7 (*d*, ^1J(C,H) = 131, C(4)); 37.7 (*d*, ^1J(C,H) = 120, C(7)); 37.0 (*d*, ^1J(C,H) = 123, C(10)); 20.9 (*q*, ^1J(C,H) = 129, 2 *Me*CO); 19.7 (*q*, ^1J(C,H) = 125, *Me*–C(2)); 14.2 (*q*, ^1J(C,H) = 128, *Me*–C(5)); 11.6 (*q*, ^1J(C,H) = 127, *Me*–C(7)); 10.9 (*q*, ^1J(C,H) = 128, *Me*–C(4)); 7.3 (*q*, ^1J(C,H) = 127, *Me*–C(10)). CI-MS (NH_3): 524 (0.21, M^+), 479 (3), 465 (7), 433 (7), 419 (9), 403 (30), 375 (29), 362 (46), 343 (22), 273 (100). Anal. calc. for $C_{27}H_{40}O_{10}$ (524.60): C 61.82, H 7.69; found: C 61.74, H 7.58.

*(1*R*,2*R*,3*R*,4*S*,4a*S*,5*R*,6*R*,7*R*,8*S*,8a*R*,9a*S*,10S,10a*R*)-1,8-Bis(acetoxymethyl)-1,3,4,6,7,8,8a,9a,10,10a-decahydro-6,10a-dihydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethyl-2*H*-2,4a-epoxyanthracen-9(5*H*)-one* ((–)-**58**).

To the crude (−)-**34**/**56** *ca.* 1:1 (5.55 mmol) in MeCN (11.5 ml) at −20°, a soln. of $(Me_4N)BH(OAc)_3$ (7 g, 26.6 mmol) in 23 ml of AcOH/MeCN 1:1 (also cooled to −20°) was added dropwise with a cannula. The mixture was stirred at −20° for 15 h, then allowed to warm to 20°, and quenched with 6 ml of 0.5M potassium sodium tartrate. The mixture was diluted with CH_2Cl_2 (80 ml) and washed with sat. aq. $NaHCO_3$ soln. (20 ml), the aq. layer back-extracted with CH_2Cl_2 (10 ml, 4×), and the combined org. layer washed with sat. aq. $NaHCO_3$ soln. (20 ml). The aq. layer was back-extracted with CH_2Cl_2 (10 ml, 4×). The combined org. layer was dried ($MgSO_4$) and evaporated. FC (20% → 60% AcOEt/CH_2Cl_2, column 50 × 150 mm, 50-ml fractions): 1.27 g (43% over the two steps) of (−)-**58** (R_f (petroleum ether/AcOEt 1:1) 0.13), 1.02 g (35%) of (−)-**34** (R_f (petroleum ether/AcOEt 1:1) 0.43), and 198 mg (7%) of the product of reduction of ketone (−)-**34**; *i.e.* of (1*R*,2*R*,3*R*,4*S*,4a*S*,5*R*,6*S*,7*S*,8*S*,8a*S*,9a*R*,10*S*,10a*R*)-1,8-bis(acetoxymethyl)-1,3,4,6,7,8,8a,9a-octahydro-6-hydroxy-3-(methoxmethoxy)-2,4,5,7,10-pentamethyl-2*H*,10*H*-2,4a:7,10a-diepoxyanthracen-9(5*H*)-one.

Data of (−)-**58**: White solid. M.p. 215–217°. $[\alpha]_{589}^{20} = -15$ (*c* = 1.2, $CHCl_3$; e.e. 90%). IR (KBr): 3525, 2605, 1735, 1705, 1465, 1370, 1245, 1145, 1040. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.60–4.55 (*AB*, MeOCH_2); 4.41 (*dd*, ^2J = 11.4, ^3J = 9.8, 1 H, CH_2–C(1)); 4.29 (*dd*, ^2J = 11.4, ^3J = 4.9, 1 H, CH_2–C(1)); 4.18–4.13 (*m*, 1 H, CH_2–C(8), H–C(6)); 4.00 (*dd*, $^2J = {}^3J$ = 10.1, 1 H, CH_2–C(8)); 3.74 (*dd*, ^3J = 10.5, ^4J = 1.6, H–C(3)); 3.38 (*s*, MeO); 2.97 (*dddd*, ^3J = 9.8, 4.9, ^4J = 1.6, H–C(1)); 2.74 (*d*, ^3J = 4.9, H–C(9a)); 2.73 (*m*, H–C(8)); 2.57 (*dq*, ^3J = 10.5, 7.3, H–C(4)); 2.48 (*d*, ^3J = 11.5, H–C(8a)); 2.29 (*m*, H–C(7)); 2.20–2.10 (*m*, H–C(5), H–C(10)); 2.05, 2.00 (2*s*, 2 MeCO); 1.46 (*s*, Me–C(2)); 1.10, 1.02 (2*d*, ^3J = 6.9, 7.4, Me–C(5), Me–C(10)); 1.03 (*d*, ^3J = 7.3, Me–C(4)); 0.89 (*d*, ^3J = 7.5, Me–C(7)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 207.9 (*s*, C(9)); 171.2, 171.0 (2*s*, 2 Me*C*O); 96.8 (*t*, ^1J(C,H) = 162, MeOCH_2O); 95.2, 85.6, 82.6 (3*s*, C(2), C(4a), C(10a)); 82.0 (*d*, ^1J(C,H) = 135, C(3)); 68.1 (*d*, ^1J(C,H) = 144, C(6)); 64.3, 63.5 (2*t*, ^1J(C,H) = 149, ^1J(C,H) = 149, *C*H_2–C(1), *C*H_2–C(8)); 56.0 (*q*, ^1J(C,H) = 132, MeO); 55.9 (*d*, ^1J(C,H) = 142, C(9a)); 48.3 (*d*, ^1J(C,H) = 130, C(8a)); 46.9 (*d*, ^1J(C,H) = 135, C(1)); 43.3, 37.9 (2*d*, ^1J(C,H) = 127, ^1J(C,H) = 122, C(5), C(10)); 38.9 (*d*, ^1J(C,H) = 132, C(4)); 34.7 (*d*, ^1J(C,H) = 127, C(7)); 33.8 (*d*, ^1J(C,H) = 129, C(8)); 21.0, 20.9 (2*q*, ^1J(C,H) = 130, 130, 2 *Me*CO); 19.7 (*q*, ^1J(C,H) = 123, *Me*–C(2)); 11.1, 11.0 (2*q*, ^1J(C,H) = 130, ^1J(C,H) = 129, *Me*–C(4), *Me*–C(5) or *Me*–C(10)); 9.6 (*q*, ^1J(C,H) = 128, *Me*–C(7)); 7.8 (*q*, ^1J(C,H) = 123, *Me*–C(5) or *Me*–C(10)). CI-MS (NH_3): 544 (3.5, $[M + H_2O]^+$), 530 (5), 526 (0.5, M^+), 467 (4, $[M - OAc]^+$), 404 (7), 377 (19), 364 (25), 345 (18), 304 (32), 293 (100). Anal. calc. for $C_{27}H_{42}O_{10}$ (526.62): C 61.58, H 8.04; found: C 61.53, H 8.05.

*Data for the Reduction Product of (−)-***34** (see above): Colorless foam. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.60, 4.56 (*AB*, ^2J = 6.6, OCH_2O); 4.52–4.44, 4.39–4.30 (2*m*, 2 CH_2O); 3.86 (*dd*, ^3J(6,5) = 10.5, ^3J(6, OH) = 4.8, H–C(6)); 3.75 (*dd*, ^3J = 10.6, ^4J = 1.7, H–C(3)); 3.38 (*s*, MeO); 2.93–2.86 (*m*, H–C(1), H–C(8)); 2.66, 2.65 (2*d*, ^3J = 4.0, 4.0, H–C(9a), H–C(8a)); 2.47 (*dq*, ^3J = 10.6, 7.4, H–C(4)); 2.41 (*dq*, ^3J = 10.5, 7.4, H–C(5)); 2.15 (*q*, ^3J = 7.1, H–C(10)); 2.01, 2.00 (2*s*, 2 MeCOO); 1.78 (*d*, ^3J = 4.8, OH); 1.47, 1.46 (2*s*, Me–C(2), Me–C(7)); 1.15 (*d*, ^3J = 7.1, Me–C(10)); 1.03 (*d*, ^3J = 7.4, Me–C(5)); 1.01 (*d*, ^3J = 7.4, Me–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 208.3 (*s*, C(9)); 171.2, 171.1 (2*s*, 2 Me*C*O); 96.6 (*t*, ^1J(C,H) = 163, OCH_2O); 93.5, 93.4, 85.5, 84.8 (4*s*, C(2), C(4a), C(7), C(10a)); 82.3 (*d*, ^1J(C,H) = 151, C(6)); 76.8 (*d*, ^1J(C,H) = 149, C(3)); 64.0, 63.8 (2*t*, ^1J(C,H) = 150, 150, *C*H_2–C(1), *C*H_2–C(8)); 55.7 (*q*, ^1J(C,H) = 142, MeO); 52.8, 52.7 (2*d*, ^1J(C,H) = 128, 129, C(8a), C(9a)); 48.0, 47.9 (2*d*, ^1J(C,H) = 146, 146, C(1), C(8)); 41.2 (*d*, ^1J(C,H) = 130, C(5)); 40.2 (*d*, ^1J(C,H) = 131, C(4)); 32.4 (*d*, ^1J(C,H) = 117, C(10)); 20.9, 20.9 (2*q*, ^1J(C,H) = 129, 129, 2 *Me*COO); 19.9, 19.6 (2*q*, ^1J(C,H) = 127, 127, *Me*–C(2), *Me*–C(7)); 11.1, 10.6 (2*q*, ^1J(C,H) = 126, 125, *Me*–C(4), *Me*–C(5)); 9.2 (*q*, ^1J(C,H) = 129, Me–C(10)).

*(1*R*,2*R*,3*R*,4*S*,4a*S*,5*R*,6*R*,7*S*,8*S*,8a*R*,9a*S*,10*S*,10a*R*)-1,8-Bis(acetoxymethyl)-1,3,4,6,7,8,8a,9a,10,10a-decahydro-6,10a-dihydroxy-3-(methoxmethoxy)-2,4,5,7,10-pentamethyl-2*H*-2,4a-epoxyanthracen-9(5*H*)-one* (**59**). A soln. of $(Me_4N)BH(OAc)_3$ (289 mg, 1.5 mmol) in anh. AcOH/MeCN 1:1 (1 ml) was added to a stirred soln. of **57** (72 mg, 0.137 mmol) in anh. MeCN (0.5 ml) at −20°. After stirring at −20° for 15 h, more $(Me_4N)BH(OAc)_3$ (100 mg) was added, and the mixture was stirred at 20° for 1 h. Then 0.5M aq. potassium sodium tartrate was added, the mixture diluted with CH_2Cl_2 (15 ml), the soln. washed with sat. aq. $NaHCO_3$ soln. (4 ml), and the aq. layer back-extracted with CH_2Cl_2 (2 ml, 4×). The combined org. layer was washed with sat. aq. $NaHCO_3$ soln. (5 ml), the aq. layer extracted with CH_2Cl_2 (2 ml, 4×), and the combined org. layer dried ($MgSO_4$) and evaporated: 71 mg (98%) of pure **59**. Colorless foam. IR (KBr): 3530, 1740, 1465, 1385, 1245, 1150, 1035. ^{1}H-NMR (400 MHz, C_6D_6): 4.78 (*dd*, ^2J = 11.3, ^3J = 9.8, 1 H, CH_2–C(1)); 4.59 (*m*, CH_2–C(8)); 4.48 (*dd*, ^2J = 11.3, ^3J = 4.9, 1 H, CH_2–C(1)); 4.30 (*s*, OCH_2O); 4.00 (*dd*, ^3J(6,7) = 11.0, ^3J(6,5) = 4.4, H–C(6)); 3.65 (*dd*, ^3J = 10.5, ^4J = 1.7, H–C(3)); 3.36 (*dddd*, ^3J = 9.8, 4.9, 5.5, ^4J = 1.7, H–C(1)); 3.15 (*s*, MeO); 2.95 (*d*, ^3J = 11.5, H–C(8a)); 2.93 (*d*, ^3J = 5.5, H–C(9a)); 2.58 (*ddd*, ^3J = 11.5, 11.5, 2.5, H–C(8)); 2.39 (*dq*, ^3J = 10.5, 7.2, H–C(4)); 2.32 (*qd*, ^3J = 7.1, 4.4, H–C(5)); 2.19 (*q*, ^3J = 6.9, H–C(10)); 2.06, 1.80 (2*s*, 2 MeCO); 1.88 (*m*, H–C(7)); 1.35 (*s*, Me–C(2)); 1.21 (*d*, ^3J = 6.2, Me–C(7)); 1.18 (*d*, ^3J = 6.9, Me–C(10)); 1.13 (*d*, ^3J = 7.1,

Me–C(5)); 0.81 (*d*, ^3J = 7.2, Me–C(4)). ^{13}C-NMR (100.6 MHz, C_6D_6): 208.6 (*s*, C(9)); 171.3, 171.0 (2*s*, 2 Me*C*OO); 97.2 (*t*, ^1J(C,H) = 163, OCH_2O); 95.8, 86.3, 82.3 (3*s*, C(4a), C(2), C(10a)); 82.8 (*d*, ^1J(C,H) = 138, C(3)); 71.9 (*d*, ^1J(C,H) = 143, C(6)); 64.8 (*t*, ^1J(C,H) = 149, *C*H_2–C(8)); 64.1 (*t*, ^1J(C,H) = 149, *C*H_2–C(1)); 56.5 (*d*, ^1J(C,H) = 129, C(9a)); 59.9 (*q*, ^1J(C,H) = 141, MeO); 52.9 (*d*, ^1J(C,H) = 124, C(8a)); 48.5 (*d*, ^1J(C,H) = 133, C(1)); 43.6 (*d*, ^1J(C,H) = 129, C(5)); 39.5 (*d*, ^1J(C,H) = 132, C(4)); 38.9 (*d*, ^1J(C,H) = 122, C(10)); 38.6 (*d*, ^1J(C,H) = 127, C(8)); 32.0 (*d*, ^1J(C,H) = 125, C(7)); 21.3, 20.9 (2*q*, ^1J(C,H) = 129, ^1J(C,H) = 129, 2 *Me*CO); 20.2 (*q*, ^1J(C,H) = 127, *Me*–C(2)); 15.8 (*q*, ^1J(C,H) = 125, Me–C(7)); 11.1 (*q*, ^1J(C,H) = 124, *Me*–C(4)); 8.8 (*q*, ^1J(C,H) = 126, *Me*–C(5)); 8.1 (*q*, ^1J(C,H) = 128, *Me*–C(10)). CI-MS (NH_3): 544 (1, $[M+H_2O]^+$), 530 (1), 526 (0.8, M^+), 509 (2), 467 (8, $[M-OAc]^+$), 404 (27), 377 (62), 364 (66), 345 (43), 293 (41), 275 (60), 257 (41), 123 (100). Anal. calc. for $C_{27}H_{42}O_{10}$ (526.62): C 61.58, H 8.04; found: C 61.60, H 8.07.

*(1*R*,2*R*,3*R*,4*S*,4a*S*,5*R*,6*R*,7*R*,8*S*,8a*R*,9a*S*,10*S*,10a*R*)-6-Acetoxy-1,8-bis(acetoxymethyl)-1,3,4,6,7,8,8a,9a,10,10a-decahydro-10a-hydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethyl-2*H*-2,4a-epoxyanthracen-9(5*H*)-one* (**60**). A mixture of (–)-**58** (282 mg, 0.535 mmol) in anh. CH_2Cl_2 (5 ml), pyridine (0.13 ml, 1.6 mmol), Me_3COCl (76 µl, 1.07 mmol) and DMAP (5 mg) was stirred at 20° for 1 h. More MeCOCl was added (0.070 ml, 0.986 mmol). After 2 h at 20°, the mixture was diluted with CH_2Cl_2 (15 ml) and washed with 0.5M aq. HCl (4 ml, 2 ×), sat. aq. $NaHCO_3$ soln. (4 ml, 2 ×), and brine (4 ml). The org. layer was dried ($MgSO_4$) and evaporated. FC (petroleum ether/AcOEt 3:2, column 20 × 150 mm, 10-ml fractions) gave 272 mg (89%) of **60**. Colorless foam. IR (KBr): 3520, 1735, 1450, 1370, 1245, 1035. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.22 (*dd*, ^3J = 5.3, 5.3, H–C(6)); 4.59, 4.56 (*AB*, ^2J = 6.7, OCH_2O); 4.43 (*dd*, ^2J = 11.2, ^3J = 9.8, 1 H, CH_2–C(1)); 4.28 (*dd*, ^2J = 11.2, ^3J = 4.9, 1 H, CH_2–C(1)); 4.14 (*dd*, ^2J = 11.7, ^3J = 3.3, 1 H, CH_2–C(8)); 4.00 (*dd*, ^2J = 11.7, ^3J = 11.5, 1 H, CH_2–C(8)); 3.73 (*dd*, ^3J = 11.5, ^4J = 1.7, H–C(3)); 3.38 (*s*, MeO); 2.96 (*dddd*, ^3J = 9.8, 5.0, 4.9, ^4J = 1.7, H–C(1)); 2.82 (*m*, H–C(8)); 2.73 (*d*, ^3J = 5.0, H–C(9a)); 2.56 (*dq*, ^3J = 11.5, 7.2, H–C(4)); 2.50 (*d*, ^3J = 11.5, H–C(8a)); 2.44 (*m*, H–C(7)); 2.25 (*dq*, ^3J = 7.5, 5.3, H–C(5)); 2.15 (*q*, ^3J = 6.9, H–C(10)); 2.09, 2.04, 2.00 (3*s*, 3 MeCO); 1.45 (*s*, Me–C(2)); 1.09 (*d*, ^3J = 6.9, Me–C(10)); 1.05 (*d*, ^3J = 7.5, Me–C(5)); 1.02 (*d*, ^3J = 7.3, Me–C(4)); 0.90 (*d*, ^3J = 7.4, Me–C(7)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 207.4 (*s*, C(9)); 171.1, 170.9, 169.9 (3*s*, 3 Me*C*O); 96.7 (*t*, ^1J(C,H) = 162, OCH_2O); 94.9, 85.4, 82.1 (3*s*, C(2), C(4a), C(10a)); 81.9 (*d*, ^1J(C,H) = 147, C(3)); 71.4 (*d*, ^1J(C,H) = 148, C(6)); 64.0 (*t*, ^1J(C,H) = 150, *C*H_2–C(8)); 63.4 (*t*, ^1J(C,H) = 152, *C*H_2–C(1)); 55.8 (*q*, ^1J(C,H) = 142, MeO); 55.7 (*d*, ^1J(C,H) = 135, C(9a)); 48.0 (*d*, ^1J(C,H) = 115, C(8a)); 46.8 (*d*, ^1J(C,H) = 130, C(1)); 40.5 (*d*, ^1J(C,H) = 130, C(5)); 38.8 (*d*, ^1J(C,H) = 135, C(4)); 37.5 (*d*, ^1J(C,H) = 124, C(10)); 33.3 (*d*, ^1J(C,H) = 128, C(8)); 31.6 (*d*, ^1J(C,H) = 130, C(7)); 21.2, 20.8, 20.8 (3*q*, ^1J(C,H) = 129, 129, 129, 3 *Me*CO); 19.6 (*q*, ^1J(C,H) = 129, Me–C(2)); 12.0 (*q*, ^1J(C,H) = 126, *Me*–C(5)); 10.9 (*q*, ^1J(C,H) = 124, *Me*–C(4)); 10.3 (*q*, ^1J(C,H) = 125, *Me*–C(7)); 7.6 (*q*, ^1J(C,H) = 127, *Me*–C(10)). CI-MS (NH_3):587 (11; $[M+H_2O]^+$), 586 (20, $[M+OH]^+$), 509 (8, $[M-OAc]^+$), 447 (15), 419 (24), 406 (31), 346 (39), 335 (100). Anal. calc. for $C_{29}H_{44}O_{11}$ + 1/3 H_2O) (574.66): C 60.62, H 7.84; found: C 60.42, H 7.95.

*(1*R*,2*R*,3*R*,4*S*,4a*S*,5*R*,6*R*,7*S*,8*S*,8a*R*,9a*S*,10*S*,10a*R*)-6-Acetoxy-1,8-bis(acetoxymethyl)-1,3,4,6,7,8,8a,9a,10,10a-decahydro-10a-hydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethyl-2*H*-2,4a-epoxyanthracen-9(5*H*)-one* (**61**). As described for **60**, from **59** (269 mg, 0.511 mmol). FC (petroleum ether/AcOEt 6:4, column 20 × 150 mm, 10-ml fractions): 243 mg (84%) of **61**. Colorless foam. IR (KBr): 3500, 1735, 1370, 1245, 1030. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.03 (*dd*, ^3J(6,7) = 11.7, ^3J(6,5) = 4.3, H–C(6)); 4.58, 4.54 (*AB*, ^2J = 6.6, OCH_2O); 4.42 (*dd*, ^2J = 11.4, ^3J = 9.2, 1 H, CH_2–C(1)); 4.36 (*dd*, ^2J = 11.9, ^3J = 2.8, 1 H, CH_2–C(8)); 4.32 (*dd*, ^2J = 11.4, ^3J = 5.5, 1 H, CH_2–C(1)); 4.00 (*dd*, ^2J = 11.9, ^3J = 2.1; 1 H, CH_2–C(8)); 3.75 (*dd*, ^3J = 10.5, ^4J = 1.7, H–C(3)); 3.37 (*s*, MeO); 2.86 (*dddd*, ^3J = 9.2, 5.5, 5.5, ^4J = 1.7, H–C(1)); 2.64 (*d*, ^3J = 5.5, H–C(9a)); 2.63 (*d*, ^3J = 11.2, H–C(8a)); 2.61 (*s*, OH); 2.58 (*dq*, ^3J = 10.5, 7.3, H–C(4)); 2.26 (*qd*, ^3J = 7.1, 4.3, H–C(5)); 2.22 (*dddd*, ^3J(8,7) = 11.7, ^3J = 11.2, 2.8, 2.1, H–C(8)); 2.14 (*q*, ^3J = 7.0, H–C(10)); 2.06, 2.05, 2.01 (3*s*, 3 MeCOO); 1.81 (*ddq*, ^3J = 11.7, 11.7, 6.5, H–C(7)); 1.44 (*s*, Me–C(2)); 1.08 (*d*, ^3J = 7.0, Me–C(10)); 1.00 (*d*, ^3J = 7.3, Me–C(4)); 0.95 (*d*, ^3J = 6.5, Me–C(7)); 0.93 (*d*, ^3J = 7.1, Me–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 207.8 (*s*, C(9)); 171.2, 171.0, 170.2 (3*s*, 3 Me*C*O); 96.8 (*t*, ^1J(C,H) = 163, OCH_2O); 94.6, 85.6, 81.1 (3*s*, C(2), C(4a), C(10a)); 82.0 (*d*, ^1J(C,H) = 168, C(3)); 74.7 (*d*, ^1J(C,H) = 150, C(6)); 63.7, 63.4 (2*t*, ^1J(C,H) = 150, ^1J(C,H) = 151, *C*H_2–C(1), *C*H_2–C(8)); 55.8 (*q*, ^1J(C,H) = 148, MeO); 55.3, 51.5 (2*d*, ^1J(C,H) = 130, ^1J(C,H) = 125, C(8a), C(9a)); 47.7 (*d*, ^1J(C,H) = 138, C(1)); 39.7 (*d*, ^1J(C,H) = 132, C(5)); 38.7 (*d*, ^1J(C,H) = 132, C(4)); 37.9 (*d*, ^1J(C,H) = 122, C(10)); 37.2 (*d*, ^1J(C,H) = 129, C(8)); 28.6 (*d*, ^1J(C,H) = 129, C(7)); 21.1, 20.9, 20.9 (3*q*, ^1J(C,H) = 130, ^1J(C,H) = 129, 129, 3 *Me*CO); 19.7 (*q*, ^1J(C,H) = 127, Me–C(2)); 15.1 (*q*, ^1J(C,H) = 126, *Me*–C(7)); 10.8 (*q*, ^1J(C,H) = 127, *Me*–C(4)); 8.8 (*q*, ^1J(C,H) = 126, *Me*–C(5)); 7.4 (*q*, ^1J(C,H) = 127, *Me*–C(10)). CI-MS (NH_3): 586 (23, $[M+H_2O]^+$), 509 (21, $[M-OAc]^+$), 447 (50), 419 (46), 406 (46), 387 (30), 257 (100), 123 (50). Anal. calc. for $C_{29}H_{44}O_{11}$ (568.66): C 61.25, H 7.80; found: C 61.12, H 8.78.

*(1*R*,2*R*,3*R*,4*S*,4a*S*,5*R*,6*R*,7*R*,8*S*,8a*R*,9a*S*,10*S*,10a*R*)-1,8-Bis(acetoxymethyl)-1,3,4,6,7,8,8a,9a,10,10a-decahydro-10a-hydroxy-6-(methoxyacetoxy)-3-(methoxymethoxy)-2,4,5,7,10-pentamethyl-2*H*-2,4a-epoxyanthracen-9(5*H*)-one* (**62**). A mixture of (−)-**58** (88 mg, 0.167 mmol), anh. CH_2Cl_2 (2 ml), anh. pyridine (40 µl, 0.5 mmol), and $MeOCH_2COCl$ (30 µl, 0.33 mmol) was stirred at 20° for 1 h, then diluted with CH_2Cl_2 (15 ml) and washed with 0.5M aq. HCl (4 ml, 2 ×), sat. $NaHCO_3$ soln. (4 ml, 2 ×), and brine (4 ml). The org. phase was dried ($MgSO_4$) and evaporated. FC (petroleum ether/AcOEt 1:1, column 18 × 90 mm, 10-ml fractions) gave 80 mg (80%) of **62**. Colorless foam. IR (KBr): 3515, 1735, 1450, 1390, 1250, 1130, 1035. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.32 (*dd*, ^3J = 5.2, 5.2, H−C(6)); 4.60–4.53 (*AB*, OCH_2O); 4.42 (*dd*, ^2J = 11.5, ^3J = 10.0, 1 H, CH_2−C(1)); 4.28 (*dd*, ^2J = 11.5, ^3J = 4.7, 1 H, CH_2−C(1)); 4.14 (*dd*, ^2J = 10.5, ^3J = 3.4, 1 H, CH_2−C(8)); 4.07 (*s*, CH_2CO); 3.99 (*dd*, ^2J = 10.5, ^3J = 10.5, 1 H, CH_2−C(8)); 3.73 (*dd*, ^3J = 10.5, ^4J = 1.5, H−C(3)); 3.48 (*s*, *Me*OCH_2CO); 3.38 (*s*, *Me*OCH_2O); 2.96 (*dddd*, ^3J = 10.0, 4.7, 5.0, ^4J = 1.5, H−C(1)); 2.83 (*m*, H−C(8)); 2.73 (*d*, ^3J = 5.0, H−C(9a)); 2.56 (*dq*, ^3J = 10.5, 7.3, H−C(4)); 2.50 (*d*, ^3J = 11.5, H−C(8a)); 2.52–2.45 (*m*, H−C(7)); 2.28 (*dq*, ^3J = 7.4, 5.2, H−C(5)); 2.15 (*q*, ^3J = 7.0, H−C(10)); 2.05, 2.00 (2*s*, 2 MeCO); 1.45 (*s*, Me−C(2)); 1.09 (*d*, ^3J = 7.0, Me−C(10)); 1.05 (*d*, ^3J = 7.4, Me−C(5)); 1.01 (*d*, ^3J = 7.3, Me−C(4)); 0.90 (*d*, ^3J = 7.5, Me−C(7)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 207.3 (*s*, C(9)); 171.2, 171.0, 169.2 (3*s*, 3 COO); 96.8 (*t*, ^1J(C,H) = 162, OCH_2O); 95.0, 85.6, 82.2 (3*s*, C(2), C(4a), C(10a)); 82.0 (*d*, ^1J(C,H) = 150, C(3)); 72.3 (*d*, ^1J(C,H) = 150, C(6)); 69.9 (*t*, ^1J(C,H) = 143, *C*H_2COO); 64.0 (*t*, ^1J(C,H) = 146, *C*H_2−C(8)); 63.5 (*t*, ^1J(C,H) = 149, *C*H_2−C(1)); 59.4 (*q*, ^1J(C,H) = 142, *Me*OCH_2COO); 55.9 (*q*, ^1J(C,H) = 142, *Me*OCH_2O); 55.9 (*d*, ^1J(C,H) = 142, C(9a)); 48.1 (*d*, ^1J(C,H) = 120, C(8a)); 47.0 (*d*, ^1J(C,H) = 133, C(1)); 40.7 (*d*, ^1J(C,H) = 129, C(5)); 38.9 (*d*, ^1J(C,H) = 135, C(4)); 37.6 (*d*, ^1J(C,H) = 123, C(10)); 33.4 (*d*, ^1J(C,H) = 130, C(8)); 31.7 (*d*, ^1J(C,H) = 131, C(7)); 20.9 (2*q*, ^1J(C,H) = 129, 2 *Me*CO); 19.7 (*q*, ^1J(C,H) = 129, *Me*−C(2)); 12.1 (*q*, ^1J(C,H) = 126, *Me*−C(5)); 11.0 (*q*, ^1J(C,H) = 125, *Me*−C(4)); 10.4 (*q*, ^1J(C,H) = 122, *Me*−C(7)); 7.7 (*q*, ^1J(C,H) = 128, *Me*−C(10)). CI-MS (NH_3): 616 (1.3, $[M+H_2O]^+$), 598 (0.3, M^+), 553 (4), 530 (6), 493 (14), 477 (13), 449 (46), 436 (51), 376 (46), 365 (100), 257 (19), 84 (98). Anal. calc. for $C_{30}H_{46}O_{12}$ (598.68): C 60.19, H 7.74; found: C 60.07, H 7.86.

*(1*R*,2*R*,3*R*,4*R*,5*R*,6*R*,7*R*,8*S*,8a*R*,10*R*,10a*S*)-6-Acetoxy-1,8-bis(acetoxymethyl)-1,3,4,5,6,7,8,8a,10,10a-decahydro-2,10a-dihydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethylanthracen-9(2*H*)-one* (**63**). To a soln. of **60** (75 mg, 0.132 mmol) in anh. THF (0.5 ml) at 0°, 1M Bu_4NF in THF (0.264 ml, 0.264 mmol, 2 equiv.) was added dropwise, and the mixture was allowed to warm to 20°. After 4 h, the solvent was evaporated at 20°. FC (petroleum ether/AcOEt 1:1 (→ AcOEt, column 10 × 150 mm, 5-ml fractions) gave 65 mg (87%) of an inseparable mixture of **63** and another product **66** in a *ca.* 4:1 ratio, the latter being probably the product of migration of one acetate from the primary-alcohol to the tertiary-alcohol moiety. **63**: Colorless oil. UV (MeCN) (mixture): 241 (12000). IR (film; mixture): 3445, 1735, 1680, 1245, 1030. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.23 (*dd*, ^3J = 5.1, 5.1, H−C(6)); 4.70–4.65 (*AB*, OCH_2O); 4.48 (*dd*, ^2J = 11.5, ^3J = 5.7, 1 H, CH_2−C(1)); 4.39 (*dd*, ^2J = 10.5, ^3J = 3.8, 1 H, CH_2−C(8)); 3.98 (*dd*, ^2J = 11.5, ^3J = 5.2, 1 H, CH_2−C(1)); 3.89 (*dd*, ^3J = 10.5, 10.5, 1 H, CH_2−C(8)); 3.45 (*d*, ^3J = 5.7, H−C(3)); 3.40 (*s*, MeO); 3.04 (*m*, H−C(1)); 2.90–2.80 (*m*, H−C(4), H−C(10)); 2.75 (*m*, H−C(8)); 2.54 (*d*, ^3J = 11.5, H−C(8a)); 2.41 (*m*, H−C(7)); 2.29 (*m*, H−C(5)); 2.11 (*s*, MeCO); 2.03 (*s*, 2 MeCO); 1.34 (*s*, Me−C(2)); 1.18 (*d*, ^3J = 7.2, Me−C(4)); 1.11 (*d*, ^3J = 7.1, Me−C(10)); 1.04 (*d*, ^3J = 7.3, Me−C(5)); 0.90 (*d*, ^3J = 7.5, Me−C(7)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 200.2 (*s*, C(9)); 171.0, 171.0, 170.7 (3*s*, 3 Me*C*O); 151.7 (*s*, C(4a)); 130.3 (*s*, C(9a)); 99.2 (*t*, ^1J(C,H) = 162, OCH_2O); 84.2 (*d*, ^1J(C,H) = 143, C(3)); 80.4 (*s*, C(10a)); 72.2 (*d*, ^1J(C,H) = 147, C(6)); 71.2 (*s*, C(2)); 64.2, 64.2 (2*t*, ^1J(C,H) = 150, 150, *C*H_2−C(1), *C*H_2−C(8)); 56.5 (*q*, ^1J(C,H) = 147, MeO); 45.6 (*d*, ^1J(C,H) = 119, C(8a)); 43.5 (*d*, ^1J(C,H) = 129, C(1)); 40.1 (*d*, ^1J(C,H) = 129, C(5)); 38.6 (*d*, ^1J(C,H) = 123, C(10)); 34.1 (*d*, ^1J(C,H) = 129, C(4)); 33.1 (*d*, ^1J(C,H) = 134, C(8)); 31.7 (*d*, ^1J(C,H) = 139, C(7)); 23.4 (*q*, ^1J(C,H) = 127, *Me*−C(2)); 21.4, 21.2, 20.9 (3*q*, ^1J(C,H) = 130, 130, 129, 3 *Me*CO); 13.6 (*q*, ^1J(C,H) = 127, *Me*−C(4)); 13.1 (*q*, ^1J(C,H) = 127, *Me*−C(5)); 10.3 (*q*, ^1J(C,H) = 127, *Me*−C(10)); 10.2 (*q*, ^1J(C,H) = 127, *Me*−C(7)). CI-MS (NH_3; mixture): 569 (0.6, M^+), 530 (8), 448 (5), 405 (6), 71 (100).

*(1*R*,2*R*,3*R*,4*R*,5*R*,6*R*,7*R*,8*S*,8a*R*,10*R*,10a*S*)-1,8-Bis(acetoxymethyl)-1,3,4,5,6,7,8,8a,10,10a-decahydro-2,10a-dihydroxy-6-(methoxyacetoxy)-3-(methoxymethoxy)-2,4,5,7,10-pentamethylanthracen-9(2*H*)-one* (**64**) *and (1*R*,2*R*,3*R*,4*R*,7*S*,8*S*)-1,2,3,4,7,8-hexahydro-2,9-dihydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethylanthracene-1,8-dimethanol 8-Acetate* (**65**). To a soln. of **62** (16 mg, 0.027 mmol) in anh. DMF (2 ml), anh. CsF (10 mg) was added, and the mixture was heated at 80° for 45 min. H_2O (3 ml) was added and the mixture extracted with Et_2O (3 ml, 3 ×) and CH_2Cl_2 (3 ml, 3 ×). The combined org. layer was washed with H_2O (3 ml, 3 ×), dried ($MgSO_4$), and evaporated. FC (AcOEt/petroleum ether 3:1 → AcOEt, column 10 × 150 mm, 5-ml fractions) gave 8 mg (50%) of **64** and 3 mg (25%) of **65**.

Data of **64**: Colorless foam. UV (MeCN): 241 (12000), 193 (4900). IR (film): 3445, 1730, 1680, 1650, 1250, 1030. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.35 (*dd*, ^3J = 5.0, 5.0, H−C(6)); 4.69, 4.67 (2*d*, ^2J = 6.8, *AB*, OCH_2O); 4.48

(*dd*, ^2J = 11.5, ^3J = 5.8, 1 H, CH_2–C(1)); 4.39 (*dd*, ^2J = 10.5, ^3J = 3.8, 1 H, CH_2–C(8)); 4.09 (*s*, MeOCH_2CO); 4.02 (*dd*, ^2J = 11.5, ^3J = 5.0, 1 H, CH_2–C(1)); 3.89 (*dd*, ^2J = 10.5, ^3J = 10.5, 1 H, CH_2–C(8)); 3.48 (*s*, *Me*OCH$_2$CO); 3.46 (*d*, ^3J = 5.0, H–C(3)); 3.41 (*s*, *Me*OCH$_2$O); 3.03 (*m*, H–C(1)); 2.94–2.83 (*m*, H–C(4), H–C(10)); 2.78 (*m*, H–C(8)); 2.58 (*d*, ^3J = 11.5, H–C(8a)); 2.48 (*m*, H–C(7)); 2.33 (*m*, H–C(5)); 2.03 (*s*, 2 MeCO); 1.35 (*s*, Me–C(2)); 1.19, 1.12 (2*d*, ^3J = 7.3, 7.0, Me–C(4), Me–C(10)); 1.05 (*d*, ^3J = 7.5, Me–C(5)); 0.90 (*d*, ^3J = 7.4, Me–C(7)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 200.3 (C(9)); 171.0, 170.9, 169.8 (3 COO); 151.6 (C(4a)); 130.4 (C(9a)); 99.1 (OCH_2O); 84.1 (C(3)); 80.3 (C(10a)); 73.0 (C(6)); 71.3 (C(2)); 70.0 (*C*H_2–CO); 64.1, 64.0 (*C*H_2–C(1), *C*H_2–C(8)); 59.5 (*Me*OCH$_2$CO); 56.6 (*Me*OCH$_2$O); 45.7 (C(8a)); 43.6 (C(1)); 40.2 (C(5)); 38.5, 34.2 (C(4), C(10)); 33.1 (C(8)); 31.6 (C(7)); 23.4 (*Me*–C(2)); 21.2, 20.9 (2 *Me*CO); 13.5, 10.3 (*Me*–C(4), *Me*–C(10)); 13.1 (*Me*–C(5)); 10.2 (*Me*–C(7)). CI-MS (NH_3): 599 (3, $[M+H]^+$), 581 (3, $[M-OH]^+$), 539 (11), 538 (11), 478 (21), 435 (21), 421 (12), 387 (11), 71 (100). Anal. calc. for $C_{30}H_{46}O_{12}$ (598.68): C 60.19, H 7.74; found: C 60.14, H 7.62.

Data of **65**: Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.5 (*m*, H–C(6)); 4.86 (*s*, OCH_2O); 4.74 (*dd*, ^2J = 8.4, ^3J = 8.4, 1 H, CH_2–C(1)); 4.33 (*dd*, ^2J = 10.8, ^3J = 6.5, 1 H, CH_2–C(8)); 4.23 (*dd*, ^3J = 12.5, ^2J = 8.4, 1 H, CH_2–C(1)); 3.95 (*dd*, ^2J = 10.8, ^3J = 7.8, 1 H, CH_2–C(8)); 3.91 (*d*, ^3J = 6.9, H–C(3)); 3.56 (*dd*, ^3J = 8.4, 12.5, H–C(1)); 3.52 (*s*, MeO); 3.49 (*m*, H–C(4)); 3.15 (*m*, H–C(8)); 2.59 (*m*, H–C(7)); 2.28 (*s*, Me–C(10)); 2.18 (*m*, Me–C(5)); 1.99 (*s*, MeCO); 1.23–1.18 (*m*, Me–C(4), Me–C(7), Me–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.2 (Me*C*O); 153.7, 136.5, 135.8, 133.6, 124.7, 123.2, 118.3 (C(5), C(9), C(9a), C(4a), C(10), C(10a), C(8a)); 133.5 (C(6)); 97.7 (OCH_2O); 86.3 (C(3)); 73.1 (*C*H_2–C(1)); 72.6 (C(2)); 62.1 (*C*H_2–C(8)); 56.2 (MeO); 49.7 (C(1)); 37.1 (C(8)); 35.8 (C(4)); 31.2 (C(7)); 23.6 (*Me*–C(5)); 21.1 (*Me*CO); 18.3 (*Me*–C(10)); 19.1, 17.4, 13.9 (*Me*–C(4), Me–C(7), Me–C(2)).

*(1*R*,2*R*,3*R*,4*R*,5*R*,6*R*,7*R*,8*S*,8a*R*,10*R*,10a*S*)-2,6-Diacetoxy-1,8-bis(acetoxymethyl)-1,3,4,5,6,7,8,8a,10,10a-decahydro-10a-hydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethylanthracen-9(2*H*)-one* (**67**). The mixture of **63** with its by-product **66** (6 mg, 0.011 mmol) was treated with pyridine (0.3 ml), Ac_2O (0.2 ml), and DMAP (1 mg). After 1 h, the solvent was removed under high vacuum. FC (petroleum ether/AcOEt 1:1, column 8 × 100 mm, 2-ml fractions) gave 6 mg (93%) of **67**. Colorless oil. UV (MeCN): 242 (93000), 193 (49000). IR (film): 1730, 1370, 1245, 1030. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.26 (*dd*, ^3J = 5.3, 5.3, H–C(6)); 4.70, 4.66 (*AB*, ^2J = 6.6, OCH_2O); 4.50 (*dd*, ^2J = 11.6, ^3J = 5.6, 1 H, CH_2–C(1)); 4.47 (*dd*, ^2J = 10.1, ^3J = 3.6, 1 H, CH_2–C(8)); 4.38 (*dd*, ^3J = 5.3, ^4J = 1.3, H–C(3)); 3.97 (*dd*, ^2J = ^3J = 10.5, 1 H, CH_2–C(8)); 3.91 (*dd*, ^2J = 11.6, ^3J = 5.8, 1 H, CH_2–C(1)); 3.55 (*ddd*, ^3J = 5.8, 5.6, ^4J = 1.3, H–C(1)); 3.41 (*s*, MeO); 2.92 (*q*, ^3J = 7.0, H–C(10)); 2.81–2.72 (*m*, H–C(8)); 2.62 (*d*, ^3J = 11.6, H–C(8a)); 2.58 (*m*, H–C(4)); 2.43 (*m*, H–C(7)); 2.31 (*qd*, ^3J = 7.1, 5.3, H–C(5)); 2.11, 2.05, 2.04, 1.87 (4*s*, 4 MeCOO); 1.72 (*s*, Me–C(2)); 1.20 (*d*, ^3J = 7.2, Me–C(4)); 1.08 (*d*, ^3J = 7.0, Me–C(10)); 1.06 (*d*, ^3J = 7.1, Me–C(5)); 0.92 (*d*, ^3J = 7.5, Me–C(7)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 199.6 (*s*, C(9)); 171.2, 170.9, 170.3, 170.1 (4*s*, 4 Me*C*O); 150.8 (*s*, C(4a)); 130.8 (*s*, C(9a)); 99.6 (*t*, ^1J(C,H) = 163, OCH_2O); 81.9, 79.7 (2*s*, C(2), C(10a)); 80.4 (*d*, ^1J(C,H) = 148, C(3)); 72.0 (*d*, ^1J(C,H) = 146, C(6)); 64.6 (*t*, ^1J(C,H) = 152, *C*H_2–C(1)); 64.2 (*t*, ^1J(C,H) = 153, *C*H_2–C(8)); 57.0 (*q*, ^1J(C,H) = 142, MeO); 45.3 (*d*, ^1J(C,H) = 119, C(8a)); 41.4 (*d*, ^1J(C,H) = 133, C(1)); 40.3 (*d*, ^1J(C,H) = 117, C(5)); 38.1 (*d*, ^1J(C,H) = 117, C(10)); 33.9 (*d*, ^1J(C,H) = 122, C(4)); 33.4 (*d*, ^1J(C,H) = 132, C(8)); 31.9 (*d*, ^1J(C,H) = 130, C(7)); 22.2, 21.4, 21.2, 20.9 (4*q*, ^1J(C,H) = 127, 129, 130, 129, 4 *Me*COO); 19.4 (*q*, ^1J(C,H) = 128, *Me*–C(2)); 13.9 (*q*, ^1J(C,H) = 128, *Me*–C(4)); 13.1 (*q*, ^1J(C,H) = 126, *Me*–C(5)); 10.7 (*q*, ^1J(C,H) = 127, *Me*–C(10)); 10.2 (*q*, ^1J(C,H) = 126, *Me*–C(7)). CI-MS (NH_3): 628 (70, $[M+H_2O]^+$), 611 (2.6, $[M+H]^+$), 610 (0.9, M^+), 551 (20), 490 (53), 447 (52), 357 (15), 279 (15), 71 (100). Anal. calc. for $C_{31}H_{46}O_{12}$ (610.69): C 60.97, H 7.59; found: C 60.97, H 7.44.

*(1*R*,2*R*,3*R*,4*R*,5*R*,6*R*,7*S*,8*S*,8a*R*,10*R*,10a*S*)-6-Acetoxy-1,8-bis(acetoxymethyl)-1,3,4,5,6,7,8,8a,10,10a-decahydro-2,10a-dihydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethylanthracen-9(2*H*)-one* (**68**). To neat **61** (180 mg, 0.317 mmol), 1M Bu_4NF in THF (1.6 ml, 1.58 mmol, 5 equiv.) was added dropwise, and the mixture was stirred at 20°. After 1 h, the solvent was evaporated. FC (petroleum ether/AcOEt 1:1 → AcOEt, column 22 × 150 mm, 10-ml fractions): 166 mg (92%) mixture of **68** and another product **69** in a *ca.* 4:1 ratio, the latter being probably the product of migration of one acetate from the primary-alcohol to the tertiary-alcohol moiety. **68**: ^{1}H-NMR (400 MHz, $CDCl_3$): 4.98 (*dd*, ^3J(6,7) = 11.5, ^3J(6,5) = 4.3, H–C(6)); 4.69 (*s*, OCH_2O); 4.57–4.48 (*m*, 2 H, CH_2–C(1), CH_2–C(8)); 4.01–3.92 (*m*, 2 H, CH_2–C(1), CH_2–C(8)); 3.45 (*d*, ^3J = 5.5, H–C(3)); 3.39 (*s*, MeO); 3.01 (*m*, H–C(1)); 2.90–2.80 (*m*, H–C(4), H–C(10)); 2.76 (*d*, ^3J = 10.9, H–C(8a)); 2.24 (*m*, H–C(5)); 2.13 (*m*, H–C(8)); 2.08, 2.02, 1.94 (3*s*, 3 MeCOO); 1.78 (*ddq*, ^3J(7,8) = 11.5, ^3J(7,6) = 11.5, ^3J = 6.1, H–C(7)); 1.32 (*s*, Me–C(2)); 1.17 (*d*, ^3J = 7.3, Me–C(4)); 1.07 (*d*, ^3J = 7.0, Me–C(10)); 0.94 (*d*, ^3J = 6.1, Me–C(7)); 0.93 (*d*, ^3J = 7.0, Me–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 199.7 (*s*, C(9)); 171.1, 170.8, 170.8 (3*s*, 3 Me*C*O); 152.6 (*s*, C(4a)); 129.8 (*s*, C(9a)); 99.2 (*t*, ^1J(C,H) = 162, OCH_2O); 84.3 (*d*, ^1J(C,H) = 142, C(3)); 80.1 (*s*, C(10a)); 75.7 (*d*, ^1J(C,H) = 149, C(6)); 71.2 (*s*, C(2)); 63.8 (2*t*, ^1J(C,H) = 151, *C*H_2–C(1), *C*H_2–C(8)); 56.5

(q, ^1J(C,H) = 142, MeO); 47.9 (d, ^1J(C,H) = 126, C(8)); 43.6 (d, ^1J(C,H) = 129, C(1)); 39.0, 38.9 (2d, ^1J(C,H) = 133, ^1J(C,H) = 121, C(5), C(10)); 36.7 (d, ^1J(C,H) = 129, C(8)); 34.3 (d, ^1J(C,H) = 126, C(4)); 28.6 (d, ^1J(C,H) = 127, C(7)); 23.4 (q, ^1J(C,H) = 121, *Me*−C(2)); 21.1, 20.9, 20.9 (3q, ^1J(C,H) = 130, ^1J(C,H) = 129, ^1J(C,H) = 129, 3 *Me*COO); 15.0, 10.0 (2q, ^1J(C,H) = 126, ^1J(C,H) = 128, *Me*−C(7); *Me*−C(5)); 13.6 (q, ^1J(C,H) = 128, *Me*−C(4)); 10.0 (q, ^1J(C,H) = 128, *Me*−C(10)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 199.7 (s, C(9)); 171.1, 170.8, 170.8 (3s, 3 Me*C*O); 152.6 (s, C(4a)); 129.8 (s, C(9a)); 99.2 (t, ^1J(C,H) = 162, OCH_2O); 84.3 (d, ^1J(C,H) = 142, C(3)); 80.1 (s, C(10a)); 75.7 (d, ^1J(C,H) = 149, C(6)); 71.2 (s, C(2)); 63.8 (2t, ^1J(C,H) = 151, *C*H_2−C(1), *C*H_2−C(8)); 56.5 (q, ^1J(C,H) = 142, MeO); 47.9 (d, ^1J(C,H) = 126, C(8)); 43.6 (d, ^1J(C,H) = 129, C(1)); 39.0, 38.9 (2d, ^1J(C,H) = 133, 121, C(5), C(10)); 36.7 (d, ^1J(C,H) = 129, C(8)); 34.3 (d, ^1J(C,H) = 126, C(4)); 28.6 (d, ^1J(C,H) = 127, C(7)); 23.4 (q, ^1J(C,H) = 121, *Me*−C(2)); 21.1, 20.9, 20.9 (3q, ^1J(C,H) = 130, 129, 129, 3 *Me*COO); 15.0, 10.0 (2q, ^1J(C,H) = 126, 128, *Me*−C(7), *Me*−C(5)); 13.6 (q, ^1J(C,H) = 128, *Me*−C(4)); 10.0 (q, ^1J(C,H) = 128, *Me*−C(10)).

*(1*R*,2*R*,3*R*,4*R*,5*R*,6*R*,7*S*,8*S*,8a*R*,10*R*,10a*S*)-2,6-Diacetoxy-1,8-bis(acetoxymethyl)-1,3,4,5,6,7,8,8a,10,10a-decahydro-10a-hydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethylanthracen-9(2*H*)-one* ((+)-**70**). A mixture of **69** and its by-product (166 mg, 0.292 mmol) was treated with anh. pyridine (2 ml), Ac_2O (1 ml), and DMAP (5 mg). After 6 h, the solvent was removed under high vacuum. FC (petroleum ether/AcOEt 1:1, column 22 × 150 ml, 10-ml fractions) gave 133 mg (75%) of (+)-**70**. Colorless oil. $[\alpha]_{589}^{20} = +68$, $[\alpha]_{577}^{20} = +68$, $[\alpha]_{546}^{20} = +66$, $[\alpha]_{435}^{20} = +100$, $[\alpha]_{405}^{20} = +105$ ($c = 0.6$, $CHCl_3$; e.e. *ca.* 90%). UV (MeCN): 242 (8700), 192 (4900). IR (film): 3490, 1735, 1680, 1370, 1250, 1030, 735. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.01 (dd, ^3J(6,7) = 11.6, ^3J(6,5) = 4.4, H−C(6)); 4.70, 4.65 (*AB*, ^2J = 6.6, OCH_2O); 4.57–4.50 (m, 2 H, CH_2−C(1), CH_2−C(8)); 4.38 (d, ^3J = 5.4, H−C(3)); 4.10 (d, ^2J = 11.7, 1 H, CH_2−C(8)); 3.91 (dd, ^2J = 11.5, ^3J = 4.9, 1 H, CH_2−C(1)); 3.57 (m, H−C(1)); 3.40 (s, MeO); 2.87 (q, ^3J = 7.0, H−C(10)); 2.82 (d, ^3J = 11.0, H−C(8a)); 2.62 (m, H−C(4)); 2.34–2.27 (m, H−C(5)); 2.18 (m, H−C(8)); 2.09, 2.06, 2.01, 1.86, 1.72 (5s, 4 MeCOO, Me−C(2)); 1.86–1.80 (m, H−C(7)); 1.20 (d, ^3J = 7.2, Me−C(4)); 1.10 (d, ^3J = 7.0, Me−C(10)); 0.97, 0.96 (2d, ^3J = 7.2, 7.2, Me−C(5), Me−C(7)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 199.1 (s, C(9)); 171.0, 170.9, 170.7, 170.0 (4s, 4 Me*C*O); 151.8 (s, C(4a)); 130.3 (s, C(9a)); 99.6 (t, ^1J(C,H) = 162, OCH_2O); 82.0, 79.3 (2s, C(2), C(10a)); 80.3 (d, ^1J(C,H) = 148, C(3)); 75.5 (d, ^1J(C,H) = 144, C(6)); 64.6 (t, ^1J(C,H) = 152, *C*H_2−C(1)); 63.8 (t, ^1J(C,H) = 150, *C*H_2−C(8)); 56.9 (q, ^1J(C,H) = 142, MeO); 47.6 (d, ^1J(C,H) = 129, C(8a)); 41.3 (d, ^1J(C,H) = 130, C(1)); 39.1 (d, ^1J(C,H) = 129, C(5)); 38.5 (d, ^1J(C,H) = 122, C(10)); 37.0 (d, ^1J(C,H) = 127, C(8)); 34.1 (d, ^1J(C,H) = 126, C(4)); 28.5 (d, ^1J(C,H) = 124, C(7)); 22.1, 21.2, 21.1, 21.0, 19.4 (5q, ^1J(C,H) = 130, 130, 130, 130, 128, 4 *Me*COO, *Me*−C(2)); 15.1 (q, ^1J(C,H) = 122, *Me*−C(5)); 13.9 (q, ^1J(C,H) = 127, *Me*−C(4)); 10.5 (q, ^1J(C,H) = 133, *Me*−C(10)); 9.9 (q, ^1J(C,H) = 126, *Me*−C(7)). CI-MS (NH_3): 611 (2, M^+), 610 (0.3), 551 (9), 490 (100), 446 (36). Anal. calc. for $C_{31}H_{46}O_{12} + 1/3\ H_2O$) (616.69): C 60.38, H 7.63; found: C 60.10, H 7.68.

*(1*R*,2*R*,3*R*,4*R*,5*R*,6*R*,7*R*,8*S*,8a*R*,10*R*,10a*S*)-1,8-Bis(acetoxymethyl)-1,3,4,5,6,7,8,8a,10,10a-decahydro-2,6,10a-trihydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethylanthracen-9(2*H*)-one* ((+)-**72**). To neat (−)-**58** (1.27 g, 2.41 mmol), 1M Bu_4NF in THF (21 ml, 21 mmol, 8.7 equiv.) was added. The mixture was stirred for 2 h at 20° and then stored at −18° overnight. The solvent was evaporated at 20°. FC (AcOEt, then AcOEt/MeOH 9:1, column 50 × 150 mm, 50-ml fractions): 1.22 g (96%) of (+)-**72**. Colorless oil. $[\alpha]_{589}^{20} = +59$ ($c = 1.2$, MeOH; e.e. *ca.* 90%). UV (MeCN): 241 (81000), 192 (30000). IR (film): 3400, 1730, 1680, 1250, 1030. ^{1}H-NMR (400 MHz, CD_3OD): 4.75, 4.71 (*AB*, ^2J = 6.5, OCH_2O); 4.54 (dd, ^2J = 11.3, ^3J = 5.7, 1 H, CH_2−C(1)); 4.49 (dd, ^2J = 10.5, ^3J = 3.7, 1 H, CH_2−C(8)); 4.16 (dd, ^3J(5,6) = ^3J(6,7) = 5.1, H−C(6)); 4.01 (dd, ^2J = 11.3, ^3J = 5.1, 1 H, CH_2−C(1)); 3.98 (dd, ^3J = ^2J = 10.5, 1 H, CH_2−C(8)); 3.52 (dd, ^3J = 5.8, ^4J = 1.1, H−C(3)); 3.43 (s, MeO); 3.10–3.02 (m, H−C(1), H−C(10)); 2.92 (m, H−C(4)); 2.76 (d, ^3J = 11.4, H−C(8a)); 2.71–2.61 (m, H−C(8)); 2.37–2.28 (m, H−C(7)); 2.28–2.19 (m, H−C(5)); 2.07, 2.06 (2s, 2 MeCO); 1.42 (s, Me−C(2)); 1.27 (d, ^3J = 7.3, Me−C(4)); 1.18 (d, ^3J = 7.1, Me−C(10)); 1.08 (d, ^3J = 7.5, Me−C(5)); 0.93 (d, ^3J = 7.4, Me−C(7)). ^{13}C-NMR (100.6 MHz, CD_3OD): 203.2 (s, C(9)); 173.0 (s, 2 Me*C*O); 153.9 (s, C(4a)); 131.7 (s, C(9a)); 100.5 (t, ^1J(C,H) = 162, OCH_2O); 85.5 (d, ^1J(C,H) = 142, C(3)); 81.4 (s, C(10a)); 72.4 (s, C(2)); 69.4 (d, ^1J(C,H) = 139, C(6)); 66.1 (t, ^1J(C,H) = 147, *C*H_2−C(8)); 65.7 (t, ^1J(C,H) = 151, *C*H_2−C(1)); 56.9 (q, ^1J(C,H) = 142, MeO); 47.2 (d, ^1J(C,H) = 112, C(8a)); 44.8, 40.2 (2d, ^1J(C,H) = 130, 124, C(1), C(10)); 43.8 (d, ^1J(C,H) = 126, C(5)); 35.9 (d, ^1J(C,H) = 128, C(7)); 35.7 (d, ^1J(C,H) = 127, C(4)); 35.0 (d, ^1J(C,H) = 131, C(8)); 24.1 (q, ^1J(C,H) = 126, *Me*−C(2)); 21.2, 20.8 (2q, ^1J(C,H) = 129, 130, 2 *Me*COO); 14.1 (q, ^1J(C,H) = 128, *Me*−C(4)); 12.5 (q, ^1J(C,H) = 126, *Me*−C(5)); 10.8 (q, ^1J(C,H) = 127, *Me*−C(10)); 9.8 (q, ^1J(C,H) = 130, *Me*−C(7)). CI-MS (NH_3): 527 (24, $[M+H]^+$), 467 (38, $[M-OAc]^+$), 405 (68), 388 (34), 363 (41), 91 (100). Anal. calc. for $C_{27}H_{42}O_{10}$ (526.62): C 61.58, H 8.04; found: C 61.50, H 8.09.

*(1*R*,2*R*,3*R*,4*R*,5*R*,6*R*,7*R*,8*S*,8a*R*,10*R*,10a*S*)-1,8-Bis(acetoxymethyl)-1,3,4,5,6,7,8,8a,10,10a-decahydro-10a-hydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethyl-2,6-bis{[2-(trimethylsilyl)ethoxy]methoxy}anthracen-*

*9(2*H*)-one* ((+)-**73**), *(1*R*,2*R*,3*R*,4*R*,5*R*,6*R*,7*R*,8*S*,8a*R*,10*R*,10a*S*)-1,8-Bis(acetoxymethyl)-1,3,4,5,6,7,8,8a,10,10a-decahydro-2,10a-dihydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethyl-6-{[2-(trimethylsilyl)ethoxy]methoxy}-anthracen-9(2*H*)-one* ((+)-**74**), *(1*R*,2*R*,3*R*,4*R*,5*R*,6*R*,7*R*,8*S*,8a*R*,10*R*,10a*S*)-1,8-Bis(acetoxymethyl)-1,3,4,5,6,7,8,8a,10,10a-decahydro-3-(methoxymethoxy)-2,4,5,7,10-pentamethyl-2,6,10a-tris{[2-(trimethylsilyl)ethoxy]-methoxy}anthracen-9(2*H*)-one* ((+)-**75**), *and (1*R*,2*R*,3*R*,4*R*,5*R*,6*R*,7*R*,8*S*,8a*R*,10*R*,10a*S*)-1,8-Bis(acetoxymethyl)-1,3,4,5,6,7,8,8a,10,10a-decahydro-2-hyroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethyl-6,10a-bis{[2-(trimethylsilyl)ethoxy]methoxy}anthracen-9(2*H*)-one* (**76**). To a suspension of (+)-**72** (1.20 g, 2.28 mmol) in anh. CH_2Cl_2 (5 ml) at 0°, $(i\text{-}Pr)_2NEt$ (1.40 ml, 7.98 mmol, 3.5 equiv.) and $Me_3SiCH_2CH_2OCH_2Cl$ (1.20 ml, 6.84 mmol, 3 equiv.) were added. After 10 min, the mixture was homogeneous. It was stirred at 20° for 7 h and then stocked at −18° overnight. The mixture was diluted with CH_2Cl_2 (50 ml) and washed with sat. soln. $NaHCO_3$ aq. (10 ml, 3 ×). The aq. layer was extracted with CH_2Cl_2 (8 ml, 3 ×) and the combined org. phase dried ($MgSO_4$) and evaporated. FC (petroleum ether/AcOEt 7:3 → AcOEt, column 50 × 150 mm, 50-ml fractions): 1.16 g (65%) of (+)-**73**, 242 mg (16%) of (+)-**74**, 68 mg (4%) of **76**, and 55 mg (3%) of (+)-**75**.

*Data of (+)-***73**; Colorless oil. $[\alpha]_{589}^{20} = +53$, $[\alpha]_{577}^{20} = +54$, $[\alpha]_{546}^{20} = +57$, $[\alpha]_{435}^{20} = +87$, $[\alpha]_{405}^{20} = +91$ (*c* = 1.1, $CHCl_3$; e.e. *ca.* 90%). UV (MeCN): 243 (11000). IR (film): 3500, 1740, 1680, 1390, 1365, 1245, 1030. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.75 (*s*, $OCH_2O-C(6)$); 4.70–4.60 (*m*, $OCH_2O-C(3)$, $OCH_2O-C(2)$); 4.52–4.45 (*m*, 2 H, $CH_2-C(1)$, $CH_2-C(8)$); 3.99 (*dd*, ^3J = 5.1, 5.1, H−C(6)); 3.95–3.89 (*m*, 2 H, $CH_2-C(1)$, $CH_2-C(8)$); 3.65 (*m*, $CH_2OCH_2O-C(6)$); 3.53 (*d*, ^3J = 5.7, H−C(3)); 3.51–3.40 (*m*, $CH_2OCH_2O-C(2)$); 3.40 (*m*, H−C(1)); 2.93 (*m*, H−C(4), H−C(10)); 2.68–2.60 (*m*, H−C(8)); 2.58 (*d*, ^3J = 11.5, H−C(8a)); 2.41 (*m*, H−C(7)); 2.23 (*m*, H−C(5)); 2.04, 2.03 (2*s*, 2 MeCOO); 1.45 (*s*, Me−C(2)); 1.18 (*d*, ^3J = 7.4, Me−C(4)); 1.12 (*d*, ^3J = 7.0, Me−C(10)); 1.04 (*d*, ^3J = 7.4, Me−C(5)); 0.88 (*d*, ^3J = 7.6, Me−C(7)); 0.95–0.83 (*m*, 2 CH_2Si); 0.03, −0.01 (2*s*, 6 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 200.3 (*s*, C(9)); 171.1, 170.9 (2*s*, 2 Me*C*O); 152.3 (*s*, C(4a)); 130.6 (*s*, C(9a)); 99.6, 89.0 (2*t*, ^1J(C,H) = 163, 162, $OCH_2O-C(3)$, $OCH_2O-C(2)$); 93.7 (*t*, ^1J(C,H) = 161, $OCH_2O-C(6)$); 83.8 (*d*, ^1J(C,H) = 143, C(3)); 80.1, 76.5 (2*s*, C(10a), C(2)); 74.7 (*d*, ^1J(C,H) = 139, C(6)); 65.5 (*t*, ^1J(C,H) = 142, $CH_2OCH_2O-C(2)$); 65.1 (*t*, ^1J(C,H) = 142, $CH_2OCH_2O-C(6)$); 65.0, 64.6 (2*t*, ^1J(C,H) = 151, ^1J(C,H) = 152, $CH_2-C(1)$, $CH_2-C(8)$); 56.8 (*q*, ^1J(C,H) = 142, MeO); 45.8 (*d*, ^1J(C,H) = 126, C(8a)); 41.3 (*d*, ^1J(C,H) = 130, C(5)); 39.6 (*d*, ^1J(C,H) = 133, C(1)); 38.6 (*d*, ^1J(C,H) = 124, C(10)); 34.3 (*d*, ^1J(C,H) = 128, C(4)); 33.6 (*d*, ^1J(C,H) = 130, C(8)); 32.6 (*d*, ^1J(C,H) = 124, C(7)); 21.2, 20.9 (2*q*, ^1J(C,H) = 129, ^1J(C,H) = 129, 2 *Me*COO); 20.3 (*q*, ^1J(C,H) = 126, *Me*−C(2)); 18.2, 17.9 (2*t*, ^1J(C,H) = 120, ^1J(C,H) = 120, 2 CH_2Si); 13.8 (*q*, ^1J(C,H) = 127, *Me*−C(4)); 12.7 (*q*, ^1J(C,H) = 127, *Me*−C(5)); 10.5 (*q*, ^1J(C,H) = 128, *Me*−C(10)); 9.9 (*q*, ^1J(C,H) = 125, *Me*−C(7)); −1.4 (*q*, ^1J(C,H) = 118, 6 MeSi). CI-MS (NH_3):805 (9, $[M+H_2O]^+$), 787 (0.5, M^+), 627 (6), 597 (5), 578 (6), 535 (5), 73 (100). Anal. calc. for $C_{39}H_{70}O_{12}Si_2$ (787.14): C 59.51, H 8.96, Si 7.14; found: C 59.56, H 8.79, Si 7.02.

*Data of (+)-***74**: Colorless oil. $[\alpha]_{589}^{20} = +37$, $[\alpha]_{577}^{20} = +39$, $[\alpha]_{546}^{20} = +38$, $[\alpha]_{435}^{20} = +48$, $[\alpha]_{405}^{20} = +37$ (*c* = 1.3, $CHCl_3$; e.e. *ca.* 90%). UV (MeCN): 241 (12000), 192 (6100). IR (film): 3420, 1740, 1680, 1470, 1385, 1250, 1030. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.76 (*s*, $OCH_2O-C(6)$); 4.70, 4.67 (*AB*, ^2J = 6.7, $OCH_2O-C(3)$); 4.48 (*dd*, ^2J = 11.4, ^3J = 5.7, 1 H, $CH_3-C(1)$); 4.36 (*dd*, ^2J = 10.5, ^3J = 3.7, 1 H, $CH_2-C(8)$); 4.05 (*dd*, ^2J = 11.4, ^3J = 5.0, 1 H, $CH_2-C(1)$); 3.98 (*dd*, ^3J = 5.2, 5.2, H−C(6)); 3.91 (*dd*, $^2J = {}^3J$ = 10.5, 1 H, $CH_2-C(8)$); 3.66 (*m*, CH_2OCH_2O); 3.47 (*d*, ^3J = 5.8, H−C(3)); 3.41 (*s*, MeO); 3.03 (*m*, H−C(1)); 2.93 (*q*, ^3J = 7.0, H−C(10)); 2.86 (*m*, H−C(4)); 2.70–2.61 (*m*, H−C(8)); 2.57 (*d*, ^3J = 11.6, H−C(8a)); 2.45–2.35 (*m*, H−C(7)); 2.23 (*m*, H−C(5)); 2.04 (*s*, 2 MeCOO); 1.34 (*s*, Me−C(2)); 1.19 (*d*, ^3J = 7.3, Me−C(4)); 1.14 (*d*, ^3J = 7.0, Me−C(10)); 1.05 (*d*, ^3J = 7.5, Me−C(5)); 0.95 (*m*, CH_2Si); 0.87 (*d*, ^3J = 7.4, Me−C(7)); 0.04 (*s*, 3 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 201.1 (*s*, C(9)); 170.9 (*s*, 2 Me*C*O); 151.5 (*s*, C(4a)); 130.4 (*s*, C(9a)); 99.0 (*t*, ^1J(C,H) = 162, $OCH_2O-C(3)$); 94.0 (*t*, ^1J(C,H) = 162, $OCH_2O-C(6)$); 84.1 (*d*, ^1J(C,H) = 146, C(3)); 80.5 (*s*, C(10a)); 75.1 (*d*, ^1J(C,H) = 147, C(6)); 71.4 (*s*, C(2)); 65.1 (*t*, ^1J(C,H) = 142, CH_2OCH_2O; 64.4, 63.8 (2*t*, ^1J(C,H) = 151, 152, $CH_2-C(1)$, $CH_2-C(8)$); 56.6 (*q*, ^1J(C,H) = 143, MeO); 46.0 (*d*, ^1J(C,H) = 126, C(8a)); 43.8 (*d*, ^1J(C,H) = 130, C(1)); 41.6 (*d*, ^1J(C,H) = 128, C(5)); 38.7 (*d*, ^1J(C,H) = 125, C(10)); 34.2 (*d*, ^1J(C,H) = 130, C(4)); 33.2 (*d*, ^1J(C,H) = 127, C(8)); 32.6 (*d*, ^1J(C,H) = 130, C(7)); 23.2 (*q*, ^1J(C,H) = 128, *Me*−C(2)); 21.1, 20.9 (2*q*, ^1J(C,H) = 129, 129, 2 *Me*COO); 18.2 (*t*, ^1J(C,H) = 119, CH_2Si); 13.5 (*q*, ^1J(C,H) = 127, MeC(4)); 12.9 (*q*, ^1J(C,H) = 122, *Me*−C(5)); 10.4 (*q*, ^1J(C,H) = 127, *Me*−C(10)); 9.8 (*q*, ^1J(C,H) = 122, *Me*−C(7)); −1.4 (*q*, ^1J(C,H) = 119, 3 *Me*Si). CI-MS (NH_3): 657 (1, M^+), 597 (3), 536 (4), 493 (3), 190 (4), 73 (100). Anal. calc. for $C_{33}H_{56}O_{11}Si$ (656.88): C 60.34, H 8.59; found: C 60.23, H 8.55.

*Data of (+)-***75**: Colorless oil. $[\alpha]_{589}^{20} = +18$ (*c* = 0.9, $CHCl_3$; e.e. *ca.* 90%). UV (MeCN): 244 (9120), 191 (5200). IR (film): 1740, 1685, 1250, 1035. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.80–4.75 (*m*, 2 OCH_2O); 4.75 (*s*, OCH_2O); 4.68, 4.65 (*AB*, ^2J = 6.7, OCH_2O); 4.57–4.49 (*m*, 4 H, 2 H of OCH_2O, $CH_2-C(1)$, $CH_2-C(8)$); 4.11 (*dd*, ^3J = 5.1, 5.1, H−C(6)); 3.97 (*dd*, $^2J = {}^3J$ = 10.3, 1 H, $CH_2-C(8)$); 3.93 (*dd*, ^2J = 11.5, ^3J = 5.3, 1 H,

$CH_2-C(1)$); 3.56 (*dd*, $^3J = 6.4$, $^4J = 1.2$, H–C(3)); 3.69–3.59, 3.50–3.41 (2*m*, 3 OCH_2CH_2); 3.40 (*s*, MeO); 3.32 (*m*, H–C(1)); 2.98 (*q*, $^3J = 7.0$, H–C(10)); 2.92 (*dq*, $^3J = 6.5$, H–C(4)); 2.70–2.61 (*m*, H–C(8)); 2.55 (*d*, $^3J = 11.4$, H–C(8a)); 2.59–2.50 (*m*, H–C(5)); 2.42 (*m*, H–C(7)); 2.04, 2.03 (2*s*, 2 MeCOO); 1.45 (*s*, Me–C(2)); 1.17, 1.16 (2*d*, $^3J = 7.4$, 7.0, Me–C(10), Me–C(4)); 1.07 (*d*, $^3J = 7.3$, Me–C(5)); 0.97–0.82 (*m*, Me–C(7), 3 CH_2Si); 0.02, 0.00 (2*s*, 9 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 199.5 (*s*, C(9)); 171.0, 170.9 (2*s*, 2 Me*C*O); 152.6 (*s*, C(4a)); 130.2 (*s*, C(9a)); 99.3, 94.1, 89.5, 89.2 (4*t*, ^1J(C,H) = 162, 161, 162, 162, 4 OCH_2O); 86.9 (*s*, C(10a)); 83.5 (*d*, ^1J(C,H) = 141, C(3)); 76.6 (*s*, C(2)); 74.8 (*d*, ^1J(C,H) = 146, C(6)); 65.5, 65.3, 65.0 (3*t*, ^1J(C,H) = 142, 142, 141, 3 OCH_2CH_2); 64.6, 64.5 (2*t*, ^1J(C,H) = 150, 149, *C*H_2–C(1), *C*H_2–C(8)); 56.7 (*q*, ^1J(C,H) = 143, MeO); 46.3 (*d*, ^1J(C,H) = 129, C(8a)); 40.2 (*d*, ^1J(C,H) = 130, C(1)); 38.9 (*d*, ^1J(C,H) = 128, C(10)); 37.5 (*d*, ^1J(C,H) = 130, C(5)); 34.3 (*d*, ^1J(C,H) = 127, C(4)); 33.9 (*d*, ^1J(C,H) = 129, C(8)); 32.8 (*d*, ^1J(C,H) = 124, C(7)); 21.2, 20.9 (2*q*, ^1J(C,H) = 129, 129, 2 *Me*COO); 19.9 (*q*, ^1J(C,H) = 126, *Me*–C(2)); 18.2, 18.0, 18.0 (3*t*, ^1J(C,H) = 120, 120, 120, 120, 3 CH_2Si); 14.0, 11.1 (2*q*, ^1J(C,H) = 127, 128, *Me*–C(4), *Me*–C(10)); 13.2 (*q*, ^1J(C,H) = 127, *Me*–C(5)); 10.0 (*q*, ^1J(C,H) = 125, *Me*–C(7)); –1.4 (*q*, ^1J(C,H) = 119, 9 MeSi). CI-MS (NH_3): 935 (4, $[M+H_2O]^+$), 662 (3), 647 (3), 441 (2), 90 (100). Anal. calc. for $C_{45}H_{84}O_{13}Si_3$ (917.40): C 58.92, H 9.23; found: C 58.81, H 9.32.

Data of **76**: Colorless oil. UV (MeCN): 242 (9300), 205 (3400). IR (film): 3440, 1735, 1680, 1385, 1250, 1030. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.75–4.63 (*m*, 3 OCH_2O); 4.54–4.48 (*m*, 2 H, CH_2–C(1), CH_2–C(8)); 4.17 (*dd*, $^2J = 11.3$, $^3J = 4.1$, 1 H, CH_2–C(1)); 4.03 (*dd*, $^3J = 5.2$, H–C(6)); 3.98 (*dd*, $^2J = {}^3J = 10.4$, 1 H, CH_2–C(8)); 3.64 (*m*, CH_2O); 3.55 (*d*, $^3J = 7.0$, H–C(3)); 3.59–3.43 (*m*, CH_2O); 3.42 (*s*, MeO); 3.06 (*m*, H–C(1)); 3.01 (*q*, $^3J = 7.2$, H–C(10)); 2.94 (*dq*, $^3J = 7.0$, H–C(4)); 2.66 (*m*, H–C(8)); 2.55 (*d*, $^3J = 11.5$, H–C(8a)); 2.49 (*qd*, $^3J = 7.4$, 5.2, H–C(5)); 2.41 (*m*, H–C(7)); 2.02 (*s*, 2 MeCOO); 1.31 (*s*, Me–C(2)); 1.23 (*d*, $^3J = 7.2$, Me–C(10)); 1.19 (*d*, $^3J = 7.3$, Me–C(4)); 1.08 (*d*, $^3J = 7.4$, Me–C(5)); 0.89 (*d*, $^3J = 7.4$, Me–C(7)); 0.95–0.80 (*m*, 2 CH_2Si); 0.03, 0.00 (2*s*, 6 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 199.3 (*s*, C(9)); 170.7 (*s*, 2 Me*C*O); 152.8 (*s*, C(4a)); 129.8 (*s*, C(9a)); 98.7, 93.9, 89.3 (3*t*, ^1J(C,H) = 167, 160, 162, 3 OCH_2O); 87.4 (*s*, C(10a)); 83.6 (*d*, ^1J(C,H) = 144, C(3)); 74.6 (*d*, ^1J(C,H) = 141, C(6)); 71.7 (*s*, C(2)); 65.9, 65.0 (2*t*, ^1J(C,H) = 142, 142, 2 CH_2O); 64.5 (*t*, ^1J(C,H) = 150, *C*H_2–C(8)); 63.1 (*t*, ^1J(C,H) = 150, *C*H_2–C(1)); 56.4 (*q*, ^1J(C,H) = 142, MeO); 46.7 (*d*, ^1J(C,H) = 122, C(8a)); 44.2 (*d*, ^1J(C,H) = 126, C(1)); 39.2 (*d*, ^1J(C,H) = 123, C(10)); 37.8 (*d*, ^1J(C,H) = 140, C(5)); 34.4 (*d*, ^1J(C,H) = 130, C(4)); 33.8 (*d*, ^1J(C,H) = 129, C(8)); 32.6 (*d*, ^1J(C,H) = 127, C(7)); 22.3 (*q*, ^1J(C,H) = 126, *Me*–C(2)); 21.1, 20.9 (2*q*, ^1J(C,H) = 129, 129, 2 *Me*COO); 18.2, 18.0 (2*t*, ^1J(C,H) = 118, 117. 2 CH_2Si); 13.7 (*q*, ^1J(C,H) = 121, *Me*–C(4)); 12.9 (*q*, ^1J(C,H) = 130, *Me*–C(5)); 10.6 (*q*, ^1J(C,H) = 127, *Me*–C(10)); 10.0 (*q*, ^1J(C,H) = 121, *Me*–C(7)); –1.4 (*q*, ^1J(C,H) = 119, 6 MeSi). CI-MS (NH_3): 805 (2, $[M+H_2O]^+$), 657 (2), 597 (4), 536 (4), 493 (5), 476 (5), 73 (100). Anal. calc. for $C_{39}H_{70}O_{12}Si_2$ (787.14): C 59.51, H 8.89; found: C 59.46, H 8.99.

*(2a*S*,3*R*,4*R*,5*R*,7*S*,8*R*,9*R*,10*S*)-2a,3,4,5,7,8,9,10-Octahydro-4-(methoxymethoxy)-3,5,6,7,9-pentamethyl-3,8-bis{[2-(trimethylsilyl)ethoxy]methoxy}-2*H*-anthra[9,1-bc]furan-10-methanol α^{10}-Acetate* (**77**). To a soln. of (+)-**73** (16 mg, 0.02 mmol) in anh. CH_2Cl_2 (0.3 ml) at –78°, 1M (i-Bu)$_2$AlH in CH_2Cl_2 (0.22 ml, 0.22 mmol, 11 equiv.) was added in 4 portions over 5 h. After 6 h at –78°, the flask was put in a bath at 0°. After stirring at 0° for 1 h, sat. aq. NH_4Cl soln. (1 ml) was added and the mixture diluted with CH_2Cl_2 (5 ml) and allowed to warm to 20°. The biphasic mixture was filtered over a *Celite* pad. The aq. phase was extracted with CH_2Cl_2 (1 ml, 3 ×), the combined org. layer dried ($MgSO_4$) and evaporated and the residue dissolved in anh. pyridine (0.5 ml) and Ac_2O (0.3 ml). After 3 h, the solvents were evaporated under high vacuum. FC (petroleum ether/Et_2O 7:3, column 8 × 120 mm, 3-ml fractions) gave 6 mg (42%) of **77**. Colorless oil. UV (MeCN): 291 (4680), 218 (17000). IR (film): 1735, 1465, 1420, 1385, 1250, 1030. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.01 (*dd*, $^2J = 11.0$, $^3J = 5.3$, 1 H, CH_2–C(10)); 4.89–4.86 (*m*, 2 H, 2 OCH_2O); 4.83–4.79 (*m*, 1 H of OCH_2O, 1 OCH_2O); 4.76–4.70 (*m*, 1 H of OCH_2O), 1 H–C(2)); 4.32–4.24 (*m*, 1 H–C(2), 1 H of CH_2–C(10)); 4.00 (*d*, $^3J = 7.0$, H–C(4)); 3.91 (*dd*, $^3J = 6.5, 4.5$, H–C(8)); 3.73–3.66 (*m*, CH_2O, 1 H of CH_2O); 3.60–3.53 (*m*, 1 H of CH_2O, H–C(2a)); 3.49 (*s*, MeO); 3.50–3.45 (*m*, H–C(5)); 3.40 (*m*, H–C(10)); 3.30 (*qd*, $^3J = 7.0$, 6.5, H–C(7)); 2.44 (*m*, H–C(9)); 2.18 (*s*, Me–C(6)); 2.06 (*s*, MeCOO); 1.29 (*s*, Me–C(3)); 1.30 (*d*, $^3J = 7.0$, Me–C(7)); 1.24 (*d*, $^3J = 7.3$, Me–C(5)); 1.10 (*d*, $^3J = 7.3$, Me–C(9)); 0.99–0.90 (*m*, 2 CH_2Si); 0.04, 0.03 (2*s*, 6 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.2 (Me*C*O); 154.9, 141.7, 135.5, 126.2, 121.9, 114.8 (C(5a), C(6), C(6a), C(10a), C(10b), C(10c)); 97.4, 94.2, 89.6 (3 OCH_2O); 82.5 (C(4)); 78.8 (C(3)); 77.8 (C(8)); 74.0 (C(2)); 65.3, 65.0 (2 CH_2O); 64.5 (*C*H_2–C(10)); 55.9 (MeO); 49.5 (C(2a)); 38.5 (C(10)); 36.4 (C(5)); 35.3 (C(7)); 33.2 (C(9)); 21.1 (*Me*COO); 18.2 (2 CH_2Si); 16.1 (*Me*–C(7)); 15.0 (*Me*–C(6)); 14.8 (*Me*–C(3)); 14.2 (*Me*–C(5)); 12.0 (*Me*–C(9)); –1.4 (6 MeSi). CI-MS (NH_3): 727 (9, $[M+H_2O]^+$), 726 (11, $[M+OH]^+$), 709 (2, M^+), 663 (4), 647 (4), 560 (36), 500 (13), 338 (68), 191 (16), 73 (100). Anal. calc. for $C_{37}H_{64}O_9Si_2$ (709.08): C 62.67, H 9.10; found: C 62.72, H 9.07.

*(1*R*,2*R*,3*R*,4*R*,4a*R*,5*R*,6*R*,7*R*,8*S*,8a*R*,9a*R*,10*R*,10a*S*)-1,8-Bis(acetoxymethyl)-1,3,4,4a,5,6,7,8,8a,9a,10,10a-dodecahydro-10a-hydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethyl-2,6-bis{[2-(trimethylsilyl)ethoxy]methoxy}-anthracen-9(2*H*)-one* (**78**). To a soln. of (+)-**73** (16 mg, 0.02 mmol) in anh. THF (0.3 ml) at 0°, 65% *Red-Al* in toluene (0.01 ml) was added. After 1 h, H_2O (2 drops) and MeOH (5 ml) were added, and the mixture was allowed to warm to 20°. $MgSO_4$ was added, and the mixture was filtered over a *Celite* pad. After evaporation, the residue was dissolved in pyridine (0.5 ml) and Ac_2O (0.3 ml) and stirred for 1 h. Evaporation under high vacuum and FC (CH_2Cl_2/AcOEt 8:2, column 8 × 120 mm, 3-ml fractions) gave 4 mg (25%) of **78**. Colorless oil. IR (film): 3480, 1740, 1470, 1390, 1250, 1145, 1105, 1040. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.95 (*d*, ^2J = 7.8, 1 H, OCH_2O); 4.75 (*d*, ^2J = 7.8, 1 H, OCH_2O); 4.74, 4.70 (2*s*, 2 OCH_2O); 4.39 (*d*, ^3J = 3.4, CH_2–C(1)); 3.98 (*dd*, ^3J = 5.1, H–C(6)); 3.95 (*dd*, ^2J = 10.8, ^3J = 4.0, 1 H, CH_2–C(8)); 3.88 (*dd*, ^2J = ^3J = 10.4, 1 H, CH_2–C(8)); 3.75–3.53 (*m*, 2 CH_2O); 3.48 (*d*, ^3J = 5.6, H–C(3)); 3.39 (*s*, MeO); 2.67–2.60 (*m*, H–C(8), H–C(8a), H–C(9a)); 2.39 (*m*, H–C(4), H–C(7)); 2.24–2.15 (*m*, H–C(1), H–C(5)); 2.03, 2.02 (2*s*, 2 MeCOO); 1.90 (*dq*, ^3J = 11.7, 6.7, H–C(10)); 1.69 (*ddd*, ^3J = 11.7, 11.7, 4.3, H–C(4a)); 1.24 (*s*, Me–C(2)); 1.03 (*d*, ^3J = 7.3, Me–C(5)); 0.98 (*d*, ^3J = 7.3, Me–C(4)); 0.96–0.92 (*m*, 2 CH_2Si); 0.88 (*d*, ^3J = 6.7, Me–C(7), Me–C(10)); 0.03, 0.02 (2*s*, 6 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 210.8 (C(9)); 170.8, 170.4 (2 Me*C*O); 97.0, 93.8, 89.9 (3 OCH_2O); 84.1 (C(3)); 83.2, 79.6 (C(2), C(10a)); 74.7 (C(6)); 65.5, 65.1 (2 CH_2O); 63.6 (*C*H_2–C(8)); 60.9 (*C*H_2–C(1)); 55.8 (MeO); 49.4, 48.1 (C(8a), C(9a)); 47.9 (C(4a)); 42.9, 41.7 (C(1), C(5)); 38.5 (C(10)); 34.6 (C(4)); 32.7 (C(8)); 32.1 (C(7)); 20.9, 20.8 (2 *Me*COO); 18.2, 18.1 (2 CH_2Si); 15.9 (*Me*–C(2)); 11.4 (*Me*–C(5)); 9.9, 9.6 (*Me*–C(7), *Me*–C(10)); 8.2 (*Me*–C(4)); −1.4, −1.5 (6 MeSi). CI-MS (NH_3): 807 (4, $[M+H_2O]^+$), 520 (3), 90 (100).

*(2a*R*,3*R*,4*R*,5*R*,6*R*,6a*S*,7*R*,8*R*,9*R*,10*S*,10a*S*,10b*S*)-2a,3,4,5,6,6a,7,8,9,10,10b-Dodecahydro-6a-hydroxy-4-(methoxymethoxy)-3,5,6,7,9-pentamethyl-3,8-bis{[2-(trimethylsilyl)ethoxy]methoxy}-2*H*-anthra[9,1-bc]furan-10-methanol* (**79**). To a soln. of (+)-**73** (103 mg, 0.131 mmol) in anh. THF (4.5 ml) at −78°, 1M $LiAlH_4$ in THF (0.262 ml, 0.262 mmol, 2.2 equiv.) was added dropwise. After 30 min, the flask was put in a bath at 0°. After stirring for 45 min, 2,2′,2″-nitrilotris[ethanol] (0.5 ml) was added dropwise, followed by Et_2O (2 ml), and the mixture was stirred at 20° for 1 h. The mixture was filtered over a *Celite* pad, which was then thoroughly washed with AcOEt. Evaporation and FC (petroleum ether/AcOEt 4:6, column 10 × 150 mm, 5-ml fractions) gave 28 mg (31%) of **79** (R_f 0.26 (petroleum ether/AcOEt 1:1)). Colorless oil. ^{1}H-NMR (400 MHz, CD_3OD): 4.90–4.75 (*m*, 3 OCH_2O); 4.09 (*dd*, ^3J = 5.3, H–C(8)); 4.02–3.91 (*m*, 2 H–C(2), 1 H of CH_2–C(10), H–C(4), H–C(10b)); 3.78–3.55 (*m*, 2 CH_2–O, 1 H of CH_2–C(10)); 3.45 (*s*, MeO); 3.06 (*m*, H–C(2a)); 2.86 (*dq*, ^3J = 7.4, H–C(5)); 2.59 (*m*, H–C(6)); 2.39 (*m*, H–C(9)); 2.27 (*qd*, ^3J = 7.0, 5.3, H–C(7)); 2.20 (*m*, H–C(10)); 1.48 (*dd*, ^3J(10,10a) = 11.3, ^3J(10a,10b) = 8.4, H–C(10a)); 1.22 (*s*, Me–C(3)); 1.14 (*d*, ^3J = 7.4, Me–C(5)); 1.05 (*d*, ^3J = 7.1, Me–C(6)); 0.97 (*d*, ^3J = 7.2, Me–C(7)); 0.94 (*d*, ^3J = 7.3, Me–C(9)); 1.02–0.91 (*m*, 2 CH_2Si); 0.08, 0.07 (2*s*, 6 MeSi). ^{13}C-NMR (100.6 MHz, CD_3OD): 132.1, 130.0 (C(5a), C(10c)); 98.2, 94.7, 90.7 (3 OCH_2O); 81.9, 80.2, 79.9, 79.1, 77.5 (C(3), C(4); C(6a), C(8), C(10b)); 67.7, 66.1, 65.9, 64.7 (4 CH_2–O); 56.2 (MeO); 44.1, 42.2, 38.9, 37.9, 36.2, 35.9 (6 of these 7 atoms: C(2a), C(5), C(6), C(7), C(9), C(10), C(10a)); 19.0 (2 CH_2Si); 14.3, 12.9, 12.4,10.1, 10.0 (*Me*–C(3), *Me*–C(5), *Me*–C(6), *Me*–C(7), *Me*–C(9)); −1.3 (6 MeSi).

*(1*R*,2*R*,3*R*,4*R*,5*R*,6*R*,7*R*,8*S*,8a*S*,9*S*,10*R*,10a*S*)-1,2,3,4,5,6,7,8,8a,9,10,10a-Dodecahydro-9,10a-dihydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethyl-2,6-bis{[2-(trimethylsilyl)ethoxy]methoxy}anthracene-1,8-dimethanol α[1],α[8]-Diacetate* ((+)-**80**) *and (1*R*,2*R*,3*R*,4*R*,5*R*,6*R*,7*R*,8*S*,8a*R*,10*R*,10a*S*)-1,2,3,4,5,6,7,8,8a,9,10,10a-Dodecahydro-10a-hydroxy-3-(methoxymethoxy)-2,4,5,7,10-pentamethyl-2,6-bis{[2-(trimethylsilyl)ethoxy]methoxy}anthracene-1,8-dimethanol α[1],α[8]-Diacetate* (**81**). To a soln. of (+)-**73** (115 mg, 0.146 mmol) in anh. THF (4.5 ml), LiBr (25 mg, 0.292 mmol, 2 equiv.) was added. The mixture was then cooled to −78°, and 1M $LiAlH_4$ in THF (0.32 ml, 0.32 mmol, 2.2 equiv.) was added dropwise. After 10 min, the flask was put in a bath at −40°. After stirring for 1 h, MeOH (3 ml) was added dropwise, and the mixture was allowed to warm to 20°. The solvents were evaporated, and the residue was dissolved in pyridine (2 ml) and Ac_2O (1.2 ml). After 2 h, the solvents were evaporated. FC (CH_2Cl_2/AcOEt 8:2, column 18 × 150 mm, 10-ml fractions) gave 47 mg (41%) of (+)-**80** and 45 mg of **81**/**79**. Removal of **79** was achieved by a 2nd FC.

*Data of (+)-***80**. Colorless oil. $[\alpha]_{589}^{20} = +20$ (c = 0.6, $CHCl_3$; e.e. *ca.* 90%). IR (film): 3475, 1735, 1370, 1250, 1035, 860, 835. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.75 (*s*, OCH_2O–C(6)); 4.68–4.61 (*m*, 6 H, 1 OCH_2O–C(2), 1 OCH_2O–C(3), CH_2–C(1), CH_2–C(8)); 4.34 (*dd*, ^2J = 12.0, ^3J = 4.7, 1 H, CH_2–C(1)); 4.09 (*dd*, ^2J = ^3J = 10.6, 1 H, CH_2–C(8)); 4.03 (*dd*, ^3J = 5.2, H–C(6)); 3.89 (*m*, H–C(9)); 3.71–3.58 (*m*, C$H_2$$OCH_2O$–C(6), H–C(3)); 3.45 (*dd*, ^2J = 9.5, ^3J = 7.9, C$H_2$$OCH_2O$–C(2)); 3.43 (*s*, MeO); 2.83 (*dq*, ^3J = 7.3, H–C(4)); 2.52 (*q*, ^3J = 7.0, H–C(10)); 2.39–2.30 (*m*, H–C(8), H–C(7)); 2.28 (*m*, H–C(1)); 2.13 (*m*, H–C(5)); 2.12, 2.05 (2*s*, 2 MeCO); 1.67 (*dd*, ^3J(8,8a) = 11.0, ^3J(8a,9) = 7.0, H–C(8a)); 1.49 (*s*, Me–C(2)); 1.05 (*d*, ^3J = 7.0, Me–C(10)); 1.02 (*d*, ^3J = 7.3, Me–C(4)); 1.00–0.90 (*m*, Me–C(5), Me–C(7), 2 CH_2Si); 0.02, 0.01 (2*s*, 6 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.4, 171.1 (2*s*, 2 Me*C*O); 137.6, 127.2 (2*s*, C(4a), C(9a)); 99.3, 93.8, 89.2 (3*t*, ^1J(C,H) = 160, 163, 160, 3

OCH_2O); 81.6 (*d*, ^1J(C,H) = 143, C(3)); 78.9, 78.0 (2*s*, C(2), C(10a)); 76.2 (*d*, ^1J(C,H) = 129, C(6)); 74.8 (*d*, ^1J(C,H) = 137, C(9)); 66.0 (*t*, ^1J(C,H) = 154, *C*H_2–C(1)); 65.4 (*t*, ^1J(C,H) = 150, *C*H_2–C(8)); 64.9 (*t*, ^1J(C,H) = 137, 2 *C*H_2OCH_2O); 56.8 (*q*, ^1J(C,H) = 142, MeO); 49.2 (*d*, ^1J(C,H) = 126, C(1)); 40.7 (*d*, ^1J(C,H) = 124, C(8a)); 40.1 (*d*, ^1J(C,H) = 128, C(5)); 39.8 (*d*, ^1J(C,H) = 125, C(8)); 37.5 (*d*, ^1J(C,H) = 126, C(10)); 33.5 (*d*, ^1J(C,H) = 127, C(4)); 33.3 (*d*, ^1J(C,H) = 128, C(7)); 21.3, 21.1 (2*q*, ^1J(C,H) = 130, ^1J(C,H) = 129, 2 *Me*CO); 20.1 (*q*, ^1J(C,H) = 126, *Me*–C(2)); 18.1, 18.0 (2*t*, ^1J(C,H) = 120, 120, 2 CH_2Si); 15.7 (*q*, ^1J(C,H) = 127, *Me*–C(4)); 9.7 (*q*, ^1J(C,H) = 127, *Me*–C(10)); 11.1, 9.4 (2*q*, ^1J(C,H) = 126, 125, *Me*–C(5), *Me*–C(7)); –1.4, –1.5 (2*q*, ^1J(C,H) = 119, 119, 2 MeSi). CI-MS (NH_3): 807 (0.4, $[M+H_2O]^+$), 789 (0.9, M^+), 771 (0.6), 736 (0.4), 711 (0.3), 663 (9), 71 (100). Anal. calc. for $C_{39}H_{72}O_{12}Si_2$ (789.16): C 59.36, H 9.20; found: C 59.38, H 9.26.

Data of **81**: Colorless oil. IR (film): 3480, 1740, 1370, 1250, 1035. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.82 (*d*, ^2J = 7.3, 1 H, OCH_2O); 4.76 (*s*, OCH_2O); 4.70–4.65 (*m*, OCH_2O, 1 H of OCH_2O); 4.53 (*dd*, ^2J = 11.8, ^3J = 3.7, 1 H, CH_2–C(1)); 4.28 (*dd*, ^2J = 11.0, ^3J = 4.1, 1 H, CH_2–C(8)); 4.09 (*dd*, ^2J = 11.8, ^3J = 6.1, 1 H, CH_2–C(1)); 4.03 (*dd*, ^3J = 5.2, H–C(6)); 3.90 (*dd*, ^2J = ^3J = 10.4, 1 H, CH_2–C(8)); 3.59 (*d*, ^3J = 5.7, H–C(3)); 3.69–3.47 (*m*, 2 CH_2O); 3.41 (*s*, MeO); 2.69 (*m*, H–C(4)); 2.44 (*m*, H–C(10)); 3.37 (*m*, H–C(1)); 2.30–2.22 (*m*, H–C(5), H–C(7), 1 H–C(9)); 2.08, 2.04 (2*s*, 2 MeCOO); 2.10–2.00 (*m*, H–C(8)); 1.75–1.60 (*m*, H–C(8a), 1 H–C(9)); 1.37 (*s*, Me–C(2)); 1.03 (*d*, ^3J = 7.4, Me–C(4)); 1.01 (*d*, ^3J = 7.3, Me–C(10)); 0.96–0.86 (*m*, 2 CH_2Si, Me–C(5), Me–C(7)); 0.03, 0.01 (2*s*, 6 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.0, 170.9 (2*s*, 2 Me*C*O); 131.8, 124.8 (2*s*, C(4a), C(9a)); 98.5, 93.7, 89.6 (3*t*, ^1J(C,H) = 163, 162, 161, 3 OCH_2O); 83.1 (*d*, ^1J(C,H) = 141, C(3)); 77.7, 75.1 (2*s*, C(2), C(10a)); 76.0 (*d*, C(6)); 65.4, 65.1, 64.9 (3*t*, ^1J(C,H) = 141, 136, 136, 2 CH_2O, *C*H_2–C(1)); 64.4 (*t*, ^1J(C,H) = 145, *C*H_2–C(8)); 56.5 (*q*, ^1J(C,H) = 142, MeO); 47.5 (*d*, ^1J(C,H) = 125, C(1)); 40.1, 33.9, 33.9 (2*d*, ^1J(C,H) = 125, 126, C(4), C(5), C(7)); 39.5 (*d*, ^1J(C,H) = 122, C(8)); 36.6 (*d*, ^1J(C,H) = 125, C(10)); 30.8 (*d*, ^1J(C,H) = 128, C(8a)); 29.5 (*t*, ^1J(C,H) = 127, C(9)); 21.2, 21.0 (2*q*, ^1J(C,H) = 130, 129, 2 *Me*COO); 18.9 (*q*, ^1J(C,H) = 126, *Me*–C(2)); 18.2, 18.0 (2*t*, ^1J(C,H) = 119, ^1J(C,H) = 119, 2 CH_2Si); 13.9 (*q*, ^1J(C,H) = 127, *Me*–C(4)); 10.3 (*q*, ^1J(C,H) = 126, *Me*–C(10)); 11.7, 9.6 (2*q*, ^1J(C,H) = 126, 125, *Me*–C(5), *Me*–C(7)); –1.4 (*q*, ^1J(C,H) = 119, 6 MeSi). CI-MS (NH_3): 791 (0.4, $[M+H_2O]^+$), 663 (0.5), 624 (0.9), 566 (1.3), 73 (100).

*(2a*R*,3*R*,4*R*,5*R*,6*R*,6a*S*,7*R*,8*R*,9*R*,10*S*,10a*S*,10b*S*)-2a,3,4,5,6,6a,7,8,9,10,10a,10b-Dodecahydro-6a-hydroxy-4-(methoxymethoxy)-3,5,6,7,9-pentamethyl-3,8-bis{[2-(trimethylsilyl)ethoxy]methoxy}-2*H*-anthra[9,1-*bc*]-10-methanol* α^{10}-*Acetate* ((+)-**82**). A soln. of **79** (28 mg, 0.041 mmol) in pyridine (1 ml) and Ac_2O (0.5 ml) was stirred at 20° overnight. Evaporation and FC (petroleum ether/AcOEt 7:3, column 10 × 150 mm, 5-ml fractions) gave 29 mg (97%) of (+)-**82**. Colorless oil. $[\alpha]_{589}^{20} = +18$ (c = 0.8, $CHCl_3$; e.e. *ca.* 90%). IR (film): 3500, 1740, 1465, 1390, 1250, 1040. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.86 (*d*, ^2J = 7.8, 1 H, CH_2O–C(3)); 4.80–4.68 (*m*, 1 H of CH_2O–C(3), 2 OCH_2O, 1 H of CH_2–C(10)); 4.04 (*dd*, ^3J = 5.2, H–C(8)); 3.97–3.84 (*m*, 5 H, 2 H–C(2), CH_2–C(10), H–C(4), H–C(10b)); 3.69–3.48 (*m*, 2 CH_2O); 3.42 (*s*, MeO); 2.98 (*m*, H–C(2a)); 2.80 (*m*, H–C(5)); 2.55 (*m*, H–C(6)); 2.45–2.32 (*m*, H–C(9), H–C(10)); 2.18 (*m*, H–C(7)); 2.04 (*s*, MeCOO); 1.44 (*dd*, ^3J(10,10a) = 11.2, ^3J(10a,10b) = 8.1, H–C(10a)); 1.19 (*s*, Me–C(3)); 1.09 (*d*, ^3J = 7.4, Me–C(5)); 1.01 (*d*, ^3J = 7.1, Me–C(6)); 0.98–0.95 (*m*, 10 H, 2 CH_2Si, Me–C(9), Me–C(7)); 0.04, 0.02 (2*s*, 6 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.1 (*s*, Me*C*O–Me); 130.2, 129.2 (2*s*, C(5a), C(10b)); 97.0, 93.7, 89.5 (3*t*, ^1J(C,H) = 162, 165, 162, 3 OCH_2O); 80.3 (*d*, ^1J(C,H) = 142, C(4)); 78.4, 78.2 (2*s*, C(6a), C(3)); 78.3 (*d*, ^1J(C,H) = 138, C(10b)); 75.7 (*d*, ^1J(C,H) = 130, C(8)); 66.6 (*t*, ^1J(C,H) = 149, C(2)); 65.0, 64.9, 64.8 (3*t*, ^1J(C,H) = 135, 148, 137, 2 CH_2O, *C*H_2–C(10)); 55.8 (*q*, ^1J(C,H) = 142, MeO); 47.8 (*d*, ^1J(C,H) = 133, C(2a)); 41.4 (*d*, ^1J(C,H) = 130, C(7)); 39.6 (*d*, ^1J(C,H) = 129, C(10)); 37.1 (*d*, ^1J(C,H) = 131, C(10a)); 36.7 (*d*, ^1J(C,H) = 127, C(6)); 34.9 (*d*, ^1J(C,H) = 127, C(5)); 33.0 (*d*, ^1J(C,H) = 129, C(9)); 21.0 (*q*, ^1J(C,H) = 130, *Me*COO); 18.2, 18.1 (2*t*, ^1J(C,H) = 118, 2 CH_2Si); 13.6 (*q*, ^1J(C,H) = 127, *Me*–C(3)); 12.1 (*q*, ^1J(C,H) = 127, *Me*–C(7)); 11.7 (*q*, ^1J(C,H) = 128, *Me*–C(5)); 9.5 (*q*, ^1J(C,H) = 128, *Me*–C(6)); 9.2 (*q*, ^1J(C,H) = 125, *Me*–C(9)); –1.44 (*q*, ^1J(C,H) = 118, 6 MeSi). CI-MS (NH_3): 747 (2, $[M+H_2O]^+$), 730 (4, $[M+H]^+$), 729 (0.9, M^+), 580 (21), 338 (53), 191 (40), 73 (100). Anal. calc. for $C_{37}H_{68}O_{10}Si_2$ (729.11): C 60.95, H 9.40; found: C 60.99, H 9.28.

*(1S,2*R*,3*R*,4*R*,4a*S*,5S,7S,8*R*,9*R*,10*R*,12S,12a*S*)-1,10-Bis(acetoxymethyl)tetradecahydro-8-(methoxymethoxy)-2,4,5,7,9-pentamethyl-3,9-bis{[2-(trimethylsilyl)ethoxy]methoxy}-6,11-epoxybenzocyclodecene-4a,6,11,12-tetrol* ((+)-**83**). Ozone (3% in O_2) was bubbled in a soln. of (+)-**80** (69 mg, 0.087 mmol) in anh. CH_2Cl_2 (5 ml) at –78° for 7 min. Then Me_2S (0.2 ml) was added and the mixture allowed to warm to 20° and stirred overnight. Solvent evaporation, FC (petroleum ether/AcOEt 3:1, column 19 × 150 mm, 10-ml fractions) gave 48 mg (66%) of **83**. Colorless oil. $[\alpha]_{589}^{25} = +50$, $[\alpha]_{577}^{25} = +52$, $[\alpha]_{546}^{25} = +59$, $[\alpha]_{435}^{25} = +96$, $[\alpha]_{405}^{25} = +114$ (c = 0.7, $CHCl_3$). IR (film): 1740, 1455, 1365, 1250, 1035. ^{1}H-NMR (400 MHz, (D_5)pyridine): 5.33 (*d*, ^2J = 8.1, 1 H, OCH_2O); 5.01 (*dd*, ^2J = 11.8, ^3J = 3.5, 1 H, CH_2–C(10)); 4.94 (*d*, ^3J = 4.0, H–C(12)); 4.90 (*d*, ^2J = 6.2, 1 H, OCH_2O); 4.89

(*s*, OCH_2O); 4.83 (*dd*, ^2J = 11.8, ^3J = 4.0, 1 H, CH_2–C(10)); 4.77 (*d*, ^2J = 6.2, 1 H, OCH_2O); 4.76 (*d*, ^2J = 8.1, 1 H, OCH_2O); 4.70–4.63 (*m*, 2 H, H–C(3), CH_2–C(1)); 4.45–4.36 (*m*, H–C(8), CH_2–C(1)); 3.98 (*m*, 1 H, CH_2OCH_2O); 3.79 (*m*, CH_2OCH_2O); 3.54 (*m*, 1 H, CH_2OCH_2O); 3.48 (*m*, H–C(1)); 3.44 (*s*, MeO); 3.04 (*dq*, ^3J = 7.2, H–C(7)); 2.77 (*dd*, ^3J = 3.5, 4.0, H–C(10)); 2.70 (*m*, H–C(2)); 2.55 (*m*, H–C(4)); 2.52 (*dd*, ^3J(1,12a) = 17.7, ^3J = 4.0, H–C(12a)); 2.41 (*q*, ^3J = 7.2, H–C(5)); 2.31, 1.97 (2*s*, 2 Me*C*OO); 1.89 (*s*, Me–C(9)); 1.31 (*d*, ^3J = 7.2, Me–C(7)); 1.18–1.09 (*m*, Me–C(4), Me–C(2), Me–C(5), CH_2Si); 1.02 (*t*, ^3J = 8.3, CH_2Si); 0.05, 0.03 (2*s*, 6 MeSi). ^{13}C-NMR (100.6 MHz, (D_5)pyridine): 170.8 (*s*, 2 Me*C*O); 111.3, 108.1 (2*s*, C(6), C(11)); 99.0, 94.0, 91.1 (3*t*, ^1J(C,H) = 162, 159, 161, 3 OCH_2O); 86.8, 77.4 (2*s*, C(4a), C(9)); 84.7 (*d*, ^1J(C,H) = 142, C(8)); 75.6 (*d*, ^1J(C,H) = 143, C(3)); 74.5 (*d*, ^1J(C,H) = 160, C(12)); 65.4, 65.0 (2*t*, 2 CH_2OCH_2O); 64.8 (*t*, CH_2–C(1)); 62.5 (*t*, ^1J(C,H) = 149, CH_2–C(10)); 59.9 (*d*, ^1J(C,H) = 125, C(10)); 56.1 (*q*, ^1J(C,H) = 143, MeO); 41.1 (2*d*, ^1J(C,H) = 128, C(7), C(4)); 40.8 (*d*, ^1J(C,H) = 125, C(5)); 39.1 (*d*, ^1J(C,H) = 118, C(12a)); 34.9 (*d*, ^1J(C,H) = 128, C(2)); 34.1 (*d*, ^1J(C,H) = 131, C(1)); 21.1, 20.8 (2*q*, ^1J(C,H) = 129, 130, 2 *Me*COO); 18.4, 18.3 (2*t*, ^1J(C,H) = 123, 2 CH_2Si); 15.5 (*q*, ^1J(C,H) = 127, *Me*–C(9)); 9.3 (*q*, ^1J(C,H) = 127, *Me*–C(7)); 11.5, 8.7, 8.2 (3*q*, ^1J(C,H) = 127, 120, 127, *Me*–C(4), *Me*–C(2), *Me*–C(5)); –1.4 (*q*, ^1J(C,H) = 119, 6 MeSi). CI-MS (NH_3): 839 (6, M^+), 673 (25), 90 (100). Anal. calc. for $C_{39}H_{74}O_{15}Si_2$ (839.17): C 55.82, H 8.89; found: C 55.88, H 8.74.

*(1*R*,2*R*,3*R*,4a*R*,4b*R*,5*S*,6*R*,7*R*,8*R*,8a*S*,9*S*,10a*R*)-3,5-Bis(acetoxymethyl)-4a,8a-dihydroxy-1-(methoxymethoxy)-2,6,8,9,10a-pentamethyl-2,7-bis{[2-(trimethylsilyl)ethoxy]methoxy}dodecahydrophenanthrene-4,10-dione* (**85**). To a soln. of (+)-**73** (30 mg, 0.038 mmol) in a mixture of CCl_4 (0.15 ml), MeCN (0.15 ml), and H_2O (0.23 ml), $NaIO_4$ (33 mg, 0.156 mmol, 4.1 equiv.) was added, followed by $RuCl_3 \cdot H_2O$ (0.5 mg, 0.002 mmol, 0.05 equiv.). The org. phase became green and the aq. phase white and cloudy. After 2.5 h, CH_2Cl_2 (5 ml) was added, the aq. phase extracted with CH_2Cl_2 (1 ml, 3 ×), and the org. phase dried ($MgSO_4$) and evaporated. FC (petroleum ether/AcOEt 4:1 → 3:1, column 10 × 150 mm, 5-ml fractions): 19 mg (61%) of a 2.5:1 mixture of the two diastereoisomers. The two diastereoisomers were separated by HPLC (petroleum ether/Et_2O/AcOEt 3:2:0.4): t_R 8 (**85**) and 6 min (isomer). **85**: Colorless oil. IR (film): 3420, 1740, 1720, 1250, 1030, 860. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.23 (*d*, ^2J = 8.3, 1 H, OCH_2O); 4.99 (*d*, ^2J = 5.2, 1 H, OCH_2O); 4.78 (*s*, H–C(1)); 4.74 (*d*, ^2J = 8.3, 1 H, OCH_2O); 4.74 (*d*, ^2J = 5.2, 1 H, OCH_2O); 4.72, 4.70 (*AB*, ^2J = 7.1, OCH_2O); 4.56 (*dd*, ^2J = ^3J = 10.3, 1 H, CH_2–C(3)); 4.36 (*s*, OH–C(4a)); 4.27 (*dd*, ^3J = 10.3, 2.0, H–C(3)); 4.15 (*dd*, ^2J = 10.3, ^3J = 2.0, 1 H, CH_2–C(3)); 3.96 (*dd*, ^3J = 5.6, H–C(7)); 3.94 (*dd*, ^2J = 11.1, ^3J = 8.7, 1 H, CH_2–C(5)); 3.79–3.72 (*m*, 1 H, CH_2CH_2Si); 3.66–3.61 (*m*, CH_2CH_2Si); 3.58 (*dd*, ^2J = 11.1, ^3J = 6.3, 1 H, CH_2–C(5)); 3.54–3.47 (*m*, 1 H, CH_2CH_2Si)); 3.38 (MeO); 3.35 (*q*, ^3J = 6.6, H–C(9)); 2.94 (*d*, ^3J = 11.0, H–C(4b)); 2.56 (*m*, H–C(5)); 2.45 (*s*, OH–C(8a)); 2.35 (*m*, H–C(6)); 2.04 (*m*, H–C(8)); 2.03, 1.96 (2*s*, 2 MeCOO); 1.15, 1.14 (2*s*, Me–C(2), Me–C(10a)); 1.07 (*d*, ^3J = 7.3, Me–C(8)); 1.03 (*d*, ^3J = 6.5, Me–C(9)); 1.01 (*d*, ^3J = 7.2, Me–C(6)); 0.95, 0.75 (*m*, 2 CH_2Si); 0.03, 0.01 (2*s*, 6 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 208.8, 204.0 (2*s*, C(4), C(10)); 171.1, 170.2 (2*s*, 2 MeCO); 99.1, 93.8, 89.1 (3*t*, ^1J(C,H) = 165, 159, 164, 3 OCH_2O); 87.5, 84.1, 83.5, (3*s*, C(2), C(8a), C(4a)); 74.9, 74.8 (2*d*, ^1J(C,H) = 145, 145, C(1), C(7)); 65.9 (*t*, ^1J(C,H) = 149, CH_2–C(5), CH_2CH_2Si); 65.3 (*t*, ^1J(C,H) = 141, CH_2CH_2Si); 58.6 (*t*, ^1J(C,H) = 149, CH_2–C(3)); 58.1 (*s*, C(10a)); 56.7 (*q*, ^1J(C,H) = 142, MeO); 48.1 (*d*, ^1J(C,H) = 131, C(3)); 44.3 (*d*, ^1J(C,H) = 124, C(9)); 42.1 (*d*, ^1J(C,H) = 126, C(8)); 35.3 (*d*, ^1J(C,H) = 128, C(5)); 34.3 (*d*, ^1J(C,H) = 130, C(6)); 32.6 (*d*, ^1J(C,H) = 127, C(4b)); 21.1, 20.6 (2*q*, ^1J(C,H) = 130, 130, 2 *Me*COO); 18.3, 15.7 (2*q*, ^1J(C,H) = 131, 129, *Me*–C(2), *Me*–C(10a)); 18.2, 18.0 (2*t*, ^1J(C,H) = 118, 119, 2 CH_2Si); 11.7 (*q*, ^1J(C,H) = 127, *Me*–C(8)); 9.0 (*q*, ^1J(C,H) = 128, *Me*–C(6)); 6.7 (*q*, ^1J(C,H) = 127, *Me*–C(9)); –1.5 (2*q*, ^1J(C,H) = 116, 6 MeSi). CI-MS (NH_3): 837 (100, $[M + H_2O]^+$), 762 (38), 704 (20), 611 (58), 492 (71), 446 (91), 417 (98), 362 (99). Anal. calc. for $C_{39}H_{70}O_{14}Si_2$ (819.14): C 57.19, H 8.61; found: C 57.10, H 8.55

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