Formal Asymmetric Synthesis of Pentalenolactone E and Pentalenolactone F 2. Construction of the Angular Diquinanoid δ-Lactone

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Received August 25, 1997

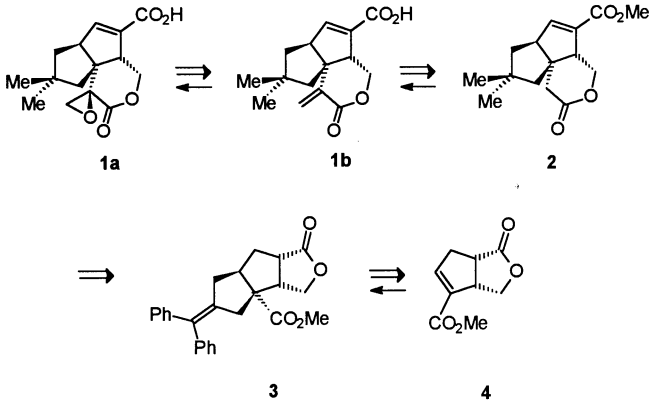
Keywords: Pentalenolactones E and F / Asymmetric synthesis / Selenide elimination / Kauffmann methylenation / Natural products

A formal asymmetric synthesis of pentalenolactone E (**1b**) and pentalenolactone F (**1a**) has been accomplished. Ozonolysis of the diphenyl-substituted triquinane **3** and Kauffmann methylenation of ketone **5** with $WOCl_3$/2 MeLi yielded the unsubstituted triquinane **9**. The crucial rearrangement of the linear triquinanoid lactone **11** to the angular triquinanoid lactone **14a** was accomplished using orthoformate and acid in methanol. Subjecting triquinanes **14a/b** to the selenoxide method gave triquinene **15**. Homologation of γ-lactone **15** to the angular diquinanoid δ-lactone **2** via a Horner-Wadsworth-Emmons or Peterson reaction of hemiacetals **16a/b** was, however, not successful. Chemoselective reduction of **14a** afforded hemiacetals **21a/b**, reaction of which with the phosphonate salt **17a** ultimately led to the ketene dithioacetal **22**. The angular intermediates **25a/b** were obtained from **22** by reduction to give the linear hemiacetals **24a/b**, which rearranged to the dithio ortholactones **25a/b** in the presence of acid. Introduction of the double bond and deprotection were accomplished via selenation of **25a/b** with *N*,*N*-diethylbenzeneselenylamide and treatment of selenides **30a/b** with silver nitrate. The unsaturated aldehydes **28** and **29** thus obtained were converted to **2** and **31**, respectively, by oxidation with manganese dioxide in the presence of sodium cyanide, methanol and acetic acid. Alkene **2** was isolated by crystallization.

Introduction

In the preceding article[1] a new strategy was established towards the angular diquinanoid δ-lactone **2** which is a precursor of pentalenolactone E (**1b**) and pentalenolactone F (**1a**) (Figure 1).The synthesis of the key triquinanoid intermediate **3** involved a stereoselective Pd-catalyzed [3+2]-cycloaddition reaction of diquinene **4**[2]. Before the final goal could be reached, however, the problems of the rearrangement of the linear to the angular triquinanoid γ-lactone[2], the homologation of the γ-lactone ring and the introduction of the double bond had to be addressed (cf. Figure 1, ref.[1]). We describe herein solutions to these problems and, thus, an asymmetric synthesis of **2**.

Figure 1. Retrosynthesis of pentalenolactone E (**1b**) and pentalenolactone F (**1a**)



Results and Discussion

Construction of the Linear Triquinanoid γ-Lactone: As a consequence of the results described in the forgoing paper[1] the synthetic plan necessitated a conversion of the diphenyl-substituted triquinane **3** into the unsubstituted triquinane **9** (Scheme 1). Thus, ozonolysis of **3** in EtOH-free and dry CH_2Cl_2, followed by reduction of the intermediate ozonide with a large excess of Me_2S[3] gave ketone **5** in 85% yield.

Wittig reaction of **5** with $Ph_3P{=}CH_2$[4] afforded, besides several minor products, derived from a reaction of the ylide with the ester group[5], the angular triquinanes **6a/b** and **7a/b** in 41% and 7% yield, respectively. Thus, in one synthetic operation the olefination and a skeletal rearrangement had occurred. This fortuitous result provided evidence for the

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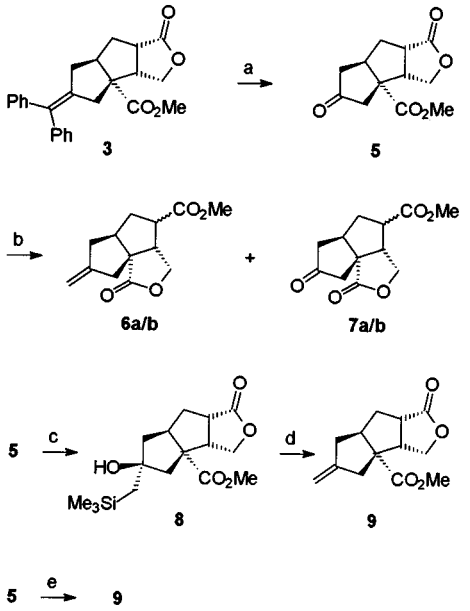
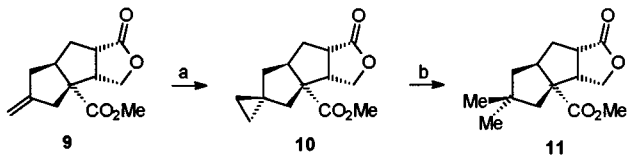
Scheme 1



Reagents and conditions: (a) 1. O_3, CH_2Cl_2, −78°C; 2. Me_2S; (b) $MePPh_3Br/NaNH_2$, CH_2Cl_2, room temp.; (c) $Cl_3CeCH_2SiMe_3$, THF, −80°C → −70°C → 25°C; (d) HF, H_2O, MeCN, room temp.; (e) $WOCl_3 \cdot 2$ THF, MeLi, THF, ether, −78°C → room temp. or $WOCl_4$, MeLi, THF, −70°C → reflux → room temp.

feasibility of the pivotal linear-angular lactone rearrangement in our retrosynthetic scheme[1]. However, attempts to modify the Wittig reaction[5][6] did not improve the yield of **6a/b**. Furthermore, the side products were difficult to separate from **6a/b**. Since conversion of **5** to **9** with $CH_2Br_2/Zn/TiCl_4$[7] failed, we turned our attention to the Peterson reaction. Treatment of **5** with $Me_3SiCH_2CeCl_2$, which was prepared from Me_3SiCH_2Li and anhydrous $CeCl_3$[8][9], gave alcohol **8** as a single isomer in 79% yield (89% conversion). The configuration of the new stereogenic center of **8** was determined by NOE experiments. The high stereoselectivity of the addition of $Me_3SiCH_2CeCl_2$ may be explained in terms of an initial coordination of this reagent to the ester group of **5**, followed by an intramolecular delivery of the trimethylsilylmethyl group. The yield of **8** was critically dependent on the conditions used for the dehydration[8] of $CeCl_3 \cdot 7\ H_2O$, as well as those of the transmetallation and the work-up[5]. Treatment of **8** with HF in aqueous MeCN afforded alkene **9** in 99% yield. However, because of the incomplete conversion of **5** and the tedious preparation of anhydrous $CeCl_3$, we searched for a more convenient alternative for the methylenation of **5**. Treatment of ketone **5** with the Kauffmann tungsten reagent, prepared either from $WOCl_3 \cdot 2$ THF or from $WOCl_4$ and 2 equiv. of MeLi in THF[10], gave in a very smooth and clean reaction alkene **9** in 97% (93%) yield, using a non-aqueous work-up procedure. Elaboration of the geminal dimethyl group of **2** starting from **9** was completed following a published procedure[11][12]. Reaction of **9** with $ZnEt_2$ and CH_2I_2 afforded in 94% yield (90% conversion) the cyclopropane derivative **10**, hydrogenation of which gave the dimethyl derivative **11** in 99% yield (Scheme 2).

Scheme 2



Reagents and conditions: (a) $ZnEt_2$, CH_2I_2, CH_2Cl_2, −80°C → room temp.; (b) H_2, Pt, AcOH, room temp.

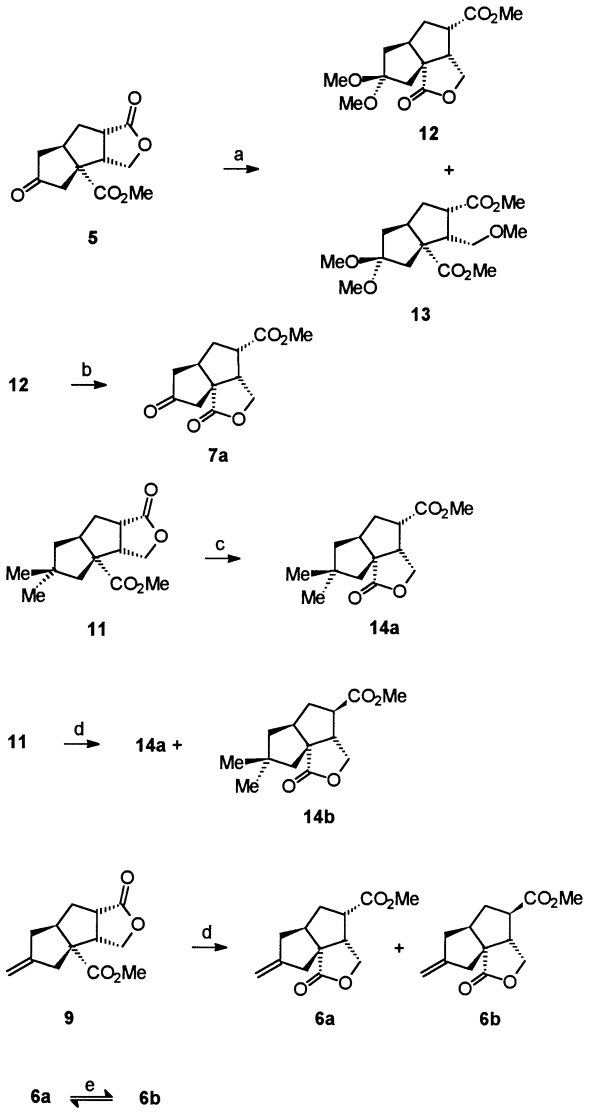
Construction of the Angular Triquinanoid γ-Lactone: Having obtained the three linear triquinanes **5**, **9**, and **11**, the stage was set for rearrangement to the angular triquinanes **7a**, **6a**, and **14a**, respectively (Scheme 3). The result of an attempted ketalization of ketone **5** gave an important clue as to the feasibility of the linear-angular lactone rearrangement. Treatment of **5** with $HC(OMe)_3$ in MeOH in the presence of *p*TsOH[13] at reflux temperature furnished ketal **12** in 87% yield. As an interesting side product, diester **13** was obtained in 9% yield. Clearly, under these conditions, not only ketalization but also a skeletal rearrangement with retention of configuration had occurred. Cleavage of ketal **12** with pyridinium *p*-toluenesulfonate in acetone gave the isomeric ketone **7a** in 97% yield. The angular structure and the configuration of **7a** were unequivocally established by X-ray analysis (Figure 2)[14].

Rearrangement of the linear triquinane **11** with $HC(OMe)_3$ in MeOH in the presence of *p*TsOH at room temperature proceeded in an analogous manner and furnished the angular triquinane **14a** as a single isomer in 98% yield. In the absence of $HC(OMe)_3$ only a minor conversion of **11** occurred. Eventually, we found that the skeletal rearrangement could also be accomplished in MeOH in the presence of a base. Treatment of **11** in MeOH with DBU at room temperature for 20 h furnished, however, a 6:1 mixture of **14a** and **14b** in 98% yield. Thus, in this case, the skeletal arrangement was accompanied by a partial epimerization. Reaction of **9** with MeOH and DBU at room temperature for 3.5 h gave a mixture of the angular triquinanes **6a** and **6b** in a ratio of 1:1 in 85% yield. After heating the mixture for 70 h to 60°C, the ratio of **14a** to **14b** shifted towards 1:2.7. No attempts were made to see whether this ratios respresented the equilibria.

Synthesis of the Angular Diquinanoid δ-Lactone: Having mastered the crucial skeletal rearrangement, we turned our attention to the introduction of the double bond in **15**. Consecutive treatment of a mixture of esters **14a/b** in THF with LDA, PhSeCl, and H_2O_2[15] furnished alkene **15** as a single isomer in 60% overall yield based on **14a/b** (Scheme 4). The position of the double bond in **15** was verified by NMR spectroscopy.

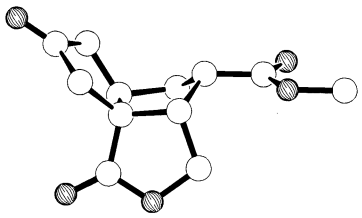
For the construction of the δ-lactone ring in **2**, we envisaged a homologation of the γ-lactone ring in **15** by the method of Lee et al.[16], which applied to the present case, requires a Horner-Wadsworth-Emmons or Peterson reaction of hemiacetals **16a/b** with **17a** or **17b** with the formation of the corresponding hydroxy ketene dithioacetal. Sub-

Scheme 3



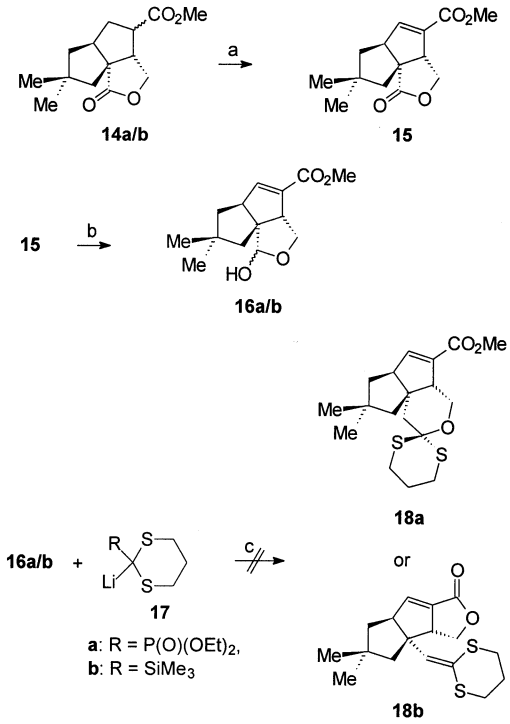
Reagents and conditions: (a) $HC(OMe)_3$, MeOH, *p*TsOH, reflux; (b) acetone, PPTS, room temp.; (c) $HC(OMe)_3$, MeOH, *p*TsOH, room temp.; (d) MeOH, DBU, room temp.; (e) MeOH, DBU, 60°C.

Figure 2. Crystal structure of **7a**



sequently, acid-catalyzed cyclization would afford the dithio ortholactone **18a**[17] or lactone **18b**. Reduction of lactone **15** with DIBAL-H[18] furnished **16a/b** in 97% yield. Unfortunately, treatment of **16a/b** with the dithiane derivatives **17a**[19] and **17b**[20] led only to recovery of the starting materials **16a/b** or to the formation of complex mixtures of products[5].

Scheme 4



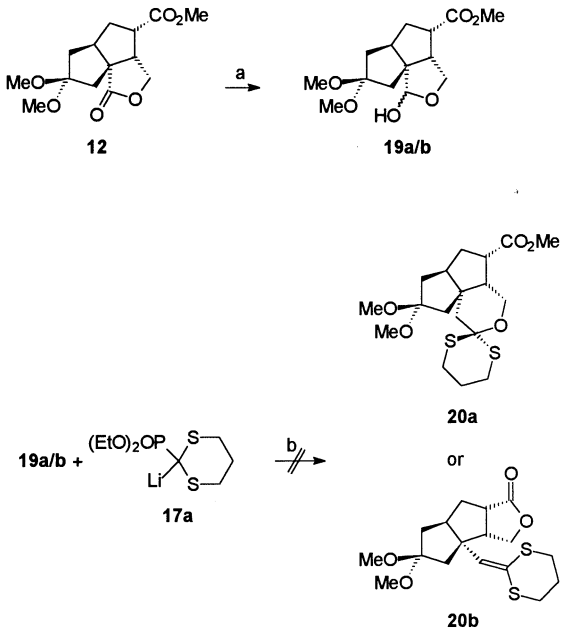
Reagents and conditions: (a) 1. LDA, THF, −80°C → room temp.; 2. PhSeCl, THF, −80°C → 0°C; 3. AcOH, H_2O_2, room temp.; (b) DIBAL-H, THF −85°C; (c) ref.[5].

We therefore turned our attention to the olefination of hemiacetals **19a/b**, which were obtained from lactone **12** via a DIBAL-H reduction in 87% yield (Scheme 5). However, reaction of **19a/b** with **17a** followed by treatment with acid led to a mixture of several products, which may have contained small amounts of ketals **20a** and **20b** or of the corresponding ketones[5]. Because of the difficulties encountered during the isolation we abandoned this route.

In the light of these unfavorable results, we focussed on the dimethyl lactone **14a**. This meant that we would have to carry out the homologation of the γ-lactone ring first and then introduce the double bond at a later stage. To this end, lactone **14a** was reduced with DIBAL-H, affording a mixture of hemiacetals **21a** and **21b** in 94% yield (Scheme 6)[21]. Reaction of **21a/b** with phosphonate **17a** led directly to the ketene dithioacetal **22** in 68% yield (78% conversion). Thus, the desired olefination and lactonization had occurred in a single synthetic step. This lactonization was, however, by no means detrimental with regard to the synthetic scheme (vide infra). Surprisingly, reaction of **21a/b** with the silyl reagent **17b** gave a mixture of ketones **23a/b** (65%) and not alkene **22**. Thus, in this case, the ester group had reacted via acylation of **17b** followed by desilylation[22].

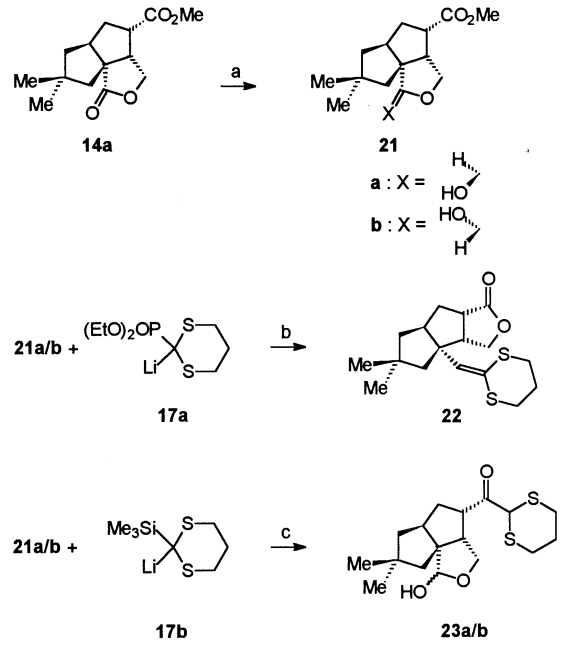
Having obtained the linear triquinane **22**, we were able to set about the completion of the δ-lactone ring and the introduction of the double bond. Reduction of **22** with DIBAL-H furnished a mixture of hemiacetals **24a/b** in a ratio of 10:1 in 96% yield (Scheme 7).

Scheme 5



Reagents and conditions: (a) DIBAL-H, THF, −80°C; (b) ref.[5].

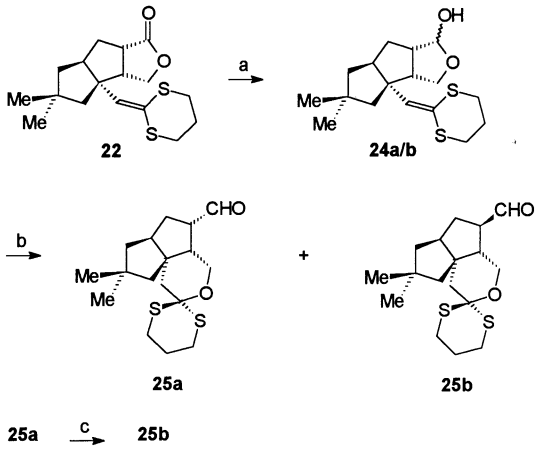
Scheme 6



Reagents and conditions: (a) DIBAL-H, THF, −80°C; (b) THF, 0°C → room temp.; (c) THF, −60°C → room temp.

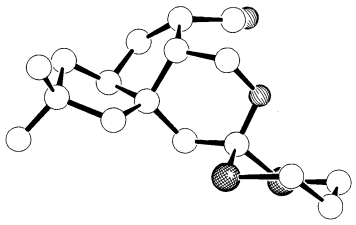
Treatment of the linear triquinanes **24a/b** with pyridinium *p*-toluenesulfonate (PPTS) in EtOH-free CH_2Cl_2 at room temperature led to formation and subsequent cyclization[23] of the corresponding hydroxy aldehyde. Thus, a mixture of the angular diquinanes **25a/b** was obtained in a ratio of 2:1 in 99% yield. Crystallization of **25a/b** afforded the pure epimeric aldehyde **25a**, the structure of which was confirmed by X-ray analysis (Figure 3)[14].

Scheme 7



Reagents and conditions: (a) DIBAL-H, THF, −80°C; (b) PPTS, CH_2Cl_2, room temp.; (c) $CDCl_3$, room temp.

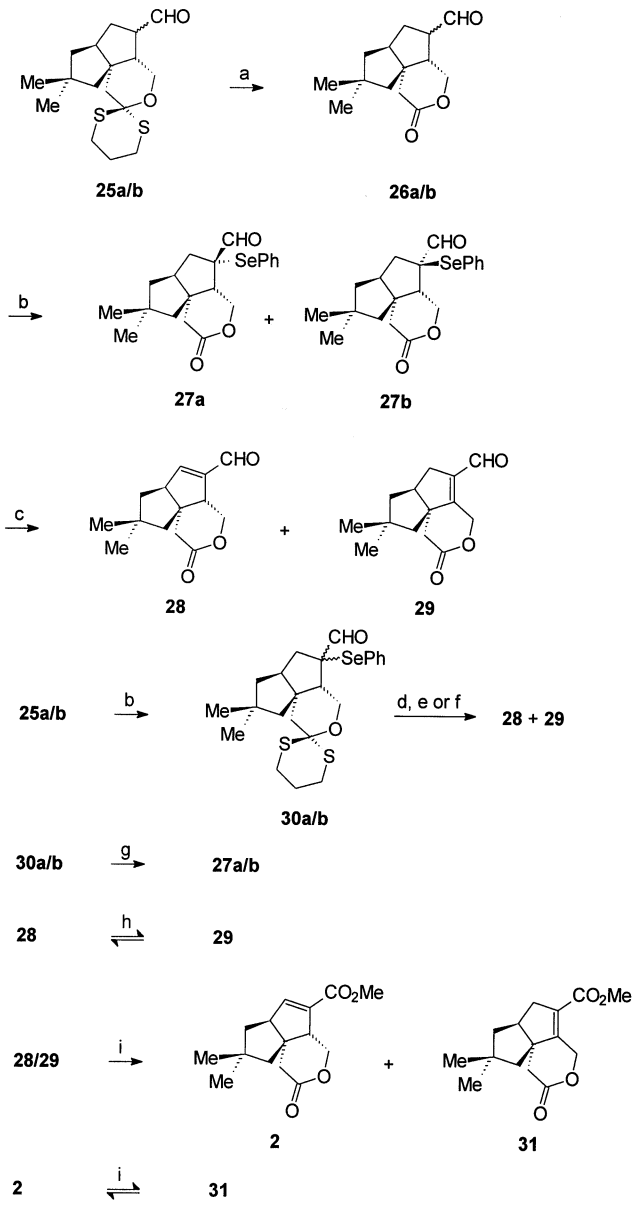
Figure 3. Crystal structure of **25a**



Thus, unmasking of the aldehyde group and formation of the dithio ortholactone ring had occurred in one step. At room temperature in $CHCl_3$ solution, slow isomerization of aldehyde **25a** to its epimer **25b** took place. With the required aldehydes **25a/b** in hand, we proceeded to investigate the introduction of the double bond by the selenoxide method[15]. Cleavage of the dithio ortholactones **25a/b** occurred readily upon treatment with $PhI(CF_3COO)_2$[24] in aqueous MeCN and gave lactones **26a/b** in 79% yield (Scheme 8).

Reaction of aldehydes **26a/b** with $PhSeNEt_2$[25] occurred selectively at the α-position of the aldehyde group and afforded a mixture of selenides **27a** and **27b** in a ratio of 7.4:1 in 88% yield. The structure of the major diastereomer **27a** was determined by NOE experiments, which proved the trans configuration of the aldehyde group to the lactone ring. Upon treatment of **27a/b** with H_2O_2 in aqueous CH_2Cl_2 oxidative elimination occurred to give a mixture of alkenes **28** and **29** in a ratio of 14:1 in 91% yield. Eventually, we found that conversion of **25a/b** to alkenes **28** and **29** could be accomplished without the oxidation step. Selenylation of aldehydes **25a/b** by reaction with $PhSeNEt_2$ in CH_2Cl_2 at room temperature gave a mixture of selenides **30a/b** in a ratio of 2.5:1 in 88% yield. Treatment of **30a/b** with $AgNO_3$ or AgO in aqueous MeCN/THF at room temperature led not only to deprotection of the lactone group, but also to clean elimination and gave a mixture of **28** and **29** in a ratio of 14:1 in 69% yield. Interestingly, if treatment of **30a/b** with $AgNO_3$ in aqueous MeCN/THF

Scheme 8



Reagents and conditions: (a) $PhI(CF_3COO)_2$, H_2O, MeCN, room temp.; (b) $PhSeNEt_2$, CH_2Cl_2, room temp.; (c) H_2O_2, H_2O, CH_2Cl_2, 0°C → room temp.; (d) AgO, THF, H_2O, room temp.; (e) $AgNO_3$, MeCN, THF, H_2O, room temp.; (f) 1. $AgNO_3$, MeCN, THF, H_2O, 0°C; 2. H_2O_2, H_2O, CH_2Cl_2, 0°C → room temp.; (g) $AgNO_3$, H_2O, MeCN, THF, 0°C; (h) MeCN, room temp.; (i) AcOH, MeOH, NaCN, MnO_2, room temp.

was carried out at 0°C, a mixture of lactones **27a/b** was obtained. Thus, the conversion of **30a/b** to **28** and **29** at room temperature occurs in a stepwise fashion with **27a/b** as intermediates. Sequential application of $AgNO_3$ and H_2O_2 to **30a/b** gave a mixture of **28** and **29** in a ratio of 7.2:1 in 91% yield. Stirring this mixture in MeCN at room temperature for several hours resulted in a change in the isomer ratio of **28** to **29** from 7.2:1 to 14:1. Thus, it seems that this ratio reflects the equilibrium between the alkenes. The structures of **28** and **29** were determined by NMR spectroscopy.

With the unsaturated aldehyde **28** in hand, the synthesis of **2** could be accomplished. The mixture of **28** and **29** (14:1) in MeOH was treated with activated MnO_2 in the presence of NaCN and AcOH[26], leading to a 9:1 mixture of esters **2** and **31** in 80% yield (Scheme 10). Ester **2** was isolated as colorless crystals either by recrystallization (43%) or by HPLC (70%). Submitting ester **31** to the above reaction conditions again led to a mixture of **2** and **31**. The ^{1}H NMR-spectroscopic data and optical rotation of crystalline **2** matched those reported for oily **2**[27][28]. Since conversions of **2** to **1b**[27][29] and of *rac*-**2** to *rac*-**1a**[29][30] have been described previously, synthesis of **2** represents a new formal asymmetric entry to compounds **1a** and **1b**.

Conclusion

An asymmetric synthesis of the angular diquinanoid δ-lactone **2**, a known precursor of pentalenolactone E (**1b**) and pentalenolactone F (**1a**), has been achieved in 23 steps and 6% overall yield. A key intermediate in this synthesis is the triquinanoid ketone **5**. It is at this point that divergence into several other pentalenolactones would appear feasible. For example, α-methylation of the cyclopentanone ring of **5** via deptotonation with a chiral lithium amide[31] followed by methylenation of the carbonyl group of the methyl derivative should facilitate the required structural changes leading ultimately to pentalenolactone B, which has not yet been synthesized.

Financial support of this work by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is gratefully acknowledged. The authors would like to thank Dr. *J. Runsink* for performing NMR experiments and Prof. Dr. *T. Kauffmann* for his advice on the preparation and application of the tungsten reagents.

Experimental Section

For a description of general techniques, see ref.[1]. iPr_2NH, MeCN, DBU, and CD_3CN were distilled from CaH_2. MeOH was distilled from Mg, CH_2Cl_2 was purified through filtration through basic Al_2O_3 and distillation from CaH_2, and $CHCl_3$ was dried with CaO and distilled. CH_2I_2 was distilled from CaH_2 and stored over Cu. *n*BuLi in *n*-hexane, MeLi in ether, $ZnEt_2$ in *n*-hexane and Me_3SiCH_2Li in *n*-pentane were standardized with diphenylacetic acid. Other starting materials were obtained either from commercial sources and used without further purification or were prepared according to the literature cited.

Methyl [3aS-(3aα,3bβ,6aβ,7aα)]-Octahydro-1,5-dioxopentaleno-[1,2-c]furan-3b(1H)-carboxylate (**5**): At −78°C, a stream of O_3/O_2 was passed through a solution of **3** (7.18 g, 18.51 mmol) in CH_2Cl_2 (700 ml) until a blue color persisted (30 min.). Excess O_3 was then removed by passing argon through the solution. Me_2S (50 ml) was added and the solution was slowly allowed to warm to room temp. Concentration of the solution in vacuo and purification of the residue by chromatography (EtOAc/*n*-hexane, 1:1) gave **5** (3.76 g, 85%) as colorless crystals: m.p. 115°C, $[\alpha]_D$ = +188.5 (*c* = 1.19, CH_2Cl_2), $[\alpha]_D$ = +186.4 (*c* = 1.83, acetone). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94 (ddd, $J_{7\alpha,6a\beta}$ = 9.0, $J_{7\alpha,7\beta}$ = 14.5, $J_{7\alpha,7a\alpha}$ = 10.5 Hz, 7-Hα, 1 H), 2.25 (ddd, $J_{6\alpha,6\beta}$ = 19.0, $J_{6\alpha,6a\beta}$ = 2.5 Hz, 6-Hα, 1 H), 2.34 (d, $J_{4\alpha,4\beta}$ = 18.5 Hz, 4-Hα, 1 H), 2.59 (ddd, $J_{7\beta,6a\beta}$ = 8.5, $J_{7\beta,7\alpha}$ = 14.5, $J_{7\beta,7a\alpha}$ = 2.5 Hz, 7-Hβ, 1 H), 2.70 (ddd, $J_{6\beta,4\beta}$ = 1.5, $J_{6\beta,6\alpha}$ = 19.0, $J_{6\beta,6a\beta}$ = 8.0 Hz, 6-Hβ,

1 H), 2.85 (dd, $J_{4\beta,4\alpha}$ = 18.5, $J_{4\beta,6\beta}$ = 1.5 Hz, 4-Hβ, 1 H), 3.16 (dq, $J_{6a\beta,6\alpha}$ = 2.5, $J_{6a\beta,7\beta}$ = 8.5 Hz, 6a-Hβ, 1 H), 3.25 (m, 3a-Hα, 7a-Hα, 2 H), 3.76 (s, OMe, 3 H), 4.08 (dd, $J_{3\beta,3\alpha}$ = 10.5, $J_{3\beta,3a\alpha}$ = 4.5 Hz, 3-Hβ, 1 H), 4.50 (dd, $J_{3\alpha,3\beta}$ = 10.5, $J_{3\alpha,3a\alpha}$ = 8.0 Hz, 3-Hα, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.53 (u), 42.76 (d), 43.76 (u), 44.01 (d), 47.20 (u), 48.54 (d), 52.72 (d, OMe), 61.33 (u, C-3b), 69.51 (u, C-3), 173.70 (u, CO), 178.72 (u, CO), 214.31 (u, C-5). − MS (EI, 70 eV); *m/z* (%): 238 [M^+] (17), 210 (10), 207 (13), 179 (45), 178 (35), 164 (11), 153 (10), 152 (16), 151 (17), 150 (30), 141 (10), 139 (12), 138 (12), 137 (11), 136 (18), 133 (14), 125 (11), 122 (17), 121 (79), 120 (10), 119 (11), 113 (12), 112 (12), 109 (15), 108 (17), 107 (26), 106 (18), 105 (45), 104 (16), 98 (13), 97 (13), 96 (12), 95 (15), 94 (13), 93 (89), 92 (49), 91 (100), 85 (18), 83 (11), 82 (42), 81 (35), 80 (14), 79 (83), 78 (34), 77 (73), 74 (21), 68 (11). − IR (KBr): $\tilde{\nu}$ = 3020 (w), 2975 (w), 2950 (m), 2910 (w), 1750 (s), 1725 (s), 1470 (w), 1430 (m), 1385 (m), 1310 (m), 1270 (m), 1250 (m), 1195 (s), 1170 (s), 1060 (m), 1025 (m), 965 (w), 910 (m), 875 (m), 640 (m). − $C_{12}H_{14}O_5$ (238.2): calcd. C 60.50, H 5.92; found C 60.24, H 5.94.

Methyl [3aS-(3aα,4β,5aβ,8aS)]- and Methyl [3aS-(3aα,4α,5aβ,8aS*)]-3,3a,4,5,5a,-6,7,8-Octahydro-7-methylene-1-oxo-1H-pentaleno[1,6a-c]furan-4-carboxylate* (**6a** and **6b**)*, and Methyl [3aS-(3aα,4α,5aβ,8aS*)]- and Methyl [3aS-(3aα,4α,5aβ,8aS*)]-3,3a,4,5,5a,6,7,8-Octahydro-1,7-dioxo-1H-pentaleno[1,6a-c]furan-4-carboxylate* (**7a** and **7b**): A suspension of $MePPh_3Br/NaNH_2$, 1.1:1, (1.76 g, 4.20 mmol) in CH_2Cl_2 (9 ml) was stirred for 30 min. at room temp. and then **5** (100 mg, 0.42 mmol) was added. After stirring the suspension for 24 h at room temp., saturated aqueous NH_4Cl was added and the aqueous phase was extracted with EtOAc. The combined organic extracts were washed with water, dried ($MgSO_4$), and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane, 1:1) gave a mixture of **6a/b** (41 mg, 41%) as a slowly crystallizing oil, m.p. 37°C, $[\alpha]_D$ = −77.8 (*c* = 1.81, CH_2Cl_2), and a mixture of **7a/b** (7.4 mg, 7%) as a colorless powder, m.p. 102°C, $[\alpha]_D$ = −59.9 (*c* = 0.65, CH_2Cl_2).

Data for **6a** (in the mixture with **6b**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.91 (ddd, *J* = 1.5, *J* = 7.5, *J* = 13.5 Hz, 5-H, 1 H), 2.22 (dddd, *J* = 8.0, *J* = 13.5, $J_{5,4\alpha}$ = 12.0 Hz, 5-H, 1 H), 2.35 (d, *J* = 15.0 Hz, 8-H, 1 H), 2.91−3.04 (m, 3 H), 3.22 (dt, *J* = 6.5, *J* = 7.0, $J_{4\alpha,5}$ = 12.0 Hz, 4-Hα, 1 H), 3.69 (s, OMe, 3 H), 4.00 (dd, $J_{3\beta,3\alpha}$ = 10.0, $J_{3\beta,3a\alpha}$ = 7.5 Hz, 3-Hβ, 1 H), 4.40 (dd, $J_{3\alpha,3\beta}$ = 10.0, $J_{3\alpha,3a\alpha}$ = 9.5 Hz, 3-Hα, 1 H), 4.90 (m, 9-H, 1 H), 4.94 (m, 9-H, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.16 (u), 40.55 (u), 44.05 (u), 47.53 (d), 48.91 (d), 49.44 (d), 52.97 (d, OMe), 59.05 (u, C-8a), 67.66 (u, C-3), 106.87 (u, C-9), 150.05 (u, C-7), 172.70 (u, CO), 181.21 (u, C-1); GC-MS (EI, 70 eV); *m/z* (%): 236 [M^+] (7), 218 (20), 205 (12), 204 (10), 190 (13), 176 (16), 160 (10), 159 (11), 150 (12), 137 (40), 136 (24), 133 (24), 132 (20), 131 (47), 130 (11), 120 (10), 119 (100), 118 (17), 117 (39), 115 (14), 106 (15), 105 (24), 100 (73), 93 (23), 92 (13), 91 (85), 79 (28), 78 (22), 77 (51), 69 (27), 68 (21), 65 (25). − Data for **6b** (in the mixture with **6a**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57 (ddd, $J_{5\alpha,5a\beta}$ = 9.5, $J_{5\alpha,4\alpha}$ = 12.5, $J_{5\alpha,5\beta}$ = 12.5 Hz, 5-Hα, 1 H), 2.08 (d, $J_{8\alpha,8\beta}$ = 16.0 Hz, 8-H, 1 H), 2.31 (ddd, *J* = 6.5, *J* = 7.5, $J_{5\beta,5\alpha}$ = 12.5 Hz, 5-Hβ, 1 H), 2.38 (d, $J_{8\alpha,8\beta}$ = 16.0 Hz, 8-H, 1 H), 2.60−2.73 (m, 3a-Hα, 5a-Hβ, 6-Hα, 6-Hβ, 4 H), 2.81 (m, 4-Hβ, 1 H), 3.71 (s, OMe, 3 H), 4.34 (dd, $J_{3\beta,3\alpha}$ = 9.0, $J_{3\beta,3a\alpha}$ = 1.5 Hz, 3-Hβ, 1 H), 4.38 (dd, $J_{3\alpha,3\beta}$ = 9.0, $J_{3\alpha,3a\alpha}$ = 6.0 Hz, 3-Hα, 1 H), 4.94 (m, 9-H, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.31 (u), 39.25 (u), 42.51 (u), 47.86 (d), 49.26 (d), 51.97 (d), 52.08 (d, OMe), 59.42 (u, C-8a), 69.76 (u, C-3), 108.65 (u, C-9), 148.41 (u, C-7), 173.31 (u, CO), 182.46 (u, C-1). − GC-MS (EI, 70 eV); *m/z* (%): 236 [M^+] (15), 190 (17), 178 (42), 177 (15), 176 (23), 150 (13), 146 (11), 137 (17), 136 (22), 132 (15), 131 (100), 130 (32), 129 (11), 119 (37), 118 (30), 117 (28), 115 (15), 113 (11), 105 (22), 100 (79), 99 (16), 93 (16), 92 (16), 91 (87), 81 (11), 79 (32), 78 (20), 77 (53), 69 (31), 68 (23), 65 (23). − $C_{13}H_{16}O_4$ (236.2): calcd. C 66.07, H 6.82; found C 65.88, H 6.78.

Data for **7a** (in the mixture with **7b**): (vide infra) GC-MS (EI, 70 eV); *m/z* (%): 238 [M^+] (11). − Data for **7b** (in the mixture with **7a**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.83 (ddd, *J* = 8.5, *J* = 9.5, *J* = 13.5 Hz, 5-H, 1 H), 2.21 (ddd, *J* = 2.5, *J* = 4.5, *J* = 19.0 Hz, 6-H, 1 H), 2.46−2.53 (m, 2 H), 2.60-2.73 (m, 4 H), 3.02−3.19 (m, 4 H), 3.72 (s, OMe, 3 H), 4.27 (dd, $J_{3\beta,3\alpha}$ = 10.0, $J_{3\beta,3a\alpha}$ = 3.5 Hz, 3-Hβ, 1 H), 4.51 (dd, $J_{3\alpha,3\beta}$ = 10.0, $J_{3\alpha,3a\alpha}$ = 7.5 Hz, 3-Hα, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.70 (u), 43.41 (u), 44.76 (d), 45.91 (u), 50.54 (d), 50.69 (d), 52.39 (u, OMe), 56.57 (u, C-8a), 70.64 (u, C-3), 173.37 (u, CO), 181.96 (u, C-1). − $C_{12}H_{14}O_5$ (238.2): calcd. C 60.50, H 5.92; found C 60.28, H 5.94.

Methyl [3aS-(3aα,3bβ,5α,6aβ,7aα)]-Octahydro-5-hydroxy-1-oxo-5-[(trimethylsilyl)methyl]pentaleno[1,2-c]furan-3b(1H)-carboxylate (**8**): At 10^{-4} Torr, $CeCl_3 \cdot 7\ H_2O$ (657 mg, 1.76 mmol) was heated from 25°C to 140°C over a period of 1 h. After heating the powder for 1 h at 140°C, it was stirred by means of a magnetic stirring bar for 1 h at 10^{-4} Torr and then slowly allowed to cool to room temp. THF (5 ml) was added and the suspension was stirred for 3.5 h at room temp. It was then cooled to −80°C and Me_3SiCH_2Li (1.50 mmol, 1.65 ml of a 0.91 M solution in *n*-pentane) was added dropwise under rapid stirring over a period of 15 min. After stirring the mixture for 1 h at −80°C, a solution of **5** (230 mg, 0.97 mmol) in THF (1.5 ml) was added and stirring was continued for 14 h at −70°C. The mixture was then warmed to 25°C, filtered though a pad of silica gel with EtOAc, and the filtrate was concentrated in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane, 1:3) gave, in addition to **5** (25 mg, 11%), **8** (250 mg, 79%) as colorless crystals: m.p. 108°C, $[\alpha]_D$ = +65.9 (*c* = 1.16, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.03 (s, $SiMe_3$, 9 H), 1.02 (s, $SiCH_2$, 2 H), 1.48 (s, OH, 1 H), 1.73 (ddd, $J_{6\alpha,4\alpha}$ = 1.5, $J_{6\alpha,6\beta}$ = 14.0, $J_{6\alpha,6a\beta}$ = 4.0 Hz, 6-Hα, 1 H), 2.02 (dd, $J_{4\alpha,4\beta}$ = 15.0, $J_{4\alpha,6\alpha}$ = 1.5 Hz, 4-Hα, 1 H), 2.08 (dd, $J_{6\beta,6\alpha}$ = 14.0, $J_{6\beta,6a\beta}$ = 9.0 Hz, 6-Hβ, 1 H), 2.17 (ddd, $J_{7\alpha,6a\beta}$ = 5.0, $J_{7\alpha,7\beta}$ = 13.5, $J_{7\alpha,7a\alpha}$ = 9.5 Hz, 7-Hα, 1 H), 2.28 (ddd, $J_{7\beta,6a\beta}$ = 7.0, $J_{7\beta,7\alpha}$ = 13.5, $J_{7\beta,7a\alpha}$ = 7.5 Hz, 7-Hβ, 1 H), 2.21 (d, $J_{4\beta,4\alpha}$ = 15.0 Hz, 4-Hβ, 1 H), 3.14 (m, 6a-Hβ, 1 H), 3.27 (dt, $J_{3a\alpha,3\alpha}$ = 8.0, $J_{3a\alpha,3\beta}$ = 7.0, $J_{3a\alpha,7a\alpha}$ = 8.5 Hz, 3a-Hα, 1 H), 3.38 (dt, $J_{7a\alpha,3a\alpha}$ = 8.5, $J_{7a\alpha,7\alpha}$ = 9.5, $J_{7a\alpha,7\beta}$ = 7.5 Hz, 7a-Hα, 1 H), 3.66 (s, OMe, 3 H), 3.86 (dd, $J_{3\beta,3\alpha}$ = 10.0, $J_{3\beta,3a\alpha}$ = 7.0 Hz, 3-Hβ, 1 H), 4.37 (dd, $J_{3\alpha,3\beta}$ = 10.0, $J_{3\alpha,3a\alpha}$ = 8.0 Hz, 3-Hα, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.28 (d, $SiMe_3$), 32.51 (u), 35.87 (u), 45.10 (d), 47.36 (d), 50.31 (u), 52.11 (d, OMe), 52.18 (d), 54.74 (u), 65.00 (u, C-3b), 69.90 (u, C-3), 83.16 (u, C-5), 175.72 (u, CO), 179.44 (u, CO). − MS (EI, 70 eV); *m/z* (%): 311 [M^+ − Me] (5), 131 (29), 119 (10), 117 (12), 105 (15), 91 (35), 79 (16), 77 (23), 75 (75), 74 (10), 73 (100), 61 (8), 59 (17), 47 (13), 45 (24), 45 (11), 41 (14). − MS (CI, 70 e V); *m/z* (%): 344 [$(M + NH_4)^+$] (100), 328 (19), 327 [M^+ + H] (66), 326 [M^+] (24), 309 (14), 90 (23). − IR (KBr): $\tilde{\nu}$ = 3461 (s), 3074 (m), 2917 (m), 2849 (m), 2427 (w), 1752 (s), 1724 (s), 1631 (m), 1479 (m), 1461 (m), 1436 (m), 1385 (s), 1322 (m), 1302 (m), 1278 (s), 1265 (s), 1244 (s), 1220 (s), 1210 (s), 1196 (s), 1169 (s), 1118 (s), 1067 (m), 1028 (s), 1013 (s), 971 (m), 948 (w), 913 (m), 882 (m), 848 (m), 764 (w). − $C_{16}H_{26}O_5Si$ (326.4): calcd. C 58.87, H 8.03; found C 58.56, H 7.82.

Methyl [3aS-(3aα,3bβ,6aβ,7aα)]-Octahydro-5-methylene-1-oxopentaleno-[1,2-c]furan-3b(1H)-carboxylate (**9**): *(a) From Silane* **8**: To a mixture of 40% aqueous HF (0.06 ml) and MeCN (4 ml) was added a solution of **8** (163 mg, 0.50 mmol) in MeCN (1 ml). After stirring the mixture for 20 min. at room temp., the solvent was

removed in vacuo. The residue was then redissolved in EtOAc and the resulting solution was filtered through a pad of silica gel with EtOAc/*n*-hexane, 1:1. Concentration of the filtrate in vacuo gave **9** (117 mg, 99%) as colorless crystals.

(b) *From* **5** *and* $WOCl_3 \cdot 2$ THF/2 MeLi: To a rapidly stirred solution of $WOCl_3 \cdot 2$ THF (11.35 g, 25.20 mmol) in THF (350 ml) at −70°C, MeLi (50.40 mmol, 31.5 ml of a 1.60 M solution in diethyl ether) was added dropwise, resulting in a color change from dark-blue to dark-brown. After stirring the mixture for 30 min. at −70°C, a solution of **5** (2.40 g, 10.08 mmol) in THF (10 ml) was added and stirring was continued for 1 h at this temp. The mixture was then allowed to warm to room temp., stirred for 30 min., heated to reflux for 40 min., recooled to room temp. and stirred for a further 12 h. Concentration of the solution in vacuo and purification of the residue by chromatography (EtOAc) gave **9** (2.30 g, 97%) as colorless crystals.

(c) *From* **5** *and* $WOCl_4$*/2 MeLi:* $WOCl_4$ (2.56 g, 7.49 mmol), which had been sublimed at 10^{-2} Torr and 105°C, was dissolved in THF (70 ml) and the solution was stirred for 30 min. at room temp. The orange-red solution was cooled to −70°C and MeLi (12.46 mmol, 14.0 ml of a 0.89 M solution in diethyl ether) was added dropwise. After stirring the dark-colored solution for 30 min. at −70°C, a solution of **5** (420 mg, 1.76 mmol) in THF (5 ml) was added. The reaction mixture was stirred for 1.5 h at −70°C, warmed to room temp., heated to reflux for 2 h, cooled to room temp. once more, and finally stirred for 12 h. The volatiles were removed in vacuo and the residue was filtered through a pad of silica gel (EtOAc). Concentration of the filtrate in vacuo gave **9** (386 mg, 93%) as colorless crystals: m.p. 103°C, $[\alpha]_D = -31.7$ (c = 0.89, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.89 (ddd, $J_{7\alpha,6a\beta}$ = 8.0, $J_{7\alpha,7\beta}$ = 14.0, $J_{7\alpha,7a\alpha}$ = 10.5 Hz, 7-Hα, 1 H), 2.24 (dddd, $J_{6\alpha,4\alpha}$ = 2.0, $J_{6\alpha,6\beta}$ = 16.5, $J_{6\alpha,6a\beta}$ = 2.5, $J_{6\alpha,8}$ = 2.0 Hz, 6-Hα, 1 H), 2.37 (ddd, $J_{7\beta,6a\beta}$ = 8.0, $J_{7\beta,7\alpha}$ = 14.0, $J_{7\beta,7a\alpha}$ = 3.5 Hz, 7-Hβ, 1 H), 2.45 (ddd, $J_{4\alpha,4\beta}$ = 17.0, $J_{4\alpha,6\alpha}$ = 2.0, $J_{4\alpha,8}$ = 2.0 Hz, 4-Hα, 1 H), 2.73 (ddd, $J_{6\beta,6\alpha}$ = 16.5, $J_{6\beta,6a\beta}$ = 8.0, $J_{6\beta,4\beta}$ = 2.5 Hz, 6-Hβ, 1 H), 2.92 (m, 4-H_β, 6a-Hβ, 2 H), 3.15 (m, 3a-Hα, 7a-Hα, 2 H), 3.72 (s, OMe, 3 H), 3.97 (dd, $J_{3\beta,3\alpha}$ = 10.5, $J_{3\beta,3a\alpha}$ = 4.5 Hz, 3-Hβ, 1 H), 4.42 (dd, $J_{3\alpha,3\beta}$ = 10.5, $J_{3\alpha,3a\alpha}$ = 8.0 Hz, 3-Hα, 1 H), 4.93 (m, 8-H, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.33 (u), 38.31 (u), 43.45 (u), 44.14 (d), 45.84 (d), 48.72 (d), 52.15 (d, OMe), 64.66 (u, C-3b), 69.93 (u, C-3), 108.40 (u, C-8), 148.02 (u, C-5), 174.79 (u, CO), 179.50 (u, CO). − MS (EI, 70 eV); *m/z* (%): 236 [M^+] (44), 208 (11), 204 (13), 190 (25), 178 (30), 177 (26), 176 (49), 151 (23), 150 (15), 132 (14), 131 (100), 130 (28), 129 (13), 119 (39), 118 (29), 117 (31), 115 (18), 105 (20), 93 (16), 92 (23), 91 (68), 79 (20), 78 (12), 77 (33), 65 (15). − IR (KBr): $\tilde{\nu}$ = 3074 (m), 2976 (s), 2918 (s), 2850 (m), 1756 (s), 1724 (s), 1662 (m), 1478 (m), 1461 (m), 1386 (s), 1322 (s), 1302 (m), 1278 (s), 1245 (s), 1231 (s), 1211 (s), 1195 (s), 1170 (s), 1119 (s), 1094 (m), 1068 (s), 1029 (s), 1014 (s), 972 (m), 933 (w), 913 (m), 883 (s), 780 (w), 766 (w), 753 (w), 709 (w), 679 (w). − $C_{13}H_{16}O_4$ (236.2): calcd. C 66.07, H 6.82; found C 66.17, H 6.89.

Methyl [3′aS-(3′aα,3′bβ,6′aβ,7′aα)]-Hexahydro-1′-oxospiro-[cyclopropane-1,5′-(1′H)-pentaleno[1,2-c]furan]-3′b(4′H)-carboxylate (**10**): To a solution of **9** (450 mg, 1.91 mmol) in CH_2Cl_2 (5 ml) was added dropwise at −80°C, $ZnEt_2$ (18.0 mmol, 18 ml of a 1.0 M solution in *n*-hexane) and under rapid stirring CH_2I_2 (5.04 g, 18.0 mmol). After stirring the mixture for 8 h at −80°C, it was allowed to warm to room temp. and treated with 2 N aqueous HCl. The solid material was removed by filtration and washed several times with EtOAc. The aqueous phase was extracted with EtOAc, and the combined organic extracts were neutralized with solid NaH_2PO_4, washed with aqueous $Na_2S_2O_7$, dried ($MgSO_4$), and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane, 1:1) gave a mixture of **10** and **9** in a ratio of 8:1. MPLC (EtOAc/*n*-hexane, 5:95) gave, in addition to **9** (49 mg, 10%), **10** (398 mg, 84%) as colorless crystals: m.p. 65°C, $[\alpha]_D$ = +102.2 (c = 1.06, CH_2Cl_2), $[\alpha]_D$ = +107.7 (c = 1.02, acetone). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.36 (m, cyclopropane, 2 H), 0.47 (m, cyclopropane, 2 H), 1.41 (dd, $J_{6'\alpha,6'\beta}$ = 13.0, $J_{6'\alpha,6'a\beta}$ = 3.5 Hz, 6′-Hα, 1 H), 1.74 (d, $J_{4'\alpha,4'\beta}$ = 13.5 Hz, 4′-Hα, 1 H), 1.97 (dd, $J_{6'\beta,6'\beta}$ = 13.0, $J_{6'\beta,6'a\beta}$ = 8.0 Hz, 6′-Hβ, 1 H), 1.99 (ddd, $J_{7'\alpha,6'a\beta}$ = 6.5, $J_{7'\alpha,7'\beta}$ = 14.0, $J_{7'\alpha,7'a\alpha}$ = 9.5 Hz, 7′-Hα, 1 H), 2.06 (d, $J_{4'\beta,4'\alpha}$ = 13.5 Hz, 4′-Hβ, 1 H), 2.29 (ddd, $J_{7'\beta,6'a\beta}$ = 9.0, $J_{7'\beta,7'\alpha}$ = 14.0, $J_{7'\beta,7'a\alpha}$ = 5.0 Hz, 7′-Hβ, 1 H), 3.02−3.18 (m, 3′-Hα, 6′-Hβ, 7′-Hα, 3 H), 3.65 (s, OMe, 3 H), 3.88 (dd, $J_{3'\beta,3'\alpha}$ = 10.0, $J_{3'\beta,3'a\alpha}$ = 6.0 Hz, 3′-Hβ, 1 H), 4.33 (dd, $J_{3'\alpha,3'\beta}$ = 10.0, $J_{3'\alpha,3'a\alpha}$ = 8.0 Hz, 3′-Hα, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.2 (u, cyclopropane), 12.3 (u, cyclopropane), 21.3 (u, C-5′), 36.0 (u), 41.8 (u), 44.7 (u), 47.1 (d), 47.2 (u), 49.8 (d), 52.0 (d, OMe), 65.5 (u, C-3′b), 69.9 (u, C-3′), 175.4 (u, CO), 179.3 (u, CO). − MS (EI, 70 eV); *m/z* (%): 250 [M^+] (32), 219 (11), 218 (11), 204 (19), 192 (58), 191 (20), 190 (52), 177 (11), 172 (10), 165 (21), 164 (15), 151 (34), 150 (12), 146 (15), 145 (100), 144 (43), 133 (38), 132 (38), 131 (36), 130 (11), 129 (28), 119 (19), 118 (14), 117 (42), 115 (15), 107 (16), 106 (29), 105 (73), 103 (10), 93 (26), 92 (16), 91 (82), 79 (40), 78 (16), 77 (42), 67 (19). − IR (KBr): $\tilde{\nu}$ = 3065 (m), 2952 (s), 2867 (s), 2764 (w), 2424 (w), 1780 (s), 1721 (s), 1633 (m), 1474 (m), 1461 (s), 1439 (s), 1385 (s), 1345 (m), 1333 (m), 1320 (m), 1283 (m), 1250 (s), 1222 (s), 1198 (s), 1179 (s), 1155 (s), 1118 (s), 1054 (s), 1029 (s), 987 (m), 973 (m), 914 (m), 891 (m), 853 (m), 782 (w), 754 (w), 724 (m), 686 (m). − $C_{14}H_{18}O_4$ (250.2): calcd. C 67.18, H 7.25; found C 67.29, H 7.24.

Methyl [3aS-(3aα,3bβ,6aβ,7aα)]-Octahydro-5,5-dimethyl-1-oxo-pentaleno-[1,2-c]furan-3b(1H)-carboxylate (**11**): PtO_2 (83.5 mg) was suspended in AcOH (14 ml) and reduced with H_2 at room temp. at 1 Torr. To the suspension of Pt was added **10** (550 mg, 2.20 mmol) and the hydrogenation was continued until the theoretical amount of H_2 had been consumed (1.5 h). The mixture was then concentrated in vacuo and the residue was filtered (EtOAc/*n*-hexane, 1:1) through a pad of silica gel. Concentration of the filtrate and azeotropic removal of AcOH with toluene in vacuo gave **11** (551 mg, 99%) as colorless crystals: m.p. 98°C, $[\alpha]_D$ = +101.0 (c = 1.64, CH_2Cl_2), $[\alpha]_D$ = +95.2 (c = 1.01, acetone). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (s, Me, 3 H), 1.03 (s, Me, 3 H), 1.27 (dd, $J_{6\alpha,6\beta}$ = 12.5, $J_{6\alpha,6a\beta}$ = 8.5 Hz, 6-Hα, 1 H), 1.54 (d, $J_{4\alpha,4\beta}$ = 13.5 Hz, 4-Hα, 1 H), 1.77 (ddd, $J_{6\beta,4\beta}$ = 2.0, $J_{6\beta,6\alpha}$ = 12.5, $J_{6\beta,6a\beta}$ = 8.0 Hz, 6-Hβ, 1 H), 1.92 (ddd, $J_{7\alpha,6a\beta}$ = 4.0, $J_{7\alpha,7\beta}$ = 13.5, $J_{7\alpha,7a\alpha}$ = 8.0 Hz, 7-Hα, 1 H), 2.19 (ddd, $J_{7\beta,6a\beta}$ = 8.0, $J_{7\beta,7\alpha}$ = 13.5, $J_{7\beta,7a\alpha}$ = 7.5 Hz, 7-Hβ, 1 H), 2.23 (dd, $J_{4\beta,4\beta}$ = 13.5, $J_{4\beta,6\beta}$ = 2.0 Hz, 4-Hβ, 1 H), 3.02 (ddd, $J_{3a\alpha,3\alpha}$ = 8.0, $J_{3a\alpha,3\beta}$ = 6.5, $J_{3a\alpha,7a\alpha}$ = 9.0 Hz, 3a-Hα, 1 H), 3.10 (ddd, $J_{7a\alpha,3a\alpha}$ = 9.0, $J_{7a\alpha,7\alpha}$ = 8.0, $J_{7a\alpha,7\beta}$ = 7.5 Hz, 7a-Hα, 1 H), 3.21 (ddd, $J_{6a\beta,6\alpha}$ = 8.5, $J_{6a\beta,6\beta}$ = 8.0, $J_{6a\beta,7\alpha}$ = 4.0, $J_{6a\beta,7\beta}$ = 8.0 Hz, 6a-Hβ, 1 H), 3.67 (s, OMe, 3 H), 3.88 (dd, $J_{3\beta,3\alpha}$ = 10.0, $J_{3\beta,3a\alpha}$ = 6.5 Hz, 3-Hβ, 1 H), 4.25 (dd, $J_{3\alpha,3\beta}$ = 10.0, $J_{3\alpha,3a\alpha}$ = 8.0 Hz, 3-Hα, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.2 (d, Me), 30.3 (d, Me), 34.6 (u), 40.2 (u, C-5), 44.5 (d), 47.6 (u), 47.7 (d), 52.0 (d), 52.1 (d, OMe), 53.2 (u), 64.7 (u, C-3b), 69.1 (u, C-3), 176.0 (u, CO), 178.9 (u, CO). − MS (EI, 70 eV); *m/z* (%): 252 [M^+] (18), 237 (10), 221 (26), 220 (100), 206 (10), 196 (22), 194 (18), 193 (30), 192 (77), 191 (13), 180 (21), 179 (16), 178 (17), 177 (32), 168 (40), 164 (33), 155 (40), 153 (14), 151 (11), 150 (13), 149 (69), 148 (15), 147 (44), 137 (16), 136 (45), 135 (46), 134 (16), 133 (24), 131 (32), 123 (22), 121 (29), 119 (26), 109 (27), 108 (19), 107 (80), 105 (32), 97 (10), 96 (48), 95 (61), 94 (18), 93 (96), 92 (20), 91 (65), 85

(18), 82 (13), 81 (26), 80 (10), 79 (61), 78 (17), 77 (57), 69 (24). − IR (KBr): $\tilde{\nu}$ = 3016 (m), 2966 (s), 2957 (s), 2928 (s), 2872 (s), 2850 (m), 2767 (w), 2738 (w), 2427 (w), 1738 (s), 1717 (s), 1634 (s), 1465 (s), 1437 (s), 1385 (s), 1342 (s), 1332 (s), 1304 (s), 1278 (s), 1252 (s), 1239 (s), 1220 (s), 1201 (s), 1193 (s), 1193 (s), 1163 (s), 1119 (s), 1094 (s), 1055 (s), 1026 (s), 997 (s), 990 (s), 965 (m), 940 (m), 919 (m), 875 (w), 841 (m), 800 (w), 773 (m). − $C_{14}H_{20}O_4$ (252.3): calcd. C 66.65, H 7.99; found C 66.73, H 7.91

Methyl [3aS-(3aα,4β,5aβ,8aS)]-3,3a,4,5,5a,6,7,8-Octahydro-7,7-dimethoxy-1-oxo-1H-pentaleno[1,6a-c]furan-4-carboxylate* (**12**) *and Dimethyl [2S-(2α,3a,3aα,6aα)]-1,2,4,5,6,6a-Hexahydro-5,5-dimethoxy-3-(methoxymethyl)-2,3a(1H)-pentalenedicarboxylate* (**13**): To a solution of **5** (200 mg, 0.84 mmol) in MeOH (4 ml) were added $HC(OMe)_3$ (265 mg, 2.50 mmol) and *p*TsOH (10 mg), and the mixture was heated to reflux for 1.5 h. A drop of piperidine was added, the mixture was concentrated in vacuo and the residue was purified by chromatography (EtOAc/*n*-hexane, 1:1). MPLC (EtOAc/*n*-hexane, 35:65) of the residue gave **12** (208 mg, 87%) and **13** (26 mg, 9%) as colorless oils.

12: $[\alpha]_D$ = −29.2 (*c* = 1.06, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.80 (ddd, $J_{6\alpha,5a\beta}$ = 4.5, $J_{6\alpha,6\beta}$ = 14.0, $J_{6\alpha,8\alpha}$ = 2.0 Hz, 6-Hα, 1 H), 1.91 (ddd, $J_{5\alpha,4\alpha}$ = 7.0, $J_{5\alpha,5\beta}$ = 13.5, $J_{5\alpha,5a\beta}$ = 2.0 Hz, 5-Hα, 1 H), 2.07 (dd, $J_{8\alpha,6\alpha}$ = 2.0, $J_{8\alpha,8\beta}$ = 14.5 Hz, 8-Hα, 1 H), 2.15 (ddd, $J_{5\beta,4\alpha}$ = 11.5, $J_{5\beta,5\alpha}$ = 13.5, $J_{5\beta,5a\beta}$ = 9.0 Hz, 5-Hβ, 1 H), 2.21 (ddd, $J_{6\beta,5a\beta}$ = 10.5, $J_{6\beta,6\alpha}$ = 14.0, $J_{6\beta,8\beta}$ = 1.0 Hz, 6-Hβ, 1 H), 2.50 (dd, $J_{8\beta,6\beta}$ = 1.0, $J_{8\beta,8\alpha}$ = 14.5 Hz, 8-Hβ, 1 H), 2.92 (dddd, $J_{5a\beta,5\alpha}$ = 2.0, $J_{5a\beta,5\beta}$ = 9.0, $J_{5a\beta,6\alpha}$ = 4.5, $J_{5a\beta,6\beta}$ = 10.5 Hz, 5a-Hβ, 1 H), 3.08 (dt, $J_{3a\alpha,3\alpha}$ = 9.5, $J_{3a\alpha,3\beta}$ = 7.0, $J_{3a\alpha,4\alpha}$ = 7.0 Hz, 3a-Hα, 1 H), 3.22 (s, α-OMe, 3 H), 3.26 (s, β-OMe, 3 H), 3.58 (dt, $J_{4\alpha,3a\alpha}$ = 7.0, $J_{4\alpha,5\alpha}$ = 7.0, $J_{4\alpha,5\beta}$ = 11.5 Hz, 4-Hα, 1 H), 3.70 (s, CO_2Me, 3 H), 3.97 (dd, $J_{3\beta,3\alpha}$ = 10.5, $J_{3\beta,3a\alpha}$ = 7.0 Hz, 3-Hβ, 1 H), 4.40 (dd, $J_{3\alpha,3\beta}$ = 10.5, $J_{3\alpha,3a\alpha}$ = 9.5 Hz, 3-Hα, 1 H) − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.35 (u), 40.82 (u), 43.17 (u), 46.92 (d), 47.07 (d), 49.15 (d, acetal-OMe), 49.17 (d), 50.18 (d, acetal-OMe), 51.84 (d, CO_2Me), 57.81 (u, C-8a), 67.75 (u, C-3), 111.20 (u, C-7), 173.19 (u, CO), 181.19 (u, C-1). − MS (EI, 70 eV); *m/z* (%): 284 [M^+] (15), 256 (9), 253 (22), 225 (38), 221 (12), 195 (18), 193 (26), 186 (52), 171 (100), 153 (13), 149 (11), 147 (11), 139 (24), 136 (23), 127 (42), 115 (23), 101 (21), 91 (34), 88 (38), 79 (27), 77 (32), 65 (15). − $C_{14}H_{20}O_6$ (284.3): calcd. C 59.15, H 7.09; found C 58.89, H 6.92.

13: $[\alpha]_D$ = + 16.9 (*c* = 1.06, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (dd, $J_{6\beta,6\alpha}$ = 13.0, $J_{6\beta,6a\beta}$ = 8.0 Hz, 6-Hβ, 1 H), 1.59 (ddd, $J_{1\beta,1\alpha}$ = 13.5, $J_{1\beta,2\beta}$ = 6.5, $J_{1\beta,6a\alpha}$ = 2.5 Hz, 1-Hβ, 1 H), 1.72 (d, $J_{4\beta,4\alpha}$ = 14.0 Hz, 4-Hβ, 1 H), 2.23 (ddd, $J_{6\alpha,4\alpha}$ = 2.5, $J_{6\alpha,6\beta}$ = 13.0, $J_{6\alpha,6a\alpha}$ = 9.0 Hz, 6-Hα, 1 H), 2.35 (ddd, $J_{1\alpha,1\beta}$ = 13.5, $J_{1\alpha,2\beta}$ = 11.0, $J_{1\alpha,6a\alpha}$ = 9.0 Hz, 1-Hα, 1 H), 2.54 (dt, $J_{3\beta,2\beta}$ = 7.0, $J_{3\beta,7}$ = 7.0 Hz, 3-Hβ, 1 H), 2.86 (dd, $J_{4\alpha,4\beta}$ = 14.0, $J_{4\alpha,6\alpha}$ = 2.5 Hz, 4-Hα, 1 H), 3.08−3.29 (m, 2-Hβ, 6a-Hα, OCH_2, 4 H), 3.10 (s, CH_2OMe, 3 H), 3.19 (s, OMe, 3 H), 3.24 (s, OMe, 3 H), 3.66 (s, CO_2Me, 3 H), 3.69 (s, CO_2Me, 3 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.45 (u), 40.77 (u), 41.72 (d), 43.91 (u), 44.72 (d), 48.73 (d, acetal-OMe), 50.20 (d, acetal-OMe), 51.38 (d), 51.53 (d, CO_2Me), 51.85 (d, CO_2Me), 58.79 (d, CH_2OMe), 59.70 (u, C-3a), 70.14 (u, CH_2O), 109.67 (u, C-5), 173.42 (u, CO), 175.25 (u, CO). − GC-MS (EI, 70 eV): *m/z* (%): 330 [M^+] (8), 315 (14), 298 (6), 285 (7), 267 (19), 266 (24), 239 (42), 234 (10), 207 (50), 193 (30), 185 (17), 167 (23), 154 (15), 147 (36), 135 (14), 133 (10), 115 (13), 105 (12), 104 (15), 103 (10), 95 (12), 91 (23), 89 (26), 88 (53), 79 (13), 77 (17), 75 (20), 65 (10). − $C_{16}H_{26}O_7$: calcd. 330.1679, found 330.1694 (MS).

Methyl [3aS-(3aα,4β,5aβ,8aS)]-Octahydro-1,7-dioxo-1H-pentaleno[1,6a-c]furan-4-carboxylate* (**7a**): To solution of **12** (110 mg, 0.39 mmol) in acetone (3 ml) was added pyridinium *p*-toluenesulfonate (10 mg). After stirring the mixture for 1 d at room temp., the solution was filtered through a pad of silica gel with EtOAc and the filtrate was concentrated in vacuo to give **13** (91 mg, 97%) as a colorless powder, which was subsequently dissolved in a minimum amount of toluene. *n*-Hexane was added to the solution until turbid, and the solution was heated until clear. Upon cooling to room temp., colorless crystals of **7a** formed: m.p. 108°C, $[\alpha]_D^{21}$ = −70.7 (*c* = 0.87, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.02 (ddd, $J_{5\alpha,4\alpha}$ = 6.5, $J_{5\alpha,5\beta}$ = 14.0, $J_{5\alpha,5a\beta}$ = 1.0 Hz, 5-Hα, 1 H), 2.08 (ddd, $J_{6\alpha,5a\beta}$ = 6.0, $J_{6\alpha,6\beta}$ = 19.0, $J_{6\alpha,8\alpha}$ = 2.0 Hz, 6-Hα, 1 H), 2.32 (dt, $J_{5\beta,4\alpha}$ = 12.5, $J_{5\beta,5\alpha}$ = 14.0, $J_{5\beta,5a\beta}$ = 7.5 Hz, 5-Hβ, 1 H), 2.47 (dd, $J_{8\alpha,6\alpha}$ = 2.0, $J_{8\alpha,8\beta}$ = 18.5 Hz, 8-Hβ, 1 H), 2.85 (ddd, $J_{6\beta,5a\beta}$ = 11.0, $J_{6\beta,6\alpha}$ = 19.0, $J_{6\beta,8\beta}$ = 2.0 Hz, 6-Hβ, 1 H), 3.08−3.19 (m, 3a-Hα, 5a-Hβ, 2 H), 3.10 (dd, $J_{8\beta,6\beta}$ = 2.0, $J_{8\beta,8\alpha}$ = 18.5 Hz, 8-Hβ, 1 H), 3.28 (dt, $J_{4\alpha,3a\alpha}$ = 6.5, $J_{\alpha,5\alpha}$ = 6.5, $J_{4\alpha,5\beta}$ = 12.5 Hz, 4-Hβ, 1 H), 3.72 (s, OMe, 3 H), 4.10 (dd, $J_{3\beta,3\alpha}$ = 10.5, $J_{3\beta,3a\alpha}$ = 7.0 Hz, 3-Hβ, 1 H), 4.49 (dd, $J_{3\alpha,3a\alpha}$ = 9.5 Hz, 3-Hα, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.3 (u), 44.1 (u), 44.5 (d), 47.0 (d), 47.9 (u), 48.7 (d), 52.3 (d, OMe), 56.6 (u, C-8a), 68.0 (u, C-3), 172.0 (u, CO), 180.4 (u, C-1), 214.3 (u, C-7). − MS (EI, 70 eV); *m/z* (%): 238 [M^+] (11), 210 (12), 180 (14), 179 (16), 152 (36), 151 (9), 150 (10), 133 (13), 125 (23), 124 (15), 121 (14), 114 (9), 107 (28), 106 (11), 105 (27), 100 (11), 99 (100), 97 (21), 96 (19), 95 (10), 93 (54), 92 (28), 91 (62), 87 (113), 82 (16), 81 (24), 80 (13), 79 (62), 78 (20), 77 (49), 69 (18), 68 (10), 67 (11), 65 (23). − $C_{12}H_{14}O_5$ (238.3): calcd. C 60.50, H 5.92; found C 60.28, H 5.94.

Methyl [3aS(3aα,4β,5aβ,8aS)]-3,3a,4,5,5a,6,7,8-Octahydro-7,7-dimethyl-1-oxo-1H-pentaleno[1,6a-c]furan-4-carboxylate* (**14a**): To a solution of **11** (103 mg, 0.41 mmol) in MeOH (4 ml) were added $HC(OMe)_3$ (200 mg, 1.89 mmol) and *p*TsOH (5 mg), and the resulting mixture was stirred for 3 h at room temp. Piperidine (0.03 ml) was added and the mixture was concentrated in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane, 1:1) gave **14a** (100 mg, 98%) as colorless crystals: m.p. 51°C, $[\alpha]_D$ = −29.1 (*c* = 1.21, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, Me, 3 H), 1.14 (s, Me, 3 H), 1.22 (dd, $J_{6\alpha,5a\beta}$ = 11.5, $H_{6\alpha,6\beta}$ = 12.5 Hz, 6-Hα, 1 H), 1.65 (d, $J_{8\alpha,8\beta}$ = 13.5 Hz, 8-Hα, 1 H), 1.77 (ddd, $J_{6\beta,5a\beta}$ = 8.0, $J_{6\beta,6\alpha}$ = 12.5, $J_{6\beta,8\beta}$ = 2.0 Hz, 6-Hβ, 1 H), 1.84 (dd, $J_{5\beta,4\alpha}$ = 6.5, $J_{5\beta,5\alpha}$ = 13.5 Hz, 5-Hα, 1 H), 2.05 (ddd, $J_{5\beta,4\alpha}$ = 13.5, $J_{5\beta,5\alpha}$ = 13.5, $J_{5\beta,5a\beta}$ = 7.5 Hz, 1 H, 5-Hβ), 2.15 (dd, $J_{8\beta,6\beta}$ = 2.0, $J_{8\beta,8\alpha}$ = 13.5 Hz, 8-Hβ, 1 H), 2.96 (m, 3a-Hα, 5a-Hβ, 2 H), 3.27 (ddd, $J_{4\alpha,3a\alpha}$ = 6.5, $J_{4\alpha,5\alpha}$ = 6.5, $J_{4\alpha,5\beta}$ = 13.5 Hz, 4-Hα, 1 H), 3.67 (s, OMe, 3 H), 3.94 (dd, $J_{3\beta,3\alpha}$ = 10.0, $J_{3\beta,3a\alpha}$ = 8.0 Hz, 3-Hβ, 1 H), 4.32 (t, $J_{3\alpha,3\beta}$ = 10.0, $J_{3\alpha,3a\alpha}$ = 10.0 Hz, 3-Hα, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.3 (d, Me), 29.2 (d, Me), 32.0 (u), 41.9 (u, C-7), 46.0 (u, CH_2), 50.3 (d), 51.0 (d), 51.9 (u), 52.0 (d, OMe), 59.6 (u, C-8a), 67.2 (u, C-3), 173.1 (u, CO), 182.4 (u, C-1). − MS (EI, 70 eV); *m/z* (%): 252 [M^+] (44), 237 (21), 234 (13), 224 (62), 222 (23), 221 (17), 220 (10), 209 (10), 208 (52), 206 (38), 194 (42), 193 (58), 192 (61), 191 (30), 190 (55), 179 (19), 178 (12), 177 (18), 175 (24), 174 (13), 165 (12), 164 (40), 163 (37), 161 (12), 150 (13), 149 (19), 148 (25), 147 (44), 146 (11), 139 (18), 138 (13), 137 (15), 135 (22), 134 (22), 133 (47), 132 (16), 131 (59), 125 (13), 123 (11), 121 (13), 119 (33), 117 (13), 112 (24), 111 (12), 109 (12), 105 (38), 100 (12), 99 (29), 95 (24), 94 (19), 93 (68), 92 (22), 91 (74), 82 (13), 81 (16), 80 (14), 79 (45), 78 (18), 77 (65), 69 (15), 67 (30). − $C_{14}H_{20}O_4$ (252.3): calcd. C 66.64, H 7.99; found C 66.77, H 8.13.

Conversion of **9** *to* **6a** and **6b**: A solution of **9** (60 mg, 0.25 mmol) in MeOH (2 ml) was treated with DBU (0.4 ml, 2.5 mmol) and stirred for 3.5 h at room temp. The mixture was then acidified with AcOH and concentrated in vacuo. The residue was dissolved in

water/EtOAc, 1:1, and the aqueous phase was extracted with EtOAc. The organic phase was washed with saturated aqueous $NaHCO_3$ and dried ($MgSO_4$). TLC analysis [EtOAc/*n*-hexane, 1:1, R_f (**6a** and **6b**) = 0.53; R_f (**9**) = 0.48] of the organic phase showed complete conversion. The organic phase was concentrated in vacuo to give a 1:1 mixture of **6a** and **6b**.

Conversion of **11** *to* **14a** *and Methyl [3aS-(3aα,4a,5aβ,8aS*)]-3,3a,4,5,-5a,6,7,8-Octahydro-7,7-dimethyl-1-oxo-1H-pentaleno[1,6a-c]furan-4-carboxylate* (**14b**): A solution of **11** (1.65 g, 6.5 mmol) in MeOH (25 ml) was treated with DBU (0.2 ml) under stirring at room temp. After stirring for 20 h, saturated aqueous NH_4Cl (10 ml) was added and the mixture was concentrated in vacuo. The residue was dissolved in EtOAc and the resulting solution was washed with saturated aqueous NH_4Cl. The organic phase was dried ($MgSO_4$), filtered through a pad of silica gel with EtOAc and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane, 1:1) gave a mixture of **14a** and **14b** (1.62 g, 98%) in a ratio of 6:1 as a slowly crystallizing oil: m.p. 49°C. − **14a**: ^{1}H NMR (400 MHz, C_5D_5N): δ = 0.99 (s, 7α-Me, 3 H), 1.13 (dd, $J_{6\alpha,5a\beta}$ = 10.5, $J_{6\alpha,6\beta}$ = 12.5 Hz, 6-Hα, 1 H), 1.23 (s, 7β-Me, 3 H), 1.45 (d, $J_{8\alpha,8\beta}$ = 13.5 Hz, 8-Hα, 1 H), 1.55 (ddd, $J_{6\beta,5a\beta}$ = 8.0, $J_{6\beta,6\alpha}$ = 12.5, $J_{6\beta,8\beta}$ = 2.5 Hz, 6-Hβ, 1 H), 1.77 (dd, $J_{5\alpha,4\alpha}$ = 6.5, $J_{5\alpha,5\beta}$ = 13.0 Hz, 5-Hα, 1 H), 2.12 (ddd, $J_{5\beta,4\alpha}$ = 7.5, $J_{5\beta,5\alpha}$ = 13.0, $J_{5\beta,5a\beta}$ = 8.0 Hz, 5-Hβ, 1 H), 2.14 (dd, $J_{8\beta,6\beta}$ = 2.5, $J_{8\beta,8\alpha}$ = 13.0 Hz, 8-Hβ, 1 H), 2.88 (ddd, $J_{5a\beta,5\beta}$ = 8.0, $J_{5a\beta,6\alpha}$ = 10.5, $J_{5a\beta,6\beta}$ = 8.0 Hz, 5aβ, 1 H), 2.95 (ddd, $J_{3a\alpha,3\alpha}$ = 10.0, $J_{3a\alpha,3\beta}$ = 8.0, $J_{3a\alpha,4\alpha}$ = 13.0 Hz, 3a-Hα, 1 H), 3.31 (ddd, $J_{4\alpha,3a\alpha}$ = 13.0, $J_{4\alpha,5\alpha}$ = 6.5, $J_{4\alpha,5\beta}$ = 6.5 Hz, 4-Hα, 1 H), 3.63 (s, OMe, 3 H), 4.07 (dd, $J_{3\beta,3\alpha}$ = 10.0, $J_{3\beta,3a\alpha}$ = 8.0 Hz, 3-Hβ, 1 H), 4.37 (dd, $J_{3\alpha,3\beta}$ = 10.0, $J_{3\alpha,3a\alpha}$ = 10.0 Hz, 3-Hα, 1 H). − GC-MS (EI, 70 eV); *m/z* (%): 252 [M^+] (3), 237 (2), 224 (10), 222 (16), 208 (13), 206 (9), 194 (15), 193 (19), 192 (17), 191 (11), 190 (18), 179 (9), 164 (15), 163 (14), 148 (12), 147 (17), 133 (29), 131 (24), 119 (16), 107 (25), 105 (22), 99 (21), 95 (19), 93 (61), 92 (24), 91 (58), 81 (17), 79 (57), 78 (19), 77 (56), 69 (23), 67 (28), 65 (23), 59 (29), 55 (61), 53 (37), 43 (37), 41 (100). − **14b**: ^{1}H NMR (400 MHz, C_5D_5N, in part): δ = 1.00 (s, 7α-Me, 3 H), 1.10 (s, 7β-Me, 3 H), 4.21 (dd, $J_{3\beta,3\alpha}$ = 10.0, $J_{3\beta,3a\alpha}$ = 8.0 Hz, 3-Hβ, 1 H), 4.31 (dd, $J_{3\alpha,3\beta}$ = 10.0, $J_{3\alpha,3a\alpha}$ = 10.0 Hz, 3-Hα, 1 H). − ^{13}C NMR (20 MHz, $CDCl_3$, in part): δ = 29.0 (d, Me), 29.4 (d, Me), 37.4 (u), 48.9 (u), 50.0 (d), 51.1 (d), 69.4 (u, C-3), 174.0 (u, CO). − GC-MS (EI, 70 eV); *m/z* (%): 252 [M^+] (11), 238 (7), 237 (45), 221 (7), 206 (8), 205 (33), 193 (13), 177 (11), 166 (18), 153 (15), 149 (22), 147 (15), 139 (23), 133 (53), 131 (20), 121 (15), 119 (17), 107 (38), 105 (36), 95 (31), 94 (19), 93 (86), 92 (29), 91 (76), 81 (19), 79 (67), 78 (22), 77 (74), 69 (27), 67 (33). − $C_{14}H_{20}O_4$ (252.3): calcd. C 66.65, H 7.99; found C 66.57, H 8.00.

Methyl [3aS-(3aα,5aβ,8aS)]-3,3a,5a,6,7,8-Hexahydro-7,7-dimethyl-1-oxo-1H-pentaleno[1,6a-c]furan-4-carboxylate* (**15**): To a solution of LDA, prepared from *i*Pr_2NH (6.0 mmol, 0.85 ml) in THF (5 ml) and *n*BuLi (6.0 mmol, 4.25 ml of a 1.38 M solution in *n*-hexane) at −80°C → 0°C, was added at −80°C a solution of a mixture of **14a/b** (1.19 g, 4.72 mmol) in THF (15 ml). After stirring the mixture for 15 min., a solution of PhSeCl (1.15 g, 6.0 mmol) in THF (12 ml) was rapidly added. After warming the mixture to 0°C, water (3 ml), AcOH (0.6 ml) and 30% aqueous H_2O_2 (2.5 ml) were added. The mixture was stirred for 1 h at 0°C, and then saturated aqueous $Na_2S_2O_7$ and EtOAc were added. The organic phase was washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane, 3:7) gave **15** (703 mg, 60%) as colorless crystals: m.p. 99°C, $[\alpha]_D$ = −137.1 (*c* = 0.22, acetone), $[\alpha]_{365}$ = −449.7 (*c* = 0.22, acetone). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (s, 3 H, Me), 1.1 (s, 3 H, Me), 1.40 (dd, $J_{6\alpha,5a\beta}$ = 7.5, $J_{6\alpha,6\beta}$ = 13.0 Hz, 1 H, 6-Hα), 1.77 (d, $J_{8\alpha,8\beta}$ = 13.5 Hz, 1 H, 8-Hα), 1.89 (dd, $J_{6\beta,5a\beta}$ = 9.5, $J_{6\beta,6\alpha}$ = 13.0 Hz, 1 H, 6-Hβ), 2.11 (d, $J_{8\beta,8\alpha}$ = 13.5 Hz, 1 H, 8-Hβ), 3.60 (dd, $J_{3a\alpha,3\alpha}$ = 8.0, $J_{3a\alpha,3\beta}$ = 3.0 Hz, 1 H, 3a-Hα), 3.61 (m, 1 H, 5a-Hβ), 3.74 (s, 3 H, OMe), 4.28 (dd, $J_{3\beta,3\alpha}$ = 10.0, $J_{3\beta,3a\alpha}$ = 3.0 Hz, 1 H, 3-Hβ), 4.48 (dd, $J_{3\alpha,3\beta}$ = 10.0, $J_{3\alpha,3a\alpha}$ = 8.0 Hz, 1 H, 3-Hα), 6.78 (m, 1 H, 5-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.70 (d, Me), 28.87 (d, Me), 43.02 (u, C-7), 45.83 (u), 50.91 (u), 51.84 (d, OMe), 53.62 (d), 59.85 (u, C-8a), 70.63 (u, C-3), 134.68 (u, C-4), 147.78 (d, C-5), 164.32 (u, CO), 182.63 (u, C-1). − MS (EI, 70 eV); *m/z* (%): 250 [M^+] (21), 235 (8), 232 (5), 219 (9), 218 (8), 205 (21), 204 (10), 193 (12), 192 (69), 191 (74), 190 (14), 177 (22), 173 (12), 163 (10), 155 (18), 147 (10), 145 (27), 137 (14), 136 (100), 135 (14), 133 (35), 132 (14), 131 (27), 128 (13), 119 (28), 118 (19), 117 (26), 115 (19), 112 (15), 106 (13), 105 (76), 91 (70), 79 (17), 78 (11), 77 (38), 65 (27). − IR (KBr): $\tilde{\nu}$ = 3071 (m), 3028 (m), 2974 (s), 2959 (s), 2931 (s), 2914 (s), 2871 (s), 2854 (s), 2769 (w), 2726 (w), 1758 (s), 1709 (s), 1627 (s), 1479 (s), 1471 (s), 1439 (s), 1385 (s), 1371 (s), 1353 (s), 1308 (s), 1283 (s), 1266 (s), 1246 (s), 1212 (s), 1207 (s), 1149 (s), 1112 (s), 1081 (s), 1055 (s), 1040 (s), 1025 (s), 993 (s), 970 (m), 955 (m), 947 (m), 929 (m), 914 (s), 903 (s), 871 (m), 830 (w), 794 (s). − $C_{14}H_{18}O_4$: calcd. 250.1205, found 250.1200 (MS). $C_{14}H_{18}O_4$ (250.2): calcd. C 67.18, H 7.25; found C 66.85, H 7.24.

Methyl [1R-(1α,3aα,5aβ,8aR)]- and Methyl [1S-(1α,3aβ,5aα,8aS*)]-3,3a,5a,6,7,8-Hexahydro-7,7-dimethyl-1-hydroxy-1H-pentaleno[1,6a-c]furan-4-carboxylate* (**16a** and **16b**): To a solution of **15** (200 mg, 0.80 mmol) in THF (7 ml) at −85°C, DIBAL-H (1.80 mmol, 1.8 ml of a 1.0 M solution in *n*-hexane) was added dropwise. After stirring the solution for 30 min., MeOH (0.24 ml), water (0.24 ml), Celite (0.48 g) and THF (6 ml) were added. The resulting suspension was allowed to warm to room temp., stirred for 15 min., and treated with Na_2SO_4 (18.0 g). The suspension was filtered and the residue was washed with EtOAc. Concentration of the filtrate in vacuo and purification of the residue by chromatography (EtOAc/*n*-hexane, 1:1) gave a mixture of **16a/b** (196 mg, 97%) in a ratio of 3:1 as a colorless oil, $[\alpha]_D$ = −59.5 (*c* = 2.02, $CDCl_3$). − **16a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 (s, β-Me, 3 H), 0.94 (s, α-Me, 3 H), 1.24 (dd, $J_{6\alpha,5a\beta}$ = 6.4, $J_{6\alpha,6\beta}$ = 12.8 Hz, 6-Hα, 1 H), 1.56 (d, $J_{8\alpha,8\beta}$ = 13.7 Hz, 8-Hα, 1 H), 1.73 (ddd, $J_{6\beta,5a\beta}$ = 9.4, $J_{6\beta,6\alpha}$ = 12.8, $J_{6\beta,8\beta}$ = 1.2 Hz, 6-Hβ, 1 H), 2.09 (dd, $J_{8\beta,6\beta}$ = 1.2, $J_{8\beta,8\alpha}$ = 13.7 Hz, 8-Hβ, 1 H), 2.90 (d, $J_{OH,1\beta}$ = 2.7 Hz, OH, 1 H), 3.09 (ddd, $J_{5a\beta,5}$ = 2.4, $J_{5a\beta,6\alpha}$ = 6.4, $J_{5a\beta,6\beta}$ = 9.4 Hz, 5a-Hβ, 1 H), 3.19 (m, 3a-Hα, 1 H), 3.66 (dd, $J_{3\beta,3\alpha}$ = 8.9, $J_{3\beta,3a\alpha}$ = 1.8 Hz, 3-Hβ, 1 H), 3.67 (s, OMe, 3 H), 4.13 (dd, $J_{3\alpha,3\beta}$ = 8.9, $J_{3\alpha,3a\alpha}$ = 7.3 Hz, 3-Hα, 1 H), 5.18 (d, $J_{1\beta,OH}$ = 2.7 Hz, 1-Hβ, 1 H), 6.62 (dd, $J_{5,3a\alpha}$ = 1.2 Hz, $J_{5,5a\beta}$ = 2.4 Hz, 5-H, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.59 (d, Me), 28.67 (d, Me), 40.20 (u, C-7), 45.65 (u), 47.33 (u), 51.55 (d, OMe), 56.42 (d), 57.41 (d), 66.13 (u, C-8a), 68.93 (u, C-3), 104.77 (d, C-1), 134.98 (u, C-4), 147.90 (u, C-5), 165.30 (u, CO). − **16b**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.93 (s, Me, 3 H), 0.96 (s, Me, 3 H), 1.18 (dd, $J_{6\beta,5a\alpha}$ = 8.2, $J_{6\beta,6\alpha}$ = 11.9 Hz, 6-Hβ, 1 H), 3.23 (m, 3a-Hβ, 1 H), 3.65 (s, OMe, 3 H), 3.71 (dd, $J_{3\alpha,3\beta}$ = 9.1, $J_{3\alpha,3a\beta}$ = 6.7 Hz, 3-Hα, 1 H), 4.12 (dd, $J_{3\beta,3\alpha}$ = 9.1, $J_{3\beta,3a\beta}$ = 9.1 Hz, 3-Hβ, 1 H), 5.16 (d, $J_{1\beta,OH}$ = 3.7 Hz, 1-Hβ, 1 H), 6.72 (dd, $J_{5,3a\beta}$ = 1.8, $J_{5,5a\alpha}$ = 2.4 Hz, 5-H, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.13 (d, Me), 28.59 (d, Me), 40.89 (u, C-7), 45.95 (u), 50.82 (d, OMe), 53.67 (u), 58.84 (d), 65.72 (u, C-8a), 70.11 (u, C-3), 104.66 (d, C-1), 134.14 (u, C-4), 149.20 (u, C-5). − MS (EI, 70 eV); *m/z* (%): 252 [M^+] (6), 234 (37), 222 (24), 221 (13), 207 (23), 206 (77), 205 (47), 193 (23), 191 (33), 190 (66), 175 (30), 166 (32), 163 (47), 162 (12), 161 (11), 151 (24), 150 (87), 148 (16), 147 (42), 146 (15), 145 (15), 138 (10), 137 (15), 135 (15), 134 (17), 133 (23), 131 (23), 121 (13), 119 (25), 118 (31), 117 (14),

107 (48), 106 (21), 105 (57), 100 (14), 93 (20), 92 (15), 91 (100), 79 (28), 78 (10), 77 (33), 69 (12), 65 (20). − IR (CH_2Cl_2): $\tilde{\nu}$ = 3420 (s), 3057 (w), 2953 (s), 2895 (s), 2865 (s), 1714 (s), 1634 (s), 1463 (s), 1439 (s), 1386 (m), 1366 (s), 1325 (m), 1308 (m), 1279 (s), 1250 (s), 1198 (s), 1119 (s), 1070 (s), 1044 (s), 1024 (s), 995 (s), 941 (m), 925 (m), 874 (w), 860 (w), 832 (w), 793 (m), 775 (m), 760 (m), 739 (s), 705 (m). − $C_{14}H_{20}O$: calcd. 252.1362, found 252.1365 (MS).

Methyl [1R-(1α,3aα,4β,5aβ,8aS)]- and Methyl [1S-(1β,3aα, 4β,5aβ,8aS*)]-3,3a,4,5,5a,6,7,8-Octahydro-7,7-dimethoxy-1-hydroxy-1H-pentaleno[1,6a-c]furan-4-carboxylate* (**19a** and **19b**): To a solution of **12** (700 mg, 2.46 mmol) in THF (50 ml) at −80°C, was added DIBAL-H (3.50 mmol, 3.5 ml of a 1 M solution in *n*-hexane). The mixture was stirred for 1 h at −80°C and then MeOH (0.5 ml) was added. After stirring the mixture for a further 10 min., the cooling bath was removed and water (1.65 ml), Celite (1.65 g)0 and Na_2SO_4 (10 g) were successively added. The suspension was stirred for 30 min. at room temp., filtered, and the residue was washed several times with diethyl ether. The combined organic extracts were concentrated in vacuo. Chromatography (EtOAc/*n*-hexane, 1:1) of the residue gave a mixture of **19a/b** (614 mg, 87%) as a slowly crystallizing oil. This oil was dissolved in toluene and *n*-hexane was added until turbid. The solution was warmed until clear. Upon cooling the solution, a mixture of **19a/b** was deposited as colorless crystals: m.p. 82°C, $[\alpha]_D$ = −39.5 (*c* = 1.39, CH_2Cl_2). − **19a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (m, $J_{6\alpha,5a\beta}$ = 9.0, $J_{6\alpha,6\beta}$ = 13.0 Hz, 6-Hα, 1 H), 1.68 (dd, $J_{5\beta,4\alpha}$ = 6.5, $J_{5\beta,5\alpha}$ = 13.5 Hz, 5-Hβ, 1 H), 1.72 (d, $J_{8\alpha,8\beta}$ = 14.0, 8-Hα, 1 H), 2.02 (ddd, $J_{5\alpha,4\alpha}$ = 8.0, $J_{5\alpha,5\beta}$ = 13.5, $J_{5\alpha,5a\beta}$ = 13.5 Hz, 5-Hα, 1 H), 2.25 (m, $J_{6\beta,8\beta}$ = 2.5 Hz, 5a-Hβ, 6-Hβ, 2 H), 2.59 (dd, $J_{8\beta,6\beta}$ = 2.5, $J_{8\beta,8\alpha}$ = 14.0 Hz, 8-Hβ, 1 H), 2.74 (dt, $J_{3a\alpha,3\alpha}$ = 9.5, $J_{3a\alpha,3\beta}$ = 5.0, $J_{3a\alpha,4\alpha}$ = 5.0 Hz, 3a-Hα, 1 H), 3.17−3.22 (m, 4-Hα, 1 H), 3.20 (s, OMe, 3 H), 3.25 (s, OMe, 3 H), 3.45 (d, $J_{OH,1\beta}$ = 2.5 Hz, OH, 1 H), 3.68 (dd, $J_{3\beta,3\alpha}$ = 9.5, $J_{3\beta,3a\alpha}$ = 5.0 Hz, 3-Hβ, 1 H), 3.69 (s, CO_2Me, 3 H), 4.08 (t, $J_{3\alpha,3\beta}$ = 9.5, $J_{3\alpha,3a\alpha}$ = 9.5 Hz, 3-Hα, 1 H), 5.17 (d, $J_{1\beta,OH}$ = 2.5 Hz, 1-Hβ, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.98 (u), 38.79 (u), 40.38 (u), 44.50 (d), 46.10 (d), 48.71 (d, acetal-OMe), 49.62 (d), 50.44 (d, acetal-OMe), 51.74 (d, CO_2Me), 63.33 (u, C-8a), 67.81 (u, C-3), 103.83 (d, C-1), 110.05 (u, C-7), 174.21 (u, CO). − **19b**: ^{1}H NMR (400 MHz, $CDCl_3$, in part): δ = 5.15 (d, $J_{1\alpha,OH}$ = 3.5 Hz, 1-Hα, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$, in part): δ = 33.96 (u), 38.89 (u), 39.54 (u), 44.23 (d), 45.10 (d), 49.06 (d), 50.07 (d, acetal-OMe), 53.42 (d, CO_2Me), 66.88 (u, C-3), 104.53 (d, C-1), 110.59 (u, C-7). − MS (EI, 70 eV); *m*/*z* (%): 286 [M^+] (5), 255 (14), 254 (36), 240 (26), 239 (25), 238 (14), 237 (82), 235 (15), 223 (29), 222 (31), 209 (13), 208 (37), 207 (11), 205 (26), 195 (12), 194 (20), 193 (19), 182 (11), 180 (13), 179 (12), 178 (11), 177 (29), 176 (11), 165 (15), 154 (20), 153 (13), 152 (14), 151 (20), 150 (12), 149 (63), 148 (17), 147 (17), 141 (35), 139 (16), 138 (10), 137 (48), 135 (31), 133 (22), 127 (31), 125 (12), 123 (21), 122 (31), 121 (21), 119 (15), 117 (36), 115 (28), 114 (23), 111 (14), 110 (18), 109 (83), 108 (10), 107 (34), 106 (10), 105 (48), 103 (13), 101 (22), 99 (10), 97 (18), 96 (14), 95 (29), 94 (11), 93 (42), 92 (18), 91 (100), 89 (28), 88 (71), 86 (11), 85 (11), 84 (18), 83 (86), 82 (12), 81 (63), 80 (11), 79 (61), 78 (16), 77 (56), 75 (24). − $C_{14}H_{22}O_6$ (286.3): calcd. C 58.73, H 7.75; found C 58.81, H 7.66.

Methyl [1R-(1α,3aα,4β,5aβ,8aR)]- and Methyl [1S-(1α,3aβ, 4α,5aα,8aS*)]-3,3a,4,5,5a,6,7,8-Octahydro-7,7-dimethyl-1-hydroxy-1H-pentaleno[1,6a-c]furan-4-carboxylate* (**21a** and **21b**): To a solution of **14a** (519 mg, 2.06 mmol) in THF (17 ml) at −80°C, DIBAL-H (2.15 mmol, 2.15 ml of a 1 M solution in *n*-hexane) was added dropwise. After stirring the mixture for 1.25 h at this temperature, MeOH (4.6 ml) was added and stirring was continued for 10 min. The cooling bath was then removed and water (2.1 ml), Celite (2.20 g) and Na_2SO_4 (11.00 g) were added. The suspension was warmed to room temp. and stirred for 1 h. It was then filtered and the residue was washed several times with EtOAc. Concentration of the filtrate in vacuo and purification of the residue by chromatography (EtOAc/*n*-hexane, 1:1) gave a mixture of **21a** and **21b** (492 mg, 94%) in a ratio of 18:1 as colorless crystals: m.p. 224°C, $[\alpha]_D$ = −105.1 (*c* = 1.00, CH_2Cl_2). − **21a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (s, Me, 3 H), 1.05 (s, Me, 3 H), 1.08 (dd, $J_{6\alpha,6\beta}$ = 12.5, $J_{6\alpha,5a\beta}$ = 10.5 Hz, 6-Hα, 1 H), 1.44 (d, $J_{8\alpha,8\beta}$ = 14.0 Hz, 8-Hα, 1 H), 1.63 (dd, $J_{5\alpha,5\beta}$ = 13.5, $J_{5\alpha,5a\beta}$ = 6.0 Hz, 5-Hα, 1 H), 1.74 (ddd, $J_{6\beta,5a\beta}$ = 8.0, $J_{6\beta,6\alpha}$ = 12.5, $J_{6\beta,8\beta}$ = 2.5 Hz, 6-Hβ, 1 H), 1.98 (dt, $J_{5\beta,4\alpha}$ = 12.5, $J_{5\beta,5\alpha}$ = 13.5, $J_{5\beta,5a\beta}$ = 8.5 Hz, 5-Hβ, 1 H), 2.13 (dd, $J_{8\beta,6\beta}$ = 2.5, $J_{8\beta,8\alpha}$ = 14.0 Hz, 8-Hβ, 1 H), 2.39 (dt, $J_{5a\beta,5\beta}$ = 8.5, $J_{5a\beta,5\alpha}$ = 6.0, $J_{5a\beta,6\alpha}$ = 10.5 Hz, 5a-Hβ, 1 H), 2.68 (ddd, $J_{3a\alpha,3\alpha}$ = 9.0, $J_{3a\alpha,3\beta}$ = 5.0, $J_{3a\alpha,4\alpha}$ = 5.5 Hz, 3a-Hα, 1 H), 2.70 (d, $J_{OH,1}$ = 2.5 Hz, OH, 1 H), 3.11 (dt, $J_{4\alpha,3a\alpha}$ = 5.5, $J_{4\alpha,5\beta}$ = 12.5 Hz, 4-Hα, 1 H), 3.65 (dd, $J_{3\beta,3\alpha}$ = 10.0, $J_{3\beta,3a\alpha}$ = 5.0 Hz, 3-Hβ, 1 H), 3.70 (s, OMe, 3 H), 4.04 (dd, $J_{3\alpha,3\beta}$ = 10.0, $J_{3\alpha,3a\alpha}$ = 9.0 Hz, 3-Hα, 1 H), 5.25 (d, $J_{1\beta,OH}$ = 2.5 Hz, 1-Hβ, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.13 (d, Me), 28.86 (d, Me), 31.91 (u), 40.25 (u, C-7), 45.87 (d), 47.19 (u), 47.58 (d), 48.82 (u), 50.93 (d), 51.71 (d, OMe), 66.47 (u, C-8a), 67.24 (u, C-3), 104.61 (d, C-1), 174.47 (u, CO). − **21b**: ^{1}H NMR (400 MHz, $CDCl_3$, in part): δ = 2.94 (d, $J_{OH,1\alpha}$ = 3.5 Hz, OH, 1 H), 5.11 (d, $J_{1\alpha,OH}$ = 2.4 Hz, 1-Hα, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.98 (d), 28.89 (d), 31.99 (u), 40.11 (u, C-7), 46.00 (d), 46.99 (u), 47.60 (d), 48.84 (u), 51.32 (d), 51.68 (d, OMe), 65.71 (u, C-8a), 67.19 (u, C-3), 104.51 (d, C-1), 174.61 (u, CO). − MS (EI, 70 eV); *m*/*z* (%): 254 [M^+] (0.5), 253 (4), 239 (2), 238 (15), 237 (100), 223 (3), 221 (4), 207 (2), 206 (1), 205 (7), 206 (1), 205 (7), 177 (3), 161 (2), 159 (5), 150 (1), 149 (6), 148 (1), 147 (4), 135 (1), 133 (2), 121 (3), 119 (3), 107 (4), 105 (4), 95 (2), 94(1), (93(5). − IR (KBr): $\tilde{\nu}$ = 3436 (m), 2955 (s), 2906 (m), 2861 (m), 2768 (w), 2427 (m), 2081 (m), 1733 (s), 1631 (m), 1486 (m), 1463 (m), 1438 (m), 1385 (s), 1330 (m), 1285 (s), 1260 (m), 1231 (m), 1208 (s), 1171 (s), 1118 (s), 1063 (s), 1045 (s), 1032 (m), 1012 (s), 999 (s), 950 (m), 938 (m), 922 (m), 900 (w), 875 (w), 849 (w), 826 (w), 757 (w). − $C_{14}H_{22}O_4$ (254.3): calcd. C 66.11, H 8.71; found C 65.89, H 8.79.

Conversion of **21a** *to* **21b**: To a solution of an 18:1 mixture of **21a** and **21b** (65 mg, 0.26 mmol) in THF (3 ml) at −80°C, *n*BuLi (0.25 mmol, 0.7 ml of a 0.36 M solution in *n*-hexane) was added dropwise over a period of 10 min. The mixture was then slowly allowed to warm to room temp. and stirred for 5 h. Saturated aqueous NH_4Cl and EtOAc were added. The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane, 1:1) gave **21b** (60 mg, 92%) as colorless crystals: m.p. 236°C, $[\alpha]_D$ = −78.5 (*c* = 1.00, CH_2Cl_2). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (s, α-Me, 3 H), 1.03 (s, β-Me, 3 H), 1.06 (dd, $J_{6\beta,5a\alpha}$ = 10.7, $J_{6\beta,6\alpha}$ = 12.7 Hz, 6-Hβ, 1 H), 1.37 (d, $J_{8\beta,8\alpha}$ = 13.7 Hz, 8-Hβ, 1 H), 1.62 (dd, $J_{5\beta,4\beta}$ = 6.1, $J_{5\beta,5\alpha}$ = 12.7 Hz, 5-Hβ, 1 H), 1.72 (ddd, $J_{6\alpha,5a\alpha}$ = 8.1, $J_{6\alpha,6\beta}$ = 12.7, $J_{6\alpha,8\alpha}$ = 2.5 Hz, 6-Hα, 1 H), 1.97 (ddd, $J_{5\alpha,4\beta}$ = 12.7, $J_{5\alpha,5\beta}$ = 12.7, $J_{5\alpha,5a\alpha}$ = 8.1 Hz, 5-Hα, 1 H), 2.00 (dd, $J_{8\alpha,6\alpha}$ = 2.5, $J_{8\alpha,8\beta}$ = 13.7 Hz, 8-Hα, 1 H), 2.38 (dt, $J_{5a\alpha,5\alpha}$ = 8.1, $J_{5a\alpha,6\alpha}$ = 8.1, $J_{5a\alpha,6\beta}$ = 10.7 Hz, 5a-Hα, 1 H), 2.61 (dt, $J_{3a\beta,3\alpha}$ = 4.2, $J_{3a\beta,3\beta}$ = 9.2 Hz, 3a-Hβ, 1 H), 3.10 (dt, $J_{4\beta,5\alpha}$ = 12.7, $J_{4\beta,5\beta}$ = 6.1 Hz, 4-Hβ, 1 H), 3.64 (dd, $J_{3\alpha,3\beta}$ = 9.5, $J_{3\alpha,3a\beta}$ = 4.2 Hz, 3-Hα, 1 H), 3.68 (s, OMe, 3 H), 3.85 (dd, $J_{3\beta,3\alpha}$ = 9.5, $J_{3\beta,3a\beta}$ = 9.2 Hz, 3-Hβ, 1 H), 5.13 (s, 1-Hβ, 1 H). − ^{13}C NMR (75 MHz, C_6D_6): δ = 27.13 (d, Me), 28.96 (d, Me), 32.45 (u), 40.13 (u, C-7), 46.38 (d), 47.32 (u), 48.06 (d), 48.87 (u), 51.14 (d, OMe), 52.04 (d), 66.04 (u, C-8a), 67.66 (u, C-3), 105.12 (d, C-1), 174.03 (u, CO). − MS (EI, 70 eV); *m*/*z* (%): 254 [M^+] (1), 253 (4), 239 (2), 238 (15) 237 (100), 221 (4), 205 (6), 177 (3), 162

(1), 159 (4), 149 (5), 147 (4), 133 (2), 121 (2), 119 (2), 107 (3), 105 (3), 99 (1), 95 (1), 93 (4).

[3aS-(3aα,3bβ,6aβ,7aα)]-Octahydro-5,5-dimethyl-3b(1H)-(1,3-dithiane-2-ylidene-methyl)-1-oxo-pentaleno[1,2-c]furan (**22**): To a solution of **17a** (H instead of Li) (645 mg, 2.54 mmol) in THF (10 ml), *n*BuLi (2.61 mmol, 1.8 ml of a 1.45 M solution in hexanes) was rapidly added at 0°C. After stirring the mixture for 10 min. at this temp., the cooling bath was removed and stirring was continued for 30 min. at room temp. The solution was recooled to 0°C and a solution of a mixture of **21a/b** (254 mg, 1.00 mmol) in THF (7 ml) was added dropwise over a period of 1 h. After stirring the mixture for 16 h at room temp., saturated aqueous NH_4Cl was added. The aqueous phase was extracted with EtOAc and the combined organic extracts were washed with saturated aqueous Na_2CO_3, dried ($MgSO_4$), and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane, 1:3) gave, in addition to a mixture of **21a/b** (56 mg, 22%), **22** (220 mg, 68%) as colorless crystals: m.p. 125°C, $[\alpha]_D$ = +97.7 (*c* = 1.11, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (s, Me, 3 H), 1.09 (s, Me, 3 H), 1.39 (dd, $J_{6\alpha,6\beta}$ = 13.5, $J_{6\alpha,6a\beta}$ = 5.5 Hz, 6-Hα, 1 H), 1.53 (d, $J_{4\alpha,4\beta}$ = 13.5 Hz, 4-Hα, 1 H), 1.76 (dd, $J_{6\beta,6\alpha}$ = 13.5, $J_{6\beta,6a\beta}$ = 7.5 Hz, 6-Hβ, 1 H), 1.88 (ddd, $J_{7\alpha,6a\beta}$ = 7.0, $J_{7\alpha,7\beta}$ = 13.5, $J_{7\alpha,7a\alpha}$ = 8.5 Hz, 7-Hα, 1 H), 2.15 (m, 7-Hβ, 5′-H, 3 H), 2.18 (d, $J_{4\beta,4\alpha}$ = 13.5 Hz, 4-Hβ, 1 H), 2.46 (m, $J_{6a\beta,6\alpha}$ = 5.5, $J_{6a\beta,6\beta}$ = 7.5, $J_{6a\beta,7\alpha}$ = 7.0, $J_{6a\beta,7\beta}$ = 8.0 Hz, 6a-Hβ, 1 H), 2.90 (t, 4′-H, 6′-H, 4 H), 3.09 (ddd, $J_{7a\alpha,3a\alpha}$ = 10.5, $J_{7a\alpha,7\alpha}$ = 8.5, $J_{7a\alpha,7\beta}$ = 5.5 Hz, 7a-Hα, 1 H), 3.38 (ddd, $J_{3a\alpha,3\alpha}$ = 8.5, $J_{3a\alpha,3\beta}$ = 6.5, $J_{3a\alpha,7a\alpha}$ = 10.5 Hz, 3a-Hα, 1 H), 4.13 (dd, $J_{3\beta,3\alpha}$ = 10.0, $J_{3\beta,3a\alpha}$ = 6.5 Hz, 3-Hβ, 1 H), 4.43 (dd, $J_{3\alpha,3\beta}$ = 10.0, $J_{3\alpha,3a\alpha}$ = 8.5 Hz, 3-Hα, 1 H), 6.60 (s, 8-H, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.4 (u), 29.2 (u), 30.1 (u), 30.6 (d, Me), 31.6 (d, Me), 34.8 (u), 39.5 (u, C-5), 44.6 (d), 46.1 (u), 50.2 (d), 53.6 (d), 55.5 (u), 60.2 (u, C-3b), 70.3 (u, C-3), 128.8 (u, C-2′), 138.6 (d, C-8), 180.2 (u, C-1). − MS (EI, 70 eV); *m/z* (%): 324 [M^+] (9), 145 (19), 135 (10), 133 (10), 132 (13), 119 (25), 107 (12), 106 (11), 105 (18), 97 (10), 93 (10), 91 (32), 85 (54), 79 (16), 77 (23), 71 (13), 67 (14), 65 (11), 59 (12), 57 (13), 55 (26), 53 (16), 47 (14), 45 (30), 43 (27), 42 (18), 41 (100), 40 (23), 39 (38). − IR (KBr): ṽ = 2925 (s), 2905 (s), 2840 (m), 1780 (s), 1730 (m), 1550 (w), 1445 (m), 1410 (w), 1355 (m), 1320 (w), 1310 (w), 1290 (w), 1265 (w), 1245 (w), 1230 (w), 1172 (m), 1160 (m), 1125 (w), 1100 (w), 1065 (w), 1020 (m), 1005 (m), 900 (w). − $C_{17}H_{24}O_2S_2$ (324.5): calcd. C 62.92, H 7.45; found C 62.78, H 7.46.

(1,3-Dithiane-2-yl)-[1R-(1α,3aα,4β,5aβ,8aR)]- and (1,3-Dithiane-2-yl)-{[1S-(1α,3aβ,4α,5aα,8aR*)]-3,3a,4,5,5a,6,7,8-octahydro-7,7-dimethyl-1-hydroxy-1H-pentaleno[1,6a-c]furan-4-yl}methanone* (**23a** and **23b**): To a solution of **17b** (H instead of Li) (115 mg, 0.60 mmol) in THF (1.2 ml) at −70°C, *n*BuLi (0.60 mmol, 0.40 ml of a 1.50 M solution in *n*-hexane) was added dropwise under rapid stirring within 1 min. The temp. of the mixture was then raised to 0°C over a period of 5 h, the cooling bath was removed, and stirring was continued for 1 h at room temp. Then, the mixture was recooled to −60°C and a solution of **21a/b** (100 mg, 0.39 mmol) in THF (1 ml) was slowly added. The the mixture was allowed to warm to room temp. over a period of 14 h and water was added. It was then extracted with EtOAc and the organic phase was washed with water, dried (Na_2SO_4), and concentrated in vacuo. Chromatography (EtOAc/*n*-hexane, 1:3) of the residue gave a mixture of **23a/b** (87 mg, 65%) as colorless crystals: m.p. 107°C, $[\alpha]_D$ = −29.84 (*c* = 0.64, diethyl ether). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (s, Me, 3 H), 1.05 (s, Me, 3 H), 1.09 (dd, $J_{6\alpha,6\beta}$ = 12.4, $J_{6\alpha,5a\beta}$ = 10.9 Hz, 6-Hα, 1 H), 1.45 (d, $J_{8\alpha,8\beta}$ = 13.5 Hz, 8-Hα, 1 H), 1.56 (dd, $J_{5\beta,4\alpha}$ = 5.7, $J_{5\beta,5\alpha}$ = 12.8 Hz, 5-Hβ, 1 H), 1.75 (ddd, $J_{6\beta,8\beta}$ = 2.4, $J_{6\beta,6\alpha}$ = 12.4, $J_{6\beta,6a\beta}$ = 8.1 Hz, 6-Hβ, 1 H), 1.98−2.18 (m, 5-Hα, 5′-Ha, 5′-He, 3 H), 2.14 (dd, $J_{8\beta,4\alpha}$ = 13.5, $J_{8\beta,6\beta}$ = 2.4 Hz, 8-Hβ, 1 H), 2.40 (ddd, $J_{5a\beta,6\alpha}$ = 10.9, $J_{5a\beta,6\beta}$ = 8.1, $J_{5a\beta,5\alpha}$ = 8.1 Hz, 5a-Hβ, 1 H), 2.40 (s, OH, 1 H), 2.52−2.63 (m, 4′-H, 6′-H, 2 H), 2.69 (ddd, $J_{3a\alpha,3\alpha}$ = 9.4, $J_{3a\alpha,3\beta}$ = 4.4, $J_{3a\alpha,4\alpha}$ = 5.7 Hz, 3a-Hα, 1 H), 3.20−3.34 (ddd, *J* = 3.0, 11.0, 14.1 Hz, 4′-H, 6′-H, 2 H), 3.47 (dt, $J_{4\alpha,3a\alpha}$ = 5.7, $J_{4\alpha,5\alpha}$ = 12.8, $J_{4\alpha,5}$ = 5.7 Hz, 4-Hα, 1 H), 3.65 (dd, $J_{3\beta,3\alpha}$ = 9.4, $J_{3\beta,3a\alpha}$ = 4.4 Hz, 3-Hβ, 1 H), 4.02 (t, $J_{3\alpha,3\beta}$ = 9.4, $J_{3\alpha,3a\alpha}$ = 9.4 Hz, 3-Hα, 1 H), 4.24 (s, 2′-H, 1 H), 5.25 (s, 1-H, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.14 (u, thioacetal), 25.96 (u, thioacetal), 26.04 (u, thioacetal), 27.06 (d, Me), 28.78 (d, Me), 31.74 (u), 40.25 (u, C-7), 45.31 (d), 47.24 (u), 47.42 (d), 48.97 (u), 51.28 (d), 51.38 (d), 66.73 (u, C-3), 66.83 (d, C-4), 104.31 (d, C-1), 203. 87 (u, CO). − IR (KBr): ṽ = 3260 (m), 2940 (s), 2915 (s), 2890 (s), 2860 (m), 1700 (s), 1455 (m), 1428 (m), 1380 (w), 1360 (m), 1340 (m), 1320 (m), 1275 (m), 1250 (m), 1183 (m), 1108 (m), 1075 (m), 1053 (s), 1035 (s), 1005 (s), 950 (m), 930 (m), 905 (m), 865 (w), 830 (w), 810 (w), 750 (w), 690 (w). − MS (EI, 70 eV); *m/z* (%): 342 [M^+] (2), 223 (6), 121 (10), 120 (15), 119 (100), 42 (6).

[1S-(1α,3aα,3bβ,6aβ,7aα)]- and [1R-(1a,3aβ,3bα,6aα,7aβ)]-Octahydro-5,5-dimethyl-3b(1H)-(1,3-dithiane-2-ylidenemethyl)-1-hydroxypentaleno[1,2-c]furan (**24a** and **24b**): To a solution of **22** (95 mg, 0.29 mmol) in THF (5 ml) at −80°C, DIBAL-H (0.35 mmol, 0.35 ml of a 1 M solution in *n*-hexane) was added dropwise over a period of 10 min. After stirring the mixture for 1.5 h at this temp., water (0.2 ml) and $MgSO_4$ (350 mg) were added. The cooling bath was then removed and the suspension was stirred rapidly for 2 h at room temp. It was then filtered and the residue was washed several times with EtOAc. Concentration of the filtrates in vacuo and purification of the residue by chromatography (EtOAc/*n*-hexane, 1:1) furnished a 10:1 mixture of **24a/b** (92 mg, 96%) as colorless crystals: m.p. 152°C, $[\alpha]_D$ = +110.7 (*c* = 1.05, diethyl ether). − **24a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (s, Me, 3 H), 1.03 (s, Me, 3 H), 1.24 (dd, $J_{6\alpha,6\beta}$ = 12.9, $J_{6\alpha,6a\beta}$ = 7.8 Hz, 6-Hα, 1 H), 1.56 (d, $J_{4\alpha,4\beta}$ = 12.9 Hz, 4-Hα, 1 H), 1.58−1.67 (m, 7-Hα, 7-Hβ, 2 H), 1.72 (ddd, $J_{6\beta,4\beta}$ = 1.7, $J_{6\beta,6\alpha}$ = 12.9, $J_{6\beta,6a\beta}$ = 7.8 Hz, 6-Hβ, 1 H), 2.08−2.17 (m, 5′-H, 5′-H, 2 H), 2.13 (dd, $J_{4\beta,4\alpha}$ = 12.9, $J_{4\beta,6\beta}$ = 1.7 Hz, 4-Hβ, 1 H), 2.49 (dq, $J_{6a\beta,6\alpha}$ = 7.8, $J_{6a\beta,6\beta}$ = 7.8, $J_{6a\beta,7}$ = 4.4, $J_{6a\beta,7}$ = 7.8 Hz, 6a-Hβ, 1 H), 2.72 (dt, $J_{7a\alpha,3a\alpha}$ = 7.5, $J_{7a\alpha,7}$ = 7.5, $J_{7a\alpha,7}$ = 8.5 Hz, 7a-Hα, 1 H), 2.83−2.91 (m, 4′-H, 6′-H, OH, 5 H), 3.29 (dt, $J_{3a\alpha,3\alpha}$ = 8.9, $J_{3a\alpha,3\beta}$ = 7.5, $J_{3a\alpha,7a\alpha}$ = 7.5 Hz, 3a-Hα, 1 H), 3.73 (dd, $J_{3\beta,3\alpha}$ = 9.2, $J_{3\beta,3a\alpha}$ = 7.5 Hz, 3-Hβ, 1 H), 4.13 (dd, $J_{3\alpha,3\beta}$ = 9.2, $J_{3\alpha,3a\alpha}$ = 8.9 Hz, 3-Hα, 1 H), 5.28 (s, 1-H, 1 H), 6.22 (s, 8-H, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$, in part): δ = 24.63 (u), 29.27 (d, Me), 29.61 (u), 30.32 (d, Me), 30.45 (u), 34.16 (u), 39.74 (u, C-5), 47.69 (u), 50.86 (d), 52.91 (d), 53.57 (d), 56.99 (u), 59.08 (u, C-3b), 70.68 (u, C-3), 103.25 (d, C-1), 126.06 (u, C-2′), 143.67 (d, C-8). − **24b**: ^{1}H NMR (300 MHz, $CDCl_3$, in part): δ = 0.93 (s, Me, 3 H), 10.6 (s, Me, 3 H), 3.84 (t, 3-Hα, 1 H), 5.52 (t, 1-Hα, 1 H), 6.19 (s, 8-H, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$, in part): δ = 46.85 (u), 54.11 (d), 68.65 (u), 142.76 (d). − MS (EI, 70 eV); *m/z* (%): 328 (12), 327 (23), 326 [M^+] (100), 324 (11), 275 (15), 269 (12), 253 (12), 252 (38), 251 (19), 239 (14), 220 (11), 219 (25), 218 (11), 205 (10), 202 (11), 195 (17), 193 (21), 192 (11), 179 (19), 173 (13), 165 (15), 161 (11), 160 (13), 159 (14), 151 (10), 149 (14), 147 (23), 145 (42), 137 (12), 135 (24), 134 (13), 133 (20), 132 (52), 131 (18), 123 (12), 119 (13), 117 (16), 115 (14), 111 (12), 109 (12), 108 (10), 107 (28), 106 (73), 105 (29), 97 (15), 95 (11), 93 (25), 91 (25), 91 (46), 87 (13), 85 (12). − IR (KBr): ṽ = 3402 (s), 3023 (w), 2953 (s), 2892 (s), 2861 (s), 2845 (s), 2510 (w), 1637 (w), 1564 (w), 1480 (w), 1462 (m), 1438 (m), 1424 (m), 1384 (m), 1366 (m), 1340 (m), 1313 (w), 1293 (m), 1282 (m), 1266 (w), 1242 (m), 1198 (m), 1174 (m), 1122 (w), 1096 (m), 1071 (s), 1044 (m), 1027 (w),

1009 (s), 982 (s), 957 (w), 913 (m), 900 (s), 886 (m), 834 (w), 819 (w), 789 (w). − $C_{17}H_{26}O_2S_2$ (326.5): calcd. C 62.53, H 8.02; found C 62.41, H 7.99.

[4′aS-(4′aα,5′b,6′aβ,9′aS)]- and [4′aS-(4′aα,5′α,6′aβ,9′aS*)]-4′,4′a,5′,6′,6′a,-7′,8′,9′-Octahydro-8′,8′-dimethylspiro[1,3-dithiane-2,2′(1H)-pentaleno-[1,6a-c]pyran]-5′-carbaldehyde* (**25a** and **25b**): To a solution of **24a/b** (240 mg, 0.74 mmol) in EtOH-free CH_2Cl_2 was added pyridinium *p*-toluenesulfonate (54 mg, 0.25 mmol). After stirring the solution for 14 h at room temp., it was concentrated in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane, 1:3) gave **25a/b** (235 mg, 98%) as a colorless powder. Single crystals of **25a** were grown by dissolving **25a/b** (10 mg) in a small amount of EtOAc and adding *n*-hexane until turbid. The solution was warmed until clear and was then slowly cooled to 4°C. In this way, **25a** was obtained as colorless plates: m.p. 112°C, $[\alpha]_D$ = −90.6 (*c* = 1.00, diethyl ether). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (s, Me, 3 H), 1.06 (s, Me, 3 H), 1.24 (dd, *J* = 9.8, *J* = 12.5 Hz, 1 H), 1.54−1.97 (m, 7 H), 2.08 (m, 2′-H, 1 H), 2.21 (ddd, *J* = 2.7, *J* = 2.7, *J* = 9.8 Hz, 1 H), 2.34−2.61 (m, 1′-H, 3′-H, 4 H), 3.00 (m, 1 H), 3.01 (ddd, *J* = 2.7, *J* = 12.8, *J* = 13.8 Hz, 1′-H or 3′-H, 1 H), 3.37 (ddd, *J* = 2.7, *J* = 12.8, *J* = 13.8 Hz, 3′-H or 1′-H, 1 H), 3.97 (dd, $J_{4\beta,4\alpha}$ = 12.5, $J_{4\beta,4a\alpha}$ = 2.4 Hz, 4-Hβ, 1 H), 4.18 (dd, $J_{4\alpha,4\beta}$ = 12.5, $J_{4\alpha,4a\alpha}$ = 3.7 Hz, 4-Hα, 1 H), 9.85 (d, $J_{CHO,5\alpha}$ = 2.4 Hz, C*H*O, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.07 (u, thioacetal), 26.16 (u, thioacetal), 27.12 (u, thioacetal), 27.28 (u), 30.36 (d, Me), 31.31 (d, Me), 41.27 (u, C-8), 46.05 (u), 47.94 (u), 47.94 (d), 51.34 (d), 51.89 (u, C-9a), 53.92 (d), 55.49 (u), 59.43 (u, C-4), 86.44 (u, C-2), 204.10 (d, CHO). − MS (EI, 70 eV); *m*/*z* (%): 326 [M$^+$] (21), 298 (31), 224 (13), 176 (10), 149 (22), 148 (24), 135 (10), 133 (10), 121 (10), 119 (16), 108 (10), 107 (18), 106 (100), 105 (12), 93 (21), 92 (16), 91 (23), 79 (17), 77 (14). − IR (KBr): ṽ = 2943 (s), 2929 (s), 2863 (s), 2830 (m), 2728 (m), 2101 (w), 2029 (w), 1999 (w), 1714 (s), 1450 (m), 1432 (m), 1412 (w), 1397 (w), 1386 (w), 1366 (m), 1338 (w), 1306 (w), 1280 (m), 1252 (w), 1239 (w), 1185 (w), 1145 (w), 1124 (w), 1110 (m), 1098 (m), 1083 (m), 1062 (m), 1046 (m), 1022 (m), 1003 (m), 974 (m), 937 (m), 907 (m), 870 (w), 841 (w), 816 (w). − $C_{17}H_{26}O_2S_2$ (326.5): calcd. C 62.53, H 8.02; found: C 62.53, H 8.32.

After having been kept in $CDCl_3$ solution for 24 h, **25a** had partially epimerized to **25b**. Data for **25b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (s, Me, 3 H), 1.06 (s, Me, 3 H), 1.19 (dd, $J_{7\alpha,6a\beta}$ = 12.1, $J_{7\alpha,7\beta}$ = 15.1 Hz, 7-Hα, 1 H), 3.45 (ddd, *J* = 3.0, *J* = 12.8, *J* = 13.8 Hz, 3′-H or 1′-H, 1 H), 3.75 (dd, $J_{4\beta,4\alpha}$ = 12.5, $J_{4\beta,4a\alpha}$ = 0.7 Hz, 4-Hβ, 1 H), 4.18 (dd, $J_{4\alpha,4\beta}$ = 12.5, $J_{4\alpha,4a\alpha}$ = 3.7 Hz, 4-Hα, 1 H), 9.74 (d, $J_{CHO,5\beta}$ = 2.0 Hz, CHO, 1 H).

[4aS-(4aα,5β,6aβ,9aS)]- and [4aS-(4aα,5α,6aβ,9aS*)]-1,2,4,4a,5,6,6a,7,8,9-Decahydro-8,8-dimethyl-2-oxopentaleno[1,6a-c]pyran-5-carbaldehyde* (**26a** and **26b**): To a solution of **25a/b** (7 mg, 21.5 μmol) in 10% H_2O/MeCN (1 ml), $PhI(CF_3COO)_2$ (15 mg, 34.9 μmol) was added at room temp. After stirring the mixture for 5 min., saturated aqueous Na_2CO_3 was added and the aqueous phase was extracted with diethyl ether. The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane, 1:1) furnished a mixture of **26a/b** (4 mg, 79%) in a ratio of 1.4:1 as a colorless oil: $[\alpha]_D$ = +9.67 (*c* = 1.20, diethyl ether). − **26a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.02 (s, β-Me, 3 H), 1.04 (s, α-Me, 3 H), 1.18 (dd, $J_{7\alpha,7\beta}$ = 13.3, $J_{7\alpha,6a\beta}$ = 8.4 Hz, 7-Hα, 1 H), 1.66 (dd, $J_{9\beta,7\beta}$ = 1.5, $J_{9\beta,9\alpha}$ = 13.7 Hz, 9-Hβ, 1 H), 1.69 (ddd, $J_{7\beta,7\alpha}$ = 13.3, $J_{7\beta,6a\beta}$ = 7.8, $J_{7\beta,9\beta}$ = 1.5 Hz, 7-Hβ, 1 H), 1.76 (d, $J_{9\alpha,9\beta}$ = 13.7 Hz, 9-Hα, 1 H), 1.91 (ddd, $J_{6\alpha,6\beta}$ = 13.6, $J_{6\alpha,5\alpha}$ = 6.0, $J_{6\alpha,6a\beta}$ = 4.7 Hz, 6-Hα, 1 H), 2.19 (ddd, $J_{6\beta,6\alpha}$ = 13.6, $J_{6\beta,5\alpha}$ = 8.7, $J_{6\beta,6a\beta}$ = 7.6 Hz, 6-Hβ, 1 H), 2.42 (dq, $J_{6a\beta,6\alpha}$ = 4.7, *J* = 8.1 Hz, 6a-Hβ, 1 H), 2.56 (d, $J_{1\alpha,1\beta}$ = 14.8 Hz, 1-Hα, 1 H), 2.60 (d, $J_{1\beta,1\alpha}$ = 14.8 Hz, 1-Hβ, 1 H), 2.78−2.82 (m, 5-Hα, 4a-Hα, 2 H), 4.06 (dd, $J_{4\alpha,4\beta}$ = 11.8, $J_{4\alpha,4a\alpha}$ = 4.8 Hz, 4-Hα, 1 H), 4.32 (dd, $J_{4\beta,4\alpha}$ = 11.8, $J_{4\beta,4a\alpha}$ = 4.3 Hz, 4-Hβ, 1 H), 9.76 (d, $J_{CHO,5\alpha}$ = 0.5 Hz, CHO, 1 H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.83 (d, β-Me), 30.95 (d, α-Me), 31.70 (u), 40.88 (u, C-8), 42.21 (u, C-1), 46.35 (d), 46.66 (u), 52.27 (d), 53.94 (u, C-9a), 56.10 (u), 56.93 (d), 69.39 (u, C-4), 172.22 (u, C-2), 201.97 (d, CHO). − **26b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.04 (s, β-Me, 3 H), 1.06 (s, α-Me, 3 H), 1.18 (t, $J_{7\alpha,7\beta}$ = 11.6 Hz, 7-Hα, 1 H), 1.48 (d, $J_{9\alpha,9\beta}$ = 13.6 Hz, 9-Hα, 1 H), 1.76 (ddd, $J_{7\beta,7\alpha}$ = 13.0, $J_{7\beta,6a\beta}$ = 7.5, $J_{7\beta,9\beta}$ = 2.4 Hz, 7-Hβ, 1 H), 1.77 (dd, $J_{6\beta,6\alpha}$ = 13.4, $J_{6\beta,5\beta}$ = 6.3 Hz, 6-Hβ, 1 H), 1.81 (dd, $J_{9\beta,9\alpha}$ = 13.6, $J_{9\beta,7\beta}$ = 2.4 Hz, 9-Hβ, 1 H), 2.11 (dt, $J_{6\alpha,6\beta}$ = 13.4, $J_{6\alpha,6a\beta}$ = 7.6, $J_{6\alpha,5\beta}$ = 7.6 Hz, 6-Hα, 1 H), 2.47 (dt, $J_{4a\alpha,4\beta}$ = 5.2, *J* = 8.5 Hz, 4a-Hα, 1 H), 2.54 (dt, $J_{6a\beta,7\beta}$ = 7.5, *J* = 11.1 Hz, 6a-Hβ, 1 H), 2.59 (d, $J_{1\alpha,1\beta}$ = 14.7 Hz, 1-Hα, 1 H), 2.69 (d, $J_{1\beta,1\alpha}$ = 14.7 Hz, 1-Hβ, 1 H), 3.23 (dddd, $J_{5\beta,CHO}$ = 1.7, $J_{5\beta,6\beta}$ = 6.3, *J* = 8.3, *J* = 13.3 Hz, 5-Hβ, 1 H), 4.07 (dd, $J_{4\alpha,4\beta}$ = 11.9, $J_{4\alpha,4a\alpha}$ = 8.8 Hz, 4-Hα, 1 H), 4.27 (dd, $J_{4\beta,4\alpha}$ = 11.9, $J_{4\beta,4a\alpha}$ = 5.2 Hz, 4-Hβ, 1 H), 9.88 (d, $J_{CHO,5\beta}$ = 1.7 Hz, C*H*O, 1 H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.41 (β-Me), 29.60 (α-Me), 30.55 (C-6), 40.70 (C-8), 42.43 (C-1), 46.19 (C-4a), 48.11 (C-7), 51.07 (C-6a), 52.25 (C-5), 52.85 (C-9a), 56.69 (C-9), 66.17 (C-4), 172.61 (C-2), 202.21 (CHO). − MS (EI, 70 eV); *m*/*z* (%): 236 [M$^+$] (7), 218 (14), 193 (39), 179 (12), 177 (36), 176 (24), 175 (10), 165 (15), 163 (13), 162 (12), 161 (24), 159 (18), 152 (10), 151 (16), 149 (29), 148 (81), 147 (21), 146 (11), 145 (11), 135 (22), 134 (13), 133 (46), 131 (16), 121 (20), 120 (24), 119 (23), 117 (13), 115 (13), 109 (21), 108 (15), 107 (51), 106 (16), 105 (38), 97 (11), 95 (29), 94 (13), 93 (58), 92 (38), 91 (72), 83 (18), 82 (26), 81 (30), 80 (11), 79 (55), 78 (14), 77 (52), 71 (13), 70 (12), 69 (26), 67 (43), 65 (25). − IR ($CHCl_3$): ṽ = 2956 (s), 2930 (s), 2867 (s), 2719 (m), 2432 (m), 2257 (w), 1745 (s), 1724 (s), 1463 (m), 1446 (m), 1431 (m), 1387 (m), 1368 (m), 1351 (m), 1280 (s), 1260 (s), 1182 (m), 1162 (m), 1120 (m), 1077 (s), 1044 (s), 910 (w), 880 (w), 825 (m). − $C_{14}H_{20}O_3$: calcd. 236.1412, found 236.1414 (MS).

[4aR-(4aα,5β,6aβ,9aR)]- and [4aR-(4aα,5α,6aβ,9aR*)]-1,2,4,4a,5,6,6a,7,8,9-Decahydro-8,8-dimethyl-2-oxo-5-phenylselenylpentaleno[1,6a-c]pyran-5-carbaldehyde* (**27a** and **27b**): To a solution of a 3:2 mixture of **26a/b** (13 mg, 55.1 μmol) in CH_2Cl_2 (1 ml), $PhSeNEt_2$ (18 mg, 79.0 μmol) was added dropwise at room temp. over a period of 10 min. After stirring the mixture for 4 h at room temp., the volatiles were removed in vacuo. Purification of the yellow oily residue by chromatography (EtOAc/*n*-hexane, 1:3) gave a mixture of **27a/b** (17 mg, 79%) in a ratio of 7.4:1 as an oil: $[\alpha]_D$ = −152.6 (*c* = 1.27, diethyl ether). − **27a**: ^{1}H NMR (500 MHz, C_6D_6): δ = 0.63 (s, β-Me, 3 H), 0.75 (dd, $J_{7\alpha,6a\beta}$ = 11.3, $J_{7\alpha,7\beta}$ = 12.9 Hz, 7-Hα, 1 H), 0.78 (s, α-Me, 3 H), 1.12 (ddd, $J_{7\beta,6a\beta}$ = 8.2, $J_{7\beta,7\alpha}$ = 12.9, $J_{7\beta,9\beta}$ = 2.3 Hz, 7-Hβ, 1 H), 1.28 (dd, $J_{9\beta,7\beta}$ = 2.3, $J_{9\beta,9\alpha}$ = 13.6 Hz, 9-Hβ, 1 H), 1.46 (d, $J_{6\alpha,6\beta}$ = 13.7 Hz, 6-Hα, 1 H), 1.50 (d, $J_{9\alpha,9\beta}$ = 13.6 Hz, 9-Hα, 1 H), 1.69 (dd, $J_{6\beta,6\alpha}$ = 13.7, $J_{6\beta,6a\beta}$ = 8.2 Hz, 6-Hβ, 1 H), 19.1 (dt, $J_{6a\beta,6\beta}$ = 8.2, $J_{6a\beta,7\alpha}$ = 11.3, $J_{6a\beta,7\beta}$ = 8.2 Hz, 6a-Hβ, 1 H), 2.14 (d, $J_{1\beta,1\alpha}$ = 14.3 Hz, 1-Hβ, 1 H), 2.22 (d, $J_{1\alpha,1\beta}$ = 14.3 Hz, 1-Hα, 1 H), 2.74 (dd, $J_{4a\alpha,4\alpha}$ = 5.1, $J_{4a\alpha,4\beta}$ = 7.2 Hz, 4a-Hα, 1 H), 3.92 (dd, $J_{4\alpha,4\beta}$ = 11.9, $J_{4\alpha,4a\alpha}$ = 5.1 Hz, 4-Hα, 1 H), 4.16 (dd, $J_{4\beta,4\alpha}$ = 11.9, $J_{4\beta,4a\alpha}$ = 7.2 Hz, 4-Hβ, 1 H), 6.92 (m, *m*- and *p*-H, 3 H), 7.27 (m, *o*-H, 2 H), 8.96 (s, CHO, 1 H). − ^{13}C NMR (125 MHz, C_6D_6): δ = 27.55 (d, β-Me), 29.37 (d, α-Me), 37.52 (u), 40.78 (u, C-8), 43.13 (u, C-1), 47.11 (d), 47.29 (u), 50.11 (d), 53.92 (u, C-9a), 54.95 (u), 66.94 (u, C-5), 69.33 (u, C-4), 129.07 (d), 129.51 (d), 135.75 (d), 137.37 (u), 170.92 (u, C-2), 190.21 (d, *C*HO). − **27b**: ^{1}H NMR (500 MHz, C_6D_6, in part): δ = 0.73 (s, Me, 3 H), 0.98 (s, Me, 3 H), 1.39 (dd, $J_{9\beta,9\alpha}$ = 14.0, $J_{9\beta,7\beta}$ =

1.3 Hz, 9-Hβ, 1 H), 1.40 (ddd, $J_{7\beta,7\alpha}$ = 12.92, $J_{7\beta,6a\beta}$ = 8.8, $J_{7\beta,9\beta}$ = 1.3 Hz, 7-Hβ, 1 H), 1.55 (d, $J_{9\alpha,9\beta}$ = 14.0 Hz, 9-Hα, 1 H), 1.57 (dd, $J_{6\alpha,6\beta}$ = 14.8, $J_{6\alpha,6a\beta}$ = 5.4 Hz, 6-Hα, 1 H), 1.82 (dd, $J_{7\alpha,7\beta}$ = 12.9, $J_{7\alpha,6a\beta}$ = 7.9 Hz, 7-Hα, 1 H), 1.97 (m, 6a-Hβ, 1 H), 2.33 (dd, $J_{6\beta,6\alpha}$ = 14.8, $J_{6\beta,6a\beta}$ = 8.2 Hz, 6-Hβ, 1 H), 3.54 (dd, $J_{4\alpha,4a\alpha}$ = 5.1, $J_{4\alpha,4\beta}$ = 11.9 Hz, 4-Hα, 1 H), 3.58 (dd, $J_{4\beta,4a\alpha}$ = 6.5, $J_{4\beta,4\alpha}$ = 11.9 Hz, 4-Hβ, 1 H), 7.40 (m, *o*-H, 2 H), 9.23 (s, CHO, 1 H). − MS (EI, 70 eV); *m/z* (%): 394 [M^+ for $C_{20}H_{24}O_3{}^{82}Se$] (21), 393 (22), 392 [M^+ for $C_{20}H_{24}O_3{}^{80}Se$] (100), 391 (10), 390 [M^+ for $C_{20}H_{24}O_3{}^{78}Se$] (51), 389 [M^+ for $C_{20}H_{24}O_3{}^{77}Se$] (23), 388 [M^+ for $C_{20}H_{24}O_3{}^{76}Se$] (23), 364 (12), 363 (37), 361 (24), 235 (25), 217 (31), 207 (28), 206 (11), 205 (40), 189 (26), 176 (13), 175 (88), 171 (14), 165 (10), 164 (11), 163 (41), 161 (19), 159 (52), 158 (28), 157 (12), 146 (13), 145 (65), 141 (10), 135 (25), 133 (34), 131 (17), 129 (14), 121 (25), 119 (29), 117 (20), 115 (15), 109 (14), 107 (52), 105 (59), 103 (10), 97 (15), 95 (23), 94 (11), 93 (46), 92 (14), 91 (85), 85 (10), 83 (20), 82 (10), 81 (25), 80 (12), 79 (60), 78 (47), 77 (98), 71 (23), 70 (12), 69 (40). − IR ($CHCl_3$): $\tilde{\nu}$ = 2960 (s), 2930 (s), 2860 (m), 2710 (w), 1750 (vs), 1710 (vs), 1580 (w), 1480 (m), 1465 (m), 1450 (w), 1440 (m), 1390 (m), 1370 (m), 1350 (w), 1315 (w), 1285 (m), 1255 (s), 1170 (m), 1160 (m), 1115 (m), 1090 (m), 1080 (m), 1055 (m), 1040 (s), 1020 (m), 975 (w), 960 (w), 840 (w). − $C_{20}H_{24}O_3{}^{80}Se$: calcd. 392.0891, found 392.0896 (MS).

[4aR-(4aα,6aβ,9aR)]-1,2,4,4a,6a,7,8,9-Octahydro-8,8-dimethyl-2-oxopentaleno[1,6a-c]pyran-5-carbaldehyde* (**28**) *and [6aS-(6aβ,9aS*)]-1,2,4,6,6a,7,8,9-Octahydro-8,8-dimethyl-2-oxopentaleno[1,6a-c]pyran-5-carbaldehyde* (**29**): *(a) From* **30a/b** with AgO: To a solution of **30a/b** (28 mg, 58 μmol) in H_2O/THF, 1:9 (5 ml), was added AgO (31 mg, 250 μmol). The suspension was stirred for 3 d at room temp., in the course of which its color changed from black to brown. The volatiles were then removed in vacuo, and the residue was suspended in EtOAc. The suspension was filtered and the solid material was washed with EtOAc. The filtrate was concentrated in vacuo and the residue was purified by chromatography (EtOAc/*n*-hexane, 1:3) to give a mixture of **28** and **29** (4 mg, 29%) in a ratio of 4.1:1 (^{1}H NMR and HPLC: RP-Phase, 5 μm, MeCN/H_2O, 1:3).

(b) From **30a/b** *with $AgNO_3$:* To a solution of **30a/b** (9 mg, 19 μmol) in MeCN/THF/water, 6:2:1 (2.5 ml), $AgNO_3$ (7 mg, 41 μmol) in water (0.5 ml) was slowly added. After stirring the mixture for 10 h at room temp., the volatiles were removed in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane, 1:1) gave a mixture of **28** and **29** (3 mg, 69%) in a ratio of 14:1 (HPLC: RP-Phase 5 μm, MeCN/H_2O, 1:3).

(c) From **30a/b** *with $AgNO_3$ and H_2O_2:* To a solution of a mixture of **30a/b** (34 mg, 71 μmol) in MeCN (3 ml), THF (1 ml), and water (0.5 ml), a solution of $AgNO_3$ (25 mg, 147 μmol) in water (0.5 ml) was added dropwise at 0°C, resulting in a yellow coloration. After stirring the mixture for 30 min. at room temp., it became turbid, and, according to TLC (EtOAc/*n*-hexane, 1:3), the selenides **30a/b** had been completely transformed to **27a/b**. The yellow solid material was removed by filtration through a pad of Celite and washed several times with diethyl ether. To the combined filtrates was added water (5 ml). The organic phase was separated, dried ($MgSO_4$) and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and to the resulting solution H_2O_2 (0.21 mmol, 1.5 ml of a 0.14 M solution in H_2O) was added at 0°C under rapid stirring. After removal of the cooling bath, the mixture was stirred rapidly for 2 h at room temp. The organic phase was separated, and the aqueous phase was washed with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane, 1:3) gave a mixture of **28** and **29** (15 mg, 91%) in a ratio of 7.2:1 (^{1}H NMR). After stirring a 7.2:1 mixture of **28** and **29** in MeCN for 30 h at room temperature, the ratio changed to 14.5:1 (HPLC: RP-Phase, 5 μm, MeCN/H_2O, 1:2).

(d) From **27a/b** *with H_2O_2:* To a rapidly stirred solution of **27a/b** (11 mg, 28 μmol) in CH_2Cl_2 (1.5 ml) at 0°C, H_2O_2 (63 μmol, 0.7 ml of a 0.09 M solution in H_2O) was added dropwise over a period of 10 min. Stirring the mixture for 15 min. at 0°C and for 20 h at room temp., followed by work-up as described above, gave a mixture of **28** and **29** (6 mg, 91%) in a ratio of 14:1 (^{1}H NMR) as colorless crystals: m.p. 108°C, $[\alpha]_D$ = −15.6 (*c* = 0.5, diethyl ether).

28: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (s, Me, 3 H), 1.08 (s, Me, 3 H), 1.42 (dd, $J_{7\alpha,6a\beta}$ = 5.7, $J_{7\alpha,7\beta}$ = 13.2 Hz, 7-Hα, 1 H), 1.72 (dd, $J_{9\beta,7\beta}$ = 0.7, $J_{9\beta,9\alpha}$ = 13.6 Hz, 9-Hβ, 1 H), 1.80 (d, $J_{9\alpha,9\beta}$ = 13.6 Hz, 9-Hα, 1 H), 1.93 (ddd, $J_{7\beta,6a\beta}$ = 9.4, $J_{7\beta,7\alpha}$ = 13.2, $J_{7\beta,9\beta}$ = 0.7 Hz, 7-Hβ, 1 H), 2.58 (d, $J_{1\beta,1\alpha}$ = 14.5 Hz, 1-Hβ, 1 H), 2.67 (d, $J_{1\alpha,1\beta}$ = 14.5 Hz, 1-Hα, 1 H), 3.23 (m, 4a-Hα, 6a-Hβ, 2 H), 4.42 (dd, $J_{4\alpha,4\beta}$ = 11.8, $J_{4\alpha,4a\alpha}$ = 4.1 Hz, 4-Hα, 1 H), 4.50 (dd, $J_{4\beta,4\alpha}$ = 11.8, $J_{4\beta,4a\alpha}$ = 3.7 Hz, 4-Hβ, 1 H), 6.91 (s, 6-H, 1 H), 9.74 (s, CHO, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.96 (d, Me), 29.45 (d, Me), 40.93 (u, C-8), 42.06 (u, C-1), 45.92 (u), 51.48 (d, C-4a), 52.18 (u, C-9a), 56.27 (u), 58.57 (d), 66.94 (u, C-4), 142.44 (u, C-5), 158.24 (d, C-6), 172.27 (u, C-2), 189.64 (d, CHO). − GC-MS (EI, 70 eV); *m/z* (%): 235 (14), 234 [M^+] (38), 216 (13), 192 (10), 188 (10), 178 (16), 177 (12), 175 (26), 173 (13), 163 (18), 162 (71), 161 (11), 160 (19), 159 (16), 147 (78), 145 (25), 133 (22), 131 (15), 128 (14), 122 (15), 120 (13), 119 (38), 117 (13), 115 (14), 107 (26), 106 (47), 105 (46), 103 (10), 93 (13), 92 (15), 91 (100), 79 (37), 78 (57), 77 (57), 65 (35).

29: ^{1}H NMR (300 MHz, $CDCl_3$, in part): δ = 5.16 (dt, $J_{4\alpha,4\beta}$ = 15.5, $J_{4,6}$ = 3.4 Hz, 4-H, 1 H), 5.59 (d, $J_{4\alpha,4\beta}$ = 15.5 Hz, 4-H, 1 H), 9.91 (s, CHO, 1 H). − GC-MS (EI, 70 eV); *m/z* (%): 234 [M^+] (10), 193 (16), 192 (100), 177 (19), 163 (15), 137 (23), 136 (30), 131 (15), 121 (16), 119 (11), 109 (25), 107 (27), 105 (21), 98 (17), 97 (10), 93 (17), 92 (10), 91 (61), 81 (13), 79 (36), 78 (10), 77 (42), 67 (10), 65 (23). − IR (KBr): $\tilde{\nu}$ = 3053 (w), 3002 (m), 2953 (s), 2927 (s), 2859 (m), 2738 (w), 1751 (s), 1739 (s), 1664 (s), 1622 (m), 1486 (m), 1464 (m), 1442 (m), 1385 (m), 1368 (m), 1357 (m), 1337 (m), 1311 (m), 1302 (m), 1282 (m), 1266 (m), 1253 (m), 1235 (m), 1205 (m), 1184 (s), 1168 (m), 1142 (m), 1098 (m), 1079 (s), 1054 (m), 1027 (m), 1006 (m), 978 (w), 931 (w), 911 (w), 875 (m), 860 (m), 829 (m), 807 (w), 784 (w), 770 (w), 750 (m), 730 (w). − $C_{14}H_{18}O_3$: calcd. 234.1256, found 234.1261 (MS).

[4'aR-(4'aα,5'α,6'aβ,9'aR)]- and [4'aR-(4'aα,5'β,6'aβ,9'aR*)]-4',4'a,5',6',6'a,7',8',9'-Octahydro-8',8'-dimethyl-5'-phenylselenylspiro[1,3-dithiane-2,2'(1H)-pentaleno[1,6a-c]pyran-5'-carbaldehyde* (**30a** and **30b**): To a solution of **25a/b** (78 mg, 0.24 mmol) in CH_2Cl_2 (1 ml) at room temp., $PhSeNEt_2$ (65 mg, 0.29 mmol) was added dropwise by means of a syringe. After stirring the solution for 4 h at room temp., the volatiles were removed in vacuo. Purification of the yellow residue by chromatography (EtOAc/*n*-hexane, 1:4) gave a mixture of **30a/b** (101 mg, 88%) in a ratio of 2.5:1 as a light-yellow oil, which crystallized after drying under high vacuum at room temp. to give colorless crystals: m.p. 81°C, $[\alpha]_D$ = −118.8 (*c* = 0.99, diethyl ether). − **30a** (in the mixture with **30b**): ^{1}H NMR (300 MHz, C_6D_6): δ = 0.79 (s, Me, 3 H), 0.89 (s, Me, 3 H), 1.26 (dd, $J_{7\beta,6a\beta}$ = 6.8, $J_{7\beta,7\alpha}$ = 13.0 Hz, 7-Hβ, 1 H), 1.34−2.30 (m, 9 H), 1.70 (dd, $J_{9\beta,9\alpha}$ = 13.9, $J_{9\beta,7\beta}$ = 1.0 Hz, 9-Hβ, 1 H), 1.79 (d, $J_{9\alpha,9\beta}$ = 13.9 Hz, 9-Hα, 1 H), 2.12 (d, $J_{1\beta,1\alpha}$ = 14.5 Hz, 1-Hβ, 1 H), 2.59 (d, $J_{1\alpha,1\beta}$ = 14.5 Hz, 1-Hα, 1 H), 2.88 (ddd, *J* = 2.4, *J* = 12.6, *J* = 14.0 Hz, 1'-H, 1 H), 3.37 (ddd, *J* = 2.4, *J* = 13.0, *J* = 14.0 Hz, 3'-H, 1 H), 4.03 (dd, $J_{4\alpha,4\beta}$ = 12.6, $J_{4\alpha,4a\alpha}$ =

2.4 Hz, 4-Hα, 1 H), 4.09 (dd, $J_{4\beta,4\alpha}$ = 12.6, $J_{4\beta,4a\alpha}$ = 4.1 Hz, 4-Hβ, 1 H), 6.90−7.01 (m, *m*- and *p*-H, 3 H), 7.48 (m, *o*-H, 2 H), 9.30 (s, CHO, 1 H). − ^{13}C NMR (75 MHz, C_6D_6): δ = 25.30 (u, thioacetal), 26.53 (u, thioacetal), 27.41 (u, thioacetal), 29.91 (d, Me), 30.78 (d, Me), 37.08 (u), 41.13 (u, C-8), 47.08 (u), 47.59 (d), 47.63 (u), 50.71 (d), 52.57 (u, C-9a), 56.38 (u), 61.47 (u, C-4), 66.18 (u, C-5), 87.22 (u, C-2), 128.94 (d), 129.11 (d), 137.20 (d), 191.23 (*C*HO) (the signal for the *i*-C was not detected). − **30b** (in the mixture with **30a**): ^{1}H NMR (300 MHz, C_6D_6, in part): δ = 0.74 (s, Me, 3 H), 0.97 (s, Me, 3 H), 3.12 (dd, *J* = 8.2, *J* = 14.7 Hz, 1 H), 3.24 (dt, *J* = 3.1, *J* = 13.0 Hz, 1′-H or 3′-H, 1 H), 3.93 (d, $J_{4\alpha,4\beta}$ = 12.6 Hz, 1 H, 4-Hα, 1 H), 9.97 (s, CHO, 1 H). − ^{13}C NMR (75 MHz, C_6D_6): δ = 25.15 (u), 25.78 (u), 25.97 (u), 27.22 (u), 31.04 (d, Me), 35.07 (d, Me), 37.50 (d, CH), 45.91 (u), 48.39 (u), 54.95 (d), 55.69 (u), 57.71 (u, C-4), 129.32 (d), 137.29 (d), 192.57 (d, CHO). − MS (EI, 70 eV); *m/z* (%): 482 [M^+ for $C_{23}H_{30}O_2S_2{}^{80}Se$] (9), 326 (17), 325 (70), 220 (14), 219 (100), 191 (40), 177 (19), 176 (42), 175 (65), 173 (12), 161 (12), 147 (28), 133 (16), 121 (14), 119 (14), 109 (13), 107 (28), 106 (55), 105 (26), 95 (12), 93 (18), 91 (38), 83 (12), 81 (21), 79 (21), 78 (11), 77 (29), 73 (10), 69 (13), 67 (15), 65 (10). − IR ($CHCl_3$): ṽ = 2954 (s), 2932 (s), 2865 (m), 1731 (m), 1699 (s), 1578 (w), 1477 (m), 1464 (m), 1448 (m), 1438 (m), 1426 (m), 1414 (w), 1386 (w), 1367 (m), 1332 (w), 1279 (m), 1155 (w), 1101 (m), 973 (w), 942 (w), 908 (m), 871 (w), 850 (w), 827 (w), 693 (m), 630 (w), 535 (w), 513 (w), 475 (w). − $C_{23}H_{30}O_2S_2{}^{80}Se$: calcd. 482.0852, found 482.0841 (MS).

Methyl [4aR-(4aα,6aβ,9aR)]-1,2,4,4a,6a,7,8,9-Octahydro-8,8-dimethyl-2-oxopentaleno[1,6a-c]pyran-5-carboxylate* (**2**): To a stir·red solution of a 14:1 mixture of **28** and **29** (9 mg, 38 μmol) in MeOH (5 ml), which contained AcOH (58 μmol, 1.1 ml of a 5.3 mM solution in MeOH), were added NaCN (9.4 mg, 0.19 mmol) and freshly prepared MnO_2 (70 mg, 0.81 mmol). After stirring the mixture for 18 h at room temp., the volatiles were removed in vacuo. The residue was suspended in diethyl ether and the suspension was filtered though a pad of Celite. The solid material was washed several times with diethyl ether and the filtrate was concentrated in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane, 1:3) gave a mixture of **2** and **31** (8 mg, 80%) in a ratio of 9:1 (^{1}H NMR) as a colorless oil, which crystallized upon storage at −25°C. Recrystallization from *n*-hexane furnished **2** (4 mg, 43%) as colorless crystals of purity ≥ 98% (HPLC: RP-Phase, 5 μm, linear gradient of MeCN/H_2O; initial ratio 40:60, after 10 min. 60:40, after 20 min. 70:30, R_t (**2**) = 9.74 min., R_t (**31**) = 11.41 min.). Concentration of the mother liquor gave a mixture of **2** and **31** (4 mg) in a ratio of 3:1 (HPLC).

2: m.p. 76°C, $[\alpha]_D$ = −58.1 (*c* = 0.26, $CHCl_3$). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.02 (s, α-Me, 3 H), 1.06 (s, β-Me, 3 H), 1.38 (ddd, $J_{7\alpha,7\beta}$ = 13.0, $J_{7\alpha,6a\beta}$ = 5.9, $J_{7\alpha,9\alpha}$ = 0.6 Hz, 7-Hα, 1 H), 1.71 (dd, $J_{9\beta,7\beta}$ = 0.9, $J_{9\beta,9\alpha}$ = 13.5 Hz, 9-Hβ, 1 H), 1.78 (d, $J_{9\alpha,9\beta}$ = 13.5 Hz, 9-Hα, 1 H), 1.87 (ddd, $J_{7\beta,7\alpha}$ = 13.0, $J_{7\beta,6a\beta}$ = 9.5, $J_{7\beta,9\beta}$ = 0.9 Hz, 7-Hβ, 1 H), 2.57 (d, $J_{1\beta,1\alpha}$ = 14.4 Hz, 1-Hβ, 1 H), 2.63 (d, $J_{1\alpha,1\beta}$ = 14.4 Hz, 1-Hα, 1 H), 3.09−3.14 (m, 6a-Hβ, 1 H), 3.18−3.21 (m, 4a-Hα, 1 H), 3.75 (s, OMe, 3 H), 4.44 (dd, $J_{4\alpha,4\beta}$ = 11.8, $J_{4\alpha,4a\alpha}$ = 4.4 Hz, 4-Hα, 1 H), 4.50 (dd, $J_{4\beta,4\alpha}$ = 11.8, $J_{4\beta,4a\alpha}$ = 4.1 Hz, 4-Hβ, 1 H), 6.84 (m, 6-H, 1 H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.09 (d, α-Me), 29.54 (d, β-Me), 40.75 (u, C-8), 42.16 (u, C-1), 45.92 (u), 51.66 (d, OMe), 51.77 (u, C-9a), 53.49 (d), 56.43 (u), 58.18 (d), 67.75 (u, C-4), 131.66 (u, C-5), 150.28 (d, C-6), 164.58 (u, C-2), 172.55 (u, CO_2Me). − MS (EI, 70 eV); *m/z* (%): 264 [M^+] (22), 233 (12), 232 (46), 206 (11), 205 (65), 204 (14), 193 (14), 192 (100), 177 (26), 173 (17), 160 (17), 145 (14), 137 (10), 136 (79), 133 (38), 132 (10), 119 (11), 117 (10), 105 (37), 91 (27), 77 (16), 70 (17), 69 (11), 65 (11). − IR ($CHCl_3$): ṽ = 2957 (m), 2930 (m), 2870 (w), 1749 (s), 1713 (s), 1634 (w), 1483 (w), 1463 (w), 1439 (m), 1384 (w), 1368 (w), 1354 (m), 1336 (w), 1272 (m), 1159 (w), 1120 (m), 1082 (m), 1030 (w), 983 (w). − $C_{15}H_{20}O_4$: calcd. 264.13616, found 264.13566 (MS).

31: ^{1}H NMR (500 MHz, $CDCl_3$, in part): δ = 1.03 (s, Me, 3 H), 1.04 (s, Me, 3 H), 1.65 (dd, *J* = 1.5, *J* = 13.3 Hz, 9-H, 1 H), 2.65 (d, $J_{1\beta,1\alpha}$ = 15.9 Hz, 1-H, 1 H), 2.72 (d, $J_{1\alpha,1\beta}$ = 15.9 Hz, 1-H, 1 H), 3.66 (s, OMe, 3 H), 4.83 (dt, $J_{4\alpha,4\beta}$ = 18.0 Hz, $J_{4,6}$ = 2.8 Hz, 4-H, 1 H), 4.88 (ddd, $J_{4\alpha,4\beta}$ = 18.0, $J_{4,6}$ = 1.8, *J* = 3.7 Hz, 4-H, 1 H).

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[21] Interestingly, by the procedure described a mixture of **21a** and **21b** in a ratio of 18:1 was obtained. Upon sequential treatment of this mixture with *n*-BuLi and water the ratio of the isomers changed to 1:18. It seems that **21a** is the product of a kinetically controlled reduction of **14a** and that **21b** is the thermodynamically more stable isomer, possibly because of an intramolecular hydrogen bond. The configuration at C-1 of **21a** and **21b** was determined by NOE experiments.

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