Stereoselective Synthesis of 5a-Ethyl-1,2,3,3a,4,5,5a,6,9a,9b-decahydro-1,3,4-trihydroxy-3a-(hydroxymethyl)-7*H*-benz[*e*]inden-7-one Derivatives

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Homochiral *Diels-Alder* cyclodimerization of (±)-6-ethenyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol (**1**) followed by oxidation gives (1*RS*,4*RS*,4a*SR*,4b*SR*,5*RS*,8*RS*,8a*RS*)-8a-ethenyl-1,3,4,4a,4b,5,6,8,8a,9-decahydro-1,4:5,8-diepoxyphenanthrene-2,7-dione (**18**). Selective hydrogenation followed by epoxidation produced (1*RS*,4*RS*,4a*RS*,5a*RS*,6a*RS*,7*RS*,10*RS*,10a*SR*,10b*RS*)-6a-ethyl-1,4,5a,6,6a,7,9,10,10a,10b-decahydro-1,4:7,10-diepoxyphenanthro[8a,9-*b*]oxirene-3,8-dione (**21**), which was solvolyzed ($Me_3SiOSO_2CF_3$, Piv_2O) with concomitant pinacol rearrangement involving an acyl-group migration to give a 6-oxo-7-oxabicyclo[2.2.1]hept-2-yl cation intermediate, which finally generated (1*RS*,3*SR*,3a*RS*,4*SR*,5a*RS*,6*RS*,9*RS*,9a*SR*,9b*SR*)-5a-ethyl-1,4,5,5a,6,7,8,9,9a,9b-decahydro-7,10-dioxo-3*H*-6,9-epoxy-1,3a-ethanonaphtho[1,2-*c*]furan-3,4-diyl bis(2,2-dimethylpropanoate) (**24**). Photo-reductive 7-oxa bridge opening of **24**, followed by water elimination and silylation, provided (1*RS*,3*SR*,3a*RS*,4*SR*,5a*SR*,9a*SR*,9b*SR*)-7-{[(*tert*-butyl)dimethylsilyl]oxy}-5a-ethyl-1,4,5,5a,9a,9b-hexahydro-10-oxo-3*H*-1,3-ethanonaphtho[1,2-*c*]furan-3,4-diyl bis(2,2-dimethylpropanoate) (**34**). Reduction of **34** with $NaBH_4$ in MeOH followed by desilylation and alcohol protection produced (1*RS*,3*RS*,3a*RS*,4*SR*,5a*SR*,9a*SR*,9b*SR*)-5a-ethyl-2,3,3a,4,5,5a,6,7,9a,9b-decahydro-1,3-bis(methoxymethoxy)-3a-[(methoxymethoxy)methyl]-7-oxo-1*H*-benz[*e*]inden-4-yl 2,2-dimethylpropanoate (**5**), a polyoxy-substituted decahydro-1*H*-benz[*e*]indene derivative with *cis-transoid-trans* junction for the two cyclohexane and the cyclopentane rings bearing an angular 3a-(oxymethyl) substituent.

Introduction. – Natural polyhydroxylated products with perhydrophenanthrene[2]) or steroidal[3]) skeletons present quite often very interesting biological properties. Recently, we have disclosed a very efficient synthesis of perhydro-8a-(hydroxymethyl)phenanthrene-1,2,4,5,7,8-hexol and of derivatives with three kinds of perpendicular protective groups of the polyol (*e.g.*, **3**) [14]. The method exploits the highly stereoselective cyclodimerization of dienol **1** to **2** (*Scheme 1*). This *Diels-Alder* cycloaddition requires homochiral matching [15], thus allowing one to prepare the polycyclic systems in both their enantiomerically pure forms, as **1** can be obtained pure in both its enantiomeric forms starting from the *Diels-Alder* adducts of furan to 1-cyanovinyl esters (naked sugars of the first generation [16]). We show here that cycloadduct **2** can be converted to decahydro-1*H*-benz[*e*]indene derivatives **4** and **5**

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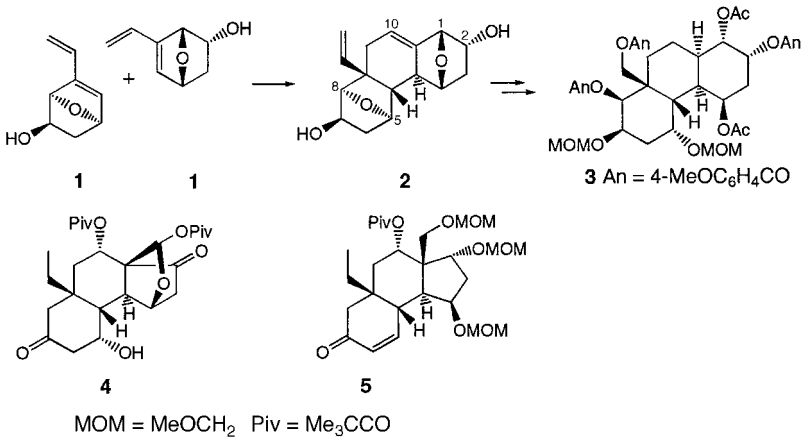
[2]) See, *e.g.*: the euryspongiols with antihistaminic activity [1]; chaparin, the bitter principle from *Castela nicholsoni* [2]; 13β,18-dihydroeurycomanol, a quassinoid from *Eurycoma longifolia* with cytotoxic activity [3]; bruceantinol [4] and bruceosides from *Brucea javanica* [5] with cytotoxic activity; α-dictalediol and β-dictalediol monoacetates from the genus *Dictyota* with cytotoxic, antibacterial, and antiviral activities [6].

[3]) See, *e.g.*: digitalis glycosides, mammalian cardiotonic factors [7]; ajugalactone from *Ajuga decumbens* [8] and ponasterone C from *Podocarpus nakaii* [9] are insect moulting inhibitors; cytotoxic incrustasterols from sponge [10]; xestobergsterols, inhibitors of histamine release [11]; ecdysteroids that play a role in plant defense against phytophagous insects [12]; contignasterol as immuno-suppressive agent [13].

with *cis-transoid-trans* junction for the two cyclohexane and the cyclopentane rings, and bearing an angular oxymethyl substituent. The work relies on the facile migration of acyl groups in pinacol rearrangements [17][18].

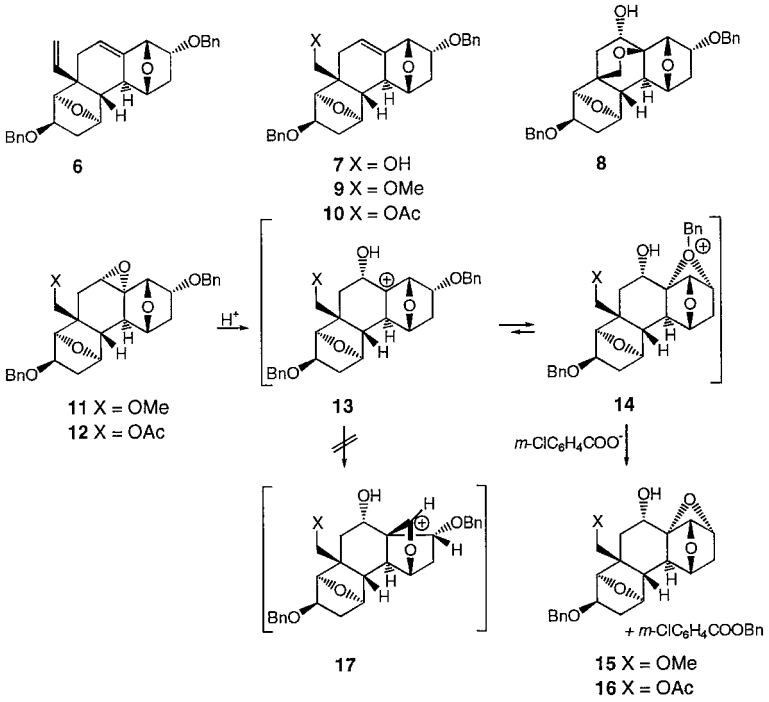
Scheme 1



Results and Discussion. – *Preamble.* Our main objective was to find a procedure to rearrange one of the two 7-oxatrinorbornyl systems to an oxy-substituted cyclopentane moiety with high stereoselectivity. We first protected diol **2** as its bisbenzyl diether **6**, and converted its ethenyl group to a hydroxymethyl substituent giving **7**. Treatment of **7** with *m*-chloroperbenzoic acid (*m*-CPBA) in $CHCl_3$ led to the formation of the 2-oxabicyclo[2.2.2]octane derivative **8** in 81% yield [19]. We then protected the primary-alcohol function of **7** as a methyl ether, giving **9**, and as an acetate, giving **10**. Epoxidation of **9** and **10** with *m*-CPBA were highly stereoselective, for steric reasons, giving the *endo* epoxy derivatives **11** and **12**, respectively. Under acidic conditions, oxiranes **11** and **12** furnished mostly oxetanes **15** and **16**, respectively, due to the facile 1,3-migration of the *endo*-(benzyloxy) group, a process implying the rearrangement of intermediates of type **13** to **14** that is more rapid than the expected pinacol rearrangement **13** to **17** (*Scheme 2*) [19]. This led us to consider the diketone **18** rather than **6** as starting material for the rearrangement; **18** was obtained in 90% yield by *Dess-Martin* periodinane [20] oxidation of diol **2** [14].

*Synthesis of 5a-Ethyl-1,2,3,3a,4,5,5a,6,9a,9b-decahydro-1,3,4-trihydroxy-3a-(hydroxymethyl)-7*H*-benz[*e*]inden-7-one Derivatives.* Catalytic hydrogenation (Pd/C, AcOEt) of dione **18** reduced first its ethenyl group to an ethyl group, and then its trisubstituted alkene unit. Conditions were found under which **19** was the major product, contaminated by 3% of the product of double hydrogenation **20** (*Scheme 3*). Treatment of this mixture **19**/**20** with dimethyldioxirane in acetone [21] provided a mixture of epoxy derivative **21** and **20**, from which **21** was isolated in 87% yield, and **20** in 3% yield. Both the hydrogenation and the epoxidation of the alkene unit of **19** preferred the *endo*-face of its 6-methylidene-7-oxabicyclo[2.2.1]heptan-2-one moiety because of steric crowding of the *exo*-face by the 8a-ethyl substituent.

Scheme 2



The ^{1}H-NMR spectrum of the perhydrogenated compound **20** showed coupling constants for vicinal proton pairs $^3J(4,4a_{endo}) = {}^3J(3_{endo},4) = {}^3J(4b_{endo},5) = {}^3J(1,10a_{endo}) \approx 0$ Hz, $^3J(3_{exo},4) = 6.0$ Hz, $^3J(5,6_{exo}) = 6.4$ Hz, $^3J(4a_{endo},10a_{endo}) = 8.9$ Hz that were typical [22] for 5-*endo*,6-*endo*-disubstituted 7-oxabicyclo[2.2.1]heptan-2-one systems and $^3J(4a,4b) \approx 0$ Hz typical for the *transoid* junction of the two 7-oxabicyclo[2.2.1]heptanes onto the cyclohexane moiety[4]). The structure of the epoxy derivative **21** was confirmed by its spectral data (see *Exper. Part*). The *endo* relative configuration of the epoxy moiety was further confirmed by the structures of the products derived from **21**, as shown below (*Scheme 3*).

Treatment of epoxy derivative **21** with $BF_3 \cdot Et_2O$ in Ac_2O/CH_2Cl_2 at $-20°$ provided a mixture of products containing *ca.* 20% of a 4 : 1 mixture of acylals **22** and **23**. A better conversion rate (*ca.* 95%) was observed when using $Me_3SiOSO_2CF_3$ in Ac_2O/CH_2Cl_2 at $-50°$. Unfortunately, **22** and **23** were unstable products that could not be separated. When Ac_2O was exchanged for pivalic anhydride (Piv_2O), the treatment of **21** with $Me_3SiOSO_2CF_3$ gave a unique product of pinacol rearrangement, the acylal **24** that could be isolated in 54% yield[5]). This result can be interpreted in terms of the formation of 7-oxabicyclo[2.2.1]hept-2-yl cation intermediate **25**, which undergoes facile acyl-group *Wagner-Meerwein* migration to generate the more stable oxyalkyl cation **26**

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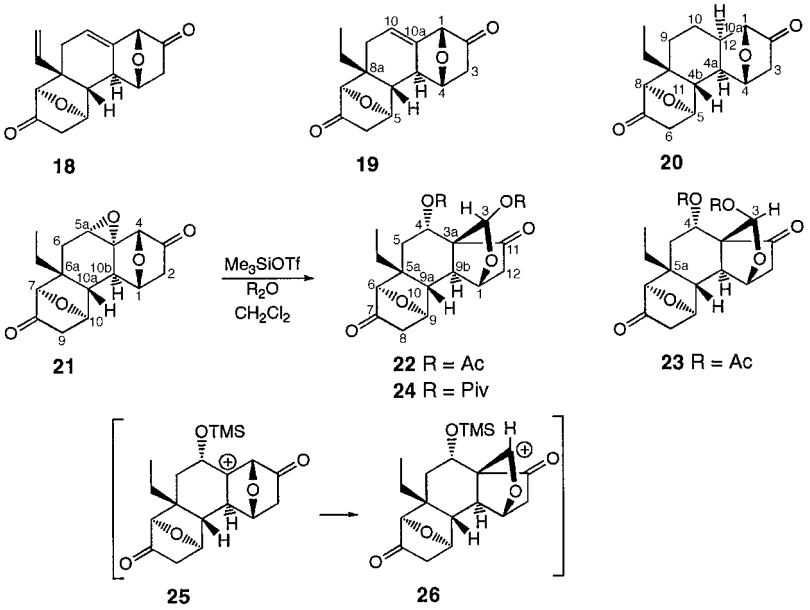
[4]) The relative configuration of the pentacyclic systems was demonstrated by further derivatization of **2** and by X-ray radiocrystallography [14].

[5]) For examples of pinacol rearrangements of 2,3-epoxy-7-oxabicyclo[2.2.1]heptane derivatives, see [23][24]. To the best of our knowledge, pinacol rearrangements of *endo*-epoxides of methylidene-7-oxabicyclo[2.2.1]heptane systems have never been reported thus far.

Scheme 3



(pinacol rearrangement). For steric reasons, the '*endo*' face of **26** is preferred for its reaction with the nucleophile giving **22** and **24** as major products. Molecular models of **22** and **23** showed severe steric repulsions between the 5a-ethyl and 3-acetoxy substituents in **23**, thus making **22** (and **24**) more stable and also more accessible. The structure of **24** was established by its spectral data.

In particular the 2D-NOESY ^{1}H-NMR of **24** showed NOEs between signals at δ 6.26 (*s*, H–C(3) of the acylal), 5.16 (*dd*, $^3J = 12.4$, 5.2 Hz, H–C(4)), and 1.83 (*dq*, $^2J = 14.8$ Hz, $^3J = 5.2$ Hz, MeCH_2) on one hand, and between δ 1.98 (*d*, $^3J = 10.9$ Hz, H–C(9b)) and 1.75 (*dd*, $^2J = 13.4$ Hz, $^3J = 12.4$ Hz, H–C(5) *anti* with respect to the 3a-ethyl group), on the other hand. The coupling constant between vicinal proton pairs measured in the ^{1}H-NMR spectrum of **24** suggests a boat conformation for the cyclohexane moiety (C(3a)–C(4)–C(5)–C(5a)–C(9a)–C(9b)), as shown in the *Figure*.

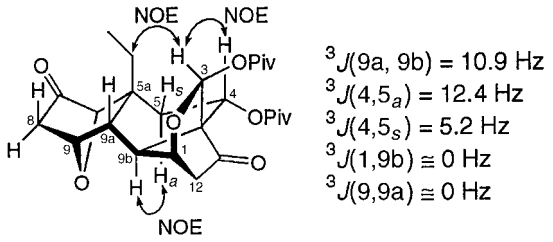
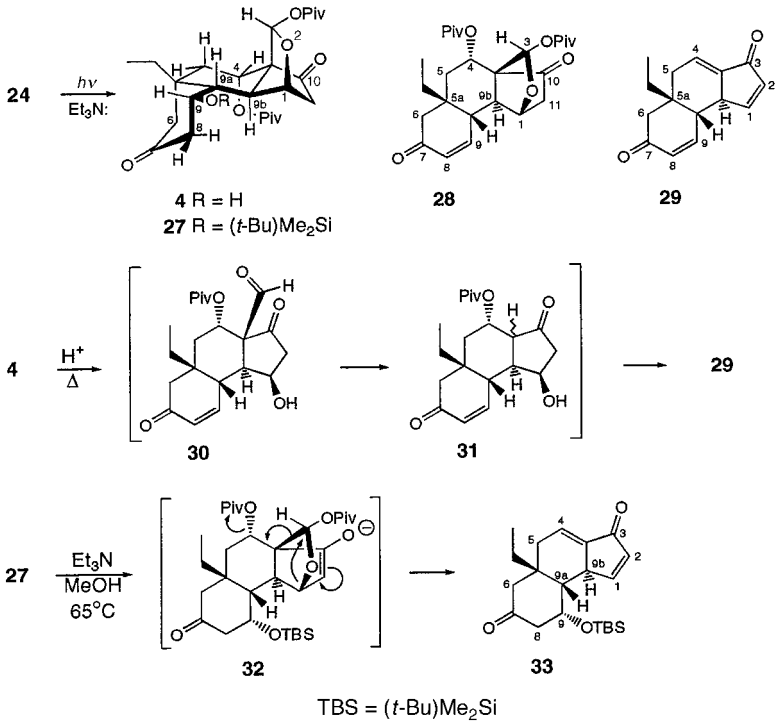


Figure. *Conformation of* **24**

Oxa-bridge opening of the 7-oxabicyclo[2.2.1]heptan-2-one unit of **24** was achieved under the photochemical reducing conditions of *Cossy* [25]. Irradiation of **24** in MeCN in the presence of Et_3N (quartz irradiator, low-pressure Hg lamps) led to a

mixture of products from which the β-hydroxy ketone **4** was isolated in 78% yield, together with the recovery of some starting material (5%). The same product **4** was obtained in only 40% yield on treating **24** with SmI_2 [26]. Silylation of **4** with (*t*-Bu)$Me_2SiOSO_2CF_3$ in the presence of 2,6-lutidine provided **27** (72%). The ^{1}H-NMR spectra of **4** and **27** suggested the conformation shown in *Scheme 4* for these compounds, a conformation which differs significantly from that proposed for **24** (see *Figure*).

Scheme 4



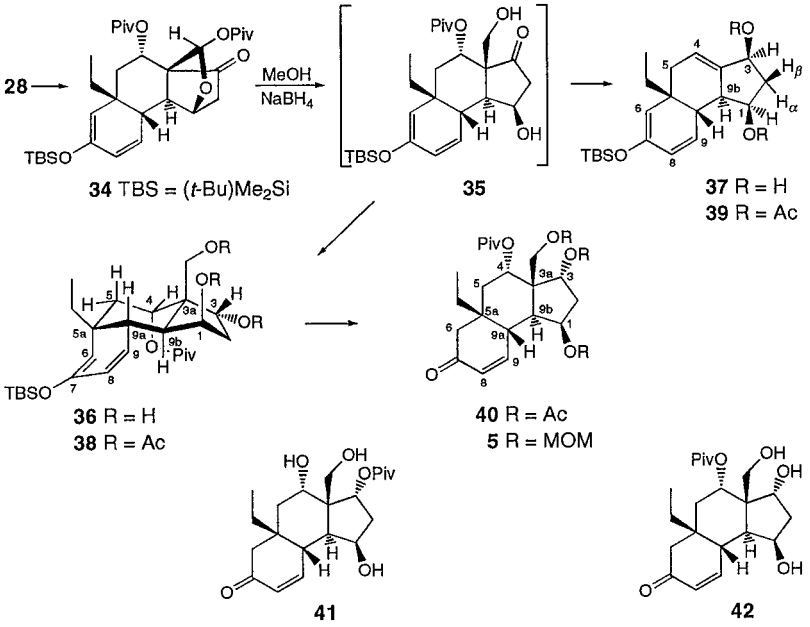
The ^{1}H-NMR spectrum of **27** showed typical coupling constants $^3J(4_{eq},5_c) = 2.2$ Hz (($c = cis$ to H–C(4)), $^3J(4,5_t) = 4.0$ Hz ($t = trans$ to H–C(4)), $^3J(8_c,9_{ax}) = 11.9$ Hz ($c = cis$ to H–C(9)), and $^3J(9,9a_{eq}) = 4.9$ Hz and $^3J(9a_{ax},H{-}9b_{ax}) = 11.7$ Hz.

When β-hydroxy ketone **4** was heated under reflux in $CHCl_3$ containing CF_3COOH, H_2O elimination occurred with the formation of enone **28** in 68% yield (*Scheme 4*). The reaction was accompanied by the formation of 5–10% of trienedione **29**, the latter compound arising probably from the hydrolysis of the acylal and formation of intermediate **30**, which undergoes a *retro-Claisen* reaction generating **31** and eliminates, in turn, 1 equiv. of H_2O and 1 equiv. of pivalic acid (*Scheme 4*). The structures of **28** and **29** were deduced from their spectral data. That of **28** was further confirmed by its product of hydrogenation **28′** (H_2/10% Pd/C, see *Exper. Part*).

The treatment of silyl-ether derivative **27** in MeOH with Et_3N did not induce the elimination of the corresponding silanol, but led to the product of fragmentation **33** in 70% yield (*Scheme 4*). This observation can be explained by a mechanism similar to that involving intermediates **30** to **31**, or by the formation of enolate intermediate **32** that could undergo β-elimination, *retro-Claisen* reaction, and β-elimination of pivaloic acid as shown in *Scheme 4*.

To make use of the acylal moiety of **4** as an angular oxymethyl substituent, we had to find a way to suppress the *retro-Claisen* fragmentation, and for that we envisioned the reduction of the keto function of the cyclopentane moiety. In order to do this without reducing the keto group of the cyclohexenone moiety, we first treated enone derivative **28** with (*t*-Bu)$Me_2SiOSO_2CF_3$ and Et_3N (20°C, 15 h). This generated the corresponding (silyloxy)diene compound **34** in 96% yield (*Scheme 5*). Probably

Scheme 5



because a greater increase in strain would have to be overcome, enolization of the 2-oxabicyclo[2.2.1]heptanone unit of **28** did not occur under the above conditions. Treatment of **34** with $NaBH_4$ in MeOH/CH_2Cl_2 (20°, 20 min) provided a mixture of the desired trihydroxy compound **36** and of the product of fragmentation **37**, the latter arising probably from the *retro*-aldolization of intermediate **35**, a reaction that competes with the reduction of its keto group. Pure **36** was obtained by flash chromatography in 61% yield, and its structure was established by its spectral data. The α-configured 3-OH group in **36** implies hydride addition to the 3-keto group of **35** on its β-face, *cis* with respect to the 3a-hydroxymethyl substituent. This stereoselectivity may be attributed to a steric factor or to lateral influence of the hydroxymethyl substituent. Interestingly, the $NaBH_4$ reduction of the intermediate ketone that led to **37** has the

opposite facial selectivity, as established by the data of its diacetate **39**. This observation can be interpreted in terms of the formation of an intermediate enone that is attacked on its α-face by the hydride for steric reasons (the β-face being impeded by the 1-hydroxy group). Acetylation (Ac_2O, pyridine, DMAP (4-(dimethylamino)pyridine)) of the mixture **36**/**37** gave polyacetates **38**/**39**, which were separated and purified (45 and 5–10% yield, resp.). Desilylation of **38** with Bu_4NF in THF provided enone derivative **40** in 98% yield. Protection of trihydroxy compound **36** with $MeOCH_2Cl$ and (i-Pr)$_2$NEt (CH_2Cl_2, 20°), followed by treatment with Bu_4NF (THF, −10°), furnished **5** (92%). Desilylation of **36** with Bu_4NF led to the migration of the pivaloyl ester from position C(4) to C(3) giving trihydroxyenone **41** in 70% yield. Difference in front strain between the 3- and 4-(pivaloyloxy)-substituted systems makes **41** more stable than its isomer **42**.

The ^{1}H-NMR spectrum of **36** showed $^3J(4_{eq},5) = 3.1$ Hz, $^3J(4,5) = 2.8$ Hz, $^3J(9a_{ax},9b_{ax}) = 12.2$ Hz, $^3J(9,9a) = 5.9$ Hz, and $^3J(1,9b) = 5.1$ Hz, all consistent with the conformation shown for this product in *Scheme 5*. The 2D-NOESY ^{1}H-NMR of **36** exhibited NOEs between δ 5.34 (*ddd*, $^3J = 7.1, 5.3, 2.7$ Hz, H–C(3)), and δ 3.79 and 3.49 ppm (2*d*, $^2J = 11.4$ Hz, CH_2OH) on one hand, and between δ 5.41 (*dd*, $^3J = 3.1, 2.8$ Hz, H–C(4)) and δ 3.49, on the other hand.

The relative configuration of the 3-acetoxy group in **39** was established by its 2D-NOESY data that showed NOEs between δ 5.59 (br. *d*, $^3J = 8.4$ Hz, H–C(3)) and δ 2.27 (*ddd*, $^2J = 16.1$ Hz, $^3J = 8.4, 4.4$ Hz, H_α–C(2)), between δ 5.24 (*dd*, $^3J = 4.5, 4.4$ Hz, H_α–C(1)) and δ 2.27 (*ddd*, $^2J = 16.1$ Hz, $^3J = 8.4, 4.4$ Hz, H_α–C(2)), and between δ 5.24 (*dd*, $^3J = 4.5, 4.4$ Hz, H_α–C(1)) and 2.43–2.39 (*m*, H–C(9b)).

The ^{1}H-NMR spectra of **5**, **40**, and **41** showed coupling constants for vicinal-proton pairs that are consistent with the structures proposed and conformations similar to that shown for **36** and **38** (*Scheme 5*). Distinction between 3-(pivaloyloxy) and 4-(pivaloyloxy) substitution in **41** was based on the coupling constants measured for δ 5.63 (*dd*, $^3J = 7.8, 3.7$ Hz, H–C(3)) and 4.23 (br. *s*, H–C(4); small $^3J(4,5)$ for equatorial H–C(4), the most deshielded proton being geminal to the pivaloyloxy substituent, the less deshielded with the secondary-alcohol function).

Conclusion. – The homochiral cyclodimerization of 6-ethenyl-7-oxabicyclo[2.2.1]-hept-5-en-2-ol (**1**) gives (1*RS*,2*RS*,4*RS*,4a*SR*,4b*SR*,5*RS*,7*RS*,8*RS*,8a*SR*)-8a-ethenyl-1,2,3,4,4a,4b,5,6,7,8,8a,9-dodecahydro-1,4:5,8-diepoxyphenanthrene-2,7-diol (**2**). Selective hydrogenation of the ethenyl group of the corresponding diketone **18**, followed by *endo*-face epoxidation of the trisubstituted alkene unit, which generated perhydrodiepoxyphenanthrooxirenedione **21**, which was converted to 5a-ethyl-1,4,5,5a,6,7,8,9,9a,9b-decahydro-7,10-dioxo-3*H*-6,9-epoxy-1,3a-ethanonaphtho[1,2-*c*]furan-3,4-diyl dipivalate (**24**). The reaction involved acid-promoted oxirane-ring opening with the formation of a tertiary 6-oxo-7-oxabicyclo[2.2.1]hept-2-yl cation intermediate **25** that underwent pinacol rearrangement (*Wagner-Meerwein* acyl shift). The 7-oxabicyclo[2.2.1]heptan-2-one moiety of **24** could be ring-opened under reductive conditions (*Cossy*'s method), and led to the corresponding β-hydroxy ketone **4**. This report discloses efficient and highly stereoselective methods for the preparation of decahydropolyhydroxy-7*H*-benz[*e*]inden-7-one derivatives such as **5** bearing an angular oxymethyl group at C(3a). Since the starting 7-oxabicyclo[2.2.1]heptyl derivatives are available in both their enantiomeric forms, the new systems described here can be prepared pure in both their enantiomeric forms also.

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Experimental Part

General. See [27][28].

*(1*RS,*3*SR,*3a*RS,*4*SR,*5a*SR,*9*RS,*9a*SR,*9b*SR*)-5a-Ethyl-1,4,5,5a,6,7,8,9,9a,9b-decahydro-9-hydroxy-7,10-dioxo-3*H-*1,3a-ethanonaphtho[1,2-*c*]*furan-3,4-diyl Bis(2,2-dimethylpropanoate)* (**4**). A soln. of **24** (150 mg, 315 μmol) and Et_3N (220 μl, 1.57 mmol) in MeCN (20 ml) in a quartz tube (∅ = 1 cm) was irradiated at 25° for 50 min in a *Gräntzel* apparatus equipped with 12 low-pressure mercury lamps. After filtration through a pad of *Florisil* and rinsing with AcOEt, the solvent was evaporated and the residue purified by FC (silica gel, 2 × 15 cm column, AcOEt/light petroleum ether 2:3): 8 mg (5%) of **24** and 117 mg (78%) of **4**. The colorless solid **4** was recrystallized from AcOEt/hexane, giving colorless needles. M.p. 152–154° (AcOEt/hexane). IR (KBr): 3440, 2970, 1765, 1735, 1280, 1145, 1080, 1015. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.36 (*s*, H–C(3)); 5.47 (*dd*, ^3J = 4.0, 2.2, H–C(4)); 5.39 (*d*, ^3J = 2.4, H–C(1)); 4.55–4.49 (*m*, H–C(9)); 2.98, 1.93 (2*d*, ^2J = 14.8, CH_2(6)); 2.71–2.40 (*m*, CH_2(8), H–C(9a), H–C(9b)); 2.54 (*d*, ^2J = 18.4, H_{syn}–C(11)); 2.43 (*dd*, ^2J = 18.4, ^3J = 2.4, H_{anti}–C(11)); 2.34 (br. *s*, OH); 1.93 (*dd*, ^2J = 16.0, ^3J = 4.0, H_{anti}–C(5)); 1.57 (*dd*, ^2J = 16.0, ^3J = 2.2, H_{syn}–C(5)); 1.29 (*q*, ^3J = 7.4, MeCH_2); 1.17, 1.16 (2*s*, Piv); 0.88 (*t*, ^3J = 7.4, MeCH_2). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 208.3, 202.6 (2*s*, C(7), C(10)); 177.7, 176.6 (2*s*, Piv); 96.5 (*d*, *J* = 181, C(3)); 80.7 (*d*, *J* = 171, C(1)); 67.8 (*d*, *J* = 141, C(9)); 63.4 (*d*, *J* = 151, C(4)); 62.9 (*s*, C(3a)); 47.5 (*t*, *J* = 120, C(6)); 45.7 (*t*, *J* = 133, C(8)); 45.6 (*d*, *J* = 133, C(9b)); 45.6 (*t*, *J* = 122, C(11)); 38.7 (*d*, *J* = 132, C(9a)); 38.6, 38.4 (2*s*, Piv); 37.6 (*s*, C(5a)); 35.3 (*t*, *J* = 126, C(5)); 31.9 (*t*, *J* = 126, MeCH_2); 26.9, 26.5 (2*q*, *J* = 127, 128, Piv); 6.9 (*q*, *J* = 126, $MeCH_2$). CI-MS (NH_3): 496 (100, $[M+NH_4]^+$), 478 (2, M^+), 394 (3), 372 (2). Anal. calc. for $C_{26}H_{38}O_8$ (478.58): C 65.25, H 8.00; found: C 65.21, H 8.01.

*(1*RS,*3*RS,*3a*RS,*4*SR,*5a*SR,*9a*SR,*9b*SR*)-5a-Ethyl-2,3,3a,4,5,5a,6,7,9a,9b-decahydro-1,3-bis(methoxymethoxy)-3a-[(methoxymethoxy)methyl]-7-oxo-1*H-*benz[*e*]*inden-4-yl 2,2-Dimethylpropanoate* (**5**). A soln. of **36** (348 mg, 720 μmol) in CH_2Cl_2 (20 ml) was cooled to 0°. After the addition of (i-Pr)$_2$EtN (2.22 ml, 13.0 mmol) and methoxymethyl chloride (0.493 ml, 5.47 mmol), the mixture was stirred at 20° for 22 h. MeOH (3 ml) was added and stirring continued for 5 min. CH_2Cl_2 (20 ml) was added and the soln. washed with a sat. aq. $NaHCO_3$ soln. (2 × 30 ml). Each aq. phase was extracted with CH_2Cl_2 (2 × 20 ml). The combined org. phase was dried ($MgSO_4$) and evaporated, the residue taken up with Et_2O, and the soln. filtered through a pad of silica gel. After solvent evaporation, the oily residue was taken up in THF (30 ml) and the soln. cooled to −10°. Then 1M Bu_4NF in THF (1.44 ml, 1.44 mmol) was added and the mixture stirred at −10° for 10 min. The mixture was filtered through a pad of *Florisil*, rinsing with Et_2O (200 ml). The solvent was evaporated and the residue purified by FC (silica gel, 2 × 12 cm column, AcOEt/light petroleum ether 2:3): 286 mg (79%) of **5**. Colorless crystals. M.p. 76–77° (hexane). UV (MeCN): 229 (10800), 195 (7000). IR (KBr): 2935, 1725, 1680, 1480, 1465, 1445, 1390, 1285, 1215, 1155, 1105, 1040, 970, 920, 755. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.89–6.85 (*m*, H–C(9)); 6.02 (*d*, ^3J = 10.1, H–C(8)); 5.80 (*dd*, ^3J = 3.5, 2.6, H–C(4)); 4.68, 4.59 (2*d*, ^2J = 6.8, OCH_2OMe); 4.61, 4.59 (2*d*, ^2J = 6.7, OCH_2OMe); 4.59, 4.37 (2*d*, ^2J = 6.8, OCH_2OMe); 5.36 (*dd*, ^3J = 7.7, 6.0, H–C(3)); 4.20–4.17 (*m*, H–C(1)); 3.69, 3.55 (2*d*, ^2J = 10.3, CH_2OCH_2OMe); 3.40, 3.38, 3.26 (3*s*, 3 OCH_2OMe); 3.24, 2.10 (2*d*, ^2J = 16.6, CH_2(6)); 2.61–2.60 (*m*, H–C(9b), H–C(9a)); 2.50 (*dd*, ^2J = 15.2, ^3J = 7.7, H_β–C(2)); 1.99 (*dd*, ^2J = 15.8, ^3J = 3.5, H–C(5)); 1.82 (*ddd*, ^2J = 15.2, ^3J = 6.0, 5.4, H_α–C(2)); 1.56, 1.37 (2*dq*, ^2J = 14.2, ^3J = 7.5, MeCH_2); 1.43 (*dd*, ^2J = 15.8, ^3J = 2.6, H–C(5)); 1.16 (*s*, Piv); 0.84 (*t*, ^3J = 7.5, *Me*CH_2). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 199.7 (*s*, C(7)); 177.1 (*s*, Piv); 150.1 (*d*, *J* = 160, C(9)); 128.8 (*d*, *J* = 165, C(8)); 96.9, 96.0, 95.9 (3*t*, *J* = 163, OCH_2OMe); 81.5, 77.5 (2*d*, *J* = 149, 147, C(1), C(3)); 69.5 (*d*, *J* = 155, C(4)); 69.5 (*t*, *J* = 144, CH_2OCH_2OMe); 56.1, 55.7, 55.1 (3*q*, *J* = 142, OCH_2OMe); 51.2 (*s*, C(3a)); 45.9, 41.2 (2*t*, *J* = 128, 130, C(2), C(6)); 45.2, 38.1 (2*d*, *J* = 127, 133, C(9a), C(9b)); 38.8, 38.3 (2*s*, Piv, C(5a)); 37.4 (*t*, *J* = 125, C(5)); 32.3 (*t*, *J* = 124, MeCH_2); 27.3 (*q*, *J* = 127, Piv); 8.0 (*q*, *J* = 125, *Me*CH_2). CI-MS (NH_3): 530 (100, $[M+NH_4]^+$), 498 (11), 481 (24), 480 (16). Anal. calc. for $C_{27}H_{44}O_9$ (512.37): C 63.26, H 8.65; found: C 63.27, H 8.57.

*(1*RS,*4*RS,*4a*RS,*4b*SR,*5*RS,*8*RS,*8a*RS,*10a*RS*)-8a-Ethyl-1,3,4,4a,4b,5,6,8,8a,9,10,10a-dodecahydro-1,4:5,8-diepoxyphenanthrene-2,7-dione* (**20**) and *(1*RS,*4*RS,*4a*RS,*5a*RS,*6a*RS,*7*RS,*10*RS,*10a*SR,*10b*RS*)-6a-Ethyl-1,4,5a,6,6a,7,9,10,10a,10b-decahydro-1,4:7,10-diepoxyphenanthro[8a,9-b]oxirene-3,8-dione* (**21**). A suspension of 10% Pd/C (40 mg) in AcOEt (40 ml) was shaken under H_2 (1 atm) for 2 h at 20°. Then **18** [14] (446 mg, 1.64 mmol) was added and the mixture shaken under H_2 until absorption of 39 ml of H_2. The mixture was filtered through *Celite* and the solvent evaporated. The residue was taken up with CH_2Cl_2 (10 ml), and 0.1M dimethyldioxirane in acetone (45 ml) was added under stirring. After staying at 20° for 15 h, the solvent was evaporated and the residue crystallized from boiling AcOEt/hexane 1:2: 297 mg (63%) of pure **21**. The mother liquor was concentrated and purified by FC (silica gel, 3 × 12 cm column, AcOEt/light petroleum ether 1:3): 11 mg (3%) of **20** and 116 mg (24%) of **21**, after recrystallization from AcOEt/hexane. Total yield of **21**: 87%.

Data of **21**: Colorless crystals. M.p. 158–159° (AcOEt/hexane). IR (KBr): 2980, 2930, 1765, 1395, 1240, 1005, 950, 900, 780, 540. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.70 (*d*, ^3J = 6.2, H–C(1)); 4.57 (*d*, ^3J = 6.0, H–C(10)); 4.02 (br. *s*, H–C(4)); 3.81 (br. *s*, H–C(7)); 3.53 (*ddd*, ^3J = 5.8, 5.5, H–C(5a)); 2.75 (*ddd*, ^2J = 17.8, ^3J = 6.2, ^4J = 1.2, H_{exo}–C(2)); 2.56 (*ddd*, ^2J = 17.5, ^3J = 6.0, ^4J = 1.0, H_{exo}–C(9)); 2.48 (*dd*, ^2J = 14.5, ^3J = 5.8, H_{eq}–C(6)); 2.38 (*d*, ^2J = 17.8, H_{endo}–C(2)); 2.13 (*d*, ^2J = 17.5, H_{endo}–C(9)); 1.75 (*dd*, ^2J = 14.5, ^3J = 5.5, H_{ax}–C(6)); 1.73, 1.70 (2*d*, ^3J = 9.8, H–C(10a), H–C(10b)); 1.54, 1.37 (2*dq*, ^2J = 14.1, ^3J = 5.5, MeCH_2); 1.17 (*q*, ^3J = 5.5, MeCH$_2$). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 209.2, 205.2 (2*s*, C(3), C(8)); 87.1, 81.7, 81.2, 78.9 (4*d*, *J* = 165, 160, 158, 174, C(1), C(4), C(7), C(10)); 63.4 (*s*, C(4a)); 54.5 (*d*, *J* = 183, C(5a)); 52.2, 46.1 (2*d*, *J* = 126, 140, C(10a), C(10b)); 48.8 (*s*, C(6a)); 43.3, 41.5 (2*t*, *J* = 135, C(2), C(9)); 31.7, 30.5 (2*t*, *J* = 130, 125, C(6), MeCH_2); 9.3 (*q*, *J* = 126, *Me*CH_2). CI-MS (NH_3): 308 (100, $[M+NH_4]^+$), 290 (20, M^+), 262 (10), 234 (19), 133 (35), 131 (31), 121 (35), 105 (33), 96 (59), 95 (37), 91 (56). Anal. calc. for $C_{16}H_{18}O_5$ (290.32): C 66.20, H 6.25; found: C 66.15, H 6.33.

Data of **20**: Colorless needles. M.p. 192–193° (AcOEt/hexane). IR (KBr): 3000, 2965, 2935, 2870, 1752, 1465, 1415, 1305, 1250, 1170, 1165, 1005, 900, 790, 565, 540, 500, 460. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.50 (*d*, ^3J = 6.0, H–C(4)); 4.48 (*d*, ^3J = 6.4, H–C(5)); 4.02 (*s*, H–C(1)); 3.88 (*s*, H–C(8)); 2.50 (*d*, ^2J = 17.7 ^3J = 6.4 ^4J = 1.4 H_{exo}–C(6)); 2.48 (*ddd*, ^2J = 17.6, ^3J = 6.0, ^4J = 1.3, H_{exo}–C(3)); 2.29–2.18 (*m*, H–C(10a)); 2.13 (*d*, ^2J = 17.7, H_{endo}–C(6)); 2.07 (*d*, ^2J = 17.6, H_{endo}–C(3)); 2.03 (*dd*, ^3J = 8.9, 8.5, H–C(4a)); 1.98–1.82 (*m*, 3 H, H–C(9), H–C(10), MeCH_2); 1.49 (*d*, ^3J = 8.5, H–C(4b)); 1.26-1.02 (*m*, 3 H, H–C(9), H–C(10) MeCH_2); 0.86 (*q*, ^3J = 7.3, *Me*CH_2). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 210.1, 208.8 (2*s*, C(2), C(7)); 87.7 (*d*, *J* = 164, C(8)); 84.7 (*d*, *J* = 168, C(1)); 83.6 (*d*, *J* = 158, C(5)); 83.0 (*d*, *J* = 162, C(4)); 52.5 (*d*, *J* = 133, C(4b)); 46.0 (*s*, C(8a)); 45.3 (*d*, *J* = 133, C(4a)); 42.4, 42.1 (2*t*, *J* = 135, 134, C(3), C(6)); 39.2 (*d*, *J* = 132, C(10a)); 28.4 (*t*, *J* = 129, MeCH_2); 25.6, 21.0 (2*t*, *J* = 128, 130, C(9), C(10)); 8.6 (*q*, *J* = 125, *Me*CH_2). ^{17}O-NMR (48.9 MHz, MeCN, 50°): 526.6, 511.4 ($\omega_{1/2}$ = 390, 570, O=C(2), O=C(7)); 61.9 ($\omega_{1/2}$ = 1020, O(11), O(12)). CI-MS (NH_3): 277 (2, $[M+H]^+$), 276 (3, M^+), 248 (46), 232 (26), 204 (100), 91 (43). Anal. calc. for $C_{16}H_{20}O_4$ (276.33): C 69.55, H 7.30; found: C 69.48, H 7.22.

*(1*RS*,3*SR*,3a*RS*,4*SR*,5a*RS*,6*RS*,9*RS*,9a*SR*,9b*SR*)-5a-Ethyl-1,4,5,5a,6,7,8,9,9a,9b-decahydro-7,10-dioxo-3*H*-6,9-epoxy-1,3a-ethanonaphtho[1,2-*c*]furan-3,4-diyl Bis(2,2-dimethylpropanoate)* (**24**). A soln. of **21** (122 mg, 0.42 mmol) and pivalic anhydride (0.68 ml, 3.35 mmol) in anh. CH_2Cl_2 (7 ml) was cooled to −50°, and $Me_3SiOSO_2CF_3$ (0.3 ml, 1.68 mmol) was added. After stirring at −45° for 4.5 h, the mixture was poured into a sat. aq. $NaHCO_3$ soln. (60 ml) under vigourous stirring. After 5 min, the stirring was stopped. The aq. phase was extracted with CH_2Cl_2 (10 ml, 4 times), the combined org. phase dried ($MgSO_4$) and evaporated, and the residue purified by FC (silica gel, 2 × 15 cm column, AcOEt/light petroleum ether 1:3): 108 mg (54%) of **24**. Colorless foam that was crystallized from AcOEt/hexane, giving colorless needles. M.p. 209–210° (AcOEt/hexane). IR (KBr): 2975, 2940, 2880, 1765, 1735, 1725, 1480, 1460, 1290, 1160, 1140, 1060, 990, 975, 955, 900, 860, 775. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.26 (*s*, H–C(3)); 5.16 (*dd*, ^3J = 12.4, 5.2, H–C(4)); 4.40 (*d*, ^3J = 6.2, H–C(9)); 4.59 (br. *s*, H–C(1)); 3.97 (*s*, H–C(6)); 2.62 (*dd*, ^2J = 17.7, ^3J = 6.2, H_{exo}–C(12)); 2.59 (*d*, ^2J = 18.1, H_{anti}–C(8)); 2.49 (*d*, ^2J = 10.9, H–C(9a)); 2.43 (*dd*, ^2J = 18.1, ^3J = 2.6, H_{syn}–C(8)); 2.21 (*d*, ^2J = 17.7, H_{endo}–C(12)); 2.04 (*dd*, ^2J = 13.4, ^3J = 5.2, H_{syn}–C(5)); 1.98 (*d*, ^3J = 10.9, H–C(9b)); 1.83, 1.30 (2*dq*, ^2J = 14.8, ^3J = 7.4, MeCH_2); 1.75 (*dd*, ^2J = 13.4, ^3J = 12.4, H_{anti}–C(5)); 1.25, 1.19 (2*s*, Piv); 0.97 (*t*, ^3J = 7.4, *Me*CH_2). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 208.3, 199.8 (2*s*, C(7), C(11)); 177.4 (*s*, Piv); 98.2 (*d*, *J* = 181, C(3)); 87.0, 80.8, 77.5 (3*d*, *J* = 166, 160, 166, C(1), C(6), C(9)); 63.7 (*d*, *J* = 149, C(4)); 60.9 (*s*, C(3a)); 52.3, 46.5 (2*d*, *J* = 128, 140, C(9a), C(9b)); 46.8, 43.1, 31.7 (3*t*, *J* = 134, 130, 135, C(5), C(8), C(12)); 46.6 (*s*, C(5a)); 38.4 (*s*, Piv); 29.2 (*t*, *J* = 123, MeCH_2); 27.1, 26.6 (2*q*, *J* = 127, Piv); 9.1 (*q*, *J* = 121, *Me*CH_2). CI-MS (NH_3): 375 (17, $[M-Piv]^+$), 319 (36), 318 (100), 291 (30), 233 (19), 188 (15). Anal. calc. for $C_{26}H_{36}O_8$ (476.57): C 65.53, H 7.61; found: C 66.01, H 7.58.

*(1*RS*,3*SR*,3a*RS*,4*SR*,5a*SR*,9*RS*,9a*SR*,9b*SR*)-9-[[(*tert*-Butyl)dimethylsilyl]oxy]-5a-ethyl-1,4,5,5a,6,7,8,9,9a,9b-decahydro-7,10-dioxo-3*H*-1,3a-ethanonaphtho[1,2-*c*]furan-3,4-diyl Bis(2,2-dimethylpropanoate)* (**27**). A soln. of **4** (119 mg, 0.25 mmol) in anh. CH_2Cl_2 (4.5 ml) was cooled to 0°, and 2,6-dimethylpyridine (113 µl, 0.98 mmol) and then (*tert*-butyl)dimethylsilyl trifluoromethanesulfonate (112 µl, 0.49 mmol) were added. After stirring at 20° for 100 min, CH_2Cl_2 (20 ml) was added. The soln. was washed with sat. aq. $NaHCO_3$ soln. (20 ml), the aq. layer extracted with CH_2Cl_2 (3 × 10 ml), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue purified by FC (silica gel, 2 × 15 cm column, Et_2O/light petroleum ether 1:3): 106 mg (72%) of **27**. Colorless oil that was crystallized from CH_2Cl_2/hexane giving colorless needles. M.p. 232–233° (CH_2Cl_2/hexane). IR (KBr): 2960, 2930, 1760, 1735, 1720, 1480, 1280, 1260, 1155, 1080, 1015, 985, 835, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.43 (*s*, H–C(3)); 5.46 (*dd*, ^3J = 4.0, 2.2, H–C(4)); 5.34 (*d*, ^3J = 2.4, H–C(1)); 4.41 (*ddd*, ^3J = 11.9, 7.2, 4.9, H–C(9)); 2.98 (*d*, ^2J = 14.8, H–C(6)); 2.62 (*d*, ^3J = 11.7, H–C(9b)); 2.62–2.58 (*m*, CH_2(8)); 2.56 (*d*, ^2J = 18.4, H_{syn}–C(11)); 2.43 (*dd*, ^2J = 18.4, ^3J = 2.4, H_{anti}–C(11)); 2.38 (*dd*, ^3J = 11.7, 4.9, H–C(9a)); 1.93

(*dd*, ^2J = 16.2, ^3J = 4.0, H_{anti}–C(5)); 1.91 (*d*, ^2J = 14.8, H–C(6)); 1.55 (*dd*, ^2J = 16.2, ^3J = 2.2, H_{syn}–C(5)); 1.30 (*q*, ^3J = 7.5, MeCH_2); 1.18, 1.16 (2*s*, Piv); 0.92 (*s*, *t*-Bu); 0.89 (*t*, ^3J = 7.5, *Me*CH_2); 0.14, 0.12 (2*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 207.8, 202.8 (2*s*, C(7), C(10)); 177.6, 177.4 (2*s*, Piv); 96.6 (*d*, *J* = 181, C(3)); 80.3 (*d*, *J* = 171, C(1)); 69.1 (*d*, *J* = 144, C(9)); 63.5 (*d*, *J* = 152, C(4)); 63.4 (*s*, C(3a)); 47.8 (*t*, *J* = 123, C(6)); 46.6 (*t*, *J* = 128, C(8)); 46.0 (*d*, *J* = 129, C(9b)); 45.9 (*t*, *J* = 134, C(11)); 39.2 (*d*, *J* = 127, C(9a)); 38.7, 38.6 (2*s*, Piv); 37.5 (*s*, C(5a)); 35.5 (*t*, *J* = 128, C(5)); 32.1 (*t*, *J* = 127, Me*C*H_2); 27.6, 26.1 (2*q*, *J* = 126, 127, Piv); 25.9 (*q*, *J* = 124, *t*-Bu); 18.2 (*s*, *t*-Bu); 7.1 (*q*, *J* = 126, *Me*CH_2); –4.7, –4.9 (2*q*, *J* = 119, Me). CI-MS (NH_3): 610 (18, $[M+NH_4]^+$), 535 (67), 321 (26), 235 (31), 161 (40), 143 (100). Anal. calc. for $C_{32}H_{52}O_8Si$ (592.85): C 64.83, H 8.84, Si 4.74; found: C 64.95, H 8.86, Si 4.61.

*(1*RS*,3*SR*,3a*RS*,4*SR*,5a*SR*,9a*SR*,9b*SR*)-5a-Ethyl-1,4,5,5a,6,7,9a,9b-octahydro-7,10-dioxo-3*H*-1,3a-ethanonaphtho[1,2-c]furan-3,4-diyl Bis(2,2-dimethylpropanoate)* (**28**) and *(5a*RS*,9a*RS*,9b*RS*)-5a-Ethyl-5a,6,9a,9b-tetrahydro-3*H*-benz[e]indene-3,7(5*H*)-dione* (**29**). A soln. of **4** (413 mg, 0.86 mmol) and CF_3COOH (1 ml) in $CHCl_3$ (20 ml) was heated under reflux for 4.5 h. After cooling to 20°, the solvent was evaporated and the residue purified by FC (silica gel, 3 × 12 cm column, AcOEt/light petroleum ether 1 : 2): 271 mg (68%) of **28** as a colorless foam that was crystallized from CH_2Cl_2/hexane and 10–20 mg (5–10%) of **29**.

Data of **28**: Colorless prisms. M.p. 218–219° (CH_2Cl_2/hexane). UV (MeCN): 229 (8100). IR (KBr): 2975, 2935, 1770, 1740, 1680, 1480, 1390, 1280, 1155, 1090, 1015, 970, 860, 765. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.01 (*dd*, ^3J = 10.1, 5.9, H–C(9)); 6.30 (*s*, H–C(3)); 6.09 (*d*, ^3J = 10.1, H–C(8)); 5.49 (*t*, ^3J = 2.9, H–C(4)); 4.82 (*d*, ^3J = 2.0, H–C(1)); 2.98, 2.17 (2*d*, ^2J = 17.2, CH_2(6)); 2.63 (*dd*, ^3J = 11.4, 5.9, H–C(9a)); 2.58 (*d*, ^2J = 18.7, H_{syn}–C(11)); 2.37 (*d*, ^3J = 11.4, H–C(9b)); 2.35 (*dd*, ^2J = 18.7, ^3J = 2.0, H_{anti}–C(11)); 1.80–1.78 (*m*, CH_2(5)); 1.64, 1.33 (2*dq*, ^2J = 14.9, ^3J = 7.5, MeCH_2); 1.16, 1.15 (2*s*, Piv); 0.82 (*t*, ^3J = 7.5, *Me*CH_2). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 201.4 (*s*, C(10)); 198.1 (*s*, C(7)); 177.5, 176.5 (2*s*, Piv); 147.7 (*d*, *J* = 154, C(9)); 129.7 (*d*, *J* = 167, C(8)); 95.8 (*d*, *J* = 181, C(3)); 77.7 (*d*, *J* = 166, C(1)); 63.5 (*d*, *J* = 152, C(4)); 63.1 (*s*, C(3a)); 51.2 (*d*, *J* = 131, C(9a)); 46.0, 44.6 (2*t*, *J* = 134, 128, C(6), C(11)); 38.7 (*s*, Piv); 37.9 (*s*, C(5a)); 37.7 (*d*, *J* = 129, C(9b)); 35.6, 31.8 (2*t*, *J* = 127, 127, C(5), Me*C*H_2); 27.1, 26.6 (2*q*, *J* = 127, 128, Piv); 7.8 (*q*, *J* = 126, *Me*CH_2). CI-MS (NH_3): 478 (23, $[M+NH_4]^+$), 360 (35), 359 (100), 329 (12), 275 (42), 274 (13), 273 (12), 152 (17). Anal. calc. for $C_{26}H_{36}O_7$ (460.57): C 67.80, H 7.88; found: C 67.76, H 7.95.

*(1*RS*,3*SR*,3a*RS*,4*SR*,5a*SR*,9a*SR*,9b*SR*)-5a-Ethyl-1,4,5,5a,6,7,8,9,9a,9b-decahydro-7,10-dioxo-3*H*-1,3a-ethanonaphtho[1,2-c]furan-3,4-diyl Bis(2,2-dimethylpropanoate)* (**28′**). A mixture of **28** (67 mg, 145 µmol) and 10% Pd/C (30 mg) in AcOEt (5 ml) was shaken under H_2 for 14 h (1 atm). After filtration through *Celite*, the solvent was evaporated: 66 mg (98%) of **28′**. Colorless needles. M.p. 186–187° ($CHCl_3$/hexane). IR (KBr): 2980, 1760, 1740, 1725, 1480, 1465, 1280, 1230, 1155, 1135, 1085, 1015, 980, 855, 755. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.30 (*s*, H–C(3)); 5.48 (*dd*, ^3J = 3.9, 2.3, H–C(4)); 4.82 (*d*, ^3J = 2.1, H–C(1)); 2.94, 1.97 (2*d*, ^2J = 14.4, CH_2(6)); 2.63 (*d*, ^3J = 11.6, H–C(9b)); 2.59 (*d*, ^2J = 18.3, H_{syn}–C(11)); 2.40 (*dd*, ^2J = 18.3, ^3J = 2.1, H_{anti}–C(11)); 2.38–2.31, 2.20–1.94 (2*m*, CH_2(8), CH_2(9), H–C(9a)); 1.82 (*dd*, ^2J = 16.0, ^3J = 3.9, H_{anti}–C(5)); 1.57 (*dd*, ^2J = 16.0, ^3J = 2.3, H_{syn}–C(5)); 1.39, 1.33 (2*dq*, ^2J = 14.5, ^3J = 7.4, MeCH_2); 1.16, 1.15 (2*s*, Piv); 0.84 (*t*, ^3J = 7.4, *Me*CH_2). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 210.1 (*s*, C(7)); 202.2 (*s*, C(10)); 177.5, 176.5 (2*s*, Piv); 96.2 (*d*, *J* = 181, C(3)); 77.8 (*d*, *J* = 166, C(1)); 63.7 (*d*, *J* = 152, C(4)); 62.9 (*s*, C(3a)); 47.8, 46.2 (2*t*, *J* = 138, 130, C(6), C(11)); 47.8, 33.1 (2*d*, *J* = 128, 125, C(9a), C(9b)); 40.4 (*s*, C(5a)); 38.7, 38.6 (2*s*, Piv); 35.9, 35.7, 31.9 (3*t*, *J* = 124, 125, 130, C(5), C(8), Me*C*H_2); 27.1, 26.6 (2*q*, *J* = 127, 128, Piv); 23.0 (*t*, *J* = 128, C(9)); 7.0 (*q*, *J* = 126, *Me*CH_2). CI-MS (NH_3): 480 (21, $[M+NH_4]^+$), 362 (55), 361 (100), 332 (54), 277 (27), 276 (32), 275 (30), 231 (73), 230 (71), 169 (53). Anal. calc. for $C_{26}H_{38}O_7$ (462.58): C 67.51, H 8.28; found: C 67.38, H 8.37.

Data of **29**: yellowish oil that polymerized quickly in the condensed state. IR (KBr): 2960, 2880, 1695, 1665, 1570, 1420, 1380, 1250, 1210, 1025, 850, 820, 785, 735. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.59 (*ddd*, ^3J = 6.0, 2.2, ^5J = 1.2, H–C(1)); 7.19 (*dd*, ^3J = 10.1, 6.0, H–C(9)); 6.74 (*dddd*, ^3J = 5.0, 3.0, ^4J = 1.8, ^5J = 1.2, H–C(4)); 6.43 (*dd*, ^3J = 6.0, ^4J = 2.3, H–C(2)); 6.16 (*d*, ^3J = 10.1, H–C(8)); 3.24 (*ddddd*, ^3J = 11.4, ^4J = 2.3, ^3J = 2.2, ^4J = 1.8, ^5J = 1.7, 1.5, H–C(9b)); 2.73, 2.37 (2*d*, ^2J = 17.5, CH_2(6)); 2.47 (*ddd*, ^2J = 20.9, ^3J = 5.0, ^5J = 1.7, H_α–C(5)); 2.16 (*ddd*, ^2J = 20.9, ^3J = 3.0, ^5J = 1.5, H_β–C(5)); 2.05 (*dd*, ^3J = 11.4, 6.0, H–C(9a)); 1.70–1.41 (*m*, MeCH_2); 0.83 (*t*, ^3J = 7.5, *Me*CH_2). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 198.2 (*s*, C(7)); 194.1 (*s*, C(3)); 156.5 (*d*, *J* = 168, C(1)); 149.0 (*d*, *J* = 159, C(9)); 137.5 (*s*, C(3a)); 137.0 (*d*, *J* = 172, C(4)); 131.3, 130.0 (2*d*, *J* = 162, 166, C(2), C(8)); 46.3, 42.2 (2*d*, *J* = 131, 135, C(9a), C(9b)); 46.2 (*t*, *J* = 128, C(6)); 40.1 (*s*, C(5a)); 37.1, 31.3 (2*t*, *J* = 127, 127, C(5), Me*C*H_2); 8.0 (*q*, *J* = 126, *Me*CH_2). CI-MS (NH_3): 246 (70, $[M+NH_4]^+$), 229 (50, $[M+H]^+$), 228 (18, M^+), 122 (80), 106 (61), 94 (100).

*(5a*RS*,9*SR*,9a*RS*,9b*RS*)-9-{[(*tert*-Butyl)dimethylsilyl]oxy}-5a-ethyl-5a,6,8,9,9a,9b-hexahydro-3*H*-benz[e]indene-3,7(5*H*)-dione* (**33**). A soln. of **27** (35 mg, 40 µmol) and Et_3N (40 µl) in MeOH (3 ml) was stirred at 65° for 140 min. After cooling to 20°, the solvent was evaporated and the residue purified by FC (silica gel, 2 × 8 cm

column, AcOEt/light petroleum ether 1:3): 15 mg (70%) of **33**. Colorless needles. M.p. 121–122° (hexane). UV (MeCN): 246 (8800). IR (KBr): 2955, 2930, 2855, 1715, 1695, 1665, 1555, 1250, 1220, 1080, 895, 830, 780, 765. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.12 (br. *d*, ^3J = 6.0, H–C(2)); 6.65 (br. *s*, H–C(4)); 6.34 (*dd*, ^3J = 6.0, 2.3, H–C(1)); 4.44 (*ddd*, ^3J = 9.9, 6.1, 4.2, H–C(9)); 3.58 (br. *d*, ^3J = 11.4, H–C(9b)); 2.72–2.64 (*m*, CH_2(8)); 2.66, 2.11 (2*d*, ^2J = 15.6, CH_2(6)); 2.41 (*ddd*, ^2J = 20.0, ^3J = 4.6, ^5J = 1.8, H–C(5)); 2.11 (*ddd*, ^2J = 20.0, ^3J = 3.3, ^5J = 1.8, H–C(5)); 1.78 (*dd*, ^3J = 11.4, 4.2, H–C(9a)); 1.32 (*q*, ^3J = 7.4, MeCH_2); 0.92 (*s*, *t*-Bu); 0.87 (*t*, ^3J = 7.4, *Me*CH_2); 0.12, 0.10 (2*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 208.3 (*s*, C(7)); 194.9 (*s*, C(3)); 161.5 (*d*, *J* = 173, C(1)); 137.9 (*s*, C(3a)); 135.1 (*d*, *J* = 172, C(4)); 129.6 (*d*, *J* = 162, C(2)); 68.9 (*d*, *J* = 137, C(9)); 48.3, 46.7 (2*t*, *J* = 129, 129, C(6), C(7)); 44.7, 39.5 (2*d*, *J* = 132, 137, C(9a), C(9b)); 38.7 (*s*, C(5a)); 36.5, 32.2 (2*t*, *J* = 126, 128, C(4), MeCH_2); 25.8 (*q*, *J* = 125, *t*-Bu); 18.0 (*s*, *t*-Bu); 7.1 (*q*, *J* = 126, *Me*CH_2); –4.7, –4.8 (2*q*, *J* = 118, Me). CI-MS (NH_3): 361 (1, $[M+H]^+$), 303 (14), 150 (35), 144 (22), 143 (100), 101 (22). Anal. calc. for $C_{21}H_{32}O_3Si$ (360.57): C 69.95, H 8.95; found: C 64.64, H 8.80.

*(1*RS*,3*SR*,3a*RS*,4*SR*,5a*SR*,9a*SR*,9b*SR*)-7-{[(*tert*-*Butyl)dimethylsilyl]oxy}-5a-ethyl-1,4,5,5a,9a,9b-hexahydro-10-oxo-3*H*-1,3-ethanonaphtho[1,2-*c*]furan-3,4-diyl Bis(2,2-dimethylpropanoate)* (**34**). A mixture of **28** (150 mg, 0.33 mmol), Et_3N (0.27 ml, 1.9 mmol), (*t*-Bu)$Me_2SiOSO_2CF_3$ (0.30 ml, 1.3 mmol) and anh. CH_2Cl_2 (7 ml) was stirred at 20° for 15 h. CH_2Cl_2 (20 ml) was added and the soln. washed with a sat. aq. $NaHCO_3$ soln. (10 ml), then with a sat. aq. NH_4Cl soln. (10 ml). Each aq. phase was extracted with CH_2Cl_2 (3 × 5 ml). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue purified by FC (silica gel, 2 × 15 cm column, Et_2O/light petroleum ether 1:5): 179 mg (96%) of **34**. Colorless oil that was crystallized from hexane giving colorless plates. M.p. 150–151° (hexane). UV (MeCN): 275 (3200). IR (KBr): 2970, 2935, 1770, 1750, 1725, 1480, 1470, 1400, 1285, 1210, 1170, 1135, 1100, 990, 930, 905, 835, 785. ^{1}H-NMR (360 MHz, $CDCl_3$): 6.26 (*s*, H–C(3)); 6.01 (*dd*, ^3J = 9.8, 5.9, H–C(9)); 5.76 (*dd*, ^3J = 9.8, ^4J = 1.9, H–C(8)); 5.39 (*dd*, ^3J = 3.3, 2.7, H–C(4)); 4.66 (*d*, ^3J = 2.4, H–C(1)); 4.66 (*d*, ^4J = 1.9, H–C(6)); 2.50 (*d*, ^2J = 18.3, H_{syn}–C(11)); 2.43 (*d*, ^3J = 11.3, H–C(9b)); 2.34 (*dd*, ^3J = 11.3, 5.9, H–C(9a)); 2.27 (*dd*, ^2J = 18.3, ^3J = 2.4, H_{anti}–C(11)); 2.02 (*dd*, ^2J = 15.7, ^3J = 2.7, H–C(5)); 1.84, 1.17 (2*dq*, ^2J = 15.1, ^3J = 7.5, MeCH_2); 1.66 (*dd*, ^2J = 15.7, ^3J = 3.3, H–C(5)); 1.18, 1.16 (2*s*, Piv); 0.91 (*s*, *t*-Bu); 0.85 (*t*, ^3J = 7.5, *Me*CH_2); 0.10, 0.09 (2*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 202.7 (*s*, C(11)); 177.7, 177.2 (2*s*, Piv); 145.6 (*s*, C(7)); 129.0, 126.1 (2*d*, *J* = 165, 161, C(8), C(9)); 114.7 (*d*, *J* = 156, C(6)); 96.1 (*d*, *J* = 181, C(3)); 78.4 (*d*, *J* = 165, C(1)); 64.1 (*d*, *J* = 152, C(4)); 62.8 (*s*, C(3a)); 51.0 (*d*, *J* = 141, C(9a)); 46.3 (*dd*, *J* = 137, 130, C(10)); 38.9, 38.7 (2*s*, Piv); 37.2 (*s*, C(5a)); 36.5 (*d*, *J* = 133, C(9b)); 35.0, 32.5 (2*t*, *J* = 125, 122, C(5), MeCH_2); 27.3, 26.7 (2*q*, *J* = 127, 128, Piv); 25.5 (*q*, *J* = 124, *t*-Bu); 17.9 (*s*, *t*-Bu); 8.8 (*q*, *J* = 125, *Me*CH_2), –4.2, –4.6 (2*q*, *J* = 118, Me). CI-MS (NH_3): 592 (12, $[M+NH_4]^+$), 575 (5, $[M+H]^+$), 574 (4, M^+), 545 (18), 444 (12), 443 (26), 360 (19), 359 (54), 342 (18), 341 (54), 331 (19), 314 (34), 313 (100), 271 (17), 237 (14), 159 (13). Anal. calc. for $C_{32}H_{50}O_7Si$ (574.83): C 66.86, H 8.77; found: C 66.91, H 8.79.

*(1*RS*,3*RS*,3a*RS*,4*SR*,5a*RS*,9a*SR*,9b*SR*)-7-{[(*tert*-*Butyl)dimethylsilyl]oxy}-5a-ethyl-2,3,3a,4,5,5a,9a,9b-octahydro-1,3-dihydroxy-3a-(hydroxymethyl)-1*H*-benz[e]inden-4-yl 2,2-Dimethylpropanoate* (**36**) *and (1*RS*,3*SR*,5a*RS*,9a*SR*,9b*SR*)-6-{[(*tert*-*Butyl)dimethylsilyl]oxy}-5a-ethyl-2,3,5,5a,9a,9b-hexahydro-1*H*-benz[e]-indene-1,3-diol* (**37**). A mixture of **34** (200 mg, 0.34 mmol), MeOH (6 ml), CH_2Cl_2 (2 ml), and $NaBH_4$ (60 mg, 1.6 mmol) was stirred at 20° for 20 min. A sat. aq. NH_4Cl soln. (10 ml) and H_2O (10 ml) were added under vigourous stirring. The mixture was extracted with CH_2Cl_2 (5 × 10 ml), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue purified by FC (silica gel, 2 × 10 cm column, AcOEt/light petroleum ether 2:1): 104 mg (61%) of **36** and 12 mg (10%) of impure **37**.

Data of **36**: Colorless oil that crystallized from hexane giving a colorless powder. M.p. 92–94° (hexane). UV (MeCN): 274 (3100). IR (KBr): 3430, 2960, 2930, 2860, 1700, 1650, 1485, 1460, 1400, 1290, 1255, 1210, 1140, 1030, 920, 840, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.90 (*dd*, ^3J = 9.9, 5.9, H–C(9)); 5.69 (*dd*, ^3J = 9.9, ^4J = 1.9, H–C(8)); 5.41 (*dd*, ^3J = 3.1, 2.8, H–C(4)); 5.34 (*ddd*, ^3J = 7.1, 5.3, 2.7, H–C(3)); 4.50 (br. *s*, H–C(6)); 4.43 (*dd*, ^3J = 6.7, 5.1, H–C(1)); 3.79, 3.49 (2*d*, ^2J = 11.4, CH_2OH); 3.58, 2.82 (2s, OH); 2.74 (*dd*, ^3J = 12.2, 5.1, H–C(9b)); 2.56 (*d*, ^3J = 5.3, OH–C(3)); 2.44 (*dd*, ^3J = 12.2, 5.9, H–C(9a)); 2.24 (*dd*, ^2J = 15.5, ^3J = 7.1, H_β–C(2)); 1.93 (*ddd*, ^2J = 15.5, ^3J = 6.7, 2.7, H_α–C(2)); 1.80 (*dd*, ^2J = 15.4, ^3J = 2.8, H–C(5)); 1.75, 1.21 (2*dq*, ^2J = 14.3, ^3J = 7.4, MeCH_2); 1.71 (*dd*, ^2J = 15.4, ^3J = 3.1, H–C(5)); 1.21 (*s*, Piv); 0.92 (*s*, *t*-Bu); 0.85 (*t*, ^3J = 7.4, *Me*CH_2); 0.11, 0.10 (2*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 178.1 (*s*, Piv); 145.1 (*s*, C(7)); 130.2 (*d*, *J* = 160, C(8)); 124.8 (*d*, *J* = 161, C(9)); 115.0 (*d*, *J* = 153, C(6)); 76.3, 73.4 (2*d*, *J* = 150, 149, C(1), C(3)); 70.3 (*d*, *J* = 152, C(4)); 63.5 (*t*, *J* = 143, CH_2OH); 51.1 (*s*, C(3a)); 47.2 (*t*, *J* = 129, C(2)); 42.9 (*d*, *J* = 130, C(9b)); 39.1 (*s*, Piv); 37.9 (*t*, *J* = 128, C(5)); 37.3 (*s*, C(5a)); 36.1 (*d*, *J* = 128, C(9a)); 33.1 (*t*, *J* = 127, C(5), MeCH_2); 27.3 (*q*, *J* = 127, Piv); 25.6 (*q*, *J* = 125, *t*-Bu); 17.9 (*s*, *t*-Bu); 8.7 (*q*, *J* = 125, *Me*CH_2); –4.1, –4.6 (2*q*, *J* = 119, Me). CI-MS (NH_3): 512 (10, $[M+NH_4]^+$), 495 (100, $[M+H]^+$), 494 (51, M^+), 477 (4), 447 (4). Anal. calc. for $C_{27}H_{46}O_6Si$ (494.75): C 65.55, H 9.37; found: C 65.47, H 9.40.

Data of **37**: see **39**.

*(1*RS*,3*RS*,3a*SR*,4*SR*,5a*RS*,9a*SR*,9b*SR*)-1,3-Diacetoxy-3a-(acetoxymethyl)-7-{[(*tert*-butyl)dimethylsilyl]oxy}-5a-ethyl-2,3,3a,4,5,5a,9a,9b-octahydro-1*H*-benz[e]inden-4-yl 2,2-Dimethylpropanoate* (**38**) and *(1*RS*,3*SR*,5a*RS*,9a*SR*, 9b*SR*)-6-{[(*tert*-Butyl)dimethylsilyl]oxy}-5a-ethyl-2,3,5,5a,9a,9b-hexahydro-1*H*-benz[e]indene-1,3-diyl Diacetate* (**39**). A mixture of **34** (90 mg, 0.16 mmol), $NaBH_4$ (30 mg, 0.79 mmol), MeOH (3 ml), and CH_2Cl_2 (0.8 ml) was stirred at 20° for 20 min. A sat. aq. NH_4Cl soln. (10 ml) and H_2O (10 ml) were added, and the mixture was extracted with CH_2Cl_2 (5 × 10 ml). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue taken up in anh. pyridine (2 ml). Ac_2O (1 ml) and 4-(dimethylamino)pyridine (2 mg) were added. After stirring at 20° for 13 h, the solvent was evaporated and the residue purified by FC (silica gel, 2 × 10 cm column, Et_2O/light petroleum ether 1:2): 44 mg (45%) of **38** and 4 mg (6%) of **39**.

Data of **38**: Colorless needles. M.p. 109–110° (hexane). UV (MeCN): 272 (3200). IR (KBr): 2960, 2935, 2860, 1745, 1655, 1400, 1370, 1285, 1250, 1210, 1165, 1140, 1035, 830, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.69 (*dd*, ^3J = 9.9, ^4J = 1.9, H–C(8)); 5.62 (*dd*, ^3J = 9.9, 5.7, H–C(9)); 5.48 (*t*, ^3J = 2.8, H–C(4)); 5.34 (*dd*, ^3J = 7.8, 5.9, H–C(3)); 5.33 (*dd*, ^3J = 5.9, 4.5, H–C(1)); 4.54 (br. *s*, H–C(6)); 4.25 (*s*, CH_2OAc); 3.03 (*dd*, ^3J = 12.3, 4.5, H–C(9b)); 2.45 (*dd*, ^2J = 15.7, ^3J = 7.8, H_β–C(2)); 2.27 (*dd*, ^3J = 12.3, 5.7, H–C(9a)); 2.11, 2.10, 1.98 (3*s*, Ac); 1.86–1.71 (*m*, H_α–C(2), CH_2(5), MeCH_2); 1.25 (*s*, Piv); 1.21 (*dq*, ^2J = 14.5, ^3J = 7.5, MeCH_2); 0.92 (*s*, *t*-Bu); 0.86 (*t*, ^3J = 7.5, *Me*CH_2); 0.11, 0.10 (2*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 177.2 (*s*, Piv); 171.3, 170.4, 170.0 (3*s*, Ac); 145.0 (*s*, C(7)); 128.6 (*d*, *J* = 164, C(8)); 125.3 (*d*, *J* = 162, C(9)); 115.2 (*d*, *J* = 156, C(6)); 76.9, 73.6 (2*d*, *J* = 153, 158, C(1), C(3)); 69.4 (*d*, *J* = 154, C(4)); 66.0 (*t*, *J* = 148, CH_2OAc); 49.6 (*s*, C(3a)); 42.8 (*d*, *J* = 128, C(9b)); 41.4 (*t*, *J* = 132, C(2)); 39.1 (*s*, Piv); 38.2 (*t*, *J* = 126, C(5)); 37.9 (*s*, C(5a)); 36.6 (*d*, *J* = 130, C(9a)); 33.5 (*t*, *J* = 127, C(5), Me*C*H_2); 27.4 (*q*, *J* = 127, Piv); 25.6 (*q*, *J* = 125, *t*-Bu); 21.6, 21.4, 20.9 (3*q*, *J* = 129, 129, 130, Ac); 17.9 (*s*, *t*-Bu); 8.7 (*q*, *J* = 125, *Me*CH_2); −4.2, −4.6 (2*q*, *J* = 119, Me). CI-MS (NH_3): 621 (22, $[M+H]^+$), 489(22), 430(19), 429(37), 369(16), 328(15), 327(41), 310(33), 309(100), 298(29), 297(78). Anal. calc. for $C_{33}H_{52}O_9Si$ (620.86): C 63.84, H 8.44; found: C 63.90, H 8.46.

Data of **39**: Colorless solid. M.p. 106–107° (hexane). IR (KBr): 2960, 2930, 2860, 1735, 1640, 1375, 1240, 1205, 1155, 1025, 945, 895, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.04 (*dd*, ^3J = 9.8, 6.0, H–C(9)); 5.89 (br. *s*, H–C(4)); 5.70 (*dd*, ^3J = 9.8, ^4J = 2.0, H–C(8)); 5.59 (br. *d*, ^3J = 8.4, H–C(3)); 5.24 (*dd*, ^3J = 4.5, 4.4, H–C(1)); 4.69 (br. *s*, H–C(6)); 2.43–2.39 (*m*, H–C(9b)); 2.27 (*ddd*, ^2J = 16.1, ^3J = 8.4, 4.4, H–C(2)); 2.15–2.10 (*m*, CH_2(5)); 2.10, 2.09 (2*s*, Ac); 2.01 (*dd*, ^3J = 9.9, 6.0, H–C(9a)); 1.95-1.87 (*m*, H–C(2), MeCH_2); 1.13 (*dq*, ^2J = 12.4, ^3J = 7.5, MeCH_2); 0.92 (*s*, *t*-Bu); 0.86 (*t*, ^3J = 7.5, *Me*CH_2); 0.12 (*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.1, 170.8 (2*s*, Ac); 147.6, 141.3 (*s*, C(3a), C(7)); 132.2, 125.4, 123.2 (3*d*, C(4), C(8), C(9)); 115.0 (*d*, C(6)); 74.3, 72.6 (2*d*, C(1), C(3)); 46.9, 37.0 (2*d*, C(9a), C(9b)); 39.4, 36.0 (2*t*, C(2), C(5)); 37.1 (*s*, C(5a)); 31.5 (*t*, Me*C*H_2); 25.7 (*q*, *t*-Bu); 21.4 (*q*, Ac); 18.1 (*s*, *t*-Bu); 9.3 (*q*, *Me*CH_2); −4.3, −4.5 (2*q*, Me). CI-MS (NH_3): 447 (2, $[M+H]^+$), 327(5), 298(9), 297(26), 237(10), 236(46), 180(21), 179(100). Anal. calc. for $C_{25}H_{38}O_5Si$ (446.66): C 67.23, H 8.58; found: C 67.37, H 8.71.

*(1*RS*,3*RS*,3a*SR*,4*SR*,5a*SR*,9a*SR*,9b*SR*)-1,3-Diacetoxy-3a-(acetoxymethyl)-5a-ethyl-2,3,3a,4,5,5a,6,7,9a,9b-decahydro-7-oxo-1*H*-benz[e]inden-4-yl 2,2-Dimethylpropanoate* (**40**). A soln. of **38** (45 mg, 0.073 mmol) in anh. THF (4 ml) was cooled to 0°, and 1M Bu_4NF in THF (0.13 ml, 0.13 mmol) was added. After stirring at 0° for 15 min, the mixture was filtered through a pad of *Florisil* (2 × 2 cm column), rinsing with AcOEt (80 ml). The solvent was evaporated and the residue purified by FC (*Florisil* 1 × 10 cm column, Et_2O/light petroleum ether 1:1): 36 mg (98%) of **40**. Colorless foam. UV (MeCN): 227 (10100). IR (KBr): 2975, 1740, 1680, 1370, 1285, 1235, 1150, 1040. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.70 (*dd*, ^3J = 10.2, 5.5, H–C(9)); 6.07 (*d*, ^3J = 10.2, H–C(8)); 5.63 (*dd*, ^3J = 3.3, 2.4, H–C(4)); 5.44 (*dd*, ^3J = 7.7, 6.0, H–C(3)); 5.40 (*dd*, ^3J = 5.5, 4.5, H–C(1)); 4.34, 4.28 (2*d*, ^2J = 12.1, CH_2OAc); 3.18, 2.18 (2*d*, ^2J = 16.5, CH_2(6)); 2.84 (*dd*, ^3J = 12.6, 4.5, H–C(9b)); 2.53 (*dd*, ^2J = 16.1, ^3J = 7.7, H_β–C(2)); 2.52 (*dd*, ^3J = 12.6, 5.5, H–C(9a)); 2.15, 2.13, 1.99 (3*s*, Ac); 1.99 (*dd*, ^2J = 16.1, ^3J = 3.3, H–C(5)); 1.93 (*ddd*, ^2J = 16.1, ^3J = 6.0, 5.5, H_α–C(2)); 1.64, 1.37 (2*dq*, ^2J = 14.4, ^3J = 7.5, MeCH_2); 1.51 (*dd*, ^2J = 16.1, ^3J = 2.4, H–C(5)); 1.24 (*s*, Piv); 0.86 (*t*, ^3J = 7.5, *Me*CH_2). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 198.5 (*s*, C(7)); 176.6 (*s*, Piv); 171.2, 170.2, 169.9 (3*s*, Ac); 148.2 (*d*, *J* = 159, C(9)); 129.4 (*d*, *J* = 167, C(8)); 76.3, 73.2 (2*d*, *J* = 156, 154, C(1), C(3)); 69.2 (*d*, *J* = 155, C(4)); 65.4 (*t*, *J* = 147, CH_2OAc); 50.5 (*s*, C(3a)); 45.7, 41.6 (2*t*, *J* = 126, 133, C(2), C(6)); 44.6, 38.5 (2*d*, *J* = 126, 125, C(9a), C(9b)); 38.9 (*s*, Piv); 38.5 (*s*, C(5a)); 37.8 (*t*, *J* = 129, C(5)); 32.3 (*t*, *J* = 128, Me*C*H_2); 27.3 (*q*, *J* = 127, Piv); 21.5, 21.3, 20.9 (3*q*, *J* = 130, Ac); 7.9 (*q*, *J* = 126, *Me*CH_2). CI-MS (NH_3): 524 (33, $[M+NH_4]^+$), 438(19), 421(17), 406(42), 405(100), 362(33), 361(48), 225(25), 213(41), 212(38), 183(32). Anal. calc. for $C_{27}H_{38}O_9$ (506.59): C 64.02, H 7.56; found: C 64.15, H 7.59.

*(1*RS*,3*RS*,3a*SR*,4*SR*,5a*SR*,9a*SR*,9b*SR*)-5a-Ethyl-2,3,3a,4,5,5a,6,7,9a,9b-decahydro-1,4-dihydroxy-3a-(hydroxymethyl)-7-oxo-1*H*-benz[e]inden-3-yl 2,2-Dimethylpropanoate* (**41**). A soln. of **36** (44 mg, 0.089 mmol) in anh. THF (3 ml) was cooled to 0°. Then 1M Bu_4NF in THF (0.13 ml, 0.13 mmol) was added. After stirring at 0°

for 50 min, the mixture was filtered through a pad of *Florisil* (2 × 2 cm), rinsing with AcOEt (80 ml). The solvent was evaporated and the residue purified by FC (silica gel, 1 × 12 cm column, AcOEt/light petroleum ether 2 : 1): 23 mg (70%) of **41**. Colorless foam. IR (KBr): 3400, 2975, 2930, 1700, 1670, 1480, 1455, 1300, 1250, 1190, 1095, 1070, 1045, 1020, 865, 625. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.06 (*dd*, ^3J = 10.2, 5.6, H–C(9)); 6.04 (*d*, ^3J = 10.2, H–C(8)); 5.63 (*dd*, ^3J = 7.8, 3.7, H–C(3)); 4.43 (*dd*, ^3J = 6.4, 4.9, H–C(1)); 4.35 (br. *s*, OH); 4.23 (br. *s*, H–C(4)); 4.18 (br. *s*, OH); 3.78, 3.47 (2*d*, ^2J = 11.4, CH_2OH); 3.56, 2.21 (2*d*, ^2J = 17.4, CH_2(6)); 3.41 (*s*, OH); 2.85 (*dd*, ^3J = 12.2, 4.9, H–C(9b)); 2.71 (*dd*, ^3J = 12.2, 5.6, H–C(9a)); 2.53 (*dd*, ^2J = 16.1, ^3J = 7.8, H_β–C(2)); 1.85 (*ddd*, ^2J = 16.1, ^3J = 6.4, 3.7, H_α–C(2)); 1.66–1.53 (*m*, CH_2(5), MeCH_2); 1.36 (*dq*, ^2J = 14.4, ^3J = 7.5, MeCH_2); 1.20 (*s*, Piv); 0.85 (*t*, ^3J = 7.5, *Me*CH_2). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 200.1 (*s*, C(7)); 177.3 (*s*, Piv); 150.0 (*d*, *J* = 159, C(9)); 129.0 (*d*, *J* = 164, C(8)); 80.3 (*d*, *J* = 158, C(3)); 71.3, 70.9 (*d*, *J* = 150, 146, C(1), C(4)); 63.4 (*t*, *J* = 144, CH_2OH); 53.2 (*s*, C(3a)); 46.2, 45.9 (2*t*, *J* = 128, 130, C(2), C(6)); 44.6 (*d*, *J* = 122, C(9b)); 38.7, 38.6 (2*s*, Piv, C(5a)); 38.5 (*d*, *J* = 130, C(9a)); 38.4 (*t*, *J* = 126, C(5)); 32.6 (*t*, *J* = 125, MeCH_2); 27.2 (*q*, *J* = 127, Piv); 8.1 (*q*, *J* = 126, *Me*CH_2). CI-MS (NH_3): 398 (11, $[M+NH_4]^+$), 381 (100, $[M+H]^+$), 380 (78, M^+), 363(8), 279(5), 260(8), 231(8), 230(14).

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