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Approach towards an EPC synthesis of nodusmicin. Part 5:☆ Stereoselective introduction of a side chain at the *cis*-decalin part of nodusmicin

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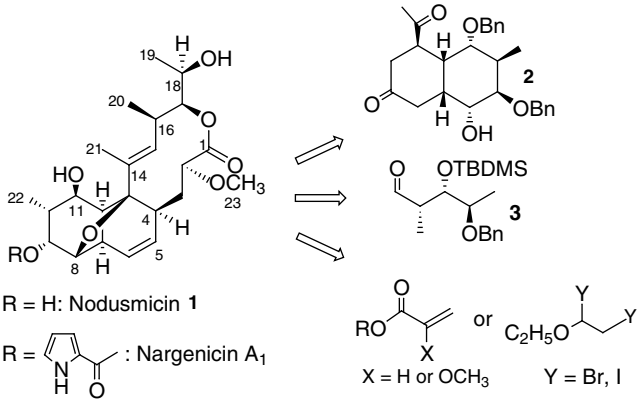
Abstract—The introduction of the side chain at C-4 of *cis*-decalin **2** and closure of the oxygen bridge are reported. Partial dehydrogenation of **2** was followed by oxymercuration and halogen–mercury exchange. Intermolecular radical addition to acrylic ester occurred from the convex face of the tricyclic compounds **7a** and **7b**. Consecutive epimerization failed. Therefore, two methods using intramolecular attachment of the side chain were developed. Formation of the β-iodoacetal of the cyclic allylic alcohol **21** permitted intramolecular radical addition generating the desired configuration at C-4 of the decalin. Likewise formation of the β bromoacetal with the *exo*-cyclic hydroxy group of tricycle **12** led via S_N2-reaction to tetrahydropyrans with the desired configuration at C-4. The oxygen bridge was introduced by dehydration of the *exo*-cyclic alcohol and consecutive oxymercuration. Mercury–oxygen exchange completed the reaction sequence.

The increasing resistance of bacterial pathogens to antibiotics necessitates the development of new and effective antibiotic species.[2] We therefore chose nodusmicin (**1**)[3,4] as a target of a convergent enantiomerically pure synthesis. This macrolide antibiotic was isolated from cultures of Saccharopolyspora hirsuta[4] and, like the structurally related nargenicins,[5] is active against Gram positive bacteria. This activity extends to drug resistant bacteria and is coupled with low toxicity and substantial oral activity.[6] These facts and its unusual structure initiated several approaches towards the synthesis of nodusmicin[7] which have culminated in the total synthesis of 18-deoxynodusmicin by Kallmerten et al.[7g]

So far we have completed the synthesis of the highly substituted oxygen bridged decalin fragment[7i,k] and have developed methods to extend the *exo*-cyclic acetyl group of bicyclic compound **2** to the unsaturated substituted side chain by adding the enantiomerically pure fragment **3**.[1] Herein we report our attempts to stereoselectively attach the remaining subunit of our convergent synthesis to the *cis*-decalin system. In anticipation of the difficulties associated with attaching this group to the already highly substituted decalin fragment,[7f] we have designed several pathways (Scheme 1).

As we have shown earlier, the ether bridge can be successfully introduced in the octalin system by oxy-mercuration.[7k] This strategy can be used to attach the ester side chain by intermolecular radical addition. Therefore, decalin **2** was partially dehydrogenated to octalindione **4** under improved conditions with ferric chloride, strong base and low temperatures. Luche reduction led to the diastereomeric octalintriols **5a** and **5b** ($1'R^*/1'S^*$=1:2.5).[7k] This mixture was transformed to the chromatographically separable crystalline oxygen bridged mercury compounds **6a** and **6b**.[8] The separated compounds were treated with iodine in methylene chloride.[9] As noted in the literature,[9,10] halogen–mercury exchange with rather unpolar solvents afforded diastereomeric mixtures of the iodides in high yields. NMR data especially NOESY experiments permitted the



Scheme 1.

☆ For Part 4 see ref. 1.

Keywords: total synthesis; antibiotic; nodusmicin; radical addition; substituted *cis*-decalins.

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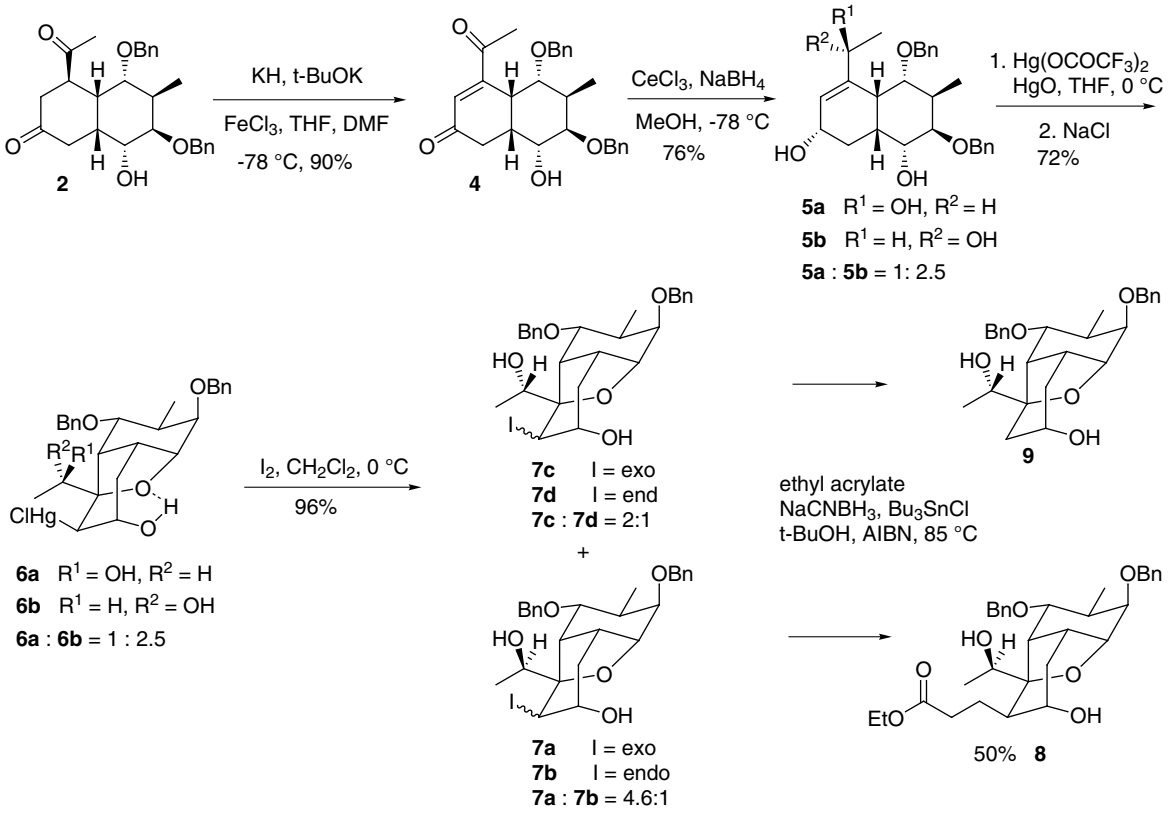
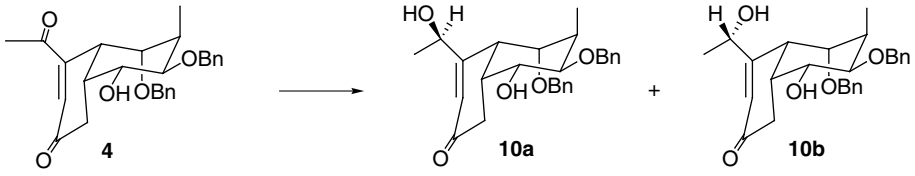


Scheme 2.

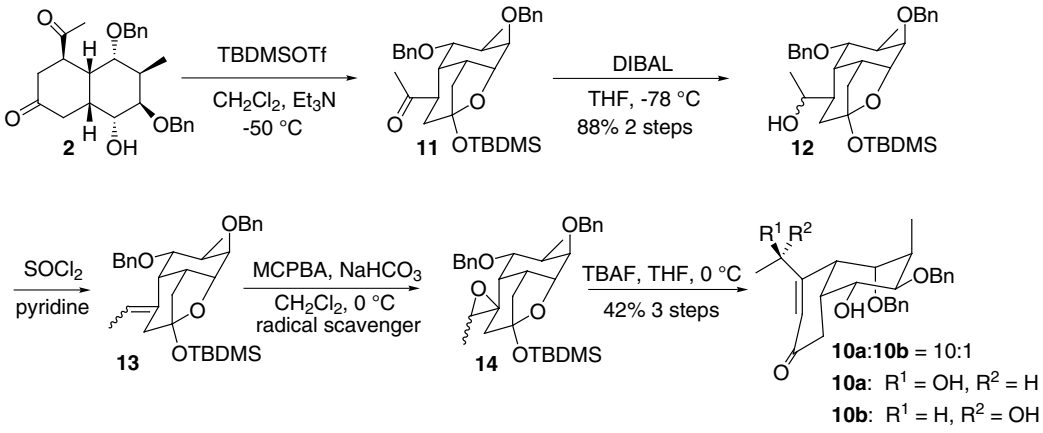
assignment of the relative configuration of the *exo*-cyclic stereocenter as well as the newly formed (cyclic) stereocenter containing the iodide substituent. The R^*-configurated alcohol **6a** led to a 4.6:1 mixture of easily separable iodides, with the *exo*-positioned iodide **7a**, derived by retention of configuration, as the main compound. The byproduct **7b** possesses a high inversion barrier leading to coalescence near room temperature. However, high temperature NMR-measurements revealed the vicinal *cis*-position of the iodide and the cyclic hydroxy group and thus the *endo*-position of the iodide. The S^*-configurated *exo*-cyclic alcohol **6b** led under identical conditions to an inseparable 2:1 mixture of *exo*- and *endo*-iodides **7c** and **7d**, indicating stronger steric hindrance on the convex face of this diastereoisomer.

Iodides **7** were treated under a variety of radical reaction conditions with acrylic esters to achieve radical addition.[11] (With radical initiators, AIBN or $h\nu$, tributyl stannanes, bis(trialkyl)stannanes,[12] tris(trimethyl)silylsilane,[13] and trialkylborane/oxygen[14] were examined as mediators.) Best results were achieved with catalytic amounts of tributylstannyl chloride and $NaCNBH_3$.[15] Even under these conditions only the R^*-configurated *exo*-cyclic alcohols **7a** and **7b** produced ester **8** in 50% yield, whereas the S^*-configurated alcohols were completely reduced to **9**[7k] due to stronger steric interactions in the main conformation which has a hydrogen bridge between the *exo*-cyclic alcohol and the benzyl ether oxygen. No addition product was detected even with the R^*-configurated alcohols when using α-methoxyacrylic ester (Scheme 2).

To improve the overall yields we looked for more selective reductants of the *exo*-cyclic ketone of **4**. We were able to achieve exclusive formation of the S^*-configurated alcohol **10b** with the reagent combination MAD/DIBAL/*n*-BuLi/toluene/−90°C.[16] However, the best results to gain the



Scheme 3.



Scheme 4.

desired R^*-configurated alcohol **10a** by hydride reduction were a meagre 1.9:1 mixture of **10a/10b** using MAD/DIBAL/methylene chloride/−90°C (Scheme 3).[17]

Thus a quite different approach was chosen to afford the R^*-configurated alcohol in good yields.

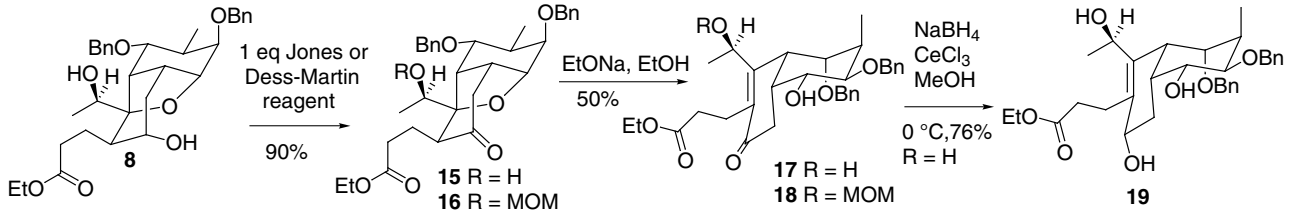
Dione **2** could be converted to the cyclic ketal **11** by treatment with *tert*-butyl dimethyl silyl triflate.[7k] Transformation to the enones **10a** and **10b** was achieved via reduction of the *exo*-cyclic ketone **11** to alcohol **12** with DIBAL, dehydration with $SOCl_2$ to olefin **13**, and epoxidation with peracid[18] to **14**. Treatment of **14** with a basic fluoride ion source removed the silyl group and concomittantly opened the epoxide via an $E1_{cb}$-reaction to provide the α,β-unsaturated ketone **10** (in a 10:1 mixture of **10a/10b**) (Scheme 4).

The relative configuration of the newly formed cyclic stereocenter had to be determined and if necessary epimerized. Therefore, the cyclic hydroxy group of **8** had to be oxidized. Due to steric reasons, the differentiation of the two hydroxy functions could be achieved by using exactly one equivalent of Dess–Martin[19] or Jones reagent[20] to provide the mono oxidized cyclic ketone **15** in good yields. NOE experiments with **15** and the corresponding methoxy methyl ether **16** revealed that irradiation at the signal of the bridgehead proton H-8 increased the intensity of two of the proton signals of the newly attached side chain. This effect is only possible if the side chain was introduced from the less hindered convex face of the molecule.

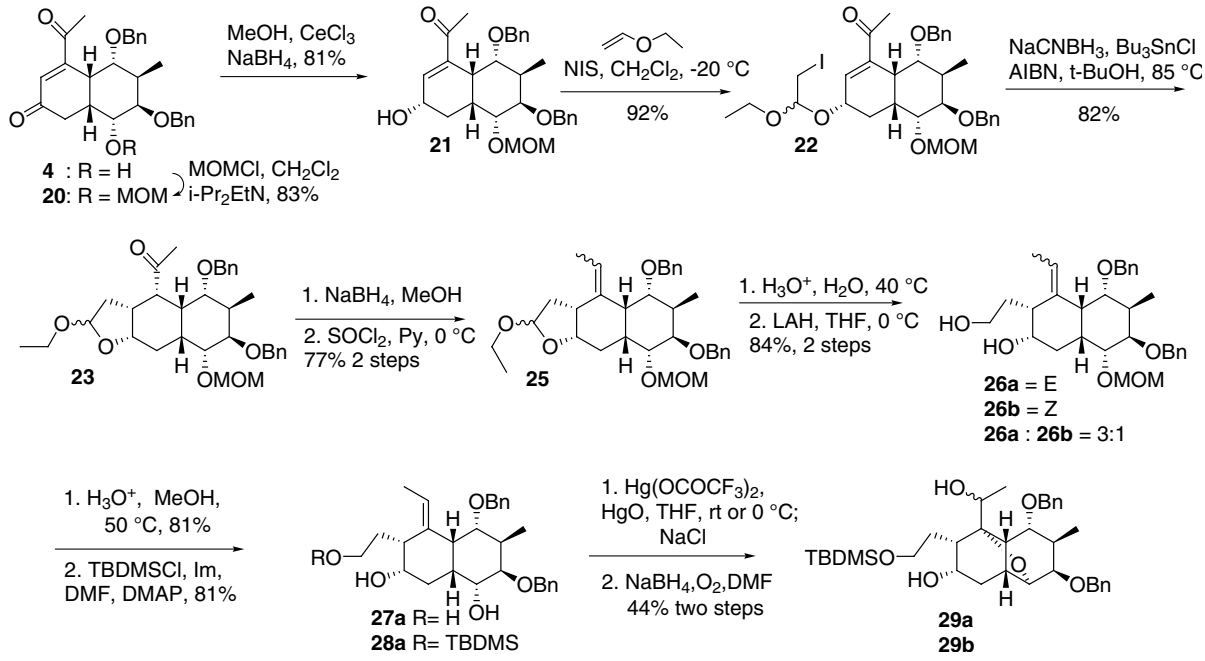
Neither acidic nor basic conditions led to epimerization of the stereogenic center of adduct **15** and **16**, respectively. The only reaction observed was $E1_{cb}$-elimination to octalinones **17** and **18**, respectively, under basic conditions. The resulting enones proved inert toward intramolecular 1,4-addition. Oxymercuration was examined as a further possibility to obtain the desired *endo* positioned side chain by reducing ketone **17** to triol **19**.[21] However, the diol **17** and its derivative **18** as well as triol **19** were inert against mercuric trifluoroacetate (Scheme 5).

To prevent addition from the sterically less hindered convex face of the molecule, we now turned to intramolecular radical reactions. We hoped to force attack from the more hindered concave side of the molecule by connecting the side chain to the cyclic *endo*-hydroxy group and then forming a fused perhydrofuran where *cis*-connection is kinetically as well as thermodynamically favored. To achieve this goal, enedione **4** was protected as MOM-ether **20** prior to regioselective reduction to **21** by inverse addition of Luche's reagent.[21c] However, the use of α-haloacetate[22] for radical cyclization purposes proved unsuccessful. Since we suspected the sp^2-center as the main reason of this failure[23] we replaced the haloester by a haloacetal.[24]

Thus allyl alcohol **21** was treated with ethyl vinyl ether and *N*-iodosuccinimide[25] to yield a diastereomeric mixture of the acetals **22a** and **22b** (1:1). Radical cyclization of these haloacetals afforded the desired heterocycles **23a** and **23b**,[26] which could be separated for analytical purposes, in good to high yield with up to 10% of the over-reduced *exo*-cyclic alcohol. The radical generated by the cyclization was quenched by hydrogen addition from the convex face of the molecule. Attempts to introduce a halogen instead of hydrogen by halogen transfer using either Co(I) complexes[27] or SmI_2 and iodine[28] led to disappointingly low yields in the halosubstituted cyclic products with reduction product **23** as the major compound.



Scheme 5.

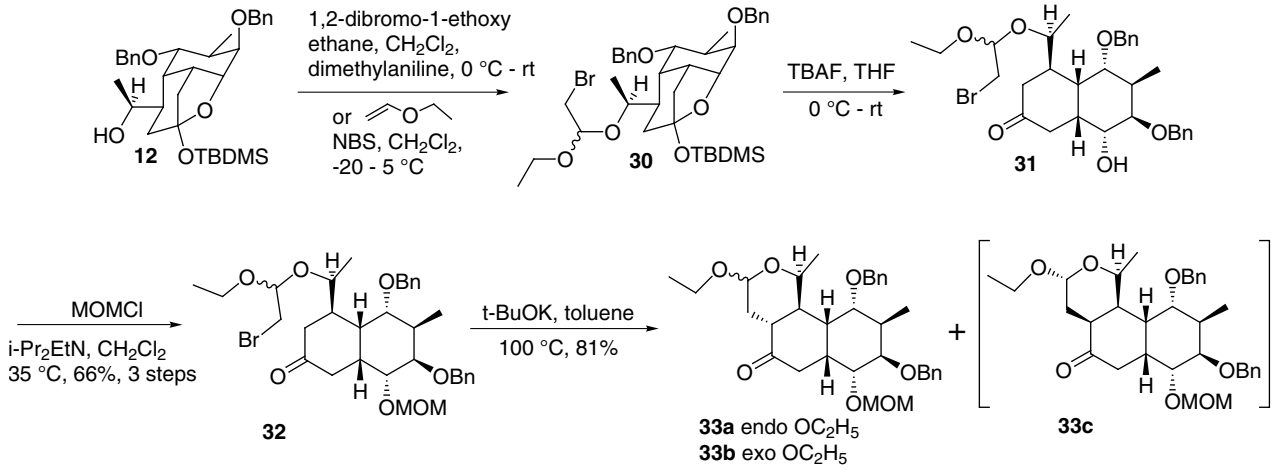


Scheme 6.

To close the ether bridge the following pathway was designed. The *exo*-cyclic keto group of **23** was converted into the trisubstituted olefins **25** (*E*/*Z*=3:1) via reduction with sodium borohydride to the inseparable epimeric *exo*-alcohols **24** and consecutive dehydration. The diols **26** were obtained by hydrolysis of the acetal and immediate reduction.

After separation on silica gel the diastereoisomers were treated individually. Hydrolysis of the methoxy methyl ether **26** to secondary alcohol **27** and regioselective protection of the primary alcohol led to silyl ether **28**. The configuration of the double bond in **28a** was determined by NOESY experiments to be in the *E*-configuration. Intramolecular oxymercuration of **28a** with mercury(II)trifluoracetate and mercury(II)oxide was very fast. Addition of sodium chloride allowed the isolation of the oxygen bridged organomercury chloride. Surprisingly **28b** (with the *Z*-configurated double bond) treated under identical conditions failed to react. Reaction of the organo-mercury compound with sodium borohydride in methanol at 0°C led to starting material **28** by *retro*-oxymercuration. Stronger basic conditions for the sodium borohydride reduction diminished this side reaction[29] but increased oxygen sensitivity which led to several products, one of them is the oxidation product **29**. To improve this desirable consecutive reaction we used Whitesides' reaction conditions—oxygen, DMF, sodium borohydride[30]—which led mainly to the epimeric *exo*-cyclic alcohols **29**. However, *retro*-oxymercuration was not totally suppressed leading to 16% of starting material **28** (Scheme 6).

A further route with an intramolecular nucleophilic substitution as the key step was developed. The *exo*-cyclic alcohol of tricyclic compound **12** was converted to the mixed acetals **30** by 1,2-dibromo-1-ethoxyethane or ethyl vinyl ether and *N* bromosuccinimide.[31] Desilylation of **30** to **31** was followed by protection of the secondary alcohol because



Scheme 7.

the desired alkylation under basic conditions in α-position to the ketone[32] was hampered by the free hydroxyl group. The cyclization rates of the two diastereoisomers of **32** under basic conditions were quite different. Nonetheless both could be transformed in high yields to the tricyclic perhydropyrans **33** when treated with *t*-BuOK in toluene at 100°C. Cyclization with the separated diastereoisomers showed that one cyclized within 5 h at 80°C whereas the other one required 15 h at 100°C. The faster cyclizing compound with the R^*-configuration at the acetalic carbon, gave a mixture of diastereomers (4:1) at 80°C. NOESY experiments revealed that the main component was the *trans* fused tetrahydropyran derivative **33a** with all three rings in a chair conformation, the ethoxy substituent in an equatorial position, and the heterocyclic methyl group in an axial position. The byproduct was the *cis*-fused tetrahydropyran derivative **33c**. The higher temperature needed for the alkylation of **32** with the S^*-configuration at the anomeric center led exclusively to the *trans*-fused pyran **33b** with all three rings in a chair conformation and both substituents of the heterocycle in an axial position (Scheme 7).

Thus we have successfully attached the side chain to the *cis* decalin (**2**) with the correct configuration at the newly formed stereocenter via two different pathways. In consequence we demonstrated with tricyclic compound **23** that closure of the ether bridge is possible. Several options for the stereo- and enantioselective extension of the side chain to the α-substituted propanoate exist.[33]

1. Experimental

1.1. General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Spectrospin AM 400-WB (400 MHz) with $CDCl_3$ as solvent at 24°C unless stated otherwise. EI mass spectra were recorded on a spectrometer 8230 (Finnigan) and FI mass spectra on a MAT 900S (Finnigan). IR spectra were recorded on a Perkin–Elmer 1600 FTIR spectrometer neat on silicon and given in wave numbers (cm^{-1}). Optical rotations were recorded on a Perkin–Elmer 241 polarimeter with the sodium D line. Melting points were obtained using a Reichert 'Kofler' hot stage microscope and are uncorrected. Silica gel (230–400 mesh ASTM, Merck) was used for flash chromatography.

1.1.1. (1*R*,6*R*,7*S*,8*R*,9*R*,10*R*)-5-Acetyl-7,9-dibenzyloxy-8-methyl-10-hydroxybicyclo [4.4.0] dec-4-en-3-one (4).[7k] *Improved procedure*. 2.27 g 35 wt% potassium hydride (20 mmol) dispersion in mineral oil (mineral oil was removed with dry petroleum ether) and 3.7 g (33 mmol) potassium *tert*-butanolate were stirred in 70 ml dry THF at room temperature under an argon atmosphere for 15 min. After cooling to 0°C 2.9 g (6.6 mmol) **2**, dissolved in 60 ml dry THF, were added with a syringe within 5 min. The yellow to orange solution was stirred at room temperature for further 25 min. After cooling to −78°C 3.2 g (20 mmol) anhydrous ferric chloride, dissolved in 100 ml dry DMF, was added with a syringe within 10 min. The dark solution was stirred at −78°C for 20 min and then quenched with aq. sat. NH_4Cl and 2% aq. HCl. The yellow aq. layer was extracted four times with ethyl acetate, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the product was purified by column chromatography with petroleum ether/ethyl acetate (2:1) to afford 2.59 g (90%) **4** as light sensitive yellowish crystals mp 111–112°C.

1.1.2. (1*R*,3*S*,4*R*,5*S*,7*R*,8*S*,9*R*,10*R*,11*R*)-9,11-Dibenzyloxy-5-hydroxy-3-(1′-hydroxyethyl)-10-methyl-2-oxatricyclo [5.4.0.0^{3,8}] undec-4-yl mercury chloride (6). A solution of 216 mg (0.49 mmol) **5a/5b** (1:2.5)[7k] in dry THF (5 ml) was treated at 0°C with 105 mg (0.245 mmol) mercury(II)trifluoroacetate and 54 mg (0.245 mmol) mercury(II)oxide under an argon atmosphere. After stirring for 1 h brine was added and the two-layer system was vigorously stirred for 15 min. The aq. layer was extracted four times with ethyl acetate, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the products were purified and separated by column chromatography with petroleum ether/ethyl acetate (1:2) to afford **6a** and **6b** (239 mg, 72%, diastereomeric ratio=1: 2.5).

6a. White crystals, mp 75–80°C. $[\alpha]^{20}_D$=+2.86° (*c*=0.7 g/100 ml in CH_2Cl_2); IR=3468 (OH), 2931 (C–H); ^{1}H NMR: δ=1.08 (d, J=6.5 Hz, 3H, 10-CH_3), 1.10 (d, J=6.5 Hz, 3H, 2′-H), 1.94 (m, J_{gem}=14.6 Hz, $J_5\sim J_7\sim$4 Hz, 1H, 6*exo*-H), 1.99 (m, J_{gem}=15 Hz, $J_5\sim J_7\sim J_4\sim$1.5 Hz, 1H, 6*endo*-H), 2.10 (d, J_9=3 Hz, 1H, 8-H), 2.29 (ddq, $J_{CH3}\sim J_{11}\sim$6 Hz, J_9=11.4 Hz, 1H, 10-H), 2.44 (dd, $J_{6ex}\sim J_{6en}\sim$2.7 Hz, 1H, 7-H), 2.79 (m, $w_{1/2}$=4.6 Hz, 1H, 4-H), 3.27 (d, J_5=10 Hz, 1H, 5-OH), 3.38 (dd, J_{10}=11 Hz, J_8=3 Hz, 1H, 9-H), 3.49 (dd, $J_1\sim J_{10}\sim$5 Hz, 1H, 11-H), 3.74 (d, $J_{1'}$=5 Hz, 1H, 1′-OH), 4.32 (dd br, J_{OH}=9.2 Hz, J_{6exo}=3 Hz, 1H, 5-H), 4.39 (d, J_{11}=5 Hz, 1H, 1-H), 4.42 (m, 1H, 1′-H), 4.43 (s, 2H, Bn), 4.47 (d, J=10.5 Hz, 1H, Bn), 4.61 (d, J=10.5 Hz, 1H, Bn), 7.0–7.4 (m, 10H, Ph); ^{13}C NMR: δ=13.52/16.15 (10-CH_3, C-2′), 37.66 (C-6), 36.06/37.96/52.65/55.20 (C-4,7,8,10), 66.96/69.70/79.53/81.35/84.79 (C-1′,1,5,9,11), 73.09/75.16 (Bn), 91.68 (C-3), 127.7–129.2 (Ph), 136.78/138.14 (Ph); MS (FI,190–240°): *m/z* (%)=420 (100) [M^+−HgCl, – OH], 91 (10) [$C_7H_7^+$]; Anal. Calcd for $C_{27}H_{33}ClHgO_5$: C=74.29%, H=7.39%, found: C=74.02%, H=7.39%.

6b. White crystals, mp 93–96°C. IR=3460 (OH), 2930 (C–H); ^{1}H NMR: 1.11 (d, J=7 Hz, 3H, 10-CH_3), 1.44 (d, J=6.5 Hz, 3H, 2′-H), 2.05–2.13 (m, 2H, 6*exo*/6*endo*-H), 2.24 (d, J_9=3 Hz, 1H, 8-H), 2.42 (ddq, J_9=11 Hz, $J_{11}\sim J_{CH3}\sim$6 Hz, 1H, 10-H), 2.62 (dd, $J_{6exo}\sim J_{6endo}\sim$3 Hz, 1H, 7-H), 2.64 (d, $J_{1'}$=3 Hz, 1H, 1′-OH), 3.29 (m, $w_{1/2}$=4.3 Hz, 1H, 4-H), 3.37 (dd, J_{10}=11 Hz, J_8=3.5 Hz, 1H, 9-H), 3.53 (dd, $J_1\sim J_{10}\sim$4.5 Hz, 1H, 11-H), 3.59 (d, J_5=9.5 Hz, 1H, 5-OH), 4.47–4.53 (m, 3H, 1′/1/5-H), 4.52 (s, 2H, Bn), 4.54 (d, J=11.5 Hz, 1H, Bn), 4.62 (d, J=11.5 Hz, 1H, Bn), 7.2–7.4 (m, 10H, Ph); ^{13}C NMR: 13.38/20.91 (10-CH_3, C-2′), 38.15 (C-6), 35.87/39.04/51.50/58.40 (C-4,7,8,10), 69.19/69.70/79.08/80.94/83.68 (C-1′,1,5,9,11), 73.15/73.33 (Bn), 93.51 (C-3), 127.7–128.7 (Ph), 137.52/138.19 (Ph); MS (FI, to 300°): *m/z* (%)=420 (100) [M^+−HgCl, – OH], 91 (10) [$C_7H_7^+$].

1.1.3. (1*R*,3*S*,5*S*,7*R*,8*S*,9*R*,10*R*,11*R*)-9,11-Dibenzyloxy-3-(1′-hydroxyethyl)-4-iodo-10-methyl-2-oxatricyclo [5.4.0.0^{3,8}] undecan-5-ol (7). For this reaction the isolated diastereo-

isomers **6a** and **6b**, respectively, were treated separately. A solution of 0.43 mmol **6** in dry methylene chloride (25 ml) was treated with 0.43 mmol iodine at 0°C under an argon atmosphere. After stirring for 30 min 10% aq. $Na_2S_2O_3$ solution was added and the two-phase system was vigorously stirred for 5 min. The aq. layer was extracted four times with methylene chloride, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the products were purified chromatographically, yielding 85–96% of **7**: **7a/b**=4.6:1, derived from **6a**, were separated with petroleum ether/diethyl ether (1:1) as eluents. The inseparable mixture of **7c/d**=2:1, derived from **6b**, was purified with petroleum ether/ethyl acetate (2:1). The iodides were used immediately after preparation.

7a (main product). Yellowish oil; $[\alpha]^{20}_D$=+38.7° (c=1.01 g/100 ml in CH_2Cl_2); IR=3460 (OH), 2936 (C–H); ^{1}H NMR: δ=1.15 (d, J=6.5 Hz, 3H, 10-CH_3), 1.28 (d, J=6.5 Hz, 3H, 2′-H), 1.95 (m, J_{gem}=15 Hz, 1H, 6*endo*-H), 2.39 (ddq, $J_{CH3}\sim J_{11}\sim$5.5 Hz, J_9=11.5 Hz, 1H, 10-H), 2.49 (ddd, J_{gem}=15 Hz, J_7=3 Hz, J_5=4.5 Hz, 1H, 6*exo*-H), 2.55 (dd, $J_{6ex}\sim J_{6en}\sim$3 Hz, 1H, 7-H), 3.22 (d, J_9=3 Hz,1H, 8-H), 3.47 (dd, J_{10}=11.5 Hz, J_8=3.5 Hz, 1H, 9-H), 3.52 (d br, J_5=8 Hz, 1H, 5-OH), 3.58 (dd, $J_1\sim J_{10}\sim$5 Hz, 1H, 11-H), 4.14 (d, $J_{1'}$=3 Hz, 1H, 1′-OH), 4.26 (m, $w_{1/2}$=15.4 Hz, J_{6ax}=4.5 Hz, 1H, 5-H), 4.33 (dq, $J_{1'}$=6.5 Hz, J_{OH}=4 Hz, 1H, 1′-H), 4.39 (m, $w_{1/2}$=4.5 Hz, 1H, 4-H), 4.44 (d, J_{11}=4.5 Hz, 1H, 1-H), 4.53 (s, 2H, Bn), 4.63 (d, J=11 Hz, 1H, Bn), 4.74 (d, J=11 Hz, 1H, Bn), 7.2–7.4 (m, 10H, Ph); ^{13}C NMR: δ=13.48/16.40 (10-CH_3, C-2′), 25.82 (C-4), 32.03 (C-6), 36.19/39.52/45.51 (C-7,8,10), 68.65/76.78/79.11/81.49/84.23 (C-1′,1,5,9,11), 73.28/74.48 (Bn), 89.31 (C-3), 127.69–128.81 (Ph), 136.60/138.13 (Ph); MS (FI, 110°): m/z (%): 564 (4) [M^+], 436 (14) [M^+-IH], 418 (28) [M^+-IH, $-H_2O$], 312 (100), 218 (29), 127 (4%) [I^+], 91 (19) [$C_7H_7^+$].

7b (by-product). White crystals, mp 132–138°C, $[\alpha]^{20}_D$=+34.78° (c=0.23 g/100 ml in CH_2Cl_2): IR: 3364 (OH), 3030 (=C–H), 2932/2874 (C–H) ^{1}H NMR (250 MHz, C_6D_6, 47°C): δ=1.15 (d, J=6.85 Hz, 3H, 10-CH_3), 1.57 (d, J=6.6 Hz, 3H, 2′-H), 1.65 (ddd, J_{gem}=13.7 Hz, J_5=7.5 Hz, J_7=2.3 Hz, 1H, 6a-H), 1.81 (ddd, J_{gem}=13.7 Hz, $J_5\sim J_7\sim$5.9 Hz, 1H, 6b-H), 2.31 (d br, J_5=6.9 Hz, 1H, 5-OH), 2.32–2.40 (m, 2H, 7/8-H), 2.83 (ddq, $J_{CH3}\sim J_{11}\sim$6.6 Hz, J_9=11.4 Hz, 1H, 10-H), 3.10–3.25 (m, 2H, 5-H/1′-OH), 3.26 (dd, J_{10}=11 Hz, J_8=3.2 Hz, 1H, 9-H), 3.49 (dd, $J_1\sim J_{10}\sim$5 Hz, 1H, 11-H), 4.29 (s, 2H, Bn), 4.31 (d, J_{11}=4.8 Hz, 1H, 1-H), 4.33 (d, J=11.2 Hz, 1H, Bn), 4.48 (d, J=11.2 Hz, 1H, Bn), 4.62 (dq, $J_{CH3}\sim J_{OH}\sim$6.6 Hz, 1H, 1′-H), 4.92 (d br, J_5=4.6 Hz, 1H, 4-H), 7.1–7.35 (m, 10H, Ph); ^{13}C NMR (250 MHz, C_6D_6, 47°C): δ=13.87/19.88 (10-CH_3,C-2′), 35.47 (C-6), 36.62/36.73/43.25 (C-7,8,10), 55.61 (C-4), 67.49/70.48/80.46/83.27/85.12 (C-1′, 1,5,9,11), 73.28/73.99 (Bn), 88.21 (C-3), 128–129 (Ph), 138.09/139.28 (Ph); MS (FI, 140°): m/z (%): 565 (33) [M^+], 456 (18) [$M^+-C_7H_7$, $-H_2O$], 437 (100) [M^+-I]; **7c/d** (inseparable mixture of isomers), yellowish oil, IR: 3422 (OH), 3030/3015 (=C–H), 2933/2899/2874 (C–H); MS (FI, 190°): m/z (%): 564 (4%) [M^+], 418 (7) [M^+-HI, $-H_2O$], 328 (10) [M^+-HI, $-H_2O$, –Bn], 314 (14), 254 (11) [M^+-HI, –Bn, –Bn], 218 (100), 127 (4%) [I^+], 108 (54), 91 (65) [$C_7H_7^+$].

1.1.4. (1″*R*,1′*R*,3′*S*,4′*R*,5′*S*,7′*R*,8′*S*,9′*R*,10′*R*,11′*R*)-Ethyl-3-[9′,11′-dibenzyloxy-3′-(1″-hydroxyethyl)-5′-hydroxy-10′-methyl-2′-oxatricyclo [5.4.0.0$^{3',8'}$] undec-4′-yl] propanoate (8). To a solution of 400 mg (0.708 mmol) **7a/b** and 7.08 mmol degassed ethyl acrylate (770 μl) in degassed *tert*-butanol (25 ml) 67 mg (1.06 mmol) sodium cyanoborohydride and 35 mg (0.212 mmol) AIBN were added. The mixture was heated to 85°C under an argon atmosphere. 0.142 mmol tri-*n*-butyltin chloride (38 μl) was added in three portions over 30 min, afterwards the solution was heated for 1 h. Then brine and water were added, the aq. layer was extracted four times with diethyl ether, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the products were purified and separated by column chromatography with petroleum ether/diethyl ether (2:1, then 1:1, then 1:2) to afford **8** as a colorless oil (~191 mg, ~50%) and **9**[7k] (~100 mg, ~32%). Polymeric impurities could not be removed completely. **8**: IR: 3480 (OH), 2929 (C–H), 1732 (CO); ^{1}H NMR: δ=1.12 (m, 1H, 3b-H), 1.14 (d, J=6.8 Hz, 3H, 10′-CH_3), 1.23 (d, J=6.4 Hz, 3H, 2″-H), 1.28 (t, J=7.1 Hz, 3H, OCH_2CH_3), 1.93 (ddd, J_{gem}=15 Hz, $J_{7'}$=3.2 Hz, $J_{5'}$=4.5 Hz, $J\sim$1, 1H, 6′b-H), 2.0 (ddd, J_{gem}=15 Hz, $J_{5'}\sim J_{7'}\sim$3.2 Hz, 1H, 6′a-H), 2.10 (d br, J_{3b}=10.8 Hz, 1H, 4′-H), 2.48–2.32 (m, 4H, 2b/3a/8′/10′-H), 2.48 (dd, $J_{6'a}\sim J_{6'b}\sim$3.1 Hz, 1H, 7′-H), 2.55 (dddd, J_{gem}=14.1 Hz, J_{3a}=10.5 Hz, J_{3b}=7.3 Hz, $J_{4'}$=1.4 Hz, 1H, 2a-H), 3.45 (dd, J_{10}=11.1 Hz, $J_{8'}$=3.1 Hz, 1H, 9′-H), 3.58 (dd, $J_{1'}\sim J_{10'}\sim$5 Hz, 1H, 11′-H), 3.65 (s, 1H, 5′-OH), 3.65 (d br, $J_{6'}$=3.5 Hz, 1H, 5′-H), 4.15 (dq, J_{CH3}=7.1 Hz, J=1 Hz, 2H, OCH_2CH_3), 4.25 (d, $J_{1''}$=3.9 Hz, 1H, 1″-OH), 4.33 (dq, J_{OH}=4.5 Hz, J_{CH3}=6.5 Hz, 1H, 1″-H), 4.39 (d, $J_{11'}$=4.6 Hz, 1H, 1′-H), 4.50 (d, J=11.7 Hz, 1H, Bn), 4.54 (d, J=11.7 Hz, 1H, Bn), 4.61 (d, J=10.8 Hz, 1H, Bn), 4.69 (d, J=11.0 Hz, 1H, Bn), 7.2–7.4 (m, 10H, Ph); ^{13}C NMR: δ=13.6/14.22/17.35 (10′-CH_3,C-2″,OCH_2CH_3), 24.26/33.39/34.0 (C-2,3,6′), 36.4/39.0/43.0/46.92 (C-4′,7′,8′,10′), 60.39 (OCH_2CH_3), 69.64/69.69/79.38/79.55/84.62 (C-1′,5′,9′,11′,1″), 73.05/74.57 (Bn), 91.49 (C-3′), 127.7–128.8 (Ph), 136.80/138.29 (Ph), 173.40 (CO); MS (FI, 190°): m/z (%): 539 (100) [M+H$^+$], 494 (45) [M+H$^+-CH_3CH_2O$], 449 (11) [$M^+-C_7H_7$], 91 (100) [$C_7H_7^+$].

1.1.5. (±)-(1*R,6*R**,7*S**,8*R**,9*R**,10*R**)-7,9-Dibenzyloxy-5-(1′-hydroxyethyl)-8-methyl-10-hydroxybicyclo [4.4.0] dec-4-en-3-one (10).** (±)-**10a**. A solution of 0.56 mmol **14** in dry THF (30 ml) was treated at 0°C with 353 mg (1.12 mmol) tetra-*n*-butylammonium fluoride trihydrate under an argon atmosphere. After stirring at 0°C for 1 h and at room temperature for 24 h sat. aq. NH_4Cl solution was added. The aq. layer was extracted three times with ethyl acetate, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the crude product was purified by column chromatography with petroleum ether/ethyl acetate (1:1.5) to afford **10a** (103.7 mg, 42% after three steps) as a colorless oil. IR: 3422 (OH), 3031.8 (=C–H), 2974/2956/2929 (C–H), 1652 (C=O); ^{1}H NMR: δ=0.96 (d, J=7.5 Hz, 3H, 8-CH_3), 1.20 (d, J=6.5 Hz, 3H, 2′-H), 1.41 (br, $w_{1/2}$=17.37 Hz, 1H, OH), 2.45–2.5 (br, 1H, OH), 2.48

(dd, J_{gem}=16.5 Hz, J_1=5 Hz, 1H, 2eq-H), 2.54 (ddd, J_{2ax}=13, J_{2eq}~J_{10}~J_6~5 Hz, 1H, 1-H), 2.57 (ddq, J_{CH3}=7.5 Hz, J_9=4.5 Hz, J_7=3 Hz, 1H, 8-H), 2.69 (dd, J_{gem}=16.6 Hz, J_1=13 Hz, 1H, 2ax-H), 2.83 (dd, J_7~J_1~3.7 Hz, 1H, 6-H), 3.68 (dd, J_6~J_8~2.5, 1H, 7-H), 3.76 (dd, J_8=5 Hz, J_{10}=10 Hz, 1H, 9-H), 3.91 (dd, J_9=10 Hz, J_1=5.5 Hz, 1H, 10-H), 4.06 (q, J_{CH3}=7 Hz, 1H, 1′-H), 4.17 (d, J=12.5 Hz, 1H, Bn), 4.36 (d, J=11.4 Hz, 1H, Bn), 4.42 (d, J=12 Hz, 1H, Bn), 4.54 (d, J=11.5 Hz, 1H, Bn), 5.95 (s, 1H, 4-H), 7.0–7.4 (m, 10H, Ph); ^{13}C NMR: δ=11.20/21.79 (8-CH_3,C-2′), 33.01/34.77/38.98 (C-1,6,8), 35.31 (C-2), 68.53/69.37/76.50/ 80.86 (C-1′,7,9,10), 71.18/71.59 (Bn), 127.96–128.53 (Ph and C-4), 137.98/138.03 (Ph), 163.40 (C-5), 201.11 (C=O); MS (FI, 150°C): *m/z* (%)=437 (100) [M+H$^+$], 391 (19) [M+H$^+$−CH_3CHOH], 267 (14), 91 (58) [$C_7H_7^+$], 57 (34); Anal. Calcd for $C_{27}H_{32}O_5$: C=74.29%, H=7.39%, found: C=74.02%, H=7.42%

10b. *MAD-solution*: A 2 M solution of trimethylalane (288 μl) in dry toluene (0.575 mmol) was added dropwise to a solution of 253 mg (1.15 mmol) 2,6-di-*t*-butyl-4-methylphenol in dry toluene (3 ml) under an argon atmosphere at room temperature. The mixture was stirred for 1 h. *DIBAL solution*: A 1 M solution of diisobutylaluminum hydride (460 μl) in hexane (0.46 mmol) was diluted with dry toluene (1 ml) and a 1.6 M solution of *n*-butyllithium in hexane (0.46 mmol=290 μl) was added at 0°C. The mixture was stirred for 10 min.

The MAD solution was cooled to −90°C and a solution of 50 mg (0.115 mmol) **4** in dry toluene (2 ml) was added. The DIBAL solution was added 10 min later. After stirring at −90°C for 1 h sat. aq. NH_4Cl solution and water were added. 2% aq. HCl was added and the aq. layer was extracted four times with ethyl acetate, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the crude product was purified by column chromatography with petroleum ether/ethyl acetate (1:2) then petroleum ether/acetone (1:1) to afford **10b** (19 mg, 39%) as a colorless oil. IR: 3430 (OH), 3032 (=C–H), 2974/2882 (C–H), 1652 (C=O); ^{1}H NMR: δ=0.95 (d, J=7 Hz, 3H, 8-CH_3), 1.10 (d, J=3.5 Hz, 1H, 1′-OH), 1.18 (d, J=6.5 Hz, 3H, 2′-H), 2.42 (br, 1H, OH), 2.43 (dd, J_7~J_1~3.5 Hz, 1H, 6-H), 2.48 (dd, J_{gem}=16 Hz, J_1=4.5 Hz, 1H, 2eq-H), 2.52–2.62 (m, 2H, 1/8-H), 2.67 (dd, J_{gem}=16 Hz, J_1=13.55 Hz, 1H, 2ax-H), 3.54 (dd, J_6~J_8~2.5 Hz, 1H, 7-H), 3.78 (dd, J_8=5 Hz, J_{10}=10 Hz, 1H, 9-H), 3.88 (dd, J_9=10 Hz, J_1=5.5 Hz, 1H, 10-H), 4.94 (dq, J_{CH3}=6 Hz, J_{OH}=3 Hz, 1H, 1′-H), 4.16 (d, J=12 Hz, 1H, Bn), 4.38 (d, J=11 Hz, 1H, Bn), 4.44 (d, J=12.6 Hz, 1H, Bn), 4.55 (d, J=11 Hz, 1H, Bn), 6.13 (s, 1H, 4-H), 7.0–7.4 (m, 10H, Ph); ^{13}C NMR: δ=11.32/22.45 (8-CH_3,C-2′), 33.17/36.50/38.66 (C-1,6,8), 35.32 (C-2), 68.21/68.46/76.51/80.63 (C-1′,7,9,10), 71.30/71.73 (Bn), 126.17 (C-4), 127.98–128.57 (Ph), 137.89/137.94 (Ph), 165.20 (C-5), 200.52 (C=O); MS (FI): *m/z* (%)=436 (100) [M$^+$]; %: Calcd for $C_{27}H_{32}O_5$: C=74.29%, H=7.39%, found: C=72.74%, H=7.28%.

1.1.6. (±)-(1*S,3*R**,4*S**,5*S**,6*R**,7*R**,8*R**,9*R**)-5,7-Dibenzyloxy-3-(1′-hydroxyethyl)-1-(*t*-butyldi-methylsilyloxy)-6-methyl-11-oxatricyclo [6.2.1.0^{4,9}] undecane (12).** A solution of 1.13 g (2.1 mmol) **2** and 10.5 mmol dry triethylamine (1.5 ml) in dry methylene chloride (90 ml) was cooled to −50°C under an argon atmosphere and 2.5 mmol *tert*-butyldimethylsilyl trifluoromethanesulfonate (584 μl) were added. After stirring for 20 min at −50°C sat. aq. $NaHCO_3$ solution was added. The aq. layer was extracted four times with methylene chloride the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the crude product **11** was dissolved in dry THF (90 ml) and cooled to −78°C under an argon atmosphere. 6.3 mmol of 1.5 M diisobutylaluminum hydride solution in toluene (4.2 ml) was added and the mixture stirred for 5 h. The reaction mixture was quenched with water (3 ml) and stirred for 30 min. The mixture was filtrated through celite and the organic layer was treated with brine and dried over Na_2SO_4. After filtration and evaporation the product was purified by column chromatography with petroleum ether/ethyl acetate (10:1) to afford **12** (1 g, 87.9% over two steps) as a colorless oil. IR: 3421 (OH), 3032 (=C–H), 2959 (C–H); ^{1}H NMR: δ=−0.01 (s, 3H, Si–CH_3), 0.00 (s, 3H, Si–CH_3), 0.77 (s, 9H, *t*-Bu), 1.00 (d, J=6 Hz, 3H, 2′-H), 1.02 (d, J=7 Hz, 3H, 6-CH_3), 1.36 (dd, J_3=6.5 Hz, J_{gem}=12.6 Hz, 1H, 2*exo*-H), 1.60 (d, J_{gem}=11.5 Hz, 1H, 10*exo*-H), 1.76 (ddd, J_{gem}=11.5 Hz, J_9~J_{2endo}~3 Hz, 1H, 10*endo*-H), 1.85 (m, J_4~4 Hz, J_{2ex}~6.5 Hz, $J_{1'}$~9 Hz, J_{2en}~13 Hz, 1H, 3-H), 1.90 (ddd, J_{gem}~J_3~12.6 Hz, J_{10en}=2 Hz, 1H, 2*endo*-H), 2.11 (ddq, J_{CH3}=7 Hz, J_7=3 Hz, J_5=10.5 Hz, 1H, 6-H), 2.31 (ddd, J_9~J_3~J_5~4.7 Hz, 1H, 4-H), 2.37 (ddd, J_4~J_8~J_{10en}~3 Hz, 1H, 9-H), 3.30 (ddq, J_{CH3}=6 Hz, J_3=8.5 Hz, J_{OH}=5 Hz, 1H, 1′-H), 3.51 (dd, J_4=4 Hz, J_6=11.04 Hz, 1H, 5-H), 3.51 (m, 1H, 7-H), 3.73 (d, $J_{1'}$=5 Hz, 1H, OH), 3.90 (dd, J_7~J_9~2.5 Hz, 1H, 8-H), 4.41 (d, J=11 Hz, 1H, Bn), 4.42 (d, J=11.6 Hz, 1H, Bn), 4.49 (d, J=11.5 Hz, 1H, Bn), 4.54 (d, J=10.5 Hz, 1H, Bn), 7.15–7.3 (m, 10H, Ph); ^{13}C NMR: δ=−2.87/−2.81 (Si–CH_3), 13.31/21.87 (6-CH_3,C-2′), 17.77 (*t*-Bu), 25.86 (*t*-Bu), 32.52/38.67/38.84/40.18 (C-3,4,6,9), 41.98/43.08 (C-2,10), 73.80/76.70/79.93/ 80.74 (C-1′,5,7,8), 73.44/73.92 (Bn), 106.58 (C-1), 127.66–128.47 (Ph), 137.20/138.45 (Ph); MS (FI, 130°C): *m/z* (%): 552 (48) [M$^+$], 494 (100) [M$^+$−*t*-Bu], 404 (12) [M$^+$−*t*-Bu, −C_7H_7], 182 (7), 91 (34) [$C_7H_7^+$], 57 (8) [*t*-Bu]; Anal. Calcd for $C_{33}H_{48}O_5Si$: C=71.7%, H=8.75%, found: C=71.47%, H=8.61%.

1.1.7. (±)-(1*R,4*R**,5*S**,6*R**,7*R**,8*R**,9*R**)-5,7-Dibenzyloxy-3-ethylidene-1-(*t*-butyldimethylsilyloxy)-6-methyl-11-oxatricyclo [6.2.1.0^{4,9}] undecane (13).** 2.8 mmol $SOCl_2$ (204 μl, freshly distilled) and dry pyridine (5 ml) were combined. A solution of 311 mg (0.56 mmol) **12** in dry pyridine (30 ml) was added slowly (over 1 h) at room temperature (The color of the solution turns to orange.) After the addition was completed the mixture was stirred for 30 min at room temperature. The reaction mixture was quenched with sat. aq. $NaHCO_3$ solution. The aq. layer was extracted four times with ethyl acetate the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation toluene was added several times and evaporated. For analytical purposes a small part of the product **13** was purified by column chromatography with petroleum ether/ethyl acetate (10:1) the rest was used without purification for the following reaction; 9.3% of an isomeric product has been formed which could not be

separated. Colorless oil; IR: 3031 (=C–H), 2931/2910/2857 (C–H); ^{1}H NMR: δ=0.00 (two s, 6H, 2Si–CH_3), 0.77 (s, 9H, *t*-Bu), 0.90 (d, J=7 Hz, 3H, 6-CH_3), 1.46 (dd, $J_{1'}$=7 Hz, J_{2en}=2.5 Hz, 3H, 2′-H), 1.65 (ddd, J_{gem}=11.0 Hz, J_9=4 Hz, J_{2en}=1.5 Hz, 1H, 10*endo*-H), 1.71 (d, J_{gem}= 11 Hz, 1H, 10*exo*-H), 1.88 (ddq, J_{CH3}=7 Hz, J_7=2.5 Hz, J_5=12 Hz, 1H, 6-H), 2.49 (m, J_4~J_8~J_{10en}~4.5 Hz, 1H, 9-H), 2.51 (d, J_{gem}=15.6 Hz, 1H, 2*exo*-H), 2.76 (m, J_{gem}=15.6 Hz, 1H, 2*endo*-H), 3.2 (dd, J_9~J_5~6.5 Hz, 1H, 4-H), 3.49 (dd, J_8~J_6~2.5 Hz, 1H, 7-H), 3.63 (dd, J_6=11.55 Hz, J_4=5.5 Hz, 1H, 5-H), 3.95 (dd, J_7~J_9~3.5 Hz, 1H, 8-H), 4.38 (d, J=11 Hz, 1H, Bn), 4.41 (d, J=10.5 Hz, 1H, Bn), 4.52 (d, J=11.6 Hz, 1H, Bn), 4.58 (d, J=11 Hz, 1H, Bn), 5.45 (m, J_{CH3}=7 Hz, 1H, 1′-H), 7.1–7.3 (m, 10H, Ph); ^{13}C NMR: δ=−2.92/−2.78 (Si–CH_3), 14.06/15.10 (6-CH_3,C-2′), 17.80 (*t*-Bu), 25.88 (*t*-Bu), 33.17/36.69/38.76 (C-4,6,9), 40.59/53.58 (C-2,10), 73.39/74.11 (Bn), 74.24/79.17/ 80.91 (C-5,7,8), 106.61 (C-1), 127.47–128.62 (Ph and C-1′), 131.11 (C-3), 138.49/138.74 (Ph); MS (FI, 80°C): *m/z* (%): 535 (100) [M+H$^+$], 478 (37) [M+H$^+$−*t*-Bu], 444 (74) [M$^+$−C_7H_7], 387 (39) [M$^+$−*t*-Bu, –C_7H_7], 298 (32), 91 (23) [$C_7H_7^+$], 84 (58), 57 (42) [*t*-Bu]; Anal. Calcd for $C_{33}H_{46}O_4Si$: C=74.11%, H=8.67%, found: C=73.81%, H=8.52%.

1.1.8. (±)-(1′*R,4′*S**,5′*R**,6′*R**,7′*R**,8′*R**,9′*R**)-5′,7′-Dibenzyloxy-1′-(*t*-butyldimethylsilyloxy)-6′-methyl-3-methylspiro{oxiran-2,3′-11′-oxatricyclo [6.2.1.0$^{4',9'}$] undecane} (14).** To a solution of 0.56 mmol of the crude material **13** in dry methylene chloride (50 ml) 1.5 g $NaHCO_3$ and 248 mg (1.12 mmol) 2,6-di-*t*-butyl-4-methylphenol were added. The mixture was cooled to 0°C under an argon atmosphere and 388 mg (2.24 mmol) MCPA was added. After stirring for 2 h 10% aq. $Na_2S_2O_3$ solution was added and the two-phase system vigorously stirred for 20 min. The aq. layer was extracted four times with methylene chloride the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation a small part of product **14** was purified by column chromatography for analytical purposes. The rest was used without purification for the following reaction. Colorless oil. IR=2930/2910/2858 (C–H); ^{1}H NMR: δ=0.00 (two s, 6H, 2Si–CH_3), 0.76 (s, 9H, *t*-Bu), 1.0 (d, J=6.5 Hz, 3H, 6′-CH_3), 1.2 (d, J=5 Hz, 3H, 3-CH_3), 1.74 (ddd, J_{gem}=11.5 Hz, $J_{9'}$=4.5 Hz, $J_{2'en}$=1.5 Hz, 1H, 10′*endo*-H), 1.81 (d, J_{gem}=14.55 Hz, 1H, 2′*exo*-H), 1.85 (d, J_{gem}=11.5 Hz, 1H, 10′*exo*-H), 2.29 (m, 1H, 4′-H), 2.29 (ddq, J_{CH3}=6.2 Hz, $J_{7'}$=2.5 Hz, 1H, 6′-H), 2.40 (d, J_{gem}=14.6 Hz, 1H, 2′*endo*-H), 2.48 (ddd, $J_{4'}$=8 Hz, $J_{8'}$~$J_{10'en}$~4 Hz, 1H, 9′-H), 2.55 (q, J_{CH3}=5.5 Hz, 1H, 3-H), 3.55 (m, 1H, 7′-H), 3.57 (dd, $J_{6'}$=12 Hz, $J_{4'}$=5 Hz, 1H, 5′-H), 3.94 (dd, $J_{7'}$~$J_{9'}$~3 Hz, 1H, 8′-H), 4.20 (d, J=11.5 Hz, 1H, Bn), 4.44 (d, J=11.5 Hz, 1H, Bn), 4.50 (d, J=11.5 Hz, 1H, Bn), 4.51 (d, J=11.5 Hz, 1H, Bn), 7.1–7.3 (m, 10H, Ph); ^{13}C NMR: δ=−2.94/−2.86 (Si–CH_3), 13.96/14.16 (3-CH_3,6′-CH_3), 17.78 (*t*-Bu), 25.85 (*t*-Bu), 33.33/34.60/37.04 (C-4′,6′,9′), 40.56/52.79 (C-2′,10′), 57.81 (spiro C), 61.69 (C-3), 72.26/73.46 (Bn), 75.21/78.44/80.63 (C-5′,7′,8′), 105.45 (C-1′), 127.29–128.28 (Ph), 138.69/138.78 (Ph); MS (FI, 95°C): *m/z* (%): 550 (18) [M$^+$], 493 (58) [M$^+$−*t*-Bu], 459 (18) [M$^+$−C_7H_7], 403 (32), 267 (43), 91 (25) [$C_7H_7^+$], 57 (100%) [*t*-Bu].

1.1.9. (+)-(1″*R*,1′*R*,3′*S*,4′*S*,7′*R*,8′*S*,9′*R*,10′*R*,11′*R*)-Ethyl 3-{3′-(1″-hydroxyethyl)-9′,11′-dibenzyloxy-10′-methyl-2′-oxatricyclo [5.4.0.0$^{3',8'}$] undecan-5′-on-4′-yl} propanoate (15). *Method a*. A 0.02 M solution of **8** in dry methylene chloride was treated with 1 equiv. of Dess–Martin reagent under an argon atmosphere at room temperature. After stirring for 30 min sat. aq. $NaHCO_3$ solution and 10% aq. $Na_2S_2O_3$ solution were added and the two phase system was vigorously stirred for 5 min. The aq. layer was extracted four times with methylene chloride, the combined organic layers were washed with brine and dried over Na_2SO_4. *Method b*. A 0.02 M solution of **8** in acetone was treated with Jones reagent under an argon atmosphere at 0°C until starting material was no longer detectable by TLC. Sat. aq. NH_4OAc solution was added, the aq. layer was extracted four times with ethyl acetate, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the product was purified by column chromatography with petroleum ether/diethyl ether (2:1, then 1:2). Both methods yielded 70–90% **15** as a colorless oil. $[\alpha]^{20}_D$=+29.87° (c=2.3 g/100 ml in CH_2Cl_2); IR: 3468 (OH), 2928/2854 (C–H), 1732 (CO); ^{1}H NMR: δ=1.06 (d, J=6.5 Hz, 3H, 10′-CH_3), 1.11 (d, J=6 Hz, 3H, 2″-H), 1.17 (t, J=7 Hz, 3H, OCH_2CH_3), 1.48 (m, J_{gem}=15.6 Hz, $J_{4'}$=13.6 Hz, J_{2a}~J_{2b}~6.5 Hz, 1H, 3b-H), 2.23–2.19 (m, 2H, 2a/2b-H), 2.20 (ddd, J_{gem}=16.6 Hz, $J_{4'}$~$J_{7'}$~2 Hz, 1H, 6′eq-H), 2.31 (ddq, J_{CH3}~6.5 Hz, $J_{9'}$=11.6 Hz, $J_{11'}$~4 Hz, 1H, 10′-H), 2.59–2.49 (m, 3H, 3a/4′/7′-H), 2.63 (dd, J_{gem}=16.6 Hz, $J_{7'}$=4 Hz, 1H, 6′*exo*-H), 2.76 (d, $J_{9'}$=3 Hz, 1H, 8′-H), 3.45 (dd, $J_{10'}$~$J_{1'}$~4.5 Hz, 1H, 11′-H), 3.52 (dd, $J_{10'}$=11.0 Hz, $J_{8'}$=3 Hz, 1H, 9′-H), 3.90 (d, $J_{11'}$=4.5 Hz, 1H, 1′-H), 4.03 (q, J=7 Hz, 2H, OCH_2CH$_3$), 4.09 (d, $J_{1''}$=4 Hz, 1H, OH), 4.24 (dq, J_{CH3}=6.5 Hz, J_{OH}=4.5 Hz, 1H, 1″-H), 4.36 (d, J=12 Hz, 1H, Bn), 4.43 (d, J=11.55 Hz, 1H, Bn), 4.58 (d, J=11 Hz, 1H, Bn), 4.65 (d, J=11 Hz, 1H, Bn), 7.15–7.35 (m, 10H, Ph); ^{13}C NMR: δ=13.57/14.18/16.75 (10′-CH_3,C-2″OCH$_2$CH_3), 23.41/31.89/42.86 (C-2,3,6′), 36.39/39.28/43.01 (C-8′,7′,10′), 56.93 (C-4′), 60.37 (OCH_2CH$_3$), 73.34/74.80 (Bn), 69.62/79.49/80.80/84.19 (C-1′,9′,11′,1″), 89.53 (C-3′), 127.71–128.83 (Ph), 136.67/138.18 (Ph), 173.04 (ester CO), 210.70 (5′-CO); MS (EI, 160°C, 70 eV): *m/z* (%): 536 (3.4) [M$^+$], 492 (8.7), 386 (15.7), 91 (100) [$C_7H_7^+$]; HRMS (EI, 200°C, 70 eV): Calcd for $C_{32}H_{40}O_7$= 536.2774, found M$^+$=536.2782; Anal. Calcd for $C_{32}H_{40}O_7$: C=71.62%, H=7.51%, found: C 71.39=%, H=7.62%.

1.1.10. (±)-(1″*R,1′*R**,3′*S**,4′*S**,7′*R**,8′*S**,9′*R**,10′*R**,11′*R**)-Ethyl 3-{3′-(1″-methoxymethyloxy-ethyl)-9′,11′-dibenzyloxy-10′-methyl-2′-oxatricyclo [5.4.0.0$^{3',8'}$] undecan-5′-on-4′-yl} propanoate (16).** To a solution of 26 mg (0.045 mmol) of (±)-**15** in dry methylene chloride (1 ml) were added 1.35 mmol *N*,*N*-diisopropylethylamine(233 μl) and 0.9 mmol chloromethyl methyl ether (68 μl) and the reaction mixture was stirred under an argon atmosphere at 40°C for 24 h. Sat. aq. $NaHCO_3$ solution was added and the aq. layer was extracted four times with methylene chloride. The combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the crude product was purified by column chromatography with petroleum ether/ethyl acetate (2:1) to afford 15.5 mg (59%) **16** as colorless oil. IR: 3063/3031(arom C–H),

2981/2854 (C–H), 1733 (CO); ^{1}H NMR: δ=1.06 (d, J=6.5 Hz, 3H, 10′-CH_3), 1.18 (t, J=7 Hz, 3H, OCH_2CH_3), 1.23 (d, J=6.5 Hz, 3H, 2″-H), 1.51 (m, 1H, 3b-H), 2.15–2.30 (m, 4H, 2a/2bor4′/10′/6b-H), 2.53 (dd, $J_{6a'}$∼$J_{6b'}$∼2 Hz, 1H, 7′-H), 2.60–2.75 (m, 3H, 3a/4′ or 2b/6′-H), 2.95 (d, $J_{9'}$=2.5 Hz, 1H, 8′-H), 3.18 (s, 3H, OCH_3), 3.34 (dd, $J_{10'}$=10 Hz, $J_{8'}$=3.5 Hz, 1H, 9′-H), 3.44 (dd, $J_{10'}$∼$J_{1'}$∼5 Hz, 1H, 11′-H), 3.86 (d, $J_{11'}$=5 Hz, 1H, 1′-H), 4.04 (q, J=7 Hz, 2H, OCH_2CH_3), 4.23 (q, J_{CH3}=6.5 Hz, 1H, 1″-H), 4.27 (d, J=7 Hz, 1H, OCH_2O), 4.36 (d, J=11.55 Hz, 1H, Bn), 4.39 (d, J=12.5 Hz, 1H, Bn), 4.43 (d, J=11.5 Hz, 1H, Bn), 4.50 (d, J=7 Hz, 1H, OCH_2O), 4.71 (d, J=12.05 Hz, 1H, Bn), 7.15–7.35 (m, 10H, Ph); ^{13}C NMR: δ=13.71/14.19/16.89 (10′-CH_3, C-2″, OCH_2CH_3), 24.0/32.30/42.96 (C-2,3,6′), 35.73/39.55/40.40 (C-4′,7′,10′), 55.31 (OCH_3), 57.20 (C-8′), 60.35 (OCH_2CH_3), 71.54/73.24 (Bn), 78.55/79.33/80.14/83.13 (C-1′,9′,11′,1″), 88.62 (C-3′), 98.07 (OCH_2O), 127.35–128.41 (Ph), 138.36/138.48 (Ph), 173.18 (ester CO), 210.82 (5′-CO).

1.1.11. (±)-(1″*R,1′*R**,6′*R**,7′*S**,8′*R**,9′*R**,10′*R**)-Ethyl 3-{5′-(1″-hydroxyethyl)-7′,9′-dibenzyloxy-10′-hydroxy-8′-methylbicyclo [4.4.0] dec-4′-en-3′-on-4′-yl} propanoate (17).** 117 mg (5 mmol) sodium were treated with dry ethanol (5 ml). A solution of 39 mg (0.073 mmol) (±)-**15** in ethanol (5 ml) was added under an argon atmosphere at 0°C. After stirring for 30 min at 0°C and 2 h at room temperature sat. aq. NH_4Cl solution was added. The aq. layer was extracted four times with ethyl acetate, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the product was purified by column chromatography with petroleum ether/ethyl acetate (2:1, then 1:1) to afford starting material (10.5 mg, 27%) and **17** (19.6 mg, 50%) as a colorless oil. IR: 3448 (OH), 3028 (=C–H), 2970/2925 (C–H), 1734 (ester CO), 1654 (CO, C=C); ^{1}H NMR: δ=0.88 (d, J=7.5 Hz, 3H, 8′-CH_3), 0.99 (t, J=7 Hz, 3H, OCH_2CH_3), 1.15 (d, J=6.5 Hz, 3H, 2″-H), 1.89 ($w_{1/2}$=8.6 Hz, 1H, OH), 2.18–2.40 (m, 6H, 1′/2′b/OH/3a or 2a/3b or 2b-H), 2.42 (ddq, J_{CH3}=7.5 Hz, $J_{7'}$=3 Hz, $J_{9'}$=5 Hz, 1H, 8′-H), 2.53–2.7 (m, 2H, 3a or 2a/2′a-H), 2.70 (dd, $J_{1'}$∼$J_{7'}$∼3.5 Hz, 1H, 6′-H), 3.67 (dd, $J_{10'}$=10.5 Hz, $J_{8'}$=5 Hz, 1H, 9′-H), 3.70 (dq, J_{CH3}=7 Hz, J_{gem}=10.55 Hz, 1H, OCH_2CH_3), 3.77 (dd, $J_{6'}$∼$J_{8'}$∼3–2.5 Hz, 1H, 7′-H), 3.80 (dd, $J_{1'}$=5 Hz, $J_{9'}$=10.5 Hz, 1H, 10′-H), 3.86 (dq, J_{CH3}=7 Hz, J_{gem}=10.55 Hz, 1H, OCH_2CH_3), 4.12 (d, J=12.55 Hz, 1H, Bn), 4.24 (d, J=11.55 Hz, 1H, Bn), 4.28 (d, J=12.05 Hz, 1H, Bn), 4.43 (d, J=11.55 Hz, 1H, Bn), 4.81 (q, J_{CH3}=6.5 Hz, 1H, 1″-H), 7.15–7.3 (m, 10H, Ph); ^{13}C NMR: δ=11.27/14.06/21.78 (8′-CH_3, C-2″, OCH_2CH_3), 20.85/33.1/35.62 (C-2,3,2′), 33.18/33.94/ 38.49 (C-1′,6′,8′), 60.41 (OCH_2CH_3), 71.01/71.91 (Bn), 67.19/68.81/76.59/82.18 (C-7′,9′,10′,1″), 127.55–128.54 (Ph), 138.03/138.53 (Ph), 135.99/156.59 (C-4′,5′), 173.88 (ester CO), 200.30 (3′-CO); MS (FI, 140°C): *m/z* (%): 537 (100) [M+H$^+$], 91 (27) [$C_7H_7^+$]; HRMS: Calcd for $C_{32}H_{40}O_7$=536.2774, found M$^+$=536.2782.

1.1.12. (±)-(1″*R,1′*R**,6′*R**,7′*S**,8′*R**,9′*R**,10′*R**)-Ethyl 3-{5′-(1″-hydroxy)ethyl-7′,9′-dibenzyloxy-10′-hydroxy-8′-methylbicyclo [4.4.0] dec-4′-en-3′-on-4′-yl} propanoate (18).** 32 mg (1.4 mmol) sodium were treated with dry ethanol (2 ml). A solution of 12 mg (0.02 mmol) **16** in ethanol (1 ml) was added under an argon atmosphere at room temperature. After stirring for 3 h sat. aq. NH_4Cl solution was added. The aq. layer was extracted four times with ethyl acetate, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the product was purified by column chromatography with petroleum ether/ethyl acetate (3:1, then 2:1) to afford (5.3 mg, 44%) **18** as a colorless oil. IR: 3568 (OH), 3028 (=C–H), 2926 (C–H), 1733.5 (ester CO), 1664 (CO, C=C); ^{1}H NMR: δ=0.95 (d, J=7.5 Hz, 3H, 8′-CH_3), 1.15 (t, J=7 Hz, 3H, OCH_2CH_3), 1.27 (d, J=6.5 Hz, 3H, 2″-H), 2.26 (t, J∼8 Hz, 2H, 2-or 3-H), 2.36 ($w_{1/2}$=6.7 Hz, 1H, OH), 2.42 (dd, $J_{2'}$=17.6 Hz, $J_{1'}$=6.5 Hz, 1H, 2′-H), 2.45–2.55 (m, 2H, 1′-H,8′-H), 2.52 (dt, J_{gem}=14 Hz, J=7.5 Hz, 1H, 3- or 2-H), 2.62 (dt, J_{gem}=13.55 Hz, J=8 Hz, 1H, 3- or 2-H), 2.72 (dd, $J_{2'}$=17.6 Hz, $J_{1'}$=13 Hz, 1H, 2′-H), 2.81(dd, $J_{1'}$∼$J_{7'}$∼3.5 Hz, 1H, 6′-H), 3.25 (s, 3H, OCH_3), 3.73 (dd, $J_{10'}$=10 Hz, $J_{8'}$=5.5 Hz, 1H, 9′-H), 3.73 (dd, $J_{6'}$∼$J_{8'}$∼3 Hz, 1H, 7′-H), 3.90 (dd, $J_{1'}$=5.5 Hz, $J_{9'}$=10 Hz, 1H, 10′-H), 3.99 (dq, J_{CH3}=7 Hz, J_{gem}=11 Hz, 1H, OCH_2CH_3), 4.02 (dq, J_{CH3}=7 Hz, J_{gem}=11 Hz, 1H, OCH_2CH_3), 4.18 (d, J=12 Hz, 1H, Bn), 4.30 (d, J=11 Hz, 2H, Bn), 4.35 (d, J=6.5 Hz, 1H, OCH_2O), 4.41 (d, J=6.5 Hz, 1H, OCH_2O), 4.48 (d, J=11.5 Hz, 1H, Bn), 4.80 (q, J_{CH3}=6.5 Hz, 1H, 1″-H), 7.0–7.3 (m, 10H, Ph); ^{13}C NMR: δ=11.67/14.59/20.83 (8′-CH_3,C-2″,OCH_2CH_3), 21.55/33.86/35.98 (C-2,3,2′), 33.48/34.81/38.99 (C-1′,6′,8′), 55.86 (OCH_3), 60.7 (OCH_2CH_3), 71.49/72.72 (Bn), 69.24/72.44/76.88/83.25 (C-7′,9′,10′,1″), 95.01 (OCH_2O), 127.56–128.95 (Ph), 138.43/138.72 (Ph), 137.01/155.13 (C-4′,5′), 173.40 (ester CO), 200.06 (3′-CO); MS (FI, 90°C): *m/z* (%): 581 (18) [M+H$^+$], 391 (84), 256 (46), 106 (100), 61(51) [$CH_3OCH_2O^+$]; HMRS: Calcd for $C_{32}H_{40}O_7$=536.2774, found M$^+$=536.2782.

1.1.13. (±)-(1″*R,1′*R**,3′*S**,6′*R**,7′*S**,8′*R**,9′*R**,10′*R**)-Ethyl 3-{5′-(1″-hydroxyethyl)-7′,9′-dibenzyloxy-3′,10′-dihydroxy-8′-methylbicyclo [4.4.0] dec-4′-en-4′-yl} propanoate (19).** To a solution of 20 mg (0.037 mmol) **17** in methanol (2 ml) 14 mg (0.037 mmol) ceric(III)chloride heptahydrate was added at 0°C under an argon atmosphere. After 20 min 3 mg (0.074 mmol) sodium borohydride were added. After stirring for 15 min sat. aq. NH_4Cl solution and water were added. The aq. layer was extracted four times with methylene chloride the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the product was purified by column chromatography with petroleum ether/ethyl acetate (1:1) to afford **19** (15 mg, 76%) as a colorless oil. IR: 3448 (OH), 3028 (=C–H), 2970/2924 (C–H), 1734 (ester CO), 1654 (C=C); ^{1}H NMR: δ=0.96 (d, J=7.5 Hz, 3H, 8′-CH_3), 1.16 (d, J=6.5 Hz, 3H, 2″-H), 1.17 (t, J=7 Hz, 3H, OCH_2CH_3), 1.33 ($w_{1/2}$=11.5 Hz, 1H, OH), 1.57 (d br, $J_{3'}$=9.5 Hz, 1H, 3′OH), 1.82 (ddd, J_{gem}∼$J_{1'}$∼13.55 Hz, $J_{3'}$=7.5 Hz, 1H, 2′ax, *endo*-H), 2.04 (dddd, $J_{2'b}$=14 Hz, $J_{6'}$∼$J_{2'a}$∼$J_{10'}$∼5 Hz, 1H, 1′-H), 2.27 (ddd, J_{gem}=13 Hz, $J_{3'}$=8 Hz, $J_{1'}$=5 Hz, 1H, 2′eq(*exo*)-H), 2.32–2.48 (m, 4H, 3a or 2a/2b/3b-H,OH), 2.52 (dd, $J_{1'}$∼$J_{7'}$∼3.5–4 Hz, 1H, 6′-H), 2.58 (ddq, J_{CH3}=7.5 Hz, $J_{7'}$=2.5 Hz, $J_{9'}$=5 Hz, 1H, 8′-H), 2.63 (m, 1H, 3a or 2a-H), 3.75 (dd, $J_{10'}$=10.5 Hz, $J_{8'}$=5 Hz, 1H, 9′-H), 3.81 (dd, $J_{6'}$∼$J_{8'}$∼3–2.5 Hz, 1H, 7′-H), 3.84 (dd, $J_{1'}$=5.5 Hz, $J_{9'}$=10 Hz, 1H, 10′-H), 4.01 (dq, J_{CH3}=7 Hz, J_{gem}=11 Hz, 1H, OCH_2CH_3), 3.95–4.07 (m, 1H, 3′-H),

4.04 (dq, J_{CH3}=7 Hz, J_{gem}=11 Hz, 1H, OCH_2CH$_3$), 4.24 (d, J=12 Hz, 1H, Bn), 4.35 (d, J=11 Hz, 1H, Bn), 4.51 (d, J=12 Hz, 1H, Bn), 4.54 (d, J=11 Hz, 1H, Bn), 4.72 (q, J_{CH3}=6.5 Hz, 1H, 1″-H), 7.15–7.3 (m, 10H, Ph); ^{13}C NMR: δ=11.50/14.22/21.41 (8′-CH$_3$,C-2″, OCH$_2$*C*H$_3$), 24.33/29.63/33.73 (C-2,3,2′), 33.05/34.03/ 38.52 (C-1′,6′,8′), 60.43 (O*C*H$_2$CH$_3$), 71.05/71.54 (Bn), 67.03/ 69.19/69.38/76.75/82.31 (C-3′,7′,9′,10′, 1″), 127.89–128.54 (Ph), 136.29/137.84 (C-4′,5′), 138.20/138.58 (Ph), 173.68 (ester CO); MS (FI, 150°C): *m/z* (%): 539 (100) [M+H$^+$], 521 (80) [M$^+$−H$_2$O], 494 (44) [M+H$^+$−CH$_3$CH$_2$O], 91 (65) [C$_7$H$_7^+$]; Anal. Calcd for C$_{32}$H$_{42}$O$_7$: C=71.35%, H=7.86%, found: C=71.08%, H=7.83%.

1.1.14. (±)-(1*R,6*R**,7*R**,8*R**,9*R**,10*S**)-2-Acetyl-8,10-dibenzyloxy-9-methyl-7-methoxymethyloxybicyclo [4.4.0] dec-2-en-4-one (20).** To a solution of 1.98 g (4.6 mmol) light sensitive **4** in dry methylene chloride (20 ml) in a brown round bottom flask were added 92 mmol *N*,*N*-diisopropylethylamine (15.9 ml) and ~65 mmol chloromethyl methyl ether (5 ml) and the reaction mixture was stirred under an argon atmosphere for 21.5 h. Sat. aq. NaHCO$_3$ solution was added and the aq. layer was extracted four times with methylene chloride. The combined organic layers were washed with brine and dried over Na$_2$SO$_4$. After filtration and evaporation the crude product was purified by column chromatography with petroleum ether/ethyl acetate (4:1) to afford 1.8 g (83%) **20** as colorless crystals mp 105°C; IR: 3028 (H–C=), 2890 (C–H), 1676 COC=CCO); ^{1}H NMR: δ=1.17 (d, J=7.3 Hz, 3H, 9-CH$_3$), 2.25 (s, 3H, COCH$_3$), 2.56 (qdd, J_{CH3}=7.4 Hz, J_8=5.1 Hz, J_{10}=2.8 Hz, 1H, 9-H), 2.6–2.65 (m, 2H, 6-H/ 5eq-H), 2.93 (dd, J_5=19 Hz, J_6=15.7 Hz, 1H, 5ax-H), 3.21(dd, J_6~5 Hz, J_{10}~2.7 Hz, 1H, 1-H), 3.36 (s, 3H, OCH$_3$), 3.55 (t, J_1~J_9~2.7 Hz, 1H, 10-H), 3.91 (dd, J_7=10.35 Hz, J_9=5.1 Hz, 1H, 8-H), 3.99 (dd, J_8=10.35 Hz, J_6=5.6 Hz, 1H, 7-H), 4.10 (d, J=12.1 Hz, 1H, Bn), 4.38 (d, J=12.1 Hz, 1H, Bn), 4.58 (d, J=11.8 Hz, 1H, Bn), 4.63 (d, J=11.6 Hz, 1H, Bn), 4.68 (d, J=6.8 Hz, 1H, OCH$_2$O), 4.86 (d, J=6.8 Hz, 1H, OCH$_2$O), 6.66 (s, 1H, 3-H), 7.05–7.4 (m, 10H, Ph); ^{13}C NMR: δ=11.79 (*C*H$_3$-9), 26.50 (*C*H$_3$CO), 33.68/35.29/ 38.62 (C-9,6,1), 36.61 (C-5), 55.96 (*C*H$_3$O), 72.37/72.59 (Bn), 75.24/75.67/81.51 (C-7,8,10), 97.27 (O*C*H$_2$O), 127.85–128.78 (Ph), 136.06 (C-3) 138.22/139.32 (Ph), 152.55 (C-2), 199.74/202.82 (CH$_3$*C*O/C-4); MS (EI): *m/z* (%)=478 (<2) [M$^+$], 446 (<2) [M$^+$−CH$_3$OH], 434 (3.5) [M$^+$−CH$_2$OCH$_3$], 433 (11) [M$^+$−CH$_3$OCH$_3$], 228 (10), 219 (25), [M$^+$], 91 (100) [C$_7$H$_7^+$]; Anal. Calcd for C$_{29}$H$_{34}$O$_6$: C=72.78%, H=7.16%, found: C=72.44%, H=7.14.

1.1.15. (±)-(1*R,4*S**,6*R**,7*R**,8*R**,9*R**,10*S**)-2-Acetyl-8,10-dibenzyloxy-9-methyl-7-methoxymethyloxybi-cyclo [4.4.0] dec-2-en-4-ol (21).** 103 mg (2.8 mmol) sodium borohydride were dissolved in methanol (30 ml) and stirred at 0°C under an argon atmosphere for 10 min. 335 mg (1.4 mmol) ceric(III)chloride heptahydrate dissolved in methanol (10 ml) were added and stirring continued at 0°C for 15 min. This reaction mixture was added dropwise within 45 min with a syringe to a solution of 650 mg (1.4 mmol) **20**, 335 mg (1.4 mmol) ceric(III)chloride heptahydrate, methylene chloride (10 ml), and methanol (40 ml) at 0°C under an argon atmosphere. After 15 min THF (5 ml) were added to improve the solubility. After stirring further 30 min at 0°C sat. aq. NH$_4$Cl solution and water were added and the aq. layer was extracted four times with ethyl acetate, the combined organic layers were washed with brine and dried over Na$_2$SO$_4$. After filtration and evaporation the crude product was purified by column chromatography with petroleum ether/ethyl acetate (2:1) to afford 544 mg (81%) **21** as colorless crystals mp 144°C. IR: 3456 (O–H), 3028 (H–C=), 2886 (C–H), 1667 (CO–C=); ^{1}H NMR: δ=1.10 (d, J=7.5 Hz, 3H, 9-CH$_3$), 1.35 (d, J_4=8.8 Hz, 1H, OH), 2.03 (ddd, J_6=13.8 Hz, J_5=12.1 Hz, J_4=9.5 Hz, 1H, 5ax-H), 2.20 (dddd, J_{5ax}=13.8 Hz, J_7=5.7 Hz, J_1=3.5 Hz, J_{5eq}=2.6 Hz, 1H, 6-H), 2.28 (s, 3H, COCH$_3$), 2.36 (ddd, J_5=12.1 Hz, J_4=7.3 Hz, J_6=2.6 Hz, 1H, 5eq-H), 2.56 (qdd, J_{CH3}=7,4 Hz, J_8=4.8 Hz, J_{10}=2.7 Hz, 1H, 9-H), 3.01 (m, $w_{1/2}$=10 Hz, 1H, 1-H), 3.38 (s, 3H, OCH$_3$), 3.64 (t, J_1~J_9~2.8 Hz, 1H, 10-H), 3.88 (dd, J_7=10.35 Hz, J_9=4.8 Hz, 1H, 8-H), 3.93 (dd, J_8=10.35 Hz, J_6=5.7 Hz, 1H, 7-H), 4.09 (d, J=11.6 Hz, 1H, Bn), 4.38 (m, J_{5ax}=9.5 Hz, J_{OH}=8.8 Hz, J_{5eq}=7.3 Hz, J_3~J_{lr}~2.6 Hz, 1H, 4-H), 4.41 (d, J=12.1 Hz, 1H, Bn), 4.59 (d, J=11.9 Hz, 1H, Bn), 4.63 (d, J=11.9 Hz, 1H, Bn), 4.71 (d, J=6.6 Hz, 1H, OCH$_2$O), 4.87 (d, J=6.6 Hz, 1H, OCH$_2$O), 6.88 (d, J_4=2.5 Hz, 1H, 3-H), 7.18–7.4 (m, 10H, Ph); ^{13}C NMR: δ=11.95 (*C*H$_3$-9), 26.06 (*C*H$_3$CO), 29.23 (C-5), 33.37/35.82/38.65 (C-9/6/1), 55.80 (*C*H$_3$O), 68.90 (C-4), 72.43/72.49 (Bn), 75.91/76.03/81.62 (C-7,8,10), 97.32 (O*C*H$_2$O), 127.73–128.79 (Ph), 139.13/ 139.59 (Ph), 139.84 (C-3), 145.28 (C-2), 198.93 (CH$_3$*C*O); MS (EI): *m/z* (%)=480 (<2) [M$^+$], 462 (<2) [M$^+$−H$_2$O], 435 (<2) [M$^+$− CH$_2$OCH$_3$], 372 (5) [M$^+$−C$_6$H$_5$CH$_2$OH], 91 (100) [C$_7$H$_7^+$]; Anal. Calcd for C$_{29}$H$_{36}$O$_6$: C=72.48%, H=7.55%, found: C=72.47%, H=7.43%.

1.1.16. (±)-(1*R,4*S**,6*R**,7*R**,8*R**,9*R**,10*S**)-2-Acetyl-8,10-benzyloxy-9-methyl-7-(methoxymethyloxy)-4-(1′,3′-dioxa-2′-iodomethylpent-1-yl)-bicyclo [4.4.0] dec-2-ene (22).** To a solution of 754 mg (1.57 mmol) **21** in dry methylene chloride 7.85 mmol ethyl vinyl ether (752 μl) and 706 mg (3.14 mmol) *N*-iodosuccinimide were added at −20°C under an argon atmosphere. After stirring for 6 h at −20°C the solvent was evaporated and the residue filtered through silica gel (petroleum ether/ethyl acetate 4:1 then 2:1) yielding **22** (979 mg, 92%) as a 1:1 diastereomeric mixture. The yellow oil was used immediately after preparation.

1.1.17. (±)-(1*R,2*S**,3*R**,4*S**,5*R**,6*R**,7*R**,8*R**,10*S**,12*R**/12*S**)-2-Acetyl-4,6-dibenzyloxy-12-ethoxy-7-(methoxymethyloxy)-5-methyl-11-oxatricyclo [8.3.0.0^{3,8}] tridecane (23).** To a solution of 1.08 g (1.59 mmol) **22** in degassed *tert*-butanol (47 ml) 150 mg (2.38 mmol) sodium cyanoborohydride and 78 mg (0.48 mmol) AIBN were added. The mixture was heated to 85°C under an argon atmosphere. 0.32 mmol tri-*n*-butyltin chloride (86 μl) were added in three portions over 40 min. Heating was continued for further 80 min. Then brine and water were added, the aq. layer was extracted four times with ethyl acetate, the combined organic layers were washed with brine and dried over Na$_2$SO$_4$. After filtration and evaporation the product was purified by column chromatography

with petroleum ether/ethyl acetate (5:1 then 1:1) to afford a 1:1 diastereomeric mixture of **23** as a colorless oil (719 mg, 82%) and the reduced product **24** (72 mg, 8%). To characterize the tricyclic compound a small part of the product mixture **23** was separated by column chromatography with petroleum ether/ethyl acetate (3:1).

23a (diastereoisomer with the higher R_f-value). IR: 3028 (=C–H), 2893 (C–H), 1710 (CO); ^{1}H NMR: δ=1.01 (d, J=7.5 Hz, 3H, 5-CH_3), 1.14 (t, J=7.5 Hz, 3H, OCH_2CH_3), 1.69 (ddd, J_{gem}=12 Hz, J_{10}=10 Hz, J_8=13 Hz, 1H, 9*endo*-H), 1.72 (dd, J_{gem}=13 Hz, J_1=7 Hz, 1H, 13*exo*-H), 1.94 (m, J_{9en}=13 Hz, J_7~J_{9en}~5.5 Hz, J_3=3.5 Hz, 1H, 8-H), 2.05 (m, J_{gem}=12.04 Hz, J_8=6 Hz, J_{10}=7 Hz, 1H, 9*exo*-H), 2.20 (s, 3H, $COCH_3$), 2.32 (ddd, J_2=7 Hz, J_4~J_8~4 Hz, 1H, 3-H), 2.47 (ddd, J_{gem}~J_1~13 Hz, J_{12}=5.5 Hz, 1H, 13*endo*-H), 2.5 (ddq, J_{CH3}=7 Hz, J_6=4.5 Hz, J_4=2.5 Hz, 1H, 5-H), 2.86 (dq, J_{13en}=13.5 Hz, J_{13ex}~J_2~J_{10}~6.5–7 Hz, 1H, 1-H), 3.14 (dd, J_1~J_3~6.5 Hz, 1H, 2-H), 3.31 (dq, J_{CH3}=7 Hz, J_{gem}=9.5 Hz, 1H, OCH_2CH_3), 3.39 (s, 3H, OCH_3), 3.64 (dq, J_{CH3}=7 Hz, J_{gem}=9.5 Hz, 1H, OCH_2CH_3), 3.79 (m, 1H, 4-H), 3.81 (dd, J_7=10.5 Hz, J_5=5 Hz, 1H, 6-H), 3.88 (dd, J_6=10.5 Hz, J_8=5.5 Hz, 1H, 7-H), 4.12 (ddd, J_{9en}=10 Hz, J_{9ex}=7 Hz, J_1=6 Hz, 1H, 10-H), 4.32 (d, J=11.0 Hz, 1H, Bn), 4.37 (d, J=11.0 Hz, 1H, Bn), 4.53 (d, J=12.05 Hz, 1H, Bn), 4.59 (d, J=12.05 Hz, 1H, Bn), 4.67 (d, J_{13en}=5.5 Hz, 1H, 12-H), 4.71 (d, J=6.5 Hz, 1H, OCH_2O), 4.85 (d, J=7 Hz, 1H, OCH_2O), 7.1–7.4 (m, 10H, Ph); ^{13}C NMR: δ=12.09/15.21 (5-CH_3, OCH_2CH_3), 26.58/33.81 (C-9,13), 29.85 ($COCH_3$), 34.46/34.47/35.64/39.47 (C-1,3,5,8), 52.03 (C-2), 55.39 (OCH3), 62.47 (OCH_2CH_3),71.52/71.98 (Bn), 75.40/75.97/79.19/80.38 (C-4,6,7,10), 96.86 (OCH_2O), 103.43 (C-12), 127–128 (Ph), 138.37/139.14 (Ph), 208.22 (CO); MS (FI,130°C): m/z (%)=552 (24) [M^+], 507 (30) [$M^+-CH_3CH_2O$], 461 (10) [$M^+-C_7H_7$], 445 (16) [$M^+-C_7H_7O$], 106 (100), 91 (44) [$C_7H_7^+$]; HRMS (EI, 180°C, 70 eV): Calcd for $C_{33}H_{44}O_7$=552.3087, found M^+=552.3098.

23b (diastereoisomer with the lower R_f-value). IR: 3028 (=C–H), 2970/2892 (C–H), 1709 (CO); ^{1}H NMR: δ=0.96 (d, J=7.5 Hz, 3H, 5-CH_3), 1.16 (t, J=7 Hz, 3H, OCH_2CH_3), 1.95 (m, J_3=3.5 Hz, J_7~J_{9ex}~5.5–6 Hz, J_{9en}=13.55 Hz, 1H, 8-H), 2.05 (m, 1H, 9*exo*-H), 2.11 (ddd, J_{gem}~J_8~13 Hz, J_{10}=11 Hz, 1H, 9*endo*-H), 2.18 (s, 3H, $COCH_3$), 2.30 (ddd, J_{gem}=13.55 Hz, J_1=7 Hz, J_{12}=5.5 Hz, 1H, 13*exo*-H), 2.44 (ddd, J_2=6 Hz, J_4~J_8~4 Hz, 1H, 3-H), 2.47 (ddq, J_{CH3}=7.5 Hz, J_4=2.5 Hz, J_6=5 Hz, 1H, 5-H), 2.61 (dddd, J_{13en}=12 Hz, J_{13ex}=7.5 Hz, J_2~J_{10}~6 Hz, 1H, 1-H), 2.75 (ddd, J_{gem}~13 Hz, J_1~11.5 Hz, J_{12}=5.5 Hz, 1H, 13*endo*-H), 3.09 (dd, J_1~J_3~6 Hz, 1H, 2-H), 3.36 (dq, J_{CH3}=7 Hz, J_{gem}=9 Hz, 1H, OCH_2CH_3), 3.38 (s, 3H, OCH_3), 3.65 (dd, J_3~J_5~3–2.5 Hz, 1H, 4-H), 3.70 (dq, J_{CH3}=7 Hz, J_{gem}=9 Hz, 1H, OCH_2CH_3), 3.73 (dd, J_7=10.55 Hz, J_5=5 Hz, 1H, 6-H), 3.87 (dd, J_6=10.5 Hz, J_8=6 Hz, 1H, 7-H), 3.94 (ddd, J_{9en}=11.04 Hz, J_{9exo}~J_1~6 Hz, 1H, 10-H), 4.21 (d, J=11.54 Hz, 1H, Bn), 4.22 (d, J=12.55 Hz, 1H, Bn), 4.28 (d, J=12.05 Hz, 1H, Bn), 4.66 (d, J=12.55 Hz, 1H, Bn), 4.69 (d, J=6.5 Hz, 1H, OCH_2O), 4.85 (d, J=7 Hz, 1H, OCH_2O), 5.15 (t, J_{13en}~J_{13ex}~5.5 Hz, 1H, 12-H), 7.1–7.4 (m, 10H, Ph); ^{13}C NMR: δ=12/15.44 (5-CH_3, OCH_2CH_3), 26.39/33.22 (C-9,13), 29.43 ($COCH_3$), 34.51/34.95/38.60/40.26 (C-1,3,5,8), 53.04 (C-2), 55.40 (OCH_3), 63.15 (OCH_2CH_3), 71.47/72.04 (Bn), 75.62/75.97/79.93/81.09 (C-4,6,7,10), 96.92 (OCH_2O), 105.72 (C-12), 127–128 (Ph), 139.15/139.22 (Ph), 207.9 (CO); MS (FI,130°C): m/z (%)=552 (44) [M^+], 507 (61) [$M^+-CH_3CH_2O$], 106 (65), 91 (100) [$C_7H_7^+$], 57 (16); HRMS (EI, 180°C, 70 eV): Calcd for $C_{33}H_{44}O_7$=552.3087, found M^+= 552.3065.

Data of the diastereomeric mixture. Anal. Calcd for $C_{33}H_{44}O_7$: C=71.71%, H=8.02%, found: C=70.18%, H=7.76%.

1.1.18. (±)-(1*R,2*S**,3*R**,4*S**,5*R**,6*R**,7*R**,8*R**,10*S**)-4,6-Dibenzyloxy-12-ethoxy-2-(1′-hydroxyethyl)-5-methyl-7-methoxymethyloxy-11-oxatricyclo [8.3.0.0^{3,8}] tridecane (24).** A solution of 464 mg (0.84 mmol) **23** in methanol (40 ml) was treated with 64 mg (1.68 mmol) sodium borohydride under an argon atmosphere at 0°C. After stirring at room temperature for 1.5 h sat. aq. NH_4Cl solution was added. The aq. layer was extracted three times with methylene chloride, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the crude product **24** (452 mg, 97%), a mixture of four diastereoisomers, was used for the following reaction. IR: 3456 (OH), 3028 (=C–H), 2969/2924 (C–H); MS (FI, 120°C): m/z (%)=554 (75) [M^+], 522 (32) [M^+-CH_3OH], 509 (100) [$M^+-CH_3CH_2O$], 91 (32) [C_7H_7]; HRMS: Calcd for $C_{33}H_{46}O_7$=554.3244, found M^+=554.3228.

1.1.19. (±)-(1*R,3*R**,4*S**,5*R**,6*R**,7*R**,8*R**,10*S**)-4,6-Dibenzyloxy-12-ethoxy-2-ethyliden-5-methyl-7-methoxymethyloxy-11-oxatricyclo [8.3.0.0^{3,8}] tridecane (25).** 4.72 mmol $SOCl_2$ (345 μl, freshly distilled) and dry pyridine (10 ml) were combined and cooled to 0°C. A solution of 524 mg (0.945 mmol) **24** in dry pyridine (50 ml) was added slowly (over 30 min). After the addition was completed the mixture was stirred for 30 min at 0°C. The reaction mixture was quenched with sat. aq. $NaHCO_3$ solution. The aq. layer was extracted four times with ethyl acetate the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation toluene was added several times and evaporated. The reaction mixture was filtered through silica gel (petroleum ether/ethyl acetate 6:1) yielding **25** (400 mg, 79%) as a colorless oil. The unseparated mixture of four diastereoisomers was used for the following reaction. IR: 3028 (=C–H), 2970/2891 (C–H); MS (FI, 90°C): m/z (%)=536 (100) [M^+], 505 (4) [M^+-CH_3O], 491 (45) [$M^+-C_2H_5O$], 391 (32), 91 (40) [C_7H_7]; HRMS: Calcd for $C_{33}H_{44}O_6$= 536.3138, found M^+=536.3135.

1.1.20. (±)-(1*R,3*R**,4*S**,6*R**,7*R**,8*R**,9*R**,10*S**)-8,10-Dibenzyloxy-2-ethyliden-3-(2′-hydroxyethyl)-9-methyl-7-(methoxymethyloxy)-bicyclo [4.4.0] decan-4-ol (26).** To a solution of 400 mg (0.746 mmol) **25** in THF (30 ml) 2% aq. HCl (15 ml) was added. The mixture was stirred at 40°C under an argon atmosphere for 2 h. The reaction mixture was quenched with sat. aq. $NaHCO_3$ solution, the aq. layer was extracted four times with ethyl acetate the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the

residue was dissolved in dry THF (50 ml). This solution was added to a suspension of 85 mg (2.24 mmol) lithium aluminum hydride in dry THF (20 ml) at 0°C. After addition was completed the mixture was stirred another 1.5 h and quenched with water (1 ml). After stirring for several min the mixture was filtered through celite and evaporated. The product was purified and separated by column chromatography with petroleum ether/ethyl acetate (1:1 then 1:2) to afford **26a** (241.5 mg, 63%) and **26b** (80.5 mg, 21%) as colorless oils.

(*E*)-**26a** (main product). IR: 3331 (OH), 3028 (=C–H), 2884 (C–H); **^{1}H** NMR: δ=0.92 (d, J=7 Hz, 3H, 9-CH_3), 1.38 (dddd, $J_{2'a}\sim J_{2'b}\sim J_3\sim$4 Hz, J_{gem}=15 Hz, 1H, 1′a-H), 1.58 (d, J=6.5 Hz, 3H, 2″-H), 1.90–1.77 (m, 2H, 1′b/5*exo*-H), 1.92 (ddd, J_4=10 Hz, J_{gem}=11.4 Hz, J_6=13 Hz, 1H, 5*endo*-H), 2.02 (m, $J_7\sim J_1\sim$5.5 Hz, J_{5en}=13.55 Hz, J_{5ex}=3 Hz, 1H, 6-H), 2.38 (dd, J_6=5.5 Hz, J_{10}=3.5 Hz, 1H, 1-H), 2.43 (ddq, J_{CH3}=7.5 Hz, J_8=4.5 Hz, J_{10}=3 Hz, 1H, 9-H), 2.51 ($w_{1/2}$=16 Hz, 2H, OH), 2.96 (dt, $J_4\sim J_{1'b}\sim$6.5 Hz, $J_{1'a}$=4 Hz, 1H, 3-H), 3.25 (dd, $J_1\sim J_9\sim$3 Hz, 1H, 10-H), 3.29 (s, 3H, OCH_3), 3.52–3.42 (m, 2H. 2′-H), 3.59 (ddd, J_{5ex}=4 Hz, J_3=6 Hz, J_{5en}=10.5 Hz, 1H, 4-H), 3.76 (dd, J_7=10.5 Hz, J_9=4.5 Hz, 1H, 8-H), 3.80 (dd, J_8=10.5 Hz, J_6=5.5 Hz, 1H, 7-H), 4.18 (d, J=11.5 Hz, 1H, Bn), 4.27 (d, J=11.5 Hz, 1H, Bn), 4.36 (d, J=12 Hz, 1H, Bn), 4.43 (d, J=12 Hz, 1H, Bn), 4.62 (d, J=6.5 Hz, 1H, OCH_2O), 4.77 (d, J=6.5 Hz, 1, OCH_2O), 5.36 (q, J_{CH3}=7 Hz, 1H, 1″-H), 7.1–7.3 (m, 10H, Ph); ^{13}C NMR: δ=11.74/13.48 (9-CH_3,C-2″), 28.30/33.69 (C-5,1′), 34.35/39.98/40.55/43.05 (C-1,3,6,9), 55.42 (OCH_3), 63.51 (C-2′), 71.64/72.21 (Bn), 73.09/74.92/75.62/88.34 (C-4,7,8,10), 96.67 (OCH_2O), 123.39 (C-1″), 127–128 (Ph) 138.69/139.21 (Ph), 143.51 (C-2); MS (FI, 110°C): m/z (%)=511 (100) [M^+], 479 (17) [M^+-CH_3OH], 450 (16) [$M^+-CH_3OCH_2O$], 386 (20), 91 (33) [C_7H_7]; HRMS: Calcd for $C_{31}H_{42}O_6$=510.2981, found M^+= 510.2997.

(*Z*)-**26b** (byproduct). IR: 3385 (OH), 3028 (=C–H), 2924/2882 (C–H); ^{1}H NMR: δ=0.98 (d, J=7.5 Hz, 3H, 9-CH_3), 1.41 (d, J=6 Hz, J=1 Hz, 3H, 2″-H), 1.50 (br, 1H, OH), 1.68 (dddd, $J_{2'a}\sim J_{2'b}\sim J_3\sim$5.5 Hz, $J_{gem}\sim$14.6 Hz, 1H, 1′a-H), 1.77 (dddd, J_{gem}=14 Hz, $J_{2'}\sim J_{2'}\sim$7 Hz, J_3=2 Hz, 1H, 1′b-H), 1.78 (m, $J_{gem}\sim J_4\sim J_6\sim$13 Hz, 1H, 5*endo*-H), 2.08 (ddd, J_{gem}=12 Hz, $J_6\sim J_4\sim$6 Hz, 1H, 5*exo*-H), 2.15 (m, J_{5en}=13 Hz, $J_{5ex}\sim J_7\sim J_1\sim$5 Hz, 1H, 6-H), 2.43 (m, 1H, 3-H), 2.46 (ddq, J_{CH3}=7.5 Hz, J_8=5 Hz, J_{10}=2.5 Hz, 1H, 9-H), 2.86 (br, 1H, OH), 2.90 (dd, $J_{10}\sim J_6\sim$3.8 Hz, 1H, 1-H), 3.30 (s, 3H, OCH_3), 3.51 (ddd, J_{gem}=11.5 Hz, $J_{1a'}$=4.5 Hz, $J_{1b'}$=7.5 Hz, 1H, 2′b-H), 3.52 (dd, $J_1\sim J_9\sim$2.5–3.5 Hz, 1H, 10-H), 3.59 (ddd, J_{gem}=11 Hz, $J_{1a'}$=5 Hz, $J_{1b'}$=6 Hz, 1H, 2′a-H), 3.79 (m, 1H, 4-H), 3.80 (dd, J_7=10.5 Hz, J_9=5 Hz, 1H, 8-H), 3.86 (dd, J_8=10 Hz, J_6=5.5 Hz, 1H, 7-H), 4.18 (d, J=11.5 Hz, 1H, Bn), 4.35 (d, J=12 Hz, 1H, Bn), 4.43 (d, J=12 Hz, 1H, Bn), 4.51 (d, J=11.5 Hz, 1H, Bn), 4.63 (d, J=6.5 Hz, 1H, OCH_2O), 4.77 (d, J=6.5 Hz, 1H, OCH_2O), 5.31 (qt, J_{CH3}=7 Hz, $J_1\sim J_3\sim$1–1.5 Hz, 1H, 1″-H), 7.1–7.3 (m, 10H, Ph); ^{13}C NMR: δ=11.62/13.54 (9-CH_3, C-2″), 29.56/32.59 (C-5,1′), 34.25/35.27/37.11/44.78 (C-1,3,6,9), 55.46 (OCH_3), 61.47 (C-2′), 71.62/72.02 (Bn), 70.23/75.30/75.34/83.03 (C-4,7,8,10), 96.58 (OCH_2O), 122.25 (C-1″), 127–128 (Ph), 137.43 (C-2), 138.57/139.17 (Ph); MS (FI, 110°C): m/z (%)=511 (100) [$M+H^+$], 479 (14) [$M+H^+-CH_3OH$], 450 (11) [$M+H^+-CH_3OCH_2O$], 391 (18), 91 (34) [C_7H_7]; HRMS: Calcd for $C_{31}H_{42}O_6$=510.2981, found M^+= 510.2996.

The following reactions were executed with the separated diastereoisomers.

1.1.21. (±)-(1*R,3*R**,4*S**,6*R**,7*R**,8*R**,9*R**,10*S**)-8,10-Dibenzyloxy-2-ethyliden-3-(2′-hydroxyethyl)-9-methylbicyclo [4.4.0] decan-4,7-diol (27).** To a solution of 222 mg (0.435 mmol) **26** in dry methanol (48 ml) 5.5 M methanolic HCl (2 ml) was added under an argon atmosphere. After stirring the reaction mixture at 50°C for 1 h sat. aq. $NaHCO_3$ solution was added. The aq. layer was extracted four times with ethyl acetate the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the reaction mixture was filtered through silica gel (petroleum ether/ethyl acetate 1:2) yielding **27** (165 mg, 81%) as a colorless oil. The substance was used immediately after preparation. IR: 3384 (OH), 3028 (=C–H), 2880 (C–H); MS (FI, 120°C): m/z (%)=467 (100) [$M+H^+$], 449 (8) [$M+H^+-H_2O$], 391 (16), 91 (42) [C_7H_7].

1.1.22. (±)-(1*R,3*R**,4*S**,6*R**,7*R**,8*R**,9*R**,10*S**)-8,10-Dibenzyloxy-2-ethyliden-3-(2′-*t*-butyldimethylsilyloxyethyl)-9-methylbicyclo [4.4.0] decan-4,7-diol (28).** To a solution of 139 mg (0.298 mmol) **27** in dry DMF (10 ml) 49 mg (3.28 mmol) *t*-butyldimethylsilyl chloride, 101 mg (1.49 mmol) imidazole and a catalytic amount of 4-*N*,*N*-dimethylamino pyridine were added under an argon atmosphere at room temperature. Stirring was continued until starting material was no longer detectable by TLC. The reaction mixture was quenched with sat. aq. $NaHCO_3$ solution. The aq. layer was extracted four times with ethyl acetate the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the product was purified by column chromatography with petroleum ether/ethyl acetate (2.5:1) to afford **28** (140 mg, 81%) as colorless oils.

(*E*)-**28a**. IR: 3448 (OH), 3028 (=C–H), 2927/2883/2857 (C–H); ^{1}H NMR: δ=0/0.1 (s/s, 6H, 2Si–CH_3), 0.85 (s, 9H, *t*-Butyl), 0.93 (d, J=7 Hz, 3H, 9-CH_3), 1.32 (dddd, J_{gem}=15.56 Hz, $J_{2'a}\sim J_{2'b}\sim J_3\sim$3 Hz, 1H, 1′b-H), 1.58 (s, 1H, OH), 1.63 (d, J=7 Hz, 3H, 2″-H), 1.77 (ddd, J_4=11 Hz, J_{gem}=12 Hz, J_6=13.5 Hz, 1H, 5*endo*-H), 1.92 (ddd, J_{gem}=12.05 Hz, $J_6\sim J_4\sim$3 Hz, 1H, 5*exo*-H), 2.0 (dddd, $J_{2'a}\sim J_3\sim$7.5 Hz, $J_{2'b}$=9 Hz, $J_{gem}\sim$15.56 Hz, 1H, 1′a-H), 2.08 (dddd, J_{5ex}=3 Hz, $J_1\sim J_7\sim$6 Hz, J_{5en}=13.55 Hz, 1H, 6-H), 2.42 (dd, J_{10}=3 Hz, J_6=5.5 Hz, 1H, 1-H), 2.50 (ddq, J_{CH3}=7.5 Hz, J_8=5 Hz, J_{10}=2.5 Hz, 1H, 9-H), 2.99 (ddd, $J_{1'a}\sim J_4\sim$7 Hz, $J_{1'b}$=2.2 Hz, 1H, 3-H), 3.34 (dd, $J_1\sim J_9\sim$3 Hz, 1H, 10-H), 3.57–3.5 (m, 2H, 2′-H), 3.59 (m, J_{5ex}=4.5 Hz, J_{5en}=10.54 Hz, J_3=7 Hz, 1H, 4-H), 3.73 (dd, J_7=10.5 Hz, J_9=5 Hz, 1H, 8-H), 3.88–3.8 (m, 1H, OH), 3.85 (dd, J_8=10 Hz, J_6=6 Hz, 1H, 7-H), 4.23 (d, J=11.55 Hz, 1H, Bn), 4.33 (s, 2H, Bn), 4.39 (d, J=11.5 Hz, 1H, Bn), 5.39 (q, J_{CH3}=6.5 Hz, 1H, 1″-H), 7.1–7.3 (m, 10H, Ph); ^{13}C NMR: δ=−5.56/−5.52 (Si–CH_3), 11.56/13.47 (9-CH_3,C-2″), 18.31 (*t*-Butyl), 25.95 (*t*-Butyl), 29.69/33.97 (C-5,1′), 32.91/39.61/40.51/42.85

(C-1,3,6,9), 64.32 (C-2′), 70.65/72.48 (Bn), 68.55/72.17/76.93/89 (C-4,7,8,10), 122.53 (C-1″), 127.41–128.46 (Ph), 138.33/138.92 (Ph), 144.55 (C-2); MS (FI, 80°C): *m/z* (%)=581 (100) [M+H$^+$], 523 (61) [M$^+$−*t*-Butyl], 91 (30) [$C_7H_7^+$]; HRMS: Calcd for $C_{35}H_{52}O_5Si$=580.3584, found M$^+$=580.3601.

(*Z*)-**28b**. IR: 3442 (OH), 3029 (=C–H), 2956/2927/2857 (C–H); ^{1}H NMR: δ=0.0 (s, 6H, 2Si–CH_3), 0.85 (s, 9H, *t*-Butyl), 0.99 (d, *J*=7 Hz, 3H, 9-CH_3), 1.49 (d, *J*=7 Hz, 3H, 2″-H), 1.56 (br, 1H, OH), 1.60 (dddd, J_{gem}=14.55 Hz, $J_{2'a}\sim J_{2'b}\sim J_3\sim$4.5 Hz, 1H, 1′b-H), 1.70 (ddd, J_4=8 Hz, $J_{gem}\sim J_6\sim$13.05 Hz, 1H, 5*endo*-H), 1.80 (dddd, $J_{2'a}\sim J_{2'b\sim}$6.5 Hz, J_3=7.5 Hz, $J_{gem}\sim$14.05 Hz, 1H, 1′a-H), 2.09 (ddd, J_{gem}=13.05 Hz, $J_6\sim J_4\sim$5 Hz, 1H, 5*exo*-H), 2.17 (dddd, $J_{5ex}\sim J_1\sim J_7\sim$5.5 Hz, J_{5en}=13 Hz, 1H, 6-H), 2.46 ($w_{1/2}$=6 Hz, 1H, OH), 2.50 (m, 1H, 3-H), 2.54 (ddq, J_{CH3}=7.5 Hz, J_8=5 Hz, J_{10}=2.5 Hz, 1, 9-H), 2.92 (dd, J_{10}=2.5 Hz, J_6=5.5 Hz, 1H, 1-H), 3.62–3.52 (m, 3H, 2′/10-H), 3.74 (m, 1H, 4-H), 3.76 (dd, J_7=10 Hz, J_9=5 Hz, 1H, 8-H), 3.91 (dd, J_8=10 Hz, J_6=6 Hz, 1H, 7-H), 4.28 (d, *J*=11.55 Hz, 1H, Bn), 4.34 (d, *J*=12.05 Hz, 1H, Bn), 4.40 (d, *J*=12 Hz, 1H, Bn), 4.44 (d, *J*=11 Hz, 1H, Bn), 5.39 (q, J_{CH3}=6.5 Hz, 1H, 1″-H), 7.1–7.3 (m, 10H, Ph); ^{13}C NMR: δ=−5.42 (Si–CH_3), 11.37/13.54 (9-CH_3,C-2″), 18.3 (*t*-Butyl), 25.95 (*t*-Butyl), 28.37/32.86 (C-5,1′), 32.71/35.14/37.56/45.17 (C-1,3,6,9), 62.81 (C-2′), 70.87/72.04 (Bn), 68.97/69.99/76.77/83.80 (C-4,7,8,10), 121.69 (C-1″), 127.8–128.5 (Ph), 137.98/138.25 (Ph), 140.38 (C-2); HRMS: Calcd for $C_{35}H_{52}O_5Si$=580.3584, found M$^+$=580.3602.

1.1.23. (±)-(1*R,3*S**,4*S**,5*S**,7*R**,8*S**,9*R**,10*R**,11*R**)-9,11-Dibenzyloxy-2-(2′-*t*-butyldimethylsilyloxyethyl)-3-(1″-hydroxyethyl)-10-methyl-2-oxatricyclo [5.4.0.0^{3,8}] undecan-5-ol (29).** A solution of 67 mg (0.115 mmol) **28a** in dry THF (2 ml) was treated at 0°C with 29 mg (0.07 mmol) mercury(II)trifluoroacetate and 15 mg (0.07 mmol) mercury(II)oxide under an argon atmosphere. After stirring until starting material was no longer detectable by TLC brine was added and the two-phase system was vigorously stirred for 15 min. The aq. layer was extracted four times with ethyl acetate, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the crude product was dissolved in DMF (2.5 ml, saturated with oxygen) (~0.05 M solution). This solution was added to a suspension of 6 mg (0.16 mmol) sodium borohydride in DMF (1 ml, saturated with oxygen) (~0.2 M solution) over 5 min, afterwards the mixture was stirred for another 30 min. Oxygen was bubbled through the solution all the time. The mixture was quenched with water, stirred for 45 min and extracted four times with methylene chloride. The combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the products were separated by column chromatography with petroleum ether/ethyl acetate (4:1 then 3:1) to afford **29** (30 mg, 44%, the diastereomeric ratio differed from reaction to reaction) and starting material (11 mg, 16%).

29a (diastereoisomer with higher R_f-value). IR: 3422 (OH), 2932/2856 (C–H); **^{1}H NMR**: δ=0.0 (s, 6H, Si–CH_3), 0.84 (s, 9H, *t*-Butyl), 1.03 (d, *J*=6.5 Hz, 3H, 10-CH_3), 1.13 (d, *J*=7 Hz, 3H, 2″-H), 1.86 (m, 1H, 6*exo*-H), 1.90 (m, 1H, 4-H), 1.94 (m, 1H, 1′-H), 2.02 (m, 1H, 1′-H), 2.06 (d, J_9=3 Hz, 1H, 8-H), 2.07 (m, J_5=2 Hz, J_7=3 Hz, J_{gem}=14–15 Hz, 1H, 6*endo*-H), 2.40 (dd, $J_{6a}\sim J_{6b}\sim$3.25 Hz, 1H, 7-H), 2.56 (ddq, J_{11}=5.5 Hz, J_9=11 Hz, J_{CH3}=7 Hz, 1H, 10-H), 3.31 (dd, J_{10}=11.05 Hz, J_8=2.5 Hz, 1H, 9-H), 3.52 (d, J_5=7.5 Hz, 1H, 5-OH), 3.57 (dd, $J_1\sim J_{10}\sim$5 Hz, 1H, 11-H), 3.60 (ddd, J_{gem}=10.6 Hz, $J_{1'}$=4 Hz, $J_{1'}$=5.5 Hz, 1H, 2′b-H), 3.72 (ddd, J_{gem}=10.5 Hz, $J_{1'}$=3.5 Hz, $J_{1'}$=7.5 Hz, 1H, 2′a-H), 3.99 (m, J_{OH}=7 Hz, $J_{6exo}\sim J_4\sim$3.5 Hz, $J_{6endo}\sim$1 Hz, 1H, 5-H), 4.38 (d, *J*=11 Hz, 1H, Bn), 4.44 (d, *J*=12 Hz, 1H, Bn), 4.49 (d, *J*~13 Hz, 1H, Bn), 4.52 (d, J_{11}=4.5 Hz, 1H, 1-H), 4.63 (d, J_{gem}=11.5 Hz, 1H, Bn), 5.18 (q, J_{CH3}=7 Hz, 1H, 1″-H), 7.2–7.4 (m, 10H, Ph), 10.05 (s, 1H, 1″-OH); ^{13}C NMR (C–H correlation): δ=−5.53/−5.52 (Si–CH_3), 13.55 (10-CH_3), 16.32 (C-2″), 18.21 (*t*-Butyl), 25.9 (*t*-Butyl), 28.66 (C-1′), 36.79 (C-6), 35.75 (C-10), 37.49 (C-7), 44.08 (C-4), 48.94 (C-8), 61.48 (C-2′), 66.34 (C-5), 72.61/72.94 (Bn), 79.40 (C-11), 81.63 (C-1), 83.36 (C-1″), 84.2 (C-9), 93.06 (C-3), 127.51–128.40 (Ph), 138.07/138.34 (Ph); MS (FI, 130°C): *m/z* (%)=596 (93) [M$^+$], 552 (7) [M$^+$−CH_3CHOH], 537 (71), 505 (34) [M$^+$− C_7H_7], 464 (40), 447 (100), 405 (22), 106 (12), 91 (49) [$C_7H_7^+$], 57 (18) [*t*-Butyl]; Anal. Calcd for $C_{35}H_{52}O_6Si$: C=70.43%, H=8.78%, found: C=70.65%, H=8.63%.

29b (diastereoisomer with the lower R_f-value). IR: 3483 (OH), 3031 (=C–H), 2928/2857 (C–H); ^{1}H NMR: δ=0.0 (s, 6H, Si–CH_3), 0.84 (s, 9H, *t*-Butyl), 1.01 (d, *J*=6.5 Hz, 3H, 10-CH_3), 1.15 (d, *J*=6.5 Hz, 3H, 2″-H), 1.97–1.82 (m, 3H, 1′/6*exo*/4-H), 2.03 (d, J_9=3 Hz, 1H, 8-H), 2.07 (m, J_5=2 Hz, J_7=3.3 Hz, J_{gem}=15.5 Hz, 1H, 6*endo*-H), 2.12 ($w_{1/2}$=7.8 Hz, 1H, 1″-OH), 2.41–2.28 (m, 2H, 1′/10-H), 2.42 (dd, $J_{6a}\sim J_{6b}\sim$3.25 Hz, 1H, 7-H), 3.27 (dd, J_{10}=11.04 Hz, J_8=3 Hz, 1H, 9-H), 3.52 (d, J_5=7.5 Hz, 1H, 5-OH), 3.53 (dd, $J_1\sim J_{10}\sim$4.5–5.5 Hz, 1H, 11-H), 3.61 (ddd, J_{gem}=10 Hz, $J_{1'}$=4.5 Hz, $J_{1'}$=5.5 Hz, 1H, 2′b-H), 3.70 (ddd, J_{gem}=10.5 Hz, $J_{1'}$=3.5 Hz, $J_{1'}$=8 Hz, 1H, 2′a-H), 3.98 (m, $w_{1/2}$=15.06 Hz, 1H, 5-H), 4.35 (d, *J*=11.54 Hz, 1H, Bn), 4.42 (d, *J*=11.55 Hz, 1H, Bn), 4.44 (d, J_{11}=4.5 Hz, 1H, 1-H), 4.49 (d, *J*=11.54 Hz, 1H, Bn), 4.64 (d, *J*=11.55 Hz, 1H, Bn), 4.72 (q, J_{CH3}=6.5 Hz, 1H, 1″-H), 7.2–7.4 (m, 10H, Ph); ^{13}C NMR: δ=−5.52 (Si–CH_3), 13.47 (10-CH_3), 16.64 (C-2″), 18.2 (*t*-Butyl), 25.89 (*t*-Butyl), 29.19 (C-1′), 36.95 (C-6), 35.80 (C-10), 38.91 (C-7), 44.17 (C-4), 48.14 (C-8), 61.65 (C-2′), 66.63 (C-5), 69.50 (C-1″), 72.36/72.79 (Bn), 79.57 (C-11), 80.67 (C-1), 84.42 (C-9), 90.88 (C-3), 127.6–128.3 (Ph), 138.19/138.47 (Ph); MS (FI, 150°C): *m/z* (%)=597 (100) [M+H$^+$], 539 (38), 91 (10) [$C_7H_7^+$]; HRMS: Calcd for $C_{35}H_{52}O_6Si$=596.3533, found M$^+$=596.3554.

1.1.24. (±)-(1*S,3*R**,4*S**,5*S**,6*R**,7*R**,8*R**,9*R**)-5,7-Dibenzyloxy-3-(4′ bromomethyl-3′,5′-dioxahept-2′-yl)-1-(*t*-butyldimethylsilyloxy)-6-methyl-11-oxatricyclo [6.2.1.0^{4,9}] undecane (30).** *Method a*. 0.4 ml (7.76 mmol) bromine was cooled to −25°C. 14 mmol ethyl vinyl ether (1.3 ml) was added slowly over 30 min. The resulting yellow solution was stirred for 30 min at −25°C and cooled to −60°C afterwards. The residue was evacuated for 45 min and after bringing to 0°C was ready for use. 270 μl (~2 mmol) of this reagent was added to a stirred solution of 220 mg (0.399 mmol) **12** and 405 μl (3.19 mmol) of freshly distilled

N,*N*-dimethylaniline in dry methylene chloride (13 ml) at 0°C under an argon atmosphere. After stirring for 15 min at 0°C and 2.5 h at room temperature sat. aq. $NaHCO_3$ solution was added. The aq. layer was extracted three times with methylene chloride, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the crude product was purified by column chromatography with petroleum ether/ethyl acetate (20:1). The *N*,*N*-dimethylaniline could not be removed completely.

Method b. To a stirred solution of 62 mg (0.112 mmol) **12** in dry methylene chloride (3 ml) 336 mmol ethyl vinyl ether (32 μl) and 40 mg (0.224 mmol) *N* bromosuccinimide were added under an argon atmosphere at −20°C. After stirring for 2 h the mixture was warmed to −5°C and stirred for another 5 h. The reaction was quenched with brine. The aq. layer was extracted four times with methylene chloride, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the crude product **30** was used for the next reaction. Using this method a part of the product lost the silylic acetal providing **31**.

For analytical purposes a small part of the product mixture **30** was separated by column chromatography the rest was used as a diasteromeric mixture for the following reaction.

30a (diastereoisomer with the higher R_f-value). IR: 3029 (=C–H), 2932/2858 (C–H); ^{1}H NMR: δ=0 (two s, 6H, 2Si–CH_3), 0.8 (s, 9H, *t*-Bu), 1.01 (t, *J*=7 Hz, 3H, 7′-H), 1.02 (d, *J*=6.5 Hz, 3H, 1′-H), 1.03 (d, *J*=6.5 Hz, 3H, 6-CH_3), 1.63 (d, J_{gem}=11.5 Hz, 1H, 10*exo*-H), 1.69 (dd, J_{gem}=14.05 Hz, J_3=7.5 Hz, 1H, 2*exo*-H), 1.74 (ddd, J_{gem}=11.6 Hz, J_9=4 Hz, J_{2en}=3 Hz, 1H, 10*endo*-H), 1.92–1.8 (m, 2H, 2*endo*/4-H), 2.14 (ddq, J_{CH3}=6.5 Hz, J_7=3.5 Hz, J_5=11 Hz, 1H, 6-H), 2.32 (ddd, J_{10en}=5.2 Hz, J_4∼J_8∼2.5 Hz, 1H, 9-H), 2.42 (ddd, $J_{2'}$=4 Hz, J_{2ex}∼J_4∼7 Hz, J_{2en}=11 Hz, 1H, 3-H), 3.03 (dd, $J_{4'}$=5 Hz, J_{gem}=10.5 Hz, 1H, CH_2Br), 3.06 (dd, $J_{4'}$=5 Hz, J_{gem}=10.5 Hz, 1H, CH_2Br), 3.25 (dq, J_{CH3}=7 Hz, J_{gem}=9 Hz, 1H, 6′-Ha), 3.40 (dd, J_6=11.05 Hz, J_4=4.5 Hz, 1H, 5-H), 3.48 (dq, J_{CH3}=7 Hz, J_{gem}=9.5 Hz, 1H, 6′-Hb), 3.51 (dd, J_8∼J_6∼3 Hz, 1H, 7-H), 3.69 (dq, J_{CH3}=6 Hz, J_3=4.5 Hz, 1H, 2′-H), 3.90 (dd, J_7∼J_9∼2.5 Hz, 1H, 8-H), 4.32 (d, *J*=11 Hz, 1H, Bn), 4.38 (t, J_{CH2}=5–6 Hz, 1H, 4′-H), 4.40 (d, *J*=11 Hz, 1H, Bn), 4.42 (d, *J*=11.55 Hz, 1H, Bn), 4.49 (d, *J*=12 Hz, 1H, Bn), 7.15–7.30 (m, 10H, Ph); ^{13}C NMR (25°C): δ=−2.84/−2.82 (Si–CH_3), 13.39/14.69/15.04 (1′,6-CH_3,7′), 17.81 (*t*-Bu), 25.91 (*t*-Bu), 32.73 (CH_2Br), 38.62/41.94 (C-2,10), 31.87/35.15/35.81/39.27 (C-3,4,6,9), 62.71 (OCH_2CH_3), 72.55/73.5 (Bn), 76.64/76.83/79.86/80.91 (C-2′,5,7,8), 100.73 (C-4′), 107.25 (C-1), 127.62–128.33 (Ph), 138.46/138.57 (Ph).

30b (diastereoisomer with the lower R_f-value). IR: 3029 (=C–H), 2932/2857 (C–H); ^{1}H NMR: δ=0 (two s, 6H, 2Si–CH_3), 0.78 (s, 9H, *t*-Bu), 0.92 (t, *J*=7 Hz, 3H, 7′-H), 1.02 (d, *J*=6.5 Hz, 3H, 1′-H), 1.03 (d, *J*=6 Hz, 3H, 6-CH_3), 1.60 (d, J_{gem}=11.55 Hz, 1H, 10*exo*(ax)-H), 1.67 (dd, J_{gem}=13.6 Hz, J_3=7.5 Hz, 1H, 2*exo*-H), 1.75 (ddd, J_{gem}=11.5 Hz, J_9=4 Hz, J_{2en}=2.5 Hz, 1H, 10*endo*-H), 1.82 (m, J_3∼J_9∼J_5∼4.5–6 Hz, 1H, 4-H), 1.87 (ddd, J_3=10.5 Hz, J_{gem}=14.05 Hz, J_{10en}=2 Hz, 1H, 2*endo*-H), 2.18 (ddq, J_{CH3}=6.5 Hz, J_7=4 Hz, J_5=10.5 Hz, 1H, 6-H), 2.32 (m, $w_{1/2}$=11.7 Hz, 1H, 9-H), 2.42 (ddd, $J_{2'}$=4 Hz, J_{2ex}=7.7 Hz, J_{2en}=10.5 Hz, J_4=6.3 Hz, 1H, 3-H), 3.07 (dq, J_{CH3}=7 Hz, J_{gem}=9 Hz, 1H, 6′-Ha), 3.10 (dd, $J_{4'}$=5.5 Hz, J_{gem}=10.5 Hz, 1H, CH_2Br), 3.14 (dd, $J_{4'}$=5 Hz, J_{gem}=10.5 Hz, 1H, CH_2Br), 3.30 (dq, J_{CH3}=7 Hz, J_{gem}=9 Hz, 1H, 6′-Hb), 3.40 (dd, J_6=11.5 Hz, J_4=4.5 Hz, 1H, 5-H), 3.53 (dd, J_8∼J_6∼3–2.5 Hz, 1H, 7-H), 3.71 (dq, J_{CH3}=6.5 Hz, J_3=4.5 Hz, 1H, 2′-H), 3.91 (dd, J_7∼J_9∼2.5 Hz, 1H, 8-H), 4.34 (d, J_{gem}=11.55 Hz, 1H, Bn), 4.40 (t, J_{CH2}=5–6 Hz, 1H, 4′-H), 4.41 (d, *J*=11.55 Hz, 1H, Bn), 4.42 (d, *J*=12 Hz, 1H, Bn), 4.49 (d, *J*=11.5 Hz, 1H, Bn), 7.15–7.30 (m, 10, Ph); ^{13}C NMR: δ=−2.81/−2.78 (Si–CH_3), 13.46/14.76/15.14 (C-1′,6-CH_3,C-7′), 17.83 (*t*-Bu), 25.93 (*t*-Bu), 32.83 (CH_2Br), 38.14/42.08 (C-2,10), 31.88/34.54/35.82/39.34 (C-3,4,6,9), 62.48 (C-6′), 72.38/73.53 (Bn), 76.98/77.27/79.84/81.07 (C-2′,5,7,8), 100.89 (C-4′), 107.26 (C-1), 127.54-128.32 (Ph), 138.56/138.58 (Ph).

Data of the diastereomeric mixture. MS (FI, 105°C): *m*/*z* (%)=702/704 (2/2) [M^+], 645/647 (92/100) [M^+−*t*-Bu], 226.8 (48), 151/153 (52/39) [$CH_3CH_2OCHCH_2Br^+$], 91 (8) [$C_7H_7^+$]; Anal. Calcd for $C_{37}H_{55}O_6SiBr$: C=63.14%, H=7.88%, found: C=62.91%, H=7.68%.

1.1.25. (±)-(1*R,5*R**,6*S**,7*S**,8*R**,9*R**,10*R**)-7,9-Dibenzyloxy-8-methyl-5-(4′-bromomethyl-3′,5′-dioxahept-2′-yl)-10-hydroxybicyclo[4.4.0]decan-3-one (31).** A solution of 345 mg (0.49 mmol) **30** (diastereomeric mixture) in THF (50 ml) was treated with 216 mg (0.686 mmol) tetra-*n*-butylammonium fluoride trihydrate under an argon atmosphere. After stirring at 0°C for 2.5 h and at room temperature for 2.5 h sat. aq. NH_4Cl solution was added. The aq. layer was extracted three times with ethyl acetate, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the crude product was purified by column chromatography with petroleum ether/ethyl acetate (3:1) to afford **31** (269 mg, 93%) as a colorless oil. For analytical purposes a small part of the product mixture **31** was separated by column chromatography the rest was used without purification for the following reaction.

31a (diastereoisomer with higher R_f-value). IR: 3456 (OH), 3028 (=C–H), 2973/2899 (C–H), 1708 (CO); ^{1}H NMR: δ=0.93 (d, *J*=7 Hz, 3H, 8-CH_3), 1.02 (d, *J*=6.5 Hz, 3H, H-1′), 1.12 (t, *J*=7 Hz, 3H, 7′-H), 1.90 (m, $w_{1/2}$=26.05 Hz, 1H, 5-H), 2.27 (dd, J_{gem}=14.6 Hz, J_5=9 Hz, 1H, 4a-H), 2.38 (m, 1H, 6-H), 2.39 (dd, J_{gem}=16.9 Hz, J_1=5.8 Hz, 1H, 2*exo*-H), 2.4 (m, 1H, OH), 2.5 (dd, J_{gem}=16.6 Hz, J_1=13 Hz, 1H, 2*endo*-H), 2.48–2.58 (m, 1H, 8-H), 2.52 (dd, J_5=6 Hz, J_{gem}=14.05 Hz, 1H, 4b-H), 2.65 (dddd, J_{2en}=12.55 Hz, J_{2ex}∼J_6∼J_{10}∼6 Hz, 1H, 1-H), 3.20 (dd, $J_{4'}$=5.5 Hz, J_{gem}=10.55 Hz, 1H, CH_2Br), 3.27 (dd, $J_{4'}$=4 Hz, J_{gem}=10.5 Hz, 1H, CH_2Br), 3.42 (m, $w_{1/2}$=7.3 Hz, 1H, 7-H), 3.49 (q, J_{CH3}=7 Hz, 2H, 6′-H), 3.53 (br, 1H, 2′-H), 3.68 (dd, J_{10}=10 Hz, J_8=5 Hz, 1H, 9-H), 3.87 (dd, J_9=10 Hz, J_1=5.5 Hz, 1H, 10-H), 4.27 (d, *J*=11.5 Hz, 1H, Bn), 4.31 (d, *J*=12 Hz, 1H, Bn), 4.47 (d, *J*=11.5 Hz, 1H, Bn), 4.48 (d, *J*=12 Hz, 1H, Bn), 4.55 (dd, J_{CH2}=5.5 Hz, J_{CH2}=4.5 Hz, 1H, 4′-H), 7.15–7.35 (m, 10, Ph); ^{13}C NMR (250 MHz, C_6D_6, 47°C): δ=11.47/15.48/17.27

(C-1′,8-CH_3,C-7′), 32.80 (CH_2Br), 39.13/42.11 (C-2,4), 33.10/33.73/38.16/43.35 (C-1,5,6,8), 63.14 (C-6′), 71.73/72.63 (Bn), 69.63/75.28/77.93/87.08 (C-2′,7,9,10), 100.1 (C-4′), 127.9–128.8 (Ph), 139.08/139.26 (Ph), 210.14 (CO); MS (EI, 160°C, 70 eV): *m/z* (%): 590/588 (2.5/2.5) [M^+], 544/542 (<1) [M^+-EtOH], 463 (10) [$M^+-Br-EtOH$], 437 (12) [$M^+-CH_3CH_2OCHCH_2Br$], 421 (20) [$M^+-CH_3CH_2OCH(O)CH_2Br$], 59 (10), 329 (25.7), 313 (25), 269 (15), 223 (23), 205 (25), 181 (51), 151/153 (60/56) [$CH_3CH_2OCHCH_2Br^+$], 123 (31), 91 (100) [$C_7H_7^+$].

31b (diastereoisomer with lower R_f-value). IR: 3460 (OH), 3029 (=C–H), 2974/2883 (C–H), 1709 (CO); ^{1}H NMR: δ=0.94 (d, J=7.5 Hz, 3H, 8-CH_3), 1.10 (d, $J_{2'}$=6.5 Hz, 3H, 1′-H), 1.14 (t, J=7 Hz, 3H, 7′-H), 1.92 (m, $w_{1/2}$=27.2 Hz, 1H, 5-H), 2.3 (m, 1H, 6-H), 2.32 (dd, J_{gem}=14.1 Hz, J_5=8.5 Hz, 1H, 4a-H), 2.4 (m, 1H, OH), 2.41 (dd, J_{gem}=16.6 Hz, J_1=6 Hz, 1H, 2*exo*-H), 2.48 (dd, J_{gem}=16.6 Hz, J_1=12.5 Hz, 1H, 2*endo*-H), 2.55 (m, 1H, 8-H), 2.57 (dd, J_5=6 Hz, J_{gem}=14.1 Hz, 1H, 4b-H), 2.65 (dddd, J_{2en}=12 Hz, $J_{2ex}\sim J_6\sim J_{10}\sim$6 Hz, 1H, 1-H), 3.22 (dd, $J_{4'}$=5.5 Hz, J_{gem}=11.6 Hz, 1H, CH_2Br), 3.26 (dd, $J_{4'}$=5.5 Hz, J_{gem}=11.6 Hz, 1H, CH_2Br), 3.4 (m, $w_{1/2}$=8 Hz, 1H, 7-H), 3.42–3.56 (m, 1H, 2′-H), 3.47 (dq, J_{CH3}=7 Hz, J_{gem}=9 Hz, 1H, 6′-Ha), 3.52 (dq, J_{CH3}=7 Hz, J_{gem}=9 Hz, 1H, 6′-Hb), 3.69 (dd, J_{10}=10 Hz, J_8=5 Hz, 1H, 9-H), 3.89 (dd, J_9=10 Hz, J_1=5.5 Hz, 1H, 10-H), 4.3 (d, J=11 Hz, 1H, Bn), 4.3 (d, J=12.7 Hz, 1H, Bn), 4.48 (d, J=11.55 Hz, 1H, Bn), 4.49 (d, J=12.55 Hz, 1H, Bn), 4.52 (t, J_{CH2}=5.5 Hz, 1H, 4′-H), 7.15–7.35 (m, 10H, Ph); ^{13}C NMR (250 MHz, C_6D_6, 47°C): δ=11.86/15.39/18.64 (C-1′,8-CH_3,C-7′), 32.55 (CH_2Br), 39.35/42.03 (C-2,4), 33.36/33.65/38.38/43.17 (C-1,5,6,8), 61.80 (O*C*H_2CH_3), 71.84/72.56 (Bn), 69.65/77.65/78.04/86.63 (C-2′,7,9,10), 102.36 (C-4′), 127–128 (Ph), 138.95/139.24 (Ph), 210.13 (CO); MS (EI, 160°C, 70 eV): *m/z* (%): 590/588 (2.5/2) [M^+], 463.2 (2.2) [$M^+-Br-EtOH$], 437 (12.4) [$M^+-CH_3CH_2OCHCH_2Br$], 421 (12.3) [$M^+-CH_3CH_2O$-CH(O)CH_2Br], 393 (3), 329 (25.7), 313 (15.1), 269 (10.2), 223 (15.2), 205 (16.5), 181 (36), 177 (11.2), 161 (12.9), 123 (23.1), 151/153 (45.8/45.1) [$CH_3CH_2OCHCH_2Br^+$], 91 (100) [$C_7H_7^+$].

Data of the diastereomeric mixture. HRMS: Calcd for $C_{31}H_{41}BrO_6$=588.2087, found M^+=588.2097.

1.1.26. (±)-(1*R,5*R**,6*S**,7*S**,8*R**,9*R**,10*R**)-7,9-Dibenzyloxy-8-methyl-5-(4′ bromomethyl-3′,5′-dioxa-hept-2′-yl)-10-(methoxymethyloxy)bicyclo[4.4.0]decan-3-one (32).** A solution of 269 mg (0.456 mmol) **31** (diastereomeric mixture) and 13.7 mmol *N*,*N*-diisopropylethyl amine (2.6 ml) in methylene chloride (13 ml) was treated with 9.11 mmol chloromethyl methyl ether (0.742 ml) unter an argon atmosphere. After stirring at 35°C for 14 h sat. aq. $NaHCO_3$ solution was added. The aq. layer was extracted three times with methylene chloride, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the crude product was purified by column chromatography with petroleum ether/ethyl acetate (4:1) to afford **32** (242 mg, 84%) as a colorless oil. The 1:1 diastereomeric mixture could not be separated. IR: 3028 (=C–H), 2971/2925 (C–H), 1713 (CO); MS (FI, 135°C): *m/z* (%)=632/634 (92/96) [M^+], 601/603 (15/16) [M^+-CH_3O], 587/589 (65/70) [$M^+-CH_3OCH_2$], 481 (20) [$M^+-CH_3CH_2OCHCH_2Br$], 197/195 (4/5) [$(CH_3CH_2O)_2CHCH_2Br$], 151/153 (8/8) [$CH_3CH_2OCHCH_2Br$], 91 (33) [C_7H_7]; Anal. Calcd for $C_{33}H_{45}BrO_7$: C=62.56%, H=7.16%, found: C=62.40%, H=6.96%.

1.1.27. (±)-(4*R,5*R**,6*R**,7*R**,8*S**,9*R**,10*S**)-6,8-Dibenzyloxy-5-(methoxymethyloxy)-13-ethoxy-7,11-dimethyl-12-oxatricyclo [8.4.0.0^{4,9}] tetradecan-2-one (33).** A solution of 230 mg (0.36 mmol) **32** (diastereomeric mixture) in dry toluene (50 ml) was treated with 89 mg (0.72 mmol) potassium *tert*-butanolate under an argon atmosphere. After stirring at 100°C for 15 h sat. aq. NH_4Cl solution was added. The aq. layer was extracted three times with diethyl ether, the combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation the crude product was purified by column chromatography with petroleum ether/ethyl acetate (4:1) to afford **33** (161 mg, 81%). For analytical purposes the diastereoisomers were separated.

33a (1*R**,11*S**,13*R**; main product). White crystals, mp: 108–113°C; IR: 3029 (=C–H), 2969/2932 (C–H), 1712 (CO); ^{1}H NMR (400 MHz, C_6D_6, 50°C): δ=1.04 (d, J=6.8 Hz, 3H, 7-CH_3), 1.08 (d, J=6.7 Hz, 3H, 11-CH_3), 1.16 (t, J=7.2 Hz, 3H, OCH_2CH_3), 1.77 (ddd, J_{13}=9.8 Hz, $J_1\sim$12.3 Hz, J_{gem}=13.1 Hz, 1H, 14b-H), 1.87 (ddd, J_{10}=11.5 Hz, $J_4\sim J_8\sim$4 Hz, 1H, 9-H), 1.99 (ddd, $J_{14b}\sim J_{10}\sim$11.9 Hz, $J_{14a}\sim$3.3 Hz, 1H, 1-H), 2.11 (m, J_{gem}=14 Hz, $J\sim$6.5 Hz, 1H, 3a-H), 2.16 (m, J_{gem}=14 Hz, $J\sim$3 Hz, 1H, 3b-H), 2.26 (m, 1H, 4-H), 2.29 (ddq, J_{CH3}=7 Hz, J_8=11 Hz, J_6=2.7 Hz, 1H, 7-H), 2.46 (ddd, $J_{13}\sim J_1\sim$2.9 Hz, J_{gem}=13.3 Hz, 1H, 14a-H), 2.93 (ddd, $J_9\sim J_1\sim$11.9 Hz, J_{11}=3.7 Hz, 1H, 10-H), 3.03 (s, 3H, O–CH_3), 3.44 (dq, J_{CH3}=7.2 Hz, J_{gem}=9.6 Hz, 1H, O*C*H_2CH_3), 3.48–3.54 (m, 3H, 5/6/8-H), 3.92 (dq, J_{CH3}=7 Hz, J_{gem}=9.4 Hz, 1H, O*C*H_2CH_3), 4.26 (d, J=11.9 Hz, 2H, Bn), 4.34 (d, J=12.5 Hz, 1H, Bn), 4.35 (s, 2H, OCH_2O), 4.38 (d, J=11.7 Hz, 1H, Bn), 4.66 (dd, J_{14a}=2.7 Hz, J_{14b}=9.8 Hz, 1H, 13-H), 5.01 (br, $w_{1/2}$=21.2 Hz, 1H, 11-H), 7.0–7.3 (m, 10H, Ph), ^{13}C NMR (400 MHz, C_6D_6, 50°C): δ=12.45/13.73/15.68 (7-CH_3,11-CH_3, OCH_2CH_3), 33.06 (C-3,14), 33.16/38.62/42.77/43.42 (C-1,4,7,9,10), 55.82 (OCH_3), 63.41 (O*C*H_2CH_3), 71.29/78.70/81.24/82.57 (C-5,6,8,11), 73.25/74.18 (Bn), 95.78 (C-13), 97.92 (OCH_2O), 127.58–128.56 (Ph), 138.95/139.07 (Ph), 207.19 (CO); MS (FI,120°C): *m/z* (%)=552 (100) [M^+], 521 (16) [$M^+-CH_3O^+$], 507 (100) [$M^+-CH_3CH_2O^+$], 91 (24) [$C_7H_7^+$].

33b (1*R**,11*S**,13*S**; main product). Colorless oil; IR: 3028 (=C–H), 2967/2921/2850 (C–H), 1702 (CO); ^{1}H NMR (250 MHz, C_6D_6, 50°C): δ=1.16 (d, J=6.8 Hz, 3H, 7-CH_3), 1.21 (t, J=7 Hz, 3H, OCH_2CH_3), 1.54 (d, J=6.6 Hz, 3H, 11-CH_3), 1.96 (ddd, J_{gem}=13.7 Hz, J_1=11.9 Hz, J_{13}=4 Hz, 1H, 14ax-H), 2.15 (ddd, J_{10}=10.7 Hz, $J_4\sim J_8\sim$4 Hz, 1H, 9-H), 2.33–2.24 (m, 2H, 3a/3b-H), 2.50–2.35 (m, 2H, 7/4-H), 2.69 (dd, J_{gem}=13.9 Hz, J_1=2.5 Hz, 1H, 14eq-H), 2.78 (ddd, $J_{14ax}\sim J_{10}\sim$10.7 Hz, J_{14eq}=3.2 Hz, 1H, 1-H), 3.06 (m, $J_1\sim J_9\sim$10.5 Hz, J_{11}=3 Hz, 1H, 10-H), 3.21 (s, 3H, O–CH_3), 3.40 (dq, J_{CH3}=6.8 Hz, J_{gem}=9.6 Hz, 1H, O*C*H_2CH_3), 3.7–3.57 (m, 3H, 5/6/8-H), 3.94 (dq,

J_{CH3}=7 Hz, J_{gem}=9.6 Hz, 1H, OCH_2CH$_3$), 4.37 (d, J=11.6 Hz, 1H, Bn), 4.39 (d, J=11.9 Hz, 1H, Bn), 4.51 (d, J=11.9 Hz, 2H, Bn), 4.52 (s, 2H, OCH$_2$O), 5.0 (br, 1H, 11-H), 5.06 (d, J_{14ax}=4 Hz, 1H, 13-H), 7.0–7.2 (m, 10H, Ph); ^{13}C NMR (250 MHz, C_6D_6, 50°C): δ=13.81/15.36/16.10 (7-CH$_3$,11-CH$_3$,OCH$_2$*C*H$_3$), 30.27/32.48 (C-3,14), 33.29/38.32/ 38.72/39.24/43.82 (C-1,4,7,9,10), 55.89 (O*C*H$_3$), 62.89 (O*C*H$_2$CH$_3$), 71.22/78.76/81.39/82.84 (C-5,6,8,11), 73.28/74.3 (Bn), 98.03 (C-13), 98.14 (OCH$_2$O), 139.12/139.24 (Ph); Anal. Calcd for $C_{33}H_{44}O_7$: C=71.71%, H=8.02%, found: C=71.42%, H=7.80%.

33c (1*S**,11*S**,13*R**; byproduct). Colorless oil; IR: 2921 (C–H), 1702 (CO); ^{1}H NMR (250 MHz, C_6D_6, 50°C): δ=1.02 (d, J=7.3 Hz, 3H, 7-CH$_3$), 1.11 (d, J_{11}=6.9 Hz, 3H, 11-CH$_3$), 1.22 (t, J=7 Hz, 3H, OCH$_2$C*H*$_3$), 1.82 (ddd, J_{13}=3.7 Hz, J_1~5.5 Hz, J_{gem}=13.7 Hz, 1H, 14b-H), 2.18 (ddd, J_9~J_{11}~4 Hz, J_1=6.8 Hz, 1H, 10-H), 2.28 (ddd, J_{gem}=14 Hz, J_1=10 Hz, J_{13}=5 Hz, 1H, 14a-H), 2.37 (m, 1H, 9-H), 2.53 (ddq, J_{CH3}=7.5 Hz, J_8=2.9 Hz, J_6=4.8 Hz, 1H, 7-H), 3.1–2.95 (m, 3H, 4/3a/3b-H), 3.20 (m, 1H, 1-H), 3.28 (m, 1H, 8-H), 3.31 (s, 3H, O–CH$_3$), 3.41 (dq, J_{CH3}=7.08 Hz, J_{gem}=9.8 Hz, 1H, OCH_2CH$_3$), 3.73 (dq, J_{CH3}=7 Hz, J_{gem}=9.6 Hz, 1H, OC*H*$_2$CH$_3$), 4.02 (dd, J_5=10.3 Hz, J_7=5 Hz, 1H, 6-H), 4.1 (dd, J_4=3.3 Hz, J_6=10.3 Hz, 1H, 5-H), 4.13 (m, 1H, 11-H), 4.11 (d, J=12 Hz, 1H, Bn), 4.34 (d, J=12 Hz, 1H, Bn), 4.56 (d, J=12 Hz, 1H, Bn), 4.68 (d, J=11 Hz, 1H, Bn), 4.69 (d, J=6.4 Hz, 1H, OCH$_2$O), 4.93 (d, J=6.4 Hz, 1H, OCH$_2$O), 4.99 (dd, J_{14a}~J_{14b}~4 Hz, 1H, 13-H), 7.0–7.3 (m, 10, Ph); ^{13}C NMR (250 MHz, C_6D_6, 50°C): δ=11.59/15.48/18.01 (7-CH$_3$,11-CH$_3$,OCH$_2$*C*H$_3$), 30.19/38.57 (C-3,14), 31.15/35.04/38.01/ 39.12/ 44.7 (C-1,4,7,9,10), 55.46 (OCH$_3$), 62.94 (O*C*H$_2$CH$_3$), 64.59/71.90/75.75/86.36 (C-5,6,8,11), 72.03/72.87 (Bn), 96.97 (C-13), 97.20 (OCH$_2$O); Anal. Calcd for $C_{33}H_{44}O_7$: C=71.71%, H=8.02%, found: C=71.96%, H=8.23%.

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