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Approach towards an EPC Synthesis of Nodusmicin – III.[1] Preparation of the Oxygen Bridged Decalin Part of Nodusmicin

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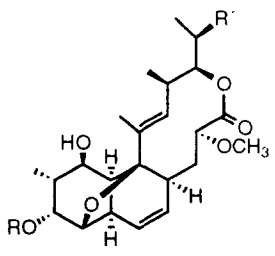
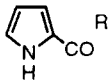
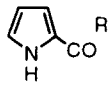
Abstract: Starting with the unsaturated 1,4-meso-diol **1**, the enantiomerically pure 4-silyloxy enone **6** is prepared in high yields via diastereomeric acetals and equilibration. Enone **6** is converted to the cis-decalinone derivative **17** with fragmentation as the key step. Consequently oxidation to the conjugated enedione **24**, reduction to the enediol **25** and intramolecular oxymercuration produces, depending on the reaction conditions, either the unsaturated tricyclic ether **27**, which constitutes a link to a known 18-deoxynargenicin synthesis, or the saturated tricyclic ether **26**, which represents the starting material for the construction of the tenmembered ring of nodusmicin.

In 1980 nodusmicin - a macrolide antibiotic - was isolated from cultures of *Saccharopolyspora hirsuta*.[2] Like the structurally related nargenicins[3] this compound is active against Gram positive bacteria. Their activity extends to drug resistant bacteria and is coupled with low toxicity and substantial oral activity.[3a,4] These facts and the unusual structural features of these compounds initiated several approaches towards the synthesis of nodusmicin,[5-7] which so far have culminated in the total synthesis of 18-deoxynargenicin by Kallmerten et al..[7c,d]



R = H, R'= OH : Nodusmicin

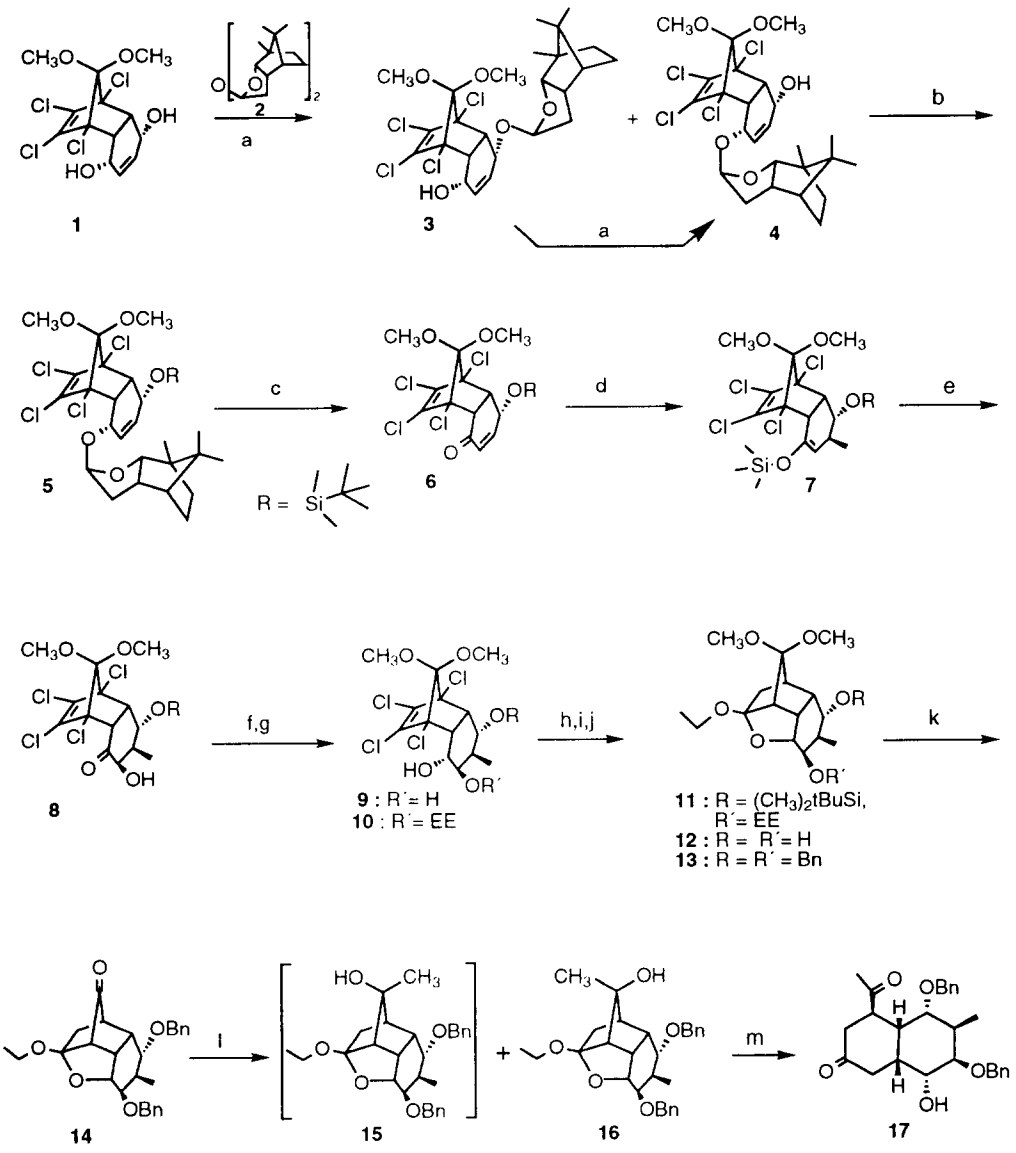
R =  R'= OH : Nargenicin A_1

R =  R'= H : 18-Deoxynargenicin A_1

R = R'= H : 18-Deoxynodusmicin

Scheme 1

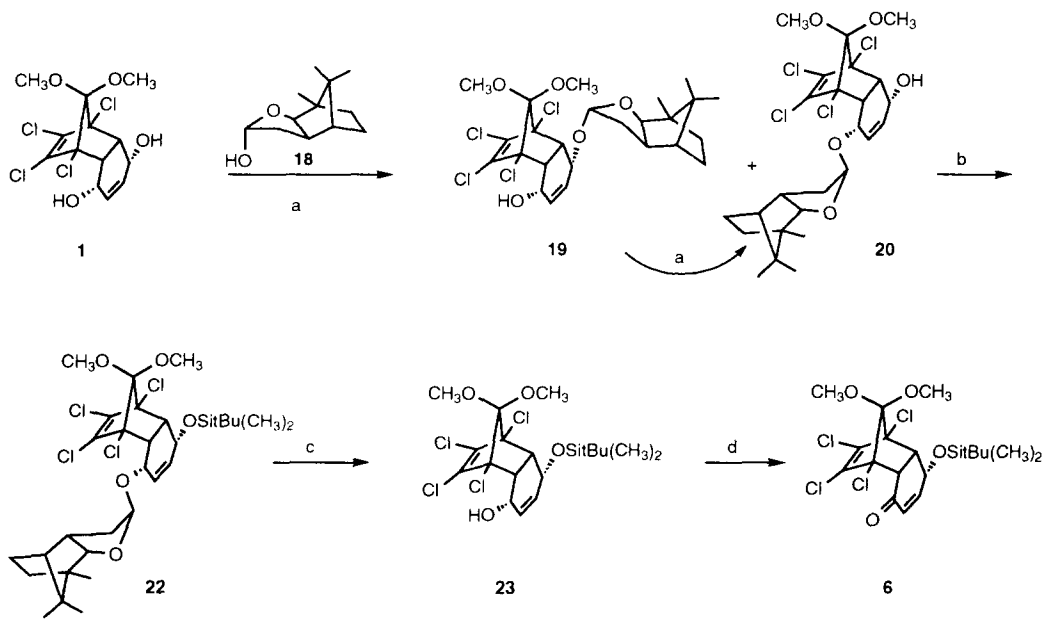
We have developed an annulation method,[8] which seemed especially suited for the synthesis of the decalin part of nodusmicin. It should permit highly stereoselective incorporation of at least 7 of the 8 stereogenic centres of this structure. As a further advantage we considered the fact, that using cheap, easily available, symmetrical starting materials a meso-diol could be constructed, which should allow the conversion of the whole material into one chiral monoalcohol.[9,1]



a) H^+, 3Å mol sieve, CH_2Cl_2, rt, 24h **b**) 4 equ. 2,6-lutidine, 2 equ. $tBu(CH_3)_2SiOSO_2CF_3$, DMF, 0°C, 2h **c**) CrO_3, H_2SO_4, acetone, 0°C, 25´ **d**) $(CH_3)_2CuLi$, $(C_2H_5)_2O$; $(C_2H_5)_3N$, $(CH_3)_3SiCl$, 0°C **e**) OsO_4 (cat.), NMO, THF/acetone/H_2O, rt, 18h **f**) $NaBH_4$, CH_3OH, 0°C, 1h **g**) $C_2H_5OC_2H_3$, PPTS, rt, 5h **h**) Na, C_2H_5OH, refl., 3h **i**) CH_3OH, H^+, rt, 15h **j**) NaH, BnBr, $Bu_4N^+I^-$, THF, refl., 2h **k**) H_3O^+/dioxane, refl., 2h **l**) $Al(CH_3)_3$, toluene, 0°C, 15h **m**) H^+, 5M $LiClO_4$, $(C_2H_5)_2O$, refl., 2h.

Scheme 2

According to Marchand's procedure,[12] meso-diol **1** (as confirmed by X-ray crystal structure analysis[11,31]) was prepared in high yields. Attempts to generate the chiral monoacetate via esterification of **1**[9] or hydrolysis of the diacetate of **1**[9] with several enzymes failed.[13] Therefore we turned to chemical methods to prepare the chiral monoalcohol. Treatment of diol **1** with half an equivalent of the dimeric lactol **2**[14] under acidic conditions led to the diastereomeric monoacetals **3** and **4** in 87% yield. To establish the absolute configuration of these diastereomers, their structures were determined by X-ray crystal structure analysis.[15] From the known absolute configuration of the lactol[14] and from the anomalous dispersion data,[15] we were able to ascertain the diastereoisomer **4** as the compound with the desired absolute configuration. We consider the preferred boat conformation with the oxygen functions in flag pole position and a strong hydrogen bridge between these two oxygens in compounds **1**, **3**, and **4** as the reason for the almost exclusive formation of the monoacetals instead of the expected statistical mixture of diol, the monoacetals and the diacetal.[1b,13] The mediocre diastereoselectivity (**3** : **4** = 5 : 6) of this reaction was of minor importance because acidic equilibration[16] of **3** again led to a 5 : 6 mixture of **3** : **4**. Yields of the acetalization as well as of the equilibration are high and separation on triethylamine deactivated silica gel is easily achieved. Thus, the chiral monoalcohol **4** was conveniently obtained in two cycles in good yields (75%). Then compound **4** was converted to the silyl ether **5**. To achieve this transformation in high yields several obstacles had to be surmounted. *t*-Butyldimethylsilyl chloride proved too unreactive for this purpose. With *t*-butyldimethylsilyl triflate as silylation agent two concurring reactions had to be suppressed. Generating the oxy anion with NaH prior to addition of *t*-butyldimethylsilyl triflate led to intramolecular nucleophilic addition to the dichlorosubstituted double bond and successive S_N'-reaction[17] at



a) $CHCl_3$, CSA, refl. **b)** $tBu(CH_3)_2SiOSO_2CF_3$, lutidine, DMF, 0°C **c)** THF, CH_3OH(0,3%) HCl, refl. **d)** CrO_3, acetone, H^+, 0°C

Scheme 3

temperatures above –30°C. Choosing –50°C and DMF as solvent **5** could be obtained in 80% yield in a slow reaction (48h). Using THF as solvent accelerated this reaction, however in this case the *t*-butyldimethylsilyl triflate acted as Lewis acid effecting partial equilibration (**4** : **3**) prior to silylation. Finally treatment of **4** with 2 equivalents of *t*-butyldimethylsilyl triflate and 4 equivalents of 2,6-lutidine in DMF at 0°C led in 2h in 100% yield to **5**, as confirmed by X-ray structure analysis.[18,31] Again DMF as solvent was crucial, because CH_2Cl_2 as solvent as described in Corey's procedure[19] led to partial equilibration prior to silylation. Hydrolysis of the acetal and oxidation of the unprotected hydroxy group were planned next. Fortunately the acidic conditions of Jones reagent[20] were sufficient to perform these two reactions in one step resulting in enone **6** in nearly quantitative yield.

An improved variant of this procedure starts with the less expensive lactol **18** as chiral auxiliary.[21] In this case the ratio between the desired acetal **20** and the diastereomeric acetal **19** is favourably changed to 1,8 : 1. The higher stability against acids and the larger difference in the Rf-values of the two acetals led to a more convenient chromatographic separation. Again the undesired **19** and small amounts of diacetal **21**, which appeared as byproduct, were easily converted into **20** by acidic equilibration. **20** was transformed to the silylether **22** according to the above mentioned procedure. Due to its greater stability against acids a method had to be developed to hydrolyze the acetal in the presence of the silyl ether.[22] Thus treatment with small amounts of methanolic hydrogen chloride in THF as solvent at elevated temperature led to the reusable methylated chiral auxiliary and high yields of **23**, which was oxidized to enone **6** by Jones reagent.

The following steps up to the decalinone **17** were performed according to the methods developed for the racemic decalinone (±)-**17**[1a] with minor variations.[23] Dimethyl copper lithium was added to the chiral enone **6** and the enolate formed was captured as silyl enolether **7** in quantitative yield by addition of trimethylsilyl chloride and triethylamine.[24] Within two steps this silyl enolether was transformed to the vicinal trans diol **9** by osmylation[25] and reduction with sodium borohydride. Starting with **5** diol **9** was prepared in 55% yield with only one chromatographic purification necessary (which also allowed to recover the chiral auxiliary as the corresponding lactone[14] in case the bislactol **2** was used). Since intramolecular nucleophilic addition to the double bond with sodium ethoxide as base was pestered with side reactions due to the newly introduced unprotected hydroxy group in exo position,[1a] this function was protected as 1-ethoxyethyl ether. Treatment of partially protected **10** with an excess of small pieces of sodium in refluxing ethanol allowed nucleophilic addition, substitution[26,8a] and dechlorination[27,8a] in one step in nearly quantitative yield. The protective groups of the tetracycle **11** were exchanged against the acid stable benzyl groups by methanolysis to the dihydroxy compound **12** and benzylation to **13**. The overall yield from **9** to **13** was 76%. The dibenzyl derivative **13** was then partially hydrolyzed to the monoketone **14** with diluted aqueous HCl in refluxing dioxane. Consequently **14** was converted to the diastereomeric tertiary alcohols **15** and **16**. Experiments with the racemic tertiary alcohols (±)-**15** and (±)-**16** had revealed[1a] that contrary to the model compounds,[8c] acidic fragmentation occurred exclusively with alcohol (±)-**16**. Therefore conditions had to be found to convert **14** to the tertiary alcohols with a high proportion of **16**. After several trials as indicated in **table 1** trimethylalane in toluene[28] at 0°C proved to be satisfactory in converting enantiomerically pure **14** to a 1 : 4.5 mixture of **15** and **16** in 80% yield. Treatment of **16** with small amounts of camphorsulfonic acid in 5M lithium perchlorate/ether solution[29] at reflux did result in the desired chiral decalinone **17** in 81% yield. Because of the drastic conditions of the last step the structure of **17** was confirmed by X-ray diffraction analysis of a single crystal.[30,31]

To effect the oxidation of dione **17** to the enedione **24** we had to develop a suitable method with a

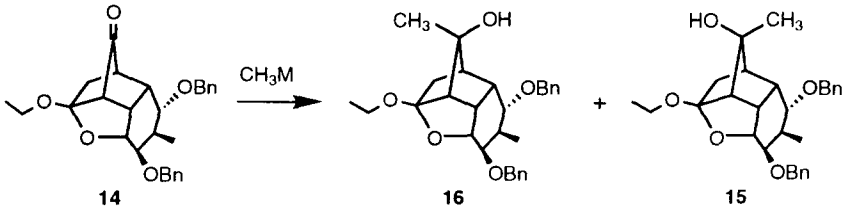
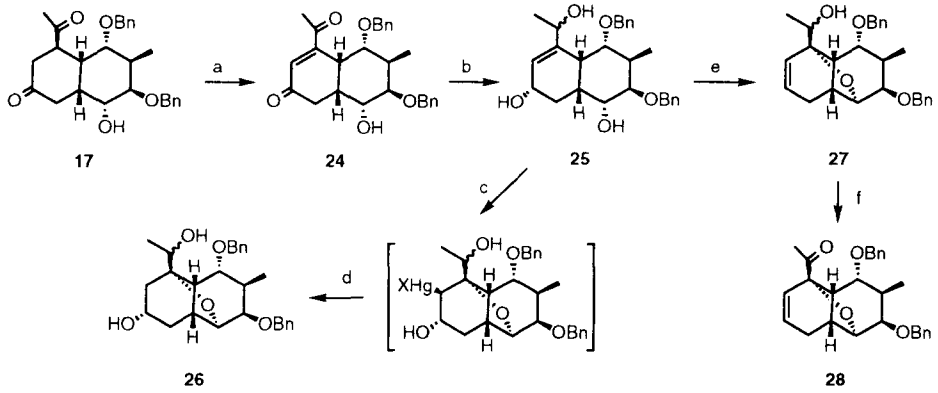


Table 1: Stereoselectivity of the addition reaction to ketone 14

CH_3M	Solvent	T(°C)	16	:	15
CH_3Li	toluene	-78	1	:	1
CH_3MgCl	hexane	0	1	:	1
-- " --	THF	-78 to -30	1	:	1
-- " --	toluene	-78	2	:	1
$CH_3MgCl/CeCl_3$	toluene	-78	1	:	8
-- " --	THF	-78	1	:	8
$(CH_3)_2CuLi$	toluene	-78	<1	:	>19
$(CH_3)_3Al$	toluene	0	4.5	:	1

model compound,[32] because the originally chosen dehydrogenation with DDQ failed under acidic as well as neutral conditions. We succeeded when oxidizing under rather drastic basic conditions. We assume the electron rich conjugated bisenolate as the reactive intermediate and its reluctant formation is due to the low kinetic as well as thermodynamic acidity of the proton geminal to the acetyl group. We arrived at this conclusion by examining the X-ray diffraction of crystalline 17.[30] Its conformation, which corresponds well with the main conformation in solution according to NMR

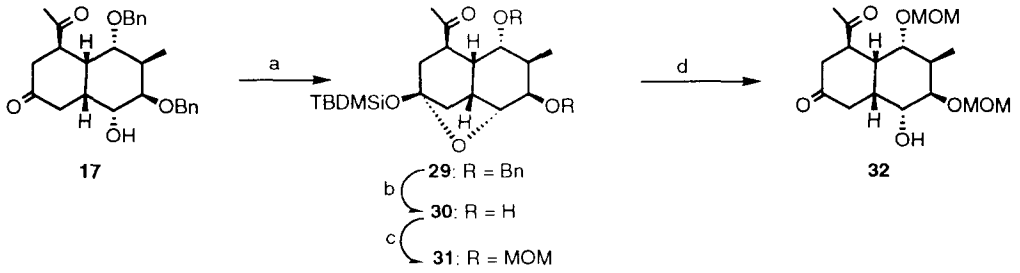


a) KH, KOt-Bu, THF; $FeCl_3$, DMF, rt b) $NaBH_4$, $CeCl_3.7H_2O$, MeOH, 0°C c) HgO, $Hg(OCOCF_3)_2$, THF, 0°C
d) $NaBH_4$, NaOH e) $Hg(OCOCF_3)_2$, THF, 0°C, then $NaBH_4$, H_2O f) CrO_3, H_2SO_4, acetone, 0°C

Scheme 4

spectroscopic data, shows the hindered proton geminal to the acetyl group perpendicularly positioned to the π-electrons of the carbonyl group. Five equivalents of potassium *t*-butoxide in DMF, which is essential as solvent, were necessary to accomplish the oxidation with a variety of oxidants (NIS, DDQ, I_2, $CuCl_2$, $FeCl_3$anh.), anhydrous ferric chloride being the most reliable one. The enedione **24**, a light sensitive compound,[32] which had to be handled in the dark, was formed in 65% yield. The intramolecular 1,4-addition of the alkoxide to the enedione, which we had anticipated, failed. Therefore we turned our attention to the electrophilic attack at the double bond[33] to obtain the cyclisation to the tricyclic ether. To provide a sufficiently electron rich double bond the diketone **24** was reduced with sodium borohydride and cerium chloride to a 1:1 mixture of the diastereomeric triols **25**. However, treatment of **25** with either iodine[34] or phenyl selenyl chloride[35] mainly led to reoxidation of the allylic alcohols. Finally the intramolecular ether formation was achieved by oxymercuration. Treatment of **25** with mercuric trifluoroacetate in THF[36] led to the organomercury compound, which immediately was consumed in a "retro oxymercuration"-reaction[37] triggered by the trifluoroacetic acid, generated by the former reaction thus yielding the unsaturated tricycle **27**. To isolate the organomercury compound we used in analogy to Giese et al.[38] a 1:1 mixture of mercuric trifluoroacetate and mercuric oxide to scavenge the liberated trifluoroacetic acid as mercuric trifluoroacetate. Both sets of reaction conditions led to useful products. The organomercury compound and/or its demercuration product **25**, prepared by reduction with sodium borohydride under basic conditions,[37] are envisaged as intermediates of our planned nodusmicin synthesis. The unsaturated alcohol **27** constitutes after oxidization to the tricyclic enone **28** an advanced intermediate in Kallmerten's improved 18-deoxynargenicin synthesis[7d] with two deviations. Firstly Kallmerten's intermediate was protected by methoxymethyl groups whereas **28** possesses two benzyl groups. The exchange of the protective groups is easily accomplished as demonstrated with the racemic diketone (±)-**17**.

Transformation of (±)-**17** to the cyclic ketal (±)-**29** with *t*-butyldimethylsilyl triflate and triethylamine under carefully controlled conditions was followed by hydrogenolysis of the benzyl groups yielding the diol (±)-**30**, which was converted to the bismethoxymethyl ether (±)-**31** with chloromethylmethyl ether and Hünig's base. Finally removal of the silyl group by fluoride restored the hydroxyketone (±)-**32** with the correct protective groups for the formal synthesis of 18-deoxynargenicin. However, this exchange could be performed within fewer steps when Kallmerten's procedure is followed with the benzyl ethers up to the removal of the phosphate group with lithium in ammonia.[7c] There



a) $tBu(CH_3)_2SiOSO_2CF_3$, Et_3N, CH_2Cl_2, -50°C **b)** H_2, Pd-C, $(i\text{-}Pr)_2O$, rt **c)** CH_3OCH_2Cl, $(i\text{-}Pr)_2NEt$, CH_2Cl_2, rt **d)** TBAF, THF, rt

Scheme 5

not only the phosphate but also the benzyl groups would be removed and the methoxymethylethers could be formed. The second deviation is more advantageous as **28** is enantiomerically pure in contrast to Kallmerten's intermediate. Therefore it is now possible to conduct Kallmerten's improved synthesis with its elegant Wittig rearrangement as key step to the enantiomerically pure (+)-18-deoxynargenicin. This should be of special interest as Magerlein at al.[4c] found more potent activity against streptococci in 18-deoxynargenicin as in the main antibiotic nargenicin.

EXPERIMENTAL[23]

General notes: ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Spectrospin WM 250 (250 MHz) or AM 400-WB (400MHZ). Tetramethylsilane served as internal standard. Mass spectra were recorded on a spectrometer CH-7(Varian) and IR spectra on a Perkin Elmer 1600 FTIR spectrometer either in solution or neat on silicon. No IR spectra are given for substances without significant bands. UV-spectra were recorded on a Hewlett Packard 8452 spectrometer. 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*R*,2*R*,6*R*,7*S*,8*S*)-1,8,9,10-Tetrachloro-11,11-dimethoxy-6-(*t*-butyldimethylsilyl)oxytricyclo[6.2.1.$0^{2,7}$]undeca-4,9-dien-3-one (6)

455mg of **5**[1b] (0.681mmol) was dissolved in 20ml of acetone and cooled to 0°C. An excess of Jones reagent was added. After stirring for 25 min at 0°C 15ml of sat. aqu. NH_4OAc and 10ml ether were added. The mixture was extracted with ether and the organic layers were washed with sat. aqu. $NaHCO_3$ and brine, dried with Na_2SO_4 and concentrated. Flash chromatography of the residue (petroleum ether / ethyl acetate 6:1) afforded **6** (306mg, 0.627 mmol, 92%) and the chiral auxiliary as lactone. - $[\alpha]_D^{20}$ = -52.0° (c = 2.96 in THF).

(+)-(1*R*,2*R*,5*S*,6*R*,7*S*,8*S*)-1,8,9,10-Tetrachloro-11,11-dimethoxy-5-methyl-6-(*t*-butyldimethylsilyl)oxy-3-(trimethylsilyl)oxytricyclo[6.2.1.$0^{2,7}$]undeca-3,9-diene (7)

$[\alpha]_D^{20}$ = +48.7° (c = 3.07 in THF).

(-)-(1*R*,2*R*,4*R*,5*R*,6*R*,7*S*,8*S*)-1,8,9,10-Tetrachloro-11,11-dimethoxy-4-hydroxy-5-methyl-6-(*t*-butyldimethylsilyl)oxytricyclo[6.2.1.$0^{2,7}$]undec-9-en-3-one (8)

$[\alpha]_D^{20}$ = -93.6° (c = 1.44 in THF).

(+)-(1*R*,2*R*,3*R*,4*R*,5*R*,6*R*,7*S*,8*S*)-1,8,9,10-Tetrachloro-3,4-dihydroxy-11,11-dimethoxy-5-methyl-6-(*t*-butyldimethylsilyl)oxytricyclo[6.2.1.$0^{2,7}$]undec-9-ene (9)

$[\alpha]_D^{20}$ = +6.7° (c = 1.48 in THF).

(+)-(1*R*,3*R*,5*R*,7*R*,8*S*,9*R*,10*S*,11*R*,12*R*)-3-Ethoxy-6,6-dimethoxy-11-methyl-2-oxatetracyclo[6.4.0.$0^{3,7}$.$0^{5,9}$]dodecan-10,12-diol (12)

$[\alpha]_D^{20}$ = +68.8° (c = 1.30 in THF).

(+)-(1*R*,3*R*,5*R*,7*R*,8*S*,9*R*,10*S*,11*R*,12*R*)-10,12-Dibenzyloxy-3-ethoxy-6,6-dimethoxy-11-methyl-2-oxatetracyclo[6.4.0.0^{3,7}.0^{5,9}]dodecane (13)

$[\alpha]_D^{20}$ = +109.0° (c = 1.05 in THF).

(+)-(1*R*,3*R*,5*R*,7*R*,8*S*,9*R*,10*S*,11*R*,12*R*)-10,12-Dibenzyloxy-3-ethoxy-11-methyl-2-oxatetracyclo[6.4.0.0^{3,7}.0^{5,9}]dodecan-6-one (14)

$[\alpha]_D^{20}$ = +109.7° (c = 1.18 in THF).

(+)-(1*R*,3*R*,5*R*,6*R*,7*S*,8*S*,9*R*,10*S*,11*R*,12*R*)-10,12-Dibenzyloxy-3-ethoxy-6,11-dimethyl-2-oxatetracyclo[6.4.0.0^{3,7}.0^{5,9}]dodecan-6-ol (15)

(+)-(1*R*,3*R*,5*R*,6*S*,7*S*,8*S*,9*R*,10*S*,11*R*,12*R*)-10,12-Dibenzyloxy-3-ethoxy-6,11-dimethyl-2-oxatetracyclo[6.4.0.0^{3,7}.0^{5,9}]dodecan-6-ol (16)

A solution of 93 mg of **14** (0.207 mmol) in 15ml of dry toluene was cooled to 0°C under an argon atmosphere. 0.6 ml of 2M trimethylaluminum solution in toluene was added with a syringe. The reaction mixture was allowed to warm up to room temperature overnight. After TLC indicated completion of the reaction 10 ml of sat. aqu. NH_4Cl was added, and the mixture was extracted with methylene chloride. The organic phase was washed with brine, dried with Na_2SO_4 and concentrated. Flash chromatography (toluene / ethyl acetate 6:1) gave **16** (62.6mg, 0.135mmol, 65%) and **15** (13.9mg, 0.030mmol, 15%) as colourless oils. - **15**: $[\alpha]_D^{20}$ = +120.8° (c = 1.52 in THF). - **16**: $[\alpha]_D^{20}$ = +110.3° (c = 1.02 in THF).

(+)-(1*R*,5*R*,6*R*,7*S*,8*R*,9*R*,10*R*)-5-Acetyl-7,9-dibenzyloxy-10-hydroxy-8-methylbicyclo[4.4.0]decan-3-one (17)

$[\alpha]_D^{20}$ = +81.5° (c = 1.28 in THF).

(-)-(1*R*,2*R*,3*S*,6*R*,7*S*,8*S*)-1,8,9,10-Tetrachloro-11,11-dimethoxy-6-{[(1'*R*,2'*R*,4'*R*,6'*R*,7'*R*)-1',10',10'-trimethyl-3'-oxatricyclo[5.2.1.0^{2,6}]dec-4-yl]oxy}tricyclo[6.2.1.0^{2,7}]undeca-4,9-dien-3-ol (19)

(-)-(1*S*,2*S*,3*R*,6*S*,7*R*,8*R*)-1,8,9,10-Tetrachloro-11,11-dimethoxy-6-{[(1'*R*,2'*R*,4'*R*,6'*R*,7'*R*)-1',10',10'-trimethyl-3'-oxatricyclo[5.2.1.0^{2,6}]dec-4-yl]oxy}tricyclo[6.2.1.0^{2,7}]undeca-4,9-dien-3-ol (20)

10.00 g of diol **1** (27.00 mmol), 5.22 g of lactol **18** (27.00 mmol) and 0.20 g of camphorsulfonic acid were dissolved in 120 ml of $CHCl_3$ (abs.). A 100 ml dropping funnel, with a reflux condenser on the top, was placed on the flask. The mixture was stirred and heated for 2 h, during which time $CHCl_3$ distilled slowly into the dropping funnel and removed water from the reaction mixture. Thereafter 1ml of triethylamine was added and the volatiles were removed under vacuum. Separation of the diastereomeric products was achieved by flash chromatography on silica gel with petroleum ether : ether (9 : 1 and 3 : 1) affording 7.63 g of **20** (13.80 mmol, 51%) and 4.30 g of **19** (7.80 mmol, 29%). The chirality of **19** was established by its conversion to (+)-**6**.

Compound **20**: m.p. 140-142°C; $[\alpha]_D^{20}$ = -12.8° (c = 1.31 in THF); **IR** (cm^{-1}): 3464, 1608; **^{1}H NMR** ($CDCl_3$, δ): 0.78 (s, 3H), 0.92 (s, 3H), 0.93 (s, 3H) C(1')CH_3, C(10')CH_3, C(10')CH_3; 0.94 (m, 2H),1.38 (m, 1H) $w_{1/2}$ = 25 Hz H(8'), H(9'), H(8'); 1.61 (d, 1H) $J_{7',8'x}$ = 4 Hz H(7'); 1.67 (ddd, 1H) $J_{9',9'}$ = 14.8 Hz, $J_{9',8'}$ = 8 Hz, $J_{9',8'}$ = 4 Hz H(9'); 2.00 (ddd, 1H) $J_{5'ax,4'}$ = 5 Hz, $J_{5'ax,6'}$ = 7 Hz, $J_{5',5'}$ = 13 Hz H(5'ax); 2.09 (dt, 1H) $J_{6',5'ax}$ = $J_{2',6'}$ = 7 Hz, $J_{6',5'eq}$ = 10.5 Hz H(6'); 2.19 (dd, 1H) $J_{5'eq,6'}$ = 10 Hz, $J_{5',5'}$ =

13 Hz H(5'eq); 2.81 (dd, 1H) $J_{2,7}$ = 11.4 Hz, $J_{2,3}$ = 4.7 Hz H(2); 3.35 (dd, 1H) $J_{2,7}$ = 11.4 Hz, $J_{6,7}$ = 4.8 Hz H(7); 3.04 (d, 1H, with D_2O exchangeable) $J_{3,OH}$ = 12 Hz OH; 3.55 (s, 3H) OCH_3; 3.58 (s, 3H) OCH_3; 3.70 (d, 1H) $J_{2',6'}$ = 7 Hz H(2'); 4.32 (t, 1H) $J_{6,5} \approx J_{6,7} \approx$ 5.4 Hz H(6); 4.37 (dt, 1H) $J_{3,2} \approx J_{3,4} \approx$ 5.4 Hz, $J_{3,OH}$ = 12 Hz H(3); 5.19 (d, 1H) $J_{4',5'ax}$ = 5 Hz H(4'); 6.38 (dd, 1H) $J_{4,5}$ = 9.3 Hz, $J_{4,3}$ = 6 Hz H(4); 6.45 (dd, 1H) $J_{4,5}$ = 9.3 Hz, $J_{5,6}$ = 6 Hz H(5); **^{13}C NMR** ($CDCl_3$, δ): 135.4, 135.0 C4, C5; 129.5, 128.7 C9, C10; 115.7 C11; 106.3 C4'; 91.3 C2'; 76.5 76.2 C1, C8; 66.1, 61.1 C3, C6; 52.9 OCH_3; 51.6 OCH_3; 51.4, 50.7 C2, C7; 48.4 C7'; 47.5, 47.0 C1', C10'; 45.2 C6'; 38.6 C5'; 32.2 C9'; 28.6 C8'; 22.8 CH_3; 20.4 CH_3; 11.5 CH_3; **MS** (m/z, %): 552/554/556 (0.1%/0.1%/0.05%, M^+); 517/519/521/523 (0.2%/0.2%/0.1%/0.05%, M^+-Cl); 338/340/342/344 (1%/1%/0.4%/0.1%, M^+-Cl-Nx); 253/255/257/259 (15%/14%/5%/1.2%, 1-dimethoxycarbonium-2,3,4-trichlorobenzene); 207/209/211 (3.5%/3.4%/1.5%, 2,3,4-trichlorobenzacylium); 179 (100%, Nx^+); 135 (45%, Nx^+-C_2H_4O); 109 (34%); 95 (52%). Nx = (1'*R*,2'*R*,4'*R*,6'*R*,7'*R*)-1',10',10'-trimethyl-3'-oxatricyclo-[5.2.1.$0^{2,6}$]dec-4-yl; Anal. Calcd for $C_{25}H_{32}Cl_4O_5$: C, 54.17; H, 5.82. Found: C, 54.31; H, 5.83.

Compound **19:** m.p. 134°C; $[\alpha]_D^{20}$ = -76.6° (c = 0.96 in THF); **IR** (cm^{-1}): 3464, 1608; **^{1}H NMR** ($CDCl_3$, δ): 0.79 (s, 3H), 0.90 (s, 3H), 0.99 (s, 3H) C(1')CH_3, C(10')CH_3, C(10')CH_3; 0.90 (m, 2H), 1.40 (m, 1H) $w_{1/2}$ = 25 Hz H(8'), H(9'), H(8'); 1.61 (d, 1H) $J_{7',8'x}$ = 4 Hz H(7'); 1.70 (m, 1H) $w_{1/2}$ = 30 Hz H(9'); 1.99 (m, 2H) H(5'ax), H(5'eq); 2.35 (dt, 1H) $J_{6',5'ax} = J_{2',6'}$ = 7 Hz, $J_{6',5'eq}$ = 10.5 Hz H(6'); 2.79 (dd, 1H) $J_{2,7}$ = 11.3 Hz, $J_{2,3}$ = 4.6 Hz H(2); 2.83 (d, 1H, with D_2O exchangeable) $J_{3,OH}$ = 12.2 Hz OH; 2.99 (dd, 1H) $J_{2,7}$ = 11.3 Hz, $J_{6,7}$ = 5.1 Hz H(7); 3.56 (s, 3H) OCH_3; 3.59 (s, 3H) OCH_3; 4.01 (d, 1H) $J_{2',6'}$ = 7.5 Hz H(2'); 4.38 (ddd, 1H) $J_{3,2}$ = 4.8 Hz, $J_{3,4}$ = 6.4 Hz, $J_{3,OH}$ = 12.2 Hz H(3); 4.64 (t, 1H) $J_{6,5} \approx J_{6,7} \approx$ 5.3 Hz H(6); 5.15 (d, 1H) $J_{4',5'ax}$ = 4.7 Hz H(4'); 6.46 (dd, 1H) $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 5.5 Hz H(5) ; 6.59 (dd, 1H) $J_{4,5}$ = 9.5 Hz, $J_{4,3}$ = 6.4 Hz H(4); **^{13}C NMR** ($CDCl_3$, δ): 138.6, 132.7 C4, C5; 129.7, 129.0 C9, C10; 115.7 C11; 100.9 C4'; 92.5 C2'; 76.3, 76.2 C1, C8; 61.4, 61.2 C3, C6; 52.9 OCH_3; 51.6 OCH_3; 51.3, 49.9 C2, C7; 48.5 C7' ; 47.8, 47.0 C1', C10'; 46.2 C6' ; 38.8 C5'; 32.2 C9'; 28.8 C8'; 22.9 CH_3; 20.2 CH_3; 11.6 CH_3; **MS** (m/z, %): 552/554/556 (0.1%/0.1%/0.05%, M^+); 517/519/521/523 (0.4/0.3/0.1%/0.05%, M^+-Cl); 338/340/342/344 (1.1%/1.1%/0.4%/0.1%, M^+-Cl-Nx); 253/255/257/259 (15%/15%/5%/1%, 1-dimethoxycarbonium-2,3,4-trichloorbenzene); 207/209/211 (1.8%/1.8%/1%, 2,3,4-trichlorobenzacylium); 179 (100%, Nx^+); 135 (33%, Nx^+-C_2H_4O); 95 (38%). Nx = (1'*R*,2'*R*,4'*R*,6'*R*,7'*R*)-1',10',10'-trimethyl-3'-oxatricyclo[5.2.1.$0^{2,6}$]dec-4-yl; Anal. Calcd for $C_{25}H_{32}Cl_4O_5$: C, 54.17; H, 5.82. Found: C, 54.17; H, 5.76.

(-)-(1*S*,2*S*,3*R*,6*S*,7*R*,8*R*)-1,8,9,10-Tetrachloro-11,11-dimethoxy-3-(*t*-butyldimethylsilyl-oxy)-6-{[(1'*R*,2'*R*,4'*R*,6'*R*,7'*R*)-1',10',10'-trimethyl-3'-oxatricyclo[5.2.1.$0^{2,6}$]dec-4-yl]oxy}tricyclo[6.2.1.$0^{2,7}$]undeca-4,9-diene (22)

10.18 g of acetal **20** (18.4 mmol) was dissolved in 500 ml of DMF(abs.) and cooled to 0°C. To this solution 6.4 ml of 2,6-lutidine (55.0 mmol) and 6.2 ml of TBDMS triflate (27.0 mmol) were added, and the reaction mixture was stirred for 4 h at 0°C under an atmosphere of argon. The reaction was quenched by sat. aqu. $NaHCO_3$ and diluted with water. After extraction with ether the organic layers were washed once with water and once with brine, and dried with Na_2SO_4. Flash chromatography on silica gel with petroleum ether : ether (50 : 1) yielded 12.3 g of **22** (18.3 mmol, 99%) as colourless oil.

$[\alpha]_D^{20}$ = -82.2° (c = 0.76 in THF); **^{1}H NMR** ($CDCl_3$, δ): 0.05 (s, 3H) $SiCH_3$; 0.08 (s, 3H) $SiCH_3$; 0.93 (s, 9H) $C(CH_3)_3$; 0.80 (s, 3H), 0.97 (s, 6H) C(1')CH_3, C(10')CH_3, C(10')CH_3; 1.00 (m, 2H), 1.41 (m, 1H) $w_{1/2}$ = 25 Hz, 1.72 (m, 1H) $w_{1/2}$ = 30 Hz H(8'), H(9'), H(8'), H(9'); 1.65 (d, 1H) $J_{7',8'x}$ = 4 Hz H(7'); 2.04 (ddd, 1H) $J_{5'ax,4'}$ = 5 Hz, $J_{5'ax,6'}$ = 7 Hz, $J_{5',5'}$ = 13 Hz H(5'ax); 2.20 (dd, 1H) $J_{5'eq,6'}$ = 10.5 Hz, $J_{5',5'}$ = 13 Hz H(5'eq); 2.34 (dt, 1H) $J_{6',5'ax} = J_{2',6'}$ = 7.5 Hz, $J_{6',5'eq}$ = 10.5 Hz; H(6') 3.11 (dd, 1H)

$J_{2,7}$ = 9.5 Hz, $J_{2,3}$ = 7.5 Hz, 3.35 (dd, 1H) $J_{2,7}$ = 9.5 Hz, $J_{6,7}$ = 7 Hz H(2), H(7); 3.53 (s, 3H) OCH_3; 3.61 (s, 3H) OCH_3; 3.88 (d, 1H) $J_{2',6'}$ = 7.5 Hz H(2'); 4.37 (dd, 1H) $J_{3,6}$ = 1.5 Hz, $J_{2,3}$ = 7.5 Hz, 4.43 (dd, 1H) $J_{3,6}$ = 1.5 Hz, $J_{6,7}$ = 7 Hz H(3), H(6); 5.31 (d, 1H) $J_{4',5'ax}$ = 5 Hz H(4'); 5.55 (s, 2H) H(4), H(5); **^{13}C NMR** ($CDCl_3$, δ): 129.7, 127.7 C4, C5; 128.9, 128.7 C9, C10; 111.9 C11; 103.3 C4'; 91.5 C2'; 76.8, 76.0 C1, C8; 68.4, 67.3 C3,C6; 52.9 OCH_3; 51.9 OCH_3; 49.5, 48.5 C7, C2; 47.6, 47.0 C1', C10'; 45.8 C7'; 45.2 C6'; 38.5 C5'; 32.5 C9'; 28.9 C8'; 25.9 $C(\underline{C}H_3)_3$; 22.9 CH_3; 20.5 CH_3; 18.1 $Si\underline{C}(CH_3)_3$; 11.7 CH_3; -4.7 $SiCH_3$; -5.1 $SiCH_3$; **MS** (m/z, %): 631/633/635 (0.6%/0.7%/0.2%, M^+-Cl); 609/611/613 (0.6%/0.9%/0.4%, M^+-*t*Bu); 471/473/475 (0.3%/0.5%/0.2%, M^+-NxO); 452/454/456/458 (6%/6%/2.1%/0.3%, M^+-Cl-Nx); 253/255/257/259 (58%/57%/20%/4%, 1-dimethoxycarbonium-2,3,4-trichlorobenzene); 200 (30%, 4-(*t*-butyldimethylsilyloxy)-buta-1,3-dien-1ol$^+$); 179 (100%, Nx^+); 135 (40%, Nx^+-C_2H_4O); 95 (52%). Nx = (1'*R*,2'*R*,4'*R*,6'*R*,7'*R*)-1',10',10'-trimethyl-3'-oxatricyclo[5.2.1.0^{2,6}]dec-4-yl; Anal. Calcd for $C_{31}H_{46}Cl_4O_5Si$: C, 55.69; H, 6.93. Found: C, 55.60; H, 6.75.

(-)-(1*R*,2*R*,3*S*,6*R*,7*S*,8*S*)-1,8,9,10-Tetrachloro-11,11-dimethoxy-6-(*t*-butyldimethylsilyl)-oxytricyclo[6.2.1.0^{2,7}]undeca-4,9-dien-3-ol (23)

To a solution of 19.7 g of **22** (29.4 mmol) in 800 ml THF (abs.) 14.7 ml of 3.2 M methanolic HCl (47 mmol) was added. The mixture was refluxed for 5 h and quenched with sat. aqu. $NaHCO_3$ after cooling to room temperature. After extraction with ethyl acetate the organic layers were washed with brine, dried with $MgSO_4$ and evaporated. Flash chromatography on silica gel with petroleum ether : ether (5 : 1 and 3 : 1) gave 11.56 g of **23** (23.6 mmol, 80%) and 5.68 g of the chiral auxiliary as methyl acetal (27.0 mmol, 92%). - $[\alpha]_D^{20}$ = -2.2° (c = 1.25 in THF)

(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 (24)

To a suspension of 70 mg of potassium hydride (1.75 mmol) in 50 ml of THF (abs.) under an atmosphere of argon 426 mg of potassium *t*-butoxide (3.48 mmol) was added and stirred for half an hour at room temperature. 305 mg of **17** (0.70 mmol) dissolved in 3ml of THF (abs.) was added slowly giving a red solution. Stirring was continued for 30 min at room temperature. Then a solution of 750 mg of anhydrous $FeCl_3$ in 50 ml of DMF (abs.) was added during 5 min and stirring was continued for 1 h. The dark brown reaction mixture was poured into 50 ml of sat. aqu. NH_4Cl and diluted with 50ml of water. After addition of a small amount of 2% aqu. HCl to dissolve precipitated iron hydroxides the mixture was extracted with ethyl acetate. The organic layers were washed with sat. aqu. $NaHCO_3$ and brine, dried with Na_2SO_4 and evaporated to give crude **24**, which is a light sensitive compound, in 65% yield. It was used for the next step without further purification. For characterization a small amount was purified by flash chromatography on silica gel with petrolether : ethyl acetate (2 : 1).

IR (cm^{-1}): 3468, 3087, 3063, 3030, 1675; **UV** (nm (ε)): 208 (7630), 242 (3500); **^{1}H NMR** ($CDCl_3$, δ): 1.08 (d, 3H) $J_{8,CH3}$ = 7.4 Hz C(8)CH_3; 2.23 (s, 3H) CH_3CO; 2.54 (b, 1H, with D_2O exchangeable) OH; 2.55-2.70 (m, 3H) H(1), H(2exo), H(8); 2.82 (dd, 1H) $J_{2,2}$ = 18.2 Hz, $J_{2,1}$ = 15.2 Hz H(2endo); 3.18 (dd, 1H) $J_{6,7}$ = 2.8 Hz, $J_{6,1}$ = 4.5 Hz H(6); 3.60 (t, 1H) $J_{7,6} \approx J_{7,8} \approx$ 2.5 Hz H(7); 3.82 (dd, 1H) $J_{9,10}$ = 10.1 Hz, $J_{9,8}$ = 5.0 Hz H(9); 4.00 (dd, 1H) $J_{9,10}$ = 10.1 Hz, $J_{10,1}$ = 5.5 Hz H(10); 4.14 (d, 1H) J_{gem} = 12.1 Hz benzyl. H; 4.41 (d, 1H) J_{gem} = 11.2 Hz benzyl. H; 4.42 (d, 1H) J_{gem} = 12.1 Hz benzyl. H; 4.61 (d, 1H) J_{gem} = 11.2 Hz benzyl. H; 6.66 (s, 1H) H(4); 7.05 - 7.11 (m, 2H) aromat. H; 7.24 - 7.37 (m, 8H) aromat. H; **^{13}C NMR** ($CDCl_3$, δ): 202.3, 199.5 C1', C3; 151.9 C5; 137.9, 137.8 aromat. C; 136.0 C4; 128.6, 128.4, 128.0, 128.0, 127.8, 127.8 aromat. C; 81.3, 76.5 C9, C7; 72.3 benzyl. C;

71.1 benzyl. C; 68.4 C10; 37.8 C6; 35.4 C2; 33.2, 33.1 C1, C8; 26.1 C2'; 11.1 C(8)$\underline{C}H_3$; **MS** (m/z, %): 434 (4.7%, M^+); 343 (33%, M^+-C_7H_7); 328 (17%, M^+-C_7H_6O); 228 (43%); 137 (43%, 3'-hydroxyacetophenone·H^+); 91 (100%, $C_7H_7^+$); 43 (60%, CH_3CO^+).

(1*R*,1'*R*,4*S*,6*R*,7*R*,8*R*,9*R*,10*S*)-8,10-Dibenzyloxy-2-(1'-hydroxyethyl)-9-methylbicyclo-[4.4.0]dec-2-en-4,7-diol (25a)

(+)-(1*R*,1'*S*,4*S*,6*R*,7*R*,8*R*,9*R*,10*S*)-8,10-Dibenzyloxy-2-(1'-hydroxyethyl)-9-methylbicyclo[4.4.0]dec-2-en-4,7-diol (25b)

Crude **24** and 0.6 g of $CeCl_3 \cdot 7H_2O$ (1.75 mmol) were dissolved in 50 ml CH_3OH (abs.) and cooled to -78°C. To this solution 0.3 g of $NaBH_4$ (7.9 mmol) was added in 3 portions within 1/2 h. After stirring for 30 min sat. aqu. NH_4Cl was added. The reaction mixture was extracted with ethyl acetate, and the organic layers were washed with brine and dried with Na_2SO_4. By flash chromatography with ethyl acetate on silica gel 156 mg of the diastereomeric products **25** (**25a** : **25b** = 2 : 3, 0.36 mmol, 51% from **17**) were obtained. Separation of these two diastereomers was not successful, only **25b** (the diastereomer, which possesses the higher Rf-value) was obtained as pure compound.

Compound **25b**: $[\alpha]_D^{20}$ = +8.0° (c = 0.71 in THF); **IR** (cm^{-1}): 3400, 3088, 3063, 3030; **^{1}H NMR** ($CDCl_3$, δ): 1.00 (d, 3H) $J_{CH3,9}$ = 6.5 Hz C(9)CH_3; 1.25 (d, 3H) $J_{CH3,1'}$ = 6.5 Hz H(2'); 1.30 (b, 2H, with D_2O exchangeable) OH, OH; 1.87 (ddd, 1H) $J_{5,5}$ = 13 Hz, $J_{5n,4}$ = 9.3 Hz, $J_{5n,6}$ = 11.8 Hz H(5endo); 2.15-2.35 (m, 3H) H(1), H(5exo), H(6); 2.55 (s, 1H, with D_2O exchangeable) OH; 2.67 (ddq, 1H) $J_{9,CH3}$ = 7.4 Hz, $J_{9,8} \approx$ 4.8 Hz, $J_{9,10} \approx$ 2.5 Hz H(9); 3.65 (t, 1H) $J_{10,1} \approx J_{10,9} \approx$ 2.5 Hz H(10); 3.81 (dd, 1H) $J_{8,7}$ = 10.2 Hz, $J_{8,9}$ = 4.9 Hz H(8); 3.91 (dd, 1H) $J_{7,8}$ = 10.2 Hz, $J_{7,6}$ = 5.5 Hz H(7); 4.05 (q, 1H) $J_{1',CH3}$ = 6.5 Hz H(1'); 4.25 (m, 1H) $w_{1/2} \approx$ 25 Hz H(4); 4.31 (d, 1H) J_{gem} = 11.9 Hz benzyl. H; 4.41 (d, 1H) J_{gem} = 11.3 Hz benzyl. H; 4.57 (d, 1H) J_{gem} = 11.9 Hz benzyl. H; 4.58 (d, 1H) J_{gem} = 11.3 Hz benzyl. H; 5.92 (d, 1H) $J_{3,4}$ = 1.6 Hz H(3); 7.20 - 7.40 (m, 10H) aromat. H; **^{13}C NMR** ($CDCl_3$, δ): 143.5 C2; 138.8, 138.4 aromat. C; 128.5, 128.5, 127.9, 127.9, 127.8, 127.6, 127.5 aromat. C, C3; 71.9 benzyl. C; 71.3 benzyl. C; 81.3, ca. 77, 68, 68.4, 68.3 C7, C8, C10, C1', C4; 38.7, 36.5, 33.5 C1, C6, C9; 28.7 C5; 23.1 C2'; 11.5 C(9)CH_3; **^{13}C NMR** (acetone-d_6, δ): 144.4 C2; 141.4, 141.0 aromat. C; 129.6, 129.6, 129.2, 129.1, 128.8, 128.7, 128.4 aromat. C, C3; 73.1, 72.4 benzyl. C; 82.8, 78.6, 70.2, 69.9, 68.6 C7, C8, C10, C1', C4; 40.3, 37.4, 36.0 C1, C6, C9; 29.9 C5; 24.8 C2'; 12.5 C(9)CH_3; **MS** (m/z, %): 438 (0.2%, M^+); 420 (6.4%, M^+-H_2O); 181 (15%); 91 (100%, $C_7H_7^+$).

(+)-(1*R*,1'*R*,3*S*,5*S*,7*R*,8*S*,9*R*,10*R*,11*R*)-9,11-Dibenzyloxy-3-(1'-hydroxyethyl)-10-methyl-2-oxatricyclo[5.4.0.0^{3,8}]undecan-5-ol (26a)

(+)-(1*R*,1'*S*,3*S*,5*S*,7*R*,8*S*,9*R*,10*R*,11*R*)-9,11-Dibenzyloxy-3-(1'-hydroxyethyl)-10-methyl-2-oxatricyclo[5.4.0.0^{3,8}]undecan-5-ol (26b)

To a stirred solution of 107 mg (0.244 mmol) of the diastereomeric mixture **25** in 10 ml of THF (abs.) at -15°C under argon were added 52.4 mg (0.123 mmol) of mercuric trifluoroacetate and 26.6 mg (0.123 mmol) of mercuric oxide. The mixture was stirred at -15°C for 4 h. Then 10ml of 2N aqu. NaOH and 130 mg of $NaBH_4$ were added. Stirring was continued at room temperature for another hour. The reaction mixture was saturated with potassium carbonate and extracted with ethyl acetate. The organic layers were washed with brine, dried with Na_2SO_4 and evaporated. Flash chromatography on silica gel with petroleum ether : ethyl acetate (4 : 1 to 1 : 2) yielded 4.7 mg (0.011 mmol, 4.5%) of **27a**, 8 mg (0.019 mmol, 8%) of **27b**, 46 mg (0.105 mmol, 43%) of **26a**, 17 mg (0.039 mmol, 16%) of **26b** and some starting material.

Compound **26a**: $[\alpha]_D^{20}$ = +52.0° (c = 0.78 in THF); **IR** (cm^{-1}): 3475, 3088, 3062, 3031; **^{1}H NMR**

($CDCl_3$, δ): 1.12 (d, 3H) $J_{CH3,10}$ = 6.8 Hz C(10)CH_3; 1.17 (d, 3H) $J_{CH3,1'}$ = 6.5 Hz C(1')CH_3; 1.84 (dd, 1H) $J_{4,4}$ = 15 Hz, $J_{4x,5}$ = 4.8 Hz H(4exo); 1.88 (ddd, 1H) $J_{6,6}$ = 14.8 Hz, $J_{6x,7}$ = 3.7 Hz, $J_{6x,5}$ = 4.9 Hz H(6exo); 2.04 (dddd, 1H) $J_{6,6}$ = 14.8 Hz, $J_{6n,7} \approx$ 3 Hz, $J_{6n,4x} \approx$ 2 Hz, $J_{6n,5} \approx$ 2.5 Hz H(6endo); 2.12 (ddd, 1H) $J_{4,4}$ = 15 Hz, $J_{4n,5} \approx J_{4n,6n} \approx$ 2 Hz H(4endo); 2.18 (d, 1H) $J_{8,9}$ = 3 Hz H(8); 2.40 (ddq, 1H) $J_{10,9}$ = 11.1 Hz, $J_{10,11}$ = 5.2 Hz, $J_{10,CH3}$ = 6.8 Hz H(10); 2.49 (m, 1H) $J_{7,6x}$ = 3.7 Hz, $J_{7,6n} \approx$ 3 Hz H(7); 3.25 (d, 1H, with D_2O exchangeable) $J_{OH,1'}$ = 4.6 Hz OH(1'); 3.42 (dd, 1H) $J_{9,8}$ = 3 Hz, $J_{9,10}$ = 11.1 Hz H(9); 3.51 (d, 1H, with D_2O exchangeable) $J_{OH,5}$ = 10.4 Hz OH(5); 3.57 (t, 1H) $J_{11,1}$ = 4.7 Hz, $J_{11,10}$ = 5.2 Hz H(11); 4.03 (m, 1H) $w_{1/2}$ = 20 Hz H(5); 4.32 (dq, 1H) $J_{1',OH}$ = 4.6 Hz $J_{1',CH3}$ = 6.5 Hz H(1'); 4.42 (d, 1H) $J_{1,11}$ = 4.7 Hz H(1); 4.48 (d, 1H) J_{gem} = 11.8 Hz benzyl. H; 4.52 (d, 1H) J_{gem} = 11.8 Hz benzyl. H; 4.59 (d, 1H) J_{gem} = 10.9 Hz benzyl. H; 4.64 (d, 1H) J_{gem} = 10.9 Hz benzyl. H; 7.26 - 7.38 (m, 10H) aromat. H; **^{13}C NMR** ($CDCl_3$, δ): 138.2, 137.1, 128.6, 128.2, 128.1, 128.0, 127.6, 127.5 aromat. C; 89.2 C3; 84.8 C1; 80.5, 79.7 C9, C11; 74.3, 72.8 benzyl. C; 67.5, 66.5 C1', C5; 48.3, 38.4, 36.0 C7, C8, C10; 37.5, 36.2 C4, C6; 16.4 C1'-$\underline{C}H_3$; 13.5 C10-$\underline{C}H_3$; **MS** (m/z, %): 438 (4%, M^+); 420 (16.5%, M^+-H_2O); 330 (15.2%, M^+-C_7H_7OH); 91 (100%, C_7H_7+); 81 (51%); 43 (33%, CH_3CO^+); HR-MS: Calcd for $C_{27}H_{34}O_5$: 438.2406. Found: 438.2379.

Compound **26b**: $[\alpha]_D^{20}$ = +47.9° (c = 0.32 in THF); **IR** (cm^{-1}): 3442, 3088, 3062, 3030; **^{1}H NMR** ($CDCl_3$, δ): 1.05 (d, 3H) $J_{CH3,1'}$ = 6.3 Hz C(1')CH_3; 1.07 (d, 3H) $J_{CH3,10}$ = 6.8 Hz C(10)CH_3; 1.63 (dd, 1H) $J_{4,4}$ = 14.8 Hz, $J_{4x,5}$ = 4.7 Hz H(4exo); 1.89 (ddd, 1H) $J_{6,6}$ = 14.8 Hz, $J_{6x,7}$ = 3.5 Hz, $J_{6x,5}$ = 4.6 Hz H(6exo); 2.08 (m, 1H) $J_{6,6}$ = 14.8 Hz H(6endo); 2.11 (d, 1H) $J_{8,9}$ = 3 Hz H(8); 2.11 (bR, 1H, with D_2O exchangeable) OH(1'); 2.36 (ddq, 1H) $J_{10,9}$ = 11.1 Hz, $J_{10,11}$ = 5.1 Hz, $J_{10,CH3}$ = 6.8 Hz H(10); 2.39 (m, 1H) $J_{4,4}$ = 14.8 Hz H(4endo); 2.53 (t, 1H) $J_{7,6x}$ = 3.5 Hz, $J_{7,6n} \approx$ 3 Hz H(7); 3.30 (dd, 1H) $J_{9,8}$ = 3 Hz, $J_{9,10}$ = 11.1 Hz H(9); 3.47 (bR, 1H, with D_2O exchangeable) OH(5); 3.57 (t, 1H) $J_{11,1}$ = 4.7 Hz, $J_{11,10}$ = 5.1 Hz H(11); 4.05 (m, 1H) $w_{1/2}$ = 14 Hz H(5); 4.36 (d, 1H) J_{gem} = 11.4 Hz benzyl. H; 4.45 (d, 1H) $J_{1,11}$ = 4.7 Hz H(1); 4.49 (d, 1H) J_{gem} = 11.8 Hz benzyl. H; 4.52 (d, 1H) J_{gem} = 11.8 Hz benzyl. H; 4.58 (q, 1H) $J_{1',CH3}$ = 6.3 Hz H(1'); 4.67 (d, 1H) J_{gem} = 11.4 Hz benzyl. H; 7.25-7.37 (m, 10H) aromat. H; **^{13}C NMR** ($CDCl_3$, δ): 138.5, 138.3, 128.5, 128.5, 127.9, 127.7 (3C) aromat. C; 90.4 C3; 83.8 C1; 80.2, 79.7 C9, C11; 73.1, 72.3 benzyl. C; 68.4, 66.6 C1', C5; 46.7, 39.3, 36.0 C7, C8, C10; 38.0, 36.0 C4, C6; 18.1 C1'-$\underline{C}H_3$; 13.6 C10-$\underline{C}H_3$; **MS** (m/z, %): 438 (0.8%, M^+); 420 (2.2%, M^+-H_2O); 330 (2.5%, M^+-C_7H_7OH); 91 (100%, C_7H_7+); HR-MS: Calcd for $C_{27}H_{34}O_5$: 438.2406. Found: 438.2392.

(+)-(1*R*,1'*R*,3*S*,7*R*,8*S*,9*R*,10*R*,11*R*)-9,11-Dibenzyloxy-3-(1'-hydroxyethyl)-10-methyl-2-oxatricyclo[5.4.0.0^{3,8}]undec-4-ene (27a)

(+)-(1*R*,1'*S*,3*S*,7*R*,8*S*,9*R*,10*R*,11*R*)-9,11-Dibenzyloxy-3-(1'-hydroxyethyl)-10-methyl-2-oxatricyclo[5.4.0.0^{3,8}]undec-4-ene (27b)

156 mg (0.356 mmol) of the diastereomeric mixture **25** (2:3) was dissolved in 20 ml of THF(abs.) and cooled to -15°C under an atmosphere of argon. 200 mg of mercuric trifluoroacetate (0.469 mmol) was added. After 1 h of stirring at -15°C 2 ml of deionized H_2O was added and stirring was continued for 20 min at -15°C, 20 min. at 0°C und 50 min. at room temperature. Thereafter 150 mg of $NaBH_4$ was added, and 15 min. later the reaction mixture was saturated with K_2CO_3. Extraction with ethyl acetate was followed by washing of the organic layers with brine, drying with Na_2SO_4 and removal of the solvent under vacuum. Flash chromatography on silica gel with petroleum ether : ethyl acetate (3 : 1) yielded 44.7 mg of **27a** (0.106 mmol, 30%), 50.2 mg of **27b** (0.119 mmol, 34 %) and 35.7 mg of starting material **25b** (0.081 mmol, 23%).

Compound **27a**: $[\alpha]_D^{20}$ = +27.1° (c = 0.89 in THF); **IR** (cm^{-1}): 3509, 3088, 3063, 3032; **^{1}H NMR** ($CDCl_3$, δ): 1.11 (d, 3H) $J_{CH3,10}$ = 6.8 Hz C(10)CH_3; 1.20 (d, 3H) $J_{CH3,1'}$ = 6.3 Hz C(1')CH_3; 2.18 (dt,

1H) $J_{6,6}$ = 18 Hz, $J_{6n,5} = J_{6n,4}$ = 3 Hz H(6endo) ; 2.44 (d, 1H) $J_{8,9}$ = 3 Hz H(8); 2.46 (qdd, 1H) $J_{10,CH3} \approx$ 6.5 Hz, $J_{10,9}$ = 10.9 Hz, $J_{10,11}$ = 5 Hz H(10); 2.55 (m, 1H) $J_{7,6x}$ = 6 Hz, $J_{7,8} \approx J_{7,6n} \approx J_{7,1} \approx$ 2 Hz H(7); 2.58 (dddd, 1H) $J_{6,6}$ = 18 Hz, $J_{6x,7}$ = 6 Hz, $J_{6x,5}$ = 4 Hz, $J_{6x,4}$ = 2 Hz H(6exo); 3.01 (d, 1H) $J_{OH,1'}$ = 5 Hz OH; 3.46 (dd, 1H) $J_{9,10}$ = 10.9 Hz, $J_{9,8}$ = 3.1 Hz H(9); 3.53 (t, 1H) $J_{11,1} \approx J_{11,10} \approx$ 5 Hz H(11); 4.09 (d, 1H) $J_{1,11}$ = 4.7 Hz H(1); 4.34 (quint, 1H) $J_{1',OH} \approx J_{1',CH3} \approx$ 6 Hz H(1'); 4.47 (d, 1H) J_{gem} = 11.9 Hz C(11)-benzyl. H; 4.52 (d, 1H) J_{gem} = 11.9 Hz C(11)-benzyl. H ; 4.56 (d, 1H) J_{gem} = 10.9 Hz C(9)-benzyl. H; 4.65 (d, 1H) J_{gem} = 10.9 Hz C(9)-benzyl. H; 5.75 (ddd, 1H) $J_{5,4}$ = 9.5 Hz, $J_{5,6x}$ = 4 Hz, $J_{5,6n}$ = 3 Hz H(5); 6.16 (dt, 1H) $J_{4,5}$ = 9.5 Hz, $J_{4,6x}$ = 2 Hz, $J_{4,6n}$ = 3 Hz; H(4); 7.24 - 7.36 (m, 10H) aromat. H. (The determination of the signals of the benzylic protons was reinforced by cross peaks in the NOESY spectrum (H_8-C_9-benzyl). The cross peak between $H_{1'}$ und H_4 determinated the shift-values of the two olefinic proton signals. The determination of the C_4-signal and the methyl group at 1.20 ppm was due to the cross peak between them.) **^{13}C NMR** ($CDCl_3$, δ): 138.6, 137.5 aromat. C; 133.0, 129.4 C5, C4; 128.7, 128.4, 128.2, 128.1, 127.7, 127.7 aromat. C; 84.9 C3 ; 85.1, 83.8, 80.5 C1, C11, C9; 74.0 benzyl. C; 73.0 benzyl. C; 67.1 C1'; 45.3, 37.2 C8, C7; 35.9 C10; 33.4 C6; 16.5 C(1')$\underline{C}H_3$; 13.7 C(10)$\underline{C}H_3$; **MS** (m/z, %): 420 (5.1%, M^+); 312 (8.5%, $M^+C_7H_7OH$); 91 (100%, C_7H_7+); 43 (27.4%, CH_3CO^+).

Compound **27b**: $[\alpha]_D^{20}$ = +56.3° (c = 1.00 in THF); **IR** (cm^{-1}): 3474, 3088, 3063, 3032; **^{1}H NMR** ($CDCl_3$, δ): 1.06 (d, 3H) $J_{CH3,10}$ = 6.8 Hz C(10)CH_3; 1.11 (d, 3H) $J_{CH3,1'}$ = 6.4 Hz C(1')CH_3; 2.17 (ddd, 1H) $J_{6,6}$ = 18 Hz, $J_{6n,5}$ = 3 Hz, $J_{6n,4}$ = 2 Hz H(6endo); 2.20 (s, 1H) OH; 2.35 (d, 1H) $J_{8,9}$ = 3 Hz H(8); 2.42 (qdd, 1H) $J_{10,CH3}$ = 6.3 Hz, $J_{10,9}$ = 11 Hz, $J_{10,11}$ = 5.5 Hz H(10); 2.55 (d, 1H) $J_{7,6x}$ = 5.5 Hz, $J_{7,8} \approx J_{7,6n} \approx J_{7,1} \approx$ 2 Hz H(7); 2.58 (dddd, 1H) $J_{6,6}$ = 18 Hz, $J_{6,7}$ = 5.5 Hz, $J_{6,5}$ = 3 Hz, $J_{6,4}$ = 2 Hz H(6exo); 3.35 (dd, 1H) $J_{9,10}$ = 11 Hz, $J_{9,8}$ = 3 Hz H(9); 3.52 (t, 1H) $J_{11,1} = J_{11,10}$ = 5 Hz H(11); 4.08 (d, 1H) $J_{1,11}$ = 4.7 Hz H(1); 4.39 (d, 1H) J_{gem} = 11.6 Hz C(9)-benzyl. H; 4.47 (d, 1H) J_{gem} = 11.9 Hz C(11)-benzyl. H; 4.53 (d, 1H) J_{gem} = 11.9 Hz C(11)-benzyl. H; 4.55 (q, 1H) $J_{1',CH3}$ = 6.3 Hz H(1'); 4.69 (d, 1H) J_{gem} = 11.6 Hz C(9)-benzyl. H; 5.75 (ddd, 1H) $J_{5,4}$ = 9.5 Hz, $J_{5,6x}$ = 3.5 Hz, $J_{5,6n}$ = 3 Hz H(5); 6.23 (dt, 1H) $J_{4,5}$ = 9.5 Hz, $J_{4,6x}$ = 2 Hz, $J_{4,6n}$ = 2 Hz H(4); 7.24-7.35 (m, 10H) aromat. H. (The shift values of the signals of the benzylic protons were established by cross peaks in the NOESY spectrum (H_8-C_9-benzyl). The cross peak between $H_{1'}$ und H_4 determined the shift values of the olefinic proton signal.) **^{13}C NMR** ($CDCl_3$, δ): 138.7, 138.2 aromat. C; 132.4 C5 or C4; 128.6, 128.4, 128.3, 127.7, 127.6, 127.6 aromat. C, C4 or C5; 86.0 C3; 84.1, 83.2, 80.3 C1, C11, C9; 73.0 benzyl. C; 72.0 benzyl. C; 68.1 C1'; 43.4, 37.8 C8, C7; 35.8 C10; 33.4 C6; 18.0 C(1')$\underline{C}H_3$; 13.6 C(10)$\underline{C}H_3$; **MS** (m/z, %): 420 (10.7%, M^+); 312 (19.9%, M^+-C_7H_7OH); 91 (100%, C_7H_7+); 43 (24.3%, CH_3CO^+).

(+)-(1*R*,3*S*,7*R*,8*S*,9*R*,10*R*,11*R*)-3-Acetyl-9,11-dibenzyloxy-10-methyl-2-oxatricyclo-[5.4.0.0^{3,8}]undec-4-ene (28)

44.7 mg of **27a** (0.106 mmol) and 50.2 mg of **27b** (0.119 mmol) were dissolved in 20 ml of acetone and cooled to 0°C. Within 5 min an excess of Jones reagent was added. After stirring for 15 min the reaction mixture was quenched by addition of sat. aqu. NH_4OAc and $NaHCO_3$ and then extracted with ethyl acetate. The organic layers were washed once with sat. aqu. $NaHCO_3$ and once with brine and dried with Na_2SO_4. Concentration of the filtrate and flash chromatography on silica gel with petroleum ether : ethyl acetate 4 : 1 gave 74.7 mg of **28** (0.178 mmol, 79%).

$[\alpha]_D^{20}$ = +79.9° (c = 1.49 in THF); **IR** (cm^{-1}): 3088, 3064, 3032, 2930, 2875, 1725, 1709; **^{1}H NMR** ($CDCl_3$, δ): 1.02 (d, 3H) $J_{CH3,10}$ = 6.8 Hz C(10)CH_3; 2.20 (s, 3H) CH_3CO; 2.22 (m, 1H) H(6endo); 2.28 (qdd, 1H) $J_{10,CH3}$ = 6.8 Hz, $J_{10,9}$ = 10.4 Hz, $J_{10,11} \approx$ 5 Hz H(10); 2.60 (d, 1H) $J_{7,6x}$ = 5.5 Hz H(7); 2.62 (dddd, 1H) $J_{6,6}$ = 18 Hz, $J_{6,7}$ = 5.5 Hz, $J_{6,5}$ = 3 Hz, $J_{6,4}$ = 2 Hz H(6exo); 2.84 (d, 1H) $J_{8,9}$ = 3.3 Hz H(8); 3.31 (dd, 1H) $J_{9,10}$ = 10.4 Hz, $J_{9,8}$ = 3.3 Hz H(9); 3.65 (t, 1H) $J_{11,1} \approx J_{11,10} \approx$ 5 Hz H(11); 4.18 (d,

1H) $J_{1,11}$ = 4.8 Hz H(1); 4.29 (d, 1H) J_{gem} = 11.6 Hz benzyl. H; 4.46 (d, 1H) J_{gem} = 11.9 Hz benzyl. H; 4.53 (d, 1H) J_{gem} = 11.9 Hz benzyl. H; 4.62 (d, 1H) J_{gem} = 11.6 Hz benzyl. H; 5.78 (ddd, 1H) $J_{5,4}$ = 9.2 Hz, $J_{5,6x}$ = 3.5 Hz, $J_{5,6n}$ = 2 Hz H(5); 5.93 (dd, 1H) $J_{4,5}$ = 9.2 Hz, $J_{4,6x}$ = 2 Hz H(4); 7.22 - 7.34 (m, 10H) aromat. H; **^{13}C NMR** ($CDCl_3$, δ): 208.5 $CH_3\underline{C}O$; 138.6, 138.1 aromat. C; 133.4 C5 or C4; 129.2, 128.4, 128.3, 127.8, 127.7, 127.7, 127.5 aromat. C, C4 or C5; 87.6 C3; 84.4, 82.5, 80.0 C1, C11, C9; 73.1 benzyl. C; 70.9 benzyl. C; 47.1 C8; 36.9, 35.2 C7, C10; 33.0 C6; 27.5 $\underline{C}H_3CO$; 13.6 C(10)$\underline{C}H_3$; **MS** (m/z, %): 312 (18%, M^+-C_7H_6O); 91 (100%, C_7H_7+); 43 (37%, CH_3CO^+); Anal. Calcd for $C_{27}H_{30}O_4$: C, 77.48; H, 7.22. Found: C, 77.21; H, 7.32.

(±)-(1*R,3*R**,4*R**,5*S**,6*R**,7*R**,8*R**,9*R**)-3-Acetyl-5,7-dibenzyloxy-1-(*t*-butyldimethylsilyloxy)-6-methyl-11-oxatricyclo[6.2.1.0^{4,9}]undecane (29)**

To a solution of 1.35 g of **17** (3.09 mmol) in 100 ml methylene chloride under an atmosphere of argon at -50°C were added 2.16 ml of triethylamine (15.5 mmol) and 0.85 ml of TBDMS triflate (3.7 mmol). This reaction mixture was stirred for 20 min and then quenched with sat. aqu. $NaHCO_3$, diluted with 50ml of water and extracted with ether. The organic layers were treated with brine and dried with Na_2SO_4. Flash chromatography on silica gel with petroleum ether : ethyl acetate 10:1 yielded 1.62 g of **29** (2.94 mmol, 95%).

IR (cm^{-1}): 3089, 3064, 3031, 1713; **^{1}H NMR** ($CDCl_3$, δ): 0.08 (s, 3H) $SiCH_3$; 0.09 (s, 3H) $SiCH_3$; 0.85 (s, 9H) $C(CH_3)_3$; 1.08 (d, 3H) $J_{6,CH3}$ = 6.7 Hz C(6)CH_3; 1.56 (dd, 1H) $J_{2x,3}$ = 9 Hz, $J_{2,2}$ = 12.8 Hz H(2exo); 1.78 (d, 1H) $J_{10,10}$ = 11.4 Hz H(10exo); 1.86 (ddd, 1H) $J_{10,10}$ = 11.4 Hz, $J_{10n,9}$ ≈ 4 Hz, $J_{10n,2n}$ ≈ 3 Hz H(10endo); 1.98 (s, 3H) CH_3CO; 2.08 (m, 1H) $J_{6,CH3}$ = 6.7 Hz, $J_{6,7}$ = 3 Hz, $J_{6,5}$ = 11 Hz H(6); 2.18 (dt, 1H) $J_{2n,10n}$ = 2 Hz, $J_{2n,3}$ ≈ $J_{2,2}$ ≈ 11 Hz H(2endo); 2.47 (m, 1H) $w_{1/2}$ = 14 Hz H(9); 3.01 (q, 1H) $J_{4,5}$ ≈ $J_{4,9}$ ≈ $J_{4,3}$ ≈ 5.5 Hz H(4); 3.14 (dt, 1H) $J_{3,2n}$ ≈ $J_{3,2x}$ ≈ 9.5 Hz, $J_{3,4}$ ≈ 6.5 Hz H(3); 3.41 (dd, 1H) $J_{5,4}$ = 4.5 Hz, $J_{5,6}$ = 11 Hz H(5); 3.60 (t, 1H) $J_{7,8}$ ≈ $J_{7,6}$ ≈ 3 Hz H(7); 4.03 (t, 1H) $J_{8,7}$ ≈ $J_{8,9}$ ≈ 2.5 Hz H(8); 4.18 (d, 1H) J_{gem} = 11.8 Hz benzyl. H; 4.36 (d, 1H) J_{gem} = 11.8 Hz benzyl. H; 4.48 (d, 1H) J_{gem} = 11.7 Hz benzyl. H; 4.54 (d, 1H) J_{gem} = 11.7 Hz benzyl. H; 7.18 - 7.33 (m, 10H) aromat. H; **^{13}C NMR** ($CDCl_3$, δ): 210.9 $CH_3\underline{C}O$; 138.6, 138.6 aromat. C; 128.3, 128.1, 128.1, 127.1, 127.6, 127.4 aromat. C; 106.9 C1; 79.8, 79.7, 77.9 C5, C7, C8, 73.7 benzyl. C; 71.5 benzyl. C; 42.5, 42.0 C2, C10; 44.8, 39.0, 34.5 C3, C4, C9; 32.2 C6; 29.2 $\underline{C}H_3CO$; 25.8 $C(\underline{C}H_3)_3$;17.8 $Si\underline{C}(CH_3)_3$; 13.4 C(6)CH_3; -2.8, -2.9 $Si(\underline{C}H_3)_2$; **MS** (m/z, %): 550 (0.5%, M^+); 91 (100%, C_7H_7+); 75 (10%, $(CH_3)_2SiOH^+$); Anal. Calcd for $C_{33}H_{46}O_5Si$: C, 71.96; H, 8.42. Found: C, 71.92; H, 8.48.

(±)-(1*R,3*R**,4*R**,5*S**,6*R**,7*R**,8*R**,9*R**)-3-Acetyl-1-(*t*-butyldimethylsilyloxy)-6-methyl-11-oxatricyclo[6.2.1.0^{4,9}]undecane-5,7-diol (30)**

A suspension of 100 mg of 10% palladium on activated carbon (wet, Degussa type E101 NE/W) in 50 ml of diisopropyl ether was stirred under an atmosphere of hydrogen for half an hour. 490 mg (0.89 mmol) of **29** dissolved in a few ml of diisopropyl ether was added, and stirring under hydrogen was continued for 16 h. The reaction mixture was filtered through Celite and the volatiles were removed under vacuum, which afforded crude diol **30** in quantitative yield.

IR (cm^{-1}): 3453, 1704; **^{1}H NMR** ($CDCl_3$, δ): 0.12 (s, 3H) $SiCH_3$; 0.14 (s, 3H) $SiCH_3$; 0.87 (s, 9H) $C(CH_3)_3$; 1.11 (d, 3H) $J_{CH3,6}$ = 6.8 Hz C(6)CH_3; 1.64 (bR, 1H, exchangeable with D_2O) OH; 1.68 (dd, 1H) $J_{2,2}$ = 12.8 Hz, $J_{2x,3}$ = 9.6 Hz H(2exo); 1.70 (bR, 1H, exchangeable with D_2O) OH; 1.74 (d, 1H) $J_{10,10}$ = 11.5 Hz H(10exo); 1.91 (ddd, 1H) $J_{10,10}$ = 11.5 Hz, $J_{10n,9}$ = 4 Hz, $J_{10n,2n}$ ≈ 2.5 Hz H(10endo); 1.98 (ddq, 1H) $J_{6,CH3}$ = 6.8 Hz, $J_{6,7}$ ≈ 3.5 Hz, $J_{6,5}$ = 11 Hz H(6); 2.18 (s, 3H) CH_3CO; 2.29 (ddd, 1H) $J_{2n,3}$ ≈ 10.6 Hz, $J_{2,2}$ = 12.8 Hz, $J_{2n,10n}$ ≈ 2.5 Hz H(2endo); 2.53 (m, 1H) $w_{1/2}$ = 13 Hz H(9); 2.74 (ddd, 1H) $J_{4,3}$ = 7 Hz, $J_{4,5}$ = 5.6 Hz, $J_{4,9}$ ≈ 4.5 Hz H(4); 3.10 (dt, 1H) $J_{3,2x}$ = 9.6 Hz, $J_{3,2n}$ ≈ 10.6 Hz, $J_{3,4}$ = 7

Hz H(3); 3.75 (dd, 1H) $J_{5,6}$ = 11 Hz, $J_{5,4}$ = 4.6 Hz H(5); 3.93 (m, 1H) $w_{1/2}$ = 8 Hz H(7); 4.01 (t, 1H) $J_{8,9} \approx J_{8,7} \approx$ 2.5 Hz H(8); **^{13}C NMR** ($CDCl_3$, δ): 212.4 $CH_3\underline{C}O$; 106.6 C1; 81.0 C8; 71.8, 71.3 C5, C7; 42.3, 41.7 C2, C10; 44.9, 38.4, 37.8 C3, C4, C9; 31.9 C6; 28.6 $\underline{C}H_3CO$; 25.8 $C(\underline{C}H_3)_3$; 17.7 $Si\underline{C}(CH_3)_3$; 12.8 C(6)CH_3; -2.8, -2.9 $Si(\underline{C}H_3)_2$; **MS** (m/z, %): 370 (7.5%, M^+); 327 (28.4%, M^+-CH_3CO); 313 (100%, M^+-*t*Bu); 295 (41.4%, M^+-*t*Bu-H_2O); 277 (14.5%); 75 (70.7%, $(CH_3)_2SiOH^+$); 73 (70%, $(CH_3)(CH_2)SiO^+$); 43 (30.8%, CH_3CO^+).

(±)-(1*R,3*R**,4*R**,5*S**,6*R**,7*R**,8*R**,9*R**)-3-Acetyl-1-(*t*-butyldimethylsilyloxy)-5,7-bis-(methoxymethyloxy)-6-methyl-11-oxatricyclo[6.2.1.0^{4,9}]undecane (31)**

To a solution of 31.2 mg (0.084 mmol) of **30** in 2ml of methylene chloride 73 µl (0.42 mmol) of diisopropylethylamine and 19 µl (0.252 mmol) of methoxymethyl chloride were added at room temperature. The mixture was stirred overnight, the volatile compounds were evaporated, and purification by flash chromatography on silica gel with petroleum ether / ethyl acetate 5 : 1 as eluent delivered 30 mg (0.072 mmol, 86%) of **31** as colourless oil.

IR (cm^{-1}): 1715; **^{1}H NMR** ($CDCl_3$, δ): 0.09 (s, 3H) $SiCH_3$; 0.06 (s, 3H) $SiCH_3$; 0.83 (s, 9H) $C(CH_3)_3$; 1.06 (d, 3H) $J_{CH3,6}$ = 6.7 Hz C(6)-CH_3; 1.54 (dd, 1H) $J_{2,2}$ = 12.8 Hz, $J_{2x,3}$ = 9.4 Hz H(2exo); 1.73 (d, 1H) $J_{10,10}$ = 11.5 Hz H(10exo); 1.87 (ddd, 1H) $J_{10,10}$ = 11.5 Hz, $J_{10n,9}$ = 4.1 Hz, $J_{10n,2n} \approx$ 2.8 Hz H(10endo); 2.09 (ddq, 1H) $J_{6,5}$ = 11.1 Hz, $J_{6,CH3}$ = 6.7 Hz, $J_{6,7} \approx$ 3.5 Hz H(6); 2.11 (s, 3H) $COCH_3$; 2.21 (ddd, 1H) $J_{2n,3}$ = 10.6 Hz, $J_{2,2}$ = 12.8 Hz, $J_{2n,10n} \approx$ 2.8 Hz H(2endo); 2.44 (m, 1H) $w_{1/2}$ = 13 Hz H(9); 2.85 (ddd, 1H) $J_{4,3}$ = 6.9 Hz, $J_{4,5}$ = 4.4 Hz, $J_{4,9} \approx$ 4.5 Hz H(4); 3.13 (dt, 1H) $J_{3,2x}$ = 9.4 Hz, $J_{3,2n}$ = 10.6 Hz, $J_{3,4}$ = 6.9 Hz H(3); 3.29 (s, 3H) OCH_3; 3.34 (s, 3H) OCH_3; 3.59 (dd, 1H) $J_{5,6}$ = 11.1 Hz, $J_{5,4}$ = 4.4 Hz H(5); 3.74 (t, 1H) $J_{7,8} \approx J_{7,6} \approx$ 3.5 Hz H(7); 3.98 (t, 1H) $J_{8,9} \approx J_{8,7} \approx$ 2.5 Hz H(8); 4.23 (d, 1H) J_{gem} = 7 Hz OCH_2O; 4.52 (d, 1H) J_{gem} = 7 Hz OCH_2O; 4.54 (d, 1H) J_{gem} = 6.9 Hz OCH_2O; 4.63 (d, 1H) J_{gem} = 6.9 Hz OCH_2O; **^{13}C NMR** ($CDCl_3$, δ): 210.9 $CH_3\underline{C}O$; 106.7 C1; 97.2, 94.4 OCH_2O; 78.7, 78.5, 76.1 C5, C7, C8; 55.9, 55.9 OCH_3; 42.4, 41.9 C2, C10; 44.7, 38.8, 34.4 C3, C4, C9; 31.3 C6; 29.1 $\underline{C}H_3CO$; 25.8 $C(\underline{C}H_3)_3$; 17.7 $Si\underline{C}(CH_3)_3$; 13.6 C(6)CH_3; -2.8, -3.0 $Si(\underline{C}H_3)_2$; **MS** (m/z, %): 458 (3.7%, M^+); 415 (27.9%, M^+-CH_3CO); 401 (24.1%, M^+-*t*-butyl); 397 (22.3%, M^+-OCH_2OCH_3); 339 (67.2%, M^+-OCH_2OCH_3-*t*-butyl); 327 (42.8%, M^+-*t*-bu$(CH_3)_2SiO$); 75 (61.9%, $(CH_3)_2SiOH^+$); 73 (84%, $(CH_3)(CH_2)SiO^+$); 45 (100%, CH_3 OCH_2+); 43 (48.2%, CH_3CO^+); Anal. Calcd for $C_{23}H_{42}O_7Si$: C, 60.23; H, 9.23. Found: C, 60.43; H, 8.95.

(±)-(1*R,5*R**,6*R**,7*S**,8*R**,9*R**,10*R**)-5-Acetyl-10-hydroxy-7,9-bis-(methoxymethyloxy)-8-methylbicyclo[4.4.0]decan-3-one (32)**

To a solution of 30 mg of **31** (0.072 mmol) in 3 ml of THF was added 34.2 mg of tetrabutylammonium fluoride trihydrate at room temperature. After stirring for 2 h 2 ml of sat. aqu. NH_4Cl was added, and the mixture was extracted with ethyl acetate. The organic layers were washed with brine and dried ($MgSO_4$). For purification 0.5 g of silica gel was added and the solvent was removed under reduced pressure. Elution of the adsorbed material through a short silica gel column (petroleum ether / acetone 2:1) afforded 24.7 mg (0.071 mmol, 99%) of **32** as a colourless solid.

m.p. 201-202°C; **IR** (cm^{-1}): 3404, 1708; **^{1}H NMR** (DMSO-d_6, δ): 1.04 (d, 3H) $J_{CH3,8}$ = 6.8 Hz C(8)-CH_3; 2.12 (s, 3H) $COC\underline{H}_3$; 2.08 - 2.16 (m, 2H) H(2,4); 2.25 (ddd, 1H) $J_{4,4}$ = 15 Hz, $J_{4,5}$ = 5.3 Hz, $J_{4,2} \approx$ 2 Hz H(4); 2.28 (ddq, 1H) $J_{8,CH3}$ = 6.8 Hz, $J_{8,9}$ = 2.6 Hz, $J_{8,7} \approx$ 11 Hz H(8); 2.37 (m, 1H) $w_{1/2}$ = 15 Hz H(1); 2.53 (dd, 1H) $J_{2,2}$ = 15.2 Hz, $J_{2,1}$ = 7 Hz H(2); 2.65 (dt, 1H) $J_{6,5}$ = 11.1 Hz, $J_{6,1} = J_{6,7}$ = 4.8 Hz H(6); 3.28 (s, 3H) OCH_3; 3.30 (s, 3H) OCH_3; 3.52 (t, 1H) $J_{9,8}$ = 2.6 Hz, $J_{9,10}$ = 3.6 Hz H(9); 3.58 - 3.69 (m, 3H) H(5,7,10); 4.20 (d, 1H) J_{gem} = 6.7 Hz OCH_2O; 4.41 (d, 1H) J_{gem} = 6.7 Hz OCH_2O; 4.56 (d, 1H) J_{gem} = 6.6 Hz OCH_2O; 4.64 (d, 1H) J_{gem} = 6.6 Hz OCH_2O; 4.93 (d, 1H, exchangeable with

D_2O) $J_{OH,10}$ = 4.7 Hz OH(10); **^{13}C NMR** ($CDCl_3$, δ): 209.6, 207.3 $CH_3\underline{C}O$, C3; 96.1, 94.3 OCH_2O; 81.3, 77.1 C7, C9; 70.4 C10; 55.0, 54.7 OCH_3; 46.5 C5; 42.6, 41.6 C2, C4; 38.8, 36.1 C1, C6; 30.1, 29.9 C8, $\underline{C}H_3CO$; 13.3 C(8)CH_3; **MS** (m/z, %): 344 (1%, M^+); 45 (100%, $CH_3OCH_2^+$); 43 (20.8%, CH_3CO^+); Anal. Calcd for $C_{17}H_{28}O_7$: C, 59.29; H, 8.19. Found: C, 59.42; H, 8.48.

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Crystal Structure of **4**: $C_{25}H_{32}Cl_4O_5$, Monoclinic, $\mathbf{P2_1}$, Z = 4, a = 13.570(10)Å, b = 13.255(8)Å, c = 14.893(8)Å, β = 89.57(4)°, R = 0.046 for 614 parameters and 3554 reflections determined at 297K, MoK$_\alpha$- radiation, Absolute structure: η = 3.2(3).
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