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Synthesis of *C*-Glycosides from Glycals or Vinylogous Lactones and Trimethylsilyl ketene acetals

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Abstract: 2,3-Unsaturated *C*-glycosides were obtained in good to excellent yields from the trimethylsilyltriflate catalyzed reaction between carbohydrate derived cyclic enolethers („glycals") and trimethylsilyl ketene acetals; under similar conditions vinylogous lactones afforded the products of an 1,4-addition reaction. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

C-Glycosides possessing a double bond between C(2) and C(3) atoms represent a very important class of compounds both in their own right [2] as well as valuable starting materials for the synthesis of certain antibiotics.[3-6] Functionalized derivatives have been accessed by the reaction of 1,5-anhydro-hex- (or pent-)-1-enitols (pyranoid glycals) or 1,4-anhydro-hex-(or pent)-1-enitols (furanoid glycals) by Lewis acid catalyzed reaction of these glycals with allylsilanes, [4, 7] olefins, [8] trimethylsilylcyanide,[9] bis(trimethylsilyl)acetylene[10] or enol ethers [5] to afford in fair yields the corresponding 2,3-unsaturated *C*-glycosides.

RESULTS AND DISCUSSION

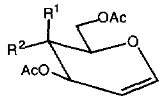
Recently the trimethylsilyltriflate (TMSOTf) catalyzed reaction between glycals and *tert*.-butoxycarbonylmethyl zinc bromide – a *Reformatsky* reagent – has been reported;[11] these reactions gave the *C*-glycosides as mixtures of the corresponding anomers in moderate (16-50%) yields.

As previously shown α-trimethylsilyl substituted esters as well as trimethylsilyl ketene acetals can be regarded as synthetic equivalents of *Reformatsky* reagents [12-14] allowing carbon chain elongation or branching reactions under very mild conditions. Therefore it seemed of interest to probe these valuable reagents with respect to both their reactivity and selectivity towards glycals and vinylogous lactones.

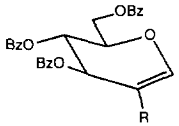
Thus, 3,4,6-tri-*O*-acetyl-D-glucal (**1**) afforded upon reaction with 1-methoxy-2-methyl-1-(trimethylsilyloxy)-propene (**2**) in the presence of TMSOTf the two products **3** and **4** (combined yield 68%) in the ratio 4:1; similarly the ketene acetal **5** gave under the same conditions exclusively **6** albeit in a rather low yield of 25%.

Reaction of the 3,4,6-tri-*O*-benzoyl-D-glucal (**7**) [15] with **2** gave 98% of **8**/**9** in the ratio 1.6:1 and from 3,4-di-*O*-acetyl-6-deoxy-L-glucal (**10**) a 1:1.1 mixture of **11** and **12** was obtained (combined yield 91%). The 3,4,6-tri-*O*-acetyl-D-galactal (**13**), however, gave under the same conditions only 64% of **14** and **15** (ratio 4.3:1) whereas the 2,3,4,6-tetra-*O*-benzoyl-1,5-anhydro-D-arabino-hex-1-enitol (**16**) gave no reaction at all;

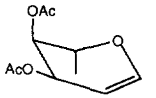
this parallels the behavior of 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-arabino-hex-1-enitol which gave no reaction with the *Reformatsky* reagent either.[11] An inseparable 1:1 mixture of anomers was also obtained for the reaction of the furanoid glycal **17** with **2** in the presence of TMSOTf and **18** was obtained in a total yield of 61%. As compared to the TMSOTf catalyzed reaction of the *Reformatsky* reagents with the glycals, usually from the trimethylsilyl ketene acetals increased yields of the products were obtained. In these reactions preferentially the β-configurated anomers were formed while for the reaction of the Reformatsky reagents with the glycals the preferred formation of the α-anomers has been reported.[11] Whereas for the reaction of the *Reformatsky* reagents it was shown [11] that no reactions occurred in ethereal solvents [16] even upon addition of $TiCl_4$ from the reaction of **1** with **2** at 0°C in the presence of TMSOTf in tetrahydrofuran 37% of **3** and 28% of **4** were isolated after chromatography. Interestingly enough, when this reaction was performed in dichloromethane a β:α selectivity of 4:1 was observed while in THF this selectivity dropped to β:α=1.3:1.[17]



1 $R^1 = H, R^2 = OAc$
13 $R^1 = OAc, R^2 = H$



7 R = H
16 R = OBz



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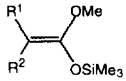
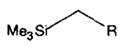
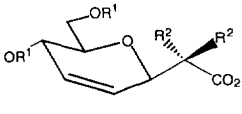


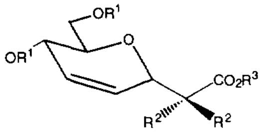
2 $R^1 = R^2 = Me$
5 $R^1 = R^2 = Et$
19 R^1 = t.-Bu, $R^2 = H$



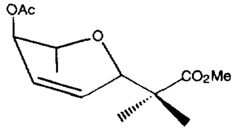
22 R = CO_2Et
26 R = CN



3 $R^1 = Ac, R^2 = R^3 = Me$
6 $R^1 = Ac, R^2 = Et, R^3 = Me$
8 $R^1 = Bz, R^2 = R^3 = Me$
23 $R^1 = Ac, R^2 = H, R^3 = Et$



4 $R^1 = Ac, R^2 = R^3 = Me$
9 $R^1 = Bz, R^2 = R^3 = Me$
24 $R^1 = Ac, R^2 = H, R^3 = Et$



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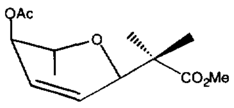

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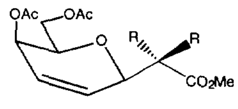
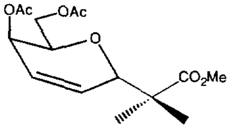


14 R = Me
25 R = H



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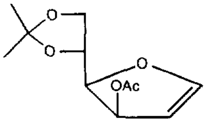

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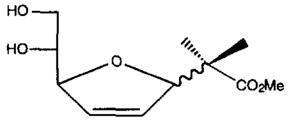

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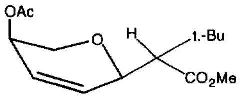
The configuration of the anomeric center was assigned on the basis of ${}^{1}H$ and ${}^{13}C$ NMR data.[18] Compound **4** possessing α-configuration at the anomeric center shows in the ${}^{13}C$ NMR spectrum for C(7) (δ = 72.47 ppm) a high field shift ($|\delta\Delta|$ = 6.5 ppm) as compared to β-configurated **3** due to a γ-gauche effect. [5, 19] The same high field shift is observed for the compounds **14/15** ($|\delta\Delta|$ = 3.4 ppm), **8/9** ($|\delta\Delta|$ = 4.9 ppm) and **11/12** ($|\delta\Delta|$ = 5.9 ppm). Usually for the β-configurated compounds δ C(7) is observed around 78 ppm whereas for the corresponding α-anomers a chemical shift δ C(7) is found in the range 72-75 ppm; therefore for **6** a β-configuration seems most likely.

As far as the ${}^{1}H$ NMR chemical shifts are concerned one would expect [5, 20, 21] that δ H-C(7)$_{\alpha\text{-anomer}}$ > δ H-C(7)$_{\beta\text{-anomer}}$; indeed $|\delta\Delta|$ = 0.4–0.5 ppm are observed.[22] To obtain an unambiguous proof for these assignments suitable crystals of **3** were grown and subjected to a single crystal X-ray analysis, the results of which are depicted in Fig. 1. As already assumed from the ${}^{1}H$ NMR data compound **3** adopts an halfchair ${}^{O}H_5$ conformation with all substituents in a pseudoequatorial orientation; the protons H-C(3) and H-C(7) are pseudoaxially oriented. [23]

A heterogeneous course of the reaction was observed using unsymmetrically substituted TMS ketene acetals in these *C*-glycosidations. Thus, D-galactal **13** afforded upon reaction with 3,3-dimethyl-1-methoxy-1-

(trimethylsilyloxy)-but-1-ene (**19**) after repeated chromatography 37% of β-configurated **20** as a 1:1 mixture of stereoisomers with respect to the newly created stereogenic center at C(2) and 33% of a mixture **21** consisting of the two other possible stereomers; these mixtures could not be separated under a variety of different chromatographic conditions.[24]



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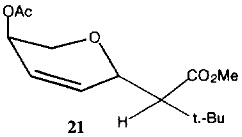

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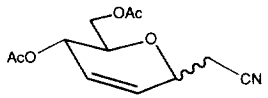
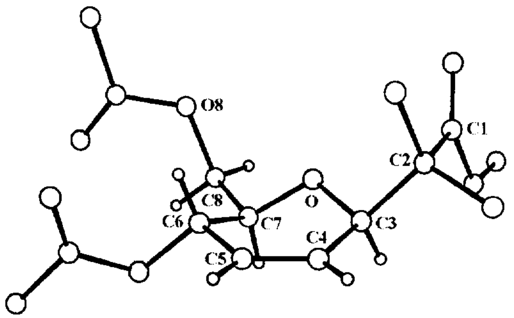


27

As previously shown, α-trimethylsilyl substituted esters can be regarded as synthetic equivalents of TMS ketene acetals.[12, 14] Following this analogy **1** was allowed to react with **22** in the presence of TMSOTf to afford the β-configurated product **23** (57%) and 24% of the α-configurated **24**, whereas for the reaction of the D-galactal derivative **13** under the same conditions the exclusive formation of β-configurated **25** was observed. Huge deterioration of **13** was found, however, for its reaction with trimethylsilyl-acetonitrile (**26**) and no products could be isolated from the complex reaction mixture. The D-glucal derivative **1** afforded under the same conditions only 20% of the elongation product **27**. This product was obtained as a 1:1 mixture (by ^{1}H NMR) of the corresponding anomers; these anomers could not be separated by chromatography.



Colorless prim (0.15 x 0.25 x 0.40 mm), monoclinic, space group $P2_1$ (#4), a = 7.101(1), b = 11.752(5), c = 9.944(5) Å, β = 97.69(2)°, V = 822.4(9) Å^3, Z =2, D_{calc} = 1.269 g.cm^{-3}, F_{000} = 336 e, $\mu_{(Mo\text{-}K_\alpha)}$ = 0.0942 mm^{-1}; radiation: Mo-K_α (λ = 0.7107 Å); 1688 unique reflections measured; structure solution: direct methods (SIR); refinement: full matrix least-squares, non-hydrogen atoms included with anisotropic discplacement parameters, hydrogen atoms refined isotropically; observed reflections included: 1371 with $I \geq 3.0\ \sigma(I)$; parameters refined: 286; R = 0.033 (weighted: R_w = 0.037); max rest electron density 0.13(4)e.Å^{-3} in final difference Fourier map.

Selected Bond Distances (in Å):

C1–C2	1.521(3)	C5–C6	1.490(4)
C2–C3	1.541(3)	C6–C7	1.516(3)
C3–C4	1.502(3)	C7–C8	1.505(4)
C3–O	1.428(3)	O–C7	1.423(3)
C4–C5	1.317(4)		

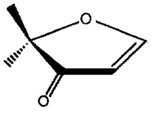
Selected Bond Angles (in °):

C2–C1–C3	107.1(2)	C4–C3–O	111.4(2)
C2–C3-O	105.8(2)	C4–C5–C6	121.6(2)
C2–C3–C4	114.3(2)	C5–C6–C7	110.5(2)
C3–C4–C5	122.0(2)	C6–C7–C8	114.0(2)
C3–O–C7	114.3(2)	C6–C7–O	107.2(2)
O–C7–C8	109.2(2)		

Fig. 1: Crystal Structure of 3, Refinement Parameters and Selected Data

An useful extension of this methodology can be expected for the reaction of vinylogous systems as represented in the 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*erythro*-hex-3-ulo-1-enitol (**28**) or the 2,2-

dimethyl-3(2H)-furanone (**29**). Thus, reaction of **29** with **2** in the presence of TMSOTf gave 58% of the desired elongation product **30** besides 7% of the dimer **31**. This dimer is formed – due to steric interactions – by a *trans* oriented attack of the educt **29** onto C(3) of the primarily formed product **30**. As previously shown, tris(dimethylaminosulfonium)difluorotrimethylsilicate (TAS-TMSF$_2$) is a suitable catalyst for the reaction of TMS ketene acetals with carbonyl compounds.[13, 14] Reaction of **29** at 0 °C with **2** in the presence of catalytic amounts of TAS-TMSF$_2$ improved the access to **30** that was then obtained in 92% yield after chromatography besides 2% of **32**.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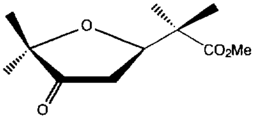

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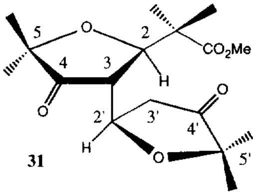

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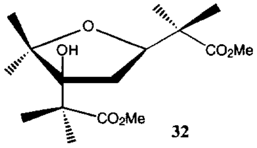

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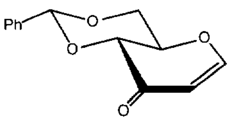
The hex-3-ulo-1-enitol **28** gave upon reaction with the TMS ketene acetal **2** in the presence of TAS-TMSF$_2$ two products [**33** (20%) and **34** (26%)] both resulting from a 1,4-addition reaction. Product **34** is characterized in its ^{1}H NMR spectrum by $^3J_{3,4a}$ = 11.5 Hz and $^3J_{6,7}$ = 9.7 Hz both coupling constants typical for *trans* diaxially oriented protons. A coupling $^4J_{4a,6}$ = 1.4 Hz is indicative for the presence of a $^6C_3$ conformation of the pyranose ring.[25]

An attack of the ketene acetal onto the *re*-face of the vinylogous system in **28** results in the intermediate formation of **35** that is subject to an enolization/reprotonation sequence leading finally to an inversion of the configuration at C(6) that is adjacent to the carbonyl group.[26] Thus, for **33** an axial/equatorial orientation of the protons H-C(6)/H-C(7) is expected [25] resulting in a $^3J_{6,7}$ = 7.8 Hz. During this reaction partial cleavage of the benzylidene acetal is observed resulting in the formation of methyl 2,2-dimethyl-3-phenyl-3-trimethylsilyloxy propionate (**36**) in 48% yield.



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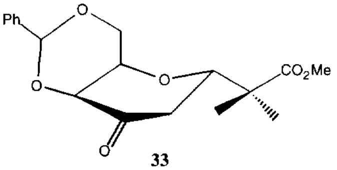

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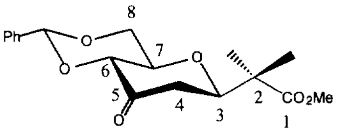

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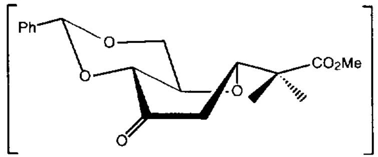

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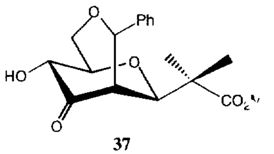

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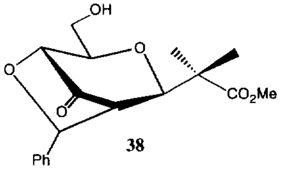

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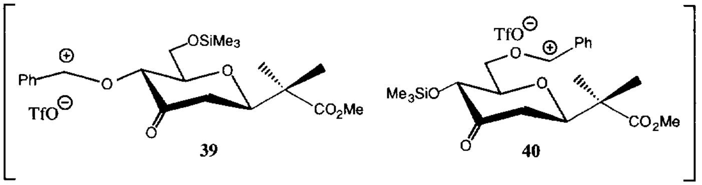

39 **40**

Interestingly enough, none of these products is found for the TMSOTf catalyzed reaction of **28** with **2**. Beside 16% of unchanged starting material **28** two products **37** (26%) and **38** (4%) could be isolated from the reaction mixture after repeated chromatography. IR, ^{1}H NMR and ^{13}C NMR spectroscopic investigation of **37** and **38** showed both the presence of a ketonic carbonyl group, the incorporation of the carbon skeleton of the ketene acetal with the proton of the benzylidene acetal missing but with its phenyl substituent still present in both molecules. The carbon C(4) show in the ^{13}C NMR spectra $\delta \approx 52$ ppm and these centers were shown to be a tertiary carbon atoms. The benzylic methine carbons are significantly shifted towards higher fields ($|\delta\Delta|$ = 16.9 and 23.9 ppm, respectively). The formation of **37**/**38** can be reasonably explained by a reaction sequence involving in a first step the formation of the desired chain elongation product **34** whose benzylidene acetal is unselectively cleaved by TMSOTf to form the carbenium ions **39**/**40** that undergo subsequently a ring closure reaction.

EXPERIMENTAL

Melting points are uncorrected (*Reichert* hot stage microscope), optical rotations were obtained using a Perkin-Elmer 243B polarimeter (1 cm micro-cell), NMR spectra (internal Me_4Si) were recorded using either a Bruker AM250 or a Varian XL300 instrument (δ given in ppm, *J* in Hz, internal Me_4Si), IR spectra (film or KBr pellet) on a Perkin-Elmer 298 instrument, MS spectra were taken either on a MAT311A or a Varian-112S instrument; for elemental analysis a Foss-Heraeus Vario EL instrument was used. TLC was performed on silica gel (Merck 5554, detection by dipping in a solution containing 10% sulfuric acid (400 *ml*), ammonium molybdate (20 g) and cerium$^{(IV)}$ sulfate (20 mg) followed by heating to 150 °C). The tetrahydrofuran was freshly distilled from sodium/benzophenone, the dichloromethane distilled from P_4O_{10} and K_2CO_3 prior to use; all reactions were performed under dry argon.

***Methyl 6,8-di-O-acetyl-3,7-anhydro-2,4,5-trideoxy-2,2-dimethyl-β-D-erythro-oct-4-enonate (3) and methyl-6,8-di-O-acetyl-3,7-anhydro-2,4,5-trideoxy-2,2-dimethyl-α-D-erythro-oct-4-enonate* (4).** To a solution of **1** (0.69 g, 2.5 mmol) and **2** (0.86 g, 4.9 mmol) in dry dichloromethane (5 *ml*) at -10 °C TMSOTf (0.5 *ml*, 2.7 mmol) was added. After stirring for 2 h at 25°C the reaction mixture was diluted with ethyl acetate (25 *ml*) and washed with ice water and brine (3 *ml* each). The organic layer was dried(Na_2SO_4), the solvent was removed under reduced pressure and the residue subjected to column chromatography (silica gel, hexane/ethyl acetate 10:1); **3** (0.43 g, 55%) and **4** (0.10 g, 13%) were obtained.

Data for **3**: mp 94-96 °C; $[\alpha]_D^{25}$ +112.92° (c = 0.27, $CHCl_3$), R_F 0.41 (hexane/ethyl acetate 3:1); IR (KBr): ν 2950*w*, 2840*w*, 1725*s*, 1430*w*, 1365*w*, 1255*bs*, 1180*m*, 1130*m*, 1075*m*, 1040*m*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.13, 1,18 (each *s*, 3 H, Me), 2.07, 2.08 (each *s*, 3 H, Me), 3.69 (*s*, 3 H, OMe), 3.67-3.73 (*m*, 1 H, H-C(7)), 4.18 (AB-part of ABX, ν_A = 4.13, J = 5.6, 11.9, ν_B = 4.23, J = 2.8, 11.9, 2 H, $H_{A,B}$-C(8)), 4.41-4.42 (*m*, 1 H, H-C(3)), 5.21-5.24 (*m*, 1 H, H-C(6)), 6.0 (*bs*, 2 H, H-C(4,5)); ^{13}C NMR (63 MHz, $CDCl_3$): δ 176.41, 170.83, 170.37 (each *s*, COO), 129.13, 127.33 (each *d*, C(4 and 5)), 78.97, 74.10, 65.61 (each *d*, C(3, 6, 7)), 63.44 (*t*, C(8)), 51.93 (*q*, OMe), 46.56 (*s*, C(2)), 21.06, 20.78, 20.55, 20.30 (each *q*, Me); MS (ei, 80 eV, 50 °C): 314 (0.01), 283 (0.5), 254 (0.2), 213 (7.8), 194 (11.7), 181 (17.4), 170 (11.32, 153 (10.6), 111 (41.1), 43 (100.0); Anal. calcd. for $C_{15}H_{22}O_7$ (314.33): C, 57.32; H, 7.05; found: C, 57.10; H, 7.00.

Data for **4**: oil; $[\alpha]_D^{25}$ +98.36° (c = 0.9, $CHCl_3$); R_F 0.30 (hexane/ethyl acetate 3:1); IR (film): ν 2980*m*, 2953*m*, 1738*s*, 1732*s*, 1471*m*, 1435*m*, 1371*m*, 1233*s*, 1196*m*, 1136*s*, 1083*m*, 1049*m*, 1020*m*, 972*m*, 911*w*, 868*w*, 606*m*, 569*w*; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.19, 1.22, 2.07, 2.08 (each *s*, 3 H, Me), 3.70 (*s*, 3 H, OMe), 4.09-4.16 (*m*, 1 H, H-C(7)), 4.19 (AB-part of ABX, ν_A = 4.07, J = 5.0, 10.1, ν_B = 4.31, J = 6.2, 10.1, 2 H, $H_{A,B}$-C(8)), 4.38 (*d*, J = 2.2, 1 H, H-C(6)), 4.93 (*bq*, J = 2.7, 5.7, 1 H, H-C(3)), 5.96 (*bs*, 2 H, H-C(4, 5)); ^{13}C NMR (63 MHz, $CDCl_3$): δ 176.3, 170.69, 170.62 (each *s*, COO), 130.85, 123.68 (each *d*, C(4 and5)), 74.17, 72.47, 64.33 (each *d*, C(3, 6, 7)), 61.90 (*t*, C(8)), 51.97 (*q*, OMe), 46.64 (*s*, C(2)), 21.20, 21.04, 20.82 (each *q*, Me); MS (ei, 80 eV, 70 °C): 314 (0.01), 283 (0.4), 254 (0.1), 213 (7.6), 194 (11.2), 181 (13.5), 170

(10.3), 111 (39.4), 43 (100.0); Anal. calcd. for $C_{15}H_{22}O_7$ (314.33): C, 57.32; H, 7.05; found: C, 57.04; H, 6.93.

In THF.- To a solution of **1** (0.71 g, 2.7 mmol) and **2** (0.65 g, 3.7 mmol) in dry THF (5 *ml*) at 0 °C TMSOTf (0.5 *ml*, 2.7 mmol) was added and stirring was continued for 1 h at 20 °C. Work up as described above followed by chromatography gave **3** (0.31 g, 37%) and **4** (0.23 g, 28%).

In acetonitrile.- From **1** (0.73 g, 2.7 mmol), **2** (0.49 g, 2.4 mmol) and TMSOTf (0.5 ml, 2.7 mmol) **3** (0.15 g, 20%) and **4** (0.05 g, 6%) were obtained after chromatographic work up; unchanged starting material **1** (0.38 g, 52%) was recovered.

***Methyl 6,8-di-O-acetyl-3,7-anhydro-2,4,5-trideoxy-2,2-diethyl-β-D-erythro-oct-4-enonate* (6).** According to the preparation of **3/4** from **1** (0.39 g, 1.45 mmol), **5** (0.49 g, 2.4 mmol) and TMSOTf (0.3 *ml*, 1.6 mmol) **6** (0.12 g, 25%) was obtained as an oil; $[\alpha]_D^{25}$ = +119.1° (*c* = 0.5, $CHCl_3$); R_F 0.47 (hexane/ethyl acetate 3:1); IR (film): ν 2968*m*, 2882*w*, 1738*s*, 1435*w*, 1371*m*, 1229*s*, 1124*m*, 1048*m*; ^1H NMR (300 MHz, $CDCl_3$): δ 0.85 (*t*, *J* = 7.5, 3 H, Me), 0.86 (*t*, *J* = 7.5, 3 H, Me), 1.61-1.76 (*m*, 4 H, 2 x CH_2), 2.06 (*s*, 3 H, Me (acetyl)), 2.08 (*s*, 3 H, Me (acetyl)), 3.66-3.73 (*m*, 1 H, H-C(7), 3.69 (*s*, 3 H, OMe), 4.17 (AB-part of ABX, ν_A = 4.13, *J* = 6.0, 11.8, ν_B = 4.22, *J* = 2.7, 11.8, 2 H, $H_{A,B}$-C(8), 4.46 (*dd*, *J* = 3.0, 4.3, 1 H, H-C(3)), 5.23-5.27 (*m*, 1 H, H-C(6)), 5.74 (*dt*, *J* = 2.2, 10.5, 1 H, H-C(5)), 5.98 (*dt*, *J* = 1.7, 10.5, 1 H, H-C(4)); ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.92, 170.51, 170.11 (each *s*, COO), 130.68, 125.68 (each *d*, C(4 and 5)), 77.07, 74.51, 65.59 (each *d*, C(3, 6, 7)), 63.36 (*t*, C(8)), 53.51 (*s*, C(2)), 51.43 (*q*, OMe), 25.21, 25.06 (each *t*, CH_2), 21.03, 20.73, 9.19, 9.07 (each *q*, Me); MS (ei, 80 eV, 75 °C): 342 (0.03), 311 (0.4), 282 (0.4), 222 (17.8), 209 (24.0), 153 (13.9), 111 (39.1), 43 (100.0); Anal. calcd. for $C_{17}H_{26}O_7$ (342.39): C, 59.64; H, 7.65; found: C, 59.48; H, 7.61.

***Methyl 3,7-anhydro-6,8-di-O-benzoyl-2,4,5-trideoxy-2,2-dimethyl-β-D-erythro-oct-4-enonate* (8)** *and* ***methyl 3,7-anhydro-6,8-di-O-benzyl-2,4,5-trideoxy-2,2-dimethyl-α-D-erythro-oct-4-enonate* (9).** According to the preparation of **3/4** from **7** (0.30 g, 0.65 mmol), **2** (0.74 g, 4.3 mmol) and TMSOTf (0.1 *ml*, 0.5 mmol) **8** (0.17 g, 60%) and **9** (0.11 g, 38%) were obtained.

Data for **8**: mp 62-64 °C; $[\alpha]_D^{25}$ +139.2° (*c* = 0.6, $CHCl_3$); R_F 0.59 (hexane/ethyl acetate 3:1); IR (KBr): ν 3063*w*, 2980*w*, 2951*w*, 1722*s*, 1602*w*, 1468*w*, 1452*s*, 1316*s*, 1272*s*, 1192*m*, 1177*m*, 1132*s*, 1109*s*, 1071*s*, 1027*s*, 998*w*, 711*s*; ^1H NMR (250 MHz, $CDCl_3$): δ 1.17 (*s*, 3 H, Me), 1.21 (*s*, 3 H, Me), 3.64 (*s*, 3 H, OMe), 4.06 (*ddd*, *J* = 3.3, 5.9, 6.6, 1 H, H-C(7)), 4.50 (AB-part of ABX, ν_A = 4.41, *J* = 5.9, 11.9, ν_B = 4.59, *J* = 3.3, 11.9, 2 H, $H_{A,B}$-C(8)), 4.50-4.55 (*m*, 1 H, H-C(3)), 5.58-5.62 (*m*, 1 H, H-C(6)), 5.85-5.90 (*m*, 1 H, H-C(5)), 5.95-6.00 (*m*, 1 H, H-C(4)); 7.34-8.06 (*m*, 10 H, H-C(Ar)); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.09 (*s*, COO, C(1)), 166.01, 165.59 (each *s*, COOPh), 129.76 (*s*, C_q(Ar)), 133.07, 132.72, 129.552, 129.42, 129.09, 128.21, 128.08, 127.17 (each *d*, C(4 and 5) and C_t(Ar)), 78.97, 74.09, 66.35 (each *d*, C(3, 6, 7)), 64,08 (*t*, C(8)), 51.86 (*q*, OMe), 46.51 (*s*, C(2)), 20.45, 20.39 (*q*, Me)); MS (ei, 80 eV, 109 °C): 438 (0.2), 407 (0.2), 337 (6.2), 274 (10.1), 215 (8.8), 194 (14.9), 181 (9.7), 105 (100.0); Anal. calcd. for $C_{25}H_{26}O_7$ (438.47): C, 68.48; H, 5.98; found: C, 68.34; H, 5.90.

Data for **9**: oil; $[\alpha]_D^{25}$ +108.5° (*c* = 0.5, $CHCl_3$); R_F 0.55 (hexane/ethyl acetate 3:1); IR (film): ν 2979*w*, 2950*w*, 1725*b*s, 1694*m*, 1602*m*, 1585*w*, 1464*w*, 1451*m*, 1435*w*, 1390*w*, 1368*w*, 1315*m*, 1266*s*, 1195*m*, 1177*m*, 1108*m*, 1070*m*, 1026*m*, 1000*w*, 951*w*; ^1H NMR (300 MHz, $CDCl_3$): δ 1.26 (*s*, 3 H, Me), 1.29 (*s*, 3 H, Me), 3.60 (*s*, 3 H, OMe), 4.53 (AB-part of ABX, ν_A = 4.42, *J* = 4.8, 11.0, ν_B = 4.64, *J* = 7.7, 11.0, 2 H, $H_{A,B}$-C(8)), 4.45-4.53 (*m*, 1 H, H-C(7)), 4.55-4.57 (*m*, 1 H, H-C(3)), 5.29-5.32 (*m*, 1 H, H-C(6)), 6.06 (*dd*, *J* = 1.4, 10.6, 1 H, H-C(5)), 6.15-6.19 (*m*, 1 H, H-C(4)), 7.42-8.31 (*m*, 10 H, H-C(Ar)); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.40 (*s*, COOMe), 166.19, 166.06 (each *s*, COOPh), 155.55 (*s*, C_q(Ar)), 133.20, 133.16, 131.43, 129.79, 129.76, 129.73, 128.41, 123.48 (each *d*, C_t(Ar) and C(4 and 5)), 74.08, 72.85, 64.81 (each *d*, C(3, 6, 7)), 62.43 (*t*, C(8)), 51.94 (*q*, OMe), 46.60 (*s*, C(2)), 21.28, 20.56 (each *q*, Me); MS (ei, 80 eV, 155 °C): 407 (0.1), 337 (8.9), 274 (1.9), 215 (8.0), 194 (17.1), 181 (10.2), 105 (100.0); Anal. calcd. for $C_{25}H_{26}O_7$ (438.47): C, 68.48; H, 5.98; found: C, 68.21; H, 5.73.

***Methyl 6-O-acetyl-3,7-anhydro-2,4,5,8-tetradeoxy-2,2-dimethyl-β-L-erythro-oct-4-enonate* (11)** *and* ***methyl 6-O-acetyl-3,7-anhydro-2,4,5,8-tetradeoxy-2,2-dimethyl-α-L-erythro-oct-4-enonate* (12).** According to the preparation of **3/4** from **10** (0.50 g, 2.3 mmol), **2** (0.84 g, 4.6 mmol) and TMSOTf (0.5 *ml*, 2.7 mmol) **11** (0.25 g, 43%) and **12** (0.28 g, 48%) were obtained.

Data for **11**: oil; $[\alpha]_D^{25}$ -108.2° (c = 1.3, CHCl$_3$); R_F 0.68 (hexane/ethyl acetate 3:1); IR (film): 2980*m*, 2939*w*, 2876*w*, 1738*s*, 1732*s*, 1470*w*, 1435*w*, 1373*m*, 1314*w*, 1235*s*, 1193*m*, 1135*s*, 1109*m*, 1079*m*, 1046*m*, 1025*m*; ^{1}H NMR (300 MHz, CDCl$_3$): 1.13 (*s*, 3 H, Me), 1.17 (*s*, 3 H, Me), 1.51 (*d*, $J_{7,8}$ = 6.2, 3 H, H-C(8)); 2.08 (*s*, 3 H, Me (acetyl)), 3.55 (*dd*, $J_{7,8}$ = 6.2, $J_{6,7}$ = 8.8, 1 H, H-C(7)), 3.69 (*s*, 3 H, OMe), 4.36-4.37 (*m*, 1 H, H-C(3)), 4.99 (*dd*, $J_{6,7}$ = 8.8, $J_{5,6}$ = 2.6, 1 H, H-C(6)), 5.72-5.76 (*m*, 2 H, H-C(4 and 5)); ^{13}C NMR (75 MHz, CDCl$_3$): 176.39 (*s*, COO), 170.28 (*s*, COO), 128.83, 127.59 (each *d*, C(4 and 5)), 78.78, 72.19, 70.91 (each *d*, C(3,6,7)), 51.79 (*q*, OMe), 46.47 (*s*, C(2)), 20.46 (*q*, 2x Me), 18.36 (*q*, Me (acetyl)); MS (ei, 80 eV, 63 °C): 225 (1.5), 212 (13.8), 196 (4.0), 181 (7.2), 170 (28.2), 155 (9.6), 137 (6.2), 111 (61.0), 95 (100.0), 43 (100.0); Anal. calcd. for $C_{13}H_{20}O_5$ (256.29): C, 60.92; H, 7.87; found: C, 60.73; H, 7.82.

Data for **12**: oil; $[\alpha]_D^{25}$ -144.8° (c = 1.4, CHCl$_3$); R_F 0.58 (hexane/ethyl acetate 3:1); IR (film): ν 2981*w*, 2951*w*, 2877*w*, 1738*s*, 1732*s*, 1470*w*, 1435*w*, 1373*m*, 1314*w*, 1236*s*, 1195*w*, 1136*s*, 1109*m*, 1079*w*, 1046*w*, 1026*w*; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.19 (*s*, 3 H, Me), 1.21 (*s*, 3 H, Me), 1.24 (*d*, $J_{7,8}$ = 6.8, 3 H, H-C(8)), 2.05 (*s*, 3 H, Me (acetyl)), 3.70 (*s*, 3 H, OMe), 4.06 (*dq*, $J_{6,7}$ = 1.7, $J_{7,8}$ = 6.8, 1 H, H-C(7)), 4.34 (*d*, $J_{3,4}$ = 2.1, 1 H, H-C(3)), 4.75 (*d*, $J_{6,7}$ = 1.7, 1 H, H-C(6)), 5.94 (*m*, 2 H, H-C(4 and 5)); ^{13}C NMR (63 MHz, CDCl$_3$): δ 176.67 (*s*, COO), 170.86 (*s*, COO), 131.27, 123.12 (each *d*, C(4 and 5)), 72.84, 70.82, 68.33 (each *d*, C(3, 6, 7)), 51.92 (*q*, OMe), 46.39 (s, C(2)), 21.14, 20.79, 15.87 (each *q*, Me); MS (ei, 80 eV, 63 °C): 257(0.1), 225 (0.1), 212 (2.0), 196 (4.3), 181 (7.9), 170 (5.7), 155 (14.5), 111 (19.4), 95 (100.0), 43 (100.0); Anal. calcd. for $C_{13}H_{20}O_5$: (256.29): C, 60.92; H, 7.87; found: C, 61.06; H, 7.87.

Methyl 6,8-di-O-acetyl-3,7-anhydro-2,4,5-trideoxy-2,2-dimethyl-β-D-threo-oct-4-enonate **(14)** ***and methyl 6,8-di-O-acetyl-3,7-anhydro-2,4,5-trideoxy-2,2-dimethyl-α-D-threo-oct-4-enonate*** **(15).** According to the preparation of **3/4** from **13** (0.81 g, 3.0 mmol), **2** (0.96 g, 5.5 mmol) and TMSOTf (0.5 *ml*, 2.7 mmol) **14** (0.49 g, 52%) was obtained as an oil besides a second fraction **15** (0.11 g, 12%) consisting of threee isomers.

Data for **14**: $[\alpha]_D^{25}$ -174.9° (c = 1.3, CHCl$_3$); R_F 0.37 (hexane/ethyl acetate 3:1); IR (film): ν 2980*m*, 2960*m*, 2880*w*, 1740*s*, 1470*m*, 1440*m*, 1370*s*, 1240*bs*, 1195*s*, 1135*s*, 1095*s*, 1050*s*, 1025*m*; ^{1}H NMR (250 MHz, CDCl$_3$): δ 1.16, 1.21, 2.04, 2.05 (each *s*, 3 H, Me), 3.69 (*s*, 3 H, OMe), 3.85-3.91 (*m*, 1 H, H-C(7)), 4.17 (AB-part of ABX, ν_A = 4.13, $J_{7,8A}$ = 5.8, $J_{8A,8B}$ = 11.3, ν_B = 4.21, $J_{7,8B}$ = 7.1, $J_{8A,8B}$ = 11.3, 2 H, $H_{A,B}$-C(8)), 4.35-4.36 (*m*, 1 H, H-C(3)), 5.03 (*dt*, J = 2.1, 2.1, 5.4, 1 H, H-C(6)), 5.95 (*dd*, J = 1.3, 10.3, 1 H, H-C(4)), 6.09 (*ddd*, J = 2.1, 5.4, 10.3, 1 H, H-C(5)); ^{13}C NMR(63 MHz, CDCl$_3$): δ 176.41, 170.66 (each *s*, COO), 132.56, 124.28 (each *d*, C(4 and 5)), 78.99, 73.32, 63.87 (each *d*, C(3,6,7)), 62.89 (*t*, C(8)), 51.89 (*q*, OMe), 46.21 (*s*, C(2)), 20.88, 20.76, 20.64, 20.43 (each *q*, Me); MS (ei, 80 eV, 89 °C): 255 (0.3), 241 (2.4), 213 (9.2), 194 (21.6), 181 (32.7), 153 (30.7), 111 (64.7), 43 (100.0); Anal. calcd. for $C_{15}H_{22}O_7$ (314.33): C, 57.32, H, 7.05; found: C, 57.05, H, 7.04.

Data for the main isomer **15**: R_F 0.33 (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, CDCl$_3$): 1.20, 1.23 (each *s*, 3 H, Me), 2.07, 2.09 (each *s*, 3 H, Me), 3.70 (*s*, 3 H, OMe), 4.12-4.17 (*m*, 1 H, H-C(7)), 4.27-4.30 (*m*, 2 H H-C(8)), 4.43-4.44 (*m*, 1 H, H-C(3)), 5.23-5.24 (*m*, 1 H, H-C(6)), 5.96-6.01 (*m*, 2 H, H-C(4,5)); ^{13}C NMR (63 MHz, CDCl$_3$): 176.22 (*s*, COOMe), 170.83, 170.39 (each *s*, COO), 129.77, 124.78 (each *d*, C(4,5)), 75.59, 70.09, 64.44 (each *d*, C(3,6,7)), 61.80 (*t*, C(8)), 51.99 (*q*, OMe), 47.42 (*s*, C(2)), 21.54, 21.27 (each *q*, Me), 20.89, 20.79 (each *q*, Me); MS (ei, 80 eV, 100 °C): 315 (84.6), 255 (6.4), 241 (4.9), 213 (6.9), 194 (12.9), 181 (11.3), 153 (25.6), 111 (34.8), 43 (100.0); HRMS calcd. for $C_{15}H_{22}O_7$: 314.1365; found: 314.1365.

Methyl 3,6-anhydro-2,2-dimethyl-2,4,5-trideoxy-α,β-D-erythro-oct-4-enonate **(18).** According to the preparation of **3/4** from **17** (0.41 g, 1.7 mmol), **2** (0.70 g, 3.9 mmol) and TMSOTf (0.4 *ml*, 2.1 mmol) (start of the reaction at -40°C, then 1 h at 25°C, chromatographic work up using hexane/ethyl acetate 3:1) gave **18** (0.24 g, 61%) as an inseparable mixture of anomers (1:1 by ^{1}H NMR); oil; $[\alpha]_D^{25}$ -88.6° (c = 1.7, CHCl$_3$); R_F 0.19 (hexane/ethyl acetate 1:1); IR (film): ν 3420*bs*, 2980*m*, 2952*m*, 2878*m*, 1720*bs*, 1667*bm*, 1471*m*, 1464*m*, 1456*w*, 1435*m*, 1418*w*, 1370*bw*, 1263*m*, 1193*w*, 1139*m*, 1068*s*, 866*w*; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.12, 1.16, 1.18, 1.22 (each *s*, 3 H, Me), 2.36 (*vbs*, 2 H, OH), 3.61-3.82 (*m*, 6 H, H-C(7), and H-C(8)), 3.68 (*s*, 3 H, OMe), 3.69 (*s*, 3 H, OMe), 4.69-4.71 (*m*, 1 H, H-C(3 oder 6)), 4.82-4.88 (*m*, 2 H, H-C(3) and H-C(6)), 5.06-5.09 (*m*, 1 H, H-C(3 oder 6)), 5.86-5.91 (*m*, 2 H, H-C(4 oder 5)), 5.99 (*m*, 2 H, H-C(4 oder 5)); ^{13}C NMR (75 MHz, CDCl$_3$): δ 176.46, 176.32 (each *s*, COO), 129.22, 128.64, 128.25, 127.98 (each *d*, C(4,5)), 91.21, 91.09, 88.14, 86.98, 73.66, 73.51 (each *d*, C(3,6,7)), 63.65, 63.32 (each *t*, C(8)), 51.89 (*q*, OMe), 47.25, 46.26 (each *s*, C(2)), 22.05, 21.21, 20.67, 20.33 (*q*, Me); MS (ei, 80 eV, 98 °C): 230 (0.3), 197 (2.4), 194 (2.3), 181 (2.3), 169 (21.4), 137 (11.4), 109 (100.0), 102 (61.9), 69 (87.8); HRMS calcd. for $C_{11}H_{18}O_5$: 230.1154; found: 230.1154.

Methyl 6,8-di-O-acetyl-3,7-anhydro-2,4,5-trideoxy-2-t-butyl-β-D-threo-oct-4-enonate **(20)** and ***methyl 6,8-di-O-acetyl-3,7-anhydro-2,4,5-trideoxy-2-t-butyl-α-D-threo-oct-4-enonate*** **(21).** According to the preparation of **3/4** from **13** (0.70 g, 2.5 mmol), **19** (0.80 g, 3.9 mmol) and TMSOTf (0.5 *ml*, 2.7 mmol) **20** (0.31 g, 37%) and **21** (0.28 g, 33%) were obtained.

Data for **20**: mixture of stereomers (1:1, by ^{1}H NMR); oil; $[\alpha]_D^{25}$ -167.0° (*c* = 1.0, $CHCl_3$); R_F 0.38 (hexane/ethyl acetate 3:1); IR (film): 2957*m*, 2874*w*, 1738*s*, 1732*s*, 1435*w*, 1372*m*, 1232*s*, 1154*m*, 1099*m*, 1049*m*; ^{1}H NMR (300 MHz, $CDCl_3$): 1.07 (*s*, 9 H, H-C(*t*-bu)), 1.09 (*s*, 9 H, H-C(*t*-bu)), 2.04, 2.06, 2.07, 2.08 (each *s*, 3 H, Me). 2.49 (*d*, $J_{2,3}$ = 9.6), 1 H, H-C(2)), 2.59 (*d*, $J_{2,3}$ = 9.6, 1 H, H-C(2)), 3.66 (*s*, 3 H, OMe), 3.67 (*s*, 3 H, OMe), 3.88 (*ddd*, *J* = 2.4, 5.1, 7.4, 1 H, H-C(7)), 4.05-4.29 (*m*, 5 H, 2 x H-C(8) and 1 x H-C(7)),4.40 (*bd*, $J_{2,3}$ = 9.6, 1 H, H-C(3)), 4.70 (*ddd*, $J_{3,6}$ = 2.1, $J_{3,4}$ = 2.1, $J_{2,3}$ = 9.6, 1 H, H-C(3)), 5.03-5.09 (*m*, 2 H, H-C(6)), 5.87-6.04 (*m*, 4H, H-C(4 and 5)); ^{13}C NMR (63 MHz, $CDCl_3$): 173.25, 173.17, 170.70, 170.58, 170.43 (each *s*, COO), 134.85, 133.51, 123.20, 123.09 (each *d*, C(4 and 5)), 74.47, 74.41, 71.93, 68.05, 63.57, 63.30 (each *d*, C(3,6,7)), 62.97, 62.72 (each *t*, C(8)), 59.01, 56.21 (each *q*, OMe), 51.24, 51.13 (each *d*, C(2)), 33.30, 33.16 (each *s*, Me(*t*-bu)), 28.64, 28.34 (each *q*, C_s(*t*-bu)), 20.89, 20.72 (each *q*, Me); MS (ei, 80 eV, 90 °C): 343 (0.4), 311 (0.3), 283 (0.3), 269 (0.5), 240 (0.2), 222 (7.6), 213 (14.0), 166 (9.1), 153 (36.4), 111 (49.3), 43 (100.0); Anal. calcd. for $C_{17}H_{26}O_7$ (342.22): C, 59.67; H, 7.66; found: C, 59.72; H, 7.55.

Data for **21**: mixture of stereomers (#:*, 1:1.5); oil; $[\alpha]_D^{25}$ -137.9° (*c* = 1.0, $CHCl_3$); R_F 0.32 (hexane/ethyl acetate 3:1); IR (film): 2956*w*, 1738*s*, 1435*w*, 1371*m*, 1232*s*, 1150*w*, 1047*w*; ^{1}H NMR (300 MHz, $CDCl_3$): 1.06 (*s*, 9 H, H-C(*t*-bu), *), 1.08 (*s*, 9 H, H-C(*t*-bu), #), 2.04 (*s*, 3 H, Me, #), 2.05 (*s*, 3 H, Me, #), 2.07 (*s*, 3 H, Me, *), 2.08 (*s*, 3 H, Me, *), 2.44 (*d*, $J_{2,3}$ = 4.9, 1 H, H-C(2), #), 2.63 (*d*, $J_{2,3}$ = 9.2, 1 H, H-C(2), *), 3.64 (*s*, 3 H, OMe, #), 3.69 (*s*, 3 H, OMe, *), 3.85 (*ddd*, *J* = 2.3, 5.3, 7.3, 1 H, H-C(7), *), 4.08-4.25 (*m*, 5 H, $H_{A,B}$-C(8), * and #, H-C(7), #), 4.44 (*bdd*, $J_{3,4}$ = 2.0, $J_{2,3}$ = 4.5, 1 H, H-C(3), #), 4.68 (*dt*, *J* = 2.7, $J_{3,4}$ = 2.7, $J_{2,3}$ = 8.8, 1 H, H-C(3), *), 5.02 (*dt*, $J_{5,6}$ = 2.5, $J_{6,7}$ = 2.5, $J_{4,6}$ = 5.6, 1 H, H-C(6), #), 5.08 (*dd*, $J_{6,7}$ = 2.3, $J_{4,6}$ = 5.3, 1 H, H-C(6), *), 5.97-6.05 (*m*, 2 H, H-C(4), * u. #), 6.15 (*dd*, $J_{5,6}$ = 1.4, $J_{4,5}$ = 10.5, 1 H, H-C(5), #), 6.19 (*dd*, $J_{5,6}$ = 3.3, $J_{4,5}$= 10.5, 1 H, H-C(5), *); ^{13}C NMR (75 MHz, $CDCl_3$): 172.67 (*), 171.75 (#), 170.50 (*), 170.41 (#) (each *s*, COO), 135.30 (#), 133.37 (*), 122.56 (#), 122.55 (*) (each *d*, C(4 and 5)), 73.84 (*), 73.75 (#), 72.04 (#), 68.66 (*), 63.72 (*), 63.61 (#) (each *d*, C(3,6,7)), 62.92 (*t*, C(8), * and #), 59.56 (*q*, OMe, #), 58.84 (*q*, OMe, *), 51.27 (*t*, C(2), *), 50.80 (*t*, C(2), #), 32.58 (*s*, C_q(*t*-bu), #), 31.86 (*s*, C_q(*t*-bu), *), 28.84 (*q*, C_s(*t*-bu), #), 28.78 (*q*, C_s(*t*-bu), *), 20.88 (*q*, Me(acetyl), *), 20.77 (*q*, Me(acetyl), #); MS (ei, 80 eV, 109 °C): 343 (0.4), 311 (0.4), 283 (0.4), 269 (0.6), 241 (0.3), 213 (15.6), 153 (42.9), 111 (51.5), 43 (100.0); HRMS calcd. for $C_{17}H_{26}O_7$: 342.1680; found: 342.1680.

Ethyl 6,8-di-O-acetyl-3,7-anhydro-2,4,5-trideoxy-β-D-erythro-oct-4-enonate **(23)** *and* ***ethyl 6,8-di-O-acetyl-3,7-anhydro-2,4,5-trideoxy-α-D-erythro-oct-4-enonate*** **(24).** According to the preparation of **3/4** from **1** (0.70 g, 2.5 mmol), **22** (1.10 g, 6.8 mmol) and TMSOTf (0.5 *ml*, 2.7 mmol) **23** (0.42 g, 57%) and **24** (0.18 g, 24%) were obtained.

Data for **23**: oil; $[\alpha]_D^{25}$ +114.2° (*c* = 1.4, $CHCl_3$); R_F 0.39 (hexane/ethyl acetate 3:1); IR (film): ν 2984*w*, 1739*s*, 1733*s*, 1684*w*, 1457*w*, 1436*w*, 1373*m*, 1237*s*, 1097*w*, 1045*m*; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.27 (*t*, *J* = 7.1, 3 H, Me), 2.04 (*s*, 3 H, Me), 2.08 (*s*, 3 H, Me), 2.55 (AB-part of ABX, ν_A = 2.47, *J* = 6.7, 15.6, ν_B = 2.62, *J* = 7.1, 15.6, 2 H, $H_{A,B}$-C(2)); 3.75 (*ddd*, *J* = 3.4, 5.5, 9.1, 1 H, H-C(7)), 4.08-4.23 (*m*, 4 H, OCH_2 and $H_{A,B}$-C(8)), 4.57-4.68 (*m*, 1 H, H-C(3)); 5.26.(*ddd*, *J* = 1.7, 4.7, 9.1, 1 H, H-C(6)), 5.76 (*dt*, *J* = 2.0, 10.3, 1 H, H-C(4)), 5.90 (*dt*, *J* = 1.7, 10.3, 1 H, H-C(5)); ^{13}C NMR (63 MHz, $CDCl_3$): δ 170.93, 170.39 (each *s*, COO), 131.65, 125.85 (each *d*, C(4 and 5)), 74.46, 71.65, 65.39 (each *d*, C(3, 6, 7)), 63.57, 60.73 (each *t*, C(8)), 40.20 (*t*, C(2)), 21.04, 20.84 (each *q*, Me), 14.21 (*q*, Me); MS (ei, 80 eV, 90 °C): 301 (1.3), 240 (0.5), 227 (0.4), 213 (5.5), 198 (16.6), 180 (17.0), 167 (21.4), 156 (43.8), 43 (100.0); Anal. calcd. for $C_{14}H_{20}O_7$ (300.31): C, 55.99; H, 6.71; found: C, 55.99; H, 6.71.

Data for **24**: oil; $[\alpha]_D^{25}$ +67.0° (*c* = 1.0, $CHCl_3$); R_F 0.12 (hexane/ethyl acetate 3:1); IR (film): ν 2983*w*, 1732*s*, 1435*w*, 1372*m*, 1231*s*, 1173*w*, 1046*m*, 972*w*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (*t*, *J* = 7.1, 3 H, Me), 2.05 (*s*, 3 H, Me), 2.09 (*s*, 3 H, Me), 2.63 (AB-part of ABX, ν_A = 2.54, *J* = 5.9, 15.2, ν_B = 2.7, *J* = 8.4, 15.2, 2 H, CH_2, H-C(2)), 3.93 (*dt*, *J* = 3.4, 6.6, 1 H, H-C(7)), 4.06-4.29 (*m*, 4 H, OCH_2 and $H_{A,B}$-C(8)) ,4.72 (*ddd*, *J* = 2.3, 5.9, 8.4, 1 H, H-C(3)), 5.16 (*ddd*, *J* = 2.2, 4.3, 6.6, 1 H, H-C(6)), 5.83 (*ddd*, *J* = 2.0, 2.7, 10.2, 1 H, H-C(4)), 5.95 (*ddd*, *J* = 1.5, 2.6, 10.2, 1 H, H-C(5)); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.56, 170.10, 169.98 (each *s*, COO), 131.62, 124.48 (each *d*, C(4 and 5)), 69.79, 68.70, 64.66 (each *d*, C(3, 6, 7)), 62.62, 60.71 (each *t*, C(8)), 38.59 (*t*, C(2)), 21.01, 20.76, 14.19 (each q, Me); MS (ei, 80 eV, 94 °C): 301 (0.3), 255 (0.3), 227 (0.9), 213 (7.8), 198 (15.4), 180 (20.2), 167 (24.3), 156 (43.5), 43 (100.0); Anal. calcd. for $C_{14}H_{20}O_7$ (300.31): C, 55.99; H, 6.71; found: C, 55.78; H, 6.70.

***Ethyl 6,8-di-O-acetyl-3,7-anhydro-2,4,5-trideoxy-β-D-threo-oct-4-enonate* (25).** According to the preparation of **3/4** from **13** (1.66 g, 5.9 mmol), **22** (1.60 g, 9.9 mmol) and TMSOTf (1 *ml*, 5.9 mmol) (chromatographic work up was performed with hexane/ethyl acetate 7:1) **25** (1.05 g, 70%) was obtained as an oil; $[\alpha]_D^{25}$ -116.1° (*c* = 0.5, $CHCl_3$); R_F 0.23 (hexane/ethyl acetate 3:1); IR (film): ν 2982*w*, 1738*s*, 1372*m*, 1236*s*, 1177*w*, 1085*w*, 1048*w*, 1029*w*, 954*w*; ^1H NMR (250 MHz, $CDCl_3$): δ 1.27 (*t*, *J* = 7.1, 3 H, Me), 2.06 (*s*, 3 H, Me), 2.07 (*s*, 3 H, Me), 2.60 (AB-part of ABX, ν_A = 2.52, $J_{2A,3}$ = 2.5, $J_{2A,2B}$ = 15.6, ν_B = 2.69, $J_{2B,3}$ = 2.7, $J_{2A,2B}$ = 15.6, 2 H, $H_{A,B}$-C(2)), 3.93 (*dt*, *J* = 2.4, 6.3, 1 H, H-C(7)), 4.13-4.22 (*m*, 4 H, OCH_2 and H-C(8)), 4.57 (*bt*, *J* = 7.2, 1 H, H-C(3)), 5.06-5.09 (*m*, 1 H, H-C(6)), 6.02-6.06 (*m*, 2 H, H-C(4 and 5)); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.41, 170.28, 170.08 (each *s*, COO), 134.53, 122.65 (each *d*, C(4 and 5)), 73.73, 71.59, 63.68 (each *d*, C(3, 6, 7)), 62.84, 60.62 (each *t*, OCH_2 and C(8)), 39.73 (*t*, C(2)), 20.91, 20.76, 14.19 (each *q*, Me); MS (ei, 80 eV, 100 °C): 301 (1.3), 241 (0.5), 213 (4.3), 198 (3.3), 180 (33.3), 167 (34.6), 156 (15.6), 111 (13.2), 81 (13.5), 43 (100.0); Anal. calcd. for $C_{14}H_{20}O_7$ (300.31): C, 55.99; H, 6.71; found: C, 55;70, H, 6.72.

***4,6-Di-O-acetyl-1,5-anhydro-2,3-dideoxy-α,β-D-erythro-hex-1-enityl-acetonitrile* (27).** According to the preparation of **3/4** from **1** (0.70, 2.5 mmol), **26** (0.7 *ml*, 5 mmol) and TMSOTf (0.5 *ml*, 2.7 mmol) (chromatographic work up with hexane/ethyl acetate 3:1) **27** (0.13 g, 20%) was obtained as an oil (as an inseparable mixture of isomers, α:β = 1:1, by ^1H NMR); R_F 0.28/0.32 (hexane/ethyl acetate 3:1); IR (film): ν 2960*w*, 2253*w*, 1745*bs*, 1695*w*, 1436*w*, 1418*w*, 1373*m*, 1235*s*, 1049*m*, 975*w*; ^1H NMR (300 MHz, $CDCl_3$): δ 2.09 (*s*, 3 H, Me), 2.10 (*s*, 6H, 2x Me), 2.11 (*s*, 3 H, Me), 2.63 (*d*, *J* = 6.1, 2 H, H-C(2)), 2.69 (*dd*, *J* = 3.3, 6.5, 2 H, H-C(2)), 3.77 (*ddd*, *J* = 2.6, 5.8, 8.8, 1 H, H-C(7)), 4.01-4.07 (*m*, 1 H, H-C(7)), 4.11-4.20 (*m*, 2 H, $H_{A,B}$-C(8)), 4.29 (AB-part of ABX, ν_A = 4.26, *J* = 2.9, 9.9, ν_B = 4.31, *J* = 6.6, 9.9, 2 H, $H_{A,B}$-C(8)), 4.46-4.51 (*m*, 1 H, H-C(6)), 4.55-4.59 (*m*, 1 H, H-C(6)), 5.11-5.14 (*m*, 1 H, H-C(3)), 5.29-5.33 (*m*, 1 H, H-C(3)), 5.85-6.04 (*m*, 4H, 2 x H-C(4 and 5)); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.57, 170.49, 170.07, 169.84 (each *s*, COO), 129.37, 128.67, 128.20, 126.38 (each *d*, 2 x C(2 and 3)), 116.25, 115.94 (each *s*, CN), 74.41, 70.78, 70.18, 67.10, 64.66, 64.07 (each *d*, 2 x C(1, 4, 5)), 63.07, 62.14 (each *t*, 2 x C(6)), 24.20, 22.86 (each *t*, 2 x $\underline{C}H_2CN$), 20.98, 20.96, 20.95, 20.78 (each *q*, Me); MS (ei, 80 eV, 78 °C): 252 (0.02), 193 (0.3), 180 (1.0), 151 (8.5), 145 (5.7), 133 (3.2), 120 (6.1), 109 (15.3), 81 (9.5); HRMS calcd. for $C_{12}H_{15}NO_5$: 253.0951; found: 253.0951.

***Methyl 2-(5,5-dimethyl-4-oxo-tetrahydrofuran-2-yl)-2-methylpropionate* (30) *and methyl-2-[3-hydroxy-5-(1-methoxycarbonyl-1-methyl-ethyl)-tetrahydrofuran-3-yl]-2-methyl-propionate* (32).** To a THF (5 *ml*) solution of **29** (0.22g, 1.96 mmol) and **2** (0.7 g, 4.0 mmol) at 0 °C catalytic amounts of tris(dimethylaminosulfonium)difluorotrimethylsilicate were added and then the mixture was stirred for 2h at 20 °C; usual work up and chromatography (silica gel, hexane/ethyl acetate 15:1) afforded **32** (0.02 g, 2%) and **30** (0.86 g, 92%) as colorless oils.

Data for **30**: R_F 0.45 (hexane/ethyl acetate 3:1); IR (film): ν 2980*s*, 2940*m*, 2880*m*, 1760*s*, 1735*s*, 1460*m*, 1435*w*, 1390*w*, 1375*w*, 1360*w*, 1030*w*, 1275*m*, 1250*w*, 1190*m*, 1175*s*, 1155*s*, 1110*s*, 1010*m*; ^1H NMR (300 MHz, $CDCl_3$): δ 1.18, 1.22, 1.23, 1.24 (each *s*, 3 H, Me), 2.47 (*bd*, *J* = 9.0, 2 H, CH_2), 3.68 (*s*, 3 H, OMe), 4.36 (*t*, *J* = 9.0, 1 H, $H_{furanyl}$-C(2)); ^{13}C NMR (62 MHz, $CDCl_3$): δ 217.13 (*s*, CO); 176.19 (*s*, COO), 81.05 (*s*, $O\underline{C}Me_2$), 77.28 (*d*, $C(2)_{furanyl}$), 51.6 (*q*, OMe), 45.26 (*s*, $\underline{C}Me_2$), 37.30 (*t*, CH_2), 24.00, 21.90, 21.02, 20.69 (each *q*, Me); MS (ei, 70 eV, 35 °C): 214 (3.3), 186 (4.3), 155 (10.0), 128 (52.9), 113 (47.4), 69 (100.0), 41 (38.5); Anal. calcd. for $C_{11}H_{18}O_4$ (214.26): C, 61.66; H, 8.46; found: C, 61.44; H, 8.37.

Data for **32**: R_F 0.57 (hexane/ethyl acetate 3:1); ^1H NMR (300 MHz, $CDCl_3$): δ 1.21, 1.22, 1.26, 1.27, 1.38, 1.51 (each *s*, 3 H, Me), 2.47-2.51 (*m*, 2 H, H-C(3)), 3.69, 3.73 (each *s*, 3 H, OMe), 4.35-4.41 (*m*, 1 H, H-C(2)), 5.47 (*s*, 1 H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175 94, 172.77 (each *s*, COO), 100.06 (*d*, C(2)), 88.91 (*s*), 80.94 (*s*), 52.61, 51.89 (each *q*, OMe), 45.66, 45.20 (each *s*), 37.27 (*t*, C(3)), 23.96, 23.25, 22.54, 21.87, 20.99, 20.65 (each *q*, Me); MS (ei, 80 eV, 40 °C): 286 (0.5), 271 (1.2), 257 (6.1), 211 (1.6), 185 (100.0), 169 (2.8), 157 (12.3), 145 (3.6), 95 (12.69, 73 (85.1); Anal. calcd. for $C_{16}H_{28}O_6$ (316.39): C, 60.74; H, 8.92; found: C, 60.52; H, 8.79.

***Methyl 2-methyl-2-(5,5,5',5'-tetramethyl-4,4'-dioxo-octahydro-[2,3']-bifuranyl-2'-yl)-propanoate* (31).** The reaction of **29** (0.34g, 3.0 mmol) with **2** (0.59 g, 3.4 mmol) in dry dichloromethane (5 *ml*) in the presence of TMSOTf (0.55 *ml*, 3.0 mmol) (0 °C then 90 min at 25 °C) afforded after work up (chromatography with hexane/ethyl acetate 15:1) **30** (0.37 g, 58%, for data: *vide infra*) and **31** (0.07 g, 7%) als colorless oils; data for **31**: R_F 0.40 (hexane/ethyl acetate 3:1); IR (film): ν 2979*m*, 2934*w*, 1755*s*, 1778*s*, 1732*s*, 1436*w*, 1377*w*, 1270*w*, 1173*m*, 1148*m*, 1112*m*, 1013*w*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17, 1.21, 1.25, 1.26, 1.27, 1.29 (each *s*, 3 H, Me), 2.31 (AB-part of ABX, ν_A = 2.50, J = 10.3, 18.4, ν_B = 2.68, *J* = 5.9, 18.4, 2 H, CH_2), 2.83 (*t*, *J* = 7.3, 1 H), 3.68 (*s*, 3 H, OMe), 4.29 (X-part of ABX, *ddd*, *J* = 5.9, 7.3, 10.3, 1 H), 4.40 (*d*, *J* = 7.3, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 216.39, 216.27 (each *s*, CO), 176.33 (*s*, COO), 81.15 (*s*), 80.37, 71.99, 52.39 (each *d*, CHO), 51.84 (*q*, OMe), 46.22 (*s*), 40.14 (*t*, CH_2), 24.36, 24.03, 23.28, 22.58, 21.44, 21.19 (each *q*, Me); MS (ei, 80 eV, 30°C): 326 (1.2), 295 (2.6), 240 (11.0), 225 (9.1), 214 (3.7), 154 (67.7), 113 (39.4), 95 (100.0); Anal. calcd. for $C_{17}H_{26}O_6$ (326.39): C, 62.56; H, 8.03; found: C, 62.35; H, 8.23.

***Methyl 3,7-anhydro-6,8-O-benzylidene-2,4-dideoxy-2,2-di-methyl-α-D-threo-5-oct-ulosonate* (33), *methyl 3,7-anhydro-6,8-O-benzylidene-2,4-dideoxy-2,2-di-methyl-β-D-erythro-5-octulosonate* (34)** and ***methyl 2,2-dimethyl-3-phenyl-3-trimethylsilyloxy-propionate* (36).** The reaction between **28** (0.47 g, 2 mmol) and **2** (0.57 g, 3.5 mmol) in the presence of catalytic amounts of $TAS\text{-}TMSF_2$ afforded after usual work up **33** (0.14 g, 20%), **34** (0.17 g, 26%) and **36** (0.27 g, 48%).

Data for **33**: mp 109-112 °C; $[\alpha]_D^{25}$ +21.7° (*c* = 0.6 $CHCl_3$); R_F 0.51 (hexane/ethyl acetate 3:1); IR (KBr): ν 2981*w*, 2949*w*, 1730*s*, 1457*w*, 1434*w*, 1396*w*, 1273*m*, 1249*w*, 1216*m*, 1192*w*, 1166*w*, 1137*s*, 1109*s*, 1071*w*, 1049*w*, 1029*w*, 823*w*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (*s*, 3 H, Me), 1.71 (*s*, 3 H, Me), 2.64 (*dd*, *J* = 2.7, 13.4, 1 H, H_A-C(4)), 2.72 (*ddd*, *J* = 1.0, 11.2, 13.4, 1 H, H_B-C(4)), 3.84 (*s*, 3 H, OMe), 4.11 (*t*, *J* = 11.2, 1 H, H_A-C(8), 4.22 (*ddd*, *J* = 1.0, 5.5, 11.2, 1 H, H_B-C(8)), 4.33 (*dd*, *J* = 2.7, 11.2, 1 H, H-C(3)), 4.80 (*ddd*, *J* = 5.5, 7.7, 11.2, 1 H, H-C(7)), 4.91 (*d*, *J* = 7.7, 1 H, H-C(6)), 5.88 (*s*, 1 H, H-$C_{benzylidene}$), 7.46-7.66 (*m*, 5 H, H-C(Ar)); ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.69 (*s*, CO), 175.42 (*s*, COO), 136.74 (*s*, C_q(Ar)), 128.94, 128.08, 125.96 (each *d*, C_t(Ar)), 97.33 (*d*, C_t(benzylidene)), 77.62, 76.57, 69.07 (each *d*, C(3, 6, 7), 64.97 (*t*, C(8)), 52.12 (*q*, OMe), 46.17 (*s*, C(2)), 42.73 (*t*, C(4)), 21.35, 19.57 (each *q*, Me); MS (ei, 80 eV, 105 °C): 334 (0.2), 333 (0.5), 303 (0.7), 247 (1.0), 233 (1.1), 199 (100.0), 139 816.9), 105 (49.3), 97 (63.9), 696 (38.1), 41 (34.3); Anal. calcd. for $C_{18}H_{22}O_6$ (334.37): C, 64.66, H, 6.63; found: C, 64.39, H, 6.36.

Data for **34**: mp 149-153 °C; $[\alpha]_D^{25}$ +36.4° (*c* = 0.6, $CHCl_3$); R_F 0.33 (hexane/ethyl acetate 3:1); IR (KBr): ν 2982*w*, 2951*w*, 2876*w*, 1734*m*, 1458*w*, 1430*w*, 1395*w*, 1268*w*, 1243*w*, 1225*w*, 1210*w*, 1192*w*, 1156*w*, 1131*m*, 1057*w*, 1020*w*, 1010*w*, 964*w*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (*s*, 3 H, Me), 1.27 (*s*, 3 H, Me), 2.51 (*dd*, *J* = 2.9, 14.0, 1 H, H_A-C(4)), 2.65 (*ddd*, *J* = 1.4, 11.5, 14.0, 1 H, H_B-C(4)), 3.70 (*s*, 3 H, OMe), 3.65-3.74 (*m*, 1 H, H-C(7)), 3.83 (*t*, *J* = 10.2, 1 H, H_A-C(8)), 4.06 (*dd*, *J* = 2.9, 11.5, 1 H, H-C(3)), 4.26 (*dd*, *J* = 1.4, 9.7, 1 H H-C(6)), 4.38 (*dd*, *J* = 4.6, 10.2, 1 H, H_B-C(8)), 5.56 (*s*, 1 H, H-$C_{benzylidene}$), 7.33-7.51 (*m*, 5H, H-C(Ar)); ^{13}C NMR (63 MHz, $CDCl_3$): δ 199.71 (*s*, CO), 175.58 (*s*, COO), 136.57 (*s*, C_q(Ar)), 129.33, 128.32, 126.43 (each *d*, C_t(Ar)), 102.04 (*d*, C_t(benzylidene)), 83.46, 82.72, 72.87 (each *d*, C(3,6,7)), 69.40 (*t*, C(8)), 52.21 (*q*, OMe), 46.24 (*s*, C(2)), 42.27 (*d*, C(4)), 20.98, 20.64 (each *q*, Me); MS (ei, 80 eV, 117 °C): 334 (3.2), 333 (3.5), 303 (3.9), 275 (4.5), 199 (17.9), 145 (66.2), 125 (63.4), 105 (100.0), 91 (74.6), 69 (87.1), 41 (70.6); Anal. calcd. for $C_{18}H_{22}O_6$ (334.37): C, 64.66, H, 6.63; found: C, 64.55, H, 6.50.

Data for **36**: oil; R_F 0.53 (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.02 (*s*, 9 H, $OSiMe_3$), 1.03 (*s*, 3 H, Me), 1.16 (*s*, 3 H, Me), 3.71 (*s*, 3 H, OMe), 5.04 (*s*, 1 H, H-C(3)), 7.29 (*bs*, 5 H, H-C(Ar)); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 177.09 (*s*, CO), 140.70 (*s*, C_q(Ar)), 127.69, 127.30, 127.28 (each *d*, C_t(Ar)), 79.16 (*d*, C(3)), 51.62 (*q*, OMe), 49.09 (*s*, C(2)), 21.73 (*q*, Me), 19.24 (*q*, Me), 0.03 (*q*, $OSiMe_3$); MS (ei, 80 eV, 55 °C): 265 (3.8), 205 (1.3), 179 (100.0), 174 (6.9), 163 (3.2), 149 (2.1), 117 (2.7), 105 (2.9), 89 (16.7), 73 (90.5); Anal. calcd. for $C_{15}H_{24}O_3Si$ (280.44): C, 64.24; H, 8.63; found: C, 64.01; H, 8.85.

***Methyl 1',8;3,7-dianhydro-2,4-dideoxy-2,2-dimethyl-4-C-(1'-phenylmethyl)-β-D-arabino-5-octulosonate* (37) *and methyl 1',6;3,7-dianhydro-2,4-dideoxy-2,2-dimethyl-4-C-(1'-phenylmethyl)-β-D-xylo-5-octulosonate* (38).** To a solution of **28** (0.20 g, 0.86 mmol) and **2** (0.24 g, 1.37 mmol) in dry dichloromethane (2 *ml*) at 0 °C TMSOTf (0.16 *ml*, 0.86 mmol) was added. After additional stirring for 1 h at 25°C work up as described for **3/4** followed by chromatography (silica gel, hexane/ethyl acetate 5:1) afforded **37** (0.07 g, 26%) and **38** (0.01 g, 4%) as colorless oils as well as unchanged educt **28** (0.03 g, 16%).

Data for **37**: R_F 0.43 (hexane/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.13, 1.25 (each *s*, 3 H, Me), 2.83 (*bs*, 1 H, H-C(4)), 3.69 (*s*, 3 H, OMe), 4.28 (*bs*, 1 H, H-C(3)), 4.37-4.51 (*m*, 4H, H-C(6, 7, 8)), 4.80 (*s*, 1 H, OH), 4.96 (*s*, 1 H, H-$C_{benzylidene}$), 7.17-7.39 (*m*, 5 H, H-C(Ar)); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.05 (*s*, CO), 176.53 (*s*, COO), 139.44 (*s*, C_q(Ar)), 128.64, 128.30, 125.38 (each *d*, C_t(Ar)), 85.18, 84.23, 78.49, 74.91 (each *d*, C(3, 6, 7) and $C_{benzylidene}$), 69.26 (*t*, C(8)), 57.81 (*q*, OMe), 52.14 (*d*, C(4)), 47.53 (*s*, C(2)), 22.61, 19.71 (each *q*, Me); MS (ei, 80 eV, 124 °C): 334 (1.4), 303 (0.5), 279 (1.0), 264 (0.1), 233 (100.0), 127 (27.8), 105 (33.0), 91 (42.69); HRMS calcd. for $C_{18}H_{22}O_6$: 334.14161; found: 334.14160.

Data for **38**: R_F 0.58 (hexane/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.03, 1.07 (each *s*, 3 H, Me), 3.10 (*d*, *J* = 3.2, 1 H, H-C(4)), 3.52 (*s*, 3 H, OMe), 4.26-4.55 (*m*, 6 H, H-C(3, 6, 7, 8) and OH), 5.11 (*d*, *J* = 2.9, 1 H, H-$C_{benzylidene}$, 7.25-7.43 (*m*, 5 H, H-C(Ar)); ^{13}C NMR (63 MHz, $CDCl_3$): δ 208.84 (*s*, CO), 176.21 (*s*, COO), 138.76 (*s*, C_q(Ar)), 128.83, 127.78, 125.25 (each *d*, C_t(Ar)), 78.19, 77.67 (2 x), 74.65 (each *d*, C(3, 6,7) and $C_{benzylidene}$), 68.94 (*t*, C(8)), 54.30 (*q*, OMe), 52.04 (*d*, C(4)), 46.79 (*s*, C(2)), 22.15, 21.41 (each *q*, Me); MS (ei, 80 eV, 139 °C): 334 (0.9), 303 (0.8), 275 (0.9), 243 (2.3), 233 (100.0), 1227 (22.4), 107 (18.0), 91 (54.7); HRMS calcd. for $C_{18}H_{22}O_6$: 334.14161; found: 334.14160

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REFERENCES AND NOTES

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16 This does not seem very surprising due to a possible complexation of the Lewis acid by the solvent; *cf.* ref. 5

17 Acetonitrile has been reported to favour the formation of α-glycosides (*cf.* Schmidt, R. R.; Rücker, E., *Tetrahedron Lett.* **1980**, *21*, 1421) due to the generation of an intermediary isonitrilium ion; for the TMSOTf catalyzed reaction of **13** with **2**, however, such an effect could be observed.

18 Interesting to note that for all pairs of anomeric *C*-glycosides in this work it was observed that the β-anomers were less polar than the α-anomers during chromatography on silica gel (hexane/ethyl acetate 10:1) and thus eluted first; *cf.* refs cited in 5 and 17.

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23 The atomic coordinates, bond lengths and angles, torsion angles and thermal parameters are available on request from the Director of the Cambridge Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB21EW. Any request should be accompanied by the full literature citation for this communication.

24 **1** gave upon reaction with **19** 93% of a 1:1 mixture (by ^{1}H NMR) of two products. According to their ^{1}H and ^{13}C NMR spectra both products show β-configuration at the anomeric center and differ only in the absolute configuration at C(2).

25 The formation of two products from the reaction of **28** with **2** is similar to the reported reaction of **28** with ethyl 2-lithio-[1,3]-dithiolane-2-carboxylate; *cf.* Paulsen, H.; Bünsch, H., *Chem. Ber.* **1978**, *111*, 3484.

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