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TETRAHEDRON

Stereoselective Synthesis of α-*C*-D-Gluco- and D-Galactopyranosyl Glycosides from an Isoprenoid Synthon

Anne Jégou, Carole Pacheco and Alain Veyrières*

Laboratoire de Synthèses et Activations de Biomolécules, CNRS ESA 6052, Ecole Nationale Supérieure de Chimie de Rennes, Campus de Beaulieu, 35700 Rennes, France

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Abstract: Addition of the allylsilane $Me_3SiCH_2C{:}CH_2CH_2CO_2Me$ to D-gluco and D-galactopyranosyl derivatives gives in good yields α-*C*-glycopyranosides which are easily converted into glycosylated β-keto esters, butenolide and dihydropyrone.

INTRODUCTION

Carbohydrate analogues in which a carbon atom substitutes the glycosidic oxygen (or nitrogen in the case of nucleosides) are defined as *C*-glycosides, or more correctly *C*-glycosyl compounds.[1,2] They became attractive as potential inhibitors of carbohydrate processing enzymes (glycosidases and glycosyl transferases) and stable mimics of glycoconjugates involved in recognition phenomena such as the adhesion of cells with viruses, bacteria, toxins and tumor cells. Many macrolide structures of biological interest, such as palytoxin, are related to *C*-glycosides. *C*-Glycosylation of pyranose or furanose units could therefore afford chiral building blocks for the synthesis of macrocyclic structures. Most often the creation of a new stereocentre at the anomeric position exploits the electrophilic character of that carbon atom. Various leaving groups generate a stabilized oxocarbenium intermediate in Lewis acid-promoted reactions. In the case of pyranosides a stereoelectronic effect[3,4] ensures that nucleophiles approach the anomeric centre mostly from the side opposite to the axial electron pair of the ring oxygen. D-Gluco- and D-galactopyranosides therefore afford α-*C*-glycosyl derivatives with excellent stereoselection.

Among *C*-nucleophiles allyltrimethylsilane offers a good reactivity with a wide variety of glycosidic activating groups. The readily available glycosyl donors, penta-*O*-acetyl-D-glucose and -D-galactose, have been efficiently allylated[5,6] in boron trifluoride etherate-promoted reactions; acetonitrile induces a fairly high α-selectivity by its ability to coordinate with intermediate oxonium ions.[7] Manipulation of the allylic appendage (most often ozonolysis) allows further integration of the pyranose unit in more elaborate stuctures.

*Corresponding author. Fax: +33 (2) 99 87 13 48

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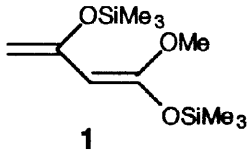
To this respect the use of functionalized allylsilanes should help in keeping the number of steps required to reach the target molecule as low as possible. Acetate[8] and halide[9] substituted allylsilanes have been occasionaly used.

Various dianion equivalents of acetoacetate have been used in the synthesis of γ-substituted-β-ketoesters. γ-Furanosyl[10,11] and pyranosyl[12] acetoacetates have been prepared by a non stereoselective Wittig reaction of phosphorane $Ph_3P{=}CHC{:}OCH_2CO_2R$ with a sugar hemi-acetal. 1,3-Bis(trimethylsilyloxy)-1-methoxybuta-1,3-diene **1**[13] and diketene **2**,[14] a cyclic enol ester, have been added to acetals in Lewis acid-promoted reactions. The silyl dienolate **3** readily available from the diketene-acetone adduct undergoes[15] enantioselective additions to aldehydes in the presence of a catalytic chiral Lewis acid. The adduct **4** between diketene and Me_3SiCH_2MgCl was obtained by a $NiCl_2$-catalyzed reaction.[16,17] Its esters **5**, **6** and **7** have been added to aldehydes and ketones,[18] iminium ions[19] and an ethoxycarbenium ion related to squaric acid.[20]



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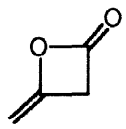

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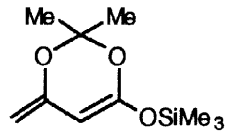

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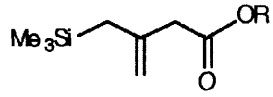


4 R = H
5 R = $SiMe_3$
6 R = p-$NO_2C_6H_4CH_2$
7 R = Me

Isopentenyl pyrophosphate and its isomerization product, dimethylallyl pyrophosphate, are five-carbon building blocks involved in the terpenoid biosynthesis.[21] These activated forms of isoprene can be chemically mimicked[18,22] by allylsilane **7**. Ozonolysis[19] of the allyl appendage affords γ-substituted acetoacetates in good yields. Alternatively, the presence of a carboxylate function allows easy double bond migration leading to conjugated products.

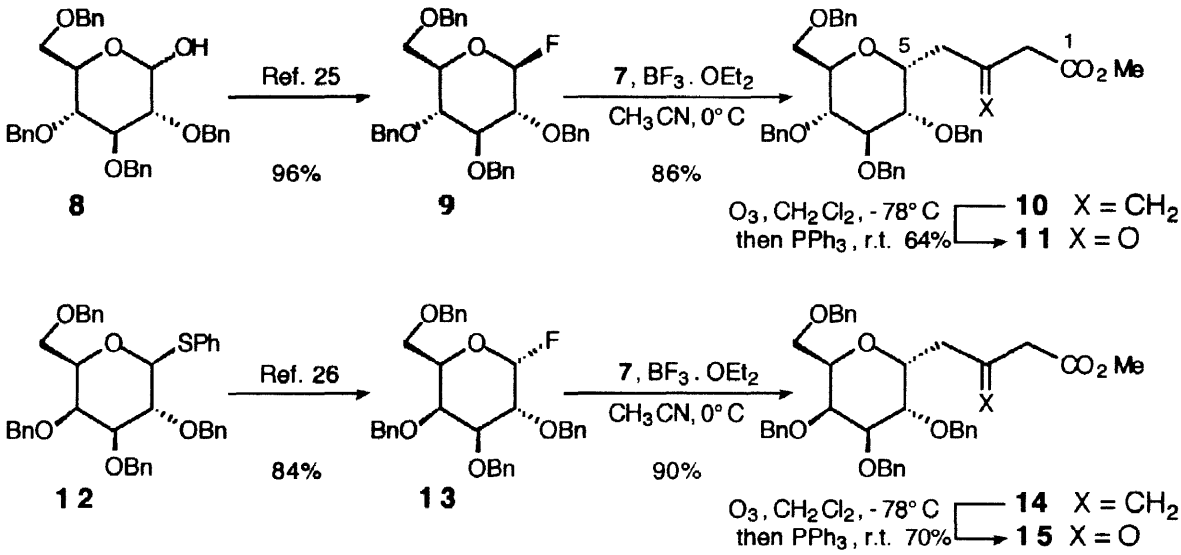
Herein we report[23] on the stereoselective addition of allylsilane **7** to oxocarbenium species generated from pyrano sugars and various transformations of the resulting *C*-glycosides.

DISCUSSION

β-D-Glucopyranose pentaacetate reacted sluggishly with allylsilane **7** and boron trifluoride etherate in acetonitrile at room temperature. A 6:1 mixture of α- and β-*C*-glycosides was obtained after 45 h in only 24% yield. No improvement resulted from changing the solvent to dichloromethane, increasing the temperature of the reaction or using trimethylsilyl trifluoromethanesulfonate (TMSOTf) as acid promoter.

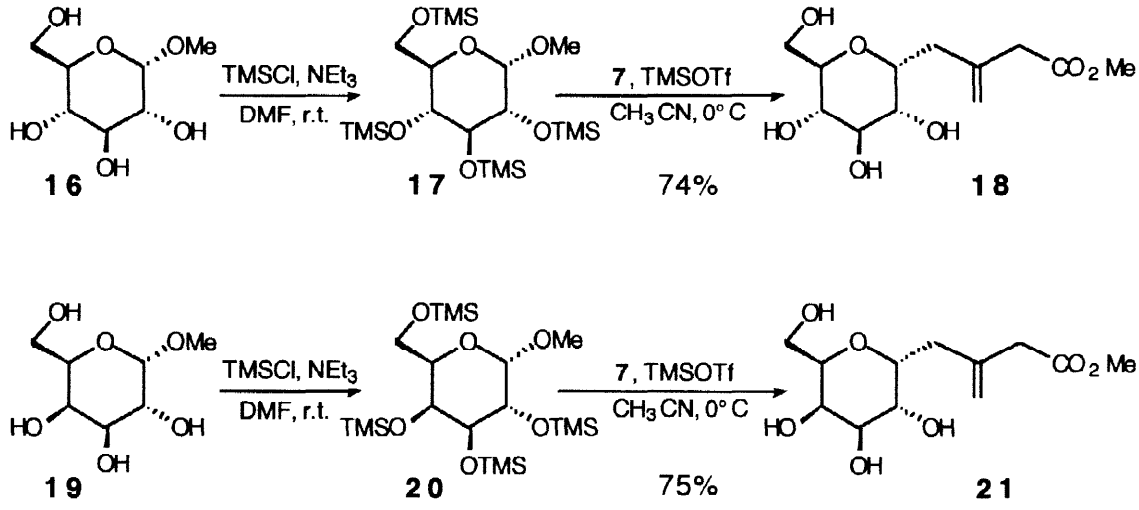
Glycosyl fluorides have been successfully used in *C*-glycosylation reactions.[24] Perbenzylated D-glucopyranosyl fluoride **9** (β:α 43:7) was quantitatively obtained[25] by reaction of commercially available tetra-*O*-benzyl-D-glucose **8** with diethylaminosulfur trifluoride (DAST) in tetrahydrofuran. The D-galactopyranosyl fluoride **13** (β:α 11:89) was prepared from the corresponding β-thiophenyl glycoside **12** as reported by Nicolaou *et al*.[26] Both fluorides **9** and **13** reacted at 0°C with allylsilane **7** and $BF_3{\cdot}OEt_2$ in acetonitrile to give *C*-glucopyranoside **10** (α:β 95:5, 86%) and *C*-galactopyranoside **14** (only α, 90%) respectively (Scheme 1). Pure **10α** crystallized from ethanol. ^1H NMR analysis of crude **10** and **14** in $CDCl_3$ allowed evaluation of diastereomeric ratios by integration of the signals corresponding to the methyl ester (singlets at δ 3.65 and 3.64 for **10α** and **10β** respectively). Signals of pyranose hydrogen atoms revealed complex mixtures of conformers at room

temperature.The expected multiplicity of anomeric H-5 in **10**α (ddd, $J_{4a,5}$ 11, $J_{4b,5}$ 3.3 and $J_{5,6}$ 5.6 Hz) was however observed in DMSO-d_6 at 80°C.



Scheme 1

Excellent yields of unprotected allyl *C*-glycosides have been obtained[27] from methyl α-D-glucopyranoside **16** by sequential *O*-trimethylsilylation, TMSOTf-promoted addition of allyltrimethylsilane and deprotection on work-up. Methyl α-D-gluco- **16** and D-galactopyranosides **19** were silylated with trimethylchlorosilane and triethylamine in *N*, *N*-dimethylformamide;[28] the crude products **17** and **20** were then treated at 0°C with allylsilane **7** and TMSOTf in acetonitrile to give unprotected *C*-glucopyranoside **18** (α:β 9:1, 74%) and *C*-galactopyranoside **21** (only α, 75%) respectively (Scheme 2). ^{1}H NMR spectra of **18** and **21** in CD_3OD showed $^4C_1$ chair conformers ($J_{6,7}$ 9.7, $J_{7,8}$ 8.7 and $J_{8,9}$ 9.7 Hz in **18**, $J_{6,7}$ 9.2 Hz in **21**) with an α-appendage at C-5 ($J_{5,6}$ 5.6 Hz in **18** and **21**).

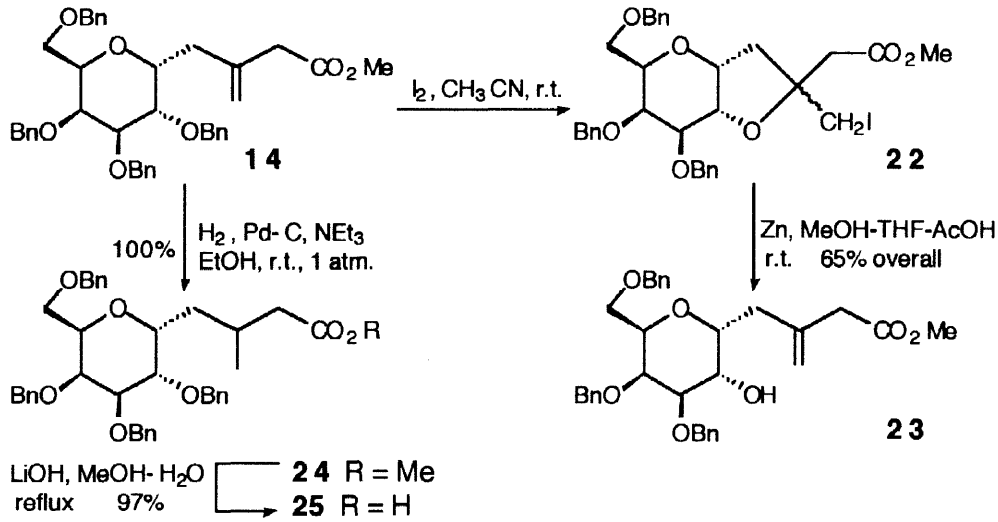


Scheme 2

Brief treatment of *C*-glucoside **10** in dichloromethane by ozone at -78°C, followed by reduction with triphenylphosphine led to the β-ketoester **11** in 64% yield. A monobenzoate resulting from regioselective oxidation of *O*-7 benzyl ether was also isolated in 6% yield; its structure was ascertained by the downfield shift of H-7 signal (δ 5.49) and the low-field signals of the aromatic hydrogens in the benzoyl group. Oxidation of benzyl ethers by ozone has been reported.[29,30] *C*-Galactoside **14** was also submitted to ozonolysis to give the β-ketoester **15** in 70% yield (Scheme 1). Its conformation was found by ^{1}H NMR analysis to be far from the chair one ($J_{5,6}$ 3.6, $J_{6,7}$ 6.6, $J_{7,8}$ 2.5 and $J_{8,9}$ 4.1 Hz). The exocyclic chain in β-ketoesters **11** and **15** had also a quite different conformation ($J_{4a,5}$ ~ 6 and $J_{4b,5}$ ~ 8 Hz) when compared to the methylene precursors **10** and **14** ($J_{4a,5}$ 10-11 and $J_{4b,5}$ 3 Hz). As already observed[12] these ketoesters were not epimerized at C-5 by methanolic 0.1 M sodium methoxide solution, since H-2a and H-2b are more acidic than H-4a and H-4b.

Regioselective debenzylation at *O*-6 of *C*-galactoside **14** was performed according to the procedure reported by Cipolla *et al*.[31] The electrophile-promoted cyclization of γ,δ-unsaturated ethers is a well known procedure[32] to make 2,5-disubstituted tetrahydrofurans. Addition of iodine to a solution of **14** in acetonitrile at room temperature gave a 3:2 mixture of C-3 epimers **22** which was submitted to reductive elimination with zinc. *C*-galactoside **23** was obtained in a 65% overall yield (Scheme 3). Addition of trichloroacetyl isocyanate[33] to an NMR sample of **23** shifted H-6 signal (δ 3.82, dd, $J_{5,6}$ 4.6, $J_{6,7}$ 10 Hz in **23**) towards lower fields (δ 5.17). The 2-*O*-unprotected *C*-galactoside will be a valuable precursor for the synthesis of α-*C*-glycosides of D-galactosaminc.[34]

Hydrogenation of **14** in the presence of palladium on charcoal and triethylamine in ethanol led to a 3:2 mixture of esters **24** in quantitative yield; saponification with lithium hydroxide in refluxing methanol–water gave the carboxylic acids **25** in 97% yield (Scheme 3).

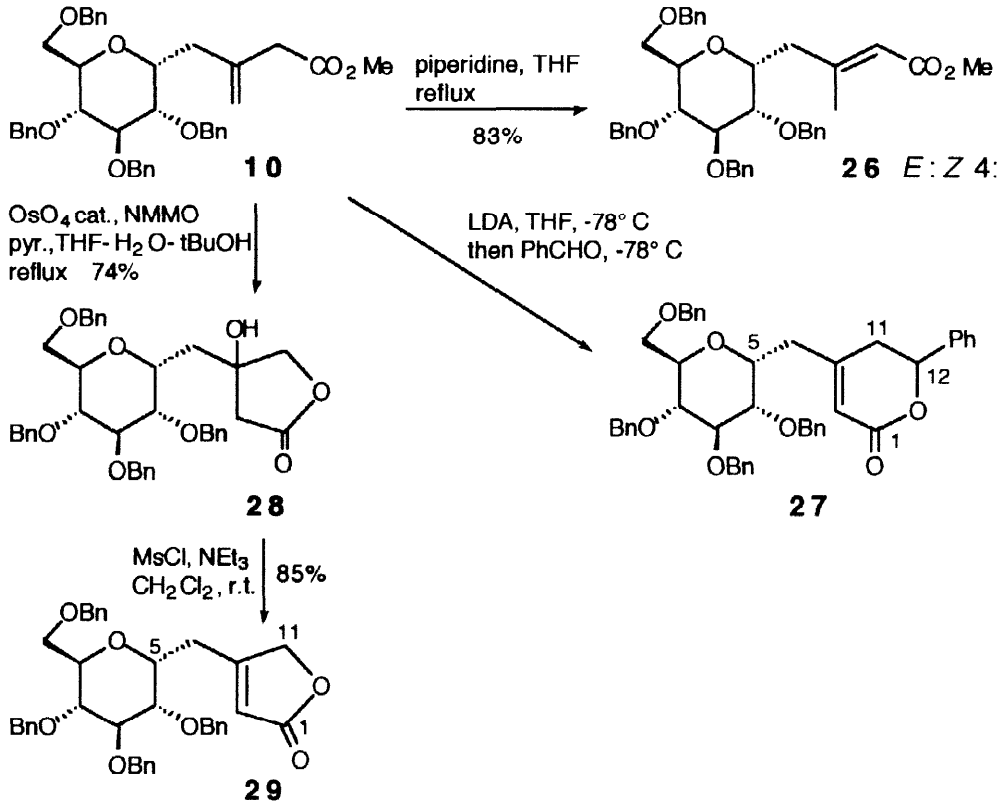


Scheme 3

Conjugation of the double bond in **10** was accomplished by treatment with piperidine in refluxing tetrahydrofuran for 3 days.[35,36] A 4:1 mixture of crystalline *E* and *Z* isomers **26** was obtained in 83% yield (Scheme 4). Assignment of the stereochemistry of these 3-disubstituted acrylates was made[37] on the basis of ^{1}H and ^{13}C chemical shifts of CH_3-3 and CH_2-4 groups. In the *E* isomer these signals occurred respectively at δ_H 2.16, δ_C 18.56 and $\delta_{H\text{-}4a}$ 2.58, $\delta_{H\text{-}4b}$ 2.48, δ_C 36.18, whereas in the *Z* isomer the following values were found: δ_H 1.92, δ_C 25.55 and $\delta_{H\text{-}4a}$ 3.34, $\delta_{H\text{-}4b}$ 2.95, δ_C 28.69. It is noticeable that attempted conjugation with

potassium *tert*-butoxide in tetrahydrofuran–*tert*-butyl alcohol led to unidentified compounds where one benzyl group had been affected.

The dienolate anion involved in conjugation experiments can be produced at low temperature by reaction of lithium diisopropylamide (LDA) in tetrahydrofuran. It is known[38] that dianionic species generated from α,β-unsaturated acids are mostly α-alkylated by carbonyl compounds at low temperatures; retroaddition and recombination to the more stable γ-alkylated product occur at higher temperatures. However the regioselectivity of addition can be dependent on the nature of the electrophile, carbonyl compounds adding preferentially to the soft nucleophilic γ-position.[39] We observed (Scheme 4) that the lithium dienolate prepared from **10** added benzaldehyde at -78°C to give the *E* γ-alkylated product which cyclized at room temperature into the α,β-unsaturated δ-lactone **27** (59%, 1:1 crystalline mixture of epimers at C-12).



Scheme 4

Finally, *C*-glucoside **10** was converted into the butenolide **29** (63% overall yield) *via* the *cis*-hydroxylation[40] of the double bond with catalytic osmium tetroxide and *N*-methyl-morpholine oxide (NMMO). The intermediate diol lactonized during the reaction to give a 7:3 mixture of epimeric alcools **28**. Treatment of **28** with methanesulfonyl chloride and triethylamine at room temperature gave rise to elimination of the intermediate tertiary sulfonate (Scheme 4).

CONCLUSION

Addition of allylsilane $Me_3SiCH_2C{:}CH_2CH_2CO_2Me$ to D-gluco and D-galactopyranosyl derivatives (most specially perbenzylated fluorides) gives access to α-*C*-glycosides which can be easily transformed into useful *C*-

glycosylated blocks by reaction of their β,γ-unsaturated ester functionality.

EXPERIMENTAL PART

General Procedures:

Melting points were determined using a Kofler hot stage apparatus under a Reichert microscope and are uncorrected. Optical rotations were measured at room temperature on a Perkin-Elmer 341 automatic polarimeter (concentration in g/100 mL). NMR spectra were recorded on a Bruker ARX-400 instrument. ^{1}H NMR were obtained at 400.13 MHz (s=singlet, d=doublet, t=triplet, m=multiplet, bd=broad). Assignments were confirmed by homonuclear 2D COSY correlated experiments. ^{13}C NMR were obtained at 100.62 MHz in the proton-decoupled mode. Heteronuclear 2D correlated spectra were recorded in order to assist in carbon resonance assignments. Chemical shifts are given in ppm relative to internal TMS (δ scale) and coupling constants (J) in Hz. Thin layer chromatography (TLC) was performed on Merck DC-Alufolien Kieselgel 60 F_{254} Art. 5554 with detection by UV light and charring with 1:10 H_2SO_4–MeOH. Flash chromatography[41] was performed on Merck Kieselgel 60 (40-63 μm). All solvents were dried and distilled according to standard laboratory procedures.[42] Elemental analyses were performed by the Service de Microanalyse du Centre National de la Recherche Scientifique (Gif-sur-Yvette, France).

Methyl 5,9-Anhydro-6,7,8,10-tetra-O-*benzyl-2,3,4-trideoxy-3*-C-*methylene*-D-glycero-D-ido-*deconate* (**10**).

To a solution of fluoride **9** (450 mg, 0.83 mmol) in dry acetonitrile (5 mL) were added at -30°C under nitrogen **7** (770 mg, 4.13 mmol), then boron trifluoride etherate (110 μL, 0.88 mmol). The reaction mixture was allowed to warm to 0°C within 45 min, then diluted with dichloromethane, and washed with saturated aqueous $NaHCO_3$ and water. The organic phase was dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography (petroleum ether–ethyl acetate, 17:3), then crystallized from ethanol to give **10** (455 mg, 86%); mp 42-45°C; $[\alpha]_D$ +20 (*c* 1, $CHCl_3$). ^{1}H NMR (DMSO-d_6, 80°C): δ 7.34-7.21 (m, 20 H, 4 Ph), 5.03 and 4.94 (2 bd s, 2 H, CH_2=), 4.83 and 4.73 (2 d, 2 H, *J* 11.5 Hz, CH_2Ph), 4.73 and 4.55 (2 d, 2 H, *J* 11.3 Hz, CH_2Ph), 4.63 (m, 2 H, CH_2Ph), 4.51 and 4.46 (2 d, 2 H, *J* 12.1 Hz, CH_2Ph), 4.23 (ddd, 1 H, $J_{4a,5}$ 11, $J_{4b,5}$ 3.3, $J_{5,6}$ 5.6 Hz, H-5), 3.78 (dd, 1 H, $J_{6,7}$ 8.8, $J_{7,8}$ 8.2 Hz, H-7), 3.70 (m, 1 H, H-9), 3.65 (dd, 1 H, H-6), 3.62-3.58 (m, 2 H, H-10a,10b), 3.60 (s, 3 H, CO_2Me), 3.46 (dd, 1 H, $J_{8,9}$ 9.4 Hz, H-8), 3.14 (bd s, 2 H, H-2a,2b), 2.60 (dd, 1 H, $J_{4a,4b}$ 15.4 Hz, H-4a) and 2.41 (dd, 1 H, H-4b); ^{13}C NMR ($CDCl_3$): δ 171.90 (C-1), 139.37, 138.80, 138.24, 138.23 and 138.08 (C-3, 4 C quat. arom.), 128.51-127.69 (20 C arom.), 116.64 (CH_2=), 82.42, 79.96, 78.03, 72.68 and 71.26 (C-5,6,7,8,9), 75.60, 75.22, 73.54 and 73.05 (4 CH_2Ph), 68.85(C-10), 51.92 (CO_2CH_3), 41.31 (C-2) and 30.75 (C-4). Anal.Calcd for $C_{40}H_{44}O_7$: C, 75.45; H, 6.96. Found: C, 75.44; H, 7.13.

Methyl 5,9-Anhydro-6,7,8,10-tetra-O-*benzyl-2,4-dideoxy*-D-glycero-D-ido-*dec-3-ulosonate* (**11**).

A solution of **10** (480 mg, 0.75 mmol) in dichloromethane (20 mL) was treated with ozone at -78°C until a persistent blue color appeared. The excess of ozone was then removed within 15 min by a stream of oxygen, then within 15 min by a stream of nitrogen at -78°C. Triphenylphosphine (590 mg, 2.25 mmol) was added and the solution was stirred at -78°C for 1 h, then at room temperature for 3 h. After evaporation the residue was

purified by flash chromatography (petroleum ether–ethyl acetate, 4:1) to give **11** (310 mg, 64%) as a syrup; $[\alpha]_D$ +33 (*c* 0.997, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.33-7.24 (m, 20 H, 4 Ph), 4.89 and 4.79 (2 d, 2 H, *J* 11.2 Hz, C*H*$_2$Ph), 4.79 and 4.56 (2 d, 2 H, *J* 11.7 Hz, C*H*$_2$Ph), 4.69 (m, 1 H, H-5), 4.61 and 4.47 (2 d, 2 H, *J* 11.2 Hz, C*H*$_2$Ph), 4.59 and 4.46 (2 d, 2 H, *J* 12.2 Hz, C*H*$_2$Ph), 3.78-3.55 (m, 6 H, H-6,7,8,9,10a,10b), 3.68 (s, 3 H, CO_2Me), 3.48 and 3.41 (2 d, 2 H, $J_{2a,2b}$ 15.8 Hz, H-2a,2b), 3.01 (dd, 1 H, $J_{4a,4b}$ 15.6, $J_{4a,5}$ 5.8 Hz, H-4a) and 2.82 (dd, 1 H, $J_{4b,5}$ 8.1 Hz, H-4b); ^{13}C NMR ($CDCl_3$) δ 200.15 (C-3), 167.42 (C-1), 138.47, 138.01, 137.87 and 137.67 (4 C quat. arom.), 128.52-127.68 (20 C arom.), 81.87, 79.06, 77.57, 72.55 and 70.83 (C-5,6,7,8,9), 75.38, 75.00, 73.51 and 73.38 (4 *C*H_2Ph), 68.73 (C-10), 52.30 (CO_2*C*H_3), 49.61 (C-2) and 40.24 (C-4). Anal. Calcd for $C_{39}H_{42}O_8$: C, 73.33; H, 6.63. Found: C, 73.25; H, 6.57.

The 7-*O*-benzoyl derivative was eluted next (28 mg, 6%). ^1H NMR ($CDCl_3$): δ 7.90, 7.51 and 7.37 (3 m, 5 H, PhCO), 5.49 (dd, 1 H, $J_{6,7} \sim J_{7,8} \sim 9.1$ Hz, H-7), 4.74 (m, 1 H, H-5) and 3.70 (m, 1 H, H-6); ^{13}C NMR ($CDCl_3$): δ 198.78 (C-3), 166.33 and 164.70 (C-1 and Ph*C*O).

Methyl 5,9-Anhydro-6,7,8,10-tetra-O-*benzyl-2,3,4-trideoxy-3*-C-*methylene*-D-glycero-L-gluco-*deconate* (**14**).

Fluoride **13** (1 g, 1.8 mmol) in dry acetonitrile (25 mL) was treated with **7** (1.37 g, 7.35 mmol) and boron trifluoride etherate (220 μL, 1.8 mmol) as described for the preparation of **10**. The crude product was purified by flash chromatography (petroleum ether–ethyl acetate, 4:1) to give **14** (1.07 g, 91%) as a syrup; $[\alpha]_D$ +33 (*c* 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.36-7.24 (m, 20 H, 4 Ph), 4.99 and 4.94 (2 d, 2 H, *J* 0.8 Hz, CH_2=), 4.76-4.42 (m, 8 H, 4 C*H*$_2$Ph), 4.19 (m, 1 H, H-5), 4.06-3.97 (m, 2 H, H-8,10a), 3.84 (m, 1 H, H-6), 3.78 (m, 1 H, H-10b), 3.70 (m, 1 H, H-7), 3.65-3.61 (m, 4 H, H-9, CO_2Me), 3.14 and 3.09 (2 d, 2 H, $J_{2a,2b}$ 15.4 Hz, H-2a,2b), 2.52 (dd, 1 H, $J_{4a,5}$ 10.4, $J_{4a,4b}$ 15.2 Hz, H-4a) and 2.39 (dd, 1 H, $J_{4b,5}$ 3.2 Hz, H-4b). Anal. Calcd for $C_{40}H_{44}O_7$: C, 75.45; H, 6.96. Found: C, 75.31; H, 6.95.

Methyl 5,9-Anhydro-6,7,8,10-tetra-O-*benzyl-2,4-dideoxy*-D-glycero-L-gluco-*dec-3-ulosonate* (**15**).

Alkene **14** (400 mg, 0.63 mmol) was treated with ozone, then with triphenylphosphine (500 mg, 1.9 mmol) as described for the preparation of **11**. The crude product was purified by flash chromatography (toluene–ethyl acetate, 9:1) to give **15** (280 mg, 70%) as a syrup; $[\alpha]_D$ +27 (*c* 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.36-7.13 (m, 20 H, 4 Ph), 4.71-4.41 (m, 9 H, 4 C*H*$_2$Ph and H-5), 4.03 (m, 1 H, H-9), 3.97 (dd, 1 H, $J_{7,8}$ 2.5, $J_{8,9}$ 4.1 Hz, H-8), 3.83 (dd, 1 H, $J_{9,10a}$ 7.6, $J_{10a,10b}$ 10.7 Hz, H-10a), 3.80 (dd, 1 H, $J_{5,6}$ 3.6, $J_{6,7}$ 6.6 Hz, H-6), 3.68 (dd, 1 H, H-7), 3.65 (s, 3 H, CO_2Me), 3.63 (dd, 1 H, $J_{9,10b}$ 4.6 Hz, H-10b), 3.48 and 3.40 (2 d, 2 H, *J* 15.8 Hz, H-2a,2b), 2.81 (dd, 1 H, $J_{4a,5}$ 7.6, $J_{4a,4b}$ 16.3 Hz, H-4a) and 2.74 (dd, 1 H, $J_{4b,5}$ 6.1 Hz, H-4b); ^{13}C NMR ($CDCl_3$): δ 200.96 (C-3), 167.62 (C-1), 138.29, 138.27, 138.22 and 137.77 (4 C quat. arom.), 128.43-127.53 (20 C arom.), 76.08, 73.73 and 67.85 (C-5,6,7,8,9), 73.31, 73.25, 73.05 and 72.87 (4 *C*H_2Ph), 67.21 (C-10), 52.20 (CO_2*C*H_3), 49.51 (C-2) and 42.11 (C-4). Anal. Calcd for $C_{39}H_{42}O_8$: C, 73.33; H, 6.63. Found: C, 73.51; H, 6.62.

Methyl 5,9-Anhydro-2,3,4-trideoxy-3-C-*methylene*-D-glycero-D-ido-*deconate* (**18**).

To a solution of methyl α-D-glucopyranoside monohydrate **16** (388 mg, 2 mmol) in dry *N*,*N*-dimethylformamide (9 mL) were successively added at 0°C under nitrogen triethylamine (1.65 mL, 12 mmol) and trimethylchlorosilane (1.5 mL, 12 mmol). The mixture was stirred for 3 h at room temperature, then diluted with pentane and washed with iced water. The organic phase was dried ($MgSO_4$), then concentrated to give **17** as a

colourless oil (882 mg, 100%).

To a solution of methyl 2,3,4,6-tetra-*O*-(trimethylsilyl)-α-D-glucopyranoside (**17**, 882 mg, 1.83 mmol) in dry acetonitrile (10 mL) were successively added at 0°C under nitrogen **7** (1 g, 7.66 mmol) and trimethylsilyl trifluoromethanesulfonate (TMSOTf, 0.98 mL, 5.43 mmol). The mixture was stirred at 0°C for 6 h, then diluted with methanol (10 mL) and neutralized with Dowex 1 X-8 (OH^-) resin. After filtration the solution was evaporated to give **18** (409 mg, 74%). A sample of **18** was purified by column chromatography (ethyl acetate–2-propanol–water, 34:6:1). ^1H NMR (CD_3OD): δ 4.97 and 4.89 (2 s, 2 H, CH_2=), 4.02 (ddd, 1 H, $J_{4a,5}$ 11.2, $J_{4b,5}$ 3.6, $J_{5,6}$ 5.6 Hz, H-5), 3.64 (dd, 1 H, $J_{9,10a}$ 2.6, $J_{10a,10b}$ 12.2 Hz, H-10a), 3.60 (s, 3 H, CO_2Me), 3.57 (dd, 1 H, $J_{9,10b}$ 4.6 Hz, H-10b), 3.52 (dd, 1 H, $J_{6,7}$ 9.7 Hz, H-6), 3.44 (dd, 1 H, $J_{7,8}$ 8.7 Hz, H-7), 3.40 (ddd, 1 H, $J_{8,9}$ 9.7 Hz, H-9), 3.22 (dd, 1 H, H-8), 3.11 (m, 2 H, H-2a,2b), 2.48 (dd, 1 H, $J_{4a,4b}$ 15.3 Hz, H-4a) and 2.40 (dd, 1 H, H-4b); ^{13}C NMR (CD_3OD): δ 173.94 (C-1), 141.54 (C-2), 116.83 (CH_2=), 76.09, 75.11, 74.53, 72.83 and 72.09 (C-5,6,7,8,9), 62.86 (C-10), 52.34 (CO_2CH_3), 42.05 (C-2) and 31.87 (C-4). Anal. Calcd for $C_{12}H_{20}O_7 \cdot 0.25\ H_2O$: C, 51.33; H, 7.36. Found: C, 51.34; H, 7.29.

Methyl 5,9-Anhydro-2,3,4-trideoxy-3-C-methylene-D-glycero-L-gluco-*deconate* (**21**).

Methyl α-D-galactopyranoside **19** (554 mg, 2.61 mmol) was silylated, then added to **7** as described for the preparation of **18** to give **21** (538 mg, 75%). An analytical sample of **21** was obtained by crystallization from ethanol; mp 103-105°C; $[\alpha]_D$ +73 (*c* 0.985, MeOH). ^1H NMR (CD_3OD): δ 5.05 and 4.96 (2 bd s, 2 H, CH_2=), 4.14 (ddd, 1 H, $J_{4a,5}$ 11.2, $J_{4b,5}$ 3.1, $J_{5,6}$ 5.6 Hz, H-5), 3.94 (m, 1 H, H-8), 3.91 (dd, 1 H, $J_{6,7}$ 9.2 Hz, H-6), 3.76-3.64 (m, 4 H, H-7,9,10a,10b), 3.67 (s, 3 H, CO_2Me), 3.18 (m, 2 H, H-2a,2b), 2.55 (dd, 1 H, $J_{4a,4b}$ 15.3 Hz, H-4a) and 2.43 (dd, 1 H, H-4b); ^{13}C NMR (CD_3OD) δ 174.00 (C-1), 141.60 (C-3), 116.75 (CH_2=), 74.79, 73.88, 71.82, 70.04 and 69.99 (C-5,6,7,8,9), 61.96 (C-10), 52.36 (CO_2CH_3), 42.08 (C-2) and 32.36 (C-4). Anal. Calcd for $C_{12}H_{20}O_7$: C, 52.17; H, 7.30. Found: C, 51.86; H, 7.27.

Methyl 5,9-Anhydro-7,8,10-tri-O-benzyl-2,3,4-trideoxy-3-C-methylene-D-glycero-L-gluco-*deconate* (**23**).

Iodine (540 mg, 2.13 mmol) was added to a solution of **14** (450 mg, 0.71 mmol) in dry acetonitrile (20 mL) at 0°C under nitrogen. The mixture was stirred overnight at room temperature, then diluted with ether (10 mL). The solution was washed with saturated aqueous $Na_2S_2O_3$ (5 mL). The aqueous phase was extracted with ether and the combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated. ^1H NMR ($CDCl_3$): **22a** δ 7.40-7.15 (m, 15 H, 3 Ph), 4.78 and 4.68 (2 d, 2 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.74 and 4.57 (2 d, 2 H, *J* 11.4 Hz, C*H*$_2$Ph), 4.56 (m, 2 H, C*H*$_2$Ph), 4.47 (dd, 1 H, $J_{4b,5}$ 5.5, $J_{5,6}$ ~ 3 Hz, H-5), 4.25 (dd, 1 H, $J_{6,7}$ 4.3 Hz, H-6), 4.20 (ddd, 1 H, $J_{8,9}$ 5.1, $J_{9,10a}$ 8.5, $J_{9,10b}$ 3 Hz, H-9), 4.01 (dd, 1 H, $J_{7,8}$ 2.5 Hz, H-8), 3.88 (dd, 1 H, $J_{10a,10b}$ 10.6 Hz, H-10a), 3.83 (dd, 1 H, H-7), 3.70-3.60 (m, 6 H, CO_2Me, CH_2I and H-10b), 3.06 and 2.97 (2 d, 2 H, *J* 15.6 Hz, H-2a,2b), 2.33 (d, 1 H, $J_{4a,4b}$ 14.4 Hz, H-4a) and 2.22 (dd, 1 H, H-4b); **22b** δ 7.40-7.15 (m, 15 H, 3 Ph), 4.84-4.65 and 4.61-4.51 (2 m, 6 H, 3 C*H*$_2$Ph), 4.47 (m, 1 H, H-5), 4.23 (m, 1 H, H-6), 4.16 (m, 1 H, H-9), 3.99 (m, 1 H, H-8), 3.85 (m, 1 H, H-10a), 3.80 (m, 1 H, H-7), 3.75-3.65 (m, 5 H, CO_2Me and CH_2I), 3.59 (m, 1 H, H-10b), 2.93, 2.73 and 2.36 (3 m, 4 H, H-2a,2b,4a,4b).

Powdered zinc (462 mg, 7.1 mmol) was added to a solution of crude **22ab** in 1:1 tetrahydrofuran–methanol (8 mL). A few drops of acetic acid were added and the mixture was stirred overnight at room temperature, then filtered over Celite and concentrated. The residue was purified by flash chromatography

(petroleum ether–ethyl acetate, 7:3) to give **23** (251 mg, 65%) as a syrup. ^{1}H NMR ($CDCl_3$): δ 7.37-7.22 (m, 15 H, 3 Ph), 5.02 and 4.97 (2 bd s, 2 H, CH_2=), 4.73, 4.72, 4.56 and 4.54 (4 d, 4 H, *J* 11.7 Hz, 2 C*H*$_2$Ph), 4.52 and 4.48 (2 d, 2 H, *J* 11.7 Hz, C*H*$_2$Ph), 4.23 (ddd, 1 H, $J_{4a,5}$ 9.7, $J_{4b,5}$ ~ $J_{5,6}$ ~ 4.6 Hz, H-5), 4.13-4.01 (m, 3 H, H-8,10a,10b), 3.82 (dd, 1 H, $J_{6,7}$ ~ 10 Hz, H-6), 3.71-3.60 (m, 2 H, H-7,9), 3.64 (s, 3H, CO_2Me), 3.16 and 3.11 (2 d, 2 H, *J* 15.8 Hz, H-2a,2b), 2.47 (dd, 1 H, $J_{4a,4b}$ 15.3 Hz, H-4a), 2.39 (dd, 1 H, H-4b); ^{1}H NMR ($CDCl_3$ + CCl_3CONCO): δ 8.67 (bd s, 1 H, NH), 7.39-7.26 (m, 15 H, 3 Ph), 5.17 (m, 1 H, H-6), 5.00 and 4.98 (2 bd s, 2 H, CH_2=), 4.76 and 4.64 (2 d, 2 H, *J* 12 Hz, C*H*$_2$Ph), 4.66 and 4.54 (2 d, 2 H, *J* 11.7 Hz, C*H*$_2$Ph), 4.55 (s, 2 H, C*H*$_2$Ph), 4.31 (m, 1 H, H-5), 4.20 (m, 1 H, H-9), 4.01 (dd, 1 H, $J_{9,10a}$ ~ 8, $J_{10a,10b}$ 11 Hz, H-10a), 3.94 (dd, 1 H, $J_{7,8}$ 2.8, $J_{8,9}$ 4.7 Hz, H-8), 3.90 (dd, 1 H, $J_{6,7}$ 5.7 Hz, H-7), 3.73 (dd, 1 H, $J_{9,10b}$ 3.9 Hz, H-10b), 3.64 (s, 3 H, CO_2Me), 3.14 and 3.08 (2 d, 2 H, *J* 15.6 Hz, H-2a,2b), 2.46 (dd, 1 H, $J_{4a,4b}$ 15.2, $J_{4a,5}$ 8.8 Hz, H-4a) and 2.34 (dd, 1 H, $J_{4b,5}$ 4.5 Hz, H-4b).

Methyl 5,9-Anhydro-6,7,8,10-tetra-O-*benzyl-2,3,4-trideoxy-3*-C-*methyl*-D-threo-L-ido *and* D-threo-L-gulo-*deconates* (**24**).

A solution of **14** (1.43 g, 2.25 mmol) and triethylamine (0.31 mL, 2.25 mmol) in ethanol (15 mL) was hydrogenated overnight in the presence of 5% palladium on charcoal at room temperature and atmospheric pressure. The mixture was filtered over Celite and the filtrate was concentrated to give **24** (1.43 g, 100%). ^{1}H NMR ($CDCl_3$): δ 7.37-7.23 (m, 20 H, 4 Ph), 4.79-4.44 (m, 8 H, 4 C*H*$_2$Ph), 4.10-3.50 (m, 7 H, H-5,6,7,8,9,10a,10b), 3.61 and 3.60 (2 s, 2x1.5 H, CO_2Me), 2.39-2.33 (m, 1 H, H-2), 2.20-2.02 (m, 2 H, H-2,3), 1.85-1.25 (4 m, 2 H, H-4), 0.97 and 0.91 (2 d, 2x1.5 H, *J* 6.6 and 6.1 Hz, Me).

5,9-Anhydro-6,7,8,10-tetra-O-*benzyl-2,3,4-trideoxy-3*-C-*methyl*-D-threo-L-ido *and* D-threo-L-gulo-*deconic acids* (**25**).

Lithium hydroxide monohydrate (327 mg, 7.8 mmol) was added to a solution of ester **24** (1 g, 1.57 mmol) in 3:1 methanol–water (16 mL). The mixture was heated at reflux for 1 h, then cooled, diluted with dichloromethane (100 mL) and washed with 10% aqueous hydrochloric acid (5 mL). The aqueous phase was extracted several times with dichloromethane and the combined organic extracts were concentrated to give **25** (950 mg, 97%) homogeneous in t.l.c. (dichloromethane–methanol, 19:1, R_f 0.42). ^{1}H NMR ($CDCl_3$): δ 0.92 and 0.87 (2 d, 2x1.5 H, *J* 6.1 and 6.6 Hz, Me).

Methyl 5,9-Anhydro-6,7,8,10-tetra-O-*benzyl-2,3,4-trideoxy-3*-C-*methyl*-D-glycero-D-ido-*dec-2-enonate* (**26***E* *and* **26***Z*).

A solution of β,γ-unsaturated ester **10** (246 mg, 0.39 mmol) in dry tetrahydrofuran (1 mL) containing piperidine (80 μL, 0.81 mmol) was heated under reflux for 72 h, then cooled, diluted with dichloromethane, washed with 0.1 M HCl and water, dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography (toluene–ethyl acetate, 19:1) to give first **26***Z* (41 mg, 17%); mp 78-80°C; $[\alpha]_D$ +46 (*c* 0.994, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.40-7.13 (m, 20 H, 4 Ph), 5.76 (bd s, 1 H, H-2), 4.95 and 4.47 (2 d, 2 H, *J* 10.7 Hz, C*H*$_2$Ph), 4.81 (m, 2 H, C*H*$_2$Ph), 4.79 and 4.69 (2 d, 2 H, *J* 11.7 Hz, C*H*$_2$Ph), 4.57 and 4.43 (2 d, 2 H, *J* 12.2 Hz, C*H*$_2$Ph), 4.40 (ddd, 1 H, $J_{4a,5}$ 11.7, $J_{4b,5}$ 3.1, $J_{5,6}$ 5.6 Hz, H-5), 3.86-3.75 (m, 3 H, H-6,7,9), 3.69-3.55 (m, 3 H, H-8,10a,10b), 3.64 (s, 3 H, CO_2Me), 3.34 (dd, 1 H, $J_{4a,4b}$ 14.2 Hz, H-4a), 2.95 (dd, 1 H, H-4b) and 1.92 (s, 3 H, Me); ^{13}C NMR ($CDCl_3$): δ 166.55 (C-1), 157.86 (C-3), 138.82, 138.42, 138.37 and

138.08 (4 C quat. arom.), 128.37-127.55 (20 C arom.), 117.59 (C-2), 82.28, 80.29, 78.07, 73.70 and 71.80 (C-5,6,7,8,9), 75.53, 74.92, 73.40 and 73.23 (4 CH_2Ph), 69.00 (C-10), 50.88 (CO_2CH_3), 28.69 (C-4) and 25.55 (Me). Anal. Calcd for $C_{40}H_{44}O_7$: C, 75.45; H, 6.96. Found: C, 75.35; H, 7.11.

26*E* was eluted next (164 mg, 67%); mp 76-78°C; $[\alpha]_D$ +49 (*c* 0.975, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.34-7.11 (m, 20 H, 4 Ph), 5.72 (bd s, 1 H, H-2), 4.93, 4.81 and 4.46 (3d, 4 H, *J* 11.2 Hz, 2 CH_2Ph), 4.73 and 4.60 (2 d, 2 H, *J* 11.7 Hz, CH_2Ph), 4.62 and 4.43 (2 d, 2 H, *J* 12.2 Hz, CH_2Ph), 4.24 (ddd, 1 H, $J_{4a,5}$ 11.2, $J_{4b,5}$ 2.5, $J_{5,6}$ 5.6 Hz, H-5), 3.78-3.57 (m, 6 H, H-6,7,8,9,10a,10b), 3.65 (s, 3 H, CO_2Me), 2.58 (dd, 1 H, $J_{4a,4b}$ 14.8 Hz, H-4a), 2.48 (dd, 1 H, H-4b) and 2.16 (d, 3 H, $J_{2,Me}$ 1 Hz, Me); ^{13}C NMR ($CDCl_3$): δ 166.99 (C-1), 156.98 (C-3), 138.76, 138.23, 138.19 and 138.11 (4 C quat. arom.), 128.68-127.72 (20 C arom.), 117.60 (C-2), 82.46, 80.03, 78.04, 72.48 and 71.64 (C-5,6,7,8,9), 75.67, 75.26, 73.65 and 73.63 (4 CH_2Ph), 68.80 (C-10), 50.97 (CO_2CH_3), 36.18 (C-4) and 18.56 (Me). Anal. Calcd for $C_{40}H_{44}O_7$: C, 75.45; H, 6.96. Found: C, 75.61; H, 6.95.

*5,9-Anhydro-6,7,8,10-tetra-*O*-benzyl-2,3,4-trideoxy-3-*C*-(2*R *and 2*S *hydroxy-2-phenylethyl)*-D-glycero-D-ido-*dec-2-enonic acid δ lactones* (**27**).

A 2.5 M solution of n-butyl lithium in hexane (36 μL, 90 μmol) was added under nitrogen to a solution of diisopropylamine (13 μL, 92 μmol) in tetrahydrofuran (200 μL) at -78°C. After 15 min at -78°C, a solution of **10** (40 mg, 60 μmol) in tetrahydrofuran (200 μL) was added. The yellow mixture was stirred for 1h at -78°C, then a solution of benzaldehyde (7 μL, 70 μmol) in tetrahydrofuran (400 μL) was added and the mixture was warmed to room temperature and stirred for an additional 5 h. Saturated aqueous NH_4Cl was added and the solution was extracted with ethyl acetate. The extract was dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography (petroleum ether–ethyl acetate, 4:1) to give first recovered **10** (13 mg, 34%), then **27** (25 mg, 59%) which crystallized; mp 110-115°C; ^1H NMR ($CDCl_3$): δ 7.40-7.22 (m, 23 H, arom.), 7.10 (m, 2 H, arom.), 5.95 and 5.93 (2 bd s, 2x0.5 H, H-2), 5.34 and 5.31 (2 dd, 2x0.5 H, *J* 3.7, 3.8, 12.3 and 12 Hz, H-12), 4.95-4.39 (4 m, 8 H, 4 CH_2Ph), 4.16 (ddd, 1 H, H-5), 3.79-3.52 (m, 6 H, H-6,7,8,9,10a,10b) and 2.76-2.33 (m, 4 H, H-4,11); ^{13}C NMR ($CDCl_3$): δ 164.61 (C-1), 157.84 and 157.69 (C-3), 138.53, 138.49, 138.42, 138.40, 137.93, 137.91, 137.87, 137.82, 137.65 and 137.58 (5 C quat. arom.), 128.62-127.75 and 126.08, 126.05 (25 C arom.), 118.21 and 117.82 (C-2), 82.02, 81.97, 79.73, 79.63, 77.69, 77.58, 71.69 and 71.65 (C-6,7,8,9), 78.74 and 78.71 (C-12), 75.55, 75.49, 75.14, 75.09, 73.89, 73.82 and 73.48 (4 CH_2Ph), 72.48 and 72.07 (C-5), 68.52 and 68.41 (C-10), 35.15, 34.86, 32.45 and 32.36 (C-4,11). Anal. Calcd for $C_{46}H_{46}O_7$: C, 77.72; H, 6.52. Found: C, 77.34; H, 6.52.

*5,9-Anhydro-6,7,8,10-tetra-*O*-benzyl-2,3,4-trideoxy-3-*C*-hydroxymethyl*-D-glycero-D-ido-*dec-2-enonic acid γ lactone* (**29**).

4-Methylmorpholine *N*-oxide (NMMO, 41 mg, 0.35 mmol) and osmium tetroxide (a few mg) were added to a solution of **10** (200 mg, 0.31 mmol) and pyridine (25 μL, 0.31 mmol) in 2:3:1 tetrahydrofuran–*tert*-butanol–water (1 mL). The mixture was heated at reflux for 24 h, then cooled, diluted with ether, washed with 20% aqueous $NaHSO_3$ and brine, dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography (petroleum ether–ethyl acetate, 13:7) to give **28** (148 mg, 74%) as a syrup. ^1H NMR ($CDCl_3$): δ 4.21 and 4.01 (2 d, 1.42 H, *J* 9.8 Hz, H-11) and 4.11 and 3.89 (2 d, 0.58 H, *J* 9.6 Hz, H-11).

Triethylamine (260 μL, 1.86 mmol) and methanesulfonyl chloride (72 μL, 0.92 mmol) were successively

added to a solution of **28** (148 mg, 0.23 mmol) in dichloromethane (3 mL). The mixture was stirred for 3 h under nitrogen, then diluted with dichloromethane, washed with brine, dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography (petroleum ether–ethyl acetate, 7:3) to give **29** (123 mg, 86%) which crystallized from ethanol; mp 113-115°C; $[\alpha]_D$ +44 (*c* 0.985, $CHCl_3$). ^1H NMR (C_6D_6): δ 7.10-6.75 (m, 20 H, 4 Ph), 5.41 (bd s, 1 H, H-2), 4.63 and 4.26 (2 d, 2 H, *J* 11.2 Hz, CH_2Ph), 4.57 (m, 2 H, CH_2Ph), 4.16 and 3.91 (2 d, 2 H, *J* 11.6 Hz, CH_2Ph), 4.06 and 3.98 (2 d, 2 H, CH_2Ph), 3.93 and 3.81 (2 dd, 2 H, $J_{2,11a}$ ~ $J_{2,11b}$ ~ 1, $J_{11a,11b}$ 17.5 Hz, H-11a,11b), 3.48 (dt, 1 H, $J_{4,5}$ ~ 7.2, $J_{5,6}$ ~ 5.9 Hz, H-5), 3.38-3.13 (m, 6 H, H-6,7,8,9,10a,10b) and 1.91 (d, 2 H, H-4a,4b); ^{13}C NMR (C_6D_6): δ 171.81 (C-1), 164.88 (C-3), 137.93, 137.66, 137.30 and 137.15 (4 C quat. arom.), 126.96-126.44 (20 C arom.), 116.18 (C-2), 80.76, 78.70, 77.11, 71.26 and 70.99 (C-5,6,7,8,9), 73.93, 73.72, 72.32, 72.29 and 71.43 (4 CH_2Ph, C-11) and 23.39 (C-4). Anal. Calcd for $C_{39}H_{40}O_7$: C, 75.46; H, 6.49. Found: C, 75.21; H, 6.54.

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