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Claisen Rearrangement of Carbohydrate-Derived Precursors Towards Highly Functionalized Cyclooctenones with L-*xylo*, D-*arabino* and L-*lyxo* Configuration and Their Diastereoselective Transformations

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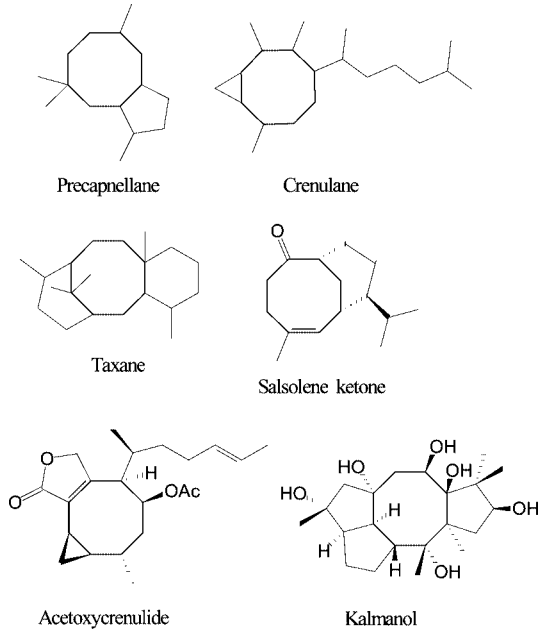
D-Glucose and D-mannose have been transformed into precursors incorporating allyl vinyl ether substructures. Both thermally and catalytically, these cyclic allyl vinyl ethers could be converted into the corresponding Claisen rearrangement products. The conformations of these enantiopure 5-cyclooctenones were studied by NMR spectroscopy and X-ray crystallography. They proved to be versatile substrates for highly stereo- and regioselective modifications.

Introduction

During the past 20 years a constantly growing number of chiral natural products containing eight-membered carbocycles have been isolated and structurally elucidated.[1] Unfortunately, interest in the synthesis of challenging natural products characterized by an eight-membered ring skeleton remained relatively low-key, probably due to problems associated with unfavourable thermodynamic factors in conventional ring-closing methods. Additionally, the known problems such as ring strain and transannular interactions represented a major drawback, although many of these compounds exhibit interesting conformational properties[2] in conjunction with biological activity. However, much progress has been made in designing synthetic approaches towards cyclooctanoid systems in recent years.[3] Scheme 1 displays a selection of both carbocyclic frameworks (precapnellane, crenulane, taxane) as well as highly functionalized compounds (salsolene ketone, acetoxycrenulide, kalmanol) featuring an eight-membered carbon ring structure.[4]

In the natural product synthesis of such complex chiral compounds, a convergent synthetic strategy may often be more advantageous than linear approaches, provided that the employed building blocks can be obtained in sufficient yields and high optical purity.

In previous communications[5] we reported on an efficient method for the construction of eight-membered rings from carbohydrate derivatives by ring enlargement using the Claisen rearrangement.[6] Further investigation of this approach appeared worthwhile to us since the ring enlargement of 2-methylene-6-vinyltetrahydropyrans originally developed by Paquette and co-workers[7] in general represents a methodical contribution to organic synthesis for the construction of medium-sized ring compounds. Moreover, the Claisen rearrangement, including its numerous modifications, has proved outstandingly efficient in natural product synthesis.[8] The application of the aluminium-catalyzed Claisen rearrangement[9] in carbohydrate chemistry has also been successfully employed by Sinaÿ[10] and van Boom[11] and their co-workers. On the other hand, Hanna and coworkers transformed properly functionalized carbohydrate derivatives into polyoxygenated cyclooctenes by ring-closing metathesis.[12]



Scheme 1. Natural product frameworks and isolated compounds.

Besides the optimization of the most critical step within this approach, the thermic Claisen rearrangement, alterna-

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tive protecting groups were employed and synthetic studies extended to monosaccharides other than D-glucose. Another objective was the introduction of additional oxygenated functionalities into the carbocyclic framework of these enantiopure building blocks. Thus, diastereoselective epoxidations, reductions, dihydroxylations and ring anellations were performed to demonstrate the outstanding suitability of sugar-derived cyclooctenones as substrates in synthetic undertakings with particular emphasis on stereoselectivity. Moreover, the potential suitability of these compounds or derivatives for use as carbohydrate-based drugs or carbohydrate mimetics[13] is currently of increasing interest owing to their unique conformational properties.

Results and Discussion

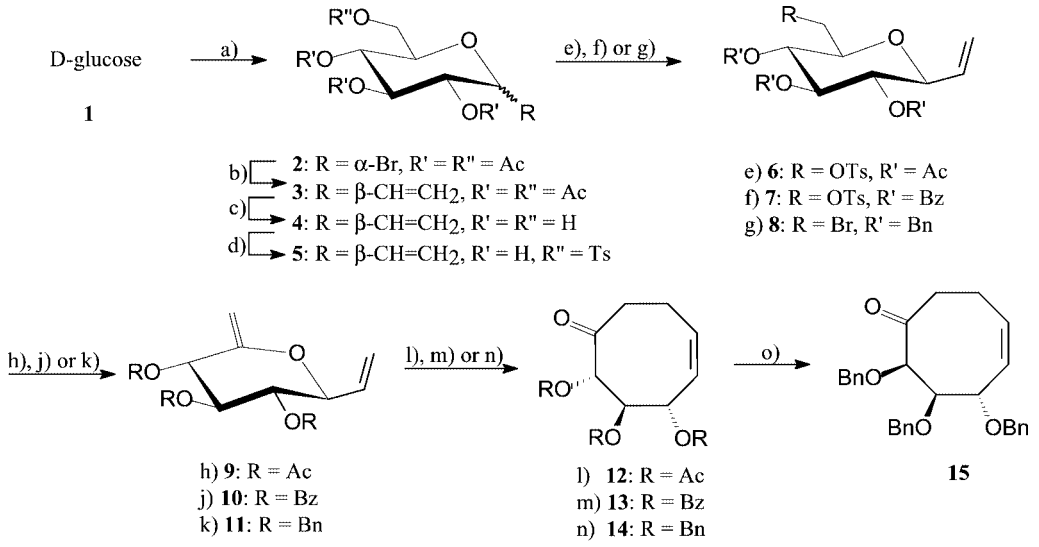
A vinyl group was introduced directly onto the anomeric carbon atom of D-glucose (**1**) by reaction of vinylmagnesium bromide with the peracetylated α-bromide **2** to give **3** (Scheme 2).[14]

As this reaction requires a large excess of the Grignard reagent and usually delivers an anomeric mixture of *C*-glycosidic products (ratio α/β = 1:5) in moderate yields (up to 45%), alternative methods were investigated. Most of these techniques, including reactions of perbenzylated derivatives with anomeric leaving groups and vinylmagnesium bromide as well as the reaction of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide with an organocuprate[15] $(CH_2CH)_2$-CuLi, led mostly to elimination products with glycal structures and were therefore unsatisfactory. However, the anomeric mixture could be separated by repeated recrystallization to obtain the pure β anomer of **3**. After deacetylation[16] to give **4** and selective tosylation to give **5**, both ester and ether protecting groups were introduced to determine the relative stability and reactivity during the planned Claisen rearrangement step. Compounds **6** and **7** with a primary tosylate underwent an elimination reaction following a standard protocol, that is, substitution of the tosylate by an iodide and elimination under basic conditions with 1.8-diazabicyclo[5.4.0]undec-7-en (DBU) in DMSO[17] to give **9** and **10** in 52 and 53% yields, respectively. Compound **8** was alternatively treated with silver fluoride in pyridine[18] to give **11** in 90% yield. The clear superiority of this latter procedure can probably be attributed to the strong basic properties of the fluoride anion in polar aprotic pyridine. In neither case did isomerization to the internal enol ether occur.

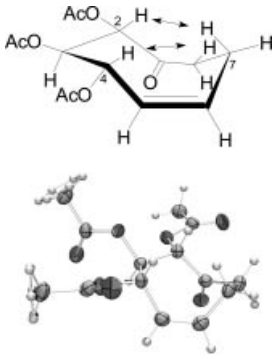
The thermal rearrangement of precursor **9**, which yielded cyclooctenone **12**, was initially performed under different reaction conditions: toluene (110 °C, 15 h, 33%), xylene (145 °C, 15 h, 73%) and nitrobenzene (210 °C, 1 h, 85%). Compound **10** was heated in xylene overnight at 145 °C to give **13** in 60% yield. Since the best results were achieved with shorter reaction times and higher temperatures, **11** was heated in nitrobenzene at 185 °C for one hour to give **14** in 81% yield.

The X-ray structure of ketone **12** revealed a boat-chair conformation with all three acetates in pseudoequatorial positions, which is in good accordance with the results obtained from NOE spectra; the distinct intramolecular interactions between 2-H, 4-H and 7-H indicate at least a closely related conformation in solution (Scheme 3). The same NO effects were observed for compounds **13** and **14**, likewise suggesting a boat-chair-like geometry.

Treatment of the benzylated ketone **14** with DBU in THF (room temp., 7 days, 80%) led to an access of cyclooctenone **15** with L-*lyxo* configuration. In contrast, acylated 5-cyclooctenones such as **12** and **13** tend to undergo elimination reactions in basic media to give the corresponding



Scheme 2. Reagents and conditions: a) ref.[35]; b) i. CH_2=CHMgBr, THF; ii. Ac_2O, py, 0 °C to room temp., 25%; c) i. NaOMe, MeOH; ii. Amberlite IR-120 H^+, 86%; d) TsCl, py, 49%; e) Ac_2O, py, 0 °C to room temp., 88%; f) BzCl, py, 0 °C to room temp., 89%;·g) i. BnBr, NaH, DMF; ii. NaBr, DMF, 80 °C, 61%; h) i. TBAI, NaI, DMSO, 80 °C; ii. DBU, DMSO, 80 °C, 53%; j) i. TBAI, NaI, DMSO, 80 °C; ii. DBU, DMSO, 80 °C, 52%; k) AgF, py, 90%; l) $PhNO_2$, 210 °C, 1 h, 85%; m) $C_6H_4(CH_3)_2$, 145 °C, 15 h, 60%; n) $PhNO_2$, 185 °C, 1 h, 81%; o) DBU, THF, 80%.



Scheme 3. X-ray structure of **12**, boat-chair conformation and NOE interactions.

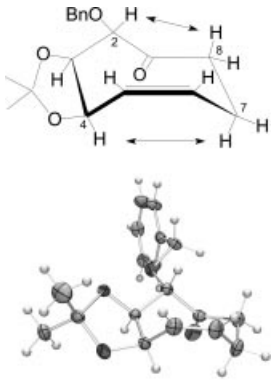
α,β-unsaturated ketones. A considerable conformational difference between **14** and **15** is rather unlikely since only minor spectral changes, including the absence of a NOE between 2-H and 4-H/7-H, were observed. Provided that a boat-chair-like conformation also applies to **15**, it appears a paradox that the benzyl residue at C-2 should prefer the pseudoaxial position. Presumably, repulsive electronic interactions between the benzyl ether oxygen atom at C-2 and the carbonyl oxygen atom within the boat-chair conformation may be a rationale for this unusual finding.

The synthesis of a second 5-cyclooctenone starting from D-mannose (**16**) again involved a Grignard reaction with vinylmagnesium bromide and subsequent deacetylation under analogous conditions as used for the glucose derivative (Scheme 4).

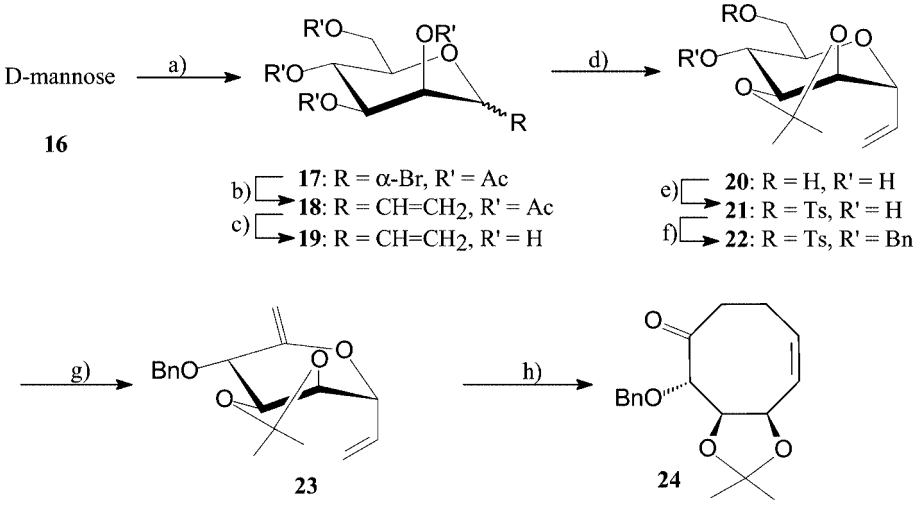
Note that the anomeric mixture obtained (**18**, ratio α/β = 1:2.5, assigned by NOE analysis) actually contained more of the β-*C*-vinyl-mannopyranoside. As the amount of the α anomer obtained was only slightly larger than that obtained in the synthesis of **3**, the anomeric effect[19] appears to be largely irrelevant. In contrast, the minimization of 1,3-diaxial interactions seems to be responsible for the stereodirecting effect during the Grignard reaction. Compound **19** was then converted into the acetonide **20**. At this stage, partial separation of the anomers was possible and the synthesis was continued with the pure α anomer to determine whether it would also fulfil the steric requirements necessary to undergo the final rearrangement step.[20] After selective tosylation and benzylation, **22** was treated with NaI/DBU in DMSO to give the mannopyranoside precursor **23**.

In order to minimize decomposition processes at elevated temperatures and to guarantee effective energy transfer onto the substrate, *n*-decane was chosen as solvent because of its higher heat capacity and toluene was added to improve solubility. The Claisen rearrangement was then performed under microwave irradiation for 1 hour at 185 °C (300 W) to give **24** in 80% yield.

In contrast to **12**, the X-ray analysis of ketone **24** actually revealed a twist-boat-chair conformation due to the (4*R*) configuration and the fused 1,3-dioxolane ring (Scheme 5). NOE experiments confirmed the same conformation in solution with NOEs between 4-H and 7-H as well as 2-H and 8-H showing that all three oxygenated residues adopt pseudoequatorial orientations.



Scheme 5. X-ray structure of **24**, twist-boat-chair conformation and NOE interactions.



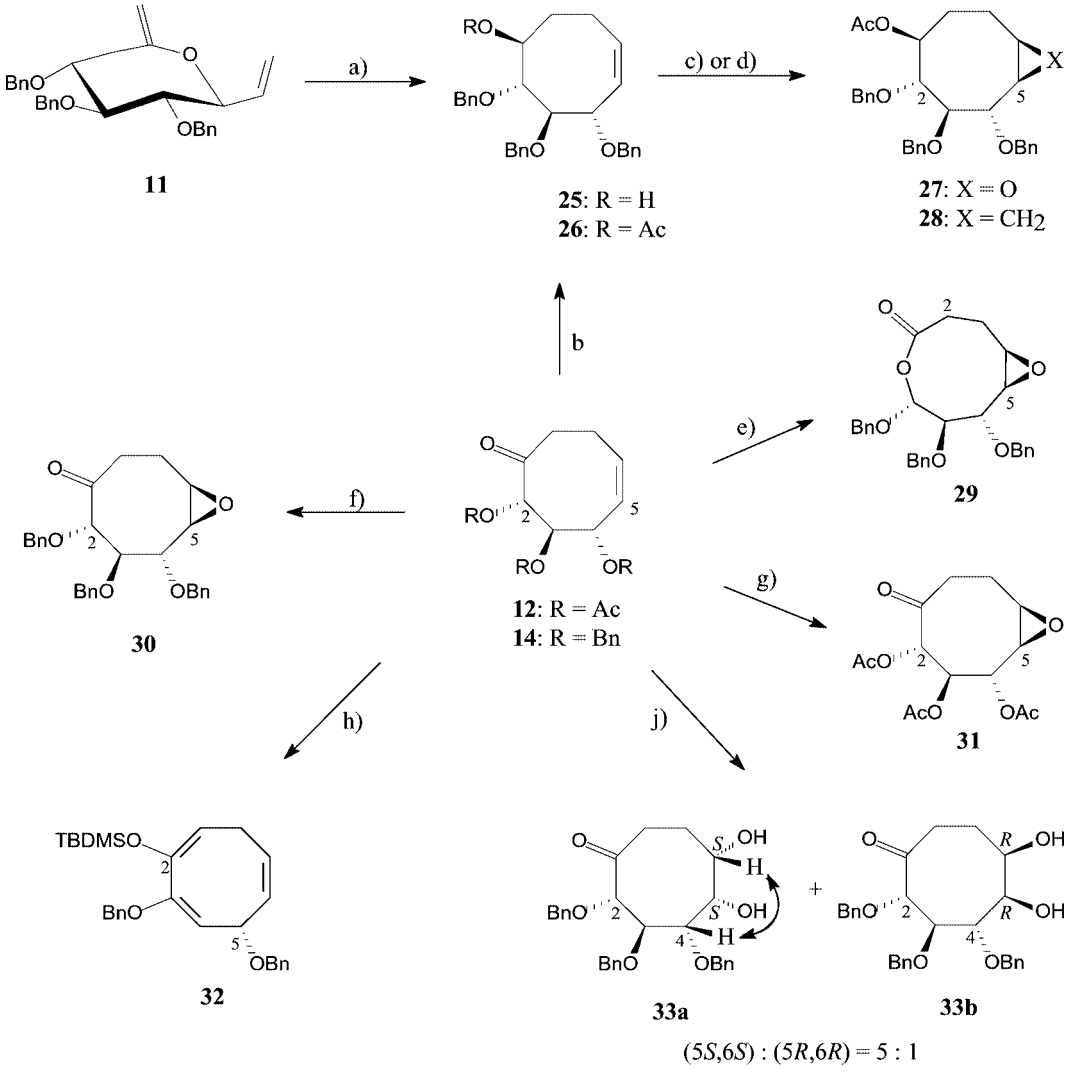
Scheme 4. Reagents and conditions: a) ref.[36]; b) i. CH_2=CHMgBr, THF, 45%; ii. Ac_2O, py, 0 °C to room temp.; c) i. NaOMe, MeOH, 100%; ii. Amberlite IR-120 H^+; d) $CH_3C(OMe)_2CH_3$, cat. *p*TsA; e) TsCl, py; f) BnBr, NaH, DMF, 77%; g) i. TBAI, NaI, DMSO, 80 °C; ii. DBU, DMSO, 80 °C, 78%; h) *n*-decane/$PhCH_3$ (ratio 4:1), 185 °C, microwave 80%.

The use of triisobutylaluminium (TIBAL)[21] as a Lewis acid catalyst in the Claisen rearrangement of cyclic substrates was originally introduced by Paquette el al.[9] Sinaÿ[10] and van Boom[11] and their co-workers converted several benzylated carbohydrate precursors into the corresponding rearrangement products. Treatment of compound **11** with TIBAL (DCM, room temp., argon) led to the diastereomeric alcohol **25** with no detection of the other diastereomer (Scheme 6).

TIBAL can thereby reduce the first-formed cyclooctenone **14** stereoselectively by transferring one of its β-hydrogen atoms with concomitant elimination of isobutene. On the other hand, the mannose precursor **23** completely failed to react under similar reaction conditions. As the number of oxygen atoms in both substrates is equal, use of the aluminium catalyst is probably incompatible with *cis* arrangements of oxygenated functionalities or even the 1,3-dioxolane ring due to chelate complex formation.

The same diastereomeric alcohol **25** and the corresponding acetate **26** could alternatively be obtained by stereospecific reduction of ketone **14** with $LiAlH_4$ in THF and, for the latter, by subsequent acetylation with acetic anhydride. The absolute configuration of the new stereogenic centre could be deduced from the large coupling constant between 1-H and 2-H ($^3J_{1,2}$ = 8.5 Hz in **25**), indicating a *trans* arrangement. van Boom and co-workers reported a 1,3-diaxial NOE interaction between 1-H and 7-H in a corresponding derivative, however, we could not verify this.[22] An X-ray analysis of a closely related compound confirmed the equatorial orientation of the newly generated hydroxy function after the TIBAL-promoted Claisen rearrangement.[23]

Epoxidation with *m*-chloroperbenzoic acid (MCPBA) and cyclopropanation with the Simmons–Smith reaction[24] (Furukawa modification[25]) of the functionalized cyclooctenone derivative **26** furnished the optically pure diastereomers **27** and **28**, respectively. This indicates a



Scheme 6. TIBAL-promoted Claisen rearrangement and stereoselective modifications. Reagents and conditions: a) iBu$_3$Al, DCM, 57%; b) $LiAlH_4$, THF, 0 °C to room temp., 88%; i. $LiAlH_4$, THF, 0 °C to room temp.; ii. Ac_2O, py, 70%, resp.; c) MCPBA, DCM, 58%; d) CH_2CI_2, Et_2Zn, DCM, 89%; e) MCPBA, DCM, 68%; f) DMD, acetone, 70%; g) MCPBA, DCM, 84%; h) i. LDA, THF, –78 °C, 1 h; ii. TBDMSCl, THF, –78 °C to room temp., 30%; j) cat. OsO_4, NMO, aq. acetone, tBuOH, 70%.

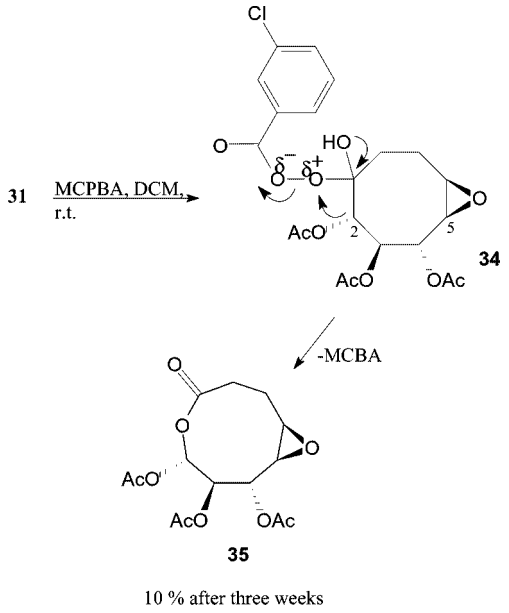
strict diastereofacial differentiation by both the peracid and the carbenoid during the attack on the double bond. The configurations could be easily deduced from the large geminal coupling constants (**27**: $^3J_{4,5}$ = 9.1 Hz; **28**: $^3J_{1,2}$ = 10.7 Hz). In the case of the cyclopropanation reaction, the *trans* diastereoselectivity appears a paradox since one would have rather expected a *cis* arrangement due to the directing effect of the allylic oxygen.[26] On the other hand, the acetoxy group was estimated to be flexible enough to exert a stereodirecting effect on the (iodomethyl)zinc reagent; thus, it may be concluded that the diastereoselectivity is promoted by a matched pair of steric and electronic interactions.

Equally interesting results were obtained by epoxidation of the cyclooctenones **12** and **14**. The latter compound reacted with MCPBA to give, as expected, the epoxidized lactone **29**. Suppression of the Baeyer–Villiger rearrangement[27] could be achieved by using dimethyldioxirane (DMD)[28] to give **30**. Again, in both cases the oxirane ring was introduced from the sterically less congested side of the π bond to give only one diastereomeric epoxide. The large coupling constants indicated once again a *trans* arrangement of the epoxide ring to the adjacent benzyl ether (**29**: $^3J_{5,6}$ = 9.2 Hz; **30**: $^3J_{4,5}$ = 9.2 Hz).

Treatment of ketone **12** with MCPBA unexpectedly furnished only the epoxidized ketone **31** without lactone formation. Examples of cyclic α-acetoxy ketones treated with MCPBA are scarce,[29] but usually the formation of the Baeyer–Villiger lactone is observed. Since the acetoxy group is reportedly an overall electron-donating function towards a cationic centre,[30] it should even promote the migration of the secondary carbon.

With the objective of detecting perhaps at least small amounts of the epoxidized lactone, **12** was treated with 2.2 equiv. MCPBA in CD_2Cl_2 in an NMR tube. An initially recorded ^{1}H NMR spectrum still showed the double-bond protons dominating together with signals of the epoxide slowly growing over several days. After one week, nearly all of **12** had reacted to give the epoxide **31** and the ^{13}C NMR spectrum still showed the signal of a quaternary carbon atom at δ = 204 ppm characterizing a ketone. However, small amounts of the epoxidized lactone **35** (approx. 10% after three weeks) were indeed formed. Most of the examples in the literature describe the reaction of α-acetoxy ketones incorporated into a six-membered ring with no further adjacent functionalities. Hence it may be reasoned that the remaining two acetoxy groups in **12** have an additional preponderating impact on the migratory tendency of the α-acetoxy group, thus largely suppressing the Baeyer–Villiger oxidation in this specific case. This appears plausible since the migration step of C-2 towards the oxygen in the α-hydroxyperoxy ester ("Criegee intermediate") **34** possesses nucleophilic character (Scheme 7).[31]

Related examples of distant effects are known in carbohydrate chemistry and involve for instance the deactivating effect of electron-withdrawing acetoxy groups relative to benzyloxy groups in glycosyl acceptors.[32] This often results in lower yields during glycosylation reactions due to the



Scheme 7. Heterolytic cleavage of the peroxidic bond and nucleophilic migration of C-2 in the formation of epoxidized lactone **35**.

significantly reduced nucleophilicity of neighbouring hydroxy functions.

The introduction of further functionalities into the carbocyclic framework was figured to be feasible by using strong, sterically hindered bases such as lithium diisopropylamide (LDA) followed by trapping the kinetic enolate as a silyl ether. Indeed it was possible to obtain the silyl enol ether **32** from **14**, but an accompanying elimination of benzyl alcohol could not be suppressed due to the high acidity of 2-H. Other bases like the slightly less basic, but more sterically hindered lithium hexamethyldisilazide (LiHMDS) did not prove to be more effective.

For the direct introduction of hydroxy functionalities, **14** was treated with catalytic amounts of osmium tetraoxide and equimolar amounts of *N*-methylmorpholine *N*-oxide.[33] The diastereomeric mixture obtained (ratio **33a/33b** = 5:1) could be partially separated. Note that the ^{1}H NMR spectrum of **33b** compared with **33a** is characterized by a marked shift of 4-H and 6-H to a lower field (approx. 0.6–0.7 ppm). Since the coupling constant between 2-H and 3-H in both diastereomers is much higher ($^3J_{2,3}$ = 8.7 Hz) than that for **14** ($^3J_{2,3}$ = 4.4 Hz) a conformational change is likely. Ketone **33a** was assigned as the (5*S*,6*S*) diastereomer since 5-H appears as a broad signal, which is a clear indication that it is flanked by two *cis* protons. Additionally, only the NOE spectrum of **33a** displays spatial proximity between 4-H and 6-H indicating a 1,3-diaxial interaction.

Conclusions

This contribution has demonstrated that monosaccharides are particularly suitable starting materials for the construction of enantiopure, highly oxygenated eight-membered rings in a limited number of synthetic steps. The crys-

tallographic structures of the glucose- and mannose-derived 5-cyclooctenones reveal interesting conformational properties and differences for the first time. The spatial arrangements of oxygenated functionalities are of particular interest with respect to carbohydrate mimetics or carbohydrate-based pharmaceuticals. Moreover, the newly generated double bond and carbonyl group offer expedient possibilities for further chemical transformations which could be demonstrated in various diastereoselective reactions. Last but not least, the largely suppressed Baeyer–Villiger rearrangement of compound **12** compared with compound **14** substantiates the nucleophilic character of the migration step in this reaction.

Experimental Section

General Remarks: Solvents were purified and dried according to standard procedures. The microwave experiment was performed in a CEM microwave system (Discover, 300 W maximum power output). The petroleum ether used was of b.p. 50–70 °C. TLC was performed on aluminium sheets coated with silica gel 60 (Merck or Macherey–Nagel) with UV detection at 254 nm and by heating with H_2SO_4 (5% in EtOH). Flash chromatography was carried out on silica gel 60 (0.04–0.063 mm; Merck, Macherey–Nagel or ICN). NMR spectra were recorded with a Bruker AMX-400 NMR spectrometer (^{1}H: 400 MHz; ^{13}C: 100 MHz) and analyzed with the respective solvent peaks as references. Mass spectra were recorded with a Bruker Biflex III (MALDI-TOF, positive reflection mode, matrix: 2,5-dihydroxybenzoic acid) and a MAT 311A (electron-impact ionization EII at 70 eV, direct inlet). Melting points were determined with a Leitz apparatus and are uncorrected. The optical rotations were measured on a Perkin–Elmer 243 or 341 polarimeter at 20 °C. Concerning nomenclature, in most cases the sugar nomenclature[34] was applied except for the more complex oligohydroxycyclooctene derivatives.

4,5,6,8-Tetra-*O*-acetyl-3,7-anhydro-1,2-dideoxy-D-*glycero*-D-*gulo*-oct-1-enitol (3): A solution of freshly prepared vinylmagnesium bromide (120 mmol) in dry THF (60 mL) was treated dropwise with a solution of α-acetobromoglucose[35] (**2**, 4.11 g, 10 mmol) in THF (50 mL). After the exothermic reaction was complete the solution was refluxed for five hours, then poured onto crushed ice and the organic phase separated. The aqueous phase was neutralized with acetic acid, then extracted twice with ethyl acetate and the combined organic phases concentrated under reduced pressure. The residue was dissolved in anhydrous pyridine (100 mL) and treated with acetic anhydride (150 mL) whilst stirring at room temperature overnight. Codistillation with toluene gave a residue which was purified on silica gel with petroleum ether/ethyl acetate (3:1). The pure material was recrystallized from diisopropyl ether to give compound **3** (890 mg, 25%) as colourless crystals. $C_{16}H_{22}O_9$, M = 358.3. $[\alpha]_D^{20}$ = +11.1 (c = 0.5, chloroform) [ref.[14] +14.1 (c = 1, chloroform)]; m.p. 98 °C (ref.[14] 103 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.00, 2.01, 2.04, 2.09 (4 s, 4×3 H, 4 Ac), 3.71 (ddd, $^3J_{6,7}$ = 9.7, $^3J_{7,8a}$ = 2.3, $^3J_{7,8b}$ = 4.9 Hz, 1 H, 7-H), 3.37 (dd, $^3J_{2,3}$ = 7.1, $^3J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 4.14 (dd, $^3J_{7,8a}$ = 4.9, $^2J_{8a,\ 8b}$ = 12.5 Hz, 1 H, 8a-H), 4.25 (dd, $^3J_{7,8b}$ = 4.9, $^2J_{8a,8b}$ = 12.5 Hz, 1 H, 8b-H), 4.94 (dd, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 5.09 (dd , $^3J_{5,6}$ = $^3J_{6,7}$ = 9.7 Hz, 1 H, 6-H), 5.23 (dd t, $^3J_{4,5}$ = $^3J_{5,6}$ = 9.7 Hz, 1 H, 5-H), 5.30 (m, 1 H, 1a-H), 5.36 (dd, m, 1 H, 1b-H), 5.75 (ddd, 1 H, 2-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.50, 20.55, 20.60, 20.66 (4 C, Ac), 62.14 (1 C, C-8), 68.38, 71.09, 73.82, 75.47, 79.34 (5 C, C-3, C-4, C-5, C-6, C-7), 120.00 (1 C, C-1), 133.08 (1 C, C-2), 169.38–170.64 (4 C, acetyl-CO_2) ppm.

3,7-Anhydro-1,2-dideoxy-D-*glycero*-D-*gulo*-oct-1-enitol (4): A solution of compound **3** (660 mg, 1.8 mmol) in dry methanol (20 mL) was chilled, then treated with sodium methoxide in methanol (0.7 mL, 1 N) and then gradually warmed to room temperature. After ester cleavage (TLC: dichloromethane/methanol, 10:1) the solution was neutralized with ion exchange resin (Amberlite IR-120 H^+), filtered and under reduced pressure concentrated to dryness. The residue was purified by column chromatography (dichloromethane/methanol, 20:1) to give **4** (300 mg, 86%) as a yellow syrup. $C_8H_{14}O_5$, M = 190.2. $[\alpha]_D^{20}$ = +6.3 (c = 0.2, methanol). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.87 (ddd, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 3.03 (dd, $^3J_{4,5}$ = $^3J_{5,6}$ = 9.4 Hz, 1 H, 5-H), 3.07–3.17 (m, 2 H, 8a-H, 8b-H), 3.41 (dd, $^3J_{5,6}$ = 9.4, $^3J_{6,7}$ = 11.7 Hz, 1 H, 6-H), 3.48 (dd, $^3J_{2,3}$ = 5.1, $^3J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 3.66 (ddd, $^3J_{6,7}$ = 11.7, $^3J_{7,8a}$ = 2.0, $^3J_{7,8b}$ = 5.6 Hz, 1 H, 7-H), 4.40 (m, 1 H, 8-OH), 4.84, 4.86, 4.89 (3 d, 3×1 H, 3 OH), 5.11, 5.28 (2 m, 2×1 H, 1a-H, 1b-H), 5.88 (ddd, 1 H, 2-H) ppm.

3,7-Anhydro-1,2-dideoxy-8-*O*-(4-tolylsulfonyl)-D-*glycero*-D-*gulo*-oct-1-enitol (5): A solution of compound **4** (200 mg, 1.1 mmol) in anhydrous pyridine (10 mL) was ice-cooled and treated with 4-toluenesulfonyl chloride (230 mg, 1.2 mmol), then gradually warmed to room temperature and stirred for two days. After TLC (dichloromethane/methanol) indicated the termination of the reaction the mixture was codistilled with toluene under reduced pressure to dryness. The residue was purified by column chromatography (dichloromethane/methanol, 20:1 to 10:1) and recrystallized from ethyl acetate to give **5** (176 mg, 49%) as colourless crystals; m.p. 125 °C. $[\alpha]_D^{20}$ = +0.4 (c = 1.0, acetone). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 2.23 (s, 3 H, CH_3), 2.89–2.94, 3.10–3.15, 3.21–3.25 (3 m, 3×1 H, 4-H, 5-H, 6-H), 3.32–3.37 (m, 1 H, 7-H), 3.47–3.51 (m, 1 H, 3-H), 3.99–4.08 (m, 2 H, 8a-H, 8b-H), 4.21–4.26 (m, 3 H, 3 OH), 4.97–5.00, 5.08–5.13 (2 m, 2×1 H, 1a-H, 1b-H), 5.73–5.81 (m, 1 H, 2-H), 7.34, 7.68 (2 d, 2×2 H, Ar) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 21.03 (1 C, Me), 70.48 (1 C, C-8), 74.40, 74.51, 77.45, 78.93, 79.99 (5 C, C-3, C-4, C-5, C-6, C-7), 115.86 (1 C, C-1), 128.24–145.25 (7 C, C-2, Ar) ppm. $C_{15}H_{20}O_7S$ (344.4): calcd. C 52.32, H 5.85; found C 50.93, H. 5.76.

4,5,6-Tri-*O*-acetyl-3,7-anhydro-1,2-dideoxy-8-*O*-(4-tolylsulfonyl)-D-*glycero*-D-*gulo*-oct-1-enitol (6): A solution of compound **5** (692 mg, 2.01 mmol) in anhydrous pyridine (20 mL) was treated under ice-cooling with acetic anhydride (10 mL), then warmed to room temperature and left for completion (TLC: petroleum ethyl/ethyl acetate, 2:1). Work up was carried out by codistillation with toluene and subsequent column chromatographic purification (petroleum ether/ethyl acetate, 5:1) and recrystallization from ethanol to give **6** (830 mg, 88%) as colourless crystals. $C_{15}H_{20}O_7S$, M = 344.4; m.p. 150–155 °C. $[\alpha]_D^{20}$ = +27.0 (c = 1.0, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.91, 1.92, 1.93 (3 s, 3×3 H, 3 Ac), 2.38 (s, 3 H, CH_3), 3.66 (ddd, $^3J_{6,7}$ = 9.5, $^3J_{7,8a}$ = 5.6, $^3J_{7,8b}$ = 2.8 Hz, 1 H, 7-H), 3.72 (dd, $^3J_{2,3}$ = 6.9, $^3J_{3,4}$ = 9.5 Hz, 1 H, 3-H), 3.99, 4.05 (2 dd, $^3J_{7,8a}$ = 5.6, $^3J_{7,8b}$ = 2.8, $^2J_{8a,8b}$ = 11.0 Hz, 2×1 H, 8a-H, 8b-H), 4.77, 4,87, 5.11 (3 dd, $^3J_{3,4}$ = $^3J_{4,5}$ = $^3J_{5,6}$ = $^3J_{5,6}$ = $^3J_{6,7}$ = 9.5 Hz, 3×1 H, 4-H, 5-H, 6-H), 5.21 (2 m, 2×1 H, 1a-H, 1b-H), 5.52–5.60 (m, 1 H, 2-H), 7.30, 7.71 (2 d, 2×2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.53, 19.60, 19.65 (3 C, Ac), 20.65 (1 C, Me), 66.90 (1 C, C-8), 67.73, 70.02, 72.66, 74.12, 78.14 (5 C, C-3, C-4, C-5, C-6, C-7), 118.83 (1 C, C-1), 127.11–144.03 (7 C, C-2, Ar) 168.39, 168.46, 169.30 (3 C, 3 acetyl-CO_2) ppm. $C_{21}H_{26}O_{10}S$ (470.5): calcd. C 53.61, H 5.57; found C 53.04, H 5.57.

3,7-Anhydro-4,5,6-tri-*O*-benzoyl-1,2-dideoxy-8-*O*-(4-tolylsulfonyl)-D-*glycero*-D-*gulo*-oct-1-enitol (7): A solution of compound **5**

(173 mg, 0.5 mmol) in a mixture of anhydrous pyridine and dichloromethane (10 mL, 1:1) was treated at 0 °C with benzoyl chloride (0.2 mL, 1.7 mmol) and then warmed to room temperature. After completion the reaction mixture was dried by codistillation with toluene, the residue purified by column chromatography (petroleum ether/ethyl acetate, 3:1) and recrystallized from ethanol to give **7** (293 mg, 89%) as colourless crystals. $C_{36}H_{32}O_{10}S$, M = 656.7; m.p. 155 °C. $[\alpha]_D^{26}$ = +23.0 (c = 1.0, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H, CH_3), 3.93–3.98 (m, 1 H, 7-H), 4.04 (dd, $^3J_{2,3}$ = 6.6, $^3J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 4.07, 4.17 (2 dd, $^3J_{7,8a}$ = 6.1, $^3J_{7,8b}$ = 2.5, $^2J_{8a,8b}$ = 11.2, 2×1 H, 8a-H, 8b-H), 5.15, 5.25 (2 d, $^3J_{1a,2}$ = 10.7, $^3J_{1b,2}$ = 17.3 Hz, 2×1 H, 1a-H, 1b-H) 5.27, 5.33, 5.75 (3 dd, $^3J_{3,4}$ = $^3J_{4,5}$ = $^3J_{5,6}$ = $^3J_{5,6}$ = $^3J_{6,7}$ = 10.0 Hz, 3×1 H, 4-H, 5-H, 6-H), 5.66–5.77 (m, 1 H, 2-H), 7.14–7.83 (m, 19 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.60 (1 C, Me), 67.32 (1 C, C-8), 68.30, 70.74, 72.92, 74.78, 78.50 (5 C, C-3, C-4, C-5, C-6, C-7), 118.99 (1 C, C-1), 127.08–143.86 (25 C, C-2, Ar), 164.14, 164.79 (3 C, 3 benzoyl-CO_2) ppm. $C_{36}H_{32}O_{10}S$ (656.7): calcd. C 65.84, H 4.91; found C 65.33, H. 4.89.

3,7-Anhydro-4,5,6-tri-*O*-benzyl-8-bromo-1,2,8-trideoxy-D-*glycero*-D-*gulo*-oct-1-enitol (8): A solution of compound **5** (445 mg, 1.3 mmol) in DMF (10 mL) was treated with benzyl bromide (1.3 mL, 10.4 mmol) and sodium hydride (225 mg, 60% in paraffin, ca. 7.8 mmol) and stirred at room temperature for 2 h. Then sodium bromide (1.3 mg, 10 mmol) was added and the mixture stirred overnight at 80 °C. For work up ethyl acetate was added and the solution washed with water and saturated sodium chloride solution, dried and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 20:1) to give **8** (418 mg, 61%) as a colourless foam. $C_{29}H_{31}BrO_4$, M = 523.5. $[\alpha]_D^{20}$ = +13.7 (c = 1.0, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.27, 3.54, 3.67 (3 dd, $^3J_{3,4}$ = $^3J_{4,5}$ = $^3J_{6,7}$ = 9.5 Hz, 3×1 H, 4-H, 5-H, 6-H), 3.41 (ddd, $^3J_{6,7}$ = 9.5, $^3J_{7,8a}$ = 4.6, $^3J_{7,8b}$ = 2.8 Hz, 1 H, 7-H), 3.54, 3.62 (2 dd, $^3J_{7,8a}$ = 4.6, $^3J_{7,8b}$ = 2.8, $^2J_{8a,8b}$ = 10.7 Hz, 2×1 H, 8a-H, 8b-H), 3.75 (dd, $^3J_{2,3}$ = 6.6, $^3J_{3,4}$ = 9.5 Hz, 1 H, 3-H), 4.59, 4.66, 4.69, 4.80, 4.86, 4.88 (6 d, 6×1 H, 3 OCH_2), 5.23, 5.41 (2 d, $^3J_{1a,2}$ = 10.2, $^3J_{1b,2}$ = 17.3 Hz, 2×1 H, 1a-H, 1b-H), 5.89 (m, 1 H, 2-H), 7.18–7.28 (m, 15 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.85 (1 C, C-8), 75.59, 75.76, 76.06 (3 C, 3×OCH_2), 77.46, 80.06, 80.26, 83.05, 86.84 (5 C, C-3, C-4, C-5, C-6, C-7), 118.87 (1 C, C-1), 128.13–138.84 (19 C, C-2, Ar) ppm. $C_{29}H_{31}BrO_4$ (523.5): calcd. C 66.54, H 5.97; found C 67.01, H 6.38.

4,5,6-Tri-*O*-acetyl-3,7-anhydro-1,2,8-trideoxy-D-*gulo*-oct-1,7-dienitol (9): A solution of compound **6** (830 mg, 1.77 mmol) in anhydrous DMSO (10 mL) was treated with tetrabutylammonium iodide (300 mg, 0.8 mmol) and sodium iodide (1.2 g, 8 mmol) and the mixture stirred at 80 °C for 2 h. Then DBU was added (0.5 mL, 3.4 mmol) and stirring continued at 80 °C for another 2 h. The mixture was filtered through Celite, diluted with water and extracted with ethyl acetate. The combined organic extracts were washed with water, dried, concentrated to dryness and the residue purified by column chromatography with petroleum ether/ethyl acetate (5:1) to give **9** (278 mg, 53%) as a yellow syrup. $C_{14}H_{18}O_7$, M = 298.3. $[\alpha]_D^{20}$ = –30.2 (c = 1.0, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94, 1.96, 2.06 (3 s, 3×3 H, 3 OAc), 3.93 (dd, $^3J_{2,3}$ = 7.1, $^3J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 4.47, 4.75 (2 s, 2×1 H, 8a-H, 8b-H), 4.98, 5.10 (2 dd, $^3J_{3,4}$ = 9.7, $^3J_{4,5}$ = 8.6, $^3J_{5,6}$ = 10.2, 2×1 H, 4-H, 5-H), 5.25 (d, $^3J_{5,6}$ = 10.2 Hz, 1 H, 6-H), 5.31–5.40 (m, 2 H, 1a-H, 1b-H), 5.68–5.76 (m, 1 H, 2-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.66, 19.69 (3 C, 3 acetyl-Me), 68.38, 70.24, 72.08, 78.77 (4 C, C-3, C-4, C-5, C-6), 95.20 (1 C, C-8), 119.28 (1 C, C-1), 131.96 (1 C, C-2), 152.24 (1C, C-7), 168.22, 168.41, 169.02 (3 C, acetyl-CO_2); EI-MS: m/z = 298 $[M]^+$; $C_{14}H_{18}O_7$ (298.3): calcd. C 56.37, H 6.08; found C 56.62, H 6.30.

3,7-Anhydro-4,5,6-tri-*O*-benzoyl-1,2,8-trideoxy-D-*gulo*-oct-1,7-dienitol (10): Tetrabutylammonium iodide (80 mg, 0.2 mmol) and sodium iodide (320 mg, 2.1 mmol) were added to a solution of compound **7** (285 mg, 0.4 mmol) in anhydrous DMSO (5 mL) and the mixture stirred at 80 °C for 2 h. Then DBU (75 µL, 0.5 mmol) was added and stirring continued at 80 °C for another 2 h. The mixture was filtered through Celite, diluted with water and extracted with ethyl acetate. The combined organic extracts were washed with water, dried, concentrated to dryness and the residue purified by column chromatography with petroleum ether/ethyl acetate (10:1) to give **10** (109 mg, 52%) as a yellow syrup. $C_{29}H_{24}O_7$, M = 485.5. $[\alpha]_D^{20}$ = +0.9 (c = 0.5, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.23, (dd, $^3J_{2,3}$ = 7.1, $^3J_{3,4}$ = 9.5 Hz, 1 H, 3-H), 4.60, 4.86 (2 dd, $^4J_{6,8a}$ = $^4J_{6,8b}$ = $^2J_{8a,8b}$ = 1.8 Hz, 2×1 H, 8a-H, 8b-H), 5.24, 5.38 (2 d, $^3J_{1a,2}$ = 10.7, $^3J_{1b,2}$ = 17.3 Hz, 2×1 H, 1a-H, 1b-H), 5.50, 5.75 (2 dd, $^3J_{3,4}$ = $^3J_{4,5}$ = $^3J_{5,6}$ = $^3J_{6,7}$ = 9.5 Hz, 2×1 H, 4-H, 5-H), 5.83–5.92 (m, 2 H, 2-H, 6-H), 7.28–7.57 (m, 9 H, Ar), 7.85–8.07 (m, 6 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 69.00, 70.67, 72.10, 79.40 (4 C, C-3, C-4, C-5, C-6), 95.64 (1 C, C-8), 119.55 (1 C, C-2), 127.30–132.51 (19 C, C-1, Ar), 152.37 (1 C, C-7), 163.98, 164.61 (3 C, CO_2) ppm. EI-MS: m/z = 484 $[M]^+$.

3,7-Anhydro-4,5,6-tri-*O*-benzoyl-1,2,8-trideoxy-D-*gulo*-oct-1,7-dienitol (11): A solution of compound **8** (410 mg, 0.78 mmol) in anhydrous pyridine (10 mL) was stirred with silver fluoride (400 mg, 3.1 mmol) under exclusion of light at room temperature for 3 days. For work up the reaction mixture was diluted with dichloromethane, filtered and the solvents evaporated by codistillation with toluene. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 20:1) to give compound **11** (312 mg, 90%) as a yellow syrup. $C_{29}H_{30}O_4$, M = 442.6. $[\alpha]_{578}^{20}$ = –5.8 (c = 1.0, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.36, (dd, $^3J_{2,3}$ = 7.6, $^3J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 3.64 (dd, $^3J_{4,5}$ = $^3J_{5,6}$ = 7.1 Hz, 1 H, 5-H), 3.88 (d, $^3J_{5,6}$ = 7.1 Hz, 1 H, 6-H), 4.03 (dd, $^3J_{3,4}$ = 9.7, $^3J_{4,5}$ = 7.1 Hz, 1 H, 4-H), 4.52–4.78 (m, 8 H, 8a-H, 8b-H, 3 OCH_2), 5.25, 5.41 (2 m, 2×1 H, 1a-H, 1b-H), 5.83–5.91 (m, 1 H, 2-H), 7.18–7.31 (m, 15 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 71.67, 73.38, 73.52 (3 C, 3 OCH_2), 77.82, 78.33, 80.95, 83.33 (4 C, C-3, C-4, C-5, C-6), 93.78 (1 C, C-8) 117.50 (1 C, C-1), 126.68–137.29 (19 C, C-2, Ar), 154.93 (1 C, C-7) ppm.

***cis*-(2*S*,3*R*,4*S*)-2,3,4-Tris(acetyloxy)cyclooct-5-enone (12):** A solution of compound **9** (60 mg, 0.2 mmol) in anhydrous toluene or xylene (5 mL) was refluxed for 15 h. Similarly, **9** (143 mg, 0.48 mmol) in anhydrous nitrobenzene (5 mL) was refluxed for 1 h. Work up and purification was carried out as described for **13**. Yields of **12**: in toluene 20 mg (33%), in xylene 44 mg (73%) and in nitrobenzene 122 mg (85%). The purified material was recrystallized from diisopropyl ether to give colourless crystals. $C_{14}H_{18}O_7$, M = 298.3; m.p. 144 °C. $[\alpha]_{578}^{20}$ = –49.5 (c = 1.0, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.98, 1.99, 2.01 (3 s, 3×3 H, 3 OAc), 2.34 (m, 1 H, 7a-H), 2.45 (dd, $^3J_{7a,8a}$ = 5.1, $^3J_{7b,8a}$ = 0, $^2J_{8a,8b}$ = 13.0 Hz, 1 H, 8a-H), 2.69 (m, 1 H, 7b-H), 2.97 (dt, $^3J_{7a,8b}$ = $^3J_{7b,8b}$ = 4.1, $^2J_{8a,8b}$ = 13.0 Hz, 1 H, 8b-H), 5.08–5.09 (m, 2 H, 2-H, 3-H), 5.34 (dd, $^3J_{3,4}$ = 6.9, $^3J_{4,5}$ = 11.5 Hz, 1 H, 4-H), 5.72–5.83 (m, 2 H, 5-H, 6-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.23, 19.59, 19.75 (3 C, 2 acetyl-Me), 21.74, 42.09 (2 C, C-7, C-8), 68.12, 68.66, 75.12 (3 C, C-2, C-3, C-4), 126.71, 132.20 (2 C, C-5, C-6), 168.22, 168.54, 169.23 (3 C, 3 acetyl-CO_2), 203.75 (1 C, C-1) ppm. $C_{14}H_{18}O_7$ (298.3): calcd. C 56.37, H 6.08; found C 56.03, H 6.14.

Crystal Data: $C_{14}H_{18}O_7$, M = 298.3, orthorhombic, a = 7.229(3), b = 10.159(4), c = 20.086(7) Å, U = 1475.1(10) Å^3, T = 173 K,

space group $P2_12_12_1$, $Z = 4$, μ(Cu-K_α) = 0.922 mm^{-1}, 3457 reflections measured, 3092 unique (R_{int} = 0.0278).

***cis*-(2*S*,3*R*,4*S*)-2,3,4-Tris(benzoyloxy)cyclooct-5-enone (13):** A solution of compound **10** (52 mg, 0.1 mmol) in anhydrous xylene (5 mL, mixture of isomers) was refluxed overnight. By codistillation with carbon tetrachloride under reduced pressure the mixture was dried and then purified by column chromatography (petroleum ether/ethyl acetate, 5:1) to give **13** (31 mg, 60%) as a colourless syrup. $C_{29}H_{24}O_7$, M = 484.5. $[\alpha]_D^{20}$ = –49.5 (c = 1.0, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43–2.50 (m, 1 H, 7_{eq}-H), 2.60 (ddd, $^3J_{7ax,8ax}$ = 13.0, $^3J_{7eq,8ax}$ = 4.9, $^2J_{8ax,8eq}$ = 12.7 Hz, 1 H, 8_{ax}-H), 2.85–2.95 (m, 1 H, 7_{ax}-H), 3.13 (ddd, $^3J_{7ax,8eq}$ = 4.1, $^3J_{7eq,8eq}$ = 4.1, $^2J_{8ax,8eq}$ = 12.7 Hz, 1 H, 8_{eq}-H), 5.53 (d, $^3J_{2,3}$ = 8.4 Hz, 1 H, 2-H), 5.62 (dd, $^3J_{4,5}$ = 7.1, $^3J_{5,6}$ = 11.2 Hz, 1 H, 4-H), 5.71 (dd, $^3J_{2,3}$ = 8.4, $^3J_{3,4}$ = 10.5 Hz, 1 H, 3-H), 5.92 (m, 1 H, 6-H), 6.22 (ddd, $^3J_{3,4}$ = 10.5, $^3J_{4,5}$ = 7.1, $^4J_{4,6}$ = 1.3 Hz, 1 H, 4-H), 7.20–7.47 (m, 10 H, Ar), 7.79–7.85 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.01 (1 C, C-7), 42.08 (1 C, C-8), 68.91 (1 C, C-4), 69.51 (1 C, C-3), 75.69 (1C, C-2), 126.88 (1 C, C-5), 127.32–132.63 (18 C, Ar), 132.38 (1 C, C-6), 164.45, 164.48, 164.74 (3 C, 3 CO_2), 203.78 (1 C, C-1) ppm. EI-MS: m/z = 484 [M]$^+$.

***cis*-(2*S*,3*R*,4*S*)-2,3,4-Tris(benzyloxy)cyclooct-5-enone (14):** A solution of compound **11** (758 mg, 1.71 mmol) in nitrobenzene (20 mL) was placed in a preheated oil bath and heated at 185 °C for one hour. After evaporation of the solvent the residue was purified by column chromatography (petroleum ether/ethyl acetate, 10:1) to give **14** (0.612 g, 1.383 mmol, 81%) as a yellow syrup. $C_{29}H_{30}O_4$, M = 442.6. $[\alpha]_D^{20}$ = +20.4 (c = 1, chloroform); IR (film): $\tilde{\nu}$ = 1719 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.14 (m, 1 H, 7a-H), 2.24 (m, 2 H, 7b-H, 8a-H), 2.71 (dt, $^3J_{7a,8b}$ = $^3J_{7b,8b}$ = 5.9, $^2J_{8a,8b}$ = 10.7 Hz, 1 H, 8b-H), 3.52 (dd, $^3J_{2,3}$ = 5.1, $^3J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 4.00 (d, $^3J_{2,3}$ = 5.1 Hz, 1 H, 2-H), 4.13 (dd, $^3J_{3,4}$ = 9.2, $^3J_{4,5}$ = 7.6 Hz, 1 H, 4-H), 4.37, 4.69 (2 s, 2×2 H, 2 OCH_2), 4.45, 4.54 (2 d, 2×1 H, OCH_2), 5.51 (dd, $^3J_{4,5}$ = 7.6, $^3J_{5,6}$ = 10.2 Hz, 1 H, 5-H), 5.84 ("m", $^3J_{5,6}$ = 10.2 Hz, 1 H, 6-H), 7.17–7.30 (m, 15 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.56, 41.20 (2 C, C-7, C-8), 70.74, 71.38, 73.47 (3 C, 3 OCH_2), 76.75, 79.24, 83.84 (3 C, C-2, C-3, C-4), 122.49–137.41 (20 C, C-5, C-6, Ar), 211.31 (1 C, C-1) ppm. MALDI-TOF-MS: m/z = 465 [M + Na]$^+$, 481 [M + K]$^+$.

***cis*-(2*R*,3*R*,4*S*)-2,3,4-Tris(benzyloxy)cyclooct-5-enone (15):** 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 20 mg, 20 µL, 134 µmol) was added to a solution of **14** (10 mg, 23 µmol) in dry THF under argon. The solution was stirred at room temperature for one week (TLC control: petroleum ether/ethyl acetate, 5:1), neutralized with *p*-toluenesulfonic acid, filtered and the solvent evaporated. Column chromatography (petroleum ether/ethyl acetate, 5:1) of the residue gave **15** (8 mg, 18 µmol, 80%) as a colourless syrup. $C_{29}H_{30}O_4$, M = 442.6. $[\alpha]_D^{20}$ = –41.8 (c = 1, chloroform). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.60–1.67 (m, 1 H, 7b-H), 2.05–2.13 (m, 1 H, 8b-H), 2.69–2.74 (ddd, 1 H, 8a-H), 3.03–3.13 (m, 1 H, 7a-H), 3.76 (dd, $^3J_{2,3}$ = 2.3, $^3J_{3,4}$ = 9.9 Hz, 1 H, 3-H), 4.23 (d, $^3J_{2,3}$ = 2.3 Hz, 1 H, 2-H), 4.38, 4.45, 4.53, 4.60, 4.68, 4.79 (6 d, 6×1 H, OCH_2), 4.90 (ddd, $^3J_{3,4}$ = 9.9, $^3J_{4,5}$ = 6.4, $^4J_{4,6}$ = 1.5 Hz, 1 H, 4-H), 5.44–5.51 ("m", $^4J_{4,6}$ = 1.5, $^3J_{5,6}$ = 10.8 Hz, 1 H, 6-H), 5.58 (dd, $^3J_{4,5}$ = 6.4, $^3J_{5,6}$ = 10.8 Hz, 1 H, 5-H), 7.05–7.36 (m, 15 H, Ar) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 22.78 (1 C, C-7), 42.53 (1 C, C-8), 72.27, 74.38, 74.90 (3 C, OCH_2), 75.37 (1 C, C-4), 83.11 (1 C, C-3), 87.62 (1 C, C-2), 127.52–128.67 (18 C, Ar), 132.21 (1 C, C-6), 133.93 (1 C, C-5) ppm. MALDI-TOF-MS: m/z = 465 [M + Na]$^+$, 481 [M + K]$^+$.

4,5,6,8-Tetra-*O*-acetyl-3,7-anhydro-1,2-dideoxy-D-*glycero*-D-*galacto*-oct-1-enitol (β anomer) and 4,5,6,8-Tetra-*O*-acetyl-3,7-anhydro-1,2-dideoxy-D-*glycero*-D-*talo*-oct-1-enitol (α anomer) (18): Under argon a solution of **17**[36] (8.19 g, 19.92 mmol) in dry THF (70 mL) was added dropwise to a solution of vinylmagnesium bromide in THF (200 mL, 1 M, 200 mmol). At the end of the exothermic reaction refluxing was continued for five hours. The reaction mixture was poured into ice–water and neutralized with acetic acid. The aqueous phase was evaporated and the residue dried for several hours in vacuo. After suspension of the residue in pyridine (150 mL) and addition of acetic anhydride (150 mL) at 0 °C the reaction mixture was stirred for two days. The mixture was then poured into ice–water and extracted with dichloromethane. After evaporation of the solvent the residue was purified by column chromatography (petroleum ether/ethyl acetate, 3:1) to give **18** (3.177 g, 8.86 mmol, 45%) as a white inseparable anomeric solid mixture (α/β ≈ 0.4:1.0). $C_{16}H_{22}O_9$, M = 358.4. β Anomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.98, 2.04, 2.09, 2.13 (4 s, 4×3 H, Ac), 3.68 (ddd, $^3J_{6,7}$ = 9.9, $^3J_{7,8a}$ = 5.6, $^3J_{7,8b}$ = 2.5 Hz, 1 H, 7-H), 4.08–4.18 ("m", $^4J_{1a,3}$ = 1.5, $^4J_{1b,3}$ = 1.5, $^3J_{2,3}$ = 5.3, $^3J_{3,4}$ = 1.3, $^3J_{7,8b}$ = 2.5, $^2J_{8a,8b}$ = 12.2 Hz, 2 H, 3-H, 8b-H), 4.27 (dd, $^3J_{7,8a}$ = 5.6, $^2J_{8a,8b}$ = 12.2 Hz, 1 H, 8a-H), 5.08 (dd, $^3J_{4,5}$ = 3.4, $^3J_{5,6}$ = 9.9 Hz, 1 H, 5-H), 5.24 (ddd, $^2J_{1a,1b}$ = 1.3, $^3J_{1b,2}$ = 10.8, $^4J_{1b,3}$ = 1.5 Hz, 1 H, 1b-H), 5.25 (dd, $^3J_{5,6}$ = $^3J_{6,7}$ = 9.9 Hz, 1 H, 6-H), 5.85 (ddd, $^2J_{1a,1b}$ = 1.3, $^3J_{1a,2}$ = 17.5, $^4J_{1a,3}$ = 1.5 Hz, 1 H, 1a-H), 5.40 (dd, $^3J_{3,4}$ = 1.3, $^3J_{4,5}$ = 3.4 Hz, 1 H, 4-H), 5.72 (ddd, $^3J_{1a,2}$ = 17.5, $^3J_{1b,2}$ = 10.8, $^3J_{2,3}$ = 5.3 Hz, 1 H, 2-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.77, 20.83, 20.86, 20.95 (4 C, Ac), 63.04 (1 C, C-8), 66.23 (1 C, C-6), 70.05 (1 C, C-4), 72.41 (1 C, C-5), 76.28 (1 C, C-7), 77.57 (1 C, C-3), 118.59 (1 C, C-1), 132.43 (1 C, C-2), 169.84, 170.35, 170.57, 170.91 (4 C, acetyl-CO_2) ppm. MALDI-TOF-MS: m/z = 381 [M + Na]$^+$, 397 [M + K]$^+$; $C_{16}H_{22}O_9$ (358.4): calcd. C 53.62, H 6.20; found C 52.95, H 6.20.

3,7-Anhydro-1,2-dideoxy-D-*glycero*-D-*galacto*-oct-1-enitol (β anomer) and 3,7-Anhydro-1,2-dideoxy-D-*glycero*-D-*talo*-oct-1-enitol (α anomer) (19): Sodium methoxide (NaOMe) was added to a solution of **18** (3.102 g, 8.660 mmol) in dry methanol (50 mL) until pH 9 was reached. The reaction mixture was stirred for several hours until TLC control (dichloromethane/methanol, 10:1) confirmed complete reaction. After neutralization with Amberlite IR-120 H$^+$ the solution was filtered and the solvent evaporated to give **19** (1.645 g, 8.649 mmol, 100%, colourless syrup) as an inseparable anomeric mixture (α/β ≈ 0.4:1.0). $C_8H_{14}O_5$, M = 190.2. β Anomer: ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ = 3.03–3.06 (m, 1 H, 7-H), 3.28–3.47, 3.57–3.69 (2 m, 5 H, 4-H, 5-H, 6-H, 8a/b-H), 3.82 (dd, $^3J_{2,3}$ = 6.1, $^3J_{3,4}$ = 1.3 Hz, 1 H, 3-H), 4.29–4.75 (br. m, 4 H, OH), 5.09 (ddd, $^2J_{1a,1b}$ = 1.5, $^3J_{1b,2}$ = 10.5, $^4J_{1b,3}$ = 1.5 Hz, 1 H, 1b-H), 5.20–5.29 ("m", $^2J_{1a,1b}$ = 1.5, $^3J_{1a,2}$ = 17.0, $^4J_{1a,3}$ = 1.5 Hz, 1 H, 1a-H), 5.84–5.95 ("m", $^3J_{1a,2}$ = 17.0, $^3J_{1b,2}$ = 10.5, $^3J_{2,3}$ = 6.1 Hz, 1 H, 2-H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ = 61.68 (1 C, C-8), 67.20, 71.79, 74.75, 78.92, 81.06 (5 C, C-3, C-4, C-5, C-6, C-7), 115.73 (1 C, C-1), 137.07 (1 C, C-2) ppm. MALDI-TOF-MS: m/z = 213 [M + Na]$^+$, 229 [M + K]$^+$.

3,7-Anhydro-1,2-dideoxy-4,5-*O*-isopropylidene-D-*glycero*-D-*talo*-oct-1-enitol (20): This compound can be prepared from **19** according to standard procedures,[37] that is, treatment of the substrate with 2,2-dimethoxypropane and a catalytic amount of acid such as *p*-toluenesulfonic acid. However, we observed its formation on treatment of a mixture of silyl ethers of compound **19** with tetrabutylammonium fluoride (TBAF) in THF containing acetone. Presumably, TBAF not only cleaves the silyl ethers but also acts as a catalyst promoting the formation of the acetonide. The anomeric mixture of the 6,8-diacetate obtained by sequential isopropylidenation and acetylation could be separated to obtain the pure α anomer which was subsequently deacetylated to give **20** as a yellow

syrup. $C_{11}H_{18}O_5$, M = 230.3. $[\alpha]_D^{20}$ = +2.0 (c = 1, methanol). ^{1}H NMR (400 MHz, CD_3OD): δ = 1.37, 1.50 (2 s, 2×3 H, Me), 3.46 (ddd, $^3J_{6,7}$ = 9.7, $^3J_{7,8a}$ = 5.7, $^3J_{7,8b}$ = 2.8 Hz, 1 H, 7-H), 3.67–3.71 ("m", $^3J_{5,6}$ = 7.5, $^3J_{6,7}$ = 9.7, $^3J_{7,8a}$ = 5.7, $^3J_{7,8b}$ = 2.8, $^2J_{8a,8b}$ = 12.0 Hz, 2 H, 6-H, 8a-H), 3.79 (dd, $^3J_{7,8b}$ = 2.8, $^2J_{8a,8b}$ = 12.0 Hz, 1 H, 8b-H), 4.06 (dd, $^3J_{4,5}$ = 6.4, $^3J_{5,6}$ = 7.5 Hz, 1 H, 5-H), 4.24 (dd, $^3J_{3,4}$ = 4.5, $^3J_{4,5}$ = 6.4 Hz, 1 H, 4-H), 4.41–4.44 ("m", $^4J_{1a,3}$ = $^4J_{1b,3}$ = 1.8, $^3J_{2,3}$ = 4.8, $^3J_{3,4}$ = 4.5 Hz, 1 H, 3-H), 5.30 (ddd, $J_{1a,1b}$ = 1.5, $J_{1b,2}$ = 10.9, $J_{1b,3}$ = 1.8 Hz, 1 H, 1b-H), 5.42 (ddd, $J_{1a,1b}$ = 1.5, $J_{1a,2}$ = 17.5, $J_{1a,3}$ = 1.8 Hz, 1 H, 1a-H), 5.94 (ddd, $J_{1a,2}$ = 17.5, $J_{1b,2}$ = 10.9, $J_{2,3}$ = 4.8 Hz, 1 H, 2-H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 26.01, 28.14 (2 C, Me), 62.81 (1 C, C-8), 70.08 (1 C, C-6), 74.81 (1 C, C-3), 75.69 (1 C, C-7), 77.64 (1 C, C-4), 79.87 (1 C, C-5), 110.21 (1 C, CMe$_2$), 118.08 (1 C, C-1), 136.81 (1 C, C-2) ppm. MALDI-TOF-MS: m/z = 253 $[M+Na]^+$, 269 $[M+K]^+$; $C_{11}H_{18}O_5$ (230.3): calcd. C 57.37, H 7.89; found C 56.06, H 7.72 (hygroscopic compound).

3,7-Anhydro-1,2-dideoxy-4,5-*O*-isopropylidene-8-*O*-(4-tolylsulfonyl)-D-*glycero*-D-*talo*-oct-1-enitol (21): p-Toluenesulfonyl chloride (308 mg, 1.62 mmol) and a catalytic amount of 4-(dimethylamino) pyridine was added to a solution of **20** (162 mg, 703 μmol) in dry pyridine (10 mL) was added at 0 °C. The solution was stirred at room temperature for two days and the reaction terminated by the addition of water. Evaporation of the solvent and column chromatography of the residue (petroleum ether/ethyl acetate, 3:1) gave **21** (228 mg, 593 μmol, 84%) as a colourless syrup. $C_{18}H_{24}O_7S$, M = 384.5. $[\alpha]_D^{20}$ = +3.4 (c = 0.5, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36, 1.50 (2 s, 2×3 H, Me), 2.44 (s, 3 H, Ts-Me), 3.62 (ddd, $^3J_{6,7}$ = 9.9, $^3J_{7,8a}$ = 4.1, $^3J_{7,8b}$ = 2.3 Hz, 1 H, 7-H), 3.87 (dd, $^3J_{5,6}$ = 7.7, $^3J_{6,7}$ = 9.9 Hz, 1 H, 6-H), 4.08 (dd, $^3J_{4,5}$ = 6.6, $^3J_{5,6}$ = 7.7 Hz, 1 H, 5-H), 4.16 (dd, $^3J_{3,4}$ = 5.3, $^3J_{4,5}$ = 6.6 Hz, 1 H, 4-H), 4.21 (dd, $^3J_{7,8b}$ = 2.3, $^2J_{8a,8b}$ = 10.9 Hz, 1 H, 8b-H), 4.31–4.36 ("m", $^3J_{2,3}$ = 5.0, $^3J_{3,4}$ = 5.32, $^3J_{7,8a}$ = 4.1, $^2J_{8a,8b}$ = 10.9 Hz, 2 H, 8a-H, 3-H), 5.28–5.36 ("m", $^2J_{1a,1b}$ = 1.3, $^3J_{1a,2}$ = 17.5, $^3J_{1b,2}$ = 10.7 Hz, 2 H, 1a/b-H), 5.79 (ddd, $^3J_{1a,2}$ = 17.5, $^3J_{1b,2}$ = 10.7, $^3J_{2,3}$ = 5.01, 1 H, 2-H), 7.34, 7.80 (2 d, 2×2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.80 (1 C, Ts-Me), 25.62, 27.76 (2 C, Me), 68.83 (1 C, C-6), 69.37 (1 C, C-8), 71.73 (1 C, C-7), 74.14 (1 C, C-3), 76.24 (1 C, C-4), 78.24 (1 C, C-5), 109.95 (1 C, CMe$_2$), 118.51 (1 C, C-1), 128.14, 130.03, 132.87, 145.11 (4 C, Ar), 134.76 (1 C, C-2) ppm. MALDI-TOF-MS: m/z = 407 $[M+Na]^+$, 423 $[M+K]^+$.

3,7-Anhydro-6-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-8-*O*-(4-tolylsulfonyl)-D-*glycero*-D-*talo*-oct-1-enitol (22): Benzyl bromide (90 μL, 129 mg, 757 μmol) and NaH (60% in paraffin, 28 mg, 700 μmol) was added to a solution of **21** (205 mg, 533 μmol) in dry DMF (12 mL). The solution was stirred for two days at room temperature. During this time extra benzyl bromide (50 μL, 72 mg, 420 μmol) and NaH (8 mg, 200 μmol) were added to effect complete conversion of the starting material. The solution was diluted with ethyl acetate and the solvent evaporated. Chromatography of the residue (petroleum ether/ethyl acetate, 5:1) gave **22** (194 mg, 409 μmol, 77%) as a colourless syrup. $C_{25}H_{30}O_7S$, M = 474.6. $[\alpha]_D^{20}$ = +7.2 (c = 1, chloroform). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.16, 1.38 (2 s, 2×3 H, Me), 1.79 (s, 3 H, Ts-Me), 3.62 (ddd, $^3J_{6,7}$ = 9.9, $^3J_{7,8a}$ = 4.3, $^3J_{7,8b}$ = 2.6 Hz, 1 H, 7-H), 3.75 (dd, $^3J_{5,6}$ = 7.0, $^3J_{6,7}$ = 9.9 Hz, 1 H, 6-H), 3.87 (dd, $^3J_{3,4}$ = 5.6, $^3J_{4,5}$ = 6.8 Hz, 1 H, 4-H), 4.02 (dd, $^3J_{4,5}$ = 6.8, $^3J_{5,6}$ = 7.0 Hz, 1 H, 5-H), 4.27 (dd, $^3J_{7,8b}$ = 2.6, $^2J_{8a,8b}$ = 10.4 Hz, 1 H, 8b-H), 4.31 (dd, $^3J_{7,8a}$ = 4.3, $^2J_{8a,8b}$ = 10.4 Hz, 1 H, 8a-H), 4.31–4.35 ("m", $^3J_{2,3}$ = 4.8, $^3J_{3,4}$ = 5.6, $^4J_{1a,3}$ = $^4J_{1b,3}$ = 1.5 Hz, 1 H, 3-H), 4.53, 4.90 (2 d, 2×1 H, OCH_2), 5.01 (ddd, $^2J_{1a,1b}$ = 1.5, $^3J_{1b,2}$ = 10.9, $^4J_{1b,3}$ = 1.5 Hz, 1 H, 1b-H), 5.22 (ddd, $^2J_{1a,1b}$ = 1.5, $^3J_{1a,2}$ = 17.6, $^4J_{1a,3}$ = 1.5 Hz, 1 H, 1a-H), 5.63 (ddd, $^3J_{1a,2}$ = 17.6, $^3J_{1b,2}$ = 10.9, $^3J_{2,3}$ = 4.8 Hz, 1 H, 2-H), 6.63–6.65, 7.08–7.21, 7.30–7.32, 7.74–7.77 (4 m, 9 H, Ar) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 21.13 (1 C, Ts-Me), 25.54, 27.69 (2 C, Me), 69.81 (1 C, C-8), 71.10 (1 C, C-7), 72.95 (1 C, OCH_2), 73.92 (1 C, C-3), 75.60 (1 C, C-6), 76.69 (1 C, C-4), 78.85 (1 C, C-5), 109.40 (1 C, CMe$_2$), 117.48 (1 C, C-1), 127.70–129.80 (12 C, Ar), 135.28 (1 C, C-2) ppm. MALDI-TOF-MS: m/z = 497 $[M+Na]^+$, 513 $[M+K]^+$.

3,7-Anhydro-6-*O*-benzyl-1,2,8-trideoxy-4,5-*O*-isopropylidene-D-*talo*-oct-1,7-dienitol (23): Tetrabutylammonium iodide (TBAI, 4.7 mg, 13 μmol), sodium iodide (26.0 mg, 173 μmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.5 μL) were added to a solution of **22** (12.0 mg, 25 μmol) in dry DMSO (0.5 mL). After stirring for 1.5 h at 80 °C more DBU (13.0 μL, 13.2 mg, 87 μmol) was added and stirring was continued for 6 h. When TLC control (petroleum ether/ethyl acetate, 3:1) showed complete conversion of the starting material the solution was diluted with water and extracted twice with dichloromethane. Column chromatography (petroleum ether/ethyl acetate, 5:1) of the residue gave **23** (6.0 mg, 20 μmol, 78%) as a colourless syrup. $C_{18}H_{22}O_4$, M = 302.4. $[\alpha]_D^{20}$ = +13.8 (c = 0.25, chloroform). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.07, 1.36 (2 s, 2×3 H, Me), 3.83 (dd, $^3J_{4,5}$ = 7.4, $^3J_{5,6}$ = 8.7 Hz, 1 H, 5-H), 4.17–4.24 ("m", $^3J_{2,3}$ = 5.6, $^3J_{4,5}$ = 7.4, $^3J_{5,6}$ = 8.7 Hz, 3 H, 3-H, 4-H, 6-H), 4.68, 4.72 (2 d, 2×1 H, OCH_2), 4.71 (s, 1 H, 8b-H), 4.81 (s, 1 H, 8a-H), 5.11 (ddd, $^2J_{1a,1b}$ = 1.3, $^3J_{1b,2}$ = 10.7, $^4J_{1b,3}$ = 1.5 Hz, 1 H, 1b-H), 5.42 (ddd, $^2J_{1a,1b}$ = 1.3, $^3J_{1a,2}$ = 17.3, $^4J_{1a,3}$ = 1.5 Hz, 1 H, 1a-H), 5.96 (ddd, $^3J_{1a,2}$ = 17.3, $^3J_{1b,2}$ = 10.7, $^3J_{2,3}$ = 5.6 Hz, 1 H, 2-H), 7.08–7.21, 7.37–7.39 (2 m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 24.62, 27.15 (2 C, Me), 72.29 (1 C, OCH_2), 75.90, 76.28, 76.81, 78.31 (4 C, C-3, C-4, C-5, C-6), 88.08 (1 C, C-8), 110.02 (1 C, CMe$_2$), 117.39 (1 C, C-1), 127.69–128.63 (6 C, Ar), 135.35 (1 C, C-2), 155.22 (1 C, C-7) ppm. MALDI-TOF-MS: m/z = 325 $[M+Na]^+$, 341 $[M+K]^+$.

***cis*-(2*S*,3*R*,4*R*)-2-Benzyloxy-3,4-(isopropylidenedioxy)cyclooct-5-en-one (24):** A solution of **23** (8.0 mg, 26 μmol) in a n-decane/toluene mixture (ratio 4:1, 5 mL) with one drop of triethylamine was heated at 185 °C under microwave irradiation for 1 h (300 W). After evaporation of the solvents the residue was purified by column chromatography (petroleum ether/ethyl acetate, 8:1) to give **24** (6.4 mg, 21 μmol, 80%) as a white solid. Colourless crystals were obtained by recrystallization from ethanol. $C_{18}H_{22}O_4$, M = 302.4; m.p. 143.7–145 °C. $[\alpha]_D^{20}$ = –16.0 (c = 0.2, chloroform). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.24, 1.47 (2 s, 2×3 H, Me), 1.55–1.60 (m, 2 H, 7a/b-H), 1.80–1.87 (m, 1 H, 8b-H), 2.12–2.17 (m, 1 H, 8a-H), 4.06 (d, $^3J_{2,3}$ = 8.6 Hz, 1 H, 2-H), 4.31 (dd, $^3J_{2,3}$ = 8.6, $^3J_{3,4}$ = 5.4 Hz, 1 H, 3-H), 4.45–4.48 ("m", $^3J_{3,4}$ = 5.4, $^3J_{4,5}$ = 6.1, $^3J_{4,6}$ = 2.0 Hz, 3 H, 4-H, OCH_2), 5.27–5.35 ("m", $^4J_{4,6}$ = 2.0, $^3J_{5,6}$ = 11.3 Hz, 1 H, 6-H), 5.60 (dd, $^3J_{4,5}$ = 6.1, $^3J_{5,6}$ = 11.3 Hz, 1 H, 5-H), 7.02–7.12, 7.30–7.32 (2 m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 23.65 (1 C, C-7), 26.26, 28.33 (2 C, Me), 44.29 (1 C, C-8), 72.45 (1 C, OCH_2), 74.02 (1 C, C-4), 78.87 (1 C, C-3), 82.74 (1 C, C-2), 127.67–128.73 (6 C, Ar), 128.60 (1 C, C-6), 133.71 (1 C, C-5) ppm. MALDI-TOF-MS: m/z = 325 $[M+Na]^+$, 341 $[M+K]^+$.

Crystal Data: $C_{18}H_{22}O_4$, M = 302.4, monoclinic, a = 7.7078(7), b = 9.8849(10), c = 10.6599(10) Å, U = 808.4(13) Å^3, T = 153 K, space group $P2_1$, Z = 2, μ(Mo-K_α) = 0.087 mm^{-1}, 9845 reflections measured, 1971 unique (R_{int} = 0.1410).

***cis*-(1*S*,2*R*,3*R*,4*S*)-2,3,4-Tris(benzyloxy)cyclooct-5-en-1-ol (25)**

Starting from Compound 11: Triisobutylaluminium (1 M in hexane, 0.08 mL, 80 μmol) was added to a solution of precursor **11** (7 mg, 16 μmol) in dry DCM (0.4 mL) under argon. The solution was stirred at room temperature overnight. After dilution with DCM and hydrolysis the organic phase was washed with 1 M HCl, filtered

by using a syringe and evaporated to give **25** (4 mg, 57%) as a colourless syrup.

Starting from Compound 14: $LiAlH_4$ (14 mg, 369 μmol) was added to a solution of **14** (92 mg, 208 μmol) in THF (4 mL) at 0 °C and the mixture was stirred overnight at room temperature. Water was added to destroy excess $LiAlH_4$. The precipitate was diluted with a small amount of 1 M sulfuric acid. The solution was diluted with chloroform and the organic phase washed with water. After another extraction of the aqueous phase with chloroform the combined organic phases were evaporated. Column chromatography of the residue (petroleum ether/ethyl acetate, 10:1) gave **25** (81 mg, 182 μmol, 88%) as a yellowish syrup. $C_{29}H_{32}O_4$, M = 444.6. $[\alpha]_D^{20}$ = –4.8 (c = 1, chloroform). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.79–1.89, 1.96–2.03, 2.52–2.61 (3 m, 4 H, 7a/b-H, 8a/b-H), 3.29 (s, 1 H, OH), 3.66 (dd, $^3J_{2,3}$ = 4.7, $^3J_{3,4}$ = 7.9 Hz, 1 H, 3-H), 3.77 (dd, $^3J_{1,2}$ = 8.5, $^3J_{2,3}$ = 4.7 Hz, 1 H, 2-H), 4.18–4.21 (m, 2 H, 1-H, OCH_2), 4.39, 4.46 (2 d, 2×1 H, OCH_2), 4.61 (d, 2 H, OCH_2), 4.78 (d, 1 H, OCH_2), 4.82 (dd, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.9 Hz, 1 H, 4-H), 5.56–5.60 ("m", $^3J_{4,5}$ = 7.9, $^3J_{5,6}$ = 10.9 Hz, 1 H, 5-H), 5.71–5.77 ("m", $^3J_{5,6}$ = 10.9 Hz, 1 H, 6-H), 7.07–7.35 (m, 15 H, Ar) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 22.21 (1 C, C-7), 32.42 (1 C, C-8), 70.71, 78.97, 81.60, 85.20 (4 C, C-1, C-2, C-3, C-4), 71.40, 73.61, 74.95 (3 C, OCH_2), 127.70–128.62, 138.93, 139.09, 139.47 (18 C, Ar), 129.76, 133.68 (2 C, C-5, C-6) ppm. MALDI-TOF-MS: m/z = 467 $[M + Na]^+$, 483 $[M + K]^+$.

***cis*-(3*S*,4*R*,5*R*)-6-Acetyloxy-3,4,5-tris(benzyloxy)cyclooctene (26):** A solution of compound **14** (27 mg, 0.06 mmol) in anhydrous tetrahydrofuran (2 mL) was stirred with $LiAlH_4$ (8 mg, 0.2 mmol) at room temperature for 2 h. Following dilution with ethyl acetate excess of $LiAlH_4$ was hydrolyzed with water and the precipitate dissolved with 1 M sulfuric acid. The organic phase was washed with a saturated sodium chloride solution and concentrated to dryness. The residue was dissolved in anhydrous pyridine (3 mL) and treated with acetic anhydride for 3 h at room temperature. Codistillation with toluene gave a residue which was purified by column chromatography (petroleum ether/ethyl acetate, 20:1) to give compound **26** (21 mg, 70%) as a colourless syrup. $[\alpha]_D^{20}$ = +3.2 (c = 1.0, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.73 (s, 3 H, Ac), 1.76 (m, 1 H, 8a-H), 1.97 (m, 2 H, 7a-H, 8b-H), 2.38 (m, 1 H, 7b-H), 3.66 (dd, $^3J_{3,4}$ = 9.2, $^3J_{4,5}$ = 3.1 Hz, 1 H, 4-H), 4.06 (dd, $^3J_{4,5}$ = 3.1, $^3J_{5,6}$ = 8.1 Hz, 1 H, 5-H), 4.36–4.53, 4.60, 4.70 (6 d, 6 H, 3 OCH_2), 4.61 (dd, $^3J_{2,3}$ = 10.7, $^3J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 5.26 (m. 1 H, 6-H), 5.55 (m, 1 H, 2-H), 5.87 (m, 1 H, 1-H), 7.24–7.37 (m, 15 H, Ar), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.03 (1 C, Ac), 21.87, 29.64 (2 C, C-7, C-8), 70.89, 72.51, 74.15 (3 C, 3 benzyl-OCH_2), 71.02, 76.42, 77.13, 84.75 (4 C, C-3, C-4, C-5, C-6), 127.25–138.93 (20 C, C-1, C-2, Ar), 170.76 (1 C, acetyl-CO_2) ppm.

***cis*-(1*S*,2*S*,3*R*,4*S*,5*R*,6*R*)-1-Acetoxy-2,3,4-tris(benzyloxy)-5,6-epoxycyclooctane (27):** 3-Chloroperbenzoic acid (approx. 70%, 23 mg, 93 μmol) was added to a solution of **26** (30 mg, 62 μmol) in dry dichloromethane (3 mL). The solution was stirred at room temperature for two days. When TLC control (petroleum ether/ethyl acetate, 5:1) showed the disappearance of the starting material the solution was diluted with ethyl acetate and washed twice with a 10% aqueous $Na_2S_2O_5$ solution, then with saturated $NaHCO_3$ and NaCl solutions. Evaporation of the organic phase and column chromatography (petroleum ether/ethyl acetate, 10:1) of the residue gave **27** (18 mg, 36 μmol, 58%) as a colourless syrup. $C_{31}H_{34}O_6$, M = 502.7. $[\alpha]_D^{20}$ = –3.0 (c = 1, dichloromethane). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.30–1.37 (m, 1 H, 8b-H), 1.50–1.60 (m, 4 H, 7b-H, Ac), 1.76–1.84 (m, 2 H, 7a-H, 8a-H), 2.78–2.82 ("m", $^3J_{5,6}$ = 4.6 Hz, 1 H, 6-H), 3.07 (dd, $^3J_{4,5}$ = 9.1, $^3J_{5,6}$ = 4.6 Hz, 1 H, 5-H), 3.71 (dd, $^3J_{2,3}$ = 3.0, $^3J_{3,4}$ = 9.1 Hz, 1 H, 3-H), 3.90 (dd, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.1 Hz, 1 H, 4-H), 3.98, 4.12 (2 d, 2×1 H, OCH_2), 4.21 (dd, $^3J_{1,2}$ = 8.4, $^3J_{2,3}$ = 3.0 Hz, 1 H, 2-H), 4.52, 4.56, 4.96, 5.11 (4 d, 4 H, OCH_2), 5.41 (ddd, $^3J_{1,2}$ = 8.4 Hz, 1 H, 1-H), 7.07–7.21, 7.41–7.49 (2 m, 15 H, Ar) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 20.84 (1 C, Ac), 23.73, 24.14 (2 C, C-7, C-8), 53.83 (1 C, C-6), 57.38 (1 C, C-5), 69.91 (1 C, C-1), 72.45, 72.95, 74.92 (3 C, OCH_2), 75.46 (1 C, C-2), 80.25 (1 C, C-4), 81.21 (1 C, C-3), 127.51–129.23, 138.42, 138.68, 139.67 (18 C, Ar), 170.08 (1 C, Ac); MALDI-TOF-MS: m/z = 525 $[M + Na]^+$, 541 $[M + K]^+$; $C_{31}H_{34}O_6$ (502.6): calcd. C 74.08, H 6.83; found C 73.51, H 6.99.

(1*R*,2*S*,3*R*,4*S*,5*S*,8*R*)-5-Acetoxy-2,3,4-tris(benzyloxy)bicyclo[6.1.0]-nonane (28): A few drops of diiodomethane and a diethylzinc solution (1 M in hexane) were added to a solution of **26** (3 mg, 6 μmol) in dry dichloromethane (0.5 mL) under argon. The solution was stirred at room temperature for 4 h. After addition of 5% HCl and dilution with dichloromethane the organic phase was evaporated. Column chromatography (petroleum ether/ethyl acetate, 20:1) of the residue gave 3 mg of a colourless syrup that after NMR spectroscopic analysis turned out to be an inseparable mixture of **28** (89%) and small amounts of **26** (approx. 11%). $C_{32}H_{36}O_5$, M = 500.7. ^{1}H NMR (500 MHz, C_6D_6): δ = 0.09 (dd, 1 H, H-9b), 0.70–0.81 (m, 2 H, 8-H, 9a-H), 0.90–0.97 ("m", $^3J_{1,2}$ = 10.7 Hz, 1 H, 1-H), 1.11 (dd, 1 H, 7b-H), 1.52–1.58 ("m", $^3J_{5,6b}$ = 5.7 Hz, 1 H, 6b-H), 1.69 (s, 3 H, Ac), 1.79–1.84 (m, 1 H, 7a-H), 1.97–2.03 ("m", $^3J_{5,6a}$ = 1.9 Hz, 1 H, 6a-H), 3.48 (dd, $^3J_{1,2}$ = 10.7, $^3J_{2,3}$ = 9.1 Hz, 1 H, 2-H), 3.81 (dd, $^3J_{2,3}$ = 9.1, $^3J_{3,4}$ = 2.8 Hz, 1 H, 3-H), 4.18 (d, 1 H, OCH_2), 4.29–4.33 ("m", $^3J_{3,4}$ = 2.8, $^3J_{4,5}$ = 8.2 Hz, 2 H, 4-H, OCH_2), 4.59 (s, 2 H, OCH_2), 4.78, 4.83 (2 d, 2×1 H, OCH_2), 5.59–5.62 ("m", $^3J_{4,5}$ = 8.2, $^3J_{5,6a}$ = 1.9, $^3J_{5,6b}$ = 5.7 Hz, 1 H, 5-H), 7.07–7.25, 7.45–7.47 (2 m, 15 H, Ar) ppm. MALDI-TOF-MS: m/z = 523 $[M + Na]^+$, 539 $[M + K]^+$.

(4*R*,5*R*,6*S*,7*R*,8*R*)-6,7,8-Tris(benzyloxy)-4,5-epoxy-octane-8-olide (29): 3-Chloroperbenzoic acid (approx. 70%, 119 mg, 483 μmol) was added to a solution of **14** (100 mg, 226 μmol) in dry dichloromethane (7 mL). The solution was stirred at room temperature until TLC control (petroleum ether/ethyl acetate, 2:1) confirmed complete conversion of the starting material. After addition of a 10% $Na_2S_2O_5$ solution the organic phase was washed with a saturated $NaHCO_3$ solution and water and the solvent evaporated. Column chromatography (petroleum ether/ethyl acetate, 8:1) of the residue gave **29** (73 mg, 154 μmol, 68%) as a colourless solid. Recrystallization from ethanol furnished white needles. $C_{29}H_{30}O_6$, M = 474.6; m.p. 105 °C. $[\alpha]_D^{20}$ = –54.9 (c = 0.5, chloroform). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.94–1.04 (m, 1 H, 3a-H), 1.70–1.89 (m, 3 H, 2a/b-H, 3b-H), 2.60 (ddd, $^3J_{4,5}$ = 3.8, $^3J_{5,6}$ = 9.2 Hz, 1 H, 4-H), 2.96 (dd, $^3J_{4,5}$ = 3.8, $^3J_{5,6}$ = 9.2 Hz, 1 H, 5-H), 3.07 (dd, $^3J_{5,6}$ = 9.2, $^3J_{6,7}$ = 9.4 Hz, 1 H, 6-H), 3.76 (dd, $^3J_{6,7}$ = 9.4, $^3J_{7,8}$ = 7.1 Hz, 1 H, 7-H), 4.64–4.94 (6 d, 6 H, 3 OCH_2), 5.96 (d, $^3J_{7,8}$ = 7.1 Hz, 1 H, 8-H), 7.05–7.19, 7.29–7.41 (2 m, 15 H, Ar) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 26.74 (1 C, C-3), 30.66 (1 C, C-2), 56.63 (1 C, C-4), 60.74 (1 C, C-5), 71.62, 74.78, 75.95 (3 C, 3 OCH_2), 77.81 (1 C, C-6), 82.83 (1 C, C-7), 98.70 (1 C, C-8), 127.66–128.65, 137.63, 139.14, 138.28 (18 C, Ar), 172.72 (1 C, C-1) ppm. MALDI-TOF-MS: m/z = 497 $[M + Na]^+$, 513 $[M + K]^+$; $C_{29}H_{30}O_6$ (474.6): calcd. C 73.39, H 6.38; found C 72.69, H 6.50.

(2*S*,3*R*,4*S*,5*R*,6*R*)-2,3,4-Tris(benzyloxy)-5,6-epoxycyclooctanone (30): A freshly prepared solution of dimethyldioxirane in acetone[38] (approx. 0.09–0.1 M, 0.7 mL, ca. 63–70 μmol) was added to a solution of **14** (19 mg, 43 μmol) in acetone (0.3 mL). The solution was stirred at room temperature for two days with two further additions of the DMD solution (0.3 and 0.6 mL, ca. 80–90 μmol). When TLC

control (petroleum ether/ethyl acetate, 3:1) showed that most of the starting material had been consumed the solvent was evaporated and the residue purified by column chromatography (petroleum ether/ethyl acetate, 12:1) to give **30** (12 mg, 26 μmol, 70%) as a colourless syrup as well as 2.5 mg of recovered **14** (6 μmol). $C_{29}H_{30}O_5$, M = 458.6. $[\alpha]_D^{20}$ = +17.6 (c = 1, dichloromethane). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.15–1.26 (m, 1 H, 7b-H), 1.82–1.93 (m, 2 H, 7a-H, 8b-H), 2.58–2.66 (m, 1 H, 8a-H), 2.76–2.81 ("m", $^3J_{5,6}$ = 4.6 Hz, 1 H, H.6), 3.05 (dd, $^3J_{4,5}$ = 9.2, $^3J_{5,6}$ = 4.6 Hz, 1 H, 5-H), 3.38 (dd, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 3.77 (dd, $^3J_{2,3}$ = 3.8, $^3J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.93 (d, $^3J_{2,3}$ = 3.8 Hz, 1 H, 2-H), 3.99 (s, 2 H, OCH_2), 4.59, 4.65, 4.68, 4.99 (4 d, 4 H, OCH_2), 7.01–7.19, 7.39–7.43 (2 m, 15 H, Ar) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 26.15 (1 C, C-7), 36.06 (1 C, C-8), 53.62 (1 C, C-6), 57.17 (1 C, C-5), 72.86, 73.50, 73.53 (3 C, OCH_2), 81.00 (1 C, C-4), 81.44 (1 C, C-3), 83.95 (1 C, C-2), 127.61–128.78 (15 C, Ar), 210.56 (1 C, CO) ppm. MALDI-TOF-MS: m/z = 482 $[M+Na]^+$, 490 $[M+K]^+$; $C_{29}H_{30}O_5$ (458.6): calcd. C 75.95, H 6.61; found C 75.97, H 7.35.

(2*S*,3*R*,4*S*,5*R*,6*R*)-2,3,4-Tris(acetyloxy)-5,6-epoxycyclooctanone (31): A solution of compound **12** (30 mg, 0.1 mmol) in anhydrous dichloromethane (2 mL) was stirred with 3-chloroperbenzoic acid (35 mg, 80%, ca. 0.2 mmol) for 3 days at room temperature. Following dilution with ethyl acetate the organic phase was washed with a saturated sodium hydrogen carbonate solution and concentrated to dryness. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 5:1 to 1:2) to give **31** (27 mg, 84%) as a colourless syrup. $C_{14}H_{18}O_8$, M = 314.3. $[\alpha]_{578}^{20}$ = –108.7 (c = 2.0, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67 (m, 1 H, 7a-H), 2.01, 2.02, 2.04 (3 s, 3×3 H, 3 Ac), 2.43 (m, 1 H, 7b-H), 2.58 (ddd, $^3J_{7a,8a}$ = $^3J_{7b,8a}$ = 4.9, $^2J_{8a,8b}$ = 13.2 Hz, 1 H, 8a-H), 2.89 (dt, $^3J_{7a,8b}$ = $^3J_{7b,8b}$ = 4.4, $^2J_{8a,8b}$ = 13.2 Hz, 1 H, 8b-H), 2.94 (dd, $^3J_{4,5}$ = 8.6, $^3J_{5,6}$ = 4.4 Hz, 1 H, 5-H), 3.07 (dt, $^3J_{5,6}$ = $^3J_{6,7a}$ = 4.4, $^3J_{6,7b}$ = 11.2 Hz, 1 H, 6-H), 4.97 (dd, $^3J_{3,4}$ = 10.7, $^3J_{4,5}$ = 8.6 Hz, 1 H, 4-H), 4.98 (d, $^3J_{2,3}$ = 7.6 Hz, 1 H, 2-H), 5.27 (dd, $^3J_{2,3}$ = 7.6, $^3J_{3,4}$ = 10.7, 1 H, 3-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.23, 19.48, 19.64 (3 C, 3 Ac), 28.68, 37.53 (2 C, C-7, C-8), 53.38, 53.99 (2 C, C-5, C-6), 69.01, 70.05, 74.53 (3 C, C-2, C-3, C-4), 168.22, 168.29, 168.89 (3 C, 3 acetyl-CO_2), 204.38 (1 C, C-1) ppm. EI-MS: m/z = 314 $[M]^+$.

(*S*)-3,5-Bis(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)cycloocta-1,3,6-triene (32): Under argon a solution of butyllithium in hexane (1.6 M, 0.11 mL, 176 μmol) was added to a solution of dry diisopropylamine (28 μL, 20 mg, 200 μmol) in dry THF (0.5 mL) at –78 °C and the mixture was stirred for ten minutes. Afterwards a solution of **14** (70 mg, 158 μmol) in THF (4 mL) was added dropwise during five minutes. Stirring was continued for one hour at –60 to –80 °C. Then *tert*-butylchlorodimethylsilane (41 mg, 272 μmol) was added and the solution was stirred at room temperature overnight. The solvent was evaporated and the residue taken up in pentane (7 mL). Removal of the precipitate by filtration and evaporation of the solvent followed by column chromatography (petroleum ether/ethyl acetate, 70:1) gave **32** (21 mg, 47 μmol, 30%) as a yellowish syrup. $C_{28}H_{36}O_3Si$, M = 448.7. $[\alpha]_D^{20}$ = –87.4 (c = 1, dichloromethane). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.13, 0.14 (2 s, 2×3 H, Me), 0.99 (s, 9 H, *tert*-butyl), 2.24–2.32, 2.80–2.86 (2 "m", $^3J_{1,8a}$ = $^3J_{1,8b}$ = 7.9 Hz, 2×1 H, 8a/b-H), 4.40, 4.52, 4.56, 4.61 (4 d, 4×1 H, OCH_2), 4.90 (d, $^3J_{4,5}$ = 6.1 Hz, 1 H, 4-H), 4.94 (dd, $^3J_{1,8a}$ = $^3J_{1,8b}$ = 7.9 Hz, 1 H, 1-H), 5.11 (dd, $^3J_{4,5}$ = 6.1, $^3J_{5,6}$ = 2.8 Hz, 1 H, 5-H), 5.43–5.48 ("m", $^3J_{6,7}$ = 11.0 Hz, 1 H, 7-H), 6.02 (ddd, $^3J_{6,7}$ = 11.0 Hz, 1 H, 6-H), 7.05–7.35 (m, 10 H, Ar) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = –4.36, –4.12 (2 C, Me), 25.44 (1 C, C-7), 25.91 (3 C, *tert*-butyl), 70.01, 70.54 (2 C, OCH_2), 75.53 (1 C, C-4), 105.87 (1 C, C-3), 108.20 (1 C, C-8), 126.27 (1 C, C-6), 127.54–128.57 (10 C, Ar), 133.40 (1 C, C-5), 137.57, 139.44 (2 C, Ar), 149.60 (1 C, C-1), 152.49 (1 C, C-2) ppm. MALDI-TOF-MS: m/z = 471 $[M+Na]^+$, 487 $[M+K]^+$; $C_{28}H_{36}O_3Si$ (448.7): calcd. C 74.95, H 8.10; found C 74.28, H 8.43.

(2*S*,3*R*,4*S*,5*S*,6*S*)-2,3,4-Tris(benzyloxy)-5,6-dihydroxycyclooctan-1-one (33a) and (2*S*,3*R*,4*S*,5*R*,6*R*)-2,3,4-Tris(benzyloxy)-5,6-dihydroxycyclooctan-1-one (33b): *N*-Methylmorpholine *N*-oxide monohydrate (7 mg, 52 μmol) and a small crystal of osmium tetraoxide (catalytic amount) were added to a solution of **14** (20 mg, 45 μmol) in a mixture of water (1.0 mL), acetone (0.9 mL) and *t*BuOH (0.1 mL). After the solution had been stirred overnight, $Na_2S_2O_5$ (2 mg, 10 μmol) was added and stirring continued for one hour. Evaporation of the solvents and purification of the residue by column chromatography (petroleum ether/ethyl acetate, 1:1) gave **33a** (8 mg, 17 μmol) as a colourless solid, **33b** (1 mg, 2 μmol) as a colourless syrup and a mixed fraction of **33a/33b** (6 mg, 13 μmol, ratio **33a/33b** = 1.0:0.2) also as a colourless syrup. The total yield amounted 15 mg of **33a/b** (32 μmol, 70%).

33a: $C_{29}H_{32}O_6$, M = 476.6; m.p. 108 °C. $[\alpha]_D^{20}$ = –4.9 (c = 0.63, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (ddd, $^2J_{8a,8b}$ = 13.4 Hz, 1 H, 8b-H), 1.76–1.83 (m, 2 H, 7a/b-H), 2.05–2.14 ("m", $^2J_{8a,8b}$ = 13.4 Hz, 1 H, 8a-H), 3.30 (dd, $^3J_{3,4}$ = 8.7, $^3J_{4,5}$ = 3.2 Hz, 1 H, 4-H), 3.34 (dd, 1 H, 6-H), 3.49 (d, $^3J_{2,3}$ = 8.7 Hz, 1 H, 2-H), 3.88 (dd, $^3J_{2,3}$ = $^3J_{3,4}$ = 8.7 Hz, 1 H, 3-H), 4.14 (br. d, $^3J_{4,5}$ = 3.2 Hz, 1 H, 5-H), 4.61, 4.64, 4.65, 4.71, 4.81, 4.85 (6 d, 6 H, OCH_2), 7.27–7.37 (15 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.13 (1 C, C-7), 31.19 (1 C, C-8), 65.82 (1 C, C-6), 72.71, 75.57, 75.71 (3 C, OCH_2), 78.82 (1 C, C-4), 81.30, 81.50, 81.67 (3 C, C-2, C-3, C-5), 127.95–128.78, 136.89, 137.92, 138.47 (18 C, Ar) ppm. MALDI-TOF-MS: m/z = 499 $[M+Na]^+$, 515 $[M+K]^+$.

33b: $C_{29}H_{32}O_6$, M = 476.6. $[\alpha]_D^{20}$ = –7.8 (c = 0.1, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.65–1.73 ("m", $^2J_{8a,8b}$ = 13.4, $^4J_{2,8b}$ = 1.5 Hz, 1 H, 8b-H), 1.83–1.89 (m, 1 H, 7b-H), 1.94–2.05 (m, 1 H, 7a-H), 2.30 (ddd, $^2J_{8a,8b}$ = 13.4 Hz, 1 H, 8a-H), 3.49 (dd, $^3J_{2,3}$ = 8.7, $^4J_{2,8b}$ = 1.5 Hz, 1 H, 2-H), 3.88 (dd, $^3J_{3,4}$ = 8.7, $^3J_{4,5}$ = 6.8 Hz, 1 H, 4-H), 3.96 (dd, $^3J_{2,3}$ = $^3J_{3,4}$ = 8.7 Hz, 1 H, 3-H), 4.01 (br. m, 1 H, 6-H), 4.19 (ddd, $^3J_{4,5}$ = 6.8 Hz, 1 H, 5-H), 4.64, 4.69, 4.73, 4.82, 4.84, 4.93 (6 d, 6 H, OCH_2), 7.28–7.36 (15 H, Ar) ppm. MALDI-TOF-MS: m/z = 499 $[M+Na]^+$, 515 $[M+K]^+$.

(4*R*,5*R*,6*S*,7*R*,8*R*)-6,7,8-Triacetoxy-4,5-epoxyoctane-8-olide (35): A solution of triacetate **12** (21 mg, 70 μmol) and 3-chloroperbenzoic acid (45 mg, 70%, ca. 183 μmol) in CD_2Cl_2 (1 mL) was kept in an NMR tube at room temperature for three weeks. After one week the epoxide **31** was the main product with ca. 10% of starting material **12** left and ca. 2% of lactone **35**. After three weeks the amount of lactone constituted approx. 10% of the mixture. $C_{14}H_{18}O_9$, M = 330.3. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 6.87 (d, $^3J_{7,8}$ = 7.6 Hz, 1 H, 8-H), 5.40 (dd, $^3J_{6,7}$ = 9.9, $^3J_{7,8}$ = 7.6 Hz, 1 H, 7-H), 4.77 (dd, $^3J_{5,6}$ = 9.2, $^3J_{6,7}$ = 9.9 Hz, 1 H, 6-H) ppm. MALDI-TOF-MS: m/z = 353.4 $[M+Na]^+$, 369.3 $[M+K]^+$.

CCDC-269566 (for **12**) and -269567 (for **24**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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