C-Disaccharides of Ketoses

Hansjörg Streicher, Armin Geyer, and Richard R. Schmidt*

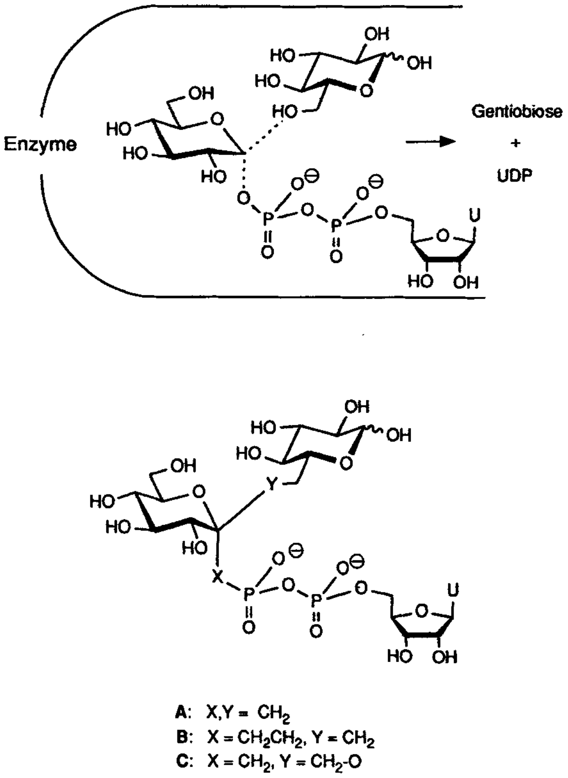
Abstract: Reaction of gluconolactone **2** with allylmagnesium bromide at low temperatures afforded ketopyranose **3**, which could easily be converted into open-chain ketoses (*R*)-**6** and (*S*)-**6**. Their reaction with lithioacetylide **9** afforded propargylic alcohol derivatives (*R*)-**10** and (*S*)-**10**, which could not be cyclized directly to the desired *C*-ketosides. They were converted by standard procedures into (*R*)-**14** and (*S*)-**14** and then into dicobalthexacarbonyl complexes (*R*)-**16** and (*S*)-**16**. A facile acid-catalyzed ring closure gave the desired *C*-ketosides (*R*)-**18**α/β and (*S*)-**18**α/β, respectively, in different ratios. In order to demonstrate that removal of the protective groups and hydrogenation of the CC triple bond proceed smoothly, (*R*)-**18**α was transformed into the deprotected target molecule (*R*)-**1**α. For the assignment of the new chiral centers at C-2/2′ and at C-8, (*S*)-**18**α was transformed into azido derivative (*S*)-**22**α, which underwent intramolecular cycloaddition to afford the spiro derivative (*S*)-**25**α. Because of the conformational constraints in this molecule, unequivocal configurational assignment was possible with the help of NMR data.

Keywords
alkynes · *C*-glycosides · cobalt complexes · cyclizations · enzyme inhibitors

Introduction

The manifold occurrence of complex oligosaccharide structures as epitopes at the cell surface[1–3] and the various biological functions attributed to these molecules[3,4] has led to a great interest in their synthesis, which has mainly been achieved by chemical and enzymatic means.[1,2,5,6] To understand these functions, structural analogues that are, for instance, stable to glycosidases or inhibitors of glycosyl transferases are required for biological testing. Carbon-bridged saccharide analogues[7,8] should play an important role because they are thought to affect the activity of glycosidases mainly by competitive inhibition,[8–11] as has meanwhile been confirmed for some representative examples.[10,12]

Of special interest are inhibitors of glycosyl transferases, which—as regio- and stereoselective catalysts—generate the complex oligosaccharide structures mainly with nucleoside mono- or diphosphate sugars as glycosyl donors.[13,14] Although knowledge of the active site of glycosyl transferases is rather limited,[15,16] investigations into some transferase inhibitors[15] indicate that the glycosyl donor and acceptor are in close proximity in the transition state in the active site of the enzyme (Scheme 1).[16] This structural orientation is also required for the generation of antibodies catalyzing glycosylation reactions. In this context, carbon-bridged sugars of type **A**–**C** are of great interest; their synthesis also offers a general approach for the formation of *C*-ketosides.[17,18,19]



Scheme 1. Schematic representation showing the generation of gentiobiose from UDP glucose and glucose.

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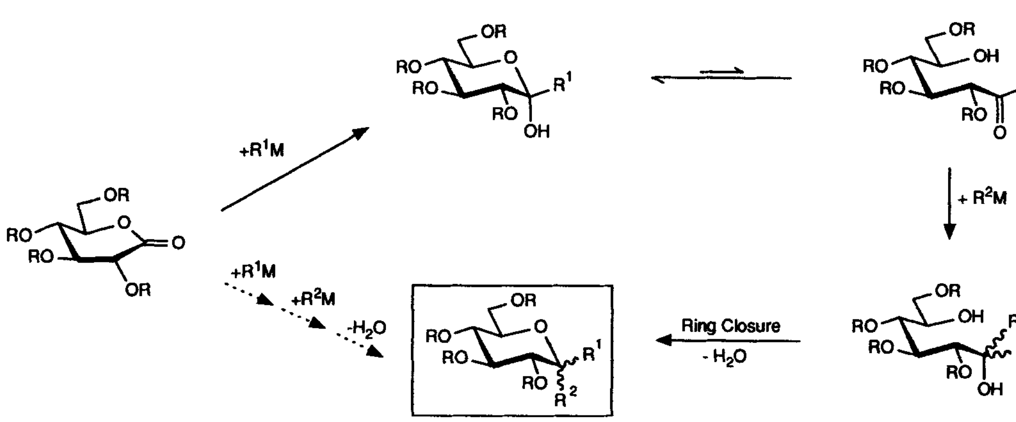
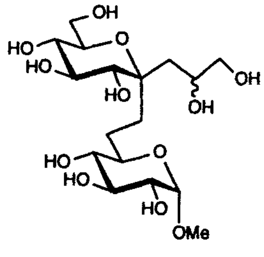
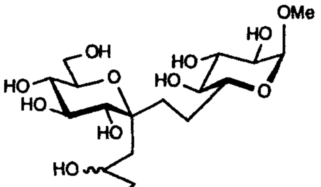


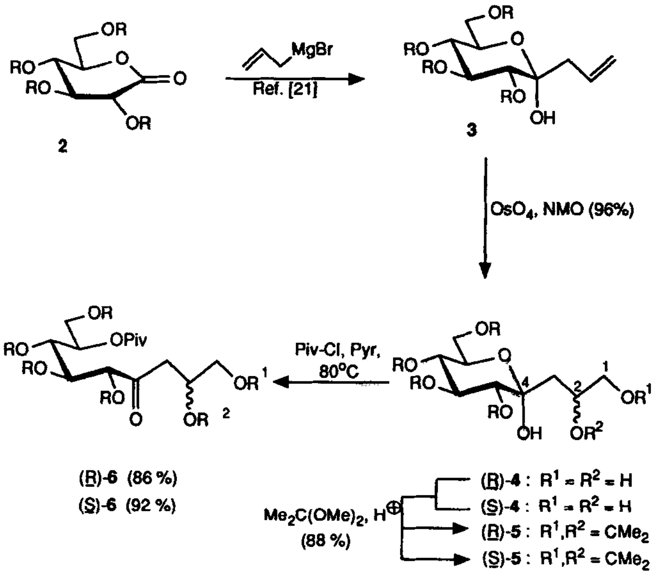
Scheme 2. General approach to the synthesis of carbon-bridged sugars of type **1**.



(R)-**1α**
(S)-**1α**



(R)-**1β**
(S)-**1β**



Scheme 3.

Results and Discussion

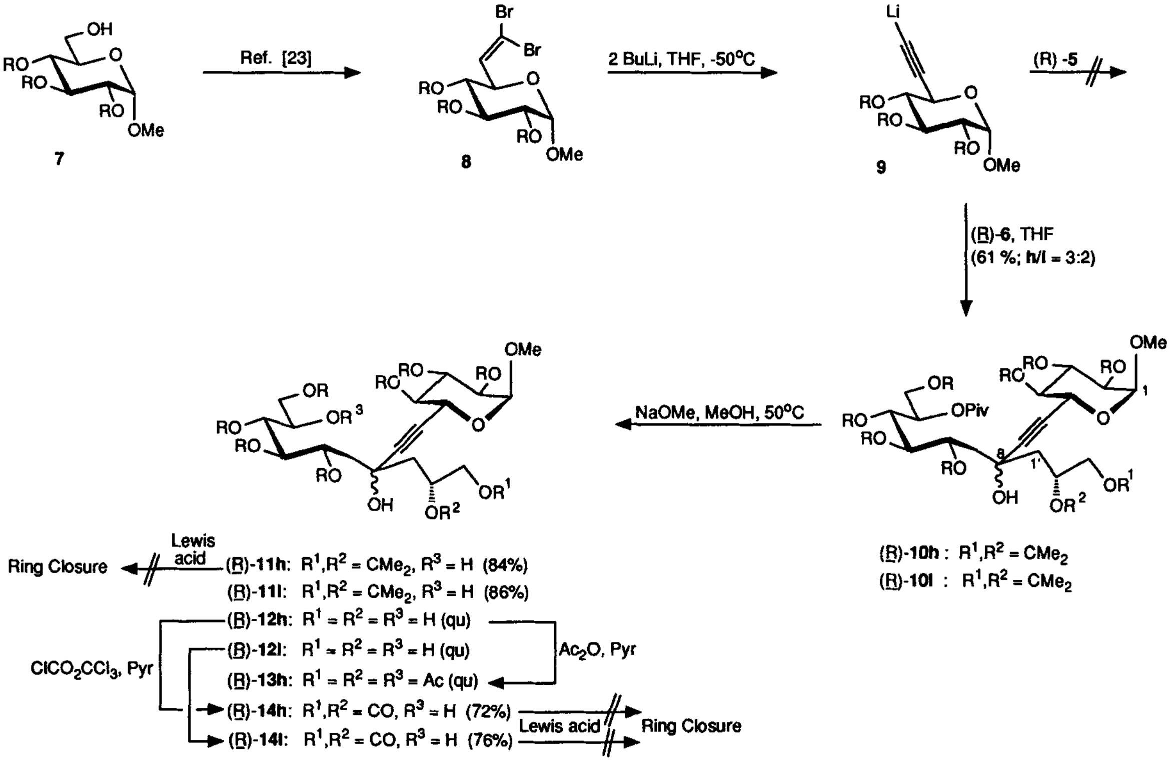
The strategy shown in Scheme 2 demonstrates that sugar lactones are promising starting materials for a general approach to carbon-bridged sugars. This scheme is based on the addition of two different functional carbon nucleophiles to the lactone carbon atom in successive steps, followed by ring closure. To study this strategy, *C*-ketosides **1** were chosen as target molecules because they contain two sugar residues and a functional C_3 moiety available for further modification.[20] For instance, phosphonate residues could be attached to the C_3 moiety in **1**, or "trisubstrate analogues"[16] could be generated.

Synthesis of the Target Molecules: Addition of a *C*-nucleophile to gluconolactone at low temperature followed by addition of a second equivalent of the nucleophile to the generated ketone moiety has already been reported.[21,22] Thus, addition of allylmagnesium bromide to D-gluconolactone **2** at −80 °C led almost exclusively to formation of compound **3**[21] (Scheme 3). Addition of a second allyl group was not observed because ring–chain tautomerism liberating the ketone moiety was too slow.

Dihydroxylation of **3** with catalytic amounts of OsO_4 and *N*-methylmorpholine *N*-oxide (NMO) as oxidizing agent afforded an approximately 2:3 mixture of (*R*)-**4** and (*S*)-**4**. *O*-Isopropylidenation with 2,2-dimethoxypropane in the presence of pyridinium *p*-toluenesulfonate as catalyst gave (*R*)-**5** and (*S*)-**5** in high overall yield, and the enantiomers could then be separated. Treatment of (*R*)-**5** and (*S*)-**5** with pivaloyl chloride (Piv-Cl) in pyridine at 80 °C provided the open-chain compounds (*R*)-**6** and (*S*)-**6**, respectively, having the desired readily accessible ketone moiety. The configuration at C-2 [(*R*) vs. (*S*)] was assigned at a later stage (see below).

Transformation of 6-*O*-deprotected glucose derivative **7** into dibromoolefin **8** and generation of lithioacetylide **9** was achieved by known procedures[23] (Scheme 4). As expected, **9** did not react with ketopyranose derivative (*R*)-**5**; however, reaction with ketone (*R*)-**6** in THF readily afforded (*R*)-**10h** and (*R*)-**10l** in a ratio of 3:2 (**h** = higher-, **l** = lower-moving spot on TLC based on (*R*)-**10**). After removal of the pivaloyl group with sodium methoxide in methanol at 50 °C [→(*R*)-**11h** and (*R*)-**11l**], attempts at direct acid-catalyzed ring closure either resulted in deisopropylidenation [→(*R*)-**12h** and (*R*)-**12l**] or no reaction took place. For a more detailed structural characterization, compound (*R*)-**12h** was transformed into tri-*O*-acetyl derivative (*R*)-**13h** with acetic anhydride in pyridine. In order to avoid deprotection during ring closure, compounds (*R*)-**12h** and (*R*)-**12l** were converted with diphosgene and pyridine into cyclic carbonates (*R*)-**14h** and (*R*)-**14l**, respectively; however, their treatment with different Lewis acids, in order to obtain the cyclized products, gave either no reaction ($ZnCl_2 \cdot OEt_2$, $BF_3 \cdot OEt_2$) or led to decomposition ($TiCl_4$).

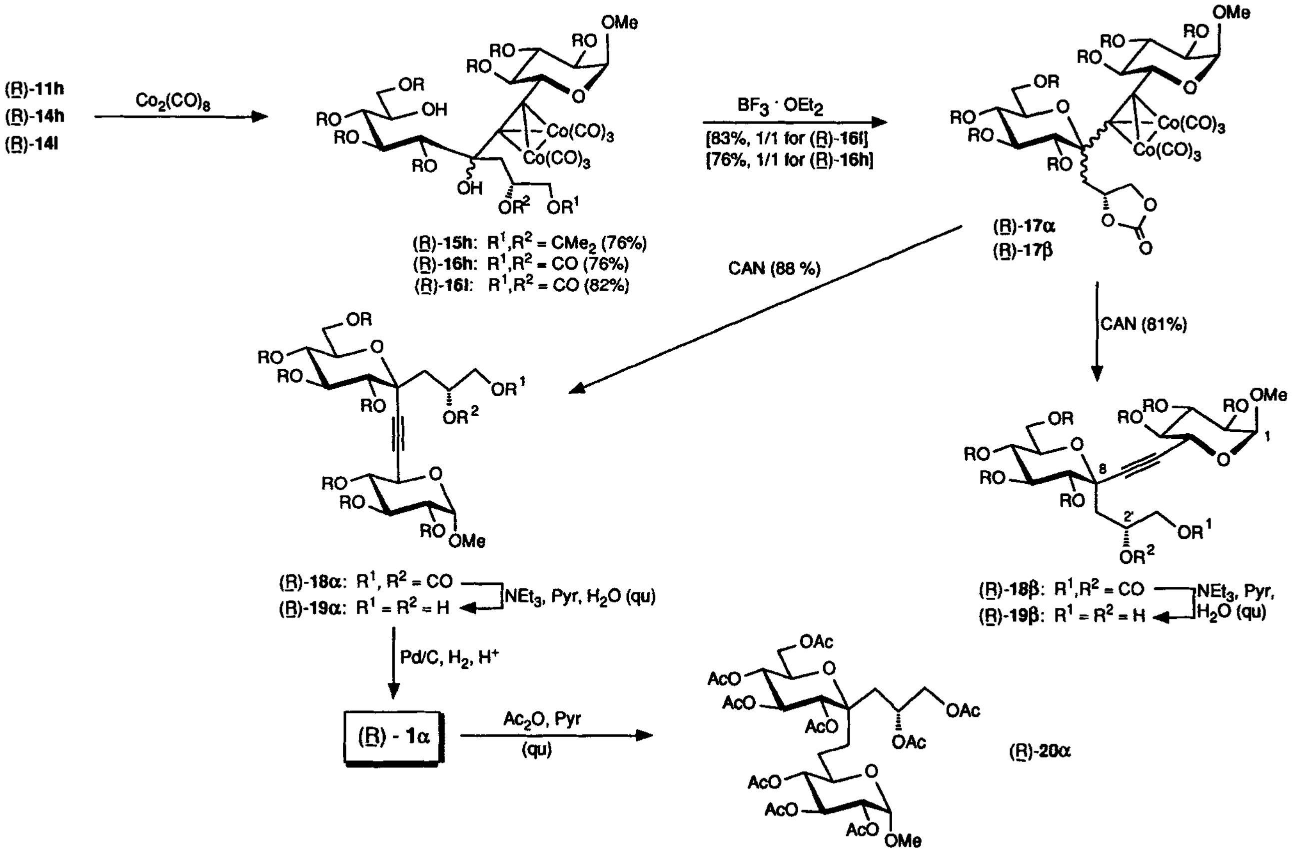
Thus, it became clear that the generation of a carbonium ion from the propargyl moiety in these systems was not a trivial matter. We therefore decided to take advantage of the known stabilization of propargylic cations in dicobalthexacarbonyl complexes.[24] To this end, (*R*)-**11h**, (*R*)-**14h**, and (*R*)-**14l** were



Scheme 4. R = benzyl.

treated with dicobaltoctacarbonyl to generate the desired dicobalthexacarbonyl complexes (*R*)-**15h**, (*R*)-**16h**, and (*R*)-**16l**, respectively, in high yields (Scheme 5); the complexes could be isolated and characterized, at least by FAB-MS.

Complexes (*R*)-**16h** and (*R*)-**16l** were particularly prone to cyclization. Upon treatment with $BF_3 \cdot OEt_2$ 1:1 mixtures of (*R*)-**17**α and (*R*)-**17**β were obtained, independent of the configuration at the carbinol carbon. The cyclized intermediates were



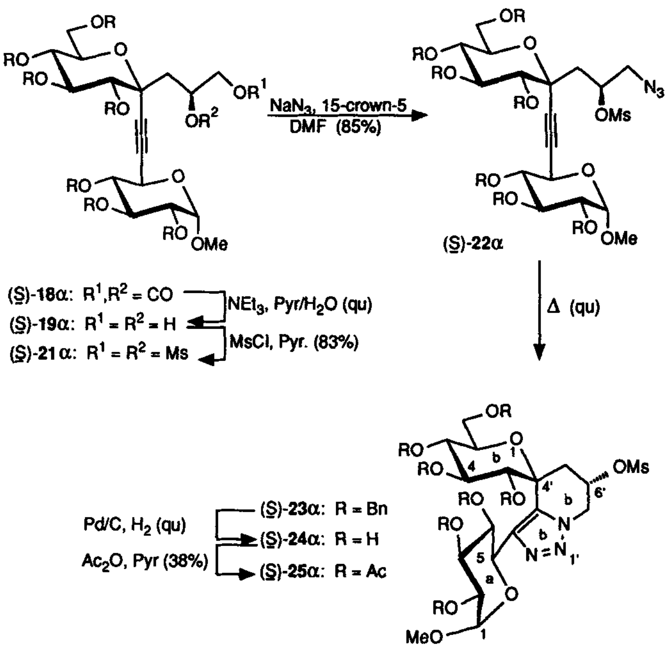
Scheme 5. R = benzyl.

separated after decomplexation with ceric ammonium nitrate (CAN) to yield compounds (*R*)-**18**α and (*R*)-**18**β. The carbonate moiety was removed by treatment with triethylamine in pyridine/water to furnish (*R*)-**19**α and (*R*)-**19**β, respectively, in high yield. Ready access of target molecules **1** (Scheme 2) was demonstrated for (*R*)-**1**α by hydrogenolytic debenzylation and concomitant hydrogenation of the CC triple bond of (*R*)-**19**α with palladium on carbon as catalyst to yield (*R*)-**1**α. To facilitate structural characterization, the latter was transformed into the per-*O*-acetyl derivative (*R*)-**20**α. Unequivocal assignment of the configuration at C-8 (α/β) of the *C*-disaccharides was achieved at a later stage (see below).

The extension of the reaction sequence described above to the (*S*) series to give the ring-closed products was quite straightforward (Scheme 6). Surprisingly, reaction of (*S*)-**6** with **9** gave a single isomer, namely, (*S*)-**10**; again, the configuration at the carbinol carbon was not assigned. Depivaloylation followed by deisopropylidenation afforded (*S*)-**12**, which was transformed into (*S*)-**14** with diphosgene carbonate. Treatment with $Co_2(CO)_8$ furnished dicobalt hexacarbonyl complex (*S*)-**16**. Treatment with $BF_3 \cdot OEt_2$ and decomplexation with CAN yielded (*S*)-**18**α and (*S*)-**18**β in a 10:1 ratio. The diastereoselectivity was thus much higher in the (*S*) series.

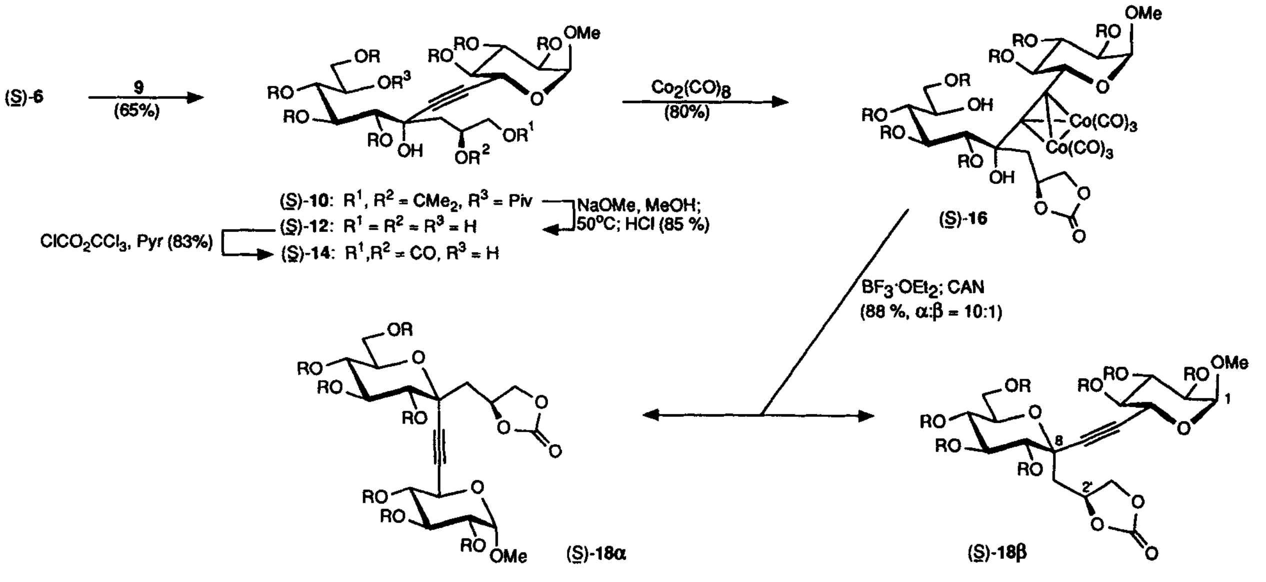
Structural Assignment: The configurations at C-2 in **4** (or C-2' in **10** or **18**) and at C-8 in **18** and derived products could not be assigned unequivocally based on ^{1}H NMR data. However, intramolecular cyclization yields structurally restricted derivatives which frequently exhibit little conformational averaging of nuclear Overhauser enhancements (NOE's) and of three-bond couplings.[24] Thus, the configuration at C-2' and at C-8 could be readily determined by NMR spectroscopy of spiro compound (*S*)-**25**α, which was readily obtained from (*S*)-**18**α (Scheme 7).

Removal of the carbonate group in (*S*)-**18**α with triethylamine in pyridine/water afforded (*S*)-**19**α; treatment with methanesulfonyl (Ms) chloride in pyridine furnished di-*O*-mesyl derivative (*S*)-**21**α. Reaction with sodium azide in DMF in the presence of 15-crown-5 led to formation of a monoazido compound (*S*)-**22**α, which underwent intramolecular cycloaddition on heating to provide the spiro compound (*S*)-**23**α. Hydrogenolytic debenzylation with palladium on carbon as catalyst [→ (*S*)-**24**α] followed by reaction with acetic anhydride in pyridine afforded (*S*)-**25**α.



Scheme 7. For **18**–**22**, R = benzyl.

Interproton couplings from the ^{1}H NMR spectra of compound (*S*)-**25**α confirmed the expected $^4C_1$ chair conformations of the two pyranose rings. The $^3J_{C,H}$ couplings were interpreted in a qualitative manner from HMBC spectra.[26] An intense heteronuclear three-bond correlation between C-7 (C-3a'; numbering of spiro compound (*S*)-**25**α is given in brackets) and H-9 (H-3b) can only arise from a *trans* arrangement of C-7–C-8–C-9–H-9 (C-3a'–C-4'–C-3b–H-3b), that is, from a D-*ido* configuration at C-8 (C-4'). A $^3J_{C-7,H-9}$ coupling of 7 Hz was extracted from a gated decoupled ^{13}C NMR spectrum with selective irradiation of H-1'^{proR} (H-5'^{proR}). Interproton distances from a NOESY spectrum[27] (τ_{mix} = 150 ms) and three-bond homo- and heteronuclear couplings allow the assignment of the diastereotopic geminal proton pairs at 1' (5') and 3' (7'). The



Scheme 6. R = benzyl.

Table 1. Interproton distances derived from a 2D NOESY spectrum of spiro compound (*S*)-**25**α, and the distances after 25 ps of molecular dynamics (MD) simulation. Numbering of protons refers to (*S*)-**25**α (Scheme 7).

		NOE [pm]	MD [pm]
H 4b	H 6b	260	258
H 3b	H 5'^{proR}	230	222
H 3b	H 5'^{proS}	250	267
H 6'	H 5'^{proR}	220	242
H 6'	H 5'^{proS}	280	259
H 6'	H 7'^{proS}	260	246
H 6'	H 7'^{proR}	230	259
H 5'^{proR}	H 7'^{proR}	270	265
H 2a	H 4b	300	282
H 4a	H 4b	300	282

NOE distances are given in Table 1. From this we conclude that C-2' (C-6') has an (*S*) configuration.

Ten distances derived from NOEs and three torsion angles were included as restraints in a molecular dynamics simulation.[28] The energy-minimized structure is shown in Figure 1. The piperidine ring with an exocyclic double bond exhibits an envelope conformation with C-1' (5) above the plane. The average restraint violation of this structure is below 10%.

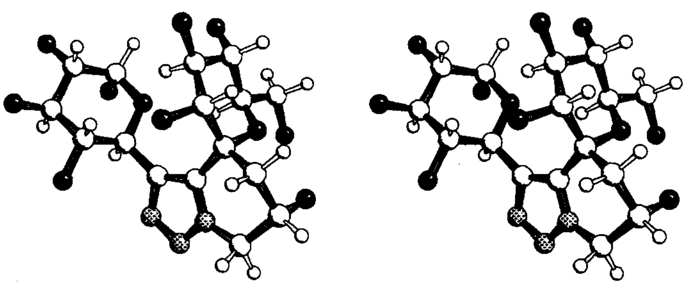


Fig. 1. Energy-minimized structure of (*S*)-**25**α.

To confirm the structural assignments, we also investigated the enantiomeric pairs (*R*)-**18**(α/β) and (*S*)-**18**(α/β), and found the NMR data to be consistent with the absolute configuration at C-8 (no data given).

Conclusion

An efficient synthesis of *C*-ketosides has been developed, based on addition of a carbon nucleophile to *O*-benzyl-protected gluconolactone at low temperature to give the expected ketopyranose. The ketose ring could be readily opened to liberate the ketone, and addition of a second nucleophile generated a carbinol moiety. After protection of the propargylic alcohol as the dicobalt hexacarbonyl complex, the key ring-closure step could be readily performed to furnish the target molecules.

Experimental Procedure

Solvents were purified according to standard procedures. Melting points (uncorrected): metal block. ^{1}H and ^{13}C NMR spectra (22 °C; TMS and the resonance of the deuterated solvent as internal standard; solvents: $CDCl_3$, 99.8%, $\delta = 7.24$; D_2O, 99.95%, $\delta = 4.63$; MeOD, 99.95%, $\delta = 3.30$): Bruker AC250 Cryospec, Jeol JNM-GX400, Bruker DRX600. IR spectra: Mattson Polaris FT-IR spectrometer (22 °C). Column chromatography: flash silica gel 60 (0.040–0.063 mm). Medium-pressure liquid chromatography (MPLC): Merck silica gel LiChroprep Si 60, 15–25 µm. Thin-layer chromatography (TLC): Merck plates, silica gel 60 F_{254}, layer thickness 0.2 mm; detection by treatment with a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (20 g) and $Ce(SO_4)_2$ (0.4 g) in 10% sulfuric acid (400 mL). Optical rotations: Perkin-Elmer polarimeter 241/MS; 1 dm cell; 22 °C. FAB-MS spectra: Finnigan MAT312; 70 eV; 70 °C.

5,6,7,9-Tetra-*O*-benzyl-1,2,3-trideoxy-α-D-*gluco*-non-1-en-4-ulopyranose (3): 2,3,4,6-Tetra-*O*-benzyl-D-*glucono*-1,5-lactone **2** [29] was converted into nonenulose **3** by the method of Kishi [21].

5,6,7,9-Tetra-*O*-benzyl-3-deoxy-α-D-*gluco*-D-*glycero*-non-4-ulopyranose [(*R*)-**4**] and **5,6,7,9-Tetra-*O*-benzyl-3-deoxy-α-D-*gluco*-L-*glycero*-non-4-ulopyranose** [(*S*)-**4**]: Ketose **3** (30 g, 51.7 mmol) and *N*-methylmorpholine *N*-oxide (9.05 g) were dissolved in a mixture of acetone/water/*t*BuOH (3:1:0.1/300 mL). OsO_4 (100 mg), dissolved in 2 mL of the same mixture, was added, and the reaction stirred until TLC indicated the absence of starting material (≈7 h). After quenching with sodium bisulfite (1.5 g) in water (75 mL) the mixture was stirred for 15 min, and the precipitate was filtered off and washed carefully with the solvent mixture. The combined filtrates were diluted with water (150 mL), adjusted to pH 7 with 10% sulfuric acid, and extracted with ethyl acetate (3 × 100 mL). The combined extracts were dried (Na_2SO_4), filtered, and concentrated. Chromatography of the residue (eluant: toluene/ethyl acetate 1:3) gave a 2:3 mixture of diastereomers (*R*)-**4** and (*S*)-**4** (30.5 g, 96%) as colorless crystals; TLC: $R_f = 0.3$ (toluene/ethyl acetate 1:2); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.38$, 1.61, 1.86, 1.93 (4dd, 4H; 3a-, 3b-H (D,L)), 3.24–3.64 (m, 12H), 3.93–4.08 (m, 6H), 4.42–4.94 (m, 16H), 7.24–7.34 (m, 40H). The crude mixture of diastereomers (*R*)-**4** and (*S*)-**4** was used for the next step without further purification.

5,6,7,9-Tetra-*O*-benzyl-3-deoxy-1,2-*O*-isopropylidene-α-D-*gluco*-D-*glycero*-non-4-ulopyranose [(*R*)-**5**] and **5,6,7,9-Tetra-*O*-benzyl-3-deoxy-1,2-*O*-isopropylidene-α-D-*gluco*-L-*glycero*-non-4-ulopyranose** [(*S*)-**5**]: The mixture of diastereomers (*R*)-**4** and (*S*)-**4** (1:1.4, 25 g, 43 mmol) was dissolved in dry, alcohol-free acetone (800 mL). 2,2-Dimethoxypropane (62.5 mL) and pyridinium *p*-toluenesulfonate (1 g) were added, and the solution was stirred overnight. Following evaporation of the solvent, the residue was chromatographed (eluant: toluene/ethyl acetate 6:1 → 1:1) to give (*R*)-**5** (10 g, colorless needles) and (*S*)-**5** (14 g, colorless oil) in a total yield of 88%.
(*R*)-**5**: Mp. 118 °C; TLC: $R_f = 0.3$ (toluene/ethyl acetate 6:1); $[\alpha]_D = -22.4$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.28$ (dd, $^3J(3a,2) = 2.5$ Hz, 1H; 3a-H), 1.32, 1.40 (2s, 6H; $C(Me)_2$), 1.93 (dd, $^2J(3b,3a) = 14.1$ Hz, $^3J(3b,2) = 10.8$ Hz, 1H; 3b-H), 3.24 (dd, $^3J(5,6) = 9.5$ Hz, $^4J(5,OH) = 1.3$ Hz, 1H; 5-H), 3.37 (dd, $^2J(1a,1b) = 8.8$ Hz, $^3J(1a,2) = 6.3$ Hz, 1H; 1a-H), 3.62–3.78 (m, 3H; 7-, 9a-, 9b-H), 3.96–4.10 (m, 3H; 1b-, 6-, 8-H), 4.46–4.97 (m, 9H; 2-H, 4 $PhCH_2$), 4.76 (d, 1H; OH), 7.14–7.35 (m, 20H; 4Ph); $C_{40}H_{46}O_8\cdot 0.25H_2O$ (659.3): calcd C 72.87, H 7.03; found C 72.92, H 7.07.
(*S*)-**5**: TLC: $R_f = 0.2$ (toluene/ethyl acetate 6:1); $[\alpha]_D = +17.2$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.25$, 1.30 (2s, 6H; $C(Me)_2$), 1.82 (dd, $^2J(3b,3a) = 14.5$ Hz, $^3J(3b,2) = 5.1$ Hz, 1H; 3b-H), 1.98 (dd, $^3J(3a,2) = 6.2$ Hz, 1H; 3a-H), 3.48–3.71 (m, 6H; 1b-, 5-, 7-, 9a-, 9b-H, OH), 3.87–3.96 (m, 3H; 1a-, 6-, 8-H), 4.20 (m, $^3J(3b,2) = 5.1$ Hz, $^3J(3a,2) = 6.2$ Hz, 1H; 2-H), 4.40–4.91 (m, 8H; 4 $PhCH_2$), 7.10–7.29 (m, 20H; 4Ph); $C_{40}H_{46}O_8\cdot 0.25H_2O$ (659.3): calcd C 72.87, H 7.03; found C 72.71 H 7.04.

5,6,7,9-Tetra-*O*-benzyl-3-deoxy-1,2-*O*-isopropylidene-8-*O*-pivaloyl-D-*gluco*-D-*glycero*-non-4-ulose [(*R*)-**6**]: (*R*)-**5** (9 g, 14.5 mmol) and pivaloyl chloride (60 mL), dissolved in pyridine (300 mL), were stirred at 80 °C for 60 h. After removal of the solvent under reduced pressure (0.2 Torr) the resulting sirup was chromatographed (eluant: toluene/ethyl acetate 9:1) to give ketone (*R*)-**6** (9.2 g, 86%) as a colorless syrup: TLC: $R_f = 0.38$ (toluene/ethyl acetate 9:1); $[\alpha]_D = +19.5$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.12$ (s, 9H; $C(Me)_3$), 1.20, 1.22 (2s, 6H; CMe_2), 2.29 (dd, $^2J(3b,3a) = 17$ Hz, $^3J(3b,2) = 5.8$ Hz, 1H; 3b-H), 2.75 (dd, $^3J(3a,2) = 7.1$ Hz, 1H; 3a-H), 3.11 (dd, $^2J(1a,1b) = 7.7$ Hz, $^3J(1a,2) = 7.7$ Hz, 1H; 1a-H), 3.62 (dd, $^2J(9a,9b) = 10.6$ Hz, $^3J(9a,8) = 5.7$ Hz, 1H; 9a-H), 3.76–3.86 (m, 3H; 1b-, 6-, 9b-H), 3.93 (dd, $^3J(7,6) = 4.6$ Hz, $^3J(7,8) = 4.6$ Hz, 1H; 7-H), 4.02–4.09 (m, 2H; 2-, 5-H), 4.34–4.68 (m, 8H; 4 $PhCH_2$), 5.14 (ddd, 1H; 8-H), 7.08–7.27 (m, 20H; 4Ph); $C_{45}H_{54}O_9$ (738.9): calcd C 73.14, H 7.37; found C 73.01, H 7.36.

5,6,7,9-Tetra-*O*-benzyl-3-deoxy-1,2-*O*-isopropylidene-8-*O*-pivaloyl-D-*gluco*-L-*glycero*-non-4-ulose [(*S*)-**6**]: Ketose (*S*)-**5** was pivaloylated as described for (*R*)-**5**. Isolation and purification by the same procedure gave (S)-**6** in 92% yield: TLC: $R_f = 0.5$ (toluene/ethyl acetate 9:1); $[\alpha]_D = +10.5$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.11$ (s, 9H; $C(Me)_3$), 1.18, 1.22 (2s, 6H; CMe_2), 2.41 (dd, $^2J(3b,3a) = 17.9$ Hz, $^3J(3b,2) = 6.9$ Hz, 1H; 3b-H), 2.94 (dd, $^3J(3a,2) = 5.8$ Hz, 1H; 3a-H), 3.20 (dd, $^2J(1a,1b) = 7.8$ Hz, $^3J(1a,2) = 7.8$ Hz, 1H; 1a-H), 3.60 (dd, $^2J(9a,9b) = 10.5$ Hz, $^3J(9a,8) = 5.8$ Hz, 1H; 9a-H), 3.81 (dd, $^3J(9b,8) = 4.3$ Hz, 1H; 9b-H), 3.86–4.06 (m, 5H; 1b-, 2-, 5-, 6-, 7-H), 4.34–4.63 (m, 8H; 4 $PhCH_2$), 5.16 (ddd, $^3J(9a,8) = 5.8$ Hz, $^3J(9a,8) = 5.8$ Hz, 1H; 8-H), 7.09–7.29 (m, 20H; 4Ph); $C_{45}H_{54}O_9$ (738.9): calcd C 73.14, H 7.37; found C 73.01, H 7.34.

Methyl 2,3,4-tri-*O*-benzyl-6-*C*-dibromomethylene-6-deoxy-α-D-glucopyranoside (8): Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (7) [30] was converted into dibromoolefine (**8**) [23,24] by a known two step procedure [30,31].

Methyl 2,3,4-tri-*O*-benzyl-6,7-dideoxy-*α*-D-glucohept-6-inopyranoside (9): Tetrahydrofuran solutions of lithioacetylide **9** [23] were generated by the following general procedure: A solution of dibromoolefin **8** in dry tetrahydrofuran was cooled to −50 °C under an atmosphere of nitrogen. BuLi (1.6 M in hexane, 2.05 equiv) was added and the solution stirred for 1 h.

Methyl 2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-8-*C*-(2′,3′-*O*-isopropylidene-L-*glycero*-propane-2′,3′-diol-1′-yl)-12-*O*-pivaloyl-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside [(*R*)-**10h** and (*R*)-**10l**]: A solution of lithioacetylide **9** in dry tetrahydrofuran (10 mL), prepared from **8** (800 mg, 1.3 mmol) was cooled to −80 °C. Ketone (*R*)-**6** (920 mg, 1.4 mmol) in dry tetrahydrofuran (10 mL) was added, and the stirred solution slowly warmed to −20 °C. After additional stirring for 30 min, the reaction was quenched with saturated ammonium chloride solution (20 mL), warmed to room temperature, and diluted with water (30 mL). After extraction with ethyl acetate (3 × 30 mL), the combined organic layers were dried (Na_2SO_4) and concentrated. Chromatography of the residue (eluant: toluene/ethyl acetate 9:1) gave (*R*)-**10h** (565 mg, colorless syrup) and (*R*)-**10l** (375 mg, colorless syrup) in a total yield of 61 %: (*R*)-**10h**: TLC: $R_f = 0.59$ (toluene/ethyl acetate 9:1); $[\alpha]_D = -7.3$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.11$ (s, 9H; C(Me)$_3$), 1.17, 1.26 (2s, 6H; CMe$_2$), 1.78–1.98 (m, 2H; 1′a-, 1′b-H), 3.23 (s, 3H; OMe), 3.33–3.44 (m, 3H; 2-, 3′a-, 4-H), 3.70–3.86 (m, 5H; 3-, 3′b-, 9-, 13a-, 13b-H), 3.95 (m, 1H; 10-H), 4.01 (m, 1H; 11-H), 4.22 (s, 1H; OH), 4.31–4.85 (m, 17H; 7PhCH$_2$, 1-, 2′-, 5-H), 5.25 (m, 1H; 12-H), 7.11–7.28 (m, 35H; 7Ph); $C_{74}H_{84}O_{14}$ (1192.4): calcd C 74.11, H 7.10; found C 73.74, H 7.08.
(*R*)-**10l**: TLC: $R_f = 0.54$ (toluene/ethyl acetate 9:1); $[\alpha]_D = +19.4$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.11$ (s, 9H; C(Me)$_3$), 1.15, 1.26 (2s, 6H; CMe$_2$), 1.90–1.97 (2dd, ^3J(1′a,2′) = 5.8 Hz, ^3J(1′b,2′) = 7.4 Hz, 2H; 1′a-, 1′b-H), 3.20 (s, 3H; OMe), 3.23–3.46 (m, 3H), 3.61–4.10 (m, 9H), 4.29–4.93 (m, 16H; 7PhCH$_2$, 1-, 5-H), 5.36 (ddd, 1H; 12-H), 7.06–7.30 (m, 35H; 7Ph); $C_{74}H_{84}O_{14}$ (1192.4): calcd C 74.11, H 7.10; found C 73.91, H 7.32.

Methyl 2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-8-*C*-(2′,3′-*O*-isopropylidene-D-*glycero*-propane-2′,3′-diol-1′-yl)-12-*O*-pivaloyl-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside [(*S*)-**10**]: Dibromoolefin **8** (5.6 g) in dry tetrahydrofuran (130 mL) was converted into lithioacetylide **9** as described above. After being cooled to −70 °C, a solution of ketone (*S*)-**6** (5.74 g, 7.8 mmol) in tetrahydrofuran (50 mL) was added. The mixture was slowly warmed to −40 °C and stirred for 1 h. The reaction was quenched with saturated ammonium chloride solution (100 mL), brought to room temperature, and diluted with water (200 mL). Following extraction with ethyl acetate (3 × 100 mL), the combined organic layers were dried (Na_2SO_4) and concentrated. The sirupy residue was chromatographed (eluant: toluene/ethyl acetate 9:1) to give (*S*)-**10** (6 g, 65 %) as a colorless oil: TLC: $R_f = 0.26$ (toluene/ethyl acetate 9:1); $[\alpha]_D = +6.8$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.10$ (s, 9H; C(Me)$_3$), 1.16, 1.26 (2s, 6H; CMe$_2$), 1.76 (dd, ^2J(1′b,1′a) = 13.4 Hz, ^3J(1′b,2′) = 5.6 Hz, 1H; 1′b-H), 2.02 (dd, ^3J(1′a,2′) = 4.5 Hz, ^2J(1′b,1′a) = 13.4 Hz, 1H; 1′a-H), 3.18 (s, 3H; OMe), 3.34–3.48 (m, 3H; 2-, 3′b-, 4-H), 3.59 (d, ^3J(9,10) = 4.4 Hz, 1H; 9-H), 3.64 (dd, ^2J(13b,13a) = 10.9 Hz, ^3J(13b,12) = 5.2 Hz, 1H; 13b-H), 3.74–3.83 (m, 2H; 3-, 13a-H), 3.88–3.96 (m, 2H; 3′a-, 11-H), 4.21 (dd, ^3J(10,9) = 4.9 Hz, ^3J(10,11) = 4.8 Hz, 1H; 10-H), 4.33–4.89 (m, 17H; 7PhCH$_2$, 1-, 2′-, 5-H), 5.25 (ddd, 1H; 12-H), 7.13–7.30 (m, 35H; 7Ph); $C_{74}H_{84}O_{14}$ (1192.4): calcd C 74.11, H 7.10; found C 73.87, H 7.09.

Methyl 2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-8-*C*-(2′,3′-*O*-isopropylidene-L-*glycero*-propane-2′,3′-diol-1′-yl)-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside [(*R*)-**11h**]: Pivaloyl ester (*R*)-**10h** (0.4 g, 0.34 mmol) was dissolved in a solution of sodium methoxide in methanol (0.5 M, 30 mL), and the mixture was stirred at 50 °C under an atmosphere of argon until TLC indicated the absence of starting material. The solution was cooled to room temperature and neutralized with Amberlite ion-exchange resin. The resin was filtered off and washed with methanol. The combined filtrates were concentrated and chromatographed (eluant toluene/ethyl acetate 2:1) to give (*R*)-**11h** (318 mg, 84 %) as a colorless syrup: TLC: $R_f = 0.4$ (toluene/ethyl acetate 4:1); $[\alpha]_D = -24$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.17$, 1.28 (2s, 6H; CMe$_2$), 1.63 (dd, ^2J(1′b,1′a) = 14.2 Hz, ^3J(1′b,2′) = 3.1 Hz, 1H; 1′b-H), 1.98 (dd, ^3J(1′a,2′) = 9.8 Hz, ^2J(1′b,1′a) = 14.2 Hz, 1H; 1′a-H), 2.96 (d, ^3J(OH,12) = 6.4 Hz, 1H; OH), 3.26 (s, 3H; OMe), 3.30–3.58 (m, 6H; 2-, 3′b-, 4-, 11-, 13a-, 13b-H), 3.66 (d, ^3J(9,10) = 5.8 Hz, 1H; 9-H), 3.75–3.84 (m, 3H; 3-, 3′a-, 10-H), 3.98 (m, 1H; 12-H), 4.21 (s, 1H; OH), 4.23 (m, 1H; 2′-H), 4.34–4.84 (m, 16H; 7PhCH$_2$, 1-, 5-H), 7.13–7.32 (m, 35H; 7Ph); $C_{69}H_{76}O_{13}$ (1113.4): calcd C 74.44, H 6.88; found C 74.43 H 6.97.

Methyl 2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-8-*C*-(2′,3′-*O*-isopropylidene-L-*glycero*-propane-2′,3′-diol-1′-yl)-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside [(*R*)-**11l**]: Compound (*R*)-**10l** was deacylated and purified as described for (*R*)-**10h**. Product (*R*)-**11l** (yield 86 %, $R_f = 0.3$, toluene/ethyl acetate 4:1) was directly used for further transformations.

Methyl 2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-8-*C*-(L-*glycero*-propane-2′,3′-diol-1′-yl)-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside [(*R*)-**12h**]: Pivaloyl ester (*R*)-**10h** (3,5 g, 2.94 mmol) was cleaved following the procedure described for (*R*)-**11h** until no more starting material was present. The pH was adjusted to 4 by addition of hydrochloric acid (2 M). Ethyl acetate was added to dissolve separated oil, and the mixture was stirred at 60 °C for 12 h. After neutralization with saturated aqueous hydrogen carbonate solution the mixture was concentrated to approximately one third of total volume, diluted with water, and extracted several times with ethyl acetate. The organic layers were dried (Na_2SO_4), concentrated and repeatedly coevaporated with dry toluene. The product (R)-**12h** (3.1 g, 98 %) was sufficiently pure for further transformations: TLC: $R_f = 0.34$ (toluene/ethyl acetate 1:1); $[\alpha]_D = -1.3$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.39$ (dd, ^2J(1′b,1′a) = 12.9 Hz, ^3J(1′b,2′) = 1 Hz, 1H; 1′b-H), 1.85 (dd, ^3J(1′a,2′) = 10.5 Hz, ^2J(1′b,1′a) = 12.9 Hz, 1H; 1′a-H), 3.15 (dd, ^2J(3′a,3′b) = 11.2 Hz, ^3J(3′a,2′) = 6 Hz, 1H; 3′a-H), 3.27 (s, 3H; OMe) 3.27–3.60 (m, 6H; 2-, 3′b-, 4-, 9-, 13a-, 13b-H), 3.72 (dd, ^3J(10,9) = 7.3 Hz, ^3J(10,11) = 4 Hz, 1H; 10-H), 3.81 (dd, ^3J(3,2) = 9.3 Hz, ^3J(3,4) = 9.3 Hz, 1H; 3-H), 3.95 (m, 1H; 12-H), 4.16 (m, 1H; 2′-H), 4.28 (dd, ^3J(11,12) = 5 Hz, ^3J(10,11) = 4 Hz, 1H; 11-H), 4.36–4.84 (m, 16H; 7PhCH$_2$, 1-, 5-H), 7.14–7.29 (m, 35H; 7Ph): $C_{66}H_{72}O_{13} \cdot H_2O$ (1091.3); calcd C 72.64, H 6.83; found C 72.78, H 6.88.

Methyl 2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-8-*C*-(L-*glycero*-propane-2′,3′-diol-1′-yl)-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside [(*R*)-**12l**]: (*R*)-**10l** was converted into (*R*)-**12l** (colorless oil) under the conditions described for (*R*)-**12h** with analogous reaction times and yields: TLC: $R_f = 0.29$ (toluene/ethyl acetate 1:1); $[\alpha]_D = +11.3$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.77$ (dd, ^2J(1′b,1′a) = 14.5 Hz, ^3J(1′b,2′) = 2.8 Hz, 1H; 1′b-H), 1.75–1.85 (br s, 1H; OH), 1.95 (dd, ^3J(1′a,2′) = 8.8 Hz, ^2J(1′b,1′a) = 14.5 Hz, 1H; 1′a-H), 3.06 (br s, 1H; OH), 3.24 (s, 3H; OMe), 3.18–4.88 (m, 28H), 4.96 (br s, 1H; OH), 7.08–7.28 (m, 35H; 7Ph); $C_{66}H_{72}O_{13} \cdot 0.5H_2O$ (1082.3): calcd C 73.24, H 6.80; found C 73.13, H 6.81.

Methyl 2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-8-*C*-D-*glycero*-propane-2′,3′-diol-1′-yl)-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside [(*S*)-**12**]: Compound (*S*)-**10** (8.5 g, 7.13 mmol) was deacylated and deisopropylidenated as described for (*R*)-**12h**. (*S*)-**12** (6.5 g, colorless syrup) was isolated in 85 % yield: TLC: $R_f = 0.39$ (toluene/ethyl acetate 1:1); $[\alpha]_D = +4.5$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.65$–1.78 (m, 2H; 1′a-, 1′b-H), 1.81 (m, 1H; OH), 2.73 (d, ^3J(OH,2′) = 3.2 Hz, 1H; OH), 2.94 (d, ^3J(OH,12) = 6.6 Hz, 1H; OH), 3.27 (s, 3H; OMe), 3.26–4.28 (m, 13H), 4.35–4.86 (m, 16H; 7PhCH$_2$, 1-, 5-H), 7.12–7.28 (m, 35H; 7Ph). Product (*S*)-**12** was used in the next step without further purification.

Methyl 12-*O*-acetyl-8-*C*-(2′,3′-di-*O*-acetyl-L-*glycero*-propane-2′,3′-diol-1′-yl)-2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside [(*R*)-**13h**]: (*R*)-**12h** (30 mg, 27 µmol) was dissolved in a mixture of pyridine and acetic anhydride (1:1, 3 mL) and left overnight. The mixture was concentrated and the residue was chromatographed (eluant toluene/ethyl acetate 6:1) to give triacetate (*R*)-**13h** (32 mg) in quantitative yield: TLC: $R_f = 0.32$ (toluene/ethyl acetate 6:1); $[\alpha]_D = -8.8$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.81$ (dd, ^2J(1′b,1′a) = 14.8 Hz, ^3J(1′b,2′) = 4.3 Hz, 1H; 1′b-H), 1.89, 1.95, 1.96 (3s, 9H; 3OAc), 2.14 (dd, ^3J(1′a,2′) = 7.2 Hz, ^2J(1′b,1′a) = 14.8 Hz, 1H; 1′a-H), 3.29 (s, 3H; OMe), 3.46–3.58 (m, 4H; 2-, 4-, 9-H, OH), 3.73 (dd, ^2J(13a,13b) = 11 Hz, ^3J(13a,12) = 5.3 Hz, 1H; 13a-H), 3.82–3.91 (m, 2H; 3-, 13b-H), 3.82–4.05 (m, 2H; 3′b-, 11-H), 4.12 (dd, ^3J(10,9) = 4.7 Hz, ^3J(10,11) = 4.7 Hz, 1H; 10-H), 4.22 (dd, ^2J(3′a,3′b) = 12 Hz, ^3J(3′a,2′) = 3.2 Hz, 1H; 3′a-H), 4.39–4.94 (m, 16H; 7PhCH$_2$, 1-, 5-H), 5.24 (m, 1H; 12-H), 5.46 (m, 1H; 2′-H), 7.18–7.34 (m, 35H; 7Ph); $C_{72}H_{78}O_{16} \cdot 2.5H_2O$ (1244.4): calcd C 69.49, H 6.72; found C 69.34, H 6.62.

Methyl 2,3,4,9,10,11,13-hepta-*O*-benzyl-8-*C*-(2′,3′-*O*-carbonyl-L-*glycero*-propane-2′,3′-diol-1′-yl)-6,7-dideoxy-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside [(*R*)-**14h**]: A solution of (*R*)-**12h** (640 mg, 0.6 mmol) in pyridine/dichloromethane (1:1, 10 mL) was cooled to −20 °C under an atmosphere of argon. Trichloromethyl chloroformate (70 µL), dissolved in dichloromethane (2 mL), was added, and the mixture was slowly warmed to room temperature. The reaction was quenched with saturated aqueous hydrogen carbonate solution (10 mL), diluted with water (10 mL), and extracted with ethyl acetate (3 × 15 mL). The organic layers were dried (Na_2SO_4) and concentrated, and the residue was chromatographed (eluant toluene/ethyl acetate 2:1) to give carbonate (*R*)-**14h** (570 mg, 72 %) as a colorless oil: TLC: $R_f = 0.43$ (toluene/ethyl acetate 2:1); $[\alpha]_D = -6.6$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.66$ (dd, ^2J(1′b,1′a) = 14.3 Hz, ^3J(1′b,2′) = 7.4 Hz, 1H; 1′b-H), 2.10 (dd, ^3J(1′a,2′) = 5.4 Hz, ^2J(1′b,1′a) = 14.3 Hz, 1H; 1′a-H), 2.91 (d, ^3J(OH,12) = 6.2 Hz, 1H; OH), 3.29 (s, 3H; OMe), 3.34–3.43 (m, 3H; 2-, 4-, OH), 3.50–3.58 (m, 3H; 3′a-, 9-, 13b-H), 3.71 (dd, ^3J(11,10) = 4.1 Hz, ^3J(11,12) = 7.5 Hz, 1H; 11-H), 3.77–3.86 (m, 2H; 3-, 13a-H), 3.95 (m, 1H; 12-H), 4.10–4.19 (m, 2H; 3′b-, 10-H), 4.34 (d, ^3J(5,4) = 10 Hz, 1H; 5-H), 4.39–4.87 (m, 16H; 7PhCH$_2$, 1-, 2′-H), 7.12–7.27 (m, 35H; 7Ph); FAB-MS (positive mode, matrix: NBOH, NaI): m/z (%): 1121 (100) [MNa$^+$ −1]. Product (*R*)-**14h** was used in the next step without further purification.

Methyl 2,3,4,9,10,11,13-hepta-*O*-benzyl-8-*C*-(2′,3′-*O*-carbonyl-L-*glycero*-propane-2′,3′-diol-1′-yl)-6,7-dideoxy-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside [(*R*)-**14l**]: (*R*)-**12l** was converted into (*R*)-**14l** (colorless oil, 76 %) in the same manner as described for (*R*)-**14h**: TLC: $R_f = 0.5$ (toluene/ethyl acetate 2:1); $[\alpha]_D = +13.5$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.65$ (dd, ^2J(1′a,1′b) = 13.4 Hz, ^3J(1′a,2′) = 10.1 Hz, 1H; 1′a-H), 2.44 (ddd, ^3J(1′b,2′) = 1 Hz,

^{4}J(1′b,OH) = 1 Hz, ^{2}J(1′a,1′b) = 13.4 Hz, 1 H; 1′b-H), 3.17 (d, ^{3}J(OH,12) = 5.6 Hz, 1 H; OH), 3.27 (s, 3 H; OMe), 3.26–3.52 (m, 4 H; 2-, 4-, 13a-, 13b-H), 3.62–3.69 (m, 2 H; 9-, 11-H), 3.81 (dd, ^{3}J(3,2) = 9.3 Hz, ^{3}J(3,4) = 9.3 Hz, 1 H; 3-H), 3.85–3.94 (m, 2 H; 3′a-, 12-H), 4.09–4.21 (m, 3 H; 3′b-, 10-H, OH), 4.29–4.83 (m, 17 H; 7 PhCH$_2$, 1-, 2′-, 5-H), 6.99–7.28 (m, 35 H; 7 Ph); $C_{67}H_{70}O_{14}\cdot 0.5\,H_2O$ (1108.3): calcd C 72.60, H 6.45; found C 72.38, H 6.43.

Methyl 2,3,4,9,10,11,13-hepta-*O*-benzyl-8-*C*-(2′,3′-*O*-carbonyl-D-*glycero*-propane-2′,3′-diol-1′-yl)-6,7-dideoxy-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside [(*S*)-**14**]: Carbonyl protection of compound (*S*)-**12** (6.4 g, 6 mmol) with trichloromethyl chloroformate (725 μL) was carried out as described for (*R*)-**14h**. Product (*S*)-**14** was isolated in 83% yield (5.3 g, colorless oil): TLC: $R_f = 0.5$ (toluene/ethyl acetate 2:1); $[\alpha]_D = +7.8$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.74 (dd, ^{2}J(1′b,1′a) = 13.3 Hz, ^{3}J(1′b,2′) = 9.7 Hz, 1 H; 1′b-H), 1.92 (dd, ^{3}J(1′a,2′) = 3.4 Hz, ^{2}J(1′b,1′a) = 13.3 Hz, 1 H; 1′a-H), 2.83 (d, ^{3}J(OH,12) = 6.4 Hz, 1 H; OH), 3.28 (s, 3 H; OMe), 3.38–3.79 (m, 7 H; 2-, 3′b-, 4-, 9-, 11-, 13b-H, OH), 3.80–3.94 (m, 3 H; 3-, 12-, 13a-H), 4.19 (dd, ^{2}J(3′a,3′b) = 9.4 Hz, ^{3}J(3′a,2′) = 7.7 Hz, 1 H; 3′a-H), 4.25 (dd, ^{3}J(10,9) = 5.4 Hz, ^{3}J(10,11) = 4.8 Hz, 1 H; 10-H), 4.36–4.87 (m, 17 H; 7 PhCH$_2$, 1-, 2′-, 5-H), 7.10–7.22 (m, 35 H; 7 Ph); $C_{67}H_{70}O_{14}\cdot 0.5\,H_2O$ (1108.3): calcd C 72.60, H 6.45; found C 72.30, H 6.42.

Hexacarbonyl{μ-[(6,7-η:6,7-η)-methyl 2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-8-*C*-(2′,3′-*O*-isopropylidene-L-*glycero*-propane-2′,3′-diol-1′-yl)-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside]}dicobalt (Co–Co) [(*R*)-**15h**]: Diol (*R*)-**11h** (67 mg, 60 μmol) was dissolved in dry dichloromethane (2 mL) under an atmosphere of argon. A solution of dicobaltoctacarbonyl (38 mg, 1.5 equiv) in dichloromethane (2 mL) was added dropwise, and the solution was stirred for 3 h. Following removal of the solvent the residue was rapidly chromatographed (eluant: toluene/ethyl acetate 6:1) to give (*R*)-**15h** (68 mg, 76%) as a dark red oil. Cobalt complex (*R*)-**15h** is stable for several days if kept at +4 °C under an atmosphere of dry argon, but nevertheless should be used as soon as possible: TLC: $R_f = 0.45$ (toluene/ethyl acetate 6:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.35, 1.39 (2 s, 6 H; CMe$_2$), 2.28 (m, 2 H; 1′a-, 1′b-H), 2.77 (bd, ^{3}J(OH,12) = 5.5 Hz, 1 H; OH), 3.13 (s, 3 H; OMe), 3.33 (dd, ^{3}J(11,10) = 7.8 Hz, ^{3}J(11,12) = 7.8 Hz, 1 H; 11-H), 3.44–3.65 (m, 5 H; 2-, 3′b-, 4-, 13a-, 13b-H), 3.84 (dd, ^{3}J(10,9) = 6 Hz, ^{3}J(11,10) = 7.8 Hz, 1 H; 10-H), 3.96–4.11 (m, 3 H; 3-, 3′a-, 12-H), 4.32 (m, 1 H; 2′-H), 4.43–5.29 (m, 18 H; 7 PhCH$_2$, 1-, 5-, 9-H, OH), 6.96–7.30 (m, 35 H; 7 Ph). Cobalt complexes (*R*)-**15h**, (*R*)-**16h**, (*S*)-**16**, (*R*)-**17**α, (*R*)-**17**β proved to be too labile to give correct elemental analyses, probably due to loss of carbon monoxide.

Hexacarbonyl{μ-[(6,7-η:6,7-η)-methyl 2,3,4,9,10,11,13-hepta-*O*-benzyl-8-*C*-(2′,3′-*O*-carbonyl-L-*glycero*-propane-2′,3′-diol-1′-yl)-6,7-dideoxy-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside]}dicobalt (Co–Co) [(*R*)-**16h**]: Carbonate (*R*)-**14h** was complexed and isolated as described for (*R*)-**14l**. Complex (*R*)-**16h** (dark red oil, yield 76%) was directly used in the cyclization reaction.

Hexacarbonyl{μ-[(6,7-η:6,7-η)-methyl 2,3,4,9,10,11,13-hepta-*O*-benzyl-8-*C*-(2′,3′-*O*-carbonyl-L-*glycero*-propane-2′,3′-diol-1′-yl)-6,7-dideoxy-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside]}dicobalt (Co–Co) [(*R*)-**16l**]: A solution of carbonate (*R*)-**14l** (600 mg, 0.55 mmol) and dicobaltoctacarbonyl (470 mg, 1.375 mmol, 2.5 equiv) in dry dichloromethane was stirred overnight under an atmosphere of dry argon. Removal of the solvent and rapid chromatography of the residue (eluant: toluene/ethyl acetate 9:1) gave (*R*)-**16l** (628 mg, 82%, dark red oil), which was handled in the same way as described for compound (*R*)-**15h**: TLC: $R_f = 0.28$ (toluene/ethyl acetate 20:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.58, 2.02 (2 brs, 2 H; 1′a-, 1′b-H), 2.60 (d, ^{3}J(OH,12) = 5.5 Hz, 1 H; OH), 3.36 (s, 3 H; OMe), 3.00–5.40 (m, 25 H), 6.96–7.30 (m, 35 H; 7 Ph); FAB-MS (positive mode, matrix: NBOH): *m*/*z* (%): 1216 (100) [$MH^+ - 6CO - H$], 1199 (5) [1216 − OH], 1185 (5) [1216 − OMe], 1126 (5) [1216 − OMe − Co].

Hexacarbonyl{μ-[(6,7-η:6,7-η)-methyl 2,3,4,9,10,11,13-hepta-*O*-benzyl-8-*C*-(2′,3′-*O*-carbonyl-D-*glycero*-propane-2′,3′-diol-1′-yl)-6,7-dideoxy-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside]}dicobalt (Co–Co) [(*S*)-**16**]: The complexation of carbonate (*S*)-**14** (2.36 g, 2.15 mmol) was carried out under the conditions described for (*R*)-**16l**. Complex (*S*)-**16** was purified in the manner previously described and isolated in 80% yield (2.38 g, dark red oil). Its spectra were identical to those described for (*R*)-**16l**. In addition, about 5% of starting material was recovered.

Hexacarbonyl{μ-[(6,7-η:6,7-η)-methyl 8,12-anhydro-2,3,4,9,10,11,13-hepta-*O*-benzyl-8-*C*-(2′,3′-O-carbonyl-L-*glycero*-propane-2′,3′-diol-1′-yl)-6,7-dideoxy-D-*glycero*-D-*gulo*(*ido*)-α-D-*gluco*-tridec-6-inopyranoside]}dicobalt (Co-Co) [(*R*)-**17**α and (*R*)-**17**β]: Cobalt complex (*R*)-**16l** (628 mg, 0.46 mmol) and $BF_3\cdot OEt_2$ (4 equiv) in dichloromethane (10 mL) were stirred under an atmosphere of dry argon until TLC indicated complete conversion to anhydro compounds (8–12 h). The reaction was quenched by addition of saturated ammonium chloride solution (15 mL), the layers were separated, and the aqueous layer was again extracted with dichloromethane (10 mL). The combined organic layers were dried (Na_2SO_4), concentrated, and rapidly chromatographed (eluant toluene/ethyl acetate 20:1) to give a 1:1 mixture of complexated *C*-glycosides (*R*)-**17**α and (*R*)-**17**β (521 mg, 83%) as a dark red oil: TLC: $R_f = 0.38$ (toluene/ethyl acetate 20:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.92 (d, 2 H; 1′a-, 1′b-H((*R*)-**17**α,(*R*)-**17**β)), 2.34 (dd, ^{2}J(1′b,1′a) = 16.7 Hz, 1 H; 1′b-H((*R*)-**17**α,(*R*)-**17**β)), 2.67 (dd, ^{3}J(1′a,2′) = 8.5 Hz, 1 H; 1′a-H((*R*)-**17**α,(*R*)-**17**β)), 3.16, 3.34 (2 s, 6 H; OMe((*R*)-**17**α,(*R*)-**17**β)), 3.31–5.34 (m, 28 H), 6.92–7.31 (m, 35 H; 7 Ph); FAB-MS (positive mode, matrix: NBOH): *m*/*z* (%): 1198 (100) [$MH^+ - 6CO - H$], 1167 (10) [1198 − OMe], 1108 (5) [1198 − OMe − Co].

Methyl 8,12-anhydro-2,3,4,9,10,11,13-hepta-*O*-benzyl-8-*C*-(2′,3′-*O*-carbonyl-L-*glycero*-propane-2′,3′-diol-1′-yl)-6,7-dideoxy-D-*glycero*-D-*ido*-α-D-*gluco*-tridec-6-inopyranoside [(*R*)-**18**α] and **Methyl 8,12-anhydro-2,3,4,9,10,11,13-hepta-*O*-benzyl-8-*C*-(2′,3′-*O*-carbonyl-L-*glycero*-propane-2′,3′-diol-1′-yl)-6,7-dideoxy-D-*glycero*-D-*gulo*-α-D-*gluco*-tridec-6-inopyranoside** [(*R*)-**18**β]: From (*R*)-**17**α,β: The 1:1 mixture of complexes (*R*)-**17**α and (*R*)-**17**β (500 mg, 0.37 mmol) was dissolved in acetone (15 mL). With stirring, 4 equiv of ceric ammonium nitrate were added in portions (gas evolution!). After 10 min the mixture was diluted with dichloromethane (50 mL) and extracted with saturated aqueous hydrogen carbonate solution (2 × 15 mL). The organic layer was dried (Na_2SO_4) and concentrated. Following filtration through silica gel (eluant: toluene/ethyl acetate 9:1) the diastereomers were separated by MPLC (same eluant) to give (*R*)-**18**α (160 mg, colorless oil) and (*R*)-**18**β (160 mg, colorless oil) in 81% yield.

From (*R*)-**16h**: Complex (*R*)-**16h** was cyclized under the conditions described above. When TLC indicated complete conversion to (*R*)-**17**α,β, the complexes were immediately cleaved by addition of 4 equiv of ceric ammonium nitrate. Isolation and purification in the manner already described gave *C*-glycosides (*R*)-**18**α and (*R*)-**18**β (1:1) in 88% yield.

(*R*)-**18**α: TLC: $R_f = 0.39$ (toluene/ethyl acetate 9:1); $[\alpha]_D = +39.2$ ($c = 1.0$ in $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.63 (dd, ^{2}J(1′b,1′a) = 13.3 Hz, ^{3}J(1′b,2′) = 10.7 Hz, 1 H; 1′b-H), 2.48 (dd, ^{3}J(1′a,2′) = 2.6 Hz, ^{2}J(1′b,1′a) = 13.3 Hz, 1 H; 1′a-H), 3.15 (d, ^{3}J(9,10) = 9.3 Hz, 1 H; 9-H), 3.34 (s, 3 H; OMe), 3.34–3.49 (m, 5 H; 2-, 4-, 11-, 13a-, 13b-H), 3.75–3.83 (m, 3 H; 3-, 10-, 12-H), 3.97 (dd, ^{2}J(3′b,3′a) = 8.8 Hz, ^{3}J(3′b,2′) = 8.8 Hz, ^{2}J(3′b,3′a) = 8.8 Hz, 1 H; 3′b-H), 4.18 (dd, ^{3}J(3′a,2′) = 8.8 Hz, 1 H; 3′a-H), 4.30–4.90 (m, 17 H; 7 PhCH$_2$, 1-, 2′-, 5-H), 7.06–7.29 (m, 35 H; 7 Ph); $C_{67}H_{68}O_{13}$ (1081.2): calcd C 74.42, H 6.34; found C 74.42, H 6.94.

(*R*)-**18**β: TLC: $R_f = 0.32$ (toluene/ethyl acetate 9:1); $[\alpha]_D = +17.5$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.09 (dd, ^{2}J(1′b,1′a) = 15.3 Hz, ^{3}J(1′b,2′) = 6.4 Hz, 1 H; 1′b-H), 2.43 (dd, ^{3}J(1′a,2′) = 5.5 Hz, ^{2}J(1′b,1′a) = 15.3 Hz, 1 H; 1′a-H), 3.29 (s, 3 H; OMe), 3.36 (dd, ^{3}J(4,3) = 9.3 Hz, ^{3}J(4,5) = 9.3 Hz, 1 H; 4-H), 3.41 (dd, ^{3}J(2,1) = 3.6 Hz, ^{3}J(2,3) = 9.4 Hz, 1 H; 2-H), 3.53–3.72 (m, 6 H; 9-, 10-, 11-, 12-, 13a-, 13b-H), 3.80 (dd, ^{3}J(4,3) = 9.3 Hz, ^{3}J(2,3) = 9.4 Hz, 1 H; 3-H), 3.90 (dd, ^{2}J(3′b,3′a) = 8.6 Hz, ^{3}J(3′b,2′) = 8.4 Hz, 1 H; 3′b-H), 4.17 (dd, ^{3}J(3′a,2′) = 7.9 Hz, ^{2}J(3′b,3′a) = 8.6 Hz, 1 H; 3′a-H), 4.28–4.90 (m, 17 H; 7 PhCH$_2$, 1-, 2′-, 5-H), 7.03–7.29 (m, 35 H; 7 Ph); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 34.38 (1′-C), 55.75 (OCH$_3$), 83.55, 85.24 (6-C, 7-C), 98.42 (1-C), 154.57 (CO$_3$). $C_{67}H_{68}O_{13}$ (1081.2): calcd C 74.42, H 6.34; found C 74.20, H 6.38.

Methyl 8,12-anhydro-2,3,4,9,10,11,13-hepta-*O*-benzyl-8-*C*-(2′,3′-*O*-carbonyl-D-*glycero*-propane-2′,3′-diol-1′-yl)-6,7-dideoxy-D-*glycero*-D-*ido*-α-D-*gluco*-tridec-6-inopyranoside [(*S*)-**18**α] and **Methyl 8,12-anhydro-2,3,4,9,10,11,13-hepta-*O*-benzyl-8-*C*-(2′,3′-*O*-carbonyl-D-*glycero*-propane-2′,3′-diol-1′-yl)-6,7-dideoxy-D-*glycero*-D-*gulo*-α-D-*gluco*-tridec-6-inopyranoside** [(*S*)-**18**β]: Complex (*S*)-**16** (2.38 g, 1.72 mmol) was dissolved in dry acetonitrile (100 mL). $BF_3\cdot OEt_2$ (0.5 equiv, 100 μL) was added, and the mixture stirred under an atmosphere of dry argon for 4 h (TLC). Ceric ammonium nitrate (2.76 g) was added in portions. When the evolution of gas had completely ceased and the original dark red solution had turned light orange, saturated aqueous hydrogen carbonate solution (150 mL) was added and the mixture was stirred for 15 min. Following dilution with water (100 mL), the mixture was extracted with dichloromethane (3 × 80 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated. Chromatography of the residue (eluant toluene/ethyl acetate 9:1) gave (*S*)-**18**β (150 mg, colorless oil) and (*S*)-**18**α (1.48 g, colorless oil) in an overall yield of 88%: (*S*)-**18**α: TLC: $R_f = 0.5$ (petroleum ether/ethyl acetate 2:1); $[\alpha]_D = +44.3$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.08 (dd, ^{2}J(1′a,1′b) = 14.1 Hz, ^{3}J(1′a,2′) = 8.6 Hz, 1 H; 1′a-H), 2.18 (dd, ^{3}J(1′b,2′) ≈ 8.6 Hz, 1 H; 1′b-H), 3.24 (d, ^{3}J(9,10) = 9.3 Hz, 1 H; 9-H), 3.35 (s, 3 H; OMe), 3.40 (dd, ^{3}J(4,3) = 9.4 Hz, ^{3}J(4,5) = 9.4 Hz, 1 H; 4-H), 3.44 (dd, ^{3}J(2,1) = 3.6 Hz, ^{3}J(2,3) = 9.7 Hz, 1 H; 2-H), 3.52 (dd, ^{2}J(13a,13b) = 11.0 Hz, ^{3}J(13a,12) = 1.8 Hz, 1 H; 13a-H), 3.55 (dd, ^{3}J(11,10) = 9.6 Hz, ^{3}J(11,12) = 9.6 Hz, 1 H; 11-H), 3.63 (dd, ^{3}J(13b,12) = 3.6 Hz, ^{2}J(13a,13b) = 11.0 Hz, 1 H; 13b-H), 3.78 (dd, ^{3}J(9,10) = 9.3 Hz, ^{3}J(11,10) = 9.6 Hz, 1 H; 10-H), 3.80 (dd, ^{3}J(4,3) = 9.4 Hz, ^{3}J(2,3) = 9.7 Hz, 1 H; 3-H), 3.82 (ddd, ^{3}J(11,12) = 9.6 Hz, ^{3}J(13a,12) = 1.8 Hz, ^{3}J(13b,12) = 3.6 Hz, 1 H; 12-H), 3.98 (dd, ^{2}J(3′a,3′b) = 8.6 Hz, ^{3}J(3′a,2′) = 8.6 Hz, 1 H; 3′a-H), 4.33 (d, ^{3}J(4,5) = 9.4 Hz, 1 H; 5-H), 4.36 (dd, ^{3}J(3′b,2′) ≈ 8.6 Hz, ^{2}J(3′a,3′b) = 8.6 Hz, 1 H; 3′b-H), 4.48 (d, 1 H; 1-H), 4.65 (m, 1 H; 2′-H), 4.41–4.90 (m, 14 H; 7 PhCH$_2$), 7.08–7.27 (m, 35 H; 7 Ph); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 42.18 (1′-C), 55.91 (OCH$_3$), 61.60 (5-C), 68.40 (13-C), 70.74 (3′-C), 73.26 (2′-C), 74.18 (8-C), 74.50 (12-C), 77.76 (11-C), 79.16 (2-C), 80.89 (3-C), 81.25 (9-C), 81.51 (7-C), 82.13 (4-C), 84.58 (10-C), 87.66 (6-C), 98.48 (1-C), 73.26–75.93 (7 PhCH$_2$), 127.14–128.48 (Ph–C), 137.60–138.52 (ipso-C), 154.6 (CO$_3$); $C_{67}H_{68}O_{13}$ (1081.2): calcd C 74.42, H 6.34; found C 71.44, H 6.25.

(*S*)-**18**β: TLC: $R_f = 0.55$ (petroleum ether/ethyl acetate 2:1); $[\alpha]_D = +20.7$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.18 (dd, ^{2}J(1′a,1′b) = 14.6 Hz, ^{3}J(1′a,2′) = 9.9 Hz, 1 H; 1′a-H), 2.52 (dd, ^{3}J(1′b,2′) = 3.8 Hz, ^{2}J(1′a,1′b) = 14.6 Hz, 1 H; 1′b-H), 3.29 (s, 3 H; OMe), 3.32 (dd, ^{3}J(11,10) = 9.5 Hz, ^{3}J(11,12) ≈ 9.6 Hz,

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1 H; 11-H), 3.39 (dd, $^3J(4,3) = 9.2$ Hz, $^3J(4,5) \approx 10.0$ Hz, 1 H; 4-H), 3.41 (dd, $^2J(13a,13b) = 10.1$ Hz, 1 H; 13a-H), 3.42 (dd, $^3J(2,1) = 3.6$ Hz, $^3J(2,3) = 9.2$ Hz, 1 H; 2-H), 3.49 (ddd, 1 H; 12-H), 3.54 (dd, $^2J(13a,13b) = 10.1$ Hz, 1 H; 13b-H), 3.55 (dd, $^3J(10,9) = 9.4$ Hz, $^3J(11,10) = 9.5$ Hz, 1 H; 10-H), 3.63 (d, $^3J(10,9) = 9.4$ Hz, 1 H; 9-H), 3.80 (dd, $^3J(2,3) = 9.2$ Hz, $^3J(4,3) = 9.2$ Hz, 1 H; 3-H), 4.18 (dd, $^2J(3'a,3'b) = 8.6$ Hz, $^3J(3'a,2') = 8.6$ Hz, 1 H; 3'a-H), 4.32 (d, $^3J(4,5) \approx 10.0$ Hz, 1 H; 5-H), 4.33 (dd, $^2J(3'a,3'b) = 8.6$ Hz, 1 H; 3'b-H), 4.46 (d, $^3J(2,1) = 3.6$ Hz, 1 H; 1-H), 4.99 (m, 1 H; 2'-H), 4.30–4.82 (m, 14 H; 7 $PhCH_2$), 7.05–7.25 (m, 35 H; 7 Ph); ^{13}C NMR (150.9 MHz, $CDCl_3$): $\delta = 32.41$ (1-C), 55.74 (OCH_3), 61.60 (5-C), 69.34 (13-C), 69.97 (3'-C), 73.43 (12-C), 73.87 (8-C), 75.35 (2'-C), 77.97 (11-C), 79.26 (2-C), 80.96 (3-C), 81.75 (4-C), 82.16 (10-C), 84.10 (9-C), 84.19 (6-C), 84.47 (7-C), 98.41 (1-C), 73.40, 73.51, 75.07, 75.23, 75.43, 75.74, 76.07 (7 $PhCH_2$), 127.42–128.51 (Ph-C), 137.57–138.54 (ipso-C), 154.62 (CO_3); $C_{67}H_{68}O_{13}$ (1081.2): calcd C 74.42, H 6.34; found C 74.44, H 6.52.

Methyl 8,12-anhydro-2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-8-*C*-(L-*glycero*-propane-2',3'-diol-1'-yl)-D-*glycero*-D-*ido*-α-D-*gluco*-tridec-6-inopyranoside [(*R*)-**19**α]: A solution of carbonate (*R*)-**18**α (100 mg, 92 μmol) in a mixture of pyridine, triethylamine, and water (1:1:1, 6 mL) was stirred at 100 °C for 4 h. Evaporation of the solvent and repeated coevaporation with dry toluene gave (*R*)-**19**α (colorless syrup) in quantitative yield and excellent purity: TLC: $R_f = 0.22$ (toluene/ethyl acetate 4:1); $[\alpha]_D = +34.5$ ($c = 1.0$ in $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.27$ (dd, 1 H; OH), 1.74 (dd, $^2J(1'b,1'a) = 14.5$ Hz, 1 H; 1'b-H), 2.08 (dd, $^3J(1'a,2') = 7.5$ Hz, 1 H; 1'a-H), 3.04 (d, 1 H; OH), 3.36 (s, 3 H; OMe), 3.27–3.89 (m, 12 H; 2-, 2'-, 3-, 3'a-, 3'b-, 4-, 9-, 10-, 11-, 12-, 13a-, 13b-H), 4.35–5.00 (m, 16 H; 7 $PhCH_2$, 1-, 5-H), 7.10–7.27 (m, 35 H; 7 Ph). Product (*R*)-**19**α was used in the next step without further purification.

Methyl 8,12-anhydro-2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-8-*C*-(L-*glycero*-propane-2',3'-diol-1'-yl)-D-*glycero*-D-*gulo*-α-D-*gluco*-tridec-6-inopyranoside [(*R*)-**19**β]: Carbonate (*R*)-**18**β was cleaved as described for (*R*)-**19**α. Diol (*R*)-**19**β was isolated in quantitative yield and sufficient purity for further transformations: TLC: $R_f = 0.25$ (toluene/ethyl acetate 2:1); $[\alpha]_D = +20.3$ ($c = 1.0$ in $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.27$ (dd, $^3J(OH,3'a(3'b)) = 7.2$ Hz, 1 H; OH), 1.76 (d, $^2J(1'b,1'a) = 14.7$ Hz, 1 H; 1'b-H), 2.16 (dd, $^3J(1'a,2') = 9.5$ Hz, 1 H; 1'a-H), 2.8 (b, 1 H; OH), 3.18–3.89 (m, 11 H; 2-, 3-, 3'a-, 3'b-, 4-, 9-, 10-, 11-, 12-, 13a-, 13b-H), 4.27 (m, 1 H; 2'-H), 4.46 (d, $^3J(1,2) = 3.5$ Hz, 1 H; 1-H), 4.31–4.87 (m, 15 H; 7 $PhCH_2$, 5-H), 7.01–7.28 (m, 35 H; 7 Ph). Product (*R*)-**19**β was used without further purification.

Methyl 8,12-anhydro-2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-8-*C*-(D-*glycero*-propane-2',3'-diol-1'-yl)-D-*glycero*-D-*ido*-α-D-*gluco*-tridec-6-inopyranoside [(*S*)-**19**α]: Compound (*S*)-**18**α (2 g, 1.85 mmol) was dissolved in a mixture of pyridine, triethylamine, and water (1:1:1, 120 mL) and heated to 80 °C for 3 h. The mixture was concentrated and coevaporated with dry toluene. Diol (*S*)-**19**α ($R_f = 0.45$, toluene/ethyl acetate 1:1) was directly used for mesylation.

Methyl 8,12-anhydro-6,7-dideoxy-8-*C*-(L-*glycero*-propane-2',3'-diol-1'-yl)-D-*glycero*-D-*ido*-α-D-*gluco*-tridecapyranoside [(*R*)-**1**α]: A suspension of diol (*R*)-**19**α (42 mg, 40 μmol) and 10% palladium on carbon (10 mg) in methanol (4 mL) and glacial acetic acid (0.5 mL) was stirred for 24 h under an atmosphere of hydrogen and then filtered through Celite. The Celite was washed with methanol, and the combined filtrates were evaporated to give (*R*)-**1**α as a clear colorless syrup: TLC: $R_f = 0.2$ (methanol/ethyl acetate 1:1); ^1H NMR (250 MHz, CD_3OD): $\delta = 1.35$–2.15 (m, 6 H; 1'a-, 1'b-, 6a-, 6b-, 7a-, 7b-H), 2.94–3.69 (m, 12 H; 2-, 3-, 3'a-, 3'b-, 4-, 5-, 9-, 10-, 11-, 12-, 13a-, 13b-H), 3.30 (s, 3 H; OMe), 3.82 (m, 1 H; 2'-H), 4.53 (d, $^3J(1,2) = 3.6$ Hz, 1 H; 1-H). For the purpose of structure elucidation and elemental analysis compound (*R*)-**1**α was acetylated to give (*R*)-**20**α.

Methyl 2,3,4,9,10,11,13-hepta-*O*-acetyl-8-*C*-(2',3'-di-*O*-acetyl-L-*glycero*-propane-2',3'-diol-1'-yl)-8,12-anhydro-6,7-dideoxy-D-*glycero*-D-*ido*-α-D-*gluco*-tridecapyranoside [(*R*)-**20**α]: Compound (*R*)-**1**α was dissolved in pyridine/acetic anhydride (1:1, 5 mL) and left overnight. Following removal of the solvent, the residue was chromatographed (eluant toluene/ethyl acetate 1:1) to give (*R*)-**20**α (30 mg, 91% from (*R*)-**19**α) as a colorless oil: TLC: $R_f = 0.29$ (toluene/ethyl acetate 1:1); $[\alpha]_D = +75.6$ ($c = 1.0$ in $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.35$–2.20 (m, 6 H; 1'a-, 1'b-, 6a-, 6b-, 7a-, 7b-H), 1.97, 1.98, 1.99, 2.00, 2.01, 2.03, 2.04, 2.07, 2.08 (9s, 27 H; 9OAc), 3.41 (s, 3 H; OMe), 3.68–3.75 (m, 2 H; 5-, 12-H), 3.94–4.14 (m, 4 H; 3'a-, 3'b-, 13a-, 13b-H), 4.79–4.94 (m, 4 H; 1-, 2-, 4-, 11-H), 5.19 (d, $^3J(9,10) = 9.8$ Hz, 1 H; 9-H), 5.32 (dd, $^3J(10,11) = 9.6$ Hz, $^3J(9,10) = 9.8$ Hz, 1 H; 10-H), 5.40 (m, 1 H; 2'-H), 5.44 (dd, $^3J(3,2) = 9.3$ Hz, $^3J(3,4) = 9.3$ Hz, 1 H; 3-H); $C_{35}H_{50}O_{21}$ (806.8): calcd C 52.10, H 6.25; found C 52.40, H 6.31.

Methyl 8,12-anhydro-2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-8-*C*-(2',3'-di-*O*-methanesulfonyl-D-*glycero*-propane-2',3'-diol-1'-yl)-D-*glycero*-D-*ido*-α-D-*gluco*-tridec-6-inopyranoside [(*S*)-**21**α]: Diol (*S*)-**19**α (2 g, 1.9 mmol) was dissolved in pyridine/dichloromethane (1:1, 100 mL), and the mixture was cooled to 0 °C. Methanesulfonyl chloride (0.59 mL) in dichloromethane (10 mL) was added dropwise under an atmosphere of dry argon. After being stirred at room temperature for 3 h, the reaction was quenched with saturated aqueous hydrogen carbonate solution (100 mL), the layers were separated, and the aqueous layer was extracted with dichloromethane (2 × 50 mL). The combined organic layers were concentrated, and the residue chromatographed (eluant: toluene/ethyl acetate 6:1). Mesylate (*S*)-**21**α was isolated as a colorless oil (1.91 g, 83%): TLC: $R_f = 0.28$ (toluene/ethyl acetate 6:1); $[\alpha]_D = +43.5$ ($c = 1.0$ in $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.94$ (dd, $^2J(1'b,1'a) = 15.1$ Hz, $^3J(1'b,2') = 4.7$ Hz, 1 H; 1'b-H), 2.27 (dd, $^3J(1'a,2') = 6.3$ Hz, $^2J(1'b,1'a) = 15.1$ Hz, 1 H; 1'a-H), 2.82, 2.86 (2s, 6 H; 2Ms), 3.22 (d, $^3J(9,10) = 9.3$ Hz, 1 H; 9-H), 3.33 (s, 3 H; OMe), 3.40–3.63 (m, 5 H; 2-, 4-, 11-, 13a-, 13b-H), 3.74–3.88 (m, 3 H; 3-, 10-, 12-H), 4.20 (dd, $^2J(3'b,3'a) = 11.7$ Hz, $^3J(3'b,2') = 5.6$ Hz, 1 H; 3'b-H), 4.33–4.96 (m, 17 H; 7 $PhCH_2$, 1-, 3'a-, 5-H), 5.06 (m, 1 H; 2'-H), 7.04–7.30 (m, 35 H; 7 Ph); $C_{68}H_{74}O_{16}S_2$ (1211.5): calcd C 67.42, H 6.16; found C 66.62, H 6.33.

Methyl 8,12-anhydro-8-*C*-(3'-azido-3'-deoxy-2'-*O*-methanesulfonyl-D-*glycero*-propane-2',3'-diol-1'-yl)-2,3,4,9,10,11,13-hepta-*O*-benzyl-6,7-dideoxy-D-*glycero*-D-*ido*-α-D-*gluco*-tridec-6-inopyranoside [(*S*)-**22**α]: A solution of (*S*)-**21**α (2.2 g, 1.82 mmol), 15-crown-5 (1.5 mL), and sodium azide (1.8 g) in dry dimethylformamide (80 mL) was stirred at 55 °C until approximately half of starting material had reacted (TLC). After cooling to room temperature, the mixture was diluted with water (80 mL) and extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with water, dried (Na_2SO_4), and concentrated. Chromatography of the residue (eluant: toluene/ethyl acetate 9:1 → 4:1) gave (*S*)-**22**α (0.9 g, 43%, colorless syrup) and triazole (*S*)-**23**α (105 mg, 5%, colorless syrup). In addition, 50% of the starting material was recovered. Repeated treatment of starting material (*S*)-**21**α in the same manner led to azide (*S*)-**22**α in 85% overall yield. Attempts to carry out the reaction in one step led to triazole (*S*)-**23**α as the major product: TLC: $R_f = 0.59$ (toluene/ethyl acetate 6:1); $[\alpha]_D = +45.6$ ($c = 1.0$ in $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.94$ (dd, $^2J(1'b,1'a) = 14.9$ Hz, $^3J(1'b,2') = 4.9$ Hz, 1 H; 1'b-H), 2.29 (dd, $^3J(1'a,2') = 6.3$ Hz, $^2J(1'b,1'a) = 14.9$ Hz, 1 H; 1'a-H), 2.88 (s, 3 H; Ms), 3.24 (d, $^3J(9,10) = 9.3$ Hz, 1 H; 9-H), 3.36 (s, 3 H; OMe), 3.38–3.71 (m, 7 H; 2-, 3'a-, 3'b-, 4-, 11-, 13a-, 13b-H), 3.76–3.90 (m, 3 H; 3-, 10-, 12-H), 4.36–5.01 (m, 17 H; 7 $PhCH_2$, 1-, 2'-, 5-H), 7.03–7.31 (m, 35 H; 7 Ph); IR (film): $\tilde{\nu} = 2106$ cm^{-1} (azide); $C_{67}H_{71}N_3O_{13}S$ (1158.4): calcd C 69.47, H 6.18, N 3.63; found C 68.82, H 6.45, N 3.70.

Methyl (5*R*)-5-*C*-[[2*R*-[2α(6'*S),3α,4β,5α,6β]]-3,4,5-tribenzyloxy-6-benzyloxymethyl-3,4,5,6,6',7'-hexahydro-6'-(methanesulfonyloxy)spiro[2*H*-pyran-2,4'(5'*H*)-[1,2,3]-triazolo[1,5-a]pyridine]-3'-yl]-2,3,4-tri-*O*-benzyl-α-D-xylopyranoside** [(*S*)-**23**α]: Triazole (*S*)-**23**α was the minor product in the synthesis of azide (*S*)-**22**α. It can be produced in almost quantitave yield by prolonged heating of (*S*)-**22**α to 60 °C with or without solvent: TLC: $R_f = 0.12$ (toluene/ethyl acetate 4:1); $[\alpha]_D = 85.6$ ($c = 1.0$ in $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.01$ (dd, $^2J(5'^{\mathrm{pro}S},5'^{\mathrm{pro}R}) = 14.8$ Hz, $^3J(5'^{\mathrm{pro}S},6') = 3.9$ Hz, 1 H; $5'^{\mathrm{pro}S}$-H), 2.41 (dd, $^3J(5'^{\mathrm{pro}R},6') = 8.2$ Hz, 1 H; $5'^{\mathrm{pro}R}$-H), 2.65 (s, 3 H; OMs), 3.04 (m, 1 H; 6b-H), 3.30 (dd, $^2J_{gem} = 10.6$ Hz, $^3J(H,6b\text{-}H) = 2.2$ Hz, 1 H; CH_2OBn), 3.39 (dd, $^3J(H,6b\text{-}H) = 5.5$ Hz, $^2J_{gem} = 10.6$ Hz, 1 H; CH_2OBn), 3.38 (s, 3 H; OMe), 3.51 (dd, $^3J(5b,4b) = 8.8$ Hz, $^3J(5b,6b) = 10.0$ Hz, 1 H; 5b-H), 3.58 (d, $^3J(3b,4b) = 9.2$ Hz, 1 H; 3b-H), 3.72 (dd, $^3J(2a,1a) = 4.0$ Hz, $^3J(2a,3a) = 9.8$ Hz, 1 H; 2a-H), 3.95 (dd, $^3J(3a,4a) = 9.5$ Hz, $^3J(2a,3a) = 9.8$ Hz, 1 H; 3a-H), 4.15 (dd, $^3J(3b,4b) = 9.2$ Hz, $^3J(5b,4b) = 8.8$ Hz, 1 H; 4b-H), 4.01–5.49 (m, 19 H; 7 $PhCH_2$, 1a-, 5b-, 5a-, $7'^{\mathrm{pro}R}$-, $7'^{\mathrm{pro}S}$-H), 5.33 (m, 1 H; 6'-H), 6.76–7.31 (m, 35 H; 7 Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 131.4$, 142.9 (triazole C); $C_{67}H_{71}N_3O_{13}S$ (1158.4): calcd C 69.47, H 6.18, N 3.63; found C 69.35, H 6.15, N 3.27.

Methyl (5*R*)-5-*C*-[[2*R*-[2α(6'*S),3α,4β,5α,6β]]-3,4,5,6,6',7'-hexahydro-3,4,5,6'-tetrahydroxy-6-(hydroxymethyl)spiro[2*H*-pyran-2,4'(5'*H*)-[1,2,3]-triazolo[1,5-a]-pyridine]-3'-yl]-α-D-xylopyranoside** [(*S*)-**24**α]: A suspension of (*S*)-**23**α (50 mg, 0.43 mmol), 10% palladium on carbon (20 mg), and formic acid (20 μL) in methanol (3 mL) was stirred under an atmosphere of hydrogen for 16 h. The mixture was filtered through Celite, and the Celite was carefully washed with methanol. The combined filtrates were neutralized by addition of aqueous ammonia and concentrated. The residue was freeze-dried (water) to remove ammonium formate: $[\alpha]_D < 1$ ($c = 1.0$ in $CHCl_3$); ^1H NMR (250 MHz, CD_3OD): $\delta = 2.42$ (dd, $^2J(5'^{\mathrm{pro}S},5'^{\mathrm{pro}R}) = 14.8$ Hz, $^3J(5'^{\mathrm{pro}S},6') = 4.3$ Hz, 1 H; $5'^{\mathrm{pro}S}$-H), 2.79 (dd, $^3J(5'^{\mathrm{pro}R},6') = 8.1$ Hz, $^2J(5'^{\mathrm{pro}S},5'^{\mathrm{pro}R}) = 14.8$ Hz, 1 H; $5'^{\mathrm{pro}R}$-H), 2.92 (m, 1 H; 6b-H), 3.15 (s, 3 H; OMs), 3.31–3.82 (m, 8 H; 3b-, 5b-H, CH_2OBn, $7'^{\mathrm{pro}R}$-, $7'^{\mathrm{pro}S}$-, 2a-, 4a-H), 3.62 (s, 3 H; OMe), 3.97, 4.04 (2m, 2 H; 4b-, 3a-H), 4.79 (d, $^3J(1a,2a) = 3.7$ Hz, 1 H; 1a-H), 5.46 (d, $^3J(5a,4a) = 9.6$ Hz, 1 H; 5a-H), 5.61 (m, 1 H; 6'-H). For the purpose of structure elucidation and elemental analysis, compound (*S*)-**24**α was acetylated to give (*S*)-**25**α.

Methyl (5*R*)-5-*C*-[[2*R*-[2α(6'*S),3α,4β,5α,6β]]-3,4,5-triacetoxy-6-acetoxymethyl-3,4,5,6,6',7'-hexahydro-6'-(methanesulfonyloxy)spiro[2*H*-pyran-2,4'(5'*H*)-[1,2,3]-triazolo[1,5-a]pyridine]-3'-yl]-2,3,4-tri-*O*-acetyl-α-D-xylopyranoside** [(*S*)-**25**α]: Compound (*S*)-**24**α (20 mg, 0.38 μmol) was dissolved in pyridine/acetic anhydride (1:1, 2 mL) and left overnight. The mixture was concentrated and the residue chromatographed (eluant: toluene/ethyl acetate 1:2) to give (*S*)-**24**α (12 mg, 38%) as a colorless oil: TLC: $R_f = 0.38$ (toluene/ethyl acetate 1:2); $[\alpha]_D = +101.2$ ($c = 1.0$ in $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): $\delta = 1.68$, 1.88, 1.95, 1.98, 2.01, 2.03, 2.16 (7s, 21 H; 7 OAc), 2.03 (d, $^2J(5'^{\mathrm{pro}S},5'^{\mathrm{pro}R}) = 15.8$ Hz, 1 H; $5'^{\mathrm{pro}S}$-H), 2.73 (dd, $^3J(5'^{\mathrm{pro}R},6') = 7.4$ Hz, $^2J(5'^{\mathrm{pro}S},5'^{\mathrm{pro}R}) = 15.8$ Hz, 1 H; $5'^{\mathrm{pro}R}$-H), 2.91 (s, 3 H; OMs), 3.21 (ddd, $^3J(6b,CH_2OBn) = 6$ Hz, $^3J(6b,CH_2OBn) = 2.3$ Hz, 1 H; 6b-H), 3.46 (s,

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3H; OMe), 3.89 (dd, $^2J_{\mathrm{gem}}(\mathrm{CH_2OBn}) = 12.4$ Hz, $^3J(\mathrm{6b,CH_2OBn}) = 6$ Hz, 1H; $\mathrm{CH_2OBn}$), 3.95 (dd, $^3J(\mathrm{6b,CH_2OBn}) = 2.3$ Hz, $^2J_{\mathrm{gem}}(\mathrm{CH_2OBn}) = 12.4$ Hz, 1H; $\mathrm{CH_2OBn}$), 4.63 (dd, $^2J(7'^{\mathrm{pro}S},7'^{\mathrm{pro}R}) = 14.1$ Hz, $^3J(7'^{\mathrm{pro}S},6') = 2.7$ Hz, 1H; $7'^{\mathrm{pro}S}$-H), 4.95 (d, $^2J(7'^{\mathrm{pro}S},7'^{\mathrm{pro}R}) = 14.1$ Hz, 1H; $7'^{\mathrm{pro}R}$-H), 5.10–5.14 (m, 3H; 1a-, 5a-, 5b-H), 5.27 (dd, $^3J(\mathrm{4b,3b}) = 9.5$ Hz, $^3J(\mathrm{4b,5b}) = 9.8$ Hz, 1H; 4b-H), 5.33 (d, $^3J(\mathrm{4b,3b}) = 9.5$ Hz, 1H; 3b-H), 5.38 (m, 1H; 6′-H), 5.57 (dd, $^3J(\mathrm{4a,3a}) = 9.8$ Hz, $^3J(\mathrm{4a,5a}) = 9.8$ Hz, 1H; 4a-H), 5.59 (dd, $^3J(\mathrm{2a,1a}) = 3.2$ Hz, $^3J(\mathrm{2a,3a}) = 9.8$ Hz, 1H; 2a-H), 5.75 (dd, $^3J(\mathrm{4a,3a}) = 9.8$ Hz, $^3J(\mathrm{2a,3a}) = 9.8$ Hz, 1H; 3a-H); ^{13}C NMR (150.9 MHz, $\mathrm{CDCl_3}$): $\delta = 20.39$–20.69 (7 $\mathrm{COCH_3}$), 39.69 ($\mathrm{SO_2CH_3}$), 41.92 (5′-C), 50.05 (7′-C), 57.20 ($\mathrm{OCH_3}$), 61.71 ($\mathrm{CH_2OBn}$), 64.42 (2a-C), 68.03 (5a-C), 69.72 (4a-C), 71.05 (6b-C), 71.12 (5b-C), 72.25 (3b-C), 72.63 (3a-C), 72.63 (6′-C), 73.74 (4b-C), 74.94 (4′-C), 98.32 (1a-C), 130.11 (3a′-C), 140.98 (3′-C), 168.26, 169.03, 169.78, 170.00, 170.08, 170.09, 170.13 (7 $\mathrm{COCH_3}$); $\mathrm{C_{32}H_{43}N_3O_{20}S}$ (821.8): calcd C 46.77, H 5.27, N 5.11; found C 46.72, H 5.26, N 4.18.

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