179. Preparation and Transmetallation of a Triphenylstannyl β-D-Glucopyranoside: A Highly Stereoselective Route to β-D-*C*-Glycosides *via* Glycosyl Dianions

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The triphenylstannyl β-D-glucopyranoside **4** was synthesized in one step from the 1,2-anhydro-α-D-glucopyranose **3** with (triphenylstannyl)lithium (*Scheme 1*). Transmetallation of **4** with excess BuLi, followed by quenching the dianion **7** with CD_3OD gave (1*S*)-1,5-anhydro-3,4,6-tri-*O*-benzyl-[1-^{2}H]-D-glucitol (**8**) in 81% yield (*Scheme 2*). Trapping of **7** with benzaldehyde, isobutyraldehyde, or acroleine gave the expected β-D-configurated products **11**, **12**, and **13** in good yields. Preparation of *C*-acyl glycosides from acid chlorides, such as acetyl or benzoyl chloride was not practicable, but addition of benzonitrile to **7** yielded 84% of the benzoylated product **14**. Treatment of **7** with MeI led to **15** (30%) along with 40% of **18**, *C*-alkylation being accompanied by halogen-metal exchange. Prior addition of lithium 2-thienylcyanocuprate increased the yield of **15** to 50% and using dimethyl sulfate instead of MeI led to 77% of **15**. No α-D-anomers could be detected, except with allyl bromide as the electrophile, which yielded in a 1:1 mixture of the anomers **16** and **17**.

Introduction. – The occurrence as natural products, the biological activity, and the analogy to *O*- and *N*-glycosides have led to intense efforts for the synthesis of *C*-glycosides [1–8]. Most of these syntheses are based on the reaction of nucleophiles with the electrophilic anomeric center, while syntheses based on an inversion of polarity of the anomeric center are relatively rare [1]. Anomeric monoanions are prone to rapid β-elimination [9]. The first successful application of the inversion of polarity of the anomeric center was the chain elongation of doubly deprotonated, 2-hydroxy-1,3-dithianes, derivatives of *aldehydo*-saccharides [10]. The first pyranosidic monoanion avoiding β-elimination used the weakly reactive anions derived from 1-deoxy-1-nitroaldoses [11–14]. Reactive glycosyl monoanions usually lack functionality in the 2-position. Such carbanions, based on 2-deoxypyranosides, have been generated by reductive lithiation of 2-deoxy-D-glycopyranosyl chlorides [15], phenyl sulfides [16], or phenyl sulfones [17], by reductive samariation of phenyl sulfones [18], by deprotonation of glycals [19–22], and by transmetalation of 2-deoxy-D-glycopyranosylstannanes [23–26] or of the corresponding alkenylstannanes [23–26].

Fully substituted, reactive carbanions have recently been generated in the context of two strategies for the synthesis of *C*-glycosides. *Sinaÿ* and coworkers used the *in situ* reaction of a transient organosamarium species in a *Barbier*-type reaction [9]. Even though the protecting group at the 2-position was varied, β-elimination could not be prevented in all cases, and the yields of β-*C*-glycosides were rather low. At about the same time, one of our groups reported that β-elimination in the 2-position is efficiently prevented at low temperatures by using a 2-hydroxypyranosyl dianion [27]. This concept has led to a stereoselective synthesis of α-D-configurated *C*-glycopyranosides.

We were interested in a stereoselective synthesis of β-D-configurated *C*-glycopyranosides from 2-hydroxy-β-D-glycopyranosylstannanes *via* 2-hydroxypyranoside dianions, formed by the concomitant transmetalation of organostannanes by organolithium compounds and deprotonation of HO–C(2). Transmetallation of organostannanes to organolithium compounds, followed by their stereoselective reaction with electrophiles [28–30] has been introduced into carbohydrate chemistry by *Sinaÿ* and coworkers, who synthesized 2-deoxy-β-*C*-glycopyranosides from β-D-glycopyranosyl-stannanes [23]. Fully protected glycosylstannanes have recently been prepared *via* glycosylidene carbenes [31]. We now report a convenient route to partially protected 2-hydroxy-β-D-glycopyranosylstannanes, their deprotonation and transmetalation to a dianion, and its reaction with electrophiles, leading to *C*-glycosides[1]).

Results and Discussion. – 1. *Preparation of the β-D-Glucopyranosylstannanes* **2** *and* **4**. First experiments had shown that the reaction of the α-D-chloride **1** with $LiSnBu_3$ leads to small amounts only of the β-D-glucopyranosylstannane **2** (*Scheme 1*), independently of the substituent (OH, OAc) at C(2). Hence, we investigated the reactivity of 1,2-anhydro-3,4,6-tri-*O*-benzyl-α-D-glucopyranose (**3**) with $LiSnR_3$. The opening of epoxides with tin reagents has been successfully applied in carbohydrate chemistry to introduce the SnR_3 moiety at positions other than C(1)[2]) [33]. The epoxide **3** is easily accessible in one step from 3,4,6-tri-*O*-benzyl-D-glucal [34].

Treatment of **3** with *ca.* 2 equiv. of $LiSnPh_3$ in THF at room temperature followed by aqueous workup with saturated aqueous NH_4Cl solution led to partial decomposition of the stannanes. However, quenching of the reaction mixture at –78° and removing the frozen aqueous phase by filtration yielded 65% of **4** together with **5** (2%), **6** (18%), and $(Ph_3Sn)_2$. The α-D-mannopyranosylstannane **5** is presumably formed from 1,2-anhydro-3,4,6-tri-*O*-benzyl-β-D-mannopyranose, an impurity in **3**. The formation of **6** is rationalized by the opening of **3** at C(2), followed by elimination of the C(3)-benzyloxy group, addition of $LiSnPh_3$ to the resulting unsaturated aldehyde, and cyclization to the pyranose **6**. Only the α-D-anomer of **6** was observed. It gives rise to two signals in the ^{119}Sn-NMR spectrum, at –103.43 and –103.87 ppm, suggesting an equilibrium between two species, of which one possesses a stabilizing interaction between the anomeric OH group and the Sn centre of the Ph_3Sn substituent.

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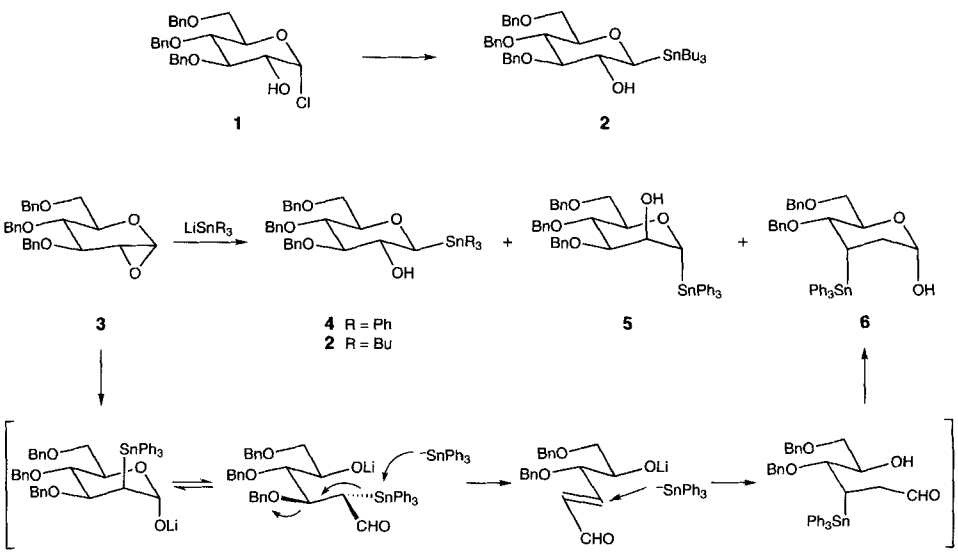
[1]) Presented in part at the VIIth European Carbohydrate Symposium, Cracow, Poland, 22.–27.8.1993, Abstract No. A 100.

[2]) In an approach to *C*-glycosides from electrophilic saccharide derivatives, *Bellosta* and *Czernecki* have shown that 1,2-anhydrosaccharides react with organocuprates to yield *C*-glycosides [32].

Scheme 1



The procedure for the preparation of $LiSnPh_3$ proved to be of crucial importance. Good results were only obtained, if $LiSnPh_3$ was freshly prepared from Li and Ph_3SnCl, according to the procedure of *Tamborsky et al.* [35]. If $LiSnPh_3$ was prepared from $(Ph_3Sn)_2$ and BuLi, or from Ph_3SnH and LDA [36], the yield of **4** was significantly lower. The Li salts, which are generated from Li and Ph_3SnCl, may thus play an important role in the reaction.

Treatment of **3** with $LiSnBu_3$ under analogous conditions as described for $LiSnPh_3$ gave only low yields (33%) of the tributylstannane **2**. Considering the difficult purification of **2**, we did not optimize its preparation.

2. *Transmetallation of* **4** *and Reaction of the Dianion* **7** *with Electrophiles.* To find suitable conditions for the generation of the dianion **7**, a solution of **4** in THF at –78° was treated with varying amounts of BuLi, followed by the addition of CD_3OD. Complete transmetallation required 10 equiv. of BuLi. Attempts to reduce the quantity of BuLi either by adding tetramethylethylenediamine, or by using a large excess of LiCl (see, *e.g.* [37] [38]), or *t*-BuLi were not successful. As a consequence of these results, 10 equiv. of BuLi and of the electrophile were added to the stannane **4** in all subsequent reactions (*Scheme 2*). The need for excess BuLi indicates a reversible Sn/Li exchange and an unfavorable position of the equilibrium [30] [39]. Alternatively, the excess may be required because of Ph/Bu exchange, or the oligomeric structure of the lithium compound. A Ph/Bu exchange is evidenced by the isolation of traces of the tributylstannane **2**. The less reactive PhLi, as generated by this process, appears not to undergo transmetallation.

Scheme 2

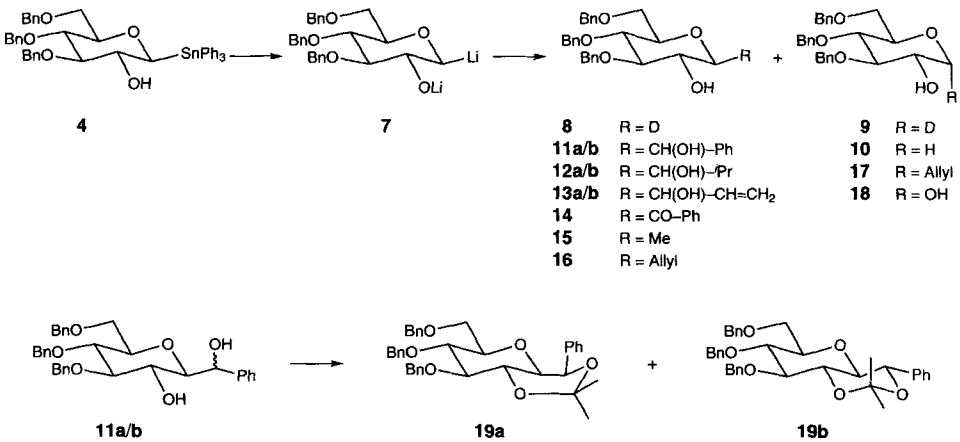


Table. *Yields and Ratios of Products of the Reaction of* **4** *with BuLi and Electrophiles*

Electrophile	Products	Total yield [%][a]	Ratio of products
MeOD	**8/9/10**	87	93 : 2 : 5
PhCHO	**11a/b**	77	58 : 42
Me_2CHCHO	**12a/b**	67	59 : 41
CH_2=CH–CHO	**13a/b**	69	60 : 40
PhCN	**14**	84	
MeI[b])	**15**	50	
$(MeO)_2SO_2$	**15**	77	
CH_2=CH–CH_2Br	**16/17**	50	50 : 50

[a]) After FC. [b]) In the presence of 10 equiv. of lithium 2-thienylcyanocuprate [40].

Deuteration of the dianion **7** resulted in an overall yield of 87% of the equatorially deuterated **8**, the axially deuterated **9** [27], and **10** [9] [27] (*Table*). The yield of **8** was calculated to be 81% from data obtained by ^{2}H- and ^{1}H-NMR spectroscopy, indicating that the stereoselectivity is ≥ 25:1 (yield of **9** < 4%). The yield of **10** was 4% and may be due to proton abstraction from the *O*-CH_2Ph groups or from the solvent. The incorporation of D in the PhCH_2 groups was 14% by ^{2}H-NMR spectroscopy. The high stereoselectivity of the reaction in favor of the equatorially deuterated product and the similar stereoselectivity observed in the synthesis of *α-C*-glycopyranosides *via* an analogous, anomeric glycosyl dianion [27], suggest that these dianions are configuratively stable at low temperature and react with retention of the configuration. The stereoselectivity is higher when the excess of BuLi is reduced, although large amounts of starting material remain [41]. This was shown by treating the tributylstannane **2** with 2 equiv. of BuLi and then with CD_3OD. Although **8**

was isolated in only 20% yield (79% based on consumed starting material), **9** could no longer be detected by ^{2}H-NMR spectroscopy (d.e. > 99%). Similar treatment of the dianion **7** with benzaldehyde, isobutyraldehyde, or acrolein led in good yield to the expected *C*-glycosides **11–13** (*Table*). Whereas **12a/b** and **13a/b** were easily separated by flash chromatography, **11a** was obtained pure by crystallization of **11a/b** from AcOEt/hexane. The diastereoisomer **11b** was enriched in the mother liquor (*ca.* 80–90%) and purified by isopropylidenation to **19b** (see below) followed by hydrolysis. The diastereoselectivity referring to the newly generated hydroxymethylene center was rather low (*ca.* 1.4:1), but always in favor of the (*R*)-diastereoisomer.

The configuration of the epimeric benzyl alcohols **11a** and **11b** was assigned on the basis of their IR and ^{1}H-NMR spectra, and confirmed by their transformation into the isopropylidene derivatives **19a** and **19b** following a procedure described for the analogous *C*-ethyl diol [22]. The benzyl alcohols **11a** and **11b** show large values for $J(2,3)$, $J(3,4)$, $J(4,5)$, and $J(5,6)$, evidencing the $^4C_1$ ring-conformation and the β-D-configuration. The IR spectrum of the crystalline (1*R*)-isomer **11a** displays an OH band at 3580 cm^{-1}, typical for a H-bond in a five-membered ring, and a small value of 2.8 Hz for $J(1,2)$. The (1*S*) diastereoisomer **11b** is characterized by $J(1,2)$ = 6.3 Hz. Its IR spectrum displays an OH band at 3580 and an additional, slightly stronger one, at 3522 cm^{-1} (H-bond in a six-membered ring). The combination of these values is only possible if the benzylic OH group in the major rotamers of **11a** and **11b** forms different H-bonds, one to the ring O-atom in the (1*R*)-isomer **11a**, and one to HO–C(3) in the (1*S*)-isomer **11b**. Isopropylidenation of the mixture **11a/b** gave selectively the acetal **19b** derived from the (1*S*)-isomer **11b**; the (1*R*)-isomer **11a** was only isopropylidenated in the presence of a large excess of dimethoxypropane, and led to poor yields of **19a**. Both **19a** and **19b** showed a large $J(1,2)$ (8.1 and 9.4 Hz), hence one of the isomers must adopt a boat-like conformation. The chemical shift values for the Me groups in the ^{13}C-NMR spectrum of **19a** (26.39 and 24.95 ppm) are indeed typical for a geminal dimethyl group of a boat conformer, while the corresponding values for **19b** (29.68 and 19.22 ppm) evidence a chair conformation (see *Scheme 2*). This confirms the configurational assignment for **11a/b**. The relative configuration of **12a/b** and of **13a/b** may then be tentatively assigned, based on the relative values for $J(3,4)$ of **12a** and **13a** (< 2 and 3.0 Hz, resp.) and for $J(6,7)$ of **12b** and **13b** (7.8 and 4.7 Hz, resp.)

Acyl chlorides proved unsuited for the preparation of *C*-acylated products. When AcCl was added to the dianion **7** at –78°, the mixture turned at once deep black, and a mixture of products were formed. Benzoyl chloride, which cannot enolize, gave small amounts of the desired product besides 12% of 3,4,6-tri-*O*-benzyl-D-glucal, suggesting that O–C(2) is benzoylated more rapidly than the anomeric center. In agreement with this hypothesis, the less reactive benzonitrile yielded 84% of **14** (*Table*), and no elimination products were observed.

C-Alkylation of the dianion **7** with MeI resulted in only 30% yield of the expected equatorially methylated **15** [20] in addition to 40% of 3,4,6-tri-*O*-benzyl-D-glucopyranose (**18**) [42] [43]. The remarkable formation of **18** might result from halogen-metal exchange [44], leading to a glycosyl iodide which is hydrolyzed during workup. The yield of **15** was raised to 50% when the dianion **7** was transformed to a higher order cuprate by adding 10

equiv. of lithium 2-thienylcyanocuprate [40] [45] before the addition of MeI. Only 15% of the by-product **18** were isolated. The yield of **15** was further increased to 77%, and the formation of **18** was suppressed when halogen-metal exchange was avoided by using dimethyl sulfate as methylating agent. EtBr was less reactive. The more highly reactive allyl bromide yielded 25% of the equatorially allylated **16** together with 25% of the anomer **17**. Formation of the α-D-anomer might again reflect halogen-metal exchange, leading to highly reactive allyllithium. That no axial diastereoisomer of the methylated analogue was obtained is then due to the low reactivity of the *in situ* generated MeLi at –78°.

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Experimental Part

General. Solvents were freshly distilled. Dimethyldioxirane was prepared according to the procedure described by *Adam et al.* [46]. Anal. TLC: *Merck* precoated silica gel *60 F254* plates; detection by treatment with a soln. of 5% $(NH_4)_6Mo_7O_{26}\cdot 4\,H_2O$, 0.1% $Ce(SO_4)_2\cdot 4\,H_2O$, and 5% H_2SO_4 in MeOH. Flash chromatography (FC): silica gel *Merck 60* (40–63 μm), HPLC: *Nucleosil Si50* (7 μm). M.p.'s are uncorrected. IR Spectra: 1–10% in CCl_4, $CHCl_3$, or CH_2Cl_2 soln. ^{1}H- and ^{13}C-NMR Spectra: at 300, 400, and 500 MHz (^{1}H) and at 50, 75, and 125 MHz (^{13}C); chemical shifts are given in ppm relative to TMS. ^{2}H-NMR Spectra ($CHCl_3$) at 76.77 MHz, $CDCl_3$ as internal standard. Coupling constants (*J*) are in Hz. In ambiguous cases, ^{1}H-NMR assignments by selective homonuclear decoupling experiments. Tin coupling constants for the isotope ^{119}Sn. FAB-MS: in NBA matrix.

Ph_3SnLi/Bu_3SnLi. Ph_3SnCl (2.5 g, 6.5 mmol) and Bu_3SnCl (2.1 g, 6.5 mmol) were added to a mixture of Li (550 mg, 79 mmol) in THF (10 ml) under Ar. Within 10–30 min, heat was evolved, and the mixture became dark olive-green. It was stirred for 2 h and directly used (*ca.* 0.3–0.5M $LiSnPh_3$/$LiSnBu_3$ in THF).

Reaction of **3** *with $LiSnPh_3$.* At 24° and under Ar, a soln. of **3** [34] (430 mg, 1 mmol) in THF (10 ml) was treated with $LiSnPh_3$ in THF (4 ml, *ca.* 1.5–2 mmol) . The mixture was stirred for 30 min, cooled to –78°, diluted with Et_2O (50 ml), and quenched with sat. NH_4Cl soln. (10 ml). The frozen aq. phase was filtered off and washed with cold (–78°) Et_2O (20 ml). The combined org. filtrates were dried ($MgSO_4$) and concentrated to give 1 g of a yellow oil. The crude was dissolved in Et_2O (25 ml), cooled to –20° and the precipitated $(Ph_3Sn)_2$ was filtered off. The filtrate was concentrated to *ca.* 5 ml and filtered again. Evaporation and FC (50 g of SiO_2, hexane/AcOEt 3:1) of the remaining oil gave 511 mg (65%) of **4**, 15 mg (2%) of **5**, and 120 mg (18%) of **6**. An anal. sample of **6** was recrystallized in hexane/AcOEt.

Triphenyl(3,4,6-tri-O-benzyl-β-D-glucopyranosyl)stannane (**4**): R_f (hexane/AcOEt 2:1) 0.46. $[\alpha]_D^{25} = +2.7$ (*c* = 1.09, $CHCl_3$). IR ($CHCl_3$): 3592*w*, 3067*m*, 3052*m*, 2905*m*, 2867*m*, 1954*w*, 1879*w*, 1815*w*, 1497*m*, 1481*m*, 1454*m*, 1430*s*, 1363*m*, 1352*m*, 1306*w*, 1261*m*, 1089*s*, 1075*s*, 1028*s*, 998*s*, 911*w*, 869*w*, 604*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.73–7.19 (*m*, 30 arom. H); 4.97 (*d*, *J* = 11.2, 1H, PhC*H*$_2$); 4.84 (*d*, *J* = 10.9, 1H, PhC*H*$_2$); 4.77 (*d*, *J* = 11.2, 1H, PhC*H*$_2$); 4.67 (*d*, *J* = 10.8, 1H, PhC*H*$_2$); 4.59 (*d*, *J* = 12.1, 1H, PhC*H*$_2$); 4.53 (*d*, *J* = 12.2, 1H, PhC*H*$_2$); 4.16 (*d*, *J* = 10.9, H–C(1)); 3.95 ('*ddd*', *J* ≈ 3.4, 8.7, 11.5, H–C(2)); 3.76 (*d*, *J* = 2.7, 2 H–C(6)); 3.67 ('*t*', *J* ≈ 9.3, H–C(4)); 3.55–3.45 (*m*, H–C(3), H–C(5)); 2.20 (*d*, *J* = 3.4, OH). ^{13}C-NMR (100 MHz, C_6D_6): 139.41 (*s*); 139.16 (*s*); 139.08 (*s*); 138.64 (3*s*, *J*(Sn,C) = 497); 138.04 (6*d*, *J*(Sn,C) = 35.7); 129.29–127.58 (*m*); 88.90 (*d*, *J*(Sn,C) = 67.9, C(3)); 83.89 (*d*, *J*(Sn,C) = 58.7, C(5)); 78.89 (*d*, C(4)); 78.34 (*d*, *J*(Sn,C) = 502, C(1)); 75.10 (*t*); 74.91 (*t*); 74.06 (*d*, *J*(Sn,C) = 9.9, C(2)); 73.59 (*t*); 69.63 (*t*, C(6)). ^{119}Sn-NMR (C_6D_6): –136.57. FAB-MS (calc. for $C_{45}H_{44}O_5{}^{120}Sn$): 718 (3, $[(Ph_3Sn)_2O]^+$), 707 (13, $[M - Ph]^+$), 351 (55, $[SnPh_3]^+$), 187 (22), 149 (33), 107 (13), 91 (100). Anal. calc. for $C_{45}H_{44}O_5Sn$ (783.55): C 68.98, H 5.66; found: C 68.98, H 5.74.

Triphenyl(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)stannane (**5**): R_f (hexane/AcOEt 2:1) 0.22. $[\alpha]_D^{25}$ = +21.4 (*c* = 0.99, $CHCl_3$). IR ($CHCl_3$): 3556*w*, 3067*m*, 2907*w*, 2868*m*, 1954*w*, 1880*w*, 1817*w*, 1496*m*, 1481*m*, 1454*m*, 1430*s*, 1362*m*, 1333*w*, 1259*w*, 1090*s*, 1074*s*, 1043*s*, 1028*m*, 998*m*, 910*w*, 859*w*, 607*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.70–7.11 (*m*, 30 arom. H); 5.31 (*d*, *J* = 2.2, *J*(Sn,H) = 39.6, H–C(1)); 4.74 (*d*, *J* = 11.5, 1H, PhCH_2); 4.59 (*d*, *J* = 12.1, 1H, PhCH_2); 4.47 (*d*, *J* = 11.3, 1H, PhCH_2); 4.45 (*d*, *J* = 12.1, 1H, PhCH_2); 4.29 (*d*, *J* = 11.4, 1H, PhCH_2); 4.27–4.24 (*m*, H–C(2)); 4.22 (*d*, *J* = 11.6, 1H, PhCH_2); 3.87 ('*t*', *J* ≈ 8.8, H–C(4)); 3.69 (*dd*, *J* ≈ 3.2, 8.4, H–C(3)); 3.68 (*dd*, *J* ≈ 4.2, 10.9, H_A–C(6)); 3.60 (*dd*, *J* = 2.2, 10.7, H_B–C(6)); 3.54 (*ddd*, *J* = 2.1, 4.5, 8.8, H–C(5)); 2.75 (*d*, *J* = 2.8, *J*(Sn,H) = 17.4, OH). ^{13}C-NMR (75 MHz, C_6D_6): 139.47 (*s*); 139.10 (*s*); 138.67 (4*s*, *J*(Sn,C) = 463); 137.75 (6*d*, *J*(Sn,C) = 36.1); 129.51–127.12 (*m*); 81.58 (*d*, C(4)); 80.23 (*d*, *J*(Sn,C) ≈ 15, C(3)); 78.22 (*d*, *J*(Sn,C) = 418, C(1)); 75.21 (*d*, *J*(Sn,C) < 10, C(5)); 74.27 (*t*); 73.54 (*t*); 71.68 (*t*); 71.04 (*d*, *J*(Sn,C) = 55.4, C(2)); 69.74 (*t*, C(6)). ^{119}Sn-NMR (C_6D_6): –140.83. FAB-MS (calc. for $C_{45}H_{44}O_5{}^{120}Sn$): 718 (4, $[(Ph_3Sn)_2O]^+$), 716 (5), 707 (2, $[M-Ph]^+$), 351 (54, $[SnPh_3]^+$), 181 (19), 91 (100). Anal. calc. for $C_{45}H_{44}O_5Sn$ (783.55): C 68.98, H 5.66; found: C 68.73, H 5.55.

4,6-Di-O-benzyl-2,3-dideoxy-3-C-(triphenylstannyl)-α-D-ribo-hexopyranose (**6**): R_f (hexane/AcOEt 2:1) 0.32. M.p. 123°. $[\alpha]_D^{25}$ = +143.8 (*c* = 1.0, $CHCl_3$). IR (CCl_4): 3600*w*, 3380*w* (br.), 3065*m*, 3050*w*, 2988*w*, 2905*w*, 2865*w*, 1949*w*, 1890*w*, 1824*w*, 1496*w*, 1481*w*, 1454*w*, 1428*m*, 1361*w*, 1305*w*, 1258*w*, 1206*w*, 1148*w*, 1118*m*, 1091*s*, 1074*s*, 1024*m*, 999*m*, 901*w*, 841*w*, 699*s*, 656*w*, 607*w*. ^{1}H-NMR (400 MHz, C_6D_6): 7.84–6.80 (*m*, 25 arom. H); 4.92 (br. *s*, H–C(1)); 4.37 (*d*, *J* = 12.4, 1H, PhCH_2); 4.32 (*d*, *J* = 12.4, 1H, PhCH_2); 4.24 (*d*, *J* = 10.9, 1H, PhCH_2); 4.10 (*ddd*, *J* = 1.8, 4.6, 9.3, H–C(5)); 4.06 (*d*, *J* = 11.0, 1H, PhCH_2); 3.90 (*dd*, *J* = 5.9, 9.5, H–C(4)); 3.69 (*dd*, *J* = 4.8, 10.7, H_A–C(6)); 3.55 (*dd*, *J* = 1.9, 10.6, H_B–C(6)); 2.59 ('*dt*', *J* ≈ 2.6, 5.5, H–C(3)); 2.10 ('*dt*', *J* ≈ 14.3, 2.1; irrad. at 4.92: *dd*, *J* = 2.6, 13.8, H_{eq}–C(2)); 2.09 (br. *s*, exchanged with D_2O, OH); 1.92 ('*dquint*', *J* ≈ 14.0, 2.6; after addn. of D_2O: *ddd*, *J* = 2.8, 5.3, 14.0; irrad. at 4.92: *dd*, *J* = 5.3, 14.0, H_{ax}–C(2)). ^{13}C-NMR (75 MHz, C_6D_6): 141.86 (3*s*); 139.00 (*s*); 138.40 (*s*); 138.15 (6*d*, *J*(SnC) = 37.9); 129.11–127.79 (*m*); 90.94 (*d*, *J*(Sn,C) < 5, C(1)); 76.87 (*d*, *J*(Sn,C) = 29.4, C(4)); 72.90 (*t*); 72.57 (*t*); 70.67 (*d*, *J*(Sn,C) < 5, C(5)); 69.81 (*t*, C(6)); 32.24 (*t*, C(2)); 28.08 (*d*, *J*(Sn,C) = 449, C(3)). ^{119}Sn-NMR (C_6D_6): –103.43; –109.88 (*d*). FAB-MS (calc. for $C_{38}H_{38}O_4{}^{120}Sn$): 601 (7, $[M-Ph]^+$), 493 (7), 351 (90, $[SnPh_3]^+$), 275 (41, $[SnPh_2+1]^+$), 197 (38, $[SnPh]^+$), 91 (100). Anal. calc. for $C_{38}H_{38}O_4Sn$ (677.43): C 67.38, H 5.65; found: C 67.18, H 5.81.

General Procedure for the Synthesis of β-C-Glucosides with **4**. Under Ar at –78°, BuLi (0.81 ml of a 1.6M soln. in hexane, 1.28 mmol) was added within 5–10 min to a soln. of **4** (100 mg, 0.128 mmol) in THF (*ca.* 2 ml). The color of the soln. changed from yellow to green. After the addition of the electrophile (1.28 mmol)[3]), the mixture was stirred for 15–45 min, diluted with Et_2O (8 ml), quenched with sat. NH_4Cl soln. (6 ml), allowed to warm to 0°, and washed with H_2O (2 × 10 ml). The org. phase was dried ($MgSO_4$) evaporated, and dried in high vacuum for 2 h. The products of the reaction with isobutyraldehyde, acrolein, and allyl bromide (see the *Table* for yields and ratios) were easily separated by FC (hexane/AcOEt 5:1 → 1:2). FC of the crude product obtained from the reactions of CD_3OD and benzaldehyde gave mixtures of **8/9/10** and **11a/b**, resp. Crystallization of **11a/b** from AcOEt/hexane gave pure **11a**, whereas the mother liquor consisted of **11b** containing **11a** (*ca.* 10–20%).

(1S)-1,5-Anhydro-3,4,6-tri-O-benzyl-[1-^{2}H]-D-glucitol (**8**): R_f (hexane/AcOEt 1:1) 0.33. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.34–7.15 (*m*, 15 arom. H); 4.92–4.52 (*m*, 3 PhCH_2); 3.70 (*m*, H–C(2)); 3.68–3.64 (*m*, 2 H–C(6)); 3.56 (*dd*, *J* = 8.7, 9.4, H–C(4)); 3.45 ('*t*', *J* = 8.6, H–C(3)); 3.39 (*ddd*, *J* = 2.7, 3.8, 9.4, H–C(5)); 3.17 (*d*, *J* = 10.3, H–C(1)). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.5 (*s*); 137.9 (*s*); 137.7 (*s*); 128.5–127.6 (*m*); 86.7 (*d*, C(3)); 79.3 (*d*, C(5)); 77.8 (*d*, C(4)); 75.0 (*t*); 74.7 (*t*); 73.5 (*t*); 70.0 (*d*, C(2)); 69.1 (*t*, C(1)); 68.7 (*t*, C(6)).

(1R)-1,5-Anhydro-3,4,6-tri-O-benzyl-[1-^{2}H]-D-glucitol [27] (**9**). Except for the ^{1}H-NMR spectrum (3.95 (*d*, *J* = 5.3, H–C(1))), **9** shows the same anal. and spectroscopic data as **8**.

(1R)-2,6-Anhydro-4,5,7-tri-O-benzyl-1-C-phenyl-D-glycero-D-gulo-heptitol (**11a**): R_f (hexane/AcOEt 2:1) 0.13. M.p. 151°. $[\alpha]_D^{25}$ = +15.0 (*c* = 1.07, $CHCl_3$). IR ($CHCl_3$): 3572*w*, 3470*w* (br.), 3090*w*, 3067*w*, 3043*w*, 3007*m*, 2911*w*, 2870*m*, 1952*w*, 1880*w*, 1811*w*, 1605*w*, 1496*m*, 1454*m*, 1396*w*, 1360*m*, 1310*w*, 1262*w*, 1099*s*, 1047*s*, 1028*s*, 947*w*, 912*w*, 862*w*, 646*w*, 600*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.41–7.20 (*m*, 20 arom. H); 4.94–4.91 (*m*, 2H, PhCH_2, H–C(1)); 4.80 (*d*, *J* = 10.9, 1H, PhCH_2); 4.76 (*d*, *J* = 11.5, 1H, PhCH_2); 4.58 (*d*, *J* = 10.9, 1H, PhCH_2); 4.52 (*d*, *J* = 12.1, 1H, PhCH_2); 4.48 (*d*, *J* = 12.1, 1H, PhCH_2); 3.72 ('*dt*', *J* ≈ 2.9, 9.1, H–C(3)); 3.67 (*d*, *J* = 3.4, 2 H–C(7)); 3.58 ('*t*', *J* ≈ 9.1, H–C(5)); 3.53 ('*t*', *J* = 8.8, H–C(4)); 3.47 (*dd*, *J* = 2.8, 9.5, H–C(2)); 3.43 ('*td*', *J* = 3.1, 9.4, H–C(6)); 3.15 (*d*, *J* = 8.4, HO–C(1)); 2.34 (*d*, *J* = 3.0, HO–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 141.52 (*s*); 138.71

[3]) In the reaction with MeI as the electrophile, the soln. was treated with lithium 2-thienylcyanocuprate [40] (10 equiv.), stirred for 5 min, and then treated with MeI (1.28 mmol).

(*s*); 138.10 (2*s*); 128.62–126.77 (*m*); 86.73 (*d*); 81.50 (*d*); 78.83 (*d*); 77.91 (*d*); 75.39 (*t*); 74.92 (*t*); 73.40 (*t*); 72.20 (*d*); 70.77 (*d*); 68.87 (*t*). FAB-MS: 1081 (22, $[2M+1]^+$), 539 (25, $[M-1]^+$), 415 (56), 307 (36), 181 (91), 154 (100), 136 (98), 107 (81), 91 (94). Anal. calc. for $C_{34}H_{36}O_6$ (540.66): C 75.53, H 6.71; found: C 75.35, H 6.81.

(1S)-2,6-Anhydro-4,5,7-tri-O-benzyl-1-C-phenyl-D-glycero-D-gulo-*heptitol* (**11b**). Pure **11b** was obtained by deisopropylidenation (48 h at r.t.) of **19b** in toluene/MeOH 4:1 in the presence of 5 equiv. of $TsOH \cdot H_2O$. FC (15 g of SiO_2; hexane/AcOEt 2:1 → 1:2) gave **19b** (15%) and **11b** (78%). R_f (hexane/AcOEt 2:1) 0.13. $[\alpha]_D^{25} = +29.7$ ($c = 0.89$, $CHCl_3$). IR ($CHCl_3$): 3580*w*, 3522*w*, 3488*w* (sh), 3090*w*, 3067*w*, 3042*w*, 2870*m*, 1952*w*, 1878*w*, 1811*w*, 1605*w*, 1496*m*, 1454*s*, 1363*m*, 1330*w*, 1264*m*, 1096*s*, 1050*s*, 1028*s*, 912*m*, 830*w*, 643*w*, 610*w*. ^{1}H-NMR (300 MHz, C_6D_6): 7.50–7.07 (*m*, 20 arom. H); 4.91 (*d*, $J = 11.8$, 1H, PhCH_2); 4.86 (*d*, $J = 11.8$, 1H, PhCH_2); 4.81 (br. *d*, $J \approx 4.9$, H–C(1)); 4.78 (*d*, $J = 11.2$, 1H, PhCH_2); 4.52 (*d*, $J = 11.2$, 1H, PhCH_2); 4.31 (*d*, $J = 12.2$, 1H, PhCH_2); 4.23 (*d*, $J = 12.1$, 1H, PhCH_2); 3.69 (br. *t*, $J \approx 8.0$, H–C(3)); 3.59–3.53 (*m*, H–C(4), H–C(5)); 3.50–3.48 (*m*, 2 H–C(7)); 3.45 (*dt*, $J = 6.3, 9.3$, H–C(2)); 3.29 (br. *s*, HO–C(1)); 3.22–3.18 (*m*, H–C(6)); 3.07 (br. *s*, HO–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 140.61 (*s*); 138.60 (*s*); 138.26 (*s*); 138.06 (*s*); 128.63–127.27 (*m*); 86.45 (*d*); 80.84 (*d*); 79.10 (*d*); 77.87 (*d*); 75.55 (*d*); 75.39 (*t*); 74.90 (*t*); 73.38 (*d* and *t*); 68.88 (*t*). FAB-MS: 1081 (2, $[2M+1]^+$), 539 (4, $[M-1]^+$), 415 (15), 207 (12), 193 (12), 181 (48), 154 (20), 147 (25), 136 (31), 107 (32), 91 (100). Anal. calc. for $C_{34}H_{36}O_6$ (540.66): C 75.53, H 6.71; found: C 75.29, H 6.96.

4,8-Anhydro-6,7,9-tri-O-benzyl-1,2-dideoxy-2-C-methyl-D-erythro-L-galacto-*nonitol* (**12a**): R_f (hexane/AcOEt 1:1) 0.34. M.p. 161°. $[\alpha]_D^{25} = +19.6$ ($c = 0.7$, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.37–7.20 (*m*, 15 arom. H); 4.95–4.50 (*m*, 3 PhCH_2); 3.78 (*dd*, $J = 7.8, 8.5$, H–C(5)); 3.69 (*m*, 2 H–C(9)); 3.56 (*m*, H–C(6), H–C(7)); 3.45 (*m*, H–C(8)); 3.40 (br. *d*, $J = 7.7$, H–C(3)); 3.29 (br. *d*, $J = 8.5$, H–C(4)); 2.93 (*s*, OH); 2.14 (*s*, OH); 1.87 (*m*, H–C(2)); 1.03 (*d*, $J = 6.7$, Me); 0.90 (*d*, $J = 6.7$, Me). ^{13}C-NMR (125 MHz, $CDCl_3$): 139.0 (*s*); 138.6 (*s*); 138.2 (*s*); 128.9–127.8 (*m*); 87.2 (*d*, C(6)); 79.1 (*d*, C(8)); 78.8 (*d*, C(4)); 78.2 (*d*, C(7)); 75.4 (*t*); 75.0 (*t*); 74.5 (*d*, C(3)); 73.6 (*t*); 70.3 (*d*, C(5)); 69.3 (*t*, C(9)); 31.5 (*d*, C(2)); 19.5 (*q*, 2 Me). Anal. calc. for $C_{31}H_{38}O_6$ (506.65): C 73.49, H 7.56; found: C 73.28, H 7.51.

2,6-Anhydro-1,3,4-tri-O-benzyl-8,9-dideoxy-8-C-methyl-L-erythro-L-gulo-*nonitol* (**12b**): R_f (hexane/AcOEt 1:1) 0.54. M.p. 107°. $[\alpha]_D^{25} = +18.0$ ($c = 0.95$, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.33–7.17 (*m*, 15 arom. H); 4.90–4.48 (*m*, 3 PhCH_2); 3.68 ('*t*', $J \approx 8.7$, H–C(5)); 3.66 (*m*, 2 H–C(1)); 3.64 (*dd*, $J = 3.2, 7.8$, H–C(7)); 3.58 ('*t*', $J = 9.0$, H–C(3)); 3.53 ('*t*', $J \approx 8.9$, H–C(4)); 3.39 (*ddd*, $J = 2.5, 3.4, 9.2$, H–C(2)); 3.20 (*s*, OH); 3.17 (*dd*, $J = 7.8, 8.9$, H–C(6)); 2.77 (*s*, OH); 2.07 (*m*, H–C(8)); 0.96 (*d*, $J = 6.9$, Me); 0.88 (*d*, $J = 6.9$, Me). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.7 (*s*); 138.4 (*s*); 137.9 (*s*); 128.5–127.7 (*m*); 86.8 (*d*, C(4)); 79.2 (*d*, C(2)); 78.8 (*d*, C(7)); 78.0 (*d*, C(3)); 77.9 (*d*, C(6)); 75.5 (*t*); 75.3 (*d*, C(5)); 75.0 (*t*); 73.6 (*t*); 69.2 (*t*, C(1)); 29.4 (*d*, C(8)); 19.4 (*q*, Me); 15.4 (*q*, Me). Anal. calc. for $C_{31}H_{38}O_6$ (506.65): C 73.49, H 7.56; found: C 73.63, H 7.31.

4,8-Anhydro-6,7,9-tri-O-benzyl-1,2-dideoxy-D-erythro-L-galacto-*non-1-enitol* (**13a**). Separated by HPLC (hexane/AcOEt 2:1). R_f (AcOEt/hexane 1:1) 0.31. M.p. 131°. $[\alpha]_D^{25} = +53.1$ ($c = 0.38$, $CHCl_3$). IR (KBr): 3376*m*, 3034*w*, 2930*m*, 2864*m*, 1674*w*, 1496*w*, 1452*m*, 1090*s*, 1058*m*, 1040*m*, 990*m*, 744*s*, 698*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.34–7.18 (*m*, 15 arom. H); 6.00 (*ddd*, $J = 5.4, 10.5, 17.2$, H–C(2)); 5.36 (*d*, $J = 17.2$, H_Z–C(1)); 5.22 (*d*, $J = 10.5$, H_E–C(1)); 4.93–4.50 (*m*, 3 PhCH_2); 4.34 (br. *s*, H–C(3)); 3.73–3.66 (*m*, H–C(5), 2 H–C(9)); 3.57 ('*t*', $J = 9.1$, H–C(7)); 3.53 ('*t*', $J = 8.7$, H–C(6)); 3.44 ('*td*', $J = 3.0, 9.3$, H–C(8)); 3.27 (*dd*, $J = 3.0, 9.6$, H–C(4)); 2.52 (*s*, HO–C(3)); 2.37 (*s*, HO–C(5)). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.4 (*s*); 137.9 (*s*); 137.8 (*s*); 136.5 (*d*, C(2)); 128.8–127.4 (*m*); 116.7 (*t*, C(1)); 86.3 (*d*, C(6)); 80.5 (*d*, C(4)); 78.9 (*d*, C(8)); 77.8 (*d*, C(7)); 75.3 (*t*); 74.9 (*t*); 73.7 (*t*); 73.4 (*d*, C(3)); 72.4 (*d*, C(5)); 68.7 (*t*, C(9)). Anal. calc. for $C_{30}H_{34}O_6$ (490.60): C 73.43, H 6.99; found: C 71.93, H 7.08.

2,6-Anhydro-1,3,4-tri-O-benzyl-8,9-dideoxy-L-erythro-L-gulo-*non-8-enitol* (**13b**). Separated by HPLC (hexane/AcOEt 2:1). R_f (hexane/AcOEt 1:1) 0.26. $[\alpha]_D^{25} = +24.6$ ($c = 0.56$, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.36–7.18 (*m*, 15 arom. H); 6.00 (*ddd*, $J = 6.3, 10.6, 17.2$, H–C(8)); 5.37 (*d*, $J = 17.2$, H_Z–C(9)); 5.22 (*d*, $J = 10.6$, H_E–C(9)); 4.96–4.50 (*m*, 3 PhCH_2); 4.34 (*dd*, $J = 4.7, 6.3$, H–C(7)); 3.72–3.66 (*m*, 2 H–C(1)); 3.62 ('*t*', $J \approx 8.9$, H–C(5)); 3.57 ('*t*', $J = 9.1$, H–C(3)); 3.52 ('*t*', $J = 8.6$, H–C(4)); 3.46 ('*td*', $J = 3.0, 9.4$, H–C(2)); 3.27 (*dd*, $J = 4.7, 9.4$, H–C(6)); 2.73 (*s*, HO–C(7)); 2.51 (*s*, HO–C(5)). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.6 (*s*); 138.2 (*s*); 138.0 (*s*); 137.7 (*d*, C(8)); 128.7–127.5 (*m*); 116.0 (*t*, C(9)); 86.6 (*d*, C(4)); 80.2 (*d*, C(6)); 79.1 (*d*, C(2)); 78.0 (*d*, C(3)); 75.3 (*t*); 74.9 (*t*); 73.4 (*t*); 71.6 (*d*, C(7)); 70.6 (*d*, C(5)); 68.9 (*t*, C(1)). Anal. calc. for $C_{30}H_{34}O_6$ (490.60): C 73.43, H 6.99; found: C 72.68, H 7.37.

2,6-Anhydro-4,5,7-tri-O-benzyl-1-C-phenyl-D-glycero-D-gulo-*heptose* (**14**): R_f (hexane/AcOEt 1:1) 0.67. $[\alpha]_D^{25} = -16.7$ ($c = 1.35$, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): 8.07 (*d*, $J = 7.8$, 2 arom. H); 7.57 (*t*, $J = 7.5$, 1 arom. H); 7.43–7.21 (*m*, 17 arom. H); 5.06–4.45 (*m*, 3 PhCH_2); 4.39 (*d*, $J = 9.3$, H–C(2)); 4.19 ('*t*', $J = 9.0$, H–C(3)); 3.80–3.72 (*m*, H_A–C(7), H–C(4), H–C(6)); 3.64 (*dd*, $J = 5.6, 10.7$, H_B–C(7)); 3.60 ('*t*', $J = 9.3$, H–C(5)); 2.98 (*s*, HO–C(3)). ^{13}C-NMR (125 MHz, $CDCl_3$); 196.7 (*s*, C(1)); 138.7 (*s*); 138.1 (2*s*); 135.2 (*s*); 133.7 (*d*); 129.7 (*d*); 128.5–

127.4 (*m*); 85.7 (*d*, C(4)); 80.3 (*d*, C(6)); 80.0 (*d*, C(2)); 77.4 (*d*, C(5)); 75.4 (*t*); 75.1 (*t*); 73.3 (*t*); 72.2 (*d*, C(3)); 69.2 (*t*, C(7)). Anal. calc. for $C_{34}H_{34}O_6$ (538.64): C 75.82, H 6.36; found: C 75.77, H 6.56.

2,6-Anhydro-4,5,7-tri-O-*benzyl-1-deoxy*-D-glycero-D-gulo-*heptitol* [20] (**15**): R_f (hexane/AcOEt 1:1) 0.51. M.p. 85–86° ([20]: 85–86°). $[\alpha]_D^{25}$ = +46.6 (*c* = 1.04, $CHCl_3$; [20]: $[\alpha]_D^{25}$ = +44.1). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.39–7.16 (*m*, 15 arom. H); 4.97–4.52 (*m*, 3 PhCH_2); 3.70 (*m*, 2 H–C(7)); 3.61 ('*t*', *J* = 9.2, H–C(5)); 3.46 ('*t*', *J* = 9.1, H–C(4)); 3.45 (*ddd*, *J* = 2.1, 4.4, 9.4, H–C(6)); 3.31 (*m*, H–C(2)); 3.23 ('*t*', *J* = 9.2, H–C(3)); 2.09 (*s*, OH); 1.31 (*d*, *J* = 6.1, 3 H–C(1)). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.5 (*s*); 138.2 (*s*); 137.8 (*s*); 129.4–127.5 (*m*); 86.6 (*d*, C(4)); 78.7 (*d*, C(6)); 78.4 (*d*, C(5)); 75.5 (*d*, C(2)); 75.2 (*d*, C(3)); 75.0 (*t*); 74.7 (*t*); 73.4 (*t*); 68.9 (*t*, C(7)); 18.2 (*t*, C(1)). Anal. calc. for $C_{28}H_{32}O_5$ (448.56): C 74.98, H 7.19; found C 75.04, H 7.82.

4,8-Anhydro-6,7,9-tri-O-*benzyl-1,2,3-trideoxy*-D-glycero-D-gulo-*non-1-enitol* (**16**): R_f (hexane/AcOEt 1:1) 0.63. $[\alpha]_D^{25}$ = +11.4 (*c* = 0.5, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.34–7.16 (*m*, 15 arom. H); 5.91 (*m*, H–C(2)); 5.12 (*d*, *J* = 17.0, H_Z–C(1)); 5.06 (*d*, *J* = 10.1, H_E–C(1)); 4.96–4.51 (*m*, 3 PhCH_2); 3.73–3.69 (*m*, 2 H–C(9)); 3.59 (*dd*, *J* = 8.9, 9.4, H–C(7)); 3.47 ('*t*', *J* = 9.0, H–C(6)); 3.41 (*ddd*, *J* = 1.9, 3.4, 9.4, H–C(8)); 3.36 ('*t*', *J* = 9.0, H–C(5)); 3.26–3.22 (*m*, H–C(4)); 2.56 (*m*, H_A–C(3), HO–C(5)); 2.30 (*m*, H_B–C(3)). ^{13}C-NMR (125 MHz, $CDCl_3$): 139.6 (*s*); 139.3 (*s*); 138.7 (*s*); 134.6 (*d*, C(2)); 129.4–128.3 (*m*); 117.0 (*t*, C(1)); 86.7 (*d*, C(6)); 79.2 (*d*, C(8)); 78.7 (*d*, C(4)); 78.5 (*d*, C(7)); 75.2 (*t*); 74.8 (*t*); 73.5 (*t*); 73.5 (*d*, C(5)); 68.9 (*t*, C(9)); 36.2 (*t*, C(3)). Anal. calc. for $C_{30}H_{34}O_5$ (474.60): C 75.92, H 7.22; found: C 75.83, H 7.02.

2,6-Anhydro-1,3,4-tri-O-*benzyl-7,8,9-trideoxy*-D-glycero-L-gulo-*non-8-enitol* (**17**): R_f (hexane/AcOEt 1:1) 0.59. $[\alpha]_D^{25}$ = +7.1 (*c* = 0.3, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.33–7.22 (*m*, 15 arom. H); 5.82 (*m*, H–C(8)); 5.12 (*d*, *J* = 17.1, H_Z–C(9)); 5.05 (*d*, *J* = 10.1, H_E–C(9)); 4.64–4.47 (*m*, 3 PhCH_2); 4.05 (*td*, *J* = 5.2, 9.8, H–C(2)); 3.92 (*ddd*, *J* = 3.0, 5.4, 8.5, H–C(6)); 3.81 (*dd*, *J* = 5.2, 10.2, H_A–C(1)); 3.75 ('*t*', *J* = 9.9, H–C(3)); 3.69 (*dd*, *J* = 5.8, 10.2, H_B–C(1)); 3.64–3.62 (*m*, H–C(4), H–C(5)); 2.91 (*s*, OH); 2.46–2.34 (*m*, 2 H–C(7)). ^{13}C-NMR (125 MHz, $CDCl_3$): 139.7 (*s*); 139.5 (*s*); 138.8 (*s*); 134.7 (*d*, C(8)); 128.5–127.6 (*m*); 117.0 (*t*, C(9)); 77.5 (*d*, C(4)); 76.8 (*t*); 74.8 (*d*, C(3)); 73.5 (*d*, C(2)); 73.3 (*t*); 73.2 (*d*, C(5)); 72.8 (*t*); 71.0 (*d*, C(6)); 68.0 (*t*, C(1)); 33.3 (*t*, C(7)). Anal. calc. for $C_{30}H_{34}O_5$ (474.60): C 75.92, H 7.22; found: C 75.96, H 6.93.

Isopropylidenation of **11a** *and* **11b**. *a*) A soln. of **11a/11b** *ca.* 1.4:1 (230 mg, 0.43 mmol) in THF (5 ml) was treated with 2,2-dimethoxypropane (31 µl, 0.25 mmol) and TsOH · H_2O (9 mg, 0.047 mmol) and stirred for 12 h at 25°. After neutralization with $NaHCO_3$ and filtration, evaporation of the filtrate and FC (15 g of SiO_2, hexane/AcOEt 2:1 → 1:2) gave **19b** (46 mg, 19%) and **11a/11b** *ca.* 2:1 (178 mg, 77%).

b) Treatment of a soln. of **11a** in THF with *ca.* 10 equiv. of 2,2-dimethoxypropane and TsOH · H_2O (0.1 equiv.) gave **19a** in low yields.

(1R)-2,6-Anhydro-4,5,7-tri-O-*benzyl-1,3*-O-*isopropylidene-1*-C-*phenyl*-D-glycero-D-gulo-*heptitol* (**19a**): R_f (hexane/AcOEt 2:1) 0.52. M.p. 91°. $[\alpha]_D^{25}$ = –19.9 (*c* = 1.11, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3067*w*, 3043*w*, 2908*m*, 2868*m*, 1951*w*, 1875*w*, 1810*w*, 1752*w*, 1606*w*, 1497*m*, 1454*m*, 1381*m*, 1317*w*, 1153*s*, 1101*s*, 1061*s*, 1028*s*, 990*m*, 912*w*, 879*m*, 834*w*, 822*w*, 635*w*, 622*w*, 605*w*. ^{1}H-NMR (300 MHz, C_6D_6): 7.48–7.07 (*m*, 20 arom. H); 5.11 (*d*, *J* ≈ 8.1, H–C(1)); 5.10 (*d*, *J* ≈ 10.9, 1H, PhCH_2); 4.97 (*d*, *J* = 11.2, 1H, PhCH_2); 4.83 (*d*, *J* = 11.5, 1H, PhCH_2); 4.60 (*d*, *J* = 11.3, 1H, PhCH_2); 4.18 (*d*, *J* = 12.7, 1H, PhCH_2); 4.09 (*d*, *J* = 12.6, 1H, PhCH_2); 4.09 ('*t*', *J* ≈ 9.4, H–C(3)); 3.75 ('*t*', *J* ≈ 8.8, H–C(4)); 3.66 ('*t*', *J* ≈ 9.0, H–C(5)); 3.53 (*dd*, *J* = 4.4, 11.9, H_A–C(7)); 3.47 (*dd*, *J* ≈ 1.7, 12, H_B–C(7)); 3.44 (*dd*, *J* = 7.8, 9.8, H–C(2)); 3.35–3.30 (*m*, H–C(6)); 1.43 (*s*, Me); 1.32 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.91 (*s*); 138.80 (*s*); 138.35 (*s*); 136.81 (*s*); 128.38–127.20 (*m*); 101.27 (*s*); 84.02 (*d*); 80.74 (*d*); 77.70 (*d*); 76.37 (*d*); 75.34 (*t*); 74.68 (*t*); 73.22 (*t*); 72.71 (*d*); 71.59 (*d*); 68.71 (*t*); 26.39 (*q*); 24.95 (*q*). FAB-MS: 579 (22, $[M-1]^+$), 415 (27), 271 (13), 181 (98), 105 (71), 92 (100), 91 (93). Anal. calc. for $C_{37}H_{40}O_6$ (580.72): C 76.53, H 6.94; found: C 76.41, H 6.87.

(1S)-2,6-Anhydro-4,5,7-tri-O-*benzyl-1,3*-O-*isopropylidene-1*-C-*phenyl*-D-glycero-D-gulo-*heptitol* (**19b**): R_f (hexane/AcOEt 2:1) 0.52. $[\alpha]_D^{25}$ = +9.6 (*c* = 1.10, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3067*m*, 2872*m*, 1952*w*, 1878*w*, 1811*w*, 1727*w*, 1606*w*, 1496*m*, 1453*m*, 1383*m*, 1366*m*, 1310*w*, 1258*m*, 1149*s*, 1101*s*, 1028*s*, 987*m*, 949*w*, 893*m*, 857*w*, 833*w*, 658*w*, 633*w*, 606*w*. ^{1}H-NMR (300 MHz, C_6D_6): 7.62–7.05 (*m*, 20 arom H); 5.07 (*d*, *J* = 11.8, 1H, PhCH_2); 5.01 (*d*, *J* = 11.3, 1H, PhCH_2); 4.84 (*d*, *J* = 11.8, 1H, PhCH_2); 4.76 (*d*, *J* = 9.4, H–C(1)); 4.63 (*d*, *J* = 11.2, 1H, PhCH_2); 4.33 (*d*, *J* = 12.1, 1H, PhCH_2); 4.25 (*d*, *J* = 12.1, 1H, PhCH_2); 3.92 ('*t*', *J* ≈ 9.2), 3.91 ('*t*', *J* ≈ 9.1, H–C(3) and H–C(5)); 3.72 ('*t*', *J* = 8.8, H–C(4)); 3.55 (*dd*, *J* = 3.7, 11.0, H_A–C(7)); 3.46 (*dd*, *J* = 1.6, 10.9, H_B–C(7)); 3.20–3.11 (*m*, H–C(2), H–C(6)); 1.53 (*s*, Me); 1.31 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.99 (2*s*); 138.37 (*s*); 138.29 (*s*); 128.38–127.26 (*m*); 99.96 (*s*); 83.89 (*d*); 79.74 (*d*); 77.32 (*d*); 76.69 (*d*); 75.25 (2*t*); 74.92 (*d*); 74.03 (*d*); 73.38 (*t*); 68.77 (*t*); 29.68 (*q*); 19.92 (*q*). FAB-MS: 579 (7, $[M-1]^+$), 415 (13), 181 (55), 91 (100). Anal. calc. for $C_{37}H_{40}O_6$ (580.72): C 76.53, H 6.94; found: C 76.43, H 7.02.

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