20. Oligosaccharide Analogues of Polysaccharides

Part 1

Concept and Synthesis of Monosaccharide-Derived Monomers

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It is proposed to study the influence of interresidue H-bonds on the structure and properties of polysaccharides by comparing them to a series of systematically modified oligosaccharide analogues where some or all of the glycosidic O-atoms are replaced by buta-1,3-diyne-1,4-diyl groups. This group is long enough to interrupt the interresidue H-bonds, is chemically versatile, and allows a binomial synthesis. Several approaches to the simplest monomeric unit required to make analogues of cellulose are described. In the first approach, allyl α-D-galactopyranoside (**1**) was transformed *via* **2** and the tribenzyl ether **3** into the triflate **4** (*Scheme 2*). Substitution by cyanide (→ **5**–**7**) followed by reduction with DIBAH led in high yield to the aldehyde **9**, which was transformed into the dibromoalkene **10** and the alkyne **11** following the *Corey-Fuchs* procedure (*Scheme 3*). The alkyne was deprotected *via* **12** or directly to the hemiacetal **13**. Oxidation to the lactone **14**, followed by addition of lithium (trimethylsilyl)acetylide $Me_3SiC{\equiv}CLi/CeCl_3$ (→ **15**) and reductive dehydroxylation afforded the disilylated dialkyne **16**. The large excess of Pd catalyst required for the transformation **11** → **13** was avoided by deallylating the dibromoalkene **10** (→ **17** → **18**), followed by oxidation to the lactone **19**, addition of $Me_3SiC{\equiv}CLi$ to the anomeric hemiketals **20** (α-D/β-D 7:2), dehydroxylation to **21**, and elimination to the monosilylated dialkyne **22** (*Scheme 3*). In an alternative approach, treatment of the epoxide **24** (from **23**) with $Me_3SiC{\equiv}CLi/Et_2AlCl$ according to a known procedure gave not only the alkyne **27** but also **25**, resulting from participation of the $MeOCH_2O$ group (*Scheme 4*). Using Me_3Al instead of Et_2AlCl increased the yield and selectivity. Deprotection of **27** (→ **28**), dibenzylation (→ **29**), and acetolysis led to the diacetate **30** which was partially deacetylated (→ **31**) and oxidized to the lactone **32**. Addition of $Me_3SiC{\equiv}CLi/TiCl_4$ afforded the anomeric hemiketals **33** (α-D/β-D 3:2) which were deoxygenated to the dialkyne **34**. This synthesis of target monomers was shortened by treating the hydroxy acetal **36** (from **27**) with $(Me_3SiC{\equiv}C)_3Al$ (*Scheme 5*): formation of the alkyne **37** (70%) by fully retentive alkynylating acetal cleavage is rationalised by postulating a participation of HOC(3). The sequence was further improved by substituting the $MeOCH_2O$ by the $(i\text{-}Pr)_3SiO$ group (*Scheme 6*); the epoxide **38** (from **23**): yielded 85% of the alkyne **39** which was transformed, on the one hand, *via* **40** into the dibenzyl ether **29**, and, on the other hand, after *C*-desilylation (→ **41**) into the dialkyne **42**. Finally, combined alkynylating opening of the oxirane and the 1,3-dioxolane rings of **38** with excess $Et_2Al\,C{\equiv}CSiMe_3$ led directly to the monomer **43** which is thus available in two steps and 77% yield from **23** (*Scheme 6*).

Introduction and Concept. – H-Bonds, the strongest and most important noncovalent bonds contributing to the interaction between molecules, are essential for carbohydrate-carbohydrate interactions and for interactions between carbohydrates and other biologically important compounds such as nucleic acids and proteins. Their role is particularly evident in polysaccharides [1–3]. The relative contribution of intra- and intermolecular H-bonds and of other relatively weak interactions to the structure and properties of polysaccharides may be studied by making and examining analogues of polysaccharides. We planned to

synthesize a series of defined oligomers[1]), where the ratio between inter- and intramolecular H-bonds is systematically varied by substituting, at regular intervals, glycosidic O-centers within a saccharide chain by other bridging units. These units should be long enough to interrupt H-bonds between adjacent saccharide units without interfering with the formation of intraresidue H-bonds[2]). The use of saccharide blocks G_n of different lengths leads to a systematic change of the ratio[3]) between intra- and intermolecular H-bonds, as illustrated in *Table 1*.

Table 1. *Intra- and Interchain Interactions in Oligosaccharide Analogues.* G denotes a monosaccharidic unit, B a bridge, as specified in the text.

xOligosaccharide analogue tetramer	x = No. of possible interchain interactions[b]) of monomeric units in two chains[c])	y = No. of possible intrachain interactions[a]) in a single chain
1. $G^1BG^2BG^3BG^4B$	4	0
2. $(GG)^1B(GG)^2B(GG)^3B(GG)^4B$	8	4
3. $(GGGG)^1B(GGGG)^2B(GGGG)^3B(GGGG)^4B$	16	12

[a]) An interaction may consist of one or several H-bonds, depending on the nature of the saccharide. Cellulose II, *e.g.* is characterized by two H-bonds between each glucose residue in a chain. [b]) Number of interactions between neighboring units only. [c]) Only pairwise interactions between chains are considered.

Apart from the above criteria, such bridging units should be rigid but allow a restricted number of conformers. They may thus impair the preorganization of single oligo- or polysaccharide chains, reduce their tendency to associate, and increase their solubility. To permit the preparation of large oligosaccharides, the bridge should allow for a convergent and, if possible, binomial synthesis. Ideally, it would be sufficiently reactive to give rise to additional series of analogues. The butadiyne moiety appears to fulfil these conditions. It will confine the linkage angle between monomers within a narrow value and can easily be modified. The choice of a butadiyne-1,4-diyl bridge allows a binomial synthesis [13][14] according to the general protocol for the synthesis of such analogues, as depicted in *Scheme 1*[4]), including, as the essential step, the cross-coupling of two selectively monodeprotected diethynyl monomers[5]).

[1]) A number of attempts to prepare polysaccharides, or at the least higher oligosaccharides, by polymerization of monomers led to the chemical and enzymatic synthesis of fairly complex oligomers [4–11]. As a rule, however, these were obtained as mixtures. Defined oligosaccharides, such as oligomers of cellulose, were prepared by stepwise synthesis; so far, this has led to a (protected) cello-octamer [12].

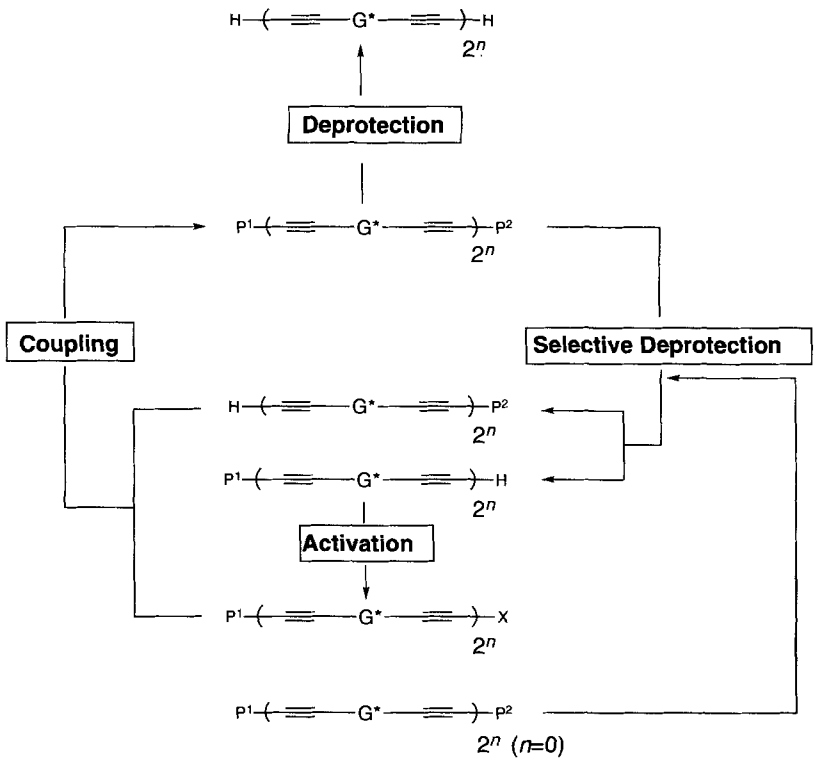
[2]) Intraresidue H-bonds may be interrupted, *e.g.* by regioselective deoxygenation.

[3]) The ratio x/y converges to 1, unless there is an unequal number of H-bonds for the intra- and interchain interaction of a G unit. For cellulose II, where two H-bonds link two sequential glucose units in a chain, but which possesses only one H-bond between each glucose unit of adjacent chains, x/y converges to a value of 2.

[4]) We propose the trivial name of acetylenosaccharides for oligosaccharide analogues where the interresidue O-atom is replaced by an alkynediyl, alkadiynediyl *etc.* moiety.

[5]) Only a few butadiyne-1,4-diyl-bridged disaccharide analogues have been reported; for an encouraging example of a *Cadiot-Chodkiewicz* cross-coupling of two ethynyl-substituted furanoses, see [15][16]. For the synthesis of a ethyne-1,2-diyl-bridged disaccharide analogue, see [17].

Scheme 1. *Binomial Synthesis of Butadiyne-1,4-diyl-Linked Analogues of Oligo- and Polysaccharides* [a])



[a]) G* stands for a mono- or oligosaccharide-derived monomeric core; n denotes the number of cycles. The synthesis starts with the monomer at the bottom of the scheme (2^n; $n = 0$). Regioselective deprotection leads to two monoprotected diynes which are activated for a cross-coupling, leading to a dimer (2^n; $n = 1$) which, in a second cycle, is subjected to regioselective deprotection and cross-coupling. Finally, complete deprotection leads to the products.

We considered the synthesis of analogues of cello-oligosaccharides as ideal to establish the feasibility and use of the above approach; in spite of the extensive research devoted to the structure of celluloses[6]) [24], many aspects concerning chain polarity (parallel and antiparallel), H-bond network, and the process of mercerization are not fully understood.

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[6]) Cellulose [18] crystallizes in the cellulose I, II, III, and IV polymorphs [19–22]. The native form is cellulose I. On the basis of NMR spectra and other evidence, native cellulose is as a composite of two crystalline forms, cellulose I_α and I_β, of which the former is prevalent in algal and bacterial celluloses (60–70% in cellulose from *Acetobacter* and *Volonia*) and the latter in celluloses from higher plants (*ca.* 60–70% in cotton) [19–23]. Cellulose II is the conversion product obtained by mercerization of native and other celluloses, while celluloses III and IV are obtained, respectively, by liquid ammonia and heat treatment of the other polymorphs. Further distinctions for celluloses III and IV can be made on the basis of the source, III_I and IV_I as obtained from cellulose I, and III_{II} and IV_{II} from cellulose II.

The synthesis of the simplest cellulose analogue according to *Scheme 1* requires a protected 1,4-dideoxy-1,4-diethynyl-β-D-glucopyranose. It has to solve the general problems in the stepwise synthesis of any large oligomer: the synthesis of monomers, realization of high yields, purification, and characterization (*cf.* [13]). Specific problems include regioselective deprotection of the ethynyl moieties, cross-coupling of two different alkynes (including the separation of hetero- from homodimers), and deprotection of the final oligomer.

In this paper, we describe the synthesis of the simplest monomers, possessing (trimethylsilyl)ethynyl substituents at C(1) and C(4), aimed both at high yields and a method which should be applicable to the synthesis of monomers derived from cellobiose and from higher cello-oligosaccharides.

Results and Discussion. – Although a number of pyranoses carrying alkynyl substituents at C(1) [25–30][17] or C(4) [31–34] were prepared, since *Zelinski* and *Meyer* made the first C(1)-alkynylated derivatives [25], only a few 1,4-dialkynylated saccharides are known [32b]. The introduction of an alkynyl moiety at C(1) by addition of an alkynyl group to a glyconolactone and subsequent reductive dehydroxylation [26] proceeds in high yields, but the introduction of the alkynyl moiety at C(4) is less satisfactory. Addition of alkynyl groups to a C(4) ketone, followed by reductive dehydroxylation did not proceed well [32]. Application of the *Corey-Fuchs* procedure [35] to a C(4)-branched aldehyde gave good results, but the synthesis of the aldehyde by methylenation of a C(4) ketone, followed by hydroboration, oxidation, and equilibration of the resulting *galacto*-aldehyde [33][32] proceeded in relatively low overall yields. The opening of epoxides is a direct way to alkynylated products [31][34]. The desired *gluco*-configuration of the product requires an inverted ($^1C_4$) chair, as realized in 1,6-anhydropyranoses. Such an approach, however, is restricted to the synthesis of diethynylated monomers derived from monosaccharides. As the goals of high yield and broad scope appeared difficult to reconcile, we have examined both methods. We have first optimized the introduction of the 4-ethynyl moiety by preparing the crucial aldehyde **9** *via* the nitrile **5**.

The *galacto*-triflate **4** (*Scheme 2*) was prepared from the allyl-galactopyranoside **1** which was, however, obtained in markedly lower yields than reported [36]. The benzylidene acetal **2** [37] was prepared in yields of up to 90% by using dimethoxytoluene (*cf.* [38]) in the presence of *Amberlist 15*[7]). Benzylation followed by reductive cleavage of the 1,3-dioxane ring [39] afforded **3**, and hence the triflate **4** as an oil which keeps well at –20°. Although substitution by a variety of (trimethylsilyl)acetylide anions [40][41] failed, dry tetrabutylammonium cyanide [42] gave smoothly the *gluco*-configurated nitrile **5** (82–84%), along with 8% of the elimination product **7** and traces of the isonitrile **6**. Reduction of a mixture **6**/**7** with diisobutylaluminium hydride (DIBAH) yielded 2% of the secondary amine **8** and 87% of the aldehyde **9** which is thus obtained in three steps and in 75% overall yield[8]) from **3**.

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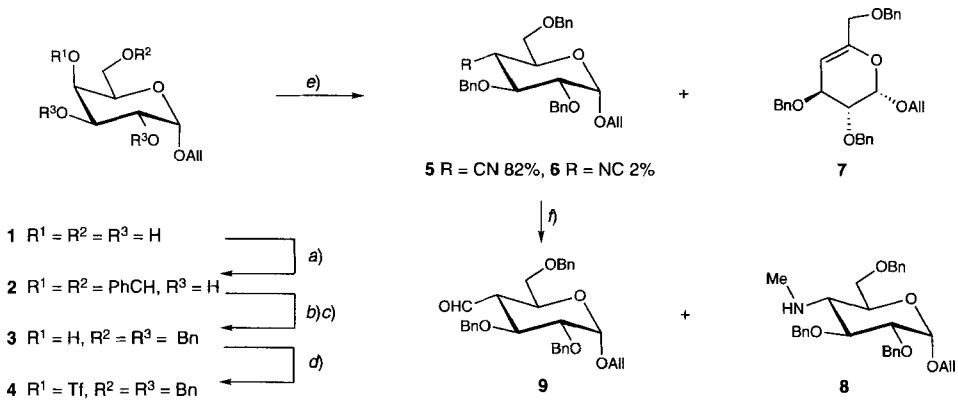
[7]) Some batches of this ion-exchanger had to be activated to ensure high yields (see *Exper. Part*).

[8]) The yield over five steps from benzyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside of the corresponding aldehyde was 57% [33]; similarly, *ca.* 30% were reported for the analogous sequence from the corresponding methyl glucoside [32].

Scheme 2



a) Benzaldehyde dimethyl acetal, *Amberlyst 15*, $CHCl_3$, reflux; 90%. *b*) *c*) $NaBH_3CN$/HCl; see [39]. *d*) Tf_2O, pyridine, CH_2Cl_2, –10 to 10°; 96%. *e*) Bu_4NCN, THF/DMF, 0° to r.t.; 82% **5**, 8% **7**; 2% **6**. *f*) DIBAH, THF/CH_2Cl_2, –20° to r.t.; 87% **9**.

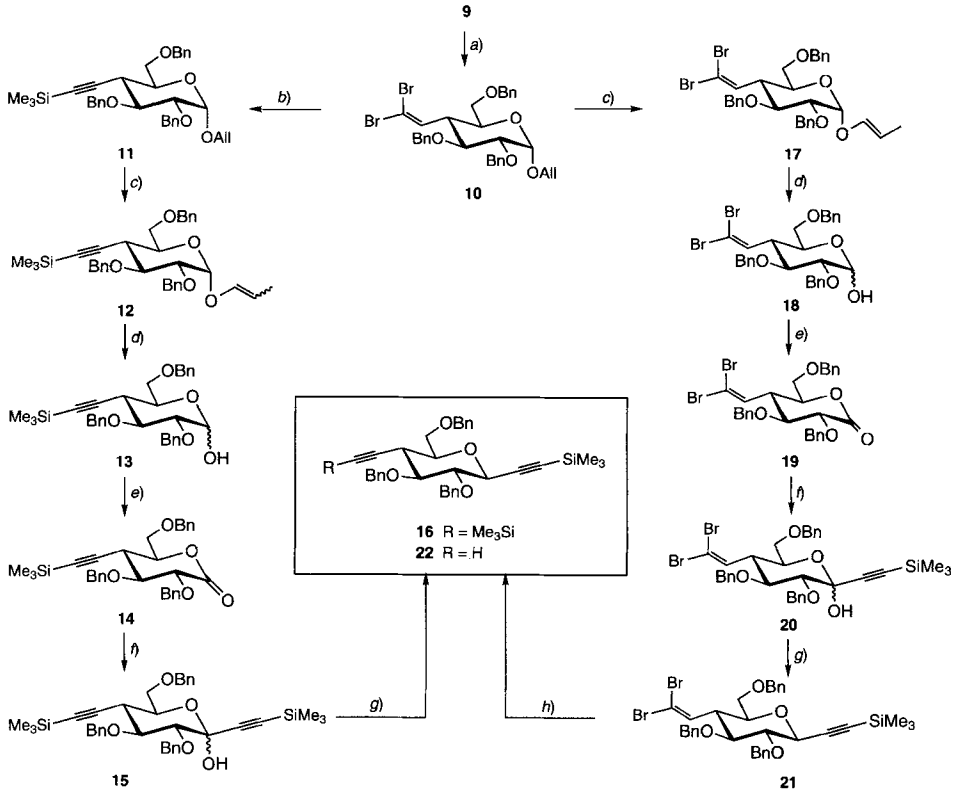
Treatment of **9** with PPh_3 and CBr_4 gave the dibromoalkene **10** in 97% yield, provided that a clear solution of PPh_3CBr_2 was used, and that Et_3N was added before quenching the reaction[9]) (*Scheme 3*). The alkyne **11** was obtained in 93% upon treating **10** with BuLi and then with Me_3SiCl. Introduction of the second ethynyl group was quite straightforward. Deallylation of **11** was best performed with $[Pd(PPh_3)_4]$ in AcOH [44][45], yielding 79% of **13** as a 2:1 α-D/β-D-mixture of anomers, while isomerization [46] of **11** to the enol ether **12** ((*E*/*Z*) 2:1) followed by treatment with $HgCl_2$ and HgO was not satisfactory. *Swern* oxidation of **13** gave the lactone **14** almost quantitatively. Addition of cerium (trimethylsilyl)acetylide [47], followed by reductive dehydroxylation [26] of the hemiacetal **15** led to the desired diethynylated derivative **16** in 43% overall yield from the hemiacetals **13**.

The large amount of $[Pd(PPh_3)_4]$ required to ensure a reasonable rate of deallylation, led to problems in the workup and is not economical. Fortunately, deallylation of the dibromoalkene **10** was straightforward. Isomerization [46] yielded exclusively (*E*)-**17**, which was hydrolyzed with $HgCl_2$/HgO in aqueous acetone; the overall yield of the anomers **18** (α-D/β-D 7:3) was 93%. Cerium (trimethylsilyl)acetylide, used for the addition at –76° to the crude lactone **19**, did not affect the dibromovinyl group. Reductive dehydroxylation of **20** afforded **21** in high yield, but the transformation of **21** into the mono- and bis(trimethylsilyl)acetylides **22** and **16** proceeded in only 42%. These transformations assured a reasonable supply of the fully protected monomer on a gram scale.

The CI-mass spectra of **5** and **9** show the $[M + NH_4]^+$ peak at *m/z* 517 and 520, respectively. The equatorial position of the C(4) substituent of **5** and **9** is evidenced by large *J*(3,4) and *J*(4,5) values (*ca.* 10.7 Hz). The formyl

[9]) PPh_3CBr_2 is quite electrophilic, and was used to cleave a variety of acetals including glucosides at –50 to –35° [43].

Scheme 3



a) PPh_3/CBr_4, CH_2Cl_2, –10° to –2°, Et_3N, H_2O; 98%. *b*) BuLi, THF, –76° to –20°, Me_3SiCl, –76° to r.t.; 93%. *c*) $[Ir(MePh_2P)_2(C_8H_{12})]PF_6$, THF, r.t.; 99%. *d*) $HgCl_2/HgO$, acetone/H_2O, r.t.; 24% for **13**; 93% for **18**. *c*) *d*) for **13**: $[Pd(PPh_3)_4]$, AcOH, 80°; 79%. *e*) $(COCl)_2$, DMSO, CH_2Cl_2, –65°, Et_3N. *f*) $CeCl_3$, $Me_3SiC{\equiv}CLi$, THF, –76°. *g*) Et_3SiH, $BF_3 \cdot Et_2O$, $MeCN/CH_2Cl_2$, –10°; 43% overall for **16** from **13**; 80% overall for **21** from **18**. *h*) BuLi, –78°, Me_3SiCl or HCl; 40%.

group of **9** resonates at 9.66 ppm (J_{vic} = 2.6 Hz), in keeping with data of analogous compounds [33]. The ^{13}C-NMR signals for C(4) of **5** and **9** appear at 35.81 and 56.64 ppm, respectively, the CN group resonates at 117.60 and the CHO group at 200.26 ppm. The enol ether **7** is characterized by an IR band at 1685 cm^{-1}, the downfield shift of H–C(4) (*d* at 5.06 ppm), and the C(4) (*d* at 99.5 ppm) and C(5) signals (*s* at 148.9 ppm). No allylic coupling between H–C(4) and H–C(6) is observed. The structure of **8** is derived from elemental analysis, the CI-MS (peak for $[M + 1]^+$ at *m/z* 504), and a weak broad IR band at 3340 cm^{-1}. The *t* (*J* = 10.0 Hz) of H–C(4) at 2.60 ppm indicates an equatorial position of the MeNH group, which is further characterized by Me signals at 2.28 and 34.33 ppm and an NH resonance at 1.39 ppm. The mass spectra of **10** and **17**–**21** display the typical 3-peak pattern for fragments containing two Br-atoms. The olefinic H resonates between 5.91 and 6.13 ppm, and the large J_{vic} with H–C(4) indicates antiperiplanar arrangement. The olefinic *s*'s appear at 93.01 to 94.01 ppm and the olefinic *d*'s at 134.77 to 135.30 ppm.

The H–C(4) signals of the acetylene derivatives resonate at *ca.* 2.7–2.9 ppm (the *dd* of H–C(4) of **14** is shifted to 3.19 ppm) with large *J*(3,4) and *J*(4,5) values (10.2–10.7 Hz; see *Table 2*) in keeping with the data for other 4-ethynylated *gluco*-derivatives [32]. The C(4) signals are at 38±1 ppm (the *d* of C(4) in **14** is shifted upfield to 35.76 ppm). C(1) and C(2) resonate at 102.3–103.7 and 91.2–91.7 ppm, respectively. The chemical shift for the ethynyl groups of the anomers **20** differ significantly from each other. The signals of the 4-ethynyl

groups resonate at 101.6–103.7 and 88.0–89.8 ppm. The IR spectra of **15** and **20** show OH bands at 3575 and 3570 cm^{-1}, but no carbonyl absorption, establishing the absence of significant concentrations of the corresponding ketones in $CHCl_3$. The ^{1}H-NMR spectrum of **20** shows an α-D/β-D ratio of 7:3; *vide infra* for the assigment of the *ddd* at 3.98 ppm to H–C(5) of the α-D-anomer and of the smaller *ddd* at 3.84 ppm to H–C(5) of the β-D-anomer, as based on the downfield shift of the H–C(5), H–C(3), C(3) and C(5) signals (hexose numbering) induced by the axial OH group. There is a weak alkynyl IR band at 2176 cm^{-1} for **16** and at 2181 and 3307 cm^{-1}, typical of a terminal alkynyl group, for **22**. The Me_3Si groups of **16** resonate at 0.17 and 0.10 ppm; the diaxial relationship of H–C(4) to H–C(5) and to H–C(3) results in a *t* at 2.79 ppm (J = 10.4 Hz). The *d* of H–C(1) at 4.05 ppm ($J(1,2)$ = 9.6 Hz) confirms the equatorial alkynyl position at C(1). The ^{1}H-NMR of **22** shows the *d* (J = 2.3 Hz) of the alkynyl H at 2.11 ppm; for the ^{13}C-NMR alkynyl signals, see *Table 2*.

Table 2. *Selected Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of H–C(1), H–C(4), C(1), and C(4), and of the Ethynyl Moieties*

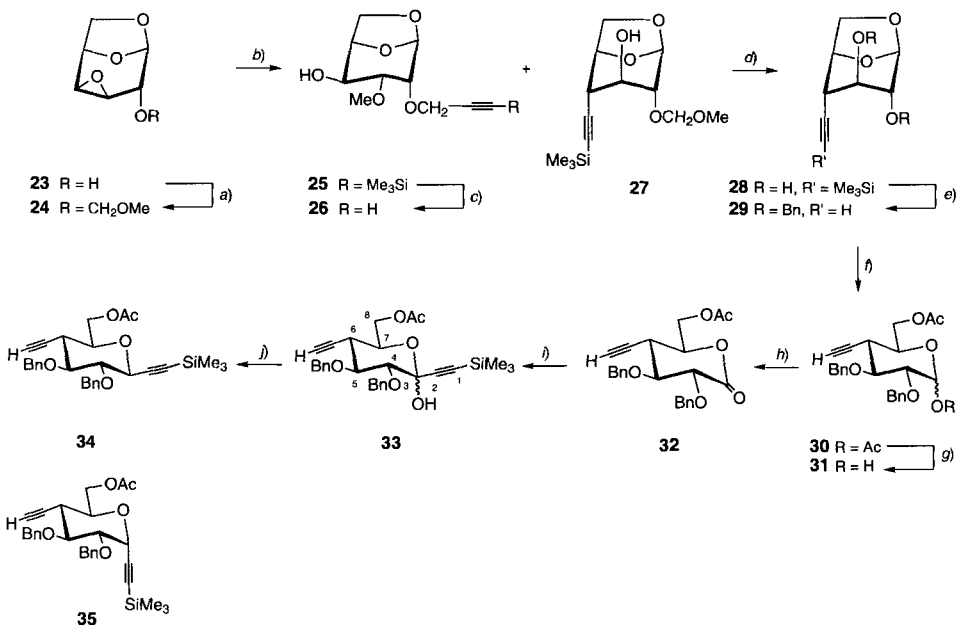
	H–C(1) ($J(1,2)$)[a]	H–C(4) ($J(3,4)$= $J(4,5)$)[a]	C(1)[a]	C(4)[a]	C(1')[b]	C(2')[b]	C(1'')[c]	C(2'')[c]
11	4.89 (3.6)	2.82 (10.6)	96.21	38.10			103.73	87.99
(*E*)-**12**	5.01 (3.5)	2.88 (10.7)	97.11	37.94			103.56	88.28
(*Z*)-**12**	4.98 (3.6)	2.89 (10.7)	97.88	37.96			103.60	88.30
α-D-**13**	5.24 (*ca.* 3.0)	2.78 (10.6)	91.91	38.10			103.54	88.45
β-D-**13**	4.69 (7.6)	2.70 (10.3)	97.54	38.32			103.27	88.95
14		3.19 (10.7)	169.24	35.76			101.55	89.81
16	4.05 (9.6)	2.79 (10.4)	70.50	38.36	103.37	91.16	102.38	88.78
α-D-**20**		2.91 (10.3)	91.65	49.43	103.68	89.23		
β-D-**20**		2.84 (10.3)	95.40	48.87	100.90	94.50		
21	4.02 (9.7)	2.85 (10.2)	70.43	49.68	102.33	91.30		
22	4.04 (9.3)	2.80 (10.2)	70.06	37.28	102.60	91.56	72.37	82.19
α-D-**30**	6.33 (3.6)	2.75 (10.8)	89.90	36.30			72.96	80.18
α-D-**31**	5.22 (2.8)	2.72 (10.5)	91.52	36.80			72.36	80.62
β-D-**31**	4.71 (7.7)	2.67 (10.6)	97.42	36.84			72.69	80.45
32		2.99 (10.5)	168.10	34.60			73.57	79.11
α-D-**33**		2.76 (10.6)	91.40	36.87	103.08	89.25	72.72	80.39
β-D-**33**		2.72 (10.6)	95.45	36.54	100.00	94.47	72.47	80.59
34	4.07 (9.6)	2.70 (10.2)	70.44	37.10	101.94	91.50	72.67	80.41
37	4.04 (9.6)	2.56 (10.3)	69.59	36.99	101.25	91.43	72.58	80.04
42	3.97 (9.2)	2.55 (10.5)	71.06	36.82	101.15	89.83	74.27	80.78
43	3.98 (9.2)	2.53 (10.2)	72.20	39.32	102.59	91.30	101.77	90.29

[a]) Numbering as for the glucosides. [b]) Ethynyl group at C(1). [c]) Ethynyl group at C(4).

In the second approach to the diethynylated monomers, we introduced the 4-ethynyl group by opening the oxirane ring of the protected 1,6:3,4-dianhydro-β-D-galactopyranose **24** with $Me_3SiC{\equiv}CLi$ in the presence of Et_2AlCl [48] (*Scheme 4*). The epoxide **24** was produced by methoxymethylation of the easily available alcohol **23** [48–50]. The alkyne **27** was then obtained under the conditions of *Magdzinski* and *Fraser-Reid* [48], but only in 69% yield. A minor product **25**[10]) (12%) was also formed, resulting from the neighboring-group participation of the $MeOCH_2$ group. The use of Me_3Al [34] instead of Et_2AlCl improved both the yield (85%) and the selectivity (10:1), while increasing the amount of $Me_3SiC{\equiv}CLi$ from 1 to 3 equiv. had no significant influence on the yield and ratio of the products. The by-product **25** was desilylated to **26** (99%).

[10]) The selectivity of the ring opening of **24** depended strongly on the source and the purity of Et_2AlCl [51]. Partially decomposed reagent transformed **24** mostly into the corresponding chlorohydrin.

Scheme 4



a) $MeOCH_2Cl$, $(i\text{-}Pr)_2NEt$, CH_2Cl_2; 97%. *b*) BuLi, $Me_3SiC{\equiv}CH$, toluene, Et_2AlCl; 69% **27**, 12% **25**. *c*) NaOH, MeOH; 99%. *d*) *Dowex 50×4* (H^+ form), MeOH; 95%. *e*) NaH, BnBr, Bu_4NI, DMF; 87%. *f*) Ac_2O, Me_3SiOTf; 95%. *g*) $BnNH_2$; 90%. *h*) DMSO, Ac_2O; 99%. *i*) $Me_3SiC{\equiv}CH$, THF, BuLi, $TiCl_4$; 96%. *j*) Et_3SiH, $BF_3 \cdot OEt_2$, MeCN, CH_2Cl_2; 90%

The introduction of the second ethynyl moiety requires opening of the 1,3-dioxolane ring. We first hydrolyzed the methoxymethyl-protected **27** [52] to the diol **28** (95%, *Scheme 4*). Acetolysis of the corresponding dibenzyl ether **29** with Me_3SiOTf (Tf = CF_3SO_2) in Ac_2O [53] led to the anomeric acetates **30** (α-D/β-D 10:1), which were regioselectively deacetylated with benzylamine[11]) [56]. Oxidation of the resulting hemiacetals **31** (α-D/β-D 1:1) with DMSO/Ac_2O [57], followed by an improved workup afforded the lactone **32** in 99% yield. This lactone was treated with $Me_3SiC{\equiv}CLi$ in THF [27] to provide a mixture (α-D/β-D 3:2) of the anomeric hemiketals **33**; none of the tautomeric hydroxy ketone was detected. Finally, reductive dehydroxylation of the hemiketal **33** with Et_3SiH in the presence of $BF_3 \cdot Et_2O$ yielded 90% of the *C*-glucoside **34** (no **35** detected; *cf.* below) which was thus obtained in an overall yield of 40.3% from **23**.

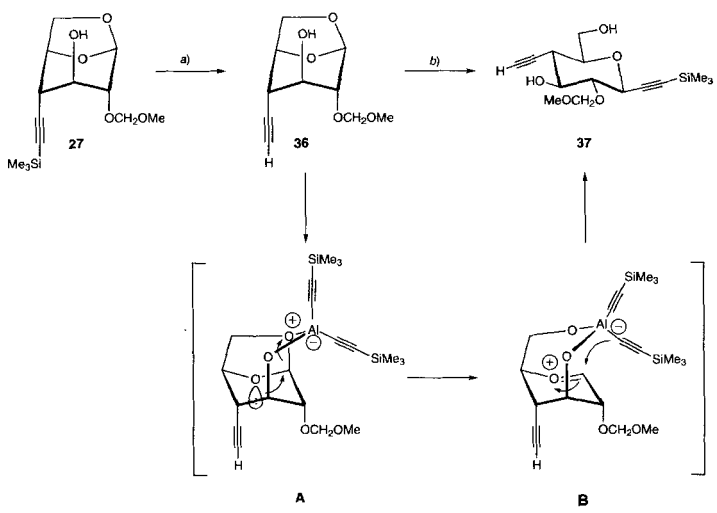
The synthesis of a dialkynylated monomer could be considerably shortened by combining the acetal cleavage with a retentive introduction of an ethynyl group. *Johnson et al.* [58] first described a *Lewis*-acid-promoted synthesis of propargyl ethers from

[11]) The opening of 1,6-anhydroglucose derivatives to glycosyl halides and reaction of the latter with alkynylstannanes to form a mixture of anomeric *C*-glycosylacetylenes or the pure α-D-anomer has been described [30][54][55].

$HC{\equiv}CSiMe_3$ and simple acetals [59], and *Yamamoto et al.* reported a retentive substitution using reagents derived from trialkylaluminium and pentafluorophenol [60]. An extension of this method to the synthesis of **37** has to take into account that cationic intermediates derived from **36** are destabilized by the σ-acceptor substituents. We relied on anchimeric assistance, hoping that it would facilitate substitution and lead to the desired stereoselectivity. Planning to introduce a (trimethylsilyl)ethynyl moiety, we desilylated **27** ($Bu_4NF \cdot 3H_2O$ [61]) to **36** (94%), to facilitate the differentiation between the two ethynyl groups of the product.

Use of $TiCl_4$ in the reaction of $Me_3SiC{\equiv}CLi$ with **36** led to a complex mixture (*cf.* [55]), while Me_3Al and Et_2AlCl did not promote the reaction, even at 100°. However, the reaction of **36** with 3 equiv. of preformed $(Me_3SiC{\equiv}C)_3Al$ (from $AlCl_3$ and $Me_3SiC{\equiv}CLi$) yielded 70% of **37** (*Scheme 5*). The alkynylating acetal opening proceeded with complete retention and is rationalized by the mechanism depicted in *Scheme 5*. One equiv. of the reagent is used to deprotonate **36** and to form an alkoxy(diethynyl)aluminium species. Intramolecular coordination of the Al center with O–C(6) leads to the aluminate complex **A**. The antiperiplanar arrangement of the lone pair at O–C(5) and the C(1)–O bond facilitates formation of the oxycarbenium ion **B** which reacts by intramolecular delivery of a (trimethylsilyl)ethynyl moiety to the cationic center.

Scheme 5

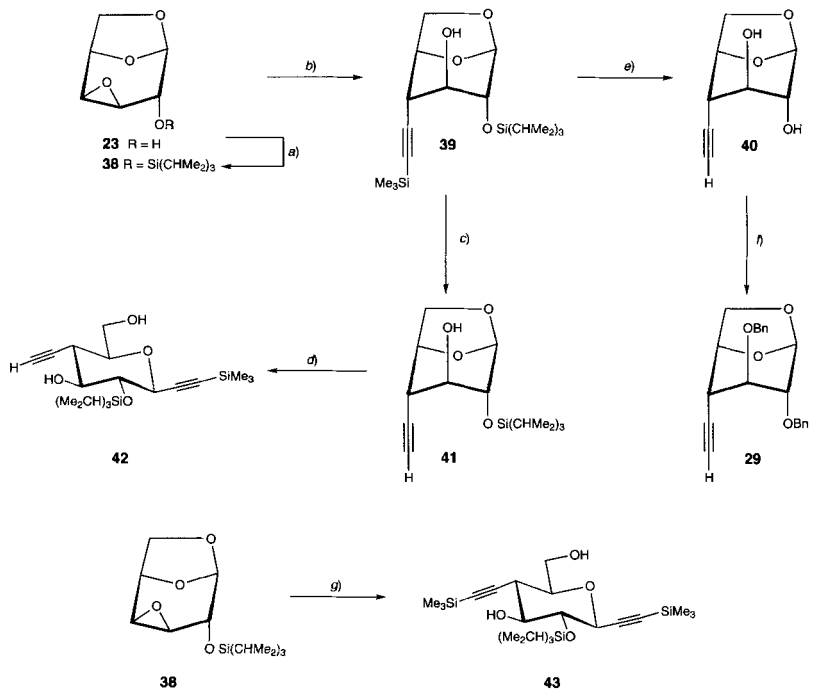


a) $Bu_4NF \cdot 3H_2O$, THF; 94%. *b*) $Me_3SiC{\equiv}CH$, BuLi, $AlCl_3$, toluene; 70%.

To improve the chemoselectivity of the opening of the methoxymethyl protected epoxide **24** (see *Scheme 4*), we prepared the analogous triisopropylsilyl ether **38** from **23** (*Scheme 6*). Indeed, reaction of **38** with $Me_3SiC{\equiv}CLi$ yielded the alkyne derivative **39** in an improved yield of 85% [62]. The latter was converted to the dibenzyl ether **29** *via* **40** (*Scheme 6*), which is thus available in an overall yield of 68% from **23**. *C*-Desilylation of **39** with NaOMe in MeOH gave 95% of **41**. The same result was obtained with 0.3 equiv.

of $Bu_4NF \cdot 3H_2O$ in THF at 0°. The alkynylating acetal cleavage of **41** proceeded under the same conditions as the one of **36**, yielding 80% of the monomer **42**. This constitutes a noticeable improvement in the synthesis of diethynylated monomers, since **42** is thus available in four steps and an overall yield of 61% from **23**, while the monomers **37** and **34** were prepared from **23** in four and nine steps in 44 and 40% yield, respectively.

Scheme 6



a) (i-Pr)$_3$SiOTf, Py; 95%. *b*) $Me_3SiC{\equiv}CH$, BuLi, Me_3Al, toluene; 85% *c*) NaOMe, MeOH; 95%. *d*) 3 equiv. of Me_3SiCCH, 3 equiv. of BuLi, 3 equiv. of $AlCl_3$, toluene; 80%. *e*) $Bu_4NF \cdot 3H_2O$, THF; 87%. *f*) NaH, BnBr, Bu_4NI, DMF; 97% *g*) 8 equiv. of $Me_3SiC{\equiv}CH$, 8 equiv. of BuLi, 8 equiv. of Et_2AlCl, toluene; 81%.

The synthesis of diethynylated monomers was, however, further improved by a one-pot ethynylating opening of the oxirane and the 1,3-dioxolane rings of **38**. As the conditions of the alkynylating acetal cleavage led to the introduction of a chloro substituent at C(4) and of a (trimethylsilyl)ethynyl moiety at the anomeric center, we reduced the concentration of chloride by substituting Et_2AlCl for $AlCl_3$. With 5 equiv. each of Et_2AlCl and $Me_3SiC{\equiv}CLi$, we obtained 45% of the fourth monomer **43** and 40% of **39**, while 8 equiv. of the reagents yielded **43** exclusively in a yield of 81%, realizing a very satisfactory synthesis of this monomer in two steps from **23** (77% yield).

The IR spectrum of **27** shows an OH band at 3560 and an alkynyl band at 2180 cm^{-1}. The small values for $J(2,3)$ and $J(3,4)$ in the ^{1}H-NMR spactrum of **27** evidence the *gluco*-configuration and the $^1C_4$ conformation. The

$MeOCH_2$ group is evidenced by 2*d* at 4.77 and 4.72 ppm (J = 7.0 Hz) and a *t* at 96.92 ppm and by the MeO signal at 3.44 and 55.8 ppm in the ^{1}H- and ^{13}C-NMR spectra, respectively. The minor product **25** shows IR absorptions at 3590 and 2170 cm^{-1}. In keeping with this, the ^{1}H-NMR spectrum shows a *d* for OH–C(4) at 2.36 ppm (J = 2.6 Hz), and the ^{13}C-NMR exhibits *s*'s at 101.1 and 92.29 ppm. The MeO group is evidenced by signals at 3.47 and 57.29 ppm, while the diequatorial ring opening is shown by the large value of J(3,4) = 9.2 Hz. That **25** is not a regio- or diastereoisomer of **27** is evidenced by the *t* at 58.51 ppm, incompatible with the MeO*CH*$_2$O group and assigned to the propargylic CH_2 group, resonating at 4.35 ppm in the ^{1}H-NMR spectrum. The desilylated **26** (from **25** and NaOH in MeOH [63]) shows coupling (J = 2.0 Hz) of the newly generated H–C(3') (*t* at 2.49 ppm) with the propargylic CH_2 group at 57.94 ppm. The anomeric configuration of **33** is deduced from a comparison of the chemical shift differences of **33** and **31** and of **33** and **35**[12]) [62]. Thus, $\Delta\delta$ between the H–C(5)/H–C(3) signals (hexose numbering) of α-D-**33** and those of α-D-**31** are 0.01/–0.11 and 0.16/0.24 ppm, as compared to $\Delta\delta$ = 0.54/0.20 and 0.37/0.07 ppm for a comparison to β-D-**31**. The $\Delta\delta$ resulting from a comparison between C(1)/C(2) in α- and β-D-**33** and in **34** is –2.25/1.14 and 2.97/–1.94 ppm, respectively; a similar comparison of C(1)/C(2) in α- and β-D-**33** to **35** gives values of –6.37/3.5 and –1.15/0.42 ppm, respectively. The configuration of the anomers of **15** and **20** (*vide supra*) was deduced in a similar way.

The β-D-configuration of **34** is shown by the *d* (J(3,4) = 9.6 Hz) of H–C(3) at 4.07 ppm and the *gluco*-configuration by J(4,5) = 9.0 Hz, J(5,6) = 10.3 Hz, and J(6,7) = 10.4 Hz. Analogous criteria as those discussed above were used for the structure assignment of compounds **37**, **42**, and **43** (see *Table 2* and *Exper. Part*).

We thank the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support.

Experimental Part

General. Solvents were distilled before use: THF from Na and benzophenone, CH_2Cl_2, amines, and MeCN from CaH_2, DMF from 4-Å molecular sieves, and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) from Na. Reactions were run under Ar. Usual workup: the mixture was diluted with Et_2O or AcOEt and the org. phase washed with brine, dried ($MgSO_4$), and evaporated. Qual. TLC: 0.25-mm precoated silica-gel plates (*Merck*, silica gel *60* F_{25}); detection by spraying the plates with 'mostain' (400 ml of 10% H_2SO_4 soln., 20 g of $(NH_4)_6Mo_7O_{24} \cdot 6H_2O$, 0.4 g of Ce $(SO_4)_2$) followed by heating at *ca.* 200°. Flash chromatography (FC): silica gel *Merck 60* (0.04–0.063 mm). M.p.'s: uncorrected. Optical rotations: 1-dm cell at 25° and 365, 436, 546, 578, and 589 nm; values at 589 nm were determined from a regression curve. IR Spectra: 3% soln. in $CHCl_3$. ^{1}H- and ^{13}C-NMR Spectra: unless otherwise stated, at 300 and 50 MHz, resp., chemical shifts δ in ppm rel. to Me_4Si (= 0 ppm) as internal standard; in ambiguous cases, ^{1}H-assignments by selective homonuclear decoupling experiments, ^{13}C assignments by ^{1}H, ^{13}C-HOMDQC spectra (^{1}H, 300 MHz). Mass spectra: chemical ionization (CI) with NH_3; at 70 eV.

Allyl 4,6-O-Benzylidene-α-D-galactopyranoside (**2**). Finely ground **1** [36] (22 g, 0.10 mol) was added to a suspension of benzaldehyde dimethyl acetal (22.0 ml, 0.145 mol) and *Amberlyst-15* ion-exchange resin (0.5 g, H^+ form)[13]) in $CHCl_3$ (350 ml). The suspension was stirred vigorously and heated to gentle reflux under N_2. MeOH was removed azeotropically by slow distillation, and fresh $CHCl_3$ was added to maintain a constant volume. After *ca.*100 min, **1** had dissolved completely. Stirring was continued until TLC showed complete disappearance of **1** (*ca.* 0.5 h). The mixture was cooled to r.t. and filtered through a glass filter half-filled with silica gel (*ca.* 100 g). The residue was washed with $CHCl_3$. Evaporation of the filtrate and washings gave a solid which was ground in a mortar under hexane (3 × 100 ml), filtered and washed with hexane. Recrystallization in boiling toluene and drying under high vacuum afforded **2** [37] (90%). R_f ($MeOH/CH_2Cl_2$ 7:93) 0.33.

Allyl 2,3,6-Tri-O-benzyl-4-O-(trifluoromethylsulfonyl)-α-D-galactopyranoside (**4**). At –10°, a freshly distilled soln. of Tf_2O (9.384 g, 33.26 mmol) in CH_2Cl_2 (20 ml) was added dropwise within 40 min to a stirred soln. of **3** [64] (13.58 g, 27.72 mmol) and pyridine (6.7 ml, 83 mmol) in CH_2Cl_2 (400 ml). The soln. was warmed

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[12]) We thank *Roland Bürli*, for a generous sample of **35** [62].

[13]) The resin was brought into the H^+ form by slowly stirring in 12N HCl for 1 h, washing with deionized H_2O to pH 7 and then with EtOH and Et_2O, heating in boiling $CHCl_3$ for 0.5 h, filtration, and washing with fresh $CHCl_3$ before use.

to 10° within 3 h, cooled to 0°, and poured into 80 ml of cold 1M aq. HCl. The org. layer was washed with sat. aq. NH_4Cl soln. (80 ml) and H_2O (3 × 80 ml) and processed as usual. Short column FC (50 g, CH_2Cl_2) gave **4** as a light orange oil (16.588 g, 96%) which was used for the next step. A sample of **4**, resulting from a parallel experiment, was purified by FC (hexane/AcOEt 92:8). Colorless oil. R_f (hexane/AcOEt 7:3) 0.52. $[\alpha]_D^{25} = +49.3$ (*c* = 1.71, $CHCl_3$). IR ($CHCl_3$): 3089*w*, 3067*w*, 3042*w*, 3007*m*, 2992*m*, 2876*m*, 1952*w*, 1878*w*, 1812*w*, 1728*w*, 1646*w*, 1603*w*, 1497*m*, 1454*m*, 1409*s*, 1353*m*, 1252*s*, 1144*s*, 1103*s*, 1057*s*, 1028*s*, 965*m*, 916*s*, 823*m*, 616*s*, 566*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.41–7.26 (*m*, 15 arom. H); 5.89 (*dddd*, *J* = 17.2, 10.3, 6.6, 5.2, H–C(2')); 5.41 (br. *d*, *J* ≈ 2.6, H–C(4)); 5.29 (*dq*, *J* = 17.2, 1.6, H–C(3')); 5.21 (*dq*, *J* = 10.3, 1.1, H–C(3')); 4.86 (*d*, *J* = 11.4, PhC*H*); 4.82 (*d*, *J* = 3.9, H–C(1)); 4.80 (*d*, *J* = 12.0, PhC*H*); 4.65 (*d*, *J* = 11.4, PhC*H*); 4.63 (*d*, *J* = 12.0, PhC*H*); 4.60 (*d*, *J* = 11.9, PhC*H*); 4.44 (*d*, *J* = 11.4, PhC*H*); 4.16–4.11 (*m*, H–C(1'), H–C(5)); 4.04–3.99 (*m*, H–C(1'), H–C(3)); 3.79 (*dd*, *J* = 10.0, 3.7, H–C(2)); 3.60 (*dd*, *J* = 9.2, 6.0, H–C(6)); 3.56 (*dd*, *J* = 9.2, 8.0, H–C(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.01 (*s*); 137.49 (*s*); 137.40 (*s*); 133.40 (*d*, C(2')); 128.53–127.76 (several *d*); 118.50 (*t*, C(3')); 96.34 (*d*, C(1)); 83.85 (*d*, C(4)); 75.13 (*d*, C(2)); 74.94 (*d*, C(3)); 73.81 (*t*, Ph*C*H$_2$); 73.67 (*t*, Ph*C*H$_2$); 73.27 (*t*, Ph*C*H$_2$); 68.82 (*t*, C(1')); 67.43 (*t*, C(6)); 67.00 (*d*, C(5)). FAB-MS: 623 (2, $[M + 1]^+$), 621 (8, $[M - 1]^+$), 181 (36), 92 (28), 91 (100). Anal. calc. for $C_{31}H_{33}F_3O_8S$ (622.65): C 59.51, H 5.32, S 5.13; found: C 59.60, H 5.54, S 4.99.

Cyanation of **4**. At 0°, a soln. of Bu_4NCN (6.181 g, 23.03 mmol, dried by stirring at 60°/0.35 mbar for 5 h) in THF (15 ml) was added over 3 min to a stirred soln. of **4** (11.935 g, 19.17 mmol) in dry DMF (120 ml). Stirring was continued for 10 min at 0° and for 1 h from 0° to r.t. Usual workup afforded a light yellow oil. FC (hexane/AcOEt 9:1) gave **5** (8.08 g, 84%, contaminated with *ca.* 2% of **6**) and **7** (0.713 g, 8%).

*Allyl 2,3,6-Tri-*O*-benzyl-4-*C*-cyano-4-deoxy-α-*D*-glucopyranoside* (**5**): Colorless oil. R_f (hexane/AcOEt 85:15) 0.16. $[\alpha]_D^{20} = +30.9$ (*c* = 0.99, $CHCl_3$). IR ($CHCl_3$): 3060*w*, 3005*m*, 2920*m*, 2870*m*, 2250*w*, 1810*w*, 1640*w*, 1590*w*, 1500*m*, 1455*m*, 1350*s*, 1260*w*, 1100*s*, 1040*s*, 1030*s*, 940*m*, 910*m*, 860*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.44–7.30 (*m*, 15 arom. H); 5.93 (*dddd*, *J* = 17.2, 10.3, 6.5, 5.3, H–C(2')); 5.34 (*dq*, *J* = 17.2, 1.5, H–C(3')); 5.26 (*dq*, *J* = 10.3, 1.1, H–C(3')); 4.95 (*d*, *J* = 10.4, PhC*H*); 4.91 (*d*, *J* = 10.4, PhC*H*); 4.86 (*d*, *J* = 3.5, H–C(1)); 4.78 (*d*, *J* = 12.0, PhC*H*); 4.64 (*d*, *J* = 12.0, 2 PhC*H*); 4.56 (*d*, *J* = 12.0, PhC*H*); 4.17 (*ddt*, *J* = 12.9, 5.3, 1.4, H–C(1')); 4.15 (*dd*, *J* = 10.9, 9.5, H–C(3)); 4.08 (*dt*, *J* ≈ 10.9, 2.8, H–C(5)); 4.02 (*ddt*, *J* = 12.9, 6.6, 1.1, H–C(1')); 3.74 (*dd*, *J* = 11.0, 3.3, H–C(6)); 3.70 (*dd*, *J* = 11.0, 2.3, H–C(6)); 3.47 (*dd*, *J* = 9.3, 3.5, H–C(2)); 3.06 (*t*, *J* = 10.8, H–C(4)). ^{13}C-NMR (50 MHz, $CDCl_3$): 137.67 (*s*); 137.61 (*s*); 137.54 (*s*); 133.10 (*d*, C(2')); 128.34–127.44 (several *d*); 118.39 (*t*, C(3')); 117.60 (*s*, CN); 96.00 (*d*, C(1)); 79.40 (*d*, C(2)); 76.15 (*d*, C(3)); 75.79 (*t*, Ph*C*H$_2$); 73.66 (*t*, Ph*C*H$_2$); 73.03 (*t*, Ph*C*H$_2$); 69.15 (*t*); 68.59 (*t*, C(6), C(1')); 67.80 (*d*, C(5)); 35.81 (*d*, C(4)). CI-MS: 517 (100, $[M + NH_4]^+$). Anal. calc. for $C_{31}H_{33}NO_5$ (499.61): C 74.53, H 6.66, N 2.80; found: C 74.71, H 6.84, N 3.01.

*Allyl 2,3,6-Tri-*O*-benzyl-4-deoxy-α-*L*-threo-hex-4-enopyranoside* (**7**): Colorless oil. R_f (hexane/AcOEt 85:15) 0.21. $[\alpha]_D^{20} = +124.8$ (*c* = 0.984, $CHCl_3$). IR ($CHCl_3$): 3070*m*, 3005*s*, 2920*s*, 2880*s*, 1955*w*, 1880*w*, 1810*w*, 1685*m*, 1500*m*, 1460*s*, 1360*m* (br.), 1310*m*, 1250*m*, 1190*m*, 1100*s*, 1070*s*, 1030*s*, 940*m*, 820*w*, 700*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.26 (*m*, 15 arom. H); 5.93 (*dddd*, *J* = 17.1, 10.4, 6.3, 5.1, H–C(2')); 5.31 (*dq*, *J* = 17.2, 1.5, H–C(3')); 5.20 (*dq*, *J* = 10.4, 1.3, H–C(3')); 5.06 (*d*, *J* = 3.1, H–C(4)); 5.03 (*d*, *J* = 2.4, H–C(1)); 4.80 (*d*, *J* = 12.3, PhC*H*); 4.75 (*d*, *J* = 12.3, PhC*H*); 4.65 (*d*, *J* = 12.0, PhC*H*); 4.62 (*d*, *J* = 12.0, PhC*H*); 4.57 (*d*, *J* = 12.0, PhC*H*); 4.53(*d*, *J* = 12.0, PhC*H*); 4.32 (*ddt*, *J* = 13.0, 5.0, 1.5, H–C(1')); 4.25 (*dd*, *J* = 6.6, 3.0, H–C(3)); 4.13 (*ddt*, *J* = 13.0, 6.3, 1.3, H–C(1')); 3.93 (*s*, 2 H–C(6)); 3.80 (*dd*, *J* = 6.5, 2.4, H–C(2)). ^{13}C-NMR (50 MHz, $CDCl_3$): 148.88 (*s*, C(5)); 138.42 (*s*); 138.13 (*s*); 137.86 (*s*); 133.71 (*d*, C(2')); 128.21–127.43 (several *d*); 117.45 (*t*, C(3')); 99.50 (*d*, C(4)); 97.12 (*d*, C(1)); 76.10 (*d*, C(2)); 73.13 (*d*, C(3)); 72.80 (*t*, Ph*C*H$_2$); 71.98 (*t*, Ph*C*H$_2$); 71.15 (*t*, Ph*C*H$_2$); 69.48 (*t*, C(6)); 68.93 (*t*, C(1')). CI-MS: 490 (100, $[M + NH_4]^+$). Anal. calc. for $C_{30}H_{32}O_5$ (472.58): C 76.25, H 6.83; found: C 75.54, H 6.82.

*Allyl 2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-formyl-α-*D*-glucopyranoside* (**9**) *and Allyl 2,3,6-Tri-*O*-benzyl-4-deoxy-4-(methylamino)-α-*D*-glucopyranoside* (**8**). At –20°, 1.2M DIBAH in toluene (1.20 ml, 1.44 mmol) was added to a stirred soln. of **5** (525 mg, 1.051 mmol; containing *ca.* 2% of **6**) in THF/CH_2Cl_2 7:23 (3 ml) over 3 min. Stirring was continued for 2 h at –20° and 5 h at r.t. The clear soln. was cooled to –10°, stirred vigorously, treated dropwise with MeOH/THF 1:1 (2 ml) and 1N HCl (2 ml), stirred for 10 min at r.t., diluted with Et_2O (70 ml), washed with aq. 1N HCl (2 × 15 ml) and H_2O (3 × 10 ml), and processed as usual. FC (hexane/AcOEt 92:8) gave **9** (461 mg, 87%) and **8** (12 mg, 2%).

Data of **9**: Colorless oil. R_f (hexane/AcOEt 17:3) 0.18. $[\alpha]_D^{20} = +14.0$ (*c* = 0.90, $CHCl_3$). IR ($CHCl_3$): 3060*w*, 3000*m*, 2920*m*, 2880*m*, 1720*s*, 1500*m*, 1460*m*, 1360*m* (br.), 1260*w* (br.), 1160*m*, 1100*s*, 1070*m*, 1040*s*, 1030*s*, 1000*m*, 940*m*, 910*w*, 700*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.66 (*d*, *J* = 2.6, CHO); 7.36–7.27 (*m*, 15 arom. H); 5.94

(*dddd*, *J* = 17.2, 10.3, 6.6, 5.2, H–C(2')); 5.33 (*dq*, *J* = 17.3, 1.5, H–C(3')); 5.23 (*dq*, *J* = 10.3, 1.3, H–C(3')); 4.93 (*d*, *J* = 10.9, PhC*H*); 4.86 (*d*, *J* = 3.5, H–C(1)); 4.75 (*d*, *J* = 12.0, PhC*H*); 4.65 (*d*, *J* = 11.9, PhC*H*); 4.60 (*d*, *J* = 10.9, PhC*H*); 4.55 (*d*, *J* = 12.0, PhC*H*); 4.45 (*d*, *J* = 12.0, PhC*H*); 4.28 (*dd*, *J* = 10.7, 9.4, H–C(3)); 4.19 (*ddt*, *J* = 13.0, 5.2, 1.4, H–C(1')); 4.10 (*dt*, *J* = 10.7, 4.2, H–C(5)); 4.00 (*ddt*, *J* = 13.1, 6.6, 1.3, H–C(1')); 3.62 (*dd*, *J* = 9.3, 3.4, H–C(2)); 3.57 (*dd*, *J* = 10.5, 4.2, H–C(6)); 3.54 (*dd*, *J* = 10.5, 4.2, H–C(6)); 2.99 (*td*, *J* = 10.7, 2.6, H–C(4)). ^{13}C-NMR (50 MHz, $CDCl_3$): 200.26 (*d*, CHO); 138.07 (*s*); 137.89 (*s*); 137.51 (*s*); 133.52 (*d*, C(2')); 128.33–127.45 (several *d*); 118.10 (*t*, C(3')); 95.72 (*d*, C(1)); 80.57 (*d*, C(2)); 75.21 (*d*, C(3)); 75.10 (*t*, PhCH_2); 73.34 (*t*, PhCH_2); 72.71 (*t*, PhCH_2); 70.13 (*t*, C(6)); 68.29 (*t*, C(1')); 67.13 (*d*, C (5)); 56.64 (*d*, C(4)). CI-MS: 520 (100, [*M* + NH_4]$^+$), 412 (79, [*M* – Bn – H]$^+$). Anal. calc. for $C_{31}H_{34}O_6$ (502.61): C 74.08, H 6.82; found: C 74.32, H 6.97.

Data of **8**: R_f (hexane/AcOEt 7:3) 0.05. $[\alpha]_D^{20}$ = +28.2 (*c* = 0.98, $CHCl_3$). IR ($CHCl_3$): 3340*w* (br.), 3070*w*, 3005*m*, 2920*s*, 2880*s*, 2810*w*, 1500*m*, 1460*s*, 1425*w*, 1360*m*, 1250*w*, 1095*s*, 1050*s*, 1030*s*. 940*m*, 920*m*, 700*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.25 (*m*, 15 arom. H); 5.95 (*dddd*, *J* = 17.2, 10.3, 6.7, 5.1, H–C(2')); 5.32 (*dq*, *J* = 17.3, 1.5, H–C(3')); 5.21 (*dq*, *J* = 10.3, 1.3, H–C(3')); 5.04 (*d*, *J* = 11.6, PhC*H*); 4.87 (*d*, *J* = 3.6, H–C(1)); 4.74 (*d*, *J* = 12.0, PhC*H*); 4.70 (*d*, *J* = 11.5, PhC*H*); 4.65 (*d*, *J* = 12.0, PhC*H*); 4.60 (*d*, *J* = 12.1, PhC*H*); 4.53 (*d*, *J* = 12.1, PhC*H*); 4.17 (*ddt*, *J* = 13.0, 5.1, 1.4, H–C(1')); 4.02 (br. *dd*, *J* ≈ 12.9, 6.7, H–C(1')); 3.81 (*t*, *J* = 9.5, H–C(3)); 3.73–3.65 (*m*, H–C(5), 2 H–C(6)); 3.60 (*dd*, *J* = 9.3, 3.6, H–C(2)); 2.60 (br. *t*, *J* ≈ 10.0, H–C(4)); 2.28 (*s*, MeN); 1.39 (br. *s*, exchange with D_2O, NH). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.69 (*s*); 138.08 (*s*); 138.03 (*s*); 133.76 (*d*, C(2')); 128.29–127.28 (several *d*); 117.80 (*t*, C(3')); 95.34 (*d*, C(1)); 80.78 (*d*, C(2)); 78.40 (*d*, C(3)); 74.88 (*t*, PhCH_2); 73.21 (*t*, PhCH_2); 72.59 (*t*, PhCH_2); 70.83 (*d*, C(5)); 69.69 (*t*, C(6)); 67.82 (*t*, C(1')); 60.20 (*d*, C(4)); 34.33 (*q*, MeN). CI-MS: 504 (100, [*M* + 1]$^+$), 414 (55). Anal. calc. for $C_{31}H_{37}NO_5$ (503.64): C 73.93, H 7.41, N 2.78; found: C 73.74, H 7.32, N 2.84.

*Allyl 2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-(2,2-dibromoethenyl)-α-*D*-glucopyranoside* (**10**). At –10 to –5°, a soln. of CBr_4 (20.548 g, 61.96 mmol) in CH_2Cl_2 (13 ml) was added within 5 min to a stirred soln. of PPh_3 (32.503 g, 123.92 mmol) in CH_2Cl_2 (55 ml). The resulting orange-brown suspension was stirred at –10° for 15 min, and decanted at –10° to give a light brown soln. and a yellow precipitate. Of the above clear soln., 60 ml were added *via* a syringe to a vigorously stirred and cooled (–10 to –6°) soln. of **9** (7.785 g, 15.49 mmol) in CH_2Cl_2 (60 ml). The brown soln. was stirred at –10 to –6° for 40 min and treated dropwise with Et_3N (15 ml) and sat. aq. $NaHCO_3$ soln. (1.5 ml). The mixture was passed through a short pad of silica gel (150 g, eluted with CH_2Cl_2). FC (CH_2Cl_2) gave **10** (9.953 g, 98%). Light-orange oil. R_f (hexane/AcOEt 17:3) 0.24. $[\alpha]_D^{20}$ = +48.0 (*c* = 1.11, $CHCl_3$). IR ($CHCl_3$): 3070*w*, 3005*m*, 2920*m*, 2880*m*, 1950*w*, 1880*w*, 1870*w*, 1630*w*, 1590*w*, 1500*m*, 1460*s*, 1370*m*, 1360*m*, 1310*w*, 1260*m*, 1150*s*, 1100*s*, 1070*s*, 1030*s*, 940*m*, 920*m*, 840*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.27 (*m*, 15 arom. H); 6.13 (*d*, *J* = 10.1, H–C(1'')); 5.95 (*dddd*, *J* = 17.2, 10.3, 6.6, 5.3, H–C(2')); 5.32 (*dq*, *J* = 17.2, 1.5, H–C(3')); 5.22 (*dq*, *J* = 10.3, 1.4, H–C(3')); 4.87 (*d*, *J* = 3.4, H–C(1)); 4.85 (*d*, *J* = 11.0, PhC*H*); 4.80 (*d*, *J* = 11.9, PhC*H*); 4.66 (*d*, *J* = 10.9, PhC*H*); 4.64 (*d*, *J* = 11.9, PhC*H*); 4.57 (*s*, PhCH_2); 4.17 (*ddt*, *J* = 13.0, 5.2, 1.4, H–C(1')); 4.03 (*ddt*, *J* = 12.9, 6.6, 1.1, H–C(1')); 3.81 (*ddd*, *J* = 10.7, 5.0, 2.5, H–C(5)); 3.79 (*t*, *J* ≈ 9.7, H–C(3)); 3.60 (*dd*, *J* = 9.4, 3.6, H–C(2)); 3.54 (*dd*, *J* = 10.7, 2.5, H–C(6)); 3.46 (*dd*, *J* = 10.7, 5.1, H–C(6)); 2.90 (*q*, *J* = 10.3, H–C(4)). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.32 (*s*); 138.24 (*s*); 137.90 (*s*); 135.46 (*d*, C(1'')); 133.76 (*d*, C(2')); 128.30–127.52 (several *d*); 118.08 (*t*, C(3')); 96.07 (*d*, C(1)); 92.86 (*s*, C(2'')); 80.29 (*d*, C(2)); 77.89 (*d*, C(3)); 75.33 (*t*, PhCH_2); 73.56 (*t*, PhCH_2); 73.13 (*t*, PhCH_2); 70.49 (*t*, C(6)); 69.26 (*d*, C(5)); 68.30 (*t*, C(1')); 49.19 (*d*, C(4)). CI-MS: 678 (58), 676 (100), 674 (62, [*M* + NH_4]$^+$). Anal. calc. for $C_{32}H_{34}Br_2O_5$ (658.42): C 58.37, H 5.21, Br 24.27; found: C 58.40, H 5.41, Br 24.01.

*Allyl 2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-[2-(trimethylsilyl)ethynyl]-α-*D*-glucopyranoside* (**11**). At –76°, a soln. of 2.37M BuLi in hexane (1.36 ml, 3.21 mmol) was added dropwise to a well stirred soln. of **10** (1.007 g, 1.529 mmol) in THF (9 ml). The yellow soln. was stirred at –76° for 3 h and at –20° for 1 h, cooled to –76°, treated with Me_3SiCl (0.29 ml, 2.29 mmol), stirred at –76° for 10 min, warmed to r.t., and worked up as usual. FC (hexane/AcOEt 96:4) afforded **11** (0.809 g, 93%). Colorless oil. R_f (hexane/AcOEt 17:3) 0.25. $[\alpha]_D^{20}$ = +6.31 (*c* = 0.935, $CHCl_3$). IR ($CHCl_3$): 3035*w*, 3005*m*, 2960*m*, 2920*m*, 2880*m*, 2180*m*, 1500*m*, 1460*s*, 1410*w*, 1360*m*, 1355*m*, 1255*s*, 1150*s*, 1095*s*, 1050*s*, 1030*s*, 1000*m*, 940*w*, 920*w*, 850*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.45–7.25 (*m*, 15 arom. H); 5.96 (*dddd*, *J* = 17.2, 10.3, 6.6, 5.2, H–C(2')); 5.34 (*dq*, *J* = 17.3, 1.6, H–C(3')); 5.23 (*dq*, *J* = 10.3, 1.6, H–C(3')); 4.95 (*d*, *J* = 10.5, PhC*H*); 4.89 (*d*, *J* = 10.5, PhC*H*); 4.86 (*d*, *J* = 3.6, H–C(1)); 4.79 (*d*, *J* = 12.2, PhC*H*); 4.65 (*d*, *J* = 12.2, PhC*H*); 4.62 (*d*, *J* = 12.3, PhC*H*); 4.56 (*d*, *J* = 12.3, PhC*H*); 4.20 (*ddt*, *J* = 12.9, 5.2, 1.4, H–C(1')); 4.04 (*ddt*, *J* = 12.9, 6.6, 1.1, H–C(1')); 3.96 (*dd*, *J* = 10.3, 9.7, H–C(3)); 3.91 (*ddd*, *J* = 10.8, 4.3, 2.3, H–C(5)); 3.74 (*dd*, *J* = 10.8, 2.3, H–C(6)); 3.70 (*dd*, *J* = 10.8, 4.4, H–C(6)); 3.45 (*dd*, *J* = 9.5, 3.6, H–C(2)); 2.82 (*t*, *J* = 10.6, H–C(4)); 0.13 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.62 (*s*); 138.20 (*s*); 138.02 (*s*); 133.73 (*d*, C(2')); 128.22–127.41 (several *d*); 117.94 (*t*, C(3')); 103.73 (*s*, C(1'')); 96.21 (*d*, C(1)); 87.99 (*s*, C(2'')); 79.48 (*d*,

C(2)); 79.37 (*d*, C(3)); 75.86 (*t*, PhCH$_2$); 73.46 (*t*, PhCH$_2$); 73.00 (*t*, PhCH$_2$); 70.33 (*d*, C(5)); 69.87 (*t*, C(6)); 68.24 (*t*, C(1')); 38.10 (*d*, C(4)); –0.17 (*q*, Me$_3$Si). CI-MS: 588 (100, [*M* + NH$_4$]$^+$). Anal. calc. for $C_{35}H_{42}O_5Si$ (570.80): C 73.65, H 7.42; found: C 73.44, H 7.32.

*Prop-1-enyl 2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-[2-(trimethylsilyl)ethynyl]-*α*-*D*-glucopyranoside* (**12**). Bis(methyldiphenylphosphine)(cycloocta-1,5-diene)iridium(I)hexafluorophosphate [46] (50 mg, 0.059 mmol) was degassed, placed under H_2, treated with THF (4 ml), and stirred for 10 min. The resulting orange soln. was degassed, flushed twice with Ar and injected into a stirred soln. of **11** (638 mg, 1.118 mmol) in THF (5 ml). The soln. was stirred for 1.5 h. Evaporation and FC (hexane/AcOEt 93:7) gave (*E*)/(*Z*)-**12** 2:1 (630 mg, 99%). Colorless oil. R_f (CH_2Cl_2) 0.57. IR ($CHCl_3$): 3060*w*, 3015*w*, 3005*m*, 2930*s*, 2900*s*, 2875*s*, 1950*w*, 1810*w*, 1680*s*, 1660*m*, 1630*w*, 1590*w*, 1500*m*, 1460*s*, 1355*s*, 1275*w*, 1250*w*, 1160*s*, 1100*s*, 1070*s*, 1040*s*, 1030*s*, 1000*m*, 920*m*, 860*w*, 840*w*, 700*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, H,H COSY; (*E*)/(*Z*) 2:1): (*E*)-**12**: 7.45–7.25 (*m*, 15 arom. H); 6.17 (br. *dq*, *J* = 12.4, 1.5, H–C(1')); 5.21 (*dq*, *J* = 12.4, 6.9, H–C(2')); 5.01 (*d*, *J* = 3.5, H–C(1)); 4.97–4.51 (*m*, 3 PhC*H*$_2$); 3.98 (*t*, *J* ≈ 10.3, H–C(3)); 3.89–3.85 (*m*, H–C(5)); 3.73–3.67 (*m*, 2 H–C(6)); 3.47 (*dd*, *J* = 9.4, 3.5, H–C(2)); 2.88 (*t*, *J* = 10.7, H–C(4)); 1.56 (*dd*, *J* = 6.9, 1.5, 3 H–C(3')); 0.12 (*s*, Me$_3$Si); (*Z*)-**12**: 6.05 (*dq*, *J* = 6.2, 1.7, H–C(1')); 4.98 (*d*, *J* = 3.6, H–C(1)); 4.65–4.59 (*m*, H–C(2')); 4.00 (*t*, *J* = 10.3, H–C(3)); 3.48 (*dd*, *J* = 9.4, 3.4, H–C(2)); 2.89 (*t*, *J* = 10.7, H–C(4)); 1.69 (*dd*, *J* = 6.8, 1.7, 3 H–C(3')); 0.13 (*s*, Me$_3$Si). ^{13}C-NMR (125 MHz, $CDCl_3$; (*E*)/(*Z*) 2:1): (*E*)-**12**: 143.04 (*d*, C(1')); 138.65 (*s*); 138.16 (*s*); 138.11 (*s*); 128.43–127.38 (several *d*); 104.76 (*d*, C(2')); 103.56 (*s*, C(1")); 97.11 (*d*, C(1)); 88.28 (*s*, C(2")); 79.45 (*d*, C(2)); 78.98 (*d*, C(3)); 76.04 (*t*, PhC*H*$_2$); 73.56 (*t*, PhC*H*$_2$); 73.24 (*t*, PhC*H*$_2$); 70.74 (*d*, C(5)); 69.69 (*t*, C(6)); 37.94 (*d*, C(4)); 12.50 (*q*, C(3')); –0.06 (*q*, Me$_3$Si); (*Z*)-**12**: 142.18 (*d*, C(1')); 138.65 (*s*); 138.30 (*s*); 138.09 (*s*); 128.43–127.38 (several *d*); 104.73 (*d*, C(2')); 103.60 (*s*, C(1")); 97.88 (*d*, C(1)); 88.30 (*s*, C(2")); 79.40 (*d*, C(2)); 79.24 (*d*, C(3)); 75.96 (*t*, PhC*H*$_2$); 73.55 (*t*, PhC*H*$_2$); 73.15 (*t*, PhC*H*$_2$); 71.03 (*d*, C(5)); 69.65 (*t*, C(6)); 37.96 (*d*, C(4)); 12.50 (*q*, C(3')); –0.06 (*q*, Me$_3$Si). FAB-MS: 569 (3, [*M* – 1]$^+$), 513 (2, [*M* – C_3H_5O]$^+$), 405 (13), 182 (11), 181 (40), 179 (11), 147 (11), 136 (13), 107 (13), 105 (13), 103 (12), 91 (100, Bn$^+$), 75 (10), 73 (40, Me$_3$Si$^+$). Anal. calc. for $C_{35}H_{42}O_5Si$ (570.80): C 73.65, H 7.42; found: C 73.71, H 7.61.

*2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glucopyranose* (**13**). a) At r.t., HgO (183 mg, 0.843 mmol) and $HgCl_2$ (331 mg, 1.22 mmol) were added to a soln. of **12** (633 mg, 1.11 mmol) in acetone/H_2O 10:1 (11 ml). The suspension was stirred for 1 h. More $HgCl_2$ (50 mg) was added to the colorless suspension, and the mixture was stirred for further 2 h. Evaporation, dilution of the residue with Et_2O, washing with sat. aq. KI soln. and H_2O (2 ×), usual workup, and FC (hexane/AcOEt 7:3) gave **13** (138 mg, 24%) as a syrup.

b) A stirred mixture of **11** (178 mg, 0.312 mmol) and [Pd(PPh$_3$)$_4$] (180 mg, 0.156 mmol) in degassed AcOH (3 ml) was heated to 80° under Ar. After 1.5 h, AcOH was removed by azeotropic evaporation with benzene. FC (hexane/AcOEt 9:1→ 82:18) gave **13** (130.4 mg, 79%). Solid. R_f (hexane/AcOEt 7:3) 0.23. IR ($CHCl_3$): 3591*m*, 3399*m* (br.), 3090*w*, 3067*m*, 3042*m*, 3007*s*, 2959*m*, 2903*m*, 2870*m*, 2360*w*, 2340*w*, 2173*m*, 1951*w*, 1877*w*, 1811*w*, 1606*w*, 1497*m*, 1454*s*, 1406*m*, 1356*m*, 1252*s*, 1086*s*, 1028*s*, 912*m*, 845*s*, 657*m*, 612*w*, 558*w*. ^{1}H-NMR (400 MHz, $CDCl_3$, H,H COSY; *α*-*D*/*β*-*D* 2:1): *α*-*D*-**13**: 7.44–7.25 (*m*, 15 arom. H); 5.24 (br. *t*, *J* ≈ 3.0, H–C(1)); 5.00–4.54 (*m*, 3 PhC*H*$_2$); 4.13 (*ddd*, *J* = 10.8, 4.8, 2.0, H–C(5)); 3.95 (*dd*, *J* = 10.4, 9.4, H–C(3)); 3.73 (*dd*, *J* = 10.6, 2.1, H–C(6)); 3.67 (*dd*, *J* = 10.6, 5.0, H–C(6)); 3.44 (*dd*, *J* = 9.3, 3.4, H–C(2)); 3.13 (*d*, *J* = 2.2, OH); 2.78 (*t*, *J* = 10.6, H–C(4)); 0.12 (*s*, Me$_3$Si); *β*-*D*-**13**: 4.69 (*dd*, *J* = 7.6, 5.4, H–C(1)); 3.85 (br. *d*, *J* ≈ 9.9, H–C(6)); 3.66–3.62 (*m*, H–C(6)); 3.60 (*dd*, *J* = 10.4, 9.0, H–C(3)); 3.60 (*ddd*, *J* = 10.4, 6.4, 1.4, H–C(5)); 3.56 (*d*, *J* = 5.4, OH); 3.25 (*dd*, *J* = 9.0, 7.8, H–C(2)); 2.70 (*t*, *J* ≈ 10.3, H–C(4)); 0.11 (*s*, Me$_3$Si). ^{13}C-NMR (100 MHz, $CDCl_3$, *α*-*D*/*β*-*D* 2:1): *α*-*D*-**13**: 138.51 (*s*); 138.00 (*s*); 137.98 (*s*); 128.48–127.62 (several *d*); 103.54 (*s*, C(1')); 91.91 (*d*, C(1)); 88.45 (*s*, C(2')); 79.47 (*d*, C(2)); 79.11 (*d*, C(3)); 75.88 (*t*, PhC*H*$_2$); 73.60 (*t*, PhC*H*$_2$); 73.34 (*t*, PhC*H*$_2$); 70.44 (*d*, C(5)); 70.00 (*t*, C(6)); 38.10 (*d*, C(4)); –0.09 (*q*, Me$_3$Si); *β*-*D*-**13**: 138.42 (*s*); 138.35 (*s*); 137.88 (*s*); 128.48–127.62 (several *d*); 103.27 (*s*, C(1')); 97.54 (*d*, C(1)); 88.95 (*s*, C(2')); 82.93 (*d*, C(2)); 82.56 (*d*, C(3)); 74.91 (*t*, PhC*H*$_2$); 74.76 (*d*, C(5)); 73.63 (*t*, PhC*H*$_2$); 73.60 (*t*, PhC*H*$_2$); 70.35 (*t*, C(6)); 38.32 (*d*, C(4)); –0.14 (*q*, Me$_3$Si). FAB-MS: 529 (15, [*M* – 1]$^+$), 513 (6, [*M* – OH]$^+$), 405 (28), 181 (60), 154 (29), 136 (35), 107 (35), 104 (26), 91 (100), 77 (25), 73 (68).

*2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glucono-1,5-lactone* (**14**). At –68°, a soln. of freshly distilled oxalyl chloride (29 µl, 0.34 mmol) in dry CH_2Cl_2 (1 ml) was treated with dry DMSO (48 µl, 0.68 mmol), stirred for 5 min, treated dropwise with a soln. of **13** (90 mg, 0.17 mmol) in CH_2Cl_2 (1.5 ml), and stirred at –68 to –55° for 40 min. After the addition of Et_3N (0.38 ml, 2.71 mmol), the suspension was stirred at –55 to –45° for 40 min, warmed to *ca.* 0° within 3 min, and neutralized (pH 7) with sat. aq. NH_4Cl soln. Usual workup

gave crude **14** as an oil (90 mg) which was used for the next step. A sample was purified by FC (hexane/AcOEt 9:1). Oil. R_f (hexane/AcOEt 7:3) 0.58. $[\alpha]_D^{20}$ = +48.1 (*c* = 1.11, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3067*m*, 3042*m*, 3008*m*, 2961*m*, 2902*m*, 2870*m*, 2178*m*, 1952*w*, 1753*s*, 1587*w*, 1497*m*, 1454*s*, 1396*w*, 1353*m*, 1252*s*, 1177*m*, 1094*s*, 1028*s*, 911*m*, 846*s*, 644*w*, 607*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.26 (*m*, 15 arom. H); 4.98 (*d*, *J* = 11.3, PhC*H*); 4.78 (*d*, *J* = 11.3, PhC*H*); 4.74 (*d*, *J* = 11.3, PhC*H*); 4.66 (*d*, *J* = 11.3, PhC*H*); 4.63 (*d*, *J* = 12.0, PhC*H*); 4.58 (*d*, *J* = 12.1, PhC*H*); 4.49 (*ddd*, *J* = 10.7, 3.5, 2.2, H–C(5)); 4.02 (*d*, *J* = 6.6, H–C(2)); 3.93 (*dd*, *J* = 8.7, 6.7, H–C(3)); 3.83 (*dd*, *J* = 11.1, 2.2, H–C(6)); 3.79 (*dd*, *J* = 11.1, 3.6, H–C(6)); 3.19 (*dd*, *J* = 10.7, 8.7, H–C(4)); 0.14 (*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 169.24 (*s*, C(1)); 137.71 (*s*); 137.43 (*s*); 136.93 (*s*); 128.48–127.69 (several *d*); 101.55 (*s*, C(1')); 89.81 (*s*, C(2')); 79.67 (*d*, C(2)); 78.49 (*d*, C(3)); 78.11 (*d*, C(5)); 74.03 (*t*, PhCH_2); 73.99 (*t*, PhCH_2); 73.76 (*t*, PhCH_2); 69.14 (*t*, C(6)); 35.76 (*d*, C(4)); –0.17 (*s*, Me_3Si). FAB-MS: 530 (10, $[M-1]^+$), 529 (23), 528 (15), 527 (32), 182 (25), 181 (63), 154 (28), 137 (35), 136 (33), 107 (32), 91 (100), 73 (53).

*4,5,8-Tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-(trimethylsilyl)-6-*C*-[2-(trimethylsilyl)ethynyl]-*D*-gluco-oct-3-ulopyranose* (**15**). $CeCl_3 \cdot 7\ H_2O$ was stirred under vacuum (0.5 Torr) for 1 h at 120° and for 1 h at 140° to give a powder (63.5 mg, *ca.* 0.258 mmol) which was cooled to 0° and treated with cold THF (0.5 ml). The suspension was stirred at r.t. for 2 h, cooled to –78°, and treated with 0.45M $Me_3SiC{\equiv}CLi$ (0.69 ml, 0.31 mmol) in THF/hexane [47]. The acetylide was freshly prepared by addition of 1.40M BuLi in hexane (1.00 ml, 1.40 mmol) to a cold (–76°) soln. of $Me_3SiC{\equiv}CH$ (0.22 ml, 1.58 mmol) in THF (2 ml) at –76° and by stirring at –76° for 40 min. The yellow suspension was stirred for 0.5 h at –78°, treated with **14** (68 mg, 0.13 mmol), and stirred at –76 to –45° for 1.5 h. Usual workup of the resulting blue soln. and FC (hexane/AcOEt 92:8) afforded **15** (71 mg, 88 %). Syrup. R_f (hexane/AcOEt 7:3) 0.49–0.61. IR ($CHCl_3$): 3573*m* (br.), 3090*m*, 3067*m*, 3042*m*, 3007*s*, 2961*s*, 2902*m*, 2869*m*, 2360*w*, 2173*m*, 1606*w*, 1497*m*, 1454*m*, 1398*m*, 1356*m*, 1253*s*, 1061*s*, 1028*s*, 911*m*, 846*s*, 628*m*. FAB-MS: 625 (1, $[M-1]^+$), 609 (2, $[M-OH]^+$), 181 (36), 92 (51), 91 (100), 75 (34), 73 (89).

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-(trimethylsilyl)-6-*C*-[2-(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-oct-1-itol* (**16**). At –10°, a soln. of **15** (34 mg, 0.054 mmol) in CH_2Cl_2/MeCN 3:7 (1 ml) was treated with a soln. of Et_3SiH in CH_2Cl_2/MeCN (0.18 ml, 0.22 mmol; taken from a soln. of 0.35 ml of Et_3SiH in 1.5 ml of MeCN/CH_2Cl_2 2:1). A soln. of $BF_3 \cdot Et_2O$ in MeCN (0.12 ml, 0.11 mmol, taken from a soln. of 0.14 ml of $BF_3 \cdot Et_2O$ in 1 ml of MeCN) was slowly added. The mixture was stirred for 1 h at –10 to 0°. Usual workup and FC (hexane/AcOEt 95:5) gave **16** (22 mg, 67%). Oil. R_f (hexane/AcOEt 7:3) 0.65. $[\alpha]_D^{20}$ = –36.9 (*c* = 1.71, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3066*w*, 3042*w*, 3007*s*, 2961*s*, 2902*m*, 2871*m*, 2176*m*, 1497*w*, 1454*m*, 1398*w*, 1358*m*, 1294*m*, 1252*s*, 1075*s*, 1028*s*, 912*w*, 846*vs*, 619*w*, 564*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.41–7.25 (*m*, 15 arom. H); 4.98 (*d*, *J* = 10.2, PhC*H*); 4.95 (*d*, *J* = 10.2, PhC*H*); 4.83 (*d*, *J* = 10.6, PhC*H*); 4.79 (*d*, *J* = 10.5, PhC*H*); 4.62 (*s*, PhCH_2); 4.05 (*d*, *J* = 9.6, H–C(3)); 3.85 (*dd*, *J* = 10.9, 1.8, H–C(8)); 3.68 (*dd*, *J* = 10.9, 5.4, H–C(8)); 3.56 (*dd*, *J* = 10.3, 8.8, H–C(5)); 3.55–3.49 (*m*, H–C(7)); 3.46 (*dd*, *J* = 9.4, 9.0, H–C(4)); 2.79 (*t*, *J* = 10.4, H–C(6)); 0.17 (*s*, Me_3Si–C(1)); 0.10 (*s*, Me_3Si–C(2')). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.38 (*d*); 138.16 (*d*); 138.12 (*d*); 128.36–127.62 (several *d*); 103.37 (*s*, C(1')); 102.38 (*s*, C(1)); 91.16 (*s*, C(2')); 88.78 (*s*, C(2)); 83.64 (*d*, C(5)); 81.85 (*d*, C(4)); 79.13 (*d*, C(7)); 75.85 (*t*, PhCH_2); 75.54 (*t*, PhCH_2); 73.64 (*t*, PhCH_2); 70.51 (*d*, C(3)); 70.22 (*t*, C(8)); 38.36 (*d*, C(6)); –0.12 (*q*, Me_3Si–C(1)); –0.29 (*q*, Me_3Si–C(2')). FAB-MS: 611 (6, $[M+1]^+$), 609 (5, $[M-1]^+$), 181 (23), 136 (24), 92 (47), 91 (100), 73 (79). Anal. calc. for $C_{37}H_{46}O_4Si_2$ (610.95): C 72.74, H 7.59; found: C 72.57, H 7.76.

*(E)-Prop-1-enyl 2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-(2,2-dibromoethenyl)-α-*D*-glucopyranoside* (**17**). The Ir catalyst [46] (14.2 mg, 0.0168 mmol) was dissolved as described for **12** and injected into a stirred soln. of **10** (276 mg, 0.419 mmol) in THF (3 ml). Stirring for 1.5 h, evaporation, and FC (hexane/AcOEt 96:4) gave **17** (252.5 mg, 91%). Colorless oil. R_f (CH_2Cl_2) 0.60. $[\alpha]_D^{20}$ = +6.3 (*c* = 1.28, $CHCl_3$). IR ($CHCl_3$): 3060*w*, 3015*w*, 3005*m*, 2930*s*, 2900*s*, 2875*s*, 1950*w*, 1810*w*, 1680*s*, 1660*m*, 1630*w*, 1590*w*, 1500*m*, 1460*s*, 1355*s*, 1275*w*, 1250*w*, 1160*s*, 1100*s*, 1070*s*, 1040*s*, 1030*s*, 1000*m*, 920*m*, 869*w*, 840*w*, 700*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.26 (*m*, 15 arom. H); 6.16 (br. *dq*, *J* = 12.4, 1.7, H–C(1')); 6.12 (*d*, *J* = 10.1, H–C(1")); 5.19 (*dq*, *J* = 12.3, 6.8, H–C(2')); 5.01 (*d*, *J* = 3.5, H–C(1)); 4.85 (*d*, *J* = 10.9, PhC*H*); 4.80 (*d*, *J* = 12.0, PhC*H*); 4.67 (*d*, *J* = 10.9, PhC*H*); 4.65 (*d*, *J* = 12.0, PhC*H*); 4.54 (*s*, PhCH_2); 3.82–3.76 (*m*, H–C(3), H–C(5)); 3.61 (*dd*, *J* = 9.3, 3.5, H–C(2)); 3.53 (*dd*, *J* = 10.8, 2.5, H–C(6)); 3.43 (*dd*, *J* = 11.0, 4.6, H–C(6)); 2.94 (*q*, *J* = 10.3, H–C(4)); 1.56 (*dd*, *J* = 6.8, 1.7, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 142.92 (*d*, C(1')); 138.15 (*s*); 138.00 (*s*); 137.77 (*s*); 135.14 (*d*, C(1")); 128.34–127.46 (several *d*); 104.66 (*d*, C(2')); 96.81 (*d*, C(1)); 93.01 (*s*, C(2")); 79.69 (*d*, C(2)); 77.70 (*d*, C(3)); 75.29 (*t*, PhCH_2); 73.38 (*t*, PhCH_2); 73.13 (*t*, PhCH_2); 70.08 (*t*, C(6)); 69.47 (*d*, C(5)); 48.80 (*d*, C(4)); 12.40 (*q*, C(3')). CI-MS: 676 (100), 678 (56), 674 (49, $[M+NH_4]^+$). Anal. calc. for $C_{32}H_{34}Br_2O_5$ (658.42): C 58.37, H 5.21, Br 24.27; found: C 58.61, H 5.49, Br 24.00.

*2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-(2,2-dibromoethenyl)-*D*-glucopyranose* (**18**). At r.t., HgO (70 mg, 0.324 mmol) and $HgCl_2$ (128 mg, 0.471 mmol) were added to a soln. of **17** (281 mg, 0.427 mmol) in acetone/H_2O 10:1 (4 ml). The suspension was stirred at r.t. for 1 h, and filtered. The filtrate was diluted with Et_2O, washed with sat. aq. KI soln. and twice with H_2O, and processed as usual. FC (hexane/AcOEt 7:3) afforded **18** (224 mg, 85%). Oil. R_f (hexane/AcOEt 7:3) 0.26. IR ($CHCl_3$): 3592*m*, 3416*m* (br.), 3089*w*, 3066*m*, 3042*m*, 3007*s*, 2870*m*, 2360*w*, 2339*w*, 1952*w*, 1877*w*, 1811*w*, 1732*m*, 1629*w*, 1587*w*, 1496*m*, 1454*s*, 1358*m*, 1310*m*, 1253*m*, 1070*s*, 1028*s*, 912*m*, 844*w*, 607*w*, 559*w*. ^{1}H-NMR (500 MHz, H,H COSY, $CDCl_3$, α-D/β-D 7:3): α-D-**18**: 7.40–7.27 (*m*, 15 arom. H); 6.09 (*d*, *J* = 10.1, H–C(1')); 5.25 (*d*, *J* = 3.5, H–C(1)); 4.82–4.51 (*m*, 3 PhC*H*$_2$); 4.02 (*ddd*, *J* = 10.7, 5.4, 2.5, H–C(5)); 3.77 (*dd*, *J* = 10.0, 9.3, H–C(3)); 3.60 (*dd*, *J* = 9.2, 3.5, H–C(2)); 3.52 (*dd*, *J* = 10.7, 2.6, H–C(6)); 3.46 (*dd*, *J* = 10.6, 5.5, H–C(6)); 3.12 (br. *s*, OH); 2.87 (*t*, *J* = 10.4, H–C(4)); β-D-**18**: 6.01 (*d*, *J* = 10.1, H–C(1')); 4.98 (*d*, *J* = 11.0, PhC*H*); 3.45–3.38 (*m*, H–C(2), H–C(3)); 3.12 (br. *s*, OH); 2.83 (*t*, *J* = 10.3, H–C(4)). ^{13}C-NMR (50 MHz, $CDCl_3$, α-D/β-D 7:3): α-D-**18**: 138.11 (*s*); 137.93 (*s*); 137.75 (*s*); 135.30 (*d*, C(1')); 128.53–127.70 (several *d*); 93.06 (*s*, C(2')); 91.67 (*d*, C(1)); 80.26 (*d*, C(2)); 77.42 (*d*, C(3)); 75.28 (*t*, PhCH$_2$); 73.79 (*d*, C(5)); 73.65 (*t*, PhCH$_2$); 73.32 (*t*, PhCH$_2$); 70.47 (*t*, C(6)); 49.04 (*d*, C(4)); β-D-**18**: 138.35 (*s*); 137.90 (*s*); 137.65 (*s*); 135.12 (*d*, C(1')); 97.51 (*d*, C(1)); 93.43 (*s*, C(2')); 83.58 (*d*, C(2)); 80.72 (*d*, C(3)); 75.14 (*t*, PhCH$_2$); 74.96 (*t*, PhCH$_2$); 73.75 (*t*, PhCH$_2$); 70.74 (*t*, C(6)); 69.29 (*d*, C(5)); 49.29 (*d*, C(4)). FAB-MS: 643 (12), 642 (8), 641(21), 639 (11, [*M* + Na]$^+$), 617 (7, [*M* + 1]$^+$), 271 (35), 182 (42), 181 (62), 179 (28), 154 (42), 137 (36), 134 (42), 107 (48), 105 (30), 92 (70), 91 (100). Anal. calc. for $C_{29}H_{30}Br_2O_5$ (618.36): C 56.33, H 4.89; found: C 56.10, H 5.11.

*2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-(2,2-dibromoethenyl)-*D*-glucono-1,5-lactone* (**19**). At –65°, a soln. of freshly distilled oxalyl chloride (53 µl, 0.62 mmol) in dry CH_2Cl_2 (2 ml) was treated with dry DMSO (88 µl, 1.24 mmol), stirred for 5 min, and treated dropwise with a soln. of **18** (191 mg, 0.309 mmol) in CH_2Cl_2 (3 ml). The soln. was stirred for 10 min at –65° and for 20 min at –40°, cooled to –76°, treated with Et_3N (0.68 ml, 4.95 mmol), warmed to 0° within *ca.* 20 min, and neutralized with sat. aq. NH_4Cl soln. untill pH *ca.* 7. Usual workup gave crude **19** as an oil (195 mg) which was used for the next step. A sample was purified by FC (hexane/AcOEt 8:2). Oil. R_f (hexane/AcOEt 7:3) 0.46. $[\alpha]_D^{20}$ = +67.9 (*c* = 0.72, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3067*w*, 3042*m*, 3008*m*, 2869*m*, 2359*w*, 2338*w*, 1952*w*, 1877*w*, 1753*s*, 1628*w*, 1588*w*, 1497*m*, 1454*s*, 1359*s*, 1299*m*, 1261*s*, 1177*m*, 1110*s*, 1028*s*, 912*w*, 865*w*, 823*w*, 609*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.37–7.24 (*m*, 15 arom. H); 6.10 (*d*, *J* = 10.1, H–C(1')); 4.95 (*d*, *J* = 11.2, PhC*H*); 4.66 (*d*, *J* = 11.8, PhC*H*); 4.63 (*d*, *J* = 11.2, PhC*H*); 4.59 (*d*, *J* = 11.9, PhC*H*); 4.56 (*d*, *J* = 11.8, 2 PhC*H*); 4.40 (*ddd*, *J* = 10.1, 4.2, 2.8, H–C(5)); 4.13 (*d*, *J* = 6.2, H–C(2)); 3.70 (*dd*, *J* = 7.0, 6.2, H–C(3)); 3.66 (*dd*, *J* = 11.1, 2.8, H–C(6)); 3.55 (*dd*, *J* = 11.0, 4.2, H–C(6)); 3.21 (*td*, *J* = 10.1, 7.1, H–C(4)). ^{13}C-NMR (125 MHz, $CDCl_3$): 168.92 (*s*, C(1)); 137.52 (*s*); 137.12 (*s*); 136.74 (*s*); 134.77 (*d*, C(1')); 128.57–127.82 (several *d*); 94.01 (*s*, C(2')); 78.18 (*d*, C(2)); 77.59 (*d*, C(3)); 77.26 (*d*, C(5)); 73.92 (*t*, PhCH$_2$); 73.71 (*t*, PhCH$_2$); 73.07 (*t*, PhCH$_2$); 69.81 (*t*, C(6)); 46.01 (*d*, C(4)). FAB-MS: 619 (1), 618 (1), 617 (4), 616 (2), 615 (5), 614 (1), 613 (2, [*M* – 1]$^+$), 147 (20), 136 (20), 91 (100), 73 (60). Anal. calc. for $C_{29}H_{28}Br_2O_5$ (616.35): C 56.51, H 4.58; found: C 56.26, H 4.71.

*4,5,8-Tri-*O*-benzyl-6-*C*-(2,2-dibromoethenyl)-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-(trimethylsilyl)-*D*-gluco-oct-3-ulopyranose* (**20**). As described for **15**, with $CeCl_3 \cdot 7H_2O$ (→ powder (49 mg, *ca.* 0.20 mmol)), cold THF (0.5 ml), 0.45M $Me_3SiC{\equiv}CLi$ (0.54 ml, 0.24 mmol), and **19** (62 mg, 0.10 mmol): **20** (65 mg, 90%). Syrup. R_f (hexane/AcOEt 7:3) 0.54. IR ($CHCl_3$): 3670*w*, 3570*m*, 3299*m*, 3089*m*, 3066*m*, 3042*m*, 3007*s*, 2959*s*, 2902*s*, 2870*s*, 2383*w*, 1630*m*, 1587*w*, 1497*s*, 1454*s*, 1357*s*, 1304*m*, 1266*s*, 1253*s*, 1124*s*, 1070*s*, 1028*s*, 989*m*, 940*m*, 910*m*, 862*s*, 847*s*, 632*m*, 612*m*, 572*w*, 553*w*. ^{1}H-NMR (500 MHz, $CDCl_3$, C,H COSY, α-D/β-D 73:27): α-D-**20**: 7.43–7.26 (*m*, 15 arom. H); 6.05 (*d*, *J* = 10.1, H–C(1')); 5.06–4.53 (*m*, 3 PhC*H*$_2$); 3.98 (*ddd*, *J* = 10.8, 4.9, 3.0, H–C(7)); 3.72 (*d*, *J* = 9.1, H–C(4)); 3.63 (*dd*, *J* = 10.2, 9.1, H–C(5)); 3.58–3.49 (*m*, 2 H–C(8)); 3.33 (br. *s*, OH); 2.91 (*q*, *J* = 10.3, H–C(6)); 0.185 (*s*, Me_3Si); β-D-**20**: 5.91 (*d*, *J* = 10.1, H–C(1')); 3.84 (*ddd*, *J* = 10.6, 5.1, 2.9, H–C(7)); 2.84 (*q*, *J* = 10.3, H–C(6)); 0.23 (*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$, α-D/β-D 73:27): α-D-**20**: 137.96 (*s*); 137.89 (*s*); 134.95 (*d*, C(1')); 129.00–127.39 (several *d*); 103.68 (*s*, C(2)); 95.40 (*s*, C(3)); 93.14 (*s*, C(2')); 91.65 (*s*, C(1)); 84.30 (*d*, C(4)); 78.27 (*d*, C(5)); 76.10 (*t*, PhCH$_2$); 75.36 (*t*, PhCH$_2$); 73.55 (*t*, PhCH$_2$); 70.91 (*d*, C(7)); 70.39 (*t*, C(8)); 49.43 (*d*, C(6)); –0.43 (*q*, Me_3Si); β-D-**20**: 138.87 (*s*); 137.96 (*s*); 137.89 (*s*); 135.18 (*d*, C(1')); 100.3 (*s*, C(3)); 93.90 (*s*); 93.25 (*s*, C(2), C(2')); 89.24 (*s*, C(1)); 84.65 (*d*, C(4)); 79.05 (*d*, C(5)); 74.97 (*t*, PhCH$_2$); 74.55 (*t*, PhCH$_2$); 73.55 (*t*, PhCH$_2$); 73.36 (*d*, C(7)); 70.47 (*t*, C(8)); 48.87 (*d*, C(6)); –0.23 (*q*, Me_3Si). FAB-MS: 713 (0.3, [*M* – 1]$^+$), 181 (34), 154 (26), 136 (36), 105 (28), 92 (45), 91 (100), 73 (69).

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-(2,2-dibromoethenyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**21**). As described for **16**, with **20** (54 mg, 0.075 mmol), CH_2Cl_2/MeCN

3:7 (1.1 ml), Et_3SiH in CH_2Cl_2/MeCN (0.20 ml, 0.15 mmol; from 0.24 ml of Et_3SiH in 1.8 ml of MeCN/CH_2Cl_2 2:1), and $BF_3 \cdot Et_2O$ in MeCN (0.11 ml, 0.096 mmol; from 0.12 ml of $BF_3 \cdot Et_2O$ in 1 ml of MeCN; 40 min): **21** (46.9 mg, 89%). Oil. R_f (hexane/AcOEt 7:3) 0.57. $[\alpha]_D^{20} = +9.6$ ($c = 1.44$, $CHCl_3$). IR ($CHCl_3$): 3066*w*, 3007*m*, 2960*m*, 2903*m*, 2868*m*, 2180*w*, 1630*w*, 1497*w*, 1454*m*, 1357*m*, 1291*m*, 1253*s*, 1071*s*, 1028*s*, 912*w*, 847*s*, 633*w*, 601*w*, 555*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.39–7.26 (*m*, 15 arom. H); 5.94 (*d*, $J = 10.2$, H–C(1')); 5.03 (*d*, $J = 10.3$, PhC*H*); 4.79 (*d*, $J = 10.3$, PhC*H*); 4.76 (*d*, $J = 11.0$, PhC*H*); 4.63 (*d*, $J = 11.0$, PhC*H*); 4.56 (*s*, PhCH_2); 4.02 (*d*, $J = 9.7$, H–C(3)); 3.61 (*dd*, $J = 9.7$, 8.8, H–C(4)); 3.55 (*dd*, $J = 10.8$, 3.1, H–C(8)); 3.51 (*dd*, $J = 10.8$, 5.1, H–C(8)); 3.40 (*ddd*, $J = 10.4$, 5.1, 3.1, H–C(7)); 3.33 (*dd*, $J = 10.2$, 8.8, H–C(5)); 2.85 (*q*, $J = 10.2$, H–C(6)); 0.18 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.04 (*s*); 137.89 (*s*); 137.81 (*s*); 134.98 (*s*, C(1')); 128.43–127.67 (several *d*); 102.33 (*s*, C(2)); 93.22 (*s*, C(2')); 91.30 (*s*, C(1)); 82.51 (*d*, C(5)); 81.85 (*d*, C(4)); 78.06 (*d*, C(7)); 75.54 (*t*, PhCH_2); 75.21 (*t*, PhCH_2); 73.68 (*t*, PhCH_2); 70.76 (*t*, C(8)); 70.44 (*d*, C(3)); 49.68 (*d*, C(6)); –0.29 (*s*, Me_3Si). FAB-MS: 699 (7), 697 (6), 695 (3, $[M-1]^+$), 181 (46), 154 (23), 136 (30), 107 (25), 92 (60), 91 (100), 73 (64). Anal. calc. for $C_{34}H_{38}Br_2O_4Si$ (698.57): C 58.46, H 5.48, Br 22.88; found: C 58.42, H 5.62, Br 22.60.

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-ethynyl-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**22**). At –76°, 1.6M BuLi in hexane (54 µl, 0.086 mmol) was added dropwise to a well stirred soln. of **21** (30 mg, 0.043 mmol) in THF (1 ml). The yellow soln. was stirred at –76° for 3 h and at –20° for 1 h, cooled to –76°, treated with 1N HCl/EtOH (0.1 ml), stirred at –76° for 10 min, warmed to r.t., and worked up as usual. FC (hexane/AcOEt 95:5) afforded **22** (9.3 mg, 40%). Colorless oil. R_f (benzene) 0.30. $[\alpha]_D^{20} = -12.6$ ($c = 0.325$, $CHCl_3$). IR ($CHCl_3$): 3307*m*, 3067*m*, 3007*s*, 2927*s*, 2870*m*, 2181*w*, 1723*w*, 1604*w*, 1497*m*, 1454*s*, 1358*m*, 1294*m*, 1252*s*, 1131*s*, 1075*s*, 1028*m*, 985*w*, 913*w*, 847*s*, 649*m*, 567*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.41–7.25 (*m*, 15 arom. H); 5.00 (*d*, $J = 10.3$, PhC*H*); 4.94 (*d*, $J = 10.6$, PhC*H*); 4.87 (*d*, $J = 10.4$, PhC*H*); 4.85 (*d*, $J = 10.6$, PhC*H*); 4.64 (*d*, $J = 12.3$, PhC*H*); 4.58 (*d*, $J = 12.4$, PhC*H*); 4.04 (*d*, $J = 9.3$, H–C(3)); 3.84 (*dd*, $J = 10.9$, 1.7, H–C(8)); 3.72 (*dd*, $J = 10.9$, 5.0, H–C(8)); 3.57 (*dd*, $J = 10.1$, 9.0, H–C(5)); 3.57–3.49 (*m*, H–C(7)); 3.49 (*t*, $J = 9.2$, H–C(4)); 2.80 (*td*, $J = 10.2$, 2.3, H–C(6)); 2.11 (*d*, $J = 2.3$, H–C(2')); 0.09 (*s*, Me_3Si–C(1)). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.66 (br. *s*); 138.43 (*s*); 128.73–127.94 (several *d*); 102.60 (*s*, C(2)); 91.56 (*s*, C(1)); 83.65 (*d*, C(5)); 82.19 (*d*, C(2')); 81.54 (*d*, C(4)); 79.33 (*d*, C(7)); 75.83 (*t*, PhCH_2); 75.53 (*t*, PhCH_2); 73.86 (*t*, PhCH_2); 72.37 (*s*, C(1')); 70.77 (*d*, C(3)); 70.32 (*t*, C(8)); 37.28 (*d*, C(6)); –0.13 (*q*, Me_3Si–C(1)). FAB-MS: 537 (2, $[M-1]^+$), 147 (22), 137 (20), 136 (27), 107 (24), 105 (20), 95 (25), 92 (26), 91 (100), 83 (25), 81 (34), 77 (22), 73 (80), 71 (23), 69 (59), 67 (27), 57 (48), 55 (60).

*1,6:3,4-Dianhydro-2-*O*-(methoxymethyl)-β-*D*-galactopyranose* (**24**). A mixture of **23** (19.0 g, 0.1319 mol), CH_2Cl_2 (25 ml), (i-Pr)$_2$EtN (67.76 ml, 0.393 mol), and $MeOCH_2Cl$ (25 ml, 0.393 mol) was stirred for 1 h at 0° and then for 3 days at r.t. Evaporation and FC (AcOEt/hexane 3:10) of the residue gave **24** (24.42 g, 97%) as an oil which crystallized under high vacuum after 1 h. R_f (AcOEt/hexane 1:2) 0.24. M.p. 53° (AcOEt/hexane). $[\alpha]_D^{25} = -36.4$ ($c = 1.76$, $CHCl_3$). IR ($CHCl_3$): 3000*m*, 2960*m*, 2900*m*, 2830*w*, 2780*w*, 1470*w*, 1450*w*, 1430*w*, 1400*w*, 1380*w*, 1350*w*, 1300*w*, 1280*w*, 1240*m*, 1160*s*, 1140*s*, 1130*s*, 1110*s*, 1070*m*, 1050*s*, 1030*s*, 1000*s*, 930*s*, 870*s*, 830*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.30 (*s*, H–C(1)); 4.85 (*t*, $J = 4.9$, H–C(5)); 4.77 (*d*, $J = 6.9$, 1 H, MeOCH_2); 4.76 (*d*, $J = 6.9$, 1 H, MeOCH_2); 3.99 (*d*, $J = 6.6$, H_{endo}–C(6)); 3.73 (br. *s*, H–C(2)); 3.63 (*t*, $J \approx 4.5$, H–C(4)); 3.53 (*dd*, $J = 6.5$, 4.8, H_{exo}–C(6)); 3.43 (*s*, MeO); 3.16 (*dd*, $J = 4.1$, 1.6, H-C(3)). ^{13}C-NMR (50 MHz, $CDCl_3$): 99.47 (*d*); 96.84 (*t*); 71.73 (*d*); 71.25 (*d*); 64.61 (*t*); 55.74 (*q*); 52.78 (*d*); 48.57 (*d*). CI-MS: 206 (100, $[M + NH_4]^+$), 189 (8, $[M + H]^+$), 157 (11), 98 (14). Anal. calc. for $C_8H_{12}O_5$ (188.17): C 51.06, H 6.42; found: C 51.10, H 6.58.

*1,6-Anhydro-4-deoxy-2-*O*-(methoxymethyl)-4-*C*-[2-(trimethylsilyl)ethynyl]-β-*D*-glucopyranose* (**27**) *and 1,6-Anhydro-3-*O*-methyl-2-*O*-[3-(trimethylsilyl)prop-2-ynyl)]-β-*D*-gulopyranose* (**25**). BuLi (1.2M in hexane; 5.86 ml, 6.4 mmol) was added dropwise to a cold (–78°) soln. of $Me_3SiC{\equiv}CH$ (0.99 ml, 7 mmol) in dry toluene (3 ml). The mixture was warmed to 20°, kept at this temp. for 15 min, treated with THF (0.01 ml) to dissolve the gelatinous precipitate, cooled again to –78°, and treated dropwise with 25% Et_2AlCl in hexane (3.04 ml, 5.8 mmol). The mixture was warmed to 20° and kept for 45 min (→ thick, white precipitate). The temp. was raised to 90°, and **24** (377 mg, 2 mmol) in toluene (3 ml) was added. After 6 h, the mixture was cooled to 0°, treated with sat. aq. NH_4Cl soln. (3 ml), and worked up normally with CH_2Cl_2. FC (AcOEt/CH_2Cl_2 1:9) of the residue gave **27** (397 mg, 69%) and **25** (67 mg, 12%) as oils.

Data of **27**: R_f (AcOEt/toluene 1:1) 0.51. $[\alpha]_D^{25} = -124.8$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3560*w*, 3440*w*, 3000*w*, 2960*m*, 2900*w*, 2180*s*, 1400*w*, 1320*w*, 1300*w*, 1250*w*, 1180*w*, 1150*w*, 1110*m*, 1045*s*, 1010*m*, 980*w*, 960*w*, 910*m*, 890*w*, 850*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.48 (br. *s*, H–C(1)); 4.77 (*d*, $J = 7.0$, 1 H, MeOCH_2); 4.72 (*d*, $J = 7.0$, 1 H, MeOCH_2); 4.64 (*dd*, $J = 4.7$, 1.6, H–C(5)); 3.92 (*d*, $J = 7.4$, H_{endo}–C(6)); 3.84 (br. *s*, irrad. at 3.03 → *t*, $J \approx 4.3$, H–C(3)); 3.68 (*dd*, $J = 7.4$, 4.8, H_{exo}–C(6)); 3.44 (*s*, MeO); 3.38 (*dd*, $J = 4.0$, 0.8, H–C(2)); 3.03

(br. *s*, OH); 2.60 (*dd*, *J* = 4.9, 1.8, H–C(4)); 0.15 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 105.26 (*s*); 102.13 (*d*); 96.92 (*t*); 87.22 (*s*); 79.98 (*d*); 75.48 (*d*); 71.1 (*d*); 68.61 (*t*); 55.80 (*q*); 38.10 (*d*); 0.009 (3*q*). CI-MS: 304 (100, $[M + NH_4]^+$), 287 (9, $[M + H]^+$), 183 (16).

Data of **25**: R_f (AcOEt/toluene 1:1) 0.32. $[\alpha]_D^{25}$ = 6.9 (*c* = 0.7, $CHCl_3$). IR ($CHCl_3$): 3590*m*, 3450*m*, 2960*s*, 2900*s*, 2820*w*, 2170*w*, 1730*w*, 1480*w*, 1440*w*, 1405*w*, 1355*m*, 1340*m*, 1325*m*, 1290*m*, 1250*s*, 1185*m*, 1145*s*, 1120*s*, 1090*s*, 1060*s*, 995*s*, 970*m*, 955*m*, 930*s*, 920*s*, 810*m*, 700*w*, 650*m*, 620*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.57 (*d*, *J* = 2.4, H–C(1)); 4.46 (*t*, *J* ≈ 4.4, H–C(5)); 4.35 (*s*, 2 H–C(1')); 4.07 (*dd*, *J* = 4.5, 2.4; irrad. at 5.57→ *d*, *J* = 4.5, H–C(2)); 4.02 (*d*, *J* = 7.6, H_{endo}–C(6)); 3.99 (br. *dd*, *J* ≈ 9.0, 4.1, H–C(4)); 3.65 (*dd*, *J* = 7.6, 4.8, H_{exo}–C(6)); 3.47 (*s*, MeO); 3.36 (*dd*, *J* = 9.2, 4.5, H–C(3)); 2.36 (br. *s*, OH–C(4)); 0.17 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 101.11 (*s*); 99.83 (*d*); 92.29 (*s*); 79.85(*d*); 74.19 (*d*); 72.26 (*d*); 68.85 (*d*); 63.76 (*t*); 58.51 (*t*); 57.29 (*q*); –0.27 (3*q*). CI-MS: 304 (100, $[M + NH_4]^+$), 256 (31), 203 (17). Anal. calc. for $C_{13}H_{22}O_5Si$ (286.4): C 54.52, H 7.74; found: C 54.63, H 7.51.

*1,6-Anhydro-3-*O*-methyl-2-*O*-(prop-2-ynyl)-β-*D*-gulopyranose* (**26**). A soln. of **25** (23 mg, 0.8 mmol) and 1M NaOH in MeOH (0.1 ml) was stirred at 25° in MeOH (2 ml) for 5 min, neutralized with 1M HCl (0.1 ml), diluted with AcOEt, washed with H_2O, dried ($MgSO_4$), and evaporated: **26** (17 mg, 99%). Oil. R_f (AcOEt/toluene 1:1) 0.16. $[\alpha]_D^{25}$ = +10.00 (*c* = 0.15, $CHCl_3$). IR ($CHCl_3$): 3599*w*, 3307*m*, 2962*m*, 2928*m*, 2856*w*, 2829*w*, 2120*w*, 1722*w*, 1603*w*, 1448*w*, 1404*w*, 1357*w*, 1328*w*, 1261*m*, 1122*s*, 1001*s*, 958*w*, 923*m*, 868*m*, 846*w*, 818*w*, 634*m*, 564*w*, 503*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.57 (*d*, *J* = 2.5, H–C(1)); 4.47 (*t*, *J* = 4.4, H–C(5)); 4.40 (*dd*, *J* = 16.0, 1.9, H–C(1')); 4.35 (*dd*, *J* = 16.0, 2.0, H'–C(1')); 4.06 (*dd*, *J* = 4.5, 2.5, H–C(2)); 4.03 (*d*, *J* ≈ 7.6, H_{endo}–C(6)); 3.99 (br. *dd*, *J* = 9.0, 4.0, H–C(4)); 3.66 (*dd*, *J* = 7.7, 5.0, H_{exo}–C(6)); 3.48 (*s*, MeO); 3.38 (*dd*, *J* = 9.0, 4.3, H–C(3)); 2.49 (*t*, *J* = 2.0, H–C(3')); 2.48 (br. *s*, OH–C(4)). ^{13}C-NMR (50 MHz, $CDCl_3$): 100.02 (*d*); 80.10 (*d*); 80.09 (*d*); 75.25 (*s*); 74.21 (*d*); 72.49 (*d*); 69.10 (*d*); 63.85 (*t*); 57.94 (*t*); 57.60 (*q*). CI-MS: 323 (100, $[M + NH_4]^+$).

*1,6-Anhydro-4-deoxy-4-*C*-[2-(trimethylsilyl)ethynyl]-β-*D*-glucopyranose* (**28**). A soln. of **27** (199 mg, 0.69 mmol) in dry MeOH (10 ml) was treated with *Dowex 50 × 4* resin (H^+; 650 mg), kept at 50° for 3 h, and filtered. The filtrate was evaporated: **28** (161 mg, 95%). White solid. R_f (AcOEt/hexane 1:2) 0.52. M.p. 84.5° (AcOEt/hexane). $[\alpha]_D^{25}$ = –126.8 (*c* = 0.51, $CHCl_3$). IR ($CHCl_3$): 3550*m*, 2960*m*, 2900*w*, 2185*w*, 1475*w*, 1450*w*, 1400*w*, 1360*w*, 1350*w*, 1320*w*, 1300*w*, 1250*m*, 1200*w*, 1180*w*, 1135*m*, 1080*m*, 1045*s*, 1010*m*, 990*w*, 930*w*, 880*m*, 850*s*, 820*w*, 780*w*, 730*s*, 665*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.51 (*s*, H–C(1)); 4.60 (*d*, *J* = 5.0, H–C(5)); 4.16 (*d*, *J* = 7.8, H_{endo}–C(6)); 4.01 (br. *dt*, *J* ≈ 8.4, 0.9, H–C(3)); 3.77 (*dd*, *J* = 7.6, 5.1, H_{exo}–C(6)); 3.54 (br. *d*, *J* = 12.1, H–C(2)); 2.75 (br. *s*, H–C(4)); 2.72 (*d*, *J* = 8.4, OH–C(3)); 2.52 (*d*, *J* = 12.1, OH–C(2)); 0.16 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 104.11 (*s*); 102.26 (*d*); 89.26 (*s*); 75.12 (*d*); 72.54 (*d*); 70.81 (*d*); 67.2 (*t*); 37.17 (*d*); –0.15 (3*q*). CI-MS: 260 (100, $[M + NH_4]^+$). Anal. calc. for $C_{11}H_{18}O_4Si$ (242.34): C 54.51, H 7.48; found: C 54.30, H 7.35.

*1,6-Anhydro-2,3-di-*O*-benzyl-4-deoxy-4-*C*-ethynyl-β-*D*-glucopyranose* (**29**). At 0°, oil-free NaH (86 mg, 3.58 mmol) was added to a soln. of **28** (124 mg, 0.51 mmol) in DMF (5 ml). The mixture was stirred for 30 min, treated dropwise with BnBr (0.3 ml, 2.56 mmol) and Bu_4NI (18 mg, 0.051 mmol), warmed to r.t., and stirred for 2 h. After cooling to 0°, excess NaH was destroyed by addition of MeOH. Normal workup and FC (Et_2O/hexane 1:23) of the residue gave **29** (156 mg, 87%). Oil. R_f (AcOEt/hexane 3.5:10) 0.42. $[\alpha]_D^{25}$ = –132.3 (*c* = 0.63, $CHCl_3$). IR ($CHCl_3$): 3300*w*, 2960w, 2900*w*, 2120*w*, 1600*w*, 1500*w*, 1455*w*, 1390*w*, 1360*w*, 1330*w*, 1250*w*, 1210*w*, 1190*w*, 1145*w*, 1080*m*, 1050*w*, 1030*m*, 1000*w*, 970*w*, 700*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35–7.27 (*m*, 10 arom. H); 5.48 (br. *s*, H–C(1)); 4.62 (br. *d*, *J* ≈ 4.6, H–C(5)); 4.61 (*d*, *J* = 12.3, PhC*H*); 4.50 (*d*, *J* = 12.4, PhC*H*); 4.48 (*d*, *J* = 12.0, PhC*H*); 4.46 (*d*, *J* = 12.0, PhC*H*); 4.08 (*d*, *J* = 6.5, H_{endo}–C(6)); 3.73 (br. *td*, *J* ≈ 3.2, 1.9, 0.9, H–C(3)); 3.72 (*dd*, *J* = 6.9, 5.4, H_{exo}–C(6)); 3.37 (br. *dd*, *J* ≈ 2.0, 1.0, H–C(2)); 2.73 (*ddd*, *J* ≈ 2.9, 1.8, 0.9, H–C(4)); 2.25 (*d*, *J* = 2.9, H–C(2')). ^{13}C-NMR (50 MHz, $CDCl_3$): 137.63 (*s*); 137.56 (*s*); 128.54–127.43 (10*d*); 100.78 (*d*); 82.83 (*d*); 76.3 (*d*); 74.97 (*d*); 74.41 (*d*); 71.95 (*t*); 71.78 (*t*); 70.66 (*s*); 67.04 (*t*); 34.7 (*d*). CI-MS: 368 (100, $[M + NH_4]^+$), 279 (11). Anal. calc. for $C_{22}H_{22}O_4$ (350.41): C 75.40, H 6.32; found: C 75.14, H 6.00.

*1,6-Di-*O*-acetyl-2,3-di-*O*-benzyl-4-deoxy-4-*C*-ethynyl-*D*-glucopyranose* (**30**). At –20°, Me_3SiOTf (13 µl, 0.076 mmol) was added dropwise to a soln. of **29** (266 mg, 0.76 mmol) in Ac_2O (4 ml). The mixture was kept at –20° for 3 h, treated with sat. aq. $NaHCO_3$ soln. (4 ml), warmed to r.t., and stirred for 30 min. Normal workup afforded **30** (317 mg, 95%; α-D/β-D 10:1). Oil. R_f (AcOE/hexane 3.5:10) 0.40. $[\alpha]_D^{25}$ = +28.21 (*c* = 0.50, $CHCl_3$).IR ($CHCl_3$): 3300*m*, 3020*w*, 2920*w*, 2860*w*, 2120*w*, 1950*w*, 1750*s*, 1500*w*, 1455*m*, 1370*m*, 1250*s*, 1150*s*, 1100*s*, 1050*m*, 1020*s*, 935*m*, 910*w*, 860*w*, 700*m*, 650*m*. ^{1}H-NMR (300 MHz, $CDCl_3$, α-D/β-D 10:1): α-D-**30**: 7.42–7.3 (*m*, 10 arom. H); 6.33 (*d*, *J* = 3.61, H–C(1)); 4.90 (*d*, *J* = 10.2, PhC*H*); 4.86 (*d*, *J* = 10.3, PhC*H*); 4.67

(*d*, *J* = 11.5, PhC*H*); 4.62 (*d*, *J* = 11.5, PhC*H*); 4.31 (*d*, *J* = 3.4, 2 H–C(6)); 4.04 (*td*, *J* = 11.0, 3.4, H–C(5)); 3.89 (*dd*, *J* = 10.4, 9.5, H–C(3)); 3.55 (*dd*, *J* = 9.3, 3.5, H–C(2)); 2.75 (*dt*, *J* = 10.7, 2.4, H–C(4)); 2.21 (*d*, *J* = 2.3, H–C(2')); 2.17 (*s*, Ac); 2.06 (*s*, Ac); β-D-**30**: 5.59 (*d*, *J* = 8.2, H–C(1)).^{13}C-NMR (50 MHz, $CDCl_3$): α-D-**30**: 170.37 (*s*); 168.94 (*s*); 138.05 (*s*); 137.37 (*s*); 120.28–127.60 (several *d*); 89.90 (*d*); 80.18 (*d*); 78.29 (2*d*); 75.71(*t*); 72.96 (*s*); 72.47 (*t*); 70.87 (*d*); 63.63 (*t*); 36.35 (*d*); 20.83 (*q*); 20.55(*q*); β-D-**30**: 93.65 (*d*); 82.18 (*d*); 80.59 (*d*); 74.94 (*t*); 73.65 (*d*); 72.87 (*t*); 36.52 (*d*). CI-MS: 470 (100, $[M + NH_4]^+$), 410 (32), 302 (23), 108 (11). Anal. calc. for $C_{26}H_{28}O_7$ (452.5): C 69.01, H 6.23; found: C 69.28, H 5.93.

6-O-Acetyl-2,3-di-O-benzyl-4-deoxy-4-C-ethynyl-D-glucopyranose (**31**). A soln. of **30** (84 mg, 0.19 mmol) in $BnNH_2$ (4 ml) was vigorously stirred at 0° for 6 h, diluted with AcOEt (3 ml), neutralized with 2M HCl (15 ml), washed with H_2O, dried ($MgSO_4$), and evaporated: **31** (70 mg, 90%, α-D/β-D 1:1) as an oil. R_f (AcOEt/hexane 1:1) 0.60. IR ($CHCl_3$): 3600*w*, 3300*m*, 3060*w*, 2920*w*, 2880*w*, 2120*w*, 1740*m*, 1500*w*, 1305*w*, 1290*w*, 1270*w*, 1245*m*, 1120*m*, 1090*m*, 1040*m*, 1030*m*, 920*w*, 700*m*, 650*m*. ^{1}H-NMR (300 MHz, $CDCl_3$, α-D/β-D 1:1): 7.40–7.27 (*m*, 10 arom. H); 5.22 (br. *t*, *J* ≈ 2.8, 0.5 H, H–C(1)); 4.96 (*d*, *J* = 10.4, 0.5 H, PhC*H*); 4.95 (*d*, *J* = 10.3, 0.5 H, PhC*H*); 4.90 (*d*, *J* = 10.2, 0.5 H, PhC*H*); 4.89 (*d*, *J* = 10.4, 0.5 H, PhC*H*); 4.86 (*d*, *J* = 10.5, 0.5 H, PhC*H*); 4.79 (*d*, *J* = 11.8, 0.5 H, PhC*H*); 4.77 (*d*, *J* = 11.0, 0.5 H, PhC*H*); 4.71 (*dd*, *J* = 7.7, 5.4, 0.5 H, H–C(1)); 4.68 (*d*, *J* = 11.8, 0.5 H, PhC*H*); 4.48 (*dd*, *J* = 12.0, 2.1, 0.5 H, H–C(6)); 4.39 (*dd*, *J* = 12.0, 2.4, 0.5 H, H–C(6)); 4.32 (*dd*, *J* = 12.0, 4.6, 0.5 H, H'–C(6)); 4.28 (*dd*, *J* = 12.0, 5.5, 0.5 H, H'–C(6)); 4.19 (*ddd*, *J* = 10.8, 4.7, 2.5, 0.5 H, H–C(5)); 3.96 (*t*, *J* = 10.4, 09.3,.0.5 H, H–C(3)); 3.65 (*dd*, *J* = 10.4, 8.9, 0.5 H, H–C(3)); 3.66 (*ddd*, *J* = 10.6, 5.7, 2.1, 0.5 H, H–C(5)); 3.45 (*dd*, *J* = 9.2, 3.5, 0.5 H, H–C(2)); 3.27 (*dd*, *J* = 9.1, 7.8, 0.5 H, H–C(2)); 3.24 (*d*, *J* = 5.5, 0.5 H, OH); 2.96 (*d*, *J* = 2.3, 0.5 H, OH); 2.72 (*dt*, *J* = 10.5, 2.3, 0.5 H, H–C(4)); 2.67 (*dt*, *J* = 10.6, 2.3, 0.5 H, H–C(4)); 2.21 (*d*, *J* = 2.0, 0.5 H, H–C(2')); 2.19 (*d*, *J* = 2.1, 0.5 H, H–C(2')); 2.09 (*s*, 1.5 H, Ac); 2.07 (*s*, 1.5 H, Ac).^{13}C-NMR (50 MHz, $CDCl_3$, α-D/β-D 2:1): α-D-**31**: 170.84 (*s*); 138.17 (*s*); 137.71 (*s*); 128.4–127.68 (several *d*); 91.52 (*d*); 80.62 (*d*); 79.49 (*d*); 78.51 (*d*); 75.77 (*t*); 73.17 (*t*); 72.36 (*s*); 68.69 (*d*); 64.18 (*t*); 36.80 (*d*); 20.72 (*q*); β-D-**31**: 97.42 (*d*); 82.81 (*d*); 82.00 (*d*); 80.45 (*d*); 74.85 (*t*); 72.85 (*t*); 72.69 (*s*); 72.36 (*d*); 36.84 (*d*). CI-MS: 428 (100, $[M + NH_4]^+$). Anal. calc. for $C_{24}H_{28}O_6$ (410.46): C 70.23, H 6.38; found: C 69.99, H 6.53

6-O-Acetyl-2,3-di-O-benzyl-4-deoxy-4-C-ethynyl-D-glucono-1,5-lactone (**32**). A soln. of **31** (51 mg, 0.112 mmol) in DMSO (1 ml) was treated with Ac_2O (0.5 ml), stirred at r.t. for 12 h, and evaporated under high vacuum at 35°. A soln. of the residue in AcOEt was processed as usual, to afford **32** (50 mg, 99%). Oil. R_f (AcOEt/hexane 1:2) 0.52. $[\alpha]_D^{25} = +54.9$ (*c* = 0.55, $CHCl_3$). IR ($CHCl_3$): 3300*w*, 2960*w*, 2940*w*, 2860*w*, 2300*w*, 1750*m*, 1500*w*, 1450*w*, 1390*w*, 1370*w*, 1350*w*, 1240*m*, 1200*w*, 1180*w*, 1110*m*, 1090*m*, 1050*w*,, 1030*w*, 910*w*, 700*m*, 650*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.32–7.25 (*m*, 10 arom. H); 4.94 (*d*, *J* = 11.4, PhC*H*); 4.70 (*s*, PhCH_2); 4.68 (*ddd*, *J* = 10.9, 4.5, 2.2, H–C(5)); 4.64 (*d*, *J* = 11.4, PhC*H*); 4.47 (*dd*, *J* = 12.4, 2.2, H–C(6)); 4.33 (*dd*, *J* = 12.5, 4.5, H'–C(6)); 4.06 (*d*, *J* = 5.4, H–C(2)); 3.98 (*dd*, *J* = 7.9, 5.4, H–C(3)); 2.99 (*ddd*, *J* = 10.6, 7.8, 2.5, H–C(4)); 2.28 (*d*, *J* = 2.5, H–C(2')); 2.10 (*s*, Ac).^{13}C-NMR (50 MHz, $CDCl_3$): 170.33 (*s*); 168.12 (*s*); 136.95 (*s*); 136.44 (*s*); 128.46–127.92 (several *d*); 79.67 (*d*); 79.11 (*d*); 77.75 (*d*); 75.5 (*d*); 73.57 (2*t*); 73.56 (*s*); 63.27 (*t*); 34.94 (*d*); 20.61 (*q*). CI-MS: 426 (100, $[M + NH_4]^+$). Anal. calc. for $C_{24}H_{24}O_6$ (408.45): C 70.58, H 5.92; found: C 70.83, H 5.63.

8-O-Acetyl-4,5-di-O-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-C-ethynyl-1-C-(trimethylsilyl)-D-gluco-oct-3-ulopyranose (**33**). At –78°, 2.4M BuLi (0.737 mmol) was added dropwise to a soln. of $Me_3SiC{\equiv}CH$ (0.1 ml, 0.737 mmol) in THF (3 ml). The mixture was kept at –78° for 30 min and then transferred by a syringe (pressure of Ar) to a cooled (–78°) soln. of **32** (215 mg, 0.526 mmol) and $TiCl_4$ (0.144 ml, 1.31 mmol) in THF (1 ml). The mixture was stirred for 1 h at –78°, treated with sat. NH_4Cl soln. (3 ml), warmed to r.t., stirred for another 30 min, diluted with AcOEt, washed with brine, dried ($MgSO_4$), and evaporated: **33** (256 mg, 96%). Oil. R_f (AcOEt/hexane 1:2) 0.54. IR ($CHCl_3$): 3570*w*, 3300*m*, 3060*w*, 3040*w*, 3000*w*, 2960*w*, 2900*w*, 2860*w*, 2160*w*, 2120*w*, 1950*w*, 1740*s*, 1500*w*, 1450*m*, 1390*w*, 1360*m*, 1250*s*, 1125*s*, 1060*s*, 1040*s*, 1030*w*, 910*w*, 860*s*, 850*s*, 700*m*, 650*m*. ^{1}H-NMR (300 MHz, $CDCl_3$, α-D/β-D 54:44): 7.41–7.26 (*m*, 10 arom. H); 5.00 (*d*, *J* = 11.6, 0.44 H, PhC*H*); 4.99 (*d*, *J* = 10.4, 0.56 H, PhC*H*); 4.93 (*d*, *J* = 11.5, 0.44 H, PhC*H*); 4.85 (*d*, *J* = 10.8, 0.56 H, PhC*H*); 4,85 (*s*, 2.24 PhCH_2); 4.80 (*d*, *J* = 10.6, 0.44 H, PhC*H*); 4.77 (*d*, *J* = 11.5, 0.44 H, PhC*H*); 4.47 (*dd*, *J* = 12.1, 2.1, 0.44 H, H–C(8)); 4.40 (*dd*, *J* = 12.2, 2.4, 0.56 H, H–C(8)); 4.33 (*dd*, *J* = 12.2, 4.8, 0.56 H, H'–C(8)); 4.27 (*ddd*, *J* = 12.2, 5.1, 0.44 H, H'–C(8)); 4.20 (*ddd*, *J* = 10.0, 4.7, 2.3, 0.56 H, H–C(7)); 4.03 (*ddd*, *J* = 10.7, 4.8, 2.0, 0.44 H, H–C(7)); 3.85 (*dd*, *J* = 10.4, 9.2, 0.56 H, H–C(5)); 3.72 (*dd*, *J* = 10.3, 9.3, 0.44 H, H–C(5)); 3.60 (*d*, *J* = 9.2, 0.56 H, H–C(4)); 3.57 (*s*, 0.44 H, OH); 3.46 (*s*, 0.56 H, OH); 3.33 (*d*, *J* = 9.2, 0.44 H, H–C(4)); 2.76 (*dt*, *J* = 10.6, 2.4, 0.56 H, H–C(6)); 2.72 (*dt*, *J* = 10.5, 2.2, 0.44 H, H–C(6)); 2.18 (*d*, *J* = 2.3, H-C(2')); 2.11 (s, Ac); 2.08 (*s*, Ac);

0.20 (*s*, Me_3Si); 0.18 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): α-D-**33**: 170.84 (*s*); 138.18 (*s*); 137.75 (*s*); 128.51–127.43 (20*d*); 103.42 (*s*); 91.69 (*s*); 89.50 (*s*); 83.41 (*d*); 80.76 (*d*); 79.19 (*d*); 75.85 (*t*); 75.68 (*t*); 72.43 (*s*); 69.83 (*d*); 63.95 (*t*); 36.57 (*d*); 20.68 (*q*); –0.71 (3*q*). β-D-**33**: 95.45 (*s*); 83.62 (*d*); 80.09 (*d*); 80.08 (*d*); 75.62 (*t*); 75.50 (*t*); 72.29 (*s*); 71.97 (*d*); 63.79 (*t*); 36.25 (*d*); 20.16 (*q*); -0.57 (3*q*). CI-MS: 524.3 (100, $[M + NH_4]^+$), 489 (18), 427 (11), 426 (40), 417 (11), 416 (39), 399 (10).

8-O-Acetyl-3,7-anhydro-4,5-di-O-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-C-ethynyl-1-C-(trimethylsilyl)-D-glycero-D-gulo-*octitol* (**34**). At 0°, a soln. of $BF_3 \cdot Et_2O$ (0.317 ml, 2.53 mmol) and Et_3SiH (0.4 ml, 2.53 mmol) in $MeCN/CH_2Cl_2$ 1:1 (8 ml) was added dropwise to a soln. of **33** (256 mg, 0.505 mmol) in $MeCN/CH_2Cl_2$ 1:1 (8 ml). The soln. was stirred for 3 h and treated with sat. aq. $NaHCO_3$ soln. (3 ml). Normal workup gave **34** (223 mg, 90%). Oil. R_f (AcOEt/hexane 1:5) 0.31. $[\alpha]_D^{25} = -45.05$ ($c = 0.475$ $CHCl_3$). IR ($CHCl_3$): 3300*m*, 3060*w*, 3020*w*, 3000*w*, 2950*w*, 2900*w*, 2860*w*, 2170*w*, 1950*w*, 1735*s*, 1495*w*, 1450*m*, 1385*w*, 1390*m*, 1355*m*, 1290*m*, 1250*m*, 1120*s*, 1070*s*, 1025*m*, 945*w*, 910*w*, 840*s*, 695*m*, 645*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.45–7.27 (*m*, 10 arom. *H*); 4.99 (*d*, $J = 10.4$, PhC*H*); 4.94 (*d*, $J = 10.6$, PhC*H*); 4.85 (*d*, $J = 10.6$, PhC*H*); 4.80 (*d*, $J = 10.4$, PhC*H*); 4.42 (*dd*, $J = 12.1, 2.0$, H–C(8)); 4.27 (*dd*, $J = 12.1, 5.6$, H'–C(8)); 4.07 (*d*, $J = 9.6$, H–C(3)); 3.59 (*ddd*, $J = 10.5, 5.5, 2.0$, H–C(7)); 3.58 (*dd*, $J = 10.3, 8.9$, H–C(5)); 3.48 (*dd*, $J = 9.6$ 9.0, H–C(4)); 2.70 (*dt*, $J = 10.5, 2.4$, H–C(6)); 2.18 (*d*, $J = 2.4$, H–C(2')); 2.09 (*s*, Ac); 0.18 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.52 (*s*); 138.09 (*s*); 137.92 (*s*); 127.75–128.47 (several *d*); 101.94 (*s*); 91.50 (*s*); 83.11 (*d*); 81.81 (*d*); 80.45 (*d*); 77.00 (*d*); 75.83 (*t*); 75.55 (*t*); 72.68 (*s*); 70.44 (*d*); 64.46 (*t*); 37.10 (*d*); 20.86 (*q*); –0.33 (3*q*). CI-MS: 508 (100, $[M + NH_4]^+$). Anal. calc. for $C_{29}H_{34}O_5Si$ (490.69): C 70.99, H 6.98; found: C 71.01, H 7.13.

*1,6-Anhydro-4-deoxy-4-C-ethynyl-2-O-(methoxymethyl)-β-*D-*glucopyranose*. (**36**). At 0°, a soln. of $Bu_4NF \cdot 3H_2O$ (82 mg, 0.262 mmol) in THF (2 ml) was added dropwise to a soln. of **27** (250 mg, 0.87 mmol) in THF (5 ml). The soln. was stirred for 1 h, treated with H_2O (2 ml), warmed to r.t., stirred for further 30 min, diluted with AcOEt, washed with brine and dried ($MgSO_4$). Evaporation afforded **36** (177 mg, 94%). Oil. R_f (AcOEt/toluene 1:1) 0.4. $[\alpha]_D^{25} = -634$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3673*w*, 3558*w*, 3428*w*, 3307*s*, 3042*w*, 3007*m*, 2959*m*, 2901*m*, 2848*w*, 2828*w*, 2122*w*, 1731*w*, 1603*w*, 1473*w*, 1443*w*, 1403*w*, 1363*w*, 1322*w*, 1301*w*, 1252*m*, 1150*s*, 1109*s*, 1078*s*, 1042*s*, 1004*m*, 972*m*, 953*m*, 916*m*, 888*m*, 871*m*, 825*w*, 649*s*, 589*w*, 552*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.51 (*s*, H–C(1)); 4.79 (*d*, $J = 7.1$, 1 H, $MeOCH_2$); 4.75 (*d*, $J = 7.0$, 1 H, $MeOCH_2$); 4.67 (*d*, $J = 4.6$, H–C(5)); 4.02 (*d*, $J = 7.1$, H_{endo}–C(6)); 3.90 (*m*, H–C(3)); 3.72 (*dd*, $J = 7.4, 4.9$, H_{exo}–C(6)); 3.45 (*s*, MeO); 3.44 (*d*, $J = 3.8$, H–C(2)); 3.09 (*d*, $J = 5.9$, OH); 2.65 (*dt*, $J = 4.1, 2.5$, H–C(4)); 2.27 (*d*, $J = 2.6$, H–C(2')). ^{13}C-NMR (50 MHz, $CDCl_3$): 101.905 (*d*); 96.80 (*t*); 82.96 (*s*); 78.7 (*d*); 75.15 (*d*); 70.87 (*d*); 70.80 (*s*); 68.12 (*t*); 55.97 (*q*); 36.66 (*d*). EI-MS: 215 ($[M + 1]^+$), 183 ($[M + 1 - MeOH]^+$). Anal. calc. for $C_{10}H_{14}O_5$ (214.22): C 56.07, H 6.59; found: C 55.88, H 6.63.

3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-C-ethynyl-4-O-(methoxymethyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-*octitol* (**37**). At –5°, 1.5M BuLi (0.5 mmol) was added dropwise to a soln. of $Me_3SiC{\equiv}CH$ (70 µl, 0.5 mmol) in toluene (3 ml). The soln. was warmed to 20°, stirred for 15 min, treated with THF (0.1 ml), and transferred into a suspension of $AlCl_3$ (67 mg, 0.5 mmol) and powdered 4 Å molecular sieves (150 mg) in toluene (2 ml). After stirring for 40 min at 20° (→ thick white precipitate), the mixture was heated to 80°, treated with a soln. of **36** (36 mg, 0168 mmol) in toluene (2 ml), stirred for 18 h, cooled to 0°, and treated with a sat. NH_4Cl soln. (4 ml). Extraction with AcOEt, washing with H_2O, drying ($MgSO_4$), treating with charcoal, evaporation and FC (AcOEt/hexane 7:17) gave **37** (36 mg, 70%) as an oil. R_f (AcOEt/toluene 1:1) 0.48. $[\alpha]_D^{25} = +184$ ($c = 0.5$, $CHCl_3$). IR: 3594*w*, 3404*m*, 3306*m*, 3042*w*, 3007*m*, 2961*m*, 2927*m*, 2855*m*, 2180*w*, 1455*w*, 1405*w*, 1369*w*, 1351*w*, 1291*m*, 1252*s*, 1150*m*, 1115*s*, 1072*s*, 1031*s*, 998*m*, 934*w*, 907*w*, 848*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.85 (*d*, $J = 6.7$, 1 H, $MeOCH_2$); 4.81 (*d*, $J = 6.8$, 1 H, $MeOCH_2$); 4.04 (*d*, $J = 9.6$, H–C(3)); 4.03 (*d*, $J = 1.6$, OH–C(5)); 3.98 (*m*, addn. of D_2O→ *dd*, $J = 11.9, 2.6$, H–C(8)); 3.76 (br. *td*, $J \approx 12.1, 5.9$, addn. of D_2O→ *dd*, $J = 12.2, 5.8$, H'–C(8)); 3.60 (*ddd*, $J = 10.2, 8.6, 1.4$, H–C(5)); 3.49 (*s*, MeO); 3.45 (*ddd*, $J = 10.3, 5.6, 2.4$, H–C(7)); 3.29 (*dd*, $J = 9.6, 8.6$, H–C(4)); 2.56 (*dt*, $J = 10.4, 2.4$, H–C(6)); 2.24 (*d*, $J = 2.4$, H–C(2')); 2.07 (br. *t*, $J \approx 6.7$, HO–C(8)); 0.17 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 101.25 (*s*); 98.26 (*t*); 91.43 (*s*); 83.34 (*d*); 80.04 (*s*); 79.00 (*d*); 74.41 (*d*); 72.56 (*d*); 69.54 (*d*); 63.32 (*t*); 56.36 (*q*); 36.99 (*d*); –0.28 (3*q*). EI-MS: 280 ($[M - MeOH]^+$). Anal. calc. for $C_{15}H_{24}O_5Si$ (312.44): C 57.66, H 7.74; found: C 57.83, H 7.58.

*1,6:3,4-Dianhydro-2-O-(triisopropylsilyl)-β-*D-*galactopyranose* (**38**). At 0°, $(i\text{-}Pr)_3SiOTf$ (8.21 ml, 30.5 mmol) was added dropwise to a soln. of **23** (4 g, 27.77 mmol) in pyridine (12 ml). The mixture was stirred for 10 h at r.t., treated with pentane (15 ml) and AcOEt (10 ml), and stirred for further 30 min. The white precipitate was

filtered off through *Celite*. Evaporation of the filtrate gave **38** (7.5 g, 95%). Oil. R_f (AcOEt/toluene 1:5) 0.49. $[\alpha]_D^{25} = -36.4$ ($c = 0.99$, $CHCl_3$). IR ($CHCl_3$): 2960*s*, 2900*s*, 2870*s*, 1470*s*, 1425*w*, 1390*m*, 1355*w*, 1310*m*, 1300*w*, 1285*w*, 1240*w*, 1200*w*, 1140*s*, 1110*s*, 1070*s*, 1030*m*, 1000*s*, 985*s*, 945*m*, 920*s*, 880*s*, 870*s*, 845*s*, 810*s*, 710*m*, 690*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.18 (*s*, H–C(1)); 4.80 (*t*, $J = 5.0$, H–C(5)); 3.93 (*d*, $J = 6.5$, H_{endo}–C(6)); 3.85 (br. *s*, H–C(2)); 3.60 (*t*, $J \approx 4.7$, H–C(4)); 3.50 (*dd*, $J = 6.5, 4.9$, H_{exo}–C(6)); 3.09 (*dd*, $J = 4.2, 1.6$, H–C(3)); 1.15–0.95 (*m*, (i-Pr)$_3$Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 101.04 (*d*); 71.6 (*d*); 66.81 (*d*); 64.37 (*t*); 52.83 (*d*); 50.36 (*d*); 17.79 (6*q*); 12.03 (3*d*). CI-MS: 318 (100, $[M + NH_4]^+$), 301 (15.24, $[M + 1]^+$). Anal. calc. for $C_{15}H_{28}O_4Si$ (300.47): C 59.96, H 9.39; found: C 60.15, H 9.30.

*1,6-Anhydro-4-deoxy-2-*O*-(triisopropylsilyl)-4-*C*-[2-(trimethylsilyl)ethynyl]-β-*D*-glucopyranose* (**39**). At –15°, 1.5M BuLi in hexane (73.3 ml, 110 mmol) was added dropwise to a soln. of $Me_3SiC{\equiv}CH$ (15.23 ml, 110 mmol) in dry toluene (100 ml). The mixture was warmed to 20°, stirred for 30 min, treated with THF (10 ml) to dissolve the gelatinous precipitate, cooled to –15°, and treated dropwise with 2M Me_3Al in hexane (55 ml, 110 mmol). Upon warming to 20° and stirring for 45 min, a thick white precipitate was formed. The suspension was heated to 80°, treated with a soln. of **38** (22 g, 0.073 mol) in toluene (60 ml), stirred for 2 h, cooled to 0°, and treated with sat. NH_4Cl soln. (10 ml). Extraction with AcOEt, washing with H_2O, drying ($MgSO_4$), evaporation and FC (AcOEt/hexane 1:10) gave **39** (24.9 g, 85%). White solid. R_f (AcOEt/hexane 1:3) 0.31. M.p. 59°. $[\alpha]_D^{25} = -69.0$ ($c = 0.85$, $CHCl_3$). IR ($CHCl_3$): 3600*w* (br.), 3000*w*, 2960*m*, 2900*m*, 2870*m*, 2180*w*, 1515*w*, 1470*w*, 1390*w*, 1370*w*, 1340*w*, 1330*w*, 1310*w*, 1295*w*, 1255*m*, 1190*w*, 1130*m*, 1105*m*, 1070*m*, 1045*m*, 1010*m*, 990*w*, 920*w*, 890*m*, 850*m*, 815*w*, 690*m*, 670*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.41 (*s*, H–C(1)); 4.62 (*d*, $J = 4.8$, H–C(5)); 3.97 (*d*, $J = 7.4$, H_{endo}–C(6)); 3.83 (br. *d*, $J \approx 6.9$, H–C(3)); 3.67 (*dd*, $J = 7.4, 4.9$, H_{exo}–C(6)); 3.62 (*s*, H–C(2)); 2.68 (*s*, H–C(4)); 2.41 (*d*, $J = 7.1$, OH); 1.14–1.05 (*m*, (i-Pr)$_3$Si); 0.13 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, C_6D_6): 106.48 (*s*); 103.41 (*d*); 86.09 (*s*); 75.253 (*d*); 73.74 (*d*); 73.42 (*d*); 67.71 (*t*); 38.7(*d*); 18.21 (6*q*); 12.46 (3*d*); 0.22 (3*q*). CI-MS: 416 (100, $[M + NH_4]^+$). Anal. calc. for $C_{20}H_{38}O_4Si_2$ (398.69): C 60.25, H 9.61; found: C 59.99, H 9.80.

*1,6-Anhydro-4-deoxy-4-*C*-ethynyl-2-*O*-(triisopropylsilyl)-β-*D*-glucopyranose* (**41**). A soln. of **39** (19 g, 0.047 mol) and 1M NaOMe in MeOH (100 ml) was stirred for 4 h at 25° in MeOH (100 ml), neutralized (*Dowex*, H^+ form), and filtered. Evaporation afforded **41** (15.2 g, 97.5%). White solid. R_f (AcOEt/hexane 1:5) 0.21. M.p. 68°. $[\alpha]_D^{25} = -65.40$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3610*w*, 3560*w*, 3310*m*, 2950*s*, 2900*m*, 2875*s*, 2130*w*, 1740*w*, 1470*m*, 1440*w*, 1390*w*, 1370*w*, 1340*w*, 1325*w*, 1315*w*, 1300*w*, 1250*m*, 1190*m*, 1130*s*, 1080*m*, 1060*s*, 1040*m*, 1000*m*, 965*w*, 920*m*, 890*s*, 870*m*, 835*w*, 810*m*, 690*m*, 660*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.44 (*s*, H–C(1)); 4.63 (*d*, $J = 4.9$, H–C(5)); 4.04 (*d*, $J = 7.5$, H_{endo}–C(6)); 3.81–3.78 (*m*, H–C(3)); 3.71 (*dd*, $J = 7.4, 4.9$, H_{exo}–(6)); 3.65 (*s*, H–C(2)); 2.67 (br. *d*, $J \approx 1.8$, H–C(4)); 2.5 (*d*, $J = 7.5$, OH–C(3)); 2.18 (*d*, $J = 2.7$ H–(2')); 1.03–0.95 (*m*, (i-Pr)$_3$Si). ^{13}C-NMR (50 MHz, C_6D_6): 103.42 (*d*); 82.60 (*d*); 75.12 (*d*); 73.33 (*d*); 73.30 (*d*); 70.78 (*s*); 67.64 (*t*); 37.70 (*d*); 18.15 (6*q*); 12.50 (3*d*). CI-MS: 344 (100, $[M + NH_4]^+$).

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-ethynyl-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol*. (**42**). At –15°, 2.3M BuLi (0.139 mol) was added dropwise to a soln. of $Me_3SiC{\equiv}CH$ (19.25 ml, 0.139 mol) in toluene (50 ml). The soln. was warmed to 20°, stirred for 30 min, diluted with THF (5 ml), and transferred into a suspension of $AlCl_3$ (18.53 g, 0.139 mol) and powdered 4 Å molecular sieves (14 g) in toluene (35 ml). Upon stirring the mixture at 20° for 45 min, a thick white precipitate formed. The mixture was heated to 100°, treated with a soln. of **41** (15.2 g, 0.046 mol) in toluene (80 ml), stirred for 18 h, cooled to 0°, and treated with sat. NH_4Cl soln. (10 ml). It was extract with AcOEt, washed with H_2O, dried ($MgSO_4$), treated with charcoal, filtered, and evaporated. The residue was purified by FC (AcOEt/hexane 1:7): **42** (15.5 g 79%). White solid. R_f (AcOEt/hexane/CH_2Cl_2 2:10:5) 0.45. M.p. 138°. $[\alpha]_D^{25} = -5.00$ ($c = 1.55$, $CHCl_3$). IR ($CHCl_3$): 3569*m*, 3300*m*, 2940*s*, 2180*w*, 1460*m*, 1410*m*, 1390*w*, 1370*w*, 1350*w*, 1330*w*, 1290*w*, 1250*m*, 1200*w*, 1140*s*, 1100*s*, 1070*m*, 1020*w*, 990*m*, 920*w*, 880*m*, 845*s*, 720*s*, 580*m*, 670*m*, 650*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.97 (*d*, $J = 9.2$, H–C(3)); 3.95 (*ddd*, $J = 12.1, 7.4, 2.5$, H–C(8)); 3.75 (*td*, $J = 12.1, 6.1$, H'–C(8)); 3.64 (*dd*, $J = 9.1, 8.3$, H–C(4)); 3.54 (*ddd*, $J = 10.2, 8.3, 2.9$, H–C(5)); 3.47 (*ddd*, $J = 10.4, 5.8, 2.6$, H–C(7)); 2.66 (*dt*, $J = 10.3, 2.4$, H–C(6)); 2.51 (*d*, $J = 3.0$, OH–C(5)); 2.23 (*d*, $J = 2.4$, H–C(2')); 2.21 (*t*, $J \approx 6.7$, OH–C(8)); 1.30–1.10 (*m*, (i-Pr)$_3$Si); 0.15 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 102.17 (*s*); 91.26 (*s*); 80.00 (*d*); 78.82 (*d*); 76.89 (*d*); 75.18 (*d*); 72.92 (*s*); 71.93 (*d*); 63.45 (*t*); 37.49 (*d*); 18.35 (6*q*); 13.05 (3*d*); –0.38 (3*q*). CI-MS: 442 (100, $[M + NH_4]^+$). Anal. calc. for $C_{22}H_{40}O_4Si_2$ (424.73): C 62.21, H9.49 ; found: C 62.47, H 9.25.

*1,6-Anhydro-4-deoxy-4-*C*-ethynyl-β-*D*-glucopyranose* (**40**). As described for **36**, with $Bu_4NF \cdot 3H_2O$ (2.28

g, 7.22 mmol) in THF (3 ml), **39** (1.44 g, 3.61 mmol) in THF (10 ml), and H_2O (3 ml). Evaporation and FC (AcOEt/hexane 1:1) gave **40** (535 mg, 87%). White solid. R_f (AcOEt/toluene 1:1) 0.14. M.p. 120°. $[\alpha]_D^{25}$ = –122.124 (c = 1.017, $CHCl_3$). IR (KBr): 3340*s* (br.), 3220*s*, 2980*m*, 2920*s*, 2865*w*, 2800*s*, 2110*w*, 1862*w*, 1630*w*, 1555*w*, 1480*s*, 1430*m*, 1380*m*, 1360*s*, 1325*s*, 1290*s*, 1250*m*, 1210*m*, 1185*s*, 1100*s*, 1080*s*, 1070*s*, 1060*s*, 990*s*, 970*m*, 940*s*, 920*s*, 890*s*, 850*s*, 820*s*, 780*m*, 740*s*, 670*s*, 620*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.53 (*s*, H–C(1)); 4.63 (*d*, J = 5.1, H–C(5)); 4.20 (*d*, J = 7.9, H_{endo}–C(6)); 4.30 (*dt*, J = 7.8, 1.6, H–C(3)); 3.80 (*dd*, J = 7.6, 5.0 H_{exo}–C(6)); 3.59 (*dt*, J = 11.8, 1.5, H–C(2)); 2.76 (*dd*, J = 2.5, 1.5, H–C(4)); 2.74 (*d*, J = 7.8, OH–C(2)); 2.48 (*d*, J = 11.9, OH–C(3)); 2.32 (*d*, J = 2.6, H–C(2')). ^{13}C-NMR (50 MHz, $CDCl_3$): 102.27 (*d*); 82.21 (*d*); 75.16 (*d*); 72.43 (2*d*); 70.64 (*s*); 67.26 (*t*); 36.01 (*d*). CI-MS: 188 (100, $[M + NH_4]^+$).

Preparation of **29** *from* **40**. At 0°, oil-free NaH (374 mg, 15.6 mmol) was added to a soln. of **40** (442 mg, 2.6 mmol) in DMF (15 ml) and treated dropwise with BnBr (1.89 ml, 13.0 mmol) and Bu_4NI (96 mg, 0.26 mmol), warmed to r.t., and stirred for 4 h. After cooling to 0°, excess NaH was destroyed by the addition of MeOH (0.5 ml). Normal workup and FC (AcOEt/hexane 1.5:10) of the residue gave **29** (885 mg, 97%) as an oil. Spectroscopic data: identical with those of a sample of **29** obtained from **28**.

*3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-6-*C*-[2-(trimethylsilyl)ethyl]-*D*-glycero-*D*-gulo-octitol*. (**43**). As described for **25/27**, with 2.4M BuLi in hexane (8.3 ml, 20 mmol), $Me_3SiC{\equiv}CH$ (2.77 ml, 20 mmol), toluene (3 ml), THF (1 ml), 25% Et_2AlCl in hexane (9.8 ml, 20 mmol), **38** (750 mg, 2.5 mmol), and toluene (20 ml; 18 h): **43** (1.0 g, 81%). White solid. R_f (AcOEt:hexane 1:5) 0.49. M.p. 188.2°. $[\alpha]_D^{25}$ = –32.08 (c = 0.67, $CHCl_3$). IR ($CHCl_3$): 3600*w*, 3010*w*, 2960*m*, 2930*m*, 2900*m*, 2870*m*, 2180*w*, 1510*w*, 1470*w*, 1410*w*, 1390*w*, 1370*w*, 1305*w*, 1330*w*, 1300*w*, 1255*m*, 1150*m*, 1110*m*, 1075*m*, 1050*m*, 1020*w*, 990*m*, 910*m*, 890*m*, 850*s*, 810*w*, 640*m*, 670*w*, 610*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.98 (*d*, J = 9.2, H–C(3)); 3.94 (*ddd*, J = 12.0, 8.0, 2.9, H–C(8)); 3.73 (*dt*, J = 12.0, 6.0, H'–C(8)); 3.63 (*dd*, J = 9.1, 8.4, H–C(4)); 3.52 (*ddd*, J = 10.0, 8.0, 2.6, H–C(5)); 3.45 (*ddd*, J = 10.3, 6.5, 2.7, H–C(7)); 2.53 (*t*, J = 10.2, H–C(6)); 2.41 (*d*, J = 2.7, OH–C(5)); 2.09 (*dd*, J = 8.1, 5.8, OH–C(8)); 1.30–1.05 (*m*, (i-Pr)$_3$Si); 0.14 (*s*, Me_3Si); 0.12 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 102.59 (*s*), 101.77 (*s*); 91.30 (*s*); 90.29 (*s*); 79.14 (*d*); 77.0 (*d*); 75:33 (*d*); 72.20 (*d*); 63.9 (*t*); 39.32 (*d*); 18.59 (6*q*); 13.20 (3*d*) 0.2 (6*q*). CI-MS: 514 (100, $[M + NH_4]^+$). Anal. calc. for $C_{25}H_{48}O_4Si_3$ (496.91): C 60.43, H 9.74; found: C 60.69, H 9.85.

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