# 109. Oligosaccharide Analogues of Polysaccharides

## Part 8

## Orthogonally Protected Cellobiose-Derived Dialkynes. A Convenient Method for the Regioselective Bromo- and Protodegermylation of Trimethylgermyl- and Trimethylsilyl-protected Dialkynes

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Dedicated to *Vlado Prelog* on the occasion of his 90th birthday

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The cellobiose-derived dialkynes **14** and **15** were prepared by glycosidation of the acceptor **9** with the thioglycosides **12** (82%) and **13** (85%), respectively. The acceptor **9** was prepared from the known alcohol **2** *via* the lactone **7** in five steps (48% overall), and the donors **12** and **13** were prepared from the alkynylated anhydroglucose derivative **10** (60% overall). Acetolytic debenzylation of **14** and **15** (→**16** and **17**, resp.) followed by deacylation of **16** yielded 60% of the cellobiose-derived dialkyne **18**. Deacylation of **14** (→**19**), methoxymethylation (→**20**) and trimethylgermylation led to the orthogonally protected dialkyne **21** (69% overall). Protodesilylation of **21** with $K_2CO_3$/MeOH gave **22** (90%), while the $Me_3Ge$ group was selectively removed with CuBr (19 mol-%) in THF/MeOH to give **20** (95%). Treatment of **21** with aqueous HCl solution led to **19** (80%). Bromodegermylation of **21** (NBS/$AgOOCCF_3$) led to a mixture of **23** (85%) and **24** (11%). Similar conditions using CuBr instead of $AgOOCCF_3$ gave exclusively the bromoalkyne **23** (93%). The temperature dependence of the $\delta$ values of the OH resonances of **18** in ($D_6$)DMSO evidence a strong intramolecular H-bond between C(5′)–O···HO–C(5).

**Introduction.** – To assess the influence of intra- and intermolecular H-bonds on the structure and properties of polysaccharides, we intend to compare native polysaccharides with a series of analogues, where the ratio between intermolecular and intramolecular H-bonds is systematically varied by substituting all or some glycosidic O-atoms by butadiynediyl units. The butadiynediyl group – apart from its favourable properties [1] – allows a binomial synthesis of the analogues [2] [3].

The synthesis of analogues of cellulose requires monomers derived from glucose, cellobiose, and higher $\beta$-D-1,4-glycanes possessing two orthogonally protected ethynyl substituents [3].

The shape of the oligosaccharide analogues is expected to be determined by the conformation of the monomeric dialkynes. The bonds to the ethynyl substituents of the glucose-derived monomer define antiparallel vectors; this monomer is calculated to give rise to essentially linear oligomers [4] [5] (*Fig. 1*). For the dialkynes derived from cellobiose and higher $\beta$-D-1,4-glycanes, one expects a conformation where the glycosidically linked pyranosyl units are alternately rotated by *ca.* 180°, resulting in a H-bond between HO–C(3) of the aglycon and O–C(5′) of the glycosyl residue, as it has been demonstrated for cellobiose [6] [7]. Here, the bonds to the ethynyl substituents define vectors that

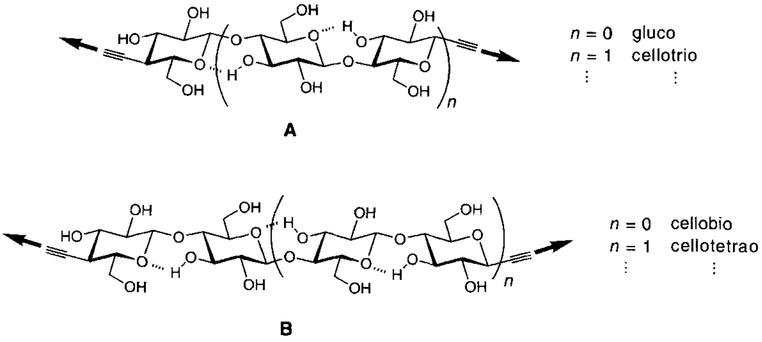

Fig. 1. *Repetitive units of the oligosaccharide analogues.* Units of type **A** possess antiparallel ethynyl substituents. Ethynyl substituents in units of type **B** define intersecting vectors.

enclose an angle of *ca.* 120°. Thus, the dialkynes derived from β-D-glucose and cello-oligosaccharides should form two classes, one comprising the monomers possessing no or an even number of glycosidic O-atoms (type **A**), and one comprising the monomers possessing an odd number of glycosidic O-atoms (type **B**). While oligomers derived from monomers of type **A** should be linear, those with odd numbers of glycosidic O-atoms (type **B**) can *a priori* form either (corrugated) linear or helical arrangements[1]).

The preparation of the glucose-derived dialkyne and its octamer have been described [3] [5] [8]. The most advantageous orthogonal protection of the dialkynes uses a *C*-$GeMe_3$ and a *C*-DOPS[2]) group; protodesilylation and bromodegermylation are selective and have led to the minimum of three steps for each cycle of the binomial synthesis [8] [9]. While the $Me_3Ge$ group is introduced in one step using $Me_3GeCl$[3]), the preparation and introduction of the DOPS-protected ethynyl group requires six steps [9]. However, the bromodegermylation of the more easily prepared, *C*-$GeMe_3$/*C*-$SiMe_3$-protected glucose-derived dialkyne was not completely regioselective and gave rise to *ca.* 3% of the corresponding bis(bromoethynyl) derivative. The separation of the monobromodialkyne from the bis(bromoethynyl) derivative and the starting material proved tedious and augured ill for the use of this protecting group couple for the preparation of higher oligomers [8].

We report the synthesis of cellobiose-derived dialkynes protected by a *C*-$GeMe_3$ and a *C*-$SiMe_3$ group, a method for their orthogonal deprotection, the fully selective bromodegermylation, and evidence for the preferred conformation of the unprotected, 1,4′-dideoxy-1,4′-diethynyl analogue of β-D-cellobiose.

**Results and Discussion.** – The synthesis of the cellobiose analogues is based on the glycosidation of a monoethynylated glycosyl acceptor by a monoethynylated glycosyl donor. The acceptor was prepared from the known alcohol **2**, which was obtained

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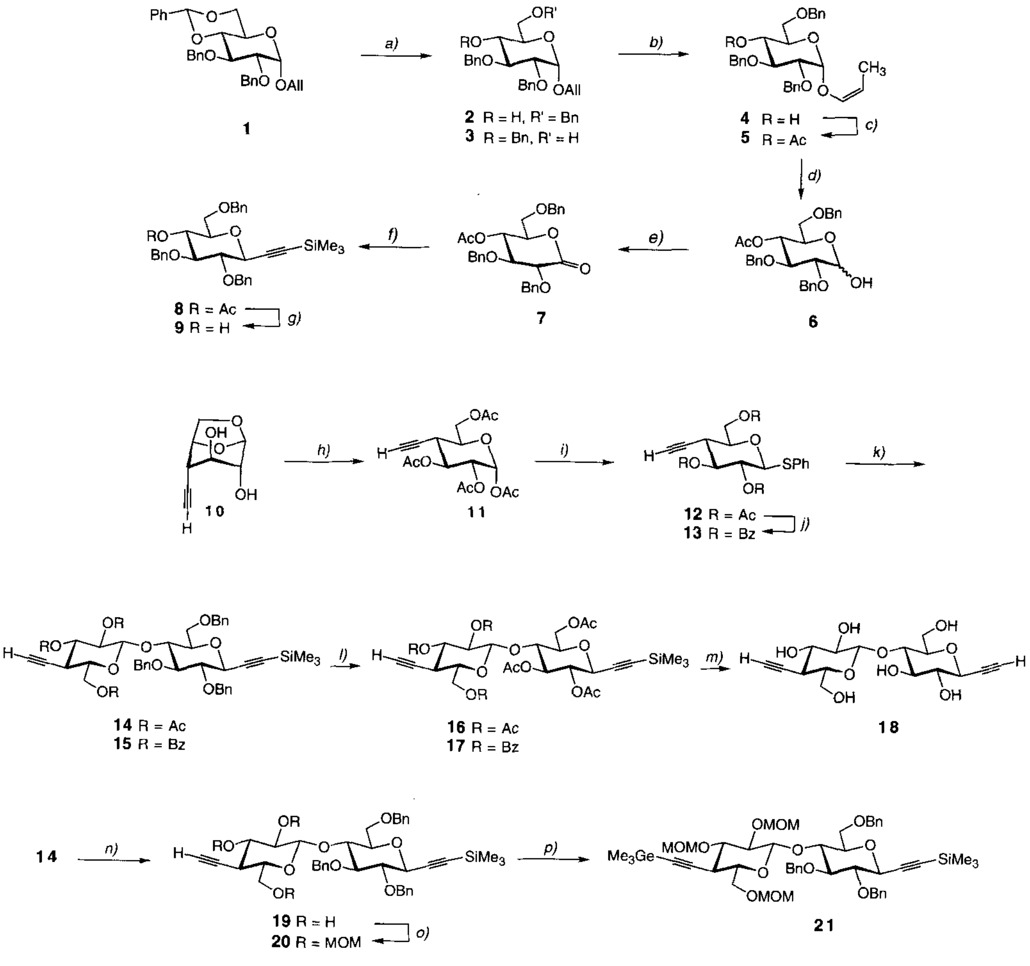
[1]) Calculations (MM3) for a cellobiose-derived octamer indicate that a helical arrangement is preferred by *ca.* 15 kcal/mol over the linear structure.

[2]) DOPS ( = [*d*imethyl(*o*xy)*p*ropyl]dimethyl*s*ilyl).

[3]) $Me_3GeCl$ is commercially available and easily prepared (see *Exper. Part*).

together with the isomer **3** (*ca.* 6:1) by reductive cleavage [10] of the 1,3-dioxane ring of the allyl α-D-glucopyranoside **1** (*Scheme 1*). Isomerization of the allyl group, (KO$^t$Bu in DMSO, → **4**), acetylation (→ **5**), and hydrolysis with $I_2$ in aqueous THF [11] resulted in a mixture of the crystalline anomers **6** (α-D-/β-D 72:28, 64% overall yield). Oxidation of **6** with *Dess-Martin*'s periodinane [12] [13] to the lactone **7** (> 95%), followed by addition

*Scheme 1*



All = $CH_2{=}CHCH_2$, Bn = $PhCH_2$, Bz = PhC(O), MOM = $MeOCH_2$

*a*) $NaCNBH_3$, HCl·$OEt_2$, 4-Å mol. sieves, THF. *b*) KO$^t$Bu, DMSO. *c*) $Ac_2O$, pyridine. *d*) $I_2$, THF/$H_2O$, pyridine; 64% overall from **1**. *e*) *Dess-Martin*'s periodinane, $CH_2Cl_2$; > 95%. *f*) 1. BuLi, HC≡CSiMe$_3$, THF; 2. $BF_3$·$OEt_2$, $Et_3SiH$, $CH_2Cl_2$/MeCN; 79%. *g*) DIBAH, THF; 95%. *h*) $CF_3COOH$, $Ac_2O$; 70%. *i*) $PhSSiMe_3$, $ZnI_2$, $CH_2Cl_2$; 78%. *j*) 1. NaOMe, MeOH, *IR 120* ($H^+$); 2. BzCl, pyridine; 78%). *k*) 1 Equiv. of **9**, NIS, TfOH (cat.), PhMe; 80–85%. *l*) $Me_3SiOTf$, $Ac_2O$; 61–66%. *m*) NaOMe, MeOH, *IR 120* ($H^+$); 96%. *n*) DIBAH, THF; 95%. *o*) $P_2O_5$, $CH_2(OMe)_2$/$CH_2Cl_2$; 75% from **14**. *p*) BuLi, $Me_3GeCl$; 93%.

of $LiC\equiv CSiMe_3$, reductive dehydroxylation [14] (→ **8**, 79%), and deacetylation with diisobutylaluminium hydride (DIBAH) in THF gave the glycosyl acceptor **9** (95%; 48% from **1**).

A number of glycosyl donors were examined4). The thioglycosides **12** and **13** gave the best results. They were prepared from the known [3] diol **10** by acetolysis to the crystalline **11** (70%). Treatment of **11** with $PhSSiMe_3$ in the presence of $ZnI_2$ [16] yielded 78% of the crystalline $\beta$-D-thioglycoside **12**, which was transformed into the crystalline tribenzoate **13** (78%) by *Zemplén* deacetylation followed by benzoylation. Treatment of a 1:1 mixture of **9** and **12** with *N*-iodosuccinimide (NIS) in the presence of catalytic amounts of trifluoromethanesulfonic acid (TfOH) [17] led in less than 5 min to a complete conversion to the dialkyne **14** that was isolated in yields of 80–86%. The yield was not affected by performing the reaction on a gram scale. Similarly, glycosidation of **9** with the benzoate **13** led to **15** that was isolated in only marginally higher yields. Acetolysis ($Ac_2O$/$Me_3SiOTf$) of the benzylated disaccharides **14** and **15** gave the esters **16** (61%) and **17** (66%), respectively. Deacetylation of the hexaacetate **16** led to the cellobiose-derived dialkyne **18** (96%).

The structure of **17** was established by X-ray analysis5) (*Fig. 2*). The two pyranose residues adopt a ${}^4C_1$-conformation, as shown by their endocyclic dihedral angles (*Table 1*). The glycosidic linkage is characterized by the dihedral angles $\Phi$(O(5′)–C(1′)–O(6)–C(6)) = −70.5° and $\Psi$(C(1′)–O(6)–C(6)–C(5)) = −58.1°. The *gg*-conformation of the benzoyloxymethyl group is characterized by the exocyclic dihedral angles $\chi^1 = -72.0°$ and $\chi^{1'} = 47.3°$, the *gt*-conformation of the acetoxymethyl group by $\chi^2 = 76.6°$ and $\chi^{2'} = 163.8°$. The ethynyl substituents are nearly linear; the bond angles C(1)–C(2)–C(3) and C(4′)–C(7′)–C(8′) are 178.2 and 178.0°, respectively. The distance between C(1) and C(8′) is 11.7 Å.

The temperature dependence of the chemical shifts of the OH resonances of **18** in $D_6$(DMSO) is shown in *Fig. 3*. A C(5′)–O···HO–C(5) intramolecular H-bond is evidenced both by the low coefficient ($\Delta\delta/\Delta T = -1.71$ ppb/°C) for HO–C(5) and the small coupling constant (${}^3J$(HO,H) = 1.7 Hz) which indicates a dihedral angle H–O–C(5)–H of *ca.* 90°. A comparable behaviour is found for methyl $\beta$-D-cellobioside

Table 1. *Selected Dihedral Angles* [°] *of* **17**

| | | | |
|---|---|---|---|
| O(5′)–C(1′)–O(6)–C(6) ($\Phi$) | −70.5 | C(1′)–O(6)–C(6)–C(5) ($\Psi$) | −58.1 |
| O(5′)–C(5′)–C(6′)–O(6′) ($\chi^1$) | −72.0 | O(7)–C(7)–C(8)–O(8) ($\chi^2$) | 76.6 |
| C(4′)–C(5′)–C(6′)–O(6′) ($\chi^{1'}$) | 47.3 | C(6)–C(7)–C(8)–O(8) ($\chi^{2'}$) | −163.8 |
| C(1′)–C(2′)–C(3′)–C(4′) | −54.2 | C(3)–C(4)–C(5)–C(6) | −55.9 |
| C(2′)–C(3′)–C(4′)–C(5′) | 53.9 | C(4)–C(5)–C(6)–C(7) | 58.1 |
| C(3′)–C(4′)–C(5′)–O(5′) | −57.0 | C(5)–C(6)–C(7)–O(7) | −61.0 |
| C(4′)–C(5′)–O(5′)–C(1′) | 65.4 | C(6)–C(7)–O(7)–C(3) | 65.0 |
| C(5′)–O(5′)–C(1′)–C(2′) | −64.9 | C(7)–O(7)–C(3)–C(4) | −63.0 |
| O(5′)–C(1′)–C(2′)–C(3′) | 57.0 | O(7)–C(3)–C(4)–C(5) | 57.3 |

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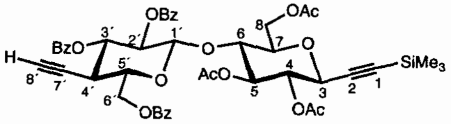
4) The thioglycosides **12** and **13** and the glycosyl fluoride, bromide, trichloroacetimidate, and phenyltetrazole, corresponding to **12**, among others [15].

5) Coordinates and thermal parameters were deposited with the *Cambridge Crystallographic Data Center*, 12 Union Road, Cambridge CB2 1EZ, England.



**17**

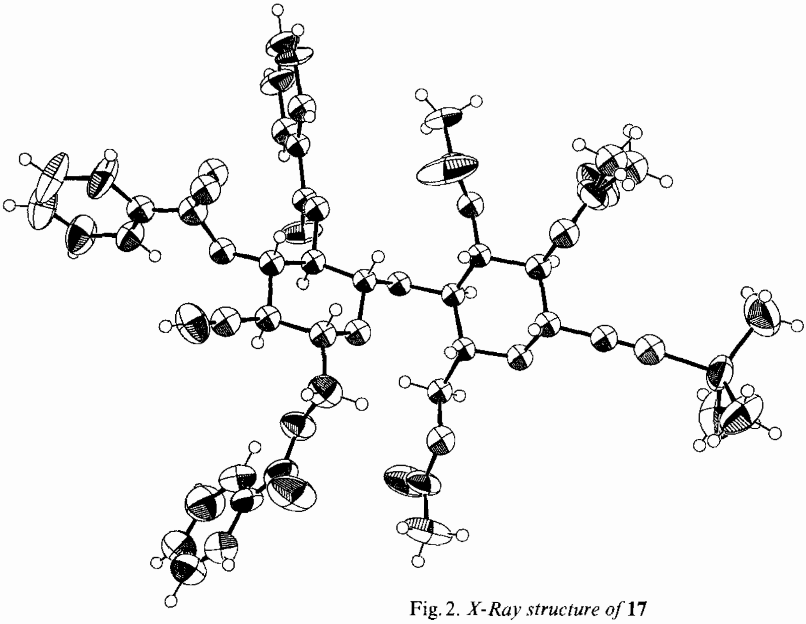


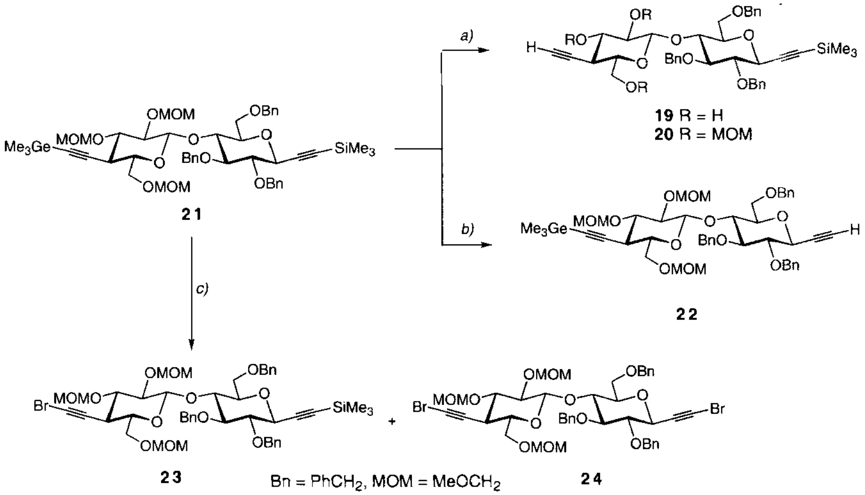
Fig. 2. *X-Ray structure of* **17**

in DMSO solution [18]; the two compounds should thus possess a very similar conformation.

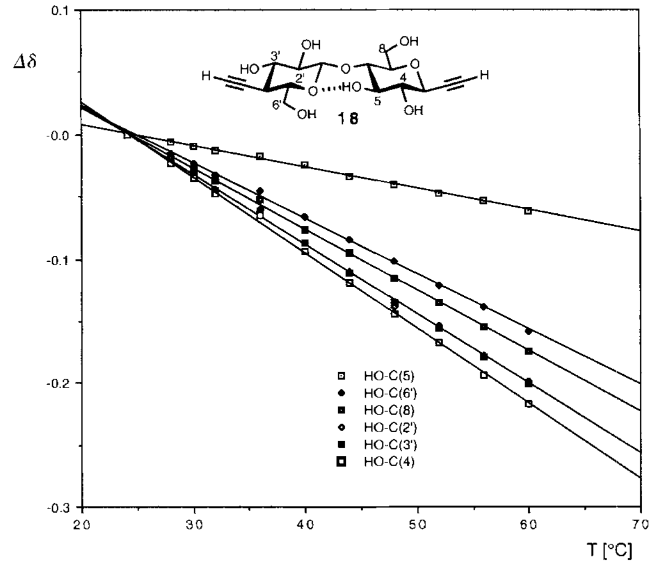
To investigate the orthogonal deprotection and selective bromodegermylation, we prepared the *C*-GeMe$_3$/*C*-SiMe$_3$ protected-dialkyne **21** (*Scheme 1*) in three steps (69% overall yield) from **14**. The protodesilylation (*Scheme 2*) of **21** with $K_2CO_3$ in MeOH to **22** (92%) proceeded without affecting the Me$_3$Ge group.

Trialkylgermyl-protected alkynes have been protodegermylated with strong acids [19] [20]. Under these conditions, *C*-SiMe$_3$-protected alkynes are expected to be stable. Heating the dialkyne **21** for 48 h at 40° in 1N aqueous methanolic HCl/THF 1:1 yielded indeed 80% of the degermylated triol **19**. No signals of desilylated products were found in the $^1$H-NMR spectrum of the reaction mixture. The bromodegermylation of **21** with *N*-bromosuccinimide (NBS) and catalytic amounts of $CF_3COOAg$ in acetone gave a mixture of the monobromodialkyne **23** (85%) and the dibromodialkyne **24** (11%) together with 1% of the starting material. The reactivity of *C*-GeMe$_3$-protected alkynes towards hard electrophiles (*vide supra*) suggests that metal ions harder than Ag$^+$ should catalyze the bromo- and the protodegermylation. Indeed, treating **21** with NBS (1.2 equiv.) and CuBr (5 mol-%) in acetone led exclusively to the monobromodialkyne **23** (93%). No trace of the dibromo-

*Scheme 2*



*a*) *Conditions A*: 1N HCl in MeOH, THF; **19** (80%); *Conditions B*: CuBr (10 mol-%), THF/MeOH; **20** (95%). *b*) $K_2CO_3$ in $CH_3OH$; 90%. *c*) *Conditions A*: CuBr (5 mol-%), NBS, acetone; **23** (93%); *Conditions B*: $CF_3COOAg$ (5 mol-%), NBS, acetone; **23** (85%), **24** (11%), **21** (1%).



| | $\Delta\delta/\Delta T$ [ppb/°C] |
|---|---|
| HO–C(5) | -1.71 |
| HO–C(6') | -4.44 |
| HO–C(8) | -4.87 |
| HO–C(2') | -5.58 |
| HO–C(3') | -5.62 |
| HO–C(4) | -6.09 |

Fig. 3. *Temperature dependence of hydroxy proton chemical shifts in the $^1$H-NMR spectrum of* **18** *in* $(D_6)$*DMSO solution*

dialkyne **24** was found in an analytical HPLC of the crude product. Catalysis by CuBr allows to perform the protodegermylation under much milder conditions. Treatment of **21** in the presence of CuBr (10 mol-%) with THF/MeOH as the proton source proceeded with exclusive degermylation to yield 95% of **20**.

Exploratory experiments indicate that a variety of *C*-$GeMe_3$/*C*-$SiMe_3$-protected dialkynes are exclusively proto- and bromodegermylated in the presence of catalytic amounts of CuBr in THF/MeOH or in acetone/NBS [21] [22].

We thank the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support, and Dr. *Bernd Schweizer*, ETHZ, for the X-ray analysis.

## Experimental Part

*General.* Solvents were distilled before use: THF, toluene, and dimethoxymethane from Na-benzophenone-ketyl, $CH_2Cl_2$ and MeOH from $CaH_2$, and acetone from $CaSO_4$. NaH dispersion was washed with pentane (5 × ) and dried for 1–2 h under high vaccum (h.v.). NIS was recrystallized from dioxane/$CCl_4$, NBS from $H_2O$. HCl in aq. MeOH was prepared by mixing 83 ml of 37% HCl soln. with 917 ml of MeOH. Reactions were run under Ar or $N_2$. Usual workup: The mixture was diluted with the indicated solvent and $H_2O$ and the aq. layer extracted 3 times with the indicated solvent. The combined org. layers were dried ($MgSO_4$) and evaporated at 40°. Qual. TLC: precoated silica-gel plates (*Merck* silica gel *60 $F_{254}$*), detection by spraying with 5% $H_2SO_4$ in EtOH followed by heating to *ca.* 200°. Flash chromatography (FC): silica gel *Merck 60* (0.04–0.063 mm). Anal. HPLC: *Spherisorb* silica (5 μm), 250 × 4.6 mm column, flow 2.5 ml/min; retention times ($t_R$) in min. M.p's: uncorrected. Optical rotations: 1-dm cell at 20 or 25°, 589 nm. FT-IR: 1–2% soln. in the indicated solvent. $^1H$- and $^{13}C$-NMR: 200, 300, 400, or 500 MHz and 50, 75, 100, or 125 MHz, resp. Mass spectra: chemical ionization (CI) with $NH_3$; fast atom bombardement (FAB; 3-NOBA = 3-nitrobenzyl alcohol) or matrix-assisted laser-desorption ionization time-of-flight MALDI-TOF MS; (sample preparation for MALDI-TOF: a soln. of the sample in DMSO was mixed with the same volume of 0.1M α-cyano-4-hydroxycinnamic acid (CCA) in $H_2O$/MeCN 1:2 containing 0.1% $CF_3COOH$.

*Allyl 2,3,6-Tri-*O*-benzyl-α-*D*-glucopyranoside* (**2**) *and Allyl 2,3,4-Tri-*O*-benzyl α-*D*-glucopyranoside* (**3**). A soln. of **1** [23] (30 g, 61.5 mmol) and $NaCNBH_3$ (14.45 g, 246 mmol) in THF (600 ml) was treated at r.t. with 4-Å molecular sieves (20 g), stirred for 5 min, treated dropwise with 1N HCl in $Et_2O$ (246 ml, 246 mmol) and stirred for further 30 min. Filtration through a pad of *Celite*, usual workup ($Et_2O$), and drying for 12 h under h.v. gave 31.2 g of a yellow suspension, which was used for the next step. FC (hexane/AcOEt 4:1) of a small sample (140 mg) gave 110 mg of **2** and 21.8 mg of **3**.

*Data of* **2**: Colourless oil. $R_f$ (hexane/AcOEt 2:1) 0.48. $[\alpha]_D^{25} = +28.0$ ($c = 0.46$, $CHCl_3$). IR ($CCl_4$): 3590*m*, 3090*m*, 3070*m*, 3030*m*, 2920*s*, 2870*s*, 1950*w*, 1500*s*, 1450*s*, 1360*s*, 1210*m*, 1100*s*, 1061*s*, 1030*s*, 990*s*, 930*m*. $^1H$-NMR (400 MHz, $CDCl_3$): see *Table 2*; additionally, 7.37–7.26 (*m*, 15 arom. H); 5.91 (*dddd*, $J = 17.1, 10.3, 5.1, 2.3$, $CH{=}CH_2$); 5.32 (*dq*, $J \approx 17.2, 1.6$), 5.22 (*dq*, $J \approx 10.4, 1.2$, $CH{=}CH_2$); 5.01 (*d*, $J = 9.5$, PhC*H*); 4.74 (*d*, $J = 11.3$, 2 PhC*H*); 4.65 (*d*, $J = 12.0$, PhC*H*); 4.59 (*d*, $J = 12.2$, PhC*H*); 4.53 (*d*, $J = 12.2$, PhC*H*); 4.17 (*ddt*, $J = 12.9, 5.2, 1.5$, 1 allyl. H); 4.01 (*ddt*, $J = 12.9, 2.4, 1.2$, 1 allyl. H); 2.34 (*d*, $J = 2.4$, HO–C(4)). $^{13}C$-NMR (100 MHz, $CDCl_3$): see *Table 2*; additionally, 138.87 (*s*); 138.11 (*s*); 138.03 (*s*); 133.76 ($CH{=}CH_2$, *d*); 128.57–126.99 (several *d*); 118.24 (*t*, $CH{=}CH_2$); 75.42 (*t*, $PhCH_2$); 73.56 (*t*, $PhCH_2$); 72.96 (*t*, $PhCH_2$); 69.45 (*t*, $OCH_2CH{=}CH_2$). CI-MS ($CH_2Cl_2$): 508.2 (12, $[M + NH_4]^+$), 450 (6, $[M + NH_4 - OAll]^+$), 433.1 (4, $[M - OAll]^+$), 399.1 (6), 341.1 (10), 325.1 (7), 253.1 (21), 240.1 (10), 217.1 (10), 203.1 (13), 181.1 (26), 147.1 (18), 108.1 (30), 91.0 (100). Anal. calc. for $C_{30}H_{34}O_6$ (490.60): C 73.45, H 6.99; found: C 73.37, H 7.30.

*Data of* **3**: Colourless oil. $R_f$ (hexane/AcOEt 2:1) 0.29. $[\alpha]_D^{25} = +44.1$ ($c = 2.56$, $CHCl_3$). IR ($CHCl_3$): 3595*m*, 3090*m*, 3070*m*, 3005*s*, 2925*m*, 2875*m*, 1952*w*, 1869*w*, 1810*w*, 1646*w*, 1605*w*, 1497*m*, 1454*s*, 1397*m*, 1360*s*, 1248*m*, 1157*s*, 1070*s*, 1028*s*, 934*m*. $^1H$-NMR (300 MHz, $CDCl_3$): see *Table 2*; additionally, 7.38–7.27 (*m*, 15 arom. H); 5.92 (*dddd*, $J = 17.1, 10.2, 5.2, 2.3$, $CH{=}CH_2$); 5.33 (*dq*, $J \approx 17.4, 1.8$), 5.22 (*dq*, $J = 10.2, 1.3$, $CH{=}CH_2$); 5.01 (*d*, $J = 10.8$, PhC*H*); 4.89 (*d*, $J = 10.9$, PhC*H*); 4.84 (*d*, $J = 11.8$, PhC*H*); 4.78 (*d*, $J = 11.8$, PhC*H*); 4.66 (*d*, $J = 12.3$, PhC*H*); 4.65 (*d*, $J = 12.2$, PhC*H*); 4.15 (*ddt*, $J = 12.9, 5.2, 1.5$, 1 allyl. H); 4.02 (*ddt*, $J = 13.0, 2.3, 1.2$, 1 allyl. H); 1.65 (br. *t*, $J \approx 6.3$, HO–C(6)). $^{13}C$-NMR (50 MHz, $CDCl_3$: see *Table 2*; additionally, 139.19 (*s*); 138.54 (2*s*); 134.08 (*d*, $CH{=}CH_2$); 128.86–128.26 (several *d*); 118.62 (*t*, $CH{=}CH_2$); 76.01 (*t*, $PhCH_2$); 75.37 (*t*, $PhCH_2$); 73.54

(*t*, Ph*C*H$_2$); 68.58 (*t*, O*C*H$_2$CH=CH$_2$). CI-MS (CH$_2$Cl$_2$): 508.2 (12, [*M* + NH$_4$]$^+$), 450 (6, [*M* − OAll]$^+$), 433.1 (4), 399.1 (6), 341.1 (10), 325.1 (7), 253.1 (21), 240.1 (10), 217.1 (10), 203.1 (13), 181.1 (26), 147.1 (18), 108.1 (30), 91.0 (100). Anal. calc. for $C_{30}H_{34}O_6$ (490.60): C 73.45, H 6.99; found: C 73.61, H 6.88.

*(Z)-Prop-1-enyl 2,3,6-Tri-*O*-benzyl-α-*D*-glucopyranoside* (**4**). A soln. of crude **2** (30 g, 61.2 mmol) in DMSO (600 ml) was treated with one batch of $^t$BuOK (27.5 g, 245 mmol) at 25°. The yellow mixture was heated for 2–3 h at 80° (→ dark brown) and cooled to r.t. Usual workup (AcOEt) and drying for 12 h under h.v. gave 29.2 g of **4** as an orange oil, which was used for the next step. A small sample (*ca.* 100 mg) was purified by FC (hexane/AcOEt 6:1). Colourless oil. $R_f$ (toluene/AcOEt 10:1) 0.34. $[\alpha]_D^{25} = +14.3$ ($c = 1.1$, CHCl$_3$). IR (CCl$_4$): 3594*m*, 3526*m*, 3090*m*, 3066*m*, 3033*m*, 2920*m*, 2866*m*, 2336*w*, 1947*w*, 1872*w*, 1806*w*, 1744*w*, 1672*m*, 1606*w*, 1497*m*, 1454*m*, 1404*m*, 1363*m*, 1344*m*, 1250*m*, 1208*m*, 1150*s*, 1105*s*, 1050*s*, 908*w*, 858*w*, 697*s*, 665*w*, 609*w*. $^1$H-NMR (200 MHz, CDCl$_3$): see *Table 2*; additionally, 7.41–7.25 (*m*, 15 arom. H); 6.03 (*dq*, *J* = 6.2, 1.7, C*H*=CHMe); 5.03 (*d*, *J* = 11.3, PhC*H*); 4.80 (*d*, *J* = 11.4, PhC*H*); 4.79 (*d*, *J* = 12.0, PhC*H*); 4.66 (*d*, *J* = 12.0, PhC*H*); 4.63 (*qd*, *J* = 6.9, 6.2, CH=C*H*Me); 4.60 (*d*, *J* = 11.6, PhC*H*); 4.51 (*d*, *J* = 12.1, PhC*H*); 2.44 (*d*, *J* = 2.0, HO–C(4)); 1.66 (*dd*, *J* = 7.0, 1.7, CH=CH*Me*). $^{13}$C-NMR (75 MHz, CDCl$_3$): see *Table 2*; additionally, 142.06 (*d*, O*C*H=CH); 138.70 (*s*); 138.01 (*s*); 137.88 (*s*); 128.44–127.63 (several *d*); 104.71 (*d*, OCH=*C*H); 75.36 (*t*, Ph*C*H$_2$); 73.45 (*t*, Ph*C*H$_2$); 72.95 (*t*, Ph*C*H$_2$); 9.52 (*q*, CH*Me*). CI-MS (CH$_2$Cl$_2$): 508.3 (7, [*M* + NH$_4$]$^+$), 450.2 (12), 433.2 (6), 341.2 (24), 325.2 (38), 307.2 (7), 271.2 (46), 235.2 (25), 217.1 (46), 181.1 (100), 91.1 (100). Anal. calc. for $C_{30}H_{34}O_6$ (490.60): C 73.45, H 6.99; found: C 73.42, H 6.98.

*(Z)-Prop-1-enyl 4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-α-*D*-glucopyranoside* (**5**). A soln. of crude **4** (24.5 g, 50 mmol) in CH$_2$Cl$_2$ (100 ml), pyridine (16 ml, 200 mmol), and Ac$_2$O (14.2 ml, 150 mmol) was stirred for 4 h at r.t. Usual workup (Et$_2$O) and drying for 12 h under h.v. gave 26.4 g of **5** as a red oil, which was used for the next step. A small sample (*ca.* 100 mg) was purified by FC (hexane/AcOEt 6:1). Colourless oil. $R_f$ (toluene/AcOEt 5:1) 0.61. $[\alpha]_D^{25} = +15.6$ ($c = 1.0$, CHCl$_3$). IR (CCl$_4$): 3090*m*, 3066*m*, 3032*m*, 2920*m*, 2865*m*, 1947*w*, 1872*w*, 1806*w*, 1748*s*, 1672*m*, 1606*w*, 1497*m*, 1453*m*, 1403*m*, 1363*m*, 1230*s*, 1104*s*, 1050*s*, 1030*s*, 908*w*, 857*w*, 697*s*, 669*w*. $^1$H-NMR (400 MHz, CDCl$_3$): see *Table 2*; additionally, 7.35–7.23 (*m*, 15 arom. H); 6.03 (*dq*, *J* = 6.2, 1.7, C*H*=CHMe); 4.90 (*d*, *J* = 11.6, PhC*H*); 4.78 (*d*, *J* = 12.1, PhC*H*); 4.67 (*d*, *J* = 11.3, PhC*H*); 4.63 (*d*, *J* = 12.0, PhC*H*); 4.63 (*qd*, *J* = 6.8, 6.2, CH=C*H*Me); 4.50 (*d*, *J* = 11.8, PhC*H*); 4.45 (*d*, *J* = 11.8, PhC*H*); 1.84 (*s*, AcO); 1.68 (*dd*, *J* = 6.9, 1.7, CH=CH*Me*). $^{13}$C-NMR (100 MHz, CDCl$_3$): see *Table 2*; additionally, 169.61 (*s*, C=O); 142.08 (*d*, O*C*H=CH); 138.60 (*s*); 138.02 (*s*); 137.79 (*s*); 128.50–127.58 (several *d*); 104.91 (*d*, OCH=*C*H); 75.22 (*t*, Ph*C*H$_2$); 73.46 (*t*, Ph*C*H$_2$); 73.33 (*t*, Ph*C*H$_2$); 20.84 (*q*, Me); 9.59 (*q*, Me). CI-MS (CH$_2$Cl$_2$): 550.3 (2, [*M* + NH$_4$]$^+$), 475.2 (4, [*M* − propenyloxy]$^+$), 383.2 (3), 307.2 (4), 271.2 (9), 241.2 (3), 217.1 (14), 181.1 (48), 91.1 (100). Anal. calc. for $C_{32}H_{36}O_7$ (532.63): C 72.16, H 6.81; found: C 72.04, H 6.70.

*4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-*D*-glucopyranose* (**6**). A soln. of crude **5** (23.2 g, 43.6 mmol) in THF/H$_2$O 4:1 (500 ml) and pyridine (14 ml, 174.4 mmol) was treated with one batch of I$_2$ (22.1 g, 87.2 mmol) at r.t. The deep violet mixture was stirred for 5 min, cooled to 0°, treated with 10% aq. Na$_2$SO$_3$ soln. (150 ml), and stirred for further 15 min (→ yellow suspension). The mixture was extracted (AcOEt), the extract washed successively with 10% aq. Na$_2$SO$_3$ soln., sat. NaHCO$_3$ soln., and brine, dried (MgSO$_4$), concentrated *ca.* 100 ml, and poured into ice-cooled hexane (1000 ml) with stirring. After 40 min, the brown precipitate was filtered off, air-dried, and recrystallized in six fractions from EtOH (95%) at +4°: 14.3 g of slightly yellow crystals. MPLC (CH$_2$Cl$_2$/AcOEt 20:1) of the mother liquor gave another 6.2 g of **6** (total 20.5 g, 64% from **1**). $R_f$ (hexane/AcOEt 1:1) 0.62. M.p. 112–113°. $[\alpha]_D^{25} = +10.9$ ($c = 1.0$, CHCl$_3$). IR (CCl$_4$): 3606*m*, 3438*m*, 3090*m*, 3066*m*, 3032*m*, 2918*m*, 2890*m*, 1947*w*, 1871*w*, 1748*s*, 1606*w*, 1497*m*, 1454*s*, 1363*s*, 1329*w*, 1230*s*, 1100*s*, 1058*s*, 1028*s*, 908*w*, 855*w*, 697*s*, 647*w*, 600*w*. $^1$H-NMR (400 MHz, CDCl$_3$; α-D/β-D-**6** 72:28): see *Table 2*; additionally, 7.51–7.24 (*m*, 15 arom, H); 4.92 (*d*, *J* = 11.1, 0.28 H), 4.86 (*d*, *J* = 11.5, 0.72 H, PhC*H*); 4.81 (*d*, *J* = 11.5, 0.28 H), 4.76 (*d*, *J* = 11.8, 0.72 H, PhC*H*); 4.73 (*d*, *J* = 11.9, 0.28 H), 4.66 (*d*, *J* = 11.8, 0.72 H, PhC*H*); 4.64 (*d*, *J* = 11.6, 0.72 H), 4.61 (*d*, *J* = 11,6, 0.28 H, PhC*H*); 4.52 (*d*, *J* = 12.0, 0.28 H), 4.51 (*d*, *J* = 12.1, 0.72 H, PhC*H*); 4.49 (*d*, *J* = 11.9, 0.28 H), 4.47 (*d*, *J* = 12.0, 0.72 H, PhC*H*); 3.46 (*d*, *J* = 2.7, 0.28 H), 3.18 (br. *d*, *J* ≈ 2.0, 0.72 H, HO–C(1)); 1.83 (*s*, 2.16 H), 1.82 (*s*, 0.84 H, AcO). $^{13}$C-NMR (100 MHz, CDCl$_3$; α-D/β-D-**6** 72:28): see *Table 2*; additionally, α-D-anomer: 169.72 (*s*, C=O); 138.50 (*s*); 137.74 (*s*); 137.91 (*s*); 128.53–127.83 (several *d*); 75.24 (*t*, Ph*C*H$_2$); 73.58 (*t*, Ph*C*H$_2$); 73.41 (*t*, Ph*C*H$_2$); 20.82 (*q*, Me); β-D-anomer: 169.75 (*s*, C=O); 138.32 (*s*); 138.18 (*s*); 137.60 (*s*); 128.42–127.63 (several *d*); 75.14 (*t*, Ph*C*H$_2$); 74.85 (*t*, Ph*C*H$_2$); 73.67 (*t*, Ph*C*H$_2$); 20.70 (*q*, Me). CI-MS (CH$_2$Cl$_2$): 510.3 (3, [*M* + NH$_4$]$^+$), 475.2 (4, [*M* − OH]$^+$), 383.2 (3), 295.2 (4), 277.2 (2), 234.1 (2), 217.1 (7), 181.1 (12), 91.1 (100). Anal. calc. for $C_{29}H_{32}O_7$ (492.57): C 70.71, H 6.55; found: C 70.49, H 6.54.

*4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-*D*-glucono-1,5-lactone* (**7**). A soln. of **6** (10 g, 20.3 mmol) in CH$_2$Cl$_2$ (100 ml) was treated with one batch of *Dess-Martin*'s periodinane (10.34 g, 24.4 mmol) at r.t. and stirred for further 30 min. Usual workup (Et$_2$O) gave 9.9 g (99%) of **7**. Colourless oil. $R_f$ (hexane/AcOEt 2:1) 0.46. $[\alpha]_D^{25} = +55.1$ ($c$ = 1.1,

$CHCl_3$). IR ($CCl_4$): 3090*w*, 3066*m*, 3033*m*, 2868*m*, 1947*w*, 1872*w*, 1767*s*, 1744*s*, 1605*w*, 1497*m*, 1454*s*, 1367*s*, 1226*s*, 1163*m*, 1125*s*, 1046*s*, 1028*s*, 909*m*, 857*m*, 697*s*. $^1$H-NMR (300 MHz, $CDCl_3$): see *Table 2*; additionally, 7.24–7.36 (*m*, 15 arom. H); 4.97 (*d*, $J = 11.3$, PhC*H*); 4.75 (*d*, $J = 11.8$, PhC*H*); 4.64 (*d*, $J = 12.0$, PhC*H*); 4.57 (*d*, $J = 11.3$, PhC*H*); 4.54 (*s*, Ph$CH_2$). $^{13}$C-NMR (50 MHz, $CDCl_3$): see *Table 2*; additionally, 169.98 (*s*, C=O); 137.59 (*s*); 137.68 (*s*); 137.04 (*s*); 128.48–128.82 (several *d*); 73.98 (*t*, Ph$CH_2$); 73.72 (*t*, Ph$CH_2$); 73.54 (*t*, Ph$CH_2$); 20.73 (*q*, Me). CI-MS ($CH_2Cl_2$): 508 (100, $[M + NH_4]^+$), 491.1 (26, $[M + H]^+$), 490.1 (70, $M^+$), 399.1 (13), 398.0 (34), 310.1 (16), 292.1 (47), 202.2 (39), 180.3 (31), 90.6 (95). Anal. calc. for $C_{29}H_{30}O_7$ (490.55): C 71.01, H 6.16; found: C 70.92, H 5.97.

*6-O-Acetyl-3,7-anhydro-4,5,8-tri-O-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1-C-(trimethylsilyl)-*D-glycero-D-gulo-*octitol* (**8**). A soln. of $HC{\equiv}CSiMe_3$ (3 ml, 21.8 mmol) in THF (180 ml) was treated at −78° dropwise with 1.24M BuLi (17.6 ml, 21.8 mmol), stirred for 10 min, treated dropwise with a soln. of **7** (8.9 g, 18.2 mmol) in THF (20 ml) within 2 min at −78°, and stirred for further 30 min. The mixture was carefully neutralized by dropwise addition of 1N methanolic HCl (21.8 ml) and warmed to r.t. Usual workup ($Et_2O$) and drying under h.v. for 3 h gave 11.2 g of an orange oil ($R_f$ (hexane/AcOEt 3:1) 0.36), which was dissolved in $CH_2Cl_2$/MeCN 1:1 (180 ml) and $Et_3SiH$ (14.4 ml, 90.8 mmol), treated dropwise with $BF_3 \cdot OEt_2$ (11.4 ml, 90.8 mmol) at −20°, stirred for further 10 min, and poured into $Et_2O$/sat. $NaHCO_3$ soln. 1:1 (200 ml). Usual workup ($Et_2O$) and MPLC (hexane/AcOEt 85:15) gave 8.2 g (79%) of **8**. Slightly-yellow oil. $R_f$ (hexane/AcOEt 3:1) 0.60. $[\alpha]_D^{25} = -21.1$ ($c = 4.0$, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3065*m*, 3010*m*, 2960*m*, 2870*m*, 2810*m*, 1740*s*, 1495*m*, 1455*m*, 1360*s*, 1295*w*, 1065*s*, 1030*s*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.38–7.23 (*m*, 15 arom. H); 5.01 (*d*, $J = 10.4$, PhC*H*); 4.99 (*t*, $J \approx 9.3$, H−C(6)); 4.82 (*d*, $J = 11.6$, PhC*H*); 4.78 (*d*, $J = 10.4$, PhC*H*); 4.59 (*d*, $J = 11.9$, PhC*H*); 4.51 (*s*, Ph$CH_2$); 4.07 (*d*, $J = 9.6$, H−C(3)); 3.65 (*t*, $J \approx 9.3$, H−C(4)); 3.54 (*t*, $J \approx 9.2$, H−C(5)); 3.52–3.46 (*m*, 2 H−C(8), H−C(7)); 1.57 (*s*, AcO); 0.18 (*s*, $SiMe_3$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 169.97 (*s*, C=O); 138.61 (*s*); 138.19 (*s*); 138.06 (*s*); 128.73–128.00 (several *d*); 102.24 (*s*, *C*≡C−Si); 92.01 (*s*, C≡*C*−Si); 83.33 (*d*, C(5)); 82.46 (*d*, C(4)); 77.81 (*d*, C(7)); 71.08 (*d*, C(6)); 70.54 (*d*, C(3)); 69.78 (*t*, C(8)); 75.83 (*t*, Ph$CH_2$); 75.51 (*t*, Ph$CH_2$); 73.92 (*t*, Ph$CH_2$); 21.09 (*q*, Me); −0.25 (*q*, $SiMe_3$). CI-MS ($CH_2Cl_2$): 590.3 (100, $[M + NH_4]^+$), 481.2 (25), 375.2 (23), 315.2 (16), 283.2 (8), 235.1 (6), 217.1 (7), 181.1 (8), 145.1 (11), 108.1 (20), 91.1 (49). Anal. calc. for $C_{34}H_{40}O_6Si$ (592.67): C 71.30, H 7.04; found: C 71.19, H 6.88.

*3,7-Anhydro-4,5,8-tri-O-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1-C-(trimethylsilyl)-*D-glycero-D-gulo-*octitol* (**9**). A soln. of **8** (32.5 g, 56.8 mmol) in THF (570 ml) was treated dropwise with 1.5M DIBAH in toluene (113.6 ml, 170.5 mmol) within 1 h at 0°, stirred for further 60 min, diluted with $CH_2Cl_2$ (500 ml), and carefully quenched with 1N aq. HCl (500 ml). Usual workup ($CH_2Cl_2$) and MPLC (hexane/AcOEt 80:20) gave 28.6 g (95%) of **9**. Colourless oil. $R_f$ (toluene/AcOEt 5:1) 0.48. $[\alpha]_D^{20} = -41.3$ ($c = 1.3$, $CHCl_3$). IR ($CCl_4$): 3585*m*, 3525*m*, 3090*m*, 3065*s*, 3030*s*, 2960*s*, 2905*s*, 2890*s*, 2180*m*, 1950*w*, 1870*w*, 1805*w*, 1735*w*, 1610*w*, 1515*m*, 1495*s*, 1455*s*, 1360*s*, 1250*s*, 1210*m*, 1090*s*, 1030*s*, 910*m*, 845*s*, 695*s*, 615*w*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.53–7.24 (*m*, 15 arom. H); 5.03 (*d*, $J = 10.5$, PhC*H*); 4.91 (*d*, $J = 11.4$, PhC*H*); 4.79 (*d*, $J = 11.4$, PhC*H*); 4.76 (*d*, $J = 10.5$, PhC*H*); 4.58 (*d*, $J = 12.1$, PhC*H*); 4.54 (*d*, $J = 12.1$, PhC*H*); 4.06 (*d*, $J = 9.6$, H−C(3)); 3.71 (*d*, $J = 4.6$, 2 H−C(8)); 3.63 (*dt*, $J \approx 9.2$, 2.2, H−C(6)); 3.58 (*t*, $J \approx 9.3$, H−C(4)); 3.41 (*t*, $J \approx 9.2$, H−C(5)); 3.40 (*dt*, $J \approx 9.3$, 4.6, H−C(7)); 2.59 (*d*, $J = 2.3$, HO−C(6)); 0.17 (*s*, $SiMe_3$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 138.89 (*s*); 138.31 (*s*); 138.03 (*s*); 128.86–128.11 (several *d*); 102.66 (*s*, *C*≡C−Si); 91.71 (*s*, C≡*C*−Si); 85.52 (*d*, C(5)); 82.10 (*d*, C(4)); 78.32 (*d*, C(7)); 72.06 (*d*, C(6)); 70.54 (*d*, C(3)); 70.52 (*t*, C(8)); 75.62 (*t*, 2 Ph$CH_2$); 74.00 (*t*, Ph$CH_2$); −0.28 (*q*, $SiMe_3$). CI-MS ($CH_2Cl_2$): 548.4 (100, $[M + NH_4]^+$), 439.3 (26), 91.0 (58). Anal. calc. for $C_{32}H_{38}O_5Si$ (530.74): C 72.42, H 7.22; found: C 72.46, H 7.42.

*1,2,3,6-Tetra-O-acetyl-4-deoxy-4-C-ethynyl-α-*D*-glucopyranose* (**11**). A soln. of **10** (10 g, 58.8 mmol) in $Ac_2O$ (200 ml) and $CF_3COOH$ (67.5 ml, 882.3 mmol) was stirred for 16 h at 40°. Usual workup (AcOEt) gave a dark brown oil, which was filtered through a pad of silica gel (AcOEt). Evaporation and crystallization from $Et_2O$/hexane gave 14.6 g (70%) of **11**. White needles. $R_f$ (hexane/AcOEt 1:1) 0.29. M.p. 54–55°. $[\alpha]_D^{20} = +65.5$ ($c = 1.50$, $CHCl_3$). IR ($CHCl_3$): 3305*m*, 3040*m*, 2980*m*, 2875*w*, 1755*s*, 1430*w*, 1370*s*, 1150*m*, 1075*s*, 1030*m*, 1010*m*, 940*m*, 910*m*, 660*m*. $^1$H-NMR (400 MHz, $CDCl_3$): see *Table 2*; additionally, 2.18 (*s*, AcO); 2.11 (*s*, AcO); 2.10 (*s*, AcO); 2.01 (*s*, AcO). $^{13}$C-NMR (100 MHz, $CDCl_3$): see *Table 2*; additionally, 170.60 (*s*, C=O); 169.93 (*s*, C=O); 169.84 (*s*, C=O); 168.93 (*s*, C=O); 20.94 (*q*, Me); 20.78 (*q*, Me); 20.69 (*q*, Me); 20.52 (*q*, Me). CI-MS ($CH_2Cl_2$): 374.2 (100, $[M + NH_4]^+$), 297.1 (56, $[M - AcO]^+$), 254.1 (7), 237.1 (15), 208.1 (7), 195.1 (11), 166.1 (12), 124.0 (13), 106.0 (5). Anal. calc. for $C_{16}H_{20}O_9$ (356.33): C 53.93, H 5.66; found: C 53.95, H 5.84.

*Phenyl 2,3,6-Tri-O-acetyl-4-deoxy-4-C-ethynyl-1-thio-β-*D*-glucopyranoside* (**12**). A soln. of **11** (178 mg, 0.5 mmol) and $PhSSiMe_3$ (0.47 ml, 2.5 mmol) in $CH_2Cl_2$ (2 ml) at 0° was treated with one batch of $ZnI_2$ (798 mg, 2.5 mmol), stirred for 4 h, and filtered through *Celite*. Usual workup ($CH_2Cl_2$) and FC (hexane/AcOEt 9:1) gave 158 mg (78%) of **12** (α-D/β-D 1:6) as a colourless oil. Crystallization from AcOEt/hexane gave pure β-D-**12**. $R_f$ (toluene/AcOEt 3:1) 0.42. M.p. 87–88°. $[\alpha]_D^{25} = -30.2$ ($c = 1.1$, $CHCl_3$). IR ($CCl_4$): 3311*m*, 3063*w*, 2956*w*, 2865*w*, 1757*s*, 1585*w*, 1479*w*, 1440*m*, 1370*m*, 1229*s*, 1082*s*, 1053*s*, 947*w*, 913*w*, 832*w*, 691*m*, 649*m*, 606*w*. $^1$H-NMR (400 MHz, $CDCl_3$): see *Table 2*; additionally, 7.51–7.46 (*m*, 2 arom. H); 7.33–7.26 (*m*, 3 arom. H); 2.09 (*s*, AcO); 2.08 (*s*, AcO); 2.06 (*s*, AcO). $^{13}$C-NMR (100 MHz, $CDCl_3$): see *Table 2*; additionally, 170.52 (*s*, C=O); 169.87 (*s*, C=O); 169.57 (*s*, C=O); 131.92 (*s*); 133.04 (*d*); 128.89–128.30 (several *d*); 20.79 (*q*, 2 Me); 20.61 (*q*, Me). CI-MS ($CH_2Cl_2$): 424.0 (51, $[M + NH_4]^+$), 297.0 (62, $[M - SPh]^+$), 237.0 (30, $[M - SPh - AcOH]^+$), 195.0 (100, $[M - SPh - AcOH - C_2H_2O]^+$), 177.0 (23), 153.0 (15), 135.0 (44), 110.0 (13), 43.0 (24). Anal. calc. for $C_{20}H_{22}O_7S$ (406.46): C 59.10, H 5.46, S 7.89; found: C 59.07, H 5.35, S 8.02.

*Phenyl 2,3,6-Tri-*O*-benzoyl-4-deoxy-4-*C*-ethynyl-1-thio-β-*D*-glucopyranoside* (**13**). A soln. of **12** (295 mg, 0.73 mmol) in MeOH was treated dropwise with 3.5M NaOMe in MeOH (0.1 ml, 0.35 mmol), stirred for 1 h, neutralized with *Amberlite IR-120* ($H^+$ form), filtered, and evaporated. The resulting colourless oil ($R_f$ ($CH_2Cl_2$ MeOH 5:1) 0.67) was dissolved in pyridine (7 ml), cooled to 0°, treated dropwise with BzCl (0.35 ml, 2.92 mmol), and stirred for 12 h. Usual workup (AcOEt) and recrystallization of the crude product in hexane/AcOEt gave 338 mg (78%) of **13**. White needles. $R_f$ (hexane/AcOEt 6:1) 0.5. M.p. 161–162°. $[\alpha]_D^{25} = +61.8$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3305*m*, 3065*m*, 3010*m*, 2950*w*, 2870*w*, 1965*w*, 1730*s*, 1600*m*, 1585*m*, 1495*w*, 1480*w*, 1450*m*, 1315*m*, 1275*s*, 1125*s*, 1090*s*, 1070*s*, 1045*w*, 1030*w*, 1000*w*. $^1$H-NMR (400 MHz, $CDCl_3$): see *Table 2*; additionally, 8.10–8.07 (*m*, 2 arom. H); 7.97–7.93 (*m*, 4 arom. H); 7.65–7.61 (*m*, 1 arom. H); 7.54–7.45 (*m*, 6 arom. H); 7.40–7.36 (*m*, 4 arom. H); 7.26–7.20 (*m*, 1 arom. H); 7.15–7.11 (*m*, 2 arom. H). $^{13}$C-NMR (100 MHz, $CDCl_3$): see *Table 2*; additionally, 166.13 (*s*, C=O); 165.56 (*s*, C=O); 165.30 (*s*, C=O); 133.31 (*s*); 133.28 (*s*); 133.06 (*s*); 132.00 (*s*); 129.89–128.20 (several *d*). CI-MS ($CH_2Cl_2$): 610.2 (15, $[M + NH_4]^+$), 483.2 (50, $[M - SPh]^+$), 361.1 (52), 239.1 (7), 122.1 (10), 110.1 (10), 105.1 (100). Anal. calc. for $C_{35}H_{28}O_7S$ (592.67): C 70.92, H 4.76, S 5.41; found: C 70.86, H 4.86, S. 5.17.

O*-(2,3,6-Tri-*O*-acetyl-4-deoxy-4-*C*-ethynyl-β-*D*-glucopyranosyl)-(1→6)-3,7-anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo-*octitol* (**14**). A soln. of **9** (2.34 g, 4.42 mmol) and **12** (1.79 g, 4.42 mmol) in toluene (45 ml) was treated with powdered 4 Å-molecular sieves (500 mg) and stirred for 30 min at r.t. The mixture was cooled to 0° and treated with one batch of NIS (2.98 g, 13.25 mmol)

Table 2. *Selected $^1$H- and $^{13}$C-NMR* ($CDCl_3$) *Data of the Glycosides* **2–7** *and* **11–13**

| | **2** | **3** | **4** | **5** | α-D-**6** | β-D-**6** | **7** | **11** | **12** | **13** |
|---|---|---|---|---|---|---|---|---|---|---|
| H−C(1) | 4.84 | 4.78 | 4.96 | 4.94 | 5.19 | 4.71 | – | 6.32 | 4.71 | 4.98 |
| H−C(2) | 3.62 | 3.52 | 3.59 | 3.63 | 3.59 | 3.59 | 4.27 | 4.97 | 4.83 | 5.30 |
| H−C(3) | 3.82 | 4.01 | 3.90 | 3.99 | 3.93 | 3.41 | 3.85 | 5.54 | 5.26 | 5.76 |
| H−C(4) | 3.62 | 3.54 | 3.79–3.65 | 5.09 | 5.00 | 4.95 | 5.29 | 2.89 | 2.79 | 3.09 |
| H−C(5) | 3.77 | 3.80–3.67 | 3.79–3.65 | 3.84 | 4.09 | 3.59–3.41 | 4.50 | 4.15 | 3.74 | 4.06 |
| $H_a$−C(6) | 3.68 | 3.80–3.67 | 3.79–3.65 | 3.48 | 3.52 | 3.59–3.41 | 3.73 | 4.40 | 4.50 | 4.86 |
| $H_b$−C(6) | 3.67 | 3.80–3.67 | 3.79–3.65 | 3.42 | 3.45 | 3.59–3.41 | 3.68 | 4.32 | 4.28 | 4.60 |
| H−C≡C | – | – | – | – | – | – | – | 2.19 | 2.15 | 2.15 |
| *J*(1,2) | 3.6 | 3.6 | 3.5 | 3.5 | 3.6 | 7.6 | – | 3.6 | 10.0 | 10.0 |
| *J*(2,3) | 9.6 | 9.1 | 9.5 | 9.6 | 9.3 | b) | 7.7 | 10.1 | 9.1 | 9.3 |
| *J*(3,4) | 8.9 | *ca.* 9.3 | 8.3 | *ca.* 9.4 | 9.4 | *ca.* 9.4 | 5.9 | *ca.* 10.3 | 10.9 | 10.9 |
| *J*(4,5) | 9.7 | *ca.* 9.3 | b) | 10.2 | 10.1 | *ca.* 9.4 | *ca.* 6.5 | 10.9 | 10.5 | 10.5 |
| *J*(5,$6_a$) | 3.8 | b) | b) | 3.0 | 3.4 | b) | 3.6 | 2.3 | 2.2 | 2.2 |
| *J*(5,$6_b$) | 3.8 | b) | b) | 4.5 | 4.8 | b) | 3.6 | 4.4 | 5.8 | 6.0 |
| *J*($6_a$,$6_b$) | 11.0 | b) | b) | 10.9 | 10.8 | b) | 10.7 | 12.0 | 12.0 | 12.0 |
| *J*(4,C≡CH) | – | – | – | – | – | – | – | 2.4 | 2.4 | 2.4 |
| C(1) | 95.67 | 95.99 | 97.25 | 97.25 | 91.27 | 97.40 | 169.34 | 89.59 | 85.90 | 86.41 |
| C(2) | 79.59 | 80.33 | 79.25 | 79.11a) | 78.91 | 81.66 | 78.48a) | 68.91a) | 70.24 | 70.66 |
| C(3) | 81.48 | 82.23 | 81.13 | 79.33a) | 79.68 | 82.81 | 78.15a) | 70.93a) | 76.72 | 77.14 |
| C(4) | 70.78a) | 77.74 | 70.43a) | 69.40a) | 70.54 | 70.75 | 70.96 | 35.52 | 35.81 | 36.47 |
| C(5) | 70.05a) | 71.16 | 70.49a) | 70.25a) | 68.88 | 73.35 | 77.21 | 69.74a) | 73.53 | 73.96 |
| C(6) | 68.24 | 68.13 | 69.16 | 68.57 | 69.02 | 69.50 | 69.33 | 63.49 | 63.98 | 64.57 |
| C≡*C*−C(4) | – | – | – | – | – | – | – | 73.40 | 73.38 | 77.15 |
| *C*≡C−C(4) | – | – | – | – | – | – | – | 77.60 | 77.71 | 77.51 |

a) Assignments may be interchanged. b) Not determined.

followed by the dropwise addition of TfOH (0.12 ml, 1.33 mmol). The dark brown mixture was stirred for further 5 min, diluted with Et$_2$O (80 ml), treated with 1M aq. Na$_2$S$_2$O$_3$ (50 ml) and 10% aq. Na$_2$SO$_3$ soln. (50 ml), stirred for 10 min (→yellow), and filtered through *Celite*. Usual workup (Et$_2$O) and FC (hexane/AcOEt 4:1→3:1) gave 3.15 g (86%) of **14** as a slightly yellow oil. $R_f$ (Et$_2$O/hexane 1:1) 0.25. $[\alpha]_D^{25} = -20.2$ ($c$ = 1.1, CHCl$_3$). IR (CHCl$_3$): 3305*m*, 3040*m*, 2955*m*, 2115*w*, 1750*s*, 1495*w*, 1455*w*, 1365*m*, 1250*m*, 1125*m*, 1065*m*, 845*m*. $^1$H-NMR (500 MHz, CDCl$_3$): see *Table 3*; additionally, 7.43–7.22 (*m*, 15 arom. H); 4.99 (*d*, $J$ = 11.0, PhC*H*); 4.89 (*d*, $J$ = 10.4, PhC*H*); 4.79 (*d*, $J$ = 12.0, PhC*H*); 4.71 (*d*, $J$ = 10.9, PhC*H*); 4.68 (*d*, $J$ = 10.4, PhC*H*); 4.46 (*d*, $J$ = 12.0, PhC*H*); 2.05 (*s*, AcO); 1.95 (*s*, AcO); 1.93 (*s*, AcO); 0.17 (*s*, SiMe$_3$). $^{13}$C-NMR (125 MHz, CDCl$_3$): see *Table 5*; additionally, 170.63 (*s*, C=O); 169.92 (*s*, C=O); 169.47 (*s*, C=O); 139.22 (*s*); 138.04 (*s*); 137.74 (*s*); 128.70–127.20 (several *d*); 75.50 (*t*, PhCH$_2$); 75.00 (*t*, PhCH$_2$); 73.70 (*t*, PhCH$_2$); 20.75 (*q*, Me); 20.66 (*q*, Me); 20.64 (*q*, Me); –0.28 (*q*, SiMe$_3$). FAB-MS (3-NOBA): 849.3 (2, [$M$ + Na]$^+$), 827.3 (5, $M^+$), 825.3 (7), 297.1 (55, [$M$ – aglycone]$^+$), 195.1 (52), 135.0 (44), 91.0 (100). Anal. calc. for C$_{46}$H$_{54}$O$_{12}$Si (827.01): C 66.81, H 6.58; found: C 66.79, H 6.74.

Table 3. *Selected $^1$H-NMR and IR Data of Dialkynes* **14–18**

| | **14**<br>CDCl$_3$ | **15**<br>C$_6$D$_6$ | **16**<br>CDCl$_3$ | **16**<br>C$_6$D$_6$ | **17**<br>CDCl$_3$ | **18**<br>CD$_3$OD | **18**<br>(D$_6$)DMSO |
|---|---|---|---|---|---|---|---|
| H–C(1) | – | – | – | – | – | 2.89 | 3.31 |
| H–C(3) | 3.99 | 3.81 | 4.13 | 3.94 | 4.02 | 3.94 | 3.85 |
| H–C(4) | 3.55 | 3.56 | 5.06 | 5.37 | 5.03 | 3.37 | 3.14 |
| H–C(5) | 3.47 | 3.40 | 5.13 | 5.27 | 5.16 | 3.56 | 3.30–3.25 |
| H–C(6) | 3.95 | 4.26 | 3.75 | 3.46 | 3.77 | 3.46 | 3.28 |
| H–C(7) | 3.24–3.29 | 2.79 | 3.55 | 3.08 | 3.44 | 3.40–3.31 | 3.30 |
| H$_a$–C(8) | 3.73 | 3.76 | 4.48 | 4.45 | 4.23 | 3.88 | 3.56 |
| H$_b$–C(8) | 3.73 | 3.41 | 4.08 | 4.04 | 4.07 | 3.82 | 3.70 |
| H–C(1′) | 4.54 | 5.01 | 4.47 | 4.18 | 4.71 | 4.40 | 4.27 |
| H–C(2′) | 4.70 | 5.66 | 4.76 | 4.96 | 5.31 | 3.15 | 2.92 |
| H–C(3′) | 5.00 | 5.89 | 5.17 | 5.32 | 5.70 | 3.51 | 3.26 |
| H–C(4′) | 2.70 | 2.90 | 2.79 | 2.58 | 3.10 | 2.48 | 2.29 |
| H–C(5′) | 3.24–3.29 | 3.56 | 3.67 | 3.24 | 3.95 | 3.56–3.48 | 3.40 |
| H$_a$–C(6′) | 4.20 | 4.66 | 4.36 | 4.28 | 4.80 | 3.92 | 3.70 |
| H$_b$–C(6′) | 4.13 | 4.45 | 4.36 | 4.23 | 4.58 | 3.72 | 3.48 |
| H–C(8′) | 2.12 | 1.56 | 2.17 | 1.70 | 2.15 | 2.56 | 2.96 |
| $J$(1,3) | – | – | – | – | – | 2.1 | 2.1 |
| $J$(3,4) | 9.7 | 9.8 | 9.6 | 9.9 | 9.9 | 9.4 | 9.7 |
| $J$(4,5) | *ca.* 9.3 | *ca.* 9.1 | *ca.* 9.6 | *ca.* 9.7 | *ca.* 9.8 | *ca.* 9.5 | *ca.* 9.3 |
| $J$(5,6) | 9.8 | *ca.* 9.4 | *ca.* 9.0 | 9.1 | *ca.* 9.4 | *ca.* 9.3 | *ca.* 9.2 |
| $J$(6,7) | 8.9 | *ca.* 9.4 | *ca.* 9.1 | 9.9 | *ca.* 9.7 | *ca.* 8.7 | *ca.* 9.2 |
| $J$(7,8$_a$) | 2.5 | 3.0 | 1.7 | 1.9 | 1.8 | 2.5 | 1.5 |
| $J$(7,8$_b$) | 2.5 | 1.4 | 5.0 | 6.5 | 5.1 | 4.0 | 5.6 |
| $J$(8$_a$,8$_b$) | 11.0 | 11.0 | 12.0 | 11.9 | 12.0 | 12.5 | 11.4 |
| $J$(1′,2′) | 8.1 | 8.1 | 7.9 | 7.9 | 7.9 | 7.9 | 7.9 |
| $J$(2′,3′) | 9.4 | 9.7 | 9.1 | 9.3 | 9.7 | 9.0 | ≈ 9.0 |
| $J$(3′,4′) | 10.8 | 10.8 | 10.8 | 11.0 | 10.9 | *ca.* 9.8 | *ca.* 10.0 |
| $J$(4′,5′) | *ca.* 10.7 | *ca.* 10.6 | *ca.* 10.4 | 10.5 | *ca.* 10.4 | *ca.* 10.3 | *ca.* 10.4 |
| $J$(5′,6′$_a$) | 2.2 | 2.5 | 3.7 | 2.4 | 2.3 | 2.1 | 1.8 |
| $J$(5′,6′$_b$) | 4.8 | 6.0 | 3.7 | 5.0 | 5.4 | 5.6 | 5.9 |
| $J$(6′$_a$,6′$_b$) | 12.1 | 11.9 | [a]) | 12.1 | 12.1 | 12.1 | 11.9 |
| $J$(4′,8′) | 2.4 | 2.4 | 2.1 | 2.4 | 2.4 | 2.3 | 2.4 |
| $\tilde{\nu}$(≡C–H) | 3305 | 3312 | 3311 | 3311 | 3311 | [a]) | [a]) |
| $\tilde{\nu}$(C≡C) | 2115 | 2183 | 2111, 2189 | 2189, 2111 | 2113 | 2125 | 2125 |
| $\tilde{\nu}$(C=O) | 1750 | 1739 | 1756 | 1755 | 1758, 1744 | – | – |

[a]) Not determined.

O-*(2,3,6-Tri-*O*-benzoyl-4-deoxy-4-*C*-ethynyl-β-*D*-glucopyranosyl)-(1 → 6)-3,7-anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo-*octitol* (**15**). As described for **14**, with **9** (54 mg, 100 μmol), **13** (60.3 mg, 100 μmol), toluene (1.5 ml), 4 Å-molecular sieves (20 mg), NIS (27 mg, 120 μmol), TfOH (1 μl), $Et_2O$ (5 ml), and 1M $Na_2S_2O_3$ (2 ml) and 10% $Na_2SO_3$ soln. (2 ml; for 5 min, → yellow). FC (toluene/AcOEt 30:1) gave 86 mg (85%) of **15**. Colourless oil. $R_f$ (toluene/AcOEt 5:1) 0.59. $[\alpha]_D^{25} = +3.2$ ($c = 0.5$, $CHCl_3$). IR ($CCl_4$): 3312*m*, 3066*m*, 3033*m*, 2958*m*, 2900*m*, 2888*m*, 2183*w*, 1739*s*, 1603*m*, 1586*w*, 1495*w*, 1452*w*, 1360*m*, 1316*m*, 1266*s*, 1210*m*, 1177*m*, 1091*s*, 1070*s*, 1028*s*, 845*m*. $^1H$-NMR (500 MHz, $C_6D_6$): see *Table 3*; additionally, 8.21–8.19 (*m*, 2 arom. H); 8.09–8.05 (*m*, 4 arom. H); 7.47–7.28 (*m*, 9 arom. H); 7.17–6.88 (*m*, 15 arom. H); 5.24 (*d*, *J* = 11.5, PhC*H*); 4.93 (*d*, *J* = 10.9, PhC*H*); 4.77 (*d*, *J* = 11.4, PhC*H*); 4.75 (*d*, *J* = 10.9, PhC*H*); 4.57 (*d*, *J* = 11.9, PhC*H*); 4.19 (*d*, *J* = 11.9, PhC*H*); 0.10 (*s*, $Me_3Si$). $^{13}C$-NMR (125 MHz, $CDCl_3$): see *Table 5*; additionally, 166.07 (*s*, C=O); 165.74 (*s*, C=O); 165.24 (*s*, C=O); 140.00–132.92 (several *s*); 133.66–127.40 (several *d*); 75.61 (*t*, Ph$CH_2$); 75.20 (*t*, Ph$CH_2$); 73.93 (*t*, Ph$CH_2$); –0.29 (*q*, $SiMe_3$). FAB-MS (3-NOBA): 1013.1 (2, $M^+$), 482.9 (49, $[M + \text{aglycon}]^+$), 360.9 (51), 181.0 (20), 154.0 (22), 135.9 (22), 104.9 (100), 90.9 (99). Anal. calc. for $C_{61}H_{60}O_{12}Si$ (1013.23): C 72.31, H 5.97; found: C 71.93, H 5.98.

O-*(2,3,6-Tri-*O*-acetyl-4-deoxy-4-*C*-ethynyl-β-*D*-glucopyranosyl)-(1 → 6)-4,5,8-tri-*O*-acetyl-3,7-anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo-*octitol* (**16**). A soln. of **14** (211.3 mg, 0.26 mmol) in $Ac_2O$ (2.5 ml) was treated at 0° dropwise with $Me_3SiOTf$ (0.56 ml, 3.12 mmol) (→ black soln.), stirred for 2.5 h, and poured carefully on ice/sat. $NaHCO_3$ soln. (10 ml). Usual workup (AcOEt) and FC (hexane/AcOEt 5:2) gave 109 mg (61%) of **16**. White solid. $R_f$ (hexane/AcOEt 2:1) 0.27. M.p. 183–184°. $[\alpha]_D^{25} = -5.1$ ($c = 1.0$, $CHCl_3$). IR ($CCl_4$): 3311*m*, 2960*m*, 2855*m*, 2189*w*, 2111*w*, 1756*s*, 1427*w*, 1366*s*, 1227*s*, 1165*m*, 1050*s*, 894*m*, 844*s*. $^1H$-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 2.14 (*s*, AcO); 2.13 (*s*, AcO); 2.05 (*s*, AcO); 2.04 (*s* AcO); 2.02 (*s*, AcO); 2.00 (*s*, AcO); 0.08 (*s*, $SiMe_3$). H-NMR (500 MHz, $C_6D_6$): see *Table 3*; additionally, 1.95 (*s*, AcO); 1.90 (*s*, AcO); 1.84 (*s*, AcO); 1.79 (*s*, AcO); 1.66 (*s*, AcO); 1.59 (*s*, AcO); 0.06 (*s*, $SiMe_3$). $^{13}C$-NMR (125 MHz, $C_6D_6$): see *Table 5*; additionally, 170.05 (*s*, C=O); 169.88 (*s*, C=O); 169.49 (*s*, C=O); 169.37 (*s*, C=O); 169.20 (*s*, C=O); 169.03 (*s*, C=O); 20.56 (*q*, Me); 20.43 (*q*, Me); 20.36 (*q*, Me); 20.26 (*q*, Me); 20.22 (*q*, Me); 20.18 (*q*, Me); –0.52 (*q*, $SiMe_3$). FAB-MS (3-NOBA): 1365.0 (2, $[2M + H]^+$), 682.9 (22, $[M + H]^+$), 368.9 (26), 297.0 (100, $[M - \text{aglycon}]^+$), 237.0 (24), 195.0 (61), 135.0 (27). Anal. calc. for $C_{31}H_{42}O_{15}Si$ (682.75): C 54.54, H 6.20; found: C 54.74, H 6.18.

O-*(4-Deoxy-4-*C*-ethynyl-β-*D*-glucopyranosyl)-(1 → 6)-3,7-anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-*D-glycero-D-gulo-*octitol* (**18**). A soln. of **16** (85 mg, 0.12 mmol) in MeOH (10 ml) at r.t. was treated with 0.1M NaOMe in MeOH (0.5 ml), stirred for 90 min, neutralized with *Amberlite IR-120* ($H^+$ form), filtered, and evaporated: 42.3 mg (96%) of **18**. White solid. $R_f$ (AcOEt/MeOH/$H_2O$ 22:3:2) 0.30. $[\alpha]_D^{25} = +18.3$ ($c = 1$, MeOH). IR (KBr): 3385*s* (br.), 2885*m*, 2125*w*, 1636*m*, 1374*m*, 1165*m*, 1030*s*, 960*m*, 893*w*, 658*m*. $^1H$.NMR (300 MHz, $CD_3OD$): see *Table 3*. $^1H$-NMR (500 MHz, ($D_6$)DMSO): see *Table 3*; additionally, 5.46 (*d*, *J* = 5.0, HO–C(4)); 5.33 (*d*, *J* = 4.9, HO–C(2')); 5.31 (*d*, *J* = 6.3, HO–C(3')); 4.77 (br. *t*, *J* ≈ 5.4, HO–C(6')); 4.63 (*d*, *J* = 1.7, HO–C(5)); 4.60 (br. *t*, *J* ≈ 5.9, HO–C(8)). $^{13}C$-NMR (125 MHz, ($D_6$)DMSO): see *Table 5*. CI-MS (MeOH): 376.2 (4, $[M + NH_4]^+$), 359.1 (6, $[M + H]^+$), 206.1 (67), 171.1 (33, $[M - \text{aglycon}]^+$), 153.1 (45), 139.1 (28), 125.1 (32), 111.1 (100), 97.1 (30), 81.0 (41), 67.0 (12), 55.0 (19), 33.0 (86). Anal. calc. for $C_{16}H_{22}O_9 \cdot CH_3OH$ (390.39): C 52.30, H 6.71; found: C 52.72, H 6.29.

O-*(2,3,6-Tri-*O*-benzoyl-4-deoxy-4-*C*-ethynyl-β-*D*-glucopyranosyl)-(1 → 6)-4,5,8-tri-*O*-acetyl-3,7-anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo-*octitol* (**17**). As described for **16**, with **15** (61 mg, 0.06 mmol), $Ac_2O$ (1 ml), $Me_3SiOTf$ (0.13 ml, 0.72 mmol; 3 h) and ice/sat. $NaHCO_3$ soln. (5 ml). FC (hexane/AcOEt 4:2) gave 34.5 mg (66%) of **17**. White solid. Crystals suitable for single-crystal X-ray analysis were obtained by slow evaporation of a soln. of **17** in $CHCl_3$ at r.t. $R_f$ (toluene/AcOEt 5:1) 0.47. $[\alpha]_D^{25} = +26.2$ ($c = 1.13$, $CHCl_3$). IR ($CCl_4$): 3311*m*, 3066*w*, 2961*m*, 2862*w*, 2338*w*, 2113*w*, 1758*s*, 1744*s*, 1602*m*, 1585*w*, 1492*w*, 1452*m*, 1366*m*, 1316*m*, 1265*s*, 1230*s*, 1178*m*, 1094*s*, 1068*s*, 1028*s*, 954*w*, 900*w*, 847*m*, 707*s*, 657*m*. $^1H$-NMR (500 MHz, $CDCl_3$): see *Table 3*; additionally, 8.14–8.11 (*m*, 2 arom. H); 7.93–7.90 (*m*, 4 arom. H); 7.65–7.62 (*m*, 1 arom. H); 7.57–7.48 (*m*, 4 arom. H); 7.39–7.34 (*m*, 4 arom, H); 2.00 (*s*, AcO); 1.96 (*s*, AcO); 1.89 (*s*, AcO); 0.13 (*s*, $SiMe_3$). $^{13}C$-NMR (125 MHz, $CDCl_3$): see *Table 5*; additionally, 170.28 (*s*, C=O); 169.89 (*s*, C=O); 169.12 (*s*, C=O); 166.09 (*s*, C=O); 165.40 (*s*, C=O); 164.48 (*s*, C=O); 133.55 (*s*); 133.42 (*s*); 133.29 (*s*); 129.88–128.36 (several *d*); 20.77 (*q*, Me); 20.54 (*q*, 2 Me); –0.49 (*q*, $SiMe_3$). FAB-MS (3-NOBA): 1737.7 (29, $[2M + H]^+$), 1351.2 (79), 869.2 (100, $[M + H]^+$), 807.1 (75), 747.1 (55), 663.4 (62), 483.1 (90, $[M - \text{aglycon}]^+$), 361.0 (85), 104.9 (99, $C_7H_5O^+$). Anal. calc. for $C_{46}H_{48}O_{15}Si$ (868.96): C 63.58, H 5.57; found: C 63.33, H 5.67.

O-*(4-Deoxy-4-*C*-ethynyl-β-*D*-glucopyranosyl)-(1 → 6)-3,7-anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo-*octitol* (**19**). From **14**: A soln. of **14** (18 g, 21.8 mmol) in THF (220 ml) was treated dropwise at 0° with 1.5M DIBAH in toluene (130.75 ml, 196.1 mmol) within 30 min, stirred for

Table 4. *Selected* $^1$*H-NMR and IR Data of the Dialkynes* **19**–**24**

| | **19**<br>$CDCl_3$/<br>$CD_3OD$ | **20**<br>$CDCl_3$ | **21**<br>$CDCl_3$ | **22**<br>$CDCl_3$ | **23**<br>$CDCl_3$ | **24**<br>$CDCl_3$ |
|---|---|---|---|---|---|---|
| H–C(1) | – | – | – | 2.52 | – | – |
| H–C(3) | 4.05 | 4.04 | 4.02 | 4.02 | 4.03 | 4.01 |
| H–C(4) | 3.54 | 3.59 | 3.58 | 3.59 | 3.58 | 3.55 |
| H–C(5) | 3.38 | 3.48 | 3.47 | 3.50 | 3.46 | 3.46 |
| H–C(6) | 3.98 | 4.06 | 4.03 | 4.05 | 4.06 | 4.02 |
| H–C(7) | 3.21 | 3.68–3.74 | 3.39–3.19 | 3.38–3.21 | 3.20 | 3.36–3.20 |
| $H_a$–C(8) | 3.78 | 3.68–3.74 | 3.74 | 3.75 | 3.68 | 3.67 |
| $H_b$–C(8) | 3.47 | 3.68–3.74 | 3.68 | 3.68 | 3.68 | 3.67 |
| H–C(1′) | 4.36 | 4.32 | 4.29 | 4.31 | 4.27 | 4.25 |
| H–C(2′) | 3.15 | 3.36–3.25 | 3.39–3.19 | 3.38–3.21 | 3.28 | 3.36–3.20 |
| H–C(3′) | 3.56 | 3.48 | 3.44 | 3.45 | 3.41 | 3.45 |
| H–C(4′) | 2.34 | 2.66 | 2.65 | 2.66 | 2.67 | 2.66 |
| H–C(5′) | 3.40 | 3.36–3.25 | 3.39–3.19 | 3.38–3.21 | 3.19 | 3.18 |
| $H_a$–C(6′) | 3.89 | 3.86 | 3.85 | 3.87 | 3.85 | 3.86 |
| $H_b$–C(6′) | 3.80 | 3.80 | 3.79 | 3.79 | 3.79 | 3.76 |
| H–C(8′) | 2.24 | 2.20 | – | – | – | – |
| *J*(1,3) | – | – | – | 2.1 | – | – |
| *J*(3,4) | 9.4 | 9.6 | 9.6 | 9.6 | 9.7 | 9.3 |
| *J*(4,5) | 10.2 | *ca.* 9.2 | *ca.* 9.3 | *ca.* 9.3 | *ca.* 9.2 | *ca.* 9.0 |
| *J*(5,6) | 9.0 | *ca.* 9.3 | *ca.* 9.7 | *ca.* 9.6 | *ca.* 9.0 | *ca.* 9.5 |
| *J*(6,7) | 10.4 | *ca.* 9.3 | *ca.* 9.7 | *ca.* 9.6 | *ca.* 10.0 | *ca.* 9.5 |
| *J*(7,$8_a$) | 2.1 | [a] | 2.0 | 2.2 | 3.3 | 3.1 |
| *J*(7,$8_b$) | 6.8 | [a] | 4.6 | 4.3 | 3.3 | 3.1 |
| *J*($8_a$,$8_b$) | 12.3 | [a] | 11.0 | 11.1 | [a] | [a] |
| *J*(1′,2′) | 7.8 | 8.0 | 8.0 | 8.0 | 8.0 | 7.8 |
| *J*(2′,3′) | 9.1 | *ca.* 9.5 | *ca.* 9.7 | 9.3 | 9.1 | *ca.* 9.9 |
| *J*(3′,4′) | 10.1 | *ca.* 9.5 | *ca.* 9.7 | 10.4 | 10.3 | *ca.* 9.7 |
| *J*(4′,5′) | 9.9 | *ca.* 10.4 | *ca.* 10.5 | *ca.* 10.5 | *ca.* 10.5 | *ca.* 10.5 |
| *J*(5′,6′$_a$) | 3.4 | 3.0 | 3.4 | 3.3 | 2.8 | 3.0 |
| *J*(5′,6′$_b$) | 2.0 | 1.6 | 1.6 | 1.7 | 1.7 | 1.7 |
| *J*(6′$_a$,6′$_b$) | 11.3 | 11.1 | 11.1 | 11.0 | 11.0 | 11.0 |
| *J*(4′,8′) | 2.4 | 2.3 | – | – | – | – |
| $\tilde{\nu}$(≡C–H) | 3311 | 3311 | – | 3311 | – | – |
| $\tilde{\nu}$(C≡C) | 2181 | 2182 | 2172 | 2171 | 2182 | 2220 |
| $\tilde{\nu}$(C=O) | – | – | – | – | – | – |

[a] Not determined.

50 min, diluted with $CH_2Cl_2$ (100 ml), and carefully quenched with 1N aq. HCl (100 ml). Usual workup ($CH_2Cl_2$) gave 16 g of **19** as a slightly yellow foam, which was used for the next step. A small sample was purified by FC (hexane/AcOEt 2:1).

From **21**: A soln. of **21** (22.6 mg, 23.8 µmol) in THF (1 ml) was treated with 1N aq. HCl in MeOH (1 ml) and heated for 48 h at 40°. Neutralization with sat. $NaHCO_3$ soln., usual workup ($CH_2Cl_2$), and short FC (hexane/AcOEt 2:1) gave 13.5 mg (80%) of **19**. Colourless foam. $R_f$ (toluene/AcOEt 1:1) 0.36. $[\alpha]^{25}_{D} = +23.6$ ($c = 1.8$, $CHCl_3$). IR ($CCl_4$): 3594*m*, 3419*m*, 3311*m*, 3090*w*, 3066*m*, 3032*m*, 2960*m*, 2874*m*, 2182*w*, 1948*w*, 1807*w*, 1741*m*, 1606*w*, 1497*m*, 1454*m*, 1399*w*, 1361*m*, 1293*w*, 1251*s*, 1212*w*, 1164*m*, 1065*s*, 1029*s*, 911*w*, 891*w*, 846*s*, 698*s*, 644*m*. $^1$H-NMR (400 MHz, $CDCl_3$/$CD_3OD$ *ca.* 98:2): see *Table 4*; additionally, 4.99 (*d*, $J = 10.3$, PhC*H*); 4.93 (*d*, $J = 10.7$, PhC*H*); 4.77 (*d*, $J = 10.3$, PhC*H*); 4.75 (*d*, $J = 10.7$, PhC*H*); 4.70 (*d*, $J = 11.9$, PhC*H*); 4.59 (*d*, $J = 11.9$, PhC*H*); 0.19 (*s*, $SiMe_3$). $^{13}$C-NMR (100 MHz, $CDCl_3$): see *Table 5*; additionally, 138.73 (*s*); 137.88 (*s*); 137.44 (*s*); 128.53–126.97 (several *d*); 75.52 (*t*, Ph$CH_2$); 75.24 (*t*, Ph$CH_2$); 73.73 (*t*, Ph$CH_2$); –0.30 (*q*, $SiMe_3$). FAB-MS

Table 5. *Selected $^{13}$C-NMR Data of the Dialkynes* **14**–**24**

| | **14**<br>$CDCl_3$ | **15**<br>$C_6D_6$ | **16**<br>$C_6D_6$ | **17**<br>$CDCl_3$ | **18**<br>$(D_6)$DMSO | **19**<br>$CDCl_3$ | **20**<br>$CDCl_3$ | **21**<br>$CDCl_3$ | **22**<br>$CDCl_3$ | **23**<br>$CDCl_3$ | **24**<br>$CDCl_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C(1) | 91.24 | 90.32 | 92.27 | 92.79 | 82.01 | 91.50 | 91.04 | 91.08 | 81.08 | 91.06 | 46.60 |
| C(2) | 102.34 | 104.14 | 100.62 | 98.91 | 75.94 | 102.26 | 102.55 | 102.61 | 74.20 | 102.50 | [b]) |
| C(3) | 70.35 | 70.55 | 69.12 | 68.86 | 69.85 | 70.43 | 70.44 | 70.49 | 69.87 | 70.38 | 70.74 |
| C(4) | 81.65 | 82.40 | 72.33 | 76.05 | 73.38 | 82.00 | 81.62 | 81.67 | 81.35 | 81.59 | 81.11 |
| C(5) | 83.88 | 83.83 | 73.65 | 73.43[a]) | 78.79 | 84.21 | 83.97 | 84.08 | 84.17 | 83.92 | 83.96 |
| C(6) | 78.90 | 77.15 | 77.28 | 76.78 | 74.22 | 78.77 | 79.29[a]) | 79.38[a]) | 79.48[a]) | 79.23[a]) | 79.18[a]) |
| C(7) | 74.45 | 78.80 | 76.96 | 72.79[a]) | 75.83 | 76.56 | 75.52 | 74.97 | 74.98 | 74.34 | 74.35 |
| C(8) | 67.68 | 68.31 | 63.89 | 64.21 | 60.24 | 68.38 | 67.98[a]) | 68.05[a]) | 68.14 | 67.94 | 67.93 |
| C(1′) | 99.81 | 100.81 | 101.41 | 100.97 | 102.90 | 102.15 | 101.55 | 101.65 | 101.71 | 101.56 | 101.63 |
| C(2′) | 72.47[a]) | 73.42 | 72.68 | 72.13[a]) | 73.96 | 74.77[a]) | 78.78[a]) | 78.88[a]) | 78.92[a]) | 78.67[a]) | 78.66[a]) |
| C(3′) | 72.81[a]) | 73.72 | 73.08 | 72.79[a]) | 79.87 | 75.29 | 78.89[a]) | 78.97[a]) | 79.01[a]) | 78.80[a]) | 78.81[a]) |
| C(4′) | 35.50 | 36.85 | 35.65 | 36.16 | 37.20 | 36.78 | 38.84 | 38.07 | 38.06 | 37.84 | 37.81 |
| C(5′) | 72.47[a]) | 73.50 | 72.93 | 71.41[a]) | 75.38 | 74.61[a]) | 74.61 | 75.61 | 78.86[a]) | 75.51 | 75.51 |
| C(6′) | 63.80 | 64.65 | 63.00 | 62.22 | 61.68 | 62.89 | 67.10 | 67.38 | 67.36 | 67.14 | 67.12 |
| C(7′) | 72.99 | 73.72 | 73.31 | 74.10 | 73.78 | 72.74 | 72.71 | 103.03 | 102.03 | 77.20 | 77.20 |
| C(8′) | 77.97 | 78.01 | 78.34 | 77.03 | 82.32 | 78.88 | 81.26 | 88.75 | 88.78 | 42.40 | 42.40 |

[a]) Assignments may be interchanged. [b]) Not determined.

(3-NOBA): 723.0 (2, $[M + Na]^+$), 699.1 (4, $[M - 1]^+$), 531.1 (9), 181.1 (34), 154.0 (17, 4, $[M -$ aglycon$]^+$), 136.0 (17), 91.0 (100). Anal. calc. for $C_{40}H_{48}O_9Si$ (700.90): C 68.55, H 6.90; found: C 68.54, H 7.02.

*O-(4-Deoxy-4-C-ethynyl-2,3,6-tris-O-(methoxymethyl)-β-*D*-glucopyranosyl)-(1→6)-3,7-anhydro-4,5,8-tri-O-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1-C-(trimethylsilyl)-*D-glycero-D-gulo-*octitol* (**20**). *Conditions A:* A mechanically stirred soln. of crude **19** (8.1 g, 11.57 mmol) in $CH_2Cl_2$ (200 ml) and $CH_2(OMe)_2$ (150 ml) was treated portionwise with $P_2O_5$ (*ca.* 40–50 g) until TLC showed complete conversion of the starting material. During the reaction, a gummy brown mass was formed and the colour of the mixture changed to green. The mixture was poured (strong evolution of $CO_2$!) into a 10-l beaker containing ice-cooled sat. $NaHCO_3$ soln. (500 ml). Usual workup (AcOEt) and FC (hexane/AcOEt 3:1) gave 7.15 g (75% from **14**) of **20**.

*Conditions B:* A soln. of **21** (106 mg, 0.11 mmol) in THF/MeOH 1:1 (2 ml) was treated at r.t. with CuBr (1.6 mg, 10 mol-%) and stirred for 3 h. Usual workup ($Et_2O$) and short FC (hexane/AcOEt 5:1) gave 91 mg (95%) of **20**. Colourless oil. $R_f$ (hexane/AcOEt 2:1) 0.76. $[\alpha]_D^{25} = +4.9$ ($c = 0.7$, $CHCl_3$). IR ($CCl_4$): 3310*m*, 3065*w*, 3030*w*, 2955*m*, 2925*m*, 2895*m*, 2824*w*, 1605*w*, 1495*w*, 1455*m*, 1360*m*, 1290*w*, 1250*m*, 1215*m*, 1155*s*, 1115*s*, 1090*s*, 1045*s*, 925*m*, 910*m*. $^1$H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 7.41–7.25 (*m*, 15 arom. H); 5.05 (*d*, $J = 11.4$, PhC*H*); 4.93 (*d*, $J = 6.6$, C*H*OMe); 4.92 (*d*, $J = 11.3$, PhC*H*); 4.90 (*d*, $J = 6.6$, C*H*OMe); 4.79 (*d*, $J = 10.6$, PhC*H*); 4.78 (*d*, $J = 6.2$, C*H*OMe); 4.75 (*d*, $J = 12.1$, PhC*H*); 4.69 (*d*, $J = 11.6$, PhC*H*); 4.66, $J = 6.3$, C*H*OMe); 4.54 (*d*, $J = 6.5$, C*H*OMe); 4.50 (*d*, $J = 6.4$, C*H*OMe); 4.49 (*d*, $J = 12.7$, PhC*H*); 3.50 (*s*, MeO); 3.39 (*s*, MeO); 3.30 (*s*, MeO); 0.20 (*s*, $SiMe_3$). $^{13}$C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 139.19 (*s*); 138.19 (*s*);137.88 (*s*); 128.57–127.28 (several *d*); 97.72 (*t*, $OCH_2O$); 97.62 (*t*, $OCH_2O$); 96.62 (*t*, $OCH_2O$); 75.56 (*t*, Ph$CH_2$); 75.27 (*t*, Ph$CH_2$); 73.59 (*t*, Ph$CH_2$); 56.61 (*q*, MeO); 56.34 (*q*, MeO); 55.26 (*q*, MeO); −0.23 (*q*, $SiMe_3$). FAB-MS (3-NOBA): 855.2 (8, $[M + Na]^+$), 831.0 (12, $[M - 2]^+$), 663.3 (100), 647.3 (98), 400.9 (22), 355.0 (28), 341.0 (31), 326.9 (43), 281.0 (100), 91.0 (100). Anal. calc. for $C_{46}H_{60}O_{12}Si$ (833.06): C 66.32, H 7.26; found: C 66.06, H 7.28.

*Chlorotrimethylgermane.* According to [24], a 250-ml autoclave equipped with a manometer and a thermometer was charged under Ar at r.t. with $GeCl_4$ (11.66 ml, 0.1 mol), $SiMe_4$ (27.44 ml, 0.2 mol), and $AlBr_3$ (1.34 g, 5 mol-%) and heated for 16 h at 225° (pressure raised to 12 bar). After cooling to r.t., the crude mixture was treated with NaCl (1 g) and the filtrate was fractionally distilled through a *Widmer* column to give 21.1 g of $SiMe_3Cl$/$SiMe_2Cl_2$ 1:1 (b.p. 55–71°) and 12.3 g (80%) of $GeMe_3Cl$. B.p. 97–102°. $^1$H-NMR (200 MHz, $CDCl_3$): 0.72 (*s*, Me).

*O-(4-Deoxy-2,3,6-tri-O-(methoxymethyl)-4-C-[(trimethylgermyl)ethynyl]-β-*D*-glucopyranosyl)-(1→6)-3,7-anhydro-4,5,8-tris-O-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1-C-(trimethylsilyl)-*D-glycero-D-gulo-*octitol* (**21**). A soln. of **20** (8.6 g, 10.34 mmol) in THF (250 ml) was metallated at −78° with 1.54M BuLi in hexane (7.4 ml, 11.37 mmol), stirred for 30 min, treated dropwise with $GeMe_3Cl$ (1.74 ml, 11.37 mmol), stirred for further 10 min, quenched with sat. $NH_4Cl$ soln. (6 ml), and warmed to r.t. Usual workup ($Et_2O$) and FC (hexane/AcOEt 5:1 → 3:1) gave 9.1 g (93%) of **21**. Colourless oil. $R_f$ (hexane/AcOEt 2:1) 0.46. $[\alpha]_D^{25} = 12.4$ ($c = 0.5$, $CHCl_3$). IR ($CCl_4$): 3311*m*, 3090*w*, 3032*w*, 2955*s*, 2927*s*, 2824*m*, 2171*w*, 1742*w*, 1641*w*, 1556*w*, 1497*w*, 1454*m*, 1361*m*, 1215*m*, 1154*s*, 1094*s*, 1043*s*, 923*m*, 833*m*, 664*m*, 610*m*. $^1$H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 7.40–7.24 (*m*, 15 arom. H); 5.06 (*d*, *J* = 10.8, PhC*H*); 5.04 (*d*, *J* = 11.2, PhC*H*); 4.94 (*d*, *J* = 10.6, PhC*H*); 4.93 (*d*, *J* = 6.0, C*H*OMe); 4.90 (*d*, *J* = 5.8, C*H*OMe); 4.77 (*d*, *J* = 10.5, PhC*H*); 4.75 (*d*, *J* = 6.1, C*H*OMe); 4.73 (*d*, *J* = 11.2, PhC*H*); 4.68 (*d*, *J* = 6.0, C*H*OMe); 4.67 (*d*, *J* = 12.0, PhC*H*); 4.52 (*d*, *J* = 6.5, C*H*OMe); 4.49 (*d*, *J* = 6.5, C*H*OMe); 4.48 (*d*, *J* = 12.0, PhC*H*); 3.50 (*s*, MeO); 3.38 (*s*, MeO); 3.30 (*s*, MeO); 0.35 (*s*, $GeMe_3$); 0.18 (*s*, $SiMe_3$). $^{13}$C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 139.26 (*s*); 138.27 (*s*); 137.99 (*s*); 128.61–127.32 (several *d*); 97.75 (*t*, $OCH_2O$); 97.71 (*t*, $OCH_2O$); 96.68 (*t*, $OCH_2O$); 75.61 (*t*, $PhCH_2$); 75.33 (*t*, $PhCH_2$); 73.54 (*t*, $PhCH_2$); 56.70 (*q*, MeO); 56.42 (*q*, MeO); 55.28 (*q*, MeO); −0.18 (*q*, $GeMe_3$, $SiMe_3$). MALDI-TOF-MS: 989.0 ($[M + K]^+$), 972.7 ($[M + Na]^+$). Anal. calc. for $C_{49}H_{68}GeO_{12}Si$ (949.76): C 61.97, H 7.22; found: C 62.04, H 7.38.

O-*(4-Deoxy-2,3,6-tris-*O*-(methoxymethyl)-4-*C*-[(trimethylgermyl)ethynyl]-β-*D*-glucopyranosyl)-(1→6)-3,7-anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-*D-glycero-D-gulo-*octitol* (**22**). A soln. of **21** (2.7 g, 2.85 mmol) in THF (15 ml) was treated at r.t. with a sat. methanolic $K_2CO_3$ soln. (2 ml), stirred for 10 min, and diluted with $CH_2Cl_2$ (15 ml) and sat. $NH_4Cl$ soln. (10 ml). Usual workup ($CH_2Cl_2$) and FC (hexane/AcOEt 5:1 → 3:1 → 1:1) gave 2.3 g (90%) of **22**. Colourless oil. $R_f$ (hexane/AcOEt 2:1) 0.46. $[\alpha]_D^{25} = +25.4$ ($c = 1.5$, $CHCl_3$). IR ($CCl_4$): 3311*m*, 3090*w*, 3032*w*, 2955*s*, 2927*s*, 2824*m*, 2171*w*, 1742*w*, 1641*w*, 1556*w*, 1497*w*, 1454*m*, 1361*m*, 1215*m*, 1154*s*, 1094*s*, 1043*s*, 923*m*, 833*m*, 664*m*, 610*m*. $^1$H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 7.40–7.24 (*m*, 15 arom. H); 5.06 (*d*, *J* = 10.8, PhC*H*); 4.94 (*d*, *J* = 6.4, C*H*OMe); 4.90 (*d*, *J* = 6.4, C*H*OMe); 4.88 (*d*, *J* = 10,4, PhC*H*); 4.80 (*d*, *J* = 10.3, PhC*H*); 4.72 (*d*, *J* = 12.0, PhC*H*); 4.69 (*d*, *J* = 6.6, C*H*OMe); 4.67 (*d*, *J* = 11.2, PhC*H*); 4.66 (*d*, *J* = 6.6, C*H*OMe); 4.53 (*d*, *J* = 6.5, C*H*OMe); 4.49 (*d*, *J* = 6.4, C*H*OMe); 4.47 (*d*, *J* = 12.1, PhC*H*); 3.50 (*s*, MeO); 3.38 (*s*, MeO); 3.30 (*s*, MeO); 0.35 (*s*, $GeMe_3$). $^{13}$C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 139.20 (*s*); 138.15 (*s*); 138.01 (*s*); 128.61–127.36 (several *d*); 97.77 (*t*, $OCH_2O$); 97.73 (*t*, $OCH_2O$); 96.69 (*t*, $OCH_2O$); 75.65 (*t*, $PhCH_2$); 75.41 (*t*, $PhCH_2$); 73.60 (*t*, $PhCH_2$); 56.71 (*q*, MeO); 56.44 (*q*, MeO); 55.29 (*q*, MeO); −0.20 (*q*, $GeMe_3$). FAB-MS (3-NOBA): 1755.1 (3, $[2M + H]^+$), 877.2 (100, $M^+$), 847.2 (23), 771.2 (20), 577.1 (65), 503.2 (54), 181.1 (80), 119.0 (90, $GeMe_3$), 91.0 (100). Anal. calc. for $C_{46}H_{60}GeO_{12}$ (877.58): C 62.96, H 6.96; found: C 62.91, H 6.92.

O-*{4-*C*-[(Bromo)ethynyl]-4-deoxy-2,3,6-tris-*O*-(methoxymethyl)-β-*D*-glucopyranosyl}-(1→6)-3,7-anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo-*octitol* (**23**) *and* O-*{4-*C*-[(Bromo)ethynyl]-4-deoxy-2,3,6-tris-*O*-(methoxymethyl)-β-*D*-glucopyranosyl}-(1→6)-3,7-anhydro-4,5,8-tri-*O*-benzyl-1-*C*-bromo-1,1,2,2-tetradehydro-1,2-dideoxy-*D-glycero-D-gulo-*octitol* (**24**). *Conditions A:* A soln. of **21** (61.9 mg, 65.25 μmol) and NBS (12.2 mg, 68.51 μmol) in acetone (1 ml) was treated with CuBr (0.47 mg, 3.26 μmol) (→ ocre soln.), stirred for 90 min, diluted with AcOEt (5 ml), and decolourized with 1M aq. $Na_2S_2O_3$ soln. (5 ml). Usual workup (AcOEt) and filtration through a pad of silica gel (elution with 10 ml of AcOEt) gave 55.6 mg (93%) of **23**. Colourless oil. Anal. HPLC (hexane/AcOEt 3:1): single peak at $t_R$ 9.0 for **23**.

*Conditions B:* A soln. of **21** (120 mg, 0.126 mmol) and NBS (24.8 mg, 0.14 mmol) in acetone (2 ml) was treated with $CF_3COOAg$ (0.84 mg, 3.8 μmol) (→ orange soln.), stirred for 60 min, diluted with AcOEt (5 ml), and decolourized with 1M aq. $Na_2S_2O_3$ soln. (5 ml). Usual workup (AcOEt) and FC (hexane/AcOEt 5:1) gave 68.1 mg (60%) of **23**. Prep. HPLC of the mixed fractions from the first FC gave another 28.3 mg (25%) of **23**, 12.9 mg (11%) of **24**, and 1.3 mg (1%) of **21** as colourless oils.

*Data of* **23**: Anal. HPLC: $t_R$ 9.0 (hexane/AcOEt 3:1). $R_f$ (hexane/AcOEt 2:1) 0.45. $[\alpha]_D^{25} = +9.1$ ($c = 1.0$, $CHCl_3$). IR ($CCl_4$): 3090*w*, 3066*m*, 3032*w*, 2955*s*, 2927*s*, 2894*s*, 2824*m*, 2183*w*, 1947*w*, 1740*w*, 1606*w*, 1497*m*, 1454*s*, 1403*m*, 1361*m*, 1292*m*, 1251*s*, 1213*m*, 1154*s*, 1117*s*, 1092*s*, 1043*s*, 923*m*, 846*s*, 674*m*. $^1$H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 7.40–7.24 (*m*, 15 arom. H); 5.02 (*d*, *J* = 11.2, PhC*H*); 5.00 (*d*, *J* = 11.2, PhC*H*); 4.91 (*d*, *J* = 6.6, C*H*OMe); 4.90 (*d*, *J* = 11.4, PhC*H*); 4.78 (*d*, *J* = 6.6, C*H*OMe); 4.76 (*d*, *J* = 6.4, C*H*OMe); 4.75 (*d*, *J* = 10.2, PhC*H*); 4.73 (*d*, *J* = 12.1, PhC*H*); 4.65 (*d*, *J* = 10.5, PhC*H*); 4.62 (*d*, *J* = 6.2, C*H*OMe); 4.52 (*d*, *J* = 6.5, C*H*OMe); 4.47 (*d*, *J* = 6.3, C*H*OMe); 4.45 (*d*, *J* = 12.7, PhC*H*); 3.50 (*s*, MeO); 3.37 (*s*, MeO); 3.30 (*s*, MeO); 0.18 (*s*, $SiMe_3$). $^{13}$C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 139.04 (*s*); 138.07 (*s*); 137.75 (*s*); 128.51–127.21 (several *d*); 97.64 (*t*, $OCH_2O$); 97.48 (*t*, $OCH_2O$); 96.48 (*t*, $OCH_2O$); 75.48 (*t*, $PhCH_2$); 75.21 (*t*, $PhCH_2$); 73.41 (*t*, $PhCH_2$); 56.32 (*q*, MeO); 55.12 (*q*, MeO); 54.97 (*q*, MeO); −0.32 (*q*, $SiMe_3$). FAB-MS (3-NOBA): 911.3 (100 $M^+$), 909.3 (70). MALDI-TOF-MS: 934.5 ($[M + Na]^+$). Anal. calc. for $C_{46}H_{59}BrO_{12}Si$ (911.95): C 60.58, H 6.52; found: C 60.64, H 6.63.

*Data of* **24**: Anal. HPLC: $t_R$ 12.7 min (hexane/AcOEt 3:1). $R_f$ (hexane/AcOEt 2:1) 0.38. IR ($CCl_4$): 3066*m*, 3032*w*, 2892*s*, 2220*m*, 1754*m*, 1453*m*, 1361*m*, 1292*m*, 1214*m*, 1154*s*, 1117*s*, 1092*s*, 1043*s*, 923*m*. $^1$H-NMR (200 MHz, $CDCl_3$): see *Table 4*; additionally, 7.37–7.25 (*m*, 15 arom. H); 5.03 (*d*, *J* = 11.2, PhC*H*); 4.91 (*d*, *J* = 6.6, C*H*OMe); 4.77 (*d*, $J = 6.5$, C*H*OMe); 4.75 (*d*, $J = 6.4$, C*H*OMe); 4.75 (*d*, $J = 11.4$, PhC*H*); 4.73 (*d*, $J = 12.2$, PhC*H*); 4.66 (*d*, $J = 12.2$, 2 PhC*H*); 4.62 (*d*, $J = 6.2$, C*H*OMe); 4.51 (*d*, $J = 6.5$, C*H*OMe); 4.48 (*d*, $J = 6.4$, C*H*OMe); 4.44 (*d*, $J = 12.1$, PhC*H*); 3.49 (*s*, MeO); 3.37 (*s*, MeO); 3.30 (*s*, MeO). $^{13}$C-NMR (50 MHz, $CDCl_3$): see *Table 5*; additionally, 139.09 (*s*); 137.94 (*s*); 137.88 (*s*); 128.63–127.34 (several *d*); 97.72 (*t*, $OCH_2O$); 97.58 (*t*, $OCH_2O$); 96.58 (*t*, $OCH_2O$); 75.58 (*t*, Ph$CH_2$); 75.30 (*t*, Ph$CH_2$); 73.53 (*t*, Ph$CH_2$); 56.30 (*q*, 2 MeO); 55.11 (*q*, MeO). FAB-MS (3-NOBA): 921.2 (26), 919.1 (53, $[M + H]^+$), 917.1 (49), 154.1 (100), 136.0 (76), 91.0 (95).

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