101. Oligosaccharide Analogues of Polysaccharides

Part 7

Synthesis of a Monosaccharide-Derived Monomer for Amylose and Cyclodextrin Analogues

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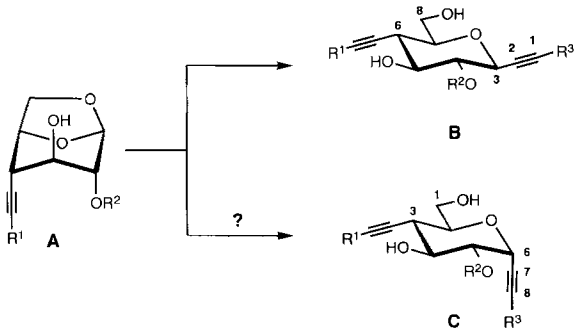
The synthesis of monomers of type **C** (*Scheme 1*) is described. In a first approach, chloro-acetyl-addition to the dioxolane **2** (*Scheme 2*), followed by treatment of the resulting chlorides **3** (α-D/β-D 1:3) with excess AgOTf and $Bu_3SnC{\equiv}CSiMe_3$ gave the axial *C*-alkynyl-glycoside **4** (31%) and the *C*-arylglycoside **5** (29%). The structure of the dialkyne **6**, obtained by deacetylation of **4**, was established by X-ray analysis. The yield of the *C*-alkynyl-glycoside was slightly improved by protecting the C(4)-ethynyl group as the triethysilyl derivative, but not by substituting the benzyl by allyl or 2,6-difluorobenzyl groups. Silylation of the diol **1** with (chloro)diethyl[2-(trimethylsilyl)ethynyl]silane (**19**) resulted in 90% of the monosilyl ether **20**. HO–C(3) of **20** should favor coordination of a *Lewis* acid to O–C(6), and intramolecular, inverting acetal opening should lead to the product of axial alkynylation. Indeed, treatment of **20** with *in situ* generated $BuAlCl_2$, followed by treatment of the crude product with 0.1M HCl in MeOH, gave the dialkynylated triol **22** in yields of 85 to 90%. Under similar conditions, the disilyl ether **21** reacted more slowly to **22** (75%). The slower reaction correlates with the assumed intramolecular interaction of the precoordinated *Lewis* acid with O–C(6) in **20**.

Introduction. – We intend to study the influence of weak interactions, particularly of H-bonds, on the structure and properties of polysaccharides. The approach we have described is based on a comparison of the native polysaccharide with systematically modified analogues, in which some or all glycosidic O-atoms are substituted by buta-1,3-diyne-1,4-diyl moieties [1].

The approach requires the synthesis of dialkynylated monomers, their orthogonal deprotection/activation, their cross-coupling, the deprotection of the products, and their comparative characterization [1–4]. To synthesize the analogues of cellulose where each glycosidic O-atom is replaced by a buta-1,3-diyne-1,4-diyl unit, we have prepared the diequatorially diethynylated monomer of type **B** by retentive, ring-opening alkynylation of 1,6-anhydro-hexopyranoses of type **A** [1] (*Scheme 1*). To prepare analogues of amylose and of cyclodextrins, we require dialkynylated monomers of type **C** possessing an axial ethynyl group at C(6)[1]). We report a comparative study of two approaches to monomers of type **C** resulting in an efficient synthesis of such a dialkyne.

[1]) The different numbering of the anhydroalditols of type **B** and **C** derives from the systematic nomenclature of carbohydrates. Thus, **B** is a 3,7-anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-ethynyl-D-*glycero*-D-*gulo*-octitol, and **C** is a 2,6-anhydro-7,7,8,8-tetradehydro-3,7,8-trideoxy-3-*C*-ethynyl-D-*glycero*-L-*gulo*-octitol.

Scheme 1

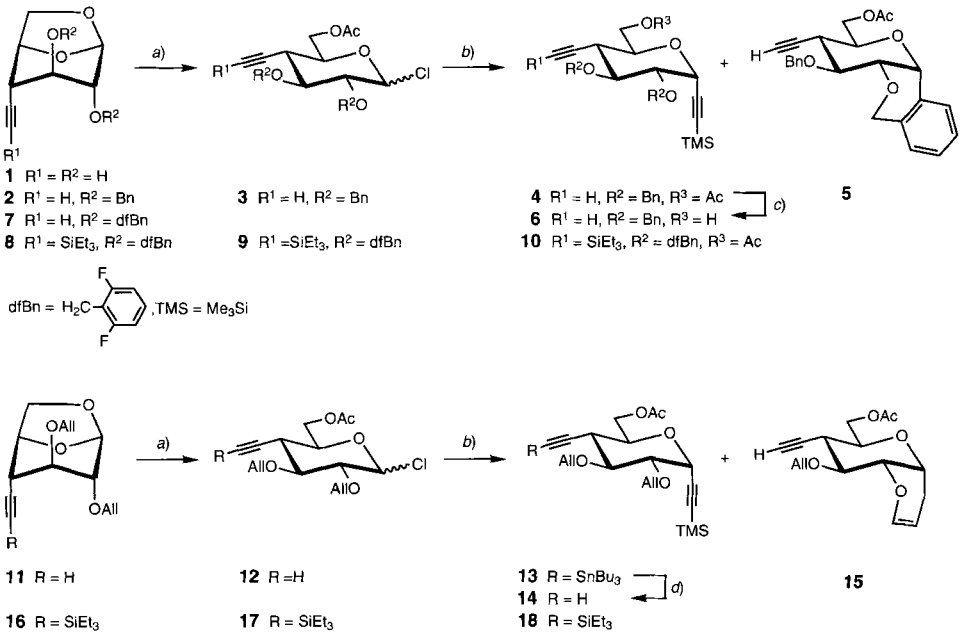


Results and Discussion. – The diol **1** [1] appeared an appropriate starting material for the synthesis of *C*-glucopyranosides of type **C**, as the alkynylating opening of the oxirane ring of a 1,6:3,4-dianhydro-*β*-D-galactopyranose derivative has led to the most efficient introduction of the C(4)-ethynyl group [1] [5] [6]. Specifically, it proved both shorter and higher-yielding than the construction of the C(4)-ethynyl substituent by transformation of an appropriately protected *galacto*-triflate by substitution of the sulfonyloxy group with cyanide followed by reduction, dibromomethylenation, and elimination. The second ethynyl substituent of the dialkynylated monomer **B** (R^1 = H, R^2 = (i-Pr)$_3$Si, R^3 = Me$_3$Si) has been introduced by retentive opening of the 1,3-dioxolane ring of the 1,6-anhydro-4-deoxy-4-*C*-ethynyl-*β*-D-glucopyranose **A** (R^1 = H, R^2 = (i-Pr)$_3$Si) [1]. Exploratory experiments to directly introduce the axial ethynyl group by acetal opening with bis(trimethylsilyl)acetylene were not promising. For this reason, and considering the axial *C*-phenylethynylation of glycosyl halides by *Zhai et al.* [7], and *Veyrières* and coworkers [8] [9], we transformed the 1,6-anhydroglucopyranose derivative **2** [1] in high yield into the glycosyl chlorides **3** (*α*-D/*β*-D 1:3) using a chloro-acetyl-addition, as described by *Gigg et al.* [10] (*Scheme 2*). Treatment of **3** with excess silver trifluoromethanesulfonate (AgOTf) and Bu$_3$SnC≡CSiMe$_3$ [11] gave the axially alkynylated *C*-glycoside **4** (31%) and the *C*-aryl-glycoside **5** (29%). The *C*-glycoside **4** was deacetylated to give the crystalline alcohol **6**. The intramolecular *Friedel-Crafts* alkylation of a BnO–C(2) is well precedented and has been extensively investigated by *Martin* and coworkers [12–16].

To suppress this cyclization, we replaced the benzyl by allyl protecting groups, converting the diol **1** to the diallyl ether **11** (94%). Chloro-acetyl-addition to **11** resulted in a high yield of the glycosyl chlorides **12** (*α*-D/*β*-D 1:2). The reaction of **12** with AgOTf and Bu$_3$SnC≡CSiMe$_3$ resulted in an even more complex mixture than the one observed by similar treatment of **3**. The stannylalkyne **13** and the desired acetylene **14** were isolated in 9% and 21% yield besides the enol ether **15** (2%), resulting from an intramolecular *C*-allylation[2]). The stannyl group of **13** was removed under mildly acidic conditions to form **14** in over 95%. The yield of the *C*-alkynylation was improved by

[2]) The diequatorial isomers of **13** and **14** have not been observed. Besides **13**–**15**, several polar products were formed which may result from the decomposition of **15**. Pure **15** decomposed under the reaction condition.

Scheme 2



1 $R^1 = R^2 = H$
2 $R^1 = H$, R^2 = Bn
7 $R^1 = H$, R^2 = dfBn
8 $R^1 = SiEt_3$, R^2 = dfBn
3 $R^1 = H$, R^2 = Bn
9 $R^1 = SiEt_3$, R^2 = dfBn
4 $R^1 = H$, R^2 = Bn, R^3 = Ac
6 $R^1 = H$, R^2 = Bn, $R^3 = H$
10 $R^1 = SiEt_3$, R^2 = dfBn, R^3 = Ac
5
11 R = H
16 $R = SiEt_3$
12 R = H
17 $R = SiEt_3$
13 $R = SnBu_3$
14 R = H
18 $R = SiEt_3$
15

a) AcCl, MeOH, 0°→r.t.; 99% of **3** (α-D/β-D 1:3), 93% of **9** (only α-D), 96% of **12** (α-D/β-D 1:2), 99% of **17** (α-D/β-D 3:7). *b*) $Bu_3SnC{\equiv}CSiMe_3$, AgOTf, CH_2Cl_2, 0°→r.t.; 31% of **4**, 29% of **5**; 39% of **10**; 9% of **13**, 21% of **14**, 2% of **15**; 44% of **18**. *c*) Camphorsulfonic acid, MeOH, reflux; 97%. *d*) HCl, MeOH, 0°; 97%.

protecting the C(4)-ethynyl group as the Et_3Si derivative. Thus, alkynylation of the glycosyl chlorides **17** (α-D/β-D 3:7, from **11** *via* **16**) yielded 44% of **18**.

An attempt to further improve the yields by substituting the benzyl by the less nucleophilic 2,6-difluorobenzyl groups [17] proved fruitless, alkynylation of the glycosyl chloride **9** (α-D) yielding only 39% of **10**, while the intermediates **7** and **8** were, again, prepared in high yields.

The structure of the dialkyne **6** was established by an X-ray analysis[3]), demonstrating that the pyranose ring adopts a flattened $^4C_1$ conformation (*Fig.*), which is shown by the values of 65.7° and −67.2° for the dihedral angles C(2)–O–C(6)–C(7) and C(4)–C(5)–C(6)–C(7), respectively. Similarly, flattened $^4C_1$ conformations are also observed for $CDCl_3$ solutions of the dialkynes **4**, **6**, **10**, **13**, **14**, and **18**, as indicated by the rather large J(5,6) values of 5.6–5.8 Hz. According to *Altona*'s equation [18], the solid-state conformer of **6** should be characterized by a J(5,6) value of 4.6 Hz. This may hint to a more flattened $^4C_1$ conformation in solution than in the crystal.

The unsatisfactory yields of the *C*-alkynylation of the glucopyranosyl chlorides **3**, **9**, **12**, and **17** prompted us to reexamine the direct alkynylating acetal cleavage of a 1,6-anhy-

[3]) Coordinates and thermal parameters were deposited with the *Cambridge Crystallographic Data Center*, 12 Union Road, Cambridge CB2 1EW, England.

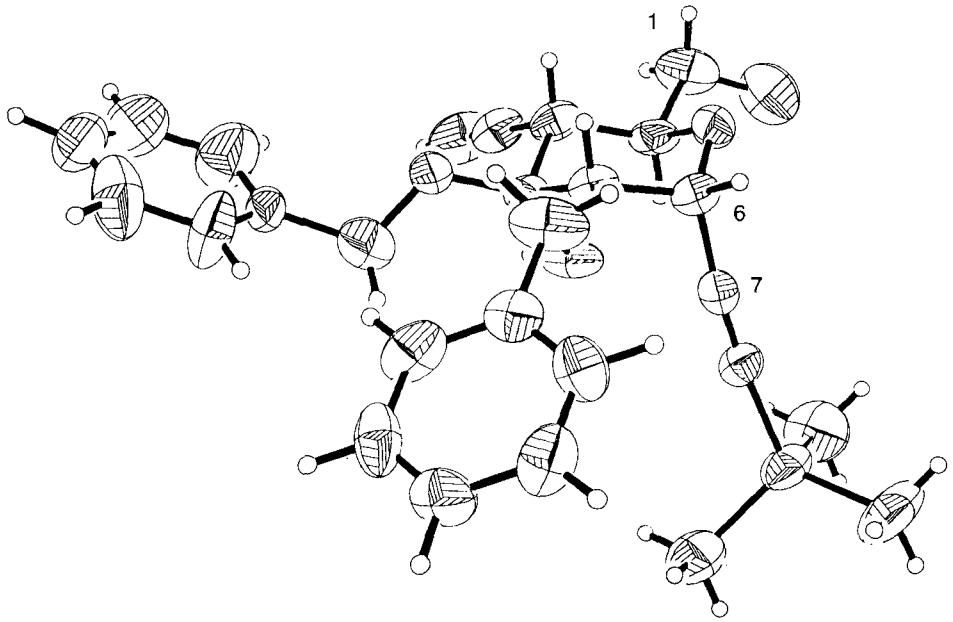
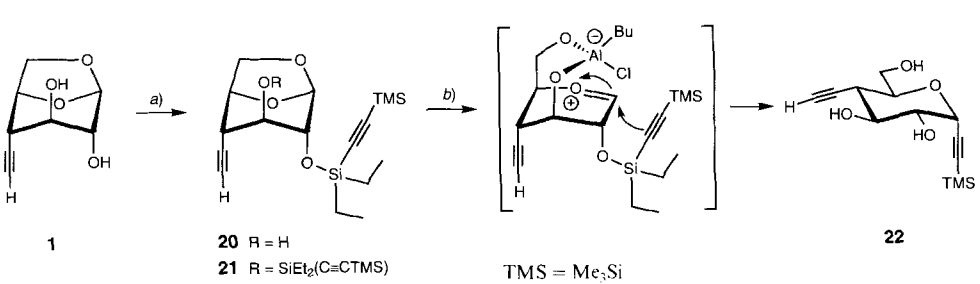


Figure. *X-Ray structure of the dialkyne* **6**

dro derivative **A**, possessing a free OH group at C(3) and an ethynylsilyloxy substituent at C(2). HO–C(3) should favor complexation of a *Lewis* acid with O–C(6), and the *C*-glycosylation by the alkynyl group bound to C(2) should be facilitated and proceed in a stereocontrolled way [19]. Silylation of the diol **1** with (chloro)diethyl[2-trimethylsilyl)-ethynyl]silane (**19**) resulted in 90% of the monosilyl ether **20** and in 7% of the disilyl ether **21** (*Scheme 3*). Treatment of **20** with *in situ* generated $BuAlCl_2$ (from $AlCl_3$ and BuLi) in toluene at 80°, followed by treatment of the crude product with 0.1M HCl in MeOH, gave the desired dialkynylated triol **22** in yields of 85–90%. Similar treatment of the disilyl ether **21** with $BuAlCl_2$ also led to **22** (75%), but the reaction proceeded *ca.* six times more

Scheme 3



1 **20** R = H; **21** R = $SiEt_2(C{\equiv}CTMS)$; **22**

TMS = Me_3Si

a) $Et_2ClSiC{\equiv}CSiMe_3$ (**19**), 2,6-dimethylpyridine, $Cl(CH_2)_2Cl$, r.t.→50°; 90% of **20**, 7% of **21**. *b*) $AlCl_3$, BuLi, toluene, 80°; HCl, MeOH, 45°; 85–90% of **22** (from **20**), 75% of **22** (from **21**).

slowly. The slower reaction correlates with the assumed intramolecular interaction of the precoordinated *Lewis* acid with O–C(6) in **20**. For larger batches, **20** and **21** were not separated; mixtures of **20**/**21** (40 g) were transformed in 85–90% into the desired monomer **22**.

We thank the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support, and Dr. *Volker Gramlich* and *Roland Schönbächler* for the X-ray analysis.

Experimental Part

General. Solvents were distilled before use: THF and toluene from Na and benzophenone, CH_2Cl_2 from CaH_2, and MeOH from Mg. NaH dispersion was washed with hexane (5 ×). Reactions were performed under Ar or N_2. Workup *A*: the mixture was diluted with the indicated solvent and H_2O, the layers were separated, and the aq. layer was extracted 3 times with the indicated solvent. The combined org. layers were dried ($MgSO_4$), and the solvent was evaporated. Workup *B*: the mixture was diluted with CH_2Cl_2 and filtered through *Celite*. The solid was washed with CH_2Cl_2, and the combined filtrates were washed successively with sat. aq. $NaHCO_3$ soln. and H_2O. After drying ($MgSO_4$), the solvent was evaporated. 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). M.p.'s: uncorrected. Optical rotations: 1-dm cell at 25°, 589 nm. FT-IR: *ca.* 2% soln. in $CHCl_3$ (or in the indicated solvent). ^{1}H- and ^{13}C-NMR: 300, 400, or 500 MHz and 75, 100, or 125 MHz, resp. Mass spectra: chemical ionization (CI) with NH_3 or fast-atom bombardment (FAB).

*6-*O*-Acetyl-2,3-di-*O*-benzyl-4-deoxy-4-*C*-ethynyl-*D*-glucopyranosyl Chloride* (**3**). A soln. of **2** (500 mg, 1.42 mmol) in AcCl (25 ml) was treated dropwise with MeOH (0.47 ml, 11.7 mmol) at 0° under Ar and stirred for 12 h at r.t. The residue obtained by evaporation at 40° followed by co-evaporation with benzene (3 ×) was dissolved in CH_2Cl_2 and the soln. washed with 5% aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated: **3** (0.61 g, 99%). Colorless oil which was used for the next step. ^{1}H-NMR (300 MHz, $CDCl_3$, α-D/β-D 1:3): 7.27–7.43 (*m*, 10 arom. H); 6.05 (*d*, *J* = 3.7, 0.3 H), 5.21 (*d*, *J* = 8.4, 0.7 H, H–C(1)); 4.98 (*d*, *J* = 10.6, 0.7 H); 4.94 (br. *s*, 0.6 H), 4.94 (*d*, *J* = 10,6, 0.7 H), 4.91 (*d*, *J* ≈ 10.3, 0.7 H); 4.81 (*d*, *J* = 10.3, 0.7 H), 4.76 (*d*, *J* = 11.9, 0.3 H), 4.71 (*d*, *J* = 11.9, 0.3 H, 2 PhCH_2); 4.47 (*dd*, *J* = 2.1, 12.2, 0.7 H), 4.38 (br. *d*, *J* ≈ 3.1, 0.6 H), 4.31 (*dd*, *J* ≈ 5.4, 12.0, 0.7 H, 2 H–C(6)); 4.18 (*td*, *J* ≈ 3.1, 10.4, 0.3 H), 3.72 (*ddd*, *J* ≈ 2.0, 5.4, 10.4, 0.7 H, H–C(5)); 4.00 (*dd*, *J* = 9.2, 10.4, 0.3 H), 3.67 (*t*, *J* ≈ 9.0, 0.7 H, H–C(3)); 3.60 (*dd*, *J* = 3.7, 9.1, 0.3 H), 3.50 (*t*, *J* = 8.5, 0.7 H, H–C(2)); 2.82 (*dt*, *J* ≈ 2.1, 10.5, 0.7 H), 2.77 (*dt*, *J* ≈ 2.1, 10.4, 0.3 H, H–C(4)); 2.24 (*d*, *J* = 2.1, C≡CH); 2.12 (*s*, 2.1 H), 2.08 (*s*, 0.9 H, Ac).

*1-*O*-Acetyl-2,6-anhydro-4,5-di-*O*-benzyl-7,7,8,8-tetradehydro-3,7,8-trideoxy-3-*C*-ethynyl-8-*C*-(trimethylsilyl)-*D*-glycero-*L*-gulo-octitol* (**4**) *and (1*R*)-6-*O*-Acetyl-1,5-anhydro-2,3-di-*O*-benzyl-4-deoxy-4-ethynyl-1,2-ortho-cyclo-*D*-glucitol* (= *(2*S*,3*S*,4*S*,4a*R*,10b*R*)-4-(Benzyloxy)-3-ethynyl-2,3,4,4a,6,10b-hexahydropyrano[3,2-c][2]-benzopyran-2-methyl Acetate*; **5**). A suspension of **3** (0.61 g, 1.42 mmol), trimethyl[2-(tributylstannyl)ethynyl]silane (2.22 ml, 6.53 mmol) and 4-Å molecular sieves (2 g) in CH_2Cl_2 (35 ml) was stirred at r.t. under Ar for 30 min. The mixture was cooled to 0°, treated with AgOTf (0.73 g, 2.84 mmol), and stirred for 5 min at 0° and for 4 h at r.t. Workup *B* and FC (hexane → hexane/Et_2O 9:1) gave **4** (219 mg, 31%) and **5** (285 mg, 29%) as colorless oils.

Data of **4**: R_f (hexane/Et_2O 3:2) 0.40. $[\alpha]_D^{20} = +80.4$ (*c* = 0.69, $CHCl_3$). IR: 3307*m*, 3090*w*, 3066*w*, 3042*w*, 3007*w*, 2960*m*, 2902*m*, 2170*w*, 1740*s* (br.), 1603*w*, 1497*m*, 1454*m*, 1387*w*, 1367*m*, 1333*w*, 1252*s*, 1144*m*, 1102*s* (br.), 1029*s*, 909*m*, 846*s*, 649*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.27–7.42 (*m*, 10 arom. H); 4.91 (*s*, PhCH_2); 4.79 (*d*, *J* = 5.6, H–C(6)); 4.71 (*d*, *J* = 12.0, PhC*H*); 4.69 (*d*, *J* = 12.0, PhC*H*); 4.40 (*dd*, *J* = 2.3, 12.0, H–C(1)); 4.34 (*dd*, *J* = 4.5, 12.1, H′–C(1)); 4.15 (*ddd*, *J* = 2.4, 4.5, 10.7, H–C(2)); 3.88 (*t*, *J* ≈ 9.8, H–C(4)); 3.48 (*dd*, *J* = 5.6, 9.2, H–C(5)); 2.63 (*dt*, *J* = 2.4, 10.6, H–C(3)); 2.19 (*d*, *J* = 2.4, C≡CH); 2.08 (*s*, Ac); 0.25 (*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 170.79 (*s*, C=O); 138.29 (*s*); 138.11 (*s*); 128.38 (2*d*); 128.34 (2*d*); 128.30 (2*d*); 127.78 (*d*); 127.75 (*d*); 127.67 (2*d*); 99.58 (*s*, *C*≡CSi); 95.62 (*s*, C≡*C*Si); 80.79 (*d*, C≡*C*H); 79.65 (*d*, C(4)); 78.62 (*d*, C(5)); 75.77 (*t*, PhCH$_2$); 72.49 (*t*, PhCH$_2$); 72.11 (*s*, *C*≡CH); 72.02 (*d*, C(2)); 67.37 (*d*, C(6)); 64.28 (*t*, C(1)); 36.70 (*d*, C(3)); 20.83 (*q*, Me); −0.11 (*q*, Me_3Si). EI-MS: 490 (< 1, M^+), 399 (12), 293 (5), 103 (7), 91 (100). Anal. calc. for $C_{29}H_{34}O_5Si$ (490.67): C 70.99, H 6.98; found: C 71.14, H 7.14.

Data of **5**: R_f (hexane/Et_2O 3:2) 0.27. $[\alpha]_D^{25} = +17.6$ (*c* = 1.39, $CHCl_3$). IR: 3306*m*, 3067*w*, 3007*m*, 2942*w*, 2108*w*, 1739*s* (br.), 1605*w*, 1495*w*, 1454*m*, 1368*m*, 1346*w*, 1333*w*, 1114*s*, 1093*s*, 1051*m*, 1028*m*, 649*m*. ^{1}H-NMR (400

MHz, $CDCl_3$): 7.44–7.47 (*m*, 2 arom. H); 7.25–7.39 (*m*, 6 arom. H); 7.01 (br. *d*, $J \approx 7.1$, 1 arom. H); 5.16 (*d*, $J = 6.2$, H–C(1)); 4.93 (*s*, PhCH_2); 4.71 (*s*, PhCH_2); 4.42 (*dd*, $J = 2.4$, 11.9, H–C(6)); 4.35 (*dd*, $J = 5.5$, 11.9, H′–C(6)); 4.12 (*dd*, $J = 6.2$, 8.6, H–C(2)); 3.81 (*dd*, $J = 8.7$, 9.7, H–C(3)); 3.68 (*ddd*, $J = 2.4$, 5.5, 10.3, H–C(5)); 2.77 (*dt*, $J = 2.4$, 10.1, H–C(4)); 2.18 (*d*, $J = 2.4$, C≡CH); 2.14 (*s*, Ac). ^{13}C-NMR (100 MHz, $CDCl_3$): 170.83 (*s*, C=O); 138.19 (*s*); 134.95 (*s*); 131.42 (*s*); 128.40 (2*d*); 128.11 (2*d*); 127.86 (*d*); 127.73 (*d*); 127.40 (*d*); 126.27 (*d*); 123.97 (*d*); 81.06 (*d*, C≡*C*H); 75.30 (*d*, C(3)); 74.06 (*d*, C(2)); 73.88 (*t*, Ph*C*H$_2$); 72.73 (*s*, *C*≡CH); 71.04 (*d*, C(5)); 69.11 (*d*, C(1)); 64.57 (*t*, C(6)); 62.96 (*t*, PhCH_2); 36.13 (*d*, C(4)); 20.89 (*q*, Me). CI-MS: 410 (20, $[M + NH_4]^+$), 393 (30, $[M + 1]^+$), 183 (39), 132 (100), 91 (51). Anal. calc. for $C_{24}H_{24}O_5$ (392.45): C 73.45, H 6.16; found: C 73.20, H 6.41.

*2,6-Anhydro-4,5-di-*O*-benzyl-7,7,8,8-tetradehydro-3,7,8-trideoxy-3-*C*-ethynyl-8-*C*-(trimethylsilyl)-*D*-glycero-*L*-gulo-octitol* (**6**). A soln. of **4** (80 mg, 0.16 mmol) and (±)-camphorsulfonic acid (13 mg, 0.06 mmol) in MeOH (14 ml) was refluxed for 10 h. Workup *A* and FC (hexane/Et_2O 1:1) gave **6** (72 mg, 97%) as a colorless oil which crystallized from pentane/$CHCl_3$. R_f (hexane/Et_2O 2:3) 0.35. M.p. 102°. $[\alpha]_D^{25} = +95.9$ ($c = 0.25$, $CHCl_3$). IR: 3596*w*, 3307*m*, 3089*w*, 3066*w*, 3042*w*, 3007*w*, 2961*m*, 2928*m*, 2170*w*, 1951*w* (br.), 1719*w*, 1603*w*, 1497*w*, 1454*m*, 1397*m*, 1363*m*, 1346*m*, 1333*m*, 1252*s*, 1120*s* (br.), 1077*s*, 1027*s*, 902*m*, 846*s* (br.), 647*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.26–7.42 (*m*, 10 arom. H); 4.90 (*s*, PhCH_2); 4.78 (*d*, $J = 5.7$, H–C(6)); 4.70 (*s*, PhCH_2); 3.73–4.04 (*m*, 2 H–C(1), H–C(2), H–C(4)); 3.46 (*dd*, $J = 5.7$, 9.2, H–C(5)); 2.61 (*dt*, $J = 2.3$, 10.4, H–C(3)); 2.18 (*d*, $J = 2.3$, C≡CH); 1.80 (*t*, $J = 6.6$, exchange with D_2O, OH–C(1)); 0.24 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.44 (*s*); 138.20 (*s*); 128.38–127.67 (several *d*); 99.80 (*s*, *C*≡CSi); 95.37 (*s*, C≡*C*Si); 81.22 (*d*, C≡*C*H); 79.66 (*d*, C(4)); 78.82 (*d*, C(5)); 75.59 (*t*, Ph*C*H$_2$); 74.27 (*d*, C(2)); 72.48 (*t*, Ph*C*H$_2$); 71.95 (*s*, *C*≡CH); 67.26 (*d*, C(6)); 63.34 (*t*, C(1)); 36.57 (*d*, C(3)); –0.06 (*q*, Me_3Si). EI-MS: 448 (< 1, M^+), 357 (11, $[M - Bn]^+$), 107 (7), 91 (100). Anal. calc. for $C_{27}H_{32}O_4Si$ (448.63): C 72.29, H 7.19; found: C 72.13, H 7.13.

X-Ray Analysis of **6**. Crystals were obtained from pentane/$CHCl_3$. $C_{27}H_{32}O_4Si$ (448.63). Orthorombic *Pbcn*; $a = 9.062$ (3), $b = 13.511$ (6), $c = 21.028$ (10) Å; $V = 2575$ (2) Å^3; $D_{calc} = 1.157$ Mg/m^3; $Z = 4$. The crystals were measured in the $\omega/2\theta$ mode on an *Syntex-P21* diffractometer (graphite monochromator, MoK_α, $\lambda = 0.71073$ Å) at 293 K. Of the 1973 total collected reflections, 1954 were independent, $R = 0.0619$, $R_w = 0.0414$. The structures were solved with the direct-methods routine of *Siemens* SHELXTL Plus (VMS).

*1,6-Anhydro-4-deoxy-2,3-bis-*O*-(2,6-difluorobenzyl)-4-*C*-ethynyl-β-*D*-glucopyranose* (**7**). A stirred suspension of 4-Å molecular sieves (0.2 g), BaO (2.09 g, 13.6 mmol), $Ba(OH)_2 \cdot 8\ H_2O$ (623 mg, 1.98 mmol), and **1** (0.40 g, 2.35 mmol) in DMF (30 ml) was treated with 2,6-difluorobenzyl bromide (2.14 g, 10.3 mmol) at r.t., stirred for 2.5 h, cooled to 0°, and diluted with Et_2O. The solids were filtered off. Workup *A* (Et_2O) and FC (hexane/Et_2O 7:3) gave **7** (933 mg, 94%). White solid. R_f (hexane/Et_2O 7:3) 0.27. M.p. 91–92°. $[\alpha]_D^{25} = -103.4$ ($c = 0.95$, $CHCl_3$). IR: 3308*m*, 3007*w*, 2967*w*, 2901*w*, 1927*w*, 1628*m*, 1594*m*, 1472*s*, 1374*w*, 1145*w*, 1090*s* (br.), 1058*s*, 1014*w*, 926*m*, 648*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.24–7.52 (*m*, 2 arom. H); 6.85–6.91 (*m*, 4 arom. H); 5.43 (br. *s*, H–C(1)); 4.75 (*td*, $J \approx 1.0$, 11.2, PhCH); 4.68 (td, $J \approx 1.0$, 11.3, PhCH); 4.64 (*t*, $J \approx 0.5$, PhCH_2); 4.57 (br. *d*, $J \approx 5.4$, H–C(5)); 3.99 (*d*, $J = 7.1$, H_{endo}–C(6)); 3.78–3.79 (*m*, H–C(3)); 3.66 (*dd*, $J = 4.5$, 7.1, H_{exo}–C(6)); 3.40 (br. *s*, H–C(2)); 2.70–2.71 (*m*, H–C(4)); 2.20 (*d*, $J = 2.7$, C≡CH). ^{13}C-NMR (100 MHz, $CDCl_3$): 162.05 (2*dd*, ^1J(C,F) = 250.8, ^3J(C,F) = 7.8); 161.97 (2*dd*, ^1J(C,F) = 250.4, ^3J(C,F) = 8.0); 130.47 (*dt*, ^3J(C,F) = 10.5); 130.43 (*dt*, ^3J(C,F) = 10.3); 113.34 (*t*, ^2J(C,F) ≈ 19.6); 113.33 (*t*, ^2J(C,F) ≈ 19.1); 111.21–111.48 (*m*, 4 arom. C); 100.83 (*d*, C(1)); 82.57 (*d*, C≡*C*H); 77.03, 76.85, 74.46 (3*d*, C(2), C(3), C(5)); 70.68 (*s*, *C*≡CH); 67.19 (*t*, C(6)); 59.63 (*tt*, ^4J(C,F) = 2.9, Ar*C*H$_2$); 59.17 (*tt*, ^4J(C,F) = 2.9, Ar*C*H$_2$); 34.23 (*d*, C(4)). Anal. calc. for $C_{22}H_{18}F_4O_4$ (422.37): C 62.56, H 4.30; found: C 62.49, H 4.46.

*1,6-Anhydro-4-deoxy-2,3-bis-*O*-(2,6-difluorobenzyl)-4-*C*-[2-(triethylsilyl)ethynyl]-β-*D*-glucopyranose* (**8**). A soln. of **7** (685 mg, 1.62 mmol) in THF (75 ml) was treated with BuLi (1.29 ml, 1.93 mmol) at –76° under Ar, stirred for 30 min, and treated with Et_3SiCl (0.38 ml, 2.27 mmol). After 35 min, the mixture was acidified to pH 2 with 0.1M HCl in MeOH. Workup *A* (Et_2O) and FC (hexane/Et_2O 12:1) gave **8** (0.827 g, 95%). Colorless oil. R_f (hexane/Et_2O 7:3) 0.60. $[\alpha]_D^{25} = -105.5$ ($c = 1.1$, $CHCl_3$). IR: 2957*s*, 2910*m*, 2876*m*, 2175*w*, 1924*w*, 1838*w*, 1750*w*, 1628*s*, 1595*s*, 1472*s*, 1414*w*, 1375*w*, 1335*w*, 1145*w*, 1091*s* (br.), 1057*s*, 1017*m*, 964*w*, 925*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.24–7.30 (*m*, 2 arom. H); 6.88–6.92 (*m*, 4 arom. H); 5.42 (br. *s*, H–C(1)); 4.73 (*td*, $J \approx 1.0$, 11.2, PhCH); 4.72 (*t*, $J \approx 1.0$, PhCH_2); 4.66 (*td*, $J \approx 1.0$, 11.2, PhCH); 4.57 (br. *d*, $J = 5.3$, H–C(5)); 3.90 (*dd*, $J \approx 0.5$, 7.0, H_{endo}–C(6)); 3.74 (*dd*, $J \approx 2.9$, 4.1, H–C(3)); 3.65 (*dd*, $J = 5.2$, 7.0, H_{exo}–C(6)); 3.36 (br. *d*, $J = 2.6$, H–C(2)); 2.68 (*dd*, $J = 1.7$, 3.8, H–C(4)); 0.97 (*t*, $J = 8.0$, 3 *Me*CH$_2$); 0.57 (*q*, $J = 8.0$, 3 MeCH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): 162.07 (2*dd*, ^1J(C,F) = 250.6, ^3J(C,F) = 7.7); 161.95 (2*dd*, ^1J(C,F) = 250.3, ^3J(C,F) = 7.7); 130.34 (*dt*, ^3J(C,F) = 10.4); 130.29 (*dt*, ^3J(C,F) = 10.3); 113.56 (*t*, ^2J(C,F) ≈ 19.2); 113.51 (*t*, ^2J(C,F) ≈ 19.5); 111.33 (2*dd*, ^2J(C,F) = 19.1); 111.27 (2*dd*, ^2J(C,F) = 19.1); 106.59 (*s*, *C*≡CSi); 101.06 (*d*, C(1)); 84.16 (*s*, C≡*C*Si); 78.69, 78.18 (2*d*, C(2), C(3)); 75.19 (*d*, C(5)); 67.95 (*t*, C(6)); 59.93, 59.14 (2*t*, Ar*C*H$_2$); 36.03 (*d*, C(4)); 7.41 (*q*, 3 *Me*CH$_2$); 4.39 (*t*, 3 MeCH_2). CI-MS: 554

(100, $[M + NH_4]^+$), 321 (71), 144 (70), 127 (93). Anal. calc. for $C_{28}H_{32}F_4O_4Si$ (536.63): C 62.67, H 6.01; found: C 62.65, H 6.04.

6-O-Acetyl-4-deoxy-2,3-bis-O-(2,6-difluorobenzyl)-4-C-[2-(triethylsilyl)ethynyl]-α-D-glucopyranosyl Chloride (**9**). As described for **3**, with **8** (168 mg, 0.31 mmol), AcCl (15 ml), and MeOH (141 µl, 3.13 mmol, at 0° under N_2, heated to 40°, and stirred for 10 h): **9** (179 mg, 93%). Colorless oil which was used for the next step. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.23–7.32 (*m*, 2 arom. H); 6.82–6.95 (*m*, 4 arom. H); 6.04 (*d*, J = 3.7, H–C(1)); 5.00 (br. *s*, PhCH_2); 4.81 (br. *d*, J = 11.6, PhC*H*); 4.72 (br. *d*, J = 11.6, PhC*H*); 4.38 (*d*, $J \approx 3.1$, 2 H–C(6)); 4.26 (*td*, J = 3.0, 10.5, H–C(5)); 3.94 (*dd*, J = 9.2, 10.4, H–C(3)); 3.56 (*dd*, J = 3.7, 9.0, H–C(2)); 2.77 (*t*, J = 10.6, H–C(4)); 2.08 (*s*, Ac); 0.96 (*t*, J = 7.9, 3 *Me*CH_2); 0.59 (*q*, J = 7.9, 3 MeCH_2).

*1-O-Acetyl-2,6-anhydro-7,7,8,8-tetradehydro-3,7,8-trideoxy-4,5-bis-O-(2,6-difluorobenzyl)-3-C-[2-(triethylsilyl)ethynyl]-8-C-(trimethylsilyl)-*D-glycero-L-gulo-*octitol* (**10**). A suspension of **9** (176 mg, 0.29 mmol), trimethyl[2-(tributylstannyl)ethynyl]silane (0.45 ml, 1.31 mmol) and 3-Å molecular sieves (0.2 g) in $Cl(CH_2)_2Cl$ (9 ml) was stirred at r.t. under Ar for 30 min. The mixture was cooled to 0°, treated with AgOTf (147 mg, 0.57 mmol), and stirred for 5 min at 0° and for 18 h at r.t. Workup *B*, FC (hexane → hexane/Et_2O 9:1), and HPLC (hexane/Et_2O 9:1) gave **10** (75 mg, 39%). Colorless oil. R_f (hexane/Et_2O 7:3) 0.43. $[\alpha]_D^{25} = +81.6$ (c = 0.55, $CHCl_3$). IR: 3007*w*, 2957*s*, 2911*m*, 2878*m*, 2172*w*, 1739*s* (br.), 1627*s*, 1595*m*, 1472*s*, 1368*m*, 1270*m*, 1087*s* (br.), 1058*s*, 1035*s*, 907*w*, 846*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.17–7.29 (*m*, 2 arom. H); 6.79–6.89 (*m*, 4 arom. H); 5.01 (br. *d*, J = 10.8, PhC*H*); 4.93 (br. *d*, J = 10.7, PhC*H*); 4.74 (*d*, J = 5.6, H–C(6)); 4.66 (br. *s*, PhCH_2); 4.37 (*dd*, J = 4.5, 12.2, H–C(1)); 4.32 (*dd*, J = 2.4, 12.2, H′–C(1)); 4.13 (*ddd*, J = 2.4, 4.5, 10.7, H–C(2)); 3.82 (br. *t*, $J \approx 9.7$, H–C(4)); 3.41 (*dd*, J = 5.6, 9.1, H–C(5)); 2.62 (*t*, J = 10.5, H–C(3)); 2.07 (*s*, Ac); 0.97 (*t*, J = 8.0, 3 *Me*CH_2); 0.57 (*q*, J = 8.0, 3 MeCH_2); 0.21 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.73 (*s*, C=O); 129.87–130.90 (several *d*); 110.88–111.39 (several *d*); 103.74 (*s*, *C*≡CSiEt$_3$); 99.22 (*s*, *C*≡CSiMe$_3$); 95.59 (*s*, C≡*C*SiMe$_3$); 85.92 (*s*, C≡*C*SiEt$_3$); 79.96, 78.88 (2*d*, C(4), C(5)); 72.31 (*d*, C(2)); 67.23 (*d*, C(6)); 64.41 (*t*, C(1)); 62.04 (*t*, Ar*C*H$_2$); 59.64 (*t*, Ar*C*H$_2$); 37.76 (*d*, C(3)); 20.83 (*q*, Me); 7.39 (*q*, 3 *Me*CH_2); 4.29 (*t*, 3 Me*C*H$_2$); −0.29 (*q*, Me_3Si). FAB-MS: 677 (37, $[M + H]^+$), 647 (100). Anal. calc. for $C_{35}H_{44}O_4F_4Si_2$ (676.89): C 62.11, H 6.55; found: C 61.87, H 6.66.

2,3-Di-O-allyl-1,6-anhydro-4-deoxy-4-C-ethynyl-β-D-glucopyranose (**11**). A soln. of **1** (2.00 g, 11.7 mmol) in DMF (200 ml) was treated with NaH (0.62 g, 25.8 mmol) and allyl bromide (4.97 ml, 58.7 mmol) at 0° under Ar, stirred for 2.5 h, and treated dropwise with MeOH (5 ml). Workup *A* (Et_2O) and FC (toluene/AcOEt 11:1) gave **11** (2.77 g, 94.3%) as a colorless oil which crystallized after 2 months at 0°. R_f (toluene/AcOEt 9:1) 0.32. M.p. 22–25°. $[\alpha]_D^{25} = +129.1$ (c = 1.07, $CHCl_3$). IR: 3307*m*, 3007*m*, 2982*m*, 2901*m*, 2861*m*, 2121*w*, 1647*w*, 1474*w*, 1454*w*, 1424*m*, 1325*m*, 1305*m*, 1142*m*, 1078*s*, 1000*s*, 932*s*, 894*m*, 866*w*, 650*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.81–5.97 (*m*, 2 *CH*=CH$_2$); 5.46 (*s*, H–C(1)); 5.30–5.33 (*m*, 1 H), 5.25–5.27 (*m*, 1 H), 5.20–5.22 (*m*, 1 H), 5.17–5.18 (*m*, 1 H, 2 CH=C*H*$_2$); 4.59 (br. *d*, $J \approx 5.5$, H–C(5)); 4.02–4.17 (*m*, H_{endo}–C(6), 4 allyl. H); 3.70 (*dd*, J = 5.5, 7.3, H_{exo}–C(6)); 3.64–3.65 (*m*, H–C(3)); 3.30 (br. *s*, H–C(2)); 2.65–2.66 (*m*, H–C(4)); 2.22 (*d*, J = 2.7, C≡CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 134.41 (*d*, *C*H=CH$_2$); 134.17 (*d*, *C*H=CH$_2$); 117.67 (*t*, CH=*C*H$_2$); 117.36 (*t*, CH=*C*H$_2$); 100.64 (*d*, C(1)); 82.85 (*d*, C≡*C*H); 76.48, 75.45, 74.41 (3*d*, C(2), C(3), C(5)); 71.01 (*t*, allyl. C); 70.61 (*s*, *C*≡CH); 67.05 (*t*, C(6)); 34.67 (*d*, C(4)). CI-MS: 265 (5), 249 (< 1, $[M - 1]^+$), 193 (12), 129 (39), 107 (22), 81 (28), 55 (56), 49 (100), 41 (51), 33 (73), 32 (41), 31 (68), 30 (42), 29 (31), 28 (38). Anal. calc. for $C_{14}H_{18}O_4$ (250.29): C 67.18, H 7.25; found: C 66.95, H 7.12.

*6-O-Acetyl-2,3-di-O-allyl-4-deoxy-4-C-ethynyl-*D*-glucopyranosyl Chloride* (**12**). At 0° under Ar, MeOH (1.32 ml, 32.7 mmol) was added dropwise to a soln. of **11** (1.04 g, 4.1 mmol) in AcCl (100 ml). The soln. was stirred overnight and evaporated at 40°. The residue was dissolved in CH_2Cl_2, washed with 5% aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated: **12** (1.31 g, 96%). Colorless oil which was used for the next step. ^{1}H-NMR (300 MHz, $CDCl_3$, α-D/β-D 1:2): 6.13 (*d*, J = 3.7, 0.3 H), 5.09 (*d*, J = 8.4, 0.7 H, H–C(1)); 5.89–6.03 (*m*, 2 *CH*=CH$_2$); 5.17–5.35 (*m*, 2 CH=C*H*$_2$); 4.17–4.48 (*m*, 0.3 H–C(5), 2 H–C(6), 4 allyl. H); 3.82 (*dd*, J = 9.2, 10.3, 0.3 H), 3.47 (*dd*, $J \approx 8.6$, 10.2, 0.7 H, H–C(3)); 3.67 (*ddd*, J = 2.1, 5.6, 10.5, 0.7 H–C(5)); 3.48 (*dd*, J = 3.7, 9.2, 0.3 H), 3.29 (br. *t*, J = 8.6, 0.7 H, H–C(2)); 2.70 (*dt*, J = 2.3, 10.5, 0.7 H), 2.69 (*dt*, J = 2.3, 10.5, 0.3 H, H–C(4)); 2.21 (*d*, J = 2.3, C≡CH); 2.10 (*s*, 2.1 H), 2.09 (*s*, 0.9 H, Ac).

Treatment of **12** *with Trimethyl[2-(tributylstannyl)ethynyl]silane and AgOTf.* A suspension of **12** (1.30 g, 3.98 mmol), trimethyl[2-(tributylstannyl)ethynyl]silane (6.20 ml, 18.3 mmol) and 3-Å molecular sieves (3.5 g) in CH_2Cl_2 (120 ml) was stirred at r.t. under Ar for 0.5 h, cooled to 0°, treated with AgOTf (2.04 g, 7.96 mmol), and stirred for 5 min at 0° and overnight at r.t. Workup *B* and FC (hexane → hexane/Et_2O 4:1) gave **13** (226 mg, 9%) and **14** (322 mg, 21%) as colorless oils and **15** (22.3 mg, 2%) as white crystals.

*Data of 1-O-Acetyl-4,5-di-O-allyl-2,6-anhydro-7,7,8,8-tetradehydro-3,7,8-trideoxy-3-C-[2-(tributylstannyl)-ethynyl]-8-C-(trimethylsilyl)-*D-glycero-L-gulo-*octitol* (**13**): R_f (hexane/Et_2O 7:3) 0.48. $[\alpha]_D^{25} = +52.0$ (c = 1.20,

$CHCl_3$). IR: 3077*w*, 2959*s*, 2922*s*, 2872*m*, 2854*m*, 2149*w*, 1739*s* (br.), 1644*w*, 1455*m*, 1416*w*, 1366*m*, 1338*w*, 1138*m*, 1072*s* (br.), 1033*m* (br.), 994*m*, 927*m*, 900*m*, 844*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.84–6.05 (*m*, 2 C*H*=CH_2); 5.31–5.34 (*m*, 1 H), 5.25–5.29 (*m*, 1 H, CH=CH_2); 5.13–5.19 (*m*, CH=CH_2); 4.78 (*d*, *J* = 5.6, H–C(6)); 4.30–4.44 (*m*, 2 H–C(1), 2 allyl. H); 4.13–4.18 (*m*, 2 allyl. H); 4.08 (*ddd*, *J* = 2.3, 4.5, 10.7, H–C(2)); 3.70 (br. *t*, *J* ≈ 9.8, H–C(4)); 3.32 (*dd*, *J* = 5.6, 9.3, H–C(5)); 2.58 (*t*, *J* = 10.4, H–C(3)); 2.08 (*s*, Ac); 1.49–1.66 (*m*, 6 H); 1.26–1.41 (*m*, 6 H); 0.85–1.00 (*m*, 15 H); 0.21 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.72 (*s*, C=O); 135.38 (*d*, *C*H=CH_2); 134.78 (*d*, *C*H=CH_2); 116.96 (*t*, CH=*C*H_2); 116.75 (*t*, CH=*C*H_2); 107.04 (*s*, *C*≡CSn); 100.09 (*s*, *C*≡CSi); 95.20 (*s*, C≡*C*Si); 86.51 (*s*, C≡*C*Sn); 80.09, 78.17 (2*d*, C(4), C(5)); 74.49 (*t*, 1 allyl. C); 72.63 (*d*, C(2)); 71.83 (*t*, 1 allyl C); 67.53 (*d*, C(6)); 64.59 (*t*, C(1)); 38.17 (*d*, C(3)); 28.88 (3*t*); 26.90 (3*t*); 20.86 (*q*, Me); 13.65 (3*q*); 11.00 (3*t*); –0.16 (*q*, Me_3Si). CI-MS: 971 (7), 970 (5), 969 (9), 968 (6), 967 (7), 682 (5), 681 (14), 680 (7), 679 (11, $[M + H]^+$), 678 (5, M^+), 677 (6), 627 (15), 626 (5), 625 (20), 624 (31), 623 (100), 622 (45), 621 (69), 620 (31), 619 (36), 291 (9), 289 (7). Anal. calc. for $C_{33}H_{56}O_5SiSn$ (679.60): C 58.32, H 8.31; found: C 58.55, H 8.04.

*Data of 1-*O*-Acetyl-4,5-di-*O*-allyl-2,6-anhydro-7,7,8,8-tetradehydro-3,7,8-trideoxy-3-*C*-ethynyl-8-*C*-(trimethylsilyl)-*D*-glycero-*L*-gulo-octitol* (**14**): R_f (hexane/Et_2O 7:3) 0.41. $[\alpha]_D^{20}$ = +70.8 (*c* = 0.96, $CHCl_3$). IR: 3307*m*, 3007*m*, 2957*s*, 2936*m*, 2912*m*, 2875*m*, 2172*m*, 1739*s* (br.), 1646*w*, 1457*m*, 1414*m*, 1386*m*, 1368*m*, 1332*m*, 1143*m*, 1077*s* (br.), 1036*s*, 932*m*, 902*m*, 846*s*, 632*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.82–6.02 (*m*, 2 C*H*=CH_2); 5.24–5.33 (*m*, CH=CH_2);5.12–5.18 (*m*, CH=CH_2); 4.77 (*d*, *J* = 5.6, H–C(6)); 4.31–4.39 (*m*, H–C(1), 2 allyl. H); 4.30 (*dd*, *J* = 4.7, 12.1, H′–C(1)); 4.11–4.14 (*m*, 2 allyl. H); 4.10 (*ddd*, *J* = 2.3, 4.6, 10.6, H–C(2)); 3.70 (*dd*, *J* ≈ 9.3, 10.2, H–C(4)); 3.31 (*dd*, *J* = 5.6, 9.2, H–C(5)); 2.53 (*dt*, *J* = 2.4, 10.5, H–C(3)); 2.17 (*d*, *J* = 2.3, C≡CH); 2.07 (*s*, Ac); 0.19 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.71 (*s*, C=O); 135.10 (*d*, *C*H=CH_2); 134.63 (*d*, *C*H=CH_2); 117.06 (*t*, 2 CH=*C*H_2); 99.66 (*s*, *C*≡CSi); 95.42 (*s*, C≡*C*Si); 80.72 (*d*, C≡*C*H); 79.15, 78.27 (2*d*, C(4), C(5)); 74.38 (*t*, 1 allyl. C); 72.00 (*d*, C(2)); 72.00 (*s*, *C*≡CH); 71.72 (*t*, 1 allyl. C); 67.44 (*d*, C(6)); 64.30 (*t*, C(1)); 36.69 (*d*, C(3)); 20.82 (*q*, Me); –0.17 (*q*, Me_3Si). CI-MS: 522 (97, $[M + NH_4]^+$), 505 (34, $[M + H]^+$), 476 (37), 475 (100), 389 (38), 235 (26), 145 (38). Anal. calc. for $C_{27}H_{44}O_5Si_2$ (504.81): C 64.24, H 8.79; found: C 64.48, H 8.90.

*Data of 9-*O*-Acetyl-6-*O*-allyl-1,5:4,8-dianhydro-2,3,7-trideoxy-7-*C*-ethynyl-*D*-glycero-*D*-ido-non-1-enitol* (= *(4aR,6S,7S,8S,8aR)-8-(Allyloxy)-7-ethynyl-4,4a,6,7,8,8a-hexahydropyrano[3,2-b]pyran-6-methyl Acetate*; **15**): R_f (hexane/Et_2O 7:3) 0.23. M.p. 74.5–75.5°. $[\alpha]_D^{25}$ = +146.8 (*c* = 0.79, $CHCl_3$). IR: 3307*m*, 3071*w*, 2942*m*, 1739*s* (br.), 1657*m* (br.), 1455*w*, 1426*w*, 1388*m*, 1367*m*, 1342*w*, 1105*s*, 1081*s*, 1053*w*, 1022*w*, 995*m* (br.), 650*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.25 (*ddd*, *J* = 1.7, 2.4, 6.1, H–C(1)); 5.96 (*tdd*, *J* = 5.9, 10.3, 17.2, C*H*=CH_2); 5.33 (*qd*, *J* = 1.6, 17.2), 5.28 (*qd*, *J* = 1.2, 10.3, CH=CH_2); 4.68 (*ddd*, *J* = 2.8, 4.9, 6.1, H–C(2)); 4.39 (*ddd*, *J* = 5.0, 6.7, 9.4, H–C(4)); 4.38 (*dd*, *J* = 2.4, 11.9, H–C(9)); 4.32 (*tdd*, *J* = 1.3, 5.9, 12.5, 1 allyl. H); 4.29 (*dd*, *J* ≈ 4.7, 11.8, H′–C(9)); 4.26 (*tdd*, *J* = 1.4, 5.9, 12.5, 1 allyl. H); 3.99 (*ddd*, *J* = 1.5, 5.0, 8.6, H–C(5)); 3.98 (*ddd*, *J* = 2.4, 4.7, 9.7, H–C(8)); 3.71 (*dd*, *J* = 8.6, 9.7, H–C(6)); 2.63 (*dt*, *J* = 2.3, 10.0, H–C(7)); 2.36 (*tdd*, *J* = 2.7, 9.2, 17.2, H–C(3)); 2.19 (*d*, *J* = 2.4, 1 C≡CH); 2.15 (*tddd*, *J* ≈ 1.5, 5.0, 6.6, 17.2, H′–C(3)); 2.09 (*s*, Ac). ^{13}C-NMR (100 MHz, $CDCl_3$): 170.82 (*s*, C=O); 140.97 (*d*, C(1)); 134.77 (*d*, *C*H=CH_2); 117.50 (*t*, CH=*C*H_2); 96.86 (*d*, C(2)); 80.95 (*d*, C≡*C*H); 75.14, 74.61 (2*d*, C(5), C(6)); 73.59 (*t*, 1 allyl. C); 72.20 (*s*, *C*≡CH); 70.61 (*d*, C(8)); 67.56 (*d*, C(4)); 64.59 (*t*, C(9)); 36.57 (*d*, C(7)); 20.88 (*q*, Me); 20.45 (*t*, C(3)). CI-MS: 310 (4, $[M + NH_4]^+$), 293 (100, $[M + H]^+$), 235 (23), 193 (10), 81 (14). Anal. calc. for $C_{16}H_{20}O_5$ (292.33): C 65.74, H 6.90; found: C 65.54, H 6.86.

Conversion of **13** *to* **14**: A soln. of **13** (193 mg, 0.28 mmol) in MeOH (4 ml) was treated with 37% HCl soln. (28 µl, 0.28 mmol) at 0°, stirred for 25 min, and neutralized with aq. $NaHCO_3$ soln. Workup *A* (Et_2O) and FC (hexane/Et_2O 9:1→4:1) gave **14** (108 mg, 97%).

*2,3-Di-*O*-allyl-1,6-anhydro-4-deoxy-4-*C*-[2-(triethylsilyl)ethynyl]-β-*D*-glucopyranose* (**16**). A soln. of **11** (1.06 g, 4.23 mmol) in THF (150 ml) was treated with BuLi (3.00 ml, 4.80 mmol) at –78° under Ar, stirred for 30 min, and treated with Et_3SiCl (1.00 ml, 5.99 mmol). After 30 min, the mixture was acidified to pH 2 with 0.1M HCl in MeOH. Workup *A* (Et_2O) and FC (hexane/Et_2O 12:1) gave **16** (1.50 g, 97%). Colorless oil. R_f (toluene/AcOEt 15:1) 0.54. $[\alpha]_D^{20}$ = –136.2 (*c* = 1.1, $CHCl_3$). IR: 2977*m*, 2957*s*, 2935*m*, 2875*s*, 2175*m*, 1646*w*, 1602*w*, 1457*m*, 1415*m*, 1383*m*, 1351*w*, 1327*w*, 1303*w*, 1109*s* (br.), 1017*s*, 1004*s*, 932*m*, 896*m*, 867*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.83–5.96 (*m*, 2 C*H*=CH_2); 5.44 (br. *s*, H–C(1)); 5.30–5.33 (*m*, 1 H), 5.26–5.27 (*m*, 1 H), 5.19–5.25 (*m*, 1 H), 5.15–5.19 (*m*, 1 H, 2 CH=CH_2); 4.57 (br. *d*, *J* ≈ 5.0, H–C(5)); 4.06–4.14 (*m*, 4 allyl. H); 3.92 (*d*, *J* = 7.1, H_{endo}–C(6)); 3.66 (*dd*, *J* = 5.2, 7.1, H_{exo}–C(6)); 3.62 (*t*, *J* ≈ 3.1, H–C(3)); 3.26 (*dd*, *J* ≈ 0.8, 3.0, H–C(2)); 2.64 (*dd*, *J* ≈ 1.4, 3.5, H–C(4)); 0.99 (*t*, *J* = 7.7, 3 *Me*CH_2); 0.58 (*q*, *J* = 7.7, 3 Me*C*H_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 134.47 (*d*, 2 *C*H=CH_2); 117.28 (*t*, CH=*C*H_2); 117.19 (*t*, CH=*C*H_2); 106.90 (*s*, *C*≡CSi); 101.17 (*d*, C(1)); 84.02 (*s*, C≡*C*Si); 77.80, 77.34, 75.06 (3*d*, C(2), C(3), C(5)); 71.55 (*t*, allyl. C); 70.92 (*t*, allyl. C); 67.99 (*t*, C(6)); 36.44 (*d*, C(4)); 7.47 (*q*, 3 *Me*CH_2); 4.41 (*t*, 3 Me*C*H_2). CI-MS: 382 (36, $[M + NH_4]^+$), 365 (3, $[M + H]^+$), 235 (33), 140 (100), 129 (89), 111 (26), 87 (20), 58 (19), 41 (79). Anal. calc. for $C_{20}H_{32}O_4Si$ (364.56): C 65.89, H 8.85; found: C 66.11, H 8.62.

6-O-Acetyl-2,3-di-O-allyl-4-deoxy-4-C-[2-(triethylsilyl)ethynyl]-D-glucopyranosyl Chloride (**17**). As described for **3**, with **16** (3.26 g, 8.94 mmol), AcCl (200 ml), and MeOH (2.96 ml, 73.1 mmol): **17** (3.94 g, 99%). Colorless oil which was used for the next step. ^{1}H-NMR (300 MHz, $CDCl_3$, α-D/β-D 3:7): 6.13 (*d*, *J* = 3.7, 0.3 H), 5.09 (*d*, *J* = 8.5, 0.7 H, H–C(1)); 5.87–6.03 (*m*, 2 C*H*=CH$_2$); 5.15–5.36 (*m*, 2 CH=C*H*$_2$); 4.17–4.47 (*m*, 0.3 H–C(5), 2 H–C(6), 4 allyl. H); 3.80 (*dd*, *J* = 9.2, 10.3, 0.3 H), 3.46 (*dd*, *J* = 8.7, 10.4, 0.7 H, H–C(3)); 3.64 (*ddd*, *J* = 1.9, 5.7, 10.6, 0.7 H–C(5)); 3.47 (*dd*, *J* = 3.7, 9.2, 0.3 H), 3.28 (*t*, *J* = 8.6, 0.7 H, H–C(2)); 2.74 (*t*, *J* = 10.5, H–C(4)); 2.19 (*s*, 2.1 H), 2.09 (*s*, 0.9 H, Ac); 0.98 (*t*, *J* = 8.0, 2.7 H), 0.97 (*t*, *J* = 7.7, 6.3 H, 3 *Me*CH$_2$); 0.59 (*q*, *J* = 7.9, 1.8 H), 0.59 (*q*, *J* = 7.9, 4.2 H, 3 MeC*H*$_2$).

1-O-Acetyl-4,5-di-O-allyl-2,6-anhydro-7,7,8,8-tetradehydro-3,7,8-trideoxy-3-C-[2-(triethylsilyl)ethynyl]-8-C-(trimethylsilyl)-D-glycero-L-gulo-octitol (**18**). As described for **12**→**13–15**, with **17** (3.94 g, 8.89 mmol), trimethyl[2-(tributylstannyl)ethynyl]silane (13.9 ml, 40.9 mmol), 3-Å molecular sieves (2 g), CH_2Cl_2 (230 ml), and AgOTf (4.57 g, 17.78 mmol). FC (hexane → hexane/Et_2O 9:1) gave **18** (1.97 g, 44%). Colorless oil. R_f (hexane/Et_2O 4:1) 0.56. $[\alpha]_D^{20} = +70.8$ (*c* = 0.96, $CHCl_3$). IR: 3083*w*, 3007*m*, 2957*s*, 2936*m*, 2912*m*, 2875*m*, 2172*m*, 1739*s* (br.), 1646*w*, 1457*m*, 1414*w*, 1386*w*, 1368*m*, 1332*w*, 1143*m*, 1077*s* (br.), 1036*s*, 932*m*, 902*m*, 846*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.88–6.04 (*m*, 2 C*H*=CH$_2$); 5.25–5.35 (*m*, CH=C*H*$_2$); 5.14–5.20 (*m*, CH=C*H*$_2$); 4.77 (*d*, *J* = 5.6, H–C(6)); 4.34–4.39 (*m*, 2 H–C(1), 2 allyl. H); 4.11–4.17 (*m*, 2 allyl. H); 4.12 (*ddd*, *J* ≈ 2.8, 4.5, 10.5, H–C(2)); 3.72 (*t*, *J* ≈ 9.7, H–C(4)); 3.33 (*dd*, *J* = 5.6, 9.5, H–C(5)); 2.59 (*t*, *J* ≈ 10.2, H–C(3)); 2.09 (*s*, Ac); 0.99 (*t*, *J* = 8.0, 3 *Me*CH$_2$); 0.59 (*q*, *J* = 7.8, 3 MeC*H*$_2$); 0.22 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.72 (*s*, C=O); 135.18 (*d*, *C*H=CH$_2$); 134.69 (*d*, *C*H=CH$_2$); 117.04 (*t*, 2 CH=*C*H$_2$); 104.20 (*s*, *C*≡CSiEt$_3$); 99.85 (*s*, *C*≡CSiMe$_3$); 95.53 (*s*, C≡*C*SiMe$_3$); 85.84 (*s*, C≡*C*SiEt$_3$); 79.65, 78.16 (2*d*, C(4), C(5)); 74.44 (*t*, 1 allyl. C); 72.36 (*d*, C(2)); 71.82 (*t*, 1 allyl. C); 67.53 (*d*, C(6)); 64.43 (*t*, C(1)); 37.89 (*d*, C(3)); 20.84 (*q*, Me); 7.44 (*q*, 3 *Me*CH$_2$); 4.35 (*t*, 3 MeCH$_2$); −0.21 (*q*, Me_3Si). CI-MS: 522 (96, $[M + NH_4]^+$), 505 (34, $[M + H]^+$), 475 (100), 389 (37), 145 (37). Anal. calc. for $C_{27}H_{44}O_5Si_2$ (504.81): C 64.24, H 8.79; found: C 64.48, H 8.90.

(Chloro)diethyl[2-(trimethylsilyl)ethynyl]silane (**19**). A soln. of Et_2SiCl_2 (49.3 g, 0.31 mol) in THF (28 ml) was treated at −16° under N_2 with a soln. of EtMgBr (0.131 mol) in THF (140 ml) within 3 h [3]. The cooling bath was removed and stirring continued for 3 h. The residue obtained by evaporation was treated with pentane, stirred vigorously for 15 min, and filtered. Fractional distillation of the filtrate gave **19** (21.9 g, 32% based on Et_2SiCl_2) and Et_2SiCl_2 (9.25 g, 19%). B.p. *ca.* 63°/0.17 mbar. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.02–1.13 (*m*, 2 *Me*CH$_2$); 0.81–0.95 (*m*, 2 MeC*H*$_2$); 0.19 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 117.77 (*s*, *C*≡CSi); 106.54 (*s*, C≡*C*Si); 9.29 (*q*, 2 *Me*CH$_2$); 6.44 (*t*, 2 MeCH$_2$); −0.34 (*q*, Me_3Si).

1,6-Anhydro-4-deoxy-2-O-{diethyl[2-(trimethylsilyl)ethynyl]silyl}-4-C-ethynyl-β-D-glucopyranose (**20**) *and 1,6-Anhydro-4-deoxy-1,3-bis-O-{diethyl[2-(trimethylsilyl)ethynyl]silyl}-4-C-ethynyl-β-D-glucopyranose* (**21**). A suspension of **1** (800 mg, 4.7 mmol) and 2,6-dimethylpyridine (2.72 ml, 23.4 mmol) in Cl(CH$_2$)$_2$Cl (20 ml) was treated with **19** (1.03 g, 4.7 mmol) and heated to 50° for 30 min. The suspension was treated with additional **19** (95 mg, 0.4 mmol), stirred for 1 h, and cooled to 0°. Workup *A* and FC (hexane/AcOEt 4:1) gave **20** (1.49 g, 90%) and **21** (188 mg, 7%) as colorless oils.

Data of **20**: R_f (hexane/AcOEt 7:3) 0.38. $[\alpha]_D^{25} = -103.1$ (*c* = 1.23, $CHCl_3$). IR: 3564*m* (br.), 3308*m*, 2962*s*, 2878*m*, 2122*w*, 1601*w*, 1459*w*, 1411*w*, 1098*s* (br.), 1055*m*, 1006*m*, 845*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.43 (br. *s*, H–C(1)); 4.61 (br. *d*, *J* = 5.0, H–C(5)); 4.02 (*d*, *J* = 7.4, H_{endo}–C(6)); 3.87–3.96 (*m*, add. of D_2O → change of signal, H–C(3)); 3.71 (*dd*, *J* ≈ 5.0, 7.4, H_{exo}–C(6)); 3.68–3.72 (*m*, H–C(2)); 2.61–2.63 (*m*, H–C(4)); 2.51 (*d*, *J* = 6.2, exchange with D_2O, HO–C(3)); 2.27 (*d*, *J* = 2.7, C≡CH); 0.96–1.03 (*m*, 2 *Me*CH$_2$); 0.61–0.82 (*m*, 2 MeC*H*$_2$); 0.19 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 117.04 (*s*, *C*≡CSi); 108.53 (*s*, C≡*C*Si); 102.74 (*d*, C(1)); 82.98 (*d*, C≡*C*H); 74.98 (*d*, C(5)); 73.55 (*d*, C(3)); 72.83 (*d*, C(2)); 70.69 (*s*, *C*≡CH); 67.77 (*t*, C(6)); 36.48 (*d*, C(4)); 6.59 (*t*, 2 MeCH$_2$); 6.43 (*q*, 2 *Me*CH$_2$); −0.21 (*q*, Me_3Si). CI-MS: 370 (65, $[M + NH_4]^+$), 255 (90), 144 (100). Anal. calc. for $C_{17}H_{28}O_4Si_2$ (352.58): C 57.91, H 8.00; found: C 57.90, H 8.02.

Data of **21**: R_f (hexane/Et_2O 9:1) 0.29. $[\alpha]_D^{25} = -136.1$ (*c* = 0.78, $CHCl_3$). IR: 3309*m*, 3307*w*, 2961*s*, 2938*m*, 2900*m*, 2878*m*, 2105*w*, 1459*m*, 1411*m*, 1099*s* (br.), 1078*s*, 1011*m*, 969*m*, 944*m*, 846*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.43 (br. *s*, H–C(1)); 4.58 (br. *d*, *J* = 5.3, H–C(5)); 4.17 (*d*, *J* = 6.8, H_{endo}–C(6)); 4.09 (*t*, *J* = 1.4, H–C(3)); 3.72 (br. *s*, H–C(2)); 3.72 (*dd*, *J* ≈ 5.3, 6.8, H_{exo}–C(6)); 2.79 (br. *s*, H–C(4)); 2.17 (*d*, *J* = 2.6, C≡CH); 0.96–1.05 (*m*, 4 *Me*CH$_2$); 0.60–0.76 (*m*, 4 MeC*H*$_2$); 0.19 (*s*, Me_3Si); 0.17 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 117.00 (*s*, *C*≡CSi); 116.47 (*s*, *C*≡CSi); 108.74 (*s*, C≡*C*Si); 108.30 (*s*, C≡*C*Si); 101.91 (*d*, C(1)); 82.80 (*d*, C≡*C*H); 74.33 (*d*, C(5)); 73.65 (*d*, C(3)); 72.06 (*d*, C(2)); 70.29 (*s*, *C*≡CH); 66.60 (*t*, C(6)); 36.76 (*d*, C(4)); 7.91 (*t*, MeCH$_2$); 6.72 (*t*, 2 MeCH$_2$); 6.58 (*q*, 2 *Me*CH$_2$); 6.52 (*q*, 2 *Me*CH$_2$); 6.45 (*t*, MeCH$_2$); −0.18 (*q*, Me_3Si); −0.21 (*q*, Me_3Si). CI-MS: 552 (31, $[M + NH_4]^+$), 424 (100). Anal. calc. for $C_{26}H_{46}O_4Si_4$ (534.99): C 58.37, H 8.67; found: C 58.16, H 8.70.

2,6-Anhydro-7,7,8,8-tetradehydro-3,7,8-trideoxy-3-C-ethynyl-8-C-(trimethylsilyl)-D-glycero-L-gulo-octitol (**22**). A suspension of $AlCl_3$ (4.39 g, 32.9 mmol) in toluene (40 ml) was treated at 0° under N_2 with BuLi (17.3 ml,

32.9 mmol), stirred for 30 min at r.t. heated to 80°, treated with a soln. of **20** (3.20 g, 9.1 mmol) in toluene (25 ml), stirred vigorously for 30 min, and cooled to 0°. Workup *B* gave a yellow oil which was treated with 0.1M HCl in MeOH (10 ml), heated to 45°, stirred for 2 h, and evaporated. FC (toluene/AcOEt 6:4→1:1) gave **22** (2.19 g, 90%). White solid. R_f(toluene/AcOEt 3:7) 0.23. M.p. 89–90°. $[\alpha]_D^{25} = +99.7$ ($c = 0.76$, $CHCl_3$). IR (CH_2Cl_2): 3588*m* (br.), 3302*m*, 2962*w*, 2926*w*, 2169*w*, 1605*w*, 1421*m*, 1389*w*, 1219*w*, 1118*w*, 1074*s* (br.), 1009*w*, 895*s*, 846*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.82 (*d*, $J = 5.6$, H–C(6)); 3.94 (*ddd*, $J \approx 2.1, 4.5, 10.5$, H–C(2)); 3.81–3.91 (*m*, 2 H–C(1)); 3.84 (br. *t*, $J \approx 10.0$, H–C(4)); 3.67–3.76 (*m*, exchange with D_2O, OH); 3.57 (br. *dd*, $J \approx 5.6, 9.7$, H–C(5)); 3.35–3.43 (*m*, exchange with D_2O, OH); 2.70–2.77 (*m*, exchange with D_2O, OH); 2,61 (*dt*, $J = 2.1, 10.3$, H–C(3)); 2.28 (*d*, $J = 2.2$, C≡CH); 0.20 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 99.18 (*s*, *C*≡CSi); 96.12 (*s*, C≡*C*Si); 80.50 (*d*, C≡*C*H); 74.19, 73.06 (2*d*, C(4), C(5)); 72.83 (*s*, *C*≡CH); 71.14 (*d*, C(2)); 68.86 (*d*, C(6)); 62.91 (*t*, C(1)); 36.84 (*d*, C(3)); –0.09 (*q*, Me_3Si). CI-MS: 286 (100, $[M + NH_4]^+$), 269 (7, $[M + H]^+$), 125 (41), 73 (91). Anal. calc. for $C_{13}H_{20}O_4Si$ (268.38): C 58.18, H 7.51; found: C 58.19, H 7.44.

Conversion of **21** *to* **22**: A suspension of $AlCl_3$ (112 mg, 0.84 mmol) in toluene (2 ml) was treated at 0° under N_2 with BuLi (0.44 ml, 0.84 mmol), stirred for 30 min at r.t., heated to 80°, treated with a soln. of **21** (122 mg, 0.23 mmol) in toluene (2 ml), stirred vigorously for 4 h (TLC: no **21** left), and cooled to 0°. Workup *B* gave a yellow oil which was treated with 0.1M HCl in MeOH (10 ml), heated to 45°, stirred for 2 h, and evaporated. FC (toluene/AcOEt 6:4→1:1) gave **22** (46 mg, 75%) as a white solid.

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