Oligosaccharide Analogues of Polysaccharides

Part 26

Mimics of Cellulose I and Cellulose II: Di- and Monoalkynyl *C*-Cellosides of 1,8-Disubstituted Anthraquinones

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The anthraquinone derivatives **T-x-x** (**x** = 2, 4, and 8), possessing two cellobiosyl, cellotetraosyl, and cellooctaosyl chains, respectively, *C*-glycosidically bonded at C(1) and C(8) were synthesised as potential mimics of cellulose I. The anthraquinone template enforces a parallel orientation of the cellodextrin chains at a distance corresponding to the one between the crystallographically independent chains of cellulose I, and the ethynyl and buta-1,3-diynyl linker units ensure an appropriate phase shift between them. The H-bonding of the **T-x-x** mimics was analysed and compared to the one of the mono-chained analogues **T-x** and of the known cellulose II mimics **N-x-x** and **N-x** where one or two cellodextrin chains are *O*-glycosidically bonded to naphthalene-1,8-diethanol, or to naphthalene-1-ethanol. The OH signals of **T-x** and **T-x-x** in solution in (D_6)DMSO were assigned on the basis of DQFCOSY, HSQC, and TOCSY (only of **T-4**, **T-4-4**, and **T-8-8**) spectra and on a comparison with the spectra of **N-x** and **N-x-x.** Hydrogen bonding was analysed on the basis of the chemical shift of OH groups and its temperature dependence, coupling constants, SIMPLE ^{1}H-NMR experiments, and ROESY spectra. **T-4-4** and **T-8-8** in (D_6)DMSO appear to adopt a V-shape arrangement of the cellosyl chains, avoiding inter-chain H-bond interactions. The well-resolved solid-state CP/MAS ^{13}C-NMR spectra of the mono-chained **T-x** (**x** = 1, 2, 4, and 8) show that only **T-8** is a close mimic of cellulose II. While the solid-state CP/MAS ^{13}C-NMR spectrum of the C_1-symmetric diglucoside **T-1-1** is well-resolved, the spectra of **T-2-2** and **T-4-4** show broad signals, and that of **T-8-8** is rather well resolved. The spectrum of **T-8-8** resembles that of cellulose I_β. A comparison of the X-ray powder-diffraction spectra of **T-8-8** and **T-8** with those of celluloses confirms that **T-8-8** is a H-bond mimic of cellulose I and **T-8** one of cellulose II.

Surprisingly, there is little difference between the CP/MAS ^{13}C-NMR spectra of the acetyl protected mono-chained *C*-glycosylated anthraquinone derivatives **A-x** and the double-chained **A-x-x** (**x** = 2, 4, and 8). The spectra of **A-4** and **A-4-4** resemble strongly the one of cellulose triacetate I (**CTA I**). The (less well-resolved) spectra of the cellooctaosides **A-8** and **A-8-8**, however, resemble the one of **CTA II**. The similarity between the solid-state CP/MAS ^{13}C-NMR spectra of **A-4** and **A-4-4** to the one of **CTA I**, and of **A-8** and **A-8-8** to the one of **CTA II** is opposite to the observations in the acetylated cellodextrin series.

The mono-chained **A-x** cellulose triacetate mimics **21** (**A-2**), **32** (**A-4**), and **55** (**A-8**) were synthesised by *Sonogashira* coupling of the cellooligosyl-ethynes **15**, **28**, and **50**, followed by selective deacetylation. Complete deacetylation provided the corresponding **T-x** mimics. The double-chained **A-x-x** mimics **24** (**A-2-2**), **35** (**A-4-4**), and **58** (**A-8-8**) were prepared from **A-x** by triflation and *Sonogashira* coupling with the cellosyl-buta-1,3-diynes **19**, **31**, and **53**. Their deacetylation provided the corresponding **T-x-x** mimics **25**, **36**, and **59**. The cellooligosyl-ethynes and cellooligosyl-buta-1,3-diynes required for the *Sonogashira* coupling were prepared by stepwise glycosylation of the partially *O*-benzylated β-cellobiosyl-ethyne and β-cellobiosyl-buta-1,3-diyne **13** and **17**, respectively, with the cellobiosyl donor **2** and the cellohexaosyl donor **47**.

Introduction. – There are at least four polymorphs of cellulose, termed cellulose I–IV [1] [2]. Common to all of them is the $^4C_1$ conformation of the 1,4-linked β-D-glucopyranosyl moieties and the intra-chain, inter-residue O(3)–H···O(5′) H-bond, as it was reviewed on several occasions ([3][4] and refs. quoted there). Most important are the native, metastable cellulose I and cellulose II, the most-stable polymorph [5]. They differ by their crystal packing, *i.e.*, by the relation between adjacent chains of the unit cell. Native cellulose I preparations of different origin show subtle differences in their X-ray diffraction pattern that were rationalised when *Atalla* and *VanderHart* found that samples of native cellulose are composed of two crystalline phases, cellulose I_α and cellulose I_β [6]. These phases are also evidenced by solid-state CP/MAS ^{13}C-NMR, *Raman* [7], and IR spectroscopy [8], and by electron diffraction [9–11]. Celluloses I_α and I_β are not only found within a single cellulose sample [11], but also along a single microfibril [12]. Their relative amounts vary between samples of different origin. Cellulose I_α-rich specimens are found in the cell walls of some algae and in bacterial cellulose, and cellulose I_β-rich specimens in cotton, wood, and ramie fibers [11–13].

The currently accepted three-dimensional structure of celluloses is mainly based on X-ray diffraction data of microcrystals and on computer modeling [14] [15]. The crystal structure of cellulose I_α and I_β, and the H-bond patterns were extensively investigated by *Sugiyama et al.* [12] and *Langan* and co-workers [14]. According to *Sugiyama et al.*, cellulose I is a composite of a triclinic cellulose I_α phase with $P1$ symmetry and a monoclinic cellulose I_β phase with $P2_1$ symmetry [12][13][16]. According to the model of *Langan et al.* [17], cellulose II (obtained from cellulose I by regeneration or mercerisation) differs from cellulose I_β mainly by the antiparallel orientation of the origin and centre chains, the *gt* conformation of the glucopyranosyl units, and intersheet H-bonds.

The structure of celluloses was also studied by solid-state CP/MAS ^{13}C-NMR spectroscopy [18]. Analysis of selectively ^{13}C-labeled celluloses resulted in an unambiguous assignment of the ^{13}C-NMR peaks [19], while analysis of cellulose fibers from various sources allowed to discriminate between chains in the interior and at the surface of the crystallites. The different conformations of chains in the interior (*tg* conformation) and at the surface (*gt* and *gg* conformation) reveal that the characteristic inter-residue C(6)OH···OHC(2′) H-bonds of native celluloses are cleaved at the surface and replaced by inter-residue C(2)OH···OHC(6′) and/or intermolecular H-bonds to H_2O or to amorphous cellulose[1]). Chains in the interior of the crystallite of native cellulose show a characteristic downfield shift of C(4) (88–91 ppm) and C(6) (65–67 ppm), as compared to C(4) and C(6) of chains at the surface that resonate at 83–85 and 62.9/61.7 ppm [20–24]. Recent calculations suggest that H-bonding leads to a shortening of the C(4)–O bonds from 1.43 to 1.36 Å and to the downfield shift of C(4) of cellulose I_α and I_β [25].

Cellotetraose and cellotriose are considered valid models of cellulose II, since single-crystal X-ray analysis of cellooligomers such as cellotetraose [26–28] and cellotriose [29] showed that their structure resembles the one of cellulose II. There are no similar model compounds for cellulose I. To this day, precise structural data defining the atomic details of native cellulose are missing. For this reason, we decided to synthe-

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[1]) The different conformations of interior and surface chains of the crystallites were also visualised by atomic-force microscopy [9].

sise model compounds of cellulose I, opting for compounds where cellodextrin chains of increasing length are attached in a parallel way to a suitable template.

We already described the design and synthesis of the cellooligomers **N-x** and **N-x-x** (**x** = 2, 3, 4, and 8)[2]) where the cellooligosyl chains are glycosidically attached to naphthalene-1-ethanol and naphthalene-1,8-diethanol (*cf. Fig. 2*) [30]. However, solid-state CP/MAS ^{13}C-NMR spectroscopy characterised the bis-cellooctaoside **N-8-8** as a mimic of cellulose II rather than of cellulose I, showing that a parallel attachment of two cellooligosaccharide chains to naphthalene-1,8-diethanol is not sufficient to generate a model for cellulose I_α or I_β [4]. It appeared necessary to design a templated model that assures a parallel orientation of the chains, and that mimicks not only the distance between the origin and centre chains of cellulose I but also the phase shift between them. MM3* Calculations (Macromodel V. 6, gas phase [31]) showed that 1-(buta-1,3-diynyl)-8-ethynylanthraquinone fulfils these conditions. It fixes the chains in a parallel orientation, and leads to a distance between two *C*-glycosidically attached cellooligosaccharide chains of 6.02 Å and to an appropriate phase shift of 2.59 Å, as discussed before [3]. A further advantage is the anticipated difference of the chemical shift of the NMR signals of the template and of the cellooligosaccharide chains.

We planned to investigate the mono- and the double-chained cellobiosyl, cellotetraosyl, and cellooctaosyl anthraquinonyl derivatives; this should allow to also study the influence of the chain length on the intramolecular, inter-chain interactions. The synthesis of the symmetric and asymmetric β-D-glucopyranosyl-ethynylated and -buta-1,3-diynylated anthraquinones, and the analysis of their H-bonding in solution were published [3]. We now describe the synthesis of the corresponding templated mono- and double-chained cellooligosides and the investigation of their H-bonding in the solid state and in DMSO solution; we also describe the synthesis and spectra of the corresponding analogues of cellulose triacetate (CTA).

Results and Discussion. – 1. *Synthesis of β-Cellobiosyl-ethyne and β-Cellobiosyl-buta-1,3-diynes.* We planned to synthesise the templated even-numbered cellooligosides (exemplified by the cellobiose derivative **A**) by coupling the corresponding ethynyl and butadiynyl *C*-glycosides, such as the protected cellobiosyl-ethyne and cellobiosyl-buta-1,3-diyne units **C** and **D** to an anthraquinone moiety **B**, as described for the synthesis of the corresponding glucosyl analogue [3] (*Fig. 1*). The required cellobiosyl *C*-glycosides should be readily available *via* a protected cellobionolactone **E** that should be obtained from commercial cellobiose octaacetate **1** [30].

Cellobiose octaacetate (**1**) was treated with HBr in AcOH to give 94%[3]) of the known bromide **2** [32] (*Scheme 1*). Glycosidation of allyl alcohol with **2** in the presence of $Hg(CN)_2$ yielded 85% of the acetylated β-cellobioside **3** [33]. Following the procedure of *Vliegenthart* and co-workers [34], **3** was deacetylated (MeONa in MeOH; yield > 98%). The resulting allyl cellobioside **4** was transformed into the benzylidene acetal **5** (89%) [35] [36] and further in 73% yield to the benzylated **6** [34] [36]. To obtain higher melting derivatives we also transformed **5** to the 4-chlorobenzyl ether **7** (83%) with a melting point *ca.* 20° higher than that of **6**. Regioselective reductive cleavage of

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[2]) For the numbering of these cellosides, see *Results and Discussion*, *Chapt. 4*.

[3]) The yield of **2** was 85–80% when the reaction was performed on a scale > 80 g.

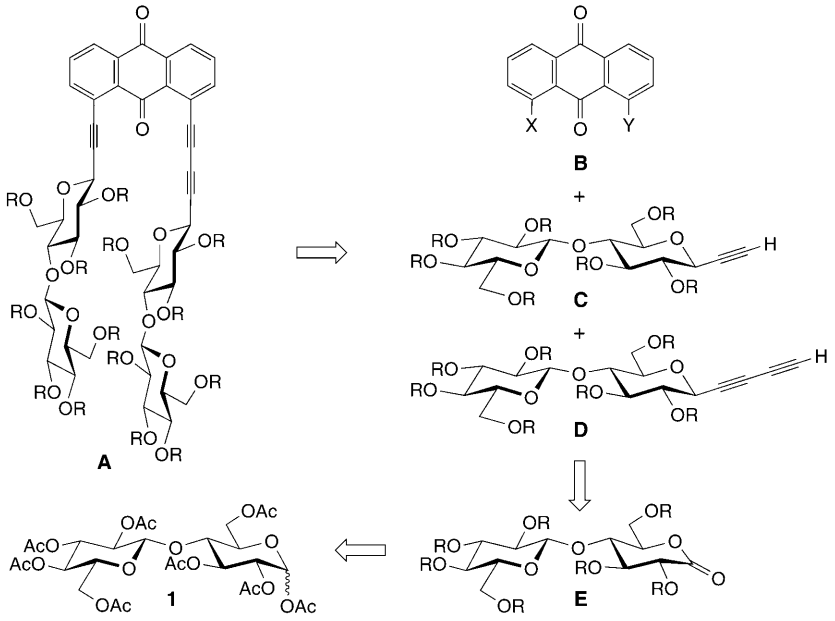
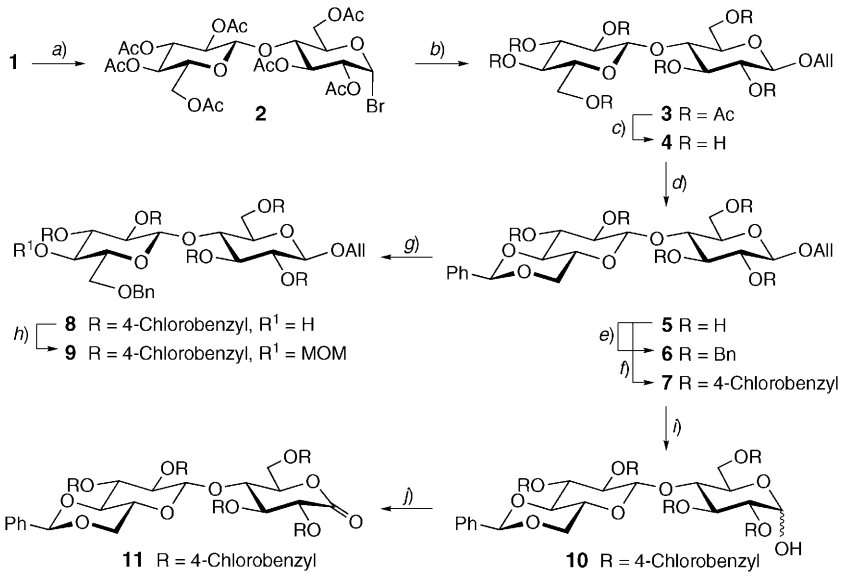


Fig. 1. *Retrosynthesis of the template-bound cellobiosyl-acetylenes and cellobiosyl-buta-1,3-diynes*

the 1,3-dioxane ring of the benzylidene acetal **7** with $NaBH_3CN$ and HCl [30] gave a mixture that was separated by flash chromatography (FC) to provide 69% of the desired secondary alcohol **8**. Reduction of **7** with $BH_3 \cdot Me_2NH/BF_3 \cdot Et_2O$ [37] followed by FC gave **8** in a lower yield (60%), while reduction of **7** with Et_3SiH and $BF_3 \cdot Et_2O$ [38] yielded 71% of **8**. Methoxymethylation of **8** gave **9** (70%) besides 17% of starting material. However, this derivative could not be converted satisfactorily to the corresponding lactone. Deallylation of **9** under standard conditions [34] followed by treatment with DMSO and Ac_2O [39] or with *Dess–Martin* periodinane [40] gave complex mixtures. We, therefore, isomerised the benzylidenated allyl glycoside **7** according to *Baudry et al.* [41], and cleaved the resulting prop-1-enyl glycosides with I_2 in THF/H_2O to obtain 87% of the hemiacetals **10**. Oxidation of **10** with DMSO and Ac_2O [39] provided 97% of crude lactone **11**.

Stereoselective methods for the preparation of β-D-hexopyranosyl-alkynes from hexonolactones are well-documented [42–46]. Treatment of the cellobionolactone **11** with 1 equiv. of lithium (trimethylsilyl)acetylide ($LiC{\equiv}CSiMe_3$) in THF led to only little conversion (*Scheme 2*). Slightly better results were obtained by using up to 2 equiv. of $LiC{\equiv}CSiMe_3$, in agreement with the reported sluggish addition of alkynyl metal reagents to cellobionolactones [47]. Cerium [45][48] or aluminium acetylides [49] performed hardly better, even when 2 equiv. of the reagent were used, and the same result was obtained upon adding $LiC{\equiv}CSiMe_3$ in the presence of *Lewis* acids, such as scandium or ytterbium triflate, in either THF or Et_2O. However, treatment of **11** with 4.5 equiv. of $LiC{\equiv}CSiMe_3$ led to complete conversion to **12** (α/β 55:45). Performing this addition on a multigram scale followed by reductive dehydroxylation and concomitant

Scheme 1



a) HBr in AcOH, $CHCl_3$; 94%. *b*) $Hg(CN)_2$, allyl alcohol; 85%. *c*) MeONa, MeOH; >98%. *d*) $PhCH(OMe)_2$, MeCN, $TsOH \cdot H_2O$; 89%. *e*) BnBr, NaH, DMF; 73%. *f*) $4\text{-}ClC_6H_4CH_2Cl$, NaH, DMF; 83%. *g*) $NaBH_3CN$, HCl in Et_2O, THF; 69%. *h*) $MeOCH_2Cl$, NaH, DMF; 70%. *i*) $[Ir(MePh_2P)_2(C_8H_{12})]PF_6$, H_2, THF, then I_2 in H_2O; 87%. *j*) Ac_2O, DMSO; 97% of crude **11**.

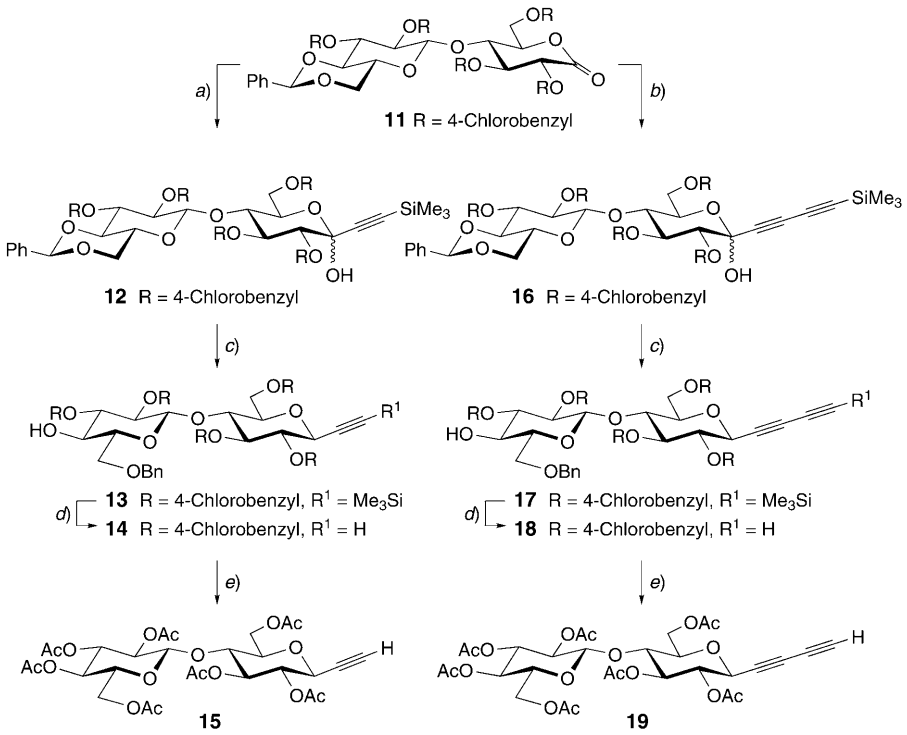
reductive opening of the 1,3-dioxane ring with Et_3SiH and $BF_3 \cdot Et_2O$ [38] yielded 72% of the β-configured alcohol **13**. *C*-Desilylation of **13** to **14** (MeONa in MeOH [50], 89%), followed by acetolytic debenzylation (TMSOTf in Ac_2O) gave the crystalline cellobiosyl-acetylene **15** (76%).

The butadiyne **19** was prepared in a similar way. Addition of the lithium acetylide derived from bis[1,4-(trimethylsilyl)buta-1,3-diyne] to the cellobionolactone **11** gave the hemiketals **16** (α/β 3:2). Concomitant dehydroxylation of **16** and reductive dioxane ring opening yielded 52% of the cellobiosyl-buta-1,3-diyne **17**. In contradistinction to the preparation of the alkyne **12**, the preparation of the butadiyne **16** required only a slight excess of the alkynyl reagent. *C*-Desilylation of **17** to **18** (87%) followed by acetolytic debenzylation gave the crystalline cellobiosyl-buta-1,3-diyne **19** (63%).

Sonogashira coupling [51–53] of the anthraquinone triflate **20** [3] and the cellobiosylacetylene **15** at 60° followed by selective deacetylation of the phenolic AcO group ($(NH_4)_2CO_3$ in DMF [3][54][55]) gave 74% of the *C*-glycoside **21** that was triflated under standard conditions to yield 96% of the aryl triflate **22** (*Scheme 3*). *Sonogashira* coupling of **22** with the cellobiosyl butadiyne **19** at room temperature [52][53] yielded 87% of the bis-*C*-cellobiosylated anthraquinone **24**. Deacetylation of **21** with MeONa in MeOH gave 95% of the mono-*C*-glycoside **23**. The corresponding bis-*C*-cellobiosyl derivative **25** was obtained in a yield of 71% by treating **24** with KCN in $MeOH/CH_2Cl_2$ [3] followed by reversed-phase column chromatography.

The ^1H- and ^{13}C-NMR data for the glucosyl units of the cellobiosyl-ethynes **13**–**15**, the cellobiosyl-buta-1,3-diynes **17**–**19**, and their template-bound derivatives **21**–**25** are

Scheme 2

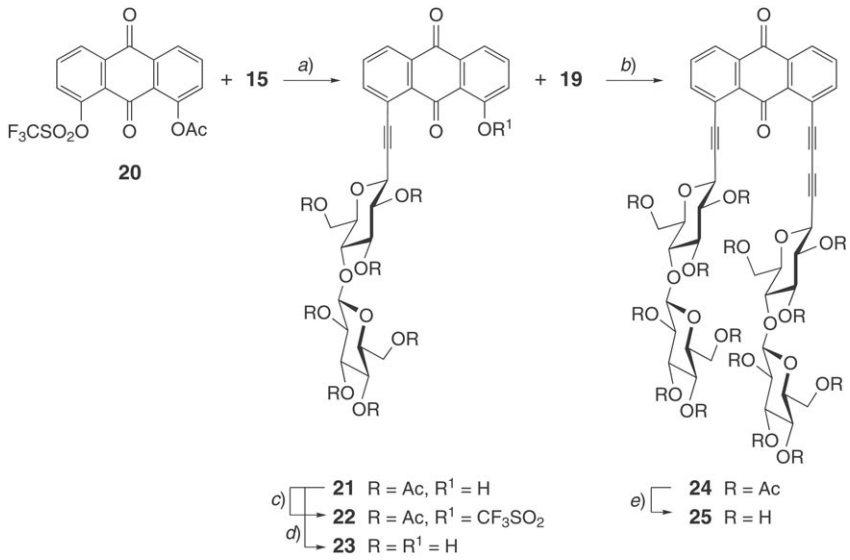


a) BuLi, $Me_3SiC{\equiv}CH$, THF, $-78°$. *b*) MeLi·LiBr, $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$, THF, $-78°$. *c*) Et_3SiH, $BF_3{\cdot}OEt_2$, CH_2Cl_2/MeCN; 72% of **13** from **11**; 52% of **17** from **11**. *d*) MeONa, THF/MeOH; 89% of **14**; 87% of **18**. *e*) Ac_2O, Me_3SiOTf, 20–25°; 76% of **15**; 63% of **19**.

listed in *Tables 5–8* in the *Exper. Part.* $^3J(1,{\equiv}CH)$ of the ethyne **14** is larger than $^5J(1,{\equiv}CH)$ of the buta-1,3-diyne **18** (2.2 *vs.* 0.6 Hz). $J(1,2)$, $J(2,3)$, $J(3,4)$, and $J(4,5)$ values evidence the $^4C_1$ conformation of all pyranosyl units. The ethynyl and the buta-1,3-diynyl group have a similar influence upon the ^{1}H- and ^{13}C-NMR chemical shifts of the sugar residues, as evidenced by the chemical shift differences ($\Delta\delta$ values) for the corresponding pairs **13**/**17**, **14**/**18**, and **15**/**19** (H–C(1^I): 0.03–0.06, other H–C: $\leq$0.03, C(1^I): 0.1–0.4, C(2^I): 0.5–0.7, and other C: $\leq$0.2 ppm)[4]). However, the anthraquinonyl moiety of **21** leads to a significant downfield shift, as evidenced by the ^{1}H-NMR $\Delta\delta$ values for the pair **21** and **16**. Large downfield shifts are observed for H–C(1^I) and H–C(2^I) (0.42 and 0.25 ppm, resp.) and smaller ones for H–C(3^I) to H–C(6^I) (0.08–0.12 ppm). Even H–C(1^{II}) to H–C(6^{II}) are shifted downfield by 0.04–0.06 ppm. Similarly, the *C*-signals of **21** are shifted downfield ($\Delta\delta$ for C(1^I): 1.1, C(2^I): 0.2, C(3^I): 0.6, and C(4^I) to C(6^{II}): $\leq$0.1 ppm). C(1^I) of the cellobiosyl-ethynes and cellobiosyl-buta-1,3-diynes res-

[4]) According to the 1996 recommendations of the nomenclature of carbohydrates, the monomer units of the cellooligosides are numbered with roman numerals in ascending order starting from the alkynylated end (corresponding to the reducing end).

Scheme 3

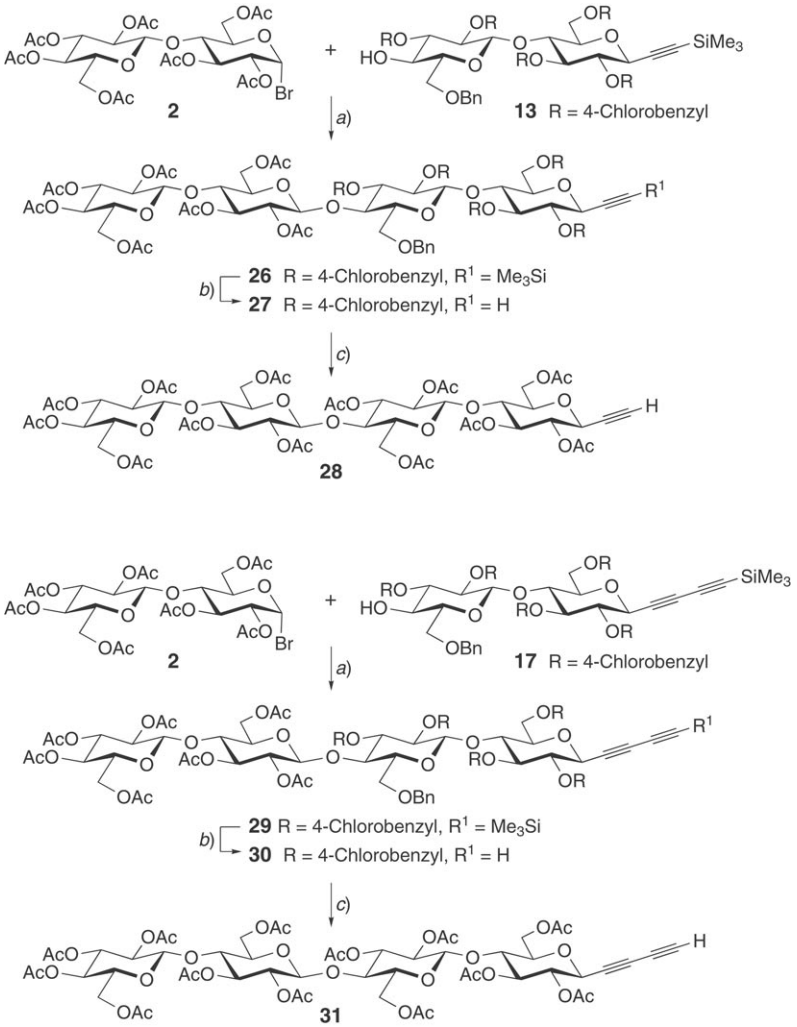


a) $[Pd(PPh_3)_2]Cl_2$, CuI, Et_3N/DMF 1:5, 60°, then $(NH_4)_2CO_3$; 74%. *b*) As *a*, but at 24° and without $(NH_4)_2CO_3$; 87%. *c*) Tf_2O, Et_3N, CH_2Cl_2; 96%. *d*) MeONa, MeOH; 95%. *e*) KCN, MeOH/CH_2Cl_2; 70%.

onates upfield at 68.3–70.4 ppm, whereas the signal for C(5^I) is shifted downfield to 76.8–79.3 ppm (compare with 74.9 ppm for the β-celloside **7**). The position of the ^{13}C-NMR signals of the ethynyl and the buta-1,3-diynyl C-atoms is characteristically influenced by the terminal substituent (Me_3Si, H, or anthraquinonyl). The assignment of the ^{1}H- and ^{13}C-NMR signals of **24** and **25** to the ethynylated or buta-1,3-diynylated chain is based on the interpretation of DQFCOSY and HSQC spectra and on a comparison with the values of the mono-chained cellobiosyl-ethynes **21** and **23**, and the mono- and double-chained glucopyranosyl-ethynes and glucopyranosyl-buta-1,3-diynes (data in [3]). Due to the shorter distance to the anthraquinonyl moiety, the ^{1}H-NMR signals of the ethynylated chain of **24** (except the one for H–C(4^I)) are shifted downfield relative to the corresponding signals of the buta-1,3-diynylated chain; strongest downfield shifts are observed for H–C(1^I), H–C(2^I), and H–C(5^I) ($\Delta\delta = 0.25$, 0.18, and 0.10 ppm, respectively).

2. *Synthesis of the Template-Bound Cellotetraosyl-ethynes and Cellotetraosyl-1,3-butadiynes.* We planned to prepare the intermediate acetylated cellotetraose *C*-glycosides **28** and **31** *via* **26** and **29** that should be obtained by *Koenigs–Knorr* glycosylation [56] with the cellobiosyl bromide **2** of the selectively protected cellobiosyl-ethyne **13** and cellobiosyl-buta-1,3-diyne **17**, respectively (*Scheme 4*). Glycosidation in toluene/CH_2Cl_2 1:1 with 4 equiv. of **2** at −35° to 25° for 2 days and in the presence of excess AgOTf yielded 84% of the crystalline cellotetraosyl-ethyne **26**, while the AgOTf-promoted glycosidation of **13** by **2** in $ClCH_2CH_2Cl$ at −35° gave only traces of **26**, and changing the solvent to CH_2Cl_2 or MeCN hardly improved the conversion. *C*-Desilyla-

Scheme 4



a) AgOTf, 3-Å mol. sieves, toluene/CH_2Cl_2; 84% of **26**; 82% of **29**. *b*) $Bu_4NF \cdot 3\,H_2O$, THF; 86% of **27**; 94% of **30**. *c*) Me_3SiOTf, Ac_2O; 76% of **28**; 65% of **31**.

tion of **26** with $Bu_4NF \cdot 3\,H_2O$ afforded 86% of **27**. Acetolytic debenzylation of **27** gave the crystalline peracetylated cellotetraosyl-ethyne **28** (76%).

The cellotetraosyl-buta-1,3-diyne **31** was similarly synthesised from the bromide **2** and the cellobiosyl-buta-1,3-diyne **17**. Glycosylation of **17** with **2** under the same conditions that we used for the synthesis of **26** yielded 82% of **29**. Desilylation of **29** gave the terminal butadiyne **30** (94%) that was transformed by acetolysis to the peracetate **31** (65%).

Sonogashira coupling of the triflated anthraquinone **20** with the cellotetraosyl-acetylene **28** under the conditions used for the preparation of the cellobiosyl-ethyne **21** and

the cellobiosyl-buta-1,3-diyne **24** produced a complex mixture (*Scheme 5*). Only little conversion resulted from performing the coupling at ambient temperature. Addition of Bu_4NI (1.5 equiv.) proved beneficial, as observed by *Yamaguchi* and co-workers [57], and the coupling of **20** with the cellotetraosyl-acetylene **28** occurred cleanly at ambient temperature[5]). Selective deacetylation of the crude coupling product and FC gave 75% of the cystalline cellotetraosylated 1-hydroxyanthraquinone **32**. Triflation under standard conditions transformed **32** to **33** (95%). The Bu_4NI-promoted coupling of this triflate with the cellotetraosyl-1,3-butadiyne **31** gave the crystalline bis-cellotetraoside **35** (59%). The mono-cellotetraoside **32** was deacetylated with MeONa in MeOH to provide 95% of **34**, while complete deacetylation of the bis-cellotetraoside **35** to **36** proved difficult. Standard methods, such as treatment with MeONa in MeOH, K_2CO_3 in MeOH, or KCN in MeOH failed to provide the desired product. Deacetylation with aqueous solutions of trialkylamines, such as Et_3N led to a very poor conversion even after 7 days, while aqueous KOH (30 equiv.) provided only small amounts of **36**. Finally, 78% of the completely deacetylated **36** were obtained by using 28–29 equiv. of Bu_4NOH in H_2O.

The ^{1}H- and ^{13}C-NMR data for the glucosyl units of the cellotetraosyl-ethynes and -buta-1,3-diynes **26**–**36** are listed in *Tables 9–12* in the *Exper. Part*. The acetoxylated and benzyloxylated centres of **26**, **27**, **29**, and **30** show the expected relative chemical shifts (^{1}H-NMR: downfield shift for acetoxylated centres, ^{13}C-NMR: downfield shift for benzyloxylated centres). The ^{1}H- and ^{13}C-NMR chemical shifts for unit I and IV of the cellotetraosyl-ethynes and -buta-1,3-diynes **28** and **31**–**36** agree well with the corresponding values for unit I and II of the peracetylated cellobiosyl-ethynes and -buta-1,3-diynes. Unit II and III of **28** and **31**–**33** show slightly shifted ^{1}H- and ^{13}C-NMR signals (^{1}H-NMR: $\Delta\delta \leq 0.03$ ppm with the exception of 0.06–0.08 ppm for H–C(2) of **28** and **31**–**33** and for H–C(5) of **32** and **33**; ^{13}C-NMR: $\Delta\delta < 0.2$ ppm). Individual ^{1}H- and ^{13}C-NMR signals are assigned to unit I of the ethynylated and buta-1,3-diynylated chain of **35**, whereas the signals for units II to IV of these chains overlap increasingly with the distance of the centres from the anthraquinonyl moiety.

3. *Synthesis of the Template-Bound Cellooctaosyl-ethynes and Cellooctaosyl-buta-1,3-diynes.* The preparation of the cellooctaosyl-alkynes according to the route described above for **36** requires a cellohexaosyl donor. Such a donor should be accessible in sufficiently large amounts by two sequential glycosidations, starting with cellobiosyl derivatives. The synthesis of the HO–C(4^{IV}) unprotected cellotetraoside **43** from the cellobiosyl bromide **2** and the cellobiosyl acceptor **38** [34][36] was described [30] (*Scheme 6*). The key step of this synthesis – the AgOTf-promoted *Koenigs–Knorr* glycosidation of **38** with 1.2 equiv. of **2** in $ClCH_2CH_2Cl$ at $-30°$ – afforded 89% of the cellotetraoside **39**. We could not reproduce the high yield by following this procedure. Even using 3 equiv. of **2** and changing the solvent to toluene/CH_2Cl_2 yielded only 50% of **39**. However, **39** was obtained in 87% yield by a TMSOTf-promoted glycosidation of **36** with the trichloroacetimidate **37** [61] in CH_2Cl_2 at $-40°$. The next steps, *i.e.*, deacetylation to **40**, benzylidenation to **41**, benzylation to **42**, and regioselective reduction to the alcohol **43** were performed according to [30], and resulted in an overall yield

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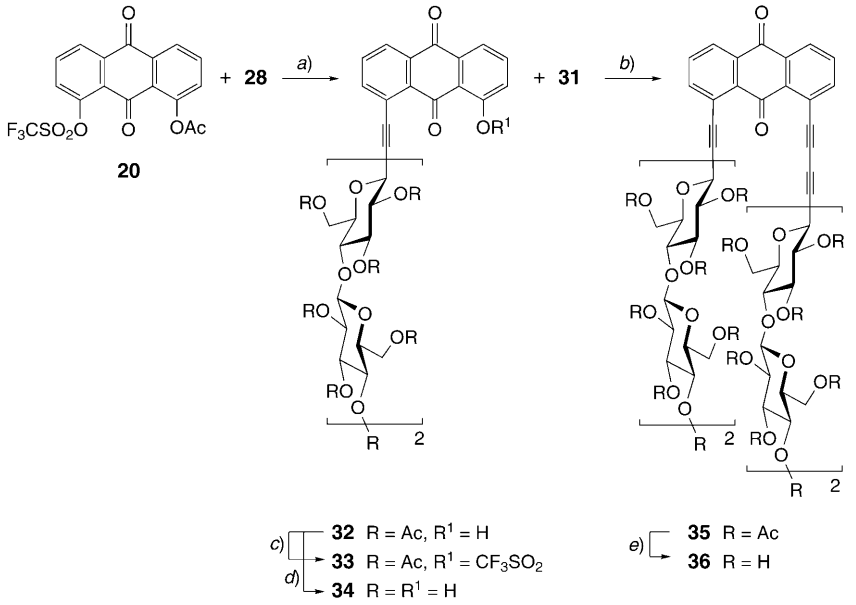
[5]) For other Bu_4NI-promoted cross couplings, see [58][59] and refs. cited therein. For a CuI-promoted *Sonogashira* coupling, see [53][60].

Scheme 5



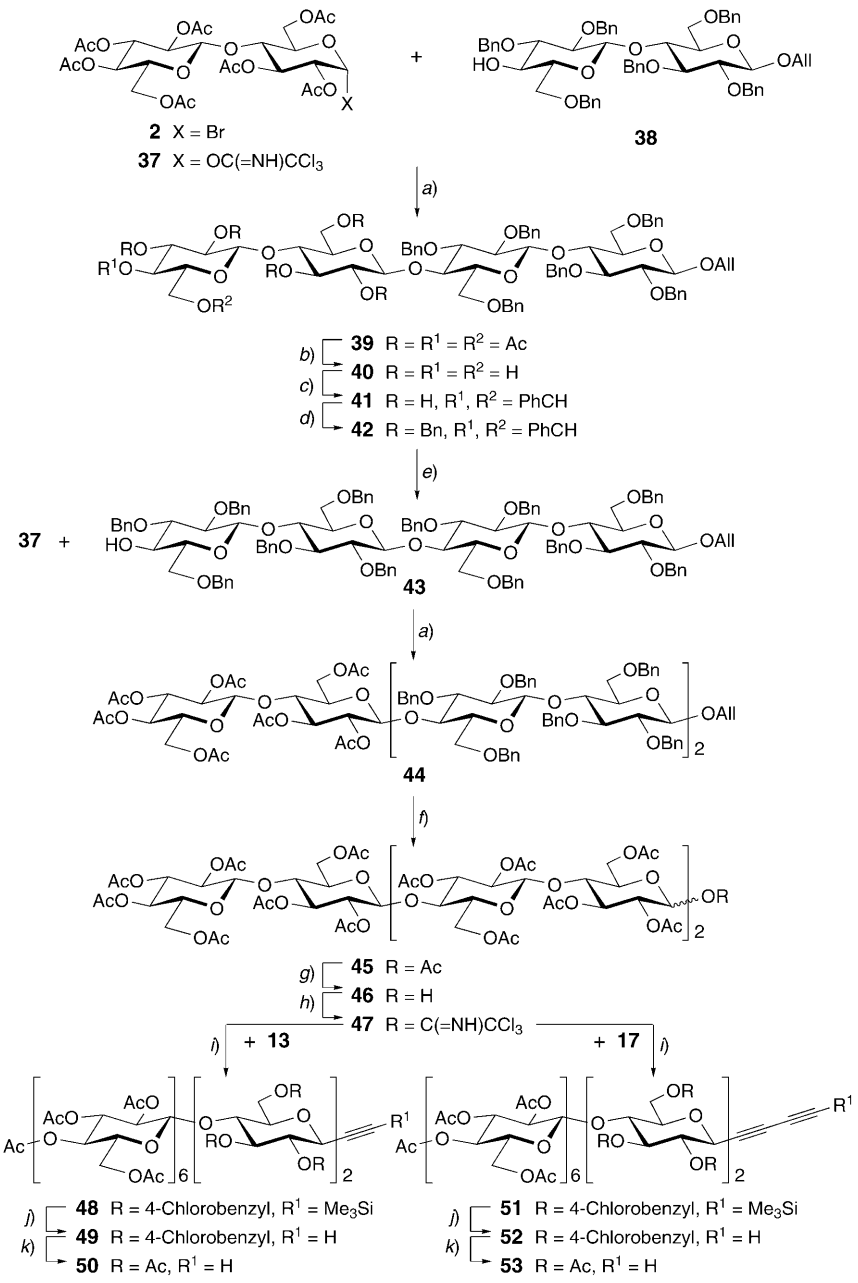
a) $[Pd(PPh_3)_2]Cl_2$, CuI, Bu_4NI, Et_3N/DMF 1:5, 24°, then $(NH_4)_2CO_3$; 75%. *b*) As *a*, but without $(NH_4)_2CO_3$; 59%. *c*) Tf_2O, Et_3N, CH_2Cl_2; 95%. *d*) MeONa, MeOH; 95%. *e*) Bu_4NOH, H_2O; 78%.

of 71%. The TMSOTf-promoted glycosidation of **43** with the trichloroacetamidate **37** in CH_2Cl_2 at −60° gave the cellohexaoside **44** (94%). Deallylation of **44** followed by hydrogenolytic debenzylation and acetylation yielded 75% of α/β-**45** 2:3[6]). Selective deacetylation of the anomeric AcO group of α/β-**45** with $(NH_4)_2CO_3$ in DMF [54] gave the hemiacetals α/β-**46** 2:1 (78%) [66] that were treated with Cl_3CCN in the presence of DBU. Crystallisation of the product from AcOEt/hexane yielded 71% of a 94:6 mixture of the trichloroacetimidates α/β-**47** [66]. The cellooctaoside **48** was obtained in 88% by a $BF_3 \cdot OEt_2$-promoted glycosylation of a slight excess of the cellobiosyl-ethyne **13** with α/β-**47** 94:6, while the TMSOTf-promoted glycosylation of **13** with a slight excess of α/β-**47** 94:6 at −78° yielded only 40% of **48**. *C*-Desilylation of **48** with $Bu_4NF \cdot 3\,H_2O$ to **49** followed by acetolytic debenzylation provided the peracetylated cellooctaosyl-ethyne **50** (75%). Similarly, the cellooctaosyl-buta-1,3-diyne **53** was synthesised *via* **51** and **52** from α/β-**47** 94:6 and the cellobiosyl-buta-1,3-diyne **17** (42% overall yield).

The Bu_4NI-promoted *Sonogashira* coupling at 0–28° of the triflate **20** with the cellooctaosyl-ethyne **50** gave 83% of the octaosylated anthraquinone **54** (*Scheme 7*). Selective deacetylation of the aromatic AcO group of **54** gave the hydroxy-anthraquinone **55** (88%) which was triflated to **56** (59%). The Bu_4NI-promoted coupling of **56** with the cellooctaosyl-1,3-butadiyne **53** gave 40% of the bis-cellooctaoside **58**. The

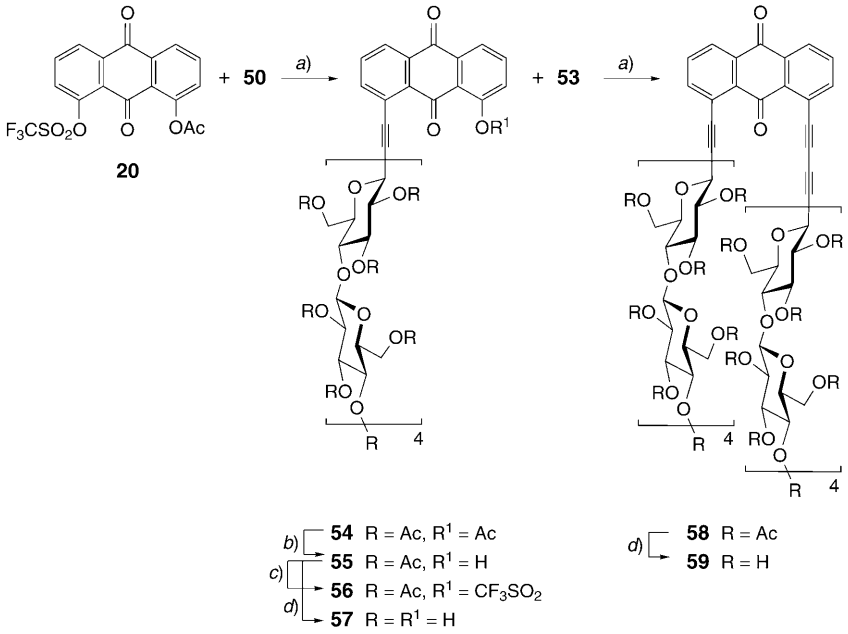
[6]) For the synthesis and NMR data of α-**45**, see [62–65].

Scheme 6



a) Me_3SiOTf, 4-Å mol. sieves, CH_2Cl_2, -40 (**38**) or $-60°$ (**43**); 87% of **39**; 94% of **44**. *b*) MeONa, MeOH; 99%. *c*) $ZnCl_2$, PhCHO; 84%. *d*) BnBr, NaH, DMF; 93%. *e*) $NaBH_3CN$, HCl, 3-Å mol. sieves, THF; 92%. *f*) H_2, $[Ir(MePh_2P)_2(C_8H_{12})]PF_6$, THF, then I_2, H_2O; $Pd(OH)_2/C$, 6 bar of H_2, AcOEt/MeOH; Ac_2O, pyridine; 75% of α/β-**45** 2:3. *g*) $(NH_4)_2CO_3$, DMF; 78% of α/β-**46** 2:1. *h*) Cl_3CCN, DBU, CH_2Cl_2; 71% of α/β-**47** 94:6. *i*) $BF_3 \cdot Et_2O$, 4-Å mol. sieves, CH_2Cl_2, $\leq -18°$; 88% of **48**; 72% of **51**. *j*) $Bu_4NF \cdot 3\,H_2O$, THF; 92% of **49**; 83% of **52**. *k*) $BF_3 \cdot OEt_2$, Ac_2O; 82 of **50**; 70% of **53**.

Scheme 7



a) $Pd(PPh_3)_2Cl_2$, CuI, Bu_4NI, Et_3N/DMF 1:5; 83% of **54**; 40% of **58**. *b*) $(NH_4)_2CO_3$, DMF; 88%. *c*) Tf_2O, Et_3N, CH_2Cl_2; 59%. *d*) Bu_4NOH, H_2O; 43% of **57**; 55% of **59**.

mono- and the bis-octaosides **55** and **58** were deacetylated with aqueous Bu_4NOH, similary to **35**, but sonification was required to dissolve the octaosides. This provided the deprotected mono-cellooctaoside **57** in 43% and the deprotected bis-cellooctaoside **59** in 55% yield.

The ^{1}H- and ^{13}C-NMR chemical shifts for unit I and VIII of the cellooctaosyl-ethynes and cellooctaosyl-buta-1,3-diynes **50**, **53**–**55**, and **57**–**59** resemble those of the terminal units of the corresponding cellobiosyl and cellotetraosyl analogues, whereas the ^{1}H- and ^{13}C-NMR signals for units II to VII of the cellooctaosyl derivatives mostly overlap (see *Tables 13* and *14* in the *Exper. Part*).

4. *Are the Template-Bound Cellooligosyl* C*-Glycosides Mimics of Cellulose I? Comparative Analysis of the Template-Bound Cellooligosyl-ethynes and Cellooligosyl-buta-1,3-diynes.* To facilitate the discussion, we have replaced the compound numbers of the oligosides of interest, designating the mono- and double-chained anthraquinonyl derivatives as **T-x** and **T-x-x** with **x** and **x-x** (**x** = 2, 4, and 8) denoting the number of glucosyl residues (*Fig. 2*,*a*). Similarly, the peracetates are labeled **A-x** and **A-x-x**. The deprotected 2-naphthylethyl cellooligosides [4], of interest as reference compounds, are designated as **N-x** and **N-x-x**. The ethynylated chain of **A-x-x** and **T-x-x** is termed *E* and the buta-1,3-diynylated chain *B*. According to carbohydrate nomenclature, the glucopyranosyl units of the cellooligosyl chains are labeled with roman numerals, as shown in *Fig. 2*,*b*, for the cellotetraoside **T-4-4**[4]). However, as the NMR signals of the internal units overlap strongly, particularly in the octaoside derivatives, we desig-

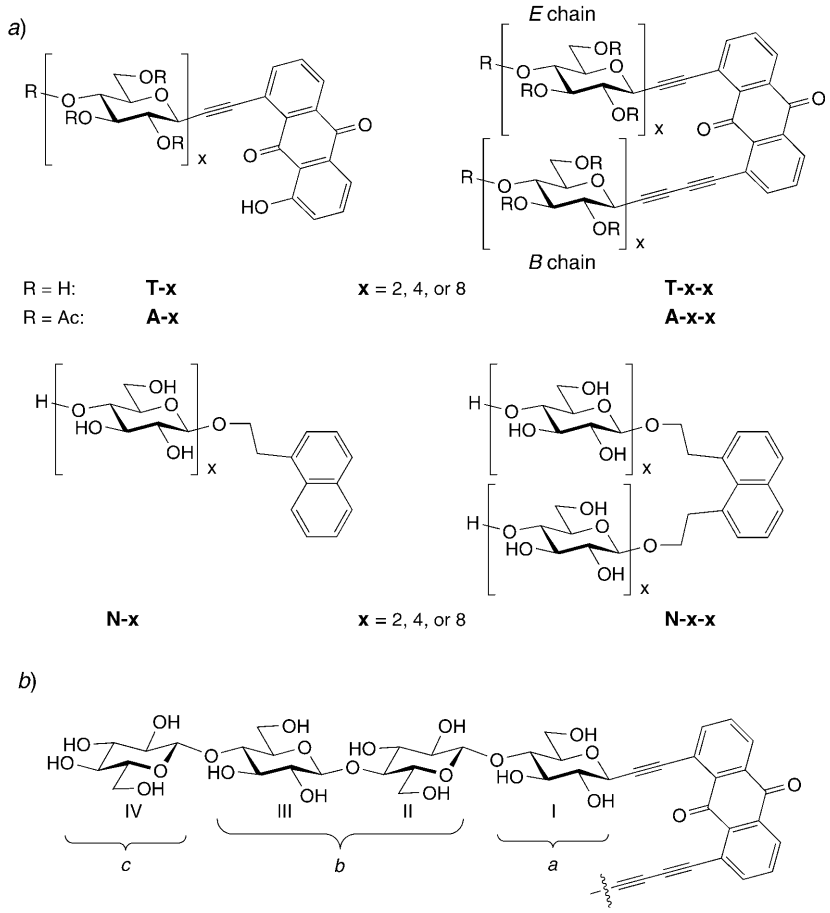


Fig. 2. a) *Numbering of the template-bound single- and double-chained cellodextrins, and labeling of the chains of* **T-x-x**, *and* b) *labeling of the glucopyranosyl units of template-bound cellodextrins*

nate units I as *a*, the terminal units as *c*, and the sum of the internal units (units II and III of tetraosides and units II–VII of octaosides) as *b*. These designations of the glucosyl residues reflect regularities in the NMR spectra, as discussed below. To further simplify the notation, the O-atoms are numbered in the same way as C-atoms.

The template-bound cellooligosaccharides **T-x** and **T-x-x** (**x** = 2, 4, and 8) are yellow-to-brownish solids that decompose upon melting. The double-chained **T-x-x** possess higher melting points than their mono-chained **T-x** analogues. The shorter **T-x** and **T-x-x** (**x** = 2 and 4) are well soluble in DMSO, DMF, and *N*,*N*-dimethylacetamide (> 40 mmol/l), slightly soluble in H_2O (< 5 mmol/l), and nearly insoluble in MeOH, EtOH, CF_3CH_2OH, AcOH, THF, dioxane, and $CHCl_3$. The solubility of **T-x** and **T-x-x** in H_2O decreases with increasing number of sugar residues. The cellooctaosides **T-8** and **T-8-8** are only soluble in DMSO. Hence, most of the NMR studies were conducted in (D_6)DMSO solution.

4.1. *Investigation of the H-Bonding of* **T-x** *and* **T-x-x** *in DMSO Solution*. The ^{1}H-NMR chemical shift of the OH groups (δ(OH)), the vicinal coupling constant (J(H,OH)), and the temperature dependence of the OH signals ($\Delta\delta$(OH)/ΔT) are useful parameters for the investigation of H-bonding of alcohols and polyols in (D_6)DMSO [67][68]. Fully solvated OH groups acting as H-donors in an intermolecular H-bond to (D_6)DMSO are characterised by a downfield shift of the OH signal, J(H,OH) values of 4.5–5.5 Hz for equatorial and of 4.2–4.4 Hz for axial OH groups, and a strong temperature dependence ($|\Delta\delta(\mathrm{OH})/\Delta T| > 4.5$ ppb/K). OH Groups acting as H-donors in an intramolecular H-bond are readily detected by an upfield shift of the OH signals, by J(H,OH) values deviating from those of fully solvated OH groups, and by a weak temperature dependence ($|\Delta\delta(\mathrm{OH})/\Delta T| < 3$ ppb/K) [67][68]. The δ(OH) values for OH groups of monosaccharides and of the terminal units of oligosaccharides are a useful reference for the interpretation of δ(OH) values for OH groups of the internal units of oligosaccharides. The H-bonding of β-cellobiose and methyl β-cellobioside [69] in (D_6)DMSO has been analysed [68]. All OH groups, with the exception of HO(3^{I}) are more or less fully solvated. A completely persistent inter-residue O(3)–H···O(5′) H-bond of methyl β-cellobioside is evidenced by J(3,OH) = 1.7 Hz, δ(HO(3)) = 4.68 ppm, and $\Delta\delta(\mathrm{HO}(3))/\Delta T = -2.6$ ppb/K.

In the templated cellooligosaccharides **N-x** and **N-x-x** (**x** = 2, 3, 4, and 8) one or two glycosidically bonded cellodextrin chains are attached to naphthalene-1-ethanol and naphthalene-1,8-diethanol. The H-bonding of solutions of these oligosaccharides in (D_6)DMSO was analysed [4]. HO(3*a*) and HO(3*b*) (δ(OH) = 4.59–4.73 ppm, J(H,OH) < 2 Hz, $\Delta\delta(\mathrm{OH})/\Delta T = -1.7$ to -2.2 ppb/K) are engaged in inter-residue H-bonds to O(5′) of the neighbouring glucosyl unit, whereas the other OH groups are involved in intermolecular H-bonds to the solvent (J(2,OH) = J(3*c*,OH) = J(4*c*,OH) = 4.5–5.3 Hz, J(6,OH) = 5.4–6.5 Hz, $\Delta\delta(\mathrm{OH})/\Delta T = -4.2$ to -7.2 ppb/K). HO(2*b*) resonates at lowest field (5.37 ppm), followed by HO(2*c*) (5.20 ppm), HO(2*a*) (5.13–5.14 ppm), HO(3*c*) (4.99 ppm), and HO(4*c*) (4.96 ppm), whereas HO(6*b*) resonates at 4.63–4.69 and HO(6*a*) and HO(6*c*) at 4.52–4.61 ppm. Only small shift differences ($\Delta\delta$(OH) values) were observed for the OH groups of the internal units *b* ($\Delta\delta(\mathrm{OH}) \leq 0.01$ ppm with the exception of 0.08 ppm for HO(3^{III}) of the cellotetraosides and HO(3^{VII}) of the cellooctaosides). Weak interchain H-bond interactions in **N-x-x** were only observed for unit *a* closest to the template.

No concentration dependence of the δ(OH) and δ(H–C(1)) values of **T-4-4** was observed in (D_6)DMSO solution at concentrations between 18 and 62 mmol (*Fig. 3*). Since all ^{1}H-NMR spectra of **T-x** and **T-x-x** were recorded at low concentration (10 mmol/l for **T-x** and 5 mmol/l for **T-x-x**), solute–solute interactions can be neglected.

All OH groups of the monoglucoside **T-1** and the diglucoside **T-1-1** are solvated in (D_6)DMSO [3]. A weakly persistent flip-flop H-bond between the two primary OH groups of the diglucoside **T-1-1** is suggested by the upfield shift of both OH groups (0.04 ppm for HO(6*E*) and 0.09 ppm for HO(6*B*) relative to HO(6) of **T-1**).

The unambiguous assignment of the OH signals of **T-x** and **T-x-x** (**x** = 2, 4, and 8) in (D_6)DMSO is based on the interpretation of DQFCOSY, HSQC, and TOCSY (only of **T-4**, **T-4-4**, and **T-8-8**) spectra and a comparison with the spectra of **N-x** and **N-x-x** (*Table 1*). The OH groups of **T-x** and **T-x-x** show similar chemical shifts as the corresponding OH groups of **N-x** and **N-x-x** except for HO(2*aE*), HO(2*aB*), and HO(6*a*)

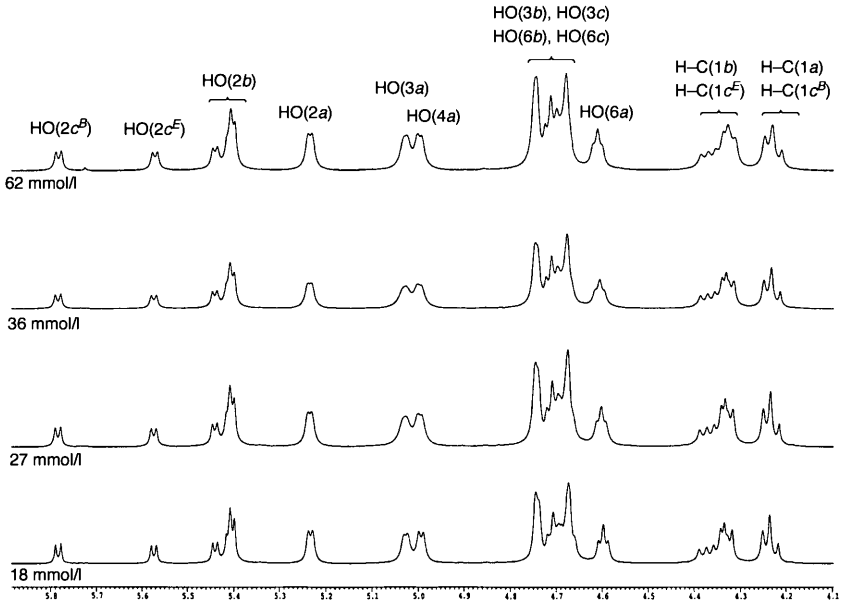


Fig. 3. *Concentration-dependence of the* ^{1}*H-NMR spectra of* **T-4-4** *in* (D_6)*DMSO: H–C(1) and OH signals*

which are shifted downfield by 0.43, 0.54, and 0.10 ppm, respectively, due to the alkynyl substituent [70]. HO(3*a*) and HO(3*b*) of **T-x** and **T-x-x** are involved in an inter-residue H-bond to O(5′) as evidenced by the upfield shift (4.75–4.65 ppm) and a small J(3,OH) value (< 1.5 Hz). The other OH groups of **T-x** and **T-x-x** are engaged in intermolecular H-bonds to (D_6)DMSO. As it was already observed for **N-4** and **N-4-4**, HO(3^{III}) of **T-4** and **T-4-4** resonates downfield to HO(3^{II}) ($\Delta\delta = 0.06–0.07$ ppm). A similar downfield shift is expected for HO(3^{VII}) of **T-8** and **T-8-8**, but overlapping HO(3) and HO(6) signals prevent an exact assignment.

A comparison of δ(OH) of the ethynylated chain *E* of the di-cellosides **T-x-x** (**x** = 2, 4, and 8) with δ(OH) of **T-x** (**x** = 2, 4, and 8; $\Delta\delta \leq 0.04$ ppm; *Table 1*) shows a weak influence of the buta-1,3-diynylated chain of **T-x-x** on the chemical shift of the OH groups of the *E* chain. These small shift differences suggest at best very weak inter-chain H-bond interactions. The OH groups of the buta-1,3-diynylated chain *B* of **T-x-x** (**x** = 2, 4, and 8) possess similar chemical shifts as the OH groups of the ethynylated chain *E* ($\Delta\delta \leq 0.03$ ppm) with the exception of HO(2*a*) which shows the expected downfield shift due to the buta-1,3-diynyl substituent (0.21 *vs.* predicted 0.16 ppm [70]). Duplication of OH signals of **T-x-x** is only observed for those OH groups that are close to the template, *i.e.*, OH groups of unit *a* and HO–C(2^{II}) (part of units *b*). This restricts the analysis by ^{1}H-NMR spectroscopy to inter-chain H-bond interactions of these OH groups of **T-x-x**.

HO(2*a*) of **T-x** (**x** = 2, 4, and 8) resonates as broad *singlet* at 5.56–5.58 ppm, whereas HO(2*aE*) and HO(2*aB*) of **T-x-x** give rise to sharp *doublet*s at 5.56–5.57 and 5.77–5.78 ppm, respectively (*Table 1*). That HO(2*a*) of **T-x** and HO(2*aE*) of **T-x-x** display the

Table 1. *^{1}H-NMR δ(OH)* [ppm] *and* J*(H,OH)* [Hz] *Values* (in parentheses) *of* **T-x** *and* **T-x-x** (**x** = 2, 4, 8) *in (D$_6$)DMSO* (assignments based on DQFCOSY and HSQC spectra and on TOCSY spectra of **T-4**, **T-4-4**, and **T-8-8**)

	T-2 *E* chain	**T-4** *E* chain	**T-8** *E* chain
HO(2*a*)	5.58[a])	5.58[a])	5.56[a])
HO(3*a*)	4.82 (< 1.5)	4.76 (< 1.5)	4.74–4.66
HO(6*a*)	4.71 (5.8)	4.68 (5.1)	4.74–4.66
HO(2*b*)		5.42 (5.0), 5.43 (5.0)	5.41 (4.9), 5.39 (*ca.* 4.4; 6 H)
HO(3*b*)		4.75 (< 1.5), 4.69 (< 1.5)	4.74–4.66
HO(6*b*)		4.71 (5.2)	4.74–4.66
HO(2*c*)	5.27 (4.7)	5.24 (4.7)	5.21 (4.8)
HO(3*c*)	5.05 (4.6)	5.04 (3.8)	5.01 (4.8)
HO(4*c*)	5.02 (4.7)	5.00 (4.9)	4.98 (5.3)
HO(6*c*)	4.64 (5.2)	4.61 (5.1)	4.58 (5.1)
	T-2-2 *E* chain, *B* chain	**T-4-4** *E* chain, *B* chain	**T-8-8** *E* chain, *B* chain
HO(2*a*)	5.57 (5.5), 5.78 (5.8)	5.56 (5.7), 5.77 (5.9)	5.56 (5.5), 5.77 (5.8)
HO(3*a*)	4.80 (< 1.5), 4.81 (< 1.5)	4.74 (< 1.5)	4.74–4.65
HO(6*a*)	4.71 (6.0)	4.72–4.65	4.74–4.65
HO(2*b*)		5.39 (2 OH; 4.9), 5.40 (4.8), 5.43 (5.0)	5.43–5.38
HO(3*b*)		4.74 (< 1.5), 4.67 (< 1.5)	4.74–4.65
HO(6*b*)		4.72–4.65	4.74–4.65
HO(2*c*)	5.25 (4.9), 5.28 (5.0)	5.22 (4.9)	5.22 (4.7)
HO(3*c*)	5.03 (4.6)	5.00 (4.9)	5.01 (4.4)
HO(4*c*)	5.00 (5.4), 5.01 (6.0)	4.98 (5.4)	4.98 (5.0)
HO(6*c*)	4.62 (5.5), 4.63 (5.5)	4.59 (5.3)	4.58 (5.2)

[a]) Broad *s*, $w_{1/2}$ = 4.7–5.0 Hz.

same chemical shift is not in agreement with an intramolecular H-bond of HO(2*a*) of **T-x** to C(9′)=O, nor is such a H-bond expected, since this C=O group acts already as H-acceptor of HO(8′) that resonates at the expected low field (12.46–12.50 ppm). A fast H/H exchange of HO(2*a*) of **T-x** is responsible for the broadening of the signals; it is probably caused by the nearby phenolic HO(8′). The vicinal *J*(H,OH) of the other OH groups of the *E* chain of **T-x-x** are similar to the corresponding coupling constants of **T-x** (Δ*J* mostly smaller than 0.3 Hz). The values of *J*(2*b*,OH) and *J*(2*c*,OH) (4.7–5.0 Hz), and of *J*(6*b*,OH) and *J*(6*c*,OH) (5.1–5.2 Hz) of **T-x** and **T-x-x** do not hint at persistent intramolecular H-bonds. The larger *J*(2*a*,OH) value of **T-x-x** (**x** = 2, 4, and 8; 5.5–5.9 Hz) and *J*(6*a*,OH) values of **T-2** and **T-2-2** (5.8–6.0 Hz) may point at weakly persistent intramolecular H-bonds. Since a small *J*(2,OH) value is expected for intra-residue O(2)–H···O(3) or O(2)–H···O(1) H-bonded glucopyranosyl species ($J < 2$ Hz [71]), these larger *J*(2*a*,OH) values of **T-x-x** evidence either an electronic influence of the π-orbitals of the buta-1,3-diynyl substituent (*cf.* [72]) or weakly persistent inter-chain H-bonds of HO(2*a*). That both factors are operating is suggested by *J*(2,OH) of the mono- and double-chained glucopyranoside analogues (5.5–5.6 *vs.* 6.0 Hz [3]).

SIMPLE ^{1}H-NMR experiments [73] with (D_6)DMSO solutions of **T-4**, **T-4-4**, **T-8**, and **T-8-8** did not show any splitting of OH signals upon titrating with D_2O or CD_3OD, corroborating the absence of strongly persistent intramolecular H-bonds between OH groups.

The temperature dependence of the OH signals of **T-x** and **T-x-x** (**x** = 2, 4, and 8) in (D_6)DMSO was determined from 298 to 348 K in 10-K intervals. $\Delta\delta$(OH)/ΔT values are listed in *Table 2*. Similarly as observed for **N-x** and **N-x-x**, a weak temperature dependence of δ(HO(3*a*)) and δ(HO(3*b*)) values of **T-x** and **T-x-x** (**x** = 2, 4; −2.0 to −2.3 ppb/K) confirms the inter-residue H-bond of HO(3*a*) and HO(3*b*) to O(5) of the adjacent glucopyranosyl moiety. The weak temperature dependence of the δ(HO(8′)) value of **T-x** (−1.5 to −1.9 ppb/K) evidences an intramolecular H-bond of HO(8′) to C(9′)=O. $\Delta\delta$(OH)/ΔT Values in the range of −4.7 to −7.2 ppb/K for all other OH groups of **T-x** and **T-x-x** evidence more or less completely solvated OH groups. The $\Delta\Delta\delta$(OH)/ΔT values for corresponding OH groups of **T-x** and the *E* chain of **T-x-x** are small ($\leq$0.4 ppb/K), except for HOC(2*a*) with $\Delta\Delta\delta$(OH)/ΔT values of 0.4–0.7 ppb/K). The slightly higher $|\Delta\delta$(HO(2*aE*)/$\Delta T|$ values of **T-x-x** may suggest that HO(2*aE*) acts as H-acceptor of a weakly persistent inter-chain H-bond.

Table 2. *Temperature Coefficients $\Delta\delta$(OH)/Δ*T [ppb/K] *of* **T-x** *and* **T-x-x** *in (D_6)DMSO*[a])

	T-2	**T-4**	**T-8**	**T-2-2** *E* chain, *B* chain	**T-4-4** *E* chain, *B* chain	**T-8-8** *E* chain, *B* chain
HO–C(8′)	−1.9	−1.9	−1.9	–	–	–
HO(2*a*)	−7.2	−6.8	−6.0	−7.9, −6.6	−7.2, −6.2	−7.4, −6.4
HO(3*a*)	−2.2	−2.3	[b])	−2.0, −2.3	−2.2	−2.4, −2.4
HO(6*a*)	−5.6	−5.0	[b])	−5.6	−5.1	[b])
HO(2*b*)	–	−5.8, −6.1	−6.0	–	−5.8 to −6.0	−5.8 to −6.2
HO(3*b*)	–	−2.3, −2.2	[b])	–	−2.2	[b])
HO(6*b*)	–	−4.7	[b])	–	−5.0 to −5.2	[b])
HO(2*c*)	−6.0	−5.7	−5.9	−6.1, −6.2	−5.7	−5.8
HO(3*c*)	−6.7	−6.3	−5.8	−6.6, −6.2	−6.3	−6.2
HO(4*c*)	−6.0	−5.9	−5.0	−5.9, −6.2	−5.7	−6.2
HO(6*c*)	−5.1	−5.3	−5.3	−5.2, −5.5	−5.2	−5.3

[a]) Spectra were recorded from 298 to 348 K in 10-K intervals. [b]) Not assigned.

H-Bonding of **N-x** and **N-x-x** (**x** = 4 and 8) was investigated by analysis of ROESY spectra [4][7]). The analysis was restricted to the cross-peaks between H–C(1) and OH signals, as the signals for H–C(2) to H–C(6) overlapped. Cross-peaks between the HO(3^n) and H–C(1^{n+1}) signals (n = 1–3 for **N-4** and **N-4-4**, and 1–7 for **N-8** and **N-8-8**) confirme the inter-residue H-bond of HO(3^n). Cross-peaks between the HO(2) and H–C(1) signals of the same unit evidence a weakly persistent O(2^n)–H···O(6^{n-1}) H-bond. Inter-chain H-bonding of **N-4-4** and **N-8-8** is restricted to unit I;

[7]) See there for the differentiation between 'true' and relayed ROEs, such as TOCSY/ROE and exchange/ROE.

a weak inter-chain H-bond between the two HO(2^{I}) groups is possible, but could not be unambiguously proven.

ROESY Spectra of **T-4**, **T-4-4**, **T-8**, and **T-8-8** were recorded under identical conditions. Signal overlap prevents the assignment of the cross-peaks involving CH groups other than H–C(1). Therefore, the analysis was again limited to interactions between H–C(1) and OH groups, and between OH groups.

The partial ROESY spectrum of **T-4** shows seven positive cross-peaks between 4.0–6.0 ppm (*Fig. 4*). All HO(2) signals show cross-peaks with the H–C(1) signal of the same residue (peaks #1 to #4). These intra-residue interactions reveal weakly persistent inter-residue H-bonds of HO(2^{IV}) to HOC(6^{III}), HO(2^{III}) to HOC(6^{II}), and HO(2^{II}) to HO(6^{I}) – as also observed for **N-4** – and a weakly persistent bifurcated H-bond of HO(2^{I}) to the acetylene and C(9′)=O groups (marked in blue in *Fig. 5*). Additional positive cross-peaks between the signals of HO(3^{III}) and H–C(1^{IV}) (peak #5), HO(3^{II}) and H–C(1^{III}) (peak #6), and HO(3^{I}) and H–C(1^{II}) (peak #7) confirm the inter-residue H-bonds of HO(3) to O(5) of the next residue (marked in red in *Fig. 5*).

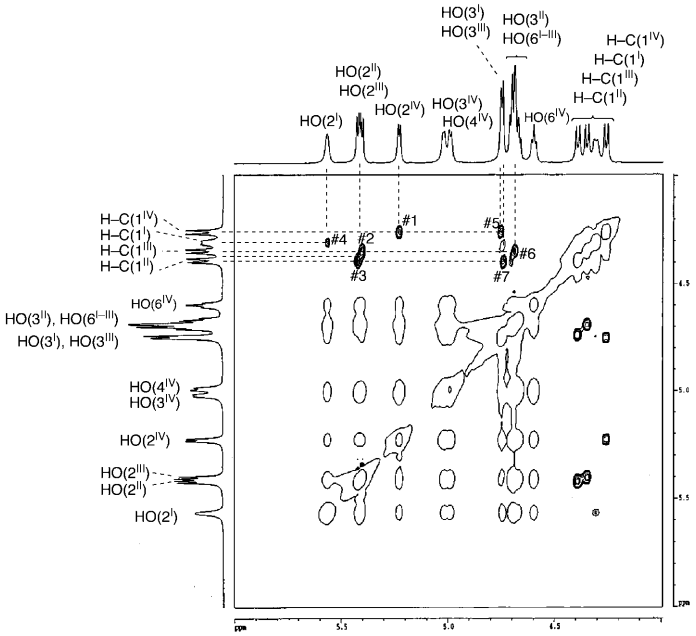


Fig. 4. *ROESY Spectrum of* **T-4**: *cross-peaks between H–C(1) and OH signals*

The partial ROESY spectrum of **T-4-4** between 4.0–6.0 ppm is depicted in *Fig. 6*. H–C(1^{I}), H–C(1^{II}), HO(2^{I}), and HO(3^{I}) of the *B* chain resonate at a position that differs from the one for the corresponding H-atoms of the *E* chain. The unambiguous assignment of the signals of **T-4-4** is based on the stronger downfield shift of HO(2^{I}) by the buta-1,3-diynyl group [70], and on the analysis of a DQFCOSY and a TOCSY spectrum. The ROESY spectrum of **T-4-4** shows cross-peaks analogous to those observed for **T-4** (peaks #1–#7); they evidence the completely persistent inter-residue

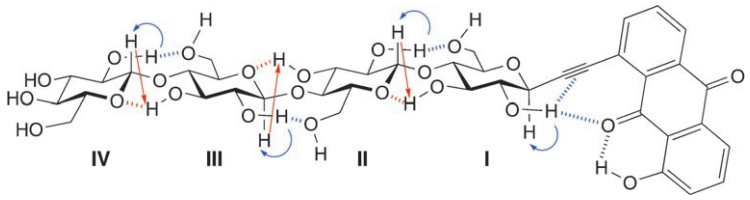


Fig. 5. *Interpretation of the ROESY spectrum of* **T-4***; arrows indicate ROE cross-peaks and hashed lines H-bonds*

O(3)–H···O(5) H-bonds and weakly persistent inter-residue H-bonds O(2)–H···O(6) (tautomer **A** in *Fig. 7*). The cross-peak pairs #4*B*/#4*E* and #7*B*/#7*E* reveal only intra-chain contacts; there are no cross-peaks for the corresponding inter-chain interactions. An additional cross-peak (#8) is observed between the signals of H–C(1^{IV}) and one HO(6) signal of the *multiplet* for HO($6^{I–III}$). For geometric reasons, it is best assigned to an intra-chain inter-residue close contact between H–C(1^{IV}) and HO(6^{III}). Analogous close contacts between H–C(1^{III}) and HO(6^{II}), and between H–C(1^{II}) and HO(6^{I}) may contribute to the cross-peaks #6 and #7. They evidence weakly persistent inter-residue H-bonds from HO(6) to HO(2) (interactions and H-bonds in green in tautomer **B**; *Fig. 7*). It is noteworthy that the cross-peaks between H–C(1) and OH signals reveal inter-residue flip-flop H-bonds between HO(6) and HO(2) of the double-

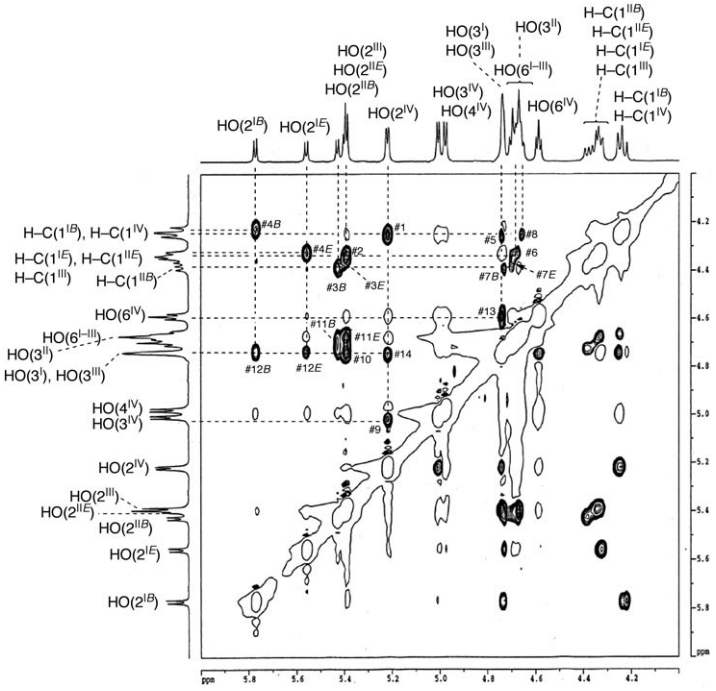


Fig. 6. *ROESY Spectrum of* **T-4-4***: cross-peaks between H–C(1) and OH signals*

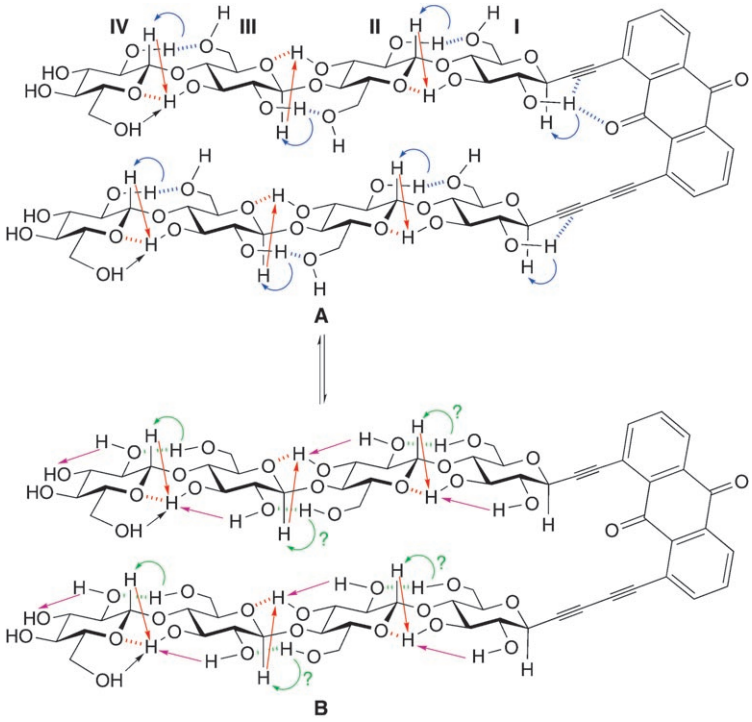


Fig. 7. *Interpretation of the ROESY spectrum of* **T-4-4**; *arrows indicate ROE cross-peaks and hashed lines H-bonds*

chained **T-4-4** and **N-4-4**, but not of the mono-chained **T-4** and **N-4** (only cross-peaks for unidirected O(2′)–H···O(6)H H-bonds).

There are several positive cross-peaks between OH groups (peaks #9 to #14) in the ROESY spectrum of **T-4-4**, whereas the ROESY spectrum of **N-4-4** showed only a single positive cross-peak between HO(2^{III}) and HO(3^{III}). The inter-residue H-bonds O(6)–H···O(2′) of tautomer **B** of **T-4-4** suggest a close intra-residue contact of HO(2) and HO(3). This is confirmed by cross-peaks between the signals of HO(2^{IV}) and HO(3^{IV}) (#9), HO(2^{III}) and HO(3^{III}) (#10), HO(2^{IIE}) and HO(3^{II}) (#11*E*), HO(2^{IIB}) and HO(3^{II}) (#11*B*), HO(2^{IE}) and HO(3^{I}) (#12*E*), and finally HO(2^{IB}) and HO(3^{I}) (#12*B*); they evidence an intra-residue close contact between HO(2) and HO(3) also for units I (marked with pink arrows in tautomer **B**). There are two additional positive cross-peaks between the broad *singlet* of HO(3^{I})/HO(3^{III}) and, on the one hand, the *triplet* of HO(6^{IV}) (#13) and, on the other hand, the *doublet* of HO(2^{IV}) (#14). Cross-peak #13 may be assigned to a close intra-chain contact between HO(6^{IV}) (*gg* conformation for HOC(6^{IV})) and HO(3^{III}), whereas cross-peak #14 cannot be assigned to an intra-chain contact (MM3* modeling predicts a H···H distance of 4.75 Å distance between HO(2^{IV}) and HO(3^{III})). A close inter-chain contact is possible between HO(2^{IVE}) and HO(3^{IIIB}) but considered improbable since there are no additional cross-peaks suggesting close contacts between OH groups of the other units, especially of unit I.

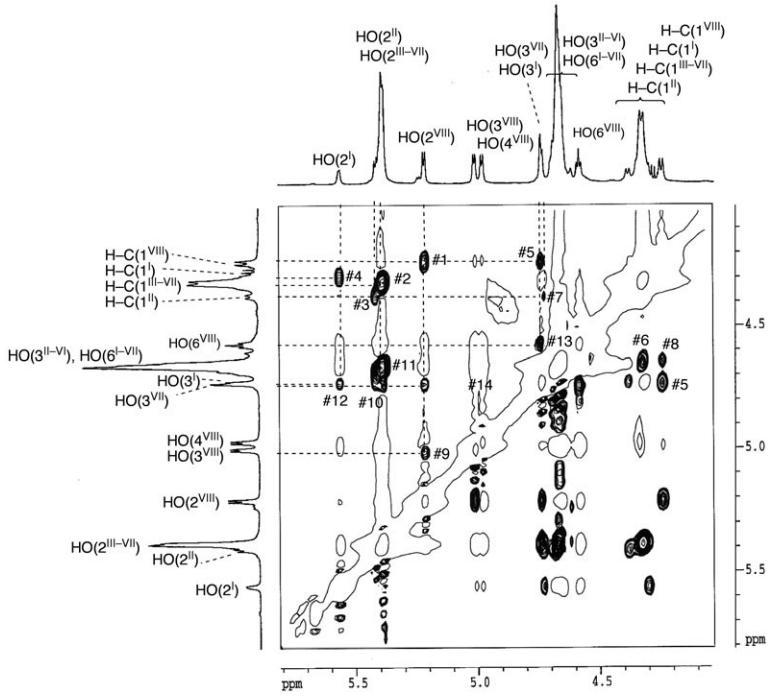


Fig. 8. *ROESY Spectrum of* **T-8**: *cross-peaks between H–C(1) and OH signals* (analogous numbering of cross-peaks as in **T-4-4**)

The ROESY spectrum of **T-8** (*Fig. 8*) shows similar cross-peaks as the ROESY spectrum of **T-4-4** for the *E* chain, confirming the inter-residue H-bond O(3)–H···O(5′) and the inter-residue flip-flop H-bond between HO(2) and HO(6′). The ROESY spectrum of **T-8-8** (*Fig. 9*) shows the same cross-peaks as the ROESY spectrum of **T-4-4** if one assumes that the cross-peaks #6, #7, #9, and #14 are hidden by strong negative absorptions. Hence, we expect that **T-4-4** and **T-8-8** adopt in (D_6)DMSO conformations which avoid inter-chain H-bond interactions. This is feasible in a V-shape arrangement of the cellooligosyl chains, as illustrated by the MM3*-calculated O(6)–H···O(2′) H-bonded tautomer of **T-8-8** in *Fig. 10* (considered a model of cellulose almost completely dissolved in DMSO). This structure suggests at best an inter-chain H-bond between HO(2^{1B}) and HO(6^{1E}). However, there are no cross-peaks between these OH signals in the ROESY spectra of **T-4-4** and **T-8-8**.

4.2. *Comparison of the CP/MAS* ^{13}*C-NMR Spectra of* **T-x** *and* **T-x-x** (**x** = 1, 2, 4, and 8) *with Those of Cellulose* I_α, I_β, *and II*. The solid-state CP/MAS ^{13}C-NMR chemical shifts of **T-x** and **T-x-x** (**x** = 1, 2, 4, and 8) are listed in *Table 3*[8]). The assignment of the signals is based on a comparison with the data in D_2O solution (especially of the glucosides **T-1** and **T-1-1**), and with the data of **N-x** and **N-x-x** in the solid state. The

[8]) We thank Prof. Dr. *Beat H. Meier*, *Ashwin Vorhofen*, and *Matthias Ernst*, Laboratory of Physical Chemistry, ETH Zurich, for the CP/MAS ^{13}C-NMR spectra of **T-x**, **T-x-x**, **A-x**, and **A-x-x**.

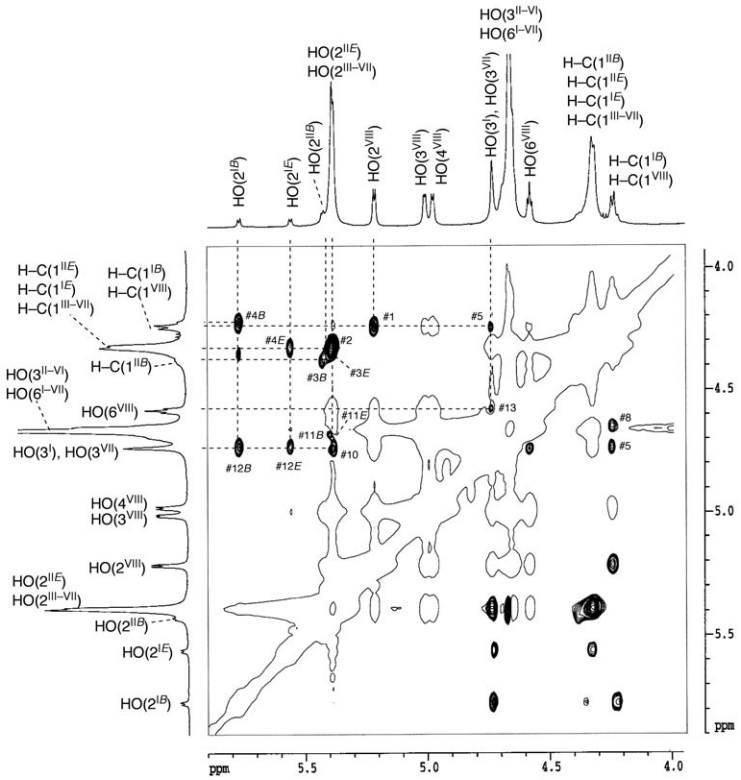


Fig. 9. *ROESY Spectrum of* **T-8-8**: *cross-peaks between H–C(1) and OH signals* (analogous numbering of cross-peaks as in **T-4-4**)

intensity of the anthraquinonyl and ethynyl signals decreases with increasing saccharide chain length; the spectra of **T-8** and **T-8-8** essentially show only signals of the central units *b*.

The solid-state CP/MAS ^{13}C-NMR spectra of the mono-chained **T-x** (**x** = 1, 2, 4, and 8) are well-resolved (*Fig. 11*). The spectrum of the glucoside **T-1** shows separate peaks for all C-atoms of the glucopyranosyl-ethynyl moiety; the δ values are very similar to those of the solution spectrum in (D_6)DMSO [3] ($\Delta\delta \leq 2.0$ ppm, with the exception of 4.6 ppm for C≡*C*–C(1)). Noteworthy are the downfield shift for C(5) resonating at 79.0 ppm, the upfield shift for C(1) appearing at 70.6 ppm, and signals for the ethynyl moiety at 94.1 and 88.6 ppm. The signals for the ethynyl group and for C(4*c*) of **T-2** and **T-4** are unambiguously assigned by a comparison with the corresponding values of **T-1** and by the decrease of their intensity in **T-4**. The duplication of the signals for C(1*c*) and C(4*a*) of **T2** (107.8/106.4 and 84.6/83.8 ppm, resp.; *Table 3*) hints at the presence of two different molecules in the unit cell. One signal is observed for each C(6*a*) and C(6*c*) (62.1/61.1 ppm). The spectrum of **T-4** exhibits the expected three peaks for C(1*b*) and C(1*c*) (109.3, 108.0, and 106.3 ppm), but in a ratio of *ca.* 3 : 2 : 1. Similarly, C(4*a*) and C(4*b*) of **T-4** give rise to two peaks at 82.4 and 83.0 ppm in a ratio larger than 3 : 1,

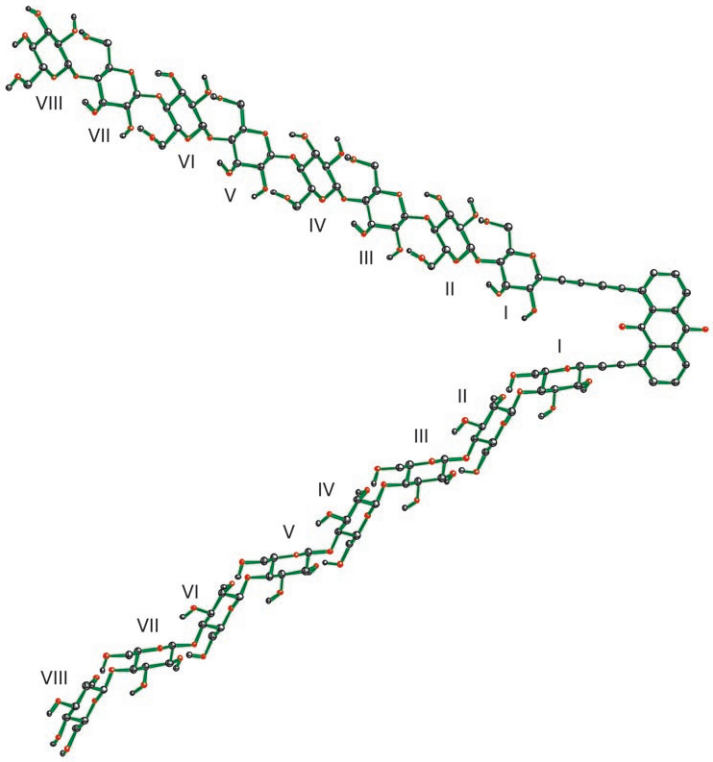


Fig. 10. *MM3*-Modeled, V-shaped conformer of* **T-8-8** *possessing inter-residue O(6)···H···O(2′) H-bonds* (H–C atoms are omitted for enhanced clarity)

whereas C(6*a*), C(6*b*), and C(6*c*) resonate as a single peak at 61.5 ppm with a weak shoulder at 61.0 ppm. The ratios for the C(1) and C(4) signals again suggest two different molecules in the unit cell. There is no downfield shift for C(4*a*) and C(6) of **T-2** and **T-4**, and of C(4*b*) of **T-4**; this clearly evidences that the cellobioside **T-2** and the cellotetraoside **T-4** are not H-bonding models for cellulose II. At best, they mimic cellulose chains at the surface of the crystallites (see *Introduction*). In contradistinction, the striking similarity of the solid-state CP/MAS ^{13}C-NMR spectrum of **T-8** and the one of cellulose II, especially the downfield shift of C(4) and C(6) at 89.9/88.7 and 63.8 ppm, respectively, reveals that the cellooctaoside **T-8** is an excellent mimic of cellulose II in the interior of the crystallite.

The solid-state CP/MAS ^{13}C-NMR spectrum of the C_1-symmetric diglucoside **T-1-1** is well-resolved (*Fig. 12* and *Table 3*). The assignment of the peaks of **T-1-1** is based on a comparison with its solution spectrum in (D_6)DMSO [3] and the solid-state spectrum of **T-1**. The solid-state CP/MAS ^{13}C-NMR spectra of **T-2-2** and **T-4-4** show only broad signals, probably due to a low degree of crystallinity. According to the upfield shift of C(4*b*) and C(4*c*) ($<$82 ppm), **T-2-2** and **T-4-4** do not mimic the H-bonds of cellulose I. The solid-state CP/MAS ^{13}C-NMR spectrum of **T-8-8** is much better resolved and

Table 3. *CP/MAS ^{13}C-NMR Chemical Shifts* [ppm] *of the Mono- and Bis*-C-*glucoside* **T-1** *and* **T-1-1**, *the Mono- and Bis*-C-*Cellodextrins* **T-x** *and* **T-x-x** (**x** = 2, 4, and 8), *and the Cellulose Polymorphs I_α, I_β* [19], *and II* [6]

	C(1) of units *c* and *b*	C(4) of units *a* and *b*[a])	C(2), C(3), C(5), C(1) of unit *a*, and C(4) of unit *c*	C(6)
T-1	–	–	79.0, 76.4, 72.5, 70.6, 68.7	61.5
T-2	107.8, 106.4	84.6, 83.8	78.5, 77.6, 77.0, 75.6, 74.3, 72.6, 68.8	62.1, 61.1
T-4	109.3, 108.0, 106.3	83.0, 82.4	78.5, 77.7, 76.4, 74.4, 72.8, 68.7	61.5
T-8	108.3, 106.2	89.9, 88.7	77.7, 76.0, 73.7	63.8
Cellulose II	108.3, 106.2	89.9, 88.7	77.8, 75.9, 73.8	64.2, 63.6
T-1-1	–	–	79–77, 74.2, 72.9, 71.9, 67.8	59.9, 59.1
T-2-2	104.2 (br.)	84.0 (br.)	76.72 (br.), 72.0 (br.)	62.7 (br.)
T-4-4	103.9 (br.)	83.5 (br.)	75.0 (br.)	62.8 (br.)
T-8-8	107.0, 105.7	89.9	76.1, 73.0	66.3, 64.3
Cellulose I_β	107.0, 105.2	90.1, 89.3	76.1, 75.3, 73.7, 72.5	66.8, 66.1
Cellulose I_α	106.3	91.0, 90.2	75.8, 73.8, 73.0, 72.0	66.5
	C(9) and C(10) of the template	C(8) of the template of **T-x**	other signals of the template	C≡C and C≡C–C≡C
T-1	185.9, 178.3	163.2	140.9, 116.0	94.1, 88.6
T-2	187.0, 179.1	160.1	144.0, 116.0	92.7, 85.6
T-4	186.9, 178.9	160.0	143.4, 116.0	92.3, 86.1
T-1-1	184.3, 180.8	–	143.6, 122.0	94.92, 86.1, 82.0, 80.7, 67.8
T-2-2	180.1 (br.)	–	141.3, 121.8	92.7 (br.)
T-4-4		–	143.0, 122.0	93.9 (br.)

[a]) Except C(4) of **T-1** and **T-1-1**.

resembles that of cellulose I_β, especially with regard to the two peaks for C(1) at 107.0 and 105.7 ppm. A broad peak for C(4) of **T-8-8** at 89.9 ppm replaces the double-headed signal for C(4) of cellulose I_β at 90.1/89.3 ppm. We conclude that **T-8-8**, unlike **N-8-8**, is indeed a H-bond mimic of cellulose I. While a comparison of **T-8-8** with **N-8-8** strongly suggests that implementation of the phase shift is crucial to mimic cellulose I, it is not yet clear which one of the three factors – the rigid linkers, the optimised distance between the chains, and the phase shift between the chains – is mostly responsible to render **T-8-8** a good mimic of cellulose I_β.

4.3. *Comparison of the X-Ray Powder-Diffraction Spectra of* **T-8** *and* **T-8-8** *with Those of Celluloses.* As several attempts to grow single crystals of **T-8** and **T-8-8** suitable for X-ray diffraction failed, we analysed these compounds by X-ray powder diffraction and compared the spectra with those of celluloses [5] (*Fig. 13*). The powder-diffraction spectra of **T-8-8** and **T-8**[9]) resemble strongly that of cellulose I and cellulose II, respectively, confirming that **T-8-8** is an oligomeric mimic of cellulose I and **T-8** of cellulose II.

[9]) We thank Prof. Dr. *Reinhard Nesper* and Dr. *Qinxing Xie*, Laboratory of Inorganic Chemistry, ETH Zurich, for the powder diffraction spectra of **T-8** and **T-8-8**.

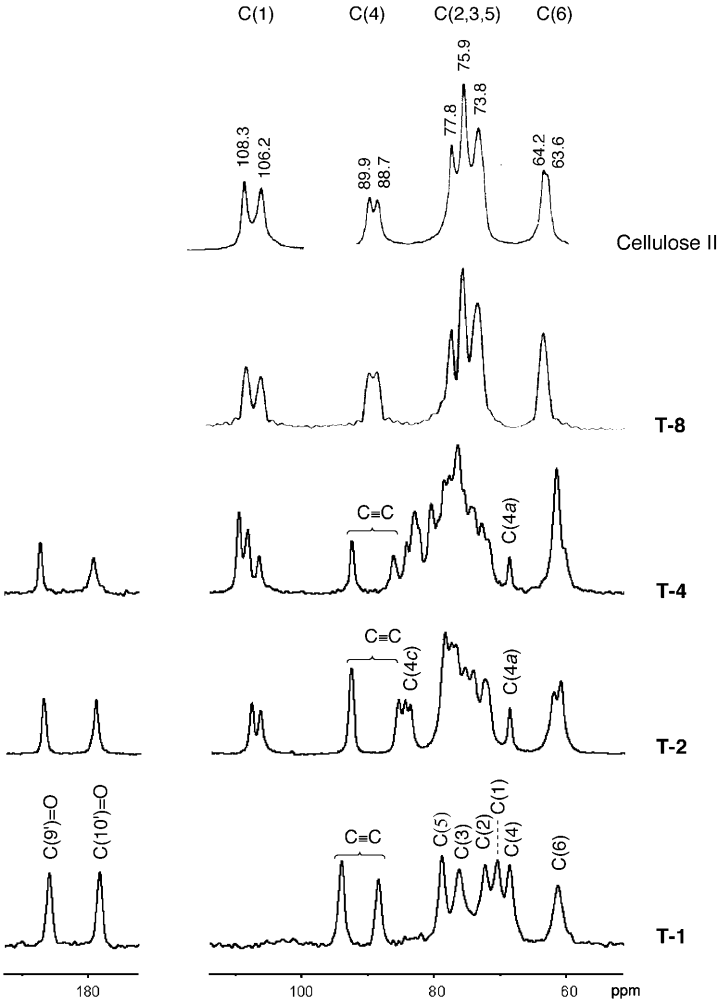


Fig. 11. *CP/MAS* ^{13}*C-NMR Spectra of* **T-x** *(***x**=1, 2, 4, and 8*) and cellulose II* (from [6])

5. *Comparison of the CP/MAS* ^{13}*C-NMR Spectra of* **A-x** *and* **A-x-x** *with Those of Cellulose Triacetates I and II.* Cellulose triacetates I (**CTA I**) and II (**CTA II**) are prepared by acetylating native cellulose I and mercerised cellulose II, respectively, and maintain the polymorphic character of cellulose [74]. Similar to cellulose I and II, **CTA I** can be transformed into **CTA II**, while the reverse process is unknown. Remarkably, both **CTA I** and **CTA II** were obtained from native celluloses by homogeneous or heterogeneous acetylation, respectively, while the same conditions transformed cellulose II only into **CTA II**. Based on the X-ray fiber-diffraction patterns and stereochemical model analysis, a parallel chain orientation was proposed for **CTA I** [75] and an antiparallel one for **CTA II** [76]. The unit cell of **CTA I** (orthorhombic, $P2_1$) contains two parallel chains, whereas the unit cell of **CTA II** (orthorhombic, $P2_12_12_1$) contains

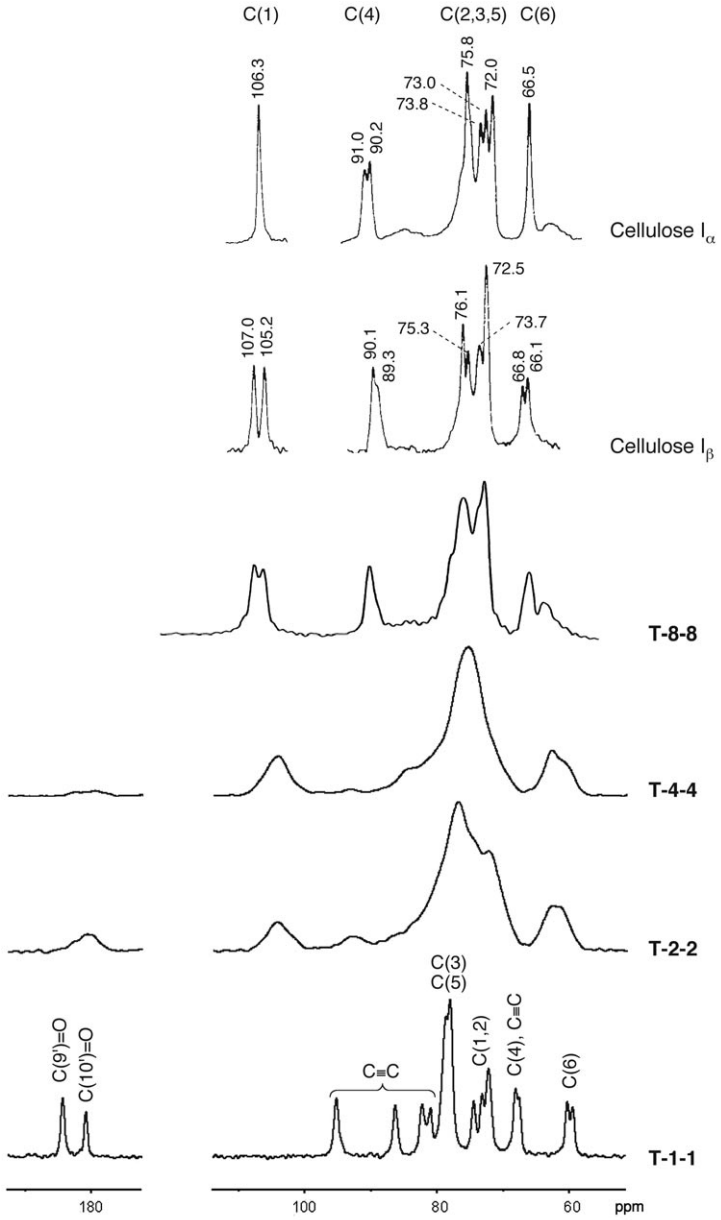


Fig. 12. *CP/MAS* ^{13}*C-NMR Spectra of* **T-x-x** (**x** = 1, 2, 4, and 8), *and cellulose* I_α *and* I_β (from [6])

two parallel and two antiparallel chains. However, there are experimental results in conflict with *Sprague*'s suggested analogy between celluloses and CTAs (see the excellent discussion in [77]) casting some doubt on the unambiguous assignment of the polarity of the chains in **CTA I** and **CTA II**.

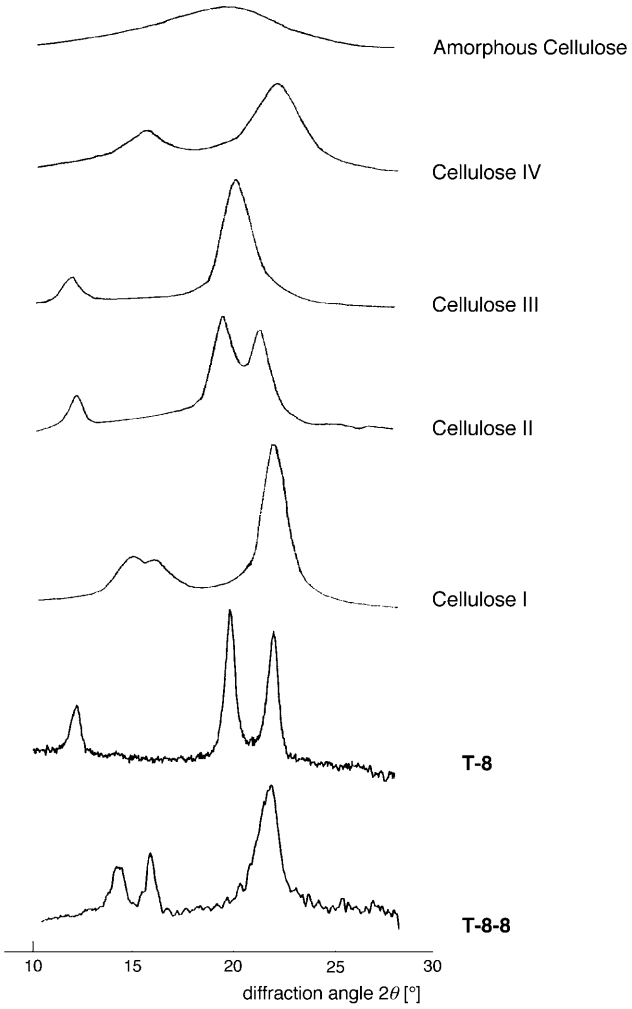


Fig. 13. *X-Ray powder-diffraction patterns of* **T-8**, **T-8-8**, *cellulose I to IV, and amorphous cellulose*

The CP/MAS ^{13}C-NMR spectra of **CTA I** and **CTA II** show characteristic differences [78]. Analysis of ^{13}C-enriched samples [79] led to a complete assignment of the signals for C(2) to C(5). The spectrum of **CTA I** displays a single set of signals, whereas **CTA II** shows a double set of signals for C(2) to C(6) evidencing two different 2,3,6-tri-*O*-acetyl-*β*-D-glucopyranosyl units [77] (*Fig. 14*). C(1) of **CTA I** resonates at 102.4 ppm, C(1) of **CTA II** at 100.4 ppm, C(6) of **CTA I** at 62.5 ppm, and C(6) of **CTA II** at 65.2 and 67.3 ppm (*Table 4*). The different values for C(6) may indicate a different orientation of the (acetoxy)methyl group, or the effect of the different environment. If *Horii*'s rule [80] should be applicable to acetylated glucopyranosides, then **CTA I** addopts the *gg*, and **CTA II** the *tg* and *gt* conformation.

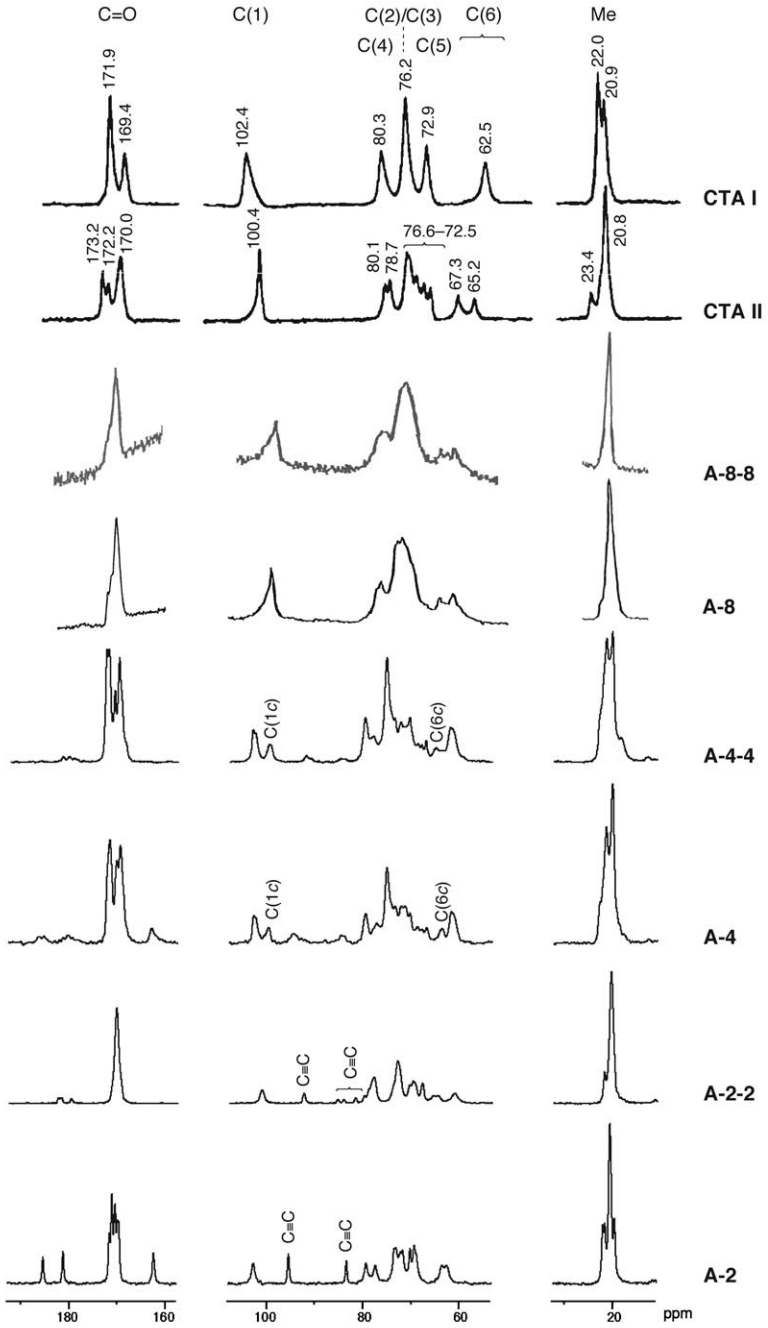


Fig. 14. *CP/MAS* ^{13}*C-NMR Spectra of* **A-x**, **A-x-x** (**x** = 2, 4, and 8), **CTA I**, *and* **CTA II** (from [78])

Table 4. *CP/MAS ^{13}C-NMR Chemical Shifts* [ppm] *of* **A-x**, **A-x-x** (**x** = 2, 4, and 8), **CTA I** [79], *and* **CTA II** [79]

	C(1) of units *c* and *b*	C≡C and C≡C–C≡C	C(4) of units *a* and *b*	C(2), C(3), C(5), C(1) of unit *a*, and C(4) of unit *c*	C(6)
A-2	103.0	95.7, 83.6	79.6, 77.6	73.3, 72.0, 70.4, 69.6	63.8, 62.9
A-4	103.1 (2 C), 100.1	94.8, 85.0	79.9 (2 C), 77.6	75.4, 73.8, 72.5, 70.7, 69.1	63.9, 62.1 (3 C)
A-8	103.4 (br.)		81.2 (br.)	76.9 (br.)	69.9, 66.9
A-2-2	101.3	92.6, 85.6, 84.3, 81.9	78.0 (br.)	73.1, 70.6, 69.9, 68.0	64.8, 61.3
A-4-4	103.0 (2 C), 99.8	92.2	80.0 (2 C), 78.2	75.5, 73.8, 72.5, 72.0, 70.7, 69.1, 68.3, 67.4	65.3, 62.4 (3 C)
A-8-8	103.4 (br.)		81.6 (br.)	76.7 (br.)	69.6, 67.0
CTA I	102.4	–	80.3	76.2 (2 C), 72.9[a])	62.5
CTA II	100.4 (2 C)	–	80.1, 78.7	76.6, 75.8 (2 C), 74.8, 73.5, 72.5[a])	67.3, 65.2

	C=O of Ac	Me of Ac	C(9) and C(10) of the template	C(8) of the template of **A-x**	Other signals of the template
A-2	171.6, 171.1, 170.5, 169.9	22.4, 21.9, 20.9, 19.9	185.4, 181.3	162.4	139.0, 115.0
A-4	172.0, 170.5, 169.8	21.7, 20.4	185.7, 180.6	163.3	139.0, 115.0
A-8	173.5	24.3			137.7
A-2-2	170.5	22.0, 20.6	182.6, 182.0, 179.9	–	141.0, 119.0
A-4-4	172.5, 172.0, 170.8, 169.9	21.8, 20.5	181.5	–	141.0, 119.0
A-8-8	173.6	24.2		–	
CTA I	171.9, 169.4	22.0, 20.9	–	–	–
CTA II	173.2, 172.2, 170.0	23.4, 20.8	–	–	–

[a]) For a complete assignment of these lines, see [77].

Surprisingly, according to the studies of the CP/MAS ^{13}C-NMR and X-ray diffraction spectra of a series of peracetylated cello-oligomers by *VanderHart et al.* [78] and *Kono et al.* [64][81], the X-ray diffraction spectra of peracetylated cellopentaose and higher cello-oligosides are similar to those of **CTA I**. In view of these results, we considered that analysis of the X-ray diffraction spectra of **A-x** and **A-x-x** (**x** = 2, 4, and 8) may contribute to understand the (apparent) opposite chain orientation in the solid state of free and acetylated higher cellodextrins.

The CP/MAS ^{13}C-NMR spectra of the template-bound peracetylated **A-x** and **A-x-x** (**x** = 2, 4, and 8), and of **CTA I** and **CTA II** are depicted in *Fig. 14*, and their chemical shift values are compiled in *Table 4*. Surprisingly, the spectra of the mono-chained **A-x** (especially of the tetraoside and octaoside) resemble the corresponding spectra of the double-chained **A-x-x**. C(1) of the tetraosides **A-4** and **A-4-4** resonates as two peaks in a 2:1 ratio at 103.4–103.1 and 101.3–99.8 ppm; the former peak is assigned to C(1*b*) and the latter one to C(1*c*). C(6) of **A-4** and **A-4-4** resonates as two peaks

in a 1:3 ratio at 65.3–63.9 and 62.4–62.1 ppm; the weaker peak was assigned to C(6*c*), and the stronger one to C(6*a*) and C(6*b*). With the exception of the signals for unit *c* that find no equivalent in the spectra of **CTA I** and **CTA II**, the spectra of **A-4** and **A-4-4** resemble the spectrum of **CTA I**. The (less well resolved) spectra of the cellooctaosides **A-8** and **A-8-8**, however, resemble strongly the spectrum of **CTA II**, particularly when considering the two peaks for C(6), the broad signals for C(4) and for C(2)/C(3)/C(5), and the single peak for the Me groups. The similarity between the solid-state CP/MAS ^{13}C-NMR spectra of **A-4** and **A-4-4** and the one of **CTA I**, and of **A-8** and **A-8-8** with the one of **CTA II** is opposite to the observations in the cellodextrin series. At first view, this result is surprising especially for **A-8-8** which possesses parallel cellosyl chains. However, the antiparallel orientation of two molecules of **A-8-8** leads to two parallel and two antiparallel chains, as required for **CTA II**. Any further analysis must resolve the question about the origin of the signal-doubling in the solid-state ^{13}C-NMR spectrum of **CTA II**. Is it due to different glucopyranosyl units in the repeating cellobiosyl moiety of all chains, to different parallel chains, or to different antiparallel chains? Better resolved diffraction analyses of **CTA II** and its oligomeric models should allow to answer this fundamental question.

6. *Conclusions.* Solid-state CP/MAS ^{13}C-NMR spectroscopy and X-ray powder-diffraction analysis reveal that **T-8** and **T-8-8** are oligomeric mimics of cellulose II and I_β, respectively. A combined analysis of the ^{1}H-NMR data (δ(OH), J(H,OH), $\Delta\delta$(OH)/ΔT, ROESY spectra) of the mono- and double-chained template-bound cellosides **T-4**, **T-8**, **T-4-4**, and **T-8-8** in (D_6)DMSO solution reveals strong intra-strand inter-residue C(3)OH···O(5′) H-bonds, weakly persistent inter-residue flip-flop H-bonds between HO(2) and HO(6′), and at best a weakly persistent inter-strand H-bond between HO(2^I) of the ethynylated chain *E* and HO(6^I) of the buta-1,3-diynylated chain *B* of **T-4-4** and **T-8-8**. The solid-state CP/MAS ^{13}C-NMR spectra of **A-4** and **A-4-4** resemble that of **CTA I**, and those of **A-8** and **A-8-8** resemble that of **CTA II**, opposite to the findings in the cellodextrin series.

We thank the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support, Mrs. *Brigitte Brandenberg* for recording the 500-MHz NMR spectra, and Prof. *Bernhard Jaun* for helpful discussions.

Experimental Part

General. See [3]. *Lewis* acids such as AgOTf, $CdCO_3$, $HgCl_2$, $Hg(CN)_2$, and $BF_3\cdot OEt_2$ were used directly without purification. IR Spectra (*ca.* 3% soln. in $CHCl_3$ or CH_2Cl_2 soln. or 1% KBr pills): *Perkin-Elmer 298* and *1600* FT-IR spectrometer. NMR Spectra: *Varian XL-300* (^{1}H: 300 MHz, ^{13}C: 75 MHz), or a *Bruker AMX-500* or *-600* (500 or 600 MHz, resp.) in deuteriated solvents ($CDCl_3$ and (D_6)DMSO, from *Dr. Glaser AG*, Basel); chemical shifts δ in ppm and couplings constants J in Hz. In ambiguous cases, ^{1}H-assignment is based on selective homonuclear decoupling experiments and 2D experiments. The CP/MAS ^{13}C-NMR experiments were performed on a *Bruker* NMR spectrometer with 500-MHz resonance frequency for ^{1}H and 125 MHz for ^{13}C. The spectrometer is equipped with a 2.5-mm MAS double resonance probe from *Chemagnetics* (Ft. Ciollins, Colorado, USA). The sample spinning frequency was 20 kHz for all samples. The contact time for cross-polarisation is 3 ms and the data-acquisition time is 25 ms. The radio-frequency field strengths are 100 and 84 kHz for the ^{1}H and the ^{13}C channel, resp. The numbers of scans collected vary from 10000 to 20000 with a repetition of 8 s for all samples.

*Allyl 4,6-*O*-Benzylidene-2,3-bis-*O*-(4-chlorobenzyl)-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-β-*D*-glucopyranoside* (**7**). A soln. of **5** [36] (36 g, 76.5 mmol) and 4-$ClC_6H_4CH_2Cl$ (93.7 g, 0.58 mol) in DMF (324 ml) was added dropwise to a cooled (0°), stirred suspension of NaH (55–65% in oil, 27.8 g) in dry DMF (396 ml). The mixture was gradually warmed to 25°, stirred overnight, cooled to 0°, treated dropwise with dry MeOH (30 ml), and poured into diluted AcOH (36 ml of AcOH in 6.0 l of H_2O). After stirring for 1 h at 0–5°, the precipitate was filtered off and washed with hexane. A soln. of the crude solid (110 g) in CH_2Cl_2 (600 ml) was washed with brine, dried (Na_2SO_4), and filtered through *Celite*. The filtrate was diluted with MeOH (2.5 l). The precipitate was filtered off, washed with MeOH and Et_2O, and dried overnight in high vacuum affording pure **7** (69.1 g, 83%). R_f (AcOEt/hexane 1:4) 0.40. M.p. 178.2°. $[\alpha]_D^{25} = +2.7$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2869*w*, 1600*w*, 1492*m*, 1408*w*, 1361*w*, 1308*w*, 1277*w*, 1162*w*, 1092*s*, 1015*m*, 931*w*, 839*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 7.50–7.10 (*m*, 25 arom. H); 5.93 (*dddd*, $J = 17.1$, 10.6, 5.9, 5.3, C*H*=CH_2); 5.49 (*s*, PhC*H*); 5.32 (*dq*, $J = 17.1$, 1.6), 5.21 (*dq*, $J = 10.6$, 1.6) (CH=CH_2); 4.86 (*d*, $J = 11.8$), 4.85 (*d*, $J = 11.2$), 4.67 (*d*, $J = 12.1$)

Table 5. *Selected ^{1}H-NMR Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of the 4-Chlorobenzylated Cellobiose Derivatives* **7**, **8**, **11**, **13**, **14**, **17**, *and* **18** *in $CDCl_3$*

	7	**8**	**11**	**13**[a])	**14**	**17**[a])	**18**
C≡CH	–	–	–	–	2.52	–	2.22
H–C(1^I)	4.40	4.40	–	3.99	3.98	4.04	4.01
H–C(2^I)	3.39	3.385	4.07	3.50	3.53	3.50	3.51
H–C(3^I)	3.48	3.49	3.92	3.43	3.44	3.45	3.44
H–C(4^I)	3.91	3.91	4.16	3.93	3.93	3.93	3.92
H–C(5^I)	3.33–3.25	3.34–3.20	4.52–4.47	3.26–3.21	3.28–3.21	3.28–3.24	3.28–3.22
H_a–C(6^I)	3.76	3.76	3.69	3.75	3.76	3.77	3.75
H_b–C(6^I)	3.63	3.65	3.61	3.63	3.63	3.63	3.61
H–C(1^{II})	4.48	4.42	4.48	4.39	4.39	4.41	4.39
H–C(2^{II})	3.33–3.25	3.23	3.34	3.20	3.21	3.22	3.21
H–C(3^{II})	3.59–3.52	3.325	3.64–3.57	3.28	3.29	3.31	3.29
H–C(4^{II})	3.59–3.52	3.63	3.64–3.57	3.60	3.61	3.62	3.59
H–C(5^{II})	3.24–3.14	3.34–3.20	3.32–3.24	3.26–3.21	3.28–3.21	3.28–3.24	3.28–3.22
H_a–C(6^{II})	4.21	3.56	4.22	3.56	3.55	3.58	3.57
H_b–C(6^{II})	3.46	3.43	3.67	3.42	3.42	3.45	3.43
HO–C(4^{II})	–	3.01	–	2.95	2.95	3.00	2.99
J(1^I,≡CH)	–	–	–	–	2.2	–	0.6
J(1^I,2^I)	7.8	7.8	–	9.6	9.7	9.4	9.3
J(2^I,3^I)	9.0	9.0	5.8	9.1	9.0	9.0	9.0
J(3^I,4^I)	9.2	9.0	5.0	8.9	8.7	8.9	8.7
J(4^I,5^I)	9.2	9.6	8.1	9.7	>9.3	9.7	9.7
J(5^I,$6a^I$)	4.0	4.0	3.8	3.4	3.3	3.5	3.3
J(5^I,$6b^I$)	2.3	2.5	2.8	1.6	1.9	1.6	1.6
J($6a^I$,$6b^I$)	10.9	10.9	11.2	11.0	11.1	11.2	11.2
J(1^{II},2^{II})	7.8	7.8	7.8	7.9	7.9	7.8	7.8
J(2^{II},3^{II})	[b])	9.0	8.8	9.1	9.0	9.0	9.0
J(3^{II},4^{II})	[b])	9.5	[b])	8.9	8.7	8.8	9.0
J(4^{II},5^{II})	[b])	9.9	[b])	9.1	8.9	9.0	9.0
J(5^{II},$6a^{II}$)	5.0	4.7	4.7	5.8	5.9	5.8	6.2
J(5^{II},$6b^{II}$)	10.6	5.9	10.6	4.8	3.4	4.8	4.7
J($6a^{II}$,$6b^{II}$)	10.6	9.7	10.6	10.0	10.0	9.9	10.0
J(4^{II},OH)	–	1.9	–	2.0	1.9	1.8	2.2

[a]) Assignments based on a DQFCOSY and a HSQC spectrum. [b]) Not assigned.

(3 PhC*H*); 4.66 (*d*, *J* = 12.4, 2 PhC*H*); 4.65 (*d*, *J* = 11.8), 4.62 (*d*, *J* = 11.5), 4.52 (*d*, *J* = 12.5) (3 PhC*H*); 4.36–4.44 (*m*, 1 allyl. H); 4.36 (*d*, *J* = 12.4, 2 PhC*H*); 4.12 (*ddt*, *J* = 13.1, 5.9, 1.4, 1 allyl. H). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 6*; additionally, 137.38, 137.07, 136.88, 136.83, 136.54, 136.38 (6*s*); 133.84 (*d*, *C*H=CH_2); 133.46, 133.45, 133.37, 133.34, 133.11 (5*s*); 128.24–129.29 (several *d*); 125.99 (2*d*); 117.35 (*t*, CH=*C*H_2); 101.20 (*d*, Ph*C*H); 74.54, 74.41, 74.14, 73.98, 72.52 (5*t*, 5 Ph*C*H_2); 70.21 (*t*, CH_2=CH*C*H_2). HR-MALDI-MS: 1113.2074 (57, $[M+Na]^+$, $C_{57}H_{55}Cl_5NaO_{11}^+$; calc. 1113.2085). Anal. calc. for $C_{57}H_{55}Cl_5O_{11}$ (1093.32): C 62.62, H 5.07; found: C 62.66, H 5.22.

Allyl 6-O-*Benzyl-2,3-bis*-O-*(4-chlorobenzyl)-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-β*-D-*glucopyranoside* (**8**). A suspension of **7** (16 g, 14.6 mmol) and $NaBH_3CN$ (10.12 g, 161 mmol) in dry THF (240 ml) was cooled to 0°, treated portionwise with sat. HCl in Et_2O (160 ml), and stirred for 4 h. After dilution with CH_2Cl_2, the yellow suspension was filtered through a pad of silica gel. The filtrate was washed with H_2O, sat. $NaHCO_3$ soln., and brine, dried (Na_2SO_4), and evaporated. Crystallisation from CH_2Cl_2/hexane and FC of the mother liquor (toluene/acetone 20 : 1) gave **8** (11.0 g, 69%). R_f (AcOEt/hexane 1 : 4) 0.08. M.p. 102–103.4°. $[\alpha]_D^{25} = +14.9$ (*c* = 1.0, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 7.40–7.10 (*m*, 25 arom. H); 5.94 (*dddd*, *J* = 17.2, 10.3, 5.9, 5.3, C*H*=CH_2); 5.33 (*dq*, *J* = 17.2, 1.6), 5.24 (*dq*, *J* = 10.3, 1.6) (CH=CH_2); 4.885 (*d*, *J* = 11.2), 4.85 (*d*, *J* ≈ 11.2), 4.835 (*d*, *J* = 11.8), 4.75 (*d*, *J* = 11.8), 4.70 (*d*, *J* = 11.8), 4.64 (*d*, *J* = 11.5) (6 PhC*H*); 4.63 (br. *d*, *J* ≈ 11.2, 2 PhC*H*); 4.55 (*d*, *J* = 12.1, PhC*H*); 4.435 (br. *s*, PhCH_2); 4.43–4.36 (*m*, 1 allyl. H); 4.39 (*d*, *J* = 12.1, PhC*H*); 4.12 (*ddt*, *J* = 13.2, 5.9, 1.4, 1 allyl. H). Anal. calc. for $C_{57}H_{57}Cl_5O_{11}$ (1095.33): C 62.50, H 5.25; found: C 62.38, H 5.34.

Allyl 6-O-*Benzyl-2,3-bis*-O-*(4-chlorobenzyl)-4*-O-*(methoxymethyl)-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)-β*-D-*glucopyranoside* (**9**). A soln. of **8** (1.2 g, 1.09 mmol) in dry DMF (30 ml) was cooled to 0°, treated with 55% NaH in oil (94 mg, 2.2 mmol) and MOMCl (176 µl, 2.2 mmol), warmed to r.t., and stirred for 4 h. The mixture was poured into H_2O. After extraction with CH_2Cl_2, the org. layer was washed with H_2O and brine, dried (Na_2SO_4), and evaporated. Crystallisation from CH_2Cl_2/hexane and FC of the mother liquor (toluene/acetone 25 : 1) gave **9** (880 mg, 70%) and **8** (200 mg, 16%). R_f (AcOEt/hexane 1 : 4) 0.28. M.p. 102.0–104.1°.

4,6-O-*Benzylidene-2,3-bis*-O-*(4-chlorobenzyl)-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tris*-O-*(4-chlorobenzyl)*-D-*glucopyranose* (**10**). At 25°, a suspension of bis(methyl(diphenyl)phosphine)(cycloocta-1,5-

Table 6. *Selected ^{13}C-NMR Chemical-Shift Values* [ppm] *of the 4-Chlorobenzylated Cellobiose Derivatives* **7**, **11**, **13**, **14**, **17**, *and* **18** *in $CDCl_3$*

	7	**11**	**13**[a])	**14**	**17**[a])	**18**
C(4′)	–	–	–	–	86.29	67.21
C(3′)	–	–	–	–	88.29	70.29
C(2′)	–	–	91.40	74.33	71.08	68.81
C(1′)	–	–	102.13	80.72	74.15	72.80
C(1^I)	102.47	168.44	70.26	69.64	70.17	70.01
C(2^I)	81.35	77.91	81.54	81.32	80.97	80.88
C(3^I)	82.24[b])	81.35[b])	83.88	83.97	83.94	83.96
C(4^I)	77.00	76.56	76.32	76.22	76.15	76.14
C(5^I)	74.88	76.68	79.19	79.28	79.28	79.31
C(6^I)	67.71	67.79	67.77	67.84	67.76	67.70
C(1^{II})	102.84	103.78	102.28	102.35	102.26	102.35
C(2^{II})	81.63	80.88	81.77	81.79	81.73	81.76
C(3^{II})	82.60[b])	81.58[b])	84.39	84.41	84.33	84.39
C(4^{II})	81.17	80.22	73.79	73.80	73.65	73.67
C(5^{II})	65.85	66.08	72.88	72.91	72.91	72.96
C(6^{II})	68.65	68.49	71.05	71.05	70.94	70.95

[a]) Assignments based on a HSQC spectrum. [b]) Assignments may be interchanged.

diene)iridium(I) hexafluorophosphate (1.16 g, 1.37 mmol) in dry THF (500 ml) was degassed and stirred under H_2 for 1 min (red suspension turns into pale yellow soln.). H_2 was replaced by Ar. The yellow soln. was treated with a soln. of **7** (50 g, 45.7 mmol) in THF (1 l), stirred for 1 h, treated with H_2O (500 ml) and I_2 (23.2 g, 91.4 mmol), stirred for 1 h, and diluted with cold 5% aq. $Na_2S_2O_3$ soln. (1 l). After evaporation of the pale yellow soln., a soln. of the residue in AcOEt was washed with brine, dried ($MgSO_4$), and evaporated. Crystallisation from Et_2O/MeOH gave **10** (41.8 g, 87%). R_f (AcOEt/hexane 1:3) 0.27. M.p. 125.6°.

*4,6-*O*-Benzylidene-2,3-bis-*O*-(4-chlorobenzyl)-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tris-*O*-(4-chlorobenzyl)-*D*-glucono-1,5-lactone* (**11**). At 26° and under Ar, a suspension of **10** (10 g, 9.5 mmol) in DMSO (24 ml) was treated with Ac_2O (20 ml) and stirred for 6 h. The clear yellow soln. was poured into cold H_2O. The separated oil was decanted, dissolved in Et_2O, washed with H_2O and brine, and dried (Na_2SO_4). After evaporation, drying of the residue under high vacuum for several hours gave crude **11** (9.7 g, 97%) as a pale brownish oil, which was used for the next step without further purification. FC (AcOEt/hexane 1:4) of a small sample gave pure **11** for microanalysis and optical rotation. R_f (AcOEt/hexane 1:3) 0.46. $[\alpha]_D^{25} = +29.0$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3034*w*, 2876*w*, 1758*m*, 1600*w*, 1493*m*, 1408*w*, 1365*w*, 1308*w*, 1276*w*, 1174*w*, 1090*s*, 1016*m*, 844*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 7.50–7.10 (*m*, 25 arom. H); 5.54 (*s*, PhC*H*); 4.87 (*d*, $J = 11.8$), 4.85 (*d*, $J = 11.8$) (2 PhC*H*); 4.70 (*d*, $J = 11.8$, 2 PhC*H*); 4.66 (*d*, $J = 12.5$), 4.63 (*d*, $J = 11.2$), 4.58 (*d*, $J = 11.5$), 4.56 (*d*, $J = 11.8$). 4.47 (*d*, $J = 11.5$), 4.37 (*d*, $J = 12.2$) (6 PhC*H*). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 6*; additionally, 136.91, 136.64, 136.25, 135.97, 135.71, 135.08 (6*s*); 134.03, 133.77, 133.48 (3*s*); 133.64 (2*s*); 128.28–129.50 (several *d*); 125.94 (2*d*); 101.30 (*d*, Ph*C*H); 74.59, 74.15, 72.70, 72.55, 72.37 (5*t*, 5 Ph*C*H_2). Anal. calc. for $C_{54}H_{49}Cl_5O_{11}$ (1051.24): C 61.70, H 4.70; found: C 61.59, H 4.88.

*6-*O*-Benzyl-2,3-bis-*O*-(4-chlorobenzyl)-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tris-*O*-(4-chlorobenzyl)-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**13**). Under Ar, a soln. of (trimethylsilyl)acetylene (11.6 ml, 82 mmol) in THF (276 ml) was cooled to −78°, treated dropwise with 1.6M BuLi in hexane (51.2 ml) over a period of 0.5 h, and stirred for 1 h. The resulting soln. was transferred into a cooled (−78°) soln. of **11** (19.1 g, 18.2 mmol) in THF (300 ml) over a period of 10 min with a canula. The pale brown soln. was stirred for 4 h, treated with sat. aq. NH_4Cl soln. (20 ml), warmed to r.t., stirred for 0.5 h, and worked up (AcOEt). Evaporation gave crude **12** (20.9 g of a pale yellow syrup, α/β 55:45) that was used for the next step without further purification.

A chilled (−40°) soln. of $BF_3 \cdot Et_2O$ (11.4 ml, 91 mmol) and Et_3SiH (23.1 ml, 145 mmol) in CH_2Cl_2/MeCN 1:1 (210 ml) was transferred *via* a canula to a stirred and chilled (−40°) soln. of crude **12** (20.9 g, *ca.* 18.2 mmol) in CH_2Cl_2/MeCN 1:1 (210 ml) over a period of 0.5 h. The mixture was stirred at −40° for 1 h, allowed to warm to −10° to −15°, stirred for 16 h, treated with sat. aq. $NaHCO_3$ soln. (200 ml), stirred for 1 h, warmed to r.t., and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 1:7) gave **13** (14.8 g, 72%). Pale yellow oil. R_f (AcOEt/hexane 1:3) 0.39. $[\alpha]_D^{25} = 11.8$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3500*w*, 3036*w*, 2916*w*, 2873*w*, 2169*w*, 1702*w*, 1600*w*, 1493*m*, 1409*w*, 1362*w*, 1308*w*, 1275*w*, 1090*s*, 1016*s*, 847*m*, 814*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 5*; additionally, 7.40–7.10 (*m*, 25 arom. H); 4.91 (*d*, $J = 11.4$), 4.89 (*d*, $J = 10.8$), 4.82 (*d*, $J = 11.6$), 4.75 (*d*, $J = 11.6$), 4.69 (*d*, $J = 10.8$), 4.66 (*d*, $J = 11.5$), 4.61 (*d*, $J = 11.4$), 4.60 (*d*, $J = 11.4$), 4.56 (*d*, $J = 12.2$), 4.46 (*d*, $J = 12.3$), 4.43 (*d*, $J = 12.3$), 4.37 (*d*, $J = 12.5$) (12 PhC*H*); 0.17 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 6*; additionally, 137.57, 137.44, 137.13, 136.64, 136.55, 136.28 (6*s*); 133.53 (2*s*); 133.51, 133.37, 132.95 (3*s*); 127.58–129.38 (several *d*); 74.57, 74.45, 74.24, 74.10, 73.69, 72.58 (6*t*, 6 Ph*C*H_2); −0.32 (*q*, Me_3Si). HR-MALDI-MS: 1155.2366 (21, $[M+Na]^+$, $C_{59}H_{61}Cl_5NaO_{10}Si^+$; calc. 1155.2374). Anal. calc. for $C_{59}H_{61}Cl_5O_{10}Si$ (1135.47): C 62.41, H 5.41; found: C 62.42, H 5.54.

*6-*O*-Benzyl-2,3-bis-*O*-(4-chlorobenzyl)-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tris-*O*-(4-chlorobenzyl)-1,2-dideoxy-*D*-glycero-*D*-gulo-oct-1-ynitol* (**14**). A soln. of **13** (6.3 g, 5.6 mmol) in THF (30 ml) was cooled to 0°, treated with a soln. of MeONa (0.6 g, 11 mmol) in MeOH (50 ml), and stirred for 1 h. After neutralisation with *Amberlist IR 120* (H^+ form), filtration, evaporation, and FC (AcOEt/hexane 1:11) gave **14** (5.28 g, 89%). Solid foam. R_f (AcOEt/hexane 1:3) 0.34. M.p. 112.9°. $[\alpha]_D^{25} = +21.9$ ($c = 1.0$, $CHCl_3$). UV ($CHCl_3$): 267 (2948), 276 (1771). IR ($CHCl_3$): 3502*w*, 3306*w*, 3007*w*, 2910*w*, 2870*w*, 1600*w*, 1493*s*, 1457*w*, 1409*w*, 1362*w*, 1308*w*, 1298*w*, 1276*w*, 1089*s*, 1016*s*, 845*w*. ^{1}H-NMR (300

MHz, $CDCl_3$): see *Table 5*; additionally, 7.40–7.10 (*m*, 25 arom. H); 4.93 (*d*, *J* = 11.2), 4.86 (*d*, *J* = 11.2), 4.82 (*d*, *J* = 11.8), 4.78 (*d*, *J* = 12.5), 4.74 (*d*, *J* = 11.8), 4.67 (*d*, *J* = 10.6) (6 PhC*H*); 4.60 (*d*, *J* = 11.5, 2 PhC*H*); 4.56 (*d*, *J* = 12.2, PhC*H*); 4.45 (*d*, *J* = 11.8, 2 PhC*H*); 4.36 (*d*, *J* = 12.5, PhC*H*). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 6*; additionally, 137.60, 137.57, 137.25, 136.76, 136.55, 136.42 (6*s*); 133.66 (2*s*); 133.70, 133.51, 133.14 (3*s*); 127.69–129.43 (several *d*); 74.64, 74.46, 74.33, 74.12, 73.70, 72.65 (6*t*, 6 Ph*C*H$_2$). HR-MALDI-MS: 1083.1973 (56, $C_{56}H_{53}Cl_5NaO_{10}^+$, $[M+Na]^+$; calc. 1083.1979). Anal. calc. for $C_{56}H_{53}Cl_5O_{10}$ (1063.29): C 63.26, H 5.02; found: C 63.32, H 5.22.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-(1 → 6)-4,5,8-tri*-O-*acetyl-3,7-anhydro-1,2-dideoxy*-D-glycero-D-gulo-*oct-1-ynitol* (**15**). A soln. of TMSOTf (17 ml, 94 mmol) in Ac_2O (10 ml) was added dropwise to a chilled (−40°) soln. of **14** (5.0 g, 4.7 mmol) in Ac_2O (92 ml). The mixture was warmed to 20°, stirred for 16 h, cooled to 0°, treated dropwise with sat. aq. $NaHCO_3$ soln. (40 ml), stirred for 0.5 h, and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 1:3) gave a colourless solid, which was recrystallised in AcOEt/hexane to afford **15** (2.3 g, 76%). Colourless needles. R_f (AcOEt/hexane 1:1) 0.26. M.p. 202°. $[\alpha]_D^{25} = -11.2$ (*c* = 1.0, $CHCl_3$). UV ($CHCl_3$): 266 (1143). IR ($CHCl_3$): 3307*w*, 3034*w*, 2953*w*, 2865*w*, 2133*w*, 1755*s*, 1603*w*, 1457*w*, 1429*w*, 1368*s*, 1249*s*, 1169*m*, 1049*s*, 905*w*, 651*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 7*; additionally, 2.48 (*d*, *J* = 1.9, C≡CH); 2.12, 2.07, 2.05, 2.01, 2.00, 1.99, 1.96 (7*s*, 7 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 8*; additionally, 170.43, 170.28, 170.14, 169.74, 169.44, 169.26, 169.02 (7*s*, 7 C=O); 20.81, 20.61, 20.57 (3*q*, 3 Me); 20.49 (*q*, 4 Me). HR-MALDI-MS: 667.1839 (65, $[M+Na]^+$, $C_{28}H_{36}NaO_{17}^+$; calc. 667.1850). Anal. calc. for $C_{28}H_{36}O_{17}$ (644.58): C 52.17, H 5.63; found: C 52.17, H 5.62.

6-O-*Benzyl-2,3-bis*-O-*(4-chlorobenzyl)-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tris*-O-*(4-chlorobenzyl)-1,2,3,4-tetradeoxy-1-(trimethylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol* (**17**). Under Ar, a soln. of 1,4-bis(trimethylsilyl)buta-1,3-diyne (0.40 g, 2.0 mmol) in THF (10 ml) was cooled to 0°, treated dropwise with 1.4M MeLi·LiBr in Et_2O (1.26 ml, 1.9 mmol) over a period of 0.5 h, and stirred for 4 h at 27°. The deep-brown-coloured soln. was transferred into a cooled (−78°) soln. of **11** (1.0 g, 0.95 mmol) in THF (10 ml) over a period of 10 min with a canula. The resulting brown soln. was stirred for 4 h at −78°, treated with sat. aq. NH_4Cl soln. (10 ml), warmed to r.t., stirred for 0.5 h, and worked up (Et_2O). Evaporation gave crude **16** (1.15 g of a brownish syrup, *α*/*β* 3:2), which was used for the next step without further purification.

A chilled (−40°) soln. of $BF_3 \cdot OEt_2$ (1.2 ml, 9.5 mmol) and Et_3SiH (2.4 ml, 152 mmol) in CH_2Cl_2/MeCN 1:1 (10 ml) was added to a stirred and chilled (−40°) soln. of crude **16** (1.15 g, *ca*. 0.95 mmol) in CH_2Cl_2/MeCN 1:1 (10 ml) over a period of 0.5 h and with a canula. The mixture was stirred at −40° for 1 h and at −10 to −15° for 16 h, treated with sat. aq. $NaHCO_3$ soln. (10 ml), warmed to r.t., stirred for 1 h, and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 1:6) gave **17** (0.58 g, 52%). Pale yellow oil. R_f (AcOEt/hexane 1:3) 0.36. $[\alpha]_D^{25} = -13.5$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3504*w*, 3034*w*, 2918*w*, 2874*w*, 2111*w*, 1703*w*, 1600*m*, 1493*m*, 1457*w*, 1409*w*, 1362*w*, 1308*w*, 1253*m*, 1090*s*, 1016*s*, 847*m*, 634*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 5*; additionally, 7.40–7.10 (*m*, 25 arom. H); 4.94 (*d*, *J* = 11.4), 4.84 (*d*, *J* = 10.9), 4.83 (*d*, *J* = 11.7), 4.76 (*d*, *J* = 11.6), 4.71 (*d*, *J* = 10.9), 4.68 (*d*, *J* = 11.5) (6 PhC*H*); 4.62 (br. *d*, *J* = 11.1, 2 PhC*H*); 4.56 (*d*, *J* = 12.2), 4.47 (*d*, *J* = 12.6), 4.45 (*d*, *J* = 12.6), 4.37 (*d*, *J* = 12.2) (4 PhC*H*); 0.23 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 6*; additionally, 137.41, 137.39, 137.08, 136.58, 136.25, 136.16 (6*s*); 133.47 (2*s*); 133.62, 133.32, 132.99 (3*s*); 127.53–129.57 (several *d*); 74.63, 74.41, 74.29, 74.07, 73.67, 72.65 (6*t*, 6 Ph*C*H$_2$); −0.53 (*q*, Me_3Si). HR-MALDI-MS: 1179.2376 (14, $[M+Na]^+$, $C_{61}H_{61}Cl_5NaO_{10}Si^+$; calc. 1179.2374). Anal. calc. for $C_{61}H_{61}Cl_5O_{10}Si$ (1159.50): C 63.19, H 5.30; found: C 63.23, H 5.41.

6-O-*Benzyl-2,3-bis*-O-*(4-chlorobenzyl)-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tris*-O-*(4-chlorobenzyl)-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol* (**18**). A soln. of **17** (50 mg, 43 μmol) in THF (0.3 ml) was cooled to 0°, treated with a soln. of MeONa (2 mg, 86 μmol) in MeOH (0.5 ml), stirred for 1 h, and passed through a pad of *Amberlite IR 120* (H^+ form, 0.5 ml wet). Evaporation of the pale yellow eluent and FC (AcOEt/hexane 1:5) gave **18** (50 mg, 87%). Pale white solid turning red on standing (it was used immediately for the next step). R_f (AcOEt/hexane 1:3) 0.45. M.p. 112.9°. $[\alpha]_D^{25} = -10.0$ (*c* = 1.0, $CHCl_3$). UV ($CHCl_3$): 267 (3697), 277 (2430). IR ($CHCl_3$): 3504*w*, 3300*w*, 3007*w*, 2910*w*, 2871*w*,

2075*w*, 1600*w*, 1492*s*, 1409*w*, 1363*w*, 1296*w*, 1089*s*, 1016*s*, 844*w*, 814*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 7.40–7.10 (*m*, 25 arom. H); 4.94 (*d*, *J* = 11.1), 4.83 (*d*, *J* = 11.5), 4.80 (*d*, *J* = 10.9), 4.75 (*d*, *J* = 11.5), 4.70 (*d*, *J* = 10.6), 4.67 (*d*, *J* = 11.5), 4.61 (*d*, *J* = 11.2), 4.60 (*d*, *J* = 11.5), 4.56 (*d*, *J* = 12.1), 4.47 (*d*, *J* = 12.5), 4.43 (*d*, *J* = 12.5), 4.36 (*d*, *J* = 11.8) (12 PhC*H*). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 6*; additionally, 137.56, 137.49, 137.21, 136.71, 136.32, 136.20 (6*s*); 133.85, 133.70, 133.62, 133.44, 133.15 (5*s*); 127.65–129.64 (several *d*); 74.72, 74.44, 74.31, 74.10, 73.67, 72.68 (6*t*, 6 Ph*C*H$_2$). HR-MALDI-MS: 1107.1965 (56, $[M+Na]^+$, $C_{58}H_{53}Cl_5NaO_{10}^+$; calc. 1107.1979). Anal. calc. for $C_{58}H_{53}Cl_5O_{10}$ (1087.31): C 64.07, H 4.91; found: C 64.17, H 5.13.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-(1 → 8)-6,7,10-tri*-O-*acetyl-5,9-anhydro-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol* (**19**). A soln. of TMSOTf (1.7 ml, 9.2 mmol) in Ac_2O (3.8 ml) was added dropwise to a chilled (−40°) soln. of **18** (0.50 g, 0.46 mmol) in Ac_2O (9 ml). The mixture was warmed to 25°, stirred for 24 h, cooled to 0°, treated dropwise with sat. aq. $NaHCO_3$ soln. (4 ml), stir-

Table 7. *Selected ^{1}H-NMR Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of the Peracetylated Cellobiosylalkynes* **15**, **19**, **21**, **22**, *and* **24** *in $CDCl_3$*

	15[a])	**19**[a])	**21**[a])	**22**[b])	**24**[a])	
					E chain[b])	*B* chain
H–C(1^I)	4.14	4.20	4.56	4.56	4.66	4.41
H–C(2^I)	5.07	5.05	5.32	5.28	5.32	5.14
H–C(3^I)	5.13	5.11	5.25	5.23	5.25	5.20
H–C(4^I)	3.76	3.76	3.87	3.85	3.86	3.89
H–C(5^I)	3.56	3.55	3.71	3.71	3.76	3.68
H$_a$–C(6^I)	4.46	4.46	4.57	4.53	4.58	4.53
H$_b$–C(6^I)	4.07	4.06	4.15	4.16	4.16	4.15
H–C(1^{II})	4.49	4.48	4.55	4.55	4.63	4.55
H–C(2^{II})	4.90	4.89	4.95	4.95	4.95	4.94
H–C(3^{II})	5.12	5.12	5.16	5.16	5.19	5.17
H–C(4^{II})	5.04	5.04	5.08	5.08	5.10	5.09
H–C(5^{II})	3.64	3.64	3.69	3.69	3.73	3.70
H$_a$–C(6^{II})	4.35	4.35	4.39	4.39	4.42	4.39
H$_b$–C(6^{II})	4.03	4.03	4.07	4.07	4.08	4.07
J(1^I, ≡CH)	2.0	0.9	–	–	–	–
J(1^I,2^I)	9.6	9.7	9.6	9.8	9.7	9.7
J(2^I,3^I)	9.3	9.6	9.4	[c])	[c])	9.4
J(3^I,4^I)	8.8	8.9	9.1	9.4	9.4	8.9
J(4^I,5^I)	9.8	9.8	9.8	9.9	9.9	9.9
J(5^I,6a^I)	5.2	5.1	5.1	5.2	4.8	5.6
J(5^I,6b^I)	1.9	2.0	1.9	1.9	1.8	2.0
J(6a^I,6b^I)	12.1	12.1	12.2	12.2	12.2	12.2
J(1^{II},2^{II})	7.9	7.9	8.0	7.9	7.9	7.9
J(2^{II},3^{II})	9.3	9.3	9.3	9.3	9.4	9.4
J(3^{II},4^{II})	9.5	9.4	9.4	9.4	9.4	9.4
J(4^{II},5^{II})	9.9	9.7	9.8	9.9	10.0	9.9
J(5^{II},6a^{II})	4.4	4.4	4.4	4.6	4.2	4.6
J(5^{II},6b^{II})	2.3	2.3	2.3	2.3	2.3	2.4
J(6a^{II},6b^{II})	12.5	12.5	12.5	12.5	12.5	12.4

[a]) Assignments based on a DQFCOSY and a HSQC spectrum. [b]) H–C(2^I) and H–C(3^I) of **22** and the *E* chain of **24** form a narrow *AB* system leading to virtual couplings with H–C(1^I) and H–C(4^I). [c]) Not assigned.

Table 8. *Selected ^{13}C-NMR Chemical-Shift Values* [ppm] *of the Peracetylated Cellobiosylalkynes* **15**, **19**, **21**, **22**, *and* **24** *in $CDCl_3$, and of the Deprotected Cellobiosylalkynes* **23** *and* **25** *in (D_6)DMSO*

	15[a])	**19**[a])	**21**[a])	**22**	**24**[a])		**23**[a])	**25**[a])	
					E chain	*B* chain		*E* chain	*B* chain
C(4′)	–	66.82	–	–	–	78.74[b])	–	–	78.82
C(3′)	–	69.84	–	–	–	78.17[b])	–	–	77.30
C(2′)	75.31	69.46	85.62	84.93	85.87	71.92	83.89	84.20	69.65
C(1′)	77.80	71.10	90.14	89.99	90.17	79.27[b])	94.51	94.02	84.20
C(1^I)	68.31	68.69	69.39	69.39	69.48	69.09	70.71	70.69	70.38
C(2^I)	71.20	70.91	71.44	71.35	71.14	71.05	73.44	73.56	73.23
C(3^I)	72.90	72.88	73.53	73.24	73.15	73.37	76.38	75.80	75.70
C(4^I)	76.14	76.02	76.28	76.38	76.31	76.09	80.04	79.98	79.81
C(5^I)	76.84	76.92	76.93	76.89	76.76	77.05	78.88	78.92	78.78
C(6^I)	62.07	61.94	62.18	62.37	62.22	62.29	60.21	60.15	60.15
C(1^{II})	100.77	100.75	100.84	100.76	100.73	100.73	103.01	103.00	103.00
C(2^{II})	71.56	71.55	71.64	71.67	71.68	71.64	73.23	73.19	73.11
C(3^{II})	73.09	73.03	72.97	73.03	73.01	72.96	76.54	76.35	76.35
C(4^{II})	67.76	67.75	67.81	67.93	67.95	67.86	69.95	69.93	69.91
C(5^{II})	71.97	71.98	72.02	72.04	72.03	71.92	76.71	76.67	76.67
C(6^{II})	61.53	61.52	61.58	61.67	61.56	61.70	60.95	60.94	60.94

[a]) Assignments based on a HSQC spectrum. [b]) Assignments may be interchanged.

red for 0.5 h, and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 1:2) gave a colourless solid, which was recrystallised in AcOEt/hexane affording **19** (0.2 g, 63%). Colourless needles. R_f (AcOEt/hexane 1:1) 0.22. M.p. 200.7°. $[\alpha]_D^{25} = -21.6$ ($c = 1.0$, $CHCl_3$). UV ($CHCl_3$): 265 (1062). IR ($CHCl_3$): 3300*w*, 3034*w*, 2954*w*, 2867*w*, 1756*s*, 1603*w*, 1428*w*, 1368*m*, 1249*s*, 1168*w*, 1051*s*, 908*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 7*; additionally, 2.20 (*d*, $J = 0.9$, C≡CH); 2.12, 2.07, 2.05, 1.99, 1.96 (5*s*, 5 AcO); 2.01 (*s*, 2 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$, assignment based on a HSQC spectrum): see *Table 8*; additionally, 170.43, 170.25, 170.14, 169.72, 169.30, 169.26, 169.01 (7*s*, 7 C=O); 20.80, 20.60, 20.51 (3*q*, 3 Me); 20.48 (*q*, 4 Me). HR-MALDI-MS: 691.1843 (43, $[M+Na]^+$, $C_{30}H_{36}NaO_{17}^+$; calc. 691.1850). Anal. calc. for $C_{30}H_{36}O_{17}$ (668.60): C 53.89, H 5.43; found: C 53.89, H 5.51.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-(1 → 6)-4,5,8-tri*-O-*acetyl-3,7-anhydro-1,2-dideoxy-1*-C-*(8-hydroxy-9,10-dioxoanthracen-1-yl)*-D-glycero-D-gulo-*oct-1-ynitol* (**21**). Under Ar, a stirred suspension of **20** (0.9 g, 2.2 mmol), $[Pd(PPh_3)_2]Cl_2$ (75 mg, 0.10 mmol), and CuI (60 mg, 0.31 mmol) in degassed Et_3N/DMF 1:5 (10 ml) was warmed to 60°, treated dropwise with a soln. of **15** (1.9 g, 2.9 mmol) in Et_3N/DMF 1:5 (6 ml) over a period of 3 h, stirred for 4 h, treated with solid $(NH_4)_2CO_3$ (0.45 g, 5.8 mmol), cooled to 23°, stirred for 12 h, treated with additional $(NH_4)_2CO_3$ (0.22 g, 2.8 mmol), and stirred for 6 h. Workup (AcOEt), evaporation, and FC (AcOEt/hexane/CH_2Cl_2 2:3:3) gave bright yellow **21** (1.4 g, 74%). R_f (AcOEt/hexane 1:1) 0.17. M.p. 263–265° (dec.). $[\alpha]_D^{25} = -4.6$ ($c = 1.0$, $CHCl_3$). UV ($CHCl_3$): 276 (16427), 373 (4481), 412 (7039), 436 (3840). IR ($CHCl_3$): 3586*w*, 3008*w*, 2954*w*, 2866*w*, 1756*s*, 1673*m*, 1640*m*, 1603*w*, 1581*w*, 1456*m*, 1435*w*, 1367*m*, 1318*w*, 1283*m*, 1166*w*, 1150*w*, 1094*w*, 1042*m*, 920*w*, 899*w*, 850*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 7*; additionally, 12.49 (*d*, $J = 0.3$, HO–C(8′)); 8.32 (*dd*, $J = 7.8$, 1.4, H–C(4′)); 7.89 (*dd*, $J = 7.7$, 1.4, H–C(2′)); 7.80 (*dd*, $J = 7.5$, 1.2, H–C(5′)); 7.73 (*t*, $J = 7.8$, H–C(3′)); 7.67 (*td*, $J \approx 7.9$, 0.3, H–C(6′)); 7.32 (*dd*, $J \approx 8.4$, 1.2, H–C(7′)); 2.16, 2.12, 2.11, 2.07, 2.06, 2.02, 1.99 (7*s*, 7 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 8*; additionally, 187.32 (*s*, C(9′)); 181.79 (*s*, C(10′)); 170.52, 170.37, 170.22, 169.92, 169.76, 169.32, 169.10 (7*s*, 7 OC=O); 162.58 (*s*, C(8′)); 140.87 (*d*, C(2′)); 136.60 (*d*, C(6′)); 134.47 (*s*, C(9′a)); 133.47 (*d*, C(3′)); 133.35 (*s*, C(4′a));

132.73 (*s*, C(10′a)); 128.24 (*d*, C(4′)); 124.82 (*d*, C(7′)); 122.03 (*s*, C(1′)); 119.33 (*d*, C(5′)); 116.3 (*s*, C(8′a)); 20.93, 20.91, 20.68, 20.62 (4*q*, 4 Me); 20.56 (*q*, 3 Me). HR-MALDI-MS: 889.2163 (60, $[M+Na]^+$, $C_{42}H_{42}NaO_{20}^+$; calc. 889.2167). Anal. calc. for $C_{42}H_{42}O_{20}$ (866.78): C 58.20, H 4.88; found: C 58.26, H 4.97.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-(1 → 6)-4,5,8-tri*-O-*acetyl-3,7-anhydro-1,2-dideoxy-1*-C-*{8-[(trifluoromethyl)sulfonyloxy]-9,10-dioxoanthracen-1-yl}*-D-glycero-D-gulo-*oct-1-ynitol* (**22**). A soln. of **21** (0.5 g, 0.58 mmol) in dry CH_2Cl_2 (8.5 ml) was treated with Et_3N (160 µl, 1.2 mmol) and cooled to −78°. The resulting red suspension was treated with freshly distilled Tf_2O (120 µl, 2 mmol), stirred for 1 h, allowed to warm to 0°, stirred for 30 min, and diluted with CH_2Cl_2 (250 ml). Workup, evaporation, and FC (AcOEt/hexane 2:3) gave **22** (0.55 g, 96%) as a pale yellow solid, which was recrystallised in AcOEt/hexane. R_f (AcOEt/hexane 1:1) 0.17. M.p. 234.1–235.4° (dec.). $[\alpha]_D^{25} = +29.7$ ($c = 1.0$, $CHCl_3$). UV ($CHCl_3$): 274 (17609), 368 (3831). IR ($CHCl_3$): 3068*w*, 2950*w*, 2870*w*, 1756*s*, 1682*m*, 1599*w*, 1434*m*, 1368*m*, 1323*m*, 1249*s*, 1157*w*, 1140*m*, 1094*w*, 1048*m*, 987*w*, 898*w*, 836*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): see *Table 7*; additionally, 8.37 (*dd*, $J = 7.8$, 1.2, H–C(4′)); 8.27 (*dd*, $J = 7.8$, 1.3, H–C(5′)); 7.89 (*dd*, $J = 7.8$, 1.3, H–C(2′)); 7.85 (*t*, $J \approx 8.0$ H–C(6′)); 7.73 (*t*, $J = 7.8$, H–C(3′)); 7.63 (br. *d*, $J \approx 8.2$, H–C(7′)); 2.05 (*s*, 2 AcO); 2.16, 2.12, 2.11, 2.02, 1.99 (5*s*, 5 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$): see *Table 8*; additionally, 181.10 (*s*, C(9′)); 179.82 (*s*, C(10′)); 170.54, 170.46, 170.22, 170.02, 169.79, 169.33, 169.10 (7*s*, 7 OC=O); 147.49 (*s*, C(8′)); 140.95 (*d*, C(2′)); 134.95 (*d*, C(6′)); 134.77 (*s*, C(9′a)); 134.48 (*s*, C(10′a)); 133.23 (*d*, C(3′)); 133.19 (*s*, C(4′a)); 128.89 (*d*, C(4′)); 127.71 (*d*, C(7′)); 127.62 (*d*, C(5′)); 126.63 (*s*, C(8′a)); 122.03 (*s*, C(1′)); 118.80 (*q*, ^1J(C,F) = 321.0, CF_3); 20.84, 20.72, 20.67, 20.62, 20.30 (5*q*, 5 Me); 20.55 (*q*, 2 Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −73.63 (*s*, CF_3). HR-MALDI-MS: 1021.1643 (12, $[M+Na]^+$, $C_{43}H_{41}F_3NaO_{22}S^+$; calc. 1021.1660). Anal. calc. for $C_{43}H_{41}F_3O_{22}S$ (998.84): C 51.71, H 4.14; found: C 51.70, H 4.24.

β-D-*Glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-1*-C-*(8-hydroxy-9,10-dioxoanthracen-1-yl)*-D-glycero-D-gulo-*oct-1-ynitol* (**23**). A stirred suspension of **21** (0.25 g, 0.29 mmol) in dry MeOH (18 ml) was treated with a soln. of 0.02M MeONa (18 ml), stirred for 6 h at 20°, treated with H_2O (10 ml), stirred for 1 h, and neutralised with *Amberlite IR-120* (H^+ form). After filtration, evaporation of the filtrate gave **23** (158 g, 95%). Bright yellow solid. R_f (*RP-18* silica gel; MeCN/H_2O 2:1) 0.33. M.p. 152.8° (dec., → green residue). $[\alpha]_D^{25} = +13.2$ ($c = 1.0$, DMSO). ^{1}H-NMR (500 MHz, (D_6)DMSO; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 1*; additionally, 12.46 (br. *s*, HO–C(8′)); 8.22 (*dd*, $J = 7.8$, 1.4, H–C(4′)); 8.00 (*dd*, $J = 7.7$, 1.4, H–C(2′)); 7.91 (*t*, $J = 7.7$, H–C(3′)); 7.79 (*t*, $J = 7.9$, H–C(6′)); 7.69 (br. *d*, $J \approx 7.5$, H–C(5′)); 7.39 (br. *d*, $J \approx 8.2$, H–C(7′)); 4.31 (br. *d*, $J = 7.9$, H–C(3^I), H–C(1^{II})); 3.81 (*dd*, $J \approx 11.8$, 5.0, H–C(8^I)); 3.73 (br. *d*, $J = 9.9$, H–C(6^{II})); 3.66 (*dd*, $J \approx 11.0$, 5.3, H′–C(8^I)); 3.46–3.30 (*m*, H–C(4^I), H–C(5^I), H–C(6^I), H–C(7^I), H′–C(6^{II})); 3.24 (*ddd*, $J \approx 9.6$, 6.2, 2.2, H–C(5^{II})); 3.19 (br. *t*, $J = 9.0$, H–C(3^{II})); 3.09 (*td*, $J \approx 9.4$, 3.4, H–C(4^{II})); 3.03 (*td*, $J \approx 8.6$, 4.1, H–C(2^{II})). ^{13}C-NMR (125 MHz, (D_6)DMSO; assignments based on a HSQC spectrum): see *Table 8*; additionally, 186.83 (*s*, C(9′)); 181.44 (*s*, C(10′)); 161.45 (*s*, C(8′)); 140.94 (*d*, C(2′)); 136.70 (*d*, C(6′)); 134.04 (*s*, C(9′a)); 133.92 (*d*, C(3′)); 132.61 (*s*, C(4′a)); 132.54 (*s*, C(10′a)); 127.26 (*d*, C(4′)); 124.28 (*d*, C(7′)); 122.06 (*d*, C(1′)); 118.50 (*d*, C(5′)); 116.27 (*s*, C(8′a)). MALDI-TOF: 573.5 ($[M+H]^+$, $C_{28}H_{29}O_{13}^+$; calc. 573.2), 595.5 ($[M+Na]^+$, $C_{28}H_{28}NaO_{13}^+$; calc. 595.1), 611.4 ($[M+K]^+$, $C_{28}H_{28}KO_{13}^+$; calc. 611.1). Anal. calc. for $C_{28}H_{28}O_{13} \cdot H_2O$ (590.53): 56.95, H 5.12; found: C 56.98, H 5.22.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-(1 → 8)-6,7,10-tri*-O-*acetyl-5,9-anhydro-1,2,3,4-tetradeoxy-1*-C-*{8-[2,3,4,6-tetra*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 6)-4,5,8-tri*-O-*acetyl-3,7-anhydro-1,2-dideoxy*-D-glycero-D-gulo-*oct-1-ynitol-1-yl]-9,10-dioxoanthracen-1-yl}*-D-glycero-D-gulo-*deca-1,3-diynitol* (**24**). Under Ar, a suspension of **21** (0.4 g, 0.40 mmol), $[Pd(PPh_3)_2]Cl_2$ (14 mg, 0.02 mmol), and CuI (11.5 mg, 0.06 mmol) in degassed Et_3N/DMF 1:5 (4 ml) was treated with a soln. of **19** (0.54 g, 0.80 mmol) in Et_3N/DMF 1:5 (4 ml) over a period of 12 h, and stirred at 24° for additional 12 h. Workup (AcOEt), evaporation, and FC (CH_2Cl_2/AcOEt 5:1 → 2:1) gave **24** (0.53 g, 87%) as a pale yellow solid, which was recrystallised in AcOEt/MeOH. R_f (AcOEt/hexane 2:1) 0.20. M.p. 302.7–304.1° (dec.). $[\alpha]_D^{25} = +14.8$ ($c = 1.0$, $CHCl_3$). UV ($CHCl_3$): 277 (30643), 289 (14415), 311 (12508), 373 (8107). IR ($CHCl_3$): 3034*w*, 2947*w*, 2867*w*, 1755*s*, 1677*w*, 1603*w*, 1574*w*, 1431*w*, 1368*m*, 1334*w*, 1249*s*, 1094*w*, 1048*m*, 908*w*, 836*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 7*; additionally, 8.31 (*dd*, $J = 7.8$, 1.4, H–C(5′)); 8.29 (*dd*, $J = 7.8$, 1.4, H–C(4′)); 7.95 (*dd*,

J = 7.8, 1.4, H–C(7′)); 7.92 (*dd*, $J \approx 7.8$, H–C(2′)); 7.72 (*t*, J = 7.8, H–C(6′)); 7.70 (*t*, $J \approx 7.8$, H–C(3′)); 2.19, 2.18, 2.16, 2.13, 2.11, 2.10, 2.07, 2.061, 2.059, 2.05, 2.02, 2.01, 2.00, 1.98 (14*s*, 14 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 8*; additionally, 181.78 (*s*, C(10′)); 179.82 (*s*, C(9′)); 170.51 (*s*, 2 OC=O); 170.43, 170.31, 170.25, 170.22, 170.19, 169.87, 169.77, 169.52, 169.36, 169.32, 169.17, 169.11 (12*s*, 12 OC=O); 142.01 (*d*, C(2′)); 141.37 (*d*, C(7′)); 135.50 (*s*, C(9′a)); 133.81 (*s*, C(8′a)); 133.72 (*s*, C(4′a)); 133.49 (*s*, C(10′a)); 132.88 (*d*, C(6′)); 132.77 (*d*, C(3′)); 128.12 (*d*, C(4′)); 127.75 (*d*, C(5′)); 122.37 (*s*, C(8′)); 121.47 (*s*, C(1′)); 20.99, 20.93, 20.90, 20.73, 20.69, 20.67, 20.65, 20.58, 20.52 (9*q*, 9 Me); 20.56 (*q*, 3 Me); 20.55 (*q*, 2 Me). HR-MALDI-MS: 1539.4000 (12, $[M+Na]^+$, $C_{72}H_{76}NaO_{36}^+$; calc. 1539.4013). Anal. calc. for $C_{72}H_{76}O_{36}$ (1517.37): C 56.99, H 5.05; found: C 57.03, H 5.17.

*β-*D*-Glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-1-*C*-{8-[β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-*D*-glycero-*D*-gulo-oct-1-ynitol-1-yl]-9,10-dioxoanthracen-1-yl}-*D*-glycero-*D*-gulo-deca-1,3-diynitol* (**25**). Under Ar, a stirred suspension of KCN (4 mg, 0.06 mmol) in dry MeOH (4.0 ml) was treated with a soln. of **24** (150 mg, 99 μmol) in CH_2Cl_2 (8 ml), stirred at 25° for 36 h, treated with H_2O (10 ml), stirred for 20 min, and diluted with H_2O (10 ml). Evaporation of the org. solvents and lyophilisation gave a pale greenish-yellow residue, which was subjected to reversed-phase (RP) FC (*Lichroprep RP-18*, 40–63 μm, MeCN/H_2O 1:5 → 1:4 → 1:3). Evaporation and lyophilisation gave **25** (65 mg, 71%) as a greenish yellow solid, which turned brown upon standing at r.t. R_f (*RP-18* silica gel; MeCN/H_2O 2:1) 0.25. ^{1}H-NMR (500 MHz, (D_6)DMSO; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 1*; additionally, 8.26 (*dd*, J = 7.7, 1.3), 8.22 (*dd*, J = 7.7, 1.4) (H–C(4′), H–C(5′)); 8.13 (*dd*, $J \approx 7.7$, 1.3), 8.03 (*dd*, $J \approx 7.8$, 1.4) (H–C(2′), H–C(7′)); 7.90 (*t*, J = 7.7), 7.89 (*t*, J = 7.9) (H–C(3′), H–C(6′)); 4.33 (*d*, J = 8.6, H–C(3^{1E})); 4.31 (*d*, J = 7.6, H–C(1^{IIE})); 4.28 (*d*, J = 7.9, H–C(1^{IIB})); 4.23 (*d*, J = 9.4, H–C(5^{1B})); 3.81 (*dd*, $J \approx 12.0$, 5.6, H–C(8^{1E})); 3.78 (*dd*, $J \approx 12.0$, 5.9, H–C(10^{1B})); 3.74–3.60 (*m*, H–C(6^{IIB}), H–C(6^{IIE}), H′–C(10^{1B}), H′–C(8^{1E})); 3.45–3.30 (*m*, H′–C(6^{IIB}), H′–C(6^{IIE}), H–C(9^{1B}), H–C(7^{1E}), H–C(8^{1B}), H–C(6^{1E}), H–C(7^{1B}), H–C(5^{1E}), H–C(6^{1B}), H–C(4^{1E})); 3.28–3.20 (*m*, H–C(5^{IIB}), H–C(5^{IIE})); 3.19–3.12 (*m*, H–C(3^{IIB}), H–C(3^{IIE})); 3.10–2.99 (*m*, H–C(4^{IIB}), H–C(4^{IIE}), H–C(2^{IIB}), H–C(2^{IIE})). ^{13}C-NMR (125 MHz, (D_6)DMSO; assignments based on a HSQC spectrum): see *Table 8*; additionally, 181.43 (*s*, C(10′)); 179.58 (*s*, C(9′)); 141.94 (*d*, C(2′)); 141.68 (*d*, C(7′)); 135.03 (*s*, C(9′a)); 133.47 (*s*, C(8′a)); 133.35 (*s*, C(4′a)); 133.27 (*d*, C(3′)); 133.22 (*d*, C(6′)); 133.10 (*s*, C(10′a)); 127.60 (*d*, C(4′)); 127.00 (*d*, C(5′)); 122.07 (*s*, C(8′)); 120.17 (*s*, C(1′)). MALDI-TOF: 929.2 ($[M+H]^+$, $C_{44}H_{49}O_{22}^+$; calc. 929.3), 951.2 ($[M+Na]^+$, $C_{44}H_{48}NaO_{22}^+$; calc. 951.3), 967.2 ($[M+K]^+$, $C_{44}H_{48}KO_{22}^+$; calc. 967.2).

*2,3,4,6-Tetra-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-6-*O*-benzyl-2,3-bis-*O*-(4-chlorobenzyl)-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tris-*O*-(4-chlorobenzyl)-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**26**). A suspension of **13** (6.7 g, 5.9 mmol), AgOTf (9.1 g, 35.4 mmol), and 3-Å molecular sieves (15 g) in dry toluene (135 ml) was stirred under Ar at 23° for 1 h, cooled to −30° to −35°, stirred for 15 min, treated with a soln. of **2** (8.24 g, 12 mmol) in CH_2Cl_2 (20 ml), stirred for 3 h, allowed to warm to r.t., and stirred for 12 h. The mixture was cooled to −35°, treated with an additional batch of **2** (8.26 g, 12 mmol) in CH_2Cl_2 (20 ml), warmed slowly to r.t., and stirred for 48 h. After cooling to −10°, the suspension was treated with Et_3N (6.0 ml), stirred for 15 min, and filtered through a pad of *Celite* (washing of the residue thoroughly with 500 ml of $CHCl_3$). The combined org. layers and washing were dried ($MgSO_4$) and evaporated. FC (AcOEt/hexane 7:12) gave **26** (8.7 g, 84%). R_f (AcOEt/hexane 2:3) 0.31. M.p. 80.7°. $[\alpha]_D^{25} = -9.5$ (c = 1.0, $CHCl_3$). IR ($CHCl_3$): 3020*m*, 2952*m*, 2916*m*, 2871*w*, 2179*w*, 1756*s*, 1601*w*, 1492*m*, 1460*w*, 1410*w*, 1363*m*, 1162*m*, 1085*s*, 1058*s*, 1020*s*, 910*w*, 842*m*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 9*; additionally, 7.40–6.95 (*m*, 25 arom. H); 5.02 (*d*, J = 11.9), 4.95 (*d*, J = 11.9), 4.87 (*d*, J = 11.6), 4.66 (*d*, J = 10.8), 4.60 (*d*, J = 12.0), 4.54 (*d*, J = 11.5), 4.53 (*d*, J = 12.2), 4.52 (*d*, J = 12.3) (8 PhC*H*); 4.51 (*d*, J = 11.5, 2 PhC*H*); 4.35 (*d*, J = 12.2), 4.27 (*d*, J = 12.0) (2 PhC*H*); 2.07, 2.02, 2.00, 1.99, 1.98, 1.95, 1.89 (7*s*, 7 AcO); 0.16 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 10*; additionally, 170.46, 170.17, 170.11, 169.69, 169.41, 169.29, 168.98 (7*s*, 7 C=O); 137.76, 137.72, 137.64, 136.57, 136.50, 136.33 (6*s*); 133.56, 133.51, 133.42, 132.98, 132.90 (5*s*); 129.35–127.83 (several *d*); 74.58, 74.33, 74.14, 74.10, 73.40, 72.53 (6*t*, 6 PhCH_2); 20.64, 20.57, 20.53, 20.50 (4*q*, 7 Me); −0.30 (*q*, Me_3Si). HR-MALDI-MS: 1773.4165 (45, $[M+Na]^+$, $C_{85}H_{95}Cl_5NaO_{27}Si^+$; calc. 1773.4170). Anal. calc. for $C_{85}H_{95}Cl_5O_{27}Si$ (1754.02): C 58.21, H 5.46; found: C 58.07, H 5.36.

Table 9. *Selected ^{1}H-NMR Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of the 4-Chlorobenzylated Cellotetraosylalkynes* **26**, **27**, **29**, *and* **30** *in $CDCl_3$*

	26[a])	**27**[b])	**29**[b])	**30**		**26**[a])	**27**[b])	**29**[b])	**30**
C≡CH	–	2.52	–	2.22					
H–C(1^{I})	3.98	3.97	4.01	3.997	H–C(1^{III})	4.49	4.49	4.49	4.48
H–C(2^{I})	3.51	3.52	3.48	3.50	H–C(2^{III})	4.80	4.80	4.79	4.79
H–C(3^{I})	3.43	3.45	3.43	3.45	H–C(3^{III})	4.953	4.95	4.95	4.95
H–C(4^{I})	3.92	3.94	3.914	3.90	H–C(4^{III})	3.66	3.66	3.67	3.66
H–C(5^{I})	3.23	3.23	3.23	3.23	H–C(5^{III})	3.11	3.11	3.11	3.11
H_a–C(6^{I})	3.72	3.74	3.73	3.73	H_a–C(6^{III})	4.24	4.24	4.24	4.24
H_b–C(6^{I})	3.63–3.56	3.63–3.56	3.64–3.57	3.63–3.58	H_b–C(6^{III})	3.91	3.91	3.91	3.91
H–C(1^{II})	4.34	4.35	4.34	4.33	H–C(1^{IV})	4.39	4.39	4.39	4.39
H–C(2^{II})	3.18	3.19	3.18	3.18	H–C(2^{IV})	4.91	4.91	4.91	4.91
H–C(3^{II})	3.28	3.29	3.29	3.28	H–C(3^{IV})	5.10	5.10	5.10	5.10
H–C(4^{II})	3.87	3.87	3.88	3.89	H–C(4^{IV})	5.05	5.05	5.06	5.06
H–C(5^{II})	3.05	3.05	3.06	3.05	H–C(5^{IV})	3.63–3.56	3.63–3.56	3.64–3.57	3.63–3.58
H_a–C(6^{II})	3.63–3.56	3.63–3.56	3.64–3.57	3.63–3.58	H_a–C(6^{IV})	4.36	4.36	4.36	4.36
H_b–C(6^{II})	3.63–3.56	3.63–3.56	3.64–3.57	3.63–3.58	H_b–C(6^{IV})	4.00	4.00	4.00	4.002
$J(1^{I},{\equiv}CH)$	–	2.3	–	0.9					
$J(1^{I},2^{I})$	9.6	9.6	9.3	9.3	$J(1^{III},2^{III})$	7.9	8.1	8.0	8.1
$J(2^{I},3^{I})$	9.0	9.0	9.0	9.0	$J(2^{III},3^{III})$	9.4	9.7	9.6	9.7
$J(3^{I},4^{I})$	8.8	8.8	8.7	8.8	$J(3^{III},4^{III})$	9.4	9.3	9.3	9.4
$J(4^{I},5^{I})$	9.9	10.0	9.8	9.9	$J(4^{III},5^{III})$	9.6	9.6	9.7	9.7
$J(5^{I},6a^{I})$	3.4	3.4	3.4	3.4	$J(5^{III},6a^{III})$	1.9	1.9	1.9	1.9
$J(5^{I},6b^{I})$	1.7	1.6	1.6	1.6	$J(5^{III},6b^{III})$	4.4	4.2	4.5	4.1
$J(6a^{I},6b^{I})$	11.1	11.1	11.2	11.1	$J(6a^{III},6b^{III})$	12.1	12.2	12.3	12.1
$J(1^{II},2^{II})$	7.9	7.9	7.6	7.8	$J(1^{IV},2^{IV})$	7.9	8.0	7.9	7.9
$J(2^{II},3^{II})$	9.0	9.0	9.0	9.1	$J(2^{IV},3^{IV})$	9.2	9.0	9.1	9.1
$J(3^{II},4^{II})$	9.0	8.8	9.0	9.2	$J(3^{IV},4^{IV})$	9.3	9.3	9.3	9.3
$J(4^{II},5^{II})$	9.8	9.8	9.8	9.8	$J(4^{IV},5^{IV})$	9.3	9.6	9.6	9.7
$J(5^{II},6a^{II})$	3.0	3.0	3.0	3.0	$J(5^{IV},6a^{IV})$	4.3	4.2	4.0	4.6
$J(5^{II},6b^{II})$	2.0	2.0	1.8	2.0	$J(5^{IV},6b^{IV})$	2.1	1.9	3.2	3.2
$J(6a^{II},6b^{II})$	[c])	[c])	[c])	[c])	$J(6a^{IV},6b^{IV})$	12.4	12.5	12.5	12.5

[a]) Assignments based on a HSQC spectrum. [b]) Assignments based on a DQFCOSY and a HSQC spectrum. [c]) Not assigned.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-6*-O-*benzyl-2,3-bis*-O-*(4-chlorobenzyl)-β*-D-*glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tris*-O-*(4-chlorobenzyl)-1,2-dideoxy*-D-glycero-D-gulo-*oct-1-ynitol* (**27**). At 0°, a stirred soln. of **26** (1.0 g, 0.57 mmol) in THF (40 ml) was treated with a soln. of $Bu_4NF \cdot 3\,H_2O$ (54 mg, 0.17 mmol) in THF (10 ml), stirred for 5 min, and treated with H_2O (10 ml). Workup (AcOEt) and FC (AcOEt/hexane 2:3) gave **27** (0.83 g, 86%). Solid foam. R_f (AcOEt/hexane 2:3) 0.23. M.p. 82°. $[\alpha]_D^{25} = -4.1$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3304*w*, 3033*w*, 2953*w*, 2871*w*, 2124*w*, 1757*s*, 1601*w*, 1492*m*, 1460*w*, 1410*w*, 1363*m*, 1162*m*, 1085*s*, 1058*s*, 1018*s*, 910*w*, 842*m*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 9*; additionally, 7.40–6.95 (*m*, 25 arom. H); 5.04 (*d*, $J = 11.8$), 4.96 (*d*, $J = 11.9$), 4.85 (*d*, $J = 10.8$), 4.67 (*d*, $J = 10.8$), 4.60 (*d*, $J = 11.9$), 4.55 (*d*, $J = 11.5$) (6 PhC*H*); 4.53 (*d*, $J = 11.5$, 2 PhC*H*); 4.52 (*d*, $J = 12.1$), 4.51 (*d*, $J = 12.0$), 4.34 (*d*, $J = 12.3$), 4.28 (*d*, $J = 12.0$) (4 PhC*H*); 2.07, 2.06, 2.00, 1.99, 1.98, 1.95, 1.89 (7*s*, 7 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 10*; additionally, 170.45, 170.17, 170.10, 169.68, 169.41, 169.29, 168.98 (7*s*, 7 C=O); 137.75, 136.57, 136.38, 136.34 (4*s*); 137.63 (2*s*); 133.60, 133.50, 133.42, 133.04, 132.91 (5*s*); 129.35–127.83 (several *d*); 74.65, 74.43, 74.16, 74.11, 73.40, 72.59 (6*t*, 6 Ph*C*H_2); 20.64, 20.57, 20.53, 20.51 (4*q*, 7 Me). HR-MALDI-MS: 1701.3779 (46, $[M + Na]^+$, $C_{82}H_{87}Cl_5NaO_{27}^+$; calc. 1701.3775). Anal. calc. for $C_{82}H_{87}Cl_5O_{27}$ (1681.84): C 58.56, H 5.21; found: C 58.39, H 5.39.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl]$_2$-(1 → 6)-4,5,8-tri*-O-*acetyl-1,2-dideoxy*-D-glycero-D-gulo-*oct-1-ynitol* (**28**). At −40°, a soln. of **27** (10.8 g, 6.4 mmol) in Ac_2O (108 ml) was treated with TMSOTf (23.2 ml, 0.13 mol), stirred for 3 h at −40°, warmed

Table 10. *Selected ^{13}C-NMR Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of the 4-Chlorobenzylated Cellotetraosylalkynes* **26**, **27**, **29**, *and* **30** *in $CDCl_3$*

	26[a])	**27**[a])	**29**[a])	**30**		**26**[a])	**27**[a])	**29**[a])	**30**
C(4′)	–	–	87.01	67.23					
C(3′)	–	–	88.36	68.88					
C(2′)	91.42	74.37	71.12	68.88					
C(1′)	102.19	80.75	74.21	72.90					
C(1^{I})	70.26	69.66	70.21	70.02	C(1^{III})	102.34	102.35	102.33	102.36
C(2^{I})	81.64	81.39	81.09	80.94	C(2^{III})	72.03	72.03	72.01	71.99
C(3^{I})	84.12	84.20	84.20	84.19	C(3^{III})	72.81	72.81	72.79	72.77
C(4^{I})	76.46	76.39	76.29	76.31	C(4^{III})	76.15	76.15	76.14	76.12
C(5^{I})	79.20	79.28	79.30	79.29	C(5^{III})	72.44	72.43	72.42	72.39
C(6^{I})	67.84	67.90	67.84	67.73	C(6^{III})	61.78	61.78	61.78	61.75
C(1^{II})	99.79	99.78	99.76	99.76	C(1^{IV})	100.82	100.82	100.81	100.81
C(2^{II})	81.66	81.66	81.62	81.59	C(2^{IV})	71.52	71.52	71.51	71.48
C(3^{II})	83.03	83.03	83.00	82.99	C(3^{IV})	72.93	72.93	72.91	72.90
C(4^{II})	76.72	76.70	76.67	76.65	C(4^{IV})	67.80	67.80	67.78	67.73
C(5^{II})	74.68	74.68	74.66	74.64	C(5^{IV})	71.95	71.96	71.94	71.92
C(6^{II})	67.63	67.63	67.59	67.56	C(6^{IV})	61.53	61.53	61.53	61.49

[a]) Assignments based on a HSQC spectrum.

to $-20°$, stirred for 24 h, warmed to $-10°$, and stirred for 20 h. After cooling to $-20°$, the mixture was treated portionwise with sat. aq. $NaHCO_3$ soln. (40 ml), and stirred for 0.5 h. Workup (AcOEt), evaporation, and FC (AcOEt/hexane 1:2 → 3:2) gave a colourless solid (7.0 g). Recrystallisation in AcOEt/hexane gave **28** (6.0 g, 76%). Colourless needles. R_f (AcOEt/hexane 3:2) 0.20. M.p. 226.4°. $[\alpha]_D^{25} = -16.8$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3305*w*, 3020*w*, 2952*w*, 2871*w*, 2138*w*, 1757*s*, 1431*w*, 1370*s*, 1160*m*, 1045*s*, 902*w*, 804*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): see *Table 11*; additionally, 2.143, 2.141, 2.13, 2.09, 2.06, 2.03, 2.02, 2.01, 2.00, 1.99, 1.983, 1.979, 1.95 (13*s*, 13 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$): see *Table 12*; additionally, 170.50, 170.35, 170.21, 170.20, 170.19, 169.80, 169.75, 169.72, 169.45, 169.33, 169.30, 169.29, 169.11 (13*s*, 13 C=O); 20.89, 20.67, 20.61, 20.59, 20.54, 20.49, 20.47 (7*q*, 7 Me); 20.80, 20.56, 20.53 (3*q*, 6 Me). HR-MALDI-MS: 1243.3527 (100, $[M+Na]^+$, $C_{52}H_{68}NaO_{33}^+$; calc. 1243.3541). Anal. calc. for $C_{52}H_{68}O_{33}$ (1221.09): C 51.15, H 5.61; found: C 51.29, H 5.61.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1 → 4)-6*-O-*benzyl-2,3-bis*-O-*(4-chlorobenzyl)-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tris*-O-*(4-chlorobenzyl)-1,2,3,4-tetradeoxy-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol* (**29**). Under Ar, a suspension of **17** (7.93 g, 6.8 mmol), AgOTf (9.1 g, 35.4 mmol), and 4-Å molecular sieves (16 g) in dry toluene (80 ml) was stirred at 25° for 1 h, cooled to $-35°$, stirred for 15 min, treated with a soln. of **2** (9.6 g, 13.7 mmol) in CH_2Cl_2 (40 ml), stirred for 3 h at $-35°$, and left for 24 h at r.t. The mixture was cooled to $-35°$, treated with an additional batch of **2** (6.5 g, 9.3 mmol) in CH_2Cl_2 (40 ml), gradually brought to r.t., and stirred for 24 h. The mixture was cooled to $-10°$, treated with Et_3N (20 ml), stirred for 15 min, and filtered through *Celite* (washing thoroughly with 500 ml of CH_2Cl_2). Evaporation and FC (AcOEt/hexane 5:9) gave **29** (10 g, 82%). R_f (AcOEt/hexane 2:3) 0.42. M.p. 84.2°. $[\alpha]_D^{25} = -30.9$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3028*m*, 2960*w*, 2877*w*, 2114*w*, 1756*s*, 1601*w*, 1519*w*, 1491*s*, 1460*w*, 1415*m*, 1363*s*, 1162*m*, 1086*s*, 1051*s*, 1017*s*, 924*m*, 910*w*, 843*s*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 9*; additionally, 7.38–6.95 (*m*, 25 arom. H); 5.03 (*d*, $J = 11.8$), 4.96 (*d*, $J = 11.9$), 4.80 (*d*, $J = 11.5$), 4.66 (*d*, $J = 10.9$), 4.60 (*d*, $J = 11.9$), 4.55 (*d*, $J = 11.4$) (6 PhC*H*); 4.53 (br. *d*, $J = 11.2$, 2 PhC*H*); 4.51 (br. *d*, $J = 11.3$, 2 PhC*H*); 4.33 (*d*, $J = 12.2$), 4.28 (*d*, $J = 12.0$) (2 PhC*H*); 2.07, 2.01, 2.00, 1.99, 1.98, 1.95, 1.89 (7*s*, 7 AcO); 0.21 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 10*; additionally, 170.45, 170.16, 170.11, 169.68, 169.40, 169.29, 168.97 (7*s*, 7 C=O); 137.73, 137.60, 137.56, 136.55, 136.32, 136.15 (6*s*);

Table 11. *Selected ^{1}H-NMR Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of the Peracetylated Cellotetraosylalkynes* **28**, **31**, **32**, **33**, *and* **35** *in $CDCl_3$*

	28	**31**	**32**[a])	**33**[b])	**35**[a]) [b])
					E chain, *B* chain
C≡CH	2.49	2.24	–	–	–
H–C(1^I)	4.14	4.21	4.54	4.54–4.51	4.60, 4.40
H–C(2^I)	5.13	5.12	5.30	5.28–5.23	5.26–5.24, 5.15–5.08
H–C(3^I)	5.12	5.11	5.23	5.28–5.23	5.26–5.24, 5.17
H–C(4^I)	3.75	3.75	3.84	3.85–3.80	3.81–3.72, 3.82
H–C(5^I)	3.63	3.64	3.69	3.69	3.71, 3.67–3.55
H_a–C(6^I)	4.47	4.47	4.56	4.54–4.51	4.56, 4.49
H_b–C(6^I)	4.09	4.093	4.13	4.13	4.15–4.06
H–C(1^{II})	4.44	4.44	4.46	4.45	4.46, 4.54
H–C(2^{II})	4.82	4.815	4.83	4.84	4.86–4.80
H–C(3^{II})	5.10	5.10	5.13	5.13	5.15–5.08
H–C(4^{II})	3.74	3.74	3.77	3.77	3.81–3.72
H–C(5^{II})	3.56	3.56	3.57	3.57	3.67–3.55
H_a–C(6^{II})	4.40	4.40	4.42	4.43–4.41	4.41
H_b–C(6^{II})	4.08	4.089	4.11	4.11	4.15–4.06
H–C(1^{III})	4.46	4.46	4.48	4.48	4.492–4.485
H–C(2^{III})	4.90	4.90	4.90	4.91	4.902–4.897
H–C(3^{III})	5.09	5.05	5.12	5.12	5.15–5.08
H–C(4^{III})	3.74	3.73	3.76	3.77	3.81–3.72
H–C(5^{III})	3.58	3.58	3.64	3.63	3.67–3.55
H_a–C(6^{III})	4.39	4.39	4.41	4.43–4.41	4.41
H_b–C(6^{III})	4.06	4.05	4.10	4.10	4.15–4.06
H–C(1^{IV})	4.48	4.48	4.51	4.51	4.50/4.495
H–C(2^{IV})	4.83	4.82	4.86	4.86	4.86–4.80
H–C(3^{IV})	5.07	5.10	5.11	5.11	5.15–5.08
H–C(4^{IV})	5.05	5.05	5.05	5.05	5.05
H–C(5^{IV})	3.57	3.57	3.60	3.61	3.67–3.55
H_a–C(6^{IV})	4.35	4.35	4.35	4.36	4.36/4.35
H_b–C(6^{IV})	4.03	4.03	4.04	4.04	4.05–4.00
$J(1^I,{\equiv}CH)$	2.2	0.9	–	–	–
$J(1^I,2^I)$	9.6	9.8	9.8	[c])	9.7, 9.6
$J(2^I,3^I)$	8.8	9.3	9.3	[c])	[c]), 9.2
$J(3^I,4^I)$	9.3	9.3	9.3	[c])	[c]), 9.2
$J(4^I,5^I)$	9.8	9.8	9.8	9.9	9.9, 9.8
$J(5^I,6a^I)$	1.9	2.0	1.9	1.8	1.9, [c])
$J(5^I,6b^I)$	4.8	4.7	5.0	5.2	4.8, [c])
$J(6a^I,6b^I)$	12.1	12.0	12.3	12.1	12.1, [c])
$J(1^{II},2^{II})$	7.9	7.9	7.9	7.9	7.8/7.8
$J(2^{II},3^{II})$	9.3	9.3	9.3	9.3	[c])
$J(3^{II},4^{II})$	9.2	9.2	9.3	9.4	[c])
$J(4^{II},5^{II})$	9.6	9.6	9.8	9.8	[c])
$J(5^{II},6a^{II})$	2.4	2.4	1.9	2.1	1.9
$J(5^{II},6b^{II})$	4.8	5.1	5.1	5.0	[c])
$J(6a^{II},6b^{II})$	12.1	12.2	12.1	12.1	12.1
$J(1^{III},2^{III})$	7.9	7.9	7.9	7.9	7.8/7.8
$J(2^{III},3^{III})$	9.3	9.3	9.3	9.3	9.5/9.3

Table 11 (cont.)

	28	**31**	**32**[a])	**33**[b])	**35**[a]) [b])
					E chain, *B* chain
$J(3^{III},4^{III})$	9.3	9.3	9.1	9.1	[c])
$J(4^{III},5^{III})$	9.7	9.7	9.7	9.8	[c])
$J(5^{III},6a^{III})$	2.2	2.2	2.1	2.3	1.9
$J(5^{III},6b^{III})$	5.1	5.2	5.0	4.9	[c])
$J(6a^{III},6b^{III})$	12.2	12.1	12.1	12.1	12.1
$J(1^{IV},2^{IV})$	7.9	8.0	7.9	7.9	7.7/7.9
$J(2^{IV},3^{IV})$	9.2	9.2	9.3	9.3	[c])
$J(3^{IV},4^{IV})$	9.6	9.6	9.2	9.2	9.4
$J(4^{IV},5^{IV})$	9.9	9.7	9.8	9.8	9.8
$J(5^{IV},6a^{IV})$	4.8	4.4	4.4	4.7	4.3/4.4
$J(5^{IV},6b^{IV})$	2.4	2.0	2.1	2.1	[c])
$J(6a^{IV},6b^{IV})$	12.5	12.5	12.5	12.5	12.5/12.5

[a]) Assignments based on a DQFCOSY and a HSQC spectrum. [b]) H–C(2^{I}) and H–C(3^{I}) of **33** and the *E* chain of **35** form a narrow *AB* system leading to virtual couplings with H–C(1^{I}) and H–C(4^{I}). [c]) Not assigned.

133.67, 133.48, 133.40, 133.05, 132.89 (5*s*); 129.62–127.83 (several *d*); 74.68, 74.43, 74.14, 74.09, 73.38, 72.62 (6*t*, 6 Ph*C*H$_2$); 20.63, 20.55, 20.51, 20.49 (4*q*, 7 Me); −0.50 (*q*, Me_3Si). HR-MALDI-MS: 1797.4162 (45, $[M+Na]^+$, $C_{87}H_{95}Cl_5NaO_{27}Si^+$; calc. 1797.4170). Anal. calc. for $C_{87}H_{95}Cl_5O_{27}Si$ (1778.04): C 58.77, H 5.39; found: C 58.69, H 5.48.

2,3,4,6-Tetra-O-*acetyl*-β-D-*glucopyranosyl-(1 → 4)-2,3,6-tri*-O-*acetyl*-β-D-*glucopyranosyl-(1 → 4)-6*-O-*benzyl-2,3-bis*-O-*(4-chlorobenzyl)*-β-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tris*-O-*(4-chlorobenzyl)-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol* (**30**). A soln. of **29** (1.0 g, 0.56 mmol) in THF (40 ml) was cooled to 0°, treated with a soln. of $Bu_4NF\cdot 3\,H_2O$ (53 mg, 0.17 mmol) in THF (10 ml), stirred for 5 min, treated with H_2O (10 ml), and warmed to r.t. Workup and FC (AcOEt/hexane 2:3) gave **30** (0.90 g, 94%) as a foamy pale yellow solid, which turned pink upon standing. It was immediately used for the next step. R_f (AcOEt/hexane 2:3) 0.26. M.p. 84.3–88.6°. $[\alpha]_D^{25} = -21.9$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3305*w*, 3028*w*, 2959*w*, 2877*w*, 2114*w*, 1757*s*, 1601*w*, 1519*w*, 1491*s*, 1460*w*, 1421*m*, 1359*s*, 1162*m*, 1086*s*, 1057*s*, 1016*s*, 929*m*, 878*w*, 843*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): see *Table 9*; additionally, 7.8–6.95 (*m*, 25 arom. H); 5.04 (*d*, $J = 12.3$), 4.96 (*d*, $J = 12.3$), 4.78 (*d*, $J = 10.8$), 4.67 (*d*, $J = 10.8$), 4.60 (*d*, $J = 11.9$), 4.54 (*d*, $J = 11.4$), 4.52 (*d*, $J = 10.5$), 4.51 (*d*, $J = 12.1$) (8 PhC*H*); 4.50 (*d*, $J = 11.8$, 2 PhC*H*); 4.34 (*d*, $J = 12.1$), 4.27 (*d*, $J = 12.0$) (2 PhC*H*); 2.07, 2.02, 2.00, 1.99, 1.98, 1.96, 1.89 (7*s*, 7 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$): see *Table 10*; additionally, 170.49, 170.20, 170.13, 169.71, 169.43, 169.31, 168.99 (7*s*, 7 C=O); 137.71, 137.57, 137.513, 136.511, 136.21, 136.00 (6*s*); 133.80, 133.50, 133.40, 133.10, 132.90 (5*s*); 129.62–127.83 (several *d*); 74.76, 74.45, 74.15, 74.11, 73.37, 72.61 (6*t*, 6 Ph*C*H$_2$); 20.65, 20.58, 20.53, 20.51 (4*q*, 7 Me). HR-MALDI-MS: 1725.3758 (49, $[M+Na]^+$, $C_{84}H_{87}Cl_5NaO_{27}^+$; calc. 1725.3775). Anal. calc. for $C_{84}H_{87}Cl_5O_{27}$ (1705.86): C 59.14, H 5.14; found: C 58.97, H 5.36.

2,3,4,6-Tetra-O-*acetyl*-β-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl*-β-D-*glucopyranosyl]$_2$-(1 → 8)-6,7,10-tri*-O-*acetyl-5,9-anhydro-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol* (**31**). A soln. of **30** (5.00 g, 2.90 mmol) in Ac_2O (50 ml) was cooled to −40°, treated with a soln. of TMSOTf (23.2 ml, 58 mmol) in Ac_2O (20 ml), stirred for 3 h, warmed to −20°, stirred for 24 h, warmed to −10°, stirred for 16 h, warmed to −5°, and stirred for 48 h. After cooling to −10°, the mixture was treated portionwise with sat. aq. $NaHCO_3$ soln. (40 ml) and stirred for 0.5 h. Workup (AcOEt), evaporation, and FC (AcOEt/hexane 1:1 → 3:2) gave a pale yellow solid (2.9 g), which was recrystallised in AcOEt/hexane to afford **31** (2.38 g, 65%). R_f (AcOEt/hexane 3:2) 0.22. M.p. 132.3° (dec.). $[\alpha]_D^{25} = -19.0$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3305*w*, 3028*w*, 2969*w*, 2888*w*, 2114*w*, 1757*s*, 1520*w*, 1427*m*, 1369*m*, 1160*m*, 1046*s*, 924*m*, 878*w*,

Table 12. *Selected* ^{13}*C-NMR Chemical-Shift Values* [ppm] *of the Peracetylated Cellotetraosylalkynes* **28**, **31**, **32**, **33**, *and* **35** *in* $CDCl_3$, *and of the Deprotected Cellotetraosylalkynes* **34** *and* **36** *in* $(D_6)DMSO$

	28	**31**	**32**[a])	**33**	**35**[a])	**34**[a])	**36**[a])
					E chain, *B* chain		*E* chain, *B* chain
C(4′)	–	66.83	–	–	–, 78.74	–	–, 78.85
C(3′)	–	69.86	–	–	–, 78.29	–	–, 77.33
C(2′)	75.38	69.60	85.65	84.94	85.92, 71.97	84.01	84.23, 69.67
C(1′)	77.80	71.13	90.16	89.93	90.24, 79.32	94.60	94.04, 84.23
C(1^{I})	68.30	68.66	69.38	69.34	69.48, 69.08	70.83	70.72, 70.41
C(2^{I})	71.27	70.99	71.53	71.35	71.20/71.12	73.53	73.57, 73.13
C(3^{I})	73.02	72.96	73.44	73.11	73.25/73.17	75.91	75.79, 75.67
C(4^{I})	76.20	76.14	76.29	76.40	76.47/76.34[b])	80.11	79.95/79.81
C(5^{I})	76.89	76.95	76.98	76.88	77.05/76.79	79.00	78.93, 78.80
C(6^{I})	62.11	62.10[c])	62.15	62.31[c])	62.31/62.20	60.31	60.17
C(1^{II})	100.53[c])	100.50	100.54	100.54	100.67/100.64	102.71	102.64/102.61
C(2^{II})	71.86[d])	71.83[d])	71.95[c])	71.91[d])	71.92[c])	73.06[b])	72.97/72.93
C(3^{II})	72.80[e])	72.87[e])	72.91[d])	72.91[e])	72.94–72.66	74.76[c])	74.64/74.61
C(4^{II})	76.15[f])	76.06	76.21[e])	76.27[f])	76.28/76.13[b])	80.41[d])	80.21/80.18
C(5^{II})	72.64[e])	72.62[e])	72.68[d])	72.68[e])	72.94–72.66	74.83	74.71
C(6^{II})	62.06	62.06[c])	62.15	62.20[c])	62.17[d])	60.31	60.20
C(1^{III})	100.52[c])	100.50	100.54	100.47	100.53	102.82	102.72
C(2^{III})	71.74[d])	71.73[d])	71.80[c])	71.76[d])	71.82[c])	72.98[b])	72.89
C(3^{III})	72.75[e])	72.79[e])	72.84[d])	72.80[e])	72.94–72.66	74.83[c])	74.71
C(4^{III})	76.07[f])	76.06	76.10[e])	76.11[f])	76.13/76.11[b])	80.34[d])	80.28
C(5^{III})	72.57[e])	72.55[e])	72.64[d])	72.64[e])	72.94–72.66	74.83	74.71
C(6^{III})	62.06	61.92[c])	62.10	62.09[c])	62.09[d])	60.31	60.20
C(1^{IV})	100.81	100.79	100.82	100.83	100.84/100.82	103.25	103.13
C(2^{IV})	71.56[d])	71.56[d])	71.61[c])	71.57[d])	71.62	73.25	73.16
C(3^{IV})	72.88[e])	72.76[e])	72.81[d])	72.76[e])	72.94–72.66	76.47	76.37
C(4^{IV})	67.73	67.73	67.79	67.74	67.79	70.04	69.94
C(5^{IV})	72.04	72.03	72.07	72.07	72.06	76.80	76.69
C(6^{IV})	61.50	61.50	61.54	61.51	61.55	61.04	60.93

[a]) Assignments based on a HSQC spectrum. [b]) [c]) [d]) Assignments may be interchanged.

849*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): see *Table 11*; additionally, 2.142, 2.140, 2.13, 2.09, 2.06, 2.03, 2.02, 2.01, 2.00, 1.99, 1.983, 1.979, 1.96 (13*s*, 13 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$): see *Table 12*; additionally, 170.51, 170.34, 170.23, 169.80, 169.77, 169.74, 169.35, 169.30, 169.12 (9*s*, 9 C=O); 170.20, 169.32 (2*s*, 4 C=O); 20.86, 20.66, 20.58, 20.48, 20.47 (5*q*, 5 Me); 20.79 (*q*, 2 Me); 20.55, 20.53 (2*q*, 6 Me). HR-MALDI-MS:1267.3526 (100, $[M+Na]^+$, $C_{54}H_{68}NaO_{33}^+$; calc. 1267.3541). Anal. calc. for $C_{54}H_{68}O_{33}$ (1245.11): C 52.09, H 5.50; found: C 52.11, H 5.66.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl]$_2$-(1 → 6)-4,5,8-tri*-O-*acetyl-3,7-anhydro-1,2-dideoxy-1*-C-*(8-hydroxy-9,10-dioxoanthracen-1-yl)*-D-glycero-D-gulo-*oct-1-ynitol* (**32**). Under Ar, a stirred suspension of **20** (0.50 g, 1.20 mmol), $[Pd(PPh_3)_2]Cl_2$ (42 mg, 0.06 mmol), CuI (34 mg, 0.18 mmol), and Bu_4NI (0.67 mg, 1.81 mmol) in degassed Et_3N/DMF 1:5 (5 ml) was treated dropwise with a soln. of **28** (1.9 g, 1.6 mmol) in Et_3N/DMF 1:5 (5 ml) over a period of 9 h at 24°. After stirring for 24 h, the mixture was treated with solid $(NH_4)_2CO_3$ (0.50 g, 6.40 mmol), and stirred for 12 h. Workup (AcOEt), evaporation, FC (AcOEt/hexane/CH_2Cl_2 2:3:3), and recrystallisation in CH_2Cl_2/MeOH gave **32** (1.3 g, 75%). Bright yellow solid. R_f (AcOEt/hexane 7:4) 0.27. M.p. 217.1°. $[\alpha]_D^{25} = -8.9$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3476*w*, 3025*m*, 2978*m*, 2897*w*, 1755*s*, 1674*w*, 1640*w*, 1575*w*,

1518*m*, 1477*w*, 1426*m*, 1368*m*, 1315*w*, 1276*w*, 1044*s*, 928*m*, 876*w*, 848*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 11*; additionally, 12.49 (*s*, OH); 8.32 (*dd*, *J* = 7.8, 1.4, H–C(4′)); 7.89 (*dd*, *J* = 7.8, 1.4, H–C(2′)); 7.81 (*dd*, *J* = 7.5, 1.2, H–C(5′)); 7.73 (*t*, *J* = 7.8, H–C(3′)); 7.67 (*dd*, *J* = 8.2, 7.7, H–C(6′)); 7.32 (*dd*, *J* = 8.4, 1.2, H–C(7′)); 2.16, 2.155, 2.151, 2.10, 2.09, 2.039, 2.037, 2.03, 2.02, 2.01, 2.00, 1.98, 1.97 (13*s*, 13 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 12*; additionally, 187.34 (*s*, C(9′)); 181.80 (*s*, C(10′)); 170.49, 170.39, 170.19, 169.92, 169.71, 169.34, 169.31, 169.30, 169.10 (9*s*, 9 C=O); 170.21, 169.74 (2*s*, 4 C=O); 162.60 (*s*, C(8′)); 140.88 (*d*, C(2′)); 136.61 (*d*, C(6′)); 134.49 (*s*, C(9′a)); 133.47 (*d*, C(3′)); 133.37 (*s*, C(4′a)); 132.75 (*s*, C(10′a)); 128.24 (*d*, C(4′)); 124.82 (*d*, C(7′)); 122.05 (*s*, C(1′)); 119.34 (*d*, C(5′)); 116.33 (*s*, C(8′a)); 20.94, 20.89, 20.82, 20.80, 20.66, 20.62, 20.56, 20.51, 20.48 (9*q*, 9 Me); 20.59, 20.53 (2*q*, 4 Me). HR-MALDI-MS: 1465.3852 (86, $[M+Na]^+$, $C_{66}H_{74}NaO_{36}^+$; calc. 1465.3858). Anal. calc. for $C_{66}H_{74}O_{36}$ (1443.29): C 54.92, H 5.17; found: C 54.78, H 5.07.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl]$_2$-(1 → 6)-4,5,8-tri*-O-*acetyl-3,7-anhydro-1,2-dideoxy-1*-C-*{8-[(trifluoromethyl)sulfonyloxy]-9,10-dioxoanthracen-1-yl}*-D-glycero-D-gulo-*oct-1-ynitol* (**33**). A stirred soln. of **32** (1.2 g, 0.83 mmol) in dry CH_2Cl_2 (19.2 ml) was treated with Et_3N (0.23 ml, 1.65 mmol) and cooled to −78°. The resulting red suspension was treated with freshly distilled Tf_2O (0.18 ml, 1.09 mmol), stirred for 1 h, allowed to warm to 0°, and diluted with CH_2Cl_2 (50 ml). Workup, evaporation, and recrystallisation in AcOEt/hexane gave **33** (1.24 g, 95%). Pale yellow solid. R_f (AcOEt/hexane 3:2) 0.22. M.p. 212.2–220.9°. $[\alpha]_D^{25} = +9.6$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3009*m*, 2974*m*, 2882*w*, 1755*s*, 1679*m*, 1598*w*, 1518*m*, 1477*w*, 1425*m*, 1367*m*, 1321*m*, 1136*w*, 1044*s*, 928*m*, 876*w*, 853*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): see *Table 11*; additionally, 8.37 (*dd*, *J* = 7.8, 1.2, H–C(4′)); 8.28 (*dd*, *J* = 7.8, 1.3, H–C(5′)); 7.89 (*dd*, *J* = 7.8, 1.3, H–C(2′)); 7.85 (*t*, *J* = 8.0, H–C(6′)); 7.73 (*t*, *J* = 7.8, H–C(3′)); 7.63 (*dd*, *J* = 8.4, 1.2, H–C(7′)); 2.16, 2.155, 2.151, 2.11, 2.10, 2.04, 2.01, 2.00, 1.99, 1.98, 1.97 (11*s*, 11 AcO); 2.03 (*s*, 2 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$): see *Table 12*; additionally, 181.10 (*s*, C(9′)); 179.83 (*s*, C(10′)); 170.51, 170.48, 170.25, 170.23, 170.20, 170.01, 169.80, 169.36, 169.12 (9*s*, 9 C=O); 169.76, 169.31 (2*s*, 4 C=O); 147.48 (*s*, C(8′)); 140.97 (*d*, C(2′)); 134.92 (*s*, C(9′a)); 134.78 (*d*, C(6′)); 134.44 (*s*, C(10′a)); 133.20 (*d* and *s*, C(3′), C(4′a)); 128.88 (*d*, C(4′)); 127.71 (*d*, C(7′)); 127.63 (*d*, C(5′)); 126.60 (*s*, C(8′a)); 122.30 (*s*, C(1′)); 118.77 (*q*, ^1J(C,F) = 320.9, CF_3); 20.87, 20.72, 20.68, 20.62, 20.60, 20.59, 20.57, 20.51, 20.49 (9*q*, 9 Me); 20.81, 20.54 (2*q*, 4 Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −73.64 (*s*, CF_3). HR-MALDI-MS: 1597.3336 (100, $[M+Na]^+$, $C_{67}H_{73}F_3NaO_{38}S^+$; calc. 1597.3350). Anal. calc. for $C_{67}H_{73}F_3O_{38}S \cdot 2\,H_2O$ (1610.37): C 49.94, H 4.82; found: C 50.16, H 4.80.

β-D-*Glucopyranosyl-[(1 → 4)-β*-D-*glucopyranosyl]$_2$-(1 → 6)-3,7-anhydro-1,2-dideoxy-1*-C-*(8-hydroxy-9,10-dioxoanthracen-1-yl)*-D-glycero-D-gulo-*oct-1-ynitol* (**34**). Under Ar, a stirred suspension of **32** (285 mg, 0.20 mmol) in dry MeOH (21 ml) was treated with a soln. of MeONa (0.296 mmol) in MeOH (21 ml), and stirred for 6.5 h at 24°. The red suspension was treated with H_2O (15 ml, → clear soln.), stirred for 4 h, neutralised with *Amberlite IR-120* resin (H^+ form), and filtered. Evaporation of the filtrate gave **34** (169 mg, 95%). Yellow solid. R_f (*RP-18* silica gel; MeCN/H_2O 2:1) 0.38. M.p 154.5° (dec., → green residue). $[\alpha]_D^{25} = +7.6$ ($c = 1.0$. DMSO). ^{1}H-NMR (500 MHz, (D_6)DMSO; assignments based on a DQFCOSY, a TOCSY, and a HSQC spectrum): see *Table 1*; additionally, 12.47 (br. *s*, HO–C(8′)); 8.23 (*d*, *J* = 7.7, H–C(4′)); 8.00 (*d*, *J* = 7.5, H–C(2′)); 7.91 (*t*, *J* = 7.7, H–C(3′)); 7.80 (*t*, *J* = 7.8, H–C(6′)); 7.70 (*d*, *J* = 7.4, H–C(5′)); 7.40 (*d*, *J* = 8.2, H–C(7′)); 4.39 (*d*, *J* = 7.8, H–C(1^{II})); 4.35 (*d*, *J* = 7.9, H–C(1^{III})); 4.31 (br. *d*, *J* = 7.6, H–C(3^{I})); 4.26 (*d*, *J* = 7.8, H–C(1^{IV})); 3.83–3.78 (*m*, H–C(8^{I}), H–C($6^{II–III}$)); 3.71 (br. *d*, *J* = 9.7, H–C(6^{IV})); 3.66–3.58 (*m*, H′–C(8^{I}), H′–C($6^{II–III}$)); 3.44–3.30 (*m*, H–C(4^{I}), H–C(5^{I}), H–C(6^{I}), H–C(7^{I}), H–C($3^{II–III}$), H–C($4^{II–III}$), H–C($5^{II–III}$), H′–C(6^{IV})); 3.24–3.12 (*m*, H–C(3^{IV}), H–C(5^{IV})); 3.13–3.03 (*m*, H–C($2^{II–III}$), H–C(4^{IV})); 3.03–2.95 (*m*, H–C(2^{IV})). ^{13}C-NMR (125 MHz, (D_6)DMSO; assignments based on a HSQC spectrum): see *Table 12*; additionally, 186.99 (*s*, C(9′)); 181.55 (*s*, C(10′)); 161.51 (*s*, C(8′)); 141.06 (*d*, C(2′)); 136.83 (*d*, C(6′)); 134.17 (*s*, C(9′a)); 134.05 (*d*, C(3′)); 132.72 (*s*, C(4′a)); 132.65 (*s*, C(10′a)); 127.39 (*d*, C(4′)); 124.35 (*d*, C(7′)); 122.17 (*d*, C(1′)); 118.50 (*d*, C(5′)); 116.38 (*s*, C(8′a)). MALDI-TOF: 919 ($[M+Na]^+$, $C_{40}H_{48}NaO_{23}^+$; calc. 919). Anal. calc. for $C_{40}H_{48}O_{23} \cdot 3$ MeOH (992.92): C 52.01, H 6.09; found: C 51.93, H 5.98.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl]$_2$-(1 → 8)-6,7,10-tri*-O-*acetyl-5,9-anhydro-1,2,3,4-tetradeoxy-1*-C-*(8-{2,3,4,6-tetra-O-acetyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri-O-acetyl-β*-D-*glucopyranosyl]$_2$-(1 → 6)-4,5,8-tri*-O-*acetyl-3,7-anhydro-1,2-dideoxy*-D-glyc-

ero-D-gulo-*oct-1-ynitol-1-yl}-9,10-dioxoanthracen-1-yl)*-D-glycero-D-gulo-*deca-1,3-diynitol* (**35**). Under Ar, a suspension of **33** (300 mg, 0.19 mmol), $[Pd(PPh_3)_2]Cl_2$ (6.7 mg, 0.01 mmol), CuI (5.5 mg, 0.03 mmol), and Bu_4NI (105 mg, 0.28 mmol) in degassed Et_3N/DMF 1:5 (3 ml) was treated dropwise with a soln. of **31** (0.80 mmol) in Et_3N/DMF 1:5 (3 ml) over a period of 12 h at 24° and stirred for 12 h. Workup (AcOEt), evaporation, and FC (CH_2Cl_2/AcOEt 5:1 → 2:1) gave **35** (303 mg, 59%) as a light yellow solid, which was recrystallised in AcOEt/MeOH. R_f (AcOEt/hexane 4:1) 0.40. M.p. 262.3–265.4°. $[\alpha]_D^{25} = +0.3$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3023*m*, 2976*m*, 2893*w*, 1754*s*, 1685*w*, 1598*w*, 1517*m*, 1476*w*, 1425*m*, 1367*m*, 1337*w*, 1316*w*, 1043*s*, 928*m*, 876*w*, 846*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 11*; additionally, 8.32 (*dd*, $J = 7.8$, 1.3), 8.29 (*dd*, $J = 7.8$, 1.4) (H–C(4′), H–C(5′)); 7.94 (*dd*, $J = 7.8$, 1.3), 7.92 (*dd*, $J = 7.5$, 1.4) (H–C(2′), H–C(7′)); 7.71, 7.70 (2*t*, $J = 7.8$, H–C(3′), H–C(6′)); 2.19, 2.17, 2.15, 2.14, 2.12, 2.042, 2.038, 2.037, 2.034, 2.00, 1.996, 1.981, 1.980, 1.97, 1.96 (15*s*, 15 AcO); 2.155, 2.09, 2.03, 2.005 (4*s*, 8 AcO); 2.007 (*s*, 3 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 12*; additionally, 181.77 (*s*, C(10′)); 179.78 (*s*, C(9′)); 170.40, 170.29, 169.81, 169.77, 169.72, 169.46, 169.32, 169.30 (8*s*, 8 C=O); 170.49, 169.75, 169.74, 169.37, 169.31, 169.11 (6*s*, 12 C=O); 170.23, 170.18 (2*s*, 6 C=O); 142.16 (*d*, C(2′)); 141.50 (*d*, C(7′)); 135.37 (*s*, C(9′a)); 133.73 (*s*, C(8′a)); 133.69 (*s*, C(4′a)); 133.50 (*s*, C(10′a)); 132.89 (*d*, C(3′)); 132.80 (*d*, C(6′)); 128.14 (*d*, C(4′)); 127.78 (*d*, C(5′)); 122.05 (*s*, C(8′)); 121.49 (*d*, C(1′)); 20.99, 20.93, 20.90, 20.82, 20.80, 20.73, 20.63, 20.56 (8*q*, 8 Me); 20.67, 20.59, 20.49 (3*q*, 6 Me); 20.57, 20.56, 20.53, 20.51 (4*q*, 12 Me). HR-MALDI-MS: 2691.7395 (47, $[M+Na]^+$, $C_{120}H_{140}NaO_{68}^+$; calc. 2691.7395). Anal. calc. for $C_{120}H_{140}O_{68}$ (2670.39): C 53.97, H 5.28; found: C 53.92, H 5.36.

*β-*D*-Glucopyranosyl-[(1 → 4)-β-*D*-glucopyranosyl]$_2$-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-1-*C*-(8-{β-*D*-glucopyranosyl-[(1 → 4)-β-*D*-glucopyranosyl]$_2$-(1 → 6)-3,7-anhydro-1,2-dideoxy-*D*-glycero-*D*-gulo-oct-1-ynitol-1-yl}-9,10-dioxoanthracen-1-yl)*-D-glycero-D-gulo-*deca-1,3-diynitol* (**36**). Under Ar, a suspension of **35** (0.10 g, 0.04 mmol) in 0.1M aq. Bu_4NOH (11 ml) was stirred for 20 h, and neutralised with *Amberlite IR-120* resin (H^+ form). The supernatant soln. was decanted from the resin and centrifuged (6000 rpm). The soln. was diluted with H_2O and lyophilised to afford **36** (46 mg, 78%). Yellowish brown solid). R_f (*RP-18*, silica gel; MeCN/H_2O 2:1) 0.50. M.p. 262.9–265.1° (dec.). $[\alpha]_D^{25} = -8.6$ ($c = 1.0$. DMSO). ^{1}H-NMR (500 MHz, (D_6)DMSO; assignments based on a DQFCOSY, a TOCSY, and a HSQC spectrum): see *Table 1*; additionally, 8.26 (*dd*, $J = 7.7$, 1.3), 8.23 (*dd*, $J = 7.7$, 1.3) (H–C(4′), H–C(5′)); 8,13 (*dd*, $J = 7.8$, 1.3), 8.03 (*dd*, $J = 7.8$, 1.3) (H–C(2′), H–C(7′)); 7.90 (*t*, $J = 7.8$), 7.89 (*t*, $J = 7.9$) (H–C(3′), H–C(6′)); 4.39 (*d*, $J = 7.8$, H–C(1^{IIIE})); 4.36 (*d*, $J = 7.8$, H–C(1^{IIE})); 4.331 (*d*, $J = 7.5$, H–C(1^{IIB}), H–C(1^{IIIB})); 4.329 (*d*, $J = 9.1$, H–C(3^{IE})); 4.25 (*d*, $J \approx 8.4$, H–C(1^{IVB}), H–C(1^{IVE})); 4.23 (*d*, $J \approx 10.0$, H–C(5^{IB})); 3.82–3.75 (*m*, H–C(8^{IE}), H–C(10^{IB}), H–C($6^{IIB-IIIB}$), H–C($6^{IIE-IIIE}$)); 3.72–3.65 (*m*, H–C(6^{IVB}), H–C(6^{IVE})); 3.64–3.55 (*m*, H′–C(8^{IE}), H′–C(10^{IB}), H′–C($6^{IIB-IIIB}$), H′–C($6^{IIE-IIIE}$)); 3.48–3.28 (*m*, H–C(4^{IE}), H–C(5^{IE}), H–C(6^{IE}), H–C(7^{IE}), H–C(6^{IB}), H–C(7^{IB}), H–C(8^{IB}), H–C(9^{IB}), H–C($3^{IIB-IIIB}$), H–C($3^{IIE-IIIE}$), H–C($4^{IIB-IIIB}$), H–C($4^{IIE-IIIE}$), H–C($5^{IIB-IIIB}$), H–C($5^{IIE-IIIE}$), H′–C(6^{IVB}), H′–C(6^{IVE})); 3.25–3.12 (*m*, H–C(3^{IVB}), H–C(3^{IVE}), H–C(5^{IVB}), H–C(5^{IVE})); 3.12–2.90 (*m*, H–C($2^{IIB-IVB}$), H–C($2^{IIE-IVE}$), H–C(4^{IVB}), H–C(4^{IVE})). ^{13}C-NMR (125 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 12*; additionally, 181.44 (*s*, C(10′)); 179.58 (*s*, C(9′)); 141.96 (*d*, C(2′)); 141.71 (*d*, C(7′)); 135.02 (*s*, C(9′a)); 133.49 (*s*, C(8′a)); 133.37 (*s*, C(4′a)); 133.27 (*d*, C(3′)); 133.22 (*d*, C(6′)); 133.09 (*s*, C(10′a)); 127.61 (*d*, C(4′)); 127.00 (*d*, C(5′)); 122.08 (*s*, C(8′)); 120.19 (*s*, C(1′)). MALDI-TOF: 1599 ($[M+Na]^+$, $C_{68}H_{88}NaO_{42}^+$; calc. 1599). Anal. calc. for $C_{68}H_{88}O_{42} \cdot 4\,H_2O$ (1649.46): C 49.51, H 5.87; found: C 49.33, H 6.39.

*Allyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* [30] (**39**). A suspension of **38** [30][34][36] (5.0 g, 5.4 mmol) and 4-Å mol. sieves in CH_2Cl_2 (190 ml) was stirred at 24° for 1 h and treated with **37** [61] (5.0 g, 6.4 mmol). The mixture was cooled to −40°, stirred for 15 min, treated dropwise with a soln. of TMSOTf (0.23 ml, 1.28 mmol) in CH_2Cl_2 (10 ml), stirred for 2 h, diluted with CH_2Cl_2, allowed to warm to r.t., and filtered through *Celite*. The filtrate was washed with aq. $NaHCO_3$ soln. Workup, evaporation, and FC (AcOEt/hexane 1:3 → 1:2) gave **39** (7.3 g, 87%). Foamy solid. R_f (AcOEt/hexane 1:1) 0.57. M.p. 230–232° ([30]: 232–234°).

*Allyl 2,3,4,6-Tetra-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl-[(1 → 4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranosyl]$_3$-(1 → 4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**44**). A sus-

pension of **43** [30] (8.0 g, 4.47 mmol) and 4-Å mol. sieves (8.0 g) in dry CH_2Cl_2 (110 ml) was stirred at 25° for 2 h, treated with **37** (4.2 g, 5.39 mmol), cooled to −60°, stirred for 30 min, treated dropwise with a soln. of TMSOTf (0.16 ml, 0.9 mmol) in CH_2Cl_2 (8 ml), stirred for 12 h, treated with solid $NaHCO_3$ (0.8 g), stirred for 30 min, warmed to 25°, and filtered through *Celite*. The filtrate was washed with sat. aq. $NaHCO_3$ soln. Workup and FC (AcOEt/cyclohexane 1:4 → 1:2) gave **44** (10.1 g, 94%). Foam. R_f (AcOEt/hexane 2:3) 0.20. M.p. 71.5–74°. $[\alpha]_D^{25} = -4.4$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3023*m*, 2872*m*, 1951*w*, 1881*w*, 1754*s*, 1604*w*, 1595*w*, 1518*m*, 1494*w*, 1454*m*, 1419*m*, 1368*s*, 1309*m*, 1153*s*, 1118*s*, 1066*s*, 922*m*, 876*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): 7.31–7.01 (*m*, 60 arom. H); 5.90 (*dddd*, $J = 17.2$, 10.5, 5.9, 5.2, C*H*=CH_2); 5.28 (*dq*, $J = 17.4$, 1.7), 5.14 (*dq*, $J = 10.5$, 1.3) (CH=CH_2); 5.09 (*d*, $J = 11.6$), 5.05 (*d*, $J = 11.6$) (2 PhC*H*); 5.05 (*t*, $J = 9.2$, H–C(3^V)); 5.04 (*d*, $J = 10.8$, PhC*H*); 5.01 (*t*, $J = 9.7$, H–C(3^{VI})); 4.92 (*d*, $J = 11.4$, PhC*H*); 4.89 (*t*, $J = 9.3$, H–C(4^{VI})); 4.86 (*dd*, $J \approx 9.2$, 8.1, H–C(2^{VI})); 4.83 (*d*, $J \approx 10.9$, PhC*H*); 4.75 (*dd*, $J = 9.7$, 8.1, H–C(2^V)); 4.68 (*d*, $J = 11.5$), 4.67 (*d*, $J = 11.1$) (2 PhC*H*); 4.66 (br. *d*, $J = 11.0$, 2 PhC*H*); 4.64 (br. *d*, $J = 10.4$, 2 PhC*H*); 4.61 (*d*, $J = 11.0$), 4.60 (*d*, $J = 11.1$), 4.58 (*d*, $J = 11.6$), 4.54 (*d*, $J = 11.6$), 4.52 (*d*, $J = 12.1$) (5 PhC*H*); 4.48 (*d*, $J = 8.1$, H–C(1^V)); 4.43 (*d*, $J = 11.9$, PhC*H*); 4.42 (*d*, $J = 7.8$, H–C(1^{IV})); 4.40 (*d*, $J = 8.0$, H–C(1^I)); 4.36 (*d*, $J = 7.7$, H–C(1^{II})); 4.37–4.33 (*m*, H–C($1^{III–VI}$), 1 allyl. H, 2 PhC*H*); 4.32 (*d*, $J = 11.2$, PhC*H*); 4.31 (*dd*, $J = 12.1$, 4.1, H–C(6^V)); 4.30 (*d*, $J = 12.1$), 4.20 (*d*, $J = 12.1$), 4.17 (*d*, $J = 12.0$), 4.15 (*d*, $J = 12.0$) (4 PhC*H*); 4.15 (*dd*, $J \approx 12.0$, 2.3, H–C(6^{VI})); 4.09–4.05 (*ddt*, $J = 13.0$, 5.9, 1.4, 1 allyl. H); 3.96 (*dd*, $J \approx 11.9$, 2.6, H′–C(6^V)); 3.94 (*t*, $J \approx 9.2$, H–C(4^I)); 3.92 (*t*, $J \approx 9.0$, H–C($4^{II–III}$)); 3.84 (*dd*, $J \approx 12.1$, 4.5, H′–C(6^{VI})); 3.83 (*t*, $J \approx 9.1$, H–C(4^{IV})); 3.78 (*dd*, $J \approx 10.9$, 4.1, H–C(6^I)); 3.68 (*dd*, $J \approx 11.0$, 3.6, H–C(6^{II})); 3.66–3.55 (*m*, H–C(5^V), H–C($6^{III–IV}$), H′–C($6^{I–III}$)); 3.62 (*t*, $J \approx 9.4$, H–C(4^V)); 3.52 (*t*, $J \approx 9.0$, H–C(3^I)); 3.48 (*dd*, $J \approx 10.9$, 3.4, H′–C(6^{IV})); 3.39 (*t*, $J \approx 8.6$, H–C(2^I), H–C(3^{II})); 3.34 (*t*, $J \approx 9.0$, H–C(3^{III})); 3.29–3.20 (*m*, H–C($2^{II–IV}$), H–C(3^{IV}), H–C(5^I)); 3.09 (*ddd*, $J = 9.7$, 3.4, 1.7, H–C(5^{II})); 3.045 (*ddd*, $J = 9.8$, 3.5, 1.6, H–C(5^{III})); 3.01 (*ddd*, $J = 9.9$, 4.3, 2.1, H–C(5^{VI})); 2.91 (*ddd*, $J = 9.9$, 3.4, 1.8, H–C(5^{IV})); 2.03, 1.97, 1.954, 1.946, 1.94, 1.87, 1.85 (7*s*, 7 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$; assignments based on a HSQC spectrum): 170.47, 170.23, 170.18, 169.72, 169.37, 169.29, 168.97 (7*s*, 7 C=O); 139.42, 139.37, 138.26 (3*s*, 6 arom. C); 138.60, 138.55, 138.42, 138.41, 138.39, 138.02 (6*s*, 6 arom. C); 134.14 (*d*, *C*H=CH_2); 128.52–126.99 (several *d*); 117.13 (*t*, CH=*C*H_2); 102.64 (*d*, C(1^{IV})); 102.54 (*d*, C(1^I)); 102.52 (*d*, C(1^{II})); 102.41 (*d*, C(1^{III})); 100.81 (*d*, C(1^{VI})); 99.69 (*d*, C(1^V)); 83.37 (*d*, C(3^I)); 83.22 (*d*, C(3^{II})); 82.94 (*d*, C(3^{III})); 82.82 (*d*, C(3^{IV})); 82.04 (*d*, C(2^I)); 82.02 (*d*, C(2^{II})); 81.82 (*d*, C(2^{IV})); 81.67 (*d*, C(2^{III})); 77.04 (*d*, C(4^I)); 76.95 (*d*, C(4^{IV})); 76.88 (*d*, C(4^{II})); 76.71 (*d*, C(4^{III})); 76.17 (*d*, C(4^V)); 75.05, 75.02, 74.98 (3*t*, 3 PhCH_2); 74.93 (2*d*), 74.56 (2*d*) (C($5^{I–IV}$)); 73.30 (*t*, PhCH_2); 73.15 (*t*, 3 PhCH_2); 72.93 (*d*, C($3^{V–VI}$)); 72.88 (*t*, 2 PhCH_2); 72.86 (*t*, 2 PhCH_2); 72.27 (*d*, C(5^{VI})); 72.05 (*d*, C(2^V)); 71.88 (*d*, C(5^V)); 71.46 (*d*, C(2^{VI})); 70.21 (*t*, 1 allyl. C); 68.16 (*t*, C(6^I)); 68.04 (*d*, C(4^{VI})); 67.75 (3*t*, C($6^{II–IV}$)); 61.82 (*t*, C(6^V)); 61.50 (*t*, C(6^{VI})); 20.67, 20.66, 20.64, 20.53, 20.52 (several *q*, 7 Me). HR-MALDI-MS: 2427.9859 (49, $[M+Na]^+$, $C_{137}H_{152}NaO_{38}^+$; calc. 2427.9859). Anal. calc. for $C_{137}H_{152}O_{38}$ (2406.69): C 68.37, H 6.37; found: C 68.51, H 6.43.

2,3,4,6-Tetra-O-*acetyl*-β-D-*glucopyranosyl*-[(1 → 4)-*2,3,6-tri*-O-*acetyl*-β-D-*glucopyranosyl*]$_4$-(1 → 4)-*1,2,3,6-tetra*-O-*acetyl*-α/β-D-*glucopyranose* (**45**). A stirred suspension of bis[methyl(diphenyl)phosphine](cycloocta-1,5-diene)iridium(I) hexafluorophosphate (52.7 mg, 0.062 mmol) in dry THF (20 ml) was degassed at 22° and stirred under H_2 for 5 min until the red suspension turned into a pale yellow soln., flushed with Ar, and treated with a soln. of **44** (5.0 g, 2.07 mmol) in THF (50 ml). After stirring for 2 h, the mixture was treated with H_2O (20 ml) and I_2 (1.09 g, 43 mmol), stirred for 3 h, and treated with a chilled 5% aq. $Na_2S_2O_3$ soln. (29 ml). Workup (AcOEt), evaporation, and FC (AcOEt/cyclohexane 1:4 → 1:2) gave the deallylated derivative of **44** (4.1 g, 83%, α/β 45:55). R_f (AcOEt/hexane 1:1) 0.25. ^{13}C-NMR (125 MHz, $CDCl_3$, α/β 45:55): 97.31 (*d*, C(1^I) of β-anomer); 91.35 (*d*, C(1^I) of α-anomer). HR-MALDI-MS: 2387.9549 (47, $[M+Na]^+$, $C_{134}H_{148}NaO_{38}^+$; calc. 2387.9546).

A suspension of the deallylated derivative of **44** (9 g, 3.8 mmol) and charcoal (10 g) in AcOEt (200 ml) was stirred for 24 h, and filtered through *Celite*. After evaporation, a soln. of the residue in acetone/MeOH 1:1 (500 ml) was treated with 20% $Pd(OH)_2$/C (3.5 g), stirred under 6 bar of H_2 for 3 days, and filtered through *Celite* (washing with 200 ml of pyridine). The combined filtrate and washings were evaporated and co-evaporated with toluene. A soln. of the pale yellow residue (4.9 g) in Ac_2O/pyridine 1:1 (60 ml) was stirred for 24 h at 23°. Evaporation, co-evaporation with toluene, and FC (AcOEt/hexane

1:1→2:1) gave α/β-D-**45** 2:3 (6.25 g, 90%). White solid. R_f (AcOEt/hexane 4:1) 0.69. M.p. 238.1–238.5°. $[\alpha]_D^{25} = -12.7$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3028*m*, 2969*m*, 2889*w*, 1751*s*, 1520*m*, 1475*w*, 1421*m*, 1369*s*, 1051*s*, 924*m*, 878*w*, 848*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; α/β-D 2:3): 6.24 (*d*, $J = 3.7$, 0.4 H), 5.65 (*d*, $J = 8.3$, 0.6 H) (H–C(1^I)). ^{13}C-NMR (125 MHz, $CDCl_3$, α/β 2:3): 91.59 (*d*, C(1^I) of β-anomer); 88.97 (*d*, C(1^I) of α-anomer). HR-MALDI-MS: 1853.5262 (100, $[M+Na]^+$, $C_{76}H_{102}NaO_{51}^+$; calc. 1853.5280). Anal. calc. for $C_{76}H_{102}O_{51}$ (1831.60): C 49.84, H 5.61; found: C 50.17, H 5.75. For ^{1}H- and ^{13}C-NMR data of α-**45**, see [63][64].

2,3,4,6-Tetra-O-*acetyl*-β-D-*glucopyranosyl*-[(1 → 4)-*2,3,6-tri*-O-*acetyl*-β-D-*glucopyranosyl*]$_4$-(1 → 4)-*2,3,6-tri*-O-*acetyl*-α/β-D-*glucopyranose* [66] (**46**). A soln. of α/β-D-**45** 2:3 (3.41 g, 1.86 mmol) in dry DMF (35 ml) was treated with $(NH_4)_2CO_3$ (0.89 g, 9.28 mmol), stirred at 23° for 36 h, poured into chilled H_2O, and extracted with AcOEt (200 ml). Workup, evaporation, and FC (AcOEt/hexane 1:1 → 3:1) gave α/β-**46** 2:1 (2.61 g, 78%). White solid. R_f (AcOEt/hexane 4:1) 0.24. M.p. 126.8°. $[\alpha]_D^{25} = -6.6$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3483*w*, 3009*m*, 2974*m*, 2882*w*, 1748*s*, 1672*m*, 1516*w*, 1476*w*, 1424*m*, 1366*s*, 1048*s*, 927*m*, 875*w*, 850*w*. ^{1}H-NMR (500 MHz, $CDCl_3$, α/β-D-**46** 2:1): 5.49 (*t*, $J = 9.7$, 0.67 H), 5.21 (*t*, $J = 9.4$, 0.33 H) (H–C(3^I)); 5.37 (*t*, $J = 3.5$, 0.67 H), 4.70 (*t*, $J = 8.0$, 0.33 H) (H–C(1^I)). HR-MALDI-MS: 1811.5138 (100, $[M+Na]^+$, $C_{74}H_{100}NaO_{50}^+$; calc. 1811.5180). Anal. calc. for $C_{74}H_{100}O_{50}$ (1789.57): C 49.67, H 4.63; found: C 49.80, H 5.82.

2,3,4,6-Tetra-O-*acetyl*-β-D-*glucopyranosyl*-[(1 → 4)-*2,3,6-tri*-O-*acetyl*-β-D-*glucopyranosyl*]$_4$-(1 → 4)-*2,3,6-tri*-O-*acetyl*-α/β-D-*glucopyranosyl Trichloroacetamidate* [66] (**47**). A soln. of α/β-D-**46** 2:1 (400 mg, 0.22 mmol) in dry CH_2Cl_2 (8 ml) was treated with Cl_3CCN (0.22 ml, 2.2 mmol) and a soln. of DBU (8.8 µl, 0.05 mmol) in CH_2Cl_2 (2 ml) and stirred for 2 h. Evaporation, FC (silica gel pre-treated with hexane/Et_3N 98:2; AcOEt/hexane 1:1 → 2:11), and crystallisation from AcOEt/hexane gave α/β-D-**47** 94:6 (308 mg, 71%). R_f (AcOEt/hexane 3:1) 0.22. M.p. 126.8°. $[\alpha]_D^{25} = +4.1$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3345*w*, 3021*m*, 2974*m*, 2882*w*, 1753*s*, 1672*w*, 1516*w*, 1475*w*, 1424*m*, 1366*m*, 1048*s*, 927*m*, 904*w*, 875*w*, 849*w*. ^{1}H-NMR (500 MHz, $CDCl_3$, α/β-D-**47** 94:6; assignments based on a HSQC and a TOCSY spectrum): data of α-D-**47**: 8.65 (*s*, NH); 6.48 (*d*, $J = 3.8$, H–C(1^I)); 5.51 (*t*, $J = 9.7$, H–C(3^I)); 5.122 (*t*, $J = 9.3$), 5.103 (*t*, $J = 9.2$, 2 H), 5.085 (*t*, $J = 9.2$), 5.083 (*t*, $J = 9.2$) (H–C($3^{II–VI}$)); 5.053 (*t*, $J = 9.6$, H–C(4^{VI})); 5.050 (*dd*, $J = 10.2$, 3.9, H–C(2^I)); 4.90 (*dd*, $J = 9.2$, 8.0, H–C(2^{VI})); 4.85 (*dd*, $J = 9.2$, 7.9, H–C(2^V)); 4.82 (*dd*, $J = 9.2$, 7.4), 4.81 (br. *dd*, $J = 9.1$, 7.6, 2 H) (H–C($2^{II–IV}$)); 4.51 (*d*, $J = 7.9$, H–C(1^{VI})); 4.47 (*d*, $J = 7.9$, H–C(1^V)); 4.45–4.38 (*m*, H–C($1^{II–IV}$), H–C($6^{I–V}$)); 4.35 (*dd*, $J = 12.5$, 4.4, H–C(6^{VI})); 4.12–4.06 (*m*, H–C(5^I), H′–C($6^{I–V}$)); 4.03 (*dd*, $J = 12.5$, 2.2, H′–C(6^{VI})); 3.81 (*t*, $J = 9.7$, H–C(4^I)); 3.76 (*t*, $J = 9.6$), 3.75 (*t*, $J = 9.6$), 3.735 (*t*, $J = 9.6$), 3.727 (*t*, $J = 9.6$) (H–C($4^{II–V}$)); 3.63 (*ddd*, $J = 9.9$, 4.3, 2.3, H–C(5^{VI})); 3.58 (*ddd*, $J = 9.8$, 4.8, 2.0, H–C(5^V)); 3.60–3.54 (*m*, H–C($5^{II–IV}$)); 2.143 (*s*, 4 AcO); 2.115, 2.088, 2.035, 2.025, 2.015, 2.008, 2.002, 1.999, 1.995, 1.982, 1.960 (11*s*, 11 AcO); 2.021, 1.957 (2*s*, 4 AcO); data of β-**47**: 8.69 (*s*, NH); 5.83 (*d*, $J = 7.5$, H–C(1^I)); 5.24 (*t*, $J = 8.6$, H–C(3^I)); 5.19 (*dd*, $J = 8.8$, 7.5, H–C(2^I)). ^{13}C-NMR (125 MHz, $CDCl_3$; α/β-D-**47** 94:6; assignments based on a HSQC and a TOCSY spectrum): data of α-**47**: 170.49, 170.22, 170.01, 169.81, 169.70, 169.42, 169.34, 169.09 (8*s*, 8 C=O); 170.18, 169.73, 169.29, 169.27 (4*s*, 8 C=O); 170.19 (4*s*, 3 C=O); 160.94 (*s*, C=NH); 100.82, 100.79, 100.56, 100.53, 100.49 (5*d*, C($1^{II–VI}$)); 92.86 (*d*, C(1^I)); 90.69 (*s*, CCl_3); 76.19 (*d*, C(4^I)); 76.09 (br. *d*, C($4^{II–V}$)); 72.88, 72.81 (4 C), 72.68, 72.63, 72.54, 72.52 (6*d*, C($3^{II–VI}$), C($5^{II–V}$)); 72.04 (*d*, C(5^{VI})); 71.91, 71.84 (2 C), 71.74 (3*d*, C($2^{II–V}$)); 71.56 (*d*, C(2^{VI})); 70.96 (*d*, C(5^I)); 69.91 (*d*, C(2^I)); 69.28 (*d*, C(3^I)); 67.72 (*d*, C(4^{VI})); 62.14, 62.05, 62.01 (2 C) (3*t*, C($6^{II–V}$)); 61.49 (*t*, C(6^{VI})); 61.33 (*t*, C(6^I)); 20.82 (*q*, 4 Me); 20.79, 20.67, 20.62, 20.61, 20.56, 20.50, 20.46 (7*q*, 7 Me); 20.58, 20.48 (2*q*, 6 Me); 20.53 (*q*, 2 Me); data of β-**47**: 160.74 (*s*, C=NH); 95.31 (*d*, C(1^I)). HR-MALDI-MS: 1954.4281 (55, $[M+Na]^+$, $C_{76}H_{100}Cl_3NO_{50}^+$; calc. 1954.4276). Anal. calc. for $C_{76}H_{100}Cl_3NO_{50}$ (1933.96): C 47.20, H 5.21; found: C 47.32, H 5.29.

2,3,4,6-Tetra-O-*acetyl*-β-D-*glucopyranosyl*-[(1 → 4)-*2,3,6-tri*-O-*acetyl*-β-D-*glucopyranosyl*]$_5$-(1 → 4)-*6*-O-*benzyl-2,3-bis*-O-*(4-chlorobenzyl)*-β-D-*glucopyranosyl*-(1 → 6)-*3,7-anhydro-4,5,8-tris*-O-*(4-chlorobenzyl)-1,2-dideoxy-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**48**). A suspension of **13** (1.55 g, 1.37 mmol), **47** (1.94 g, 1.0 mmol), and powdered 4-Å molecular sieves (3.00 g) in dry CH_2Cl_2 (25 ml) was stirred under Ar at 24° for 2 h, cooled to −18° (ice/NaCl bath), treated dropwise with $BF_3 \cdot OEt_2$ (0.15 ml, 1.15 mmol) over 10 min, stirred for 2 h, treated with solid $NaHCO_3$ (0.06 g), warmed to r.t., and filtered through *Celite*. Workup, evaporation, and FC (toluene/acetone 5:1 → 4:1) gave **48** (2.58

g, 88%). R_f (toluene/acetone 3:2) 0.73. M.p. 128.7–129.7°. $[\alpha]_D^{25} = -14.8$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3030*w*, 2929*w*, 2872*w*, 2179*w*, 1756*s*, 1600*w*, 1492*w*, 1367*m*, 1160*m*, 1088*s*, 1054*s*, 1017*m*, 905*w*, 845*w*, 810*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a HSQC and a TOCSY spectrum): 7.39–7.12 (*m*, 23 arom. H); 6.97 (*d*, $J = 7.5$, 2 arom. H); 5.115 (*t*, $J = 9.3$, H–C(3^{VIII})); 5.091 (*t*, $J = 9.1$), 5.077 (*t*, $J = 9.1$), 5.066 (*t*, $J = 9.1$), 5.051 (*t*, $J = 9.2$) (H–C($3^{IV–VII}$)); 5.043 (*t*, $J = 9.6$, H–C(4^{VIII})); 5.00 (*d*, $J = 11.9$), 4.939 (*d*, $J = 12.2$), 4.865 (*d*, $J = 10.5$) (3 PhC*H*); 4.932 (*t*, $J = 9.2$, H–C(3^{III})); 4.890 (*dd*, $J = 9.2$, 7.9, H–C(2^{VIII})); 4.813 (*dd*, $J = 9.1$, 7.8), 4.801 (*dd*, $J = 9.1$, 7.9), 4.794 (*dd*, $J = 9.1$, 7.8), 4.783 (*dd*, $J = 9.1$, 7.9), 4.773 (*dd*, $J = 9.5$, 7.9) (H–C($2^{III–VII}$)); 4.65 (*d*, $J = 10.8$), 4.59 (*d*, $J = 11.9$), 4.537 (*d*, $J = 11.6$), 4.523 (*d*, $J = 12.5$), 4.513 (*d*, $J \approx 12.5$), 4.500 (*d*, $J \approx 10.5$), 4.489 (*d*, $J \approx 11.6$) (7 PhC*H*); 4.480 (*d*, $J \approx 7.7$), 4.469 (*d*, $J = 7.7$), 4.437 (*d*, $J = 7.7$), 4.424 (*d*, $J = 7.7$), 4.418 (*d*, $J = 7.8$) (H–C($1^{IV–VIII}$)); 4.42–4.32 (*m*, H–C($6^{IV–VIII}$)); 4.346 (*d*, $J = 7.9$, H–C(1^{III})); 4.330 (*d*, $J = 7.7$, H–C(1^{II})); 4.342 (*d*, $J = 11.8$), 4.265 (*d*, $J = 12.0$) (2 PhC*H*); 4.236 (*dd*, $J = 12.5$, 2.0, H–C(6^{III})); 4.105–4.03 (*m*, H′–C($6^{IV–VII}$)); 4.03 (*dd*, $J = 12.6$, 2.2, H′–C(6^{VIII})); 3.97 (*d*, $J = 9.6$, H–C(3^{I})); 3.92 (*t*, $J = 9.4$, H–C(6^{I})); 3.885 (*dd*, $J \approx 12.5$, 4.6, H′–C(6^{III})); 3.85 (*t*, $J = 9.3$, H–C(4^{II})); 3.746 (*t*, $J = 9.3$), 3.727 (*t*, $J = 9.3$), 3.722 (*t*, $J = 9.3$), 3.708 (*t*, $J = 9.1$) (H–C($4^{IV–VII}$)); 3.75–3.71 (*m*, H–C(8^{I})); 3.628 (*t*, $J = 9.5$, H–C(4^{III})); 3.625 (*ddd*, $J = 9.8$, 4.4, 2.4, H–C(5^{VIII})); 3.616 (*dd*, $J \approx 12.5$, 2.0, H′–C(8^{I})); 3.59–3.47 (*m*, 2 H–C(6^{II}), H–C($5^{IV–VII}$)); 3.495 (*t*, $J = 9.3$, H–C(4^{I})); 3.42 (*t*, $J = 8.9$, H–C(5^{I})); 3.27 (*t*, $J = 9.0$, H–C(3^{II})); 3.24 (*ddd*, $J = 9.5$, 3.4, 1.7, H–C(7^{I})); 3.17 (*dd*, $J = 9.1$, 7.9, H–C(2^{II})); 3.10 (*ddd*, $J = 9.9$, 4.2, 2.1, H–C(5^{III})); 3.04 (*ddd*, $J = 10.0$, 3.4, 1.7, H–C(5^{II})); 2.133, 2.129, 2.126, 2.109, 2.079, 2.026, 2.015, 2.009, 1.999, 1.993, 1.989, 1.987, 1.973, 1.950, 1.947, 1.944, 1.938, 1.934, 1.882 (19*s*, 19 AcO); 0.16 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$; assignments based on a HSQC and a TOCSY spectrum): 170.44, 170.17, 170.07, 169.63, 169.33, 169.29, 169.22, 169.15, 169.04 (9*s*, 9 C=O); 170.14 (*s*, 4 C=O); 169.68, 169.66, 169.25 (3*s*, 6 C=O); 137.70, 137.69, 137.66, 136.53, 136.48, 136.31 (6*s*, 6 arom. C); 133.53, 133.48, 133.39, 132.93, 132.88 (5*s*, 5 arom. C); 129.31, 129.20, 128.96, 128.82, 128.61, 128.53, 128.41, 128.32, 128.28, 128.24, 128.22, 127.76 (12*d*, 24 arom. C); 128.10 (*d*, 1 arom. C); 102.29 (*d*, C(1^{II})); 102.17 (*s*, *C*≡CSi); 100.78, 100.64, 100.52, 100.49, 100.43 (5*d*, C($1^{III–VII}$)); 99.77 (*d*, C(1^{VIII})); 91.39 (*s*, C≡*C*Si); 84.09 (*d*, C(5^{I})); 82.99 (*d*, C(3^{II})); 81.65 (*d*, C(2^{II})); 81.61 (*d*, C(4^{I})); 79.17 (*d*, C(7^{I})); 76.40 (*d*, C(4^{II})); 76.23 (*d*, C(6^{I})); 76.04 (br. *d*, C($4^{III–VII}$)); 74.67 (*d*, C(5^{II})); 74.54, 74.29, 74.11, 74.07, 73.36, 72.63 (6*t*, 6 Ph*C*H$_2$); 72.88, 72.82 (br.), 72.80, 72.71 (4*d*, C($3^{III–VIII}$), C($5^{IV–VII}$)); 72.55 (*d*, C(5^{III})); 72.51 (*d*, C(5^{VIII})); 72.49, 72.44, 72.04, 71.86, 71.76, 71.58 (6*d*, C($2^{III–VIII}$)); 70.24 (*d*, C(3^{I})); 67.81 (*t*, C(8^{I})); 67.77 (*d*, C(4^{VIII})); 67.62 (*t*, C(6^{II})); 62.07, 62.05, 62.00, 61.67, 61.51 (2 C) (5*t*, C($6^{III–VIII}$)); 20.76–20.45 (several *q*, 19 Me); −0.33 (*q*, Me_3Si). HR-MALDI-MS: 2925.8295 (4, $[M+Na]^+$, $C_{133}H_{159}Cl_5NaO_{59}Si^+$, calc. 2925.7551). Anal. calc. for $C_{133}H_{159}Cl_5O_{59}Si$ (2907.03): C 54.95, H 5.51; found: C 54.88, H 5.65.

2,3,4,6-Tetra-O-*acetyl*-*β*-D-*glucopyranosyl*-[(1 → 4)-*2,3,6-tri*-O-*acetyl*-*β*-D-*glucopyranosyl*]$_5$-(1 → 4)-*6*-O-*benzyl*-*2,3-bis*-O-*(4-chlorobenzyl)*-*β*-D-*glucopyranosyl*-(1 → 6)-*3,7-anhydro*-*4,5,8-tris*-O-*(4-chlorobenzyl)*-*1,2-dideoxy*-D-glycero-D-gulo-*oct*-*1-ynitol* (**49**). A stirred soln. of **48** (0.40 g, 0.14 mmol) in THF (15 ml) was cooled to 0°, treated with a soln. of $Bu_4NF \cdot 3\,H_2O$ (15 mg, 48 μmol) in THF (1.5 ml), stirred for 15 min, and treated with sat. aq. NH_4Cl soln. (5 ml). Workup and FC gave **49** (0.36 g, 92%). R_f (AcOEt/hexane 2:1) 0.20. M.p. 122.2°. $[\alpha]_D^{25} = -11.7$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3307*w*, 3029*w*, 3015*w*, 2872*w*, 1757*s*, 1600*w*, 1492*w*, 1411*w*, 1367*m*, 1160*m*, 1088*s*, 1058*s*, 1017*m*, 905*w*, 843*w*, 810*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35–7.10 (*m*, 23 arom. H); 6.96 (*d*, $J = 7.8$, 2 arom. H); 5.113 (*t*, $J = 9.3$, H–C(3^{VIII})); 5.084 (*t*, $J = 9.0$), 5.070 (*t*, $J = 9.0$), 5.065 (*t*, $J = 9.0$), 5.045 (*t*, $J = 9.3$) (H–C($3^{IV–VII}$)); 5.040 (*t*, $J = 9.6$, H–C(4^{VIII})); 4.982 (*d*, $J = 12.0$), 4.938 (*d*, $J = 12.0$), 4.873 (*d*, $J = 11.1$) (3 PhC*H*); 4.923 (*t*, $J = 9.3$, H–C(3^{III})); 4.892 (*t*, $J \approx 8.4$, H–C(2^{VIII})); 4.85–4.73 (*m*, H–C($2^{III–VII}$)); 4.66 (*d*, $J = 11.4$), 4.585 (*d*, $J = 12.3$) (2 PhC*H*); 4.55–4.40 (*m*, H–C($1^{II–VIII}$), H–C($6^{IV–VIII}$), 6 PhC*H*); 4.256 (*d*, $J = 12.0$, PhC*H*); 4.236 (br. *d*, $J = 12.3$, H–C(6^{III})); 4.12–3.99 (*m*, H′–C($6^{IV–VIII}$)); 3.963 (*dd*, $J = 9.1$, 2.1, H–C(3^{I})); 3.927 (*t*, $J \approx 9.4$, H–C(6^{I})); 3.92–3.84 (*m*, H′–C(6^{III})); 3.857 (*t*, $J = 9.0$, H–C(4^{II})); 3.78–3.66 (*m*, H–C($4^{IV–VII}$)); 3.66–3.45 (*m*, 2 H–C(8^{I}), 2 H–C(6^{II}), H–C(4^{III}), H–C($5^{IV–VIII}$)); 3.51 (*t*, $J = 9.3$, H–C(4^{I})); 3.41 (*t*, $J = 9.0$, H–C(5^{I})); 3.275 (*t*, $J = 9.0$, H–C(3^{II})); 3.235 (br. *d*, $J \approx 9.6$, H–C(7^{I})); 3.17 (*dd*, $J = 9.0$, 7.8, H–C(2^{II})); 3.08 (br. *d*, $J \approx 9.9$, H–C(5^{III})); 3.04 (br. *d*, $J \approx 9.9$, H–C(5^{II})); 2.52 (*d*, $J = 2.1$, C≡CH); 2.13–1.87 (several *s*, 19 AcO). HR-MALDI-MS: 2853.7135 (32, $[M+Na]^+$, $C_{130}H_{151}Cl_5NaO_{59}^+$; calc. 2853.7150). Anal. calc. for $C_{130}H_{151}Cl_5O_{59}$ (2834.85): C 55.08, H 5.37; found: C 55.19, H 5.61.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl]$_6$-(1 → 6)-4,5,8-tri*-O-*acetyl-1,2-dideoxy*-D-glycero-D-gulo-*oct-1-ynitol* (**50**). A soln. of **49** (0.60 g, 0.21 mmol) in Ac_2O (6 ml) was cooled to −18° (ice/NaCl bath), treated with $BF_3 \cdot OEt_2$ (0.54 ml, 4.23 mmol), stirred for 1 h, warmed to 24°, stirred for additional 2 d, poured into chilled sat. aq. $NaHCO_3$ soln. (30 ml), and stirred vigorously for 0.5 h. Workup (AcOEt), evaporation, and FC (AcOEt/hexane 1:1 → 5:2) gave **50** (0.41 g, 82%). White solid. R_f (toluene/acetone 3:2) 0.44. M.p. 263.7° (dec.). $[\alpha]_D^{25} = -18.8$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3307*w*, 3029*w*, 2958*w*, 2872*w*, 1756*s*, 1600*w*, 1429*w*, 1368*m*, 1162*m*, 1051*s*, 952*w*, 902*w*, 836*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 13*; additionally, 2.139, 2.137, 2.125, 2.084, 2.053, 2.031, 2.020, 2.008, 2.004, 1.991, 1.952 (11*s*, 11 AcO); 2.133, 1.948 (2*s*, 6 AcO); 2.013 (*s*, 4 AcO); 1.978, 1.950 (2*s*, 4 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 14*; additionally, 170.41, 170.26, 169.70, 169.62, 169.37, 169.26, 169.01 (7*s*, 7 C=O); 170.13, 170.12, 169.21 (3*s*, 9 C=O); 170.11, 169.19 (2*s*, 4 C=O); 169.66 (*s*, 5 C=O); 20.81, 20.59, 20.53 (3*q*, 3 Me); 20.73, 20.50 (2*q*, 8 Me); 20.71, 20.48, 20.46 (3*q*, 9 Me); 20.40 (*q*, 5 Me). HR-MALDI-MS: 2395.6891 (90, $[M+Na]^+$, $C_{100}H_{132}NaO_{65}^+$; calc. 2395.6921). Anal. calc. for $C_{100}H_{132}O_{65}$ (2374.10): C 50.59, H 5.60; found: C 50.68, H 5.76.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl]$_5$-(1 → 4)-6*-O-*benzyl-2,3-bis*-O-*(4-chlorobenzyl)-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tris*-O-*(4-chlorobenzyl)-1,2,3,4-tetradeoxy-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol* (**51**). A suspension of **17** (0.72 g, 0.62 mmol), *α*/*β*-**47** 8:1 (1.09 g, 0.56 mmol) and powdered 4-Å mol. sieves (1.0 g) in dry CH_2Cl_2 (16 ml) was stirred under Ar at 28° for 2 h, cooled to −40°, treated dropwise with $BF_3 \cdot OEt_2$ (82 µl, 0.65 mmol) over 10 min, slowly warmed to −20°, stirred for 1 h, treated with solid $NaHCO_3$ soln. (0.12 g), and filtered through *Celite*. The filtrate was washed with aq. $NaHCO_3$ soln. Workup, evaporation, and FC (AcOEt/cyclohexane 1:2→1:1) gave **51** (1.35 g, 72%). R_f (toluene/acetone 3:2) 0.71. M.p. 126.7° (dec.). $[\alpha]_D^{25} = -28.4$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3029*w*, 3014*w*, 2872*w*, 2112*w*, 1756*s*, 1711*m*, 1492*w*, 1414*w*, 1366*m*, 1227*s*, 1160*m*, 1088*m*, 1055*s*, 1017*w*, 908*w*, 845*w*, 810*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.37–7.13 (*m*, 23 arom. H); 6.96 (*d*, $J = 7.2$, 2 arom. H); 5.113 (*t*, $J = 9.3$, H−C(3^{VIII})); 5.11–4.99 (*m*, H−C($3^{IV–VII}$), H−C(4^{VIII}), 1 PhC*H*); 4.936 (*d*, $J = 11.1$, PhC*H*); 4.922 (*t*, $J = 9.3$, H−C(3^{III})); 4.891 (*t*, $J \approx 8.4$, H−C(2^{VIII})); 4.84–4.72 (*m*, H−C($2^{III–VII}$), 1 PhC*H*); 4.644 (*d*, $J = 11.1$), 4.580 (*d*, $J = 12.3$) (2 PhC*H*); 4.54–4.28 (*m*, H−C($1^{II–VIII}$), H−C($6^{IV–VIII}$), 6 PhC*H*); 4.255 (*d*, $J = 12.0$, PhC*H*); 4.235 (br. *d*, $J = 12.3$, H−C(6^{III})); 4.11–3.98 (*m*, H′−C($6^{IV–VIII}$)); 3.995 (*d*, $J = 9.0$, H−C(5^{I})); 3.91–3.83 (*m*, H′−C(6^{III})); 3.895 (*t*, $J = 9.3$, H−C(8^{I})); 3.855 (*t*, $J = 9.3$, H−C(4^{II})); 3.78–3.65 (*m*, H−C(10^{I}), H−C($4^{IV–VII}$)); 3.66–3.42 (*m*, H′−C(10^{I}), 2 H−C(6^{II}), H−C(4^{III}), H−C($5^{IV–VIII}$)); 3.470 (*t*, $J = 9.0$, H−C(6^{I})); 3.425 (*t*, $J = 9.0$, H−C(7^{I})); 3.276 (*t*, $J = 9.0$, H−C(3^{II})); 3.25–3.19 (*m*, H−C(9^{I})); 3.167 (*dd*, $J = 9.0$, 8.1, H−C(2^{II})); 3.07 (br. *d*, $J \approx 10.0$, H−C(5^{III})); 3.04 (br. *d*, $J \approx 10.0$, H−C(5^{II})); 2.137, 2.134, 2.130, 2.113, 2.082, 2.029, 2.018, 2.012, 2.002, 1.996, 1.993, 1.988, 1.976, 1.950, 1.947, 1.945, 1.938 (6 H), 1.881 (18*s*, 19 AcO); 0.20 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.29–168.90 (several *s*, 19 C=O); 137.53, 137.46, 137.39, 136.35, 136.13, 135.96 (6*s*, 6 arom. C); 133.54, 133.34, 133.26, 132.89, 132.75 (5*s*, 5 arom. C); 129.50, 129.15 (2*d*, 4 arom. C); 128.91–128.12 (several *d*, 19 arom. C); 127.66 (*d*, 2 arom. C); 102.26 (*d*, C(1^{II})); 100.74 (2 C), 100.60, 100.48 (2 C) (3*d*, C($1^{III–VII}$)); 99.68 (*d*, C(1^{VIII})); 88.32 (*s*, *C*≡CSi); 86.93 (*s*, C≡*C*Si); 84.15 (*d*, C(7^{I})); 82.92 (*d*, C(3^{II})); 81.55 (*d*, C(2^{II})); 81.01 (*d*, C(6^{I})); 79.24 (*d*, C(9^{I})); 76.28, 76.24 (2*d*, C(8^{I}), C(4^{II})); 76.04 (br. *d*, C($4^{III–VII}$)); 74.68 (*d*, C(5^{II})); 74.60, 74.42, 74.12 (2 C), 73.32, 72.58 (5*t*, 6 Ph*C*H$_2$); 72.84, 72.76 (br.), 72.50 (br.) (3*d*, C($3^{III–VIII}$), C($5^{III–VIII}$)); 72.00 (2 C), 71.78 (2 C), 71.70, 71.52 (4*d*, C($2^{III–VIII}$)); 70.17 (*d*, C(5^{I})); 67.71 (*t*, C(10^{I})); 67.67 (*d*, C(4^{VIII})); 67.62 (*t*, C(6^{II})); 62.02 (br., 4 C), 61.59, 61.47 (3*t*, C($6^{III–VIII}$)); 20.89–20.62 (several *q*, 19 Me); −0.37 (*q*, Me_3Si); *s*s of *C*≡*C*Si hidden by other signals. HR-MALDI-MS: 2949.7831 (20, $[M+Na]^+$, $C_{135}H_{159}Cl_5NaO_{59}Si^+$; calc. 2949.7551). Anal. calc. for $C_{135}H_{159}Cl_5O_{59}Si$ (2931.05): C 55.32, H 5.47; found: C 55.31, H 5.60.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl]$_5$-(1 → 4)-6*-O-*benzyl-2,3-bis*-O-*(4-chlorobenzyl)-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tris*-O-*(4-chlorobenzyl)-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol* (**52**). A soln. of **51** (0.82 g, 0.28 mmol) in THF (25 ml) was cooled to 0°, treated with a soln. of $Bu_4NF \cdot 3\,H_2O$ (30.8 mg, 0.10 mmol) in THF (2.5 ml), stirred for 30 min, and treated with sat. aq. NH_4Cl soln. (10 ml). Workup and FC (AcOEt/cyclohexane 1:1 → 3:2) gave **52** (0.66 g, 83%). Foamy solid. R_f (toluene/acetone 2:1) 0.55. M.p. 118.2° (dec.). $[\alpha]_D^{25} = -26.3$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3306*w*, 3030*w*, 2958*w*, 2872*w*, 1756*s*, 1600*w*, 1492*w*, 1367*m*,

Table 13. *Selected ^{1}H-NMR Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of the Peracetylated Cellooctaosylalkynes* **50**, **53**–**55**, *and* **58** *in* $CDCl_3$

	50[a])	**53**	**54**[b])	**55**	**58**[b])
					E chain, *B* chain
C≡CH	2.49	2.20	–	–	–
H–C(1^{I})	4.141	4.192	4.522	4.532	4.593, 4.39
H–C(1^{II})	4.471	4.462	4.471	4.48–4.34	4.49–4.39
H–C($1^{III–VII}$)	4.425 (5 H)	4.46–4.39	4.439 (2 H), 4.427 (3 H)	4.48–4.34	4.49–4.39
H–C(1^{VIII})	4.471	4.462	4.497	4.496	4.49–4.39
H–C(2^{I})	5.078	5.043	5.27–5.20	5.30	5.28–5.22, 5.14–5.08
H–C($2^{II–VII}$)	4.820 (2 H), 4.800 (4 H)	4.85–4.76	4.854, 4.813, 4.805 (4 H)	4.850, 4.818, 4.804 (4 H)	4.839 (2 H), 4.803 (10 H)
H–C(2^{VIII})	4.895	4.895	4.898	4.878	4.897
H–C(3^{I})	5.118	5.108	5.27–5.20	5.22	5.28–5.22, 5.188
H–C($3^{II–VII}$)	5.093, 5.091, 5.074 (4 H)	5.125–5.03	5.114, 5.101, 5.084, 5.080 (3 H)	5.15–5.04	5.14–5.06
H–C(3^{VIII})	5.121	5.117	5.120	5.108	5.14–5.06
H–C(4^{I})	3.77–3.69	3.79–3.67	3.810	3.829	3.818, 3.772
H–C($4^{II–VII}$)	3.77–3.69	3.79–3.67	3.752 (2 H), 3.733, 3.730, 3.723 (2 H)	3.748 (2 H), 3.717 (3 H), 3.687	3.730 (6 H), 3.724 (6 H)
H–C(4^{VIII})	5.048	5.043	5.050	5.044	5.050
H–C(5^{I})	3.59–3.52	3.59–3.50	3.670	3.71–3.66	3.592
H–C($5^{II–VII}$)	3.59–3.52	3.59–3.50	3.597, 3.575–3.52 (5 H)	3.59–3.50	3.57–3.52
H–C(5^{VIII})	3.630	3.623	3.631	3.628	3.632
H_a–C(6^{I})	4.415–4.36	4.44–4.35	4.54–4.50	4.577	4.58–4.50
H_a–C($6^{II–VII}$)	4.415–4.36	4.44–4.35	4.41–4.36	4.48–4.34	4.41–4.35
H_a–C(6^{VIII})	4.350	4.35	4.351	4.350	4.352
H_b–C(6^{I})	4.115–4.035	4.12–4.02	4.114	4.15–4.04	4.14–4.03
H_b–C($6^{II–VII}$)	4.115–4.035	4.12–4.02	4.125–4.04	4.15–4.04	4.14–4.03
H_b–C(6^{VIII})	4.028	4.018	4.030	4.023	4.030
$J(1^{I},{\equiv}CH)$	2.1	0.9	–	–	–
$J(1^{I},2^{I})$	9.6	9.9	9.6	9.6	9.6, [c])
Other *J*(1,2)	7.7–8.0	7.8–8.1	7.8–8.0	7.8–8.1	7.8–8.0
J(2,3)	9.2–9.6	9.0–9.6	9.1–9.3	9.0–9.6	9.0–9.6
J(3,4)	9.2–9.4	9.0–9.6	9.1–9.3	9.0–9.6	9.0–9.6
J(4,5)	9.7–9.9	9.3–9.9	9.7–9.9	9.3–9.9	9.3–9.9
$J(5^{VIII},6a^{VIII})$	4.3	4.2	4.3	4.2	4.1
$J(5^{VIII},6b^{VIII})$	2.2	2.1	2.2	2.4	2.5
Other *J*(5,6a)	[c])	[c])	2.0	[c])	[c])
Other *J*(5,6b)	[c])	[c])	4.9	[c])	[c])
J(6a,6b)	12.5	12.5	12.5	12.3	12.5

[a]) Assignments based on a DQFCOSY and a HSQC spectrum. [b]) Assignments based on a DQFCOSY spectrum. [c]) Not assigned.

Table 14. *Selected ^{13}C-NMR Chemical-Shift Values* [ppm] *of the Peracetylated Cellooctaosylalkynes* **50**, **53**, **54**, *and* **58** *in $CDCl_3$, and of the Deprotected Cellooctaosylalkynes* **57** *and* **59** *in (D_6)DMSO*

	50[a])	**53**	**54**	**58**	**57**	**59**
				E chain, *B* chain		*E* chain, *B* chain
C(4′)	–	66.82	–	–, 78.68	–	–, 78.80
C(3′)	–	69.80	–	–, 78.31	–	–, 77.33
C(2′)	75.31	69.48	85.90	85.92, 71.97	83.89	84.23, 69.68
C(1′)	77.72	71.12	88.93	90.20, 79.31	94.53	94.05, 84.23
C(1^{I})	68.22	68.66	69.49	69.45, 69.05	70.74	70.72, 70.41
C(1^{II})	100.73	100.73	100.81	100.81	103.13	103.13 (2 C)
C($1^{III–VIII}$)	100.48, 100.43 (4 C), 100.37	100.43	100.56, 100.51 (4 C), 100.49	100.81 (2 C), 100.56 (4 C), 100.52 (6 C)	103.13, 102.72 (4 C), 102.61	103.13 (2 C), 102.72 (10 C)
C(2^{I})	71.20	70.95	71.41	71.13/71.08	73.44	73.57/73.14
C($2^{II–VII}$)	71.74 (5 C), 71.65	71.77 (5 C), 71.71	71.88, 71.83 (4 C), 71.73	71.82 (8 C), 71.73 (4 C)	73.15, 72.97, 72.88 (4 C)	73.14 (2 C), 72.87 (10 C)
C(2^{VIII})	71.48	71.52	71.57	71.56	73.15	73.14 (2 C)
C(3^{I})	72.94	72.86	73.18	73.21/73.12	75.84	75.79/75.68
C($3^{II–VII}$)	72.72 (5 C), 72.67	72.76	72.52 (br.)	72.70 (3 C), 72.54 (9 C)	74.65 (6 C)	74.65 (12 C)
C(3^{VIII})	72.80	72.81	72.63	72.63	76.38	76.38 (2 C)
C($4^{I–VII}$)	76.11, 76.05, 76.00 (5 C)	76.03	76.39, 76.19, 76.08 (4 C)	76.09	80.27 (6 C), 80.01	80.27 (12 C), 79.95/79.82
C(4^{VIII})	67.64	67.67	67.72	67.71	69.94	69.94 (2 C)
C(5^{I})	76.81	77.20	76.92	76.48, 76.20	78.91	78.94/78.80
C($5^{II–VII}$)	72.55, 72.44 (5 C)	72.55 (2 C), 72.47 (4 C)	72.88, 72.81 (4 C), 72.79	72.88 (3 C), 72.80 (9 C)	74.72 (6 C)	74.71 (12 C)
C(5^{VIII})	71.96	72.00	72.04	72.03	76.70	76.69 (2 C)
C($6^{I–VII}$)	62.05, 61.98 (3 C), 61.94 (3 C)	61.99	62.25, 62.18, 62.05 (5 C)	62.25, 62.01 (8 C), 61.48 (3 C)	60.94, 60.20 (6 C)	60.93 (2 C), 60.19 (12 C)
C(6^{VIII})	61.41	61.46	61.49	61.48	60.94	60.93 (2 C)

[a]) Assignments based on a HSQC spectrum.

1160*w*, 1088*s*, 1055*s*, 1017*m*, 904*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.38–7.10 (*m*, 23 arom. H); 6.96 (*d*, *J* = 7.8, 2 arom. H); 5.108 (*t*, *J* = 9.3, H–C(3^{VIII})); 5.10–4.99 (*m*, H–C($3^{IV–VII}$), H–C(4^{VIII}), 1 PhC*H*); 4.936 (*d*, *J* ≈ 10.8, PhC*H*); 4.918 (*t*, *J* = 9.3, H–C(3^{III})); 4.887 (*t*, *J* ≈ 8.4, H–C(2^{VIII})); 4.84–4.72 (*m*, H–C($2^{III–VII}$), 1 PhC*H*); 4.647 (*d*, *J* = 10.8), 4.580 (*d*, *J* = 12.0) (2 PhC*H*); 4.56–4.28 (*m*, H–C($1^{II–VIII}$), H–C($6^{IV–VIII}$), 6 PhC*H*); 4.25 (*d*, *J* = 12.3, PhC*H*); 4.23 (br. *d*, *J* = 12.3, H–C(6^{III})); 4.12–3.98 (*m*, H′–C($6^{IV–VIII}$)); 3.98 (br. *d*, *J* = 9.3, H–C(5^{I})); 3.90–3.83 (*m*, H′–C(6^{III})); 3.89 (*t*, *J* = 9.3, H–C(8^{I})); 3.85 (*t*, *J* = 9.3, H–C(4^{II})); 3.78–3.65 (*m*, H–C(10^{I}), H–C($4^{IV–VII}$)); 3.66–3.45 (*m*, H′–C(10^{I}), 2 H–C(6^{II}), H–C(4^{III}), H–C($5^{IV–VIII}$)); 3.48 (*t*, *J* = 8.7, H–C(6^{I})); 3.43 (*t*, *J* = 8.7, H–C(7^{I})); 3.265 (*t*, *J* = 9.0, H–C(3^{II})); 3.26–3.18 (*m*, H–C(9^{I})); 3.16 (*dd*, *J* ≈ 8.5, H–C(2^{II})); 3.08 (br. *d*, *J* ≈ 10.0, H–C(5^{III})); 3.03 (br. *d*, *J* ≈ 10.0, H–C(5^{II})); 2.22 (br. *s*, C≡CH); 2.12–1.86 (several *s*, 19 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.29–168.89 (several *s*, 19 C=O); 137.52, 137.45, 137.36, 136.34, 136.04, 135.86 (6*s*, 6 arom. C); 133.60, 133.38, 133.26, 132.91, 132.75 (5*s*, 5 arom. C); 129.45, 129.18, 128.84, 128.76, 128.52, 128.22 (6*d*,

12 arom. C); 128.44 (*d*, 4 arom. C); 128.15 (*d*, 6 arom. C); 128.05 (*d*, 1 arom. C); 127.65 (*d*, 2 arom. C); 102.26 (*d*, C(1^{II})); 100.73, 100.59, 100.47 (2 C), 100.41 (4*d*, C($1^{III–VII}$)); 99.68 (*d*, C(1^{VIII})); 84.13 (*d*, C(7^{I})); 82.92 (*d*, C(3^{II})); 81.54 (*d*, C(2^{II})); 80.88 (*d*, C(6^{I})); 79.23 (*d*, C(9^{I})); 76.25, 76.22 (2*d*, C(8^{I}), C(4^{II})); 76.04 (br. *d*, C($4^{III–VII}$)); 74.73 (*d*, C(5^{II})); 74.60, 74.42, 74.12 (2 C), 73.32, 72.57 (5*t*, 6 Ph*C*H_2); 72.85, 72.75 (br.), 72.49 (br.) (3*d*, C($3^{III–VIII}$), C($5^{III–VIII}$)); 71.99 (2 C), 71.78 (2 C), 71.70, 71.52 (4*d*, C($2^{III–VIII}$)); 70.17 (*d*, C(5^{I})); 70.00 (*s*, C≡*C*–*C*≡CH); 67.67 (*t*, C(10^{I})); 67.67 (*d*, C(4^{VIII})); 67.62 (*t*, C(6^{II})); 67.21 (*s*, C≡C–C≡*C*H); 62.03 (br., 4 C), 61.63, 61.47 (3*t*, C($6^{III–VIII}$)); 20.89–20.66 (several *q*, 19 Me); *s* of *C*≡C–C≡CH hidden by other signals. Anal. calc. for $C_{132}H_{151}Cl_5O_{59}$ (2858.87): C 55.46, H 5.32; found: C 55.49, H 5.46.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl]$_6$-(1 → 8)-5,9-anhydro-6,7,10-tri*-O-*acetyl-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol* (**53**). A soln. **52** (2.13 g, 0.75 mmol) in Ac_2O (20 ml) was cooled to −18° (ice/NaCl bath), treated with $BF_3 \cdot OEt_2$ (1.90 ml, 15.01 mmol), warmed to 31°, stirred for 3 d, poured into a chilled sat. aq. $NaHCO_3$ soln. (60 ml), and stirred vigorously for 0.5 h. Workup (AcOEt), evaporation, and FC (AcOEt/hexane 1:1 → 5:2) gave **53** (1.26 g, 70%). Pale yellow solid. R_f (toluene/acetone 3:2) 0.49. M.p. 165.2° (dec.). $[\alpha]_D^{25} = -20.6$ ($c = 1.03$, $CHCl_3$). IR ($CHCl_3$): 3300*w*, 3029*w*, 2969*w*, 2119*w*, 1756*s*, 1602*w*, 1430*w*, 1368*m*, 1162*w*, 1054*s*, 904*w*, 846*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 13*; additionally, 2.135, 2.002, 1.975 (3*s*, 6 AcO); 2.130 (*s*, 5 AcO); 2.082, 2.060, 2.029, 2.018, 1.988 (5*s*, 5 AcO); 2.011 (*s*, 4 AcO); 1.944 (br. *s*, 5 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 14*; additionally, 170.30, 170.10, 168.90 (3*s*, 3 C=O); 170.00, 169.54 (2*s*, 14 C=O); 169.16 (*s*, 2 C=O); 169.10 (*s*, 6 C=O); 20.89 (br. *q*, 5 Me); 20.75 (*q*, 2 Me); 20.66 (br. *q*, 13 Me); 20.89 (*q*, 5 Me). HR-MALDI-MS: 2419.6950 (83, $[M+Na]^+$, $C_{102}H_{132}NaO_{65}^+$; calc. 2419.6921). Anal. calc. for $C_{102}H_{132}O_{65}$ (2398.13): C 51.09, H 5.55; found: C 51.08, H 5.78.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl]$_6$-(1 → 6)-4,5,8-tri*-O-*acetyl-3,7-anhydro-1,2-dideoxy-1*-C-*(8-acetoxy-9,10-dioxoanthracen-1-yl)*-D-glycero-D-gulo-*oct-1-ynitol* (**54**). Under Ar, a suspension of **20** (0.38 g, 0.93 mmol), $[Pd(PPh_3)_2]Cl_2$ (29.6 mg, 0.04 mmol), CuI (24.1 mg, 0.13 mmol), and Bu_4NI (0.47 g, 1.26 mmol) in degassed Et_3N/DMF 1:5 (20 ml) was cooled to 0°, treated dropwise with a soln. of **50** (2.0 g, 0.84 mmol) in Et_3N/DMF 1:5 (20 ml) over a period of 10 h (with a syringe pump), warmed to 28°, stirred for 6 h, and poured into ice/H_2O (400 ml). Workup (AcOEt), evaporation, and FC (toluene/acetone 3:1) gave **54** (1.85 g, 83%). Bright yellow solid. R_f (toluene/acetone 3:2) 0.49. M.p. 219.6° (dec.). $[\alpha]_D^{25} = -9.4$ ($c = 1.03$, $CHCl_3$). IR ($CHCl_3$): 3029*w*, 2951*w*, 2863*w*, 1756*s*, 1598*w*, 1434*w*, 1368*m*, 1323*w*, 1205*m*, 1160*w*, 1054*m*, 902*w*, 846*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY spectrum): see *Table 13*; additionally, 8.27 (*dd*, $J = 7.8$, 1.4, H–C(4′)); 8.23 (*dd*, $J = 7.8$, 1.3, H–C(5′)); 7.83 (*dd*, $J = 7.8$, 1.4, H–C(2′)); 7.78 (*t*, $J = 7.9$, H–C(6′)); 7.68 (*t*, $J = 7.8$, H–C(3′)); 7.43 (*dd*, $J = 8.0$, 1.3, H–C(7′)); 2.50 (*s*, AcO–C(8′)); 2.153, 2.150, 2.144, 2.140, 2.139, 2.137, 2.136, 2.086, 2.085, 2.034, 2.032, 2.023, 2.022, 2.020, 2.007, 2.005, 1.993, 1.979, 1.962 (19*s*, 19 AcO); 2.016, 1.954 (2*s*, 4 AcO); 1.953 (br. *s*, 2 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$): see *Table 14*; additionally, 181.99 (*s*, C(9′)); 180.56 (*s*, C(10′)); 170.49, 170.37, 169.86, 169.70, 169.68, 169.34, 169.10 (7*s*, 7 C=O); 170.22 (*s*, 4 C=O); 170.20 (*s*, 3 C=O); 169.74 (*s*, 5 C=O); 169.30 (*s*, 7 C=O); 150.17 (*s*, C(8′)); 140.79 (*d*, C(2′)); 134.72 (*s*, C(9′a)); 134.62 (*d*, C(3′)); 134.46 (*s*, C(4′a)); 133.53 (*s*, C(10′a)); 132.75 (*d*, C(6′)); 130.25 (*d*, C(4′)); 127.72 (*d*, C(7′)); 125.51 (*d*, C(5′)); 125.46 (*s*, C(1′)); 121.77 (*s*, C(8′a)); 21.22 (*q*, *Me*C(=O)–C(8′)); 20.94, 20.79, 20.70, 20.67, 20.61, 20.56 (7*q*, 7 Me); 20.81, 20.48 (2*q*, 10 Me); 20.58 (*q*, 6 Me); 20.54 (*q*, 2 Me). HR-MALDI-MS: 2659.7390 (36, $[M+Na]^+$, $C_{116}H_{140}NaO_{69}^+$; calc. 2659.7344). Anal. calc. for $C_{116}H_{140}O_{69}$ (2638.34): C 52.81, H 5.35; found: C 52.94, H 5.43.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl]$_6$-(1 → 6)-4,5,8-tri*-O-*acetyl-3,7-anhydro-1,2-dideoxy-1*-C-*(8-hydroxy-9,10-dioxoanthracen-1-yl)*-D-glycero-D-gulo-*oct-1-ynitol* (**55**). A stirred soln. of **54** (1.63 g, 0.62 mmol) in DMF (30 ml) was treated with $(NH_4)_2CO_3$ (0.18 g, 1.92 mmol), stirred for 10 h at 26°, and poured into chilled H_2O (300 ml). Workup, evaporation, and FC (AcOEt/cyclohexane 3:1→3:2) gave **55** (1.42 g, 88%). White solid. R_f (toluene/acetone 3:2) 0.48. M.p. 227° (dec.). ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 13*; additionally, 12.50 (*s*, OH); 8.33 (*dd*, $J = 7.8$, 1.2, H–C(4′)); 7.89 (*dd*, $J = 7.8$, 1.2, H–C(2′)); 7.81 (*dd*, $J = 7.5$, 1.2, H–C(5′)); 7.73 (*t*, $J = 7.7$, H–C(3′)); 7.67 (*t*, $J = 7.8$, H–C(6′)); 7.32 (*dd*, $J = 8.4$, 1.2, H–C(7′)); 2.151, 2.134, 2.030, 2.019, 2.016 (5*s*, 10 AcO); 2.137, 2.013, 1.949 (3*s*, 9 AcO); 2.106, 2.082, 2.003, 1.989, 1.977, 1.958 (6*s*, 6 AcO). HR-MALDI-MS: 2617.7270 (40, $[M+Na]^+$, $C_{114}H_{138}NaO_{68}^+$; calc. 2617.7238).

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl]$_6$-(1 → 6)-4,5,8-tri*-O-*acetyl-3,7-anhydro-1,2-dideoxy-1*-C-*{8-[(trifluoromethyl)sulfonyloxy]-9,10-dioxoanthracen-1-yl}*-D-glycero-D-gulo-*oct-1-ynitol* (**56**). A soln. of **55** (140 mg, 0.05 mmol) in dry CH_2Cl_2 (1.2 ml) was treated with Et_3N (22 µl, 0.16 mmol) and cooled to −78°. The resulting red suspension was treated with Tf_2O (18 µl, 0.11 mmol), stirred for 1 h, diluted with CH_2Cl_2, and warmed to r.t. Workup, evaporation, and crystallisation from CH_2Cl_2/MeOH gave **56** (81 mg, 59%). Yellow solid. R_f (toluene/acetone 3:2) 0.48. M.p. 237° (dec.). HR-MALDI-MS: 2749.6744 (26, $[M+Na]^+$, $C_{115}H_{137}F_3NaO_{70}S^+$; calc. 2749.6731).

β-D-Glucopyranosyl-[(1 → 4)-β-D-glucopyranosyl]$_6$-(1 → 6)-3,7-anhydro-1,2-dideoxy-1-C-*(8-hydroxy-9,10-dioxoanthracen-1-yl)*-D-glycero-D-gulo-*oct-1-ynitol* (**57**). A suspension of **55** (180 mg, 0.07 mmol) in 0.1M aq. Bu_4NOH (2.7 ml, 2.7 mmol) was sonicated for 20 min, stirred for 2 d at 26°, and neutralised with *Amberlite IR-120* resin (H^+ form). The supernatant was decanted, centrifuged (4000 rpm), and diluted with H_2O. Lyophilisation gave **57** (46 mg, 43%). Yellowish brown solid. M.p. 138° (dec., → green residue). IR (KBr): 3400*s*, 2892*m*, 2119*w*, 1664*m*, 1636*m*, 1579*w*, 1454*m*, 1364*m*, 1317*m*, 1284*m*, 1240*m*, 1200*m*, 1158*s*, 1071*s*, 896*m*, 746*m*, 665*m*, 611*w*. ^{1}H-NMR (600 MHz, (D_6)DMSO; assignments based on a DQFCOSY spectrum): see *Table 1*; additionally, 12.48 (br. *s*, HO−C(8′)); 8.24 (*d*, *J* = 7.7, H−C(4′)); 8.01 (*d*, *J* = 6.7, H−C(2′)); 7.91 (*t*, *J* = 7.7, H−C(3′)); 7.81 (*t*, *J* = 8.4, H−C(6′)); 7.73 (*d*, *J* = 7.9, H−C(5′)); 7.41 (*d*, *J* = 8.5, H−C(7′)); 4.38 (*d*, *J* = 7.8, H−C(1^{VII})); 4.32 (br. *d*, *J* ≈ 7.5, H−C(3^{I}), H−C($1^{II–VI}$)); 4.24 (*d*, *J* = 7.8, H−C(1^{VIII})); 3.79 (br. *s*, H−C(8^{I}), H−C($6^{II–VII}$)); 3.70 (br. *d*, *J* = 9.8, H−C(6^{VIII})); 3.57 (br. *s*, H′−C(8^{I}), H′−C($6^{II–VII}$)); 3.42–3.26 (*m*, H−C(4^{I}), H−C(5^{I}), H−C(6^{I}), H−C(7^{I}), H′−C(6^{VIII}), H−C($3^{II–VII}$), H−C($4^{II–VII}$), H−C($5^{II–VII}$)); 3.26–3.13 (*m*, H−C(3^{VIII}), H−C(5^{VIII})); 3.07–2.89 (*m*, H−C($2^{II–VIII}$), H−C(4^{VIII})). ^{13}C-NMR (151 MHz, (D_6)DMSO): see *Table 14*; additionally, 186.94 (*s*, C(9′)); 181.50 (*s*, C(10′)); 161.36 (*s*, C(8′)); 141.95 (*d*, C(2′)); 136.74 (*d*, C(6′)); 134.11 (*s*, C(9′a)); 133.95 (*d*, C(3′)); 132.63 (*s*, C(4′a)); 132.60 (*s*, C(10′a)); 127.28 (*d*, C(4′)); 124.20 (*d*, C(7′)); 122.10 (*d*, C(1′)); 118.60 (*d*, C(5′)); 116.32 (*s*, C(8′a)). MALDI-TOF: 1567.5 ($[M+Na]^+$, $C_{64}H_{88}NaO_{43}^+$; calc. 1567.6). Anal. calc. for $C_{64}H_{88}O_{43}\cdot 2\,H_2O$ (1581.39): C 48.61, H 5.86; found: C 48.79, H 6.09.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl]$_6$-(1 → 8)-6,7,10-tri*-O-*acetyl-5,9-anhydro-1,2,3,4-tetradeoxy-1*-C-*(8-{2,3,4,6-tetra*-O-*acetyl-β*-D-*glucopyranosyl-[(1 → 4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl]$_6$-(1 → 6)-4,5,8-tri*-O-*acetyl-3,7-anhydro-1,2-dideoxy*-D-glycero-D-gulo-*oct-1-ynitol-1-yl}-9,10-dioxoanthracen-1-yl)*-D-glycero-D-gulo-*deca-1,3-diynitol* (**58**). Under Ar, a soln. of **56** (0.43 g, 0.16 mmol), $[Pd(PPh_3)_2]Cl_2$ (5.5 mg, 7.9 µmol), CuI (4.5 mg, 5.5 µmol), and Bu_4NI (88 mg, 55 µmol) in degassed DMF/Et_3N 5:1 (1.8 ml) was cooled to −18° (ice/NaCl bath), treated dropwise with a soln. of **53** (0.42 g, 0.18 mmol) in degassed DMF/Et_3N 5:1 (1.8 ml) over 10 h (with a syringe pump), warmed to 28°, stirred for 16 h, and poured into chilled H_2O (80 ml). Workup (AcOEt), evaporation, and FC (toluene/acetone 3:1→2:1) gave **58** (0.31 g, 40%). Yellow solid. R_f (toluene/acetone 1:1) 0.56. M.p. 166.2° (dec.). $[\alpha]_D^{25} = -8.1$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3029*w*, 2957*w*, 2873*w*, 2142*w*, 1756*s*, 1677*w*, 1566*w*, 1431*w*, 1368*m*, 1316*w*, 1161*w*, 1052*s*, 953*w*, 903*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY spectrum): see *Table 13*; additionally, 8.32 (*dd*, *J* = 7.8, 1.3), 8.29 (*dd*, *J* = 7.8, 1.3) (H−C(4′), H−C(5′)); 7.95 (*dd*, *J* = 7.7, 1.3), 7.92 (*dd*, *J* = 7.7, 1.3) (H−C(2′), H−C(7′)); 7.72 (*t*, *J* = 7.8), 7.70 (*t*, *J* = 7.8) (H−C(3′), H−C(6′)); 2.185, 2.166, 2.119, 1.962 (4*s*, 4 AcO); 2.144, 2.033, 2.020, 2.006, 1.993, 1979 (6*s*, 18 AcO); 2.141, 2.137 (2*s*, 10 AcO); 2.085, 2.027, 2.001 (3*s*, 6 AcO); 2.023, 2.017, 1.953 (3*s*, 12 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$): see *Table 14*; additionally, 181.75 (*s*, C(10′)); 179.76 (*s*, C(9′)); 170.50–169.09 (several *s*, 50 C=O); 142.24 (*d*, C(2′)); 141.55 (*d*, C(7′)); 135.29 (*s*, C(9′a)); 133.69 (*s*, C(8′a)); 133.61(*s*, C(4′a)); 133.46 (*s*, C(10′a)); 132.90 (*d*, C(3′)); 132.81 (*d*, C(6′)); 128.15 (*d*, C(4′)); 127.77 (*d*, C(5′)); 122.35 (*s*, C(8′)); 121.46 (*d*, C(1′)); 21.00, 20.93, 20.91, 20.74 (4*q*, 4 Me); 20.81 (*q*, 9 Me); 20.79 (*q*, 4 Me); 20.67 (*q*, 3 Me); 20.58 (*q*, 10 Me); 20.56, 20.53 (2*q*, 12 Me); 20.47 (*q*, 8 Me). HR-MALDI-MS: 4996.4282 (7, $[M+Na]^+$, $C_{216}H_{268}NaO_{132}^+$; calc. 4996.4156). Anal. calc. for $C_{216}H_{268}O_{132}$ (4976.41): C 52.13, H 5.43; found: C 52.15, H 5.57.

β-D-Glucopyranosyl-[(1 → 4)-β-D-glucopyranosyl]$_6$-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-1-C-*(8-{β-D-glucopyranosyl-[(1 → 4)-β-D-glucopyranosyl]$_6$-(1 → 6)-3,7-anhydro-1,2-dideoxy*-D-glycero-D-gulo-*oct-1-ynitol-1-yl}-9,10-dioxoanthracen-1-yl)*-D-glycero-D-gulo-*deca-1,3-diynitol* (**59**). A suspension of **58** (150 mg, 0.03 mmol) in 0.1M aq. Bu_4NOH (30 ml, 3.0 mmol) was sonicated for 20 min, stirred for 2 d at 26°, and neutralised with *Amberlite IR-120* resin (H^+ form). The supernatant was decanted and cen-

trifuged (4000 rpm, washing with H_2O). Lyophilisation gave **59** (48 mg, 55%). Yellowish brown solid. M.p. 268° (dec., → green residue). IR (KBr): 3368*s*, 2899*m*, 2143*w*, 1673*m*, 1633*m*, 1572*w*, 1430*m*, 1372*m*, 1334*s*, 1256*m*, 1199*m*, 1160*s*, 1067*s*, 897*w*, 801*m*, 741*m*, 662*s*, 599*s*. ^{1}H-NMR (600 MHz, (D_6)DMSO; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 1*; additionally, 8.26 (*d*, *J* = 7.9), 8.23 (*d*, *J* = 8.4) (H–C(4′), H–C(5′)); 8,13 (*d*, *J* = 7.5), 8.03 (*dd*, *J* = 7.4) (H–C(2′), H–C(7′)); 7.90 (*t*, *J* = 7.4), 7.89 (*t*, *J* = 8.4) (H–C(3′), H–C(6′)); 4.33–4.27 (*m*, H–C(3^{1E}), H–C(5^{1B}), H–C($1^{II–VIIIB/E}$)); 3.80–3.79 (*m*, H–C(8^{1E}), H–C(10^{1B}), H–C($6^{II–VIIB/E}$)); 3.70–3.69 (*m*, H–C($6^{VIIIB/E}$)); 3.57 (br. *s*, H′–C(8^{1E}), H′–C(10^{1B}), H′–C($6^{II–VIIB/E}$)); 3.45–3.33 (*m*, H–C(4^{1E}), H–C(5^{1E}), H–C(6^{1E}), H–C(7^{1E}), H–C(6^{1B}), H–C(7^{1B}), H–C(8^{1B}), H–C(9^{1B}), H–C($3^{II–VIIB/E}$), H–C($4^{II–VIIB/E}$), H–C($5^{II–VIIB/E}$), H′–C($6^{IVB/E}$)); 3.20–3.15 (*m*, H–C($3^{VIIIB/E}$), H–C($5^{VIIIB/E}$)); 3.07–2.99 (*m*, H–C($4^{VIIIB/E}$), H–C($2^{II–VIIIB/E}$)). ^{13}C-NMR (151 MHz, $CDCl_3$): see *Table 14*; additionally, 181.44 (*s*, C(10′)); 179.57 (*s*, C(9′)); 141.97 (*d*, C(2′)); 141.71 (*d*, C(7′)); 135.02 (*s*, C(9′a)); 133.49 (*s*, C(8′a)); 133.37 (*s*, C(4′a)); 133.28 (*d*, C(3′), C(6′)); 133.09 (*s*, C(10′a)); 127.58 (*d*, C(4′)); 127.00 (*d*, C(5′)); 122.09 (*s*, C(8′)); 120.19 (*s*, C(1′)). MALDI-TOF: 2899.8 ($[M+Na+4\,H]^+$, $C_{116}H_{172}NaO_{82}^+$; calc. 2899.9). Anal. calc. for $C_{116}H_{168}O_{82}\cdot 8\,H_2O$ (3018.65): C 46.15, H 6.14; found: C 46.06, H 6.24.

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