Oligosaccharide Analogues of Polysaccharides

Part 21[1])

Towards New Cellulose I Mimics: Synthesis of Dialkynyl *C*-glucosides of *peri*-Substituted Anthraquinone

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The bis-*C*-glucoside **2** has been synthesised as the first representative of a series of templated glucosides and cellooligosaccharides that mimick part of the unit cell of cellulose I. As expected, there are, at best, weakly persistent H-bonds between the two glucosyl residues in (D_6)DMSO and (D_7)DMF solution. The acetylated oct-1-ynitol **7** and deca-1,3-diynitol **12** were prepared from the gluconolactone **5** (*Scheme 1*). Coupling of **12** to PhI and 2-iodothiophene yielded **13** and **14**, respectively, while dimerisation of the benzylated and acetylated deca-1,3-diynitols **10** and **12** afforded the bis-*C*-glucosyloctatetrayne **15** and the less stable **16**, respectively. The 2-glucosylthiophene **17** was obtained by treating the *C*-silylated deca-1,3-diynitol **9** with Na_2S. Cross-coupling of (trimethylsilyl)acetylene (TMSA) with 1,8-bis(triflyloxy)-9,10-anthraquinone (**20**) at elevated temperature gave the dialkynylated **21**; its structure was established by X-ray analysis (*Scheme 2*). Sequential coupling of **6** or **7** and TMSA to **20** gave the symmetric dialkyne **21**, the mixed dialkynes **23** (from **6**) and **25** (from **7**), and the symmetric diglucoside **36** (from **7**) in modest yields; a stepwise coupling to the acetylated monotriflate **28** proved advantageous. It led to the oct-1-ynitol **29** and the deca-1,3-diynitol **33** that were transformed into the triflates **30** and **34**, respectively. Coupling of the triflate **34** to the oct-1-ynitol **7** gave the unsymmetric bis-*C*-glucoside **35**; this was obtained in higher yields by coupling the triflate **30** to the deca-1,3-diynitol **12**. Coupling of the bistriflate **20** with either **7** or **12** afforded the symmetric bis-*C*-glucosides **36** and **37**, respectively. Deacetylation (KCN in MeOH) of **35**–**37** provided the unsymmetric bis-*C*-glucoside **2** and the symmetric analogues **3** and **4**.

Introduction. – There are at least four different polymorphs of cellulose. The most important ones are cellulose I, the native, metastable form, and cellulose II, the most stable one [2][3]. These two differ in their crystal-packing, *i.e.*, in the relation between adjacent chains of the unit cell, as it has been reviewed on several occasions [4][5][2]).

The cellulose chains in crystalline cellulose I are oriented in a parallel[3]) sense and in cellulose II in an antiparallel one (*Fig. 1*; **I** and **II** *vs.* **III**). Cellulose I largely predominates in the cell walls of the alga *Valonia ventricosa*. Two models have been proposed for this cellulose, both derived from X-ray diffraction data. The one of *Gardner* and *Blackwell* ('*G-B* model', **I**) is based on a monoclinic unit cell, and that of *Sarko* and *Muggli* ('*S-M* model', **II**) is based on a triclinic unit cell. These models agree in the parallel orientation of the chains, but differ in the unit-cell indexing. Neither of

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1) Part 20: see [1].

2) For a recent neutron diffraction study of cellulose II, see [6].

3) Parallel packing means that all downstream (= reducing) ends of the nearest adjacent chains in the unit cell point in the same direction, while antiparallel packing means that the downstream ends of nearest adjacent chains in the unit cell point in opposite directions.

the above models rationalizes all X-ray reflections[4]). Moreover, native celluloses of different origin show subtle differences in their X-ray diffraction pattern. The 'extra' reflections and the differences were rationalized after the finding of *Atalla* and *VanderHart* that native celluloses are composites of two crystalline phases, cellulose I_α and cellulose I_β [8][9]. These phases were evidenced by solid state CP/MAS ^{13}C-NMR and later supported by *Raman* [10] and IR spectroscopy [11], and also by electron-diffraction studies [12]. According to *Sugiyama et al.*, cellulose I is a composite of a triclinic I_α phase **IV** with P_1 symmetry and a monoclinic I_β phase **V** with P_{21} symmetry [13][14]. Cellulose I_α has only one independent chain in the unit cell that resembles the *S-M* model **II** of cellulose I [15] (**IV** and **II** in *Fig. 1*), although the *S-M* unit cell comprises two independent chains. The centre chain **E** of **II** is equidistant (5.93 Å) from the adjacent origin chains **A** and **C**; the centre and origin chains are staggered by *ca.* + 2.6 Å (**II-A**) and *ca.* −2.6 Å (**II-B**), respectively. Thus, there is continuous translation of the chains in the $1\bar{1}0$ plane in either upward or downward direction. The unit cell of *Sugiyama*'s I_α phase **IV** lacks a centre chain, but the origin chains (**A** and **D**, or **B** and **C**) are also staggered by 2.6 Å, and the distance between **A** and **D**, or **B** and **C** (5.93 Å) is the same as between the centre and origin chains in the *S-M* model **II**.

The unit cell of *Sugiyama*'s I_β-phase **V** is similar to the two-chain unit cell **I** (*G-B*) of cellulose I. The centre chain **E** of **V** is at a distance of 6.01 Å from its origin neighbours **A** and **C**; centre and origin chains are staggered by *ca.* 2.7 Å. Thus, there is an alternative translation of **E** in its $1\bar{1}0$ plane either upward ('parallel-up', **V-A**) or downward direction ('parallel-down', **V-B**) relative to the origin chains **A** and **C**. A recent crystal structure re-analysis of pure *Valonia* cellulose I_β phase [16] confirmed the crystal dimensions ($a = 8.16$ Å, $b = 7.82$ Å, $c = 10.32$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 97.5°$) and a parallel-up packing for this allomorph. A highly pure cellulose I_α phase was isolated recently from the alga *Glaucocystis nostochinearum*, but the details of the crystal structure have not yet been published [17].

For the unit cells of both the *G-B* and the *S-M* models, **I** and **II**, respectively, are postulated H-bonds between the origin chains **A** and **B** ($a = 8.15 - 8.17$ Å) and also between **C** and **D**, but not between the asymmetric elements **A** and **E**, nor between **E** and either **B**, **C**, or **D**. However, **E** forms H-bonds to the centre chains of the adjacent unit cells. In the one-chain cellulose I_α model **IV** of *Sugiyama* are H-bonds between the (minor) diagonal elements **D** and **B** postulated that cannot be directly compared to the H-bonds in the *S-M* model **II**. The cellulose I_β model **V** of *Sugiyama* is similar to the *G-B* model **I** of cellulose I also with regard to H-bonds.

Single-crystal analysis of cellotriose [18] and cellotetraose have led *Saenger* and co-workers to propose cellotetrose as a model of cellulose II [19][20]. There are no similar models for cellulose I. In search of such a model, we intended to mimic the relationship between the independent chains **A** and **E** of *Sugiyama*'s model **V** of cellulose I_β. Since the crystal coordinates have, to the best of our knowledge, not been published, we used the coordinates of the *G-B* model **I**. We chose to mimic chains **A** and **E**, considering that there are no H-bonds between them and speculating that this will favour intermolecular H-bonding and crystallization. The distance between **A** and **E** (6.01 Å)

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[4]) To explain the 'extra' reflections, *Gardner* and *Blackwell* proposed a (not fully satisfactory) eight-chain model [7].

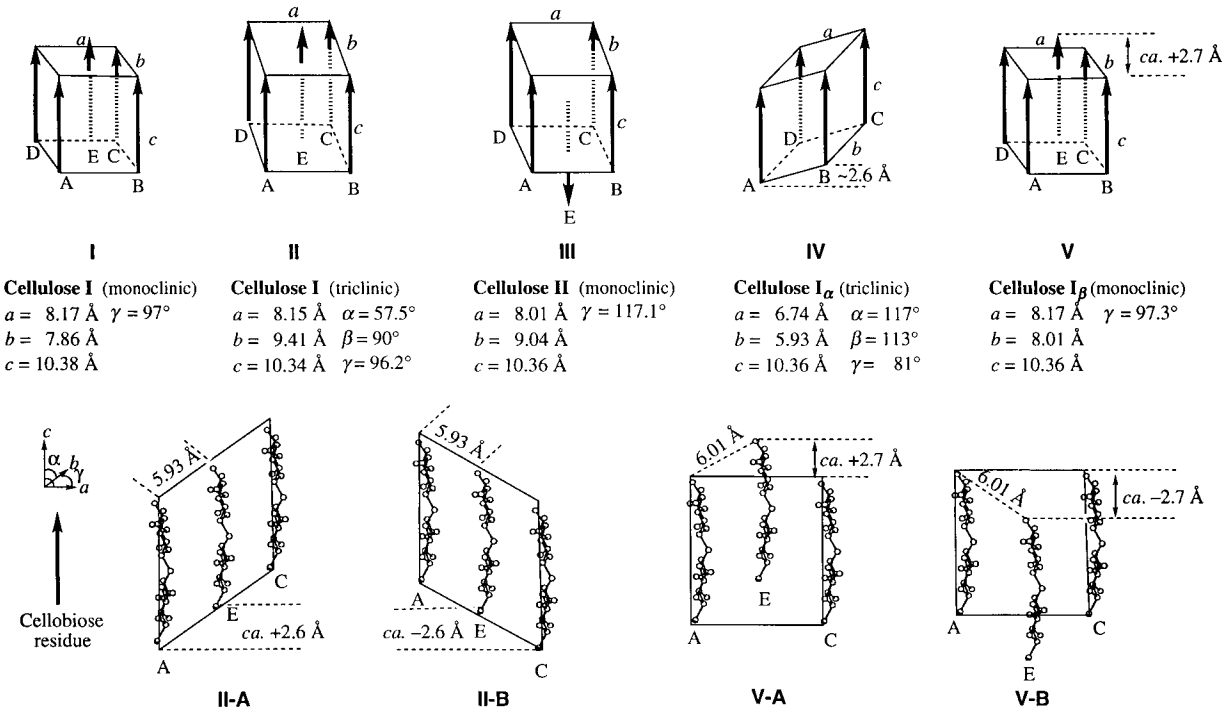

Fig. 1. *Schematic representation of unit cells* **I**–**V** (arrows indicate the cellobiose residues) *proposed for cellulose I, II, I_α and I_β*, i.e. **I**: *unit cell for cellulose I* [7], **II**: *unit cell of cellulose I* [15], **III**: *unit cell for cellulose II* [7], **IV**: *unit cell for cellulose I_α* [13], and **V**: *unit cell for cellulose I_β* [13]. Views of parallel-up (**II-A**) and parallel-down chain packing (**II-B**) in the $(1\bar{1}0)$ plane of **II** [15] indicate a phase shift of *ca.* 2.6 Å. Views of parallel-up (**V-A**) and parallel-down chain packing (**V-B**) in the $(1\bar{1}0)$ plane of **V** [7] indicate a phase shift of *ca.* 2.7 Å.

rather than between **B** and **E** (6.60 Å)[5]) was chosen, since a shorter distance might lead to a simpler template. To prepare the first model compounds, we have glycosylated naphthalene-1,8-diethanol with cellooligosaccharides [21]. The resulting glycosides possess two cellodextrin chains in parallel orientation and have been characterised in solution and in the solid state [1]. The distance between the O-atoms of the template amounts to 6.01 Å in the optimum conformation, corresponding to the distance between the **A** and **E** chains. However, the maximum phase shift (*ca.* 1.5 Å) characterising the staggering of the two chains in the model is smaller than the phase shift in the unit cell of cellulose I (2.7 Å). Perhaps as a result of the inaccurate phase shift and the chain flexibility, the solid state CP/MAS ^{13}C-NMR spectrum of the (naphthalene-1,8-diethyl)bis[cellooctaoside] resembles that of cellulose II evidencing an antiparallel packing in the solid state of this model compound.

We have now designed an improved model, based on a template that allows us to attach two parallel cellooligosaccharide chains, corresponding to the **A** and **E** chains in the unit cell of cellulose I_β, but restricts their conformational mobility and imposes a correct phase shift.

Results and Discussion. – 1. *The Template.* An improved template should impose a distance between the chains of ideally 6.01 Å and a phase shift (staggering) of ideally 2.7 Å. MM3* Calculations (Macromodel V.6, gas phase [22]) showed that an anthraquinone[6]) carrying a 1-butadiynyl and 8-ethynyl substituent should be a suitable template. *C*-Glycosylation should lead to a series of model compounds **1** of cellulose I, carrying cellodextrin chains of increasing length (*Fig. 1*). The calculated distance $c = 6.02$ Å and the phase shift $d = 2.59$ Å of conformer **2A** of the bis-*C*-glucoside **2** compare well to the corresponding distances in *G-B*'s cellulose I model **I** (*Fig. 2*; for the distances $a = 5.14$ and $b = 5.30$ Å, see below). The conformations that are accessible by rotation about the C,C bonds to the ethyndiyl and the buta-1,3-diynediyl groups of **2** are specified with the help of the dihedral angles $C(2)-C(1)\cdots C(1_A)-O(5_A)$ and $C(7)-C(8)\cdots C(1_B)-O(5_B)$. MM3* Calculations showed that only conformer **2A**, characterised by the dihedral angles $C(2)-C(1)\cdots C(1_A)-O(5_A)$ of 78° and $C(7)-C(8)\cdots C(1_B)-O(5_B)$ of $-108°$ and by a $C(1_A)\cdots C(1_B)$ distance of 6.02 Å, mimics the relationship between the cellulose chains **A** and **E** of *Sugiyama*'s model **V** of cellulose I_β. No intramolecular, interchain H-bonds are possible in this (stacked) conformer. The conformer obtained by rotating the glucosyl moieties of **2A** by 180° each is much less stable. Interchain H-bonds are feasible in the minimum energy conformation **2B**, characterised by dihedral angles $C(2)-C(1)\cdots C(1_A)-O(5_A)$ of 73° and $C(7)-C(8)\cdots C(1_B)-O(5_B)$ of 0°, and a $C(1_A)\cdots C(1_B)$ distance of 6.2 Å, and evidenced by $C(2_A)O\cdots OC(2_B)$ and $C(3_A)O\cdots OC(3_B)$ distances of 2.5 to 3.4 Å. Several other conformers may also form such H-bonds.

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[5]) The distances between the origin chains **A** and **B** to the centre chain **E** depend on the crystal parameters. Mean distances of $\mathbf{A}\cdots\mathbf{E}$ and $\mathbf{B}\cdots\mathbf{E}$ for the monoclinic unit cell **I** are 6.01 ± 0.05 and 6.60 ± 0.06 Å, respectively. The phase shift between the origin and centre chains **A** and **E** is 2.70 ± 0.08 Å.

[6]) 1,8-Diethynylanthracene has been used as a template to induce H-bond interactions between DNA base pairs [23]. 1,8-Diethynylanthracene also has been used in the preparation of cyclophanes [24] in an attempt to generate cellulose I mimics by *Hoffmann* [25].

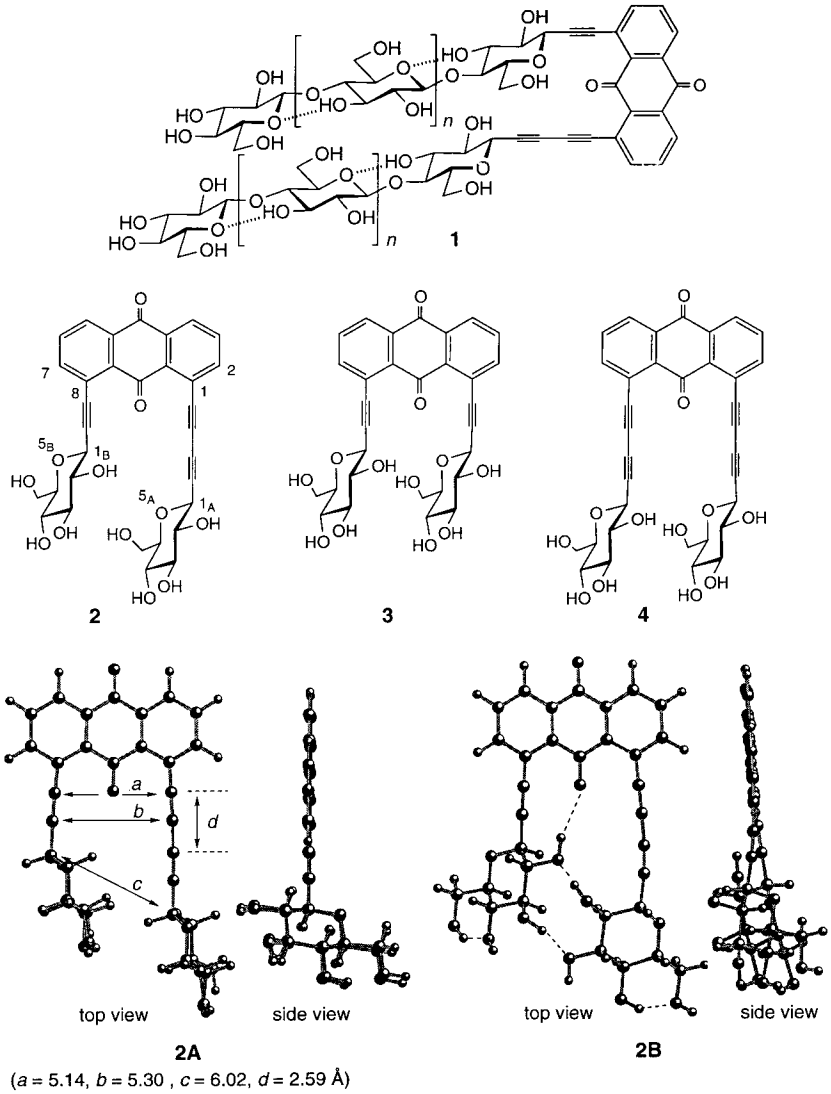
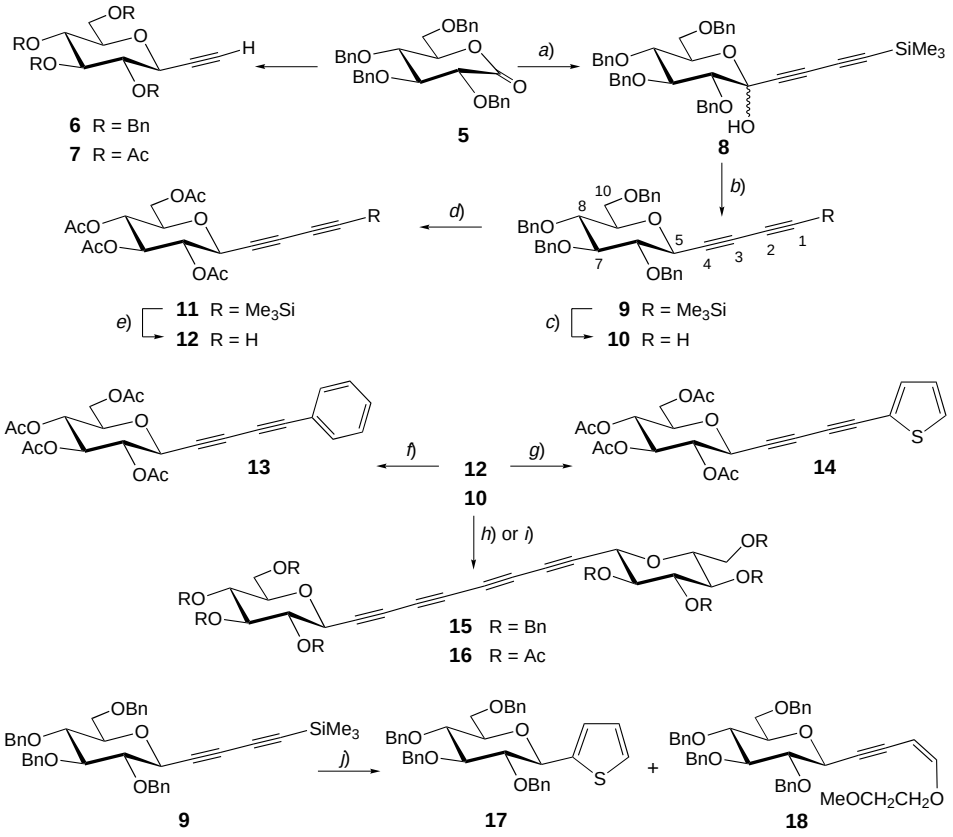


Fig. 2. *The targeted templated bis-cellooligosaccharides* **1** *as model for cellulose* I_β, *the parent unsymmetric bis-glucoside* **2**, *and the symmetric bis-glucosides* **3** *and* **4**. Two preferred conformers of **2** were obtained by MM3* modelling: **2A** lacking any interstrand H-bonds and mimicking the conformation of cellulose I_β, and **2B** as an example of a conformer possessing interchain H-bonds.

2. *Synthesis of the Bis-*C*-glucosides* **2**–**4**. We intended to prepare the unsymmetric bis-*C*-glucoside **2** (the first member of the planned series of templated cellodextrins **1**; *Fig. 2*) by sequential Pd-catalysed cross-couplings [26–29] of the acetylene **7** [30] and the butadiyne **12** to an 1,8-dihalo- or 1,8-bis(sulfonyloxy)anthraquinone (*Scheme 1*). The symmetric bis-*C*-glucosides **3** and **4** should be available in a similar way; they are of

Scheme 1



a) Bis(trimethylsilyl)butadiyne, MeLi/LiBr, THF. *b*) $BF_3 \cdot Et_2O$, Et_3SiH, CH_2Cl_2/MeCN 1:1; 76% from **5**. *c*) NaOMe, MeOH; 83%. *d*) TMSOTf, Ac_2O; 60% of **11** from **9**; 79% of **12** from **10**. *e*) $Bu_4NF \cdot 3\,H_2O$, THF; 95%. *f*) PhI, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N/DMF 1:5; 49%. *g*) C_4H_3SI, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N/DMF 1:5; 70%. *h*) Cu_2Cl_2, O_2, pyridine; 70% of **15** from **10**. *i*) $Cu_2Cl_2 \cdot$ TMEDA, O_2, acetone; 96% of **16** from **12**. *j*) $Na_2S \cdot 9\,H_2O$, 2-methoxyethanol; 64% of **17** and 5% of **18**.

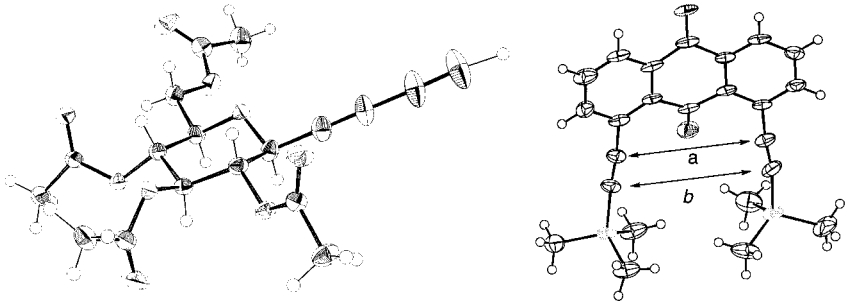
interest for a comparative ^{1}H-NMR study of the intra- and intermolecular association of these *C*-glucosides.

The protected glucosylacetylenes **6** and **7** [30] had been prepared from the gluconolactone **5**. An attempt to obtain the required glucosyl-butadiyne **11** by transforming **7** into the corresponding bromoalkyne [30] and cross-coupling with (trimethylsilyl)acetylene under *Sonogashira* conditions yielded only traces of **11**. However, addition of 1-(trimethylsilyl)buta-1,3-diyne [31][32] to the lactone **5** and reductive deoxygenation [33] of the resulting hemiketal **8** gave the equatorial glucosyl-butadiyne **9** in an overall yield of 76%. No traces of its anomer could be detected. Desilylation and acetolytic debenzylation of **9** yielded 64% of the crystalline tetraacetate **12**. Inverting the order of deprotection steps led to a slightly lower yield of **12** (55%).

We have first cursorily examined the cross-coupling of **12** to iodobenzene and 2-iodothiophene and the dimerisation of **10** and **12**. *Sonogashira*-type cross-coupling of **12** (2 equiv.) with PhI at 25° gave 30% of **13**, while coupling of the monoalkyne **7** required elevated temperatures (70–80°) [34][35]. The higher reactivity of the diyne **12** is probably due to the enhanced acidity of the buta-1,3-diynyl group. The higher acidity is evidenced by a successful deuteration of **12** in CD_3OD within 6–8 h at 25°, while the monoalkyne **7** was not deuterated even after 2 days. Coupling of **12** and PhI at 50–55° gave only 26% of **13** that proved poorly stable under these conditions. The butadiyne **12** decomposed already at 25° under coupling conditions within 3 h. Slow addition (9 h) of **12** under otherwise identical conditions at ambient temperature raised the yield of **13** to 49%. Coupling of **12** to 2-iodothiophene was more favourable, yielding 70% of **14**.

Glaser coupling [36][37] of **10** yielded 70% of the benzylated tetrayne **15**, whereas the tetraacetate **12** remained unaffected under these reaction conditions. However, *Hay* coupling [38] of **12** proceeded smoothly, yielding 96% of the acetylated tetrayne **16**. The crystalline acetylated tetrayne **16** decomposed largely within 5–6 h at 25°, or within 24 h at 0°, while the equally crystalline benzylated tetrayne **15** proved stable at 0° for several months. The diyne **9** reacted with Na_2S in methoxyethanol to give the 2-thienyl-*C*-glycoside **17** (64%) besides the ynenol ether **18** (5%), in keeping with the known reactivity of buta-1,3-diynes [39] and an earlier transformation of a related glycosylbuta-1,3-diyne [30].

The equatorial position of the buta-1,3-diynyl group of **12** was evidenced by $J(5,6) = 9.7$ Hz. The structure of **12** was confirmed by a single-crystal X-ray analysis (*Fig. 3*)[7]. It shows the β-D-*gluco*-configuration, the *gt* conformation for the $AcOCH_2$ group, and the expected linearity of the buta-1,3-diynyl substituent.



12 **21**

(*a* = 5.20 Å and *b* = 5.62 Å)

Fig. 3. *X-Ray crystal structures of the oct-1-ynitol* **12** *and the 1,8-diethynylanthraquinone* **21**

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[7]) The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No CCDC-152428 (**12**) and No CCDC-152429 (**21**). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

Selected ^{1}H-NMR chemical shifts and coupling constants of **9**–**18** in C_6D_6 are compiled in *Table 2* in the *Exper. Part*; they are in keeping with the expected structure and the data of known analogues [40]. The ^{13}C-NMR chemical shifts for C(5) to C(10) of the benzyl ethers **9**, **10**, **15**, **17**, and **18** (*Table 3* in the *Exper. Part*) agree well with those of benzylated β-D-glucopyranosyl derivatives [40][41]. The unambiguous assignment of **35** (HSQC.GRASP spectrum, see below) was used for the assignment of C(5) to C(10) of the acetates **11**–**14** and **16**. As expected, C(6), C(7), and C(8) of the acetates show the same relative chemical shifts as C(6), C(7), and C(8) of the benzyl ethers, but resonate at higher field by *ca.* 11 to 12 ppm. The C(5) of the acetates **11**–**14** and **16** resonates at 69.3–69.5 ppm, *ca.* 1 ppm upfield to C(5) of the benzyl ethers **9**, **10**, **15**, **17**, and **18**. The transformation of the buta-1,3-diynyl substituent is evidenced by a strong downfield shift for C(5) of the thiophene **17** ($\Delta\delta = 8$ ppm). The enol ether structure of **18** is evidenced by a deshielding of H–C(1) (5.99 ppm) and C(1) (156.85 ppm) and by a shielding of H–C(2) (4.77 ppm) and C(2) (84.5 ppm). The value $J(1,2) = 6.2$ Hz reveals the (*Z*)-configuration of **18**.

A compilation of published data of acetylenes and buta-1,3-diynes shows a strong dependence of the chemical shifts for the acetylenic C-atoms upon their substituents (H *vs.* alkyl, aryl, and trialkylsilyl) [42]. Alkylation of buta-1,3-diyne ($\delta(C(1)) = 64.5$ ppm, $\delta(C(2)) = 68.2$ ppm [43]) leads to a strong downfield shift of the C(α)-atom (*ca.* 13–15 ppm) and to a weak upfield shift of the C(β)-atom (*ca.* 2–3 ppm), silylation to a strong downfield shift of both the C(α)- (*ca.* 18 ppm) and C(β)-atom (*ca.* 25 ppm), and arylation to a downfield shift of the C(α)- (*ca.* 17 ppm), C(β)- (*ca.* 5 ppm), and C(δ)-atom (*ca.* 6 ppm). The assignment for C(1) to C(4) of **9**–**14** is based on these shifts. A tentative assignment is given for C(1) to C(4) of the octa-1,3,5,7-tetraynes **15** and **16**.

A bis-1,8-sulfonate of anthraquinone appeared an advantageous partner for the cross-coupling, considering the lengthy preparation of 1,8-diiodo-9,10-anthraquinone [44]. The crystalline bis-triflate **20** was prepared in a yield of 76% from commercially available chrysazin (**19**; *Scheme 2*). Similarly, the crystalline monotriflate **28** was obtained in 77% yield from the monoacetate **27** [45].

Sonogashira coupling[8]) of the bis-triflate **20** to (trimethylsilyl)acetylene (3 equiv.) at ambient temperature yielded 63% of the crystalline dialkyne **21**. The yield was improved to 73% by conducting the reaction at a higher temperature (90–100°) for 2 h and in the absence of CuI [47].

The structure of **21** was established by a single-crystal X-ray analysis (*Fig. 3*)[7]). The distances $a = 5.20$ and $b = 5.62$ Å between the alkyne units of **21** were longer than those predicted for **2A** by the MM3* force-field calculations ($a = 5.14$ and $b = 5.47$ Å; *Fig. 2*). The anthraquinone moiety shows a slight distortion from planarity, probably due to the bulky Me_3Si groups, which may also be responsible for the longer than expected distances *a* and *b*.

Sequential coupling of the benzylated glucosylacetylene **6** and (trimethylsilyl)acetylene to the bis-triflate **20** (80–85°, DMF, Et_3N, $Pd(PPh_3)_2Cl_2$) gave 33% of the unsymmetric **23** besides 6% of the symmetric dialkyne **21**. Sequential coupling of the

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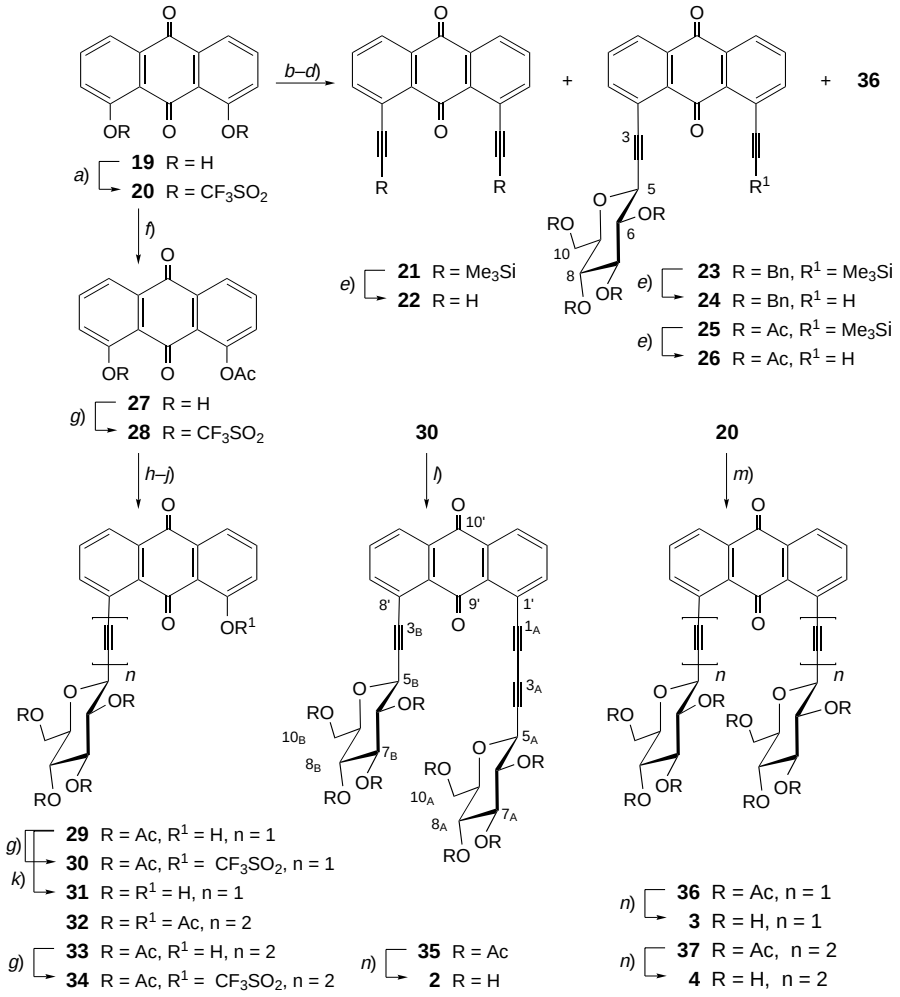
[8]) Exploratory experiments to couple trimethyl- and tributylalkynylstannanes [46] to **20** failed in the presence of various Pd catalysts (*e.g.*, $Pd(PPh_3)_3$, $Pd(PPh_3)_2Cl_2$), and in several solvents (DMF, toluene, THF).

Scheme 2



a) Tf_2O, pyridine; 76.5%. *b*) $Me_3SiC{\equiv}CH$, $Pd(PPh_3)_2Cl_2$, Et_3N, DMF; 73% of **21**. *c*) $Pd(PPh_3)_2Cl_2$, **6**, Et_3N, DMF, then $Me_3SiC{\equiv}CH$; 6% of **21** and 33% of **23**. *d*) $Pd(PPh_3)_2Cl_2$, **7**, Et_3N, DMF, then $Me_3SiC{\equiv}CH$, 5% of **21**, 21% of **25**, and 34% of **36**. *e*) KF, EtOH; 94% of **22**; 80.5% of **24**; 57% of **26**. *f*) $B(OH)_3$, Ac_2O; 94%. *g*) Tf_2O, Et_3N, CH_2Cl_2; 94% of **28**; 97% of **30**; 95% of **34**. *h*) $Pd(PPh_3)_2Cl_2$, CuI, **7**, Et_3N/DMF 1:5; 62% of **29**. *i*) $Pd(PPh_3)_2Cl_2$, CuI, **12**, Et_3N/DMF 1:5; 58% of **32** and 5% of **33**. *j*) As *i*, then $(NH_4)_2CO_3$; 63% of **33**. *k*) NaOMe, MeOH; 83%. *l*) $Pd(PPh_3)_2Cl_2$, CuI, **12**, Et_3N/DMF 1:5; 76%. *m*) $Pd(PPh_3)_2Cl_2$, CuI, Bu_4NI, **7** or **12**; 47% of **36**; 38% of **37**. *n*) KCN, MeOH/THF; 78% of **2**; 92% of **3**; 88% of **4**.

acetylated glucosylacetylene **7** (1.2 equiv.) and (trimethylsilyl)acetylene (1.5 equiv.) to **20** under similar conditions gave only 20% of the desired **25**. A larger excess of **7** (2.75 equiv.) led to a mixture of **21** (5%), **25** (21%), and **36** (24%), which were separated by FC. The reaction did not proceed in toluene or MeCN. Attempts to simultaneously couple the acetylated glucosylacetylene **7** and the acetylated glucosyl-

buta-1,3-diyne **12** (1.75 equiv. each) to **20** led to an ominous number of spots on TLC; the products were not separated. Desilylation of **21**, **23**, and **25** with KF in EtOH [48] gave the terminal acetylenes **22**, **24**, and **26**, respectively.

To circumvent the difficult separation and to increase the yield of the coupling, we adopted a stepwise approach. The Ac-protected monotriflate **28** was subjected to an iodide-accelerated *Sonogashira* coupling [49][50] with the diyne **12** to give a mixture of **32** (58%) and **33** (5%). Selective deacetylation of **32** with $(NH_4)_2CO_3$ in DMF [51][52] gave **33** (90%). Transforming **28** to **33** without isolating **32** increased the overall yield from 57 to 62%. Triflation of **33** gave **34** (97%), which was coupled to the acetylene **7** at 70° to yield 43% of the unsymmetric bis-*C*-glucoside **35**. Inverting the sequence by first coupling **28** and the glucosylacetylene **7**, followed by *in situ* deacetylation to the phenol **29**, triflation of **29** to **30**, and coupling of **30** to **12** gave **35** in an improved overall yield of 45%. Coupling of the bis-triflate **20** with either the monoalkyne **7** or the diyne **12** yielded 47 and 38% of the symmetric bis-*C*-glucosides **36** and **37**, respectively.

Deacetylation of the monoacetylene **29** with NaOMe/MeOH gave 83% of the phenol **31**, while deacetylation of **35** with NaOMe/MeOH or K_2CO_3/MeOH led to several products, presumably on account of the base-sensitive buta-1,3-diyne moiety. However, KCN in MeOH transformed **34**–**36** in 78–92% to the deprotected *C*-glucosides **2**–**4**, respectively.

The ^{13}C-NMR chemical shifts for the anthraquinonyl moieties of **19**–**36** and **2**–**4** are listed in *Table 4* in the *Exper. Part*. Characteristic shifts are observed for phenols, aryl acetates, and aryl sulfonates [53–56]. The introduction of an ethynyl or a buta-1,3-diynyl substituent leads to a strong upfield shift of C(1′) and C(8′) (120.5–123.5 ppm) and to a surprisingly strong downfield shift of C(2′) and C(7′) (140.9–142.4 ppm instead of the expected 137.7 ppm [57][58]). Only small $\Delta\delta$ values (< 1.6 ppm) are observed for all aromatic C-atoms of the oct-1-ynitol *vs.* the deca-1,3-diynitol substituted anthraquinones (**29** *vs.* **33**, **30** *vs.* **34**, **36** *vs.* **37**, and **3** *vs.* **4**). These differences are also visible for the asymmetric diglucosides **35** and **2**. The protected phenols **20**, **28**, **30**, **32**, and **34**, and the 1,8-dialkynylated anthraquinones **21**–**26**, **35**–**37**, and **2**–**4** are characterised by two *s* at 179.6–182.7 ppm for the quinonyl C=O groups. In the phenols **27**, **29**, and **33**, one of these C=O groups resonates downfield at 187.0–188.1 ppm ($CDCl_3$). This downfield shift, together with that of the C(8′) *s* at 162.7–162.9 ppm, evidences a completely persistent intramolecular H-bond from the phenolic OH to the buried O=C(9′), as documented for many related compounds [53]. This intramolecular H-bond is corroborated by a downfield shift for the phenolic OH of **27**, **29**, and **33** (12.55–12.73 ppm; C_6D_6). The intramolecular H-bond of the corresponding deprotected phenol **31** persists even in (D_6)DMSO, as evidenced by similar downfield shifts (δ(O=C(9′)) = 187.1, δ(C(6′)) = 161.5, δ(OH) = 12.48 ppm) and by a low temperature dependence ($\Delta\delta$(OH)/ΔT = – 1.5 ppb/K).

Selected ^{1}H- and ^{13}C-NMR chemical shifts and coupling constants for the oct-1-ynitol and deca-1,3-diynitol chains of **23**–**26**, **29**, **30**, and **32**–**37** are collected in *Tables 5* and *6* in the *Exper. Part*[9]). The chemical shift of the glucosyl-*H* (C_6D_6) is influenced by

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[9]) In the *Theoretical Part*, and in the *Tables 1*, *5*, and *6*, the same numbering as for the deca-1,3-diynitol chain is used for the oct-1-ynitol chains of **23**–**25**, **29**–**31**, **35**, and **36**. The deca-1,3-diynitol chain of **35** and **2** is labelled with A and the oct-1-ynitol chain with B.

the size of the substituent in *peri*-position; bulkier substituents lead to poorer solvation and, thus, to a downfield shift. This is evidenced by the downfield shift of the corresponding glucosyl-*H* of the trimethylsilyl ethers **23** and **25** as compared to the unprotected butadiynes **24** and **25**, respectively ($\Delta\delta = 0.03 - 0.17$ ppm). The poorer solvation contributes to a downfield shift of the oct-1-ynitol-*H* as compared to those of the corresponding deca-1,3-diynitol-*H*. The influence of the *peri*-substituent and of the anthraquinonyl moiety on the chemical shift of the monoglucosylated alkynes **29** and **30**, and alkadiynes **33** and **34** decreases with increasing distance to the glucosyl-*H*. Thus, the $\Delta\delta$ values for corresponding glucosyl-*H* of the alkyne/dialkyne pairs **29**/**33** and **30**/**34** decrease in the order of 0.31 – 0.34 ppm for H–C(5), 0.25 – 0.27 ppm for H–C(6), 0.15 – 0.16 ppm for H–C(7) and H–C(8), and 0.07 – 0.14 ppm for H–C(9), H–C(10a), and H–C(10b). The symmetrically substituted, two-chain anthraquinones **36** and **37** give rise to symmetric ^{1}H- and ^{13}C-NMR half-spectra, evidencing the magnetic equivalence of the glucosyl units, whereas the unsymmetric anthraquinone **35** is characterised by two sets of signals for the glucosyl units. The glucosyl-*H* signals of the diglucosides **35** – **37** are shifted downfield relative to those of the monoglucosides **30** and **34**, in agreement with the bulkier *peri*-substituent.

The *C*-glucosides **2** – **4** are well-soluble in DMSO, DMF, DMA, and pyridine (> 40 mM), much less soluble in H_2O, MeCN, and glycerol at 60° (< 5 mM), and nearly insoluble in EtOH, MeOH, acetone, AcOH, Et_3N, nitrobenzene, $MeNO_2$, and trifluoroethanol. A solution of **2** in (D_5)pyridine turned dark on standing at room temperature. Its ^{1}H-NMR spectrum showed broadened OH signals after one day and then progressive broadening and finally disappearance of these signals. We have thus confined NMR studies to solutions in (D_6)DMSO and (D_7)DMF inasmuch as H-bonding in (D_6)DMSO of mono- and oligosaccharides is well-investigated [1][59][60].

The ^{1}H-NMR spectra of the symmetric distranded *C*-glucosides **3** and **4** in (D_6)DMSO are characterised by three *d*'s for HO–C(6), HO–C(7), HO–C(8), and a *t* for HO–C(10), while the spectrum of **2** shows six well-resolved OH *d*'s and two OH *t*'s (*Table 1*). The OH signals of **2** and **3** were unambiguously assigned on the basis of DQFCOSY.GRASP spectra. The OH signals of **4** are characterized by similar shifts than those of the deca-1,3-diynitol chain of **2** and the OH signals of the monoglucoside **31** by similar shifts than those of the oct-1-ynitol chain of **2**; the OH signals were assigned accordingly.

The ^{1}H-NMR spectra of **2** and **3** in (D_6)DMSO at 22° and a concentration of 10, 40, and 80 mM showed no dependence of δ(OH) and J(H,OH) on the concentration and, thus, provide no evidence for any association. Temperature-dependence coefficients $\Delta\delta$(OH)/ΔT of – 4.4 to – 7.6 ppb/K reveal more or less completely solvated OH groups of **2** – **4** (*Table 1*). The HO–C(8) of the monoglucoside **31** cannot form strong intermolecular H-bonds, but shows a relatively weak temperature dependence ($\Delta\delta/\Delta T = -4.7$ ppb/K). Hence, $\Delta\delta$(OH)/ΔT values between – 4.4 and – 5.5 ppb/K may not necessarily indicate intramolecular H-bonds in **2** – **4**. SIMPLE ^{1}H-NMR Spectroscopy of **2** – **4** did not lead to signal splitting, as would be expected for weakly persistent interchain H-bonds [1].

The analysis of δ(OH) and J(OH) values should allow detection of even weakly persistent intramolecular H-bonds [59][60]. For this analysis, one must know how the replacement of an OH by an ethynyl or buta-1,3-diynyl group affects δ(OH) and J(OH)

Table 1. *^{1}H-NMR Chemical Shifts, Coupling Constants, and Temperature Coefficients for the OH Groups of* **31**, **3**, **4**, *and* **2** *in (D_6)DMSO and of* **2** *in (D_7)DMF Solution*[9])

		31	**3**[a])	**4**	**2** in (D_6)DMSO[a])		**2** in (D_7)DMF	
					A	B	A	B
δ(OH)[b])	HO–C(6)	5.38 (5.31)	5.24 (5.31)	5.60 (5.51)	5.62	5.39	5.78	5.43
[ppm]	HO–C(7)	5.09 (5.01)	5.07 (5.01)	5.13 (5.06)	5.15	5.11	5.25	5.16
	HO–C(8)	4.99 (4.91)	4.97 (4.91)	5.01 (4.91)	5.06	5.03	5.13	5.13
	HO–C(10)	4.62 (4.55)	4.60 (4.55)	4.62 (4.55)	4.71	4.66	4.85	4.70
J(H,OH)	HO–C(6)	5.6	5.5	5.6	6.0	5.8	5.6	4.7
[Hz]	HO–C(7)	4.7	4.3	4.4	4.7	4.7	3.7	3.7
	HO–C(8)	5.0	5.3	5.0	5.4	5.4	3.7	3.7
	HO–C(10)	5.6	5.0	5.9	6.0	5.7	6.2	5.9
$\Delta\delta$(OH)/ΔT	HO–C(6)	– 6.5	– 6.2	– 4.6	– 6.3	– 7.6	– 7.4	– 10.6
[ppb/K][c])	HO–C(7)	– 6.2	– 5.7	– 5.2	– 6.8	– 7.1	– 8.7	– 9.8
	HO–C(8)	– 4.7	– 5.3	– 4.7	– 6.0	– 5.9	– 8.3	– 8.3
	HO–C(10)	– 5.7	– 5.5	– 4.4	– 5.7	– 5.9	– 8.9	– 9.4

[a]) Assignment based on a 500-MHz DQFCOSY.GRASP spectrum. [b]) Calculated δ(OH) (see text) in parenthesis. [c]) Spectra were recorded from 298 to 348 K in 10-K intervals for solutions in (D_6)DMSO and from 298 to 248 K in 10-K intervals for solutions in (D_7)DMF.

of fully solvated remaining OH groups. An analysis of the ^{1}H-NMR spectra of β-D-glucopyranosyl moieties, *C*-substituted by ethynyl and buta-1,3-diynyl groups in the 1- and 4-positions [61–63], led to the following increments: substitution of HO–C(1) of β-D-glucopyranose by an ethynyl group leads to a downfield shift of 0.50 ppm for HO–C(2), of 0.2 ppm for HO–C(3), and of 0.1 ppm for HO–C(4) and HO–C(6); substitution of HO–C(1) of β-D-glucopyranose by a buta-1,3-diynyl substituent leads to a downfield shift of 0.70 ppm for HO–C(2), of 0.25 ppm for HO–C(3), and of 0.1 ppm for HO–C(4) and HO–C(6) [64]. Both substitutions are accompanied by an increase of J(2,OH) from *ca.* 5 to 6 Hz.

The J(H,OH) values of the diglucosides **2**–**4** are similar to those of the monoglucoside **31** and typical for more or less completely solvated OH groups (*Table 1*)[9]). In agreement with the above findings, J(6,OH) = 5.6–6.0 Hz is larger than J(7,OH) = 4.3–4.7 Hz and J(8,OH) = 5.0–5.4 Hz. Based on the experimental δ(OH) values of 4.81 ppm for HO–C(2), HO–C(3), and HO–C(4), and of 4.45 ppm for HO–C(6) of β-D-glucopyranose [65], and on the above-mentioned increments, the chemical-shift values for fully solvated OH groups of **31** and **2**–**4** may be calculated (values in parentheses in *Table 1*). A comparison of the calculated and experimental values for the monoglucoside **31** evidences the influence of the anthraquinonyl moiety; it leads to an additional downfield shift of *ca.* 0.1 ppm for HO–C(6), HO–C(7), and HO–C(8), and one of 0.07 ppm for HO–C(10). Interchain H-bonds should easily be detected by comparison of the δ(OH) values of the diglucosides with those of parent monoglucosides. Unfortunately, no experimental data are available for an anthraquinone bearing a single deca-1,3-diynitol substituent. We, therefore, assumed a similar influence of the anthraquinonyl moiety on the δ(OH) values of the deca-1,3-diynitol and the oct-1-ynitol substituents, and compared the experimental with the calculated δ(OH) values. According to these values, all OH groups of **2**–**4** are completely solvated with the exception of HO–C(6) of **3** (upfield shift of 0.14 ppm) and

HO–C(10A) and HO–C(10B) of **2** (downfield shift of 0.09 and 0.04 ppm, resp.). A weakly persistent flip-flop H-bond between the two HO–C(6) is expected to lead to a weak downfield shift [59][60], but this may not always be so, since a similar upfield shift has been observed for an 1,2-bis(oct-1-ynitol-1-yl)benzene, where such a flip-flop H-bond appears probable [35]. Alternatively, this upfield shift may be rationalised by cooperative O(6A)–H···O(6B)–H···O=C(9′) H-bonds. The weak downfield shifts of both HO–C(10A) and HO–C(10B) of **2** suggest a weakly persistent flip-flop H-bond between the primary OH groups.

Hydrogen bonding of **2** was also studied for a solution in (D_7)DMF (*Table 1*), a slightly weaker H-bond acceptor than (D_6)DMSO[10]). The OH signals are broader than in (D_6)DMSO indicating a faster H/H exchange. Thus, the smaller J(H,OH) observed may be due to this faster H/H exchange and not to stronger intramolecular H-bonds (see [60] for similar cases). The $\Delta\delta$(OH)/ΔT values are larger in (D_7)DMF than in (D_6)DMSO[11]). The interpretation of the δ(OH) values for solutions in (D_7)DMF is difficult in the absence of reliable reference compounds and shift increments.

The complete or almost complete absence of interchain H-bonds in (D_6)DMSO and (D_7)DMF solutions of **2** is in agreement with the expectation that oligomers of the templated model **1** (*Fig. 2*) may be useful mimics of cellulose I_β.

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Experimental Part

General. Solvents were distilled before use. Standard workup means that the reaction mixture was diluted with CH_2Cl_2 or AcOEt, and the org. layer was washed with brine and dried (Na_2SO_4). For coupling reactions, the solvents were degassed by vigorous purging with Ar for 20 min. Qual. TLC: 0.25-mm precoated *Merck* silica gel *60F-254/Merck RP 18254 S* plates, detection by heating with mostain (400 ml of 10% H_2SO_4 soln., 20 g of $(NH_4)_6Mo_7O_{24}\cdot 6\,H_2O$, 0.4 g of $Ce(SO_4)_2$) and/or by UV at 254 nm. Flash chromatography (FC): silica gel *Fluka 60* (0.04–0.063 mm). M.p. uncorrected. Optical rotations: 1-dm cell at 25°. UV Spectra: λ_{max} in nm (ε). IR Spectra: KBr disc or 2% CH_2Cl_2 soln. ^{1}H- and ^{13}C-NMR spectra chemical shifts δ in ppm and coupling constants J in Hz; ^{1}H assignments based on selective homonuclear decoupling experiments and ^{13}C assignments based on DEPT, and on comparison with published literature. CI-MS and FAB-MS: 3-nitrobenzyl alcohol and NH_3 as matrix; molecular ions of the substances with molecular weight >1000 were detected by MALDI-TOF mass spectrometry with either α-cyano-4-hydroxycinnamic acid (CCA, 0.05–0.1M in MeCN/EtOH) or indole-3-acetic acid (IAA, 0.05M in THF).

5,9-Anhydro-6,7,8,10-tetra-O-*benzyl-1,2,3,4-tetradeoxy-1-(trimethylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol* (**9**). Under Ar, a stirred and cooled (0°) soln. of 1,4-bis(trimethylsilyl)buta-1,3-diyne (2.65 g, 13.6 mmol) in THF (35 ml) was treated dropwise with 1.4M MeLi/LiBr in hexane (10.22 ml) over a period of 0.5 h and stirred for 4.5 h at 20°. The deep-brown-coloured soln. was transferred into a cooled (−78°) soln. of **5** (7.0 g, 13 mmol) in THF (35 ml) over a period of 10 min by a canula. The resulting pale brown soln. was stirred for 1.0 h, treated with sat. aq. NH_4Cl soln. (20 ml), stirred for 0.5 h, and worked up (Et_2O). Evaporation gave a brownish syrup (crude α-D-**8**/β-D-**8** 3:2, 8.55 g), which was taken to the next step without any further purification.

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[10]) The ability of a solvent to act as an H-acceptor in a solute-to-solvent H-bond is defined by the β scale. The β value is 0.76 for DMSO and 0.69 for DMF [66].

[11]) Only a few $\Delta\delta$(OH)/ΔT values of alcohols in (D_7)DMF are known; −5.8 to −8.2 ppb/K for completely solvated OH groups, and −1.8 ppb/K for a intramolecularly H-bonded OH group (deduced from the NMR plots in [67][68]); the $\Delta\delta$(OH)/ΔT values for **2** are in keeping with completely solvated OH groups.

At 0°, a soln. of $BF_3 \cdot Et_2O$ (17.8 ml, 142 mmol) and Et_3SiH (11.4 ml, 72 mmol) in CH_2Cl_2/MeCN 1:1 (30 ml) was added by a canula to a stirred and chilled (0°) soln. of crude α-D-**8**/β-D-**8** (8.5 g, 12.9 mmol) in CH_2Cl_2/MeCN 1:1 (40 ml) during 0.5 h. The mixture was stirred for 2.5 h, treated with sat. aq. $NaHCO_3$ soln. (28.5 ml), stirred for 15 min, and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 1:16) gave **9** (6.28 g, 76% from **5**) as a colourless-to-pale-yellow oil.

Data of Crude α-D-**8**/β-D-**8**: R_f (AcOEt/hexane 1:2) 0.76. FAB-MS: 683 (9, $[M+Na]^+$), 667 (11, $[M+Li]^+$), 659 (3, $[M-1]^+$), 535 (100).

Data of **9**: R_f (AcOEt/hexane 1:3) 0.86. $[\alpha]_D^{25} = -32.8$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 268 (2649). IR (CH_2Cl_2): 3090*w*, 3034*w*, 2960*w*, 2905*m*, 2871*m*, 2111*w*, 1606*w*, 1497*m*, 1454*m*, 1421*m*, 1399*w*, 1361*m*, 1209*w*, 1132*m*, 1092*s*, 1068*s*, 1028*m*, 999*m*, 896*m*, 867*s*, 847*s*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 2*; additionally, 7.40–7.00 (*m*, 20 arom. H); 4.95 (*d*, $J = 10.9$, PhC*H*); 4.85 (*d*, $J = 11.2$, PhC*H*); 4.81 (*d*, $J \approx 11.0$, PhC*H*); 4.75 (*d*, $J \approx 12.0$, PhC*H*); 4.71 (*d*, $J = 10.9$, PhC*H*); 4.58 (*d*, $J = 11.5$, PhC*H*); 4.47 (*d*, $J = 11.8$, PhC*H*); 4.35 (*d*, $J = 12.1$, PhC*H*); 0.03 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Table 3*; additionally, 138.51, 137.80 (2*s*); 138.06 (*s*, 2 C); 128.60–127.76 (several *d*); 75.72, 75.59, 75.11, 73.55 (4*t*, 4 Ph*C*H$_2$); −0.65 (*q*, Me_3Si). FAB-MS: 643 (4, $[M-1]^+$), 181 (68), 91 (100). Anal. calc. for $C_{41}H_{44}O_5Si \cdot 0.66\ H_2O$ (656.76): C 74.97, H 6.96; found: C 74.92, H 7.08.

5,9-Anhydro-6,7,8,10-tetra-O-*benzyl-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol* (**10**). At 0°, a soln. of **9** (3.0 g, 4.65 mmol) in THF (25 ml) was treated with a soln. of MeONa (0.5 g, 9.3 mmol) in MeOH (50 ml), stirred for 1 h, and passed through a pad of cation-exchange resin (*IR-120*, H^+ form, 20 ml wet). Evaporation of the neutral eluent and FC (AcOEt/hexane 1:11) gave **10** (2.20 g, 83%), which was used immediately in the next step. Pale yellow liquid (changed to dark brown within several hours at 25°). R_f (AcOEt/hexane 1:7) 0.39. $[\alpha]_D^{25} = -33.3$ ($c = 1.0$, $CHCl_3$). UV ($CHCl_3$): 281 (165). IR (CH_2Cl_2): 3295*m*, 3090*w*, 3034*w*, 2909*w*, 2871*m*, 2068*w*, 1605*w*, 1497*m*, 1479*w*, 1454*m*, 1398*w*, 1361*m*, 1293*w*, 1210*w*, 1133*m*, 1092*s*, 1068*s*, 1028*m*, 999*w*, 914*w*, 822*w*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 2*; additionally, 7.40–7.00 (*m*, 20 arom. H); 4.89 (*d*, $J = 10.9$, PhC*H*); 4.85 (*d*, $J = 11.5$, PhC*H*); 4.81 (*d*, $J \approx 10.5$, PhC*H*); 4.75 (*d*, $J = 11.5$, PhC*H*); 4.69 (*d*, $J = 10.9$, PhC*H*); 4.57 (*d*, $J = 11.2$, PhC*H*); 4.45 (*d*, $J = 12.1$, PhC*H*); 4.33 (*d*, $J = 12.1$, PhC*H*); 1.50 (*d*, $J = 0.9$, H–C(1)). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Table 3*; additionally, 138.48, 137.68 (2*s*); 138.01 (*s*, 2 C); 128.52–127.78 (several *d*); 75.72, 75.61, 75.11, 73.55 (4*t*, 4 Ph*C*H$_2$). EI-MS: 572 (15, M^+), 481 (57), 181 (21), 91 (100).

6,7,8,10-Tetra-O-*acetyl-5,9-anhydro-1-(trimethylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol* (**11**). At −40°, a soln. of TMSOTf (1.94 ml, 10.7 mmol) in Ac_2O (4 ml) was added dropwise to a stirred soln. of **9** (0.87 g, 1.34 mmol) in Ac_2O (30 ml). The mixture was slowly warmed to 20°, stirred for 12 h, stirred at 40° for 0.5 h, cooled to 0°, treated slowly with sat. aq. $NaHCO_3$ soln. (3.6 ml), stirred for 0.5 h, and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 1:5) afforded a colourless solid, which was recrystallized in AcOEt/hexane to give needles of **11** (0.365 g, 60%). R_f(AcOEt/hexane 1:2) 0.23. M.p. 128.9° (dec). $[\alpha]_D^{25} = -32.8$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 268 (977). IR (CH_2Cl_2): 3068*w*, 2962*w*, 2867*w*, 2300*w*, 2112*w*, 1756*s*, 1606*w*, 1424*w*, 1373*m*, 1301*w*, 1229*s*, 1097*m*, 1050*s*, 918*w*, 850*m*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 2*; additionally, 1.67, 1.65, 1.64, 1.62 (4*s*, 4 AcO); −0.02 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Table 3*; additionally, 170.82, 170.38, 169.44, 169.26 (4*s*, 4 C=O); 20.59 (*q*, Me); 20.46 (*q*, 2 Me); 20.41 (*q*, Me); −0.61 (*q*, Me_3Si). EI-MS: 452 (1, M^+), 259 (25), 217 (46), 85 (66), 83 (100), 49 (57). Anal. calc. for $C_{21}H_{28}O_9Si$ (452.53): C 55.74, H 6.24; found: C 55.56, H 6.16.

6,7,8,10-Tetra-O-*acetyl-5,9-anhydro*-D-glycero-D-gulo-*deca-1,3-diynitol* (**12**). *From* **10**: At −40°, a soln. of TMSOTf (3.7 ml, 27.9 mmol) in Ac_2O (10 ml) was added dropwise to a stirred soln. of **10** (2.0 g, 3.5 mmol) also in Ac_2O (30 ml). The soln. was slowly brought to 20°, stirred at r.t. for 12 h and at 40° for 0.5 h, cooled to 0° and treated slowly with sat. aq. $NaHCO_3$ soln. (10 ml), stirred for 0.5 h, and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 1:3) afforded a colourless solid, which was recrystallized in AcOEt/hexane to give needles of **12** (1.05 g, 79%).

From **11**: At 0°, a soln. of $Bu_4NF \cdot 3\ H_2O$ (11 mg, 0.03 mmol) in THF (2 ml) was added dropwise to a stirred soln. of **11** (50 mg, 0.11 mmol) also in THF (2 ml). The soln. was treated with H_2O (2 ml) and stirred at 20° for 0.5 h, and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 1:3) afforded a colourless solid, which was recrystallized in AcOEt/hexane to give needles of **12** (40 mg, 95%). R_f (AcOEt/hexane 1:2) 0.23. M.p. 129° (dec). $[\alpha]_D^{25} = -21.5$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 270 (19). IR (CH_2Cl_2): 3295*m*, 3068*w*, 2958*w*, 2874*w*, 2244*w*, 2100*w*, 1757*s*, 1422*w*, 1369*m*, 1303*w*, 1228*s*, 1174*w*, 1099*m*, 1049*s*, 982*w*, 958*w*, 911*w*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 2*; additionally, 1.67, 1.63 (2*s*, 2 AcO); 1.65 (br. *s*, 2 AcO); 1.43 (*d*, $J = 0.9$, H–C(1)). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Table 3*; additionally, 170.80, 170.36, 169.42, 169.23 (4*s*, 4 C=O); 20.59, 20.44 (2*q*, 2 Me); 20.39 (*q*, 2 Me). EI-MS: 380 (3, M^+), 259 (26), 200 (22), 187 (33), 158 (40), 145 (60), 139 (100), 97 (25), 43 (22). Anal. calc. for $C_{18}H_{20}O_9$ (380.3): C 56.84, H 5.30; found: C 56.92, H 5.46.

Table 2. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of* **9**–**18** *in C_6D_6 Solution*[a])

	9	**10**	**11**	**12**	**13**	**14**	**15**[b])	**16**[b])	**17**[b])	**18**
H–C(5)	3.93	3.86	3.85	3.78	3.98	3.95	3.81	3.74	4.46	4.24
H–C(6)	3.56	3.51	5.32	5.28	5.40	5.38	3.48	5.24	3.58	3.54
H–C(7)	3.43	3.41	5.20	5.18	5.25	5.24	3.40	5.25	3.72	3.75
H–C(8)	3.70	3.69	5.14	5.13	5.19	5.18	3.69	5.05	3.89	3.77
H–C(9)	3.12	3.10	3.03	3.02	3.10	3.08	3.08	3.03	3.46	3.25
H_a–C(10)	3.64	3.62	4.16	4.16	4.22	4.19	3.62	4.16	3.76	3.68
H_b–C(10)	3.58	3.55	3.95	3.95	3.99	3.98	3.56	3.95	3.68	3.63
J(1,5)	–	0.9	–	0.9	–	–	–	–	–	[c])
J(5,6)	9.7	9.7	10.0	9.7	10.0	10.0	9.3	9.7	9.3	9.7
J(6,7)	9.0	9.3	9.0	9.0	9.3	9.3	9.0	9.3	9.0	9.0
J(7.8)	9.3	9.0	9.3	9.0	9.3	9.0	9.0	9.0	9.3	9.3
J(8,9)	9.8	9.9	9.9	9.7	9.7	9.7	9.7	9.7	9.7	10.0
J(9,10a)	3.7	3.4	4.7	4.7	4.7	4.7	3.6	5.0	3.7	4.3
J(9,10b)	1.9	1.9	1.9	2.2	2.2	2.2	1.9	2.2	1.9	1.9
J(10a,10b)	11.2	11.2	12.3	12.5	12.5	12.5	11.2	12.5	11.2	11.5

[a]) Assignments are based on homonuclear decoupling experiments for all the compounds. [b]) Same numbering as for **12**. [c]) $J(2,5) = 1.6$ Hz.

Table 3. *Selected ^{13}C-NMR Chemical Shifts* [ppm] *of* **9**–**18** *in $CDCl_3$ Solution*

	9	**10**	**11**	**12**	**13**	**14**	**15**[a])	**16**[a])	**17**[a])	**18**
C(1)	87.31	67.42	86.53	66.78	79.51	77.63	61.78[b])	61.50[b])	126.23[b])	156.85
C(2)	87.99	70.32[b])	89.20	69.57[b])	72.70	72.65	70.82[b])	71.61[b])	125.49[b])	84.49
C(3)	71.11	68.56[b])	70.69	69.51[b])	71.84	71.66	63.91[b])	64.40[b])	126.57[b])	81.17
C(4)	74.33	73.30	71.97	71.27	75.43	76.84	75.66	72.10	142.18	89.31
C(5)	70.16	70.00	69.01	68.80	69.25	69.27	70.21	68.98	78.18	70.56
C(6)	81.94	81.73	70.76	70.64	70.87	70.80	81.52	70.53	84.65	82.50
C(7)	85.96	85.96	73.49	73.36	73.51	73.49	86.03	73.29	86.55	85.98
C(8)	79.23	79.25	67.88	67.80	67.94	67.91	79.36	67.73	79.64	78.89
C(9)	77.52	77.42	76.01	76.08	76.05	76.05	77.42	76.21	77.62	77.71
C(10)	68.68	68.59	61.87	61.79	61.92	61.89	68.54	61.74	68.91	68.86

[a]) Same numbering as for **12**. [b]) Assignment may be interchanged.

X-Ray Analysis of **12**. Crystals were obtained from AcOEt/hexane. $C_{18}H_{20}O_9$ (380.34). Orthorhombic *P*212121; $a = 5.491$ (2) Å, $b = 14.198$ (8) Å, $c = 24.749$ (9) Å. $V = 1930$ (2) Å^3. $Z = 4$. $D_{calc} = 1.309$ Mg/m^3. From a crystal of size $0.35 \times 0.30 \times 0.20$ mm 2163 reflexions were measured on an *Enraf Nonius CAD-4* diffractometer with CuK_α radiation (graphite monochromator, $\lambda = 1.54184$ Å) [69]. The structure was solved by direct method with SHELXS-96 [70]. The non-H-atoms were refined anisotropically with SHELXL-97 [71]. H-atoms were obtained from a difference *Fourier* map and refined with constrained isotropic displacement parameters. Drawings of the molecule were performed with PLUTO [72] and ORTEP [73].

6,7,8,10-Tetra-O-*acetyl-5,9-anhydro-1,2,3,4-tetradeoxy-1-phenyl*-D-glycero-D-gulo-*deca-1,3-diynitol* (**13**). A stirred suspension of C_6H_5I (50 mg, 0.25 mmol), $Pd(PPh_3)_2Cl_2$ (8.6 mg, 0.012 mmol) and CuI (7.0 mg, 0.04 mmol) in Et_3N/DMF 1:5 (1.0 ml, degassed) was treated with a soln. of **12** (186 mg, 0.49 mmol) in Et_3N/DMF 1:5 (1.0 ml) over a period of 9 h at 20°. The soln. was stirred overnight and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 2:5) gave **13** (54 mg, 49%) as a colourless solid, which was recrystallized in AcOEt/hexane. R_f (AcOEt/hexane 1:2) 0.34. M.p. 158.3°. $[\alpha]_D^{25} = -43.9$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 301 (2680), 291 (13906), 278 (9783). IR (CH_2Cl_2): 3068*w*, 2958*w*, 2246*w*, 1757*s*, 1604*w*, 1492*w*, 1421*w*, 1369*m*, 1229*s*, 1136*w*, 1098*m*, 1047*m*, 920*w*, 896*w*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 2*; additionally, 7.22–7.14 (*m*, 3 arom. H); 6.90–6.76 (*m*, 2 arom. H); 1.70, 1.69, 1.68, 1.64 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Table 3*; additionally, 170.83, 170.40, 169.47, 169.33 (4*s*, 4 C=O); 132.81 (*d*, 2 C); 129.74 (*d*); 128.53 (*d*, 2 C);

120.99 (*s*); 20.60, 20.43 (2*q*, 2 Me); 20.49 (*q*, 2 Me). EI-MS: 913 (2, $[2M+1]^+$), 593 (20), 457 (100, $[M+1]^+$), 397 (25), 263 (33), 221 (30). Anal. calc. for $C_{24}H_{24}O_9$ (456.44): C 63.15, H 5.30; found: C 63.16, H 5.42.

6,7,8,10-Tetra-O-*acetyl-5,9-anhydro-1,2,3,4-tetradeoxy-1-(2-thienyl)*-D-glycero-D-gulo-*deca-1,3-diynitol* (**14**). A stirred suspension of C_4H_3SI (100 mg, 0.48 mmol), $Pd(PPh_3)_2Cl_2$ (16.7 mg, 0.024 mmol), and CuI (13.6 mg, 0.07 mmol) in degassed Et_3N/DMF 1:5 (1.0 ml) was treated with a soln. of **12** (272 mg, 0.71 mmol) in Et_3N/DMF 1:5 (1.0 ml) over a period of 4 h at 20°, stirred for 5 h, and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 2:5) gave **14** (154 mg, 70%) as a colourless solid, which was recrystallized in AcOEt/hexane. R_f (AcOEt/hexane 1:3) 0.28. M.p. 166.9–167.5°. $[\alpha]_D^{25} = -52.9$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 310 (15956), 297 (16904). IR (CH_2Cl_2): 3068*m*, 2987*m*, 2235*w*, 1757*s*, 1422*s*, 1369*m*, 1302*w*, 1229*s*, 1098*m*, 1049*m*, 896*s*, 856*w*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 2*; additionally, 6.89 (*dd*, $J \approx 3.7$, 1.0, H–C(3′)); 6.49 (*dd*, $J \approx 5.1$, 1.1, H–C(5′)); 6.31 (*dd*, $J = 5.0$, 3.7, H–C(4′)); 1.68, 1.67, 1.66, 1.63 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Table 3*; additionally, 170.83, 170.40, 169.46, 169.33 (4*s*, 4 C=O); 135.21 (*d*, C(3′)); 129.39 (*d*, C(5′)); 127.26 (*d*, C(4′)); 121.17 (*s*, C(2′)); 20.62 (*q*, Me); 20.49 (*q*, 2 Me); 20.43 (*q*, Me). EI-MS: 463 (1.2, $[M+1]^+$), 282 (25), 269 (33), 240 (26), 227 (100). Anal. calc. for $C_{22}H_{22}O_9S$ (462.47): C 57.14, H 4.79; found: C 57.02, H 4.58.

*1,1′-(Octa-1,3,5,7-tetrayne-1,8-diyl)bis[(1*S*)-1,5-anhydro-2,3,4,6-tetra*-O-*benzyl*-D-*glucitol]* (**15**). A soln. of **10** (150 mg, 0.26 mmol) in dry pyridine (4.2 ml) was treated with Cu_2Cl_2 (26 mg, 0.26 mmol), stirred under O_2 for 2.5 h at 35°, diluted with AcOEt (25 ml), and washed successively with sat. NH_4Cl and 3N HCl (20 ml). Workup and a fast FC (AcOEt/hexane 1:6) gave **15** (105 mg, 70%) as a white solid, which decomposed on standing at 25° (under day-light) but was stable at 0° for several months. R_f(AcOEt/hexane 1:7) 0.12. M.p. 149° (dec). $[\alpha]_D^{25} = -110.6$ ($c = 1.0$, $CHCl_3$). UV ($CHCl_3$): 364 (129), 338 (220), 316 (224), 282 (404). IR (CH_2Cl_2): 3089*w*, 3033*w*, 2909*w*, 2871*m*, 2232*w*, 2088*w*, 1955*w*, 1875*w*, 1815*w*, 1605*w*, 1497*m*, 1454*m*, 1398*w*, 1361*m*, 1210*w*, 1132*m*, 1092*s*, 1069*s*, 1028*m*, 997*m*, 914*w*, 883*w*, 832*w*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 2*; additionally, 7.40–7.04 (*m*, 20 arom. H); 4.85 (*d*, $J = 11.2$, PhC*H*); 4.82 (*d*, $J = 11.2$, PhC*H*); 4.80 (*d*, $J = 10.9$, PhC*H*); 4.76 (*d*, $J = 11.5$, PhC*H*); 4.66 (*d*, $J = 10.9$, PhC*H*); 4.58 (*d*, $J = 11.2$, PhC*H*); 4.45 (*d*, $J = 11.8$, PhC*H*); 4.33 (*d*, $J = 11.8$, PhC*H*). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Table 3*; additionally, 138.41, 137.51 (2*s*); 137.98 (*s*, 2 C); 128.62–127.83 (several *d*); 75.75, 75.66, 75.14, 73.59 (4*t*, 4 Ph*C*H_2). MALDI-MS: 1165 ($[M+Na]^+$). Anal. calc. for $C_{76}H_{70}O_{10}$ (1143.36): C 79.84, H 6.17; found: C 79.77, H 6.26.

*1,1′-(Octa-1,3,5,7-tetrayne-1,8-diyl)bis[(1*S*)-2,3,4,6-tetra*-O-*acetyl-1,5-anhydro*-D-*glucitol]* (**16**). A stirred soln. of **12** (50 mg, 0.13 mmol) in acetone (0.5 ml) was saturated with O_2, treated with freshly prepared $Cu_2Cl_2 \cdot$TMEDA complex (0.17 ml), and stirred at 25° for 4 h. After evaporation, a soln. of the residue in AcOEt was washed with 3N HCl (4.2 ml) and subjected to aqueous workup. Evaporation and a rapid FC (AcOEt/hexane 1:1) gave **16** (48 mg, 96%) as a white solid, which changes colour to deep brown on standing at 20°. R_f(AcOEt/hexane 1:1) 0.08. M.p. 151.2–153.7° (dec). UV ($CHCl_3$): 354 (214), 331 (241), 310 (214), 281 (261). IR (CH_2Cl_2): 3041*w*, 2958*w*, 2867*w*, 2092*w*, 1758*s*, 1606*w*, 1430*w*, 1368*m*, 1302*w*, 1229*s*, 1097*m*, 1048*m*, 906*w*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 2*; additionally, 1.68, 1.66, 1.64, 1.63 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Table 3*; additionally, 170.77, 170.30, 169.39, 169.18 (4*s*, 4 C=O); 20.57, 20.43 (2*q*, 2 Me); 20.39 (*q*, 2 Me). FAB-MS: 1517 (1, $[2M+1]^+$), 759 (100, $[M+1]^+$), 699 (25), 579 (22).

Treatment of **9** *with* $Na_2S \cdot 9\,H_2O$. A stirred soln. of **9** (0.75 g, 1.16 mmol) in 2-methoxyethanol was treated with solid $Na_2S \cdot 9\,H_2O$ (1.12 g, 4.65 mmol). The mixture was heated to 120° for 5 min, cooled to 25°, stirred for 2 h, diluted with AcOEt/hexane 3:5 (20 ml), and filtered through *Celite*. Evaporation and FC (AcOEt/hexane 1:11) gave **17** (0.45 g, 64%) as a colourless solid and **18** (35 mg, 5%) as an oil. Compound **17** was recrystallized from AcOEt/hexane.

*(1*R*)-1,5-Anhydro-2,3,4,6-tetra*-O-*benzyl-1*-C-*(2-thienyl)*-D-*glucitol* (**17**). R_f(AcOEt/hexane 1:3) 0.68. M.p. 102.4–104.3°. $[\alpha]_D^{25} = +22.2$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 264 (1522). IR (CH_2Cl_2): 3037*w*, 2869*m*, 1956*w*, 1880*w*, 1813*w*, 1605*w*, 1496*w*, 1452*m*, 1359*m*, 1294*w*, 1209*m*, 1094*s*, 1068*s*, 1028*m*, 911*w*, 833*w*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 2*; additionally, 7.00–7.40 (*m*, 21 arom. H); 6.90 (*dd*, $J = 5.3$, 1.3, H–C(5′)); 6.72 (*dd*, $J = 5.3$, 3.7, H–C(4′)); 4.95 (*d*, $J = 11.2$, PhC*H*); 4.91 (*d*, $J = 11.2$, PhC*H*); 4.88 (*d*, $J = 11.2$, PhC*H*); 4.69 (*d*, $J = 11.2$, PhC*H*); 4.58 (*d*, $J = 12.8$, PhC*H*); 4.54 (*d*, $J = 10.9$, PhC*H*); 4.45 (*d*, $J = 12.1$, PhC*H*); 4.11 (*d*, $J = 10.9$, PhC*H*). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Table 3*; additionally, 138.75, 138.51, 138.27, 137.88 (4*s*); 128.51–127.62 (several *d*); 75.64, 75.12, 75.08, 73.51 (4*t*, 4 Ph*C*H_2). FAB-MS: 1213 (1, $[2M+1]^+$), 605 (43, $[M-1]^+$), 499 (30), 391 (32), 307 (32), 253 (71), 181 (100). Anal. calc. for $C_{38}H_{38}O_5S$ (606.77): C 75.22, H 6.31; found: C 75.37, H 6.41.

*(*Z*)-5,9-Anhydro-6,7,8,10-tetra*-O-*benzyl-2,3,4-trideoxy-1*-O-*(2-methoxyethyl)*-D-glycero-D-gulo-*deca-1-en-3-ynitol* (**18**). R_f (AcOEt/hexane 1:3) 0.39. IR (CH_2Cl_2): 3068*w*, 2987*m*, 2306*w*, 1653*w*, 1558*w*, 1497*w*, 1422*s*, 1362*w*, 1238*w*, 1156*w*, 1095*w*, 1066*w*, 1028*w*, 896*s*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 2*; additionally, 7.50 (*d*, $J = 7.2$, 2 arom. H); 7.30–7.00 (*m*, 18 arom. H); 5.99 (*d*, $J = 6.2$, H–C(1)); 5.36 (*d*, $J = 10.9$, PhC*H*); 4.94

(d, J = 11.5, PhC*H*); 4.87 (d, J = 10.6, PhC*H*); 4.85 (d, J = 11.5, PhC*H*); 4.78 (d, J = 11.5, PhC*H*); 4.60 (d, J = 12.2, PhC*H*); 4.50 (d, J = 12.5, PhC*H*); 4.47 (dd, $J \approx 6$, 1.9, H–C(2)); 4.37 (d, J = 12.1, PhC*H*); 3.42, 3.41 (2*t*, J = 4.7, $MeOCH_2CH_2$); 2.96 (t, J = 4.7, $MeOCH_2$); 2.90 (*s*, MeO). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Table 3*; additionally, 138.78, 138.41, 138.23, 138.20 (4*s*); 128.64–127.65 (several *d*); 75.64, 75.24, 75.03, 73.47 (4*t*, 4 $PhCH_2$); 72.42, 71.53 (2*t*, $MeOCH_2CH_2$); 58.99 (*q*, MeO). FAB-MS: 1298 (1, $[2M+1]^+$), 649 (47, $[M+1]^+$), 181 (100).

1,8-Bis[(trifluoromethyl)sulfonyloxy]-9,10-anthraquinone (**20**). A stirred soln. of **19** (5.0 g, 20.8 mmol) in pyridine (85 ml) at $-10°$ (ice/NaCl) was treated dropwise with Tf_2O (10.25 ml, 62.5 mmol) over a period of 0.5 h, stirred at 0° for 44 h, and worked up (CH_2Cl_2). Evaporation and FC (AcOEt/hexane 1:8) gave **20** (8.03 g, 76.5%) as a yellow solid, which was recrystallized in CH_2Cl_2/hexane. R_f (AcOEt/hexane 1:9) 0.2. M.p. 138.4°. UV ($CHCl_3$): 326 (5597), 271 (7870). IR (CH_2Cl_2): 3089*w*, 1686*s*, 1597*m*, 1435*s*, 1320*s*, 1228*s*, 1192*m*, 1157*m*, 1139*s*, 962*s*, 860*s*, 824*s*, 794*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.38 (dd, J = 7.8, 1.2, H–C(4)); 7.91 (t, $J \approx 7.9$, H–C(3)); 7.69 (dd, $J \approx 8.2$, 1.1, H–C(2)). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Table 4*; additionally, 118.75 (q, ^1J(C,F) = 321.1, 2 CF_3). ^{19}F-NMR (282 MHz, $CDCl_3$): –73.03 (*s*, 2 CF_3). EI-MS: 504 (30, M^+), 348 (37), 307

Table 4. *^{13}C-NMR Chemical Shifts* [ppm] *for the Aromatic C-Atoms of* **19**–**30** *and* **32**–**37** *in $CDCl_3$ and of* **31** *and* **2**–**4** *in (D_6)DMSO Solution*[9])[a])

	19 [53]	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**
C(1′)	162.6	147.48	123.50	122.77	122.69	122.74	121.86	122.21	150.63	150.56	122.07
C(2′)	124.6	129.39	141.47	141.68	141.13[b])	141.57[b])	140.94[b])	141.48[b])	130.26	130.78	141.08
C(3′)	137.2	135.42	132.36	132.82	132.36[c])	132.64	132.55[c])	132.82	135.56	135.01[b])	133.61
C(4′)	120.0	127.69	127.19	127.65	[e])	[e])	127.20	127.80[c])	126.02	125.58	128.37
C(5′)					[e])	[e])	127.62	127.76[c])	119.42	127.72	119.44
C(6′)					132.33[c])	132.64	132.48[c])	132.82	136.71	135.31[b])	136.73
C(7′)					141.05[b])	141.53[b])	140.73[b])	141.75[b])	124.87	128.93	124.90
C(8′)					123.40	123.01	123.26	122.61	162.74	147.56	162.76
C(9′)	193.1	178.89	180.41	180.98	180.16	180.51	180.33	180.60	188.09	180.26	187.58
C(10′)	181.5	180.12	182.67	182.35	182.50	182.50	182.28	182.28	181.85	181.20	182.01
C(4′a)	115.8	134.58	133.56	133.75	133.59[d])	133.74[c])	133.53[d])	133.76[d])	135.40	134.17	133.46
C(10′a)					133.51[d])	133.70[c])	133.53[d])	133.66[d])	132.75	134.17	132.80
C(8′a)					134.92[d])	135.00[c])	134.87[d])	134.78[d])	116.59	126.63	116.38
C(9′a)	133.6	126.22	134.64	134.92	134.73[d])	134.55[c])	134.69[d])	134.41[d])	124.69	126.63	134.58

	30	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**2**	**3**	**4**
C(1′)	122.35	122.13	121.39	121.54	121.98	121.49	122.07	121.88	120.54	122.13	120.56
C(2′)	141.18	141.16	141.81	141.70	141.81	142.23	141.05	142.35	142.15	140.91	142.24
C(3′)	133.33	134.10	132.86	133.57	133.35	133.01	132.91	133.05	133.73[b])	133.68	133.75
C(4′)	127.83	127.03	128.11	128.62	129.09[b])	128.22	127.93	128.23	127.98	127.03	127.92
C(5′)	127.72	118.74	125.58	119.53	127.78	127.88			127.36		
C(6′)	134.89	136.90	134.84	136.83	135.03	132.88			133.52[b])		
C(7′)	128.95	124.36	130.45	124.97	129.14[b])	141.57			141.85		
C(8′)	147.60	161.49	150.51	162.92	147.73	122.36			122.40		
C(9′)	180.05	187.12	180.30	187.04	179.57	179.97	180.43	179.56	180.13	180.90	179.76
C(10′)	181.28	181.65	182.01	181.80	181.09	181.95	182.14	181.78	181.86	182.07	181.54
C(4′a)	133.00	132.72	133.75	133.57	133.43	133.78[b])	133.69	133.74	133.66[c])	133.44	133.50
C(10′a)	135.05	132.72	136.15	132.80	135.66	133.56[b])			133.66[c])		
C(8′a)	126.88	116.45	125.35	116.20	126.33	133.88[b])			133.79[c])		
C(9′a)	134.55	134.23	134.53	134.74	135.03	135.55[b])	134.29	135.18	135.44[c])	134.23	135.01

[a]) Assignments for phenols, phenol acetates, and sulfonates based on the assignments for **19**, its *O*-acetylated, *O*-methylated, and *O*-propylated derivatives [53–56]; assignments for acetylenes and buta-1,3-diynes based on the assignment for anthraquinone [53][56] and the increments for an ethynyl group [57]. [b]) [c]) [d]) Assignment may be interchanged. [e]) Hidden by signals of the Bn groups.

(51), 291 (25), 279 (55), 251 (50), 223 (77), 210 (25), 182 (34), 157 (33), 126 (56), 69 (100). Anal. calc. for $C_{16}H_6F_6O_8S_2$ (504.34): C 38.10, H 1.20; found: C 37.98, H 1.12.

1,8-Bis[(trimethylsilyl)ethynyl]-9,10-anthraquinone (**21**). A stirred soln. of **20** (0.5 g, 0.99 mmol) and $Pd(PPh_3)_2Cl_2$ (100 mg, 0.13 mmol) in freshly distilled, degassed DMF (20 ml) at 20° was treated with Et_3N (1.2 ml) and $Me_3SiC{\equiv}CH$ (0.49 ml, 3.47 mmol), heated to 90–100° for 2 h, cooled to 20°, stirred for 2 h, and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 1:49) gave **21** (0.29 g, 73%) as a yellow solid, which was recrystallized in hexane/pentane. R_f (AcOEt/hexane 2:8) 0.62. M.p. 153.7°. UV ($CHCl_3$): 374 (8569), 273 (40210). IR (CH_2Cl_2): 3041*w*, 2986*w*, 2963*w*, 2900*w*, 2148*w*, 1677*s*, 1606*w*, 1586*w*, 1573*w*, 1456*w*, 1428*w*, 1323*s*, 1238*m*, 1217*w*, 1158*w*, 1088*w*, 1027*w*, 956*m*, 896*m*, 851*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.26 (*dd*, $J\approx7.7$, 1.5, H–C(4)); 7.94 (*dd*, $J\approx7.7$, 1.5, H–C(2)); 7.67 (*t*, $J\approx7.7$, H–C(3)); 0.35 (*s*, Me_3Si). ^{1}H-NMR (300 MHz, C_6D_6): 8.00 (*dd*, $J=7.8$, 1.3, H–C(4)); 7.57 (*dd*, $J\approx7.6$, 1.4, H–C(2)); 6.82 (*t*, $J=7.8$, H–C(3)); 0.47 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): See *Table 4*; additionally, 103.76, 102.08 (2*s*, 2 C≡CSiMe$_3$); –0.20 (*q*, 2 Me_3Si). EI-MS: 400 (100, M^+), 385 (35), 73 (48). Anal. calc. for $C_{24}H_{24}O_2Si_2$ (400.62): C 71.95, H 6.04; found: C 71.82, H 5.81.

X-Ray Analysis of **21**. Crystals were obtained from hexane/pentane by slow diffusion. $C_{24}H_{24}O_2Si_2$ (400.61). Monoclinic $P21/c$; $a=9.283$ (8) Å, $b=12.02$ (6) Å, $c=20.732$ (10) Å; $\beta=92.44$ (5)°; $V=2313$ (12) Å^3; $Z=4$. $D_{calc}=1.151$ Mg/m^3. From a crystal of size $0.30\times0.20\times0.20$ mm, 4396 reflexions were measured on an *Enraf Nonius CAD-4* diffractometer with CuK_α radiation (graphite monochromator, $\lambda=1.54184$ Å) [69]. The structure was solved by direct methods with SIR 97 [74]. The non-H-atoms were refined anisotropically with SHELXL-97 [71]. The H-atoms were calculated at idealised positions and included in the structure factor calculation with fixed isotropic displacement parameters. Drawings of the molecule were performed with PLUTO [72] and ORTEP [73].

1,8-Diethynyl-9,10-anthraquinone (**22**). A stirred soln. of **21** (50 mg, 0.125 mmol) in EtOH (5.0 ml) was treated with solid KF (22.1 mg, 0.38 mmol) at 20°, stirred at 60° for 3 h, evaporated, and worked up (AcOEt). Evaporation and FC (CH_2Cl_2/hexane 1:1) gave **22** (30 mg, 94%) as a pale greenish solid, which was recrystallized in AcOEt/pentane. R_f(AcOEt/hexane 1:5) 0.35. M.p. 170–175° (dec). UV ($CHCl_3$): 363 (6990), 271 (29102). IR (CH_2Cl_2): 3289*m*, 3056*w*, 2100*w*, 1678*s*, 1572*m*, 1433*w*, 1322*s*, 1156*w*, 1011*w*, 917*w*, 850*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.34 (*dd*, $J\approx7.7$, 1.5, H–C(4)); 8.00 (*dd*, $J\approx7.7$, 1.5, H–C(2)); 7.75 (*t*, $J\approx7.7$, H–C(3)); 3.63 (*s*, C≡CH). ^{1}H-NMR (300 MHz, C_6D_6): 8.02 (*dd*, $J=7.8$, 1.3, H–C(4)); 7.47 (*dd*, $J\approx7.8$, 1.5, H–C(2)); 6.80 (*t*, $J\approx7.8$, H–C(3)); 3.22 (*s*, C≡CH). ^{13}C-NMR (50 MHz, $CDCl_3$): See *Table 4*; additionally, 84.30 (*s*, 2 *C*≡CH); 82.24 (*s*, 2 C≡*C*H). EI-MS: 256 (100, M^+), 200 (55), 100 (20). Anal. calc. for $C_{18}H_8O_2$ (256.25): C 84.37, H 3.15; found: C 84.52, H 2.86.

3,7-Anhydro-4,5,6,8-tetra-O-*benzyl-1,2-dideoxy-1*-C-*{8-[(trimethylsilyl)ethynyl]-9,10-anthraquinon-1-yl}*-D-glycero-D-gulo-*oct-1-ynitol* (**23**). Under Ar, a soln. of **20** (0.5 g, 0.992 mmol), $Pd(PPh_3)_2Cl_2$ (74.3 mg, 0.11 mmol), and **6** (0.71 g, 1.29 mmol) in freshly distilled and degassed DMF (20 ml) at 20° was treated with Et_3N (1.2 ml), stirred at 80–85° for 1 h, treated with $Me_3SiC{\equiv}CH$ (0.21 ml, 1.49 mmol), stirred for 2 h, cooled to 20°, and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 1:7) gave **21** (25 mg, 6%) as a solid and **23** (0.278 g, 33%) as an oil.

Data of **23**: R_f(AcOEt/hexane 1:3) 0.50. $[\alpha]_D^{25}=+5.4$ ($c=1$, $CHCl_3$). UV ($CHCl_3$): 368 (4466), 276 (16556). IR (CH_2Cl_2): 3041*m*, 2987*m*, 2686*w*, 2155*w*, 1677*m*, 1587*w*, 1572*w*, 1497*w*, 1454*m*, 1422*s*, 1361*m*, 1324*m*, 1215*w*, 1157*m*, 1092*m*, 1068*m*, 1028*m*, 1001*w*, 896*s*, 850*m*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 5*; additionally, 8.02 (*dd*, $J\approx7.8$, 1.3), 7.99 (*dd*, $J\approx8.1$, 1.3) (H–C(4′), H–C(5′)); 7.60 (br. *d*, $J=7.2$, 2 arom. H); 7.59 (*dd*, $J=7.8$, 1.3), 7.48 (*dd*, $J\approx7.5$, 1.2) (H–C(2′), H–C(7′)); 7.38 (br. *d*, $J\approx7.2$, 2 arom. H); 7.33 (br. *d*, $J\approx7.2$, 2 arom. H); 7.27 (br. *d*, $J\approx7.2$, 2 arom. H); 7.22–6.95 (*m*, 11 arom. H); 6.98 (br. *t*, $J\approx7.3$, 1 arom. H); 6.83 (*t*, $J\approx7.8$), 6.80 (*t*, $J\approx7.8$) (H–C(3′), H–C(6′)); 5.69 (*d*, $J=10.9$, PhC*H*); 5.16 (*d*, $J=11.2$, PhC*H*); 5.06 (*d*, $J=11.2$, PhC*H*); 4.97 (*d*, $J=11.2$, PhC*H*); 4.91 (*d*, $J=11.2$, PhC*H*); 4.69 (*d*, $J=11.2$, PhC*H*); 4.53 (*d*, $J=12.1$, PhC*H*); 4.41 (*d*, $J=12.1$, PhC*H*); 0.46 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Tables 4* and *6*; additionally, 138.72, 138.37, 138.06, 138.01 (4*s*); 128.38–127.07 (several *d*); 103.68, 102.14 (2*s*, *C*≡*C*SiMe$_3$); 75.61, 75.38, 75.11, 73.54 (4*t*, 4 PhCH_2); –0.03 (*q*, Me_3Si). CI-MS: 868 (5, $[M+NH_4]^+$), 91 (100).

3,7-Anhydro-4,5,6,8-tetra-O-*benzyl-1,2-dideoxy-1*-C-*(8-ethynyl-9,10-anthraquinon-1-yl)*-D-glycero-D-gulo-*oct-1-ynitol* (**24**). A soln. of **23** (175 mg, 0.205 mmol) in EtOH (40 ml) was treated with solid KF (36.5 mg, 0.62 mmol), stirred for 4.5 h, evaporated, and worked up (CH_2Cl_2). Evaporation and FC (CH_2Cl_2/hexane 9:1) gave **24** (129 mg, 80.5%) as a pale yellow solid, which was recrystallized in CH_2Cl_2/hexane. R_f(AcOEt/hexane 1:3) 0.42. M.p. 172.5–174.5° (dec.). $[\alpha]_D^{25}=+26.4$ ($c=1$, $CHCl_3$). UV ($CHCl_3$): 364 (6212), 276 (16443). IR (CH_2Cl_2): 3297*m*, 3033*w*, 2909*w*, 2870*m*, 1677*s*, 1605*w*, 1587*m*, 1574*m*, 1497*m*, 1454*m*, 1430*m*, 1361*m*, 1325*s*, 1212*w*, 1132*m*, 1092*s*, 1067*s*, 1028*m*, 997*m*, 914*w*, 850*w*, 803*m*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 5*;

Table 5. *Selected ^{1}H-NMR Chemical Shifts* [ppm][a]) *and Coupling Constants* [Hz] *of* **23**–**26**, **29**, **30**, *and* **32**–**37** *in C_6D_6 Solution*[9])

	23	**24**	**25**	**26**	**29**	**30**	**32**	**33**	**34**	**35**		**36**	**37**
										A	B		
H–C(5)	4.60	4.48	4.56	4.31	4.37	4.30	4.05	4.06	3.96	4.13	4.35	4.46	4.19
H–C(6)	4.16	4.11	5.77	5.72	5.71	5.73	5.45	5.46	5.46	5.51	5.75	5.72	5.50
H–C(7)	3.78	3.69	5.53	5.47	5.43	5.44	5.28	5.28	5.28	5.32	5.54	5.52	5.39
H–C(8)	3.96	3.87	5.41	5.38	5.36	5.37	5.22	5.21	5.21	5.38	5.40	5.42	5.28
H–C(9)	3.51	3.39	3.35	3.18	3.21	3.14	3.11	3.11	3.10	3.36	3.31	3.43	3.36
H_a–C(10)	3.79	3.74	4.36	4.30	4.29	4.33	4.24	4.22	4.22	4.36	4.41	4.42	4.34
H_b–C(10)	3.79	3.74	4.13	4.06	4.09	4.06	4.02	4.02	4.00	4.12	4.23	4.21	4.12
J(5,6)	9.7	9.7	10.0	10.0	10.0	10.3	10.0	10.0	10.0	10.0	10.0	10.0	9.7
J(6,7)	9.3	9.3	9.7	9.3	9.3	9.3	9.3	9.3	9.3	9.3	9.3	9.7	9.3
J(7,8)	9.0	9.0	9.3	9.3	9.3	9.3	9.3	9.0	9.3	9.3	9.3	9.3	9.3
J(8,9)	9.7	9.7	9.8	9.7	9.7	10.0	9.8	9.7	9.7	10.0	10.0	10.0	10.0
J(9,10a)	2.8	2.8	4.5	4.1	4.7	4.7	4.2	4.7	5.0	4.0	4.7	4.4	4.7
J(9,10b)	2.8	2.8	2.2	1.9	2.2	2.0	2.2	2.2	2.2	2.2	2.2	2.2	2.2
J(10a,10b)	[b])	[b])	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5

[a]) Assignments are based on homonuclear decoupling experiments. [b]) Not assigned.

additionally, 8.01 (*dd*, $J \approx 7.8$, 1.3, H–C(4′), H–C(5′)); 7.66 (br. *d*, 2 arom. H); 7.52 (*dd*, $J \approx 7.6$, 1.4), 7.44 (*dd*, $J \approx 7.6$, 1.4) (H–C(2′), H–C(7′)); 7.35 (br. *t*, 4 arom. H); 7.24 (br. *d*, 2 arom. H); 7.00–7.22 (*m*, 12 arom. H); 6.81 (*t*, $J = 7.8$), 6.79 (*t*, $J \approx 7.6$) (H–C(3′), H–C(6′)); 5.83 (*d*, $J = 11.2$, PhC*H*); 5.16 (*d*, $J = 11.2$, PhC*H*); 5.03 (*d*, $J = 11.5$, PhC*H*); 4.91 (*d*, $J = 10.9$, PhC*H*); 4.88 (*d*, $J = 10.9$, PhC*H*); 4.64 (*d*, $J = 11.2$, PhC*H*); 4.53 (*d*, $J = 12.1$, PhC*H*); 4.41 (*d*, $J = 11.8$, PhC*H*); 3.06 (*s*, C≡CH). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Tables 4* and *6*; additionally, 138.80, 138.72, 138.25, 138.22 (4*s*); 128.48–127.46 (several *d*); 84.23 (*s*, C≡CH); 82.16 (*s*, C≡*C*H); 75.72, 75.42, 75.09, 73.59 (4*t*, 4 Ph*C*H_2). FAB-MS: 1558 (2, $[2M+1]^+$), 779 (100, $[M+1]^+$), 581 (20). Anal. calc. for $C_{52}H_{42}O_7$ (778.89): C 80.19, H 5.43; found: C 80.02, H 5.54.

Treatment of **20** *with* **7** *and $Me_3SiC{\equiv}CH$*. Under Ar, a soln. of **20** (0.25 g, 0.49 mmol) and **7** (0.48 g, 1.36 mmol) in freshly distilled, degassed DMF (10 ml) was treated with Et_3N (0.6 ml) at 20°, followed by a soln. of $Pd(PPh_3)_2Cl_2$ (35 mg, 0.049 mmol) in DMF (5.0 ml), stirred at 85–90° for 45 min, cooled to 60°, treated with $Me_3Si{\equiv}CH$ (0.21 ml, 1.49 mmol), stirred for 2 h at 85–90°, cooled to 20°, and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 1:3 → 2:3) gave **21** (16 mg, 5%), **25** (130 mg, 21%), and **36** (110 mg, 24%). Compound **36**, a pale yellow solid, was recrystallized in CH_2Cl_2/MeOH.

4,5,6,8-Tetra-O-*acetyl-3,7-anhydro-1,2-dideoxy-1*-C-*{8-[(trimethylsilyl)ethynyl]-9,10-anthraquinonyl}*-D-glycero-D-gulo-*oct-1-ynitol* (**25**). Oil. R_f(AcOEt/hexane 1:2) 0.18. $[\alpha]_D^{25} = +44.3$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 368 (4479), 276 (14894). IR (CH_2Cl_2): 3068*w*, 2960*w*, 2149*w*, 1757*s*, 1677*m*, 1587*w*, 1573*w*, 1458*w*, 1430*m*, 1368*m*, 1324*m*, 1228*s*, 1099*w*, 1064*m*, 1041*m*, 982*w*, 958*w*, 901*w*, 872*w*, 850*m*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 5*; additionally, 8.00 (*dd*, $J \approx 7.8$, 1.3), 7.95 (*dd*, $J \approx 7.8$, 1.3), (H–C(4′), H–C(5′)); 7.54 (*dd*, $J \approx 7.8$, 1.3), 7.42 (*dd*, $J \approx 7.5$, 1.3) (H–C(2′), H–C(7′)); 6.82 (*t*, $J \approx 7.8$), 6.76 (*t*, $J \approx 7.8$) (H–C(3′), H–C(6′)); 2.13, 1.73, 1.71, 1.70 (4*s*, 4 AcO); 0.47 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Tables 4* and *6*; additionally, 170.74, 170.22, 169.67, 169.41 (4*s*, 4 OC=O); 103.70, 101.98 (2*s*, *C*≡*C*SiMe$_3$); 20.94, 20.78, 20.65, 20.58 (4*q*, 4 Me); −0.16 (*q*, Me_3Si). FAB-MS: 1317 (2, $[2M+1]^+$), 659 (100, $[M+1]^+$), 72 (22).

4,5,6,8-Tetra-O-*acetyl-3,7-anhydro-1,2-dideoxy-1*-C-*(8-ethynyl-9,10-anthraquinon-1-yl)*-D-glycero-D-gulo-*oct-1-ynitol* (**26**). Under Ar, a stirred soln. of **25** (100 mg, 0.148 mmol), in dry EtOH (25 ml) was treated with solid KF (26 mg, 0.45 mmol) at 20°, heated to 50°, stirred for 0.5 h, and evaporated. Workup (AcOEt), evaporation, and FC (AcOEt/hexane 1:2) gave **26** (50 mg, 57%) as a pale yellow solid, which was recrystallized in AcOEt/hexane. R_f (AcOEt/hexane 1:2) 0.19. M.p. 178.6–180.6° (dec). $[\alpha]_D^{25} = +38.5$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 362 (5080), 276 (12779). IR (CH_2Cl_2): 3297*w*, 3068*w*, 2955*w*, 2878*w*, 2111*w*, 1754*s*, 1676*m*, 1575*w*, 1430*w*, 1372*m*, 1324*m*, 1229*s*, 1090*m*, 1041*s*, 908*w*, 850*w*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 5*; additionally, 8.02 (*dd*, $J \approx 7.8$, 1.2), 7.97 (*dd*, $J \approx 7.8$, 1.2) (H–C(4′), H–C(5′)); 7.46 (*dd*, $J \approx 7.8$, 1.2), 7.42 (*dd*, $J \approx 7.8$, 1.2) (H–C(2′), H–C(7′)); 6.81 (*t*, $J \approx 7.8$), 6.76 (*t*, $J \approx 7.8$) (H–C(3′), H–C(6′)); 3.27 (*s*, C≡CH); 2.22, 1.75, 1.70,

Table 6. *^{13}C-NMR Chemical Shifts* [ppm][a]) *for the Oct-1-ynitol and Deca-1,3-dynitol Moieties of* **23**–**26**, **29**, **30**, *and* **32**–**37** *in $CDCl_3$, and of* **31** *and* **2**–**4** *in (D_6)DMSO Solution*[9])

	23	**24**	**25**	**26**	**29**	**30**	**32**	**33**	**34**
C(1)	–	–	–	–	–	–	78.68[b])	79.67[b])	79.46[b])
C(2)	–	–	–	–	–	–	77.79[b])	77.97[b])	77.15[b])
C(3)	84.60	84.80	86.04	86.13	85.83	85.12	72.18	71.97	71.99
C(4)	92.14	92.92	88.76	89.35	89.93	89.73	78.04[b])	78.70[b])	78.28[b])
C(5)	70.84	70.84	69.78	69.69	69.54	69.51	69.35	69.36	69.36
C(6)	82.29	82.39	70.88	70.92	71.16	70.90	70.89	70.87	70.77
C(7)	86.19	86.30	73.57	73.70	73.81	73.65	73.57	73.54	73.57
C(8)	79.20	79.23	68.28	68.23	68.05	68.25	67.94	67.94	68.01
C(9)	77.68	77.78	76.05	76.01	76.08	76.00	76.13	76.18	76.13
C(10)	68.89	68.98	62.07	62.10	62.04	62.12	61.94	61.94	61.97
	35[a])		**36**	**37**	**31**	**2**[a])		**3**[a])	**4**
	A	B				A	B		
C(1)	79.15[b])	–	–	79.52[b])	–	79.22	–	–	79.16
C(2)	78.28[b])	–	–	78.15[b])	–	77.49	–	–	77.32
C(3)	72.20	86.03	86.20	72.45	83.85	69.86	84.35	83.95	69.62
C(4)	79.15[b])	89.83	80.39	78.41[b])	95.01	84.71	94.45	94.01	84.92
C(5)	69.22	69.60	69.61	69.33	71.18	71.05	71.36	71.06	70.89
C(6)	70.80	70.87	71.13	70.88	73.83	73.69	74.19	74.10	73.50
C(7)	73.52	73.59	73.55	73.52	77.73	77.80	77.80	77.51	77.67
C(8)	68.30	67.88	68.28	68.00	69.95	69.97	70.10	69.99	69.75
C(9)	76.08	75.88	75.98	76.03	81.19	81.32	81.21	81.05	81.30
C(10)	62.07	61.89	62.10	62.00	61.12	61.31	61.31	61.12	61.09

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

1.68 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Tables 4* and *6*; additionally, 170.92, 170.50, 169.9, 169.60 (4*s*, 4 OC=O); 84.28 (*s*, *C*≡CH); 82.37 (*s*, C≡*C*H); 20.92, 20.70, 20.57, 20.48 (4*q*, 4 Me). FAB-MS: 1173 (8, $[2M+1]^+$), 587 (100, $[M+1]^+$).

9,10-Dihydro-8-hydroxy-9,10-dioxoanthracen-1-yl Acetate (**27**). Under Ar, at 25°, a soln. of **19** (8.0 g, 0.033 mol) in Ac_2O (160 ml) was treated with boric acid (8.1 g, 0.131 mol). The suspension was heated at 90° for 21 h, allowed to cool to 25° and poured in cold water (1.1 l). The orange precipitate was filtered off, dissolved in $CHCl_3$ (400 ml), and worked up. Evaporation and recrystallisation in AcOEt/hexane gave **27** (8.8 g, 94%) [45] as orange crystals. R_f(AcOEt/hexane 1:7) 0.20. M.p. 171.5°. IR (KBr): 3456*w*, 3099*w*, 1766*s*, 1673*s*, 1633*s*, 1593*s*, 1579*m*, 1492*w*, 1443*m*, 1364*m*, 1345*m*, 1317*w*, 1287*s*, 1245*s*, 1187*s*, 1087*w*, 1064*w*, 1014*w*, 972*w*, 919*w*, 893*m*, 850*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 12.55 (*s*, OH); 8.26 (*dd*, *J* = 7.8, 1.3, H–C(4)); 7.80 (*t*, *J* = 7.8, H–C(3)); 7.78 (*dd*, *J* = 7.5, 1.3, H–C(5)); 7.64 (*t*, *J* = 7.9, H–C(6)); 7.41 (*d*, *J* = 7.8, H–C(2)); 7.28 (*dd*, *J* = 7.8, 0.9, H–C(7)); 2.47 (*s*, AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Table 4*; additionally, 169.68 (*s*, OC=O); 21.04 (*q*, Me).

9,10-Dihydro-9,10-dioxo-8-[(trifluoromethyl)sulfonyloxy]anthracen-1-yl Acetate (**28**). Under Ar, a suspension of **27** (4.0 g, 14.2 mmol) in dry CH_2Cl_2 (80 ml) was treated at 25° with distilled Et_3N (3.95 ml, 28.4 mmol), stirred for 15 min, cooled to −78°, treated dropwise with Tf_2O (3.0 ml, 18.4 mmol), stirred for 30 min, allowed to warm to 0°, and stirred for 1 h. The mixture was diluted with CH_2Cl_2, treated with H_2O (5 ml), stirred for 30 min, and worked up. Evaporation, FC (AcOEt/hexane 1:9), and recrystallization in AcOEt/hexane gave **28** (5.0 g, 85%) as yellow crystals. R_f (AcOEt/hexane 1:2) 0.4. M.p. 134.9°. UV ($CHCl_3$): 333 (4868), 273 (7216). IR (CH_2Cl_2): 3005*w*, 1769*m*, 1681*s*, 1595*m*, 1432*s*, 1369*w*, 1319*s*, 1214*s*, 1193*s*, 1157*m*, 1139*m*, 1037*w*, 1008*m*, 962*m*, 888*m*, 855*m*, 844*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.37 (*dd*, *J* = 7.8, 1.3), 8.24 (*dd*, *J* = 7.8, 1.2) (H–C(4), H–C(5)); 7.85 (*t*, *J* = 8.1), 7.82 (*t*, *J* = 7.8) (H–C(3), H–C(6)); 7.61 (br. *d*, *J* = 8.1), 7.48 (*dd*, *J* = 8.1, 1.2) (H–C(2), H–C(7)); 2.49 (*s*, AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Table 4*; additionally, 169.86 (*s*, OC=O); 118.81 (*q*, ^1J(C,F) = 321, CF_3); 20.88 (*q*, Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −73.29 (*s*, CF_3).

EI-MS: 415 (0.3, $[M+1]^+$), 372 (100), 260 (19), 211 (68), 155 (22). Anal. calc. for $C_{17}H_9F_3O_7S$ (414.31): C 49.28, H 2.19; found: C 49.40, H 2.03.

4,5,6,8-Tetra-O-*acetyl-3,7-anhydro-1,2-dideoxy-1*-C-*(8-hydroxy-9,10-anthraquinonyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**29**). Under Ar, a stirred suspension of **28** (1.5 g, 3.6 mmol), $Pd(PPh_3)_2Cl_2$ (127 mg, 0.18 mmol), and CuI (103 mg, 0.54 mmol) in degassed Et_3N/DMF 1:5 (15 ml) was treated with a soln. of **7** (2.65 g, 7.24 mmol) in Et_3N/DMF 1:5 (15 ml) over a period of 3 h at 60°, stirred for 3 h, and treated with solid $(NH_4)_2CO_3$ (0.7 g, 7.3 mmol), and stirred at 23° for 12 h. After treatment with additional $(NH_4)_2CO_3$ (0.35 g, 3.65 mmol), stirring was continued for 8 h. Workup (AcOEt), evaporation, and FC (AcOEt/hexane/CH_2Cl_2 1:2:0.3) gave bright yellow **29** (1.3 g, 62%), which was recrystallized in CH_2Cl_2/MeOH. R_f (AcOEt/hexane 1:1) 0.33. M.p. 225.7–227.7 (dec). $[\alpha]_D^{25} = +11.8$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 434 (4532), 410 (6302), 386 (5608), 368 (4954), 275 (12114). IR (CH_2Cl_2): 3056*w*, 2963*w*, 2879*w*, 2100*w*, 1754*s*, 1674*m*, 1641*m*, 1605*w*, 1579*w*, 1454*m*, 1433*w*, 1368*m*, 1316*m*, 1237*s*, 1155*w*, 1094*m*, 1042*s*, 960*w*, 901*w*, 849*w*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 5*; additionally, 12.83 (*s*, ArOH), 8.02 (*dd*, $J = 7.8, 1.6$), 7.66 (*dd*, $J = 7.2, 1.6$) (H–C(4′), H–C(5′)); 7.38 (*dd*, $J = 7.8, 1.2$), 6.96 (*dd*, $J = 8.4, 1.6$) (H–C(2′), H–C(7′)); 6.90 (*dd*, $J \approx 8.4, 7.2$, H–C(6′)); 6.78 (*t*, $J \approx 7.8$, H–C(3′)); 2.03, 1.74, 1.69, 1.68 (4*s*, 4 AcO). ^{13}C-NMR (50 MHz, $CDCl_3$): See *Tables 4* and *6*; additionally, 170.91, 170.54, 169.67, 169.55 (4*s*, 4 OC=O); 20.77, 20.70, 20.56, 20.49 (4*q*, 4 Me). FAB-MS: 1157 (6, $[2M+1]^+$), 579 (100, $[M+1]^+$), 537 (24). Anal. calc. for $C_{30}H_{26}O_{12}$ (578.52): C 62.28, H 4.53; found: C 62.24, H 4.75.

4,5,6,8-Tetra-O-*acetyl-3,7-anhydro-1,2-dideoxy-1*-C-*{[(8-trifluoromethyl)sulfonyloxy]-9,10-anthraquinon-1-yl}*-D-glycero-D-gulo-*oct-1-ynitol* (**30**). A stirred soln. of **29** (0.9 g, 1.55 mmol) in dry CH_2Cl_2 (18 ml) was treated with Et_3N (430 µl, 3.1 mmol) at 23° and cooled to −78°. The resulting red suspension was treated with freshly distilled Tf_2O (330 µl, 2 mmol), allowed to warm to 0°, stirred for 30 min, and diluted with CH_2Cl_2 (250 ml). Workup, evaporation, and FC (AcOEt/hexane 1:2) gave pale yellow solid **30** (1.07 g, 97%), which was recrystallized in AcOEt/hexane. R_f (AcOEt/hexane 1:1) 0.55. M.p. 205.5–206.4° (dec). $[\alpha]_D^{25} = +53.3$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 366 (3637), 274 (13626). IR (CH_2Cl_2): 3068*w*, 2956*w*, 2111*w*, 1754*s*, 1682*m*, 1599*w*, 1430*m*, 1373*m*, 1322*m*, 1223*s*, 1140*m*, 1094*m*, 1042*m*, 899*w*, 836*m*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 5*; additionally, 7.88 (*dd*, $J = 7.8, 1.3$), 7.86 (*dd*, $J = 7.8, 1.3$) (H–C(4′), H–C(5′)); 7.36 (*dd*, $J = 7.8, 1.6$), 6.84 (br. *d*, $J \approx 7.8$) (H–C(2′), H–C(7′)); 6.72 (*t*, $J = 7.8$), 6.69 (*t*, $J \approx 7.9$) (H–C(3′), H–C(6′)); 2.20, 1.72, 1.72, 1.69 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Tables 4* and *6*; additionally, 170.96, 170.40, 170.02, 169.65 (4*s*, 4 OC=O); 118.86 (*q*, $^1J(C,F) = 322$, CF_3); 20.64, 20.59, 20.54, 20.51 (4*q*, 4 Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −73.00 (*s*, CF_3). FAB-MS: 2131 (0.5, $[3M+1]^+$), 1421 (57, $[2M+1]^+$), 711 (100, $[M+1]^+$), 669 (61), 651 (54), 475 (46). Anal. calc. for $C_{31}H_{25}F_3O_{14}S$ (710.58): C 52.40, H 3.55; found: C 52.59, H 3.64.

3,7-Anhydro-1,2-dideoxy-1-C-*(8-hydroxy-9,10-anthraquinon-1-yl)*-D-glycero-D-gulo-*oct-1-ynitol* (**31**). Under Ar, a stirred suspension of **29** (68 mg, 0.12 mmol) in dry MeOH (5.0 ml) was treated with a soln. of MeONa (9.5 mg, 0.18 mmol) in MeOH (5.0 ml) and stirred for 6 h at 24°. The deep red suspension was treated with H_2O (4.0 ml) and neutralised with dry *Amberlyst IR-120*. Filtration and evaporation gave **31** (40 mg, 83%). Yellow solid. R_f (*RP-18* silica gel; MeCN/H_2O 1:2) 0.10. M.p. 140° (dec). $[\alpha]_D^{25} = -184.5$ ($c = 1$, DMSO). IR (KBr): 3417*s*(br.), 2925*w*, 2859*w*, 1665*m*, 1636*s*, 1578*m*, 1458*m*, 1374*w*, 1357*m*, 1319*w*, 1288*m*, 1242*s*, 1203*m*, 1082*m*, 1028*w*, 923*w*, 847*m*. ^{1}H-NMR (300 MHz, (D_6)DMSO): See *Table 1*; additionally, 12.48 (*s*, HO–C(8′)); 8.24 (*dd*, $J = 7.8, 1.3$, H–C(4′)); 8.02 (*dd*, $J = 7.8, 1.6$, H–C(2′)); 7.91 (*t*, $J = 7.8$, H–C(3′)); 7.81 (*t*, $J = 7.9$, H–C(6′)); 7.72 (*dd*, $J = 7.8, 1.3$, H–C(5′)); 7.41 (*dd*, $J \approx 7.9, 1.3$, H–C(7′)); 4.20 (*d*, $J = 9.7$, H–C(3)); 3.72 (br. *dd*, $J = 11.2, 5.0$, H_a–C(8)); 3.45 (*dt*, $J = 11.5, 5.3$, H_b–C(8)); 3.28–3.08 (*m*, H–C(4), H–C(5), H–C(6), H–C(7)). ^{13}C-NMR (75 MHz, (D_6)DMSO): See *Tables 4* and *6*. HR-MALDI-TOF-MS: 433.088 ($C_{22}H_{18}NaO_8^+$, $[M+Na]^+$; calc. 433.089).

Coupling of **28** *with* **12**. *a*) Under Ar, a stirred suspension of **28** (100 mg, 0.242 mmol), $Pd(PPh_3)_2Cl_2$ (8.5 mg, 0.012 mmol), and CuI (6.9 mg, 0.036 mmol) in degassed Et_3N/DMF 1:5 (1.0 ml) was treated with a soln. of **12** (184 mg, 0.48 mmol) in Et_3N/DMF 1:5 (1.0 ml) over a period of 8 h, stirred for additional 12 h, and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 1:2) gave **32** (90 mg, 58%) and **33** (7.3 mg, 5%).

b) Under Ar, a stirred suspension of **28** (414 mg, 1 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol), and CuI (28.6 mg, 0.15 mmol) in degassed Et_3N/DMF 1:5 (4.0 ml) was treated with a soln. of **12** (761 mg, 2.0 mmol) in Et_3N/DMF 1:5 over a period of 9.0 h at 23°, stirred for additional 18 h, treated with solid $(NH_4)_2CO_3$ (155 mg, 2 mmol), stirred for 3 h, treated with additional $(NH_4)_2CO_3$ (155 mg, 2 mmol), stirred 18 h, and worked up (AcOEt). Evaporation and FC (AcOEt/hexane 1:2.8) gave bright yellow solid **33** (380 mg, 63%).

6,7,8,10-Tetra-O-*acetyl-5,9-anhydro-1,2,3,4-tetradeoxy-1-(8-acetoxy-9,10-anthraquinon-1-yl)*-D-glycero-D-gulo-*deca-1,3-diynitol* (**32**). R_f(AcOEt/hexane 1:1) 0.33. M.p. 203–215.6° (dec). $[\alpha]_D^{25} = -32.5$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 374 (5371), 310 (13448), 292 (12278), 279 (15786). IR (CH_2Cl_2): 3041*w*, 2945*w*, 2240*w*, 2155*w*, 1758*s*, 1678*s*, 1596*m*, 1573*w*, 1435*w*, 1369*m*, 1332*m*, 1228*s*, 1195*s*, 1158*w*, 1099*m*, 1036*m*, 959*w*, 913*w*, 896*w*, 853*w*.

^{1}H-NMR (300 MHz, C_6D_6): See *Table 5:* additionally, 8.00 (*dd*, $J \approx 7.3$, 1.7), 7.89 (*dd*, $J = 7.8$, 1.6) (H–C(4′), H–C(5′)); 7.18 (*dd*, $J \approx 7.8$, 1.2), 6.88 (*dd*, $J \approx 7.9$, 1.7) (H–C(2′), H–C(7′)); 6.94 (*t*, $J \approx 7.8$), 6.66 (*t*, $J = 7.6$) (H–C(3′), H–C(6′)); 2.34 (*s*, AcO–C(8′)); 1.76, 1.71, 1.68, 1.65 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Tables 4* and *6*; additionally, 170.85, 170.43, 169.96, 169.49, 169.26 (5*s*, 5 OC=O); 21.15, 20.64, 20.46 (3*q*, 3 Me); 20.51 (*q*, 2 Me). FAB-MS: 1289 (5, $[2\,M+1]^+$), 645 (100, $[M+1]^+$), 307 (40). Anal. calc. for $C_{34}H_{28}O_{13}$ (644.58): C 63.35, H 4.38; found: C 63.19, H 4.53.

6,7,8,10-Tetra-O-*acetyl-5,9-anhydro-1,2,3,4-tetradeoxy-1-(8-hydroxy-9,10-anthraquinon-1-yl)*-D-glycero-D-gulo-*deca-1,3-diynitol* (**33**). R_f(AcOEt/hexane 1:1) 0.42. M.p. 160–180° (dec). $[\alpha]_D^{25} = -39.2$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 435 (5968), 411 (8443), 395 (8760), 309 (11454), 281 (18337). IR (CH_2Cl_2): 2992*w*, 2971*w*, 2236*w*, 2154*w*, 1757*s*, 1674*m*, 1639*m*, 1600*w*, 1580*w*, 1455*w*, 1435*w*, 1368*m*, 1326*w*, 1237*s*, 1155*w*, 1098*w*, 1052*m*, 960*w*, 918*w*, 850*w*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 5*; additionally, 12.73 (*s*, OH), 7.99 (*dd*, $J = 7.8$, 1.2), 7.64 (*dd*, $J = 7.2$, 1.6) (H–C(4′), H–C(5′)); 7.20 (*dd*, $J = 7.8$, 1.2), 6.94 (*dd*, $J = 8.4$, 1.6) (H–C(2′), H–C(7′)); 6.88 (*dd*, $J \approx 8.3$, 7.0, H–C(6′)); 6.73 (*t*, $J = 7.8$, H–C(3′)); 1.77, 1.69, 1.68, 1.65 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Tables 4* and *6*; additionally, 170.86, 170.41, 169.49, 169.39 (4*s*, 4 OC=O); 20.64, 20.53, 20.49, 20.44 (4*q*, 4 Me). FAB-MS: 1205 (12, $[2\,M+1]^+$), 603 (100, $[M+1]^+$), 154 (17). Anal. calc. for $C_{32}H_{26}O_{12}$ (602.54): C 63.79, H 4.35; found: C 63.79, H 4.47.

6,7,8,10-Tetra-O-*acetyl-5,9-anhydro-1,2,3,4-tetradeoxy-1-{8-[(trifluoromethyl)sulfonyloxy]-9,10-anthraquinon-1-yl}*-D-glycero-D-gulo-*deca-1,3-diynitol* (**34**). A soln. of **33** (50 mg, 0.08 mmol) in dry CH_2Cl_2 (1.0 ml) was treated with Et_3N (23 µl, 0.17 mmol) at 23° and cooled to −78°. The resulting red suspension was treated with freshly distilled Tf_2O (18 µl, 0.11 mmol), allowed to warm to 0°, stirred for 30 min, diluted with CH_2Cl_2 (10 ml), treated with few drops of H_2O, stirred for 15 min, and worked up. Evaporation and FC (AcOEt/hexane 2:5) gave **34** (58 mg, 95%). R_f (AcOEt/hexane 1:1) 0.40. M.p. 192.9°–193° (dec). $[\alpha]_D^{25} = -6.6$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 383 (4210), 312 (11458), 294 (10816), 275 (14153). IR (CH_2Cl_2): 3041*w*, 2956*w*, 2233*w*, 2153*w*, 1757*s*, 1682*m*, 1598*w*, 1584*w*, 1572*w*, 1434*m*, 1369*m*, 1330*m*, 1316*m*, 1218*s*, 1156*m*, 1140*m*, 1098*m*, 1046*m*, 952*m*, 896*w*, 861*m*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 5*; additionally, 7.86 (*dd*, $J = 7.8$, 1.3), 7.84 (*dd*, $J = 7.8$, 1.6) (H–C(4′), H–C(5′)); 7.17 (*dd*, $J = 7.8$, 1.3), 6.86 (br. *d*, $J \approx 7.8$) (H–C(2′), H–C(7′)); 6.68 (*t*, $J = 7.8$), 6.67 (*t*, $J = 7.8$) (H–C(3′), H–C(6′)); 1.92, 1.70, 1.68, 1.65 (4*s*, AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Tables 4* and *6*; additionally, 170.90, 170.43 (2*s*, 2 OC=O); 169.54 (*s*, 2 OC=O); 118.86 (*q*, ^1J(C,F) = 321, CF_3); 20.62, 20.51, 20.44, 20.41 (4*q*, 4 Me). ^{19}F-NMR (282 MHz, $CDCl_3$): −72.97 (*s*, CF_3). FAB-MS: 2203 (2, $[3\,M+1]^+$), 1469 (30, $[2\,M+1]^+$), 735 (46, $[M+1]^+$), 499 (100). HR-MS: 735.0989 ($[C_{33}H_{26}F_3O_{14}S]^+$; calc. 735.0995).

6,7,8,10-Tetra-O-*acetyl-5,9-anhydro-1,2,3,4-tetradeoxy-1*-C-*[8-(4,5,6,8-tetra*-O-*acetyl-3,7-anhydro-1,2-dideoxy*-D-glycero-D-gulo-*oct-1-ynitol-1-yl)-9,10-anthraquinon-1-yl]*-D-glycero-D-gulo-*deca-1,3-diynitol* (**35**). Under Ar, a stirred suspension of **30** (1.0 g, 1.47 mmol), $Pd(PPh_3)_2Cl_2$ (49.4 mg, 0.07 mmol), and CuI (40.2 mg, 0.2 mmol) in degassed Et_3N/DMF 1:5 (10 ml) was treated with a soln. of **12** (1.07 g, 2.8 mmol) in Et_3N/DMF 1:5 (10 ml) over a period of 9 h at 21–23°. After stirring for additional 12 h and workup (AcOEt), evaporation and FC (AcOEt/hexane 1:1) gave light yellow **35** (1.0 g, 76%), which was recrystallized in CH_2Cl_2/MeOH. R_f (AcOEt/hexane 1:1) 0.27. M.p. 205.1–206.3° (dec). $[\alpha]_D^{25} = +16.8$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 373 (8721), 311 (13292), 288 (14543), 281 (23987). IR (CH_2Cl_2): 3068*w*, 2958*w*, 2878*w*, 2238*w*, 2144*w*, 1754*s*, 1677*m*, 1606*w*, 1565*w*, 1430*w*, 1373*m*, 1333*w*, 1312*w*, 1230*s*, 1096*m*, 1043*s*, 907*w*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 5*; additionally, 7.96 (*dd*, $J \approx 7.8$, 1.2, H–C(4′), H–C(5′)); 7.38 (*dd*, $J \approx 7.6$, 1.4, H–C(7′)); 7.21 (*dd*, $J \approx 7.6$, 1.4, H–C(2′)); 6.76 (*t*, $J = 7.8$, H–C(6′)); 6.71 (*t*, $J = 7.8$, H–C(3′)); 2.48, 1.82, 1.82, 1.79, 1.73, 1.72, 1.70, 1.67 (8*s*, 8 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): See *Tables 4* and *6*; additionally, 170.95, 170.81, 170.07, 169.60, 169.49, 169.41 (6*s*, 6 OC=O); 170.38 (*s*, 2 OC=O); 20.75, 20.70, 20.64, 20.57, 20.52 (5*q*, 5 Me); 20.47 (*q*, 3 Me). FAB-MS: 1881 (100, $[2\,M+1]^+$), 941 (86, $[M+1]^+$), 881 (34). Anal. calc. for $C_{48}H_{44}O_{20}\cdot 0.5\,H_2O$ (949.86): C 60.69, H 4.78; found: C 60.64, H 4.95.

1,1′-C-*(9,10-Anthraquinon-1,8-diyl)bis[4,5,6,8-tetra*-O-*acetyl-3,7-anhydro-1,2-dideoxy*-D-glycero-D-gulo-*oct-1-ynitol]* (**36**). Under Ar, a stirred suspension of **20** (0.5 g, 0.99 mmol), $Pd(PPh_3)_2Cl_2$ (69.5 mg, 0.1 mmol), CuI (56.5 mg, 0.3 mmol), and Bu_4NI (1.09 g, 2.9 mmol) in degassed Et_3N/DMF 1:5 (5 ml) was treated with a soln. of **7** (1.06 g, 3.0 mmol) in Et_3N/DMF 1:5 (5 ml) over a period of 5 h at 60°. After stirring for additional 2 h, workup (AcOEt), evaporation, and FC (AcOEt/hexane 2:3) gave pale orange solid **36** (0.43 g, 47%), which was recrystallized in CH_2Cl_2/MeOH. R_f(AcOEt/hexane 1:1) 0.19. M.p. 181.3–184.0° (dec). $[\alpha]_D^{25} = +69.7$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 365 (6865), 276 (19931). IR (CH_2Cl_2): 3041*w*, 2958*w*, 1757*s*, 1676*m*, 1588*w*, 1574*w*, 1460*w*, 1431*w*, 1368*m*, 1328*m*, 1228*s*, 1099*m*, 1065*m*, 1042*s*, 916*w*, 850*w*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 5*; additionally, 7.98 (*dd*, $J \approx 7.9$, 1.4, H–C(4′)); 7.52 (*dd*, $J \approx 7.6$, 1.4, H–C(2′)); 6.80 (*t*, $J = 7.8$, H–C(3′)); 2.14, 1.76, 1.75, 1.68 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Tables 4* and *6*; additionally, 170.82, 170.40, 169.86,

169.59 (4*s*, 8 OC=O); 20.77, 20.65, 20.54, 20.47 (4*q*, 8 Me). FAB-MS: 1833 (5, $[2M+1]^+$), 917 (100, $[M+1]^+$). Anal. calc. for $C_{46}H_{44}O_{20}\cdot 0.5\ H_2O$ (925.84): C 59.67, H 4.90; found: C 59.52, H 4.98.

*1,1′-C-(9,10-Anthraquinon-1,8-diyl)bis[6,7,8,10-tetra-*O*-acetyl-5,9-anhydro-1,2,3,4-tetradeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol]* (**37**). Under Ar, a stirred suspension of **20** (0.6 g, 1.19 mmol), $Pd(PPh_3)_2Cl_2$ (83.5 mg, 0.12 mmol), CuI (62 mg, 0.32 mmol), and Bu_4NI (1.32 g, 0.36 mmol) in degassed Et_3N/DMF 1:5 (6 ml) was treated with a soln. of **12** (1.36 g, 3.57 mmol) in Et_3N/DMF 1:5 (6 ml) over a period of 9 h at 20–23°. After stirring for additional 12 h, workup (AcOEt), evaporation, and FC (AcOEt/hexane 1:1) gave pale orange solid **37** (0.44 g, 38%), which was recrystallized in CH_2Cl_2/MeOH. R_f (AcOEt/hexane 2:1) 0.40. M.p. 189.8° (dec). $[\alpha]_D^{25} = +13.0$ ($c = 1$, $CHCl_3$). UV ($CHCl_3$): 382 (7772), 311 (16498), 295 (15206), 279 (23468). IR (CH_2Cl_2): 3041*w*, 2957*w*, 2878*w*, 2238*w*, 2152*w*, 1754*s*, 1677*m*, 1572*w*, 1429*w*, 1373*m*, 1335*m*, 1231*s*, 1148*w*, 1096*m*, 1048*s*, 949*w*, 905*w*, 854*w*. ^{1}H-NMR (300 MHz, C_6D_6): See *Table 5*; additionally, 7.95 (*dd*, $J = 7.8$, 1.6, H–C(4′)); 7.23 (*dd*, $J \approx 7.6$, 1.4, H–C(2′)); 6.73 (*t*, $J = 7.8$, H–C(3′)); 2.00, 1.76, 1.75, 1.66 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): See *Tables 4* and *6*; additionally, 170.89, 170.42 (2*s*, 4 OC=O); 169.53 (*s*, 4 OC=O); 20.66 (*q*, 4 Me), 20.50, 20.45 (2*q*, 4 Me). FAB-MS: 1929 (100, $[2M+1]^+$), 965 (69, $[M+1]^+$). Anal. calc. for $C_{50}H_{44}O_{20}\cdot H_2O$ (982.89): C 61.10, H 4.72; found: C 61.25, H 4.77.

General Procedure for the Deprotection of **35**–**37**. At 25°, a stirred suspension of KCN (1.75 mg, 0.025 mmol) and **35**, **36**, or **37** (0.05 mmol) in MeOH (2.5 ml) was treated with THF (5.0 ml) until a clear soln. was formed. After stirring for 3–4 h, the pale greenish-yellow soln. was passed through a small pad of silica gel (elution with MeOH/Et_2O 1:1), and the filtrate was evaporated. A suspension of the residue in hot MeOH was stirred for 15 min and filtered. Drying of the pale yellow solid gave **2** (78%), **3** (92%), or **4** (88%), resp.

*5,9-Anhydro-1,2,3,4-tetradeoxy-1-*C*-[8-(3,7-anhydro-1,2-dideoxy-*D-glycero-D-gulo-*oct-1-ynitol-1-yl)-9,10-anthraquinon-1-yl]-*D-glycero-D-gulo-*deca-1,3-diynitol* (**2**). R_f(*RP-18* silica gel, MeCN/H_2O 1:2) 0.21. M.p. 219.4–224.3 (dec). $[\alpha]_D^{25} = -15.3$ ($c = 1$, DMSO). IR (KBr): 3520*m*, 3348*m*, 2922*w*, 2230*w*, 2140*w*, 1733*w*, 1666*m*, 1566*w*, 1431*w*, 1338*m*, 1288*w*, 1083*m*, 1051*m*, 1027*m*, 903*w*, 848*w*. ^{1}H-NMR (500 MHz, (D_6)DMSO, assignment based on a DQFCOSY.GRASP and a HSQC.GRASP spectrum): See *Table 1*; additionally, 8.23 (*dd*, $J = 7.8$, 1.3), 8.19 (*dd*, $J \approx 7.7$, 1.4) (H–C(4′), H–C(5′)); 8.08 (*dd*, $J \approx 7.8$, 1.3), 8.00 (*dd*, $J \approx 7.8$, 1.3) (H–C(2′), H–C(7′)); 7.87 (*t*, $J = 7.7$), 7.86 (*t*, $J = 7.7$) (H–C(3′), H–C(6′)); 4.20 (*d*, $J = 9.5$, H–C(3B)); 4.11 (*d*, $J = 9.4$, H–C(5A)); 3.72–3.57 (*m*, H_a–C(10A), H_a–C(8B)); 3.53–3.42 (*m*, H_b–C(10A), H_b–C(8B)); 3.34 (*td*, $J = 9.4$, 5.8, H–C(4B)); 3.27–3.21 (*m*, H–C(6A), H–C(7A), H–C(7B)); 3.20–3.14 (*m*, H–C(8A), H–C(9A), H–C(5B)); 3.08 (*td*, $J = 9.0$, 5.3, H–C(6B)). ^{13}C-NMR (125 MHz, (D_6)DMSO, assignment based on a HSQC.GRASP spectrum): See *Tables 4* and *6*. FAB-MS: 605 (100, $[M+1]^+$), 338 (89). Anal. calc. for $C_{32}H_{28}O_{12}$ (604.57): C 63.57, H 4.67; found: C 63.41, H 4.86.

*1,1′-C-(9,10-Anthraquinon-1,8-diyl)bis[3,7-anhydro-1,2-dideoxy-*D-glycero-D-gulo-*oct-1-ynitol]* (**3**). R_f(*RP-18* silica gel, MeCN/H_2O 1:2) 0.32. M.p. >170° (dec). $[\alpha]_D^{25} = -0.4$ ($c = 1$, DMSO). IR (KBr): 3380*m*, 2910*w*, 1670*m*, 1569*w*, 1431*w*, 1329*m*, 1239*w*, 1081*m*, 1024*m*, 900*w*, 850*w*, 801*w*. ^{1}H-NMR (500 MHz, (D_6)DMSO, assignment based on a DQFCOSY.GRASP and a HSQC.GRASP spectrum): See *Table 1*; additionally, 8.20 (*dd*, $J = 7.7$, 1.4, H–C(4′)); 7.98 (*dd*, $J = 7.7$, 1.4, H–C(2′)); 7.86 (*t*, $J = 7.7$, H–C(3′)); 4.25 (*d*, $J = 9.6$, H–C(3)); 3.71 (*ddd*, $J = 12.1$, 5.7, 1.9, H_a–C(8)); 3.47 (*dt*, $J = 12.0$, 6.0, H_b–C(8)); 3.40 (*td*, $J = 9.2$, 5.0, H–C(4)); 3.22–3.28 (*m*, H–C(5), H–C(7)); 3.15 (*td*, $J = 9.3$, 4.6, H–C(6)); ^{13}C-NMR (75 MHz, (D_6)DMSO, assignment based on a HSQC.GRASP spectrum): See *Tables 4* and *6*. FAB-MS: 581 (7, $[M+1]^+$), 307 (100). Anal. calc. for $C_{30}H_{28}O_{12}\cdot 0.33\ H_2O$ (604.50): C 59.60, H 5.11; found: C 59.77, H 5.31.

*1,1′-C-(9,10-Anthraquinon-1,8-diyl)bis[5,9-anhydro-1,2,3,4-tetradeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol]* (**4**). R_f(*RP-18* silica gel, MeCN/H_2O 1:2) 0.10. $[\alpha]_D^{25} = -2.3$ ($c = 1$, DMSO). IR (KBr): 3361*m*, 2873*w*, 2233*w*, 2144*w*, 1736*w*, 1670*m*, 1566*w*, 1429*w*, 1338*m*, 1288*m*, 1081*m*, 1033*m*, 848*w*. ^{1}H-NMR (300 MHz, (D_6)DMSO): See *Table 1*; additionally, 8.26 (*dd*, $J = 7.7$, 1.4, H–C(4′)); 8.14 (*dd*, $J = 7.7$, 1.4, H–C(2′)); 7.91 (*t*, $J = 7.8$, H–C(3′)); 4.15 (*d*, $J = 9.0$, H–C(5)); 3.69 (br. *dd*, $J = 11.4$, 6.0, H_a–C(10)); 3.44 (*dt*, $J = 11.5$, 6.0, H_b–C(10)); 3.28–3.16 (*m*, H–C(6), H–C(7), H–C(9)); 3.11 (br. *td*, $J = 9.0$, 5.3, H–C(8)). ^{13}C-NMR (75 MHz, (D_6)DMSO): See *Tables 4* and *6*. FAB-MS: 629 (55, $[M+1]^+$), 307 (100).

REFERENCES

[1] B. Bernet, J. Xu, A. Vasella, *Helv. Chim. Acta* **2000**, *83*, 2072.

[2] G. Meshitsuka, A. Isogai, in 'Chemical Modification of Lignocellulosic Materials', Ed. D. N.-S. Hon, Marcel Dekker, Inc., New York, 1996, p. 11.

[3] R. H. Marchessault, A. Sarko, *Adv. Carbohydr. Chem.* **1967**, *22*, 421.

[4] T. Kondo, in 'Polysaccharides: Structural Diversity and Functional Versatality', Ed. S. Dumitriu, Marcel Dekker, Inc., New York, 1998, p. 131.
[5] J. Sugiyama, T. Imai, *Trends Glycosci. Glycotechnol*. **1999**, *11*, 23.
[6] P. Langan, Y. Nishiyama, H. Chanzy, *J. Am. Chem. Soc*. **1999**, *121*, 9940.
[7] K. H. Gardner, J. Blackwell, *Biopolymers* **1974**, *13*, 1975.
[8] R. H. Atalla, D. L. Vanderhart, *Science* **1984**, *223*, 283.
[9] D. L. Vanderhart, R. H. Atalla, *Macromolecules* **1984**, *17*, 1465.
[10] J. H. Wiley, R. H. Atalla, *ACS Symposium Series* **1987**, *340*, 151.
[11] A. J. Michell, *Carbohydr. Res.* **1988**, *173*, 185; A. J. Michell, *Carbohydr. Res.* **1993**, *241*, 47.
[12] J. Sugiyama, J. Persson, H. Chanzy, *Macromolecules* **1991**, *24*, 2461; J. Sugiyama, T. Okano, H. Yamamoto, F. Horii, *Macromolecules* **1990**, *23*, 3196.
[13] J. Sugiyama, R. Vuong, H. Chanzy, *Macromolecules* **1991**, *24*, 4168.
[14] T. Imai, J. Sugiyama, *Macromolecules* **1998**, *31*, 6275.
[15] A. Sarko, R. Muggli, *Macromolecules* **1974**, *7*, 486.
[16] V. L. Finkenstadt, R. P. Millane, *Macromolecules* **1998**, *31*, 7776.
[17] T. Imai, J. Sugiyama, T. Itoh, R. Horii, *J. Struct. Biol*. **1999**, *127*, 248.
[18] S. Raymond, B. Henrissat, D. T. Qui, A. Kvik, H. Chanzy, *Carbohydr. Res.* **1995**, *277*, 209; S. Raymond, A. Heyraud, D. T. Qui, A. Kvick, H. Chanzy, *Macromolecules* **1995**, *28*, 2096.
[19] K. Gessler, N. Krauss, T. Steiner, C. Betzel, A. Sarko, W. Saenger, *J. Am. Chem. Soc*. **1995**, *117*, 11397; K. Gessler, N. Krauss, T. Steiner, C. Betzel, C. Sandmann, W. Saenger, *Nature* **1994**, *266*, 1027.
[20] B. J. Poppleton, A. M. Mathieson, *Nature* **1968**, *219*, 1046.
[21] J. Xu, A. Vasella, *Helv. Chim. Acta* **1999**, *82*, 1728.
[22] F. Mohamadi, N. G. J. Richards, W. C. Guida, R. Liskamp, C. Caufield, M. Lipton, G. Chang, T. Hendrickson, W. C. Still, *J. Comput. Chem*. **1990**, *11*, 440.
[23] J. L. Sessler, R. Wang, *Angew. Chem.*, *Int. Ed*. **1998**, *37*, 1726; J. L. Sessler, R. Wang, *J. Am. Chem. Soc*. **1996**, *118*, 9808.
[24] G. T. Crisp, P. D. Turner, *Tetrahedron* **2000**, *56*, 8335.
[25] B. Hoffmann, Diplomarbeit, ETH-Zürich, 1997.
[26] K. Sonogashira, in 'Comprehensive Organic Synthesis', Eds. B. M. Trost and I. Fleming, Oxford, 1991, 3, p. 521.
[27] I. B. Campbell, 'The Sonogashira Cu-Pd-Catalysed Alkyne Coupling Reaction', in 'Organocopper Reagents: A Practical Approach', Ed. R. J. K. Taylor, Oxford University Press, Oxford, 1994, p. 217.
[28] L. Brandsma, S. F. Vasilevsky, H. D. Verkruijsse, 'Application of Transition Metal Catalysts in Organic Synthesis', Springer-Verlag, Berlin, 1998.
[29] K. Ritter, *Synthesis* **1993**, 735.
[30] J. Alzeer, Diss. ETH-Zürich No. 11383, 1995.
[31] A. B. Homes, C. L. D. Jenning-White, A. H. Schulthess, B. Akinde, D. R. M. Walton, *J. Chem. Soc.*, *Chem. Commun*. **1979**, 840.
[32] F. Freeman, D. S. H. L. Kim, E. Rodriguez, *J. Org. Chem*. **1993**, *58*, 2317.
[33] M. D. Lewis, J. K. Cha, Y. Kishi, *J. Am. Chem. Soc*. **1982**, *104*, 4976.
[34] T. Lowary, M. Meldal, A. Helmboldt, A. Vasella, K. Bock, *J. Org. Chem*. **1998**, *63*, 9057.
[35] J. Xu, A. Egger, B. Bernet, A. Vasella, *Helv. Chim. Acta* **1996**, *79*, 2004.
[36] C. Glaser, *Chem. Ber*. **1869**, *2*, 422.
[37] G. Eglinton, W. McCrae, 'The Coupling of Acetylenic Compounds', Interscience Publishers, New York, 1963.
[38] A. S. Hay, *J. Org. Chem*. **1962**, *27*, 3320.
[39] K. E. Schulte, J. Reisch, L. Hörner, *Angew. Chem.* **1960**, *72*, 920.
[40] J. Alzeer, A. Vasella, *Helv. Chim. Acta* **1995**, *78*, 177.
[41] P. R. Muddasani, E. Bozo, B. Bernet, A. Vasella, *Helv. Chim. Acta* **1994**, *77*, 257.
[42] B. Bernet, unpublished results.
[43] G. A. Kalabin, A. G. Proidakov, S. I. Radchenko, *J. Org. Chem. USSR* **1980**, *16*, 442.
[44] H. O. House, D. G. Koepsell, W. J. Campbell, *J. Org. Chem*. **1972**, *37*, 1003.
[45] F. Dimroth, *Chem. Ber*. **1921**, *54*, 3033; M. P. Cava, Z. Ahmed, N. Benfaremo, R. A. Murphy, G. J. Omalley, *Tetrahedron* **1984**, *40*, 4767; K. Krohn, U. Müller, W. Priyono, B. Sarstedt, A. Stoffregen, *Liebigs Ann. Chem*. **1984**, 306.
[46] J. K. Stille, J. H. Simpson, *J. Am. Chem. Soc*. **1987**, *109*, 2138.

[47] Q.-Y. Chen, Z.-Y. Yang, *Tetrahedron Lett*. **1986**, *27*, 1171.
[48] H. E. Katz, *J. Org. Chem*. **1989**, *54*, 2179.
[49] C. Cai, A. Vasella, *Helv. Chim. Acta* **1995**, *78*, 2053.
[50] N. A. Powell, S. D. Rychnovsky, *Tetrahedron Lett*. **1996**, *37*, 7901.
[51] M. Mikamo, *Carbohydr. Res.* **1989**, *191*, 150.
[52] G. Blay, M. L. Cardona, M. B. Garcia, J. R. Pedro, *Synthesis* **1989**, 438.
[53] A. Arnone, G. Fronza, R. Mondelli, J. S. Pyrek, *J. Magn. Reson*. **1977**, *28*, 69.
[54] Y. Berger, A. Castonguay, P. Brassard, *Org. Magn. Reson*. **1980**, *14*, 103.
[55] L. Echegoyen, Y. Hafez, R. C. Lawson, J. Demendoza, T. Torres, *J. Org. Chem*. **1993**, *58*, 2009.
[56] K. Danielsen, *Magn. Reson. Chem*. **1995**, *33*, 823.
[57] E. Pretsch, T. Clerc, J. Seibl, W. Simon, 'Table of Spectral Data for Structure Determination of Organic Compounds', Springer-Verlag, Berlin, 1989, p. C120.
[58] P. A. A. Klusener, J. C. Hanekamp, L. Brandsma, P. von Ragué Schleyer, *J. Org. Chem*. **1990**, *55*, 1311.
[59] B. Bernet, A. Vasella, *Helv. Chim. Acta* **2000**, *83*, 995.
[60] B. Bernet, A. Vasella, *Helv. Chim. Acta* **2000**, *83*, 2055.
[61] J. Alzeer, A. Vasella, *Helv. Chim. Acta* **1995**, *78*, 1219.
[62] A. Ernst, W. B. Schweizer, A. Vasella, *Helv. Chim. Acta* **1998**, *81*, 2157.
[63] T. V. Bohner, O.-S. Becker, A. Vasella, *Helv. Chim. Acta* **1999**, *82*, 198.
[64] B. Bernet, A. Vasella, in preparation.
[65] B. Gillet, D. Nicole, J.-J. Delpuech, B. Gross, *Org. Magn. Reson*. **1981**, *17*, 28.
[66] M. J. Kamlet, J. L. M. Abboud, M. H. Abraham, R. W. Taft, *J. Org. Chem*. **1983**, *48*, 2877; M. J. Kamlet, J. F. Gal, P. C. Maria, R. W. Taft, *J. Chem. Soc., Perkin Trans. 2* **1985**, 1583.
[67] I. Mc Ewen, M. Rönnqvist, P. Ahlberg, *J. Am. Chem. Soc*. **1993**, *115*, 3989.
[68] I. B. Yanachkov, G. W. Wright, *J. Org. Chem*. **1994**, *59*, 6739.
[69] Enraf-Nonius, *CAD-4 Software. Enraf-Nonius Delft*, The Netherlands, 1989.
[70] G. M. Sheldrick, 'Program for the Solution of Crystal Structures', University of Göttingen, Germany, 1993.
[71] G. M. Sheldrick, 'Program for the Refinement of Crystal Structures', University of Göttingen, Germany, 1997.
[72] F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, B. G. Hummelink-Peters, O. Kennard, W. D. S. Motherwell, J. R. Rodgers, D. G. Watson, *Acta Cryst.*, *Sect B* **1976**, *35*, 2331.
[73] C. K. Johnson, 'ORTEP II, Report ORNL-5138', Oak Ridge National Laboratory, Tennessee, 1976.
[74] A. Altomare, B. Carrozzini, C. G. L. C. Giacovazzo, A. Guagliardi, A. G. Moliterni, A. Rizzi, 'A Package for Crystal Structure Solution by Direct Methods and Refinement', 1997, Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche, Bari, 1997.

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