Functionalised Bicyclic *exo*-Glycals by Alkynol Cycloisomerisation of Hydroxy 1,3-Diynes and Hydroxy Haloalkynes

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Herrn Prof. Dr. *Rolf Huisgen* mit den besten Wünschen herzlich zugeeignet.

Functionalised bicyclic *exo*-glycals are readily obtained by base-catalysed (typically MeONa in MeOH) alkynol cycloisomerisation of ethynylated cyclic saccharides. Thus, base treatment of the phenylethynyl- and halogenoethynylated 1-*O*-acetyl-ribofuranoses **22**–**24** and the 4-ethynylated 1-thioglucopyranosides **30**–**33** gave – after deacetylation – selectively the (*Z*)-configured exocyclic enol ethers **26**–**28** (84–91%) and **34**–**37** (63–76%), respectively, resulting from a *trans*-5-*exo-dig* cyclisation. The ring closure to the *trans*-dioxahexahydroindans **34**–**37** is favoured by a concerted intramolecular protonation of the intermediate vinyl anion by the neighbouring HO–C(3). Cycloisomerisation of the 6-*O*-acetyl-4-(phenylethynyl)-1-thio-α-D-glucopyranoside **39** occurred *via* the corresponding phenylethynylated allenes to provide the *galacto*-configured (*Z*)- and (*E*)-*cis*-dioxahexahydroindans **40** (30%) and **41** (51%). Surprisingly, the HO–C(4) unprotected α-D-galactopyranosyl-buta-1,3-diyne **15** and the β-D-glucopyranosyl-buta-1,3-diyne **51** (and its 2-bromoethynyl analogue) undergo a 6-*exo-dig* ring closure to the 2,5-dioxabicyclo[2.2.2]octanes **16**–**19** and **52**/**53**, respectively, the ring closure requiring a boat conformation ($B_{1,4}$ for **15**, $^{1,4}B$ for **51**). Ring strain (*anti*-reflex effect) prevents an alkynol cycloisomerisation of 4-(phenylbuta-1,3-diynyl, bromoethynyl, or iodoethynyl)levoglucosan **56**–**59**, and **56** reacted by elimination to the hex-1-ene-3,5-diyne **59** (82%), while isomerisation of **57** and **58** led to epimeric mixtures of the haloallenes **60** (82%) and **61** (68%).

Introduction. – *exo*-Glycals are versatile synthetic intermediates used for the preparation of, *e.g.*, ulosides [1–3], substituted *endo*-glycals, and functionalised *C*-glycosides; their chemistry has recently been summarised by *Taillefumier* and *Chapleur* [4][1]). Methods for the synthesis of *exo*-glycals comprise the *Wittig*-type olefination of glyconolactones and glycosylphosphonium salts, the methylenation of glyconolactones with *Tebbe* and *Petasis* reagent, addition–elimination reaction, reductive elimination of ketopyranosyl bromides, cyclisation of ethenylated alditols induced by electrophiles, followed by elimination, and the *Ramberg–Bäcklund* rearrangement of glycosyl sulfones.

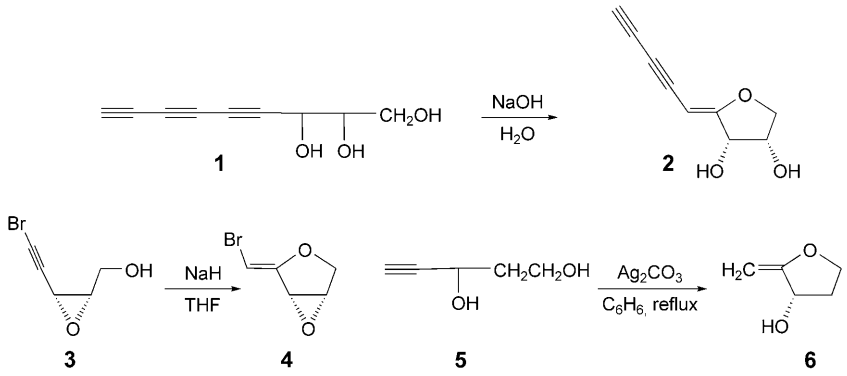
While alkynol cyclisation (cycloisomerisation) has been used as early as 1959 for the structure elucidation of hydroxylated oligoacetylenes, as illustrated by the high-yielding cyclisation of **1** to **2** [9][10] (*Scheme 1*), this facile cyclisation has, surprisingly, not been used for the transformation of carbohydrates into *exo*-glycals, nor has the high yielding base- or Ag^+-promoted cyclisation of hydroxylated haloalkynes and terminal alkynes, such as **3** to **4** and **5** to **6** [11–14] found such an application[2]). Acceptor-

[1]) For more recent reports, see [5–8].

[2]) Alk-3-ynols and alk-4-ynols undergo a ready formal 5-*endo-dig* and 6-*endo-dig* cyclisation to *endo*-glycals *via* transition-metal (Mo, Cr, W, Ru, Pd) vinylidene intermediates (see [15–17] and [18] for a recent review). Sequential cyclisation and addition of alkynols to the resulting *endo*-glycals was used for the preparation of oligosaccharides [16][19].

substituted acetylenes cyclise under basic conditions exclusively to 2-methylideneoxolanes; a 1*H*-isochromene derivative was identified as an isomerisation product from the corresponding 1-methylidene-1,3-dihydroisobenzofuran [20][21].

Scheme 1



In the context of the synthesis of acetylenosaccharides (see, *e.g.*, [22–25] and [26] for a recent review), we investigated the alkynol cycloisomerisation of buta-1,3-diynylated and haloethynylated alcohols to *exo*-glycals, and report the results of the cyclisation of glycofuranose- and glycopyranose-derived hydroxyacetylenes.

Results and Discussion. – To further evaluate the pronounced electrophilic properties of buta-1,3-diynes and haloalkynes, we calculated the orbital energies of acetylene (**7**), buta-1,3-diyne (**9**), the halogenated acetylenes **11**–**13**, HCN (**8**), and propiolonitrile (**10**) using the semi-empirical programs AM1 [27] and PM3 [28]) implemented in the AMPAC 6.55 package [29]. The electrophilicity of these compounds correlates with the energy and coefficients of the LUMO (*Table 1*). According to both AM1 and PM3 calculations, the LUMO energies of **8**–**13** are more or less below the one of acetylene (**7**), except for the iodoacetylene **13**, as calculated by PM3 (similar energy). The LUMO energy of buta-1,3-diyne (**9**) is markedly lower than that of acetylene (**7**) and HCN (**8**) (AM1: $\Delta E(\mathbf{9/7}) = 1.375$, $\Delta E(\mathbf{9/8}) = 1.047$; PM3: $\Delta E(\mathbf{9/7}) = 1.286$, $\Delta E(\mathbf{9/8}) = 0.734$ eV), evidencing a much higher electrophilicity. The propiolonitrile (**10**) is even more electrophilic (AM1: $\Delta E(\mathbf{10/7}) = 1.809$, $\Delta E(\mathbf{10/8}) = 1.481$; PM3: $\Delta E(\mathbf{10/7}) = 1.862$, $\Delta E(\mathbf{10/8}) = 1.310$ eV). The LUMO energy of the halogenated acetylenes **11**–**13** is higher than the one of buta-1,3-diyne (**9**), suggesting a reduced electrophilicity. According to the AM1 calculation, the LUMO energy drops from chloro- to bromo- and iodoacetylene, while PM3 calculation led to an inverse sequence. This difference is probably due to the decreasing accuracy in semi-empirical calculations of atoms of the lower rows; the high LUMO energy resulting in the PM3 calculation of the iodide **13** suggests that the heavier atoms are less well implemented in PM3 than in AM1, and that iodoacetylene (**13**) and bromoacetylene (**12**) are better acceptors for nucleophiles than chloroacetylene (**11**).

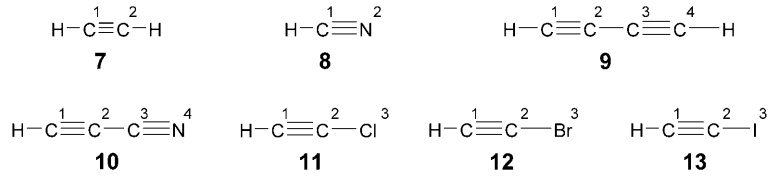


Table 1. *Energy and Coefficients of the LUMO of* **7**–**13** *Obtained by AM1 and PM3 Calculations*

	Energy [eV]		Coefficient at							
			atom 1		atom 2		atom 3		atom 4	
	AM1	PM3	AM1	PM3	AM1	PM3	AM1	PM3	AM1	PM3
7	2.053	2.009	−0.71	−0.71	0.71	0.71				
8	1.725	1.457	−0.73	−0.72	0.69	0.69				
9	0.678	0.723	−0.57	−0.56	0.43	0.43	0.43	0.43	−0.57	−0.56
10	0.244	0.147	−0.61	−0.60	0.47	0.46	0.40	0.42	−0.49	−0.51
11	1.663	1.713	−0.71	−0.71	0.69	0.69	−0.15	−0.17		
12	1.447	1.763	−0.72	−0.72	0.68	0.69	−0.14	−0.10		
13	1.412	2.025	−0.72	−0.71	0.68	0.69	−0.11	−0.11		

Both AM1 and PM3 calculations result in similar coefficients for the LUMO orbitals of **7**–**13** (*Table 1*). The largest coefficient at C(1) of **9**–**13** predict that nucleophilic attack is favoured at the unsubstituted acetylenic C-atom.

The regioselectivity of the addition of (hard) nucleophiles to acetylenes is also influenced by the charge distribution. AM1 and PM3 calculations led to similar net atomic charges for **7**–**13** (*Table 2*). That **8**–**10** are more electrophilic than acetylene (**7**) is predicted by the lower net atomic charge on C(1) of **8**–**10**. A higher reactivity towards hard nucleophiles of the buta-1,3-diyne (**9**) internal C-atoms is predicted on the basis of their lower net atomic charge. The net atomic charges of propiolonitrile (**10**) are in keeping with an expected attack of hard nucleophiles at the cyano C-atom. The net atomic charge of C(1) decreases in the series chloro-, bromo-, to iodoacetylene indicating the same relative reactivity as deduced from the LUMO energy values of the AM1 calculation.

Table 2. *Net Atomic Charges of* **7**–**13** *Obtained by AM1 and PM3 Calculations*

	Net atomic charge at							
	atom 1		atom 2		atom 3		atom 4	
	AM1	PM3	AM1	PM3	AM1	PM3	AM1	PM3
7	−0.22	−0.19	−0.22	−0.19				
8	−0.19	−0.16	−0.05	−0.07				
9	−0.17	−0.15	−0.06	−0.05	−0.06	−0.05	−0.17	−0.15
10	−0.10	−0.08	−0.10	−0.08	−0.02	0.00	−0.01	−0.04
11	−0.18	−0.16	−0.21	−0.32	0.16	0.28		
12	−0.14	−0.12	−0.32	−0.30	0.22	0.23		
13	−0.12	−0.14	−0.40	−0.34	0.29	0.28		

Alkynol Cycloisomerisation of α-D-Glucopyranosylbuta-1,3-diynes. Exploratory experiments performed in 1995 to cyclise partially protected 4-buta-1,3-diynylated glucopyranosides failed. However, treatment of the C_2-symmetric di(α-D-glucopyranosyl)buta-1,3-diyne **15** obtained from **14** [30][31] with excess $Na_2S \cdot 9\,H_2O$ in boiling $MeOCH_2CH_2OH$ gave the ynenol ether **16** (60%, *Entry 1* in *Table 3*), an *exo*-glycal, and not the expected thiophene (*Scheme 2*). Similarly, benzylation of **15** with NaH and BnBr in DMF at 0° gave a mixture of the perbenzylated *exo*-glycals **18** (53%) and **19** (21%). This result was rather surprising, considering that the alkynol cycloisomerisation of **15** requires a conformational change of the pyranosyl ring from a chair to a $B_{1,4}$ boat. Best yields of **16** (70%) were obtained with K_2CO_3 albeit in a slower reaction (24 h vs. 0.6 h; *Entry 3*); increasing the strength of the base lowered the yield of **19** (*Entries 1–3*).

Scheme 2

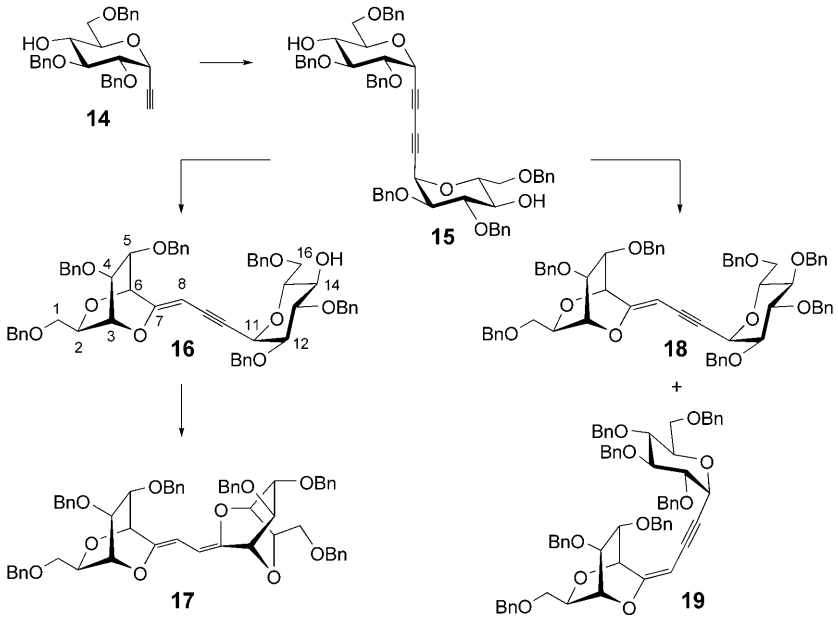


Table 3. *Conditions and Yields in the Alkynol Cycloisomerisation of* **15** *and* **16**

Entry	Starting material	Solvent	Base (8–10 equiv.) and reagent	Conditions	Products and yields
1	**15**	$MeOCH_2CH_2OH$	$Na_2S \cdot 9\,H_2O$	0.6 h at reflux	60% of **16**
2	**15**	$MeOCH_2CH_2OH$	$MeOCH_2CH_2ONa$	48 h at reflux	45% of **16**
3	**15**	$MeOCH_2CH_2OH$	K_2CO_3	24 h at reflux	70% of **16**
4	**15**	DMF	NaH, BnBr	3 h at 0°	53% of **18**, 21% of **19**
5	**16**	$MeOCH_2CH_2OH$	$Na_2S \cdot 9\,H_2O$	0.6 h at reflux	no reaction
6	**16**	$MeOCH_2CH_2OH$	$MeOCH_2CH_2ONa$	48 h at reflux	10% of **17**
7	**16**	$MeOCH_2CH_2OH$	K_2CO_3	24 h at reflux	37% of **17**
8	**16**	DMF	NaH	3 h at 0°	no reaction

While no product of double ring closure could be detected in the crude product of **15**, we obtained the doubly ring-closed, C_2-symmetric dienol ether **17** by subjecting the ynenol ether **16** to the same conditions as **15**, although the yields of the second cyclisation were distinctly lower (37% with K_2CO_3, 10% with $MeOCH_2CH_2Na$; *Entries 7* and *6* in *Table 3*).

The enol ether moiety of **16**–**19** is evidenced by an IR band of medium strength at 1654–1662 cm^{-1}. The ^1H- and ^{13}C-NMR spectra of **16**, **18**, and **19** evidence an α-D-glucopyranosylethynyl moiety (^{13}C-NMR: 2 *s*s at 87.6–85.8 and at 84.6–83.5 ppm for C(10) and C(9), resp., 6 BnO groups in **16**, and 7 BnO groups in **18** and **19**). HO–C(14) of **16** resonates as *d* at 2.40 ppm, and $J(14,OH) = 1.7$ Hz evidences an intramolecular H-bond to BnO–C(13), which is corroborated by the IR band at 3590 cm^{-1} (*cf.* [32][33]). The NMR spectra of **16** and **18** are very similar apart from the replacement of OH by OBn and reveal the same configuration. H–C(8) of **16** and **18** resonates as a *d* at 4.64–4.66 ppm, whereas the *d* of H–C(8) of **19** is shifted downfield to 5.15 ppm due to the neighbouring O–C(3), allowing to unambiguously assign the (*E*)-configuration to **19** and the (*Z*)-configuration to **16** and **18**. This assignment is confirmed by strong NOEs between H–C(8) and H–C(6) of **16** (8–14%). H–C(8) of **16**, **18**, and **19** couples with H–C(11) ($J(8,11) = 1.9–2.0$ Hz), but not with H–C(6). These couplings evidence the 2,5-dioxabicyclo[2.2.2]octane skeleton of **16**, **18**, and **19** and a 6-*exo-dig* alkynol cycloisomerisation of **15**[3]). H–C(6) of **19** is *cis*-oriented to the ethynyl group and, therefore, resonates downfield as a broad *d* at 5.11 ppm ($J(5,6) = 3.6$ Hz), whereas the signal of H–C(6) of **18** appears upfield at 4.07–4.09 ppm. Due to virtual coupling [37] (H–C(4) and H–C(5) resonate as a narrow *AB* system at 3.91–3.88 ppm), H–C(6) of **16** and **18** shows an additional splitting (**16**: $J = 3.5$ and 1.9, **18**: $J = 2.0$ and 1.4 Hz). As it is typical for enol ethers, the *s* of C(7) appears at low field (**16**/**18**: 159.6, **19**: 161.8 ppm) and the *d* of C(8) at high field (**16**/**18**: 83.4–83.6, **19**: 85.35 ppm). The NMR spectra of **17** show a single set of signals and evidence the C_2-symmetry. H–C(8) resonates as *s* at 5.39 ppm (no allylic coupling). The upfield shift of the *d* of H–C(6) (4.14 ppm, $J(5,6) = 3.0$ Hz) ascertains the (*Z*,*Z*)-configuration. The *s* of C(7) of **17** appears at 146.6 and the *d* of C(8) at 97.9 ppm.

The formation of 2,5-dioxabicyclo[2.2.2]octanes in the alkynol cycloisomerisation of **15** and **16** agrees well with the result of the semi-empirical calculation, *i.e.*, an enhanced electrophilicity at the terminal C-atoms of the buta-1,3-diyne moiety. The lower yields of **17** than of **16** (see *Table 3*) evidence the decreased electrophilicity of the alkynylated enol ether. The cycloisomerisation promoted by K_2CO_3, $Na_2S \cdot 9\ H_2O$, and $MeOCH_2CH_2ONa$ led selectively to the (*Z*)-configured enol ethers **16** and **17**, whereas cyclisation of **15** promoted by NaH led to a *ca.* 7:3 mixture (*Z*)-**18**/(*E*)-**19**. NaH did not promote the cyclisation of **16** (*Entry 8* in *Table 3*). That a rather weak base in a protic solvent and at higher temperature led to the best results of the cycloisomerisation suggests that a fast chair–boat interconversion, and particularly a concerted protonation of the evolving linear *trans*-vinyl anion[4]) are favourable. Protonation of a fully fledged vinyl anion as resulting from the NaH-promoted cyclisation results in a mixture of the (*E*)- and (*Z*)-ynenol ethers **18** and **19**.

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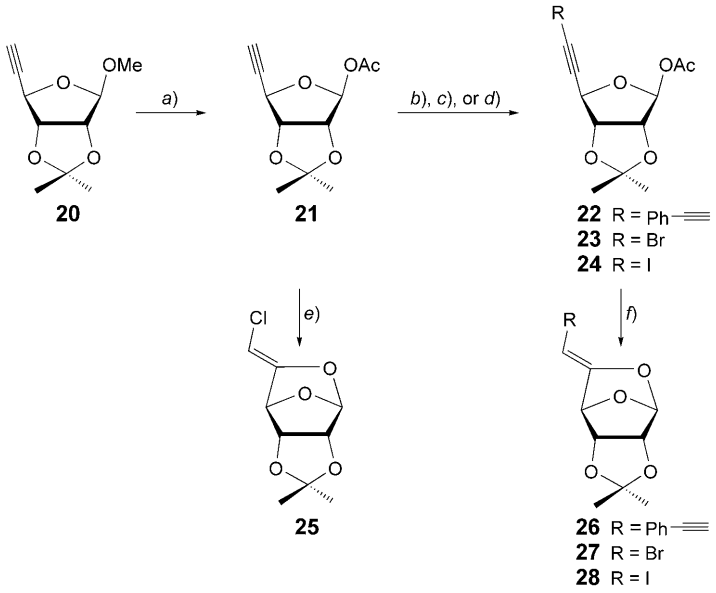
[3]) A 7-*endo-dig* alkynol cycloisomerisation of **15** would lead to a 2,5-dioxabicyclo-[3.2.2]non-6-ene skeleton. One expects a vicinal coupling $J(6,7)$ of 6.6 Hz (MM3* modeling [34]) and the absence of a coupling between H–C(7) and H–C(11); compare with corresponding values of 8 and 9.5 Hz of a bicyclo[3.2.2]non-7-ene and a bicyclo[3.2.2]non-8-en-7-one, respectively [35][36].

[4]) As shown by AM1 calculations, deprotonation at C(1′) of (*E*)- and (*Z*)-6-(but-2-ynylidene)-2,5-dioxabicyclo[2.2.2]octane leads to the same almost linear (*Z*)-vinyl anion (C=C$^-$–C bond angle = 163°, O–C=C$^-$–C dihedral angle −0.2°), whereas deprotonation of 6-methylidene-2,5-dioxabicyclo[2.2.2]octane gives two trihedral anions (C=C$^-$–H bond angles = 122–125°). The (*E*) anion is favoured by an anomeric effect. Treatment of 2-(but-2-ynyl)phenol with aqueous NaOH led indeed selectively to the (*Z*)-configured enol ether [38].

The successful alkynol cycloisomerisation of **15** prompted us to further investigate such cyclisations of monosaccharides.

Alkynol Cycloisomerisation of D-ribo-*Hex-5-ynofuranoses.* The alkyne **20** was prepared from D-ribose (22% overall yield) *via* a *Corey–Fuchs* reaction [39]. Acetolysis of **20** (AcOH, Ac_2O, and conc. H_2SO_4) in THF at room temperature gave 81% of the β-D-configured acetate **21**[5]) (*Scheme 3*). *Sonogashira* coupling between **21** and PhC≡CBr yielded 81% of the butadiyne **22**. Treatment of **21** with NBS and catalytic amounts of $AgNO_3$ [41] or with *N*-iodosuccinimide (NIS) and 1.5 equiv. of $AgNO_3$ [41][42] gave the bromide **23** (95%) and the iodide **24** (80%), respectively. Chlorination of **21** with *N*-chlorosuccinimide (NCS) was sluggish. Treatment of **21** with 5.25% aqueous NaOCl [42] led to complete chlorination, but also cleaved the anomeric AcO group. The intermediate hemiacetal cyclised *in situ* to the chloro-enol ether **25** (90%). Deacetylation of **22**–**24** with MeONa in MeOH was accompanied by cyclisation to the *exo*-glycals **26** (91%), **27** (84%), and **28** (91%), respectively. The cyclisation of the halides **23** and **24** occurred at room temperature (overnight) and that of the butadiyne **22** at 78° (4 h).

Scheme 3



a) Ac_2O, conc. H_2SO_4, AcOH/THF 1:1; 81%. *b*) (Bromoethynyl)benzene, $[Pd_2(dba)_3]$, CuI, $P(fur)_3$, Et_3N, DMF; 81% of **22**. *c*) NBS, $AgNO_3$, acetone; 95% of **23**. *d*) NIS, $AgNO_3$, NH_3/H_2O, acetone; 80% of **24**. *e*) NaOCl, H_2O; 90%. *f*) MeONa, MeOH; 91% of **26**; 84% of **27**; 91% of **28**.

The *ribo*-hexofuranosides **21**–**28** show couplings of *ca.* 0 Hz for *J*(1,2) and *J*(3,4) (*Table 4* in the *Exper. Part*). This evidences an E_O conformation also for the acetates **21**–**24** where the C(1) and C(4) substituents are pseudoaxial. The enol–ether moiety of **26**–**28** is evidenced by an IR band at 1692–1674 cm^{-1}. The *s* of the

[5]) For the use of an anomeric mixture containing **21**, see [40].

olefinic H–C(6) resonates at 4.94 (**26**) and 5.82–5.83 ppm (**25**, **27**, and **28**). The absence of coupling between H–C(6) and H–C(4) agrees with a 3-methylidene-2,7-dioxabicyclo[2.2.1]heptane but not with a 2,8-dioxabicyclo[3.2.1]oct-3-ene skeleton, where a vicinal coupling of *ca.* 6 Hz between the olefinic and bridgehead H is expected. H–C(4) of **25**–**28** resonates at 4.93–4.95 ppm at a similar position as H–C(4) of **21**–**24** (4.87–4.97 ppm); the absence of a downfield shift evidences the (*Z*)-configuration. The *s* of C(5) appears at 155.2 (**26**), 153.0 (**28**), 148.7 (**27**), and 146.8 ppm (**25**). As expected, C(6) resonates as a *d* at high field and the chemical shift is strongly influenced by the substituent (88.6 ppm for the chloride **25**, 80.1 ppm for the acetylene **26**, 74.5 ppm for the bromide **27**, and 41.6 ppm for the iodide **28**). The signals for the C≡C group of **26** were assigned according to [43], C(7) resonating at 82.61 and C(8) at 92.43 ppm.

The (*Z*)-configuration of **25**–**28** (dihedral angle O–C(5)–C(6)–X (X = C(7) or halogen) $\leq \pm 1.0^\circ$) was established by X-ray crystal-structure analysis. The unit cell of **26**–**28** contains a single molecule, whereas the unit cell of the chloride **25** contains two slightly different molecules (*Fig. 1*)[6]). The analysis shows typical bond lengths and bond angles, such as C(1)–OC(5) of 1.453–1.472 Å, C(5)–O of 1.366–1.397 Å, C(5)=C(6) of 1.307–1.328 Å, O–C(5)=C(6) of 124.1–125.9°, and C(5)–C(6)–X (X = C(7) or halogen) of 122.3–127.8°. The C–Hal bond lengths are 1.735 and 1.741 Å (chloride **25**), 1.869 Å (bromide **27**), and 2.063 Å (iodide **28**). The C≡C bond length of **26** is 1.199 Å, and a slight deviation of the acetylene group from linearity is indicated by the bond angles C(6)–C(7)≡C(8) of 172.3° and C(7)≡C(8)–C(1′) of 176.8°. The π-planes of the enol-ether moiety and the Ph group of **26** are orthogonal.

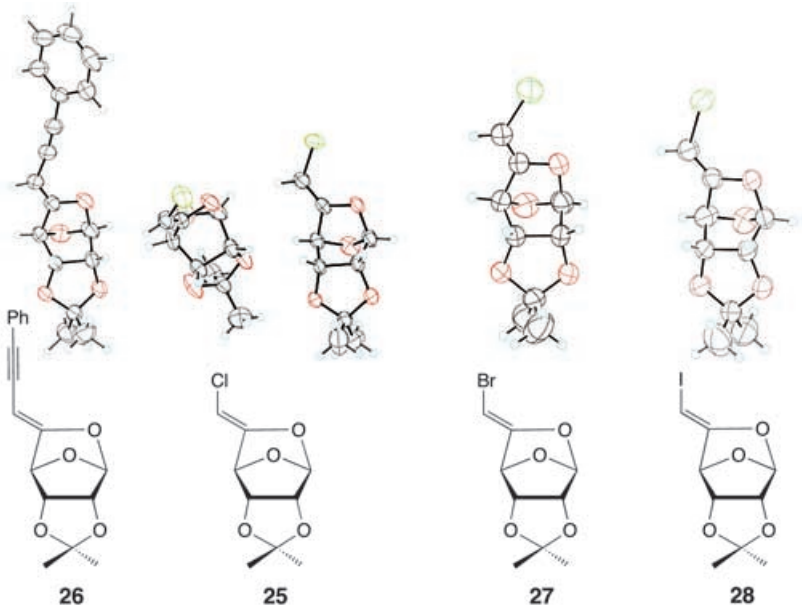


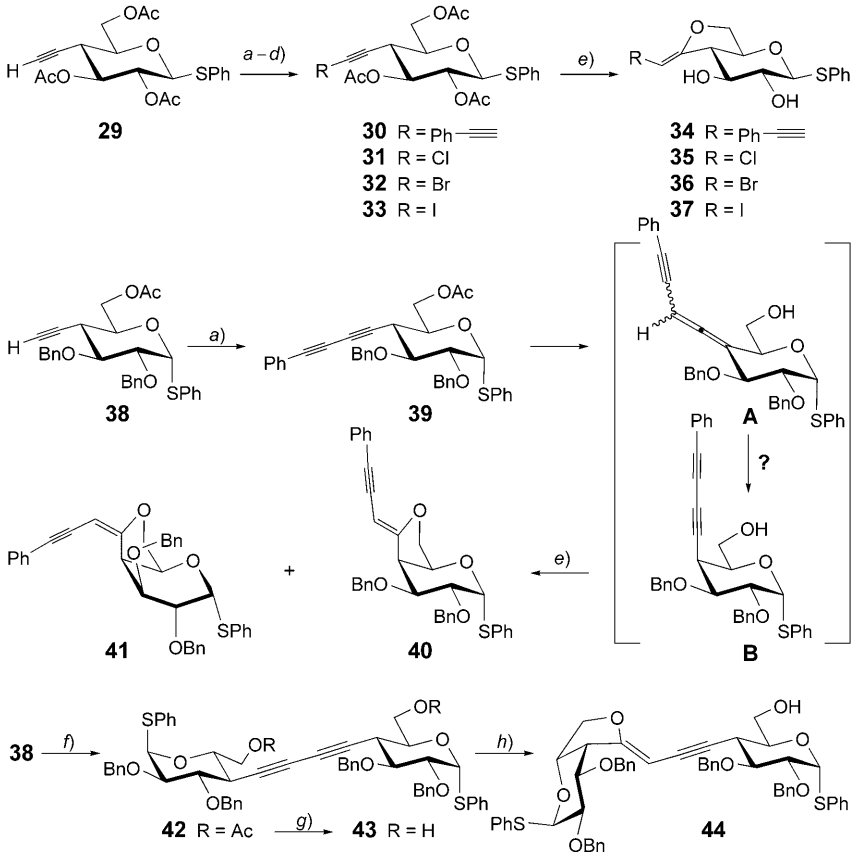
Fig. 1. *Crystal structure of the 1-5-anhydro*-D-ribo-*hex-5-enofuranoses* **25**–**28**

[6]) The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-248024 (**26**), CCDC-248027 (**27**), CCDC-248026 (**28**), CCDC-248025 (**25**), CCDC-248028 (**57**), and CCDC-248029 (**59**). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax. +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

The exclusive formation of **25**–**28** shows that a 5-*exo-dig* alkynol cycloisomerisation of D-*ribo*-hex-5-ynofuranoses is favoured, probably by proximity of the reacting centers, although a 6-*endo-dig* cyclisation does not suffer from additional steric strain. However, a 5-*exo-dig* alkynol cycloisomerisation of C(6)O unprotected 4-ethynyl-glucopyranosides leading to *trans*-dioxahexahydroindans is sterically disfavoured. We wondered whether such glucopyranosides would undergo a 6-*endo-dig* cyclisation to *trans*-dioxadecalins.

*Alkynol Cycloisomerisation of 4-Ethynyl-*D*-glucopyranosides.* The buta-1,3-diyne **30** (82%), the bromide **32** (83%), and the iodide **33** (73%; *Scheme 4*) were prepared from the 4-ethynyl-1-thio-β-D-glucopyranoside **29** [44], similarly as described for the synthesis of **22**–**24**. The chloride **31** was obtained in 64% yield by lithiation of **29** in

Scheme 4



a) (Bromoethynyl)benzene, $[Pd_2(dba)_3]$, CuI, $P(fur)_3$, Et_3N, DMF; 82% of **30**, 82% of **39**. *b*) BuLi, then NCS, THF; 64% of **31**. *c*) NBS, $AgNO_3$, THF; 83% of **32**. *d*) NIS, $AgNO_3$, NH_3/H_2O, acetone; 73% of **33**. *e*) MeONa, MeOH, reflux; 76% of **34**, 63% of **35**, 74% of **36**, 64% of **37**, 30% of **40**, and 51% of **41**. *f*) $Cu(OAc)_2$, pyridine; 88%. *g*) NaOH, THF/MeOH/H_2O, 60°; 99%. *h*) $Na_2S \cdot 9\,H_2O$, 2-methoxyethanol; 20% of **44** and *ca.* 10% of an unassigned 4 : 3 : 2 mixture.

THF with BuLi at $-78°$, followed by chlorination with NCS. Treatment of **30**–**33** with MeONa in boiling MeOH for 4 h led to deacetylation and selective cyclisation of the intermediate triols to the *gluco*-configured exocyclic enol ethers **34**–**37** (63–76%).

The buta-1,3-diyne **39** (82%) was obtained by *Sonogashira* coupling of 4-ethynyl-1-thio-α-D-glucopyranoside **38** [30] and (bromo-ethynyl)benzene, while *Eglinton* coupling of **38** yielded 88% of the C_2-symmetric acetylated buta-1,3-diyne **42** (*Scheme 4*). MeONa in MeOH (4 h at reflux) transformed the acetate **39** into the corresponding alcohol, which cyclised *in situ* to the *galacto*-configured (*Z*)- and (*E*)-ynenol ethers **40** (30%) and **41** (51%). Treatment of the diyne **42** with NaOH in THF/MeOH/H_2O for 15 min at 60° led in 99% yield to the diol **43**. Boiling the diol **43** and $Na_2S \cdot 9\,H_2O$ in 2-methoxyethanol for 30 min led to the *gluco*- and *galacto*-configured enol ether **44** (20%), and to a 4:3:2 mixture of alkenes (*ca.* 10%) that were not isolated[7]). Heating **43** in 2-methoxymethanol in the presence of excess K_2CO_3 or treatment of **43** with NaH in DMF at 0° did not afford **44**.

The *gluco*-configuration of **30**–**37**, **39**, **42**, **43**, and of the directly alkynylated moiety of **44** is evidenced by large J(3,4) and J(4,5) values (9.7–11.1 Hz), whereas the *galacto*-configuration of **40** and **41** is revealed by distinctly smaller J(3,4) and J(4,5) values (3.4–7.0 Hz; see *Tables 5* and *6* in the *Exper. Part*). In agreement with the *galacto*-configuration, the olefinic H–C(2′) of **44** resonates as a br. *s* showing a $w_{1/2}$ value of 8.7 Hz. The *trans*-annulation of **34**–**37** is also evidenced by large J(5,6a) and J(5,6b) values (6.6–6.7 and 9.6–9.7 Hz, resp.) whereas small J(5,6a) and J(5,6b) values (0–4.2 Hz) reveal the *cis*-annulation of **40**, **41**, and **44**. Characteristic geminal J(6a,6b) values (**34**–**37**: 7.8–8.0; **40**, **41**, and **44**: 10.0–10.1 Hz) reflect the different orientation of both H–C(6) and the lone pairs at O–C(6) (cf. [45]). The *galacto*-configuration of **40** and **41** was corroborated by NOEs between H–C(3) and H–C(4) (7.5–12%; see *Exper. Part*).

The olefinic H-atom of the *gluco*-configured enol ethers **34**–**37** resonates as a *d* at 5.15–5.45 ppm (*Table 5* in the *Exper. Part*). The chemical shift depends only weakly on the substituents and evidences that **34**–**37** possess the same configuration of the C=C bond. J(4,CH=C) of 2.1–2.4 Hz is compatible with an allylic coupling of an exocyclic enol ether, but also with a vicinal coupling of an endocyclic enol ether (according to MM3* calculation both couplings are 2.6 Hz). An endocyclic enol ether may, however, be excluded as it should show similar $J(5,6_{eq})$, $J(5,6_{ax})$, and $J(6_{eq},6_{ax})$ values as the corresponding 4,6-*O*-benzylidene acetal (typically 4.5, 10.5, and 10.5 Hz, resp.). The olefinic H-atom of the *galacto*-configured enol ethers **40** and **41** resonates as a *d* at 5.98 and 5.34 ppm, respectively (*Table 6* in the *Exper. Part*). The large $\Delta\delta$ value (0.64 ppm) is suggestive of an (*E*)/(Z)-pair. Since the olefinic H-atom of both isomers is close to an O-atom ((*Z*)-isomer to BnO–C(4); (*E*)-isomer to O–C(6)), the relative deshielding does not allow an unambiguous assignment of the configuration although a comparison with the *gluco* analogue **34** suggests the (*Z*)-configuration for **40**. Moreover, the coupling of the olefinic H-atom with H–C(4) (**40**: 2.2, **41**: 1.9 Hz) and the small $J(5,6_{eq})$ and $J(5,6_{ax})$ values of **40** (0 and 2.2 Hz, resp.) do not allow to exclude the structure of an endocyclic enol ether. The structure of an exocyclic enol ether is, however, evidenced by cross-peaks in the HMBC spectrum of **40** between H–C(3) and the *s* at 164.23 ppm, between H–C(5) and the *s* at 164.23 ppm, and between H–C(2′) and C(1)/C(2)/C(6) of the PhC≡C moiety. Similar cross-peaks are missing in the HMBC spectrum of **41**, but here $J(5,6_a) = 3.1$ and $J(5,6_b) = 6.0$ Hz exclude an endocyclic enol ether (according to MM3* calculation $J(5,6_a) = 1.0$ and $J(5,6_b) = 3.0$ Hz). The (*Z*)-configuration of **40** was evidenced by NOEs for H–C(4) (2.6%) and H–C(2) (2.4%) observed upon irradiation of H–C(2′). As expected, no NOE was observed upon irradiation of H–C(2′) of the (*E*)-configured **41**. In addition, the C(1′) *s* of the enol ether moiety of **40** and **41** show the same relative shifts (**40**: 164.2, **41**: 168.6 ppm) as the (*Z*)- and (*E*)-lactone oximes and hydrazones (cf. [46–48]). H–C(2′) of the dimer **44** resonates as a *t* at 5.31 ppm. It shows an allylic coupling with $H–C(4_{Gal})$ and a homopropargylic coupling with $H–C(4_{Glc})$ (both 1.5 Hz). Signal overlap for H–C(2), H–C(3), H–C(5), and H_a–C(6) of the galactose unit of **44** prevents an assignment of J(2,3), J(3,4), J(4,5), and $J(5,6_a)$, while the similarity of

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7) The ^{1}H-NMR spectrum of this mixture showed two signals at 5.18 and 5.14 ppm for olefinic H-atoms, and two signals at 3.33 and 2.92 ppm for H–C(4) of the glucopyranosyl residues.

δ(H–C(2′) and $J(5,6_b)$ of the galactose unit of **44** and the corresponding values of **40** indicates the (*Z*)-configuration.

The conformations of the pyranose ring of **40** and **41** differ. A flattened $^4C_1$ is evidenced for the (*Z*)-configured **40** by $J(1,2) = 4.8$, $J(2,3) = 10.0$, $J(3,4) = 5.6$, and $J(4,5) = 3.4$ Hz (*Table 6* in the *Exper. Part*). The $^4C_1$ conformer of the (*Z*)-configured **41** is destabilised by a steric interaction between PhC≡C and both BnO groups, and a boat conformation is preferred. MM3* modeling of the $^OS_2$ conformer of **41** predicts vicinal coupling constants that are similar to the experimentally determined ones.

Only products of a formal 5-*exo-dig* alkynol cycloisomerisation of **30**–**33**, **39**, and **43** were observed. There is a striking difference between the β-D-glucopyranosides **30**–**33** affording only the *gluco*-configured (Z)-enol ethers and the α-D-glucopyranosides **39** and **43** affording a (E)/(Z) mixture of the *galacto*-configured enol ethers. We assume that this difference results from a neighbouring group participation of HO–C(3) and not from the different anomeric configuration, cyclisation to a strained *trans*-dioxahexahydroindan being favoured by concerted protonation of the evolving vinyl anion by HO–C(3) of the intermediate triols derived from **30**–**33**. In the absence of this intramolecular protonation, the alcohol derived from **39** (and similarly **43**) may equilibrate with the allenes **A** and further with the *galacto* isomer **B** (*Scheme 4*). The allenes **A** may cyclise to the *cis*-dioxahexahydroindans **40** and **41** by an 5-*exo-dig* processs, leading to an intermediate dihydrofuran that isomerises to the product by migration of the double bond. Such a process appears more probable than a direct 5-*endo-dig* cyclisation[8])[9]). Alternatively, the *galacto*-configured buta-1,3-diyne **B** may cyclise to the *cis*-dioxahexahydroindans **40** and **41**. It is not clear why this cyclisation with NaOMe in MeOH (concerted intermolecular protonation of the emerging vinyl anion) leads preferentially to the sterically disfavoured **41**, unless protonation leading to **41** is (sterically?) favoured.

Alkynol Cycloisomerisation of β-D-Galactopyranosylethynes. The configuration at C(1) and C(4) of the α-D-glucopyranosylethynes (*Scheme 2*) and of the β-D-galactopyranosylethynes **49**–**51** (*Scheme 5*) differ, but the alkynyl and the hydroxy substituents of all these compounds are *cis*-oriented. One expects that the galactopyranosyl C-glycosides **49**–**51** will cyclise about as readily as the *gluco*-alkynols **14** and **15** and lead to epimeric 1,5-dioxabicyclo[2.2.2]octanes. The β-D-galactopyranosylethyne **49** was prepared from the diol **45** [63] by standard reactions. 4-Methoxybenzylation of **45** (→**46**), deallylation (→**47**), and *Swern* oxidation yielded the galactono-1,5-lactone **48** in 65% overall yield. The anomeric 1-ethynylated galactopyranoses were obtained

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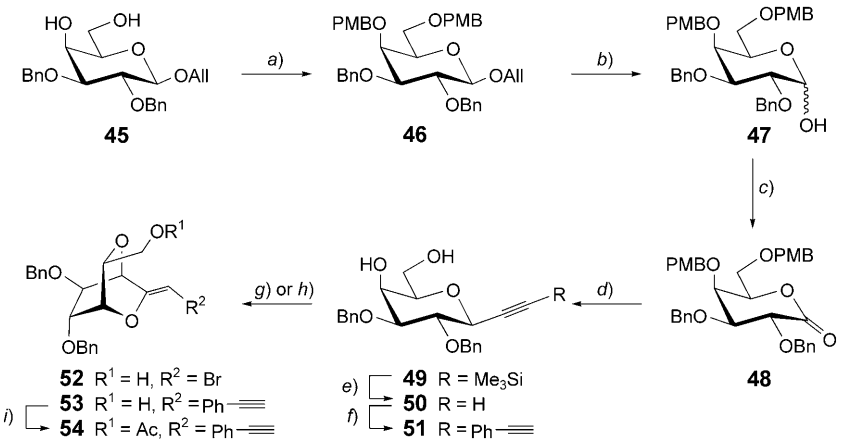
[8]) Treatment of allenic alcohols with various bases induces a 5-*exo-dig* cyclisation to endocyclic enol ethers by attack on the central sp hybridised C-atom of the allenyl moiety [49–52]. However, treatment of (–)-marasin, a buta-1,3-diynylated allenylethanol, with aqueous NaOH resulted in the formation of (*Z*)-2-(penta-2,4-diynylidene)oxolane [53][54]. The protic and *Lewis* acid (silver salts or BF_3) catalysed 5-*endo-dig* and 6-*endo-dig* cyclisation of α- and β-allenic alcohols to 2,5-dihydrofurans and 3,6-dihydro-2*H*-pyrans have been described (see [55–57]). The HgO- or $Pd(PPh_3)_4$-catalysed allenol cycloisomerisation gave endo- [58][59] and exocyclic enol ethers [60].

[9]) A 5-*exo-dig* cyclisation, followed by migration of the double bond, or a 5-*endo-dig* cyclisation appears more probable than isomerisation to the corresponding triynol, followed by a 5-*exo-dig* cyclisation, considering that distillation of pent-4-yn-1-ol (possessing an isolated, non-activated C≡C bond) in the presence of a catalytic amount of $NaNH_2$ gave 2-methylideneoxolane [61][62].

by treating **48** with lithium (trimethylsilyl)acetylide and reduced with Et_3SiH and $BF_3 \cdot Et_2O$. Under these conditions, the 4-methoxybenzyl ethers were also cleaved (compare [64]) and the diol **49** was isolated in 63% yield. *C*-Desilylation (NaOMe in MeOH) to **50** and *Sonogashira* coupling with (bromoethynyl)benzene gave 85% of the buta-1,3-diyne **51**. Bromination of **50** with NBS and $AgNO_3$ in THF at room temperature led to the bromoacetylene which cyclised *in situ* to the enol ether **52** (93%). Cyclisation of **51** (NaOMe in MeOH) yielded 93% of the ynenol ether **53** which was acetylated to **54** (95%).

Scheme 5



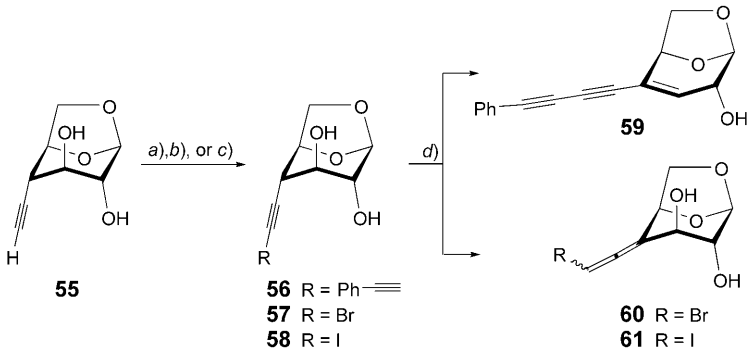
a) PMBCl (=4-methoxybenzyl chloride), NaH, DMF; 90%. *b*) [Ir(COD)(PPh_2Me)PF_6], H_2, THF, then I_2 and H_2O; 82%. *c*) DMSO/Ac_2O 2:1; 88%. *d*) BuLi, $Me_3SiC{\equiv}CH$, THF; Et_3SiH, $BF_3 \cdot Et_2O$, CH_2Cl_2/MeCN 1:1; 63%. *e*) MeONa, MeOH; 93%. *f*) (Bromoethynyl)benzene, [$Pd_2(dba)_3$], CuI, P(fur)$_3$, Et_3N, DMF; 85%. *g*) **50**, NBS, $AgNO_3$, THF; 93% of **52**. *h*) **51**, MeONa, MeOH; 93% of **53**. *i*) Ac_2O, pyridine; 95%.

The β-D-configuration of the galactopyranosylethynes **49**–**51** is evidenced by $J(1,2) = 9.6–9.9$ Hz (*Table 7* in the *Exper. Part*). HO–C(4) of **49**–**51** resonates as a *dd* at 2.64–2.70 ppm. In $CDCl_3$, the small $J(4,OH) =$ 1.5–2.0 Hz and the *W*-coupling with H–C(5) (1.0–1.5 Hz) evidence an intramolecular H-bond of HO–C(4) to BnO–C(3) (*cf.* [65]). $J(6_b,OH) = 7.2–8.4$ Hz, and $J(6_a,OH) = 3.3–4.8$ Hz of the diols **49**–**51** and the monoalcohols **52** and **53** reveal an intramolecular H-bond of HO–C(6) to O–C(5). The enol ether moiety of **52**–**54** is evidenced by an IR band at 1658–1664 cm^{-1}. The small coupling between the olefinic H-atom and H–C(1) of **52**–**54** ($\leq$1.0 Hz) reveals the dioxabicyclo[2.2.2]octane structure, and allows us to exclude a dioxabicyclo[3.2.2]nonane structure (*cf. Sect. 2.1*). The upfield shift of H–C(1) at 4.24–4.29 ppm evidences the (*Z*)-configuration of **52**–**54**, which is corroborated by NOEs of 9–14% between H–C(1) and H–C(2′) of **53** (see *Exper. Part*).

As expected from the cyclisation of the α-D-*gluco*-analogues **15** and **16**, a 6-*exo*-*dig* alkynol cycloisomerisation of **51** and the corresponding bromoacetylene required the conformational change from $^4C_1$ to $^{1,4}B$, and the bromoacetylene cyclised already under the mild conditions of its preparation. No 2-methylidene-3,9-dioxabiyclo[3.3.2]nonane resulting from a 6-*exo*-*dig* alkynol cycloisomerisation involving the primary OH group and requiring a change of the ring conformation from $^4C_1$ to $^1C_4$ was found.

Attempted Alkynol Cycloisomerisation of 4-Ethynylated Levoglucosans. We explored the limits of strain compatible with alkynol cyclisation by attempting to cyclise the 4-ethynylated levoglucosan derivatives **56**–**58**, which are easily accessible from the known diol **55** [66] (*Scheme 6*). Due to the short CH_2O bridge in levoglucosans, the distance between the axial substituents at C(2) and C(4) is considerably larger than the typical distance between 1,3-diaxial substituents of cyclohexane (*anti*-reflex effect; see [67] and refs. cit. therein). Thus, the O···O distance between the 1,3-diaxial OH groups is 3.299 Å in crystalline levoglucosan, but only 2.768 Å in crystalline 1,3,5-methylidyne-*myo*-inositol [67]. A 5-*endo-dig* alkynol cycloisomerisation of 4-ethynylated levoglucosans would lead to a severely strained *anti*-2,8,9-trioxatricyclo[4.2.1.1^{2,5}]decane[10]).

Scheme 6



a) (Bromoethynyl)benzene, [$Pd_2(dba)_3$], CuI, P(fur)$_3$, Et_3N, DMF; 76% of **56**. *b*) NBS, $AgNO_3$, THF; 92% of **57**. *c*) NIS, $AgNO_3$, NH_3, acetone/H_2O; 87% of **58**. *d*) MeONa or *t*-BuOK, MeOH; 82% of **59**, 62% of **60**, 68% of **61**.

The solid-state structure of **57** was determined by X-ray analysis (*Fig. 2*)[6]). The distance between O–C(2) and C(1′) is 3.196 Å. HO–C(2) is involved in a intramolecular H-bond to OC(5) (OH···OC(5) distance 2.395 Å, H–C(2)–O–H dihedral angle −159.6°), whereas HO–C(3) is engaged in an intermolecular H-bond to O–C(6). The ethynyl moiety does not act as additional H-acceptor of the intermolecular H-bond revealed by the OH···C(1′) distance of 2.732 Å. It is slightly bent, as indicated by the bond angles for C(4)–C(1′)–C(2′) and C(1′)–C(2′)–Br of 175.6 and 177.8°, respectively.

Treatment of the buta-1,3-diyne **56** with MeONa in MeOH gave the diynenitol **59** in 82% yield. A similar treatment of the bromide **57** and the iodide **58** (with *t*-BuOK instead of MeONa) led to a 9:1 mixture of the epimeric bromoallenes **60** (82%) and to a 1:1 mixture of the epimeric iodoallenes **61** (68%). As expected, no cyclisation products could be found in the crude products obtained from **56**–**58**.

In $CDCl_3$ solution, HO–C(2) of **56**–**58** is engaged in a bifurcated intramolecular H-bond to O–C(5) and the acetylene group as evidenced by J(2,OH) = 11.8–11.9 Hz, and HO–C(3) forms an intramolecular H-bond to O–C(6) (J(3,OH) = 7.7–7.8 Hz). J(2,OH) of **59** = 11.2 Hz evidences in solution a bifurcated intramolecular

[10]) *anti*-2,8,9-Trioxatricyclo[4.2.1.1^{2,5}]decanes are not known. *anti*-2,8,9-Tricyclo[4.2.1.1^{2,5}]decane is 23.7 kcal/mol higher in energy than the isomeric adamantane [68].

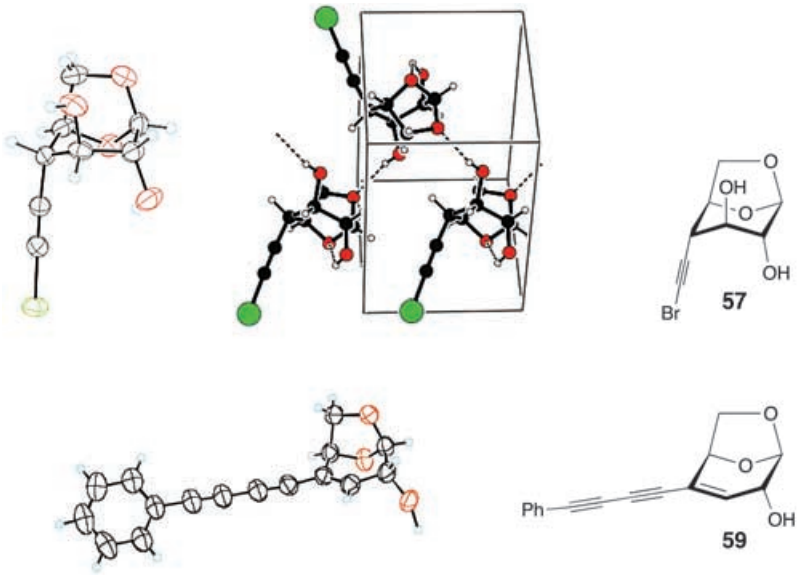


Fig. 2. *Crystal structure of the 4-ethynylated levoglucosans* **57** *and* **59**

H-bond to O–C(5) and the C=C bond. In the solid state of **59**, however, HO–C(2) is involved only in intermolecular H-bonding (*Fig. 2*). *J*(2,OH) and *J*(3,OH) values of the allenes **60** and **61** are 8.2–8.7 and 6.8–7.1 Hz, and evidence intramolecular H-bonds to O–C(5) and O–C(6), respectively. The C=CH group of **59** is evidenced by the IR band at 1680 cm^{-1}, the downfield shift of H–C(3) at 6.23 ppm, and the downfield shift of C(3) (*d* at 133.5 ppm) and C(4) (*s* at 125.36 ppm). The allenyl moieties of **60** and **61** show the expected spectroscopic characteristics (*cf.* [69]); *i.e.*, an IR band at 1964 and 1955 cm^{-1}, a strong downfield shift of C(1′) at 198.6 and 201.0 ppm, a weak upfield shift for C(4) at 108.6 and 102.1 ppm, and a strong upfield shift for C(2′) at 73.1/73.2 and 39.0/38.3 ppm, respectively.

Conclusions. – Base-promoted alkynol cycloisomerisation of hydroxybuta-1,3-diynes and haloalkynes occurs readily, and a 5- or a 6-*exo-dig* ring closure to *exo*-methylidene-tetrahydofurans and -pyrans is preferred. If this ring closure is disfavoured by ring strain, isomerisation to the isomeric allenes is preferred over an alkynol cycloisomerisation. In keeping with earlier work on non-carbohydrate alkynols, our results show that alkynol cycloisomerisation is favoured by cumulated triple bonds, a 1-iodo 1-bromo, 1-chloro, 1-phenylchalcogeno (S or Se), or 1-(hetero)aryl substituent, and the proximity of the reacting groups [11][12]. Alkynol cycloisomerisation promises to become a useful additional route to (further functionalised) *exo*-glycals.

We thank Dr. *B. Schweizer* for the crystal-structure determination, *C. Jäger* for the help in the synthesis of the *galacto*-dimers, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support.

Experimental Part

General. See [30].

1,1′-[Buta-1,3-diyne-1,4-diyl]bis[2,3,6-tri-O-*benzyl*-α-D-*glucopyranosyl]* (**15**). Under Ar, a soln. of $Cu(OAc)_2$ (11.9 g, 65.7 mmol) in pyridine (110 ml) was heated to 60°, stirred for 3 h, treated with a soln. of **14** [30] (11.9 g, 65.7 mmol) in pyridine (10 ml), stirred for 1 h, and evaporated. Pyridine was removed by co-

evaporation with toluene. FC (hexane/AcOEt 5:1 → 1:1) gave **15** (1.24 g, 83%). R_f (hexane/AcOEt 3:1) 0.28. $[\alpha]_D^{25} = +189.2$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3587*m*, 3510*w*, 3089*w*, 3066*w*, 2913*m*, 2871*m*, 2157*w*, 1603*w*, 1496*m*, 1454*m*, 1364*m*, 1330*m*, 1248*m*, 1069*s*, 1028*s*, 910*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.42–7.24 (*m*, 15 arom. H); 5.03 (*d*, $J = 11.4$, PhC*H*); 4.81 (*d*, $J = 5.8$, H–C(1)); 4.78 (*d*, $J = 11.1$), 4.73 (*d*, $J = 12.0$), 4.69 (*d*, $J = 12.0$), 4.59 (*d*, $J = 12.3$), 4.54 (*d*, $J = 12.0$) (5 PhC*H*); 3.95 (br. *dt*, $J \approx 9.6, 3.9$, H–C(5)); 3.79 (*t*, $J = 9.1$, H–C(3)); 3.73 (*dd*, $J = 10.5, 4.2$, H–C(6)); 3.69 (*dd*, $J = 10.5, 3.3$, H′–C(6)); 3.615 (*dd*, $J = 9.3, 5.8$, H–C(2)); 3.62 (*td*, $J = 9.2, 2.3$, addn. of D_2O → *t*, $J = 9.2$, H–C(4)); 2.44 (*d*, $J = 2.3$, exchange with D_2O, HO–C(4)). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.59, 137.74, 137.55 (3*s*); 128.50–127.66 (several *d*); 82.54 (*d*, C(3)); 78.52 (*d*, C(2)); 75.54, 73.72, 73.02 (3*t*, 3 Ph*C*H_2); 74.81 (*s*, C≡*C*–C(1)); 73.15 (*s*, *C*≡C–C(1)); 73.89 (*d*, C(5)); 70.54 (*d*, C(4)); 69.44 (*t*, C(6)); 67.44 (*d*, C(1)). HR-MALDI-MS: 937.391 ($[M + Na]^+$, $C_{58}H_{58}NaO_{10}^+$; calc. 937.392).

(7Z)-2,6:3,7:11,15-Trianhydro-1,4,5,12,13,16-hexa-O-*benzyl-8,9,10-trideoxy*-D-erythro-L-ido-L-gulo-*hexadec-7-en-9-ynitol* (**16**). *a*) A soln. of **15** (355 mg, 0.38 mmol) in $MeOCH_2CH_2OH$ (10 ml) was treated with $Na_2S \cdot 9\ H_2O$ (745.5 mg, 3.10 mmol), stirred for 40 min under reflux, cooled to 23°, diluted with AcOEt (0.5 ml) and hexane (0.8 ml), stirred for 30 min, and filtered through *Celite*. Evaporation of the filtrate and FC (hexane/AcOEt 10:1 → 3:1) gave **16** (212 mg, 60%).

b) A soln. of **15** (20 mg, 22 μmol) in $MeOCH_2CH_2OH$ (3 ml) was treated with K_2CO_3 (24 mg, 0.17 mmol), kept for 24 h at reflux, and evaporated. A soln. of the residue in AcOEt (10 ml) was washed with H_2O (5 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 10:1 → 3:1) gave **16** (14 mg, 70%). R_f (hexane/AcOEt 3:1) 0.85. $[\alpha]_D^{25} = +150.6$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3590*w*, 3066*w*, 2917*m*, 2870*m*, 2209*w*, 1661*m*, 1603*w*, 1496*m*, 1454*m*, 1335*m*, 1094*s*, 1027*s*, 909*w*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a DQFCOSY.-GRASP and a HSQC.GRASP spectrum): 7.38–7.22 (*m*, 30 arom. H); 4.98 (*d*, $J = 11.1$, PhC*H*); 4.98 (*dd*, $J = 5.5, 2.0$, H–C(11)); 4.75 (*d*, $J = 11.4$), 4.72 (*d*, $J = 11.9$), 4.65 (*d*, $J = 11.8$) (3 PhC*H*); 4.66 (*d*, $J = 2.0$, irrad. at 4.09 → NOE of 14%, H–C(8)); 4.59 (*d*, $J = 12.1$), 4.45 (*s*, irrad. at 4.09 → NOE of 5%, 2 H), 4.53 (*d*, $J = 11.4$, 2 H), 4.49 (*d*, $J = 11.9$), 4.47 (*d*, $J = 11.6$), 4.41 (*d*, $J = 11.9$) (8 PhC*H*); 4.43–4.42 (*m*, H–C(3)); 4.38 (br. *t*, $J \approx 6.5$, H–C(2)); 4.09 (*dd*, $J = 3.5, 1.9$, with virtual coupling, irrad. at 4.61 → NOE of 8%, H–C(6)); 4.01 (*dt*, $J \approx 9.6, 3.9$, H–C(15)); 3.91–3.89 (*m*, irrad. at 4.09 → NOE of 7%, H–C(4), H–C(5)); 3.82 (*t*, $J = 9.1$, H–C(13)); 3.73 (*dd*, $J = 10.7, 4.2$, H–C(16)); 3.68 (*dd*, $J = 10.6, 3.4$, H′–C(16)); 3.65 (*d*, $J = 6.4$, 2 H–C(1)); 3.63 (*dd*, $J = 9.4, 5.6$, H–C(12)); 3.61 (br. *t*, $J = 8.8$, H–C(14)); 2.40 (*d*, $J = 1.7$, HO–C(14)). ^{13}C-NMR (75 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 159.55 (*s*, C(7)); 138.92, 138.32, 137.06, 137.90, 137.52, 137.35 (6*s*); 128.32–127.47 (several *d*); 87.44 (*s*, C(10)); 83.56 (*s*, C(9)); 83.43 (*d*, C(8)); 82.20 (*d*, C(13)); 80.55, 79.53 (2*d*, C(4), C(5)); 78.71 (*d*, C(12)); 75.41 (*d*, C(2)); 75.12, 73.37, 73.15, 72.28, 71.77, 71.43 (6*t*, 6 Ph*C*H_2); 72.79 (*d*, C(15)); 70.99 (*d*, C(3)); 70.64 (*d*, C(14)); 69.76 (*t*, C(1)); 69.52 (*t*, C(16)); 69.04 (*d*, C(6)); 67.27 (*d*, C(11)). HR-MALDI-MS: 937.393 ($[M + Na]^+$, $C_{58}H_{58}NaO_{10}^+$; calc. 937.392).

(7Z,9Z)-2,6:3,7:10,14:11,15-Tetraanhydro-1,4,5,12,13,16-hexa-O-*benzyl-8,9-dideoxy*-D-erythro-L-ido-L-gulo-*hexadeca-7,9-dienitol* (**17**). *a*) A soln. of **16** (27 mg, 29.5 μmol) in $MeOCH_2CH_2OH$ (3 ml) was treated with K_2CO_3 (40.7 mg, 0.29 mmol), kept for 48 h at reflux, and evaporated. A soln. of the residue in AcOEt (10 ml) was washed with H_2O (8 ml), and the aq. layer was extracted with AcOEt (3 × 10 ml). The combined org. layers were washed with brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 10:1 → 3:1) gave **17** (10 mg, 37%).

b) A soln. of **16** (20 mg, 21.9 μmol) in $MeOCH_2CH_2OH$ (2 ml) was treated 1M $MeOCH_2CH_2ONa$ in $MeOCH_2CH_2OH$ (200 μl, 0.22 mmol), kept for 70 h at reflux, and evaporated. A soln. of the residue in AcOEt (10 ml) was washed with H_2O (8 ml), and the aq. layer was extracted with AcOEt (3 x 10 ml). The combined org. layers were washed with brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 10:1 → 3:1) gave **17** (2 mg, 10%). R_f (hexane/AcOEt 3:1) 0.62. $[\alpha]_D^{25} = +139.2$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3089*w*, 3066*w*, 2961*m*, 2869*m*, 1654*m*, 1604*w*, 1496*m*, 1454*m*, 1363*m*, 1324*m*, 1261*s*, 1101*s*, 1027*s*, 909*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39–7.23 (*m*, 15 arom. H); 5.39 (*s*, H–C(8)); 4.60 (*d*, $J = 12.3$), 4.55 (*d*, $J = 12.0$), 4.51 (*d*, $J = 12.0$), 4.50 (*d*, $J = 12.0$), 4.49 (*d*, $J = 11.9$), 4.41 (*d*, $J = 12.0$) (6 PhC*H*); 4.41–4.34 (*m*, H–C(2), H–C(3)); 4.14 (*d*, $J = 3.0$, H–C(6)); 3.92–3.86 (*m*, H–C(4), H–C(5)); 3.65 (*d*, $J \approx 6.0$, 2 H–C(1)). ^{13}C-NMR (75 MHz, $CDCl_3$): 146.59 (*s*, C(7)); 137.91, 137.63, 137.47 (3*s*); 128.33–127.56 (several *d*); 97.88 (*d*, C(8)); 81.17, 79.70 (2*d*, C(4), C(5)); 75.93 (*d*, C(2)); 73.21, 71.68, 71.17 (3*t*, 3 Ph*C*H_2); 70.58 (*d*, C(3)); 70.05 (*t*, C(1)); 69.86 (*d*, C(6)). HR-MALDI-MS: 937.391 ($[M + Na]^+$, $C_{58}H_{58}NaO_{10}^+$; calc. 937.392).

Benzylation of **15**. Under Ar, a soln. of **15** (737 mg, 0.80 mmol) in DMF (36 ml) was cooled to 0°, treated with 60% NaH in oil (270 mg, 8.0 mmol), stirred for 15 min, treated with BnBr (478 μl, 5.02 mmol), stirred for 3 h, treated dropwise with MeOH (1.0 ml), and diluted with H_2O (30 ml) and Et_2O (50 ml). After separation of the layers, the aq. layer was extracted with Et_2O (2 × 50 ml). The combined org. layers were washed with brine, dried ($MgSO_4$), and evaporated. FC (hexane/Et_2O 10:1 → 5:1) gave **18** (391 mg, 53%) and **19** (155 mg, 21%).

Data of (Z)-*2,6:3,7:11,15-Trianhydro-1,4,5,12,13,14,16-hepta*-O-*benzyl-8,9,10-trideoxy*-D-erythro-L-ido-L-gulo-*hexadeca-7-en-9-ynitol* (**18**). R_f (hexane/AcOEt 3:1) 0.70. $[\alpha]_D^{25} = +166.4$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3088*w*, 3066*w*, 2917*m*, 2867*m*, 2209*w*, 1662*m*, 1496*m*, 1454*m*, 1363*m*, 1089*s*, 1027*s*, 910*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignment based on a HSQC.GRASP spectrum): 7.38–7.21 (*m*, 33 arom. H); 7.14–7.13 (*m*, 2 arom. H); 4.98 (*d*, $J = 11.2$, PhC*H*); 4.97 (*dd*, $J = 5.6, 2.0$, H–C(11)); 4.84 (*d*, $J = 10.6$), 4.81 (*d*, $J = 10.9$), 4.72 (*d*, $J = 11.9$), 4.68 (*d*, $J = 11.9$) (4 PhC*H*); 4.64 (*d*, $J = 2.0$, H–C(8)); 4.62 (*d*, $J = 12.1$), 4.54 (*s*, 2 H), 4.51 (*d*, $J = 11.6$), 4.48 (*d*, $J = 11.0$, 2 H), 4.47 (*d*, $J = 12.1$), 4.45 (*d*, $J = 11.6$), 4.41 (*d*, $J = 12.0$) (9 PhC*H*); 4.43–4.42 (*m*, H–C(3)); 4.38 (br. *t*, $J \approx 6.8$, H–C(2)); 4.07 (*dd*, $J = 2.0, 1.4$, with virtual coupling, H–C(6)); 4.04 (*ddd*, $J = 9.9, 3.3, 2.1$, H–C(15)); 3.99 (*t*, $J = 9.2$, H–C(13)); 3.89–3.88 (*m*, H–C(4), C(5)); 3.77 (*dd*, $J = 10.8, 3.5$, H–C(16)); 3.68 (*dd*, $J = 10.8, 2.0$, H′–C(16)); 3.65 (*dd*, $J = 9.4, 5.5$, H–C(12)); 3.63 (*d*, $J = 6.7$, 2 H–C(1)); 3.61 (*t*, $J = 9.7$, H–C(14)). ^{13}C-NMR (75 MHz, $CDCl_3$; assignment based on a HSQC.GRASP spectrum): 159.57 (*s*, C(7)); 138.92, 138.32, 138.12, 138.00, 137.89, 137.51, 137.35 (7*s*); 128.49–127.52 (several *d*); 87.64 (*s*, C(10)); 83.60 (*s*, C(9)); 83.57 (*d*, C(8)); 83.09 (*d*, C(13)); 80.64, 79.63 (2*d*, C(4), C(5)); 79.25 (*d*, C(12)); 77.59 (*d*, C(14)); 75.60, 75.47, 75.13, 73.39, 72.57, 71.83, 71.48 (7*t*, 7 PhCH_2); 75.47 (*d*, C(2)); 73.20 (*d*, C(15)); 71.03 (*d*, C(3)); 69.84 (*t*, C(1)); 69.12 (*d*, C(6)); 68.62 (*t*, C(16)); 67.34 (*d*, C(11)). HR-MALDI-MS: 1027.442 ($[M + Na]^+$, $C_{65}H_{64}NaO_{10}^+$; calc. 1027.445).

Data of (E)-*2,6:3,7:11,15-Trianhydro-1,4,5,12,13,14,16-hepta*-O-*benzyl-8,9,10-trideoxy*-D-erythro-L-ido-L-gulo-*hexadeca-7-en-9-ynitol* (**19**). R_f (hexane/AcOEt 3:1) 0.75. $[\alpha]_D^{25} = +65.4$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3089*w*, 3066*w*, 2925*m*, 2868*m*, 2208*w*, 1654*m*, 1496*m*, 1454*m*, 1364*m*, 1090*s*, 1027*s*, 910*w*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on a DQFCOSY.GRASP and a HSQC.GRASP spectrum): 7.32–7.19 (*m*, 33 arom. H); 7.12–7.10 (*m*, 2 arom. H); 5.15 (*d*, $J = 1.9$, H–C(8)); 5.11 (br. *d*, $J = 3.6$, H–C(6)); 4.93 (*d*, $J = 10.9$, PhC*H*); 4.86 (*dd*, $J = 5.6, 1.9$, H–C(11)); 4.78 (*d*, $J = 10.8$), 4.77 (*d*, $J = 10.9$), 4.66 (*d*, $J = 11.4$), 4.64 (*d*, $J = 11.4$), 4.61 (*d*, $J = 12.0$), 4.53 (*d*, $J = 12.1$), 4.50 (*d*, $J = 11.9$), 4.48 (*s*, 2 H), 4.48 (*d*, $J = 12.0$), 4.43 (*d*, $J = 11.6$), 4.39 (*d*, $J = 12.2$), 4.27 (*d*, $J = 11.3$) (13 PhC*H*); 4.39–4.34 (*m*, H–C(2), H–C(3)); 3.93–3.91 (*m*, H–C(15)); 3.91 (*t*, $J = 9.1$, H–C(13)); 3.89 (*t*, $J = 3.5$, irrad. at 5.11 → *d*, $J = 3.5$, H–C(5)); 3.80 (*dt*, $J = 3.4, 1.6$, irrad. at 4.36 → *d*, $J = 3.4$, H–C(4)); 3.67 (br. *d*, $J = 6.7$, irrad. at 4.36 → *s*, 2 H–C(1)); 3.63 (*dd*, $J = 10.7, 3.5$, H–C(16)); 3.61 (*t*, $J = 9.8$, H–C(14)); 3.60 (*dd*, $J = 9.4, 5.7$, H–C(12)); 3.48 (*dd*, $J = 10.7, 2.0$, H′–C(16)). ^{13}C-NMR (75 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 161.76 (*s*, C(7)); 138.80, 138.30, 138.00, 137.90, 137.85, 137.40, 137.39 (7*s*); 128.56–127.53 (several *d*); 85.86 (*s*, C(10)); 84.59 (*s*, C(9)); 85.35 (*d*, C(8)); 83.40 (*d*, C(14)); 80.42 (*d*, C(4)); 79.04 (*d*, C(12)); 78.73 (*d*, C(5)); 77.50 (*d*, C(14)); 75.66, 75.09, 73.48, 73.44, 73.29, 72.81, 71.77 (7*t*, 7 PhCH_2); 75.44 (*d*, C(2)); 73.48 (*d*, C(15)); 71.50 (*d*, C(3)); 69.97 (*t*, C(1)); 68.45 (*t*, C(16)); 67.44 (*d*, C(11)); 65.33 (*d*, C(6)). HR-MALDI-MS: 1027.438 ($[M + Na]^+$, $C_{65}H_{64}NaO_{10}^+$; calc. 1027.445).

1-O-*Acetyl-5,6-dideoxy-2,3*-O-*isopropylidene-β*-D-ribo-*hex-5-ynofuranose* (**21**). A suspension of **20** [39] (500 mg, 2.5 mmol) in THF (5 ml) was treated with AcOH (5 ml) and Ac_2O (1.4 g, 13.9 mmol), cooled to 5°, stirred for 0.5 h, treated dropwise with conc. H_2SO_4 (0.25 ml) over a period of 5 min, and stirred at 23° for 12 h. The mixture was poured on ice (20 g), stirred for 1 h, and extracted with AcOEt (3 × 20 ml). The combined org. fractions were washed with sat. $NaHCO_3$ soln. (20 ml), H_2O (20 ml) and brine (20 ml), dried ($MgSO_4$), and evaporated. FC (hexane/Et_2O 2:1) gave **21** (460 mg, 81%). White solid. R_f (hexane/Et_2O 1:1) 0.63. M.p. 75–76°. $[\alpha]_D^{25} = -102.3$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3307*m*, 3029*w*, 2995*w*, 2943*w*, 2124*w*, 1746*s*, 1602*w*, 1458*w*, 1430*w*, 1376*s*, 1228*s*, 1204*m*, 1159*m*, 1104*s*, 1058*m*, 1015*s*, 971*s*, 922*w*, 864*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 2.01 (*s*, AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 169.19 (*s*, C=O); 21.08 (*q*, Me). ESI-MS: 211 ($[M - Me]^+$). Anal. calc. for $C_{11}H_{14}O_5$ (226.23): C 58.40, H 6.24; found: C 58.24, H 6.21.

1-O-*Acetyl-5,6,7,8-tetradeoxy-2,3*-O-*isopropylidene-8*-C-*phenyl-β*-D-ribo-*octa-5,7-diynofuranose* (**22**). A suspension of $[Pd_2(dba)_3]$ (15.7 mg, 0.0339 mmol), CuI (5.26 mg, 0.0274 mmol), P(fur)$_3$ (16 mg, 0.068 mmol), **21** (310 mg, 1.37 mmol), and (bromoethynyl)benzene (250 mg, 1.37 mmol) in DMF (5 ml) was degassed twice and stirred at 22° for 5 min. The mixture was treated with Et_3N (0.7 ml) and stirred for 12 h at 22°. The soln. was diluted with Et_2O (20 ml), and treated with H_2O (20 ml) and 0.1M aq. HCl (5.5 ml). The org. layer was washed with H_2O (2 × 15 ml), and the aq. layer was extracted with Et_2O (4 × 15 ml). The combined org. fractions were dried ($MgSO_4$) and evaporated. FC (hexane/AcOEt 4:1) gave **22** (360 mg, 81%). Pale yellow solid. R_f (hexane/AcOEt 2:1) 0.56. M.p. 86–87°. $[\alpha]_D^{25} = -112.1$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3030*w*, 3014*w*, 2981*w*, 2246*w*, 1747*s*, 1491*w*, 1443*w*, 1384*m*, 1376*m*, 1227*s*, 1204*m*, 1159*m*, 1101*s*, 1054*s*, 1014*m*, 971*s*, 877*w*, 861*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 7.50–7.25 (*m*, 5 arom. H); 2.13 (*s*, AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 169.36 (*s*, C=O); 132.52 (2*d*); 129.48 (*d*); 128.40 (2*d*); 121.05 (*s*); 21.22 (*q*, Me). MALDI-MS: 349 ($[M + Na]^+$). HR-MALDI-MS: 349.1045 ($[M + Na]^+$, $C_{19}H_{18}NaO_5^+$; calc. 349.1046). Anal. calc. for $C_{19}H_{18}O_5$ (326.35): C 69.93, H 5.56; found: C 70.08, H 5.57.

Table 4. *Selected ^{1}H- and ^{13}C-NMR Chemical Shifts* [ppm], *and Coupling Constants* [Hz] *of the Unsaturated* D-ribo-*Hexofuranoses* **21**–**28** *in* $CDCl_3$

	21	**22**	**23**	**24**	**26**[a])	**25**	**27**	**28**
H–C(1)	6.21	6.24	6.20	6.20	5.86	5.34	5.28	5.07
H–C(2)	4.94	4.99	4.93	4.93	4.54	4.50	4.51	4.51
H–C(3)	4.82	4.84	4.81	4.81	4.44	4.41	4.41	4.41
H–C(4)	4.88	4.995	4.87	4.97	4.95	4.93	4.93	4.95
H–C(6)	2.55[b])	–	–	–	4.94	5.82	5.82	5.83
Me_2C	1.47, 1.33	1.48, 1.34	1.46, 1.32	1.45, 1.31	1.47, 1.32	1.46, 1.31	1.46, 1.31	1.45, 1.30
J(1,2)	0	0	0	0	0	0	0	0
J(2,3)	6.0	5.4	5.4	5.7	5.4	5.4	5.4	5.7
J(3,4)	0	0	0	0	0	0	0	0
C(1)	102.16	101.96	102.03	101.98	103.12	102.89	102.95	102.83
C(2)	85.21	85.07	84.98	85.18	80.62	80.67	80.71	80.74
C(3)	84.99	84.99	84.94	84.94	78.06	79.45	80.06	80.23
C(4)	75.92	76.55	76.76	77.30	78.93	78.17	77.99	77.88
C(5)	80.64	79.67	77.23	91.13	155.21	146.79	148.70	152.97
C(6)	75.24	71.82	48.01	5.12	80.09	88.58	74.53	41.57
C(7)	–	72.78	–	–	82.61	–	–	–
C(8)	–	78.63	–	–	92.43	–	–	–
Me_2C	113.37	113.54	113.45	113.42	114.08	113.94	114.02	114.04
Me_2C	26.40, 25.18	26.42, 25.25	26.39, 25.19	26.38, 25.19	25.99, 25.63	25.92, 25.55	25.96, 25.60	25.92, 25.57

[a]) Assignment based on a DQFCOSY and a HSQC spectrum, and on a NOE (2.5%) observed for H–C(2) upon irradiation of H–C(1). [b]) $^4J(4,6) = 2.4$ Hz.

1-O-*Acetyl-6*-C-*bromo-5,6-dideoxy-2,3*-O-*isopropylidene-β*-D-ribo-*hex-5-ynofuranose* (**23**). A suspension of **21** (56 mg, 0.25 mmol) and NBS (60 mg, 0.336 mmol) in acetone (3 ml) was treated with $AgNO_3$ (6 mg, 0.036 mmol) and stirred for 30 min at 22°. After evaporation, the residue was partitioned between H_2O and AcOEt. The aq. layer was extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4:1) gave **23** (71 mg, 95%). White solid. R_f (hexane/AcOEt 4:1) 0.43. M.p. 63–64°. $[\alpha]_D^{25} = -76.8$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3027*w*, 3015*m*, 2218*w*, 1746*s*, 1376*m*, 1313*w*, 1159*m*, 1100*s*, 1055*m*, 1014*m*, 971*s*, 927*w*, 865*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 2.08 (*s*, AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 169.30 (*s*, C=O); 21.17 (*q*, Me). HR-EI-MS: 290.9689 (97, $[M - Me]^+$, $C_{10}H_{10}{}^{81}BrO_5$, calc. 290.9691), 288.9715 (100, $[M - Me]^+$, $C_{10}H_{10}{}^{79}BrO_5$; calc. 288.9712). Anal. calc. for $C_{11}H_{13}BrO_5$ (305.12): C 43.30, H 4.29; found: C 43.08, H 4.13.

1-O-*Acetyl-5,6-dideoxy-6*-C-*iodo-2,3*-O-*isopropylidene-β*-D-ribo-*hex-5-ynofuranose* (**24**). A suspension of **21** (56 mg, 0.25 mmol) in acetone (3 ml) was added dropwise to a stirred soln. of $AgNO_3$ (65 mg, 0.38 mmol) and diluted NH_3/H_2O (1 drop) in H_2O (3 ml). The mixture was stirred for 5 min at 22°, treated with NIS (90 mg, 0.4 mmol), and stirred for 30 min (the mixture became homogeneous after *ca.* 5 min and then turbid again). After evaporation, the residue was partitioned between H_2O and AcOEt. The aq. layer was extracted with AcOEt (3 × 15 ml). The combined org. layers were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4:1) gave **24** (70 mg, 80%). White solid. R_f (hexane/AcOEt 4:1) 0.52. M.p. 59–60°. $[\alpha]_D^{25} = -60.8$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3027*m*, 3015*w*, 2929*m*, 2852*m*, 2190*w*, 1733*s*, 1602*w*, 1246*s*, 1159*w*, 1100*m*, 1046*m*, 1013*m*, 971*m*, 864*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 2.08 (*s*, AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 169.33 (*s*, C=O); 21.23 (*q*, Me). HR-EI-MS: 337.9612 (11, $[M - Me]^+$, $C_{10}H_{10}{}^{128}IO_5^+$; calc. 337.9607), 336.9577 (100, $[M - Me]^+$, $C_{10}H_{10}{}^{126}IO_5^+$; calc. 336.9573). Anal. calc. for $C_{11}H_{13}IO_5$ (352.13): C 37.52, H 3.72; found: C 37.55, H 3.79.

(*Z*)-*1,5-Anhydro-6*-C-*chloro-6-deoxy-2,3*-O-*isopropylidene-β*-D-ribo-*hex-5-enofuranose* (**25**). A suspension of **21** (240 mg, 1.06 mmol) in 5.25% aq. NaOCl (35 ml) was stirred at 22° for 16 h (the mixture became homogeneous within 30 min), diluted with H_2O (10 ml), and extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (20 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 2:1) gave **25** (208 mg, 90%). White solid. R_f (hexane/AcOEt 4:1) 0.45. M.p. 71–72°. $[\alpha]_D^{25} = -25.3$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*. ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*. EI-MS: 203 ($[M - Me]^+$).

X-Ray Analysis of **25**[6]). Recrystallisation of **25** in Et_2O/hexane 4:1 gave crystals suitable for X-ray analysis: $C_9H_{11}ClO_4$ (218.636); orthorhombic $P2_12_12_1$; $a = 5.55290(10)$, $b = 9.2059(2)$, $c = 40.4710(10)$ Å. V = 2068.85 Å^3; Z = 8; $D_{calc.} = 1.404$ Mg/m^3. Intensities were measured on an *Enraf-Nonius CAD-4* diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 152 K, θ range 0.998–29.575°. Of the 5331 total collected reflections, 5319 independent reflections were observed. $R = 0.0658$, $R_w = 0.1654$.

(Z)-*1,5-Anhydro-6,7,8-trideoxy-2,3*-O-*isopropylidene-8*-C-*phenyl-β*-D-ribo-*oct-5-en-7-ynofuranose* (**26**). A suspension of **22** (50 mg, 0.15 mmol) in dry MeOH (3 ml) was treated with one batch of MeONa (30 mg, 0.56 mmol) and kept at reflux for 4 h. After evaporation, the residue was treated with soln. of 0.1M HCl (0.5 ml) in H_2O (10 ml), and extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (cyclohexane/AcOEt 4:1) gave **26** (40 mg, 91%). White solid. R_f (cyclohexane/AcOEt 4:1) 0.53. M.p. 74–75°. $[\alpha]_D^{25} = +13.2$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3030*w*, 3013*w*, 2939*w*, 2204*w*, 1950*w*, 1683*m*, 1597*w*, 1491*m*, 1456*w*, 1443*w*, 1384*m*, 1376*m*, 1356*m*, 1316*m*, 1231*s*, 1204*m*, 1158*m*, 1138*s*, 1091*s*, 1056*m*, 971*m*, 925*s*, 865*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): see *Table 4*; additionally, 7.45–7.26 (*m*, 5 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): see *Table 4*; additionally, 131.35 (*d*); 128.13 (2*d*); 127.96 (2*d*); 123.26 (*s*). HR-MALDI-MS: 307.0950 ($[M + Na]^+$, $C_{17}H_{16}NaO_4^+$; calc. 307.0941). Anal. calc. for $C_{17}H_{16}O_4$ (284.31): C 71.96, H 5.81; found: C 71.82, H 5.67.

X-Ray Analysis of **26**[6]). Recrystallisation of **26** in Et_2O/hexane 4:1 gave crystals suitable for X-ray analysis: $C_{17}H_{16}O_4$ (284.311); orthorhombic $P2_12_12_1$; $a = 5.5724(2)$, $b = 16.1789(5)$, $c = 16.5834(5)$ Å. V = 1495.08 Å^3; Z = 4; $D_{calc.} = 1.263$ Mg/m^3. Intensities were measured on an *Enraf-Nonius CAD-4* diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 202 K, θ range 0.998–31.507°. Of the 4757 total collected reflections, 4738 independent reflections were observed. $R = 0.0616$, $R_w = 0.1552$.

(Z)-*1,5-Anhydro-6*-C-*bromo-6-deoxy-2,3*-O-*isopropylidene-β*-D-ribo-*hex-5-enofuranose* (**27**). A suspension of **23** (100 mg, 0.33 mmol) in dry MeOH (3 ml) was treated with one batch of MeONa (30 mg, 0.56 mmol), stirred at 22° overnight, and evaporated. The residue was treated with a soln. of 0.1M HCl (0.5 ml) in H_2O (10 ml) and extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4:1) gave **27** (72 mg, 84%). White solid. R_f (hexane/AcOEt 4:1) 0.55. M.p. 118–119°. $[\alpha]_D^{25} = -34.9$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3105*w*, 3029*m*, 2993*m*, 2941*m*, 1692*m*, 1457*m*, 1384*s*, 1376*s*, 1340*m*, 1284*s*, 1233*s*, 1204*s*, 1158*m*, 1122*s*, 1090*s*, 1048*s*, 971*s*, 927*s*, 865*m*, 830*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*. ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*. Anal. calc. for $C_9H_{11}BrO_4$ (263.09): C 41.09, H 4.21; found: C 41.31, H 4.13.

X-Ray Analysis of **27**[6]). Recrystallisation of **27** in Et_2O/hexane 4:1 gave crystals suitable for X-ray analysis: $C_9H_{11}BrO_4$ (263.092); orthorhombic $P2_12_12_1$; $a = 5.6059(2)$, $b = 9.3515(3)$, $c = 19.8996(7)$ Å. V = 1043.21 Å^3; Z = 4; $D_{calc.} = 1.675$ Mg/m^3. Intensities were measured on an *Enraf-Nonius CAD-4* diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 298 K, θ range 0.998–26.733°. Of the 2064 total collected reflections, 2051 independent reflections were observed. $R = 0.0556$, $R_w = 0.1828$.

(Z)-*1,5-Anhydro-6-deoxy-6*-C-*iodo-2,3*-O-*isopropylidene-β*-D-ribo-*hex-5-enofuranose* (**28**). A suspension of **24** (36 mg, 0.1 mmol) in dry MeOH (3 ml) was treated with one batch of MeONa (10 mg, 0.2 mmol), stirred at 22° overnight, and evaporated. The residue was treated with a soln. of 0.1M HCl (0.5 ml) in H_2O (10 ml) and extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4:1) gave **28** (28 mg, 91%). White solid. R_f (hexane/AcOEt 4:1) 0.52. M.p. 130–132°. $[\alpha]_D^{25} = -24.1$ ($c = 0.96$, $CHCl_3$). IR ($CHCl_3$): 3095*w*, 3029*w*, 3011*m*, 2983*m*, 2959*m*, 1674*m*, 1457*w*, 1384*m*, 1376*m*, 1340*w*, 1283*m*, 1231*s*, 1228*s*, 1205*s*, 1159*m*, 1113*s*, 1087*s*, 1044*m*, 971*m*, 927*s*, 880*m*, 865*s*, 829*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*. ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*. HR-EI-MS: 296.0877 (9, $[M - Me]^+$, $C_8H_8{}^{128}IO_4^+$, calc. 296.0875), 295.0926 (100, $[M - Me]^+$, $C_8H_8{}^{126}IO_4^+$, calc. 295.0928), 295 ($[M - Me]^+$). Anal. calc. for $C_9H_{11}IO_4$ (310.09): C 34.86, H 3.58; found: C 35.00, H 3.66.

X-Ray Analysis of **28**[6]). Recrystallisation of **28** in Et_2O/hexane 4:1 gave crystals suitable for X-ray analysis: $C_9H_{11}IO_4$ (310.087); orthorhombic $P2_12_12_1$; $a = 5.6538(2)$, $b = 20.4230(6)$, $c = 9.4368(3)$ Å. V = 1089.64 Å^3; Z = 4; $D_{calc.} = 1.890$ Mg/m^3. Intensities were measured on an *Enraf-Nonius CAD-4* diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 298 K, θ range 0.998–28.700°. Of the 5274 total collected reflections, 2798 independent reflections were observed. $R = 0.0386$, $R_w = 0.1282$.

Phenyl 2,3,6-Tri-O-*acetyl-4-deoxy-4*-C-*(4-phenylbuta-1,3-diyn-1-yl)-1-thio-β*-D-*glucopyranoside* (**30**). A suspension of $[Pd_2(dba)_3]$ (6 mg, 0.0125 mmol), CuI (2 mg, 0.01 mmol), P(fur)$_3$ (6 mg, 0.0125 mmol), **29** [44] (253 mg, 0.5 mmol), and (bromoethynyl)benzene (91 mg, 0.5 mmol) in DMF (3 ml) was degassed twice and stirred for 5 min at 22°. The mixture was treated with Et_3N (0.3 ml) and stirred for 12 h at 22°. The soln. was diluted with Et_2O (10 ml), treated with H_2O (10 ml), and 0.1M aq. HCl (3 ml). The org. layer was washed with H_2O (2 × 15 ml), and the aq. layer was extracted with Et_2O (4 × 10 ml). The combined org. fractions were dried

($MgSO_4$) and evaporated. FC (hexane/AcOEt 4:1) gave **30** (246 mg, 82%). White solid. R_f (hexane/AcOEt 4:1) 0.46. M.p. 128–129°. $[\alpha]_D^{25} = -10.7$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3029*w*, 3014*w*, 2953*w*, 2336*w*, 1751*s*, 1600*w*, 1491*w*, 1479*w*, 1441*w*, 1372*w*, 1231*s*, 1227*s*, 1051*m*, 909*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 7.50–7.26 (*m*, 10 arom. H); 2.11 (*s*, AcO); 2.09 (*s*, 2 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 170.37, 169.63, 169.42 (3*s*, 3 C=O); 140.63 (*s*); 133.06 (2*d*); 132.56 (2*d*); 129.37 (*d*); 128.83 (2*d*); 128.35 (2*d*); 128.30 (*d*); 121.05 (*s*); 20.94 (*q*, 2 Me); 20.82 (*q*, Me). HR-MALDI-MS: 529.1297 ($[M + Na]^+$, $C_{28}H_{26}NaO_7S^+$; calc. 529.1291). Anal. calc. for $C_{28}H_{26}O_7S$ (506.58): C 66.21, H 5.26; found: C 66.39, H 5.17.

Table 5. *Selected ^{1}H- and ^{13}C-NMR Chemical Shifts* [ppm], *and Coupling Constants* [Hz] *of the 1-Thio-β-*D*-glucopyranosides* **30**–**37** *in $CDCl_3$*

	30	**31**	**32**	**33**	**34**	**35**	**36**	**37**
H–C(1)	4.71	4.69	4.68	4.68	4.67	4.66	4.65	4.65
H–C(2)	4.84	4.81	4.79	4.80	3.35	3.33	3.33	3.33
H–C(3)	5.27	5.22	5.21	5.22	3.87	3.84	3.84	3.86
H–C(4)	2.97	2.79	2.78	2.91	2.67	2.61	2.56	2.54
H–C(5)	3.78	3.72	3.72	3.73	3.80	3.79	3.77	3.79
H_a–C(6)	4.52	4.47	4.46	4.46	4.42	4.39	4.38	4.39
H_b–C(6)	4.29	4.24	4.22	4.24	4.06	4.01	4.01	4.03
H–C(2′)	–	–	–	–	5.15	5.44	5.38	5.16
HO–C(2)	–	–	–	–	2.80	2.76	2.82	2.70
HO–C(3)	–	–	–	–	2.67	2.61	2.67	2.58
J(1,2)	9.9	9.9	9.9	9.9	9.6	9.9	9.6	9.6
J(2,3)	9.0	9.0	9.0	9.0	8.7	8.5	8.1	8.1
J(3,4)	10.8	10.8	10.8	11.1	10.8	10.5	10.7	10.5
J(4,5)	10.5	10.5	10.5	10.4	10.8	10.5	10.7	10.5
J(4,2′)	–	–	–	–	2.1	2.4	2.1	2.1
J(5,6a)	2.2	2.1	2.1	2.2	6.6	6.7	6.9	6.7
J(5,6b)	5.4	5.7	5.7	5.7	9.6	9.6	9.6	9.7
J(6a,6b)	12.0	12.0	12.0	12.0	8.0	7.8	7.8	7.8
J(2,OH)	–	–	–	–	≤ 2.0	2.4	2.7	2.4
J(3,OH)	–	–	–	–	≤ 2.0	≤ 2.0	3.0	2.4
C(1)	85.86	85.82	85.78		90.68	89.06	90.91	90.63
C(2)	70.22	70.16	70.17		73.54	73.55	73.77	73.60
C(3)	73.28	73.41	73.36		74.47	74.29	74.54	74.28
C(4)	36.97	36.28	37.05		49.34	48.99	49.80	49.90
C(5)	76.50	76.53	76.42		76.88	77.17	75.77	77.50
C(6)	64.11	64.06	64.05		69.87	69.60	69.86	69.61
C(1′)	[a])	73.41	73.87		161.98	152.31	154.31	157.83
C(2′)	69.71	63.28	44.81		79.83	90.66	77.49	43.56
C(3′)	73.06	–	–		83.64	–	–	–
C(4′)	76.25	–	–		91.97	–	–	–

[a]) Hidden by the signals of $CDCl_3$.

*Phenyl 2,3,6-Tri-*O*-acetyl-4-*C*-(2-chloroethynyl)-4-deoxy-1-thio-β-*D*-glucopyranoside* (**31**). A suspension of **29** (101 mg, 0.25 mmol) in THF (3 ml) was cooled to −78°, treated with 1.6M BuLi in hexane (0.2 ml, 0.3 mmol), and stirred for 3 min. The mixture was transferred *via* a cannula to a stirred, cooled (−78°) soln. of NCS (34 mg, 0.32 mmol) in THF (3 ml). The resulting mixture was slowly warmed to ambient temp., when TLC showed complete conversion. After addition of sat. aq. NH_4Cl soln. (5 ml), the aq. layer was extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (cyclohexane/AcOEt 4:1) gave **31** (70 mg, 64%). White solid. R_f (hexane/AcOEt 4:1) 0.62. M.p. 123–124°. $[\alpha]_D^{25} = -28.5$ ($c = 1.05$, $CHCl_3$). IR ($CHCl_3$): 3030*w*, 3009*w*, 2957*w*, 2873*w*, 2245*w,* 1752*s*, 1584*w*,

1479*w*, 1440*w*, 1372*m*, 1234*s*, 1227*s*, 1050*s*, 954*w*, 913*w*, 830*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 7.49–7.28 (*m*, 5 arom. H); 2.10, 2.08, 2.07 (3*s*, 3 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 170.36, 169.61, 169.40 (3*s*, 3 C=O); 132.93 (2*d*); 131.70 (*s*); 128.81 (2*d*); 128.23 (*d*); 20.92 (*q*, 2 Me); 20.76 (*q*, Me). HR-MALDI-MS: 465.0551 (32, $[M + Na]^+$, $C_{20}H_{21}{}^{37}ClNaO_7S^+$; calc. 465.0565), 463.0591 (100, $[M + Na]^+$, $C_{20}H_{21}{}^{35}ClNaO_7S^+$, calc. 463.0594). Anal. calc. for $C_{20}H_{21}ClO_7S$ (440.90): C 54.48, H 4.80; found: C 54.51, H 5.05.

Phenyl 2,3,6-Tri-O-*acetyl-4*-C-*(2-bromoethynyl)-4-deoxy-1-thio-β*-D-*glucopyranoside* (**32**). A suspension of **29** (101 mg, 0.25 mmol) and NBS (60 mg, 0.336 mmol) in acetone (3 ml) was treated with $AgNO_3$ (6 mg, 0.036 mmol) and stirred for 30 min at 22°. After evaporation, the residue was partitioned between H_2O and AcOEt. The aq. layer was extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4:1) gave **32** (101 mg, 83%). White solid. R_f (hexane/AcOEt 4:1) 0.58. M.p. 84–85°. $[\alpha]_D^{25} = -28.8$ ($c = 1.04$, $CHCl_3$). IR ($CHCl_3$): 3029*m*, 3013*m*, 2955*w*, 2871*w*, 2220*w*, 1753*s*, 1584*w*, 1479*w*, 1440*w*, 1372*m*, 1231*s*, 1081*m*, 1050*s*, 954w, 911*m*, 828*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 7.47–7.26 (*m*, 5 arom. H); 2.08, 2.06, 2.04 (3*s*, 3 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 170.34, 169.56, 169.38 (3*s*, 3 C=O); 132.91 (2*d*); 131.70 (*s*); 128.79 (2*d*); 128.21 (*d*); 20.92 (*q*, 2 Me); 20.74 (*q*, Me). HR-MALDI-MS: 509.0068 (97, $[M + Na]^+$, $C_{20}H_{21}{}^{81}BrNaO_7S^+$; calc. 509.0069), 507.0090 (100, $[M + Na]^+$, $C_{20}H_{21}{}^{79}BrNaO_7S^+$; calc. 507.0089). Anal. calc. for $C_{20}H_{21}BrO_7S$ (485.35): C 49.49, H 4.36; found: C 49.64, H 4.34.

Phenyl 2,3,6-Tri-O-*acetyl-4-deoxy-4*-C-*(2-iodoethynyl)-1-thio-β*-D-*glucopyranoside* (**33**). A soln. of $AgNO_3$ (65 mg, 0.38 mmol) in H_2O (3 ml) was treated with dil. NH_3/H_2O (1 drop), dropwise with a suspension of **29** (101 mg, 0.25 mmol) in acetone (3 ml), NIS (90 mg, 0.4 mmol), and stirred for 30 min (the mixture became homogeneous after *ca.* 5 min and then became turbid again). After evaporation, the residue was partitioned between H_2O and AcOEt. The aq. layers were extracted with AcOEt (3 × 15 ml). The combined org. layers were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4:1) gave **33** (109 mg, 73%). White solid. R_f (hexane/AcOEt 4:1) 0.62. M.p. 123–124°. $[\alpha]_D^{25} = -121.6$ ($c = 1.04$, $CHCl_3$). IR ($CHCl_3$): 3030*m*, 3011*m*, 2957*w*, 2872*w*, 2118*w*, 1953*w*, 1752*s*, 1584*w*, 1479*m*, 1440*m*, 1372*s*, 1240*s*, 1081*s*, 1051*s*, 953w, 913*m*, 868*w*, 826*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 7.48–7.27 (*m*, 5 arom. H); 2.09, 2.08, 2.06 (3*s*, 3 AcO). HR-MALDI-MS: 555.9987 (22, $[M + Na]^+$, $C_{20}H_{21}{}^{127}INaO_7S^+$; calc. 555.9984), 554.9951 (100, $[M + Na]^+$, $C_{20}H_{21}{}^{126}INaO_7S^+$; calc. 554.9950).

Phenyl (Z)-*4^I,6-Anhydro-4-deoxy-4*-C-*(4-phenyl-1-hydroxybut-1-en-3-yn-1-yl)-1-thio-β*-D-*glucopyranoside* (**34**). A suspension of **30** (51 mg, 0.1 mmol) in dry MeOH (3 ml) was treated with one batch of MeONa (20 mg, 0.37 mmol) and kept at reflux for 4 h. After evaporation, the residue was treated with a soln. of 0.1M HCl (0.5 ml) in H_2O (10 ml) and extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4:1) gave **34** (29 mg, 76%). R_f (hexane/AcOEt 4:1) 0.40. $[\alpha]_D^{25} = -114.9$ ($c = 1.02$, $CHCl_3$). IR ($CHCl_3$): 3586*w*, 3500–3150*w* (br.), 3064*w*, 3029*w*, 3012*m*, 2901*w*, 2199*w*, 1669*m*, 1596*w*, 1490*m*, 1480*m*, 1441*m*, 1360*m*, 1303*w*, 1247*m*, 1177*m*, 1130*m*, 1109*m*, 1089*m*, 1070*m*, 1044*m*, 1008*s*, 914*w*, 862*w*, 825*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 7.56–7.25 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 133.04 (2*d*); 131.23 (2*d*); 130.80 (*s*); 129.15 (2*d*); 128.62 (*d*); 128.01 (2*d*); 127.51 (*d*); 123.76 (*s*). HR-MALDI-MS: 403.0973 ($[M + Na]^+$, $C_{22}H_{20}NaO_4S^+$; calc. 403.0975). Anal. calc. for $C_{22}H_{20}O_4S$ (380.46): C 69.45, H 5.30; found: C 69.53, H 5.50.

Phenyl (Z)-*4^I,6-Anhydro-4*-C-*(2-chloro-1-hydroxyethenyl)-4-deoxy-1-thio-β*-D-*glucopyranoside* (**35**). A suspension of **31** (44 mg, 0.1 mmol) in dry MeOH (3 ml) was treated with one batch of MeONa (20 mg, 0.37 mmol) and kept at reflux for 4 h. After evaporation, the residue was treated with a soln. of 0.1M HCl (0.5 ml) in H_2O (10 ml), and extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (cyclohexane/AcOEt 2:1) gave **35** (20 mg, 63%). White solid. R_f (cyclohexane/AcOEt 2:1) 0.52. M.p. 85–86°. $[\alpha]_D^{25} = -158.8$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3586*m*, 3391*w* (br.), 3113*w*, 3028*w*, 3008*m*, 2960*s*, 2928*s*, 2901*m*, 2873*s*, 1690*w*, 1650*w*, 1583*w*, 1481*m*, 1441*m*, 1383*m*, 1354*m*, 1308*m*, 1284*w*, 1175*m*, 1131*s*, 1110*s*, 1090*m*, 1071*m*, 1034*s*, 1004*s*, 893*m*, 826*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 7.55–7.33 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 133.02 (2*d*); 130.71 (*s*); 129.16 (*d*); 128.67 (2*d*). HR-MALDI-MS: 339.0246 (32, $[M + Na]^+$, $C_{14}H_{15}{}^{37}ClNaO_4S^+$; calc. 339.0248), 337.0280 (100, $[M + Na]^+$, $C_{14}H_{15}{}^{35}ClNaO_4S^+$; calc. 337.0277). Anal. calc. for $C_{14}H_{15}ClO_4S$ (398.86): C 54.20, H 4.80; found: C 54.16, H 4.82.

Phenyl (Z)-*4^I,6-Anhydro-4*-C-*(2-bromo-1-hydroxyethenyl)-4-deoxy-1-thio-β*-D-*glucopyranoside* (**36**). A suspension of **32** (48 mg, 0.1 mmol) in dry MeOH (3 ml) was treated with one batch of MeONa (20 mg, 0.37 mmol) and kept at reflux for 4 h. After evaporation, the residue was treated with a soln. of 0.1M HCl (0.5 ml) in H_2O (10 ml) and extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with

brine (10 ml), dried ($MgSO_4$), and evaporated. FC (cyclohexane/AcOEt 2:1) gave **36** (27 mg, 74%). R_f (cyclohexane/AcOEt 2:1) 0.46. $[\alpha]_D^{25} = -93.6$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3524*w* (br.), 3450*w* (br.), 3029*s*, 2986*s*, 2941*m*, 2907*m*, 2875*m*, 1732*s*, 1573*w*, 1478*w*, 1465*s*, 1446*s*, 1374*s*, 1251*s*, 1197*m*, 1158*m*, 1096*s*, 1046*s*, 1004*m*, 940*m*, 918*m*, 847*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 7.54–7.26 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 133.37 (2*d*); 131.06 (*s*); 129.52 (2*d*); 129.02 (*d*). HR-MALDI-MS: 382.9758 (97, $[M + Na]^+$, $C_{14}H_{15}{}^{81}BrNaO_4S^+$; calc. 382.9752), 380.9776 (100, $[M + Na]^+$, $C_{14}H_{15}{}^{79}BrNaO_4S^+$; calc. 380.9772). Anal. calc. for $C_{14}H_{15}BrO_4S$ (359.24): C 46.81, H 4.21; found: C 46.85, H 4.36.

Phenyl (Z)-*4^I,6-Anhydro-4-deoxy-4*-C-*(1-hydroxy-2-iodoethenyl)-1-thio-β*-D-*glucopyranoside* (**37**). A suspension of **33** (53 mg, 0.1 mmol) in dry MeOH (3 ml) was treated with one batch of MeONa (20 mg, 0.37 mmol) and kept at reflux for 4 h. After evaporation, the residue was treated with a soln. of 0.1M HCl (0.5 ml) in H_2O (10 ml), and extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (cyclohexane/AcOEt 2:1) gave **37** (26 mg, 64%) R_f (cyclohexane/AcOEt 2:1) 0.45. M.p. 66–67°. $[\alpha]_D^{25} = -99.7$ ($c = 0.98$, $CHCl_3$). IR ($CHCl_3$): 3587*w* (br.), 3416*w* (br.), 3027*w*, 2984*m*, 1731*s*, 1478*w*, 1441*w*, 1375*s*, 1249*s*, 1110*m*, 1046*s*, 940*w*, 846*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 7.54–7.32 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 133.03 (2*d*); 130.69 (*s*); 129.16 (2*d*); 128.66 (*d*). HR-ESI-MS: 429.9687 (16, $[M + Na]^+$, $C_{14}H_{15}{}^{127}INaO_4S^+$; calc. 429.9689), 428.9625 (100, $[M + Na]^+$, $C_{14}H_{15}{}^{126}INaO_4S^+$; calc. 428.9628).

Phenyl 6-O-*Acetyl-2,3-di*-O-*benzyl-4-deoxy-4*-C-*(4-phenylbuta-1,3-diyn-1-yl)-1-thio-α*-D-*glucopyranoside* (**39**). A suspension of $[Pd_2(dba)_3]$ (6 mg, 0.0125 mmol), CuI (2 mg, 0.01 mmol), P(fur)$_3$ (6 mg, 0.0125 mmol), **38** [30] (251 mg, 0.5 mmol) and (bromoethynyl)benzene (91 mg, 0.5 mmol) in DMF (3 ml) was degassed twice and stirred at 22° for 5 min. The mixture was treated with Et_3N (0.3 ml) and stirred for 12 h at 22°. The soln. was diluted with Et_2O (10 ml), and treated with H_2O (10 ml) and 0.1M aq. HCl (3 ml). The org. layer was washed with H_2O (2 × 15 ml), and the aq. layer was extracted with Et_2O (4 × 10 ml). The combined org. fractions were dried ($MgSO_4$) and evaporated. FC (hexane/AcOEt 4:1) gave **39** (246 mg, 82%). Pale yellow solid. R_f (hexane/AcOEt 4:1) 0.48. M.p. 126–128°. $[\alpha]_D^{25} = -149.6$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3066*w*, 3032*m*, 3012*m*, 2245*w*, 2144*w*, 1951*w*, 1880*w*, 1741*s*, 1584*w*, 1491*m*, 1481*m*, 1454*m*, 1441*m*, 1368*m*, 1239*s*, 1206*w*, 1126*s*, 1087*s*, 1038*s*, 1028*s*, 910*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 6*; additionally, 7.53–7.26 (*m*, 20 arom. H); 4.95 (*s*, PhCH_2); 4.78, 4.72 (2*d*, $J = 11.7$, PhCH_2); 2.02 (*s*, AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 6*; additionally, 170.48 (*s*, C=O); 137.93, 137.43, 133.56 (3*s*); 132.54 (2*d*); 131.67 (2*d*); 127.33–129.20 (several *d*); 121.40 (*s*); 76.61, 72.62 (2*t*, 2 PhCH_2); 20.90 (*q*, Me). MALDI-MS: 625 ($[M + Na]^+$). HR-MALDI-MS: 625.2012 ($[M + Na]^+$, $C_{38}H_{34}NaO_5S^+$; calc. 625.2019). Anal. calc. for $C_{38}H_{34}O_5S$ (602.75): C 75.72, H 5.69; found: C 75.94, H 5.96.

Treatment of **39** *with MeONa.* A suspension of **39** (60 mg, 0.1 mmol) in dry MeOH (3 ml) was treated with one batch of MeONa (20 mg, 0.37 mmol) and kept at reflux for 4 h. After evaporation, the residue was treated with a soln. of 0.1M HCl (0.5 ml) in H_2O (10 ml), and extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4:1) gave **41** (28 mg, 51%) and **40** (17 mg, 30%).

Data of Phenyl (Z)-4^I,6-Anhydro-2,3-di-O-*benzyl-4-deoxy-4*-C-*(1-hydroxy-4-phenylbut-1-en-3-yn-1-yl)-1-thio-α*-D-*galactopyranoside* (**40**). R_f (hexane/AcOEt 4:1) 0.52. $[\alpha]_D^{25} = +11.8$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3066*w*, 3030*m*, 3014*s*, 2930*w*, 2195*w*, 1951*w*, 1879*w*, 1807*w*, 1648*s*, 1596*m*, 1584*m*, 1489*m*, 1481*m*, 1454*m*, 1440*w*, 1354*w*, 1293*w*, 1262*m*, 1172*s*, 1091*s*, 1047*s*, 1027*s*, 999*m*, 987*m*, 931*w*, 911*w*, 872*w*, *842w*, 820*w*. ^{1}H-NMR (500 MHz, C_6D_6): see *Table 6*; additionally, 7.52–7.46 (*m*, 2 arom. H); 7.42–7.34 (*m*, 2 arom. H); 7.29–7.24 (*m*, 4 arom. H); 7.16–7.01 (*m*, 8 arom. H); 6.99–6.82 (*m*, 4 arom. H); 4.51, 4.46 (2*d*, $J = 11.7$, PhCH_2); 4.34, 4.29 (2*d*, $J = 11.4$, PhCH_2); 4.18 (*t*, $J \approx 3.0$, irrad. at 4.01 → NOE of 3.9%, H–C(5)); 4.11 (*dd*, $J = 10.0$, 4.8, irrad. at 5.98 → NOE of 2.4%, H–C(2)); 3.42 (*dd*, $J = 10.1$, 2.5, irrad. at 4.18 → NOE of 3.8%, H′–C(6)); 2.72 (*dt*, $J \approx 5.6$, 3.4, irrad. at 5.98 → NOE of 2.6%, irrad. at 4.18 → NOE of 7.4%, irrad. at 4.01 → NOE of 12%, H–C(4)). ^{13}C-NMR (125 MHz, C_6D_6): see *Table 6*; additionally, 138.59 (2*s*); 135.35 (*s*); 131.46 (2*d*), 130.67 (2*d*); 129.16 (2*d*); 126.86–128.63 (several *d*); 125.33 (*s*); 73.23, 72.77 (2*t*, 2 PhCH_2). MALDI-MS: 583 ($[M + Na]^+$). HR-MALDI-MS: 583.1920 ($[M + Na]^+$, $C_{36}H_{32}NaO_4S^+$; calc. 583.1914).

Data of Phenyl (E)-*4^I,6-Anhydro-2,3-di*-O-*benzyl-4-deoxy-4*-C-*(1-hydroxy-4-phenylbut-1-en-3-yn-1-yl)-1-thio-α*-D-*galactopyranoside* (**41**). R_f (hexane/AcOEt 4:1) 0.62. $[\alpha]_D^{25} = +37.3$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3066*w*, 3033*w*, 3013*s*, 2930*m*, 2893*w*, 2196*w*, 1950*w*, 1878*w*, 1807*w*, 1731*w*, 1648*m*, 1595*w*, 1584*w*, 1489*m*, 1481*m*, 1454*m*, 1440*w*, 1377*m*, 1350*w*, 1307*m*, 1262*m*, 1173*m*, 1101*s*, 1067*m*, 1047*s*, 1027*s*, 999*m*, 987*m*, 931*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 6*; additionally, 7.54–7.19 (*m*, 20 arom. H); 4.93 (*ddd*, $J = 7.0$, 5.9, 3.2, irrad. at 3.68 → NOE of 10.5%, H–C(5)); 4.77 (*d*, $J = 12.0$), 4.565 (*d*, $J = 11.8$) (PhCH_2); 4.570 (*dd*, $J \approx 5.7$, 4.2, irrad. at 3.68 → NOE of 7.5%, H–C(3)); 4.558 (*d*, $J = 11.4$), 4.47 (*d*, $J = 12.0$) (PhCH_2); 4.22 (*dd*, $J = 10.0$, 6.0, irrad. at

Table 6. *Selected ^{1}H- and ^{13}C-NMR Chemical Shifts* [ppm], *and Coupling Constants* [Hz] *of the 1-Thio-β-*D*-glucopyranosides* **39**–**44**

	39 $CDCl_3$	**40**[a]) C_6D_6	**41**[a]) $CDCl_3$	**42** $CDCl_3$	**43** $CDCl_3$	**44** (Glc) $CDCl_3$	**44** (Gal)
H–C(1)	5.64	5.65	5.73	5.64	5.60	5.61	5.65
H–C(2)	3.80	4.11	3.64	3.79	3.75	3.76	4.20–4.13
H–C(3)	3.92	4.01	4.57	3.90	3.88	3.89	4.20–4.13
H–C(4)	2.85	2.72	3.68	2.79	2.81	2.81	3.53[b])
H–C(5)	4.57	4.18	4.93	4.56	4.35	4.36	4.20–4.13
H_a–C(6)	4.35	3.91	4.36	4.33	3.87–3.70	3.94–3.84	4.20–4.13
H_b–C(6)	4.31	3.42	4.22	4.29	3.87–3.70	3.82–3.72	4.11
H–C(2′)	–	5.98	5.34	–	–	–	5.31[c])
J(1,2)	5.5	4.8	5.0	5.4	5.1	5.4	4.0
J(2,3)	9.3	10.0	4.2	9.3	9.3	9.3	[d])
J(3,4)	9.9	5.6	5.7	9.9	9.9	9.7	[d])
J(4,5)	10.8	3.4	7.0	10.5	10.5	10.5	[d])
J(4,2′)	–	2.2	1.9	–	–	–	1.5
J(5,6a)	4.2	0	3.1	3.6	2.1	3.0	[d])
J(5,6b)	3.6	2.5	6.0	2.4	4.8	5.4	2.7
J(6a,6b)	11.1	10.1	10.0	10.8	[d])	[d])	10.0
C(1)	86.99	87.29	85.31	86.90	87.10		
C(2)	79.52[e])	76.76	74.14	79.33[e])	79.54[e])		
C(3)	79.40[e])	75.10	71.60	78.99[e])	79.03[e])		
C(4)	38.20	46.11	43.46	37.86	37.39		
C(5)	69.34	72.13	70.21	69.24	71.66		
C(6)	64.32	74.27	75.19	64.21	62.94		
C(1′)	79.03	164.23	168.59	74.82	75.10		
C(2′)	68.94	81.61	80.85	68.49	68.35		
C(3′)	73.67	86.70	87.00	–	–		
C(4′)	76.16	92.64	92.30	–	–		

[a]) Assignment based on selective homodecoupling experiments, and a HSQC and a HMBC spectrum. [b]) *J*(2′,H–C(4) of Glc) = 1.5 Hz. [c]) Br. *s*; $w_{1/2}$ = 8.7 Hz. [d]) Not assigned. [e]) Assignments may be interchanged.

4.93 → NOE of 3.5%, H′–C(6)); 3.68 (*ddd*, *J* ≈ 7.2, 5.6, 1.8, irrad. at 4.93 → NOE of 9%, H–C(4)); no NOE observed upon irrad. at 5.34. ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 6*; additionally, 137.73, 137.02, 135.74 (3*s*); 130.65 (2*d*), 130.09 (2*d*); 128.95–126.50 (several *d*); 124.13 (*s*); 74.37, 73.73 (2*t*, 2 Ph*C*H$_2$). MALDI-MS: 583 ([*M* + Na]$^+$). HR-MALDI-MS: 583.1919 ([*M* + Na]$^+$, $C_{36}H_{32}NaO_4S^+$; calc. 583.1914).

*4,4′-(Buta-1,3-diyne-1,4-diyl)bis(phenyl 6-*O*-Acetyl-2,3-di-*O*-benzyl-4-deoxy-1-thio-α-*D*-glucopyranoside)* (**42**). Under Ar, a soln. of $Cu(OAc)_2$ (6.7 g, 36.88 mmol) in pyridine (72 ml) was stirred at 60° for 3 h, treated with a soln. of **38** (900 mg, 1.84 mmol) in pyridine (10 ml), stirred for 1 h, cooled to r.t., and evaporated. Pyridine was removed by two co-distillations with toluene. FC (hexane/AcOEt 5:1 → 1:1) gave **42** (795 mg, 88%). R_f (hexane/AcOEt 1:1) 0.38. ^{1}H-NMR (75 MHz, $CDCl_3$): see *Table 6*; additionally, 7.50–7.24 (*m*, 15 arom. H); 4.93 (*d*, *J* = 10.8), 4.88 (*d*, *J* = 10.5), 4.77 (*d*, *J* = 12.0), 4.71 (*d*, *J* = 11.7) (4 PhC*H*); 2.01 (*s*, AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 6*; additionally, 170.40 (*s*, C=O); 137.86, 137.38 (2*s*); 133.48 (*s*); 131.66 (2*d*); 128.91 (2*d*); 128.40 (2*d*); 128.30 (2*d*); 128.14 (2*d*); 127.98 (2*d*); 127.93, 127.76, 127.31 (3*d*); 76.11, 72.57 (2*t*, 2 Ph*C*H$_2$); 20.87 (*q*, Me). MALDI-MS: 1025 ([*M* + Na]$^+$).

*4,4′-(Buta-1,3-diyne-1,4-diyl)bis(phenyl 2,3-Di-*O*-benzyl-4-deoxy-1-thio-α-*D*-glucopyranoside)* (**43**). A soln. of **42** (600 mg, 0.6 mmol) in THF/MeOH/H_2O 4:4:1 (45 ml) was treated with 1M MeONa in MeOH (3 ml), heated for 15 min to 60°, cooled to r.t., treated with *Amberlite IR-120* (H^+ form), and stirred for 5 min. Filtration, evaporation of the filtrate, and FC (hexane/AcOEt 5:1 → 1:1) gave **43** (549 mg, 99%). R_f (hexane/AcOEt 1:1) 0.47. ^{1}H-NMR (75 MHz, $CDCl_3$): see *Table 6*; additionally, 7.49–7.26 (*m*, 15 arom. H); 4.92 (*d*, *J* = 11.1), 4.88 (*d*, *J* = 11.1), 4.77 (*d*, *J* = 11.7), 4.71 (*d*, *J* = 11.7) (4 PhC*H*); 1.57 (br. *s*, OH). ^{13}C-NMR (75 MHz,

$CDCl_3$): see *Table 6*; additionally, 137.96, 137.44 (2*s*); 133.40 (*s*); 132.03 (2*d*); 128.98 (2*d*); 128.37 (2*d*); 128.26 (2*d*); 128.09 (2*d*); 127.98 (2*d*); 127.89, 127.68, 127.46 (3*d*); 75.95, 72.66 (2*t*, 2 PhCH$_2$). MALDI-MS: 941 ([*M* + Na]$^+$).

Treatment of **43** *with* $Na_2S \cdot 9\,H_2O$. A soln. of **43** (50 mg, 32.6 μmol) in $MeOCH_2CH_2OH$ (3 ml) was treated with $Na_2S \cdot 9\,H_2O$ (8 mg, 32.6 μmol), kept for 30 min at reflux, and cooled to 23°. The suspension was diluted with AcOEt (0.5 ml) and hexane (0.8 ml), stirred for 30 min at 23°, and filtered over *Celite*. Evaporation of the filtrate and FC (hexane/AcOEt 20 : 1 → 10 : 1) gave a unknown 4 : 3 : 2 mixture (5.5 mg, *ca*. 10%) and **44** (10 mg, 20%).

*Data of Phenyl 2,3-Di-*O*-benzyl-4-deoxy-4-[(*Z*)-4-(phenyl 2,3-Di-*O*-benzyl-4-deoxy-1-thio-α-*D*-galacto-pyranosid-4-*C*,6-*O*-ylidene)but-3-en-1-yn-1-yl]-1-thio-α-*D*-glucopyranoside* (**44**). R_f (toluene/AcOEt 2 : 1) 0.48. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 6*; additionally, 7.55 – 7.21 (*m*, 30 arom. H); 4.88 (2*d*, *J* = 10.2, PhCH_2); 4.82 – 4.70 (*m*, 6 PhC*H*); 1.72 (*t*, *J* = 6.6, HO–C(6)).

Data of the 4 : 3 : 2 Mixture. R_f (toluene/AcOEt 2 : 1) 0.69. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.79 (*s*, 0.2 H), 5.72 (*d*, *J* = 10.2, 0.2 H), 5.68 (*d*, *J* = 4.5, 0.8 H), 5.66 (*d*, *J* ≈ 4.8, 1.2 H) (2 H–C(1)); 5.18 (*d*, *J* = 1.0, 0.4 H); 5.14 (*t*, *J* ≈ 1.5, 0.6 H) (1 olef. H); 3.43 (*td*, *J* ≈ 6.3, 2.5, 0.4 H), 3.33 (br. *t*, *J* = 10.5, 0.2 H), 2.92 (*td*, *J* = 10.5, 2.5, 0.6 H) (1.2 H–C(4)).

*Allyl 2,3-Di-*O*-benzyl-4,6-bis-*O*-(4-methoxybenzyl)-β-*D*-galactopyranoside* (**46**). A soln. of **45** [63] (80 mg, 0.2 mmol) in DMF (5 ml) was cooled to 0° and treated with 60% NaH in mineral oil (26 mg, 0.67 mmol) in small portions. After the evolution of gas had ceased (*ca*. 30 min), the mixture was treated with 4-methoxybenzyl chloride (0.1 ml, 0.73 mmol) and Bu_4NI (4 mg, 0.01 mmol), stirred at r.t. for 16 h, diluted with Et_2O (10 ml), and treated dropwise with H_2O (5 ml). The layers were separated, and the org. layer was washed with brine, dried ($MgSO_4$), and evaporated. FC (cyclohexane/AcOEt 8 : 1) gave **46** (115 mg, 90%). R_f (cyclohexane/AcOEt 4 : 1) 0.52. $[\alpha]_D^{25} = -10.5$ (*c* = 1.10, $CHCl_3$). IR ($CHCl_3$): 3020*s*, 2958*m*, 2937*m*, 2912*m*, 2860*m*, 2839*m*, 1884*w*, 1612*s*, 1586*m*, 1513*s*, 1465*m*, 1442*m*, 1421*w*, 1384*w*, 1361*m*, 1302*m*, 1248*s*, 1173*s*, 1110*m*, 1072*m*, 1035*s*, 1011*w*, 919*w*, 895*w*, 825*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 7*; additionally, 7.40 – 7.18 (*m*, 14 arom. H); 6.93 – 6.78 (*m*, 4 arom. H); 5.95 (*dddd*, *J* = 17.2, 10.5, 6.0, 5.4, $CH_2=CH$); 5.33 (*dq*, *J* = 17.1, 1.8), 5.18 (*dq*, *J* = 10.8, 1.8) ($CH_2=CH$); 4.95 (*d*, *J* = 11.1), 4.86 (*d*, *J* = 11.4), 4.77 (*d*, *J* = 10.5), 4.76 (*d*, *J* = 12.0), 4.70 (*d*, *J* = 12.0), 4.58 (*d*, *J* = 11.4), 4.41 (*d*, *J* ≈ 11.2), 4.35 (*d*, *J* = 11.1) (8 ArC*H*); 4.41 (*ddt*, *J* = 12.9, 5.1, 1.8), 4.12 (*ddt*, *J* = 12.9, 6.0, 1.5) (CH_2=CHCH_2); 3.81, 3.79 (2*s*, 2 MeO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 7*; additionally, 159.14, 158.95 (2*s*); 138.63, 138.45 (2*s*); 134.11 (*d*, CH_2=*C*H); 130.72, 129.90 (2*s*); 129.84 – 127.40 (several *d*); 116.89 (*t*, *C*H_2=CH); 113.74 (2*d*); 113.45 (2*d*); 75.25, 73.94, 73.18, 72.99 (4*t*, 4 Ar*C*H_2); 70.11 (*t*, CH_2=CH*C*H_2); 55.30, 55.27 (2*q*, 2 MeO). MALDI-MS: 663 ([*M* + Na]$^+$). HR-MALDI-MS: 663.2920 ([*M* + Na]$^+$, $C_{39}H_{44}NaO_8^+$; calc. 663.2928). Anal. calc. for $C_{39}H_{44}O_8$ (640.77): C 73.10, H 6.92; found: C 73.11, H 7.05.

*2,3-Di-*O*-benzyl-4,6-bis-*O*-(4-methoxybenzyl)-*D*-galactopyranose* (**47**). A suspension of [Ir(COD)(PPh_2-Me)PF_6] (6 mg, 0.007 mmol) in dry THF (3 ml) was degassed and stirred under H_2 for 10 min at 25° (red suspension turned into yellow soln.). After replacement of H_2 by Ar, the yellow soln. was treated with a soln. of **46** (110 mg, 0.225 mmol) in THF (5 ml), stirred for 1 h, treated with H_2O (10 ml) and I_2 (114 mg, 0.45 mmol), stirred for 1 h, and treated with chilled 5% $Na_2S_2O_3$ soln. (10 ml). After evaporation, a soln. of the residue in AcOEt was washed with brine, dried ($MgSO_4$), and evaporated. FC (cyclohexane/AcOEt 5 : 1) gave **47** (85 mg, 82%). R_f (cyclohexane/AcOEt 2 : 1) 0.55. $[\alpha]_D^{25} = +4.3$ (*c* = 1.10, $CHCl_3$). IR ($CHCl_3$): 3416*w* (br.), 3021*s*, 3014*s*, 2936*w*, 2914*w*, 2873*w*, 2839*w*, 1612*m*, 1586*w*, 1514*s*, 1465*w*, 1455*w*, 1363*w*, 1302*m*, 1249*s*, 1173*m*, 1154*w*, 1093*s*, 1037*s*, 909*m*, 827*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; α-*D*-**47**/β-*D*-**47** 55 : 45): 7.49 – 7.30 (*m*, 7 arom. H); 7.38 – 7.19 (*m*, 7 arom. H); 6.88 – 6.81 (*m*, 4 arom. H); 5.29 (*t*, *J* ≈ 3.2, addn. of D_2O → *d*, *J* = 3.2, 0.55 H–C(1)); 4.93 (*d*, *J* = 10.8, 0.55 H), 4.86 (*d*, *J* = 11.4, 0.45 H), 4.85 (*d*, *J* = 11.7, 0.55 H), 4.82 (*d*, *J* = 12.0, 0.45 H), 4.80 (*d*, *J* = 12.0, 0.55 H), 4.77 (*d*, *J* = 12.0, 0.45 H), 4.75 (*d*, *J* = 10.5, 0.55 H), 4.73 (*d*, *J* = 10.5, 0.45 H), 4.71 (*d*, *J* = 10.5, 0.55 H), 4.70 (*d*, *J* = 11.7, 0.45 H) (5 PhC*H*); 4.65 (*dd*, *J* = 7.5, 6.6, addn. of D_2O → *d*, *J* = 7.5, 0.45 H–C(1)); 4.55 (*d*, *J* = 11.4, 0.45 H), 4.53 (*d*, *J* = 11.1, 0.55 H), 4.43 (br. *d*, *J* = 11.7, 1 H), 4.33 (*d*, *J* = 11.7, 0.55 H), 4.32 (*d*, *J* = 11.7, 0.45 H) (3 PhC*H*); 4.15 (*t*, *J* ≈ 6.4, 0.55 H–C(5)); 4.03 (*dd*, *J* = 9.3, 3.6, 0.55 H–C(2)); 3.93 (br. *s*, 0.55 H–C(4)); 3.91 (*dd*, *J* = 9.3, 2.7, 0.55 H–C(3)); 3.85 (*d*, *J* = 3.0, 0.45 H–C(4)); 3.80, 3.795, 3.79 (3*s*, 2 MeO); 3.765 (*dd*, *J* = 9.6, 7.5, 0.45 H–C(2)); 3.760 (*d*, *J* = 6.6, exchanged with D_2O, 0.45 HO–C(1)); 3.60 – 3.45 (*m*, 0.45 H–C(5), 1.55 H–C(6)); 3.435 (*dd*, *J* = 9.3, 2.5, 0.45 H–C(3)); 3.420 (*dd*, *J* = 9.3, 6.9, 0.45 H–C(6)); 3.38 (*d*, *J* = 2.4, exchanged with D_2O, 0.55 HO–C(1)). ^{13}C-NMR (75 MHz, $CDCl_3$, α-*D*-**47**/β-*D*-**47** 55 : 45): signals of α-*D*-**47**: 159.15, 159.06 (2*s*); 138.59, 138.20 (2*s*); 130.62 (*s*); 129.87 (2*d*); 129.84 (*s*); 129.56 (2*d*); 128.31 (2*d*); 128.23 (2*d*); 127.92 (2*d*); 127.68 (*d*); 127.48 (*d*); 127.42 (2*d*); 113.74 (2*d*); 113.58 (2*d*); 91.84 (*d*, C(1)); 78.80 (*d*, C(3)); 76.62 (*d*, C(2)); 74.19 (*t*, PhCH_2); 74.17 (*d*, C(4)); 73.46, 73.12, 72.94 (3*t*, 3PhCH_2); 69.52 (*d*, C(5)); 68.79 (*t*, C(6)); 55.32 (*q*, 2 MeO); signals of β-*D*-**47**: 159.19, 159.06 (2*s*); 138.54, 138.35 (2*s*); 130.56 (*s*); 129.84 (2*d*);

Table 7. *Selected ^{1}H- and ^{13}C-NMR Chemical Shifts* [ppm], *and Coupling Constants* [Hz] *of the* D-*Galactopyranose Derivatives* **46** *and* **48**–**54** *in* $CDCl_3$

	46	**48**	**49**	**50**	**51**	**52**[a])	**53**[a])[b])	**54**[a])
H–C(1)	4.41	–	4.03	4.01	4.15	4.29	4.24	4.28
H–C(2)	3.87	4.46	3.87	3.87	3.91	3.75–3.73	3.77	3.77
H–C(3)	3.58–3.47	3.86	3.48	3.50	3.51	3.73–3.71	3.75	3.74
H–C(4)	4.62	4.14	4.03	4.04	4.06	4.59	4.60	4.55
H–C(5)	3.86	4.30	3.43	3.45	3.47	3.98	4.00	4.11
H_a–C(6)	3.58–3.47	3.67	3.95	3.96	3.94	3.79	3.83	4.31
H_b–C(6)	3.58–3.47	3.61	3.79	3.79	3.80	3.68	3.73	4.20
HO–C(4)	–	–	2.70	2.64	2.73	–	–	–
HO–C(6)	–	–	2.24	2.11	2.28	1.77	1.78	–
H–C(2′)	–	–	–	2.54	–	5.21	4.81	4.83
J(1,2′)	–	–	–	2.1	–	0.9	0.6	≤1.0
J(1,2)	7.5	–	9.6	9.9	9.6	2.4	2.0	2.0
J(2,3)	8.1	9.6	9.0	8.7	9.0	[c])	≤2.0	≤2.0
J(3,4)	4.2	2.4	3.3	3.0	3.3	1.5	≤1.0	≤1.0
J(4,5)	≤1.0	1.2	1.8	1.0	1.2	1.5	≤1.0	≤1.0
J(5,6_a)	1.8	8.1	6.6	6.6	6.6	6.9	6.5	6.3
J(5,6_b)	7.8	5.7	4.5	4.5	4.5	7.2	7.2	6.3
J(6_a,6_b)	[c])	9.0	11.7	11.7	11.7	11.4	11.1	11.1
J(4,OH)	–	–	1.5	2.0	1.5	–	–	–
J(5,OH)	–	–	1.5	1.0	1.0	–	–	–
J(6_a,OH)	–	–	4.5	4.8	3.3	4.5	4.5	–
J(6_b,OH)	–	–	8.4	8.7	7.5	7.5	7.2	–
C(1)	102.89	169.87	70.30	69.70	70.50	69.56	69.77	69.71
C(2)	79.61	77.43[d])	78.47	78.13	78.06[d])	80.02	80.10	79.96
C(3)	82.42	80.13	81.29	81.37	81.42	80.35	80.59	80.36
C(4)	73.45	71.96	67.76	67.62	67.60	71.09	71.22	71.54
C(5)	72.84	77.31[d])	77.97	77.99	78.03[d])	74.84	74.94	72.62
C(6)	68.59	67.17	62.86	62.86	62.79	61.97	62.13	63.45
C(1′)	–	–	102.13	80.74	79.08[e])	152.33	159.61	159.14
C(2′)	–	–	91.11	74.15	70.70	78.37	82.35	82.60
C(3′)	–	–	–	–	73.21	–	83.25	83.14
C(4′)	–	–	–	–	78.70[e])	–	93.47	93.87

[a]) Same numbering as **50** and **51**. [b]) Assignment based on a DQFCOSY, a HSQC, and a HMBC spectrum. [c]) Not assigned. [d]) [e]) Assignments may be interchanged.

129.73 (*s*); 129.61 (2*d*); 128.32 (4*d*); 128.10 (2*d*); 127.54 (*d*); 127.52 (*d*); 127.46 (2*d*); 113.77 (2*d*); 113.58 (2*d*); 97.76 (*d*, C(1)); 82.25 (*d*, C(3)); 80.80 (*d*, C(2)); 75.11, 74.07 (2*t*, 2 Ph*C*H_2); 73.62 (*d*, C(4)); 73.20 (*t*, Ph*C*H_2); 73.01 (*d*, C(5)); 72.94 (*t*, Ph*C*H_2); 68.68 (*t*, C(6)); 55.32 (*q*, 2 MeO). MALDI-MS: 623 ($[M + Na]^+$). HR-MALDI-MS: 623.2614 ($[M + Na]^+$, $C_{36}H_{40}NaO_8^+$; calc. 623.2615).

*2,3-Di-*O*-benzyl-4,6-bis-*O*-(4-methoxybenzyl)-*D*-galactono-1,5-lactone* (**48**). A suspension of **47** (672 mg, 1.12 mmol) in DMSO (6 ml) was treated with Ac_2O (3 ml) and stirred for 6 h. The clear yellow soln. was added dropwise to cold stirred H_2O. After extraction with CH_2Cl_2, evaporation and crystallisation from hexane gave **48** (590 mg, 88%). R_f (cyclohexane/AcOEt 5:1) 0.45. $[\alpha]_D^{25} = +151.4$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3067*w*, 3021*s*, 3014*m*, 2959*w*, 2936*w*, 2914*w*, 2875*w*, 2839*w*, 1748*s*, 1612*m*, 1586*w*, 1514*s*, 1465*m*, 1455*m*, 1442*w*, 1361*m*, 1302*m*, 1249*s*, 1174*m*, 1103*s*, 1061*m*, 1035*s*, 910*w*, 847*w*, 824*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 7*; additionally, 7.49–7.30 (*m*, 10 arom. H); 7.29–7.10 (*m*, 4 arom. H); 6.91–6.80 (*m*, 4 arom. H); 5.18 (*d*, $J = 11.4$), 4.84 (*d*, $J = 10.8$), 4.78 (*d*, $J = 11.1$), 4.74 (*d*, $J = 12.6$), 4.67 (*d*, $J = 12.0$), 4.54 (*d*, $J = 10.8$), 4.46 (*d*, $J = 11.4$), 4.39 (*d*, $J = 11.7$) (8 Ph*CH*); 3.80, 3.79 (2*s*, 2 MeO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 7*; additionally, 159.29, 159.18 (2*s*); 137.69, 137.44 (2*s*); 129.78 (*s*); 129.60 (2*d*); 129.56 (2*d*); 129.36 (*s*); 128.36 (2*d*); 128.33 (2*d*); 128.25 (2*d*);

127.77 (*d*); 127.68 (*d*); 127.38 (2*d*); 113.80 (2*d*); 113.67 (2*d*); 75.27, 74.30, 73.30, 72.72 (4*t*, 4 Ph*C*H$_2$); 55.30 (2 MeO). MALDI-MS: 621 ([*M* + Na]$^+$). HR-MALDI-MS: 621.2467 ([*M* + Na]$^+$, $C_{36}H_{38}NaO_8^+$; calc. 621.2459). Anal. calc. for $C_{36}H_{38}O_8$ (598.69): C 72.22, H 6.40; found: C 72.23, H 6.51.

*1-(2,3-Di-*O*-benzyl-β-*D*-galactopyranosyl)-2-(trimethylsilyl)ethyne* (**49**). Under Ar, a stirred and cooled (− 78°) soln. of $Me_3SiC{\equiv}CH$ (0.3 ml, 2 mmol) in THF (8 ml) was treated dropwise with 1.6M BuLi in hexane (1.2 ml) over a period of 0.5 h and stirred for 1 h. This soln. was transferred into a cooled (− 78°) soln. of **48** (240 mg, 0.4 mmol) in THF (8 ml) over a period of 10 min with a canula. The resulting pale brown soln. was stirred for 4 h at − 78°, treated with sat. aq. NH_4Cl soln. (2 ml), warmed to r.t., stirred for 0.5 h, and worked up (AcOEt). After evaporation, a soln. of the residue (280 mg) in CH_2Cl_2/MeCN 1:1 (5 ml) was cooled to − 40°, treated with a soln. of $BF_3 \cdot Et_2O$ (0.3 ml, 2.3 mmol) and Et_3SiH (0.6 ml, 3.6 mmol) in CH_2Cl_2/MeCN 1:1 (5 ml) using a canula over a period of 0.5 h. The mixture was stirred at − 40° for 1 h and at − 10 to − 15° for 16 h, treated with sat. aq. $NaHCO_3$ soln. (5 ml), stirred for 1 h at − 10 to − 15°, and worked up (AcOEt). Evaporation and FC (cyclohexane/AcOEt 5:1) gave **49** (101 mg, 63%). Pale yellow oil. R_f (cyclohexane/AcOEt 5:1) 0.42. $[\alpha]_D^{25} = -52.6$ ($c = 1.1$, $CHCl_3$). IR ($CHCl_3$): 3577*w* (br.), 3350*w* (br.), 3090*w*, 3067*w*, 3032*w*, 3013*m*, 2961*m*, 2876*m*, 2180*w*, 1951*w*, 1875*w*, 1810*w*, 1732*w*, 1606*w*, 1497*w*, 1454*m*, 1365*m*, 1297*m*, 1251*s*, 1091*s*, 1028*m*, 910*w*, 846*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 7*; additionally, 7.42 – 7.28 (*m*, 10 arom. H); 4.99 (*d*, *J* = 10.5), 4.83 (*d*, *J* = 10.5) (Ph*C*H_2); 4.73 (*s*, Ph*C*H_2); 0.19 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 7*; additionally, 137.95, 137.49 (2*s*); 128.45 (2*d*); 128.25 (2*d*); 128.07 (2*d*); 127.95 (2*d*); 127.72 (2*d*); 75.78, 72.36 (2*t*, 2 Ph*C*H$_2$); 0.16 (*q*, Me_3Si). MALDI-MS: 463 ([*M* + Na]$^+$). HR-MALDI-MS: 463.1906 ([*M* + Na]$^+$, $C_{25}H_{32}NaO_5Si^+$; calc. 463.1911).

*(2,3-Di-*O*-benzyl-β-*D*-galactopyranosyl)ethyne* (**50**). A suspension of **49** (88 mg, 0.2 mmol) in dry MeOH (5 ml) was treated with one batch of MeONa (20 mg, 0.37 mmol), kept at reflux for 10 h, and evaporated. The residue was treated with a soln. of 0.1M HCl (0.5 ml) in H_2O (10 ml), and extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. Crystallisation from i-PrOH gave **50** (68 mg, 93%). White solid. M.p. 133 – 134°. $[\alpha]_D^{25} = -52.6$ ($c = 1.1$, $CHCl_3$). IR ($CHCl_3$): 3572*w* (br.), 3307*w*, 3031*w*, 3009*w*, 2929*w*, 2853*w*, 2256*w*, 1603*w*, 1497*w*, 1454*w*, 1374*s*, 1298*w*, 1265*s*, 1249*s*, 1093*s*, 1046*m*, 1002*w*, 941*w*, 918*w*, 846*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 7*; additionally, 7.40 – 7.26 (*m*, 10 arom. H); 4.99, 4.84 (2*d*, *J* = 10.5, Ph*C*H_2); 4.73 (*s*, Ph*C*H_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 7*; additionally, 137.82, 137.41 (2*s*); 128.48 (2*d*); 128.27 (2*d*); 128.14 (2*d*); 127.99, 127.78 (2*d*); 127.75 (2*d*); 75.81, 72.30 (2*t*, 2 Ph*C*H$_2$). MALDI-MS: 391 ([*M* + Na]$^+$). HR-MALDI-MS: 391.1521 ([*M* + Na]$^+$, $C_{22}H_{24}NaO_5^+$; calc. 391.1516). Anal. calc. for $C_{22}H_{24}O_5$ (368.43): C 71.72, H 6.57; found: C 71.68, H 6.71.

*1-(2,3-Di-*O*-benzyl-β-*D*-galactopyranosyl)-4-phenylbuta-1,3-diyne* (**51**). A suspension of $[Pd_2(dba)_3]$ (6 mg, 0.0125 mmol), CuI (2 mg, 0.01 mmol), $P(fur)_3$ (6 mg, 0.0125 mmol), **50** (184 mg, 0.5 mmol), and (bromoethynyl)benzene (91 mg, 0.5 mmol) in DMF (3 ml) was degassed twice and stirred at 22° for 5 min. The mixture was treated with Et_3N (0.3 ml) and stirred for 12 h at 22°. The soln. was diluted with Et_2O (10 ml), and treated with H_2O (10 ml) and 0.1M aq. HCl (3 ml). After separation of the layers, the aq. layer was extracted with Et_2O (4 × 10 ml), and the Et_2O layer was washed with H_2O (2 × 15 ml). The combined org. fractions were dried ($MgSO_4$) and evaporated. FC (cyclohexane/AcOEt 3:1) gave **51** (198 mg, 85%). R_f (cyclohexane/AcOEt 3:1) 0.47. $[\alpha]_D^{25} = -146.6$ ($c = 1.1$, $CHCl_3$). IR ($CHCl_3$): 3581*w* (br.), 3442*w* (br.), 3067*w*, 3032*w*, 3013*m*, 2928*m*, 2876*m*, 2242*w*, 1952*w*, 1881*w*, 1807*w*, 1672*w*, 1597*w*, 1554*w*, 1492*w*, 1454*m*, 1443*w*, 1367*m*, 1291*m*, 1091*s*, 1028*m*, 1013*m*, 985*w*, 914*w*, 884*w*, 834*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 7*; additionally, 7.75 – 7.72 (*m*, 1 arom. H); 7.53 – 7.48 (*m*, 2 arom. H); 7.45 – 7.40 (*m*, 2 arom. H); 7.40 – 7.30 (*m*, 8 arom. H); 7.19 – 7.15 (*m*, 1 arom. H); 6.58 – 6.54 (*m*, 1 arom. H); 4.98, 4.86 (2*d*, *J* = 10.2, Ph*C*H_2); 4.74 (*s*, Ph*C*H_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 7*; additionally, 137.68, 137.41 (2*s*); 132.55 (2*d*); 128.49 (2*d*); 129.33 (*d*); 128.33 (6*d*); 128.02 (*d*); 127.85 (*d*); 127.76 (2*d*); 121.17 (*s*); 75.89, 72.32 (2*t*, 2 Ph*C*H$_2$). MALDI-MS: 491 ([*M* + Na]$^+$). HR-MALDI-MS: 491.1829 ([*M* + Na]$^+$, $C_{30}H_{28}NaO_5^+$; calc. 491.1829).

(Z)-*2,6:3,7-Dianhydro-4,5-di-*O*-benzyl-8-bromo-8-deoxy-*L*-glycero-*L*-galacto-oct-7-enitol* (**52**). A suspension of **50** (92 mg, 0.25 mmol) and NBS (60 mg, 0.336 mmol) in acetone (3 ml) was treated with $AgNO_3$ (6 mg, 0.036 mmol) and stirred for 30 min at 22°. After evaporation, the residue was partitioned between H_2O and AcOEt. The aq. layer was extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (cyclohexane/AcOEt 4:1) gave **52** (113 mg, 93%). R_f (cyclohexane/AcOEt 2:1) 0.55. $[\alpha]_D^{25} = -156.2$ ($c = 1.02$, $CHCl_3$). IR ($CHCl_3$): 3594*w*, 3416*w* (br.), 3107*w*, 3090*w*, 3067*w*, 3031*m*, 3013*m*, 2944*w*, 2885*m*, 1664*m*, 1603*w*, 1496*w*, 1454*m*, 1363*m*, 1265*s*, 1146*s*, 1103*s*, 1038*s*, 1028*s*, 993*m*, 912*w*, 884*w*, 860*w*, 821*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 7*; additionally, 7.39 – 7.29 (*m*, 10 arom. H); 4.66, 4.64 (2*d*, *J* = 12.0, 2 Ph*C*H); 4.53 (*d*, *J* = 12.0, 2 Ph*C*H). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 7*; additionally, 137.24, 137.04 (2*s*); 128.45 (2*d*); 128.42 (2*d*); 128.07 (*d*); 128.02 (2*d*); 127.92 (2*d*); 127.82 (*d*);

71.01, 70.47 (2*t*, 2 Ph*C*H$_2$). HR-MALDI-MS: 471.0601 (97, $[M + Na]^+$, $C_{22}H_{23}Na^{81}BrO_5^+$; calc. 471.0601), 469.0616 (100, $[M + Na]^+$, $C_{22}H_{23}Na^{79}BrO_5^+$; calc. 469.0621).

(Z)-*2,6 : 3,7-Dianhydro-4,5-di*-O-*benzyl-8,9,10-trideoxy-10*-C-*phenyl*-L-glycero-L-galacto-*dec-7-en-9-ynitol* (**53**). A suspension of **51** (47 mg, 0.1 mmol) in dry MeOH (3 ml) was treated with one batch of MeONa (20 mg, 0.37 mmol), kept at reflux for 10 h, and evaporated. The residue was treated with a soln. of 0.1M HCl (0.5 ml) in H_2O (10 ml) and extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (cyclohexane/AcOEt 4 : 1) gave **53** (44 mg, 93%). R_f (cyclohexane/AcOEt 2 : 1) 0.50. $[\alpha]_D^{25} = -220.8$ ($c = 1.05$, $CHCl_3$). IR ($CHCl_3$): 3429*w* (br.), 3066*w,* 3031*m,* 3013*m*, 2929*w*, 2892*w*, 2200*w*, 1951*w*, 1879*w*, 1808*w*, 1779*w*, 1658*m*, 1596*w*, 1490*m*, 1454*m*, 1442*w*, 1381*m*, 1362*m*, 1317*m*, 1279*m*, 1171*s*, 1106*s*, 1076*s*, 1036*m*, 1028*m*, 996*m*, 928*w*, 914*w*, 876*w*, 844*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 7*; additionally, 7.46 – 7.40 (*m*, 2 arom. H); 7.39 – 7.25 (*m*, 13 arom. H); 4.81 (*s*, irrad. at 4.24 → NOE of 9%, H−C(8)); 4.67, 4.66 (2*d*, $J = 12.0$, 2 PhC*H*); 4.54 (*d*, $J = 12.0$, 2 PhC*H*); 4.24 (*dd*, $J = 2.1$, 0.6, irrad. at 4.81 → NOE of 14%, H−C(6)); 3.77 (br. *s*, irrad. at 4.24 → NOE of 7%, H−C(5)). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 7*; additionally, 137.14, 137.06 (2*s*); 131.37 (2*d*); 128.49 (2*d*); 128.44 (2*d*); 128.07 (2*d*); 128.04 (*d*); 128.00 (2*d*); 127.92 (*d*); 127.89 (2*d*); 127.73 (*d*); 123.70 (*s*); 71.04, 70.51 (2*t*, 2 Ph*C*H$_2$). MALDI-MS: 491 ($[M + Na]^+$). HR-MALDI-MS: 491.1834 ($[M + Na]^+$, $C_{30}H_{28}NaO_5^+$; calc. 491.1829). Anal. calc. for $C_{30}H_{28}O_5$ (468.55): C 76.90, H 6.02; found: C 76.66, H 6.22.

(Z)-*1*-O-*Acetyl-2,6 : 3,7-dianhydro-4,5-di*-O-*benzyl-8,9,10-trideoxy-10*-C-*phenyl*-L-glycero-L-galacto-*dec-7-en-9-ynitol* (**54**). A suspension of **53** (47 mg, 0.1 mmol) in pyridine (3 ml) was treated with Ac_2O (66 µl, 0.16 mmol) and stirred overnight at 25°. Co-evaporation three times with toluene and FC (cyclohexane/AcOEt 4 : 1) gave **54** (49 mg, 95%). R_f (cyclohexane/AcOEt 2 : 1) 0.58. IR ($CHCl_3$): 3107*w,* 3090*w,* 3067*w,* 3029*m*, 3014*m*, 2928*s*, 2852*m*, 2260*w*, 1952*w*, 1731*s*, 1664*m*, 1603*w*, 1496*w*, 1453*m*, 1374*m*, 1250*s*, 1146*m*, 1102*s*, 1043*s*, 993*m*, 909*w*, 885*w*, 860*w*, 821*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 7*; additionally, 7.46 – 7.41 (*m*, 2 arom. H); 7.39 – 7.25 (*m*, 13 arom. H); 4.83 (*s*, H−C(8)); 4.66, 4.65 (2*d*, $J = 12.0$, 2 PhC*H*); 4.55, 4.53 (2*d*, $J = 12.0$, 2 PhC*H*); 2.10 (*s*, AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 7*; additionally, 170.48 (*s*, C=O); 137.06, 136.97 (2*s*); 131.33 (2*d*); 128.45 (2*d*); 128.40 (2*d*); 128.02 (3*d*); 127.95 (2*d*); 127.89 (*d*); 127.85 (2*d*); 127.68 (*d*); 123.67 (*s*); 71.00, 70.52 (2*t*, 2 Ph*C*H$_2$); 20.93 (*q*, Me).

1,6-Anhydro-4-deoxy-4-C-*(4-phenylbuta-1,3-diyn-1-yl)-β*-D-*glucopyranose* (**56**). A suspension of $[Pd_2(dba)_3]$ (6 mg, 0.0125 mmol), CuI (2 mg, 0.01 mmol), P(fur)$_3$ (6 mg, 0.0125 mmol), **55** [66] (85 mg, 0.5 mmol), and (bromoethynyl)benzene (91 mg, 0.5 mmol) in DMF (3 ml) was degassed twice and stirred at 22° for 5 min. The mixture was treated with Et_3N (0.3 ml) and stirred for 12 h at 22°. The soln. was diluted with Et_2O (10 ml), and treated with H_2O (10 ml) and 0.1M aq. HCl (3 ml). The Et_2O layer was washed with H_2O (2 × 15 ml), and the aq. layer was extracted with Et_2O (4 × 10 ml). The combined org. fractions were dried ($MgSO_4$) and evaporated. FC (cyclohexane/AcOEt 1 : 1) gave **56** (102 mg, 76%). White solid. R_f (cyclohexane/AcOEt 1 : 1) 0.43. M.p. 128 – 129°. $[\alpha]_D^{25} = -41.5$ ($c = 1.02$, $CHCl_3$). IR ($CHCl_3$): 3561*m*, 3385*w* (br.), 3028*w*, 3014*w*, 2960*w*, 2928*w*, 2906*w*, 2855*w*, 2246*w*, 2148*w*, 1730*w*, 1597*w*, 1491*w*, 1442*w*, 1347*w*, 1297*w*, 1264*w*, 1180*w*, 1135*m*, 1111*w*, 1049*s*, 1013*m*, 987*m*, 928*m*, 886*m*, 849*w*, 814*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.52 – 7.47 (*m*, 2 arom. H); 7.37 – 7.29 (*m*, 3 arom. H); 5.56 (br. *s*, H−C(1)); 4.69 (br. *d*, $J = 4.8$, H−C(5)); 4.22 (*d*, $J = 7.8$, H_{endo}−C(6)); 4.07 (*dquint.*, $J = 7.8$, 1.5, addition of D_2O → *quint.*, $J = 1.5$, H−C(3)); 3.83 (*dd*, $J = 7.8$, 5.1, H_{exo}−C(6)); 3.61 (br. *d*, $J = 11.6$, addn. of D_2O → br. *s*, H−C(2)); 2.94 (br. *s*, H−C(4)); 2.72 (*d*, $J = 7.8$, exchanged with D_2O, HO−C(3)); 2.43 (*d*, $J = 11.9$, exchanged with D_2O, HO−C(2)). ^{13}C-NMR (75 MHz, $CDCl_3$): 132.51 (2*d*); 129.26 (*d*); 128.36 (2*d*); 121.27 (*s*); 102.22 (*d*, C(1)); 80.59 (*s*, C(1′)); 77.33 (*s*, C(4′)); 75.07 (*d*, C(5)); 73.33 (*s*, C(3′)); 72.47 (*d*, C(3)); 70.47 (*d*, C(2)); 68.82 (*s*, C(2′)); 67.38 (*t*, C(6)); 37.20 (*d*, C(4)). HR-MALDI-MS: 293.0787 ($[M + Na]^+$, $C_{16}H_{14}NaO_4$; calc. 293.0784). Anal. calc. for $C_{16}H_{14}O_4 \cdot 0.5\ H_2O$ (279.28): C 68.74, H 5.37; found: C 68.48, H 5.87.

1,6-Anhydro-4-C-*(2-bromoethynyl)-4-deoxy-β*-D-*glucopyranose* (**57**). A suspension of **55** (85 mg, 0.5 mmol) and NBS (120 mg, 0.67 mmol) in acetone (5 ml) was treated with $AgNO_3$ (12 mg, 0.072 mmol) and stirred for 30 min at 22°. After evaporation, the residue was partitioned between H_2O and AcOEt. The aq. layer was extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 1 : 1) gave **57** (115 mg, 92%). White solid. R_f (hexane/AcOEt 1 : 1) 0.56. M.p. 145 – 146°. $[\alpha]_D^{25} = -75.5$ ($c = 1.01$, $CHCl_3$). IR ($CHCl_3$): 3562*m*, 3393*w* (br.), 3027*w*, 3014*w*, 2961*w*, 2906*w*, 2215*w*, 1602*w*, 1476*w*, 1399*w*, 1348*w*, 1300*w*, 1182*w*, 1134*m*, 1064*s*, 1048*s*, 1008*m*, 986*m*, 929*w*, 884*w*, 851*w*, 817*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.53 (br. *s*, H−C(1)); 4.63 (br. *d*, $J = 5.0$, H−C(5)); 4.18 (*d*, $J = 7.8$, H_{endo}−C(6)); 4.00 (*dquint.*, $J = 7.8$, 1.5, addition of D_2O → *quint.*, $J = 1.5$, H−C(3)); 3.80 (*dd*, $J = 7.5$, 5.1, H_{exo}−C(6)); 3.57 (br. *d*, $J = 11.5$, addition of D_2O → br. *s*, H−C(2)); 2.80 (br. *s*, H−C(4)); 2.67 (*d*, $J = 7.7$, exchanged with D_2O, HO−C(3)); 2.37 (*d*, $J = 11.8$, exchanged with D_2O, HO−C(2)). ^{13}C-NMR (75 MHz,

$CDCl_3$): 102.12 (*d*, C(1)); 78.00 (*s*, C(1′)); 75.02 (*d*, C(5)); 72.20 (*d*, C(3)); 70.41 (*d*, C(2)); 67.26 (*t*, C(6)); 43.46 (*s*, C(2′)); 37.29 (*d*, C(4)). HR-MALDI-MS: 272.9557 (97, $[M + Na]^+$, $C_8H_9{}^{81}BrNaO_4^+$; calc. 272.9561), 270.9578 (100, $[M + Na]^+$, $C_8H_9{}^{79}BrNaO_4^+$; calc. 270.9576). Anal. calc. for $C_8H_9BrO_4$ (249.06): C 38.58, H 3.64; found: C 38.64, H 3.86.

X-Ray Analysis of **57**[6]). Recrystallisation of **57** in Et_2O/hexane 4:1 gave crystals suitable for X-ray analysis: $C_8H_9BrO_4$ (249.065); monoclinic $P2_1$; $a = 7.3149(3)$, $b = 6.8396(3)$, $c = 8.9967(3)$ Å, $\beta = 101.902(2)°$. $V = 440.44(3)$ Å^3; $Z = 2$; $D_{calc.} = 1.878$ Mg/m^3. Intensities were measured on an *Enraf-Nonius CAD-4* diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 298 K, θ range 0.998–27.485°. Of the 1883 total collected reflections, 1877 independent reflections were observed. $R = 0.0282$, $R_w = 0.0862$.

*1,6-Anhydro-4-deoxy-4-*C*-(2-iodoethynyl)-β-*D*-glucopyranose* (**58**). A soln. of $AgNO_3$ (65 mg, 0.38 mmol) and dil. NH_3/H_2O (one drop) in H_2O (3 ml) was treated dropwise with a suspension of **55** (43 mg, 0.25 mmol) in acetone (3 ml), stirred for 5 min, treated with NIS (90 mg, 0.4 mmol), and stirred for 30 min at 22° (the mixture became clear after 5 min and then turbid again). After evaporation, the residue was partitioned between H_2O and AcOEt. The aq. layer was extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (cylcohexane/AcOEt 2:1) gave **58** (64 mg, 87%). White solid. R_f (cyclohexane/AcOEt 2:1) 0.43. M.p. 75–76°. $[\alpha]_D^{25} = -60.1$ ($c = 1.02$, $CHCl_3$). IR ($CHCl_3$): 3560*m*, 3401*w* (br.), 3027*w*, 3014*w*, 2967*w*, 2906*w*, 2253*w*, 1602*w*, 1475*w*, 1397*w*, 1348*w*, 1321*w*, 1299*w*, 1227*w*, 1182*w*, 1134*m*, 1080*w*, 1052*m*, 1046*s*, 1007*m*, 986*w*, 909*s*, 884*w*, 850*w*, 817*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.50 (br. *s*, H–C(1)); 4.62 (br. *d*, $J = 5.0$, H–C(5)); 4.15 (*d*, $J = 7.5$, H_{endo}–C(6)); 4.00 (br. *d*, $J = 6.9$, addition of $D_2O \rightarrow$ br. *s*, H–C(3)); 3.77 (*dd*, $J = 7.5$, 5.0, H_{exo}–C(6)); 3.55 (br. *d*, $J = 11.2$, addition of $D_2O \rightarrow$ br. *s*, H–C(2)); 2.98 (*d*, $J = 6.9$, exchanged with D_2O, HO–C(3)); 2.89 (br. *d*, $J = 1.9$, H–C(4)); 2.56 (*d*, $J = 11.5$, exchanged with D_2O, HO–C(2)). ^{13}C-NMR (75 MHz, $CDCl_3$): 102.13 (*d*, C(1)); 92.08 (*s*, C(1′)); 75.22 (*d*, C(5)); 72.41 (*d*, C(3)); 70.52 (*d*, C(2)); 67.28 (*t*, C(6)); 38.34 (*d*, C(4)); 31.07 (*s*, C(2′)). HR-ESI-MS: 318.9423 (100, $[M + Na]^+$, $C_8H_9INaO_4^+$; calc. 318.9443). Anal. calc. for $C_8H_9IO_4$ (296.06): C 32.46, H 3.06; found: C 32.35, H 3.15.

*1,6-Anhydro-4-deoxy-4-*C*-(4-phenylbuta-1,3-diyn-1-yl)-β-*D*-erythro-hex-3-enopyranose* (**59**). A suspension of **56** (27 mg, 0.1 mmol) in dry MeOH (3 ml) was treated with one batch of MeONa (20 mg, 0.37 mmol) and kept at reflux for 10 h. After evaporation, the residue was treated with a soln. of 0.1M HCl (0.5 ml) in H_2O (10 ml) and extracted with AcOEt (3 × 15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4:1) gave **59** (21 mg, 82%). R_f (hexane/AcOEt 2:1) 0.46. $[\alpha]_D^{25} = -7.6$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3579*w*, 3386*w* (br.), 3028*w*, 2988*w*, 2928*s*, 2852*s*, 2209*w*, 1680*w*, 1598*w*, 1491*w*, 1450*m*, 1375*m*, 1360*w*, 1249*s*, 1130*m*, 1045*m*, 930*w*, 904*w*, 872*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.53–7.48 (*m*, 2 arom. H); 7.40–7.29 (*m*, 3 arom. H); 6.23 (*dd*, $J = 4.4$, 1.9, H–C(3)); 5.54 (*t*, $J = 1.6$, H–C(1)); 4.75 (*d*, $J = 3.7$, H–C(5)); 3.81 (*d*, $J = 6.9$, H_{endo}–C(6)); 3.75 (*dd*, $J = 6.9$, 4.0, H_{exo}–C(6)); 3.74 (*ddd*, $J = 11.0$, 4.5, 1.5, addition of D_2O: *dd*, $J = 4.5$, 1.5, H–C(2)); 1.86 (*d*, $J = 11.2$, exchanged with D_2O, HO–C(2)). ^{13}C-NMR (75 MHz, $CDCl_3$): 133.50 (*d*, C(3)); 132.42 (2*d*); 129.50 (*d*); 128.39 (2*d*); 125.36 (*s*, C(4)); 121.09 (*s*); 101.96 (*d*, C(1)); 83.55 (*s*, C(4′)); 78.27 (*s*, C≡C); 73.57 (*d*, C(5)); 73.09 (*s*, C≡C); 69.11 (*t*, C(6)); 65.50 (*d*, C(2)); *s* of C≡C hidden by signals of $CDCl_3$. HR-MALDI-MS: 275.0677 ($[M + Na]^+$, $C_{16}H_{12}NaO_3^+$; calc. 275.0679). Anal. calc. for $C_{16}H_{12}O_3$ (252.27): C 76.18, H 4.79; found: C 76.11, H 4.87.

X-Ray Analysis of **59**[6]). Recrystallisation of **59** in Et_2O/hexane 4:1 gave crystals suitable for X-ray analysis: $C_{16}H_{12}O_3$ (252.269); orthorhombic $P2_12_12_1$; $a = 7.1054(2)$, $b = 9.4375(3)$, $c = 19.4351(7)$ Å. $V = 1303.26$ Å^3; $Z = 4$; $D_{calc.} = 1.286$ Mg/m^3. Intensities were measured on an *Enraf-Nonius CAD-4* diffractometer with Mo$K\alpha$ radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 298 K, θ range 0.998–27.485°. Of the 2937 total collected reflections, 2920 independent reflections were observed. $R = 0.0444$, $R_w = 0.1298$.

*1,6-Anhydro-4-*C*-(2-bromoethenylidene)-4-deoxy-β-*D*-glucopyranose* (**60**). A suspension of **57** (50 mg, 0.2 mmol) in dry MeOH (3 ml) was treated with one batch of MeONa (20 mg, 0.37 mmol) and kept at reflux for 10 h. After evaporation, the residue was treated with a soln. of 0.1M HCl (0.5 ml) in H_2O (10 ml) and extracted with AcOEt (3 × 10 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4:1) gave **60** (43 mg, 82%). R_f (hexane/AcOEt 2:1) 0.48. $[\alpha]_D^{25} = -47.7$ ($c = 1.02$, $CHCl_3$). IR ($CHCl_3$): 3564*m*, 3401*w* (br.), 3027*m*, 3015*m*, 2968*w*, 2902*w*, 1964*w*, 1730*w*, 1602*w*, 1475*w*, 1394*w*, 1347*w*, 1300*w*, 1123*s*, 1048*s*, 1009*m*, 976*m*, 946*w*, 930*m*, 909*s*, 890*m*, 849*w*, 818*w*. IR (KBr): 3432*s* (br.), 3051*m*, 2963*m*, 2926*m*, 2903*m*, 1964*w*, 1631*w* (br.), 1471*w*, 1432*m*, 1397*m*, 1361*w*, 1345*m*, 1309*m*, 1285*m*, 1266*m*, 1212*w*, 1150*s*, 1128*s*, 1064*s*, 1029*s*, 982*m*, 947*s*, 926*s*, 892*s*, 854*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; 9:1 mixture of diastereoisomers): signals of the minor diastereoisomer: 6.27 (*d*, $J = 1.2$, H–C(2′)); 5.51 (br. *s*, H–C(1)); 5.02 (*d*, $J = 4.7$, H–C(5)); 4.30 (br. *d*, $J \approx 7.0$, addition of $D_2O \rightarrow$ br. *s*, H–C(3)); 4.20 (*d*, $J = 7.2$, H_{endo}–C(6)); 3.87 (*dd*, $J = 7.4$, 4.7, H_{exo}–C(6)); 3.70 (br. *dq*, $J \approx 8.4$, 1.5, addition of $D_2O \rightarrow$ br. *s*, H–C(2)); 2.37 (*d*, $J = 6.8$, exchanged

with D_2O, HO–C(3)); 2.20 (*d*, *J* = 8.7, exchanged with D_2O, HO–C(2)); signals of the minor diastereoisomer: 6.24 (br. *s*, H–C(2′)); 5.05 (*d*, *J* = 4.7, H–C(5)); 4.12 (*d*, *J* = 7.2, H_{endo}–C(6)); 2.43 (*d*, *J* = 6.8, exchanged with D_2O, HO–C(3)); 2.26 (*d*, *J* = 8.7, exchanged with D_2O, HO–C(2)). ^{13}C-NMR (75 MHz, $CDCl_3$; 9:1 mixture of diastereoisomers): signals of the major diastereoisomer: 198.59 (*s*, C(1′)); 108.58 (*s*, C(4)); 102.55 (*d*, C(1)); 75.49 (*d*, C(5)); 73.50 (*d*, C(3)); 73.08 (*d*, C(2′)); 70.88 (*t*, C(6)); 69.40 (*d*, C(2)); signals of the minor diastereoisomer: 73.2 (*d*, C(2′)); 69.5 (*d*, C(2)). HR-MALDI-MS: 272.9555 (97, $[M + Na]^+$, $C_8H_9{}^{81}BrNaO_4^+$; calc. 272.9561), 270.9577 (100, $[M + Na]^+$, $C_8H_9{}^{79}BrNaO_4^+$; calc. 270.9576).

*1,6-Anhydro-4-deoxy-4-*C*-(2-iodoethenylidene)-β-*D*-glucopyranose* (**61**). A suspension of **58** (50 mg, 0.2 mmol) in dry MeOH (3 ml) was treated with one batch of *t*-BuOK (41 mg, 0.37 mmol) and kept at reflux for 10 h. After evaporation, the residue was treated with a soln. of 0.1M HCl (0.5 ml) in H_2O (10 ml) and extracted with AcOEt (3 × 10 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (cyclohexane/AcOEt 4:1) gave **61** (12 mg, 68%). R_f (hexane/AcOEt 2:1) 0.49. $[\alpha]_D^{25} = -54.2$ (*c* = 1.05, $CHCl_3$). IR ($CHCl_3$): 3563*m*, 3405*m* (br.), 3027*m*, 3015*m*, 2963*m*, 2929*m*, 2901*m*, 2852*w*, 1955*w*, 1602*w*, 1474*w*, 1392*m*, 1345*m*, 1300*w*, 1127*s*, 1056*s*, 1000*m*, 975*m*, 945*m*, 930*m*, 890*m*, 848*m*. ^{1}H-NMR (300 MHz, $CDCl_3$; 1:1 mixture of diastereoisomers): 6.07, 6.05 (2*t*, *J* = 0.8, H–C(2′)); 5.50 (br. *s*, H–C(1)); 5.04, 5.02 (2 br. *d*, *J* = 4.5, H–C(5)); 4.35–4.28 (br. *s*, H–C(3)); 4.18, 4.13 (2*d*, *J* = 7.5, H_{endo}–C(6)); 3.86, 3.83 (2*dd*, *J* = 7.5, 4.5, H_{exo}–C(6)); 3.69 (br. *d*, *J* = 8.0, H–C(2)); 2.48, 2.41 (2*d*, *J* = 7.1, HO–C(3)); 2.27, 2.23 (2*d*, *J* = 8.2, HO–C(2)). ^{13}C-NMR (75 MHz, $CDCl_3$; 1:1 mixture of diastereoisomers): 201.03 (*s*, C(1′)); 102.65, 102.58 (2*d*, C(1)); 102.09 (*s*, C(4)); 75.16, 73.36 (2*d*, C(5)); 72.66, 72.33 (2*d*, C(3)); 70.30, 70.08 (2*t*, C(6)); 69.62, 68.87 (2*d*, C(2)); 38.97, 38.29 (2*d*, C(2′)). HR-ESI-MS: 318.9443 (100, $[M + Na]^+$, $C_8H_9INaO_4^+$; calc. 318.9443).

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