Available online at www.sciencedirect.com
ScienceDirect
Carbohydrate Research 342 (2007) 2031–2048
Carbohydrate RESEARCH

Modification of methyl *O*-propargyl-D-glucosides: model studies for the synthesis of alkynyl based functional polysaccharides

Pascal F. Tankam,[a,b] Petra Mischnick,[b,*] Henning Hopf[a,*] and Peter G. Jones[c]

[a]*Technical University Braunschweig, Institute of Organic Chemistry, Hagenring 30, D-38106 Braunschweig, Germany*
[b]*Technical University Braunschweig, Institute of Food Chemistry, Schleinitzstr. 20, D-38106 Braunschweig, Germany*
[c]*Technical University Braunschweig, Institute of Inorganic and Analytical Chemistry, Hagenring 30, D-38106 Braunschweig, Germany*

Received 18 March 2007; received in revised form 1 May 2007; accepted 9 May 2007
Available online 18 May 2007

Abstract—Methyl 4,6-*O*-benzylidene-2,3-di-*O*-propargyl-α-D-glucoside (**2**) has been prepared and its structure determined, including its X-ray structural analysis. For comparison the structure of the corresponding allyl derivative has also been determined by X-ray crystallography. Glucoside **2** is a versatile starting material for numerous novel derivatives such as diols, a diester, a diacid, and a dialdehyde. Subjecting **2** to a Mannich reaction leads to a (bis)amine in excellent yields. The click reaction between **2** and benzyl azide furnishes a (bis)triazole as the main product. Deprotection of **2** furnishes a (bis)propargyl ether, which can be converted by the methodology developed for **2** to the corresponding (bis)acetylenes; click reaction with benzyl azide converts **2** into a (bis)triazole.

Keywords: Acetylenic carbohydrates; Propargyl ethers; Glucan derivatives; X-ray crystallography

1. Introduction

Polysaccharides have been chemically modified in various ways to change their physical and/or biological properties, thus allowing a broader range of application. Most reported chemical modifications of starch and cellulose are base-induced etherifications. The distribution of substituents in these processes, which are usually kinetically controlled, depends primarily on base concentration and spatial requirements, favoring the most acidic or the primary position of the glycosyl unit, respectively.[1] Functional groups are most often introduced directly by polymer-analogous reactions, for example, carboxy groups by substitution with chloroacetate.

Transformation of a reactive intermediate to a range of products with various functionalities offers an alternative approach, thus decoupling functional group interconversion from the steric and electronic effects of the polysaccharide backbone. In this way, polysaccharide derivatives with various functionalities, but identical substitution patterns, could become available, since the latter are established and can be tuned in the first step. Unsaturated ethers can serve as such intermediates. Dubber and Lindhorst introduced hydroxyalkyl, thio, and amino groups into glucose via *O*-allyl ethers.[2] Cyclodextrin sulfonates were obtained by addition of hydrogen sulfite to allyl modified cyclodextrins by Wenz and Höfler.[3] Slaghek et al. prepared *O*-(2,3-epoxy)propyl ethers from allyl starches.[4] If one proceeds one step further and formally removes hydrogen from the alkenyl group, the geometry of the resulting acetylenic function corresponds to a rigid carbon rod with an acidic hydrogen at the tip. Such alkynyl groups comprise several special properties, such as solvent-dependent self-association and a wide range of reactivities. Self-association rests on the ability of acetylenic groups to act both as a hydrogen bond acceptor and a donor. When linked to a polymeric backbone, supramolecular structures associated with cooperative effects can be expected.

* Corresponding authors. Tel.: +49 (0)531 391 7201; fax: +49 (0)531 391 7230 (P.M.); tel.: +49 (0)531 391 5255; fax: +49 (0)531 391 5388 (H.H.); e-mail addresses: p.mischnick@tu-bs.de; h.hopf@tu-bs.de

0008-6215/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2007.05.007

A very important category of reactions of the terminal alkynyl group employs the corresponding acetylide in substitutions, for example, of alkyl halides, and additions, for example, to carbonyl compounds. In all these transformations the C≡C-triple bond is retained, whereas it is lost by addition reactions to the sp-hybridized carbon atoms. Into a third category fall copper-catalyzed homogeneous C–C-coupling reactions, enabling oligomerization, or cross-linking reactions. By using higher homologues, spacer lengths can be varied in all these cases. Hydrogenation of the functionalized acetylenic group allows transformation of the rigid, slim spacer to a flexible, more space filling structural feature. These 'multi-talent' properties of the acetylenic function make it a promising motif for chemical modification of polysaccharides. Fusion of carbohydrate and acetylene chemistry links an oxygen rich, strictly stereoregular, hydrophilic polymer with a carbon rich, rod-like hydrophobic reactive group.

Carbohydrate *O*-propargyl ethers have been used for the formation of glycophanes by Belghiti et al.[5] Novel thiosaccharides have been prepared by addition of a glucosesulfenic acid to a propargyl glycoside by Aversa et al.[6] The chemistry of acetyleno saccharides has recently been reviewed.[7] *C*-Glycosyl compounds and *O*-alkynyl glycosides have since 1995 been the object of a series of systematic studies of oligosaccharide analogues of polysaccharides by Vasella and co-workers.[8] De novo synthesis of a cellulose-analogue stiffened by buta-1,3-diynyl spacers and staggered linkage of propargyl cellooligosaccharides to a core molecule contributed significantly to the understanding of cellulose structure.[9] The Swiss workers also prepared *O*-propargyl derivatives to insert a diynyl spacer or a triazole bridge into a cyclodextrin ring by 1,3-dipolar cycloaddition of the corresponding ring-opened propargyl- and azido-functionalized saccharide.[10]

Since the definition of the Cu(I)-catalyzed variant of the Huisgen 1,3-dipolar cycloaddition of azides and alkynes to afford 1,2,3-triazoles as 'click-chemistry' by Sharpless and co-workers[11] and Meldal et al.,[12] the use of propargyl ethers in carbohydrate chemistry has drastically increased.[13,14] For example, 'click-chemistry' has been applied to carbohydrate-alkynyl derivatives for the generation of synthetic receptors.[15,16]

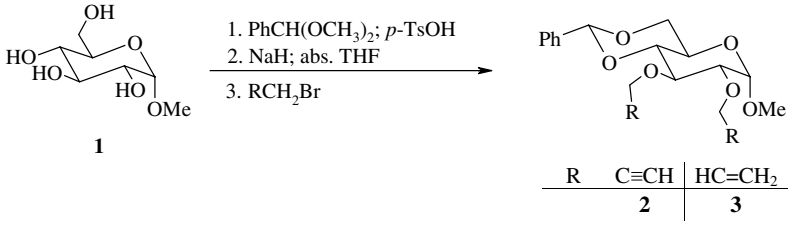
We now report on model studies performed with benzylidene-protected methyl 2,3-di-*O*-propargyl-α-D-glucopyranoside and also with the free pyranoside to investigate the applicability of typical acetylenic reactions to multiple carbohydrate alkynyl ethers. Subsequently, propargyl starches (PgS) have been prepared and selected reactions have been applied to these polysaccharide ethers in polymer-analogous modifications.[17]

2. Results and discussion

2.1. Preparation and structure of methyl 4,6-*O*-benzylidene-2,3-di-*O*-propargyl-α-D-glucoside (2)

Beside glucose, propargyl starches will comprise up to seven glucose derivatives with the patterns 2-, 3-, 6-, 2,3-, 2,6-, 3,6-, and 2,3,6-*O*-propargyl. For our exploratory studies we employed methyl 4,6-*O*-benzylidene-2,3-di-*O*-propargyl-α-D-glucoside (**2**). Full protection of the sugar OH was chosen in a first step to exclude interference with protic groups and to simplify isolation and purification of the products. Two neighboring reactive groups should give a first impression on the efficiency of multiple reactions, on decoupling of the relative reactivities from the sugar core, and possible interactions between the two acetylenic groups in close proximity. Therefore, the 2,3-di-*O*-propargyl-glucoside was chosen as the simplest appropriate, but adequately complex model compound. Since partly derivatized polysaccharides inevitably are complex mixtures, their characterization is difficult and limited. Thus, the model studies described in this paper should enable the production and characterization of defined and uniform compounds. To prepare acetylene derivative **2**, methyl α-D-glucoside (**1**) was reacted with benzaldehyde dimethylacetal,[18] and the resulting intermediate subsequently etherified in THF by treatment with NaH followed by reaction with propargyl bromide (Scheme 1; R: C≡CH).

The structure assignment of **2** is straightforward and rests on the spectroscopic and analytical data given in Section 3; the two ethynyl groups are readily identified by the corresponding signals in the ^{1}H ($\delta = 2.43$ and 2.46 ppm) and ^{13}C NMR spectra ($\delta = 79.91$, 74.32 and



Scheme 1. Preparation of methyl 4,6-*O*-benzylidene-2,3-di-*O*-propargyl-α-D-gluco-pyranoside (**2**) and methyl 4,6-*O*-benzylidene-2,3-di-*O*-allyl-α-D-glucopyranoside (**3**).

79.88, 74.80 ppm), respectively, as well as the typical acetylene bands in the vibrational spectrum ($\tilde{\nu} = 3304\ cm^{-1}$ (s) and 3273 (s)). Furthermore, since we were interested in the exact structural parameters of **2**, an X-ray structural investigation was carried out on single crystals obtained by recrystallization from aqueous methanol (Fig. 1).

To investigate whether the linear structure of the propargyl substituent in **2** influences bond angles and lengths of the sugar core, we also prepared the (bis)allyl derivative **3** (Scheme 1; R: $CH{=}CH_2$) corresponding to **2**, employing a method already described in the literature.[19] Again, single crystals were obtained from petroleum ether and the structure of **3** is reproduced in Figure 2.

The molecular structures of compounds **2** and **3** are shown in Figures 1 and 2. The structures of the glucose cores are closely similar, with an rms deviation of 0.026 Å for a fit of atoms O1,4,5,6 and C1–8 (Fig. 3);

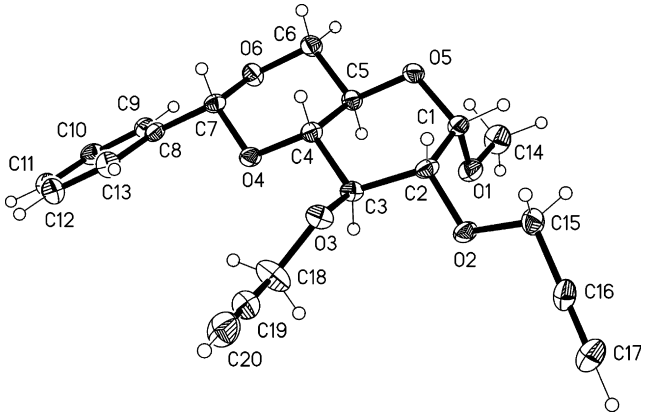


Figure 1. Ellipsoid representation (50% level) of compound **2** in the crystal.

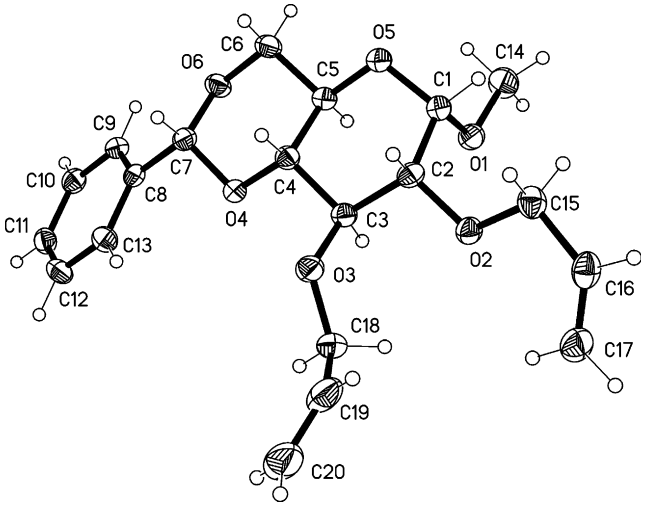


Figure 2. Ellipsoid representation (50% level) of compound **3** in the crystal.

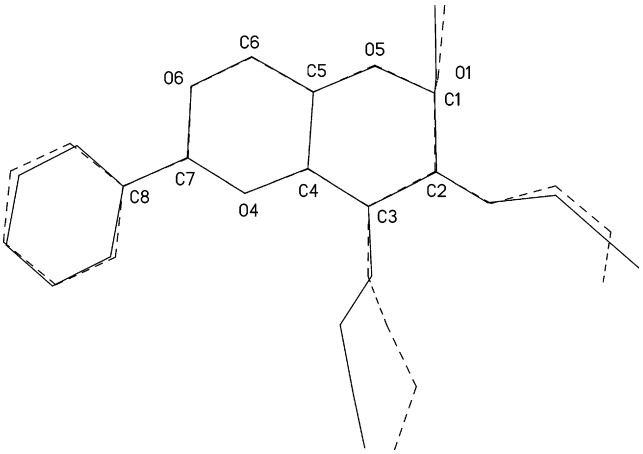


Figure 3. Least-squares fit of compounds **2** (solid lines) and **3** (broken lines).

atoms O2 and O3 deviate by 0.20 and 0.12 Å, respectively. Minor differences are observed in the angle C2–C3–O3 (106.6°, 109.5(1)°), the orientation of the phenyl ring (torsion angle O4–C7–C8–C9 −121.2°, −135.2(2)°) and the side chain orientations corresponding to torsion angles C1–C2–O2–C15 (76.5°, 67.0(2)°) and O5–C1–O1–C14 (58.6°, 64.0(2)°). The major difference in conformation is seen in the torsion angle C2–C3–O3–C18 (−143.7°, −100.5(2)°). The distance between the midpoints of the side chain multiple bonds amounts to 6.23 and 5.05 Å, respectively. The triple bonds are hence significantly further apart than their corresponding olefinic moieties.

Although the cell constants are similar and the space group is the same, the compounds are not isostructural. This is seen in the packing diagrams (Figs. 4 and 5). In

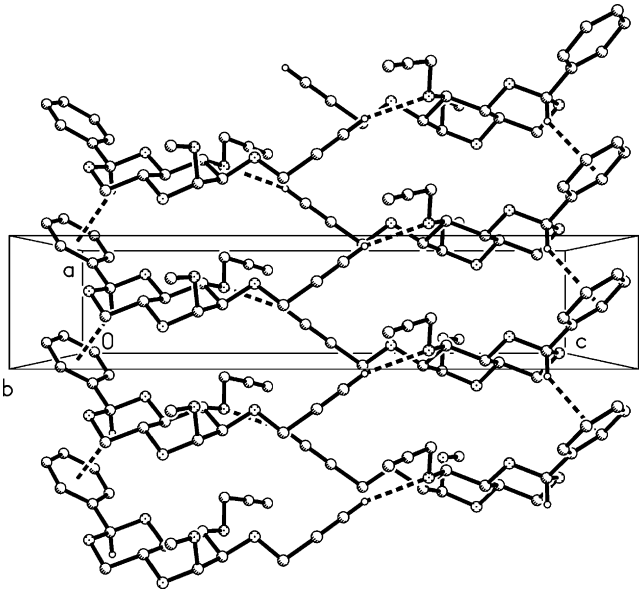


Figure 4. Packing diagram of compound **2**.

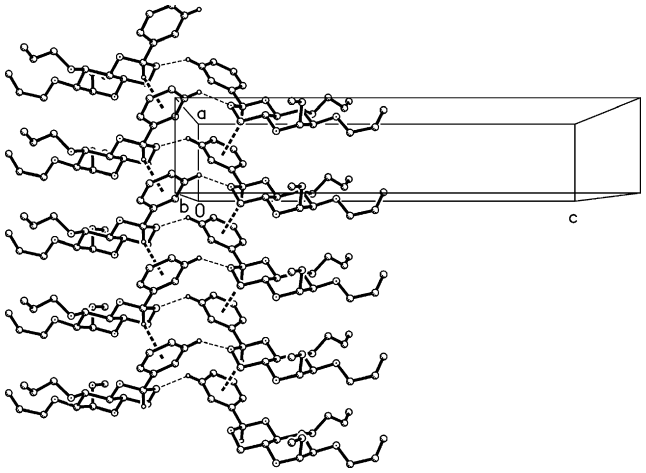


Figure 5. Packing diagram of compound **3**.

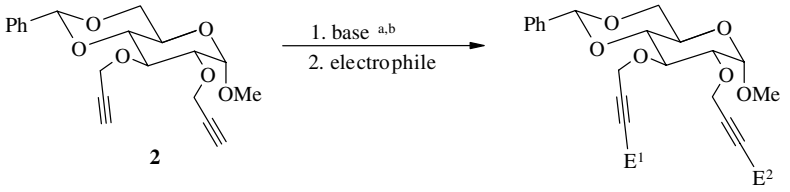
compound **2**, the most significant contacts are from the acetylenic hydrogen H17 to O3 (normalized distance 2.34 Å, angle 161°, operator $-\frac{1}{2}+x,\frac{1}{2}-y,-z$) and from C7–H7 to the centroid of the phenyl ring (2.60 Å, 143°, $1+x,y,z$), leading to the formation of layers parallel to the *ac* plane. For compound **3**, an analogous C7–H7···phenyl interaction is observed (2.46 Å, 154°, $1+x,y,z$), which combines with the weak hydrogen bond C10–H10···O6 (2.46 Å, 131°, $-\frac{1}{2}+x,\frac{1}{2}-y,1-z$) to form broad molecular ribbons parallel to the *x* axis.

2.2. The chemical behavior of the diacetylene derivative 2

First, reactions based on CH-acidity were studied, and the results of these experiments are collected in Table 1.

In an exploratory experiment (entry 1), deprotonation of **2** with ethyl magnesium bromide was investigated by quenching the resulting (bis)acetylide with D_2O. Exchange was found to be nearly quantitative: No ethynyl proton and no isomerization to allenic groups could be detected by ^1H NMR spectroscopic analysis in the raw hydrolyzate, and after work-up the (bis)deuterated product **4** was isolated in 78% yield. Its spectroscopic data—together with those of all the other products from Table 1—can be found in Section 3. For further reac-

Table 1. Functionalization of terminal alkynes with various electrophiles



2 **4-14**

Entry	Product	E	Product		Time (h)	Yield (%)
			E^1	E^2	Step 1/Step 2	
1	**4**	D_2O	D	D	3[a]/18	78
2	**5**	$(CH_3)_3SiCl$	$Si(CH_3)_3$	$Si(CH_3)_3$	0.5[b]/24	84
3	**6**	CH_3I	CH_3	CH_3	1[b]/24	85
4	**7a**	$(CH_2O)_n$	CH_2OH	CH_2OH	1[b]/14	74
	7b		CH_2OH	H		5[c]
	7c		H	CH_2OH		
5	**8a**	CH_3CHO	$CH(CH_3)OH$	$CH(CH_3)OH$	1[b]/24	75
	8b		$CH(CH_3)OH$	H		10[c]
	8c		H	$CH(CH_3)OH$		
6	**9a**	$(CH_3)_2CO$	$C(CH_3)_2OH$	$C(CH_3)_2OH$	3[a]/14	70
	9b		$C(CH_3)_2OH$	H		23[c]
	9c		H	$C(CH_3)_2OH$		
7	**10a**	$CH_2(O)CH_2$	CH_2CH_2OH	CH_2CH_2OH	1[b]/13	46
	10b		CH_2CH_2OH	H		17[c]
	10c		H	CH_2CH_2OH		
8	**11a**	$(CH_3)_2NCHO$	CHO	CHO	1[b]/2	30
	11b		CHO	H		4[c]
	11c		H	CHO		
9	**12**	CO_2	COOH	COOH	2[b]/2	40
10	**13a**	CH_3OCOCl	$COOCH_3$	$COOCH_3$	1[b]/2	53
	13b		$COOCH_3$	H		6[c]
	13c		H	$COOCH_3$		
11	**14**	Et_2NH/CH_2O	CH_2NEt_2	CH_2NEt_2	—/48	87

[a] EtMgBr; room temp., abs. THF.
[b] *n*-BuLi; −78 °C; abs. THF.
[c] Combined yield of the two positional isomers.

tions either ethyl magnesium bromide or butyl lithium was employed in the anionization in step 1 (Table 1). With both trimethylsilyl chloride (entry 2) and methyl iodide (entry 3) as the electrophile (step 2, Table 1) the results are very similar, and the silylated and methylated products **5** and **6**, respectively, are again isolated in good yields. In the next series of experiments, aldehydes and ketones were employed as the quenching reagents. With formaldehyde the primary diol **7a** was obtained in 74% yield (entry 4). In this case the two isomeric mono alcohols **7b** and **c** (combined yield 5%) are also isolated, evidently resulting from either incomplete formation of the carbanion intermediate or incomplete quenching of it. With acetaldehyde (entry 5) and acetone (entry 6) very similar results are obtained, the fully functionalized products **8a** and **9a** being accompanied by their monosubstituted precursors **8b**,**c** and **9b**,**c**, which are produced in sizeable amounts here. Since in experiment 5 the quenching reagent is prochiral, diastereomers of methyl 4,6-*O*-benzylidene-2,3,-di-*O*-(4-hydroxy-pent-2-ynyl)-α-D-glucoside **8a** are generated, as can be inferred from doubling of selected signals in the respective ^{13}C NMR spectra (see Section 3).

Monosubstituted regioisomers were always obtained in a 1:1 ratio as estimated by GLC analysis, therefore confirming the expected (see above) decoupling of local reactivity from the sugar core. In contrast, methyl α-D-glucosides show a strongly preferred reactivity of the 2-OH group, which is the most acidic due to the electron-withdrawing effect of the anomeric center and the deprotonation supporting effect of the α-glycosidic oxygen. Column chromatography of the monosubstituted product mixture in several cases provides one pure regioisomer and an enriched fraction of the other, with the impurity of the slower eluting isomer lying in the 16–30% range. In Section 3, spectroscopic data are only listed for the analytically pure compounds. The 2- and 3-modified isomers could be differentiated by their EI-mass spectra, as will be discussed later.

A primary alcohol group was also introduced by addition of **2** to ethylene oxide (entry 7), yielding 46% of methyl 4,6-*O*-benzylidene-2,3-di-*O*-(5-hydroxy-hex-2-ynyl)-α-D-glucoside **10a** as a homologue of **7a**, and 17% of the 1:1 mixture of monoalcohols **10b** and **c** (cf. Table 1). While oxirane represents a lower oxidation state—compared to the aldehydes—additions to carbon dioxide (entry 9) and methyl chloroformate (entry 10) were carried out as examples for a higher oxidation state. Six percent of the mono- and 53% of the dimethyl ester **13a** could be isolated, while the work-up procedure for the much more polar carboxylic acid derivatives **12** from the reaction with carbon dioxide was more difficult.

To fill the gap between the oxidation states of alcohols and carboxylic acids, the glucose acetylide was finally reacted with dimethylformamide (entry 8). The conjugated dialdehyde **11a** could be isolated in 30% yield, accompanied by 4% of the regioisomeric monoaldehydes (Table 1), which again were produced in 1:1-ratio.

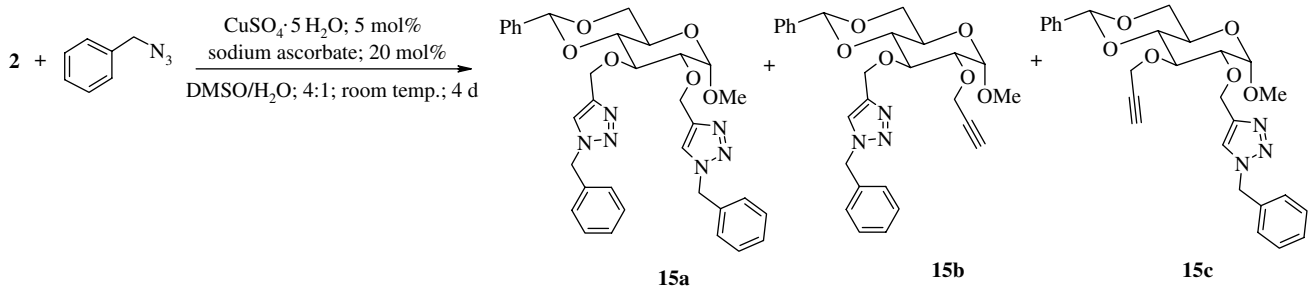
In a final derivatization a Mannich reaction[20] was performed with **2** (entry 11). We were pleased to find that the corresponding (bis)*tert*-amine **14** was produced in excellent yield, no monosubstituted products being obtained in this instance.

Recently there have been several reports on the use of carbohydrates in 'click-chemistry' processes.[21–25] To test the behavior of **2** in this dipolar cycloaddition we kept a mixture of it and benzyl azide for 4 days at room temperature in Me_2SO (Scheme 2).

After work-up (bis)adduct **15a** was isolated in 71% yield, the mono addition products **15b** (2%) and **15c** (10%) being obtained as minor side products. Obviously this reaction can be optimized further and hence constitutes—like many of the functionalizations summarized in Table 1—a preparatively efficient process.

2.3. Mass spectrometry

Because most of the spectroscopic data of the regioisomers formed by incomplete reaction of 2,3-di-*O*-propargyl glucoside **2** are very similar, they cannot easily be distinguished. However, EIMS allows a clear differentiation of the 2-O- and 3-O-functionalized propargyl glucosides. The fragmentation of glycoside derivatives has been thoroughly investigated by Kochetkov and Chizhov.[26,27] Fragmentation of methyl 4,6-*O*-benzylidene-hexopyranosides has been described by Bosso et al.[28] Besides the typical fragments of a benzaldehyde derivative at



Scheme 2. Copper(I)-catalyzed synthesis of 1,4-disubstituted 1,2,3-triazoles.

m/*z* 77, 91 and 105, fragments with *m*/*z* 179, *m*/*z* 162, and especially *m*/*z* 149 are formed, the latter including C-6, C-5, O-6, and O-5 of the sugar part. The corresponding M−149 ion is also observed and indicates substitution or modification at O-2 and O-3 by the corresponding mass shifts. Two additional fragments indicate substitution at both O-2 and O-3 without differentiation. One is the C_2-fragment, assigned as H_1^i according to Kochetkov and Chizhov, which preferably contains C-2 and C-3 (i.e., H_1^2): $[R^3O–CH{=}CH–OR^2]^+$. From the C_3-fragments the usually dominating linear F_1^2 ion comprising C-2, C-3, and C-4 is inhibited, because O-4 is involved in the benzylidene ring. Thus cyclic G_1^5 is preferred bearing the substituents of two adjacent C-atoms: $[R^3O–CH(–CH–)CH–OR^2]^+$. To differentiate between positions 2 and 3, there are two diagnostically valuable ring cleavage fragments, which only bear the substituents at position 3. One is a rearrangement product J_1^1, including 1-$CHOCH_3$ and OR^3 $[R^3O–CH{=}OCH_3]^+$. In the mass spectra of the modified methyl 4,6-*O*-benzylidene-2,3-di-*O*-propargyl-glucosides, a characteristic second fragment containing only R^3 is observed at a *m*/*z* 26 u higher than J_1^1. This is presumably related to the F_1^1 ion and has the structure $[R^3O–CH{=}CH–CH{=}OCH_3]^+$. Further fragments are formed by loss of OCH_3, (M−31), cleavage of the alkynyl residue $[M–CH_2–C{\equiv}C–E]^+$, while $[CH_2–C{\equiv}C–E]^+$ itself is also observed with an abundance of up to 100% relative intensity (*m*/*z* 53 for **6**). Special fragmentations such as loss of water and formation of the isopropyl cation (*m*/*z* 43) are observed for the tertiary alcohols **9a**–**c**.

Relative intensities of the fragment ions mentioned are listed in Table 2. For those compounds, for which the fragmentation of the sugar core dominates, the rearrangement ion J_1^1 is very intensive or even the most abundant (**2**, **4**, **7a**–**c**, **8a**–**c**, **9a**–**c**, **10a**,**b**). If the substituent itself forms a stable ion, as observed for the trimethylsilyl-propynyl (**5**) or the 2-butynyl derivative (**6**), the relative intensity of this sugar derived fragment ion decreases. The same trend is observed for the C_2 and C_3 fragments from cross-ring cleavage (H_1^2, G_1^5), while the other R^3-containing fragment F_1^1 has around 10% relative intensity for most of the derivatives. Modification at position 3 can be recognized by the corresponding mass shift of J_1^1 and F_1^1, while the 2-regioisomer shows *m*/*z* 99 with 100% relative intensity and *m*/*z* 125 like parent compound **2**. There are some systematic differences in relative ion intensities of the regioisomers. For nearly all 3-modified derivatives the intensity of the molecular ion is higher than for the 2-modified isomer, with the biggest difference for the carboxy methyl esters **13b** and **c** (17% vs 2%) and significant differences for the hydroxymethyl and the hydroxyethyl derivatives **7b**,**c** and **8b**,**c** (both 6% vs 1% relative intensity). On the other hand, $[M-149]^+$ with the structure $[O{=}CH–CH(OR^3)–CH(OR^2)–CH–OCH_3]^+$ is always observed with a three- to sevenfold higher abundance for the 2-regioisomer. For the tertiary alcohol **9a**–**c** and to a minor extent even for the secondary alcohol **8a**–**c**, loss of water is observed. As basic ion of **9b** modified in position 3, $(CH_3)_2CH^+$ is detected at *m*/*z* 43, while for the 2-isomer **9c** rearrangement product at *m*/*z* 99 dominates the mass spectrum as outlined above.

Since nitrogen stabilizes the positive charge very well, fragmentation of the nitrogen-containing compounds **14** and **15a**–**c** is no longer typical for the carbohydrate part. Because of the additional benzyl residue in triazole **15**, the tropylium ion at *m*/*z* 91 dominates the mass spectrum. The ring cleavage fragments of the glucose part (F, G, H, J) can still be detected but with a very low relative intensity. R is registered at *m*/*z* 172, but *m*/*z* 144, presumably a secondary ion of R, maybe by the loss of N_2, occurs with higher relative intensity of 28%. The mass spectrum of the other nitrogen-containing compound **14** is also dominated by non-carbohydrate fragments such as *m*/*z* 56 (100% relative intensity), 110 and 125.

2.4. The chemical behavior of methyl 2,3-di-*O*-propargyl-α-D-glucopyranoside (16)

Having completed our studies on pyranoside **2** we next turned our attention to the unprotected (bis)propargyl ether **16** (Scheme 3), employing this as a model compound for the ultimately intended propargylated starch.

Since **16**, readily available in quantitative yield by acid-catalyzed hydrolysis of **2**, contains acidic OH-groups that might interfere with the functionalization of the terminal triple bonds, we thought it desirable to subject the unprotected carbohydrate derivative to a selection of the processes described above. As the results summarized in Scheme 3 show, the anionization of **16** and the subsequent trapping of the (bis)acetylide with an electrophile can be performed effortlessly. Although these trapping experiments were not optimized, the yield of the desired products **17** is satisfactory in most cases. Only in the case of silylation with trimethylsilyl chloride did we observe the formation of a product in which reaction had taken place at the oxygen atoms as well (formation of **17c**). From the reaction of **16** with benzyl azide, known for its high compatibility with functional groups, adduct **18** was isolated in 81% yield. It thus appears likely that the corresponding experiments can also be performed with the biopolymer: the accompanying publication confirms this.[17] All products **17a**–**h** and **18** were characterized by the usual spectroscopic methods as described in Section 3.

2.5. Conclusion

Propargyl ethers of carbohydrates are versatile intermediates for further functionalization. A range of nucleophilic reactions of the acetylide and a cycloaddition

Table 2. Mass spectral data (EIMS) of methyl 4,6-*O*-benzylidene-2,3-di-*O*-propargyl-D-glucoside (**2**) and its products **4**–**15** functionalized according to Table 1

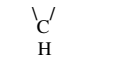
	E^1	E^2	M	A_1[a]	M−149[b]	*m/z* 149[b]	G_1^{5c}	H_1^{2d}	F_1^{1e}	J_1^{1f}	*m/z* 105	*m/z* 91	*m/z* 77	$M-R^{2/3}$	$R^{2/3}$	Special fragments
2	H	H	358 (0.8)	327 (2)	209 (46)	(55 − *x*)	149 (*x*)	136 (44)	125 (11)	99 (100)	(49)	(34)	(36)	319 (3)		
4	D	D	360 (2)	329 (2)	211 (24)	(25)	151 (19)	138 (28)	126 (8)	100 (100)	(59)	(37)	(29)	320 (0.7)		
5	$Si(CH_3)_3$	$Si(CH_3)_3$	502 (1)	471 (n.d.)	353 (0.3)	(43)	293 (8)	280 (3)	197 (20)	171 (45)	(33)	(30)	(9)	391 (12)	111 (90)	*m/z* 73 (100)
6	CH_3	CH_3	386 (0.7)	355 (0.1)	237 (1)	(22)	177 (7)	164 (5)	139 (6)	113 (39)	(55)	(44)	(34)	333 (6)	53 (100)	
7a	CH_2OH	CH_2OH	418 (0.5)	387 (n.d.)	269 (0.1)	(39)	209 (17)	196 (10)	155 (8)	129 (100)	(31)	(29)	(46)	349 (n.d.)	69 (36)	
7c	H	CH_2OH	388 (1)	357 (0.2)	239 (23)	(23)	179 (14)	166 (22)	125 (10)	99 (100)	(34)	(29)	(16)	319 (0.2)		
7b	CH_2OH	H	388 (6)	357 (0.7)	239 (8)	(33)	179 (17)	166 (23)	155 (7)	129 (100)	(45)	(39)	(21)	319 (0.4)		M−H_2O (1)
8a	$CH(CH_3)OH$	$CH(CH_3)OH$	446 (1)	415 (n.d.)	297 (0.8)	(55)	237 (14)	224 (6)	169 (6)	143 (100)	(67)	(62)	(39)	363 (0.2)	83 (38)	M−H_2O (1)
8c	H	$CH(CH_3)OH$	402 (1)	371 (n.d.)	253 (18)	(25)	193 (9)	180 (15)	125 (8)	99 (100)	(34)	(24)	(15)	319 (0.3)	83 (12)	M−H_2O (0.8)
8b	$CH(CH_3)OH$	H	402 (6)	371 (0.3)	253 (4)	(39)	193 (12)	180 (6)	169 (5)	143 (78)	(50)	(36)	(22)	319 (0.7)	83 (26)	M−H_2O (4)
9a	$C(CH_3)_2OH$	$C(CH_3)_2OH$	474 (0)	443 (n.d.)	325 (0.1)	(45)	265 (13)	252 (2)	183 (4)	157 (72)	(26)	(21)	(12)	377 (n.d.)	97 (38)	M−H_2O (0.7) *m/z* 43 (100)
9c	H	$C(CH_3)_2OH$	416 (0.1)	385 (n.d.)	267 (22)	(32)	207 (22)	194 (12)	125 (10)	99 (100)	(34)	(23)	(13)	319 (0.3)	97 (43)	M−H_2O (0.8) *m/z* 43 (58)
9b	$C(CH_3)_2OH$	H	416 (0.2)	385 (n.d.)	267 (3)	(48)	207 (12)	194 (11)	183 (3)	157 (94)	(45)	(35)	(21)	319 (0.7) 377 (n.d.)	97 (43)	M−H_2O (4) *m/z* 43 (100)
10a	CH_2CH_2OH	CH_2CH_2OH	446 (0.2)	415 (0.1)		(48)	237 (8)	224 (4)	169 (44)	143 (100)	(46)	(52)	(17)	363 (0.5)	83 (36)	*m/z* 221 (16)
10c	H	CH_2CH_2OH	402 (1)	371 (0.2)	253 (2)	(27)	193 (12)	180 (20)	125 (26)	99 (100)	(44)	(32)	(17)	319 (0.3) 363 (0.4)	83 (16)	
10b	CH_2CH_2OH	H	402 (12)	371 (2)	253 (3)	(57)	193 (12)	180 (20)	125 (12)	143 (100)	(70)	(76)	(30)	319/363 (n.d.)	83 (36)	
11a	CHO	CHO	414 (2)	383 (0.4)	265 (2)	(36)	205 (6)	192 (8)	153 (4)	127 (14)	(100)	(60)	(72)	347 (0.5)	67 (8)	
11c	H	CHO	386 (2)	355 (1)	237 (13)	(42)	177 (18)	164 (32)	125 (9)	99 (100)	(73)	(49)	(46)	319 (0.7)	67 (10)	
11b	CHO	H	386 (3)	355 (1)	237 (5)	(39)	177 (18)	164 (36)	153 (8)	127 (34)	(100)	(68)	(51)	347 (0.4)	67 (15)	
13a	$COOCH_3$	$COOCH_3$	474 (8)	443 (7)[g]	325 (2)	(63)	265 (10)	252 (11)	183 (6)	157 (32)	(100)	(58)	(27)	377 (0.7)	97 (23)	M−CH_3 (5) M−157 (6) M−251 (21)
13c	H	$COOCH_3$	416 (2)	385 (3)	267 (13)	(42)	207 (17)	194 (21)	125 (9)	99 (100)	(72)	(45)	(27)	319/377 (n.d.)	97 (17)	M−CH_3 (1)
13b	$COOCH_3$	H	416 (17)	385 (4)	267 (5)	(42)	207 (21)	194 (29)	183 (7)	157 (52)	(100)	(60)	(39)	319/377 (n.d.)	97 (24)	M−CH_3 (5)
14	$CH_2N(C_2H_5)_2$	$CH_2N(C_2H_5)_2$	528 (4)	497 (0.4)	379 (0.2)	(14)	319 (n.d.)	306 (n.d.)	210 (14)	184 (n.d.)	(39)	(38)	(28)	404 (2)		*m/z* 125 (72) *m/z* 110 (50) *m/z* 56 (100)
15a	$C_6H_5CH_2N_3$	$C_6H_5CH_2N_3$	624 (1)	593 (1)	475 (n.d.)	(4)	415 (4)	402 (n.d.)	258 (5)	232 (n.d.)	(12)	(100)[h]	(10)	452 (2)	172 (28)	*m/z* 144 (28)
15c	H	$C_6H_5CH_2N_3$	491 (1)	460 (2)	342 (3)	(12)	282 (10)	269 (n.d.)	125 (5)	99 (3)	(21)	(100)[h]	(15)	319 (0.5)	172 (5)	*m/z* 144 (28) *m/z* 258 (5)
15b	$C_6H_5CH_2N_3$	H	491 (0.6)	460 (3)	342 (1)	(10)	282 (2)	269 (0.7)	258 (2)	232 (2)	(33)	(100)[h]	(21)	319 (n.d.)	172 (9)	*m/z* 144 (28)

n.d. = not detected.

[a] M−OCH_3.

[b] 149: PhCH=O(6)–CH_2–CH=O(5).

[c] R^3O–CH–CH–OR^2.

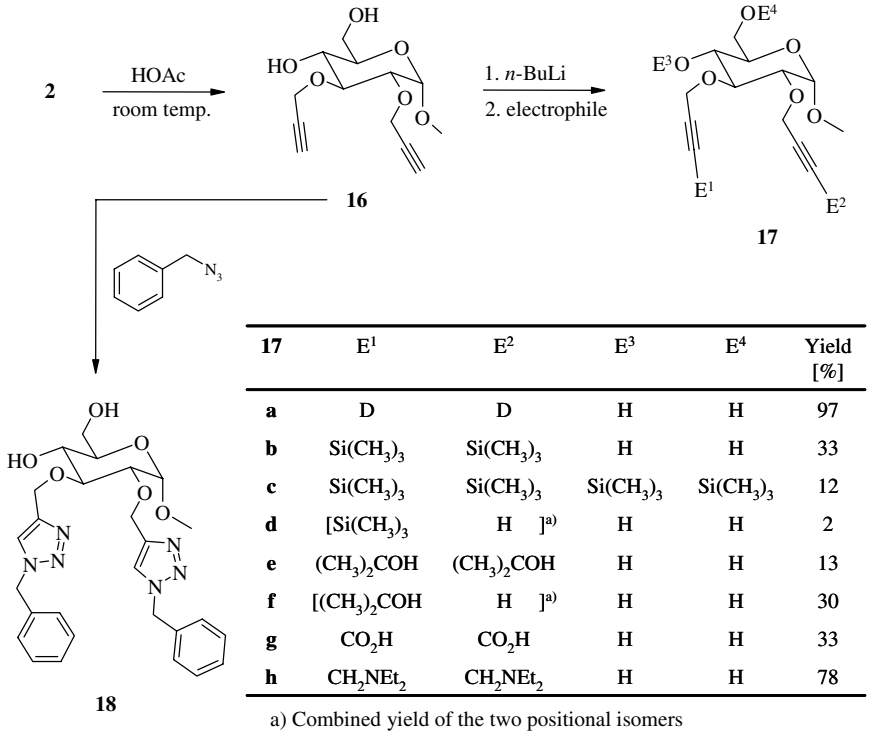
[d]


[e] R^3O–CH=CH–CH=OCH_3.

[f] R^3O–CH=OCH_3.

[g] Mainly from ester.

[h] Additional from the Bn-substituent.



17	E^1	E^2	E^3	E^4	Yield [%]
a	D	D	H	H	97
b	$Si(CH_3)_3$	$Si(CH_3)_3$	H	H	33
c	$Si(CH_3)_3$	$Si(CH_3)_3$	$Si(CH_3)_3$	$Si(CH_3)_3$	12
d	$[Si(CH_3)_3$	H]a)	H	H	2
e	$(CH_3)_2COH$	$(CH_3)_2COH$	H	H	13
f	$[(CH_3)_2COH$	H]a)	H	H	30
g	CO_2H	CO_2H	H	H	33
h	CH_2NEt_2	CH_2NEt_2	H	H	78

a) Combined yield of the two positional isomers

Scheme 3. Selected reactions of methyl 2,3-di-*O*-propargyl-α-D-glucopyranoside (**16**).

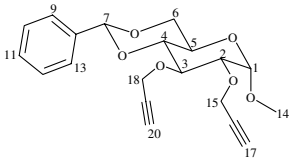
reaction have been successfully performed with a 4,6-*O*-benzylidene protected di-*O*-propargyl methyl glucoside and also with the deprotected propargyl derivative as model compounds. In the next step, propargyl starches will be produced with degrees of substitution (DS) <3, and selected reactions will be applied to these polysaccharide propargyl ethers.

3. Experimental

3.1. General remarks

Melting points were measured with a Büchi 530 melting point apparatus, uncorr. For thin-layer chromatography (TLC) Macherey-Nagel Polygram Sil G/UV_{254} plates were used. Column chromatography was performed with Kieselgel 60 (70–230 mesh) from E. Merck, Darmstadt. ^1H and ^{13}C NMR-spectra were recorded with a Bruker DRX-400 at 400.1 and 100.6 MHz, respectively. The chemical shifts are given with respect to tetramethylsilane (^1H: δ 0 ppm) and $CDCl_3$ (^{13}C: δ 77.0 ppm). The numbering system for the atoms of the different carbohydrate derivatives is shown in the structure below; for all other derivatives this scheme was employed analogously. IR: Bruker Tensor 27. UV–vis: Varian Cary 100 Bio. GC: Agilent 6890 (30 m analytical column). GC–MS: Hewlett Packard 5890 (30 m analytical column). ESI mass spectra: Thermofinnigan MAT95XLT. High resolution mass spectra: Thermofinnigan MAT95.

3.2. Methyl 4,6-*O*-benzylidene-2,3-di-*O*-propargyl-α-D-glucopyranoside (2)



2

To a soln of 9.50 g (33.7 mmol) of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside[18] in 320 mL of anhydrous THF is added 5.88 g (0.25 mol) of sodium hydride. The suspension was stirred for 30 min and cooled with an ice-salt bath. With vigorous stirring 50 mL (53.4 g, 0.45 mol) of propargyl bromide is added over 1 h, and the reaction mixture is stirred for 3 days at room temp. MeOH is added carefully until gas formation ceases (destruction of excess sodium hydride). The solvent was removed under diminished pressure and the residue is taken up in 250 mL of CH_2Cl_2 and 150 mL of water. After phase separation the organic phase is carefully washed with water and dried with magnesium sulfate. The solvent is removed and the raw product is purified by column chromatography (flash silica gel, 8:1 hexane–EtOH): 8.40 g (70%) of **2**, colorless needles, mp 78–79 °C. ^1H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 2.43 (t, 1H, 1H, 20-H, $^4J_{20,18} = 2.40$), 2.46 (t, 1H, 17-H, $^4J_{17,15} = 2.39$), 3.44 (s, 3H, 14-H, OCH_3), 3.60 (t, 1H, 4-H, $^3J_{4,3} = 9.25$), 3.70 (dd, 1H, 2-H, $^3J_{2,1} = 3.76$,

$^3J_{2,3} = 9.25$), 3.74 (t, 1H, 6-H_a, $^3J_{6a,5} = 10.0$), 3.83 (ddd, 1H, 5-H, $^3J_{5,4} = 9.40$, $^3J_{5,6a} = 10.0$, $^3J_{5,6b} = 4.57$), 3.99 (t, 1H, 3-H, $^3J_{3,2} = 9.25$), 4.29 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.57$, $^2J_{6a,6b} = 10.0$), 4.37–4.49 (m, 4H, 15-, 18-$H_{a,b}$), 4.88 (d, 1H, 1-H, $^3J_{1,2} = 3.76$), 5.53 (s, 1H, 7-H, Ph–CH), 7.35–7.49 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.19 (s, C-8), 128.96 (d, C-11), 128.19 (d, C-10, -12), 126.02 (d, C-9, -13), 101.32 (d, C-7), 99.24 (d, C-1), 81.96 (d, C-4), 79.91 (s, C-19), 79.88 (s, C-16), 77.88 (d C-2, -3), 74.80 (d, C-17), 74.32 (d, C-20), 68.99 (t, C-6), 62.08 (d, C-5), 59.99 (t, C-18), 59.36 (t, C-15), 55.24 (q, C-14). IR (diamond-ATR): $\tilde{\nu} = 3304\ cm^{-1}$ (s), 3273 (s), 3039 (m), 2922 (m), 2870 (m), 2131 (m), 1454 (s), 1375 (s), 1081 and 1041 (vs), 752 and 697 (s). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 192 nm (4.11), 205 (3.95), 256 (2.34), 261 (2.28). GC–MS: m/z (%) = 358 (0.8) [M^+], 327 (2), 209 (46), 149 (55), 136 (44), 125 (11), 105 (49), 99 (100), 91 (34), 77 (36). Anal. Calcd for $C_{20}H_{22}O_6$ (358.39): C, 67.03; H, 6.19. Found: C, 67.02; H, 6.04.

3.3. General procedure for substituting the terminal triple bonds of methyl 4,6-*O*-benzylidene-2,3-di-*O*-propargyl-α-D-glucopyranoside (2)

(a) *With ethyl magnesium bromide as base*: A solution of ethyl magnesium bromide in diethyl ether is placed in a 25 mL three-necked flask equipped with a stirring bar and a reflux condenser. Under stirring **2** in anhydrous THF is added within 15 min, and the mixture stirred for 3 h at room temp. The mixture is cooled to 0 °C, the electrophile is added, and the mixture stirred at room temp. overnight. The mixture is dried with sodium sulfate, the solvent is removed and the raw product is purified by silica gel column chromatography.

(b) *With n-butyl lithium as base:* To a solution of **2** in anhydrous THF is added within 15 min a *n*-butyl lithium solution (1.6 M) in hexane at −78 °C. Stirring is continued for further 30 min, the reaction temperature is raised to 0 °C, and the electrophile is added in THF. After stirring overnight at room temp., the reaction mixture is hydrolyzed and carefully extracted with CH_2Cl_2. The combined organic layers are dried with magnesium sulfate, the solvent is removed under diminished pressure, and the remainder purified by silica gel column chromatography.

3.4. Methyl 4,6-*O*-benzylidene-2,3-di-*O*-(prop-2-ynyl-3-*d*)-α-D-glucopyranoside (4)

According to general procedure (a), **4** is prepared from ethyl magnesium bromide in diethyl ether (147 mg, 1.1 mmol, 0.4 mL), and 180 mg (0.5 mmol) of **2** in 4 mL of THF with 0.4 mL of deuterium oxide: 141 mg (78%) of **4**, mp 75 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 3.44 (s, 3H, 14-H, OCH_3), 3.60 (t, 1H, 4-H, $^3J_{4,3} = 9.25$), 3.70 (dd, 1H, 2-H, $^3J_{2,1} = 3.77$, $^3J_{2,3} = 9.25$), 3.74 (t, 1H, 6-H_a, $^3J_{6a,5} = 10.0$), 3.83 (ddd, 1H, 5-H, $^3J_{5,4} = 9.41$, $^3J_{5,6a} = 10.0$, $^3J_{5,6b} = 4.57$), 3.99 (t, 1H, 3-H, $^3J_{3,2} = 9.25$), 4.29 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.57$, $^2J_{6a,6b} = 10.0$), 4.37–4.49 (m, 4H, 15-, 18-$H_{a,b}$), 4.88 (d, 1H, 1-H, $^3J_{1,2} = 3.77$), 5.53 (s, 1H, 7-H, Ph–CH), 7.34–7.49 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.21 (s, C-8), 128.97 (d, C-11), 128.20 (d, C-10, -12), 126.04 (d, C-9, -13), 101.34 (d, C-7), 99.26 (d, C-1), 81.97 (d, C-4), 79.46 (s, C-19), 79.24 (s, C-16), 77.90 (d, C-2, -3), 74.81 (d, C-17), 74.32 (d, C-20), 69.00 (t, C-6), 62.09 (d, C-5), 59.99 (t, C-18), 59.36 (t, C-15), 55.26 (q, C-14). IR (diamond-ATR): $\tilde{\nu} = 3038\ cm^{-1}$ (w), 2991 (w), 2921 (m), 2871 (m), 2597 and 2582 (m), 1990 (m), 1454 (s), 1375 (s), 1082 and 1047 (vs), 754 and 697 (s). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 191 nm (4.31), 204 (4.00). EIMS (70 eV): m/z (%) = 360 (2) [M^+], 211 (24), 149 (25), 138 (28), 126 (8), 105 (59), 100 (100), 91 (37), 77 (29). HRMS: calcd 360.154, found m/z 360.154 ± 1 ppm. Anal. Calcd for $C_{20}H_{20}D_2O_6$: C, 66.65; H, 6.71. Found: C, 66.08; H, 6.37.

3.5. Methyl 4,6-*O*-benzylidene-2,3-di-*O*-(3-trimethylsilyl-propyn-2-yl)-α-D-gluco-pyranoside (5)

According to general procedure (b), **5** is prepared from 359 mg (1.0 mmol) of **2** in 7 mL of anhydrous THF, 1.7 mL (2.72 mmol) of *n*-butyl lithium solution and 0.35 mL (2.72 mmol) of trimethylsilyl chloride in 0.6 mL THF: 421 mg (84%) of **5**, slightly yellow oil. ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ −0.03 (s, 9H, 18-H), 0.00 (s, 9H, 22-H), 3.26 (s, 3H, 14-H, OCH_3), 3.41 (t, 1H, 4-H, $^3J_{4,3} = 9.24$), 3.49 (dd, 1H, 2-H, $^3J_{2,1} = 3.78$, $^3J_{2,3} = 9.24$), 3.56 (t, 1H, 6-H_a, $^3J_{6a,5} = 9.86$), 3.64 (ddd, 1H, 5-H, $^3J_{5,4} = 9.17$, $^3J_{5,6a} = 9.86$, $^3J_{5,6b} = 4.37$), 3.73 (t, 1H, 3-H, $^3J_{3,2} = 9.24$), 4.10 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.37$, $^2J_{6a,6b} = 9.86$), 4.18–4.32 (m, 4H, 15-, 19-$H_{a,b}$), 4.70 (d, 1H, 1-H, $^3J_{1,2} = 3.78$), 5.35 (s, 1H, 7-H, Ph–CH), 7.15–7.31 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.28 (s, C-8), 128.93 (d, C-11), 128.19 (d, C-10, -12), 126.09 (d, C-9, -13), 101.94 (s, C-20), 101.90 (s, C-16), 101.32 (d, C-7), 99.37 (d, C-1), 91.58 (s, C-21), 90.80 (s, C-17), 81.75 (d, C-4), 78.59 (d, C-2), 78.15 (d, C-3), 69.02 (t, C-6), 62.11 (d, C-5), 60.98 (t, C-19), 60.13 (t, C-15), 55.26 (q, C-14), −0.19 (q, C-18, -22). IR (diamond-ATR): $\tilde{\nu} = 2958\ cm^{-1}$ (m), 2933 (m), 2863 (m), 2176 (w), 1453 (m), 1369 (s), 1082 and 1052 (vs), 756 and 697 (s). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 192 nm (4.30), 202 (4.00), 227 (3.16). GC–MS: m/z (%) = 502 (1) [M^+], 429 (0.3), 391 (12), 293 (8), 280 (3), 197 (20), 171 (45), 149 (43), 105 (33), 111 (90), 91 (30), 73 (100).

HRMS: $C_{26}H_{38}O_6Si_2$: calcd 502.220, found m/z 502.220 ± 1 ppm.

3.6. Methyl 4,6-*O*-benzylidene-2,3-di-*O*-(but-2-ynyl)-α-D-glucopyranoside (6)

According to general procedure (b), **6** is prepared from 359 mg (1.0 mmol) of **2** in 7 mL of anhydrous THF, 1.4 mL (2.2 mmol) of *n*-butyl lithium solution, 0.7 mL (4.0 mmol) of HMPA, and 0.15 mL (2.4 mmol) of methyl iodide. After stirring overnight, 25 mL of diethyl ether is added and the mixture extracted three times with 15 mL portions of dil. aqueous hydrochloric acid. After washing with water, the mixture is dried with magnesium sulfate. Solvent removal provides a solid residue that is purified by silica gel column chromatography (16:4:0.5 pentane–diethyl ether–ethanol): 330 mg (85%) of **6**, colorless needles, mp 76–77 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 1.81 (t, 3H, 22-H, $^5J_{22,19} = 2.36$), 1.85 (t, 3H, 18-H, $^5J_{18,15} = 2.34$), 3.44 (s, 3H, 14-H, OCH_3), 3.58 (t, 1H, 4-H, $^3J_{4,3} = 9.27$), 3.68 (dd, 1H, 2-H, $^3J_{2,1} = 3.76$, $^3J_{2,3} = 9.27$), 3.73 (t, 1H, 6-H_a, $^3J_{6a,5} = 10.0$), 3.83 (ddd, 1H, 5-H, $^3J_{5,4} = 9.39$, $^3J_{5,6a} = 10.0$, $^3J_{5,6b} = 4.52$), 3.91 (t, 1H, 3-H, $^3J_{3,2} = 9.27$), 4.28 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.52$, $^2J_{6a,6b} = 10.0$), 4.34–4.45 (m, 4H, 15-, 19-$H_{a,b}$), 4.87 (d, 1H, 1-H, $^3J_{1,2} = 3.76$), 5.53 (s, 1H, 7-H, Ph–CH), 7.33–7.50 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.30 (s, C-8), 128.84 (d, C-11), 128.11 (d, C-10, -12), 126.04 (d, C-9, -13), 101.25 (d, C-7), 99.30 (d, C-1), 82.68 (s, C-16), 82.11 (s, C-20), 81.76 (d, C-4), 77.95 (d, C-2), 77.61 (d, C-3), 75.41 (s, C-21), 75.23 (s, C-17), 68.99 (t, C-6), 62.15 (d, C-5), 60.65 (t, C-15), 59.73 (t, C-19), 55.19 (q, C-14), 3.64 (q, C-18), 3.61 (q, C-22). IR (diamond-ATR): $\tilde{\nu} = 3039\ cm^{-1}$ (w), 2970 (m), 2919 (m), 2868 (m), 2239 (w), 1452 (m), 1375 (s), 1079 and 1048 (vs), 750 and 695 (s). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 192 nm (4.28), 204 (3.97), 223 (2.91). EIMS (70 eV): m/z (%) = 386 (0.7) [M^+], 333 (6), 177 (7), 164 (5), 149 (22), 139 (6), 113 (39), 105 (55), 91 (44), 77 (34), 53 (100). HRMS: calcd 386.173, found m/z 386.170 ± 7 ppm. Anal. Calcd for $C_{22}H_{26}O_6$ (386.44): C, 68.38; H, 6.78. Found: C, 67.39; H, 6.76.

3.7. Methyl 4,6-*O*-benzylidene-2,3-di-*O*-(4-hydroxy-but-2-ynyl)-α-D-glucopyranoside (7a)

According to general procedure (b), **7a** is prepared from 359 mg (1.0 mmol) of 2 in 7 mL of THF, 1.5 mL (2.4 mmol) of *n*-butyl lithium solution, and 110 mg (3.6 mmol) of paraformaldehyde. A slight increase in temperature is noted and compensated by cooling with an ice-water bath. The reaction mixture is heated to 40–45 °C for 2.5 h and stirred at room temp. overnight. The mixture is added to a solution of 3 g of ammonium chloride in water with vigorous stirring, the phases are separated, and the aqueous layer is washed thoroughly with ether. After solvent removal, the remainder is separated by silica gel column chromatography (10:1 diethyl ether–hexane): Fraction 1: 4.2 mg (1%) of **2**; fraction 2: 7 mg (2%) of **7b**, slightly yellow oil; fraction 3: 13 mg (3%) **7b** and **7c** (ratio 1:2), slightly yellow oil; fraction 4: 310 mg (74%) of **7a**, colorless solid, mp 86–88 °C. Compound **7a**: ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 2.80 (br s, 2H, 2OH), 3.36 (s, 3H, 14-H, OCH_3), 3.50 (t, 1H, 4-H, $^3J_{4,3} = 9.26$), 3.56 (dd, 1H, 2-H, $^3J_{2,1} = 3.77$, $^3J_{2,3} = 9.26$), 3.65 (t, 1H, 6-H_a, $^3J_{6a,5} = 9.98$), 3.74 (ddd, 1H, 5-H, $^3J_{5,4} = 9.36$, $^3J_{5,6a} = 9.98$, $^3J_{5,6b} = 4.49$), 3.89 (t, 1H, 3-H, $^3J_{3,2} = 9.26$), 4.17 (t, 2H, 22-$H_{a,b}$, $^5J_{22,19} = 1.77$), 4.20 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.49$, $^2J_{6a,6b} = 9.98$), 4.23 (t, 2H, 18-$H_{a,b}$, $^5J_{18,15} = 1.77$), 4.35–4.45 (m, 4H, 15-, 19-$H_{a,b}$), 4.78 (d, 1H, 1-H, $^3J_{1,2} = 3.77$), 5.45 (s, 1H, 7-H, Ph–CH), 7.27–7.42 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.16 (s, C-8), 129.02 (d, C-11), 128.21 (d, C-10, -12), 126.04 (d, C-9, -13), 101.40 (d, C-7), 98.89 (d, C-1), 85.27 (s, C-17), 84.77 (s, C-21), 81.74 (d, C-4), 81.73 (s, C-20), 81.41 (s, C-16), 78.12 (d, C-2), 77.54 (d, C-3), 68.92 (t, C-6), 62.13 (d, C-5), 60.26 (t, C-19), 59.49 (t, C-15), 55.22 (q, C-14), 50.79 (t, C-22), 50.78 (t, C-18). IR (diamond-ATR): $\tilde{\nu} = 3414\ cm^{-1}$ (br m), 2919 (m), 2865 (m), 2247 (w), 1453 (m), 1371 (s), 1077 (vs), 1050 (s), 751 and 700 (s). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 191 nm (4.35), 205 (3.98), 256 (2.50). GC–MS: m/z (%) = 418 (0.5) [M^+], 209 (17), 196 (10), 149 (39), 129 (100), 105 (31), 91 (29), 69 (36). HRMS: calcd 418.162, found m/z 418.162 ± 2 ppm. Anal. Calcd for $C_{22}H_{26}O_8$ (418.44): C, 63.15; H, 6.26. Found: C, 63.20; H, 6.33.

3.8. Methyl 4,6-*O*-benzylidene-3-*O*-(4-hydroxy-but-2-ynyl)-2-*O*-propargyl-α-D-gluco-pyranoside (7b)

^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 1.86 (br s, 1H, OH), 2.47 (t, 1H, 17-H, $^4J_{17,15} = 2.39$), 3.44 (s, 3H, 14-H, OCH_3), 3.58 (t, 1H, 4-H, $^3J_{4,3} = 9.28$), 3.68 (dd, 1H, 2-H, $^3J_{2,1} = 3.77$, $^3J_{2,3} = 9.28$), 3.73 (t, 1H, 6-H_a, $^3J_{6a,5} = 10.07$), 3.83 (ddd, 1H, 5-H, $^3J_{5,4} = 9.40$, $^3J_{5,6a} = 10.07$, $^3J_{5,6b} = 4.58$), 3.98 (t, 1H, 3-H, $^3J_{3,2} = 9.28$), 4.23 (t, 2H, 21-$H_{a,b}$, $^5J_{21,18} = 1.81$), 4.29 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.58$, $^2J_{6a,6b} = 10.07$), 4.41–4.52 (m, 4H, 15-, 18-$H_{a,b}$), 4.88 (d, 1H, 1-H, $^3J_{1,2} = 3.77$), 5.53 (s, 1H, 7-H, Ph–CH), 7.35–7.50 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.28 (s, C-8), 129.05 (d, C-11), 128.24 (d, C-10, -12), 126.09 (d, C-9, -13), 101.44 (d, C-7), 99.21 (d, C-1), 84.56 (s, C-20), 82.11 (s, C-19), 81.83 (d, C-4), 79.86 (s, C-16), 78.22 (d, C-2), 77.72 (d, C-3), 74.87 (s, C-17), 69.02 (t, C-6), 62.21 (d, C-5), 60.28 (t, C-18), 59.33 (t, C-15), 55.28 (q, C-14), 51.12 (t, C-21). IR (diamond-ATR): $\tilde{\nu} = 3438\ cm^{-1}$ (br s), 3283 (m), 2922 (m), 2867 (m), 2243 (w), 2117 (w), 1453 (m), 1370 (s), 1079 (vs), 1048 (s),

750 and 698 (s). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 192 nm (4.21), 195 (4.11), 232 (3.44). GC–MS: m/z (%) = 388 (6) [M^+], 239 (8), 179 (17), 166 (23), 149 (33), 129 (100), 105 (45), 91 (39), 77 (21), 69 (45). HRMS: $C_{21}H_{24}O_7$: calcd 388.152, found m/z 388.155 ± 7 ppm.

3.9. Methyl 4,6-*O*-benzylidene-2-*O*-(4-hydroxy-but-2-ynyl)-3-*O*-propargyl-α-D-glucopyranoside (7c)

GC–MS: m/z (%) = 388 (1) [M^+], 239 (23), 179 (14), 166 (22), 149 (23), 125 (10), 105 (34), 99 (100), 91 (29), 77 (16), 69 (26). HRMS: $C_{21}H_{24}O_7$: calcd 388.152, found m/z 388.152 ± 1 ppm.

3.10. Methyl 4,6-*O*-benzylidene-2,3-di-*O*-(4-hydroxy-pent-2-ynyl)-α-D-gluco-pyranoside (8a)

According to general procedure (b), **8a** is prepared from 359 mg (1.0 mmol) of **2** in 7 mL of THF, 1.5 mL (2.4 mmol) of *n*-butyl lithium solution, and 118 mg (2.7 mmol) of dry acetaldehyde. The raw product is purified by silica gel column chromatography (12:1 diethylether–hexane). Fraction 1: 15 mg (4%) of **2**; fraction 2: 14 mg (3%) of **8b**; slightly yellow oil; fraction 3: 27 mg (7%) **8b** and **8c** (ratio 1:6), slightly yellow oil; fraction 4: 337 mg (75%) of a diastereomeric mixture of diols **8a**, viscous, slightly yellow oil. Compound **8a**: ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 1.33 (d, 3H, 24-H, $^3J_{24,23}$ = 6.60), 1.39 (d, 3H, 19-H, $^3J_{19,18}$ = 6.61), 2.44 (br s, 2H, 2OH), 3.37 (s, 3H, 14-H, OCH_3), 3.50 (t, 1H, 4-H, $^3J_{4,3}$ = 9.26), 3.57 (dd, 1H, 2-H, $^3J_{2,1}$ = 3.74, $^3J_{2,3}$ = 9.26), 3.66 (t, 1H, 6-H_a, $^3J_{6a,5}$ = 10.0), 3.75 (ddd, 1H, 5-H, $^3J_{5,4}$ = 9.34, $^3J_{5,6a}$ = 10.0, $^3J_{5,6b}$ = 4.48), 3.89 (t, 1H, 3-H, $^3J_{3,2}$ = 9.26), 4.21 (dd, 1H, 6-H_b, $^3J_{6b,5}$ = 4.48, $^2J_{6a,6b}$ = 10.0), 4.33–4.41 (m, 4H, 15-, 20-$H_{a,b}$), 4.43–4.53 (m, 2H, 18-, 23-H), 4.78 (d, 1H, 1-H, $^3J_{1,2}$ = 3.74), 5.46 (s, 1H, 7-H, Ph–CH), 7.27–7.42 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$, C* refers to the diasteromeric product): δ 137.20 (s, C-8), 129.03 (d, C-11), 128.22 (d, C-10, -12), 126.08 (d, C-9, -13), 101.41 (d, C-7), 98.99 (d, C-1), 98.96 (d, C*-1), 88.77 (s, C-16), 88.32 (s, C-21), 88.28 (s, C*-21), 81.76 (d, C-4), 81.73 (d, C*-4), 80.16 (s, C-22), 79.87 (s, C-17), 78.26 (d, C-2), 78.22 (d, C*-2), 77.57 (d, C-3), 77.52 (d, C*-3), 68.96 (t, C-6), 62.16 (d, C-5), 62.14 (d, C*-5), 60.33 (t, C-20), 60.28 (t, C*-20), 59.46 (t, C-15), 59.43 (t, C*-15), 58.13 (d, C-18, -23), 55.25 (q, C-14), 24.13 (q, C-19), 24.06 (q, C*-19), 23.96 (q, C-24), 23.94 (q, C*-24). IR (diamond-ATR): $\tilde{\nu}$ = 3408 cm^{-1} (br vs), 2980 (m), 2932 (m), 2867 (m), 1452 (m), 1369 (m), 1148 (m), 1074 and 1048 (vs), 751 and 699 (s). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 191 nm (4.43), 204 (3.98), 256 (2.49). EIMS (70 eV): m/z (%) = 446 (1) [M^+], 237 (14), 224 (6), 169 (6), 149 (55), 143 (100), 105 (67), 91 (62), 83 (38), 77 (39). HRMS: $C_{24}H_{30}O_8$ (446.49): calcd 446.194, found 446.192 ± 4 ppm. Anal. Calcd for $C_{24}H_{30}O_8$ (446.49): C, 64.56; H, 6.77. Found: C, 64.31; H, 6.94.

3.11. Methyl 4,6-*O*-benzylidene-3-*O*-(4-hydroxy-pent-2-ynyl)-2-*O*-propargyl-α-D-glucopyranoside (8b)

^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 1.39 (2 × d, 3H, 22-H, $^3J_{22,21}$ = 6.55), 1.90 (br s, 1H, OH), 2.46 (t, 1H, 17-H, $^4J_{17,15}$ = 2.38), 3.34 (s, 3H, 14-H, OCH_3), 3.58 (t, 1H, 4-H, $^3J_{4,3}$ = 9.26), 3.69 (dd, 1H, 2-H, $^3J_{2,1}$ = 3.76, $^3J_{2,3}$ = 9.26), 3.74 (t, 1H, 6-H_a, $^3J_{6a,5}$ = 10.05), 3.83 (ddd, 1H, 5-H, $^3J_{5,4}$ = 9.41, $^3J_{5,6a}$ = 10.05, $^3J_{5,6b}$ = 4.61), 3.98 (t, 1H, 3-H, $^3J_{3,2}$ = 9.26), 4.29 (dd, 1H, 6-H_b, $^3J_{6b,5}$ = 4.61, $^2J_{6a,6b}$ = 10.05), 4.39–4.52 (m, 5H, 15-, 18-$H_{a,b}$ and 21-H), 4.88 (d, 1H, 1-H, $^3J_{1,2}$ = 3.76), 5.53 (s, 1H, 7-H, Ph–CH), 7.35–7.50 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$; C* refers to the diastereomeric product): δ 137.26 (s, C-8), 129.05 (d, C-11), 128.24 (d, C-10, -12), 126.09 (d, C-9, -13), 101.42 (d, C-7), 99.20 (d, C-1), 88.20 (s, C-19), 88.16 (s, C*-19), 81.80 (d, C-4), 80.30 (s, C-20), 79.87 (s, C-16), 78.20 (d, C-2), 77.71 (d, C-3), 74.87 (d, C-17), 69.01 (t, C-6), 62.19 (d, C-5), 60.28 (t, C-18), 59.30 (t, C-15), 58.28 (d, C-21), 55.28 (q, C-14), 24.04 (q, C-22), 24.02 (q, C*-22). IR (diamond-ATR): $\tilde{\nu}$ = 3465 cm^{-1} (br vs), 3283 (m), 3066 and 3038 (w), 2980 (m), 2931 (m), 2867 (m), 1452 (m), 1370 (s), 1150 (s), 1080 and 1049 (vs), 751 and 698 (s). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 191 nm (4.28), 203 (3.98), 255 (2.74). GC–MS: m/z (%) = 402 (6) [M^+], 384 (4), 253 (4), 209 (5), 193 (12), 180 (6), 169 (5), 149 (39), 143 (78), 105 (50), 91 (36), 83 (26), 77 (22). HRMS: $C_{22}H_{26}O_7$: calcd 402.168, found m/z 402.165 ± 6 ppm.

3.12. Methyl 4,6-*O*-benzylidene-2-*O*-(4-hydroxy-pent-2-ynyl)-3-*O*-propargyl-α-D-glucopyranoside (8c)

GC–MS: m/z (%) = 402 (1) [M^+], 384 (0.8), 253 (18), 209 (4), 193 (9), 180 (15), 149 (25), 125 (8), 105 (34), 99 (100), 91 (24), 83 (12), 77 (15). HRMS: $C_{22}H_{26}O_7$: calcd 402.168, found m/z 402.165 ± 7 ppm.

3.13. Methyl 4,6-*O*-benzylidene-2,3-di-*O*-(4-hydroxy-4-methyl-pent-2-ynyl)-α-D-glucopyranoside (9a)

According to general procedure (a), **9a** is prepared from ethyl magnesium bromide in diethyl ether (147 mg, 1.1 mmol, 0.4 mL), and 180 mg (0.5 mmol) of **2** in 4 mL of THF with 103 mg (1.77 mmol) of acetone in 0.13 mL of ether at 50 °C for 2.5 h. The raw product is purified by silica gel column chromatography (8:1 hexane–ethanol). Fraction 1: 8.7 mg (5%) **2**; fraction 2: 48 mg (23%) **9b** and **9c** (1:1 ratio), yellow oil; fraction 3: 166 mg (70%) **9a**, slightly yellow oil. Compound **9a**:

^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 1.39 (s, 6H, 19-H, 19′-H), 1.45 (s, 3H, 24-H), 1.46 (s, 3H, 24′-H), 2.40 (br s, 2H, 2OH), 3.37 (s, 3H, 14-H, OCH_3), 3.51 (t, 1H, 4-H, $^3J_{4,3} = 9.26$), 3.57 (dd, 1H, 2-H, $^3J_{2,1} = 3.76$, $^3J_{2,3} = 9.26$), 3.66 (t, 1H, 6-H_a, $^3J_{6a,5} = 9.97$), 3.76 (ddd, 1H, 5-H, $^3J_{5,4} = 9.30$, $^3J_{5,6a} = 9.97$, $^3J_{5,6b} = 4.48$), 3.88 (t, 1H, 3-H, $^3J_{3,2} = 9.26$), 4.21 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.48$, $^2J_{6a,6b} = 9.97$), 4.31–4.42 (m, 4H, 15-, 20-$H_{a,b}$), 4.78 (d, 1H, 1-H, $^3J_{1,2} = 3.76$), 5.46 (s, 1H, 7-H, Ph–CH), 7.28–7.43 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.27 (s, C-8), 129.03 (d, C-11), 128.22 (d, C-10, -12), 126.12 (d, C-9, -13), 101.44 (d, C-7), 99.07 (d, C-1), 91.50 (s, C-22), 91.02 (s, C-17), 81.70 (d, C-4), 78.38 (d, C-2), 78.05 (s, C-16, -21), 77.49 (d, C-3), 68.98 (t, C-6), 65.02 (s, C-23), 64.93 (s, C-18), 62.21 (d, C-5), 60.32 (t, C-20), 59.40 (t, C-15), 55.27 (q, C-14), 31.28 (q, C-19), 31.20 (q, C-24), 31.13 (q, C-24′). IR (diamond-ATR): $\tilde{\nu} = 3384\ cm^{-1}$ (br s), 2980 (m), 2932 (m), 2865 (m), 2252 (w), 1454 (m), 1363 (s), 1167 (s), 1083 and 1042 (vs), 731 and 697 (s). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 192 nm (4.58), 202 (4.03), 226 (3.02), 256 (2.91). GC–MS: m/z (%) = 456 (0.7) [$M^+ - H_2O$], 265 (13), 252 (2), 157 (72), 149 (45), 105 (26), 97 (38), 91 (21), 77 (12), 43 (100).

3.14. Methyl 4,6-*O*-benzylidene-2,3-di-*O*-(5-hydroxy-pent-2-ynyl)-α-D-glucopyranoside (10a)

According to general procedure (b), **10a** is prepared from 359 mg (1.0 mmol) of **2** in 7 mL of THF, 1.5 mL (2.4 mmol) of *n*-butyl lithium solution, and 265 mg (4.1 mmol, 0.3 mL) of condensed (−27 °C) ethylene oxide with 2 mL of Me_2SO added as a co-solvent (temperature increase to 45 °C). The raw product is purified by silica gel chromatography (60:1 diethyl ether–ethanol): Fraction 1: 32 mg (9%) of **2**; fraction 2: 43 mg (11%) of **10c**, highly viscous oil; fraction 3: 25 mg (6%) **10b** and **c** (ratio 5:1, viscous oil); fraction 4: 205 mg (46%) of **10a**, highly viscous, slightly yellow oil. Compound **10a**: ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 2.41–2.50 (m, 4H, 19-, 24-$H_{a,b}$), 2.81 (br s, 2H, 2OH), 3.44 (s, 3H, 14-H, OCH_3), 3.58 (t, 1H, 4-H, $^3J_{4,3} = 9.38$), 3.64 (dd, 1H, 2-H, $^3J_{2,1} = 3.70$, $^3J_{2,3} = 9.38$), 3.67–3.76 (m, 5H, 6-H_a, and 18-, 23-$H_{a,b}$), 3.83 (ddd, 1H, 5-H, $^3J_{5,4} = 9.47$, $^3J_{5,6a} = 10.0$, $^3J_{5,6b} = 4.58$), 4.11 (t, 1H, 3-H, $^3J_{3,2} = 9.38$), 4.29 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.58$, $^2J_{6a,6b} = 10.0$), 4.34–4.46 (m, 4H, 15-, 20-$H_{a,b}$), 4.86 (d, 1H, 1-H, $^3J_{1,2} = 3.70$), 5.53 (s, 1H, 7-H, Ph–CH), 7.34–7.49 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.22 (s, C-8), 128.96 (d, C-11), 128.17 (d, C-10, -12), 126.07 (d, C-9, -13), 101.41 (d, C-7), 98.92 (d, C-1), 84.60 (s, C-22), 84.55 (s, C-17), 81.91 (d, C-4), 78.05 (s, C-21), 77.85 (d, C-2), 77.72 (s, C-16), 76.32 (d, C-3), 68.97 (t, C-6), 62.37 (d, C-5), 60.86 (t, C-23), 60.82 (t, C-18), 60.54 (t, C-20), 59.61 (t, C-15), 55.22 (q, C-14), 23.37 (t, C-24), 23.26 (t, C-19). IR (diamond-ATR): $\tilde{\nu} = 3424\ cm^{-1}$ (br s), 2914 (m), 2870 (m), 2228 (w), 1453 (m), 1370 (m), 1075 (vs), 1045 (s), 752 and 700 (s). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 191 nm (4.39), 204 (3.96), 255 (2.50). GC–MS: m/z (%) = 446 (0.2) [M^+], 237 (8), 224 (4), 169 (44), 149 (48), 143 (100), 105 (46), 91 (52), 83 (36), 77 (17). Anal. Calcd for $C_{24}H_{30}O_8$ (446.49): C, 64.56; H, 6.77. Found: C, 64.48; H, 6.99.

3.15. Methyl 4,6-*O*-benzylidene-2-*O*-(5-hydroxy-pent-2-ynyl)-3-*O*-propargyl-α-D-glucopyranoside (10c)

^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 2.04 (br s, 1H, OH), 2.44 (t, 1H, 22-H, $^4J_{22,20} = 2.40$), 2.47–2.52 (m, 2H, 19-$H_{a,b}$), 3.44 (s, 3H, 14-H, OCH_3), 3.60 (t, 1H, 4-H, $^3J_{4,3} = 9.27$), 3.67–3.76 (m, 4H, 2-H, 6-H_a and 18-$H_{a,b}$), 3.83 (ddd, 1H, 5-H, $^3J_{5,4} = 9.40$, $^3J_{5,6a} = 9.98$, $^3J_{5,6b} = 4.48$), 3.97 (t, 1H, 3-H, $^3J_{3,2} = 9.27$), 4.29 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.48$, $^2J_{6a,6b} = 9.98$), 4.39–4.49 (m, 4H, 15-, 20-$H_{a,b}$), 4.86 (d, 1H, 1-H, $^3J_{1,2} = 3.74$), 5.54 (s, 1H, 7-H, Ph–CH), 7.34–7.50 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.17 (s, C-8), 128.94 (d, C-11), 128.17 (d, C-10, -12), 126.03 (d, C-9, -13), 101.31 (d, C-7), 99.02 (d, C-1), 84.07 (s, C-17), 81.86 (d, C-4), 79.90 (s, C-21), 77.97 (s, C-16), 77.72 (d, C-2), 77.66 (d, C-3), 74.35 (d, C-22), 68.96 (t, C-6), 62.09 (d, C-5), 60.87 (t, C-18), 60.03 (t, C-20), 59.56 (t, C-15), 55.23 (q, C-14), 23.17 (t, C-19). IR (diamond-ATR): $\tilde{\nu} = 3472\ cm^{-1}$ (br s), 3284 (m), 3066 and 3037 (w), 2916 (m), 2868 (m), 2228 (w), 2118 (w), 1453 (m), 1370 (m), 1076 (vs), 1048 (vs), 752 and 698 (s). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 191 nm (4.50), 205 (4.09), 222 (3.39). GC–MS: m/z (%) = 402 (1) [M^+], 221 (16), 193 (12), 180 (20), 149 (27), 125 (26), 105 (44), 99 (100), 91 (32), 83 (16), 77 (17). HRMS: $C_{22}H_{26}O_7$: calcd 402.168, found m/z 402.166 ± 4 ppm.

3.16. Methyl 4,6-*O*-benzylidene-3-*O*-(5-hydroxy-pent-2-ynyl)-2-*O*-propargyl-α-D-glucopyranoside (10b)

GC–MS: m/z (%) = 402 (12) [M^+], 193 (12), 180 (20), 149 (51), 143 (100), 105 (70), 91 (76), 83 (36), 77 (30). HRMS: $C_{22}H_{26}O_7$: calcd 402.168, found m/z 402.170 ± 5 ppm.

3.17. Methyl 4,6-*O*-benzylidene-2,3-di-*O*-(4-oxo-but-2-ynyl)-α-D-glucopyranoside (11a)

According to general procedure (b), **11a** is prepared from 359 mg (1.0 mmol) of **2** in 7 mL of THF, 1.6 mL (2.56 mmol) of *n*-butyl lithium solution, and 0.5 mL (6.5 mmol) DMF. For work-up the reaction mixture is added to a cold mixture (5 °C) of 10% aqueous KH_2PO_4 solution and 20 mL of MTBE. After solvent removal the

raw product is purified by silica gel chromatography (3:2 hexane–ethyl acetate): Fraction 1: 5.6 mg (2%) of **2**; fraction 2: **11b** and **11c** (ratio 1:1), yellow oil; fraction 3: 124 mg (30%) of **11a**, slightly yellow oil. Compound **11a**: ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 3.46 (s, 3H, 14-H, OCH_3), 3.61 (t, 1H, 4-H, $^3J_{4,3} = 9.17$), 3.65 (dd, 1H, 2-H, $^3J_{2,1} = 3.78$, $^3J_{2,3} = 9.17$), 3.75 (t, 1H, 6-H_a, $^3J_{6a,5} = 10.06$), 3.84 (ddd, 1H, 5-H, $^3J_{5,4} = 9.37$, $^3J_{5,6a} = 10.06$, $^3J_{5,6b} = 4.54$), 4.00 (t, 1H, 3-H, $^3J_{3,2} = 9.17$), 4.30 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.54$, $^2J_{6a,6b} = 10.06$), 4.57–4.69 (m, 4H, 15-, 19-$H_{a,b}$), 4.88 (d, 1H, 1-H, $^3J_{1,2} = 3.78$), 5.54 (s, 1H, 7-H, Ph–CH), 7.35–7.48 (m, 5H, Ph), 9.12 (s, 1H, 22-H), 9.25 (s, 1H, 18-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 176.27 (d, C-22), 176.01 (d, C-18), 136.98 (s, C-8), 129.18 (d, C-11), 128.31 (d, C-10, -12), 126.04 (d, C-9, -13), 101.56 (d, C-7), 98.77 (d, C-1), 92.17 (s, C-20), 91.71 (s, C-16), 85.74 (s, C-17), 85.34 (s, C-21), 81.80 (d, C-4), 78.67 (d, C-2, -3), 68.92 (t, C-6), 62.06 (d, C-5), 59.83 (t, C-19), 59.29 (t, C-15), 55.34 (q, C-14). IR (diamond-ATR): $\tilde{\nu} = 2916\ cm^{-1}$ (m), 2866 (w), 2251 and 2197 (w), 1667 (s), 1452 (m), 1371 (m), 1078 and 1048 (vs), 750 and 698 (s). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 191 nm (4.44), 207 (4.14), 221 (4.00). EIMS (70 eV): m/z (%) = 414 (2) [M^+], 205 (6), 192 (8), 149 (36), 127 (14), 105 (100), 91 (60), 77 (72). HRMS: calcd 414.131, found m/z 414.129 ± 5 ppm. Anal. Calcd for $C_{22}H_{22}O_8$ (414.40): C, 63.76; H, 5.35. Found: C, 63.07; H, 5.62.

3.18. Methyl 4,6-*O*-benzylidene-2,3-di-*O*-(3-carboxy-prop-2-ynyl)-α-D-glucopyranoside (12)

According to general procedure (b), **12** is prepared from 180 mg (0.50 mmol) of **2** in 6 mL of THF, 0.76 mL (1.2 mmol) of *n*-butyl lithium solution, and excess dry ice. After work-up **12** is isolated as microcrystalline needles (89 mg, 40%), mp 150–152 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 3.40 (s, 3H, 14-H, OCH_3), 3.46–3.97 (m, 5H, 2-, 3-, 4-, 5-H and 6-H_a), 4.25 (br s, 1H, 6-H_b), 4.38–4.54 (m, 4H, 15-, 19-$H_{a,b}$), 4.86 (br s, 1H, 1-H), 5.50 (s, 1H, 7-H, Ph–CH), 7.34–7.43 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 156.35 (s, C-22), 156.22 (s, C-18), 137.60 (s, C-8), 129.28 (d, C-11), 128.49 (d, C-10, -12), 126.43 (d, C-9, -13), 101.72 (d, C-7), 98.78 (d, C-1), 82.11 (s, C-17, -21), 81.84 (d, C-4), 79.11 (d, C-2), 78.66 (d, C-3), 78.35 (s, C-16), 78.12 (s, C-20), 68.12 (t, C-6), 62.36 (d, C-5), 59.38 (t, C-19), 59.22 (t, C-15), 55.38 (q, C-14). IR (diamond-ATR): $\tilde{\nu} = 3480\ cm^{-1}$ (br s), 3069 and 3040 (w), 2919 (m), 2867 (m), 2241 (m), 1708 (s), 1452 (m), 1378 (s), 1080 and 1046 (vs), 750 and 698 (s). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 191 nm (4.47), 201 (4.24), 241 (3.27). MS (ESI-MS): m/z (%) = 469 (100) [M+Na]$^+$, 425 (17). HRMS: $C_{22}H_{22}O_{10}$+Na: calcd 469.111, found m/z 469.112 ± 2 ppm.

3.19. Methyl 4,6-*O*-benzylidene-2,3-di-*O*-(3-methoxy-carbonyl-prop-2-ynyl)-α-D-glucopyranoside (13a)

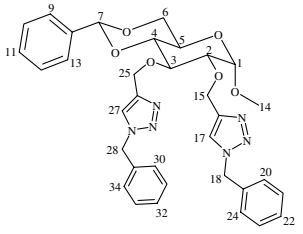
According to general procedure (b), **13a** is prepared from 359 mg (1.0 mmol) of **2** in 7 mL of THF, 1.4 mL (2.24 mmol) of *n*-butyl lithium solution, and 428 mg (4.6 mmol, 0.35 mL) of methyl chloroformate in 1.5 mL THF. After work-up the residue is separated by silica gel chromatography (2:1 hexane–ethyl acetate): Fraction 1: 38.4 mg (11%) of **2**; fraction 2: 24.0 mg (6%) **13b** and **c** (ratio 1:1); fraction 3: 253 mg (53%) of 13a, colorless oil. Compound **13a**: ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 3.45 (s, 3H, 14-H, OCH_3), 3.58–3.65 (m, 2H, 2-, 4-H), 3.68–3.86 (m, 8H, 5-H, 6-H_a, 19- and 24-H), 3.96 (t, 1H, 3-H, $^3J_{3,2} = 9.18$), 4.29 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.43$, $^2J_{6a,6b} = 9.84$), 4.48–4.62 (m, 4H, 15-, 20-$H_{a,b}$), 4.89 (d, 1H, 1-H, $^3J_{1,2} = 3.78$), 5.53 (s, 1H, 7-H, Ph–CH), 7.35–7.48 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 153.53 (s, C-23), 153.41 (s, C-18), 137.02 (s, C-8), 129.06 (d, C-11), 128.25 (d, C-10, -12), 126.04 (d, C-9, -13), 101.46 (d, C-7), 98.94 (d, C-1), 83.71 (s, C-17), 83.59 (s, C-22), 81.81 (d, C-4), 78.78 (s, C-16), 78.59 (s, C-21), 78.05 (d, C-2), 77.44 (d, C-3), 68.94 (t, C-6), 61.98 (d, C-5), 59.70 (t, C-20), 59.25 (t, C-15), 55.34 (q, C-14), 52.81 (q, C-19), 52.70 (q, C-24). IR (diamond-ATR): $\tilde{\nu} = 2954\ cm^{-1}$ (m), 2919 (m), 2865 (w), 2241 (m), 1713 (s), 1436 (s), 1372 (m), 1249 (vs), 1087 and 1048 (vs), 749 and 699 (s). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 192 nm (4.39), 204 (4.24). GC–MS: m/z (%) = 474 (8) [M^+], 459 (5), 443 (7), 317 (6), 265 (10), 252 (11), 223 (21), 157 (32), 149 (63), 105 (100), 91 (58), 77 (27). Anal. Calcd for $C_{24}H_{26}O_{10}$ (474.46): C, 60.66; H, 5.52. Found: C, 60.53; H, 5.77.

3.20. Methyl 4,6-*O*-benzylidene-2,3-di-*O*-(4-diethyl-amino-but-2-ynyl)-α-D-glucopyranoside (14)

In 1.5 mL of anhydrous Me_2SO 180 mg (0.50 mmol) of **2**, 99 mg (1.34 mmol) of diethylamine, 0.4 mL aqueous formaldehyde solution (35%) and 5 mg (0.026 mmol) of copper(I) iodide are dissolved. The solution is stirred for 48 h at 30 °C, and the reaction terminated by addition of 3 mL of a 2 M sodium hydroxide solution. The product mixture is extracted thoroughly with ether, the combined organic phases are dried with magnesium sulfate, and the solvent is removed under diminished pressure. Silica gel column chromatography (20:1:1.05 diethyl ether–pentane–ethanol–Et_3N) provides 230 mg (87%) of **14**, slightly yellow, viscous oil. ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 1.03 (t, 6H, 20-H, $^3J_{20,19} = 7.18$), 1.07 (t, 6H, 26-H, $^3J_{26,25} = 7.18$), 2.48–2.58 (m, 8H, 19-$H_{a,b}$ and 25-$H_{a,b}$), 3.42 (t, 2H, 18-Ha,b, $^5J_{18,15} = 1.88$), 3.44 (s, 3H, 14-H, OCH_3), 3.46 (t, 2H, 24-Ha,b, $^5J_{24,21} = 1.80$), 3.58 (t, 1H, 4-H, $^3J_{4,3} = 9.26$), 3.71 (dd, 1H, 2-H, $^3J_{2,1} = 3.76$,

$^3J_{2,3} = 9.26$), 3.74 (t, 1H, 6-H_a, $^3J_{6a,5} = 9.85$), 3.83 (ddd, 1H, 5-H, $^3J_{5,4} = 9.25$, $^3J_{5,6a} = 9.85$, $^3J_{5,6b} = 4.42$), 3.98 (t, 1H, 3-H, $^3J_{3,2} = 9.26$), 4.29 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.42$, $^2J_{6a,6b} = 9.85$), 4.39–4.53 (m, 4H, 15-, 21-$H_{a,b}$), 4.85 (d, 1H, 1-H, $^3J_{1,2} = 3.76$), 5.53 (s, 1H, 7-H, Ph–CH), 7.34–7.50 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.26 (s, C-8), 128.90 (d, C-11), 128.13 (d, C-10, -12), 126.02 (d, C-9, -13), 101.29 (d, C-7), 99.34 (d, C-1), 81.87 (d, C-4), 81.52 (s, C-22), 80.96 (s, C-16), 80.79 (s, C-17), 80.62 (s, C-23), 77.80 (d, C-2), 77.58 (d, C-3), 68.99 (t, C-6), 62.16 (d, C-5), 60.37 (t, C-21), 59.54 (t, C-15), 55.21 (q, C-14), 47.19 (t, C-25), 47.09 (t, C-19), 40.91 (t, C-18), 40.86 (t, C-24), 12.52 (q, C-20), 12.50 (q, C-26). IR (diamond-ATR): $\tilde{\nu} = 2970\ cm^{-1}$ (s), 2932 (m), 2870 (m), 1454 (m), 1373 (s), 1322 (m), 1080 and 1051 (vs), 750 and 698 (s). UV (acetonitrile): λ_{max} ($\lg \varepsilon$) = 191 nm (4.47), 202 (4.17), 255 (2.33). EIMS (70 eV): m/z (%) = 528 (4) [M^+], 499 (1), 456 (2), 442 (4), 149 (14), 125 (72), 110 (50), 105 (39), 91 (38), 77 (28), 56 (100), 53 (57). HRMS: calcd 528.319, found m/z 528.319 ± 1 ppm. Anal. Calcd for $C_{30}H_{44}N_2O_6$ (528.68): C, 68.15; H, 8.39; N, 5.30. Found: C, 68.15; H, 8.47; N, 5.42.

3.21. (Bis) *N*-benzyl triazole 15a of methyl 4,6-*O*-benzylidene-2,3-di-*O*-propargyl-α-D-glucopyranoside (2)



15a

To a solution of 359 mg (1.0 mmol) of **2** in 10 mL of a Me_2SO–water mixture (4:1) is added 270 mg (2.03 mmol) of benzyl azide. A freshly prepared solution of 80 mg (0.4 mmol) sodium L-ascorbate in 0.4 mL of water and 25 mg (0.1 mmol) of copper(II) sulfate pentahydrate is added, and the mixture is stirred for 4 days at room temp. The reaction mixture is diluted with 30 mL of water and cooled with an ice-water bath: a white-brown precipitate is formed, which is removed by filtration and washed twice with 20 mL portions of cold water, and dried under vacuum. Silica gel column chromatography with diethyl ether–pentane–ethanol (10:0.5:0.5) provides four fractions: Fraction 1: 12 mg (3%) of **2**; fraction 2: 12 mg (2%) of **15b**; fraction 3: 49 mg (10%) of **15c**; fraction 4: 442 mg (71%) of **15a**, colorless needles, mp 124–126 °C. Compound **15a**: ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 3.35 (s, 3H, 14-H, OCH_3), 3.54 (t, 1H, 4-H, $^3J_{4,3} = 9.27$), 3.60 (dd, 1H, 2-H, $^3J_{2,1} = 3.68$, $^3J_{2,3} = 9.27$), 3.70 (t, 1H, 6-H_a, $^3J_{6a,5} = 10.0$), 3.79 (ddd, 1H, 5-H, $^3J_{5,4} = 9.33$, $^3J_{5,6a} = 10.0$, $^3J_{5,6b} = 4.49$), 3.92 (t, 1H, 3-H, $^3J_{3,2} = 9.27$), 4.26 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.49$, $^2J_{6a,6b} = 10.0$), 4.77 (d, 1H, 1-H, $^3J_{1,2} = 3.68$), 4.80 (s, 2H, 15-$H_{a,b}$), 4.86–4.96 (m, 2H, 25-$H_{a,b}$), 5.30–5.38 (m, 2H, 28-$H_{a,b}$), 5.42–5.53 (m, 3H, 7-H and 18-$H_{a,b}$), 7.14–7.47 (m, 15H, Ph. H), 7.52 (s, 1H, 27-H), 7.67 (s, 1H, 17-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 145.92 (s, C-26), 145.18 (s, C-16), 137.31 (s, C-8), 134.76 (s, C-19), 134.68 (s, C-29), 129.01 (2 × d, C-21, -23 and C-11), 128.92 (d, C-31, -33), 128.63 (d, C-22), 128.50 (d, C-32), 128.23 (d, C-10, -12), 128.14 (d, C-20, -24), 127.92 (d, C-30, -34), 126.07 (d, C-9, -13), 123.22 (d, C-17), 122.70 (d, C-27), 101.42 (d, C-7), 98.57 (d, C-1), 81.76 (d, C-4), 79.30 (d, C-2), 78.23 (d, C-3), 68.99 (t, C-6), 66.51 (t, C-25), 64.89 (t, C-15), 62.19 (d, C-5), 55.17 (q, C-14), 54.06 (t, C-18), 53.86 (t, C-28). IR (diamond-ATR): $\tilde{\nu} = 3068$ and $3033\ cm^{-1}$ (w), 2978 (w), 2934 (m), 2873 (m), 1496 (m), 1454 (s), 1433 (s), 1366 (s), 1322 (s), 1078 (vs), 1052 (vs), 754 (s), 699 (s). UV (acetonitrile): λ_{max} ($\lg \varepsilon$) = 193 nm (4.88), 205 (4.51), 257 (2.83). EIMS (70 eV): m/z (%) = 624 (1) [M^+], 415 (4), 258 (5), 173 (28), 144 (28), 105 (12), 91 (100), 77 (10). Anal. Calcd for $C_{34}H_{36}N_6O_6$ (624.69): C, 65.37; H, 5.81; N, 13.45. Found: C, 65.43; H, 5.88; N, 13.48.

3.22. Mono *N*-benzyl triazole 15b of methyl 4,6-*O*-benzylidene-2,3-di-*O*-propargyl-α-D-glucopyranoside (2)

^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 2.39 (t, 1H, 17-H, $^4J_{17,15} = 2.4$), 3.43 (s, 3H, 14-H, OCH_3), 3.59 (t, 1H, 4-H, $^3J_{4,3} = 9.27$), 3.69 (dd, 1H, 2-H, $^3J_{2,1} = 3.69$, $^3J_{2,3} = 9.27$), 3.73 (t, 1H, 6-H_a, $^3J_{6a,5} = 10.04$), 3.82 (ddd, 1H, 5-H, $^3J_{5,4} = 9.37$, $^3J_{5,6a} = 10.04$, $^3J_{5,6b} = 4.54$), 3.96 (t, 1H, 3-H, $^3J_{3,2} = 9.27$), 4.29 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.54$, $^2J_{6a,6b} = 10.04$), 4.33–4.34 (m, 2H, 15-$H_{a,b}$), 4.87 (d, 1H, 1-H, $^3J_{1,2} = 3.69$), 4.91–5.01 (m, 2H, 18-$H_{a,b}$), 5.34–5.41 (m, 2H, 21-$H_{a,b}$), 5.52 (s, 1H, 7-H, Ph–CH), 7.14–7.47 (m, 11H, Ph. Ha. 20-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 146.19 (s, C-19), 137.31 (s, C-8), 134.77 (s, C-22), 129.06 (d, C-11), 128.99 (d, C-24, -26), 128.59 (d, C-25), 128.30 (d, C-10, -12), 127.97 (d, C-23, -27), 126.13 (d, C-9, -13), 122.38 (d, C-20), 101.51 (d, C-7), 99.15 (d, C-1), 81.89 (d, C-4), 79.84 (s, C-16), 78.56 (d, C-2, -3), 74.80 (d, C-17), 69.04 (t, C-6), 66.64 (t, C-18), 62.26 (d, C-5), 59.19 (t, C-15), 55.28 (q, C-14), 53.97 (t, C-21). IR (diamond-ATR): $\tilde{\nu} = 3287\ cm^{-1}$ (m), 3066 and 3035 (w), 2931 (m), 2867 (m), 2249 (w), 2116 (w), 1497 (m), 1455 (s), 1372 (s), 1081 (vs), 1048 (vs), 727 and 698 (s). UV (acetonitrile): λ_{max} ($\lg \varepsilon$) = 192 nm (4.76), 204 (4.34). EIMS (70 eV): m/z (%) = 491 (0.6) [M^+], 452 (2), 172 (9), 149 (10), 144 (28), 105 (33), 91 (100), 77 (21).

HRMS: $C_{27}H_{29}N_3O_6$: calcd 490.198, found m/z 490.197 ± 2 ppm.

3.23. Mono *N*-benzyl triazole 15c of methyl 4,6-*O*-benzylidene-2,3-di-*O*-propargyl-α-D-glucopyranoside (2)

^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 2.32 (t, 1H, 27-H, $^4J_{27,25} = 2.41$), 3.34 (s, 3H, 14-H, OCH_3), 3.55 (t, 1H, 4-H, $^3J_{4,3} = 9.26$), 3.60 (dd, 1H, 2-H, $^3J_{2,1} = 3.73$, $^3J_{2,3} = 9.26$), 3.70 (t, 1H, 6-H_a, $^3J_{6a,5} = 9.95$), 3.79 (ddd, 1H, 5-H, $^3J_{5,4} = 9.27$, $^3J_{5,6a} = 9.95$, $^3J_{5,6b} = 4.46$), 3.94 (t, 1H, 3-H, $^3J_{3,2} = 9.26$), 4.26 (dd, 1H, 6-H_b, $^3J_{6b,5} = 4.46$, $^2J_{6a,6b} = 9.95$), 4.35–4.47 (m, 2H, 25-$H_{a,b}$), 4.75 (d, 1H, 1-H, $^3J_{1,2} = 3.73$), 4.85–4.92 (m, 2H, 15-$H_{a,b}$), 5.46–5.56 (m, 3H, 7- and 18-$H_{a,b}$), 7.26–7.49 (m, 10H, Ph. H), 7.57 (s, 1H, 17-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 145.54 (s, C-16), 137.25 (s, C-8), 134.57 (s, C-19), 129.07 (d, C-21, -23), 128.92 (d, C-11), 128.73 (d, C-22), 128.16 (d, C-10, -12), 128.14 (d, C-20, -24), 126.03 (d, C-9, -13), 122.83 (d, C-17), 101.29 (d, C-7), 98.73 (d, C-1), 81.90 (d, C-4), 80.17 (s, C-26), 78.94 (d, C-2), 77.66 (d, C-3), 74.18 (d, C-27), 68.98 (t, C-6), 65.19 (t, C-15), 62.07 (d, C-5), 59.97 (t, C-25), 55.16 (q, C-14), 54.38 (t, C-18). IR (diamond-ATR): $\tilde{\nu} = 3286\ cm^{-1}$ (m), 3067 and 3035 (w), 2931 (m), 2867 (m), 2248 (w), 2118 (w), 1497 (m), 1455 (s), 1372 (s), 1080 (vs), 1049 (vs), 727 (s), 698 (s). UV (acetonitrile): λ_{max} (lg ε) = 192 nm (4.78), 204 (4.33). EIMS (70 eV): m/z (%) = 491 (1) [M^+], 258 (5), 172 (5), 149 (12), 144 (28), 125 (3), 105 (21), 99 (13), 91 (100), 77 (15). HRMS: $C_{27}H_{29}N_3O_6$: calcd 491.205, found m/z 491.202 ± 6 ppm.

3.24. Methyl 2,3-di-*O*-propargyl-α-D-glucopyranoside (16)

A solution of 300 mg (0.84 mmol) of methyl-4,6-*O*-benzyliden-2,3-di-*O*-propargyl-α-D-glucopyranoside (**2**) in 16 mL of acetic acid (70%) was kept at room temp. for 16 h. Water (40 mL) was added to the reaction mixture, and the hydrolyzate was carefully extracted with CH_2Cl_2. After separation of the aqueous phase this was saturated with sodium chloride and extracted several times with CH_2Cl_2. The combined organic phases were dried (sodium sulfate), the solvent was evaporated, and the remaining oily residue purified by column chromatography (silica gel, diethyl ether–hexane = 24:1): 218 mg (96%) of **16** as a colorless, viscous oil. ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 2.42 (br s, 2H, 2OH), 2.48 (t, 1H, 13-H, $^4J_{13,11} = 2.4$), 2.51 (t, 1H, 10-H, $^4J_{10,8} = 2.4$), 3.44 (s, 3H, 17-H, OCH_3), 3.56–3.89 (m, 6H, 2-, 3-, 4-, 5-H and 6-$H_{a,b}$), 4.34 (dd, 2H, 8-$H_{a,b}$, $^4J_{8,10} = 2.4$), 4.37–4.54 (2 dd, 2H, 11-$H_{a,b}$, $^4J_{11,13} = 2.4$, $^2J_{11a,11b} = 15.8$), 4.92 (d, 1H, 1-H, $^3J_{1,2} = 3.6$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 97.93 (d, C-1), 80.66 (d, C-3), 80.47 (s, C-12), 79.52 (s, C-9), 79.22 (d, C-2), 75.06 (d, C-10), 74.87 (d, C-13), 70.76 (d, C-5), 69.96 (d, C-4), 62.28 (t, C-6), 60.28 (t, C-11), 58.34 (t, C-8), 55.17 (q, C-7). IR (diamond-ATR): $\tilde{\nu} = 3426\ cm^{-1}$ (br s), 3285 (s), 2928 (m), 2842 (w), 2118 (m), 1448 (m), 1357 (m), 1156 (m), 1088 (vs), 1046 (vs). UV (acetonitrile): λ_{max} (lg ε) = 191 nm (3.14), 235 (2.58). EIMS (70 eV): m/z (%) = 270 (26) [M^+], 239 (2), 136 (38), 125 (10), 111 (50), 99 (100), 85 (82), 73 (63), 61 (48), 57 (79). HRMS: $C_{13}H_{18}O_6$: calcd 270.110, found m/z 270.110 ± 2 ppm. Anal. Calcd for $C_{13}H_{18}O_6$ (270.28): C, 57.77; H, 6.71. Found: C, 56.57; H, 6.62.

3.25. Methyl 2,3-di-*O*-(prop-2-ynyl-3-*d*)-α-D-glucopyranoside (17a)[17]

According to general procedure (b), 205 mg (0.76 mmol) of **16** in 7 mL of THF was metalated with 2.2 mL *n*-butyl lithium solution (3.49 mmol, 1.6 M in hexane), and the reaction mixture quenched with 1 mL (55.3 mmol) of deuterium oxide. After work-up (see above) 201 mg (97%) of **17a** was isolated as a viscous oil. ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 2.42 (br s, 2H, 2OH), 3.37 (s, 3H, 7-H, OCH_3), 3.47–3.82 (m, 6H, 2-, 3-, 4-, 5-H and 6-$H_{a,b}$), 4.22–4.27 (m, 2H, 8-$H_{a,b}$) 4.31–4.46 (dd, 2H, 11-$H_{a,b}$, $^2J_{11a,11b} = 15.8$), 4.85 (d, 1H, 1-H, $^3J_{1,2} = 3.7$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 97.92 (d, C-1), 80.65 (d, C-3), 80.00 (s, C-12), 79.18 (d, C-2), 79.02 (s, C-9), 74.59 (d, C-10), 74.41 (d, C-13), 70.79 (d, C-5), 69.85 (d, C-4), 62.14 (t, C-6), 60.24 (t, C-11), 58.35 (t, C-8), 55.14 (q, C-7). IR (diamond-ATR): $\tilde{\nu} = 3421\ cm^{-1}$ (br vs), 2927 (m), 2869 (m), 2838 (w), 2576 (m), 1997 (m), 1449 (m), 1356 (m), 1155 (m), 1088 (vs), 1045 (vs). UV (acetonitrile): λ_{max} (lg ε) = 193 nm (3.16), 238 (2.68). EIMS (70 eV): m/z (%) = 272 (0.6) [M^+], 138 (53), 126 (10), 112 (50), 100 (100), 73 (44), 61 (32), 57 (28). HRMS: $C_{13}H_{16}D_2O_6$: calcd 272.123, found m/z 272.122 ± 1 ppm.

3.26. Methyl 2,3-di-*O*-(3-trimethylsilyl-prop-2-ynyl)-α-D-glucopyranoside (17b)

According to general procedure (b), 193 mg (0.72 mmol) of **16** in 5 mL of THF was metalated with 2.3 mL of *n*-butyl lithium solution (3.52 mmol, 1.6 M in hexane). After quenching with trimethylsilyl chloride (0.65 mL, 5.12 mmol) and work-up, three fractions were obtained: Fraction 1 (47 mg, 12%) of **17c** as a viscous oil; fraction 2 (97 mg, 33%) of **17b**, and fraction 3 (5 mg, 2%) of **17d**, viscous oil, as a mixture of two positional isomers. Fraction 2: colorless solid, mp 113–114 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 0.00 (2s, 18 H, 11-, 15-H), 1.91 (br s, 2H, 2OH), 3.27 (s, 3H, 7-H, OCH_3), 3.31–3.73 (m, 6H, 2-, 3-, 4-, 5-H and 6-$H_{a,b}$), 4.06–4.15 (dd, 2H, 8-$H_{a,b}$, $^2J_{8a,8b} = 16.2$), 4.16–4.34 (dd, 2H,

12-$H_{a,b}$, $^2J_{12a,12b} = 16.2$), 4.77 (d, 1H, 1-H, $^3J_{1,2} = 3.6$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 102.61 (s, C-13), 101.54 (s, C-9), 98.14 (d, C-1), 92.01 (s, C-14), 91.92 (s, C-10), 81.07 (d, C-3), 79.74 (d, C-2), 70.78 (d, C-5), 70.15 (d, C-4), 62.65 (t, C-6), 61.16 (t, C-12), 59.38 (t, C-8), 55.20 (q, C-7), −0.23 (q, C-11), −0.28 (q, C-15). IR (diamond-ATR): $\tilde{\nu} = 3463\ cm^{-1}$ (br vs), 2961 (m), 2912 (m), 2848 (w), 2189, 2172 (w), 1345 (m), 1150 (m), 1088 (s), 1047 (vs). UV (acetonitrile): λ_{max} ($lg\,\varepsilon$) = 191 nm (3.49), 195 (3.40), 205 (3.14), 218 (2.59), 224 (2.42). EIMS (70 eV): m/z (%) = 414 (7) [M^+], 341 (1), 303 (2), 293 (6), 280 (6), 183 (21), 171 (39), 111 (61), 83 (58), 73 (100). Anal. Calcd for $C_{19}H_{34}O_6Si_2$ (414.64): C, 55.04; H, 8.26. Found: C, 54.91; H, 8.33.

3.26.1. Side products: Mixture of methyl 2-*O*-propargyl-3-*O*-(3-trimethylsilyl-prop-2-ynyl)-α-D-glucopyranoside and methyl 3-*O*-propargyl-2-*O*-(3-trimethylsilyl-prop-2-ynyl)-α-D-glucopyranoside (17d). ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 0.00 (2s, 18H, 11-, 14′-H), 1.62 (br s, 4H, 4 OH), 2.28 and 2.31 (2t, 2H, 14-H and 10′-H, $^4J_{14,12} = 2.4$, $^4J_{10',8'} = 2.4$), 3.26 (s, 6H, 7-, 7′-H, OCH_3), 3.32–3.71 (m, 12H, 2-, 2′-, 3-, 3′-, 4-, 4′-, 5-, 5′-H and 6-, 6′-$H_{a,b}$), 4.05–4.34 (m, 8H, 8-, 12-$H_{a,b}$, and 8′-, 11′-$H_{a,b}$), 4.74 (d, 2H, 1-, 1′-H, $^3J_{1,2} = 3.5$, $^3J_{1',2'} = 3.6$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 101.43 (s, C-9), 98.07 (d, C-1), 98.00 (d, C-1′), 92.02 (s, C-10), 81.07 (d, C-3), 80.57 (d, C-3, -13), 79.82 (d, C-2), 75.00 (d, C-10′), 74.85 (d, C-14), 70.66 (d, C-5), 70.15 (d, C-4′), 70.07 (d, C-4), 62.50 (t, C-6), 60.26 (t, C-12), 59.31 (t, C-8), 55.20 (q, C-7), −0.24 (q, C-11), −0.28 (q, C-14′). IR (diamond-ATR): $\tilde{\nu} = 3403\ cm^{-1}$ (br vs), 3291 (m), 2958 (m), 2928 (m), 2853 (w), 2177 (w), 2118 (w), 1450 (m), 1358 (m), 1153 (m), 1088 (vs), 1045 (vs).

3.26.2. Methyl 4,6-di-*O*-(trimethylsilyl)-2,3-di-*O*-(3-trimethylsilyl-prop-2-ynyl)-α-D-glucopyranoside (17c). ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 0.00 (s, s, 18H, 11-, 16-H), 0.02 (s, 9H, 17-H), 0.03 (s, 9H, 15-H), 3.26 (s, 3H, 7-H, OCH_3), 3.27–3.75 (m, 6H, 2-, 3-, 4-, 5-H and 6-$H_{a,b}$), 4.12–4.34 (m, 4H, 8-, 12-$H_{a,b}$), 4.63 (d, 1H, 1-H, $^3J_{1,2} = 3.6$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 102.87 (s, C-13, -13), 97.70 (d, C-1), 91.78 (s, C-10, -14), 80.12 (d, C-3), 79.31 (d, C-2), 70.68 (d, C-5), 70.31 (d, C-4), 62.92 (t, C-6), 60.90 (t, C-8, -12), 55.42 (q, C-7), 0.06 (q, C-16), −0.06 (q, C-11), −0.26 (q, C-15), −1.93 (q, C-17). IR (diamond-ATR): $\tilde{\nu} = 2960\ cm^{-1}$ (m), 2905 (m), 2178 (w), 1450 (m), 1366 (m), 1150 (m), 1040 (vs). UV (acetonitrile): λ_{max} ($lg\,\varepsilon$) = 193 nm (3.95), 200 (3.93), 208 (4.01), 216 (4.06), 224 (3.90). GC–MS: m/z (%) = 558 (62) [M^+], 271 (68), 255 (11), 197 (8), 171 (8), 155 (56), 111 (27), 83 (23), 73 (100). HRMS: $C_{25}H_{50}O_6Si_4$: calcd 558.268, found m/z 558.270 ± 4 ppm.

3.27. Methyl 2,3-di-*O*-(4-hydroxy-4-methyl-pent-2-ynyl)-α-D-glucopyranoside (17e)

According to general procedure (b), 295 mg (1.09 mmol) of **16** in 6 mL of THF was metalated with 7.0 mL of *n*-butyl lithium solution (11.2 mmol, 1.6 M in hexane). After quenching with acetone (1.2 mL, 16.34 mmol) and work-up (see above), three fractions were obtained: fraction 1: 29 mg (10%) of substrate **16**, fraction 2: **17f** (108 mg, 30%) as a mixture of positional isomers, fraction 3 (54 mg, 13%) of **17e**: viscous oil. ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 1.50 (s, 6H, 17-, 19′-H), 1.51 (s, 6H, 12-, 12′-H), 3.26 (br s, 2H, 2OH), 3.44 (s, 3H, 7-H, OCH_3), 3.59–3.90 (m, 6H, 2-, 3-, 4-, 5-H and 6-$H_{a,b}$), 4.04 (br s, 2H, 2OH), 4.29–4.58 (m, 4H, 8-, 13-$H_{a,b}$), 4.90 (d, 1H, 1-H, $^3J_{1,2} = 3.5$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 97.88 (d, C-1), 91.80 (s, C-10), 91.71 (s, C-15), 80.46 (d, C-3), 78.84 (d, C-2), 78.47 (s, C-14), 77.55 (s, C-9), 71.01 (d, C-5), 69.40 (d, C-4), 64.80 (s, C-16), 64.77 (s, C-11), 61.68 (t, C-6), 60.59 (t, C-13), 58.50 (t, C-8), 55.25 (q, C-7), 31.23 (q, C-12), 31.17 (q, C-17, -17′), 31.12 (q, C-12′). IR (diamond-ATR): $\tilde{\nu} = 3379\ cm^{-1}$ (br vs), 2981 (m), 2934 (m), 1456 (m), 1361 (s), 1168 (s), 1090, 1065 (vs), 1038 (vs). UV (acetonitrile): λ_{max} ($lg\,\varepsilon$) = 193 nm (3.44), 197 (3.20). GC–MS: m/z (%) = 368 (3) [$M^+ - H_2O$], 265 (7), 252 (7) , 169 (17), 157 (57), 97 (59), 80 (74), 43 (100). HRMS: $C_{19}H_{30}O_8$–H_2O=$C_{19}H_{28}O_7$: calcd 368.183, found m/z 368.181 ± 6 ppm. Anal. Calcd for $C_{19}H_{30}O_8$ (386.44): C, 59.05; H, 7.82; Found: C, 55.75; H, 7.66.

3.27.1. Side products: Mixture of methyl 3-*O*-(4-hydroxy-4-methyl-pent-2-ynyl)-2-*O*-propargyl-α-D-glucopyranoside and methyl 2-*O*-(4-hydroxy-4-methyl-pent-2-ynyl)-3-*O*-propargyl-α-D-glucopyranoside (17f). ^{1}H NMR (400.1 MHz, $CDCl_3$, J in Hz): δ 1.50–1.51 (s, s, 12H, 12-, 12″-H and 15′-, 15″-H), 2.49, 2.52 (t, t, 2H, 15-, 10′-H, $^4J_{15,13} = 2.4$, $^4J_{10',8'} = 2.4$), 2.88 (br s, 6H, 6 OH), 3.44 (s, s, 6H, 7-, 7′-H, OCH_3), 3.54–3.86 (m, 12H, 2-, 2′-, 3-, 3′-, 4-, 4′-, 5-, 5′-H and 6-, 6′-$H_{a,b}$), 4.28–4.56 (m, 8H, 8-, 13-$H_{a,b}$ and 8′-, 11′-$H_{a,b}$), 4.90–4.92 (m, 2H, 1-, 1′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 97.99 (d, C-1′), 97.95 (d, C-1), 91.71 (s, C-10), 91.67 (s, C-13′), 80.61 (d, C-3), 80.51 (d, C-3′), 79.63 (s, C-9′, -14), 79.20 (d, C-2′), 79.04 (d, C-2), 78.63 (s, C-12′), 77.66 (s, C-9), 75.05 (d, C-10′), 74.92 (d, C-15), 70.93 (d, C-5′), 70.88 (d, C-5), 69.76 (d, C-4′), 69.64 (d, C-4), 64.88 (s, C-11, -14′), 62.05 (t, C-6), 61.93 (t, C-6′), 60.48 (t, C-11′), 60.31 (t, C-13), 58.60 (t, C-8), 58.36 (t, C-8′), 55.19 (q, C-7, -7′), 31.21 (q, C-12, -12″), 31.16 (q, C-15′, -15″). IR (diamond-ATR): $\tilde{\nu} = 3392\ cm^{-1}$ (br s), 3289 (s), 2981 (m), 2932 (m), 2117 (w), 1451 (m), 1362 (s), 1158 (s), 1091 (vs), 1053 (vs). UV (acetonitrile): λ_{max} ($lg\,\varepsilon$) = 191 nm (3.46), 208 (3.28).

3.28. Methyl 2,3-di-*O*-(3-carboxy-prop-2-ynyl)-α-D-glucopyranoside (17g)

According to general procedure (b), 202 mg (0.75 mmol) of **16** in 5 mL of THF was metalated with 2.9 mL of *n*-butyl lithium solution (4.64 mmol, 1.6 M in hexane). Gaseous carbon dioxide was passed through the acetylide solution for 1 h, and the reaction mixture worked-up as described above. After solvent removal 87 mg (33%) of **17g** was isolated, colorless crystals, mp 131–133 °C. ^{1}H NMR (400.1 MHz, CD_3COCD_3, *J* in Hz): δ 3.37 (s, 3H, 7-H, OCH_3), 3.39–3.80 (m, 6H, 2-, 3-, 4-, 5-H and 6-$H_{a,b}$), 4.44–4.63 (m, 4H, 8-, 12-$H_{a,b}$), 4.91 (br s, 1H, 1-H, $^3J_{1,2} = 3.5$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 153.97 (s, C-15), 153.82 (s, C-11), 98.50 (d, C-1), 84.93 (s, C-14), 84.46 (s, C-10), 82.67 (d, C-3), 80.54 (d, C-2), 78.90 (s, C-9), 78.39 (s, C-13), 72.90 (d, C-5), 71.37 (d, C-4), 62.42 (t, C-6), 60.30 (t, C-12), 58.32 (t, C-8), 55.04 (q, C-7). IR (diamond-ATR): $\tilde{\nu} = 3416\ cm^{-1}$ (br s), 2922 (s), 2852 (m), 2240 (m), 1696 (vs), 1442 (m), 1356 (m), 1251 (s), 1156 (m), 1091 (vs). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 193 nm (3.83), 204 (3.87). MS (ESI-MS): *m*/*z* (%) = 381 (100) $[M + Na]^+$, 337 (39). Anal. Calcd for $C_{15}H_{18}O_{10}$ (358.30): C, 50.28; H, 5.06. Found: C, 50.49; H, 5.94.

3.29. Methyl 2,3-di-*O*-(4-diethylamino-but-2-ynyl)-α-D-glucopyranoside (17h)

To 1.5 mL of anhydrous Me_2SO were added 136 mg (0.50 mmol) **16**, 99 mg (1.34 mmol) diethylamine, 0.8 mL aqueous formaldehyde (35%), and 5.5 mg (0.029 mmol) of copper(I) iodide. The reaction mixture was stirred for 55 h at 30 °C and after work-up (as described above for **14**) 173 mg (78%) of **17h** was obtained as a colorless, highly viscous oil. ^{1}H NMR (400.1 MHz, $CDCl_3$, *J* in Hz): δ 1.04–1.08 (t, t, 12H, 19-, 19′-H, and 13-, 13′-H, $^3J_{19,18} = {}^3J_{19',18'} = {}^3J_{13,12} = {}^3J_{13',12'} = 7.2$), 2.52–2.57 (q, q, 8H, 18-, 18′-$H_{a,b}$ and 12-, 12′-$H_{a,b}$, $^3J_{18,19} = {}^3J_{18',19'} = {}^3J_{12,13} = {}^3J_{12',13'} = 7.2$), 3.09 (br s, 2H, 2OH), 3.43 (s, 3H, 7-H, OCH_3), 3.45 (s, s, 4H, 11-, 17-Ha,b), 3.48–3.87 (m, 6H, 2-, 3-, 4-, 5-H and 6-$H_{a,b}$), 4.31–4.53 (m, 4H, 8-, 14-$H_{a,b}$), 4.88 (d, 1H, 1-H, $^3J_{1,2} = 3.5$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 98.09 (d, C-1), 81.65 (s, C-9), 81.55 (s, C-15), 81.41 (s, C-16), 80.45 (d, C-3), 80.42 (s, C-10), 78.91 (d, C-2), 70.97 (d, C-5), 70.14 (d, C-4), 62.31 (t, C-6), 60.53 (t, C-14), 58.65 (t, C-8), 55.10 (q, C-7), 47.15 (t, C-12, -12′), 47.06 (t, C-18, -18′), 40.90 (t, C-11), 40.83 (t, C-17), 12.42 (q, C-13, -13′), 12.29 (q, C-19, -19′). IR (diamond-ATR): $\tilde{\nu} = 3323\ cm^{-1}$ (br s), 2971 (s), 2930 (m), 1458 (m), 1353 (m), 1324 (s), 1155 (m), 1089 (s), 1050 (vs). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 191 nm (4.22). EIMS (70 eV): *m*/*z* (%) = 440 (4) $[M^+]$, 411 (2), 368 (5), 354 (4), 316 (3), 125 (100), 110 (85), 86 (41), 58 (39), 56 (38). HRMS: $C_{23}H_{40}N_2O_6$: calcd 440.288, found *m*/*z* 440.288 ± 1 ppm. Anal. Calcd for $C_{23}H_{40}N_2O_6$ (440.57): C, 62.70; H, 9.15; N, 6.36. Found: C, 62.36; H, 9.51; N, 6.88.

3.30. (Bis) *N*-benzyl-triazole of methyl 2,3-di-*O*-propargyl-α-D-glucopyranoside (18)

To a solution of 203 mg (0.75 mmol) of **16** in Me_2SO–water (4:1) is added 20 mg (1.5 mmol) of benzylazide, 60 mg (0.3 mmol) of sodium-L-ascorbate in 0.25 mL of water, and 19 mg (0.08 mmol) of copper(II) sulfate pentahydrate. After 5.5 d at room temp., the reaction mixture is diluted with 25 mL of water and extracted carefully with CH_2Cl_2. The combined organic phases are dried (magnesium sulfate), the solvent is removed under diminished pressure, and the raw product purified by silica gel chromatography with diethyl ether–ethanol (5:1): 325 mg (81%) of **18**, as colorless crystals, mp 48–50 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 3.31 (s, 3H, 7-H, OCH_3), 3.40 (br s, 2H, 2OH), 3.48–3.82 (m, 6H, 2-, 3-, 4-, 5-H and 6-$H_{a,b}$), 4.77 (d, 1H, 1-H, $^3J_{1,2} = 3.5$ Hz), 4.76 (s, 2H, 8-$H_{a,b}$), 4.79–4.95 (m, 2H, 18-$H_{a,b}$), 5.41–5.51 (m, 4H, 11-, 21-$H_{a,b}$), 7.23–7.37 (m, 10H, Ph–H), 7.49 (s, 1H, 20-H), 7.57 (s, 1H, 10-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 145.79 (s, C-19), 145.14 (s, C-9), 134.52 (s, C-12), 134.36 (s, C-22), 129.05 (d, C-14, -16), 129.03 (d, C-24, -26), 128.73 (d, C-15), 128.68 (d, C-25), 128.10 (d, C-13, -17 and C-23, -27), 122.92 (d, C-10), 122.27 (d, C-20), 97.71 (d, C-1), 82.10 (d, C-3), 79.58 (d, C-2), 71.04 (d, C-5), 70.62 (d, C-4), 65.70 (t, C-18), 64.36 (t, C-8), 62.31 (t, C-6), 54.93 (q, C-7), 54.16 (t, C-11), 54.07 (t, C-21). IR (diamond-ATR): $\tilde{\nu} = 3368\ cm^{-1}$ (br s), 3091 and 3067 cm^{-1} (w), 2918 (m), 2838 (w), 1497 (m), 1456 (m), 1437 (m), 1331 (m), 1088 (s), 1025 (vs). UV (acetonitrile): λ_{max} ($\lg\varepsilon$) = 192 nm (4.78), 206 (4.34), 258 (2.59). EIMS (70 eV): *m*/*z* (%) = 536 (0.3) $[M^+]$, 505 (1), 364 (2), 332 (13), 188 (11), 173 (28), 144 (28), 91 (100). MS (ESI-MS): *m*/*z* (%) = 559 (100) $[M+Na]^+$. HRMS: $C_{27}H_{32}N_6O_6$+Na: calcd 559.228, found *m*/*z* 559.288 ± 1 ppm. Anal. Calcd for $C_{34}H_{36}N_6O_6$ (624.69): C, 60.44; H, 6.01; N, 15.66. Found: C, 59.57; H, 6.08; N, 15.43.

3.31. X-ray structure determinations

Numerical details are presented in Table 3. *Data collection*: Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (Bruker SMART 1000 CCD). Measurements were performed with monochromated Mo Kα radiation. *Structure refinement*: The structures were refined anisotropically against F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen). H atoms were included using a riding model. In the absence of significant anomalous scatterers, Friedel opposite reflections were

Table 3. Details of X-ray structure analyses of **2** and **3**

Compound	**2**	**3**
Formula	$C_{20}H_{22}O_6$	$C_{20}H_{26}O_6$
M_r	358.38	362.41
Habit	colorless needle	colorless lath
Crystal size/mm	$0.45 \times 0.07 \times 0.07$	$0.45 \times 0.14 \times 0.09$
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Cell constants		
a/Å	4.5735(8)	4.7360(6)
b/Å	18.117(3)	17.009(2)
c/Å	21.527(4)	23.330(2)
V/Å^3	1783.7	1879.3
Z	4	4
D_x/Mg m^{-3}	1.335	1.281
μ/mm^1	0.10	0.09
$F(000)$	760	776
T/°C	−140	−140
$2\theta_{max}$	60	57.4
No. of reflections		
Measured	14,318	19,513
Independent	3047	2835
R_{int}	0.046	0.075
Parameters	236	236
wR (F^2, all refl.)	0.099	0.098
R (F, $>4\sigma(F)$)	0.041	0.039
S	1.03	1.02
Max. $\Delta\rho$/e Å^{-3}	0.30	0.25

merged and the absolute configuration of D-glucose was assumed.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC 288653 (**2**), 288654 (**3**). Copies may be requested free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, England (e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment

Financial support of P.F.T. by the DAAD is gratefully acknowledged.

References

1. Mischnick, P.; Heinrich, J.; Gohdes, M.; Wilke, O.; Rogmann, N. *Macromol. Chem. Phys.* **2001**, *201*, 1985–1995.
2. Dubber, M.; Lindhorst, T. K. *Carbohydr. Res.* **1998**, *310*, 35–41.
3. Wenz, G.; Höfler, Th. *Carbohydr. Res.* **1999**, *322*, 153–165.
4. Slaghek, T. M.; Timmermans, J. W.; Fester, G. K. Patent WO0187986, 2001, CAN 136:7993.
5. Belghiti, T.; Joly, J.-P.; Didierjeau, C.; Dahaoi, S.; Chapleur, Y. S. *Tetrahedron* **2002**, *43*, 1441–1443.
6. Aversa, M. C.; Barattucci, A.; Bilardo, M. C.; Bonaccorsi, P.; Fiannetto, P.; Rollin, P.; Tatibouët, A. *J. Org. Chem.* **2005**, *70*, 7389–7396.
7. Bernet, B.; Vasella, A. Acetylenosaccharides. In *Acetylene Chemistry. Chemistry, Biology and Material Science*; Diederich, F., Stang, P. J., Tykwinski, R. R., Eds.; Wiley-VCH, 2005; pp 174–231.
8. Alzee, J.; Cai, C.; Vasella, A. *Helv. Chim. Acta* **1995**, *78*, 242–264.
9. Murty, K. V. S. N.; Xie, T.; Bernet, B.; Vasella, A. *Helv. Chim. Acta* **2006**, *89*, 675–730.
10. Hoffmann, B.; Bernet, B.; Vasella, A. *Helv. Chim. Acta* **2002**, *85*, 265–287.
11. Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021.
12. Tornøe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057–3064.
13. Wilkinson, B. L.; Bornaghi, L. F.; Poulsen, S.-A.; Houston, T. A. *Tetrahedron* **2006**, *62*, 8115–8125.
14. Bock, V. D.; Hiemstra, H.; van Maarseveen, J. H. *Eur. J. Org. Chem.* **2006**, 51–68, and references cited therein.
15. Hasegawa, T.; Umeda, M.; Numata, M.; Li, C.; Bae, A.-H.; Fujisawa, T.; Haraguchi, S.; Sakurai, K.; Shinkai, S. *Carbohydr. Res.* **2006**, *341*, 35–40.
16. Dörner, S.; Westermann, B. *Chem. Commun.* **2005**, 2852–2854.
17. Tankam, P. F.; Müller, R.; Mischnick, P.; Hopf, H. *Carbohydr. Res.*, in press, doi:10.1016/j.carres.2007.05.017.
18. Evans, M. E. *Carbohydr. Res.* **1972**, *21*, 473–475.
19. Wu, X.; Kong, F.; Lu, D.; Li, G. *Carbohydr. Res.* **1992**, *235*, 163–178.
20. Bieber, L. W.; Da Silva, M. F. *Tetrahedron Lett.* **2004**, *45*, 8281–8283.
21. Bodine, K. D.; Gin, D. Y.; Gin, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 1638–1639.
22. Himo, F.; Lovell, T.; Hilgraf, R.; Rostovtsev, V. V.; Noodleman, L.; Sharpless, K. B.; Fokin, V. V. *J. Am. Chem. Soc.* **2005**, *127*, 210–216.
23. Rodionov, V. O.; Fokin, V. V.; Finn, M. G. *Angew. Chem.* **2005**, *117*, 2250–2255; . *Angew. Chem., Int. Ed.* **2005**, *44*, 2210–2215.
24. Wu, P.; Feldman, A. K.; Nugent, A. F.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Fréchet, J. M. J.; Sharpless, K. B.; Fokin, V. V. *Angew. Chem.* **2004**, *116*, 4018–4022; *Angew. Chem., Int. Ed.* **2004**, *43*, 3928–3932.
25. Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem.* **2002**, *114*, 2708–2711; *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599.
26. Kochetkov, N. K.; Chizhov, O. S. *Adv. Carbohydr. Chem.* **1966**, *21*, 39–93.
27. Kochetkov, N. K.; Chizhov, O. S. *Tetrahedron* **1965**, *21*, 2029–2047.
28. Bosso, C.; Defaye, J.; Gadelle, A.; Ulrich, J. *Org. Mass Spectrom.* **1977**, *12*, 493–499.