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Stereoselective synthesis of epoxyalkyl glycoside precursors of glycosyl glycerol analogues from alkenyl glycosides of *N*-acetyl-D-glucosamine derivatives†

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Abstract—The synthesis of epoxyalkyl glycoside derivatives of *N*-acetyl-D-glucosamine is described. Epoxidation of the corresponding alkenyl glycosides with *m*-CPBA took place with different stereoselectivity depending on the nature of the unsaturated system and the protecting groups on the sugar moiety. The configuration of the newly formed stereogenic centres has been confirmed unequivocally by chemical correlation.

1. Introduction

Oxiranes are important intermediates in organic synthesis, because their electrophilic or nucleophilic opening leads to 1,2-difunctionalized systems or to the formation of new carbon–carbon bonds.[2–4] This chemical reactivity is responsible for the biological activity exhibited by compounds bearing an oxirane moiety. Thus, they can present cytotoxic activity, and hence have been studied for use as anti-cancer agents.[5] It is noteworthy that in a strategy to obtain new highly selective drugs against carcinoma cells in rapid growth, which have a great demand for primary metabolites such as carbohydrates, the latter are used as antitumour agent carrier.[6–8] This line of research is one of the components of our work, and previously we have described the synthesis of compounds with potential antitumour activity by linkage of the alkylating moiety—chlorambucil or cyclophosphamide—widely used clinically in the treatment of different types of cancer[9,10]—to different positions of various aminosugars.[1,11–14] We want to broaden this approach and use oxiranes as alkylating moiety. At the same time, the epoxyalkyl glycosides of some sugars have been studied as potential inhibitors of several endoglycosidases. Thus, epoxypropyl glycosides of *N*-acetyl-D-glucosamine, di-*N*-acetylchitobiose and tri-*N*-acetylchitotriose have been prepared as inhibitors of lysozyme,[15] while epoxyalkyl cellobiosides have been synthesized as inhibitors of cellulases.[16,17] It has also been reported that the inhibition of several endoglucanases by oligosaccharidic epoxyalkyl glycosides shows a remarkable specificity not only with respect to the sugar moiety but also with respect to the chain length and the configuration of the aglycone.[18,19] Furthermore, it is noteworthy that certain glycosyl glycerols, an important class of compounds widely distributed in plants, animals and bacteria,[20] have shown tumour inhibitory activity;[21–25] and they can be obtained from epoxyalkyl glycosides and subsequent ring opening reaction.[16] Thus, we became very interested in investigating a good method to obtain the epoxyalkyl glycosides of aminosugars with high stereoselectivity.

We believe that a straightforward means to achieve this might be the oxidation of alkenyl glycosides, for the following (and other) reasons.

(a) Alkenyl glycosides are readily obtained, and the oxidation of alkenes to oxiranes is very well known and easily performed;

(b) published precedent works on the oxidation of alkenyl glycosides are scarce, and refer mostly to allyl glycosides of sugars;[26–28] those referring to the epoxidation of alkenyl glycosides derived from *N*-acetyl-D-glucosamine are even fewer in number;[29] and

(c) we have used 2-aminosugars as chiral templates in the stereoselective synthesis of numerous compounds (2-aminoglycals,[30] 2-nitrosugars,[14] chiral oxazolidi-

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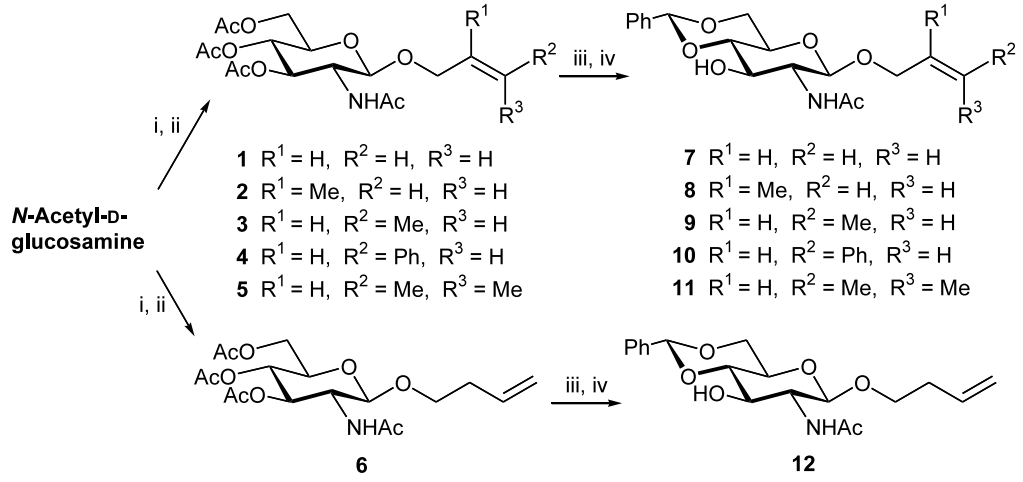
nes,[31] chiral epoxyamides,[32] compounds with potential anti-cancer activity[11–13]), and we anticipated that the glucosamine moiety could serve as a chiral inductor in the oxidation reaction and as carrier agent in the derivatives with potential biological activity.

We have already published preliminary assays for the preparation of epoxyalkyl glycosides by oxidation of alkenyl glycosides of D-glucosamine,[1] and observed that the reaction takes place with high stereoselectivity. We have also explored the preparation of glycosyl aminoglycerols by further ring opening reaction with nitrogen nucleophiles.[33]

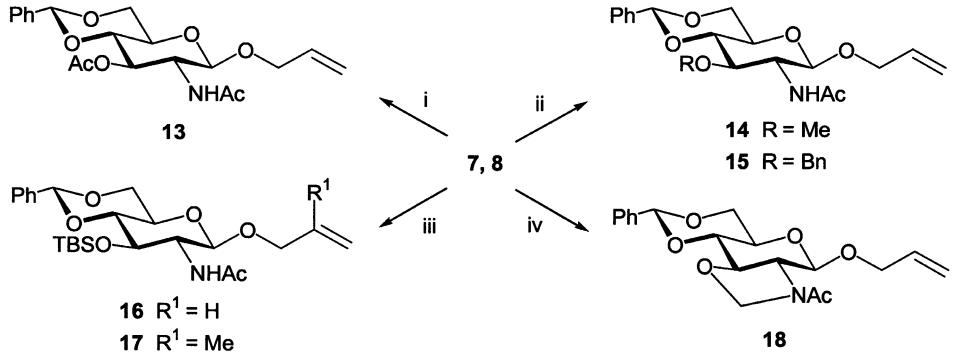
Herein, we report on a study of the oxidation of a wide range of alkenyl glycosides derived from D-glucosamine with *m*-chloroperoxybenzoic acid (*m*-CPBA), aiming to analyze the influence that the different groups on the double bond and the protecting groups of the sugar hydroxyls have on the stereoselectivity of the reaction. We also present unequivocal chemical proof of the configuration of the major diastereoisomer obtained in the oxidation reaction. The new compounds obtained can be converted into new glycosyl glycerols representing a pool of compounds, of differing—but related—structure, with a potentially broad spectrum of biological activity.

2. Results and discussion

The oxidation of the alkenyl glucopyranosides **1**–**18** was studied (Schemes 1 and 2) in an attempt to determine the effect of their different structural features on the stereofacial differentiation of the diastereotopic faces of the double bond in the epoxidation reaction. They can be divided into two groups, according to their higher or lower conformational flexibility: the peracetylated derivatives **1**, **2**, **4**, **5**, and those possessing a benzylidene group between positions 4 and 6 of the tetrahydropyran ring, resulting in a more rigid structural model **7**–**18**. This was important to study because the only work published on oxidations of the alkenyl glycosides of D-glucosamine deals solely with the oxidation of **1**,[29] and we ourselves have observed greater stereoselectivity in the oxidation of the more rigid compounds.[33] Because of the possible influence of the group at position 3 of the sugar on the stereochemical course of the reaction, we have further divided the benzylidene derivatives into two groups: compounds with the C-3 hydroxyl group free (**7**–**12**), and compounds with the C-3 hydroxyl group blocked with protecting groups, in analogy to the peracetylated derivatives (**13**–**18**). Finally, within each group, the glycosides are differentiated by the number and type of substituents on the double bond.



Scheme 1. *Reagents*: (i) AcCl; (ii) Unsaturated alcohol/$Hg(CN)_2$; (iii) NaMeO/MeOH; (iv) PhCHO/$ZnCl_2$.



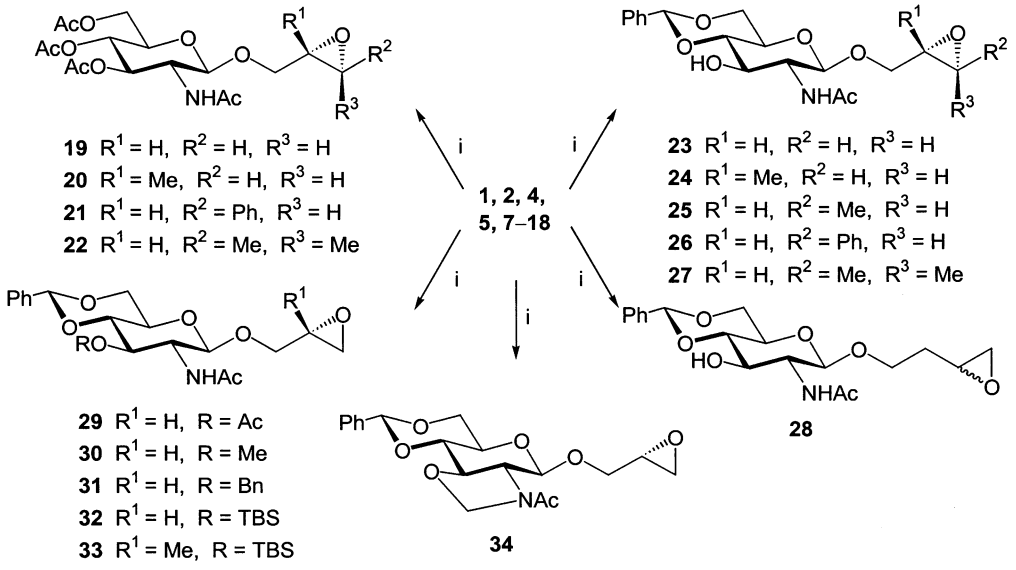
Scheme 2. *Reagents*: (i) Ac_2O/Py; (ii) MeI/KOH/18-crown-6/THF or BnBr/CH_2Cl_2/50% NaOH/H_2O/TBABr; (iii) TBSCl/imidazole/DMF; (iv) CH_2Br_2/CH_2Cl_2/50% NaOH/H_2O/TBABr/reflux.

The alkenyl glucopyranoses **1**–**12** were obtained from *N*-acetyl-D-glucosamine in excellent yields using the procedure previously described for alkyl glucopyranosides[11,12,34] (Scheme 1). The compounds **1**, **6** and **7** have been described previously in the literature.[15,35,36] The reaction of 2-acetamide-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride[37] with the corresponding unsaturated alcohol gave compounds **1**–**6**, which were transformed into the compounds **7**–**12** by deacetylation, and subsequent reaction with benzaldehyde. The NMR spectra showed signals corresponding to the unsaturated moiety incorporated into the sugar molecule in the glycosidation reaction. The ^{1}H NMR spectra showed signals at 6.60–4.80 ppm corresponding to the double bond, the characteristic signals corresponding to the sugar moiety, a doublet for H-1 at 4.70–4.50 ppm for the compounds **1**–**12**, two triplets for H-3 and H-4 at 5.20 and 4.90 ppm, respectively, for **1**–**6**, and a singlet at 5.50 ppm corresponding to the benzylidene group in compounds **7**–**12**.

The syntheses of compounds **13**–**18** were carried out from **7** or **8** as indicated in Scheme 2. The ^{1}H NMR spectra of these compounds showed the signals corresponding to the protecting group present: a singlet at 2.07 ppm for **13**, a singlet at 3.35 ppm for **14**, two signals at 4.70–4.50 ppm for **15**, three singlets at 0.79, –0.03 and –0.10 for **16** (similar for **17**), and two signals at 5.48 and 4.80–4.70 for **18**.

The reaction of **1**, **2**, **4**, **5**, **7**–**18** with *m*-CPBA in dichloromethane at different temperatures gave the corresponding oxiranes **19**–**34**. In all cases, the major isomer was isolated and purified by recrystallization from ethanol or by flash chromatography on silica gel (Scheme 3, Table 1). The ^{1}H NMR spectra for these compounds showed the characteristic signals of the oxirane system at 3.85 and 3.20 ppm for **21** and **26**, and at 3.10–2.50 for the other compounds (Table 2). The ^{13}C NMR spectra showed signals between 62 and 44 ppm for every one the compounds **19**–**34**.

The diastereomeric excess (d.e.), determined using ^{1}H NMR, is shown in Table 1, from which certain inferences can be drawn. For their analysis, the starting alkenyl glycosides can be grouped into the three groups defined above. The first comprises the peracetylated derivatives (compounds **1**, **2**, **4**, **5**); the second is the benzylidene derivatives with the 3-hydroxyl group free (compounds **7**–**12**); and the third is the benzylidene derivatives with the 3-hydroxyl group blocked (compounds **13**–**18**). As expected, the d.e. of the oxidation reaction is higher when the reaction temperature is lowered. The d.e. obtained for the compounds of the first group (entries 1–8) are lower than those for the corresponding compounds of the second group with the same aglycone (entries 9–20) measured at the same temperature, probably because of the greater rigidity of the latter compounds. So, at 10°C, compounds **23**, **24**, **26** and **27** are obtained with d.e. of 93, 82, 70 and 49%, respectively, while compounds **19**, **20**, **21** and **22** are obtained with d.e. of 72, 74, 60 and 34%, respectively. The d.e. of the alkenyl glycosides of the third group (entries 21–26) are again lower than those for the corresponding compounds of the second group with the same aglycone (entries 10 and 12) measured at the same temperature. This effect is very marked for the oxidation of **18**, a compound in which, besides not having the hydroxyl group at position 3 of the sugar, also does not have the N–H bond by formation of an oxazolidine bridge between these two positions. This supports the idea of the formation of a hydrogen bond between the NH group and the peroxyacid, preferentially stabilizing the transition state related to electrophilic addition to the *Re*-face (see below) of the double bond,[33] and further suggests additional stabilization of this transition state, probably by formation of a hydrogen bridge between the hydroxyl group at position 3 and the acetamido group. At the same time, intra-group comparison of the different alkenyl glycosides by the degree of substitution of the double-bond carbons shows that diastereoselectivity generally decreases slightly when a



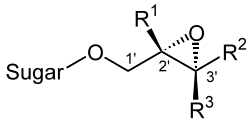
Scheme 3. *Reagents*: (i) *m*-CPBA/CH_2Cl_2.

Table 1. Epoxidation of alkenyl glucosides **1**, **2**, **4**, **5**, **7**–**18** with *m*-CPBA

Entry	Starting compound	Temperature (°C)	Reaction time[a] (days)	Reaction product	Yield[b] (%)	D.e.[c] (%)
1	**1**	10	5	**19**[d]	75	72
2	**1**	−15	55	**19**	42	80
3	**2**	10	4	**20**	68	78
4	**2**	−15	60	**20**	57	95
5	**4**	10	6	**21**	69	60
6	**4**	−15	80	**21**	67	88
7	**5**	10	6	**22**	71	35
8	**5**	−15	90	**22**	52	43
9	**7**	10	2	**23**	74	93
10	**7**	−15	90	**23**	48	100
11	**8**	10	6	**24**	69	86
12	**8**	−15	33	**24**	49	97
13	**9**	10	1	**25**	81	66
14	**9**	−15	30	**25**	66	82
15	**10**	10	2	**26**	72	75
16	**10**	−15	24	**26**	65	87
17	**11**	10	6	**27**	73	49
18	**11**	−15	70	**27**	58	61
19	**12**	10	2	**28**	70	27
20	**12**	−15	35	**28**	59	36
21	**13**	−15	20	**29**	82	70
22	**14**	−15	60	**30**	47	74
23	**15**	−15	14	**31**	85	68
24	**16**	−15	30	**32**	83	64
25	**17**	−15	14	**33**	76	74
26	**18**	−15	72	**34**	62	23

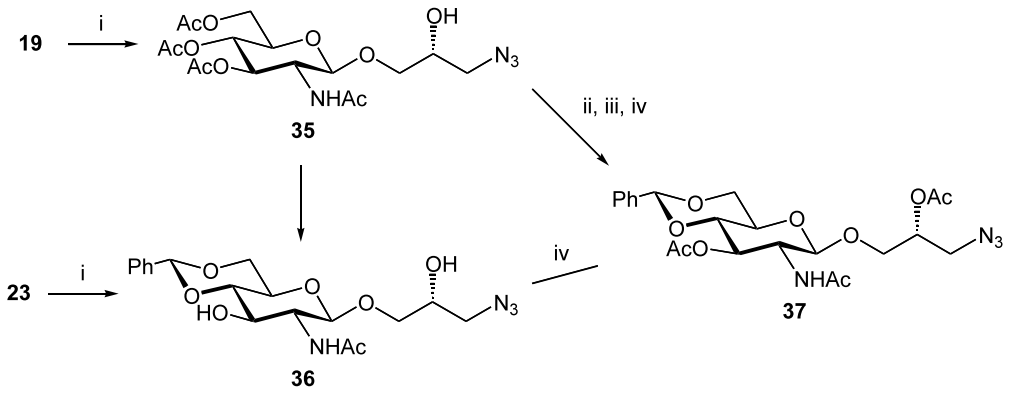
[a] Reaction time approximated (TLC showed that all starting compound had been consumed).
[b] Yields refer to compounds obtained in each reaction after isolation and purification.
[c] Determined by relative integration in the ^{1}H NMR spectra of reaction mixtures.
[d] Literature: temperature 20°C; yield 71%; d.e. 68% (Ref. 29).

Table 2. NMR data (δ, ppm) in $CDCl_3$ for the oxirane protons, and anomeric proton and carbon in compounds **19**–**34**



Entry	Compound	H-2′	H_A-3′; H_B-3′	H-1 minor/major	C-1 major/minor
1	**19**[a]	3.12	2.75; 2.67	4.75/4.63	
2	**19**	3.12	2.76; 2.68/2.53[b]	4.74/4.62	101.3/100.7
3	**20**	–	2.82; 2.55	4.67/4.54	101.6/101.2
4	**21**	3.17	3.85; –	4.81/4.65	101.6/100.8
5	**22**	2.92	–; –	4.79/4.70	101.8/100.2
6	**23**[c,d]	3.05	2.70; 2.56	4.54/4.51	101.8/101.6
7	**24**	–	2.95; 2.66	4.67/4.44	102.9/102.8
8	**25**	3.10	2.89; –	4.68/4.49	101.7/101.6
9	**26**[d]	3.24	3.85; –	4.59/4.55	102.0/101.9
10	**27**	2.99	–; –	4.75/4.67	101.7/101.3
11	**28**	3.06	2.81; 2.56	4.62/4.53	101.7/101.4
12	**29**	3.06	2.76; 2.64/2.51[b]	4.55/4.43	102.5/102.1
13	**30**	3.11	2.77; 2.65/2.55[b]	5.05/4.95	101.2/101.1
14	**31**	3.10	2.76; 2.64/2.52[b]	4.96/4.9–4.8	101.0/100.7
15	**32**	3.11	2.76; 2.66/2.52[b]	4.98/4.90	100.8/100.5
16	**33**	–	2.81; 2.57	4.92/4.80	101.2/100.8
17	**34**[d,e]	3.15	2.73; 2.50	4.96/4.95	103.5/103.3

[a] Reference 29.
[b] δ H_B for the major/minor isomers.
[c] Reference 33.
[d] NMR spectrum recorded in DMSO-d_6.
[e] ^{1}H NMR spectrum recorded at 80°C.



Scheme 4. *Reagents*: (i) $NaN_3/LiClO_4/CH_3CN$; (ii) NaMeO/MeOH; (iii) $PhCHO/ZnCl_2$; (iv) Ac_2O/Py.

single substituent is introduced at the unsaturated carbons (see, for example, the entries for compounds **24**–**26** with respect to **23**) and decreases notably when the allylic system is doubly substituted (see the entry for **22** with respect to **19**, and **27** with respect to **23**). Finally, when the aglycone is a homoallylic system (compound **12**, entries 19 and 20), the oxidation product **28** is obtained with very low stereoselectivity.

In conclusion, the structural features favouring high stereoselectivity in the oxidation of alkenyl glycosides of *N*-acetyl-D-glucosamine derivatives by *m*-CPBA, are, probably in this order: the fact that the alkenyl glycoside is an allyl glycoside; the existence of the N–H bond in the acetamido group; the presence of an acetal group between positions 4 and 6 of the pyranose ring, making the system rigid; and the presence of a free hydroxyl group at position 3. The existence of all these features in compound **7** explains why, at low temperature, its oxidation product—compound **23**—can be obtained with total diastereoselectivity.

Regarding the stereochemistry of the new stereogenic centre created in the formation of the oxirane, Peter et al.[29] demonstrated unequivocally that, in compound **19** (the major diastereoisomer), the configuration is *R* at position 2′ (see Table 2). They also observe that the anomeric proton of this major compound **19** (C-2′ *R*) resonates at higher field (or possesses a lower δ) than the minor diastereoisomer, (C-2′ *S*), and on this basis, assign the *R*-configuration for the other oxiranes (different to those presented here) described in their work.

In all of the cases examined (as shown in Table 2) the major stereoisomer also presents a lower chemical shift in ^{1}H NMR for the value of the anomeric proton (as in **19**) and a higher chemical displacement value for the anomeric carbon in ^{13}C NMR. Thus, it can be tentatively stated that the *Re*-face of the double bond is the more reactive to the electrophilic agent.

To rule out the possibility that the presence of the benzylidene ring condensed with the tetrahydropyran ring in compounds **7**–**18** might invert the reactivity of the diastereotopic faces of the alkene and the chemical displacement of the anomeric protons of the oxiranes formed (compounds **23**–**34**), we went on to the chemical assignment of the stereochemistry of one of the benzylidene oxiranes (**23**) of defined stereochemistry (by correlation here with **19**).[29] Thus, **36** was synthesized independently from **19** and **23**[33] (Scheme 4). The chemical displacement values shown in its ^{1}H and ^{13}C NMR spectra were identical to the signals for the major diastereoisomer. Both compounds **36** were transformed independently into **37**; again, the NMR spectra were identical. The ^{1}H and ^{13}C NMR spectra of a mixture of compound **37** obtained by the two routes present a single set of signals. The foregoing proves the *R*-configuration at position 2′ of **23**, and by extension, recognizes the *Re*-face as the more reactive in all cases.

3. Experimental

3.1. General

Evaporations were conducted under reduced pressure. Preparative chromatography was performed on Silica Gel 60 (E. Merck). Kieselgel 60 F_{254} (E. Merck) was used for TLC. Melting points are uncorrected. Optical rotations were obtained on a Bellingham+Stanley Ltd P-20 polarimeter at 25°C. Mass spectra were recorded on a Micromass AUTOSPECQ mass spectrometer, CI at 150 eV, and HR mass measurements with resolutions of 10000. FAB mass spectra were recorded on a Kratos MS-80-RFA using a thioglycerol matrix. NMR spectra were recorded at 25°C on a Bruker AC-200 spectrometer at 200 MHz for ^{1}H and 50 MHz for ^{13}C, and on a Bruker AMX-500 spectrometer at 500 MHz for ^{1}H and 125 MHz for ^{13}C. The chemical shifts are reported in ppm on the δ scale relative to TMS. COSY, DEPT, and CHCORR experiments were performed to assign the signals in the NMR spectra.

3.2. Alkenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosides, 1–6

A solution of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride[37] (18.3 g, 50 mmol) in dry nitromethane (40 mL) was added dropwise, with exclusion of moisture, to a stirred mixture of the corresponding unsaturated alcohol (25 mL) in anhydrous toluene

(40 mL) containing 4 Å molecular sieves (30 g) and mercury(II) cyanide (12.5 g). The mixture was stirred at room temperature for 1–2 days. When TLC showed that all of the chloride had reacted, the mixture was diluted with ethyl acetate and filtered through a pad (12 cm diameter×1 cm height) of alumina. The organic layer was washed with an aqueous saturated solution of sodium bicarbonate and water, then dried (Na_2SO_4) and concentrated. Suspension of the residue with stirring in hexane for 1 h gave a solid that was filtered off and washed with hexane. Recrystallization from ethanol gave the pure peracetate.

3.2.1. 2-Methyl-2-propenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside, 2. Yield 17.0 g (85%); mp 165–166°C; $[\alpha]_D$ +36.9 (*c* 0.6, CH_2Cl_2); MS (CI): *m*/*z* 402 (65%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 5.84 (d, 1H, $J_{2,NH}$ 8.9 Hz, NH), 5.24 (t, 1H, $J_{2,3}=J_{3,4}$ 9.4 Hz, H-3), 5.02 (t, 1H, $J_{3,4}=J_{4,5}$ 9.5 Hz, H-4), 4.90, 4.85 (2bs, 2H, C=CH_2), 4.60 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.3–3.8 (m, 5H, H-2, H-6, H-6′, OCH_2R), 3.65 (m, 1H, H-5), 2.03, 1.98, 1.97, 1.89 (4s, 4CH_3CO), 1.66 (s, 3H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.9, 170.7, 170.2, 169.3 (4C=O), 140.9 (C=CH_2), 113.2 (C=CH_2), 99.5 (C-1), 72.8 (OCH_2R), 72.4 (C-4), 71.6 (C-3), 68.7 (C-5), 62.1 (C-6), 54.5 (C-2), 23.2 (CH_3CON), 20.7, 20.6, 20.5 (3CH_3COO), 19.2 (CH_3). HRMS (EI): $[M]^{+\bullet}$, found 401.167637. $C_{18}H_{27}NO_9$ requires 401.168582. Anal. calcd for $C_{18}H_{27}NO_9$: C, 53.86; H, 6.78; N, 3.49. Found: C, 53.81; H, 6.67; N, 3.53%.

3.2.2. *trans*-2-Butenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside, 3. Yield 13.6 g (68%); mp 163–164°C; $[\alpha]_D$ −28.3 (*c* 0.8, CH_2Cl_2); MS (CI): *m*/*z* 402 (40%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 5.8–5.6 (m, 3H, NH, CH=CH), 5.28 (t, 1H, $J_{2,3}=J_{3,4}$ 9.6 Hz, H-3), 5.02 (t, 1H, $J_{3,4}=J_{4,5}$ 9.4 Hz, H-4), 4.69 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.3–3.9 (m, 4H, H-6, H-6′, OCH_2R), 3.80 (m, 1H, H-2), 3.66 (m, 1H, H-5), 2.05, 1.99, 1.98, 1.91 (4s, 4CH_3CO), 1.67 (d, 3H, *J* 6.5 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.8, 170.7, 170.3, 169.4 (4C=O), 130.7, 126.2 (CH=CH), 99.2 (C-1), 72.3 (C-4), 71.6 (C-3), 69.8 (OCH_2R), 68.6 (C-5), 62.1 (C-6), 54.7 (C-2), 23.3 (CH_3CON), 20.7, 20.6, 20.5 (3CH_3COO), 17.8 (CH_3). HRMS (CI): $[M+H]^+$, found 402.176338. $C_{18}H_{28}NO_9$ requires 402.176407. Anal. calcd for $C_{18}H_{27}NO_9$: C, 53.86; H, 6.78; N, 3.49. Found: C, 53.53; H, 6.79; N, 3.48%.

3.2.3. *trans*-3-Phenyl-2-propenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside, 4. Yield 18.7 g (81%); mp 175–176°C; $[\alpha]_D$ −24.0 (*c* 1.0, DMF); MS (CI): *m*/*z* 464 (5%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 6.58 (d, 1H, J_{trans} 16.0 Hz, CH_2CH=CHPh), 6.20 (m, 1H, CH_2CH=CHPh), 5.49 (d, 1H, $J_{2,NH}$ 8.8 Hz, NH), 5.28 (t, 1H, $J_{2,3}=J_{3,4}$ 9.3 Hz, H-3), 5.07 (t, 1H, $J_{3,4}=J_{4,5}$ 9.6 Hz, H-4), 4.76 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.48 (ddd, 1H, J_{gem} 12.8 Hz, *J* 5.6 Hz, ^4J 1.4 Hz, C$H_A$$H_B$CH=CHPh), 4.3–4.1 (m, 3H, $CH_A$$H_B$CH=CHPh, H-6, H-6′), 3.87 (m, 1H, H-2), 3.69 (m, 1H, H-5), 2.06, 2.01, 2.00, 1.93 (4s, 4CH_3CO). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.9, 170.7, 170.2, 169.4 (4C=O), 136.3, 133.3, 128.6, 127.9, 126.5, 124.6 (CH=CHPh), 99.6 (C-1), 72.3 (C-4), 71.8 (C-3), 69.7 (OCH_2R), 68.6 (C-5), 62.1 (C-6), 54.8 (C-2), 23.4 (CH_3CON), 20.7, 20.6, 20.5 (3CH_3COO). Anal. calcd for $C_{23}H_{29}NO_9$: C, 59.60; H, 6.31; N, 3.02. Found: C, 59.37; H, 6.19; N, 2.97%.

3.2.4. 3-Methyl-2-butenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside, 5. Yield 15.1 g (73%); mp 138–139°C; $[\alpha]_D$ +50.0 (*c* 0.6, $CHCl_3$); MS (CI): *m*/*z* 416 (27%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 5.96 (d, 1H, $J_{2,NH}$ 8.8 Hz, NH), 5.3–5.1 [m, 2H, H-3, CH=C(CH_3)$_2$], 4.98 (t, 1H, $J_{3,4}=J_{4,5}$ 9.6 Hz, H-4), 4.65 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.2–4.0 (m, 4H, H-6, H-6′, OCH_2R), 3.78 (m, 1H, H-2), 3.64 (m, 1H, H-5), 2.01, 1.96, 1.95, 1.88 (4s, 4CH_3CO), 1.68, 1.60 [2s, 6H, CH=C(CH_3)$_2$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.7, 170.6, 170.5, 169.3 (4C=O), 139.0 [CH=C(CH_3)$_2$], 119.5 [CH=C(CH_3)$_2$], 98.8 (C-1), 72.3 (C-4), 71.6 (C-3), 68.8 (C-5), 65.0 (OCH_2R), 62.2 (C-6), 54.6 (C-2), 25.7, 23.2, 20.6, 20.5, 20.4, 17.8 (6CH_3). HRMS (CI): $[M+H]^+$, found 416.192050. $C_{19}H_{30}NO_9$ requires 416.192057. Anal. calcd for $C_{19}H_{29}NO_9$: C, 54.93; H, 7.04; N, 3.37. Found: C, 54.93; H, 6.98; N, 3.37%.

3.3. Alkenyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosides, 7–12

To a solution of **1**–**6** (25 mmol) in methanol (100 mL) was added a solution of sodium methoxide (2.0 mmol) in methanol (20 mL). After 30 min at room temperature, the mixture was neutralized by addition of Dowex 50 resin (H^+ form), filtered, and evaporated. The solid obtained was dissolved in benzaldehyde (100 mL), and zinc chloride (5 g) was added. The mixture was stirred for 2 days and then poured into hexane/water (1:1) (500 mL) with stirring. The precipitate was filtered off, washed with water and with hexane, and then recrystallized from ethanol.

3.3.1. 2-Methyl-2-propenyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 8. Yield 6.1 g (67%); mp 262–264°C; $[\alpha]_D$ −50.0 (*c* 1.0, DMF); MS (CI): *m*/*z* 364 (85%) $[M+H]^+$. ^1H NMR (200 MHz, DMSO-d_6): δ 7.84 (d, 1H, $J_{2,NH}$ 8.2 Hz, NH), 7.5–7.3 (m, 5H, Ph), 5.59 (s, 1H, PhCH), 5.28 (d, 1H, $J_{3,OH}$ 4.9 Hz, OH), 4.92, 4.83 (2bs, 2H, C=CH_2), 4.45 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.20 (dd, 1H, $J_{5,6e}$ 4.6 Hz, $J_{6e,6a}$ 10.1 Hz, H-6$_e$), 4.08 (d, 1H, J_{gem} 13.0 Hz, OC$H_A$$H_B$R), 3.87 (d, 1H, J_{gem} 13.0 Hz, $OCH_A$$H_B$R), 3.73 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 9.9 Hz, H-6$_a$), 3.6–3.3 (m, 4H, H-2, H-3, H-4, H-5), 1.81 (s, 3H, CH_3CON), 1.64 (s, 3H, CH_3). ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.0 (C=O), 141.5 (C=CH_2), 137.7, 128.8, 128.0, 126.3 (Ph), 111.8 (C=CH_2), 101.0 (C-1), 100.7 (PhCH), 81.3 (C-4), 71.9 (OCH_2R), 70.3 (C-3), 67.9 (C-6), 65.9 (C-5), 56.1 (C-2), 23.0 (CH_3CON), 19.0 (CH_3). HRMS (CI): $[M+H]^+$, found 364.176046. $C_{19}H_{26}NO_6$ requires 364.176013. Anal. calcd for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85. Found: C, 62.69; H, 6.77; N, 4.06%.

3.3.2. *trans*-2-Butenyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 9. Yield 8.5 g (94%); mp 236–238°C; $[\alpha]_D$ −57.7 (*c* 1.0, DMF); MS (CI): *m*/*z* 364 (45%) $[M+H]^+$. ^1H NMR (200 MHz, DMSO-d_6): δ 7.82 (d, 1H, $J_{2,NH}$ 8.5 Hz, NH), 7.5–7.3 (m, 5H, Ph), 5.7–5.4 (m, 3H, PhCH, CH=CH), 5.28 (d, 1H, $J_{3,OH}$ 5.3

Hz, OH), 4.47 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.3–4.1 (m, 2H, H-6_e, OC$\underline{H}_A\underline{H}_B$R), 3.91 (dd, 1H, J 6.0 Hz, J_{gem} 12.3 Hz, OC$H_A\underline{H}_B$R), 3.72 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 9.9 Hz, H-6_a), 3.6–3.2 (m, 4H, H-2, H-3, H-4, H-5), 1.80 (s, 3H, CH_3CON), 1.65 (d, 3H, J 6.2 Hz, CH_3). ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.2 (C=O), 137.8, 128.9, 128.1, 126.4 (Ph), 128.2, 127.4 (C$\underline{H}$=C$\underline{H}$), 100.8 (C-1), 100.7 (PhC$\underline{H}$), 81.3 (C-4), 70.4 (C-3), 68.9 (OCH_2R), 67.9 (C-6), 66.0 (C-5), 56.2 (C-2), 23.1 (C$\underline{H}_3$CON), 17.6 (CH_3). HRMS (CI): [M+H]$^+$, found 364.175819. $C_{19}H_{26}NO_6$ requires 364.176013. Anal. calcd for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85. Found: C, 62.63; H, 6.87; N, 3.88%.

3.3.3. *trans*-3-Phenyl-2-propenyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 10. Yield 9.2 g (87%); mp 252–253°C; $[\alpha]_D$ −90.0 (*c* 1.2, DMF); MS (FAB): *m*/*z* 448 (100%) [M+Na]$^+$. ^{1}H NMR (200 MHz, DMSO-d_6): δ 7.90 (d, 1H, $J_{2,NH}$ 8.4 Hz, NH), 7.5–7.2 (m, 10H, 2Ph), 6.59 (d, 1H, J_{trans} 16.0 Hz, CH_2CH=C$\underline{H}$), 6.27 (dt, 1H, J 5.4 Hz, J_{trans} 16.0 Hz, CH_2C$\underline{H}$=CH), 5.60 (s, 1H, PhC$\underline{H}$), 5.32 (d, 1H, $J_{3,OH}$ 5.2 Hz, OH), 4.56 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.37 (ddd, 1H, J_{gem} 12.3 Hz, J 6.0 Hz, ^4J 1.3 Hz, OC$\underline{H}_A\underline{H}_B$CH=CH), 4.2–4.1 (m, 2H, H-6_e, OC$H_A\underline{H}_B$CH=CH), 3.75 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 9.9 Hz, H-6_a), 3.6–3.3 (m, 4H, H-2, H-3, H-4, H-5), 1.83 (s, 3H, CH_3CON). ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.2 (C=O), 137.7, 131.0, 128.9, 128.7, 128.0, 127.6, 126.3, 126.0 (Ph, CH=CHPh), 101.0 (C-1), 100.7 (PhC$\underline{H}$), 81.3 (C-4), 70.4 (C-3), 68.7 (OCH_2R), 67.9 (C-6), 66.0 (C-5), 56.2 (C-2), 23.2 (C$\underline{H}_3$CON), 17.6 (CH_3). HRMS (CI): [M+H]$^+$, found 426.191285. $C_{24}H_{28}NO_6$ requires 426.191663. Anal. calcd for $C_{24}H_{27}NO_6$: C, 67.75; H, 6.40; N, 3.29. Found: C, 67.53; H, 6.41; N, 3.16%.

3.3.4. 3-Methyl-2-butenyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 11. Yield 7.1 g (75%); mp 164–166°C; $[\alpha]_D$ −34.6 (*c* 1.0, DMF); MS (CI): *m*/*z* 378 (20%) [M+H]$^+$. ^{1}H NMR (200 MHz, DMSO-d_6): δ 7.80 (d, 1H, $J_{2,NH}$ 8.6 Hz, NH), 7.5–7.3 (m, 5H, Ph), 5.58 (s, 1H, PhC$\underline{H}$), 5.3–5.1 [m, 2H, OH, C$\underline{H}$=C$(CH_3)_2$], 4.49 (d, 1H, $J_{1,2}$ 8.1 Hz, H-1), 4.2–3.9 (m, 3H, H-6_e, OCH_2R), 3.75 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 9.9 Hz, H-6_a), 3.6–3.3 (m, 4H, H-2, H-3, H-4, H-5), 1.81 (s, 3H, CH_3CON), 1.69, 1.59 [2s, 6H, CH=C(C$\underline{H}_3)_2$]. ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.1 (C=O), 137.8, 128.9, 128.0, 126.4 (Ph), 136.6 [C$\underline{H}$=C$(CH_3)_2$], 120.5 [CH=C$\underline{(CH_3)_2}$], 100.7 (PhC$\underline{H}$), 100.5 (C-1), 81.3 (C-4), 70.5 (C-3), 67.9 (OCH_2R), 66.0 (C-5), 64.6 (C-6), 56.2 (C-2), 23.1 (C$\underline{H}_3$CON), 25.5, 19.0 [CH=C(C$\underline{H}_3)_2$]. HRMS (CI): [M+H]$^+$, found 378.191480. $C_{20}H_{28}NO_6$ requires 378.191663. Anal. calcd for $C_{20}H_{27}NO_6$: C, 63.65; H, 7.21; N, 3.71. Found: C, 63.39; H, 6.99; N, 3.97%.

3.3.5. 3-Butenyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 12. Yield 6.0 g (66%); mp 235–236°C; $[\alpha]_D$ −44.4 (*c* 0.9, DMF); MS (CI): *m*/*z* 364 (100%) [M+H]$^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 6.0–5.7 (m, 2H, NH, C$\underline{H}$=CH_2), 5.51 (s, 1H, PhC$\underline{H}$), 5.08 (m, 2H, CH=C$\underline{H}_2$), 4.64 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 3.6–3.4 (m, 4H, H-2, H-3, H-4, H-5), 2.34 (m, 2H, OCH_2C$\underline{H}_2$R), 2.02 (s, 3H, CH_3CON). ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.2 (C=O), 137.0, 129.2, 128.3, 126.3 (Ph), 134.9 (C$\underline{H}$=CH_2), 117.0 (CH=C$\underline{H}_2$), 101.9 (C-1), 100.5 (PhC$\underline{H}$), 81.5 (C-4), 71.2 (C-3), 68.8 ($OC\underline{H}_2CH_2$R), 68.5 (C-6), 66.3 (C-5), 59.2 (C-2), 33.8 ($OCH_2C\underline{H}_2$R), 23.6 (C$\underline{H}_3$CON). HRMS (CI): [M+H]$^+$, found 364.175683. $C_{19}H_{26}NO_6$ requires 364.176013. Anal. calcd for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85. Found: C, 62.73; H, 6.93; N, 3.86%.

3.4. Allyl 2-acetamido-3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosides, 13

Allyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside **7** (3.5 g, 10 mmol) was acetylated in the usual way with acetic anhydride/pyridine (1:1) (40 mL). The reaction mixture was kept overnight at room temperature and then poured into ice–water. The precipitate obtained was isolated by filtration and, recrystallized from ethanol, yielded 3.7 g (95%); mp 283–284°C; $[\alpha]_D$ −77.1 (*c* 0.7, CH_2Cl_2); MS (CI): *m*/*z* 392 (60%) [M+H]$^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 5.98 (d, 1H, $J_{2,NH}$ 9.5 Hz, NH), 5.77 (m, 1H, C$\underline{H}$=CH_2), 5.48 (s, 1H, PhC$\underline{H}$), 5.3–5.1 (m, 3H, H-3, CH=C$\underline{H}_2$), 4.44 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.3–4.05 (m, 3H, H-2, H-6_e, OC$\underline{H}_A\underline{H}_B$R), 3.89 (m, 1H, OC$H_A\underline{H}_B$R), 3.8–3.65 (m, 2H, H-4, H-6_a), 3.52 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.6 Hz, $J_{5,6e}$ 4.7 Hz, H-5), 2.07 (s, 3H, CH_3COO), 1.95 (s, 3H, CH_3CON). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.4, 170.2 (2C=O), 136.9, 129.1, 128.2, 126.0 (Ph), 133.5 (C$\underline{H}$=CH_2), 117.4 (CH=C$\underline{H}_2$), 101.2 (C-1), 101.1 (PhC$\underline{H}$), 78.6 (C-4), 72.0 (C-3), 70.0 (OCH_2R), 68.6 (C-6), 66.2 (C-5), 54.3 (C-2), 23.3 (C$\underline{H}_3$CON), 20.9 (C$\underline{H}_3$COO). HRMS (CI): [M+H]$^+$, found 392.170795. $C_{20}H_{26}NO_7$ requires 392.170928. Anal. calcd for $C_{20}H_{25}NO_7$: C, 61.37; H, 6.44; N, 3.58. Found: C, 61.21; H, 6.35; N, 3.62%.

3.5. Alkenyl 2-acetamido-3-*O*-alkyl-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosides, 14 and 15

3.5.1. Allyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-β-D-glucopyranoside, 14. To a solution of **7** (3.5 g, 10 mmol) in dry THF (50 mL) were added, successively, freshly powdered potassium hydroxide (1.0 g, 17.9 mmol), 18-crown-6 (150 mg, 0.5 mmol), and methyl iodide (20.8 mmol). The mixture was stirred at room temperature, and the reaction was monitored by TLC at the end of the reaction. The mixture was then diluted with dichloromethane, and washed several time with water and dried (Na_2SO_4). Evaporation of the organic phase gave the pure methylated product. The solid obtained, purified by crystallization from ethanol, yielded 2.3 g (64%); mp 290–291°C; $[\alpha]_D$ −103.4 (*c* 0.7, DMF); MS (CI): *m*/*z* 364 (100%) [M+H]$^+$. ^{1}H NMR (200 MHz, DMSO-d_6): δ 7.96 (d, 1H, $J_{2,NH}$ 8.7 Hz, NH), 7.5–7.3 (m, 5H, Ph), 5.82 (m, 1H, C$\underline{H}$=CH_2), 5.65 (s, 1H, PhC$\underline{H}$), 5.15 (m, 2H, CH=C$\underline{H}_2$), 4.52 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.3–4.1 (m, 2H, H-6_e, OC$\underline{H}_A\underline{H}_B$R), 4.00 (m, 1H, OC$H_A\underline{H}_B$R), 3.77 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.1 Hz, H-6_a), 3.6–3.4 (m, 4H, H-2, H-3, H-4, H-5), 3.35 (s, 3H, OCH_3), 1.82 (s, 3H, CH_3CON). ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.0 (C=O), 137.6, 128.8, 128.1, 126.0

(Ph), 134.5 (CH=CH_2), 116.2 (CH=CH_2), 101.0 (C-1), 100.2 (PhCH), 80.6 (C-4), 79.5 (C-3), 69.0 (OCH_2R), 67.8 (C-6), 65.6 (C-5), 59.0 (OCH_3), 54.2 (C-2), 22.9 (CH_3CON). HRMS (CI): $[M+H]^+$, found 364.175979. $C_{19}H_{26}NO_6$ requires 364.176013. Anal. calcd for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85. Found: C, 62.49; H, 6.70; N, 3.85%.

3.5.2. Allyl 2-acetamido-3-*O*-benzyl-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 15. To a solution of **7** (3.5 g, 10 mmol) in distilled dichloromethane (200 mL), benzyl bromide (2.5 mL, 21.0 mmol), 50% aqueous sodium hydroxide solution (200 mL) and tetrabutylammonium bromide (32 mg, 0.10 mmol) were added. The reaction mixture was stirred vigorously at room temperature for 3 h. The organic phase was washed with water until neutral, dried ($MgSO_4$), and the solvent was removed under reduced pressure to give a solid which, purified by crystallization from ethyl acetate–ethanol, yielded 3.1 g (71%); mp 270–272°C; $[\alpha]_D$ −37.6 (*c* 1.0, DMF); MS (CI): *m*/*z* 440 (10%) $[M+H]^+$. ^1H NMR (200 MHz, DMSO-d_6): δ 8.00 (d, 1H, $J_{2,NH}$ 8.4 Hz, NH), 7.5–7.2 (m, 10H, 2Ph), 5.81 (m, 1H, CH=CH_2), 5.70 (s, 1H, PhCH), 5.18 (m, 2H, CH=CH_2), 4.72 (d, 1H, J_{gem} 11.9 Hz, PhC$H_A$$H_B$O), 4.6–4.5 (m, 2H, PhC$H_A$$H_B$O, H-1), 4.3–4.15 (m, 2H, H-6_e, OC$H_A$$H_B$R), 4.01 (m, 1H, OC$H_A$$H_B$R), 3.8–3.6 (m, 4H, H-2, H-3, H-4, H-6_a), 3.46 (m, 1H, H-5), 1.81 (s, 3H, CH_3CON). ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.1 (C=O), 138.7, 137.6, 129.7, 128.8, 128.1, 128.0, 127.4, 126.0 (2Ph), 134.5 (CH=CH_2), 116.3 (CH=CH_2), 100.9 (C-1), 100.1 (PhCH), 80.9 (C-4), 78.6 (C-3), 73.2 (PhCH_2O), 69.0 (OCH_2R), 67.8 (C-6), 65.6 (C-5), 54.6 (C-2), 23.0 (CH_3CON). HRMS (CI): $[M+H]^+$, found 440.207175. $C_{25}H_{30}NO_6$ requires 440.207313. Anal. calcd for $C_{25}H_{29}NO_6$: C, 68.32; H, 6.65; N, 3.19. Found: C, 68.15; H, 6.97; N, 3.34%.

3.6. Alkenyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosides, 16 and 17

To a solution of **7**, **8** (10 mmol) in dry DMF (30 mL), imidazole (3.4 g, 50 mmol) and *tert*-butyldimethylsilyl chloride (3.8 g, 25 mmol) were added and the mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with dichloromethane, washed with water, dried (Na_2SO_4), filtered and the filtrate evaporated to dryness to give a white solid, which was purified by flash chromatography on silica gel using hexane–ethyl acetate (7:1).

3.6.1. Allyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside, 16. Yield 3.8 g (82%); mp 98–99°C; $[\alpha]_D$ −66.3 (*c* 1.0, CH_2Cl_2); MS (CI): *m*/*z* 464 (60%) $[M+H]^+$. ^1H NMR (200 MHz, DMSO-d_6): δ 7.91 (d, 1H, $J_{2,NH}$ 9.0 Hz, NH), 7.5–7.3 (m, 5H, Ph), 5.82 (m, 1H, CH=CH_2), 5.63 (s, 1H, PhCH), 5.17 (m, 2H, CH=CH_2), 4.50 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.3–4.1 (m, 2H, H-6_e, OC$H_A$$H_B$R), 3.99 (m, 1H, OC$H_A$$H_B$R), 3.8–3.4 (m, 5H, H-2, H-3, H-4, H-5, H-6_a), 1.78 (s, 3H, CH_3CON), 0.75 [s, 9H, $OSi(CH_3)_2C(CH_3)_3$], −0.03, −0.10 [2s, 6H, $OSi(CH_3)_2C(CH_3)_3$]. ^{13}C NMR (50 MHz, DMSO-d_6): δ 168.8 (C=O), 137.6, 128.8, 128.0, 126.2 (Ph), 134.6 (CH=CH_2), 116.2 (CH=CH_2), 100.8 (C-1), 100.7 (PhCH), 81.5 (C-4), 72.3 (C-3), 68.9 (OCH_2R), 67.8 (C-6), 65.6 (C-5), 56.0 (C-2), 25.6 [$OSi(CH_3)_2C(CH_3)_3$], 23.1 (CH_3CON), 17.9 [$OSi(CH_3)_2C(CH_3)_3$], −4.2, −5.0 [$OSi(CH_3)_2C(CH_3)_3$]. HRMS (CI): $[M+H]^+$, found 464.246313. $C_{24}H_{38}NO_6Si$ requires 464.246842. Anal. calcd for $C_{24}H_{37}NO_6Si$: C, 62.17; H, 8.04; N, 3.02. Found: C, 62.11; H, 7.90; N, 3.15%.

3.6.2. 2-Methyl-2-propenyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside, 17. Yield 3.4 g (71%); mp 132–133°C; $[\alpha]_D$ −30.4 (*c* 0.9, CH_2Cl_2); MS (CI): *m*/*z* 478 (75%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 5.87 (d, 1H, $J_{2,NH}$ 8.1 Hz, NH), 5.46 (s, 1H, PhCH), 4.90 (m, 3H, C=CH_2, H-1), 4.3–4.2 (m, 2H, H-6_e, OC$H_A$$H_B$R), 3.95 (d, 1H, J_{gem} 12.6 Hz, OC$H_A$$H_B$R), 3.73 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6_a), 3.5–3.3 (m, 4H, H-2, H-3, H-4, H-5), 1.95 (s, 3H, CH_3CON), 1.69 (s, 3H, CH_3), 0.79 [s, 9H, $OSi(CH_3)_2C(CH_3)_3$], −0.02, −0.08 [2s, 6H, $OSi(CH_3)_2C(CH_3)_3$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.0 (C=O), 141.1 (C=CH_2), 137.2, 128.9, 128.1, 126.2 (Ph), 112.8 (C=CH_2), 101.7 (C-1), 99.5 (PhCH), 82.5 (C-4), 73.0 (OCH_2R), 71.1 (C-3), 68.7 (C-6), 65.8 (C-5), 59.2 (C-2), 25.7 [$OSi(CH_3)_2C(CH_3)_3$], 23.7 (CH_3CON), 19.3 (CH_3), 18.1 [$OSi(CH_3)_2C(CH_3)_3$], −4.2, −5.0 [$OSi(CH_3)_2C(CH_3)_3$]. HRMS (CI): $[M+H]^+$, found 478.261653. $C_{25}H_{40}NO_6Si$ requires 478.262492. Anal. calcd for $C_{25}H_{39}NO_6Si$: C, 62.86; H, 8.23; N, 2.93. Found: C, 62.79; H, 8.18; N, 3.01%.

3.7. Allyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-methylidene-β-D-glucopyranoside, 18

To a solution of allyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside **7** (10 mmol) in distilled dichloromethane (50 mL), dibromomethane (50 mL), 50% aqueous sodium hydroxide solution (100 mL), and tetrabutylammonium bromide (6.5 mg, 0.02 mmol) were added. The reaction mixture was vigorously stirred under reflux for 2 days, then cooled to room temperature. The organic phase was washed with water until neutral, dried ($MgSO_4$), and the solvent was removed under reduced pressure to give a solid which was purified by flash chromatography on silica gel using hexane–ethyl acetate (15:10) as eluent, yielding 3.5 g (97%); mp 94–95°C; $[\alpha]_D$ −21.5 (*c* 1.0, CH_2Cl_2); MS (CI): *m*/*z* 362 (100%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.96 (d, 1H, $J_{2,NH}$ 8.7 Hz, NH), 7.5–7.3 (m, 5H, Ph), 5.90 (m, 1H, CH=CH_2), 5.60 (s, 1H, PhCH), 5.48 (d, 1H, J_{gem} 5.3 Hz, OC$H_A$$H_B$N), 5.28 (m, 2H, CH=$CH_2$), 4.8–4.7 (m, 2H, OC$H_A$$H_B$N, H-1), 4.5–4.3 (m, 2H, OC$H_A$$H_B$R, H-$6_e$), 4.14 (m, 1H, OC$H_A$$H_B$R), 4.0–3.8 (m, 3H, H-3, H-4, H-6_a), 3.50 (m, 1H, H-5), 3.37 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.2 Hz, H-2), 2.22 (s, 3H, CH_3CON). ^{13}C NMR (50 MHz, $CDCl_3$): δ 173.3 (C=O), 136.5, 129.3, 128.3, 126.2 (Ph), 132.8 (CH=CH_2), 118.7 (CH=CH_2), 102.8 (C-1), 101.6 (PhCH), 82.4 (OCH_2N), 82.0 (C-4), 79.2 (C-3), 70.6 (OCH_2R), 69.1 (C-5), 68.5 (C-6), 62.0 (C-2), 23.2

($C\underline{H}_3CON$). Anal. calcd for $C_{19}H_{23}NO_6$: C, 63.15; H, 6.41; N, 3.88. Found: C, 62.88; H, 6.55; N, 3.82%.

3.8. Epoxidation of alkenyl glucosides with *m*-chloroperoxybenzoic acid

To a solution of either **1**, **2**, **4**, **5** or **7**–**18** (1.5 mmol) in distilled dichloromethane (300 mL), *m*-chloroperoxybenzoic acid (Aldrich 57–86%) (3.0 g) was added and the suspension was stirred. When TLC showed that all starting compound had been consumed, the reaction mixture was washed successively with a 5% aqueous solution of sodium hydroxide and water, dried ($MgSO_4$), filtered, and the filtrate evaporated to dryness. Diastereomeric excess (d.e.) was determined by ^{1}H NMR. The solids obtained were purified by recrystallization from ethanol or by flash chromatography on silica gel.

3.8.1. Epoxidation of peracetyl derivatives

3.8.1.1. (*R*)-2,3-Epoxy-2-methylpropyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside, 20. Mp 152–154°C; $[\alpha]_D$ +16.6 (*c* 0.8, DMF); MS (CI): *m*/*z* 418 (15%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.64 (d, 1H, $J_{2,NH}$ 8.8 Hz, NH major), 5.53 (d, $J_{2,NH}$ 8.6 Hz, NH minor), 4.67 (d, $J_{1,2}$ 8.4 Hz, H-1 minor), 4.54 (d, $J_{1,2}$ 8.5 Hz, H-1 major), 2.82, 2.55 [2d, 2H, J_{gem} 5.1 Hz, $OCH_2C(CH_3)(O)C\underline{H}_2$], 2.06, 2.01, 2.00, 1.99, 1.94 (4s, 12H, $4CH_3CO$), 1.33 (s, CH_3 minor), 1.29 (s, CH_3 major). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.9, 170.7, 170.3, 170.2, 169.3 (4C=O), 101.6 (C-1 major), 101.2 (C-1 minor) 72.7, 72.5, 71.9, 71.8 (C-4, C-3), 69.6 (C-5 minor), 68.4 (C-5 major), 70.6 [$O\underline{C}H_2C(CH_3)(O)CH_2$ minor], 69.8 [$O\underline{C}H_2C(CH_3)(O)CH_2$ major], 62.0 (C-6 major), 61.5 (C-6 minor), 56.1 [$OCH_2\underline{C}(CH_3)(O)CH_2$ minor], 56.0 [$OCH_2\underline{C}(CH_3)(O)CH_2$ major], 54.2 (C-2 major), 51.0 (C-2 minor), 51.6 [$OCH_2C(CH_3)(O)\underline{C}H_2$ minor], 50.4 [$OCH_2C(CH_3)(O)\underline{C}H_2$ major], 23.2, 23.0, 20.9, 20.7, 20.6, 20.5, 18.3, 18.1 ($5CH_3$). HRMS (CI): $[M+H]^+$, found 418.171028. $C_{18}H_{28}NO_{10}$ requires 418.171322. Anal. calcd for $C_{18}H_{27}NO_{10}$: C, 51.79; H, 6.52; N, 3.36. Found: C, 51.52; H, 6.33; N, 3.48%.

3.8.1.2. (2*S*,3*S*)-2,3-Epoxy-3-phenylpropyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside, 21. Mp 141–142°C; $[\alpha]_D$ −32.0 (*c* 1.0, DMF); MS (CI): *m*/*z* 480 (35%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 5.78 (d, 1H, $J_{2,NH}$ 8.9 Hz, NH), 5.18 (t, 1H, $J_{2,3}=J_{3,4}$ 9.5 Hz, H-3), 5.06 (t, 1H, $J_{3,4}=J_{4,5}$ 9.4 Hz, H-4), 4.81 (d, $J_{1,2}$ 8.5 Hz, H-1 minor), 4.65 (d, $J_{1,2}$ 8.4 Hz, H-1 major), 4.25 [dd, 1H, J_{gem} 12.2 Hz, J 4.6 Hz, $OC\underline{H}_AH_BCH(O)CHPh$], 4.14 [dd, 1H, J_{gem} 12.5 Hz, J 2.2 Hz, $OCH_A\underline{H}_BCH(O)CHPh$], 4.05–3.95 (m, 3H, H-2, H-6, H-6′), 3.85 [d, 1H, J 2.0 Hz, $OCH_2CH(O)C\underline{H}Ph$], 3.68 (m, 1H, H-5), 3.17 [m, 1H, $OCH_2C\underline{H}(O)CHPh$], 2.07, 2.02, 2.01, 1.93 (4s, $4CH_3CO$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.9, 170.7, 170.3, 169.3 (4C=O), 136.4, 134.5, 128.5, 128.4, 125.6 (Ph), 101.6 (C-1 major), 100.8 (C-1 minor), 72.5 (C-4), 71.9 (C-3), 68.3 (C-5), 67.0 [$O\underline{C}H_2CH(O)CHPh$], 62.0 (C-6), 60.8 [$OCH_2\underline{C}H(O)CHPh$], 55.1 (C-2), 54.3 [$OCH_2CH(O)\underline{C}HPh$], 23.3 ($\underline{C}H_3CON$), 20.8, 20.7, 20.6 ($3\underline{C}H_3COO$). HRMS (EI): $[M]^{+\bullet}$, found 479.177804. $C_{23}H_{29}NO_{10}$ requires 479.179147. Anal. calcd for $C_{23}H_{29}NO_{10}$: C, 57.61; H, 6.10; N, 2.92. Found: C, 57.38; H, 6.00; N, 3.10%.

3.8.1.3. (*S*)-2,3-Epoxy-3-methylbutyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside, 22. Mp 156–158°C; $[\alpha]_D$ +13.9 (*c* 0.9, DMF); MS (CI): *m*/*z* 432 (65%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.82 (2d, 1H, $J_{2,NH}$ 8.4 Hz, 9.0 Hz, NH), 4.79 (d, $J_{1,2}$ 8.3 Hz, H-1 minor), 4.70 (d, $J_{1,2}$ 8.4 Hz, H-1 major), 2.92 [m, 1H, $OCH_2C\underline{H}(O)C(CH_3)_2$], 2.04, 1.99, 1.98, 1.92, 1.90 (4s, 12H, $4CH_3CO$), 1.28, 1.24 [2s, 6H, $OCH_2CH(O)C(C\underline{H}_3)_2$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.9, 170.7, 170.3, 169.4, 169.3 (4C=O), 101.8 (C-1 major), 100.2 (C-1 minor) 72.5, 72.1, 71.9, 71.8 (C-4, C-3), 68.6 (C-5 minor), 68.4 (C-5 major), 68.3 [$O\underline{C}H_2CH(O)C(CH_3)_2$ major], 67.9 [$O\underline{C}H_2CH(O)C(CH_3)_2$ minor], 62.1 (C-6 minor), 62.0 (C-6 major), 62.2 [$OCH_2\underline{C}H(O)C(CH_3)_2$ major], 61.1 [$OCH_2\underline{C}H(O)C(CH_3)_2$ minor], 58.2 [$OCH_2CH(O)\underline{C}(CH_3)_2$ minor], 57.7 [$OCH_2CH(O)C\underline{(CH_3)_2}$ major], 54.8 (C-2 minor), 54.3 (C-2 major), 24.6, 24.5, 23.3, 20.7, 20.6, 18.9, 18.7 ($6CH_3$). HRMS (CI): $[M+H]^+$, found 432.185043. $C_{19}H_{30}NO_{10}$ requires 432.186972. Anal. calcd for $C_{19}H_{29}NO_{10}$: C, 52.89; H, 6.78; N, 3.25. Found: C, 52.66; H, 6.57; N, 3.39%.

3.8.2. Epoxidation of 4,6-*O*-benzylidene derivatives

3.8.2.1. (*R*)-2,3-Epoxy-2-methylpropyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 24. Mp 274–276°C; $[\alpha]_D$ −69.1 (*c* 1.0, DMF); MS (CI): *m*/*z* 380 (100%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 6.85 (d, 1H, $J_{2,NH}$ 3.8 Hz, NH), 5.54 (s, 1H, $PhC\underline{H}$), 4.67 (d, $J_{1,2}$ 8.4 Hz, H-1 minor), 4.44 (d, $J_{1,2}$ 8.4 Hz, H-1 major), 4.31 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.3 Hz, H-6_e), 3.40 (m, 1H, H-5), 2.95, 2.66 [2d, 2H, J_{gem} 4.9 Hz, $OCH_2C(CH_3)(O)C\underline{H}_2$], 2.05 (s, 3H, CH_3CON), 1.39 (s, CH_3 minor), 1.34 (s, CH_3 major). ^{13}C NMR (50 MHz, $CDCl_3$): δ 173.1 (C=O), 137.0, 129.1, 128.2, 126.3 (Ph), 102.9 (C-1 major), 102.8 (C-1 minor), 101.9 ($PhC\underline{H}$), 81.3 (C-4), 73.3 (C-3), 69.5 [$O\underline{C}H_2C(CH_3)(O)CH_2$], 68.4 (C-6), 66.3 (C-5), 59.6 (C-2), 57.1 [$OCH_2\underline{C}(CH_3)(O)CH_2$], 49.6 [$OCH_2C(CH_3)(O)\underline{C}H_2$], 23.0 ($\underline{C}H_3CON$), 18.2 [$OCH_2C(\underline{C}H_3)(O)CH_2$]. HRMS (CI): $[M+H]^+$, found 380.171042. $C_{19}H_{26}NO_7$ requires 380.170928. Anal. calcd for $C_{19}H_{25}NO_7$: C, 60.15; H, 6.64; N, 3.69. Found: C, 60.10; H, 6.70; N, 3.71%.

3.8.2.2. (2*S*,3*S*)-2,3-Epoxybutyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 25. Mp 258–260°C; $[\alpha]_D$ −76.7 (*c* 0.7, DMF); MS (CI): *m*/*z* 380 (100%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 6.70 (d, 1H, $J_{2,NH}$ 4.8 Hz, NH), 5.54 (s, 1H, $PhC\underline{H}$), 4.68 (d, $J_{1,2}$ 8.3 Hz, H-1 minor), 4.49 (d, $J_{1,2}$ 8.4 Hz, H-1 major), 4.31 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.4 Hz, H-6_e), 4.08 [dd, 1H, J_{gem} 13.3 Hz, J 2.1 Hz, $OC\underline{H}_AH_BCH(O)CHCH_3$], 3.74 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6_a), 3.40 (m, 1H, H-5), 3.10 [m, 1H, $OCH_2C\underline{H}(O)CHCH_3$], 2.89 [m, 1H, $OCH_2CH(O)C\underline{H}CH_3$], 2.05 (s, 3H, CH_3CON), 1.40 [d, J 5.3 Hz, $OCH_2CH(O)CHC\underline{H}_3$ major]. ^{13}C NMR (50

MHz, DMSO-d_6): δ 169.2 (C=O), 137.7, 128.9, 128.0, 126.4 (Ph), 101.7 (C-1 major), 101.6 (C-1 minor), 100.7 (PhCH), 81.2 (C-4), 70.3 (C-3), 69.0 [OCH$_2$CH(O)CHCH$_3$ minor], 68.8 [OCH$_2$CH(O)CHCH$_3$ major], 67.8 (C-6), 66.0 (C-5), 56.9 [OCH$_2$CH(O)CHCH$_3$ minor], 56.7 [OCH$_2$CH(O)CHCH$_3$ major], 56.1 (C-2), 51.3 [OCH$_2$CH(O)CHCH$_3$ minor], 51.2 [OCH$_2$CH(O)CHCH$_3$ major], 23.1 (CH$_3$CON), 17.1 [OCH$_2$CH(O)CHCH$_3$]. HRMS (CI): [M+H]$^+$, found 380.171278. $C_{19}H_{26}NO_7$ requires 380.170928. Anal. calcd for $C_{19}H_{25}NO_7$: C, 60.15; H, 6.64; N, 3.69. Found: C, 59.88; H, 6.64; N, 3.82%.

3.8.2.3. (2*S*,3*S*)-2,3-Epoxy-3-phenylpropyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 26. Mp 248–250°C; $[\alpha]_D$ −88.3 (*c* 1.2, DMF); MS (FAB): *m*/*z* 464 (100%) [M+Na]$^+$. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.84 (d, 1H, $J_{2,NH}$ 8.8 Hz, NH), 7.5–7.2 (m, 10H, 2Ph), 5.59 (s, 1H, PhCH), 5.28 (d, 1H, $J_{3,OH}$ 5.5 Hz, OH), 4.59 (d, $J_{1,2}$ 8.2 Hz, H-1 minor), 4.55 (d, $J_{1,2}$ 8.2 Hz, H-1 major), 4.19 (dd, $J_{5,6e}$ 5.0 Hz, $J_{6e,6a}$ 10.2 Hz, H-6$_e$ major), 4.11 (dd, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.2 Hz, H-6$_e$ minor), 3.85 [m, 2H, OCH$_A$H$_B$CH(O)CHPh], 3.78 [dd, 1H, J_{gem} 12.3 Hz, J 5.0 Hz, OCH$_A$H$_B$CH(O)CHPh], 3.73 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6$_a$), 3.62 (m, 1H, H-3), 3.56 (m, 1H, H-2), 3.44 (t, 1H, $J_{3,4}=J_{4,5}$ 9.6 Hz, H-4), 3.35 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.8 Hz, $J_{5,6e}$ 4.9 Hz, H-5), 3.24 [m, 1H, OCH$_2$CH(O)CHPh], 1.82 (s, 3H, CH$_3$CON major), 1.80 (s, 3H, CH$_3$CON minor). ^{13}C NMR (125 MHz, DMSO-d_6): δ 169.3 (C=O), 137.7, 137.0, 128.9, 128.5, 128.2, 128.1, 126.4, 125.9 (2Ph), 102.0 (C-1 major), 101.9 (C-1 minor), 100.7 (PhCH), 81.2 (C-4), 70.4 (C-3), 68.8 [OCH$_2$CH(O)CHPh minor], 68.3 [OCH$_2$CH(O)CHPh major], 67.8 (C-6), 66.0 (C-5), 60.3 [OCH$_2$CH(O)CHPh minor], 60.1 [OCH$_2$CH(O)CHPh major], 56.1 (C-2), 55.3 [OCH$_2$CH(O)CHPh minor], 54.9 [OCH$_2$CH(O)CHPh major], 23.1 (CH$_3$CON). HRMS (CI): [M+H]$^+$, found 442.185556. $C_{24}H_{28}NO_7$ requires 442.186578. Anal. calcd for $C_{24}H_{27}NO_7$: C, 65.29; H, 6.16; N, 3.17. Found: C, 65.13; H, 6.11; N, 3.11%.

3.8.2.4. (*S*)-2,3-Epoxy-3-methylbutyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 27. Mp 188–190°C; $[\alpha]_D$ −64.9 (*c* 1.0, DMF); MS (CI): *m*/*z* 394 (80%) [M+H]$^+$. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.5–7.3 (m, 5H, Ph), 6.35 (d, $J_{2,NH}$ 5.7 Hz, NH minor), 6.18 (d, $J_{2,NH}$ 5.8 Hz, NH major), 5.53 (s, 1H, PhCH), 4.75 (d, $J_{1,2}$ 8.3 Hz, H-1 minor), 4.67 (d, $J_{1,2}$ 8.3 Hz, H-1 major), 4.30 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.3 Hz, H-6$_e$), 3.76 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.1 Hz, H-6$_a$), 2.99 [dd, 1H, J 3.5 Hz, 7.9 Hz, OCH$_2$CH(O)C(CH$_3$)$_2$], 2.04 (s, CH$_3$CON major), 2.02 (s, CH$_3$CON minor), 1.34, 1.31 [2s, OCH$_2$CH(O)C(CH$_3$)$_2$ minor], 1.33, 1.29 [2s, OCH$_2$CH(O)C(CH$_3$)$_2$ major]. ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.2 (C=O), 137.7, 128.8, 128.0, 126.3 (Ph), 101.7 (C-1 major), 101.3 (C-1 minor), 100.7 (PhCH), 81.2 (C-4), 70.4 (C-3 major), 70.3 (C-3 minor), 67.8 [OCH$_2$CH(O)C(CH$_3$)$_2$], 67.5 (C-6), 66.0 (C-5), 61.1 [OCH$_2$CH(O)C(CH$_3$)$_2$ major], 60.6 [OCH$_2$CH(O)C(CH$_3$)$_2$ minor], 57.3 [OCH$_2$CH(O)C(CH$_3$)$_2$ minor], 57.2 [OCH$_2$CH(O)C(CH$_3$)$_2$ major], 56.2 (C-2 minor), 56.1 (C-2 major), 24.4, 18.6 [OCH$_2$CH(O)C(CH$_3$)$_2$], 23.1 (CH$_3$CON). HRMS (EI): [M]+•, found 393.178388. $C_{20}H_{27}NO_7$ requires 393.178753. Anal. calcd for $C_{20}H_{27}NO_7$: C, 61.06; H, 6.92; N, 3.56. Found: C, 61.00; H, 6.86; N, 3.61%.

3.8.2.5. 3,4-Epoxybutyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 28. Two stereoisomers were obtained. Reaction at 10°C: mp 251–253°C; $[\alpha]_D$ −64.5 (*c* 0.9, DMF); MS (CI): *m*/*z* 380 (100%) [M+H]$^+$. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.5–7.3 (m, 5H, Ph), 6.70 (2d, 1H, $J_{2,NH}$ 4.7 Hz, NH), 5.55 (s, 1H, PhCH), 4.62 (d, $J_{1,2}$ 8.3 Hz, H-1 minor), 4.53 (d, $J_{1,2}$ 8.3 Hz, H-1 major), 4.30 (m, 1H, H-6$_e$), 3.06 [m, 1H, OCH$_2$CH$_2$CH(O)CH$_2$], 2.81, 2.56 [2m, 2H, OCH$_2$CH$_2$CH(O)CH$_2$], 2.04 (s, 3H, CH$_3$CON), 1.60 [m, 2H, OCH$_2$CH$_2$CH(O)CH$_2$]. ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.1 (C=O), 137.8, 128.9, 128.0, 126.4 (Ph), 101.7 (C-1 major), 101.4 (C-1 minor), 100.7 (PhCH), 81.3 (C-4), 70.4 (C-3), 67.9 [OCH$_2$CH$_2$CH(O)CH$_2$], 66.0 (C-5), 65.8 (C-6), 56.0 (C-2), 49.2 [OCH$_2$CH$_2$CH(O)CH$_2$], 46.3 [OCH$_2$CH$_2$CH(O)CH$_2$ major], 46.2 [OCH$_2$CH$_2$CH(O)CH$_2$ minor], 32.3 [OCH$_2$CH$_2$CH(O)CH$_2$ major], 32.1 [OCH$_2$CH$_2$CH(O)CH$_2$ minor], 23.0 (CH$_3$CON). HRMS (CI): [M+H]$^+$, found 380.170892. $C_{19}H_{26}NO_7$ requires 380.170928. Anal. calcd for $C_{19}H_{25}NO_7$: C, 60.15; H, 6.64; N, 3.69. Found: C, 60.09; H, 6.66; N, 3.96%.

3.8.3. Epoxidation of 4,6-*O*-benzylidene-3-*O*-protected derivatives

3.8.3.1. (*R*)-2,3-Epoxypropyl 2-acetamido-3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 29. From **13**: Yield 0.50 g (82%); mp 279–280°C; $[\alpha]_D$ −64.0 (*c* 1.0, CH$_2$Cl$_2$); MS (CI): *m*/*z* 408 (15%) [M+H]$^+$. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.5–7.3 (m, 5H, Ph), 5.96, 5.94 (2d, 1H, $J_{2,NH}$ 9.5 Hz, NH), 5.48 (s, 1H, PhCH), 5.21 (m, 1H, H-3), 4.55 (d, $J_{1,2}$ 8.5 Hz, H-1 minor), 4.43 (d, $J_{1,2}$ 8.4 Hz, H-1 major), 4.30 (dd, 1H, $J_{5,6e}$ 4.7 Hz, $J_{6e,6a}$ 10.3 Hz, H-6$_e$), 3.06 [m, 1H, OCH$_2$CH(O)CH$_2$], 2.76 [m, 1H, OCH$_2$CH(O)CH$_{cis}$H$_{trans}$], 2.64 [dd, J_{trans} 2.7 Hz, J_{gem} 5.2 Hz, OCH$_2$CH(O)CH$_{cis}$H$_{trans}$ major], 2.51 [dd, J_{trans} 2.6 Hz, J_{gem} 4.8 Hz, OCH$_2$CH(O)CH$_{cis}$H$_{trans}$ minor], 2.06 (s, 3H, CH$_3$COO), 1.97 (s, CH$_3$CON major), 1.96 (s, CH$_3$CON minor). ^{13}C NMR (50 MHz, CDCl$_3$): δ 171.3, 170.3 (C=O), 136.9, 129.1, 128.2, 126.0 (Ph), 102.5 (C-1 major), 102.1 (C-1 minor), 101.3 (PhCH), 78.5 (C-4), 71.9 (C-3), 70.7 [OCH$_2$CH(O)CH$_2$ minor], 68.5 [OCH$_2$CH(O)CH$_2$ major], 67.7 (C-6), 66.3 (C-5), 54.3 (C-2), 50.8 [OCH$_2$CH(O)CH$_2$ minor], 50.4 [OCH$_2$CH(O)CH$_2$ major], 44.2 [OCH$_2$CH(O)CH$_2$ minor], 43.8 [OCH$_2$CH(O)CH$_2$ major], 23.3 (CH$_3$CON), 20.9 (CH$_3$COO). HRMS (CI): [M+H]$^+$, found 408.165674. $C_{20}H_{26}NO_8$ requires 408.165842. Anal. calcd for $C_{20}H_{25}NO_8$: C, 58.96; H, 6.19; N, 3.44. Found: C, 58.92; H, 6.13; N, 3.51%.

From **23**: An aliquot of compound **23** (0.75 mmol) was acetylated in the usual way with acetic anhydride/pyri-

dine (1:1) (4 mL). The reaction mixture was kept overnight at room temperature and then poured into ice–water. The precipitate obtained was isolated by filtration and, recrystallized from ethanol–water, gave **29** as only one stereoisomer. Yield 0.28 g (92%); MS (FAB): m/z 430 (100%) $[M+Na]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 5.95 (d, 1H, $J_{2,NH}$ 9.3 Hz, NH), 5.48 (s, 1H, PhCH), 5.20 (t, 1H, $J_{2,3}=J_{3,4}$ 9.9 Hz, H-3), 4.46 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.31 (dd, 1H, $J_{5,6e}$ 4.7 Hz, $J_{6e,6a}$ 10.3 Hz, H-6_e), 3.50 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.6 Hz, $J_{5,6e}$ 4.7 Hz, H-5), 3.08 [m, 1H, $OCH_2CH(O)CH_2$], 2.76 [m, 1H, $OCH_2CH(O)CH_{cis}H_{trans}$], 2.64 [dd, 1H, J_{trans} 2.7 Hz, J_{gem} 5.2 Hz, $OCH_2CH(O)CH_{cis}H_{trans}$], 2.06 (s, 3H, CH_3COO), 1.97 (s, 3H, CH_3CON). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.3, 170.3 (C=O), 136.9, 129.1, 128.2, 126.1 (Ph), 102.5 (C-1), 101.3 (PhCH), 78.5 (C-4), 71.8 (C-3), 68.5 [$OCH_2CH(O)CH_2$], 67.7 (C-6), 66.4 (C-5), 54.4 (C-2), 50.4 [$OCH_2CH(O)CH_2$], 43.8 [$OCH_2CH(O)CH_2$], 23.3 (CH_3CON), 20.9 (CH_3COO).

3.8.3.2. (*R*)-2,3-Epoxypropyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-β-D-glucopyranoside, 30. Yield 0.27 g (47%); mp 211–212°C; $[\alpha]_D$ +102.2 (c 0.5, CH_2Cl_2); MS (CI): m/z 380 (100%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 5.83 (d, 1H, $J_{2,NH}$ 7.7 Hz, NH), 5.52 (s, 1H, PhCH), 5.05 (d, $J_{1,2}$ 8.2 Hz, H-1 minor), 4.95 (d, $J_{1,2}$ 8.2 Hz, H-1 major), 4.31 (dd, 1H, $J_{5,6e}$ 4.3 Hz, $J_{6e,6a}$ 10.3 Hz, H-6_e), 3.11 [m, 1H, $OCH_2CH(O)CH_2$], 2.77 [m, $OCH_2CH(O)CH_{cis}H_{trans}$], 2.65 [dd, J_{trans} 2.7 Hz, J_{gem} 5.1 Hz, $OCH_2CH(O)CH_{cis}H_{trans}$ major], 2.55 [dd, J_{trans} 2.6 Hz, J_{gem} 5.2 Hz, $OCH_2CH(O)CH_{cis}H_{trans}$ minor], 2.01 (s, 3H, CH_3CON). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.1 (C=O), 137.2, 129.0, 128.2, 126.0 (Ph), 101.2 (C-1 major), 101.1 (C-1 minor), 100.6 (PhCH), 82.3 (C-4), 78.4 (C-3), 69.2 [$OCH_2CH(O)CH_2$], 68.7 (C-6), 65.9 (C-5), 57.6 (C-2), 50.7 [$OCH_2CH(O)CH_2$ minor], 50.3 [$OCH_2CH(O)CH_2$ major], 44.2 [$OCH_2CH(O)CH_2$], 29.7 (CH_3O), 23.7 (CH_3CON). HRMS (CI): $[M+H]^+$, found 380.169608. $C_{19}H_{26}NO_7$ requires 380.170928. Anal. calcd for $C_{19}H_{25}NO_7$: C, 60.15; H, 6.64; N, 3.69. Found: C, 59.90; H, 6.62; N, 3.80%.

3.8.3.3. (*R*)-2,3-Epoxypropyl 2-acetamido-3-*O*-benzyl-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 31. Yield 0.58 g (85%); mp 263–264°C; $[\alpha]_D$ −54.0 (c 1.0, CH_2Cl_2); MS (FAB): m/z 478 (97%) $[M+Na]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.6–5.5 (m, 2H, NH, PhCH), 4.96 (d, $J_{1,2}$ 8.3 Hz, H-1 minor), 4.9–4.8 (m, H-1 major, $PhCH_AH_BO$), 4.62 (d, 1H, J_{gem} 11.9 Hz, $PhCH_AH_BO$), 4.33 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.3 Hz, H-6_e), 3.10 [m, 1H, $OCH_2CH(O)CH_2$], 2.76 [m, 1H, $OCH_2CH(O)CH_{cis}H_{trans}$], 2.64 [dd, J_{trans} 2.7 Hz, J_{gem} 5.2 Hz, $OCH_2CH(O)CH_{cis}H_{trans}$ major], 2.52 [dd, J_{trans} 2.6 Hz, J_{gem} 5.2 Hz, $OCH_2CH(O)CH_{cis}H_{trans}$ minor], 1.89 (s, CH_3CON major), 1.87 (s, CH_3CON minor). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.5 (C=O), 138.3, 137.3, 129.0, 128.4, 128.3, 128.2, 127.8, 126.0 (2Ph), 101.2 (PhCH), 101.0 (C-1 major), 100.7 (C-1 minor), 82.6 (C-4), 76.5 (C-3), 74.4 ($PhCH_2O$), 70.8 [$OCH_2CH(O)CH_2$ minor], 68.9 [$OCH_2CH(O)CH_2$ major], 68.7 (C-6), 66.0 (C-5), 57.1 (C-2), 50.8 [$OCH_2CH(O)CH_2$ minor], 50.3 [$OCH_2CH(O)CH_2$ major], 44.2 [$OCH_2CH(O)CH_2$], 23.6 (CH_3CON). HRMS (CI): $[M+H]^+$, found 456.201254. $C_{25}H_{30}NO_7$ requires 456.202228. Anal. calcd for $C_{25}H_{29}NO_7$: C, 65.92; H, 6.42; N, 3.07. Found: C, 65.67; H, 6.46; N, 3.12%.

3.8.3.4. (*R*)-2,3-Epoxypropyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside, 32. Yield 0.60 g (83%); mp 125–127°C; $[\alpha]_D$ −66.0 (c 1.0, CH_2Cl_2); MS (CI): m/z 480 (100%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 5.67 (d, 1H, $J_{2,NH}$ 8.1 Hz, NH), 5.46 (s, 1H, PhCH), 4.98 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1 minor), 4.90 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1 major), 3.11 [m, 1H, $OCH_2CH(O)CH_2$], 2.76 [m, 1H, $OCH_2CH(O)CH_{cis}H_{trans}$], 2.66 [dd, J_{trans} 2.7 Hz, J_{gem} 5.2 Hz, $OCH_2CH(O)CH_{cis}H_{trans}$ major], 2.52 [dd, J_{trans} 2.7 Hz, J_{gem} 5.2 Hz, $OCH_2CH(O)CH_{cis}H_{trans}$ minor], 2.01 (s, CH_3CON minor), 1.96 (s, CH_3CON major), 0.79 [s, 9H, $OSi(CH_3)_2C(CH_3)_3$], −0.01, −0.07 [2s, 6H, $OSi(CH_3)_2C(CH_3)_3$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.3 (C=O), 137.1, 129.0, 128.1, 126.3 (Ph), 101.8 (PhCH), 100.8 (C-1 major), 100.5 (C-1 minor), 82.4 (C-4), 71.2 (C-3), 70.5 [$OCH_2CH(O)CH_2$ minor], 68.7 [$OCH_2CH(O)CH_2$ major, C-6], 66.0 (C-5), 59.1 (C-2), 50.8 [$OCH_2CH(O)CH_2$ minor], 50.4 [$OCH_2CH(O)CH_2$ major], 44.2 [$OCH_2CH(O)CH_2$ minor], 44.1 [$OCH_2CH(O)CH_2$ major], 25.7 [$OSi(CH_3)_2C(CH_3)_3$], 23.8 (CH_3CON), 18.1 [$OSi(CH_3)_2C(CH_3)_3$], −4.1, −5.0 [$OSi(CH_3)_2C(CH_3)_3$]. HRMS (CI): $[M+H]^+$, found 480.241486. $C_{24}H_{38}NO_7Si$ requires 480.241756. Anal. calcd for $C_{24}H_{37}NO_7Si$: C, 60.10; H, 7.78; N, 2.92. Found: C, 60.14; H, 7.80; N, 3.03%.

3.8.3.5. (*R*)-2,3-Epoxy-2-methylpropyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside, 33. Yield 0.56 g (76%); mp 137–139°C; $[\alpha]_D$ −42.5 (c 0.8, CH_2Cl_2); MS (CI): m/z 494 (50%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 5.64 (d, 1H, $J_{2,NH}$ 8.3 Hz, NH), 5.46 (s, 1H, PhCH), 4.92 (d, $J_{1,2}$ 8.4 Hz, H-1 minor), 4.80 (d, $J_{1,2}$ 8.5 Hz, H-1 major), 4.29 (dd, 1H, $J_{5,6e}$ 4.2 Hz, $J_{6e,6a}$ 10.2 Hz, H-6_e), 2.81, 2.57 [2d, 2H, J_{gem} 5.1 Hz, $OCH_2C(CH_3)(O)CH_2$], 1.98 (s, 3H, CH_3CON), 1.35 [s, $OCH_2C(CH_3)(O)CH_2$ minor], 1.30 [s, $OCH_2C(CH_3)(O)CH_2$ major], 0.79 [s, 9H, $OSi(CH_3)_2C(CH_3)_3$], −0.14, −0.07 [2s, 6H, $OSi(CH_3)_2C(CH_3)_3$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.1 (C=O), 137.1, 129.0, 128.1, 126.2 (Ph), 101.8 (PhCH), 101.2 (C-1 major), 100.8 (C-1 minor), 82.3 (C-4), 73.2 [$OCH_2C(CH_3)(O)CH_2$ minor], 71.5 (C-3 major), 71.4 (C-3 minor), 70.6 [$OCH_2C(CH_3)(O)CH_2$ major], 68.7 (C-6), 66.0 (C-5), 58.9 (C-2 minor), 58.7 (C-2 major), 55.8 [$OCH_2C(CH_3)(O)CH_2$], 51.6 [$OCH_2C(CH_3)(O)CH_2$ minor], 50.9 [$OCH_2C(CH_3)(O)CH_2$ major], 25.7 [$OSi(CH_3)_2C(CH_3)_3$], 23.7 (CH_3CON), 18.3 [$CH_2C(CH_3)(O)CH_2$], 18.1 [$OSi(CH_3)_2C(CH_3)_3$], –4.1, –5.0 [$OSi(CH_3)_2C(CH_3)_3$]. HRMS (CI): $[M+H]^+$, found

494.258167. $C_{25}H_{40}NO_7Si$ requires 494.257406. Anal. calcd for $C_{25}H_{39}NO_7Si$: C, 60.82; H, 7.96; N, 2.84. Found: C, 60.59; H, 7.80; N, 2.87%.

3.8.3.6. (*R*)-2,3-Epoxypropyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-methylidene-β-D-glucopyranoside, 34. Two stereoisomers were obtained. Yield 0.35 g (62%); mp 198–199°C; $[\alpha]_D$ +82.8 (*c* 1.1, CH_2Cl_2); MS (CI): *m*/*z* 378 (15%) $[M+H]^+$. ^1H NMR (200 MHz, DMSO-d_6, 80°C): δ 7.6–7.3 (m, 5H, Ph), 5.70 (s, 1H, PhC$\underline{H}$), 5.27 (d, 1H, J_{gem} 5.0 Hz, OC$\underline{H}_A\underline{H}_B$N), 4.96, 4.95 (2d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.72 (d, 1H, J_{gem} 5.0 Hz, OC$H_A\underline{H}_B$N), 3.15 [m, 1H, OCH$_2$C$\underline{H}$(O)CH$_2$], 2.73, 2.60 [2m, 2H, OCH$_2$CH(O)-C$\underline{H}_2$], 2.14 (s, CH_3CON minor), 2.13 (s, CH_3CON major). ^{13}C NMR (50 MHz, $CDCl_3$): δ 179.5 (C=O), 136.4, 129.2, 128.2, 126.1 (Ph), 103.5 (C-1 major), 103.3 (C-1 minor), 101.5 (PhCH), 82.2 (OCH$_2$N), 81.8 (C-4), 79.0 (C-3), 71.1 [OC$\underline{H}_2$CH(O)CH$_2$ minor], 70.1 [OC$\underline{H}_2$CH(O)CH$_2$ major], 69.1 (C-5), 68.4 (C-6), 61.9 (C-2 major), 61.6 (C-2 minor), 50.2 [OCH$_2$C$\underline{H}$(O)CH$_2$ minor], 50.0 [OCH$_2$C$\underline{H}$(O)CH$_2$ major], 44.3 [OCH$_2$CH(O)C$\underline{H}_2$ major], 44.2 [OCH$_2$CH(O)C$\underline{H}_2$ minor], 23.2 (C$\underline{H}_3$CON). HRMS (CI): $[M+H]^+$, found 378.154586. $C_{19}H_{24}NO_7$ requires 378.155277. Anal. calcd for $C_{19}H_{23}NO_7$: C, 60.47; H, 6.14; N, 3.71. Found: C, 60.40; H, 6.05; N, 3.80%.

3.9. Azide ring-opening reaction

3.9.1. (*R*)-3-Azido-2-hydroxypropyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside 35. To a solution of compound **19** (0.81 g, 2.0 mmol) in acetonitrile (20 mL), lithium perchlorate (0.43 g, 4.0 mmol) and sodium azide (0.52 g, 8.0 mmol) were added. The mixture was stirred at room temperature for 30 days, with stirring. It was then poured into ice-water, and the precipitate obtained was filtered off, dried, and recrystallized from ethanol. Two stereoisomers were obtained in 87:13 ratio (74% d.e.). Yield 0.58 g (65%); mp 104–105°C; $[\alpha]_D$ +55.6 (*c* 0.9, AcOEt); MS (FAB): *m*/*z* 469 (100%) $[M+Na]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 5.88 (d, 1H, $J_{2,NH}$ 8.8 Hz, NH), 4.63 (d, $J_{1,2}$ 8.4 Hz, H-1 major), 4.61 (d, $J_{1,2}$ 8.3 Hz, H-1 minor), 3.43 [d, *J* 4.6 Hz, OCH$_2$CH(OH)C$\underline{H}_2$N$_3$ minor], 3.32 [d, *J* 5.2 Hz, OCH$_2$CH(OH)C$\underline{H}_2$N$_3$ major], 2.07, 2.02, 2.01, 2.00, 1.94 (4s, 12H, 4CH_3CO). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.1, 170.9, 170.7, 169.3 (4C=O), 101.8 (C-1), 72.3 [OC$\underline{H}_2$CH(OH)CH$_2$N$_3$], 72.2, (C-4), 71.9 (C-3), 69.7 [OCH$_2$C$\underline{H}$(OH)CH$_2$N$_3$ major], 69.5 [OCH$_2$C$\underline{H}$(OH)-CH$_2$N$_3$ minor], 68.3 (C-5), 62.0 (C-6), 54.5 (C-2 minor), 54.3 (C-2 major), 53.1 [OCH$_2$CH(OH)C$\underline{H}_2$N$_3$ major], 52.8 [OCH$_2$CH(OH)C$\underline{H}_2$N$_3$ minor], 23.3 (C$\underline{H}_3$CON), 20.7, 20.6, 20.5 (3C$\underline{H}_3$COO). HRMS (CI): $[M+H]^+$, found 447.172302. $C_{17}H_{27}N_4O_{10}$ requires 447.172719. Anal. calcd for $C_{17}H_{26}N_4O_{10}$: C, 45.74; H, 5.87; N, 12.55. Found: C, 45.61; H, 5.70; N, 12.62%.

3.9.2. (*R*)-3-Azido-2-hydroxypropyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 36. To a solution of compound **35** (0.67 g, 1.5 mmol) in methanol (15 mL) was added a solution of sodium methoxide (1.0 mmol) in methanol (2 mL). After 30 min at room temperature, the mixture was neutralized by addition of Dowex 50 resin (H^+ form), filtered, and evaporated. The solid obtained was dissolved in benzaldehyde (10 mL), and zinc chloride (0.5 g) was added. The mixture was stirred for 2 days and then poured into hexane/water (1:1) (50 mL) with stirring. The precipitate was filtered off, washed with water and with hexane, and then recrystallized from ethanol. Yield 0.43 g (70%); mp 228–229; MS (CI): *m*/*z* 409 (5%) $[M+H]^+$. ^1H NMR (200 MHz, DMSO-d_6): δ 7.86 (d, $J_{2,NH}$ 8.4 Hz, NH minor), 7.83 (d, $J_{2,NH}$ 8.4 Hz, NH major), 7.5–7.3 (m, 5H, Ph), 5.59 (s, 1H, PhC$\underline{H}$), 5.28 (m, 2H, 2OH), 4.47 (d, $J_{1,2}$ 7.8 Hz, H-1 minor), 4.44 (d, $J_{1,2}$ 7.8 Hz, H-1 major), 4.19 (dd, 1H, $J_{5,6e}$ 4.3 Hz, $J_{6e,6a}$ 10.1 Hz, H-6$_e$), 1.1 (s, 3H, CH_3CON). ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.3 (C=O), 137.7, 129.9, 128.1, 126.4 (Ph), 102.2 (C-1 major), 102.0 (C-1 minor), 100.7 (PhCH), 81.2 (C-4), 70.4 [OC$\underline{H}_2$CH(OH)CH$_2$N$_3$], 70.3 (C-3), 68.6 [OCH$_2$C$\underline{H}$(OH)CH$_2$N$_3$], 67.8 (C-6), 66.0 (C-5), 56.1 (C-2), 53.2 [OCH$_2$CH(OH)C$\underline{H}_2$N$_3$], 23.1 (C$\underline{H}_3$CON). HRMS (CI): $[M+H]^+$, found 409.171958. $C_{18}H_{25}N_4O_7$ requires 409.172325. Anal. calcd for $C_{18}H_{24}N_4O_7$: C, 52.94; H, 5.92; N, 13.72. Found: C, 52.88; H, 5.87; N, 13.80%.

3.9.3. (*R*)-2-Acetoxy-3-azidopropyl 2-acetamido-3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, 37. Compound **36** (100 mg, 0.25 mmol) was acetylated in the usual way with acetic anhydride/pyridine (1:1) (5 mL). The reaction mixture was kept overnight at room temperature and then poured into ice–water. The precipitate obtained was isolated by filtration and recrystallized from ethanol, giving compound **37** as a white solid. Only one stereoisomer was obtained. Yield 109 mg (89%); mp 218–219°C; $[\alpha]_D$ −64.9 (*c* 1.0, CH_2Cl_2); MS (CI): *m*/*z* 493 (70%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5-7.3 (m, 5H, Ph), 5.90 (d, 1H, $J_{2,NH}$ 9.4 Hz, NH), 5.49 (s, 1H, PhC$\underline{H}$), 5.20 (t, 1H, $J_{2,3} = J_{3,4}$ 9.9 Hz, H-3), 5.05 [m, 1H, OCH$_2$C$\underline{H}$(OAc)CH$_2$N$_3$], 4.40 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.30 (dd, 1H, $J_{5,6e}$ 4.8 Hz, $J_{6e,6a}$ 10.4 Hz, H-6$_e$), 4.11 (m, 1H, H-2), 3.41 [d, 2H, *J* 4.7 Hz, OCH$_2$CH(OAc)C$\underline{H}_2$N$_3$], 2.08, 2.07, 1.95 (3s, 9H, 3CH_3CO). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.5, 170.2, 170.1, (3C=O), 136.8, 129.1, 128.3, 126.0 (Ph), 102.0 (C-1), 101.3 (PhCH), 78.5, (C-4), 71.7 (C-3), 70.5 [OCH$_2$C$\underline{H}$(OAc)CH$_2$N$_3$], 68.5 [OC$\underline{H}_2$CH(OAc)CH$_2$N$_3$], 67.0 (C-6), 66.4 (C-5), 54.1 (C-2), 50.5 [OCH$_2$CH(OAc)C$\underline{H}_2$N$_3$], 23.3 (C$\underline{H}_3$CON), 20.9, 20.8, (2C$\underline{H}_3$COO). Anal. calcd for $C_{22}H_{28}N_4O_9$: C, 53.65; H, 5.73; N, 11.38. Found: C, 53.82; H, 5.53; N, 11.12%.

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