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Stereoselective synthesis of oxiranes as a source of isoserine analogues using D-glucosamine and D-glucose derivatives as chiral templates☆

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Abstract—The synthesis of alkyl (*R*)-4,6-*O*-(2,3-epoxypropylidene) hexopyranoside derivatives from *N*-acetyl-D-glucosamine and D-glucose is described. The reaction of epoxidation with *m*-CPBA of the corresponding alkenylidene derivatives took place with different stereoselectivities depending upon the substitution of the unsaturated system, the protecting groups of the hydroxyl group at carbon three of the sugar moiety, and its configuration. The ring-opening reaction of these oxiranes with nitrogen nucleophiles gave phenylisoserine precursors.

1. Introduction

Stereoselective transformations from natural products are one of the most-effective procedures for the preparation of enantiomerically pure compounds of biological and pharmacological interest. Carbohydrates are important chiral templates for numerous asymmetric transformations.[2] Our group has been using 2-aminosugars as chiral templates in the stereoselective synthesis of different compounds (2,3-diaminoglucoses,[3] chiral oxazolidines,[4] and compounds with potential anti-cancer activity[3,5,6]). Due to the important role of oxiranes as intermediates in the asymmetric synthesis of chiral 1,2-difunctionalized compounds, we have recently developed a method for the stereoselective epoxidation of olefins. The olefinic chain was joined to different positions of a sugar molecule, acting as chiral inductor via various functions (glycoside, amide). The chiral epoxyalkyl glycosides[1,7] and the chiral epoxyamides[8] obtained can be transformed into different types of compounds. This method has enabled us to synthesize derivatives of glycosyl glycerol analogues that have been used as alkylating-agent carrier systems.[9] Our current aim is to obtain chiral oxiranes on a moiety that can be easily separated from the sugar.

Our primary interest in the synthesis of sugar-derived oxiranes is twofold. On the one hand, they are interesting in themselves, because compounds, which have an oxirane ring are reactive substances that act as alkylating agents, making them potential anti-cancer drugs. Moreover, as the oxirane fragment is joined to a sugar molecule, lipophilic moieties can bond, modulating the hydrophilic–lipophilic balance of the compound, enabling greater selectivity in the transport and localization of the drug.[10–12] In addition, the lability of the bond between the oxirane moiety and sugar provides ready release of the active fraction in the organism.

On the other hand, the oxiranes are compounds suitable for transformation into other compounds of biological interest. Those worthy of note are the α-hydroxy-β-aminoacids derived from isoserine, which are nonproteinogenic aminoacids, and important members of the β-aminoacid family. Isoserine derivatives constitute the essential fragment in natural products of high therapeutic value,[13] such as taxol (an anti-cancer agent), whose side chain is *N*-acyl-(2*R*,3*S*)-phenylisoserine, bestatin (a dipeptide modifier of the immune response), in which one of the aminoacids is (2*S*,3*R*)-2-hydroxy-3-amino-3-phenylbutyric acid, and the kinostatins (potent inhibitors of the HIV-1 protease), in which one of the constituent aminoacids is (2*S*,3*S*)-2-hydroxy-3-amino-3-phenylbutyric acid. Due to the β-aminoalcohol properties of these

☆ Potential anti-cancer drugs, Part 7. For Part 6, see: Ref. 1.

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compounds, one procedure that can be used for their synthesis is regio- and stereoselective opening with amines of chiral oxirane—linking this method with our line of research. Consequently, we began the synthesis of modified, enantiomerically pure isoserines, using sugars as chiral inductors, in order to study the effect of stereochemistry and the formation of alkyl analogues on their biological activity.

The aim was to obtain chiral oxiranes on a skeleton that could be transformed easily into modified isoserines, joined to a modified sugar moiety that acts as chiral inductor (and transporter in such case) via a labile bond enabling easy separation, chemically or enzymatically.

We believe that a straightforward manner to achieve this might be the oxidation of cinnamal acetals formed between positions 4 and 6 of a sugar molecule, for the following reasons: (a) these acetals are readily obtained compounds, and the reaction of oxidation of alkenes to oxiranes is well known and easy to perform; (b) to the best of our knowledge, there are no published precendents on the oxidation of cinnamal acetals of sugars; (c) we have used 2-aminosugars as chiral templates in the stereoselective synthesis of numerous compounds (2-aminoglycals,[14] 2-nitrosugars,[15] chiral oxazolidines,[4] chiral epoxyamides,[8] compounds with potential anticancer activity,[3,5,6] and epoxyalkyl glycosides[1,7]), and we think that the glucosamine moiety could serve as a chiral inductor in the oxidation reaction and as a carrier agent in derivatives with potential biological activity; and (d) the acetalic bond is labile, and the chiral inductor can be separated easily.

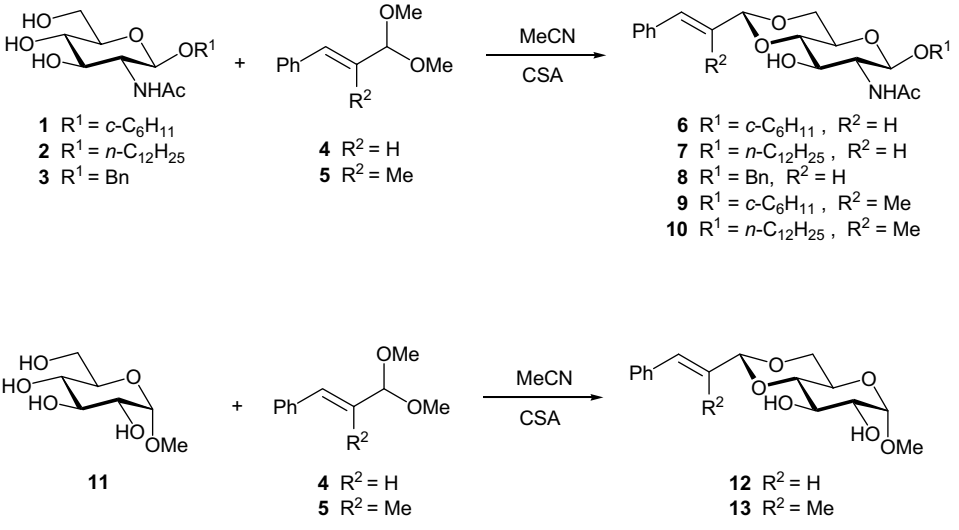
Herein, we report the epoxidation of the double bond of *trans*-cinnamaldehyde and α-methyl-*trans*-cinnamaldehyde, which have previously formed an acetal with the 4- and 6-hydroxyls of the alkyl glycoside of *N*-acetyl-D-glucosamine and D-glucose. Additionally, in order to find the substrate giving the best yields and diastereomeric excesses, we have used chiral substrates varying in (a) the anomeric configuration and the nature of the aglycon; (b) the substituent on carbon two of the sugar, *N*-acetyl-D-glucosamine, and D-glucose; (c) the protection of the hydroxyl group on carbon three; and (d) the configuration of carbon three: *gluco* and *allo* configuration.

The new compounds obtained are capable of being converted into new phenylisoserine analogues. We report the preliminary studies of the ring-opening reaction of an oxirane with two nitrogen nucleophiles, sodium azide, and piperidine.

2. Results and discussion

(*R*)-4,6-*O*-Alkenylidene hexopyranosides, whose oxidation has been studied are compounds **6**–**10** and **12**–**24** (Schemes 1–4). An attempt was made to study 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 three groups: compounds with a *gluco* configuration and the C-3 hydroxyl group free **6**–**10**, **12**, and **13**; compounds with the C-3 hydroxyl group blocked **14**–**23**, and the compound with an *allo* configuration **24**.

(*R*)-4,6-*O*-Alkenylidene glucopyranosides **6**–**10** were obtained by reaction of alkyl 2-acetamido-2-deoxy-D-glucopyranosides[5,16] **1**–**3** and *trans*-cinnamaldehyde dimethyl acetal **4** or α-methyl-*trans*-cinnamaldehyde dimethyl acetal **5** in good yields using the procedure described by Murphy et al.[17] for the formation of acetals using aldehyde dimethyl acetal as reagent. The same method was used for the preparation of compounds **12** and **13** from methyl α-D-glucopyranoside **11** (Scheme 1). The reagent α-methyl-*trans*-cinnamaldehyde dimethyl acetal **5**, obtained by the procedure described in the preparation of *trans*-cinnamaldehyde dimethyl acetal[18] **4**, was characterized by its mass and NMR spectra.



1 R^1 = *c*-C_6H_{11}
2 R^1 = *n*-$C_{12}H_{25}$
3 R^1 = Bn

4 R^2 = H
5 R^2 = Me

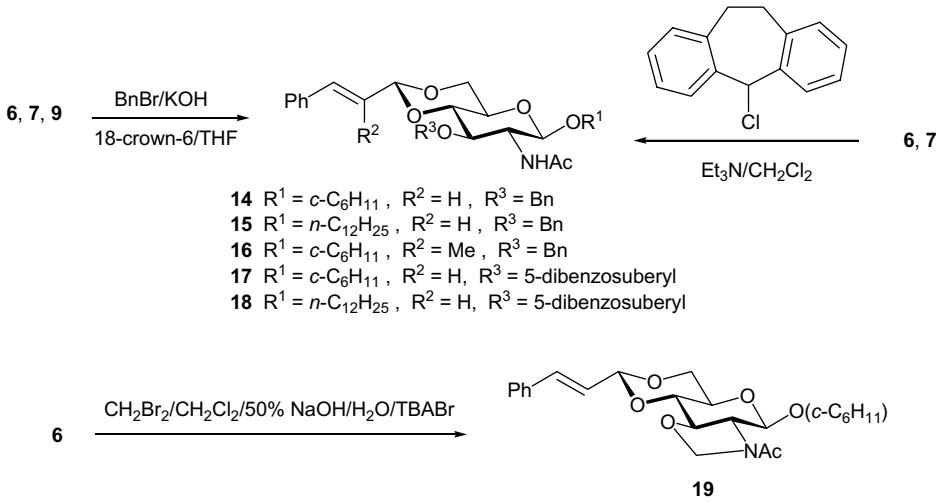
6 R^1 = *c*-C_6H_{11}, R^2 = H
7 R^1 = *n*-$C_{12}H_{25}$, R^2 = H
8 R^1 = Bn, R^2 = H
9 R^1 = *c*-C_6H_{11}, R^2 = Me
10 R^1 = *n*-$C_{12}H_{25}$, R^2 = Me

11

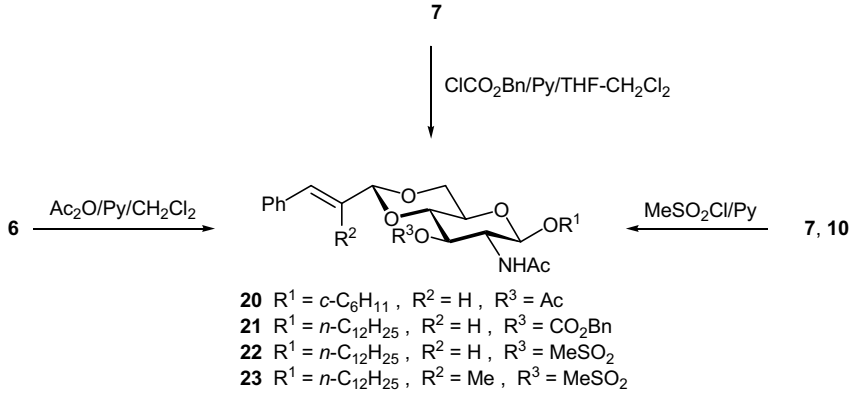
4 R^2 = H
5 R^2 = Me

12 R^2 = H
13 R^2 = Me

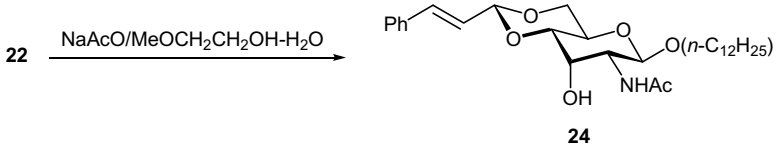
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

The NMR spectra for compounds **6**–**10**, **12**, and **13** showed signals corresponding to the unsaturated moiety incorporated into the sugar molecule in the acetalation reaction. The ^{1}H spectra showed a signal at 5.2–5.0 ppm corresponding to the acetal proton, and another at 6.8–6.6 ppm corresponding to the olefinic proton at the α-position to the phenyl group. Compounds **6**–**8** and **12** showed a signal at 6.2–6.1 ppm corresponding to the other olefinic proton, while compounds **9**, **10**, and **13** showed a singlet at 1.9–1.8 ppm corresponding to the methyl group on the double bond. Compounds **6**–**10**, **12**, and **13** showed a doublet at 4.7–4.0 ppm for H-1 as characteristic signal of the sugar moiety.

The syntheses of compounds **14**–**18** were carried out from **6**, **7**, or **9** by means of several alkylation processes of the C-3 hydroxyl group as indicated in Scheme 2. The ^{1}H NMR spectra of these compounds showed the signals corresponding to the protecting group introduced: two doublets at 4.88 and 4.63 ppm for **14**, **15**, and **16**, a singlet at 5.65 ppm corresponding to the suberyl group for **17** and **18**, and two doublets at 5.52 and 4.73 ppm for **19**.

Compounds **6**, **7**, and **10** were acylated with different reagents, giving compounds **20**–**23** (Scheme 3). Compound **20** showed a singlet at 1.74 ppm in ^{1}H and a signal at 20.6 ppm in the ^{13}C NMR spectra, corresponding to the acetyl group. The ^{13}C NMR spectrum of **21** gave a signal at 155.1 ppm for the new carbonyl group introduced. Compounds **22** and **23** showed characteristic signals corresponding to the methanosulfonyl group at

3.03 ppm in the ^{1}H and at 38.5 ppm in the ^{13}C NMR spectra.

Compound **24** was synthesized from compound **22** by the same procedure described for similar compounds[4] (Scheme 4). ^{1}H NMR showed mayor chemical shifts for the signals corresponding to H-2 (4.10 ppm) and H-3 (4.21 ppm), and a change in the multiplicity, with respect to compound **7**, the isomer of *gluco* configuration.

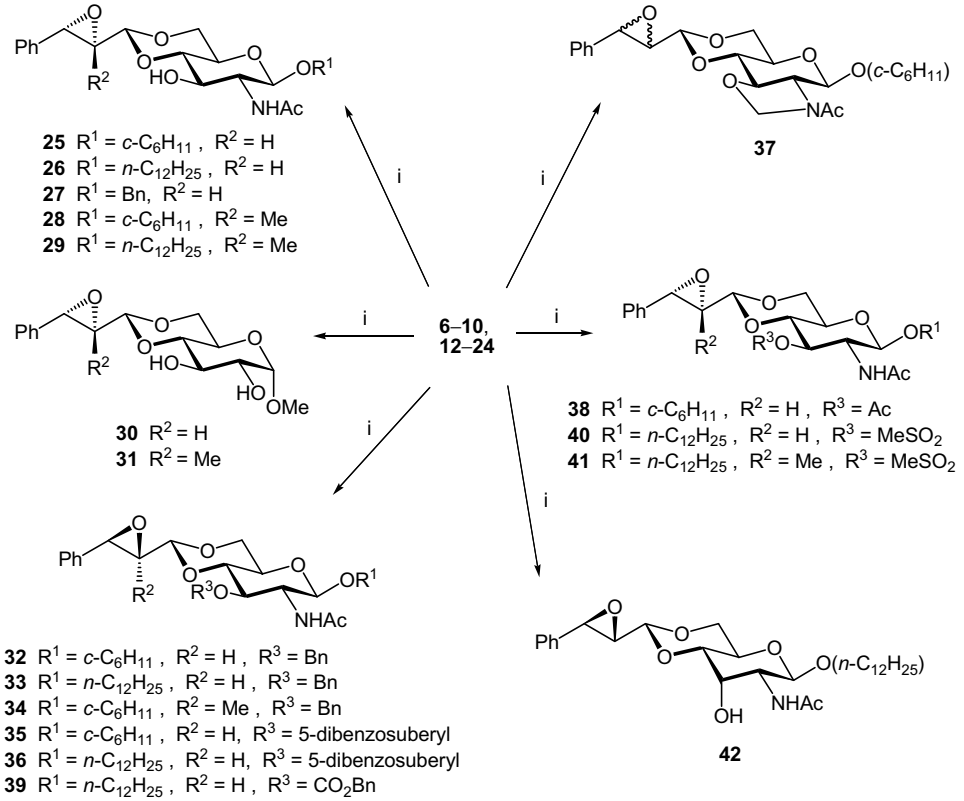
The reaction of **6**–**10** and **12**–**24** with *m*-CPBA in chloroform at different temperatures gave the corresponding oxiranes **25**–**42**. The compounds were isolated and purified by flash chromatography on silica gel (Scheme 5, Table 1). The ^{1}H NMR spectra for these compounds showed the characteristic signals of the oxirane system at 3.9 and 3.3 ppm for **25**–**27**, **30**, **32**, **33**, **35**–**40**, and **42**, and at 4.15 and 1.10 ppm for the other compounds. The ^{13}C NMR spectra showed signals between 62 and 54 ppm for each of the compounds **25**–**42**.

The diastereomeric excesses (de), determined using ^{1}H NMR, are shown in Table 1, from which certain inferences can be drawn. For their analysis, the starting (*R*)-4,6-*O*-propylidene acetals can be grouped into the three groups defined above. The first group comprises of the compounds with the 3-hydroxyl group free (**6**–**10**, **12**, and **13**); the second group is the compounds with the 3-hydroxyl group blocked (**14**–**23**), and the third is compound **24** with an *allo* configuration. As expected, in the oxidation of a compound, the de is higher when the reaction temperature is lower. With regard to the degree of substitution of the double bond, the results show that the de obtained when the substituent on the double bond is R^2 = Me (entries 4, 5, 7, 11, and 19) is higher

Table 1. Epoxidation of (*R*)-4,6-*O*-propenylidene derivatives **6**–**10**, **12**–**24** with *m*-CPBA at −15 °C

Entry	Starting compound	Reaction product	Yield[a] (%)	De[b] (%)	Major oxirane configuration
1	**6**	**25**	84	42	2*R*,3*S*
2	**7**	**26**	77	34	2*R*,3*S*
3	**8**	**27**	58	42	2*R*,3*S*
4	**9**	**28**	81	74	2*R*,3*S*
5	**10**	**29**	72	56	2*R*,3*S*
6	**12**	**30**	77	46	2*R*,3*S*
7	**13**	**31**	78	72	2*R*,3*S*
8	**14**	**32**	82	28	2*S*,3*R*
9	**15**	**33**	86	22	2*S*,3*R*
10	**15**	**33**	89[c]	13[c]	2*S*,3*R*
11	**16**	**34**	86	34	2*S*,3*R*
12	**17**	**35**	72	36	2*S*,3*R*
13	**17**	**35**	80[c]	32[c]	2*S*,3*R*
14	**18**	**36**	69	24	2*S*,3*R*
15	**19**	**37**	65	0	
16	**20**	**38**	68	0	
17	**21**	**39**	72	12	2*S*,3*R*
18	**22**	**40**	75	2	2*R*,3*S*
19	**23**	**41**	68	12	2*R*,3*S*
20	**24**	**42**	60	66	2*S*,3*R*

[a] Yields refer to compounds obtained in each reaction after isolation and purification.
[b] Determined by integration in ^{1}H NMR spectra of reaction mixtures.
[c] Reaction at room temperature.



Scheme 5. Reagent: (i) *m*-CPBA/$CHCl_3$.

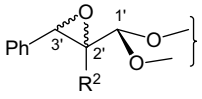
than when R^2 = H (entries 1, 2, 6, 8, and 18). Thus, compounds **28**, **29**, **31**, **34**, and **41** were obtained with des of 74%, 56%, 72%, 34%, and 12%, respectively, while compounds **25**, **26**, **30**, **32**, and **40** were obtained with des of 42%, 34%, 46%, 28%, and 2%, respectively. With regard to the functionalization of position three of the sugar, the results show that the compounds of the first group (*gluco* configuration, hydroxyl 3 free) present des higher than those for the corresponding compounds of the second group (same configuration, hydroxyl 3 blocked). Thus, the de for **25** was 42%, while the des for compounds **32**, **35**, and **38** were 28%, 36%, and 0%, respectively; for **28** the de was 74%, while that for **34** was 34%. These results support the idea of the formation of a hydrogen bond between the 3-OH group and the peroxyacid in the transition state related to the electrophilic addition to the double bond that controls the stereochemical course of the reaction, and are similar to those found in the epoxidation reaction of alkenyl glycosides[1,7,19] with *m*-CPBA. In the case of the alkenyl glycosides, it has been demonstrated that the reactive face in the epoxidation reaction is the *Re* face (see, e.g., Ref. 1). Given that the distance between the 2-NH and the double bond of the glycoside and their relative disposition are the same as those observed between the 3-OH and the double bond of the propylidene acetals presented herein, we tentatively propose that the more-reactive face of the double bond is the same in both types of compound—that is the *Re*,*Re* face of the propylidene acetals with the 3-hydroxyl group free.

With regard to the configuration of position three of the sugars, it is remarkable that the epoxidation of compound **24**, with an *allo* configuration, led to compound **42**, with a de of 66%, the highest de obtained for the oxidation of a compound derived from cinnamaldehyde.

At the same time, it is important to analyze the chemical shifts of the protons corresponding to the oxidized acetal system in the ^{1}H NMR spectra (Table 2). The signal for H-3′ is easily identifiable in the ^{1}H spectra at approximately 4 ppm, as a doublet for compounds with R^2 = H and as a singlet for compounds with R^2 = Me. In all spectra for the compounds of the first group (3-hydroxyl group free) with R^2 = H (**25**, **26**, **27**, and **30**), the doublet corresponding to H-3′ of the major isomer appeared at lower chemical shift than that of the minor isomer (entries 1, 2, 3, and 6), so that we assign the same configuration in the oxirane ring (2*R*,3*S*) to the major isomer for each of these compounds, bearing in mind the above remarks.

Comparison of the signal for H-3′ of compounds **25** and **26** with that of the compounds in the second group (3-hydroxyl group blocked) showed changes in the previously described pattern. Compounds **32** and **35** present the doublet of the major isomer at higher chemical shift than that of the minor isomer (a different profile to that presented by compound **25**). Compounds **33**, **36**, and **39** present a profile for the H-3′ doublets similar to that presented by compounds **32** and **35**, but different to that presented by compound **26**. We assigned the (2*S*,3*R*)-configuration for the oxirane ring of the major isomer of compounds **32**, **33**, **35**, **36**, and **39**, which have the 3-hydroxyl group blocked with an aromatic protecting group (see below). Compound **40**, however, (in which the hydroxyl group on three is blocked with a nonaromatic protecting group) presents the same profile as

Table 2. ^{1}H NMR data (δ, ppm) for the acetalic group in compounds with the oxirane ring **25**–**42**



Entry	Compound	H-1′	H-2′	CH_3	H-3′
1	**25**	4.62(M)/4.60(m)	3.29(M)/	—	3.99(m)/3.98(M)
2	**26**	4.63(M)/4.62(m)		—	3.99(m)/3.98(M)
3	**27**	4.67(M)/	3.24(M)/	—	4.00(m)/3.94(M)
4	**28**	4.47(M)/4.43(m)	—	1.00(M)/0.99(m)	
5	**29**	4.47(M)/4.44(m)	—	1.11(M)/1.09(m)	4.14(M)/4.13(m)
6	**30**	4.69(M)/4.65(m)	3.22(M)/	—	3.99(m)/3.97(M)
7	**31**	4.47(M)/4.41(m)	—	1.10(M)/1.09(m)	4.16(M)/4.11(m)
8	**32**		3.30(M)/3.27(m)	—	4.00(M)/3.97(m)
9	**33**	4.70(M)/4.64(m)	3.20(M)/	—	3.96(M)/3.93(m)
10	**34**	4.47(M)/4.40(m)	—	1.12(M)/1.10(m)	4.15(M)/4.10(m)
11	**35**	4.61(M)/4.59(m)		—	3.97(M)/3.93(m)
12	**36**	4.60(M)/		—	3.96(M)/3.93(m)
13	**37**	4.65		—	3.99/3.93
14	**38**	4.59	3.14	—	3.89/3.87
15	**39**	4.64(M)/4.56(m)	3.16(M)/	—	3.92(M)/3.88(m)
16	**40**	4.63(m)/4.53(M)	3.15(M)/	—	3.91(m)/3.89(M)
17	**41**	4.52(m)/4.34(M)	—		1.08(m)/1.04(M)
18	**42**	4.68(M)/4.65(m)	3.19(M)/	—	3.93(M)/3.91(m)

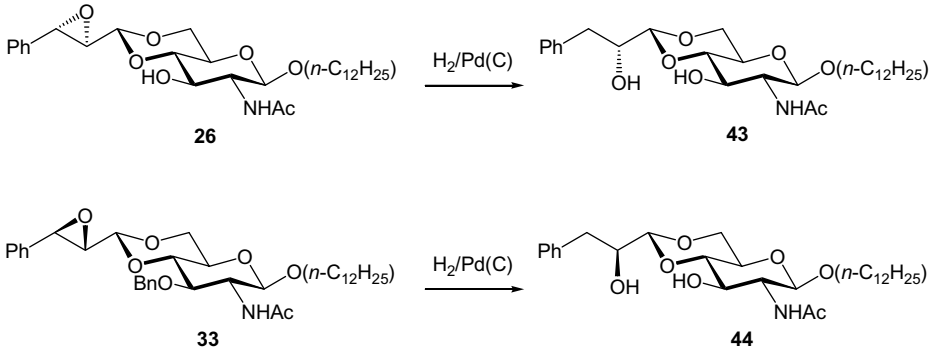
(M) For the major isomer.
(m) For the minor isomer.

compound **26**, meaning that we assigned a (2*R*,3*S*)-configuration for the major isomer of compound **40**.

Comparison of the H-3′ signal for compound **42** (third-group compound) with that for compound **26** shows that the profiles for the two compounds are different. We assign the (2*S*,3*R*)-configuration for the oxirane ring of the major isomer of compound **42**.

In order to demonstrate that the ^{1}H spectra profiles for the compounds of the first and second groups are different because the face of the double bond is more reactive in the epoxidation is different in the two groups of compounds, we carried out the hydrogenolysis of compounds **26** and **33** (Scheme 6). The hydrogenolysis of **26** led to compound **43**, and that of **33** to **44**. Table 3 shows the chemical shift for the most-characteristic protons in the ^{1}H NMR spectra of compounds **43** and **44**. The results confirm that the major isomer of compound **43** has a different configuration to that of the major isomer of compound **44**, implying that the compounds derived from **26** and **33** have different configurations.

We also studied the ring-opening reactions of oxirane **28** with two different nitrogen nucleophiles (sodium azide and piperidine), giving compounds **45** and **46**, in good yield and diastereomeric excess (Scheme 7). In both cases, the oxirane ring reacted regioselectively via the least-substituted carbon (benzylic carbon). The ^{13}C NMR spectra showed the characteristic signals corresponding to CHN_3 at 69.0 ppm (for **45**), to $CHNR_2$ at 73.4 ppm, and to CH_2NCH_2 at 53.1 ppm (for **46**). Compounds **45** and **46** have an α-hydroxy-β-aminoacetal structure, and can be used as precursors of phenylisoserine analogues.

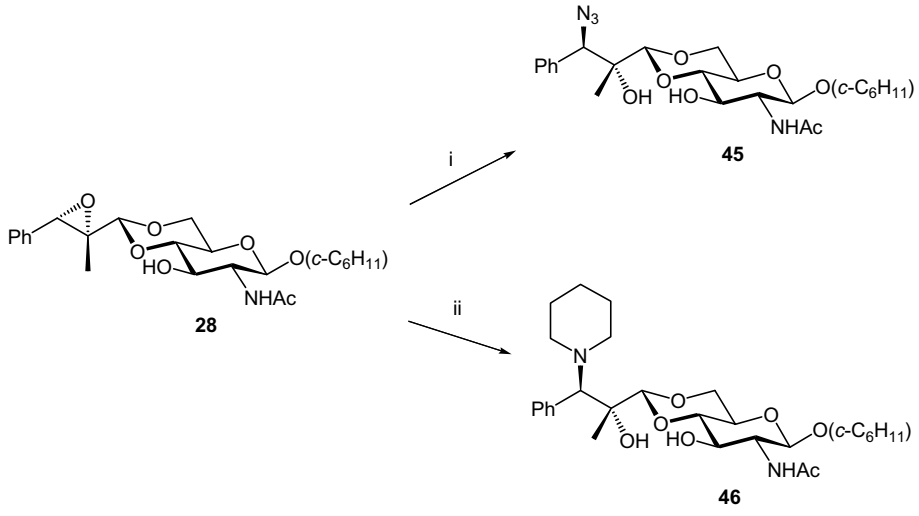


Scheme 6.

Table 3. ^{1}H NMR data (δ, ppm) for compounds **43** and **44**

Entry	Compd	H-1′	H_A-3′	H_B-3′	H-1	H-6_e
1	**43**	4.46(M)/4.41(m)	2.94(m)/2.89(M)	2.79(M)/2.75(m)	4.61(M)/4.59(m)	4.22(M)/4.18(m)
2	**44**	4.45(m)/4.43(M)	2.96(M)/2.91(m)	2.82(m)/2.73(M)	4.65(m)/4.62(M)	4.25(m)/4.20(M)

(M) For the major isomer.
(m) For the minor isomer.



Scheme 7. Reagents: (i) $NaN_3/LiClO_4/CH_3CN$; (ii) piperidine/$LiClO_4/CH_3CN$.

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 were obtained on a Stuart Melting Point Apparatus SMP 10 and are uncorrected. Optical rotations were obtained on a Perkin Elmer Polarimeter Model 341 at 25 °C. Mass spectra were recorded on a Micromass AUTOSPECQ mass spectrometer, EI at 70 eV and CI at 150 eV; HR mass measurements with resolutions of 10,000. 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.

3.1.1. α-Methyl-*trans*-cinnamaldehyde dimethyl acetal 5. A mixture of α-methyl-*trans*-cinnamaldehyde (35 mL, 0.25 mol), trimethylorthoformate (33 mL, 0.30 mol), anhydrous methanol (225 mL), and anhydrous camphorsulfonic acid (0.25 g) was stirred at room temperature for 4 days. At the end of this time, the alcohol was removed with a rotary evaporator, and the residue was distilled, yielding 36 g (75%); MS (FAB): *m/z* 215 (10%) $[M+Na]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 6.67 [s, 1H, PhC*H*= C(CH_3)-$CH(OCH_3)_2$], 4.66 [s, 1H, PhCH=C(CH_3)C*H*(OCH_3)$_2$], 3.39 [s, 6H, PhCH=C(CH_3)CH(OC*H*$_3$)$_2$], 1.90 [s, 3H, PhCH=C(C*H*$_3$)CH(OCH_3)$_2$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 136.4–127.5 (Ph), 133.8 [PhCH=*C*(CH_3)-$CH(OCH_3)_2$], 126.1 [Ph*C*H=C(CH_3)CH(OCH_3)$_2$], 106.7 [PhCH=C(CH_3)*C*H(OCH_3)$_2$], 52.5 [PhCH=C(CH_3)- CH(O*C*H$_3$)$_2$], 12.5 [PhCH=C(*C*H$_3$)-$CH(OCH_3)_2$]. HRMS (FAB): $[M+Na]^+$, found 215.104763. $C_{12}H_{16}O_2$ Na requires 215.104800.

3.2. Alkyl 2-acetamido-(*R*)-4,6-*O*-alkenylidene-2-deoxy-β-D-glucopyranosides 6–10

To a suspension of alkyl 2-acetamido-2-deoxy-β-D-glucopyranoside **1**–**3** (15.0 mmol) in acetonitrile (90 mL) was added the corresponding aldehyde dimethylacetal **4**, **5** (25.0 mmol), and anhydrous camphorsulfonic acid (15 mg). The mixture was stirred at room temperature until the reaction was complete (1–2 weeks, TLC). The reaction mixture was then filtered, the solid stirred in hexane and the mixture filtered again; the solid was stirred in water, and the product obtained by filtration. The product was recrystallized from 96% ethanol.

3.2.1. *c*-Hexyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside 6. Yield 4.4 g (71%); mp 260–262 °C; $[\alpha]_D = -108.0$ (*c* 0.5, MeOH); MS (CI): *m/z* 418 (57%) $[M+H]^+$. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.8 (d, 1H, $J_{2,NH}$ 9.0 Hz, NH), 7.5–7.3 (m, 5H, Ph), 6.76 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.23 (dd, 1H, J_{trans} 16.1 Hz, *J* 5.1 Hz, PhCH=C*H*CH), 5.22 (d, 1H, $J_{3,OH}$ 5.8 Hz, OH), 5.19 (d, 1H, *J* 5.1 Hz, PhCH=CHC*H*), 4.53 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.10 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.1 Hz, H-6_e), 3.6–3.5 (m, 3H, H-3, H-6_a, OCHR), 3.38 (m, 1H, H-2), 3.28 (t, 1H, $J_{3,4} = J_{4,5}$ 9.2 Hz, H-4), 3.22 (dd, 1H, $J_{4,5} = J_{5,6a}$ 9.5 Hz, $J_{5,6e}$ 4.8 Hz, H-5), 1.79 (s, 3H, CH_3CON), 1.7–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.0 (C=O), 135.6–126.7 (Ph), 133.1 (Ph*C*H=CHCH), 125.3 (PhCH=*C*HCH), 100.3, 100.0 (C-1, PhCH=CH*C*H), 81.1 (C-4), 75.9 (OCHR), 70.3 (C-3), 67.6 (C-6), 65.8 (C-5), 56.6 (C-2), 32.9–22.8 [$(CH_2)_5$], 23.1 (*C*H_3CON). HRMS (CI): $[M+H]^+$, found 418.221858. $C_{23}H_{32}NO_6$ requires 418.222963. Anal. Calcd for $C_{23}H_{31}NO_6$: C, 66.17; H, 7.48; N, 3.35. Found: C, 65.88; H, 7.33; N, 3.33.

3.2.2. 1-Dodecyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside 7. Yield 5.7 g (75%); mp 252–254 °C; $[\alpha]_D = -68.0$ (*c* 1.0, EtOH); MS (CI): *m/z* 504 (19%) $[M+H]^+$. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.71 (d, 1H, $J_{2,NH}$ 8.9 Hz, NH), 7.5–7.3 (m, 5H, Ph), 6.76 (d, 1H, J_{trans} 16.2 Hz, PhC*H*=CHCH), 6.21 (dd, 1H, J_{trans} 16.2 Hz, *J* 5.0 Hz, PhCH=C*H*CH), 5.20 (d, 1H, *J* 5.0 Hz, PhCH=CHC*H*), 5.13 (d, 1H, $J_{3,OH}$ 5.6 Hz, OH), 4.43 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.11 (dd, 1H, $J_{5,6e}$ 4.8 Hz, $J_{6e,6a}$ 10.1 Hz, H-6_e), 3.66 (m, 1H, OCH_AH$_B$R), 3.61 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.1 Hz, H-6_a), 3.58 (m, 1H, H-3), 3.47 (m, 1H, H-2), 3.38 (m, 1H, OCH$_A$$H_B$R), 3.30 (t, 1H, $J_{3,4} = J_{4,5}$ 9.3 Hz, H-4), 3.2 (m, 1H, H-5), 1.80 (s, 3H, CH_3CON), 1.4–1.2 [m, 20H, $(CH_2)_{10}$], 0.85 (t, 3H, *J* 6.8 Hz, CH_3). ^{13}C NMR (125 MHz, DMSO-d_6): δ 169.0 (C=O), 135.6–126.7 (Ph), 133.1 (Ph*C*H=CHCH), 125.3 (PhCH=*C*HCH), 101.4 (C-1), 100.1 (PhCH=CH*C*H), 81.0 (C-4), 70.4 (C-3), 68.5 (OCH_2R), 67.5 (C-6), 65.8 (C-5), 56.2 (C-2), 31.1–21.9 [$(CH_2)_{10}$], 22.8 (*C*H_3CON), 13.7 (CH_3). HRMS (EI): $[M]^{+\cdot}$, found 503.324320. $C_{29}H_{45}NO_6$ requires 503.324689. Anal. Calcd for $C_{29}H_{45}NO_6$: C, 69.15; H, 9.00; N, 2.78. Found: C, 69.24; H, 8.99; N, 2.79.

3.2.3. Benzyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside 8. Yield 3.9 g (61%); mp 268–269 °C; $[\alpha]_D = -54.2$ (*c* 1.0, DMF); MS (CI): *m/z* 426 (100%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.4–7.3 (m, 10H, 2Ph), 6.80 (d, 1H, J_{trans} 16.0 Hz, PhC*H*=CHCH), 6.19 (dd, 1H, J_{trans} 16.0 Hz, *J* 4.7 Hz, PhCH=C*H*CH), 5.47 (d, 1H, $J_{2,NH}$ 5.4 Hz, NH), 5.21 (d, 1H, *J* 4.7 Hz, PhCH=CHC*H*), 4.90 (d, 1H, J_{gem} 12.0 Hz, OCH_AH$_B$Ph), 4.62 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 4.57 (d, 1H, J_{gem} 12.0 Hz, OCH$_A$$H_B$Ph), 4.31 (dd, 1H, $J_{6e,6a}$ 10.2 Hz, $J_{5,6e}$ 4.7 Hz, H-6_e), 4.00 (t, 1H, $J_{2,3} = J_{3,4}$ 8.2 Hz, H-3), 3.73 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.2 Hz, H-6_a), 3.6–3.3 (m, 3H, H-2, H-4, H-5), 1.95 (s, 3H, CH_3CON). ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.2 (C=O), 138.0–126.8 (Ph), 133.2 (Ph*C*H=CHCH), 125.2 (PhCH=*C*HCH), 101.5, 100.4 (PhCH=CH*C*H, C-1), 81.0 (C-4), 70.4 (C-3), 70.0 (O*C*H_2Ph), 67.5

(C-6), 66.0 (C-5), 56.1 (C-2), 23.1 (CH_3CON). HRMS (CI): $[M+H]^+$, found 426.190361. $C_{24}H_{28}NO_6$ requires 426.191663. Anal. Calcd for $C_{24}H_{27}NO_6$: C, 67.76; H, 6.35; N, 3.29. Found: C, 67.63; H, 6.41; N, 3.24.

3.2.4. *c*-Hexyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-(*E*-2-methyl-3-phenyl-2-propenylidene)-β-D-glucopyranoside 9. Yield 5.2 g (81%); mp 174–175 °C; $[\alpha]_D = -155.6$ (*c* 0.3, EtOH); MS (EI): *m/z* 431 (26%) $[M]^{+\cdot}$. ^1H NMR (500 MHz, DMSO-d_6): δ 7.8 (d, 1H, $J_{2,NH}$ 9.0 Hz, NH), 7.5–7.3 (m, 5H, Ph), 6.65 [s, 1H, PhC*H*=C(CH_3)CH, 5.23 (d, 1H, $J_{3,OH}$ 5.8 Hz, OH), 5.04 [s, 1H, PhCH=C(CH_3)C*H*], 4.56 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.12 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.2 Hz, H-6_e), 3.61 (dd, 1H, $J_{2,3} = J_{3,4}$ 9.5 Hz, $J_{3,OH}$ 5.6 Hz, H-3), 3.59 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.1 Hz, H-6_a), 3.52 (m, 1H, OCHR), 3.36 (dd, 1H, $J_{1,2}$ 8.4 Hz, $J_{2,3}$ 9.3 Hz, H-2), 3.28 (t, 1H, $J_{3,4} = J_{4,5}$ 9.2 Hz, H-4), 3.22 (m, 1H, H-5), 1.83 [d, 3H, ^4J 1.2 Hz, PhCH=C(C*H*$_3$)CH], 1.72 (s, 3H, CH_3CON), 1.7–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (125 MHz, DMSO-d_6): δ 168.2 (C=O), 135.5–127.4 (Ph), 133.4 [PhCH=*C*(CH_3)CH], 126.2 [Ph*C*H=C(CH_3)CH], 103.1 [PhCH(CH_3)*C*H], 99.2 (C-1), 80.3 (C-4), 75.1 (OCHR), 69.5 (C-3), 66.9 (C-6), 65.1 (C-5), 56.0 (C-2), 32.1–22.0 [$(CH_2)_5$], 22.3 (*C*H_3CON), 12.3 (CH_3). HRMS (EI): $[M]^{+\cdot}$, found 431.230877. $C_{24}H_{33}NO_6$ requires 431.230788. Anal. Calcd for $C_{24}H_{33}NO_6$: C, 66.80; H, 7.71; N, 3.25. Found: C, 66.55; H, 7.52; N, 3.39.

3.2.5. 1-Dodecyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-(*E*-2-methyl-3-phenyl-2-propenylidene)-β-D-glucopyranoside 10. Yield 5.4 g (70%); mp 214–215 °C; $[\alpha]_D = -53.3$ (*c* 0.8, EtOH); MS (CI): *m/z* 518 (100%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 6.66 [s, 1H, PhC*H*=C(CH_3)CH], 5.75 (d, 1H, $J_{2,NH}$ 5.4 Hz, NH), 5.01 [s, 1H, PhCH=C(CH_3)C*H*], 4.67 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.26 (dd, 1H, $J_{5,6e}$ 4.3 Hz, $J_{6e,6a}$ 10.1 Hz, H-6_e), 4.12 (dd, 1H, $J_{2,3} = J_{3,4}$ 8.9 Hz, H-3), 3.9–3.8 (m, 1H, OC$H_A$$H_B$R), 3.69 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 9.8 Hz, H-6_a), 3.5–3.3 (m, 4H, H-2, H-4, H-5, OC$H_A$$H_B$R), 2.04 (s, 3H, CH_3CON), 1.90 [d, 3H, ^4J 1.4 Hz, PhCH=C(C*H*$_3$)CH], 1.6–1.2 [m, $(CH_2)_{10}$], 0.86 (t, 3H, *J* 6.5 Hz, CH_3). ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.1 (C=O), 136.3–128.3 (Ph), 134.1 [PhCH=*C*(CH_3)CH], 127.1 [Ph*C*H=C(CH_3)CH], 104.0 101.6 [(C-1), PhCH(CH_3)*C*H], 81.0 (C-4), 70.4 (C-3), 68.7 (OCH_2R), 67.6 (C-6), 66.0 (C-5), 56.3 (C-2), 31.4–22.2 [$(CH_2)_{10}$], 23.0 (*C*H_3CON), 14.0 (CH_3), 13.1 [PhCH=C(*C*H_3)CH]. HRMS (EI): $[M]^{+\cdot}$, found 517.340208. $C_{30}H_{47}NO_6$ requires 517.340339. Anal. Calcd for $C_{30}H_{47}NO_6$: C, 69.60; H, 9.15; N, 2.71. Found: C, 69.27; H, 8.90; N, 2.71.

3.3. Methyl (*R*)-4,6-*O*-alkenylidene-α-D-glucopyranosides 12 and 13

To a solution of methyl α-D-glucopyranoside **11** (15.0 mmol) in acetonitrile (90 mL) was added the corresponding aldehyde dimethylacetal **4**, **5** (25.0 mmol) and camphorsulfonic acid (15 mg). The mixture was stirred at room temperature for 3 days. After checking by TLC that all of the starting material had reacted, triethylamine was added until pH 7. The reaction mixture was evaporated to a reduced volume (≅15 mL) and left overnight at 5 °C. Compound **6** precipitated and was obtained by filtration and purified by column chromatography. In the case of **7**, after neutralization of the acidic medium, the reaction mixture was evaporated and a syrup obtained. Column chromatography gave the pure compound **7** in good yield.

3.3.1. Methyl (*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-α-D-glucopyranoside 12. Column chromatography using dichloromethane–methanol (30:1) yielded 4.2 g (90%); mp 152–153 °C; $[\alpha]_D = +97.2$ (*c* 1.4, CH_2Cl_2); MS (CI): *m/z* 309 (55%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 6.79 (d, 1H, J_{trans} 16.2 Hz, PhC*H*=CHCH), 6.18 (dd, 1H, J_{trans} 16.2 Hz, *J* 4.8 Hz, PhCH=C*H*CH), 5.15 (dd, 1H, *J* 4.8 Hz, ^4J 0.8 Hz, PhCH=CHC*H*), 4.8 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.15 (dd, 1H, $J_{5,6e}$ 3.8 Hz, $J_{6e,6a}$ 9.2 Hz, H-6_e), 3.90 (t, 1H, $J_{2,3} = J_{3,4}$ 9.2 Hz, H-3), 3.7–3.5 (m, 3H, H-2, H-5, H-6_a), 3.4–3.3 (m, 4H, H-4, OCH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 135.6–126.8 (Ph), 134.2 (Ph*C*H=CHCH), 124.0 (PhCH=*C*HCH), 100.9 (PhCH=CH*C*H), 99.8 (C-1), 80.4 (C-4), 72.7 (C-2), 71.1 (C-3), 68.4 (C-6), 62.2 (C-5), 55.3 (OCH_3). HRMS (EI): $[M]^{+\cdot}$, found 308.125585. $C_{16}H_{20}O_6$ requires 308.125989. Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 62.17; H, 6.49.

3.3.2. Methyl (*R*)-4,6-*O*-(*E*-2-methyl-3-phenyl-2-propenylidene)-α-D-glucopyranoside 13. Column chromatography using dichloromethane–methanol (30:1) yielded 3.2 g (67%); mp 105–106 °C; $[\alpha]_D = +119.1$ (*c* 1.1, CH_2Cl_2); MS (CI): *m/z* 323 (75%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 6.64 [d, 1H, ^4J 1.2 Hz, PhC*H*=C(CH_3)CH], 4.96 [s, 1H, PhCH=C(CH_3)C*H*], 4.73 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.18 (dd, 1H, $J_{5,6e}$ 3.6 Hz, $J_{6e,6a}$ 8.9 Hz, H-6_e), 3.90 (t, 1H, $J_{2,3} = J_{3,4}$ 9.2 Hz, H-3), 3.7–3.5 (m, 3H, H-2, H-5, H-6_a), 3.4–3.3 (m, 4H, H-4, OCH_3), 1.90 [d, 3H, ^4J 1.2 Hz, PhCH=C(C*H*$_3$)CH]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 136.5–128.0 (Ph), 133.6 [PhCH=*C*(CH_3)CH], 126.9 [Ph*C*H=C(CH_3)CH], 105.2 [PhCH=C(CH_3)*C*H], 99.8 (C-1), 80.4 (C-4), 72.8 (C-2), 71.4 (C-3), 68.5 (C-6), 62.3 (C-5), 55.4 (OCH_3), 13.0 [PhCH=C(*C*H_3)CH]. HRMS (EI): $[M]^{+\cdot}$, found 322.141336. $C_{17}H_{22}O_6$ requires 322.141639. Anal. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.57; H, 6.87.

3.4. Alkyl 2-acetamido-(*R*)-4,6-*O*-alkenylidene-3-*O*-alkyl-2-deoxy-β-D-glucopyranosides 14–18

Method A: To a cooled solution (5 °C) of alkyl 2-acetamido-(*R*)-4,6-*O*-alkenylidene-2-deoxy-β-D-glucopyranosides **6**, **7**, **9** (6.0 mmol) in fresh distilled THF (60 mL) were added, successively, freshly powdered potassium hydroxide (2.0 g, 35.7 mmol), 18-crown-6 (120 mg, 0.4 mmol), and benzyl bromide (8.4 mmol). The reaction mixture was stirred at this temperature for 3 h, and left overnight at room temperature, then diluted with dichloromethane (60 mL) and washed successively with water and an aqueous saturated solution of sodium bicarbonate, dried over $MgSO_4$, filtered, and the filtrate

evaporated to dryness. The solid obtained was purified by flash chromatography on silica gel.

3.4.1. *c*-Hexyl 2-acetamido-3-*O*-benzyl-2-deoxy-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside 14. Column chromatography using dichloromethane–methanol (120:1) yielded 2.2 g (73%); mp 245–246 °C; $[\alpha]_D$ = +5.5 (*c* 1.1, $CHCl_3$); MS (CI): *m/z* 508 (22%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.3 (m, 10H, 2Ph) 6.78 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.18 (dd, 1H, *J* 4.4 Hz, J_{trans} 16.1 Hz, PhCH=C*H*CH), 5.73 (d, 1H, $J_{2,NH}$ 7.4 Hz, NH), 5.16 (dd, 1H, *J* 4.5 Hz, ^4J 0.9 Hz, PhCH=CHC*H*), 5.11 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.88 (d, 1H, J_{gem} 11.8 Hz, OC*H*$_A$H$_B$Ph), 4.64 (d, 1H, J_{gem} 11.8 Hz, OCH$_A$*H*$_B$Ph), 4.36 (t, 1H, $J_{2,3} = J_{3,4}$ 8.5 Hz, H-3), 4.25 (dd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 10.2 Hz, H-6$_e$), 3.68 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.2 Hz, H-6$_a$), 3.6–3.4 (m, 3H, H-4, H-5, OCHR), 3.1 (m, 1H, H-2), 1.9–1.2 [m, 13H, CH_3CON, $(CH_2)_5$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.3 (C=O), 136.7–126.8 (Ph), 133.7 (Ph*C*H=CHCH), 124.5 (PhCH=*C*HCH), 100.6, 98.4 (PhCH=CH*C*H, C-1), 82.5 (C-4), 77.7 (C-3), 76.3 (OCHR), 74.5 (O*C*H$_2$Ph), 68.5 (C-6), 65.7 (C-5), 58.5 (C-2), 33.4–24.0 [$(CH_2)_5$], 23.8 (*C*H$_3$CON). HRMS (CI): $[M+H]^+$, found 508.268461. $C_{30}H_{38}NO_6$ requires 508.269913. Anal. Calcd for $C_{30}H_{37}NO_6$: C, 70.98; H, 7.35; N, 2.76. Found: C, 70.72; H, 7.41; N, 2.72.

3.4.2. 1-Dodecyl 2-acetamido-3-*O*-benzyl-2-deoxy-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside 15. Column chromatography using dichloromethane–methanol (140:1) yielded 2.9 g (81%); mp 189–190 °C; $[\alpha]_D$ = +48.0 (*c* 0.5, $CHCl_3$); MS (EI): *m/z* 593 (26%) $[M]^{+\cdot}$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.3 (m, 10H, 2Ph) 6.79 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.18 (dd, 1H, *J* 4.4 Hz, J_{trans} 16.1 Hz, PhCH=C*H*CH), 5.56 (d, 1H, $J_{2,NH}$ 7.7 Hz, NH), 5.18 (dd, 1H, *J* 4.4 Hz, ^4J 0.8 Hz, PhCH=CHC*H*), 4.93 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.88 (d, 1H, J_{gem} 11.5 Hz, OC*H*$_A$H$_B$Ph), 4.62 (d, 1H, J_{gem} 11.8 Hz, OCH$_A$*H*$_B$Ph), 4.3–4.2 (m, 2H, H-3, H-6$_e$), 3.8–3.4 (m, 5H, H-4, H-5, H-6$_a$OCH$_2$R), 3.24 (t, 1H, $J_{1,2} = J_{2,3}$ 8.3 Hz, H-2), 1.86 (s, 3H, CH_3CON), 1.5–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3H, *J* 6.5 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.3 (C=O), 138.5–126.9 (Ph), 133.8 (Ph*C*H=CHCH), 124.5 (PhCH= *C*HCH), 100.7, 100.3 (PhCH=CH*C*H, C-1), 82.5 (C-4), 76.4 (C-3), 74.5 (O*C*H$_2$Ph), 70.2 (OCH$_2$R), 68.5 (C-6), 65.8 (C-5), 58.0 (C-2), 31.9–22.7 [$(CH_2)_{10}$], 23.6 (*C*H$_3$CON), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found 594.379054. $C_{36}H_{52}NO_6$ requires 594.379464. Anal. Calcd for $C_{36}H_{51}NO_6$: C, 72.82; H, 8.66; N, 2.36. Found: C, 73.06; H, 7.8.54; N, 2.15.

3.4.3. *c*-Hexyl 2-acetamido-3-*O*-benzyl-2-deoxy-(*R*)-4,6-*O*-(*E*-2-methyl-3-phenyl-2-propenylidene)-β-D-glucopyranoside 16. Column chromatography using dichloromethane–methanol (120:1) yielded 2.5 g (80%); mp 233–234 °C; $[\alpha]_D$ = +17.5 (*c* 1.1, $CHCl_3$); MS (CI): *m/z* 522 (20%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.3 (m, 10H, 2Ph) 6.70 [s, 1H, PhC*H*=C(CH_3)CH], 5.68 (d, 1H, $J_{2,NH}$ 7.3 Hz, NH), 5.15 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.99 [s, 1H, PhCH=C(CH_3)C*H*], 4.87 (d, 1H, J_{gem} 11.7 Hz, OC*H*$_A$H$_B$Ph), 4.63 (d, 1H, J_{gem} 11.7 Hz, OCH$_A$*H*$_B$Ph), 4.39 (t, 1H, $J_{2,3} = J_{3,4}$ 8.5 Hz, H-3), 4.27 (dd, 1H, $J_{5,6e}$ 4.4 Hz, $J_{6e,6a}$ 10.2 Hz, H-6$_e$), 3.69 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.2 Hz, H-6$_a$), 3.6–3.4 (m, 3H, H-4, H-5, OCHR), 3.04 (m, 1H, H-2), 1.92 [d, 3H, ^4J 1.4 Hz, PhCH=C(C*H*$_3$)CH], 1.86 (s, 3H, CH_3CON), 1.8–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.3 (C=O), 138.4, 136.7, 129.1, 128.3, 128.1, 127.7 (Ph), 133.8 [PhCH=*C*(CH$_3$)CH], 126.9 [Ph*C*H=C(CH$_3$)CH], 104.2 [PhCH=C(CH$_3$)*C*H], 98.2 (C-1), 82.6 (C-4), 77.6 (C-3), 76.0 (OCHR), 74.5 (O*C*H$_2$Ph), 68.6 (C-6), 65.8 (C-5), 58.7 (C-2), 33.4–24.1 [$(CH_2)_5$], 23.8 (*C*H$_3$CON), 13.4 [PhCH=C(*C*H$_3$)CH]. HRMS (CI): $[M+H]^+$, found 522.282827. $C_{31}H_{40}NO_6$ requires 522.285563. Anal. Calcd for $C_{31}H_{39}NO_6$: C, 71.38; H, 7.54; N, 2.69. Found: C, 71.10; H, 7.32; N, 2.40.

Method B: To a cooled solution (5 °C) of alkyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranosides **6**, **7** (2.0 mmol) in distilled dichloromethane (200 mL) were added triethylamine (20 mL) and 5-chlorodibenzosuberane (6.0 mmol). The reaction mixture was stirred at this temperature for 3 h and left at room temperature for 48 h. The mixture was washed with water, dilute hydrochloric acid, and aqueous saturated solution of sodium bicarbonate, dried over $MgSO_4$, and evaporated. The pure product was obtained by column chromatography in good yield.

3.4.4. *c*-Hexyl 2-acetamido-2-deoxy-3-*O*-(5-dibenzosuberyl)-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside 17. Column chromatography using hexane–ethyl acetate (3.2:1) yielded 0.75 g (62%); mp 221–222 °C; $[\alpha]_D$ = −44.1 (*c* 1.0, $CHCl_3$); MS (FAB): *m/z* 632 (63%) $[M+Na]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.2 (m, 13H, Ph) 6.80 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.22 (dd, 1H, J_{trans} 16.1 Hz, *J* 5.5 Hz, PhCH=C*H*CH), 5.65 (s, 1H, CH suberyl group), 5.13 (m, 2H, NH, PhCH=C*H*CH), 4.88 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.3–4.1 (m, 2H, H-3, H-6$_e$), 3.7–2.8 [m, 9H, H-2, H-4, H-5, H-6$_a$, OCHR, $(CH_2)_2$ suberyl group], 1.61 (s, 3H, CH_3CON). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.7 (C=O), 135.9–125.8 (Ph), 133.9 (Ph*C*H=CHCH), 124.6 (PhCH=*C*HCH), 101.0, 99.1 (C-1, PhCH=CH*C*H), 82.7 (C-4), 77.6 (C-3), 76.4 (OCHR, CH suberyl group), 68.6 (C-6), 65.8 (C-5), 57.5 (C-2), 33.3–23.7 [$(CH_2)_5$, $(CH_2)_2$ suberyl group], 23.3 (*C*H$_3$CON). HRMS (EI): $[M]^{+\cdot}$, found 609.310537. $C_{38}H_{43}NO_6$ requires 609.309039. Anal. Calcd for $C_{38}H_{43}NO_6$: C, 74.85; H, 7.11; N, 2.30. Found: C, 74.72; H, 7.09; N, 2.26.

3.4.5. 1-Dodecyl 2-acetamido-2-deoxy-3-*O*-(5-dibenzosuberyl)-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside 18. Column chromatography using hexane–ethyl acetate (3.4:1) yielded 0.9 g (64%); mp 217–218 °C; $[\alpha]_D$ = −41.6 (*c* 1.1, $CHCl_3$); MS (CI): *m/z* 696 (10%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.2 (m, Ph) 6.81 (d, 1H, J_{trans} 16.4 Hz, PhC*H*=CHCH), 6.23 (dd, 1H, *J* 4.8 Hz, J_{trans} 16.4 Hz, PhCH=C*H*CH), 5.64 (s, 1H, CH suberyl group), 5.13 (d, 1H, *J* 4.8 Hz, PhCH=CHC*H*), 4.97 (d, 1H, $J_{2,NH}$ 7.0 Hz, NH), 4.67 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.25 (dd, 1H, $J_{5,6e}$ 4.8 Hz, $J_{6e,6a}$ 10.3 Hz, H-6$_e$), 4.05 (t, 1H,

$J_{2,3} = J_{3,4}$ 9.4 Hz, H-3), 3.8–2.9 [m, 10H, H-4, H-5, H-2, H-6_a, OCH_2R, $(CH_2)_2$ suberyl group], 1.63 (s, 3H, CH_3CON), 1.5–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3H, *J* 6.5 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.7 (C=O), 135.8–125.8 (Ph), 134.1 (Ph*C*H=CHCH), 124.5 (PhCH=*C*HCH), 101.1 (PhCH=CH*C*H, C-1), 82.7 (C-4), 76.4 (C-3, CH suberyl group), 70.0 (OCH_2R), 68.6 (C-6), 65.8 (C-5), 56.4 (C-2), 32.8–22.6 [$(CH_2)_{10}$, $(CH_2)_2$ suberyl group], 23.2 (*C*H_3CON), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found 696.425146. $C_{44}H_{58}NO_6$ requires 696.426414. Anal. Calcd for $C_{44}H_{57}NO_6$: C, 75.94; H, 8.26; N, 2.01. Found: C, 76.05; H, 8.14; N, 1.94.

3.5. *c*-Hexyl 2-acetamido-2-deoxy-2-*N*-3-*O*-methylidene-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside 19

To a solution of *c*-hexyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside **6** (2.5 mmol) in distilled dichloromethane (50 mL) were added dibromomethane (50 mL), 50% aqueous sodium hydroxide solution (100 mL), and tetrabutylammonium bromide (6.5 mg, 0.02 mmol). The reaction mixture was stirred vigorously under reflux for 2 days, then cooled to room temperature. The organic phase was washed with water until neutral, dried over $MgSO_4$, and the solvent removed under reduced pressure to give a solid, which was purified by flash chromatography on silica gel using hexane–ethyl acetate (3.2:1) as eluent, yielding 0.80 g (82%); mp 151–152 °C; $[\alpha]_D = -17.9$ (*c* 1.3, $CHCl_3$); MS (CI): *m*/*z* 430 (100%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 6.79 (d, 1H, J_{trans} 16.2 Hz, PhC*H*=CHCH), 6.16 (dd, 1H, *J* 4.6 Hz, J_{trans} 16.4 Hz, PhCH=C*H*CH), 5.52 (d, 1H, J_{gem} 5.5 Hz, OCH_AH_BN), 5.23 (dd, 1H, *J* 4.6 Hz, ^4J 0.9 Hz, PhCH=CHC*H*), 4.77 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.73 (d, 1H, J_{gem} 5.5 Hz, OCH_AH_BN), 4.29 (dd, 1H, $J_{5,6e}$ 4.7 Hz, $J_{6e,6a}$ 10.4 Hz, H-6_e), 3.9–3.8 (m, 3H, H-3, H-4, H-6_a), 3.7 (m, 1H, OCHR), 3.5–3.3 (m, 2H, H-2, H-5), 2.25 (s, 3H, CH_3CON), 2.0–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 173.9 (C=O), 135.7–126.9 (Ph), 134.4 (Ph*C*H=CHCH), 123.6 (PhCH=*C*HCH), 102.2, 100.8 (PhCH=CH*C*H, C-1), 82.5 (C-4), 82.3 (OCH_2N), 78.9, 78.4 (C-3, OCHR), 69.1 (C-2), 68.4 (C-6), 62.2 (C-5), 33.6–23.2 [$(CH_2)_5$], 24.0 (*C*H_3CON). HRMS (EI): $[M]^{+\cdot}$, found 429.216742. $C_{24}H_{31}NO_6$ requires 429.215138. Anal. Calcd for $C_{24}H_{31}NO_6$: C, 67.11; H, 7.27; N, 3.26. Found: C, 66.86; H, 7.37; N, 3.21.

3.6. Alkyl 2-acetamido-3-*O*-acyl-2-deoxy-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranosides 20 and 21.

3.6.1. *c*-Hexyl 2-acetamido-3-*O*-acetyl-2-deoxy-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside 20. To a solution of *c*-hexyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside **6** (2.0 mmol) in distilled dichloromethane (250 mL) were added acetic anhydride (6 mL) and dry pyridine (6 mL). The reaction mixture was stirred overnight at room temperature and then washed successively with water, dilute aqueous solution of acetic acid, saturated aqueous solution of sodium bicarbonate, and water, dried over $MgSO_4$, filtered, and the filtrate evaporated to dryness. The solvent was removed under reduced pressure to give a solid, which was purified by flash chromatography on silica gel using diethyl ether–hexane (10:1) as eluent. Yield 0.60 g (63%); mp 251–252 °C; $[\alpha]_D = -70.4$ (*c* 1.1, $CHCl_3$); MS (CI): *m*/*z* 460 (27%) $[M+H]^+$. ^1H NMR (500 MHz, DMSO-d_6): δ 7.92 (d, 1H, $J_{2,NH}$ 9.3 Hz, NH), 7.5–7.3 (m, 5H, Ph) 6.71 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.20 (dd, 1H, *J* 5.1 Hz, J_{trans} 16.1 Hz, PhCH=C*H*CH), 5.22 (d, 1H, *J* 5.1 Hz, PhCH=CHC*H*), 5.11 (t, 1H, $J_{2,3} = J_{3,4}$ 9.9 Hz, H-3), 4.69 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.15 (dd, 1H, $J_{5,6e}$ 5.0 Hz, $J_{6e,6a}$ 10.2 Hz, H-6_e) 3.7–3.6 (m, 3H, H-2, H-4, H-6_a), 3.44 (m, 1H, OCHR), 3.38 (m, 1H, $J_{4,5} = J_{5,6a}$ 10.0 Hz, $J_{5,6e}$ 5.1 Hz, H-5), 1.96 (s, 3H, CH_3CON), 1.74 (s, 3H, CH_3COO), 1.7–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.7, 169.0 (2C=O), 135.4–126.8 (Ph), 133.3 (Ph*C*H=CHCH), 124.8 (PhCH=*C*HCH), 100.2, 99.6 (PhCH=CH*C*H, C-1), 77.8 (C-4), 76.3 (OCHR), 71.9 (C-3), 67.4 (C-6), 65.6 (C-5), 54.1 (C-2), 32.9–22.9 [$(CH_2)_5$], 22.7 (*C*H_3CON), 20.6 (*C*H_3COO). HRMS (EI): $[M]^{+\cdot}$, found 459.224705. $C_{25}H_{33}NO_7$ requires 459.225703. Anal. Calcd for $C_{25}H_{33}NO_7$: C, 65.35; H, 7.24; N, 3.05. Found: C, 65.37; H, 7.23; N, 3.00.

3.6.2. 1-Dodecyl 2-acetamido-3-*O*-benzyloxycarbonyl-2-deoxy-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside 21. To a cooled solution of 1-dodecyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside **7** (2.0 mmol) in THF–dichloromethane (5:3) (80 mL) were very slowly added dry pyridine (7 mL), and benzyl chloroformate (1.5 mL, 10 mmol). The reaction mixture was stirred at room temperature for 2 days, then diluted with dichloromethane (20 mL), washed successively with water, dilute aqueous solution of hydrochloric acid (3 × 20 mL), saturated aqueous solution of sodium bicarbonate (3 × 20 mL), and water, dried over $MgSO_4$, filtered, and the filtrate evaporated to dryness. The solvent was removed under reduced pressure to give a solid, which was purified by recrystallization from 96% ethanol. Yield 0.93 g (73%); mp 151–152 °C; $[\alpha]_D = -58.2$ (*c* 0.8, $CHCl_3$); MS (CI): *m*/*z* 638 (26%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph) 6.72 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.11 (dd, 1H, *J* 4.7 Hz, J_{trans} 16.1 Hz, PhCH=C*H*CH), 5.73 (d, 1H, $J_{2,NH}$ 8.7 Hz, NH), 5.3–5.1 (m, 3H, H-3, OCH_2Ph), 5.09 (d, 1H, ^4J 0.8 Hz, *J* 4.7 Hz, PhCH=CHC*H*), 4.68 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.27 (dd, 1H, $J_{5,6e}$ 4.3 Hz, $J_{6e,6a}$ 10.2 Hz, H-6_e) 3.9–3.2 (m, 6H, H-2, H-4, H-5, H-6_a, OCH_2R), 1.87 (s, 3H, CH_3CON), 1.5–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3H, *J* 6.5 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.1, 155.1 (2C=O), 135.7–126.8 (Ph), 134.1 (Ph*C*H=CHCH), 123.9 (PhCH=*C*HCH), 101.3, 100.9 (PhCH=CH*C*H, C-1), 78.5 (C-4), 75.4 (C-3), 70.2, 69.9 (OCH_2Ph, OCH_2R), 68.3 (C-6), 65.9 (C-5), 55.3 (C-2), 31.9–22.6 [$(CH_2)_{10}$], 23.1 (*C*H_3CON), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found 638.369213. $C_{37}H_{52}NO_8$ requires 638.369293. Anal. Calcd for $C_{37}H_{51}NO_8$: C, 69.68; H, 8.06; N, 2.20. Found: C, 69.75; H, 7.95; N, 2.07.

3.7. 1-Dodecyl 2-acetamido-(*R*)-4,6-*O*-(*E*-2-alkyl-3-phenyl-2-propenylidene)-2-deoxy-3-*O*-methanosulfonyl-β-D-glucopyranosides 22 and 23

To a cooled solution (0 °C) of 1-dodecyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside **7** or 1-dodecyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-(*E*-2-methyl-3-phenyl-2-propenylidene)-β-D-glucopyranoside **10** (2.0 mmol) in dry pyridine (25 mL) was slowly added methanosulfonyl chloride (0.4 mL, 5.0 mmol). The reaction mixture was kept overnight at 5 °C, then poured into water (150 mL) with stirring, and the precipitate isolated by filtration. The pure compounds were obtained by recrystallization from 96% ethanol.

3.7.1. 1-Dodecyl 2-acetamido-2-deoxy-3-*O*-methanosulfonyl-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside 22. Yield 0.91 g (78%); mp 161–163 °C; $[\alpha]_D = -68.0$ (*c* 1.0, EtOH); MS (CI): *m*/*z* 582 (36%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph) 6.75 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.10 (dd, 1H, *J* 5.0 Hz, J_{trans} 16.1 Hz, PhCH=C*H*CH), 5.90 (d, 1H, $J_{2,NH}$ 7.7 Hz, NH), 5.2–5.1 (m, 2H, H-3, PhCH=CHC*H*), 5.06 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 4.30 (dd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 10.2 Hz, H-6$_e$) 3.9–3.3 (m, 6H, H-2, H-4, H-5, H-6$_a$, OCH_2R), 3.04 (s, 3H, CH_3SO_3), 2.00 (s, 3H, CH_3CON), 1.5–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3H, *J* 6.5 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.2 (C=O), 135.4–126.9 (Ph), 134.7 (Ph*C*H=CHCH), 123.6 (PhCH=*C*HCH), 101.1, 100.3 (PhCH=CH*C*H, C-1), 78.9, 78.8 (C-4, C-3), 70.5 (OCH_2R), 68.3 (C-6), 65.4 (C-5), 57.1 (C-2), 38.6 (CH_3SO_3), 31.9–22.6 [$(CH_2)_{10}$], 23.0 (*C*H_3CON), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found 582.308948. $C_{30}H_{48}NO_8S$ requires 582.310065. Anal. Calcd for $C_{30}H_{47}NO_8S$: C, 61.97; H, 8.15; N, 2.41; S, 5.50. Found: C, 61.72; H, 7.95; N, 2.32; S, 5.50.

3.7.2. 1-Dodecyl 2-acetamido-2-deoxy-3-*O*-methanosulfonyl-(*R*)-4,6-*O*-(*E*-2-methyl-3-phenyl-2-propenylidene)-β-D-glucopyranoside 23. Yield 0.90 g (76%); mp 162–163 °C; $[\alpha]_D = -19.4$ (*c* 0.8, CH_2Cl_2); MS (FAB): *m*/*z* 618 (36%) $[M+Na]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 6.63 [br s, 1H, PhC*H*=C(CH_3)CH], 5.97 (d, 1H, $J_{2,NH}$ 7.6 Hz, NH), 5.21 (t, 1H, $J_{2,3}$ 9.4 Hz, H-3), 5.11 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 4.98 [s, 1H, PhCH=C(CH_3)C*H*], 4.31 (dd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 10.2 Hz, H-6$_e$) 3.8–3.3 (m, 6H, H-2, H-4, H-5, H-6$_a$, OCH_2R), 3.02 (s, 3H, CH_3SO_3), 2.00 (s, 3H, CH_3CON), 1.87 [d, 3H, ^4J 1.4 Hz, PhCH=C(C*H*$_3$)CH], 1.5–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3H, *J* 6.2 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.4 (C=O), 136.2–128.2 (Ph), 133.1 [PhCH=*C*(CH_3)CH], 127.2 [Ph*C*H=C(CH_3)CH], 104.9, 100.2 [PhCH=C(CH_3)*C*H, C-1], 78.9, 78.6 (C-4, C-3), 70.9 (OCH_2R), 68.3 (C-6), 65.4 (C-5), 57.3 (C-2), 38.4 (CH_3SO_3), 31.9–22.7 [$(CH_2)_{10}$], 23.4 (*C*H_3CON), 14.1 (CH_3), 13.1 [PhCH=C(*C*H_3)CH]. HRMS (CI): $[M+H]^+$, found 596.324272. $C_{31}H_{50}NO_8S$ requires 596.325715. Anal. Calcd for $C_{31}H_{49}NO_8S$: C, 62.49; H, 8.29; N, 2.35; S, 5.38. Found: C, 62.77; H, 8.49; N, 2.42; S, 5.40.

3.8. 1-Dodecyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-allopyranoside 24

A solution of 1-dodecyl 2-acetamido-2-deoxy-3-*O*-methanosulfonyl-(*R*)-4,6-*O*-(*E*-3-phenyl-2-propenylidene)-β-D-glucopyranoside **22** (1.16 g, 2.0 mmol) and anhydrous sodium acetate (1.10 g) in 96:4 2-methoxyethanol-water (15 mL) was heated at reflux temperature for 12 h. After cooling, the mixture was poured into water and the precipitate collected by filtration and recrystallized from ethanol. Yield 0.81 g (81%); mp 231–233 °C; $[\alpha]_D = +20.0$ (*c* 1.0, EtOH); MS (CI): *m*/*z* 504 (73%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.4–7.3 (m, 5H, Ph), 6.77 (d, 1H, J_{trans} 16.2 Hz, PhC*H*=CHCH), 6.16 (dd, 1H, J_{trans} 16.2 Hz, *J* 4.8 Hz, PhCH=C*H*CH), 6.00 (d, 1H, $J_{2,NH}$ 9.0 Hz, NH), 5.21 (d, 1H, *J* 4.8 Hz, PhCH=CHC*H*), 4.62 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.3–4.2 (m, 2H, H-3, H-6$_e$), 4.10 (ddd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{1,2} = J_{2,NH}$ 8.8 Hz, $J_{2,3}$ 2.9 Hz, H-2) 3.9–3.3 (m, 5H, H-4, H-5, H-6$_a$, OCH_2R), 2.00 (s, 3H, CH_3CON), 1.5–1.1 [m, 20H, $(CH_2)_{10}$], 0.85 (t, 3H, *J* 6.1 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.8 (C=O), 135.5–126.8 (Ph), 134.3 (Ph*C*H=CHCH), 124.0 (PhCH=*C*HCH), 101.1, 100.1 (PhCH=CH*C*H, C-1), 78.4, (C-4), 69.8 (OCH_2R), 68.8 (C-6), 68.6 (C-3), 65.2 (C-5), 52.2 (C-2), 31.8–22.6 [$(CH_2)_{10}$], 23.3 (*C*H_3CON), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found 504.330959. $C_{29}H_{46}NO_6$ requires 504.332514. Anal. Calcd for $C_{29}H_{45}NO_6$: C, 69.15; H, 9.00; N, 2.78. Found: C, 68.83; H, 9.09; N, 2.77.

3.9. Epoxidation with *m*-chloroperoxybenzoic acid

To a solution of the different (*R*)-4,6-*O*-propenylidene derivatives **6**–**10**, **12**–**24** (2.0 mmol) in chloroform (150 mL) was added a solution of *m*-chloroperoxybenzoic acid (Aldrich 57–86%) (3.0 g) in chloroform (50 mL), previously dried over $MgSO_4$. The reaction mixture was kept at −15 °C until TLC showed that all of the starting compound had been consumed (2-months), after which the solution was washed successively with 5% aqueous sodium hydroxide (7 × 30 mL) and water, dried over $MgSO_4$, filtered, and the filtrate evaporated to dryness. The diastereomeric excess (de) was determined by ^{1}H NMR. The solids obtained were purified by recrystallization from either ethanol or by flash chromatography on silica gel.

3.9.1. *c*-Hexyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-[(2*R*,3*S*)-2,3-epoxy-3-phenylpropylidene]-β-D-glucopyranoside 25. Two stereoisomers were obtained in 71:28 ratio (42% de). The pure diastereoisomeric mixture was obtained by recrystallization from 96% ethanol. Yield 0.70 g (84%); mp 209–210 °C; $[\alpha]_D = -123.6$ (*c* 0.3, DMF); MS (CI): *m*/*z* 434 (100%) $[M+H]^+$. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.80 (d, 1H, $J_{2,NH}$ 9.0 Hz, NH), 7.5–7.3 (m, 5H, Ph), 5.24 (br s, 1H, OH), 4.62 [d, *J* 4.6 Hz, PhCH(O)CHC*H* major], 4.60 [d, *J* 4.6 Hz, PhCH(O)CHC*H* minor], 4.53 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.11 (m, 1H, H-6$_e$), 3.99 [d, J_{trans} 2,0 Hz, PhC*H*(O)-CHCH minor], 3.98 [d, J_{trans} 2,0 Hz, PhC*H*(O)CHCH major], 3.6–3.5 (m, 2H, H-3, OCHR), 3.37 (t, $J_{5,6a} = J_{6e,6a}$ 9.5 Hz, H-6$_a$ major), 3.29 [dd, J_{trans} 2.0 Hz, *J*

4.6 Hz, PhCH(O)C*H*CH major], 3.25 (m, 3H, H-2, H-4, H-5), 1.81 (s, CH_3CON minor), 1.79 (s, CH_3CON major), 1.7–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (125 MHz, DMSO-d_6): δ 169.0 (C=O minor), 168.9 (C=O major), 136.0–126.0 (Ph), 100.0 (C-1), 99.6 [PhCH(O)CH*C*H minor], 99.4 [PhCH(O)CH*C*H major], 81.0 (C-4 major), 80.8 (C-4 minor), 75.9 (OCHR), 70.2 (C-3 minor), 70.1 (C-3 major), 67.5 (C-6 minor), 67.3 (C-6 major), 65.6 (C-5), 60.2 [Ph*C*H(O)CHCH minor], 60.1 [Ph*C*H(O)CHCH major], 56.5 (C-2), 54.7 [PhCH(O)*C*HCH major], 54.4 [PhCH(O)*C*HCH minor], 32.9–23.0 [$(CH_2)_5$], 23.1 (CH_3CON major), 23.1 (CH_3CON minor). HRMS (EI): $[M]^{+\cdot}$, found 433.210378. $C_{23}H_{31}NO_7$ requires 433.210053. Anal. Calcd for $C_{23}H_{31}NO_7$: C, 63.73; H, 7.21; N, 3.23. Found: C, 63.80; H, 6.95; N, 3.30.

3.9.2. 1-Dodecyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-[(2*R*,3*S*)-2,3-epoxy-3-phenylpropylidene]-β-D-glucopyranoside 26. Two stereoisomers were obtained in 67:33 ratio (34% de). The pure diastereoisomeric mixture was obtained by recrystallization from 96% ethanol. Yield 0.80 g (77%); mp 251–252 °C; $[\alpha]_D = -62.0$ (*c* 1.2, DMF); MS (CI): *m*/*z* 520 (40%) $[M+H]^+$. ^1H NMR (200 MHz, DMSO-d_6): δ 7.84 (d, 1H, $J_{2,NH}$ 9.4 Hz, NH), 7.4–7.3 (m, 5H, Ph), 5.34 (br s, 1H, OH), 4.63 [d, *J* 4.6 Hz, PhCH(O)CHC*H* major], 4.62 [d, *J* 4.5 Hz, PhCH(O)CHC*H* minor], 4.41 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.11 (m, 1H, H-6_e), 3.99 [d, J_{trans} 1.9 Hz, PhC*H*(O)CHCH minor], 3.98 [d, J_{trans} 1.9 Hz, PhC*H*(O)CHCH major], 3.7–3.2 [m, 8H, PhCH(O)C*H*CH, OCH_2R, H-2, H-3, H-4, H-5, H-6_a], 1.79 (s, CH_3CON minor), 1.78 (s, CH_3CON major), 1.5–1.2 [m, 20H, $(CH_2)_{10}$], 0.84 (t, 3H, *J* 6.4 Hz, CH_3). ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.0 (C=O), 136.0–126.1 (Ph), 101.6 (C-1), 99.5 [PhCH(O)CH*C*H minor], 99.4 [PhCH(O)CH*C*H major], 80.9 (C-4 major), 80.8 (C-4 minor), 70.3 (C-3), 68.7 (OCH_2R), 67.4 (C-6 minor), 67.3 (C-6 major), 65.8 (C-5), 60.1 [Ph*C*H(O)CHCH], 56.1 (C-2), 54.7 [PhCH(O)*C*HCH major], 54.5 [PhCH(O)*C*HCH minor], 31.3–22.1 [$(CH_2)_{10}$], 23.0 (CH_3CON), 14.0 (CH_3). HRMS (EI): $[M]^{+\cdot}$, found 519.322610. $C_{29}H_{45}NO_7$ requires 519.319603. Anal. Calcd for $C_{29}H_{45}NO_7$: C, 67.03; H, 8.73; N, 2.69. Found: C, 66.74; H, 8.58; N, 2.63.

3.9.3. Benzyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-[(2*R*,3*S*)-2,3-epoxy-3-phenylpropylidene]-β-D-glucopyranoside 27. Two stereoisomers were obtained in 71:29 ratio (42% de). The pure diastereoisomeric mixture was obtained by column chromatography using dichloromethane–methanol (50:1) as eluent. Yield 0.5 g (58%); mp 254–256 °C; $[\alpha]_D = -52.0$ (*c* 1.0, DMF); MS (CI): *m*/*z* 442 (11%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.3 (m, 10H, 2Ph), 5.5 (m, 1H, NH), 4.89 (d, 1H, J_{gem} 12.1 Hz, OCH_AH$_B$Ph), 4.67 [d, *J* 4.0 Hz, PhCH(O)CHC*H* major], 4.62 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.56 (d, 1H, J_{gem} 12.1 Hz, OCH$_A$*H*$_B$Ph), 4.27 (m, 1H, H-6_e), 4.00 (m, 1H, H-3), 4.00 [d, J_{trans} 1.9 Hz, PhC*H*(O)CHCH minor], 3.94 [d, J_{trans} 1.9 Hz, PhC*H*(O)CHCH major], 3.7–3.4 [m, 4H, H-2, H-4, H-5, H-6_a], 3.24 [dd, 1H, J_{trans} 1.7 Hz, *J* 4.0 Hz, PhCH(O)C*H*CH major], 1.95 (s, 3H, CH_3CON). ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.2 (C=O), 137.9–126.1 (Ph), 101.5 (C-1), 99.6 [PhCH(O)CH*C*H minor], 99.5 [PhCH(O)CH*C*H major], 80.9 (C-4), 70.7 (C-3), 70.2 (O*C*H$_2$Ph), 67.3 (C-6), 65.9 (C-5), 60.1 [Ph*C*H(O)CHCH], 56.1 (C-2), 54.8 [PhCH(O)*C*HCH major], 54.5 [PhCH(O)*C*HCH minor], 23.1 (CH_3CON). HRMS (EI): $[M]^{+\cdot}$, found 441.175649. $C_{24}H_{27}NO_7$ requires 441.178753. Anal. Calcd for $C_{24}H_{27}NO_7$: C, 65.30; H, 6.18; N, 3.17. Found: C, 65.19; H, 6.34; N, 2.98.

3.9.4. *c*-Hexyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-[(2*R*,3*S*)-2,3-epoxy-2-methyl-3-phenylpropylidene]-β-D-glucopyranoside 28. Two stereoisomers were obtained in 87:13 ratio (74% de). The pure diastereoisomeric mixture was obtained by recrystallization from 96% ethanol. Yield 0.72 g (81%); mp 184–185 °C; $[\alpha]_D = -83.3$ (*c* 0.5, DMF); MS (CI): *m*/*z* 448 (46%) $[M+H]^+$. ^1H NMR (200 MHz, DMSO-d_6): δ 7.79 (d, 1H, $J_{2,NH}$ 8.8 Hz, NH), 7.4–7.2 (m, 5H, Ph), 5.29 (d, 1H, $J_{3,OH}$ 5.5 Hz, OH), 4.57 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.47 [s, PhCH(O)C(CH$_3$)C*H* major], 4.43 [s, PhCH(O)C(CH$_3$)C*H* minor], 4.2–4.1 [m, 2H, H-6_e, PhC*H*(O)C(CH$_3$)CH], 3.6–3.5 (m, 3H, OCHR, H-3, H-6_a), 3.3–3.2 (m, 3H, H-2, H-4, H-5), 1.79 (s, 3H, CH_3CON), 1.7–1.2 [m, 10H, $(CH_2)_5$], 1.00 [s, PhCH(O)C(C*H*$_3$)CH major], 0.99 [s, PhCH(O)C(C*H*$_3$)CH minor]. ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.0 (C=O), 134.7–126.4 (Ph), 102.5 [PhCH(O)C(CH$_3$)*C*H minor], 102.2 [PhCH(O)C(CH$_3$)*C*H major], 99.8 (C-1), 80.9 (C-4 major), 80.7 (C-4 minor), 75.8 (OCHR), 70.0 (C-3), 67.5 (C-6 minor), 67.4 (C-6 major), 65.8 (C-5), 62.2 [PhCH(O)*C*(CH$_3$)CH], 59.8 [Ph*C*H(O)C(CH$_3$)CH major], 59.6 [Ph*C*H(O)C(CH$_3$)CH minor], 56.8 (C-2), 32.9–22.8 [$(CH_2)_5$], 23.1 (CH_3CON), 10.7 [PhCH(O)C(*C*H$_3$)CH major], 10.5 [PhCH(O)C(*C*H$_3$)CH minor]. HRMS (CI): $[M+H]^+$, found 448.233465. $C_{24}H_{34}NO_7$ requires 448.233528. Anal. Calcd for $C_{24}H_{33}NO_7$: C, 64.41; H, 7.43; N, 3.13. Found: C, 64.14; H, 7.47; N, 3.30.

3.9.5. 1-Dodecyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-[(2*R*,3*S*)-2,3-epoxy-2-methyl-3-phenylpropylidene]-β-D-glucopyranoside 29. Two stereoisomers were obtained in 78:22 ratio (56% de). The pure diastereoisomeric mixture was obtained by recrystallization from 96% ethanol. Yield 0.77 g (72%); mp 221–222 °C; $[\alpha]_D = -57.1$ (*c* 0.7, $CHCl_3$); MS (CI): *m*/*z* 534 (72%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 5.86 (d, 1H, $J_{2,NH}$ 5.4 Hz, NH), 4.69 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.47 [s, PhCH(O)C(CH$_3$)C*H* major], 4.44 [s, PhCH(O)C(CH$_3$)C*H* minor], 4.25 (dd, 1H, $J_{5,6e}$ 4.2 Hz, $J_{6e,6a}$ 10.3 Hz, H-6_e), 4.14 [s, PhC*H*(O)C(CH$_3$)CH major], 4.13 [s, PhC*H*(O)C(CH$_3$)CH minor], 3.82 (m, 1H, OCH_AH$_B$R), 3.7–3.3 (m, 5H, H-2, H-4, H-5, H-6_a, OCH$_A$*H*$_B$R), 2.03 (s, 3H, CH_3CON), 1.6–1.2 [m, 20H, $(CH_2)_{10}$], 1.11 [s, PhCH(O)C(C*H*$_3$)CH major, 1.09 [s, PhCH(O)C(C*H*$_3$)CH minor], 0.86 (t, 3H, *J* 6.5 Hz, CH_3). ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.0 (C=O), 134.7–126.5 (Ph), 102.6 [PhCH(O)C(CH$_3$)*C*H minor], 102.3 [PhCH(O)C(CH$_3$)*C*H major], 101.5 (C-1), 80.9 (C-4 major), 80.6 (C-4 minor), 70.2 (C-3), 68.7 (OCH_2R), 67.4 (C-6 minor), 67.3 (C-6 major), 65.9 (C-5 major), 65.6 (C-5 minor), 62.2 [PhCH(O)*C*(CH$_3$)CH], 59.8 [Ph*C*H(O)C(CH$_3$)CH major], 59.7 [Ph*C*H(O)-

C(CH_3)CH minor], 56.3 (C-2), 31.3–22.1 [(CH_2)$_{10}$], 23.0 (*C*H_3CON), 14.0 (CH_3), 10.7 [PhCH(O)C(*C*H_3)CH major], 10.5 [PhCH(O)C(*C*H_3)CH minor]. HRMS (CI): $[M+H]^+$, found 534.342345. $C_{30}H_{48}NO_7$ requires 534.343078. Anal. Calcd for $C_{30}H_{47}NO_7$: C, 67.51; H, 8.88; N, 2.62. Found: C, 67.36; H, 8.96; N, 2.58.

3.9.6. Methyl (*R*)-4,6-*O*-[(2*R*,3*S*)-2,3-epoxy-3-phenylpropylidene]-α-D-glucopyranoside 30. Two stereoisomers were obtained in 73:27 ratio (46% de). The pure diastereoisomeric mixture was obtained by column chromatography using dichloromethane–methanol (30:1) as eluent. Yield 0.50 g (77%); mp 76–78 °C; $[\alpha]_D$ = +61.4 (*c* 1.0, $CHCl_3$); MS (EI): *m*/*z* 324 (7%) $[M]^{+\cdot}$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 4.75 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.69 [d, *J* 3.6 Hz, PhCH(O)CHC*H* major], 4.65 [d, *J* 3.6 Hz, PhCH(O)CHC*H* minor], 4.18 (dd, 1H, $J_{5,6e}$ 4.3 Hz, $J_{6e,6a}$ 9.7 Hz, H-6$_e$), 3.99 [d, J_{trans} 2.1 Hz, PhC*H*(O)CHCH minor], 3.97 [d, J_{trans} 2.1 Hz, PhC*H*(O)CHCH major], 3.90 (t, $J_{2,3} = J_{3,4}$ 9.2 Hz, H-3 minor), 3.88 (t, $J_{2,3} = J_{3,4}$ 9.2 Hz, H-3 major), 3.7–3.5 (m, 3H, H-2, H-5, H-6$_a$), 3.39 (s, 3H, OCH_3), 3.31 (t, $J_{3,4} = J_{4,5}$ 9.2 Hz, H-4), 3.22 [dd, 1H, J_{trans} 2.1 Hz, *J* 3.6 Hz, PhCH(O)C*H*CH]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 135.8–125.9 (Ph), 99.8, 99.3 [PhCH(O)CH*C*H, C-1], 80.5 (C-4), 72.7 (C-2), 71.2 (C-3), 68.4 (C-6), 62.1 (C-5), 60.5 [Ph*C*H(O)CHCH], 55.4 [OCH_3, PhCH(O)-*C*HCH]. HRMS (EI): $[M]^{+\cdot}$, found 324.210381. $C_{16}H_{20}O_7$ requires 324.120903. Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.25; H, 6.22. Found: C, 59.04; H, 6.25.

3.9.7. Methyl (*R*)-4,6-*O*-[(2*R*,3*S*)-2,3-epoxy-2-methyl-3-phenylpropylidene]-α-D-glucopyranoside 31. Two stereoisomers were obtained in an 86:14 ratio (72% de). The pure diastereoisomeric mixture was obtained by column chromatography using dichloromethane–methanol (30:1) as eluent. Yield 0.53 g (78%); mp 87–89 °C; $[\alpha]_D$ = +66.2 (*c* 0.9, $CHCl_3$); MS (EI): *m*/*z* 338 (8%) $[M]^{+\cdot}$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 4.75 (d, 1H, $J_{1,2}$ 3.9 Hz, H-1), 4.47 [s, PhCH(O)-C(CH_3)C*H* major], 4.41 [s, 1H, PhCH(O)C(CH_3)C*H* minor], 4.20 (dd, 1H, $J_{5,6e}$ 4.1 Hz, $J_{6e,6a}$ 9.4 Hz, H-6$_e$), 4.16 [s, PhC*H*(O)C(CH_3)CH major], 4.11 [s, PhC*H*(O)C(CH_3)CH minor], 3.89 (t, 1H, $J_{2,3} = J_{3,4}$ 9.2 Hz, H-3), 3.7–3.5 (m, 3H, H-2, H-5, H-6$_a$), 3,40 (s, 3H, OCH_3), 3.31 (t, 1H, $J_{3,4}$ 9.2 Hz, H-4), 1.10 [s, PhCH(O)C(C*H*$_3$)CH major], 1.09 [s, PhCH(O)-C(C*H*$_3$)CH minor]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 134.6–126.6 (Ph), 102.8, 99.8 PhCH(O)C(CH_3)*C*H, C-1], 80.6 (C-4), 72.7 (C-2), 71.4 (C-3), 68.5 (C-6), 62.5 [PhCH(O)*C*(CH_3)CH], 62.2 (C-5), 60.5 [Ph*C*H(O)-C(CH_3)CH], 55.4 (OCH_3), 11.3 [PhCH(O)C(*C*H_3)CH major], 11.0 [PhCH(O)C(*C*H_3)CH minor]. HRMS (EI): $[M]^{+\cdot}$, found 338.136406. $C_{17}H_{22}O_7$ requires 338.136553. Anal. Calcd for $C_{17}H_{22}O_7$: C, 60.35; H, 6.55. Found: C, 60.05; H, 6.57.

3.9.8. *c*-Hexyl 2-acetamido-3-*O*-benzyl-2-deoxy-(*R*)-4,6-*O*-[(2*S*,3*R*)-2,3-epoxy-3-phenylpropylidene]-β-D-glucopyranoside 32. Two stereoisomers were obtained in a 64:36 ratio (28% de). The pure diastereoisomeric mixture was obtained by recrystallization from 96% ethanol. Yield 0.86 g (82%); mp 225–226 °C; $[\alpha]_D$ = −29.3 (*c* 0.6, $CHCl_3$); MS (CI): *m*/*z* 524 (83%) $[M+H]^+$. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.96 (d, 1H, $J_{2,NH}$ 8.9 Hz, NH), 7.4–7.2 (m, 10H, 2Ph), 4.7–4.5 [m, 4H, H-1, OC*H*$_2$Ph, PhCH(O)CHC*H*], 4.14 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 9.9 Hz, H-6$_e$), 4.00 [d, J_{trans} 2.0 Hz, PhC*H*(O)CHCH major], 3.97 [d, J_{trans} 2.0 Hz, PhC*H*(O)CHCH minor], 3.7–3.5 (m, 5H, OCHR, H-2, H-3, H-4, H-6$_a$), 3.37 (m, 1H, H-5), 3.30 [dd, J_{trans} 2.0 Hz, *J* 4.1 Hz, PhCH(O)C*H*CH major], 3.27 [dd, 1H, J_{trans} 2.0 Hz, *J* 4.3 Hz, PhCH(O)C*H*CH minor], 1.80 (s, 3H, CH_3CON), 1.7–1.2 [m, 10H, (CH_2)$_5$]. ^{13}C NMR (125 MHz, DMSO-d_6): δ 169.2 (C=O), 1368.0–125.2 (Ph), 99.0 (C-1), 98.6 [PhCH(O)CH*C*H minor], 98.4 [PhCH(O)CH*C*H major], 79.9 (C-4 minor), 79.8 (C-4 major), 77.6 (C-3 major), 77.5 (C-3 minor), 75.2 (O*C*H$_2$Ph), 72.3 (OCHR), 66.8 (C-6 major), 66.6 (C-6 minor), 64.6 (C-5), 59.4 [Ph*C*H(O)CHCH minor], 59.3 [Ph*C*H(O)CHCH major], 54.3 (C-2 minor), 54.2 (C-2 major), 53.8 [PhCH(O)*C*HCH major], 53.7 [PhCH(O)*C*HCH minor], 32.1–22.1 [(CH_2)$_5$], 23.1 (*C*H_3CON). HRMS (CI): $[M+H]^+$, found 524.264828. $C_{30}H_{38}NO_7$ requires 524.264904. Anal. Calcd for $C_{30}H_{37}NO_7$: C, 68.81; H, 7.12; N, 2.67. Found: C, 68.57; H, 6.95; N, 2.62.

3.9.9. 1-Dodecyl 2-acetamido-3-*O*-benzyl-2-deoxy-(*R*)-4,6-*O*-[(2*S*,3*R*)-2,3-epoxy-3-phenylpropylidene]-β-D-glucopyranoside 33. Two stereoisomers were obtained in a 61:39 ratio (22% de). The pure diastereoisomeric mixture was obtained by column chromatography using dichloromethane–methanol (100:1) as eluent. Yield 1.0 g (86%); mp 159–160 °C; $[\alpha]_D$ = −0.5 (*c* 1.7, CH_2Cl_2); MS (CI): *m*/*z* 610 (95%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.3–7.2 (m, 10H, 2Ph), 5.54 (d, 1H, $J_{2,NH}$ 7.7 Hz, NH), 4.96 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.87 (d, J_{gem} 11.7 Hz, OCH_AH$_B$Ph major), 4.83 (d, 1H, J_{gem} 11.7 Hz, OCH_AH$_B$Ph minor), 4.70 [d, *J* 3.3 Hz, PhCH(O)CHC*H* major], 4.64 [d, *J* 3.3 Hz, PhCH(O)CHC*H* minor], 4.61 (d, J_{gem} 11.7 Hz, OCH$_A$*H*$_B$Ph major), 4.59 (d, J_{gem} 11.7 Hz, OCH$_A$*H*$_B$Ph minor), 4.3–4.2 (m, 2H, H-3, H-6$_e$), 3.96 [d, J_{trans} 2.0 Hz, PhC*H*(O)CHCH major], 3.93 [d, J_{trans} 2.0 Hz, PhC*H*(O)CHCH minor], 3.20 [dd, J_{trans} 2.0 Hz, *J* 3.3 Hz, PhCH(O)C*H*CH major], 1.86 (s, CH_3CON minor), 1.85 (s, CH_3CON major), 1.5–1.2 [m, 10H, (CH_2)$_{10}$], 0,86 (t, 3H, *J* 6.5 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): 170.3 (C=O), 138.4–125.7 (Ph), 100.2 (C-1), 99.7 [PhCH(O)CH*C*H minor], 99.4 [PhCH(O)CH*C*H major], 82.6 (C-4), 76.2 (C-3), 74.5 (O*C*H$_2$Ph), 70.2 (OCH$_2$ R), 68.4 (C-6), 65.6 (C-5), 60.8 [Ph*C*H(O)CHCH], 58.1 (C-2), 55.2 [PhCH(O)*C*HCH minor], 55.0 [PhCH(O)*C*HCH major], 31.9–22.6 [(CH_2)$_{10}$], 23.5 (*C*H_3CON), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found 609.371674. $C_{36}H_{51}NO_7$ requires 609.366554. Anal. Calcd for $C_{36}H_{51}NO_7$: C, 70.91; H, 8.43; N, 2.30. Found: C, 70.79; H, 7.8.22; N, 2.28.

3.9.10. *c*-Hexyl 2-acetamido-3-*O*-benzyl-2-deoxy-(*R*)-4,6-*O*-[(2*S*,3*R*)-2,3-epoxy-2-methyl-3-phenylpropylidene]-β-D-glucopyranoside 34. Two stereoisomers were obtained in a 67:33 ratio (34% de). The pure diastereoisomeric mixture was obtained by column chromatography using dichloromethane–methanol (120:1) as eluent. Yield 0.88 g (86%); mp 199–200 °C; $[\alpha]_D$ = +9.7 (*c* 0.5,

$CHCl_3$); MS (CI): *m/z* 538 (32%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 5.80 (d, 1H, $J_{2,NH}$ 7.2 Hz, NH), 5.16 (d, $J_{1,2}$ 8.3 Hz, H-1 major), 5.15 (d, $J_{1,2}$ 8.3 Hz, H-1 minor), 4.87 (d, 1H, J_{gem} 11.6 Hz, OCH_AH_BPh), 4.64 (d, J_{gem} 11.6 Hz, OCH_AH_BPh minor), 4.63 (d, J_{gem} 11.6 Hz, OCH_AH_BPh major), 4.47 [s, PhCH(O)C(CH_3)C*H* major], 4.40 [s, PhCH(O)C(CH_3)C*H* minor], 4.15 [s, PhC*H*(O)-C(CH_3)CH major], 4.10 [s, PhC*H*(O)C(CH_3)CH minor], 3.7–3.4 (m, 4H, H-2, H-4, H-6_a, OCHR), 3.03 (m, 1H, H-5), 1.87 (s, CH_3CON minor), 1.86 (s, CH_3CON major), 1.7–1.2 [m, 10H, $(CH_2)_5$], 1.12 [s, PhCH(O)-C(C*H*$_3$)CH major], 1.10 [s, PhCH(O)C(C*H*$_3$)CH minor]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.4 (C=O), 138.2–126.5 (Ph), 102.9 [PhCH(O)C(CH_3)*C*H minor], 102.5 [PhCH(O)C(CH_3)*C*H major], 98.1 (C-1), 82.5, (C-4), 77.6 (C-3), 75.6 (OCHR), 74.5 (O*C*H_2Ph), 72.3 68.4 (C-6), 65.5 (C-5), 62.4 [PhCH(O)*C*(CH_3)CH], 60.4 [Ph*C*H(O)C(CH_3)CH minor], 60.1 [Ph*C*H(O)-C(CH_3)CH major], 58.6 (C-2), 33.3–23.7 [$(CH_2)_5$], 23.5 (*C*H_3CON), 11.5 [PhCH(O)C(*C*H_3)CH major], 10.8 [PhCH(O)C(*C*H_3)CH minor]. HRMS (CI): $[M+H]^+$, found 538.280744. $C_{31}H_{40}NO_7$ requires 538.280478. Anal. Calcd for $C_{31}H_{39}NO_7$: C, 69.25; H, 7.31; N, 2.61. Found: C, 69.20; H, 7.31; N, 2.36.

3.9.11. *c*-Hexyl 2-acetamido-2-deoxy-3-*O*-(5-dibenzosuberyl)-(*R*)-4,6-*O*-[(2*S*,3*R*)-2,3-epoxy-3-phenylpropylidene]-β-D-glucopyranoside 35. Two stereoisomers were obtained in a 68:32 ratio (36% de). The pure diastereoisomeric mixture was obtained by recrystallization from 96% ethanol. Yield 0.94 g (72%); mp 186–188 °C; $[\alpha]_D = -30.0$ (*c* 0.7, DMF); MS (CI): *m/z* 626 (10%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.1 (m, 13H, Ph), 5.65 (s, OCH suberyl group major), 5.60 (s, OCH suberyl group minor), 5.19 (d, 1H, $J_{2,NH}$ 7.5 Hz, NH), 4.93 (d, $J_{1,2}$ 8.3 Hz, H-1 major), 4.90 (d, $J_{1,2}$ 8.3 Hz, H-1 minor), 4.61 [d, *J* 3.8 Hz, PhCH(O)CHC*H* major], 4.59 [d, *J* 3.8 Hz, PhCH(O)CHC*H* minor], 4.3–4.1 (m, 2H, H-3, H-6_e), 3.97 [d, J_{trans} 2.0 Hz, PhC*H*(O)CHCH major], 3.93 [d, J_{trans} 2.0 Hz, PhC*H*(O)-CHCH minor], 3.7–2.8 [m, 10H, OCHR, H-4, H-5, H-2, H-6_a, PhCH(O)C*H*CH, $(CH_2)_2$ suberyl group], 2.04 (s, CH_3CON major), 2.00 (s, CH_3CON minor), 1.8–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.8 (C=O), 130.7–125.9 (Ph), 99.9 [PhCH(O)CH*C*H], 98.9 (C-1), 82.7 (C-4), 77.0 (C-3), 76.4 (OCH suberyl group), 75.0 (OCHR), 68.5 (C-6), 65.6 (C-5), 60.7 [Ph*C*H(O)CHCH minor], 60.6 [Ph*C*H(O)CHCH major], 57.7 (C-2), 55.4 [PhCH(O)*C*HCH major], 55.2 [PhCH(O)*C*HCH minor], 33.3–23.4 [$(CH_2)_5$, $(CH_2)_2$ suberyl group], 23.7 (*C*H_3CON). HRMS (CI): $[M+H]^+$, found 626.308667. $C_{38}H_{44}NO_7$ requires 626.311778. Anal. Calcd for $C_{38}H_{43}NO_7$: C, 72.94; H, 6.93; N, 2.24. Found: C, 72.60; H, 6.86; N, 2.28.

3.9.12. 1-Dodecyl 2-acetamido-2-deoxy-3-*O*-(5-dibenzosuberyl)-(*R*)-4,6-*O*-[(2*S*,3*R*)-2,3-epoxy-3-phenylpropylidene]-β-D-glucopyranoside 36. Two stereoisomers were obtained in a 62:38 ratio (24% de). The pure diastereoisomeric mixture was obtained by recrystallization from 96% ethanol. Yield 1.0 g (69%); mp 184–185 °C; $[\alpha]_D = -53.2$ (*c* 0.7, CH_2Cl_2); MS (CI): *m/z* 712 (8%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.1 (m, 13H, Ph), 5.62 (s, OCH suberyl group major), 5.56 (s, OCH suberyl group minor), 5.02 (m, 1H, NH), 4.71 (d, $J_{1,2}$ 8.3 Hz, H-1 major), 4.68 (d, $J_{1,2}$ 8.3 Hz, H-1 minor), 4.60 [d, 1H, *J* 3.8 Hz, PhCH(O)CHC*H*], 4.3–4.0 (m, 2H, H-6_e, H-3), 3.96 [d, J_{trans} 1.9 Hz, PhC*H*(O)CHCH major], 3.93 [d, J_{trans} 1.9 Hz, PhC*H*(O)CHCH minor], 3.8–2.8 [m, 11H, H-2, H-4, H-5, H-6_a, OCH_2R, $(CH_2)_2$ suberyl group, PhCH(O)C*H*CH], 1.64 (s, 3H, CH_3CON), 1.5–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3H, *J* 6.8 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.8 (C=O), 130.7–125.9 (Ph), 100.9 (C-1), 99.9 [PhCH(O)-CH*C*H], 82.7 (C-4), 75.3 (OCH suberyl group, C-3), 70.1 (OCH_2R), 68.5 (C-6), 65.7 (C-5), 60.8 [Ph*C*H(O)CHCH major], 60.6 [Ph*C*H(O)CHCH minor], 56.9 (C-2), 55.4 [PhCH(O)*C*HCH minor], 55.1 [PhCH(O)*C*HCH major], 32.8–22.7 [$(CH_2)_{10}$, $(CH_2)_2$ suberyl group], 23.4 (*C*H_3CON), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found 712.419050. $C_{44}H_{58}NO_7$ requires 712.421329. Anal. Calcd for $C_{44}H_{57}NO_7$: C, 74.23; H, 8.07; N, 1.97. Found: C, 73.98; H, 7.90; N, 1.73.

3.9.13. *c*-Hexyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-(2,3-epoxy-3-phenylpropylidene)-2-*N*-3-*O*-methylidene-β-D-glucopyranoside 37. Two stereoisomers were obtained without diastereoisomeric excess. The pure diastereoisomeric mixture was obtained by recrystallization from 96% ethanol. Yield 0.6 g (65%); mp 152–153 °C; $[\alpha]_D = -40.7$ (*c* 0.5, CH_2Cl_2); MS (CI): *m/z* 446 (100%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 5.49 (d, 1H, J_{gem} 5.5 Hz, OCH_AH_BN), 4.8–4.7 (m, 2H, OCH_AH_BN, H-1), 4.65 [d, 1H, *J* 4.2 Hz, PhCH(O)CHC*H*], 4.3–4.2 (m, 2H, H-3, H-6_e), 3.99, 3.93 [2d, 1H, J_{trans} 1.9 Hz, PhC*H*(O)CHCH], 3.8–3.2 [m, 6H, H-2, H-4, H-5, H-6_a, OCHR, PhCH(O)C*H*CH], 2.24 (s, 3H, CH_3CON), 1.7–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.8 (C=O), 135.9–125.8 (Ph), 102.2 (C-1), 100.0, 99.1 [PhCH(O)CH*C*H], 82.4 (OCH_2N), 82.1 (C-4), 78.9, 78.5 (C-3, OCHR), 68.9 (C-2), 68.3 (C-6), 62.2 (C-5), 60.5, 60.4 [Ph*C*H(O)-CHCH], 55.6, 54.8 [PhCH(O)*C*HCH], 33.6-23.7 [$(CH_2)_5$], 23.2 (*C*H_3CON). HRMS (CI): $[M+H]^+$, found 446.218439. $C_{24}H_{32}NO_7$ requires 446.217878. Anal. Calcd for $C_{24}H_{31}NO_7$: C, 64.70; H, 7.01; N, 3.14. Found: C, 64.44; H, 6.81; N, 2.95.

3.9.14. *c*-Hexyl 2-acetamido-3-*O*-acetyl-2-deoxy-(*R*)-4,6-*O*-(2,3-epoxy-3-phenylpropylidene)-β-D-glucopyranoside 38. Two stereoisomers were obtained without diastereoisomeric excess. The pure diastereoisomeric mixture was obtained by column chromatography using diethyl ether–hexane–methanol (9:1:0.3) as eluent. Yield 0.6 g (68%); mp 201–202 °C; $[\alpha]_D = -35.5$ (*c* 0.9, DMF); MS (CI): *m/z* 476 (24%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 6.20, 6.17 (2d, 1H, $J_{2,NH}$ 9.4 Hz, NH), 5.25 (m, 1H, H-3), 4.63 (d, 1H, $J_{1,2}$ 8.6 Hz, H-1), 4.59 [d, 1H, *J* 3.7 Hz, PhCH(O)CHC*H*], 4.24 (m, 1H, H-6_e), 3.98 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 9.4 Hz, H-6_a), 3.89, 3.87 [2d, 1H, J_{trans} 1.9 Hz, PhC*H*(O)CHCH], 3.7–3.4 (m, 4H, H-2, H-4, H-5, OCHR), 3.14 [m, 1H, PhCH(O)C*H*CH], 2.08, 2.06 (2s, 3H, CH_3COO), 1.92 (s, 3H, CH_3CON), 1.7–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C

NMR (50 MHz, $CDCl_3$): δ 171.1, 169.9 (2C=O), 135.6–125.4 (Ph), 99.8 (C-1), 99.3, 99.0 [PhCH(O)CH*C*H], 78.0 (C-4), 77.0 (C-3), 71.5 (OCHR), 68.0 (C-6), 65.5 (C-5), 60.2, 60.1 [Ph*C*H(O)CHCH], 55.0, 54.7 [2PhCH(O)-*C*HCH], 54.4 (C-2), 32.8–23.2 [$(CH_2)_5$], 23.0 (CH_3CON), 20.6 (CH_3COO). HRMS (EI): $[M]^{+\cdot}$, found 475.219945. $C_{25}H_{33}NO_8$ requires 475.220617. Anal. Calcd for $C_{25}H_{33}NO_8$: C, 63.14; H, 6.99; N, 2.95. Found: C, 62.86; H, 6.83; N, 2.81.

3.9.15. 1-Dodecyl 2-acetamido-3-*O*-benzyloxycarbonyl-2-deoxy-(*R*)-4,6-*O*-[(2*S*,3*R*)-2,3-epoxy-3-phenylpropylidene]-β-D-glucopyranoside 39. Two stereoisomers were obtained in a 56:44 ratio (12% de). The pure diastereoisomeric mixture was obtained by recrystallization from 96% ethanol. Yield 0.9 g (72%); mp 103–104 °C; $[\alpha]_D = -45.2$ (*c* 0.6, $CHCl_3$); MS (CI): *m*/*z* 654 (17%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.3–7.2 (m, 10H, 2Ph), 5.61 (d, $J_{2,NH}$ 8.5 Hz, NH major), 5.60 (d, $J_{2,NH}$ 8.5 Hz, NH minor), 5.3–5.1 (m, 2H, $PhCH_2OCO$, H-3), 4.76 (d, $J_{1,2}$ 8.3 Hz, H-1 major), 4.74 (d, $J_{1,2}$ 8.3 Hz, H-1 minor), 4.64 [d, *J* 3.3 Hz, PhCH(O)CHC*H* major], 4.56 [d, *J* 3.9 Hz, PhCH(O)CHC*H* minor], 4.27 (m, 1H, H-6_e), 3.92 [d, J_{trans} 2.0 Hz, PhC*H*(O)CHCH major], 3.88 [d, J_{trans} 2.0 Hz, PhC*H*(O)CHCH minor], 3.8–3.4 (m 6H, H-2, H-4, H-5, H-6_a, OCH_2R), 3.16 [m, 1H, PhCH(O)C*H*CH], 1.78 (s, CH_3CON major), 1.77 (s, CH_3CON minor), 1.5–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3H, *J* 6.5 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.2, 155.0 (2C=O), 136.0–125.8 (Ph), 101.1 (C-1), 99.7 [PhCH(O)CH*C*H minor], 99.4 [PhCH(O)CH*C*H major], 78.6 (C-4 major), 78.5 (C-4 minor), 74.9 (C-3), 70.3, 70.0 ($PhCH_2OCO$, OCH_2R), 68.2 (C-6), 65.8 (C-5), 60.5 [Ph*C*H(O)CHCH major], 60.4 [Ph*C*H(O)CHCH minor], 55.6 [PhCH(O)*C*HCH major], 55.4 [PhCH(O)*C*HCH minor], 54.9 (C-2), 31.9–22.6 $[(CH_2)_{10}]$, 23.0 (CH_3CON), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found 654.362872. $C_{37}H_{52}NO_9$ requires 654.364208. Anal. Calcd for $C_{37}H_{51}NO_9$: C, 67.97; H, 7.86; N, 2.14. Found: C, 67.78; H, 7.78; N, 2.10.

3.9.16. 1-Dodecyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-[(2*R*,3*S*)-2,3-epoxy-3-phenylpropylidene]-3-*O*-methanosulfonyl-β-D-glucopyranoside 40. Two stereoisomers were obtained in a 51:49 ratio (2% de). The pure diastereoisomeric mixture was obtained by column chromatography using hexane–ethyl acetate (1.2:1) as eluent. Yield 0.9 g (75%); mp 125–126 °C; $[\alpha]_D = -30.8$ (*c* 0.9, CH_2Cl_2); MS (CI): *m*/*z* 598 (7%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 5.89 (d, $J_{2,NH}$ 7.6 Hz, NH major), 5.87 (d, $J_{2,NH}$ 7.6 Hz, NH minor), 5.23 (t, 1H, $J_{2,3} = J_{3,4}$ 9.4 Hz, H-3), 5.10 (d, 1H, $J_{1,2}$ 8.1 Hz, H-1), 4,63 [d, *J* 3.2 Hz, PhCH(O)-CHC*H* minor], 4.53 [d, *J* 4.6 Hz, PhCH(O)CHC*H* major], 4.28 (m, 1H, H-6_e), 3.91 [d, J_{trans} 1.9 Hz, PhC*H*(O)-CHCH minor], 3.89 [d, J_{trans} 1.9 Hz, PhC*H*(O)CHCH major], 3.79 (m, 1H, OCH_AH_BR), 3.6–3.3 (m, 5H, H-2, H-4, H-5, H-6_a, OCH_AH_BR), 3.15 [m, 1H, PhCH(O)C*H*CH], 3.12 (s, CH_3SO_2 major), 3.05 (s, CH_3SO_2 minor), 2.00 (s, 3H, CH_3CON), 1.5–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3H, *J* 6.4 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.3 (C=O), 135.6–125.6 (Ph), 100.3 (C-1), 99.2 [PhCH(O)CH*C*H], 78.8, 78.5 (C-4, C-3), 70.5 (OCH_2R), 68.2 (C-6), 65.2 (C-5), 60.3, 60.2 [Ph*C*H(O)CHCH], 56.9, 56.9 (C-2), 55.6 [PhCH(O)-*C*HCH major], 54.7 [PhCH(O)*C*HCH minor], 38.7, 38.5 (CH_3SO_2), 31.9–22.6 $[(CH_2)_{10}]$, 23.4 (CH_3CON), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found 598.305657. $C_{30}H_{48}NO_9S$ requires 598.304979. Anal. Calcd for $C_{30}H_{47}NO_9S$: C, 60.28; H, 7.65; N, 2.34. Found: C, 60.55; H, 7.67; N, 2.43.

3.9.17. 1-Dodecyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-[(2*R*,3*S*)-2,3-epoxy-2-methyl-3-phenylpropylidene]-3-*O*-methanosulfonyl-β-D-glucopyranoside 41. Two stereoisomers were obtained in a 56:44 ratio (12% de). The pure diastereoisomeric mixture was obtained by column chromatography using hexane–ethyl acetate (1.2:1) as eluent. Yield 0.8 g (68%); mp 139–140 °C; $[\alpha]_D = -30.4$ (*c* 0.9, $CHCl_3$); MS (CI): *m*/*z* 612 (13%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 5.96 (m, 1H, NH), 5.24 (m, 1H, H-3), 5.14 (d, $J_{1,2}$ 8.1 Hz, H-1 major), 5.13 (d, $J_{1,2}$ 8.0 Hz, H-1 minor), 4.52 [s, PhCH(O)C(CH_3)C*H* minor], 4.34 [s, PhCH(O)-C(CH_3)C*H* major], 4.28 (m, 1H, H-6_e), 4.09 [s, PhC*H*(O)C(CH_3)CH minor], 4.03 [s, PhC*H*(O)-C(CH_3)CH major], 3.81 (m, 1H, OCH_AH_BR) 3.7–3.3 (m, 5H, H-2, H-4, H-5, H-6_a, OCH_AH_BR), 3.13 (s, CH_3SO_2 major), 3.08 (s, CH_3SO_2 minor), 2.00 (s, 3H, CH_3CON), 1.5–1.2 [m, 20H, $(CH_2)_{10}$], 1.08 [s, PhCH(O)C(C*H*$_3$)CH minor], 1.04 [s, PhCH(O)-C(C*H*$_3$)CH major], 0.86 (t, 3H, *J* 6.4 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.4 (C=O), 134.4–126.3 (Ph), 103.7 [PhCH(O)C(CH_3)*C*H major], 102.5 [PhCH(O)C(CH_3)*C*H minor], 100.1 (C-1), 78.8, 78.7 (C-4, C-3), 70.6 (OCH_2R), 68.2 (C-6), 65.3 (C-5), 62.1 [PhCH(O)*C*(CH_3)CH major], 62.0 [PhCH(O)-*C*(CH_3)CH minor], 60.9 [Ph*C*H(O)C(CH_3)CH major], 60.0 [Ph*C*H(O)C(CH_3)CH minor], 57.4 (C-2), 38.7 (CH_3SO_2 major), 38.5 (CH_3SO_2 minor), 31.9–22.7 $[(CH_2)_{10}]$, 23.4 (CH_3CON), 14.1 (CH_3), 11.5 [PhCH(O)-C(*C*H$_3$)CH minor], 10.6 [PhCH(O)C(*C*H$_3$)CH major]. HRMS (CI): $[M+H]^+$, found 612.320568. $C_{31}H_{50}NO_9S$ requires 612.320630. Anal. Calcd for $C_{31}H_{49}NO_9S$: C, 60.87; H, 8.07; N, 2.29. Found: C, 60.65; H, 7.93; N, 2.49.

3.9.18. 1-Dodecyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-[(2*S*,3*R*)-2,3-epoxy-3-phenylpropylidene]-β-D-allopyranoside 42. Two stereoisomers were obtained in an 83:17 ratio (66% de). The pure diastereoisomeric mixture was obtained by column chromatography using dichloromethane–methanol (60:1) as eluent. Yield 0.6 g (60%); mp 212–213 °C; $[\alpha]_D = -40.9$ (*c* 1.1, DMF); MS (CI): *m*/*z* 520 (18%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 5.96 (d, 1H, $J_{2,NH}$ 9.1 Hz, NH), 4.68 [d, *J* 3.8 Hz, PhCH(O)CHC*H* major], 4.65 [d, *J* 3.8 Hz, PhCH(O)CHC*H* minor], 4.61 (d, $J_{1,2}$ 8.5 Hz, H-1 major), 4.57 (d, $J_{1,2}$ 8.5 Hz, H-1 minor), 4.3–4.2 (m, 2H, H-3, H-6_e), 4.08 (dt, 1H, $J_{1,2}$ 8.5 Hz, $J_{2,3}$ 2.8 Hz, $J_{2,NH}$ 9.0 Hz, H-2), 3.93 [d, J_{trans} 2.0 Hz, PhC*H*(O)CHCH major], 3.91 [d, J_{trans} 2.0 Hz, PhC*H*(O)CHCH minor], 3.87 (dt, 1H, $J_{4,5} = J_{5,6a}$ 10.0 Hz, $J_{5,6e}$ 4.7 Hz, H-5), 3.80 (m, 1H, OCH_AH_BR), 3.61 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.2 Hz, H-6_a minor), 3.60 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.2 Hz, H-6_a major), 3.46 (dd, 1H,

$J_{3,4}$ 2.4 Hz, $J_{4,5}$ 9.6 Hz, H-4), 3.40 (m, 1H, OCH_AH_BR), 3.19 [dd, 1H, J_{trans} 2.0 Hz, J 3.8 Hz, PhCH(O)C*H*CH], 2.08 (s, CH_3CON minor), 1.99 (s, CH_3CON major), 1.5–1.2 [m, 20H, $(CH_2)_{10}$], 0.85 (t, 3H, J 6.9 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.6 (C=O), 135.7–125.8 (Ph), 100.2 (C-1), 99.8 [PhCH(O)CH*C*H], 78.4 (C-4), 69.9 (OCH_2R), 68.7 (C-6), 68.5 (C-3), 63.1 (C-5), 60.7 [PhCH(O)*C*HCH], 55.4 [Ph*C*H(O)CHCH], 52.1 (C-2), 31.9–22.7 [$(CH_2)_{10}$], 23.3 (CH_3CON), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found 520.326261. $C_{29}H_{46}NO_7$ requires 520.327428. Anal. Calcd for $C_{29}H_{45}NO_7$: C, 67.03 H, 8.73; N, 2.55. Found: C, 66.96; H, 8.55; N, 2.45.

3.10. Hydrogenolysis reactions

A solution of compound **26** or **33** (0.5 mmol) in methanol (10 mL) was hydrogenolyzed over 10% Pd(C) (50 mg) at room temperature and atmospheric pressure. TLC indicated complete reaction after 2 days. The mixture was diluted with methanol, the catalyst filtered off and washed with methanol, and the filtrate concentrated to dryness under reduced pressure.

3.10.1. 1-Dodecyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-[(2*R*)-2-hydroxy-3-phenylpropylidene]-β-D-glucopyranoside 43. Two stereoisomers were obtained in a 72:28 ratio (44% de). The pure diastereoisomeric mixture was obtained by column chromatography using dichloromethane–methanol (20:1) as eluent. Yield 0.18 g (70%); mp 188–190 °C; $[\alpha]_D = -23.2$ (c 0.8, DMF); MS (CI): m/z 522 (41%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.1 (m, 5H, Ph), 6.30 (d, $J_{2,NH}$ 6.4 Hz, NH minor), 6.09 (d, $J_{2,NH}$ 6.3 Hz, NH major), 4.61 (d, $J_{1,2}$ 8.3 Hz, H-1 major), 4.59 (d, $J_{1,2}$ 8.4 Hz, H-1 minor), 4.46 [d, J 3.3 Hz, $PhCH_2CH(OH)CH$ major], 4.41 [d, J 5.6 Hz, $PhCH_2CH(OH)CH$ minor], 4.22 (dd, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 10.4 Hz, H-6_e major), 4.18 (dd, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 10.4 Hz, H-6_e minor), 2.94 [dd, J 3.6 Hz, J_{gem} 14.0 Hz, $PhCH_AH_BCH(OH)CH$ minor], 2.89 [dd, J 4.9 Hz, J_{gem} 14.0 Hz, $PhCH_AH_BCH(OH)CH$ major], 2.79 [dd, J 8.5 Hz, J_{gem} 14.0 Hz, $PhCH_AH_BCH(OH)CH$ major], 2.75 [dd, J 8.6 Hz, J_{gem} 14.0 Hz, $PhCH_AH_BCH(OH)CH$ minor], 1.98 (s, CH_3CON major), 1.94 (s, CH_3CON minor), 1.6–1.2 [m, 20H, $(CH_2)_{10}$], 0.84 (t, 3H, J 6.9 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.0 (C=O), 138.0–126.4 (Ph), 101.6 (C-1), 100.8 [$PhCH_2CH(OH)CH$], 81.1 (C-4 major), 80.9 (C-4 minor), 72.8 [$PhCH_2CH(OH)CH$ minor], 72.5 [$PhCH_2CH(OH)CH$ major], 70.9 (C-3), 70.1 (OCH_2R), 68.1 (C-6), 66.2 (C-5), 58.4 (C-2 major), 57.9 (C-2 minor), 38.0 [$PhCH_2CH(OH)CH$ minor], 37.5 [$PhCH_2$ CH(OH)CH major], 31.9–22.7 [$(CH_2)_{10}$], 23.4 (CH_3CON), 14.1 (CH_3). Anal. Calcd for $C_{29}H_{47}NO_7$: C, 66.77; H, 9.08; N, 2.68. Found: C, 66.62; H, 8.96; N, 2.65.

3.10.2. 1-Dodecyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-[(2*S*)-2-hydroxy-3-phenylpropylidene]-β-D-glucopyranoside 44. Two stereoisomers were obtained in a 62:38 ratio (24% de). The pure diastereoisomeric mixture was obtained by column chromatography using dichloromethane–methanol (20:1) as eluent. Yield 0.19 g (74%); mp 183–184 °C; $[\alpha]_D = -29.7$ (c 0.7, DMF); MS (CI): m/z 522 (35%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 5.83 (d, $J_{2,NH}$ 6.0 Hz, NH major), 5.75 (d, $J_{2,NH}$ 6.2 Hz, NH minor), 4.65 (d, $J_{1,2}$ 8.4 Hz, H-1 minor), 4.62 (d, $J_{1,2}$ 8.5 Hz, H-1 major), 4.45 [d, J 3.7 Hz, $PhCH_2CH(OH)CH$ minor], 4.43 [d, J 5.0 Hz, $PhCH_2CH(OH)CH$ major], 4.25 (dd, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 10.4 Hz, H-6_e minor), 4.20 (dd, $J_{5,6e}$ 4.7 Hz, $J_{6e,6a}$ 10.4 Hz, H-6_e major), 2.96 [dd, J 4.1 Hz, J_{gem} 14.0 Hz, $PhCH_AH_BCH(OH)CH$ major], 2.91 [dd, J 5.4 Hz, J_{gem} 14.0 Hz, $PhCH_AH_BCH(OH)CH$ minor], 2.82 [dd, J 8.3 Hz, J_{gem} 14.0 Hz, $PhCH_AH_BCH(OH)CH$ minor], 2.73 [dd, J 8.6 Hz, J_{gem} 14.0 Hz, $PhCH_AH_BCH(OH)CH$ major], 2.01 (s, CH_3CON minor), 2.00 (s, CH_3CON major), 1.6–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3H, J 6.9 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.9 (C=O), 137.9–126.4 (Ph), 101.8 (C-1), 100.8 [$PhCH_2CH(OH)CH$ minor], 100.7 [$PhCH_2CH(OH)CH$ major], 81.2 (C-4 major), 81.1 (C-4 minor), 72.8 [$PhCH_2CH(OH)CH$ minor], 72.5 [$PhCH_2CH(OH)CH$ major], 71.0 (C-3 major), 70.8 (C-3 minor), 70.1 (OCH_2R), 68.1 (C-6), 66.2 (C-5 major), 66.0 (C-5 minor), 58.9 (C-2 major), 58.5 (C-2 minor), 38.0 [$PhCH_2CH(OH)CH$ minor], 37.8 [$PhCH_2CH(OH)CH$ major], 31.9–22.6 [$(CH_2)_{10}$], 23.5 (CH_3CON), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found 522.341338. $C_{29}H_{48}NO_7$ requires 522.343078.

3.11. Ring-opening nucleophilic reactions

3.11.1. *c*-Hexyl 2-acetamido-(*R*)-4,6-*O*-[(2*R*,3*R*)-3-azido-2-hydroxy-2-methyl-3-phenylpropylidene]-2-deoxy-β-D-glucopyranoside 45. To a solution of compound **28** (0.26 g, 0.58 mmol) in acetonitrile (25 mL) were added lithium perchlorate (0.19 g, 1.8 mmol) and sodium azide (0.30 g, 4.6 mmol). The mixture was stirred at 80 °C for 9 days. The salts were filtered off, and the filtrate concentrated to a small volume. Water was added slowly until a white precipitate was formed. Two stereoisomers were obtained in a 93:7 ratio (86% de). The solid was isolated by filtration, and recrystallized from 96% ethanol. Yield 0.20 g (70%); mp 228–230 °C; $[\alpha]_D = -18.1$ (c 0.9, DMF); MS (CI): m/z 491 (35%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 6.13 (br s, 1H, NH), 4.8–4.7 [m, 2H, H-1, $PhCH(N_3)C(CH_3)(OH)CH$], 4.25 [s, 1H, $PhCH(N_3)C(CH_3)(OH)CH$], 4.20 (dd, $J_{5,6e}$ 4.8 Hz, $J_{6e,6a}$ 10.4 Hz, H-6_e), 4.04 (t, 1H, $J_{2,3} = J_{3,4}$ 9.3 Hz, H-3), 3.49 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.3 Hz, H-6_a), 3.4–3.3 (m, 3H, H-2, H-5, OCHR), 3.17 (t, 1H, $J_{3,4} = J_{4,5}$ 9.2 Hz, H-4), 2.00 (s, CH_3CON major), 1.99 (s, CH_3CON minor), 1.8–1.1 [m, 13H, $(CH_2)_5$, $PhCH(N_3)C(CH_3)(OH)CH$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.0 (C=O), 135.8–126.6 (Ph), 102.8 (C-1), 98.9 [$PhCH(N_3)C(CH_3)(OH)CH$ major], 98.8 [$PhCH(N_3)C(CH_3)(OH)CH$ minor], 81.2 (C-4), 77.9 (OCHR), 75.1 [$PhCH(N_3)C(CH_3)(OH)CH$], 70.7 (C-3 major), 70.0 (C-3 minor), 69.0 [$PhCH(N_3)C(CH_3)(OH)CH$], 68.3 (C-6 major), 67.9 (C-6 minor), 66.0 (C-5 major), 65.9 (C-5 minor), 59.1 (C-2 major), 58.8 (C-2 minor), 33.4–23.8 [$(CH_2)_5$], 23.6 (CH_3CON), 18.8 [$PhCH(N_3)C(CH_3)(OH)CH$]. HRMS (CI): $[M+H]^+$, found 491.251897. $C_{24}H_{35}N_4O_7$ requires 491.250575. Anal. Calcd for $C_{24}H_{34}N_4O_7$: C, 58.76; H, 6.99; N, 11.42. Found: C, 58.63; H, 7.12; N, 11.31.

3.11.2. *c*-Hexyl 2-acetamido-2-deoxy-(*R*)-4,6-*O*-[(2*R*, 3*R*)-2-hydroxy-2-methyl-3-phenyl-3-(1-piperidyl)propylidene]-β-D-glucopyranoside 46. To a solution of compound **28** (0.10 g, 0.22 mmol) in acetonitrile (10 mL) were added lithium perchlorate (24 mg, 0.23 mmol) and piperidine (0.30 g, 4.6 mmol). The mixture was kept at room temperature for 2-months and then poured into water. The precipitate obtained was isolated by filtration and recrystallized from 96% ethanol. Only one stereoisomer was obtained. Yield 0.75 g (63%); mp 209–210 °C; $[\alpha]_D = -11.0$ (*c* 0.3, DMF); MS (CI): *m*/*z* 533 (15%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 5.77 (d, 1H, $J_{2,NH}$ 5.7 Hz, NH), 4.80 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.12 (dd, $J_{5,6e}$ 5.0 Hz, $J_{6e,6a}$ 10.3 Hz, H-6_e), 4.08 [s, 1H, PhCH(NR_2)C(CH_3)(OH)C*H*], 4.04 (t, 1H, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3), 3.54 [s, 2H, PhC*H*(NR_2)C(CH_3)(OH)CH, OCHR], 3.36 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.3 Hz, H-6_a), 3.22 (dt, 1H, $J_{5,6e}$ 4.9 Hz, $J_{4,5} = J_{5,6a}$ 10.3 Hz, H-5), 3.09 (m, 1H, H-2), 2.80 (t, 1H, $J_{3,4} = J_{4,5}$ 9.6 Hz, H-4), 2.3–1.1 [m, 20H, 2(CH_2)$_5$], 1.98 (s, 3H, CH_3CON), 1.40 [s, 3H, PhCH(NR_2)C(C*H*$_3$)(OH)CH]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.4 (C=O), 135.8–127.0 (Ph), 103.2 (C-1), 98.5 [PhCH(NR_2)C(CH_3)(OH)*C*H], 81.3 (C-4), 77.7 (OCHR), 77.4 [PhCH(NR_2)*C*(CH_3)(OH)CH], 73.4 [Ph*C*H(NR_2)C(CH_3)(OH)CH], 70.4 (C-3), 68.2 (C-6), 66.2 (C-5), 59.3 (C-2), 53.1 (CH_2NCH_2), 33.4–23.8 [(CH_2)$_3$, (CH_2)$_5$], 23.6 (*C*H$_3$CON), 20.4 [PhCH(NR_2)C(*C*H$_3$)(OH)CH]. HRMS (CI): $[M+H]^+$, found 533.322800. $C_{29}H_{45}N_2O_7$ requires 533.322677. Anal. Calcd for $C_{29}H_{44}N_2O_7$: C, 65.39; H, 8.33; N, 5.26. Found: C, 65.54; H, 8.20; N, 5.02.

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References

1. Vega-Pérez, J. M.; Candela, J. I.; Blanco, E.; Iglesias-Guerra, F. *Tetrahedron: Asymmetry* **2002**, *13*, 2471–2483.
2. Kunz, H.; Rück, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 336–358.
3. Vega-Pérez, J. M.; Candela, J. I.; Blanco, E.; Iglesias-Guerra, F. *Tetrahedron* **1999**, *55*, 9641–9650.
4. Vega-Pérez, J. M.; Vega, M.; Blanco, E.; Iglesias-Guerra, F. *Tetrahedron: Asymmetry* **2001**, *12*, 135–147.
5. Iglesias-Guerra, F.; Romero, I.; Alcudia, F.; Vega-Pérez, J. M. *Carbohydr. Res.* **1998**, *308*, 57–62.
6. Iglesias-Guerra, F.; Candela, J. I.; Bautista, J.; Alcudia, F.; Vega-Pérez, J. M. *Carbohydr. Res.* **1999**, *316*, 71–84.
7. Vega-Pérez, J. M.; Candela, J. I.; Romero, I.; Blanco, E.; Iglesias-Guerra, F. *Eur. J. Org. Chem.* **2000**, 3949–3956.
8. Vega-Pérez, J. M.; Vega, M.; Blanco, E.; Iglesias-Guerra, F. *Tetrahedron: Asymmetry* **2001**, *12*, 3189–3203.
9. Iglesias-Guerra, F.; Candela, J. I.; Blanco, E.; Alcudia, F.; Vega-Pérez, J. M. *Chirality* **2002**, *14*, 199–203.
10. Halmos, T.; Santarromana, M.; Antonakis, K.; Scherman, D. *Eur. J. Pharmacol.* **1996**, *318*, 477–484.
11. Lin, T. S.; Fischer, P. H.; Prusoff, W. H. *J. Med. Chem.* **1980**, *23*, 1235–1237.
12. Yamashita, M.; Takahashi, C. *Heterocycles* **1993**, *36*, 651–654.
13. Fringuelli, F.; Pizzo, F.; Rucci, M.; Vaccaro, L. *J. Org. Chem.* **2003**, *68*, 7041–7045.
14. Iglesias-Guerra, F.; Candela, J. I.; Espartero, J. L.; Vega-Pérez, J. M. *Tetrahedron Lett.* **1994**, *35*, 5031–5034.
15. Vega-Pérez, J. M.; Candela, J. I.; Iglesias-Guerra, F. *J. Org. Chem.* **1997**, *62*, 6608–6611.
16. Gross, P. H.; Jeanloz, R. W. *J. Org. Chem.* **1967**, *32*, 2759–2763.
17. Murphy, P. V.; O'Brien, J. L.; Gorey-Feret, L. J.; Smith, A. B. *Tetrahedron* **2003**, *59*, 2259–2271.
18. Padwa, A.; Blacklock, T.; Tremper, A. *Org. Synth.* **1988**, *6*, 893–896.
19. Peter, M. G.; Boldt, P.-C.; Petersen, S. *Liebigs Ann. Chem.* **1992**, 1275–1279.