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Stereoselective synthesis of oxiranes using oxazolidines derived from 2-amino-2-deoxy-D-allose as chiral auxiliaries†

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Abstract—The synthesis of 2,3-epoxyamide derivatives of 2-amino-2-deoxy-D-allose is described. Epoxidation of the corresponding α,β-unsaturated amides with *m*-CPBA took place with better stereoselectivity when an oxazolidine ring was fused to the 2,3-positions of the sugar molecule. In most cases, both stereoisomers could be isolated and characterized. The stereochemistry of the new stereogenic centers was then determined by cleavage of the oxirane moiety from the chiral auxiliary, which was also recovered.

1. Introduction

Chiral 1,3-oxazolidines are widely used in asymmetric synthesis. They are usually prepared by reaction of carbonyl compounds (mainly aldehydes) with chiral β-amino alcohols—ephedrine, norephedrine, phenylglycinol, prolinol are among the most commonly used.[2–7] Bicyclic oxazolidines have also been prepared by condensation of a chiral β-amino alcohol with dialkyl γ- and δ-chloroketones[8] and with keto-acids,[9–12] generating in the process a new stereogenic center with high stereoselectivity. Many authors have studied the reactivity of the oxazolidine ring with nucleophilic agents, a good approach to the asymmetric synthesis of chiral nitrogenated compounds (amines, pyrrolidines, piperidines, α-amino aldehydes, etc.).[13–17] At the same time, various asymmetric transformations (Diels–Alder cycloadditions, nucleophile addition, epoxidations) have been carried out on α,β-unsaturated carbonyl compounds derived from chiral oxazolidines.[3,4,18,19]

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.[20–22] They are prepared by oxidation of the appropriate alkene,[23–27] or alternatively from aldehydes by employing either the Darzens reaction or a sulphur ylide-mediated approach.[28–32]

Carbohydrates are polyfunctional molecules with several stereogenic centers, making them important chiral templates for numerous asymmetric transformations.[33] As part of our work, we have used 2-aminosugars with *gluco*-, *allo*- and *altro*-configuration as chiral starting materials in the synthesis of numerous compounds (2-aminoglycals, 2-nitrosugars, compounds with potential anti-cancer activity).[34–39] In previous papers, we have reported the synthesis of oxazolidines from 2-amino-2-deoxy-D-glucose and D-allose derivatives with different groups on C(2) of the oxazolidine ring, and the reactivity of these compounds with nucleophiles.[1,40–43] We have also reported the stereoselective epoxidation of allyl glucopyranoside derivatives and their reactivity with different nucleophiles.[44]

Herein, we describe the use of the oxazolidines derived from 2-amino-2-deoxy-D-allose as chiral auxiliaries in the asymmetric synthesis of the oxiranes of α,β-unsaturated amides.

2. Results and discussion

The alkyl 2-acylamino-(*R*)-4,6-*O*-benzylidene-2-deoxy-D-allopyranosides **4**–**10** were obtained in excellent yields from benzyl or dodecyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-D-allopyranosides **1**,[45] **2**[45] and **3**[36] by reaction with the corresponding activated unsaturated acid. We have used three different methods for these reactions, depending on the acid derived and the condensing agent (Scheme 1). The NMR spectra showed signals corresponding to the unsaturated moiety incorporated to the sugar molecule in the reaction. In the ^{1}H spectra,

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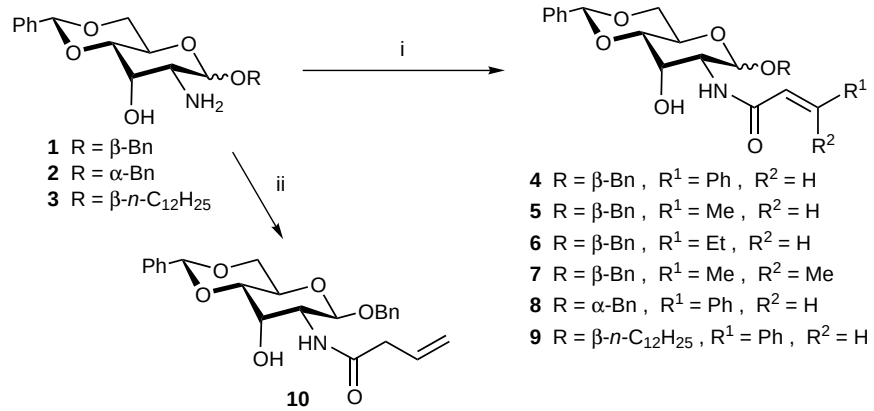
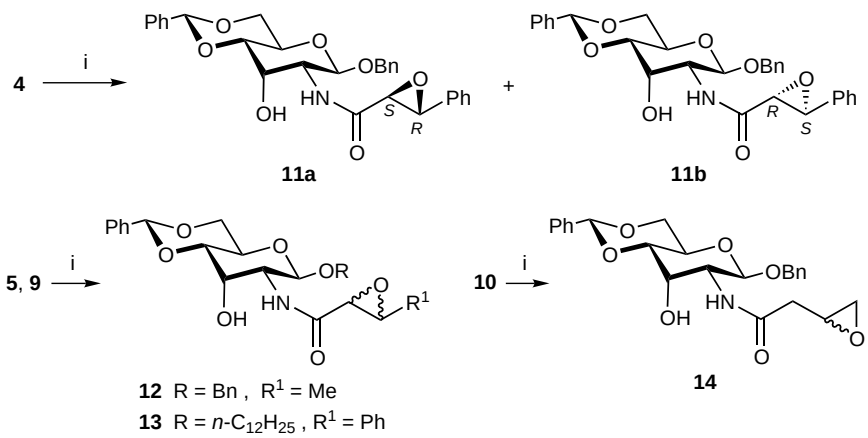


Scheme 1. (i) Method A: *trans*-PhCH=CHCOCl/Py/CH_2Cl_2 (**4**, **8**, **9**); Method B: R^1R^2C=$CHCO_2H$/pentachlorophenol trichloroacetate/Et_3N/THF (**5**, **6**, **7**); (ii) Method C: CH_2=$CHCH_2CO_2H$/DCC/DMAP/CH_2Cl_2.

two doublets at 6.4 and 7.6 ppm for compounds **4**, **8** and **9**, two multiplets at 5.7 and 6.9 ppm for **5** and **6**, a multiplet at 5.53 ppm for **7** and two multiplets at 5.80 and 5.14 ppm for **10** were observed. The ^{13}C spectra showed two signals at approximately 120 and 145 ppm for each one of these compounds.

We have studied the effect of the stereogenic centers of the sugar in the stereofacial differentiation of the diastereotopic faces of the double bond in the epoxidation reaction, and used ^1H NMR to determine the diastereomeric excess (de) in each case. The reaction of **4**, **5**, **9** and **10** with *m*-chloroperbenzoic acid (*m*-CPBA) in dichloromethane at room temperature gave the corresponding oxiranes **11**–**14**, which were isolated as mixtures of stereoisomers (Scheme 2, Table 1). The ^1H NMR spectrum for **11** contained two doublets at 3.62 and 3.51 ppm, corresponding to the oxirane protons of the major isomer. For the minor isomer, an isolated doublet was observed at 3.55 ppm, corresponding to the oxirane proton in α-position to the carbonyl group. Compounds **12**, **13** and **14** showed signals between 3.5 and 2.3 ppm for the oxirane system. The ^{13}C spectra showed signals at 60–55 ppm for **11**, **12**, and **13** and at 48.7 and 39.7 ppm for **14**. The results of this reaction, shown in Table 1, indicate that the de is low when the reaction is carried out at room temperature (entries 1, 3, 4, 5) and somewhat better when the reaction is performed at −10°C (entry 2), although at the cost of a considerable increase in reaction time. Moreover, the solubility of compounds **4**, **5**, **9** and **10** in dichloromethane at −10°C is much lower than at room temperature, which means having to use greater amounts of solvent and oxidant for the same amount of starting material.

Epoxides **11**, **12** and **14**, used as stereoisomeric mixtures, were ring-opened with lithium aluminum hydride, giving the hydroxylamides **15**, **16** and **17** (Scheme 3). The reaction of **11** gave only one regioisomer **15**, which was characterized as its diacetyl derivative **18**. The reaction of **12** gave **16** and **17** in 1:3 ratio. The ^1H NMR spectrum shows two signals for methyl group, a triplet at 0.87 ppm for **16**, and a doublet at 1.17 ppm for **17**, with relative integral of 1:3. Compound **14** afforded **17** as the sole product.

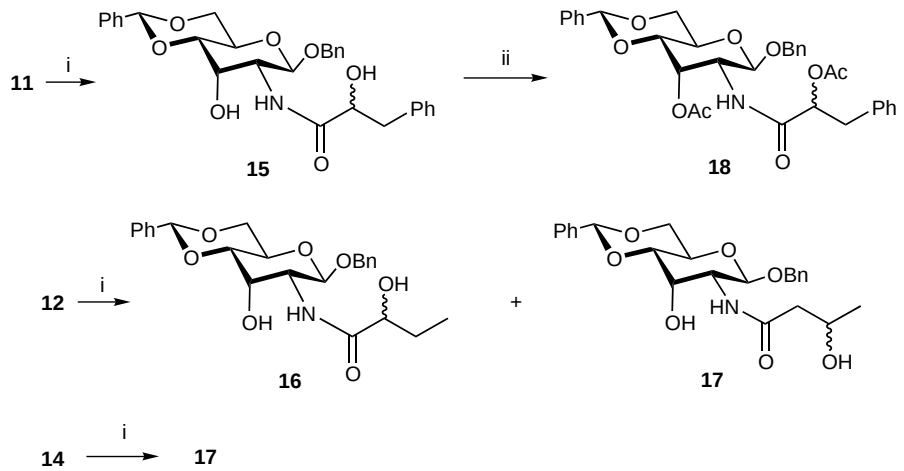


Scheme 2. (i) *m*-CPBA/CH_2Cl_2.

Table 1. Epoxidation of unsaturated amides **4**, **5**, **9**, **10**, **19**–**22**, **24** and **26** with *m*-CPBA at room temperature

Entry	Starting compound	Reaction time[a] (days)	Reaction product	Yield[b] (%)	De[c] (%)
1	**4**	2	**11**	80	26
2	**4**	10[d]	**11**	71	40
3	**5**	3	**12**	95	16
4	**9**	3	**13**	91	0
5	**10**	2	**14**	85	12
6	**19**	2	**27**	85	94
7	**20**	2	**28**	80	44
8	**21**	2	**29**	83	46
9	**22**	3	**30**	78	48
10	**24**	3	**32**	94	76
11	**26**	2	**33**	75	50

[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 integration in ^{1}H NMR spectra of reaction mixtures.
[d] Reaction at −10°C.

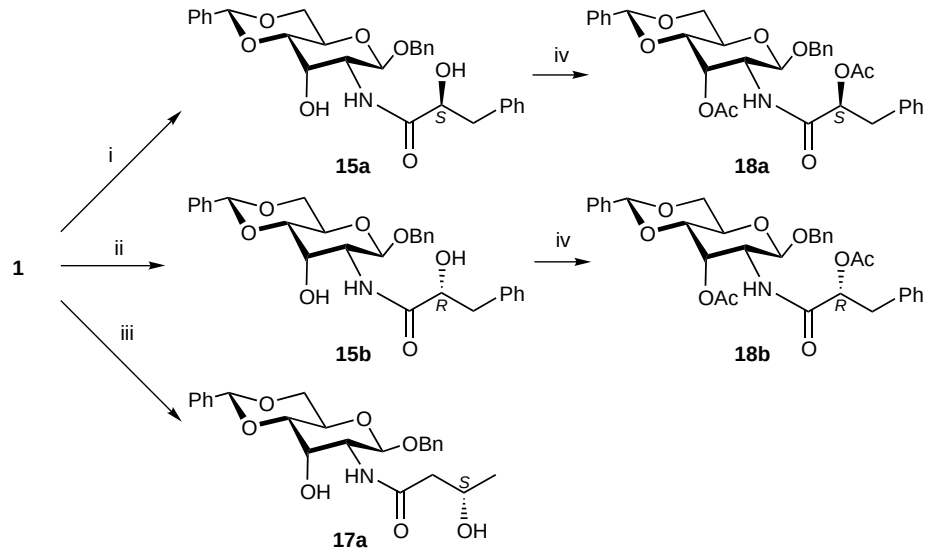


Scheme 3. (i) $LiAlH_4$/THF/−10°C; (ii) Ac_2O/Py/CH_2Cl_2.

With the aim of demonstrating the regiochemistry of the oxirane ring opening reaction of **11**, **12**, and **14**, and the stereochemistry of the major stereoisomer of oxiranes **11**, we obtained compounds **15a**, **15b** and **17a** by unequivocal synthesis from compound **1** and the corresponding enantiomerically pure acid, and their diacetyl derivatives **18a** and **18b** (Scheme 4). The NMR data, shown in Tables 2 and 3, indicates that in the stereoisomeric mixture **15** (Table 2) and **18** (Table 3), the major isomer has (*S*)-configuration at the stereogenic carbon in the α-position of the amide group (**15a** and **18a**), and thus the major stereoisomer in the oxirane **11** has (2*S*,3*R*)-configuration (**11a**) (Scheme 2).

We have also studied the epoxidation of α,β-unsaturated amides derived from sugar-oxazolidines. The formation of a new ring between positions 2 and 3 of the sugar increases the rigidity of the chiral auxiliary, and thus enables greater stereoselectivity in the epoxidation reaction. The alkyl 2-*N*-acyl-2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-methylidene-D-allopyranosides **19**–**24** were obtained in good yield from compounds **4**–**9** by reaction with dibromomethane under phase-transfer conditions, using a methodology described previously by our research group[1,41,42] (Scheme 5). The NMR spectra showed signals corresponding to the methylidene group introduced in the reaction. In the ^{1}H spectra, two doublets between 5.35 and 5.15 ppm were observed in each case. The ^{13}C spectra contained a signal at 82–80 ppm for each compound.

The synthesis of compound **26** was carried out from **10** in two steps (Scheme 5). The treatment of **10** with acetone–dichloromethane (1:1) containing magnesium sulphate as a dehydrating agent gave the oxazolidine **25**, characterized by its mass spectrum {MS (CI) *m*/*z* 398 (100%) $[M+H]^+$}. It was used without further purification because of its low stability (oxazolidine ⇌ imine equilibrium has been described for compounds with this structure).[2] The reaction of **25** with crotonyl chloride/pyridine in dichloromethane at 0°C yielded compound **26** (65% from **10**). The NMR data confirm the presence of the isopropylidene group (1.64 and 1.58 ppm in ^{1}H spectrum, 26.5 and 23.8 ppm in ^{13}C spectrum) and the crotonyl group (three signals at 6.90, 6.48 and 1.75 ppm in ^{1}H spectrum, 163.3, 140.9, 124.5 and 17.7 ppm in ^{13}C spectrum).



Scheme 4. (i) (*S*)-(−)-3-Phenyllactic acid/DCC/NHS/dioxane; (ii) (*R*)-(+)-3-phenyllactic acid/DCC/NHS/dioxane; (iii) (*S*)-(+)-3-hydroxybutyric acid/DCC/NHS/dioxane; (iv) $Ac_2O/Py/CH_2Cl_2$.

Table 2. Comparison of the NMR data (δ, ppm) for the stereoisomeric mixture **15** and the diastereomerically pure compounds **15a** and **15b**

Entry	Signal assigned	**15** major isomer/minor isomer	**15a** (*S*-configuration)	**15b** (*R*-configuration)
1	NH	6.93/6.83	6.88	6.79
2	$OCH_A\underline{H}_BPh$	4.57/4.55	4.57	4.56
3	$CH(OH)CH_A\underline{H}_BPh$	2.75/2.87	2.77	2.89
4	$\underline{C}H(OH)CH_2Ph$	73.1/72.8	73.0	72.8
5	$CH(OH)\underline{C}H_2Ph$	41.0/40.7	41.0	40.7

Table 3. Comparison of the NMR data (δ, ppm) for the stereoisomeric mixture **18** and the diastereomerically pure compounds **18a** and **18b**

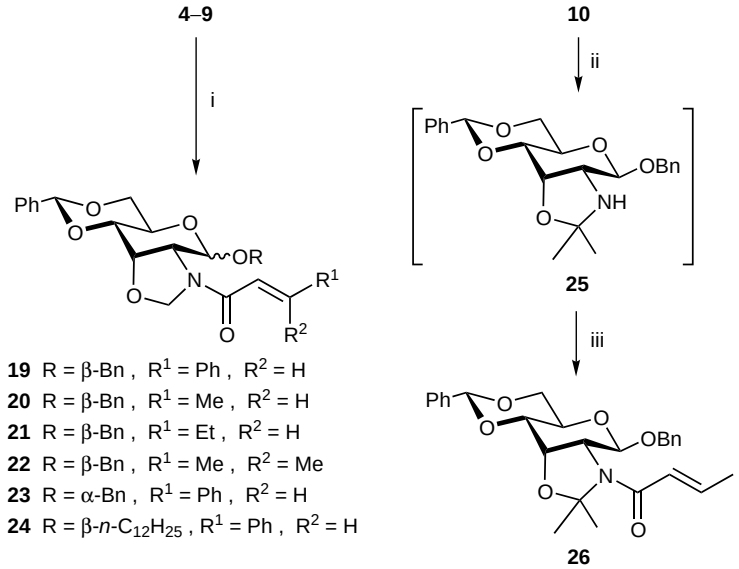
Entry	Signal assigned	**18** major isomer/minor isomer	**18a** (*S*-configuration)	**18b** (*R*-configuration)
1	NH	5.96/6.05	6.00	6.06
2	H-3	5.67/5.63	5.68	5.64
3	$2CH_3CO$	2.05, 1.90/2.04, 1.94	2.05, 1.91	2.05, 1.95
4	$\underline{C}H(OAc)CH_2Ph$	74.3/74.1	74.3	74.1
5	$CH(OAc)\underline{C}H_2Ph$	37.2/36.8	37.2	36.8

The reaction of **19**–**24** and **26** with *m*-CPBA in dichloromethane at room temperature gave the corresponding oxiranes **27**–**33** as mixtures of stereoisomers with good yields and with de of between 44 and 94% (Scheme 6, Table 1). In most cases, both stereoisomers were isolated by column chromatography, the major isomer always having the higher R_f. The NMR data for the oxirane system in compounds **27**–**33** are shown in Table 4. In the ^1H NMR spectra of these compounds, the signal corresponding to the α-protons of the oxirane ring appears with a greater chemical shift in the minor isomer, while the chemical shift of the β-proton is greater for the major isomer. In all ^{13}C spectra of these compounds, the two signals corresponding to the oxirane carbons appear with the greater chemical shift in the major isomer.

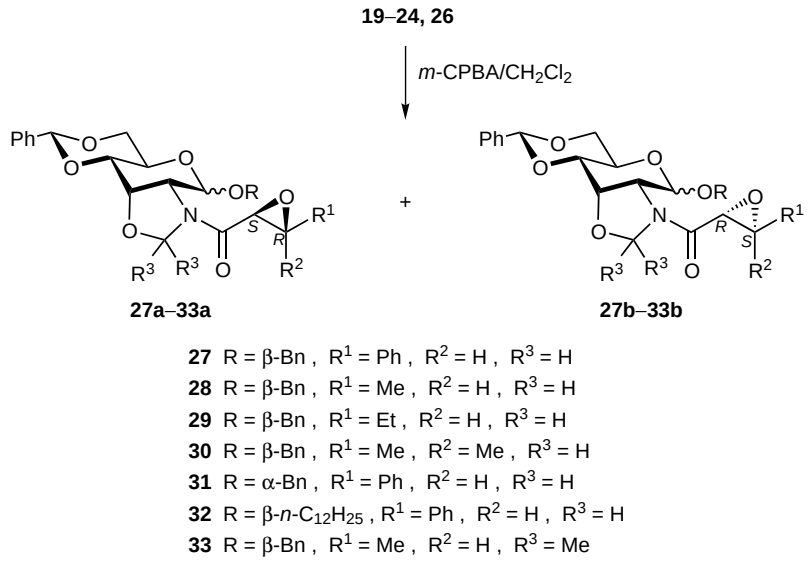
The absolute stereochemistry of the 2,3-epoxyamides was deduced by correlation with the (2*R*,3*R*)-(+)-3-phenylglycidol obtained from **27** or **32**. The reaction of the major isomer of **27** or **32** with sodium borohydride in THF at room temperature yielded a sugar derivative identified by MS as compound **1** or **3**, and another identified by MS, NMR, and $[\alpha]_D$ data as (2*R*,3*R*)-(+)-3-phenylglycidol **34** (Scheme 7). The results indicate that the major stereoisomer of the α,β-epoxyamides has (2*S*,3*R*)-configuration at the oxirane ring.

3. Conclusions

In conclusion, we have presented a stereoselective synthesis of α,β-epoxyamides derived from alkyl allopyran-



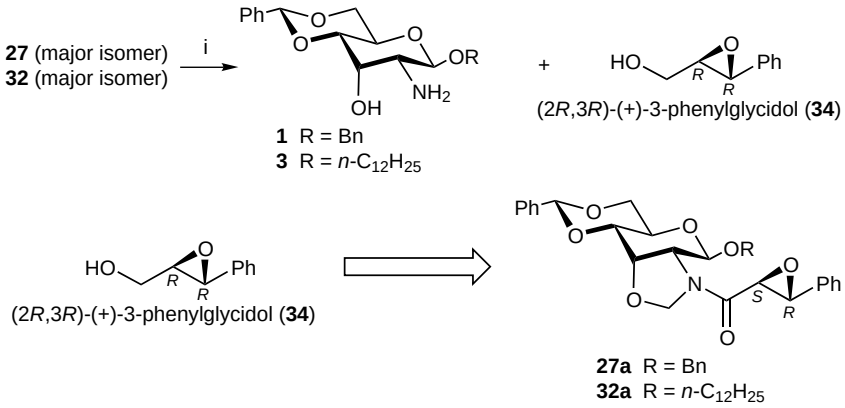
Scheme 5. (i) CH_2Br_2/CH_2Cl_2/TBABr/50% NaOH/H_2O/reflux; (ii) acetone/CH_2Cl_2/$MgSO_4$; (iii) *trans*-CH_3CH=$CHCOCl$/Py/CH_2Cl_2/0°C.



Scheme 6.

Table 4. NMR data (δ, ppm) for the oxiranes **27**–**30**, **32** and **33**

Entry	Compound	C<u>H</u>(O)CHR[1]	CH(O)C<u>H</u>R[1]	<u>C</u>H(O)CHR[1]	CH(O)<u>C</u>HR[1]
1	**27a**	3.95	4.23	58.2	56.6
2	**28a**	3.43	3.24	54.5	53.9
3	**28b**	3.75	3.22	54.4	53.8
4	**29a**	3.49	3.19	58.7	52.5
5	**29b**	4.0–3.7	3.15	58.6	52.4
6	**30**	3.33	–	60.7	56.8
7	**32a**	3.97	4.3–4.2	58.8	58.1
8	**32b**	4.09	4.15	58.5	57.8
9	**33a**	3.47	3.23	55.0	54.5
10	**33b**	4.0–3.7	3.17	54.3	54.3



Scheme 7. (i) $NaBH_4$/THF.

osides, with good yields, in which the 2-amino-2-deoxy-D-allose moiety acts as an effective chiral auxiliary. When positions 2 and 3 of the sugar participate in an oxazolidine ring, (a) the starting compounds are more soluble in dichloromethane, (b) the stereoselectivity of the epoxidation reaction increases considerably, (c) both stereoisomers can be separated and isolated using column chromatography, (d) the α,β-epoxyamide can be separated from the sugar moiety and e) the chiral auxiliary (sugar) can be recovered.

4. Experimental

4.1. 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. Infrared (IR) spectra were obtained on a Jasco FT/IR-410 spectrophotometer. 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 ^1H and 50 MHz for ^{13}C, and on a Bruker AMX-500 spectrometer at 500 MHz for ^1H and 125 MHz for ^{13}C. The chemical shifts are reported in ppm on the δ scale relative to TMS, COSY, DEPT and CHCOOR experiments were performed to assign the signals in the NMR spectra.

4.2. Alkyl 2-acylamino-(*R*)-4,6-*O*-benzylidene-2-deoxy-D-allopyranosides 4–10, 15a, 15b, 17a

4.2.1. Method A. To a solution of either alkyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside **1**–**3** (3.0 mmol) and dry pyridine (15 mL) in distilled dichloromethane (300 mL), cooled to 0°C, cinnamoyl chloride (1.0 g, 6.0 mmol) was added slowly and the reaction mixture was stirred overnight at room temperature. The reaction mixture was diluted with dichloromethane and washed successively with water, saturated aqueous sodium bicarbonate and water, dried ($MgSO_4$), filtered and the filtrate evaporated to dryness to give a solid which was purified by flash chromatography on silica gel.

4.2.1.1. Benzyl (*R*)-4,6-*O*-benzylidene-2-deoxy-2-(*trans*-3-phenyl-2-propenamido)-β-D-allopyranoside 4. Column chromatography using dichloromethane-methanol (150:1) as eluent yielded 1.24 g (85%). Mp 238–239°C; $[\alpha]_D$ −74.1 (*c* 0.5, CH_2Cl_2); MS (CI): *m*/*z* 488 (43%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.65 (d, 1H, J_{trans} 15.6 Hz, CH=CHPh), 7.5–7.2 (m, 15H, 3Ph), 6.35 (d, 1H, J_{trans} 15.6 Hz, CH=CHPh), 6.06 (d, 1H, $J_{2,NH}$ 9.3 Hz, NH), 5.60 (s, 1H, PhCH), 4.90 (d, 1H, J_{gem} 12.5 Hz, OCH_AH_BPh), 4.74 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.59 (d, 1H, J_{gem} 12.5 Hz, OCH_AH_BPh), 4.5–4.3 (m, 2H, H-2, H-6_e), 4.29 (t, 1H, $J_{2,3}=J_{3,4}$ 2.7 Hz, H-3), 3.97 (dt, 1H, $J_{4,5}=J_{5,6a}$ 10.0 Hz, $J_{5,6e}$ 4.5 Hz, H-5), 3.82 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6_a), 3.70 (dd, 1H, $J_{3,4}$ 2.7 Hz, $J_{4,5}$ 9.2 Hz, H-4). ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.5 (C=O), 138.8 (CH=CHPh), 137.7–126.4 (3Ph), 122.4 (CH=CHPh), 100.7 (PhCH), 99.4 (C-1), 78.5 (C-4), 70.2 (OCH_2Ph), 68.3 (C-6), 67.5 (C-3), 63.0 (C-5), 52.9 (C-2). Anal. calcd for $C_{29}H_{29}NO_6$: C, 71.44; H, 6.00; N, 2.87. Found: C, 71.48; H, 6.13; N, 2.86%.

4.2.1.2. Benzyl (*R*)-4,6-*O*-benzylidene-2-deoxy-2-(*trans*-3-phenyl-2-propenamido)-α-D-allopyranoside 8. Column chromatography using hexane–ethyl acetate (15:10) as eluent yielded 1.31 g (90%). Mp 207–208°C; $[\alpha]_D$ +92.0 (*c* 0.4, Cl_2CH_2); MS (CI): *m*/*z* 488 (75%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.62 (d, 1H, J_{trans} 15.6 Hz, COCH=CHPh), 7.5–7.3 (m, 15H, 3Ph), 6.44 (d, 1H, $J_{2,NH}$ 7.6 Hz, NH), 6.42 (d, 1H, J_{trans} 15.6 Hz, COCH=CHPh), 5.62 (s, 1H, PhCH), 5.02 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1), 4.78 (d, 1H, J_{gem} 11.9 Hz, OCH_AH_BPh), 4.53 (d, 1H, J_{gem} 11.9 Hz, OCH_AH_BPh), 4.44 (dd, 1H, $J_{5,6e}$ 4.0 Hz, $J_{6e,6a}$ 9.4 Hz, H-6_e), 4.3–4.1 (m, 3H, H-2, H-3, H-5), 3.79 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 9.4 Hz, H-6_a), 3.69 (dd, 1H, $J_{3,4}$ 2.8 Hz, $J_{4,5}$ 9.4 Hz, H-4). ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.3 (C=O), 141.9 (CH=CHPh), 137.0–126.2 (3Ph), 120.0 (CH=CHPh), 101.9 (PhCH), 97.5 (C-1), 78.5 (C-4), 70.7 (OCH_2Ph), 69.1 (C-6), 68.3 (C-3), 57.8 (C-5), 49.4 (C-2). HRMS (EI): $[M]^{+\bullet}$, found 487.200556. $C_{29}H_{29}NO_6$ requires 487.199488. Anal. calcd for $C_{29}H_{29}NO_6$: C, 71.44; H, 6.00; N, 2.87. Found: C, 71.19; H, 6.22; N, 2.78%.

4.2.1.3. 1-Dodecyl (*R*)-4,6-*O*-benzylidene-2-deoxy-2-(*trans*-3-phenyl-2-propenamido)-β-D-allopyranoside 9. Column chromatography using dichloromethane–methanol (180:1) as eluent yielded 1.44 g (85%). Mp 232–233°C; $[\alpha]_D$ −80.0 (*c* 0.5, DMF); MS (CI): *m*/*z* 566 (100%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.66 (d, 1H, J_{trans} 15.6 Hz, CH=CHPh), 7.5–7.3 (m, 10H, 2Ph), 6.45 (d, 1H, J_{trans} 15.6, CH=CHPh), 6.32 (d, 1H, $J_{2,NH}$ 9.2 Hz, NH), 5.56 (s, 1H, PhCH), 4.73 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.4–4.3 (m, 3H, H-2, H-3, H-6$_e$), 3.98 (m, 1H, $J_{4,5}=J_{5,6a}$ 9.6 Hz, $J_{5,6e}$ 4.6 Hz, H-5), 3.9–3.7 (2H, H-6$_a$, OCH_AH_BR), 3.66 (dd, 1H, $J_{3,4}$ 2.2 Hz, $J_{4,5}$ 9.3 Hz, H-4), 3.44 (m, 1H, OCH_AH_BR), 1.5–1.1 [m, 20H, $(CH_2)_{10}$], 0.85 (t, 3H, *J* 6..6 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.4 (C=O), 141.6 (CH=CHPh), 137.0–126.1 (2Ph), 120.4 (CH=CHPh), 101.6 (PhCH), 100.4 (C-1), 78.7 (C-4), 70.1 (OCH_2R), 69.1 (C-6), 68.8 (C-3), 63.3 (C-5), 52.2 (C-2), 31.9–22.6 [$(CH_2)_{10}$], 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found 566,348086. $C_{34}H_{48}NO_6$ requires 566,348164. Anal. calcd for $C_{34}H_{47}NO_6$: C, 72.18; H, 8.37; N, 2.48. Found: C, 71.93; H, 8.42; N, 2.55%.

4.2.2. Method B. To a solution of the corresponding α,β-unsaturated acid (4.5 mmol) in distilled and dry THF (75 mL), was added triethylamine (9 mL) and the mixture was stirred at room temperature for 30 min. Then pentachlorophenol trichloroacetate (2.80 g, 6.8 mmol) was added, and the mixture was stirred for 3 h. After this time, a solution of alkyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside **1** or **3** (3.0 mmol) in distilled and dry THF (75 mL) was added and the reaction mixture was stirred for a further 8 h. The solvent was evaporated to a volume of 10–15 mL and the mixture was poured into ice-water. The precipitate obtained was isolated by filtration, washed with water and dissolved in dichloromethane. The solution was washed successively with 5% aqueoussodium hydroxide and water, dried ($MgSO_4$), filtered and the filtrate was evaporated to dryness to give a solid, which was purified by flash chromatography on silica gel.

4.2.2.1. Benzyl (*R*)-4,6-*O*-benzylidene-2-(*trans*-2-butenamido)-2-deoxy-β-D-allopyranoside 5. Column chromatography using dichloromethane–methanol (100:1) as eluent yielded 1.17 g (90%). Mp 234–235°C; $[\alpha]_D$ −92.3 (*c* 0.4, CH_2Cl_2); MS (CI): *m*/*z* 426 (92%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 6.86 (m, 1H, CH=CHCH$_3$), 5.85 (d, 1H, $J_{2,NH}$ 9.1 Hz, NH), 5.75 (dq, 1H, J_{trans} 15.2 Hz, ^4J 1.6 Hz, CH=CHCH$_3$), 5.58 (s, 1H, PhCH), 4.88 (d, 1H, J_{gem} 12.5 Hz, OCH_AH_BPh), 4.70 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 4.57 (d, 1H, J_{gem} 12.5 Hz, OCH_AH_BPh), 4.39 (dd, 1H, $J_{5,6e}$ 4.7 Hz, $J_{6e,6a}$ 9.7 Hz, H-6$_e$), 4.3–4.0 (m, 2H, H-2, H-3), 3.95 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.7 Hz, $J_{5,6e}$ 4.7 Hz, H-5), 3.80 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 9.7 Hz, H-6$_a$), 3.67 (dd, 1H, $J_{3,4}$ 2.4 Hz, $J_{4,5}$ 9.7 Hz, H-4), 1.85 (dd, 3H, *J* 6.7 Hz, ^4J 1.6 Hz, CH=CHCH$_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.4 (C=O), 140.7 (CH=CHCH$_3$), 137.3–124.9 (2Ph), 120.0 (CH=CHCH$_3$), 101.7 (PhCH), 99.1 (C-1), 78.7 (C-4), 70.5 (OCH_2Ph), 69.1 (C-6), 68.7 (C-3), 63.3 (C-5), 51.6 (C-2), 17.8 (CH=CHCH$_3$). Anal. calcd for $C_{24}H_{27}NO_6$: C, 67.75; H, 6.40; N, 3.29. Found: C, 67.46; H, 6.20; N, 3.33%.

4.2.2.2. Benzyl 4,6-*O*-benzylidene-2-deoxy-2-(*trans*-2-pentenamido)-β-D-allopyranoside 6. Column chromatography using dichloromethane–methanol (120:1) as eluent yielded 1.19 g (90%). Mp 243–244°C; $[\alpha]_D$ −77.1 (*c*, 0.7, $CHCl_3$); MS (CI): *m*/*z* 440 (20%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 6.92 (dt, 1H, J_{trans} 15.3 Hz, *J* 6.3 Hz, CH=CHCH$_2$CH$_3$), 5.86 (d, 1H, $J_{2,NH}$ 9.2 Hz, NH), 5.72 (dt, 1H, J_{trans} 15.3 Hz, ^4J 1.7 Hz, CH=CHCH$_2$CH$_3$), 5.59 (s, 1H, PhCH), 4.88 (d, 1H, J_{gem} 12.5 Hz, OCH_AH_BPh), 4.69 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.58 (d, 1H, J_{gem} 12.5 Hz, OCH_AH_BPh), 4.40 (dd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 9.9 Hz, H-6$_e$), 4.3–4.2 (m, 2H, H-2, H-3), 3.95 (m, 1H, H-5), 3.80 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 9.9 Hz, H-6$_a$), 3.67 (dd, 1H, $J_{3,4}$ 2.4 Hz, $J_{4,5}$ 9.2 Hz, H-4), 2.21 (m, 2H, CH=CHCH$_2$CH$_3$), 1.06 (t, 3H, *J* 7.4 Hz, CH=CHCH$_2$CH$_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.6 (C=O), 146.9 (CH=CHCH$_2$CH$_3$), 137.3–126.1 (2Ph), 122.4 (CH=CHCH$_2$CH$_3$), 101.7 (PhCH), 99.1 (C-1), 78.7 (C-4), 70.4 (OCH_2Ph), 69.1 (C-6), 68.8 (C-3), 63.3 (C-5), 51.7 (C-2), 25.1 (CH=CHCH$_2$CH$_3$), 12.4 (CH=CHCH$_2$CH$_3$). HRMS (CI): $[M+H]^+$, found 440.207031. $C_{25}H_{30}NO_6$ requires 440.207313. Anal. calcd for $C_{25}H_{29}NO_6$: C, 68.32; H, 6.65; N, 3.19. Found: C, 68.00; H, 6.79; N, 3.29%.

4.2.2.3. Benzyl (*R*)-4,6-*O*-benzylidene-2-deoxy-2-(3-methyl-2-butenamido)-β-D-allopyranoside 7. Column chromatography using dichloromethane–methanol (135:1) as eluent yielded 1.25 g (95%). Mp 208–209°C; $[\alpha]_D$ −91.1 (*c* 0.5, CH_2Cl_2); MS (CI): *m*/*z* 440 (99%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.2 (m, 10H, 2Ph), 5.78 (d, 1H, $J_{2,NH}$ 9.1 Hz, NH), 5.59 (s, 1H, PhCH), 5.53 [m, 1H, CH=C(CH$_3$)$_2$], 4.89 (d, 1H, J_{gem} 12.5 Hz, OCH_AH_BPh), 4.68 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 4.57 (d, 1H, J_{gem} 12.5 Hz, OCH_AH_BPh), 4.39 (dd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 9.9 Hz, H-6$_e$), 4.3–4.2 (m, 2H, H-2, H-3), 3.93 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.9 Hz, $J_{5,6e}$ 4.5 Hz, H-5), 3.80 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 9.9 Hz, H-6$_a$), 3.66 (dd, 1H, $J_{3,4}$ 2.3 Hz, $J_{4,5}$ 9.2 Hz, H-4), 2.15, 1.84 [2d, 6H, ^4J 1.3 Hz, CH=C(CH$_3$)$_2$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.3 (C=O), 151.7 [CH=C(CH$_3$)$_2$], 137.4–126.1 (2Ph), 118.4 [CH=C(CH$_3$)$_2$], 101.7 (PhCH), 99.3 (C-1), 78.7 (C-4), 70.4 (OCH_2Ph), 69.1 (C-6), 68.9 (C-3), 63.3 (C-5), 51.4 (C-2), 27.2, 19.9 [CH=C(CH$_3$)$_2$]. HRMS (CI): $[M+H]^+$, found 440.204192. $C_{25}H_{30}NO_6$ requires 440.207313. Anal. calcd for $C_{25}H_{29}NO_6$: C, 68.32; H, 6.65; N, 3.19. Found: C, 68.03; H, 6.62; N, 3.15%.

4.2.3. Method C. To a solution of benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside **1** (1.07 g, 3.0 mmol) in distilled dichloromethane (100 mL) were sequentially added vinylacetic acid (0.3 mL, 3.5 mmol), 4-(*N*,*N*-dimethylamino)pyridine (0.01 g, 0.08 mmol), and *N*,*N*′-dicyclohexylcarbodiimide (0.7 g, 3.3 mmol), and the mixture was stirred at room temperature for 4 h. The solid was removed by filtration, and the filtrate was diluted with dichloromethane and washed successively with 1 N aqueous acetic acid, saturated aqueous sodium bicarbonate, and water, dried ($MgSO_4$), filtered, and the filtrate evaporated to dryness. The solid was purified by flash chromatography on silica gel, using dichloromethane–methanol (130:1) as eluent, to give **10**.

4.2.3.1. Benzyl (*R*)-4,6-*O*-benzylidene-2-(3-butenamido)-2-deoxy-β-D-allopyranoside 10. Yield 1.15 g (90%). Mp 241–242°C; $[\alpha]_D$ −117.7 (*c* 0.5, CH_2Cl_2); MS (CI): *m/z* 426 (100%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.2 (m, 10H, 2Ph), 6.00 (d, 1H, $J_{2,NH}$ 8.6 Hz, NH), 5.80 (m, 1H, $CH_2C\underline{H}=CH_2$), 5.58 (s, 1H, PhC<u>H</u>), 5.14 (m, 2H, $CH_2CH=C\underline{H}_2$), 4.88 (d, 1H, J_{gem} 12.5 Hz, $OC\underline{H}_AH_BPh$), 4.68 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.57 (d, 1H, J_{gem} 12.5 Hz, $OCH_A\underline{H}_BPh$), 4.39 (dd, 1H, $J_{5,6e}$ 4.4 Hz, $J_{6e,6a}$ 9.8 Hz, H-6_e), 4.25–4.20 (m, 2H, H-2, H-3), 3.95 (m, 1H, $J_{4,5}=J_{5,6a}$ 9.8 Hz, $J_{5,6e}$ 4.4 Hz, H-5), 3.78 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 9.8 Hz, H-6_a), 3.65 (dd, 1H, $J_{3,4}$ 2.2 Hz, $J_{4,5}$ 9.2 Hz, H-4), 2.99 (dt, 2H, *J* 7.1 Hz, ^4J 1.2 Hz, $C\underline{H}_2CH=CH_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.0 (C=O), 137.3–126.1 (2Ph), 131.1 ($CH_2\underline{C}H=CH_2$), 119.8 ($CH_2CH=\underline{C}H_2$), 101,7 (Ph<u>C</u>H), 99.0 (C-1), 78.7 (C-4), 70.5 ($O\underline{C}H_2Ph$), 69.1 (C-6), 68.7 (C-3), 63.3 (C-5), 51.9 (C-2), 41.6 ($\underline{C}H_2CH=CH_2$). Anal. calcd for $C_{24}H_{27}NO_6$: C, 67.75; H, 6.40; N, 3.29. Found: C, 67.50; H, 6.36; N, 3.27%.

4.2.4. Method D. To a solution of the hydroxyacid [(*S*)-(–)-3-phenyllactic acid, (*R*)-(+)-3-phenyllactic acid or (*S*)-(+)-3-hydroxybutyric acid] (1.2 mmol) in dry dioxane (20 mL) *N*-hydroxysuccinimide (0.17 g, 1.5 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.30 g, 1.5 mmol) were added and the mixture was stirred at room temperature for 2 h. The solid was removed by filtration, and to the filtrate, a solution of benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside **1** (0.36 g, 1.0 mmol) and triethylamine (0.2 mL, 1.4 mmol) in dry dioxane (20 mL) was added and the mixture was stirred overnight at room temperature. The solution was poured into water, and the precipitate was filtered and washed with water. The solid was dissolved in dichloromethane and washed successively with saturated aqueous sodium bicarbonate and water, dried ($MgSO_4$), filtered and the filtrate evaporated to dryness. The solid obtained was purified by flash chromatography on silica gel.

4.2.4.1. Benzyl (*R*)-4,6-*O*-benzylidene-2-deoxy-2-[(*S*)-2-hydroxy-3-phenylpropanamido]-β-D-allopyranoside 15a. Column chromatography using dichloromethane–methanol (55:1) as eluent yielded 0.39 g (77%). Mp 248–249°C; $[\alpha]_D$ −142.3 (*c* 0.5, DMF); MS (CI): *m/z* 506 (22%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.2 (m, 15H, 3Ph), 6.88 (d, 1H, $J_{2,NH}$ 9.0 Hz, NH), 5.60 (s, 1H, C<u>H</u>Ph), 4.89 (d, 1H, J_{gem} 12.4 Hz, $OC\underline{H}_AH_BPh$), 4.73 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.57 (d, 1H, J_{gem} 12.4 Hz, $OCH_A\underline{H}_BPh$), 4.40 (dd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 9.8 Hz, H-6_e), 4.3–4.2 [m, 3H, H-2, H-3, C<u>H</u>(OH)CH_2Ph], 3.94 (m, 1H, H-5), 3.80 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6_a), 3.67 (dd, 1H, $J_{3,4}$ 2.3 Hz, $J_{4,5}$ 9.2 Hz, H-4), 3.23 [dd, 1H, J_{gem} 14.0 Hz, *J* 4.2 Hz, CH(OH)$C\underline{H}_AH_B$Ph], 2.77 [dd, 1H, J_{gem} 14.0 Hz, *J* 8.9 Hz, CH(OH)$CH_A\underline{H}_B$Ph], 2.38 (m, 2H, 2OH). ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.6 (C=O), 138.8–126.0 (3Ph), 100.7 (<u>C</u>HPh), 99.5 (C-1), 78.6 (C-4), 73.0 [<u>C</u>H(OH)CH_2Ph], 70.0 ($O\underline{C}H_2Ph$), 68.3 (C-6), 67.6 (C-3), 63.0 (C-5), 51.7 (C-2), 41.0 [CH(OH)<u>C</u>H_2Ph]. Anal. calcd for $C_{29}H_{31}NO_7$: C, 68.90; H, 6.18; N, 2.77. Found: C, 69.00; H, 6.23; N, 2.82%.

4.2.4.2. Benzyl (*R*)-4,6-*O*-benzylidene-2-deoxy-2-[(*R*)-2-hydroxy-3-phenylpropanamido]-β-D-allopyranoside 15b. Column chromatography using dichloromethane–methanol (65:1) as eluent yielded 0.34 g (67%). Mp 270–271°C; $[\alpha]_D$ −48.7 (*c* 0.6, DMF); MS (FAB): *m/z* 528 (13%) $[M+Na]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.2 (m, 15H, 3Ph), 6.79 (d, 1H, $J_{2,NH}$ 8.6 Hz, NH), 5.59 (s, 1H, PhC<u>H</u>), 4.90 (d, 1H, J_{gem} 12.4 Hz, $OC\underline{H}_AH_BPh$), 4.70 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 4.56 (d, 1H, J_{gem} 12.4 Hz, $OCH_A\underline{H}_BPh$), 4.39 (dd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 9.8 Hz, H-6_e), 4.30 (dd, 1H, $J_{1,2}$ 8.2 Hz, $J_{2,3}$ 4.2 Hz, H-2), 4.2–4.1 [m, 2H, H-3, C<u>H</u>(OH)CH_2Ph], 3.93 (m, 1H, H-5), 3.80 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6_a), 3.65 (dd, 1H, $J_{3,4}$ 2.3 Hz, $J_{4,5}$ 9.2 Hz, H-4), 3.18 [dd, 1H, J_{gem} 14.0 Hz, *J* 4.0 Hz, CH(OH)$C\underline{H}_AH_B$Ph], 2.89 [dd, 1H, J_{gem} 14.0 Hz, *J* 8.1 Hz, CH(OH)$CH_A\underline{H}_B$Ph], 2.17 (m, 2H, 2OH). ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.1 (C=O), 136.9–126.1 (3Ph), 101.8 (Ph<u>C</u>H), 99.0 (C-1), 78.7 (C-4), 72.8 [<u>C</u>H(OH)CH_2Ph], 70.7 ($O\underline{C}H_2Ph$), 69.1 (C-6), 68.6 (C-3), 63.3 (C-5), 51.8 (C-2), 40.7 [CH(OH)<u>C</u>H_2Ph]. Anal. calcd for $C_{29}H_{31}NO_7$: C, 68.90; H, 6.18; N, 2.77. Found: C, 68.57; H, 6.44; N, 2.78%.

4.2.4.3. Benzyl (*R*)-4,6-*O*-benzylidene-2-deoxy-2-[(*S*)-3-hydroxybutanamido]-β-D-allopyranoside 17a. Column chromatography using dichloromethane–methanol (20:1) as eluent yielded 0.32 g (72%). Mp 221–222; $[\alpha]_D$ −96.2 (*c* 0.4, DMF); MS (CI): *m/z* 444 (16%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.2 (m, 10H, 2Ph), 6.08 (d, 1H, $J_{2,NH}$ 9.2 Hz, NH), 5.59 (s, 1H, PhC<u>H</u>), 4.90 (d, 1H, J_{gem} 12.4 Hz, $OC\underline{H}_AH_BPh$), 4.70 (d, 1H, $J_{1,2}$ 8,2 Hz, H-1), 4.57 (d, 1H, J_{gem} 12.4 Hz, $OCH_A\underline{H}_BPh$), 4.40 (dd, 1H, $J_{5,6e}$ 4,4 Hz, $J_{6e,6a}$ 99 Hz, H-6_e), 4.24 (m, 2H, H-2, H-3), 4.17 [m, 1H, $CH_2C\underline{H}$(OH)CH_3], 3.94 (dt, 1H, $J_{5,6e}$ 4.4 Hz, $J_{4,5}=J_{5,6a}$ 9.5 Hz, H-5), 3.81 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6_a), 3.66 (dd, 1H, $J_{3,4}$ 2.3 Hz, $J_{4,5}$ 9.3 Hz, H-4), 2.3–2.2 [m, 2H, $C\underline{H}_2$CH(OH)CH_3], 1.18 [d, 3H, *J* 6.3 Hz, CH_2CH(OH)$C\underline{H}_3$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.8 (C=O), 129.3–126.1 (2Ph), 101.8 (Ph<u>C</u>H), 99.1 (C-1), 78.6 (C-4), 70.7 ($O\underline{C}H_2Ph$), 69.0 (C-6), 68.6 (C-3), 64.8 [$CH_2\underline{C}H$(OH)CH_3], 63.4 (C-5), 51.7 (C-2), 44.1 [$\underline{C}H_2$CH(OH)CH_3], 22.7 [CH_2CH(OH)<u>C</u>H_3]. HRMS (CI): $[M+H]^+$, found 444.201102. $C_{24}H_{30}NO_7$ requires 444.202228. Anal. calcd for $C_{24}H_{29}NO_7$: C, 65.00; H, 6.59; N, 3.16. Found: C, 64.89; H, 6.61; N, 3.28%.

4.2.5. Acetyl derivatives from 15a and 15b. To a solution of **15a** or **15b** (0.25 g, 0.5 mmol) in distilled dichloromethane (20 mL), pyridine (0.5 mL) and acetic anhydride (0.5 mL) were added and the reaction mixture was stirred overnight at room temperature. The solution was washed successively with water, 1N solution of acetic acid, saturated aqueous sodium bicarbonate and water, then dried ($MgSO_4$) and filtered and the filtrate evaporated to dryness. The solid obtained was purified by flash chromatography on silica gel.

4.2.5.1. Benzyl 2-[(*S*)-2-acetoxy-3-phenylpropanamido]-3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside 18a. Column chromatography using dichloromethane–methanol (120:1) as eluent yielded 0.26 g (88%). Mp 216–217°C; $[\alpha]_D$ −95.6 (*c* 0.6, CH_2Cl_2); MS (CI): *m*/*z* 590 (22%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.1 (m 15H, 3Ph), 6.00 (d, 1H, $J_{2,NH}$ 8.4 Hz, NH), 5.68 (t, 1H, $J_{2,3}=J_{3,4}$ 2.6 Hz, H-3), 5.52 (s, 1H, PhCH), 5.32 [dd, 1H, *J* 4.9 Hz, *J* 7.6 Hz, CH(OAc)CH_2Ph], 4.88 (d, 1H, J_{gem} 12.2 Hz, OCH_AH_BPh), 4.68 (d, 1H, $J_{1,2}$ 8.6 Hz, H-1), 4.58 (d, 1H, J_{gem} 12.2 Hz, OCH_AH_BPh), 4.4–4.3 (m, 2H, H-2, H-6_e), 3.9–3.7 (m, 3H, H-4, H-5, H-6_a), 3.22 [dd, 1H, J_{gem} 14.3 Hz, *J* 4.9 Hz, CH(OAc)CH_AH_B Ph], 3.06 [dd, 1H, J_{gem} 14.3 Hz, *J* 7.6 Hz, CH(OAc)CH_AH_BPh], 2.05, 1.91 (2s, 6H, $2CH_3CO$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.6, 169.3, 169.2 (3C=O), 136.9–125.8 (3Ph), 101.2 (PhCH), 98.5 (C-1), 76.8 (C-4), 74.3 [CH(OAc)CH_2Ph], 70.1 (OCH_2Ph), 69.3 (C-3), 68.8 (C-6), 64.3 (C-5), 51.0 (C-2), 37.2 [CH(OAc)CH_2Ph], 20.6, 20.5 ($2CH_3CO$). Anal. calcd for $C_{33}H_{35}NO_9$: C, 67.22; H, 5.98; N, 2.38. Found: C, 67.08; H, 6.01; N, 2.51.

4.2.5.2. Benzyl 2-[(*R*)-2-acetoxy-3-phenylpropanamido]-3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside 18b. Column chromatography using dichloromethane–methanol (100:1) as eluent yielded 0.27 g (92%). Mp 197–198°C; $[\alpha]_D$ −91.5 (*c* 0.6, CH_2Cl_2); MS (CI): *m*/*z* 590 (32%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.1 (m, 15H, 3Ph), 6.06 (d, 1H, $J_{2,NH}$ 8.8 Hz, NH), 5.64 (t, 1H, $J_{2,3}=J_{3,4}$ 2.6 Hz, H-3), 5.54 (s, 1H, PhCH), 5.29 [dd, 1H, *J* 7.4 Hz, *J* 5.4 Hz, CH(OAc)CH_2Ph], 4.86 (d, 1H, J_{gem} 12.2 Hz, OCH_AH_BPh), 4.67 (d, 1H, $J_{1,2}$ 8.6 Hz, H-1), 4.56 (d, 1H, J_{gem} 12.2 Hz, OCH_AH_BPh), 4.4–4.3 (m, 2H, H-2, H-6_e), 3.9–3.7 (m, 3H, H-4, H-5, H-6_a), 3.23 [dd, 1H, J_{gem} 14.3 Hz, *J* 5.4 Hz, CH(OAc)CH_AH_BPh], 3.06 [dd, 1H, J_{gem} 14.3 Hz, *J* 7.4 Hz, CH(OAc)CH_AH_BPh], 2.05, 1.95 (2s, 6H, $2CH_3CO$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.9, 169.2, 168.2 (3C=O), 136.9–125.9 (3Ph), 101.2 (PhCH), 98.6 (C-1), 77.6 (C-4), 74.1 [CH(OAc)CH_2Ph], 70.3 (OCH_2Ph), 69.0 (C-3), 68.9 (C-6), 64.3 (C-5), 50.9 (C-2), 36.8 [CH(OAc)CH_2Ph], 20.7 ($2CH_3CO$). Anal. calcd for $C_{33}H_{35}NO_9$: C, 67.22; H, 5.98; N, 2.38. Found: C, 67.14; H, 6.03; N, 2.41%.

4.3. Alkyl 2-*N*-acyl-2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-methylidene-D-allopyranosides 19–24, 26

To a solution of either alkyl 2-acylamino-(*R*)-4,6-*O*-benzylidene-2-deoxy-D-allopyranoside **4**–**9** (2.5 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.

4.3.1. Benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-methylidene-2-*N*-(*trans*-3-phenyl-2-propenoyl)-β-D-allopyranoside 19. Column chromatography using dichloromethane–methanol (220:1) as eluent yielded 1.00 g (80%). Mp 194–195°C; $[\alpha]_D$ +73.9 (*c* 0.6, CH_2Cl_2); MS (CI): *m*/*z* 500 (100%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, 1H, J_{trans} 15.6 Hz, CH=CHPh), 7.5–7.2 (m, 15H, 3Ph), 7.05 (d, 1H, J_{trans} 15.6 Hz, CH=CHPh), 5.62 (s, 1H, PhCH), 5.32 (2d, 2H, J_{gem} 5.6 Hz, OCH_2N), 4.98 (d, 1H, J_{gem} 10.7 Hz, OCH_AH_BPh), 4.77 (d, 1H, $J_{1,2}$ 7.4 Hz, H-1), 4.56 (d, 1H, J_{gem} 10.7 Hz, OCH_AH_BPh), 4.50–4.45 (m, 2H, H-3, H-6_e), 4.18 (dd, 1H, $J_{1,2}$ 7.4 Hz, $J_{2,3}$ 4.3 Hz, H-2), 4.05 (dt, 1H, $J_{5,6e}$ 5.1 Hz, $J_{4,5}=J_{5,6a}$ 9.8 Hz, H-5), 3.91 (dd, 1H, $J_{3,4}$ 3.1 Hz, $J_{4,5}$ 9.6 Hz, H-4), 3.84 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.2 Hz, H-6_a). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.7 (C=O), 142.9 (CH=CHPh), 136.7–126.2 (3Ph), 118.7 (CH=CHPh), 102.7 (PhCH), 101.2 (C-1), 80.8 (OCH_2N), 76.8 (C-3), 76.4 (C-4), 72.3 (OCH_2Ph), 69.0 (C-6), 63.4 (C-5), 59.1 (C-2). Anal. calcd for $C_{30}H_{29}NO_6$: C, 72.13; H, 5.85; N, 2.80. Found: C, 71.97; H, 5.69; N, 2.90%.

4.3.2. Benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-*N*-(*trans*-2-butenoyl)-2-deoxy-2-*N*-3-*O*-methylidene-β-D-allopyranoside 20. Column chromatography using dichloromethane–methanol (180:1) as eluent yielded 0.76 g (70%). Mp 155–156°C; $[\alpha]_D$ −7.8 (*c* 0.8, CH_2Cl_2); MS (CI): *m*/*z* 438 (66%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.2 (m, 10H, 2Ph), 6.96 (m, 1H, CH=CHCH$_3$), 6.43 (d, 1H, J_{trans} 15.1 Hz, CH=CHCH$_3$), 5.58 (s, 1H, PhCH), 5.21 (bs, 2H, OCH_2N), 4.92 (d, 1H, J_{gem} 11.2 Hz, OCH_AH_BPh), 4.66 (d, 1H, $J_{1,2}$ 7.2 Hz, H-1), 4.55 (d, 1H, J_{gem} 11.2 Hz, OCH_AH_BPh), 4.5–4.4 (m, 2H, H-3, H-6_e), 4.1–3.7 (m, 4H, H-2, H-4, H-5, H-6_a), 1.75 (d, 3H, *J* 6.7 Hz, CH=CHCH$_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.6 (C=O), 142.6 (CH=CHCH$_3$); 136.6–126.3 (2Ph), 123.1 (CH=CHCH$_3$), 102.7 (PhCH), 101.0 (C-1), 80.6 (OCH_2N), 76.7 (C-4), 76.4 (C-3), 72.1 (OCH_2Ph), 69.0 (C-6), 63.4 (C-5), 59.0 (C-2), 17.9 (CH=CHCH$_3$). Anal. calcd for $C_{25}H_{27}NO_6$: C, 68.64; H, 6.22; N, 3.20. Found: C, 68.44; H, 6.14; N, 3.11%.

4.3.3. Benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-methylidene-2-*N*-(*trans*-2-pentenoyl)-β-D-allopyranoside 21. Column chromatography using dichloromethane–methanol (200:1) as eluent yielded 1.00 g (90%). Mp 68–69°C; $[\alpha]_D$ −32.7 (*c* 0.6, $CHCl_3$); MS (CI): *m*/*z* 452 (82%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.6–7.2 (m, 10H, 2Ph), 7.00 (m, 1H, CH=CHCH$_2$CH$_3$), 6.37 (d, 1H, J_{trans} 15.3 Hz, CH=CHCH$_2$CH$_3$), 5.57 (s, 1H, PhCH), 5.21 (bs, 2H, OCH_2N), 4.91 (d, 1H, J_{gem} 11.1 Hz, OCH_AH_BPh), 4.66 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1), 4.53 (d, 1H, J_{gem} 11.1 Hz, OCH_AH_BPh), 4.5–4.4 (m, 2H, H-6_e, H-3), 4.1–3.7 (m, 4H, H-2, H-4, H-5, H-6_a), 2.09 (m, 2H, CH=CHCH$_2$CH$_3$), 0.88 (t, 3H, *J* 7.4 Hz, CH=CHCH$_2$CH$_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.9 (C=O), 148.8 (CH=CHCH$_2$CH$_3$), 136.7–126.2 (2Ph), 120.5 (CH=CHCH$_2$CH$_3$), 102.7 (PhCH), 101.0 (C-1), 80.7 (OCH_2N), 76.7 (C-4), 76.4 (C-3), 72.1

(OCH$_2$Ph), 69.0 (C-6), 63.4 (C-5), 59.0 (C-2), 25.2 (CH=CHCH$_2$CH$_3$), 12.0 (CH=CHCH$_2$CH$_3$). HRMS (EI): $[M]^{+\bullet}$, found 451.198802. $C_{26}H_{29}NO_6$ requires 451.199488. Anal. calcd for $C_{26}H_{29}NO_6$: C, 69.16; H, 6.47; N, 3.10. Found: C, 68.88; H, 6.64; N, 3.14%.

4.3.4. Benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-(3-methyl-2-butenoyl)-2-*N*-3-*O*-methylidene-β-D-allopyranoside 22. Column chromatography using hexane–ethyl acetate (3:1) as eluent yielded 0.85 g (75%). Mp 136–137°C; $[\alpha]_D$ −14.2 (*c* 0.7, CH_2Cl_2); MS (CI): *m*/*z* 452 (100%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 6.19 [s, 1H, CH=C(CH$_3$)$_2$], 5.57 (s, 1H, PhCH), 5.19 (m, 2H, OCH$_2$N), 4.92 (d, 1H, J_{gem} 11.2 Hz, OCH$_A$H$_B$Ph), 4.66 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1), 4.55 (d, 1H, J_{gem} 11.2 Hz, OCH$_A$H$_B$Ph), 4.5–4.4 (m, 2H, H-3, H-6$_e$), 4.1–3.7 (m, 4H, H-2, H-4, H-5, H-6$_a$), 2.12, 1.70 [2s, 6H, CH=C(CH$_3$)$_2$]. ^{13}C NMR 50 MHz, $CDCl_3$): δ 165.9 (C=O), 153.6 [CH=C(CH$_3$)$_2$], 136.7–126.3 (2Ph), 116.8 [CH=C(CH$_3$)$_2$], 102.8 (PhCH), 101.2 (C-1), 80.5 (OCH$_2$N), 76.7 (C-4), 76.5 (C-3), 72.1 (OCH$_2$Ph), 69.1 (C-6), 63.4 (C-5), 59.4 (C-2), 27.3, 20,3 [CH=C(CH$_3$)$_2$]. Anal. calcd for $C_{26}H_{29}NO_6$: C, 69.16; H, 6.47; N, 3.10. Found: C, 68.96; H, 6.43; N, 3.09%.

4.3.5. Benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-methylidene-2-*N*-(*trans*-3-phenyl-2-propenoyl)-α-D-allopyranoside 23. Column chromatography using hexane–ethyl acetate (15:10) as eluent yielded 1.11 g (89%). Mp 108–109°C; $[\alpha]_D$ +196.1 (*c* 0.5, CH_2Cl_2); MS (CI): *m*/*z* 500 (37%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.75, 7.68 (2d, 1H, J_{trans} 15.4 Hz, CH=CHPh), 7.6–7.1 (m, 15H, 3Ph), 6.34, 6.30 (2d, 1H, J_{trans} 15.4 Hz, CH=CHPh), 5.62 (s, 1H, PhCH), 5.38 (d, 1H, $J_{1,2}$ 5.4 Hz, H-1), 5.30, 5.21 (2d, 2H, *J* 2.0 Hz, OCH$_2$N), 4.71, 4.70 (2d, 1H, J_{gem} 11.9 Hz, OCH$_A$H$_B$Ph), 4.63 (dd, 1H, $J_{5,6e}$ 5.0 Hz, $J_{6e,6a}$ 9.8 Hz, H-6$_e$), 4.48 (d, 1H, J_{gem} 11.9 Hz, OCH$_A$H$_B$Ph), 4.4–4.2 (m, 3H, H-2, H-3, H-5), 3.89 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{4,5}$ 9.5 Hz, H-5), 3.73 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6$_a$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 162.5 (C=O), 143.6, 143.3 (CH=CHPh), 137.5–126.3 (Ph), 117.2, 117.1 (CH=CHPh), 102.7 (PhCH), 95.7, 94.8 (C-1), 82.0, 80.5 (OCH$_2$N), 76.5, 76.4 (C-4), 73.9 (C-3), 70.6 (OCH$_2$Ph), 69.6, 69.2 (C-6), 56.7 (C-5), 56.0, 55.8 (C-2). HRMS (EI): $[M]^{+\bullet}$, found 499.199545. $C_{30}H_{29}NO_6$ requires 499.199488. Anal. calcd for $C_{30}H_{29}NO_6$: C, 72.13; H, 5.85; N, 2.80. Found: C, 72.02; H, 5.90; N, 2.78%.

4.3.6. 1-Dodecyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-methylidene-2-*N*-(*trans*-3-phenyl-2-propenoyl)-β-D-allopyranoside 24. Column chromatography using hexane–ethyl acetate (34:10) as eluent yielded 1.17 g (81%). Mp 109–110°C; $[\alpha]_D$ −32.4 (*c* 0.6, CH_2Cl_2); MS (CI): *m*/*z* 578 (100%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.69 (d, 1H, J_{trans} 15.6 Hz, CH=CHPh), 7.6–7.3 (m, 10H, 2Ph), 7.10 (d, 1H, J_{trans} 15.6 Hz, CH=CHPh), 5.58 (s, 1H, PhCH), 5.35 (d, 1H, J_{gem} 5.8 Hz, NCH$_A$H$_B$O), 5.27 (d, 1H, J_{gem} 5.8 Hz, NCH$_A$H$_B$O), 4.59 (d, 1H, $J_{1,2}$ 7.4 Hz, H-1), 4.5–4.4 (m, 2H, H-3, H-6$_e$), 4.13 (dd, 1H, $J_{1,2}$ 7.4 Hz, $J_{2,3}$ 4.3 Hz, H-2), 4.1–3.8 (m, 3H, H-4, H-5, OCH$_A$H$_B$R), 3.78 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6$_a$), 3.44 (m, 1H, OCH$_A$H$_B$R), 1.6–1.1 [m, 20H, (CH$_2$)$_{10}$], 0.86 (t, 3H, *J* 6.5 Hz, CH$_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.7 (C=O), 142,6 (CH=CHPh), 136.7–126.3 (Ph), 118.7 (CH=CHPh), 102.8, 102.1 (C-1, PhCH), 80.9 (NCH$_2$O), 76.8 (C-4), 76.5 (C-3), 71.1 (OCH$_2$R), 69.1 (C-6), 63.4 (C-5), 59.2 (C-2), 31.9–22.7 [(CH$_2$)$_{10}$], 14.1 (CH$_3$). HRMS (CI): $[M+H]^+$, found 578.347399. $C_{35}H_{48}NO_6$ requires 578.348164. Anal. calcd for $C_{35}H_{47}NO_6$: C, 72.76; H, 8.20; N, 2.42. Found: C, 72.54; H, 8.31; N, 2.47%.

4.4. Benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-*N*-(*trans*-2-butenoyl)-2-deoxy-2-*N*-3-*O*-isopropylidene-β-D-allopyranoside 26

A solution of benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside **1** (1.0 g, 2.8 mmol) in dry acetone (100 mL) was stirred at room temperature for 3 h. Distilled dichloromethane (100 mL) and anhydrous magnesium sulphate (2.0 g) were added, and the suspension was stirred for two weeks. Then, the reaction mixture was filtered through a pad of kieselguhr (4 cm diameter×0.5 cm height) and the filtrate was evaporated to dryness. The compound obtained, benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-isopropylidene-β-D-allopyranoside **25** {MS (CI) *m*/*z* 398 (100%) $[M+1]^+$}, was used without further purification. To a solution of **25** in distilled dichloromethane (100 mL) at 0°C, dry pyridine (10 mL) and crotonyl chloride (0.5 mL, 5.2 mmol) were added. The reaction mixture was stirred overnight at room temperature, and then poured into ice water. The organic phase was washed successively with water, saturated aqueous sodium bicarbonate and water. The solution was dried ($MgSO_4$), filtered and evaporated to dryness. The solid obtained was purified by column chromatography using hexane–ethyl acetate (32:10) as eluent, yield: 0.72 g (55%). Mp 86–87°C; $[\alpha]_D$ −16.9 (*c* 0.7, CH_2Cl_2); EM (CI): *m*/*z* 466 (100%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.6–7.3 (m, 10H, 2Ph), 6.90 (m, 1H, CH=CHCH$_3$), 6.48 (d, 1H, J_{trans} 15.0 Hz, CH=CHCH$_3$), 5.56 (s, 1H, PhCH), 4.88 (d, 1H, J_{gem} 11.4 Hz, OCH$_A$H$_B$Ph), 4.65 (d, 1H, $J_{1,2}$ 7.4 Hz, H-1), 4.52 (d, 1H, J_{gem} 11.4 Hz, OCH$_A$H$_B$Ph), 4.5–4.4 (m, 2H, H-3, H-6$_e$), 4.1–3.7 (m, 3H, H-2, H-5, H-6$_a$), 1.75 (d, 3H, *J* 6.6, CH=CHCH$_3$), 1.64, 1.58 [2s, 6H, OC(CH$_3$)$_2$N]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 163.3 (C=O), 140.9 (CH=CHCH$_3$), 136.7–126.2 (2Ph), 124.5 (CH=CHCH$_3$), 102.5 (PhCH), 100.7 (C-1), 96.9 [OC(CH$_3$)$_2$N], 76.5 (C-4), 72.3 (C-3), 71.4 (OCH$_2$Ph), 68.9 (C-6), 63.1 (C-5), 60.4 (C-2), 26.5, 23.8 [OC(CH$_3$)$_2$N], 17.7 (CH=CHCH$_3$). HRMS (EI): $[M]^{+\bullet}$, found 465.214076. $C_{27}H_{31}NO_6$ requires 465.215138. Anal. calcd for $C_{27}H_{31}NO_6$: C, 69.66; H, 6.71; N, 3.01. Found: C, 69.61; H, 6.78; N, 3.07%.

4.5. Epoxidation of the unsaturated amides with *m*-chloroperoxybenzoic acid

To a solution of either **4**, **5**, **9**, **10**, **19**–**24**, **26** (1.5 mmol) in distilled dichloromethane (300 mL), *m*-chloroperoxybenzoic acid (Aldrich 57–86%) (3.0 g) was added and the suspension was stirred at room temperature. When TLC showed that all starting compound had been consumed (2–3 days), the reaction mixture was washed successively with 5% aqueous sodium hydroxide and water, dried ($MgSO_4$), filtered and the filtrate evaporated to dryness. The solid obtained was purified by flash chromatography on silica gel.

4.5.1. Benzyl (*R*)-4,6-*O*-benzylidene-2-deoxy-2-[(*E*)-2,3-epoxy-3-phenylpropanamido]-β-D-allopyranoside 11. Two stereoisomers were obtained in 63:37 ratio (26% de). Column chromatography using dichloromethane–methanol (125:1) as eluent allowed the purification of two stereoisomers but not their separation. Yield 0.60 g (80%). Mp 255–256°C; $[\alpha]_D$ −61.5 (*c* 0.5, DMF); MS (CI): *m*/*z* 504 (22%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$) (for the major isomer **11a**): δ 7.5–7.1 (m 15H, 3Ph), 6.71 (d, 1H, $J_{2,NH}$ 9.2 Hz, NH), 5.61 (s, 1H, PhCH), 4.93 (d, 1H, J_{gem} 12.3 Hz, OCH_AH_BPh), 4.77 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 4.57 (d, 1H, J_{gem} 12.3 Hz, OCH_AH_BPh), 4.42 (dd, 1H, $J_{5,6e}$ 4.6 Hz, $J_{6e,6a}$ 10.0 Hz, H-6_e), 4.3–4.2 (m, 2H, H-2, H-3), 3.99 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.6 Hz, $J_{5,6e}$ 4.6 Hz, H-5), 3.82 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6_a), 3.68 (m, 1H, H-4), 3.62, [d, 1H, J_{trans} 1.9 Hz, CH(O)CHPh], 3.51 [d, 1H, J_{trans} 1.9 Hz, CH(O)CHPh]. ^{13}C NMR (50 MHz, $CDCl_3$) (for the major isomer **11a**): δ 167.2 (C=O), 136.9–125.7 (Ph), 101.8 (PhCH), 99.2 (C-1), 78.7 (C-4), 70.9 (OCH_2Ph), 69.0 (C-6), 68.6 (C-3), 63.5 (C-5), 58.9, [CH(O)CHPh], 58.7 [CH(O)CHPh], 51.4 (C-2). HRMS (EI): $[M]^{+\bullet}$, found 503.193733. $C_{29}H_{29}NO_7$ requires 503.194403. Anal. calcd for $C_{29}H_{29}NO_7$: C, 69.17; H, 5.80; N, 2.78. Found: C, 68.96; H, 5.80; N, 2.70%.

When an identical reaction was carried out at −10°C, compound **11** was obtained with a de of 40%.

4.5.2. Benzyl (*R*)-4,6-*O*-benzylidene-2-deoxy-2-[(*E*)-2,3-epoxybutanamido]-β-D-allopyranoside 12. Two stereoisomers were obtained in 58:42 ratio (16% de). Column chromatography using dichloromethane–methanol (125:1) as eluent allowed the purification of two stereoisomers but not their separation. Yield 0.63 g (95%). Mp 243–244°C; $[\alpha]_D$ −101.1 (*c* 0.5, DMF); MS (CI): *m*/*z* 442 (10%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.2 (m, 10H, 2Ph), 6.53 (m, 1H, $J_{2,NH}$ 6.7 Hz, NH), 5.58, 5.57 (2s, 1H, PhCH), 4.90, 4.86 (2d, 1H, J_{gem} 12.3 Hz, OCH_AH_BPh), 4.70, 4.67 (2d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.59, 4.51 (2d, 1H, J_{gem} 12.3 Hz, OCH_AH_BPh), 4.39 (dd, 1H, $J_{5,6e}$ 4.4 Hz, $J_{6e,6a}$ 9.9 Hz, H-6_e), 4.3–4.1 (m, 2H, H-2, H-3), 3.96 (m, 1H, H-5), 3.79 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 9.9 Hz, H-6_a), 3.66 (m, 1H, H-4), 3.21, 3.17 [2d, 1H, J_{trans} 2.1 Hz, CH(O)CHCH$_3$], 3.00, 2.64 [2dq, 1H, J_{trans} 2.1 Hz, *J* 5.1 Hz, CH(O)CHCH$_3$], 1.38, 1.29 [2d, 3H, *J* 5.1 Hz, CH(O)CHCH$_3$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 168.3 (C=O), 137.1–126.2 (2Ph), 101.74, 101.71 (PhCH), 99.2, 98.8 (C-1), 78.7, 78.6 (C-4), 70.8, 70.7 (OCH_2Ph), 69.0 (C-6), 68.6, 68.5 (C-3), 63.34, 63.29 (C-5), 56.2 [CH(O)CHCH$_3$], 55.8, 55.6 [CH(O)CHCH$_3$], 51.6, 51.2 (2C-2), 17.5, 17.4 [CH(O)CHCH$_3$]. HRMS (EI): $[M]^{+\bullet}$, found 441.178846. $C_{24}H_{27}NO_7$ requires 441.178753. Anal. calcd for $C_{24}H_{27}NO_7$: C, 65.29; H, 6.16; N, 3.17. Found: C, 64.98; H, 6.35; N, 3.14%.

4.5.3. 1-Dodecyl (*R*)-4,6-*O*-benzylidene-2-deoxy-2-[(*E*)-2,3-epoxy-3-phenylpropanamido]-β-D-allopyranoside 13. Two stereoisomers were obtained in 1:1 ratio. Column chromatography using dichloromethane–methanol (100:1) as eluent allowed the purification of two stereoisomers but not their separation. Yield 0.79 g (91%). Mp 189–190°C; $[\alpha]_D$ −147.8 (*c* 0.3, DMF); MS (CI): *m*/*z* 582 (16%) $[M+H]^{+\bullet}$ ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 6.73, 6.69 (2d, 1H, $J_{2,NH}$ 8.7 Hz, NH), 5.59 (s, 1H, PhCH), 4.69, 4.68 (2d, 1H, $J_{1,2}$ 8,4 Hz, H-1), 4.38 (dd, 1H, $J_{5,6e}$ 4.8 Hz, $J_{6e,6a}$ 10.0 Hz, H-6_e), 4.28 (m, 1H, H-3), 4.2–3.7 [m, 5H, H-2, H-5, H-6_a, OCH_AH_BR, CH(O)CHPh], 3.66 (dd, 1H, $J_{3,4}$ 2.5 Hz, $J_{4,5}$ 9.3 Hz, H-4), 3.56, 3.54 [2d, 1H, J_{trans} 2.0 Hz CH(O)CHPh], 3.44 (m, 1H, OCH_AH_BR), 1.6–1.2 [m, 10H, $(CH_2)_{10}$], 0.85 (t, 3H, *J* 6.4 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.1 (C=O), 136.9–125.7 (Ph), 101.6 (PhCH), 100.0, 99.9 (C-1), 78.6 (C-4), 70.2, 70.0 (OCH_2R), 69.0 (C-6), 68.5 (C-3), 63.3 (C-5), 58.9 [CH(O)CHPh], 58.6 [CH(O)CHPh], 51.6 (C-2), 31.8–22.6 [$(CH_2)_{10}$], 14.1 (CH_3). HRMS (EI): $[M]^{+\bullet}$, found 581.334319. $C_{34}H_{47}NO_7$ requires 581.335253. Anal. calcd for $C_{23}H_{47}NO_7$: C, 70.20; H, 8.14; N, 2.41. Found: C, 70.11; H, 8.12; N, 2.38%.

4.5.4. Benzyl (*R*)-4,6-*O*-benzylidene-2-deoxy-2-(3,4-epoxybutanamido)-β-D-allopyranoside 14. Two stereoisomers were obtained in 56:44 ratio (12% de). Column chromatography using dichloromethane–methanol (100:1) as eluent allowed the purification of two stereoisomers but not their separation. Yield 0.56 g (85%). Mp 240–241°C; $[\alpha]_D$ −110.3 (*c* 0.6, DMF); MS (CI): *m*/*z* 442 (19%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 6.26 (m, 1H, NH), 5.60 (s, 1H, PhCH), 4.90 (d, 1H, J_{gem} 12.3 Hz, OCH_AH_BPh), 4.73, 4.72 (2d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.59, 4.57 (2d, 1H, J_{gem} 12.3 Hz, OCH_AH_BPh), 4.40 (dd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 9.9 Hz, H-6_e), 4.3–4.2 (m, 2H, H-2, H-3), 3.95 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.7 Hz, $J_{5,6e}$ 4.5 Hz, H-5), 3.81 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 9.9 Hz, H-6_a), 3.67 (dd, 1H, $J_{3,4}$ 2.4 Hz, $J_{4,5}$ 9.2 Hz, H-4), 3.21, 3.12 [2m, 1H, $CH_2CH(O)CH_2$], 2.80 [m, 1H, $CH_AH_BCH(O)CH_2$], 2.6–2.5 [m, 2H, $CH_AH_BCH(O)CH_{cis}H_{trans}$], 2.41 (bs, 1H, OH), 2.34, 2.26 [2dd, 1H, J_{gem} 6.8 Hz, J_{trans} 3.1 Hz, $CH_2CH(O)CH_{cis}H_{trans}$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 168.7 (C=O), 129.3–126.1 (2Ph), 101.7 (PhCH), 99.2 (C-1), 78.6 (C-4), 70.8 (OCH_2Ph), 69.1 (C-6), 68.7 (C-3), 63.3 (C-5), 51.9 (C-2), 48.7 [$CH_2CH(O)CH_2$], 47.1 [$CH_2CH(O)CH_2$], 39.8, 39.6 [$CH_2CH(O)CH_2$]. Anal. calcd for $C_{24}H_{27}NO_7$: C, 65.29; H, 6.16; N, 3.17. Found: C, 65.05; H, 6.24; N, 3.27%.

4.5.5. Benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-[(2*S*,3*R*)-2,3-epoxy-3-phenylpropanoyl]-2-*N*-3-*O*-methylidene-β-D-allopyranoside 27. Two stereoisomers were obtained in 97:3 ratio [94% de for the (2*S*,3*R*)-isomer]. The major isomer **27a** (major R_f) was isolated by column chromatography using hexane–ethyl acetate (25:10) as eluent, yield: 0.66 g (85%). Mp 171–172°C; $[\alpha]_D$ +62.5 (*c* 0.5, $CHCl_3$); MS (CI): *m*/*z* 516 (25%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.51–6.9 (m, 15H, 3Ph), 5.58 (s, 1H, PhC$\underline{H}$), 5.19 (dd, 2H, J_{gem} 5.7 Hz, OCH_2N), 4.6–4.3 (m, 6H, H-1, H-2, H-3, H-6_e, $OC\underline{H}_2Ph$), 4.23 [d, 1H, J_{trans} 1.7 Hz, CH(O)C$\underline{H}$Ph], 3.95 [d, 1H, J_{trans} 1.7 Hz, C$\underline{H}$(O)CHPh], 3.9–3.7 (m, 3H, H-4, H-5, H-6_a). ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.2 (C=O), 136.6–126.0 (3Ph), 102.8 (Ph$\underline{C}$H), 99.7 (C-1), 80.9 (OCH_2N), 76.8 (C-3), 76.3 (C-4), 71.4 ($O\underline{C}H_2Ph$), 68.9 (C-6), 63.7 (C-5), 58.7 (C-2), 58.2 [$\underline{C}$H(O)CHPh], 56.6 [CH(O)$\underline{C}$HPh]. Anal. calcd for $C_{30}H_{29}NO_7$: C, 69.89; H, 5.67; N, 2.72. Found: C, 69.83; H, 5.79; N, 2.70%.

4.5.6. Benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-[(*E*)-2,3-epoxybutanoyl]-2-*N*-3-*O*-methylidene-β-D-allopyranoside 28. Two stereoisomers were obtained in 72:28 ratio [44% de for the (2*S*,3*R*)-isomer]. Both isomers were isolated by column chromatography using hexane–ethyl acetate (17:10) as eluent, yield: 0.54 g (80%).

4.5.6.1. Major isomer 28a (major R_f). Mp 113–114°C; $[\alpha]_D$ −21.1 (*c* 0.6, CH_2Cl_2); MS (CI): *m*/*z* 454 (36%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.5–7.2 (m, 10H, 2Ph), 5.61 (s, 1H, PhC$\underline{H}$), 5.17 (dd, 2H, J_{gem} 5.5 Hz, OCH_2N), 4.96 (d, 1H, J_{gem} 11.4 Hz, $OC\underline{H}_AH_BPh$), 4.67 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.56 (d, 1H, J_{gem} 11.4 Hz, $OCH_A\underline{H}_BPh$), 4.5–4.4 (m, 2H, H-3, H-6_e), 4.28 (dd, 1H, $J_{1,2}$ 7.6 Hz, $J_{2,3}$ 4.2 Hz, H-2), 3.99 (m, 1H, $J_{4,5}=J_{5,6a}$ 9.9 Hz, $J_{5,6e}$ 5.0 Hz, H-5), 3.91 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{4,5}$ 9.9 Hz, H-4), 3.80 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 9.9 Hz, H-6_a), 3.43 [d, 1H, J_{trans} 1.8 Hz, C$\underline{H}$(O)CHCH$_3$], 3.24 [dq, 1H, J_{trans} 1.8 Hz, *J* 5.1 Hz, CH(O)C$\underline{H}$CH$_3$], 0.96 (d, 3H, *J* 5.1 Hz, CH(O)CHC$\underline{H}_3$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.1 (C=O), 136.6–126.2 (2Ph), 102.7 (Ph$\underline{C}$H), 100.5 (C-1), 80.8 (OCH_2N), 76.8 (C-3), 76.3 (C-4), 71.8 ($O\underline{C}H_2Ph$), 68.9 (C-6), 63.8 (C-5), 58.7 (C-2), 54.5 [$\underline{C}$H(O)CHCH$_3$], 53.9 [CH(O)$\underline{C}$HCH$_3$], 16.3 [CH(O)CH$\underline{C}$H$_3$]. Anal. calcd for $C_{25}H_{27}NO_7$: C, 66.21; H, 6.00; N, 3.09. Found: C, 66.07; H, 6.18; N, 2.97%.

4.5.6.2. Minor isomer 28b (minor R_f). Mp 83–84°C; $[\alpha]_D$ −102.7 (*c* 0.4, CH_2Cl_2); MS (CI): *m*/*z* 454 (53%) $[M+H]^+$; ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.58 (s, 1H, PhC$\underline{H}$), 5.14 (dd, 2H, J_{gem} 5.6 Hz, OCH_2N), 4.92 (d, 1H, J_{gem} 11.3 Hz, $OC\underline{H}_AH_BPh$), 4.7–4.6 (m, 2H, H-1, $OCH_A\underline{H}_BPh$), 4.4–4.2 (m, 2H, H-3, H-6_e), 4.11 (dd, 1H, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 4.2 Hz, H-2), 4.0–3.8 (m, 3H, H-4, H-5, H-6_a), 3.75 [d, 1H, J_{trans} 2.1 Hz, C$\underline{H}$(O)CHCH$_3$], 3.22 [dq, 1H, J_{trans} 2.1 Hz, *J* 5.1 Hz, CH(O)C$\underline{H}$CH$_3$], 1.31 [d, 3H, *J* 5.1 Hz, CH(O)CHC$\underline{H}_3$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.4 (C=O), 136.6–126.3 (2Ph), 102.8 (Ph$\underline{C}$H), 100.0 (C-1), 80.8 (OCH_2N), 77.0 (C-3), 76.4 (C-4), 71.9 ($O\underline{C}H_2Ph$), 68.9 (C-6), 63.6 (C-5), 58.6 (C-2), 54.4 [$\underline{C}$H(O)CHCH$_3$], 53.8 [CH(O)$\underline{C}$HCH$_3$], 17,2 [CH(O)CH$\underline{C}$H$_3$]. HRMS (CI): $[M+H]^+$, found 454.184981. $C_{25}H_{28}NO_7$ requires 454.186578. Anal. calcd for $C_{25}H_{27}NO_7$: C, 66.21; H, 6.00; N, 3.09. Found: C, 65.98; H, 5.99; N, 3.18%.

4.5.7. Benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-[(*E*)-2,3-epoxypentanoyl]-2-*N*-3-*O*-methylidene-β-D-allopyranoside 29. Two stereoisomers were obtained in 73:27 ratio [46% de for the (2*S*,3*R*)-isomer]. Both isomers were isolated by column chromatography using hexane–ethyl acetate (17:10) as eluent, yield: 0.58 g (83%).

4.5.7.1. Major isomer 29a (major R_f). Mp 78–79°C; $[\alpha]_D$ −53.6 (*c* 0.5; CH_2Cl_2); MS (CI): *m*/*z* 468 (19%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.2 (m, 10H, 2Ph), 5.59 (s, 1H, PhC$\underline{H}$), 5.17 (dd, 2H, J_{gem} 5.2 Hz, OCH_2N), 4.93 (d, 1H, J_{gem} 11.4 Hz, $OC\underline{H}_AH_BPh$), 4.64 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.54 (d, 1H, J_{gem} 11.4 Hz, $OCH_A\underline{H}_BPh$), 4.5–4.4 (m, 2H, H-3, H-6_e), 4.29 (dd, 1H, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 4.2 Hz, H-2), 4.0–3.9 (m, 2H, H-4, H-5), 3.78 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6_a), 3.49 [d, 1H, J_{trans} 2.0 Hz, C$\underline{H}$(O)CHCH$_2$CH$_3$], 3.19 [dt, 1H, J_{trans} 2.0 Hz, *J* 4.1 Hz, CH(O)C$\underline{H}$CH$_2$CH$_3$], 1.5–1.2 [m, 2H, CH(O)CHC$\underline{H}_2$CH$_3$], 0.76 [t, 3H, *J* 7.5 Hz, CH(O)CHCH$_2$C$\underline{H}_3$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.4 (C=O), 136.6–126.3 (2Ph), 102.8 (Ph$\underline{C}$H), 100.4 (C-1), 80.9 (OCH_2N), 76.8 (C-3), 76.4 (C-4), 71.8 ($O\underline{C}H_2Ph$), 69.0 (C-6), 63.9 (C-5), 59.5 (C-2), 58.7 [$\underline{C}$H(O)CHCH$_2$CH$_3$], 52.5 [CH(O)$\underline{C}$HCH$_2$CH$_3$], 23.7 [CH(O)CH$\underline{C}$H$_2$CH$_3$], 9.2 [CH(O)CHCH$_2$C$\underline{H}_3$]. Anal. calcd for $C_{26}H_{29}NO_7$: C, 66.80; H, 6.25; N, 3.00. Found: C, 66.56; H, 6.19; N, 3.04%.

4.5.7.2. Minor isomer 29b (minor R_f). Mp 80–81°C; $[\alpha]_D$ −144.2 (*c* 0.4; CH_2Cl_2); MS (CI): *m*/*z* 468 (33%) $[M+H]^+$; ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.57 (s, 1H, PhC$\underline{H}$), 5.14 (dd, J_{gem} 5.6 Hz, 2H, OCH_2N), 4.91 (d, 1H, J_{gem} 11.2 Hz, $OC\underline{H}_AH_BPh$), 4.66 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.64 (d, 1H, J_{gem} 11.2 Hz, $OCH_A\underline{H}_BPh$), 4.5–4.4 (m, 2H, H-3, H-6_e), 4.12 (dd, 1H, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 4.3 Hz, H-2), 4.0–3.7 [m, 4H, H-4, H-5, H-6_a, C$\underline{H}$(O)CHCH$_2$CH$_3$], 3.15 [m, 1H, CH(O)-C$\underline{H}$CH$_2$CH$_3$], 1.61 [m, 2H, CH(O)CHC$\underline{H}_2$CH$_3$], 0.90 (t, 3H, *J* 7.5 Hz, CH(O)CHCH$_2$C$\underline{H}_3$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.7 (CO), 136.6–126.2 (2Ph), 102.8 (Ph$\underline{C}$H), 100.1 (C-1), 80.8 (OCH_2N), 77.0 (C-3), 76.3 (C-4), 71.9 ($O\underline{C}H_2Ph$), 69.0 (C-6), 63.6 (C-5), 59.3 (C-2), 58.6 [$\underline{C}$H(O)CHCH$_2$CH$_3$], 52.4 [CH(O)$\underline{C}$HCH$_2$-CH$_3$], 24.3 [CH(O)CH$\underline{C}$H$_2$CH$_3$], 9.4 [CH(O)CHCH$_2$-C$\underline{H}_3$]. HRMS (CI): $[M+H]^+$, found 468.201746. $C_{26}H_{30}NO_7$ requires 468.202228. Anal. calcd for $C_{26}H_{29}NO_7$: C, 66.80; H, 6.25; N, 3.00. Found: C, 66.62; H, 6.39; N, 2.88%.

4.5.8. Benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-(2,3-epoxy-3-methylbutanoyl)-2-*N*-3-*O*-methylidene-β-D-allopyranoside 30. Two stereoisomers were obtained in 74:26 ratio (48% de). Column chromatography using hexane–ethyl acetate (15:10) as eluent allowed the

purification of two stereoisomers but not their separation. Yield 0.55 g (78%). Mp 82–83°C; $[\alpha]_D$ −37.9 (*c* 0.6, CH_2Cl_2); MS (CI): *m/z* 468 (40%) $[M+H]^+$; ^1H NMR (500 MHz, $CDCl_3$) (for the major isomer): δ 7.5–7.2 (m, 10H, 2Ph), 5.59 (s, 1H, PhCH), 5.14 (m, 2H, OCH_2N), 4.97 (d, 1H, J_{gem} 11.6 Hz, OCH_AH_BPh), 4.63 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.58 (d, 1H, J_{gem} 11.6 Hz, OCH_AH_BPh), 4.5–4.4 (m, 3H, H-2, H-3, H-6_e), 4.00 (m, 1H, H-5), 3.89 (dd, 1H, $J_{3,4}$ 3.1 Hz, $J_{4,5}$ 9.6 Hz, H-4), 3.81 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6_a), 3.33 [s, 1H, CH(O)C$(CH_3)_2$], 1.29, 1.17 [2s, 6H, CH(O)C$(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$) (for the major isomer): δ 165.6 (C=O), 136.7–126.2 (2Ph), 102.7 (PhCH), 100.1 (C-1), 80.4 (OCH_2N), 76.7 (C-3), 76.3 (C-4), 71.6 (OCH_2Ph), 69.0 (C-6), 63.8 (C-5), 60.7 [CH(O)C$(CH_3)_2$], 58.0 (C-2), 56.8 [CH(O)C$(CH_3)_2$], 23.7, 19.1 [CH(O)C$(CH_3)_2$]. HRMS (EI): $[M]^{+\bullet}$, found 467.194004. $C_{26}H_{29}NO_7$ requires 467.194403. Anal. calcd for $C_{26}H_{29}NO_7$: C, 66.80; H, 6.25; N, 3.00. Found: C, 66.55; H, 6.19; N, 2.95%.

4.5.9. Benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-[(*E*)-2,3-epoxy-3-phenylpropanoyl]-2-*N*-3-*O*-methylidene-α-D-allopyranoside 31. MS (CI): *m/z* 516 (20%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): complex spectrum, stereoisomers, and conformers mixture. Anal. calcd for $C_{30}H_{29}NO_7$: C, 69.89; H, 5.67; N, 2.72. Found: C, 69.61; H, 5.92; N, 2.58%.

4.5.10. 1-Dodecyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-[(*E*)-2,3-epoxy-3-phenylpropanoyl]-2-*N*-3-*O*-methylidene-β-D-allopyranoside 32. Two stereoisomers were obtained in 88:12 ratio [76% de for the (2*S*,3*R*)-isomer]. Both isomers were isolated by column chromatography using hexane–ethyl acetate (32:10) as eluent, yield: 0.84 g (94%).

4.5.10.1. Major isomer 32a (major R_f). Mp 67–68°C; $[\alpha]_D$+40.4 (*c* 0.5, Cl_2CH_2); MS (CI): *m/z* 594 (35%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.57 (s, 1H, PhCH), 5.29 (d, 1H, J_{gem} 5.7 Hz, OCH_AH_BN), 5.18 (d, 1H, J_{gem} 5.7 Hz, OCH_AH_BN), 4.5–4.4 (m, 2H, H-1, H-3), 4.37 (dd, 1H, $J_{5,6e}$ 4.4 Hz, $J_{6e,6a}$ 10.0 Hz, H-6_e), 4.3–4.2 [m, 2H, H-2, CH(O)CHPh], 3.97 [d, 1H, J_{trans} 1.7 Hz, CH(O)CHPh], 3.9–3,8 (m, 2H, H-4, H-5), 3.73 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6_a), 3.56 (m, 1H, OCH_AH_BR), 3,20 (m, 1H, OCH_AH_BR). ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.2 (C=O), 136.6–125.9 (2Ph), 102.6 (PhCH), 101.2 (C-1), 80.9 (OCH_2N), 76.8 (C-4), 76.1 (C-3), 70.6 (OCH_2R), 68.8 (C-6), 63.5 (C-5), 58.8 [CH(O)CHPh], 58.1 [CH(O)CHPh], 56.3 (C-2), 31.8–22.6 [$(CH_2)_{10}$], 14.0 (CH_3). Anal. calcd for $C_{35}H_{47}NO_7$: C, 70.80; H, 7.98; N, 2.36. Found: C, 70.52; H, 8.14; N, 2.54%.

4.5.10.2. Minor isomer 32b (minor R_f). MS (CI): *m/z* 594 (40%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.54 (PhCH), 5.33 (d, 1H, J_{gem} 5.6 Hz, OCH_AH_BN), 5.17 (d, 1H, J_{gem} 5.6 Hz, OCH_AH_BN), 4.60 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.15 [d, 1H, J_{trans} 1.9 Hz, CH(O)CHPh], 4.09 [d, 1H, J_{trans} 1.9 Hz, CH(O)CHPh]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 101.7 (C-1), 80.9 (OCH_2N), 71.1 (OCH_2R), 63.5 (C-5), 58.5 [CH(O)CHPh], 57.8 [CH(O)CHPh], 56.6 (C-2). HRMS (EI): $[M]^{+\bullet}$, found 593.334479. $C_{35}H_{47}NO_7$ requires 593.335253.

4.5.11. 1-Benzyl 2-amino-(*R*)-4,6-*O*-benzylidene-2-deoxy-2-*N*-[(*E*)-2,3-epoxybutanoyl]-2-*N*-3-*O*-isopropylidene-β-D-allopyranoside 33. Two stereoisomers were obtained in 75:25 ratio [50% de for the (2*S*,3*R*)-isomer]. Both isomers were isolated by column chromatography using hexane–ethyl acetate (17:10) as eluent, yield: 0.54 g (75%).

4.5.11.1. Major isomer 33a (major R_f). Mp 90–91°C; $[\alpha]_D$ −18.2 (*c* 0.6, CH_2Cl_2); MS (CI): *m/z* 482 (81%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.60 (s, 1H, PhCH), 4.90 (d, 1H, J_{gem} 11.8 Hz, OCH_AH_BPh), 4.66 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 4.61 (d, 1H, J_{gem} 11.8 Hz, OCH_AH_BPh), 4.55 (t, 1H, $J_{2,3}=J_{3,4}$ 3.7 Hz, H-3), 4.46 (dd, 1H, $J_{5,6e}$ 5.1 Hz, $J_{6e,6a}$ 10.2 Hz, H-6_e), 4.28 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 3.7 Hz, H-2), 3.96 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.9 Hz, $J_{5,6e}$ 5.1 Hz, H-5), 3.87 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{4,5}$ 9.9 Hz, H-4), 3.81 (t, 1H, $J_{5,6e}=J_{6e,6a}$ 9.9 Hz, H-6_a), 3.47 [d, 1H, J_{trans} 1.7 Hz, CH(O)CHCH$_3$], 3.23 [dq, 1H, J_{trans} 1.7 Hz, J 5.2 Hz, CH(O)CHCH$_3$], 1.61, 1.53 [2s, 6H, OC$(CH_3)_2$N], 1.09 [d, 3H, J 5.2 Hz, CH(O)CHCH$_3$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.0 (C=O), 136.7–126.3 (2Ph), 102.8 (PhCH), 100.1 (C-1), 97.7 [OC$(CH_3)_2$N], 76.9 (C-4), 72.7 (C-3), 71.3 (OCH_2Ph), 69.0 (C-6), 63.8 (C-5), 60.1 (C-2), 55.0 [CH(O)CHCH$_3$], 54.5 [CH(O)CHCH$_3$], 26.3, 23.7 [OC$(CH_3)_2$N], 16.6 [CH(O)CHCH$_3$]. Anal. calcd for $C_{27}H_{31}NO_7$: C, 67.35; H, 6.49; N, 2.91. Found: C, 67.14; H, 6.53; N, 2.91%.

4.5.11.2. Minor isomer 33b (minor R_f). Mp 182–183°C; $[\alpha]_D$ −105.3 (*c* 0.3, CH_2Cl_2); MS (CI): *m/z* 482 (40%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.2 (m, 10H, 2Ph), 5.56 (s, 1H, PhCH), 4.91 (d, 1H, J_{gem} 11.7 Hz, OCH_AH_BPh), 4.65 (d, 1H, J_{gem} 11.7 Hz, OCH_AH_BPh), 4.62 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.5–4.4 (m, 2H, H-3, H-6_e), 4.08 (dd, 1H, $J_{1,2}$ 7.6 Hz, $J_{2,3}$ 4.0 Hz, H-2), 4.0–3.7 [m, 4H, H-4, H-5, H-6_a, CH(O)CHCH$_3$], 3.17 [dq, 1H, J_{trans} 1.8 Hz, J 5.0 Hz, CH(O)CHCH$_3$], 1.54, 1.36 [2s, 6H, OC$(CH_3)_2$N)], 1.35 [d, 3H, J 5.0 Hz, CH(O)CHCH$_3$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.1 (C=O), 136.7–126.4 (2Ph), 102.9 (PhCH), 99.5 (C-1), 97.7 [OC$(CH_3)_2$N], 76.7 (C-4), 72.8 (C-3), 71.2 (OCH_2Ph), 69.1 (C-6), 63.6 (C-5), 60.0 (C-2), 54.3 [CH(O)CHCH$_3$], 26.2, 23.6 [OC$(CH_3)_2$N], 17.2 [CH(O)CHCH$_3$]. HRMS (EI): $[M]^{+\bullet}$, found 481.209446. $C_{27}H_{31}NO_7$ requires 481.210053. Anal. calcd for $C_{27}H_{31}NO_7$: C, 67.35; H, 6.49; N, 2.91. Found: C, 67.07; H, 6.51; N, 2.89%.

4.6. Reaction of epoxyamides with metallic hydrides

4.6.1. General procedure for reaction with lithium aluminum hydride. A stirred solution of either **11**, **12** or **14** (0.5 mmol) in dry THF (30 mL) was cooled to −10°C under an argon atmosphere. Lithium aluminum hydride

solution in THF (1 M, 0.8 mmol) was added and the reaction mixture was stirred for 3–6 h and then allowed to warm to room temperature. Saturated aqueous sodium sulphate solution (0.25 mL) was added dropwise. The solid was removed by filtration and washed with anhydrous THF and the filtrate was then concentrated to dryness.

4.6.1.1. Benzyl (*R*)-4,6-*O*-benzylidene-2-deoxy-2-(2-hydroxy-3-phenylpropanamido)-β-D-allopyranoside 15. Only one regioisomer was obtained as stereoisomeric mixture from **11**. MS (CI): *m/z* 506 (20%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 6.93 (d, 1H, $J_{2,NH}$ 9.0 Hz, NH), 4.57 (d, 1H, J_{gem} 12.1 Hz, OCH_AH_BPh), 2.75 [dd, 1H, J_{gem} 14.0 Hz, J 8.5 Hz, $CH(OH)CH_AH_BPh$] (for the major isomer); 6.83 (d, 1H, $J_{2,NH}$ 8.7 Hz, NH), 4.55 (d, 1H, J_{gem} 12.5 Hz, OCH_AH_BPh), 2.87 [dd, 1H, J_{gem} 14.0 Hz, J 8.2 Hz, $CH(OH)CH_AH_BPh$] (for the minor isomer). ^{13}C NMR (50 MHz, $CDCl_3$): δ 73.1 [$CH(OH)CH_2Ph$], 41.0 [$CH(OH)CH_2Ph$] (for the major isomer); 72.8 [$CH(OH)CH_2Ph$], 40.6 [$CH(OH)CH_2Ph$] (for the minor isomer). **15** was acetylated for its characterization.

*4.6.1.1.1. Benzyl 2-(2-acetoxy-3-phenylpropanamido)-3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside **18***. Compound **15** was acetylated in the usual way with acetic anhydride/pyridine/dichloromethane, and purified by column chromatography using dichloromethane–methanol (125:1) as eluent, yield: 0.23 g (78%); MS (CI): *m/z* 590 (35%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 15H, 3Ph), 6.05 (d, $J_{2,NH}$ 8.7 Hz, NH minor isomer), 5.96 (d, $J_{2,NH}$ 8.4 Hz, NH major isomer), 5.67 (bs, H-3 major isomer), 5.63 (bs, H-3 minor isomer), 5.53 (PhCH), 5.31 [m, 1H, $CH(OAc)CH_2Ph$], 4.87, 4.85 (2d, 1H, J_{gem} 12.3 Hz, OCH_AH_BPh), 4.67, 4.65 (2d, 1H, $J_{1,2}$ 8.6 Hz, H-1), 4.57, 4.55 (2d, 1H, J_{gem} 12.3 Hz, OCH_AH_BPh), 4.4–4.3 (m, 2H, H-6_e, H-2), 3.9–3.7 (m, 3H, H-4, H-5, H-6_a), 3.2–3.0 [m, 2H, $CH(OAc)CH_2Ph$], 2.05, 1.90 (2s, CH_3 major isomer), 2.04, 1.94 (2s, CH_3 minor isomer). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.0, 169.7, 169.4, 169.3,169.2, 168.2 (3C=O), 137.0–125.4 (3Ph), 101.3, 101.2 (CHPh), 98.6, 98,5 (C-1), 76.9 (C-4), 74.3 [$CH(OAc)CH_2Ph$ major isomer], 74.1 [$CH(OAc)CH_2Ph$ minor isomer], 70.3, 70.2 (OCH_2Ph), 69.4, 69.1 (C-3), 68.8 (C-6), 64.3 (C-5), 51.0 (C-2), 37.2 [$CH(OAc)CH_2Ph$ major isomer], 36.8 [$CH(OAc)CH_2Ph$ minor isomer], 20.8, 20.7, 20.6, 20.5 ($2CH_3CO$). Anal. calcd for $C_{33}H_{35}NO_9$: C, 67.22; H, 5.98; N, 2.38. Found: C, 66.94; H, 5.92; N, 2.53%.

4.6.1.2. Benzyl (*R*)-4,6-*O*-benzylidene-2-deoxy-2-(3-hydroxybutanamido)-β-D-allopyranoside 17. The reaction of compound **14** gave **17** as a stereoisomeric mixture, which was purified by crystallization from ethanol, yield: 0.19 g (86%). Mp 214–215; $[\alpha]_D$ −113.1 (*c* 0.5, DMF); MS (CI): *m/z* 444 (29%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 6.16, 6.12 (2d, 1H, $J_{2,NH}$ 8.5 Hz, NH), 5.59 (s, 1H, PhCH), 4.89, 4.88 (2d, 1H, J_{gem} 12.3 Hz, OCH_AH_BPh), 4.70, 4.69 (2d, 1H, $J_{1,2}$ 8.1 Hz, H-1), 4.56 (d, 1H, J_{gem} 12.3 Hz, OCH_AH_BPh), 4.40 (dd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 9.8 Hz, H-6_e), 4.3–4.1 [m, 3H, H-2, H-3, $CH_2CH(OH)CH_3$], 3.96 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.3 Hz, $J_{5,6e}$ 4.5 Hz, H-5), 3.80 (t, 1H, $J_{5,6a}=J_{6a,6e}$ 10.0 Hz, H-6_a), 3.66 (dd, 1H, $J_{3,4}$ 1.9 Hz, $J_{4,5}$ 9.3 Hz, H-4), 2.4–2.1 [m, 2H, $CH_2CH(OH)CH_3$], 1.17 [d, 3H, J 6.3 Hz, $CH_2CH(OH)CH_3$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.8 (C=O), 136.9–126.1 (2Ph), 101.7 (PhCH), 99.0 (C-1), 78.6 (C-4), 70.6 (OCH_2Ph), 69.0 (C-6), 68.7, 68.6 (C-3), 64.8, 64.7 [$CH_2CH(OH)CH_3$], 63.3 (C-5), 51.7, 51.6 (C-2), 44.1 [$CH_2CH(OH)CH_3$], 22.6 [$CH_2CH(OH)CH_3$]. HRMS (EI): $[M]^{+\bullet}$, found 444.201322. $C_{24}H_{30}NO_7$ requires 444.202228.

From compound **12**, using the described conditions, two regioisomers were obtained: **16** and **17** in 1:3 ratio. ^1H NMR (200 MHz, $CDCl_3$): δ 1.17 [d, J 6.3 Hz, $CH_2CH(OH)CH_3$] (for **17**), 0.87 [t, J 7.2 Hz, $CH(OH)CH_2CH_3$] (for **16**). ^{13}C NMR (50 MHz, $CDCl_3$): δ 22.6 [$CH_2CH(OH)CH_3$] (for **17**), 9.1 [$CH(OH)CH_2CH_3$] (for **16**).

4.6.2. General procedure for reaction with sodium borohydride. To a solution of **27a** or **32a** (0.5 mmol) in dry THF (50 mL) was added sodium borohydride (12 mg, 0.32 mmol) and the reaction mixture was stirred at room temperature until completion of the reaction. When TLC showed that all of the starting compound had been consumed (1 week), the solvent was co-evaporated with methanol to give a solid which was purified by flash chromatography on silica gel. The elution with hexane–ethyl acetate (2:1) gave the compound **34**, which was identified as (2*R*,3*R*)-(+)-3-phenylglycidol. The posterior elution with dichloromethane–methanol (60:1) gave the sugar moiety **1** or **3**.

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