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Stereoselective epoxidation of alkenylidene acetals derived from carbohydrates with D-*allo*, D-*altro*, D-*galacto*, D-*gluco* and D-*xylo* configurations☆

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Abstract—The synthesis of 2,3-epoxypropylidene acetals of sugar derivatives from *N*-acetyl-2-amino-2-deoxy-D-allopyranose, D-altropyranose, D-galactopyranose, *N*-acetyl-D-glucosamine, D-glucofuranose and D-xylofuranose is described. The epoxidation with *m*-CPBA of the corresponding alkenylidene derivatives took place with different stereoselectivities depending upon the sugar configuration, the protecting group of the hydroxyl groups of the sugar, and the substitution of the unsaturated system. The analysis of the ring-opening reaction of these oxiranes by hydrogenolysis enabled the assignation of their configuration at the new stereogenic centres.

1. Introduction

Stereoselective epoxidation of alkenes is a versatile method used for inducing chirality into organic molecules, and the resulting oxirane moiety can be transformed into a variety of target molecules.[2,3] Chiral oxiranes are very important building blocks for the synthesis of enantiomerically pure complex molecules of biologically active compounds.[4–6] Carbohydrates contain several functional groups and stereogenic centres in one molecular unit, which allows the use of carbohydrates as tools in stereochemical differentiations, as the starting materials in ex-chiral pool syntheses of interesting enantiopure compounds,[7] as chiral template in asymmetric transformations,[8] and as chiral auxiliaries in stereoselective synthesis.[9,10] We have used aminosugars as chiral templates in the stereoselective synthesis of diaminosugars, chiral oxazolidines and compounds with potential anti-cancer activity.[11–14] Oxiranes are key intermediates in the asymmetric synthesis of chiral 1,2-difunctionalised compounds of biological and pharmacological interest, such as α-hydroxy-β-aminoacids derived from isoserine, which are the most-important members of the β-aminoacid family. Isoserine derivatives constitute as an essential fragment in natural products of high therapeutic value,[4] 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 important role of oxiranes in stereoselective synthesis, we have developed a method for the stereoselective epoxidation of an olefin moiety linked to different positions of a carbohydrate molecule, acting as a chiral inductor via various functionalities (glycoside, amide, acetal). The chiral epoxyalkyl glycosides,[15,16] chiral epoxyamides[17] and the chiral epoxyacetals[1] obtained, can be transformed into different types of compound. This method has enabled us to synthesise derivatives of glycosyl glycerol analogues that have been used as alkylating-agent carrier systems,[18] and phenylisoserine precursors,[1] whose acetal function can be easily hydrolysed in the organism, separating the active fraction of the sugar moiety.

Our work (the initial efforts) on the epoxidation of olefins joined to carbohydrates via glycoside or amide bonds has recently been reviewed in depth by Adam and Zhang.[9] Their review shows that, apart from our contribution, there are very few references with regards to the use of carbohydrates as chiral auxiliaries in stereoselective epoxidation reactions, and, in those rare cases, it always takes the form

☆ Potential anticancer drugs, Part 7. For Part 6, see: Ref. 1.

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of the union of the chiral auxiliary (2-hydroxyglucosides) to the olefin substrate, via the glycoside bond. Broadening this line, we also proposed the union of the olefin to the carbohydrate via a more labile bond. Thus, the new chiral fragment, oxiranes or derivatives obtained from it, can be more easily separated from the chiral auxiliary by chemical or enzymatic hydrolysis. This approach presents several advantages: (1) the easier union of the olefin and the chiral auxiliary; (2) greater variability in the structural and stereochemical aspects of the chiral auxiliary that can affect the stereoselection; (3) widening the potential range of chiral auxiliaries available, via a simple, inexpensive and environmentally friendly chemistry and (4) the above-mentioned easier separation of the acetal function to liberate the biologically evaluable substrate.

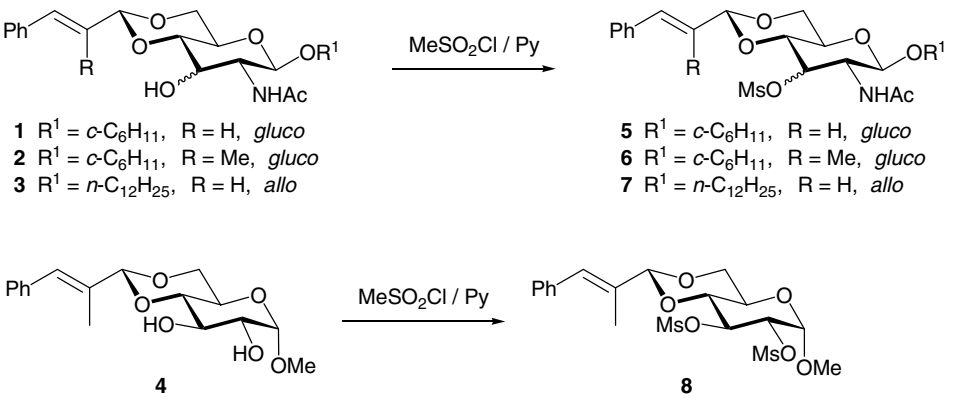
In a previous paper,[1] we have carried out the epoxidation of (*R*)-4,6-*O*-propenylidene acetals, derivatives of D-glucosamine and D-glucose, showing the important role of the hydroxyl group at the 3-position of the sugar in the diastereoselectivity of the reaction. Higher diastereoisomeric excesses (des) were obtained when the hydroxyl group was unprotected. We also proved that higher des could be obtained with an *allo* derivative as the substrate of the epoxidation reaction (its hydroxyl group at the 3-position is unprotected) than with its analogue having a *gluco* configuration. Herein, we report the epoxidation reaction, with *m*-chloroperoxybenzoic acid, of the double bond of acetals of *trans*-cinnamaldehyde and α-methyl-*trans*-cinnamaldehyde with different monosaccharide derivatives of alkyl 2-acetamido-2-deoxy-D-allopyranoside, alkyl D-altropyranoside, alkyl D-galactopyranoside, alkyl 2-acetamido-2-deoxy-D-glucopyranoside, 1,2-*O*-isopropylidene-D-glucofuranose and 1,2-*O*-isopropylidene-D-xylofuranose, in order to diversify the carbohydrate moiety, which acts as a chiral inductor for obtaining the best diastereomeric excesses.

2. Results and discussion

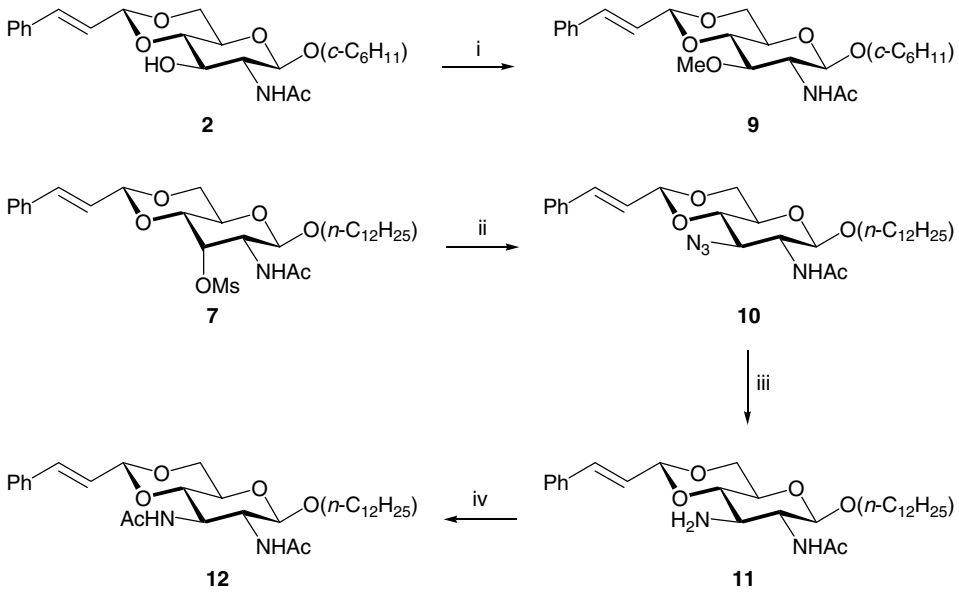
Compounds **2**–**8** (Scheme 1) were used as the precursors of propenylidene acetals **9**, **12**–**17** and **23**–**28** (Schemes 2–5), whose oxidation was carried out (Scheme 6). With the aim of analysing the stereofacial differentiation of the diastereotopic faces of the double bond in the epoxidation reaction depending on the configuration of the sugar moiety, we have classified the starting compounds as a function of the sugar configuration: glucopyranose derivatives **9** and **12**; allopyranose derivatives **13**–**16**; altropyranose derivative **17**; galactopyranose derivatives **23** and **24**; glucofuranose derivatives **25** and **26**; and xylofuranose derivatives **27** and **28**.

The reaction of alkyl (*R*)-4,6-*O*-alkenylidene-D-glucopyranoside derivatives **1**–**4** with methanosulfonyl chloride and pyridine gave the corresponding methanosulfonyl derivatives **5**–**8** in good yields (Scheme 1). These compounds showed characteristic signals corresponding to the methanosulfonyl group at 3.1–3.0 ppm in ^{1}H and at 39–38 ppm in their ^{13}C NMR spectra. Compound **9** was obtained by 3-*O*-methylation reaction of (*R*)-4,6-*O*-alkenylidene-D-glucopyranoside derivative **2** with methyl iodide and 18-crown-6 as a catalyst (Scheme 3). The ^{13}C NMR spectrum of compound **9** showed a signal at 60.6 ppm corresponding to the new methyl group. The reaction of (*R*)-4,6-*O*-alkenylidene-3-*O*-methanosulfonyl-D-allopyranoside derivative **7** with sodium azide gave the corresponding 3-*O*-azido-D-glucopyranoside derivative **10,** which was hydrogenated to give the amine **11** and then acetylated, to give **12**, a compound with the *gluco* configuration and the structure of a 2,3-diacetamido derivative. The NMR spectra of **12** confirmed the presence of two acetamido groups, thus the acetamido groups showed two singlets at 1.64 and 1.63 ppm in the ^{1}H spectrum, and signals at 170.7, 23.6 and 23.5 ppm in the ^{13}C spectrum; the signal corresponding to C-3 was observed at 68.2 ppm.

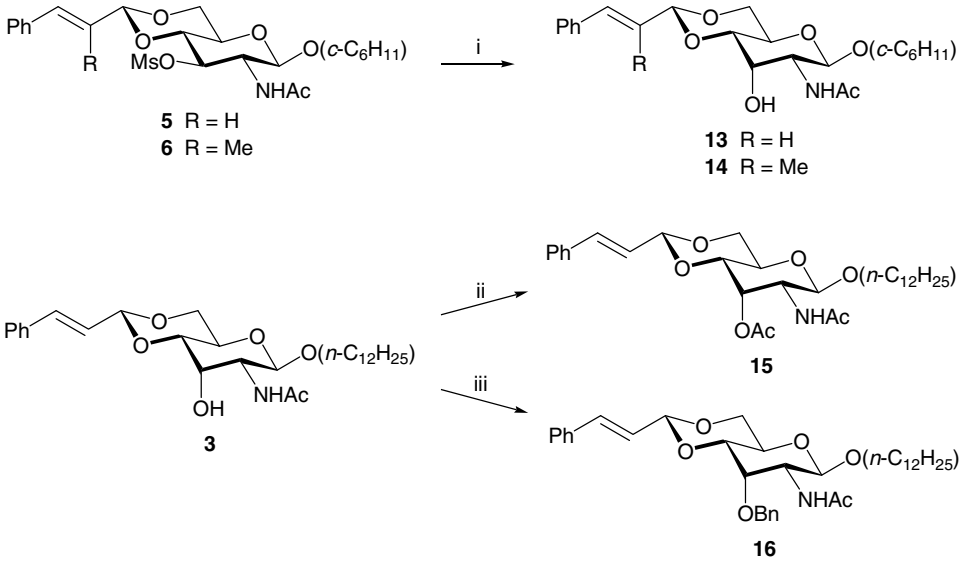
Compounds **5** and **6** were transformed into (*R*)-4,6-*O*-alkenylidene-D-allopyranoside derivatives **13** and **14** with sodium acetate in 2-methoxyethanol–water, by a configuration inversion described for similar compounds[1,12,13] (Scheme 2). ^{1}H NMR showed the signal corresponding to H-2 as a double triplet at 4.10 ppm, characteristic of an *allo* configuration. In order to obtain other *allo*-configuration compounds with the 3-OH of the sugar protected, as substrates for the epoxidation, we proceeded to the 3-O-acetylation and the 3-O-benzylation of **3**, which gave compounds **15** and **16**, respectively. Compound **15** showed a singlet at 2.15 ppm in the ^{1}H NMR spectrum, and a signal



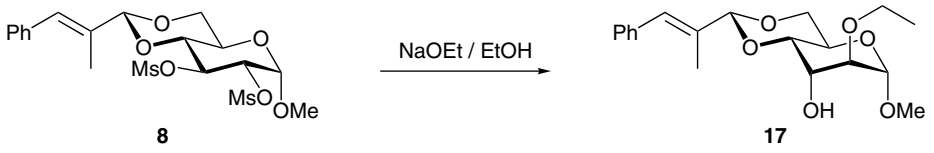
Scheme 1.



Scheme 2. Reagents and conditions: (i) MeI/KOH/18-crown-6/THF; (ii) NaN_3/DMF; (iii) $NaBH_4$/DMF; (iv) Ac_2O/Py/CH_2Cl_2.



Scheme 3. Reagents and conditions: (i) NaOAc/$MeOCH_2CH_2OH$–H_2O; (ii) Ac_2O/Py/CH_2Cl_2; (iii) BnBr/KOH/18-crown-6/THF.

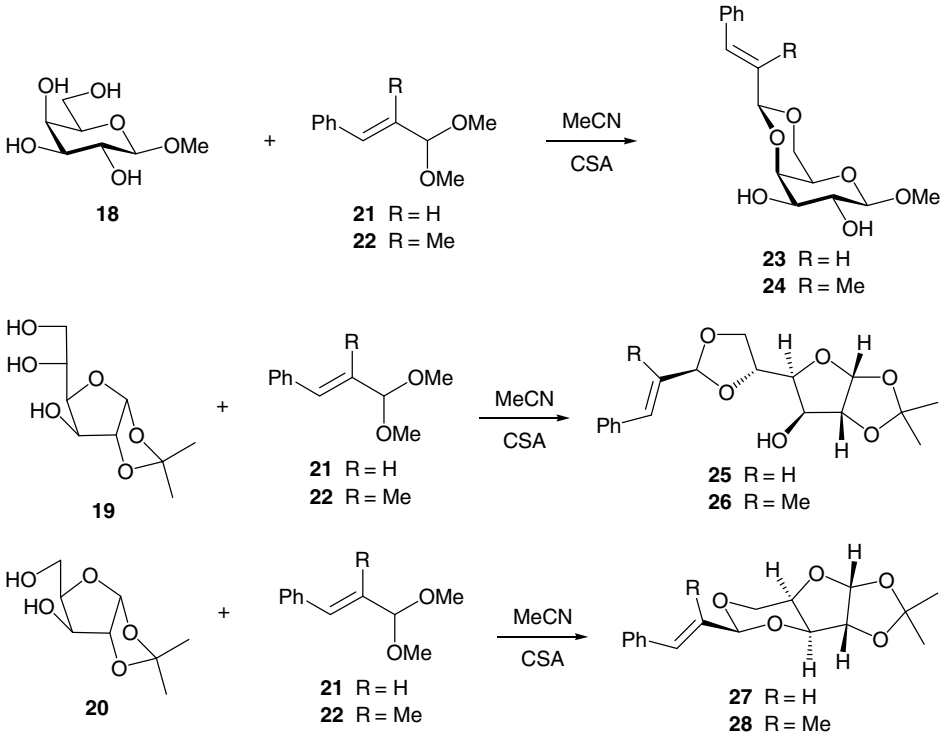


Scheme 4.

at 21.0 ppm in the ^{13}C, corresponding to the acetyl group. The NMR spectra of compound **16** showed the signals corresponding to the protecting group introduced: doublets at 5.03 and 4.55 ppm in ^{1}H, and a signal at 74.8 ppm in ^{13}C.

The synthesis of compound **17**, a derivative with an *altro* configuration, was carried out from **8** by the treatment with sodium ethoxide in ethanol, via the corresponding intermediate 2,3-anhydro-D-allopyranoside derivative (not isolated) (Scheme 4). The ^{1}H NMR of **17** showed a singlet at 4.68 ppm for H-1 ($J_{1,2} \approx 0$ Hz) and a double doublet at 3.58 ppm ($J_{2,3}$ 1.0, $J_{3,4}$ 3.0 Hz), characteristic signals of α-glycosides in an *altro* configuration.

Methyl (*S*)-4,6-*O*-alkenylidene-β-D-galactopyranosides **23** and **24** were obtained by the reaction of methyl β-D-galactopyranoside **18** and *trans*-cinnamaldehyde dimethyl ace-



Scheme 5.

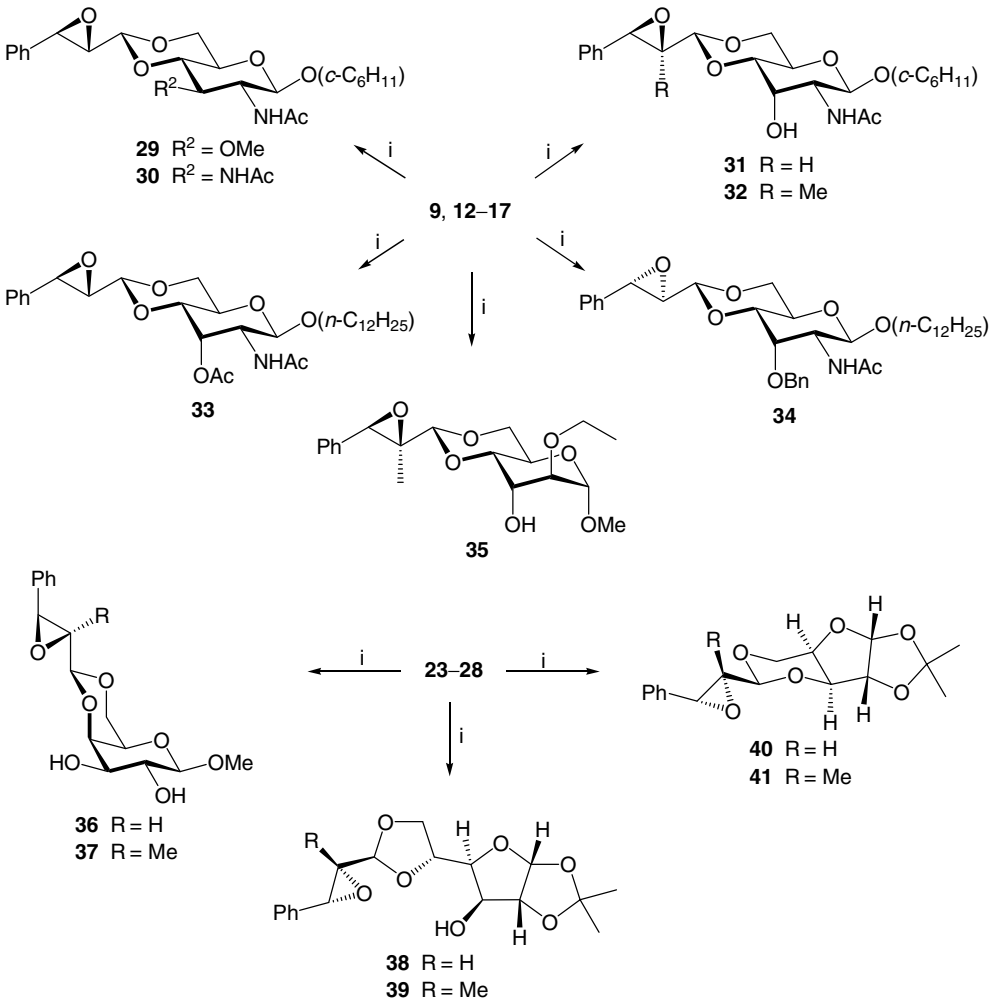
tal[19] **21** or α-methyl-*trans*-cinnamaldehyde dimethyl acetal[1] **22** in good yields, using the procedure described by Murphy et al.[20] for the formation of acetals using aldehyde dimethyl acetal as a reagent. The same method has been used for the preparation of 1,2-isopropylidene-(*S*)-5,6-*O*-alkenylidene-α-D-glucofuranoses **25** and **26** from 1,2-isopropylidene-α-D-glucofuranose **19**, and 1,2-isopropylidene-(*S*)-3,5-*O*-alkenylidene-α-D-xylofuranoses **27** and **28** from 1,2-isopropylidene-α-D-xylofuranose **20** (Scheme 5). The NMR spectra for compounds **23**–**28** showed signals corresponding to the olefin moiety incorporated into the carbohydrate molecule in the acetalation reaction.

Compound **23** was obtained as only one stereoisomer, as shown in its NMR spectra. The ^{1}H spectrum showed a signal at 5.17 ppm corresponding to the acetal proton, signals at 6.75 and 6.23 ppm for the olefinic protons, and another at 4.17 ppm corresponding to H-1 as a characteristic signal of the β-galactopyranoside moiety. Compound **24** was obtained as a mixture of two stereoisomers in 76% de (NMR data). The major diastereoisomer was isolated by column chromatography, and characterised from the ^{1}H NMR spectrum: a singlet at 6.60 ppm corresponding to the olefinic proton, a singlet at 4.96 ppm for the acetal proton, a doublet at 1.89 ppm corresponding to the methyl group on the double bond, and a doublet at 4.14 ppm for H-1 of the sugar moiety, as the most-characteristic signals. 2D-NOESY experiments led us to establish the (*S*)-configuration at the acetal carbon for compounds **23** and **24**.

In the syntheses of compounds **25** and **26**, two stereoisomers were obtained in each case, in 68% and 38% de, respectively. The two diastereoisomers of **25** and **26** were separated by column chromatography. In both cases, 2D-NOESY experiments established an (*S*)-configuration at the acetal carbon for the major isomer. Compound (*S*)-**25** showed signals at 6.76 and 6.14 ppm for the olefinic protons, at 5.47 ppm for the acetal proton, and at 6.03 ppm for H-1 of the glucofuranose moiety in the ^{1}H NMR spectrum. Compound (*R*)-**25** showed signals at 6.72, 6.12, 5.58 and 5.93 ppm for the same protons. The ^{1}H NMR spectrum of (*S*)-**26** showed signals at 6.65, 5.26 and 1.89 ppm for the unsaturated acetal function incorporated into the 5,6-hydroxyl groups of the α-D-glucofuranose derivative. The ^{1}H NMR spectrum of (*R*)-**26** showed the same signals at 6.64, 5.41 and 1.89 ppm, respectively.

Compound **27** was obtained as only one stereoisomer, with an (*S*)-configuration at the acetal carbon. Compound **28** was obtained as a mixture of two stereoisomers in 74% de (NMR spectra), which were separated by column chromatography. The incorporation of an unsaturated acetal function into the 3,5-hydroxyl groups of the 1,2-*O*-isopropylidene-α-D-xylofuranose was observed from the NMR spectra, thus compound **27** showed signals at 6.77, 6.14 and 5.09 ppm, compound (*S*)-**28** at 6.66, 4.90 and 1.89 ppm, and compound (*R*)-**28** at 6.52, 5.13 and 1.91 ppm.

The reaction of **9**, **12**–**17** and **23**–**28** with *m*-CPBA in chloroform gave the corresponding oxiranes **29**–**41**. The compounds were isolated and purified by flash chromatography on silica gel (Scheme 6). The NMR data for compounds **29**–**41** showed the characteristic signals corresponding to the oxirane ring at 3.9 and 3.2 ppm in the ^{1}H spectra, and at 61 and 55 ppm in the ^{13}C spectra for **29**–**31**,



Scheme 6. Reagent and conditions: (i) *m*-CPBA/$CHCl_3$/−15 °C.

33, **34**, **36**, **38** and **40**; and at 4.1 and 1.1 ppm in the ^1H spectra, and at 63 and 61 ppm in the ^{13}C spectra for **32**, **35**, **37**, **39** and **41**.

The de in each case was determined by ^1H NMR (Table 1). For their analysis, the oxiranes obtained **29**–**41** have been listed in the order of the carbohydrate configuration: *gluco-pyranose* for compounds **29** and **30**, *allopyranose* for **31**–**34**, *altropyranose* for **35**, *galactopyranose* for **36** and **37**, *gluco-furanose* for **38** and **39**, and *xylofuranose* for **40** and **41**. In order to compare the results, we have included, in Table 1, three compounds previously studied:[1] 1-dodecyl 2-acetamido-2-deoxy-4,6-*O*-[(1*R*,2*R*,3*S*)-2,3-epoxy-3-phenylpropylidene]-β-D-glucopyranoside **42**, 1-dodecyl 2-acetamido-2-deoxy-4,6-*O*-[(1*R*,2*R*,3*S*)-2,3-epoxy-2-methyl-3-phenylpropylidene]-β-D-glucopyranoside **43**, and 1-dodecyl 2-acetamido-3-*O*-benzyl-2-deoxy-4,6-*O*-[(1*R*,2*R*,3*S*)-2,3-epoxy-3-phenylpropylidene]-β-D-glucopyranoside **44**.

With regards to the degree of substitution of the double bond of the starting propylidene acetals, the experimental data show that the des obtained from α-methyl-*trans*-cinnamaldehyde acetals (entries 2, 7, 12, 14 and 16) are higher than those from *trans*-cinnamaldehyde acetals (entries 1, 6, 11, 13 and 15). Thus, compounds **43**, **32**, **37**, **39** and **41** were obtained with des of 56%, 72%, 74%, 60% and 30%, respectively, while compounds **42**, **31**, **36**, **38** and **40** were obtained with des of 34%, 68%, 26%, 56% and 22%, respectively.

With regard to the functionalisation of carbon 3 of the carbohydrate with pyranose ring, the results show that the compounds with the free 3-hydroxyl group (entries 1 and 6) present higher des than those for the corresponding compounds with the 3-hydroxyl group blocked (entries 3, 4, 8 and 9). Thus, compound **42** was obtained with 34% de, while compounds **44** and **29** were obtained with des of 22% and 14%, respectively. Compound **31** was obtained with 68% de, while compounds **15** and **16** were obtained with des of 20% and 28%, respectively.

The des also depend upon the configuration of the carbohydrate moiety. Thus, oxiranes obtained from α-methyl-*trans*-cinnamaldehyde acetal derivatives with the 3-hydroxyl group free—**43** (*gluco* configuration), **32** (*allo* configuration) and **37** (*galacto* configuration)—showed des of 56%, 72% and 74%, respectively. Equally, oxiranes obtained from *trans*-cinnamaldehyde acetal derivatives with

Table 1. Epoxidation of 3-phenylpropenylidene derivatives **9**, **12**–**17**, **23**–**28**

Entry	Starting compound	Reaction product	Yield[a] (%)	De[b] (%)	Major oxirane configuration
1		**42**[c]	77	34	(2*R*,3*S*)
2		**43**[c]	72	56	(2*R*,3*S*)
3		**44**[c]	86	22	(2*S*,3*R*)
4	**9**	**29**	90	14	(2*S*,3*R*)
5	**12**	**30**	82	0	
6	**13**	**31**	72	68	(2*S*,3*R*)
7	**14**	**32**	72	72	(2*S*,3*R*)
8	**15**	**33**	80	20	(2*S*,3*R*)
9	**16**	**34**	83	28	(2*R*,3*S*)
10	**17**	**35**	86	34	(2*S*,3*R*)
11	**23**	**36**	67	26	(2*R*,3*S*)
12	**24**	**37**	62	74	(2*R*,3*S*)
13	**25**	**38**	84	56	(2*S*,3*R*)
14	**26**	**39**	71	60	(2*S*,3*R*)
15	**27**	**40**	89	22	(2*S*,3*R*)
16	**28**	**41**	84	30	(2*S*,3*R*)

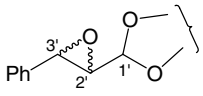
[a] Yields refer to compounds obtained in each reaction after isolation and purification.
[b] Determined by integration in the ^{1}H NMR spectra of reaction mixtures.
[c] Ref. 1.

the free 3-hydroxyl group—**42** (*gluco* configuration), **31** (*allo* configuration) and **36** (*galacto* configuration)—showed des of 34%, 68% and 26%, respectively. When the des of oxiranes obtained from *trans*-cinnamaldehyde acetal derivatives with the 3-hydroxyl group blocked are compared, a similar behaviour is observed, thus compounds **44** and **29** (*gluco* configuration) were obtained with des of 22% and 14%, respectively, lower than that of **34** (*allo* configuration), obtained with 28% de.

In order to assign the configuration on the stereogenic centres in the oxirane ring formed in the oxidation reaction, it is important to analyse the chemical shifts of the protons and the carbons corresponding to the oxidised acetal system in the NMR spectra (Tables 2 and 3). For oxiranes derived from *trans*-cinnamaldehyde (Table 2), the signal corresponding to H-3′ is easily identifiable in the ^{1}H spectra at approximately 4 ppm as a doublet, and the signal for C-3′ in ^{13}C at approximately 55 ppm. In a previous paper,[1] we assigned the (2*R*,3*S*) configuration to the major isomer of compound **42**, and we can observe that the doublet corresponding to H-3′ of the major isomer appeared at a lower chemical shift than that of the minor isomer, and that the signal for C-3′ of the major isomer appeared at a higher chemical shift than that of the minor isomer. Compound **44** showed a different profile in H-3′ and C-3′ to that of compound **42**, by which we assigned a (2*S*,3*R*)-configuration for the major isomer of compound **44**. Compound **29** showed the same profile as **44**—both of which are compounds with a *gluco* configuration and with the 3-hydroxyl group blocked. Compounds **31** and **34** (*allo* configuration) showed different profiles in the H-3′ and C-3′ signals, by which different configurations have been assigned to them. On the basis of these profiles, we have assigned the configuration of the remaining compounds as shown in Table 2.

For oxiranes derived from α-methyl-*trans*-cinnamaldehyde (Table 3), the ^{13}C NMR spectra showed signals at approximately 103, 62, 60 and 11 ppm, for C-1′, C-2′, C-3′ and methyl group on the oxirane ring, respectively. The ^{1}H and ^{13}C NMR spectra of **43**[1] showed the signal corresponding to CH_3 of the major isomer at a higher chemical shift than that of the minor isomer, whereas the signal for C-1′ of the major isomer appeared at a lower chemical shift to that of the minor isomer. As a result we assigned a (2*R*,3*S*)-configuration to the major isomer of compound **43**. Compounds **32** (*allo* configuration) and **43** (*gluco* configuration) showed different profiles in C-1′ and CH_3 signals, by which we assigned a (2*S*,3*R*)-configuration to the major isomer of compound **32**. Compound **35** (*altro* configuration) showed the same profile as **32** in the signals corresponding to C-1′ and C-2′, whereas compound **37** (*galacto* configuration) showed a different profile to that of **32** in the signals corresponding to C-2′, C-3′ and CH_3. We assigned a (2*S*,3*R*)-configuration to the major isomer of compound **35**, and a (2*R*,3*S*)-configuration to the major isomer of compound **37**. Compounds **39** (*glucofuranose* configuration) and **41** (*xylofuranose* configuration) showed the same profile as **32** for C-1′, C-2′, C-3′ and CH_3 in the ^{13}C spec-

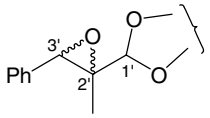
Table 2. NMR data (δ, ppm) for the acetal group in oxiranes derived from *trans*-cinnamaldehyde



Entry	Compound	H-1′	H-2′	H-3′	C-1′	C-2′	C-3′
1	**42**[a]	4.63(M)/4.62(m)		3.99(m)/3.98(M)	99.5(m)/99.4(M)	60.1	54.7(M)/54.5(m)
2	**44**[a]	4.70(M)/4.64(m)	3.20	3.96(M)/3.93(m)	99.7(m)/99.4(M)	60.8	55.2(m)/55.0(M)
3	**29**	4.65(M)/4.61(m)	3.20(m)/3.18(M)	3.95(M)/3.92(m)	99.7(m)/99.4(M)	61.0(M)/60.7(m)	55.3(m)/55.1(M)
4	**31**	4.67(M)/4.63(m)	3.18	3.93(M)/3.91(m)	100.0(M)/99.8(m)	60.7(M)/60.5(m)	56.3(m)/55.4(M)
5	**33**	4.70(M)/4.61(m)	3.12	3.90(M)/3.86(m)	99.9(m)/99.4(M)	60.6(m)/60.5(M)	55.4(m)/54.9(M)
6	**34**	4.65(M)/4.61(m)	3.19	3.95(m)/3.91(M)	99.9	60.9(m)/60.7(M)	53.3(M)/53.1(m)
7	**36**	4.65(M)/4.61(m)	3.29	3.96(m)/3.95(M)	100.2(m)/99.7(M)	61.0(m)/60.8(M)	55.4(M)/55.3(m)
8	**38**	4.97(M)/4.94(m)	3.18	3.95(M)/3.91(m)	93.9(m)/93.7(M)	61.2	55.3
9	**40**	4.56(m)/4.54(M)	3.18	3.96(M)/3.93(m)	98.2(M)/98.0(m)	61.0(M)/60.9(m)	55.3(M)/55.1(m)

(M) For the major isomer.
(m) For the minor isomer.
[a] Ref. 1.

Table 3. NMR data (δ, ppm) for the acetal group in oxiranes derived from α-methyl-*trans*-cinnamaldehyde



Entry	Compound	H-1′	CH_3	H-3′	C-1′	C-2′	CH_3	C-3′
1	**43**[a]	4.47(M)/4.44(m)	1.11(M)/1.09(m)	4.14(M)/4.13(m)	102.6(m)/102.3(M)	62.2	10.7(M)/10.5(m)	59.8(M)/59.7(m)
2	**32**	4.47(M)/4.44(m)	1.09		103.2(M)/102.9(m)	62.4(M)/62.3(m)	11.4(m)/11.1(M)	60.7(M)/60.5(m)
3	**35**	4.50	1.12(M)/1.11(m)	4.09	104.0(M)/103.9(m)	62.5(M)/62.4(m)	11.0	60.7(m)/60.6(M)
4	**37**	4.51(M)/4.41(m)	1.12	4.14	102.5	63.1(m)/62.9(M)	11.3(M)/11.2(m)	60.7(m)/60.4(M)
5	**39**	4.74(M)/4.73(m)	1.08(m)/1.07(M)		96.5	62.1(M)/62.0(m)	11.0(m)/10.7(M)	60.4(M)/60.2(m)
6	**41**	4.37(m)/4.32(M)	1.08(m)/1.07(M)	4.09(m)/4.08(M)	101.4(M)/101.1(m)	62.6(M)/60.6(m)	11.0(m)/10.7(M)	60.6(M)/60.3(m)

(M) For the major isomer.
(m) For the minor isomer.
[a] Ref. 1.

tra; therefore, we assigned the (2*S*,3*R*) configuration to the major isomer of compounds **39** and **41**.

The stereochemical results obtained here with **31** and **32** (*allo* configuration) are remarkable, compared with those obtained from their corresponding *gluco* analogues **42** and **43**.[1] This can be explained within the general framework used to explain the asymmetric induction in the oxidation of β-alkenyl glycosides. In the case of the oxidation of the β-alkenyl glycosides, it has been shown that the reactive face is the *Re* face.[18,21,22] This is seen above all when there is a hydrogen-bond-donating group (OH or NHCOR) at the 2-position. This suggests the formation of a hydrogen bond between the reagent and the 2-OH or 2-NH group. Indeed, when the 2-OH is blocked, the stereoselectivity falls dramatically. The arrangement and distance of the 3-OH group of *gluco* configuration and the double bond of the acetal propylidene group, compounds **42** and **43** (Fig. 1a), are the same as that of the β-alkenyl glycosides, and thus the coordinated oxidant reacts with the 3-OH by the same reactive face in both cases. When the chiral auxiliary has an *allo* configuration, compounds **31** and **32**, the coordinated oxidant with the 3-OH reacts with the alkene via the face opposite to that in the former cases (Fig. 1b).

In order to demonstrate that the ^{1}H and ^{13}C spectra profiles for the oxiranes are related with the reactive face of the double bond in the epoxidation reaction, we carried out the hydrogenolysis of **34**, **38**, **40**, **42**, **44** and **47** (Scheme 7). Table 4 shows the NMR data for the acetal group in hydrogenated compounds **45**, **46** and **48**–**51**. The data in Table 4 indicate that the major isomer of compound **45** has a different configuration to that of the major isomer of compound **46**, implying that the major isomers of compounds **42** and **44** have different configurations (a *gluco* configuration at the 3-position free versus a *gluco* configuration at the 3-position blocked). The same reasoning can be applied to compounds **48** and **49**, showing that the major isomers of compounds **47** *allo* configuration) and **34** (*galacto* configuration) have different configurations. Compounds **50** and **51** show the same profile in the data of Table 4, and therefore we have assigned the same configuration, implying that the major isomers of compounds **38** and **40** have the same configurations.

3. Conclusion

In conclusion, we were able to establish that (a) the more reactive face in the epoxidation reaction of propylidene acetals presented herein with a *glucopyranose* and a *galactopyranose* configuration with the 3-hydroxyl free is the *Re*,*Re* face, whereas the *Si*,*Si* face is the more reactive for compounds with an *glucopyranose* configuration with the 3-hydroxyl blocked; (b) the more reactive face in the epoxidation reaction of propylidene acetals presented herein with *allopyranose* configuration with the 3-hydroxyl free is the *Si*,*Si* face, whereas the same compounds with the 3-hydroxyl blocked show the *Re*,*Re* face as the more reactive; (c) the propylidene acetals presented herein with a *glucofuranose* and a *xylofuranose* configuration react preferably by the *Si*,*Si* face in the epoxidation reaction. In summary, the stereochemistry of the oxirane obtained

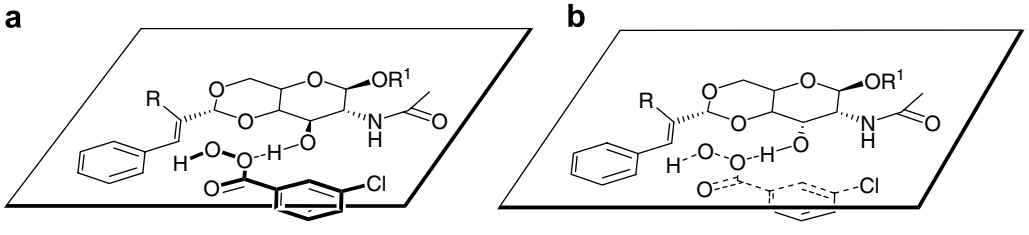
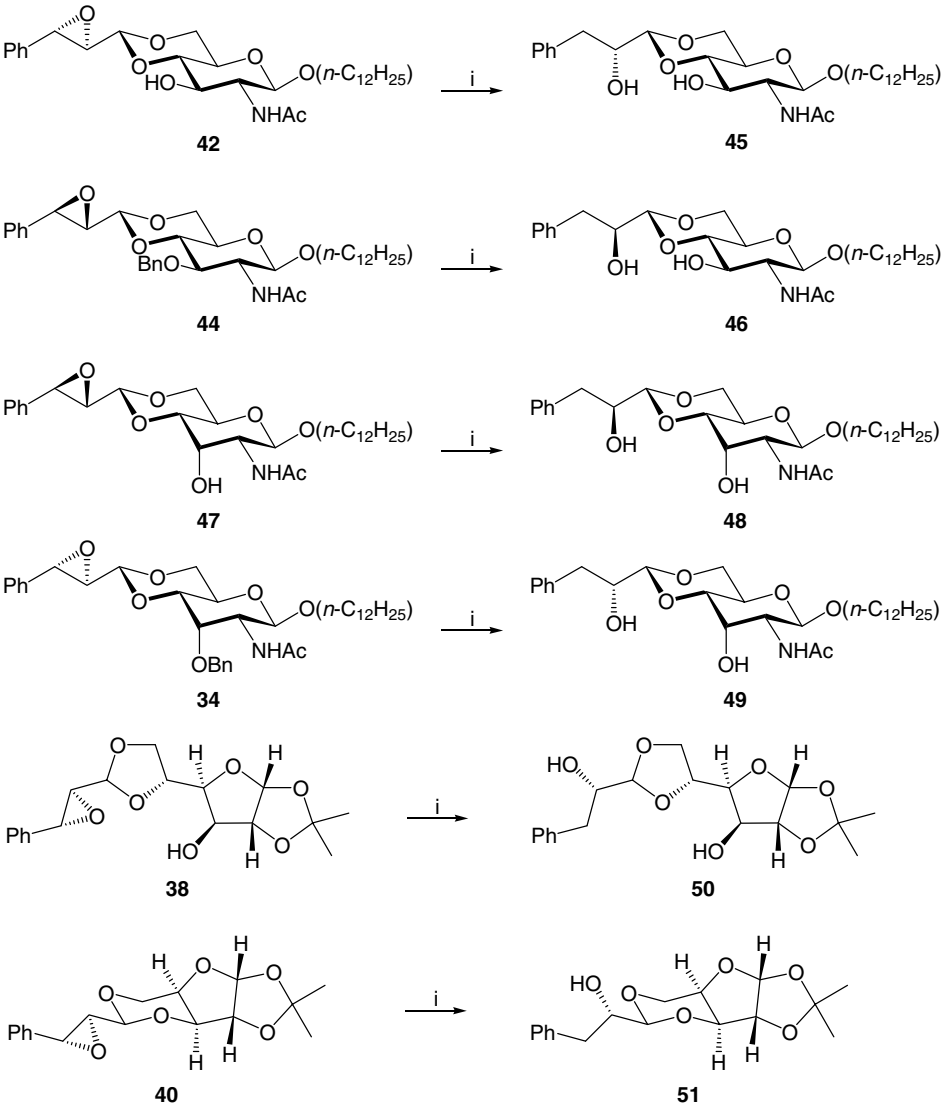
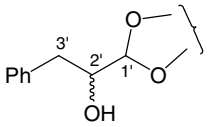


Figure 1.



Scheme 7. Reagents and conditions: (i) H_2/Pd(C).

Table 4. NMR data (δ, ppm) for compounds **45**, **46**, **48**–**51**



Entry	Compound	H-1′	H_A-3′	H_B-3′	C-1′	C-2′	C-3′
1	**45**[a]	4.46(M)/4.41(m)	2.94(m)/2.89(M)	2.79(M)/2.75(m)	100.8	72.8(m)/72.5(M)	38.0(m)/37.5(M)
2	**46**[a]	4.45(m)/4.43(M)	2.96(M)/2.91(m)	2.82(m)/2.73(M)	102.1(M)/101.9(m)	72.8(M)/72.7(m)	38.0(m)/37.8(M)
3	**48**	4.46(m)/4.45(M)	2.88(M)/2.86(m)	2.81(M)/2.79(m)	101.5(m)/101.4(M)	72.9(M)/72.8(m)	38.3(m)/38.2(M)
4	**49**	4.46(M)/4.45(m)	2.88(m)/2.86(M)	2.80(m)/2.78(M)	101.5(M)/101.4(m)	72.9(m)/72.8(M)	38.3(M)/38.2(m)
5	**50**	4.80(M)/4.75(m)	2.96(M)/2.94(m)	2.75(M)/2.70(m)	93.4(m)/93.3(M)	72.8(M)/72.7(m)	37.7(m)/37.3(M)
6	**51**	4.31	2.94(M)/2.90(m)	2.73	99.8(M)/99.7(m)	72.8(M)/72.7(m)	37.4(m)/37.3(M)

(M) For the major isomer.
(m) For the minor isomer.
[a] Ref. 1.

by the epoxidation of a propylidene acetal, in the conditions described, depends on the sugar configuration and on whether the hydroxyl group on carbon 3 of the sugar is free or blocked.

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 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. NMR spectra were recorded at 25 °C on a Bruker AMX300 spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C, and on a Bruker AV500 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, HSQC and NOESY experiments were performed to assign the signals in the NMR spectra.

4.2. Alkyl 2-acetamido-4,6-*O*-(*R*)-alkenylidene-2-deoxy-3-*O*-methanosulfonyl-β-D-hexopyranosides 5–7

To a cooled solution (0 °C) of the alkyl 2-acetamido-4,6-*O*-(*R*)-alkenylidene-2-deoxy-β-D-hexopyranosides **1**–**3** (3.0 mmol) in dry pyridine (35 mL) was slowly added methanosulfonyl chloride (0.6 mL, 7.5 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 recrystallisation from 96% ethanol.

4.2.1. *c*-Hexyl 2-acetamido-2-deoxy-3-*O*-methanosulfonyl-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-glucopyranoside 5. Yield 1.20 g (78%); mp 196–198 °C; $[\alpha]_D = -72.7$ (*c* 1.0, DMF); MS (EI): *m*/*z* 495 (24%) $[M]^{+\cdot}$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 6.75 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.10 (dd, 1H, J_{trans} 16.1 Hz, *J* 5.1 Hz, PhCH=C*H*CH), 5.89 (d, 1H, $J_{2,NH}$ 7.4 Hz, NH), 5.3 (m, 2H, H-1, H-3), 5.14 (dd, 1H, ^4J 0.6 Hz, *J* 5.1 Hz, PhCH=CHC*H*), 4.20 (dd, 1H, $J_{5,6e}$ 4.3 Hz, $J_{6e,6a}$ 10.3 Hz, H-6_e), 3.7–3.4 (m, 4H, H-4, H-5, H-6_a, OCHR), 3.26 (ddd, 1H, $J_{1,2}$ 8.1 Hz, $J_{2,3}$ 9.1 Hz, $J_{2,NH}$ 7.4 Hz, H-2), 3.01 (s, 3H, CH_3SO_2), 1.99 (s, 3H, CH_3CON), 1.7–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.3 (C=O), 135.4–126.9 (Ph), 134.7 (Ph*C*H=CHCH), 123.6 (PhCH=*C*HCH), 101.1 (PhCH=CH*C*H), 98.4 (C-1), 78.9, 78.5, 78.1 (C-3, C-4, OCHR), 68.4 (C-6), 65.3 (C-5), 57.8 (C-2), 38.5 (CH_3SO_2), 33.3–23.7 [$(CH_2)_5$], 23.5 (*C*H_3CON). HRMS (CI): $[M+H]^+$ found: 496.200110. $C_{24}H_{34}NO_8S$ requires 496.200514. Anal. Calcd for $C_{24}H_{33}NO_8S$: C, 58.16; H, 6.71; N, 2.83. Found: C, 57.96; H, 6.82; N, 2.76.

4.2.2. *c*-Hexyl 2-acetamido-2-deoxy-3-*O*-methanosulfonyl-4,6-*O*-[(*R*,*E*)-2-methyl-3-phenyl-2-propenylidene]-β-D-glucopyranoside 6. Yield 1.10 g (73%); mp 169–170 °C; $[\alpha]_D = -14.8$ (*c* 0.9, $CHCl_3$); MS (CI): *m*/*z* 510 (25%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 6.63 [s, 1H, PhC*H*=C(CH_3)CH], 5.89 (d, 1H, $J_{2,NH}$ 7.4 Hz, NH), 5.3 (m, 2H, H-1, H-3), 4.97 [s, 1H, PhCH=C(CH_3)C*H*], 4.30 (dd, 1H, $J_{5,6e}$ 5.0 Hz, $J_{6e,6a}$ 10.5 Hz, H-6_e), 3.68 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.5 Hz, H-6_a), 3.6 (m, 2H, H-2, OCHR), 3.51 (dt, 1H, $J_{4,5} = J_{5,6a}$ 9.8 Hz, $J_{5,6e}$ 5.0 Hz, H-5), 3.24 (dd, 1H, $J_{3,4}$ 9.4 Hz, $J_{4,5}$ 9.8 Hz, H-4), 3.01 (s, 3H, CH_3SO_2), 1.99 (s, 3H, CH_3CON), 1.87 [d, 3H, *J* 1.5 Hz, PhCH=C(C*H*$_3$)CH], 1.7–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.4 (C=O), 136.4–128.2 (Ph), 133.3 [PhCH=*C*(CH_3)CH], 127.2 [Ph*C*H=C(CH_3)CH], 105.0 [PhCH=C(CH_3)*C*H], 98.4 (C-1), 79.0, 78.6, 78.1 (C-3, C-4, OCHR), 68.4 (C-6), 65.4 (C-5), 58.0 (C-2), 38.4 (CH_3SO_2) 33.4–23.7 [$(CH_2)_5$], 23.5 (*C*H_3CON), 13.1 [PhCH=C(*C*H$_3$)CH]. HRMS (CI): $[M+H]^+$, found: 510.212721. $C_{25}H_{36}NO_8S$ requires 510.216164. Anal. Calcd for $C_{25}H_{35}NO_8S$: C, 58.92; H, 6.92; N, 2.75. Found: C, 58.63; H, 6.83; N, 2.68.

4.2.3. 1-Dodecyl 2-acetamido-2-deoxy-3-*O*-methanosulfonyl-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-allopyranoside 7. Yield 1.41 g (80%); mp 168–169 °C; $[\alpha]_D = -72.0$ (*c* 1.0, DMF); MS (EI): *m*/*z* 581 (35%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.3 (m, 5H, Ph), 6.75 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.07 (dd, 1H, J_{trans} 16.1 Hz, *J* 4.6 Hz, PhCH=C*H*CH), 5.70 (d, 1H, $J_{2,NH}$ 8.5 Hz, NH), 5.22 (t, 1H, $J_{2,3} = J_{3,4}$ 2.6 Hz, H-3), 5.19 (dd, 1H, *J* 4.6 Hz, ^4J 1.0 Hz, PhCH=CHC*H*), 4.61 (d, 1H, $J_{1,2}$ 8.6 Hz, H-1), 4.30 (dd, 1H, $J_{5,6e}$ 5.0 Hz, $J_{6e,6a}$ 10.4 Hz, H-6_e), 4.23 (dt, 1H, $J_{1,2} = J_{2,NH}$ 8.6 Hz, $J_{2,3}$ 2.6 Hz, H-2), 3.9–3.8 (m, 2H, H-4, OC$H_A$$H_B$R), 3.7–3.5 (m, 2H, H-5, H-6_a), 3.43 (m, 1H, OC$H_A$$H_B$R), 3.01 (s, 3H, CH_3SO_2) 2.01 (s, 3H, CH_3CON), 1.6–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3, *J* 7.0 Hz, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 169.2 (C=O), 135.4–126.7 (Ph), 133.4 (Ph*C*H=CHCH), 124.6 (PhCH=*C*HCH), 100.2 (PhCH=CH*C*H), 98.8 (C-1), 77.9 (C-4), 74.8 (C-3), 69.2 (C-6), 67.7 (OCH_2R), 63.3 (C-5), 51.7 (C-2), 38.8 (CH_3SO_2), 31.3–22.1 [$(CH_2)_{10}$], 22.4 (CH_3CON), 13.9 (CH_3). HRMS (EI): $[M]^{+\cdot}$, found: 581.300561. $C_{30}H_{47}NO_8S$ requires 581.302240. Anal. Calcd for $C_{30}H_{47}NO_8S$: C, 61.94; H, 8.14; N, 2.41; S, 5.51. Found: C, 62.04; H, 8.25; N, 2.49; S, 5.12.

4.3. Methyl 2,3-di-*O*-methanosulfonyl-4,6-*O*-[(*R*,*E*)-2-methyl-3-phenyl-2-propenylidene]-α-D-glucopyranoside 8

To a cooled solution (0 °C) of methyl 4,6-*O*-[(*R*,*E*)-2-methyl-3-phenyl-2-propenylidene]-α-D-glucopyranoside **4** (2.6 g, 8.0 mmol) in dry pyridine (15 mL) was slowly added methanosulfonyl chloride (2.6 mL, 32.5 mmol). The reaction mixture was kept overnight at 5 °C, then poured into water (150 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The organic solvent was dried over $MgSO_4$, filtered, and evaporated to dryness. The pure compound was obtained by flash chromatography using hexane–ethyl acetate (2.5:1) as eluent. Yield: 2.3 g (60%); mp 144–146 °C; $[\alpha]_D = +64.4$ (*c* 0.8, $CHCl_3$); MS (CI): *m*/*z* 479 (35%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.3 (m, 5H, Ph), 6.64 [s, 1H, PhC*H*=C(CH_3)CH], 5.04 (t, 1H, $J_{2,3} = J_{3,4}$ 9.6 Hz, H-3), 5.00 [s, 1H, PhCH=C(CH_3)C*H*], 4.99 (d, 1H, $J_{1,2}$ 4.5 Hz, H-1), 4.59 (d,d, 1H, $J_{1,2}$ 4.5 Hz, $J_{2,3}$ 9.6 Hz, H-2) 4.27 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.4 Hz, H-6_e), 3.85 (dt, 1H, $J_{4,5} = J_{5,6a}$ 9.8 Hz, $J_{5,6e}$ 4.9 Hz, H-5), 3.66 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.4 Hz, H-6_a), 3.62 (t 1H,

$J_{3,4} = J_{4,5}$ 9.6 Hz, H-4), 3.47 (s, 3H, OCH_3), 3.16, 3.06 (2s, 6H, $2CH_3SO_2$), 1.90 [d, 3H, ^4J 1.3 Hz, PhCH=C(CH_3)CH]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.2–128.3 (Ph), 133.0 [PhCH=*C*(CH$_3$)CH], 127.4 [Ph*C*H=C(CH$_3$)CH], 105.3 [PhCH=C(CH$_3$)*C*H], 99.0 (C-1), 78.9 (C-4), 77.3 (C-3), 75.9 (C-2), 68.4 (C-6), 62.3 (C-5), 56.2 (OCH_3), 39.8, 38.8 ($2CH_3SO_2$), 13.1 [PhCH=C(*C*H$_3$)CH]. HRMS (CI): $[M+H]^+$, found: 479.103323. $C_{19}H_{27}O_{10}S$ requires 479.104566. Anal. Calcd for $C_{19}H_{27}O_{10}S_2$: C, 47.69; H, 5.48; S, 13.40. Found: C, 47.81; H, 5.78; S, 13.00.

4.4. Alkyl-2-acetamido-3-*O*-alkyl-2-deoxy-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-hexopyranoside 9 and 16

To a cooled solution (5 °C) of *c*-hexyl 2-acetamido-2-deoxy-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-glucopyranoside **2** and 1-dodecyl-2-acetamido-2-deoxy-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-allopyranoside **3** (2.0 mmol) in freshly distilled THF (20 mL) were added, successively, freshly powdered potassium hydroxide (0.70 g, 11.9 mmol), 18-crown-6 (40 mg, 0.13 mmol), and the corresponding alkyl halide (2.8 mmol). The reaction mixture was stirred at this temperature for 3 h, and then left overnight at room temperature, after which the mixture was diluted with dichloromethane (20 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.

4.4.1. *c*-Hexyl 2-acetamido-2-deoxy-3-*O*-methyl-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-glucopyranoside 9. The solid obtained was purified by flash chromatography on silica gel, using dichloromethane–methanol (80:1) as eluent. Yield 0.62 g (71%); mp 196–197 °C; $[\alpha]_D = -10.3$ (*c* 0.7, $CHCl_3$); MS (CI): *m*/*z* 432 (23%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.3 (m, 5H, Ph), 6.77 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.16 (dd, 1H, J_{trans} 16.1 Hz, *J* 4.5 Hz, PhCH=C*H*CH), 5.80 (d, 1H, $J_{2,NH}$ 7.4 Hz, NH), 5.17 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 5.14 (d, 1H, *J* 4.5 Hz, PhCH=CHC*H*), 4.3–4.2 (m, 2H, H-3, H-6$_e$), 3.65 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.0 Hz, H-6$_a$), 3.59 (m, 4H, OCHR, OCH_3), 3.5–3.4 (m, 2H, H-4, H-5), 2.95 (dd, 1H, $J_{1,2}$ 8.3 Hz, $J_{2,3}$ 9.4 Hz, H-2), 1.98 (s, 3H, CH_3CON), 1.8–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6 (C=O), 136.0–126.9 (Ph), 133.8 (PhCH=*C*HCH), 124.6 (Ph*C*H=CHCH), 100.7 (PhCH=CH*C*H), 98.2 (C-1), 82.4 (C-4), 77.9 (C-3), 77.8 (OCHR), 68.6 (C-6), 65.8 (C-5), 60.6 (OCH_3), 59.1 (C-2), 33.5–23.9 [$(CH_2)_5$], 23.7 (*C*H$_3$CON). HRMS (CI): $[M+H]^+$, found: 432.237391. $C_{24}H_{34}NO_6$ requires 432.238613. Anal. Calcd for $C_{24}H_{33}NO_6$: C, 66.80; H, 7.71; N, 3.25. Found: C, 66.69; H, 7.85; N, 3.24.

4.4.2. 1-Dodecyl 2-acetamido-3-*O*-benzyl-2-deoxy-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-allopyranoside 16. The solid obtained was purified by flash chromatography on silica gel, using dichloromethane–methanol (100:1) as eluent. Yield 1.0 g (83%); mp 190–191 °C; $[\alpha]_D = -76.3$ (*c* 1.0, CH_2Cl_2); MS (CI): *m*/*z* 594 (17%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.3 (m, 5H, Ph), 6.83 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.22 (dd, 1H, J_{trans} 16.1 Hz, *J* 4.8 Hz, PhCH=C*H*CH), 5.64 (d, 1H, $J_{2,NH}$ 8.8 Hz, NH), 5.18 (dd, 1H, *J* 4.8 Hz, ^4J 0.9 Hz, PhCH=CHC*H*), 5.03 (d, 1H, J_{gem} 11.7 Hz, OCH_AH_BPh), 4.58 (dd, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.55 (d, 1H, J_{gem} 11.7 Hz, OCH_AH_BPh), 4.33 (dd, 1H, $J_{5,6e}$ 5.2 Hz, $J_{6e,6a}$ 10.5 Hz, H-6$_e$), 4.11 (m, 2H, H-2, H-3), 4.00 (dt, 1H, $J_{5,6e}$ 5.2 Hz, $J_{4,5} = J_{5,6a}$ 10.1 Hz, H-5), 3.88 (m, 1H, OCH_AH_BR), 3.71 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.4 Hz, H-6$_a$), 3.65 (dd, 1H, $J_{3,4}$ 1.9 Hz, $J_{4,5}$ 9.5 Hz, H-4), 3.41 (m, 1H, OCH_AH_BR), 1.86 (s, 3H, CH_3CON), 1.6–1.3 [m, 20H, $(CH_2)_{10}$], 0.90 (t, 3H, *J* 7.0 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.2 (C=O), 135.9–126.9 (Ph), 134.1 (Ph*C*H=CHCH), 124.6 (PhCH=*C*HCH), 101.3 (PhCH=CH*C*H), 100.4 (C-1), 80.1 (C-4), 76.0 (C-3), 74.8 (OCH_2Ph), 69.8 (OCH_2R), 69.0 (C-6), 63.8 (C-5), 52.0 (C-2), 31.9–22.7 [$(CH_2)_{10}$], 23.2 (*C*H$_3$CON), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found: 594.379108. $C_{36}H_{52}NO_6$ requires 594.379464. Anal. Calcd for $C_{36}H_{51}NO_6$: C, 72.82; H, 8.66; N, 2.36. Found: C, 72.72; H, 8.88; N, 2.46.

4.5. 1-Dodecyl 2-acetamido-3-azido-2,3-dideoxy-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-glucopyranoside 10

To a solution of 1-dodecyl 2-acetamido-2-deoxy-3-*O*-methanosulfonyl-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-allopyranoside **7** (1.2 g, 2.0 mmol) in dimethylformamide (4 mL), sodium azide (0.2 g, 3.0 mmol) was added. The reaction mixture was heated at 80 °C for 12 h. After cooling, the mixture was poured into water and the precipitate collected by filtration. The pure compound was obtained by flash chromatography on silica gel, using dichloromethane–methanol (250:1) as eluent. Yield 0.34 g (64%); mp 202–204 °C; MS (CI): *m*/*z* 529 (24%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.3 (m, 5H, Ph), 6.79 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.16 (dd, 1H, J_{trans} 16.1 Hz, *J* 4.3 Hz, PhCH=C*H*CH), 5.70 (d, 1H, $J_{2,NH}$ 7.5 Hz, NH), 5.17 (dd, 1H, *J* 4.3 Hz, ^4J 0.9 Hz, PhCH=CHC*H*), 5.00 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 4.44 (d, 1H, $J_{2,3} = J_{3,4}$ 10.0 Hz, H-3), 4.26 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.5 Hz, H-6$_e$), 3.81 (m, 1H, OCH_AH_BR), 3.65 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.3 Hz, H-6$_a$), 3.5–3.4 (m, 2H, H-5, OCH_AH_BR), 3.67 (t, 1H, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-4), 3.04 (ddd, 1H, $J_{1,2}$ 8.2 Hz, $J_{2,3}$ 10.0 Hz, $J_{2,NH}$ 7.5 Hz, H-2), 2.00 (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 (125 MHz, $CDCl_3$): δ 170.7 (C=O), 135.8–126.9 (Ph), 134.2 (Ph*C*H=CHCH), 123.9 (PhCH=*C*HCH), 100.8 (PhCH=CH*C*H), 99.9 (C-1), 80.3 (C-4), 70.3 (OCH_2R), 68.5 (C-6), 66.9 (C-3), 60.9 (C-5), 57.8 (C-2), 31.9–22.7 [$(CH_2)_{10}$], 23.5 (*C*H$_3$CON), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found: 529.337701. $C_{29}H_{45}N_4O_5$ requires 529.338996. Anal. Calcd for $C_{29}H_{44}N_4O_5$: C, 65.88; H, 8.39; N, 10.60. Found: C, 65.59; H, 8.26; N, 10.71.

4.6. 1-Dodecyl 2-acetamido-3-amino-2,3-dideoxy-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-glucopyranoside 11

To a solution of 1-dodecyl 2-acetamido-3-azido-2,3-dideoxy-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-glucopyranoside **10** (0.8 g, 1.5 mmol) in dimethylformamide (6 mL), sodium borohydride (3.0 mmol) was added. The reaction mixture was heated at 70 °C for 4 days. After cooling, the mixture was poured into water and the precipitate collected by filtration. The pure compound was obtained

by flash chromatography on silica gel, using dichloromethane–methanol (20:1) as eluent. Yield 0.48 g (96%); mp 230–232 °C; MS (CI): *m*/*z* 503 (53%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.4–7.3 (m, 5H, Ph), 6.77 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.16 (dd, 1H, J_{trans} 16.1 Hz, *J* 4.7 Hz, PhCH=C*H*CH), 5.53 (d, 1H, $J_{2,NH}$ 8.0 Hz, NH), 5.14 (d, 1H, *J* 4.7 Hz, PhCH=CHC*H*), 4.69 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.03 (dd, 1H, $J_{5,6e}$ 5.0 Hz, $J_{6e,6a}$ 10.4 Hz, H-6_e), 3.81 (m, 1H, OCH_AH_BR), 3.65 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.3 Hz, H-6_a), 3.5–3.4 (m, 3H, H-2, H-5, OCH_AH_BR), 3.34 (t, 1H, $J_{2,3} = J_{3,4}$ 9.2 Hz, H-3), 3.21 (t, 1H, $J_{3,4} = J_{4,5}$ 9.2 Hz, H-4), 2.01 (s, 3H, CH_3CON), 1.3–1.1 [m, 20H, $(CH_2)_{10}$], 0.85 (t, 3H, *J* 6.8 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6 (C=O), 134.2–126.9 (Ph), 134.0 (Ph*C*H=CHCH), 124.3 (PhCH=*C*HCH), 101.2 (C-1), 101.1 (PhCH=CH*C*H), 82.3 (C-4), 69.8 (OCH_2R), 68.5 (C-6), 67.5 (C-3), 58.1 (C-5), 53.8 (C-2), 31.8-22.6 [$(CH_2)_{10}$], 23.6 (CH_3CON), 14.0 (CH_3). HRMS (CI): $[M+H]^+$, found: 503.349902. $C_{29}H_{47}N_2O_5$ requires 503.348498. Anal. Calcd for $C_{29}H_{46}N_2O_5$: C, 69.29; H, 9.22; N, 5.57. Found: C, 68.98; H, 9.45; N, 5.46.

4.7. 1-Dodecyl 2,3-diacetamido-2,3-dideoxy-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-glucopyranoside 12

To a solution of 1-dodecyl 2-acetamido-3-amino-2,3-dideoxy-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-glucopyranoside **11** (0.8 g, 1.5 mmol) in distilled dichloromethane (50 mL), dry pyridine (5 mL) and acetic anhydride (5 mL) were added. The reaction mixture was stirred overnight at room temperature and then washed successively with water, diluted 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 dichloromethane–methanol (50:1) as eluent. Yield 0.20 g (72%); mp 169–170 °C; MS (CI): *m*/*z* 545 (16%) $[M+H]^+$. ^1H NMR (500 MHz, DMSO-D_6): δ 7.7–7.6 (m, 2H, 2NH), 7.4–7.2 (m, 5H, Ph), 6.62 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.11 (dd, 1H, J_{trans} 16.1 Hz, *J* 5.3 Hz, PhCH=C*H*CH), 5.03 (d, 1H, *J* 5.3 Hz, PhCH=CHC*H*), 4.39 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.03 (dd, 1H, $J_{5,6e}$ 5.1 Hz, $J_{6e,6a}$ 10.1 Hz, H-6_e), 3.88 (m, 1H, OCH_AH_BR), 3.6–3.3 (m, 6H, H-2, H-3, H-4, H-5, H-6_a, OCH_AH_BR), 1.64, 1.63 (2s, 6H, $2CH_3CON$), 1.3–1.1 [m, 20H, $(CH_2)_{10}$], 0.76 (t, 3H, *J* 6.8 Hz, CH_3). ^{13}C NMR (125 MHz, DMSO-d_6): δ 170.7 (2C=O), 134.3–127.6 (Ph), 134.0 (Ph*C*H=CHCH), 125.9 (PhCH=*C*HCH), 103.3 (C-1), 101.4 (PhCH=CH*C*H), 78.8 (C-4), 69.5 (OCH_2R), 68.3 (C-6), 68.2 (C-3), 55.63 (C-5), 54.74 (C-2), 32.1–22.9 [$(CH_2)_{10}$], 23.6, 23.5 ($2CH_3CON$), 14.7 (CH_3). HRMS (CI): $[M+H]^+$, found: 545.358114. $C_{31}H_{49}N_2O_6$ requires 545.359063. Anal. Calcd for $C_{31}H_{48}N_2O_6$: C, 68.35; H, 8.88; N, 5.14. Found: C, 68.08; H, 8.80; N, 5.20.

4.8. *c*-Hexyl 2-acetamido-4,6-*O*-(*R*)-alkenylidene-2-deoxy-β-D-allopyranosides 13 and 14

A solution of *c*-hexyl 2-acetamido-2-deoxy-3-*O*-methanosulfonyl-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-glucopyranoside **5** or *c*-hexyl 2-acetamido-2-deoxy-3-*O*-methanosulfonyl-4,6-*O*-[(*R*,*E*)-2-methyl-3-phenyl-2-propenylidene]-β-D-glucopyranoside **6** (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.

4.8.1. *c*-Hexyl 2-acetamido-2-deoxy-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-allopyranoside 13. Column chromatography using dichloromethane–methanol (100:1) yielded 0.74 g (88%); mp 197–198 °C; $[\alpha]_D = -86.9$ (*c* 0.7, CH_2Cl_2); MS (CI): *m*/*z* 418 (26%) $[M+H]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ 7.4–7.3 (m, 5H, Ph), 6.77 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.15 (dd, 1H, J_{trans} 16.1 Hz, *J* 4.8 Hz, PhCH=C*H*CH), 5.88 (d, 1H, $J_{2,NH}$ 9.1 Hz, NH), 5.20 (dd, 1H, *J* 4.8 Hz, ^4J 1.0 Hz, PhCH=CHC*H*), 4.72 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.3–4.2 (m, 2H, H-3, H-6_e), 4.08 (dt, 1H, $J_{1,2} = J_{2,NH}$ 8.8 Hz, $J_{2,3}$ 3.0 Hz, H-2), 3.87 (dt, 1H, $J_{5,6e}$ 4.9 Hz, $J_{5,6a} = J_{4,5}$ 10.0 Hz, H-5), 3.68 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.4 Hz, H-6_a), 3.59 (m, 1H, OCHR), 3.54 (dd, 1H, $J_{3,4} = 2.5$ Hz, $J_{4,5}$ 9.5 Hz, H-4), 2.00 (s, 3H, CH_3CON), 1.8–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5 (C=O), 135.7–126.9 (Ph), 134.4 (Ph*C*H=CHCH), 124.1 (PhCH=*C*HCH), 101.2 (PhCH=CH*C*H), 98.7 (C-1), 78.4 (C-4), 77.2 (OCHR), 68.9 (C-6), 68.8 (C-3), 63.3 (C-5), 54.5 (C-2), 33.4–23.6 [$(CH_2)_5$], 23.5 (CH_3CON). HRMS (CI): $[M+H]^+$, found: 418.222785. $C_{23}H_{32}NO_6$ requires 418.222963. Anal. Calcd for $C_{23}H_{31}NO_6$: C, 66.17; H, 7.48; N, 3.35. Found: C, 65.94; H, 7.44; N, 3.34.

4.8.2. *c*-Hexyl 2-acetamido-2-deoxy-4,6-*O*-[(*R*,*E*)-2-methyl-3-phenyl-2-propenylidene]-β-D-allopyranoside 14. Column chromatography using dichloromethane–methanol (120:1) yielded 0.72 g (83%); mp 147–148 °C; $[\alpha]_D = -56.6$ (*c* 0.9, $CHCl_3$); MS (CI): *m*/*z* 432 (10%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 6.67 [s, 1H, PhC*H*=C(CH_3)CH], 5.90 (d, 1H, $J_{2,NH}$ 9.2 Hz, NH), 5.03 [s, 1H, PhCH=C(CH_3)C*H*], 4.08 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.27 (dd, 1H, $J_{5,6e}$ 5.1 Hz, $J_{6e,6a}$ 10.3 Hz, H-6_e), 4.25 (m, 1H, H-3), 4.09 (dt, 1H, $J_{1,2}$ 8.5 Hz, $J_{2,3}$ 2.5 Hz, $J_{2,NH}$ 9.0 Hz, H-2), 3.87 (dt, 1H, $J_{4,5}$ 9.5 Hz, $J_{5,6e}$ 5.0 Hz, $J_{5,6a}$ 10.0 Hz, H-5), 3.68 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.3 Hz, H-6_a), 3.59 (m, 1H, OCHR), 3.54 (dd, 1H, $J_{3,4} = 2.5$ Hz, $J_{4,5}$ 10.0 Hz, H-4), 2.00 (s, 3H, CH_3CON), 1.90 [d, 3H, ^4J 1.3 Hz, PhCH=C(CH_3)CH], 1.7–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4 (C=O), 136.5–128.1 (Ph), 133.6 [PhCH=*C*(CH_3)CH], 127.0 [Ph*C*H=C(CH_3)CH], 104.9 [PhCH=C(CH_3)*C*H], 98.7 (C-1), 78.4 (C-4), 77.2 (OCHR), 70.0 (C-3), 68.9 (C-6), 63.3 (C-5), 52.3 (C-2), 33.3–23.6 [$(CH_2)_5$], 23.4 (CH_3CON), 13.2 [PhCH=C(*C*H_3)CH]. HRMS (CI): $[M+H]^+$, found: 432.235370. $C_{24}H_{34}NO_6$ requires 432.238613. Anal. Calcd for $C_{24}H_{33}NO_6$: C, 66.80; H, 7.71; N, 3.25. Found: C, 66.62; H, 7.60; N, 3.24.

4.9. 1-Dodecyl 2-acetamido-3-*O*-acetyl-2-deoxy-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-allopyranoside 15

To a solution of 1-dodecyl 2-acetamido-2-deoxy-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-β-D-allopyranoside **3** (1 g, 2.0 mmol) in distilled dichloromethane (100 mL),

dry pyridine (6 mL) and acetic anhydride (6 mL) were added. The reaction mixture was stirred overnight at room temperature and then washed successively with water, diluted 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 dichloromethane–methanol (100:1) as eluent. Yield 0.93 g (85%); mp 154–155 °C; $[\alpha]_D = -67.4$ (*c* 1.0, $CHCl_3$); MS (CI): *m/z* 546 (20%) $[M+H]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ 7.4–7.3 (m, 5H, Ph), 6.71 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.08 (dd, 1H, J_{trans} 16.1 Hz, *J* 4.3 Hz, PhCH=C*H*CH), 5.67 (t, 1H, $J_{2,3} = J_{3,4}$ 2.9 Hz, H-3), 5.39 (d, 1H, $J_{2,NH}$ 8.6 Hz, NH), 5.14 (d, 1H, *J* 4.3 Hz, ^4J 1.1 Hz, PhCH=CHC*H*), 4.60 (d, 1H, $J_{1,2}$ 8.6 Hz, H-1), 4.26 (dd, 1H, $J_{5,6e}$ 5.0 Hz, $J_{6e,6a}$ 10.0 Hz, H-6_e), 4.22 (dd, 1H, $J_{1,2}$ 8.6 Hz, $J_{2,3}$ 3.0 Hz, H-2), 3.9–3.8 (m, 2H, H-5, OCH_AH_BR), 3.7–3.6 (m, 2H, H-4, H-6_a), 3.4 (m, 1H, OCH_AH_BR), 2.15 (s, 3H, CH_3COO), 1.96 (s, 3H, CH_3CON), 1.5–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3H, *J* 6.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 169.4 (2C=O), 135.8–126.9 (Ph), 133.9 (Ph*C*H=CHCH), 124.1 (PhCH=*C*HCH), 100.8, 100.0 (C-1, PhCH=CH*C*H), 77.2 (C-4), 69.8 (C-3), 69.7 (OCH_2R), 68.9 (C-6), 64.4 (C-5), 51.3 (C-2), 31.9–22.7 [$(CH_2)_{10}$], 23.2 (CH_3CON), 21.0 (CH_3COO), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found: 546.340455. $C_{31}H_{48}NO_7$ requires 546.343078. Anal. Calcd for $C_{31}H_{47}NO_7$: C, 68.23; H, 8.68; N, 2.57. Found: C, 67.97; H, 8.62; N, 2.52.

4.10. Methyl 2-*O*-ethyl-4,6-*O*-[(*R*,*E*)-2-methyl-3-phenyl-2-propenylidene]-α-D-altropyranoside 17

To a solution of sodium ethoxide (9.0 mmol) in ethanol (15 mL) was added methyl 2,3-di-*O*-methanosulfonyl-4,6-*O*-[(*R*,*E*)-2-methyl-3-phenyl-2-propenylidene]-α-D-glucopyranoside **8** (1.4 g, 3.0 mmol). The mixture was heated at reflux with stirring for 8 h. The reaction mixture was cooled to room temperature, poured into water (50 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The organic extracts were dried over $MgSO_4$, filtered, and evaporated to dryness. Flash chromatography, using hexane–ethyl acetate as eluent, gave the pure compound as a syrup. Yield 0.7 g (77%); $[\alpha]_D = +79.5$ (*c* 0.9, CH_2Cl_2); MS (CI): *m/z* 351 (55%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 6.67 [s, 1H, PhC*H*=C(CH_3)CH], 5.09 [s, 1H, PhCH=C(CH_3)C*H*], 4.68 (br s, 1H, H-1), 4.25 (dd, 1H, $J_{5,6e}$ 5.1 Hz, $J_{6e,6a}$ 10.2 Hz, H-6_e), 4.14 (m, 1H, H-2), 4.08 (dt, 1H, $J_{4,5} = J_{5,6a}$ 10.1 Hz, $J_{5,6e}$ 5.1 Hz, H-5), 3.82 (dd, 1H, $J_{3,4}$ 3.0 Hz, $J_{4,5}$ 9.9 Hz, H-4), 3.74 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.2 Hz, H-6_a), 3.61 (m, 2H, OCH_2CH_3), 3.58 (dd, 1H, $J_{2,3}$ 1.0 Hz, $J_{3,4}$ 3.0 Hz, H-3), 3.42 (s, 3H, OCH_3), 1.92 [d, 3H, ^4J 1.5 Hz, PhCH=C(CH_3)CH], 1.21 (t, 3H, *J* 7.0 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.8–128.1 (Ph), 134.1 [PhCH=*C*(CH_3)CH], 126.9 [Ph*C*H=C(CH_3)CH], 105.5 [PhCH=C(CH_3)*C*H], 100.4 (C-1), 77.5 (C-3), 76.4 (C-4), 68.9 (C-6), 67.3 (C-2), 66.4 (OCH_2CH_3), 58.3 (C-5), 55.6 (OCH_3), 15.5 (OCH_2CH_3), 13.2 [PhCH=C(*C*H_3)CH]. HRMS (CI): $[M]^{+\cdot}$, found: 350.173107. $C_{19}H_{26}O_6$ requires 350.172939.

4.11. General procedure for the synthesis of α,β-unsaturated acetals

To a solution of the corresponding sugars **18**–**20** (5.0 mmol) in acetonitrile (30 mL), aldehyde dimethylacetal **21**[19] or **22**[1] (10.0 mmol) and camphorsulfonic acid (10 mg) were added. The mixture was stirred at room temperature until a check by TLC showed that all the starting material had reacted. Triethylamine was then added until pH 7. The reaction mixture was evaporated, and a syrup was obtained. Column chromatography gave the pure compounds **23**–**28** in good yields.

4.11.1. Methyl 4,6-*O*-[(*S*,*E*)-3-phenyl-2-propenylidene]-β-D-galactopyranoside 23. Column chromatography on silica gel, using dichloromethane–methanol (40:1) as eluent yielded 1.30 g (85%); mp 159–160 °C; $[\alpha]_D = -35.5$ (*c* 0.9, CH_2Cl_2); MS (CI): *m/z* 309 (46%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 6.75 (d, 1H, J_{trans} 16.2 Hz, PhC*H*=CHCH), 6.23 (dd, 1H, J_{trans} 16.2 Hz, *J* 5.2 Hz, PhCH=C*H*CH), 5.17 (dd, 1H, *J* 5.2 Hz, ^4J 0.8 Hz, PhCH=CHC*H*), 4.25 (dd, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.5 Hz, H-6_e), 4.17 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.09 (dd, 1H, $J_{3,4}$ 3.9 Hz, $J_{4,5}$ 0.9 Hz, H-4), 3.96 (dd, 1H, $J_{5,6a}$ 1.9 Hz, $J_{6e,6a}$ 12.6 Hz, H-6_a), 3.74 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 9.7 Hz, H-2), 3.66 (m, 1H, H-3), 3.54 (s, 3H, OCH_3), 3.39 (m, 1H, H-5). ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.8–126.9 (Ph), 134.2 (Ph*C*H=CHCH), 124.8 (PhCH=*C*HCH), 103.9 (C-1), 101.0 (PhCH=CH*C*H), 75.0 (C-4), 72.6 (C-3), 71.6 (C-2), 68.8 (C-6), 66.7 (C-5), 57.2 (OCH_3). HRMS (EI): $[M]^{+\cdot}$, found: 308.125448. $C_{16}H_{20}O_6$ 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.

4.11.2. Methyl 4,6-*O*-[(*S*,*E*)-2-methyl-3-phenyl-2-propenylidene]-β-D-galactopyranoside 24. Two stereoisomers were obtained in an 88:12 ratio (76% de). Column chromatography on silica gel, using dichloromethane–methanol (70:1) as eluent, separated the major diastereoisomer. Yield 1.2 g (73%); mp 148–150 °C; $[\alpha]_D = -55.1$ (*c* 0.8, CH_2Cl_2); MS (CI): *m/z* 323 (20%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.2–7.1 (m, 5H, Ph), 6.60 [s, 1H, PhC*H*=C(CH_3)CH], 4.96 [s, 1H, PhCH=C(CH_3)C*H*], 4.23 (d, 1H, $J_{5,6e}$ 1.3 Hz, $J_{6e,6a}$ 12.4 Hz, H-6_e), 4.14 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.06 (dd, 1H, $J_{3,4}$ 3.5 Hz, $J_{4,5}$ 0.7 Hz, H-4), 3.93 (dd, 1H, $J_{5,6a}$ 1.8 Hz, $J_{6e,6a}$ 12.5 Hz, H-6_a), 3.68 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 9.6 Hz, H-2), 3.63 (m, 1H, H-3), 3.52 (s, 3H, OCH_3), 3.36 (m, 1H, H-5), 1.89 [d, 3H, ^4J 1.3 Hz, PhCH=C(CH_3)CH]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.7 [PhCH=*C*(CH_3)CH], 134.2–126.9 (Ph), 129.1 [Ph*C*H=C(CH_3)CH], 104.6 [PhCH=C(CH_3)*C*H], 103.8 (C-1), 74.9 (C-4), 72.8 (C-3), 71.7 (C-2), 68.8 (C-6), 66.7 (C-5), 57.2 (OCH_3), 13.1 [PhCH=C(*C*H_3)CH]. HRMS (EI): $[M]^{+\cdot}$, found: 322.141873. $C_{17}H_{22}O_6$ requires 322.141639. Anal. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 62.98; H, 6.65.

4.11.3. 1,2-*O*-Isopropylidene-5,6-*O*-[(*S*,*E*)-3-phenyl-2-propenylidene]-α-D-glucofuranose 25. Two stereoisomers were obtained in an 84:16 ratio (68% de). Column chromatography on silica gel, using hexane–ethyl acetate (2.5:1) as eluent, separated the major diastereoisomer. Yield 0.76 g

(45%); mp 152–154 °C; $[\alpha]_D = +26.4$ (*c* 1.0, CH_2Cl_2); MS (CI): *m*/*z* 335 (90%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 6.76 (d, 1H, J_{trans} 16.2 Hz, PhC*H*=CHCH), 6.14 (dd, 1H, J_{trans} 16.2 Hz, *J* 5.1 Hz, PhCH=C*H*CH), 6.03 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 5.47 (d, 1H, *J* 5.0 Hz, PhCH=CHC*H*), 4.62 (d, 1H,$J_{1,2}$ 3.7 Hz, H-2), 4.36 (d, 1H, $J_{3,4}$ 2.2 Hz, H-3), 4.28 (dd, 1H, $J_{5,6A}$ 7.1 Hz, $J_{5,6B}$ 4.3 Hz, H-5), 4.07 (m, 1H, H-4), 4.00 (dd, 1H, $J_{5,6A}$ 7.1 Hz, $J_{6A,6B}$ 11.6 Hz, H-6_A), 3.88 (dd, 1H, $J_{5,6B}$ 4.3 Hz, $J_{6A,6B}$ 11.6 Hz, H-6_B), 1.50, 1.32 [2s, 6H, $C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.7–126.9 (Ph), 134.3 (Ph*C*H=CHCH), 124.6 (PhCH=*C*HCH), 113.7 [*C*$(CH_3)_2$], 105.4 (C-1), 94.2 (PhCH=CH*C*H), 83.8 (C-2), 77.7 (C-3), 73.7 (C-5), 73.1 (C-4), 62.0 (C-6), 26.7, 26.2 [C(*C*$H_3)_2$]. HRMS (EI): $[M]^{+\cdot}$, found: 334.136352. $C_{18}H_{22}O_6$ requires 334.137616. Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.40; H, 6.92.

For the minor diastereoisomer (*R*) configuration: ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, Ph), 6.72 (d, 1H, J_{trans} 16.0 Hz, PhC*H*=CHCH), 6.12 (dd, 1H, J_{trans} 16.0 Hz, *J* 6.1 Hz, PhCH=C*H*CH), 5.93 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 5.58 (d, 1H, *J* 6.1 Hz, PhCH=CHC*H*), 4.52 (d, 1H, $J_{1,2}$ 3.6 Hz, H-2), 4.40 (m, 1H, $J_{4,5} = 7.8$ Hz, $J_{5,6A} = J_{5,6B}$ 6.3 Hz, H-5), 4.36 (d, 1H,$J_{3,4}$ 2.8 Hz, H-3), 4.27 (dd, 1H, $J_{5,6A} = 6.3$ Hz, $J_{6A,6B}$ 8.6 Hz, H-6_A), 4.17 (dd, 1H, $J_{4,5} = 7.8$ Hz, $J_{2,3}$ 2.8 Hz, H-4), 3.98 (dd, 1H, $J_{5,6B}$ 6.3 Hz, $J_{6A,6B}$ 8.6 Hz, H-6_B), 1.49, 1.30 [2s, 6H, $C(CH_3)_2$].

4.11.4. 1,2-*O*-Isopropylidene-5,6-*O*-[(*S*,*E*)-2-methyl-3-phenyl-2-propenylidene]-α-D-glucofuranose 26. Two stereoisomers were obtained in a 69:31 ratio (38% de). Column chromatography on silica gel, using hexane–ethyl acetate (3.5:1) as eluent, separated the major diastereoisomer. Yield 0.71 g (41%); mp 161–162 °C; $[\alpha]_D = +12.7$ (*c* 0.9, CH_2Cl_2); MS (CI): *m*/*z* 349 (15%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 6.65 [s, 1H, PhC*H*=C(CH_3)CH], 6.02 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.26 [s, 1H, PhCH=C(CH_3)C*H*], 4.63 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.36 (d, 1H, $J_{3,4}$ 2.3 Hz, H-3), 4.30 (m, 1H, $J_{5,6A}$ 7.9 Hz, $J_{5,6B}$ 4.3 Hz, H-5), 4.05 (m, 1H, H-4), 4.01 (dd, 1H, $J_{5,6A} = 7.9$ Hz, $J_{6A,6B}$ 11.5 Hz, H-6_A), 3.86 (dd, 1H, $J_{5,6B}$ 4.3 Hz, $J_{6A,6B}$ 11.5 Hz, H-6_B), 1.89 [d, 3H, *J* 1.3 Hz, PhCH=C(C*H*$_3$)CH], 1.50, 1.32 [2s, 6H, $C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.7–128.1 (Ph), 134.1 [PhCH=*C*(CH_3)CH], 127.0 [Ph*C*H=C(CH_3)CH], 111.9 [$(CH_3)_2$*C*], 105.0 (C-1), 97.3 [PhCH=C(CH_3)*C*H], 84.0 (C-2), 77.7 (C-3), 73.9 (C-5), 73.0 (C-4), 61.8 (C-6), 26.8, 26.2 [C(*C*$H_3)_2$], 12.9 [PhCH=C(*C*H_3)CH]. HRMS (EI): $[M]^{+\cdot}$, found: 348.157511. $C_{19}H_{24}O_6$ requires 348.157289. Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 65.10; H, 6.74.

For the minor diastereoisomer (*R*)-configuration: ^1H NMR (500 MHz, $CDCl_3$): δ 7.4–7.2 (m, Ph), 6.64 [s, 1H, PhC*H*=C(CH_3)CH], 5.93 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 5.41 [s, 1H, PhCH=C(CH_3)C*H*], 4.51 (d, 1H, $J_{1,2}$ 3.6 Hz, H-2), 4.41 (m, 1H, $J_{4,5} = 7.5$ Hz, $J_{5,6A} = J_{5,6B}$ 6.5 Hz, H-5), 4.36 (d, 1H, $J_{3,4}$ 2.7 Hz, H-3), 4.31 (dd, 1H, $J_{5,6A} = 6.5$ Hz, $J_{6A,6B}$ 8.5 Hz, H-6_A), 4.18 (dd, 1H, $J_{4,5} = 7.6$ Hz, $J_{2,3}$ 2.8 Hz, H-4), 3.97 (dd, 1H, $J_{5,6B}$ 6.5 Hz, $J_{6A,6B}$ 8.5 Hz, H-6_B), 1.85 [d, 3H, *J* 1.9 Hz, PhCH=C(C*H*$_3$)CH], 1.50, 1.29 [2s, 6H, $C(CH_3)_2$].

4.11.5. 1,2-*O*-Isopropylidene-3,5-*O*-[(*S*,*E*)-3-phenyl-2-propenylidene]-α-D-xylofuranose 27. Column chromatography on silica gel, using hexane–ethyl acetate (7:1) as eluent, yielded 0.93 g (61%); mp 164–165 °C; $[\alpha]_D = +12.3$ (*c* 0.8, CH_2Cl_2); MS (EI): *m*/*z* 304 (65%) $[M]^{+\cdot}$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 6.77 (d, 1H, J_{trans} 16.2 Hz, PhC*H*=CHCH), 6.14 (dd, 1H, J_{trans} 16.2 Hz, *J* 4.8 Hz, PhCH=C*H*CH), 6.05 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.09 (dd, 1H, *J* 4.8 Hz, *J* 1.1 Hz, PhCH=CHC*H*), 4.60 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.37 (d, 1H, $J_{5e,5a}$ 13.2 Hz, H-5_e), 4.31 (d, 1H, $J_{3,4}$ 1.9 Hz, H-3), 4.12 (m, 1H, H-4), 4.09 (dd, 1H, $J_{4,5}$ 2.0 Hz, $J_{5e,5a}$ 13.2 Hz, H-5_a), 1.50, 1.32 [2s, 6H, $C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.8–126.9 (Ph), 134.1 (Ph*C*H=CHCH), 124.6 (PhCH=*C*HCH), 111.9 [*C*$(CH_3)_2$], 105.7 (C-1), 98.9 (PhCH=CH*C*H), 83.9 (C-2), 78.7 (C-3), 72.2 (C-4), 66.5 (C-5), 26.8, 26.2 [C(*C*$H_3)_2$]. HRMS (EI): $[M]^{+\cdot}$, found: 304.130302. $C_{17}H_{20}O_5$ requires 304.131074. Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 66.70; H, 6.30.

4.11.6. 1,2-*O*-Isopropylidene-3,5-*O*-[(*S*,*E*)-2-methyl-3-phenyl-2-propenylidene]-α-D-xylofuranose 28. Two stereoisomers were obtained in an 87:13 ratio (74% de). Column chromatography on silica gel, using hexane–ethyl acetate (10.5:1) as eluent, separated the major diastereoisomer. Yield 0.87 g (50%); mp 86–88 °C; $[\alpha]_D = -3.9$ (*c* 0.7, CH_2Cl_2); MS (EI): *m*/*z* 318 (70%) $[M]^{+\cdot}$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 6.66 [s, 1H, PhC*H*=C(CH_3)CH], 6.05 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.90 [s, 1H, Hz, PhCH=C(CH_3)C*H*], 4.61 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.39 (d, 1H, $J_{5e,5a}$ 13.1 Hz, H-5_e), 4.32 (d, 1H, $J_{3,4}$ 2.0 Hz, H-3), 4.08 (m, 1H, H-4), 4.05 (dd, 1H, $J_{4,5}$ 2.0 Hz, $J_{5e,5a}$ 13.1 Hz, H-5_a), 1.89 [d, 3H, *J* 1.4 Hz, PhCH=C(C*H*$_3$)CH], 1.50, 1.32 [2s, 6H, $C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.7–128.1 (Ph), 134.0 [PhCH=*C*(CH_3)CH], 126.9 [Ph*C*H=C(CH_3)CH], 111.8 [*C*$(CH_3)_2$], 105.7 (C-1), 102.4 [PhCH=C(CH_3)*C*H], 83.9 (C-2), 78.8 (C-3), 72.3 (C-4), 66.6 (C-5), 26.8, 26.2 [C(*C*$H_3)_2$], 13.1 [PhCH=C(*C*H_3)CH]. HRMS (EI): $[M]^{+\cdot}$, found: 318.145744. $C_{18}H_{22}O_5$ requires 318.146724. Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 67.80; H, 6.43.

For the minor diastereoisomer (*R*) configuration: ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, Ph), 6.52 [s, 1H, PhC*H*=C(CH_3)CH], 6.04 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.13 [s, 1H, Hz, *J* PhCH=C(CH_3)C*H*], 4.58 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.30 (d, 1H, $J_{5e,5a}$ 13.3 Hz, H-5_e), 4.23 (d, 1H, $J_{3,4}$ 2.0 Hz, H-3), 4.00 (br s, 1H, H-4), 3.93 (dd, 1H, $J_{4,5}$ 1.9 Hz, $J_{5e,5a}$ 13.3 Hz, H-5_a), 1.91 [d, 3H, *J* 1.4 Hz, PhCH=C(C*H*$_3$)CH], 1.47, 1.32 [2s, 6H, $C(CH_3)_2$].

4.12. General procedure for epoxidation of alkenyl sugar derivatives with *m*-CPBA

To solutions of the different propenylidene derivatives **9**, **12**–**17** and **23**–**28** (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 the starting compounds had been consumed (1 month) The solution was then 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.

4.12.1. *c*-Hexyl 2-acetamido-2-deoxy-4,6-*O*-[(1*R*,2*S*,3*R*)-2,3-epoxy-3-phenylpropylidene]-3-*O*-methyl-β-D-glucopyranoside 29. Two stereoisomers were obtained in a 57:43 ratio (14% de). The pure diastereoisomeric mixture was obtained by flash chromatography on silica gel, using dichloromethane–methanol (125:1) as eluent. Yield 0.81 g (90%); mp 149–151 °C; $[\alpha]_D = -14.3$ (*c* 0.6, CH_2Cl_2); MS (CI): *m*/*z* 448 (37%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.3 (m, 5H, Ph), 5.87 (d, 1H, $J_{2,NH}$ 6.9 Hz, NH), 5.18 (d, $J_{1,2}$ 8.3 Hz, H-1 major), 5.16 (d, $J_{1,2}$ 8.3 Hz, H-1 minor), 4.65 [d, *J* 3.4 Hz, PhCH(O)CHC*H* major], 4.61 [d, *J* 3.6 Hz, PhCH(O)CHC*H* minor], 4.3–4.2 (m, 2H, H-3, H-6$_e$), 3.95 [d, J_{trans} 1.9 Hz, PhC*H*(O)CHCH major], 3.92 [d, J_{trans} 1.9 Hz, PhC*H*(O)CHCH minor], 3.6–3.3 (m, 7H, H-4, H-5, OCHR, H-6$_a$, CH_3O), 3.20 [dd, *J* 3.4 Hz, J_{trans} 2.0 Hz, PhCH(O)C*H*CH minor], 3.18 [dd, *J* 3.4 Hz, J_{trans} 2.1 Hz, PhCH(O)C*H*CH major], 2.91 (m 1H, H-2), 1.99 (s, 3H, CH_3CON), 1.8–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6 (C=O), 136.1–125.8 (Ph), 99.7 [PhCH(O)CH*C*H minor], 99.4 [PhCH(O)CH*C*H major], 98.3 (C-1 major), 98.1 (C-1 minor), 82.5 (C-4), 81.8 (OCHR), 77.8 (C-3), 68.7 (C-6 major), 68.5 (C-6 minor), 65.6 (C-5), 61.0 [PhCH(O)*C*HCH major], 60.7 [PhCH(O)*C*HCH minor], 60.5 (CH_3O), 59.1 (C-2), 55.3 [Ph*C*H(O)CHCH minor], 55.1 [Ph*C*H(O)CHCH major], 33.5–23.9 [$(CH_2)_5$], 23.7 (*C*H_3CON). HRMS (CI): $[M+H]^+$, found: 448.233577. $C_{24}H_{34}NO_7$ requires 448.233528. Anal. Calcd for $C_{24}H_{33}NO_7$: C, 64.41; H, 7.43; N, 3.13. Found: C, 64.10; H, 7.00; N, 2.86.

4.12.2. 1-Dodecyl 2,3-diacetamido-2,3-dideoxy-4,6-*O*-[(1*R*)-2,3-epoxy-3-phenylpropylidene]-β-D-glucopyranoside 30. Two stereoisomers were obtained in a 50:50 ratio. The pure diastereoisomeric mixture was obtained by flash chromatography on silica gel, using dichloromethane–methanol (60:1) as eluent. Yield 0.90 g (82%); MS (CI): *m*/*z* 561 (10%) $[M+H]^+$. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.78, 7.74 (2d, 2H, $J_{2,NH}$ 9.3 Hz, 2NH), 7.3–7.2 (m, 5H, Ph), 4.60, 4.51 [2d, 1H, *J* 4.8 Hz, PhCH(O)CHC*H*], 4.48 (d, 1H, $J_{1,2}$ 7.4 Hz, H-1), 4.13 (dd, 1H, $J_{5,6e}$ 4.7 Hz, $J_{6e,6a}$ 10.2 Hz, H-6$_e$), 3.98 (m, 1H, OCH_AH$_B$R), 3.94, 3.89 [2d, 1H, J_{trans} 1.8 Hz, PhC*H*(O)CHCH], 3.7–3.3 (m, 6H, H-2, H-3, H-4, H-5, H-6$_a$, OCH$_A$*H*$_B$R), 3.24 [dd, 1H, *J* 4.8 Hz, J_{trans} 1.9 Hz, PhCH(O)C*H*CH], 1.78, 1.74, 1.73, 1.72 (4s, 6H, 2CH_3CON), 1.3–1.1 [m, 20H, $(CH_2)_{10}$], 0.84 (t, 3H, *J* 6.9 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.7, 171.1 (2C=O), 136.1–125.8 (Ph), 102.6, 102.5 (C-1), 99.7, 99.5 [PhCH(O)CH*C*H], 78.7 (C-4), 70.2 (C-3), 68.4, 67.7 (C-6, OCH_2R), 60.7, 60.5 (C-5), 55.2, 55.1 [PhCH(O)*C*HCH], 54.9, 54.8 (C-2), 53.4, 53.0 [Ph*C*H(O)CHCH], 32.1–22.9 [$(CH_2)_{10}$], 23.3, 22.7 (2CH_3CON), 14.1 (CH_3). HRMS (CI): $[M+H]^{+\cdot}$, found: 561.350236. $C_{31}H_{49}N_2O_7$ requires 561.353977. Anal. Calcd for $C_{31}H_{48}N_2O_7$: C, 66.40; H, 8.63; N, 5.00. Found: C, 66.03; H, 8.88; N, 4.84.

4.12.3. *c*-Hexyl 2-acetamido-2-deoxy-4,6-*O*-[(1*R*,2*S*,3*R*)-2,3-epoxy-3-phenylpropylidene]-β-D-allopyranoside 31. Two stereoisomers were obtained in an 84:16 ratio (68% de). The pure diastereoisomeric mixture was obtained by flash chromatography on silica gel, using dichloromethane–methanol (100:1) as eluent. Yield 0.62 g (72%); mp 199–200 °C; $[\alpha]_D = -15.7$ (*c* 0.6, CH_2Cl_2); MS (CI): *m*/*z* 434 (15%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 5.97 (d, 1H, $J_{2,NH}$ 9.1 Hz, NH), 4.71 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.67 [d, *J* 3.9 Hz, PhCH(O)CHC*H* major], 4.63 [d, *J* 4.0 Hz, PhCH(O)CHC*H* minor], 4.3–4.2 (m, 2H, H-3, H-6$_e$), 4.05 (dt, 1H, $J_{1,2} = J_{2,NH}$ 8.8 Hz, $J_{2,3}$ 3.0 Hz, H-2), 3.93 [d, J_{trans} 1.8 Hz, PhC*H*(O)CHCH major], 3.91 [d, J_{trans} 1.9 Hz, PhC*H*(O)CHCH minor], 3.86 (dt, 1H, $J_{4,5} = 9.5$ Hz, $J_{5,6a}$ 10.2 Hz, $J_{5,6e}$ 5.0 Hz, H-5), 3.6–3.5 (m, 2H, H-6$_a$, OCHR), 3.46 (dd, 1H, $J_{3,4} = 2.3$ Hz, $J_{4,5}$ 9.5 Hz, H-4), 3.18 [dd, 1H, *J* 4.0 Hz, J_{trans} 1.8 Hz, PhCH(O)C*H*CH], 2.09 (s, CH_3CON minor), 1.99 (s, CH_3CON major), 1.9–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.6 (C=O), 135.8–125.9 (Ph), 100.0 [PhCH(O)CH*C*H major], 99.8 [PhCH(O)CH*C*H minor], 98.7 (C-1 major), 98.6 (C-1 minor), 78.6 (C-4 minor), 78.4 (C-4 major), 77.4 (OCHR), 69.0 (C-6 major), 68.8 (C-6 minor), 68.7 (C-3 minor), 68.6 (C-3 major), 63.1 (C-5 major), 62.9 (C-5 minor), 60.7 [PhCH(O)*C*HCH major], 60.5 [PhCH(O)*C*HCH minor], 56.3 [Ph*C*H(O)CHCH minor], 55.4 [Ph*C*H(O)CHCH major], 52.6 (C-2 minor), 52.5 (C-2 major), 33.3–23.6 [$(CH_2)_5$], 23.4 (*C*H_3CON). HRMS (CI): $[M+H]^+$, found: 434.218804. $C_{23}H_{32}NO_7$ requires 434.217878. Anal. Calcd for $C_{23}H_{31}NO_7$: C, 63.73; H, 7.21; N, 3.23. Found: C, 63.23; H, 7.16; N, 3.31.

4.12.4. *c*-Hexyl 2-acetamido-2-deoxy-4,6-*O*-[(1*R*,2*S*,3*R*)-2,3-epoxy-2-methyl-3-phenylpropylidene]-β-D-allopyranoside 32. Two stereoisomers were obtained in an 86:14 ratio (72% de). The pure diastereoisomeric mixture was obtained by flash chromatography on silica gel, using dichloromethane–methanol (100:1) as eluent. Yield 0.64 g (72%); mp 154–155 °C; $[\alpha]_D = -46.5$ (*c* 0.6, CH_2Cl_2); MS (CI): *m*/*z* 448 (16%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 5.94 (d, 1H, $J_{2,NH}$ 9.2 Hz, NH), 4.70 (d, 1H, $J_{1,2}$ 8.5 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], 4.3–4.2 (m, 2H, H-3, H-6$_e$), 4.1–4.0 [m, 2H, H-2, PhC*H*(O)C(CH_3)CH], 3.84 (dt, 1H, $J_{4,5} = J_{5,6a}$ 9.5 Hz, $J_{5,6e}$ 5.1 Hz, H-5), 3.62 (t, $J_{6e,6a} = J_{5,6a}$ 10.4 Hz, H-6$_a$ minor), 3.60 (t, $J_{6e,6a} = J_{5,6a}$ 10.4 Hz, H-6$_a$ major), 3.56 (m, 1H, OCHR), 3.47 (dd, 1H, $J_{3,4} = 2.3$ Hz, $J_{4,5}$ 9.4 Hz, H-4), 2.14 (s, CH_3CON major), 2.10 (s, CH_3CON minor), 1.09 [s, 3H, PhCH(O)C(C*H*$_3$)CH], 1.7–1.2 [m, 10H, $(CH_2)_5$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.5 (C=O), 134.7–126.6 (Ph), 103.2 [PhCH(O)C(CH_3)*C*H major], 102.9 [PhCH(O)C(CH_3)*C*H minor], 98.7 (C-1 major), 98.6 (C-1 minor), 78.5 (C-4 minor), 78.3 (C-4 major), 77.3 (OCHR), 68.9 (C-6 major), 68.8 (C-6 minor), 68.7 (C-3 major), 68.6 (C-3 minor), 63.2 (C-5), 62.4 [PhCH(O)*C*(CH_3)CH major], 62.3 [PhCH(O)*C*(CH_3)CH minor], 60.7 [Ph*C*H(O)C(CH_3)CH major], 60.5 [Ph*C*H(O)C(CH_3)CH minor],

52.4 (C-2 minor), 52.3 (C-2 major), 33.3–23.6 [$(CH_2)_5$], 23.4 (CH_3CON), 11.4 (CH_3 minor), 11.1 (CH_3 major). HRMS (CI): $[M+H]^+$, found: 448.232893. $C_{24}H_{34}NO_7$ requires 448.233528. Anal. Calcd for $C_{24}H_{33}NO_7$: C, 64.41; H, 7.43; N, 3.13. Found: C, 64.60; H, 7.47; N, 3.19.

4.12.5. 1-Dodecyl 2-acetamido-3-*O*-acetyl-2-deoxy-4,6-*O*-[(1*R*,2*S*,3*R*)-2,3-epoxy-3-phenylpropylidene]-β-D-allopyranoside 33. Two stereoisomers were obtained in a 61:39 ratio (20% de). The pure diastereoisomeric mixture was obtained by flash chromatography on silica gel, using dichloromethane–methanol (100:1) as eluent. Yield 0.90 g (80%); mp 135–136 °C; $[\alpha]_D = -64.7$ (*c* 0.8, CH_2Cl_2); MS (CI): *m*/*z* 562 (25%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 5.66 (t, 1H, $J_{2,3} = J_{3,4}$ 2.8 Hz, H-3), 5.33 (d, 1H, $J_{2,NH}$ 8.3 Hz, NH), 4.70 [d, *J* 3.0 Hz, PhCH(O)CHC*H* major], 4.61 [d, *J* 3.0 Hz, PhCH(O)CHC*H* minor], 4.59 (d, 1H, $J_{1,2}$ 8.7 Hz, H-1), 4.26 (dd, 1H, $J_{5,6e}$ 5.2 Hz, $J_{6e,6a}$ 10.2 Hz, H-6_e), 4.20 (dd, 1H, $J_{1,2}$ 8.3 Hz, $J_{2,3}$ 3.0 Hz, H-2), 3.90 [d, J_{trans} 1.9 Hz, PhC*H*(O)CHCH major], 3.86 [d, J_{trans} 1.9 Hz, PhC*H*(O)CHCH minor], 3.8–3.7 (m, 2H, H-5, OCH_AH_BR), 3.6–3.5 (m, 2H, H-4, H-6_a), 3.41 (m, 1H, OCH_AH_BR), 3.12 [dd, 1H, *J* 3.0 Hz, J_{trans} 1.9 Hz, PhCH(O)C*H*CH], 2.15 (s, CH_3COO minor), 2.14 (s, CH_3COO major), 1.97 (s, CH_3CON major), 1.95 (s, CH_3CON minor), 1.5–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3H, *J* 6.7 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.6 (C=O minor), 169.4 (C=O major), 136.2–125.8 (Ph), 100.1 (C-1 major), 100.0 (C-1 minor), 99.9 [PhCH(O)CH*C*H minor], 99.4 [PhCH(O)CH*C*H major], 77.2 (C-4 minor), 76.9 (C-4 major), 69.7 (OCH_2R), 69.6 (C-3 major), 69.4 (C-3 minor), 68.7 (C-6), 64.3 (C-5 major), 64.2 (C-5 minor), 60.6 [PhCH(O)*C*HCH minor], 60.5 [PhCH(O)*C*HCH major], 55.4 [Ph*C*H(O)CHCH minor], 54.9 [Ph*C*H(O)CHCH major], 51.4 (C-2 minor), 51.2 (C-2 major), 31.9–22.7 $[(CH_2)_{10}]$, 23.2 (CH_3CON), 21.0 (CH_3COO minor), 20.9 (CH_3COO major), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found: 562.339285. $C_{31}H_{48}NO_8$ requires 562.337993. Anal. Calcd for $C_{31}H_{47}NO_8$: C, 66.29; H, 8.43; N, 2.49. Found: C, 65.90; H, 8.26; N, 2.75.

4.12.6. 1-Dodecyl 2-acetamido-3-*O*-benzyl-2-deoxy-4,6-*O*-[(1*R*,2*R*,3*S*)-2,3-epoxy-3-phenylpropylidene]-β-D-allopyranoside 34. Two stereoisomers were obtained in a 64:36 ratio (28% de). The pure diastereoisomeric mixture was obtained by flash chromatography on silica gel, using dichloromethane–methanol (150:1) as eluent. Yield 1.0 g (83%); mp 146–148 °C; $[\alpha]_D = -80.0$ (*c* 1.2, CH_2Cl_2); MS (CI): *m*/*z* 610 (10%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 5.65 (d, $J_{2,NH}$ 9.1 Hz, NH minor), 5.64 (d, 1H, $J_{2,NH}$ 9.1 Hz, NH major), 4.97 (d, J_{gem} 11.6 Hz, PhCH_AH_BO minor), 4.93 (d, J_{gem} 11.7 Hz, PhCH_AH_BO major), 4.65 [d, *J* 3.6 Hz, PhCH(O)CHC*H* major], 4.61 [d, *J* 3.7 Hz, PhCH(O)CHC*H* minor], 4.54 (d, $J_{1,2}$ 8.3 Hz, H-1 major), 4.53 (d, $J_{1,2}$ 8.3 Hz, H-1 minor), 4.51 (d, J_{gem} 11.6 Hz, PhCH_AH_BO minor), 4.49 (d, J_{gem} 11.7 Hz, PhCH_AH_BO major), 4.29 (dd, $J_{5,6e}$ 5.2 Hz, $J_{6e,6a}$ 10.5 Hz, H-6_e major), 4.27 (dd, $J_{5,6e}$ 5.1 Hz, $J_{6e,6a}$ 10.7 Hz, H-6_e minor), 4.05 (m, 2H, H-2, H-3), 3.97 (dt, 1H, $J_{5,6e}$ 5.2 Hz, $J_{4,5} = J_{5,6a}$ 10.1 Hz, H-5), 3.95 [d, J_{trans} 1.9 Hz, PhC*H*(O)CHCH minor], 3.91 [d, J_{trans} 1.9 Hz, PhC*H*(O)CHCH major], 3.77 (m, 1H, OCH_AH_BR), 3.6–3.5 (m, 2H, H-4, H-6_a), 3.37 (m, 1H, OCH_AH_BR), 3.19 [dd, 1H, J_{trans} 1.9 Hz, *J* 3.6 Hz, PhCH(O)C*H*CH major], 3.17 [dd, 1H, J_{trans} 1.9 Hz, *J* 3.6 Hz, PhCH(O)C*H*CH minor], 1.82 (s, 3H, CH_3CON), 1.6–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3H, *J* 7.0 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3 (C=O major), 169.2 (C=O minor), 138.3–125.8 (Ph), 100.5, 100.4, 100.1, 99.9 [C-1, PhCH(O)CH*C*H], 80.0 (C-4 major), 79.7 (C-4 minor), 75.8 (C-3), 74.8 (Ph*C*H_2O major), 74.6 (Ph*C*H_2O minor), 69.8 (OCH_2R), 68.9 (C-6 major), 68.7 (C-6 minor), 63.8 (C-5 minor), 63.6 (C-5 major), 60.9 [PhCH(O)*C*HCH minor], 60.7 [PhCH(O)*C*HCH major], 55.3 [Ph*C*H(O)CHCH major], 55.1 [Ph*C*H(O)CHCH minor], 52.0 (C-2 major), 51.8 (C-2 minor), 31.9–22.7 $[(CH_2)_{10}]$, 23.2 (CH_3CON), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found: 610.376842. $C_{36}H_{52}NO_7$ requires 610.374379. Anal. Calcd for $C_{36}H_{51}NO_7$: C, 70.91; H, 8.43; N, 2.30. Found: C, 70.56; H, 8.51; N, 2.23.

4.12.7. Methyl 4,6-*O*-[(1*R*,2*S*,3*R*)-2,3-epoxy-2-methyl-3-phenylpropylidene]-2-*O*-ethyl-α-D-altropyranoside 35. Two stereoisomers were obtained in a 67:33 ratio (34% de). The pure diastereoisomeric mixture was obtained as a syrup by flash chromatography on silica gel, using hexane–ethyl acetate (2.5:1) as eluent. Yield 0.6 g (86%); $[\alpha]_D = +72.8$ (*c* 0.8, $CHCl_3$); MS (EI): *m*/*z* 366 (4%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.3 (m, 5H, Ph), 4.67 (br s, H-1 minor), 4.66 (br s, H-1 major), 4.50 [bs, 1H, PhCH(O)C(CH_3)C*H*], 4.24 (dd, $J_{5,6e}$ 5.1 Hz, $J_{6e,6a}$ 10.5 Hz, H-6_e minor), 4.22 (dd, $J_{5,6e}$ 5.1 Hz, $J_{6e,6a}$ 10.5 Hz, H-6_e major), 4.16 (m, 1H, H-2), 4.09 [br s, 1H, PhC*H*(O)C(CH_3)CH], 4.05 (dt, 1H, $J_{4,5} = J_{5,6a}$ 10.0 Hz, $J_{5,6e}$ 5.0 Hz, H-5), 3.76 (dd, $J_{3,4}$ 3.0 Hz, $J_{4,5}$ 9.9 Hz, H-4 major), 3.75 (dd, $J_{3,4}$ 3.0 Hz, $J_{4,5}$ 9.9 Hz, H-4 minor), 3.67 (t, $J_{5,6a} = J_{6e,6a}$ 10.3 Hz, H-6_a minor), 3.66 (t, $J_{5,6a} = J_{6e,6a}$ 10.3 Hz, H-6_a major), 3.61 (m, 2H, OCH_2CH_3), 3.58 (dd, 1H, $J_{2,3}$ 1.0 Hz, $J_{3,4}$ 3.2 Hz, H-3), 3.41 (s, 3H, OCH_3), 1.21 (t, *J* 7.1 Hz, OCH_2CH_3 minor), 1.20 (t, *J* 7.0 Hz, OCH_2CH_3 major), 1.12 [s, PhCH(O)C(CH_3)CH major], 1.11 [s, PhCH(O)C(CH_3)CH minor]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.9–126.0 (Ph), 104.0 [PhCH(O)C(CH_3)*C*H major], 103.9 [PhCH(O)C(CH_3)*C*H minor], 100.5 (C-1 major), 100.3 (C-1 minor), 77.5 (C-3), 76.4 (C-4 minor), 76.3 (C-4 major), 68.8 (C-6 major), 68.7 (C-6 minor), 67.1 (C-2 minor), 66.9 (C-2 major), 66.4 (OCH_2CH_3), 62.5 [PhCH(O)*C*(CH_3)CH major], 62.4 [PhCH(O)*C*(CH_3)CH minor], 60.7 [Ph*C*H(O)C(CH_3)CH minor], 60.6 [Ph*C*H(O)C(CH_3)CH major], 58.2 (C-5 minor), 58.1 (C-5 major), 55.7 (OCH_3 major), 55.6 (OCH_3 minor), 15.4 (OCH_2CH_3), 11.0 [PhCH(O)C(*C*H_3)CH]. HRMS (EI): $[M]^{+\cdot}$, found: 366.167623. $C_{19}H_{26}O_7$ requires 366.167854.

4.12.8. Methyl 4,6-*O*-[(1*S*,2*R*,3*S*)-2,3-epoxy-3-phenylpropylidene]-β-D-galactopyranoside 36. Two stereoisomers were obtained in a 63:37 ratio (26% de). The pure diastereoisomeric mixture was obtained as a pure syrup by flash chromatography on silica gel, using hexane–ethyl acetate (1:3.5) as eluent. Yield 0.4 g (67%); $[\alpha]_D = -3.2$ (*c* 0.9, CH_2Cl_2); MS (EI): *m*/*z* 324 (7%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 4.65 [d, *J* 4.1 Hz, PhCH(O)CHC*H* major], 4.61 [d, *J* 4.2 Hz, PhCH(O)CHC*H* minor],

4.24 (dd, 1H, $J_{5,6e}$ 1.4 Hz, $J_{6e,6a}$ 12.4 Hz, H-6$_e$), 4.15 (d, $J_{1,2}$ 7.5 Hz, H-1 major), 4.13 (d, $J_{1,2}$ 8.1 Hz, H-1 minor), 4.03 (m, 1H, H-4), 3.96 [d, J_{trans} 2.0 Hz, PhC*H*(O)CHCH minor], 3.95 [d, J_{trans} 2.0 Hz, PhC*H*(O)CHCH major], 3.90 (dd, 1H, $J_{5,6a}$ 1.9 Hz, $J_{6e,6a}$ 12.4 Hz, H-6$_a$), 3.69 (dd, 1H, $J_{1,2}$ 7.6 Hz, $J_{2,3}$ 9.8 Hz, H-2), 3.63 (m, 1H, H-3), 3.54 (s, OCH_3 minor), 3.53 (s, OCH_3 major), 3.40 (m, 1H, H-5), 3.29 [dd, 1H,J_{trans} 2.0 Hz, *J* 4.0 Hz, PhCH(O)C*H*CH]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.9–125.7 (Ph), 103.9 (C-1 minor), 103.7 (C-1 major), 100.2 [PhCH(O)CH*C*H minor], 99.7 [PhCH(O)CH*C*H major], 75.1 (C-4), 72.6 (C-3 minor), 72.4 (C-3 major), 71.4 (C-2 major), 71.3 (C-2 minor), 68.8 (C-6 major), 68.7 (C-6 minor), 66.7 (C-5), 61.0 [PhCH(O)*C*HCH minor], 60.8 [PhCH(O)*C*HCH major], 57.3 (OCH_3 minor), 57.0 (OCH_3 major), 55.4 [Ph*C*H(O)CHCH major], 55.3 [Ph*C*H(O)CHCH minor]. HRMS (EI): $[M]^{+\cdot}$, found: 324.119644. $C_{16}H_{20}O_7$ requires 324.120903.

4.12.9. Methyl 4,6-*O*-[(1*S*,2*R*,3*S*)-2,3-epoxy-2-methyl-3-phenylpropylidene]-β-D-galactopyranoside 37. Two stereoisomers were obtained in an 87:13 ratio (74% de). The pure diastereoisomeric mixture was purified by flash chromatography on silica gel, using dichloromethane–methanol (70:1) as eluent. Yield 0.4 g (62%); mp 151–153 °C; $[\alpha]_D = -4.9$ (*c* 0.7, CH_2Cl_2); MS (EI): *m*/*z* 338 (15%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.2–7.1 (m, 5H, Ph), 4.51 [s, PhCH(O)C(CH_3)C*H* major], 4.41 [s, PhCH(O)C(CH_3)C*H* minor], 4.26 (d, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.4 Hz, H-6$_e$), 4.16 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1), 4.14 [s, 1H, PhC*H*(O)C(CH_3)CH], 4.04 (dd, 1H, $J_{3,4}$ 3.5 Hz, $J_{4,5}$ 1.1 Hz, H-4), 3.91 (dd, 1H, $J_{5,6a}$ 2.0 Hz, $J_{6e,6a}$ 12.6 Hz, H-6$_a$), 3.66 (dd, 1H, $J_{1,2}$ 7.2 Hz, $J_{2,3}$ 9.7 Hz, H-2), 3.62 (m, 1H, H-3), 3.55 (s, OCH_3 major), 3.53 (s, OCH_3 minor), 3.41 (m, 1H, H-5), 1.12 [s, 3H, PhCH(O)C(C*H*$_3$)CH]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.7–126.7 (Ph), 103.9 (C-1), 102.5 [PhCH(O)C(CH_3)*C*H], 75.1 (C-4), 72.8 (C-3 minor), 72.7 (C-3 major), 71.6 (C-2 minor), 71.5 (C-2 major), 68.8 (C-6 major), 68.7 (C-6 minor), 66.8 (C-5 major), 66.6 (C-5 minor), 63.1 [PhCH(O)*C*(CH_3)CH minor], 62.9 [PhCH(O)*C*(CH_3)CH major], 60.7 [Ph*C*H(O)C(CH_3)CH minor], 60.4 [Ph*C*H(O)C(CH_3)CH major], 57.2 (OCH_3 major), 57.1 (OCH_3 minor), 11.3 [PhCH(O)C(*C*H$_3$)CH major], 11.2 [PhCH(O)C(*C*H$_3$)CH minor]. HRMS (EI): $[M]^{+\cdot}$, found: 338.134483. $C_{17}H_{22}O_7$ requires 338.136553. Anal. Calcd for $C_{17}H_{22}O_7$: C, 60.35; H, 6.55. Found: C, 60.18; H, 6.61.

4.12.10. 5,6-*O*-[(1*S*,2*S*,3*R*)-2,3-Epoxy-3-phenylpropylidene]-1,2-*O*-isopropylidene-α-D-glucofuranose 38. Two stereoisomers were obtained in a 78:22 ratio (56% de). The pure diastereoisomeric mixture was obtained by flash chromatography on silica gel, using hexane–ethyl acetate (2:1) as eluent. Yield 0.60 g (84%); mp 128–130 °C; $[\alpha]_D = +2.6$ (*c* 0.7, $CHCl_3$); MS (CI): *m*/*z* 351 (10%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 6.00 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.97 [d, *J* 4.0 Hz, PhCH(O)CHC*H* major], 4.94 [d, *J* 4.0 Hz, PhCH(O)CHC*H* minor], 4.62 (d, $J_{1,2}$ 3.7 Hz, H-2 major), 4.59 (d, $J_{1,2}$ 3.8 Hz, H-2 minor), 4.33 (d, $J_{3,4}$ 2.3 Hz, H-3 major), 4.30 (d, $J_{3,4}$ 2.4 Hz, H-3 minor), 4.23 (m, 1H, H-5), 4.09 (m, H-4 minor), 4.08 (m, H-4 major), 3.95 [d, J_{trans} 2.1 Hz, PhC*H*(O)CHCH major], 3.94 (dd, 1H, $J_{5,6A}$ 7.7 Hz, $J_{6A,6B}$ 11.6 Hz, H-6$_A$), 3.91 [d, J_{trans} 1.8 Hz, PhC*H*(O)CHCH minor], 3.88 (dd, 1H, $J_{5,6B}$ 4.3 Hz, $J_{6A,6B}$ 11.7 Hz, H-6$_B$), 3.18 [dd, 1H, J_{trans} 2.1 Hz, *J* 4.0 Hz, PhCH(O)C*H*CH], 1.48, 1.31 [2s, C(CH_3)$_2$ major], 1.47, 1.30 [2s, C(CH_3)$_2$ minor]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.9–125.9 (Ph), 112.0 [*C*(CH_3)$_2$], 105.0 (C-1), 93.9 [PhCH(O)CH*C*H minor], 93.7 [PhCH(O)CH*C*H major], 83.8 (C-2), 77.7 (C-3), 73.8 (C-5), 73.4 (C-4 minor), 73.3 (C-4 major), 62.3 (C-6 minor), 62.2 (C-6 major), 61.2 [PhCH(O)*C*HCH], 55.3 [Ph*C*H(O)CHCH], 26.7, 26.1 [C(*C*H$_3$)$_2$]. HRMS (CI): $[M+H]^+$, found: 351.145125. $C_{18}H_{23}O_7$ requires 351.144378. Anal. Calcd for $C_{18}H_{22}O_7$: C, 61.71; H, 6.33. Found: C, 61.62; H, 6.06.

4.12.11. 5,6-*O*-[(1*S*,2*S*,3*R*)-2,3-Epoxy-2-methyl-3-phenylpropylidene]-1,2-*O*-isopropylidene-α-D-glucofuranose 39. Two stereoisomers were obtained in an 80:20 ratio (60% de). The pure diastereoisomeric mixture was obtained by flash chromatography on silica gel, using hexane–ethyl acetate (4:1) as eluent Yield 0.52 g (71%); mp 138–140 °C; $[\alpha]_D = +1.4$ (*c* 0.7, $CHCl_3$); MS (CI): *m*/*z* 365 (10%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.3 (m, 5H, Ph), 5.99 (d, $J_{1,2}$ 3.7 Hz, H-1 major), 5.93 (d, $J_{1,2}$ 3.6 Hz, H-1 minor), 4.74 [s, PhCH(O)C(CH_3)C*H* major], 4.73 [s, PhCH(O)C(CH_3)C*H* minor], 4.63 (d, $J_{1,2}$ 3.7 Hz, H-2 major), 4.61 (d, $J_{1,2}$ 3.7 Hz, H-2 minor), 4.33 (d, 1H, $J_{3,4}$ 2.4 Hz, H-3), 4.25 (m, 1H, H-5), 4.1–4.0 [m, 2H, H-4, PhC*H*(O)C(CH_3)CH], 3.97 (dd, 1H, $J_{5,6A} = 7.2$ Hz, $J_{6A,6B}$ 11.6 Hz, H-6$_A$), 3.88 (dd, 1H, $J_{5,6B}$ 4.5 Hz, $J_{6A,6B}$ 11.6 Hz, H-6$_B$), 1.49, 1.32 [2s, 6H, C(CH_3)$_2$], 1.08 [s, PhCH=C(C*H*$_3$)CH minor], 1.07 [s, PhCH=C(C*H*$_3$)CH major]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.8–126.6 (Ph), 112.0 [*C*(CH_3)$_2$], 105.3 (C-1 minor), 105.0 (C-1 major), 96.5 [PhCH(O)C(CH_3)*C*H], 85.2 (C-2 minor), 83.9 (C-2 major), 77.7 (C-3 minor), 77.6 (C-3 major), 73.8 (C-5 major), 73.6 (C-5 minor), 73.3 (C-4 minor), 73.2 (C-4 major), 62.9 (C-6), 62.1 [PhCH(O)*C*(CH_3)CH major], 62.0 [PhCH(O)*C*(CH_3)CH minor], 60.4 [Ph*C*H(O)C(CH_3)CH major], 60.2 [Ph*C*H(O)C(CH_3)CH minor], 26.9, 26.3 [C(*C*H$_3$)$_2$ minor], 26.8, 26.2 [C(*C*H$_3$)$_2$ major], 11.0 [PhCH(O)C(*C*H$_3$)CH minor], 10.7 [PhCH(O)C(*C*H$_3$)CH major]. HRMS (CI): $[M+H]^+$, found: 365.158425. $C_{19}H_{25}O_7$ requires 365.160028. Anal. Calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64. Found: C, 62.61; H, 6.66.

4.12.12. 3,5-*O*-[(1*S*,2*S*,3*R*)-2,3-Epoxy-3-phenylpropylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose 40. Two stereoisomers were obtained in a 61:39 ratio (22% de). The pure diastereoisomeric mixture was obtained by flash chromatography on silica gel, using hexane–ethyl acetate (9:1) as eluent. Yield 0.6 g (89%); mp 99–100 °C; $[\alpha]_D = +6.5$ (*c* 0.8, $CHCl_3$); MS (EI): *m*/*z* 320 (10%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 6.02 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.60 (d, $J_{1,2}$ 3.7 Hz, H-2 major), 4.57 (d, $J_{1,2}$ 3.8 Hz, H-2 minor), 4.56 [d, *J* 3.9 Hz, PhCH(O)CHC*H* minor], 4.54 [d, *J* 3.9 Hz, PhCH(O)-CHC*H* major], 4.36 (d, $J_{5e,5a}$ 12.9 Hz, H-5$_e$ minor), 4.33 (d, $J_{5e,5a}$ 13.1 Hz, H-5$_e$ major), 4.27 (d, $J_{3,4}$ 1.8 Hz, H-3 major), 4.25 (d, $J_{3,4}$ 1.8 Hz, H-3 minor), 4.07 (m, 1H, H-4), 3.99 (dd, 1H, $J_{4,5a}$ 1.9 Hz, $J_{5e,5a}$ 13.1 Hz, H-5$_a$), 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], 3.18 [dd, 1H, J_{trans}

1.9 Hz, *J* 4.1 Hz, PhCH(O)C*H*CH], 1.47, 1.32 [2s, 6H, $C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.0–126.0 (Ph), 111.9 [$C(CH_3)_2$], 105.7 (C-1 major), 105.6 (C-1 minor), 98.2 [PhCH(O)CH*C*H major], 98.0 [PhCH(O)CH*C*H minor], 83.7 (C-2), 78.6 (C-3 major), 78.5 (C-3 minor), 72.3 (C-4), 66.4 (C-5 minor), 66.3 (C-5 major), 61.0 [PhCH(O)*C*HCH major], 60.9 [PhCH(O)*C*HCH minor], 55.3 [Ph*C*H(O)CHCH major], 55.1 [Ph*C*H(O)CHCH minor], 26.7, 26.1 [$C(CH_3)_2$]. HRMS (EI): $[M]^{+\cdot}$, found: 320.125720. $C_{17}H_{20}O_6$ requires 320.125989. Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29. Found: C, 63.50; H, 5.95.

4.12.13. 3,5-*O*-[(1*S*,2*S*,3*R*)-2,3-Epoxy-2-methyl-3-phenylpropylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose 41. Two stereoisomers were obtained in a 65:35 ratio (30% de). The pure diastereoisomeric mixture was obtained by flash chromatography on silica gel, using hexane–ethyl acetate (8:1) as eluent. Yield 0.56 g (84%); mp 136–138 °C; $[\alpha]_D = +7.6$ (*c* 0.9, $CHCl_3$); MS (EI): *m*/*z* 334 (10%) $[M]^{+\cdot}$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 6.02 (d, $J_{1,2}$ 3.7 Hz, H-1 major), 6.00 (d, $J_{1,2}$ 3.6 Hz, H-1 minor), 4.62 (d, $J_{1,2}$ 3.7 Hz, H-2 major), 4.59 (d, $J_{1,2}$ 3.8 Hz, H-2 minor), 4.37 [s, PhCH(O)C(CH_3)C*H* minor], 4.35 (m, 1H, H-5_e), 4.32 [s, PhCH(O)C(CH_3)C*H* major], 4.27 (m, 1H, H-3), 4.09 [s, PhC*H*(O)C(CH_3)CH minor], 4.08 [s, PhC*H*(O)C(CH_3)CH major], 4.06 (m, 1H, H-4), 3.98 (dd, $J_{4,5a}$ 2.1 Hz, $J_{5e,5a}$ 13.3 Hz, H-5_a minor), 3.97 (dd, $J_{4,5a}$ 2.1 Hz, $J_{5e,5a}$ 13.3 Hz, H-5_a major), 1.54, 1.31 [2s, C(CH_3)$_2$ minor], 1.48, 1.32 [2s, $C(CH_3)_2$ major], 1.08 [s, PhCH(O)C(C*H*$_3$)CH minor], 1.07 [s, PhCH(O)C(C*H*$_3$)-CH major]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.9–126.6 (Ph), 111.9 [$C(CH_3)_2$], 105.7 (C-1 major), 105.6 (C-1 minor), 101.4 [PhCH(O)C(CH_3)*C*H major], 101.0 [PhCH(O)C(CH_3)*C*H minor], 83.8 (C-2), 78.6 (C-3 major), 78.5 (C-3 minor), 72.3 (C-4), 66.4 (C-5 minor), 66.3 (C-5 major), 62.7 [PhCH(O)*C*(CH_3)CH minor], 62.6 [PhCH(O)-*C*(CH_3)CH major], 60.6 [Ph*C*H(O)C(CH_3)CH major], 60.3 [Ph*C*H(O)C(CH_3)CH minor], 26.7, 26.2 [$C(CH_3)_2$], 11.0 [PhCH(O)C(*C*H$_3$)CH minor], 10.7 [PhCH(O)C(*C*H$_3$)CH major]. HRMS (EI): $[M]^{+\cdot}$, found: 334.139740. $C_{18}H_{22}O_6$ requires 334.141639. Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.67; H, 6.84.

4.13. Hydrogenolysis reactions

A solution of compounds **47**, **34**, **38** or **40** (0.5 mmol) in methanol (10 mL) was hydrogenolysed over 10% Pd (C) (50 mg) at room temperature and atmospheric pressure. TLC indicated complete reaction after one night for **47**, **38**, and **40**, and after 2 days for **34**. The mixture was diluted with methanol, after which the catalyst was filtered off and washed with methanol, and the filtrate then concentrated to dryness under reduced pressure. Compounds **48**–**51** were obtained as mixtures of diastereoisomers.

4.13.1. 1-Dodecyl 2-acetamido-2-deoxy-4,6-*O*-[(1*R*,2*S*)-2-hydroxy-3-phenylpropylidene]-β-D-allopyranoside 48. Two stereoisomers were obtained in an 85:15 ratio (70% de). The pure diastereoisomeric mixture was purified by flash chromatography on silica gel, using dichloromethane–methanol (40:1) as eluent. Yield 0.20 g (77%); mp 162–164 °C; $[\alpha]_D = -33.6$ (*c* 0.7, $CHCl_3$); MS (CI): *m*/*z* 522 (20%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 6.00 (d, 1H, $J_{2,NH}$ 9.0 Hz, NH), 4.61 (d, $J_{1,2}$ 8.5 Hz, H-1 major), 4.56 (d, $J_{1,2}$ 8.1 Hz, H-1 minor), 4.46 [d, *J* 3.3 Hz, PhCH_2CH(OH)C*H* minor], 4.45 [d, *J* 3.3 Hz, PhCH_2CH(OH)C*H* major], 4.28 (dd, $J_{5,6e}$ 5.1 Hz, $J_{6e,6a}$ 10.5 Hz, H-6_e minor), 4.24 (m, 1H, H-3), 4.22 (dd, $J_{5,6e}$ 5.0 Hz, $J_{6e,6a}$ 10.3 Hz, H-6_e major), 4.04 (dt, 1H, $J_{2,3}$ 2.9 Hz, $J_{1,2}$ 8.8 Hz, H-2), 3.9–3.8 (m, 3H, H-4, H-5, OC$H_A$$H_BR, PhCH_2$C*H*(OH)CH), 3.55 (t, $J_{5,6a} = J_{6e,6a}$ 10.4 Hz, H-6_a minor) 3.54 (t, $J_{5,6a} = J_{6e,6a}$ 10.4 Hz, H-6_a major), 3.4 (m, 2H, H-4, OC$H_A$$H_B$R), 2.88 [dd, J_{gem} 13.9 Hz, *J* 5.7 Hz, PhC$H_A$$H_B$CH(OH)CH major], 2.86 [dd, J_{gem} 13.5 Hz, *J* 5.5 Hz, PhC$H_A$$H_B$CH(OH)CH minor], 2.81 [dd, J_{gem} 13.9 Hz, *J* 7.9 Hz, PhC$H_A$$H_B$CH(OH)CH major], 2.79 [dd, J_{gem} 14.0 Hz, *J* 7.8 Hz, PhC$H_A$$H_B$-CH(OH)CH minor], 1.97 (s, CH_3CON major), 1.95 (s, CH_3CON minor), 1.7–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3H, *J* 6.9 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.7 (C=O), 137.4–126.7 (Ph), 101.5 [PhCH_2CH(OH)*C*H minor], 101.4 [PhCH_2CH(OH)*C*H major], 100.2 (C-1), 78.4 (C-4 minor), 78.3 (C-4 major), 72.9 [PhCH_2*C*H(OH)CH major], 72.8 [PhCH_2*C*H(OH)CH minor], 69.9 (OCH_2R), 68.7 (C-6), 68.6 (C-3), 63.3 (C-5), 52.4 (C-2 minor), 52.3 (C-2 major), 38.3 [Ph*C*H$_2$CH(OH)CH minor], 38.2 [Ph*C*H$_2$CH(OH)CH major], 31.9–22.7 [$(CH_2)_{10}$], 23.4 (*C*H$_3$CON major), 23.3 (*C*H$_3$CON minor), 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found: 522.339611. $C_{29}H_{48}NO_7$ requires 522.343078. Anal. Calcd for $C_{29}H_{47}NO_7$: C, 66.77; H, 9.08; N, 2.68. Found: C, 66.43; H, 8.95; N, 6.82.

4.13.2. 1-Dodecyl 2-acetamido-2-deoxy-4,6-*O*-[(1*R*,2*R*)-2-hydroxy-3-phenylpropylidene]-β-D-allopyranoside 49. Two stereoisomers were obtained in a 68:32 ratio (36% de). The pure diastereoisomeric mixture was purified by flash chromatography on silica gel, using dichloromethane–methanol (40:1) as eluent. Yield 0.19 g (73%); mp 140–141 °C; $[\alpha]_D = -35.8$ (*c* 0.9, $CHCl_3$); MS (CI): *m*/*z* 522 (22%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 6.03, 6.00 (2d, $J_{2,NH}$ 9.1 Hz, 2NH), 4.60 (d, $J_{1,2}$ 8.4 Hz, H-1 major), 4.59 (d, $J_{1,2}$ 8.4 Hz, H-1 minor), 4.46 [d, *J* 3.2 Hz, PhCH_2CH(OH)C*H* major], 4.45 [d, *J* 3.2 Hz, PhCH_2CH(OH)C*H* minor], 4.3–4.2 (m, 2H, H-3, H-6e), 4.03 (dt, 1H, $J_{2,3}$ 2.9 Hz, $J_{1,2}$ 8.8 Hz, H-2), 3.9–3.8 [m, 3H, H-5, OC$H_A$$H_BR, PhCH_2$C*H*(OH)CH], 3.55 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 10.4 Hz, H-6_a), 3.4 (m, 2H, H-4, OC$H_A$$H_B$R), 2.88 [dd, J_{gem} 13.8 Hz, *J* 5.6 Hz, PhC$H_A$$H_B$-CH(OH)CH minor], 2.86 [dd, J_{gem} 13.8 Hz, *J* 5.5 Hz, PhC$H_A$$H_B$CH(OH)CH major], 2.80 [dd, J_{gem} 13.9 Hz, *J* 7.9 Hz, PhC$H_A$$H_B$CH(OH)CH minor], 2.78 [dd, J_{gem} 14.0 Hz, *J* 7.8 Hz, PhC$H_A$$H_B$CH(OH)CH major], 1.97 (s, CH_3CON major), 1.95 (s, CH_3CON minor), 1.7–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (t, 3H, *J* 6.9 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.7 (C=O), 137.4–126.7 (Ph), 101.5 [PhCH_2CH(OH)*C*H major], 101.4 [PhCH_2CH-(OH)*C*H minor], 100.2 (C-1 minor), 100.1 (C-1 major), 78.4 (C-4 major), 78.2 (C-4 minor), 72.9 [PhCH_2*C*H-(OH)CH minor], 72.8 [PhCH_2*C*H(OH)CH major], 69.9 (OCH_2R), 68.8 (C-6), 68.7 (C-3 major), 68.6 (C-3 minor), 63.3 (C-5), 52.4 (C-2 major), 52.3 (C-2 minor), 38.3 [Ph*C*H$_2$CH(OH)CH major], 38.2 [Ph*C*H$_2$CH(OH)CH minor], 31.9–22.7 [$(CH_2)_{10}$], 23.4 (*C*H$_3$CON major), 23.3 (*C*H$_3$CON minor), 14.1 (CH_3). HRMS (CI): $[M+H]^+$,

found: 522.339611. $C_{29}H_{48}NO_7$ requires 522.343078. Anal. Calcd for $C_{29}H_{47}NO_7$: C, 66.77; H, 9.08; N, 2.68. Found: C, 66.43; H, 8.95; N, 6.82.

4.13.3. 5,6-*O*-[(1*S*,2*S*)-2-Hydroxy-3-phenylpropylidene]-1,2-*O*-isopropylidene-α-D-glucofuranose 50. Two stereoisomers were obtained in an 80:20 ratio (60% de). The pure diastereoisomeric mixture was obtained by flash chromatography on silica gel, using dichloromethane–methanol (40:1) as eluent. Yield 0.13 g (74%); $[\alpha]_D = +12.6$ (*c* 0.7, CH_2Cl_2); MS (CI): *m*/*z* 353 (20%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 5H, Ph), 5.98 (d, $J_{1,2}$ 3.5 Hz, H-1 major), 5.96 (d, $J_{1,2}$ 3.3 Hz, H-1 minor), 4.80 [d, *J* 4.5 Hz, $PhCH_2CH(OH)CH$ major], 4.75 [d, *J* 4.5 Hz, $PhCH_2CH(OH)CH$ minor], 4.62 (d, $J_{1,2}$ 3.7 Hz, H-2 major), 4.55 (d, $J_{1,2}$ 3.7 Hz, H-2 minor), 4.25 (d, $J_{3,4}$ 2.0 Hz, H-3 minor), 4.23 (d, $J_{3,4}$ 2.1 Hz, H-3 major), 4.21 (m, 1H, H-5), 3.99 (m, H-4 minor), 3.95 (m, H-4 major), 3.9–3.7 [m, 3H, H-6_A, H-6_B, $PhCH_2CH(OH)CH$], 2.96 [dd, *J* 4.2 Hz, J_{gem} 14.0 Hz, $PhCH_AH_BCH(OH)CH$ major], 2.94 [dd, *J* 4.1 Hz, J_{gem} 14.1 Hz, $PhCH_AH_BCH(OH)CH$ minor], 2.75 [dd, *J* 8.5 Hz, J_{gem} 14.0 Hz, $PhCH_AH_BCH(OH)CH$ major], 2.70 [dd, *J* 8.5 Hz, J_{gem} 14.0 Hz, $PhCH_AH_BCH(OH)CH$ minor], 1.47, 1.30 [2s, $C(CH_3)_2$ minor], 1.45, 1.28 [2s, $C(CH_3)_2$ major]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.9–126.0 (Ph), 111.9 [$C(CH_3)_2$ minor], 111.8 [$C(CH_3)_2$ major], 104.9 (C-1 minor), 104.8 (C-1 major), 93.4 [$PhCH_2CH(OH)CH$ minor], 93.3 [$PhCH_2CH(OH)CH$ major], 83.8 (C-2 minor), 83.7 (C-2 major), 77.5 (C-3 minor), 77.4 (C-3 major), 74.6 (C-5 major), 74.5 (C-5 minor), 74.0 (C-4 major), 73.0 (C-4 minor), 72.8 [$PhCH_2CH(OH)CH$ major], 72.7 [$PhCH_2CH(OH)CH$ minor], 61.7 (C-6 minor), 61.6 (C-6 major), 37.7 [$PhCH_2CH(OH)CH$ minor], 37.3 [$PhCH_2CH(OH)CH$ major], 26.6, 26.1 [$C(CH_3)_2$]. HRMS (CI): $[M+H]^+$, found: 353.159327. $C_{18}H_{25}O_7$ requires 353.160028.

4.13.4. 3,5-*O*-[(1*S*,2*S*)-2-Hydroxy-3-phenylpropylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose 51. Two stereoisomers were obtained in a 63:37 ratio (26% de). The pure diastereoisomeric mixture was obtained by flash chromatography on silica gel, using dichloromethane–methanol (100:1) as eluent. Yield 0.12 g (77%); $[\alpha]_D = +10.2$ (*c* 0.7, CH_2Cl_2); MS (CI): *m*/*z* 323 (30%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 6.00 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.58 (d, $J_{1,2}$ 4.0 Hz, H-2 major), 4.56 (d, $J_{1,2}$ 4.1 Hz, H-2 minor), 4.31 [m, 2H, H-5_e, $PhCH_2CH(OH)CH$], 4.21 (d, $J_{3,4}$ 2.0 Hz, H-3 major), 4.19 (d, $J_{3,4}$ 2.3 Hz, H-3 minor), 4.02 (m, 1H, H-4), 3.92 (dd, $J_{4,5a}$ 2.0 Hz, $J_{5e,5a}$ 13.3 Hz, H-5_a major), 3.89 (dd, $J_{4,5a}$ 2.0 Hz, $J_{5e,5a}$ 13.2 Hz, H-5_a minor), 3.81 [m, 1H, $PhCH_2CH(OH)CH$], 2.94 [dd, *J* 4.0 Hz, J_{gem} 13.9 Hz, $PhCH_AH_BCH(OH)CH$ major], 2.90 [dd, *J* 3.7 Hz, J_{gem} 14.0 Hz, $PhCH_AH_BCH(OH)CH$ minor], 2.73 [dd, 1H, *J* 8.2 Hz, J_{gem} 13.9 Hz, $PhCH_AH_BCH(OH)CH$], 1.46, 1.30 [2s, 6H, $C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.7–126.3 (Ph), 111.8 [$C(CH_3)_2$], 105.5 (C-1), 99.8 [$PhCH_2CH(OH)CH$ major], 99.7 [$PhCH_2CH(OH)CH$ minor], 83.7 (C-2), 78.4 (C-3), 72.8 [$PhCH_2CH(OH)CH$ major], 72.7 [$PhCH_2CH(OH)CH$ minor], 72.3 (C-4 minor), 72.2 (C-4 major), 66.2 (C-5 major), 66.1 (C-5 minor), 37.4 [$PhCH_2CH(OH)CH$ minor], 37.3 [$PhCH_2CH(OH)CH$ major], 26.6, 26.1 [$C(CH_3)_2$]. HRMS (EI): $[M]^{+\bullet}$, found: 322.141253. $C_{17}H_{22}O_6$ requires 322.141639.

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