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Stereoselective Dihydroxylation Reaction of Alkenyl β-D-Hexopyranosides: A Methodology for the Synthesis of Glycosylglycerol Derivatives and 1-*O*-Acyl-3-*O*-β-D-glycosyl-*sn*-glycerol Analogues

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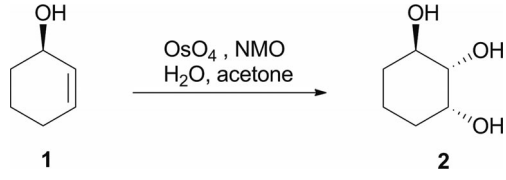
A variety of new glycosylglycerol derivatives have been prepared by stereoselective dihydroxylation of a range of alkenyl β-D-hexopyanosides under Donohoe's conditions. We have studied the relationship between the diastereoisomeric excess and the structural features of the precursor (sugar and alkenyl moieties). The stereochemical yields demonstrated that the presence of a hydrogen-bond donor group (OH, NHAc) at the 2-position of the sugar moiety is required to obtain high levels of stereofacial discrimination. New 1-*O*-acyl-3-*O*-β-D-glycosyl-*sn*-glycerol analogues were obtained by functionalisation of the primary hydroxy group with a fatty acid. Preliminary cytotoxic activity assays of both glycosylglycerol and glycoglycerolipid analogues are also presented.

Introduction

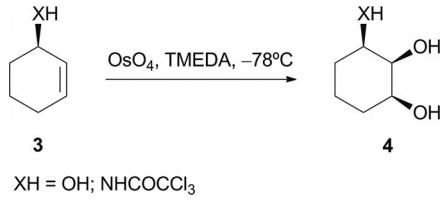
Osmium-mediated dihydroxylation is one of the most synthetically useful reactions and is tolerant of a wide array of functional groups. The basic premise of the reaction is the *syn* addition of the hydroxy groups across a C=C bond to produce 1,2-glycols.[1–6] The utility of this reaction in the field of organic synthesis is enhanced by the easy transformation of the 1,2-diol products into other synthetically useful intermediates. This becomes more important when these synthetic intermediates are the precursors of products with biological activity.[7]

In the field of diastereoselective dihydroxylation of substituted alkenes, the most useful compounds that have been subjected to these protocols are cyclic allylic alcohols and amides. In 1983, Kishi and co-workers reported a thorough study of the dihydroxylation of allylic alcohols and showed that the double bond is oxidised from the face opposite the hydroxy group under standard conditions (OsO_4/NMO), being driven by steric factors[8] (Scheme 1).

Donohoe et al. disclosed the use of an osmium tetroxide–tetramethylethylenediamine (TMEDA) complex for the synthesis of the *syn* diol. The product is obtained as a consequence of a hydrogen bond formed between the hydroxy group of the allylic alcohol and the oxo ligands, which act as efficient hydrogen-bonding acceptors, and thus the dihydroxylation occurs on the same face as the hydroxy group of the allylic alcohol.[9] They also reported the direct dihydroxylation of a range of cyclic allylic amides with this system, describing the same hydrogen-bonding control leading to the *syn* stereoisomer[10] (Scheme 2).



Scheme 1. Hydroxy-directed dihydroxylation.



Scheme 2. TMEDA-stereocontolled reaction.

Our research group has a long-term interest in the use of carbohydrates in asymmetric processes. In this sense, we have employed carbohydrate derivatives as chiral templates for the stereoselective synthesis of different compounds: diamino sugars, chiral oxazolidines, highly functionalised new

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β-enamino ketones and compounds with potential anti-cancer activity.[11]

On the other hand, searching for new methods for the stereoselective synthesis of relevant functions such as cyclopropanes[12] and oxiranes, our research involves the use of carbohydrates as chiral inducers in asymmetric transformations of olefins, with the olefinic chain joined to different positions of the sugar moiety through various functions.

Focusing on the development of epoxidation reactions of olefins with high stereocontrol (diastereoselectivity), our group has described the stereoselective epoxidation of olefin moieties linked through various functionalities (glycoside,[13,14] amide[15] and acetal[16]) to different positions of carbohydrate residues with *m*-chloroperoxybenzoic acid as oxidant under mild conditions. The different types of chiral epoxides obtained (epoxy glycosides, epoxy amides and epoxy acetals) can be transformed into a variety of compounds.

Herein we present our research focused on the development of stereoselective osmium-mediated dihydroxylation reactions employing carbohydrate derivatives as chiral templates. To prepare the compounds to be dihydroxylated, first we decided to join the alkenyl moiety to the sugar residue through a glycosidic bond. Previously we have described the stereoselective epoxidation reactions of a variety of alkenyl β-D-*gluco*- and β-D-*galacto*-pyranoside derivatives as an efficient methodology for obtaining new chiral epoxyalkyl-β-D-hexopyranoside derivatives.[13,14,17] We attempted to assess the behaviour of alkenyl glycosides as chiral templates in osmium-mediated dihydroxylation reactions. Secondly, we had to decide on the appropriate sugar residue to act as chiral inductor. We have chosen β-D-*galacto*- and β-D-*gluco*-pyranoside derivatives with different substitution patterns at the 2- and 3-positions of the sugar moiety. Thirdly, a range of allylic alcohols were used in the glycosylation reaction to explore both the stereoselectivity and the substrate scope of the reaction.

With a view to addressing this goal, we present herein our choice of scaffold, namely structure **5**,[13] to act as precursor as it fulfils all the requirements stated above (Figure 1).

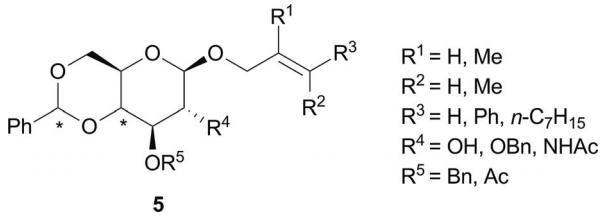

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Figure 1. General structure of the alkenyl β-D-hexopyranosides.

Glycolipids are glycoconjugates that are widespread in bacteria, plants and animals. They serve a variety of functions in nature. Glycoglycerolipids are one of a class of glycolipids that are common constituents of plant cell membranes and bacterial cell walls. They consist of one or more monosaccharide units and fatty acid residues linked by a glycerol moiety. A large number of natural glycoglycerolipids have been found to have biological and pharmacological activities, including antitumour, HIV-1 infection inhibitory and antiinflammatory activities.[18]

Natural acyl mono- and diglycosylglycerols, generally galactolipids in which the sugar is linked to the 3-position of *sn*-glycerol, have attracted attention as antitumour-promoting compounds.[19] The search for effective chemo-preventing agents is focused on the synthesis of new glycoglycerolipid analogues and biological evaluation to clarify the structural features necessary for the antitumour-promoting activity.[20] In this context we have started a research program based on the synthesis of new glycoglycerolipid analogues. We present herein new glycosylglycerol analogues **6**, obtained by an easy and efficient dihydroxylation of alkenyl β-D-*gluco*- and β-D-*galacto*-pyranoside derivatives (Figure 2). Finally the lipophilic chain was linked to the glycosylglycerol skeleton through an ester and/or amide function, producing new glycoglycerolipid analogues.

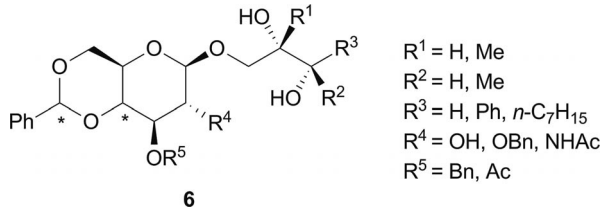

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Figure 2. General structure of the new glycosylglycerol analogues.

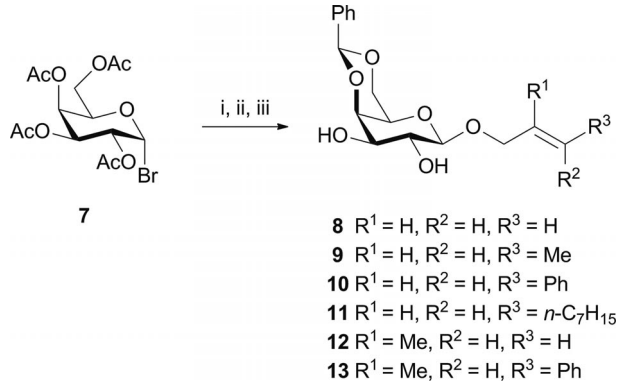
Biological tests of both glycosylglycerol and glycoglycerolipid analogues are in an initial state and preliminary results are presented.

Results and Discussion

Development of Stereoselective Osmium-Mediated Dihydroxylation Reactions: Synthesis of New Glycosylglycerol Analogues

To synthesise the new glycosylglycerol analogues we have developed a highly diastereoselective osmium-mediated dihydroxylation reaction of alkenyl β-D-hexopyranoside derivatives. We have employed D-galactose, D-glucose and 2-acetamido-2-deoxy-D-glucose as sugar precursors. Our objective was to achieve a set of functionalised substances with a well-defined stereochemistry that differ in the type of incorporated alkenyl moiety as well as in the sugar residue and its substituents.

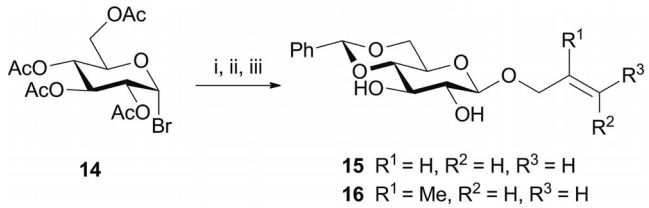
The alkenyl β-D-galactopyranosides were prepared following a short synthetic sequence that starts from the commercially available α-D-acetobromogalactose **7**. These alkenyl 4,6-*O*-(*S*)-benzylidene-D-galactopyranosides **8**–**13** have been described previously by our group and were obtained in good chemical yields (87–92%) as a single diastereoisomer[13] (Scheme 3).



Scheme 3. Reagents and conditions: (i) $HOCH_2CR^1{=}CR^2R^3$, $MeNO_2$/PhMe, $Hg(CN)_2$, 50 °C, 2–3 h; (ii) NaMeO, MeOH; (iii) $PhCH(OMe)_2$, MeCN, CSA, 87–92%.

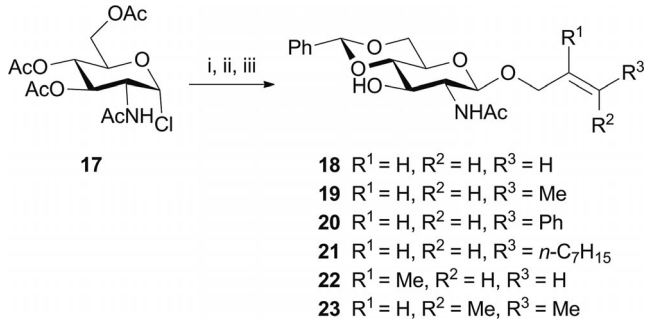
In all the NMR spectra the proton of the 4,6-*O*-(*S*)-benzylidene acetal appears as a singlet between 5.55 and 5.57 ppm, and the anomeric proton as a doublet at around 4.30 ppm in those cases in which its signal is resolved.

By using 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**14**) as the starting material and employing the same methodology we prepared alkenyl β-D-glucopyranoside derivatives **15**[21] and **16** in good yields (Scheme 4).



Scheme 4. Reagents and conditions: (i) $HOCH_2CR^1{=}CR^2R^3$, $MeNO_2$/PhMe (1:1), $Hg(CN)_2$, 50 °C, 2–3 h; (ii) NaMeO, MeOH; (iii) $PhCH(OMe)_2$, MeCN, CSA (10 mg), 81%.

The reaction of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride (**17**)[22] with the corresponding unsaturated alcohols gave the corresponding acetylated intermediates, which were subjected to deacetylation, and subsequent reaction with benzaldehyde dimethyl acetal gave compounds **18**–**23** (Scheme 5). Compound **18** has previously been described in the literature[23] and compounds

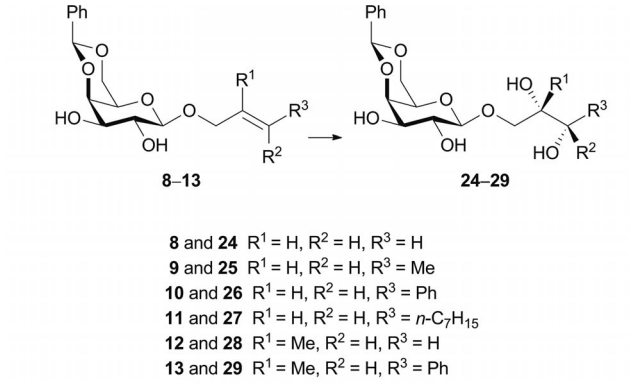


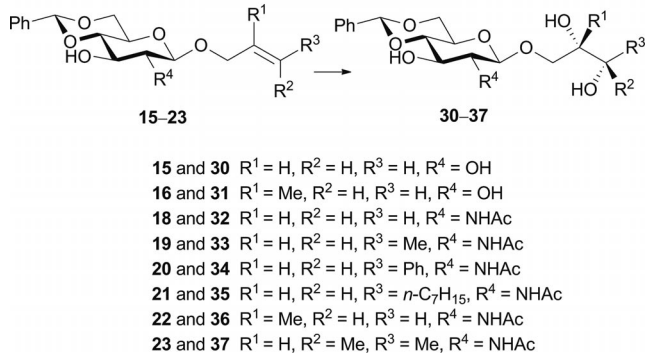
Scheme 5. Reagents and conditions: (i) $HOCH_2CR^1{=}CR^2R^3$, $MeNO_2$/PhMe (1:1), $Hg(CN)_2$, 1–2 d; (ii) NaMeO, MeOH; (iii) $PhCH(OMe)_2$, MeCN, CSA (10 mg), 80–90%.

19, **20** and **22**–**23** have previously been synthesised by our group.[14]

With the alkenyl β-D-hexopyranoside derivatives in hand, we performed assays to develop an effective stereoselective dihydroxylation of the double bond. First, we tried standard catalytic conditions (OsO_4 catalytic/NMO) with compounds **12** (*galacto* derivative) and **15** (*gluco* derivative), but the reactions showed no stereoselectivity. We then looked at the work of Donohoe and co-workers, who reported the direct dihydroxylation of a range of cyclic allylic alcohols and amides with the formation of the *syn* stereoisomer with high stereocontrol.[9,10]

The 2,3-dihydroxyalkyl β-D-hexopyranosides **24**–**37** were synthesised by employing Donohoe's conditions: sugar derivatives (1.0 mmol), TMEDA (1.1 mmol) and OsO_4 (1.05 mmol). Compounds **8**–**13**, **15**, **16** and **18**–**23** were used as precursors. This is the first report of the dihydroxylation of alkenyl sugar derivatives employing these conditions (Scheme 6). The dihydroxylated derivatives were isolated in satisfactory chemical yields (50–90%). Stereochemical yields (*de*s) were established by ^1H NMR spectroscopy and are summarised in Table 1.





Scheme 6. Reagents and conditions: TMEDA, OsO_4, CH_2Cl_2, –78 °C, 2 h.

The diastereoisomeric excesses of the products from the dihydroxylation of D-galactose derivatives were low (entries 1–6) with the exception of compounds **24** and **28**, which were obtained with high *de* (60 and 78%, respectively, entries 1 and 5). The presence of the methyl group at the 2-position of the olefin seems to slightly increase the diastereoisomeric excess [compare entry 1 (R^1 = H) vs. entry 5 (R^1 = Me) and entry 3 (R^1 = H) vs. entry 6 (R^1 = Me)].

Table 1. Asymmetric osmium-mediated dihydroxylation of alkenyl β-D-galactopyranosides derivatives **8**–**13** and β-D-glucopyranosides derivatives **15**, **16** and **18**–**23**.

Entry	Compd.	R^1	R^2	R^3	R^4	Yield[a] [%]	*de*[b] [%]
1	**24**	H	H	H	–	88	60
2	**25**	H	H	Me	–	53	9
3	**26**	H	H	Ph	–	52	–
4	**27**	H	H	*n*-C_7H_{15}	–	80	9
5	**28**	Me	H	H	–	91	78
6	**29**	Me	H	Ph	–	66	13
7	**30**	H	H	H	OH	60	–
8	**31**	Me	H	H	OH	72	43
9	**32**	H	H	H	NHAc	92	>99
10	**33**	H	H	Me	NHAc	75	>99
11	**34**	H	H	Ph	NHAc	82	>99
12	**35**	H	H	*n*-C_7H_{15}	NHAc	65	>99
13	**36**	Me	H	H	NHAc	81	>99
14	**37**	H	Me	Me	NHAc	63	50

[a] Yields after column chromatography. [b] Diastereoisomeric excesses were determined by relative integration of the ^{1}H NMR spectra of the reaction mixtures.

In the case of the D-glucose derivatives, as for the D-*galacto* derivatives, the diastereoselectivity increased when a methyl group is present at the 2-position of the olefin moiety [entry 7 (R^1 = H) vs. entry 8 (R^1 = Me)].

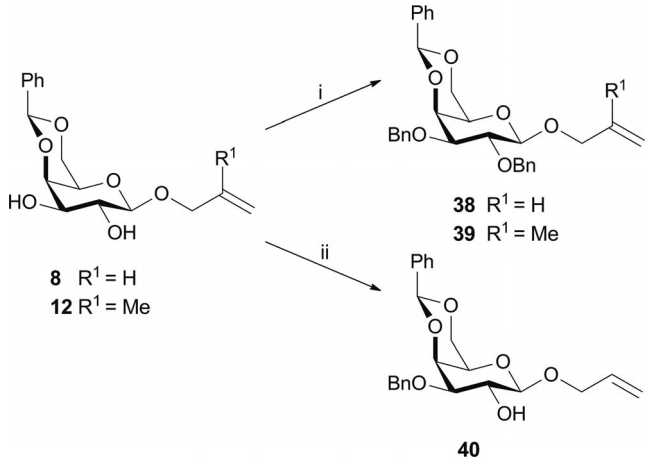
The alkenyl 2-acetamido-2-deoxy-D-glucopyranoside derivatives reacted in virtually all cases with practically complete stereoselectivity (entries 9–14). The diastereomeric excess was only moderate (50%) in the reaction of the 3,3-disubstituted olefin, compound **37** (entry 14).

In view of the results presented in Table 1, we can conclude that the best chiral inductor is the residue of 2-acetamido-2-deoxy-D-glucopyranoside, which provided total stereoselectivity regardless of the structure of the alkenyl moiety. For the same alkenyl residue, the D-galactose derivatives gave lower levels of stereoselectivity (compare entries 1–5 vs. entries 9–13) with moderate-to-good *de* values obtained with terminal olefins. For the D-glucopyranoside derivatives the diastereomeric excess decreased even more.

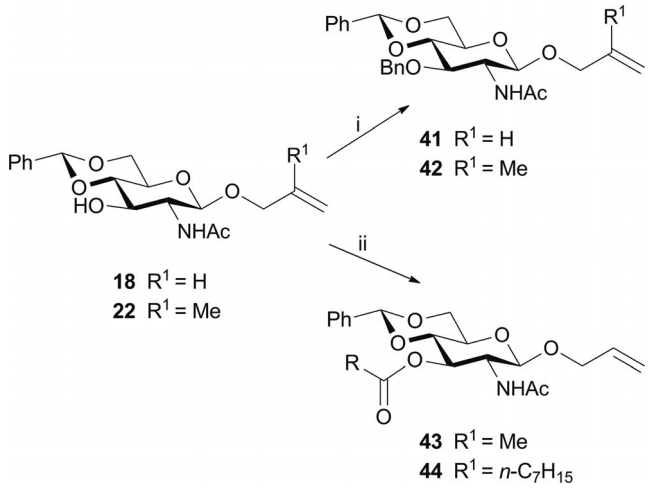
To have a higher number of substrates to subject to dihydroxylation and focusing primarily on analysing the influence of hydroxy groups at the 2- and 3-positions of the sugar on the stereochemical yields, we also prepared mono- and diprotected derivatives. We chose those substrates that yielded diols in high diastereoisomeric excesses, that is, those derived from D-galactose and 2-acetamido-2-deoxy-D-glucose.

We carried out dibenzylation and selective monobenzylation reactions (selective at the 3-position) with the *galacto* derivatives **8**[24] and **12**. In both cases we employed the same method but with rigorous control of the amounts of reagents and of the reaction time (3 h and 20 min, respectively) according to a method previously described[13] for the preparation of monoprotected derivatives (Scheme 7).

The alkenyl 2-acetamido-2-deoxy-β-D-glucopyranoside derivatives **18** and **22** were also subjected to the 3-*O*-protection reaction. To protect the hydroxy group we decided to employ both ether (benzyl) and ester (acetyl and capriloyl) functions. Compounds **41**–**44**[14] were synthesised in high yields (Scheme 8).

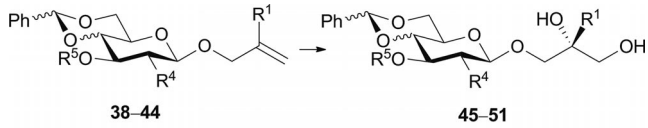


Scheme 7. Reagents and conditions: (i) KOH, 18-crown-6, BnBr, THF, 3 h, 58%; (ii) KOH, 18-crown-6, BnBr, THF, 20 min, 88%.



Scheme 8. Reagents and conditions: (i) KOH, 18-crown-6, BnBr, THF, 3 h, 70%; (ii) DAMP, acid chloride, CH_2Cl_2, 0 °C, 3 h, 60–80%.

Compounds **38**–**44** were then subjected to osmium-mediated dihydroxylation under the same conditions as described above (Scheme 9). The chemical and stereochemical yields are presented in Table 2.



38 and **45** R^1 = H, R^4 = OBn, R^5 = Bn, *galacto*
39 and **46** R^1 = Me, R^4 = OBn, R^5 = Bn, *galacto*
40 and **47** R^1 = H, R^4 = OH, R^5 = Bn, *galacto*
41 and **48** R^1 = H, R^4 = NHAc, R^5 = Bn, *gluco*
42 and **49** R^1 = Me, R^4 = NHAc, R^5 = Bn, *gluco*
43 and **50** R^1 = H, R^4 = NHAc, R^5 = $COCH_3$, *gluco*
44 and **51** R^1 = H, R^4 = NHAc, R^5 = *n*-$C_7H_{15}CO$, *gluco*

Scheme 9. Reagents and conditions: TMEDA, OsO_4, CH_2Cl_2, –78 °C, 2 h.

Table 2. Asymmetric osmium-mediated dihydroxylation of alkenyl β-D-hexopyranosides derivatives **38**–**44**.

Entry	Compd.	R^1	R^4	R^5	Sugar	Yield[a] [%]	*de*[b] [%]
1	**45**	H	OBn	Bn	*galacto*	82	–
2	**46**	Me	OBn	Bn	*galacto*	70	20
3	**47**	H	OH	Bn	*galacto*	66	68
4	**48**	H	NHAc	Bn	*gluco*	78	>99
5	**49**	Me	NHAc	Bn	*gluco*	75	>99
6	**50**	H	NHAc	$COCH_3$	*gluco*	81	>99
7	**51**	H	NHAc	$CO(CH_2)_6CH_3$	*gluco*	82	43

[a] Yields after column chromatography. [b] Diastereoisomeric excesses were determined by relative integration of the ^{1}H NMR spectra of the reaction mixtures.

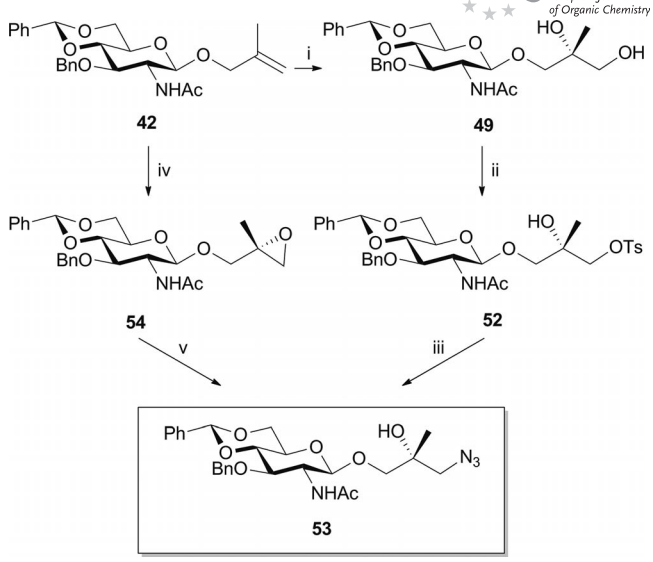
As can be seen from Table 2, 2,3-di-*O*-benzyl *galacto* derivatives **45** and **46** were obtained with low *de* values (entries 1 and 2). Compounds **24** and **28**, *galacto* derivatives with the same alkenyl moiety but with the 2- and 3-positions unprotected, gave high *de* values (60 and 78%, respectively, Table 1, entries 1 and 5). Compound **47**, the 3-*O*-benzyl *galacto* derivative, was obtained in high stereochemical yield (68%). Based on this result it can be concluded that the presence of a OH group at the 2-position of the sugar is determinant for the stereoselectivity of the reaction, attributed to the formation of a hydrogen bridge.[9,10]

However, the 3-*O*-protection of 2-acetamido-2-deoxy *gluco* derivatives (benzyl ether and acetyl ester) did not affect the stereochemical yield. Compounds **48**–**50** were essentially obtained as one diastereoisomer (entries 4–6). This suggests that the amide function at the 2-position also acts as a hydrogen-bond donor and directs the stereochemical course of the reaction. When a capriloyl ester is present at the 3-position the *de* falls (43%, entry 7), probably due to steric interactions.

Stereochemical Assignment

Our next objective was the assignment of the configurations of the new stereogenic centres in the glycol moieties formed in the dihydroxylation reactions. With this goal in mind we prepared the azide derivative **53** from two different compounds through short synthetic sequences. We employed compound **49**, a new glycosylglycerol analogue obtained by the dihydroxylation reaction, and the appropriate epoxyalkyl derivative **54** as precursors (Scheme 10). Note that this epoxide has previously been prepared in high diastereomeric yield from the alkenyl glucopyranoside **42** by a stereoselective epoxidation reaction; it was assigned an *R* configuration.[14]

We compared the chemical shifts of the easily identifiable protons and carbons of compound **53**, obtained by each of the two routes. The ^{1}H and ^{13}C NMR spectra of **53** prepared from glycol **49** present a single set of signals (*de* > 99%). In contrast, compound **53** was obtained as a diastereomeric mixture (70% *de*) from the epoxyalkyl derivative **54**. The chemical shifts of the protons of the major diastereoisomer were identical to the single signals of compound **53** obtained from **49** (Table 3). These correlation



Scheme 10. Reagents and conditions: (i) TMEDA, OsO_4, CH_2Cl_2, –78 °C, 2 h, 75%; (ii) DAMP, tosyl chloride, CH_2Cl_2, 0 °C, 5 h, 82%; (iii) NaN_3, DMF, 70 °C, 18 h, 82%; (iv) *m*-CPBA (Aldrich 57–86%), CH_2Cl_2, –15 °C, 1 month, 83%; (v) NaN_3, $LiClO_4$, CH_3CN, 80 °C, 10 h, 82%.

studies led us to assign the *R* configuration to the glycol formed and, by extension, the *Re* notation to the most reactive face. We tentatively propose the mechanism shown in Figure 3.

Table 3. NMR spectroscopic data for characteristic protons in compound **53** obtained by two routes.[a]

Entry	Compd.	δ [ppm]				
		NH	1-H	3-H	CH_3CON	*de*[b] [%]
		M/m	M/m	M/m	M/m	
1	**53**[c]	5.32	4.77	3.92	1.88	>99
2	**53**[d]	5.32/5.38	4.77/4.83	3.92/4.02	1.88/1.89	71

[a] M/m represents major/minor diastereomer. [b] Diastereoisomeric excesses were determined by relative integration of the ^{1}H NMR spectra of the reaction mixtures. [c] Compound **53** obtained from compound **49** as precursor. [d] Compound **53** obtained from compound **54** as precursor.

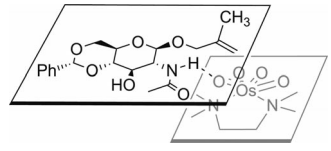
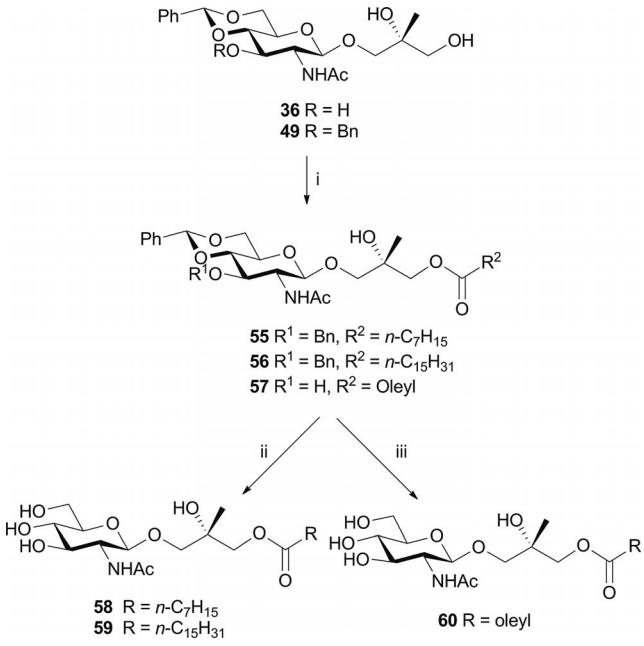


Figure 3. Mechanism tentatively proposed to explain the *Re* face attack favored.

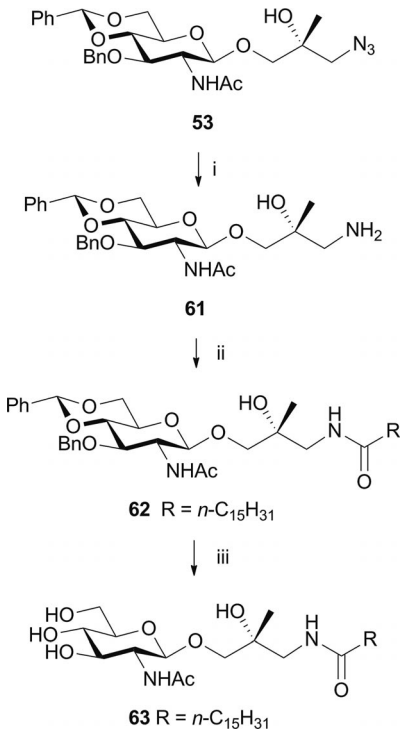
Synthesis of New Glycoglycerolipid Analogues

In the design of new glycoglycerolipids, the structural features usually taken into consideration are the nature of the saccharidic residue, the anomeric configuration of the glycosidic linkage and the length and position of the acyl residue situated on one of the primary hydroxy groups of the glycerol moiety.[20]

Three key issues must be addressed in our planned synthesis of glycoglycerolipds. First, the glycerol moiety must be attached to the sugar. Our synthetic approach involved the preparation of an optically active glycerol moiety linked to the β-hexopyranoside residue (the β configuration is present in natural bioactive glycosylglycerols)[19] through the stereoselective dihydroxylation of alkenyl β-D-hexopyranosides. Other synthetic approaches involve glycosylation with an optically active glycerol component yielding different α/β stereoselectivities.[25] Secondly, *O*-acylation of the primary hydroxy group with a fatty acid must be performed. We have employed capriloyl and palmitoyl moieties as examples of short and medium fatty acid residues and, with the objective of expanding the acyl residues on the primary OH, the oleyl residue was also used. Thirdly, the protecting groups must be eliminated. In this way, compounds **58**–**60** were obtained in high yields (Scheme 11).



Scheme 11. Reagents and conditions: (i) DAMP, acid chloride, CH_2Cl_2, 0 °C, 3 h, 50–78%; (ii) H_2/Pd-C, 4 bar; (iii) 80% acetic acid/water, 60 °C, 5 h, 85%.



Scheme 12. Reagents and conditions: (i) H_2/Pd-C, 1 bar, 4 h; (ii) DAMP, acyl chloride, CH_2Cl_2, 0 °C, 3 h, 71%; (iii) H_2/Pd-C, 4 bar, 24 h, 80%.

Finally, we planned the synthesis of analogues in which the lipophilic chain is linked to the glycosylglycerol skeleton through bonds chemically and enzymatically more stable than an ester. The designed analogue should be an isoster of our acylglycosylglycerol. We chose the amide function taking advantage of the azido derivative **53** prepared for the stereochemical study and performed its selective reduction to the amino group and subsequent acylation (Scheme 12).

Evaluation of Cytotoxic Activity

To examine the cytotoxic activity of our compounds against cancer cells they were tested in vitro against A549 human lung cancer cells by using the MTT method. To evaluate the selectivity of our compounds towards tumour and normal cells, they were also tested in an MTT assay against MRC5 human non-malignant lung fibroblasts (for conditions of the MTT assay, see the Exptl. Sect.). We carried out these early biological tests to evaluate both the cytotoxicity and selectivity of the glycosylglycerol and glycoglycerolipid analogues.

First, we evaluated the 1-*O*-acyl-3-*O*-2-acetamido-2-deoxy-β-D-glucopyranosyl-*sn*-glycerol derivatives **58**–**60** and the analogue **63** with an amide function. As reference compound we employed cisplatin, a drug with cytotoxic activity, to truly gauge the effectiveness of our compounds.

The viability of human lung cancer cells A549 and human non-malignant lung fibroblasts MRC5 treated for 48 h with several concentrations of each compound is shown in Figures 4–7.

Figure 4 shows the results for compound **58**, the capriloyl derivative, which showed low cytotoxic activity ($IC_{50} >$ 1000 μM).

Figure 5 and Figure 7 show the results for compounds **59** and **63**, both palmitoyl derivatives with an ester or amide function. As can be seen, in spite of showing cytotoxic activity (IC_{50} = 44.80 and 81.97 μM, respectively, for the reference compound IC_{50} = 11.67), these compounds did not show selective activity towards the cancer cell line.

However, compound **60** showed an intermediate situation. Its activity was less than those of **59** and **63** (IC_{50} = 362.00 μM), but in this case the cancer cells were more susceptible than normal cells to its cytotoxic activity (Figure 6).

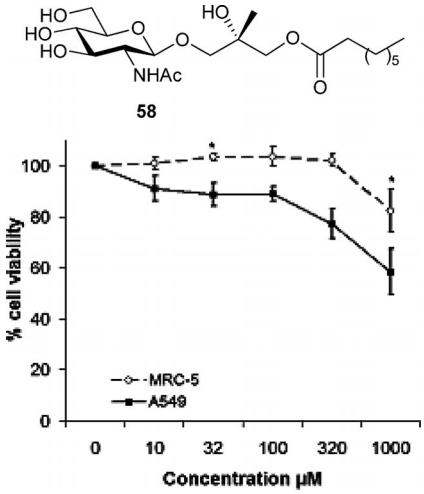


Figure 4. Percentage cell viability (± SEM) in A549 and MRC5 cells exposed to compound **58** for 48 h determined by the MTT assay.

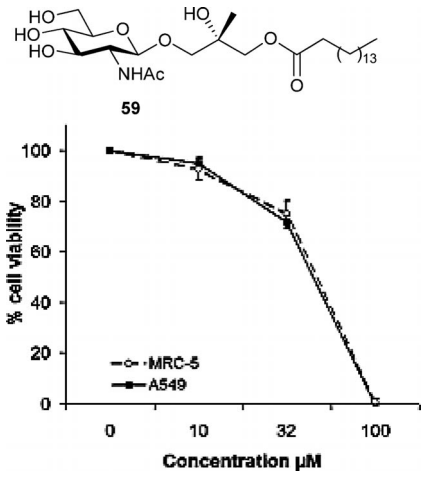


Figure 5. Percentage cell viability (± SEM) in A549 and MRC5 cells exposed to compound **59** for 48 h determined by the MTT assay.

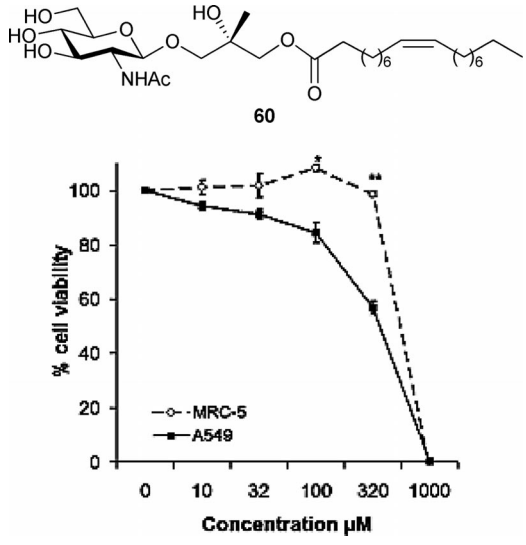


Figure 6. Percentage cell viability (± SEM) in A549 and MRC5 cells exposed to compound **60** for 48 h determined by the MTT assay.

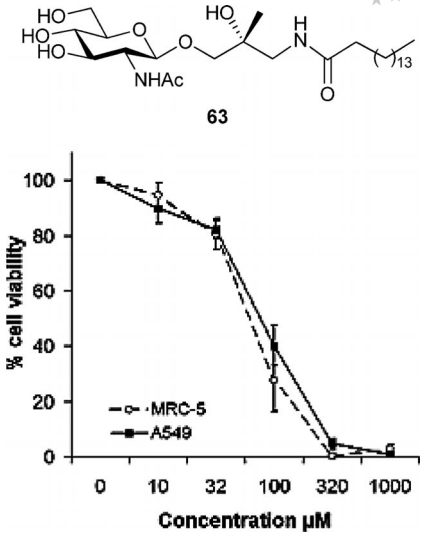


Figure 7. Percentage cell viability (± SEM) in A549 and MRC5 cells exposed to compound **63** for 48 h determined by the MTT assay.

These four compounds have the same sugar and glycerol moieties. The only different structural feature between them is the acyl group at the 1-position of the glycerol. The presence of the oleyl group in compound **60** increases the selectivity against cancer cells in this kind of compounds.

We also evaluated the glycosylglycerol analogues **27** and **36**, *galacto* and *gluco* derivatives, respectively (Figures 8 and 9).

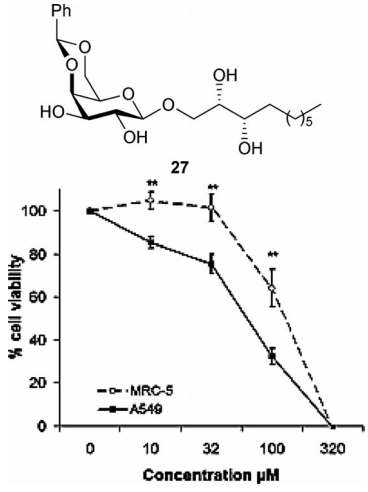


Figure 8. Percentage cell viability (± SEM) in A549 and MRC5 cells exposed to compound **27** for 48 h determined by the MTT assay.

Figure 8 shows the results of compound **27**. In addition to showing cytotoxic activity (IC_{50} = 63.58 μM), this compound also showed selectivity; the viability of normal cells MRC-5 was higher than the viability of cancer cells A549.

Compound **36** was chosen for cytotoxicity testing because it is the glycol precursor of the acyl glycerol analogues that were tested. As shown in Figure 9, it was neither biologically active nor selective.

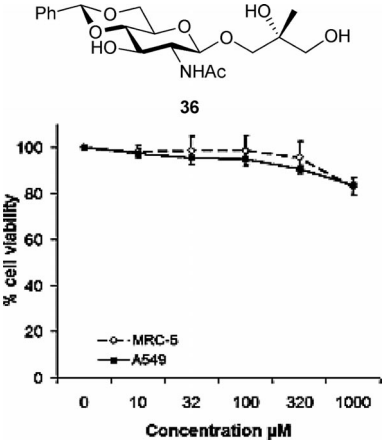


Figure 9. Percentage cell viability (± SEM) in A549 and MRC5 cells exposed to compound **36** for 48 h determined by the MTT assay.

Conclusions

We have described the stereoselective dihydroxylation of alkenyl β-D-hexopyranosides under Donohoe's conditions. We have demonstrated the decisive role of a hydrogen-bond donor group (OH, NHAc) at the 2-position of the sugar moiety in the stereochemical control of the reaction. We have also studied the influence of the sugar residue on the stereoselectivity of the reaction. The 2-acetamido-2-deoxy-β-D-glucopyranoside derivative was found to be the best chiral inductor, giving >99% *de* irrespective of the structure of the alkene. The chiral agent capability of the D-galactose residue was lower and dependent on the structure of the alkene moiety.

By using different sugar moieties and allylic alcohols this becomes an efficient methodology for the stereoselective synthesis of a wide variety of new glycosylglycerol analogues and, by their use as precursors, of new 1-*O*-acyl-3-*O*-β-D-glycosyl-*sn*-glycerol analogues.

We have also presented our preliminary results on cytotoxicity assays.

At present we are preparing more compounds by this methodology and studying the relationship between the structural features of our compounds (sugar, alkenyl and acyl moieties) and their cytotoxic activity and selectivity.

Experimental Section

Materials and General Methods: Evaporations were conducted under reduced pressure. Preparative chromatography was performed on silica gel 60 (E. Merck). Kieselgel 60 F254 (E. Merck) was used for TLC. Melting points were obtained with an SMP 10 Stuart Melting Point apparatus. Optical rotations were obtained with a Perkin–Elmer Polarimeter Model 341 at 25 °C. Mass spectra were recorded with a Micromass AUTOSPECQ mass spectrometer: EI at 70 eV and CI at 150 eV, HR measurements with resolutions of 10000. FAB-MS were recorded by using a thioglycerol matrix. NMR spectra were recorded at 25 °C with a Bruker AMX500 and AV500 spectrometers 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, HSQC and NOESY experiments were performed to assign the signals in the NMR spectra.

Alkenyl β-D-Glucopyranosides 16 and 21: Mercury cyanide (2.54 g, 10.0 mmol), 4 Å molecular sieves (5 g) and the corresponding unsaturated alcohol (10.0 mmol) were added to a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**14**; 2.06 g, 5.0 mmol) in nitromethane/toluene (1:1, 30 mL). The mixture was heated at 50 °C with stirring until TLC showed that all the starting material had reacted (2–3 h). The solid was filtered through Celite and washed with toluene. The organic layer was washed with an aqueous saturated solution of sodium hydrogen carbonate and brine, then dried ($MgSO_4$), evaporated to dryness and purified by column chromatography. For compound **21**, with 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosyl chloride as starting material, the glycosidation reaction was carried out at room temperature for 1–2 d. A solution of sodium methoxide (1 mmol) in methanol (5 mL) was added to a solution of the corresponding acetylated alkenyl β-D-glucopyranoside in methanol (50 mL). After 30 min at room temperature, the solution was neutralised by the addition of Dowex 50 resin (H^+ form), filtered and the solvents evaporated to dryness. Benzaldehyde dimethyl acetal (10.0 mmol) and camphorsulfonic acid (10 mg) were added to a solution of the corresponding alkenyl β-D-glucopyranoside in acetonitrile (30 mL). The mixture was stirred at room temperature until TLC showed that all the starting material had reacted. Then triethylamine was added until pH 7. The reaction mixture was evaporated and the compound obtained was purified by column chromatography to give compounds **16** and **21** in good yields.

2-Methyl-2-propenyl 4,6-*O*-(*R*)-Benzylidene-β-D-glucopyranoside (16): Purification by column chromatography using hexane/ethyl acetate (1.5:1) as eluent gave the compound as a white solid; yield 1.30 g (81%); m.p. 98–99 °C. $[\alpha]_D$ = –52.0 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.79 [s, 3 H, $OCH_2C(CH_3)$=CH], 3.45 (m, 1 H, 5-H), 3.53–3.59 (m, 2 H, 2-H, 3-H), 3.79 (t, *J* = 10.3 Hz, 1 H, 6_a-H), 3.84 (t, *J* = 9.1 Hz, 1 H, 4-H), 4.07, 4.28 [2 d, *J* = 12.4 Hz, 2 H, $OCH_2C(CH_3)$=CH_2], 4.35 (dd, *J* = 5.0, 10.4 Hz, 1 H, 6_e-H), 4.44 (d, *J* = 7.8 Hz, 1 H, 1-H), 4.96, 5.04 [2 m, 2 H, $OCH_2C(CH_3)$=CH_2], 5.57 (s, 1 H, PhC*H*), 7.3–7.5 (m, 5 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.5 [$OCH_2C(CH_3)$=CH_2], 66.4 (C-5), 68.7 (C-6), 73.2 (C-4), 73.3 [$OCH_2C(CH_3)$=CH_2], 74.6 (C-2), 80.6 (C-3), 101.9 (C-1), 102.0 (PhCH), 113.5 [$OCH_2C(CH_3)$=CH_2], 126.3–137.0 (Ph), 140.8 [$OCH_2C(CH_3)$=CH_2] ppm. MS (FAB): *m*/*z* (%) = 345 (60) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{17}H_{22}O_6Na$ [M + Na]$^+$ 345.1314; found 345.1320. $C_{17}H_{22}O_6$ (322.14): calcd. C 63.34, H 6.88; found C 63.21, H 6.62.

(*E*)-2-Decenyl 2-Acetamido-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (21): Purification by column chromatography using dichloromethane/methanol (20:1) as eluent gave a white solid; yield 1.60 g (72%); m.p. 230–231 °C. $[\alpha]_D$ = –31.0 (*c* = 0.5, MeOH). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 0.85 [t, *J* = 6.9 Hz, 3 H, OCH_2CH=$CH(CH_2)_6CH_3$], 1.20–1.35 [m, 10 H, OCH_2CH=$CHCH_2(CH_2)_5CH_3$], 1.80 (s, 3 H, CH_3CON), 1.98 [m, 2 H, OCH_2CH=$CHCH_2(CH_2)_5CH_3$], 3.30 (m, 1 H, 5-H), 3.41 (t, *J* = 9.3 Hz, 1 H, 4-H), 3.49 (m, 1 H, 2-H), 3.61 (m, 1 H, 3-H), 3.71 (t, *J* = 10.2 Hz, 1 H, 6_a-H), 3.93 [dd, *J* = 6.0, 12.5 Hz, 1 H, OCH_AH_BCH=$CH(CH_2)_6CH_3$], 4.11 [dd, *J* = 5.5, 12.5 Hz, 1 H, OCH_AH_BCH=$CH(CH_2)_6CH_3$], 4.18 (dd, *J* = 4.8, 9.8 Hz, 1 H, 6_e-H), 4.49 (d, *J* = 8.4 Hz, 1 H, 1-H), 5.23 (d, *J* = 5.6 Hz, 1 H, OH), 5.58 (s, 1 H, PhC*H*), 5.43 [m, 1 H, OCH_2CH=$CH(CH_2)_6CH_3$], 5.63 [m, 1 H, OCH_2CH=$CH(CH_2)_6CH_3$], 7.3–7.5 (m, 5 H, Ph), 7.78 (d, *J* = 9.0 Hz, 1 H, NH) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 13.8 [OCH_2CH=$CH(CH_2)_6CH_3$], 22.0 (CH_3CON), 23.0–31.6 [OCH_2CH=$CH(CH_2)_6CH_3$], 56.2 (C-2), 65.9 (C-5), 67.9 (C-6), 68.9 [OCH_2CH=$CH(CH_2)_6CH_3$], 70.4 (C-3), 81.3 (C-4), 100.6 (PhCH),

100.8 (C-1), 126.0 [$OCH_2CH{=}CH(CH_2)_6CH_3$], 133.2 [$OCH_2CH{=}CH(CH_2)_6CH_3$], 126.0–137.7 (Ph), 169.1 (C=O) ppm. MS (FAB): *m*/*z* (%) = 470 (100) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{25}H_{37}NO_6Na$ $[M + Na]^+$ 470.2519; found 470.2504. $C_{25}H_{37}NO_6$ (459.26): calcd. C 67.09, H 8.33, N 3.13; found C 66.83, H 8.51, N 3.39.

Allyl 2-Acetamido-4,6-*O*-(*R*)-benzylidene-3-*O*-capriloyl-2-deoxy-β-D-glucopyranoside (44): DAMP (2 mmol) and capriloyl chloride (1 mmol) were added to a solution of **18** (0.5 mmol) in dry dichloromethane (30 mL) precooled to 0 °C. The reaction mixture was stirred at 0 °C until TLC showed that all the starting material had reacted (3 h). The organic phase was successively washed with diluted hydrochloric acid, water and an aqueous saturated solution of sodium hydrogen carbonate, dried ($MgSO_4$), filtered and the filtrate was evaporated to dryness. The compound was obtained as a white solid by column chromatography using hexane/ethyl acetate (2:1) as eluent; yield 0.26 g (54%); m.p. 201–202 °C. $[\alpha]_D$ = –63.0 (*c* = 0.3, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 [t, *J* = 7.0 Hz, 3 H, $CH_3(CH_2)_5CH_2CO_2$], 1.2–1.6 [m, 10 H, $CH_3(CH_2)_5CH_2CO_2$], 1.95 (s, 3 H, CH_3CON), 2.32 [m, 2 H, $CH_3(CH_2)_5CH_2CO_2$], 3.51 (m, 1 H, 5-H), 3.70 (t, *J* = 9.4 Hz, 1 H, 4-H), 3.80 (t, *J* = 10.3 Hz, 1 H, 6_a-H), 4.02 (m, 1 H, $OCH_AH_BCH{=}CH_2$), 4.17 (m, 1 H, 2-H), 4.30–4.35 (m, 2 H, 6_e-H, $OCH_AH_BCH{=}CH_2$), 4.55 (d, *J* = 8.5 Hz, 1 H, 1-H), 5.15–5.30 (m, 2 H, 3-H, $OCH_2CH{=}CH_2$), 5.51 (s, 1 H, PhC*H*), 5.58 (d, *J* = 9.4 Hz, 1 H, NH), 5.85 (m, 1 H, $OCH_2CH{=}CH_2$), 7.35–7.45 (m, 5 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 [$CH_3(CH_2)_6CO_2$], 23.3 (CH_3CON), 22.6–34.3 [$CH_3(CH_2)_6CO_2$], 54.6 (C-2), 66.6 (C-5), 68.7 (C-6), 70.0 ($OCH_2CH{=}CH_2$), 71.5 (C-3), 78.7 (C-4), 101.2 (C-1), 101.4 (PhCH), 117.6 ($OCH_2CH{=}CH_2$), 126.1–137.0 (Ph), 133.6 ($OCH_2CH{=}CH_2$), 170.0 (CH_3CON), 174.2 [$CH_3(CH_2)_6CO_2$] ppm. MS (FAB): *m*/*z* (%) = 498 (30) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{26}H_{37}NO_7Na$ $[M + Na]^+$ 498.2468; found 498.2480. $C_{26}H_{37}NO_7$ (475.26): calcd. C 65.66, H 7.84, N 2.95; found C 65.66, H 8.03, N 3.04.

2,3-Dihydroxyalkyl β-D-Hexopyranosides 24–37 and 45–51: A solution of 0.5 M OsO_4 (1.05 mmol) in dichloromethane was added to a solution of sugar derivatives **8**–**13**, **15**, **16**, **18**–**23** and **38**–**44** (1.0 mmol) and TMEDA (1.1 mmol) in dry dichloromethane precooled to –78 °C (50 mL). The solution turned brown-black and was stirred at –78 °C until TLC showed that all the starting material had reacted (2 h). Ethylenediamine (5.0 mmol) was added to the crude reaction mixture at room temperature and the resulting solution stirred for 48 h, during which time a brown precipitate formed. The solution was concentrated under reduced pressure and the resulting residue dissolved in methanol/ethyl acetate (1:4) and filtered through Celite. The organic phase was evaporated to dryness and the compounds obtained were purified by flash chromatography on silica gel. The diastereomeric excesses (*de*) were determined by ^{1}H NMR spectroscopy.

(2*R*)-2,3-Dihydroxypropyl 4,6-*O*-(*S*)-Benzylidene-β-D-galactopyranoside (24): Two diastereoisomers were obtained in a 4:1 ratio (60% *de*). The pure diastereomeric mixture was obtained as a white solid by column chromatography using dichloromethane/methanol (7:1) as eluent; yield 0.33 g (88%); m.p. 141–142 °C. $[\alpha]_D$ = +7.0 (*c* = 0.5, MeOH). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 3.36–3.51 [m, 6 H, 2-H, 3-H, $OCH_AH_BCH(OH)CH_2OH$], 3.63 (m, 1 H, 5-H), 3.71 [dd, *J* = 5.4, 9.7 Hz, 0.8 H, $OCH_AH_BCH(OH)CH_2OH$ major], 3.84 [dd, *J* = 4.3, 10.1 Hz, 0.2 H, $OCH_AH_BCH(OH)CH_2OH$ minor], 4.06–4.08 (m, 3 H, 4-H, 6_a-H, 6_e-H), 4.22 (d, *J* = 7.6 Hz, 0.8 H, 1-H major), 4.24 (d, *J* = 7.3 Hz, 0.2 H, 1-H minor), 4.51 [m, 1 H, $OCH_AH_BCH(OH)CH_2OH$], 4.63 [d, *J* = 5.2 Hz, 0.8 H, $OCH_AH_BCH(OH)CH_2OH$ major], 4.67 [d, *J* = 4.3 Hz, 0.2 H, $OCH_AH_BCH(OH)CH_2OH$ minor], 4.91 (d, *J* = 6.1 Hz, 1 H, 2-OH), 4.99 (d, *J* = 4.4 Hz, 1 H, 3-OH), 5.57 (s, 1 H, PhC*H*), 7.3–7.5 (m, 5 H, Ph) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 63.4 (C-5 minor), 63.4 (C-5 major), 66.4 [$OCH_2CH(OH)CH_2OH$], 69.1 (C-6), 70.5 [$OCH_2CH(OH)CH_2OH$], 70.8 (C-2 major), 71.0 (C-2 minor), 71.6 (C-3 major), 71.8 (C-3 minor), 72.2 (C-4 minor), 72.3 (C-4 major), 76.5 [$OCH_2CH(OH)CH_2OH$], 100.2 (C-1), 104.1 (PhCH), 126.8–139.1 (Ph) ppm. MS (FAB): *m*/*z* (%) = 365 (100) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{16}H_{24}O_8Na$ $[M + Na]^+$ 365.1212; found 365.1224.

(2*S*,3*S*)-2,3-Dihydroxybutyl 4,6-*O*-(*S*)-Benzylidene-β-D-galactopyranoside (25): Two stereoisomers were obtained in a 1.2:1 ratio (9% *de*). The pure diastereomeric mixture was obtained as a pale-yellow syrup by column chromatography using dichloromethane/methanol (10:1) as eluent; yield 0.19 g (53%). $[\alpha]_D$ = –21.2 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.19, 1.21 [2 d, *J* = 6.4 Hz, 3 H, $OCH_2CH(OH)CH(OH)CH_3$], 3.46 (m, 1 H, 5-H), 3.55–3.85 [m, 5 H, 2-H, 3-H, $OCH_AH_BCH(OH)CH(OH)CH_3$], 3.95 [dd, *J* = 5.8, 11.1 Hz, 0.45 H, $OCH_AH_BCH(OH)CH(OH)CH_3$ minor], 4.0–4.1 [m, 1.55 H, 6_a-H, $OCH_AH_BCH(OH)CH(OH)CH_3$ major], 4.17 (m, 1 H, 4-H), 4.30 (d, *J* = 12.4 Hz, 1 H, 6_e-H), 4.34, 4.35 (2 d, *J* = 7.7 Hz, 1 H, 1-H), 5.52 (s, 1 H, PhC*H*), 7.2–7.5 (m, 5 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.3, 19.4 [$OCH_2CH(OH)CH(OH)CH_3$], 66.8 (C-5), 68.0, 68.1 (C-2), 69.0 (C-6), 71.6 [$OCH_2CH(OH)CH(OH)CH_3$], 72.7 (C-3), 74.0 [$OCH_2CH(OH)CH(OH)CH_3$], 75.2 (C-4), 101.4 (PhCH), 103.5, 103.6 (C-1), 126.4–137.4 (Ph) ppm. MS (FAB): *m*/*z* (%) = 379 (100) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{17}H_{24}O_8Na$ $[M + Na]^+$ 379.1369; found 379.1356.

2,3-Dihydroxy-3-phenylpropyl 4,6-*O*-(*S*)-Benzylidene-β-D-galactopyranoside (26): Two stereoisomers were obtained in a 1:1 ratio. The pure diastereomeric mixture was obtained as a pale-yellow solid by column chromatography using dichloromethane/methanol (7:1) as eluent; yield 0.22 g (52%); m.p. 130–131 °C. $[\alpha]_D$ = –17.0 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.32, 3.34 (2 s, 1 H, 5-H), 3.51 [dd, *J* = 6.6, 10.7 Hz, 0.5 H, $OCH_AH_BCH(OH)CH(OH)Ph$], 3.60–3.65 [m, 1.5 H, 3-H, $OCH_AH_BCH(OH)CH(OH)Ph$], 3.75–3.90 [m, 3 H, 2-H, $OCH_AH_BCH(OH)CH(OH)Ph$], 3.98 (m, 1 H, 6_a-H), 4.10 (m, 1 H, 4-H), 4.22 (d, *J* = 12.4 Hz, 1 H, 6_e-H), 4.26, 4.28 (2 d, *J* = 7.8 Hz, 1 H, 1-H), 4.64, 4.77 [2 d, *J* = 6.6 Hz, 1 H, $OCH_2CH(OH)CH(OH)Ph$], 5.47, 5.49 (2 s, 1 H, PhC*H*), 7.0–7.5 (m, 10 H, 2 Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 66.6, 66.7 (C-5), 69.0 (C-6), 70.7 (C-2), 71.3 [$OCH_2CH(OH)CH(OH)Ph$], 71.5 (C-3), 72.6 [$OCH_2CH(OH)CH(OH)Ph$], 74.9 [$OCH_2CH(OH)CH(OH)Ph$], 75.4 (C-4), 101.3 (PhCH), 103.1, 103.6 (C-1), 137.6–126.4 (2 Ph) ppm. MS (FAB): *m*/*z* (%) = 441 (100) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{22}H_{26}O_8Na$ $[M + Na]^+$ 441.1525; found 441.1536. $C_{22}H_{26}O_8$ (418.16): calcd. C 63.15, H 6.26; found C 63.24, H 6.30.

(2*S*,3*S*)-2,3-Dihydroxydecenyl 4,6-*O*-(*S*)-Benzylidene-β-D-galactopyranoside (27): Two stereoisomers were obtained in a 1.2:1 ratio (9% *de*). The pure diastereomeric mixture was obtained as a pale-yellow syrup by column chromatography using dichloromethane/methanol (20:1) as eluent; yield 0.35 g (80%). $[\alpha]_D$ = –14.1 (*c* = 0.6, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 [t, *J* = 7.0 Hz, 3 H, $OCH_2CH(OH)CH(OH)(CH_2)_6CH_3$], 1.25–1.30 [m, 12 H, $OCH_2CH(OH)CH(OH)(CH_2)_6CH_3$], 1.75 (s, 1 H, OH), 3.39 (m, 0.45 H, 5-H minor), 3.41 (m, 0.55 H, 5-H major), 3.6–3.7 [m, 3 H, 3-H, $OCH_2CH(OH)CH(OH)(CH_2)_6CH_3$], 3.75–3.80 [m, 2 H, 2-H, $OCH_AH_BCH(OH)CH(OH)(CH_2)_6CH_3$], 4.00 [m, 1 H, $OCH_AH_BCH(OH)CH(OH)(CH_2)_6CH_3$], 4.02 (m, 1 H, 6_a-H), 4.11 (m, 1 H, 4-H), 4.27 (m, 1 H, 6_e-H), 4.32, 4.33 (2 d, *J* = 7.8 Hz, 1 H, 1-H), 5.49 (s, 0.45

H, PhC*H* minor), 5.50 (s, 0.55 H, PhC*H* major), 7.3–7.5 (m, 5 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 [$OCH_2CH(OH)CH(OH)(CH_2)_6\mathit{C}H_3$], 22.6–33.6 [$OCH_2CH(OH)CH(OH)(\mathit{C}H_2)_6CH_3$], 66.7 (C-5 minor), 66.8 (C-5 major), 69.1 (C-6), 71.3 (C-2), 71.8 [$OCH_2CH(OH)\mathit{C}H(OH)(CH_2)_6CH_3$ minor], 72.1 [$OCH_2CH(OH)\mathit{C}H(OH)(CH_2)_6CH_3$ major], 72.4 [$OCH_2\mathit{C}H(OH)CH(OH)(CH_2)_6CH_3$ minor], 72.5 [$O\mathit{C}H_2CH(OH)CH(OH)(CH_2)_6CH_3$ minor], 72.6 (C-3), 72.7 [$O\mathit{C}H_2CH(OH)CH(OH)(CH_2)_6CH_3$ major], 72.8 [$OCH_2\mathit{C}H(OH)CH(OH)(CH_2)_6CH_3$ major], 75.4 (C-4), 101.3 (Ph*C*H), 103.3 (C-1 major), 103.5 (C-1 minor), 126.5–137.5 (Ph) ppm. MS (FAB): *m*/*z* (%) = 463 (100) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{23}H_{36}O_8Na$ $[M + Na]^+$ 463.2308; found 463.2323.

(2*R*)-2,3-Dihydroxy-2-methylpropyl 4,6-*O*-(*S*)-Benzylidene-β-D-galactopyranoside (28): Two diastereoisomers were obtained in an 8.1:1 ratio (78% *de*). The pure diastereomeric mixture was obtained as a pale-yellow syrup by column chromatography using dichloromethane/methanol (7:1) as eluent; yield 0.33 g (91%). $[\alpha]_D$ = +5.0 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.10 [s, 2.67 H, $OCH_2C(C\mathit{H}_3)(OH)CH_2OH$ major], 1.12 [s, 0.33 H, $OCH_2C(C\mathit{H}_3)(OH)CH_2OH$ minor], 3.39 (m, 1 H, 5-H), 3.43 [d, *J* = 11.4 Hz, 0.89 H, $OCH_2C(CH_3)(OH)CH_A\mathit{H}_BOH$ major], 3.47 [d, *J* = 11.3 Hz, 0.11 H, $OCH_2C(CH_3)(OH)CH_A\mathit{H}_BOH$ minor], 3.52 [d, *J* = 10.5 Hz, 1 H, $OCH_A\mathit{H}_BC(CH_3)(OH)CH_2OH$], 3.61 [d, *J* = 11.4 Hz, 1 H, $OCH_2C(CH_3)(OH)C\mathit{H}_AH_BOH$], 3.65 (dd, *J* = 9.7, 3.7 Hz, 1 H, 3-H), 3.75 (dd, *J* = 7.7, 9.7 Hz, 1 H, 2-H), 3.80 [d, *J* = 10.4 Hz, 0.11 H, $OC\mathit{H}_AH_BC(CH_3)(OH)CH_2OH$ minor], 4.00 (dd, *J* = 1.7, 12.6 Hz, 1 H, 6_a-H), 3.92 [d, *J* = 10.5 Hz, 0.89 H, $OC\mathit{H}_AH_BC(CH_3)(OH)CH_2OH$ major], 4.10 (d, *J* = 3.6 Hz, 1 H, 4-H), 4.25 (dd, *J* = 1.2, 12.5 Hz, 1 H, 6_e-H), 4.32 (d, *J* = 7.8 Hz, 0.11 H, 1-H minor), 4.34 (d, *J* = 7.7 Hz, 0.89 H, 1-H major), 5.48 (s, 1 H, PhC*H*), 7.3–7.6 (m, 5 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.3 [$OCH_2C(\mathit{C}H_3)(OH)CH_2OH$ major], 22.7 [$OCH_2C(\mathit{C}H_3)(OH)CH_2OH$ minor], 66.8 (C-5), 67.8 [$OCH_2C(CH_3)(OH)\mathit{C}H_2OH$ minor], 67.9 [$OCH_2C(CH_3)(OH)\mathit{C}H_2OH$ major], 69.1 (C-6), 71.3 (C-2 minor), 71.4 (C-2 major), 72.3 (C-3), 72.6 [$OCH_2\mathit{C}(CH_3)(OH)CH_2OH$], 75.5 (C-4), 75.9 [$O\mathit{C}H_2C(CH_3)(OH)CH_2OH$], 101.3 (Ph*C*H), 103.7 (C-1), 126.4–137.6 (Ph) ppm. MS (FAB): *m*/*z* (%) = 379 (100) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{17}H_{24}O_8Na$ $[M + Na]^+$ 379.1369; found 379.1390.

(2*S*,3*S*)-2,3-Dihydroxy-2-methyl-3-phenylpropyl 4,6-*O*-(*S*)-Benzylidene-β-D-galactopyranoside (29): Two stereoisomers were obtained in a 1.3:1 ratio (13% *de*). The pure diastereomeric mixture was obtained as a white solid by column chromatography using dichloromethane/methanol (20:1) as eluent; yield 0.4 g (66%); m.p. 150–151 °C. $[\alpha]_D$ = –9.5 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 0.90 [s, 1.71 H, $OCH_2C(C\mathit{H}_3)(OH)CH(OH)Ph$ major], 0.97 [s, 1.29 H, $OCH_2C(C\mathit{H}_3)(OH)CH(OH)Ph$ minor], 3.15 [d, *J* = 9.7 Hz, 0.43 H, $OCH_A\mathit{H}_BC(CH_3)(OH)CH(OH)Ph$ minor], 3.4–3.5 [m, 3.57 H, 2-H, 3-H, 5-H, $OCH_A\mathit{H}_BC(CH_3)(OH)CH(OH)Ph$ major], 3.52 [d, *J* = 9.8 Hz, 0.57 H, $OC\mathit{H}_AH_BC(CH_3)(OH)CH(OH)Ph$ major], 3.81 [d, *J* = 9.8 Hz, 0.43 H, $OC\mathit{H}_AH_BC(CH_3)(OH)CH(OH)Ph$ minor], 4.0–4.1 (m, 3 H, 4-H, 6_e-H, 6_a-H), 4.18 (d, *J* = 7.4 Hz, 0.43 H, 1-H minor), 4.25 (d, *J* = 7.4 Hz, 0.57 H, 1-H major), 4.55 [s, 1 H, $OCH_2C(CH_3)(O\mathit{H})CH(OH)Ph$], 4.55 [d, *J* = 4.7 Hz, 0.43 H, $OCH_2C(CH_3)(OH)C\mathit{H}(OH)Ph$ minor], 4.62 [d, *J* = 4.7 Hz, 0.57 H, $OCH_2C(CH_3)(OH)C\mathit{H}(OH)Ph$ major], 4.88 (d, *J* = 5.6 Hz, 1 H, 2-OH), 4.99 [d, *J* = 4.8 Hz, 0.57 H, $OCH_2C(CH_3)(OH)CH(O\mathit{H})Ph$ major], 5.03, 5.04 (2 d, *J* = 3.9 Hz, 1 H, 3-OH), 5.11 [d, *J* = 4.8 Hz, 0.43 H, $OCH_2C(CH_3)(OH)CH(O\mathit{H})Ph$ minor], 5.55 (s, 0.43 H, PhC*H* minor), 5.56 (s, 0.57 H, PhC*H* major), 7.2–7.5 (m, 10 H, 2 Ph) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 20.6 [$OCH_2C(\mathit{C}H_3)(OH)CH(OH)Ph$ major], 21.4 [$OCH_2C(\mathit{C}H_3)(OH)CH(OH)Ph$ minor], 65.9 (C-5 major), 66.0 (C-5 minor), 68.6 (C-6), 70.2 (C-2 minor), 70.3 (C-2 major), 71.7 (C-3), 73.6 [$OCH_2\mathit{C}(CH_3)(OH)CH(OH)Ph$ minor], 73.7 [$OCH_2\mathit{C}(CH_3)(OH)CH(OH)Ph$ major], 73.9 [$O\mathit{C}H_2C(CH_3)(OH)CH(OH)Ph$ major], 74.3 [$O\mathit{C}H_2C(CH_3)(OH)CH(OH)Ph$ minor], 75.4 [$OCH_2C(CH_3)(OH)\mathit{C}H(OH)Ph$ major], 75.7 [$OCH_2C(CH_3)(OH)\mathit{C}H(OH)Ph$ minor], 75.9 (C-4), 99.7 (Ph*C*H minor), 99.8 (Ph*C*H major), 103.9 (C-1 major), 104.1 (C-1 minor), 126.2–142.1 (2 Ph) ppm. MS (FAB): *m*/*z* (%) = 455 (100) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{23}H_{28}O_8Na$ $[M + Na]^+$ 455.1682; found 455.1676. $C_{23}H_{28}O_8$ (432.18): calcd. C 63.88, H 6.53; found C 63.81, H 6.60.

2,3-Dihydroxypropyl 4,6-*O*-(*R*)-Benzylidene-β-D-glucopyranoside (30): Two stereoisomers were obtained in a 1:1 ratio. Purification by column chromatography using dichloromethane/methanol (10:1) as eluent gave a white solid; yield 0.20 g (60%); m.p. 182–183 °C. $[\alpha]_D$ = –21.0 (*c* = 0.5, MeOH). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 3.10 (m, 1 H, 2-H), 3.28–3.42 [m, 5.5 H, 3-H, 4-H, 5-H, $OCH_A\mathit{H}_BCH(OH)C\mathit{H}_2OH$], 3.49 [dd, *J* = 4.6, 9.8 Hz, 0.5 H, $OCH_A\mathit{H}_BCH(OH)CH_2OH$], 3.60–3.70 [m, 2.5 H, 6_a-H, $OC\mathit{H}_AH_BC\mathit{H}(OH)CH_2OH$], 3.77 [dd, *J* = 4.4, 10.0 Hz, 0.5 H, $OC\mathit{H}_AH_BCH(OH)CH_2OH$], 4.18 (dd, *J* = 4.0, 10.6 Hz, 1 H, 6_e-H), 4.34, 4.35 (2 d, *J* = 7.5 Hz, 1 H, 1-H), 4.46 [m, 1 H, $OCH_2CH(OH)CH_2O\mathit{H}$], 4.58, 4.61 [2 d, *J* = 3.0, 3.8 Hz, 1 H, $OCH_2CH(O\mathit{H})CH_2OH$], 5.25 (s, 2 H, 2-OH, 3-OH), 5.55 (s, 1 H, PhC*H*), 7.35–7.45 (m, 5 H, Ph) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 62.7, 62.8 [$OCH_2\mathit{C}H(OH)CH_2OH$], 65.8 (C-5), 67.9 (C-6), 70.3, 70.4 [$OCH_2CH(OH)\mathit{C}H_2OH$], 71.2, 71.5 [$O\mathit{C}H_2CH(OH)CH_2OH$], 72.6, 72.7 (C-3), 74.3, 74.4 (C-2), 80.6 (C-4), 100.6 (Ph*C*H), 103.8, 103.9 (C-1), 126.3–137.7 (Ph) ppm. MS (FAB): *m*/*z* (%) = 365 (100) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{16}H_{22}O_8Na$ $[M + Na]^+$ 365.1212; found 365.1202. $C_{16}H_{22}O_8$ (342.34): calcd. C 56.13, H 6.48; found C 56.24, H 6.41.

(2*R*)-2,3-Dihydroxy-2-methylpropyl 4,6-*O*-(*R*)-Benzylidene-β-D-glucopyranoside (31): Two stereoisomers were obtained in a 2.5:1 ratio (43% *de*). The pale-yellow syrup was purified by column chromatography using dichloromethane/methanol (10:1) as eluent; yield 0.26 g (72%). $[\alpha]_D$ = –18.0 (*c* = 0.5, MeOH). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.00 [s, 2.1 H, $OCH_2C(C\mathit{H}_3)(OH)CH_2OH$ major], 1.03 [s, 0.9 H, $OCH_2C(C\mathit{H}_3)(OH)CH_2OH$ minor], 3.13 (m, 1 H, 2-H), 3.20 [m, 1 H, $OCH_2C(CH_3)(OH)CH_A\mathit{H}_B(OH)$], 3.26–3.32 [m, 2 H, $OCH_A\mathit{H}_BC(CH_3)(OH)C\mathit{H}_AH_BOH$], 3.35–3.45 (m, 3 H, 3-H, 4-H, 5-H), 3.62, 3.63 [2 d, *J* = 9.8 Hz, 1 H, $OC\mathit{H}_AH_BC(CH_3)(OH)CH_2OH$], 3.69 (m, 1 H, 6_a-H), 4.18 (dd, *J* = 4.5, 10.6 Hz, 1 H, 6_e-H), 4.23 [s, 0.7 H, $OCH_2C(CH_3)(O\mathit{H})CH_2OH$ major], 4.24 [s, 0.3 H, $OCH_2C(CH_3)(O\mathit{H})CH_2OH$ minor], 4.34, 4.35 (2 d, *J* = 7.7 Hz, 1 H, 1-H), 4.45 [m, 1 H, $OCH_2C(CH_3)(OH)CH_2O\mathit{H}$], 5.25 (m, 1.2 H, 2-OH, 3-OH), 5.29 (d, *J* = 4.5 Hz, 0.7 H, 2-OH), 5.56 (s, 1 H, PhC*H*), 7.40–7.45 (m, 5 H, Ph) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 21.5 [$OCH_2C(\mathit{C}H_3)(OH)CH_2OH$], 65.8 (C-5), 66.0 [$OCH_2C(CH_3)(OH)\mathit{C}H_2OH$], 67.9 (C-6), 71.5 [$OCH_2\mathit{C}(CH_3)(OH)CH_2OH$], 72.6 (C-3), 74.1 [$O\mathit{C}H_2C(CH_3)(OH)CH_2OH$], 74.5 (C-2), 80.6 (C-4), 100.6 (Ph*C*H), 104.2 (C-1), 137.8–126.3 (Ph) ppm. MS (FAB): *m*/*z* (%) = 379 (100) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{17}H_{24}O_8Na$ $[M + Na]^+$ 379.1369; found 379.1366.

(2*R*)-2,3-Dihydroxypropyl 2-Acetamido-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (32): Only one stereoisomer was obtained (>99% *de*). A white solid was obtained after column chromatography by using dichloromethane/methanol (10:1) as eluent; yield 0.35 g (92%); m.p. 201–202 °C. $[\alpha]_D$ = –23.6 (*c* = 0.5, MeOH). ^{1}H

NMR (500 MHz, [D$_6$]DMSO): δ = 1.80 (s, 3 H, CH_3CON), 3.38 (m, 1 H, 3-H), 3.49–3.52 [m, 3 H, 2-H, 4-H, OCH$_A$$H_B$CH(OH)-CH$_2$OH], 3.57–3.60 [m, 2 H, 5-H, OCH_AH$_B$CH(OH)CH$_2$OH], 3.72 (t, J = 10.0 Hz, 1 H, 6$_a$-H), 4.19 (dd, J = 5.0, 10.1 Hz, 1 H, 6$_e$-H), 4.46 (d, J = 8.4 Hz, 1 H, 1-H), 5.58 (s, 1 H, PhCH), 7.35–7.55 (m, 5 H, Ph), 7.81 (d, J = 8.8 Hz, 1 H, NH) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 23.0 (*C*H$_3$CON), 48.6 (C-2), 56.2 (C-5), 62.9 (C-6), 65.9 (C-3), 70.2 [OCH$_2$CH(OH)*C*H$_2$OH], 70.4 [O*C*H$_2$CH-(OH)CH$_2$OH], 70.8 [OCH$_2$*C*H(OH)CH$_2$OH], 81.2 (C-4), 100.6 (Ph*C*H), 102.1 (C-1), 126.3–137.7 (Ph), 169.3 (C=O) ppm. MS (FAB): *m*/*z* (%) = 406 (80) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{18}H_{25}NO_8Na$ [M + Na]$^+$ 406.1478; found 406.1493. $C_{18}H_{25}NO_8$ (383.16): calcd. C 56.39, H 6.57, N 3.65; found C 56.74, H 6.70, N 3.54.

(2*S*,3*S*)-2,3-Dihydroxybutyl 2-Acetamido-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (33): Only one stereoisomer was obtained (>99% *de*). Purification by column chromatography using dichloromethane/methanol (10:1) as eluent gave a white solid; yield 0.30 g (75%); m.p. 221–222 °C. [a]$_D$ = –34.2 (c = 0.5, MeOH). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.00 [d, J = 6.5 Hz, 3 H, OCH$_2$-CH(OH)CH(OH)CH_3], 1.80 (s, 3 H, CH_3CON), 3.25–3.35 (m, 2 H, 3-H, 5-H), 3.40 (d, J = 9.0 Hz, 1 H, 4-H), 3.46 [m, 1 H, OCH-$_A$$H_B$CH(OH)CH(OH)CH$_3$], 3.50 (m, 1 H, 2-H), 3.55–3.65 [m, 3 H, OCH_AH$_B$CH(OH)CH(OH)CH$_3$], 3.70 (t, J = 10.1 Hz, 1 H, 6$_a$-H), 4.12 [m, 1 H, OCH$_2$CH(OH)CH(OH)CH$_3$], 4.20 (dd, J = 5.0 Hz, 1 H, 6$_e$-H), 4.36 [m, 1 H, OCH$_2$CH(OH)CH(OH)CH$_3$], 4.47 (d, J = 8.5 Hz, 1 H, 1-H), 5.23 (m, 1 H, 3-OH), 5.58 (s, 1 H, PhCH), 7.4–7.5 (m, 5 H, Ph), 7.7 (d, J = 8.9 Hz, 1 H, NH) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 18.9 [OCH$_2$CH(OH)CH(OH)*C*H$_3$], 23.0 (*C*H$_3$CON), 56.2 (C-2), 65.9 (C-5), 66.7 [OCH$_2$CH-(OH)*C*H(OH)CH$_3$], 67.8 (C-6), 70.4 (C-3), 70.6 [O*C*H$_2$CH(OH)-CH(OH)CH$_3$], 72.8 [OCH$_2$*C*H(OH)CH(OH)CH$_3$], 81.2 (C-4), 100.6 (Ph*C*H), 101.9 (C-1), 126.3–137.7 (Ph), 169.3 (C=O) ppm. MS (FAB): *m*/*z* (%) = 420 (100) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{19}H_{27}NO_8Na$ [M + Na]$^+$ 420.1634; found 420.1644. $C_{19}H_{27}NO_8$ (397.17): calcd. C 57.42, H 6.85, N 3.52; found C 57.39, H 6.46, N 3.14.

(2*S*,3*S*)-2,3-Dihydroxy-3-phenylpropyl 2-Acetamido-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (34): Only one stereoisomer was obtained (>99% *de*). Purification by column chromatography using dichloromethane/methanol (15:1) as eluent gave a white solid; yield 0.38 g (82%); m.p. 205–206 °C. [a]$_D$ = –37.0 (c = 0.5, MeOH). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.81 (s, 3 H, CH_3CON), 3.41 (t, J = 9.0 Hz, 1 H, 4-H), 3.70 (t, J = 10.1 Hz, 1 H, 6$_a$-H), 4.16 (dd, J = 5.0, 10.1 Hz, 1 H, 6$_e$-H), 4.48 (d, J = 8.0 Hz, 1 H, 1-H), 4.54 (d, J = 3.9 Hz, 1 H, 3-OH), 5.58 (s, 1 H, PhCH), 7.20–7.45 (m, 10 H, Ph), 7.78 (d, J = 8.7 Hz, 1 H, NH) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 23.0 (*C*H$_3$CON), 56.2 (C-2), 65.8 (C-5), 67.8 (C-6), 73.4 (C-3), 81.2 (C-4), 100.6 (Ph*C*H), 102.1 (C-1), 126.3–143.3 (Ph), 169.2 (C=O) ppm. MS (CI): *m*/*z* (%) = 460 (20) [M + H]$^+$. HRMS (CI): calcd. for $C_{24}H_{30}NO_8$ [M + H]$^+$ 460.1971; found 460.1969. $C_{24}H_{29}NO_8$ (459.19): calcd. C 62.73, H 6.36, N 3.05; found C 62.55, H 6.51, N 3.47.

(2*S*,3*S*)-2,3-Dihydroxydecyl 2-Acetamido-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (35): Only one stereoisomer was obtained (>99% *de*). Purification by column chromatography using dichloromethane/methanol (15:1) as eluent gave a white solid; yield 0.31 g (65%); m.p. 232–233 °C. [a]$_D$ = –39.0 (c = 0.5, MeOH). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 0.85 [t, J = 7.0 Hz, 3 H, OCH$_2$-CH(OH)CH(OH)(CH$_2$)$_6$CH_3], 1.23–1.38 [m, 10 H, OCH$_2$CH(OH)-CH(OH)CH$_2$(CH_2)$_5$CH$_3$], 1.80 (s, 3 H, CH$_3$CON), 3.29–3.539 [m, 8 H, 2-H, 4-H, 5-H, OCH$_A$$H_BCH$(OH)C$H$(OH)C$H_2$(CH$_2$)$_5CH_3$], 3.56–3.61 [m, 2 H, 3-H, OCH_AH$_B$CH(OH)CH(OH)(CH$_2$)$_5$CH$_3$], 3.70 (t, J = 10.1 Hz, 1 H, 6$_a$-H), 4.20 (dd, J = 5.0, 10.1 Hz, 1 H, 6$_e$-H), 4.31 [d, J = 5.8 Hz, 1 H, OCH$_2$CH(OH)CH(OH)(CH$_2$)$_6$-CH$_3$], 4.46 (d, J = 8.4 Hz, 1 H, 1-H), 5.22 (d, J = 5.5 Hz, 1 H, 3-OH), 5.58 (s, 1 H, PhCH), 7.34–7.45 (m, 5 H, Ph), 7.76 (d, J = 8.9 Hz, 1 H, NH) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 13.9 [OCH$_2$CH(OH)CH(OH)(CH$_2$)$_6$*C*H$_3$], 23.0 (*C*H$_3$CON), 22.0–32.6 [OCH$_2$CH(OH)CH(OH)(*C*H$_2$)$_6$CH$_3$], 56.2 (C-2), 65.9 (C-5), 67.8 (C-6), 70.2 [O*C*H$_2$CH(OH)CH(OH)(CH$_2$)$_6$CH$_3$], 70.5 [OCH$_2$-CH(OH)*C*H(OH)(CH$_2$)$_6$CH$_3$], 70.7 (C-3), 71.4 [OCH$_2$*C*H(OH)-CH(OH)(CH$_2$)$_6$CH$_3$], 81.3 (C-4), 100.6 (Ph*C*H), 102.1 (C-1), 126.3–137.7 (Ph), 169.2 (C=O) ppm. MS (FAB): *m*/*z* (%) = 504 (100) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{25}H_{39}NO_8Na$ [M + Na]$^+$ 504.2573; found 504.2574. $C_{25}H_{39}NO_8$ (481.58): calcd. C 62.35, H 8.16, N 2.91; found C 61.97, H 8.27, N 2.86.

(2*R*)-2,3-Dihydroxy-2-methylpropyl 2-Acetamido-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (36): Only one stereoisomer was obtained (>99% *de*). A white solid was obtained after column chromatography using dichloromethane/methanol (10:1) as eluent; yield 0.32 g (81%); m.p. 218–219 °C. [a]$_D$ = –22.2 (c = 0.5, MeOH). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 0.9 [s, 3 H, OCH$_2$C-(OH)(CH_3)CH$_2$OH], 1.80 (s, 3 H, CH_3CON), 3.16 [m, 2 H, OCH$_2$-C(OH)(CH$_3$)CH_2OH], 3.28 [d, J = 10.5 Hz, 1 H, OCH$_A$$H_B$-C(OH)(CH$_3$)CH$_2$OH], 3.42–3.47 (m, 2 H, 3-H, 4-H), 3.48 [d, J = 10.5 Hz, 1 H, OCH_AH$_B$C(OH)(CH$_3$)CH$_2$OH], 3.54–3.58 (m, 2 H, 2-H, 5-H), 3.72 (t, J = 10.1 Hz, 1 H, 6$_a$-H), 4.12 [s, 1 H, OCH$_2$-C(OH)(CH$_3$)CH$_2$OH], 4.20 (dd, J = 4.9, 10.1 Hz, 1 H, 6$_e$-H), 4.39 [t, J = 6.0 Hz, 1 H, OCH$_2$C(OH)(CH$_3$)CH$_2$OH], 4.42 (d, J = 7.9 Hz, 1 H, 1-H), 5.26 (d, J = 5.2 Hz, 1 H, 3-OH), 5.58 (s, 1 H, PhCH), 7.2–7.5 (m, 5 H, Ph), 7.79 (d, J = 8.4 Hz, 1 H, NH) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 21.4 [OCH$_2$C(OH)(*C*H$_3$)-CH$_2$OH], 23.0 (*C*H$_3$CON), 56.1 (C-2), 65.9 [OCH$_2$C(OH)(CH$_3$)-*C*H$_2$OH], 66.2 (C-3), 67.9 (C-6), 70.3 (C-5), 71.5 [OCH$_2$*C*-(OH)(CH$_3$)CH$_2$OH], 73.9 [O*C*H$_2$C(OH)(CH$_3$)CH$_2$OH], 81.3 (C-4), 100.7 (Ph*C*H), 102.6 (C-1), 126.4–137.8 (Ph), 169.3 (C=O) ppm. MS (FAB): *m*/*z* (%) = 420 (100) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{19}H_{27}NO_8Na$ [M + Na]$^+$ 420.1634; found 420.1624. $C_{19}H_{27}NO_8$ (397.17): calcd. C 57.42, H 6.85, N 3.52; found C 57.42, H 7.01, N 3.41.

(2*S*)-2,3-Dihydroxy-3-methylbutyl 2-Acetamido-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (37): Two stereoisomers were obtained in a 3:1 ratio (50% *de*). The pure diastereomeric mixture was obtained as a white solid by column chromatography using dichloromethane/methanol (12:1) as eluent; yield 0.26 g (63%); m.p. 202–203 °C. [a]$_D$ = –15.0 (c = 0.5, MeOH). ^{1}H NMR (500 MHz, [D$_6$]-DMSO): δ = 1.04, 0.98 [2 s, 6 H, OCH$_2$CH(OH)C(CH_3)$_2$OH], 1.80 (s, 0.75 H, CH_3CON minor), 1.81 (s, 2.25 H, CH_3CON major), 3.42 (t, J = 9.2 Hz, 1 H, 4-H), 3.48 (m, 1 H, 2-H), 3.60 (m, 1 H, 3-H), 3.71 (t, J = 10.1 Hz, 1 H, 6$_a$-H), 3.84 [d, J = 7.4 Hz, 1 H, OCH_A-H$_B$CH(OH)C(CH$_3$)$_2$OH], 4.09 [m, 1 H, OCH$_2$CH(OH)C(CH$_3$)$_2$OH], 4.20 (m, 1 H, 6$_e$-H), 4.32 [m, 1 H, OCH$_2$CH(OH)C(CH$_3$)$_2$OH], 4.48 (d, J = 8.3 Hz, 0.25 H, 1-H minor), 4.51 (d, J = 8.3 Hz, 0.75 H, 1-H major), 5.23 (m, 1 H, 3-OH), 5.58 (s, 1 H, PhCH), 7.2–7.5 (m, 5 H, Ph), 7.77 (d, J = 8.7 Hz, 0.75 H, NH major), 7.80 (d, J = 8.9 Hz, 0.25 H, NH minor) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 23.1 (*C*H$_3$CON), 24.7, 26.7 [OCH$_2$CH(OH)C(*C*H$_3$)$_2$OH], 56.3 (C-2), 65.9 (C-5), 67.9 (C-6), 70.6, 70.8, 70.5 [O*C*H$_2$CH(OH)*C*(CH$_3$)$_2$OH, C-3], 76.1 [OCH$_2$*C*H(OH)C(CH$_3$)$_2$OH], 81.3 (C-4), 100.7 (Ph*C*H), 101.7 (C-1 minor), 102.1 (C-1 major), 126.3–137.7 (Ph), 169.5 (C=O) ppm. MS (FAB): *m*/*z* (%) = 434 (60) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{20}H_{29}NO_8Na$ [M + Na]$^+$ 434.1791; found 434.1781. $C_{20}H_{29}NO_8$ (411.19): calcd. C 58.38, H 7.10, N 3.40; found C 58.74, H 6.74, N 3.43.

2,3-Dihydroxypropyl 2,3-Di-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside (45): Two stereoisomers were obtained in a 1:1 ratio. Purification by column chromatography using hexane/ethyl acetate (1:2) as eluent gave a white solid; yield 0.43 g (82%); m.p. 134–135 °C. $[\alpha]_D$ = +17.0 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 [m, 1 H, $OCH_2CH(OH)CH_2OH$], 1.55 [s, 1 H, $OCH_2CH(OH)CH_2OH$], 3.36 (s, 1 H, 5-H), 3.58 (dd, *J* = 9.5, 3.4 Hz, 1 H, 3-H), 3.6–3.7 [m, 3 H, $OCH_AH_BCH(OH)CH_AH_BOH$, 2-H], 3.80–3.90 [m, 3 H, $OCH_AH_BCH(OH)CH_2OH$, $OCH_2CH(OH)CH_AH_BOH$], 4.02 (d, *J* = 12.4, *J* = 1.7 Hz, 1 H, 6_a-H), 4.13 (d, *J* = 3.4 Hz, 1 H, 4-H), 4.27 (d, *J* = 12.3 Hz, 1 H, 6_e-H), 4.30 (d, *J* = 7.8 Hz, 0.5 H, 1-H), 4.40 (d, *J* = 7.8 Hz, 0.5 H, 1-H), 4.75 (s, 2 H, $PhCH_2O$-3), 4.80 (m, 2 H, $PhCH_2O$-2), 5.49 (s, 1 H, PhCH), 7.3–7.6 (m, 15 H, 3 Ph) ppm. ^{13}C NMR (125 MHz, $[D_6]$DMSO): δ = 21.2 $[OCH_2C(OH)(CH_3)CH_2OH]$, 62.4 $[OCH_2C(OH)(CH_3)CH_2OH]$, 66.6 (C-5), 67.4 (C-6), 69.1 ($PhCH_2O$), 71.8 $[OCH_2C(OH)(CH_3)CH_2OH]$, 72.5 (C-4), 73.6 $[OCH_2C(OH)(CH_3)CH_2OH]$, 74.4 ($PhCH_2O$), 75.2 (C-2), 78.8 (C-3), 101.4 (PhCH), 104.1 (C-1), 126.4–138.4 (3 Ph) ppm. MS (FAB): *m*/*z* (%) = 545 (80) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{30}H_{34}O_8Na$ $[M + Na]^+$ 545.2151; found 545.2132.

(2*R*)-2,3-Dihydroxy-2-methylpropyl 2,3-Di-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside (46): Two diastereoisomers were obtained in a 1.5:1 ratio (20% *de*). The pure diastereomeric mixture was obtained as a white solid by column chromatography using hexane/ethyl acetate (1:2) as eluent; yield 0.37 g (70%); m.p. 136–137 °C. $[\alpha]_D$ = +22.0 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.13 [s, 1.8 H, $OCH_2C(OH)(CH_3)CH_2OH$ major], 1.15 [s, 1.2 H, $OCH_2C(OH)(CH_3)CH_2OH$ minor], 2.40 [m, 1 H, $OCH_2C(OH)(CH_3)CH_2OH$], 3.02, 3.03 [2 s, 1 H, $OCH_2C(OH)(CH_3)CH_2OH$], 3.36 (s, 1 H, 5-H), 3.43 (m, 1 H, 3-H), 3.5–3.6 [m, 2.6 H, $OCH_AH_B(OH)C(CH_3)CH_2OH$, $OCH_2(OH)C(CH_3)CH_AH_BOH$ major, 2-H], 3.66 [d, *J* = 10.4 Hz, 0.4 H, $OCH_2(OH)C(CH_3)CH_AH_BOH$ minor], 3.77 [d, *J* = 10.4 Hz, 0.4 H, $OCH_2C(OH)(CH_3)CH_AH_BOH$ minor], 3.85–3.90 [m, 1.6 H, $OCH_AH_BC(OH)(CH_3)CH_2OH$, $OCH_2C(OH)(CH_3)CH_AH_BOH$ major], 4.02 (d, *J* = 10.7 Hz, 1 H, 6_a-H), 4.13 (d, *J* = 3.5 Hz, 1 H, 4-H), 4.27 (d, *J* = 12.3 Hz, 1 H, 6_e-H), 4.44 (d, *J* = 7.8 Hz, 0.4 H, 1-H minor), 4.46 (d, *J* = 7.8 Hz, 0.6 H, 1-H major), 4.75 (s, 2 H, $PhCH_2O$-3), 4.85 (m, 2 H, $PhCH_2O$-2), 5.49 (s, 1 H, PhCH), 7.2–7.6 (m, 15 H, 3 Ph) ppm. ^{13}C NMR (125 MHz, $[D_6]$DMSO): δ = 63.6 $[OCH_2CH(OH)CH_2OH]$, 66.6 (C-5), 69.2 (C-6), 70.7 ($PhCH_2O$), 71.9 $[OCH_2CH(OH)CH_2OH]$, 72.4 (C-4), 73.7 $[OCH_2CH(OH)CH_2OH]$, 75.5 ($PhCH_2O$), 78.3 (C-2), 79.7 (C-3), 101.3 (PhCH), 104.4 (C-1), 126.4–129.0 (3 Ph) ppm. MS (FAB): *m*/*z* (%) = 559 (80) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{31}H_{36}O_8Na$ $[M + Na]^+$ 559.2308; found 559.2345. $C_{31}H_{36}O_8$ (536.24): calcd. C 69.39, H 6.76; found C 69.34, H 6.76.

(2*R*)-2,3-Dihydroxypropyl 3-*O*-Benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside (47): Two stereoisomers were obtained in a 5.2:1 ratio (68% *de*). The pure diastereomeric mixture was obtained as a white solid by column chromatography using dichloromethane/methanol (10:1) as eluent; yield 0.28 g (66%); m.p. 138–139 °C. $[\alpha]_D$ = +13.0 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (500 MHz, $[D_6]$DMSO): δ = 3.35 [m, 2 H, $OCH_2CH(OH)CH_2OH$], 3.45–3.50 [m, 4 H, 2-H, 3-H, 5-H, $OCH_AH_BCH(OH)CH_2OH$], 3.62 [m, 1 H, $OCH_2CH(OH)CH_2OH$], 3.68 [dd, *J* = 5.9, 10.0 Hz, 1 H, $OCH_AH_BCH(OH)CH_2OH$], 4.0–4.1 (m, 2 H, 6_e-H, 6_a-H), 4.25 (d, *J* = 7.8 Hz, 0.84 H, 1-H major), 4.35 (d, *J* = 3.1 Hz, 1 H, 4-H), 4.51 [t, *J* = 5.8 Hz, 1 H, $OCH_2CH(OH)CH_2OH$], 4.60 (d, *J* = 12.2 Hz, 1 H, OCH_AH_BPh), 4.64 [d, *J* = 5.3 Hz, 1 H, $OCH_2CH(OH)CH_2OH$], 4.68 (d, *J* = 12.2 Hz, 1 H, OCH_AH_BPh), 4.98 (d, *J* = 4.2 Hz, 0.16 H, 2-OH minor), 5.19 (d, *J* = 4.2 Hz, 0.84 H, 2-OH major), 5.58 (s, 1 H, PhCH), 7.25–7.45 (m, 10 H, 2 Ph) ppm. ^{13}C NMR (125 MHz, $[D_6]$DMSO): δ = 62.9 $[OCH_2CH(OH)CH_2OH]$, 65.8 (C-5), 68.7 (C-6), 69.2 (C-2 major), 69.3 (C-2 minor), 70.3 ($PhCH_2O$), 70.5 $[OCH_2CH(OH)CH_2OH]$, 71.1 $[OCH_2CH(OH)CH_2OH]$, 72.5 (C-4), 79.1 (C-3), 99.7 (PhCH), 103.4 (C-1 major), 103.5 (C-1 minor), 126.1–138.8 (2 Ph) ppm. MS (FAB): *m*/*z* (%) = 455 (100) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{23}H_{28}O_8Na$ $[M + Na]^+$ 455.1682; found 455.1680. $C_{23}H_{28}O_8$ (432.18): calcd. C 63.88, H 6.53; found C 63.59, H 6.89.

(2*R*)-2,3-Dihydroxypropyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (48): Only one stereoisomer was obtained (>99% *de*). Purification by column chromatography using dichloromethane/methanol (15:1) as eluent gave a white solid; yield 0.37 g (78%); m.p. 274–275 °C. $[\alpha]_D$ = –13.0 (*c* = 0.5, MeOH). ^{1}H NMR (500 MHz, $[D_6]$DMSO): δ = 1.81 (s, 3 H, CH_3CON), 3.52 (m, 1 H, 3-H), 3.61 [m, 1 H, $OCH_AH_BCH(OH)CH_2OH$], 3.67–3.69 (m, 2 H, 2-H, 4-H), 3.76 (t, *J* = 10.1 Hz, 1 H, 6_a-H), 7.95 (d, *J* = 7.8 Hz, 1 H, NH), 4.23 (dd, $J_{5,6e}$ = 5.0, $J_{6e,6a}$ = 10.1 Hz, 1 H, 6_e-H), 4.44 [t, *J* = 5.2 Hz, 1 H, $OCH_2CH(OH)CH_2OH$], 4.53 (d, *J* = 7.5 Hz, 1 H, 1-H), 4.56–4.58 [m, 2 H, $PhCH_AH_BO$, $OCH_2CH(OH)CH_2OH$], 4.70 (d, *J* = 12.1 Hz, 1 H, $PhCH_AH_BO$), 5.69 (s, 1 H, PhCH), 7.2–7.5 (m, 10 H, 2 Ph) ppm. ^{13}C NMR (125 MHz, $[D_6]$DMSO): δ = 23.0 (CH_3CON), 54.6 (C-2), 62.8 $[OCH_2CH(OH)CH_2OH]$, 65.6 (C-5), 67.8 $[OCH_2CH(OH)CH_2OH]$, 70.2 (C-6), 70.9 $[OCH_2CH(OH)CH_2(OH)]$, 73.1 ($PhCH_2O$), 78.7 (C-3), 80.9 (C-4), 100.1 (PhCH), 101.9 (C-1), 126.0–144.4 (2 Ph), 169.1 (C=O) ppm. MS (FAB): *m*/*z* (%) = 496 (100) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{25}H_{31}NO_8Na$ $[M + Na]^+$ 496.1947; found 496.1944. $C_{25}H_{31}NO_8$ (473.20): calcd. C 63.41, H 6.60, N 2.96; found C 63.35, H 6.71, N 2.76.

(2*R*)-2,3-Dihydroxy-2-methylpropyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (49): Only one stereoisomer was obtained (>99% *de*). A white solid was obtained after purification by column chromatography using dichloromethane/methanol (15:1) as eluent; yield 0.36 g (75%); m.p. 263–265 °C. $[\alpha]_D$ = –43.5 (*c* = 0.5, MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.10 [s, 3 H, $OCH_2C(CH_3)(OH)CH_2OH$], 1.89 (s, 3 H, CH_3CON), 2.53 [m, 1 H, $OCH_2C(CH_3)(OH)CH_2OH$], 2.98 [s, 1 H, $OCH_2C(CH_3)(OH)CH_2(OH)$], 3.39 [dd, *J* = 6.9, 11.3 Hz, 1 H, $OCH_2C(CH_3)(OH)CH_AH_BOH$], 3.45–3.50 [m, 2 H, 5-H, $OCH_AH_BC(CH_3)(OH)CH_2OH$], 3.55–3.62 [m, 2 H, 2-H, $OCH_2C(CH_3)(OH)CH_AH_BOH$], 3.72 (t, *J* = 9.3 Hz, 1 H, 4-H), 3.79 (t, *J* = 10.3 Hz, 1 H, 6_a-H), 3.84 [d, *J* = 10.0 Hz, 1 H, $OCH_AH_BC(CH_3)(OH)CH_2OH$], 3.89 (t, *J* = 9.5 Hz, 1 H, 3-H), 4.35 (dd, *J* = 5.0, 10.4 Hz, 1 H, 6_e-H), 4.65 (d, *J* = 12.0 Hz, 1 H, $PhCH_AH_BO$), 4.75 (d, *J* = 8.3 Hz, 1 H, 1-H), 4.90 (d, *J* = 12.0 Hz, 1 H, $PhCH_AH_BO$), 5.37 (d, *J* = 7.8 Hz, 1 H, NH), 5.58 (s, 1 H, PhCH), 7.25–7.55 (m, 10 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.2 $[OCH_2C(CH_3)(OH)CH_2OH]$, 23.5 (CH_3CON), 56.5 (C-2), 66.2 $[OCH_2C(CH_3)(OH)CH_2OH]$, 67.8 (C-5), 68.6 (C-6), 71.6 $[OCH_2C(CH_3)(OH)CH_2OH]$, 74.1 ($PhCH_2O$), 75.8 $[OCH_2C(CH_3)(OH)CH_2OH]$, 76.5 (C-3), 82.5 (C-4), 101.3 (PhCH), 102.2 (C-1), 126.0–138.2 (Ph), 171.0 (C=O) ppm. MS (FAB): *m*/*z* (%) = 510 (100) $[M + Na]^+$. HRMS (FAB): calcd. for $C_{26}H_{33}NO_8Na$ $[M + Na]^+$ 510.2104; found 510.2120. $C_{26}H_{33}NO_8$ (487.22): calcd. C 64.05, H 6.82, N 2.87; found C 63.89, H 6.72, N 2.80.

(2*R*)-2,3-Dihydroxypropyl 2-Acetamido-3-*O*-Acetyl-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (50): Only one stereoisomer was obtained (>99% *de*). Purification by column chromatography using dichloromethane/methanol (15:1) as eluent gave a white solid; yield 0.34 g (81%); m.p. 237–238 °C. $[\alpha]_D$ = –5.2 (*c* =

0.5, MeOH). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.78 (s, 3 H, CH_3CON), 1.94 (s, 3 H, CH_3COO), 3.25–3.30 [m, 2 H, OCH$_2$CH(OH)CH_2OH], 3.42 [dd, J = 5.8, 9.8 Hz, 1 H, OCH$_A H_B$CH(OH)CH$_2$OH], 3.50–3.55 [m, 2 H, 5-H, OCH$_2$CH-(OH)CH$_2$OH], 3.60 [dd, J = 5.8, 9.8 Hz, 1 H, OCH_AH$_B$CH(OH)-CH$_2$OH], 3.70–3.80 (m, 3 H, 2-H, 4-H, 6$_a$-H), 4.23 (dd, J = 5.0, 10.2 Hz, 1 H, 6$_e$-H), 4.64 (d, J = 8.5 Hz, 1 H, 1-H), 5.10 (t, J = 10.0 Hz, 1 H, 3-H), 5.62 (s, 1 H, PhCH), 7.30–7.35 (m, 5 H, Ph), 7.91 (d, J = 9.2 Hz, 1 H, NH) ppm. ^{13}C NMR (125 MHz, [D$_6$]-DMSO): δ = 20.5 (*C*H$_3$CONH), 22.7 (*C*H$_3$COO), 53.7 (C-2), 62.8 [OCH$_2$CH(OH)*C*H$_2$OH], 65.7 (C-5), 67.6 (C-6), 70.1 [OCH$_2$*C*H-(OH)CH$_2$OH], 71.1 [O*C*H$_2$CH(OH)CH$_2$OH], 71.9 (C-3), 78.0 (C-4), 100.2 (Ph*C*H), 101.4 (C-1), 126.1–137.3 (Ph), 169.2 (CH$_3$*C*ON), 169.7 (CH$_3$*C*OO) ppm. MS (FAB): *m*/*z* (%) = 448 (100) [M + Na]$^+$. HRMS (FAB): calcd. for C$_{20}$H$_{27}$NO$_9$Na [M + Na]$^+$ 448.1584; found 448.1573. C$_{20}$H$_{27}$NO$_9$ (425.17): calcd. C 56.46, H 6.40, N 3.29; found C 56.47, H 6.36, N 3.09.

(2*R*)-2,3-Dihydroxypropyl 2-Acetamido-3-*O*-capriloyl-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (51): Two stereoisomers were obtained in a 2.5:1 ratio (43% *de*). Purification by column chromatography using dichloromethane/methanol (10:1) as eluent gave a pale-yellow syrup; yield 0.53 g (82%). [α]$_D$ = –30.0 (c = 1.0, MeOH). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 0.81 [t, J = 7.0 Hz, 3 H, CH_3(CH$_2$)$_5$CH$_2$CO$_2$], 1.1–1.5 [m, 10 H, CH$_3$(CH_2)$_5$CH$_2$CO$_2$], 1.74 (s, 0.9 H, CH_3CON minor), 2.20 [m, 2 H, CH$_3$(CH$_2$)$_5$-CH_2CO$_2$], 1.75 (s, 2.1 H, CH_3CON major), 3.3–3.6 [m, 4 H, 5-H, OCH$_2$CH(OH)CH_2OH], 3.70–3.85 [m, 5 H, 2-H, 4-H, 6$_a$-H, OCH_2CH(OH)CH$_2$OH], 4.26 (m, 1 H, 6$_e$-H), 4.62 (d, J = 8.5 Hz, 0.3 H, 1-H minor), 4.76 (d, J = 8.5 Hz, 0.7 H, 1-H major), 5.04 (t, J = 9.9 Hz, 0.7 H, 3-H major), 5.12 (t, J = 9.9 Hz, 0.3 H, 3-H minor), 5.62 (s, 1 H, PhCH), 7.34 (m, 5 H, Ph), 7.78 (d, J = 9.4 Hz, 0.7 H, NH major), 7.92 (d, J = 9.4 Hz, 0.3 H, NH minor) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 13.9 [*C*H$_3$(CH$_2$)$_6$CO$_2$], 22.6 (*C*H$_3$CON), 22.0–33.5 [CH$_3$(*C*H$_2$)$_6$CO$_2$], 53.4 (C-2 major), 53.6 (C-2 minor), 65.9 (C-5), 67.7 (C-6), 68.9 [O*C*H$_2$CH(OH)CH$_2$OH], 70.1 [OCH$_2$*C*H(OH)CH$_2$OH], 71.0 [OCH$_2$CH(OH)*C*H$_2$OH], 71.7 (C-3), 78.2 (C-4), 100.2 (Ph*C*H), 101.6 (C-1 minor), 102.0 (C-1 major), 126.0–137.4 (Ph), 169.1 (CH$_3$*C*ON), 172.3 [CH$_3$(CH$_2$)$_5$CH$_2$-*C*O$_2$] ppm. MS (FAB): *m*/*z* (%) = 532 (60) [M + Na]$^+$. HRMS (FAB): calcd. for C$_{26}$H$_{39}$NO$_9$Na [M + Na]$^+$ 532.2523; found 532.2507.

Stereochemical Assignment

Synthesis of (2*S*)-2-Hydroxy-2-methyl-3-tosyloxypropyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (52): DAMP (2.0 mmol) and tosyl chloride (1.1 mmol) were added to a solution of the glycol derivative **49** (1.0 mmol) in dry dichloromethane (50 mL) cooled to 0 °C. The mixture was stirred at 0 °C until TLC showed that all the starting material had reacted (ca. 5 h). The organic phase was washed with diluted hydrochloric acid, water and saturated sodium hydrogen carbonate, and the organic layer was evaporated to dryness. Only one stereoisomer was obtained (100% *de*). A white solid was obtained after purification by column chromatography using hexane/ethyl acetate (1:2) as eluent; yield 0.53 g (82%); m.p. 234–235 °C. [α]$_D$ = –8.0 (c = 0.3, CH$_2$Cl$_2$). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.12 [s, 3 H, OCH$_2$C(CH_3)(OH)CH$_2$OTs], 1.88 (s, 3 H, CH_3CON), 2.45 (s, 3 H, C$_6$H$_4$CH_3), 3.41 [d, J = 10.0 Hz, 1 H, OCH$_A H_B$C(CH$_3$)(OH)-CH$_2$OTs], 3.46 (m, 1 H, 5-H), 3.56 (m, 1 H, 2-H), 3.70 (t, J = 9.4 Hz, 1 H, 4-H), 3.75 [d, J = 10.0 Hz, 1 H, OCH_AH$_B$C(CH$_3$)-(OH)CH$_2$OTs], 3.79 (t, J = 10.3 Hz, 1 H, 6$_a$-H), 3.84 [d, J = 9.5 Hz, 1 H, OCH$_2$C(CH$_3$)(OH)CH$_A$CH_BOTs], 3.90 (t, J = 9.6 Hz, 1 H, 3-H), 3.95 [d, J = 9.5 Hz, 1 H, OCH$_2$C(CH$_3$)(OH)CH_ACH$_B$OTs], 4.34 (dd, J = 5.0, 10.4 Hz, 1 H, 6$_e$-H), 4.65 (d, J = 12.0 Hz, 1 H, PhCH$_A H_B$O), 4.73 (d, J = 8.4 Hz, 1 H, 1-H), 4.89 (d, J = 12.0 Hz, 1 H, PhCH_AH$_B$O), 5.40 (d, J = 7.7 Hz, 1 H, NH), 5.59 (s, 1 H, PhCH), 7.30–7.80 (m, 14 H, Ar) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 21.1 [OCH$_2$C(*C*H$_3$)(OH)CH$_2$OTs], 21.6 (C$_6$H$_4$*C*H$_3$), 23.5 (*C*H$_3$CON), 56.4 (C-2), 66.1 (C-5), 68.7 (C-6), 70.8 [OCH$_2$*C*(CH$_3$)(OH)CH$_2$OTs], 72.9 [OCH$_2$C(CH$_3$)(OH)*C*H$_2$OTs], 73.3 [O*C*H$_2$C(CH$_3$)(OH)CH$_2$OTs], 74.2 (Ph*C*H$_2$O), 76.5 (C-3), 82.4 (C-4), 101.3 (Ph*C*H), 101.8 (C-1), 126.0–145.1 (3 Ar), 170.6 (C=O) ppm. MS (FAB): *m*/*z* (%) = 664 (30) [M + Na]$^+$. HRMS (FAB): C$_{32}$H$_{35}$NO$_{11}$SNa [M + Na]$^+$ 664.1829; found 664.1840. C$_{32}$H$_{35}$NO$_{11}$S (641.19): calcd. C 59.90, H 5.50, N 2.18, S 5.00; found C 60.24, H 5.82, N 2.01.

Synthesis of (2*R*)-3-Azido-2-hydroxy-2-methylpropyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (53)

From 52: Sodium azide (2.0 mmol) was added to a solution of the tosyl derivative **52** (1.0 mmol) in dry DMF (20 mL) and the reaction was heated at 70 °C (18 h). The reaction mixture was diluted with dichloromethane, successively washed with water and brine, and the organic phase was evaporated to dryness. Only one stereoisomer was obtained (100% *de*). Purification by flash chromatography on silica gel using hexane/ethyl acetate (1:2) as eluent gave a white solid; yield 0.42 g (82%); m.p. 192–193 °C. [α]$_D$ = +2.0 (c = 0.5, MeOH). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.17 [s, 3 H, OCH$_2$C(CH_3)(OH)CH$_2$N$_3$], 1.88 (s, 3 H, CH_3CON), 3.27 [s, 2 H, OCH$_2$C(CH$_3$)(OH)CH_2N$_3$], 3.39 [d, J = 9.9 Hz, 1 H, OCH$_A H_B$C(CH$_3$)(OH)CH$_2$N$_3$], 3.48 (m, 1 H, 5-H), 3.57 (m, 1 H, 2-H), 3.72 (t, J = 9.2 Hz, 1 H, 4-H), 3.77–3.82 [m, 2 H, 6$_a$-H, OCH_AH$_B$C(CH$_3$)(OH)CH$_2$N$_3$], 3.92 (t, J = 9.5 Hz, 1 H, 3-H), 4.35 (dd, J = 5.0, 10.5 Hz, 1 H, 6$_e$-H), 4.66 (d, J = 12.0 Hz, 1 H, PhCH$_A H_B$O), 4.77 (d, J = 8.3 Hz, 1 H, 1-H), 4.90 (d, J = 12.0 Hz, 1 H, PhCH_AH$_B$O), 5.32 (d, J = 7.8 Hz, 1 H, NH), 5.58 (s, 1 H, PhCH), 7.3–7.5 (m, 10 H, 2 Ph) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 22.0 [OCH$_2$C(*C*H$_3$)(OH)CH$_2$N$_3$], 23.6 (*C*H$_3$CON), 56.7 (C-2), 57.6 [OCH$_2$C(CH$_3$)(OH)*C*H$_2$N$_3$], 66.1 (C-5), 68.7 (C-6), 72.2 [OCH$_2$*C*(CH$_3$)(OH)CH$_2$N$_3$], 74.2 (Ph*C*H$_2$O), 74.5 [O*C*H$_2$C(CH$_3$)(OH)CH$_2$N$_3$], 76.5 (C-3), 82.5 (C-4), 101.3 (Ph*C*H), 101.9 (C-1), 126.0–138.2 (2 Ph), 170.7 (C=O) ppm. MS (FAB): *m*/*z* (%) = 535 (50) [M + Na]$^+$. HRMS (FAB): calcd. for C$_{26}$H$_{32}$N$_4$O$_7$Na [M + Na]$^+$ 535.2169; found 535.2153. C$_{26}$H$_{32}$N$_4$O$_7$ (512.23): calcd. C 60.93, H 6.29, N 10.93; found C 60.66, H 6.51, N 10.97.

From 54: Lithium perchlorate (2.0 mmol) and sodium azide (4.0 mmol) were added to a solution of the oxirane derivative **54** (1.0 mmol) in dry CH$_3$CN (70 mL) and the reaction was heated at 80 °C (10 h). The reaction mixture was poured into water and the compound was extracted with ethyl acetate (50 mL). The reaction mixture was diluted with CH$_2$Cl$_2$ (50 mL). The organic phase was washed with water (2 × 40 mL), dried and the solvents evaporated to dryness. A white solid was obtained after purification by column chromatography using hexane/ethyl acetate (1:2) as eluent. Two stereoisomers were obtained in a 6:1 ratio (71% *de*); yield 0.42 g (82%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.16 [s, 0.42 H, OCH$_2$C(CH_3)(OH)CH$_2$N$_3$ minor], 1.17 [s, 2.58 H, OCH$_2$C(CH_3)(OH)CH$_2$N$_3$ major], 1.88 (s, 2.58 H, CH_3CON major), 1.89 (s, 0.42 H, CH_3CON minor), 3.27 [s, 2 H, OCH$_2$C(CH$_3$)(OH)CH_2N$_3$], 3.39 [d, J = 9.9 Hz, 1 H, OCH$_A H_B$C-(CH$_3$)(OH)CH$_2$N$_3$], 3.48 (m, 1 H, 5-H), 3.57 (m, 1 H, 2-H), 3.70 (t, J = 9.1 Hz, 0.14 H, 4-H minor), 3.72 (t, J = 9.3 Hz, 0.86 H, 4-H major), 3.78–3.82 [m, 2 H, 6$_a$-H, OCH_AH$_B$C(CH$_3$)(OH)CH$_2$N$_3$], 3.92 (t, J = 9.5 Hz, 0.86 H, 3-H major), 4.02 (t, J = 9.5 Hz, 0.14 H, 3-H minor), 4.35 (dd, J = 5.0, 10.5 Hz, 0.86 H, 6$_e$-H major),

4.40 (dd, J = 4.9, 10.5 Hz, 0.14 H, 6_e-H minor), 4.66 (d, J = 12.0 Hz, 1 H, PhCH$_A$H$_B$O), 4.77 (d, J = 8.3 Hz, 0.86 H, 1-H major), 4.83 (d, J = 8.3 Hz, 0.14 H, 1-H minor), 4.90 (d, J = 12.0 Hz, 1 H, PhCH$_A$H$_B$O), 5.32 (d, J = 7.8 Hz, 0.86 H, NH major), 5.38 (d, J = 7.9 Hz, 0.14 H, NH minor), 5.58 (s, 1 H, PhCH), 7.3–7.5 (m, 10 H, 2 Ph) ppm. MS (FAB): m/z (%) = 535 (40) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{26}H_{32}N_4O_7Na$ [M + Na]$^+$ 535.2169; found 535.2191.

Synthesis of Glycoglycerolipid Analogues

Selective Acylation Reaction: DAMP (1 mmol) and acid chloride (0.5 mmol) were added to a solution of **49** and **61** (0.5 mmol) in dry dichloromethane (30 mL) precooled to 0 °C. The reaction mixture was stirred at 0 °C until TLC showed that all the starting material had reacted (3 h). The organic phase was successively washed with diluted hydrochloric acid, water and an aqueous saturated solution of sodium hydrogen carbonate, dried ($MgSO_4$), filtered and the filtrate was evaporated to dryness. The compounds obtained were purified by flash chromatography on silica gel.

(2*S*)-3-Capriloyloxy-2-hydroxy-2-methylpropyl 2-Acetamido-3-*O*-benzyl 4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (55): A white solid was obtained by column chromatography using hexane/ethyl acetate (1:3) as eluent; yield 0.31 g (50%); m.p. 150–151 °C. $[\alpha]_D$ = –2.0 (c = 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 0.87 [t, J = 7.1 Hz, 3 H, OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 1.16 [s, 3 H, OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 1.25–1.70 [m, 10 H, OCH$_2$C(CH$_3$)(OH)CH$_2$OCOCH$_2$(CH$_2$)$_5$CH$_3$], 1.88 (s, 3 H, CH$_3$CON), 2.34 [t, J = 7.5 Hz, 2 H, OCH$_2$C(CH$_3$)(OH)CH$_2$OCOCH$_2$(CH$_2$)$_5$CH$_3$], 3.40 [d, J = 9.8 Hz, 1 H, OCH$_A$H$_B$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 3.47–3.51 (m, 2 H, 2-H, 5-H), 3.69 (t, J = 9.3 Hz, 1 H, 4-H), 3.76–3.81 [m, 2 H, 6_a-H, OCH$_A$H$_B$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 3.93 [d, J = 11.2 Hz, 1 H, OCH$_2$C(CH$_3$)(OH)CH$_A$H$_B$OCO(CH$_2$)$_6$CH$_3$], 4.01 (t, J = 9.5 Hz, 1 H, 3-H), 4.10 [d, J = 11.2 Hz, 1 H, OCH$_2$C(CH$_3$)(OH)CH$_A$H$_B$OCO(CH$_2$)$_6$CH$_3$], 4.34 (dd, J = 5.0, 10.2 Hz, 1 H, 6_e-H), 4.64 (d, J = 11.9 Hz, 1 H, PhCH$_A$H$_B$O), 4.85 (d, J = 8.4 Hz, 1 H, 1-H), 4.90 (d, J = 11.9 Hz, 1 H, PhCH$_A$H$_B$O), 5.47 (d, J = 7.8 Hz, 1 H, NH), 5.57 (s, 1 H, PhCH), 7.26–7.55 (m, 10 H, 2 Ph) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 14.1 [OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 21.4 [OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 22.6 (CH$_3$CON), 24.9–34.2 [OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 57.1 (C-2), 66.1 (C-5), 67.8 [OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 68.7 (C-6), 71.2 [OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 74.4 [OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 74.3 (PhCH$_2$O), 76.5 (C-3), 82.6 (C-4), 101.3 (PhCH), 101.7 (C-1), 126.0–138.2 (2 Ph), 170.7 (CH$_3$CON), 173.8 [OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$] ppm. MS (FAB): m/z (%) = 636 (80) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{34}H_{47}NO_9Na$ [M + Na]$^+$ 636.3149; found 636.3135. $C_{34}H_{47}NO_9$ (613.33): calcd. C 66.54, H 7.72, N 2.28; found C 66.39, H 7.32, N 2.63.

(2*S*)-2-Hydroxy-2-methyl-3-palmitoyloxypropyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (56): Only one stereoisomer was obtained (>99% *de*). A white solid was obtained after purification by column chromatography using dichloromethane/methanol (20:1) as eluent; yield 0.56 g (78%); m.p. 142–143 °C. $[\alpha]_D$ = –5.0 (c = 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 [t, J = 6.9 Hz, 3 H, OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_{14}$CH$_3$], 1.16 [s, 3 H, OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_{14}$CH$_3$], 1.25–1.29 [m, 26 H, OCH$_2$C(CH$_3$)(OH)CH$_2$OCOCH$_2$(CH$_2$)$_{13}$CH$_3$], 1.88 (s, 3 H, CH$_3$CON), 2.33 [t, J = 7.7 Hz, 2 H, OCH$_2$C(CH$_3$)(OH)CH$_2$OCOCH$_2$(CH$_2$)$_{13}$CH$_3$], 3.42–3.51 [m, 3 H, 2-H, 5-H, OCH$_A$H$_B$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_{14}$CH$_3$], 3.69 (t, J = 9.2 Hz, 1 H, 4-H), 3.76–3.80 [m, 2 H, 6_a-H, OCH$_A$H$_B$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_{14}$(CH$_3$)], 3.94 [d, J = 11.2 Hz, 1 H, OCH$_2$C(CH$_3$)(OH)CH$_A$H$_B$OCO(CH$_2$)$_{14}$CH$_3$], 4.03 (t, J = 9.5 Hz, 1 H, 3-H), 4.08 [d, J = 11.2 Hz, 1 H, OCH$_2$C(CH$_3$)(OH)CH$_A$H$_B$OCO(CH$_2$)$_{14}$CH$_3$], 4.34 (dd, J = 5.0, 10.2 Hz, 1 H, 6_e-H), 4.64 (d, J = 11.9 Hz, 1 H, PhCH$_A$H$_B$O), 4.86 (d, J = 8.4 Hz, 1 H, 1-H), 4.90 (d, J = 11.9 Hz, 1 H, PhCH$_A$H$_B$O), 5.52 (d, J = 7.8 Hz, 1 H, NH), 5.57 (s, 1 H, PhCH), 7.3–7.5 (m, 10 H, 2 Ph) ppm. ^{13}C NMR (125 MHz, DMSO): δ = 14.1 [OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_{14}$CH$_3$], 21.4 [OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_{14}$CH$_3$], 23.5 (CH$_3$CON), 24.7–34.2 [OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_{14}$CH$_3$], 57.2 (C-2), 66.1 (C-5), 67.8 [OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_{14}$CH$_3$], 68.7 (C-6), 71.2 [OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_{14}$CH$_3$], 173.7 [OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_{14}$CH$_3$], 74.3 (PhCH$_2$O), 74.4 [OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_{14}$CH$_3$], 76.6 (C-3), 82.6 (C-4), 101.3 (PhCH), 101.7 (C-1), 126.0–129.0 (2 Ph), 170.7 (CH$_3$CON) ppm. MS (FAB): m/z (%) = 748 (30) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{42}H_{63}NO_9Na$ [M + Na]$^+$ 748.4401; found 748.4405. $C_{42}H_{63}NO_9$ (725.45): calcd. C 69.49, H 8.75, N 1.93; found C 69.69, H 8.97, N 1.80.

(2*R*)-2-Hydroxy-2-methyl-3-palmitamidopropyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (62): A white solid was obtained after purification by column chromatography using dichloromethane/methanol (80:1) as eluent; yield 0.51 g (71%); m.p. 195–196 °C. $[\alpha]_D$ = –12.0 (c = 0.5, MeOH). ^{1}H NMR (500 MHz, DMSO): δ = 0.85 [t, J = 6.8 Hz, 3 H, OCH$_2$C(CH$_3$)(OH)CH$_2$NHCO(CH$_2$)$_{14}$CH$_3$], 0.98 [s, 3 H, OCH$_2$C(CH$_3$)(OH)CH$_2$NHCO(CH$_2$)$_{14}$CH$_3$], 1.15–1.30 [m, 26 H, OCH$_2$C(CH$_3$)(OH)CH$_2$NHCOCH$_2$(CH$_2$)$_{13}$CH$_3$], 1.83 (s, 3 H, NCH$_3$CO), 2.12 [t, J = 7.7 Hz, 2 H, OCH$_2$C(CH$_3$)(OH)CH$_2$NHCOCH$_2$(CH$_2$)$_{13}$CH$_3$], 3.1–3.8 [m, 7 H, 2-H, 3-H, 4-H, 5-H, 6_a-H, OCH$_2$C(CH$_3$)(OH)CH$_2$NHCO(CH$_2$)$_{14}$CH$_3$], 4.22 (dd, J = 5.0, 10.1 Hz, 1 H, 6_e-H), 4.47 (d, J = 8.2 Hz, 1 H, 1-H), 4.55 [s, 1 H, OCH$_2$C(CH$_3$)(OH)CH$_2$NHCO(CH$_2$)$_{14}$CH$_3$], 4.59 (d, J = 11.9 Hz, 1 H, PhCH$_A$H$_B$O), 4.71 (d, J = 11.9 Hz, 1 H, PhCH$_A$H$_B$O), 5.68 (s, 1 H, PhCH), 7.20–7.43 (m, 5 H, Ph), 7.52 [t, J = 5.85 Hz, 1 H, OCH$_2$C(CH$_3$)(OH)CH$_2$NHCO(CH$_2$)$_{14}$CH$_3$], 7.92 (d, J = 8.6 Hz, 1 H, CH$_3$CONH) ppm. MS (FAB): m/z (%) = 747 (30) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{42}H_{64}N_2O_8Na$ [M + Na]$^+$ 747.4560; found 747.4544. $C_{42}H_{64}N_2O_8$ (724.47): calcd. C 69.58, H 8.90, N 3.86; found C 69.42, H 8.89, N 3.66.

Deprotection Reactions: Solutions of compounds **55**, **56** and **62** (0.5 mmol) in dry methanol (10 mL) were each subjected to hydrogenolysis over 10% Pd/C (50 mg) at room temperature under hydrogen (4 bar) for 24 h. The mixture was diluted with methanol and the catalyst filtered off and washed with methanol. The filtrate was concentrated to dryness under reduced pressure.

(2*S*)-3-Capriloyloxy-2-hydroxy-2-methylpropyl 2-Acetamido-2-deoxy-β-D-glucopyranoside (58): Purification by column chromatography using dichloromethane/methanol (10:1) as eluent gave a pale-yellow syrup; yield 0.37 g (85%). $[\alpha]_D$ = –11.0 (c = 0.3, MeOH). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 0.85 [t, J = 7.1 Hz, 3 H, OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 1.01 [s, 3 H, OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 1.2–1.6 [m, 10 H, OCH$_2$C(CH$_3$)(OH)CH$_2$OCOCH$_2$(CH$_2$)$_5$CH$_3$], 1.75 (s, 3 H, CH$_3$CON), 2.29 [t, J = 7.4 Hz, 2 H, OCH$_2$C(CH$_3$)(OH)CH$_2$OCOCH$_2$(CH$_2$)$_5$CH$_3$], 3.00 (m, 2 H, 4-H, 5-H), 3.26 [d, J = 9.6 Hz, 1 H, OCH$_A$H$_B$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 3.30–3.45 (m, 3 H, 2-H, 3-H, 6_A-H), 3.52 [d, J = 9.6 Hz, 1 H, OCH$_A$H$_B$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 3.66 (m, 1 H, 6_B-H), 3.80 [d, J = 10.9 Hz, 2 H, OCH$_2$C(CH$_3$)(OH)CH$_2$OCO(CH$_2$)$_6$CH$_3$], 4.23 (d,

J = 8.4 Hz, 1 H, 1-H), 4.51 (t, J = 5.8 Hz, 1 H, 6-OH), 4.60 [s, 1 H,$OCH_2C(CH_3)(OH)CH_2OCO(CH_2)_6CH_3$], 4.88 (d, J = 5.3 Hz, 1 H, 3-OH), 4.98 (d, J = 4.1 Hz, 1 H, 4-OH), 7.64 (d, J = 8.9 Hz, 1 H, NH) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 13.9 [$OCH_2C(CH_3)(OH)CH_2OCO(CH_2)_6\mathit{C}H_3$], 21.7 [$OCH_2C(\mathit{C}H_3)$-$(OH)CH_2OCO(CH_2)_6CH_3$], 22.9 ($\mathit{C}H_3CON$), 22.0–33.4 [$OCH_2C(CH_3)(OH)CH_2OCO(\mathit{C}H_2)_6CH_3$], 55.4 (C-2), 61.0 (C-6), 67.9 [$OCH_2C(CH_3)(OH)\mathit{C}H_2OCO(CH_2)_6CH_3$], 69.9 (C-5), 70.6 [$OCH_2\mathit{C}(CH_3)(OH)CH_2OCO(CH_2)_5CH_3$], 73.4 [$O\mathit{C}H_2C(CH_3)$-$(OH)CH_2OCO(CH_2)_6CH_3$], 73.9 (C-3), 76.9 (C-4), 101.9 (C-1), 169.1 ($CH_3\mathit{C}ON$), 172.8 [$OCH_2C(CH_3)(OH)CH_2O\mathit{C}O(CH_2)_6$-$CH_3$] ppm. MS (FAB): m/z (%) = 458 (100) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{20}H_{37}NO_9Na$ [M + Na]$^+$ 458.2366; found 458.2383.

(2*S*)-2-Hydroxy-2-methyl-2-palmitoyloxypropyl 2-Acetamido-2-deoxy-β-D-glucopyranoside (59): The pure compound was obtained as a white solid by column chromatography using dichloromethane/methanol (10:1) as eluent; yield 0.46 g (85%); m.p. 112–113 °C. $[a]_D$ = –8.0 (c = 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 0.84 [t, J = 7.0 Hz, 3 H, $OCH_2C(CH_3)(OH)CH_2OCO$-$(CH_2)_{14}C\mathit{H}_3$], 1.01 [s, 3 H, $OCH_2C(C\mathit{H}_3)(OH)CH_2OCO$-$(CH_2)_{14}CH_3$], 1.2–1.6 [m, 28 H, $OCH_2C(CH_3)(OH)CH_2OCO$-$(C\mathit{H}_2)_{14}CH_3$], 1.75 (s, 3 H, CH_3CON), 2.28 [t, J = 7.5 Hz, 2 H, $OCH_2C(CH_3)(OH)CH_2OCOC\mathit{H}_2(CH_2)_{13}CH_3$], 3.04–3.06 (m, 2 H, 4-H, 5-H), 3.25–3.30 [m, 2 H, 3-H, $OCH_A\mathit{H}_BC(CH_3)(OH)$-$CH_2OCO(CH_2)_{14}CH_3$], 3.36 (m, 1 H, 2-H), 3.44 (m, 1 H, 6_A-H), 3.52 [d, J = 9.7 Hz, 1 H, $OC\mathit{H}_AH_BC(CH_3)(OH)CH_2OCO$-$(CH_2)_{14}CH_3$], 3.67 (m, 1 H, 6_B-H), 3.81 [dd, J = 10.9 Hz, 2 H, $OCH_2C(CH_3)(OH)C\mathit{H}_2OCO(CH_2)_{14}CH_3$], 4.24 (d, J = 8.4 Hz, 1 H, 1-H), 4.47 (t, J = 5.8 Hz, 1 H, 6-OH), 4.56 [s, 1 H, $OCH_2C(CH_3)(O\mathit{H})CH_2OCO(CH_2)_{14}CH_3$], 4.84 (d, J = 5.3 Hz, 1 H, 3-OH), 4.93 (d, J = 4.9 Hz, 1 H, 4-OH), 7.61 (d, J = 9.4 Hz, 1 H, NH) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 13.9 [$OCH_2C(CH_3)(OH)CH_2OCO(CH_2)_{14}\mathit{C}H_3$], 21.7 ($\mathit{C}H_3CON$), 22.9 [$OCH_2C(\mathit{C}H_3)(OH)CH_2OCO(CH_2)_{14}CH_3$], 22.0–33.5 [$OCH_2C$-$(CH_3)(OH)CH_2OCO(\mathit{C}H_2)_{14}CH_3$], 55.4 (C-2), 61.0 (C-6), 67.9 [$OCH_2C(CH_3)(OH)\mathit{C}H_2OCO(CH_2)_{14}CH_3$], 69.9 [$OCH_2\mathit{C}(CH_3)$-$(OH)CH_2OCO(CH_2)_{14}CH_3$], 70.6 (5-C), 73.4 [$O\mathit{C}H_2C(OH)(CH_3)$-$CH_2OCO(CH_2)_{14}CH_3$], 73.9 (C-3), 76.9 (C-4), 101.9 (C-1), 170.7 ($CH_3\mathit{C}ON$), 172.8 [$OCH_2C(CH_3)(OH)CH_2O\mathit{C}O(CH_2)_{14}$-$CH_3$] ppm. MS (FAB): m/z (%) = 570 (100) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{28}H_{53}NO_9Na$ [M + Na]$^+$ 570.3618; found 570.3583. $C_{28}H_{53}NO_9$ (547.37): calcd. C 61.40, H 9.75, N 2.56; found C 61.59, H 9.62, N 2.55.

(2*R*)-2-Hydroxy-2-methyl-3-palmitamidopropyl 2-Acetamido-2-deoxy-β-D-glucopyranoside (63): A pale-yellow syrup was obtained after column chromatography using dichloromethane/methanol (10:1) as eluent; yield 0.43 g (80%). $[a]_D$ = –14.3 (c = 0.3, MeOH). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 0.84 [t, J = 6.8 Hz, 3 H, $OCH_2C(CH_3)(OH)CH_2NHCOCH_2(CH_2)_{13}C\mathit{H}_3$], 0.96 [s, 3 H, $OCH_2C(C\mathit{H}_3)(OH)CH_2NHCOCH_2(CH_2)_{13}CH_3$], 1.20–1.27 [m, 26 H, $OCH_2C(CH_3)(OH)CH_2NHCOCH_2(C\mathit{H}_2)_{13}CH_3$], 1.82 (s, 3 H, $NHCOC\mathit{H}_3$), 2.12 [t, J = 7.4 Hz, 2 H, $OCH_2C(CH_3)(OH)$-$CH_2NHCOC\mathit{H}_2(CH_2)_{13}CH_3$], 4.20 (d, J = 8.5 Hz, 1 H, 1-H), 7.54 [t, J = 5.80 Hz, 1 H, $OCH_2C(CH_3)(OH)CH_2N\mathit{H}COCH_2$-$(CH_2)_{13}CH_3$], 7.71 (d, J = 8.9 Hz, 1 H, NH) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 13.9 [$OCH_2C(OH)(CH_3)CH_2OCO$-$(CH_2)_{14}\mathit{C}H_3$], 22.5 [$OCH_2C(OH)(\mathit{C}H_3)CH_2NHCO(CH_2)_{14}CH_3$], 22.9 ($\mathit{C}H_3CON$), 22.0–33.5 [$OCH_2C(CH_3)(OH)CH_2NHCO$-$(\mathit{C}H_2)_{14}CH_3$], 45.8 [$OCH_2C(CH_3)(OH)\mathit{C}H_2NHCO(CH_2)_{14}CH_3$], 55.4 (C-2), 61.0 (C-6), 70.5 [$OCH_2\mathit{C}(CH_3)(OH)CH_2NHCO$-$(CH_2)_{14}CH_3$], 71.0 (C-5), 74.4 [$O\mathit{C}H_2C(CH_3)(OH)$-$CH_2NHCO(CH_2)_{14}CH_3$], 74.7 (C-3), 77.0 (C-4), 102.0 (C-1), 169.5 ($CH_3\mathit{C}ON$), 173.0 [$OCH_2C(CH_3)(OH)CH_2NH\mathit{C}O(CH_2)_{14}$-$CH_3$] ppm. MS (FAB): m/z (%) = 569 (100) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{28}H_{54}N_2O_8Na$ [M + Na]$^+$ 569.3778; found 569.3795.

Synthesis of (2*S*)-2-Hydroxy-2-methyl-3-oleoyloxypropyl 2-Acetamido-2-deoxy-β-D-glucopyranoside (60): A solution of compound **57** (0.4 mmol) in 80% acetic acid/water (20 mL) was heated at 60 °C. The reaction was monitored until TLC showed that all the starting material had reacted (5 h). Then the reaction mixture was cooled to room temperature. The pH of the solution was adjusted to 7.5 with saturated aqueous sodium hydrogen carbonate solution and the aqueous solution was extracted with dichloromethane. The organic layer was washed with water and saturated aqueous sodium chloride solution, dried with $MgSO_4$ and concentrated under reduced pressure. The syrup was purified by column chromatography using dichloromethane/methanol (10:1) as eluent; yield 0.46 g (85%). $[a]_D$ = –22.0 (c = 0.3, MeOH). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 0.85 [t, J = 7.0 Hz, 3 H, $OCH_2C(CH_3)(OH)$-$CH_2OCO(CH_2)_7CH{=}CH(CH_2)_7C\mathit{H}_3$], 1.02 [s, 3 H, OCH_2C-$(C\mathit{H}_3)(OH)CH_2OCO(CH_2)_7CH{=}CH(CH_2)_7CH_3$], 1.20–1.55 [m, 22 H, $OCH_2C(CH_3)(OH)CH_2OCOCH_2(C\mathit{H}_2)_5CH_2CH{=}CHCH_2$-$(C\mathit{H}_2)_6CH_3$], 1.76 (s, 3 H, CH_3CON), 1.95–2.00 [m, 4 H, $OCH_2C(CH_3)(OH)CH_2OCO(CH_2)_6C\mathit{H}_2CH{=}CHC\mathit{H}_2(CH_2)_6CH_3$], 2.28 [t, J = 7.3 Hz, 2 H, $OCH_2C(CH_3)(OH)CH_2OCOC\mathit{H}_2$-$(CH_2)_6CH{=}CH(CH_2)_7CH_3$], 3.04–3.08 (m, 2 H, 4-H, 5-H), 3.25–3.50 [m, 4 H, 2-H, 3-H, 6_A-H, $OCH_A\mathit{H}_BC(CH_3)(OH)CH_2OCO$-$(CH_2)_7CH{=}CH(CH_2)_7CH_3$], 3.53 [d, J = 9.6 Hz, 1 H, $OC\mathit{H}_AH_BC(CH_3)(OH)CH_2OCO(CH_2)_7CH{=}CH(CH_2)_7CH_3$], 3.66 (m, 1 H, 6_B-H), 3.81 [dd, J = 11.0 Hz, 2 H, $OCH_2C(CH_3)(OH)$-$C\mathit{H}_2OCO(CH_2)_7CH{=}CH(CH_2)_7CH_3$], 4.25 (d, J = 8.2 Hz, 1 H, 1-H), 4.48 (t, J = 5.8 Hz, 1 H, 6-OH), 4.56 [s, 1 H, $OCH_2C(CH_3)(O\mathit{H})CH_2OCO(CH_2)_7CH{=}CH(CH_2)_7CH_3$], 4.85 (d, J = 5.1 Hz, 1 H, 3-OH), 4.94 (d, J = 4.7 Hz, 1 H, 4-OH), 5.31 [m, 2 H, $OCH_2C(CH_3)(OH)CH_2OCO(CH_2)_7C\mathit{H}{=}C\mathit{H}(CH_2)_7CH_3$], 7.61 (d, J = 8.9 Hz, 1 H, NH) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 13.9 [$OCH_2C(CH_3)(OH)CH_2OCO(CH_2)_7$-$CH{=}CH(CH_2)_7\mathit{C}H_3$], 21.7 [$OCH_2C(\mathit{C}H_3)(OH)CH_2OCO(CH_2)_7$-$CH{=}CH(CH_2)_7CH_3$], 22.9 ($\mathit{C}H_3CON$), 22.0–33.4 [$OCH_2C$-$(CH_3)(OH)CH_2OCO(\mathit{C}H_2)_7CH{=}CH(\mathit{C}H_2)_7CH_3$], 55.4 (C-2), 60.9 (C-6), 67.9 [$OCH_2C(CH_3)(OH)\mathit{C}H_2OCO(CH_2)_7CH{=}CH$-$(CH_2)_7CH_3$], 69.9 [$OCH_2\mathit{C}(CH_3)(OH)CH_2OCO(CH_2)_7CH{=}CH$-$(CH_2)_7CH_3$], 70.6 (C-5), 73.5 [$O\mathit{C}H_2C(CH_3)(OH)CH_2OCO$-$(CH_2)_7CH{=}CH(CH_2)_7CH_3$], 73.9 (C-3), 76.9 (C-4), 101.9 (C-1), 129.6 [$OCH_2C(CH_3)(OH)CH_2OCO(CH_2)_7\mathit{C}H{=}\mathit{C}H(CH_2)_7CH_3$], 169.0 ($CH_3\mathit{C}ON$), 172.7 [$OCH_2C(CH_3)(OH)CH_2O\mathit{C}O(CH_2)_7$-$CH{=}CH(CH_2)_7CH_3$] ppm. MS (FAB): m/z (%) = 596 (100) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{30}H_{55}NO_9Na$ [M + Na]$^+$ 596.3775; found 596.3795.

Synthesis of (2*R*)-3-Amino-2-hydroxy-2-methylpropyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-2-deoxy-β-D-glucopyranoside (61): A solution of compound **53** (0.5 mmol) in dry methanol (10 mL) was subjected to hydrogenolysis over 10% Pd/C (50 mg) at room temperature under hydrogen (1 bar) for 4 h. The mixture was diluted with methanol and the catalyst was filtered off and washed with methanol. The filtrate was concentrated to dryness under reduced pressure. The compound was detected by MS and used without purification in the deprotection reaction. MS (FAB): m/z (%) = 569 (40) [M + Na]$^+$. HRMS (FAB): calcd. for $C_{26}H_{34}N_2O_7Na$ [M + Na]$^+$ 509.2264; found 509.2258.

Bioactivity

Cell Culture: The human A549 lung cancer cell line and the human lung fibroblastic MRC-5 cell line were maintained in DMEM sup-

plemented with 2 mM glutamine, 50 μg/mL penicillin, 50 μg/mL streptomycin and 10% foetal bovine serum. Cell lines were cultured at 37 °C in a humidified atmosphere containing 5% CO_2. Cell culture reagents were obtained from Life Technologies.

Cell Proliferation Assay: The MTT assay is a colorimetric technique that allows the quantitative determination of cell viability. It is based on the capability of viable cells to transform the MTT salt [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide] into a formazan dye. Exponentially growing cells were seeded into 96-well plates and drugs were added after 24 h. Following an incubation period of 48 h, the medium was removed and MTT (125 μL, 1 mg/mL in medium) was added to each well for 5 h. Then 20% sodium dodecyl sulfate (80 μL) in 0.02 M HCl was added, plates were incubated for 10 h at 37 °C and optical densities were measured at 540 nm on a multi-well plate spectrophotometer reader. Cell viability was expressed as a percentage relative to controls. All data were averaged from at least three independent experiments and were expressed as mean ± standard deviation of the means (e.s.d. values).

Supporting Information (see footnote on the first page of this article): ^{1}H NMR spectra for the reported new compounds.

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