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Alkenyl β-D-galactopyranoside derivatives as efficient chiral templates in stereoselective cyclopropanation and epoxidation reactions

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ABSTRACT

The synthesis of a wide range of alkenyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranosides is described. The cyclopropanation and epoxidation reactions of these compounds were developed. Cyclopropanation reactions took place with high stereoselectivity giving diastereomeric excesses of up to 100%. As a part of our aim in studying hydroxyl-directed reactions, their epoxidation with *m*-CPBA was carried out. High diastereomeric excesses (80–100%) were obtained when the hydroxyl group at C-2 of the auxiliary was unprotected. The β-D-galactopyranoside moiety constitutes as an interesting auxiliary, due to its efficient chirality transfer capability as well as providing a way to obtain a variety of glycolipid derivatives.

1. Introduction

Given the close relationship between therapeutic activity and chirality, the preparation of enantiomerically pure compounds, to be tested and/or used as potential drugs, is currently a great challenge in organic and pharmaceutical chemistries. The use of chiral auxiliaries to achieve stereoselectivity is an important strategy in asymmetric synthesis in order to obtain enantiomerically enriched compounds.[1] In this context, carbohydrates, which contain several functional groups and stereogenic centres in one molecular unit, are effective tools as chiral inducers.[2,3]

One of our lines of research, the search for new methods to prepare enantiomerically pure substances, is centred on the development of methods for the synthesis of synthetic and/or functionally relevant functions, such as the cyclopropanes and oxiranes, via the stereoselective transformation of alkenes, employing carbohydrates as chiral inducers. The fragment, which contains the double bond to be transformed, is incorporated into different positions of the sugar residue by means of different organic functions.

Due to the presence of cyclopropane rings in a variety of natural products and biologically active compounds,[4] and their nature as versatile synthetic intermediaries for the preparation of more functionalised cycloalkanes and acyclic compounds,[5] the development of efficient methods for the synthesis of chiral non-racemic cyclopropane moieties is an important aim in asymmetric synthesis. General methods for this stereoselective synthesis have recently been reviewed.[6] One synthetic strategy is based on the stereoselective addition of the methylene group to substituted allylic alcohols and to α,β-unsaturated carbonyl compounds joined to different chiral auxiliaries.[7] There are only a few precedents for the stereoselective synthesis of cyclopropanes using carbohydrates as chiral auxiliaries.[8–12] Our group has recently published the stereoselective cyclopropanation (using the diiodomethane/diethyl zinc system) of a wide range of alkenes linked via an acetal function to different backbones of sugar moieties.[13,14] It is important to note that the union of the olefin to the carbohydrate via an acetal function allowed the easy separation of the new chiral cyclopropane fragment and the chiral auxiliary by mild acid hydrolysis.

Chiral epoxides are widely employed in organic synthesis because they are useful synthetic intermediates that can easily be transformed into a variety of target molecules[15] (via their opening reaction which allows the obtention of 1,2-difunctionalised compounds and the formation of new carbon–carbon bonds). The functional group is itself an essential structural moiety of many natural products and biologically active compounds.[16] Its chemical reactivity is responsible for the biological activity exhibited by the compounds that contain the function; certain glycosyl glycidols (oxiranes derived from alkenyl glycosides) have cytotoxic activity and can be used as alkylating agents in anticancer chemotherapy.[17] The development of efficient methods to gain access to chiral epoxides with high enantiomeric excesses is an important goal of many research groups, including our own.

The enantioselective epoxidation of non-functionalised olefins is one of the most useful processes in synthetic transformations for the introduction of functional groups into organic molecules. Over the last few years we have developed methods for the stereoselective epoxidation of olefins, involving the use of chiral catalysts or chiral auxiliaries, both of which are derived from sugars. With regard to the first, we have recently described the synthesis of new chiral ketones and their use as catalysts in the enantioselective dioxirane-mediated epoxidation of a wide range of arylalkenes.[18] For the second, we have developed the stereoselective

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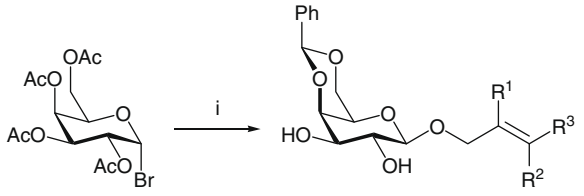
epoxidation of olefins with *m*-CPBA. The olefinic chain was joined to different positions of a sugar molecule, acting as a chiral auxiliary via various functions: glycoside, amide and acetal. The chiral epoxyalkyl glycosides,[19] epoxyamides[20] and epoxyacetals[21,22] obtained can be transformed into different types of compound. This method has enabled us to synthesise derivatives of glycosylglycerol analogues which have been used as an alkylating-agent carrier system[23] and phenylisoserine precursors[21,22] whose acetal function can be easily hydrolysed in the organism to separate the active fraction of the sugar moiety.

Herein we continue to investigate the development of effective methods for the selective cyclopropanation and epoxidation of alkenes. In the present case, the substrates chosen as carriers of the double bond for the stereoselective transformations are a wide range of allyl alcohols that join to the chiral auxiliary via a glycosidic bond with D-galactose as the carbohydrate inducer of chirality. We chose this carbohydrate as the auxiliary; (a) because there are few references describing the use of chiral auxiliaries derived from D-galactose in these reactions on double bonds,[24] and thus to assess its capacity as a chirality agent; and (b) because D-galactose is a frequent sugar in glycolipid complexes such as glycerolipids, phosphatidic acids and sphingolipids, substances that have gained great interest as regulatory agents of cell proliferation, and thus are possibly useful in the treatment of cancer.[25] The synthesis of the derivatives or analogues of these natural products is a focus of attention. On this point it is of interest that the stereoselective synthesis of the cyclopropane and oxirane functions of the substituents on the anomeric position of D-galactosyl derivatives is shown to be an effective procedure for obtaining synthetic intermediaries and analogues of those natural compounds for their subsequent biological evaluation.



1

2 R^1 = H , R^2 = H, R^3 = H
3 R^1 = H , R^2 = H, R^3 = Ph
4 R^1 = H , R^2 = H, R^3 = Me
5 R^1 = H , R^2 = H, R^3 = *n*-C_7H_{15}
6 R^1 = H , R^2 = Me, R^3 = Me
7 R^1 = Me , R^2 = H, R^3 = H
8 R^1 = Me , R^2 = H, R^3 = Ph

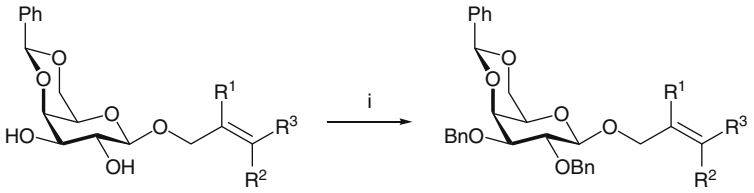
Scheme 1. Reagents and conditions: (i) (1) $HOCH_2CR^1{=}CR^2R^3$/$MeNO_2$–PhMe (1:1)/$Hg(CN)_2$/50 °C/2–3 h; (2) NaMeO/MeOH; (3) $PhCH(OMe)_2$/MeCN/CSA.

2. Results and discussion

Herein we report the highly diastereoselective cyclopropanation and epoxidation reactions of substituted allylic alcohols linked to a carbohydrate moiety readily available from commercial α-D-acetobromogalactose **1**. The double bond was incorporated into the sugar by a simple glycosidation reaction, and via a short synthetic sequence we obtained the new alkenyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranosides **2**–**8**. By this means we achieved a set of functionalised substances with a well-defined stereochemistry, and with a double bond susceptible to transformation into compounds with diverse but constitutionally similar chemical features (Scheme 1). These alkenyl derivatives are obtained in good chemical yields and as single diastereoisomers. In all cases, the proton of 4,6-*O*-(*S*)-benzylidene acetal appears as a singlet between 5.57 and 5.55 ppm, while the proton at the anomeric position appears as a doublet at around 4.30 ppm in those cases where its signal is resolved.

In order to have a higher number of substrates to study the reactions and to analyse the effect of the free hydroxyl groups at the 2- and 3-position of the sugar and/or the aromatic residues of the protecting groups introduced into both the chemical and stereochemical yields obtained in the cyclopropanation and epoxidation reactions, and at the same time to attempt to resolve the possible problems caused by the solubilities of the alkenyl derivatives in the solvents used in these reactions (caused by the presence of the OH at the 2- and 3-position of the sugar), the compounds **9**–**15** were obtained by the introduction of benzyl ethers (Scheme 2). In all cases, the signals for the two pairs of diastereotopic benzyl protons (2-OCH_2Ph and 3-OCH_2Ph) appear between 4.9 and 4.7 ppm.

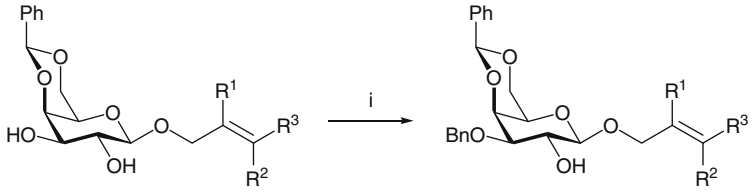
It has been reported that β-D-glucopyranosides with a free hydroxyl group at the 2-position are efficient chiral auxiliaries for stereoselective reactions of cyclopropanation and epoxidation of allyl alcohols present on the aglyclone.[8,19,26] The presence of the OH at the 2-position of the sugar is a determinant for the stereoselectivity of the reactions of epoxidation and cyclopropanation of allyl β-D-glucopyranosides, and can be attributed to the OH presumably acting as an anchor point of the reagent from which it is transferred preferentially to one of the faces of the double bond which determines the configuration of the major diastereoisomer obtained. Thus, our next aim in adding to the range of compounds in which we were going to carry out both reactions of transformation of the double bond was the synthesis of the 3-O-benzylated derivatives. We obtained compounds that conserve a free OH at the 2-position of the sugar and are soluble in the appropriate solvents, in order to evaluate whether in these new galactosyl derivatives the 2-OH group is determinant in the stereochemical control of the reaction. The bibliography describes the



2–**8**

9 R^1 = H , R^2 = H, R^3 = H
10 R^1 = H , R^2 = H, R^3 = Ph
11 R^1 = H , R^2 = H, R^3 = Me
12 R^1 = H , R^2 = H, R^3 = *n*-C_7H_{15}
13 R^1 = H , R^2 = Me, R^3 = Me
14 R^1 = Me , R^2 = H, R^3 = H
15 R^1 = Me , R^2 = H, R^3 = Ph

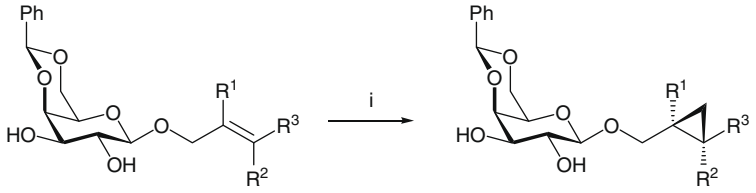
Scheme 2. Reagents: (i) BnBr/KOH/18-crown-6/THF.



2–8

16 R^1 = H , R^2 = H, R^3 = H
17 R^1 = H , R^2 = H, R^3 = Ph
18 R^1 = H , R^2 = H, R^3 = Me
19 R^1 = H , R^2 = H, R^3 = *n*-C_7H_{15}
20 R^1 = H , R^2 = Me, R^3 = Me
21 R^1 = Me , R^2 = H, R^3 = H
22 R^1 = Me , R^2 = H, R^3 = Ph

Scheme 3. Reagents: (i) BnBr/KOH/18-crown-6/THF.



3 R^1 = H , R^2 = H, R^3 = Ph
6 R^1 = H , R^2 = Me, R^3 = Me

23 R^1 = H , R^2 = H, R^3 = Ph
24 R^1 = H , R^2 = Me, R^3 = Me

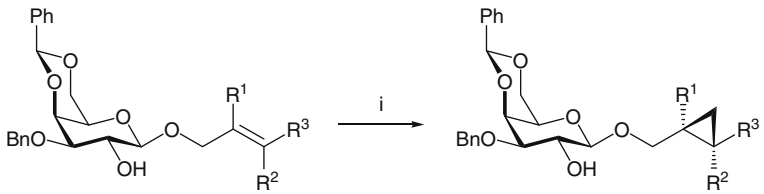
Scheme 4. Reagents: (i) $CH_2I_2/ZnEt_2/CH_2Cl_2$.

benzylation mediated by butyltin oxide which takes place with high chemoselectivity towards the 3-position of the allyl 4,6-*O*-benzylidene-β-galactopyranoside to give the 3-*O*-benzyl ether, a reaction that requires heating and reaction times of around 24 h.[27] We have developed a method for the selective monobenzylation of the hydroxyl at position 3 of the sugar, using the same method as for the dibenzylation, although with rigorous control of the equivalents of reagents and, mainly, of the reaction time (20–30 min) (for general conditions see Experimental) (Scheme 3). We achieved marked improvements over the previously described procedure with regard to shorter reaction times, no need for heating and applicability to a variety of alkenyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranosides with products **16**–**22** being obtained. In all cases the signal due to the benzyl protons appears at around 4.7 ppm.

The next step was to tackle the cyclopropanation of the new alkenyl derivatives by the general method of Simmons–Smith. This cyclopropanation reaction had been studied in allyl β-D-glucopyranosides in toluene, which takes place with high diastereoisomeric excesses.[8b,9–12] As our products, with a free OH at at the 2- and 3-position of the sugar, are not very soluble in toluene, we decided to use CH_2Cl_2 as the solvent, and chose for this assay, compounds **3** and **6** (Scheme 4). Compounds **23** and **24** were obtained in 57% and 22% of diastereoisomeric excess, respectively (determined by ^{1}H NMR).

For the assays of the cyclopropanation reaction in toluene, we chose the alkenyl glycoside analogues of **2** and **3**, which are soluble in that solvent and hence give the corresponding dibenzylated and monobenzylated derivatives. The cyclopropanation reaction of compounds **10** and **13** (2,3-di-*O*-benzyl-derived substrates) in toluene does not take place. We attribute this to the steric hindrance exerted by the benzyl group at the 2-position of the sugar, obstructing the access of the reagent to the double bond. However, the reaction of compounds **17** and **20** (3-*O*-benzyl-derived) yielded compounds **25** and **26** with 100% diastereoisomeric excess. This led us to subject the remaining 3-O-benzylated derivatives, compounds **18**, **19** and **22**, to the cyclopropanation reaction to give compounds **27**, **28** and **29** (Scheme 5). The excesses continued to be high: 74–100% (Table 1).

All the cyclopropyl derivatives with a Ph at the 2-position of the cyclopropane ring present the signals of the 2H of the methylenic bridge at around 0.9–1.0 ppm while those of the H of the methines



17 R^1 = H , R^2 = H, R^3 = Ph
18 R^1 = H , R^2 = H, R^3 = Me
19 R^1 = H , R^2 = H, R^3 = *n*-C_7H_{15}
20 R^1 = H , R^2 = Me, R^3 = Me
22 R^1 = Me , R^2 = H, R^3 = Ph

25 R^1 = H , R^2 = H, R^3 = Ph
26 R^1 = H , R^2 = Me, R^3 = Me
27 R^1 = H , R^2 = H, R^3 = Me
28 R^1 = H , R^2 = H, R^3 = *n*-C_7H_{15}
29 R^1 = Me , R^2 = H, R^3 = Ph

Scheme 5. Reagents: (i) $CH_2I_2/ZnEt_2/PhCH_3$.

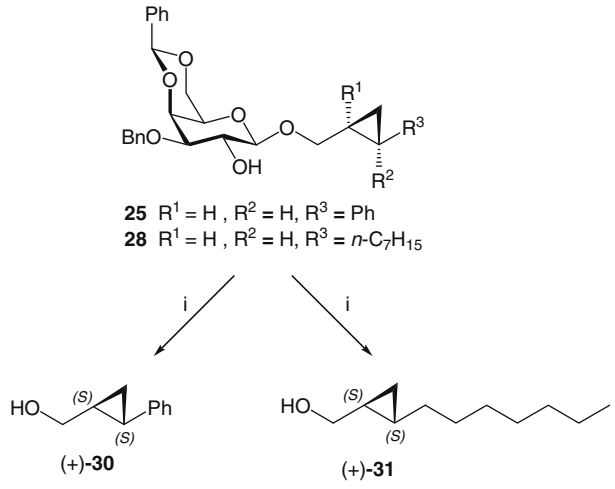
Table 1
Cyclopropanation of alkenyl galactopyranosides **17**–**20** and **22** produced via Scheme 5

Entry	Starting compound	Reaction product	Yield[a] (%)	De[b] (%)	Major cyclopropane configuration
1	**17**	**25**	95	100	(2*S*,3*S*)
2	**18**	**27**	91	84	(2*S*,3*S*)
3	**19**	**28**	91	100	(2*S*,3*S*)
4	**20**	**26**	91	100	(2*S*)
5	**22**	**29**	67	78	(2*S*,3*R*)

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

of the cycle between 1.5 ppm and 1.8 ppm. For the 2-alkyl cyclopropyl derivatives, those signals appeared at around 0.2–0.5 ppm and 0.7–0.9 ppm, respectively.

In order to assign the absolute configuration of the stereogenic centres generated in the cyclopropanation reaction, the cyclopropyl derivatives **25** and **28** (obtained with some 100% diastereoisomeric excess) were treated with triflic anhydride in pyridine; subsequent heating in aqueous DMF in the presence of pyridine yielded the enantiomerically pure cyclopropylcarbinols **30** and **31**.[9] Comparison of the specific rotations of these compounds with those reported in the literature enabled us to assign the absolute stereochemistry of the cyclopropane ring for compounds **30**[14,28] and **31**[14] (Scheme 6); in both cases the enantiomer obtained had an (*S*,*S*)-configuration. The reactive face is the same in the two cases—its notation being (*Si*,*Si*) for compound **17** (with one aromatic substituent on carbon three of the allyl moiety) and (*Si*,*Re*) for compound **19** (with one alkyl substituent on carbon three). It should be emphasised that our research group had already described the enantioselective synthesis of the cyclopropylcarbinol enantiomers of **30** and **31**, employed as a chiral auxiliary 1,2-*O*-isopropylidene-α-D-xylofuranose and incorporating the alkene via an acetal function that is readily cleaved off.[14] The configurations of the other cyclopropanes listed in Table 1 were established from analysis of the chemical shifts of the protons and the carbons of the cyclopropane system and anomeric position in the NMR data.



Scheme 6. Reagents and conditions: (i) (1) Tf_2O/Py (95%); (2) DMF/Py/H_2O/160 °C.

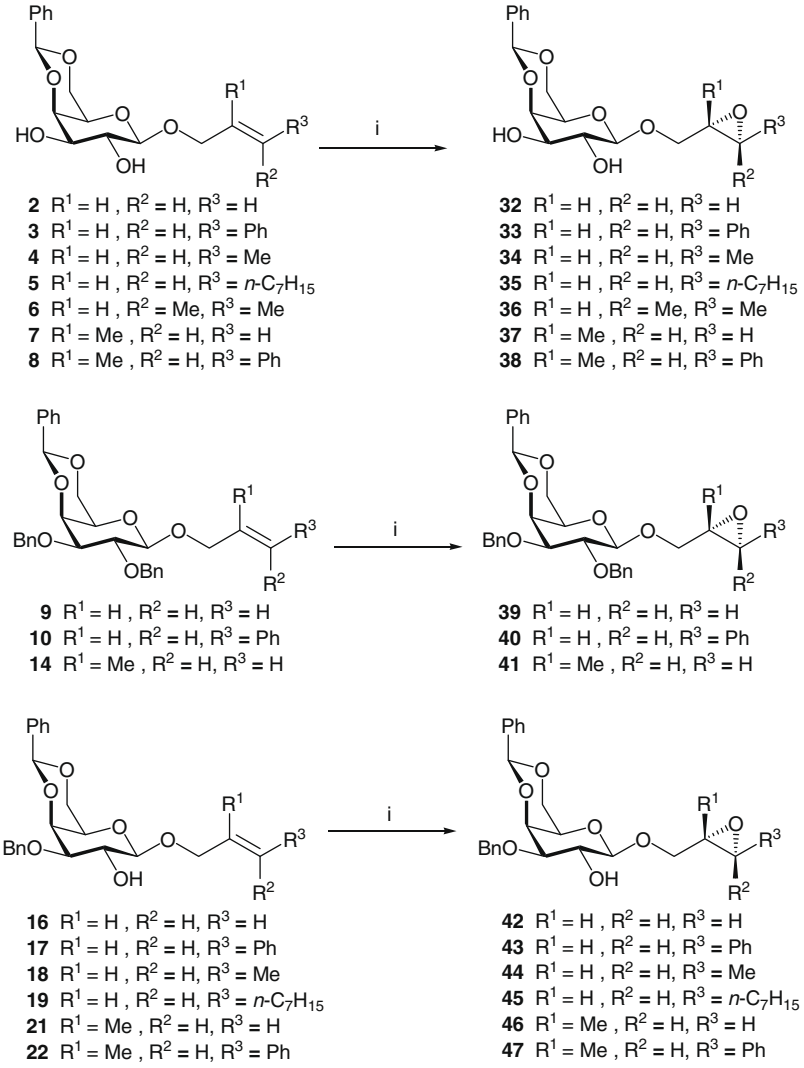
The second part of the study, which was within our line of work centred on the development of new sugar-derived chiral inducers for *hydroxyl-group-directed* reactions, was to subject the newly synthesised β-allyl galactopyranosides to an epoxidation reaction with *m*-CPBA. This general method is of interest not only because it enables access to chiral-substituted epoxyalcohols, but also because it undoubtedly provides a procedure for the synthesis of a variety of compounds by oxirane opening, for example, glycolipids, in the present context: the employment of D-galactose derivatives as chiral template acquires added value. Our group has already described the use of this method for the synthesis of chiral epoxyalkyl glucosides with high diastereoisomeric excesses,[19] and derivatives of glycosylglycerol analogues that have been used as an alkylating agent carrier system.[23] The aim of this work was to obtain epoxyalkyl galactopyranosides and to study the influence of both the configuration of the sugar (*galacto*) and the role of the OH at the 2- and 3-position of the sugar on the stereoselectivity of the epoxidation reaction. In all cases the reaction was performed in chloroform at −15 °C for the time necessary until plate detection showed that all the starting material had been consumed (for reaction conditions see Experimental). The reaction of compounds **2–8** (with the free OH at the 2- and 3-position of the sugar) yielded compounds **32**–**38**. Compounds **9, 10** and **14** (2,3-di-*O*-benzyl derivatives) yielded the compounds **39**–**41**. The epoxidation of the 3-*O*-benzyl derivatives **16–19**, **21** and **22** yielded compounds **42–47** (Scheme 7).

The diastereoisomeric excesses were established by ^{1}H NMR (Table 2). For their analysis, the epoxyalkyl β-D-galactopyranosides were grouped into three groups. The first group comprises those substrates with a free OH at the 2- and 3-position of the sugar residue (compounds **32–38**); the second group comprises those epoxides obtained by using 2,3-di-*O*-benzyl derivative as a chiral inducer (compounds **39–41**); and the third group comprises those in which the chiral auxiliary is a 3-*O*-benzyl derivative (compounds **42–47**). As can be seen in Table 2, the compounds obtained with the largest diastereoisomeric excesses are **32–38** and **42–47**, with values between 77% and 100%. However, the excesses obtained fall drastically (9–23%), and in one case to zero, for compounds **39–41**. This demonstrates that the presence of the OH at the 2-position of the sugar is the determinant for the stereoselectivity of the epoxidation reaction of the double bond with *m*-CPBA attributed to the formation of a hydrogen bridge between the OH group and the peroxyacid.

The stereoselectivity generated due to the directing role of the group at the 2-position of the sugar able to form hydrogen bridges with the peroxyacid has already been described in the epoxidation reactions of alkenyl β-D-glucopyranoside derivatives[26] (OH group at the 2-position of the sugar) and by ourselves in the epoxidation reaction of alkenyl glycoside derived from *N*-acetyl-D-glucosamine (acetamido group on 2),[19] in both cases the reactive face being *Re*. Our group has also described the stereoselectivity in the epoxidation reaction of propenylidene acetals derived from glucopyranosides, allopyranosides, glucofuranosides and xylofuranosides, and how the stereochemistry of the major oxirane obtained depends on the configuration of the sugar residue employed as a chiral auxiliary and whether the OH at the 3-position of the sugar is free or protected; the asymmetric induction is greater when it is free.[20,21]

In order to assign the configuration to the stereogenic centres in the oxirane ring formed in the epoxidation reaction, the chemical shifts of the easily identifiable protons and carbons must be analysed and compared with the signals of epoxyalkyl β-D-glucopyranoside analogues previously described.[19] For this, we compared the chemical displacements and profile of the signals of the protons and carbons of epoxyalkyl 2-acetamido-(*R*)-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside analogues **49–52** (Scheme 8), whose epoxyalkyl moieties on the anomeric position are analogous to those present on compounds **32–47** (Table 3).

In most of the cases examined (as shown in Table 3), the major stereoisomer presents a lower chemical shift in ^{1}H NMR for the anomeric proton, and a higher chemical displacement for the anomeric carbon in ^{13}C NMR. At the same time, the signals of the carbons of the oxirane ring and of the allyl methylene appear at lower values of chemical displacement for the major stereoisomer than



Scheme 7. Reagents and conditions: (i) *m*-CPBA/$CHCl_3$/−15 °C.

Table 2
Epoxidation of alkenyl galactopyranosides **2**–**10**, **14**, **16**–**19**, **21** and **22** produced via Scheme 7

Entry	Starting compound	Reaction product	Yield[a] (%)	De[b] (%)	Major oxirane configuration[c]
1	**2**	**32**	63	100	(2*R*)
2	**3**	**33**	72	85	(2*S*,3*S*)
3[b]	**4**	**34**	56	80	(2*S*,3*S*)
4	**5**	**35**	74	80	(2*S*,3*S*)
5	**6**	**36**	92	23	(2*S*)
6	**7**	**37**	79	88	(2*R*)
7	**8**	**38**	80	76	(2*S*,3*S*)
8	**9**	**39**	90	23	(2*R*)
9	**10**	**40**	72	9	(2*S*,3*S*)
10	**14**	**41**	90	0	-
11	**16**	**42**	61	77	(2*R*)
12	**17**	**43**	87	73	(2*S*,3*S*)
13	**18**	**44**	98	84	(2*S*,3*S*)
14	**19**	**45**	80	86	(2*S*,3*S*)
15	**21**	**46**	79	88	(2*R*)
16	**22**	**47**	85	81	(2*S*,3*S*)

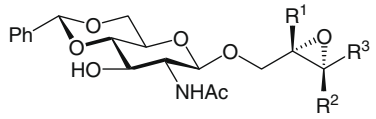
[a] Yields refer to compounds obtained in each reaction after isolation and purification.
[b] Determined by relative integration in the ^1H NMR spectra of reaction mixture.
[c] Deduced by comparative studies of NMR data, Table 3.

for the minor stereoisomer in those compounds whose signals are spread for each diastereoisomer.

From these correlation studies we were able to assign the notation for the more reactive face (in all cases studied it was always the same): *Re,Re* in compounds with one aromatic substituent on the C-3; *Re* in compounds whereby both substituents on the C-3 are the same and *Re,Si* in compounds with one alkyl substituent on C-3; as well as the absolute configuration of the major stereoisomer for compounds **32–47** as shown in Table 3.

3. Conclusions

Herein we have described the synthesis of a wide range of new alkenyl β-D-galactopyranoside derivatives and their use as chiral templates for the stereoselective transformation of the double bond moiety. Their cyclopronation and epoxidation reactions took place with high diastereoisomeric excesses, up to 100%. The des in both reactions were found to depend on the presence of the OH group at the 2-position of the unprotected sugar, which determines the selective transfer of the reagent from one face to the double bond. The excellent chemical and stereochemical yields obtained allow us to consider the D-galactose moiety as an effective chiral



48 R^1 = H , R^2 = H, R^3 = Ph
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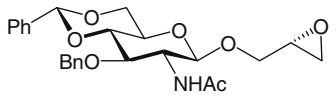
50 R^1 = H, R^2 = Me, R^3 = Me
51 R^1 = Me , R^2 = H, R^3 = H



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Scheme 8. Alkenyl glucopyranosides previously described.[19]

auxiliary; this methodology as an attractive way to obtain new chiral cycloalkyl and epoxyalkyl β-D-galactopyranoside derivatives that can be employed as precursors of glycolipid analogues.

4. Experimental

4.1. General

Evaporations were conducted under reduced pressure. Preparative chromatography was performed on Silica Gel 60 (E. Merck). Kieselgel 60 F_{254} (E. Merck) was used for TLC. Melting points were obtained on a Stuart Melting Point Apparatus SMP 10 and are uncorrected. Optical rotations were obtained on a Perkin Elmer Polarimeter Model 341 at 25 °C. Mass spectra were recorded on a Micromass AUTOSPECQ mass spectrometer: EI at 70 eV and CI at 150 eV, HR mass measurements with resolutions of 10,000. FAB mass spectra were recorded using a thioglycerol matrix. NMR spectra were recorded at 25 °C on a Bruker AMX500 spectrometer and on a Bruker AV500 spectrometer at 500 MHz for ^{1}H and 125 MHz for ^{13}C. The chemical shifts are reported in ppm on the δ scale relative to TMS. COSY, HSQC and NOESY experiments were performed to assign the signals in the NMR spectra.

4.2. General procedure for the synthesis of alkenyl glycosides 2–8

To a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide **1** (2.06 g, 5.0 mmol) in nitromethane–toluene (1:1) (30 mL), 4 Å molecular sieves (5 g), mercury cyanide (2.54 g, 10.0 mmol) and the corresponding unsaturated alcohol (10.0 mmol) were added. 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 dichloromethane. The organic layer was washed with an aqueous saturated solution of sodium bicarbonate and brine, then dried ($MgSO_4$), evaporated to dryness and purified by column chromatography. To a solution of the corresponding alkenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside in methanol (50 mL), a solution of sodium methoxide (1 mmol) in methanol (5 mL) was added. After 30 min at room temperature, the solution was neutralised by the addition of Dowex 50 resin (H^+ form), filtered and evaporated to dryness. To a solution of the corresponding alkenyl β-D-galactopyranoside in acetonitrile (30 mL), benzaldehyde dimethylacetal (10.0 mmol) and camphorsulfonic acid (10 mg) were added. 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 **2**–**9** in good yields.

4.2.1. Allyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 2[27]

The solid was purified by column chromatography using hexane–ethyl acetate (1:4) as eluent. Yield 1.1 g (72.2%). MS (CI): *m/z* 309 (40%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, 1Ph), 5.94 (m, $OCH_2CH{=}CH_2$), 5.53 (s, 1H, PhC*H*), 5.25 (m, 2H, $OCH_2CH{=}CH_2$), 4.42 (ddd, 1H, J_{gem} 12.6 Hz, *J* 5.3 Hz, ^4J 1.5 Hz, $OCH_AH_BCH{=}CH_2$), 4.31 (m, 2H, H-6_e, H-1), 4.19 (dd, 1H, $J_{3,4}$ 3.7 Hz, $J_{4,5}$ 1.0 Hz, H-4), 4.12 (ddd, 1H, J_{gem} 12.5 Hz, *J* 6.9 Hz, ^4J 1.1 Hz, $OCH_AH_BCH{=}CH_2$), 4.06 (dd, 1H, $J_{5,6a}$ 1.9 Hz, $J_{6e,6a}$ 12.5 Hz, H-6_a), 3.77 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 9.5 Hz, H-2), 3.67 (dd, 1H, $J_{2,3}$ 9.5 Hz, $J_{3,4}$ 3.7 Hz, H-3), 3.45 (m, 1H, H-5), 2.52 (m, 2H, 2OH).

4.2.2. (*E*)-3-Phenyl-2-propenyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 3

The solid was purified by column chromatography using hexane–ethyl acetate (1:4) as eluent. Yield 1.2 g (92%); mp 185–186 °C; $[\alpha]_D = -22.8$ (*c* 0.5, CH_2Cl_2); MS (CI): *m/z* 385 (5%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.2 (m, 10H, 2Ph), 6.65 (d, 1H, J_{trans} 16.0 Hz, $OCH_2CH{=}CHPh$), 6.34 (ddd, 1H, J_{trans} 16.0 Hz, *J* 5.8 Hz, *J* 6.8 Hz, $OCH_2CH{=}CHPh$), 5.57 (s, 1H, PhC*H*), 4.61 (ddd, 1H, J_{gem} 12.5 Hz, *J* 5.8 Hz, ^4J 1.5 Hz, $OCH_AH_BCH{=}CHPh$), 4.41 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 4.37 (dd, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.5 Hz, H-6_e), 4.32 (ddd, 1H, J_{gem} 12.5 Hz, *J* 6.9 Hz, ^4J 1.3 Hz, $OCH_AH_BCH{=}CHPh$), 4.22 (dd, 1H, $J_{3,4}$ 3.9 Hz, $J_{4,5}$ 1.1 Hz, H-4), 4.10 (dd, 1H, $J_{5,6a}$ 1.9 Hz, $J_{6e,6a}$ 12.5 Hz, H-6_a), 3.82 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 9.6 Hz, H-2), 3.71 (m, 1H, H-3), 3.50 (m, 1H, H-5), 2.52 (m, 2H, 2OH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.5–126.4 (2Ph), 133.5 ($OCH_2CH{=}CHPh$), 125.0 ($OCH_2CH{=}CHPh$), 101.6 (C-1), 101.5 (PhCH), 75.3 (C-4), 72.8 (C-3), 71.9 (C-2), 69.9 ($OCH_2CH{=}CHPh$), 69.2 (C-6), 66.8 (C-5). HRMS (CI): $[M+H]^+$, found 385.1641. $C_{22}H_{25}O_6$ requires 385.1651. Anal. Calcd for $C_{22}H_{24}O_6$: C, 68.74; H, 6.29. Found: C, 68.57; H, 6.41.

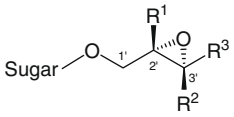
4.2.3. (*E*)-2-Butenyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 4

The solid was purified by column chromatography using hexane–ethyl acetate (1:4) as eluent. Yield 1.4 g (87%); mp 178–180 °C; $[\alpha]_D = -43.1$ (*c* 1.0, CH_2Cl_2); MS (FAB): *m/z* 345 (100%) $[M+Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 5.77 (m, 1H, $OCH_2CH{=}CHCH_3$), 5.63 (m, 1H, $OCH_2CH{=}CHCH_3$), 5.56 (s, 1H, PhC*H*), 4.4–4.3 (m, 3H, $OCH_AH_BCH{=}CHCH_3$, H-1, H-6_e), 4.21 (dd, 1H, $J_{3,4}$ 3.8 Hz, $J_{4,5}$ 1.0 Hz, H-4), 4.1–4.0 (m, 2H, H-6_a, $OCH_AH_BCH{=}CHCH_3$), 3.78 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 9.6 Hz, H-2), 3.70 (m, 1H, H-3), 3.48 (m, 1H, H-5), 2.50 (m, 2H, 2OH), 1.73 (dd, 3H, *J* 6.5 Hz, ^4J 1.1 Hz, $OCH_2CH{=}CHCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.4, 129.2, 128.2, 126.4 (Ph), 130.8 ($OCH_2CH{=}CHCH_3$), 126.6 ($OCH_2CH{=}CHCH_3$), 101.5 (PhCH), 101.4 (C-1), 75.3 (C-4), 72.8 (C-3), 71.8 (C-2), 70.0 ($OCH_2CH{=}CHCH_3$), 69.2 (C-6), 66.7 (C-5), 17.8 ($OCH_2CH{=}CHCH_3$). HRMS (FAB): $[M+Na]^+$, found 345.1297. $C_{17}H_{22}O_6Na$ requires 345.1314. Anal. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.41; H, 6.74.

4.2.4. (*E*)-2-Decenyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 5

The solid was purified by column chromatography using hexane–ethyl acetate (1:2) as eluent. Yield 2.4 g (87%); mp 164–165 °C; $[\alpha]_D = -14.6$ (*c* 1.0, CH_2Cl_2); MS (CI): *m/z* 407 (5%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.3 (m, 5H, Ph), 5.74 [m, 1H, OCH_2-$CH{=}CH(CH_2)_6CH_3$], 5.60 [m, 1H, $OCH_2CH{=}CH(CH_2)_6CH_3$], 5.55 (s,

Table 3
Comparative analysis of NMR data (δ, ppm) in $CDCl_3$ for the oxirane carbons and anomeric proton and carbon in compounds **32**–**47** versus **48**–**52**



Entry	Product	C-1′ minor/major	C-2′ minor/major	C-3′ minor/major	H-1 minor/major	C-1 major/minor	Major oxirane configuration
1	**32**[a]	69.0	50.7	44.6	4.4–4.5	103.2	(2*R*)
2	**33**	68.7/68.2	60.5	56.2/55.9	4.46/4.39	103.3/102.6	(2*S*,3*S*)
3	**34**	68.6	57.9/57.7	52.2	4.40/4.35	103.1	(2*S*,3*S*)
4	**35**	68.8	56.9/56.7	56.3/56.0	4.41/4.33	103.3/102.3	(2*S*,3*S*)
5	**36**	68.0	61.7	58.3/57.9	4.33/4.25	102.7	(2*S*)
6	**37**	71.0	56.2	51.3	4.40/4.35	103.6	(2*R*)
7	**38**	71.5/71.3	62.8	60.7/60.4	4.49/4.40	103.7	(2*S*,3*S*)
8	**39**	70.5	50.8/50.6	44.6/44.3	4.49/4.44	103.7/103.4	(2*R*)
9	**40**	69.2	61.4/60.8	56.3/56.0	4.56/4.51	103.8/103.6	(2*S*,3*S*)
10	**41**[b]	72.0	55.8	51.7/51.6	4.49/4.44	103.5/103.2	-
11	**42**	68.9	50.7/50.5	44.6	4.43/4.38	103.3/103.1	(2*R*)
12	**43**	68.1	61.2/61.0	56.2/56.0	4.50/4.44	103.5/103.2	(2*S*,3*S*)
13	**44**	68.5	57.7	52.4	4.42/4.35	103.5	(2*S*,3*S*)
14	**45**	68.7	56.8	56.4	4.43/4.35	103.5	(2*S*,3*S*)
15	**46**	70.9	56.2	51.4	4.43/4.34	103.7	(2*R*)
16	**47**	71.3	62.7	61.2/60.4	4.51/4.43	103.9/103.6	(2*S*,3*S*)
17	**48**[c]	68.8/68.3	60.3/60.1	55.3/54.9	4.59/4.55	102.1/101.9	(2*S*,3*S*)
18	**49**[c]	69.0/68.8	56.9/56.7	51.3/51.2	4.68/4.49	101.7/101.6	(2*S*,3*S*)
19	**50**[c]	67.8	60.5	57.3/57.2	4.75/4.67	101.7/101.3	(2*S*)
20	**51**[c]	69.5	57.1	49.6	4.67/4.44	102.9/102.8	(2*R*)
21	**52**[c]	70.8/68.9	50.8/50.3	44.2	4.96/4.90	101.0/100.7	(2*R*)

[a] Only one stereoisomer obtained.
[b] No de.
[c] Ref. 19.

1H, PhC*H*), 4.39 [dd, 1H, J_{gem} 11.7 Hz, *J* 6.0 Hz, OCH_AH_BCH=$CH(CH_2)_6CH_3$], 4.35–4.30 (m, 2H, H-1, H-6_e), 4.21 (d, 1H, $J_{3,4}$ 3.7 Hz, H-4), 4.10–4.05 [m, 2H, H-6_a, OCH_AH_BCH=$CH(CH_2)_6CH_3$], 3.77 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 9.5 Hz, H-2), 3.69 (m, 1H, H-3), 3.47 (m, 1H, H-5), 2.52 (m, 2H, 2OH), 2.05 [m, 2H, OCH_2CH=$CHCH_2$-$(CH_2)_5CH_3$], 1.40–1.25 [m, 10H, OCH_2CH=$CHCH_2(CH_2)_5CH_3$], 0.88 [t, 3H, *J* 6.9 Hz, OCH_2CH=$CH(CH_2)_6CH_3$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.4, 129.2, 128.2, 126.4 (Ph), 136.2 [OCH_2CH=$CH(CH_2)_6CH_3$], 125.1 [OCH_2CH=$CH(CH_2)_6CH_3$], 101.5 (PhCH), 101.4 (C-1), 75.3 (C-4), 72.7 (C-3), 71.8 (C-2), 70.1 [OCH_2CH=$CH(CH_2)_6CH_3$], 69.2 (C-6), 66.7 (C-5), 32.3, 31.8, 29.2, 29.1, 29.0, 22.6 [OCH_2CH=$CH(CH_2)_6CH_3$], 14.1 [OCH_2CH=$CH(CH_2)_6CH_3$]. HRMS (CI): $[M+H]^+$, found 407.2413. $C_{23}H_{35}O_6$ requires 407.2434. Anal. Calcd for $C_{23}H_{34}O_6$: C, 67.96; H, 8.43. Found: C, 67.91; H, 8.14.

4.2.5. 3-Methyl-2-butenyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 6

The solid was purified by column chromatography using hexane–ethyl acetate (1:4) as eluent. Yield 1.85 g (86%); mp 177–178 °C; $[\alpha]_D$ = −26.5 (*c* 1.0, CH_2Cl_2); MS (FAB): *m/z* 358 (65%) $[M+Na]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 5.56 (s, 1H, PhC*H*), 5.38 [m, 1H, OCH_2CH=$C(CH_3)_2$], 4.40 [dd, J_{gem} 11.7 Hz, *J* 6.4 Hz, OCH_AH_BCH=$C(CH_3)_2$], 4.35 (dd, 1H, $J_{5,6e}$ 1.2 Hz, $J_{6e,6a}$ 12.5 Hz, H-6_e), 4.32 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.22–4.17 [m, 2H, H-4, OCH_AH_BCH=$C(CH_3)_2$], 4.09 (dd, 1H, $J_{5,6a}$ 1.8 Hz, $J_{6e,6a}$ 12.5 Hz, H-6_a), 3.80 (dd, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 9.5 Hz, H-2), 3.70 (m, 1H, H-3), 3.47 (m, 1H, H-5), 2.51 (m, 2H, 2OH), 1.77, 1.69 [2s, 6H, OCH_2CH=$C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3 [OCH_2CH=$C(CH_3)_2$], 137.5, 129.2, 128.2, 126.4 (Ph), 120.0 [OCH_2CH=$C(CH_3)_2$], 101.5 (PhCH), 101.3 (C-1), 75.3 (C-4), 72.8 (C-3), 71.8 (C-2), 69.2 (C-6), 66.7 (C-5), 65.5 [OCH_2CH=$C(CH_3)_2$], 25.8, 18.0 [OCH_2CH=$C(CH_3)_2$]. HRMS (FAB): $[M+Na]^+$, found 358.1375. $C_{18}H_{24}O_6Na$ requires 358.1392. Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19. Found: C, 64.34; H, 7.27.

4.2.6. 2-Methyl-2-propenyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 7

The compound was purified by column chromatography using hexane–ethyl acetate (1:4) as eluent to obtain a syrup. Yield 1.1 g (70%); $[\alpha]_D$ = −21.6 (*c* 0.8, CH_2Cl_2); MS (CI): *m/z* 323 (5%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 5.55 (s, 1H, PhC*H*), 5.03, 4.94 [2 m, 2H, $OCH_2C(CH_3)$=CH_2], 4.4–4.3 [m, 3H, H-1, H-6_e, $OCH_AH_BC(CH_3)$=CH_2], 4.21 (dd, 1H, $J_{3,4}$ 3.8 Hz, $J_{4,5}$ 0.8 Hz, H-4), 4.10–4.05 [m, 2H, H-6_a, $OCH_AH_BC(CH_3)$=CH_2], 3.80 (dd, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 9.6 Hz, H-2), 3.70 (dd, 1H, $J_{2,3}$ 9.6 Hz, $J_{3,4}$ 3.8 Hz, H-3), 3.46 (m, 1H, H-5), 2.60 (m, 2H, 2OH), 1.77 [s, 3H, $OCH_2C(CH_3)$=CH_2]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.2 [$OCH_2C(CH_3)$=CH_2], 137.5, 129.2, 128.2, 126.4 (Ph), 113.3 [$OCH_2C(CH_3)$=CH_2], 101.4 (PhCH), 101.3 (C-1), 75.3 (C-4), 72.7 [C-3, $OCH_2C(CH_3)$=CH_2], 71.8 (C-2), 69.1 (C-6), 66.7 (C-5), 19.6 [$OCH_2C(CH_3)$=CH_2]. HRMS (CI): $[M+H]^+$, found 323.241457. $C_{17}H_{23}O_6$ requires 323.243364.

4.2.7. (*E*)-2-Methyl-3-phenyl-2-propenyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 8

The compound was purified by column chromatography using hexane–ethyl acetate (1:3) as eluent to obtain a syrup. Yield 1.11 g (74%); $[\alpha]_D$ = −27.4 (*c* 1.0, CH_2Cl_2); MS (EI): *m/z* 398 (3%) $[M]^{+\cdot}$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.6–7.2 (m, 10H, 2Ph), 6.56 [s, 1H, $OCH_2C(CH_3)$=$CHPh$], 5.56 (s, 1H, PhC*H*), 4.46 [d, 1H, J_{gem} 12. Hz, $OCH_AH_BC(CH_3)$=CHPh], 4.4–4.3 (m, 2H, H-1, H-6_e), 4.25–4.20 [m, 2H, H-4, $OCH_AH_BC(CH_3)$=CHPh], 4.09 (d, 1H, $J_{6e,6a}$ 12.5 Hz, H-6_a), 3.83 (m, 1H, H-2), 3.71 (m, 1H, H-3), 3.470 (m, 1H, H-5), 2.67 (m, 2H, 2OH), 1.95 [s, 3H, $OCH_2C(CH_3)$=CHPh]. ^{13}C NMR

(125 MHz, $CDCl_3$): δ 137.5–126.4 [2Ph, $OCH_2C(CH_3)$=CHPh], 101.4 (PhCH), 101.3 (C-1), 75.3 [$OCH_2C(CH_3)$=CHPh], 75.2 (C-4), 72.7 (C-3), 71.8 (C-2), 69.1 (C-6), 66.7 (C-5), 15.7 [$OCH_2C(CH_3)$=CHPh]. HRMS (EI): $[M]^{+\cdot}$, found 398.1738. $C_{23}H_{26}O_6$ requires 398.1729.

4.3. Synthesis of 2,3-di-*O*-benzyl derivatives 9–15

To a cooled solution (5 °C) of sugar derivatives **2**–**8** (1.0 mmol) in freshly distilled THF (20 mL) were added, successively, freshly powdered potassium hydroxide (0.7 g, 8.33 mmol), 18-crown-6 (20–30 mg) and benzyl bromide (0.5 mL, 4.1 mmol). The reaction mixture was stirred at this temperature for 3 h, left overnight at room temperature, then diluted with dichloromethane (30 mL) and washed successively with water and an aqueous saturated solution of sodium bicarbonate, dried ($MgSO_4$), filtered and the filtrate was evaporated to dryness.

4.3.1. Allyl 2,3-di-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 9[27]

The compound was purified by column chromatography using hexane–ethyl acetate (3:1) as eluent to obtain a syrup. Yield 0.3 g (77%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.3 (m, 15H, 3Ph), 5.95 (m, 1H, OCH_2CH=CH_2), 5.48 (s, 1H, PhC*H*), 5.32 (m, 2H, OCH_2CH=CH_2), 4.85 (m, 4H, 2-PhCH_2O, 3-PhCH_2O), 4.44 (m, 2H, OCH_AH_BCH=CH_2, H-1), 4.29 (dd, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_e), (ddd, 1H, J_{gem} 12.9 Hz, *J* 5.9 Hz, ^4J 1.3 Hz, OCH_AH_BCH=CH_2), 4.09 (dd, 1H, $J_{3,4}$ 3.7 Hz, $J_{4,5}$ 1.0 Hz, H-4), 4.00 (dd, 1H, $J_{5,6a}$ 1.8 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_a), 3.86 (dd, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 9.6 Hz, H-2), 3.54 (dd, 1H, $J_{2,3}$ 9.6 Hz, $J_{3,4}$ 3.7 Hz, H-3), 3.30 (m, 1H, H-5).

4.3.2. (*E*)-3-Phenyl-2-propenyl 2,3-di-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 10

The compound was purified by column chromatography using hexane–ethyl acetate (3:1) as eluent to obtain a syrup. Yield 0.4 g (77%); $[\alpha]_D$ = −30.3 (*c* 0.4, CH_2Cl_2); MS (FAB): *m/z* 587 (82%) $[M+Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.2 (m, 20H, 4Ph), 6.65 (d, 1H, J_{trans} 16.0 Hz, OCH_2CH=*CH*Ph), 6.31 (dt, 1H, J_{trans} 16.0 Hz, *J* 5.9 Hz, OCH_2CH=CHPh), 5.51 (s, 1H, PhC*H*), 4.97, 4.84 (2d, 2H, J_{gem} 10.9 Hz, 2-PhCH_2O), 4.79, 4.75 (2d, 2H, J_{gem} 12.4 Hz, 3-PhCH_2O), 4.60 (dd, 1H, J_{gem} 13.0 Hz, *J* 5.8 Hz, OCH_AH_BCH=CHPh), 4.51 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.35–4.30 (m, 2H, OCH_AH_BCH=CHPh, H-6_e), 4.12 (d, 1H, $J_{3,4}$ 3.5 Hz, H-4), 4.03 (dd, 1H, $J_{5,6a}$ 1.7 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_a), 3.91 (dd, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 9.7 Hz, H-2), 3.58 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.33 (m, 1H, H-5). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.0–126.5 (4Ph), 132.5 (OCH_2CH=CHPh), 125.6 (OCH_2CH=CHPh), 102.6 (C-1), 101.4 (PhCH), 79.3 (C-3), 78.5 (C-2), 75.3 (2-PhCH_2O), 74.0 (C-4), 72.1 (3-PhCH_2O), 69.8 (OCH_2CH=CHPh), 69.3 (C-6), 66.5 (C-5). HRMS (FAB): $[M+Na]^+$, found 587.2382. $C_{36}H_{35}O_6Na$ requires 587.2410.

4.3.3. (*E*)-2-Butenyl 2,3-di-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 11

The solid was purified by column chromatography using hexane–ethyl acetate (3:1) as eluent. Yield 0.4 g (85%); mp 135–136 °C; $[\alpha]_D$ = +16.0 (*c* 1.0, CH_2Cl_2); MS (FAB): *m/z* 525 (10%) $[M+Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60–7.25 (m, 15H, 3Ph), 5.76 (m, 1H, OCH_2CH=*CH*CH_3), 5.63 (m, 1H, OCH_2CH=$CHCH_3$), 5.50 (s, 1H, PhC*H*), 4.95 (d, 1H, J_{gem} 10.8 Hz, 2-PhCH_AH_BO), 4.80–4.70 (m, 3H, 2-PhCH_AH_BO, 3-PhCH_2O), 4.44 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.38 (dd, 1H, J_{gem} 11.9 Hz, *J* 5.9 Hz, OCH_AH_BCH=$CHCH_3$), 4.31 (dd, 1H, $J_{5,6e}$ 1.3 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_e), 4.11–4.06 (m, 2H, H-4, OCH_AH_BCH=$CHCH_3$), 4.01 (dd, 1H, $J_{5,6a}$ 1.6 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_a), 3.86 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.6 Hz, H-2), 3.56 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.7 Hz, H-3), 3.31 (m, 1H, H-5), 1.71 (dd, 3H, *J* 6.4 Hz, ^4J 1.0 Hz, OCH_2CH=$CHCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.0–126.6 (3Ph, OCH_2CH=$CHCH_3$), 102.5 (C-1), 101.4 (PhCH), 79.3 (C-3), 78.5 (C-2), 75.3 (2-PhCH_2O), 74.1 (C-4), 72.1 (3-PhCH_2O), 70.1 (OCH_2CH=$CHCH_3$), 69.3 (C-6), 66.4 (C-5), 17.8 (OCH_2CH=$CHCH_3$). HRMS (FAB): $[M+Na]^+$, found 525.2248. $C_{31}H_{34}O_6Na$ requires 525.2253. Anal. Calcd for $C_{31}H_{34}O_6$: C, 74.08; H, 6.82. Found: C, 73.83; H, 6.81.

4.3.4. (*E*)-2-Decenyl 2,3-di-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 12

The solid was purified by column chromatography using hexane–ethyl acetate (3:1) as eluent. Yield 0.5 g (85%); mp 181–182 °C; $[\alpha]_D$ = +20.1 (*c* 1.0, CH_2Cl_2); MS (FAB): *m/z* 609 (10%) $[M+Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60–7.25 (m, 15H, 3Ph), 5.74 [m, 1H, OCH_2CH=*CH*$(CH_2)_6CH_3$], 5.60 [m, 1H, OCH_2CH=$CH(CH_2)_6CH_3$], 5.50 (s, 1H, PhC*H*), 4.95 (d, 1H, J_{gem} 10.9 Hz, 2-PhCH_AH_BO), 4.80–4.70 (m, 3H, 2-PhCH_AH_BO, 3-PhCH_2O), 4.44 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.40 [dd, 1H, J_{gem} 12.0 Hz, *J* 5.8 Hz, OCH_AH_BCH=$CH(CH_2)_6CH_3$], 4.31 (dd, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_e), 4.11–4.07 [m, 2H, H-4, OCH_AH_BCH=$CH(CH_2)_6CH_3$], 4.01 (dd, 1H, $J_{5,6a}$ 1.8 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_a), 3.87 (dd, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 9.7 Hz, H-2), 3.56 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.7 Hz, H-3), 3.30 (m, 1H, H-5), 2.04 [m, 2H, OCH_2CH=$CHCH_2(CH_2)_5CH_3$], 1.40–1.20 [m, 10H, OCH_2CH=$CHCH_2$-$(CH_2)_5CH_3$], 0.88 [t, 3H, *J* 7.0 Hz, OCH_2CH=$CH(CH_2)_6CH_3$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.0–126.5 (3Ph), 135.0 [OCH_2CH=*CH*$(CH_2)_6$-CH_3], 125.7 [OCH_2CH=$CH(CH_2)_6CH_3$], 102.6 (C-1), 101.4 (PhCH), 79.3 (C-3), 78.5 (C-2), 75.2 (2-PhCH_2O), 74.1 (C-4), 72.1 (3-PhCH_2O), 70.2 [OCH_2CH=$CH(CH_2)_6CH_3$], 69.3 (C-6), 66.4 (C-5), 32.3, 31.8, 29.2, 29.1, 22.6 [OCH_2CH=$CH(CH_2)_6CH_3$], 14.1 [OCH_2CH=$CH(CH_2)_6CH_3$]. HRMS (FAB): $[M+Na]^+$, found 609.3224. $C_{37}H_{46}O_6Na$ requires 609.3192. Anal. Calcd for $C_{37}H_{46}O_6$: C, 75.74; H, 7.90. Found: C, 75.89; H, 7.90.

4.3.5. 3-Methyl-2-butenyl 2,3-di-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 13

The solid was purified by column chromatography using hexane–ethyl acetate (3:1) as eluent. Yield 0.4 g (74%); mp 177–178 °C; $[\alpha]_D$ = −50.3 (*c* 1.0, CH_2Cl_2); MS (FAB): *m/z* 539 (5%) $[M+Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.2 (m, 15H, 3Ph), 5.50 (s, 1H, PhC*H*), 5.41 [m, 1H, OCH_2CH=$C(CH_3)_2$], 4.95 (d, 1H, J_{gem} 10.8 Hz, 2-PhCH_AH_BO), 4.80–4.73 (m, 3H, 2-PhCH_AH_BO, 3-PhCH_2O), 4.45 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.40 [dd, J_{gem} 11.8 Hz, *J* 6.5 Hz, OCH_AH_BCH=$C(CH_3)_2$], 4.31 (dd, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.2 Hz, H-6_e), 4.21 [dd, J_{gem} 11.8 Hz, *J* 7.4 Hz, OCH_AH_BCH=$C(CH_3)_2$], 4.10 (dd, 1H, $J_{3,4}$ 3.7 Hz, $J_{4,5}$ 0.7 Hz, H-4), 4.02 (dd, 1H, $J_{5,6a}$ 1.8 Hz, $J_{6e,6a}$ 12.2 Hz, H-6_a), 3.86 (dd, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 9.7 Hz, H-2), 3.56 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.7 Hz, H-3), 3.30 (m, 1H, H-5), 1.76, 1.68 [2s, 6H, OCH_2CH=$C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.0 [OCH_2CH=*C*$(CH_3)_2$], 138.6–126.6 (3Ph), 120.7 [OCH_2CH=$C(CH_3)_2$], 102.4 (C-1), 101.4 (PhCH), 79.4 (C-3), 78.5 (C-2), 75.2 (2-PhCH_2O), 74.1 (C-4), 72.1 (3-PhCH_2O), 69.3 (C-6), 66.4 (C-5), 65.7 [OCH_2CH=$C(CH_3)_2$], 25.8, 18.0 [OCH_2CH=$C(CH_3)_2$]. HRMS (FAB): $[M+Na]^+$, found 539.2416. $C_{32}H_{36}O_6$ requires 539.2410. Anal. Calcd for $C_{32}H_{36}O_6Na$: C, 74.39; H, 7.02. Found: C, 74.57; H, 7.21.

4.3.6. 2-Methyl-2-propenyl 2,3-di-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 14

The solid was purified by column chromatography using hexane–ethyl acetate (3:1) as eluent. Yield 0.3 g (58%); mp 140–141 °C; $[\alpha]_D$ = +36.3 (*c* 0.9, CH_2Cl_2); MS (CI): *m/z* 503 (2%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.3 (m, 15H, 3Ph), 5.50 (s, 1H, PhC*H*), 5.05, 4.91 [2 m, 2H, $OCH_2C(CH_3)$=CH_2], 4.96 (d, 1H, J_{gem} 10.8 Hz, 2-PhCH_AH_BO), 4.80–4.73 (m, 3H, 2-PhCH_AH_BO, 3-PhCH_2O), 4.43 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.34 [d, J_{gem} 12.7 Hz, $OCH_AH_BC(CH_3)$=CH_2], 4.31 (dd, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_e), 4.11 (dd, 1H, $J_{3,4}$ 3.7 Hz, $J_{4,5}$ 0.8 Hz, H-4), 4.06 [d 1H, J_{gem} 12.7 Hz, $OCH_AH_BC(CH_3)$=CH_2], 4.02 (dd, 1H, $J_{5,6a}$ 1.8 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_a), 3.89 (dd, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 9.7 Hz, H-2), 3.57 (dd, 1H, $J_{2,3}$

9.7 Hz, $J_{3,4}$ 3.7 Hz, H-3), 3.31 (m, 1H, H-5), 1.78 [s, 3H, $OCH_2C(CH_3)$=CH_2]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.5 [$OCH_2C(CH_3)$=CH_2], 138.8–126.5 (3Ph), 112.7 [$OCH_2C(CH_3)$=CH_2], 102.3 (C-1), 101.3 (PhCH), 79.4 (C-3), 78.5 (C-2), 75.3 (2-PhCH_2O), 74.0 (C-4), 72.7 [$OCH_2C(CH_3)$=CH_2], 72.1 (3-PhCH_2O), 69.3 (C-6), 66.4 (C-5), 19.6 [$OCH_2C(CH_3)$=CH_2]. HRMS (CI): $[M+H]^+$, found 503.2414. $C_{31}H_{35}O_6$ requires 503.2433. Anal. Calcd for $C_{31}H_{34}O_6$: C, 74.08; H, 6.82. Found: C, 74.13; H, 6.65.

4.3.7. (*E*)-2-Methyl-3-phenyl-2-propenyl 2,3-di-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 15

The solid was purified by column chromatography using hexane–ethyl acetate (3:1) as eluent. Yield 0.5 g (74%); $[\alpha]_D$ = −27.4 (*c* 1.0, CH_2Cl_2); MS (FAB): *m/z* 601 (60%) $[M+Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.2 (m, 20H, 4Ph), 6.58 [s, 1H, $OCH_2C(CH_3)$=C*H*Ph], 5.51 (s, 1H, PhC*H*), 4.99 (d, 1H, J_{gem} 10.8 Hz, 2-PhCH_AH_BO), 4.84 (d, 1H, J_{gem} 10.8 Hz, 2-PhCH_AH_BO), 4.79 (d, 1H, J_{gem} 12.4 Hz, 3-PhCH_AH_BO), 4.76 (d, 1H, J_{gem} 12.4 Hz, 3-PhCH_AH_BO), 4.50–4.45 [m, 2H, H-1, $OCH_AH_BC(CH_3)$=CHPh], 4.34 (dd, 1H, $J_{5,6e}$ 0.8 Hz, $J_{6e,6a}$ 12.3 Hz, H-6$_e$), 4.22 [d, 1H, J_{gem} 12.4 Hz, $OCH_AH_BC(CH_3)$=CHPh], 4.13 (d, 1H, $J_{3,4}$ 3.5 Hz, H-4), 4.04 (dd, 1H, $J_{5,6a}$ 1.4 Hz, $J_{6e,6a}$ 12.3 Hz, H-6$_a$), 3.93 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.6 Hz, H-2), 3.59 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.34 (m, 1H, H-5), 1.94 [s, 3H, $OCH_2C(CH_3)$=CHPh]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8–126.4 [2Ph, $OCH_2C(CH_3)$=CHPh], 102.2 (PhCH), 101.3 (C-1), 79.4 (C-3), 78.5 (C-2), 75.4 (2-PhCH_2O), 75.1 [$OCH_2C(CH_3)$=CHPh], 74.0 (C-4), 72.0 (3-PhCH_2O), 69.2 (C-6), 66.4 (C-5), 15.7 [$OCH_2C(CH_3)$=CHPh]. HRMS (FAB): $[M+Na]^+$, found 601.2532. $C_{37}H_{38}O_6$ requires 601.2566. Anal. Calcd for $C_{37}H_{38}O_6$: C, 76.79; H, 6.62. Found: C, 76.74; H, 6.59.

4.4. Synthesis of 3-*O*-benzyl derivatives 16–22

To a cooled solution (5 °C) of sugar derivatives **2**–**8** (3.0 mmol) in freshly distilled THF (20 mL) were added, successively, freshly powdered potassium hydroxide (1.0 g, 11.9 mmol), 18-crown-6 (60 mg, 0.2 mmol) and benzyl bromide (0.4 mL, 3.4 mmol). The reaction mixture was stirred at this temperature for 20 min, then diluted with dichloromethane (30 mL) and washed successively with water and an aqueous saturated solution of sodium bicarbonate, dried ($MgSO_4$), filtered and the filtrate was evaporated to dryness.

4.4.1. Allyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 16[27]

The compound was purified by column chromatography using hexane–ethyl acetate (1.5:1) as eluent to obtain a syrup. Yield (calculated from the amount of starting material transformed) 0.7 g (88%); MS (FAB): *m/z* 421 (50%) $[M+Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.94 (m, 1H, OCH_2CH=CH_2), 5.44 (s, 1H, PhC*H*), 5.24 (m, 2H, OCH_2CH=CH_2), 4.78, 4.74 (2 br s, 2H, 3-PhCH_2O), 4.41 (ddd, 1H, J_{gem} 12.5 Hz, *J* 5.3 Hz, ^4J 1.5 Hz, OCH_AH_BCH=CH_2), 4.34 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.29 (dd, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.3 Hz, H-6$_e$), 4.12 (m, 2H, OCH_AH_BCH=CH_2, H-4), 4.01 (m, 2H, H-2, H-6$_a$), 3.48 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.34 (m, 1H, H-5). HRMS (FAB): $[M+Na]^+$, found 421.1628. $C_{23}H_{26}O_6Na$ requires 421.1627.

4.4.2. (*E*)-3-Phenyl-2-propenyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 17

The compound was purified by column chromatography using hexane–ethyl acetate (2:1) as eluent to obtain a syrup. Yield (calculated from the amount of starting material transformed) 0.4 g (67%); $[\alpha]_D$ = −35.1 (*c* 1.0, CH_2Cl_2); MS (CI): *m/z* 475 (2%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.2 (m, 15H, 3Ph), 6.64 (d, 1H, J_{trans} 16.0 Hz, OCH_2CH=C*H*Ph), 6.33 (ddd, 1H, J_{trans} 16.0 Hz, *J* 5.7 Hz, *J* 6.9 Hz, OCH_2CH=CHPh), 5.47 (s, 1H, PhC*H*), 4.78, 4.74 (2d, 2H, J_{gem} 12.4 Hz, PhCH_2O), 4.59 (ddd, 1H, J_{gem} 13.0 Hz, *J* 5.8 Hz, ^4J 1.5 Hz, OCH_AH_BCH=CHPh), 4.42 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.35–4.30 (m, 2H, H-6$_e$, OCH_AH_BCH=CHPh), 4.14 (dd, 1H, $J_{3,4}$ 3.6 Hz, $J_{4,5}$ 1.0 Hz, H-4), 4.1–4.0 (m, 2H, H-2, H-6$_a$), 3.51 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.37 (m, 1H, H-5). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1–126.4 (3Ph), 133.3 (OCH_2CH=CHPh), 125.2 (OCH_2CH=CHPh), 101.7 (C-1), 101.2 (PhCH), 79.3 (C-3), 73.2 (C-4), 71.6 (PhCH_2O), 70.1 (C-2), 69.6 (OCH_2CH=CHPh), 69.3 (C-6), 66.7 (C-5). HRMS (CI): $[M+H]^+$, found 475.2072. $C_{29}H_{31}O_6$ requires 475.2121.

4.4.3. (*E*)-2-Butenyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 18

The solid was purified by column chromatography using hexane–ethyl acetate (2:1) as eluent. Yield (calculated from the amount of starting material transformed) 0.2 g (35%); mp 153–155 °C; $[\alpha]_D$ = +8.2 (*c* 0.5, CH_2Cl_2); MS (FAB): *m/z* 435 (35%) $[M+Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55–7.25 (m, 10H, 2Ph), 5.75 (m, 1H, OCH_2CH=C*H*CH_3), 5.63 (m, 1H, OCH_2CH=$CHCH_3$), 5.46 (s, 1H, PhC*H*), 4.76 (m, 2H, PhCH_2O), 4.4–4.3 (m, 2H, OCH_AH_BCH=$CHCH_3$, H-1), 4.31 (dd, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.3 Hz, H-6$_e$), 4.13 (dd, 1H, $J_{3,4}$ 3.6 Hz, $J_{4,5}$ 0.9 Hz, H-4), 4.09–3.99 (m, 3H, OCH_AH_BCH=$CHCH_3$, H-2, H-6$_a$), 3.50 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.35 (m, 1H, H-5), 2.41 (d, 1H, $J_{2,OH}$ 1.8 Hz, OH), 1.72 (dd, 3H, *J* 6.4 Hz, ^4J 1.2 Hz, OCH_2CH=$CHCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2–126.4 (2Ph), 130.5 (OCH_2CH=$CHCH_3$), 126.8 (OCH_2CH=$CHCH_3$), 101.6 (C-1), 101.2 (PhCH), 79.2 (C-3), 73.3 (C-4), 71.6 (PhCH_2O), 70.1 (C-2), 69.7 (OCH_2CH=$CHCH_3$), 69.3 (C-6), 66.7 (C-5), 17.8 (OCH_2CH=$CHCH_3$). HRMS (FAB): $[M+Na]^+$, found 435.1790. $C_{24}H_{28}O_6Na$ requires 435.1784. Anal. Calcd for $C_{24}H_{28}O_6$: C, 69.88; H, 6.84. Found: C, 69.57; H, 7.21.

4.4.4. (*E*)-2-Decenyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 19

The solid was purified by column chromatography using hexane–ethyl acetate (2:1) as eluent. Yield (calculated from the amount of starting material transformed) 0.4 g (77%); mp 118–120 °C; $[\alpha]_D$ = −44.0 (*c* 0.3, CH_2Cl_2); MS (FAB): *m/z* 519 (85%) $[M+Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60–7.25 (m, 10H, 2Ph), 5.74 [m, 1H, OCH_2CH=C*H*$(CH_2)_6CH_3$], 5.59 [m, 1H, OCH_2CH=$CH(CH_2)_6CH_3$], 5.46 (s, 1H, PhC*H*), 4.76 (s, 2H, PhCH_2O), 4.40–4.35 [m, 2H, H-1, OCH_AH_BCH=$CH(CH_2)_6CH_3$], 4.30 (dd, 1H, $J_{5,6e}$ 1.2 Hz, $J_{6e,6a}$ 12.3 Hz, H-6$_e$), 4.13 (d, 1H, $J_{3,4}$ 3.5 Hz, H-4), 4.09–4.00 [m, 3H, H-2, H-6$_a$, OCH_AH_BCH=$CH(CH_2)_6CH_3$], 3.50 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.34 (m, 1H, H-5), 2.45 (d, 1H, $J_{2,OH}$ 1.7 Hz, OH), 2.04 [m, 2H, OCH_2CH=$CHCH_2(CH_2)_5CH_3$], 1.40–1.20 [m, 10H, OCH_2CH=$CHCH_2(CH_2)_5CH_3$], 0.88 [t, 3H, *J* 6.9 Hz, OCH_2CH=$CH(CH_2)_6CH_3$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1–126.4 (2Ph), 136.0 [OCH_2CH=C*H*$(CH_2)_6CH_3$], 125.2 [OCH_2CH=$CH(CH_2)_6CH_3$], 101.5 (C-1), 101.1 (PhCH), 79.2 (C-3), 73.2 (C-4), 71.5 (PhCH_2O), 70.0 [OCH_2CH=$CH(CH_2)_6CH_3$], 69.9 (C-2), 69.3 (C-6), 66.6 (C-5), 32.3, 31.8, 29.2, 29.1, 29.0, 22.6 [OCH_2CH=$CH(CH_2)_6CH_3$], 14.1 [OCH_2CH=$CH(CH_2)_6CH_3$]. HRMS (FAB): $[M+Na]^+$, found 519.2713. $C_{30}H_{40}O_6Na$ requires 519.2723. Anal. Calcd for $C_{30}H_{40}O_6$: C, 72.55; H, 8.12. Found: C, 72.80; H, 8.40.

4.4.5. 3-Methyl-2-butenyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 20

The solid was purified by column chromatography using hexane–ethyl acetate (1.5:1) as eluent. Yield (calculated from the amount of starting material transformed) 0.3 g (66%); mp 188–190 °C; $[\alpha]_D$ = +11.0 (*c* 1.0, CH_2Cl_2); MS (CI): *m/z* 427 (5%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60–7.25 (m, 10H, 2Ph), 5.46 (s, 1H, PhC*H*), 5.39 [m, 1H, OCH_2CH=$C(CH_3)_2$], 4.76 (s, 2H, PhCH_2O), 4.38 [dd, J_{gem} 11.7 Hz, *J* 6.5 Hz, OCH_AH_BCH=$C(CH_3)_2$], 4.34–4.30

(m, 2H, H-1, H-6_e), 4.20 [dd, J_{gem} 11.7 Hz, J 7.8 Hz, $OCH_AH_BCH{=}C(CH_3)_2$], 4.12 (dd, 1H, $J_{3,4}$ 3.6 Hz, $J_{4,5}$ 0.9 Hz, H-4), 4.05–3.00 (m, 2H, H-2, H-6_a), 3.50 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.34 (m, 1H, H-5), 2.41 (d, 1H, $J_{2,OH}$ 1.9 Hz, OH), 1.76, 1.68 [2s, 6H, $OCH_2CH{=}C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8 [$OCH_2CH{=}C(CH_3)_2$], 138.0–126.6 (2Ph), 120.2 [$OCH_2CH{=}C(CH_3)_2$], 101.5 (C-1), 101.2 (Ph*C*H), 79.2 (C-3), 73.3 (C-4), 71.6 ($PhCH_2O$), 70.1 (C-2), 69.3 (C-6), 66.8 (C-5), 65.3 [$OCH_2CH{=}C(CH_3)_2$], 25.8, 18.0 [$OCH_2CH{=}C(CH_3)_2$]. HRMS (CI): $[M+H]^+$, found 427.2098. $C_{25}H_{31}O_6$ requires 427.2121. Anal. Calcd for $C_{25}H_{30}O_6$: C, 70.40; H, 7.09. Found: C, 70.00; H, 6.86.

4.4.6. 2-Methyl-2-propenyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 21

The solid was purified by column chromatography using hexane–ethyl acetate (2:1) as eluent. Yield (calculated from the amount of starting material transformed) 0.3 g (67%); mp 156–157 °C; $[\alpha]_D$ = +6.2 (*c* 0.5, CH_2Cl_2); MS (FAB): *m/z* 435 (50%) $[M+Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.5–7.2 (m, 10H, 2Ph), 5.46 (s, 1H, Ph*C*H), 5.02, 4.93 [2m, 2H, $OCH_2C(CH_3){=}CH_2$], 4.76 (s, 2H, $PhCH_2O$), 4.34 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.32–4.28 (m, 2H, H-6_e, $OCH_AH_BC(CH_3){=}CH_2$], 4.13 (dd, 1H, $J_{3,4}$ 3.6 Hz, $J_{4,5}$ 0.9 Hz, H-4), 4.09–4.01 [m, 3H, $OCH_AH_BC(CH_3){=}CH_2$, H-2, H-6_a], 3.50 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.35 (m, 1H, H-5), 2.41 (d, 1H, $J_{2,OH}$ 2.0 Hz, OH), 1.78 [s, 3H, $OCH_2C(CH_3){=}CH_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.3 [$OCH_2C(CH_3){=}CH_2$], 138.2–126.4 (2Ph), 113.1 [$OCH_2C(CH_3){=}CH_2$], 101.5 (C-1), 101.2 (Ph*C*H), 79.3 (C-3), 73.3 (C-4), 72.5 [$OCH_2C(CH_3){=}CH_2$], 71.6 ($PhCH_2O$), 70.1 (C-2), 69.3 (C-6), 66.7 (C-5), 19.6 [$OCH_2C(CH_3){=}CH_2$]. HRMS (FAB): $[M+Na]^+$, found 435.1792. $C_{24}H_{28}O_6Na$ requires 435.1784.

4.4.7. (*E*)-2-Methyl-3-phenyl-2-propenyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 22

The solid was purified by column chromatography using hexane–ethyl acetate (3:1) as eluent. Yield 0.3 g (60%); mp 126–127 °C; $[\alpha]_D$ = −27.4 (*c* 1.0, CH_2Cl_2); MS (FAB): *m/z* 511 (65%) $[M+Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.2 (m, 15H, 3Ph), 6.55 [s, 1H, $OCH_2C(CH_3){=}CHPh$], 5.47 (s, 1H, Ph*C*H), 4.78, 4.75 (2d, 2H, J_{gem} 12.4 Hz, $PhCH_2O$), 4.45 [d, 1H, J_{gem} 12.2 Hz, $OCH_AH_BC(CH_3){=}CHPh$], 4.40 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.34 (dd, 1H, $J_{5,6e}$ 1.4 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_e), 4.22 [d, 1H, J_{gem} 12.2 Hz, $OCH_AH_BC(CH_3){=}CHPh$], 4.14 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 4.09 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.6 Hz, H-2), 4.04 (dd, 1H, $J_{5,6a}$ 1.8 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_a), 3.52 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.37 (m, 1H, H-5), 2.45 (s, 1H, OH), 1.94 [d, 3H, ^4J 1.1 Hz, $OCH_2C(CH_3){=}CHPh$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1–126.6 (3Ph), 134.2 [$OCH_2C(CH_3){=}CHPh$], 127.9 [$OCH_2C(CH_3){=}CHPh$], 101.4 (C-1), 101.1 (Ph*C*H), 79.2 (C-3), 74.9 [$OCH_2C(CH_3){=}CHPh$], 73.2 (C-4), 71.6 ($PhCH_2O$), 70.1 (C-2), 69.3 (C-6), 66.7 (C-5), 15.6 [$OCH_2C(CH_3){=}CHPh$]. HRMS (FAB): $[M+Na]^+$, found 511.2081. $C_{30}H_{32}O_6Na$ requires 511.2097. Anal. Calcd for $C_{30}H_{32}O_6$: C, 73.75; H, 6.60. Found: C, 73.50; H, 6.62.

4.5. General procedure for cyclopropanation of unsaturated glycosides

To a solution of the corresponding unsaturated glycosides **3**, **6**, **17**–**20**, **22** (1.0 mmol) in dry toluene (10–30 mL) at −15 °C were added 1.0 M diethylzinc in hexane (5.0 mL, 5.0 mmol) and diiodomethane (0.8 mL, 10.0 mmol). The reaction mixture was stirred for 1 h at −15 °C, and then kept at room temperature until TLC showed that all the starting material had reacted (~12 h). The reaction mixture was diluted with dichloromethane and the reaction was quenched with saturated ammonium chloride solution. The organic layer was dried ($MgSO_4$), filtered and evaporated to dryness. The compounds obtained were purified by flash chromatography on silica gel. The diastereomeric excess (de) was determined by ^{1}H NMR.

4.5.1. (2*S*,3*S*)-(2-Phenylcyclopropyl)methyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 23

Two stereoisomers were obtained in a 3.7:1 ratio (57% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography using dichlorometane–methanol (30:1) as eluent. Yield 0.3 g (74%); $[\alpha]_D$ = −22.1 (*c* 1.0, CH_2Cl_2); MS (FAB): *m/z* 421 (50%) $[M+Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.0 (m, 10H, 2Ph), 5.56 (s, 0.21H, Ph*C*H minor), 5.54 (s, 0.79H, Ph*C*H major), 4.38 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.22–4.19 (m, 2H, H-4, H-6_e), 4.02 (dd, 1H, $J_{5,6a}$ 1.6 Hz, $J_{6e,6a}$ 12.4 Hz, H-6_a), 3.86 [dd, 1H J_{gem} 10.7 Hz, J 7.0 Hz, $OCH_AH_BCH(CH_2)CHPh$], 3.77 (m, 1H, H-2), 3.71 (m, 1H, H-3), 3.66 [dd, 1H, J_{gem} 10.8 Hz, J 6.7 Hz, $OCH_AH_BCH(CH_2)CHPh$], 3.48 (m, 0.21H, H-5 minor), 3.43 (m, 0.79H, H-5 major), 2.49 (m, 2H, 2OH), 1.87 [m, 1H, $OCH_2CH(CH_2)CHPh$], 1.52 [m, 1H, $OCH_2CH(CH_2)Ph$], 1.01 [m, 1H, $OCH_2CH(CH_AH_B)CHPh$], 0.95 [m, 1H, $OCH_2CH(CH_AH_B)CHPh$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.4–125.6 (2Ph), 102.4 (C-1 major), 102.1 (C-1 minor), 101.4 (Ph*C*H), 75.4 (C-4), 73.4 (C-3), 72.6 [$OCH_2CH(CH_2)C(CH_3)_2$], 71.7 (C-2), 69.1 (C-6 minor), 69.0 (C-6 major), 66.7 (C-5), 22.7 [$OCH_2CH(CH_2)CHPh$ minor] 22.3 [$OCH_2CH(CH_2)CHPh$ major], 21.7 [$OCH_2CH(CH_2)CHPh$ minor], 21.6 [$OCH_2CH(CH_2)CHPh$ major], 14.3 [$OCH_2CH(CH_2)CHPh$ major], 14.1 [$OCH_2CH(CH_2)CHPh$ minor]. HRMS (FAB): $[M+Na]^+$, found 421.1607. $C_{23}H_{26}O_6Na$ requires 421.1627.

4.5.2. (2*S*)-3-Methyl-2,3-methylidenebutyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 24

Two stereoisomers were obtained in a 1.5:1 ratio (20% de). The pure diastereomeric mixture was obtained as a solid by column chromatography using dichloromethane–methanol (10:1) as eluent. Yield 0.3 g (85%); mp 159–160 °C; $[\alpha]_D$ = −36.5 (*c* 1.0, CH_2Cl_2); MS (CI): *m/z* 351 (5%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55–7.35 (m, 5H, Ph), 5.56 (s, 0.40H, Ph*C*H minor), 5.55 (s, 0.60H, Ph*C*H major), 4.36 (d, 0.60H, $J_{1,2}$ 7.6 Hz, H-1 major), 4.33 (m, 1H, H-6_e), 4.29 (d, 0.40H, $J_{1,2}$ 7.6 Hz, H-1 minor), 4.21 (m, 1H, H-4), 4.09 (m, 1H, H-6_a), 4.04 [dd, 0.40H J_{gem} 10.7 Hz, J 6.6 Hz, $OCH_AH_BCH(CH_2)C(CH_3)_2$ minor], 3.89 [dd, 0.60H J_{gem} 10.8 Hz, J 7.5 Hz, $OCH_AH_BCH(CH_2)C(CH_3)_2$ major], 3.77 (m, 1H, H-2), 3.71 (m, 1H, H-3), 3.63 [dd, 1H, J_{gem} 10.8 Hz, J 7.3 Hz, $OCH_AH_BCH(CH_2)C(CH_3)_2$ major], 3.50–3.45 [m, 1.40H, H-5, $OCH_AH_BCH(CH_2)C(CH_3)_2$ minor], 2.49 (m, 2H, 2OH), 1.11, 1.10, 1.09, 1.08 [4s, 6H, $OCH_2CH(CH_2)C(CH_3)_2$], 0.95 [m, 1H, $OCH_2CH(CH_2)C(CH_3)_2$], 0.54, 0.16 [2 m, 2H, $OCH_2CH(CH_2)C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.6–126.4 (2Ph), 102.2 (C-1 major), 102.1 (C-1 minor), 101.4 (Ph*C*H), 75.4 (C-4), 72.8 (C-3 major), 72.7 (C-3 minor) 71.8 (C-2 major), 71.7 (C-2 minor), 70.7 [$OCH_2CH(CH_2)C(CH_3)_2$], 69.2 (C-6), 66.7 (C-5 major), 66.6 (C-5 minor) 27.2, 20.0 [$OCH_2CH(CH_2)C(CH_3)_2$ minor], 27.1, 20.0 [$OCH_2CH(CH_2)C(CH_3)_2$ major], 23.5 [$OCH_2CH(CH_2)C(CH_3)_2$ minor], 23.3 [$OCH_2CH(CH_2)C(CH_3)_2$ major], 18.8 [$OCH_2CH(CH_2)C(CH_3)_2$], 16.1 [$OCH_2CH(CH_2)C(CH_3)_2$ minor], 15.7 [$OCH_2CH(CH_2)C(CH_3)_2$ major]. HRMS (CI): $[M+H]^+$, found 351.1801. $C_{19}H_{27}O_6$ requires 351.1808. Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48. Found: C, 65.35; H, 7.42.

4.5.3. (2*S*,3*S*)-(2-Phenylcyclopropyl)methyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 25

Only one stereoisomer was obtained (100% de). The syrup was purified by column chromatography using hexane–ethyl acetate (2:1) as eluent. Yield 0.5 g (95%); $[\alpha]_D$ = −22.5 (*c* 0.8, CH_2Cl_2); MS (EI): *m/z* 488 (3%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.0 (m, 15H, 2Ph), 5.44 (s, 1H, Ph*C*H), 4.78, 4.75 (2d, 2H, $PhCH_2O$), 4.39 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.15 (dd, 1H, $J_{5,6e}$ 1.3 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_e), 4.12 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 4.02 (dt, 1H, $J_{1,2}$ = $J_{2,3}$ 7.8 Hz, $J_{2,OH}$ 1.8 Hz, H-2), 3.96 (dd, 1H, $J_{5,6a}$ 1.8 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_a),

3.87 [dd, 1H, J_{gem} 10.7 Hz, J 7.0 Hz, OCH_AH$_B$CH(CH$_2$)CHPh], 3.64 [dd, 1H, J_{gem} 10.8 Hz, J 6.7 Hz, OCH$_A$$H_B$CH(CH$_2$)CHPh], 3.50 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.30 (m, 1H, H-5), 2.43 (d, 1H, $J_{2,OH}$ 1.8 Hz, OH), 1.85 [m, 1H, OCH$_2$CH(CH$_2$)CHPh], 1.51 [m, 1H, OCH$_2$CH(CH$_2$)Ph], 1.00 [m, 1H, OCH$_2$CH(CH_AH$_B$)CHPh], 0.94 [m, 1H, OCH$_2$CH(CH$_A$$H_B$)CHPh]. ^{13}C NMR (125 MHz, CDCl$_3$): δ 142.5–125.6 (3Ph), 102.5 (C-1), 101.1 (PhCH), 79.1 (C-3), 73.2 (C-4), 73.1 [OCH$_2$CH(CH$_2$)CHPh], 71.5 (PhCH$_2$O), 70.1 (C-2), 69.2 (C-6), 66.7 (C-5), 22.3 [OCH$_2$CH(CH$_2$)CHPh], 21.5 [OCH$_2$CH(CH$_2$)CHPh], 14.3 [OCH$_2$CH(CH$_2$)CHPh]. HRMS (EI): [M]$^{+\cdot}$, found 488.2184. $C_{30}H_{32}O_6$ requires 488.2199.

4.5.4. (2*S*)-3-Methyl-2,3-methylidenebutyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 26

Only one stereoisomer was obtained (100% de). The syrup was purified by column chromatography using hexane–ethyl acetate (1.5:1) as eluent. Yield 0.4 g (91%); $[\alpha]_D$ = −56.6 (*c* 0.3, CH_2Cl_2); MS (EI): *m/z* 440 (5%) [M]$^{+\cdot}$. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.55–7.25 (m, 10H, 2Ph), 5.46 (s, 1H, PhC*H*), 4.77 (s, 2H, PhCH_2O), 4.38 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.30 (dd, 1H, $J_{5,6e}$ 1.4 Hz, $J_{6e,6a}$ 12.3 Hz, H-6$_e$), 4.12 (d, 1H, $J_{3,4}$ 3.3 Hz, H-4), 4.04–4.00 (m, 2H, H-2, H-6$_a$), 3.87 [dd, J_{gem} 10.8 Hz, J 7.5 Hz, OCH_AH$_B$CH(CH$_2$)C(CH$_3$)$_2$], 3.62 [dd, 1H, J_{gem} 10.8 Hz, J 7.2 Hz, OCH$_A$$H_B$CH(CH$_2$)C(CH$_3$)$_2$], 3.51 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.34 (m, 1H, H-5), 2.45 (d, 1H, $J_{2,OH}$ 1.7 Hz, OH), 1.09, 1.07 [2s, 6H, OCH$_2$CH(CH$_2$)C(CH_3)$_2$], 0.94 [m, 1H, OCH$_2$CH-(CH$_2$)C(CH$_3$)$_2$], 0.53 [dd, 1H, J_{gem} 4.5 Hz, J 8.5 Hz, OCH$_2$CH-(CH_AH$_B$)C(CH$_3$)$_2$], 0.15 [dd, 1H, J_{gem} 4.6 Hz, J 4.9 Hz, OCH$_2$CH-(CH$_A$$H_B$)C(CH$_3$)$_2$]. ^{13}C NMR (125 MHz, CDCl$_3$): δ 138.2–126.4 (2Ph), 102.2 (C-1), 101.2 (PhCH), 79.1 (C-3), 73.3 (C-4), 71.5 (PhCH$_2$O), 70.4 [OCH$_2$CH(CH$_2$)C(CH$_3$)$_2$], 70.1 (C-2), 69.3 (C-6), 66.7 (C-5), 27.2, 20.0 [OCH$_2$CH(CH$_2$)C(*C*H$_3$)$_2$], 23.3 [OCH$_2$*C*H(CH$_2$)C(CH$_3$)$_2$], 18.8 [OCH$_2$CH(*C*H$_2$)C(CH$_3$)$_2$], 15.7 [OCH$_2$CH(CH$_2$)*C*(CH$_3$)$_2$]. HRMS (EI): [M]$^{+\cdot}$, found 440.2202. $C_{26}H_{32}O_6$ requires 440.2199.

4.5.5. (2*S*,3*S*)-2,3-Methylidenebutyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 27

Two stereoisomers were obtained in an 11.5:1 ratio (84% de). The pure diastereomeric mixture was obtained as a solid by column chromatography using hexane–ethyl acetate (2:1) as eluent. Yield 0.4 g (91%); $[\alpha]_D$ = −12.8 (*c* 0.5, CH_2Cl_2); MS (FAB): *m/z* 449 (50%) [M+Na]$^+$. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.55–7.25 (m, 10H, 2Ph), 5.46 (s, 1H, PhC*H*), 4.77 (s, 2H, PhCH_2O), 4.39 (d, 0.08H, $J_{1,2}$ 7.8 Hz, H-1 minor), 4.35 (d, 0.92H, $J_{1,2}$ 7.8 Hz, H-1 major), 4.29 (dd, 1H, $J_{5,6e}$ 1.6 Hz, $J_{6e,6a}$ 12.3 Hz, H-6$_e$), 4.12 (dd, 1H, $J_{3,4}$ 3.6 Hz, $J_{4,5}$ 0.9 Hz, H-4), 4.05–4.00 (m, 2H, H-2, H-6$_a$), 3.75 [dd, J_{gem} 10.6 Hz, J 7.0 Hz, OCH_AH$_B$CH(CH$_2$)CHCH$_3$], 3.50 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.42 [dd, 1H, J_{gem} 10.6 Hz, J 7.1 Hz, OCH$_A$$H_B$CH(CH$_2$)CHCH$_3$], 3.33 (m, 1H, H-5), 2.45 (s, 1H, OH), 1.05 [d, 3H, J 6.0 Hz, OCH$_2$-CH(CH$_2$)CHCH_3], 0.85, 0.66 [2m, 2H, OCH$_2$CH(CH$_2$)CHCH$_3$], 0.39, 031 [2m, 2H, OCH$_2$CH(CH_2)CHCH$_3$]. ^{13}C NMR (125 MHz, CDCl$_3$): δ 138.2–126.4 (2Ph), 102.4 (C-1), 101.1 (PhCH), 79.2 (C-3), 73.6 (C-4), 73.3 [OCH$_2$CH(CH$_2$)CHCH$_3$], 71.6 (PhCH$_2$O), 70.1 (C-2) , 69.3 (C-6), 66.7 (C-5), 19.0, 18.4, 11.7, 11.2 [OCH$_2$*C*H(CH$_2$)C*H*CH$_3$]. HRMS (FAB): [M+Na]$^+$, found 449.1914. $C_{25}H_{30}O_6$Na requires 449.1940.

4.5.6. (2*S*,3*S*)-2,3-Methylidenedecyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 28

Only one stereoisomer was obtained (100% de). The syrup was purified by column chromatography using hexane–ethyl acetate (3:1) as eluent. Yield 0.5 g (91%); $[\alpha]_D$ = −27.4 (*c* 0.5, CH_2Cl_2); MS (FAB): *m/z* 533 (50%) [M+Na]$^+$. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.55–7.25 (m, 10H, 2Ph), 5.46 (s, 1H, PhC*H*), 4.77 (s, 2H, PhCH_2O), 4.36 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.29 (dd, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.3 Hz, H-6$_e$), 4.12 (dd, 1H, $J_{3,4}$ 3.3 Hz, $J_{4,5}$ 0.8 Hz, H-4), 4.03–4.00 (m, 2H, H-2, H-6$_a$), 3.82 [dd, J_{gem} 10.6 Hz, J 6.7 Hz, OCH_AH$_B$CH(CH$_2$)-CH(CH$_2$)$_5$CH$_3$], 3.50 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.36 [dd, 1H, J_{gem} 10.6 Hz, J 7.5 Hz, OCH$_A$$H_B$CH(CH$_2$)CH(CH$_2$)$_5CH_3$], 3.32 (m, 1H, H-5), 2.46 (s, 1H, OH), 1.4–1.2, [m, 10H, OCH$_2$CH(CH$_2$)CH-(CH_2)$_5$CH$_3$], 0.90–0.83 [m, 4H, OCH$_2$CH(CH$_2$)CH(CH$_2$)$_5$CH_3], 0.61 [m, 1H, OCH$_2$CH(CH$_2$)CH(CH$_2$)$_5$CH$_3$], 0.41–033 [m, 2H, OCH$_2$-CH(CH_2)CH(CH$_2$)$_5$CH$_3$]. ^{13}C NMR (125 MHz, CDCl$_3$): δ 138.0–125.3 (2Ph), 102.1 (C-1), 101.1 (PhCH), 78.9 (C-3), 73.6 [OCH$_2$CH(CH$_2$)-CH(CH$_2$)$_5$CH$_3$], 73.2 (C-4), 71.5 (PhCH$_2$O), 70.1 (C-2), 69.2 (C-6), 66.6 (C-5), 33.6–29.4 [OCH$_2$CH(CH$_2$)CH(*C*H$_2$)$_5$CH$_3$], 22.7 [OCH$_2$*C*H-(CH$_2$)CH(CH$_2$)$_5$CH$_3$], 17.8 [OCH$_2$CH(CH$_2$)CH(CH$_2$)$_5$CH$_3$], 14.1 [OCH$_2$-CH(*C*H$_2$)CH(CH$_2$)$_5$CH$_3$], 10.1 [OCH$_2$CH(CH$_2$)CH(CH$_2$)$_5$CH$_3$]. HRMS (FAB): [M+Na]$^+$, found 533.2874. $C_{31}H_{42}O_6$Na requires 533.2879.

4.5.7. (1*S*,2*R*)-(1-Methyl-2-phenylcyclopropyl)methyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 29

Two stereoisomers were obtained in an 8.1:1 ratio (78% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography using hexane–ethyl acetate (3:1) as eluent. Yield 0.3 g (67%); $[\alpha]_D$ = +34.0 (*c* 0.8, CH_2Cl_2); MS (FAB): *m/z* 525 (15%) [M+H]$^+$. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.60–7.15 (m, 15H, 3Ph), 5.48 (s, 1H, PhC*H*), 4.78 (s, 2H, PhCH_2O), 4.40 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.31 (dd, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.3 Hz, H-6$_e$), 4.15 (d, 1H, $J_{3,4}$ 2.7 Hz, H-4), 4.08–4.02 (m, 2H, H-2, H-6$_a$), 3.87 [d, 0.11H J_{gem} 10.3 Hz, OCH_AH$_B$C(CH$_3$)(CH$_2$)CHPh minor], 3.82 [d, 0.89H J_{gem} 10.2 Hz, OCH_AH$_B$C(CH$_3$)(CH$_2$)CHPh major], 3.60–3.50 [m, 2H, OCH$_A$$H_B$C(CH$_3$)(CH$_2$)CHPh, H-3), 3.64 (m, 1H, H-5), 2.43 (s, 1H, OH), 2.11 [m, 1H, OCH$_2$C(CH$_3$)(CH$_2$)C*H*Ph], 0.97 [m, 1H, OCH$_2$-C(CH$_3$)(CH_AH$_B$)CHPh], 0.90–0.85 [m, 4H, OCH$_2$CH(CH_3)(CH$_A$$H_B$)-CHPh]. ^{13}C NMR (125 MHz, CDCl$_3$): δ 138.9–125.8 (3Ph), 102.7 (C-1), 101.1 (PhCH), 79.1 (C-3), 77.7 [OCH$_2$C(CH$_3$)(CH$_2$)CHPh], 73.4 (C-4), 71.6 (PhCH$_2$O), 70.3 (C-2), 69.3 (C-6), 66.8 (C-5), 26.6 [OCH$_2$-C(CH$_3$)(CH$_2$)CHPh], 22.6 [OCH$_2$*C*(CH$_3$)(CH$_2$)CHPh], 16.3 [OCH$_2$C-(*C*H$_3$)(CH$_2$)CHPh], 15.8 [OCH$_2$C(CH$_3$)(*C*H$_2$)CHPh]. HRMS (FAB): [M+Na]$^+$, found 525.2250. $C_{31}H_{34}O_6$Na requires 525.2253.

4.6. Separation of chiral auxiliary[9]

To a solution of compound **25** or **28** (1.0 mmol) in dichloromethane (2 mL) cooled to −20 °C, pyridine (17 mmol) and trifluoromethanesulfonic anhydride (4.8 mmol) were added over 20 min. The reaction mixture was then warmed slowly to 0 °C over 1 h and stirred at that temperature until TLC analysis showed complete consumption of the starting material. The reaction mixture was diluted with dichloromethane and washed with saturated aqueous sodium bicarbonate and brine, and the organic layer was dried ($MgSO_4$) and evaporated to dryness. The residue was dissolved in dimethylformamide (100 mL) and pyridine (2 mL) and water (2 mL) were added. The reaction mixture was heated at 150 °C for 30 min and then cooled to room temperature. The solution was diluted with diethyl ether–ethyl acetate (1:1) (100 mL) and washed successively with 10% aqueous hydrochloric acid and water. The organic layer was dried ($MgSO_4$) and evaporated to dryness. The compound obtained was purified by column chromatography using hexane–ethyl acetate mixtures as eluent.

4.6.1. (1*S*,2*S*)-*trans*-1-Hydroxymethyl-2-phenylcyclopropane (+)-30[29]

A syrup was obtained. Yield 48 mg (60%); $[\alpha]_D$ = +69.3 (*c* 0.8, CH_2Cl_2), {lit.[29b] for (*R*,*R*)-enantiomer $[\alpha]_D$ = −56.2 (*c* 0.60, $CHCl_3$) for 75% ee}; MS (CI): *m/z* 149 (20%) [M+H]$^+$. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.6–7.1 (m, 5H, Ph), 3.63 [dd, 2H, J 6.8 Hz, J_{gem} 11.3 Hz, HOCH_2CH(CH$_2$)CHPh], 1.84 [m, 1H, HOCH$_2$CH(CH$_2$)C*H*Ph], 1.47 [m, 1H, HOCH$_2$C*H*(CH$_2$)CHPh], 0.98 [m, 2H, HOCH$_2$CH(CH_2)CHPh]. ^{13}C NMR (125 MHz, CDCl$_3$): δ 136.7–128.1 (Ph), 66.5 [HOCH$_2$-CH(CH$_2$)CHPh], 25.2 [HOCH$_2$*C*H(CH$_2$)CHPh], 21.3 [HOCH$_2$CH(CH$_2$)-*C*HPh], 13.7 [HOCH$_2$CH(*C*H$_2$)CHPh].

4.6.2. (1*S*,2*S*)-*trans*-1-Heptyl-2-hydroxymethylcyclopropane (+)-31

A syrup was obtained. Yield 100 mg (75%); $[\alpha]_D$ = +16.8 (*c* 0.5, CH_2Cl_2), {lit.[14] *ent*-form $[\alpha]_D$ = –17.6 (*c* 0.50, CH_2Cl_2)}; MS (CI): *m/z* 171 (5%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 3.44 [m, 2H, $HOCH_2CH(CH_2)CH(CH_2)_6CH_3$], 1.60–1.15 [m, 13H, $HOCH_2CH(CH_2)$-$CH(CH_2)_6CH_3$], 0.88 [t, 3H, *J* 6.9 Hz, $HOCH_2CH(CH_2)CH(CH_2)_6CH_3$], 0.83 [m, 1H, $HOCH_2CH(CH_2)CH(CH_2)_6CH_3$], 0.59 [m, 1H, $HOCH_2$-$CH(CH_2)CH(CH_2)_6CH_3$], 0.36, 0.30 [2 m, 2H, $HOCH_2CH(CH_2)CH$-$(CH_2)_6CH_3$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 67.3 [$HOCH_2CH(CH_2)$-$CH(CH_2)_6CH_3$], 33.6, 31.9, 29.6, 29.4, 29.3, 22.7 [$HOCH_2CH(CH_2)$-$CH(CH_2)_6CH_3$], 21.2 [$HOCH_2CH(CH_2)CH(CH_2)_6CH_3$], 17.4 [$HOCH_2$-$CH(CH_2)CH(CH_2)_6CH_3$], 14.1 [$HOCH_2CH(CH_2)CH(CH_2)_6CH_3$], 9.9 [$HOCH_2CH(CH_2)CH(CH_2)_6CH_3$].

4.7. General procedure for the epoxidation of unsaturated glycosides

To a solution of the corresponding unsaturated glycosides **2**–**10**, **14**, **16**–**19**, **21** and **22** (1.0 mmol) in chloroform (75 mL) was added a solution of *m*-chloroperoxybenzoic acid (Aldrich 57–86%) (1.5 g) in chloroform (25 mL), previously dried over $MgSO_4$. The reaction mixture was kept at −15 °C until TLC showed that all starting compound had been consumed (7 days); then, the solution was washed successively with 5% aqueous sodium hydroxide (7 × 30 mL) and water, dried ($MgSO_4$), filtered and the filtrate was evaporated to dryness. The diastereomeric excess (de) was determined by ^1H NMR.

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

4.7.1.1. (2*R*)-2,3-Epoxypropyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 32. Only one stereoisomer was obtained (100% de). The pure compound was obtained as a syrup by column chromatography using hexane–ethyl acetate (1:5) as eluent. Yield 0.2 g (63%); $[\alpha]_D$ = −31.2 (*c* 0.5, CH_2Cl_2); MS (CI): *m/z* 325 (5%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.6–7.3 (m, 5H, Ph), 5.55 (s, 1H, PhC*H*), 4.4–4.3 (m, 2H, H-1, H-6_e), 4.21 (d, 1H, $J_{3,4}$ 3.5 Hz, H-4), 4.02 (d, 1H, $J_{6e,6a}$ 12.4 Hz, H-6_a), 3.98 [dd, 1H, J_{gem} 12.0 Hz, *J* 4.4 Hz, $OCH_AH_BCH(O)CH_2$], 3.90 [dd, 1H, J_{gem} 12.0 Hz, *J* 3.0 Hz, $OCH_AH_BCH(O)CH_2$], 3.78 (m, 1H, H-2), 3.70 (m, 1H, H-3), 3.49 (m, 1H, H-5), 3.25 [m, 1H, $OCH_2CH(O)CH_2$], 2.83 [m, 1H, $OCH_2CH(O)$-CH_AH_B], 2.78 [m, 1H, $OCH_2CH(O)CH_AH_B$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.4–126.4 (Ph), 103.2 (C-1), 101.4 (PhCH), 75.2 (C-4), 72.7 (C-3), 71.7 (C-2), 69.1 (C-6), 69.0 [$OCH_2CH(O)CH_2$], 66.8 (C-5), 50.7 [$OCH_2CH(O)CH_2$], 44.6 [$OCH_2CH(O)CH_2$]. HRMS (CI): $[M+H]^+$, found 325.1287. $C_{16}H_{21}O_7$ requires 325.1287.

4.7.1.2. (2*S*,3*S*)-2,3-Epoxy-3-phenylpropyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 33. Two stereoisomers were obtained in a 12.5:1 ratio (85% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography using hexane–ethyl acetate (1:4) as eluent. Yield 0.3 g (72%); $[\alpha]_D$ = −26.5 (*c* 0.4, CH_2Cl_2); MS (FAB): *m/z* 423 (100%) $[M+Na]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.6–7.2 (m, 10H, 2Ph), 5.55 (s, 0.93H, PhC*H* major), 5.54 (s, 0.07H, PhC*H* minor), 4.46 (d, 0.07H, $J_{1,2}$ 7.8 Hz, H-1 minor), 4.39 (d, 0.93H, $J_{1,2}$ 7.7 Hz, H-1 major), 4.33 (dd, 0.93H, $J_{5,6e}$ 1.4 Hz, $J_{6e,6a}$ 12.5 Hz, H-6_e major), 4.26 (dd, 0.07H, $J_{5,6e}$ 1.4 Hz, $J_{6e,6a}$ 12.5 Hz, H-6_e minor), 4.21 (d, 1H, $J_{3,4}$ 3.0 Hz, H-4), 4.15–4.05 [m, 2H, OCH_AH_B-$CH(O)CHPh$, H-6_a], 4.01 [dd, 1H, J_{gem} 12.1 Hz, *J* 2.8 Hz, OCH_AH_B-$CH(O)CHPh$], 3.96 [d, 1H, *J* 2.0 Hz, $OCH_2CH(O)CHPh$], 3.81 (m, 1H, H-2), 3.70 (m, 1H, H-3), 3.49 (m, 1H, H-5), 3.33 [m, 0.07H, OCH_2-$CH(O)CHPh$ minor], 3.28 [m, 0.93H, $OCH_2CH(O)CHPh$ major], 3.04 (s, 1H, 2-OH), 2.68 (s, 1H, 3-OH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.5–125.8 (2Ph), 103.3 (C-1 major), 102.6 (C-1 minor), 101.4 (PhCH), 75.2 (C-4), 72.7 (C-3), 71.7 (C-2 major), 71.2 (C-2 minor), 69.1 (C-6), 68.7 [$OCH_2CH(O)CHPh$ minor], 68.2 [$OCH_2CH(O)CHPh$ major], 66.8 (C-5), 60.5 [$OCH_2CH(O)CHPh$], 56.2 [$OCH_2CH(O)CHPh$ minor], 55.9 [$OCH_2CH(O)CHPh$ major]. HRMS (FAB): $[M+Na]^+$, found 423.1441. $C_{22}H_{24}O_7Na$ requires 423.1420.

4.7.1.3. (2*S*,3*S*)-2,3-Epoxybutyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 34. Two stereoisomers were obtained in a 9:1 ratio (80% de). The pure diastereomeric mixture was obtained as a solid by column chromatography using hexane–ethyl acetate (1:6) as eluent. Yield 0.2 g (56%); mp 149–150 °C; $[\alpha]_D$ = −37.2 (*c* 0.5, CH_2Cl_2); MS (FAB): *m/z* 361 (100%) $[M+Na]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.50–7.30 (m, 5H, Ph), 5.55 (s, 1H, PhC*H*), 4.40 (d, 0.10H, $J_{1,2}$ 7.7 Hz, H-1 minor), 4.35–4.30 (m, 1.90H, H-1 major, H-6_e), 4.21 (d, 1H, $J_{3,4}$ 3.7 Hz, H-4), 4.09 (dd, 1H, $J_{5,6a}$ 1.8 Hz, $J_{6e,6a}$ 12.5 Hz, H-6_a), 4.00 [dd, 0.90H J_{gem} 12.0 Hz, *J* 4.3 Hz, OCH_AH_B-$CH(O)CHCH_3$ major], 3.84 [dd, 0.90H J_{gem} 12.0 Hz, *J* 3.2 Hz, OCH_AH_B-$CH(O)CHCH_3$ major], 3.77 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 9.4 Hz, H-2), 3.68 (dt, 1H, $J_{2,3}$ 9.4 Hz, $J_{3,4}$ 3.7 Hz, $J_{3,OH}$ 8.7 Hz, H-3), 3.58 [dd, 0.10H J_{gem} 11.9 Hz, *J* 6.0 Hz, $OCH_AH_BCH(O)CHCH_3$ minor], 3.49 (m, 1H, H-5), 3.07 [m, 1H, $OCH_2CH(O)CHCH_3$], 2.96 [m, 1H, $OCH_2CH(O)CHCH_3$], 2.92 (s, 1H, 2-OH), 2.56 (d, 1H, $J_{3,OH}$ 8.6 Hz, 3-OH), 1.34 [d, 3H, *J* 5.3 Hz, $OCH_2CH(O)CHCH_3$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.4–126.4 (Ph), 103.3 (C-1), 101.4 (PhCH), 75.2 (C-4), 72.7 (C-3), 71.7 (C-2), 69.1 (C-6), 68.6 [$OCH_2CH(O)CHCH_3$], 66.8 (C-5), 57.9 [OCH_2-$CH(O)CHCH_3$ minor], 57.7 [$OCH_2CH(O)CHCH_3$ major], 52.2 [OCH_2-$CH(O)CHCH_3$], 17.2 [$OCH_2CH(O)CHCH_3$ major], 15.3 [$OCH_2CH(O)$-$CHCH_3$ minor]. HRMS (FAB): $[M+Na]^+$, found 361.1244. $C_{17}H_{22}O_7Na$ requires 361.1263. Anal. Calcd for $C_{17}H_{22}O_7$: C, 60.35; H, 6.55. Found: C, 59.95; H, 6.35.

4.7.1.4. (2*S*,3*S*)-2,3-Epoxydecyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 35. Two stereoisomers were obtained in an 8.9:1 ratio (80% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography using hexane–ethyl acetate (1:6) as eluent. Yield 0.3 g (74%); $[\alpha]_D$ = −17.3 (*c* 0.5, CH_2Cl_2); MS (FAB): *m/z* 445 (100%) $[M+Na]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.55–7.30 (m, 5H, Ph), 5.55 (s, 1H, PhC*H*), 4.41 (d, 0.10H, $J_{1,2}$ 7.8 Hz, H-1 minor), 4.33–4.31 (m, 1.90H, H-1 major, H-6_e), 4.20 (d, 1H, $J_{3,4}$ 3.7 Hz, H-4), 4.15 [dd, 0.10H J_{gem} 12.0 Hz, *J* 2.9 Hz, $OCH_AH_BCH(O)CH(CH_2)_6CH_3$ minor], 4.08 (dd, 1H, $J_{5,6a}$ 1.8 Hz, $J_{6e,6a}$ 12.5 Hz, H-6_a), 3.99 [dd, 0.90H J_{gem} 12.0 Hz, *J* 4.1 Hz, OCH_AH_B-$CH(O)CH(CH_2)_6CH_3$ major], 3.85 [dd, 0.90H J_{gem} 12.0 Hz, *J* 2.8 Hz, $OCH_AH_BCH(O)CH(CH_2)_6CH_3$ major], 3.76 (dd, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 9.4 Hz, H-2), 3.68 (dt, 1H, $J_{2,3}$ 9.5 Hz, $J_{3,4}$ 3.7 Hz, $J_{3,OH}$ 8.6 Hz, H-3), 3.54 [dd, 0.10H J_{gem} 12.0 Hz, *J* 6.3 Hz, $OCH_AH_BCH(O)CH(CH_2)_6CH_3$ minor], 3.48 (m, 1H, H-5), 3.08 (s, 0.90H, 2-OH major), 3.04 (s, 0.10H, 2-OH minor), 3.02–2.97 [m, 2H, $OCH_2CH(O)CH(CH_2)_6CH_3$], 2.64 (d, 1H, $J_{3,OH}$ 8.6 Hz, 3-OH), 1.6–1.2 [m, 12H, $OCH_2CH(O)$-$CH(CH_2)_6CH_3$], 0.88 [t, 3H, *J* 7.0 Hz, $OCH_2CH(O)CH(CH_2)_6CH_3$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.5–126.4 (Ph), 103.3 (C-1 major), 102.3 (C-1 minor), 101.4 (PhCH), 75.2 (C-4), 72.7 (C-3 major), 72.6 (C-3 minor), 71.7 (C-2 major), 71.2 (C-2 minor), 69.1 (C-6), 68.8 [$OCH_2CH(O)CH(CH_2)_6CH_3$], 66.8 (C-5), 56.9, 56.3 [OCH_2-$CH(O)CH(CH_2)_6CH_3$ minor], 56.7, 56.0 [$OCH_2CH(O)CH(CH_2)_6CH_3$ major], 31.7, 31.6, 29.3, 29.1, 25.9, 22.6 [$OCH_2CH(O)CH(CH_2)_6CH_3$], 14.1 [$OCH_2CH(O)CH(CH_2)_6CH_3$]. HRMS (FAB): $[M+Na]^+$, found 445.2215. $C_{23}H_{34}O_7Na$ requires 445.2202.

4.7.1.5. (2*S*)-2,3-Epoxy-3-methylbutyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 36. Two stereoisomers were obtained in a 1.6:1 ratio (23% de). The pure diastereomeric mixture was obtained as a solid by column chromatography using hexane–ethyl acetate (1:4) as eluent. Yield 0.3 g (92%); mp 148–149 °C, $[\alpha]_D$ = −17.3 (*c* 1.0, CH_2Cl_2); MS (FAB): *m/z* 375 (100%) $[M+Na]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.55–7.30 (m, 5H, Ph), 5.51 (s, 1H, PhC*H*), 4.33–4.25 (m, 2H, H-1, H-6_e), 4.15–4.00 (m, 2H, H-4, H-6_a), 3.95 [dd, 0.38H J_{gem} 11.5 Hz, *J* 6.0 Hz, $OCH_AH_BCH(O)C(CH_3)_2$ minor], 3.81–3.74 [m, 1.62H, H-2, $OCH_AH_BCH(O)C(CH_3)_2$ major], 3.69–

3.59 [m, 2H, H-3, $OCH_AH_BCH(O)C(CH_3)_2$], 3.42 (m, 1H, H-5), 3.06 [m, 1H, $OCH_2CH(O)C(CH_3)_2$], 2.72, 2.59 (2 m, 2H, 2OH), 1.33, 1.29 [2*s*, 1.14H, $OCH_2CH(O)C(CH_3)_2$ minor], 1.30, 1.27 [2s, 1.86H, $OCH_2CH(O)C(CH_3)_2$ major]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.6–126.4 (Ph), 102.7 (C-1), 101.3 (PhCH), 75.4 (C-4 major), 75.3 (C-4 minor), 72.6 (C-3 minor), 72.5 (C-3 major), 71.5 (C-2 major), 71.2 (C-2 minor), 69.1 (C-6), 68.0 [$OCH_2CH(O)C(CH_3)_2$], 66.7 (C-5), 61.7 [$OCH_2CH(O)C(CH_3)_2$], 58.3 [$OCH_2CH(O)C(CH_3)_2$ minor], 57.9 [$OCH_2CH(O)C(CH_3)_2$ major], 24.6, 18.8 [$OCH_2CH(O)C(CH_3)_2$ minor], 24.5, 18.9 [$OCH_2CH(O)C(CH_3)_2$ major]. HRMS (FAB): $[M+Na]^+$, found 375.1438. $C_{18}H_{24}O_7Na$ requires 375.1420. Anal. Calcd for $C_{18}H_{24}O_7$: C, 61.35; H, 6.86. Found: C, 60.56; H, 6.88.

4.7.1.6. (2*R*)-2,3-Epoxy-2-methylpropyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 37. Two stereoisomers were obtained in a 15:1 ratio (88% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography using hexane–ethyl acetate (1:4) as eluent. Yield 0.3 g (79%); $[\alpha]_D = -19.2$ (*c* 0.9, CH_2Cl_2); MS (CI): *m/z* 339 (50%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.3 (m, 5H, Ph), 5.57 (s, 0.06H, PhC*H* minor), 5.55 (s, 0.94H, PhC*H* major), 4.40 (d, 0.06H, *J* 7.8 Hz, H-1 minor), 4.35–4.30 (m, 1.94H, H-1 major, H-6_e), 4.20 (dd, 1H, $J_{3,4}$ 3.7 Hz, $J_{4,5}$ 0.8 Hz, H-4), 4.08 (dd, 1H, $J_{5,6a}$ 1.8 Hz, $J_{6e,6a}$ 12.5 Hz, H-6_a), 4.01 [d, 1H J_{gem} 11.7 Hz, $OCH_AH_BC(CH_3)(O)CH_2$], 3.78 (m, 0.06H, H-2 minor) 3.76 (dd, 0.94H, $J_{1,2}$ 7.6 Hz, $J_{2,3}$ 9.6 Hz, H-2 major), 3.7–3.6 [m, 2H, H-3, $OCH_AH_BC(CH_3)(O)CH_2$], 3.47 (m, 1H, H-5), 2.97 [d, 1H, J_{gem} 4.9 Hz, $OCH_2C(CH_3)(O)CH_AH_B$], 2.64 [d, 1H, J_{gem} 4.9 Hz, $OCH_2C(CH_3)(O)CH_AH_B$], 1.34 (s, 0.18H, $OCH_2C(CH_3)(O)CH_2$ minor], 1.38 (s, 2.88H, $OCH_2C(CH_3)(O)CH_2$ major]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.5–126.4 (Ph), 103.6 (C-1), 101.4 (PhCH), 75.2 (C-4), 72.8 (C-3), 71.8 (C-2), 71.0 [$OCH_2C(CH_3)(O)CH_2$], 69.1 (C-6), 66.8 (C-5), 56.2 [$OCH_2C(CH_3)(O)CH_2$], 51.3 [$OCH_2C(CH_3)(O)CH_2$], 18.6 [$OCH_2C(CH_3)(O)CH_2$]. HRMS (CI): $[M+H]^+$, found 339.1446. $C_{17}H_{23}O_7$ requires 339.1444.

4.7.1.7. (2*S*,3*S*)-2,3-Epoxy-2-methyl-3-phenylpropyl 4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 38. Two stereoisomers were obtained in a 7.3:1 ratio (76% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography using hexane–ethyl acetate (1:4) as eluent. Yield 0.3 g (80%); $[\alpha]_D = -20.1$ (*c* 0.7, CH_2Cl_2); MS (EI): *m/z* 414 (8%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.2 (m, 10H, 2Ph), 5.56 (s, 1H, PhC*H*), 4.49 (d, 0.12H, $J_{1,2}$ 7.8 Hz, H-1 minor), 4.40 (d, 0.88H, $J_{1,2}$ 7.8 Hz, H-1 major), 4.36 (dd, 1H, $J_{5,6e}$ 1.4 Hz, $J_{6e,6a}$ 12.4 Hz, H-6_e), 4.29 [s, 1H, $OCH_2C(CH_3)(O)CHPh$], 4.22 (d, 1H, $J_{3,4}$ 3.0 Hz, H-4), 4.14 [d, 1H, J_{gem} 12.0 Hz, $OCH_AH_BC(CH_3)(O)CHPh$], 4.10 (dd, 1H, $J_{5,6a}$ 1.8 Hz, $J_{6e,6a}$ 12.4 Hz, H-6_a), 3.85–3.80 [m, 2H, $OCH_AH_BC(CH_3)(O)CHPh$, H-2], 3.75 (m, 0.12H, H-3 minor), 3.73 (m, 0.88H, H-3 major), 3.51 (m, 1H, H-5), 1.10 [s, 3H, $OCH_2C(CH_3)(O)CHPh$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.4–126.4 (2Ph), 103.7 (C-1), 101.4 (PhCH), 75.2 (C-4), 72.6 (C-3), 71.7 (C-2), 71.5 [$OCH_2C(CH_3)(O)CHPh$ minor], 71.3 [$OCH_2C(CH_3)(O)CHPh$ major], 69.1 (C-6), 66.8 (C-5), 62.8 [$OCH_2C(CH_3)(O)CHPh$], 60.7 [$OCH_2C(CH_3)(O)CHPh$ minor], 60.4 [$OCH_2C(CH_3)(O)CHPh$ major], 13.8 [$OCH_2C(CH_3)(O)CHPh$]. HRMS (EI): $[M]^{+\cdot}$, found 414.1686. $C_{23}H_{26}O_7$ requires 414.1679.

4.7.2. Epoxidation of 4,6-*O*-benzylidene-2,3-di-*O*-benzyl derivatives

4.7.2.1. (2*R*)-2,3-Epoxypropyl 2,3-di-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 39. Two stereoisomers were obtained in a 1.6:1 ratio (23% de).The pure diastereomeric mixture was obtained as a solid by column chromatography using hexane–ethyl acetate (3:1) as eluent. Yield 0.5 g (90%); mp 131–132 °C; $[\alpha]_D = +52.9$ (*c* 0.5, CH_2Cl_2); MS (EI): *m/z* 504 (10%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.1 (m, 10H, 2Ph), 5.55 (s, 1H, PhC*H*), 4.96, 4.86 (2d, 1H, J_{gem} 10.8 Hz, 2-PhCH_AH_BO), 4.81–4.76 (m, 3H, 2-PhCH_AH_BO, 3-PhCH_2O) 4.49 (d, 0.39H, $J_{1,2}$ 7.8 Hz, H-1 minor), 4.44 (d, 0.61H, $J_{1,2}$ 7.8 Hz, H-1 major), 4.28 (dd, 1H, $J_{5,6e}$ 5.0 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_e), 4.14 (d, 0.39H, $J_{3,4} = J_{4,5}$ 3.2 Hz, H-4 minor), 4.12 (d, 0.61H, $J_{3,4} = J_{4,5}$ 3.5 Hz, H-4 major), 4.02 (d, 0.61H, J_{gem} 12.2, H-6_a major), 4.01 (d, 0.39H, J_{gem} 12.4, H-6_a minor), 3.98 (d, 0.39H, $J_{2,3} = J_{3,4}$ 4.8 Hz, H-3 minor), 3.95 (d, 0.61H, $J_{2,3} = J_{3,4}$ 4.7 Hz, H-3 major), 3.9–3.8 [m, 2H, $OCH_AH_BCH(O)CH_2$, H-2] , 3.6–3.5 (m, 1H, $OCH_AH_BCH(O)CH_2$), 3.33 (br s, 1H, H-5), 3.22 [m, 1H, $OCH_2CH(O)CH_2$], 2.83 [m, 1H, $OCH_2CH(O)CH_AH_B$], 2.72 [dd, 0.61H, *J* 2.7 Hz, *J* 4.9 Hz, $OCH_2CH(O)CH_AH_B$ major], 2.60 [dd, 0.39H, *J* 2.7 Hz, *J* 4.9 Hz, $OCH_2CH(O)CH_AH_B$ minor]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.7–126.4 (3Ph), 103.7 (C-1 major), 103.4 (C-1 minor), 101.3 (PhCH), 79.1 (C-3 major), 79.0 (C-3 minor), 78.4 (C-2 minor), 78.3 (C-2 major), 75.3 (2-PhCH_2O), 73.9 (C-4 minor), 73.8 (C-4 mayor), 72.1 (3-PhCH_2O minor), 72.0 (3-PhCH_2O major), 70.5 [$OCH_2CH(O)CH_2$], 69.4 (C-6 minor), 69.2 (C-6 major), 66.5 (C-5 major), 66.4 (C-5 minor), 50.8 [$OCH_2CH(O)CH_2$ minor], 50.6 [$OCH_2CH(O)CH_2$ major], 44.5 [$OCH_2CH(O)CH_2$]. HRMS (EI): $[M]^{+\cdot}$, found 504.2109. $C_{30}H_{32}O_7$ requires 504.2148.

4.7.2.2. (2*S*,3*S*)-2,3-Epoxy-3-phenylpropyl 2,3-di-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 40. Two stereoisomers were obtained in a 1.2:1 ratio (9% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography using hexane–ethyl acetate (3:1) as eluent. Yield 0.4 g (72%); $[\alpha]_D = -30.3$ (*c* 0.4, CH_2Cl_2); MS (EI): *m/z* 580 (10%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.2 (m, 20H, 4Ph), 5.52 (s, 0.55H, PhC*H* major), 5.50 (s, 0.45H, PhC*H* minor), 4.96 (d, 0.55H, J_{gem} 10.6 Hz, 2-PhCH_AH_BO major), 4.94 (d, 0.45H, J_{gem} 10.6 Hz, 2-PhCH_AH_BO minor), 4.8–4.7 (m, 3H, 2-PhCH_AH_BO, 3-PhCH_2O), 4.56 (d, 0.45H, $J_{1,2}$ 7.9 Hz, H-1 minor), 4.51 (d, 0.55H, $J_{1,2}$ 7.9 Hz, H-1 major), 4.38 (m, 0.45H, H-6_e minor), 4.32 (m, 0.55H, H-6_e major), 4.2–4.1 (m, 2H, H-4, H-6_a), 4.0–3.9 [m, 3H, H-2, $OCH_AH_BCH(O)CHPh$, $OCH_2CH(O)CHPh$], 3.80 (d, 0.45H, $J_{2,3} = J_{3,4}$ 5.0 Hz, H-3 minor), 3.78 (d, 0.55H, $J_{2,3} = J_{3,4}$ 5.1 Hz, H-3 major), 3.36 (m, 0.45H, H-5 minor), 3.33 (m, 0.55H, H-5 major), 3.30 [m, 0.45H, $OCH_2CH(O)CHPh$ minor], 3.27 [m, 0.55H, $OCH_2CH(O)CHPh$ major] .^{13}C NMR (125 MHz, $CDCl_3$): δ 138.7–125.7 (4Ph), 103.8 (C-1 major), 103.6 (C-1 minor), 101.3 (PhCH major), 101.2 (PhCH minor), 79.1 (C-3), 78.4 (C-2 major), 78.3 (C-2 minor), 75.4 (2-PhCH_2O minor), 75.3 (2-PhCH_2O major), 73.9 (C-4), 72.0 (3-PhCH_2O), 69.2 [$OCH_2CH(O)CHPh$], 68.3(C-6) 66.6 (C-5), 61.4 [$OCH_2CH(O)CHPh$ minor], 60.8 [$OCH_2CH(O)CHPh$ major], 56.3 [$OCH_2CH(O)CHPh$ minor], 56.0 [$OCH_2CH(O)CHPh$ major]. HRMS (EI): $[M]^{+\cdot}$, found 580.2466. $C_{36}H_{36}O_7$ requires 580.2461.

4.7.2.3. 2,3-Epoxy-2-methylpropyl 2,3-di-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 41. Two stereoisomers were obtained in a 1:1 ratio (0% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography using hexane–ethyl acetate (3:1) as eluent. Yield 0.5 g (90%); $[\alpha]_D = +35.8$ (*c* 1.0, CH_2Cl_2); MS (EI): *m/z* 518 (10%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.2 (m, 15H, 3Ph), 5.50 (s, 1H, PhC*H*), 4.96, 4.92 (2d, 1H, J_{gem} 10.8 Hz, 2-PhCH_AH_BO), 4.8–4.7 (m, 3H, 2-PhCH_AH_BO, 3-PhCH_2O), 4.49, 4.44 (2d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.29 (2dd, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_e), 4.11 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 4.05–3.80 [m, 3H, H-2, H-6_a, $OCH_AH_BC(CH_3)(O)CH_2$], 3.7–3.5 [m, 2H, $OCH_AH_BC(CH_3)(O)CH_2$, H-3), 3.32 (m, 1H, H-5), 2.88, 2.73 [2d, 1H, J_{gem} 5.0, 4.7 Hz, $OCH_2C(CH_3)(O)CH_AH_B$], 2.63, 2.61 [2d, 1H, J_{gem} 4.7, 5.0 Hz, $OCH_2C(CH_3)(O)CH_AH_B$], 1.43, 1.40 (2s, 3H, $OCH_2C(CH_3)(O)CH_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.4–126.4 (3Ph), 103.5, 103.2 (2C-1), 101.2 (PhCH), 79.3,79.2 (2C-3), 78.4, 78.3 (2C-2) 75.3 (2-PhCH_2O), 73.9 (C-4), 71.7 (3-PhCH_2O), 72.0 [$OCH_2C(CH_3)(O)CHPh$], 69.2 (C-6), 66.5 (C-5), 55.8 [$OCH_2C(CH_3)(O)CH_2$], 51.7, 51.6 [2$OCH_2C(CH_3)(O)CH_2$], 18.7, 18.5 [2$OCH_2C(CH_3)(O)CHPh$]. HRMS (EI): $[M]^{+\cdot}$, found 5518.2282. $C_{31}H_{34}O_7$ requires 518.2305.

4.7.3. Epoxidation of 4,6-*O*-benzylidene-3-*O*-benzyl derivatives

4.7.3.1. (2*R*)-2,3-Epoxypropyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 42. Two stereoisomers were obtained in a 7.5:1 ratio (76% de). The pure diastereomeric mixture was obtained as a solid by column chromatography using hexane–ethyl acetate (1:2) as eluent. Yield 0.3 g (61%). mp 200–201 °C; $[\alpha]_D = -43.2$ (*c* 0.5, CH_2Cl_2); MS (FAB): *m/z* 437 (70%) $[M+Na]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.4–7.1 (m, 10H, 2Ph), 5.55 (s, 1H, PhC*H*), 4.75 (s, 2H, PhCH_2O) 4.43 (d, 0.12H, $J_{1,2}$ 7.8 Hz, H-1 minor), 4.38 (d, 0.88H, $J_{1,2}$ 7.8 Hz, H-1 major), 4.31 (dd, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_e) 4.15 (d, 0.12H, $J_{3,4}$ 3.5 Hz, H-4 minor), 4.13 (d, 0.88H, $J_{3,4}$ 3.5 Hz, H-4 major), 4.01–3.8 [m, 3H, OCH_AH_BCH(O)CH_2, H-2], 3.88 (dd, 1H, $J_{6e,6a}$ 12.4 Hz, $J_{5,6a}$ 3.3 Hz, H-6_a), 3.52 (dd, 0.12H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 8.0 Hz, H-3 minor), 3.49 (dd, 0.88H, $J_{3,4}$ 3.5 Hz, $J_{2,3}$ 8.1 Hz, H-3 major), 3.38 (br s, 1H, H-5), 3.25 [m, 1H, $OCH_2CH(O)CH_2$], 2.82 [m, 1H, $OCH_2CH(O)$-CH_AH_B], 2.77 [m, 1H, $OCH_2CH(O)CH_AH_B$], 2.67 (br s, 1H, 2-OH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.0–126.2 (2Ph), 103.3 (C-1 major), 103.1 (C-1 minor), 101.0 (PhCH), 79.0 (C-3), 73.1 (C-4 minor), 73.0 (C-4 major), 71.6 (PhCH_2O minor), 71.5 (PhCH_2O major), 70.1 (C-2), 69.3 (C-6 minor), 69.2 (C-6 major), 68.9 [$OCH_2CH(O)CHCH_3$], 66.7 (C-5), 50.7 [$OCH_2CH(O)CH_2$ minor], 50.5 [$OCH_2CH(O)CH_2$ major], 44.6 [$OCH_2CH(O)CH_2$] HRMS (CI): $[M+Na]^+$, found 413.1586. $C_{23}H_{26}O_7Na$ requires 413.1576. Anal. Calcd for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32. Found: C, 66.60; H, 6.06.

4.7.3.2. (2*S*,3*S*)-2,3-Epoxy-3-phenylpropyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 43. Two stereoisomers were obtained in a 6.5:1 ratio (74% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography using hexane–ethyl acetate (1:1) as eluent. Yield 0.2 g (87.3%); $[\alpha]_D = -20.4$ (*c* 0.4, CH_2Cl_2); MS (EI): *m/z* 490 (12%) $[M]^{+\cdot}$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.6–7.2 (m, 15H, 3Ph), 5.55 (s, 0.87H, PhC*H* major), 5.54 (s, 0.13H, PhC*H* minor), 4.70 (s, 2H, PhCH_2O) 4.50 (d, 0.13H, $J_{1,2}$ 7.8 Hz, H-1 minor), 4.44 (d, 0.87H, $J_{1,2}$ 7.7 Hz, H-1 major), 4.33 (dd, 1H, $J_{5,6e}$ 1.4 Hz, $J_{6e,6a}$ 12.5 Hz, H-6_e), 4.20 (d, 0.13H, $J_{3,4}$ 3.0 Hz, H-4 minor), 4.18 (d, 0.87H, $J_{3,4}$ 3.0 Hz, H-4 major), 4.1–3.9 [m, 4H, OCH_2-CH(O)CHPh, H-2, H-6_a], 3.52 (dd, 0.13H, $J_{3,4}$ 3.5 Hz, $J_{2,3}$ 8.0 Hz, H-3 minor), 3.49 (dd, 0.87H, $J_{3,4}$ 3.5 Hz, $J_{2,3}$ 8.1 Hz, H-3 major) 3.42 (m, 1H, H-5), 3.33 [m, 0.87H, $OCH_2CH(O)CHPh$ minor], 3.30 [m, 0.13H, $OCH_2CH(O)CHPh$ major], 2.94 [m, 0.13H, $OCH_2CH(O)CHPh$ minor], 2.90 [m, 0.87H, $OCH_2CH(O)CHPh$ major], 2.73 (br s, 1H, 2-OH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.5–125.8 (3Ph), 103.5 (C-1 major), 103.2 (C-1 minor), 101.2 (PhCH), 79.2 (C-3 major), 79.1 (C-3 minor), 73.1 (C-4 mayor), 71.6 (PhCH_2O), 70.1 (C-2), 69.3 (C-6 major), 69.2 (C-6 minor), 68.1 [O$CH_2CH(O)CHPh$], 66.8 (C-5), 61.2 [$OCH_2CH(O)CHPh$ minor], 61,0 [$OCH_2CH(O)CHPh$ major], 56.2 [$OCH_2CH(O)CHPh$ minor], 56.0 [$OCH_2CH(O)CHPh$ major]. HRMS (EI): $[M]^{+\cdot}$, found 490.1992. $C_{29}H_{30}O_7$ requires 490.1992.

4.7.3.3. (2*S*,3*S*)-2,3-Epoxybutyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 44. Two stereoisomers were obtained in an 11.5:1 ratio (84% de). The pure diastereomeric mixture was obtained as a solid by column chromatography using hexane–ethyl acetate (1:1) as eluent. Yield 0.4 g (98%); mp 119–120 °C; $[\alpha]_D = +15.3$ (*c* 1.0, CH_2Cl_2); MS (FAB): *m/z* 451 (95%) $[M+Na]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.60–7.25 (m, 10H, 2Ph), 5.46 (s, 1H, PhC*H*), 4.76 (s, 2H, PhCH_2O), 4.42 (d, 0.08H, $J_{1,2}$ 7.8 Hz, H-1 minor), 4.35 (d, 0.92H, $J_{1,2}$ 7.8 Hz, H-1 major), 4.30 (d, 1H, $J_{6e,6a}$ 12.4 Hz, H-6_e), 4.12 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 4.05–3.95 [m, 3H, H-2, H-6_a, OCH_AH_BCH(O)$CHCH_3$], 3.83 [dd, 0.92H J_{gem} 12.1 Hz, *J* 3.4 Hz, $OCH_AH_BCH(O)CHCH_3$ major], 3.60 [dd, 0.08H J_{gem} 12.0 Hz, *J* 3.6 Hz, $OCH_AH_BCH(O)CHCH_3$ minor], 3.49 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.5 Hz, H-3), 3.37 (m, 1H, H-5), 3.07 [m, 1H, OCH_2-$CH(O)CHCH_3$], 2.95 [m, 1H, $OCH_2CH(O)CHCH_3$], 2.72 (s, 1H, OH), 1.33 [d, 3H, *J* 5.3 Hz, $OCH_2CH(O)CHCH_3$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1–126.3 (2Ph), 103.5 (C-1), 101.1 (PhCH), 79.0 (C-3), 73.1 (C-4), 71.6 (PhCH_2O), 70.1 (C-2), 69.3 (C-6), 68.5 [OCH_2-$CH(O)CHCH_3$], 66.7 (C-5), 57.7 [$OCH_2CH(O)CHCH_3$], 52.4 [OCH_2-$CH(O)CHCH_3$], 17.2 [$OCH_2CH(O)CHCH_3$]. HRMS (FAB): $[M+Na]^+$, found 451.1767. $C_{24}H_{28}O_7Na$ requires 451.1733. Anal. Calcd for $C_{24}H_{28}O_7$: C, 67.28; H, 6.59. Found: C, 67.02; H, 6.49.

4.7.3.4. (2*S*,3*S*)-2,3-Epoxydecyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 45. Two stereoisomers were obtained in a 13.6:1 ratio (86% de). The pure diastereomeric mixture was obtained as a solid by column chromatography using hexane–ethyl acetate (1.5:1) as eluent. Yield 0.4 g (80%); mp 129–130 °C; $[\alpha]_D = +21.5$ (*c* 1.0, CH_2Cl_2); MS (FAB): *m/z* 535 (95%) $[M+Na]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.55–7.25 (m, 10H, 2Ph), 5.55 (s, 1H, PhC*H*), 4.77 (s, 2H, PhCH_2O), 4.43 (d, 0.07H, $J_{1,2}$ 7.8 Hz, H-1 minor), 4.35 (d, 0.93H, $J_{1,2}$ 7.8 Hz, H-1 major), 4.30 (dd, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_e), 4.12 (dd, 1H, $J_{3,4}$ 3.6 Hz, $J_{4,5}$ 0.8 Hz, H-4), 4.05–3.95 [m, 3H, H-2, H-6_a, OCH_AH_BCH(O)$CH(CH_2)_6CH_3$], 3.84 [dd, 1H J_{gem} 12.2 Hz, *J* 3.2 Hz, $OCH_AH_BCH(O)CH(CH_2)_6CH_3$], 3.49 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.37 (m, 1H, H-5), 2.97 [m, 2H, OCH_2-$CH(O)CH(CH_2)_6CH_3$], 2.71 (s, 1H, OH), 1.6–1.2 [m, 12H, OCH_2-$CH(O)CH(CH_2)_6CH_3$], 0.88 [t, 3H, *J* 7.0 Hz, $OCH_2CH(O)CH(CH_2)_6$-CH_3]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2–126.4 (2Ph), 103.5 (C-1), 101.1 (PhCH), 79.1 (C-3), 73.2 (C-4), 71.6 (PhCH_2O), 70.1 (C-2), 69.3 (C-6), 68.7 [$OCH_2CH(O)CH(CH_2)_6CH_3$], 66.8 (C-5), 56.8, 56.4 [$OCH_2CH(O)CH(CH_2)_6CH_3$], 31.7, 31.6, 29.3, 29.2, 25.9, 22.6 [OCH_2-$CH(O)CH(CH_2)_6CH_3$], 14.1 [$OCH_2CH(O)CH(CH_2)_6CH_3$]. HRMS (FAB): $[M+Na]^+$, found 535.2656. $C_{30}H_{40}O_7Na$ requires 535.2672. Anal. Calcd for $C_{30}H_{40}O_7$: C, 70.29; H, 7.86. Found: C, 70.29; H, 7.66.

4.7.3.5. (2*R*)-2,3-Epoxy-2-methylpropyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 46. Two stereoisomers were obtained in a 16.2:1 ratio (88% de). The pure diastereomeric mixture was obtained as a solid by column chromatography using hexane–ethyl acetate (1:2) as eluent. Yield 0.3 g (79%); mp 158–159 °C; $[\alpha]_D = +27.8$ (*c* 0.5, CH_2Cl_2); MS (FAB): *m/z* 451 (100%) $[M+Na]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.55–7.25 (m, 10H, 2Ph), 5.46 (s, 0.06H, PhC*H* minor), 5.45 (s, 0.94H, PhC*H* major), 4.77 (s, 2H, PhCH_2O), 4.43 (d, 0.06H, $J_{1,2}$ 7.8 Hz, H-1 minor), 4.34 (d, 0.94H, $J_{1,2}$ 7.8 Hz, H-1 major), 4.29 (dd, 1H, $J_{5,6e}$ 1.5 Hz, $J_{6e,6a}$ 12.3 Hz, H-6_e), 4.11 (dd, 1H, $J_{3,4}$ 3.6 Hz, $J_{4,5}$ 0.9 Hz, H-4), 4.05–3.95 [m, 3H, H-2, H-6_a, O$CH_AH_BC(CH_3)(O)CH_2$], 3.68 [d, 0.94H, J_{gem} 11.8 Hz, $OCH_AH_BC(CH_3)(O)CH_2$ major], 3.60 [d, 0.06H, J_{gem} 11.8 Hz, $OCH_AH_BC(CH_3)(O)CH_2$ minor], 3.48 (dd, 1H, $J_{2,3}$ 9.6 Hz, $J_{3,4}$ 3.6 Hz, H-3), 3.35 (m, 1H, H-5), 2.96 [d, 1H, J_{gem} 4.9 Hz, $OCH_2C(CH_3)(O)$-CH_AH_B], 2.82 (s, 1H, OH), 2.63 [d, 1H, J_{gem} 4.9 Hz, $OCH_2C(CH_3)(O)$-CH_AH_B], 1.38 (s, 3H, $OCH_2C(CH_3)(O)CH_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2–126.4 (2Ph), 103.7 (C-1), 101.1 (PhCH), 79.1 (C-3), 73.3 (C-4), 71.6 (PhCH_2O), 70.9 [$OCH_2C(CH_3)(O)CH_2$], 70.1 (C-2), 69.2 (C-6), 66.8 (C-5), 56.2 [$OCH_2C(CH_3)(O)CH_2$], 51.4 [OCH_2C-$(CH_3)(O)CH_2$], 18.6 [$OCH_2C(CH_3)(O)CH_2$]. HRMS (FAB): $[M+Na]^+$, found 451.1731. $C_{24}H_{28}O_7Na$ requires 451.1733. Anal. Calcd for $C_{24}H_{28}O_7$: C, 67.28; H, 6.59. Found: C, 67.25; H, 6.54.

4.7.3.6. (2*S*,3*S*)-2,3-Epoxy-2-methyl-3-phenylpropyl 3-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-β-D-galactopyranoside 47. Two stereoisomers were obtained in a 9.4:1 ratio (81% de). The pure diastereomeric mixture was obtained as a solid by column chromatography using hexane–ethyl acetate (1.5:1) as eluent. Yield 0.4 g (85%); mp 78–79 °C; $[\alpha]_D = +21$ (*c* 1.0, CH_2Cl_2); MS (FAB): *m/z* 527 (5%) $[M+Na]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.6–7.2 (m, 15H, 3Ph), 5.48 (s, 1H, PhC*H*), 4.78 (s, 2H, PhCH_2O), 4.51 (d, 0.10H, $J_{1,2}$ 7.8 Hz, H-1 minor), 4.43 (d, 0.90H, $J_{1,2}$ 7.7 Hz, H-1 major), 4.34–4.30 [m, 2H, H-6_e, $OCH_2C(CH_3)(O)CHPh$], 4.14–4.10 [m, 2H, H-4, O$CH_AH_BC(CH_3)(O)CHPh$], 4.07–4.03 (m, 2H, H-2, H-6_a), 3.85 [d, 0.90H, J_{gem} 12.1 Hz, $OCH_AH_BC(CH_3)(O)CHPh$ major], 3.78 [d,

0.90H, J_{gem} 11.9 Hz, $OCH_AH_BC(CH_3)(O)CHPh$ minor], 3.52 (dd, 1H, $J_{2,3}$ 9.6 Hz, $J_{3,4}$ 3.5 Hz, H-3), 3.40 (m, 1H, H-5), 2.94, 2.90 (2s, 1H, OH), 1.17 [s, 0.30H, $OCH_2C(CH_3)(O)CHPh$ minor], 1.09 [s, 2.70H, $OCH_2C(CH_3)(O)CHPh$ major]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2–126.3 (3Ph), 103.9 (C-1 major), 102.6 (C-1 minor), 101.1 (PhCH), 79.1 (C-3), 73.3 (C-4), 71.6 ($PhCH_2O$), 71.3 [$OCH_2C(CH_3)(O)CHPh$], 70.3 (C-2), 69.2 (C-6), 66.8 (C-5), 62.7 [$OCH_2C(CH_3)(O)CHPh$], 61.2 [$OCH_2C(CH_3)(O)CHPh$ minor], 60.4 [$OCH_2C(CH_3)(O)CHPh$ major], 13.8 [$OCH_2C(CH_3)(O)CHPh$]. HRMS (FAB): $[M+Na]^+$, found 527.2042. $C_{30}H_{32}O_7Na$ requires 527.2042. Anal. Calcd for $C_{30}H_{32}O_7$: C, 71.41; H, 6.39. Found: C, 71.29; H, 6.54.

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