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Stereoselective cyclopropanation of unsaturated acetals, using carbohydrates with D-*gluco*, L-*rhamno* and D-*xylo* configurations as chiral auxiliaries

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ABSTRACT

The stereoselective synthesis of (2-phenylcyclopropyl)methylidene acetals of sugar derivatives from methyl D-glucopyranoside, dodecyl *N*-acetyl-2-amino-2-deoxy-D-glucopyranoside, 1,2-*O*-isopropylidene-D-glucofuranose, methyl L-rhamnopyranoside and 1,2-*O*-isopropylidene-D-xylofuranose, as a chiral auxiliary, is described. The cyclopropanation reaction of the corresponding alkenylidene derivatives with $CH_2I_2/ZnEt_2$ took place with different stereoselectivity, depending on the configuration on the acetal carbon, the size of the acetal ring, the sugar configuration, the protecting group of the hydroxyl groups of the sugar and the substitution of the unsaturated system. The stereochemistry of the new stereogenic centres was then determined by acid hydrolysis of the cyclopropane moiety of the chiral auxiliary, which was also recovered.

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1. Introduction

The importance of chiral, non-racemic cyclopropane moieties in a number of natural and synthetic compounds, as well as in molecules used to probe biological and pharmacological processes, has led to intensive efforts to develop efficient methods for their construction.[1–10] Cyclopropanes have also been used as versatile synthetic intermediates in the synthesis of more-functionalised cycloalkanes and acyclic compounds.[11–13]

General methods have been used for building the cyclopropane ring, and have been reviewed recently.[5,11] The enantioselective methylenative cyclopropanation methods for prochiral alkenes can be classified in to two categories: (a) a synthetic strategy involving the stereoselective addition of a methylene group to substituted allylic alcohols or α,β-unsaturated carbonyl compounds linked to different chiral auxiliaries;[14–16] and (b) the use of chiral catalysts in the enantioselective cyclopropanation of achiral alkenes.[17–20]

Carbohydrates are used as tools in stereochemical differentiations: as starting materials in the syntheses of interesting enantiopure compounds;[21] as chiral templates in asymmetric transformations;[22] and as chiral auxiliaries in stereoselective syntheses.[23,24] However, there are only few precedents of the use of carbohydrates as chiral auxiliaries in the asymmetric cyclopropanation reaction of olefins,[25–29] the most important being those in which the chiral auxiliary is linked to the olefin moiety via a glycosidic bond, making the final separation difficult.

In view of the scarcity of the antecedents found on the use of sugars as chiral auxiliaries in the Simmons–Smith cyclopropanation reaction, and because of our interest and experience in carbohydrate chemistry,[30–40] we proposed to use new carbohydrate derivatives as chiral auxiliaries in the stereoselective synthesis of cyclopropanes.

In this paper, we have studied the cyclopropanation reaction, with the diiodomethane/diethylzinc system, of the double bond of acetals of *trans*-cinnamaldehyde and α-methyl-*trans*-cinnamaldehyde with different monosaccharide derivatives of alkyl D-glucopyranoside, alkyl 2-acetamido-2-deoxy-D-glucopyranoside, 1,2-*O*-isopropylidene-D-glucofuranose, alkyl rhamnopyranoside and 1,2-*O*-isopropylidene-D-xylofuranose. In order to find the substrate giving the best yields and diastereomeric excesses, we have diversified the chiral substrate, varying the carbohydrate configuration, the protection of the hydroxyl groups and the size of the sugar and acetal rings. The union of the olefin to the carbohydrate across an acetal function allowed easy separation of the new chiral cyclopropane fragment from the chiral auxiliary by acid hydrolysis.

2. Results and discussion

The synthesis of the alkenylidene acetals, substrates of the cyclopropanation reaction, has been carried out from commercial compounds or compounds previously described by us.[39,40] Methyl 2,3-*O*-(*E*-3-phenyl-2-propenylidene)-α-L-rhamnopyranosides **4** and **5** were obtained by reaction of methyl α-L-rhamnopyranoside **1** and *trans*-cinnamaldehyde dimethyl acetal[41] **2** in good

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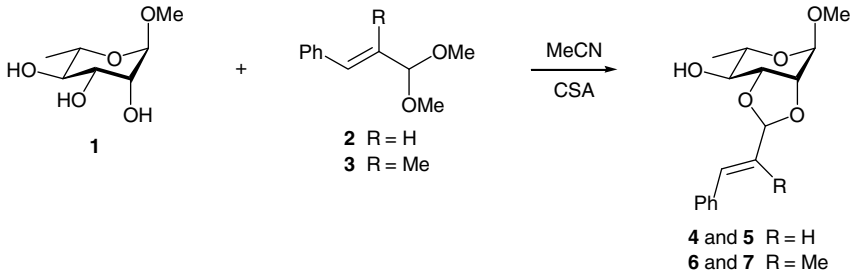


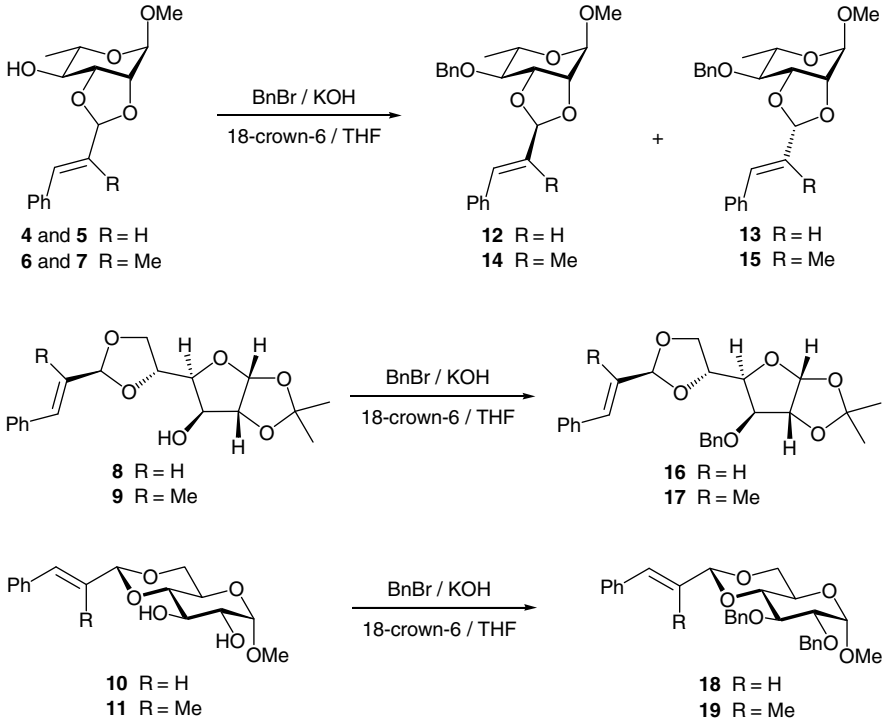
Scheme 1.

yields, using the procedure described by Murphy et al.[42] for the formation of acetals using aldehyde dimethyl acetal as reagent. Compounds **4** and **5** were obtained as a diastereomeric mixture in a 1:1 ratio, as their NMR spectra showed. The same method was used for the preparation of methyl 2,3-*O*-(*E*-2-methyl-3-phenyl-2-propenylidene)-α-L-rhamnopyranosides **6** and **7** from **1** and α-methyl-*trans*-cinnamaldehyde dimethyl acetal[39] **3** (Scheme 1). Compounds **6** and **7** were obtained as a diastereomeric mixture in a 2.2:1 ratio. The NMR spectra for mixtures **4** and **5**, and **6** and **7** showed signals corresponding to the olefin moiety incorporated into the methyl α-L-rhamnopyranoside molecule in the acetalation reaction.

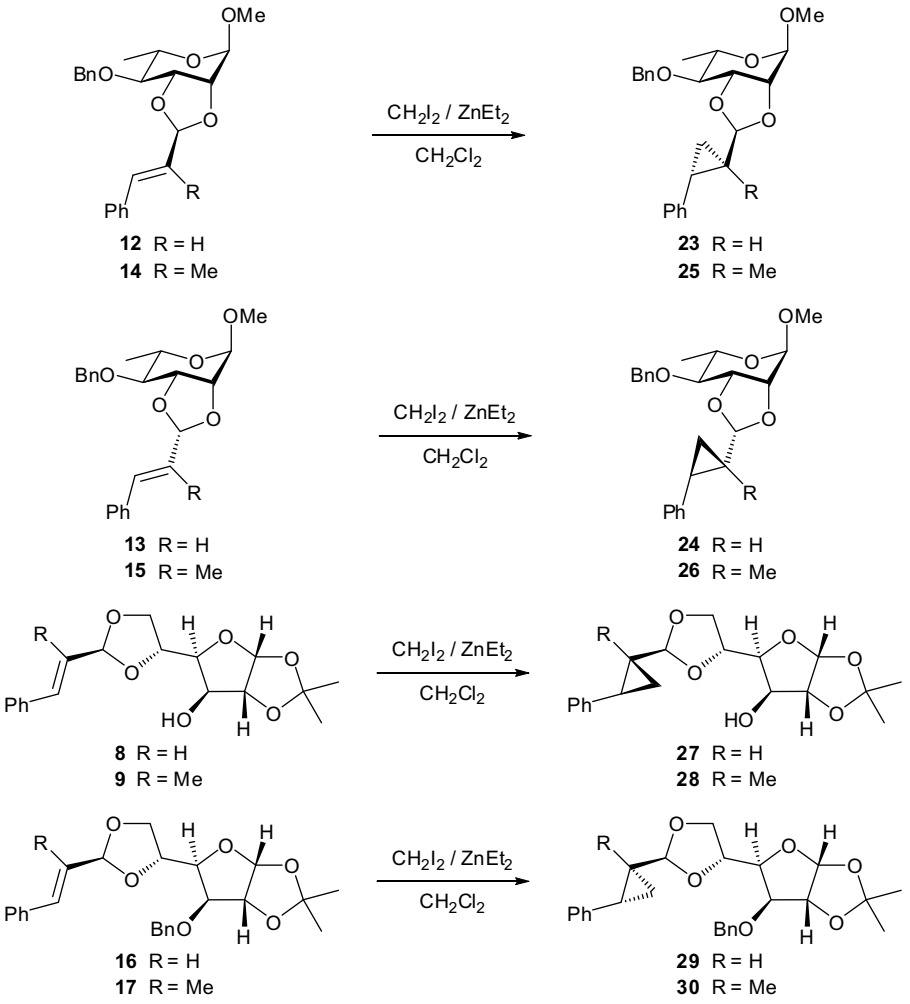
Compounds **4**–**11** were transformed into their *O*-benzyl derivatives **12**–**19** with benzyl bromide and 18-crown-6 as a catalyst (Scheme 2). The two diastereoisomers **12** and **13**, obtained from the mixture of **4** and **5**, were separated by column chromatography. Compounds **14** and **15** were obtained as two diastereoisomers from a mixture of **6** and **7**, and were separated by column chromatography. In each case, 2D-NOESY experiments established, at the acetal carbon, an (*S*)-configuration for the major isomers **12** and **14**, and an (*R*)-configuration for the minor isomers **13** and **15**.

The cyclopropanation reactions of compounds **8**–**22** were carried out using the $CH_2I_2/ZnEt_2$ system as a reagent and dichloromethane as a solvent (Schemes 3 and 4). Compounds **23**, **24**, **27** and **29**–**37** were isolated and purified by flash chromatography on silica gel. When the starting compounds were **9**, **14** and **15**, the cyclopropanation reactions gave the lowest yields of compounds **28**, **25** and **26**, which were detected by ^{1}H NMR but not isolated.

The diastereomeric excess (de) in each case was determined by ^{1}H NMR, and is shown in Table 1. The starting propylidene acetals have been classified into two groups, depending on the acetal ring size. The first group comprises compounds with an acetal ring of five members (Scheme 3); they are listed as a function of the carbohydrate configuration: α-L-*rhamnopyranose* for compounds **12** and **13**, and α-D-*glucofuranose* for compounds **8**, **9**, **16** and **17**. The second group comprises compounds with acetal ring of six members (Scheme 4); they are also listed in the order of the carbohydrate configuration: α-D-*glucopyranose* for compounds **10**, **11** and **18**–**20**, and α-D-*xylofuranose* for compounds **21** and **22**. Within the two groups, the compounds differ in the acetal carbon configuration, in the degree of substitution of the double bond and in the presence of a free hydroxyl group or a blocked hydroxyl group. With regard to the degree of substitution of the double bond of the starting propylidene acetals, the experimental data show that the diastereomeric excesses (des) obtained from *trans*-cinnamaldehyde acetals (entries 1–4, 6, 8, 10 and 11) are higher than those from α-methyl-*trans*-cinnamaldehyde acetals (entries 5, 7, 9 and



Scheme 2.

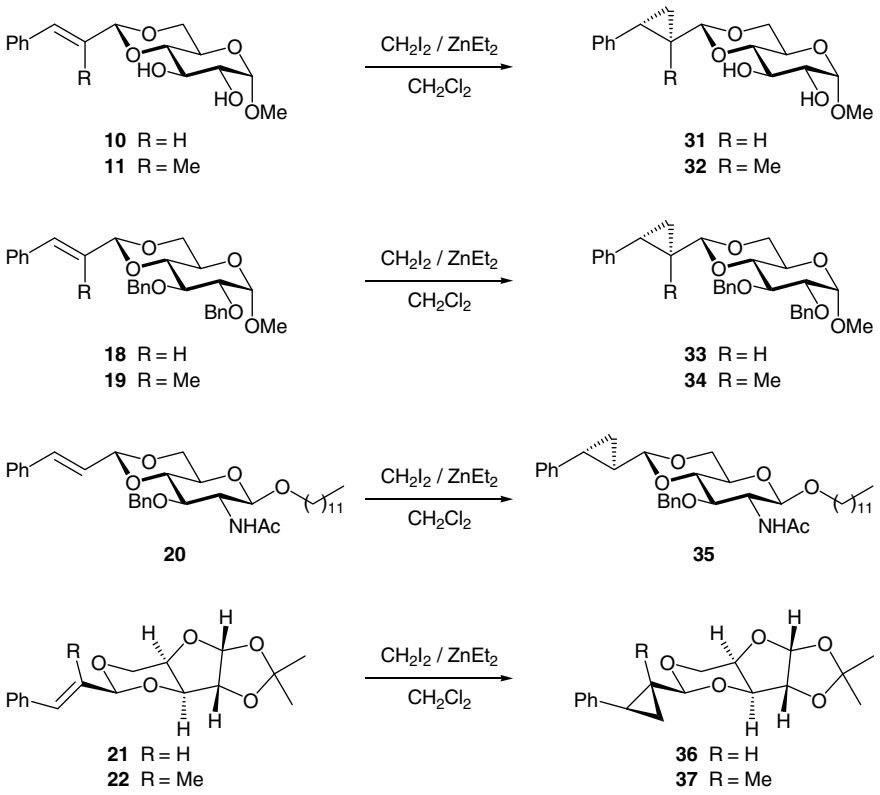


Scheme 3.

12). Thus, compounds **29**, **31**, **33** and **36** were obtained with des of 4.8%, 20%, 33% and 80%, respectively, while compounds **30**, **32**, **34** and **37** were obtained with des of 0%, 4.8%, 4.8% and 50%, respectively.

In the group of compounds with an acetal ring of five members (Scheme 3), we can observe that in those with α-L-*rhamnopyranose* configuration, **23** and **24**, the des depend on the configuration of the acetal carbon; thus, compound **23**, with an (*S*)-configuration on the acetal carbon, was obtained in 26% de, whereas **24**, with an (*R*)-configuration on the acetal carbon, was obtained in 57% de. The des of the compounds with α-D-*glucofuranose* configuration **27**, **29** and **30** were very different (Table 1, entries 3, 4 and 5) depending on the functionalisation on carbon 3 of the carbohydrate; compound **27**, with the 3-hydroxyl group free, was obtained in 49% de, whereas compounds **29** and **30**, with the 3-hydroxyl group blocked, were obtained with des of 4.8% and 0%, respectively. In the group of compounds with acetal ring of six members (Scheme 4), the des depended on the configuration of the carbohydrate moiety. The results show that the compounds **36** and **37** (with α-D-*xylofuranose* configuration) (entries 11 and 12) present des higher than the compounds **31**–**35** (with D-*glucopyranose* configuration) (entries 6–10). Thus, compounds **31**, **33**, **35** and **36**, obtained from *trans*-cinnamaldehyde acetal derivatives, showed des of 20%, 33%, 46% and 80%, respectively. Equally, cyclopropanes **32**, **34** and **37**, obtained from α-methyl-*trans*-cinnamaldehyde acetal derivatives, showed des of 4.8%, 4.8% and 50%, respectively.

In order to assign the configuration at the stereogenic centres in the cyclopropane ring formed in the cyclopropanation reaction, we proceeded to the separation of the chiral auxiliary by hydrolysis with 80% acetic acid and subsequent reduction with sodium borohydride to give the corresponding hydroxymethylcyclopropane and recovery of the carbohydrate derivative (Scheme 5). The absolute stereochemistry of the cyclopropane ring, (2*R*,3*R*) for **23**, (2*S*,3*S*) for **24**, (2*R*,3*S*) for **32**, (2*R*,3*R*) for **36** and (2*R*,3*S*) for **37**, was deduced by correlation with (1*R*,2*R*)-*trans*-1-hydroxymethyl-2-phenylcyclopropane[29,43] (−)-**38** obtained from **23** or **36**, by correlation with (1*S*,2*S*)-*trans*-1-hydroxymethyl-2-phenylcyclopropane[25,44] (+)-**38** obtained from **24**, and by correlation with (1*R*,2*S*)-*E*-1-hydroxymethyl-1-methyl-2-phenylcyclopropane[45,46] (−)-**40** obtained from **32** or **37**. The configuration of the other cyclopropanes listed in Table 1 was established on the basis of the analysis of the chemical shifts of the protons and the carbons corresponding to the cyclopropane acetal system in the NMR spectra. For cyclopropanes derived from *trans*-cinnamaldehyde, the signal corresponding to H-1′ is easily identifiable in the ^{1}H NMR spectra at approximately 5.0–4.4 ppm as a doublet, and the signals for C-1′, C-2′, C-3′ and C-4′ are identifiable in the ^{13}C NMR spectra at approximately 107–96, 25, 19 and 12 ppm, respectively. Compound **29** showed the same profile in H-1′, C-1′, C-2′ and C-3′ as that of compound **24**, so that we assigned (2*S*,3*S*) for the major isomer of compound **29**. Compound **27** showed the same profile in H-1′ as **23** and a different profile to that of **24** and **29**; moreover, com-



Scheme 4.

Table 1
Cyclopropanation of 3-phenylpropenylidene derivatives **8**–**22** in CH_2Cl_2

Entry	Starting compound	Reaction product	Yield[a] (%)	de[b] (%)	Major cyclopropane configuration
1	**12**	**23**	81	26	(2*R*,3*R*)
2	**13**	**24**	75	56.5	(2*S*,3*S*)
3	**8**	**27**	66	49	(2*R*,3*R*)
4	**16**	**29**	64	4.8	(2*S*,3*S*)
5	**17**	**30**	60	0	—
6	**10**	**31**	65	20	(2*R*,3*R*)
7	**11**	**32**	62	4.8	(2*R*,3*S*)
8	**18**	**33**	66	33	(2*R*,3*R*)
9	**19**	**34**	74	4.8	(2*R*,3*S*)
10	**20**	**35**	76	46	(2*R*,3*R*)
11	**21**	**36**	85	80	(2*R*,3*R*)
12	**22**	**37**	87	50	(2*R*,3*S*)

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

pounds **27** and **29** present a different sign for $[\alpha]_D$. We assigned (2*R*,3*R*) for the major isomer of compound **27**. Compounds **31** and **33** showed the same profiles as **23**, so that the same configurations have been assigned to them. For cyclopropanes derived from α-methyl-*trans*-cinnamaldehyde, the signal corresponding to H-1′ is easily identifiable in the ^{1}H spectra at approximately 4.7–4.2 ppm as a singlet, and the signals for C-1′, C-3′ and C-4′ are identifiable in the ^{13}C NMR spectra at approximately 106–103, 25 and 14 ppm, respectively. Compound **34** showed the same profile in H-1′, C-1′, C-3′ and C-4′ as that of compounds **32** and **37**, so we assigned (2*R*,3*S*) for the major isomer of compound **34**.

3. Conclusion

In conclusion, in the cyclopropanation reaction of propylidene acetals presented here, (a) the *Re*,*Re* face is the more reactive in compounds with *gluco* and *xylo* configuration, whereas the compounds with *rhamno* configuration present the *Re*,*Re* or *Si*,*Si* face as the more reactive, depending on the configuration of the acetal carbon; (b) the diastereomeric excesses (des) found depend on the carbohydrate configuration; (c) we have not found a direct relationship between the reactivity (de) and the protection (or not) of the hydroxyl groups of the sugar; (d) of the sugars used as chiral auxiliaries in this work, the best (best de) was 1,2-*O*-isopropylidene-α-D-xylofuranose. We have chosen this chiral auxiliary for the optimisation of the cyclopropanation reaction in a wide range of alkenes, whose results will be reported in forthcoming articles.

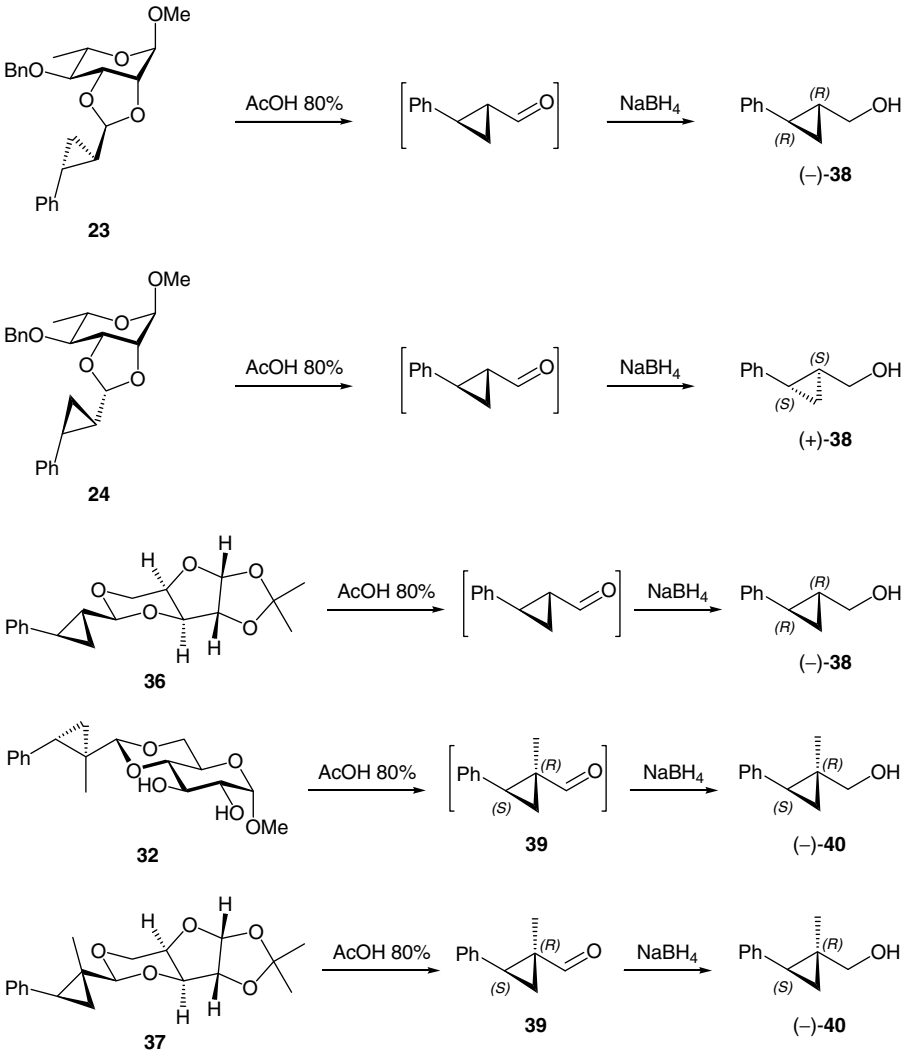
4. Experimental

4.1. General

Evaporations were conducted under reduced pressure. Preparative chromatography was performed on Silica Gel 60 (E. Merck). Kieselgel 60 F_{254} (E. Merck) was used for TLC. Melting points were obtained on a Stuart Melting Point Apparatus SMP 10 and are uncorrected. Optical rotations were obtained on a Perkin Elmer Polarimeter Model 341 at 25 °C. Mass spectra were recorded on a Micromass AUTOSPECQ mass spectrometer: EI at 70 eV and CI at 150 eV, HR mass measurements with resolutions of 10,000. NMR spectra were recorded at 25 °C on a Bruker 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, DEPT, HSQC and NOESY experiments were performed to assign the signals in the NMR spectra.

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

To a solution of methyl α-L-rhamnopyranoside **1** (0.89 g, 5.0 mmol) in acetonitrile (30 mL), the aldehyde dimethylacetal



Scheme 5.

2[41] or **3**[39] (10.0 mmol) and camphorsulfonic acid (10 mg) were added. The mixture was stirred at room temperature until a check by TLC showed that all the starting material had reacted. Then, triethylamine was added until pH 7. The reaction mixture was evaporated, and a syrup was obtained. Column chromatography gave the compounds **4** and **5** or **6** and **7**, in good yields.

4.2.1. Methyl 2,3-*O*-(*E*-3-phenyl-2-propenylidene)-α-L-rhamnopyranoside 4 and 5

Two stereoisomers were obtained in a 1:1 ratio. The pure diastereomeric mixture was obtained as a solid by column chromatography, using hexane–ethyl acetate (6:1) as eluent. Yield 1.15 g (79%); mp 136–138 °C; $[\alpha]_D = -13.0$ (*c* 1.1, CH_2Cl_2); MS (EI): *m*/*z* 292 (30%) $[M]^{+\cdot}$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 6.79 (d, 0.5H, J_{trans} 16.0 Hz, PhC*H*=CHCH B), 6.73 (d, 0.5H, J_{trans} 15.9 Hz, PhC*H*=CHCH A), 6.19 (dd, 0.5H, J_{trans} 16.0 Hz, *J* 6.5 Hz, PhCH=C*H*CH B), 6.13 (dd, 0.5H, J_{trans} 15.9 Hz, *J* 6.0 Hz, PhCH=C*H*CH A), 5.75 (d, 0.5H, *J* 6.0 Hz, PhCH=CHC*H* A), 5.53 (dd, 0.5H, *J* 6.5 Hz, ^4J 0.6 Hz, PhCH=CHC*H* B), 4.94 (s, 0.5H, H-1 B), 4.91 (s, 0.5H, H-1 A), 4.28 (dd, 0.5H, $J_{2,3}$ 5.4 Hz, $J_{3,4}$ 7.5 Hz, H-3 A), 4.15 (dd, 0.5H, $J_{2,3}$ 5.0 Hz, $J_{3,4}$ 7.0 Hz, H-3 B), 4.09 (m, 1H, H-2), 3.69 (m, 1H, H-5), 3.44 (m, 1H, H-4), 3.41 (s, 1.5H, OCH_3 B), 3.39 (s, 1.5H, OCH_3 A), 2.40 (d, 0.5H, $J_{4,OH}$ 4.6 Hz, OH B), 2.38 (d, 0.5H, $J_{4,OH}$ 4.4 Hz, OH A), 1.34 (d, 1.5H, $J_{5,6}$ 6.3 Hz, CH_3 A), 1.32 (d, 1.5H, $J_{5,6}$ 6.3 Hz, CH_3 B). ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.8, 134.4 (Ph*C*H=CHCH), 128.6–127.0 (Ph), 125.3, 125.2 (PhCH=*C*HCH), 104.5, 103.3 (PhCH=CH*C*H), 98.1, 97.8 (C-1), 79.1, 77.9 (C-3), 77.6, 75.3 (C-2), 74.9, 72.0 (C-4), 65.8, 65.4 (C-5), 55.0, 54.9 (OCH_3), 17.5, 17.4 (C-6). HRMS (EI): $[M]^{+\cdot}$, found 292.130072. $C_{16}H_{20}O_5$ requires 292.131074. Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.80; H, 7.14.

4.2.2. Methyl 2,3-*O*-(*E*-2-methyl-3-phenyl-2-propenylidene)-α-L-rhamnopyranoside 6 and 7

Two stereoisomers were obtained in a 22:10 ratio (37.5% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography, using hexane–ethyl acetate (10:1) as eluent. Yield 1.40 g (92%); $[\alpha]_D = -6.8$ (*c* 1.6, CH_2Cl_2); MS (CI): *m*/*z* 307 (98%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.4–7.2 (m, 10H, Ph), 6.74 [s, 0.31H, PhC*H*=C(CH_3)CH minor], 6.66 [s, 0.69H, PhC*H*=C(CH_3)CH major], 5.59 [s, 0.69H, PhCH=C(CH_3)C*H* major], 5.36 [d, 0.31H, ^4J 0.5 Hz, PhCH=C(CH_3)C*H* minor], 4.94 (s, 0.31H, H-1 minor), 4.91 (s, 0.69H, H-1 major), 4.34 (dd, 0.69H, $J_{2,3}$ 5.5 Hz, $J_{3,4}$ 7.4 Hz, H-3 major), 4.19 (t, 0.31H, $J_{2,3} = J_{3,4}$ 6.5 Hz, H-3 minor), 4.12 (m, 1H, H-2), 3.71 (m, 1H, H-5), 3.50 (m, 1H, H-4), 3.42 (s, 0.93H, OCH_3 minor), 3.40 (s, 2.07H, OCH_3 major), 2.40 (m, 0.31H, $J_{4,OH}$ 5.0 Hz, OH minor), 2.34 (m, 0.69H, $J_{4,OH}$ 4.4 Hz, OH major), 1.94 [d, 0.93H, ^4J 1.5 Hz, PhCH=C(C*H*$_3$)CH minor], 1.86 (d, 2.07H, ^4J 1.4 Hz, PhCH=C(C*H*$_3$)CH A), 1.35 [d, 2.07H, $J_{5,6}$ 6.3 Hz, CH_3 major], 1.32 (d, 0.93H, $J_{5,6}$ 6.3 Hz, CH_3 minor). ^{13}C

NMR (125 MHz, $CDCl_3$): δ 136.6, 136.5 [PhCH=*C*(CH_3)CH], 131.0, 129.9 [PhCH=C(CH_3)CH], 129.1–127.1 (Ph), 107.8, 106.9 [PhCH=C(CH_3)*C*H], 98.3, 98.2 (C-1), 79.5, 77.7 (C-3), 77.3, 76.2 (C-2), 74.1, 71.6 (C-4), 66.2, 65.3 (C-5), 55.0, 54.9 (OCH_3), 17.7, 17.5 (C-6), 12.3, 12.0 [PhCH=C(*C*H_3)CH]. HRMS (CI): $[M+H]^+$, found 307.154013. $C_{17}H_{23}O_5$ requires 307.15455.

4.3. *O*-Benzyl derivatives 12–19

To a cooled solution (5 °C) of sugar derivatives **4**–**11** (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 (4.8 mmol for each hydroxyl group in **4**–**11**). The reaction mixture was stirred at this temperature for 3 h, and 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 ($MgSO_4$) and filtered, and the filtrate evaporated to dryness.

4.3.1. From 4 and 5

Two stereoisomers were obtained in a 1:1 ratio. Both stereoisomers were isolated as solid compounds by column chromatography, using hexane–ethyl acetate (15:1) as eluent. Yield 1.09 g (95%).

4.3.1.1. Methyl 4-*O*-benzyl-2,3-*O*-[(*S*,*E*)-3-phenyl-2-propenylidene]-α-L-rhamnopyranoside 12 (major R_f). Mp 79–80 °C; $[\alpha]_D = -63.2$ (*c* 1.2, CH_2Cl_2); MS (CI): *m*/*z* 383 (10%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, Ph), 6.76 (d, 1H, J_{trans} 15.9 Hz, PhC*H*=CHCH), 6.15 (dd, 1H, J_{trans} 15.9 Hz, *J* 6.1 Hz, PhCH=C*H*CH), 5.67 (d, 1H, *J* 6.1 Hz, PhCH=CHC*H*), 4.94 (d, 1H, J_{gem} 11.6 Hz, PhCH_AH_BO), 4.89 (s, 1H, H-1), 4.70 (d, 1H, J_{gem} 11.6 Hz, PhCH_AH_BO), 4.48 (dd, 1H, $J_{2,3}$ 5.6 Hz, $J_{3,4}$ 7.0 Hz, H-3), 4.08 (d, 1H, $J_{2,3}$ 5.5 Hz, H-2), 3.72 (m, 1H, H-5), 3.37 (s, 3H, OCH_3), 3.25 (dd, 1H, $J_{3,4}$ 7.1 Hz, $J_{4,5}$ 9.7 Hz, H-4), 1.33 (d, 3H, $J_{5,6}$ 6.3 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2–127.0 (Ph), 135.7 (PhCH=CHCH), 125.4 (PhCH=*C*HCH), 103.1 (PhCH=CH*C*H), 98.0 (C-1), 79.3 (C-3), 78.0 (C-4), 75.4 (C-2), 73.0 (PhCH_2O), 64.2 (C-5), 54.9 (OCH_3), 17.8 (C-6). HRMS (EI): $[M]^{+\cdot}$, found 382.178694. $C_{23}H_{26}O_5$ requires 382.178024. Anal. Calcd for $C_{23}H_{26}O_5$: C, 72.23; H, 6.85. Found: C, 72.54; H, 7.08.

4.3.1.2. Methyl 4-*O*-benzyl-2,3-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-α-L-rhamnopyranoside 13 (minor R_f). Mp 116–118 °C; $[\alpha]_D = -36.0$ (*c* 0.7, CH_2Cl_2); MS (CI): *m*/*z* 383 (15%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.5–7.2 (m, 10H, Ph), 6.80 (d, 1H, J_{trans} 16.0 Hz, PhC*H*=CHCH), 6.13 (dd, 1H, J_{trans} 16.0 Hz, *J* 6.6 Hz, PhCH=C*H*CH), 5.53 (d, 1H, *J* 6.6 Hz, PhCH=CHC*H*), 4.94 (s, 1H, H-1), 4.89 (d, 1H, J_{gem} 11.7 Hz, PhCH_AH_BO), 4.67 (d, 1H, J_{gem} 11.7 Hz, PhCH_AH_BO), 4.33 (t, 1H, $J_{2,3} = J_{3,4}$ 6.5 Hz, H-3), 4.09 (dd, 1H, $J_{2,3}$ 6.0 Hz, ^4J 0.6 Hz, H-2), 3.73 (m, 1H, H-5), 3.39 (s, 3H, OCH_3), 3.24 (dd, 1H, $J_{3,4}$ 6.9 Hz, $J_{4,5}$ 9.9 Hz, H-4), 1.31 (d, 3H, $J_{5,6}$ 6.2 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2–127.1 (Ph), 135.6 (PhCH=CHCH), 125.7 (PhCH=*C*HCH), 104.5 (PhCH=CH*C*H), 97.7 (C-1), 81.0 (C-4), 78.2 (C-3), 77.9 (C-2), 72.7 (PhCH_2O), 64.5 (C-5), 54.8 (OCH_3), 17.8 (C-6). HRMS (EI): $[M]^{+\cdot}$, found 382.179407. $C_{23}H_{26}O_5$ requires 382.178024. Anal. Calcd for $C_{23}H_{26}O_5$: C, 72.23; H, 6.85. Found: C, 72.15; H, 6.88.

4.3.2. From 6 and 7

Two stereoisomers were obtained in a 22:10 ratio. Both stereoisomers were isolated as syrups by column chromatography, using hexane–ethyl acetate (21:1) as eluent. Yield 1.06 (89%).

4.3.2.1. Methyl 4-*O*-benzyl-2,3-*O*-[(*S*,*E*)-2-methyl-3-phenyl-2-propenylidene]-α-L-rhamnopyranoside 14 (major R_f). $[\alpha]_D = -43.8$ (*c* 1.2, CH_2Cl_2); MS (CI): *m*/*z* 397 (15%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.4–7.2 (m, 10H, Ph), 6.66 [s, 1H, PhC*H*=C(CH_3)CH], 5.49 [s, 1H, PhCH=C(CH_3)C*H*], 4.95 (d, 1H, J_{gem} 11.6 Hz, PhCH_AH_BO), 4.90 (s, 1H, H-1), 4.72 (d, 1H, J_{gem} 11.6 Hz, PhCH_AH_BO), 4.53 (dd, 1H, $J_{2,3}$ 5.5 Hz, $J_{3,4}$ 7.2 Hz, H-3), 4.09 (d, 1H, $J_{2,3}$ 5.5 Hz, H-2), 3.72 (m, 1H, H-5), 3.38 (s, 3H, OCH_3), 3.27 (dd, 1H, $J_{3,4}$ 7.2 Hz, $J_{4,5}$ 9.7 Hz, H-4), 1.89 [d, 3H, ^4J 1.4 Hz, PhCH=C(*C*H_3)CH], 1.34 (d, 3H, $J_{5,6}$ 6.2 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1–127.1 (Ph), 136.6 [PhCH=*C*(CH_3)CH], 130.0 [PhC*H*=C(CH_3)CH], 106.8 [PhCH=C(CH_3)*C*H], 98.1 (C-1), 79.7 (C-4), 77.3 (C-3), 76.3 (C-2), 73.0 (PhCH_2O), 64.1 (C-5), 54.9 (OCH_3), 17.8 (C-6), 12.0 [PhCH=C(*C*H_3)CH]. HRMS (CI): $[M+H]^+$, found 397.198103. $C_{24}H_{29}O_5$ requires 397.201499.

4.3.2.2. Methyl 4-*O*-benzyl-2,3-*O*-[(*R*,*E*)-2-methyl-3-phenyl-2-propenylidene]-α-L-rhamnopyranoside 15 (minor R_f). $[\alpha]_D = -6.0$ (*c* 0.6, CH_2Cl_2); MS (CI): *m*/*z* 397 (20%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.4–7.2 (m, 10H, Ph), 6.77 [s, 1H, PhC*H*=C(CH_3)CH], 5.38 [d, 1H, ^4J 0.6 Hz, PhCH=C(CH_3)C*H*], 4.97 (s, 1H, H-1), 4.93 (d, 1H, J_{gem} 11.6 Hz, PhCH_AH_BO), 4.64 (d, 1H, J_{gem} 11.6 Hz, PhCH_AH_BO), 4.37 (t, 1H, $J_{2,3} = J_{3,4}$ 6.6 Hz, H-3), 4.15 (dd, 1H, $J_{2,3}$ 6.6 Hz, ^4J 0.6 Hz, H-2), 3.74 (m, 1H, H-5), 3.40 (s, 3H, OCH_3), 3.33 (dd, 1H, $J_{3,4}$ 6.6 Hz, $J_{4,5}$ 9.8 Hz, H-4), 1.93 [d, 3H, ^4J 1.4 Hz, PhCH=C(*C*H_3)CH], 1.33 (d, 3H, $J_{5,6}$ 6.2 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3–127.1 (Ph), 136.6 [PhCH=*C*(CH_3)CH], 130.8 [PhC*H*=C(CH_3)CH], 107.6 [PhCH=C(CH_3)*C*H], 98.0 (C-1), 81.4 (C-4), 77.9 (C-2, C-3), 72.6 (PhCH_2O), 64.2 (C-5), 54.7 (OCH_3), 18.0 (C-6), 12.4 [PhCH=C(*C*H_3)CH]. HRMS (CI): $[M+H]^+$, found 397.199113. $C_{24}H_{29}O_5$ requires 397.201499.

4.3.3. 3-*O*-Benzyl-5,6-*O*-[(*S*,*E*)-3-phenyl-2-propenylidene]-1,2-*O*-isopropylidene-α-D-glucofuranose 16

The syrup obtained was purified by flash chromatography on silica gel, using hexane–ethyl acetate (5:1) as eluent. Yield 0.92 g (72%); $[\alpha]_D = -4.7$ (*c* 0.8, CH_2Cl_2); MS (CI): *m*/*z* 425 (40%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.4–7.2 (m, 10H, Ph), 6.80 (d, 1H, J_{trans} 16.0 Hz, PhC*H*=CHCH), 6.20 (dd, 1H, J_{trans} 16.1 Hz, *J* 5.0 Hz, PhCH=C*H*CH), 6.09 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 5.71 (d, 1H, *J* 5.0 Hz, PhCH=CHC*H*), 4.68 (d, 1H, $J_{1,2}$ 3.6 Hz, H-2), 4.65, 4.60 (2d, 2H, J_{gem} 12.2 Hz, PhCH_2O), 4.52 (d, 1H, $J_{3,4}$ 2.3 Hz, H-3), 4.39 (t, 1H, $J_{5,6A} = J_{5,6B}$ 4.2 Hz, H-5), 4.19 (m, 1H, H-4), 3.95 (dd, 1H, $J_{5,6A}$ 4.2 Hz, $J_{6A,6B}$ 10.5 Hz, H-6_A), 3.81 (dd, 1H, $J_{5,6B}$ 4.2 Hz, $J_{6A,6B}$ 10.5 Hz, H-6_B), 1.58, 1.38 [2s, 6H, C(CH_3)$_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.7–126.9 (Ph), 133.7 (PhCH=CHCH), 126.7 (PhCH=*C*HCH), 111.6 [*C*(CH_3)$_2$], 104.7 (C-1), 94.85 (PhCH=CH*C*H), 83.9 (C-2), 76.7 (C-3), 73.4 (C-5), 73.5 (C-4), 73.5 (PhCH_2O), 71.4 (C-6), 26.6, 26.0 [C(*C*H_3)$_2$]. HRMS (EI): $[M]^{+\cdot}$, found 424.183759. $C_{18}H_{22}O_6$ requires 424.188589.

4.3.4. 3-*O*-Benzyl-5,6-*O*-[(*S*,*E*)-2-methyl-3-phenyl-2-propenylidene]-1,2-*O*-isopropylidene-α-D-glucofuranose 17

The syrup obtained was purified by flash chromatography on silica gel, using hexane–ethyl acetate (12.5:1) as eluent. Yield 0.90 g (71%); $[\alpha]_D = -10.7$ (*c* 0.8, CH_2Cl_2); MS (CI): *m*/*z* 439 (25%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.2 (m, 10H, Ph), 6.64 [s, 1H, PhC*H*=C(CH_3)CH], 6.04 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.46 [s, 1H, PhCH=C(CH_3)C*H*], 4.64 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.61, 4.58 (2d, 2H, J_{gem} 12.2 Hz, PhCH_2O), 4.48 (d, 1H, $J_{3,4}$ 2.0 Hz, H-3), 4.36 (t, 1H, $J_{5,6A} = J_{5,6B}$ 4.0 Hz, H-5), 4.15 (m, 1H, H-4), 3.92 (dd, 1H, $J_{5,6A}$ 4.0 Hz, $J_{6A,6B}$ 10.4 Hz, H-6_A), 3.78 (dd, 1H, $J_{5,6B}$ 4.0 Hz, $J_{6A,6B}$ 10.4 Hz, H-6_B), 1.90 [d, 3H, ^4J 1.5 Hz, PhCH=C(*C*H_3)CH], 1.54, 1.35 [2s, 6H, C(CH_3)$_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.7–128.1 (Ph),

134.1 [PhCH=C(CH_3)CH], 127.0 [PhCH=*C*(CH_3)CH], 111.9 [*C*(CH_3)$_2$], 105.0 (C-1), 97.3 [PhCH=C(CH_3)*C*H], 84.0 (C-2), 77.7 (C-3), 73.9 (C-5), 73.6 (PhCH_2O), 73.0 (C-4), 61.8 (C-6), 26.8, 26.2 [C(CH_3)$_2$], 12.9 [PhCH=C(*C*H_3)CH]. HRMS (EI): $[M]^{+\cdot}$, found 438.202348. $C_{19}H_{24}O_6$ requires 438.204239.

4.3.5. Methyl 2,3-di-*O*-benzyl-4,6-*O*-[(*R*,*E*)-3-phenyl-2-propenylidene]-α-D-glucopyranoside 18

The syrup obtained was purified by flash chromatography on silica gel, using hexane–ethyl acetate (8:1) as eluent. Yield 1.17 g (80%); $[\alpha]_D$ = +6.8 (*c* 0.9, CH_2Cl_2); MS (CI): *m*/*z* 489 (10%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.2 (m, 15H, Ph), 6.81 (d, 1H, J_{trans} 16.1 Hz, PhC*H*=CHCH), 6.19 (dd, 1H, J_{trans} 16.1 Hz, *J* 4.3 Hz, PhCH=*C*HCH), 5.17 (dd, 1H, *J* 4.3 Hz, ^4J 1.2 Hz, PhCH=CHC*H*), 4.9–4.7 (m, 4H, 2 Ph*C*H_2O), 4.59 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.20 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.2 Hz, H-6$_e$), 4.01 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.3 Hz, H-3), 3.6–3.5 (m, 3H, H-2, H-5, H-6$_a$), 3.5 (m, 1H, H-4), 3.4 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 128.4–126.8 (Ph), 133.6 (Ph*C*H=CHCH), 124.5 (PhCH=*C*HCH), 100.7 (PhCH=CH*C*H), 99.2 (C-1), 81.9 (C-4), 79.2 (C-2), 78.6 (C-3), 75.3, 73.7 (2 PhCH_2O), 68.8 (C-6), 62.3 (C-5), 55.2 (OCH_3). HRMS (CI): $[M+H]^+$, found 489.226908. $C_{30}H_{33}O_6$ requires 489.227714.

4.3.6. Methyl 2,3-di-*O*-benzyl-4,6-*O*-[(*R*,*E*)-2-methyl-3-phenyl-2-propenylidene]-α-D-glucopyranoside 19

The syrup obtained was purified by flash chromatography on silica gel, using hexane–ethyl acetate (8:1) as eluent. Yield 1.11 g (74%); $[\alpha]_D$ = +29.2 (*c* 1.1, CH_2Cl_2); MS (CI): *m*/*z* 503 (5%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.5–7.3 (m, 15H, Ph), 6.70 [s, 1H, PhC*H*=C(CH_3)CH], 4.98 [s, 1H, PhCH=C(CH_3)C*H*], 4.91(d, 1H, J_{gem} 11.3 Hz, Ph*C*H_AH$_B$O), 4.9–4.8 (2d, 2H, J_{gem} 12.3 Hz, J_{gem} 11.3 Hz, Ph*C*H_DH$_E$O, PhCH_A*H*$_B$O), 4.71 (d, 1H, J_{gem} 12.2 Hz, PhCH_D*H*$_E$O), 4.59 (d, 1H, $J_{1,2}$ 3.70 Hz, H-1), 4.21 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.2 Hz, H-6$_e$), 4.02 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.3 Hz, H-3), 3.77 (dt, 1H, $J_{5,6e}$ 4.5 Hz, $J_{4,5}$ = $J_{5,6a}$ 10.0 Hz, H-5), 3.62 (t, 1H, $J_{5,6a}$ 10.3 Hz, H-6$_a$), 3.54 (dd, 1H, $J_{1,2}$ 3.7 Hz, $J_{2,3}$ 9.3 Hz, H-2), 3.50 (dd, 1H, $J_{3,4}$ 9.30 Hz, $J_{4,5}$ 10.0 Hz, H-4), 3.40 (s, 3H, OCH_3), 1.94 [d, 3H, ^4J 2.4 Hz, PhCH=C(C*H*$_3$)CH]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 128.1–127.5 (Ph), 129.1 [Ph*C*H=C(CH_3)CH], 128.3 [PhCH=*C*(CH_3)CH], 104.2 [PhCH=C(CH_3)*C*H], 99.2 (C-1), 81.9 (C-4), 79.2 (C-2), 78.5 (C-3), 75.3, 73.8 (2 PhCH_2O), 68.9 (C-6), 62.4 (C-5), 55.3 (OCH_3), 13.5 [PhCH=C(*C*H_3)CH]. HRMS (CI): $[M+H]^{+\cdot}$, found 503.241457. $C_{31}H_{35}O_6$ requires 503.243364.

4.4. General procedure for cyclopropanation of α,β-unsaturated acetals

To a solution of the corresponding unsaturated acetal **8**–**22** (1.0 mmol) in dry dichloromethane (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 left at room temperature until TLC showed that all the starting material had reacted (~12 h). The reaction was diluted with dichloromethane and quenched with saturated ammonium chloride solution. The organic layer was dried ($MgSO_4$), filtered and evaporated to dryness. Compounds obtained were purified by flash chromatography on silica gel. The diastereomeric excess (de) was determined by ^{1}H NMR.

4.4.1. Methyl 4-*O*-benzyl-2,3-*O*-[(1*S*,2*R*,3*R*)-(2-phenylcyclopropyl)methylidene]-α-L-rhamnopyranoside 23

Two stereoisomers were obtained in a 17:10 ratio (26% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography, using hexane–ethyl acetate (15:1) as eluent. Yield 0.32 g (81%); $[\alpha]_D$ = −17.8 (*c* 1.0, CH_2Cl_2); MS (CI): *m*/*z* 397 (45%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.1 (m, 10H, Ph), 4.99 [d, 0.63H, *J* 5.0 Hz, PhCH(CH_2)CHC*H* major], 4.95 [d, 0.37H, *J* 5.2 Hz, PhCH(CH_2)CHC*H* minor], 4.90 (2d, 1H, J_{gem} 11.7 Hz, Ph*C*H_AH$_B$O), 4.86 (s, 0.63H, H-1 major), 4.85 (s, 0.37H, H-1 minor), 4.69 (2d, 1H, J_{gem} 11.7 Hz, PhCH_A*H*$_B$O), 4.44 (m, 1H, H-3), 4.03 (m, 1H, H-2), 3.69 (m, 1H, H-5), 3.37 (s, 1.89H, OCH_3 major), 3.36 (s, 1.11H, OCH_3 minor), 3.17 (dd, 1H, $J_{3,4}$ 7.2 Hz, $J_{4,5}$ 9.8 Hz, H-4), 2.05 [m, 1H, Ph*C*H(CH_2)CHCH], 1.45 [m, 1H, PhCH(CH_2)*C*HCH], 1.32 (d, 3H, $J_{5,6}$ 6.3 Hz, CH_3), 1.15 [m, 1H, PhCH(*C*H_AH$_B$)CHCH], 0.98 [m, 1H, PhCH(CH$_A$*H*$_B$)CHCH]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.7–125.8 (Ph), 105.0 [PhCH(CH_2)CH*C*H minor], 104.7 [PhCH(CH_2)CH*C*H major], 98.0 (C-1), 79.2 (C-3), 77.3 (C-4 minor), 77.2 (C-4 major), 75.65 (C-2 major), 75.60 (C-2 minor), 72.9 (PhCH_2O minor), 72.8 (Ph*C*H_2O major), 64.1 (C-5), 54.8 (OCH_3), 25.7 [PhCH(CH_2)*C*HCH minor], 25.5 [PhCH(CH_2)*C*HCH major], 19.5 [Ph*C*H(CH_2)CHCH major], 19.2 [Ph*C*H(CH_2)CHCH minor], 17.8 (C-6), 11.6 [PhCH(*C*H_2)CHCH minor], 11.2 [PhCH(*C*H_2)CHCH major]. HRMS (EI): $[M]^{+\cdot}$, found 396.192959. $C_{24}H_{28}O_5$ requires 396.193674.

4.4.2. Methyl 4-*O*-benzyl-2,3-*O*-[(1*R*,2*S*,3*S*)-(2-phenylcyclopropyl)methylidene]-α-L-rhamnopyranoside 24

Two stereoisomers were obtained in a 36:10 ratio (57% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography, using hexane–ethyl acetate (15:1) as eluent. Yield 0.30 g (75%); $[\alpha]_D$ = −15.3 (*c* 1.2, CH_2Cl_2); MS (EI): *m*/*z* 396 (15%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.1 (m, 10H, Ph), 4.95 (s, 0.78H, H-1 major), 4.94 (s, 0.22H, H-1 minor), 4.92 (d, 0.22H, J_{gem} 11.7 Hz, Ph*C*H_AH$_B$O minor), 4.88 (d, 0.78H, J_{gem} 11.7 Hz, Ph*C*H_AH$_B$O major), 4.85 [d, 0.22H, *J* 6.0 Hz, PhCH(CH_2)CHC*H* minor], 4.79 [d, 0.78H, *J* 6.0 Hz, PhCH(CH_2)CHC*H* major], 4.66 (2d, 1H, J_{gem} 11.7 Hz, PhCH_A*H*$_B$O), 4.30 (m, 1H, H-3), 4.06 (m, 1H, H-2), 3.73 (m, 1H, H-5), 3.41 (s, 2.34H, OCH_3 major), 3.40 (s, 0.66H, OCH_3 minor), 3.27 (dd, 0.22H, $J_{3,4}$ 6.8 Hz, $J_{4,5}$ 9.9 Hz, H-4 minor), 3.22 (dd, 0.78H, $J_{3,4}$ 6.8 Hz, $J_{4,5}$ 9.9 Hz, H-4 major), 2.12 [m, 1H, Ph*C*H(CH_2)CHCH], 1.49 [m, 1H, PhCH(CH_2)*C*HCH], 1.35 (d, 0.66H, $J_{5,6}$ 6.3 Hz, CH_3 minor), 1.30 (d, 2.34H, $J_{5,6}$ 6.3 Hz, CH_3 major), 1.20 [m, 0.22H, PhCH(*C*H_AH$_B$)CHCH minor], 1.15 [m, 0.78H, PhCH(*C*H_AH$_B$)CHCH major], 0.98 [m, 1H, PhCH(CH$_A$*H*$_B$)CHCH]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.6–125.9 (Ph), 106.9 [PhCH(CH_2)CH*C*H major], 106.2 [PhCH(CH_2)CH*C*H minor], 97.8 (C-1), 81.0 (C-4 minor), 80.9 (C-4 major), 78.0 (C-3 major), 77.9 (C-3 minor), 77.8 (C-2 major), 77.7 (C-2 minor), 72.7 (Ph*C*H_2O minor), 72.5 (Ph*C*H_2O major), 64.5 (C-5 minor), 64.3 (C-5 major), 54.8 (OCH_3), 25.5 [PhCH(CH_2)*C*HCH major], 25.2 [PhCH(CH_2)*C*HCH minor], 19.9 [Ph*C*H(CH_2)CHCH major], 19.7 [Ph*C*H(CH_2)CHCH minor], 17.9 (C-6), 12.0 [PhCH(*C*H_2)CHCH minor], 11.7 [PhCH(*C*H_2)CHCH major]. HRMS (EI): $[M]^{+\cdot}$, found 396.193339. $C_{24}H_{28}O_5$ requires 396.193674.

4.4.3. 1,2-*O*-Isopropylidene-5,6-*O*-[(1*S*,2*R*,3*R*)-(2-phenylcyclopropyl)methylidene]-α-D-glucofuranose 27

Two stereoisomers were obtained in a 29:10 ratio (49% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography, using hexane–ethyl acetate (5:1) as eluent. Yield 0.23 g (66%); $[\alpha]_D$ = −6.3 (*c* 1.1, CH_2Cl_2); MS (EI): *m*/*z* 348 (10%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.1 (m, 5H, Ph), 5.97 (d, $J_{1,2}$ 3.7, H-1 minor), 5.95 (d, $J_{1,2}$ 3.60, H-1 major), 4.88 [d, 0.74H, *J* 5.5, PhCH(CH_2)CHC*H* major], 4.73 [d, 0.26H, *J* 5.5, PhCH(CH_2)CHC*H* minor], 4.63 (d, 0.26H, $J_{1,2}$ 3.7 Hz, H-2 minor), 4.53 (d, 0.74H, $J_{1,2}$ 3.6 Hz, H-2 major), 4.48 (d, 0.26H, $J_{3,4}$ 2.5 Hz, H-3 minor), 4.36 (d, 0.74H, $J_{3,4}$ 2.7 Hz, H-3 major), 4.28 (dd, 1H, $J_{4,5}$ 8.0 Hz, $J_{5,6A}$ 6.4 Hz, H-5), 4.18 (dd, 1H, $J_{3,4}$ 2.7 Hz, $J_{4,5}$ 8.0 Hz, H-4), 3.95 (dd, 1H, $J_{5,6A}$ 6.4 Hz, J_{gem} 8.6 Hz, H-6$_A$), 3.82 (d, 1H, J_{gem} 8.6 Hz, H-6$_B$), 2.06 [m, Ph*C*H(CH_2)CHCH major], 1.95 [m, Ph*C*H(CH_2)CHCH minor], 1.48 [m, 1H, PhCH(CH_2)*C*HCH], 1.21 [m, PhCH(*C*H_AH$_B$)CHCH

minor], 1.12 [m, PhCH(CH_AH_B)CHCH major], 1.03 [m, 1H, PhCH(CH_AH_B)CHCH]. HRMS (EI): $[M]^{+\cdot}$, found 348.157228. $C_{19}H_{24}O_6$ requires 348.157289.

4.4.4. 3-*O*-Benzyl-1,2-*O*-isopropylidene-5,6-*O*-[(1*S*,2*S*,3*S*)-(2-phenylcyclopropyl)methylidene]-α-D-glucofuranose 29

Two stereoisomers were obtained in an 11:10 ratio (4.8% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography, using hexane–ethyl acetate (7:1) as eluent. Yield 0.28 g (64%); $[\alpha]_D$ = +12.9 (*c* 1.2, CH_2Cl_2); MS (CI): *m*/*z* 439 (5%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.1 (m, 10H, Ph), 6.02 (d, 0.48H, $J_{1,2}$ 4.0 Hz, H-1 minor), 6.00 (d, 0.52H, $J_{1,2}$ 4.0 Hz, H-1 major), 4.91 [d, 0.48H, *J* 5.0 Hz, PhCH(CH_2)CHC*H* minor], 4.86 [d, 0.52H, *J* 5.0 Hz, PhCH(CH_2)CHC*H* major], 4.59 (2d, 1H, $J_{1,2}$ 4.1 Hz, H-2), 4.56 (s, 2H, PhCH_2O), 4.36 (d, 1H, $J_{3,4}$ 2.1 Hz, H-3), 4.28 (m, 1H, H-5), 4.09 (m, 1H, H-4), 3.83 (m, 1H, H-6_A), 3.70 (m, 1H, H-6_B), 2.01 [m, 1H, PhC*H*(CH_2)CHCH], 1.49, 1.33 [2s, 6H, $C(CH_3)_2$], 1.45 [m, 1H, PhCH(CH_2)C*H*CH], 1.12 [m, 1H, PhCH(CH_AH_B)CHCH], 0.90 [m, 1H, PhCH(CH_AH_B)CHCH]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.7–128.1 (Ph), 111.6 [$C(CH_3)_2$], 104.7 (C-1), 96.7 [PhCH(CH_2)CHCH major], 96.4 [PhCH(CH_2)CHCH minor], 84.0 (C-2), 77.8 (C-3 major), 77.7 (C-3 minor), 73.5 (C-4), 73.4 (PhCH_2O), 72.3 (C-5), 71.3 (C-6), 26.6, 26.0 [$C(CH_3)_2$], 25.5 [PhCH(CH_2)CHCH major], 25.4 [PhCH(CH_2)CHCH minor], 19.3 [PhCH(CH_2)CHCH major], 19.1 [PhCH(CH_2)CHCH minor], 11.8 [PhCH(CH_2)CHCH major], 11.7 [PhCH(CH_2)CHCH minor]. HRMS (CI): $[M+H]^+$, found 439.213282. $C_{26}H_{31}O_6$ requires 439.212064.

4.4.5. 3-*O*-Benzyl-1,2-*O*-isopropylidene-5,6-*O*-[(1*S*,2*R*,3*S*)-(1-methyl-2-phenylcyclopropyl)methylidene]-α-D-glucofuranose 30

Two stereoisomers were obtained in a 1:1 ratio. The pure diastereomeric mixture was obtained as a syrup by column chromatography, using hexane–ethyl acetate (12.5:1) as eluent. Yield 0.27 g (60%); $[\alpha]_D$ = +16.6 (*c* 2.7, CH_2Cl_2); MS (CI): *m*/*z* 453 (5%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.1 (m, 10H, Ph), 6.00, 5.99 (2d, 1H, $J_{1,2}$ 4.0 Hz, H-1), 4.74 [s, 0.5H, PhCH(CH_2)C(CH_3)C*H*], 4.67 [s, 0.5H, PhCH(CH_2)CHC*H*], 4.62, 4.60 (2d, 1H, $J_{1,2}$ 4.1 Hz, H-2), 4.57 (s, 2H, PhCH_2O), 4.36 (d, 1H, $J_{3,4}$ 2.1 Hz, H-3), 4.30 (m, 1H, H-5), 4.09 (m, 1H, H-4), 3.82 (m, 1H, H-6_A), 3.73 (m, 1H, H-6_B), 2.19 [m, 1H, PhC*H*(CH_2)C(CH_3)CH], 1.53, 1.35 [2s, 6H, $C(CH_3)_2$], 1.11 [dd, 0.5H, J_{gem} 5.0 Hz, *J* 8.9 Hz, PhCH(CH_AH_B)-C(CH_3)CH], 1.06 [dd, 0.5H, J_{gem} 5.0 Hz, *J* 8.9 Hz, PhCH(CH_AH_B)-C(CH_3)CH], 0.80 [m, 4H, PhCH(CH_AH_B)C(CH_3)CH]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.6–125.8 (Ph), 111.7, 11.6 [$C(CH_3)_2$], 104.8 (C-1), 99.2, 98.7 [PhCH(CH_2)C(CH_3)CH], 84.1 (C-2), 77.8, 77.7 (C-3), 73.5 (PhCH_2O), 73.44, 73.39 (C-4), 72.3, 72.2 (C-5), 71.2, 71.1 (C-6), 26.7, 26.1 [$C(CH_3)_2$], 25.3, 25.2 [PhCH(CH_2)C(CH_3)CH], 24.9, 24.6 [PhCH(CH_2)C(CH_3)CH], 13.7, 13.3 [PhCH(CH_2)C(CH_3)CH], 13.6 [PhCH(CH_2)C(CH_3)CH]. HRMS (CI): $[M+H]^+$, found 453.227332. $C_{27}H_{33}O_6$ requires 453.227714.

4.4.6. Methyl 4,6-*O*-[(1*R*,2*R*,3*R*)-(2-phenylcyclopropyl)-methylidene]-α-D-glucopyranoside 31

Two stereoisomers were obtained in a 15:10 ratio (20% de). Column chromatography, using dichloromethane–methanol (30:1) as eluent, gave the major diastereoisomer separated as a syrup. Yield 0.21 g (65%); $[\alpha]_D$ = +82.8 (*c* 1.0, CH_2Cl_2); MS (CI): *m*/*z* 323 (65%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.5–7.1 (m, 5H, Ph), 4.79 (d, 1H, $J_{1,2}$ 3.9 Hz, H-1), 4.59 [d, 1H, *J* 3.9 Hz, PhCH(CH_2)CHC*H*], 4.17 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.2 Hz, H-6_e), 3.90 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.3 Hz, H-3), 3.7–3.5 (m, 3H, H-2, H-5, H-6_a), 3.46 (s, 3H, OCH_3), 3.31 (t, 1H, $J_{3,4}$ = $J_{4,5}$ 9.4 Hz, H-4), 2.10 [m, 1H, PhC*H*(CH_2)CHCH], 1.55, 1.20, 0.90 [3m, 3H, PhCH(CH_2)C*H*CH]. ^{13}C NMR (500 MHz, $CDCl_3$): δ 128.3–125.7 (Ph), 102.2 [PhCH(CH_2)CHCH], 99.7 (C-1), 80.4 (C-4), 72.8 (C-2), 71.8 (C-3), 68.4 (C-6), 62.3 (C-5), 55.5 (OCH_3), 24.8 [PhCH(CH_2)CHCH], 19.4 [PhCH(CH_2)CHCH], 11.8 [PhCH(CH_2)CHCH]. HRMS (EI): $[M]^{+\cdot}$, found 322.142677. $C_{17}H_{22}O_6$ requires 322.141639.

4.4.7. Methyl 4,6-*O*-[(1*R*,2*R*,3*S*)-(1-methyl-2-phenylcyclopropyl)methylidene]-α-D-glucopyranoside 32

Two stereoisomers were obtained in an 11:10 ratio (4.8% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography, using hexane–ethyl acetate (6:1) as eluent. Yield 0.21 g (62%); $[\alpha]_D$ = +94.0 (*c* 1.0, CH_2Cl_2); MS (CI): *m*/*z* 337 (50%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.1 (m, 5H, Ph), 4.8 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.36 [s, 0.60H, PhCH(CH_2)C(CH_3)C*H* major], 4.26 [s, 0.40H, PhCH(CH_2)C(CH_3)C*H* minor], 4.20 (m, 1H, H-6_e), 3.93 (m, 1H, H-3), 3.7–3.6 (m, 2H, H-2, H-5), 3.56 (m, 1H, H-6_a), 3.46 (1s, 3H, OCH_3), 3.31 (m, 1H, H-4), 2.33 [dd, 0.60H, *J* 8.8 Hz, *J* 6.7 Hz, PhC*H*(CH_2)C(CH_3)CH major], 2.31 [dd, 0.40H, *J* 8.8 Hz, *J* 6.5 Hz, PhC*H*(CH_2)C(CH_3)CH minor], 1.30 [m, 1H, PhCH(CH_AH_B)C(CH_3)CH], 0.90 [m, 1H, PhCH(CH_AH_B)C(CH_3)CH], 0.87 [s, 1.80H, PhCH(CH_2)C(CH_3)CH major], 0.86 [s, 1.20H, PhCH(CH_2)C(CH_3)CH minor]. ^{13}C NMR (500 MHz, $CDCl_3$): δ 136.7–128.1 (Ph), 105.9 [PhCH(CH_2)C(CH_3)*C*H minor], 105.0 [PhCH-(CH_2)C(CH_3)*C*H major], 99.1 (C-1), 81.9 (C-4 minor), 81.7 (C-4 major), 78.9 (C-2), 78.4 (C-3 major), 78.3 (C-3 minor), 75.1, 73.3 (2 PhCH_2O), 68.7 (C-6 major), 68.6 (C-6 minor), 62.4 (C-5 major), 62.3 (C-5 minor), 55.3 (OCH_3), 25.1 [PhCH(CH_2)C(CH_3)CH minor], 24.9 [PhCH(CH_2)C(CH_3)CH major], 24.8 [PhCH(CH_2)C(CH_3)CH], 14.5 [PhCH(CH_2)C(CH_3)CH major], 14.0 [PhCH(CH_2)C(CH_3)CH minor], 13.8 [PhCH(CH_2)C(CH_3)CH minor], 13.6 [PhCH(CH_2)C(CH_3)CH major]. HRMS (EI): $[M]^{+\cdot}$, found 337.165533. $C_{18}H_{24}O_6$ requires 337.165114.

4.4.8. Methyl 2,3-di-*O*-benzyl-4,6-*O*-[(1*R*,2*R*,3*R*)-(2-phenylcyclopropyl)methylidene]-α-D-glucopyranoside 33

Two stereoisomers were obtained in a 2:1 ratio (33% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography, using hexane–ethyl acetate (8:1) as eluent. Yield 0.33 g (66%); $[\alpha]_D$ = +79.9 (*c* 0.8, CH_2Cl_2); MS (EI): *m*/*z* 502 (50%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.1 (m, 15H, Ph), 5.0–4.7 (m, 4H, 2PhCH_2O), 4.63 [d, 0.67H, *J* 4.2 Hz, PhCH(CH_2)CHC*H* major], 4.61 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.51 [d, 0.33H, *J* 4.7 Hz, PhCH(CH_2)CHC*H* minor], 4,16 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.2 Hz, H-6_e), 4.00 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.3 Hz, H-3), 3.72 (dt, 1H, $J_{5,6e}$ 4.8 Hz, $J_{4,5}$ = $J_{5,6a}$ 9.7 Hz, H-5), 3.6–3.5 (m, 2H, H-2, H-6_a), 3.43 (s, 3H, OCH_3), 3.40 (t, 1H, $J_{3,4}$ 9.4 Hz, H-4), 2.21 [m, 0.33H, PhC*H*(CH_2)CHCH minor], 2.12 [m, 0.67H, PhC*H*(CH_2)CHCH major], 1.51 [m, 1H, PhCH(CH_2)C*H*CH], 1.25 [m, 0.67H, PhCH(CH_AH_B)CHCH major], 1,03 [m, 0.33H, PhCH(CH_AH_B)CHCH minor], 0.97 [m, 1H, PhCH(CH_AH_B)CHCH]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.7–128.1 (Ph), 102.8 [PhCH(CH_2)CHCH minor], 101.9 [PhCH(CH_2)CHCH major], 99.2 (C-1), 81.9 (C-4 minor), 81.7 (C-4 major), 79.2 (C-2), 78.5 (C-3 major), 78.4 (C-3 minor), 75.2, 73.7 (2 PhCH_2O), 68.7 (C-6), 62.3 (C-5), 55.3 (OCH_3), 25.1 [PhCH(CH_2)CHCH minor], 25.0 [PhCH(CH_2)CHCH major], 19.5 [PhCH(CH_2)CHCH major], 19.3 [PhCH(CH_2)CHCH minor], 11.7 [PhCH(CH_2)CHCH minor], 11.4 [PhCH(CH_2)CHCH major]. HRMS (EI): $[M]^{+\cdot}$, found 502.234491. $C_{31}H_{34}O_6$ requires 502.235539.

4.4.9. Methyl 2,3-di-*O*-benzyl-4,6-*O*-[(1*R*,2*R*,3*S*)-(1-methyl-2-phenylcyclopropyl)methylidene]-α-D-glucopyranoside 34

Two stereoisomers were obtained in an 11:10 ratio (4.8% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography, using dichloromethene–methanol (60:1) as eluent. Yield 0.38 g (74%); $[\alpha]_D$ = +31.4 (*c* 0.9, CH_2Cl_2); MS (EI): *m*/*z* 516 (5%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.1 (m, 15H, Ph), 5.0–4.7 (m, 4H, 2CH_2Ph), 4.62 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.45 [s, 0.52H, PhCH(CH_2)C(CH_3)C*H* major], 4.32 [s, 0.42H,

PhCH(CH_2)C(CH_3)C*H* minor], 4.18 (m, 1H, H-6_e), 4.02 (m, 1H, H-3), 3.70 (m, 1H, H-5), 3.52 (m, 1H, H-2), 3.45 (m, 2H, H-4, H-6_a), 3.43 (2s, 6H, OCH_3 major, OCH_3 minor), 2.37 [dd, 0.52H, J_{cis} 8.8 Hz, J_{trans} 6.5 Hz, PhC*H*(CH_2)C(CH_3)CH major], 2.31 [dd, 0.42H, J_{cis} 8.8 Hz, J_{trans} 6.5 Hz, PhC*H*(CH_2)C(CH_3)CH minor], 1.23 [dd, 0.52H, J_{gem} 5.0 Hz, J_{cis} 8.9 Hz, PhCH(CH_{cis}H$_{trans}$)C(CH_3)CH major], 1.19 [dd, 0.42 H, J_{gem} 5.0 Hz, J 9.0 Hz, PhCH(CH_{cis}H$_{trans}$)C(CH_3)CH minor], 0.90 [m, 4H, PhCH(CH_AH_B)C(CH_3)CH]. ^{13}C NMR (500 MHz, $CDCl_3$): δ 136.7–128.1 (Ph), 105.9 [PhCH(CH_2)C(CH_3)*C*H minor], 105.0 [PhCH(CH_2)C(CH_3)*C*H major], 99.1 (C-1), 81.9 (C-4 minor), 81.7 (C-4 major), 78.9 (C-2), 78.4 (C-3 major), 78.3 (C-3 minor), 75.1, 73.3 (2 PhCH_2O), 68.6 (C-6 minor), 68.7 (C-6 major), 62.4 (C-5 major), 62.3 (C-5 minor), 55.3 (OCH_3 minor), 55.2 (OCH_3 major), 25.1 [Ph*C*H(CH_2)C(CH_3)CH minor], 24.9 [Ph*C*H(CH_2)C(CH_3)CH major], 24.8 [PhCH(CH_2)*C*(CH_3)CH], 14.5 [PhCH(CH_2)C(*C*H_3)CH major], 14.0 [PhCH(*C*H_2)C(CH_3)CH minor], 13.8 [PhCH(CH_2)C(*C*H_3)CH minor], 13.6 [PhCH(*C*H_2)C(CH_3)CH major]. HRMS (EI): $[M]^{+\cdot}$, found 516.248457. $C_{32}H_{36}O_6$ requires 516.251189.

4.4.10. 1-Dodecyl 2-acetamido-3-*O*-benzyl-2-deoxy-4,6-*O*-[(1*R*,2*R*,3*R*)-(2-phenylcyclopropyl)methylidene]-β-D-glucopyranoside 35

Two stereoisomers were obtained in a 27:10 ratio (46% de). The pure diastereomeric mixture was obtained as a syrup by column chromatography, using dichloromethane–methanol (80:1) as eluent. Yield 0.46 g (76%); $[\alpha]_D$ = +4.0 (*c* 4.6, CH_2Cl_2); MS (CI): *m*/*z* 608 (45%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6–7.1 (m, 10H, Ph), 5.55 (d, 1H, $J_{2,NH}$ 7.2 Hz, NH), 4.90 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.8–4.5 [m, 3H, PhCH(CH_2)CHC*H*, Ph*C*H_2O], 2.10 [m, 1H, PhC*H*(CH_2)CHCH], 1.90 (s, 2.19H, CH_3CON major), 1.83 (s, 0.81H, CH_3CON minor), 1.48 [m, 1H, PhCH(CH_2)CHCH], 1.4–1.2 [m, 20H, $(CH_2)_{10}$], 1.17 [m, 1H, PhCH(CH_AH_B)CHCH], 0.98 [m, 1H, PhCH(CH_AH_B)CHCH], 0.90 (t, 3H, J 6.8 Hz, CH_3). HRMS (CI): $[M+H]^+$, found 607.38806. $C_{37}H_{54}NO_6$ requires 607.38729.

4.4.11. 1,2-*O*-Isopropylidene-3,5-*O*-[(1*S*,2*R*,3*R*)-(2-phenylcyclopropyl)methylidene]-α-D-xylofuranose 36

Two stereoisomers were obtained in a 9:1 ratio (80% de). Column chromatography, using hexane–ethyl acetate (8:1) as eluent, gave the major diastereoisomer separated as a solid. Yield 0.27 g (85%); mp 108–110 °C; $[\alpha]_D$ = −60.4 (*c* 1.0, CH_2Cl_2); MS (CI): *m*/*z* 319 (40%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.1 (m, 5H, Ph), 6.03 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.42 [d, 1H, J 4.7 Hz, PhCH(CH_2)CHC*H*], 4.58 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.32 (d, 1H, $J_{5e,5a}$ 13.3 Hz, H-5_e), 4.22 (d, 1H, $J_{3,4}$ 1.9 Hz, H-3), 4.04 (m, 1H, H-4), 4.32 (d, 1H, $J_{5e,5a}$ 13.3 Hz, H-5_a), 2.07 [m, 1H, PhC*H*(CH_2)CHCH], 1.50, 1.32 [2s, 6H, C(CH_3)$_2$], 1.45 [m, 1H, PhCH(CH_2)C*H*CH], 1.14 [m, 1H, PhCH(CH_AH_B)CHCH], 0.92 [m, 1H, PhCH(CH_AH_B)CHCH]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.8–125.7 (Ph), 111.7 [*C*(CH_3)$_2$], 105.6 (C-1), 100.3 [PhCH(CH_2)CH*C*H], 83.8 (C-2), 78.5 (C-3), 72.2 (C-4), 66.4 (C-5), 26.7, 26.1 [C(*C*H_3)$_2$], 25.1 [PhCH(CH_2)CHCH], 19.1 [PhCH(CH_2)CHCH], 11.6 [PhCH(*C*H_2)CHCH]. HRMS (CI): $[M+H]^+$, found 319.155503. $C_{18}H_{23}O_5$ requires 319.15459. Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.09; H, 6.62. Found: C, 66.80; H, 6.30.

4.4.12. 1,2-*O*-Isopropylidene-3,5-*O*-[(1S,2R,3S)-(1-methyl-2-phenylcyclopropyl)methylidene]-α-D-xylofuranose 37

Two stereoisomers were obtained in a 3:1 ratio (50% de). Column chromatography, using hexane–ethyl acetate (11:1) as eluent, gave the major diastereoisomer separated as a solid. Yield 0.29 g (87%); mp 112–114 °C; $[\alpha]_D$ = −12.9 (*c* 0.9, CH_2Cl_2); MS (CI): *m*/*z* 333 (40%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4–7.1 (m, 5H, Ph), 6.03 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.59 (d, 1H, $J_{1,2}$ 3.8 Hz, H-2), 4.34 (d, 1H, $J_{5e,5a}$ 13.2 Hz, H-5_e), 4.26 [s, 0.75H, PhCH(CH_2)C(CH_3)C*H* major], 4.24 (d, 1H, $J_{3,4}$ 2.1 Hz, H-3), 4.21 [s, 0.25H, PhCH(CH_2)C(CH_3)C*H* minor], 4.05 (m, 1H, H-4), 3.95 (dd, 1H, $J_{4,5a}$ 2.2 Hz, $J_{5e,5a}$ 13.2 Hz, H-5_a), 2.26 [dd, 0.75H, J_{cis} 8.9 Hz, J_{trans} 6.4 Hz, PhC*H*(CH_2)C(CH_3)CH major], 2.23 [dd, 0.25H, J_{cis} 8.9 Hz, J_{trans} 6.4 Hz, PhC*H*(CH_2)C(CH_3)CH minor], 1.51, 1.34 [2s, 6H, C(CH_3)$_2$], 1.14 [dd, 1H, J_{gem} 5.1 Hz, J_{cis} 8.9 Hz, PhCH(CH_{cis}H$_{trans}$)C(CH_3)CH], 0.81 [s, 3H, PhCH(CH_2)C(CH_3)CH], 0.79 [m, 1H, PhCH(CH_{cis}-H_{trans})C(CH_3)CH]. ^{13}C NMR (500 MHz, $CDCl_3$): δ 138.5–125.9 (Ph), 111.8 [*C*(CH_3)$_2$], 105.7 (C-1), 103.4 [PhCH(CH_2)C(CH_3)*C*H minor], 103.1 [PhCH(CH_2)C(CH_3)*C*H major], 84.0 (C-2), 78.7 (C-3 minor), 78.6 (C-3 major), 72.4 (C-4), 66.5 (C-5), 26.8, 26.2 [C(*C*H_3)$_2$], 25.2 [PhCH(CH_2)*C*(CH_3)CH], 24.8 [Ph*C*H(CH_2)C(CH_3)CH minor], 24.7 [Ph*C*H(CH_2)C(CH_3)CH major], 14.0 [PhCH(CH_2)C(*C*H_3)CH], 13.7 [PhCH(*C*H_2)C(CH_3)CH]. HRMS (CI): $[M+H]^+$, found 333.169907. $C_{19}H_{25}O_5$ requires 333.170199. Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.66; H, 7.28. Found: C, 68.48; H, 7.21.

4.5. Separation of chiral auxiliary

A solution of the cyclopropylmethylidene acetal **23**, **24**, **32**, **36** or **37** (0.4 mmol) in 80% acetic acid in water (20 mL) was heated at 60 °C, and the reaction was monitored until TLC showed that all the starting material had reacted (0.5 h). Then, the reaction mixture was cooled to room temperature. The pH of the solution was adjusted to 7.5 with saturated aqueous sodium bicarbonate solution, and the aqueous solution was extracted with ethyl acetate. The organic layer was washed with water and saturated aqueous sodium chloride solution, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel, using hexane–ethyl acetate (7:1) as eluent. The sugar was recovered in good yield (70–85%) by elution with dichloromethane–methanol mixture.

The aldehyde obtained was dissolved in ethanol (5 mL), and sodium borohydride (22 mg, 0.58 mmol) was added at room temperature. The reaction mixture was stirred for 1.5 h at room temperature, and the reaction was quenched with saturated aqueous ammonium chloride solution. After evaporation of the solvent, the solution was diluted with water and *tert*-butyl methyl ether. The organic layer was washed with water and saturated aqueous sodium chloride solution, dried ($MgSO_4$) and concentrated under reduced pressure. The compound obtained was purified by flash chromatography on silica gel, using hexane–ethyl acetate (4:1) as eluent.

4.5.1. (1*R*,2*R*)-trans-1-Hydroxymethyl-2-phenylcyclopropane[29,43] (−)-38

^{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, PhCH(CH_2)CHC*H*$_2$OH], 1.84 [m, 1H, PhC*H*(CH_2)CHCH_2OH], 1.47 [m, 1H, PhCH(CH_2)C*H*CH_2OH], 0.98 [m, 2H, PhCH(CH_2)CHCH_2OH]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.7–128.1 (Ph), 66.5 [PhCH(CH_2)CHCH_2OH], 25.2 [PhCH-(CH_2)CHCH_2OH], 21.3 [PhCH(CH_2)CHCH_2OH], 13.7 [PhCH(CH_2)-CHCH_2OH].

4.5.1.1. From 23. Yield 46 mg (77%); $[\alpha]_D$ = −22.1 (c 1.0, CH_2Cl_2). {lit.[43] $[\alpha]_D$ = −92 (*c* 1.23, EtOH)}.

4.5.1.2. From 36. Yield 50 mg (84%); $[\alpha]_D$ = −75.6 (*c* 1.0, CH_2Cl_2).

4.5.2. (1*S*,2*S*)-*trans*-1-Hydroxymethyl-2-phenylcyclopropane[25,44] (+)-38

4.5.2.1. From 24. Yield 45 mg (75%); $[\alpha]_D$ = +46.0 (*c* 1.0, CH_2Cl_2). {lit.[44] $[\alpha]_D$ = +18.0 (*c* 0.84, $CHCl_3$ as 39% ee)}.

4.5.3. (1*R*,2*S*)-*E*-1-Methyl-2-phenylcyclopropanecarboxaldehyde[16] 39

Yield 40 mg (63%) from **37**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 [s, 1H, PhCH(CH_2)C(CH_3)C*H*O], 7.6–7.1 (m, 5H, Ph), 2.73 [dd, 1H, J_{cis} 9.2 Hz, J_{trans} 7.2 Hz, PhC*H*(CH_2)C(CH_3)CHO], 1.68 [dd, 1H,

J_{gem} 5.3 Hz, J_{cis} 9.3 Hz, PhCH($CH_{cis}H_{trans}$)C(CH_3)CHO], 1.43 [dd, 1H, J_{gem} 5.4 Hz, J_{trans} 7.2 Hz, PhCH($CH_{cis}H_{trans}$)C(CH_3)CHO], 0.98 [s, 3H, PhCH(CH_2)C(CH_3)CHO]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.7 [PhCH(CH_2)C(CH_3)*C*HO], 136.7–128.1 (Ph), 34.3 [PhCH(CH_2)-*C*(CH_3)CHO], 29.9 [PhCH(CH_2)C(CH_3)CHO], 17.7 [PhCH(*C*H_2)C-(CH_3)CHO], 11.5 [PhCH(CH_2)C(*C*H_3)CHO].

4.5.4. (1*R*,2*S*)-*E*-1-Hydroxymethyl-1-methyl-2-phenyl-cyclopropane[45,46](−)-40

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3–7.1 (m, 5H, Ph), 3.56 [d, 2H, J_{gem} 11.0 Hz, PhCH(CH_2)C(CH_3)C*H*$_2$OH], 2.05 [dd, 1H, J_{cis} 8.7 Hz, J_{trans} 6.0 Hz, PhC*H*(CH_2)C(CH_3)CH_2OH], 1.52 (s, 1H, OH), 0.94 [dd, 1H, J_{gem} 5.0 Hz, J_{cis} 8.8 Hz, PhCH(*CH*$_{cis}$H$_{trans}$)C(CH_3)CH_2OH], 0.89 [s, 3H, PhCH(CH_2)C(*CH*$_3$)CH_2OH], 0.86 [m, 1H, PhCH($CH_{cis}H_{trans}$)C(CH_3)-CH_2OH]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.7–128.1 (Ph), 71.7 [PhCH(CH_2)C(CH_3)CH_2OH], 29.7 [PhCH(CH_2)C(CH_3)CH_2OH], 26.8 [PhC*H*(CH_2)C(CH_3)CH_2OH], 15.7 [PhCH(*C*H_2)C(CH_3)CH_2OH], 15.1 [PhCH(CH_2)C(*C*H_3)CH_2OH].

4.5.4.1. From 32. Yield 35 mg (89%); $[\alpha]_D = -6.1$ (*c* 1.1, CH_2Cl_2). {lit.[45] $[\alpha]_D = -1.4$ (*c* 5.00, $CHCl_3$ as 5% ee)}.

4.5.4.2. From 37. Yield 32 mg (80%); $[\alpha]_D = -16.6$ (*c* 1.0, CH_2Cl_2). {lit.[46] $[\alpha]_D = -15.1$ (*c* 0.12, $CHCl_3$)}.

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