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The use of 1,2-*O*-isopropylidene-α-D-xylofuranose as a chiral auxiliary in asymmetric cyclopropanation reactions

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ABSTRACT

The stereoselective synthesis of cyclopropylmethylidene acetals derived from 1,2-*O*-isopropylidene-D-xylofuranose, as a chiral auxiliary, is described. The Simmons–Smith cyclopropanation reaction of the corresponding alkenylidene derivatives with $CH_2I_2/ZnEt_2$, in different reaction conditions, took place with high stereoselectivity. The diastereomeric excess in each case depended on the solvent and the temperature used in the reaction. The absolute configuration of the new stereogenic centres formed was determined by acid hydrolysis of the cyclopropane moiety of the chiral auxiliary, which was also recovered.

1. Introduction

The importance of chirality is well recognised, mainly in connection with the fact that nearly all natural products are chiral and their physiological or pharmacological properties depend upon their recognition by chiral receptors, which will interact only with molecules of the proper absolute configuration. At the same time, the chiral cyclopropane moiety is present in a number of natural and synthetic compounds, as well as in molecules used to probe biological and pharmacological processes;[1–6] thus, optically active 2-substituted 1-cyclopropanecarboxylates, especially 2-phenyl-1-cyclopropanecarboxylates, are very useful intermediates in the synthesis of chiral compounds, and are present in many biologically important substances.[7,8] Compounds containing cyclopropanes have been used extensively as a probe to solve mechanistic problems.[9,10] In the last few years, efforts have been made to develop new and more efficient methods for the preparation of these entities in enantiomerically pure form. General methods for the stereoselective synthesis of the cyclopropane ring have been reviewed recently.[2,11–13] Enantioselective methylenation cyclopropanation methods for prochiral alkenes have been carried out using chiral auxiliaries[9,14–16] or chiral catalysts.[17–20] Cyclopropanes have also been used as versatile synthetic intermediate in the synthesis of more functionalised cycloalkanes and acyclic compounds.[13,21,22]

Carbohydrates contain several functional groups and stereogenic centres in one molecular unit, which allows the use of carbohydrates as tools in stereochemical differentiations, as the starting materials in syntheses of interesting enantiopure compounds,[23–26] as chiral templates in asymmetric transformations[27] and as chiral auxiliaries in stereoselective syntheses.[28–37] However, there are few precedents for the use of carbohydrates as chiral auxiliaries in the asymmetric cyclopropanation reaction of olefins,[38–42] 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 a previous paper[43] we used sugar derivatives as chiral auxiliaries in the Simmons–Smith cyclopropanation reaction. We studied the cyclopropanation reaction, using 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 diversified the chiral substrate, varyied the carbohydrate configuration, protected the hydroxyl groups and the size of the sugar and acetal rings. We found that the best diastereomeric excesses were obtained when 1,2-*O*-isopropylidene-D-xylofuranose was used as a chiral auxiliary.

For this reason, we have chosen 1,2-*O*-isopropylidene-D-xylofuranose as a chiral auxiliary for the optimisation of the Simmons–Smith cyclopropanation with a wide range of alkenes, under different experimental conditions of solvents and temperatures. The results obtained are reported in this paper. It is important to point out that the union of the olefin to the carbohydrate across an acetal function allowed easy separation of the new chiral cyclopropane fragment and the chiral auxiliary by acid hydrolysis, obtaining functionalised chiral cyclopropanes which can be used as building blocks in different synthetic routes.

2. Results and discussion

The synthesis of the new alkenylidene acetals **13–24**, substrates for the cyclopropanation reaction, has been carried out by reaction

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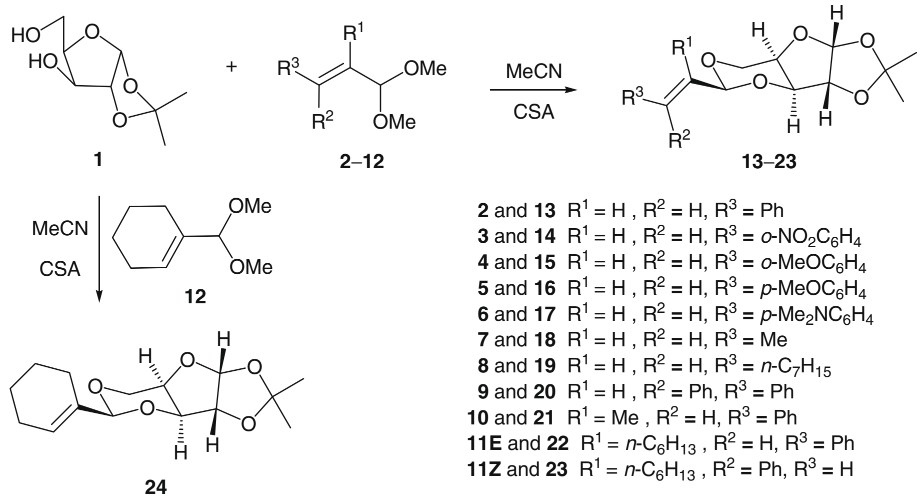
of 1,2-*O*-isopropylidene-D-xylofuranose **1** and the corresponding unsaturated aldehyde dimethyl acetals **2**–**12** in good yields, employing the procedure described by Murphy et al.[44] for the formation of acetals using the aldehyde dimethyl acetal as a reagent (Scheme 1). Compounds **13**–**24** were obtained as only one stereoisomer, in all cases with an (*S*)-configuration at the acetal carbon, established by 2D-NOESY experiments in each case. The reaction of **1** with α-hexylcinnamaldehyde dimethyl acetal (**11E** + **11Z**) gave two compounds **22** and **23** as a stereoisomeric mixture. Column chromatography was used to separate compounds **22** and **23**, whose configurations *E* and *Z*, respectively, were determined by 2D-NOESY experiments.

The cyclopropanation reactions of compounds **13**–**16**, **18**–**22** and **24** were carried out using the $CH_2I_2/ZnEt_2$ system as a reagent and different solvents and reaction temperatures, giving compounds **25**–**34** (Scheme 2), which were isolated and purified by flash chromatography on silica gel. The compound obtained from **17** was not recovered, it is assumed that it partitioned into the aqueous layer on work-up when aqueous ammonium chloride was added. However, subsequent extraction after this layer had been made alkaline with sodium hydroxide did not provide any appreciable amount of material. When the starting compound was **23**, the reaction gave a complex mixture of cyclopropanes detected by ^1H NMR but not isolated. The diastereomeric excess (de) in each case was determined by ^1H NMR, and is shown in Table 1. The data shown in the table indicate that the diastereomeric excesses (des) obtained in the cyclopropanation of the compounds studied are different depending on the solvent and temperature used in the reaction. The des are higher when lower temperatures are used. At temperatures below −20 °C, the solubility of the starting material is low and the times of reaction are considerably longer. With regard to solvent, the experimental data show that the des obtained in 1,2-dichloroethane or toluene are higher than those from dichloromethane. The combined use of low temperature and 1,2-dichloroethane as a solvent gave the best result in des: compounds **30** and **31** were both obtained with 100% de using these temperature and solvent conditions. With regard to the degree of substitution of the double bond in the starting propylidene acetals, the experimental data show that (a) the de obtained from *trans*-cinnamaldehyde acetal (R^1 = H, entry 2) was higher than those obtained from α-alkyl-*trans*-cinnamaldehyde acetal ($R^1 \neq$ H, entries 18 and 19); thus, compound **25** was obtained with 82% de, while compounds **32** and **33** were obtained with des of 76% and 66%, respectively; (b) in this same aspect, compound **30** (R^1 = H, entry 12) was obtained with 100% de, while **34** ($R^1 \neq$ H, entry 20) was obtained with 67% de; (c) the des obtained from propylidene acetals with hindered substituents on carbon three were higher than those obtained from acetals with smaller substituents on carbon three; thus, compounds **27** (R^3 = *o*-$MeOC_6H_4$) and **30** (R^3 = *n*-C_7H_{15}) were obtained with des of 77% (entry 7) and 100% (entry 12), while compounds **28** (R^3 = *p*-$MeOC_6H_4$) and **29** (R^3 = CH_3) were obtained with des of 46% (entry 8) and 60% (entry 10); (d) the des obtained from propylidene acetals with two substituents on carbon three were higher than those obtained from acetals with one substituent on carbon three; thus, compound **31** (R^2 = R^3 = Ph) gave 100% de (entry 15) while compound **25** (R^2 = H, R^3 = Ph) gave 82% de (entry 2).

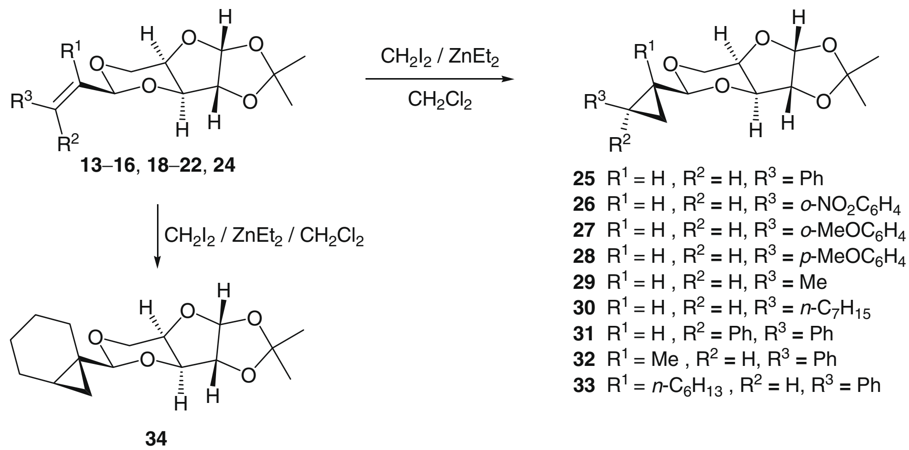
In order to assign the configuration of the stereogenic centres in the cyclopropane ring formed during the cyclopropanation reaction, we proceeded to separate the chiral auxiliary by hydrolysis with 80% acetic acid and subsequent reduction with sodium borohydride to give the corresponding hydroxymethylcyclopropane, with recovery of the carbohydrate derivative (Scheme 3). The absolute stereochemistry of the cyclopropane ring, (2*R*,3*R*) for **25**, **26** and **30**, (2*R*) for **31**, and (2*R*,3*S*) for **32**, was deduced by correlation with (1*R*,2*R*)-*trans*-1-hydroxymethyl-2-phenylcyclopropane[45] (−)-**35** obtained from **25**, by correlation with (1*R*,2*R*)-*trans*-1-hydroxymethyl-2-(*o*-nitrophenyl)cyclopropane[46] (+)-**36** obtained from **26**, by correlation with (1*R*)-1-hydroxymethyl-2,2-diphenycloproprane[46,47] (+)-**38** obtained from **31**, and by correlation with (1*R*,2*S*)-*E*-1-hydroxymethyl-1-methyl-2-phenylcyclopropane[48] (−)-**39** obtained from **32**. The configuration of the other cyclopropanes listed in Table 1 was established from the analysis of the chemical shifts of the protons and the carbons corresponding to the cyclopropane acetal system in the NMR spectra.

3. Conclusion

In conclusion, in the cyclopropanation reaction of propylidene acetals derived from 1,2-*O*-isopropylidene-D-xylofuranose presented here, (a) in all cases studied the more reactive face is always the same one; its notation being *Re*,*Re* in compounds with one aromatic substituent on carbon three, *Re* when the compound has two substituents on carbon three, and *Re,Si* in compounds with one alkyl substituent on carbon three; (b) the diastereomeric excesses (des) were found to depend on the solvent and the reaction temperature, the best des being obtained when 1,2-dichloroethane



Scheme 1.

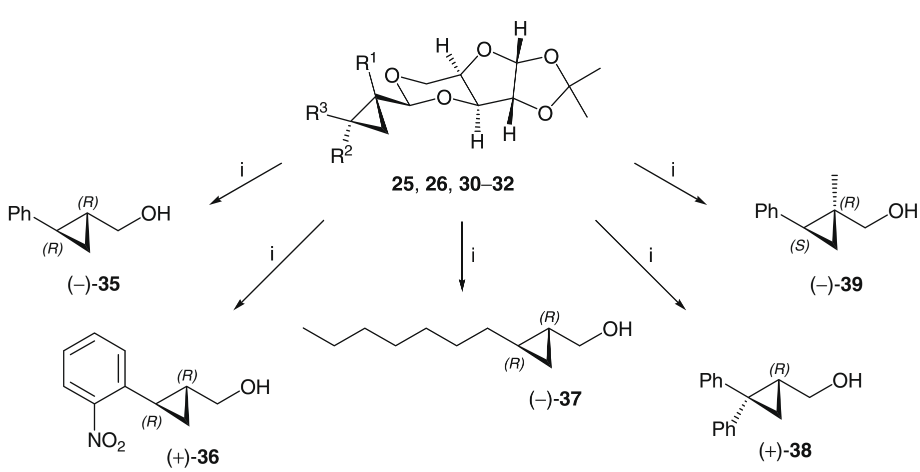


Scheme 2.

Table 1
Cyclopropanation of α,β-unsaturated acetal derivatives **13–24**

Entry	Starting compound	Reaction product	Solvent	Temp (°C)	Yield[a] (%)	De[b] (%)	Major cyclopropane configuration
1	**13**	**25**[c]	CH_2Cl_2	−15	85	80	(2*R*,3*R*)
2	**13**	**25**	$ClCH_2CH_2Cl$	−20 to 0	77	82	(2*R*,3*R*)
3	**14**	**26**	CH_2Cl_2	−20 to 0		75	(2*R*,3*R*)
4	**14**	**26**	PhMe	−20 to 0		75	(2*R*,3*R*)
5	**14**	**26**	$ClCH_2CH_2Cl$	−20 to 0	84	78	(2*R*,3*R*)
6	**15**	**27**	CH_2Cl_2	−20 to 0		33	(2*R*,3*R*)
7	**15**	**27**	$ClCH_2CH_2Cl$	−30	86	77	(2*R*,3*R*)
8	**16**	**28**	$ClCH_2CH_2Cl$	−30	77	46	(2*R*,3*R*)
9	**18**	**29**	CH_2Cl_2	−20 to 0		56	(2*R*,3*R*)
10	**18**	**29**	PhMe	−20 to 0	76	65	(2*R*,3*R*)
11	**18**	**29**	$ClCH_2CH_2Cl$	−20 to 0		60	(2*R*,3*R*)
12	**19**	**30**	$ClCH_2CH_2Cl$	−20 to 0	74	100	(2*R*,3*R*)
13	**20**	**31**	CH_2Cl_2	−20 to 0		82	(2*R*)
14	**20**	**31**	PhMe	−20 to 0		85	(2*R*)
15	**20**	**31**	$ClCH_2CH_2Cl$	−20 to 0	69	100	(2*R*)
16	**20**	**31**	$ClCH_2CH_2Cl$	20		20	(2*R*)
17	**21**	**32**[c]	CH_2Cl_2	−15	87	50	(2*R*,3*S*)
18	**21**	**32**	$ClCH_2CH_2Cl$	−20 to 0	75	76	(2*R*,3*S*)
19	**22**	**33**	$ClCH_2CH_2Cl$	−20 to 0	72	66	(2*R*,3*S*)
20	**24**	**34**	$ClCH_2CH_2Cl$	−20 to 0	79	67	(2*R*,3*R*)

[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.
[c] Ref. 43.



Scheme 3. Reagents: (i) 1. AcOH 80%; 2. $NaBH_4$.

and the lowest temperature are used; (c) 1,2-*O*-isopropylidene-D-xylofuranose is a good chiral auxiliary in the reaction of cyclopropanation of propylidene acetals.

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 ^1H and at 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 synthesis of α,β-unsaturated acetals

To a solution of 1,2-*O*-isopropylidene-α-D-xylofuranose **1** (0.95 g, 5.0 mmol) in acetonitrile (30 mL), the aldehyde dimethylacetals **2**–**12** (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 the product obtained was chromatographed, giving compounds **13**–**23** in good yields.

4.2.1. 1,2-*O*-Isopropylidene-3,5-*O*-[(*S*,*E*)-3-(2-nitrophenyl)-2-propenylidene]-α-D-xylofuranose 14

The solid was purified by column chromatography, using hexane–ethyl acetate (4:1) as eluent. Yield 1.57 g (90%); mp 70–71 °C, $[\alpha]_D = -12.5$ (*c* 0.6, CH_2Cl_2); MS (CI): *m/z* 350 (100%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.9–7.4 (m, 4H, Ar), 7.21 (d, 1H, J_{trans} 15.9 Hz, ArC*H*=CHCH), 6.07 (dd, 1H, J_{trans} 15.9 Hz, *J* 4.6 Hz, ArCH=C*H*CH), 6.00 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.12 (d, 1H, *J* 4.5 Hz, ArCH=CHC*H*), 4.56 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.34–4.31 (m, 2H, H-3, H-5e), 4.06–4.03 (m, 2H, H-4, H-5a), 1.45, 1.28 [2s, 6H, $C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.0–124.6 (Ar), 129.7 (ArCH=*C*HCH), 129.4 (Ar*C*H=CHCH), 111.9 [$C(CH_3)_2$], 105.6 (C-1), 98.1 (ArCH=CH*C*H), 83.7 (C-2), 78.6 (C-3), 72.1 (C-4), 66.4 (C-5), 26.7, 26.1 [$C(CH_3)_2$]. HRMS (CI): $[M+H]^+$, found 350.123545, $C_{17}H_{20}NO_7$ requires 350.123977. Anal. Calcd for $C_{17}H_{19}NO_7$: C, 58.45; H, 5.48; N, 4.01. Found: C, 58.48; H, 5.46; N, 4.25.

4.2.2. 1,2-*O*-Isopropylidene-3,5-*O*-[(*S*,*E*)-3-(2-methoxyphenyl)-2-propenylidene]-α-D-xylofuranose 15

The solid was purified by column chromatography, using hexane–ethyl acetate (3.5:1) as eluent. Yield 1.34 g (80%); mp 168–169 °C, $[\alpha]_D = +5.4$ (*c* 1.0, CH_2Cl_2); MS (CI): *m/z* 335 (100%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.4–6.8 (m, 4H, Ar), 7.08 [d, 1H, J_{trans} 16.2 Hz, ArCH=CHCH], 6.22 [dd, 1H, J_{trans} 16.2 Hz, *J* 5.1 Hz, ArCH=CHCH], 6.07 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.10 [dd, 1H, *J* 5.0 Hz, ^4J 1.0 Hz, ArCH=CHCH], 4.62 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.39 (d, 1H, $J_{5e,5a}$ 13.1 Hz, H-5e), 4.33 (d, 1H, $J_{3,4}$ 1.9 Hz, H-3), 4.09 (m, 1H, H-4), 4.06 (dd, 1H, $J_{4,5a}$ 2.0 Hz, $J_{5e,5a}$ 13.1 Hz, H-5a), 3.84 (s, 3H, OCH_3), 1.51, 1.34 [2s, 6H, $C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.2–110.8 (Ar), 129.4 [ArCH=CHCH], 124.8 [ArCH=CHCH], 111.8 [$C(CH_3)_2$], 105.7 (C-1), 99.6 [ArCH=CHCH], 83.9 (C-2), 78.7 (C-3), 72.2 (C-4), 66.4 (C-5), 55.4 (OCH_3), 26.7, 26.2 [$C(CH_3)_2$]. HRMS (CI): $[M+H]^+$, found 335.1492. $C_{18}H_{23}O_6$ requires 335.1495. Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.65; H, 6.77.

4.2.3. 1,2-*O*-Isopropylidene-3,5-*O*-[(*S*,*E*)-3-(4-methoxyphenyl)-2-propenylidene]-α-D-xylofuranose 16

The solid was purified by column chromatography, using hexane–ethyl acetate (4:1) as eluent. Yield 1.39 g (83%); mp 164–166 °C, $[\alpha]_D = +13.0$ (*c* 1.0, CH_2Cl_2); MS (EI): *m/z* 334 (85%) $[M]^{+\cdot}$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–6.8 (m, 4H, Ar), 6.72 [d, 1H, J_{trans} 16.1 Hz, ArCH=CHCH], 6.07 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 6.03 [dd, 1H, J_{trans} 16.1 Hz, *J* 5.0 Hz, ArCH=CHCH], 5.08 [d, 1H, *J* 5.0 Hz, ArCH=CHCH], 4.62 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.39 (d, 1H, $J_{5e,5a}$ 13.2 Hz, H-5e), 4.33 (d, 1H, $J_{3,4}$ 1.7 Hz, H-3), 4.09 (m, 1H, H-4), 4.06 (dd, 1H, $J_{4,5a}$ 1.8 Hz, $J_{5e,5a}$ 13.2 Hz, H-5a), 3.80 (s, 3H, OCH_3), 1.51, 1.34 [2s, 6H, $C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8–113.9 (Ar), 133.6 [ArCH=CHCH], 122.2 [ArCH=CHCH], 111.8 [$C(CH_3)_2$], 105.6 (C-1), 99.1 [ArCH=CHCH], 83.8 (C-2), 78.6 (C-3), 72.2 (C-4), 66.4 (C-5), 55.2 (OCH_3), 26.7, 26.1 [$C(CH_3)_2$]. HRMS (EI): $[M]^{+\cdot}$, found 334.1406. $C_{18}H_{22}O_6$ requires 334.1416. Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.37; H, 6.59.

4.2.4. 3,5-*O*-[(*S*,*E*)-3-(4-Dimethyaminophenyl)-2-propenylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose 17

The syrup was purified by column chromatography, using hexane–ethyl acetate (4.5:1) as eluent. Yield 1.53 g (88%); $[\alpha]_D = +19.3$ (*c* 1.0, CH_2Cl_2); MS (CI): *m/z* 348 (65%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–6.8 (m, 4H, Ar), 6.69 [d, 1H, J_{trans} 16.2 Hz, ArCH=CHCH], 6.07 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.97 [dd, 1H, J_{trans} 16.2 Hz, *J* 5.2 Hz, ArCH=CHCH], 5.07 [dd, 1H, *J* 5.2 Hz, ^4J 1.0 Hz, ArCH=CHCH], 4.61 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.38 (d, 1H, $J_{5e,5a}$ 13.2 Hz, H-5e), 4.32 (d, 1H, $J_{3,4}$ 1.9 Hz, H-3), 4.08 (m, 1H, H-4), 4.05 (dd, 1H, $J_{4,5a}$ 2.0 Hz, $J_{5e,5a}$ 13.1 Hz, H-5a), 2.96 [s, 6H, $N(CH_3)_2$], 1.51, 1.34 [2s, 6H, $C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.3 [ArCH=CHCH], 128.0–112.1 (Ar), 120.0 [ArCH=CHCH], 111.8 [$C(CH_3)_2$], 105.7 (C-1), 99.7 [ArCH=CHCH], 83.9 (C-2), 78.7 (C-3), 72.2 (C-4), 66.4 (C-5), 40.3 [$(NCH_3)_2$], 26.7, 26.2 [$C(CH_3)_2$]. HRMS (EI): $[M]^{+\cdot}$, found 347.1723. $C_{19}H_{25}NO_5$ requires 347.1733. Anal. Calcd for $C_{19}H_{25}NO_5$: C, 65.69; H, 7.25; N, 4.03. Found: C, 65.35; H, 7.17; N, 4.15.

4.2.5. 3,5-*O*-[(*S*,*E*)-2-Butenylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose 18

The compound was purified by column chromatography, using hexane–ethyl acetate (7:1) as eluent, obtaining a syrup. Yield 0.93 g (77%); $[\alpha]_D = -6.2$ (*c* 1.1, CH_2Cl_2); MS (CI): *m/z* 243 (100%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 6.01 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 5.91 (m, 1H, CH_3CH=CHCH), 5.48 (m, 1H, CH_3CH=CHCH), 4.85 (d, 1H, *J* 5.3 Hz, CH_3CH=CHC*H*), 4.54 (d, 1H, $J_{1,2}$ 3.6 Hz, H-2), 4.30 (d, 1H, $J_{5e,5a}$ 13.3 Hz, H-5e), 4.23 (d, 1H, $J_{3,4}$ 1.7 Hz, H-3), 4.01 (m, 1H, H-4), 3.97 (dd, 1H, $J_{4,5a}$ 1.9 Hz, $J_{5e,5a}$ 13.2 Hz, H-5a), 1.70 (dd, 3H, ^4J 1.1 Hz, *J* 6.6 Hz, CH_3CH=CHCH), 1.46, 1.29 [2s, 6H, $C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 131.4 (CH_3CH=CHCH), 127.2 (CH_3CH=CHCH), 111.6 [$C(CH_3)_2$], 105.5 (C-1), 99.2 (CH_3CH=CHCH), 83.7 (C-2), 78.4 (C-3), 72.0 (C-4), 66.2 (C-5), 26.6, 26.0 [$C(CH_3)_2$], 17.5 (CH_3CH=CHCH). HRMS (CI): $[M+H]^+$, found 243.123087. $C_{12}H_{19}O_5$ requires 243.123249.

4.2.6. 3,5-*O*-[(*S*,*E*)-2-Decenylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose 19

The compound was purified by column chromatography, using hexane–ethyl acetate (8:1) as eluent, obtaining a syrup. Yield 1.30 g (80%); $[\alpha]_D = -3.6$ (*c* 1.3, CH_2Cl_2); MS (EI): *m/z* 326 (20%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 6.04 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.93 (m, 1H, RCH_2CH=CHCH), 5.49 (m, 1H, RCH_2CH=CHCH), 4.88 (d, 1H, *J* 5.4 Hz, RCH_2CH=CHC*H*), 4.58 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.33 (d, 1H, $J_{5e,5a}$ 13.2 Hz, H-5e), 4.26 (d, 1H, $J_{3,4}$ 1.8 Hz, H-3), 4.04 (m, 1H, H-4), 3.99 (dd, 1H, $J_{4,5a}$ 1.9 Hz, $J_{5e,5a}$ 13.2 Hz, H-5a), 2.05 (m, 2H, $RCH_2CH{=}CHCH$), 1.49, 1.32 [2s, 6H, $C(CH_3)_2$], 1.4–1.2 [m, $(CH_2)_5$], 0.87 (t, 3H, *J* 6.9 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.8 ($RCH_2CH{=}CHCH$), 125.7 ($RCH_2CH{=}CHCH$), 111.8 [$C(CH_3)_2$], 105.6 (C-1), 99.3 ($RCH_2CH{=}CHCH$), 83.8 (C-2), 78.5 (C-3), 72.1 (C-4), 66.3 (C-5), 32.0, 31.8, 29.2, 29.1, 28.5, 22.6 [$(CH_2)_6$], 26.7, 26.1 [$C(CH_3)_2$], 14.1 (CH_3). HRMS (EI): $[M]^{+\cdot}$, found 326.2085. $C_{18}H_{30}O_5$ requires 326.2093.

4.2.7. 3,5-*O*-[(*S*)-3,3-Diphenyl-2-propenylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose 20

The solid was purified by column chromatography, using hexane–ethyl acetate (8:1) as eluent. Yield 1.80 g (94%); mp 188–189 °C, $[\alpha]_D = -53.7$ (*c* 1.0, CH_2Cl_2); MS (EI): *m/z* 380 (100%) $[M]^{+\cdot}$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.4–7.2 (m, 10H, Ph), 6.08–6.07 (m, 2H, $Ph_2C{=}CHCH$, H-1), 4.84 (d, 1H, *J* 7.3 Hz, $Ph_2C{=}CHCH$), 4.61 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.31 (d, 1H, $J_{5e,5a}$ 13.3 Hz, H-5e), 4.17 (d, 1H, $J_{3,4}$ 2.0 Hz, H-3), 3.98 (m, 1H, H-4), 3.87 (dd, 1H, $J_{4,5a}$ 2.0 Hz, $J_{5e,5a}$ 13.3 Hz, H-5a), 1.48, 1.34 [2s, 6H, $C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.1 ($Ph_2C{=}CHCH$), 141.0–127.9 (2Ph), 123.8 ($Ph_2C{=}CHCH$), 111.8 [$C(CH_3)_2$], 105.6 (C-1), 97.5 ($Ph_2C{=}CHCH$], 83.9 (C-2), 78.2 (C-3), 72.0 (C-4), 66.1 (C-5), 26.7, 26.2 [$C(CH_3)_2$]. HRMS (EI): $[M]^{+\cdot}$, found 380.1616. $C_{23}H_{24}O_5$ requires 380.1624. Anal. Calcd for $C_{23}H_{24}O_5$: C, 72.61; H, 6.36. Found: C, 72.59; H, 6.38.

4.2.8. 3,5-*O*-[(*S*,*E*)-2-Hexyl-3-phenyl-2-propenylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose 22

The syrup was purified by column chromatography, using hexane–ethyl acetate (8:1) as eluent. Yield 1.40 g (72%); $[\alpha]_D = +15.0$ (*c* 1.0, CH_2Cl_2); MS (CI): *m/z* 389 (80%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 6.71 [s, 1H, $PhCH{=}C(C_6H_{13})CH$], 6.06 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.96 [d, 1H, ^4J 0.9 Hz, $PhCH{=}C(C_6H_{13})CH$], 4.63 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.41 (d, 1H, $J_{5e,5a}$ 13.2 Hz, H-5e), 4.33 (d, 1H, $J_{3,4}$ 2.0 Hz, H-3), 4.10 (m, 1H, H-4), 4.05 (dd, 1H, $J_{4,5a}$ 2.0 Hz, $J_{5e,5a}$ 13.2 Hz, H-5a), 2.31 [m, 2H, $PhCH{=}C(CH_2R)CH$], 1.52, 1.35 [2s, 6H, $C(CH_3)_2$], 1.3–1.2 [m, $(CH_2)_4$], 0.87 (t, 3H, *J* 7.1 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.5 [$PhCH{=}C(C_6H_{13})CH$], 136.9–128.1 (Ph), 126.8 [$PhCH{=}C(C_6H_{13})CH$], 111.8 [$C(CH_3)_2$], 105.7 (C-1), 101.3 [$PhCH{=}C(C_6H_{13})CH$], 84.0 (C-2), 78.9 (C-3), 72.3 (C-4), 66.7 (C-5), 31.5, 29.5, 28.7, 27.6, 22.6 [$(CH_2)_5$], 26.8, 26.2 [$C(CH_3)_2$], 14.0 (CH_3). HRMS (CI): $[M+H]^+$, found 389.2313. $C_{23}H_{33}O_5$ requires 389.2328.

4.2.9. 3,5-*O*-[(*S*,*Z*)-2-Hexyl-3-phenyl-2-propenylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose 23

The syrup was purified by column chromatography, using hexane–ethyl acetate (8:1) as eluent. Yield 0.40 g (21%); $[\alpha]_D = -52.9$ (*c* 1.2, CH_2Cl_2); MS (CI): *m/z* 389 (65%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ph), 6.51 [s, 1H, $PhCH{=}C(C_6H_{13})CH$], 6.04 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.15 [s, 1H, $PhCH{=}C(C_6H_{13})CH$], 4.58 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.31 (d, 1H, $J_{5e,5a}$ 13.2 Hz, H-5e), 4.23 (d, 1H, $J_{3,4}$ 2.0 Hz, H-3), 4.01 (m, 1H, H-4), 3.92 (dd, 1H, $J_{4,5a}$ 2.0 Hz, $J_{5e,5a}$ 13.2 Hz, H-5a), 2.30 [m, 2H, $PhCH{=}C(CH_2R)CH$], 1.6–1.2 [m, $(CH_2)_4$], 1.49, 1.34 [2s, 6H, $C(CH_3)_2$], 0.90 (t, 3H, *J* 7.0 Hz, CH_3). HRMS (CI): $[M+H]^+$, found 389.2316. $C_{23}H_{33}O_5$ requires 389.2328.

4.2.10. 3,5-*O*-[(*S*)-(1-Cyclohexenyl)methylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose 24

The compound was purified by column chromatography, using hexane–ethyl acetate (10:1) as eluent, obtaining a solid. Yield 1.33 g (94%); mp 94–95 °C, $[\alpha]_D = -2.8$ (*c* 1.0, CH_2Cl_2); MS (EI): *m/z* 282 (100%) $[M]^{+\cdot}$. ^1H NMR (500 MHz, $CDCl_3$): δ 6.03 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.91 (s, 1H, $CH{=}CCH$), 4.74 (s, 1H, $CH{=}CCH$), 4.58 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.34 (d, 1H, $J_{5e,5a}$ 13.2 Hz, H-5e), 4.26 (d, 1H, $J_{3,4}$ 1.9 Hz, H-3), 4.04 (m, 1H, H-4), 3.99 (dd, 1H, $J_{4,5a}$ 1.9 Hz, $J_{5e,5a}$ 13.2 Hz, H-5a), 2.06–2.04 (m, 4H, $2CH_2$), 1.63–1.59 (m, 4H, $2CH_2$), 1.49, 1.33 [2s, 6H, $C(CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.7 ($CH{=}CCH$), 126.7 ($CH{=}CCH$), 111.7 [$C(CH_3)_2$], 105.6 (C-1), 101.5 ($CH{=}CCH$), 83.9 (C-2), 78.6 (C-3), 72.2 (C-4), 66.5 (C-5), 26.7, 26.2 [$C(CH_3)_2$], 24.7, 23.0, 22.2, 22.1 ($4CH_2$). HRMS (EI): $[M]^{+\cdot}$, found 282.1457. $C_{15}H_{22}O_5$ requires 282.1467. Anal. Calcd for $C_{15}H_{22}O_5$: 63.81; H, 7.85. Found: 63.80; H, 7.93.

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

To a solution of the corresponding unsaturated acetals **13–16**, **18–22** and **24** (1.0 mmol) in dry solvent (10–30 mL) at the corresponding temperature (Table 1) 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 −5 °C, and then kept at room temperature until a check by 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. Compounds obtained were purified by flash chromatography on silica gel. The diastereomeric excesses (des) were determined by ^1H NMR, and are shown in Table 1.

4.3.1. 1,2-*O*-Isopropylidene-3,5-*O*-[(1*S*,2*R*,3*R*)-(2-phenylcyclopropyl)methylidene]-α-D-xylofuranose 25

Two stereoisomers were obtained in a 10:1 ratio (82% de), using 1,2-dichloroethane as the reaction solvent. The solid was purified by column chromatography, using hexane–ethyl acetate (8:1) as eluent. Yield 0.25 g (77%); $[\alpha]_D = -61.7$ (*c* 1.0, CH_2Cl_2). {lit.[43] $[\alpha]_D = -60.4$ (*c* 1.0, CH_2Cl_2 as 80% de)}.

4.3.2. 1,2-*O*-Isopropylidene-3,5-*O*-{(1*S*,2*R*,3*R*)-2-[(2-nitrophenyl)cyclopropyl]methylidene}-α-D-xylofuranose 26

Two stereoisomers were obtained in an 8.1:1 ratio (78% de), using 1,2-dichloroethane as the reaction solvent. The syrup was purified by column chromatography, using hexane–ethyl acetate (5:1) as eluent. Yield 0.30 g (84%); $[\alpha]_D = -42.8$ (*c* 0.9, CH_2Cl_2); MS (EI): *m/z* 363 (5%) $[M]^{+\cdot}$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.8–7.2 (4H, Ar), 6.06 (d, 0.89H, $J_{1,2}$ 3.7 Hz, H-1 major), 6.03 (d, 0.11H, $J_{1,2}$ 3.7 Hz, H-1 minor), 4.59 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.54 [d, 0.89H, *J* 4.3 Hz, $ArCH(CH_2)CHCH$ major], 4.52 [s, 0.11H, *J* 4.3 Hz, $ArCH(CH_2)CHCH$ minor], 4.32 (d, 1H, $J_{5e,5a}$ 13.2 Hz, $H\text{-}5_e$), 4.24 (d, 1H, $J_{3,4}$ 1.9 Hz, H-3), 4.05 (m, 1H, H-4), 3.96 (dd, 1H, $J_{4,5a}$ 2.0 Hz, $J_{5e,5a}$ 13.2 Hz, $H\text{-}5_a$), 2.55 [m, 1H, $ArCH(CH_2)CHCH$], 1.50, 1.34 [2s, 6H, $C(CH_3)_2$], 1.46 [m, 1H, $ArCH(CH_2)CHCH$], 1.27 [m, 1H, $ArCH(CH_AH_B)CHCH$], 0.92 [m, 1H, $ArCH(CH_AH_B)CHCH$]. ^{13}C NMR (500 MHz, $CDCl_3$): δ 150.9–124.2 (Ar), 111.8 [$C(CH_3)_2$], 105.7 (C-1), 99.6 [$ArCH(CH_2)CHCH$ minor], 99.2 [$ArCH(CH_2)CHCH$ major], 83.9 (C-2), 78.7 (C-3 minor), 78.5 (C-3 mayor), 72.3 (C-4), 66.4 (C-5), 26.7, 26.2 [$C(CH_3)_2$], 24.5 [$ArCH(CH_2)CHCH$], 16.6 [$ArCH(CH_2)CHCH$ minor], 16.4 [$ArCH(CH_2)CHCH$ major], 10.1 [$ArCH(CH_2)CHCH$ minor], 9.8 [$ArCH(CH_2)CHCH$ major]. HRMS (EI): $[M]^{+\cdot}$, found 363.133598. $C_{18}H_{21}NO_7$ requires 363.131802.

4.3.3. 1,2-*O*-Isopropylidene-3,5-*O*-{(1*S*,2*R*,3*R*)-2-[(2-methoxyphenyl)cyclopropyl]methylidene}-α-D-xylofuranose 27

Two stereoisomers were obtained in a 7.7:1 ratio (77% de), using 1,2-dichloroethane as the reaction solvent. The syrup was purified by column chromatography using hexane–ethyl acetate (4:1) as eluent. Yield 0.30 g (86%); $[\alpha]_D = -60.6$ (*c* 1.0, CH_2Cl_2); MS (EI): *m/z* 348

(70%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.2–6.8 (4H, Ar), 6.04 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.60 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.40 [d, 0.88H, J 5.0 Hz, $ArCH(CH_2)CHCH$ major], 4.37 [s, 0.12H, J 5.0 Hz, $ArCH(CH_2)CHCH$ minor], 4.32 (d, 1H, $J_{5e,5a}$ 13.2 Hz, H-5_e), 4.23 (d, 1H, $J_{3,4}$ 1.9 Hz, H-3), 4.05 (m, 1H, H-4), 3.95 (2dd, 1H, $J_{4,5a}$ 2.0 Hz, $J_{5e,5a}$ 13.3 Hz, H-5_a), 3.85 (s, 0.36H, OCH_3 minor), 3.84 (s, 2.64H, OCH_3 major), 2.27 [m, 1H, $ArCH(CH_2)CHCH$], 1.54 [m, 1H, $ArCH(CH_2)CHCH$], 1.50, 1.33 [2s, 6H, $C(CH_3)_2$], 1.13 [m, 1H, $ArCH(CH_AH_B)CHCH$], 0.85 [m, 1H, $ArCH(CH_AH_B)CHCH$]. ^{13}C NMR (500 MHz, $CDCl_3$): δ 158.1, 129.9, 126.7, 125.7, 120.5, 110.3 (Ar), 111.8 [$C(CH_3)_2$], 105.7 (C-1), 101.0 [$ArCH(CH_2)CHCH$ minor], 100.9 [$ArCH(CH_2)CHCH$ major], 83.8 (C-2), 78.7 (C-3 minor), 78.6 (C-3 major), 72.3 (C-4), 66.4 (C-5), 55.5 (OCH_3), 26.7, 26.1 [$C(CH_3)_2$], 23.6 [$ArCH(CH_2)CHCH$ minor], 23.5 [$ArCH(CH_2)CHCH$ major], 13.9 [$ArCH(CH_2)CHCH$], 11.0 [$ArCH(CH_2)CHCH$ minor], 10.9 [$ArCH(CH_2)CHCH$ major]. HRMS (EI): $[M]^{+\cdot}$, found 348.1573. $C_{19}H_{24}O_6$ requires 348.1573.

4.3.4. 1,2-*O*-Isopropylidene-3,5-*O*-{(1*S*,2*R*,3*R*)-2-[(4-methoxyphenyl)cyclopropyl]methylidene}-α-D-xylofuranose 28

Two stereoisomers were obtained in a 2:1 ratio (46% de), using 1,2-dichloroethane as the reaction solvent. The syrup was purified by column chromatography, using hexane–ethyl acetate (3:1) as eluent. Yield 0.27 g (77%); $[\alpha]_D = -36.9$ (*c* 1.0, CH_2Cl_2); MS (EI): *m/z* 348 (65%) $[M]^{+\cdot}$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.1–6.7 (4H, Ar), 6.04 (m, 1H, H-1), 4.58 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.35 [d, 0.67H, J 5.0 Hz, $ArCH(CH_2)CHCH$ major], 4.37 [s, 0.33H, J 5.0 Hz, $ArCH(CH_2)CHCH$ minor], 4.32 (2d, 1H, $J_{5e,5a}$ 13.2 Hz, H-5_e), 4.24 (d, 1H, $J_{3,4}$ 1.8 Hz, H-3), 4.04 (m, 1H, H-4), 3.94 (2dd, 1H, $J_{4,5a}$ 2.0 Hz, $J_{5e,5a}$ 13.3 Hz, H-5_a), 3.77 (s, 1.00H, OCH_3 minor), 3.77 (s, 2.00H, OCH_3 major), 2.00 [m, 1H, $ArCH(CH_2)CHCH$], 1.50, 1.33 [2s, 6H, $C(CH_3)_2$], 1.41 [m, 1H, $ArCH(CH_2)CHCH$], 1.09 [m, 1H, $ArCH(CH_AH_B)CHCH$], 0.85 [m, 1H, $ArCH(CH_AH_B)CHCH$]. ^{13}C NMR (500 MHz, $CDCl_3$): δ 157.8–127.3 (Ar), 113.7 [$C(CH_3)_2$], 105.6 (C-1), 100.7 [$ArCH(CH_2)CHCH$ minor], 100.6 [$ArCH(CH_2)CHCH$ major], 83.8 (C-2), 78.7 (C-3 minor), 78.6 (C-3 major), 72.2 (C-4), 66.4 (C-5), 55.3 (OCH_3), 26.7, 26.1 [$C(CH_3)_2$], 24.9 [$ArCH(CH_2)CHCH$ minor], 24.7 [$ArCH(CH_2)CHCH$ major], 18.6 [$ArCH(CH_2)CHCH$ minor], 18.5 [$ArCH(CH_2)CHCH$ major], 11.3 [$ArCH(CH_2)CHCH$ minor], 11.2 [$ArCH(CH_2)CHCH$ major]. HRMS (EI): $[M]^{+\cdot}$, found 348.1561. $C_{19}H_{24}O_6$ requires 348.1573.

4.3.5. 1,2-*O*-Isopropylidene-3,5-*O*-[(1*S*,2*R*,3*R*)-(2-methylcyclopropyl)methylidene]-α-D-xylofuranose 29

Two stereoisomers were obtained in a 4.7:1 ratio (65% de), using toluene as the reaction solvent. The solid was purified by column chromatography, using hexane–ethyl acetate (7:1) as eluent. Yield 0.19 g (76%); mp 74–75 °C; $[\alpha]_D = -21.2$ (*c* 1.0, CH_2Cl_2); MS (CI): *m/z* 257 (100%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.03 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.56 (d, 1H, $J_{1,2}$ 3.6 Hz, H-2), 4.30 (d, 1H, $J_{5e,5a}$ 13.2 Hz, H-5_e), 4.16 (m, 1H, H-3), 4.11 [d, 1H, J 5.0 Hz, $CH_3CH(CH_2)CHCH$ minor], 4.04 [d, 1H, J 5.3 Hz, $CH_3CH(CH_2)CHCH$ major], 4.01 (m, 1H, H-4), 3.89 (m, 1H, H-5_a), 1.48, 1.32 [2s, 6H, $C(CH_3)_2$], 1.03 [m, 3H, $CH_3CH(CH_2)CHCH$], 0.9–0.8 [m, 2H, $CH_3CH(CH_2)CHCH$], 0.59 [m, 1H, $CH_3CH(CH_AH_B)CHCH$], 0.30 [m, 1H, $CH_3CH(CH_AH_B)CHCH$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 111.7 [$C(CH_3)_2$ major], 111.6 [$C(CH_3)_2$ minor], 105.6 (C-1), 102.2 [$CH_3CH(CH_2)CHCH$ major], 101.8 [$CH_3CH(CH_2)CHCH$ minor], 83.8 (C-2), 78.6 (C-3 minor), 78.5 (C-3 major), 72.2 (C-4), 66.4 (C-5), 26.7, 26.1 [$C(CH_3)_2$], 22.9 [$CH_3CH(CH_2)CHCH$ major], 22.7 [$CH_3CH(CH_2)CHCH$ minor], 18.2 [$CH_3CH(CH_2)CHCH$ minor], 18.2 [$CH_3CH(CH_2)CHCH$ major], 9.6 [$CH_3CH(CH_2)CHCH$], 9.4 [$CH_3CH(CH_2)CHCH$ major], 9.3 [$CH_3CH(CH_2)CHCH$ minor]. HRMS (CI): $[M+H]^+$, found 257.138960. $C_{13}H_{21}O_5$ requires 257.138899. Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87. Found: C, 60.97; H, 7.93.

4.3.6. 3,5-*O*-[(1*S*,2*R*,3*R*)-(2-Heptylcyclopropyl)methylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose 30

Only one stereoisomer was obtained (100% de). The syrup was purified by column chromatography, using hexane–ethyl acetate (10:1) as eluent. Yield 0.25 g (74%); $[\alpha]_D = -26.7$ (*c* 1.0, CH_2Cl_2); MS (CI): *m/z* 341 (30%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.02 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.56 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.29 (d, 1H, $J_{5e,5a}$ 13.2 Hz, H-5_e), 4.16 (d, 1H, J 1.9 Hz, H-3), 4.05 [d, 1H, J 5.8 Hz, $RCH_2CH(CH_2)CHCH$], 4.00 (m, 1H, H-4), 3.89 (dd, 1H, $J_{4,5a}$ 1.9 Hz, $J_{5e,5a}$ 13.2 Hz, H-5_a), 1.48, 1.31 [2s, 6H, $C(CH_3)_2$], 1.4–1.1 [m, $(CH_2)_6$], 0.87 [m, 4H, $CH_3(CH_2)_5CH_2CH(CH_2)CHCH$], 0.80 [m, 1H, $RCH_2CH(CH_2)CHCH$], 0.55 [m, 1H, $RCH_2CH(CH_AH_B)CHCH$], 0.32 [m, 1H, $RCH_2CH(CH_AH_B)CHCH$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 111.7 [$C(CH_3)_2$], 105.6 (C-1), 102.2 [$RCH_2CH(CH_2)CHCH$], 83.8 (C-2), 78.5 (C-3), 72.2 (C-4), 66.4 (C-5), 33.3, 31.9, 29.3, 29.2, 22.6 [$(CH_2)_6$]. 26.7, 26.1 [$C(CH_3)_2$], 21.7 [$RCH_2CH(CH_2)CHCH$], 15.3 [$RCH_2CH(CH_2)CHCH$], 14.1 (CH_3), 8.4 [$RCH_2CH(CH_2)CHCH$],]. HRMS (CI): $[M+H]^+$, found 341.2320. $C_{19}H_{33}O_5$ requires 341.2328.

4.3.7. 3,5-*O*-[(1*S*,2*R*)-(2,2-Diphenylcyclopropyl)methylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose 31

Only one stereoisomer was obtained (100% de), using 1,2-dichloroethane as the reaction solvent. The syrup was purified by column chromatography, using hexane–ethyl acetate (6:1) as eluent. Yield 0.27 g (69%); $[\alpha]_D = +77.0$ (*c* 1.1, CH_2Cl_2); MS (CI): *m/z* 395 (10%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.5–7.1 (10H, 2Ph), 6.12 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.69 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 4.28 (d, 1H, $J_{5e,5a}$ 13.3 Hz, H-5_e), 3.92 (m, 2H, H-3, H-4), 4.76 (dd, 1H, $J_{4,5a}$ 2.0 Hz, $J_{5e,5a}$ 13.3 Hz, H-5_a), 3.62 [d, 1H, J 7.8 Hz, $(Ph)_2C(CH_2)CHCH$], 2.05 [m, 1H, $(Ph)_2C(CH_2)CHCH$], 1.53, 1.40 [2m, 2H, $(Ph)_2C(CH_2)CHCH$], 1.50, 1.38 [2s, 6H, $C(CH_3)_2$]. ^{13}C NMR (500 MHz, $CDCl_3$): δ 145.6–126.1 (2Ph), 111.7 [$C(CH_3)_2$], 105.7 (C-1), 101.5 [$(Ph)_2C(CH_2)CHCH$], 83.9 (C-2), 78.5 (C-3), 72.1 (C-4), 66.5 (C-5), 34.9 [$(Ph)_2C(CH_2)CHCH$], 28.7 [$(Ph)_2C(CH_2)CHCH$], 26.7, 26.2 [$C(CH_3)_2$], 16.9 [$(Ph)_2C(CH_2)CHCH$]. HRMS (CI): $[M+H]^+$, found 395.1859. $C_{24}H_{27}O_5$ requires 395.1858.

4.3.8. 1,2-*O*-Isopropylidene-3,5-*O*-[(1*S*,2*R*,3*S*)-(1-methyl-2-phenylcyclopropyl)methylidene]-α-D-xylofuranose 32

Two stereoisomers were obtained in a 6.5:1 ratio (76% de), using 1,2-dichloroethane as the reaction solvent. The solid was purified by column chromatography, using hexane–ethyl acetate (11:1) as eluent. Yield 0.25 g (75%); $[\alpha]_D = -17.8$ (*c* 0.9, CH_2Cl_2). {lit.[43] $[\alpha]_D = -12.9$ (*c* 0.9, CH_2Cl_2 as 50% de)}.

4.3.9. 3,5-*O*-[(1*S*,2*R*,3*S*)-(1-Hexyl-2-phenylcyclopropyl)methylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose 33

Two stereoisomers were obtained in a 4.9:1 ratio (66% de), using 1,2-dichloroethane as the reaction solvent. The syrup was purified by column chromatography, using hexane–ethyl acetate (18:1) as eluent. Yield 0.29 g (72%); $[\alpha]_D = -16.9$ (*c* 0.9, CH_2Cl_2); MS (CI): *m/z* 403 (50%) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3–7.1 (5H, Ph), 6.02 (d, 0.82H, $J_{1,2}$ 3.7 Hz, H-1 major), 6.00 (d, 0.18H, $J_{1,2}$ 3.6 Hz, H-1 minor), 4.59 (d, 0.82H, $J_{1,2}$ 3.7 Hz, H-2 major), 4.59 (d, 0.18H, $J_{1,2}$ 3.7 Hz, H-2 minor), 4.52 [s, 0.82H, $PhCH(CH_2)C(C_6H_{13})CH$ major], 4.50 [s, 0.18H, $PhCH(CH_2)C(C_6H_{13})CH$ minor], 4.33 (d, 1H, $J_{5e,5a}$ 13.2 Hz, H-5_e), 4.23 (m, 1H, H-3), 4.05 (m, 1H, H-4), 3.94 (dd, 1H, $J_{4,5a}$ 1.8 Hz, $J_{5e,5a}$ 13.2 Hz, H-5_a), 2.35 [m, 1H, $PhCH(CH_2)C(C_6H_{13})CH$], 1.51, 1.34 [2s, 6H, $C(CH_3)_2$], 1.3–0.8 [m, 15H, $PhHC(CH_2)C(C_6H_{13})CH$]. ^{13}C NMR (500 MHz, $CDCl_3$): δ 138.7–125.7 (Ph), 111.8 [$C(CH_3)_2$], 105.7 (C-1), 101.0 [$PhC(CH_2)C(C_6H_{13})CH$ minor], 100.8 [$PhC(CH_2)C(C_6H_{13})CH$ major], 84.0 (C-2), 78.7 (C-3 minor), 78.5 (C-3 major), 72.4 (C-4), 66.5 (C-5), 31.6–14.1 [$PhCH(CH_2)C(C_6H_{13})CH$], 26.8, 26.2 [$C(CH_3)_2$], 12.2 [$PhCH(CH_2)C(C_6H_{13})CH$]. HRMS (CI): $[M+H]^+$, found 403.2486. $C_{24}H_{35}O_5$ requires 403.2484.

4.3.10. 1,2-*O*-Isopropylidene-3,5-*O*-[(1*S*,2*R*,3*R*)-(1,2-methylidenecyclohexyl)methylidene]-α-D-xylofuranose 34

Two stereoisomers were obtained in a 5:1 ratio (67% de), using 1,2-dichloroethane as the reaction solvent. The syrup was purified by column chromatography, using hexane–ethyl acetate (10:1) as eluent. Yield 0.23 g (79%); $[\alpha]_D = -10.0$ (*c* 1.0, CH_2Cl_2); MS (CI): *m/z* 297 (15%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 6.00 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.56 (d, 0.18H, $J_{1,2}$ 3.7 Hz, H-2 minor), 4.54 (d, 0.82H, $J_{1,2}$ 3.7 Hz, H-2 major), 4.30, 4.28 (2d, 1H, $J_{5e,5a}$ 13.2 Hz, H-5_e), 4.16 (d, 0.18H, *J* 1.9 Hz, H-3 minor), 4.15 (d, 0.82H, *J* 1.9 Hz, H-3 major), 3.98 [m, 0.18H, $CH(CH_2)CC\mathit{H}$ minor], 3.93 [m, 0.82H, $CH(CH_2)CC\mathit{H}$ major], 3.90–3.85 (m, 2H, H-4, H-5_a), 2.0–1.0 (m, 8H, $4CH_2$ cyclohexyl), 1.48, 1.32 [2s, 6H, $C(CH_3)_2$], 0.98 [m, 1H, $C\mathit{H}(CH_2)CCH$], 0.69 [m, 1H, $CH(C\mathit{H}_AH_B)CCH$], 0.26 [dd, 0.82H, J_{gem} 4.6 Hz, *J* 5.8 Hz, $CH(CH_A\mathit{H}_B)CCH$ major], 0.22 [dd, 0.18H, J_{gem} 4.6 Hz, *J* 5.8 Hz, $CH(CH_A\mathit{H}_B)CCH$ minor]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 111.7 [$\mathit{C}(CH_3)_2$], 105.7 (C-1), 104.8 [$CH(CH_2)C\mathit{C}H$ major], 104.5 [$CH(CH_2)C\mathit{C}H$ minor], 83.9 (C-2), 78.6 (C-3 minor), 78.5 (C-3 major), 72.3 (C-4), 66.5 (C-5 minor), 66.4 (C-5 major), 26.7, 26.1 [$C(\mathit{C}H_3)_2$], 23.8, 23.1, 22.0, 21.5, 21.0 (cyclohexyl), 14.1 [$\mathit{C}H(CH_2)CCH$ major], 14.0 [$\mathit{C}H(CH_2)CCH$ minor], 13.7 [$CH(\mathit{C}H_2)CCH$ major], 13.6 [$CH(\mathit{C}H_2)CCH$ minor]. HRMS (CI): $[M+H]^+$, found 297.1689. $C_{16}H_{25}O_5$ requires 297.1702.

4.4. Separation of the chiral auxiliary

A solution of the cyclopropylmethylidene acetals **25**, **26** and **30**–**32** (0.4 mmol) in 80% acetic acid in water (20 mL) was heated at 60 °C, and the reaction was monitored until a check by 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 ($MgSO_4$) 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 mixture as eluent.

4.4.1. (1*R*,2*R*)-*trans*-1-Hydroxymethyl-2-phenylcyclopropane[45] (−)-35

A syrup was obtained. Yield 48 mg (81%); $[\alpha]_D = -78.2$ (*c* 1.1, CH_2Cl_2), {lit.[45] $[\alpha]_D = -92$ (*c* 1.23, EtOH)}; MS (CI): *m/z* 149 (20%) $[M+H]^+$. ^1H 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, $PhCH(CH_2)CHC\mathit{H}_2OH$], 1.84 [m, 1H, $PhC\mathit{H}(CH_2)CHCH_2OH$], 1.47 [m, 1H, $PhCH(CH_2)C\mathit{H}CH_2OH$], 0.98 [m, 2H, $PhCH(C\mathit{H}_2)CHCH_2OH$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.7–128.1 (Ph), 66.5 [$PhCH(CH_2)CH\mathit{C}H_2OH$], 25.2 [$PhCH(CH_2)\mathit{C}HCH_2OH$], 21.3 [$Ph\mathit{C}H(CH_2)CHCH_2OH$], 13.7 [$PhCH(\mathit{C}H_2)CHCH_2OH$].

4.4.2. (1*R*,2*R*)-*trans*-1-Hydroxymethyl-2-(2-nitrophenyl)cyclopropane[46] (+)-36

A syrup was obtained. Yield 60 mg (78%); $[\alpha]_D = +25.1$ (*c* 0.9, CH_2Cl_2); MS (CI): *m/z* 194 (5%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.9–7.2 (m, 4H, Ar), 3.75 [dd, 1H, *J* 5.8 Hz, J_{gem} 11.4 Hz, $ArCH(CH_2)CHC\mathit{H}_AH_BOH$], 3.55 [dd, 1H, *J* 7.4 Hz, J_{gem} 11.4 Hz, $ArCH(CH_2)CHCH_A\mathit{H}_BOH$], 2.30 [m, 1H, $ArC\mathit{H}(CH_2)CHCH_2OH$], 1.88 (s, 1H, OH), 1.35 [m, 1H, $ArCH(CH_2)C\mathit{H}CH_2OH$], 1.08, 0.90 [2 m, 2H, $ArCH(C\mathit{H}_2)CHCH_2OH$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.7, 136.6, 132.9, 128.6, 126.8, 124.4 (Ar), 66.2 [$ArCH(CH_2)CH\mathit{C}H_2OH$], 24.7 [$ArCH(CH_2)\mathit{C}HCH_2OH$], 19.1 [$Ar\mathit{C}H(CH_2)CHCH_2OH$], 11.1 [$ArCH(\mathit{C}H_2)CHCH_2OH$]. HRMS (CI): $[M+H]^+$, found 194.0817. $C_{10}H_{12}NO_3$ requires 194.0817.

4.4.3. (1*R*,2*R*)-*trans*-1-Heptyl-2-hydroxymethylcyclopropane (−)-37

A syrup was obtained. Yield 59 mg (87%); $[\alpha]_D = -17.6$ (*c* 0.5, CH_2Cl_2); MS (CI): *m/z* 171 (5%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 3.43 [m, 2H, $CH_3(CH_2)_6CH(CH_2)CHC\mathit{H}_2OH$], 1.42–1.15 [m, 13H, $CH_3(C\mathit{H}_2)_6CH(CH_2)CHCH_2O\mathit{H}$], 0.88 [t, 3H, *J* 7.0 Hz, $C\mathit{H}_3(CH_2)_6$-$CH(CH_2)CHCH_2OH$], 0.83 [m, 1H, $CH_3(CH_2)_6CH(CH_2)C\mathit{H}CH_2OH$], 0.59 [m, 1H, $CH_3(CH_2)_6C\mathit{H}(CH_2)CHCH_2OH$], 0.36, 0.30 [2m, 2H, $CH_3(CH_2)_6CH(C\mathit{H}_2)CHCH_2OH$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 67.3 [$CH_3(CH_2)_6CH(CH_2)CH\mathit{C}H_2OH$], 33.6, 31.9, 29.6, 29.4, 29.3, 22.7 [$CH_3(\mathit{C}H_2)_6CH(CH_2)CHCH_2OH$], 21.2 [$CH_3(CH_2)_6\mathit{C}H(CH_2)CHCH_2OH$], 17.4 [$\mathit{C}H_3(CH_2)_6CH(CH_2)CHCH_2OH$], 14.1 [$CH_3(CH_2)_6CH(CH_2)$-$\mathit{C}HCH_2OH$], 9.9 [$CH_3(CH_2)_6CH(\mathit{C}H_2)CHCH_2OH$].

4.4.4. (1*R*)-1,1-Diphenyl-2-hydroxymethylcyclopropane[46,47] (+)-38

A syrup was obtained. Yield 76 mg (85%); $[\alpha]_D = +21.1$ (*c* 0.5, CH_2Cl_2), {lit.[47] $[\alpha]_D = +167$ (*c* 0.30, $CHCl_3$)}; MS (CI): *m/z* 225 (40%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.5–7.2 (m, 10H, 2Ph), 3.67 [m, 2H, $Ph_2C(CH_2)CHC\mathit{H}_2OH$], 3.10 (s, 1H, OH), 2.43 [m, 1H, Ph_2C-$(CH_2)C\mathit{H}CH_2OH$], 1.60 [m, 2H, $Ph_2C(C\mathit{H}_2)CHCH_2OH$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.1, 128.1, 126.8, 126.1 (2Ph), 77.9 [$Ph_2\mathit{C}$-$(CH_2)CHCH_2OH$], 63.2 [$Ph_2C(CH_2)CH\mathit{C}H_2OH$], 38.9 [$Ph_2C(CH_2)$-$\mathit{C}HCH_2OH$], 27.2 [$Ph_2C(\mathit{C}H_2)CHCH_2OH$]. HRMS (CI): $[M+H]^+$, found 225.1285. $C_{16}H_{17}O$ requires 225.1279.

4.4.5. (1*R*,2*S*)-*E*-1-Hydroxymethyl-1-methyl-2-phenylcyclopropane[48] (−)-39

Yield 32 mg (80%); $[\alpha]_D = -23.7$ (*c* 1.0, CH_2Cl_2), {lit.[48] $[\alpha]_D = -15.1$ (*c* 0.12, $CHCl_3$)}; MS (CI): *m/z* 163 (20%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3–7.1 (m, 5H, Ph), 3.56 [d, 2H, J_{gem} 11.0 Hz, $PhCH(CH_2)C(CH_3)C\mathit{H}_2OH$], 2.05 [dd, 1H, J_{cis} 8.7 Hz, J_{trans} 6.0 Hz, $PhC\mathit{H}(CH_2)C(CH_3)CH_2OH$], 1.52 (s, 1H, OH), 0.94 [dd, 1H, J_{gem} 5.0 Hz, J_{cis} 8.8 Hz, $PhCH(C\mathit{H}_{cis}H_{trans})C(CH_3)CH_2OH$], 0.89 [s, 3H, $PhCH(CH_2)C(C\mathit{H}_3)CH_2OH$], 0.86 [m, 1H, $PhCH(CH_{cis}\mathit{H}_{trans})C(CH_3)CH_2OH$]. ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.7–128.1 (Ph), 71.7 [$PhCH(CH_2)C(CH_3)\mathit{C}H_2OH$], 29.7 [$PhCH(CH_2)\mathit{C}(CH_3)CH_2OH$], 26.8 [$Ph\mathit{C}H(CH_2)C(CH_3)CH_2OH$], 15.7 [$PhCH(\mathit{C}H_2)C(CH_3)CH_2OH$], 15.1 [$PhCH(CH_2)C(\mathit{C}H_3)CH_2OH$].

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References

1. Salaün, J. *Top. Curr. Chem.* **2000**, *207*, 1–67.
2. Pellissier, H. *Tetrahedron* **2008**, *64*, 7041–7095.
3. Kim, A.; Hong, J. H. *Eur. J. Med. Chem.* **2007**, *42*, 487–493.
4. Zhang, A.; Li, F.; Ding, C.; Yao, Q.; Knappi, B. I.; Bidlack, J. M.; Neumeyer, J. L. *J. Med. Chem.* **2007**, *50*, 2747–2751.
5. Kuramochi, K.; Matsui, R.; Matsubara, Y.; Nakai, J.; Sunoki, T.; Arai, S.; Nagata, S.; Nagahara, Y.; Mizushina, Y.; Ikekita, M.; Kobayashi, S. *Bioorg. Med. Chem.* **2006**, *14*, 2151–2161.

6. Bender, D. M.; Peterson, J. A.; McCarthy, J. R.; Gunaydin, H.; Takano, Y.; Houk, K. N. *Org. Lett.* **2008**, 509–511.
7. Högberg, M.; Sahlberg, C.; Engelhardt, P.; Noréen, R.; Kangasmetsä, J.; Johansson, N. G.; Vrang, L.; Zhang, H.; Sahlberg, B.-L.; Unge, T.; Lövgren, S.; Fridborg, K.; Bäckbro, K. *J. Med. Chem.* **1999**, *42*, 4150–4160.
8. Huang, K.; Huang, Z.-Z. *Synlett* **2005**, 1621–1623.
9. Mitra, D.; Sengupta, A.; Biradha, K.; Basak, A. *Tetrahedron: Asymmetry* **2008**, *19*, 2678–2681.
10. Baldwin, J. E.; Adlington, R. M.; Domayne-Hayman, B. P.; Knight, G.; Ting, H.-H. *J. Chem. Soc., Chem. Commun.* **1987**, 1661–1663.
11. Cativiela, C.; Díaz-de-Villegas, M. D. *Tetrahedron: Asymmetry* **2000**, *11*, 645–732.
12. Donaldson, W. *Tetrahedron* **2001**, *57*, 8589–8627.
13. Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977–1050.
14. Mash, E. A.; Nelson, K. A. *Tetrahedron* **1987**, *43*, 679–692.
15. Vallgarda, J.; Hacksell, U. *Tetrahedron Lett.* **1991**, *32*, 5625–5628.
16. Dubs, M.; Dieks, H.; Günther, W.; Kötteritzsch, M.; Poppitz, W.; Schönecker, B. *Tetrahedron Lett.* **2002**, *43*, 2499–2503.
17. Balsells, J.; Walsh, P. J. *J. Org. Chem.* **2000**, *65*, 5005–5008.
18. Charette, A. B.; Janes, M. K.; Lebel, H. *Tetrahedron: Asymmetry* **2003**, *14*, 867–872.
19. Long, J.; Du, H.; Li, K.; Shi, Y. *Tetrahedron Lett.* **2005**, *46*, 2737–2740.
20. Du, H.; Long, J.; Shi, Y. *Org. Lett.* **2006**, 2827–2829.
21. Davies, H. M. L. *Tetrahedron* **1993**, *49*, 5203–5223.
22. Corsaro, A.; Pistarà, V.; Catelani, G.; D'Andrea, F.; Adamo, R.; Chiacchio, M. A. *Tetrahedron Lett.* **2006**, *47*, 6591–6594.
23. Hollingsworth, R. I.; Wang, G. *Chem. Rev.* **2000**, *100*, 4267–4282.
24. Iglesias-Guerra, F.; Romero, I.; Alcudia, F.; Vega-Pérez, J. M. *Carbohydr. Res.* **1998**, *308*, 57–62.
25. Iglesias-Guerra, F.; Candela, J. I.; Bautista, J.; Alcudia, F.; Vega-Pérez, J. M. *Carbohydr. Res.* **1999**, *316*, 71–84.
26. Vega-Pérez, J. M.; Candela, J. I.; Iglesias-Guerra, F. *J. Org. Chem.* **1997**, *62*, 6608–6611.
27. Kunz, H.; Rück, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 336–358.
28. Adam, W.; Zhang, A. *Synlett* **2005**, 1047–1072.
29. Pleuss, N.; Zech, G.; Furman, B.; Kunz, H. In *Sugars as Chiral Auxiliaries*; Levy, D. E., Fügedi, P., Eds.; The Organic Chemistry of Sugars; Taylor & Francis Group: Boca Raton, 2006; pp 427–488.
30. Iglesias-Guerra, F.; Candela, J. I.; Blanco, E.; Alcudia, F.; Vega-Pérez, J. M. *Chirality* **2002**, *14*, 199–203.
31. Vega-Pérez, J. M.; Candela, J. I.; Blanco, E.; Iglesias-Guerra, F. *Tetrahedron* **1999**, *55*, 9641–9650.
32. Vega-Pérez, J. M.; Vega, M.; Blanco, E.; Iglesias-Guerra, F. *Tetrahedron: Asymmetry* **2001**, *12*, 135–147.
33. Vega-Pérez, J. M.; Candela, J. I.; Romero, I.; Blanco, E.; Iglesias-Guerra, F. *Eur. J. Org. Chem.* **2000**, 3949–3956.
34. Vega-Pérez, J. M.; Candela, J. I.; Blanco, E.; Iglesias-Guerra, F. *Tetrahedron: Asymmetry* **2002**, *13*, 2471–2483.
35. Vega-Pérez, J. M.; Vega, M.; Blanco, E.; Iglesias-Guerra, F. *Tetrahedron: Asymmetry* **2001**, *12*, 3189–3203.
36. Vega-Pérez, J. M.; Vega, M.; Blanco, E.; Iglesias-Guerra, F. *Tetrahedron: Asymmetry* **2004**, *15*, 3617–3633.
37. Vega-Pérez, J. M.; Vega, M.; Blanco, E.; Iglesias-Guerra, F. *Tetrahedron: Asymmetry* **2007**, *18*, 1850–1867.
38. Charette, A. B.; Côté, B.; Marcoux, J.-F. *J. Am. Chem. Soc.* **1991**, *113*, 8166–8167.
39. Charette, A. B.; Côté, B. *J. Org. Chem.* **1993**, *58*, 933–936.
40. Charette, A. B.; Turcotte, N.; Marcoux, J.-F. *Tetrahedron Lett.* **1994**, *35*, 513–516.
41. Ferreira, V. F.; Leao, R. A. C.; Silva, F. C.; Pinheiro, S.; Lhoste, P.; Sinou, D. *Tetrahedron: Asymmetry* **2007**, *18*, 1217–1223.
42. Kang, J.; Lim, G. J.; Yoon, S. K.; Kim, M. Y. *J. Org. Chem.* **1995**, *60*, 564–577.
43. Vega-Pérez, J. M.; Periñán, I.; Vega, M.; Iglesias-Guerra, F. *Tetrahedron: Asymmetry* **2008**, *19*, 1720–1729.
44. Murphy, P. V.; O'Brien, J. L.; Gorey-Feret, L. J.; Smith, A. B. *Tetrahedron* **2003**, *59*, 2259–2271.
45. Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726–728.
46. Turnbull, M. D. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1241–1247.
47. Walborsky, H. M.; Barash, L.; Young, A. E.; Impastato, F. J. *J. Am. Chem. Soc.* **1961**, *83*, 2517–2525.
48. Nishii, Y.; Wakimura, K.; Tsuchiya, T.; Nakamura, S.; Tanabe, Y. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1243–1249.