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Structural modification of carbohydrates via functionalised organolithium intermediates: EPC preparation of branched-chain functionalised sugars

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Abstract

The reductive opening of epoxides **1**, **9**, **13** derived from D-glucose and **18** derived from D-fructose using lithium and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (DTBB) in THF at −78°C allows the formation of β-oxido organolithium derivatives (**2**, **10**, **14** and **19**), which, by reaction with different electrophiles [H_2O, D_2O, Me_3SiCl, PhCHO, Me_2CO, Et_2CO, $(CH_2)_5CO$, CO_2] at the same temperature yields, after hydrolysis with water, the expected branched-chain functionalised carbohydrates. An alternative route for compound **11**, derived from the epoxide **9**, consists of the deprotonation of the chlorohydrin **12** followed by the same protocol of lithiation-reaction with an electrophile. The application of this methodology to the oxetane **4** allows compound **6** to be obtained through the corresponding γ-functionalised organolithium intermediates **5**. Finally, the addition of the dianions **25** (resulting from the DTBB-catalysed lithiation of phthalan and isochroman) to the ketones **8** and **23**, derived from D-glucose and D-fructose, respectively, allowed the stereoselective functionalisation at the 3-position of the sugars, giving the corresponding diols **26** and **27**, which can cyclise to the corresponding heterocycles **28** and **29**, respectively, under Mitsunobu reaction conditions.

1. Introduction

Carbohydrates are the most abundant organic compounds in nature.[1] Considering their biological activity, they play an important role in molecular recognition, cell signalling, biomolecular transport, the immune system and, in fact, in virtually every essential biological process.[2] From a chemical point of

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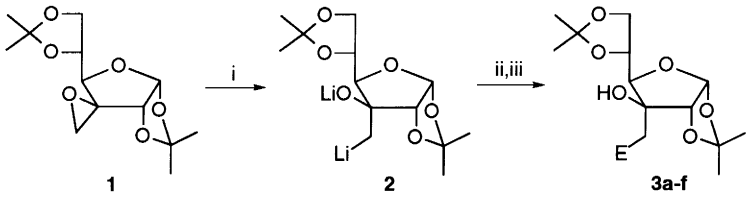
view, carbohydrates constitute one of the most important families of the chiral pool of natural products, which can be used for the preparation of enantiopure molecules.[3] In particular, naturally occurring D-glucose is one of the molecules most used in the so-called EPC (enantiomerically pure compounds) synthesis, which uses natural products as starting materials and a source of chirality.[4] In recent years much effort has been focused on the preparation of branched-chain functionalised carbohydrates, bearing mainly an alcohol functionality at the branching carbon atom, due to their presence as glycosidic components of many antibiotics.[5] On the other hand, during the last decade we have developed a new methodology for the preparation of organolithium compounds consisting of the use of lithium powder and a catalytic amount of an arene, naphthalene or 4,4′-di-*tert*-butylbiphenyl (DTBB) being the most commonly used.[6–9] This methodology has allowed us to generate organolithium reagents starting from non-halogenated materials,[10] functionalised organolithium intermediates[11] (starting from chlorinated precursors,[12] ethers,[13] thioethers,[14] sulfones[15] and saturated heterocycles[16]) and polylithiated synthons.[17] Among the different methods for generating functionalised organolithium compounds, the reductive opening of epoxides using lithium and a stoichiometric[18] or catalytic[19] amount of an arene has been shown to be effective for the generation of β-oxido-functionalised organolithium derivatives. In this paper, we describe the application of the aforementioned arene-catalysed lithiation of epoxides derived from carbohydrates such as glucose or fructose derivatives.[20]

2. Results and discussion

The reaction of the protected epoxy D-glucose **1** with an excess of lithium (1:14 molar ratio) and a catalytic amount of DTBB (1:0.1 molar ratio, 5 mol%) in THF at −78°C for 2 h followed by treatment with different electrophiles [E^+=H_2O, D_2O, Me_3SiCl, PhCHO, Me_2CO, $(CH_2)_5CO$] at the same temperature for 10 min afforded, after hydrolysis with water, the expected products **3a**–**f**, the corresponding intermediate **2** probably being involved in the process (Scheme 1 and Table 1). In the case of prochiral carbonyl compounds, such as benzaldehyde, a 2:3 diastereomeric mixture was isolated (Table 1, entry 4), which was separated by chromatography (neutral silica gel, hexane:ethyl acetate), giving the corresponding pure diastereomers. The unequivocal assignment of the stereochemistry of both formed stereocentres in diols **3d** and **3d′** was performed by single-crystal analysis of compound **3d′** (Fig. 1).[21]



Scheme 1. *Reagents and conditions*: (i) Li, DTBB (5%), THF, −78°C, 2 h; (ii) E^+=H_2O, D_2O, Me_3SiCl, PhCHO, Me_2CO, $(CH_2)_5CO$, −78°C, 10 min; (iii) H_2O, –78 to 20°C

Since oxetanes can be reductively opened using lithium and a catalytic amount of DTBB,[22] we applied the above-mentioned methodology to the oxetane derivative **4**, but performing the lithiation step at −40°C. In this case, the reaction with different electrophiles [H_2O, D_2O, PhCHO, Me_2CO, $(CH_2)_5CO$] always gave the 'reduced' product **6a** (E=H; >95% yield) except for the deuterolysis in which a 98% yield of compound **6b** was obtained with only 55% of deuterium incorporation (MS) (Scheme 2). It seems that, under these reaction conditions, the intermediate **5** partially decomposed by abstracting a proton from the

Table 1
Preparation of compounds **3** from the epoxide **1**

Entry	Electrophile E+	Product[a] No.	Product[a] E	Yield (%)[b]
1	H_2O	**3a**	H	95
2	D_2O	**3b**	D	95[c]
3	Me_3SiCl	**3c**	Me_3Si	50 (70)
4	PhCHO	**3d+3d'**	PhCHOH	50 (65)[d]
5	Me_2CO	**3e**	Me_2COH	20 (55)
6	$(CH_2)_5CO$	**3f**	$(CH_2)_5COH$	60

[a] All products **3** were ≥95% pure (300 MHz ^1H NMR and/or GLC). [b] Isolated yield after column chromatography (neutral silica gel, hexane/ethyl acetate) based on the starting material **1**; in parenthesis GLC yield. [c] 75% Deuterium incorporation (from MS). [d] 2/3 Diastereomeric mixture (75 MHz ^{13}C NMR).

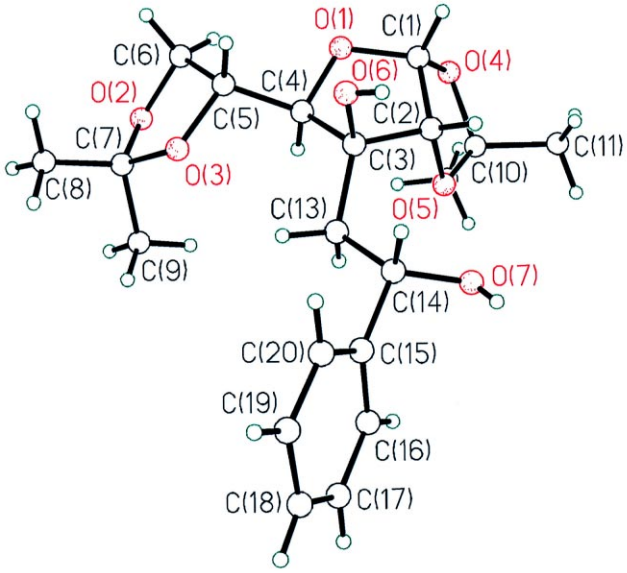
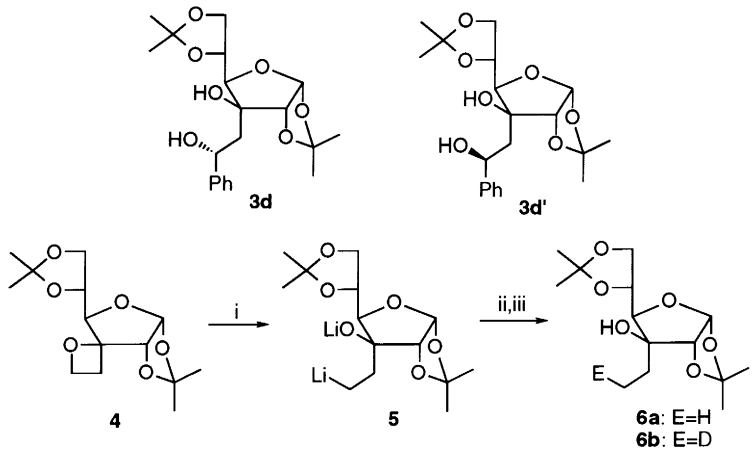


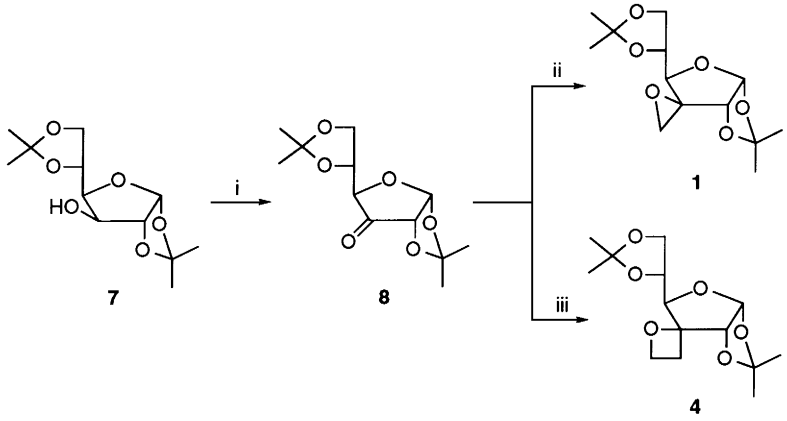
Fig. 1.

reaction medium, probably from the THF, thus giving the corresponding product **6a** instead of reacting with the electrophile, except in the case of deuterium oxide.



Scheme 2. *Reagents and conditions*: (i) Li, DTBB (5%), THF, −40°C, 3 h; (ii) E^+=H_2O, D_2O, –40°C, 10 min; (iii) H_2O, –40 to 20°C

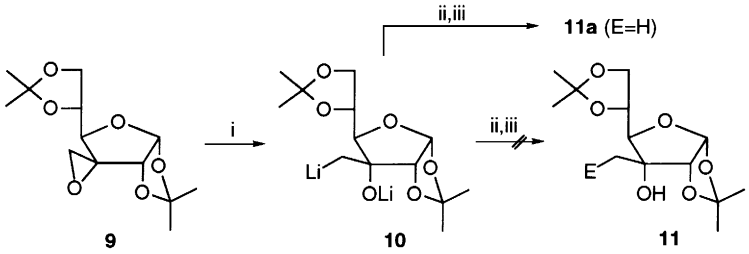
Starting materials **1** and **4** were prepared from commercially available compound **7**, which was oxidised with pyridinium chlorochromate (PCC) in CH_2Cl_2 to give the ketone **8**, followed by treatment with a stoichiometric amount or an excess of trimethylsulfoxonium iodide in 80–85% yield (Scheme 3).[22d]



Scheme 3. *Reagents and conditions*: (i) PCC, Ac_2O, CH_2Cl_2, 20°C, 30 min; (ii) KOBu^t (1 equiv.), Me_3SOI (1 equiv.), Bu^{t}OH, 50°C, 2.5 h; (iii) KOBu^t (4 equiv.), Me_3SOI (4 equiv.), Bu^{t}OH, 50°C, 1.5 h

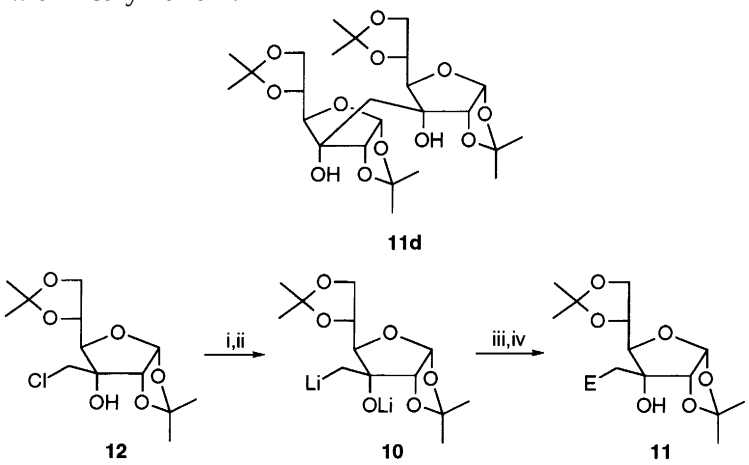
When the epimeric epoxide **9** was submitted to the same procedure as shown in Scheme 1 and using various electrophiles [H_2O, D_2O, PhCHO, Et_2CO, $(CH_2)_5CO$] we always isolated the same product **11a** resulting from a lithium/hydrogen exchange. In this case, the corresponding dianion **10** seemed to be very unstable and decomposed during the lithiation time (2 h), under the reaction conditions employed, by abstraction of a proton from the reaction medium (Scheme 4).[23]

In order to avoid the former problem we lithiated the chlorohydrin **12**, previously deprotonated with Bu^{n}Li in THF at −78°C, using the same procedure as above, so that the corresponding intermediate **10** was formed in only 30 min, and its decomposition could be avoided and compounds **11** could be isolated, after reaction with D_2O, $(CH_2)_5CO$ and compound **8** (Scheme 5 and Table 2). In the last case, the stereochemistry of compound **11d** is that corresponding to the attack of intermediate **10** to the upper face of the ketone **8**.[24] A definitive proof of the C_2 symmetry in compound **11d** is observed in its NMR spectra



Scheme 4. *Reagents and conditions*: (i) Li, DTBB (5%), THF, −78°C, 2 h; (ii) E^+=H_2O, D_2O, PhCHO, Et_2CO, $(CH_2)_5CO$, −78°C; (iii) H_2O

(see the Experimental part). The stereochemistry of compound **11a** was confirmed by its preparation by reaction of ketone **8** with methyllithium.



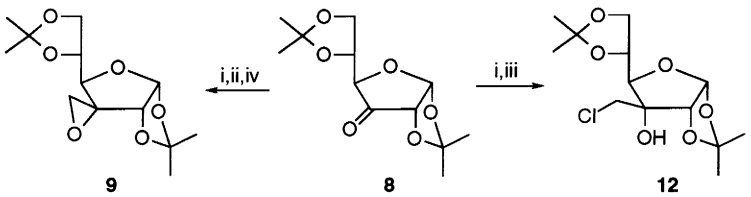
Scheme 5. *Reagents and conditions*: (i) Bu^nLi, THF, −78°C; (ii) Li, DTBB (5%), THF, −78°C, 30 min; (iii) E^+=D_2O, $(CH_2)_5CO$, **8**, –78 to 0°C; (iv) H_2O

Table 2
Preparation of compounds **11** from the chlorohydrin **12**

Entry	Electrophile E^+	Product[a] No.	Product[a] E	Yield (%)[b]
1	D_2O	**11b**	D	65 (78)
2	$(CH_2)_5CO$	**11c**	$(CH_2)_5COH$	61
3	**8**	**11d**	-	20 (63)

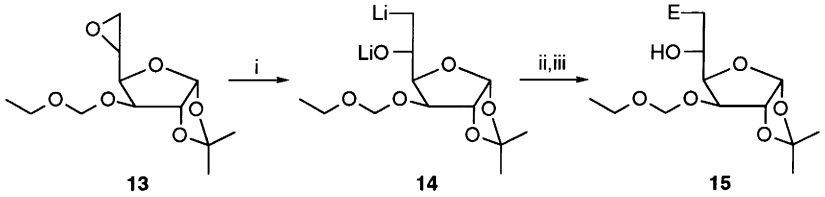
[a] All products **12** were ≥93% pure (300 MHz ^1H NMR and/or GLC). [b] Isolated yield after column chromatography (neutral silica gel, hexane/ethyl acetate) based on the starting material **12**; in parenthesis GLC yield.

Starting materials **9** and **12** were prepared from ketone **8** by reaction with in situ generated chloromethyllithium (from chloroiodomethane and Bu^nLi), the only difference being the reaction temperature for the hydrolysis: at low temperature the chlorohydrin **12** did not cyclise to the epoxide **9**, but at room temperature this was the reaction product formed (Scheme 6).



Scheme 6. *Reagents and conditions*: (i) $ClCH_2I$, LiBr, THF, 10 min; (ii) Bu^nLi, THF, −78 to 20°C; (iii) as (ii) but at −78°C and then H_2O, −78 to 0°C; (iv) H_2O

Another epoxide derived from D-glucose is compound **13**, which was lithiated and reacted with electrophiles [H_2O, D_2O, PhCHO, Me_2CO, $(CH_2)_5CO$, CO_2] using the same procedure shown in Scheme 1. Thus, the expected compounds **15** were isolated, dianion **14** probably being involved as an intermediate (Scheme 7 and Table 3). Also in this case, when benzaldehyde was used as electrophile, a 3:1 diastereomeric mixture of compounds **15c** and **15c′** was obtained (Table 3, entry 3).



Scheme 7. *Reagents and conditions*: (i) Li, DTBB (5%), THF, −78°C, 2.5 h; (ii) E^+=H_2O, D_2O, PhCHO, Me_2CO, $(CH_2)_5CO$, CO_2, −78°C, 10 min; (iii) H_2O, −78 to 20°C

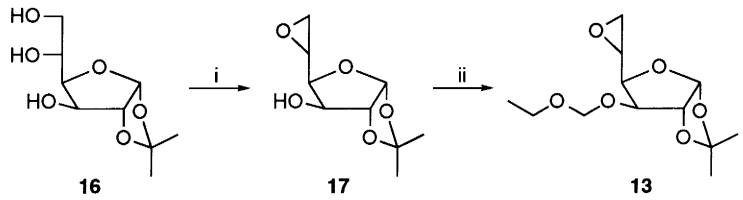
Table 3
Preparation of compounds **15** from the epoxide **13**

Entry	Electrophile E+	Product[a] No.	Product[a] E	Yield (%)[b]
1	H_2O	**15a**	H	95
2	D_2O	**15b**	D	95[c]
3	PhCHO	**15c+15c'**	PhCHOH	80[d]
4	Me_2CO	**15d**	Me_2COH	25
5	$(CH_2)_5CO$	**15e**	$(CH_2)_5COH$	65
6	CO_2	**15f**	CO_2H	34

[a] All products **15** were ≥95% pure (300 MHz ^1H NMR and/or GLC). [b] Isolated yield after column chromatography (neutral silica gel, hexane/ethyl acetate) based on the starting material **13**. [c] 90% Deuterium incorporation (from MS). [d] 3/1 Diastereomeric mixture (75 MHz ^{13}C NMR).

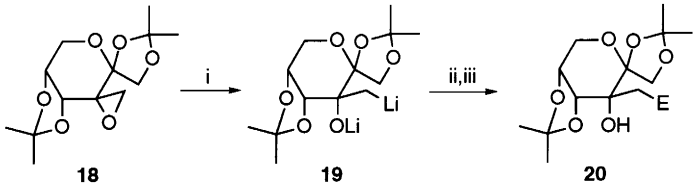
The preparation of the starting epoxide **13** was carried out starting from the commercially available triol **16**, which was treated with diisopropyl azodicarboxylate (DIAD) and triphenylphosphine in benzene at reflux, to give the epoxide **17**.[25] This epoxide was finally protected with chloromethyl ethyl ether to give **13** (Scheme 8).

In order to establish the scope of the methodology described in this paper, we applied this procedure to the epoxide **18** derived from D-fructose. This compound was used as a 4:1 diastereomeric mixture, which could not be separated chromatographically, the major compound being the structure **18**. After lithiation



Scheme 8. *Reagents and conditions*: (i) PPh_3, DIAD, PhH reflux, 2.5 h; (ii) Bu^nLi, $ClCH_2OEt$, THF, −78 to 20°C

and reaction with different electrophiles, compounds **20** were isolated resulting from the reaction of the major diasteroisomer, except for compound **20** with E=D, in which the same 4:1 mixture (**20b** and **20b′**) was obtained and separated chromatographically (Scheme 9 and Table 4). Also in this case, a dimer **20f** was prepared in poor yield when the ketone **23** was used as electrophilic component (Table 4, entry 6). Also for compound **20f** a C_2 symmetry was observed in the NMR spectra (compare to compound **11d**; see the Experimental part). The stereochemistry of compounds **18** and **20** was also confirmed by preparation of **20a** by reaction of ketone **23** with methyllithium (62% isolated yield).[24] The use of benzaldehyde afforded an 8:1 mixture of diastereomers **20c** and **20c′**, resulting from the major intermediate **19**.



Scheme 9. *Reagents and conditions*: (i) Li, DTBB (5%), THF, −78°C, 2 h; (ii) E^+=H_2O, D_2O, PhCHO, Et_2CO, $(CH_2)_5CO$, **23**, −78°C, 10 min; (iii) H_2O, −78 to 20°C

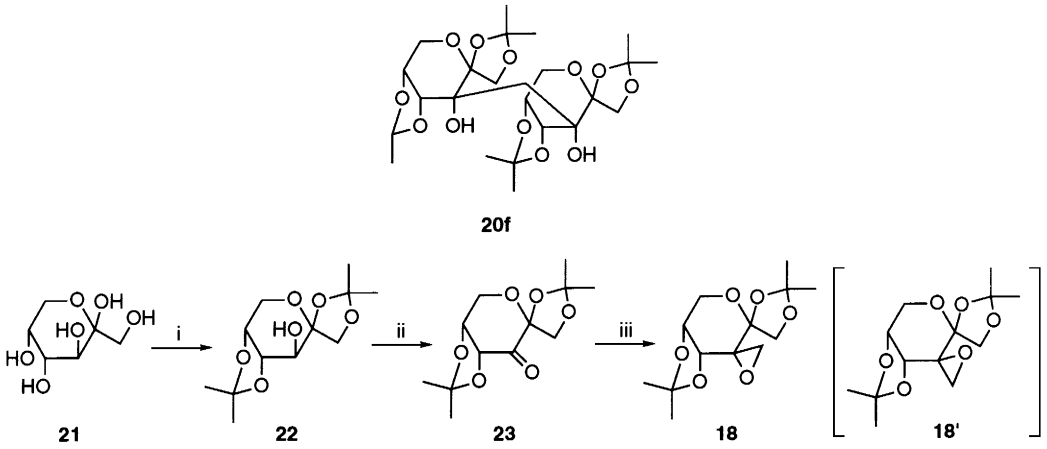
Table 4
Preparation of compounds **20** from the epoxide **18**

Entry	Electrophile E^+	Product[a] No.	Product[a] E	Yield (%)[b]
1	H_2O	**20a**	H	95[c]
2	D_2O	**20b+20b'**	D	95[c,d]
3	PhCHO	**20c+20c'**	PhCHOH	75[e]
4	Et_2CO	**20d**	Et_2COH	40
5	$(CH_2)_5CO$	**20e**	$(CH_2)_5COH$	42
6	**23**	**20f**	-	15

[a] All products **20** were ≥97% pure (300 MHz ^1H NMR and/or GLC). [b] Isolated yield after column chromatography (neutral silica gel, hexane/ethyl acetate) based on the starting material **18**. [c] A 4:1 diastereomeric mixture was obtained (75 MHz ^{13}C NMR). [d] 90% Deuterium incorporation (from MS). [e] A 8/1 Diastereomeric mixture corresponding to the structures **20** (OH group down).

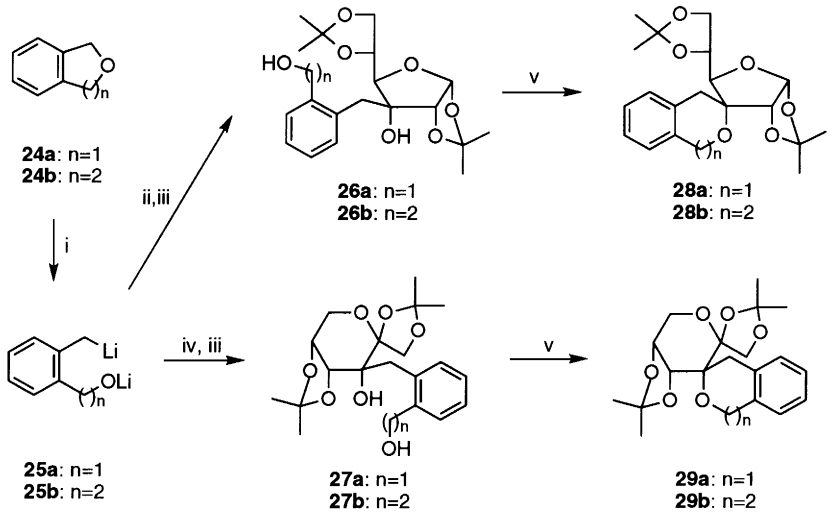
The mentioned 4:1 diastereomeric mixture of epoxides **18** and **18′** was prepared starting from the commercially available D-fructose **21**, which was converted into the compound **22** by reaction with 2,2-dimethoxypropane in acetone under perchloric acid catalysis. Compound **22** was oxidised with PCC in

CH_2Cl_2 and acetic anhydride to give the ketone **23**, which finally afforded the epoxides **18** and **18′** using the same methodology as for epoxide **1** (Scheme 10).



Scheme 10. *Reagents and conditions*: (i) $Me_2C(OMe)_2$, $HClO_4$ cat., Me_2CO, 0°C, 6 h; (ii) PCC, Ac_2O, CH_2Cl_2, 30 min; (iii) $KOBu^t$ (1 equiv.), Me_3SOI (1 equiv.), Bu^tOH, 50°C, 2.5 h

In the final part of this study we use a different approach to prepare the branched-chain functionalised sugars, which consisted of adding functionalised organolithium compounds to ketone **8** or **23** in a stereoselective manner. As organolithium component we used dianions **25a** and **25b**, easily accessible by DTBB-catalysed lithiation of phthalan **24a**[26] and isochroman **24b**,[27] respectively. Once intermediates **25** were generated, the reaction with ketone **8** or **23** at −78°C for 10 min afforded, after hydrolysis, the expected compounds **26** or **27**, respectively (Scheme 11). These diols can be easily cyclised under Mitsunobu-type reaction conditions to yield heterocycles **28** or **29**, respectively (Scheme 11).



Scheme 11. *Reagents and conditions*: (i) Li, DTBB (2.5%), THF, −78 to 20°C, 30 min; (ii) **8**, −78°C, 10 min; (iii) H_2O, −78 to 20°C; (iv) **23**, −78°C, 10 min; (v) PPh_3, DIAD, PhH reflux, 3 h

In conclusion, we have reported here a new way to prepare branched-chain functionalised carbohydrates involving functionalised organolithium compounds derived from the carbohydrate or by using an external organolithium derivative and a ketone, derived from a sugar, as the chiral source.

3. Experimental

3.1. General

Melting points were obtained with a Reichert Thermovar apparatus. FT-IR spectra were obtained on a Nicolet Impact 400D spectrophotometer. NMR spectra were recorded on a Bruker AC-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) using $CDCl_3$ as solvent and TMS as internal standard; chemical shifts are given in δ (ppm) and coupling constants (J) are given in hertz. ^{13}C NMR assignments were made on the basis of DEPT experiments. Mass spectra (EI) were obtained at 70 eV on a Shimadzu QP-5000 spectrometer, fragment ions in *m/z* with relative intensities (%) in parentheses. Elemental analyses were performed by the Microanalyses Service at the University of Alicante. High resolution mass spectra were performed by the corresponding service at the University of Alicante using a Finnigan MAT 95 S apparatus. The purity of volatile products and the chromatographic analyses (GLC) were determined with a Hewlett–Packard HP-5890 instrument equipped with a flame ionisation detector and a 12 m capillary column (0.2 mm diam., 0.33 mm film thickness), using nitrogen (2 ml/min) as carrier gas, $T_{injector}$=275°C, T_{column}=60°C (3 min) and 60–270°C (15°C/min). Thin layer chromatography (TLC) was carried out on Schleicher & Schuell F1500/LS 254 plates coated with a 0.2 mm layer of silica gel; R_f values are given under these conditions. Column chromatography was performed using silica gel 60 of 35–70 mesh. All starting materials were commercially available (Acros, Aldrich, Fluka) of the best grade and were used without further purification. THF was dried over benzophenone ketyl under an argon atmosphere and distilled before use.

3.2. Preparation of compound **8**

To a dichloromethane solution (70 ml) of commercially available D-glucose derivative **7** (5.2 g, 20 mmol) was added acetic anhydride (8 ml, 84.6 mmol) and PCC (13 g, 60 mmol) and the mixture was stirred at 25°C for 30 min. Then the resulting mixture was filtrated and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) to give 1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-ulose **8**:[28] (83% yield) R_f 0.31 (hexane:ethyl acetate, 4;1); ν (film) 1774 (C=O), 1215 cm^{-1} (CO); δ_H 1.34 (6H, s, 2×CH_3), 1.44 (3H, s, CH_3), 1.46 (3H, s, CH_3), 4.02–4.05 (2H, m, C*H*CH*H*), 4.35–4.40 (2H, m, C*H*CHCH*H*), 4.36 (1H, d, *J*=4.6, C*H*CHO_2), 6.14 (1H, d, *J*=4.6, OC*H*O); δ_C 25.3, 25.9, 27.1, 27.5 (4×CH_3), 64.3 (CH_2O), 76.3 (*C*HCH_2), 77.2 (CH_2CH*C*H), 78.9 (*C*HCHO_2), 103.1 (OCHO), 110.4, 114.3 [2×*C*$(CH_3)_2$], 176.2 (CO); *m/z* 243 [$M^+-(CH_3)$, 5.5%], 101 (56), 85 (17), 71 (10), 59 (12), 43 (100) [found: $M^+-(CH_3)$, 243.0825; $C_{11}H_{15}O_6$ requires: M, 243.0869]; $[\alpha]_D^{20}$=+131.5 [*c* 1.27 (CH_2Cl_2)] {lit.[28b] $[\alpha]_D^{20}$=+107 ($CHCl_3$)}.

3.3. Preparation of epoxide **1**

To a *tert*-butanol solution (30 ml) of trimethylsulfoxonium iodide (3.30 g, 15 mmol) was added a *tert*-butanol solution (30 ml) of potassium *tert*-butoxide (1.80 g, 16 mmol) at 50°C under argon. After 30 min at this temperature, a new *tert*-butanol solution (15 ml) of ketone **8** (3.77 g, 14.6 mmol) was added and stirring was continued for 3 h. Then the resulting mixture was evaporated (15 mmHg) and the resulting residue was hydrolysed with water (30 ml) and extracted with ethyl acetate (3×40 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) to give 3,3′-anhydro-3-*C*-hydroxymethyl-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose **1**:[29] (82% yield) R_f 0.48 (hexane:ethyl acetate, 4:1); ν

(film) 1213, 1166 cm^{-1} (CO); δ_H 1.27 (3H, s, CH_3), 1.32 (3H, s, CH_3), 1.34 (3H, s, CH_3), 1.40 (3H, s, CH_3), 3.09 (1H, d, *J*=4.9, OC*H*HC), 3.17 (1H, d, *J*=4.9, OCH*H*C), 4.00–4.04 (3H, m, CH_2CH), 4.29 (1H, d, *J*=3.7, C*H*CHO_2), 4.37 (1H, d, *J*=6.7, C*H*$CHCH_2$), 5.95 (1H, d, *J*=3.7, OCHO); δ_C 25.2, 26.4, 26.8, 26.9 (4×CH_3), 46.3 (CH_2C), 65.05 (CH_2*C*), 66.9 (*C*H_2CH), 72.9 (*C*$HCHCH_2$), 76.4 (*C*HCH_2), 84.5 (*C*$HCHO_2$), 104.2 (OCHO), 109.5, 112.6 [2×*C*$(CH_3)_2$]; *m/z* 257 [$M^+-(CH_3)$, 4.3%], 101 (26), 59 (12), 43 (100) [found: $M^+-(CH_3)$, 257.1029; $C_{12}H_{17}O_6$ requires: M, 257.1025]; $[\alpha]_D^{20}$=+55.5 [*c* 1.08 (CH_2Cl_2)] {lit.[29] $[\alpha]_D^{20}$=+55 [*c* 1.7 (MeOH)]}.

3.4. Preparation of oxetane **4**

To a *tert*-butanol solution (30 ml) of trimethylsulfoxonium iodide (8.80 g, 40 mmol) was added a *tert*-butanol solution (30 ml) of potassium *tert*-butoxide (4.48 g, 40 mmol) at 50°C under argon. After 30 min at this temperature, a new *tert*-butanol solution (10 ml) of ketone **8** (2.58 g, 10 mmol) was added and stirring was continued for 3 h. Then the resulting mixture was evaporated (15 mmHg) and the resulting residue was hydrolysed with water (30 ml) and extracted with ethyl acetate (3×40 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) to give 3,3′-anhydro-3-*C*-(3-hydroxyethyl)-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose **4**: (83% yield) R_f 0.46 (hexane:ethyl acetate, 4:1); ν (film) 1215, 1076 cm^{-1} (CO); δ_H 1.34 (3H, s, CH_3), 1.41 (3H, s, CH_3), 1.48 (6H, s, 2×CH_3), 2.77–2.86 (2H, m, CH_2CH_2O), 3.89 (1H, d, *J*=7.6, C*H*$CHCH_2$), 4.02 (1H, dd, *J*=8.5, 5.8, CHC*H*H), 4.14 (1H, dd, *J*=8.5, 6.4, CHCH*H*), 4.48–4.56 (1H, m, C*H*CH_2), 4.57–4.61 (2H, m, OCH_2CH_2), 4.67 (1H, d, *J*=3.5, C*H*CHO_2), 5.79 (1H, d, *J*=3.5, OCHO); δ_C 23.7, 25.4, 26.4, 26.9 (4×CH_3), 31.2 (OCH_2CH_2), 67.5 (OCH_2CH_2), 73.2 (CH_2CO), 77.2 (*C*H_2CH), 82.05 (CH*C*HCH_2), 85.5 (*C*$HCHCH_2$), 90.9 (CH*C*HO_2), 104.05 (OCHO), 109.3, 112.1 [2×*C*$(CH_3)_2$]; *m/z* 272 [$M^+-(CH_3)$, 2.0%], 271 (13), 111 (11), 101 (90), 99 (20), 97 (19), 95 (13), 85 (12), 83 (16), 73 (16), 72 (19), 71 (13), 69 (11), 59 (24), 55 (20), 43 (100), 42 (21) [found: $M^+-(CH_3)$, 217.1176; $C_{13}H_{19}O_6$ requires: M, 271.1181]; $[\alpha]_D^{20}$=+27.9 [*c* 0.98 (CH_2Cl_2)].

3.5. Preparation of epoxide **9**

To a suspension of lithium bromide (0.79 g, 9.1 mmol) in THF (15 ml) were added chloroiodomethane (0.66 ml, 9.1 mmol) and ketone **8** (1.7 g, 6.5 mmol) at 25°C under argon. The reaction mixture was cooled down to −78°C and 1.6 M *n*-butyllithium hexane solution (4.5 ml, 7.8 mmol) was added dropwise. The reaction mixture was allowed to get to 25°C overnight and was hydrolysed with water (30 ml) and extracted with ethyl acetate (3×30 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) to give 3,3′-anhydro-3-*C*-hydroxymethyl-1,2;5,6-di-*O*-isopropylidene-α-D-allofuranose **9**:[28a] (30% yield) R_f 0.15 (hexane:ethyl acetate, 4:1); ν (film) 1074, 1020 cm^{-1} (CO); δ_H 1.32 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.40 (3H, s, CH_3), 1.63 (3H, s, CH_3), 2.99 (1H, d, *J*=5.2, OC*H*HC), 3.39 (1H, d, *J*=5.2 OCH*H*C), 3.91 (1H, dd, *J*=7.3, 4.9, C*H*CHH), 3.96–4.08 (2H, m, C*H*C*H*H), 4.25 (1H, d, *J*=6.7, C*H*$CHCH_2$), 4.43 (1H, d, *J*=3.7, C*H*CHO_2), 5.87 (1H, d, *J*=4.3, OCHO); δ_C 25.2 (CH_3), 26.5 (2×CH_3), 26.8 (CH_3), 26.9 (CH_2), 64.3 (CH_2), 67.0 (*C*HCH_2), 75.1 (CH*C*H_2), 75.7 (*C*$HCHCH_2$), 80.5 (*C*$HCHO_2$), 103.8 (OCHO), 109.9, 113.6 [2×*C*$(CH_3)_2$]; *m/z* 257 [$M^+-(CH_3)$, 0.4%], 101 (17), 59 (20), 55 (18), 44 (12), 43 (100), 41 (16); $[\alpha]_D^{20}$=+85.6 [*c* 1.20 (CH_2Cl_2)].

3.6. Preparation of chlorohydrin **12**

To a suspension of lithium bromide (1.31 g, 14.7 mmol) in THF (20 ml) were added chloroiodomethane (1.08 ml, 15.6 mmol) and ketone **8** (2.7 g, 10.5 mmol) at 25°C under argon. The reaction mixure was cooled down to −78°C and a 1.6 M *n*-butyllithium hexane solution (9.3 ml, 14.9 mmol) was added dropwise. The reaction mixture was stirred at the same temperature for 30 min and hydrolysed with water (30 ml). After that, it was extracted with ethyl acetate (3×30 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) to give 3-*C*-chloromethyl-1,2;5,6-di-*O*-isopropylidene-α-D-allofuranose **12**: (20%) R_f 0.30 (hexane:ethyl acetate, 4:1); m.p. 122–123°C (dichloromethane/pentane); ν (KBr) 3675–3028 (OH), 1210, 1081, 1016 (CO), 800–600 cm^{-1} (CCl); δ_H 1.36 (3H, s, CH_3), 1.39 (3H, s, CH_3), 1.46 (3H, s, CH_3), 1.61 (3H, s, CH_3), 3.01 (1H, s, OH), 3.60 (1H, d, *J*=12.2, C*H*HCl), 3.89–3.97 (3H, m, CH*H*Cl, C*HCH*CH_2), 4.09–4.16 (2H, m, CHC*H*$_2$), 4.64 (1H, d, *J*=3.7, C*H*CHO_2), 5.80 (1H, d, *J*=3.7, OCHO); δ_C 25.1, 26.5, 26.6, 26.65 (4×CH_3), 45.5 (CH_2Cl), 67.9 ($CHCH_2O$), 73.0 (*C*HCH_2O), 79.2 (COH), 80.9 (*C*$HCHCH_2$), 82.1 (*C*$HCHO_2$), 103.8 (OCHO), 110.0, 112.9 [2×*C*(CH_3)]; *m/z* 293 [$M^+-(CH_3)$, 7.0%], 101 (33), 72 (12), 59 (46), 55 (19), 43 (100), 41 (14). Anal. calcd for $C_{13}H_{21}ClO_6$: C, 50.57; H, 6.85; found: C, 50.36; H, 6.63. $[\alpha]_D^{20}$=+23.4 [*c* 1.20 (CH_2Cl_2)].

3.7. Preparation of epoxide **17**

To a benzene solution (40 ml) of commercially available D-glucose derivative **16** (1.0 g, 4.54 mmol) and triphenylphosphine (1.31 g, 4.98 mmol) in the presence of 4 Å molecular sieves under argon was added dropwise diisopropyl azodicarboxylate (0.97 ml, 4.98 mmol) at 25°C. The reaction mixture was heated at 80°C for 2.5 h. Then the resulting mixture was evaporated (15 mmHg) and the resulting residue was hydrolysed with water (30 ml) and extracted with ethyl acetate (3×40 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) to give 5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose **17**:[30] (80% yield) R_f 0.28 (hexane:ethyl acetate, 3:2); ν (film) 3538–3140 (OH), 1083, 1065 cm^{-1} (CO); δ_H 1.32 (3H, s, CH_3), 1.48 (3H, s, CH_3), 2.87 (1H, dd, *J*=4.6, 2.7, OC*H*H), 2.97–3.00 (1H, m, OCH*H*), 3.30 (1H, br s, OH), 3.40–3.43 (1H, m, C*H*CH_2), 4.00–4.03 (1H, m, C*H*$CHCH_2$), 4.24–4.29 (1H, m, C*H*OH), 4.52 (1H, d, *J*=3.7, C*H*CHO_2), 5.98 (1H, d, *J*=3.7, OCHO); δ_C 26.1, 26.7 (2×CH_3), 45.9 (CH_2O), 50.3 (*C*HCH_2), 75.2 (COH), 79.2 (*C*$HCHCH_2$), 85.0 (*C*$HCHO_2$), 104.9 [*C*(CH_3)$_2$], 111.8 (OCHO); *m/z* 187 [$M^+-(CH_3)$, 12.2%], 59 (82), 57 (13), 55 (15), 43 (100); $[\alpha]_D^{20}$=−25.0 [*c* 1.00 ($CHCl_3$)] {lit.[30] $[\alpha]_D^{20}$=−25 [*c* 1 ($CHCl_3$)]}.

3.8. Preparation of epoxide **13**

To a THF solution (40 ml) of epoxide **17** (0.91 g, 4.56 mmol) at −78°C under argon was added dropwise a 1.6 M *n*-butyllithium hexane solution (3.64 ml, 5.47 mmol). After 5 min at the same temperature, chloromethyl ethyl ether (0.92 ml, 5.47 mmol) was added and the reaction mixture was allowed to rise to 25°C overnight and then hydrolysed with water (30 ml) and extracted with ethyl acetate (3×40 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) to give 5,6-anhydro-3-*O*-ethoxymethyl-1,2-*O*-isopropylidene-α-D-glucofuranose **13**: (79% yield) R_f 0.60 (hexane:ethyl acetate, 3:2); ν (film) 1088, 1031 cm^{-1} (CO); δ_H 1.24 (3H, t, *J*=6.9, CH_2CH_3), 1.47 (3H,

s, CH_3), 1.49 (3H, s, CH_3), 2.76–2.78 (1H, m, CHC*H*H), 2.87–2.92 (1H, m, CHCH*H*), 3.20–3.24 (1H, m, C*H*CH_2), 3.60–3.71 (2H, m, C*H*$_2CH_3$), 3.76 (1H, dd, *J*=7.0, 3.0, C*H*CHCH_2), 4.31 (1H, d, *J*=3.0, C*H*OCH_2O), 4.62 (1H, d, *J*=3.5, C*H*CHO_2), 4.77–4.83 (2H, m, OCH_2O), 5.92–5.98 (1H, m, OCHO); δ_C 14.9 (CH_2*C*H_3), 26.1, 26.7 (2×CH_3), 46.8 (CHCH*C*H_2), 48.1 (CH*C*HCH_2), 63.8 (*C*H_2CH_3), 79.4 (*C*HOCH_2O), 81.4 (*C*HCHCH_2), 83.1 (*C*HCHO_2), 94.3 (OCH_2O), 105.2 (OCHO), 111.9 (OCO); *m/z* 245 [$M^+-(CH_3)$, 5.5%], 129 (30), 117 (16), 85 (25), 73 (12), 69 (12), 59 (100), 57 (15), 55 (36) 43 (84) [found: M^+, 260.1251; $C_{12}H_{20}O_6$ requires: M, 260.1259]; $[\alpha]_D^{20}=-38.8$ [*c* 1.44 (CH_2Cl_2)].

3.9. Preparation of ketone **23**

To a suspension of D-fructose (18.42 g, 100 mmol) and 2,2-dimethoxypropane (7.4 ml, 60 mmol) in acetone (370 ml) was added perchloric acid (4.3 ml, 70%) at 0°C. The reaction mixture was stirred at the same temperature for 6 h. After that, a saturated ammonium hydroxide aqueous solution (5 ml) was added. Then the resulting mixture was evaporated (15 mmHg) and the resulting residue was hydrolysed with water (30 ml) and extracted with dichloromethane (3×40 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was compound **22** and was used for the preparation of ketone **23** without further purification. To a dichloromethane solution (80 ml) of D-fructose derivative **22** (7.74 g, 30 mmol) were added acetic anhydride (12 ml, 126.9 mmol) and PCC (19.5 g, 90 mmol) and the mixture was stirred at 25°C for 30 min. Then the resulting mixture was filtrated and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) to give 1,2;4,5-di-*O*-isopropylidene-β-D-fructopyranos-3-ulose **23**:[31] (91% yield) R_f 0.23 (hexane:ethyl acetate, 4:1); m.p. 96–97°C (dichloromethane/pentane) (lit.[31b] m.p. 102–103°C); ν (KBr) 1748 (C=O), 1229, 1099 cm^{-1} (CO); δ_H 1.40 (6H, s, 2×CH_3), 1.46 (3H, s, CH_3), 1.55 (3H, s, CH_3), 3.99 (1H, d, *J*=9.5, CC*H*HO), 4.12 (1H, d, *J*=13.4, CHC*H*HO), 4.39 (1H, dd, *J*=13.4, 1.8, CHCH*H*O), 4.55 (1H, dd, *J*=5.5, 1.2, C*H*CHCO), 4.61 (1H, d, *J*=9.5, CC*H*HO), 4.73 (1H, d, *J*=5.5, CHCO); δ_C 26.0 (2×CH_3), 26.5 (CH_3), 27.1 (CH_3), 60.1 (CH*C*H_2O), 70.0 (*C*HCH_2O), 75.8 (CCH_2O), 77.9 (*C*HCO), 104.1 (*C*CH_2O), 110.6, 113.8 [2×*C*$(CH_3)_2$], 196.9 (CO); *m/z* 243 [$M^+-(CH_3)$, 9.0%], 117 (33), 114 (36), 85 (36), 72 (11), 59 (72), 58 (10), 56 (14), 43 (100), 42 (47), 41 (23); $[\alpha]_D^{20}=-100.9$ [*c* 1.35 (CH_2Cl_2)].

3.10. Preparation of epoxide **18**

To a *tert*-butanol solution (50 ml) of trimethylsulfoxonium iodide (4.58 g, 20.8 mmol) was added a *tert*-butanol solution (50 ml) of potassium *tert*-butoxide (2.33 g, 20.8 mmol) at 50°C under argon. After 30 min at this temperature, a new *tert*-butanol solution (50 ml) of ketone **22** (5.38 g, 20.8 mmol) was added and stirring was continued for 3 h. Then the resulting mixture was evaporated (15 mmHg) and the resulting residue was hydrolysed with water (30 ml) and extracted with ethyl acetate (3×40 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) to give 3,3′-anhydro-3-*C*-hydroxymethyl-1,2;4,5-di-*O*-isopropylidene-β-D-psicopyranose **18**: (83% yield) R_f 0.55 (hexane:ethyl acetate, 3:2); ν (film) 1096, 1021 cm^{-1} (CO); δ_H 1.32 (3H, s, CH_3), 1.33 (3H, s, CH_3), 1.48 (3H, s, CH_3), 1.54 (3H, s, CH_3), 2.68 (1H, d, *J*=5.5, CHCC*H*HO), 3.22 (1H, d, *J*=5.5, CHCCH*H*O), 3.83–3.84 (1H, m, CHC*H*HO), 4.01–4.08 (3H, m, CHCH*H*O, C*H*CH_2O, CC*H*HO), 4.23 (1H, d, *J*=9.1, CCH*H*O), 4.39 (1H, d, *J*=7.3, C*H*CHCH2); δ_C 25.1 (CH_3), 25.9 (CH_3), 26.1 (2×CH_3), 48.6 (CHC*C*H_2O), 63.8 (CH*C*CH_2O, CH*C*H_2O), 73.5 (CC*C*H_2O), 75.0 (*C*HCH_2O), 75.8 (*C*HCHCH_2O), 110.4 (2×*C*CH_3), 110.8 (C*C*CH_2O);

m/z 257 [$M^+-(CH_3)$, 15%], 139 (14), 72 (29), 59 (15), 55 (12), 43 (100), 42 (25), 41 (15) (found: M^+, 272.1280; $C_{13}H_{20}O_6$ requires: M, 272.1260); $[\alpha]_D{}^{20}=-120.1$ [*c* 1.20 (CH_2Cl_2)].

*3.11. DTBB-catalysed lithiation of epoxides **1**, **9**, **13** and **18**, and reaction with electrophiles. Isolation of compounds **3**, **11**, **15** and **20**. General procedure*

To a cooled (−78°C) blue suspension of lithium powder (0.10 g, 14.0 mmol) and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (0.04 g, 0.15 mmol) in THF (5 ml) was added the corresponding epoxide (1.0 mmol) uner argon and the mixture was stirred at the same temperature for 2 h in the case of compounds **1**, **9** and **18** and 2.5 h in the case of compounds **13**. Then the corresponding electrophile (1.2 mmol; 0.5 ml in the case of water and deuterium oxide; CO_2 was bubbled for 30 min) was added at −78°C and the temperature was allowed to rise to 20°C overnight. The resulting mixture was hydrolysed with water (20 ml) and extracted with ethyl acetate (3×20 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) and/or recrystallised to yield pure products **3**, **11**, **15** and **20**. Yields are included in Tables 1, 3 and 4. Physical, spectroscopic and analytical data follow.

*3.11.1. 1,2;5,6-Di-*O*-isopropylidene-3-*C*-methyl-α-*D*-glucofuranose **3a**[29]*

R_f 0.31 (hexane:ethyl acetate, 4:1); ν (film) 3664–3061 (OH), 1215, 1076 cm^{-1} (CO); δ_H 1.32 (3H, s, CH_3), 1.35 (3H, s, CH_3), 1.44 (3H, s, CH_3), 1.47 (3H, s, CH_3), 1.51 (3H, s, CH_3), 2.14 (1H, br s, OH), 3.80 (1H, d, *J*=7.6, C*H*CHCH$_2$), 3.97–4.02 (1H, m, OC*H*H), 4.12–4.17 (1H, m, OCH*H*), 4.23 (1H, d, *J*=3.5, C*H*CHO$_2$), 4.25–4.30 (1H, m, C*H*CH$_2$), 5.86 (1H, d, *J*=3.5, OCHO); δ_C 20.0, 25.2, 26.4, 26.7, 27.1 (5×CH_3), 67.7 (CH*C*H$_2$), 73.6 (*C*HCH$_2$), 80.05 (*C*HCHCH$_2$), 83.1 (*C*HCHO$_2$), 87.65 (COH), 104.6 (OCHO), 109.6, 112.3 [2×*C*(CH$_3$)$_2$]; *m/z* 259 [$M^+-(CH_3)$, 16.6%], 159 (16), 101 (48), 100 (44), 99 (11), 85 (30), 83 (19), 73 (11), 72 (13), 71 (13), 59 (67), 55 (14), 43 (100), 42 (16) [found: $M^+-(CH_3)$, 259.1158; $C_{12}H_{19}O_6$ requires: M, 259.1182]; $[\alpha]_D{}^{20}=+21.1$ [*c* 0.72 (CH_2Cl_2)] {lit.[29] $[\alpha]_D{}^{20}=+23$ [*c* 1.0 (Me_2CO)]}.

*3.11.2. 3-*C*-Deuteriomethyl-1,2;5,6-di-*O*-isopropylidene-α-*D*-glucofuranose **3b***

R_f 0.31 (hexane:ethyl acetate, 4:1); ν (film) 3664–3061 (OH), 1215, 1076 cm^{-1} (CO); δ_H 1.32 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.44 (3H, s, CH_3), 1.47 (2H, s, CH_2D), 1.51 (3H, s, CH_3), 2.35 (1H, br s, OH), 3.80 (1H, d, *J*=7.6, C*H*CHCH$_2$), 3.98–4.02 (1H, m, OC*H*H), 4.11–4.16 (1H, m, OCH*H*), 4.23 (1H, d, *J*=3.5, C*H*CHO$_2$), 4.25–4.32 (1H, m, C*H*CH$_2$), 5.86 (1H, d, *J*=3.5, OCHO); δ_C 19.6 (t, J_{CD}=19.5, CH_2D), 25.2, 26.4, 26.65, 27.1 (4×CH_3), 67.7 (CH*C*H$_2$), 73.5 (*C*HCH$_2$), 79.9 (*C*HCHCH$_2$), 83.0 (*C*HCHO$_2$), 87.6 (COH), 104.5 (OCHO), 109.5, 112.2 [2×*C*(CH$_3$)$_2$]; *m/z* 260 [$M^+-(CH_3)$, 9.3%], 101 (39), 100 (40), 85 (23), 84 (10), 72 (14), 59 (63), 55 (10), 44 (63), 43 (100), 42 (16) [found: $M^+-(CH_3)$, 260.1247; $C_{12}H_{18}DO_6$ requires: M, 260.1244]; $[\alpha]_D{}^{20}=+22.9$ [*c* 1.25 (CH_2Cl_2)].

*3.11.3. 1,2;5,6-Di-*O*-isopropylidene-3-*C*-(trimethylsilylmethyl)-α-*D*-glucofuranose **3c***

R_f 0.27 (hexane:ethyl acetate, 4:1); ν (film) 3643–3117 (OH), 1069, 1013 cm^{-1} (CO); δ_H 0.18 [9H, s, Si(CH$_3$)$_3$], 1.21 (2H, s, CH$_2$Si), 1.31 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.45 (3H, s, CH_3), 1.50 (3H, s, CH_3), 1.95 (1H, br s, OH), 3.81 (1H, d, *J*=6.7, C*H*CHCH$_2$), 3.96–4.01 (1H, m, OC*H*H), 4.11–4.16 (1H, m, OCH*H*), 4.25 (1H, d, *J*=3.7, C*H*CHO$_2$), 4.25–4.29 (1H, m, C*H*CH$_2$), 5.83 (1H, d, *J*=3.7, OCHO); δ_C 0.3 [Si(CH$_3$)$_3$], 21.5 (CH$_2$Si), 25.2, 26.2, 26.6, 27.1 (4×CH_3), 67.7 (COH), 74.1 (CH$_2$O), 82.7 (*C*HCH$_2$O), 84.5 (*C*HCHCH$_2$), 86.1 (*C*HCHO$_2$), 104.6 (OCHO), 109.6, 112.0 [2×*C*(CH$_3$)$_2$]; *m/z* 331 [$M^+-(CH_3)$, 0.1%], 115 (45), 101 (19), 100 (47), 85 (26), 75 (34), 73 (76), 59 (25), 55 (10), 45 (19), 44

(27), 43 (100) [found: $M^+-(CH_3)$, 331.1585; $C_{15}H_{27}O_6Si$ requires: M, 331.1577]; $[\alpha]_D^{20}$=+27.8 [*c* 1.18 (CH_2Cl_2)].

*3.11.4. (2′*R*)-3-*C*-(2-Hydroxy-2-phenylmethyl)-1,2;5,6-di-*O*-isopropylidene-α-*D*-glucofuranose **3d***

Minor isomer: R_f 0.29 (hexane:ethyl acetate, 4:1); ν (film) 3691–3107 (OH), 3033 (ArCH), 1065 cm^{-1} (CO); δ_H 1.34 (3H, s, CH_3), 1.37 (6H, s, 2×CH_3), 1.51 (3H, s, CH_3), 2.02–2.07 (1H, m, COHC*H*H), 2.25–2.33 (1H, m, COHCH*H*), 2.66 (1H, br s, OH), 2.88 (1H, br s, OH), 3.83 (1H, d, *J*=6.7, C*H*CHCH$_2$), 4.00–4.13 (2H, m, OCHC*H*$_2$), 4.38–4.42 (1H, m, OC*H*CH$_2$), 4.60 (1H, d, *J*=3.4, C*H*CHO$_2$), 5.19–5.23 (1H, m, C*H*OH), 5.93 (1H, d, *J*=3.4, OCHO), 7.12–7.40 (5H, m, ArH); δ_C 25.3, 26.6, 26.7, 27.2 (4×CH_3), 39.5 (*C*H$_2$COH), 67.2 (CH$_2$*C*OH), 73.0 (CH$_2$*C*HOH), 73.7 (CH$_2$O), 82.1 (*C*HCH$_2$O), 83.6 (*C*HCHCH$_2$), 85.9 (*C*HCHO$_2$), 104.8 (OCHO), 109.1, 112.4 [2×*C*(CH$_3$)$_2$], 125.6, 128.1, 128.7 (ArCH), 144.0 (ArC); *m/z* 289 [$M^+-(PhCH_2)$, 1.6%], 105 (13), 104 (13), 101 (18), 100 (20), 85 (13), 59 (12), 58 (14), 44 (32), 43 (100), 42 (11) [found: $M^+-(CH_3, CH_3COCH_3, H_2O)$, 289.1081; $C_{16}H_{17}O_5$ requires: M, 289.1076]; $[\alpha]_D^{20}$=+33.3 [*c* 1.11 (CH_2Cl_2)].

*3.11.5. (2′*S*)-3-*C*-(2-Hydroxy-2-phenylmethyl)-1,2;5,6-di-*O*-isopropylidene-α-*D*-glucofuranose **3d′***

Major isomer:[21] R_f 0.24 (hexane:ethyl acetate, 4:1); m.p. 94–95°C (dichloromethane/pentane); ν (KBr) 3708–3118 (OH), 3061, 3036 (ArCH), 1222, 1063 cm^{-1} (CO); δ_H 1.28 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.41 (3H, s, CH_3), 1.49 (3H, s, CH_3), 2.25–2.28 (2H, m, COHC*H*$_2$), 3.00 (1H, br s, OH), 3.70 (1H, br s, OH), 3.88 (1H, d, *J*=7.3, C*H*CHCH$_2$), 4.00 (1H, dd, *J*=8.5, 6.1, CHC*H*H), 4.14 (1H, dd, *J*=8.5, 6.1, CHCH*H*), 4.35–4.41 (2H, m, OC*H*CH$_2$, C*H*CHO$_2$), 5.23–5.29 (1H, m, C*H*OH), 5.82 (1H, d, *J*=3.4, OCHO), 7.11–7.37 (5H, m, ArH); δ_C 25.4, 26.4, 26.6, 27.1 (4×CH_3), 40.4 (*C*H$_2$COH), 67.8 (CH$_2$*C*OH), 71.2 (CH$_2$*C*HOH), 72.9 (CH$_2$O), 81.2 (*C*HCH$_2$O), 84.1 (*C*HCHCH$_2$), 87.4 (*C*HCHO$_2$), 104.3 (OCHO), 109.5, 112.2 [2×*C*(CH$_3$)$_2$], 125.6, 127.6, 128.5 (ArCH), 144.4 (ArC); *m/z* 322 [$M^+-(2\times CH_3, H_2O)$, 0.6%], 105 (14), 104 (15), 101 (14), 100 (21), 85 (14), 59 (13), 58 (15), 44 (18), 43 (100), 42 (10) [found: $M^+-(CH_3)$, 369.1605; $C_{19}H_{25}O_7$ requires: M, 365.1600]; $[\alpha]_D^{20}$=+19.5 [*c* 1.12 (CH_2Cl_2)].

*3.11.6. 3-*C*-(2-Hydroxy-2-methylpropyl)-1,2;5,6-di-*O*-isopropylidene-α-*D*-glucofuranose **3e***

R_f 0.27 (hexane:ethyl acetate, 4:1); ν (film) 3670–3074 (OH), 1165, 1069 cm^{-1} (CO); δ_H 1.32 (3H, s, CH_3), 1.35 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.44 (3H, s, CH_3), 1.47 (3H, s, CH_3), 1.49 (3H, s, CH_3), 1.95 (1H, d, *J*=14.9, C*H*HCOH), 2.16 (1H, d, *J*=14.9, CH*H*COH), 2.37 (1H, br s, OH), 3.77 (1H, d, *J*=6.4, C*H*CHCH$_2$), 4.03–4.13 (2H, m, CHC*H*$_2$), 4.34–4.41 (1H, m, C*H*CH$_2$), 4.50 (1H, d, *J*=3.4, C*H*CHO$_2$), 5.11 (1H, br s, OH), 5.87 (1H, d, *J*=3.4, OCHO); δ_C 25.45, 26.5, 26.7, 27.2 (4×CH_3), 28.9, 33.7 [COH(*C*H$_3$)$_2$], 40.0 (*C*H$_2$C), 67.4 [*C*OH(CH$_3$)$_2$], 73.1 (*C*OHCH$_2$), 77.2 (CH$_2$O), 81.5 (*C*HCH$_2$), 84.2 (*C*HCHCH$_2$), 86.2 (*C*HCHO$_2$), 105.0 (OCHO), 109.1, 112.0 [2×*C*(CH$_3$)$_2$]; *m/z* 299 [$M^+-(CH_3, H_2O)$, 1.6%], 241 (12), 143 (35), 111 (11), 101 (55), 100 (68), 97 (10), 85 (55), 83 (29), 73 (11), 72 (15), 71 (31), 59 (76), 58 (12), 57 (17), 56 (13), 55 (33), 44 (10), 43 (100), 42 (18) [found: $M^+-(CH_3)$, 317.1555; $C_{15}H_{25}O_7$ requires: M, 317.1600]; $[\alpha]_D^{20}$=+27.8 [*c* 1.50 (CH_2Cl_2)].

*3.11.7. 3-*C*-(1-Hydroxycyclohexylmethyl)-1,2;5,6-di-*O*-isopropylidene-α-*D*-glucofuranose **3f***[32]

R_f 0.34 (hexane:ethyl acetate, 4:1); m.p. 108–109°C (dichloromethane/pentane); ν (KBr) 3689–3093 (OH), 1222, 1158 cm^{-1} (CO); δ_H 1.32 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.44 (3H, s, CH_3), 1.50 (3H, s, CH_3), 1.30–1.96 [10H, m, (CH$_2$)$_5$], 2.00–2.08 (2H, m, COHC*H*$_2$), 2.47 (2H, br s, 2×OH), 3.78 (1H, d, *J*=7.3, C*H*CHCH$_2$), 4.01–4.13 (2H, m, CHC*H*$_2$), 4.34–4.41 (1H, m, C*H*CH$_2$), 4.46 (1H, d, *J*=3.1, C*H*CHO$_2$), 5.85 (1H, d, *J*=3.1, OCHO); δ_C 21.8, 21.9, 25.3 (3×CH_2), 25.45, 26.5, 26.7, 27.25 (4×CH_3), 36.6, 39.15, 41.15 (3×CH_2), 67.3 [COH(CH$_2$)$_5$], 73.1 (*C*OHCH), 74.0 (CH$_2$O), 81.3 (*C*HCH$_2$), 84.2

(*C*HCHCH$_2$), 86.4 (*C*HCHO$_2$), 105.0 (OCHO), 109.0, 111.9 [2×*C*(CH$_3$)$_2$]; *m/z* 357 [M$^+$−(CH$_3$), 0.6%], 281 (23), 183 (21), 143 (52), 101 (83), 100 (100), 99 (36), 95 (35), 85 (71), 81 (43), 71 (38), 67 (21), 59 (62), 57 (21), 55 (63), 43 (98), 42 (28); $[\alpha]_D^{20}$=+30.1 [*c* 1.79 (CH$_2$Cl$_2$)].

3.11.8. 1,2;5,6-Di-O-*isopropylidene-3*-C-*methyl*-α-D-*allofuranose* ***11a***[28a]

R_f 0.13 (hexane:ethyl acetate, 4:1) (48% yield); ν (film) 3637–3107 (OH), 1076, 1008 cm^{-1} (CO); δ_H 1.28 (3H, s, CH$_3$), 1.35 (3H, s, CH$_3$), 1.36 (3H, s, CH$_3$), 1.45 (3H, s, CH$_3$), 1.59 (3H, s, CH$_3$), 2.68 (1H, br s, OH), 3.78 (1H, d, *J*=7.3, C*H*CHCH$_2$), 3.98 (1H, dd, *J*=11.1, 8.1, C*H*H), 4.07–4.13 (2H, m, C*H*CH*H*), 4.17 (1H, d, *J*=3.7, C*H*CHO$_2$), 5.7 (1H, d, *J*=3.7, OCHO); δ_C 19.5, 25.2, 26.4, 26.6, 26.7 (5×CH$_3$), 67.7 (CH*C*H$_2$), 73.7 (*C*HCH$_2$), 77.4 (*C*HCHCH$_2$), 81.4 (*C*HCHO$_2$), 84.7 (COH), 103.6 (OCHO), 109.5, 112.8 [2×*C*(CH$_3$)$_2$]; *m/z* 259 [M$^+$−(CH$_3$), 6.4%], 101 (16), 100 (24), 85 (13), 59 (39), 55 (14), 44 (13), 43 (100) [found: M$^+$−(CH$_3$), 259.1176; $C_{12}H_{19}O_6$ requires: M, 259.1182]; $[\alpha]_D^{20}$=+23.7 [*c* 1.26 (CH$_2$Cl$_2$)].

3.11.9. 6-Deoxy-3-O-*ethoxymethyl-1,2*-O-*isopropylidene*-α-D-*glucofuranose* ***15a***

R_f 0.38 (hexane:ethyl acetate, 3:2); ν (film) 3645–3106 (OH), 1082, 1025 cm^{-1} (CO); δ_H 1.24 (3H, t, *J*=7.0, CH$_2$C*H*$_3$), 1.34 (3H, d, *J*=6.1, CHC*H*$_3$), 1.50 (3H, s, CH$_3$), 1.56 (3H, s, CH$_3$), 3.06 (1H, d, *J*=4.6, OH), 3.56–3.71 (2H, m, C*H*$_2$CH$_3$), 3.93 (1H, dd, *J*=8.2, 2.7, C*H*CHOH), 3.98–4.02 (1H, m, C*H*OH), 4.22 (1H, d, *J*=2.7, C*H*CHCHOH), 4.56 (1H, d, *J*=3.7, C*H*CHO$_2$), 4.75 (1H, d, *J*=6.4, OC*H*HO), 4.80 (1H, d, *J*=6.4, OCH*H*O), 5.92 (1H, d, *J*=3.7, OCHO); δ_C 14.9 (CH$_2$*C*H$_3$), 20.4 (CHOH*C*H$_3$), 26.3, 26.8 (2×CH$_3$), 64.4 (*C*H$_2$CH$_3$), 64.9 (*C*HOCH$_2$O), 81.7 (CHOH), 83.6 (*C*HCHOH), 84.1 (*C*HCHO$_2$), 95.6 (OCH$_2$O), 105.1 (OCHO), 111.8 (OCO); *m/z* 247 [M$^+$−(CH$_3$), 0.5%], 113 (32), 85 (13), 59 (100), 55 (11), 45 (21), 44 (11), 43 (72) [found: M$^+$−(CH$_3$), 247.1176; $C_{11}H_{19}O_6$ requires: M, 247.1182]; $[\alpha]_D^{20}$=−48.2 [*c* 1.10 (CH$_2$Cl$_2$)].

3.11.10. 6-Deoxy-6-deuterio-3-O-*ethoxymethyl-1,2*-O-*isopropylidene*-α-D-*glucofuranose* ***15b***

R_f 0.38 (hexane:ethyl acetate, 3:2); ν (film) 3645–3106 (OH), 1082, 1025 cm^{-1} (CO); δ_H 1.26 (3H, t, *J*=3.6, CH$_2$C*H*$_3$), 1.31 (6H, s, 2×CH$_3$), 1.32–1.35 (2H, m, CH$_2$D), 3.10 (1H, d, *J*=4.9, OH), 3.56–3.74 (2H, m, C*H*$_2$CH$_3$), 3.93 (1H, dd, *J*=8.1, 2.9, C*H*CHOH), 3.99–4.10 (1H, m, C*H*OH), 4.23 (1H, d, *J*=3.0, C*H*OCH$_2$O), 4.56 (1H, d, *J*=3.8, C*H*CHO$_2$), 4.75 (1H, d, *J*=6.4, OC*H*HO), 4.80 (1H, d, *J*=6.4, OCH*H*O), 5.90 (1H, d, *J*=3.8, OCHO); δ_C 14.9 (CH$_2$*C*H$_3$), 20.1 (t, J_{CD}=20.1, *C*H$_2$D), 26.2, 26.7 (2×CH$_3$), 64.4 (*C*H$_2$CH$_3$), 64.8 (*C*HOCH$_2$O), 81.7 (CHOH), 83.6 (*C*HCHOH), 84.0 (*C*HCHO$_2$), 95.5 (OCH$_2$O), 105.1 (OCHO), 111.8 (OCO); *m/z* 248 [M$^+$−(CH$_3$), 0.3%], 113 (38), 85 (20), 84 (11), 71 (11), 60 (11), 59 (100), 55 (17), 46 (16), 45 (14), 44 (21), 43 (82), 41 (32) [found: M$^+$, 263.1475; $C_{12}H_{21}DO_6$ requires: M, 263.1479]; $[\alpha]_D^{20}$=−41.3 [*c* 1.46 (CH$_2$Cl$_2$)].

*3.11.11. (1′*S*)-6-Deoxy-3*-O-*ethoxymethyl-6*-C-*(hydroxyphenylmethyl)-1,2*-O-*isopropylidene*-α-D-*glucofuranose* ***15c***

Major isomer: R_f 0.27 (hexane:ethyl acetate, 3:2); ν (film) 3682–3085 (OH), 3024 (ArH), 1085, 1031 cm^{-1} (CO); δ_H 1.22 (3H, t, *J*=7.0, CH$_2$C*H*$_3$), 1.30 (3H, s, CH$_3$), 1.49 (3H, s, CH$_3$), 2.00–2.10 (1H, m, CHOHC*H*H), 2.20 (1H, dd, *J*=14.6, 7.9, CHOHCH*H*), 3.24 (1H, br s, OH), 3.51–3.70 (2H, m, C*H*$_2$CH$_3$), 3.78 (1H, br s, OH), 4.10 (2H, m, C*H*C*H*OH), 4.20 (1H, m, C*H*CHCHOH), 4.53 (1H, d, *J*=3.7, C*H*CHO$_2$), 4.72 (1H, d, *J*=6.7, OC*H*HO), 5.08–5.11 (1H, m, CHPh), 4.77 (1H, d, *J*=6.7, OCH*H*O), 5.88 (1H, d, *J*=3.7, OCHO), 7.22–7.40 (5H, m, ArH); δ_C 14.9 (CH$_2$*C*H$_3$), 26.3, 26.8 (2×CH$_3$), 41.7 (CHOH*C*H$_2$), 64.6 (*C*H$_2$CH$_3$), 66.3 (*C*HOCH$_2$O), 71.5 (*C*HCHOH), 82.0 (PhCHOH), 82.2 (*C*HCHOH), 83.6 (*C*HCHO$_2$), 95.9 (OCH$_2$O), 105.1 (OCHO), 111.9 (OCO), 125.6, 127.1, 128.3

(ArCH), 144.5 (ArC); *m/z* 335 [$M^+-(CH_3, H_2O)$, 0.2%], 113 (31), 105 (16), 77 (10), 59 (100), 43 (36) [found: $M^+-(2H_2O, CH_3COCH_3)$, 274.1208; $C_{16}H_{18}O_4$ requires: M, 274.1205]; $[\alpha]_D^{20}=-18.2$ [*c* 1.00 (CH_2Cl_2)].

*3.11.12. (1′*R*)-6-Deoxy-3*-O-*ethoxymethyl-6*-C-*(hydroxyphenylmethyl)-1,2*-O-*isopropylidene-α*-D-*glucofuranose **15c′***

Minor isomer: R_f 0.34 (hexane:ethyl acetate, 3:2); ν (film) 3658–3113 (OH), 3058, 3054 (ArH), 1085, 1024 cm^{-1} (CO); δ_H 1.25 (3H, t, *J*=3.7, CH_2CH_3), 1.30 (3H, s, CH_3), 1.46 (3H, s, CH_3), 1.84–1.96 (1H, m, CHOHC*H*H), 2.15–2.20 (1H, m, C*H*OHCH*H*), 3.57–3.79 (2H, m, CH_2CH_3), 3.82 (1H, br s, OH), 3.98 (1H, dd, *J*=8.2, 2.7, C*H*CHOH), 4.16 (1H, m, C*H*OH), 4.19 (1H, br s, OH), 4.21 (1H, d, *J*=3.0, C*H*CHCHOH), 4.55 (1H, d, *J*=3.7, C*H*CHO_2), 4.76 (1H, d, *J*=6.7, OC*H*HO), 4.84 (1H, d, *J*=6.7, OCH*H*O), 5.00–5.03 (1H, m, CHPh), 5.89 (1H, d, *J*=3.7, OCHO), 7.24–7.40 (5H, m, ArH); δ_C 14.9 (CH_2CH_3), 26.3, 26.7 (2×CH_3), 42.8 (CHOH*C*H_2), 64.5 (*C*H_2CH_3), 69.7 (*C*HOCH_2O), 75.0 (*C*HCHOH), 81.5 (PhCHOH), 82.7 (*C*HCHOH), 83.6 (*C*HCHO_2), 95.8 (OCH_2O), 105.1 (OCHO), 112.0 (OCO), 125.6, 127.4, 128.3 (ArCH), 144.4 (ArC); *m/z* 321 [$M^+-(CH_2CH_3, H_2O)$, 0.6%], 113 (16), 105 (15), 77 (10), 59 (100), 43 (39) [found: $M^+-(2H_2O, CH_3COCH_3)$, 274.1208; $C_{16}H_{18}O_4$ requires: M, 274.1205]; $[\alpha]_D^{20}=-38.3$ [*c* 1.15 (CH_2Cl_2)].

3.11.13. 6-Deoxy-3-O-*ethoxymethyl-6*-C-*[(1-hydroxy-1-methyl)ethyl]-1,2*-O-*isopropylidene-α*-D-*glucofuranose **15d**[32]*

R_f 0.34 (hexane:ethyl acetate, 3:2); ν (film) 3670–3087 (OH), 1083, 1033 cm^{-1} (CO); δ_H 1.26 (3H, t, *J*=7.0, CH_2CH_3), 1.27 (3H, s, CH_3), 1.31 (3H, s, CH_3), 1.33 (3H, s, CH_3), 1.49 (3H, s, CH_3), 1.73 (1H, dd, *J*=14.6, 11.0, CHOHC*H*H), 1.78 (1H, dd, *J*=14.6, 2.4, CHOHCH*H*), 3.42 (1H, br s, OH), 3.59–3.77 (2H, m, CH_2CH_3), 3.97 (1H, dd, *J*=8.5, 3.0, CHOHC*H*), 4.08 (1H, br s, OH), 4.22–4.27 (2H, m, C*H*OH, C*H*OCH_2O), 4.56 (1H, d, *J*=3.7, C*H*CHO_2), 4.77 (1H, d, *J*=6.1, OC*H*HO), 4.84 (1H, d, *J*=6.1, OCH*H*O), 5.90 (1H, d, *J*=3.7, OCHO); δ_C 14.9 (CH_2CH_3), 26.3, 26.8 (2×CH_3), 27.9, 31.6 (2×COH*C*H_3), 45.2 (CHOH*C*H_2), 64.4 (*C*H_2CH_3), 66.8 (*C*HOCH_2O), 71.3 (COH), 81.5 (CHOH), 83.6 (*C*HCHOH), 95.8 (OCH_2O), 105.0 (OCHO), 111.9 (OCO); *m/z* 305 [$M^+-(CH_3)$, 0.4%], 59 (100), 43 (71); $[\alpha]_D^{20}=-17.0$ [*c* 1.15 (CH_2Cl_2)].

3.11.14. 6-Deoxy-3-O-*ethoxymethyl-6*-C-*(1-hydroxycyclohexyl)-1,2*-O-*isopropylidene-α*-D-*glucofuranose **15e***

R_f 0.34 (hexane:ethyl acetate, 3:2); ν (film) 3648–3115 (OH), 1086, 1024 cm^{-1} (CO); δ_H 1.22–1.25 (3H, m, CH_2CH_3), 1.31 (3H, s, CH_3), 1.49 (3H, s, CH_3), 1.55–1.71 [12H, m, $(CH_2)_5$, CH_2COH], 3.23 (1H, br s, OH), 3.59–3.75 (2H, m, CH_2CH_3), 3.96 (1H, dd, *J*=8.4, 2.7, C*H*CHOH), 4.06 (1H, br s, OH), 4.22 (1H, d, *J*=2.7, CH_2OCH), 4.22–4.26 (1H, m, C*H*OH), 4.56 (1H, d, *J*=3.7, C*H*CHO_2), 4.75 (1H, d, *J*=6.4, OC*H*HO), 4.83 (1H, d, *J*=6.4, OCH*H*O), 5.90 (1H, d, *J*=3.7, OCHO); δ_C 14.9 (CH_2CH_3), 22.1, 22.3, 25.8 (3×CH_2), 26.3, 26.8 (2×CH_3), 36.1, 40.1 (2×CH_2), 43.5 (CHOH*C*H_2), 64.4 (*C*H_2CH_3), 66.0 (CHOH), 72.2 (COH), 81.3 (CH_2OCH), 83.1 (*C*HOHCH), 83.6 (*C*HCHO_2), 95.7 (OCH_2O), 105.1 (OCHO), 111.9 (OCO); *m/z* 314 [$M^+-(CH_3CH_2OH)$, 0.1%], 113 (38), 85 (13), 81 (15), 71 (12), 59 (100), 57 (19), 55 (33), 44 (21), 43 (65), 42 (10) [found: $M^+-(CH_3CH_2OH)$, 314.1707; $C_{16}H_{26}O_6$ requires: M, 314.1729]; $[\alpha]_D^{20}=-23.5$ [*c* 1.35 (CH_2Cl_2)].

3.11.15. 6-C-*Carboxy-6-deoxy-3*-O-*ethoxymethyl-1,2*-O-*isopropylidene-α*-D-*glucofuranose **15f**[32]*

R_f 0.12 (hexane:ethyl acetate, 3:2); ν (film) 3694–3043 (OH), 1723 (C=O), 1084, 1029 cm^{-1} (CO); δ_H 1.24 (3H, t, *J*=7.1, CH_2CH_3), 1.31 (3H, s, CH_3), 1.49 (3H, s, CH_3), 2.58 (1H, dd, *J*=16.5, 9.5,

CHOHC*H*H), 2.88 (1H, dd, *J*=16.5, 2.4, CHOHCH*H*), 3.56–3.76 (2H, m, C*H*$_2$CH$_3$), 4.06 (1H, dd, *J*=8.8, 2.7, C*H*CHOH), 4.23 (1H, d, *J*=2.7, C*H*CHCHOH), 4.24–4.33 (1H, m, C*H*OH), 4.57 (1H, d, *J*=3.4, C*H*CHO$_2$), 4.76 (1H, d, *J*=6.7, OC*H*HO), 4.81 (1H, d, *J*=6.7, OCH*H*O), 5.88 (1H, d, *J*=3.4, OCHO); δ_C 14.8 (CH$_2$*C*H$_3$), 26.2, 26.8 (2×CH$_3$), 38.6 (CHOH*C*H$_2$), 64.4 (*C*H$_2$CH$_3$), 65.1 (CHOH), 81.1 (*C*HOCH$_2$), 81.8 (*C*HCHOH), 83.6 (*C*HCHO$_2$), 95.7 (OCH$_2$O), 105.1 (OCHO), 112.0 (OCO), 177.2 (CO$_2$H); $[\alpha]_D^{20}=-19.9$ [*c* 0.89 (CH$_2$Cl$_2$)].

3.11.16. 1,2;4,5-Di-O-*isopropylidene-3*-C-*methyl-β*-D-*psicopyranose* ***20a***

Major isomer: R_f 0.62 (hexane:ethyl acetate, 3:2); ν (film) 3623–3122 (OH), 1215, 1044 cm^{-1} (CO); δ_H 1.24 [3H, s, C(OH)C*H*$_3$], 1.39 (3H, s, CH$_3$), 1.42 (3H, s, CH$_3$), 1.49 (3H, s, CH$_3$), 1.60 (3H, s, CH$_3$), 2.53 (1H, br s, OH), 3.97 (1H, d, *J*=9.8, CC*H*HO), 4.06 (1H, d, *J*=5.5, C*H*CHCH$_2$), 4.10–4.18 (3H, m, CHCH$_2$), 4.30 (1H, d, *J*=9.8, CC*H*HO); δ_C 20.2 [C(OH)*C*H$_3$], 25.5, 25.7, 25.8, 26.2 (4×CH$_3$), 59.7 (CH*C*H$_2$), 70.4 (COH), 71.6 (C*C*H$_2$), 71.8 (*C*HCH$_2$), 75.5 (*C*HCHCH$_2$), 106.9, 108.9 [2×*C*(CH$_3$)$_2$], 112.3 (*C*CH$_2$O); *m/z* 259 [M$^+$−(CH$_3$), 4.6%], 157 (10), 99 (20), 85 (12), 79 (11), 59 (36), 52 (11), 43 (100), 42 (11) [found: M$^+$−(CH$_3$), 259.1187; C$_{12}$H$_{19}$O$_6$ requires: M, 259.1182]; $[\alpha]_D^{20}=-118.7$ [*c* 1.10 (CH$_2$Cl$_2$)].

3.11.17. 3-C-*Deuteriomethyl-1,2;4,5-di*-O-*isopropylidene-β*-D-*psicopyranose* ***20b***

Major isomer: R_f 0.62 (hexane:ethyl acetate, 3:2); ν (film) 3645–3078 (OH), 1220, 1097, 1030 cm^{-1} (CO); δ_H 1.23 (2H, m, CH$_2$D), 1.39, 1.42, 1.49, 1.60 (12H, s, 4×CH$_3$), 2.51 (1H, br s, OH), 3.97 (1H, d, *J*=9.5, CC*H*HO), 4.06 (1H, d, *J*=5.5, C*H*CHCH$_2$), 4.14–4.21 (3H, m, CHCH$_2$O), 4.30 (1H, d, *J*=9.5, CC*H*HO); δ_C 19.5 (t, J_{CD}=19.5, CH$_2$D), 25.5, 25.7, 25.8, 26.2 (4×CH$_3$), 59.7 (*C*HCH$_2$O), 70.3 (COH), 71.6 (C*C*H$_2$O), 71.8 (*C*HCH$_2$O), 75.5 (*C*HCHCH$_2$O), 106.9 (*C*CH$_2$O), 108.9, 112.3 [2×*C*(CH$_3$)$_2$]; *m/z* 260 [M$^+$−(CH$_3$), 8.0%], 158 (18), 117 (14), 100 (36), 99 (15), 85 (23), 84 (16), 72 (13), 59 (64), 57 (16), 55 (10), 43 (100), 42 (29), 41 (18) [found: M$^+$, 275.1440; C$_{13}$H$_{21}$DO$_6$ requires: M, 275.1479]; $[\alpha]_D^{20}=-123.7$ [*c* 1.30 (CH$_2$Cl$_2$)].

3.11.18. 3-C-*Deuteriomethyl-1,2;4,5-di*-O-*isopropylidene-β*-D-*fructopyranose* ***20b′***

Minor isomer: R_f 0.52 (hexane:ethyl acetate, 3:2); ν (film) 3645–3078 (OH), 1220, 1077, 1030 cm^{-1} (CO); δ_H 1.31 (2H, m, CH$_2$D), 1.35, 1.44, 1.49, 1.51 (12H, s, 4×CH$_3$), 2.53 (1H, br s, OH), 3.81 (1H, d, *J*=12.8, C*H*CHCH$_2$), 3.90 (1H, d, *J*=9.8, CC*H*HO), 4.19–4.23 (3H, m, C*H*C*H*C*H*HO), 4.30 (1H, dd, *J*=7.3, 2.4, CC*H*HO); δ_C 21.8 (t, J_{CD}=20.7, CH$_2$D), 24.8, 25.7, 26.0, 26.4 (4×CH$_3$), 62.6 (*C*HCH$_2$O), 71.3 (COH), 72.3 (C*C*H$_2$O), 73.0 (*C*HCH$_2$O), 77.9 (*C*HCHCH$_2$O), 105.9 (*C*CH$_2$O), 109.0, 110.5 [2×*C*(CH$_3$)$_2$]; *m/z* 260 [M$^+$−(CH$_3$), 9.0%], 158 (16), 117 (13), 100 (31), 99 (13), 85 (20), 84 (14), 72 (19), 59 (51), 57 (14), 55 (10), 44 (100), 43 (53), 42 (27) [found: M$^+$, 275.1440; C$_{13}$H$_{21}$DO$_6$ requires: M, 275.1479]; $[\alpha]_D^{20}=-89.6$ [*c* 0.85 (CH$_2$Cl$_2$)].

*3.11.19. (2′*R*)-3*-C-*(2-Hydroxy-2-phenylethyl)-1,2;4,5-di*-O-*isopropylidene-β*-D-*psicopyranose* ***20c***

Major isomer: m.p. 126–127°C (dichloromethane/pentane); R_f 0.40 (hexane:ethyl acetate, 3:2); ν (KBr) 3606–3278 (OH), 3016, 3004 (ArH), 1217, 1089, 1040 cm^{-1} (CO); δ_H 1.36 (3H, s, CH$_3$), 1.43 (3H, s, CH$_3$), 1.46 (3H, s, CH$_3$), 1.68 (3H, s, CH$_3$), 1.93 (2H, d, *J*=5.5, COHC*H*$_2$), 2.71 (2H, br s, 2×OH), 3.94 (1H, d, *J*=9.8, CC*H*HO), 4.17–4.38 (4H, m, C*H*CH$_2$O, CC*H*HO), 4.62 (1H, d, *J*=1.8, C*H*CHCH$_2$O), 5.13 (1H, m, C*H*OH), 7.24–7.41 (5H, m, ArH); δ_C 25.1 (CH$_3$), 25.6 (CH$_3$), 25.7 (CH$_3$), 26.3 (CH$_3$), 45.1 [C(OH)*C*H$_2$], 59.6 (CH*C*H$_2$O), 68.9 (CHOH), 71.7 (C*C*H$_2$O), 72.3 (*C*HCH$_2$O), 75.9 (*C*HCHCH$_2$), 77.2 (COH), 107.5 (*C*CH$_2$O), 109.3, 112.6 [2×*C*(CH$_3$)$_2$], 125.7, 126.9, 128.2 (ArCH), 144.9 (ArC); *m/z* 347 [M$^+$−(H$_2$O, CH$_3$), 8%], 131 (12), 114 (23), 105 (20), 104 (24), 85 (14), 77 (11), 59 (15), 55 (11), 44

(10), 43 (100), 42 (21), 41 (12). Anal. calcd for $C_{20}H_{28}O_7$: C, 63.14; H, 7.41; found: C, 63.07; H, 7.11. $[\alpha]_D^{20}=-123.5$ [*c* 0.98 (CH_2Cl_2)].

*3.11.20. (2′S)-3-*C*-(2-Hydroxy-2-phenylethyl)-1,2;4,5-di-*O*-isopropylidene-β-*D*-psicopyranose* ***20c′***

Minor isomer: R_f 0.44 (hexane:ethyl acetate, 3:2); ν (film) 3670–3133 (OH), 3006, 3000 (ArH), 1225, 1069, 1026 cm^{-1} (CO); δ_H 1.37 (3H, s, CH_3), 1.45 (3H, s, CH_3), 1.46 (3H, s, CH_3), 1.65 (3H, s, CH_3), 2.96 (1H, d, *J*=16.2, COHC*H*H), 3.16 (1H, d, *J*=16.2, COHCH*H*), 3.46 (1H, d, *J*=9.8, CC*H*HO), 3.73 (1H, d, *J*=9.8, CCH*H*O), 4.03–4.18 (3H, m, C*H*C*H*CH_2, O*H*), 4.24–4.28 (1H, m, PhC*H*OH), 4.67 (1H, d, *J*=13.4, CHC*H*HO), 4.92 (1H, d, *J*=13.4, CHCH*H*O), 5.29 (1H, br s, OH), 7.09–7.28 (5H, m, ArH); δ_C 24.5 (CH_3), 25.1 (CH_3), 26.2 (CH_3), 26.6 (CH_3), 41.1 (COH*C*H_2), 63.7 (CH*C*H_2O), 70.7 (CHOH), 72.3 (C*C*H_2O), 72.6 (*C*HCH_2O), 73.6 (*C*HCHCH_2), 73.9 (COH), 105.2 (*C*CH_2O), 109.4, 110.2 [2×*C*$(CH_3)_2$], 125.8, 127.5, 128.4 (ArCH), 144.1 (ArC); *m/z* 347 [$M^+-(H_2O, CH_3)$, 13.5%], 131 (11), 105 (19), 104 (17), 59 (11), 55 (15), 44 (10), 43 (100), 42 (18), 41 (12) [found: $M^+-(H_2O, CH_3)$, 347.1521; $C_{19}H_{23}O_6$ requires: M, 347.1495]; $[\alpha]_D^{20}=-57.7$ [*c* 1.33 (CH_2Cl_2)].

*3.11.21. 3-*C*-(2-Ethyl-2-hydroxybutyl)-1,2;4,5-di-*O*-isopropylidene-β-*D*-psicopyranose* ***20d***

R_f 0.48 (hexane:ethyl acetate, 3:2); ν (film) 3555–3107 (OH), 1218, 1053 cm^{-1} (CO); δ_H 0.90 (6H, dd, *J*=14.6, 7.3, 2×CH_2C*H*$_3$), 1.26–1.63 (4H, m, 2×C*H*$_2$$CH_3$), 1.34 (3H, s, CH_3), 1.46 (3H, s, CH_3), 1.49 (3H, s, CH_3), 1.51 (3H, s, CH_3), 1.81 [1H, d, *J*=15.0, C(OH)C*H*H], 1.96 [1H, d, *J*=15.0, C(OH)CH*H*], 2.82 (1H, br s, OH), 3.67 (1H, m, CHC*H*H), 3.87 (1H, d, *J*=10.1, CCH*H*O), 4.18 (1H, d, *J*=10.1, CC*H*HO), 4.24–4.35 (3H, m, C*H*CH*H*, O*H*), 4.69 (1H, d, *J*=7.3, C*H*CHCH_2); δ_C 7.5, 8.2 (2×CH_2*C*H_3), 24.4, 25.1, 26.3, 26.6 (4×C*C*H_3), 31.9, 33.7 (2×*C*$H_2$$CH_3$), 36.1 (COH*C*$H_2$), 64.0 (CH*C*$H_2$O), 72.6 (C*C*$H_2$O), 73.0 (*C*HC$H_2$O), 74.3 ($CH_3CH_2$*C*OH), 75.6 (*C*HCHC$H_2$), 76.1 (C*C*COH), 105.7, 109.1 [2×*C*$(CH_3)_2$], 109.6 (*C*CH_2O); *m/z* 345 [$M^+-(CH_3)$, 1.0%], 197 (18), 111 (13), 99 (13), 87 (12), 85 (22), 83 (23), 79 (11), 69 (11), 59 (38), 57 (59), 55 (26), 45 (15), 43 (100), 42 (15), 41 (25) [found: $M^+-(CH_3)$, 345.1912; $C_{17}H_{29}O_7$ requires: M, 345.1913]; $[\alpha]_D^{20}=-46.2$ [*c* 1.00 (CH_2Cl_2)].

*3.11.22. 3-*C*-(1-Hydroxycyclohexylmethyl)-1,2;4,5-di-*O*-isopropylidene-β-*D*-psicopyranose* ***20e***

R_f 0.56 (hexane:ethyl acetate, 3:2); ν (film) 3665–3101 (OH), 1214, 1067, 1012 cm^{-1} (CO); δ_H 1.32–1.70 (10H, m, 5×CH_2), 1.35, 1.47, 1.48, 1.51 (12H, s, 4×CH_3), 1.77 (1H, d, *J*=15.3, COHC*H*H), 2.02 (1H, m, COHCH*H*), 2.85 (1H, br s, OH), 3.68 (1H, dd, *J*=12.8, 1.8, CHC*H*HO), 3.88 (1H, d, *J*=10.1, CCH*H*O), 4.18 (1H, d, *J*=10.1, CC*H*HO), 4.27–4.32 (3H, m, C*H*CH*H*O, O*H*), 4.68 (1H, d, *J*=7.3, C*H*CHCH_2); δ_C 22.1, 24.5, 25.1, 25.5, 26.2, 26.6 [4×CH_3, 3×CH_2, C(OH)*C*H_2C(OH)], 38.5 [C(OH)*C*$H_2$$CH_2$], 40.2 [C(OH)C$H_2$*C*$H_2$], 41.0 [C(OH)*C*$H_2$$CH_2$], 63.8 (CH*C*$H_2$O), 72.5 (C*C*$H_2$O), 72.9 (*C*HC$H_2$O), 74.3 [CH*C*(OH)C], 76.0 (*C*HCHCH_2), 105.7 (O*C*CH_2), 109.0, 109.7 [2×*C*$(CH_3)_2$]; *m/z* 354 [$M^+-(H_2O)$, 0.4%], 339 [$M^+-(CH_3, H_2O)$, 5.0%], 123 (12), 117 (10), 95 (49), 94 (10), 85 (20), 81 (19), 79 (11), 67 (16), 59 (53), 57 (17), 55 (28), 43 (100), 42 (20), 41 (33) [found: $M^+-(CH_3)$, 357.1907; $C_{18}H_{29}O_7$ requires: M, 357.1913]; $[\alpha]_D^{20}=-60.8$ [*c* 1.30 (CH_2Cl_2)].

3.11.23. Compound ***20f***

M.p. 232–233°C (dichloromethane/pentane); R_f 0.49 (hexane:ethyl acetate, 3:2); ν (KBr) 3634–3150 (OH), 1220, 1079 cm^{-1} (CO); δ_H 1.39 (6H, s, 2×CH_3), 1.47 (12H, s, 4×CH_3), 1.61 (6H, s, 2×CH_3), 1.94 (2H, s, CCH_2C), 4.01 (2H, d, *J*=9.8, 2×CC*H*HO), 4.05–4.18 (4H, m, 2×CHC*H*$_2$), 4.25–4.29 (2H, m, 2×C*H*CH_2), 4.35 (2H, d, *J*=6.1, 2×C*H*CHCH_2), 4.44 (2H, d, *J*=9.8, 2×CC*H*HO), 4.58 (2H, br s, 2×OH); δ_C 24.9, 25.4, 26.2, 26.6 (8×CH_3), 43.4 (C*C*H_2C), 60.7 (2×CH*C*H_2), 70.6 (2×C*C*H_2), 71.0 (2×*C*OH), 72.5 (2×*C*HCH_2), 75.8 (2×*C*HCHCH_2), 107.1, 109.2, 111.9 [4×*C*$(CH_3)_2$, (2×*C*CH_2O)];

m/z 317 [$M^+-(215)$, 0.2%], 85 (17), 59 (22), 43 (100), 42 (12), 41 (10). Anal. calcd for $C_{25}H_{40}O_{12}$: C, 56.38; H, 7.57; found: C, 56.10; H, 7.57. $[\alpha]_D^{20}=-104.6$ [*c* 1.00 (CH_2Cl_2)].

*3.12. Preparation of compounds **11a** and **20a** by addition of methyllithium to ketones **8** and **23***

A 1.6 M methyllithium diethyl ether solution (0.5 ml, 0.8 mmol) was added at −78°C to the corresponding ketone (0.5 mmol) THF solution (5 ml) under argon at −78°C. After 10 min at this temperature the reaction mixture was hydrolysed with water (15 ml), allowed to reach 25°C and extracted with ethyl acetate (3×20 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) to yield the title compounds. Yields are given in the text. Physical and spectroscopic data are given above.

*3.13. DTBB-catalysed lithiation of the oxetane **4**. Isolation of compounds **6**. General procedure*

To a cooled (–40°C) blue suspension of lithium powder (0.10 g, 14.0 mmol) and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (0.04 g, 0.15 mmol) in THF (6 ml) was added oxetane **4** (0.27 g, 1.0 mmol) under argon and the mixture was stirred at the same temperature for 3 h. Then the corresponding electrophile (1.2 mmol; 0.5 ml in the case of water and deuterium oxide) was added at –40°C and the temperature was allowed to rise to 20°C overnight. The resulting mixture was hydrolysed with water (20 ml) and extracted with ethyl acetate (3×20 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) and/or recrystallised to yield pure products **6**. Yields are given in the text. Physical, spectroscopic and analytical data follow.

*3.13.1. 3-*C*-Ethyl-1,2;5,6-di-*O*-isopropylidene-α-*D*-glucofuranose **6a***

R_f 0.32 (hexane:ethyl acetate, 4:1); ν (film) 3670–3099 (OH), 1075 cm^{-1} (CO); δ_H 1.05 (3H, t, *J*=7.4, CH_2CH_3), 1.32 (3H, s, CH_3), 1.35 (3H, s, CH_3), 1.42 (3H, s, CH_3), 1.51 (3H, s, CH_3), 1.81 (2H, q, *J*=7.4, CH_2CH_3), 2.34 (1H, br s, OH), 3.81 (1H, d, *J*=7.6, $CHCHCH_2$), 3.99 (1H, dd, *J*=8.5, 5.5, $CHCHCHH$), 4.12 (1H, dd, *J*=8.5, 6.4, $CHCHCHH$), 4.24–4.28 (1H, m, $CHCHCH_2$), 4.31 (1H, d, *J*=3.4, $CHCHO_2$), 5.85 (1H, d, *J*=3.4, OCHO); δ_C 7.9 (CH_2CH_3), 25.1 (CH_2CH_3), 25.6, 26.4, 26.6, 27.1 (4×CH_3), 67.65 (OCH_2), 73.45 (COH), 82.9 ($CHCH_2O$), 83.5 ($CHCHCH_2$), 85.2 ($CHCHO_2$), 104.5 (OCHO), 109.4, 112.2 [2×$C(CH_3)_2$]; *m/z* 273 [$M^+-(CH_3)$, 5.0%], 101 (37), 100 (30), 85 (19), 71 (12), 59 (34), 57 (40), 55 (12), 43 (100), 42 (10) [found: $M^+-(CH_3)$, 273.1340; $C_{13}H_{21}O_6$ requires: M, 273.1338]; $[\alpha]_D^{20}=+25.5$ [*c* 0.69 (CH_2Cl_2)].

*3.13.2. 3-*C*-(2-Deuterioethyl)-1,2;5,6-di-*O*-isopropylidene-α-*D*-glucofuranose **6b***

R_f 0.32 (hexane:ethyl acetate, 4:1); ν (film) 3657–3112 (OH), 1074 cm^{-1} (CO); δ_H 1.05 (2H, t, *J*=7.3, CH_2D), 1.32 (3H, s, CH_3), 1.35 (3H, s, CH_3), 1.43 (3H, s, CH_3), 1.51 (3H, s, CH_3), 1.81 (2H, t, *J*=7.3, CH_2CH_2D), 2.10 (1H, br s, OH), 3.81 (1H, d, *J*=7.6, $CHCHCH_2$), 3.98 (1H, dd, *J*=8.5, 5.5, $CHCHCHH$), 4.10–4.15 (1H, m, $CHCHCHH$), 4.24–4.28 (1H, m, $CHCHCH_2$), 4.31 (1H, d, *J*=3.4, $CHCHO_2$), 5.85 (1H, d, *J*=3.4, OCHO); δ_C 7.7 (t, J_{CD}=20.7, CH_2D), 25.2 (CH_3), 25.7 (CH_2CH_2D), 26.4, 26.6, 27.2 (3×CH_3), 67.7 (OCH_2), 73.6 (COH), 83.0 ($CHCH_2$), 83.5 ($CHCHCH_2$), 85.2 ($CHCHO_2$), 104.6 (OCHO), 109.5, 112.3 [2×$C(CH_3)_2$]; *m/z* 274 [$M^+-(CH_3)$, 4.0%], 101 (39), 100 (45), 85 (27), 72 (11), 71 (14), 59 (50), 58 (28), 57 (35), 55 (10), 44 (14), 43 (100), 42 (13) [found: $M^+-(CH_3)$, 274.1394; $C_{13}H_{20}DO_6$ requires: M, 274.1401]; $[\alpha]_D^{20}=+28.5$ [*c* 1.26 (CH_2Cl_2)].

3.14. Preparation of compounds **11** from the chlorohydrin **12**. General procedure

A 1.6 M *n*-butyllithium hexane solution (0.69 ml, 1.1 mmol) was added to a chlorohydrin **12** (0.31 g, 1.0 mmol) THF solution (5 ml) under argon at −78°C. After 10 min at this temperature, the resulting solution was transferred via cannula to a cooled (−78°C) blue suspension of lithium powder (0.10 g, 14.0 mmol) and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (0.04 g, 0.15 mmol) in THF (5 ml) under argon. The mixture was stirred at the same temperature for 30 min. Then the corresponding electrophile (1.1 mmol; 0.5 ml in the case of deuterium oxide) was added at −78°C and the temperature was allowed to rise to 20°C overnight. The resulting mixture was hydrolysed with water (20 ml) and extracted with ethyl acetate (3×20 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) and/or recrystallised to yield pure products **11**. Yields are included in Table 2. Physical, spectroscopic and analytical data follow.

3.14.1. 3-C-Deuteriomethyl-1,2;5,6-di-O-isopropylidene-α-D-allofuranose **11b**

M.p. 123–124°C (dichloromethane/pentane); R_f 0.19 (hexane:ethyl acetate, 4:1); ν (KBr) 3625–3113 (OH), 1267, 1076, 1014 cm^{-1} (CO); δ_H 1.27 (2H, s, CH_2D), 1.35 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.45 (3H, s, CH_3), 1.59 (3H, s, CH_3), 2.68 (1H, s, OH), 3.78 (1H, d, *J*=6.7, C*H*CHCH$_2$), 3.90–3.96 (1H, m, CHC*H*H), 4.07–4.13 (2H, m, C*H*CH*H*), 4.17 (1H, d, *J*=3.7, C*H*CHO$_2$), 5.7 (1H, d, *J*=3.7, OCHO); δ_C 18.9 (t, J_{CD}=20.1, CH_2D), 25.2, 26.4, 26.6, 26.7 (4×CH_3), 67.7 (CH*C*H$_2$), 73.7 (*C*HCH$_2$), 77.3 (*C*HCHCH$_2$), 81.4 (*C*HCHO$_2$), 84.7 (COH), 103.5 (OCHO), 109.5, 112.8 [2×*C*(CH$_3$)$_2$]; *m/z* 260 [M$^+$−(CH$_3$), 6.7%], 101 (19), 100 (26), 85 (11), 72 (11), 59 (48), 55 (15), 44 (53), 43 (100), 42 (14), 41 (13). Anal. calcd for $C_{13}H_{21}DO_6$: C, 56.71; H, 8.42; found: C, 5.79; H, 8.86. $[\alpha]_D^{20}$=+26.2 [*c* 1.35 (CH_2Cl_2)].

3.14.2. 3-C-(1-Hydroxycyclohexylmethyl)-1,2;5,6-di-O-isopropylidene-α-D-allofuranose **11c**

M.p. 122–123°C (dichloromethane/pentane); R_f 0.22 (hexane:ethyl acetate, 4:1); ν (KBr) 3665–3083 (OH), 1214, 1085, 1018 cm^{-1} (CO); δ_H 1.36 (6H, s, 2×CH_3), 1.44 (3H, s, CH_3), 1.58 (3H, s, CH_3), 1.24–1.68 (10H, m, 5×CH_2), 1.73–1.77 (1H, m, COHC*H*H), 2.00 (1H, d, *J*=15.3, COHCH*H*), 2.82 (1H, br s, OH), 3.08 (1H, br s, OH), 3.76 (1H, d, *J*=7.3, C*H*CHCH$_2$), 3.92 (1H, dd, *J*=7.9, 5.5, CHC*H*CHO), 4.07–4.18 (2H, m, C*H*C*H*HO), 4.94 (1H, d, *J*=3.7, C*H*CHO$_2$), 5.71 (1H, d, *J*=3.7, OCHO); δ_C 21.9, 22.2 (2×CH_2), 25.3, 25.6 (2×CH_3), 26.6 (CH_2), 26.7 (2×CH_3), 39.7 (CH_2), 40.8 (COH*C*H$_2$), 67.6 (O*C*H$_2$CH), 71.9 (COH), 73.3 (OCH$_2$*C*H), 80.0 (COH), 81.5 (OCH$_2$CH*C*H), 83.3 (*C*HCHO$_2$), 103.7 (OCHO), 109.6, 112.5 [2×*C*(CH$_3$)$_2$]; *m/z* 357 [M$^+$−(CH$_3$), 0.12%], 101 (22), 100 (10), 95 (14), 85 (11), 73 (15), 71 (14), 67 (10), 59 (17), 55 (16), 44 (23), 43 (100), 42 (14), 41 (29). Anal. calcd for $C_{19}H_{32}O_7$: C, 61.27; H, 8.66; found: C, 61.19; H, 8.66. $[\alpha]_D^{20}$=−7.5 [*c* 1.00 (CH_2Cl_2)].

3.14.3. Compound **11d**

M.p. 169–170°C (dichloromethane/pentane); R_f 0.32 (hexane:ethyl acetate, 3:2); ν (KBr) 3691–3133 (OH), 1260, 1068, 1030 cm^{-1} (CO); δ_H 1.37 (12H, s, 4×CH_3), 1.45 (6H, s, 2×CH_3), 1.59 (6H, s, 2×CH_3), 1.91 (2H, s, CCH$_2$C), 2.81 (2H, br s, 2×OH), 3.78 (2H, dd, *J*=12.5, 7.5, 2×CHC*H*HO), 3.93–3.97 (2H, m, 2×CHCH*H*O), 4.07–4.12 (4H, m, 2×C*H*C*H*CH$_2$), 5.26 (2H, d, *J*=3.4, 2×C*H*CHO$_2$), 5.77 (2H, d, *J*=3.4, 2×OCHO); δ_C 25.3, 26.6, 26.7 (8×CH_3), 32.9 (C*C*H$_2$C), 67.8 (2×CH*C*H$_2$O), 73.1 (2×*C*HCH$_2$O), 79.6 (2×*C*HCHCH$_2$), 80.5 (2×*C*HCHO$_2$), 82.8 (2×COH), 103.8 (2×OCHO), 109.7, 112.5 [4×*C*(CH$_3$)$_2$]; *m/z* 515 [M$^+$−(OH), 3.8%], 207 (11), 101 (15), 58 (10), 57 (18), 56 (10), 55 (12),

44 (56), 43 (100), 42 (18), 41 (27). Anal. calcd for $C_{25}H_{40}O_{12}$: C, 56.38; H, 7.57; found: C, 56.69; H, 7.50. $[\alpha]_D^{20}$=+32.7 [*c* 1.05 (CH_2Cl_2)].

*3.15. Reaction of intermediates **25** with ketones **8** and **25**. Isolation of compounds **26** and **27**. General procedure*

To a cooled (−78°C) blue suspension of lithium powder (0.10 g, 14.0 mmol) and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (0.04 g, 0.15 mmol) in THF (6 ml) was added phthalan or isochroman **24** (1.0 mmol) under argon and the mixture was allowed to reach 25°C in 30 min. After that, it was cooled down to −78°C and a THF solution (0.5 ml) of ketones **8** or **23** (1.0 mmol) was added dropwise. Stirring was continued at the same temperature for 10 min, hydrolysed with water (30 ml) and extracted with ethyl acetate (3×20 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) and/or recrystallised to yield pure products **26** and **27**. Yields (based on the starting material **25**), physical, spectroscopic and analytical data follow.

3.15.1. 3-C-*[2-(Hydroxymethyl)phenylmethyl]-1,2;5,6-di*-O-*isopropylidene*-α-D-*allofuranose **26a***

M.p. 119–120°C (dichloromethane/pentane) (58% yield); R_f 0.39 (hexane:ethyl acetate, 3:2); ν (KBr) 3600–3106 (OH), 3000 (ArH), 1069, 1006 cm^{-1} (CO); δ_H 1.25 (3H, s, CH_3), 1.41 (3H, s, CH_3), 1.48 (3H, s, CH_3), 1.54 (3H, s, CH_3), 2.67 (1H, d, *J*=14.4, COHC*H*H), 3.44 (1H, d, *J*=14.4, COHCH*H*), 3.46–3.57 (2H, br s, 2×OH), 3.89 (1H, d, *J*=8.2, C*H*CHCH$_2$), 3.96–4.00 (1H, m, CHC*H*H), 4.14–4.19 (1H, m, CHCH*H*), 4.26–4.31 (1H, m, C*H*CH$_2$), 4.34 (1H, d, *J*=3.5, C*H*CHO$_2$), 4.55 (1H, d, *J*=12.1, C*H*HOH), 4.75 (1H, d, *J*=12.1, CH*H*OH), 5.85 (1H, d, *J*=3.5, OCHO), 7.14–7.43 (4H, m, ArH); δ_C 25.3 (CH_3), 26.4 (CH_3), 26.6 (2×CH_3), 33.9 (PhCH$_2$), 63.0 (CH_2OH), 67.9 (CH_2O), 73.2 (*C*HCH$_2$O), 79.3 (*C*HCHCH$_2$), 80.5 (COH), 82.6 (*C*HCHO$_2$), 103.4 (OCHO), 109.7, 112.4 [2×*C*(CH_3)$_2$], 127.3, 127.7, 130.6, 131.9 (ArCH), 134.3, 140.9 (ArC); *m/z* 347 [M^+−(CH_3, H_2O), 0.8%], 145 (12), 104 (25), 101 (17), 100 (11), 85 (11), 44 (24), 43 (100), 42 (10). Anal. calcd for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42; found: C, 62.91; H, 7.12. $[\alpha]_D^{20}$=+26.6 [*c* 0.98 (CH_2Cl_2)].

3.15.2. 3-C-*[2-(2-Hydroxyethyl)phenylmethyl]-1,2;5,6-di*-O-*isopropylidene*-α-D-*allofuranose **26b***

M.p. 112–113°C (dichloromethane/pentane) (67% yield); R_f 0.16 (hexane:ethyl acetate, 3:2); ν (KBr) 3680–3052 (OH), 3022 (ArH), 1071 cm^{-1} (CO); δ_H 1.26 (3H, s, CH_3), 1.40 (3H s, CH_3), 1.50 (3H, s, CH_3), 1.55 (3H, s, CH_3), 2.72 (1H, d, *J*=14.8, PhC*H*HC), 2.85 (1H, br s, OH), 2.87–3.06 (2H, m, PhCH$_2$C*H*$_2$), 3.31 (1H, d, *J*=14.8, PhCH*H*C), 3.38 (1H, br s, OH), 3.80–3.88 (3H, m, C*H*$_2$OH, C*H*CHCH$_2$), 3.99 (1H, dd, *J*=8.2, 5.8, CHC*H*H), 4.17 (1H, dd, *J*=8.2, 6.2, CHCH*H*), 4.24 (1H, d, *J*=3.7, C*H*CHO$_2$), 4.28–4.35 (1H, m, C*H*CH$_2$), 5.82 (1H, d, *J*=3.7, OCHO), 7.19–7.40 (4H, m, ArH); δ_C 25.4, 26.4, 26.6, 26.7 (4×CH_3), 33.2 (PhC*H*$_2$C), 35.9 (PhCH$_2$*C*H$_2$), 63.4 (CH_2OH), 67.9 (CH_2O), 73.2 (COH), 79.9 (*C*HCH$_2$), 80.4 (*C*HCHCH$_2$), 82.7 (*C*HCHO$_2$), 103.6 (OCHO), 109.7, 112.5 [2×*C*(CH_3)$_2$], 126.4, 127.1, 129.8, 132.1 (ArCH), 134.7, 138.1 (ArC); *m/z* 379 [M^+−(CH_3), 0.15%], 117 (10), 101 (21), 100 (18), 85 (12), 71 (12), 59 (17), 54 (11), 44 (55), 43 (100), 42 (13). Anal. calcd for $C_{21}H_{30}O_7$: C, 63.46; H, 7.65; found: C, 63.46; H, 7.65. $[\alpha]_D^{20}$=+32.2 [*c* 1.00 (CH_2Cl_2)].

3.15.3. 3-C-*[2-(Hydroxymethyl)phenylmethyl]-1,2;4,5-di*-O-*isopropylidene*-β-D-*psicopyranose **27a***

M.p. 181–182°C (dichloromethane/pentane) (80% yield); R_f 0.41 (hexane:ethyl acetate, 3:2); ν (KBr) 3498–3091 (OH), 3060, 3023 (ArCH), 1209, 1076 cm^{-1} (CO); δ_H 1.27 (3H, s, CH_3), 1.39 (3H, s, CH_3), 1.53 (3H, s, CH_3), 1.57 (3H, s, CH_3), 3.03 (1H, d, *J*=14.6, PhC*H*H), 3.07 (1H, br s, OH),

3.14 (1H, d, *J*=14.6, PhCH*H*), 3.43 (1H, br s, OH), 3.96 (1H, d, *J*=9.8, CC*H*HO), 4.05–4.13 (1H, m, C*H*CHHO), 4.20–4.25 (2H, m, CHCH*H*O, PhC*H*HOH), 4.35 (1H, d, *J*=5.5, PhCH*H*OH), 4.42 (1H, d, *J*=9.8, CCH*H*O), 4.64–4.66 (2H, m, C*H*C*H*CH_2O), 7.21–7.39 (4H, m, ArH); δ_C 25.2, 25.3, 25.8, 26.5 (4×CH_3), 37.4 ($PhCH_2$), 59.9 (*C*HCH_2O), 63.3 ($PhCH_2OH$), 71.5 (C*C*H_2O), 72.3 (*C*HCH_2O), 75.4 (*C*HCHCH_2), 107.0 (*C*CH_2O), 108.9, 112.4 [2×*C*$(CH_3)_2$], 127.0, 127.1 (ArCH), 127.4 (COH), 130.3, 132.5 (ArCH), 134.7, 140.5 (2ArC); *m/z* 362 [$M^+-(H_2O)$, 2.5%], 145 (10), 129 (11), 117 (12), 115 (12), 105 (12), 104 (27), 103 (10), 91 (12), 85 (15), 59 (15), 58 (10), 55 (12), 44 (24), 43 (100), 42 (15), 41 (14). Anal. calcd for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42; found: C, 63.22; H, 7.31. $[\alpha]_D^{20}=-52.1$ [*c* 1.10 (CH_2Cl_2)].

3.15.4. 3-C-*[2−(2-Hydroxyethyl)phenylmethyl]-1,2;4,5-di*-O-*isopropylidene-β*-D-*psicopyranose* ***27b***

R_f 0.27 (hexane:ethyl acetate, 3:2) (85% yield); ν (film) 3649–3112 (OH), 3071 (ArCH), 1213, 1078, 1060 cm^{-1} (CO); δ_H 1.25, 1.40, 1.53, 1.56 (12H, s, 4×CH_3), 1.91 (1H, br s, OH), 2.88 (1H, br s, OH), 2.95 (1H, d, *J*=14.0, PhC*H*HC), 3.06–3.12 (3H, m, PhCH*H*O, Ph*C*H_2CH_2), 3.91 (2H, m, $PhCH_2CH_2$), 3.96 (1H, d, *J*=9.5, CC*H*HO), 4.04–4.09 (1H, m, CHC*H*H), 4.16–4.21 (2H, m, C*H*CH*H*), 4.29 (1H, d, *J*=6.1, C*H*CHCH_2), 4.43 (1H, d, *J*=9.5, CCH*H*O), 7.13–7.36 (4H, m, ArH); δ_C 25.2, 25.3, 25.7, 26.5 (4×CH_3), 35.4, 37.2 (2×$PhCH_2$), 60.0 (CH_2OH), 63.2 (CH*C*H_2O), 71.5 (C*C*H_2O), 72.4 (*C*HCH_2O), 72.6 (COH), 75.2 (*C*HCHCH_2), 107.1 (*C*CH_2O), 108.8, 112.3 [2×*C*$(CH_3)_2$], 125.7, 126.8, 129.1, 132.5 (ArCH), 135.5, 138.1 (ArC); *m/z* 379 [$M^+-(CH_3)$, 0.5%], 201 (14), 129 (10), 118 (12), 117 (31), 115 (14), 105 (10), 91 (11), 85 (16), 59 (41), 57 (12), 55 (11), 43 (100), 42 (14), 41 (16), 40 (10) [found: $M^+-(CH_3)$, 379.1776; $C_{20}H_{27}O_7$ requires: M, 379.1757]; $[\alpha]_D^{20}=-74.6$ [*c* 1.00 (CH_2Cl_2)].

3.16. Cyclisation of compounds ***26*** *and* ***27****. Isolation of compounds* ***28*** *and* ***29****. General procedure*

To a benzene solution (5 ml) of diols **26** or **27** (0.25 mmol) and triphenylphosphine (0.16 g, 0.6 mmol) in the presence of 4 Å molecular sieves (0.5 g) under argon was added dropwise diisopropyl azodicarboxylate (0.12 ml, 0.6 mmol) at 25°C. The reaction mixture was heated at 80°C for 3 h. Then the resulting mixture was evaporated (15 mmHg) and the resulting residue was hydrolysed with water (10 ml) and extracted with ethyl acetate (3×20 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel, hexane:ethyl acetate) to give compounds **28** and **29**. Yields (based on the starting materials **26** and **27**), physical, spectroscopic and analytical data follow.

3.16.1. Compound ***28a***

M.p. 123–124°C (dichloromethane/pentane) (50% yield); R_f 0.31 (hexane:ethyl acetate, 4:1); ν (KBr) 3035, 3023 (ArH), 1076, 1039 cm^{-1} (CO); δ_H 1.27 (3H, s, CH_3), 1.32 (3H, s, CH_3), 1.46 (3H, s, CH_3), 1.61 (3H, s, CH_3), 2.44 (1H, d, *J*=15.9, CC*H*HPh), 3.25 (1H, d, *J*=15.9, CCH*H*Ph), 3.99 (1H, dd, *J*=8.1, 5.0, CHC*H*HO), 4.11 (1H, d, *J*=5.8, C*H*CHCH_2), 4.12–4.24 (2H, m, C*H*CH_2, CHCH*H*), 4.19 (1H, d, *J*=3.7, C*H*CHO_2), 4.90 (1H, d, *J*=15.3, OC*H*HPh), 5.01 (1H, d, *J*=15.3, OC*H*HPh), 5.69 (1H, d, *J*=3.7, OCHO), 7.04–7.23 (4H, m, ArH); δ_C 25.3, 26.5, 26.6, 26.9 (4×CH_3), 30.0 (C*C*H_2Ph), 65.2 (CH*C*H_2), 67.6 (OCH_2Ph), 73.5 (*C*HCHCH_2), 80.8 (*C*HCH_2), 81.1 (*C*CH_2Ph), 81.9 (*C*HCHO_2), 103.6 (OCHO), 109.6, 113.0 [2×*C*$(CH_3)_2$], 124.3, 126.4, 126.6, 128.9 (ArCH), 130.8, 135.1 (ArC); *m/z* 347 [$M^+-(CH_3)$, 1.8%], 145 (18), 117 (13), 104 (21), 101 (24), 100 (23), 85 (23), 72 (10), 59 (10), 55 (12), 44 (12), 43 (100), 42 (12) [found: $M^+-(CH_3)$, 347.1495; $C_{19}H_{23}O_6$ requires: M, 347.1496]; $[\alpha]_D^{20}=+128.0$ [*c* 1.00 (CH_2Cl_2)].

*3.16.2. Compound **28b***

R_f 0.37 (hexane:ethyl acetate, 4:1) (70% yield); ν (film) 3053 (ArCH), 1083 cm^{-1} (CO); δ_H 1.20 (3H, s, CH_3), 1.38 (3H, s, CH_3), 1.47 (3H, s, CH_3), 1.56 (3H, s, CH_3), 2.61 (1H, d, *J*=15.1, CC*H*HPh), 2.74 (1H, dd, *J*=15.6, 4.9, CH_2C*H*HPh), 3.31–3.39 (1H, m, CH_2CH*H*Ph), 3.51 (1H, d, *J*=15.1, CCH*H*Ph), 3.75 (1H, m, C*H*HCH_2Ph), 4.02–4.04 (1H, m, CHC*H*H), 4.07–4.18 (4H, m, C*H*C*H*CH*H*, C*H*CHO_2), 4.25–4.31 (1H, m, CH*H*CH_2Ph), 5.66 (1H, d, *J*=3.7, OCHO), 7.02–7.26 (4H, m, ArH); δ_C 25.5, 26.5, 26.6, 27.1 (4×CH_3), 38.7 (C*C*H_2Ph), 39.7 (CH_2*C*H_2Ph), 66.0 (*C*H_2CH_2Ph), 67.2 (CH*C*H_2), 73.3 (*C*HCHCH_2), 79.7 (*C*HCH_2), 81.8 (*C*CH_2Ph), 82.7 (*C*HCHO_2), 103.4 (OCHO), 109.4, 112.8 [2×*C*$(CH_3)_2$], 126.6, 127.1, 129.4, 130.2 (ArCH), 136.6, 141.4 (2×ArC); *m/z* 361 [$M^+-(CH_3)$, 1.7%], 118 (18), 117 (22), 115 (11), 101 (23), 100 (23), 91 (11), 85 (20), 71 (11), 59 (10), 55 (15), 44 (12), 43 (100), 42 (11) [found: $M^+-(CH_3)$, 361.1651; $C_{20}H_{25}O_6$ requires: M, 361.1651]; $[\alpha]_D^{20}$=+41.8 [*c* 1.00 (CH_2Cl_2)].

*3.16.3. Compound **29a***

R_f 0.64 (hexane:ethyl acetate, 3:2) (45% yield); ν (film) 3029 (ArCH), 1262, 1092, 1025 cm^{-1} (CO); δ_H 1.37 (3H, s, CH_3), 1.45 (6H, s, 2×CH_3), 1.46 (3H, s, CH_3), 2.97 (1H, d, *J*=16.2, PhC*H*H), 3.16 (1H, d, *J*=16.2, PhCH*H*), 3.47 (1H, d, *J*=9.8, CC*H*HO), 3.73 (1H, d, *J*=9.8, CCH*H*O), 4.06 (1H, dd, *J*=13.1, 2.1, CHC*H*HO), 4.14–4.18 (2H, m, C*H*CHCH*H*O), 4.24–4.28 (1H, m, C*H*CH_2O), 4.67 (1H, d, *J*=13.4, PhC*H*HO), 4.92 (1H, d, *J*=13.4, PhCH*H*O), 7.09–7.26 (4H, m, ArH); δ_C 25.8, 26.0, 26.3, 26.5 (4×CH_3), 32.1 (PH*C*H_2C), 60.9 (CH*C*H_2O), 66.8 (PhCH_2O), 71.3 (*C*HCH_2O), 71.4 (C*C*H_2O), 73.7 (*C*HCHCH_2O), 77.7 (*C*CHCHCH_2), 106.6, 109.5 [2×*C*$(CH_3)_2$], 111.6 (*C*CH_2O), 124.4, 126.3, 127.2, 127.8 (ArCH), 134.1, 136.7 (ArC); *m/z* 362 (M^+, 5.5%), 173 (14), 145 (15), 144 (15), 129 (11), 117 (16), 116 (13), 115 (13), 105 (14), 104 (27), 100 (12), 85 (20), 59 (19), 55 (14), 44 (16), 43 (100), 42 (18), 41 (17) [found: M^+, 362.1740; $C_{20}H_{26}O_6$ requires: M, 362.1729]; $[\alpha]_D^{20}$=−83.3 [*c* 0.94 (CH_2Cl_2)].

*3.16.4. Compound **29b***

R_f 0.66 (hexane:ethyl acetate, 3:2) (40% yield); ν (film) 3067 (ArH), 1247, 1215, 1053 cm^{-1} (CO); δ_H 1.16 (3H, s, CH_3), 1.46 (3H, s, CH_3), 1.50 (3H, s, CH_3), 1.53 (3H, s, CH_3), 2.82 (1H, m, PhC*H*HCH_2), 3.12 (1H, d, *J*=15.9, PhC*H*HC), 3.28 (1H, m, PhCH*H*CH_2), 3.65 (1H, dd, *J*=12.8, 7.3, CHC*H*HO), 3.68 (1H, d, *J*=15.9, PhCH*H*C), 3.91–4.19 (5H, m, C*H*C*H*CH*H*O, PhCH_2C*H*$_2$O), 4.20 (1H, d, *J*=9.8, CC*H*HO), 4.39 (1H, d, *J*=9.8, CCH*H*O), 7.04–7.26 (4H, m, ArH); δ_C 25.85 (2×CH_3), 26.8, 27.9 (2×CH_3), 38.1 (Ph*C*H_2C), 39.2 (Ph*C*H_2CH_2), 62.6 (CH*C*H_2O), 63.9 (C*C*H_2O), 67.55 (PhCH_2*C*H_2), 70.1 (*C*HCH_2O), 74.5 (PhCH_2*C*), 74.9 (*C*HCHCH_2O), 106.6, 109.9 [2×*C*$(CH_3)_2$], 110.3 [*C*CH_2O], 126.6, 126.9, 129.3, 130.1 (ArCH), 136.5, 139.6 (ArC); *m/z* 376 (M^+, 2.6%), 176 (11), 118 (13), 117 (25), 115 (13), 100 (15), 91 (11), 85 (15), 59 (16), 55 (11), 44 (24), 43 (100), 42 (16), 41 (17) [found: M^+, 376.1926; $C_{21}H_{28}O_6$ requires: M, 376.1886]; $[\alpha]_D^{20}$=−19.4 [*c* 1.45 (CH_2Cl_2)].

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21. (a) Crystal data (deposited at the Cambridge Crystallographic Data Centre): $C_{20}H_{28}O_7$, M=380.42; monoclinic, a=14.5447(13), b=6.6448(10), c=21.591(3) Å, β=91.129(9)°; U=2086.3(5) Å; space group $P2_1$; Z=4; D_c=1.211 Mg·m^{-3}; λ=0.71073 Å; μ=0.091 mm^{-1}; F(000)=816; T=24–25±1°C. Intensity data were measured on a CAD–4 diffractometer. The data were reduced by routine methods.[21b] The structure was solved by direct methods[21c] and refined to all 3037 unique F_o^2 by full matrix least squares.[21d] Most of the hydrogen atoms were seen in difference Fourier maps, but for the final refinement all H atoms were placed at idealised positions and refined as rigid atoms, with the exception of the OH and the methyl group hydrogens, which were located in Fourier calculations; these groups were refined as rigid rotators. Final $wR2$=0.1440 for all data and 499 parameters; $R1$=0.0547 for 2366 $F_o>4\alpha(F_o)$. The enantiomorph was fixed according to the known stereochemistry of four of the chiral centres in the molecule. (b) Data were processed on an AlphaStation 200 4:166 (OpenVMS Alpha V6.2), using the program XCAD4B (K. Harms, University of Marburg) and the commercial package SHELXTL-PLUS Release 5.05/V, © 1996, Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin. (c) SHELXS-97: Fortran program for crystal structure solution, ©1997, G. M. Sheldrick. (d) SHELXL-97: Fortran program for crystal structure solution, © 1997, G. M. Sheldrick.
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