Synthesis of β-D-talopyranosides and β-D-mannopyranosides *via* intramolecular nucleophilic substitution

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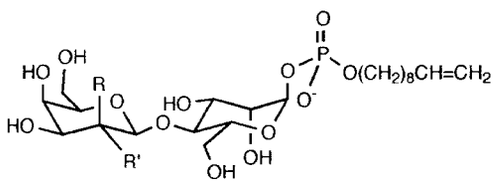
The selective and efficient syntheses of β-D-talopyranosides and β-D-mannopyranosides were achieved from β-D-galactopyranosides and β-D-glucopyranosides, respectively, that carry a benzoyl group at O-3 and a triflyl group at O-2. The transformation was performed in the presence of an alcohol *via* intramolecular nucleophilic attack of the benzoyl group with inversion of configuration at C-2 that provided, first, the formation of the corresponding 2,3-(alkyl orthobenzoates) of the desired β-D-talopyranosides or β-D-mannopyranosides, followed by acidic opening of the cyclic orthoesters.

Introduction

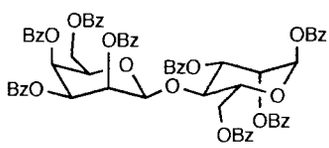
It has been shown recently[1] that the β-D-galactopyranosyl-(1→4)-α-D-mannopyranosyl phosphate **1** is an effective exogenous acceptor for the elongating α-D-mannopyranosylphosphate transferase of the *Leishmania* lipophosphoglycan biosynthesis. In order to predict which sugar hydroxy groups may be involved in enzyme–substrate recognition events chemical synthesis of some structural analogues of the substrate **1** has been designed. In the framework of this project chemical synthesis of the octa-*O*-benzoyl-β-D-talopyranosyl-(1→4)-α-D-mannopyranose **3** has been undertaken. The latter will be used for the preparation of the biosyl phosphate **2**, which is an epimer of the acceptor **1** at C-2′.

As well as the chemical synthesis of β-D-mannopyranosides,[2,3] the synthesis of β-D-talopyranosides is rather difficult to perform *via* standard glycosylation techniques, since both the neighbouring group participation and the anomeric effect uniformly favour the formation of α-D-manno- and α-D-talopyranosides. Great effort has been undertaken to develop alternative methods for β-D-mannoside synthesis.[2–11] Since synthesis of β-D-glucopyranosides is relatively easy owing to favourable neighbouring group assistance,[2] methods based on epimerization of β-D-glucosides to β-D-mannosides have appeared. Epimerization at C-2 can be achieved either *via* an oxidation to give the 2-uloses followed by reduction,[4,5] or *via* an S_N2 reaction.[6–9] Chemical syntheses of methyl and benzyl β-D-talopyranosides[12,13] were carried out from the corresponding β-D-galactopyranosides *via* an oxidation–reduction at C-2. Since the reduction is not completely stereoselective,[13] the corresponding β-D-galactosides were formed to various extents in addition to β-D-talosides.



1 R = H, R′ = OH

2 R = OH, R′ = H



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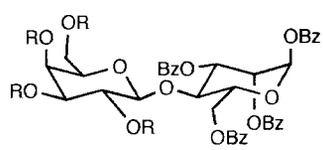
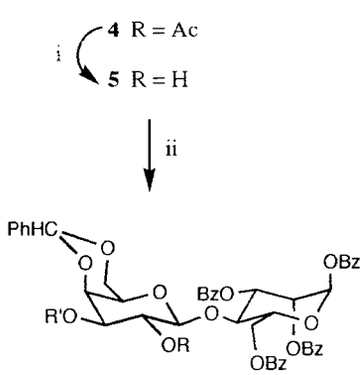
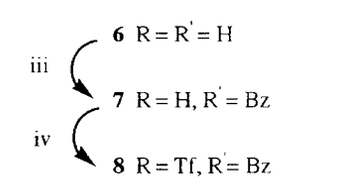






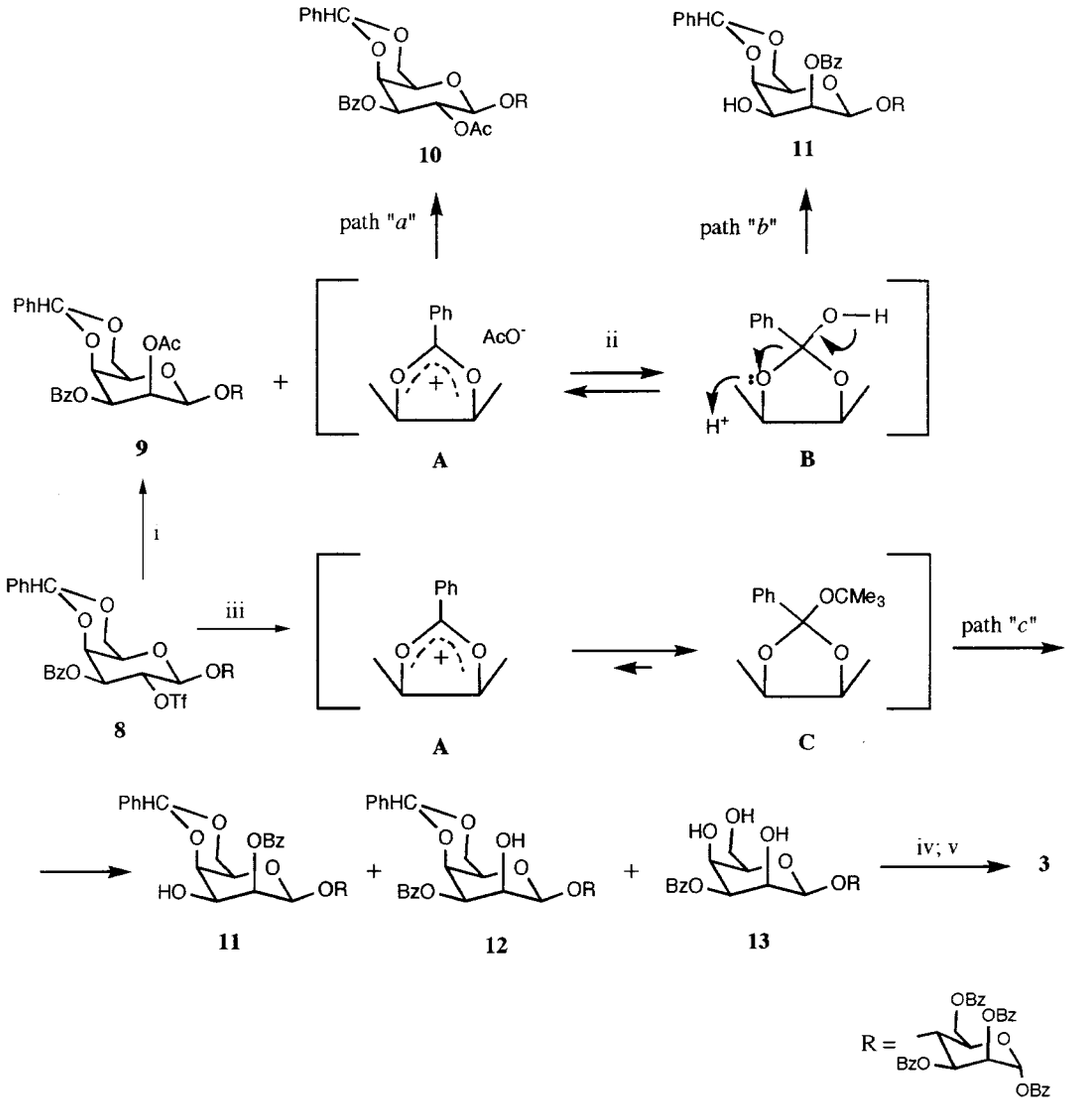
Scheme 1 *Reagents*: i, HCl, MeOH–CH_2Cl_2; ii, $PhCH(OMe)_2$, $TsOH·H_2O$, MeCN; iii, *N*-benzoylimidazole, $CHCl_3$; iv, Tf_2O, CH_2Cl_2–pyridine.

Results and discussion

We attempted to synthesize the disaccharide **3** starting from the easily available 3′-*O*-benzoyl-2′-*O*-triflyl-β-D-galactoside **8** *via* an S_N2 reaction with inversion of configuration at C-2′ using AcO^- as an external nucleophile.

The triflate **8** (Scheme 1) was prepared from the disaccharide **4**[14] in a few steps. The disaccharide **4** was converted into benzylidene derivative **6** (56%) by O-deacetylation[15] with HCl in methanol followed by treatment of the resulting tetraol **5** with α,α-dimethoxytoluene in acetonitrile in the presence of $TsOH·H_2O$. The diol **6** was then selectively benzoylated with *N*-benzoylimidazole in chloroform to give the 3-*O*-benzoate **7** (85%), which reacted with triflic anhydride in dichloromethane in the presence of pyridine to give the triflate **8** in 90% yield.

However, the reaction of the triflate **8** with caesium acetate in



Scheme 2 *Reagents*: i, CsOAc, 18-crown-6, toluene; ii, water; iii, Bu′OH, 2,4,6-collidine, toluene; iv, 80% AcOH; v, BzCl, pyridine.

the presence of 18-crown-6 gave a mixture of one D-galactose **10** and two D-taloside **9** and **11** derivatives (Scheme 2). The expected 2-*O*-acetyl-β-D-taloside **9**, arising as a result of direct intermolecular nucleophilic displacement of the triflate group, was formed in 29% yield only. Two other products **10** (24%) and **11** (26%) seemed to arise by 3′-*O*-benzoyl neighbouring group participation *via* the formation of the acyloxonium intermediate **A**. Opening the intermediate **A** by the nucleophilic attack of the AcO^- at C-2 (path "*a*") gives the 2-*O*-acetyl-β-D-galactoside **10** with *trans*-2,3-diol configuration. The 2-*O*-benzoyl-β-D-taloside **11** with *cis*-2,3-diol configuration seems to arise as a result of opening of the orthoacid **B** (path "*b*"), that could form from the cyclic cation **A** either in the presence of traces of water or during aqueous work-up of the reaction mixture.

Analogous neighbouring group participation by acyloxy groups in reactions of nucleophilic displacement of methane- or toluene-sulfonate resulting in products other than those formed by direct intermolecular attack is known from the literature.[16] Some attempts were undertaken [17,18] to use it for aimed syntheses of rare sugars. However, using trifluoromethanesulfonate (triflate) as a very effective leaving group for S_N2 inversion in sugars normally [19] led to products of intermolecular nucleophilic substitution. This is also true for conversion of some 3-*O*-acyl-2-*O*-triflyl-D-glucopyranosides to the corresponding D-mannopyranosides.[9,20] An intermolecular S_N2 reaction at C-2 in the 4′,6′-*O*-benzylidene-β-D-galactopyranoside **8** seems to meet steric hindrance that makes predominant an intramolecular displacement of 2-triflate with participation of the neighbouring 3-benzoate.

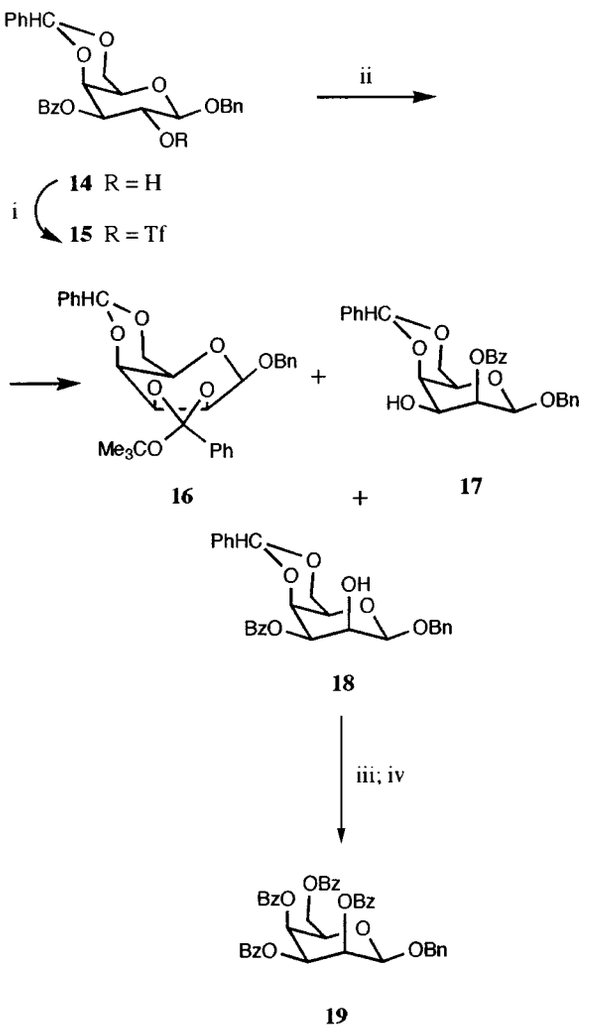
Probably, the neighbouring group effect could be inhibited using allyl or benzyl protection at O-3. Examples of intermolecular epimerization of 3-*O*-alkyl-β-D-glucosides to β-D-mannosides are summarized in refs. 2, 3, 6, 7 and 19. Gunther and Kunz [8] developed an intramolecular version of the epimerization of β-D-glucopyranosides to β-D-mannopyranosides using the *N*-phenylcarbamoyl group as a neighbouring group active protection at O-3. Stabilization of the 2,3-(*N*-phenylcarbamoyl)oxonium intermediate was achieved by forming the corresponding 2,3-iminocarbonate, which embodied the desired *cis*-2,3-diol structure and prevented the formation of products with *trans*-2,3-diol orientation.

We supposed that stabilization of the acyloxonium intermediate **A** in a form of the corresponding 2′,3′-orthoester **C** would exclude path "*a*" (Scheme 2) and give products predominantly with β-D-*talo*-configuration (path "*c*"). Indeed, alcoholysis of the triflate **8** with *tert*-butyl alcohol in the presence of 2,4,6-trimethylpyridine (2,4,6-collidine) in boiling toluene gave the β-D-talosides **11**–**13** in a total yield of 71%. It seems that the acidity of 2,4,6-collidinium triflate (formed *in situ*) is sufficient for opening of the cyclic orthoester **C** to give the β-D-talosides **11** and **12**, as well as for partial debenzylidenation of the 3-*O*-benzoate **12** to form the triol **13**.

When the interaction of the triflate **8** with *tert*-butyl alcohol followed by acid hydrolysis and conventional benzoylation

were carried out without isolation of intermediates, the desired β-D-talopyranosyl-(1→4)-α-D-mannopyranose octabenzoate **3** was obtained in an overall yield of 76%. The *talo*-configuration of the non-reducing monosaccharide residue in the disaccharides **3**, **9** and **11**–**13** was clearly confirmed by the characteristic values of $J_{1',2'}$ (<1 Hz) and $J_{2',3'}$ (2.0–3.5 Hz) in ^{1}H NMR spectra.

The same sequence of reactions gave a good result in the synthesis of benzyl 2,3,4,6-tetra-*O*-benzoyl-β-D-talopyranoside **19** (65%) from the 2-*O*-triflyl-β-D-galactoside **15** (Scheme 3).

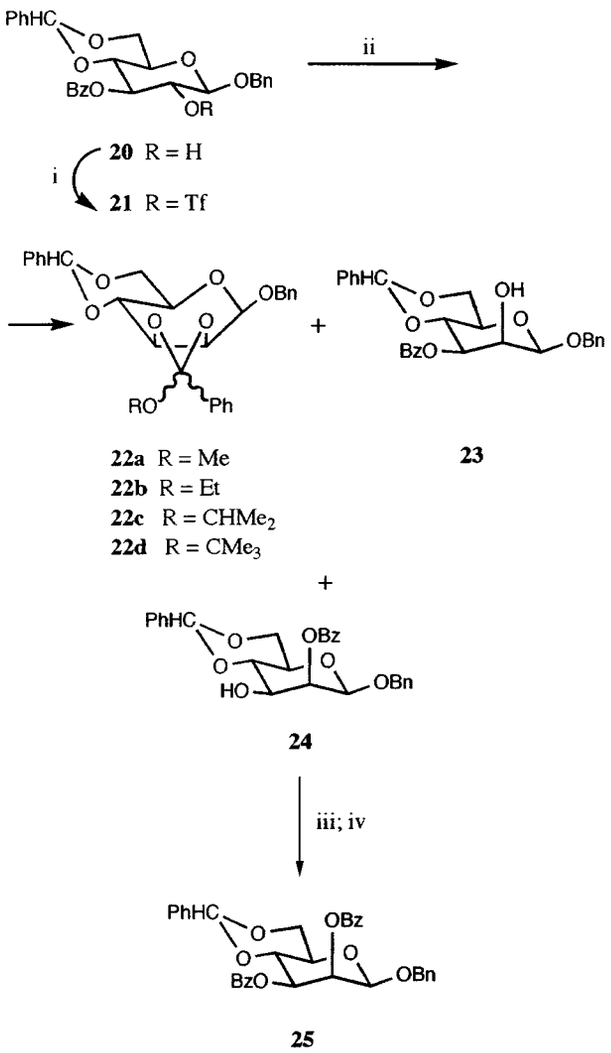


Scheme 3 *Reagents (and selected conditions)*: i, Tf_2O, CH_2Cl_2–pyridine; ii, Bu^{t}OH, 2,4,6-collidine, toluene; iii, 80% AcOH (70 °C); iv, BzCl, pyridine.

Analysis of products of the reaction of the triflate **15** with *tert*-butyl alcohol showed the formation of the orthoester **16** (12%) along with the isomeric 2- and 3-*O*-benzoyl-β-D-talosides **17** (48%) and **18** (10%) that confirmed the proposed pathway of the reaction through cyclic orthoesters. It should be noted that, unlike the reaction of the 2′-*O*-triflyl-β-D-galactoside **8** with *tert*-butyl alcohol (Scheme 2), no product of debenzylidenation was noticed during the transformation of the 2-*O*-triflyl-β-D-galactoside **15** to the β-D-talosides **16**–**18**.

The structures of the β-D-talosides **17**–**19** were clearly confirmed by ^{1}H NMR data ($J_{1,2}$ <1 Hz, $J_{2,3}$ ~3 Hz). In comparison with the β-D-talosides, the signals of 1-H and 2-H in the ^{1}H NMR spectrum of the orthoester **16** showed unusually large coupling constants of $J_{1,2}$ 2.3 Hz and $J_{2,3}$ 6.8 Hz. The difference seems to be due to the presence of the 2,3-orthoester ring system, which forces the D-taloside ring to adopt an $^OH_5$ conformation. Analogous changes of ^{1}H NMR data were observed for 2,3-carbonates of β-D-mannopyranose.[8] The molecular mass of the orthoester **16** was confirmed by electrospray mass spectrometry (ESMS) (see Experimental section).

Further, the method was extended for the synthesis of the β-D-mannoside **25** starting from the 2-*O*-triflyl-β-D-glucoside **21** (Scheme 4). Investigation of the reaction of the triflate **21**



Scheme 4 *Reagents (and selected conditions)*: i, Tf_2O, CH_2Cl_2–pyridine; ii, an alcohol (see Table 1), 2,4,6-collidine, toluene; iii, 80% AcOH (rt); iv, BzCl, pyridine.

with different alcohols in the presence of 2,4,6-collidine was carried out, the results obtained being summarized in Table 1. It turned out that the triflate **21** gave the unstable orthoester **22d**, converting partly into the isomeric monobenzoates **23** and **24** during the reaction, in the case of sterically hindered *tert*-butyl alcohol only. The use of methyl, ethyl or isopropyl alcohols in this reaction gave the orthoesters **22a**–**22c** (as pairs of diastereoisomers) and only traces of the products **23** and **24**. In the reaction with ethyl alcohol the diastereoisomeric 2,3-(ethyl orthobenzoates) **22b-1** (20%) and **22b-2** (75%) were purified by column chromatography and their structures were confirmed by ^{1}H NMR and mass-spectrometry data. As for the β-D-talopyranoside 2,3-orthoester **16**, the larger values of $J_{1,2}$ ~2.5 and $J_{2,3}$ ~6.7 Hz in ^{1}H NMR spectra of compounds **22b-1** and **22b-2** (in a contrast with those of the β-D-mannoside **25**) indicated, probably, an $^OH_5$ conformation for the pyranose ring.

The reaction of the triflate **21** with any alcohol in the presence of 2,4,6-collidine followed by mild acid hydrolysis (which opens the cyclic orthoester) and subsequent benzoylation gave the β-D-mannoside **25** in an overall yield of ~90%. The ^{1}H NMR data of compound **25**, including characteristic values

Table 1 Conditions and products of the reaction[a] of the triflate **21** with different alcohols in toluene in the presence of 2,4,6-collidine (1.2 equiv.) at 110 °C

Alcohol	Reaction time (*t*/h)	Yield of the corresponding orthoester **22** (%)	Formation of the monobenzoates (**23** + **24**)[b] (%)	Yield of the dibenzoate **25**[c] (%)
MeOH (15 equiv.)	3	>90[b] (**22a**)	traces	90
EtOH (15 equiv.)	2	95[d] (**22b**)	traces	89
Pr^{i}OH (15 equiv.)	1.5	>90[b] (**22c**)	traces	89
Bu^{t}OH (30 equiv.)	4	~25[b] (**22d**)	~75	91

[a] See Scheme 4. [b] Estimated by TLC. [c] The dibenzoate **25** was prepared from the sum of products (**22** + **23** + **24**) by hydrolysis with 80% AcOH followed by standard benzoylation (see Experimental section). [d] The diastereoisomers **22b-1** (20%) and **22b-2** (75%) were isolated.

of $J_{1,2}$ <1.0 and $J_{2,3}$ 3.6 Hz, confirmed the β-D-mannoside configuration.

It should be noted that treatment of the orthoesters **22a**–**d** with 80% AcOH gave the 2-*O*- and 3-*O*-benzoates **24** and **23**, respectively, in approximately equal proportion, as was detected by TLC. According to the literature data,[21] formation of the sole β-D-mannoside **24** with axial orientation of the O-benzoyl group would be expected. Possibly, the presence of 4,6-*O*-acetal protection in the orthoesters **22a**–**d** makes both O-2 and O-3 equally available for the reaction with acid that gives the isomeric benzoates **23** and **24**, respectively. The formation of the isomeric 2-*O*- (**11** and **17**) and 3-*O*-benzoates (**12** and **18**) of 4,6-*O*-benzylidene-β-D-talopyranoside can be explained similarly.

Thus, we report a novel, simple and convenient method of synthesis of β-D-talopyranosides and β-D-mannopyranosides based on an intramolecular nucleophilic attack of the 3-*O*-benzoyl group with inversion of configuration of C-2 in the corresponding 3-*O*-benzoyl-2-*O*-triflyl-β-D-galactopyranosides and -β-D-glucopyranosides, respectively. The method can be considered as a useful alternative to intermolecular epimerization† of analogous 3-*O*-benzyl (or allyl)-2-*O*-triflyl derivatives, because (1) the starting 3-benzoates (like compounds **7**, **14** or **20**) are much easier to furnish than are the corresponding 3-benzyl (or allyl) ethers and (2) the following de-O-benzylation (de-O-allylation) may not be compatible with generic synthetic strategy. The method can be especially utilitarian when an intermolecular inversion at C-2 is not effective for some reason (*e.g.*, steric hindrance because of bulky aglycone or protecting groups). It should be particularly recommended for the preparation of β-D-talosides since it seems to be practically more convenient and efficient than the oxidation–reduction approach which has been described earlier.[12,13] Orthogonally protected products resulting from opening of the intermediate orthoesters (*e.g.*, derivatives **11** and **12**, **17** and **18** or **23** and **24**) can be easily separated by flash chromatography and used as glycosyl acceptors for the synthesis of branched D-mannose- and D-talose-containing oligosaccharides.

Experimental

General procedures

Mps were determined on a Reichert hot-plate apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 141 polarimeter; $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. NMR spectra (^{1}H at 200 and 500 MHz and ^{13}C{^{1}H} at 50.3 and 125 MHz) were recorded with Bruker AM-200 and AM-500 spectrometers for solutions in $CDCl_3$, unless otherwise indicated. Chemical shifts (δ) are given relative to those for Me_4Si; *J*-values are given in Hz. ES mass spectra were recorded with a VG Quattro system (VG Biotech, UK). TLC was performed on Kieselgel 60 F_{254} (Merck) with *A*, chloroform–methanol (9:1); *B*, toluene–ethyl acetate (7:3); *C*, toluene–ethyl acetate (4:1); *D*, dichloromethane–ethyl acetate (9:1); and *E*, toluene–ethyl acetate (9:1) as developers and detection under UV light or by charring with sulfuric acid–water–ethanol (15:85:5). Flash-column chromatography (FCC) was performed on Kieselgel 60 (0.040–0.063 mm) (Merck). Dichloromethane, acetonitrile and toluene were freshly distilled from CaH_2. Solutions worked up were concentrated under reduced pressure at <40 °C.

4,6-*O*-Benzylidene-β-D-galactopyranosyl-(1→4)-1,2,3,6-tetra-*O*-benzoyl-α-D-mannopyranose 6

A solution of HCl in MeOH [prepared at 0 °C from acetyl chloride (0.8 cm^3) and methyl alcohol (20 cm^3)] was added to a solution of the compound **4**[14] (2.34 g, 2.52 mmol) in CH_2Cl_2 (6 cm^3) and the resulting solution was kept at 20 °C for 44 h; TLC (solvent *A*) then showed the formation of one major product (R_f 0.48; presumably the O-deacetylated derivative **5**). The mixture was concentrated to dryness and toluene was evaporated off from the residue. The residue was dissolved in acetonitrile (50 cm^3), and $PhCH(OMe)_2$ (0.57 cm^3, 3.78 mmol) and TsOH (50 mg) were added to the solution. After 16 h at 20 °C the solution was treated with Et_3N (0.5 cm^3), the mixture was concentrated to dryness and toluene was evaporated off from the residue. FCC (3:2 toluene–ethyl acetate) gave *4′,6′-O-benzylidene derivative* **6** (1.34 g, 56%), mp 130–132 °C (from toluene); $[\alpha]_D^{25}$ +8 (*c* 1, $CHCl_3$); R_f 0.1 (solvent *B*) (Found: C, 66.7; H, 5.2. $C_{47}H_{42}O_{15}$ requires C, 66.7; H, 5.0%); δ_H($CDCl_3$ + D_2O) 2.60 (1 H, s, 5′-H), 3.41 (1 H, dd, $J_{2',3'}$ 9.5, $J_{3',4'}$ 3.6, 3′-H), 3.41 (1 H, d, $J_{6a',6b'}$ 10.2, 6′-H^a), 3.62 (1 H, d, 6′-H^b), 3.63 (1 H, dd, $J_{1',2'}$ 7.7, 2′-H), 3.84 (1 H, d, 4′-H), 4.31 (1 H, ddd, $J_{5,6a}$ 1.8, $J_{5,6b}$ 2.6, 5-H), 4.38 (1 H, d, 1′-H), 4.47 (1 H, t, $J_{3,4} = J_{4,5} = 9.8$, 4-H), 4.52 (1 H, dd, $J_{6a,6b}$ 12.1, 6-H^a), 4.99 (1 H, dd, 6-H^b), 5.23 (1 H, s, PhC*H*), 5.77 (1 H, dd, $J_{1,2}$ 1.8, $J_{2,3}$ 3.2, 2-H), 5.97 (1 H, dd, 3-H), 6.49 (1 H, d, 1-H) and 7.18–8.12 (25 H, m, 5 × Ph).

3-*O*-Benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-1,2,3,6-tetra-*O*-benzoyl-α-D-mannopyranose 7

Benzoyl chloride (0.15 cm^3, 1.311 mmol) was added to a stirred and cooled (0 °C) solution of imidazole (0.18 g, 2.622 mmol) in anhydrous $CHCl_3$ (3 cm^3). After 30 min, the mixture was filtered and the solids were washed with $CHCl_3$ (3 × 2 cm^3). The filtrate and washings were added to a solution of the diol **6** (0.74 g, 0.874 mmol) in $CHCl_3$ (5 cm^3) and the mixture was stirred under reflux for 12 h. The reaction mixture was diluted with CH_2Cl_2, washed successively with saturated aq. $NaHCO_3$ and water, dried by filtration through cotton wool and concentrated. FCC [toluene–ethyl acetate (95:5) ⟶ (9:1)] of the residue gave the *3′-O-benzoate* **7** (0.72 g, 86%), mp 132–134 °C (from Et_2O–hexane); $[\alpha]_D^{25}$ +89.5 (*c* 1, $CHCl_3$); R_f 0.49 (solvent *C*) (Found: C, 67.8; H, 4.8. $C_{54}H_{46}O_{16}$ requires C, 68.2; H, 4.9%); δ_H 2.75 (1 H, s, 5′-H), 3.50 (1 H, d, $J_{6a',6b'}$ 11.9, 6′-H^a), 3.78 (1 H, d, 6′-H^b), 4.18 (1 H, dd, $J_{1',2'}$ 7.1, $J_{2',3'}$ 9.9, 2′-H), 4.20 (1 H, d, $J_{3',4'}$ 3.6, 4′-H), 4.40 (1 H, dt, $J_{5,6a} = J_{5,6b} = 1.5$, 5-H), 4.54 (1 H, dd, $J_{6a,6b}$ 11.8, 6-H^a), 4.60 (1 H, t, $J_{3,4} = J_{4,5} = 9.2$, 4-H), 4.68 (1 H, d, 1′-H), 4.97 (1 H, dd, 3′-H), 5.29 (1 H, dd, 6-H^b), 5.32 (1 H, s, PhC*H*), 5.89 (1 H, dd, $J_{1,2}$ 1.1, $J_{2,3}$ 3.1, 2-H),

† So far, the intermolecular epimerization has been described[2,3,6,7,19] for the preparation of β-D-mannosides only (not for β-D-talosides).

6.09 (1 H, dd, 3-H), 6.60 (1 H, d, 1-H) and 7.10–8.20 (30 H, m, 6 × Ph).

3-*O*-Benzoyl-4,6-*O*-benzylidene-2-*O*-trifluoromethylsulfonyl-β-D-galactopyranosyl-(1→4)-1,2,3,6-tetra-*O*-benzoyl-α-D-mannopyranose 8

Triflic anhydride (0.573 cm^3, 3.408 mmol) was added dropwise to a cooled (−60 °C), stirred solution of compound **7** (0.81 mg, 0.852 mmol) in CH_2Cl_2 (15 cm^3) containing pyridine (0.67 cm^3, 8.52 mmol), and then the reaction mixture was allowed to warm to rt. After 1 h, the mixture was diluted with CH_2Cl_2, washed successively with ice-cold 0.1 mol dm^{-3} HCl, ice-cold saturated aq. $NaHCO_3$ and water, dried by filtration through cotton wool and concentrated. Toluene was evaporated off from the residue. FCC [toluene–ethyl acetate (95:5) ⟶ (9:1)] gave the 2′-*O*-triflate **8** (0.824 g, 89%) as an amorphous solid; $[\alpha]_D^{25}$ +68 (*c* 1, $CHCl_3$); R_f 0.59 (solvent *C*); δ_H 3.30 (1 H, s, 5′-H), 3.82 (1 H, d, $J_{6a',6b'}$ 12.2, 6′-H^a), 4.07 (1 H, d, 6′-H^b), 4.46 (1 H, d, $J_{3',4'}$ 3.2, 4′-H), 4.47 (1 H, dt, $J_{5,6a} = J_{5,6b} = 2.2$, 5-H), 4.77 (1 H, dd, $J_{6a,6b}$ 12.7, 6-H^a), 4.83 (1 H, t, $J_{3,4} = J_{4,5} = 9.5$, 4-H), 4.86 (1 H, dd, 6-H^b), 5.03 (1 H, d, $J_{1',2'}$ 7.1, 1′-H), 5.25 (1 H, dd, $J_{2',3'}$ 10.2, 2′-H), 5.29 (1 H, dd, 3′-H), 5.37 (1 H, s, PhC*H*), 5.96 (1 H, dd, $J_{1,2}$ 2.0, $J_{2,3}$ 3.3, 2-H), 6.02 (1 H, dd, 3-H), 6.60 (1 H, d, 1-H) and 7.22–8.22 (30 H, m, 6 × Ph).

Reaction of the triflate 8 with CsOAc

A mixture of the CsOAc (77 mg, 0.4 mmol) and 18-crown-6 (10 mg, 0.04 mmol) was dried by evaporation of anhydrous toluene therefrom. The residue was suspended in the same solvent (1 cm^3) and a solution of the triflate **8** (108 mg, 0.1 mmol) in toluene (1 cm^3) was added. The reaction mixture was stirred under reflux for 1.5 h, then diluted with CH_2Cl_2 and washed successively with saturated aq. $NaHCO_3$ and water, dried by filtration through cotton wool and concentrated. FCC [toluene–ethyl acetate (95:5) ⟶ (2:1)] of the residue provided, first, *2-O-acetyl-3-O-benzoyl-4,6-O-benzylidene-β-D-galactopyranosyl-(1→4)-1,2,3,6-tetra-O-benzoyl-α-D-mannopyranose* **10** (24 mg, 24%) as an amorphous solid; $[\alpha]_D^{25}$ +83 (*c* 1, $CHCl_3$); R_f 0.55 (solvent *C*) (Found: C, 67.4; H, 5.2. $C_{56}H_{48}O_{17}$ requires C, 67.7; H, 4.9%); δ_H 1.90 (3 H, s, Ac), 2.80 (1 H, s, 5′-H), 3.47 (1 H, d, $J_{6a',6b'}$ 12.4, 6′-H^a), 3.75 (1 H, d, 6′-H^b), 4.23 (1 H, d, $J_{3',4'}$ 3.1, 4′-H), 4.36 (1 H, dt, $J_{5,6a} = J_{5,6b} = 2.3$, 5-H), 4.51 (1 H, dd, $J_{6a,6b}$ 12.1, 6-H^a), 4.64 (1 H, t, $J_{3,4} = J_{4,5} = 9.6$, 4-H), 4.77 (1 H, dd, 6-H^b), 4.80 (1 H, d, $J_{1',2'}$ 7.6, 1′-H), 5.00 (1 H, dd, $J_{2',3'}$ 10.8, 3′-H), 5.30 (1 H, s, PhC*H*), 5.55 (1 H, dd, 2′-H), 5.85 (1 H, dd, $J_{1,2}$ 1.0, $J_{2,3}$ 2.7, 2-H), 6.03 (1 H, dd, 3-H), 6.53 (1 H, d, 1-H) and 7.10–8.20 (30 H, m, 6 × Ph).

Continued elution gave *2-O-acetyl-3-O-benzoyl-4,6-O-benzylidene-β-D-talopyranosyl-(1→4)-1,2,3,6-tetra-O-benzoyl-α-D-mannopyranose* **9** (29 mg, 29%) as an amorphous solid; $[\alpha]_D^{25}$ −13.5 (*c* 1, $CHCl_3$); R_f 0.49 (solvent *C*) (Found: C, 67.7; H, 5.1%); δ_H 2.10 (3 H, s, Ac), 3.18 (1 H, br, 5′-H), 3.68 (1 H, dd, $J_{5',6a'}$ ~1.5, $J_{6a',6b'}$ 12.6, 6′-H^a), 3.72 (1 H, br, 4′-H), 3.83 (1 H, d, 6′-H^b), 4.31 (1 H, ddd, $J_{5,6a}$ 2.0, $J_{5,6b}$ 2.5, 5-H), 4.55 (1 H, dd, $J_{6a,6b}$ 12.2, 6-H^a), 4.81 (1 H, t, $J_{3,4} = J_{4,5} = 9.5$, 4-H), 4.90 (1 H, dd, 6-H^b), 4.93 (1 H, br, $J_{1',2'}$ <1, 1′-H), 5.19 (1 H, t, $J_{2',3'} = J_{3',4'} = 2.7$, 3′-H), 5.23 (1 H, br d, 2′-H), 5.34 (1 H, s, PhC*H*), 5.84–5.89 (2 H, m, 2- and 3-H), 6.52 (1 H, br, 1-H) and 6.90–8.20 (30 H, m, 6 × Ph); δ_C 29.70 (*Me*CO), 62.80 (C-6), 66.07 (C-2′), 67.32 (C-5′), 68.79 (C-6′), 69.51 (C-2, -3′), 70.52 (C-3), 70.91 (C-4′), 71.52 (C-4), 71.93 (C-5), 91.18 (C-1), 98.11 (C-1′), 100.79 (Ph*C*H), 126.3–137.3 (Ph) and 164.0–168.5 (C=O).

Further elution gave *2-O-benzoyl-4,6-O-benzylidene-β-D-talopyranosyl-(1→4)-1,2,3,6-tetra-O-benzoyl-α-D-mannopyranose* **11** (25 mg, 26%) as an amorphous solid; $[\alpha]_D^{25}$ −43 (*c* 1, $CHCl_3$); R_f 0.15 (solvent *C*), 0.48 (solvent *D*) (Found: C, 68.0; H, 5.0. $C_{54}H_{46}O_{16}$ requires C, 68.2; H, 4.9%); δ_H 2.88 (1 H, br, 5′-H), 3.59 (1 H, dd, $J_{5',6a'}$ ~ 1.5, $J_{6a',6b'}$ 12.4, 6′-H^a), 3.74 (1 H, d, 6′-H^b), 3.90 (1 H, t, $J_{2',3'} = J_{3',4'} = 3.2$, 3′-H), 3.98 (1 H, d, 4′-H), 4.25 (1 H, ddd, $J_{5,6a}$ 2.1, $J_{5,6b}$ 1.8, 5-H), 4.59 (1 H, dd, $J_{6a,6b}$ 12.3, 6-H^a), 4.69 (1 H, t, $J_{3,4} = J_{4,5} = 9.7$, 4-H), 4.73 (1 H, br, $J_{1',2'}$ <1, 1′-H), 5.02 (1 H, dd, 6-H^b), 5.41 (1 H, s, PhC*H*), 5.72 (1 H, br d, 2′-H), 5.82 (1 H, dd, $J_{1,2}$ 1.6, $J_{2,3}$ 2.9, 2-H), 5.89 (1 H, dd, 3-H), 6.52 (1 H, d, 1-H) and 6.90–8.20 (30 H, m, 6 × Ph); δ_C 62.56 (C-6), 67.20 (C-5′), 68.09 (C-3′), 68.52 (C-6′), 69.19 (C-2), 69.32 (C-2′), 70.14 (C-3), 71.25 (C-5), 72.76 (C-4′), 72.8 (C-4), 91.11 (C-1), 99.91 (C-1′), 100.96 (Ph*C*H), 128.2–137.4 (Ph) and 164.0–166.2 (C=O).

Reaction of the triflate 8 with *tert*-butyl alcohol

A solution of the triflate **8** (108 mg, 0.1 mmol), *tert*-butyl alcohol (0.283 cm^3, 3 mmol) and 2,4,6-collidine (0.016 cm^3, 0.12 mmol) in toluene (2 cm^3) was stirred under reflux for 3 h. The reaction mixture was diluted with CH_2Cl_2, washed successively with saturated aq. $NaHCO_3$ and water, and dried by filtration through cotton wool. The filtrate was concentrated to dryness and toluene was evaporated off from the residue (3 × 2 cm^3). FCC [toluene–ethyl acetate (95:5) ⟶ (8:2)] gave, first, *3-O-benzoyl-4,6-O-benzylidene-β-D-talopyranosyl-(1→4)-1,2,3,6-tetra-O-benzoyl-α-D-mannopyranose* **12** (13 mg, 13%) as an amorphous solid; $[\alpha]_D^{25}$ +53 (*c* 1, $CHCl_3$); R_f 0.52 (solvent *C*) (Found: C, 68.1; H, 5.0%); δ_H($CDCl_3$ + D_2O) 2.94 (1 H, br, 5′-H), 3.53 (1 H, d, $J_{6a',6b'}$ 12.2, 6′-H^a), 3.68 (1 H, d, 6′-H^b), 4.14 (1 H, d, $J_{2',3'}$ 2.2, 2′-H), 4.26 (1 H, d, $J_{3',4'}$ 2.2, 4′-H), 4.46 (1 H, dt, $J_{5,6a} = J_{5,6b} = 1.9$, 5-H), 4.61 (1 H, dd, $J_{6a,6b}$ 12.0, 6-H^a), 4.62 (1 H, t, $J_{3,4} = J_{4,5} = 9.5$, 4-H), 4.66 (1 H, s, 1′-H), 4.95 (1 H, t, 3′-H), 4.98 (1 H, dd, 6-H^b), 5.27 (1 H, s, PhC*H*), 5.88 (1 H, dd, $J_{1,2}$ 1.4, $J_{2,3}$ 3.0, 2-H), 6.09 (1 H, dd, 3-H), 6.56 (1 H, d, 1-H) and 7.15–8.20 (30 H, m, 6 × Ph).

Continued elution provided a mixture of two products, which was re-subjected to FCC [dichloromethane–ethyl acetate (10:0) ⟶ (9:1)] to give compound **11** (40 mg, 42%) and 3-*O*-benzoyl-β-D-talopyranosyl-(1→4)-1,2,3,6-tetra-*O*-benzoyl-α-D-mannopyranose **13** (14 mg, 16%) as an amorphous solid; $[\alpha]_D^{25}$ −10 (*c* 1, $CHCl_3$); R_f 0.15 (solvent *C*), 0.34 (solvent *D*); δ_H($CDCl_3$ + D_2O) 3.39–3.56 (3 H, m, 5′-H and 6′-H_2), 3.94 (1 H, d, $J_{2',3'}$ 2.0, 2′-H), 4.30 (1 H, d, $J_{3',4'}$ 2.0, 4′-H), 4.35 (1 H, ddd, $J_{5,6a}$ 1.2, $J_{5,6b}$ 2.4, 5-H), 4.60 (1 H, dd, $J_{6a,6b}$ 11.7, 6-H^a), 4.75 (1 H, s, 1′-H), 4.80 (1 H, t, 3′-H), 4.90 (1 H, dd, 6-H^b), 5.14 (1 H, t, $J_{3,4} = J_{4,5} = 9.4$, 4-H), 5.86 (1 H, dd, $J_{1,2}$ 1.8, $J_{2,3}$ 3.1, 2-H), 6.00 (1 H, dd, 3-H), 6.54 (1 H, d, 1-H) and 7.10–8.20 (25 H, m, 5 × Ph); ESMS(−): *m/z* 896.6 (100%, [M + ^{35}Cl]$^-$) and 898.7 (45%, [M + ^{37}Cl]$^-$) ($C_{47}H_{42}O_{16}$ requires *M*, 862.2).

2,3,4,6-Tetra-*O*-benzoyl-β-D-talopyranosyl-(1→4)-1,2,3,6-tetra-*O*-benzoyl-α-D-mannopyranose 3

A solution of the triflate **8** (108 mg, 0.1 mmol), *tert*-butyl alcohol (0.283 cm^3, 3 mmol) and 2,4,6-collidine (0.016 cm^3, 0.12 mmol) in toluene (2 cm^3) was stirred under reflux for 4 h. The reaction mixture was diluted with CH_2Cl_2, washed successively with ice-cold 0.1 mol dm^{-3} HCl, ice-cold saturated aq. $NaHCO_3$ and water, and dried by filtration through cotton wool. The filtrate was concentrated to dryness and toluene was evaporated off from the residue (3 × 2 cm^3). The residue was dissolved in 80% AcOH (5 cm^3) and the reaction mixture was kept for 2 h at 70 °C before the solution was concentrated to dryness and toluene was evaporated off from the residue (3 × 5 cm^3). The residue was dissolved in pyridine (2 cm^3), and benzoyl chloride (0.093 cm^3, 0.8 mmol) was added to the solution. After 16 h, the reaction mixture was diluted with CH_2Cl_2, washed successively with saturated aq. $NaHCO_3$ and water, dried by filtration through cotton wool and concentrated. FCC (95:5 toluene–ethyl acetate) of the residue gave the *disaccharide* **3** (89 mg, 76%) as an amorphous solid; $[\alpha]_D^{25}$ −42 (*c* 1, $CHCl_3$); R_f 0.62 (solvent *C*) (Found: C, 69.5; H, 4.8. $C_{68}H_{54}O_{19}$ requires C, 69.5; H, 4.6%); δ_H 3.97 (1 H, ddd, $J_{5',6a'}$ 8.0, $J_{5',6b'}$ 5.0, 5′-H), 4.15 (1 H, dd, $J_{6a',6b'}$ 10.2, 6′-H^a), 4.22 (1 H, dd, 6′-H^b), 4.35 (1 H,

ddd, $J_{5,6a}$ 1.8, $J_{5,6b}$ 1.4, 5-H), 4.72 (1 H, dd, $J_{6a,6b}$ 12.0, 6-H^a), 4.81 (1 H, dd, 6-H^b), 4.86 (1 H, t, $J_{3,4} = J_{4,5} = 9.8$, 4-H), 5.12 (1 H, br, $J_{1',2'} < 1$, 1′-H), 5.51 (1 H, t, $J_{2',3'} = J_{3',4'} = 3.5$, 3′-H), 5.75 (1 H, dd, $J_{1,2}$ 1.5, $J_{2,3}$ 2.4, 2-H), 5.83 (1 H, br d, 2′-H), 5.91 (1 H, d, 4′-H), 5.98 (1 H, dd, 3-H), 6.59 (1 H, d, 1-H) and 7.10–8.20 (40 H, m, 8 × Ph).

Benzyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-*O*-trifluoromethylsulfonyl-β-D-galactopyranoside 15

This compound was prepared by O-trifylation of the galactoside **14**[22] (0.32 g, 0.7 mmol) with triflic anhydride (0.47 cm^3, 2.8 mmol) in CH_2Cl_2 (10 cm^3) in the presence of pyridine (0.550 cm^3, 7 mmol), as described for the preparation of the triflate **8**. FCC (95:5 toluene–ethyl acetate) gave the triflate **15** (0.405 g, 97%) as an amorphous solid; $[\alpha]_D^{25}$ +79 (*c* 1, $CHCl_3$); R_f 0.54 (solvent *C*); δ_H 3.62 (1 H, s, 5-H), 4.12 (1 H, d, $J_{6a,6b}$ 12.0, 6-H^a), 4.42 (1 H, d, 6-H^b), 4.60 (1 H, s, 4-H), 4.76 (1 H, d, $J_{1,2}$ 7.0, 1-H), 4.77 and 5.02 (2 H, AB q, *J* 11.4, C*H*$_2$Ph), 5.35 (2 H, m, 2- and 3-H), 5.53 (1 H, s, PhC*H*) and 7.25–8.20 (15 H, m, 3 × Ph); ESMS(−): *m*/*z* 629 (100%, $[M + {}^{35}Cl]^-$) and 631 (45%, $[M + {}^{37}Cl]^-$) ($C_{28}H_{25}F_3O_9S$ requires *M*, 594.2).

Reaction of the triflate 15 with *tert*-butyl alcohol

A solution of the triflate **15** (180 mg, 0.303 mmol), *tert*-butyl alcohol (0.857 cm^3, 9.09 mmol) and 2,4,6-collidine (0.05 cm^3, 0.353 mmol) in toluene (4 cm^3) was stirred under reflux for 6 h. The reaction mixture was diluted with CH_2Cl_2, washed successively with saturated aq. $NaHCO_3$ and water, and dried by filtration through cotton wool. The filtrate was concentrated to dryness and toluene was evaporated off from the residue (3 × 2 cm^3). FCC [toluene–ethyl acetate (95:5) ⟶ (8:2)] gave, first, benzyl 4,6-*O*-benzylidene-2,3-*O*-(1-*tert*-butoxybenzylidene)-β-D-talopyranoside **16** (20 mg, 12%) as an amorphous solid; $[\alpha]_D^{25}$ +74 (*c* 1, $CHCl_3$); R_f 0.65 (solvent *C*); δ_H 1.20 (9 H, s, Me_3C), 4.03 (1 H, d, $J_{4,5}$ 1.5, 5-H), 4.10 (1 H, d, $J_{6a,6b}$ 12.9, 6-H^a), 4.38 (1 H, d, 6-H^b), 4.61 (1 H, dd, $J_{1,2}$ 2.3, $J_{2,3}$ 6.8, 2-H), 4.62 and 4.78 (2 H, AB q, *J* 11.2, C*H*$_2$Ph), 4.79 (1 H, dd, $J_{3,4}$ 4.3, 4-H), 5.06 (1 H, d, 1-H), 5.47 (1 H, s, PhC*H*), 5.70 (1 H, dd, 3-H) and 7.20–8.15 (15 H, m, 3 × Ph); ESMS(−): *m*/*z* 553.0 (100%, $[M + {}^{35}Cl]^-$) and 555.0 (45%, $[M + {}^{37}Cl]^-$) ($C_{31}H_{34}O_7$ requires *M*, 518.2).

Continued elution provided *benzyl 3-O-benzoyl-4,6-O-benzylidene-β-D-talopyranoside* **18** (15 mg, 10%), mp 181–183 °C (from isopropyl alcohol); $[\alpha]_D^{25}$ +8 (*c* 1, $CHCl_3$) [lit.,[12] mp 185–187 °C (from Pr^{i}OH); $[\alpha]_D^{24}$ −13.8 (*c* 1.1, CH_2Cl_2)]; R_f 0.43 (solvent *C*) (Found: C, 70.1; H, 5.7. Calc. for $C_{27}H_{26}O_7$: C, 70.1; H, 5.7%); δ_H($CDCl_3$ + D_2O) 3.49 (1 H, s, 5-H), 4.04 (1 H, d, $J_{2,3}$ 2.5, 2-H), 4.13 (1 H, d, $J_{6a,6b}$ 11.9, 6-H^a), 4.45 (1 H, d, $J_{3,4}$ 2.5, 4-H), 4.48 (1 H, d, 6-H^b), 4.50 (1 H, s, 1-H), 4.78 and 5.03 (2 H, AB q, *J* 12.2, C*H*$_2$Ph), 5.01 (1 H, t, 3-H), 5.50 (1 H, s, PhC*H*) and 7.20–8.15 (15 H, m, 3 × Ph).

Further elution gave *benzyl 2-O-benzoyl-4,6-O-benzylidene-β-D-talopyranoside* **17** (68 mg, 48%), mp 188–190 °C (from CH_2Cl_2–hexane); $[\alpha]_D^{25}$ −65 (*c* 1, $CHCl_3$) [lit.,[12] mp 181–183 °C (from Pr^{i}OH); $[\alpha]_D^{25}$ −61 (*c* 0.6, $CHCl_3$)]; R_f 0.11 (solvent *C*) (Found: C, 69.9; H, 5.7%); δ_H 3.40 (1 H, br, 5-H), 3.92 (1 H, t, $J_{2,3} = J_{3,4} = 4.1$, 3-H), 4.16 (1 H, dd, $J_{5,6a}$ 1.7, $J_{6a,6b}$ 11.8, 6-H^a), 4.18 (1 H, d, 4-H), 4.50 (1 H, dd, $J_{5,6b}$ 0.7, 6-H^b), 4.56 (1 H, s, 1-H), 4.70 and 4.93 (2 H, AB q, *J* 12.4, C*H*$_2$Ph), 5.59 (1 H, d, 2-H), 5.60 (1 H, s, PhC*H*) and 7.10–8.05 (15 H, m, 3 × Ph).

Benzyl 2,3,4,6-tetra-*O*-benzoyl-β-D-talopyranoside 19

A reaction of the triflate **15** (60 mg, 0.1 mmol) with *tert*-butyl alcohol (0.28 cm^3, 3 mmol) in toluene (2 cm^3) in the presence of 2,4,6-collidine (0.016 cm^3, 0.12 mmol), subsequent acid hydrolysis (2 cm^3 of 80% AcOH; 70 °C; 2 h) and benzoylation with benzoyl chloride (0.058 cm^3, 0.5 mmol) were accomplished as described for the preparation of the disaccharide **3**. FCC (95:5 toluene–ethyl acetate) gave the *β-D-taloside* **19** (45 mg, 65%) as an amorphous solid; $[\alpha]_D^{25}$ −56 (*c* 1, $CHCl_3$); R_f 0.68 (solvent *C*) (Found: C, 71.2; H, 5.2. $C_{41}H_{34}O_{10}$ requires C, 71.7; H, 5.0%); δ_H 4.27 (1 H, dd, $J_{5,6a}$ 7.5, $J_{5,6b}$ 3.4, 5-H), 4.60 (1 H, dd, $J_{6a,6b}$ 11.3, 6-H^a), 4.80 and 5.00 (2 H, AB q, *J* 12.8, C*H*$_2$Ph), 4.85 (1 H, dd, 6-H^b), 4.87 (1 H, s, 1-H), 5.55 (1 H, t, $J_{2,3} = J_{3,4} = 2.8$, 3-H), 5.82 (1 H, d, 2-H), 5.86 (1 H, d, 4-H) and 7.20–8.15 (25 H, m, 5 × Ph).

Benzyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-*O*-trifluoromethylsulfonyl-β-D-glucopyranoside 21

This compound was prepared by O-triflylation of the glucoside **20**[23] (0.41 g, 0.887 mmol) with triflic anhydride (0.6 cm^3, 3.55 mmol) in CH_2Cl_2 (10 cm^3) in the presence of pyridine (0.7 cm^3, 8.87 mmol), as described for the preparation of the triflate **8**. FCC [95:5 toluene–ethyl acetate] gave the triflate **21** (0.4 g, 76%) as an amorphous solid; $[\alpha]_D^{20}$ −64 (*c* 0.5, $CHCl_3$); R_f 0.65 (solvent *E*); δ_H 3.63 (1 H, dt, $J_{4,5} = J_{5,6a} = 10.0$, 5-H), 3.63 (1 H, t, $J_{3,4}$ 10.0, 4-H), 3.67 (1 H, t, $J_{6a,6b}$ 10.0, 6-H^a), 4.45 (1 H, dd, $J_{5,6b}$ 5.2, 6-H^b), 4.78 and 4.98 (2 H, AB q, *J* 12.0, C*H*$_2$Ph), 4.84 (1 H, d, $J_{1,2}$ 7.4, 1-H), 4.93 (1 H, dd, $J_{2,3}$ 10.0, 2-H), 5.52 (1 H, s, PhC*H*), 5.78 (1 H, t, 3-H) and 7.28–8.17 (15 H, m, 3 × Ph); ESMS(−): *m*/*z* 629.0 (100%, $[M + {}^{35}Cl]^-$) and 631.0 (45%, $[M + {}^{37}Cl]^-$) ($C_{28}H_{25}F_3O_9S$ requires *M*, 594.2).

Benzyl 4,6-*O*-benzylidene-2,3-*O*-(1-ethoxybenzylidene)-β-D-mannopyranoside 22b

A solution of the triflate **21** (60 mg, 0.1 mmol), EtOH (0.088 cm^3, 1.5 mmol) and 2,4,6-collidine (0.016 cm^3, 0.12 mmol) in toluene (2 cm^3) was stirred under reflux for 2 h. The reaction mixture was diluted with CH_2Cl_2, washed successively with saturated aq. $NaHCO_3$ and water, and dried by filtration through cotton wool. The filtrate was concentrated to dryness and toluene was evaporated off from the residue (3 × 2 cm^3). FCC (95:5 toluene–ethyl acetate) gave two isomeric orthoesters: **22b-1** (10 mg, 20%), amorphous solid; $[\alpha]_D^{25}$ −40 (*c* 1, $CHCl_3$); R_f 0.56 (solvent *E*); δ_H 1.12 (3 H, t, C*H*$_3$CH$_2$), 3.47 (1 H, dt, $J_{4,5} = J_{5,6a} = 9.9$, $J_{5,6b}$ 4.3, 5-H), 3.70–3.90 (3 H, m, 6-H^a and CH$_3$C*H*$_2$), 4.21 (1 H, dd, $J_{1,2}$ 2.4, 2-H), 4.29 (1 H, t, $J_{2,3} = J_{3,4} = 6.3$, 3-H), 4.39 (1 H, dd, $J_{6a,6b}$ 10.4, 6-H^b), 4.61 (1 H, dd, 4-H), 4.66 and 4.93 (2 H, AB q, *J* 11.9, C*H*$_2$Ph), 4.96 (1 H, d, 1-H), 5.60 (1 H, s, PhC*H*) and 7.25–7.75 (15 H, m, 3 × Ph); ESMS(−): *m*/*z* 525.0 (100%, $[M + {}^{35}Cl]^-$) and 527.0 (45%, $[M + {}^{37}Cl]^-$) ($C_{29}H_{30}O_7$ requires *M*, 490.2); and **22b-2** (37 mg, 75%), amorphous solid; $[\alpha]_D^{25}$ −77 (*c* 1, $CHCl_3$); R_f 0.50 (solvent *E*); δ_H 1.17 (3 H, t, C*H*$_3$CH$_2$), 3.35–3.70 (4 H, m, 6-H$_2$ and CH$_3$C*H*$_2$), 4.27–4.40 (2 H, m, 4- and 5-H), 4.57 and 4.85 (2 H, AB q, *J* 12.0, C*H*$_2$Ph), 4.64 (1 H, dd, $J_{1,2}$ 2.6, 2-H), 4.71 (1 H, t, $J_{2,3} = J_{3,4} = 7.1$, 3-H), 4.99 (1 H, d, 1-H), 5.48 (1 H, s, PhC*H*) and 7.20–7.75 (15 H, m, 3 × Ph); ESMS(−): *m*/*z* 525.0 (100%, $[M + {}^{35}Cl]^-$) and 527.0 (45%, $[M + {}^{37}Cl]^-$).

Benzyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-mannopyranoside 25

A reaction of the triflate **21** (1 equiv.) with an alcohol (amount of alcohol and reaction time are given in Table 1) in the presence of 2,4,6-collidine (1.2 equiv.) was accomplished as described for the preparation of the orthoester **22b**. The residue was dissolved in 80% AcOH (2 cm^3) and the mixture was kept for 1 h at rt before being concentrated, and toluene was evaporated off from the residue (3 × 5 cm^3). Subsequent benzoylation (as described for the preparation of the disaccharide **3**) followed by FCC [toluene–ethyl acetate (100:0) ⟶ (95:5)] gave the *mannoside* **25** (89–91% yield), mp 79–81 °C (from Et_2O); $[\alpha]_D^{25}$ −115 (*c* 1, $CHCl_3$); R_f 0.60 (solvent *E*) (Found: C, 71.9; H, 5.3. $C_{34}H_{30}O_8$ requires C, 72.1; H, 5.3%); δ_H 3.63 (1 H, dt, $J_{4,5} = J_{5,6a} = 9.5$, 5-H), 4.04 (1 H, t, $J_{6a,6b}$ 9.5, 6-H^a), 4.29 (1 H, t, $J_{3,4}$ 9.5, 4-H), 4.47 (1 H, dd, $J_{5,6b}$ 4.4, 6-H^b), 4.72 and 4.92 (2 H,

AB q, J 12.0, CH_2Ph), 4.90 (1 H, br, 1-H), 5.51 (1 H, dd, $J_{2,3}$ 3.6, 3-H), 5.64 (1 H, s, PhCH), 5.94 (1 H, br d, 2-H) and 7.25–8.15 (20 H, m, 4 × Ph).

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