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Stereoselective *O*-glycosylation reactions using glycosyl donors with diphenylphosphinate and propane-1,3-diyl phosphate leaving groups

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Abstract—Glycosyl donors having a diphenylphosphinate and a propane-1,3-diyl phosphate leaving group were easily prepared by the addition of the anomeric hydroxyl group of 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranose to diphenylphosphinic and propane-1,3-diyldioxyphosphoryl chlorides. These glycosyl donors were selectively glycosylated with a number of primary and secondary oxygen nucleophiles in the presence of trimethylsilyl triflate (TMSOTf). The use of 1,3-diyl phosphate resulted in the stereoselective formation of β-*O*-linked glycosides. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The involvement of oligosaccharide structures in biological processes such as neuronal development, fertilisation, proliferation of cells, metastasis[1] and in inducing the antibody response which is responsible for the protection of the organism during infection[2a] has markedly increased the interest in synthetic oligosaccharides.[2b] Thus, efforts to develop new methods for the synthesis of oligosaccharides, glycoconjugates, either chemically or chemoenzymatically have increased greatly over the past decade.[3] Of the many *O*-glycosylation reactions[4] available for oligosaccharide synthesis, the most efficient are those where the stereochemical outcome of the reaction is facilitated by neighbouring group participation. Whereas this method works very satisfactorily to synthesise *trans*-1,2-glycosides/oligosaccharides,[5] the synthesis of *cis*-1,2-glycosides can be problematic. *S*-Glycosyl phosphoroimidothioates have been reported to afford 1,2-*cis*-glycosides.[6] There have been a number of reports regarding glycosyl donors that contain a phosphorus atom in the leaving group at the anomeric centre and the coupling reactions of glycosyl diphenylphosphates, glycosyl diphenylphosphinimidates, glycosyl phosphoramidates and dimethylphosphinothioates as glycosyl donors have been investigated.[7,8]

We have studied a series of glycosylation reactions and we recently reported part of this work concerning the stereoselective *O*-glycosylation reactions using 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranosyl phosphinate and phosphates,[9] D-manno-, L-fuco- and D-galactopyranosyl phosphates[10] in the presence of catalytic trimethylsilyl triflate (TMSOTf) as an activator. We report herein a synthesis of glycosyl donors having diphenylphosphinyl and propane-1,3-diyl phosphate leaving groups and their use in glycosylation. The use of the diphenylphosphinate function for *N*-protection and coupling of amino acids has been elegantly demonstrated by Kenner and Ramage[11] in their studies encompassing the synthesis of lysozyme. We reasoned that employment of the diphenylphosphinate function for the activation of the anomeric centre of D-glucopyranose should provide access to *O*-glycosides. In addition to these studies we chose to investigate the chemistry of propane-1,3-diyl phosphate as the leaving group as this would provide a comparison of the effect of pK_a on the leaving group ability and also allow predictions of the influence that steric factors may have in subsequent coupling reactions at the anomeric centre.

2. Results and discussion

With these considerations in mind we commenced an investigation of the coupling at the anomeric centre of 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranose. The choice of this derivative was influenced by the prime consider-

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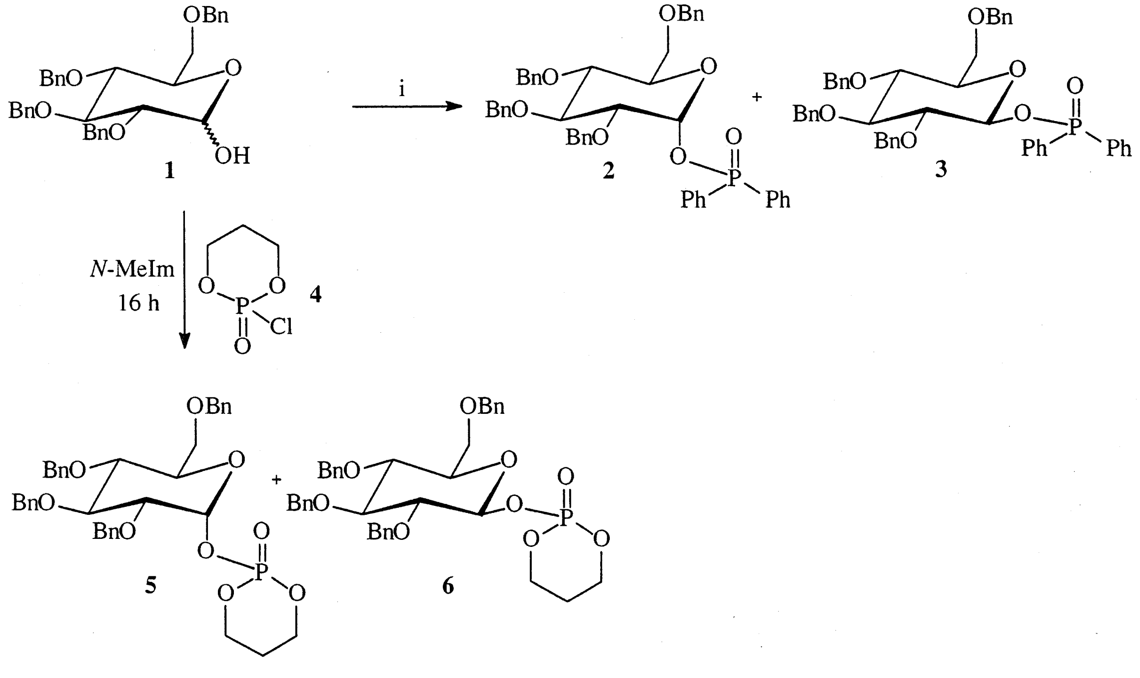
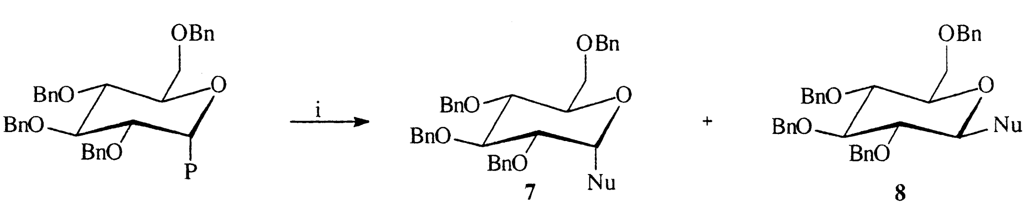
ation that there would be no participation in the coupling reaction of the C(2) substituent. An additional factor was that a successful outcome to this chemistry would provide access to *O*-glycopyranosides.

The 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranose **1** was prepared as reported by Fletcher.[12] Treatment of **1** with diphenylphosphinic chloride and *N*-methylimidazole resulted in the formation of the phosphinates **2** and **3** (Scheme 1), which were separable by flash column chromatography in a ratio of 10:1, respectively, in combined yield of 95%. The stereochemical assignment of the anomeric centre in compounds **2** and **3** was based upon the ^{1}H NMR coupling constants for C(1); in the case of compound **2** the resonance was observed as a doublet at δ_H 5.99 with a $J_{1,2}$ of 3.3 Hz and $J_{H\text{-}P}$ of 11.9 Hz, whilst for compound **3** a doublet at δ_H 5.32 with $J_{1,2}$ of 7.9 Hz and $J_{H\text{-}P}$ of 11.9 Hz was seen. For convenience we conducted all of the studies with an anomeric mixture of **2** and **3**. We were pleased to find that these phosphinates could be stored at −20°C for four months without any significant decomposition, as evidenced by TLC and ^{1}H NMR analysis. Similar treatment of **1** with propane-1,3-diyldioxyphosphoryl chloride **4** resulted in the formation of the phosphates **5** and **6**, which proved to be inseparable by chromatography, in a yield of 65% and a ratio of 10:1 based on ^{1}H NMR analysis, as a mixture of colourless crystalline diastereoisomers with an mp of 101–103°C. In the case of the phosphate **5** the resonance for the C(1)H at δ_H 5.85 exhibited couplings of $J_{1,2}=3.3$ Hz and $J_{H\text{-}P}=10.6$ Hz, whilst in the case of the phosphate **6** the anomeric resonance was observed at δ_H 5.24 as an apparent triplet with $J_{1,2,}=7.3$ and $J_{H\text{-}P}=13.2$ Hz. We were pleased to observe that like the diphenylphosphinate derivatives **2** and **3** the propane-1,3-diyl phosphates **5** and **6** did not display any appreciable decomposition upon storage at −20°C for a similar period of time.

With these phosphinates and phosphates in hand we examined their reactions with a range of primary/secondary amino acid- and carbohydrate-based nucleophiles (Fig. 1). In the first instance we chose to examine the reaction of **2** with *n*-butanol, without the addition of a Lewis acid, which resulted in the isolation of the corresponding phosphinate ester and recovery of 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranose. However, adding one equivalent of TMSOTf in the reaction at −78°C resulted in the desired displacement of the diphenylphosphinate function and formation a glycosidic linkage at the anomeric centre (Scheme 2). Flash column chromatographic purification on silica enabled separation of the two stereoisomers in a combined isolated yield of 90% (Table 1). As a result of this finding we investigated the reaction of the mixture of phosphinates **2** and **3** with *n*-butanol in the presence of a stoichiometric amount of TMSOTf and we found



Scheme 1. *Reagents and conditions*: (i) Ph_2POCl, Me*N*Im, CH_2Cl_2, rt, 16 h.



Scheme 2. *Reagents and conditions*: (i) 1 equiv. of nucleophile, 1 equiv. TMSOTf, −78°C, 25 min.

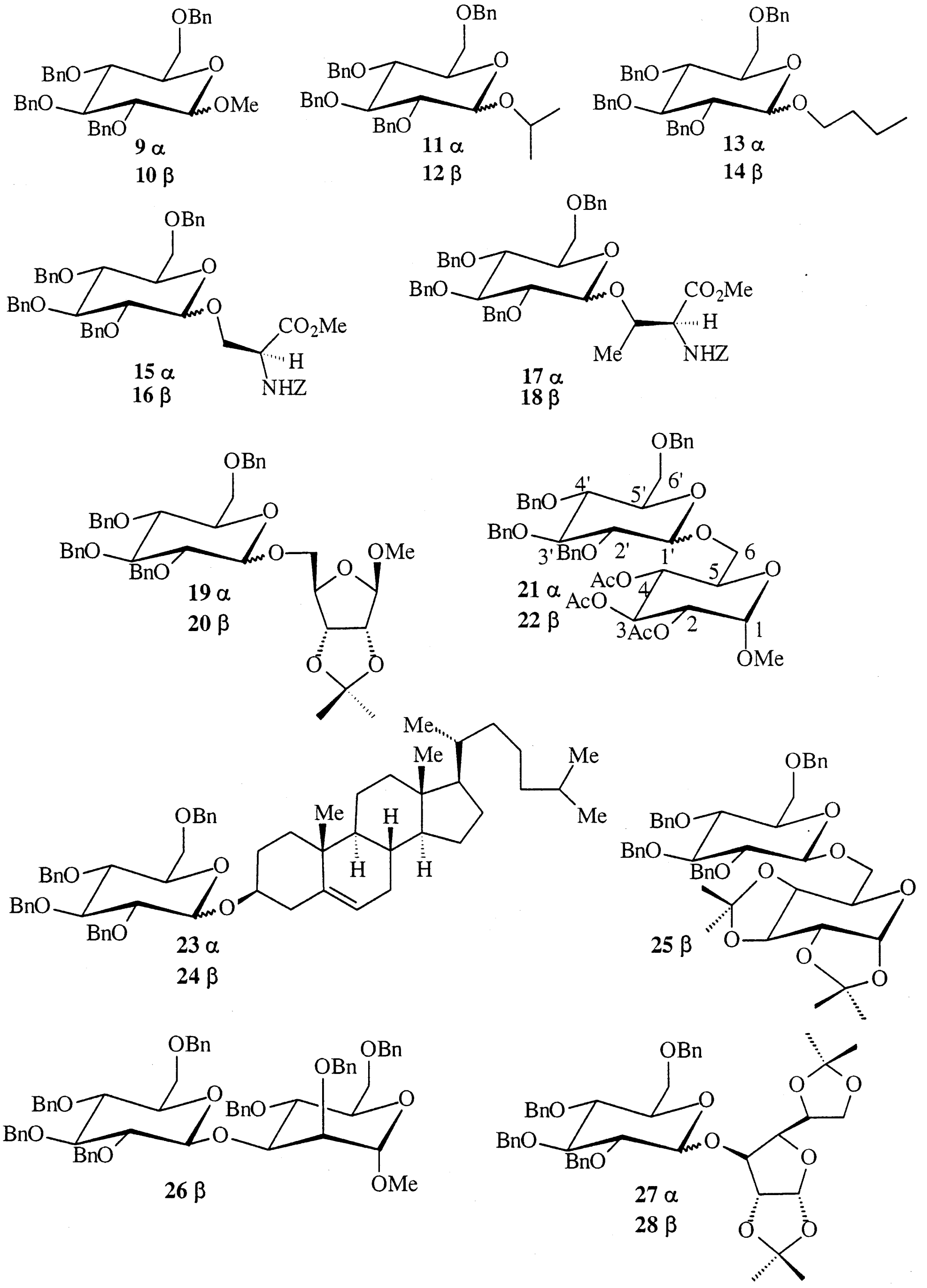


Figure 1.

Table 1. Reactions of phosphinate donors **2** and **3** conducted in dichloromethane

Product	% Yield	Ratio (α:β)
9, **10**	94	1:4
11, **12**	93	1:3.5
13, **14**	90	1:2
15, **16**	88	1:2.5
17, **18**	94	2:1
19, **20**	92	1:2
21, **22**	84	1:3
23, **24**	85	1:2

little difference in the stereochemical outcome of the reaction employing this anomeric mixture. In all of our subsequent studies we employed this mixture of anomeric phosphinates **2** and **3**. In all reactions the yields were excellent; however, the observed stereoselectivity in these cases was invariably poor, being in the order of 3:1 in favour of the desired β-isomer. The stereochemistry of the products was established by ^{1}H and ^{13}C NMR analysis. In this respect ^{13}C NMR data proved particularly useful in that the β-isomers had chemical shifts above δ 100 ppm, whilst the α-isomer had resonances at ca. δ 96 ppm,[13] thus allowing facile assignment of the newly formed stereocentre.

We next investigated the chemistry of the propane-1,3-diyl phosphates **5** and **6** as the glycosyl donors. In all reactions studied, the displacement reaction proceeded smoothly and resulted in isolation of *O*-glycosides in good yields after chromatographic purification (Scheme 2). In all cases we were able to isolate both the α- and β-isomers in pure form. To our surprise the employment of serine and threonine as acceptors resulted in the formation of products wherein the α-isomer was dominant (Table 2); this may be a result of a hydrogen bonding interaction with the N–H, resulting in delivery from the α-face of the glucose.

In the case of acceptors that were carbohydrate based we observed improved stereoselectivity, in that only the β-anomers were isolated in good yield. Glycosylation of the C(6)–OH of the acceptor with propane-1,3-diyl phosphates **5** and **6** gave the disaccharides **22** and **25** in good yield with complete β-selectivity. In the case of secondary alcohol acceptor C(3)OH with phosphates **5** and **6** gave the disaccharides **27** and **28** in 67% yield with high β-selectivity (α:β = 1:12). This was particularly encouraging as at C(2) we have a 2-*O*-benzyl function that is non-participating in glycosylation reactions and would be expected to result in the formation of α-glycosides. Based upon these findings one could in principle use *O*-benzyl protected sugars as starting materials and by changing the activating group of the glycosyl donor either diastereoisomer can be obtained, removing the need for differentially protected glycoside precursors.

In these studies we have established that 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranose can provide access to O-linked glycosides with good stereoselectivity in the cases where propane-1,3-diyl phosphate functions as the anomeric leaving group, adding to the methodology available for the synthesis of complex carbohydrates.

3. Experimental

3.1. General methods

^{1}H NMR spectra were recorded in CDCl$_3$ (unless stated otherwise) on a JEOL GSX 270 NMR spectrometer and are reported as follows: chemical shifts δ (ppm) [number of protons, multiplicity, coupling constants *J* (Hz), and assignment]. Residual protic solvent CHCl$_3$ (δ_H 7.26 ppm) was used as the internal reference. ^{13}C NMR spectra were recorded in CDCl$_3$ at 67.8 MHz on a JEOL GSX 270 NMR spectrometer using central resonance of CDCl$_3$ (δ_C 77.0 ppm) as the internal reference. ^{31}P NMR spectra were recorded in CDCl$_3$ at 109.25 MHz using a JEOL GSX 270 NMR spectrometer, using trimethyl phosphate as the external reference. IR spectra were recorded on a UNICAM series FTIR spectrometer. Mass spectra were obtained on an AEI MS 902 or VG ZAB-E spectrometer. Microanalyses were performed by MEDAC Ltd, Surrey, UK. Mps were determined on a GallenKamp capillary melting point apparatus and are uncorrected. Optical rotations were measured in CHCl$_3$ solution using a Bellingham & Stanley ADP 220 polarimeter. Flash chromatography was carried out using Fluka silica gel 60 (230–400 mesh) unless otherwise indicated. Analytical TLC was performed using pre-coated aluminium plates (Merck Kiselgel 60 F$_{254}$) and visualised by UV, phosphomolybdic acid or basic aqueous potassium permanganate solutions. 'Petrol' refers to petroleum spirit (distillation range 40–60°C), which was distilled prior to use, and ether refers to diethyl ether (Et$_2$O).

All reactions were carried out under an argon or nitrogen atmosphere in oven-dried glassware unless otherwise stated. The sole solvent used for the glycosylation reaction was CH$_2$Cl$_2$, which was distilled from calcium hydride. Aqueous solutions are saturated unless otherwise specified.

3.2. General procedure for the synthesis of 2,3,4,6-tetra-*O*-benzyl-1-*O*-diphenylphosphinyl-α,β-D-glucopyranosyl-2-oxides 2 and 3

2,3,4,6-Tetra-*O*-benzyl-α,β-D-glucopyranose **1** (2.5 g, 4.63 mmol) was dissolved in CH$_2$Cl$_2$ (20 mL) and the solution was cooled to 0°C. Diphenylphosphinic chloride (1.36 g, 5.74 mmol) and 1-methylimidazole (0.76 g, 9.25 mmol) were added dropwise over 15 min to the above solution and stirring was continued for 16 h, with gradual warming to room temperature. The sol-

Table 2. Reactions of phosphate donors **5** and **6** conducted in dichloromethane

Product	% Yield	Ratio (α:β)	Chemical shift for anomeric C(1) proton δ_{ppm}[a]
9, **10**	96	3:7	4.80, 4.29
11, **12**	98	3:7	4.87, 4.45
13, **14**	99	β-only[a]	4.76, 4.39
15, **16**	91	2:1	5.08, 4.34
17, **18**	83	2:1	4.88, 4.30
19, **20**	68	β-only[a]	4.78, 4.22
21, **22**	72	β-only[a]	5.45, 4.38
23, **24**	88	1:4	4.92, 4.49
25	73	β-only[b]	4.58
26	79	β-only[b]	4.51
27, **28**	67	1:12[b]	4.63

[a] In these cases the α-isomer chemical shifts were recorded for the compounds obtained using diphenylphosphinate activation of the anomeric centre (Table 1).

[b] Reactions carried out only with phosphate donors **5** and **6**.

vent was removed, and the oily residue dissolved in CH_2Cl_2 (20 mL) and evaporated a second time to remove traces of 1-methylimidazole. A solution of residue in CH_2Cl_2 (20 mL) was washed with ice-water (25 mL), saturated aq. $NaHCO_3$ solution (2×25 mL) and water (25 mL). The organic layer was dried over Na_2SO_4 and solvent removed in vacuo. The oily residue was purified by column chromatography over silica (Et_2O–petrol 3:1) to afford phosphinates **2** and **3** (ratio 10:1) (3.2 g, 95%), $[\alpha]^{24}_{Dmix}=+83.3$ (*c* 4.3, $CHCl_3$).

For isomer **2**, IR (film) ν_{max} 1592, 1210 cm^{-1}; δ_H 3.62–3.77 (4H, m), 3.86–4.07 (2H, m), 4.36 (1H, d, *J* 11.9), 4.47 (1H, d, *J* 10.5), 4.51 (1H, d, *J* 11.9), 4.60 (1H, d, *J* 11.2), 4.73 (1H, d, *J* 11.2), 4.80 (1H, d, *J* 10.6), 4.85 (1H, d, *J* 10.6), 4.96 (1H, d, *J* 11.2), 5.99 (1H, dd, $J_{1,2}$ 11.9, 3.3), 7.10–7.84 (30H, m); δ_C 68.08, 72.10, 73.21, 74.64, 76.67, 79.14, 79.20, 81.13, 84.28, 92.79 (C-1), 127.41, 127.45, 127.48, 127.53, 127.67, 127.77, 127.81, 127.90, 128.04, 128.11, 128.14, 128.19, 128.24, 130.31, 131.05, 131.21, 131.44, 131.48, 131.55, 131.59, 131.69, 131.88, 131.97, 131.99, 132.02, 132.40, 137.57, 137.70, 137.86, 138.01, 138.22, 138.40; δ_P (161.70 MHz; $CDCl_3$) 32.50; *m*/*z* (CI, NH_3) [found: (M+NH_4), 758.3246. $C_{46}H_{49}NO_7P$ requires *m*/*z* 758.3247].

For isomer **3**, δ_H 3.60–3.80 (4H, m), 3.85–4.07 (2H, m), 4.36 (1H, d, *J* 11.8), 4.45 (1H, d, *J* 10.5), 4.50 (1H, d, *J* 11.9), 4.60 (1H, d, *J* 11.2), 4.73 (1H, d, *J* 11.2), 4.80 (1H, d, *J* 10.5), 4.85 (1H, d, *J* 10.5), 5.01 (1H, d, *J* 11.2), 5.32 (1H, dd, $J_{1,2}$ 11.9, 7.9), 7.10–7.84 (30H, m); δ_C 96.0 (C-1); δ_P 32.72; *m*/*z* (EI) [found: (M+H), 741.2971. $C_{46}H_{46}PO_7$ requires *m*/*z* 741.2981].

3.3. 2,3,4,6-Tetra-*O*-benzyl-α,β-D-glucopyranosyl-1,3-diyl phosphates 5 and 6

To a mixture of 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranose **1** (2 g, 3.69 mmol), at 0°C, was added a solution of propane-1,3-diyldioxyphosphoryl chloride[10] **4** (1.16 g, 7.39 mmol) in CH_2Cl_2 (20 mL) followed by 1-methylimidazole (0.60 g, 7.39 mmol), under N_2. The above reaction mixture was allowed to warm to rt and stirring was continued for a total of 16 h. The solvent was removed under reduced pressure and the resulting residue was dissolved in CH_2Cl_2 (25 mL), washed with saturated aq. $NaHCO_3$ (10 mL) and water (10 mL). The organic layer was dried over anhydrous Na_2SO_4 and in vacuo. The residue was purified by column chromatography on silica gel (Et_2O–petrol 5:1) to afford inseparable α- and β-anomers **5** and **6** (1.62 g, 65%), mp 101–103°C; $[\alpha]^{24}_{Dmix}=+65.7$ (*c* 1.4, $CHCl_3$).

For isomer **5**, IR (KBr) ν_{max} 1600, 1214 cm^{-1}; δ_H 1.55–1.63 (1H, m, J_{PH} 15.2), 2.14–2.28 (1H, m, J_{PH} 15.2), 3.61–3.78 (4H, m), 3.89–3.99 (2H, m), 4.15–4.41 (4H, m), 4.44 (1H, d, *J* 11.9), 4.52 (1H, d, *J* 11.9), 4.56 (1H, d, *J* 11.9), 4.63 (1H, d, *J* 11.2), 4.71 (1H, d, *J* 11.9), 4.80 (1H, d, *J* 10.6), 4.84 (1H, d, *J* 11.2), 4.94 (1H, d, *J* 11.2), 5.85 (1H, dd, $J_{1,2}$ 10.6, 3.3), 7.13–7.37 (20H, m); δ_C 25.84 (d, *J* 7.01), 68.14, 68.65 (d, *J* 7.01), 68.86 (d, *J* 7.01), 72.58, 73.06, 73.54, 75.24, 75.51, 76.94, 79.03, 81.09, 94.78 (C-1), 127.60, 127.68, 127.76, 127.81, 127.86, 127.88, 129.95, 128.25, 128.32 (2C), 128.38 (2C), 137.50, 137.84, 137.90, 138.47; δ_P (109.25 MHz; $CDCl_3$) −10.99; microanalysis: found: C, 67.4; H, 6.3; P, 4.7. $C_{37}H_{41}O_9P$ requires: C, 67.3; H, 6.3; P 4.7%. For isomer **6**, δ_H 5.24 (1H, dd, $J_{1,2}$ 13.2, 7.3); δ_C 98.44; δ_P −10.60; *m*/z_{mix} (EI) [found (M$^+$), 660.6993. $C_{37}H_{41}O_9P$ requires *m*/*z* 660.6993].

3.4. General procedure for the synthesis of 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranosides 7 and 8

To a stirred solution of glycosyl donor (0.25 g, 0.37 mmol) in CH_2Cl_2 (5 mL) at −78°C was added TMSOTf (0.084 g, 0.37 mmol). After a period of 2 min a solution of the glycosyl acceptor (0.37 mmol) in CH_2Cl_2 (2 mL) was added to this mixture. The resultant mixture was stirred for a further 3 min and then allowed to warm to 0°C (ca. 20 min). The mixture was diluted by the addition of CH_2Cl_2 (10 mL) and washed with saturated aq. $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated in vacuo and the residue was purified by column chromatography to give compounds **7** and **8**.

3.5. Methyl-*O*-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose 9[14]

$[\alpha]^{22}_D=+36.2$ (*c* 1.2, $CHCl_3$) {lit.[14e] $[\alpha]_D=+40.0$ (*c* 1.0, $CHCl_3$); lit.[14d] $[\alpha]_D=+21.2$ (*c* 1.0, $CHCl_3$)}; IR (film) ν_{max} 1606 cm^{-1}; δ_H 3.37 (3H, s), 3.46 (1H, d, *J* 7.3), 3.53 (1H, dd, *J* 9.9, 4.0), 3.61–3.65 (2H, m), 3.68–3.72 (1H, m), 3.94 (1H, t, *J* 9.2), 4.44 (1H, d, *J* 11.9), 4.49 (1H, unresolved), 4.57, (1H, *J* 12.5), 4.63 (1H, d, *J* 11.9), 4.77 (1H, d, *J* 9.9), 4.79 (1H, d, *J* 10.6), 4.80 (1H, d, $J_{1,2}$ 3.3), 4.84 (1H, d, *J* 10.6), 4.95 (1H, d, *J* 10.6), 7.11–7.33 (20H, m); δ_C 55.18, 68.58, 70.13, 73.41, 73.52, 75.03, 75.77, 76.58, 79.92, 82.19, 98.25 (C-1), 127.50, 127.61, 127.69, 127.89 (2C), 127.93 (2C), 138.02, 138.25 (2C), 138.89; *m*/*z* (CI, NH_3) [found: (M+NH_4), 572.3012. $C_{35}H_{42}NO_6$ requires *m*/*z* 572.3012].

3.6. Methyl-*O*-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranose 10[14]

$[\alpha]^{22}_D=+11.4$ (*c* 2.0, $CHCl_3$) {lit.[14b] $[\alpha]_D=+12.2$ (*c* 3.0, $CHCl_3$); lit.[14c] $[\alpha]_D=+12.6$ (*c* 3.0, $CHCl_3$); lit.[14f] $[\alpha]_D=+11.0$ (*c* 5.3, dioxan)}; IR (film) ν_{max} 1610 cm^{-1}; δ_H 3.42–3.48 (2H, m), 3.55 (3H, s), 3.60 (1H, dd, *J* 7.3, 4.6), 3.63 (1H, d, *J* 9.2), 3.69–3.73 (2H, m), 4.29 (1H, d, $J_{1,2}$ 7.9), 4.50 (1H, d, *J* 10.6), 4.54 (1H, unresolved), 4.58 (1H, d, *J* 10.6), 4.62 (1H, d, *J* 11.9), 4.68 (1H, d, *J* 11.2), 4.76 (1H, d, *J* 10.6), 4.79 (1H, d, *J* 10.6), 4.91 (1H, d, *J* 10.6), 7.12–7.32 (20H, m); δ_C 56.84, 68.81, 73.32, 74.54, 74.76 (2C), 75.46, 77.77, 82.20, 84.54, 104.59 (C-1), 127.46 (2C), 127.61 (2C), 127.70 (2C), 127.80, 127.93, 128.21 (2C), 138.10 (2C), 138.48, 138.55; *m*/*z* (CI, NH_3) [found: (M+NH_4), 572.3012. $C_{35}H_{42}NO_6$ requires *m*/*z* 572.3012].

3.7. Isopropyl-*O*-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose 11[15]

$[\alpha]_D^{21}=+48.6$ (*c* 4.4, $CHCl_3$) {lit.[15c] $[\alpha]_D=+28.0$ (*c* 0.4, $CHCl_3$)}; IR (film) ν_{max} 1592 cm^{-1}; δ_H 1.16 (3H, d, *J* 5.9), 1.21 (3H, d, *J* 5.9), 3.43–3.60 (2H, m), 3.64 (1H, d, *J* 9.2), 3.71 (1H, dd, *J* 10.6, 4.0), 3.82–3.86 (1H, m), 3.89 (1H, d, *J* 5.9) 3.96 (1H, t, *J* 9.2), 4.45 (1H, d, *J* 9.2), 4.59 (1H, d, *J* 9.2), 4.63 (1H, d, *J* 9.9), 4.74 (1H, d, *J* 11.9), 4.81 (1H, d, *J* 10.6), 4.83 (1H, d, *J* 10.6), 4.85 (1H, d, *J* 9.9), 4.87 (1H, d, $J_{1,2}$ 3.9), 4.98 (1H, d, *J* 10.6), 7.11–7.33 (20H, m); δ_C 21.22, 23.20, 68.64, 69.13, 70.11, 73.17, 73.50, 75.15, 75.69, 76.59, 80.02, 82.19, 94.86 (C-1), 127.56, 127.73, 127.93 (2C), 128.02 (2C), 128.19, 128.41 (2C), 138.08, 138.36 (2C), 139.06; *m*/*z* (CI, NH_3) [found: $(M+NH_4)$, 600.3325. $C_{37}H_{46}NO_6$ requires *m*/*z* 600.3376].

3.8. Isopropyl-*O*-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranose 12[15]

$[\alpha]_D^{21}=+22.5$ (*c* 4.0, $CHCl_3$) {lit.[15b] $[\alpha]_D=+11.0$ (*c* 1.0, $CHCl_3$)}; IR (film) ν_{max} 1600 cm^{-1}; δ_H 1.22 (3H, d, *J* 5.6), 1.30 (3H, d, *J* 5.9), 3.41–3.47 (2H, m), 3.53 (1H, d, *J* 9.2), 3.59–3.68 (3H, m), 3.72 (1H, d, *J* 8.6), 3.99 (1H, t, *J* 5.9), 4.45 (1H, d, $J_{1,2}$ 7.3), 4.52 (1H, d, *J* 11.2), 4.58 (1H, d, *J* 12.5), 4.69 (1H, d, *J* 11.2), 4.76 (1H, d, *J* 10.6), 4.80 (1H, d, *J* 10.6), 4.91 (1H, d, *J* 11.2), 4.95 (1H, d, *J* 11.2), 7.12–7.32 (20H, m); δ_C 22.16, 23.68, 69.13, 72.22, 73.35, 74.73, 74.79, 74.86, 75.57, 76.58, 82.28, 84.81, 102.16 (C-1), 127.47, 127.56, 127.63 (2C), 127.79, 127.90, 128.11, 128.27 (2C), 138.17, 138.28, 138.55, 138.68; *m*/*z* (CI, NH_3) [found: $(M+NH_4)$, 600.3325. $C_{37}H_{46}NO_6$ requires *m*/*z* 600.3336].

3.9. Butyl-*O*-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose 13[16]

$[\alpha]_D^{22}=+42.5$ (*c* 1.2, $CHCl_3$); IR (film) ν_{max} 1600 cm^{-1}; δ_H 0.89 (3H, t, *J* 7.3), 1.33–1.42 (2H, m), 1.56–1.65 (2H, m), 3.38–346 (1H, m), 3.53–3.66 (4H, m), 3.68 (1H, dd, *J* 10.6, 8.6), 3.75–3.80 (1H, m), 3.96 (1H, t, *J* 9.2), 4.43 (1H, d, *J* 11.9), 4.45 (1H, d, *J* 11.2), 4.58 (1H, d, *J* 10.6), 4.62 (1H, d, *J* 9.9), 4.75 (1H, d, *J* 11.9), 4.76 (1H, d, $J_{1,2}$ 4.0), 4.79 (1H, d, *J* 10.6), 4.81 (1H, d, *J* 10.6), 4.97 (1H, d, *J* 11.2), 7.11–7.36 (20H, m); δ_C 13.82, 19.34, 31.44, 67.83, 68.55, 70.07, 73.05, 73.41, 75.02, 75.60, 76.58, 80.14, 82.09, 96.86 (C-1), 127.47, 127.61, 127.75, 127.87 (2C), 137.97, 138.28, 138.36, 138.94; *m*/*z* (CI, NH_3) [found: $(M+NH_4)$, 614.3482. $C_{38}H_{48}NO_6$ requires *m*/*z* 614.3482].

3.10. Butyl-*O*-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranose 14

Mp 69–71°C; $[\alpha]_D^{22}=+16.5$ (*c* 1.3, $CHCl_3$); IR (KBr) ν_{max} 1592 cm^{-1}; δ_H 0.91 (3H, t, *J* 7.3), 1.35–1.71 (4H, m), 3.41–3.50 (2H, m), 3.52–3.69 (4H, m), 3.73 (1H, dd, *J* 10.6, 2.0), 3.97 (1H, dt, *J* 12.5, 5.9), 4.39 (1H, d, $J_{1,2}$ 7.9), 4.51 (1H, d, *J* 11.2), 4.55 (1H, d, *J* 11.9), 4.61 (1H, d, *J* 12.5), 4.71 (1H, d, *J* 10.6), 4.76 (1H, d, *J* 11.2), 4.80 (1H, d, *J* 10.6), 4.91 (1H, d, *J* 10.6), 4.93 (1H, d, *J* 10.6), 7.10–7.31 (20H, m); δ_C 13.85, 19.29, 31.82, 67.88, 69.02, 69.78, 73.45, 74.85, 74.98, 75.66, 77.96, 82.29, 84.72, 103.60 (C-1), 127.58, 127.64, 127.76, 127.89, 127.99, 128.19, 128.37, 138.23, 138.32, 138.61, 138.74; *m*/*z* (HRMS, EI) [found: (M^+), 596.3138. $C_{38}H_{44}O_6$ requires *m*/*z* 596.3138].

3.11. *N*-Benzyloxycarbonyl-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-L-serine methyl ester 15

$[\alpha]_D^{23}=+28.8$ (*c* 9.2, $CHCl_3$); IR (film) ν_{max} 3424, 1722, 1214, 1070 cm^{-1}; δ_H 3.50–3.55 (2H, m), 3.54 (1H, dd, *J* 9.2, 3.3), 3.71 (3H, s), 3.73 (2H, s), 3.88 (1H, d, *J* 9.2), 4.13 (1H, d, *J* 7.9), 4.41 (1H, d, *J* 11.9), 4.47 (1H, d, *J* 12.5), 4.49 (1H, d, *J* 10.6), 4.52 (2H, appt. d, *J* 9.2), 4.74 (1H, d, *J* 8.6), 4.80 (1H, d, *J* 10.6+1H, unresolved), 4.91 (1H, d, *J* 10.6), 4.93 (1H, unresolved), 5.08 (1H, d, $J_{1,2}$ 3.3), 5.10 (2H, s), 6.02 (1H, d, *J* 7.9), 7.10–7.31 (25H, m); δ_C 52.53, 54.52, 67.02, 68.23, 69.68, 70.02, 73.00, 75.08, 75.60, 76.58, 79.88, 81.65, 81.80, 98.65 (C-1), 127.41, 127.58, 127.67, 127.79, 127.90, 128.10, 128.34 (2C), 136.23, 137.85, 138.03, 138.16, 138.51, 138.74, 155.99, 170.48; *m*/*z* (CI, NH_3) [found: $(M+NH_4)$, 779.36697. $C_{46}H_{53}N_2O_{10}$ requires *m*/*z* 779.3670].

3.12. *N*-Benzyloxycarbonyl-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-L-serine methyl ester 16

$[\alpha]_D^{23}=-8.6$ (*c* 3.7, $CHCl_3$); IR (film) ν_{max} 3432, 1742, 1216, 1070 cm^{-1}; δ_H 3.39 (2H, m), 3.50 (1H, dd, *J* 9.9, 4.0), 3.67 (3H, s), 3.73 (2H, s), 3.81 (1H, d, *J* 9.2), 4.10 (1H, d, *J* 7.9), 4.34 (1H, bs, H-1), 4.37 (1H, d, *J* 11.9), 4.43 (1H, d, *J* 10.6), 4.52 (2H, unresolved), 4.67 (1H, d, *J* 11.9), 4.70 (1H, d, *J* 8.6), 4.77 (2H, unresolved), 4.85 (1H, d, *J* 8.6), 4.89 (1H, d, *J* 11.2), 5.10 (2H, s), 5.73 (1H, d, *J* 7.9), 7.10–7.31 (25H, m); δ_C 52.53, 54.52, 67.02, 68.54, 70.83, 73.41, 74.91 (2C), 75.60, 76.58, 79.88, 81.65, 84.52, 103.86 (C-1), 127.58, 127.67, 127.79, 127.90, 128.10, 128.34, 136.23, 137.85 (2C), 138.03, 138.16, 138.51, 138.74, 155.99, 170.48.

3.13. *N*-Benzyloxycarbonyl-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-L-threonine methyl ester 17

$[\alpha]_D^{23}=+35.5$ (*c* 1.7, $CHCl_3$); IR (film) ν_{max} 3428, 1724, 1216, 1070 cm^{-1}; δ_H 1.32 (3H, d, *J* 6.6), 3.34–3.37 (3H, m), 3.46–3.50 (4H, m), 3.66 (3H, s), 3.75 (1H, d, *J* 10.6, 3.3), 3.84 (1H, d, *J* 9.24), 4.41 (1H, d, *J* 11.9), 4.45 (1H, d, *J* 8.6), 4.46 (1H, d, *J* 11.9+1H, unresolved), 4.65 (1H, d, *J* 11.9), 4.78 (1H, d, *J* 11.2), 4.86 (1H, d, *J* 11.9), 4.88 (1H, d, $J_{1,2}$ 4.0), 4.93 (1H, d, *J* 10.6), 5.12 (1H, s), 5.88 (1H, d, *J* 8.6), 7.09–7.33 (25H, m); δ_C 18.98, 52.31, 58.71, 67.02, 68.27, 70.94, 73.02, 74.65, 75.10 (2C), 76.68, 79.52, 81.62, 84.58, 97.91 (C-1), 127.49, 127.81, 127.90, 128.00. 128.29 (2C), 128.43, 137.79, 138.02, 138.14, 138.52, 138.62, 156.72, 170.70; *m*/*z* (CI, NH_3) [found: $(M+NH_4)$, 807.3857. $C_{47}H_{55}N_2O_{10}$ requires *m*/*z* 807.3857].

3.14. *N*-Benzyloxycarbonyl-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-L-threonine methyl ester 18

$[\alpha]_D^{23}=-12.0$ (*c* 2.2, $CHCl_3$); IR (film) ν_{max} 3438, 1725, 1267, 1070 cm^{-1}; δ_H 1.30 (3H, d, *J* 6.6), 3.34–3.37 (3H, m), 3.45–3.50 (4H, m), 3.60 (3H, s), 3.70 (1H, dd, *J*

10.6, 3.3), 3.80 (1H, d, *J* 9.2), 4.30 (1H, d, $J_{1,2}$ 8.6), 4.36 (1H, d, *J* 11.9), 4.41 (1H, d, *J* 12.5), 4.42 (1H, d, *J* 9.9), 4.50 (1H, d, *J* 11.2), 4.76 (1H, d, *J* 11.2), 4.82 (2H, unresolved), 4.89 (1H, d, *J* 11.2), 5.12 (1H, s), 5.78 (1H, d, *J* 8.6), 7.09–7.33 (25H, m); δ_C 17.67, 52.37, 58.85, 67.05 (2C), 68.62, 73.44, 74.70, 74.94, 75.48, 77.55, 81.78 (2C), 84.48, 101.52 (C-1), 127.67, 127.83, 127.94 (2C), 128.04, 128.31, 136.24, 137.92, 138.02, 138.14, 138.52, 138.62, 156.72, 171.08; *m*/*z* (CI, NH_3) [found: (M+NH_4), 807.3861. $C_{47}H_{55}N_2O_{10}$ requires *m*/*z* 807.3857].

3.15. Methyl 2,3-*O*-isopropylidene-(2′,3′,4′,6′-tetra-*O*-benzyl-α-D-glucopyranosyl)-β-D-ribofuranoside 19

$[\alpha]_D^{25}$ = +33.3 (*c* 1.3, $CHCl_3$); IR (film) ν_{max} 1604 cm^{-1}; δ_H 1.30 (3H, s), 1.46 (3H, s), 3.27 (3H, s), 3.43–3.59 (2H, m), 3.62–3.66 (2H, m), 3.68–3.70 (3H, m), 3.76 (1H, d, *J* 9.9), 3.96 (1H, t, *J* 9.2), 4.35 (1H, t, $J_{1,2}$ 5.9, H-1), 4.39 (1H, d, *J* 11.2), 4.43 (1H, d, *J* 11.9), 4.55 (1H, d, *J* 11.9), 4.58 (1H, d, *J* 11.9), 4.75 (1H, d, *J* 11.9), 4.78 (1H, d, $J_{1',2'}$ 3.3, H-1′), 4.81 (1H, d, *J* 11.2), 4.83 (1H, d, *J* 5.3), 4.94 (1H, d, *J* 11.2), 4.95 (1H, d, *J* 11.2), 4.98 (1H, s), 7.11–7.33 (20H, m); δ_C 25.07, 26.46, 54.83, 69.71, 70.52, 73.05, 73.47, 74.99, 75.60, 80.21, 81.86, 82.03, 82.19, 84.63, 84.84, 85.12, 98.07 (C-1′), 109.27 (C-1), 112.33, 127.49, 127.63, 127.70, 127.75, 127.81 (2C), 128.31 (2C), 137.97, 138.34, 138.42, 138.91; *m*/*z* (CI, NH_3) [found: (M+NH_4), 744.3752. $C_{43}H_{54}NO_{10}$ requires *m*/*z* 744.3748].

3.16. Methyl 2,3-*O*-isopropylidene-(2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl)-β-D-ribofuranoside 20

$[\alpha]_D^{25}$ = −5.5 (*c* 0.7, $CHCl_3$); IR (film) ν_{max} 1600 cm^{-1}; δ_H 1.24 (3H, s), 1.36 (3H, s), 3.34–3.49 (2H, m), 3.51 (3H, s), 3.52–3.55 (2H, s), 3.58 (1H, d, *J* 6.6, 2.0), 3.63–3.66 (2H, m), 3.68 (1H, dd, *J* 5.9, 2.0), 4.22 (1H, d, $J_{1',2'}$ 7.92, H-1′), 4.42 (1H, d, $J_{1,2}$ 5.9, H-1), 4.43 (1H, d, *J* 11.2), 4.45 (1H, d, *J* 12.5), 4.50 (1H, d, *J* 8.6), 4.53 (1H, d, *J* 12.5), 4.61 (1H, d, *J* 10.6), 4.69 (1H, d, *J* 11.2), 4.72 (1H, d, *J* 10.6), 4.73 (1H, d, *J* 2.6), 4.83 (1H, d, *J* 11.2), 4.87 (1H, d, *J* 10.6), 4.98 (1H, s), 7.18–7.30 (20H, m); δ_C 24.82, 26.41, 57.07, 68.97, 73.50, 74.73, 74.88, 74.99, 75.64, 77.47, 77.91, 82.34, 84.67, 84.73, 86.50, 87.69, 104.72 (C-1′), 106.75 (C-1), 112.35, 127.59, 127.61, 127.74, 127.77, 127.87, 127.93, 127.96, 128.09, 128.35 (2C), 138.16, 138.22, 138.58, 138.65; *m*/*z* (CI, NH_3) [found: (M+NH_4), 744.3748. $C_{43}H_{54}NO_{10}$ requires *m*/*z* 744.3748].

3.17. Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2′,3′,4′,6′-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1-6)-α-D-glucopyranose 21[17]

$[\alpha]_D^{21}$ = + 59.2 (*c* 1.5, $CHCl_3$); IR (film) ν_{max} 3019, 1745, 1369, 1216, 1041 cm^{-1}; δ_H 1.94 (3H, s), 2.01 (3H, s), 2.07 (3H, s), 3.36 (3H, s), 3.42–3.50 (4H, m), 3.57–3.65 (2H, m), 3.70–3.74 (1H, m), 3.80 (1H, d, *J* 8.6), 3.88 (1H, t, *J* 9.2), 4.30 (1H, d, *J* 12.5), 4.41 (1H, d, *J* 12.5), 4.42 (1H, d, *J* 11.2), 4.54 (1H, d, *J* 11.9), 4.59 (1H, unresolved), 4.70 (1H, d, *J* 12.5), 4.78 (1H, d, *J* 10.6), 4.82 (1H, unresolved), 4.83–4.89 (3H, m), 5.45 (1H, d, $J_{1',2'}$ 1.3, H-1′), 5.57 (1H, d, $J_{1,2}$ 4.6, H-1), 7.10–7.35 (20H, m); δ_C 20.65 (2C), 20.90, 55.13, 62.71, 68.49, 70.72, 71.03, 71.58, 73.40, 73.64, 74.80, 75.45, 75.58, 80.21, 81.25, 84.71, 96.51 (C-1), 99.00 (C-1′), 127.50, 127.63, 127.72, 127.79, 127.92, 128.18, 128.28, 128.31 (2C), 128.45, 137.82, 138.03, 138.23, 138.48, 138.66, 169.72, 170.22, 170.31.

3.18. Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl)-(1-6)-α-D-glucopyranose 22[17]

$[\alpha]_D^{21}$ = +65.5 (*c* 3.3, $CHCl_3$); IR (thin film) ν_{max} 3011, 1748, 1370, 1221, 1051 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.99 (3H, s), 2.02 (3H, s), 2.08 (3H, s), 3.29 (3H, s), 3.41–3.55 (3H, m), 3.64–3.80 (2H, m), 3.84–3.97 (4H, m), 4.38 (1H, d, $J_{1',2'}$ 8.6, H-1′), 4.46 (1H, d, *J* 11.9), 4.49 (1H, d, *J* 11.9), 4.56 (1H, d, *J* 11.9), 4.58 (1H, d, *J* 10.6), 4.64 (1H, d, *J* 11.2), 4.74 (1H, d, *J* 11.2), 4.81–4.85 (3H, m), 4.89 (1H, d, *J* 10.6), 4.91 (1H, d, *J* 11.2), 5.36 (1H, app t, $J_{1,2}$ 4.6, H-1), 7.03–7.27 (20H, m); δ_C 20.68, 20.70, 29.59, 66.83, 68.43, 69.51, 70.24, 70.82, 73.15, 74.67, 74.82, 75.12, 75.47, 80.21, 81.27, 82.49, 84.71, 96.61 (C-1), 102.93 (C-1′), 127.52, 127.65, 127.68, 127.72, 127.77, 127.87, 127.92, 127.99, 128.18, 128.32, 128.34, 128.51, 137.72, 138.06, 138.34, 138.50, 170.10, 170.29, 170.40; *m*/*z* (CI, NH_3) [found: (M+NH_4), 860.3867. $C_{47}H_{58}NO_{14}$ requires *m*/*z* 860.3857].

3.19. Cholesteryl-*O*-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose 23[18]

$[\alpha]_D^{24}$ = +44.8 (*c* 2.2, $CHCl_3$) {lit.[18b] $[\alpha]_D$ = +48.0 (*c* 2.0, $CHCl_3$)}; IR (film) ν_{max} 1596 cm^{-1}; δ_H 0.68 (3H, s), 0.85 (3H, s), 0.88 (3H,s), 1.01 (3H, s), 1.07–1.23 (4H, m), 1.25 (3H, s), 1.28–2.43 (21H, m), 3.47 (1H, s), 3.53 (1H, dd, *J* 9.9, 4.0), 3.56 (1H, dd, *J* 9.2, 3.3), 3.60–3.67 (3H, m), 3.72–3.86 (2H, m), 3.97 (1H, t, *J* 9.3), 4.10 (1H, d, *J* 7.26), 4.42 (1H, d, *J* 12.5), 4.44 (1H, d, *J* 10.6), 4.59 (1H, d, *J* 12.5), 4.63 (1H, d, *J* 11.9), 4.75 (1H, d, *J* 12.5), 4.80 (1H, d, *J* 10.6), 4.83 (1H, d, *J* 10.6), 4.92 (1H, d, $J_{1,2}$ 4.0), 4.99 (1H, d, *J* 10.6), 5.28 (1H, s), 7.11–7.35 (20H, m); δ_C 11.84, 18.72, 19.36, 21.07, 22.53, 22.77, 23.83, 24.28, 27.58, 27.99, 28.21, 29.62, 29.66, 31.92, 35.73, 35.76, 36.21, 36.79, 37.15, 39.53, 39.82, 39.83, 42.35, 50.18, 56.22, 56.82, 68.78, 70.16, 73.01, 73.44, 75.07, 75.61, 76.77, 78.02, 80.07, 82.14, 94.75 (C-1), 121.70, 127.48, 127.59, 127.65, 127.81, 127.88 (2C), 127.94, 128.10, 128.32 (2C), 128.34 (2C), 128.35, 128.40, 138.10, 138.36, 139.07, 140.88.

3.20. Cholesteryl-*O*-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranose 24[18]

$[\alpha]_D^{24}$ = −0.7 (*c* 1.4, $CHCl_3$) {lit.[18c] $[\alpha]_D$ = −0.5 (*c* 1.6, $CHCl_3$)}; IR (film) ν_{max} 1600 cm^{-1}; δ_H 0.68 (3H, s), 0.85 (3H, s), 0.88 (3H, s), 0.91–0.96 (4H, m), 1.03 (3H, s), 1.08–1.22 (4H, m), 1.25 (3H, s), 1.33–2.38 (21H, m), 3.41–3.47 (2H, m), 3.51 (1H, t, *J* 9.2), 3.60–3.67 (2H, m), 3.72 (1H, d, *J* 8.6), 4.49 (1H, bs, H-1), 4.51 (1H, d, *J* 10.6), 4.52 (1H, d, *J* 11.9), 4.59 (1H, d, *J* 11.9), 4.70 (1H, d, *J* 11.2), 4.76 (1H, d, *J* 10.6), 4.80 (1H, d, *J* 10.6), 4.90 (1H, d, *J* 11.2), 4.96 (1H, d, *J* 10.6), 5.35 (1H, s), 7.15–7.33 (20H, m); δ_C 11.90, 18.79, 19.44, 21.14, 22.58, 22.82 (2C), 23.89, 24.33, 28.05, 28.26, 29.73 (2C), 30.05, 31.99 (2C), 35.83, 36.27, 36.82, 37.40, 39.19, 39.59, 39.89, 42.42, 50.32, 56.28, 56.86, 69.33, 73.47, 74.93 (2C), 75.67, 78.15, 79.74, 82.48, 84.95, 102.33 (C-1), 121.96, 127.56, 127.72, 127.92, 128.01, 128.21, 128.39 (2C), 138.32, 138.46, 138.69, 138.83, 140.72; *m*/*z* (CI, NH_3) [found: ($M+NH_4$), 926.6298. $C_{61}H_{84}NO_6$ requires *m*/*z* 926.6299].

3.21. 6-*O*-(2′,3′,4′,6′-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1-6)-1,2:3,4-di-isopropylidene-α-D-galactopyranose 25

$[\alpha]_D^{23}=-8.6$ (*c* 0.7, $CHCl_3$); IR (film) ν_{max} 1605 cm^{-1}; δ_H 1.27 (6H, s), 1.46 (3H, s), 1.51 (3H, s), 3.44 (1H, dd, *J* 8.57, 4.0), 3.57–3.81 (4H, m), 3.96 (1H, dd, *J* 9.2, 5.9), 4.07 (1H, d, *J* 3.3, 1.3), 4.41 (1H, dd, *J* 4.0, 4.0), 4.23–4.38 (2H, m), 4.45 (1H, d, *J* 11.9), 4.46 (1H, dd, *J* 5.9, 3.3), 4.49 (1H, dd, *J* 5.3, 4.0), 4.58 (1H, bs), 4.70 (1H, d, *J* 11.2), 4.71 (1H, d, *J* 11.2), 4.75 (1H, d, *J* 11.2), 4.81 (1H, d, *J* 11.2), 4.81 (1H, d, *J* 11.2), 4.95 (1H, d, *J* 10.6), 5.04 (1H, d, *J* 11.2), 5.56 (1H, d, $J_{1,2}$ 5.3), 7.13–7.71 (20H, m); δ_C 24.41, 25.00, 25.97, 26.00, 65.67, 67.34, 70.63, 70.65, 70.78, 73.48, 74.75, 74.93, 74.97, 75.63, 77.73, 81.62, 81.96, 84.55, 96.36, 104.38, 108.56, 109.36, 127.46, 127.51, 127.59, 127.62, 127.69, 127.81, 127.87, 127.93, 128.19, 128.34 (2C), 128.63, 138.16, 138.18, 138.37, 138.72; *m*/*z* (CI, NH_3) [found: ($M+NH_4$), 800.4017 $C_{46}H_{58}NO_{11}$ requires *m*/*z* 800.4010].

3.22. Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl)-(1-3)-α-D-mannopyranose 26

$[\alpha]_D^{21}=+21.9$ (*c* 0.6, $CHCl_3$); IR (film) ν_{max} 1602 cm^{-1}; δ_H 3.36 (3H, s), 3.72–3.78 (4H, m), 3.92 (1H, d, *J* 4.62), 3.94 (1H, d, *J* 2.6), 4.01–4.05 (4H, m), 4.19 (1H, d, *J* 3.3, 2.6), 4.51 (1H, bs+1H, d, *J* 10.6), 4.54 (1H, d, *J* 11.9+1H, unresolved); 4.55 (1H, d, *J* 9.9 +1H, unresolved), 4.57 (2H, dd, *J* 11.2, 9.2), 4.59 (1H, d, *J* 9.2), 4.62 (1H, d, *J* 12.5), 4.67 (1H, d, *J* 10.6), 4.69 (1H, d, *J* 11.9), 4.73 (1H, d, *J* 11.9), 4.74 (1H, d, *J* 12.5), 4.78 (1H, d, *J* 1.3), 4.95 (1H, d, *J* 11.2), 5.31 (1H, d, *J* 1.3), 7.20–7.41 (35H, m); δ_C 54.75, 69.12, 69.67, 71.78, 72.12, 72.15, 72.25, 72.61, 73.31, 73.33, 74.39, 74.72, 75.00, 75.11, 75.58, 77.47, 78.47, 79.86, 98.49, 99.93, 126.89, 126.95, 127.27, 127.34, 127.37, 127.40, 127.45, 127.54, 127.61, 127.63 (2C), 128.06, 128.12, 128.14, 128.22, 128.24, 128.29, 128.31, 138.31, 138.35 (2C), 138.43, 138.47, 138.50, 138.78; *m*/*z* (CI, NH_3) [found: (M+Na), 1009.4502. $C_{62}H_{66}NaO_{11}$ requires *m*/*z* 1009.4503].

3.23. 3-*O*-(2′,3′,4′,6′-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1-3)-1,2:5,6-di-isopropylidene-α-D-glucofuranose 28

$[\alpha]_D^{25}=+20.0$ (*c* 0.8, $CHCl_3$); IR (film) ν_{max} 1605 cm^{-1}; δ_H 1.27 (6H, s), 1.30 (3H, s), 1.33 (3H, s), 3.63–3.85 (4H, m), 3.87 (1H, dd, *J* 9.2, 2.6), 3.99–4.06 (2H, m), 4.16 (1H, d, *J* 3.3), 4.26 (1H, d, *J* 4.0), 4.29 (1H, d, *J* 2.6), 4.32 (1H, d, *J* 6.6), 4.50 (1H, d, *J* 11.2), 4.54 (1H, d, *J* 9.9), 4.55 (1H, d, *J* 11.9), 4.56 (1H, d, *J* 3.3), 4.63 (1H, bs), 4.64 (1H, d, *J* 9.9), 4.66 (1H, d, *J* 11.9), 4.69 (1H, d, *J* 11.2), 4.86 (1H, d, *J* 10.6), 4.87 (1H, d, *J* 10.6), 5.98 (1H, d, $J_{1,2}$ 3.3), 7.26–7.36 (20H, m); δ_C 22.66, 23.95, 26.54, 27.15, 65.54, 66.92, 69.12, 70.94, 71.78, 72.17, 72.46, 73.21, 74.66, 74.84, 74.94, 79.27, 79.85, 83.98, 97.53, 100.87, 106.36, 112.20, 127.46, 127.53, 127.68, 127.76, 127.82, 127.89, 127.97, 128.10, 128.24, 128.30, 128.32, 128.37, 128.41, 128.83, 138.40, 138.48, 138.53, 138.63; *m*/*z* (CI, NH_3) [found: ($M+NH_4$), 800.4019. $C_{46}H_{58}NO_{11}$ requires *m*/*z* 800.4010].

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