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A new glycosylation strategy for the synthesis of mannopyranosides

Gurdial Singh * and Hariprasad Vankayalapati

Department of Chemistry, University of Sunderland, Sunderland, SR1 3SD, UK

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Abstract

Activation of the anomeric centre of 1-*O*-2,3,4,6-tetra-*O*-benzyl-D-mannopyranosyl propane-1,3-diyl phosphate in the presence of trimethylsilyl triflate allowed the preparation of α- or β-manno-linked glycosides.

1. Introduction

The elucidation of the roles that carbohydrates play in biological processes has resulted in a resurgence of interest in their chemistry leading to an increased demand for oligosaccharides for biological studies.[1] One of the most challenging problems in this field is the diastereoselective formation of β-mannopyranosides.[2] A major reason that makes this a difficult problem is that the formation of a β-glycomannoside bond is strongly disfavoured by the anomeric effect of the pyranose ring.

Analysis of the coupling reaction of a glycosyl donor with a glycosyl acceptor leads to the conclusion that one would like to favour an S_N2-like process over and above an S_N1 displacement, which on electronic grounds leads to an axial glycosidic bond formation. In the case of glycomannoside this preponderance for axial bond formation is further enhanced by the presence of the adjacent C-2 axial C–O bond which retards the equatorial approach of the acceptor/nucleophile. This is especially true in the case of ester protecting groups which actively promote axial glycoside bond formation through anchimeric assistance. A solution to this problem is to employ an axial mannosyl donor that has a non-participating protecting group which reacts in a concerted process or to have a process in which the reaction is faster than equilibration of the axial and equatorial donors. As a direct consequence of this there have been some ingenious strategies developed by a number of workers in order to solve this problem. Of particular note are the glycosidations via intramolecular aglycon delivery.[3] Other successful approaches have involved the stereoselective reduction of substituted 2-ulopyranosides and the inversion reaction of

* Corresponding author. E-mail: gurdial.singh@sunderland.ac.uk

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β-D-gluco configured compounds to a β-D-manno configuration.[4] Other strategies have included the α-selective quenching of 1-alkoxy-1-mannosyl radicals by hydrogen donors[5] and the insertion of mannosyl carbenes into O–H bonds of acceptor alcohols; however, these afford predominantly α-mannosides.[6] The alkylation of anomeric alkoxides with electrophiles has been investigated by Schmidt and co-workers.[7]

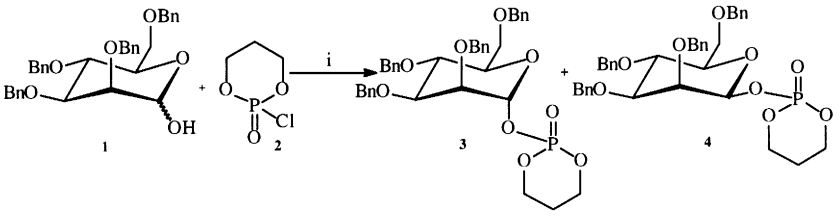
Recently, there have been a number of reports using direct mannosylation reactions.[8] However, all of these have some drawbacks associated with them and thus there is still a need for efficient formation of β-mannosides.

2. Results and discussion

In order to extend the scope of this methodology we decided to investigate the possibility of using the propane-1,3-diyl phosphate group for coupling of a mannosyl donor with glycosyl and amino acid(s) acceptors.

Our attraction to this approach was derived from the fact that we had recently employed this grouping to successfully prepare β-gluco-, galacto- and fucosides in good yields and excellent diastereoselectivity.[9] One of the major considerations in adopting this approach was the principle that one should be able to utilise the same coupling reagent for the synthesis of oligosaccharides and peptides, although in the former case we are forming a glycosidic bond rather than an amide bond; however, the leaving group is the same in both reactions. Furthermore, the introduction of the cyclic phosphate group would allow us to assess the influence of steric requirements at the anomeric centre.

Treatment of 2,3,4,6-tetra-*O*-benzyl-D-mannopyranose **1** with propane-1,3-diyl phosphoryl chloride **2** in the presence of *N*-methylimidazole resulted in the formation of the phosphates **3** and **4,** that were inseparable by flash chromatography, in 68% yield (ratio ca. 19:1). The anomeric mixture of these phosphates was characterised by ^{1}H, ^{13}C and ^{31}P NMR analysis. In general, these phosphates were relatively easy to prepare and they have proven to be stable in that they have been stored at 4°C for 4 months without any noticeable decomposition as evidenced by ^{1}H NMR (Scheme 1).



Scheme 1. (i) 2 equiv. Me*N*Im, DCM, rt, 16 h

Initial experiments employing Bu_3SnOTf and TESOTf as the activators resulted in the formation of the disaccharides in 10–20% yield along with recovery of the donor and acceptors employed. We thus proceeded to study the reactions of the phosphates **3** and **4** with a range of primary and secondary nucleophiles (Table 1), using a catalytic amount of TMSOTf as the activator to effect the glycosidic bond formation. In the case of simple alcohol nucleophiles the displacement reaction proceeded smoothly and resulted in the formation of α- or β-*O*-linked glycosides in good yield. Similar results were obtained using amino acid-derived alcohols. In the case where we had an anomeric acetoxy function in 1,3,4,6-tetra-*O*-acetyl-α-D-galactopyranose we were unable to obtain any β-glycomannoside, and this may be due to severe steric interactions resulting in the approach of the incoming nucleophile from the α-face only. A comparable result was obtained when 2,3-*O*-isopropylidene-D-ribonolactone was used as

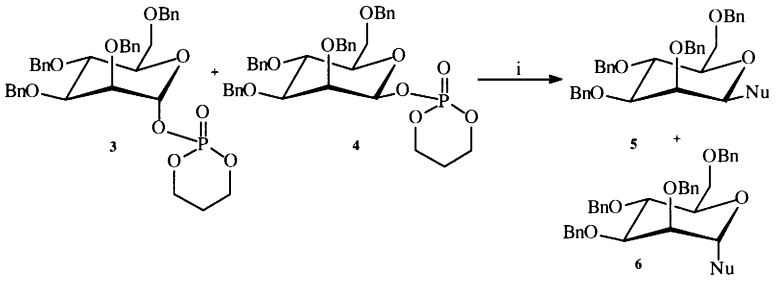
the nucleophile. In the case where the acceptor contained an *O*-isopropylidene protecting group we observed some deprotection of this function during the course of the reactions. However, the partially deprotected saccharides and starting sugars (catalytic reactions) could be readily separated from the required compound by flash chromatography. On the other hand, the use of an excess amount of TMSOTf resulted in the exclusive formation of α-mannopyranosides, in high yields, suggesting that the yield and anomeric configuration were influenced by the reaction conditions, such as the ratio of the activator and the temperature.

Table 1

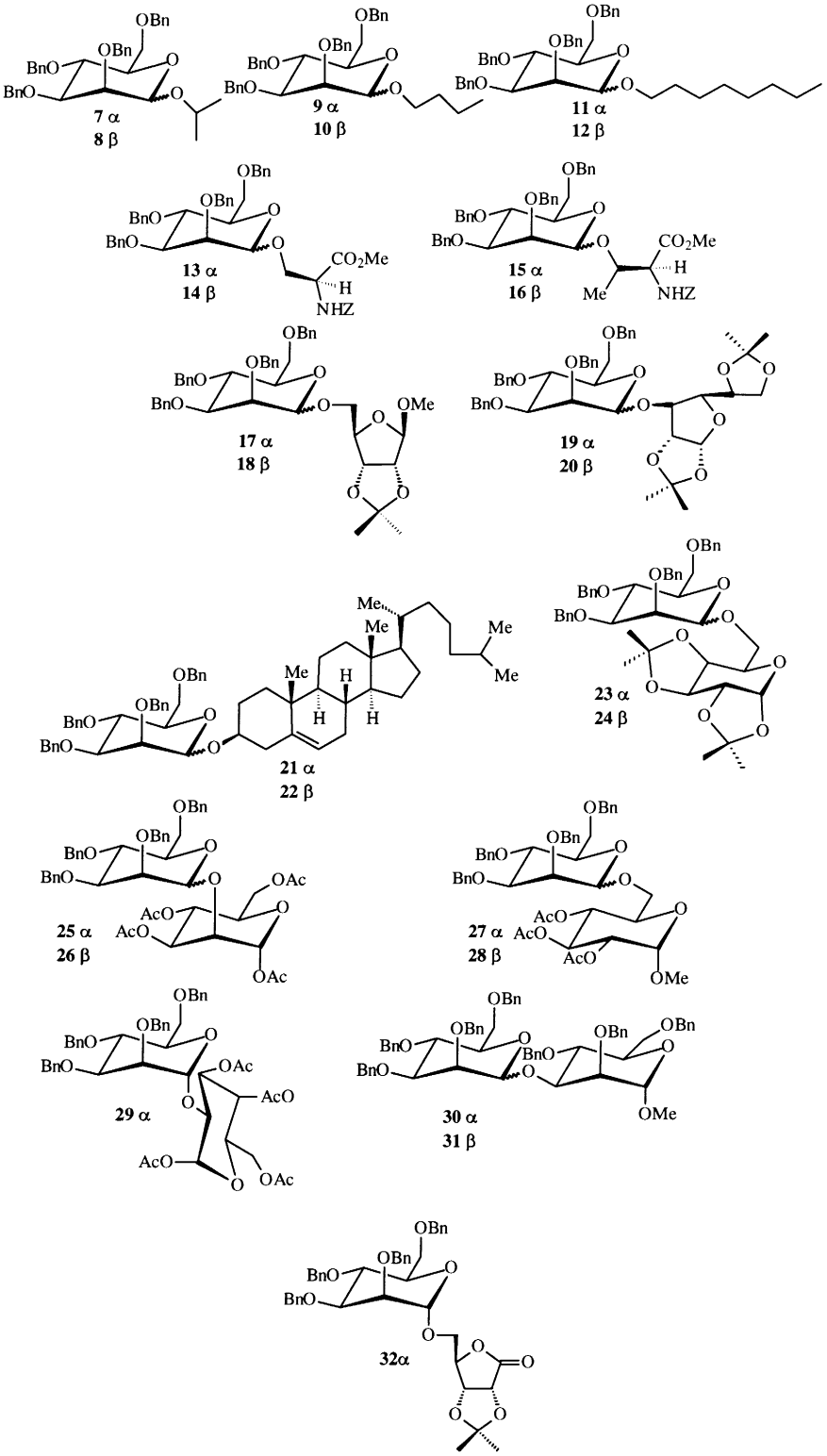
Product	% Yield[§] (0.2 eq cat)[#]; ratio [α : β]	% Yield[§] (1.5 eq)[†]; ratio [α : β]	Coupling Constant ^{13}C-^{1}H (α) Hz	Coupling Constant ^{13}C-^{1}H (β) Hz
7, 8	76 [1:1]	89 [α only]	171.6	156.3
9, 10	77 [2:3]	96 [α only]	171.1	153.9
11, 12	73 [1:1]	81 [α only]	169.3	153.9
13, 14	63 [4:1]	87 [α only]	172.4	157.1
15, 16	61 [3:2]	87 [α only]	173.4	157.1
17, 18	59 [1:1]	75 [α only]	170.6	155.3
19, 20	47 [9:1]	79 [α only]	171.2	not resolved
21, 22	78 [1:1]	91 [α only]	171.9	155.5
23, 24	63 [1:1]	69 [α only]	169.3	156.0
25, 26	46 [3:2]	50 [α only]	174.5	162.0
27, 28	67 [1:1]	79 [α only]	170.6	161.2
29	56 [α only]	53 [α only]	174.5	-
30, 31	57 [1:1]	61 [α only]	171.3	156.0
32	57 [α only]	76 [α only]	171.2	-

[§] All yields are for isolated products. # Reaction time 10-15 mins. † Reaction time 60 mins.

To ascertain the mode of formation of the β-glycosides we monitored the reactions using ^{31}P NMR (−78°C) but we were unable to detect any intermediates. On the other hand, when we treated pure 1-*n*-butyl-β-mannopyranoside with a catalytic amount of TMSOTf we observed its conversion to the α-isomer (0°C, 10 min) in 90% isolated yield, suggesting that the β-anomer is formed as the result of a kinetic reaction via a tightly bound ion-pair (Scheme 2).



Scheme 2. (i) 1 equiv. of nucleophile, cat. 0.2 or 1–1.5 equiv. TMSOTf, −78°C to 0°C


7 α
8 β
9 α
10 β
11 α
12 β
13 α
14 β
15 α
16 β
17 α
18 β
19 α
20 β
21 α
22 β
23 α
24 β
25 α
26 β
27 α
28 β
29 α
30 α
31 β
32α

In all of the examples investigated we were gratified to observe that we had attained our goal of stereoselectivity in the formation of α- or β-mannosides using various glycosyl acceptors. This is particularly encouraging as we have a 2-*O*-benzyl protecting group which is non-participating in glycosylation reactions and would be expected to result in the formation of the α-glycosides. As a result of these findings one could, in principle, use *O*-benzyl protected sugars as starting materials and by changing the amount of TMSOTf used for the glycosylation reaction either of the desired stereoisomers can be obtained, thus alleviating the need for differentially protected starting sugars. The stereochemistry of products was established by ^{1}H and ^{13}C NMR analysis. The ^{13}C–^{1}H NMR were particularly useful as the axial H-1 signal in the β-isomers **5** exhibited a coupling constant between 150 and 165 Hz whilst the corresponding equatorial H-1 signal gave a value in the range of 165–175 Hz, allowing assignment of the newly formed stereocentre.[10] Furthermore, the chemical shifts of the α- and β-mannopyranosides were in agreement with those reported in the literature.[8f]

In summary, we have established that 2,3,4,6-tetra-*O*-benzyl-D-mannopyranose can be converted into *O*-linked glycosides in one step with stereoselectivity using donor propane-1,3-diyl phosphate as the leaving group, adding to the methodology useful for the glycosylation where the protecting groups are normally labile towards Lewis acids. Furthermore, the reaction times for these coupling procedures are invariably short and can be used for the synthesis of complex polysaccharides.

3. Experimental

^{1}H NMR spectra were measured at 270 MHz with a JEOL GSX 270 FT NMR spectrometer. Chemical shifts were measured relative to internal tetramethylsilane (δ: 0). ^{13}C NMR spectra were recorded at 67.8 MHz on the same instrument with internal $(CH_3)_4Si$ (δ: 0, $CDCl_3$). IR spectra were recorded on a UNICAM series FT- instrument. Mass spectra were recorded on AEI MS 902 or VG ZAB-E instruments. Microanalyses were performed by MEDAC Ltd, Surrey. Melting points were determined on GallenKamp capillary melting point apparatus and are uncorrected. Optical rotations were measured in chloroform solution using a Bellingham & Stanley ADP 220 polarimeter. Flash chromatography was performed using Fluka silica gel 60 (230–400 mesh) and the solvent petroleum ether (boiling range 40–60°C) was distilled prior to use. Thin layer chromatography was carried out using pre-coated aluminium plates (Merck Kieselgel 60 F_{254}) which were visualised under UV light and then with either phosphomolybdic acid or basic aqueous potassium permanganate as appropriate. All anhydrous reactions were carried out under argon or nitrogen. Anhydrous transfers were done with standard syringe techniques; all glassware was pre-dried overnight. Dichloromethane was distilled from calcium hydride and stored over 4 Å molecular sieves.

*3.1. 2-Chloro-1,3,2-dioxaphosphacyclohexane-2-oxide **2***

A solution of propane-1,3-diol (5 g, 65 mmol) and triethylamine (18 ml, 130 mmol) in dichloromethane (30 ml) and a solution of phosphorus oxychloride (10 g, 65 mmol) in dichloromethane (35 ml) were added slowly and simultaneously with stirring to dichloromethane (35 ml) at 0°C. The reaction mixture was stirred at the same temperature for 20 min and a further 30 min at rt. The solvents were removed in vacuo, the solid was extracted with diethyl ether and filtered, and the filtrate was evaporated to dryness to give white crystalline product **2** (62%). Mp: 43–45°C (lit.[11], 39–42°C); ^{1}H NMR (270 MHz, $CDCl_3$), δ: 1.85–1.92 (1H, d, H-5_{eq}, J_{P-H}=15.17 Hz), 2.34–2.51 (1H, m, H-5_{ax}), 4.46–4.65 (4H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$), δ: 25.31, 70.31, 70.42.

3.2. 2,3,4-6-Tetra-O-benzyl-1-O-1′,3′,2′-dioxaphosphacyclohexane-α,β-D-mannopyranosyl-2-oxide **3** and **4**

To 2,3,4,6-Tetra-*O*-benzyl-α,β-D-mannopyranose **1** (5 g, 9.3 mmol) dissolved in dry dichloromethane (50 ml) at 0°C under inert atmosphere was added with stirring propane-1,3-diyl phosphoryl chloride (18.5 mmol) and 1-methylimidazole (18.5 mmol) within 5 min. Stirring was continued for 16 h at rt. The solvent was then removed and the oily residue redissolved in dichloromethane and evaporated in order to remove traces of 1-methylimidazole. The resulting residue was dissolved in dichloromethane (50 ml), and washed with aq. $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4) and the solvent removed in vacuo. The residue was purified by flash chromatography (elution with 5:1 diethyl ether:petroleum ether) to give inseparable α and β anomers (**3** and **4**) in 68% yield. $[\alpha]_D^{20}$=+10.8 (*c* 3.5, $CHCl_3$); **3**: ^{1}H NMR (270 MHz, $CDCl_3$), δ: 1.37–1.43 (1H, m, H-5ax, J_{P-H}=15.2 Hz), 1.93–2.07 (1H, m, H-5eq, J_{P-H}=15.2 Hz), 3.70–3.79 (2H, m), 3.89–4.11 (4H, m), 4.13–4.40 (4H, m), 4.42 (1H, d, *J*=11.2 Hz), 4.45 (1H, d, *J*=11.9 Hz), 4.51 (1H, d, *J*=11.2 Hz), 4.52 (1H, d, *J*=8.6 Hz), 4.58 (1H, d, *J*=11.9 Hz), 4.60 (1H, d, *J*=10.6 Hz), 4.66 (1H, d, *J*=12.5 Hz), 4.86 (1H, d, *J*=11.2 Hz), 5.79 (1H, dd, H-1α, *J*=8.6, 2.0 Hz), 7.17–7.44 (20H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) **3** (major), δ: 25.17, 68.51, 68.61, 71.55, 72.51, 73.00 (2C), 73.79 (2C), 74.37, 74.44, 74.74, 75.64, 81.05, 95.39 (C-1), 127.00, 127.12, 127.16, 127.22, 127.30, 127.52, 127.60, 127.80, 127.87, 127.96 (2C), 137.34, 137.70, 137.75, 137.80; **4** (minor): ^{1}H NMR (270 MHz, $CDCl_3$), δ: 5.29 (1H, d, H-1β, *J*=7.3 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$), δ: 95.91 (C-1); ^{31}P NMR (109.25 MHz, $CDCl_3$), δ: 11.19 (compound **3**), −10.72 (compound **4**); ν_{max} (film) 1215 cm^{-1}; HRMS (EI) calcd for $C_{37}H_{41}O_9P$: 660.2488. Found: 661.2566 (M+H); anal. calcd for $C_{37}H_{41}O_9P$: C, 67.3; H, 6.3; P, 4.7. Found: C, 67.5; H, 6.3; P, 4.4.

3.3. General procedure for the synthesis of 2,3,4,6-tetra-O-benzyl-α,β-D-mannopyranosides **5** and **6**

To a stirred solution of glycosyl propane 1,3-diyl-phosphate (0.3 mmol) in dichloromethane (5 ml) at –78°C under an argon atmosphere was added TMSOTf (cat. 0.2 equiv. and/or 1.5 equiv.) and, after 2 min, a solution of glycosyl acceptor (0.3 mmol) in dichloromethane (3 ml) was added. The reaction mixture was stirred at −78°C for 30 min and then allowed to warm up to 0°C before being quenched with saturated aqueous $NaHCO_3$ (10 ml) and extracted with dichloromethane (10 ml). The organic phase was dried (Na_2SO_4), concentrated in vacuo and the residue purified by column chromatography.

3.4. Isopropyl-O-2,3,4,6-tetra-O-benzyl-α-D-mannopyranose **7**

$[\alpha]_D^{21}$=+20.5 (*c* 1.6, $CHCl_3$); ^{1}H NMR, δ: 1.04 (3H, d, *J*=5.94 Hz), 1.14 (3H, d, *J*=5.93 Hz), 3.70–3.78 (2H, m), 3.81–3.85 (1H, m), 3.87–3.94 (2H, m), 3.96–4.03 (2H, m), 4.48 (1H, d, *J*=10.56 Hz), 4.51 (1H, d, *J*=10.22 Hz), 4.61 (1H, d, *J*=11.88 Hz), 4.65 (1H, d, *J*=11.87 Hz), 4.68 (1H, d, *J*=12.53 Hz,), 4.76 (1H, d, *J*=12.53 Hz), 4.85 (2H, d, *J*=10.55 Hz), 4.96 (1H, d, *J*=1.98 Hz), 7.12–7.40 (20H, m); ^{13}C NMR, δ: 21.20, 23.20, 29.67, 68.86, 69.34, 71.74, 72.12, 72.61, 73.31, 75.17, 75.26, 80.38, 95.82, 127.41, 127.47, 127.54, 127.57, 127.73, 127.84, 128.08, 128.26, 128.30, 128.32 (3), 138.50 (2C), 138.69 (2C); HRMS (EI) calcd for $C_{37}H_{42}O_6$: 582.2981. Found: 582.2953.

3.5. Isopropyl-O-2,3,4,6-tetra-O-benzyl-β-D-mannopyranose **8**

$[\alpha]_D^{21}$=−16.2 (*c* 1.4, $CHCl_3$); ^{1}H NMR, δ: 0.84 (3H, d, *J*=5.94 Hz), 0.88 (3H, d, *J*=5.93 Hz), 3.42–3.52 (1H, m), 3.85–3.97 (4H, m), 3.99–4.06 (2H, m), 4.28 (1H, $_{app}$t, *J*=6.6 Hz), 4.40 (1H, d,

J=11.88 Hz), 4.44 (1H, d, *J*=9.89 Hz), 4.52 (1H, d, *J*=9.89 Hz), 4.60 (1H, d, *J*=12.54 Hz), 4.63 (1H, d, *J*=12.54 Hz), 4.68 (1H, d, *J*=11.88 Hz), 4.75 (1H, d, *J*=12.55 Hz), 4.92 (1H, d, *J*=12.53 Hz), 7.10–7.50 (20H, m); ^{13}C NMR, δ: 21.16, 23.16, 29.64, 69.27, 69.79, 71.28, 72.07, 73.35, 74.07, 74.97, 75.85, 82.51, 99.57, 127.27, 127.38, 127.43, 127.51, 127.70, 127.76, 127.80, 127.98, 128.01, 128.22, 128.27, 128.42, 138.21, 138.37, 138.44, 138.64.

3.6. *Butyl*-O-*2,3,4,6-tetra*-O-*benzyl*-α-D-*mannopyranose* **9**

$[\alpha]_D^{18}$=+30.0 (*c* 2.2, $CHCl_3$); ^{1}H NMR, δ: 0.86 (3H, t, *J*=7.26 Hz,), 1.26–1.40 (2H, m), 1.43–1.55 (2H, m), 3.31–3.46 (2H, m), 3.62–3.80 (4H, m), 3.88 (1H, dd, *J*=9.24, 2.60 Hz), 3.96 (1H, dt, *J*=9.24, 4.6 Hz), 4.49 (1H, d, *J*=10.56 Hz), 4.52 (1H, d, *J*=11.87 Hz), 4.60 (1H, d, *J*=10.56 Hz), 4.62 (1H, s), 4.67 (1H, d, *J*=11.87 Hz), 4.69 (1H, d, *J*=10.55 Hz), 4.73 (1H, d, *J*=12.54 Hz), 4.86 (1H, d, *J*=10.55 Hz), 4.90 (1H, d, *J*=12.54 Hz), 7.14–7.39 (20H, m); ^{13}C NMR, δ: 13.78, 19.27, 30.26, 67.26, 69.31, 71.77, 72.10, 72.52, 73.27, 74.92, 75.02, 75.07, 80.31, 97.81, 127.35, 127.44, 127.46, 127.51, 127.58, 127.63, 127.72, 127.98, 128.20, 128.24 (2C), 128.26, 138.44 (2C), 138.48, 138.57; HRMS (EI) calcd for $C_{38}H_{44}O_6$: 596.3138. Found: 596.3140 (M).

3.7. *Butyl*-O-*2,3,4,6-tetra*-O-*benzyl*-β-D-*mannopyranose 10*

Mp: 66–68°C. $[\alpha]_D^{18}$=−36.8 (*c* 2.5 $CHCl_3$); ^{1}H NMR, δ: 0.92–0.97 (3H, t, *J*=7.26 Hz), 1.34–1.48 (2H, m), 1.50–1.74 (2H, m), 3.38–3.52 (2H, m), 3.71–3.86 (4H, m), 3.89 (1H, d, *J*=7.3 Hz), 3.99 (1H, dt, *J*=6.6, 2.63 Hz), 4.3 (1H, b s), 4.40 (1H, d, *J*=11.88 Hz), 4.48 (1H, d, *J*=11.88 Hz), 4.51 (1H, d, *J*=11.21 Hz), 4.56 (1H, d, *J*=11.87 Hz), 4.60 (1H, d, *J*=10.56 Hz), 4.85 (1H, d, *J*=12.53 Hz), 4.88 (1H, d, *J*=10.55 Hz), 4.97 (1H, d, *J*=12.53 Hz), 7.14–7.52 (20H, m); ^{13}C NMR, δ: 13.86, 19.26, 31.75, 69.63, 69.74, 71.34, 73.41, 73.69 (2C), 74.99, 75.07, 75.94, 82.38, 101.69, 127.30, 127.40, 127.51, 127.53, 127.57, 127.78, 128.01 (2C), 128.24, 128.27, 128.29, 128.35, 138.21, 138.27, 138.50, 138.84; HRMS (CI, NH_3) anal. calcd for $C_{38}H_{48}O_6N$: 614.3482. Found: 614.3481 ($M+NH_4$).

3.8. *Octyl*-O-*2,3,4,6-tetra*-O-*benzyl*-α-D-*mannopyranose* **11**

$[\alpha]_D^{21}$=+25.6 (*c* 5.0, $CHCl_3$); ^{1}H NMR, δ: 0.85 (3H, t, *J*=7.26 Hz), 1.26–1.51 (12H, m), 3.31 (1H, dt, *J*=9.23, 6.6 Hz), 3.63 (1H, dd, *J*=9.9, 2.64 Hz), 3.74–3.80 (4H, m), 3.88–4.02 (2H, m), 4.49 (1H, d, *J*=9.9 Hz), 4.52 (1H, d, *J*=11.87 Hz), 4.62 (2H, unresolved), 4.65 (1H, d, *J*=11.87 Hz), 4.69 (1H, d, *J*=10.55 Hz), 4.73 (1H, d, *J*=1.98 Hz), 4.86 (2H, dd, *J*=10.55 Hz), 7.14–7.36 (20H, m); ^{13}C NMR, δ: 14.01, 22.60, 26.08, 29.16, 29.31, 29.37, 31.77, 67.62, 69.31, 71.75, 72.11, 72.51, 73.29, 74.88, 75.03, 75.09, 80.32, 97.81, 127.38, 127.46, 127.48, 127.53, 127.59, 127.70, 127.75, 127.94, 128.23, 128.26, 128.29 (2C), 138.46 (2C), 138.50, 138.60; HRMS (EI) calcd for $C_{42}H_{52}O_6$: 652.3764. Found: 653.3842 (M+H).

3.9. *Octyl*-O-*2,3,4,6-tetra*-O-*benzyl*-β-D-*mannopyranose* **12**

$[\alpha]_D^{21}$=−5.3 (*c* 6.4, $CHCl_3$); ^{1}H NMR, δ: 0.85 (3H, t, *J*=6.6 Hz), 1.26–1.69 (12H, m), 3.31 (1H, dt, *J*=9.23, 6.6 Hz), 3.61 (1H, dd, *J*=9.89, 2.64 Hz), 3.70–3.84 (4H, m), 3.88–4.00 (2H, m), 4.39 (1H, d, *J*=11.89 Hz), 4.44 (1H, d, *J*=9.23 Hz), 4.47 (1H, d, *J*=11.22 Hz), 4.52 (1H, d, *J*=9.89 Hz), 4.56 (1H, d, *J*=11.21 Hz), 4.60 (1H, d, *J*=11.22 Hz), 4.61 (1H, b s), 4.65 (1H, d, *J*=12.53 Hz), 4.98 (1H, d, *J*=12.53 Hz), 7.14–7.48 (20H, m); ^{13}C NMR, δ: 13.99, 22.53, 26.00, 29.08, 29.23, 29.29, 31.69, 67.52, 69.24,

69.64, 71.72, 72.44, 73.34, 73.42, 74.89, 75.88, 82.28, 101.61, 127.22, 127.30, 127.43, 127.51, 127.60, 127.65, 127.70, 127.90, 127.93, 128.17 (2C), 128.27, 138.13, 138.31, 138.52, 138.77; HRMS (EI) calcd for $C_{42}H_{52}O_6$: 652.3764. Found: 653.3843 (M+H).

3.10. N-*Benzyloxycarbonyl*-O-*(2,3,4,6-tetra*-O-*benzyl-α*-D-*mannopyranosyl)*-L-*serine methyl ester* ***13***

$[\alpha]_D^{22}$=+37.3 (*c* 5.2, $CHCl_3$); ^{1}H NMR, δ: 3.66 (3H, s), 3.67–3.72 (3H, m), 3.76–3.80 (2H, m), 3.88 (1H, dd, *J*=8.58, 2.64 Hz), 3.93 (1H, t, *J*=8.57 Hz), 4.45 (1H, d, *J*=10.55 Hz), 4.49 (1H, unresolved), 4.56 (2H, dd, *J*=11.87, 8.58 Hz), 4.59 (1H, d, *J*=11.87 Hz), 4.61 (1H, d, *J*=11.88 Hz), 4.63 (1H, d, *J*=11.21 Hz), 4.65 (1H, d, *J*=12.53 Hz), 4.70 (1H, d, *J*=11.87 Hz), 4.79 (1H, d, *J*=1.97 Hz), 4.80 (1H, d, *J*=11.22 Hz), 5.08 (2H, s), 5.75 (1H, d, *J*=8.58 Hz), 7.12–7.32 (25H, m); ^{13}C NMR, δ: 52.44, 54.28, 67.03, 68.75, 68.90, 72.28, 72.34, 72.65, 73.24, 74.65, 74.70, 74.90, 79.55, 92.20, 127.40, 127.57, 127.69 (2C), 127.92, 128.10, 128.23, 128.25, 128.27, 128.31, 128.44, 136.10, 138.14, 138.23, 138.27, 138.30, 155.92, 170.40; ν_{max} (film) 3360, 1721, 1612, 775 cm^{-1}; HRMS (EI) calcd for $C_{46}H_{49}O_{10}N$: 775.3356. Found: 776.3424 (M+H).

3.11. N-*Benzyloxycarbonyl*-O-*(2,3,4,6-tetra*-O-*benzyl-β*-D-*mannopyranosyl)*-L-*serine methyl ester* ***14***

$[\alpha]_D^{22}$=+12.3 (*c* 2.1, $CHCl_3$); ^{1}H NMR, δ: 3.44–3.52 (1H, m), 3.63 (3H, s), 3.66–3.69 (2H, m), 3.76–3.81 (2H, m), 3.92 (1H, dt, *J*=7.91, 3.95 Hz), 3.95 (1H, dd, *J*=8.58, 4.62 Hz), 4.35 (1H, s), 4.44 (1H, d, *J*=11.21 Hz), 4.50 (1H, d, *J*=11.21 Hz), 4.51 (1H, d, *J*=10.55 Hz), 4.55 (1H, d, *J*=11.22 Hz), 4.58 (1H, d, *J*=11.21 Hz), 4.60 (1H, d, *J*=11.88 Hz), 4.62 (1H, d, *J*=11.87 Hz), 4.69 (1H, d, *J*=12.53 Hz), 4.71 (1H, d, *J*=12.53 Hz), 4.86 (1H, d, *J*=10.55 Hz), 5.15 (2H, s), 5.71 (1H, d, *J*=8.57 Hz), 7.12–7.42 (25H, m); ^{13}C NMR, δ: 52.31, 54.11, 69.11, 69.42, 71.42, 71.88, 73.23, 73.43, 74.70, 74.80, 75.82, 79.61, 81.90, 101.47, 127.29, 127.33, 127.45, 127.58, 127.64, 127.71, 127.80, 127.84, 127.97, 128.02, 128.16, 128.19, 128.26, 128.36, 138.06, 138.31, 138.37, 138.40, 138.44, 155.80, 170.22.

3.12. N-*Benzyloxycarbonyl*-O-*(2,3,4,6-tetra*-O-*benzyl-α*-D-*mannopyranosyl)*-L-*threonine methyl ester* ***15***

$[\alpha]_D^{18}$=+33.9 (*c* 1.8, $CHCl_3$); ^{1}H NMR, δ: 1.26 (3H, d, *J*=6.6 Hz), 3.56 (3H, s), 3.66–3.80 (4H, m), 3.89–3.98 (2H, m), 4.27–4.35 (2H, m), 4.45 (1H, d, *J*=10.55 Hz), 4.49 (1H, d, *J*=11.87 Hz), 4.53 (1H, d, *J*=11.88 Hz), 4.58 (1H, d, *J*=11.21 Hz), 4.62 (1H+unresolved 1H, d, *J*=11.22 Hz), 4.72 (1H, d, *J*=3.29 Hz), 4.83 (1H, d, *J*=11.21 Hz), 4.86 (1H, d, *J*=10.56 Hz), 5.13 (2H, s), 5.22 (1H, d, *J*=9.89 Hz), 7.13–7.40 (25H, m); ^{13}C NMR, δ: 18.43, 52.27, 58.58, 67.25, 69.15, 72.13, 72.36 (2C), 73.33, 74.54, 74.80, 75.11, 76.26, 79.30, 99.56, 127.45, 127.52, 127.60, 127.66 (2C), 127.81, 127.87, 127.94, 128.00, 128.18, 128.25, 128.32 (2C), 128.34, 128.54, 136.08, 138.13, 138.24, 138.29 (2C), 156.51, 170.99; ν_{max} (film) 1723, 1513, 1215 cm^{-1}; *m/z* (CI, NH_3) calcd for $C_{47}H_{55}O_{10}N_2$: 807.3857. Found: 807.3857 (M+NH_4); anal. calcd for $C_{47}H_{51}O_{10}N$: C, 71.47; H, 6.51; N, 1.77. Found: C, 71.34; H, 6.52; N, 1.52.

3.13. N-*Benzyloxycarbonyl*-O-*(2,3,4,6-tetra*-O-*benzyl-β*-D-*mannopyranosyl)*-L-*threonine methyl ester* ***16***

M.p. 106–108°C; $[\alpha]_D^{18}$=−10.4 (*c* 1.2, $CHCl_3$); ^{1}H NMR, δ: 1.23 (3H, d, *J*=6.6 Hz), 3.33–3.37 (1H, m), 3.46–3.56 (2H, m), 3.63 (3H, s), 3.71 (1H, t, J=9.89 Hz), 3.81 (1H, d, *J*=2.64 Hz), 3.90–3.97 (1H, m), 4.28–4.37 (2H, m), 4.39 (1H, b s), 4.48 (1H, d, *J*=11.88 Hz), 4.49 (1H, d, *J*=11.87 Hz), 4.52 (1H, d,

J=11.21 Hz), 4.56 (1H, d, *J*=11.87 Hz), 4.59 (1H, d, *J*=11.87 Hz), 4.71 (1H, d, *J*=12.53 Hz), 4.84 (1H, d, *J*=12.53 Hz), 4.86 (1H, d, *J*=11.22 Hz), 5.12 (2H, s), 5.73 (1H, d, *J*=8.58 Hz), 7.14–7.43 (25H, m); ^{13}C NMR, δ: 16.89, 52.43, 67.05, 69.33, 71.53, 73.32, 73.52 (2C), 73.81, 74.36, 74.58, 75.14, 75.95, 82.21, 98.66, 127.34, 127.43, 127.56, 127.63, 127.68, 127.72, 127.84, 127.90, 127.94, 128.00, 128.10, 128.13, 128.27, 128.31, 128.35, 128.38, 128.49, 136.36, 138.16, 138.40, 138.47, 138.84, 156.77, 170.89; ν_{max} (film) 1723, 1513, 1215 cm^{-1}; HRMS (CI, NH_3) calcd for $C_{47}H_{55}O_{10}N_2$: 807.3857. Found: 807.3877 (M+NH_4).

3.14. Methyl 2,3-O-isopropylidene-(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)-β-D-ribofuranoside **17**

$[\alpha]_D^{21}$=+15.8 (*c* 3.2, $CHCl_3$); ^{1}H NMR, δ: 1.31 (3H, s), 1.47 (3H, s), 3.32 (3H, s), 3.65–3.81 (4H, m), 3.86–3.90 (3H, m), 3.95–4.01 (1H, m), 4.28 (1H, d, *J*=1.32 Hz), 4.49 (1H, d, *J*=2.64 Hz), 4.52 (1H, d, *J*=1.98 Hz), 4.57 (1H, d, *J*=12.53 Hz), 4.64 (2H, dd, *J*=11.22 Hz), 4.69 (1H, d, *J*=11.21 Hz), 4.73 (1H, d, *J*=12.54 Hz), 4.77 (1H, d, *J*=1.98 Hz), 4.81 (1H, d, *J*=11.87 Hz), 4.82 (1H, d, *J*=5.94 Hz), 4.86 (1H, d, *J*=11.22 Hz), 5.05 (1H, s), 7.14–7.39 (20H, m); ^{13}C NMR, δ: 24.79, 26.37, 54.67, 65.18, 69.32, 71.71, 72.07, 72.57, 73.32, 74.61, 74.93, 75.00, 80.21, 81.89, 86.53, 87.65, 98.96, 106.72, 111.84, 127.40, 127.48, 127.53, 127.56, 127.62, 127.71, 127.77, 127.88, 128.24 (2C), 128.27, 128.30, 138.53 (2C), 138.43, 138.37.

3.15. Methyl 2,3-O-isopropylidene-(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)-β-D-ribofuranoside **18**

$[\alpha]_D^{21}$=−23.2 (*c* 2.9, $CHCl_3$); ^{1}H NMR, δ: 1.26 (3H, s), 1.50 (3H, s), 3.23 (3H, s), 3.33–3.45 (2H, m), 3.69–3.75 (2H, m), 3.83–3.94 (3H, m), 3.95–4.04 (1H, m), 4.28 (1H, d, *J*=3.3 Hz), 4.37 (1H, d, *J*=1.98 Hz), 4.40 (1H, d, *J*=5.94 Hz), 4.48 (1H, d, *J*=12.53 Hz), 4.51 (1H, d, *J*=11.21 Hz), 4.53 (1H, d, *J*=12.53 Hz), 4.56 (1H, d, *J*=10.56 Hz), 4.59 (1H, d, *J*=12.53 Hz), 4.63 (1H, d, *J*=12.53 Hz), 4.67 (1H, d, *J*=2.64 Hz), 4.71 (1H, d, *J*=11.87 Hz), 4.85 (1H, d, *J*=10.55 Hz), 5.20 (1H, d, *J*=1.98 Hz), 7.14–7.50 (20H, m); ^{13}C NMR, δ: 25.05, 26.44, 54.81, 68.56, 69.12, 71.47, 72.11, 72.25, 72.63, 73.42, 74.79 (2C), 80.01, 82.07, 85.04, 85.23, 101.36, 109.36, 112.32, 127.39, 127.43, 127.51, 127.55, 127.61, 127.66, 127.69, 127.72, 127.91, 128.01, 128.06, 128.25, 138.08, 138.35 (2C), 138.44; *m/z* (Electrospray, NH_3) calcd for $C_{43}H_{54}NO_{10}$: 744.4. Found: 744.2 (M+NH_4).

3.16. 3-O-(2,3,4,6-Tetra-O-benzyl-α-D-mannopyranosyl)-(1–3)-1,2:5,6-di-O-isopropylidine-α-D-glucofuranose **19**

$[\alpha]_D^{22}$=+13.3 (*c* 3.2, $CHCl_3$); ^{1}H NMR, δ: 1.21 (3H, s), 1.32 (3H, s), 1.40 (3H, s), 1.47 (3H, s), 3.75–3.84 (4H, m), 4.96–4.00 (2H, m), 4.02–4.11 (3H, m), 4.26 (1H, s), 4.47 (1H, d, *J*=10.56 Hz), 4.55 (1H, d, *J*=3.3 Hz), 4.56 (1H, d, *J*=11.87 Hz), 4.60 (1H, d, *J*=10.56 Hz), 4.63 (1H, d, *J*=12.53 Hz), 4.64 (1H, d, *J*=12.53 Hz), 4.64 (1H, d, *J*=3.3 Hz), 4.69 (1H, d, *J*=11.88 Hz), 4.72 (1H, d, *J*=12.53 Hz), 4.86 (1H, d, *J*=10.56 Hz), 5.23 (1H, d, *J*=1.98 Hz), 5.79 (1H, d, *J*=3.3 Hz), 7.14–7.39 (20H, m); ^{13}C NMR, δ: 25.50, 26.01, 26.25, 26.83, 67.64, 69.25, 72.07, 72.25, 72.50, 72.65, 73.44, 74.26, 74.75, 75.23, 79.55, 80.61, 81.30, 83.62, 98.89, 105.21, 109.24, 111.87, 127.48, 127.59, 127.61, 127.64, 127.66, 127.71, 127.79 (2C), 128.09, 128.27, 128.31, 128.32 (2C), 128.36, 138.11, 138.22, 138.25, 138.33.

3.17. 3-O-*(2,3,4,6-Tetra*-O-*benzyl-β*-D-*mannopyranosyl)-(1–3)-1,2:5,6-di*-O-*isopropylidine-α*-D-*glucofuranose* ***20***

$[\alpha]_D^{22}=-22.2$ (*c* 1.5, $CHCl_3$); ^{1}H NMR, δ: 1.18 (3H, s), 1.26 (3H, s), 1.29 (3H, s), 1.34 (3H, s), 3.66–3.91 (4H, m), 3.97–4.01 (2H, m), 4.03–4.11 (3H, m), 4.15 (1H, d, *J*=3.96 Hz), 4.27 (1H, s), 4.47 (1H, d, *J*=10.56 Hz), 4.51 (1H, d, *J*=11.87 Hz, +1H, unresolved), 4.56 (1H, d, *J*=1.32 Hz), 4.61 (1H, unresolved), 4.67 (1H, s), 4.67 (1H, d,11.87 Hz), 4.69, (1H, d, *J*=10.56 Hz), 4.72 (1H, d, *J*=12.53 Hz), 4.86 (1H, d, *J*=10.56 Hz), 5.97 (1H, d, *J*=3.3 Hz), 7.15–7.36 (20H, m); ^{13}C NMR, δ: 25.42, 25.93, 26.68, 26.72, 67.54, 69.03, 69.04, 72.05, 72.32, 72.42, 72.48, 72.50, 73.35, 74.73, 74.83, 79.45, 81.21, 83.53, 100.74, 105.15, 109.15, 112.07, 127.29, 127.41, 127.52, 127.58, 127.64, 127.71, 127.87, 128.00,128.14, 128.19, 128.24, 128.28, 138.01, 138.13, 138.15, 138.24; HRMS (CI, NH_3) calcd for $C_{46}H_{58}NO_{11}$: 800.4010. Found: 800.4010 (M+NH_4).

3.18. Cholesteryl-O-*2,3,4,6-tetra*-O-*benzyl-α*-D-*mannopyranose* ***21***

$[\alpha]_D^{20}=+13.7$ (*c* 2.6, $CHCl_3$); ^{1}H NMR, δ: 0.67 (3H, s), 0.85 (3H, s), 0.88 (3H, s), 0.90–0.96 (2H, m), 0.97 (3H, s), 1.00–1.23 (6H, m), 1.25 (3H, m), 1.29–2.41 (21H, m), 3.42–3.52 (2H, m), 3.71–3.92 (3H, m), 3.94 (1H, dd, *J*=9.23, 2.64 Hz), 4.48 (1H, d, *J*=10.56 Hz), 4.49 (1H, d, *J*=11.87 Hz), 4.56 (1H, d, *J*=10.55 Hz), 4.63 (1H, unresolved), 4.65 (1H, d, *J*=11.87 Hz), 4.68 (1H, d, *J*=12.54 Hz), 4.74 (1H, d, *J*=12.54 Hz), 4.86 (1H, d, *J*=11.31 Hz), 5.03 (1H, d, *J*=1.98 Hz), 5.32 (1H, d, *J*=5.62 Hz), 7.14–7.69 (20H, m); ^{13}C NMR, δ: 11.82, 18.69, 19.23, 21.02, 22.53, 22.78, 23.79, 24.25, 27.59, 27.97, 28.19, 29.66, 31.85, 31.88, 35.75, 36.16, 36.64, 36.97, 39.49, 39.75, 39.84, 42.29, 50.06, 56.13, 56.74, 69.37, 71.75, 72.10, 72.54, 73.27, 75.13, 75.15, 75.28, 80.36, 95.78, 121.80, 127.30, 127.36, 127.45, 127.50, 127.55 (2C), 127.74 (2C), 127.78, 128.00, 128.03, 128.22, 128.29 (2C), 138.23, 138.47, 138.52, 138.67, 140.59.

3.19. Cholesteryl-O-*2,3,4,6-tetra*-O-*benzyl-β*-D-*mannopyranose* ***22***

M.p. 123–125°C; $[\alpha]_D^{20}=-8.4$ (*c* 1.2, $CHCl_3$); ^{1}H NMR, δ: 0.67 (3H, s), 0.85 (3H, s), 0.88 (3H, s), 0.91–0.93 (2H, m), 0.97 (3H, s), 1.03 (3H, s), 1.06–2.35 (27H, m), 3.42–3.59 (2H, m), 3.69–3.92 (3H, m), 3.94 (1H, dd, *J*=8.58, 2.64 Hz), 4.41 (1H, d, *J*=11.88 Hz), 4.49 (1H, b s), 4.52 (1H, d, *J*=10.55 Hz), 4.56 (1H, d, *J*=10.55 Hz), 4.59 (1H, d, *J*=12.53 Hz), 4.60 (1H, unresolved), 4.87 (1H, d, *J*=12.54 Hz), 4.89 (1H, d, *J*=10.55 Hz), 4.98 (1H, unresolved), 5.26 (1H, d, *J*=4.62 Hz), 7.15–7.50 (20H, m); ^{13}C NMR, δ: 11.82, 18.69, 19.29, 19.39, 21.02, 22.53, 22.78, 23.79, 24.26, 27.97, 28.19, 31.82, 31.88, 35.75, 36.17, 36.64, 36.74, 36.97, 39.49, 39.76, 39.85, 42.29, 42.31, 50.07, 50.17, 69.40, 71.77, 72.54, 73.35, 73.76, 75.16, 75.18, 75.88, 78.65, 80.37, 99.72, 121.80, 127.29, 127.35, 127.44, 127.49, 127.51, 127.54, 127.73, 128.00, 128.02, 128.21, 128.27, 128.29, 128.44, 138.24, 138.44, 138.53, 138.60, 140.60; *m/z* (FAB) calcd for $C_{61}H_{80}O_6Na$: 931.6. Found: 931.2 (M+Na).

3.20. 6-O-*(2,3,4,6-Tetra*-O-*benzyl-α*-D-*mannopyranosyl)-(1–6)-1,2:3,4-di*-O-*isopropylidine-α*-D-*galactopyranose* ***23***

$[\alpha]_D^{20}=-2.6$ (*c* 2.3, $CHCl_3$); ^{1}H NMR, δ: 1.32 (6H, s), 1.43 (3H, s), 1.50 (3H, s), 3.66–3.80 (4H, m), 3.81–3.86 (2H, m), 3.89 (1H, d, *J*=2.64 Hz), 3.92–4.06 (3H, d), 4.14 (1H, dd, *J*=7.92, 1.32 Hz), 4.29 (1H, dd, *J*=5.28, 2.64 Hz), 4.48 (1H, d, *J*=10.56 Hz), 4.50 (1H, d, *J*=11.87 Hz), 4.53 (1H, d, *J*=12.54 Hz), 4.58 (1H+unresolved 1H, d, *J*=11.87 Hz), 4.62 (1H, d, *J*=10.55 Hz), 4.66 (1H, d, *J*=11.88 Hz),

4.85 (1H, d, *J*=11.21 Hz), 5.02 (1H, d, 1.32 Hz), 5.51 (1H, d, *J*=5.27 Hz), 7.13–7.40 (20H, m); ^{13}C NMR, δ: 24.52, 24.85, 25.93, 26.08, 65.25, 65.35, 69.09, 70.56, 70.63, 70.88 (2C), 72.04, 72.30, 73.27, 74.59, 74.83, 75.02, 80.01, 96.31, 97.26, 108.51, 109.30, 127.37, 127.43, 127.48, 127.51, 127.58 (2C), 127.75 (2C), 127.97 (2C), 128.23 (2C), 128.25 (2C), 138.30, 138.43, 138.50, 138.58; HRMS (EI) calcd for $C_{46}H_{54}O_{11}$: 782.3666. Found: 783.3744 (M+H).

*3.21. 6-*O*-(2,3,4,6-Tetra-*O*-benzyl-β-*D*-mannopyranosyl)-(1–6)-1,2:3,4-di-*O*-isopropylidine-α-*D*-galactopyranose* ***24***

$[\alpha]_D^{20}$=−72.6 (*c* 2.7, $CHCl_3$); ^{1}H NMR, δ: 1.32 (3H, s), 1.33 (3H, s), 1.44 (3H, s), 1.48 (3H, s), 3.39–3.48 (2H, m), 3.59 (1H, dd, *J*=8.57, 1.98 Hz), 3.72–3.81 (2H, m), 3.86 (1H, t, *J*=9.23 Hz), 4.00 (1H, d, *J*=2.63 Hz), 4.10 (1H, d, *J*=8.58 Hz), 4.20 (1H, t, *J*=4.61 Hz), 4.24 (1H, d, *J*=1.98 Hz), 4.31–4.35 (2H, m), 4.42 (1H, d, *J*=11.22 Hz), 4.46 (1H, b s), 4.48 (1H, d, *J*=11.22 Hz), 4.57 (1H, d, *J*=11.87 Hz), 4.59 (1H, d, *J*=10.55 Hz), 4.62 (1H, d, *J*=12.53 Hz), 4.89 (1H, d, *J*=10.55 Hz), 4.90 (1H, d, *J*=12.53 Hz), 5.00 (1H, d, *J*=12.54 Hz), 5.59 (1H, d, *J*=5.28 Hz), 7.13–7.15 (20H, m); ^{13}C NMR, δ: 24.35, 25.02, 25.92, 25.97, 68.02, 69.48, 69.84, 70.46, 70.73, 71.00, 71.58, 72.62, 73.39, 73.52, 74.73, 75.05, 75.70, 81.84, 96.38, 102.32, 108.68, 109.43, 127.33, 127.42, 127.49, 127.54, 127.57 (2C), 127.87, 127.97, 128.11, 128.24 (2C), 128.25 (2C), 128.63, 138.07, 138.39 (2C), 138.62.

*3.22. 1,3,4,6-Tetra-*O*-acetyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-mannopyranosyl)-(1–2)-α-*D*-mannopyranose* ***25***

$[\alpha]_D^{22}$=+ 57.0 (*c* 1.7, $CHCl_3$); ^{1}H NMR, δ: 2.00 (3H, s), 2.06 (3H, s), 2.07 (3H, s), 2.12 (3H, s), 3.43–3.51 (1H, m), 3.56–3.57 (2H, m), 3.66–3.83 (4H, m), 3.88–3.95 (2H, m), 4.04 (1H, t, *J*=9.24 Hz), 4.18 (1H, dd, *J*=5.28, 4.62 Hz), 4.45 (1H, d, *J*=11.87 Hz), 4.49 (1H, d, *J*=10.55 Hz), 4.62 (1H, d, *J*=11.22 Hz), 4.68 (1H, d, *J*=12.53 Hz), 4.73 (1H, d, *J*=11.22 Hz), 4.75 (1H, d, *J*=12.53 Hz), 4.84 (1H, d, *J*=10.55 Hz), 5.04 (1H, d, *J*=1.32 Hz), 5.11 (1H, d, *J*=11.21 Hz), 5.24 (1H, d, *J*=6.59 Hz), 5.26 (1H, d, *J*=3.3 Hz), 7.16–7.42 (20H, m); ^{13}C NMR, δ: 20.56, 20.60, 20.62, 20.72, 62.25, 66.05, 68.58, 68.67, 68.84, 69.26, 72.77, 72.84, 73.03, 73.25, 74.43, 74.76, 75.01, 79.32, 92.48, 93.60, 127.40, 127.59, 127.69 (2C), 127.78, 127.86, 127.90, 128.22. 128.26, 128.29, 128.35, 128. 45, 137.95, 138.23, 138.27 (2C), 169.49, 169.75, 169.78, 170.53.

*3.23. 1,3,4,6-Tetra-*O*-acetyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-mannopyranosyl)-(1–2)-α-*D*-mannopyranose* ***26***

$[\alpha]_D^{22}$=−15.3 (*c* 1.3, $CHCl_3$); ^{1}H NMR, δ: 2.00 (s, 3H), 2.06 (s, 3H), 2.06 (3H, s), 2.12 (3H, s), 3.43–3.47 (1H, m), 3.56–3.72 (3H, m), 3.79–3.94 (3H, m), 3.97–4.11 (2H, m), 4.17 (1H, dd, *J*=5.28 Hz), 4.28 (1H, t, *J*=7.25 Hz), 4.47 (1H, d, *J*=11.22 Hz), 4.49 (1H, d, *J*=11.22 Hz), 4.53 (1H, d, J=11.88 Hz), 4.60 (1H, b s), 4.63 (1H, d, *J*=11.21 Hz), 4.67 (1H, d, *J*=12.54 Hz), 4.71 (1H, d, *J*=10.55 Hz), 4.86 (1H, d, *J*=10.56 Hz), 5.01 (1H, d, *J*=12.53 Hz), 5.10 (1H, d, *J*=1.98 Hz), 5.27 (1H, d, *J*=5.98 Hz), 7.13–7.37 (20H, m), ^{13}C NMR, δ: 20.51, 20.60 (2C), 20.73, 62.25, 66.06, 69.47, 72.19, 72.48, 72.55, 72.62, 72.67, 72.87, 73.48, 74.68, 74.85, 75.01, 79.56, 90.93, 98.85, 127.44, 127.48, 127.57, 127.68 (2C), 128.19, 128.24, 128.33, 128.34 (2C), 138.15, 138.15 (2C), 138.34, 138.52, 168.75, 169.41, 169.56, 170.55; *m/z* (CI, NH_3) calcd for $C_{48}H_{54}NO_{15}Na$: 892.9. Found: 892.6 (M+Na).

*3.24. Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-mannopyranosyl)-(1–6)-α-*D*-gluco-pyranose* ***27***

$[\alpha]_D^{18}$=+ 57.8 (*c* 1.7, $CHCl_3$); ^{1}H NMR, δ: 1.76 (3H, s), 1.96 (6H, s), 3.29 (3H, s), 3.50–3.66 (3H, m), 3.69–3.79 (3H, m), 3.85 (1H, dd, *J*=9.23, 3.3 Hz), 4.11–4.24 (2H, m), 4.38–4.41 (3H, m), 4.43 (1H, d, *J*=10.56 Hz), 4.51 (2H, unresolved), 4.65 (1H, d, *J*=10.55 Hz), 4.69 (1H, d, *J*=9.9 Hz), 4.70 (1H, d, *J*=9.89 Hz), 4.77 (1H, d, *J*=11.21 Hz), 4.92 (1H, d, *J*=11.21 Hz), 5.14 (1H, d, *J*=1.32 Hz), 5.36 (1H, t, *J*=9.89 Hz), 7.01–7.29 (20H, m); ^{13}C NMR, δ: 20.61, 20.64, 22.61, 55.17, 62.90, 68.11, 68.74, 68.75, 69.59, 70.97, 71.38, 72.08, 72.21, 72.58, 73.21, 74.51, 74.94, 79.72, 96.54, 100.68, 127.40, 127.51.127.72, 127.76, 127.91, 128.04, 128.09, 128.26 (2C), 128.44, 128.78, 138.26, 138.36, 138.39, 138.47, 169.62, 170.24, 170.52; ν_{max} (film) 3019, 1743, 1369 cm^{-1}.

*3.25. Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-mannopyranosyl)-(1–6)-α-*D*-gluco-pyranose* ***28***

$[\alpha]_D^{18}$=+ 22.4 (*c* 1.4, $CHCl_3$); ^{1}H NMR, δ: 1.83 (3H, s), 2.03 (6H, s), 3.36 (3H, s), 3.41–3.66 (3H, m), 3.72–3.77 (3H, m), 3.80–3.85 (2H, m), 3.98 (1H, t, *J*=8.58 Hz), 4.17 (1H, dd, *J*=9.23, 3.3 Hz), 4.39 (1H, d, *J*=2.63 Hz), 4.41 (1H, d, *J*=11.88 Hz), 4.43 (1H, b s), 4.45 (1H, d, *J*=11.87 Hz), 4.60–4.68 (3H, m), 4.71 (1H, d, *J*=11.21 Hz), 4.75 (1H, d, *J*=9.9 Hz), 4.80 (1H, d, *J*=10.56 Hz), 5.01 (1H, s), 5.42 (1H, t, *J*=9.23 Hz), 7.11–7.30 (20H, m); ^{13}C NMR, δ: 20.64 (2C), 20.73, 55.20, 62.91, 68.15, 68.81, 71.00, 72.24, 72.75, 73.22, 73.35, 74.50, 74.55, 74.58, 75.75, 76.16, 79.30, 96.57, 100.72, 127.41, 127.51, 127.57, 127.71, 127.78, 127.87, 128.22 (2C), 128.31 (2C), 138.30 (2C), 138.35, 138.43, 169.60, 170.21, 170.48; ν_{max} (film) 3019, 1743, 1369 cm^{-1}; *m/z* (Electrospray, NH_3) calcd for $C_{47}H_{58}NO_{14}$: 860.4. Found: 860.2 ($M+NH_4$).

*3.26. 1,3,4,6-Tetra-*O*-acetyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-mannopyranosyl)-(1–2)-α-*D*-galacto-pyranose* ***29***

$[\alpha]_D$=+60.6 (*c* 2.8, $CHCl_3$); ^{1}H NMR, δ: 1.95 (6H, s), 2.03 (3H, s), 2.09 (3H, s), 3.55 (1H, s), 3.70 (3H, s), 3.85 (2H, s), 3.95–4.02 (2H, m), 4.06–4.08 (2H, m), 4.32 (1H, d, *J*=7.25, 3.3 Hz), 4.32 (1H, d, *J*=10.55 Hz), 4.47 (2H, unresolved), 4.58 (1H, d, *J*=11.87 Hz), 4.62 (1H, d, *J*=11.87 Hz), 4.70 (1H, d, *J*=12.53 Hz), 4.85 (1H, d, *J*=11.21 Hz), 5.09 (1H, s), 5.20 (1H, d, *J*=10.55 Hz), 5.25 (1H, s), 6.44 (1H, d, *J*=2.63 Hz), 7.04–7.39 (20H, m); ^{13}C NMR, δ: 20.22, 20.56 (2C), 20.84, 61.34, 67.37, 67.54, 68.09, 68.91, 69.51, 71.82, 71.18, 72.25, 73.27, 73.86, 74.42, 74.75, 79.26, 89.46, 94.48, 127.32, 127.42, 127.50, 127.53, 127.56, 127.65 (2C), 127.98, 128.10, 128.21 (2C), 128.27, 138.12, 138.23, 138.24, 138.61, 168.94, 170.03, 170.05, 170.28; ν_{max} (film) 1751 cm^{-1}; *m/z* (Electrospray, NH_3) calcd for $C_{48}H_{58}NO_{15}$: 888.4. Found: 888.1.

*3.27. Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-mannopyranosyl)-(1–3)-α-*D*-manno-pyranose* ***30***

$[\alpha]_D^{20}$=+25.0 (*c* 3.8, $CHCl_3$); ^{1}H NMR, δ: 3.29 (3H, s), 3.65–3.71 (4H, m), 3.74–3.78 (2H, m), 3.86–3.87 (2H, m), 3.90–3.98 (3H, m), 4.12–4.17 (1H, m), 4.43 (1H, b s), 4.48 (1H, d, *J*=11.21 Hz), 4.49 (1H, d, *J*=11.88 Hz), 4.50 (1H, d, *J*=11.87 Hz), 4.53 (1H, d, *J*=11.21 Hz), 4.56 (1H, d, *J*=9.89 Hz), 4.57 (1H, d, *J*=9.94 Hz), 4.59 (1H, d, *J*=11.87 Hz), 4.61 (1H, d, *J*=11.21 Hz), 4.62 (1H, d, *J*=11.87 Hz), 4.64 (1H, d, *J*=9.90 Hz), 4.65 (1H, d, *J*=11.88 Hz), 4.67–4.72 (2H, m), 4.88 (1H, d, *J*=11.21 Hz),

5.23 (1H, d, *J*=1.98 Hz), 7.12–7.38 (35H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$), δ: 54.73, 69.14, 69.69, 71.80, 72.15, 72.19, 72.30, 72.63, 73.34, 73.36, 74.42, 74.75, 75.02, 75.14, 75.61, 77.53, 78.49, 79.88, 98.52, 99.96, 126.98, 127.30, 127.32, 127.40, 127.43, 127.48, 127.57, 127.64 (2C), 127.67 (2C), 128.14, 128.15, 128.16, 128.24, 128.27, 128.32, 128.33, 138.32, 138.36 (2C), 138.45, 138.50, 138.51, 138.79; ν_{max} (film) 1600 cm^{-1}; HRMS (EI) calcd for $C_{62}H_{66}O_{11}$: 986.4605. Found: 986.4605.

*3.28. Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-mannopyranosyl)-(1–3)-α-*D*-mannopyranose **31***

$[\alpha]_D^{20}$=+2.4 (*c* 2.5, $CHCl_3$); ^{1}H NMR, δ: 3.29 (3H, m), 3.54 (3H, s), 3.70–3.80 (4H, m), 3.81–3.86 (1H, m), 3.89–3.90 (2H, m), 3.92–4.17 (2H, m), 4.29 (1H, b s), 4.42 (1H, d, *J*=11.87 Hz), 4.46 (1H, d, *J*=11.88 Hz), 4.49 (1H, d, *J*=9.24 Hz), 4.52 (1H, d, *J*=9.23 Hz), 4.53 (1H, d, *J*=10.56 Hz), 4.55 (1H, d, *J*=12.53 Hz), 4.60 (1H, d, *J*=10.56 Hz), 4.62 (1H, d, *J*=12.53 Hz), 4.72 (1H, d, *J*=1.97 Hz), 4.80 (1H, d, *J*=12.54 Hz), 4.88 (2H, dd, *J*=10.56 Hz), 4.91 (1H, d, *J*=9.89 Hz), 4.95 (2H, dd, *J*=11.87 Hz), 7.12–7.47 (35H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$), δ: 55.49, 65.48, 68.90, 69.27, 69.68, 70.76, 71.41, 72.15, 72.53, 73.33, 73.84, 74.73, 74.99, 75.04, 75.09, 75.97, 80.22, 82.44, 97.17, 100.27, 127.29, 127.40, 127.42, 127.48, 127.51, 127.56, 127.61, 127.64, 127.70, 127.76, 127.79, 127.85, 127.97, 128.03, 128.26 (2C), 128.28 (2C), 128.35, 137.34, 138.30, 138.37, 138.44, 138.47, 138.49, 138.53; ν_{max} (film) 1600 cm^{-1}; *m/z* (Electrospray, NH_3) calcd for $C_{62}H_{70}NO_{11:}$ 1004.5. Found: 1004.8.

*3.29. 2,3-*O*-Isopropylidine-(2,3,4,6-tetra-*O*-benzyl-α-*D*-mannopyranosyl)-(1–4)-*D*-ribono-1,4-lactone **32***

$[\alpha]_D^{22}$=+4.2 (*c* 2.8, $CHCl_3$); ^{1}H NMR, δ: 1.35 (3H, s), 1.46 (3H, s), 3.55–3.58 (2H, m), 3.60–3.64 (3H, m), 3.70–3.71 (2H, m), 3.81 (1H, dd, *J*=9.9, 1.23 Hz), 3.88 (1H, t, *J*=9.24 Hz), 4.23 (1H, d, *J*=5.28 Hz), 4.47 (1H, d, *J*=10.56 Hz), 4.50 (1H, d, *J*=11.21 Hz), 4.52 (1H, d, *J*=11.21 Hz), 4.59 (2H, dd, *J*=1.97, 12.53 Hz), 4.60 (2H, dd, *J*=10.56, 9.9 Hz), 4.66 (1H, d, *J*=12.54 Hz), 4.77 (1H, s), 4.87 (1H, d, *J*=10.56 Hz), 7.17–7.39 (20H, m); ^{13}C NMR, δ: 25.54, 26.72, 67.28, 69.14, 71.23, 72.72, 72.84, 73.42, 74.51, 74.55, 75.23, 75.27, 76.53, 78.35, 80.50, 99.08, 113.29, 127.55, 127.67, 127.72, 127.75, 127.79, 127.86, 127.91, 127.97, 128.16, 128.31, 128.37 (2C), 128.31, 128.52, 137.73, 137.77, 138.01, 138.1, 173.80; ν_{max} 1789 cm^{-1}; *m/z* (Electrospray, NH_3) calcd for $C_{42}H_{50}NO_{10}$: 728.3. Found: 728.5 (M+NH_4).

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