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Synthesis of a Glucuronic Acid-Containing Thioglycoside Trisaccharide Building Block and Its Use in the Assembly of *Cryptococcus Neoformans* Capsular Polysaccharide Fragments**

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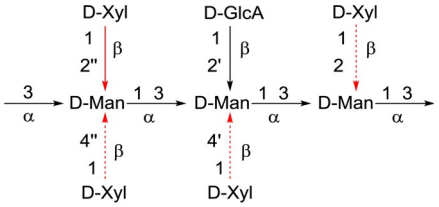
As part of an ongoing project aimed at identifying protective capsular polysaccharide epitopes for the development of vaccine candidates against the fungal pathogen *Cryptococcus neoformans*, the synthesis and glycosylation properties of a naphthalenylmethyl (NAP) orthogonally protected trisaccharide thioglycoside, a common building block for construction of serotype B and C capsular polysaccharide structures, were investigated. Ethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→4)]-6-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-1-thio-α-D-mannopyranoside was prepared and used both as a donor and an acceptor in glycosylation reactions to obtain spacer equipped hexa- and heptasaccharide structures suitable either for continued elongation or for deprotection and printing onto a glycan array or conjugation to a carrier protein. The glycosylation reactions proceeded with high yields and α-selectivity, proving the viability of the building block approach also for construction of 4-*O*-xylosyl-containing *C. neoformans* CPS structures.

Introduction

Cryptococcus neoformans is a fungal pathogen which causes severe infections in immunocompromised individuals, for example, AIDS patients and patients going through organ transplantation.[1] *C. neoformans* is surrounded by capsular polysaccharides (CPSs), primarily the glucurono-xylo-mannan (GXM)-polysaccharide comprising 90–95% of the total capsule mass. The structure of the GXM is believed to be built up of triads, that is, substituted α-(1→3) linked trisaccharide mannans, as depicted in Figure 1. β-glucuronic acid residues are linked to position 2 of the mannose backbone, together with a heterogeneous pattern of 2- and/or 4-β-xylose substituents. The amount of xylose substitution is the major determinant for the serotyping, with serotype B and C being the more substituted. GXM is also heterogeneously acetylated with the acetate positioned at the 6-OH of the mannose backbone but not present in the residues carrying 4-*O*-xylose.[2] The acetylation is believed to be important for virulence for Serotypes A and D.[3]



Xylose substitution

Serotype	2	2''	4'	4''
A	X	X		
B	X	X	X	
C	X	X	X	X
D		X		

Figure 1. Suggested structures of *C. neoformans* GXM serotype triads.

Our main focus is on Serotypes A and D, which are the most common ones in human infections, but we are also interested in 4-*O*-xylosyl containing motifs usually attributed to Serotypes B and C, since these structures, owing to the large heterogeneity of the CPS, are present in minor quantities also in CPSs serotyped as A or D. Furthermore, Serotype C structures have the lowest degree of acetylation, which should simplify structure–activity interpretation of immunological results. A building block synthetic strategy for Serotype A and D structures using 2-O-substituted disaccharides (**I**–**III**, Figure 2)[4–9] has been developed, but the use of 2,4-di-O-substituted trisaccharide building blocks has not been investigated in detail. The syntheses of both the 2,4-di-*O*-Xyl (**IV**, Figure 2)[10] and the 2-*O*-GlcA-[4-*O*-Xyl] (**V**, Figure 2)[6,11] substituted trisaccharide thioglycoside building blocks have been published, but only the former has been used in glycosylations and then only as

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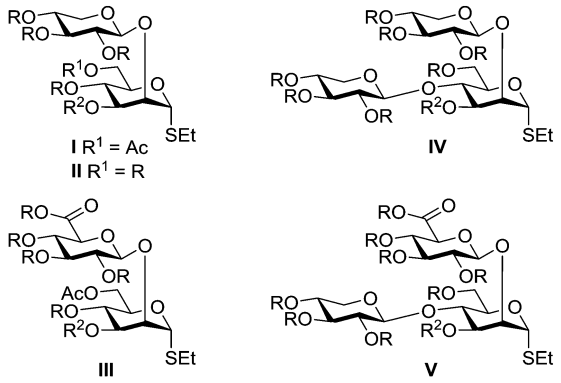


Figure 2. Desired thioglycoside building blocks. R = persistent protecting group, orthoghonal to the acetyl group; R^2 = temporary protecting group, orthoghonal to R and acetyl groups.

a donor. The potential use of block **V** as donor or as acceptor to form heavily branched 2,3,4-tri-substituted mannose motifs has not been explored.

A slightly different approach to the one we are pursuing has been investigated by Zhao and Kong[12,13] on the syntheses of non-acetylated methyl glycoside structures of Serotype B. These capsular polysaccharide fragments were prepared following a mixed convergent-linear strategy. In particular, the xylose-substituted trisaccharide mannan backbone was constructed before, and the glucuronic acid (GlcA) was introduced in the final step.

When the mannose residue involved in the glycosylation was at the nonreducing end in a hexasaccharide acceptor (Figure 3 A), no reaction was observed with methyl 2,3,4-tri-*O*-acetyl bromo- or trichloroacetimidate GlcA donors.[12]

However, when the mannose residue was at the reducing end of the hexasaccharide acceptor (Figure 3 B), the glycosylation proceeded smoothly (78% yield), affording the target non-acetylated heptasaccharide structural motif.[13] Noteworthy, this latter strategy failed when the same glycosylation was performed on Serotype C heptasaccharide acceptor (Figure 3, C).[14] The conflicting outcomes of GlcA glycosylation decrease the attractiveness of this strategy in the preparation of larger GXM fragments.

Herein, our recent efforts in the preparation of the orthogonally protected building block type **V** are reported together with its use in the construction of larger spacer-containing acetylated part structures following a convergent approach.

Results and Discussion

In our previous synthesis,[6] building block **V** was prepared with an allyl group as the temporary protecting group in position 3. However, in light of results obtained in attempts to remove the allyl group on disaccharide thioglycosides, showing its incompatibility with the thioethyl group,[9] the allyl group was changed into a naphthalenylmethyl protecting group (NAP) in the new synthesis (Scheme 1).

Starting from compound **1**,[7] the benzylidene ring was opened regioselectively with $NaCNBH_3$/HCl[15] obtaining compound 4-OH acceptor **2** in 93% yield. The coupling of **2** and **3**[16] was carried out using trimethylsilyl trifluoromethanesulfonate (TMSOTf) in the presence of (commercial) acid-washed molecular sieves to prevent orthoester formation and afford compound **4** in 70% yield. At this stage, benzoyl groups, which ensured the stereoselective course of the glycosylation, were removed and the primary OH was selectively protected by reaction with *tert*-butyldimethylsilyl chloride (TBDMSCl) giving **6** in 61% yield over two steps. The remaining hydroxy groups were *per*-benzylated (→**7**, 77%) before compound **8** was obtained in an almost quantitative yield (96%) by reaction with tetra-*n*-butylammonium fluoride (TBAF).

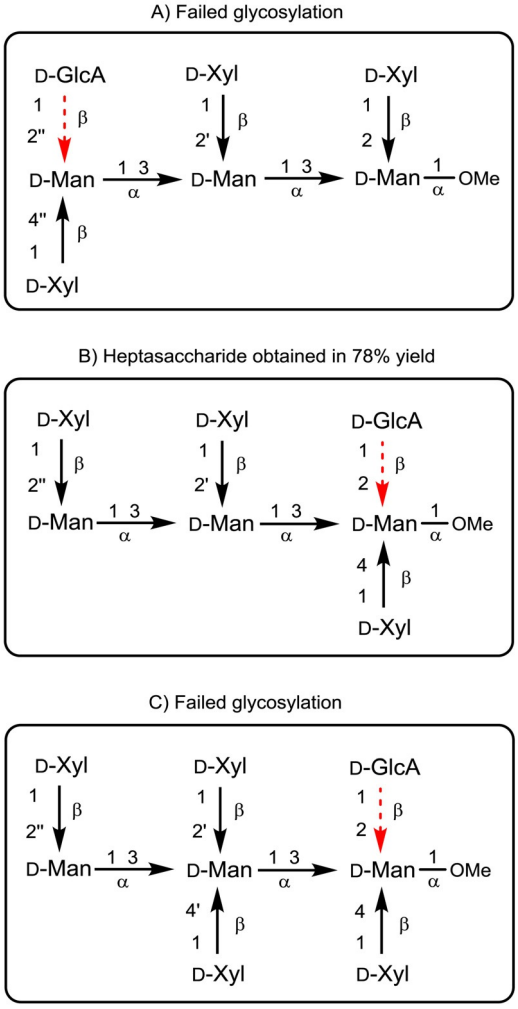
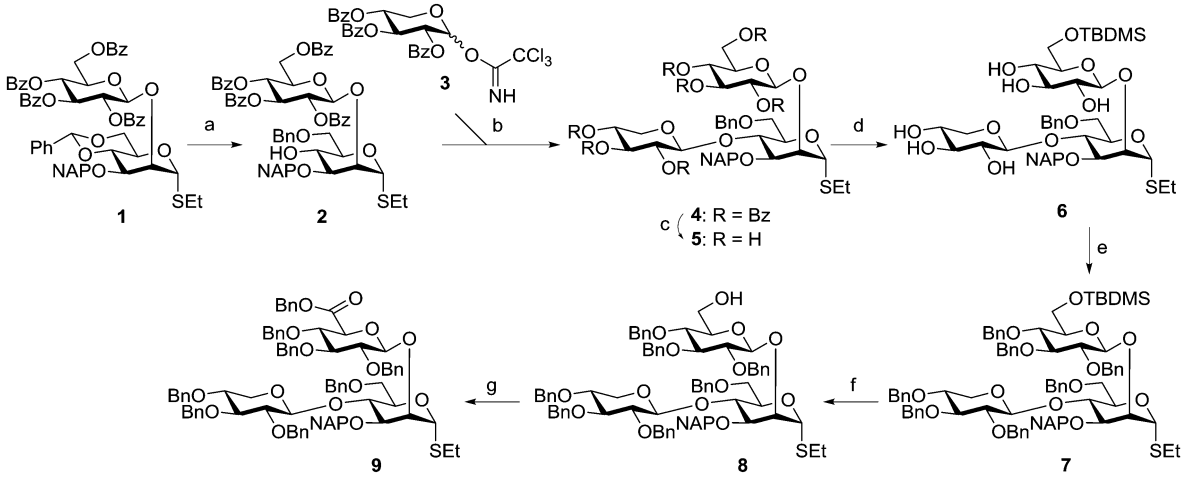


Figure 3. Schematic representation of GlcA glycosylation of xylose-substituted trisaccharide mannan backbone, reported previously.[12–14]

NMR analysis of compound **8** at 25 °C in $CDCl_3$ gave unexpected results, which included broad peaks in the ^{1}H NMR spectrum and even missing carbon peaks in the ^{13}C NMR spectrum (Figure 4).

By carrying out the NMR experiments at 50 °C (Figure 4 B), sharper peaks (^{1}H NMR) and expected peaks (^{13}C NMR) were observed. In particular, the cross peak for C−1′ as well as the two anomeric carbons for C−1′ and C−1″ were visible. Still, no signal was observed for position 4 of the mannose residue.



Scheme 1. *Reagents and conditions*: a) $NaCNBH_3$, HCl (1 M in Et_2O), THF, pH 1–2, 20 °C, 30 min, 93%; b) TMSOTf, CH_2Cl_2, AW-300 MS, −78 °C→0 °C, o/n, 70%; c) 1. NaOMe, MeOH, 20 °C, o/n; 2. Dowex H^+ ion-exchange resin, 80%; d) TBDMSCl, pyridine, DMAP, 20 °C, 4 h, 76%; e) NaH, BnBr, DMF, 0 °C→20 °C, o/n, 77%; f) TBAF trihydrate, THF, 20 °C, 2 h, 96%; g) 1) TEMPO, BAIB, CH_2Cl_2/H_2O (2:1), 20 °C; 2) Cs_2CO_3, BnBr, DMF, 0 °C→20 °C, 2 h, 60%.

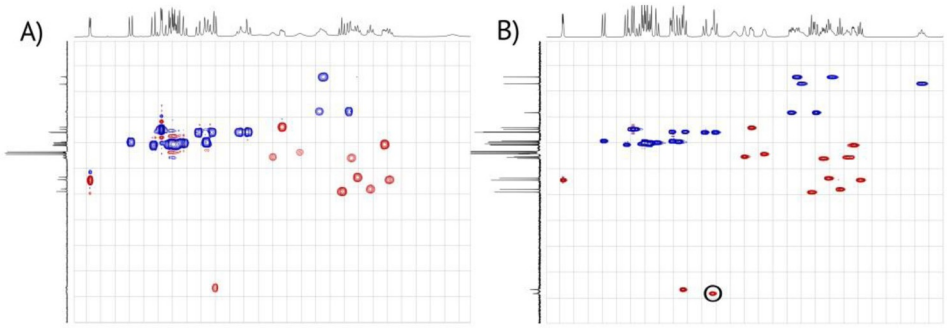
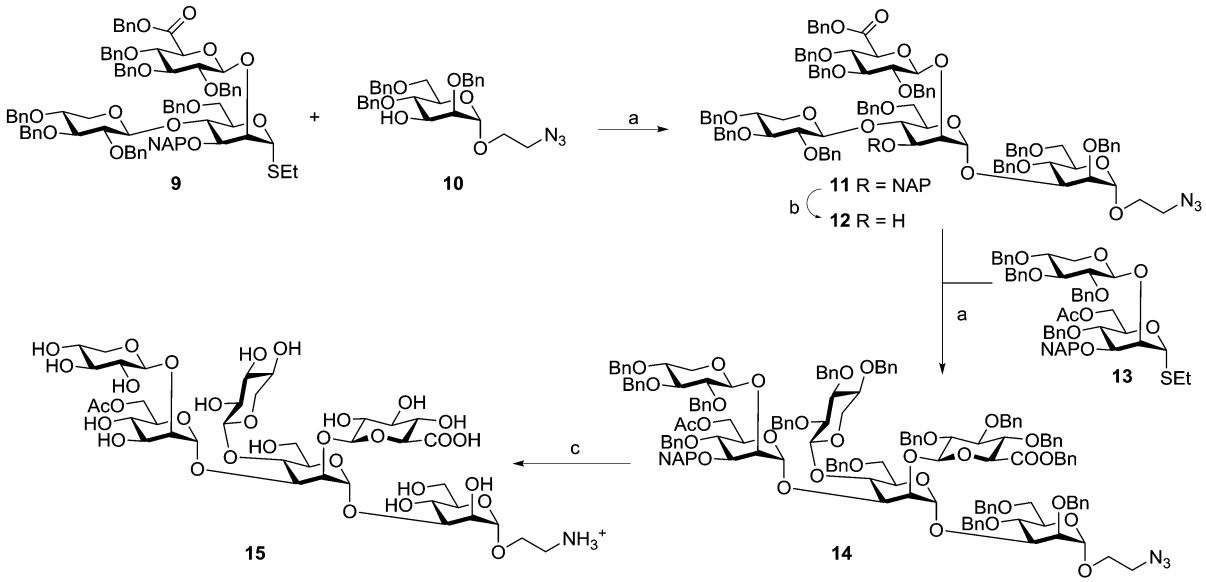


Figure 4. A) ^1H–^{13}C HSQC spectrum of compound **8** at 25 °C; B) ^1H–^{13}C HSQC spectrum of compound **8** at 50 °C; the now visible anomeric cross peak is highlighted.

This behaviour is in agreement with hindered rotation for compound **8**.[17] Interestingly, the NMRs of the related compounds **7** and **9** do not show this behaviour.

Final oxidation with the (2,2,6,6-tetramethylpiperidin-1-yl)oxyl-[bis(acetoxy)iodo]benzene (TEMPO-BAIB)[18] system followed by benzylation of the crude (Cs_2CO_3, BnBr) afforded the desired building block **9** in satisfactory 60% yield.



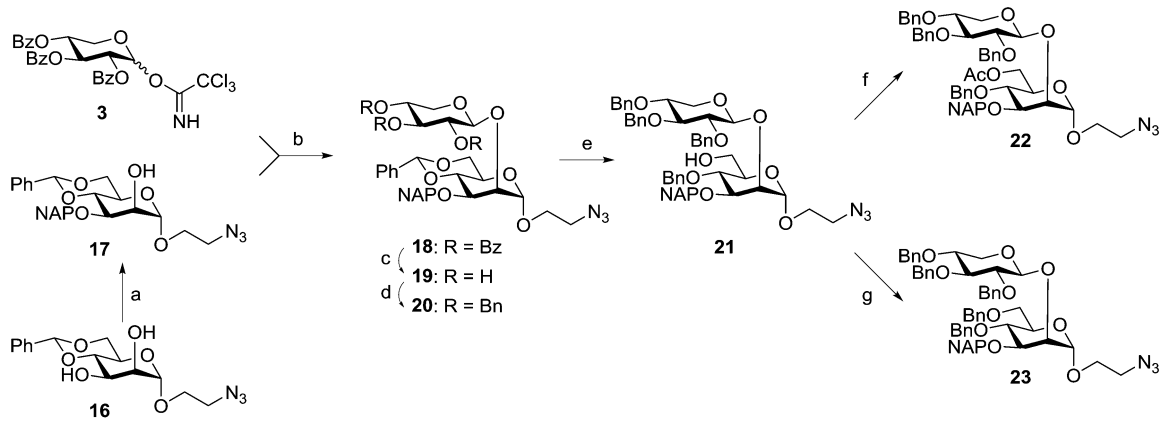
Scheme 2. *Reagents and conditions*: a) DMTST, Et_2O, 0 °C→20 °C, 1.5 h, 95% for **11**, 79% for **14**; b) DDQ, CH_2Cl_2/H_2O (10:1), 20 °C, 60 min, 74%; c) H_2/Pd–C (30 bar), EtOAc, H_2O, AcOH, 67%.

Prepared trisaccharide **9** was tested in a dimethyl(methylthio)sulfonium trifluoromethansulfonate (DMTST)-promoted glycosylation with the spacer-containing derivative **10**[10] (Scheme 2) and afforded α-linked tetrasaccharide **11** as the sole product in 95% yield, demonstrating excellent donor properties of trisaccharide **9** to monosaccharide acceptors.

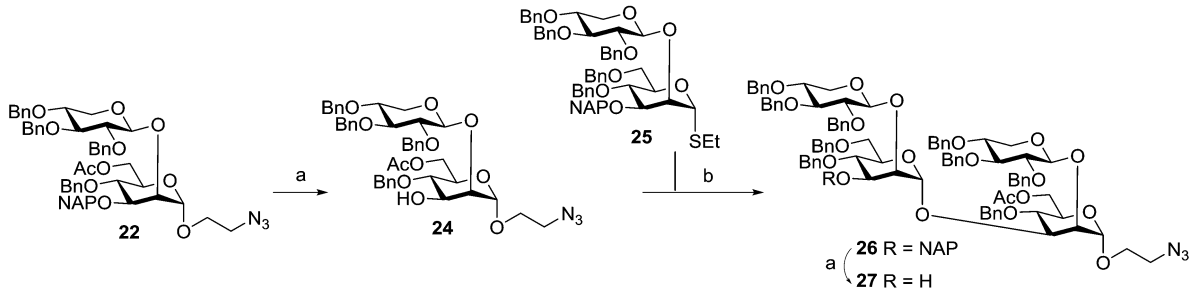
The removal of the naphthalenylmethyl protecting group by reaction with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in a mixture of dichloromethane/water proceeded in 74% yield to obtain acceptor **12** ready for testing the possibility of obtaining 2,3,4-tri-O-glycosylated structures. Thus, acceptor **12** was reacted with disaccharide thioglycoside **13**[9] again using DMTST as promoter. Satisfactorily, hexasaccharide **14** was obtained with complete α-selectivity and in high yield (79%) and was then completely deprotected by means of hydrogenolysis to afford **15** in 67% yield. This rather unusual GXM structural motif was reported recently by Nimrichter et al.[19] who characterised a substituted triad from encapsulated cells that had only been described in polysaccharide fractions from a hypocapsular mutant. NMR data for **15** are in good agreement with the one reported for the polysaccharide: anomeric reported values: 4.45 ppm (GlcA), 4.35 ppm (2-*O*-Xyl), 4.25 ppm (4-*O*-Xyl); found for **15** 4.47 ppm (GlcA), 4.40 ppm (2-*O*-Xyl), 4.31 ppm (4-*O*-Xyl).

A more complex acceptor than the monosaccharide **10** was then prepared to further investigate the donor properties of trisaccharide **9** (Scheme 3 and 4). Spacer-equipped acceptor **17**, obtained from **16**[10] in 88% yield, was coupled with trichloroacetimidate donor **3**[16] using *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBDMSOTf) in the presence of acid-washed molecular sieves yielding disaccharide **18** in 86% yield. Benzoyl groups, again utilised for their anchimeric assistance in the glycosylation reaction, were exchanged for benzyl groups affording **20** in 77% yield over two steps. The opening of the benzylidene ring was this time performed using Bu_2BOTf/BH_3[20] to afford the opposite regioselectivity to compound **1**, giving the 6-OH compound **21** (76%), which was either acetylated (→**22**, 93%) or benzylated (→**23**, 95%). The 6-*O*-acetyl disaccharide **22** was then chosen for the preparation of a tetrasaccharide acceptor for the consecutive construction of the spacer-containing *C. neoformans* Serotype B heptasaccharide triad motif which followed our standard sequence of reactions: NAP removal followed by DMTST-promoted glycosylation (Scheme 4).

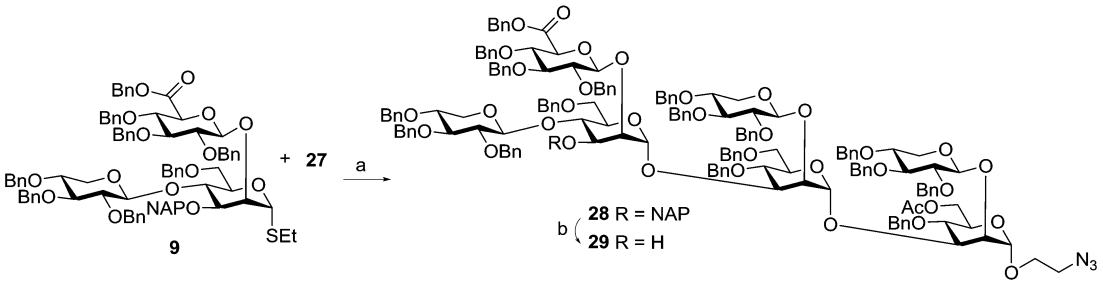
The first reaction gave disaccharide acceptor **24** in 73% yield, while the glycosylation with **25**[9] afforded tetrasaccharide **26** in 85% yield, which was in turn converted into the new acceptor **27** (80% yield). As mentioned in the introduction,



Scheme 3. *Reagents and conditions*: a) Bu_2SnO, Bu_4NBr, NapBr, toluene, reflux, 3 h, 88%; b) TBDMSOTf, CH_2Cl_2, AW-300 MS, −78 °C→20 °C, o/n, 86%; c) 1. NaOMe, MeOH, 20 °C; 2. Dowex H^+ ion-exchange resin, 86%; d) NaH, BnBr, DMF, 0 °C→20 °C, 3 h, 90%; e) Bu_2BOTf, BH_3 (1 M in THF), CH_2Cl_2, 0 °C, 90 min, 76%; f) Ac_2O, pyridine, 20 °C, 3 h, 93%; g) NaH, BnBr, DMF, 0 °C→20 °C, 2 h, 95%.



Scheme 4. *Reagents and conditions*: a) DDQ, CH_2Cl_2/H_2O (10:1), 20 °C, 60 min, 73% for **24**, 80% for **27**; b) DMTST, Et_2O, 0 °C→20 °C, 3.5 h, 85%.



Scheme 5. *Reagents and conditions*: a) DMTST, Et_2O, DMTST, Et_2O, 0 °C→20 °C, 3.5 h, 83%; b) DDQ, CH_2Cl_2/*t*BuOH (10:1), 20 °C, 1.5 h, 68%.

acetates are heterogenously present on the 6-OH of mannose residues if no 4-*O*-xylose substituents are present. By choosing the correct combination from the set of thioglycoside donors (**13** and **25**) and spacer-containing acceptors (**24** and the one that can be prepared from **23** after NAP removal), and by following the same sequence of reactions reported in Scheme 4, all possible acetylation patterns on the tetrasaccharide motif can be obtained, permitting following investigation into the effect of the acetylation pattern on the immune response.

Finally, building block **9** was used in the glycosylation reaction with **27** to prepare the desired structural motif (Scheme 5).

The reaction proceeded smoothly (83%) and permitted, for the first time, the synthesis of monoacetyl heptasaccharide **28**. This result, together with the preparation of tetrasaccharide **11**, confirmed the versatility of the proposed convergent strategy which allows for installation of the GlcA containing trisaccharide in every position of the mannan triad thus overcoming the problems encountered previously with different strategies. Derivative **28** could be completely deprotected by hydrogenolysis, as shown for **14**, and used to prepare a candidate vaccine after conjugation with an immunogenic protein, or could be employed as an acceptor after removal of the NAP group (→**29**, 68%), to further elongate the GXM fragment.

Conclusions

In conclusion, an efficient synthesis of a GlcA-containing trisaccharide thioglycoside building block corresponding to *Cryptococcus neoformans* Serotype B and C glucurono-xylo-mannan (GXM) oligosaccharide structure has been developed. The naphthalenylmethyl (NAP)-protected building block was shown to be a most efficient glycosyl donor to both monosaccharide and more complex acceptors in dimethyl(methylthio)-sulfonium-trifluoromethansulfonate (DMSTS)-promoted glycosylation reactions which proceeded with high yields and complete α-selectivity. Subsequent removal of the 2-NAP temporary protecting group converted obtained saccharides into new acceptors, which were shown to work well in following glycosylation reactions allowing effective construction of heavily branched 2,3,4-subtituted motifs. Thus, the presented strategy permitted the preparation of both a hexasaccharide (**14**) and a Serotype B heptasaccharide structural motif, and the results demonstrate the possible synthesis of any *C. neoformans* GXM structure from the various available mono-, di-, and trisaccharide building blocks.

Experimental Section

General: Thin-layer chromatography (TLC) was carried out on precoated 60 F_{254} silica gel alumina plates (Merck) using UV light and/or 8% H_2SO_4 and/or AMC-solution (ammonium molybdate, cerium (IV) sulphate, 10% H_2SO_4 [5:0.1:100, *w/w/v*] for visualisation. Flash column chromatography was performed on silica gel (Merck, pore size 60 Å, particle size 40–63 μm). NMR spectra were recorded in $CDCl_3$ (internal Me_4Si $d=0.00$ ppm) at 25 °C on a Varian instrument (500 MHz for ^1H and 125 MHz for ^{13}C or 600 MHz for ^1H and 150 MHz for ^{13}C, VNMRS 500 MHz or 600 MHz, Palo Alto, USA). Coupling constants are given in Hertz (Hz). High-resolution mass spectrometry (HRMS) spectra were recorded on a Micromass LCT instrument (Waters, Milford, USA) using electrospray ionisation (ESI) in either the positive or negative modes. Optical rotations were measured with a PerkinElmer 343 polarimeter (Waltham, USA) at the sodium D-line (589 nm) at 20 °C using a 1 dm cell. All reactions containing air- and moisture-sensitive reagents were carried out under an Ar atmosphere. Organic phases were dried over $MgSO_4$ before evaporation, which was performed under reduced pressure at temperatures not exceeding 40 °C.

Ethyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl-(1→2)-6-O-benzyl-3-O-(2-naphthalenylmethyl)-1-thio-α-D-mannopyranoside (2). Sodium cyanoborohydride (223 mg, 3.56 mmol) was added to a solution of acetal **1** (612 mg, 0.59 mmol) in dry tetrahydrofuran (THF, 25 mL) containing crushed molecular sieves (3 Å, 150 mg). A 1 M solution of HCl in Et_2O (9.0 mL, 9.0 mmol) was added dropwise at 20 °C (until pH 1–2). The reaction mixture was stirred until no starting material was detected by TLC (toluene/EtOAc, 6:1). After 30 min, Et_3N (2.5 mL, 17.80 mmol) was added, followed by dropwise addition of MeOH (10 mL). CH_2Cl_2 (20 mL) was added, the solids were removed by filtration through a short pad of Celite, concentrated in vacuo, and then redissolved and co-evaporated with MeOH (3×50 mL). Purification by flash column chromatography (SiO_2, 100 mL, 4.5 cm, toluene→toluene/EtOAc, 96:4→93:7→90:10→87:13→85:15→80:20→75:25) gave **2** (571 mg, 93%) as a colourless, amorphous solid: $R_f=0.32$ (toluene/EtOAc, 6:1); $[\alpha]_D^{20}+6.7$ (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=7.96–7.88$ (m, 6H), 7.87–7.81 (m, 2H), 7.79–7.66 (m, 4H), 7.54–7.38 (m, 7H), 7.36–7.32 (m, 2H), 7.31–7.14 (m, 11H), 5.93 (t, *J* 9.7, 1H), 5.70–5.61 (m, 1H), 5.27 (d, *J* 1.0, 1H), 5.01 (d, *J* 7.9, 1H), 4.91 (d, *J* 11.5, 1H), 4.65 (dd, *J* 3.1, *J* 12.1, 1H), 4.57 (d, *J* 11.5, 1H), 4.48 (dd, *J* 5.7, *J* 12.1, 1H), 4.32 (dd, *J* 1.7, *J* 2.9, 1H), 4.26 (s, 2H), 4.21–4.15 (m, 1H), 3.96 (ddd, *J* 3.3, *J* 6.6, *J* 9.7, 1H), 3.81 (t, *J* 9.4, 1H),

3.68 (dd, *J* 3.1, *J* 9.2, 1H), 3.58 (dd, *J* 3.3, *J* 10.7, 1H), 3.27 (dd, *J* 6.6, *J* 10.7, 1H), 2.55–2.38 (m, 3H), 1.15 ppm (t, *J* 7.4, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.2, 166.0, 165.3, 164.9, 138.5, 135.2, 133.6, 133.4, 133.3, 133.2, 133.2, 133.1, 130.0, 129.9, 129.9, 129.8, 129.7, 129.6, 129.0, 128.9, 128.6, 128.5, 128.4, 128.4, 128.3, 128.1, 127.8, 127.5, 127.5, 127.1, 126.2, 126.1, 126.0, 99.8, 81.2, 77.9, 75.5, 73.4, 73.0, 72.7, 71.9, 71.86, 70.9, 70.9, 69.9 68.1, 63.4, 25.4, 14.8; HRMS (ESI): $[M-H]^-$ *m/z* calcd for $C_{60}H_{55}O_{14}S$: 1031.3313, found: 1031.3279; Anal. calcd for $C_{60}H_{55}O_{14}S$: C 69.75, H 5.46, S 3.10, found: C 69.43, H 5.43, S 3.28.

Ethyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→4)]-6-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-1-thio-α-D-mannopyranoside (4). A catalytic amount of TMSOTf (20 μL, 11 μmol) was added to a solution of donor **3**[16] (88 mg, 0.145 mmol) and acceptor **2** (116 mg, 0.113 mmol) in dry CH_2Cl_2 (5 mL) containing crushed molecular sieves (AW-300, 40 mg) kept at −78 °C in an atmosphere of nitrogen. The temperature was then allowed to rise to 20 °C overnight (TLC, toluene-EtOAc, 6:1). The reaction mixture was neutralised with Et_3N (16 μL, 0.113 mmol), the solids were removed by filtration, and the filtrate was concentrated in vacuo to a yellowish foam. Purification by flash column chromatography (SiO_2, 100 mL, 4.5 cm, toluene→toluene/tOAc, 98:2→96:4→94:6 →92:8→90:10→88:12→86:14) gave **4** (118 mg, 70%) as a colourless foam: R_f = 0.46 (toluene/EtOAc, 9:1); $[\alpha]_D^{20}$ + 5.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93–7.83 (m, 14H), 7.77–7.69 (m, 4H), 7.56–7.42 (m, 7H), 7.39–7.19 (m, 20H), 7.10–7.03 (m, 2H), 5.90 (t, *J* 9.7 Hz, 1H), 5.71–5.62 (m, 2H), 5.53 (t, *J* 8.2 Hz, 1H), 5.26 (dd, *J* 6.5 Hz, *J* 8.2 Hz, 1H), 5.20 (d, *J* 2.9 Hz, 1H), 5.16 (td, *J* 4.9 Hz, *J* 8.1 Hz, 1H), 5.02 (d, *J* 7.9 Hz, 1H), 4.94 (d, *J* 11.3 Hz, 1H), 4.73 (d, *J* 6.2 Hz, 1H), 4.68 (d, *J* 11.4 Hz, 1H), 4.61 (dd, *J* 3.1 Hz, *J* 12.1 Hz, 1H), 4.44 (dd, *J* 5.2 Hz, *J* 12.1 Hz, 1H), 4.20 (bs, 1H), 4.15–4.09 (m, 3H), 4.01–3.88 (m, 4H), 3.34 (dd, *J* 1.9 Hz, *J* 10.8 Hz, 1H), 3.27 (dd, *J* 5.9 Hz, *J* 10.9 Hz, 1H), 3.02 (dd, *J* 8.3 Hz, *J* 12.1 Hz, 1H), 2.44–2.30 (m, 2H), 1.06 ppm (t, *J* 7.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.1, 165.9, 165.5, 165.5, 165.3, 165.2, 164.9, 138.6, 135.6, 133.5, 133.4, 133.3, 133.3, 133.3, 133.2, 133.1, 133.0, 130.0, 130.0, 129.9, 129.9, 129.9, 129.8, 129.7, 129.5, 129.4, 129.4, 129.0, 128.9, 128.5, 128.5, 128.5, 128.4, 128.4, 128.2, 128.2, 128.0, 127.8, 127.5, 127.4, 127.2, 126.6, 126.1, 125.9, 100.8, 100.6, 81.3, 77.3, 77.1, 76.2, 73.1, 72.9, 72.6, 72.2, 71.9, 71.5, 71.4 (2C), 69.8, 69.5, 69.3, 63.3, 61.9, 25.2, 14.7 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{86}H_{76}O_{21}NaS$: 1499.4498, found: 1499.4547; Anal. calcd for $C_{86}H_{76}O_{21}S$: C 69.91, H 5.18, S 2.17, found: C 69.75, H 5.28, S 2.43.

Ethyl β-D-glucopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→4)]-6-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-1-thio-α-D-mannopyranoside (5). A catalytic amount of sodium methoxide (75 mg, 1.38 mmol) was added to a solution of **4** (4.10 g, 2.77 mmol) in dry MeOH (150 mL). The mixture was stirred at 20 °C overnight (TLC, CH_2Cl_2–MeOH, 9:1). After complete conversion, Dowex (H^+) acidic ion-exchange resin was added for neutralisation, the resin was filtered off, washed with MeOH (30 mL), and the filtrate was concentrated in vacuo. Purification by flash column chromatography (SiO_2, 600 mL, 7.5 cm, DCM→DCM/MeOH, 95:5→90:10→88:12→86:14→84:16→83:17→82:18) gave **5** (1.68 g, 80%) as a colourless, amorphous solid: R_f = 0.13 (CH_2Cl_2/MeOH, 9:1); $[\alpha]_D^{20}$ + 45.6 (*c* 1.0, MeOH); ^{1}H NMR (600 MHz, DMSO) δ 7.93 (1H, s), 7.88–7.84 (1H, m), 7.81 (m, 2H), 7.56 (dd, 1.6 Hz, *J* 8.5 Hz, 1H), 7.48–7.43 (m, 2H), 7.43–7.28 (m, 4H), 7.27–7.23 (m, 1H), 5.40 (d, *J* 2.0 Hz, 1H), 5.10 (d, *J* 4.8 Hz, 1H), 4.94–4.83 (m, 5H), 4.69–4.60 (m, 2H), 4.53 (d, *J* 11.9 Hz, 1H), 4.44 (d, *J* 11.9 Hz, 1H), 4.39 (t, *J* 5.6 Hz, 1H), 4.33 (d, *J* 7.8 Hz, 1H), 4.22 (d, *J* 7.4 Hz, 1H), 4.19 (t, *J* 2.8 Hz, 1H), 4.00–3.90 (m, 2H), 3.86 (dd, *J* 4.8 Hz, *J* 11.1 Hz, 1H), 3.75 (dd, *J* 1.6 Hz, *J* 11.2 Hz, 1H), 3.73–3.64 (m, 2H), 3.61 (dd, *J* 3.4 Hz, *J* 8.3 Hz, 1H), 3.42–3.35 (m, 1H), 3.32–3.27 (m, 1H), 3.19–3.09 (m, 2H), 3.09–2.96 (m, 4H), 2.88 (dd, *J* 10.2 Hz, *J* 11.5 Hz, 1H), 2.64–2.49 (m, 2H), 1.16 ppm (t, *J* 7.4 Hz, 3H); ^{13}C NMR (125 MHz, DMSO): δ = 138.6, 136.6, 132.8, 132.4, 128.2, 127.6, 127.5, 127.4, 127.3, 126.2, 126.0, 125.9, 125.6, 103.9, 101.6, 81.8, 77.2, 76.8, 76.7, 76.6, 74.7, 74.1, 73.9, 73.1, 72.2, 71.7, 70.3, 70.3, 69.7, 68.8, 65.9, 61.5, 24.5, 14.9 ppm; HRMS (ESI): $[M-H]^-$ *m/z* calcd for $C_{37}H_{47}O_{14}S$: 747.2687, found: 747.2702.

Ethyl 6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→4)]-6-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-1-thio-α-D-mannopyranoside (6). *tert*-Butyldimethylchlorosilane (82 mg, 0.55 mmol) and a catalytic amount of DMAP (1 mg, 8 μmol) were added to a solution of **5** (273 mg, 0.36 mmol) in dry pyridine (10 mL), and the mixture was stirred at 20 °C for 4 h. The progress of the reaction was followed by TLC (DCM/MeOH, 9:1). The mixture was concentrated in vacuo, and then redissolved and coevaporated with toluene (3×30 mL) (water bath temperature of rotary evaporator: < 30 °C). Purification by flash column chromatography (SiO_2, DCM→DCM/MeOH, 95:5→94:6→93:7→92:8→91:9→90:10) gave **6** (240 mg, 76%) as colourless, amorphous solid: R_f = 0.35 (CH_2Cl_2/MeOH, 9:1); $[\alpha]_D^{20}$ + 31.5 (*c* 0.89, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82–7.74 (m, 4H), 7.53 (d, *J* 8.5 Hz, 1H), 7.47–7.39 (m, 2H), 7.35–7.19 (m, 5H), 5.32 (s, 1H), 4.85 (d, *J* 11.5 Hz, 1H), 4.78 (d, *J* 11.5 Hz, 1H), 4.59 (d, *J* 12.0 Hz, 1H), 4.51 (d, *J* 12.0 Hz, 1H), 4.43–4.36 (m, 2H), 4.31–4.19 (m, 3H), 4.13–4.07 (m, 2H), 3.93–3.77 (m, 6H), 3.73–3.64 (m, 3H), 3.55–3.40 (m, 4H), 3.35–3.26 (m, 3H), 3.00 (t, *J* 10.6 Hz, 1H), 2.89 (bs, 1H), 2.61–2.46 (m, 2H), 1.20 (t, *J* 7.4 Hz, 1H), 0.84 (s, 9H), 0.00 (s, 3H), 0.00 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.6, 134.8, 133.3, 133.2, 128.6, 128.2, 128.2, 128.1, 128.0, 127.8, 127.7, 126.7, 126.2, 126.1, 103.2, 100.7, 82.6, 77.0, 76.3, 76.1, 75.6, 74.2, 74.0, 73.7, 73.5, 72.3, 72.2, 72.0, 71.5, 69.7, 68.7, 65.6, 64.3, 25.9, 25.6, 18.3, 15.0, −5.3, −5.4 ppm; HRMS (ESI): $[M-H]^-$ *m/z* calcd for $C_{43}H_{61}O_{14}SSi$: 861.3551, found: 861.3558

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl-(1→2)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→4)]-6-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-1-thio-α-D-mannopyranoside (7). NaH (100 mg, 2.49 mmol, 60% oil dispersion) was washed with pentane (3×10 mL) prior to use. NaH was added portionwise to a solution of **6** (239 mg, 0.27 mmol) in dry DMF (10 mL) at 0 °C in an atmosphere of nitrogen. After 15 min, benzyl bromide (236 μL, 2.00 mmol) was added dropwise at 0 °C under vigorous stirring. The temperature was then allowed to rise to 20 °C overnight (TLC, toluene/EtOAc, 9:1). After complete consumption of the starting material, residual NaH was quenched with MeOH (1 mL), and then with H_2O (50 mL). The resulting mixture was extracted once with EtOAc (40 mL), the layers were separated, and the organic layer was washed with brine (1×40 mL), dried over $MgSO_4$, and concentrated in vacuo. Purification by flash column chromatography (SiO_2, toluene→toluene/EtOAc, 97:3→94:6→92:8→91:9) gave **7** (300 mg, 77%) as a colourless syrup. R_f = 0.61 (toluene/EtOAc, 9:1); $[\alpha]_D^{20}$ + 29.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (s, 1H), 7.85–7.74 (m, 3H), 7.62 (d, *J* 9.7 Hz, 1H), 7.49–7.13 (m, 35H), 7.10–7.02 (m, 2H), 5.47 (d, *J* 2.1 Hz, 1H), 5.14 (d, *J* 10.4 Hz, 1H), 5.06 (d, *J* 12.4 Hz, 1H), 4.94 (d, *J* 11.0 Hz, 1H), 4.87–4.69 (m, 7H), 4.66 (m, 2H), 4.57–4.50 (m, 3H), 4.38–4.22 (m, 5H), 4.08–4.02 (m, 1H), 3.92–3.75 (m, 5H), 3.68–3.51 (m, 5H), 3.43 (t, *J* 8.9 Hz, 1H), 3.37–3.28 (m, 2H), 2.90 (dd, *J* 10.1 Hz, *J* 11.6 Hz, 1H), 2.68–2.54 (m, 2H), 1.26 (t, *J* 7.4 Hz, 3H), 0.85 (s, 9H), 0.01 (s, 3H), 0.00 ppm (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 138.9, 138.8,

138.8, 138.7, 138.4, 138.4, 138.3, 136.3, 133.4, 133.0, 129.1, 129.0, 128.5, 128.4, 128.4, 128.2, 128.2, 128.2, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4, 126.8, 126.6, 125.9, 125.6, 103.4, 102.0, 85.0, 84.1, 82.4, 81.8, 78.3, 77.5, 76.4, 76.3, 75.7, 75.5, 75.4, 75.0, 75.0, 74.9, 74.6, 73.0, 72.9, 71.9, 71.1, 69.0, 63.6, 62.7, 26.2, 26.1, 25.5, 18.4, 15.0, −5.1, −5.2 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{85}H_{98}O_{14}NaSSi$: 1425.6344, found: 1425.6320.

Ethyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→4)]-6-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-1-thio-α-D-mannopyranoside (8). TBAF trihydrate (52 mg, 0.16 mmol) was added to a solution of **7** (153 mg, 0.11 mmol) in THF (5 mL), and the mixture was stirred at 20 °C for 2 h (TLC, toluene/EtOAc, 9:1). After complete consumption of the starting material, the reaction mixture was concentrated in vacuo. Purification by flash column chromatography (SiO_2, toluene→toluene/EtOAc, 93:7→90:10→87:13→84:16→81:19→78:22→75:25) gave **8** (135 mg, 96%) as a colourless, amorphous solid: R_f = 0.39 (toluene/EtOAc, 6:1); $[\alpha]_D^{20}$ + 34.5 (*c* 0.42, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.77 (m, 4H, H_{ar}), 7.56–7.54 (m, 1H, H_{ar}), 7.48–7.44 (m, 2H, H_{ar}), 7.38–7.36 (m, 2H, H_{ar}), 7.32–7.20 (m, 31H, H_{ar}), 7.12–7.11 (m, 2H, H_{ar}), 5.37 (d, 1H, *J* 3.4 Hz, H-1), 5.09 (d, 1H, *J* 10.4 Hz, PhCH_2), 4.93 (d, 1H, *J* 11.1 Hz, PhCH_2), 4.90–4.84 (ABq, 2H, PhCH_2), 4.82–4.70 (m, 6H, PhCH_2), 4.63–4.50 (m, 5H, H-1′, PhCH_2), 4.35–4.26 (m, 3H, H-1″, PhCH_2), 4.17 (m, 1H, H-4), 4.09 (m, 1H, H-2), 4.04–4.02 (m, 1H, H-5), 3.92 (m, 1H, H-3), 3.78–3.73 (m, 3H, H-6a, H-6′a, H-5″a), 3.63–3.49 (m, 5H, H-6b, H-2′, H-3′, H-6′b, H-4″), 3.43–3.39 (m, 2H, H-4′, H-3″), 3.33–3.29 (m, 1H, H-5′), 3.27 (t, 1H, *J* 8.4 Hz, H-2″), 2.86–2.80 (m, 1H, H-5″b), 2.69–2.56 (m, 2H, SC$H_2$$CH_3$), 1.26 ppm (t, 3H, *J* 7.4 Hz, SCH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.7, 138.7, 138.5, 138.5, 138.3 (2C), 138.0, 136.1, 133.2, 133.0 ($C_{ar,quart}$), 128.8, 128.44, 128.40, 128.33, 128.28, 128.22, 128.21, 128.17, 128.1, 128.0, 127.9, 127.83, 127.78, 127.76, 127.7, 127.6, 127.51, 127.47, 127.4, 126.7, 126.1, 125.8 (C_{ar}), 104.1 (C-1″), 103.2 (C-1′), 84.5 (C-3′), 84.0 (C-3″), 82.2 (2C, C-1, C-2″), 81.7 (C-2′), 78.0 (C-4″), 77.8 (C-2), 77.6 (C-4′), 77.0 (C-3), 75.6 (PhCH_2), 75.4 (PhCH_2), 75.4 (C-5′), 75.1 (PhCH_2), 75.0 (PhCH_2), 74.8 (PhCH_2), 73.0 (PhCH_2), 73.0 (PhCH_2), 72.4 (NapCH_2), 72.0 (C-5), 69.0 (C-6), 63.6 (C-5″), 62.2 (C-6′), 25.4 (SCH_2CH_3), 15.0 ppm (SCH_2CH_3). The signal of C-4 could not be observed; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{79}H_{84}O_{14}NaS$: 1311.5479, found: 1311.5487.

Ethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→4)]-6-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-1-thio-α-D-mannopyranoside (9). TEMPO (2 mg, 13 μmol) and BAIB (300 mg, 0.93 mmol) were added to a vigorously stirred solution of **8** (116 mg, 90 μmol) in CH_2Cl_2/H_2O (12 mL, 3:1), and the mixture was stirred at 20 °C for 4 h. The progress of the reaction was carefully monitored by TLC (toluene/EtOAc, 9:1). The reaction was quenched by adding 10% aq. $Na_2S_2O_3$ solution (10 mL). The resulting mixture was extracted once with EtOAc (20 mL), the layers were separated, and the organic layer was washed with brine (1×10 mL), dried over $MgSO_4$, and concentrated in vacuo. Cs_2CO_3 (57 mg, 0.17 mmol) was added to a solution of the crude in dry DMF (3 mL) at 20 °C. After 15 min, benzyl bromide (22 μL, 0.18 mmol) was added dropwise at 0 °C. The temperature was then allowed to rise to 20 °C over 16 h (TLC, toluene/EtOAc 9:1). After complete consumption of the starting material, water (10 mL) was added, and the resulting mixture was extracted with Et_2O (2×15 mL), the layers were separated, and the organic layer was dried over $MgSO_4$, and concentrated in vacuo. Purification by flash column chromatography (SiO_2, toluene→toluene-EtOAc, 70:30) gave **9** (75 mg, 60%) as a pale yellow syrup: R_f = 0.45 (toluene/EtOAc, 9:1); $[\alpha]_D^{20}$ + 31.7 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.77 (m, 3H), 7.74 (d, *J* 8.4 Hz, 1H), 7.59–6.97 (m, 43H), 5.39 (s, 1H), 5.11 (d, *J* 10.1 Hz, 1H), 5.07–5.00 (m, 2H), 4.92–4.85 (m, 2H), 4.84–4.77 (m, 2H), 4.77–4.69 (m, 4H), 4.65–4.60 (m, 2H), 4.55–4.50 (m, 2H), 4.48–4.44 (m, 2H), 4.37 (d, *J* 7.5 Hz, 1H), 4.31–4.24 (m, 2H), 4.21 (s, 2H), 4.05 (dd, *J* 3.8 Hz, *J* 9.6 Hz, 1H), 3.94 (d, *J* 9.8 Hz, 1H), 3.88–3.74 (m, 4H), 3.67–3.53 (m, 4H), 3.43 (t, *J* 8.9 Hz, 1H), 3.33–3.29 (m, 1H), 2.92–2.87 (m, 1H), 2.65–2.54 (m, 2H), 1.25 ppm (t, *J* 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.1, 138.8, 138.8, 138.7, 138.5, 138.4, 138.3, 138.0, 136.2, 135.1, 133.4, 133.1, 129.3, 128.8, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.5, 127.5, 127.4, 126.8, 126.6, 125.9, 125.7, 103.5, 102.8, 84.2, 84.1, 82.5, 82.0, 81.1, 79.0, 78.5, 76.6, 76.3, 75.8, 75.6, 75.2, 75.2, 75.1, 74.9, 74.4, 73.0, 73.0, 72.0, 71.5, 68.9, 67.4, 63.7, 25.7, 15.1 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{86}H_{88}O_{15}NaS$: 1415.5742, found: 1415.5712.

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→4)]-6-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-α-D-mannopyranoside (11). A mixture of **10** (10 mg, 19.3 μmol), **9** (40 mg, 29 μmol), and crushed molecular sieves (4 Å, 20 mg) in dry Et_2O (2 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C, freshly prepared DMTST (15 mg, 60 μmol) was added, and the reaction mixture was stirred at 0 °C for 30 min. The progress of the reaction was carefully monitored by TLC (toluene/EtOAc, 9:1). The cooling bath was removed and stirring was continued at 20 °C for 1 h. Et_2O (5 mL) was added, and the reaction was quenched with Et_3N (50 μL) at 0 °C. The solids were removed by filtration through a pad of Celite, and the filtrate was concentrated in vacuo. Purification by flash column chromatography (SiO_2, toluene/EtOAc, 97:3→70:30) gave **11** (34 mg, 95%) as a colourless syrup: R_f = 0.56 (toluene/EtOAc, 9:1); $[\alpha]_D^{20}$ + 7.5 (*c* 1.0, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.77 (s, 1H), 7.72–7.63 (m, 3H), 7.53 (d, *J* 8.4, Hz, 1H), 7.41–6.98 (m, 57H), 5.20 (d, *J* 1.7 Hz, 1H), 5.08 (d, *J* 10.5 Hz, 1H), 5.05–4.99 (m, 2H), 4.86–4.76 (m, 4H), 4.76–4.34 (m, 16H), 4.30–4.15 (m, 4H), 4.11 (dd, *J* 9.5, 3.1 Hz, 1H), 4.06 (d, *J* 7.8 Hz, 1H), 4.01–3.89 (m, 3H), 3.90–3.39 (m, 15H), 3.34–3.26 (m, 3H), 3.22 (ddd, *J* 13.2, 6.1, 3.7 Hz, 1H), 2.93 ppm (dd, *J* 11.9, 9.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 168.2, 138.8, 138.8, 138.7, 138.7, 138.5, 138.4, 138.4, 138.4, 138.4, 138.4, 136.4, 135.2, 133.4, 133.0, 129.2, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.6, 127.6, 127.6, 127.5, 127.4, 127.3, 126.9, 126.8, 126.8, 125.9, 125.7, 103.7 (J_{C-H} 161 Hz), 103.2 (J_{C-H} 162.5 Hz), 99.7 (J_{C-H} 172 Hz), 98.0 (J_{C-H} 171.5 Hz), 84.2, 83.6, 82.6, 81.0, 78.8, 78.7, 78.5, 78.4, 75.7, 75.6, 75.6, 75.5, 75.0, 74.9, 74.8, 74.6, 74.6, 74.6, 74.1, 73.5, 73.2, 73.0, 72.8, 72.7, 72.4, 72.0, 69.1, 67.3, 66.7, 63.7, 50.5 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{113}H_{115}O_{21}N_3Na$: 1872.7921, found: 1872.7861.

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→4)]-6-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-α-D-mannopyranoside (12). DDQ (10 mg, 44 μmol) was added to a vigorously stirred solution of **11** (34 mg, 18 μmol) in CH_2Cl_2/*t*BuOH (4.4 mL, 10:1) at 20 °C. The progress of the reaction was monitored by TLC (toluene/EtOAc, 9:1). After 60 min, the reaction was quenched by adding satd. $NaHCO_3$ solution (15 mL). The resulting mixture was extracted once with CH_2Cl_2 (20 mL), the layers were separated, and the organic layer was washed with, 10% aq. $Na_2S_2O_3$ solution (1×15 mL), dried over $MgSO_4$, and concentrated in vacuo to a yellow oil. Purification by flash column chromatography (SiO_2, toluene→toluene/EtOAc, 97:3→70:30) gave **12** (23 mg,

74%) as a colourless syrup: R_f = 0.24 (toluene/EtOAc, 9:1); $[\alpha]_D^{20}$ + 10.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.51–6.92 (m, 55H), 5.22 (d, *J* 1.6 Hz, 1H), 5.11 (s, 2H), 5.03 (d, *J* 10.6 Hz, 1H), 4.85–4.76 (m, 4H), 4.74–4.70 (m, 2H), 4.69–4.56 (m, 8H), 4.52–4.48 (m, *2H*), 4.44 (d, *J* 10.6 Hz, 1H), 4.39 (d, *J* 11.0 Hz, 1H), 4.25 (d, *J* 7.8 Hz,1H), 4.18 (d, *J* 11.8 Hz, 1H), 4.15–4.11 (m, 2H), 4.06 (dt, *J* 9.2, 3.8 Hz, 1H), 4.04–4.00 (m, 2H), 3.99–3.88 (m, 5H), 3.83 (ddd, *J* 10.1, 6.0, 3.6 Hz, 1H), 3.76 (ddd, *J* 9.9, 4.9, 1.9 Hz, 1H), 3.74–3.68 (m, 2H), 3.68–3.59 (m, 5H), 3.53 (ddd, *J* 10.7, 7.0, 3.6 Hz, 1H), 3.47 (t, *J* 9.1 Hz, 1H), 3.44–3.40 (m, *2H*), 3.36–3.28 (m, 3H), 3.24 (ddd, *J* 13.2, 6.1, 3.7 Hz, 1H), 3.13 ppm (t, *J* 11.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 168.2, 138.7, 138.6, 138.6, 138.4, 138.4, 138.3, 138.3, 138.2, 138.2, 135.3, 129.0, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 127.4, 127.1, 126.8, 104.0, 103.1, 100.1, 97.9, 84.1, 83.5, 81.9, a80.9, 79.4, 79.0, 78.3 (2C), 78.0, 77.9, 75.8, 75.7, 75.2, 74.9, 74.8, 74.8, 74.5, 74.4, 73.5, 73.5, 73.1, 72.6, 72.5, 72.0, 69.1, 68.9, 68.5, 67.3, 66.8, 64.3, 50.5 ppm. HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{102}H_{107}O_{21}N_3Na$: 1732.7205, found: 1732.7264.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranosyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)][2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→4)]-6-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-α-D-mannopyranoside (14). A mixture of **12** (22 mg, 13 μmol), **13**[9] (18 mg, 20 μmol), and crushed molecular sieves (4 Å, 20 mg) in dry Et_2O (3 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C, freshly prepared DMTST (14 mg, 56 μmol) was added, and the reaction mixture was stirred at 0 °C for 30 min. The progress of the reaction was carefully monitored by TLC (toluene/EtOAc, 9:1). The cooling bath was removed, and stirring was continued at 20 °C for 1 h. Et_2O (6 mL) was added and the reaction was quenched with Et_3N (40 μL, 0.20 mmol) at 0 °C. The solids were removed by filtration through a pad of Celite, and the filtrate was concentrated in vacuo. Purification by flash column chromatography (SiO_2, toluene→toluene/EtOAc, 95:5→60:40) gave **14** (26 mg, 79%) as a colourless syrup: R_f = 0.47 (toluene/EtOAc, 9:1); $[\alpha]_D^{20}$ −4.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.95 (s, 1H), 7.82–7.74 (m, 3H), 7.64 (dd, *J* 8.3, 1.5 Hz, 1H), 7.48 −6.91 (m, 78H), 5.64 (d, *J* 1.4 Hz, 1H), 5.25 (s, 1H), 5.13 (d, *J* 10.4 Hz, 1H), 5.08 (m, 2H), 4.99 (m, 2H), 4.87 (d, *J* 10.9 Hz, 1H), 4.85–4.72 (m, 5H), 4.72–4.44 (m, 18H), 4.41–4.34 (m, 4H), 4.33–4.20 (m, 6H), 4.20–4.15 (m, 2H), 4.13–4.08 (m, 1H), 4.06 (d, *J* 7.5 Hz, 1H), 4.03–3.81 (m, 10H), 3.78–3.71 (m, 2H), 3.71–3.60 (m, 6H), 3.59–3.53 (m, 2H), 3.49 (t, *J* 8.5 Hz, 1H), 3.43–3.33 (m, 3H), 3.28–3.24 (m, 2H), 3.24–3.15 (m, 2H), 2.96 (t, *J* 11.3 Hz, 1H), 1.63 ppm (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 170.9, 168.2, 139.0, 138.9, 138.8, 138.8, 138.8, 138.7, 138.6, 138.6, 138.4, 138.2, 138.2 (3C), 138.1, 136.7, 135.5, 133.5, 133.1, 129.2, 128.8, 128.8, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 127.9, 127.9, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.4, 127.3, 127.3, 127.1, 127.1, 126.7, 125.9, 125.8, 104.3 (J_{C-H} 161 Hz), 103.7 (J_{C-H} 162 Hz), 102.9 (J_{C-H} 159.5 Hz), 100.1 (J_{C-H} 171.6 Hz), 99.6 (J_{C-H} 176.4 Hz), 98.0 (J_{C-H} 169.8 Hz), 84.1, 84.0, 83.5, 82.6, 81.1, 81.0, 79.5, 79.2, 79.2, 79.1, 79.0, 78.4, 78.0, 75.7, 75.6, 75.5, 75.5, 75.4, 75.0, 75.0, 74.9, 74.7, 74.7, 74.6, 74.5, 74.4, 74.3, 73.7, 73.6, 73.3, 73.1, 73.0, 72.5, 72.5, 72.0, 71.7, 70.6, 69.1, 68.2, 67.2, 66.9, 64.3, 64.1, 64.0, 50.5, 20.8 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{154}H_{159}O_{31}N_3Na$: 2569.0855, found: 2569.0840.

2-Aminoethyl β-D-xylopyranosyl-(1→2)-6-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[β-D-glucopyranosyluronate-(1→2)][β-D-xylopyranosyl-(1→4)]-α-D-mannopyranosyl-(1→3)-α-D mannopyranoside (15). 10% w Pd/C (17 mg, 16.1 mmol) was added to a solution of compound **14** (26 mg, 12.4 mmol) in AcOEt/H_2O/AcOH (4:2:1, 1.75 mL). The mixture was hydrogenolysed in a high-pressure reactor (Berghof, Eningen, Germany) at 20 °C (*p* = 30 bar). After 48 h, the solids were removed by filtration using a 'sandwich filter' (3 frits stacked on top of each other in the following order: 20 μm, 10 μm, 5 μm), rinsed with H_2O (3×2 mL) and EtOH (3×2 mL), and the filtrate was concentrated in vacuo. Purification by reversed-phase chromatography (C-18, H_2O/MeOH, 9:1→8:2→7:3→6:4→2:8→0:10), followed by freeze-drying gave **15** (7.0 mg, 67%) as a colourless, amorphous solid; $[\alpha]_D^{20}$ + 6.0 (*c* 0.40, H_2O); ^{1}H NMR (500 MHz, D_2O): δ = 5.25 (s, 1H), 5.17 (s, 1H), 4.90 (s, 1H), 4.47 (d, *J* 7.8 Hz, 1H), 4.40 (d, *J* 7.8 Hz, 1H), 4.37–4.33 (m, 2H), 4.31 (d, *J* 7.8 Hz, 1H), 4.26–4.12 (m, 5H), 4.11–3.86 (m, 10H), 3.84–3.57 (m, 10H), 3.54–3.20 (m, 9H), 2.17 ppm (s, 3H); ^{13}C anomeric signals taken from Heteronuclear Single Quantum Coherence (HSQC) spectroscopy: 103.7, 102.8, 101.7, 100.9, 99.8, 99.6 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{38}H_{63}O_{31}NNa$: 1052.3282, found: 1052.3330.

2-Azidoethyl 4,6-*O*-benzylidene-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (17). A solution **16** (10.0 g, 29.6 mmol) and dibutyltin oxide (9.96 g, 40.0 mmol) in anhydrous toluene (320 mL) was heated at reflux with continuous removal of water (Dean–Stark trap). After 3 h, the mixture was concentrated to half volume, tetrabutylammonium iodide (14.8 g, 40.0 mmol) and 2-(bromomethyl)naphthalene (7.21 g, 32.6 mmol) were added, and the reaction mixture was brought to reflux for another 3 h. To the reaction mixture, EtOAc (400 mL) was added, and the organic layer was then washed sequentially with water (3×200 mL), 10% aq. KF-solution (3×200 mL), and brine (2×200 mL), dried over $MgSO_4$, and concentrated in vacuo to a yellow oily residue. Purification by flash column chromatography (SiO_2, pentane→pentane/Et_2O, 50:50→35:65→25:75→15:85) gave **17** (12.5 g, 88%) as a pale yellow syrup: R_f = 0.33 (toluene/EtOAc, 3:1); $[\alpha]_D^{20}$ + 28.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85–7.36 (m, 12H), 5.63 (s, 1H), 4.99 (d, *J* 12.0 Hz, 1H), 4.91 (d, *J* 1.5 Hz,1H), 4.90 (d, *J* 12.0 Hz, 1H), 4.30–4.24 (m, 1H, H-6a), 4.16–4.12 (m, 2H), 3.99 (dd, *J* 3.0 Hz, *J* 9.0 Hz, 1H), 3.89–3.83 (m, 3H), 3.60 (ddd, *J* 3.7 Hz, *J* 6.8 Hz, *J* 10.6 Hz, 1H), 3.42–3.32 (m, 2H,), 2.74 ppm (d, *J* 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.7, 135.5, 133.4, 133.2, 129.1, 128.4, 128.4, 128.1, 127.8, 126.8, 126.3, 126.3, 126.1, 125.9, 101.9, 100.4, 78.8, 75.6, 73.2, 69.9, 69.0, 66.9, 63.9, 50.5 ppm; HRMS (ESI): $[M+H]^+$ *m/z* calcd for $C_{26}H_{28}N_3O_6$: 478.1978, found: 478.1972.

2-Azidoethyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (18). A catalytic amount of TBDMSOTf (335 μL, 1.46 mmol) was added to a solution of **3**[16] (8.89 g, 14.66 mmol) and **17** (7.00 g, 14.66 mmol) in dry CH_2Cl_2 (125 mL) containing crushed molecular sieves (AW-300, 180 mg) kept at −78 °C in an atmosphere of nitrogen. The temperature was then allowed to rise to 20 °C overnight (TLC, toluene/EtOAc, 6:1). The reaction mixture was neutralised with Et_3N (1.23 mL, 8.79 mmol), the solids were removed by filtration, and the filtrate was concentrated in vacuo to a yellowish foam. Purification by flash column chromatography (SiO_2, toluene→toluene/EtOAc, 98:2→96:4→94:6→92:8→90:10→88:12→86:14) gave **18** (11.70 g, 86%) as a colourless, amorphous solid: R_f = 0.42 (toluene/EtOAc, 9:1); $[\alpha]_D^{20}$ −48.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.23–8.22 (m, 2H), 8.08–8.07 (m, 2H), 7.97–7.95 (m, 2H), 7.87 (m, 1H), 7.81–7.78 (m, 2H), 7.71–7.69 (m, 1H), 7.58–7.36 (m, 15H), 7.27–7.24 (m, 2H), 5.61 (t, *J* 4.2 Hz, 1H), 5.35–5.32 (m, 1H), 5.15 (d, *J* 3.0 Hz, 1H), 5.11 (s, 1H), 5.10 (d, *J* 2.4 Hz,

1H), 5.06–4.98 (ABq, 2H), 4.95 (dd, *J* 13.0 Hz, *J* 1.6 Hz, 1H), 4.87 (d, *J* 1.6 Hz, 1H), 4.30 (dd, *J* 3.4 Hz, *J* 1.6 Hz 1H), 4.10–4.05 (m, 2H), 3.99 (t, *J* 9.5 Hz, 1H), 3.82–3.76 (m, 2H), 3.75–3.70 (m, 1H), 3.55–3.50 (m, 1H), 3.48 (t, 1H, *J* 10.5 Hz), 3.37–2.27 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.8, 165.5, 165.1, 137.9, 136.1, 133.7, 133.6, 133.2, 130.6, 130.3, 130.2, 129.8, 129.6, 129.5, 129.2, 128.7, 128.6, 128.5, 128.3, 128.2, 127.9, 126.5, 126.4, 126.3, 126.0, 125.9, 101.7, 98.4, 96.8, 78.7, 75.0, 74.7, 73.3, 68.9, 68.5, 68.1, 67.5, 67.0, 64.7, 59.6, 50.6 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{52}H_{47}N_3O_{13}Na$: 944.3007, found: 944.2960.

2-Azidoethyl β-D-xylopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (19). A catalytic amount of sodium methoxide (68 mg, 1.27 mmol) was added to a solution of **18** (11.70 g, 12.69 mmol) in dry MeOH (250 mL). The mixture was swirled at 20 °C overnight (TLC, CH_2Cl_2/MeOH, 9:1). After complete conversion, Dowex (H^+) acidic ion exchange resin was added for neutralisation, the resin was filtered off, washed with MeOH (50 mL), and the filtrate was concentrated in vacuo. Purification by flash column chromatography (SiO_2, DCM→DCM/MeOH, 99:1→98:2→97:3→96:4→95:5) gave **19** (11.70 g, 86%) as a colourless, amorphous solid: R_f = 0.39 (DCM/MeOH, 9:1); $[\alpha]_D^{20}$ −1.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82–7.78 (m, 3H), 7.75–7.73 (m, 1H), 7.52–7.44 (m, 5H), 7.40–7.36 (m, 3H), 5.66 (s, 1H), 5.05 (d, *J* 11.7 Hz, 1H,), 4.88 (d, *J* 11.7 Hz, 1H,), 4.85 (d, *J* 1.5 Hz, 1H,), 4.53 (d, *J* 7.0 Hz, 1H,), 4.27–4.35 (m, 1H), 4.21–4.17 (m, 2H), 4.08 (dd, *J* 3.0 Hz, *J* 9.0 Hz, 1H,), 4.05–4.02 (m, 2H), 3.89–3.81 (m, 3H), 3.64–3.58 (m, 2H), 3.49–3.46 (m, 2H), 3.37 (m, 2H), 3.26 (dd, *J* 9.5 Hz. *J* 11.5 Hz, 1H,), 3.14 (s br, 1H), 2.67 ppm (s br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.4, 134.6, 133.2, 133.1, 129.0, 128.3, 128.0, 127.7, 127.4, 126.1, 101.7, 101.3, 100.0, 79.3, 74.8, 74.5, 74.5, 71.6, 69.8, 69.5, 68.7, 66.7, 65.3, 64.1, 50.4 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{31}H_{35}N_3O_{10}Na$: 632.2220, found: 632.2195.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (20). NaH (3.81 g, 95.61 mmol, 60% oil dispersion) was washed with pentane (3×100 mL) prior to use. NaH was added portionwise to a solution of **19** (12.96 g, 21.24 mmol) in dry DMF (200 mL) kept at 0 °C under an atmosphere of nitrogen. After 15 min, benzyl bromide (10.09 mL, 84.96 mmol) was added dropwise at 0 °C under vigorous stirring. The temperature was then allowed to rise to 20 °C over 3 h (TLC, toluene/EtOAc, 6:1). After complete consumption of the starting material, residual NaH was quenched with MeOH, and then with H_2O (300 mL). The resulting mixture was extracted once with EtOAc (600 mL), the layers were separated, and the organic layer was washed with brine (1× 400 mL), dried over $MgSO_4$, and concentrated in vacuo. Purification by flash column chromatography (SiO_2, toluene→toluene/EtOAc, 98:2→96:4→94:6→92:8→90:10→88:12) gave **20** (16.87 g, 90%) as a colourless syrup: R_f = 0.55 (toluene/EtOAc, 6:1); $[\alpha]_D^{20}$ −8.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86 (m, 1H), 7.81–7.79 (m, 1H), 7.76–7.74 (m, 1H), 7.68–7.66 (m, 1H), 7.52–7.48 (m, 3H),7.44–7.42 (m, 2H), 7.39–7.27 (m, 18H), 5.61 (s, 1H), 4.98 (d, *J* 10.5 Hz, 1H), 4.95 (d, *J* 1.6 Hz, 1H),4.91–4.85 (m, 4H), 4.73–4.69 (m, 2H), 4.61 (d, *J* 11.6 Hz, 1H), 4.45 (d, *J* 7.2 Hz, 1H), 4.28 (m, 1H), 4.21–4.17 (m, 2H), 4.03–3.99 (m, 2H), 3.86–3.78 (m, 3H), 3.66 (ddd, *J* 5.2 Hz, *J* 8.3 Hz, *J* 9.5 Hz, 1H), 3.59 (t, *J* 8.8 Hz, 1H), 3.56–3.49 (m, 2H), 3.35 (ddd, *J* 3.5 Hz, *J* 7.1 Hz, *J* 13.3 Hz, 1H,), 3.30–3.23 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.7, 138.3, 138.1, 137.6, 136.0, 133.3, 132.9, 128.8, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 126.3, 126.1, 125.8, 125.6, 103.9, 101.6, 99.1, 83.8, 81.5, 78.4, 77.8, 76.2, 75.5, 75.1, 74.2, 73.3, 71.9, 68.9, 66.7, 64.6, 64.1, 50.3 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{52}H_{53}N_3O_{10}Na$: 902.3629, found: 902.3613.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (21). A 1 M solution of BH_3 in THF (23.6 mL, 23.6 mmol) was added to a solution of **20** (2.08 g, 2.36 mmol) in dry CH_3CN (40 mL) kept at 0 °C under an atmosphere of nitrogen. After 5 min, a 1 M solution of Bu_2BOTf (2.36 mL, 2.36 mmol) was added dropwise at 0 °C, and the reaction mixture was stirred for 90 min (TLC, toluene-EtOAc, 6:1). After complete consumption of the starting material, the reaction was quenched with Et_3N (10 mL), followed by dropwise addition of MeOH (10 mL) at 0 °C. The mixture was concentrated in vacuo, and the residue was redissolved and co-evaporated with MeOH (3×50 mL). The syrupy residue was redissolved in MeOH, the solids were removed by filtration through a short pad of Celite, and the filtrate was concentrated in vacuo. Purification by flash column chromatography (SiO_2, toluene→toluene/EtOAc, 97:3→94:6→91:9→88:12→85:15→82:18→79:21) gave **21** (1.59 g, 76%) as a colourless syrup: R_f = 0.16 (toluene/EtOAc, 6:1); $[\alpha]_D^{20}$ +6.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81–7.80 (m, 2H), 7.76–7.74 (m, 1H), 7.71–7.69 (m, 1H), 7.52–7.50 (m, 1H), 7.47–7.43 (m, 2H), 7.37–7.26 (m, 20H), 5.01–4.98 (m, 2H), 4.94–4.92 (m, 2H), 4.86 (ABq, *J* 12.0 Hz, 2H), 4.76–4.70 (m, 3H), 4.62–4.59 (m, 2H), 4.42 (d, *J* 7.5 Hz, 1H), 4.16 (m, 1H), 4.00–3.97 (m, 2H), 3.90 (t, *J* 9.5 Hz, 1H), 3.82–3.76 (m, 2H), 3.72–3.63 (m, 3H), 3.58 (t, *J* 8.8 Hz, 1H), 3.54–3.49 (m, 2H), 3.36–3.32 (ddd, 1H), 3.29–3.21 (m, 2H), 1.62 ppm (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.7, 138.6, 138.4, 138.1, 135.6, 133.3, 133.1, 128.5, 128.38, 128.37, 128.3, 127.99, 127.97, 127.94, 127.92, 127.89, 127.87, 127.8, 127.7, 127.6, 127.5, 127.1, 126.5, 125.9, 125.8, 103.8, 98.2, 83.9, 81.2, 78.1, 77.5, 75.5, 75.2, 74.8 (2C), 74.79, 74.4, 73.4, 72.4, 71.5, 66.6, 64.2, 62.5, 50.4 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{52}H_{55}N_3O_{10}Na$: 904.3785, found: 904.3763.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (22). Acetic anhydride (2.44 mL, 25.76 mmol) was added to a solution of **21** (2.84 g, 1.47 mmol) in dry pyridine (50 mL) at 20 °C, and the mixture was stirred for 3 h (TLC, toluene/EtOAc, 9:1). The reaction mixture was concentrated in vacuo, and then redissolved and co-evaporated with toluene (3×100 mL). Purification by flash column chromatography (SiO_2, toluene→toluene/EtOAc, 97:3→94:6→91:9→88:12→85:15) gave **22** (2.76 g, 93%) as a colourless syrup: R_f = 0.25 (toluene/EtOAc, 9:1); $[\alpha]_D^{20}$ +11.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83–7.80 (m, 2H), 7.76 (m, 1H), 7.72–7.69 (m, 1H), 7.52 (m, 1H), 7.48–7.44 (m, 2H), 7.39–7.25 (m, 20H), 5.06 (d, *J* 10.0 Hz, 1H), 4.99 (d, *J* 11.5 Hz, 1H), 4.95–4.93 (m, 2H), 4.90–4.84 (m, 2H), 4.75–4.72 (m, 2H), 4.63–4.61 (m, 2H), 4.56 (d, *J* 11.0 Hz, 1H), 4.40 (d, *J* 7.0 Hz, 1H), 4.35–4.29 (m, 2H), 4.16 (m, 1H), 4.02–3.98 (m, 2H), 3.95 (t, *J* 9.5 Hz), 3.84–3.80 (m, 2H), 3.70–3.65 (m, 1H), 3.58–3.51 (m, 3H), 3.35 (ddd, *J* 3.5 Hz, *J* 7.1 Hz, *J* 13.3 Hz, 1H), 3.28 (ddd, *J* 3.0 Hz, *J* 6.0 Hz, *J* 9.8 Hz, 1H), 3.24 (t, *J* 11.0 Hz, 1H), 1.75 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 138.8, 138.2, 138.1, 135.5, 133.3, 133.1, 128.8–125.8, 104.1, 98.2, 83.9, 81.4, 78.2, 77.4, 75.6, 75.2, 75.1, 75.0, 73.8, 73.4, 71.5, 70.2, 66.6, 64.2, 63.3, 50.4, 20.5 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{54}H_{57}N_3O_{11}Na$: 946.3891, found: 946.3876.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4,6-di-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (23). NaH (155 mg, 3.88 mmol, 60% oil dispersion) was washed with pentane (3×10 mL) prior to use. NaH was added portionwise to a solution of **21** (0.98 g, 1.11 mmol) in dry DMF (40 mL)

kept at 0 °C under an atmosphere of nitrogen. After 15 min, benzyl bromide (395 μL, 3.33 mmol) was added dropwise at 0 °C under vigorous stirring. The temperature was then allowed to rise to 20 °C over 2 h (TLC, toluene/EtOAc, 6:1). After complete consumption of the starting material, residual NaH was quenched with MeOH (2 mL), and then with H_2O (80 mL). The resulting mixture was extracted once with EtOAc (160 mL), the layers were separated, and the organic layer was washed with brine (1×100 mL), dried over $MgSO_4$ and concentrated in vacuo. Purification by flash column chromatography (SiO_2, toluene→toluene/EtOAc, 98:2→96:4→94:6→92:8→90:10) gave **23** (1.03 g, 95%) as a colourless syrup: R_f = 0.38 (toluene/EtOAc, 9:1); $[\alpha]_D^{20}$ + 7.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82–7.80 (m, 2H, H), 7.75–7.73 (m, 1H), 7.70–7.68 (m, 1H), 7.52–7.50 (m, 1H), 7.47–7.15 (m, 27H), 5.06 (d, *J* 10.5 Hz, 1H), 4.95–4.92 (m, 3H), 4.90–4.82 (ABq, 2H), 4.75–4.71 (m, 2H), 4.61 (d, *J* 10.5 Hz, 1H), 4.55–4.52 (m, 2H), 4.42–4.40 (m, 3H), 4.15 (s, 1H), 4.03–3.96 (m, 3H), 3.84 (ddd, *J* 3.5 Hz, *J* 5.8 Hz, *J* 10.7 Hz, 1H), 3.81–3.77 (m, 1H), 3.75–3.64 (m, 3H), 3.57–3.49 (m, 3H), 3.35 (ddd, *J* 3.5 Hz, *J* 7.2 Hz, *J* 13.3 Hz, 1H), 3.29–3.21 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.9, 138.6, 138.6, 138.3, 138.2, 135.7, 133.3, 133.1, 128.9, 128.5, 128.3, 128.2, 128.2, 128.0, 127.95, 127.92, 127.87, 127.64, 127.60, 127.54, 127.51, 127.47, 127.4, 127.1, 126.5, 125.9, 125.7, 104.1, 98.2, 84.0, 81.2, 78.3, 77.4, 75.5, 75.2 (2C), 75.0, 74.4, 73.4, 73.3, 72.1, 71.6, 69.5, 66.5, 64.2, 50.4 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{59}H_{61}N_3O_{10}Na$,: 994.4255, found: 994.4252.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (24). DDQ (393 mg, 1.73 mmol) was added to a vigorously stirred solution of **23** (1.00 g, 1.08 mmol) in CH_2Cl_2/H_2O (44 mL, 10:1) at 20 °C. Additional amounts of DDQ (295 mg, 1.30 mmol) were added after 20 min. More DDQ (295 mg, 1.30 mmol) was added after 40 min. The progress of the reaction was carefully monitored by TLC (toluene/EtOAc, 6:1). After 60 min, the reaction was quenched by adding 10% aq. $Na_2S_2O_3$ solution (200 mL). The resulting mixture was extracted once with CH_2Cl_2 (200 mL), the layers were separated, and the organic layer was washed sequentially with sat. $NaHCO_3$ solution (3×150 mL), and brine (1×150 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (SiO_2, toluene→toluene/EtOAc, 96:4→93:7→90:10→87:13→84:16→80:20). The first fraction to appear in the eluate contained recovered starting material (51 mg). Solvent removal of the second and main fraction gave **24** (624 mg, 73%) as a colourless syrup: R_f = 0.26 (toluene/EtOAc, 6:1); $[\alpha]_D^{20}$ + 42.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.24 (m, 20H), 4.99 (d, *J* 11.0 Hz, 1H), 4.93–4.86 (m, 3H), 4.74–4.69 (m, 3H), 4.64–4.61 (m, 2H), 4.37 (dd, *J* 2.0 Hz, *J* 12.0 Hz, 1H), 4.34 (d, *J* 8.0 Hz, 1H), 4.27 (dd, *J* 4.5 Hz, *J* 12.0 Hz, 1H), 4.03 (td, *J* 3.4 Hz, *J* 9.2 Hz, 1H), 3.97–3.91 (m, 2H), 3.84–3.78 (m, 2H), 3.66–3.50 (m, 4H), 3.42–3.36 (m, 2H), 3.34–3.28 (m, 1H), 3.23 (dd, *J* 11.7 Hz, *J* 10.3 Hz, 1H,), 3.17 (d, *J* 9.5 Hz, 1H), 1.87 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.7, 138.6, 138.3, 138.0, 137.9, 128.6–127.7, 104.4, 98.4, 83.8, 81.5, 80.7, 77.6, 76.3, 75.9, 75.4, 75.0, 73.7, 71.0, 70.0, 66.7, 64.4, 63.6, 50.4, 20.7 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{43}H_{49}N_3O_{11}Na$: 806.3265, found: 806.3230; Anal. calcd for $C_{43}H_{49}N_3O_{11}$: C 65.89, H 6.30, N 5.36, found: C 65.70, H 6.27, N 5.31.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4,6-di-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (26). A mixture of **24** (66 mg, 84.2 μmol), **25**[9] (119 mg, 125.6 μmol), and crushed molecular sieves (4 Å, 20 mg) in dry Et_2O (6 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C, freshly prepared DMTST (64 mg, 248 μmol) was added, and the reaction mixture was stirred at 0 °C for 30 min. The progress of the reaction was carefully monitored by TLC (toluene/EtOAc, 9:1). The cooling bath was removed, and stirring was continued at 20 °C for 3 h. Et_2O (8 mL) was added and the reaction was quenched with Et_3N (200 μL) at 0 °C. The solids were removed by filtration through a pad of Celite, and the filtrate was concentrated in vacuo. Purification by flash column chromatography (SiO_2, toluene/EtOAc, 95:5→7:3) gave **26** (119 mg, 85%) as a colourless syrup: R_f = 0.66 (toluene/EtOAc, 9:1); $[\alpha]_D^{20}$ + 3.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80 (m, 1H), 7.76–7.74 (m, 1H), 7.70–7.67 (m, 2H), 7.50–7.48 (m, 1H), 7.42–7.14 (m, 47H), 5.19 (s, 1H), 5.06 (d, *J* 11.0 Hz, 1H), 5.01 (d, *J* 12.0 Hz, 1H), 4.97 (d, *J* 10.5 Hz, 1H), 4.86–4.76 (m, 7H), 4.69 (d, *J* 12.0 Hz, 1H), 4.64 (d, *J* 10.0 Hz, 1H), 4.58–4.55 (m, 3H), 4.49 (d, *J* 11.0 Hz, 1H), 4.45 (d, *J* 12.0 Hz, 1H), 4.39 (d, *J* 12.0 Hz, 2H), 4.34–4.20 (m, 6H), 4.12–4.08 (m, 3H), 3.98–3.93 (m, 4H), 3.84–3.68 (m, 6H), 3.58–3.53 (m, 1H), 3.50–3.36 (m, 5H), 3.33–3.25 (m, 2H), 3.22–3.17 (m, 1H), 3.06 (t, *J* 10.8 Hz, 1H), 2.77 (t, *J* 10.8 Hz, 1H), 1.84 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 139.3, 138.95, 138.9, 138.86, 138.6, 138.5, 138.4, 138.1, 138.0, 136.0, 133.3, 133.0, 128.9, 128.7, 128.6, 128.44, 128.37, 128.35, 128.33, 128.30, 128.28, 128.2, 128.1, 128.0, 127.90, 127.88, 127.85, 127.81, 127.79, 127.77, 127.75, 127.70, 127.6, 127.49, 127.47, 127.45, 127.42, 127.35, 127.1, 126.8, 126.6, 126.0, 125.8, 104.3, 103.7, 100.3 ($J_{C-1,H-1}$ 170 Hz), 98.4 ($J_{C-1,H-1}$ 175 Hz), 83.8, 83.4, 81.6, 81.0, 78.5 (2C), 77.7, 77.4, 77.1, 75.8, 75.6, 75.3, 75.12, 75.09, 74.9, 74.7, 74.4, 73.4, 73.2, 72.5 (2C), 72.2, 70.3, 69.9, 66.6, 63.9, 63.5, 63.2, 50.3, 20.7 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{100}H_{105}N_3O_{20}Na$: 1690.7189, found: 1690.7153; Anal. calcd for $C_{100}H_{105}N_3O_{20}$: C 71.97, H 6.34, N 2.52, found: C 71.99, H 6.32, N 2.54.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (27). DDQ (22 mg, 99 μmol) was added to a vigorously stirred mixture of compound **26** (104 mg, 62 μmol) in CH_2Cl_2/H_2O (11 mL, 10:1) at 20 °C. Additional amounts of DDQ (17 mg, 75 μmol) were added after 20 min. More DDQ (17 mg, 75 μmol) was added after 40 min. The progress of the reaction was carefully monitored by TLC (toluene/EtOAc, 6:1). After 60 min, the reaction was quenched by adding 10% aq. $Na_2S_2O_3$ solution (20 mL). The resulting mixture was extracted once with CH_2Cl_2 (50 mL), the layers were separated, and the organic layer was washed sequentially with sat. $NaHCO_3$ solution (3×30 mL), and brine (1×30 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (SiO_2, toluene→toluene/EtOAc, 96:4→93:7→90:10 →87:13→84:16→81:19→78:22). The first fraction to appear in the eluate contained recovered starting material (13 mg). Solvent removal of the second and main fraction gave **27** (76 mg, 80%) as a colourless foam: R_f = 0.25 (toluene/EtOAc, 6:1); $[\alpha]_D^{20}$ + 13.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38–7.13 (m, 45H), 5.19 (s, 1H), 4.99–4.94 (m, 2H), 4.94 (d, *J* 11.0 Hz, 1H), 4.88–4.80 (m, 6H), 4.69 (d, *J* 11.5 Hz, 1H), 4.66–4.57 (m, 5H), 4.51 (s, 2H), 4.36–4.24 (m, 6H), 4.13–4.06 (m, 3H), 3.99 (dd, *J* 5.5 Hz, *J* 12.0 Hz, 1H), 3.90 (t, *J* 9.5 Hz, 1H), 3.85–3.83 (m, 2H), 3.80–3.68 (m, 5H), 3.60 (t, *J* 9.3 Hz, 1H), 3.57–3.49 (m, 2H), 3.46 (t, *J* 9.3 Hz, 1H), 3.44–3.39 (m, 2H), 3.36 (t, *J* 9.0 Hz, 1H), 3.30–3.26 (m, 2H), 3.24–3.19 (m, 1H), 3.07–3.03 (m, 2H), 2.85 (t, *J* 11.3 Hz, 1H), 1.84 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 139.2, 138.8, 138.7, 138.4, 138.3, 138.20, 138.16, 138.0, 128.7, 128.64, 128.58, 128.4, 128.29, 128.28, 128.23, 128.20, 127.95, 127.85, 127.83, 127.79, 127.77, 127.74, 127.71, 127.64 127.56, 127.54, 127.50, 127.46, 127.44,

127.36, 126.7, 104.4, 104.0, 100.9, 98.3, 83.8, 83.2, 81.4, 80.8, 80.7, 78.8, 77.7, 77.3, 77.1, 75.5, 75.5, 75.1, 74.7, 74.7, 74.6, 74.4, 73.4, 73.3, 72.6, 71.9, 70.8, 70.4, 69.8, 66.5, 63.9, 63.5, 63.1, 50.3, 20.6 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{89}H_{97}N_3O_{20}Na$: 1550.6563, found: 1550.6541.

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→4)]-6-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (28). A mixture of **27** (31 mg, 20.3 μmol), **9** (41 mg, 29.4 μmol), and crushed molecular sieves (4 Å, 20 mg) in dry Et_2O (3 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C, freshly prepared DMTST (22 mg, 88 μmol) was added, and the reaction mixture was stirred at 0 °C for 30 min. The progress of the reaction was carefully monitored by TLC (toluene/EtOAc, 9:1). The cooling bath was removed, and stirring was continued at 20 °C for 3 h. Et_2O (8 mL) was added and the reaction was quenched with Et_3N (200 μL) at 0 °C. The solids were removed by filtration through a pad of Celite, and the filtrate was concentrated in vacuo. Purification by flash column chromatography (SiO_2, toluene/EtOAc, 98:2→80:20) gave **28** (48 mg, 83%) as a colourless syrup: R_f = 0.44 (toluene/EtOAc, 9:1); $[\alpha]_D^{20}$ −18.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82–7.78 (m, 2H), 7.71 (d, *J* 8.1 Hz, 1H), 7.67 (d, *J* 8.4 Hz, 1H), 7.51 (d, *J* 8.4 Hz, 1H), 7.45–6.99 (m, 87H), 5.25 (s, 1H), 5.16 (s, 1H), 5.08–4.90 (m, 5H), 4.86–4.70 (m, 8H), 4.69–5.58 (m, 7H), 4.57–4.39 (m, 9H), 4.38–4.27 (m, 7H), 4.27–4.14 (m, 8H), 4.14–3.98 (m, 8H), 3.88 (d, *J* 3.1 Hz, 1H), 3.84 (d, *J* 7.7 Hz, 1H), 3.83–3.58 (m, 9H), 3.58–3.34 (m, 11H), 3.32–3.14 (m, 4H), 3.13–3.04 (m, 2H), 2.95–2.83 (m, 2H), 1.78 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.8, 168.1, 139.0, 139.0, 138.9, 138.9, 138.8, 138.7, 138.7, 138.7, 138.6, 138.6, 138.6, 138.5, 138.4, 138.3, 138.2, 138.1, 136.3, 135.2, 133.3, 133.0, 129.2, 128.8, 128.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 1278.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.5, 127.5, 127.5, 127.4, 127.4, 127.4, 127.4, 127.3, 127.2, 127.2, 126.0, 125.9, 125.8, 104.5 (J_{C-H} 160 Hz), 103.8 (J_{C-H} 161.5 Hz), 103.6 (J_{C-H} 163.5 Hz), 102.8 (J_{C-H} 162.5 Hz), 101.3 (J_{C-H} 172.5 Hz), 99.4 (J_{C-H} 170 Hz), 98.4 (J_{C-H} 171.5 Hz), 84.4, 84.0, 83.4, 83.4, 82.6, 81.7, 81.5, 80.9, 79.5, 79.1, 78.8, 78.8, 78.6, 78.5, 78.2, 76.3 (2C), 75.6 (2C), 75.5 (2C), 75.3 (3C), 75.0 (2C), 74.8, 74.6, 74.5 (2C), 74.3, 73.7 (2C), 73.6, 73.2, 73.1, 72.8, 72.8, 72.6, 72.4, 71.9, 70.5, 69.7 (2C), 67.2, 66.6, 63.7, 63.6, 63.5, 63.4, 50.4, 20.7 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{173}H_{179}N_3O_{35}Na$: 2881.2217, found: 2881.2205.

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→4)]-6-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (29). DDQ (7.2 mg, 32 μmol) was added to a vigorously stirred solution of **27** (45 mg, 15.7 μmol) in CH_2Cl_2/*t*BuOH (1.6 mL, 10:1) at 20 °C. The progress of the reaction was monitored by TLC (toluene/EtOAc, 9:1). After 60 min, the reaction was quenched by adding satd. $NaHCO_3$ solution (6 mL). The resulting mixture was extracted once with CH_2Cl_2 (10 mL), the layers were separated, and the organic layer was washed with 10% aq. $Na_2S_2O_3$ solution (6 mL), dried over $MgSO_4$, and concentrated in vacuo to a yellow oil. Purification by flash column chromatography (SiO_2, toluene/EtOAc, 94:6→70:30) gave **29** (42.8 mg, 68%) as a colourless syrup: R_f = 0.40 (toluene/EtOAc, 9:1); $[\alpha]_D^{20}$ −9.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57–6.86 (m, 85H), 5.33 (s, 1H), 5.16 (s, 1H), 5.14–5.06 (m, 2H), 5.05–4.98 (m, 3H), 4.88–4.78 (m, 6H), 4.76–4.54 (m, 13H), 4.53–4.40 (m, 6H), 4.38–4.18 (m, 9H), 4.17–3.89 (m, 15H), 3.85–3.75 (m, 2H), 3.75–3.34 (m, 17H), 3.33–3.27 (m, 2H), 3.22 (ddd, *J* 13.1, 6.4, 3.8 Hz, 1H), 3.17–3.04 (m, 4H), 2.93 (dd, *J* 11.6, 9.3 Hz, 1H), 1.79 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.8, 168.1, 139.0, 139.0, 138.9, 138.8, 138.7, 138.6, 138.6, 138.6, 138.5, 138.5, 138.5, 138.3, 138.3, 138.2, 138.2, 138.0, 135.4, 129.2, 128.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.5, 127.4, 125.9, 104.5, 104.0, 103.4, 102.7, 101.2, 99.9, 98.3, 84.3, 84.0, 83.4 (2C), 82.0, 81.7, 81.3, 80.5, 79.8, 79.0, 78.9, 78.6, 78.4, 78.2, 78.1, 77.9, 77.9, 77.4, 75.6, 75.6, 75.5, 75.4 (2C), 75.3, 75.2, 74.9, 74.8, 74.6, 74.5, 74.2, 74.0, 73.6 (2C), 73.4, 73.2, 73.2, 73.0, 72.0, 71.9, 70.5, 69.7, 68.9, 68.2, 67.2, 66.7, 64.2, 63.9, 63.7, 63.3, 50.4, 20.8 ppm; HRMS (ESI): $[M+Na]^+$ *m/z* calcd for $C_{162}H_{171}N_3O_{35}Na$: 2741.1591, found: 2741.1567.

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