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Synthesis of complex-type glycans derived from parasitic helminths

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Abstract—Chemical syntheses of complex-type glycans derived from the eggs of parasitic helminths, *Schistosoma mansoni* and *Schistosoma japonicum* were achieved. In addition, their analogs, which lack xylose and/or fucose residue(s), are described. These branched sugar chains were synthesized regio- and stereoselectively by using β-mannosylation, desilylation under high-pressure and glycosylation in frozen solvent as key transformations.

Keywords: Parasitic helminths; Glycoprotein; Complex-type glycans

1. Introduction

A majority of proteins produced by eukaryotes are glycoproteins, which carry asparagine (Asn)-linked (N-linked) oligosaccharides (*N*-glycans).[1] Although these glycans are structurally diverse, they share a common feature, carrying the core pentasaccharide that consists of three mannose and two *N*-acetylglucosamine residues ($Man_3GlcNAc_2$). Eukaryotic *N*-glycans are introduced in the endoplasmic reticulum (ER) as a tetradecasaccharide ($Glc_3Man_9GlcNAc_2$). They are then processed by various glycosidases and glycosyltransferases to generate highly diverse glycans.[2] *N*-Glycans play important roles in numerous biological events, such as development, signal transduction, cell–cell recognition, malignant transformation, and immune response.[3] They are also functional in modulating protein folding, transport, and degradation.[4]

Recently, novel *N*-glycans have been identified from bacteria,[5] plants,[6] and parasites.[7] They are attracting attention, in terms of relationships with allergy, infection, and pathogenicity. Our interest has been directed to the synthesis of complex-type *N*-glycans **1** and **2**, which were found in the eggs of parasitic helminths, *Schistosoma mansoni* and *Schistosoma japonicum* (Chart 1).[8] They share structural elements with higher eukaryotes. Namely, they are linked to the side chain of Asn through GlcNAc and carry the common pentasaccharide $Man_3GlcNAc_2$. However, they have relatively short chain length, lacking outer galactose and sialic acid residues. They are instead decorated by D-xylose and L-fucose residues, which are linked to mannose (Xylβ1→2Man) and innermost *N*-acetylglucosamine (Fucα1→3GlcNAc), respectively. Interestingly, plant derived *N*-glycans also have these residues. It has been shown that these structures are antigenic to human,[9] and contribute to IgE binding to plant allergens.[10] Helminth *N*-glycans have an additional Fuc, which is α-(1→6) linked to the innermost GlcNAc, as is often observed in mammalian complex-type glycans.

Schistosomes chronically infect more than 200 million people in developing countries.[11] Infection with *S. mansoni* induces T_H2 type immune response,[12] which was ascribed to adjuvant activities of carbohydrates.[13] Curiously, individuals infected with the parasite acquire resistance to allergy.[14] The so-called 'IgE blocking hypothesis' implies that the polyclonal IgE antibody produced after parasite infection saturates the IgE

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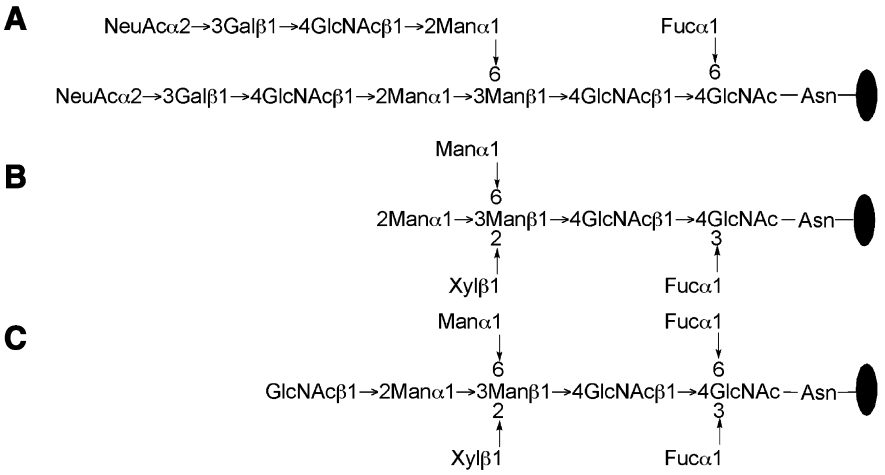
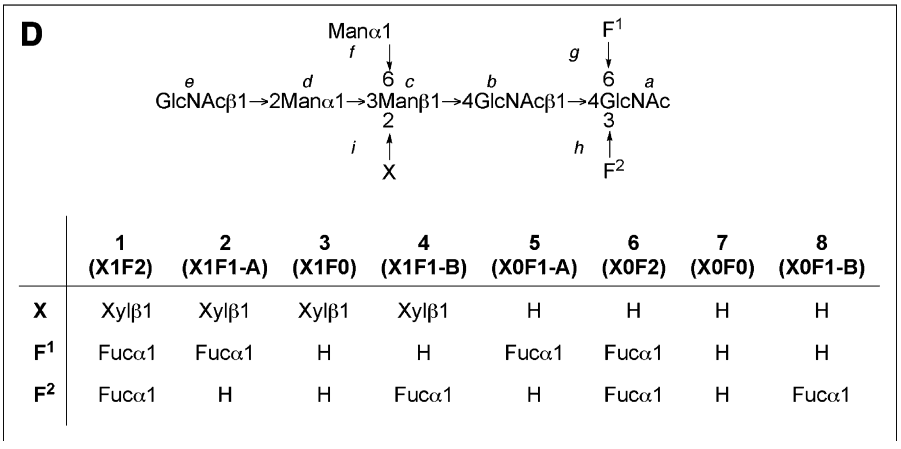




	1 (X1F2)	2 (X1F1-A)	3 (X1F0)	4 (X1F1-B)	5 (X0F1-A)	6 (X0F2)	7 (X0F0)	8 (X0F1-B)
X	Xylβ1	Xylβ1	Xylβ1	Xylβ1	H	H	H	H
F^1	Fucα1	Fucα1	H	H	Fucα1	Fucα1	H	H
F^2	Fucα1	H	H	Fucα1	H	Fucα1	H	Fucα1

Chart 1. Typical structures of animal (A), plant (B), and helminth (C) derived *N*-glycans. (D) Oligosaccharides synthesized in this study.

receptors on mast cells and blocks the binding of specific IgE antibody. On the other hand, the rapid increase of allergic diseases in urban area is explained by the 'hygiene hypothesis'. It advocates that the highly hygienic environment caused drastically reduced infection, which promotes the outbreak of the allergy.[15] More recently, a new theory has emerged, which advocates the role of IL-10 in anti-inflammatory network for inhibiting the allergy. Long-term parasite infection upregulates the production of this cytokine in the presence of regulatory T cells. However, a precise understanding of the roles of glycoprotein glycans in these phenomena has been difficult to identify, because of the limited access to these molecules.

In addition to their biomedical significance, highly complex branching of **1** and **2** attracted our attention. In particular, the construction of triply branched substitution patterns on GlcNAc^a and Man^c was anticipated to be challenging. Described herein is the full detail of our synthetic studies toward mono- (**2**) and difucosylated (**1**) xylosylated glycans,[16] as well as a series of their analogs systematically lacking Fuc and/or Xyl residues (**3**–**8**). It is our perspective that a comparison of their activities may provide information as for the contribution of each sugar residue on the immunostimulant activity of helminth/plant glycans.

2. Results and discussion

2.1. General synthetic plan

In order to approach **1**–**8** in a systematic manner, we settled on the use of xylosylated (**9**) and non-xylosylated (**12**) donors, (1→6)-fucosylated (**10**), and non-fucosylated (**13**) glucosamine components, and fucosyl donor

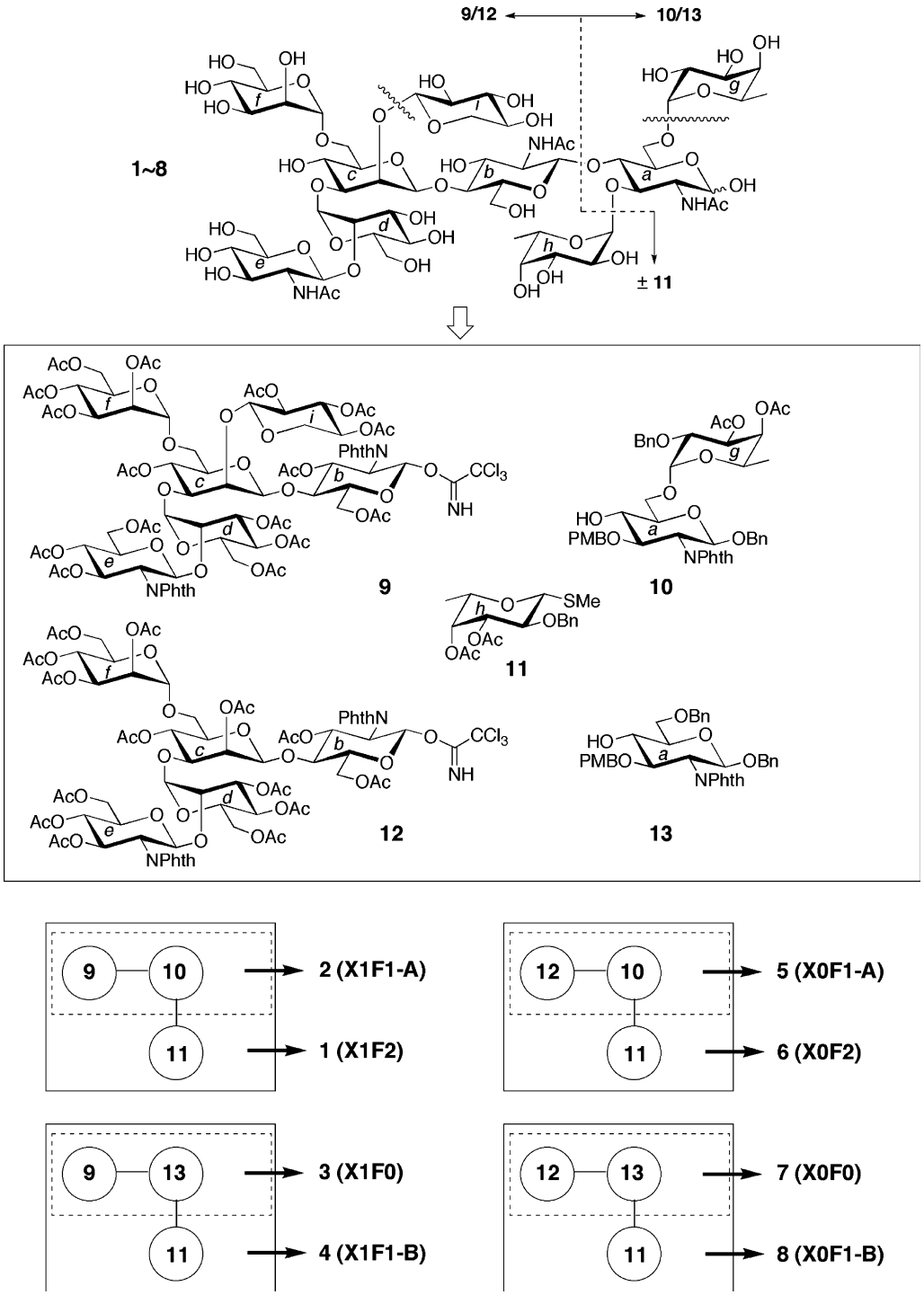
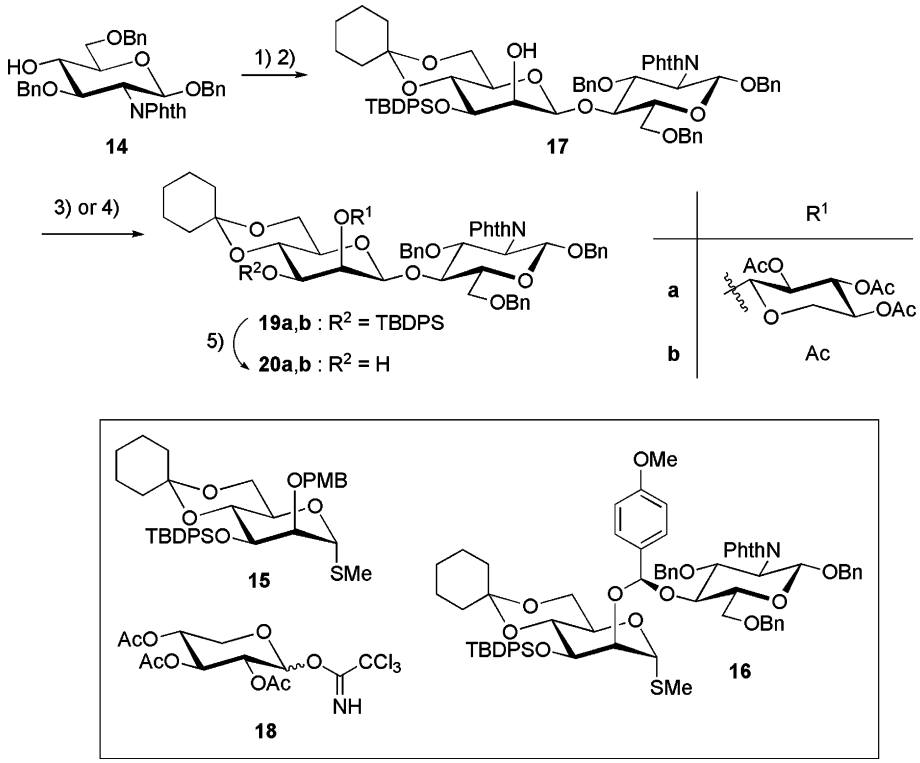


Chart 2. Design of synthetic blocks.

11[17] (Chart 2). We expected that the combination of these fragments [(**9** or **12**) × (**10** or **13**) × (+ or −**11**)] would provide **1**–**8**, with a uniform set of reactions.

2.2. Synthesis of hexa- and pentasaccharide donors

As precursors of hexa- and pentasaccharide donors (**9** and **12**), β-mannoside containing fragments (**20a** and **20b**) were prepared (Scheme 1). To begin with, compound **14**[18] was subjected to the intramolecular aglycon delivery process (IAD) using **15** as a donor[19] to give **17** as a pure β-isomer, through intermediacy of hemiacetal **16**. This reaction was particularly suitable for our purpose, because it simultaneously liberated the 2-OH of β-mannose. Thus, product **17** was immediately subjected to the next glycosylation with trichloroacetimidate[20]



Scheme 1. Reagents and conditions: (1) **15** (1.2 equiv), DDQ (1.25 equiv), MS 4 Å, CH_2Cl_2, rt, 1.5 h; (2) MeOTf (3.5 equiv), DTBMP (4 equiv), MS 4 Å, $(ClCH_2)_2$, 45 °C, 24 h, 82% (two steps); (3) **18** (3 equiv), TMSOTf (2 equiv), CH_2Cl_2, −40 °C, 2 h, 67% for **19a**; (4) Ac_2O, Py, DMAP (0.1 equiv), rt, 12 h, 97%; (5) HF·Py, DMF, 1 GPa, 12 h, 88% for **20a**, 89% for **20b**.

18[21] as a xylosyl donor to afford **19a**. This reaction required somewhat forcing conditions (3 equiv of **18**, 2 equiv of TMSOTf), reflecting the steric hindrance of **17**; the reacting OH was axially orientated and had unfavorable gauche interactions with two bulky groups (OTBDPS and heavily protected glucosamine).

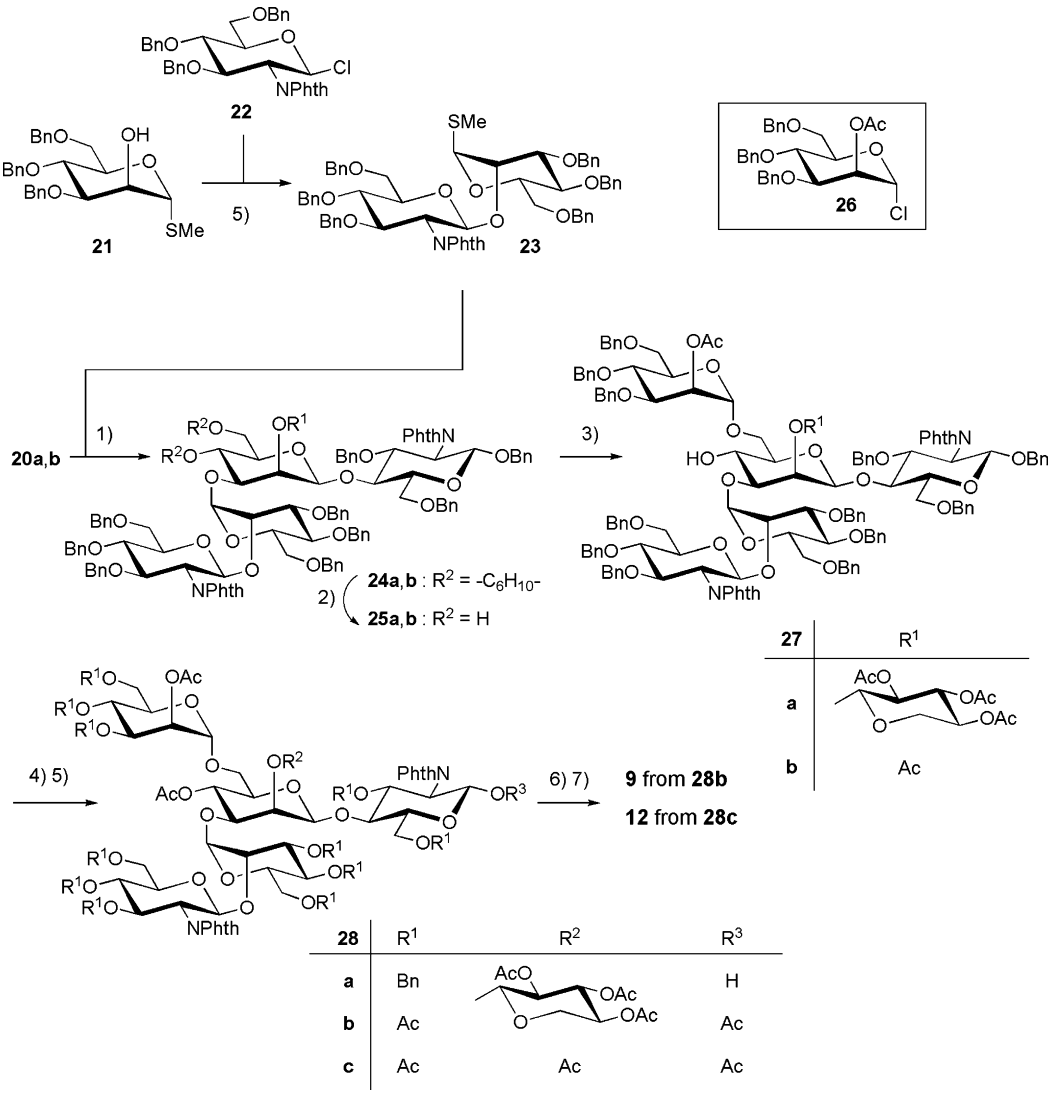
In order to liberate the hydroxy group for further glycosylation, **19a** was subjected to the deprotection of the TBDPS group. Treatment with tetra-*n*-butylammonium fluoride (TBAF) and acetic acid (1:1) in DMF gave the desilylated product **20a** in 75% yield. However, in this case, the product isolation was rather cumbersome, presumably due to the occurrence of acetyl migration. This transformation was achieved more cleanly under high-pressure conditions[22] using HF-pyridine to provide **20a** in 88% yield. In comparison, when the same reaction was conducted under atmospheric pressure, otherwise identical conditions, no product formation was observed. In the same fashion, desilylation of compound **19b**, which was obtained by acetylation of **17**, provided **20b**.

Preparation of the GlcNAc1→2Man component **23** was conducted by the reaction of **21**[23] and chloride **22**[24] under standard conditions (Scheme 2). Disaccharide **23** was then coupled with **20a** and **20b**, through activation with MeOTf,[25] to give **24a** and **24b**, respectively. Both were converted to diols **25a** and **25b** after acidic removal of the cyclohexylidene group. Glycosylation with mannosyl chloride **26**[26] proceeded regioselectively to give hexa- **27a** and pentasaccharide **27b**, without complexity.

In order to convert them to hexa/pentasaccharide donors, our initial plan was to undertake the selective deprotection of the anomeric benzyl group. Thus, **27a** was acetylated and treated under modified Bieg conditions[27] using Pd–Al_2O_3 as a catalyst and cyclohexene as a hydrogen source. In fact, this reaction indeed gave hemiacetal **28a** in 60% yield. However, its isolation was difficult by the contamination of other debenzylated products. We then settled on a three-step procedure, which involved complete debenzylation, peracetylation and selective deacetylation.

Complete debenzylation of **27a** was far less straightforward than expected. Namely, hydrogenolysis under standard conditions [H_2, $Pd(OH)_2$, EtOH–EtOAc–water] and subsequent acetylation gave rise to the formation of side products having one of their phthaloyl groups saturated. After extensive screening, it was found that this complication could be avoided by employing the hydrogen transfer protocol[28] using $Pd(OH)_2$ in 2:1:1 cyclohexane–EtOH–AcOH.[†] The debenzylated product was isolated as peracetate **28b**, which was converted to trichloroacetimidate **9** in a standard fashion.

[†] The proportion of the solvent was critical. A smaller proportion of AcOH resulted in incomplete deprotection.



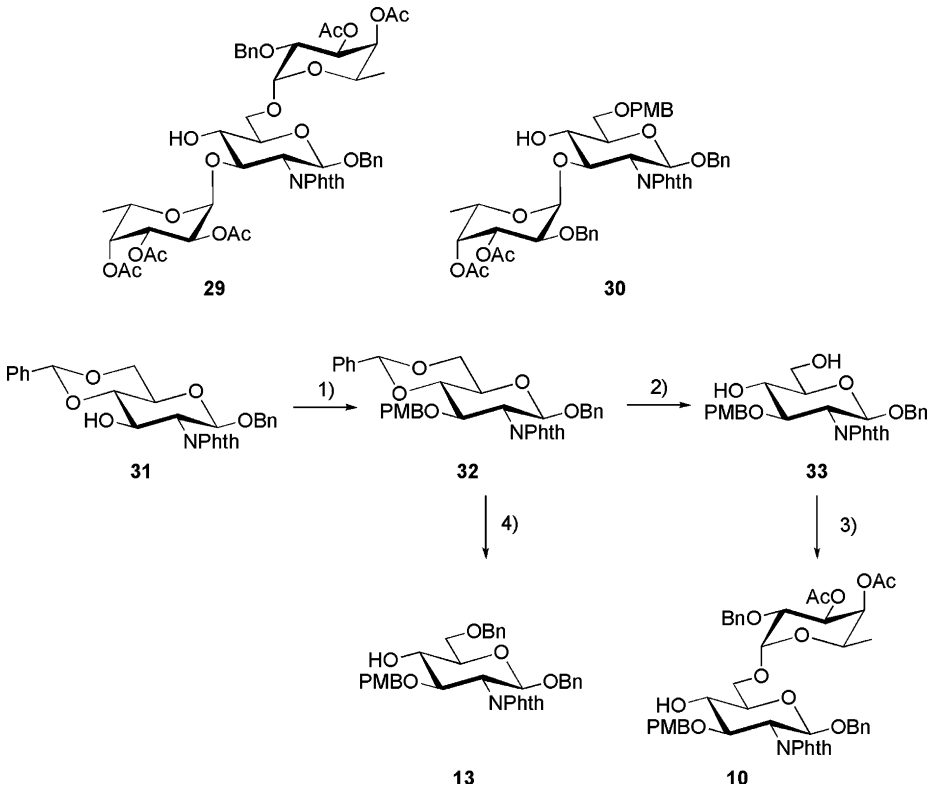
Scheme 2. Reagents and conditions: (5) **22** (1.27 equiv), AgOTf (2.5 equiv), MS 4 Å, $(ClCH_2)_2$–toluene (2:1), −40 °C, 1 h, 63%; (1) **23** (1.5 equiv), MeOTf (4.5 equiv), DTBMP (4.5 equiv), MS 4 Å, toluene, 50 °C, 12 h, 94% for **24a**; 9 h, 79% for **24b**; (2) $TsOH{\cdot}H_2O$ (2.5 equiv), CH_3CN, rt, 9 h, 91% for **25a**; 12 h, 86% for **25b**; (3) **26** (1.2 equiv), AgOTf (2.4 equiv), MS 4 Å, $(ClCH_2)_2$–toluene (2 :1), −30 °C to rt, 2.5 h, 77% for **27a**; 6 h, 89% for **27b**; (4) $Pd(OH)_2$, cyclohexene–EtOH–AcOH (2:1:1), reflux, 60 h; (5) Ac_2O, Py, rt, 6 h, 93% for **28b** (two steps); 7 h, 94% for **28c** (two steps); (6) $N_2H_4{\cdot}AcOH$ (1.3 equiv), DMF, rt, 2 h; (7) DBU (0.95 equiv), Cl_3CCN, rt, 12 h, 75% for **9**, (two steps); 74% for **12** (two steps).

In the same manner, the non-xylosylated pentasaccharide **27b** was converted to **12** via **28c**.

2.3. Synthesis of xylosylated glycans

With designed donors **9** and **12** in place, we initially explored the possibility to combine them with difucosylated trisaccharide, to complete the synthesis of **1** and **6** in a most convergent manner. To explore this possibility, the reaction of **9** with a potential acceptor **29** was conducted (Scheme 3). However, several attempts to achieve this coupling resulted in complete failure, suggesting the severe congestion of the hydroxy group, which was sandwiched by two sugar residues. To alleviate the steric hindrance, we then prepared 3-O-fucosylated disaccharide **30** as an alternative acceptor. However, its reaction with **9** gave the coupled product only in low (<10%) yield.

We selected 6-O-fucosylated disaccharide **10** as an acceptor, hoping that it had less steric hindrance than **29** or **30**, because of the conformational flexibility of the C-6 position. The synthesis of **10** was conducted as shown in Scheme 3. Thus, compound **31**[18] was converted to its *p*-methoxybenzyl (PMB) ether **32** using PMB trichloroacetimidate and $La(OTf)_2$[29] and then to diol **33**. The latter was regioselectively glycosylated with **11** to give **10**. To our delight, the coupling of **9** with **10** (1.5 equiv) proceeded smoothly under standard trichloroacetimidate conditions[20] to give octasaccharide **34** in a satisfactory yield (Scheme 4).



Scheme 3. Reagents and conditions: (1) **30** (3 equiv), $La(OTf)_3$ (0.12 equiv), CH_2Cl_2, rt, 20 h, 79%; (2) $TsOH{\cdot}H_2O$ (3.5 equiv), CH_3CN–MeOH (1:1), rt, 11 h, 78%; (3) **11** (1.2 equiv), MeOTf (3.6 equiv), DTBMP (3.6 equiv), MS 4 Å, CPME, rt, 22 h, 66%; (4) $BH_3{\cdot}NMe_3$ (5 equiv), $A1Cl_3$ (5 equiv), THF, rt, 20 h, 66%.

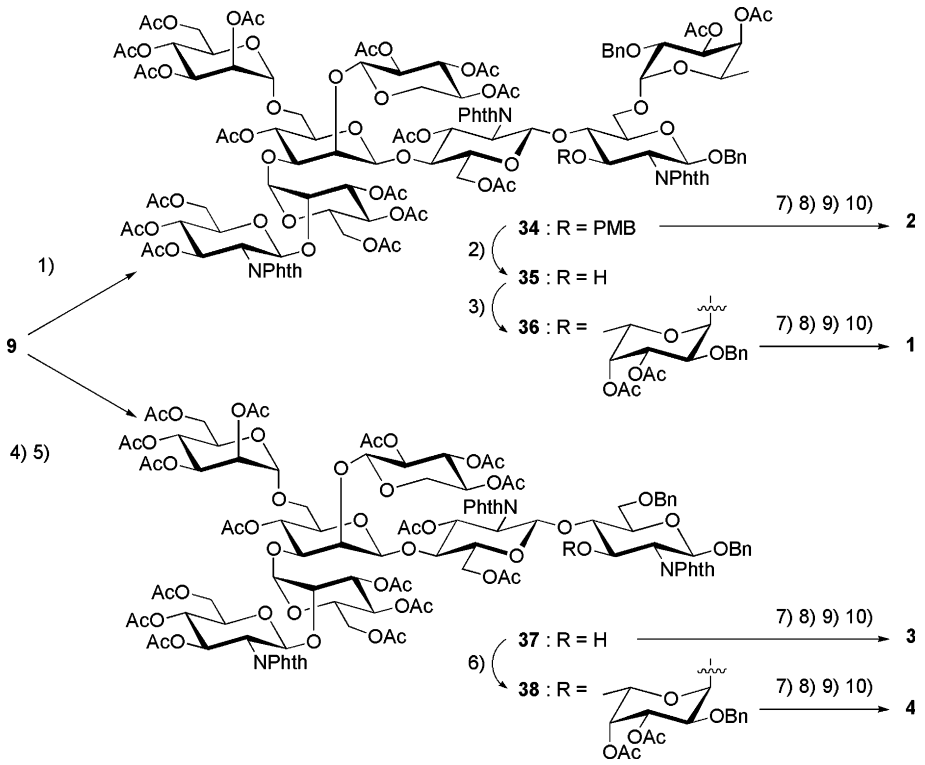
In order to introduce the (1→3)-linked fucose, the *p*-methoxybenzyl group of **34** had to be removed. However, under standard conditions (DDQ, H_2O, CH_2Cl_2), this reaction was rather sluggish, requiring 6.5 equiv of DDQ for completion. Although the desired **35** was obtained, the yield was only modest (56%) and concomitant formation of monodebenzylated product (18%) hampered the facile isolation of **35**. This difficulty was alleviated by using manganese(III) acetate as a co-oxidant.[30] Namely, treatment of **34** with a small excess of DDQ and 3.6 equiv of $Mn(OAc)_3{\cdot}2H_2O$ in CH_2Cl_2 gave 97% yield of **35**. Conversion of **9** to **37** was conducted in a similar manner; glycosylation with **13** was followed by the removal of the PMB group to give **37** in 72% yield from **9**.

Introduction of the fucose residue to **35** was conducted using **11**, through activation with MeOTf. Since this reaction was anticipated to be difficult, we were encouraged to observe the formation of the desired product **36** in ~50% yield (estimated from MALDI-TOFMS) by using ~5 equiv of **11**. However, the separation of **36** from unreacted **35** was impossible in a preparative scale and we were obliged to identify the conditions that lead to complete consumption of **35**. Since we recently found that MeOTf promoted glycosylation using methylthio glycoside could be accelerated under frozen conditions in *p*-xylene (mp 12–13 °C),[31] we decided to apply these conditions to the coupling between **35** and **11**. Gratifyingly, when the coupling was conducted in *p*-xylene at 4 °C, nearly complete conversion was achieved and nonasaccharide **36** was obtained in 90% yield. On another hand, fucosylation of **37** with **11** proceeded smoothly under standard solution conditions, possibly reflecting the reduced steric hindrance of **37** compared to **35**, providing **38** in high yield.

With the successfully assembled nona-**36**, hepta-**34**, **38**, and hexasaccharide **37** in hand, these compounds were subjected to complete deprotection in a uniform manner. Thus, sequential dephthaloylation, acetylation, O-deacetylation, and debenzylation provided **1** (X1F2), **2** (X1F1-A), **3** (X1F0), and **4** (X1F1-B).

2.4. Synthesis of non-xylosylated glycans

The synthesis of a series of non-xylosylated glycans **5**–**8** was conducted, essentially as described for **1**–**4**, except that pentasaccharide **12** was employed as a common donor (Scheme 5). Coupling with disaccharide **10** gave **39**, which was converted to **40** and glycosylated with **11** under frozen conditions to give **41**. On the other hand, coupling of **12** and **13** (2 equiv) was followed by PMB deprotection to give **42** in 81% yield. Further glycosylation with **11** gave **43**. Compounds **39**, **41**, **42**, and



Scheme 4. Reagents and conditions: (1) **10** (1.5 equiv), TMSOTf (0.2 equiv), CH_2Cl_2, −78 to −40 °C, 4.5 h, 74%; (2) DDQ (1.2 equiv), $Mn(OAc)_3{\cdot}2H_2O$ (3.6 equiv), rt, 24 h, 97%; (3) **11** (3 equiv), MeOTf (7.5 equiv), DTBMP (4.5 equiv), MS 4 Å, *p*-xylene, 4 °C, 90%; (4) **13** (2 equiv), TMSOTf (0.2 equiv), CH_2Cl_2, −78 to −50 °C, 1.5 h; (5) DDQ (0.96 equiv), $Mn(OAc)_3{\cdot}2H_2O$ (2.9 equiv), CH_2Cl_2, rt, 12 h, 72% (two steps); (6) **11** (2 equiv), MeOTf (6 equiv), DTBMP (5 equiv), MS 4 Å, CPME, rt, 23 h, 85%; (7) $(H_2NCH_2)_2$, *n*-BuOH, 85 °C, 12 h; (8) Ac_2O, Py, rt, 6 h; (9) MeONa, MeOH, rt, 12 h; (10) $Pd(OH)_2$, aq MeOH, rt, 12 h, 87% for **1** (four steps), 73% for **2** (four steps), 88% for **3** (four steps), 68% for **4** (four steps).

43 thus obtained were deprotected to give **5** (X0F1-A), **6** (X0F2), **7** (X0F0), and **8** (X0F1-B).

In conclusion, the systematic synthesis of complex-type *N*-glycans **1** and **2** found in the eggs of parasites, *S. mansoni* and *S. japonicum*, as well as their analogs lacking fucose and/or xylose residues was accomplished. These compounds are expected to be valuable in order to reveal the structure activity relationship of plant- and helminth-derived oligosaccharides.

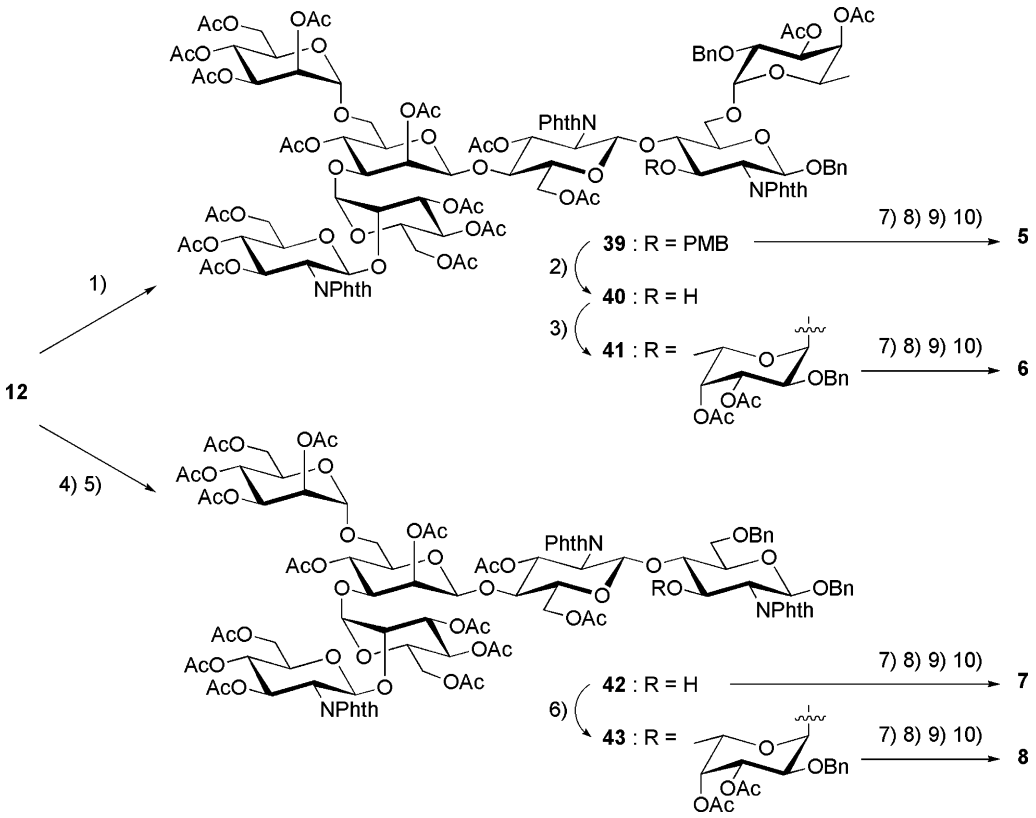
3. Experimental

3.1. General

^1H and ^{13}C NMR spectra were measured on a JEOL EX-400 spectrometer in $CDCl_3$ and were referenced to Me_4Si unless otherwise stated. Silica gel column chromatography was performed using Silica Gel-60 (E. Merck). MALDI-TOFMS spectra were recorded in the positive ion mode on an AXIMA CFR (Shimadzu/KRATOS) equipped with a nitrogen laser with an emission wavelength of 337 nm. High-resolution ESI-TOF mass spectra were obtained with a JEOL AccuTOF JMS-T700LCK equipment with CF_3CO_2Na as an internal standard.

3.2. Benzyl (3-*O*-*tert*-butyldiphenylsilyl-4,6-*O*-cyclohexylidene-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (17)

To a mixture of **15** (48.5 mg, 83.7 μmol) and **14** (57.0 mg, 87.8 μmol) and preactivated MS 4 Å (0.5 g) in dry CH_2Cl_2 (2.5 mL) was added DDQ (23.7 mg, 114 μmol) at 0 °C, and the mixture was stirred for 3 h, during which time the temperature was raised to room temperature. The reaction was quenched with aq ascorbic acid (0.7%)–citric acid (1.3%)–NaOH (0.9%) and filtered through Celite, which was rinsed with EtOAc. The filtrate was separated and the organic layer was washed with satd aq $NaHCO_3$ and brine, successively, and dried over Na_2SO_4. After concentration under diminished pressure, the mixed acetal **16** was used for the next reaction without further purification. To a mixture of mixed acetal **16** and DTBMP (68.8 mg, 335 μmol), which were coevaporated with toluene, in dry 1,2-dichloroethane (8.0 mL) were added MS 4 Å (0.9 g) and MeOTf (32.1 μL, 284 μmol) at room temperature. The mixture was stirred at 45 °C for 15 h and cooled down to room



Scheme 5. Reagents and conditions: (1) **10** (1.5 equiv), TMSOTf (0.2 equiv), CH_2Cl_2, −78 to −40 °C, 4.5 h, 70%; (2) DDQ (1.3 equiv), $Mn(OAc)_3{\cdot}2H_2O$ (3.9 equiv), rt, **13** h, 92%; (3) **11** (3 equiv), MeOTf (7.5 equiv), DTBMP (4.5 equiv), MS 4 Å, *p*-xylene, 4 °C, frozen condition, 84 h, 80%; (4) 13 (2 equiv), TMSOTf (0.2 equiv), CH_2Cl_2, −78 to −50 °C, 2 h; (5) DDQ (1.05 equiv), $Mn(OAc)_3{\cdot}2H_2O$ (3.1 equiv), CH_2Cl_2, rt, 12 h, 81% (two steps); (6) **11** (2 equiv), MeOTf (5.5 equiv), DTBMP (5 equiv), MS 4 Å, CPME, rt, 20.5 h, 92%; (7) $(H_2NCH_2)_2$, *n*-BuOH, 85 °C, 12 h; (8) Ac_2O, Py, rt, 6 h; (9) MeONa, MeOH, rt, 12 h; (10) $Pd(OH)_2$, aq MeOH, rt, 12 h, 75% for **5** (four steps), 74% for **6** (four steps), 74% for **7** (four steps), 69% for **8** (four steps).

temperature. The reaction was quenched with Et_3N (1.0 mL), eluted with EtOAc, and filtered through Celite, which was rinsed with EtOAc. The filtrate was washed with satd aq $NaHCO_3$ and brine, successively, and dried over Na_2SO_4. After concentration under diminished pressure, the residue was purified by preparative TLC (2:1 hexane–EtOAc) to give 72.4 mg (82% in two steps) of compound **17**; $[\alpha]_D$ +17.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.87–6.82 (m, 29H, Ar), 5.10 (d, *J* 8.3 Hz, 1H, H-1^{GlcN}), 4.82–4.79 (m, 2H, PhCH_2), 4.61 (d, *J* 12.2 Hz, 1H, PhC*H*H), 4.49–4.39 (m, 3H, H-1^{Man}, PhCH_2), 4.34–4.13 (m, 3H, PhC*H*H, 2,3-H^{GlcN}), 4.03–3.98 (m, 2H, H-4^{Man}, H-4^{GlcN}), 3.78–3.44 (m, 7H, H-2,3,6^{Man}, H-5,6^{GlcN}), 2.90–2.84 (m, 1H, H-5^{Man}), 2.61 (br, 1H, 2-OH^{Man}), 1.98–1.41 (m, 10H, cyclohexyl), 1.14 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 138.5, 137.6, 137.1, 136.2, 135.8, 133.8, 133.4, 132.6, 131.5, 129.9, 129.7, 128.3, 128.0, 127.8, 127.7, 127.6, 127.4, 126.8, 123.0, 100.2, 99.8, 97.5, 78.8, 74.5, 74.4, 73.4, 73.1, 71.3, 70.8, 69.8, 68.1, 67.6, 61.2, 55.7, 38.0, 27.7, 26.9, 25.6, 22.6, 22.3, 19.3. Anal. Calcd for $C_{63}H_{69}NO_{12}Si$: C, 71.36; H, 6.56; N, 1.32. Found: C, 71.33; H, 6.52; N, 1.25.

3.3. Benzyl (2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→2)-(3-*O*-*tert*-butyldiphenylsilyl-4,6-*O*-cyclohexylidene-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (19a)

A mixture of preactivated molecular sieves 4 Å (120 mg) and compounds **18** (63.1 mg, 150 μmol) and **17** (52.8 mg, 49.8 μmol) in CH_2Cl_2 (2.5 mL) was stirred at −40 °C for 30 min. TMSOTf (18 μL, 0.10 mmol) was added and stirred at the same temperature for 2 h. The reaction was quenched with Et_3N (30 μL), stirred at −40 °C for 5 min and filtered through Celite. The filtrate was diluted with EtOAc, washed with brine, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was purified by preparative TLC (3:2 hexane–EtOAc) to afford 44.0 mg (67%) of compound **19a** and 6.2 mg (12%) of recovered **17**. Compound **19a**: $[\alpha]_D$ −34.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.80–6.74 (m, 29H, Ar), 5.11–5.03 (m, 3H, H-1^{GlcN}, H-$1,3^{Xyl}$), 4.96 (dd, *J* 5.1, 7.1 Hz, 1H, H-2^{Xyl}), 4.80–4.69 (m, 3H, H-4^{Xyl}, PhCH_2), 4.52 (d, *J* 12.2 Hz, 1H, PhC*H*H), 4.43 (d, *J* 12.5 Hz, 1H, Ph*H*H), 4.35 (br s, 1H, H-1^{Man}), 4.31 (d, *J* 12.2 Hz, 1H, Ph*H*H), 4.20–4.11 (m, 4H, H-2,3^{GlcN}, H-5a^{Xyl}, PhC*H*H), 3.93 (t, *J*

9.5 Hz, 1H, H-4^{Man}), 3.89–3.83 (m, 1H, H-4^{GlcN}), 3.76 (d, *J* 2.9 Hz, 1H, H-2^{Man}), 3.72–3.64 (m, 2H, H-3,6a^{Man}), 3.60–3.57 (m, 1H, H-6a^{GlcN}), 3.46 (t, *J* 10.4 Hz, 1H, H-6b^{Man}), 3.37–3.29 (m, 2H, H-5,6b^{GlcN}), 3.13 (dd, $J = 6.7$, 12.1 Hz, 1H, H-5b^{Xyl}), 2.84–2.76 (m, 1H, H-5^{Man}), 2.08 (s, 3H, CH_3CO), 2.02 (s, 3H, CH_3CO), 1.89 (s, 3H, CH_3CO), 1.81–1.25 (m, 10H, cyclohexyl), 1.10 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170, 169.3, 168.8, 167.4, 138.3, 137.6, 137.0, 136.4, 136.0, 134.3, 133.4, 131.4, 129.5, 129.4, 128.3, 128.0, 127.7, 127.4, 127.3, 127.2, 126.8, 123.0, 102.4, 99.8, 98.5, 97.2, 80.4, 75.5, 74.8, 74.5, 73.4, 72.6, 70.7, 70.2, 69.7, 69.5, 68.7, 68.5, 68.3, 61.4, 60.8, 55.6, 38.0, 27.7, 27.0, 26.0, 22.7, 22.4, 21.0, 20.9, 20.8, 19.5; HRESIMS: found *m*/*z* 1340.52077 [M+Na]$^+$, calcd for $C_{74}H_{83}O_{19}NSiNa$ 1340.52262.

3.4. Benzyl (2-*O*-acetyl-3-*O*-*tert*-butyldiphenylsilyl-4,6-*O*-cyclohexylidene-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (19b)

To a mixture of **17** (56.2 mg, 53.0 μmol) in pyridine (1.0 mL) were added Ac_2O (0.1 mL) and DMAP (5 mg) at room temperature and the mixture was stirred for 16 h at the same temperature and evaporated under diminished pressure. After concentration, the residue was purified by preparative TLC (4:1 hexane–EtOAc) to give 56.4 mg (97%) of **19b**; $[\alpha]_D$ −3.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–6.81 (m, 29H, Ar), 5.01–4.99 (m, 1H, H-1^{GlcN}), 4.94 (d, *J* 3.4 Hz, 1H, H-2^{Man}), 4.73 (d, *J* 12.2 Hz, 1H, PhC*H*H), 4.72 (d, *J* 12.2 Hz, 1H, PhC*H*H), 4.58 (d, *J* 12.0 Hz, 1H, PhC*H*H), 4.42 (d, *J* 12.2 Hz, 1H, PhC*H*H), 4.38 (br s, 1H, H-1^{Man}), 4.29 (d, *J* 12.2 Hz, 1H, PhC*H*H), 4.23 (d, *J* 12.0 Hz, 1H, PhC*H*H), 4.14–4.07 (m, 2H, H-2,3^{GlcN}), 3.98–3.86 (m, 1H, H-4^{GlcN}), 3.89 (t, *J* 9.6 Hz, 1H, H-4^{Man}), 3.69–3.60 (m, 3H, H-3,6a^{Man}, H-6a^{GlcN}), 3.52–3.44 (m, 2H, H-6b^{Man}, H-6b^{GlcN}), 3.40–3.38 (br, 1H, H-5^{GlcN}), 2.81–2.75 (m, 1H, H-5^{Man}), 2.13 (s, 3H, CH_3CO), 1.96–1.33 (m, 10H, cyclohexyl), 1.04 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 167.5, 138.5, 137.8, 137.0, 136.2, 133.7, 133.4, 133.3, 131.5, 129.8, 129.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.1, 126.9, 123.0, 99.7, 99.1, 97.2, 78.8, 76.7, 74.4, 73.3, 72.1, 71.6, 70.7, 70.1, 68.1, 67.7, 61.1, 55.6, 37.8, 27.7, 26.8, 25.6, 22.6, 22.4, 21.2, 19.3; HRESIMS: found *m*/*z* 1124.46041 [M+Na]$^+$, calcd for $C_{65}H_{71}O_{13}NSiNa$ 1124.45924.

3.5. Benzyl (2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→2)-(4,6-*O*-cyclohexylidene-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (20a)

To a Teflon reaction vessel was introduced compound **19a** (1.40 g, 1.06 mmol) in DMF (4 mL) containing 10% HF·pyridine. It was compressed to 1.0 GPa and left for 12 h. The resulting mixture was diluted with EtOAc and washed with satd aq $NaHCO_3$ and brine, successively. The organic layer was dried over $MgSO_4$ and evaporated under diminished pressure. The residue was purified by silica gel column chromatography (1:1 hexane–EtOAc) to afford 1.10 g (88%) of compound **20a**; $[\alpha]_D$ −35.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–6.77 (m, 19H, Ar), 5.18 (t, *J* 7.6 Hz, 1H, H-3^{Xyl}), 5.07–5.05 (m, 1H, H-1^{GlcN}), 4.96–4.87 (m, 3H, H-1,2,4^{Xyl}), 4.79–4.70 (m, 3H, PhCH_2), 4.56 (br s, 1H, H-1^{Man}), 4.49–4.45 (m, 2H, PhCH_2), 4.28 (d, *J* 12.2 Hz, 1H, PhC*H*H), 4.23–4.17 (m, 3H, H-2,3^{GlcN}, H-5a^{Xyl}), 3.98–3.93 (m, 1H, H-4^{GlcN}), 3.84 (d, *J* 3.2 Hz, 1H, H-2^{Man}), 3.73–3.72 (m, 2H, H-6^{GlcN}), 3.66–3.56 (m, 2H, H-4,6a^{Man}), 3.52–3.48 (m, 1H, H-5^{GlcN}), 3.42–3.31 (m, 3H, H-3,6b^{Man}, H-5b^{Xyl}), 2.97–2.91 (m, 1H, H-5^{Man}), 2.87 (d, *J* 9.3 Hz, 1H, 3-OH^{Man}), 2.07 (s, 3H, CH_3CO), 2.02 (s, 6H, CH_3CO), 1.99–1.32 (m, 10H, cyclohexyl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 169.3, 169.0, 167.5, 138.4, 137.4, 136.9, 133.4, 131.4, 128.5, 128.0, 127.9, 127.7, 127.4, 127.3, 126.8, 123.0, 102.1, 99.9, 99.8, 97.3, 80.8, 77.5, 74.6, 74.4, 73.8, 70.8, 70.6, 70.4, 70.1, 68.5, 68.4, 68.2, 61.4, 61.1, 55.6, 38.0, 27.9, 25.7, 22.9, 22.6, 21.2, 20.9, 20.8. Anal. Calcd for $C_{58}H_{65}NO_{19}$: C, 64.49; H, 6.07; N, 1.30. Found: C, 64.39; H, 5.99; N, 1.26.

3.6. Benzyl (2-*O*-acetyl-4,6-*O*-cyclohexylidene-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (20b)

Compound **19a** (2.05 g, 1.86 mmol) was desilylated as described for compound **20a**. Purification by silica gel column chromatography (7:3→3:2 toluene–EtOAc linear gradient) afforded 1.43 g (89%) of compound **20b**: $[\alpha]_D$ −3.82 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–6.80 (m, 19H, Ar), 5.21 (d, *J* 3.4 Hz, 1H, H-2^{Man}), 5.08–5.02 (m, 1H, H-1^{GlcN}), 4.78–4.74 (m, 3H, PhCH_2), 4.64 (br s, 1H, H-1^{Man}), 4.49–4.44 (m, 2H, PhCH_2), 4.34 (d, *J* 12.2 Hz, 1H, PhC*H*H), 4.20–4.14 (m, 2H, H-2,3^{GlcN}), 4.09–4.05 (m, 1H, H-4^{GlcN}), 3.81 (dd, *J* 3.1, 11.1 Hz, 1H, H-6a^{GlcN}), 3.74–3.67 (m, 3H, H-4,6a^{Man}, H-6b^{GlcN}), 3.51–3.46 (m, 3H, H-3,6b^{Man}, H-5^{GlcN}), 3.00–2.94 (m, 1H, H-5^{Man}), 2.14 (s, 3H, CH_3CO), 2.09 (d, *J* 3.7 Hz, 1H, 3-OH^{Man}), 1.98–1.36 (m, 10H, cyclohexyl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 167.4, 138.4, 137.6, 136.9, 133.4, 131.4, 128.4, 127.9, 127.8, 127.7, 127.5, 127.4, 126.9, 123.0, 99.9, 99.3, 97.2, 79.3, 77.2, 76.8, 74.5, 74.4, 73.5, 71.2, 70.7, 70.2, 70.1, 68.2, 67.8, 61.0, 55.7, 37.9, 28.0, 25.6, 22.8, 22.6, 21.2; HRESIMS: found *m*/*z* 886.33992 [M+Na]$^+$, calcd for $C_{49}H_{53}O_{13}NNa$ 886.34146.

3.7. Methyl (3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (23)

A mixture of preactivated molecular sieves 4 Å (8 g) and AgOTf (3.39 g, 13.2 mmol) in toluene (40 mL) was stirred at −40 °C for 30 min. A mixture of **22** (3.95 g, 6.61 mmol) and **21** (2.46 g, 5.19 mmol) in 1,2-dichloroethane (80 mL) was added dropwise and the reaction was stirred for 1 h. It was quenched with Et_3N (2 mL) and satd aq $NaHCO_3$. After being stirred for 15 min, the resulting mixture was diluted with EtOAc, and filtered through Celite. The filtrate was washed with brine, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was purified by silica gel column chromatography (20:1 toluene–EtOAc) to afford 3.42 g (63%) of **23**; $[\alpha]_D$ +41.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.58–7.49 (m, 4H, Phth), 7.34–6.81 (m, 30H, Ar), 5.27 (d, *J* 7.8 Hz, 1H, H-1^{GlcN}), 4.86–4.74 (m, 5H, H-1^{Man}, PhCH_2), 4.65–4.44 (m, 5H, PhCH_2), 4.39–4.29 (m, 3H, H-2,3^{GlcN}, PhC*H*H), 4.15 (t, *J* 2.5 Hz, 1H, H-2^{Man}), 4.01 (d, *J* 12.0 Hz, 1H, PhC*H*H), 3.96 (d, *J* 12.0 Hz, 1H, PhC*H*H), 3.82–3.68 (m, 6H, H-4,5,6^{GlcN}, H-3,5^{Man}), 3.46 (t, *J* 9.1 Hz, 1H, H-4^{Man}), 3.37 (dd, *J* 1.8, 10.9 Hz, 1H, H-6a^{Man}), 2.92 (dd, *J* 6.6, 10.9 Hz, 1H, H-6b^{Man}), 1.90 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 137.9, 137.8, 137.7, 133.3, 131.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 127.3, 127.2, 127.1, 122.9, 96.4, 82.6, 79.7, 79.0, 77.9, 75.1, 75.0, 74.8, 74.7, 73.6, 72.7, 71.8, 70.7, 69.8, 69.3, 55.8, 13.8; HRESIMS: found *m*/*z* 1064.40541 $[M+Na]^+$, calcd for $C_{63}H_{63}O_{11}NNa$ 1064.40195.

3.8. Benzyl (3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→2)]-(4,6-*O*-cyclohexylidene-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (24a)

A mixture of preactivated molecular sieves 4 Å (6 g), compounds **23** (3.14 g, 3.0 mmol) and **20a** (2.16 g, 2.0 mmol), and DTBMP (1.85 g, 9.0 mmol) in toluene (80 mL) was stirred at room temperature for 30 min. MeOTf (1.0 mL, 9 mmol) was added and stirred at the same temperature for 1.5 h. Then the mixture was warmed up to 50 °C and was stirred for 12 h. The reaction was cooled to ambient temperature, quenched with Et_3N (1.3 mL) and filtered through Celite. The filtrate was diluted with EtOAc, washed with brine, dried over $MgSO_4$ and evaporated under diminished pressure. The residue was purified by silica gel column chromatography (6:1 toluene–EtOAc) to afford 3.90 g (94%) of compound **24a**; $[\alpha]_D$ −21.5 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.62–6.79 (m, 53H, Ar), 5.26 (d, *J* 7.8 Hz, 1H, H-1^{GlcN2}), 5.04 (d, *J* 8.1 Hz, 1H, H-1^{GlcN1}), 4.96–4.74 (m, 9H, H-1^{Man2}, H-1,2,3^{Xyl}, PhCH_2), 4.68–4.32 (m, 12H, H-2,3^{GlcN2}, H-4^{Xyl}, PhCH_2), 4.22–4.11 (m, 5H, H-1^{Man1}, H-2^{Man2}, H2,3^{GlcN1}, PhC*H*H), 4.04–3.93 (m, 3H, PhCH_2), 3.89–3.72 (m, 8H, H-2^{Man1}, H-3,5^{Man2}, H-4^{GlcN1}, H-4,6^{GlcN2}, H-5a^{Xyl}), 3.64–3.61 (m, 1H, H-5^{GlcN2}), 3.58–3.50 (m, 2H, H-4,6a^{Man1}), 3.45–3.21 (m, 7H, H-6b^{Man1}, H-4,6a^{Man2}, H-5,6^{GlcN1}, H-5b^{Xyl}), 3.15 (dd, *J* 3.1, 10.1 Hz, 1H, H-3^{Man1}), 2.74 (dd, *J* 7.1, 10.5 Hz, 1H, H-6b^{Man2}), 2.54–2.48 (m, 1H, H-5^{Man1}), 1.94 (s, 3H, CH_3CO), 1.89 (s, 3H, CH_3CO), 1.88 (s, 3H, CH_3CO), 1.73–1.25 (m, 10H, cyclohexyl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 169.1, 168.8, 167.3, 138.7, 138.4, 138.3, 138.1, 137.9, 137.8, 137.7, 137.6, 137.0, 133.4, 133.2, 131.7, 131.4, 128.7, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.1, 127.0, 126.7, 123.0, 101.5, 99.3, 99.1, 98.1, 97.3, 96.6, 79.7, 79.6, 79.4, 76.2, 76.1, 75.7, 72.2, 75.1, 74.9, 74.8, 74.6, 74.1, 73.7, 73.2, 72.8, 71.8, 71.7, 70.8, 70.0, 69.7, 69.5, 69.3, 68.2, 67.9, 61.3, 60.5, 55.9, 55.5, 38.0, 27.9, 25.7, 23.5, 22.7, 21.0, 20.9, 20.7. Anal. Calcd for $C_{120}H_{124}N_2O_{30}$: C, 69.48; H, 6.03; N, 1.35. Found: C, 69.51; H, 6.01; N, 1.23.

3.9. Benzyl (3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2-*O*-acetyl-4,6-*O*-cyclohexylidene-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (24b)

Compound **20b** (1.12 g, 1.30 mmol) was glycosylated with **23** as described for **24a**. Purification by silica gel column chromatography (4:1→2:1 hexane–EtOAc then 9:1→8:1 toluene–EtOAc, linear gradient) afforded 1.91 g (79%) of **24b**; $[\alpha]_D$ −11.7 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.62–6.81 (m, 53H, Ar), 5.23 (d, *J* 7.6 Hz, 1H, H-1^{GlcN2}), 5.04 (d, *J* 3.4 Hz, 1H, H-2^{Man1}), 4.99 (d, *J* 7.8 Hz, 1H, H-1^{GlcN1}), 4.84–4.68 (m, 6H, H-1^{Man2}, PhCH_2), 4.65–4.31 (m, 11H, H-2,3^{GlcN2}, PhCH_2), 4.25 (d, *J* 12.2 Hz, 1H, PhC*H*H), 4.19 (br s, 1H, H-1^{Man1}), 4.14–3.98 (m, 6H, H-2^{Man2}, H-2,3^{GlcN1}, PhCH_2), 3.92 (t, *J* 8.9 Hz, 1H, H-4^{GlcN1}), 3.76–3.72 (m, 3H, H-4,6^{GlcN2}), 3.70–3.58 (m, 4H, H-6a^{Man1}, H-3,5^{Man2}, H-5^{GlcN2}), 3.56–3.39 (m, 5H, H-4,6b^{Man1}, H-4^{Man2}, H-6^{GlcN1}), 3.35–3.27 (m, 3H, H-3^{Man1}, H-6a^{Man2}, H-5^{GlcN1}), 2.72 (dd, *J* 6.6, 11.0 Hz, 1H, H-6b^{Man2}), 2.64–2.58 (m, 1H, H-5^{Man1}), 1.86 (s, 3H, CH_3CO), 1.75–1.23 (m, 10H, cyclohexyl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 167.4, 138.7, 138.4, 138.3, 137.9, 137.8, 137.7, 137.6, 136.9, 133.3, 131.6, 131.4, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.1, 127.0, 126.9, 123.0, 99.5, 98.7, 97.7, 97.2, 96.0, 79.6, 79.4, 78.2, 77.2, 76.6, 75.3, 75.0, 74.8, 74.3, 74.0, 73.6, 73.2, 72.5, 72.2, 71.6, 70.8, 70.7, 70.2, 70.1, 69.4, 67.8,

67.2, 61.2, 55.8, 55.6, 53.5, 38.0, 31.0, 28.1, 25.7, 23.3, 22.8, 20.9. Anal. Calcd for $C_{111}H_{112}N_2O_{24}$: C, 71.75; H, 6.08; N, 1.51. Found: C, 71.78; H, 6.07; N, 1.51.

3.10. Benzyl (3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→2)]-(β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (25a)

To a stirred soln of **24a** (29.9 mg, 14.4 μmol) in MeCN (1 mL) was added $TsOH·H_2O$ (6.8 mg, 36.0 μmol). The mixture was stirred for 9 h at room temperature and the reaction was quenched with Et_3N (0.1 mL). The resulting mixture was diluted with EtOAc, washed with satd aq $NaHCO_3$ and brine, successively, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was purified by preparative TLC (1:1 hexane–EtOAc) to afford 26.0 mg (91%) of compound **25a**; $[\alpha]_D$ −7.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.64–6.77 (m, 53H, Ar), 5.34 (d, *J* 8.3 Hz, 1H, H-1^{GlcN2}), 5.08–4.98 (m, 4H, H-1^{Man2}, H-1^{GlcN1}, H-$1,3^{Xyl}$), 4.92–4.87 (br, 1H, H-4^{Xyl}), 4.85–4.73 (m, 7H, H-2^{Xyl}, PhCH_2), 4.59 (d, *J* 12.2 Hz, 1H, PhC*H*H), 4.54–4.41 (m, 9H, H-1^{Man1}, H-3^{GlcN2}, PhCH_2), 4.39–4.24 (m, 5H, H-3^{GlcN1}, H-2^{GlcN2}, PhCH_2), 4.19–4.14 (m, 2H, H-2^{Man2}, H-2^{GlcN1}), 4.02–3.99 (m, 3H, H-$5a^{Xyl}$, PhCH_2), 3.85–3.75 (m, 6H, H-$2,6a^{Man1}$, H-$3,5^{Man2}$, H-4^{GlcN1}, H-5^{GlcN2}), 3.69–3.64 (m, 2H, H-4^{Man2}, H-4^{GlcN2}), 3.61–3.50 (m, 4H, H-4^{Man1}, H-6^{GlcN1}, H-$6a^{GlcN2}$), 3.43–3.35 (m, 4H, H-$6b^{Man1}$, H-$6a^{Man2}$, H-5^{GlcN1}, H-$6b^{GlcN2}$), 3.21–3.15 (m, 2H, H-3^{Man1}, H-$5b^{Xyl}$), 3.06 (d, *J* 4.9 Hz, 1H, 4-OH^{Man1}), 2.88–2.81 (m, 2H, H-5^{Man1}, H-$6b^{Man2}$), 2.17 (br, 1H, 6-OH^{Man1}), 1.96 (s, 3H, CH_3CO), 1.95 (s, 3H, CH_3CO), 1.93 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 169.2, 167.5, 138.3, 138.2, 138.1, 137.8, 137.5, 136.9, 133.4, 131.5, 131.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 127.3, 127.2, 127.1, 126.9, 123.1, 101.1, 100.0, 97.1, 97.0, 96.4, 79.7, 79.1, 79.0, 77.2, 77.1, 76.1, 75.0, 74.8, 74.7, 74.6, 74.3, 73.9, 73.5, 73.5, 73.4, 73.2, 72.9, 71.2, 70.7, 70.5, 70.4, 69.5, 68.6, 68.4, 65.4, 62.2, 61.3, 56.0, 55.6, 31.0, 21.2, 20.9. Anal. Calcd for $C_{114}H_{116}N_2O_{30}$: C, 68.66; H, 5.86; N, 1.40. Found: C, 68.37; H, 5.81; N, 1.37.

3.11. Benzyl (3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (25b)

Compound **24b** (1.85 g, 996 μmol) was treated with TsOH as described for the preparation of **25a**. The crude product was purified by silica gel column chromatography (3:1 toluene–EtOAc) to afford 1.52 g (86%) of compound **25b**; $[\alpha]_D$ +4.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.64–6.77 (m, 53H, Ar), 5.27 (d, *J* 7.8 Hz, 1H, H-1^{GlcN2}), 5.12 (d, *J* 3.2 Hz, 1H, H-2^{Man1}), 5.04 (d, *J* 8.3 Hz, 1H, H-1^{GlcN1}), 4.96 (d, *J* = 2.7 Hz, 1H, H-1^{Man2}), 4.84–4.74 (m, 4H, PhCH_2), 4.71–4.40 (m, 10H, H-1^{Man1}, PhCH_2), 4.36–4.25 (m, 5H, H-$2,3^{GlcN2}$, PhCH_2), 4.17–3.98 (m, 6H, H-2^{Man2}, H-$2,3,4^{GlcN1}$, PhCH_2), 3.77–3.75 (br, 1H, H-$6a^{GlcN2}$), 3.71–3.62 (m, 8H, H-$6a^{Man1}$, H-$3,5^{Man2}$, H-6^{GlcN1}, H-$4,5,6b^{GlcN2}$), 3.55–3.40 (m, 4H, H-$4,6b^{Man1}$, H-4^{Man2}, H-5^{GlcN1}), 3.37–3.33 (m, 2H, H-3^{Man1}, H-$6a^{Man2}$), 3.18 (d, *J* 4.9 Hz, 1H, 4-OH^{Man1}), 2.91–2.87 (m, 2H, H-5^{Man1}, H-$6b^{Man2}$), 1.99 (br, 1H, 6-OH^{Man1}), 1.60 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 167.4, 138.2, 138.1, 137.9, 137.7, 137.5, 137.0, 133.5, 131.4, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 127.1, 123.1, 98.1, 97.2, 96.8, 96.4, 79.6, 79.3, 78.0, 77.9, 77.2, 76.8, 75.4, 75.2, 75.1, 74.8, 74.7, 74.4, 74.3, 74.0, 73.9, 73.6, 73.4, 72.8, 71.4, 71.2, 70.8, 70.7, 69.9, 69.2, 67.9, 66.4, 62.3, 55.8, 55.6, 21.2. Anal. Calcd for $C_{105}H_{104}N_2O_{24}$: C, 70.93; H, 5.90; N, 1.58. Found: C, 70.95; H, 5.86; N, 1.45.

3.12. Benzyl (3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-*O*-[(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)]-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→2)]-(β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (27a)

A mixture of preactivated molecular sieves 4 Å (200 mg) and AgOTf (7.8 mg, 30 μmol) in toluene (1 mL) was stirred at 0 °C for 30 min, then cooled to −30 °C. After being stirred for 10 min, a mixture of **26** (7.7 mg, 15 μmol) and **25a** (25.1 mg, 12.6 μmol) in 1,2-dichloroethane (2.0 mL) was added dropwise and the whole mixture was stirred at −30 °C for 30 min, then warmed up to ambient temperature. The mixture was stirred for 2.5 h and the reaction was quenched with Et_3N (20 μL). The resulting mixture was diluted with EtOAc and filtered through Celite. The filtrate was washed with satd aq $NaHCO_3$ and brine, successively, dried over $MgSO_4$ and evaporated under diminished pressure. The residue was purified by preparative TLC (4:1 toluene–EtOAc) to afford 23.9 mg (77%) of **27a**; $[\alpha]_D$ −3.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.63–6.70 (m, 68H, Ar), 5.33–5.32 (m, 1H, H-2^{Man3}), 5.29 (d, *J* 8.3 Hz, 1H, H-1^{GlcN2}), 5.11–4.98 (m, 3H, H-1^{GlcN1}, H-$2,3^{Xyl}$), 4.91 (d, *J* 1.7 Hz, 1H, H-1^{Man2}), 4.88–4.72 (m, 10H, H-1^{Man3}, H-$1,4^{Xyl}$, PhCH_2), 4.67–4.20 (m, 20H, H-1^{Man1}, H-2^{Man2}, H-3^{GlcN1}, H-2,3-H^{GlcN2}, PhCH_2), 4.13 (dd, *J* 8.4, 10.4 Hz, 1H, H-2^{GlcN1}), 4.07 (d, *J* 12.2 Hz,

1H, PhC*H*H), 4.01 (d, *J* 12.2 Hz, 1H, PhC*H*H), 3.92–3.68 (m, 15H, H-2,6a^{Man1}, H-3,4,5^{Man2}, H-3,4,5,6^{Man3}, H-4^{GlcN1}, H-4,5,6a^{GlcN2}, H-5a^{Xyl}), 3.54–3.47 (m, 3H, H-4^{Man1}, H-6^{GlcN1}), 3.43–3.32 (m, 4H, H-6b^{Man1}, H-6a^{Man2}, H-5^{GlcN1}, H-6b^{GlcN2}), 3.17–3.09 (m, 3H, H-3^{Man1}, 4-OH^{Man1}, H-5b^{Xyl}), 2.93–2.85 (m, 2H, H-5^{Man1}, H-6b^{Man2}), 2.08 (s, 3H, C*H*$_3$CO), 1.95 (s, 6H, C*H*$_3$CO), 1.90 (s, 3H, C*H*$_3$CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 169.7, 169.1, 168.9, 167.4, 138.6, 138.2, 138.1, 137.9, 137.8, 137.0, 133.3, 131.4, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 127.1, 127.0, 126.9, 123.0, 101.7, 100.3, 97.8, 97.5, 97.1, 96.6, 80.0, 79.5, 79.2, 78.3, 77.4, 77.2, 76.3, 75.2, 75.0, 74.8, 74.6, 74.2, 74.1, 73.4, 73.2, 72.8, 71.7, 71.6, 71.5, 71.3, 70.7, 70.6, 70.5, 69.2, 69.1, 68.6, 67.5, 66.3, 61.8, 56.0, 55.6, 31.0, 21.2, 21.0, 20.9; HRESIMS: found *m*/*z* 2489.95692 $[M+Na]^+$, calcd for $C_{143}H_{146}O_{36}N_2Na$ 2489.95529.

3.13. Benzyl (3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-[(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)]-(2-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (27b)

Compound **25a** (1.48 g, 832 μmol) was glycosylated with chloride **26** as described for the preparation of compound **27a**. The crude product was purified by silica gel column chromatography (5:2→1:1 hexane–EtOAc, linear gradient) to afford 1.67 g (89%) of **27b**; $[\alpha]_D$ +14.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–6.69 (m, 68H, Ar), 5.30–5.29 (m, 1H, H-2^{Man3}), 5.27 (d, *J* 7.8 Hz, 1H, H-1^{GlcN2}), 5.13 (d, *J* 3.2 Hz, 1H, H-2^{Man1}), 4.98 (d, *J* 8.3 Hz, 1H, H-1^{GlcN1}), 4.95 (d, *J* 2.0 Hz, 1H, H-1^{Man2}), 4.84 (d, *J* 1.7 Hz, 1H, H-1^{Man3}), 4.82–4.70 (m, 7H, PhC*H*$_2$), 4.64–4.57 (m, 3H, PhC*H*$_2$), 4.52–4.25 (m, 14H, H-1^{Man1}, H-2,3^{GlcN2}, PhC*H*$_2$), 4.22 (d, *J* 11.0 Hz, 1H, PhC*H*H), 4.16 (br s, 1H, H-2^{Man2}), 4.13–4.03 (m, 4H, H-2,3-H^{GlcN1}, PhC*H*$_2$), 3.93 (br, 1H, H-4^{GlcN1}), 3.83–3.77 (m, 4H, H-5^{Man2}, H-3,4,6a^{Man3}), 3.71–3.55 (m, 12H, H-4,6a^{Man1}, H-2,3,5^{Man2}, H-5,6b^{Man3}, H-6^{GlcN1}, H-4,5,6a^{GlcN2}), 3.47 (br, 1H, H-6b^{GlcN2}), 3.38–3.30 (m, 3H, H-5^{GlcN1}, H-3,6b^{Man1}), 3.17 (d, *J* 5.1 Hz, 1H, 4-OH^{Man1}), 2.94–2.89 (m, 2H, H-5^{Man1}, H-6b^{Man2}), 1.95 (s, 3H, C*H*$_3$CO), 1.94 (s, 3H, C*H*$_3$CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 169.5, 167.2, 138.4, 138.3, 138.2, 138.1, 138.0, 137.8, 137.7, 133.3, 131.5, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 127.3, 127.2, 127.1, 126.9, 122.9, 98.7, 97.9, 97.8, 97.1, 96.5, 79.6, 79.3, 78.6, 78.3, 77.2, 76.4, 75.2, 75.1, 74.9, 74.7, 74.3, 74.2, 73.5, 73.4, 73.2, 72.7, 71.7, 71.6, 71.1, 70.6, 69.9, 69.1, 68.8, 68.4, 68.1, 67.2, 66.6, 55.8, 55.7, 21.0; HRESIMS: found *m*/*z* 2273.89419 $[M+Na]^+$; calcd for $C_{134}H_{134}O_{30}N_2Na$ 2273.89191.

3.14. (3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→2)]-(4-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-1,3,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose (28b)

To a stirred soln of **27a** (247 mg, 100 μmol) in cyclohexene (20 mL), EtOH (10 mL), and AcOH (10 mL) was added 20% $Pd(OH)_2$ (250 mg). The mixture was heated under reflux for 60 h and filtered through Celite. The filtrate was evaporated under diminished pressure, and the residue was dissolved in pyridine (10 mL) and Ac_2O (5 mL). The mixture was stirred for 6 h and quenched with EtOH (10 mL) at ice-cold temperature. The resulting mixture was evaporated, diluted with EtOAc, washed with 1 M HCl and brine, successively, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was purified by preparative TLC (1:4 hexane–EtOAc) to afford 180 mg (93%) of **28b**; $[\alpha]_D$ −17.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.70 (m, 8H, Ar), 6.44 (d, *J* 9.0 Hz, 1H), 5.87 (t, *J* 9.0 Hz, 1H), 5.66 (dd, *J* 9.0, 10.5 Hz, 1H), 5.31–5.28 (m, 3H), 5.19–5.02 (m, 5H), 4.98–4.91 (m, 2H), 4.79–4.76 (m, 3H), 4.63 (br s, 1H), 4.48 (br s, 1H), 4.42–4.24 (m, 7H), 4.08–3.82 (m, 9H), 3.76–3.68 (m, 3H), 3.57–3.42 (m, 4H), 2.26 (s, 3H, C*H*$_3$CO), 2.16–1.94 (m, 42H, C*H*$_3$CO), 1.88 (s, 3H, C*H*$_3$CO), 1.84 (s, 3H, C*H*$_3$CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5 × 2, 170.4, 170.0, 169.8 × 2, 169.7, 169.5, 169.4, 169.2, 169.1, 168.9, 168.3, 167.2, 134.3, 131.2, 123.5, 99.5, 98.8, 98.2, 97.2, 97.0, 89.6, 74.1, 73.3, 72.5, 72.1, 70.6, 69.6, 69.2, 68.8, 68.7, 68.6, 68.0, 67.8, 65.8, 65.5, 62.3, 62.1, 62.0, 61.8, 54.3, 53.4, 21.0, 20.9, 20.8, 20.7, 20.6 × 2, 20.5 × 2, 20.4; HRESIMS: found *m*/*z* 1955.52682 $[M+Na]^+$; calcd for $C_{85}H_{100}O_{49}N_2Na$ 1955.52923.

3.15. (3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-(2,4-di-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-1,3,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl (28c)

Compound **27a** (226 mg, 100 μmol) was submitted to sequential debenzylation and acetylation as described for **28b**. Purification by preparative TLC (1:5 hexane–EtOAc) afforded 166 mg (97%) of **28c**; $[\alpha]_D$ +5.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.70 (m, 8H, Ar), 6.41 (d, *J* 8.8 Hz, 1H), 5.87 (dd, *J* 8.3, 10.7 Hz, 1H), 5.64 (t, *J* 9.8 Hz, 1H), 5.40–5.22 (m, 5H), 5.14–5.09 (m, 2H), 5.02 (t, *J* 9.5 Hz, 1H), 4.82 (br s, 1H), 4.75 (dd, *J* 3.4, 10.5 Hz, 1H), 4.59–4.57 (m, 2H), 4.40–4.28 (m, 6H), 4.17–4.02 (m, 4H), 3.97–3.90 (m, 2H), 3.86–3.71 (m, 6H), 3.58–3.47 (m, 2H), 2.30 (s,

3H, CH_3CO), 2.17–1.92 (m, 39H, CH_3CO), 1.66 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5 × 2, 170.2, 170.0 × 2, 169.9, 169.6 × 2, 169.2, 169.1, 168.2, 167.1, 134.3, 131.1, 123.4, 98.3, 97.5, 97.0, 96.7, 89.7, 74.0, 73.9 × 2, 73.1, 72.8, 72.1, 69.3, 69.2 × 3, 69.0, 68.8, 68.6, 67.6, 65.7, 64.9, 62.3, 62.1, 62.0, 61.8, 54.3, 53.4, 21.0, 20.9, 20.8, 20.7 × 3, 20.6, 20.5, 20.4 × 2; HRESIMS: found *m/z* 1739.47052 $[M+Na]^+$; calcd for $C_{76}H_{88}O_{43}N_2Na$ 1739.46585.

3.16. (3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→2)]-(4-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (9)

To a stirred soln of **28b** (43.8 mg, 22.7 μmol) in DMF (3 mL) was added hydrazine acetate (2.7 mg, 30 μmol). The mixture was stirred for 2 h, washed with brine, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was dissolved in trichloroacetonitrile (5 mL). Then DBU (3.2 μL, 22 μmol) was added and the reaction was stirred for 12 h. The resulting mixture was evaporated under diminished pressure and the residue was purified by preparative TLC (1:4 hexane–EtOAc containing 1% Et_3N) to afford 36.4 mg (79%) of **9**; $[\alpha]_D$ −13.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H, N*H*), 7.83–7.64 (m, 8H, Ar), 6.54 (d, *J* 8.8 Hz, 1H), 5.88 (dd, *J* 8.8, 10.5 Hz, 1H), 5.64 (dd, *J* 9.0, 10.5 Hz, 1H), 5.33–5.26 (m, 3H), 5.18–5.01 (m, 5H), 4.96–4.92 (m, 2H), 4.77–4.73 (m, 3H), 4.62 (br s, 1H), 4.50–4.45 (m, 2H), 4.41–4.22 (m, 6H), 4.11–3.81 (m, 9H), 3.75–3.68 (m, 3H), 3.57–3.43 (m, 4H), 2.24 (s, 3H, CH_3CO), 2.14–1.82 (m, 45H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.4, 170.0, 169.9, 169.8, 169.7, 169.5 × 2, 169.4, 169.2, 169.1, 168.9, 160.3, 134.3, 131.2, 131.1, 123.5, 99.6, 98.8, 98.2, 97.3, 97.0, 93.4, 90.1, 74.1, 73.5, 72.7, 72.1, 70.6, 69.7, 69.2, 68.9 × 2, 68.8, 68.7, 68.2, 67.8, 65.8, 65.6, 62.3, 62.2, 61.9 × 2, 54.4, 53.5, 21.1, 21.0, 20.9, 20.8, 20.7, 20.6 × 2, 20.5, 20.4; HRESIMS: found *m/z* 2056.43055 $[M+Na]^+$; calcd for $C_{85}H_{98}O_{48}N_3Cl_3Na$ 2056.42830.

3.17. (3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-(2,4-di-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (12)

Compound **28c** (56.9 mg, 33.1 μmol) was submitted to anomeric deacetylation and trichloroacetimidate formation as described for **9** to afford 44.6 mg (74%, two steps) of **12**; $[\alpha]_D$ +10.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H, N*H*), 7.81–7.66 (m, 8H, Ar), 6.53 (d, *J* 9.0 Hz, 1H), 5.89 (dd, *J* 9.0, 10.7 Hz, 1H), 5.63 (t, *J* 9.5 Hz, 1H), 5.39 (t, *J* 10.0 Hz, 1H), 5.31 (dd, *J* 3.2, 10.0 Hz, 1H), 5.24–5.22 (m, 3H), 5.13–5.07 (m, 2H), 5.00 (t, *J* 9.5 Hz, 1H), 4.81 (br s, 1H), 4.74 (dd, *J* 3.2, 10.0 Hz, 1H), 4.59–4.57 (m, 2H), 4.46–4.26 (m, 6H), 4.18–3.92 (m, 6H), 3.85–3.70 (m, 6H), 3.56–3.47 (m, 2H), 2.29 (s, 3H, CH_3CO), 2.15–1.93 (m, 36H, CH_3CO), 1.82 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5 × 2, 170.2, 170.0 × 2, 169.9, 169.8, 169.7, 169.6, 169.2 × 2, 160.2, 134.4, 134.3, 131.2, 131.0, 123.6, 123.5, 98.4, 97.5, 97.0, 96.8, 93.6, 90.1, 74.1, 73.8, 73.4, 73.0, 72.1, 70.6, 69.3 × 2, 69.2 × 2, 69.1 × 2, 68.8, 68.6, 67.6, 65.6, 65.0, 62.3, 62.2, 61.9, 61.8, 54.3, 53.4, 21.1, 21.0, 20.9, 20.8 × 2, 20.7 × 2, 20.6, 20.5 × 2, 20.4; HRESIMS: found *m/z* 1840.36317 $[M+Na]^+$; calcd for $C_{76}H_{86}O_{42}N_3Cl_3Na$ 1840.36491.

3.18. Benzyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-*p*-methoxybenzyl-2-phthalimido-β-D-glucopyranoside (32)

To a stirred soln of **31** (975 mg, 2.0 mmol) in CH_2Cl_2 (10 mL) were added PMB–OC(NH)CCl_3 (5.0 mmol) in CH_2Cl_2 (10 mL), and La(OTf)$_3$ (117 mg, 0.2 mmol), successively, and stirring was continued for 17 h. Additional amounts of PMB–OC(NH)CCl_3 (1.0 mmol) in CH_2Cl_2 (2 mL), and La(OTf)$_3$ (23.4 mg, 0.04 mmol) were added. The mixture was stirred for 3 h and quenched with Et_3N (2 mL). The resulting mixture was diluted with EtOAc, washed with satd aq $NaHCO_3$ and brine, successively, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was purified by silica gel column chromatography (5:1→4:1 hexane–EtOAc) and recrystallization from 2-propanol to afford 954 mg (79%) of **32**; $[\alpha]_D$ +10.4 (*c* 1.0, $CHCl_3$); mp 125–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (br, 3H, Ar), 7.52–7.50 (m, 3H, Ar), 7.40–7.35 (m, 3H, Ar), 7.03–6.97 (m, 4H, Ar), 6.87 (d, *J* 8.5 Hz, 2H, Ar), 6.33 (d, *J* 8.5 Hz, 2H, Ar), 5.61 (s, 1H, benzylidene-H), 5.18 (d, *J* 8.5 Hz, 1H, H-1^{GlcN}), 4.68 (d, *J* 12.4 Hz, 1H, ArC*H*H), 4.68 (d, *J* 12.2 Hz, 1H, ArC*H*H), 4.47–4.34 (m, 4H, ArCH_2, H-3,6a^{GlcN}), 4.20 (dd, *J* 8.4, 10.3 Hz, 1H, H-2^{GlcN}), 3.86 (t, *J* 10.3 Hz, 1H, H-6b^{GlcN}), 3.79 (t, *J* 9.3 Hz, 1H, H-4^{GlcN}), 3.64–3.56 (m, 4H, H-5^{GlcN}, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 158.7, 137.2, 136.8, 133.5, 131.5, 130.0, 129.6, 128.9, 128.2, 128.1, 127.6, 127.5, 126.0, 123.0, 113.2, 101.3, 97.8, 83.0, 74.0, 73.6, 71.1, 68.8, 66.1, 55.9, 54.9; HRESIMS: found *m/z* 630.20998 $[M+Na]^+$; calcd for $C_{36}H_{33}O_8NNa$ 630.21039.

3.19. Benzyl 2-deoxy-3-*O*-*p*-methoxybenzyl-2-phthalimido-β-D-glucopyranoside (33)

To a stirred soln of **32** (27.2 mg, 44.8 μmol) in MeCN (1 mL) and MeOH (1 mL), was added TsOH·H_2O

(29.9 mg, 157 μmol). The reaction mixture was stirred for 11 h at room temperature and was then quenched with Et_3N (50 μL). The resulting mixture was diluted with EtOAc, washed with satd aq $NaHCO_3$ and brine, successively, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was purified by preparative TLC (1:2 hexane–EtOAc) to afford 18.2 mg (78%) of **33**; $[\alpha]_D$ −4.8 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.78–7.57 (br, 4H, Ar), 7.10–6.94 (m, 7H, Ar), 6.50–6.47 (m, 2H, Ar), 5.17 (d, *J* 8.3 Hz, 1H, H-1^{GlcN}), 4.74 (d, *J* 12.2 Hz, 1H, ArC*H*H), 4.55 (d, *J* 12.2 Hz, 1H, ArC*H*H), 4.48 (d, *J* 12.2 Hz, 1H, ArC*H*H), 4.42 (d, *J* 12.2 Hz, 1H, ArC*H*H), 4.22 (dd, *J* 8.3, 10.5 Hz, 1H, H-3^{GlcN}), 4.14 (dd, *J* 8.3, 10.5 Hz, 1H, H-2^{GlcN}), 3.95–3.90 (m, 1H, H-6a^{GlcN}), 3.86–3.79 (m, 1H, H-6b^{GlcN}), 3.76–3.70 (m, 1H, H-4^{GlcN}), 3.61 (s, 3H, OCH_3), 3.52–3.48 (m, 1H, H-5^{GlcN}), 2.48 (d, *J* 3.7 Hz, 1H, 4-OH^{GlcN}), 2.05 (t, *J* 6.5 Hz, 1H, 6-OH^{GlcN}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 158.8, 137.0, 133.6, 131.5, 130.1, 129.4, 128.1, 127.6, 123.1, 113.5, 97.6, 78.7, 75.2, 74.0, 72.1, 71.2, 62.4, 55.6, 54.9; HRESIMS: found *m*/*z* 542.17507 $[M+Na]^+$; calcd for $C_{29}H_{29}O_8NNa$ 542.17909.

3.20. Benzyl (3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→6)-2-deoxy-3-*O*-*p*-methoxybenzyl-2-phthalimido-β-D-glucopyranoside (10)

A mixture of preactivated molecular sieves 4 Å (800 mg), **11** (168 mg, 455 μmol) and **33** (169 mg, 325 μmol), and DTBMP (281 mg, 1.37 mmol) in cyclopentyl methyl ether (CPME) (15 mL) was stirred at room temperature for 30 min. MeOTf (1 M 1,2-dichloroethane soln, 1.4 mL) was added. After being stirred for 8 h at room temperature, **11** (36.0 mg, 97.5 μmol) in CPME (1 mL), and MeOTf (1 M 1,2-dichloroethane soln, 290 μL) were added, successively, and stirred for 14 h at the same temperature. The reaction was quenched with Et_3N (1 mL) and filtered through Celite. The filtrate was diluted with EtOAc, washed with brine, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was purified by silica gel column chromatography (3:1→2:1 hexane–EtOAc, linear gradient) to afford 179 mg (66%) of **10**; $[\alpha]_D$ −65.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.76–7.50 (br, 4H, Ar), 7.35–7.25 (m, 5H, Ar), 7.06–6.99 (m, 5H, Ar), 6.90 (d, *J* 8.5 Hz, 2H, Ar), 6.40 (d, *J* 8.5 Hz, 2H, Ar), 5.33 (dd, *J* 3.4, 10.2 Hz, 1H, H-3^{Fuc}), 5.30–5.29 (m, 1H, H-4^{Fuc}), 5.10–5.08 (m, 1H, H-1^{GlcN}), 4.88 (d, *J* 3.7 Hz, 1H, H-1^{Fuc}), 4.72 (d, *J* 12.2 Hz, 2H, ArCH_2), 4.63–4.57 (m, 2H, ArCH_2), 4.41 (d, *J* 12.2 Hz, 1H, ArC*H*H), 4.38 (d, *J* 12.2 Hz, 1H, ArC*H*H), 4.26–4.21 (br, 1H, H-5^{Fuc}), 4.17–4.13 (m, 2H, H-2,3-H^{GlcN}), 3.95 (dd, *J* 4.2, 11.2 Hz, 1H, H-6a^{GlcN}), 3.88–3.83 (m, 3H, H-4,6b^{GlcN}, H-2^{Fuc}), 3.60–3.54 (m, 4H, H-5^{GlcN}, OCH_3), 3.33 (d, *J* 3.4 Hz, 1H, 4-OH^{GlcN}), 2.14 (s, 3H, CH_3CO), 1.99 (s, 3H, CH_3CO), 1.10 (d, *J* 6.6 Hz, 3H, 6-CH_3^{Fuc}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 169.8, 158.6, 137.6, 137.0, 133.5, 131.5, 130.4, 129.5, 128.4, 128.0, 127.9, 127.5, 127.4, 123.1, 122.9, 113.3, 98.0, 97.2, 77.7, 73.8, 73.7, 73.6, 73.4, 73.3, 71.6, 70.6, 70.3, 68.5, 64.8, 55.5, 54.9, 20.9, 20.8, 15.9. Anal. Calcd for $C_{46}H_{49}NO_{14}$: C, 65.78; H, 5.88; N, 1.67. Found: C, 65.42; H, 5.70; N, 1.60.

3.21. Benzyl 6-*O*-benzyl-2-deoxy-3-*O*-*p*-methoxybenzyl-2-phthalimido-β-D-glucopyranoside (13)

To a stirred soln of compound **32** (30.4 mg, 50.0 μmol) in THF (2 mL) was added $BH_3{\cdot}NMe_3$ (18.2 mg, 250 μmol) at room temperature, then $AlCl_3$ (33.3 mg, 250 μmol) was added at ice-cold temperature. After being stirred for 20 h at room temperature, the mixture was quenched with water (2 mL) and 1 M HCl (5 mL). The resulting mixture was diluted with EtOAc, washed with brine, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was purified by preparative TLC (1:1 hexane–EtOAc) to afford 20.0 mg (66%) of **13**; $[\alpha]_D$ −7.8 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.77–6.99 (m, 14H, Ar), 6.94 (d, *J* 8.5 Hz, 2H, Ar), 6.42 (d, *J* 8.5 Hz, 2H, Ar), 5.14 (d, *J* 7.8 Hz, 1H, H-1^{GlcN}), 4.77 (d, *J* 12.4 Hz, 1H, ArC*H*H), 4.67–4.57 (m, 3H, ArCH_2), 4.47–4.42 (m, 2H, ArCH_2), 4.23–4.14 (m, 2H, H-2,3^{GlcN}), 3.86–3.76 (m, 3H, H-4,6^{GlcN}), 3.65–3.60 (m, 1H, H-5^{GlcN}), 3.59 (s, 3H, OCH_3), 2.93 (d, *J* 2.7 Hz, 1H, 4-OH^{GlcN}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 158.6, 137.6, 137.0, 133.5, 131.5, 130.2, 129.4, 128.4, 128.0, 127.8, 127.7, 127.5, 127.4, 123.1, 122.9, 113.3, 97.3, 78.2, 74.2, 73.8, 73.7, 73.6, 70.7, 70.6, 55.4, 54.8; HRESIMS: found *m*/*z* 623.22545 $[M+Na]^+$; calcd for $C_{36}H_{35}O_8NNa$ 623.22604.

3.22. Benzyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→2)]-(4-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→6)]-2-deoxy-3-*O*-*p*-methoxybenzyl-2-phthalimido-β-D-glucopyranoside (34)

A mixture of preactivated molecular sieves 4 Å (200 mg) and compounds **9** (44.1 mg, 21.7 μmol) and **10** (36.5 mg, 43.4 μmol) in CH_2Cl_2 (2 mL) was stirred at −78 °C for 30 min. TMSOTf (0.05 M CH_2Cl_2 soln, 87 μL) was added and the reaction was stirred at −40 °C for 4.5 h. The reaction was quenched with Et_3N (50 μL) and filtered through Celite. The filtrate was diluted with EtOAc, washed with satd aq $NaHCO_3$ and brine, successively, dried over $MgSO_4$, and evaporated under

diminished pressure. The residue was purified by preparative TLC (1:3 hexane–EtOAc) to afford 43.8 mg (74%) of **34** and 19.7 mg (54% recovery) of **10**. Compound **34**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–6.81 (m, 24H, Ar), 6.22 (d, *J* 8.3 Hz, 2H, Ar), 5.81 (dd, *J* 9.3, 10.8 Hz, 1H), 5.66 (dd, *J* 9.3, 10.8 Hz, 1H), 5.52 (d, *J* 8.3 Hz, 1H), 5.29–4.85 (m, 15H), 4.76–4.22 (m, 17H), 4.15–3.62 (m, 19H), 3.55–3.29 (m, 8H), 2.23 (s, 3H, CH_3CO), 2.11–1.84 (m, 51H, CH_3CO), 1.03 (d, *J* 6.3 Hz, 3H, 6-CH_3^{Fuc}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.4, 170.3, 170.2, 169.9, 169.8, 169.7, 169.6, 169.5, 169.4, 169.3, 169.1, 169.0, 168.8, 168.0, 167.1, 158.2, 138.0, 136.8, 134.6, 134.3, 133.1, 131.4, 131.2, 131.1, 130.8, 129.5, 128.3, 127.9, 127.6, 127.3, 127.2, 123.7, 123.4, 122.6, 113.0, 99.5, 98.6, 98.0, 97.4, 97.0, 96.9, 96.8, 96.5, 76.2, 75.6, 74.1, 73.9, 72.6, 72.3, 72.2, 72.1, 71.7, 70.7, 70.1, 70.0, 69.5, 69.3, 68.9, 68.7, 68.5, 67.9, 65.8, 65.6, 65.4, 64.2, 62.3, 62.1, 62.0, 61.9, 55.7, 55.1, 54.7, 54.4, 21.1, 21.0, 20.9, 20.8, 20.7, 20.6, 16.0; HRESIMS: found *m*/*z* 2734.82033 $[M+Na]^+$; calcd for $C_{129}H_{145}O_{61}N_3Na$ 2734.82341.

3.23. Benzyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→2)]-(4-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→6)]-2-deoxy-2-phthalimido-β-D-glucopyranoside (35)

To a mixture of **33** (13.9 mg, 5.12 μmol) in dry CH_2Cl_2 (1.5 mL) were added $Mn(OAc)_3{\cdot}2H_2O$ (4.9 mg, 18 μmol) and DDQ (1.4 mg, 6.1 μmol) successively at room temperature. After being stirred for 48 h at the same temperature, the reaction was quenched with satd aq $NaHCO_3$ and diluted with EtOAc. The organic layer was washed with an aq soln of ascorbic acid (0.7%)–citric acid (1.3%)–NaOH (0.9%) and brine, successively, dried over Na_2SO_4, and evaporated under diminished pressure. The residue was purified by preparative TLC (1:2 toluene–EtOAc) to afford 12.9 mg (97%) of **35**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–6.94 (m, 22H, Ar), 5.83–5.78 (m, 1H), 5.66 (dd, *J* 9.0, 10.7 Hz, 1H), 5.38 (d, *J* 8.3 Hz, 1H), 5.32–5.26 (m, 3H), 5.16–5.06 (m, 6H), 5.02 (t, *J* 5.4 Hz, 1H), 4.98–4.92 (m, 2H), 4.87–4.85 (m, 2H), 4.79 (d, *J* 1.2 Hz, 1H), 4.73–4.71 (m, 2H), 4.65–4.57 (m, 4H), 4.43–4.21 (m, 10H), 4.14–3.63 (m, 17H), 3.52–3.29 (m, 7H), 2.25 (s, 3H, CH_3CO), 2.16 (s, 3H, CH_3CO), 2.09–1.84 (m, 48H, CH_3CO), 0.98 (d, *J* 6.3 Hz, 3H, 6-CH_3^{Fuc}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.4, 170.3, 170.2, 170.0, 169.9, 169.8, 169.6, 169.4, 169.3, 169.1, 169.0, 168.7, 167.7, 138.1, 136.8, 134.6, 134.3, 133.7, 131.6, 131.2, 128.4, 128.0, 127.6, 127.4, 127.3, 127.2, 123.4, 98.7, 98.5, 98.2, 98.0, 97.3, 97.2, 97.0, 96.9, 77.1, 74.2, 73.0, 72.6, 72.3, 72.2, 72.1, 71.4, 70.7, 70.4, 69.9, 69.6, 69.5, 69.3, 69.1, 69.0, 68.8, 68.5, 68.4, 67.9, 67.7, 65.7, 65.5, 64.2, 62.4, 62.3, 62.2, 61.9, 55.9, 54.5, 54.4, 21.1, 21.0, 20.9, 20.8, 20.7, 20.6, 20.5, 16.0; HRESIMS: found *m*/*z* 2614.76628 $[M+Na]^+$; calcd for $C_{121}H_{137}O_{60}N_3Na$ 2614.76589.

3.24. Benzyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→2)]-(4-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→6)]-[(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-2-deoxy-2-phthalimido-β-D-glucopyranoside (36)

To a mixture of **11** (4.3 mg, 12 μmol) and **35** (10.1 mg, 3.89 μmol), DTBMP (3.6 mg, 18 μmol) and preactivated MS 4 Å (0.25 g) in dry *p*-xylene (5 mL) was added MeOTf (35.4 μL, 167 μmol) at room temperature. The mixture was rapidly mixed and frozen by liquid nitrogen. The mixture was stored in a refrigerator at 4 °C for 84 h and defrosted at room temperature. The reaction was quenched with Et_3N and the mixture was filtrated through Celite. The filtrate was diluted with EtOAc, washed with brine, dried over Na_2SO_4, and evaporated under diminished pressure. After gel filtration (Bio-Beads SX-3, 1:1 toluene–EtOAc), to a mixture of the residue, **11** (4.3 mg, 12 μmol), DTBMP (3.6 mg, 17.5 μmol) and preactivated MS 4 Å (0.25 g) in dry *p*-xylene (5 mL) was added MeOTf (35.4 μL, 167 μmol) at room temperature. The mixture was rapidly mixed and frozen by liquid nitrogen. The mixture was stored in a refrigerator at 4 °C for 84 h and defrosted at room temperature. The reaction was quenched with Et_3N and the mixture was filtrated through Celite. The filtrate was diluted with EtOAc, washed with brine, dried over Na_2SO_4 and evaporated under diminished pressure. The residue was purified by gel filtration (Bio-Beads SX-3, 1:1 toluene–EtOAc), then by preparative TLC (1:2 hexane–EtOAc) to afford 10.2 mg (90%) of **36**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–6.85 (m, 27H, Ar), 5.76–5.71 (m, 1H), 5.68–5.63 (m, 1H), 5.59 (d, *J* 8.3 Hz, 1H), 5.32–4.53 (m, 26H), 4.41–3.25 (m, 35H), 2.22–1.79 (m, 60H, CH_3CO), 1.11 (d, *J* 6.3 Hz, 3H, 6-CH_3^{Fuc}), 1.03 (d, *J* 6.3 Hz, 3H, 6-CH_3^{Fuc}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 170.5, 170.4, 170.3. 170.2, 169.9, 169.7, 169.6, 169.5, 169.4, 169.3, 169.1, 169.0, 168.8, 167.9, 166.8, 137.9, 137.8, 136.6, 134.4, 133.7, 131.5, 131.3, 131.2, 131.1, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.4, 127.3, 127.2, 123.6, 123.4, 100.6, 98.8, 98.3, 98.0, 97.4, 96.9, 96.4, 96.3, 95.8, 77.6, 76.4, 74.2, 74.0, 73.8, 73.0, 72.6, 72.2, 72.1, 71.8,

71.7, 70.7, 70.5, 70.2, 70.0, 69.3, 69.1, 69.0, 68.9, 68.8, 68.7, 68.6, 68.3, 65.7, 65.6, 65.4, 64.6, 64.3, 62.6, 62.3, 62.1, 61.9, 60.0, 56.5, 55.1, 54.4, 21.1, 21.0, 20.9, 20.8, 20.7, 20.6, 20.5, 16.0; HRESIMS: found *m*/*z* 2934.88712 $[M+Na]^+$; calcd for $C_{138}H_{157}O_{66}N_3Na$ 2934.89188.

3.25. Benzyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→2)]-(4-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (37)

A mixture of preactivated molecular sieves 4 Å (200 mg) and compounds **9** (75.5 mg, 37.1 μmol) and **13** (45.2 mg, 74.2 μmol) in CH_2Cl_2 (3 mL) was stirred at −78 °C for 20 min. TMSOTf (0.05 M CH_2Cl_2 soln, 148 μL) was added and the reaction was stirred at −50 °C for 1.5 h. It was then quenched with Et_3N (100 μL) and filtered through Celite. The filtrate was diluted with EtOAc, washed with satd aq $NaHCO_3$ and brine, successively, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was purified by chromatography on Bio-Beads SX-3 (toluene) and then with preparative TLC (1:3 hexane–EtOAc) to afford the protected heptasaccharide. It was then dissolved in CH_2Cl_2 (3 mL), and $Mn(OAc)_3{\cdot}2H_2O$ (28.7 mg, 107 μmol) and DDQ (8.1 mg, 35.8 μmol) were added, successively. After being stirred for 12 h at room temperature, the reaction was quenched with satd aq $NaHCO_3$ and diluted with EtOAc. The organic layer was washed with water and brine, successively, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was purified by preparative TLC (2:7 toluene–EtOAc) to afford 62.8 mg (72%, two steps) of **37**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.00 (m, 22H, Ar), 5.85 (br, 1H), 5.66 (br, 1H), 5.45 (d, $J = 8.8$ Hz, 1H), 5.31–5.25 (m, 3H), 5.17–4.98 (m, 5H), 4.95–4.92 (br, 1H), 4.87 (d, $J = 3.2$ Hz, 1H), 4.79–4.69 (m, 4H), 4.60 (br, 1H), 4.50 (br, 1H), 4.44–4.22 (m, 9H), 4.14–3.93 (m, 10H), 3.86–3.68 (m, 8H), 3.57–3.42 (m, 5H), 3.24 (br, 2H), 2.26 (s, 3H, C*H*$_3$CO), 2.10–1.79 (m, 45H, C*H*$_3$CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.3, 170.2, 169.8, 169.7, 169.6, 169.5, 169.4, 169.3, 169.2, 169.0, 168.9, 168.7, 167.4, 166.8, 137.8, 136.9, 134.2, 133.7, 131.5, 131.2, 131.1, 127.9, 127.3, 127.1, 127.0, 123.4, 123.1, 98.7, 98.4, 98.2, 97.2, 97.0, 81.7, 74.2, 73.9, 72.7, 72.6, 72.2, 72.1, 70.6, 70.5, 69.7, 69.4, 69.3, 69.2, 68.9, 68.7, 68.6, 68.5, 68.3, 68.2, 67.9, 67.6, 65.6, 65.5, 62.5, 62.3, 62.2, 61.8, 55.9, 54.6, 54.3, 21.1, 21.0, 20.9, 20.8, 20.7, 20.6, 20.5, 20.4; HRESIMS: found *m*/*z* 2384.68627 $[M+Na]^+$; calcd for $C_{111}H_{123}O_{54}N_3Na$ 2384.68686.

3.26. Benzyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→2)]-(4-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-2-deoxy-2-phthalimido-β-D-glucopyranoside (38)

A mixture of preactivated molecular sieves 4 Å (200 mg), **11** (8.5 mg, 23.0 μmol) and **37** (27.1 mg, 11.5 μmol), and DTBMP (11.8 mg, 57.5 μmol) in cyclopentyl methyl ether (CPME) (2 mL) was stirred at room temperature for 20 min, and MeOTf (6.5 μL, 57.5 μmol) was added. After being stirred at the same temperature for 10 h, an additional amount of MeOTf (1.3 μL, 11.5 μmol) was added, then stirred for 13 h. The reaction was quenched with Et_3N (50 μL) and filtered through Celite. The filtrate was diluted with EtOAc, washed with brine, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was purified by preparative TLC (1:3 toluene–EtOAc) and then chromatography with Bio-Beads SX-3 (toluene) to afford 26.3 mg (85%) of **38**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85–6.90 (m, 27H, Ar), 5.73–5.63 (m, 2H), 5.47 (d, J 8.5 Hz, 1H), 5.30–5.07 (m, 10H), 5.00 (dd, J 3.4, 10.2 Hz, 1H), 4.93–4.88 (m, 3H), 4.78–4.52 (m, 9H), 4.41–4.15 (m, 12H), 4.09–3.81 (m, 9H), 3.74–3.49 (m, 10H), 3.39–3.34 (m, 2H), 2.24 (s, 3H, C*H*$_3$CO), 2.10–1.80 (m, 51H, C*H*$_3$CO), 1.11 (d, J 6.6 Hz, 3H, 6-CH_3^{Fuc}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.4, 170.3, 169.9, 169.7, 169.6, 169.5, 169.4, 169.3, 169.2, 169.1, 169.0, 168.9, 167.7, 167.4, 166.9, 138.1, 137.8, 136.8, 134.3, 134.2, 134.1, 133.7, 131.6, 131.3, 131.2, 128.5, 128.2, 127.9, 127.5, 127.4, 127.3, 127.2, 127.1, 123.4, 123.3, 100.4, 98.8, 98.5, 97.9, 97.1, 96.9, 96.7, 96.2, 96.0, 77.6, 75.9, 74.6, 74.2, 73.6, 73.4, 72.8, 72.3, 72.2, 72.1, 72.0, 71.9, 71.6, 71.0, 70.7, 70.6, 70.5, 70.1, 69.3, 69.0, 68.9, 68.8, 68.7, 68.2, 68.0, 65.7, 65.5, 64.6, 62.6, 62.2, 61.9, 56.3, 55.1, 54.4, 21.1, 21.0, 20.9, 20.8, 20.7, 20.6, 16.0; HRESIMS: found *m*/*z* 2704.80928 $[M+Na]^+$; calcd for $C_{128}H_{143}O_{60}N_3Na$ 2704.81284.

3.27. (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(α-D-mannopyranosyl)-(1→3)-[(α-D-mannopyranosyl)-(1→6)]-[(β-D-xylopyranosyl)-(1→2)]-(β-D-mannopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-[(α-L-fucopyranosyl)-(1→6)]-[(α-L-fucopyranosyl)-(1→3)]-2-acetamido-2-deoxy-D-glucopyranose (1)

Compound **36** (9.4 mg, 3.22 μmol) was treated with ethylenediamine (50 μL) in *n*-BuOH (1.5 mL) at 85 °C. The resulting mixture was evaporated under diminished pressure and the residue was dissolved in pyridine (1 mL). Subsequently, Ac_2O (0.5 mL) was added at

ice-water temperature, and the reaction was stirred for 6 h at room temperature. The mixture was quenched with EtOH (2 mL) at ice-cold temperature and evaporated under diminished pressure. The residue was dissolved in MeOH (1.5 mL) and MeONa (5 mg) was added. After being stirred for 12 h, the mixture was quenched with Amberlyst-15 and filtered. The filtrate was evaporated under diminished pressure and the residue was purified by Sep-Pak® (C_{18}, 0–50% aq MeOH). Fractions containing the nonasaccharide were collected and concentrated. The residue was dissolved in aq MeOH (20 mL) and 20% $Pd(OH)_2$ (5 mg) was added. The mixture was stirred under an H_2 atmosphere at room temperature for 12 h and then filtered through Celite. The filtrate was evaporated under diminished pressure and filtered through ultrafree®-MC by centrifugation, then the residue was purified by FPLC (Pharmacia, column: Super Peptide 10/300GL, water) to afford 4.3 mg (87%) of **1**; ^{1}H NMR (400 MHz, D_2O, acetone at δ 2.22): δ 5.14 (br s, 1H, H-1$^{\alpha Man}$), 5.11 (d, J 3.9 Hz, 1H, H-1$^{\alpha 1\rightarrow 3Fuc}$), 5.06 (d, J 3.4 Hz, 0.6H, H-1$^{\alpha GlcN}$), 4.92 (d, J 3.9 Hz, 1H, H-1$^{\alpha 1\rightarrow 6Fuc}$), 4.91 (br s, 1H, H-1$^{\alpha Man}$), 4.85 (br s, 1H, H-1$^{\beta Man}$), 4.71–4.66 (m, 1.4H, H-1$^{\beta GlcN}\times 2$), 4.51 (d, J 8.5 Hz, 1H, H-1$^{\beta GlcN}$), 4.45 (d, J 7.6 Hz, 1H, H-1$^{\beta Xyl}$), 4.25 (br s, 1H, H-2$^{\beta Man}$), 3.26 (t, J 11.0 Hz, 1H), 2.05–2.02 (m, 9H, CH_3CO), 1.27 (d, J 6.6 Hz, 3H, 6-CH_3^{Fuc}), 1.22 (d, J 6.6 Hz, 1.2H, 6-CH_3^{Fuc}), 1.20 (d, J 6.6 Hz, 1.8H, 6-CH_3^{Fuc}); ^{13}C NMR (125 MHz, D_2O, acetone at δ 30.89): δ 175.4 × 2, 175.1, 174.9, 105.9, 101.2, 100.7, 100.3, 100.0, 99.8, 99.7 × 2, 81.6, 80.1 × 2, 78.8, 77.8, 77.7, 77.2, 76.5, 75.9, 75.0, 74.3, 74.0, 73.9, 73.4, 73.1, 72.7, 72.5, 71.1, 70.9, 70.6, 70.5, 70.2, 70.1, 69.9 × 2, 69.2, 68.8, 68.4, 67.9, 67.5, 67.3, 67.2, 66.1 × 2, 62.4, 61.6, 61.3, 56.0, 55.7, 54.6, 23.9, 23.0, 22.9, 22.7, 20.7, 16.2, 16.0; HRESIMS: found m/z 1560.55120 $[M+Na]^+$; calcd for $C_{59}H_{99}O_{43}N_3Na$ 1560.55499.

3.28. (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(α-D-mannopyranosyl)-(1→3)-[(α-D-mannopyranosyl)-(1→6)]-[(β-D-xylopyranosyl)-(1→2)]-(β-D-mannopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-[(α-L-fucopyranosyl)-(1→6)]-2-acetamido-2-deoxy-D-glucopyranose (2)

Compound **34** (13.1 mg, 4.83 μmol) was submitted sequentially to dephthaloylation, acetylation, O-deacetylation, and debenzylation as described for compound **1** to afford 4.9 mg (73%, four steps) of **2**; ^{1}H NMR (400 MHz, D_2O, acetone at δ 2.22): δ 5.17 (d, J 3.4 Hz, 0.67H, H-1$^{\alpha GlcN}$), 5.13 (br s, 1H, H-1$^{\alpha Man}$), 4.91 (br s, 1H, H-1$^{\alpha Man}$), 4.90–4.88 (m, 1H, H-1$^{\alpha 1\rightarrow 6Fuc}$), 4.87 (br s, 1H, H-1$^{\beta Man}$), 4.67–4.64 (m, 1.33H, H-1$^{\beta GlcN}\times 2$), 4.51 (d, J 8.5 Hz, 1H, H-1$^{\beta GlcN}$), 4.44 (d, J 7.8 Hz, 1H, H-1$^{\beta Xyl}$), 4.25 (br s, 1H, H-2$^{\beta Man}$), 3.25 (t, J 11.0 Hz, 1H), 2.08–2.03 (m, 9H, CH_3CO), 1.22–1.20 (m, J 6.6 Hz, 3H, 6-CH_3^{Fuc}); ^{13}C NMR (125 MHz, D_2O, acetone at δ 30.89): δ 175.4, 175.3, 175.1, 105.8, 101.7, 101.2, 100.4, 100.3, 100.2, 100.0, 99.8, 95.6 × 2, 91.2, 80.3, 79.6, 79.3, 77.8, 77.2, 76.5, 75.9, 75.0, 74.3, 74.0, 73.9, 73.4, 72.8, 72.5, 71.1, 70.6, 70.5, 70.2, 70.1, 69.9, 69.8 × 2, 68.8 67.9, 67.7, 67.5, 67.3, 67.2, 66.1, 65.6, 62.4, 61.6, 61.3, 60.8, 60.7, 56.9, 56.0, 55.7 × 2, 55.6, 54.4, 23.0, 22.5, 16.0; HRESIMS: found m/z 1414.49218 $[M+Na]^+$, calcd for $C_{53}H_{89}O_{39}N_3Na$ 1414.49709.

3.29. (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(α-D-mannopyranosyl)-(1→3)-*O*-[(α-D-mannopyranosyl)-(1→6)]-[(β-D-xylopyranosyl)-(1→2)]-(β-D-mannopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-2-acetamido-2-deoxy-D-glucopyranose (3)

Compound **37** (12.0 mg, 5.08 μmol) was submitted sequentially to dephthaloylation, acetylation, O-deacetylation, and debenzylation as described for **1** to afford 5.6 mg (88%, four steps) of **3**: ^{1}H NMR (400 MHz, D_2O, acetone at δ 2.22): δ 5.18 (d, J 1.7 Hz, 0.62H, H-1$^{\alpha GlcN}$), 5.13 (br s, 1H, H-1$^{\alpha Man}$), 4.91 (br s, 1H, H-1$^{\alpha Man}$), 4.87 (br s, 1H, H-1$^{\beta Man}$), 4.69–4.68 (m, 0.38H, H-1$^{\beta GlcN}$), 4.61–4.59 (m, 1H, H-1$^{\beta GlcN}$), 4.51 (d, J 8.3 Hz, 1H, H-1$^{\beta GlcN}$), 4.43 (d, J 7.5 Hz, 1H, H-1$^{\beta Xyl}$), 4.25 (d, J 2.7 Hz, 1H, H-2$^{\beta Man}$), 4.03 (d, J 3.2 Hz, 1H, H-2$^{\alpha Man}$), 3.24 (t, J 11.0 Hz, 1H), 2.07–2.03 (m, 9H, CH_3CO); ^{13}C NMR (100 MHz, D_2O, acetone at δ 30.89): δ 175.0, 174.9, 174.7, 105.6, 101.8, 101.0, 100.2, 100.1, 99.7, 95.3, 90.9, 80.2, 80.1, 79.9, 79.7, 77.6, 77.1, 76.4, 75.9, 75.1, 74.9, 74.2, 73.8, 73.3, 73.0, 72.6, 71.0, 70.6, 70.5, 70.4, 70.0, 69.8, 69.0, 67.7, 67.2, 67.1, 65.9, 65.5, 62.3, 61.5, 61.2, 60.6, 56.7, 55.9, 55.6, 54.2, 23.0, 22.8, 22.5, 20.7; HRESIMS: found m/z 1268.44085 $[M+Na]^+$; calcd for $C_{47}H_{79}O_{35}N_3Na$ 1268.43918.

3.30. (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(α-D-mannopyranosyl)-(1→3)-[(α-D-mannopyranosyl)-(1→6)]-[(β-D-xylopyranosyl)-(1→2)]-(β-D-mannopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-[(α-L-fucopyranosyl)-(1→3)]-2-acetamido-2-deoxy-D-glucopyranose (4)

Compound **38** (13.6 mg, 5.07 μmol) was submitted sequentially to dephthaloylation, acetylation, O-deacetylation, and debenzylation as described for **1** to afford 4.8 mg (68%, four steps) of **4**: ^{1}H NMR (400 MHz, D_2O, acetone at δ 2.22): δ 5.14 (br s, 1H, H-1$^{\alpha Man}$), 5.11 (d, J 3.7 Hz, 1H, H-1$^{\alpha 1\rightarrow 3Fuc}$), 5.07 (d, J 3.4 Hz, 0.55H, H-1$^{\alpha GlcN}$), 4.91 (br s, 1H, H-1$^{\alpha Man}$), 4.84 (br s, 1H, H-1$^{\beta Man}$), 4.69–4.67 (m, 0.45H, H-1$^{\beta GlcN}$), 4.56–4.52 (m, 2H, H-1$^{\beta GlcN}\times 2$), 4.47 (d, J 7.6 Hz, 1H, H-1$^{\beta Xyl}$), 4.25 (d, J 2.7 Hz, 1H, H-2$^{\beta Man}$), 4.15 (d, J 2.9 Hz, 1H, H-2$^{\alpha Man}$), 3.25 (t, J 11.0 Hz, 1H), 2.07–2.02 (m, 9H, CH_3CO), 1.27 (d, J 6.6 Hz, 3H, 6-CH_3^{Fuc}); ^{13}C NMR (100 MHz, D_2O, acetone at δ 30.89): δ 175.0 × 2,

174.7, 174.5, 105.6, 101.0, 100.9, 100.2 × 2, 99.6, 98.9, 91.3, 81.3, 79.8, 77.5, 77.0, 76.4, 75.9, 75.1, 74.9, 74.2, 73.8 × 2, 73.3, 73.1, 72.9, 72.6, 71.9, 71.0, 70.5, 70.3, 69.9, 69.8 × 2, 68.3, 67.8, 67.2, 67.1, 65.9, 65.5, 62.3, 61.6, 61.5, 61.2, 57.4, 55.9, 55.7, 54.5, 23.0, 22.9, 22.8, 22.7, 20.7, 16.2; HRESIMS: found *m/z* 1414.49839 $[M+Na]^+$; calcd for $C_{53}H_{89}O_{39}N_3Na$ 1414.49709.

3.31. Benzyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-(2,4-di-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→6)]-2-deoxy-3-*O*-*p*-methoxybenzyl-2-phthalimido-β-D-glucopyranoside (39)

Compound **12** (44.6 mg, 24.5 μmol) was glycosylated with **10** as described for **34** to afford 43.0 mg (70%) of **39**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–6.88 (m, 22H, Ar), 6.83 (d, *J* 8.5 Hz, 2H, Ar), 6.23 (d, *J* 8.5 Hz, 2H, Ar), 5.79 (dd, *J* 9.3, 10.7 Hz, 1H), 5.64 (dd, *J* 9.3, 10.7 Hz, 1H), 5.55 (d, *J* 8.3 Hz, 1H), 5.32–5.21 (m, 6H), 5.17–5.10 (m, 3H), 5.08–4.97 (m, 2H), 4.92–4.90 (m, 1H), 4.77–4.73 (m, 3H), 4.69–4.65 (m, 2H), 4.59–4.56 (m, 2H), 4.44–4.00 (m, 16H), 3.96–3.93 (m, 1H), 3.89–3.64 (m, 10H), 3.52–3.43 (m, 5H), 3.37–3.26 (m, 2H), 2.27 (s, 3H, C*H*$_3$CO), 2.27–1.84 (m, 45H, C*H*$_3$CO), 1.01 (d, *J* 6.6 Hz, 3H, 6-C*H*$_3^{Fuc}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.4, 170.3, 170.2, 170.0, 169.9, 169.8, 169.7, 169.6, 169.5, 169.4, 169.0, 167.8, 167.1, 158.1, 137.9, 136.7, 134.4, 134.3, 133.1, 131.6, 131.3, 131.0, 130.7, 129.5, 128.3, 128.2, 127.9, 127.8, 127.5, 127.3, 127.2, 123.7, 123.4, 122.9, 122.5, 122.9, 98.3, 97.3, 96.9, 96.7, 96.5, 77.2, 76.4, 76.0, 75.4, 74.2, 74.0, 73.6, 72.5, 72.2, 72.1, 71.9, 71.7, 70.6, 70.0, 69.9, 69.5, 69.3, 69.2, 68.8, 68.6, 67.4, 65.6, 64.8, 64.1, 62.3, 62.0, 61.8, 60.4, 55.6, 55.0, 54.7, 54.3, 21.1, 20.9, 20.8, 20.7, 20.6, 20.5, 20.4, 15.9, 14.3; HRESIMS: found *m/z* 2518.76413 $[M+Na]^+$; calcd for $C_{120}H_{133}O_{55}N_3Na$ 2518.76002.

3.32. Benzyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-(2,4-di-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→6)]-2-deoxy-2-phthalimido-β-D-glucopyranoside (40)

To a stirred soln of **39** (27.5 mg, 11.0 μmol) in CH_2Cl_2 (1.5 mL) were added $Mn(OAc)_3{\cdot}2H_2O$ (11.5 mg, 42.9 mmol) and DDQ (3.2 mg, 14.3 mmol), successively. After being stirred for 13 h at room temperature, the reaction was quenched with satd aq $NaHCO_3$ and diluted with EtOAc. The organic layer was washed with water and brine, successively, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was purified by preparative TLC (1:3 toluene–EtOAc) to afford 24.0 mg (92%) of **40**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–6.95 (m, 22H, Ar), 5.74 (dd, *J* 9.3, 10.7 Hz, 1H), 5.64 (dd, *J* 9.3, 10.7 Hz, 1H), 5.39–5.04 (m, 11H), 4.95 (t, *J* 9.6 Hz, 1H), 4.89 (d, *J* 3.6 Hz, 1H), 4.80 (d, *J* 1.5 Hz, 1H), 4.76–4.73 (m, 2H), 4.66–4.58 (m, 3H), 4.47 (br s, 1H), 4.40–4.01 (m, 13H), 3.88–3.67 (m, 11H), 3.46–3.41 (m, 4H), 3.39–3.34 (m, 1H), 3.26–3.22 (m, 1H), 2.30 (s, 3H, C*H*$_3$CO), 2.15–1.84 (m, 45H, C*H*$_3$CO), 0.98 (d, *J* 6.6 Hz, 3H, 6-C*H*$_3^{Fuc}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.4, 170.2, 170.1, 170.0, 169.9, 169.8, 169.7, 169.6, 169.1, 167.7, 166.7, 138.1, 136.9, 134.5, 134.3, 133.7, 131.6, 131.1, 130.8, 128.4, 128.0, 127.5, 127.4, 127.3, 127.2, 123.9, 123.4, 98.3, 97.8, 97.3, 97.0, 96.9, 96.2, 80.2, 74.1, 74.0, 73.8, 73.3, 72.9, 72.5, 72.2, 72.1, 71.5, 70.6, 70.3, 70.0, 69.5, 69.5, 69.4, 69.3, 69.2, 69.1, 68.9, 68.7, 67.4, 65.6, 65.0, 64.1, 62.3, 62.2, 62.0, 61.8, 55.9, 54.4, 54.3, 29.8, 21.2, 21.0, 20.9, 20.8, 20.7, 20.6, 16.0; HRESIMS: found *m/z* 2398.70293 $[M+Na]^+$, calcd for $C_{112}H_{125}O_{54}N_3Na$ 2398.70251.

3.33. Benzyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-(2,4-di-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→6)]-[(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-2-deoxy-2-phthalimido-β-D-glucopyranoside (41)

A mixture of preactivated molecular sieves 4 Å (200 mg), compounds **11** (9.50 mg, 25.9 μmol) and **40** (20.5 mg, 8.62 μmol), and DTBMP (8.0 mg, 38.8 mmol) in *p*-xylene (1.5 mL) was stirred at room temperature for 30 min. Subsequently, MeOTf (7.3 μL, 64.7 μmol) was added, and the mixture was rapidly mixed and frozen by liquid nitrogen. The mixture was stored in a refrigerator at 4 °C for 84 h and was defrosted at room temperature. Et_3N (100 μL) was added to quench MeOTf and the mixture was filtered through Celite. The filtrate was diluted with EtOAc, washed with brine, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was purified by chromatography with Bio-Beads SX-3 (toluene) and then by preparative TLC (1:3 toluene–EtOAc) to afford 18.7 mg (80%) of **41**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85–6.87 (m, 27H, Ar), 5.79 (dd, *J* 8.8, 10.7 Hz, 1H), 5.67–5.62 (m, 2H), 5.29–5.08 (m, 12H), 4.94–4.86 (m, 3H), 4.77–4.53 (m, 8H), 4.43–3.67 (m, 27H), 3.59–3.50 (m, 3H), 3.43–3.36 (m, 2H), 2.25 (s, 3H, C*H*$_3$CO), 2.10–1.79 (m, 51H, C*H*$_3$CO), 1.11 (d, *J* 6.6 Hz, 3H, 6-C*H*$_3^{Fuc}$), 1.00 (d, *J* 6.3 Hz, 1H, 6-C*H*$_3^{Fuc}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.5, 170.4,

170.3, 169.9, 169.8, 169.6, 169.5, 169.4, 169.1, 169.0, 167.7, 166.9, 137.9, 137.8, 136.6, 134.3, 134.1, 133.7, 131.5, 131.3, 131.2, 131.1, 128.5, 128.2, 128.0, 127.9, 127.6, 127.4, 127.3, 127.2, 123.6, 123.4, 98.5, 98.3, 98.0, 97.1, 97.0, 96.5, 96.4, 96.3, 96.0, 77.2, 75.0, 74.1, 73.6, 72.7, 72.6, 72.2, 72.1, 72.0, 71.9, 71.8, 71.7, 71.6, 71.5, 70.7, 70.4, 70.2, 69.9, 69.4, 69.3, 69.0, 68.9, 68.8, 68.7, 68.2, 65.7, 64.9, 64.8, 64.6, 64.2, 62.6, 62.4, 61.9, 61.8, 56.5, 54.9, 54.3, 21.1, 20.9, 20.8, 20.7, 20.6, 20.5, 20.3, 16.0, 15.9; HRESIMS: found *m/z* 2718.82648 $[M+Na]^+$; calcd for $C_{129}H_{145}O_{60}N_3Na$ 2718.82849.

3.34. Benzyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-(2,4-di-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-2-deoxy-2-phthalimido-β-D-glucopyranoside (42)

Compound **12** (79.1 mg, 43.5 μmol) was submitted sequentially to glycosylation with **13** and de-*p*-methoxybenzylation as described for **37**. The crude product was purified by preparative TLC (1:3 toluene–EtOAc) to afford 75.7 mg (81%, two steps) of **42**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.00 (m, 22H, Ar), 5.84 (dd, *J* 8.8, 10.7 Hz, 1H), 5.64 (dd, *J* 9.3, 10.7 Hz, 1H), 5.42 (d, *J* 8.5 Hz, 1H), 5.39–5.28 (m, 2H), 5.23–5.06 (m, 6H), 4.99 (t, *J* 9.4 Hz, 1H), 4.81 (d, *J* 1.5 Hz, 1H), 4.75–4.71 (m, 2H), 4.69 (br s, 2H), 4.57–4.01 (m, 17H), 3.87–3.67 (m, 8H), 3.53–3.49 (m, 2H), 3.41–3.37 (br, 1H), 3.23 (br, 2H), 2.30 (s, 3H, CH_3CO), 2.16 (s, 3H, CH_3CO), 2.10–1.90 (s, 33H, CH_3CO), 1.83 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 170.5, 170.4, 170.3, 170.2, 170.0, 169.9, 169.8, 169.7, 169.2, 169.1, 167.6, 166.9, 137.9, 137.0, 134.4, 134.2, 133.8, 131.6, 131.3, 131.1, 130.9, 128.0, 127.9, 127.4, 127.3, 127.1, 123.6, 123.4, 98.6, 98.3, 97.5, 97.1, 97.0, 96.2, 81.7, 77.2, 76.7, 74.6, 74.1, 73.9, 73.7, 73.0, 72.8, 72.2, 72.1, 70.6, 69.7, 69.4, 69.2, 69.1, 68.9, 68.8, 68.7, 68.6, 68.1, 67.5, 65.6, 65.0, 62.4, 62.3, 62.1, 61.8, 55.9, 54.5, 54.3, 21.1, 20.9, 20.8, 20.7, 20.6, 20.5, 20.4; HRESIMS: found *m/z* 2168.62060 $[M+Na]^+$; calcd for $C_{102}H_{111}O_{48}N_3Na$ 2168.62347.

3.35. Benzyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-*O*-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-(2,4-di-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-2-deoxy-2-phthalimido-β-D-glucopyranoside (43)

A mixture of pre-activated molecular sieves 4 Å (200 mg), compounds **11** (11.8 mg, 32.0 μmol) and **42** (34.4 mg, 16.0 μmol), and DTBMP (16.4 mg, 80.0 μmol) in cyclopentyl methyl ether (CPME) (2.5 mL) was stirred at room temperature for 20 min. MeOTf (9.1 μL, 80.0 μmol) was added. After being stirred at the same temperature for 16 h, MeOTf (0.9 μL, 8.0 μmol) was added, and the reaction then stirred for 4.5 h. It was quenched with Et_3N (50 μL) and filtered through Celite. The filtrate was diluted with EtOAc, washed with brine, dried over $MgSO_4$, and evaporated under diminished pressure. The residue was purified by chromatography with Bio-Beads SX-3 (toluene) and then by preparative TLC (2:5 toluene–EtOAc) to afford 36.3 mg (92%) of **43**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86–6.91 (m, 27H, Ar), 5.71 (dd, *J* 9.0, 10.5 Hz, 1H), 5.65 (dd, *J* 9.0, 10.7 Hz, 1H), 5.41 (d, *J* 8.3 Hz, 1H), 5.31–5.09 (m, 10H), 4.93 (d, *J* 8.3 Hz, 1H), 4.88 (d, *J* 3.4 Hz, 1H), 4.79 (dd, *J* 3.4, 10.5 Hz, 1H), 4.74 (d, *J* 1.2 Hz, 1H), 4.70–4.66 (m, 2H), 4.62–4.59 (m, 2H), 4.55–4.52 (m, 3H), 4.50–4.17 (m, 9H), 4.13–3.71 (m, 13H), 3.66–3.38 (m, 7H), 2.28 (s, 3H, CH_3CO), 2.13–1.82 (s, 45H, CH_3CO), 1.10 (d, *J* 6.3 Hz, 3H, 6-CH_3^{Fuc}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.2, 170.1, 169.9, 169.8, 169.7, 169.5, 169.4, 169.3, 169.1, 169.0, 167.8, 166.8, 138.0, 137.8, 136.8, 134.3, 134.1, 133.7, 131.5, 131.2, 131.1, 128.2, 128.1, 127.9, 127.5, 127.4, 127.3, 127.2, 123.5, 123.4, 123.3, 98.4, 98.1, 97.6, 97.0, 96.7, 96.3, 95.9, 76.2, 74.6, 74.5, 74.1, 73.7, 72.8, 72.8, 72.3, 72.1, 72.0, 71.9, 71.8, 71.6, 70.7, 70.4, 70.2, 70.0, 69.9, 69.3, 69.2, 69.1, 68.9, 68.8, 68.7, 68.1, 65.7, 64.9, 64.6, 62.6, 62.3, 62.0, 61.8, 56.3, 55.0, 54.3, 21.1, 21.0, 20.9, 20.8, 20.7, 20.6, 20.5, 16.0; HRESIMS: found *m/z* 2488.74856 $[M+Na]^+$; calcd for $C_{119}H_{131}O_{54}N_3Na$ 2488.74946.

3.36. (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(α-D-mannopyranosyl)-(1→3)-*O*-[(α-D-mannopyranosyl)-(1→6)]-(β-D-mannopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-[(α-L-fucopyranosyl)-(1→6)]-2-acetamido-2-deoxy-D-glucopyranose (5)

Compound **39** (12.6 mg, 5.05 μmol) was submitted sequentially to dephthaloylation, acetylation, O-deacetylation, and hydrogenation as described for **1** to afford 4.8 mg (75%, four steps) of **5**; ^{1}H NMR (400 MHz, D_2O, acetone at δ 2.22): δ 5.17 (d, *J* 2.7 Hz, 0.67H, H-1$^{\alpha GlcN}$), 5.11 (br s, 1H, H-1$^{\alpha Man}$), 4.91 (br s, 1H, H-1$^{\alpha Man}$), 4.89–4.88 (m, 1H, H-1$^{\alpha 1\rightarrow 6Fuc}$), 4.77 (br s, 1H, H-1$^{\beta Man}$), 4.69–4.64 (m, 1.33H, H-1$^{\beta GlcN}\times 2$), 4.54 (d, *J* 8.3 Hz, 1H, H-1$^{\beta GlcN}$), 4.24 (br s, 1H, H-2$^{\beta Man}$), 4.18 (br s, 1H, H-2$^{\alpha Man}$), 2.09–2.03 (m, 9H, CH_3CO), 1.22–1.20 (m, 3H, 6-CH_3^{Fuc}); ^{13}C NMR (100 MHz, D_2O, acetone at δ 30.89): δ 175.0, 174.9, 174.7, 101.5, 100.9, 100.1, 99.8, 95.5, 91.0, 80.9, 80.3, 79.5, 77.0, 76.4, 74.9, 74.7, 74.1, 73.8, 73.2, 72.6, 72.4, 70.9, 70.7, 70.4, 70.0, 69.9, 69.7, 69.0, 68.8, 67.9, 67.4, 67.3, 66.5, 62.3, 61.5, 61.2, 60.5, 55.9, 55.5, 54.3, 23.0, 22.8, 22.6, 20.7, 16.0;

HRESIMS: found m/z 1282.45092 $[M+Na]^+$; calcd for $C_{48}H_{81}O_{35}N_3Na$ 1282.45483.

3.37. (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-*O*-(α-D-mannopyranosyl)-(1→3)-*O*-[(α-D-mannopyranosyl)-(1→6)]-(β-D-mannopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-[(α-L-fucopyranosyl)-(1→6)]-[(α-L-fucopyranosyl)-(1→3)]-2-acetamido-2-deoxy-D-glucopyranose (6)

Compound **41** (18.2 mg, 6.75 μmol) was submitted sequentially to dephthaloylation, acetylation, O-deacetylation, and debenzylation as described for **1** to afford 7.0 mg (74%, four steps) of **6**; ^{1}H NMR (400 MHz, D_2O, acetone at δ 2.22): δ 5.11 (br s, 2H, H-1$^{\alpha Man}$, H-1$^{\alpha 1\rightarrow 3Fuc}$), 5.06 (d, J 3.4 Hz, 0.66H, H-1$^{\alpha GlcN}$), 4.92–4.91 (m, 2H, H-1$^{\alpha Man}$, H-1$^{\alpha 1\rightarrow 6Fuc}$), 4.74 (br s, 1H, H-1$^{\beta Man}$), 4.69–4.65 (m, 1.33H, H-1$^{\beta GlcN}\times 2$), 4.54 (d, J 8.3 Hz, 1H, H-1$^{\beta GlcN}$), 4.25 (br s, 1H, H-2$^{\beta Man}$), 2.06–2.02 (m, 9H, CH_3CO), 1.27 (d, J 6.8 Hz, 3H, 6-CH_3^{Fuc}), 1.22–1.20 (m, 3H, 6-CH_3^{Fuc}); ^{13}C NMR (125 MHz, D_2O, acetone at δ 30.89): δ 175.4, 174.9, 101.1, 100.8, 100.7, 100.4, 100.3, 100.0, 95.5 × 2, 95.4, 91.6, 81.7 × 2, 81.0, 77.1, 76.5, 75.2, 75.1, 74.8, 74.3, 73.9, 73.4, 73.2, 73.0, 72.7, 72.5, 71.0, 70.9, 70.8, 70.6, 70.2, 70.1, 69.9, 69.8, 69.1, 68.8. 68.4, 68.0, 67.5 × 2, 67.3, 66.6, 62.4, 61.7 × 2, 61.6, 61.3, 56.0, 55.6, 54.6, 23.0, 22.9, 22.7, 20.7, 16.2, 16.0; HRESIMS: found m/z 1428.50948 $[M+Na]^+$; calcd for $C_{54}H_{91}O_{39}N_3Na$ 1428.51274.

3.38. (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(α-D-mannopyranosyl)-(1→3)-[(α-D-mannopyranosyl)-(1→6)]-(β-D-mannopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-2-acetamido-2-deoxy-D-glucopyranose (7)

Compound **42** (16.2 mg, 7.55 μmol) was submitted sequentially to dephthaloylation, acetylation, O-deacetylation, and debenzylation as described for **1** to afford 6.2 mg (74%, four steps) of **7**: ^{1}H NMR (400 MHz, D_2O, acetone at δ 2.22): δ 5.18 (d, J 2.4 Hz, 0.65H, H-1$^{\alpha GlcN}$), 5.12 (br s, 1H, H-1$^{\alpha Man}$), 4.91 (d, J 1.5 Hz, 1H, H-1$^{\alpha Man}$), 4.77 (br s, 1H, H-1$^{\beta Man}$), 4.71–4.68 (m, 0.35H, H-1$^{\beta GlcN}$), 4.61–4.59 (m, 1H, H-1$^{\beta GlcN}$), 4.54 (d, J 8.3 Hz, 1H, H-1$^{\beta GlcN}$), 4.25 (br s, 1H, H-2$^{\beta Man}$), 4.18 (m, 1H, H-2$^{\alpha Man}$), 2.07–2.03 (m, 9H, CH_3CO); ^{13}C NMR (125 MHz, D_2O, acetone at δ 30.89): δ 175.4 × 3, 175.1, 102.0, 101.1, 100.3 × 2, 95.5, 95.6, 91.1, 81.0, 80.3, 79.9, 77.1, 76.5, 75.3, 75.0, 74.8, 74.2, 73.9, 73.4, 73.1 72.7, 71.1, 70.9, 70.7, 70.6, 70.5 × 2, 70.1, 69.9, 69.1, 68.0, 67.4, 66.6, 66.5, 62.4, 61.6, 61.3, 60.6, 56.0, 55.5, 54.3, 23.0, 22.9, 22.5; HRESIMS: found m/z 1136.39830 $[M+Na]^+$; calcd for $C_{42}H_{71}O_{31}N_3Na$ 1136.39692.

3.39. (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(α-D-mannopyranosyl)-(1→3)-*O*-[(α-D-mannopyranosyl)-(1→6)]-(β-D-mannopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-[(α-L-fucopyranosyl)-(1→3)]-2-acetamido-2-deoxy-D-glucopyranose (8)

Compound **43** (12.4 mg, 5.03 μmol) was submitted sequentially to dephthaloylation, acetylation, O-deacetylation, and debenzylation as described for compound **1** to afford 4.4 mg (69%, four steps) of **8**: ^{1}H NMR (400 MHz, D_2O, acetone at δ 2.22): δ 5.11 (br s, 2H, H-1$^{\alpha Man}$, H-1$^{\alpha 1\rightarrow 3Fuc}$), 5.07 (d, J 3.4 Hz, 0.55H, H-1$^{\alpha GlcN}$), 4.91 (br s, 1H, H-1$^{\alpha Man}$), 4.74 (br s, 1H, H-1$^{\beta Man}$), 4.71–4.67 (m, 0.45H, H-1$^{\beta GlcN}$), 4.57–4.53 (m, 2H, H-1$^{\beta GlcN}\times 2$), 4.25 (br s, 1H, H-2$^{\beta Man}$), 4.18 (d, J 2.0 Hz, 1H, H-2$^{\alpha Man}$), 2.05–2.02 (m, 9H, CH_3CO), 1.27 (d, J 6.8 Hz, 3H, 6-CH_3^{Fuc}); ^{13}C NMR (100 MHz, D_2O, acetone at δ 30.89): δ 175.0 × 2, 174.7, 100.9, 100.2, 100.1, 100.0, 91.3, 81.4, 80.8, 76.9, 76.4, 75.9, 75.1, 74.7, 74.4, 74.3, 74.1, 73.8, 73.2, 72.8, 72.6, 70.9, 70.7, 70.5, 70.4, 69.9, 69.8, 69.0, 68.3, 67.9, 67.3, 66.5, 66.4, 62.3, 61.5, 61.2, 55.9, 55.6, 54.5, 23.0, 22.8, 22.7, 20.7, 16.2; HRESIMS: found m/z 1282.45501 $[M+Na]^+$; calcd for $C_{48}H_{81}O_{35}N_3Na$ 1282.45483.

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