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Comprehensive synthesis of ER related high-mannose-type sugar chains by convergent strategy

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Abstract—Systematic synthesis of high-mannose-type sugar chains of asparagine-linked glycoproteins is described. To construct the target sugar chains, we employed the convergent route, using three oligosaccharide components, the common hexasaccharide, branched tri-, tetra- and pentasaccharides, and mono-, di-, and triglucosyl fragments. Construction of the β-mannoside linkage was performed using *p*-methoxybenzyl-assisted intramolecular aglycon delivery. The hexasaccharide fragment was coupled with the branched mannooligosaccharide donors such as M5, M4B, M4C, and M3 to give undecasaccharide (M9), decasaccharide (M8B and M8C), and nonasaccharide (M7), respectively. Incorporation of mono-, di-, and triglucosyl fragments toward them gave tetradecasaccharide (G3M9), tridecasaccharide (G2M9), dodecasaccharide (G1M9), undecasaccharide (G1M8B and G1M8C), and decasaccharide (G1M7), respectively.

1. Introduction

N-Glycosylation of secretory and membrane-bound proteins is an essential and highly conserved protein modification of eukaryotes[1] (Fig. 1). The key step of protein N-glycosylation pathway is the en bloc transfer of a triglucosylated high-mannose-type tetradecasaccharide ($Glc_3Man_9GlcNAc_2$; G3M9) from lipid carrier dolichyl pyrophosphate (Dol-PP) to asparagine (Asn) residue of Asn-X-Ser/Thr sequences of nascent polypeptide chains. It occurs during their translocation across the endoplasmic reticulum (ER) membrane.[2] This transformation is catalyzed by a large multisubunit enzyme, oligosaccharyltransferase (OST) complex. Subsequently, glucosidase I, an integral membrane protein with a luminally oriented catalytic domain, removes the terminal α1-2 linked glucose residue of the triglucosyl sequence. Trimming of penultimate glucose residues takes place by the action of glucosidase II to give $Glc_1Man_9GlcNAc_2$ (G1M9) and then $Man_9GlcNAc_2$ (M9) glycoforms.[3,4]

Partial trimming of mannose residues also occurs in the ER, which is initiated by two distinct enzymes, ER α1-2 mannosidases I and II. The proposed function of the former enzyme is to remove the terminal sugar of the middle branch to generate the M8B isomer, which is the proposed ligand of mannosidase-like protein (MLP).[5,6] On the other hand, mannosidase II preferentially releases the terminal mannose linked to the α1-6 branch to yield M8C isomer. An additional mannosidase that may be involved in early processing is Man9 mannosidase, which has an ability to trim M9 to $Man_7GlcNAc_2$ (M7) and eventually $Man_5GlcNAc_2$ (M5).[7]

Recent investigations have revealed the fundamental roles of these N-linked high-mannose-type glycans in protein quality control (folding, transport, and degradation).[8–11] A number of proteins, such as calreticulin (CRT), calnexin (CNX), ER-Golgi intermediate compartment (ERGIC)-53, vesicular integral membrane protein (VIP) 36, and mannosidase-like proteins (MLP, EDEM/Htm1p/Mnl1p) have been revealed or suggested to recognize these N-linked glycans. CNX and CRT are ER-resident lectin-chaperones that specifically recognize monoglucosylated glycans, most typically G1M9.[12,13] They constitute CNX/CRT cycle, together with UDP-Glc: glycoprotein glucosyltransferase (UGGT). Intriguingly, the latter enzyme functions as the 'folding sensor', glucosylating prematurely deglucosylated glycoproteins having M9, M8 or M7 glycans and regenerate monoglucosylated structures G1M9∼7, in order that they can engage in multiple rounds of interactions with CNX/CRT.[14] On the other hand, ERGIC-53 and VIP36 are cargo receptors that mediate glycoprotein transport between ER and Golgi,[15] while MLPs are proposed to capture malfolded glycoproteins destined for degradation. Although MLPs are considered to recognize M8B, their lectin activity is yet to be revealed.

These functions of high-mannose-type glycans in protein quality control are attracting recent attention. Most of the

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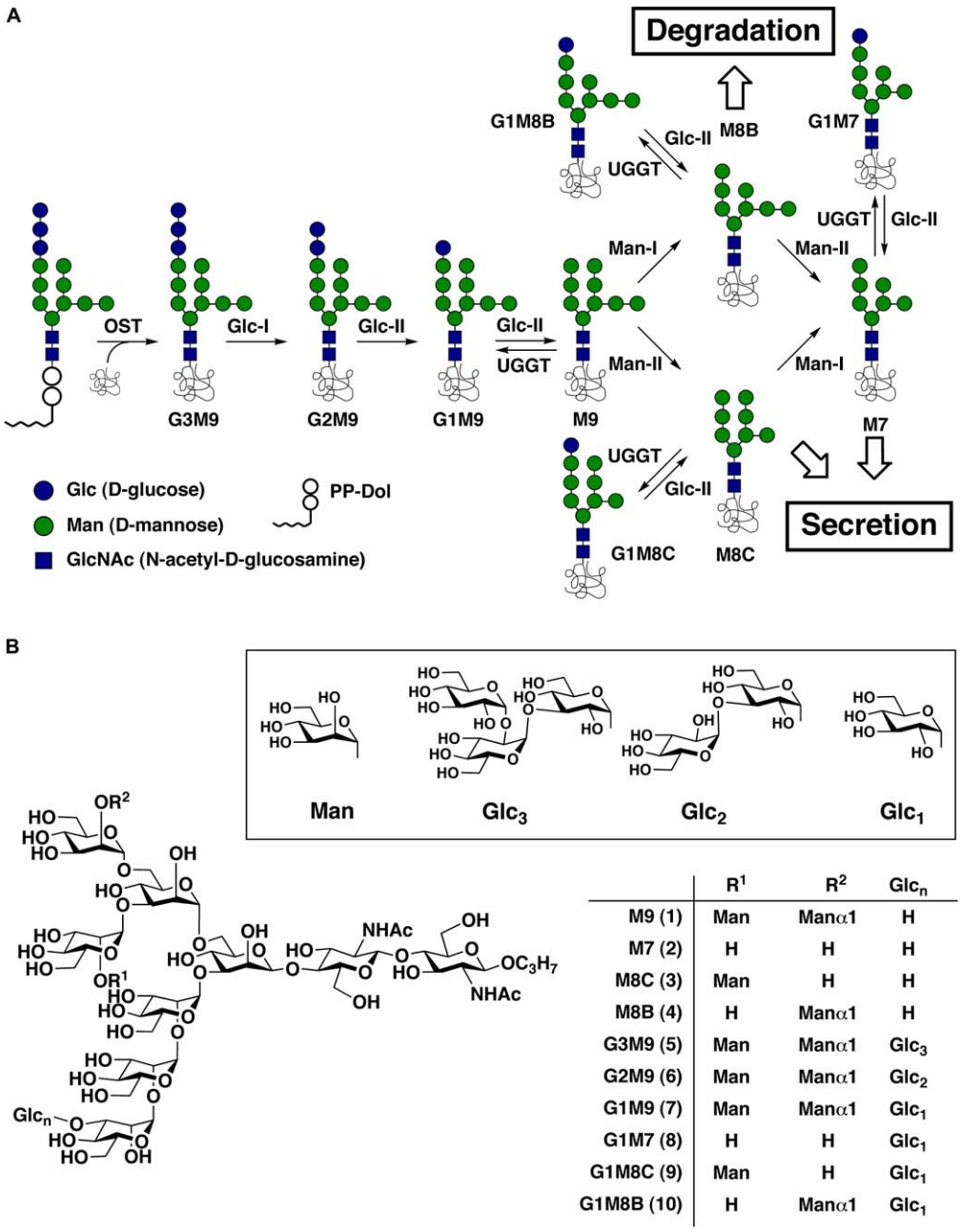


	R^1	R^2	Glc_n
M9 (1)	Man	Manα1	H
M7 (2)	H	H	H
M8C (3)	Man	H	H
M8B (4)	H	Manα1	H
G3M9 (5)	Man	Manα1	Glc_3
G2M9 (6)	Man	Manα1	Glc_2
G1M9 (7)	Man	Manα1	Glc_1
G1M7 (8)	H	H	Glc_1
G1M8C (9)	Man	H	Glc_1
G1M8B (10)	H	Manα1	Glc_1

Figure 1. (A) Glycoprotein glycan processing in ER. (B) Structure of ER-type *N*-glycans synthesized in this study.

previous studies were conducted with glycoproteins or glycan chains derived from biological sources. In order to gain precise understanding of carbohydrate–protein interplays in protein quality control, access to homogeneous and structurally defined oligosaccharides is highly important. With this respect, approaches based on chemical synthesis are more advantageous, in terms of their flexibility and ability to provide homogeneous glycans in larger amount. We wish to describe here the results of our program toward comprehensive synthesis of ER-related *N*-glycans.[11] Parts of this study have been reported in preliminary forms (M9 and G1M9,[16] M8B and G1M8B,[17] G2M9 and G3M9.[18]

Considering the diversity of the targets, we adopted a convergent strategy as shown in Figure 2. Thus, fragments corresponding to an invariant hexasaccharide **11**, branched penta-, tri-, and tetramannoside (**M5**, **M3**, **M4B**, and **M4C**) fragments, and mono-, di-, and triglucoside donors (**G1**, **G2**, and **G3**) were chosen. Combination of these fragments should allow for the construction of all types of high-mannose-type sugar chains.

2. Results and discussion

2.1. Synthesis of an invariant hexasaccharide

Synthesis of hexasaccharide **11** was carried out as depicted in Scheme 1. It started with the preparation of trisaccharide **25**. Its β-mannoside linkage was constructed using the 2-*O*-*p*-methoxybenzyl (PMB) equipped thioglycoside **20** as a donor. Thus, coupling with the 4-*O*-unprotected fluoride

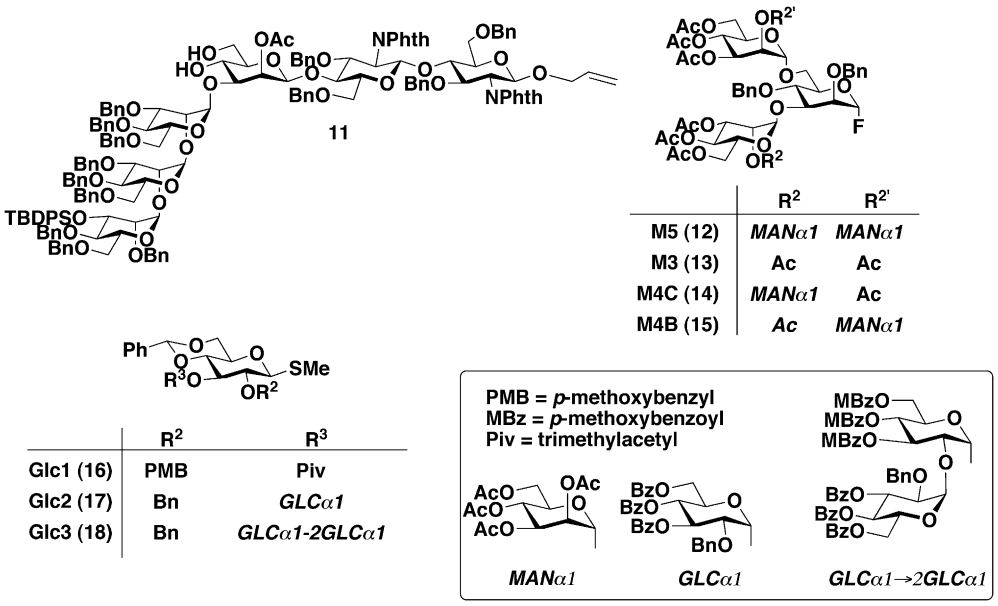


Figure 2. Designed oligosaccharide fragments.

19 was conducted according to our standard protocol; DDQ-mediated formation of the mixed acetal and subsequent intramolecular aglycon delivery (IAD) that was promoted by MeOTf to afford disaccharide **21** as a single stereoisomer in 84% yield (two steps).[19,20] NMR of **21** revealed the presence of newly formed β-mannoside linkage [δ_H 4.37 ($J_{1,2}$=~0 Hz), δ_C 99.7 ($^1J_{C-H}$=159 Hz)].[21] After acetylation, it was condensed with a reducing-end GlcN component **23** through the activation with Cp_2HfCl_2/AgOTf[22,23] to give **24**. Subsequent desilylation proceeded most cleanly under high-pressure conditions (1 GPa) with HF/pyridine[24] to give **25**.

The linear mannotriose **31** was synthesized in a stepwise manner. Coupling of a thiomannoside **26** with chloride **27** was performed under standard conditions (AgOTf/CH_2Cl_2) to give mannobiose **28**,[25,26] which was deacetylated to **29**. As the third mannose residue, the 3-*O*-TBDPS protected fluoride **30** was used and trisaccharide **31** was obtained in a quantitative yield. Three anomeric signals appeared in the region of α-Man linkage [δ_H 5.75, 5.54 and 5.21 (s)], while that of β-Man linkage is typically less than 5 ppm,[27] confirming its stereochemistry. Coupling with **25** was achieved using MeOTf to afford hexasaccharide **32**. Although rigorous assignment of αMan1-3Man linkage was not made at this stage, homogeneity of isolated **32** was obvious and we assumed its stereochemical integrity based on well-established intrinsic α-selectivity of mannosyl donor as well as on our own results. Subsequent removal of the cyclohexylidene group completed the synthesis of the common hexasaccharide fragment **11**.

2.2. Synthesis of oligomannose branch

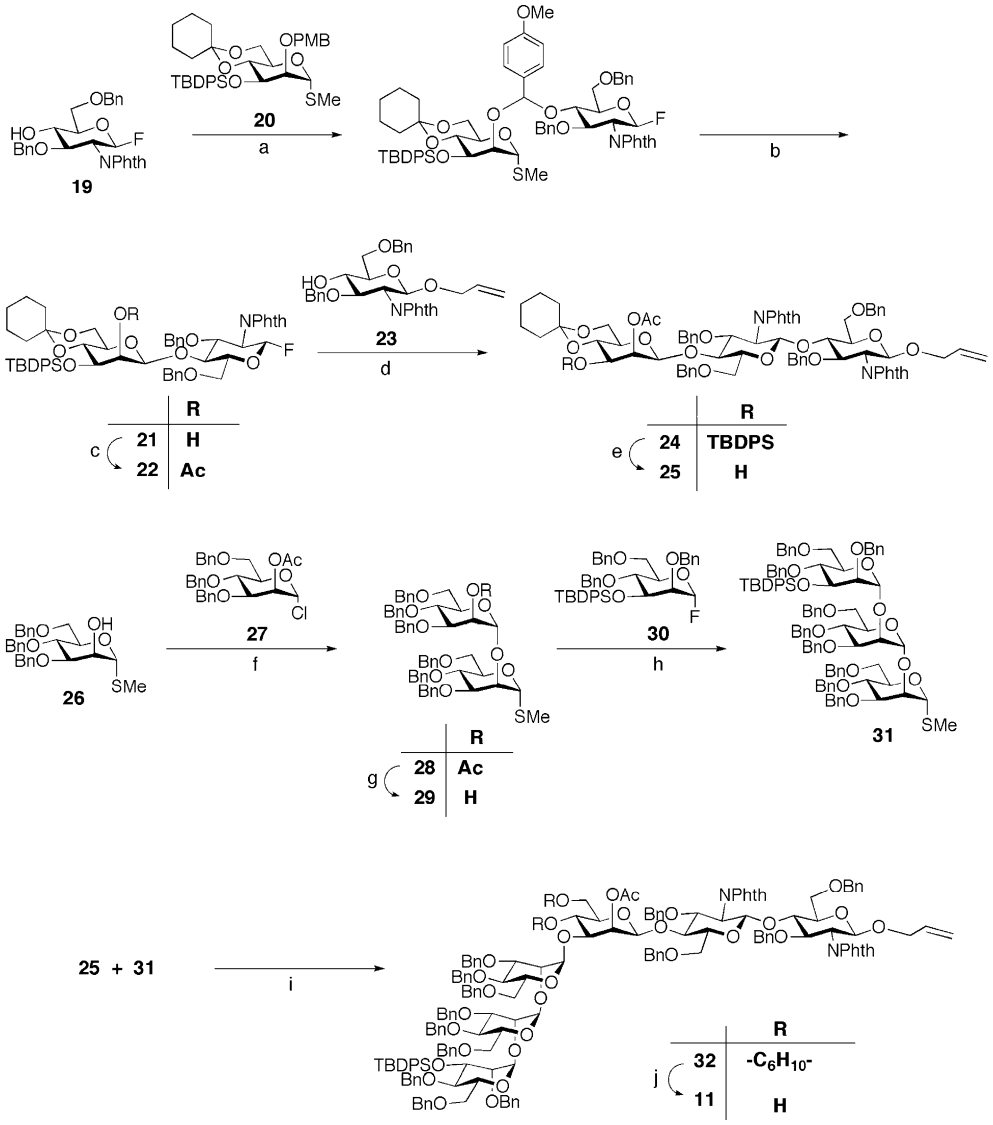
Syntheses of branched mannooligosaccharide fragments, M5 (**12**), M3 (**13**), M4C (**14**), and M4B (**15**) were conducted as shown in Scheme 2. Preparation of **12** and **13** was straightforward, being achieved by double glycosylation of diol **35** with **33**/**34** to give **36**/**37**, spectral data of which were identical with previous reported ones.[17,28] They were treated with *N*-bromosuccinimide (NBS)/diethylaminosulfur trifluoride (DAST)[29] to give corresponding fluorides **12** [δ_H 5.66 (d, $^2J_{H-F}$=51.5 Hz)] and **13** [δ_H 5.59 (d, $^2J_{H-F}$=52.0 Hz)] in 89% and 76% yield, respectively. These were used as M5 (**12**) and M3 (**13**) donors for subsequent transformations.

Construction of the heterogeneously branched M4C fragment necessitated the discrimination of *O*-3 and *O*-6 positions. To that end, compound **35** was regioselectively protected by treatment with chloroacetic anhydride (CAc_2O) in toluene/dichloromethane (1:1) at 60 °C to give 6-*O*-CAc derivative **39**.[30] The latter was glycosylated with a disaccharide donor **38**[28] using TfOH as a promoter to give trisaccharide **40** [δ_C 100.57, 99.17, and 84.27 (*C*-1)]. Subsequent removal of the chloroacetyl group provided **41**, which was further glycosylated with **34**, giving branched tetramannoside **42** in 50% yield [δ_C 100.52, 99.16, 97.79, and 84.58 (*C*-1)]. M4B fragment **43** was synthesized from diol **35** as previously reported.[30] These branched oligosaccharides were converted to fluoride **14** [δ_H 5.52 ($^2J_{H-F}$=50.7 Hz)] and **15** [δ_H 5.66 ($^2J_{H-F}$=50.8 Hz)] using NBS–DAST.

2.3. Synthesis of oligoglucose fragments

Mono-, di-, and triglucosyl donors were designed as **16**, **17**, and **18**, respectively (Fig. 2, Scheme 3). Our previous studies revealed that 4,6-*O*-benzylidene-protected thioglucoside was highly suitable for α-selective glucosylation at C-3 position of mannose. The G1 donor **16** was synthesized from **44**. For the synthesis of disaccharide (**17**) and trisaccharide (**18**) fragments, **48** and **52** were chosen as donors, respectively. We anticipated that the presence of electron-withdrawing acyloxy groups[31] at 3-, 4-, and 6-positions would be favorable for the stereoselective formation of α-glucosidic linkages (vide infra).

For the preparation of these donors, the 2-OH derivative **49** and hemiacetal **47** were chosen as key intermediates. These compounds were prepared from glucosyl bromides via cyclic acetals, as described by Suzuki et al.[32,33] Hemiacetal



Scheme 1. Reagents and conditions: (a) DDQ, CH_2Cl_2, rt, 3 h; (b) MeOTf, $ClCH_2CH_2Cl$, 45 °C, 23 h (84% two steps); (c) Ac_2O, DMAP, pyr., 40 °C, 8 h (97%); (d) Cp_2HfCl_2, AgOTf, CH_2Cl_2, −10 °C, 4 h (78%); (e) 10% HF–pyr., DMF, 1 GPa; (f) AgOTf, $ClCH_2CH_2Cl$, −30 °C to rt, 12 h (83%); (g) NaOMe, MeOH/THF, rt, 12 h (95%); (h) Cp_2HfCl_2, AgOTf, CH_2Cl_2, −45 to −20 °C, 1 h (99%); (i) MeOTf, $ClCH_2CH_2Cl$, rt, 12 h (82%); (j) $TsOH\cdot H_2O$, CH_3CN, rt, 6 h (74%).

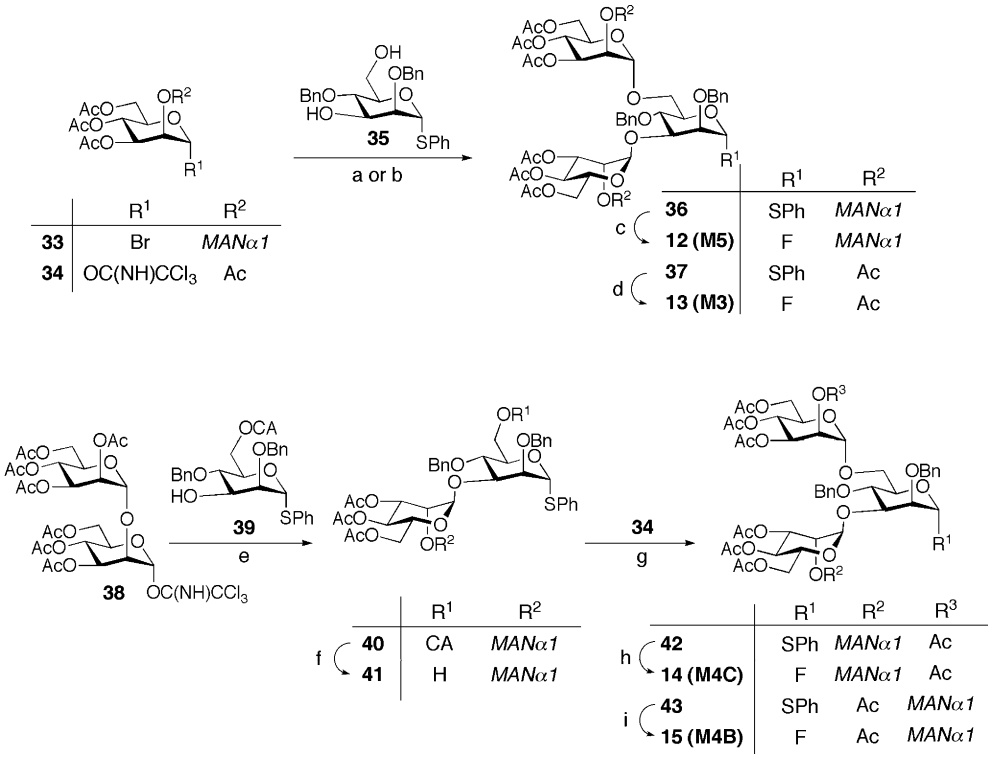
47 was converted to fluoride **48** using DAST and used for the glycosylation with **46** through activation with Cp_2HfCl_2/AgOTf. It afforded disaccharide **17** as a single stereoisomer [δ_H 5.73 (d, J=3.6 Hz, H-1$^{\alpha\text{-Glc}}$)] in 63% yield. The G3 fragment **18** was synthesized by the stepwise elongation of glucose residues from the non-reducing end. To begin with, glycosylation of **49** with **48** using Cp_2HfCl_2/AgOTf afforded disaccharide **50** as a single stereoisomer [δ_H 5.14 (d, J= 3.6 Hz, H-1$^{\alpha\text{-Glc}}$)] in 92% yield. Removal of the *p*-methoxybenzyl group using DDQ afforded hemiacetal **51** that was converted to α-imidate **52**. Coupling of **52** and **46** through activation with TMSOTf in toluene provided trisaccharide **18** in 45% yield, whose ^{1}H NMR reveled the presence of three anomeric protons with α-configuration [δ_H 5.82 (J=3.6 Hz), 5.40 (s), 4.93 (J=3.2 Hz)].

2.4. Systematic synthesis of high-mannose-type glycans

With all fragments in hand, the construction of high-mannose-type skeletons (undeca-, deca-, and nonasaccharide) and the introduction of glucose fragments were undertaken as shown in Scheme 4.

Pentamannoside **12** was used as the glycosyl donor to react with diol **11** using Cp_2HfCl_2/AgOTf in toluene to provide undecasaccharide **53** in 87% yield as a single stereoisomer, which is currently obtainable in multigram quantity (see Section 4). Similar conditions were applied to **13**, **14**, and **15**, and nonasaccharide **55**, as well decasaccharides **57** and **59** were obtained in 77%, 75%, and 84% yield, respectively. Although we were not able to confirm rigorously their stereochemistry at this stage, contamination of stereoisomer was not detectable by 400 MHz NMR in each case. Since selective formation of β-isomer is highly unlikely, we assumed their structure as depicted. Full confirmation was made after complete deprotection (vide infra).

In order to incorporate the pendant glucose residue(s), removal of the TBDPS group from **53**, **55**, **57**, and **59** was required. Mindful of the difficulty we previously encountered



Scheme 2. Reagents and conditions: (a) **33**, AgOTf, $ClCH_2CH_2Cl$, −30 °C to rt (72%); (b) **34**, TfOH, $ClCH_2CH_2Cl$, −20 °C (39%); (c) NBS, DAST, CH_2Cl_2, −20 to −10 °C (89%); (d) NBS, DAST, CH_2Cl_2, −30 °C to rt (76%); (e) TfOH, $ClCH_2CH_2Cl$, −20 to −10 °C (84%); (f) DABCO, EtOH, 50 °C (95%); (g) TfOH, $ClCH_2CH_2Cl$, −20 to −10 °C (50%); (h) NBS, DAST, CH_2Cl_2, −40 to −30 °C (87%); (i) NBS, DAST, CH_2Cl_2, −30 °C to rt (90%).

in the deprotection of TBDPS groups installed at the *O*-3-position of mannose, all of these reactions were conducted with HF/pyridine under high-pressure reaction conditions.[24] For instance, treatment of undecasaccharide **53** in DMF with 10% HF/pyridine at 30 °C under 1 GPa for 24 h cleanly gave the desired product **54** in 95% yield. In a similar manner, **56**, **58,** and **60** were obtained from **55**, **57**, and **59** in 86%, 70% and 97% yield, respectively.

As we hoped, incorporation of mono-, di-, and triglucosyl fragment proceeded selectively to provide desired α-linked products. Namely, MeOTf-promoted coupling of the undecasaccharide **54** with triglucoside **18** gave tetradecasaccharide **61** in 57% yield, and tridecasaccharide **62** was obtained in 85% yield under similar conditions, when **17** was used as the donor. Introduction of a glucose residue to M9, M7, M8C, and M8B type of sugar chain was achieved using the donor **16** to give **63**, **64**, **65**, and **66** in 93%, 86%, 91%, and 79% yield, respectively.

Finally, deprotection of these compounds afforded the ER-type sugar chains in good yield. Figure 3 showed the ^1H NMR spectra of these compounds, which were in good agreement with those reported for closely related compounds.[34]

3. Conclusion

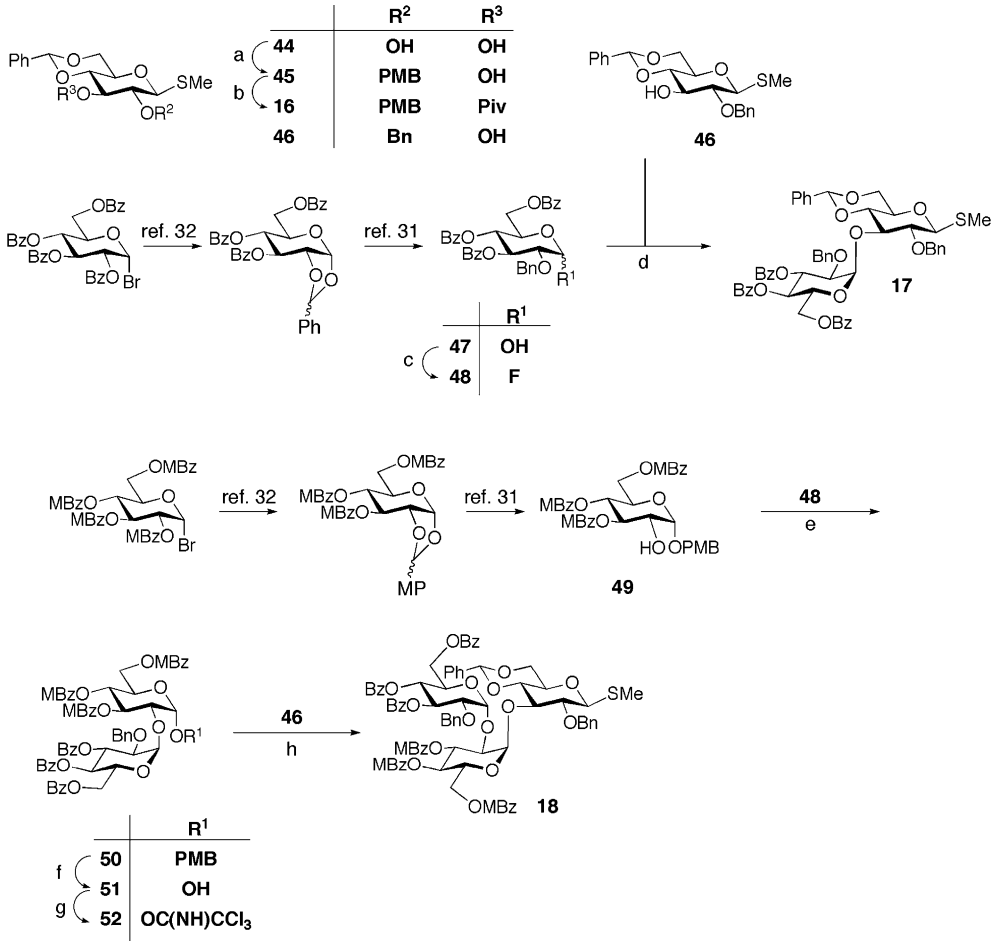
In summary, convergent and stereoselective synthetic route to ER-related *N*-glycan chains was established. Although oligosaccharides were prepared as chemically inert *n*-propyl glycosides in this study, tactics for the incorporation of probes and proteins have been established.[11,35–38] Currently, these glycan chains and derivatives are in extensive use as molecular probes to clarify various issues related to glycoprotein quality control system, including specificities of protein–oligosaccharide interactions and glycan processing enzymes. These results will be reported in due course.

4. Experimental

4.1. General

^1H and ^{13}C NMR spectra were measured on JEOL EX-400 spectrometer in $CDCl_3$ and were referenced to Me_4Si unless otherwise mentioned. Silica gel column chromatography was performed using Silica gel-60 (E Merck). Preparative thin layer chromatography (PTLC) was developed on E Merck Silica Gel 60 F_{254} plates (0.5 mm thickness). MALDI-TOF MS spectra were recorded in the positive ion mode on an AXIMA CFR (Shimadzu/KRATOS) equipped with nitrogen laser with an emission wavelength of 337 nm. High-resolution fast atom bombardment mass spectrometry was performed on a JEOL IMS-HX-100 mass spectrometer.

4.1.1. Compound 22. Under ice-water cooling, a mixture of DDQ (3.16 g, 15.9 mmol) and molecular sieves 4 Å (15 g) in CH_2Cl_2 (40 mL) was stirred under Ar. A solution of **20** (9.90 g, 15.3 mmol) and **19** (6.25 g, 12.7 mmol) in CH_2Cl_2 (60 mL) was added and the mixture was stirred at room temperature for 3 h. It was then quenched with aq solution of ascorbic acid (0.7%)/citric acid (1.3%)/NaOH (0.9%), stirred for 5 min, diluted with CH_2Cl_2/brine, and filtered

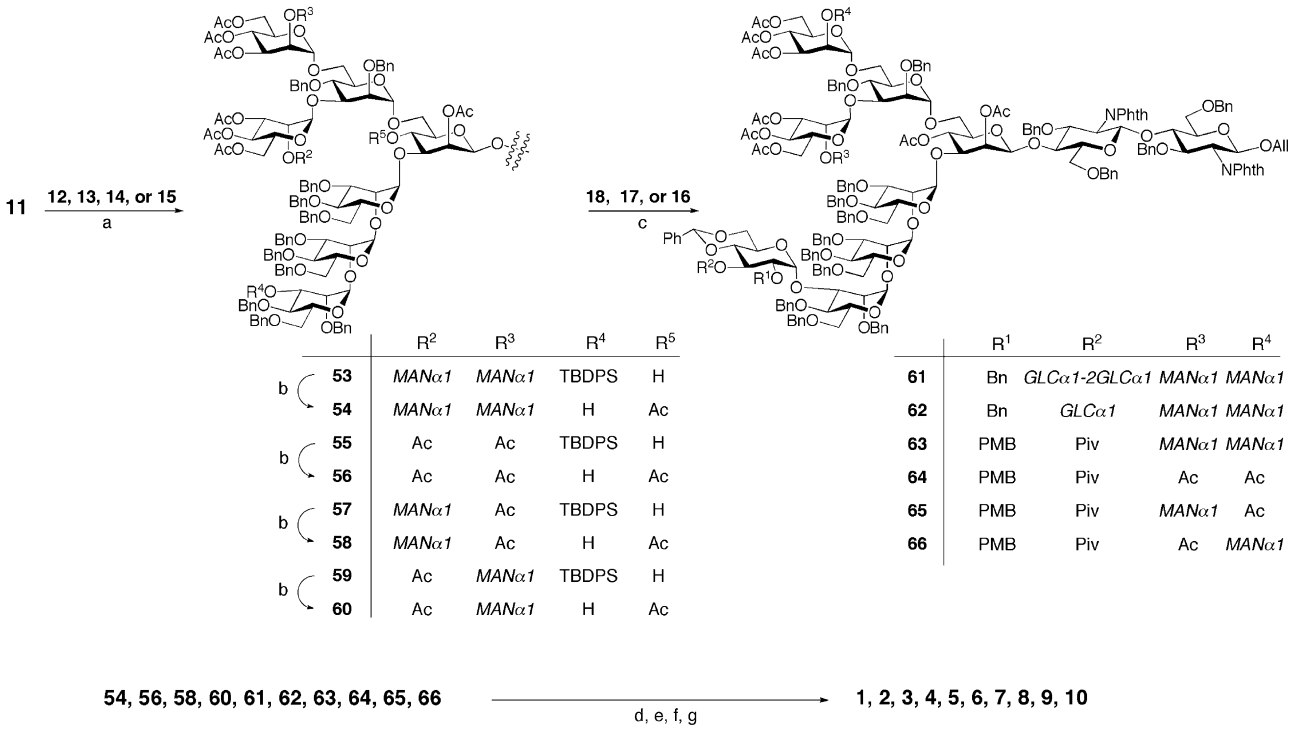


Scheme 3. Reagents and conditions: (a) PMBCl, Bu_4NHSO_4, aq NaOH, 45 °C (52%); (b) PivCl, pyr., 0 °C to rt (61%); (c) DAST (92%); (d) Cp_2HfCl_2, AgOTf, toluene/ether, −40 °C (63%); (e) Cp_2HfCl_2, AgOTf, CH_2Cl_2, −10 °C (90%); (f) DDQ, CH_2Cl_2, H_2O, rt (73%); (g) CCl_3CN, DBU, CH_2Cl_2, 0 °C, 1 h (quant.); (h) TMSOTf, toluene, −40 °C (45%).

through Celite. The filtrate was washed with aq $NaHCO_3$ and the organic layers were dried over Na_2SO_4 and evaporated in vacuo. The residue was mixed with 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) (10.66 g, 51.91 mmol) and co-evaporated with toluene three times. The residue was stirred at room temperature with molecular sieves 4 Å (30 g) in $ClCH_2CH_2Cl$ (200 mL). Then, a solution of 1 M MeOTf in $ClCH_2CH_2Cl$ (36.1 mL, 36.1 mmol) was added at 0 °C and stirred at 45 °C for 23 h. The reaction was quenched with Et_3N, diluted with EtOAc/aq $NaHCO_3$, and filtered through Celite. The filtrate was washed with aq $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was subjected to a silica gel column chromatography (hexane/EtOAc, 5:1) to afford **21** (10.14 g, 82%). Disaccharide **21** and DMAP (122 mg) were dissolved in-pyridine (20 mL) and Ac_2O (10 mL). The mixture was stirred at 40 °C for 8 h and evaporated in vacuo. The residue was diluted with EtOAc, and washed with aq HCl, brine, aq $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, and evaporated in vacuo to give **22** (10.27 g, 97%). Physical data were consistent with those reported previously (Ref. 16).

4.1.2. Compound 24. To a stirred mixture of Cp_2HfCl_2 (3.73 g, 9.62 mmol), AgOTf (5.19 g, 20.2 mmol), and molecular sieves 4 Å (14.5 g) in dry CH_2Cl_2 (500 mL) was added a solution of **22** (19.52 g, 19.25 mmol) and **23** (12.23 g, 23.10 mmol) in dry CH_2Cl_2 (800 mL) at −10 °C. The mixture was stirred for 4 h. Insoluble materials were removed by passage through Celite, and the filtrate was then diluted with CH_2Cl_2, and washed with brine, aq $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, and evaporated in vacuo. The residue was subjected to a silica gel column chromatography (toluene/EtOAc, 20:1 to 10:1) to afford compound **24** (22.90 g, 78%). Physical data were consistent with those reported previously (Ref. 16).

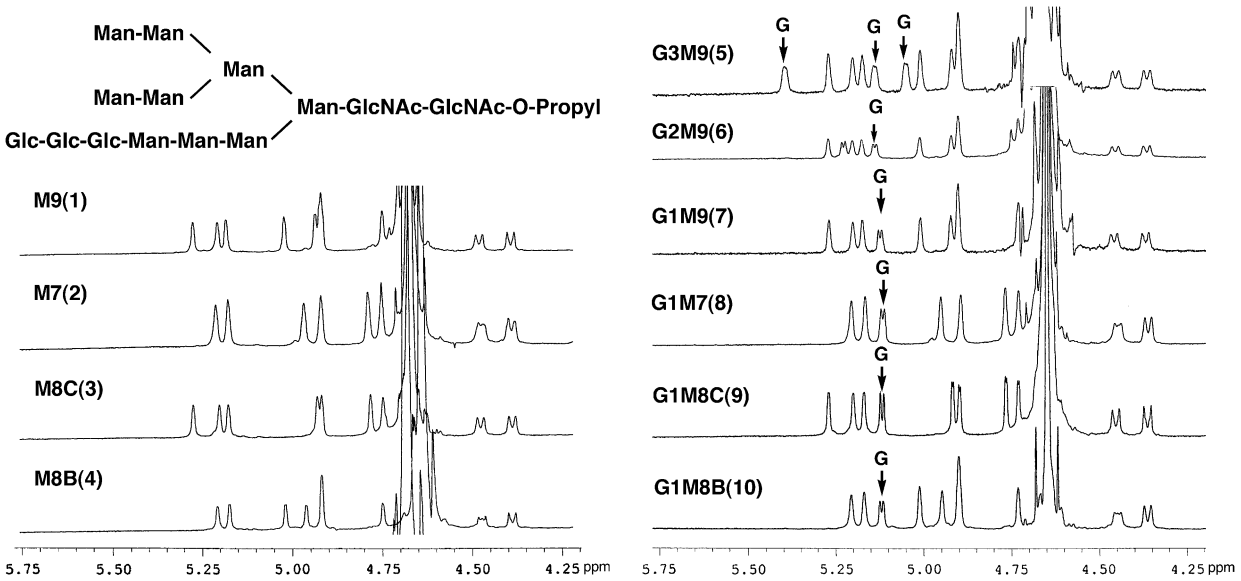
4.1.3. Compound 25. Compound **24** (16.0 g, 10.5 mmol) was dissolved in DMF (24 mL) containing 10% HF/pyridine. The mixture was divided to eight portions and transferred to 3 mL Teflon reaction vessels. It was compressed to 1.0 GPa and left at 30 °C for 5 h. Combined mixture was diluted with EtOAc and washed with aq $NaHCO_3$ and brine, successively. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The combined mixtures were subjected to a silica gel column chromatography (hexane/EtOAc=2:1–3:2) to give compound **25** (11.1 g, 86% yield) as a colorless solid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.64–7.00 (m, 28H), 5.50 (m, 1H), 5.27 (d, 1H, J=2.4 Hz), 5.23 (d, 1H, J=8.0 Hz), 5.01–4.91 (m, 3H), 4.84 (d, 1H, J=12.8 Hz), 4.83 (d, 1H, J=12.8 Hz), 4.68 (br s, 1H), 4.58 (d, 1H, J=12.0 Hz),



	R^2	R^3	R^4	R^5
53	*MANα1*	*MANα1*	TBDPS	H
54	*MANα1*	*MANα1*	H	Ac
55	Ac	Ac	TBDPS	H
56	Ac	Ac	H	Ac
57	*MANα1*	Ac	TBDPS	H
58	*MANα1*	Ac	H	Ac
59	Ac	*MANα1*	TBDPS	H
60	Ac	*MANα1*	H	Ac

	R^1	R^2	R^3	R^4
61	Bn	*GLCα1-2GLCα1*	*MANα1*	*MANα1*
62	Bn	*GLCα1*	*MANα1*	*MANα1*
63	PMB	Piv	*MANα1*	*MANα1*
64	PMB	Piv	Ac	Ac
65	PMB	Piv	*MANα1*	Ac
66	PMB	Piv	Ac	*MANα1*

Scheme 4. Reagents and conditions: (a) Cp_2HfCl_2, AgOTf, toluene, −30 to −10 °C; **12** (87%), **13** (77%), **14** (75%), **15** (84%); (b) (1) Ac_2O, pyr., 50 °C; (2) 10% HF–pyr., DMF, 1 Gpa; **54** (95%), **56** (86%), **58** (70%), **60** (97%); (c) MeOTf, CH_2CH_2, cyclohexane, (1) **61** (**54**+**18**; 57%), **62** (**54**+**17**; 85%), **63** (**54**+**16**; 93%), **64** (**56**+**16**; 86%), **65** (**58**+**16**; 91%), **66** (**60**+**16**; 79%); (d) ethylenediamine, *n*-BuOH; (e) Ac_2O, pyr.; (f) NaOMe, MeOH; (g) $Pd(OH)_2$/C, aq AcOH, H_2, **1** (54%), **2** (84%), **3** (47%), **4** (87%), **5** (56%), **6** (65%), **7** (54%), **8** (84%), **9** (66%), **10** (58%).



	GlcNAc (Hz)		Man								Glc (Hz)		
M9 (1)	4.36 (*J*=7.5)	4.45 (*J*=7.6)	4.73	4.90	4.90	4.92	5.01	5.17	5.20	5.27	***	***	***
M7 (2)	4.36 (*J*=6.8)	4.45 (*J*=6.6)	4.73	4.77	4.91	4.96	***	5.17	5.21	***	***	***	***
M8C (3)	4.36 (*J*=7.6)	4.45 (*J*=7.6)	4.73	4.77	4.91	4.92	***	5.17	5.20	5.27	***	***	***
M8B (4)	4.36 (*J*=8.0)	4.45 (*J*=7.5)	4.73	4.90	4.90	4.95	5.01	5.17	5.20	***	***	***	***
G3M9 (5)	4.36 (*J*=6.8)	4.45 (*J*=7.2)	4.76	4.90	4.90	4.92	5.01	5.17	5.20	5.27	5.04(*J*=3.2)	5.13(*J*=2.4)	5.39(*J*=2.4)
G2M9 (6)	4.35 (*J*=6.8)	4.57 (*J*=7.0)	4.71	4.89	4.89	4.90	5.00	5.16	5.19	5.26	***	5.12(*J*=3.9)	5.21(*J*=3.6)
G1M9 (7)	4.37 (*J*=7.5)	4.46 (*J*=7.3)	4.73	4.90	4.90	4.92	5.01	5.17	5.20	5.27	***	5.12(*J*=3.7)	***
G1M7 (8)	4.36 (*J*=7.3)	4.44 (*J*=6.6)	4.73	4.77	4.90	4.95	***	5.17	5.21	***	***	5.11(*J*=3.6)	***
G1M8C (9)	4.36 (*J*=8.0)	4.45 (*J*=7.5)	4.73	4.77	4.90	4.92	***	5.17	5.20	5.27	***	5.11(*J*=4.0)	***
G1M8B (10)	4.36 (*J*=7.2)	4.45 (*J*=6.8)	4.68	4.90	4.90	4.95	5.01	5.17	5.21	***	***	5.11(*J*=3.9)	***

Figure 3. ^{1}H NMR spectra of high-mannose-type oligosaccharides.

4.51–4.36 (m, 5H), 4.23–4.09 (m, 7H), 3.87 (m, 1H), 3.73–3.69 (m, 2H), 3.61–3.38 (m, 6H), 3.29 (m, 1H), 3.18 (m, 1H), 2.98 (m, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.16, 167.22, 138.52, 138.42, 138.08, 137.69, 137.61, 133.73, 133.55, 133.28, 131.52, 131.25, 128.82, 128.34, 128.06, 128.02, 127.92, 127.84, 127.70, 127.61, 127.58, 127.38, 127.29, 127.13, 126.86, 126.64, 125.10, 123.41, 122.19, 116.93, 99.87, 99.09, 97.02, 98.87, 78.92, 76.82, 75.71, 74.47, 74.44, 73.16, 72.93, 72.71, 71.35, 71.24, 70.38, 70.15, 69.43, 68.15, 67.82, 67.60, 61.02, 60.35, 56.54, 55.66, 41.99, 37.92, 27.99, 27.07, 25.62, 25.07, 22.82, 22.58, 21.53, 21.16, 21.11, 14.30; HRMS (FAB) *m/z* calcd for $C_{73}H_{76}N_2O_{19}Na$ 1307.4940 $(M+Na)^+$, found 1307.4940.

4.1.4. Compound 28. A mixture of AgOTf (12.7 g, 49.6 mmol) and molecular sieves 4 Å (30 g) in dry toluene (105 mL) was stirred at −40 °C for 30 min. A solution of compounds **27** (10.8 g, 21.3 mmol) and **26** (8.5 g, 18 mmol) in dry $ClCH_2CH_2Cl$ (159 mL) was added dropwise over 40 min and the mixture was stirred at −30 °C for 1 h and at ambient temperature for 12 h. The reaction was quenched with TEA (20 mL). The reaction mixture was diluted with EtOAc and filtered through Celite. The filtrate was washed with aq $NaHCO_3$ and brine, successively. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was subjected to a silica gel column chromatography (hexane/EtOAc, 10:1 to 1:1) to afford **28** (14.1 g, 83%). Physical data were consistent with those reported previously (Ref. 16).

4.1.5. Compound 29. To a stirred solution of **28** (14.1 g, 14.8 mmol) in THF/MeOH (1:1, 148 mL) was added 28% NaOMe/MeOH (1.0 mL) at room temperature. The mixture was stirred for 12 h, neutralized with Amberlyst 15 (H^+) resin, and evaporated in vacuo. The residue was subjected to a silica gel column chromatography (hexane/EtOAc, 5:1 to 1:1) to give **29** (12.9 g, 95%). Physical data were consistent with those reported previously (Ref. 16).

4.1.6. Compound 31. To a stirred mixture of Cp_2HfCl_2 (5.71 g, 15.0 mmol), AgOTf (7.74 g, 30.1 mmol), and molecular sieves 4 Å (5 g) in dry CH_2Cl_2 (200 mL) was added a solution of **30** (8.04 g, 11.6 mmol) and **29** (9.17 g, 10.0 mmol) in dry CH_2Cl_2 (50 mL) at −45 °C. The mixture was gradually warmed up to −20 °C and stirred for 1 h. The reaction was quenched with TEA (20 mL) and processed as described for **28**. The residue was subjected to a silica gel column chromatography (hexane/EtOAc, 10:1 to 5:1) to afford the compound **31** (15.9 g, 99%). Physical data were consistent with those reported previously (Ref. 16).

4.1.7. Compound 32. A mixture of **25** (2.73 g, 2.12 mmol), **31** (5.05 g, 3.19 mmol), and molecular sieves 4 Å (15 g) in dry CH_2Cl_2 (200 mL) was stirred at −40 °C for 30 min, to which was added 1 M MeOTf (31.8 mL, 31.8 mmol) in $ClCH_2CH_2Cl$. The mixture was stirred at −40 °C for 30 min and at ambient temperature (12 h). The reaction was quenched with TEA (10 mL) and processed as described for **28**. The residue was subjected to a silica gel column chromatography (toluene/EtOAc, 30:1) to afford **32** (4.92 g, 82%). Physical data were consistent with those reported previously (Ref. 16).

4.1.8. Compound 11. To a stirred solution of compound **32** (4.29 g, 1.74 mmol) in dry CH_3CN was added *p*-toluenesulfonic acid monohydrate (0.83 g, 4.4 mmol) and stirred for 6 h at room temperature. The reaction was quenched with TEA (0.1 mL) and concentrated in vacuo. The residue was subjected to a silica gel column chromatography (toluene/EtOAc, 10:1) to afford the compound **11** (3.54 g, 74%). Physical data were consistent with those reported previously (Ref. 16).

4.1.9. Compound 36. A mixture of AgOTf (14.8 g, 57.6 mmol), molecular sieves 4 Å (100 g), and compound **35** (5.64 g, 12.8 mmol) in dry $ClCH_2CH_2Cl$ (100 mL) was stirred at 0 °C for 30 min, then cooled at −30 °C. The mixture was added a solution of **33** (20.2 g, 28.9 mmol) in dry $ClCH_2CH_2Cl$ (100 mL) dropwise over 15 min. The reaction mixture was stirred at −30 °C for 1 h and at ambient temperature (12 h). It was then quenched with TEA (1 mL) and processed as described for **28**. The residue was subjected to silica gel column chromatography (hexane/EtOAc, 1:1 to 1:3) to afford **36** (21.0 g, 72%). Physical data were consistent with those reported previously (Ref. 28).

4.1.10. Compound 12. A mixture of compound **36** (6.00 g, 3.56 mmol) and NBS (948 mg, 5.33 mmol) in CH_2Cl_2 (100 mL) was added DAST (1.41 mL, 10.6 mmol) at −30 °C. The mixture was stirred at −30 °C for 1 h and at ambient temperature (3 h). The reaction mixture was processed as described for **28**. The residue was subjected to a silica gel column chromatography (hexane/EtOAc, 3:2) to afford **12** (5.05 g, 89%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.29 (m, 10H), 5.66 (d, 1H, J=51.5 Hz), 5.40–5.21 (m, 10H), 5.07 (br s, 1H), 4.89 (d, 1H, J=12 Hz), 4.81–4.64 (m, 4H), 4.20–3.71 (m, 19H), 2.15 (s, 3H), 2.13 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.087 (s, 3H), 2.07 (s, 3H), 2.05 (s, 9H), 2.04 (s, 3H), 2.03 (s, 6H), 2.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.73, 170.55, 170.39, 170.31, 170.13, 169.61, 169.57, 169.54, 169.34, 169.30, 169.20, 169.10, 137.48, 137.08, 128.51, 128.40, 127.84, 127.73, 127.55, 127.15, 105.51, 100.08, 99.25, 99.14, 99.08, 78.38, 77.78, 77.49, 75.79, 75.45, 74.91, 74.25, 73.44, 72.41, 70.10, 69.91, 69.83, 69.67, 69.53, 69.27, 69.10, 68.55, 68.40, 66.25, 66.19, 66.11, 65.90, 62.45, 62.28, 62.13, 61.89, 20.86, 20.81, 20.68, 20.52; MALDI-TOF mass *m/z* calcd for $C_{72}H_{91}FO_{39}Na$ 1621.5 $(M+Na)^+$, found 1622.2.

4.1.11. Compound 37. A mixture of **35** (1.11 g, 2.45 mmol), TfOH (20 μL), and molecular sieves AW 300 (6 g) in dry $ClCH_2CH_2Cl$ (20 mL) was stirred at −20 °C for 30 min. The donor **33** (2.90 g, 5.89 mmol) in dry $ClCH_2CH_2Cl$ (5 mL) was added dropwise over 10 min. The reaction was quenched with aq $NaHCO_3$ and processed as described for **28**. The residue was subjected to a silica gel column chromatography (hexane/EtOAc, 5:1 to 1:1) to afford **37** (1.01 g, 39%). Physical data were consistent with those reported previously (Ref. 28).

4.1.12. Compound 13. A mixture of compound **37** (229 mg, 0.206 mmol) and NBS (73.4 mg, 0.412 mmol) in CH_2Cl_2 (2 mL) was added DAST (82 μL, 0.62 mmol) at −40 °C. The reaction mixture was stirred at −30 °C for 1 h and then at ambient temperature. After 12 h, MeOH (0.1 mL)

was added and the mixture was diluted with EtOAc, washed successively with aq $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was subjected to a silica gel column chromatography (toluene/EtOAc, 5:1 to 2:1) to afford compound **13** (162 mg, 76%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.24 (m, 10H), 5.59 (d, 1H, J=52.0 Hz), 5.40–5.17 (m, 9H), 5.15 (br s, 1H), 4.90 (d, 1H, J=2.0 Hz), 4.87 (d, 1H, J=11.6 Hz), 4.80 (d, 1H, J=12.4 Hz), 4.71 (d, 1H, J=12.4 Hz), 4.64 (d, 1H, J=11.6 Hz), 4.21 (dd, 1H, J=4.8, 12.0 Hz), 4.14–3.72 (m, 16H), 2.14 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.36, 170.26, 170.16, 169.47, 169.43, 169.37, 169.32, 169.27, 169.24, 137.18, 137.09, 128.48, 128.41, 128.34, 128.32, 128.22, 127.85, 127.72, 127.66, 127.57, 127.56, 105.26, 99.05, 97.94, 75.05, 73.90, 73.85, 72.60, 69.37, 69.31, 68.92, 68.84, 68.71, 68.47, 66.38, 66.13, 66.06, 65.98, 62.46, 62.23, 20.92, 20.75, 20.69, 20.59; MALDI-TOF mass m/z calcd for $C_{48}H_{59}FO_{23}Na$ 1045.3 $(M+Na)^+$, found 1045.4.

4.1.13. Compound 40. A mixture of compound **39** (0.497 g, 0.939 mmol), TfOH (10 μL), and molecular sieves AW 300 (4 g) in dry $ClCH_2CH_2Cl$ (10 mL) was stirred at −20 °C for 30 min. A solution of the glycosyl donor **38** (0.90 g, 1.2 mmol) in dry $ClCH_2CH_2Cl$ (10 mL) was added dropwise over 10 min and stirred at −10 °C for 8 h. The reaction was quenched with aq $NaHCO_3$ and processed as described for **28**. The residue was subjected to a silica gel column chromatography (toluene/EtOAc, 5:1 to 1.5:1) to afford compound **40** (0.89 g, 84%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.27 (m, 15H), 5.66 (d, 1H, H-1), 5.38–5.23 (m, 6H), 4.85 (d, 1H, J=11.6 Hz), 4.77 (d, 1H, J=11.6 Hz), 4.71 (d, 1H, J=1.6 Hz), 4.60 (d, 1H, J=11.6 Hz), 4.50 (d, 1H, J=11.6 Hz), 4.37–3.93 (m, 16H), 2.15 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.42, 170.24, 170.05, 169.48, 169.39, 169.08, 168.89, 166.56, 166.56, 137.31, 136.95, 133.23, 131.30, 128.99, 128.39, 128.34, 127.99, 127.71, 127.65, 127.61, 127.34, 100.57, 99.17, 84.27, 81.01, 78.72, 77.75, 75.24, 74.16, 71.05, 70.63, 69.98, 69.60, 69.29, 69.05, 68.30, 66.19, 65.86, 64.53, 62.60, 62.31, 40.63, 20.93, 20.82, 20.75, 20.73, 20.71; MALDI-TOF mass m/z calcd for $C_{54}H_{63}ClO_{23}SNa$ 1169.3 $(M+Na)^+$, found 1168.5.

4.1.14. Compound 41. Trisaccharide **40** (453 mg, 0.423 mmol) was dissolved in EtOH (20 mL) and treated with DABCO (300 mg) at 50 °C for 2 h. The mixture was neutralized with Amberlist 15 E [H^+]. Insoluble materials were removed by filtration and the filtrate was concentrated in vacuo. The residue was subjected to a silica gel column chromatography (toluene/EtOAc, 3:1 to 1:1) to give **41** (430 mg, 95%). Physical data were consistent with those reported previously (Ref. 28).

4.1.15. Compound 42. A mixture of compound **41** (377 mg, 0.352 mmol), TfOH (15 μL), and molecular sieves AW 300 (4 g) in dry $ClCH_2CH_2Cl$ (10 mL) was stirred at −20 °C for 10 min. A solution of glycosyl donor **34** (472 mg, 0.958 mmol) in dry $ClCH_2CH_2Cl$ (10 mL) was added dropwise over 10 min and stirred at −10 °C for 1 h. Resulting mixture was processed as described for **28**. The residue was subjected to a silica gel column chromatography (hexane/EtOAc, 5:1 to 1:2) to afford **42** (249 mg 50%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.27 (m, 15H), 5.62 (d, 1H, J=1.2 Hz), 5.36–5.21 (m, 9H), 4.89 (d, 1H, J=10.8 Hz), 4.81 (d, 1H, J=12.0 Hz), 4.70 (d, 1H, J=2.0 Hz), 4.64 (d, 1H, J=11.6 Hz), 4.49 (d, 1H, J=12.4 Hz), 4.23–3.80 (m, 17H), 2.15 (s, 3H), 2.14 (s, 3H), 2.12 (s, 6H), 2.10 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.49, 170.31, 169.98, 169.51, 169.45, 169.35, 169.33, 169.10, 168.95, 137.66, 137.14, 133.64, 131.35, 129.08, 128.43, 128.33, 127.60, 127.55, 127.42, 127.39, 100.52, 99.16, 97.79, 84.58, 78.74, 77.82, 75.23, 74.62, 72.22, 71.00, 70.04, 69.63, 69.38, 69.29, 68.99, 68.95, 68.37, 66.70, 66.22, 66.08, 65.92, 62.58, 62.29, 62.15, 20.99, 20.85, 20.83, 20.79, 20.77, 20.75; MALDI-TOF mass m/z calcd for $C_{66}H_{80}O_{31}SNa$ 1423.4 $[M+Na]^+$, found 1422.7.

4.1.16. Compound 14. Compound **42** (180 mg, 0.128 mmol) was treated with NBS (68 mg, 0.39 mmol) and DAST (51 μL, 0.39 mmol) as described for **13** and purified by silica gel column chromatography (toluene/EtOAc, 5:1 to 2:3) to afford compound **14** (146 mg, 87%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.05 (m, 10H), 5.52 (d, 1H, J=50.7 Hz), 5.27–5.10 (m, 7H), 4.80–4.53 (m, 5H), 4.17–3.57 (m, 14H), 2.04 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H), 1.94 (s, 6H), 1.93 (s, 6H), 1.92 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.52, 170.40, 170.29, 170.05, 169.58, 169.51, 169.49, 169.22, 169.06, 137.49, 137.11, 128.84, 128.49, 128.41, 128.36, 128.03, 127.86, 127.79, 127.68, 127.63, 127.60, 127.51, 127.40, 105.17, 100.26, 99.14, 98.02, 78.71, 77.81, 75.01, 73.97, 73.44, 72.44, 69.84, 69.53, 69.34, 69.24, 69.03, 68.82, 68.43, 68.34, 66.23, 66.12, 66.04, 65.90, 62.46, 62.16, 20.83, 20.71, 20.66, 20.63, 20.50; MALDI-TOF mass m/z calcd for $C_{60}H_{75}FO_{31}Na$ 1333.4 $(M+Na)^+$, found 1333.0.

4.1.17. Compound 15. Compound **43** (537 mg, 0.382 mmol) was treated with NBS (135 mg, 0.759 mmol) and DAST (0.10 mL, 0.75 mmol) as described for **13** and purified by silica gel column chromatography (toluene/EtOAc, 5:1 to 2:1) to afford compound **15** (452 mg, 90%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.29 (m, 10H), 5.66 (d, 1H, J=50.8 Hz), 5.41–5.10 (m, 23H), 4.89–4.64 (m, 5H), 4.21–3.75 (m, 30H), 2.11 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.06 (s, 6H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.81, 170.47, 170.43, 170.09, 169.64, 169.60, 169.49, 169.30, 169.28, 137.32, 137.18, 136.92, 128.89, 128.61, 128.53, 128.34, 128.08, 127.86, 127.78, 127.67, 127.45, 125.16, 105.51, 100.08, 99.25, 99.14, 99.08, 77.41, 75.94, 75.42, 75.10, 74.24, 73.86, 72.61, 71.89, 69.95, 69.71, 69.31, 69.10, 69.02, 68.73, 68.61, 68.43, 66.29, 66.16, 65.98, 62.50, 62.34, 61.99, 20.85, 20.71, 20.66, 20.56; MALDI-TOF mass m/z calcd for $C_{60}H_{75}FO_{31}Na$ 1333.4 $(M+Na)^+$, found 1332.7.

4.1.18. Compound 16. To a stirred solution of compound **44** (73.0 mg, 0.245 mmol), p-methoxybenzyl chloride (41 μL), Bu_4NHSO_4 (40 mg) in CH_2Cl_2 (4 mL) was added 5% aq

NaOH (0.5 mL). The mixture was stirred at 45 °C for 12 h. The reaction mixture was diluted with $CHCl_3$ and washed with brine. The organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue was subjected to a PTLC (toluene/EtOAc, 8:1) to afford compound **45** (53.2 mg, 52%) and its regioisomer (33.0 mg, 32%). Compound **45** (327 mg, 0.782 mmol) was dissolved in pyridine (3 mL) and added PivCl (0.57 mL) at 0 °C. The mixture was stirred at room temperature for 12 h. The reaction was added MeOH (1 mL) and evaporated in vacuo, The residue was diluted with EtOAc and washed with aq $CuSO_4$, brine, satd aq $NaHCO_3$, and brine. The organic layer was dried over $NaSO_4$ and evaporated in vacuo. The residue was crystallized from 2-propanol to give **16** (238 mg, 61%) as a colorless needles: mp 124–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–6.85 (m, 9H), 5.58 (s, 1H), 5.41 (t, 1H, J=9.2 Hz), 4.52 (d, 1H, J=9.2 Hz), 4.58–4.53 (m, 2H), 4.38 (dd, 1H, J=4.8, 10.4 Hz), 3.97 (s, 3H), 3.63 (t, 1H, J=9.6 Hz), 3.55–3.51 (m, 2H), 2.26 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.01, 159.26, 136.86, 129.58, 129.38, 128.79, 128.07, 125.80, 113.75, 100.97, 86.31, 79.15, 79.14, 74.75, 74.33, 70.19, 68.63, 55.31, 27.23, 13.46; Anal. Calcd for $C_{27}H_{34}O_7S$: C, 64.52; H, 6.92; S, 6.38. Found: C, 64.26; H, 6.77; S, 6.20.

4.1.19. Compound 48. To a solution of compound **47** (378 mg, 0.649 mmol) in CH_2Cl_2 (10 mL) was added DAST (171 μL, 1.30 mmol) at −40 °C for 30 min. MeOH (0.5 mL) was added to the reaction mixture, which was diluted with EtOAc and washed successively with aq $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, concentrated and subjected to a silica gel column chromatography (toluene/EtOAc, 5:1) to afford **48** (348 mg, 92%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.06 (m, 20H), 5.64–5.53 (m, 2H), 5.44 (dd, 1H, J=6.0, 46.0 Hz), 4.74 (d, 1H, J=12.0 Hz), 4.62–4.53 (m, 3H), 4.38 (dd, 1H, J=5.2, 12.4 Hz), 4.16 (m, 1H), 3.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.12 (d, J=220.1 Hz), 77.72 (d, J=25.1 Hz), 73.62, 72.81, 72.02, 68.67, 62.89; MALDI-TOF mass m/z calcd for $C_{34}H_{29}FO_8Na$ 607.6 $(M+Na)^+$, found 607.7.

4.1.20. Compound 17. A mixture of Cp_2HfCl_2 (187 mg, 0.493 mmol), AgOTf (273 mg, 1.06 mmol), and molecular sieves 4 Å (1.4 g) was added a solution of compounds **48** (160 mg, 0.274 mmol) and **46** (107 mg, 0.274 mmol) in ether/toluene (2:1, 30 mL) at −40 °C. The mixture was stirred at −40 °C for 9 h. The reaction was quenched with TEA and processed as described for **28**. The residue was subjected to a column of Bio-Beads SX-4 (toluene) to afford **17** (165 mg, 63%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–6.69 (m, 30H), 6.01 (t, 1H, J=9.6 Hz), 5.73 (d, 1H, J=3.6 Hz), 5.47 (s, 1H), 5.41 (t, 1H, J=9.9 Hz), 5.20 (d, 1H, J=10.4 Hz), 4.93 (d, 1H, J=10.4 Hz), 4.51 (d, 1H, J=9.6 Hz), 4.36 (dd, 1H, J=4.8, 10.4 Hz), 4.25–4.11 (m, 3H), 3.89 (t, 1H, J=9.6 Hz), 3.83–3.75 (m, 2H), 3.69 (t, 1H, J=9.2 Hz), 3.60 (dd, 1H, J=3.6, 10.0 Hz), 3.54 (m, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.83, 165.60, 165.06, 137.11, 136.77, 136.73, 133.08, 132.86, 132.69, 129.76, 129.71, 129.62, 129.58, 129.42, 129.38, 128.91, 128.85, 128.35, 128.19, 128.10, 128.05, 128.02, 128.01, 127.97, 127.68, 127.52, 127.41, 127.19, 126.33, 125.13, 102.21, 95.56, 86.09, 81.97, 78.62, 75.54, 75.17, 71.33, 70.57, 69.87, 69.02, 68.72, 67.56, 62.05, 21.42, 12.85; MALDI-TOF mass m/z calcd for $C_{55}H_{52}O_{13}SNa$ 975.3 $(M+Na)^+$, found 975.7.

4.1.21. Compound 50. A mixture of Cp_2HfCl_2 (80.9 mg, 0.213 mmol), AgOTf (110 mg, 0.426 mmol), and molecular sieves 4 Å (1.4 g) in dry CH_2Cl_2 (2 mL) was stirred at −10 °C. A solution of glycosyl donor **48** (83.5 mg, 0.142 mmol) and glycosyl acceptor **49** (52 mg 0.070 mmol) in dry CH_2Cl_2 (2 mL) was added. The mixture was stirred at −10 °C for 7 h and processed as described for **28**. The residue was subjected to a column of Bio-Beads SX-4 (toluene) to afford compound **50** (82 mg, 90%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.12 (m, 36H), 6.03 (t, 1H, J=9.6 Hz), 5.82 (t, 1H, J=9.6 Hz), 5.41 (t, 1H, J=9.6 Hz), 5.29 (t, 1H, J=9.6 Hz), 5.14 (d, 1H, J=3.6 Hz), 4.93 (d, 1H, J=3.2 Hz), 4.66 (d, 1H, J=11.6 Hz), 4.51 (d, 1H, J=11.6 Hz), 4.48–4.40 (m, 2H), 4.35–4.28 (m, 2H), 4.22 (m, 1H), 4.05–3.98 (m, 3H), 3.82 (s, 3H), 3.77 (s, 3H), 3.73 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.85, 165.76, 165.18, 165.07, 165.02, 164.97, 163.48, 163.29, 163.18, 159.31, 137.31, 133.01, 132.92, 132.82, 131.93, 131.66, 130.01, 129.69, 129.58, 129.57, 128.73, 128.59, 128.30, 128.16, 128.13, 127.78, 122.12, 121.68, 121.25, 113.83, 113.55, 96.91, 94.98, 72.56, 71.78, 71.23, 69.83, 69.72, 69.36, 68.11, 67.99, 63.12, 62.64, 55.40, 55.21, 55.15; MALDI-TOF mass m/z calcd for $C_{72}H_{66}O_{21}Na$ 1289.4, found 1290.3.

4.1.22. Compound 52. To a solution of **50** (264 mg, 0.209 mmol) in CH_2Cl_2 (5 mL) was added DDQ (273 mg, 1.20 mmol), followed by H_2O (1 mL). The mixture was stirred at room temperature for 12 h, diluted with EtOAc, quenched with ascorbate buffer. The organic layer was washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was subjected to a silica gel column chromatography (hexane/EtOAc, 5:1 to 2:3) to give hemiacetal **51** (175 mg, 73%): MALDI-TOF mass m/z calcd for $C_{64}H_{58}O_{20}Na$ 1169.3 $(M+Na)^+$, found 1169.8. Hemiacetal **51** (157 mg, 0.137 mmol) was dissolved in CCl_3CN (1 mL) and CH_2Cl_2 (1 mL) and added DBU (10 μL) at 0 °C. After stirring for 1 h, the mixture was subjected to a silica gel column chromatography (toluene/EtOAc, 10:1 to 3:1 in 0.1% TEA) to give **52** (177 mg, quant.) as a slightly yellow amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.02–6.63 (m, 33H), 6.13 (t, 1H, J=10.0 Hz), 5.77 (t, 1H, J=9.8 Hz), 5.57 (t, 1H, J=10.1 Hz), 5.34 (t, 1H, J=10.0 Hz), 5.08 (d, 1H, J=3.4 Hz), 4.35 (dd, 1H, J=5.3, 12.4 Hz), 4.25 (m, 2H), 4.11 (m, 1H), 3.94 (m, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.69 (dd, 1H, J=3.4, 10.0 Hz), 3.57 (s, 3H).

4.1.23. Compound 18. A mixture of **52** (65 mg, 0.057 mmol), **46** (16 mg, 0.042 mmol), and molecular sieves AW 300 (700 mg) in dry toluene (3 mL) was stirred at −40 °C for 30 min, to which was added TMSOTf (5 μL). The mixture was stirred at −40 °C for 2 h, then quenched with TEA (20 μL) and processed as described for **28**. The residue was subjected to a column of Bio-Beads SX-4 (toluene/EtOAc, 1:1), then PTLC (toluene/EtOAc, 5:1) to afford **18** (28 mg, 45%) as a white solid: R_f 0.48 (toluene/EtOAc, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–6.63 (m, 42H), 6.14 (t, 1H, J=10.0 Hz), 5.86 (t, 1H, J=10.0 Hz), 5.82

(d, 1H, J=3.6 Hz), 5.45 (t, 1H, J=10.0 Hz), 5.40 (s, 1H), 5.27 (t, 1H, J=10.0 Hz), 5.19–5.02 (m, 2H), 4.93 (d, 1H, J=3.2 Hz), 4.65–4.16 (m, 9H), 3.94 (dd, 1H, J=3.7, 10.5 Hz), 3.83, 3.81, 3.65 (dd, 1H, J=3.2, 10.0 Hz), 3.58 (t, 1H, J=9.3 Hz), 3.50 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.94, 165.66, 165.20, 165.10, 164.85, 163.40, 163.13, 138.15, 137.38, 136.87, 133.01, 132.86, 131.83, 131.68, 129.64, 129.59, 129.52, 129.15, 128.58, 128.43, 128.26, 128.15, 128.11, 127.74, 127.45, 126.03, 122.36, 121.64, 121.33, 113.53, 113.37, 95.95, 95.03, 86.05, 81.41, 78.74, 76.60, 75.54, 74.57, 70.98, 70.83, 69.98, 69.52, 69.17, 68.47, 67.84, 67.77, 62.93, 62.21, 55.40, 55.07, 13.01; MALDI-TOF mass m/z calcd for $C_{85}H_{80}O_{24}SNa$ 1539.5 $(M+Na)^+$, found 1540.2.

4.1.24. Compound 53. A mixture of AgOTf (465 mg, 1.81 mmol), Cp_2HfCl_2 (344 mg, 0.906 mmol), and molecular sieves 4 Å (6 g) in dry toluene (50 mL) was stirred at room temperature for 30 min, then cooled at −30 °C. A solution of donor **12** (1.45 g, 0.906 mmol) and acceptor **11** (1.66 g, 0.604 mmol) in dry toluene (10 mL) was added dropwise over 5 min. The mixture was stirred at −10 °C for 4 h. The reaction was quenched with TEA (1 mL) and processed as described for **28**. The residue was subjected to a silica gel column chromatography (hexane/EtOAc, 1:1 to 2:3) to afford **53** (2.27 g, 87%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–6.70 (m, 93H), 5.56 (m, 1H), 5.39–5.20 (m, 15H), 4.98–3.20 (m, 96H), 3.10 (m, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.02 (s, 6H), 2.01 (s, 3H), 1.98 (s, 12H), 1.97 (s, 3H), 1.96 (s, 3H), 1.94 (s, 3H), 1.91 (s, 3H), 1.89 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.71, 170.45, 170.14, 169.96, 169.91, 169.58, 169.48, 169.38, 169.25, 169.17, 168.94, 167.90, 167.29, 138.63, 138.43, 138.29, 138.23, 138.18, 138.10, 138.06, 137.90, 137.76, 137.66, 133.61, 133.35, 131.60, 131.26, 128.42, 128.23, 128.11, 128.06, 127.86, 127.77, 127.70, 127.65, 127.59, 127.56, 127.50, 127.36, 127.27, 127.07, 126.72, 123.29, 123.00, 117.00, 101.11, 99.90, 99.31, 99.08, 98.62, 96.91, 79.79, 79.45, 79.17, 78.48, 78.25, 75.88, 75.26, 75.03, 74.86, 74.58, 74.42, 74.34, 74.21, 73.37, 73.19, 73.07, 72.76, 72.58, 72.47, 72.25, 72.18, 71.60, 71.15, 70.04, 69.83, 69.58, 69.51, 69.31, 69.11, 69.00, 68.80, 68.72, 68.55, 68.26, 68.05, 67.93, 67.43, 67.27, 67.09, 66.22, 66.10, 65.87, 65.45, 62.02, 61.83, 61.53, 56.49, 55.56, 38.68, 30.33, 28.88, 27.15, 23.73, 22.94, 21.42, 20.87, 20.81, 20.76, 20.63, 20.60, 20.57, 19.34, 14.03, 10.95; MALDI-TOF mass m/z calcd for $C_{236}H_{260}O_{73}N_2Na$ 4343.6 $(M+Na)^+$, found 4343.5; Anal. Calcd for $C_{236}H_{260}N_2O_{73}Si$: C, 65.60; H, 6.07; N, 0.65. Found: C, 65.56; H, 6.12; N, 0.56.

4.1.25. Compound 54. To a stirred solution of compound **53** (2.27 g, 0.525 mmol) and DMAP (6.4 mg) in pyridine (40 mL) was added acetic anhydride (20 mL). The mixture was stirred at 50 °C for 12 h. To the mixture was added methanol (20 mL) and volatiles were removed by evaporation in vacuo. The residue was diluted with EtOAc and washed successively with aq $CuSO_4$, brine, aq $NaHCO_3$, and brine. The organic layer was dried ($MgSO_4$) and evaporated in vacuo. The residue was subjected to a silica gel column chromatography (hexane/EtOAc 5:1 to 1:3) to give the acetylated undecasaccharide (2.22 g, 97%). The acetylated compound (2.22 g, 0.509 mmol) was dissolved in a 3 mL Teflon reaction vessel in DMF (2 mL) containing 10% HF/pyridine. It was compressed to 1.0 GPa and left at 30 °C for 24 h and the resultant mixture was diluted with EtOAc and washed successively with aq $NaHCO_3$ and brine, successively. The organic layer was dried over $MgSO_4$ and evaporated in vacuo. The residue was subjected to a silica gel column chromatography (hexane/EtOAc 10:1 to 1:2) to give **54** (1.99 g, 95%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–6.71 (m, 83H), 5.59 (m, 1H), 5.41–5.11 (m, 16H), 5.01–4.91 (m, 5H), 4.86–4.77 (m, 7H), 4.69–4.14 (m, 23H), 4.33–4.23 (m, 57H), 3.48 (m, 1H), 3.26 (m, 1H), 2.07–3.14 (m, 2H), 2.11 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.04 (s, 6H), 2.02 (s, 3H), 2.00 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H), 1.96 (s, 3H), 1.91 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.71, 170.45, 170.14, 169.96, 169.91, 169.58, 169.48, 169.38, 169.25, 169.17, 168.94, 167.90, 167.29, 138.63, 138.43, 138.29, 138.23, 138.10, 138.06, 137.90, 137.76, 137.66, 133.61, 133.35, 131.60, 131.26, 128.42, 128.23, 128.11, 128.06, 127.88, 127.77, 127.70, 127.65, 127.59, 127.50, 127.36, 127.27, 127.07, 126.72, 123.29, 123.00, 117.00, 101.14, 100.77, 99.29, 99.18, 98.68, 98.56, 98.33, 96.96, 96.86, 79.90, 79.71, 78.91, 78.00, 77.53, 77.20, 76.23, 75.74, 75.05, 74.81, 74.70, 74.60, 74.43, 74.29, 74.03, 73.34, 73.21, 73.05, 72.86, 72.76, 72.67, 72.59, 72.50, 72.02, 71.87, 71.56, 71.47, 70.83, 70.07, 69.87, 69.63, 69.57, 69.39, 69.18, 69.05, 68.90, 68.71, 68.54, 68.67, 67.99, 67.21, 66.28, 66.11, 65.88, 65.48, 62.00, 61.89, 61.43, 56.56, 55.61, 20.95, 20.85, 20.71, 20.68, 20.64, 20.60, 20.54; MALDI-TOF mass m/z calcd for $C_{222}H_{244}N_2NaO_{74}$ 4144.5 $(M+Na)^+$, found 4144.2; Anal. Calcd for $C_{222}H_{244}N_2O_{74}$: C, 64.65; H, 5.96; N, 0.68. Found: C, 64.44; H, 5.97; N, 0.65.

4.1.26. Compound 55. A mixture of AgOTf (80 mg, 0.31 mmol), Cp_2HfCl_2 (52 mg, 0.14 mmol), and molecular sieves 4 Å (2 g) in dry toluene (4 mL) was stirred at room temperature for 30 min, then cooled at −30 °C. To a solution of **13** (128 mg, 0.125 mmol) and **11** (208 mg, 0.0759 mmol) in dry toluene (15 mL) the mixture was added dropwise over 5 min. The mixture was stirred at −10 °C for 12 h. The mixture was processed as described for **53** and purified by PTLC (toluene/EtOAc, 3:1) to afford **55** (219 mg, 77%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–6.68 (m, 93H), 5.56 (m, 1H), 5.35–5.14 (m, 10H), 4.99–3.23 (m, 98H), 3.13 (m, 1H), 2.12 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H), 1.92 (s, 3H), 1.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.23, 169.41, 169.34, 138.53, 138.44, 138.41, 138.19, 138.16, 138.05, 138.00, 137.97, 137.92, 137.86, 137.82, 137.77, 137.60, 135.95, 135.87, 133.48, 133.20, 129.33, 128.28, 128.19, 128.09, 128.06, 128.00, 127.95, 127.86, 127.82, 127.70, 127.64, 127.50, 127.32, 127.30, 127.22, 127.19, 127.16, 127.07, 126.83, 126.73, 126.58, 116.84, 100.91, 99.80, 99.49, 99.26, 97.51, 96.87, 79.74, 79.38, 78.20, 75.28, 75.03, 74.89, 74.40, 74.32, 73.91, 73.42, 73.10, 72.80, 72.55, 72.36, 72.17, 71.43, 71.08, 70.98, 69.35, 69.32, 69.21, 69.01, 68.52, 68.32, 67.98, 67.38, 67.06, 66.20, 65.93, 65.80, 62.20, 62.14, 56.49, 55.58, 20.92, 20.85, 20.76, 20.71, 20.68, 19.39; MALDI-TOF mass m/z calcd for $C_{212}H_{228}O_{74}N_2SiNa$ 3764.5 $(M+Na)^+$, found 3764.4;

Anal. Calcd for $C_{212}H_{228}N_2O_{57}Si$: C, 68.01; H, 6.14; N, 0.75. Found: C, 67.77; H, 6.19; N, 0.69.

4.1.27. Compound 56. Compound **55** (205 mg, 0.0548 mmol) was acetylated and desilylated as described for **54**. The residue was subjected to a PTLC (toluene/EtOAc 2:1) to give **56** (168 mg, 86%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–6.72 (m, 83H), 5.58 (m, 1H), 5.38 (d, 1H, J=2.9 Hz), 5.34–3.49 (m, 93H), 3.46–3.31 (m, 2H), 3.34–3.18 (m, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.99 (s, 6H), 1.97 (s, 3H), 1.94 (s, 3H), 1.93 (s, 3H), 1.92 (s, 3H), 1.91 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.31, 170.03, 169.48, 169.44, 163.31, 169.28, 169.23, 167.77, 167.15, 138.54, 138.35, 138.32, 138.21, 138.12, 138.05, 137.98, 137.94, 137.84, 137.81, 137.71, 137.65, 133.61, 133.50, 131.31, 131.16, 128.34, 128.24, 128.14, 128.11, 128.05, 128.03, 127.98, 127.87, 127.80, 127.77, 127.69, 127.65, 127.61, 127.56, 127.52, 127.46, 127.41, 127.31, 127.27, 127.22, 127.19, 127.15, 127.01, 126.78, 126.65, 123.32, 122.89, 116.95, 101.08, 100.68, 99.18, 98.32, 97.45, 96.92, 96.77, 79.85, 79.53, 78.78, 77.95, 77.82, 77.20, 76.20, 75.69, 75.04, 74.85, 74.78, 74.69, 74.55, 74.38, 74.29, 74.01, 73.86, 73.33, 73.17, 73.04, 72.85, 72.72, 72.64, 72.49, 72.00, 71.83, 71.63, 71.50, 71.43, 71.18, 70.85, 69.39, 69.26, 69.17, 69.03, 68.95, 68.69, 68.60, 68.37, 67.98, 67.86, 67.22, 66.71, 66.23, 65.93, 65.68, 62.24, 62.00, 56.54, 55.61, 21.04, 20.94, 20.90, 20.83, 20.75, 20.66; MALDI-TOF mass m/z calcd for $C_{198}H_{212}O_{58}N_2Na$ 3568.4 $(M+Na)^+$, found 3568.1; Anal. Calcd for $C_{198}H_{212}N_2O_{58}$: C, 67.03; H, 6.02; N, 0.79. Found: C, 66.86; H, 6.00; N, 0.75.

4.1.28. Compound 57. A mixture of AgOTf (84.9 mg, 0.330 mmol), Cp_2HfCl_2 (62.8 mg, 0.165 mmol), and molecular sieves 4 Å (5 g) in dry toluene (8 mL) was stirred at room temperature for 30 min, then cooled at −30 °C. To a solution of **14** (146 mg, 0.111 mmol) and **11** (268 mg, 0.0978 mmol) in dry toluene (15 mL) the mixture was added dropwise over 5 min and stirred at −10 °C for 3 h. The reaction mixture was processed as described for **53** and purified by silica gel column chromatography (toluene/EtOAc, 5:1 to 1:1) to afford **57** (295 mg, 75%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–6.72 (m, 93H), 5.64 (m, 1H), 5.34–3.22 (m, 104H), 3.14 (m, 1H), 2.16 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 2.04 (s, 6H), 2.03 (s, 6H), 2.02 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H), 1.94 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.36–169.30, 138.45–126.76, 116.91, 101.08, 99.68, 99.58, 99.25, 98.62, 97.79, 97.51, 96.94, 96.85, 56.53, 55.58, 27.22, 20.93, 20.84, 20.76, 20.70, 20.66, 19.42, 14.29; MALDI-TOF mass m/z calcd for $C_{224}H_{244}O_{65}N_2SiNa$ 4052.6 $(M+Na)^+$, found 4053.7; Anal. Calcd for $C_{224}H_{244}N_2O_{65}Si$: C, 66.72; H, 6.10; N, 0.69. Found: C, 66.50; H, 6.13; N, 0.61.

4.1.29. Compound 58. Compound **57** (275 mg, 0.0682 mmol) was acetylated and desilylated as described for **54**. Purification by silica gel column chromatography (hexane/EtOAc, 5:1 to 1:1) gave **58** (182 mg, 70%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–6.73 (m, 83H), 5.58 (m, 1H), 5.54 (d, 1H, J=4.8 Hz), 5.40–3.12 (m, 107H), 2.10 (s, 3H), 2.03 (s, 9H), 2.02 (s, 3H), 1.99 (s, 6H), 1.98 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H), 1.89 (s, 6H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.36–169.30, 138.35–127.00, 116.95, 101.15, 100.59, 99.30, 98.69, 98.29, 97.49, 96.91, 96.80, 79.89, 79.65, 78.97, 77.95, 77.64, 77.14, 77.02, 76.67, 76.18, 75.71, 75.05, 74.86, 74.79, 74.62, 74.40, 74.26, 74.01, 73.05, 72.86, 72.74, 72.65, 72.56, 71.86, 71.52, 71.45, 71.14, 70.85, 70.03, 69.58, 69.15, 69.02, 68.96, 68.76, 68.65, 68.49, 68.39, 67.97, 67.86, 67.28, 66.18, 66.10, 65.87, 65.51, 62.21, 62.05, 61.43, 56.58, 55.62, 21.54, 20.90, 20.84, 20.76, 20.68; MALDI-TOF mass m/z calcd for $C_{210}H_{228}O_{66}N_2Na$ 3856.5 $(M+Na)^+$, found 3857.6; Anal. Calcd for $C_{210}H_{228}N_2O_{66}$: C, 65.75; H, 5.99; N, 0.73. Found: C, 65.76; H, 6.19; N, 0.68.

4.1.30. Compound 59. A mixture of AgOTf (103 mg, 0.401 mmol), Cp_2HfCl_2 (77.7 mg, 0.201 mmol), and molecular sieves 4 Å (4 g) in dry toluene (5 mL) was stirred at room temperature for 30 min, then cooled at −30 °C. To a solution of **15** (381 mg, 0.291 mmol) and **11** (550 mg, 0.201 mmol) in dry toluene (45 mL) the mixture was added dropwise over 5 min. The reaction mixture was stirred at −10 °C for 3 h and processed as described for **53**. The residue was subjected to a silica gel column chromatography (hexane/EtOAc, 1:1 to 2:3) to afford **59** (682 mg, 84%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–6.70 (m, 93H), 5.57 (m, 1H), 5.37–5.12 (m, 12H), 5.01–3.43 (m, 89H), 3.30 (m, 2H), 3.22 (m, 2H), 3.11 (m, 1H), 2.00 (s, 6H), 1.92 (s, 9H), 1.92 (s, 3H), 1.90 (s, 6H), 1.88 (s, 3H), 1.87 (s, 3H), 1.84 (s, 3H), 1.83 (s, 3H), 1.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.60, 170.13, 170.01, 169.35, 169.30, 169.29, 169.07, 138.49, 138.45, 138.42, 138.23, 138.21, 138.09, 138.03, 137.84, 137.79, 136.00, 135.92, 133.54, 128.31, 128.22, 128.13, 128.05, 128.00, 127.90, 127.83, 127.75, 127.73, 127.61, 127.56, 127.37, 127.35, 127.31, 127.21, 127.13, 127.10, 126.91, 126.80, 126.60, 126.45, 116.91, 101.01, 99.97, 99.41, 99.09, 98.41, 96.93, 96.87, 79.78, 79.50, 79.10, 78.28, 77.71, 77.56, 77.20, 75.86, 75.32, 75.05, 74.89, 74.48, 74.34, 73.89, 73.41, 73.22, 73.16, 72.81, 72.61, 72.47, 72.21, 71.77, 71.53, 71.29, 71.14, 69.94, 69.77, 69.64, 69.38, 69.21, 69.05, 68.91, 68.63, 68.56, 68.37, 68.02, 67.48, 67.32, 67.01, 66.29, 66.15, 65.94, 65.81, 62.11, 61.90, 56.53, 55.63, 27.26, 20.99, 20.91, 20.84, 20.73, 19.45; MALDI-TOF mass m/z calcd for $C_{224}H_{244}O_{65}N_2SiNa$ 4053.5 $(M+Na)^+$, found 4053.8; Anal. Calcd for $C_{224}H_{244}N_2O_{65}Si$: C, 66.72; H, 6.10; N, 0.69. Found: C, 66.51; H, 6.13; N, 0.66.

4.1.31. Compound 60. Compound **59** (303 mg, 0.0751 mmol) was acetylated and desilylated as described for **54**. Purification by silica gel column chromatography (toluene/EtOAc, 5:1 to 1:1) afforded **60** (285 mg, 97%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–6.73 (m, 83H), 5.58 (m, 1H), 5.38–4.40 (m, 46H), 4.32–3.45 (m, 48H), 3.67 (m, 1H), 3.31 (m, 1H), 3.23 (m, 1H), 3.17 (m, 1H), 2.11 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.64, 170.08, 169.73, 169.50, 169.43, 169.34, 169.15, 138.53, 138.36, 138.31, 138.18, 138.13, 138.05, 138.02, 137.98, 137.82, 137.76, 137.66, 133.54, 128.37, 128.28, 128.19, 128.14, 128.09, 128.07, 128.02, 127.95, 127.87, 127.82, 127.13,

127.66, 127.60, 127.56, 127.42, 127.32, 127.30, 127.23, 127.12, 127.03, 126.68, 126.42, 117.00, 101.07, 100.78, 99.17, 98.33, 97.11, 96.94, 96.82, 79.90, 79.62, 78.76, 77.98, 77.74, 77.55, 77.20, 76.23, 75.73, 75.08, 74.86, 74.64, 74.42, 74.34, 74.06, 73.68, 73.38, 73.21, 73.07, 72.86, 72.79, 72.66, 72.55, 72.47, 72.03, 71.88, 71.68, 71.54, 71.47, 71.27, 70.85, 69.96, 69.63, 69.44, 69.22, 69.05, 68.91, 68.73, 68.65, 68.55, 68.37, 68.21, 68.00, 67.18, 66.28, 66.17, 65.90, 65.77, 62.10, 62.00, 61.94, 56.53, 55.64, 21.06, 20.96, 20.87, 20.80, 20.76, 20.73; MALDI-TOF mass *m/z* calcd for $C_{210}H_{228}O_{66}N_2Na$ 3856.5 $(M+Na)^+$, found 3856.6; Anal. Calcd for $C_{210}H_{228}N_2O_{66}$: C, 65.75; H, 5.99; N, 0.73. Found: C, 65.76; H, 5.89; N, 0.75.

4.1.32. Compound 61. A mixture of **18** (28.1 mg, 0.0185 mmol), **54** (49.8 mg, 0.0120 mmol), DTBMP (38 mg, 0.012 mmol), and molecular sieves 4 Å (500 mg) in dry $ClCH_2CH_2Cl$ (1 mL) and cyclohexane (4 mL) was stirred at room temperature for 2 h, then added 1 M MeOTf (0.15 mL, 0.15 mmol) in $ClCH_2CH_2Cl$. The reaction mixture was stirred at 50 °C for 12 h. The reaction was quenched with TEA (0.1 mL). The mixture was diluted with EtOAc and filtered through Celite. The filtrate was washed with aq $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was subjected to a column of Bio-Beads SX-4 (toluene/EtOAc, 1:1), then PTLC (toluene/EtOAc, 1:2) to afford **61** (38.1 mg, 57%) as a colorless amorphous: R_f 0.75 (toluene/EtOAc, 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–6.56 (m, 125H), 6.10 (t, 1H, J=10.0 Hz), 5.76 (t, 1H, J=10.0 Hz), 5.66 (d, 1H, J=3.2 Hz), 5.55–5.47 (m, 1H), 5.43 (t, 1H, J=10.0 Hz), 2.03, 2.00, 1.99, 1.96, 1.95, 1.93, 1.92, 1.91, 1.91, 1.90, 1.89, 1.88; MALDI-TOF mass *m/z* calcd for $C_{306}H_{320}N_2O_{98}Na$ 5612.9 $(M+Na)^+$, found 5611.3.

4.1.33. Compound 62. A mixture of **17** (30.6 mg, 0.0321 mmol), **54** (77.4 mg, 0.0188 mmol), DTBMP (52 mg, 0.26 mmol), and molecular sieves 4 Å (500 mg) in dry $ClCH_2CH_2Cl$ (3 mL) and cyclohexane (9 mL) was stirred at room temperature for 30 min then added 1 M MeOTf (0.2 mL, 0.2 mmol) in $ClCH_2CH_2Cl$. The reaction mixture was stirred at 50 °C for 12 h and processed as described for **61**. Purification by PTLC (toluene/EtOAc, 5:4) afforded **62** (80.4 mg, 85%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–6.61 (m, 113H), 5.94 (t, 1H, J=9.0 Hz), 5.65 (d, 1H, J=4.0 Hz), 5.63–5.54 (m, 1H), 5.42–3.45 (m, 124H), 3.30 (m, 1H), 3.25–3.18 (m, 2H), 2.10 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.98 (s, 6H), 1.97 (s, 3H), 1.96 (s, 3H), 1.95 (s, 3H), 1.90 (s, 3H), 1.89 (s, 3H); MALDI-TOF mass *m/z* calcd for $C_{276}H_{292}N_2O_{87}Na$ 5052.2 $(M+Na)^+$, found 5052.4; Anal. Calcd for $C_{276}H_{292}N_2O_{87}$: C, 65.91; H, 5.85; N, 0.56. Found: C, 65.51; H, 5.80; N, 0.49.

4.1.34. Compound 63. A mixture of **54** (500 mg, 0.121 mmol), **16** (244 mg, 0.485 mmol), DTBMP (117 mg, 0.558 mmol), and molecular sieves 4 Å (5 g) in dry $ClCH_2CH_2Cl$ (11 mL) and cyclohexane (55 mL) was stirred at room temperature for 30 min, then added 1 M MeOTf (0.68 mL, 0.68 mmol) in $ClCH_2CH_2Cl$. The reaction mixture was stirred at 50 °C for 12 h and processed as described for **61**. Purification by PTLC (toluene/EtOAc, 1:2) afforded **63** (555 mg, 93%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–6.64 (m, 92H), 5.71 (t, 1H, J=9.8 Hz), 5.58 (m, 1H), 5.41 (s, 1H), 5.38 (br d, 1H, J=2.8 Hz), 5.36–3.42 (m, 117H), 3.33 (m, 1H), 3.23 (m, 1H), 3.17 (m, 2H), 2.10 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 9H), 1.97 (s, 3H), 1.96 (s, 3H), 1.95 (s, 3H), 1.90 (s, 3H), 1.88 (s, 3H), 1.71 (s, 9H); MALDI-TOF mass *m/z* calcd for $C_{248}H_{274}N_2O_{81}Na$ 4601.8 $(M+Na)^+$, found 4601.7; Anal. Calcd for $C_{248}H_{274}N_2O_{81}$: C, 65.05; H, 6.03; N, 0.61. Found: C, 64.51; H, 5.97; N, 0.58.

4.1.35. Compound 64. A mixture of **56** (36.7 mg, 0.0103 mmol), **16** (36.6 mg, 0.0728 mmol), DTBMP (30 mg, 0.14 mmol), and molecular sieves 4 Å (1.0 g) in dry $ClCH_2CH_2Cl$ (2 mL) and cyclohexane (4 mL) was stirred at room temperature for 30 min, then added 1 M MeOTf (0.100 mL, 0.100 mmol) in $ClCH_2CH_2Cl$. The reaction mixture was stirred at 45 °C for 19 h and processed as described for **61**. The mixture was subjected to a PTLC (toluene/EtOAc, 3:4) to afford **64** (35.6 mg, 86%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–6.42 (m, 92H), 5.72 (t, 1H, J=9.6 Hz), 5.58 (m, 1H), 5.42 (s, 1H), 5.38 (d, 1H, J=3.2 Hz), 5.34–3.45 (m, 102H), 3.33 (m, 2H), 3.23 (m, 1H), 3.18 (m, 2H), 2.05 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H), 1.93 (s, 3H), 1.92 (s, 3H), 1.91 (s, 3H), 1.88 (s, 3H), 1.17 (s, 9H); MALDI-TOF mass *m/z* calcd for $C_{224}H_{242}N_2O_{65}Na$ $(M+Na)^+$ 4022.6, found 4022.5; Anal. Calcd for $C_{224}H_{242}N_2O_{65}$: C, 67.22; H, 6.09; N, 0.70. Found: C, 67.43; H, 6.35; N, 0.56.

4.1.36. Compound 65. A mixture of **58** (71.2 mg, 0.0186 mmol), **16** (37.9 mg, 0.0754 mmol), DTBMP (70.3 mg, 0.570 mmol), and molecular sieves 4 Å (2.0 g) in dry $ClCH_2CH_2Cl$ (4 mL) and cyclohexane (10 mL) was stirred at room temperature for 30 min, then added 1 M MeOTf (0.400 mL, 0.400 mmol) in $ClCH_2CH_2Cl$. The reaction mixture was stirred at 45 °C for 12 h. The mixture was processed as described for **61** and purified by PTLC (toluene/EtOAc, 3:4) to afford **65** (72.5 mg, 91%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–6.63 (m, 92H), 5.71 (t, 1H, J=10.0 Hz), 5.90 (m, 1H), 5.41 (br s, 2H), 5.33–3.14 (m, 114H), 2.10 (s, 3H), 2.03 (s, 9H), 2.02 (s, 3H), 2.00 (s, 3H), 1.99 (s, 6H), 1.98 (s, 3H), 1.96 (s, 3H), 1.90 (s, 3H), 1.88 (s, 3H), 1.16 (s, 9H); MALDI-TOF mass *m/z* calcd for $C_{236}H_{258}N_2O_{73}Na$ 4310.6 $(M+Na)^+$, found 4311.7; Anal. Calcd for $C_{236}H_{258}N_2O_{73}$: C, 66.06; H, 6.06; N, 0.65. Found: C, 65.81; H, 5.92; N, 0.59.

4.1.37. Compound 66. A mixture of **60** (276 mg, 0.0719 mmol), **16** (111 mg, 0.221 mmol), DTBMP (83.5 mg, 0.407 mmol), and molecular sieves 4 Å (3.0 g) in dry $ClCH_2CH_2Cl$ (10 mL) and cyclohexane (20 mL) was stirred at room temperature for 30 min, then added 1 M MeOTf (0.288 mL, 0.288 mmol) in $ClCH_2CH_2Cl$. The reaction mixture was stirred at 45 °C for 60 h and processed as described for **61**. Purification by PTLC (toluene/EtOAc, 1:2) afforded **66** (245 mg, 79%) as a colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–6.64 (m, 92H), 5.72 (t, 1H, J=9.3 Hz), 5.58 (m, 1H), 5.42 (s, 1H), 5.38–3.30 (m, 112H), 3.20 (m, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H),

1.96 (s, 3H), 1.95 (s, 3H), 1.95 (s, 3H), 1.93 (s, 3H), 1.91 (s, 3H), 1.71 (s, 9H); MALDI-TOF mass *m/z* calcd for $C_{236}H_{258}N_2O_{73}Na$ 4310.6 $(M+Na)^+$, found 4311.2; Anal. Calcd for $C_{236}H_{258}N_2O_{73}$: C, 66.06; H, 6.06; N, 0.65. Found: C, 65.94; H, 6.02; N, 0.59.

4.1.38. Compound 1 (M9). A solution of undecasaccharide **51** (28.7 mg, 0.00696 mmol) in *n*-butanol (2 mL) containing 0.5 mL ethylenediamine was stirred at 90 °C for 15 h. Volatiles were removed by evaporation in vacuo and the residue was dissolved in pyridine (0.3 mL). The solution was treated with Ac_2O (0.2 mL) at 0 °C for 24 h and evaporated in vacuo. The residue was dissolved in MeOH (5 mL) and 1 N NaOMe/MeOH (0.1 mL) was added at 0 °C. The mixture was stirred at 60 °C for 12 h, neutralized with Amberlyst 15 (H^+) resin, and evaporated in vacuo. The residue was applied to a gel filtration chromatography (Sephadex LH20, $CHCl_3$/MeOH, 1:1) to collect the deacetylated compound and evaporated in vacuo. The residue was hydrogenated over $Pd(OH)_2$/C (20 wt %, 5 mg) in 60% aq AcOH (5 mL) at room temperature for 24 h. The mixture was filtered through Celite. The filtrate was concentrated in vacuo. The residue was subjected to a gel filtration (Sephadex LH 20, H_2O) to afford **1** (7.3 mg, 54%) as a white powder: ^1H NMR (400 MHz, D_2O) δ 5.27 (br s, 1H), 5.20 (br s, 1H), 5.17 (br s, 1H), 5.01 (br s, 1H), 4.92 (br s, 1H), 4.90 (br s, 2H), 4.73 (br s, 1H), 4.45 (d, 1H, J=7.6 Hz), 4.36 (d, 1H, J=7.8 Hz), 4.09 (br s, 1H), 4.02–3.37 (m, 67H), 1.93 (s, 3H), 1.88 (s, 3H), 1.40 (m, 2H), 0.72 (t, 3H, J=7.3 Hz); MALDI-TOF mass *m/z* calcd for $C_{73}H_{124}N_2O_{56}Na$ 1947.7 $(M+Na)^+$, found 1947.7.

4.1.39. Compound 2 (M7). A solution of nonasaccharide **56** (100 mg, 0.0282 mmol) in *n*-butanol (3 mL) containing 2 mL of ethylenediamine was stirred at 90 °C for 15 h. Volatiles were removed by evaporation in vacuo and the residue was dissolved in pyridine (3 mL). The solution was treated with Ac_2O (1.5 mL) at 0 °C for 24 h and evaporated in vacuo to give acetylated compound (quantitative yield). The acetylated compound (22.6 mg, 0.0067 mmol) was hydrogenated over $Pd(OH)_2$/C (20 wt %, 20 mg) in a mixture of MeOH (10 mL) and 60% aq AcOH (5 mL) at room temperature for 24 h. The mixture was filtered through Celite. The filtrate was concentrated in vacuo. The residue was dissolved in MeOH (5 mL) and 1 N NaOMe/MeOH (0.1 mL). The mixture was stirred at 60 °C for 12 h, neutralized with Amberlyst 15 (H^+) resin, and evaporated in vacuo. The residue was subjected to a Sep-Pak C18 cartridge (500 mg, Waters) (H_2O only to H_2O/MeOH=20:1) to give **2** (9.1 mg, 84%) as a white powder: ^1H NMR (400 MHz, D_2O) δ 5.21 (br s, 1H), 5.17 (br s, 1H), 4.96 (br s, 1H), 4.91 (br s, 1H), 4.77 (br s, 1H), 4.73 (br s, 1H), 4.45 (br d, 1H, J=6.6 Hz), 4.36 (d, 1H, J=6.8 Hz), 4.10 (br s, 1H), 4.01 (br s, 1H), 3.97–3.37 (m, 54H), 1.93 (s, 3H), 1.89 (s, 3H), 1.41 (m, 2H), 0.73 (t, 3H, J=7.3 Hz); MALDI-TOF mass *m/z* calcd for $C_{61}H_{104}N_2O_{46}Na$ 1623.6 $(M+Na)^+$, found 1624.7.

4.1.40. Compound 3 (M8C). In a manner as described for **1**, decasaccharide **58** (14.5 mg, 0.00378 mmol) was subjected to a series of reactions. Purification by gel filtration (Sephadex LH20, H_2O) gave compound **3** (6.0 mg, 87%) as a white powder: ^1H NMR (400 MHz, D_2O) δ 5.27 (br s, 1H), 5.20 (br s, 1H), 5.17 (br s, 1H), 4.92 (br s, 1H), 4.91 (br s, 1H), 4.77 (br s, 1H), 4.73 (br s, 1H), 4.45 (d, 1H, J=7.6 Hz), 4.36 (d, 1H, J=7.6 Hz), 4.10 (br s, 1H), 4.02–3.38 (m, 54H), 1.94 (s, 3H), 1.89 (s, 3H), 1.41 (m, 2H), 0.73 (t, 3H, J=7.3 Hz); MALDI-TOF mass *m/z* calcd for $C_{67}H_{114}N_2O_{51}Na$ 1785.6 $(M+Na)^+$, found 1785.2.

4.1.41. Compound 4 (M8B). Decasaccharide **60** (28.7 mg, 0.00748 mmol) was subjected to a series of reactions in a manner as described for **1**. The mixture was subjected to a Sep-Pak C18 cartridge (500 mg, Waters) (H_2O only to H_2O/MeOH, 20:1) to give **4** (6.2 mg, 47%) as a white powder. ^1H NMR (400 MHz, D_2O) δ 5.20 (br s, 1H), 5.17 (br s, 1H), 5.01 (br s, 1H), 4.95 (br s, 1H), 4.90 (br s, 2H), 4.73 (br s, 1H), 4.45 (br d, 1H, J=7.5 Hz), 4.36 (d, 1H, J=8.0 Hz), 4.09 (br d, 1H, J=2.4 Hz), 4.01–3.36 (m, 54H), 1.93 (s, 3H), 1.89 (s, 3H), 1.41 (m, 2H), 0.72 (t, 3H, J=7.3 Hz); MALDI-TOF mass *m/z* calcd for $C_{67}H_{114}N_2O_{51}Na$ 1785.6 $(M+Na)^+$, found 1786.3.

4.1.42. Compound 5 (G3M9). Tetradecasaccharide **61** (26.7 mg, 0.00477 mmol) was subjected to a series of reactions in a manner as described for **1**. The mixture was purified by Sep-Pak C18 cartridge (500 mg, Waters, H_2O only to H_2O/MeOH, 20:1), then with HPLC (column Fluofix, H_2O) to give **5** (6.5 mg, 56%) as a white powder: ^1H NMR (400 MHz, D_2O) δ 5.39 (d, 1H, J=2.4 Hz), 5.27 (br s, 1H), 5.20 (br s, 1H), 5.17 (br s, 1H), 5.13 (br d, 1H, J=2.4 Hz), 5.04 (br d, 1H, J=3.2 Hz), 5.01 (br s, 1H), 4.12 (br s, 1H), 4.90 (br s, 2H), 4.76 (br s, 1H), 4.45 (d, 1H, J=7.2 Hz), 4.36 (d, 1H, J=6.8 Hz), 4.10 (br s, 2H), 4.02–3.30 (m, 84H), 1.93 (s, 3H), 1.89 (s, 3H), 1.40 (m, 2H), 0.72 (t, 3H, J=7.6 Hz); MALDI-TOF mass *m/z* calcd for $C_{91}H_{154}N_2O_{71}Na$ 2433.8 $(M+Na)^+$, found 2432.8.

4.1.43. Compound 6 (G2M9). Tridecasaccharide **62** (80.4 mg, 0.0160 mmol) in *n*-butanol (2 mL) containing ethylenediamine (1 mL) was stirred at 80 °C for 12 h. Volatiles were removed by evaporation in vacuo and the residue was dissolved in pyridine (4 mL). The solution was treated with Ac_2O (2 mL) and stirred at 40 °C for 12 h and evaporated in vacuo. The residue was diluted with EtOAc and washed with 1 N HCl, brine, aq $NaHCO_3$, and brine. The organic layer was dried (Na_2SO_4) and evaporated in vacuo. The residue was dissolved in MeOH (10 mL) and 1 N NaOMe/MeOH (0.5 mL) was added at 0 °C. The mixture was stirred at 40 °C for 5 h, neutralized with Amberlyst 15 (H^+) resin, and evaporated in vacuo. The residue was subjected to a PTLC ($CHCl_3$/MeOH, 5:1) to give the deacetylated compound (44 mg, 72%). The deacetylated compound (28.8 mg, 0.00745 mmol) was hydrogenated over $Pd(OH)_2$–C (20 wt %, 20 mg) in 50% aq AcOH (5 mL) at room temperature for 12 h. The mixture was filtered through Celite. The filtrate was concentrated in vacuo. The residue was subjected to a Sep-Pak C18 cartridge (500 mg, Waters) (H_2O only to H_2O/MeOH, 20:1) to give **6** (11.0 mg, 65%) as a white powder: ^1H NMR (400 MHz, D_2O) δ 5.26 (br s, 1H), 5.21 (d, 1H, J=3.6 Hz), 5.19 (br s, 1H), 5.16 (br s, 1H), 5.12 (d, 1H, J=3.9 Hz), 5.00 (br s, 1H), 4.90 (br s, 1H), 4.89 (br s, 2H), 4.71 (br s, 1H), 4.57 (br d, 1H, J=7.0 Hz), 4.35 (br d, 1H, J=6.8 Hz), 4.09 (br s, 2H), 4.01–3.30 (m, 80H), 1.92 (s, 3H), 1.88 (s, 3H), 1.40 (m, 2H), 0.71 (t, 3H, J=7.3 Hz); MALDI-TOF mass *m/z* calcd for $C_{85}H_{144}N_2O_{66}Na$ 2271.8 $(M+Na)^+$, found 2271.4.

4.1.44. Compound 7 (G1M9). Dodecasaccharide **63** (34.7 mg, 0.00757 mmol) was subjected to a series of reactions in a manner as described for **1**. Subsequent purification by gel filtration (Sephadex LH 20, H_2O) afforded compound **7** (8.5 mg, 54%) as a white powder: ^{1}H NMR (400 MHz, D_2O) δ 5.27 (br s, 1H), 5.20 (br s, 1H), 5.17 (br s, 1H), 5.12 (d, 1H, J=3.7 Hz), 5.01 (br s, 1H), 4.92 (br s, 1H), 4.90 (br s, 2H), 4.73 (br s, 1H), 4.46 (d, 1H, J=7.3 Hz), 4.37 (d, 1H, J=7.5 Hz), 4.10 (br s, 2H), 4.02–3.24 (m, 71H), 1.94 (s, 3H), 1.89 (s, 3H), 1.41 (m, 2H), 0.73 (t, 3H, J=7.3 Hz); MALDI-TOF mass m/z calcd for $C_{79}H_{134}N_2O_{61}Na$ 2109.7(M+Na)$^+$, found 2109.4.

4.1.45. Compound 8 (G1M7). Decasaccharide **64** (35.6 mg, 0.00898 mmol) was subjected to a series of reactions in a manner as described for **1**. The mixture was subjected to a Sep-Pak C18 cartridge (2 g, Waters) (H_2O only to H_2O/MeOH, 10:1) to give **8** (15.1 mg, 84%) as a white powder: ^{1}H NMR (400 MHz, D_2O) δ 5.21 (br s, 1H), 5.17 (br s, 1H), 5.11 (d, 1H, J=3.6 Hz), 4.95 (br s, 1H), 4.90 (br s, 1H), 4.77 (br s, 1H), 4.73 (br s, 1H), 4.44 (br d, 1H, J=6.6 Hz), 4.36 (d, 1H, J=7.3 Hz), 4.10 (br s, 2H), 4.01–3.24 (m, 61H), 1.93 (s, 3H), 1.89 (s, 3H), 1.41 (m, 2H), 0.72 (t, 3H, J=7.3 Hz); MALDI-TOF mass m/z calcd for $C_{67}H_{114}N_2O_{51}Na$ 1785.6 (M+Na)$^+$, found 1785.6.

4.1.46. Compound 9 (G1M8C). Undecasaccharide **65** (68.8 mg, 0.0160 mmol) was subjected to a series of reactions in a manner as described for **1**. The mixture was subjected to a Sep-Pak C18 cartridge (2 g, Waters) (H_2O only to H_2O/MeOH, 20:1) to give **9** (20.7 mg, 66%) as a white powder: ^{1}H NMR (400 MHz, D_2O) δ 5.27 (br s, 1H), 5.20 (br s, 1H), 5.17 (br s, 1H), 5.11 (d, 1H, J=4.0 Hz), 4.92 (br s, 1H), 4.90 (br s, 1H), 4.77 (br s, 1H), 4.73 (br s, 1H), 4.45 (d, 1H, J=7.5 Hz), 4.36 (d, 1H, J=8.0 Hz), 4.09 (br s, 2H), 3.97–3.21 (m, 67H), 1.94 (s, 3H), 1.89 (s, 3H), 1.41 (m, 2H), 0.73 (t, 3H, J=7.3 Hz); MALDI-TOF mass m/z calcd for $C_{73}H_{124}N_2O_{56}Na$ 1947.7 (M+Na)$^+$, found 1947.5.

4.1.47. Compound 10 (G1M8B). Undecasaccharide Compound **66** (24.2 mg, 0.00564 mmol) was subjected to a series of reactions in a manner as described for **1**. The mixture was subjected to a Sep-Pak C18 cartridge (500 mg, Waters) (H_2O only to H_2O/MeOH, 20:1) to give **10** (6.3 mg, 58%) as a white powder: ^{1}H NMR (400 MHz, D_2O) δ 5.21 (br s, 1H), 5.17 (br s, 1H), 5.11 (d, 1H, J=3.9 Hz), 5.01 (br s, 1H), 4.95 (br s, 1H), 4.90 (br s, 2H), 4.68 (br s, 1H), 4.45 (d, 1H, J=6.8 Hz), 4.36 (d, 1H, J=7.2 Hz), 4.10 (br s, 2H), 3.01–3.26 (m, 67H), 1.93 (s, 3H), 1.89 (s, 3H), 1.40 (m, 2H), 0.72 (t, 3H, J=7.3 Hz); MALDI-TOF mass m/z calcd for $C_{73}H_{124}N_2O_{56}Na$ 1947.7 (M+Na)$^+$, found 1948.6.

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