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Synthetic studies on glycosphingolipids from protostomia phyla: synthesis of glycosphingolipids and related carbohydrate moieties from the parasite *Schistosoma mansoni*

Takayuki Kanaya [a], Frank Schweizer [b,c], Tadahiro Takeda [a], Fumiyuki Kiuchi [a], Noriyasu Hada [a,*]

[a] Faculty of Pharmacy, Keio University, 1-5-30 Shibakoen, Minato-ku, Tokyo 105-8512, Japan
[b] Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2
[c] Department of Medical Microbiology, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

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ABSTRACT

Stereocontrolled syntheses of three neutral glycosphingolipids and six oligosaccharide derivatives found from the parasite *Schistosoma mansoni* have been accomplished. A pentasaccharide glycosphingolipid β-D-Gal*p*-(1→4)-[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAc-(1→3)-β-D-Gal*p*NAc-(1→4)-β-D-Glc*p*-(1↔1)-Cer (**1**), two hexasaccharide glycosphingolipids α-L-Fuc*p*-(1→3)-β-D-Gal*p*-(1→4)-[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAc-(1→3)-β-D-Gal*p*NAc-(1→4)-β-D-Glc*p*-(1↔1)-Cer (**2**) and β-D-Gal*p*-(1→4)-[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAc-(1→3)-β-D-Glc*p*NAc-(1→3)-β-D-Gal*p*NAc-(1→4)-β-D-Glc*p*-(1↔1)-Cer (**3**), together with their non-reducing end tri- and tetrasaccharides, β-D-Gal*p*-(1→4)-[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAcOR (**4**) and α-L-Fuc*p*-(1→3)-β-D-Gal*p*-(1→4)-[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAcOR (**5**), were synthesized by block synthesis. Moreover, non-reducing end oligosaccharides of schistosomal glycosphingolipids, β-D-Gal*p*-NAc-(1→4)-[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAcOR (**6**), α-L-Fuc*p*-(1→3)-β-D-Gal*p*NAc-(1→4)-[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAcOR (**7**), α-L-Fuc*p*-(1→3)-β-D-Gal*p*NAc-(1→4)-[α-L-Fuc*p*-(1→2)-α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAcOR (**8**) and α-L-Fuc*p*-(1→3)-β-D-Gal*p*NAc-(1→4)-[α-L-Fuc*p*-(1→2)-α-L-Fuc*p*-(1→2)-α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAcOR (**9**) [R = 2-(trimethylsilyl)ethyl], were synthesized as probes to explore their diagnostic potential to detect schistosomiasis from patients' sera.

1. Introduction

Schistosomiasis is a human parasitic disease caused by the digenetic blood flukes of the genus *Schistosoma* that affect more than 200 million people in the tropics.[1] There is no vaccine to prevent the disease, and although drug therapy is effective in most cases, reinfection is common in endemic areas.[2] Schistosomes produce a variety of remarkable and complex glycoconjugates such as glycoproteins and glycosphingolipids.[3] It has been known for more than a quarter century that glycosylated antigens play a major role in the development of the characteristic innate humoral immune response in infected hosts.[4] In the past decade, many studies have investigated global structural features of glycans derived from schistosomal glycoprotein and glycolipid preparations in particular from *Schistosoma mansoni* and *Schistosoma japonicum*.[5] *S. mansoni* adult worm- and egg-derived glycoproteins contain common N-linked oligomannose structures that occur in most eukaryotic organisms. Typical elements of the complex antennary N-linked glycans from adult worm are β-D-Gal*p*NAc-(1→4)-β-D-Glc*p*NAc (LacdiNAc, LDN), β-D-Gal*p*NAc-(1→4)-[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAc (fucosylated LacdiNAc, LDN-F), and β-D-Gal*p*NAc-(1→4)-[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAc (Lewis X, Le^X).[6] On the other hand, novel core types have been identified along with the conventional type 1 [β-D-Gal*p*-(1→3)-β-D-Gal*p*NAc] and type 2 [β-D-Gal*p*-(1→3)-[β-D-Glc*p*NAc-(1→6)]-β-D-Gal*p*NAc] in the O-linked glycans of schistosoma. Several unusually long and complex O-glycan chains were found which are multifucosylated.[7] Furthermore, some of the fucosylated schistosome glycosphingolipids in cercariae are dominated not only by terminal Le^X groups, but also abundantly express pseudo-Lewis Y (Le^Y) variants of α-L-Fuc*p*-(1→3)-β-D-Gal*p*-(1→4)-[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAc-structures[8] Makaaru et al.[9] have shown that *S. mansoni* glycolipids from adult worms consisting of a β-D-Gal*p*NAc-(1→4)-β-D-Glc*p*-(1↔1)-Cer sequence called 'schisto-core' instead of the more common mammalian β-D-Gal*p*-(1→4)-β-D-Glc*p*-(1↔1)-Cer core structure, and this core structure is also found in other unique glycan sequences from eggs and cercariae (Fig. 1). Thus, *S. mansoni* synthesizes a multitude of complex carbohydrates, including both parasite- and stage-specific glycans. These glycoconjugates are interesting from two points of view. One is their antigenicity against sera of schistosomiasis patients and the other is their function in immune responses against host mammals. Therefore, schistosome glycans and glycoconjugates are good targets not only for immunodiagnostic purposes but also for vaccine developments. Chemical synthesis of glycoconjugates provides not only access to large amounts of structurally

* Corresponding author. Tel.: +81 3 5400 2666; fax: +81 3 5400 2556.
E-mail address: hada-nr@pha.keio.ac.jp (N. Hada).

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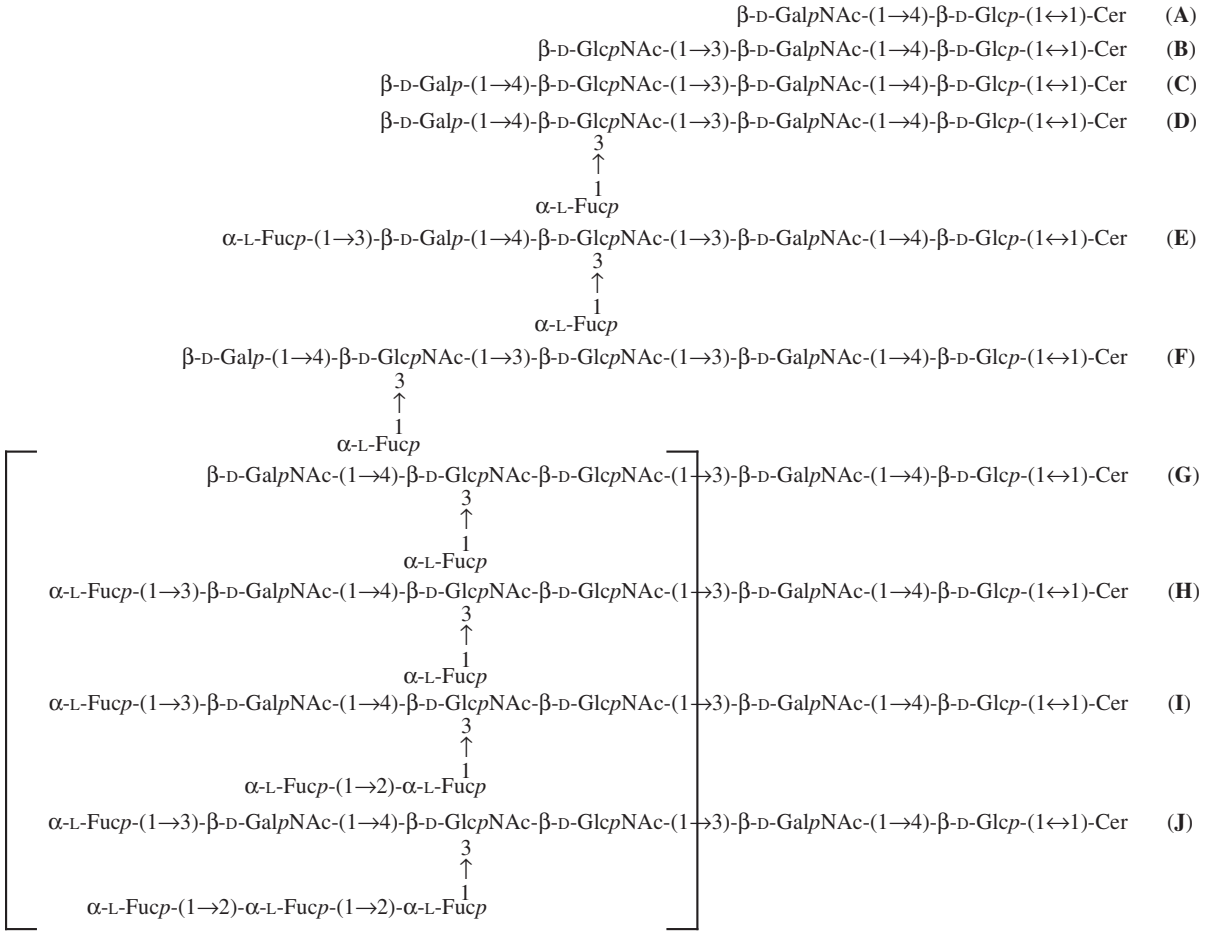


Figure 1. Structures of glycosphingolipid (**A–J**) from *Schistosoma mansoni*.

well-defined natural compounds, but also to a variety of structurally related non-natural compounds.

In the course of our studies on natural oligosaccharides, we are interested in the unique glycolipids and glycoproteins found in various parasites. We initiated a program to study biological functions of various parasitic glycoconjugates and have (a) devised synthetic strategies for their preparation and (b) examined their antigenicity against patient sera.[10] In our previous paper,[11] we reported the total syntheses of di-, tri-, and tetrasaccharide glycolipids of schistosoma (**A**, **B**, and **C**, Fig. 1) and examined their antigenicity by an enzyme linked immunosorbent assay (ELISA). However, these glycolipids did not react with sera of patients suffering from schistosomiasis (data not shown), most likely because of insufficient size of the presented carbohydrate epitope. In this study, we describe total syntheses of glycosphingolipids **1**–**3** (**D**–**F)** together with the non-reducing end fragments of **D** and **E**, that is Le^X (**4**) and pseudo Le^Y (**5**). In addition, we describe syntheses of the non-reducing oligosaccharide fragments **6**–**9** that are precursors of glycosphingolipids **G**–**J** (Fig. 2). These compounds are expected to be good probes to clarify the structural requirements for antigenicity against sera of schistosomiasis patients.

2. Results and discussion

2.1. Total synthesis of glycosphingolipid 1 and its non-reducing end trisaccharide 4

Glycosphingolipid **1** which contains the Le^X trisaccharide and schisto-core disaccharide [β-D-Gal*p*NAc-(1→4)-β-D-Glc*p*] sequence was prepared by block synthesis of corresponding disaccharide acceptor **14** and trisaccharide donor **13** (Scheme 1). Initially, we attempted to synthesize the trisaccharide donor via glycosylation of LacNAc acceptor **10**[11] with phenyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-fucopyranoside[12] using *N*-iodosuccinimide (NIS)/trifluoromethanesulfonic acid (TfOH) as promoter.[13] However, this resulted in poor yield of corresponding trisaccharide because of a side reaction leading to a formation of an NIS–fucose complex. In contrast, significantly improved yield of the trisaccharide was obtained with fucosyl imidate donor **11**[14] bearing benzoyl protecting groups at 3- and 4-positions. Glycosylation of **10** with **11** in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf)[15] and 4 Å molecular sieves (MS 4 Å) in CH_2Cl_2 afforded desired trisaccharide (**12**) in 79% yield. The nature of the new glycosidic linkage was determined by the coupling constant of anomeric proton (H-1 of Fuc, δ = 5.33 ppm, J = 4.9 Hz). Removal of the 2,2,2-trichloroethoxycarbonyl (Troc) group and N-acetylation of **12** with Zn–Ac_2O–AcOH,[16] followed by debenzylation with catalytic hydrogenolysis over 10% Pd/C in THF and acetylation afforded O-acetylated intermediate. Zemplén-based deacetylation of the intermediate and purification by Sephadex LH-20 column chromatography furnished Le^X trisaccharide **4**. Once we had an access to the trisaccharide derivative **12**, it was used as a precursor for the synthesis of the target glycosphingolipid **1**. Selective removal of 2-(trimethylsilyl)ethyl (TMS-ethyl) group in **12** with trifluoroacetic acid (TFA) in CH_2Cl_2, followed by treatment with CCl_3CN in the presence of 1,8-diazabicyclo[5,4,0]-7-undecene (DBU)[17] provided corresponding α-trichloroacetimidate **13** in 73% yield. Glycosylation of **13** with schisto core derivative **14**[11] in the presence of TMSOTf and MS 4 Å in CH_2Cl_2 produced desired pentasaccharide **15** in 78% yield. The anomeric proton of newly established anomeric center

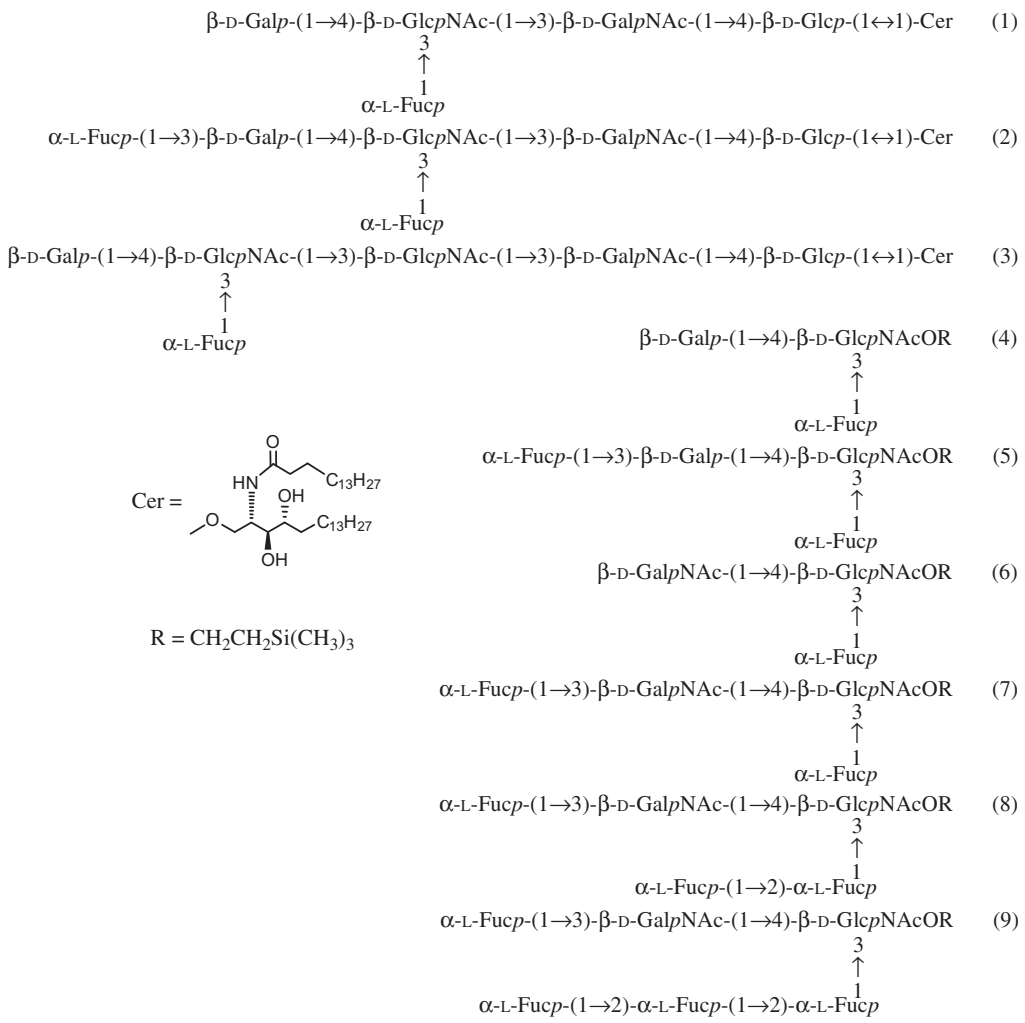
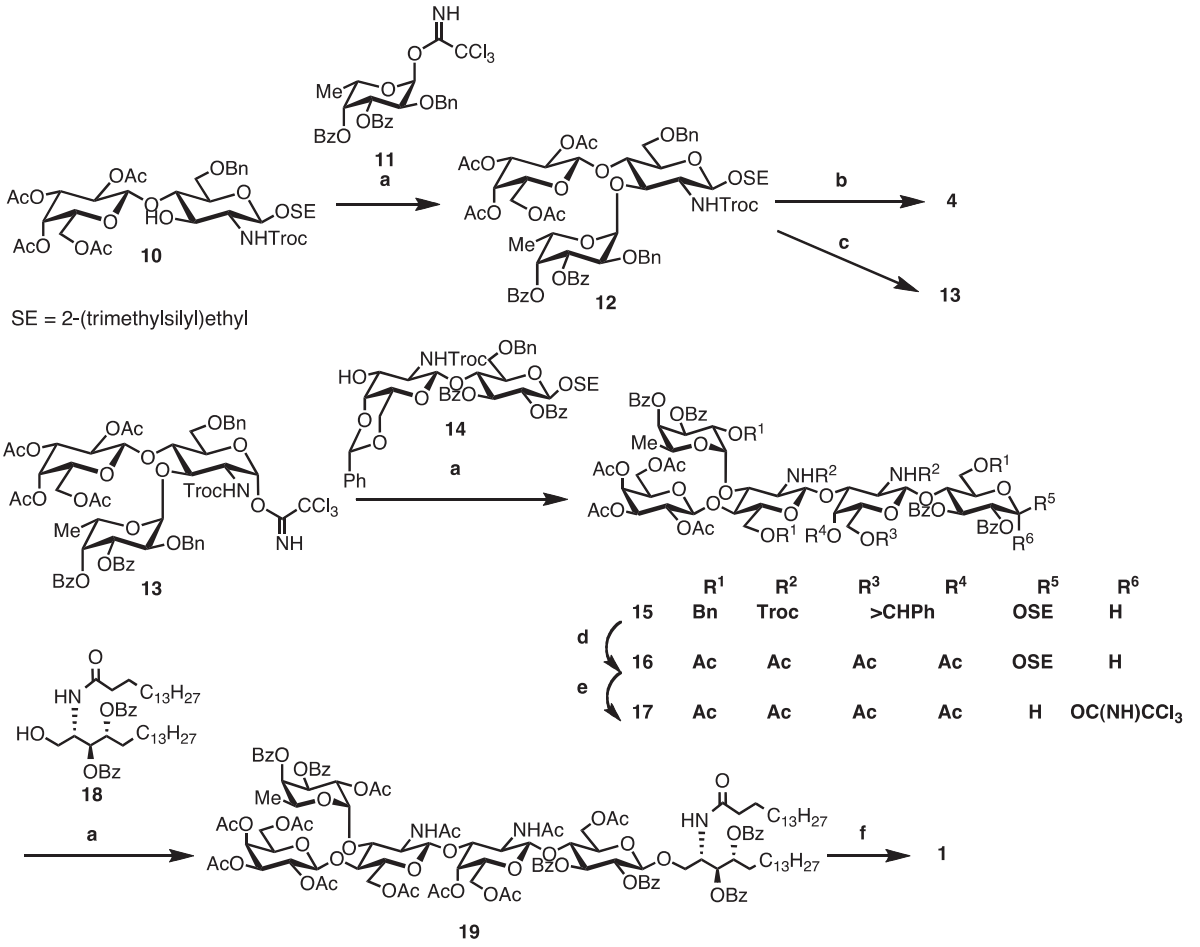


Figure 2. Structures of target compounds (**1**–**9**).

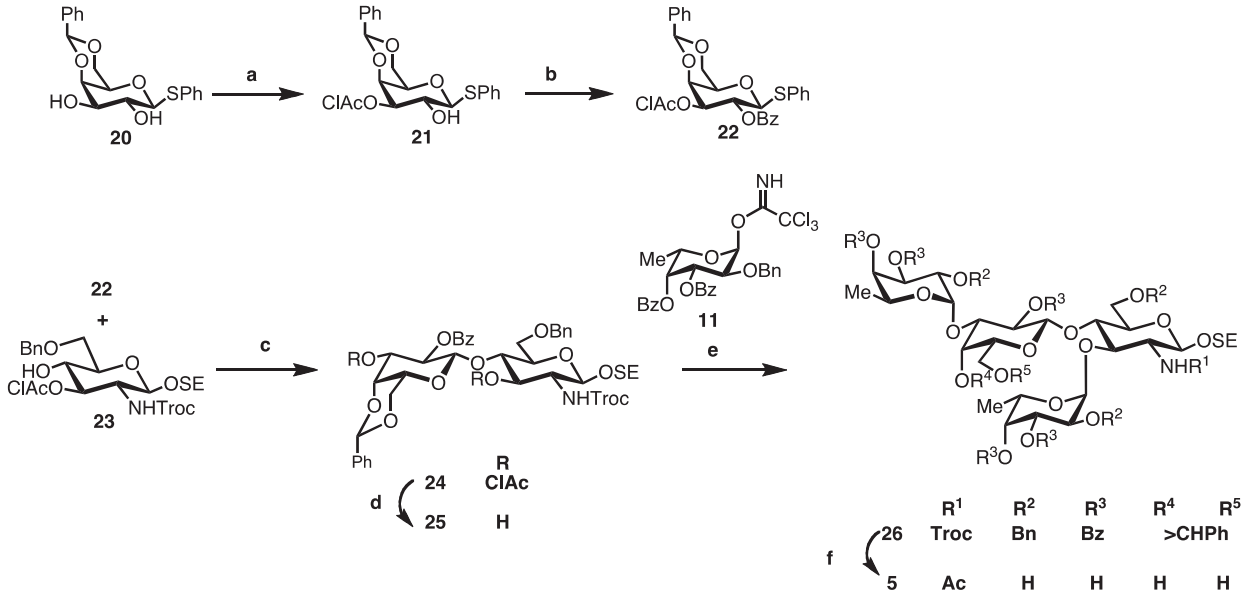
appeared as a doublet at δ 4.72 (J = 8.0 Hz) indicating exclusive formation of β-anomeric linkage. Removal of the Troc-protecting group of **15**, followed by catalytic hydrogenation over 10% Pd-C in MeOH–AcOH and acetylation gave protected pentasaccharide analog **16**. Compound **16** was exposed to TFA and resulted hemiacetal was converted into glycosyl imidate **17** using standard conditions. In a synthesis of glycosyl ceramide, a phytoceramide acceptor gives lower yield compared to, for example, an azidosphingosine. However, we employed a ceramide type acceptor because of the easy conversion to the final product. TMSOTf-promoted glycosylation of phytoceramide acceptor, (2*S*,3*R*,4*R*)-3,4-di-*O*-benzoyl-2-hexadecanamido-octadecane-1,3,4-triol **18**[18] with glycosyl imidate donor **17** afforded desired protected glycosphingolipid-based β-glycoside **19** in 23% yield. Finally, standard deacetylation of **19** and purification by column chromatography on Sephadex LH-20 furnished glycolipid **1** (Scheme 1). The structure and purity of **1** were demonstrated by its ^{1}H NMR and HR-FABMS data.

2.2. Total synthesis of glycosphingolipid 2 and its non-reducing end tetrasaccharide 5

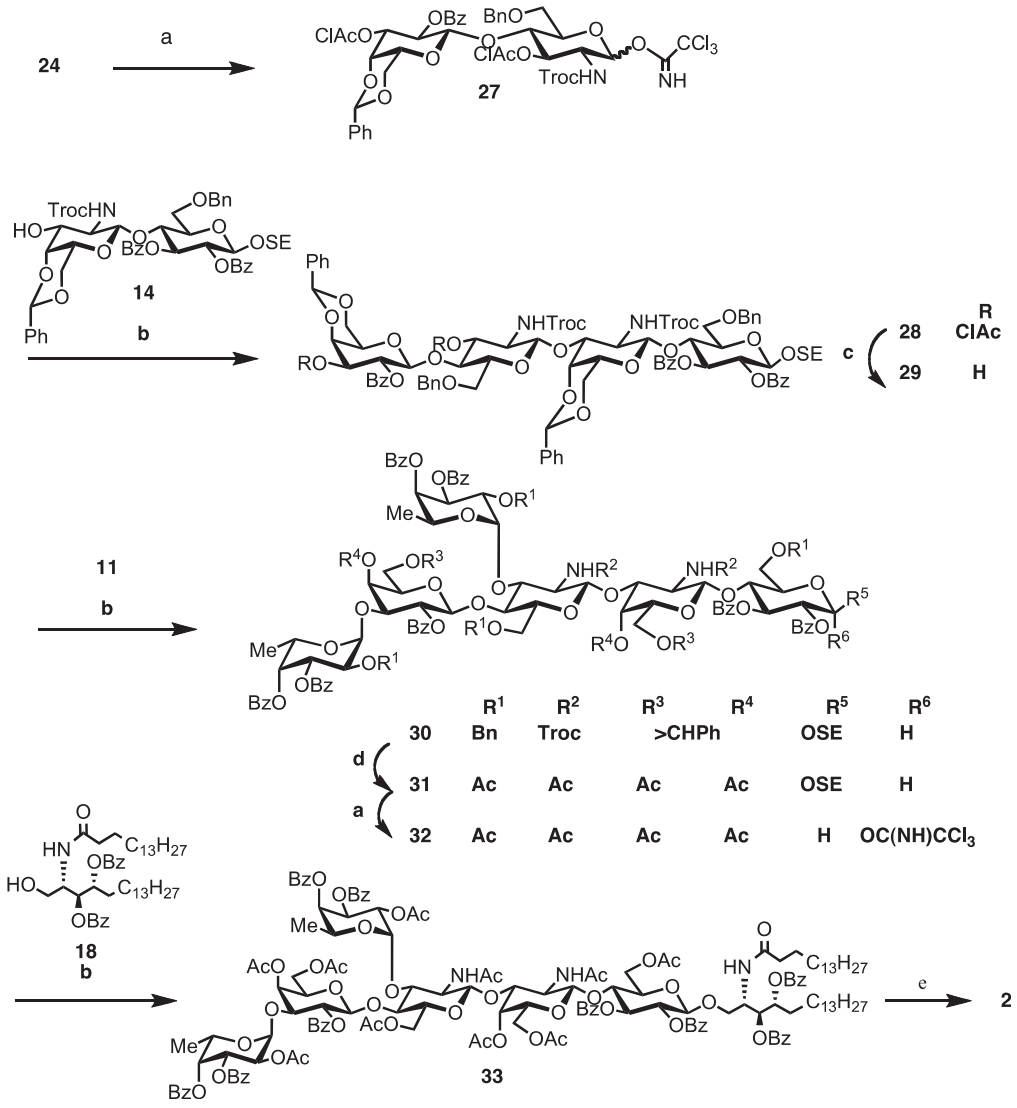
Glycosphingolipid **2** contains pseudo Le^Y tetrasaccharide {α-L-Fuc*p*-(1→3)]-β-D-Gal*p*-(1→4)-[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAc-}, in which the terminal Fuc-residue is bound to 3-position of galactose instead of 2-position in Le^Y structure {L-Fuc*p*-(1→2)-β-D-Gal*p*-(1→4)-[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAc-}, at the non-reducing end. Prior to the synthesis of glycosphingolipid **2**, pseudo Le^Y tetrasaccharide derivative **5** was synthesized (Scheme 2). Galactopyranosyl donor **22** was obtained from phenyl 4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (**20**),[19] by a two-step procedure. Regioselective chloroacetylation of the in situ prepared stannylidene derivative of **20** with chloroacetyl chloride produced **21** in 75% yield. This chloroacetylation was found to be highly regio-specific in this case. Benzoylation of **21** in pyridine resulted in partial replacement of the chloroacetyl group with a benzoyl group. Thus, this reaction had to be carried out under a milder condition to prevent cleavage of the chloroacetyl group and treatment with benzoyl chloride in CH_2Cl_2/pyridine (5:3) mixture successfully gave glycosyl donor **22** in 85% yield. Glycosylation of the donor **22** with acceptor **23**[13] in the presence of NIS, TfOH, and MS 4 Å in CH_2Cl_2 afforded desired disaccharide **24** in 84% yield. The anomeric proton of the galactose unit appeared as a doublet at δ 4.63 (J = 8.3 Hz), indicating a β-linkage formation. The two chloroacetyl groups in **24** were cleaved by treatment with pyridine/H_2O yielding diol **25** in 70% yield. Glycosylation of the diol acceptor **25** with glycosyl donor **11** in the presence of TMSOTf produced tetrasaccharide **26** in 82% yield. The presence of two α-inter fucosidic linkages in **26** was indicated by two doublets at δ 5.36 and 5.04 ppm both showing the same small homonuclear coupling constant of 3.6 Hz in the ^{1}H NMR spectrum. Removal of the Troc-protecting group of **26** was achieved with Zn



Scheme 1. Reagents and conditions: (a) TMSOTf, MS 4 Å, CH_2Cl_2, **12** 79%, **15** 78%, **19** 23%; (b) (1) Zn, Ac_2O, AcOH; (2) Pd-C/H_2, THF-MeOH; (3) Ac_2O/pyridine, 58% (three steps); (4) MeONa, MeOH, 86%; (c) (1) TFA, CH_2Cl_2; (2) CCl_3CN, DBU, CH_2Cl_2, 73% (two steps); (d) (1) Zn, Ac_2O, AcOH; (2) Pd-C/H_2, MeOH/AcOH; (3) Ac_2O/pyridine, 37% (three steps); (e) (1) TFA, CH_2Cl_2; (2) CCl_3CN, DBU, CH_2Cl_2, quant. (two steps); (f) MeONa, 1,4-dioxane/MeOH, 65%.



Scheme 2. Reagents and conditions: (a) (1) Bu_2SnO, toluene; (2) Bu_4NBr, chloroacetyl chloride, DMF, 75%; (b) benzoyl chloride, CH_2Cl_2/pyridine, 85%; (c) NIS, TfOH, MS 4 Å, CH_2Cl_2, 84%; (d) pyridine, H_2O, 70%; (e) TMSOTf, MS 4 Å, CH_2Cl_2, 82%; (f) (1) Zn, Ac_2O, AcOH; (2) Pd-C/H_2, AcOH/MeOH; (3) Ac_2O/pyridine; (4) NaOMe, MeOH, 23% (four steps).



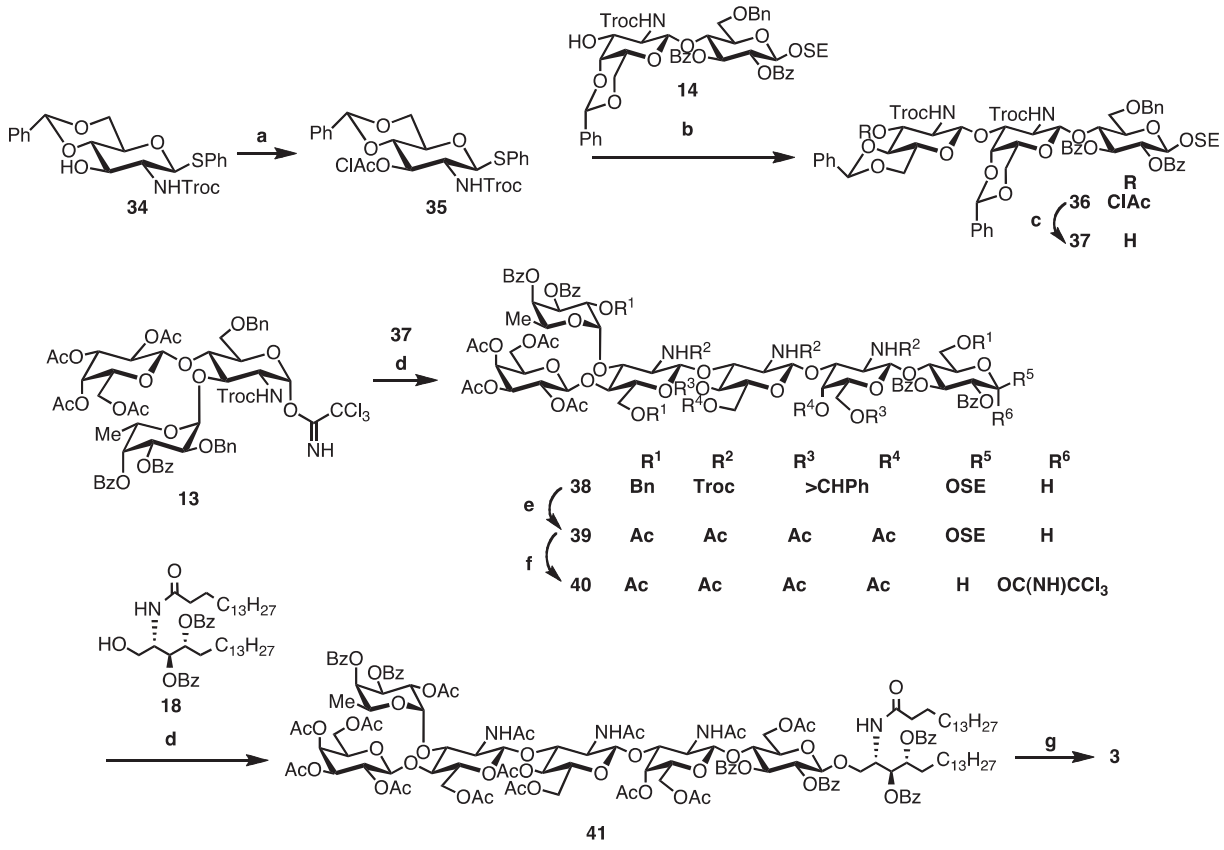
Scheme 3. Reagents and conditions: (a) (1) CF_3CO_2H/CH_2Cl_2, MS 4 Å; (2) DBU, CCl_3CN, CH_2Cl_2, **27** 64% (two steps), **32** 82% (two steps); (b) TMSOTf, MS 4 Å, CH_2Cl_2, **28** 65%, **30** 72%, **33** 28%; (c) pyridine, H_2O, quant.; (d) 1) Zn, Ac_2O, AcOH; (2) Pd-C/H_2, MeOH/AcOH; (3) Ac_2O/pyridine, 43% (three steps); (e) MeONa, dioxane/MeOH, quant.

Ac_2O and AcOH mixture, followed by catalytic hydrogenation over 10% Pd-C in MeOH–AcOH, acetylation and deacetylation provided tetrasaccharide **5** which was purified by column chromatography on Sephadex LH-20 (Scheme 2).

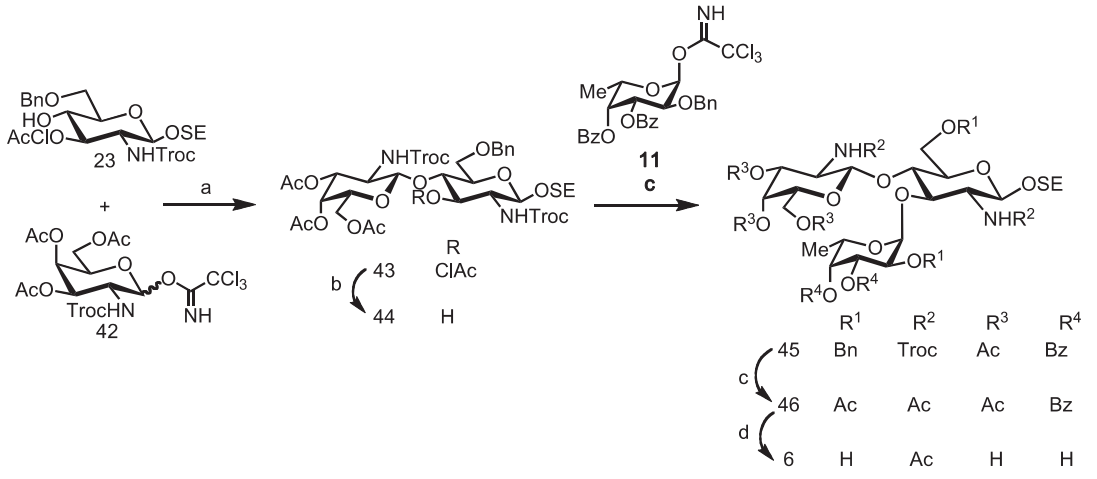
Hexasaccharide-based core of glycosphingolipid **2** containing pseudo Le^Y tetrasaccharide moiety was planned to be synthesized by double glycosylation with fucosyl imidate **11** of tetrasaccharide acceptor **29** which can be obtained by glycosylation of donor **27** with schisto core disaccharide acceptor **14** (Scheme 3). Disaccharide donor **27** was prepared from protected disaccharide **24** by cleavage of the anomeric TMS-ethyl protecting group and conversion of resulted hemiacetal into imidate. During the deprotection of TMS-ethyl group, presence of MS 4 Å was necessary to prevent hydrolysis of the benzylidene acetal in the molecule. Linear tetrasaccharide acceptor **29** was synthesized by TMSOTf promoted glycosylation of acceptor **14** with the donor **27** followed by removal of the chloroacetyl group with aqueous pyridine in 65% yield over two steps. Having obtained the tetrasaccharide acceptor **29**, we performed TMSOTf-promoted glycosylation of **29** with fucopyranosyl donor **11** in dichloromethane at −60 °C, which produced desired hexasaccharide **30** (72%), as evidenced by ^{1}H NMR spectroscopy (H-1 of Fuc a,b, δ 5.30 and 5.03 ppm, J = 3.6 Hz). Reduction of the Troc groups of **30** with Zn–AcOH followed by debenzylidenation and debenzylation with catalytic hydrogenolysis over 10% Pd/C in MeOH/AcOH and acetylation afforded **31** in 43% yield over three steps. Selective removal of the TMS-ethyl group in **31** with TFA, followed by exposure of resulted hemiacetal to CCl_3CN and DBU afforded corresponding α-trichloroacetimidate **32**. TMSOTf-promoted glycosylation of phytosphingosine-based lipid **18** with the glycosyl donor **32** was carried out in the presence of TMSOTf and MS 4 Å to afford desired β-glycoside **33** in 23% yield. Finally, removal of the acyl groups in **33** under Zemplén conditions and column chromatography on Sephadex LH-20 furnished desired glycolipid **2** (Scheme 3). The structure and purity of **2** were demonstrated by its ^{1}H NMR and HR-FABMS data.

2.3. Total synthesis of glycosphingolipid 3

Glycosphingolipid **3** is a hexasaccharide containing an additional Glc*p*NAc moiety between the Le^X trisaccharide and the schisto core disaccharide. The hexasaccharide portion of **3** can be synthesized by glycosylation of a linear trisaccharide-based acceptor **37** with the previously prepared trisaccharide imidate donor **13**. The synthesis of acceptor **37** started from known phenyl 4,6-*O*-benzylidene-2-



Scheme 4. Reagents and conditions: (a) chloroacetyl chloride, CH_2Cl_2/pyridine, 99%; (b) NIS, TfOH, MS 4 Å, CH_2Cl_2, 73%; (c) pyridine, H_2O, 86%; (d) TMSOTf, MS 4 Å, CH_2Cl_2, **38** 63%, **41** 20%; (e) (1) Zn, Ac_2O, AcOH; (2) Pd-C/H_2, MeOH/AcOH; (3) Ac_2O/pyridine, 40% (three steps); (f) (1) CF_3CO_2H/CH_2Cl_2, MS 4 Å; (2) DBU, CCl_3CN, CH_2Cl_2, 77% (two steps); (g) MeONa, dioxane/MeOH, 79%.

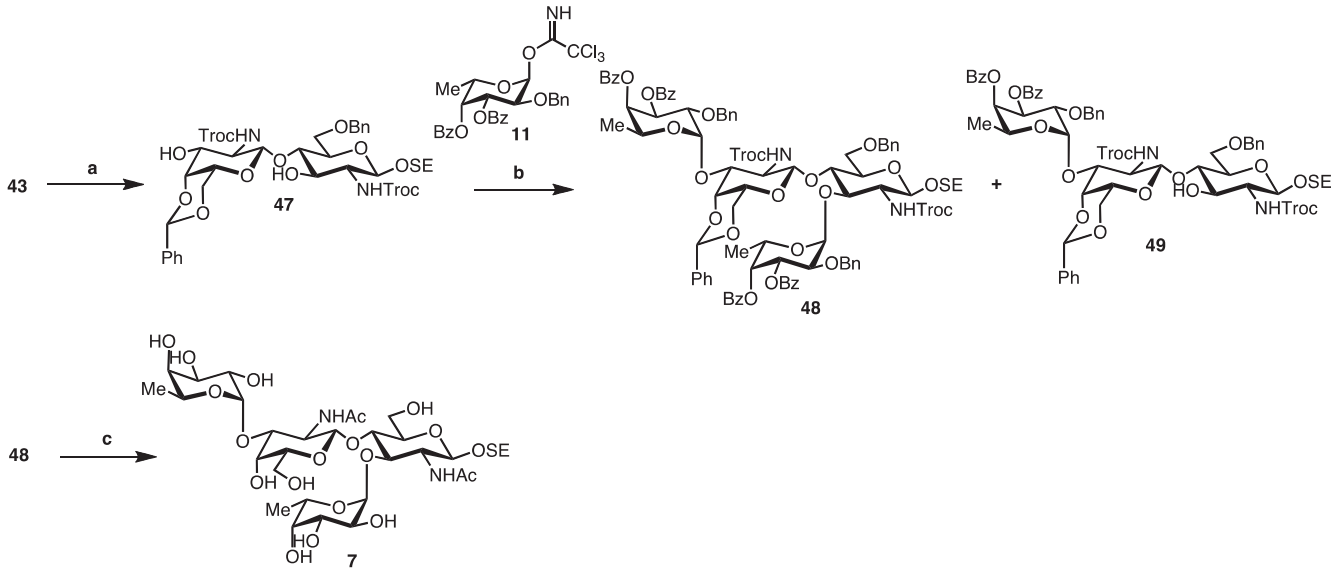


Scheme 5. Reagents and conditions: (a) TMSOTf, MS 4 Å, CH_2Cl_2, **43** 79%, **45** 80%; (b) pyridine, H_2O, 70%; (c) (1) Zn, Ac_2O, AcOH; (2) Pd-C/H_2, MeOH/AcOH; (3) Ac_2O/pyridine, 44% (three steps); (d) MeONa, MeOH, 94%.

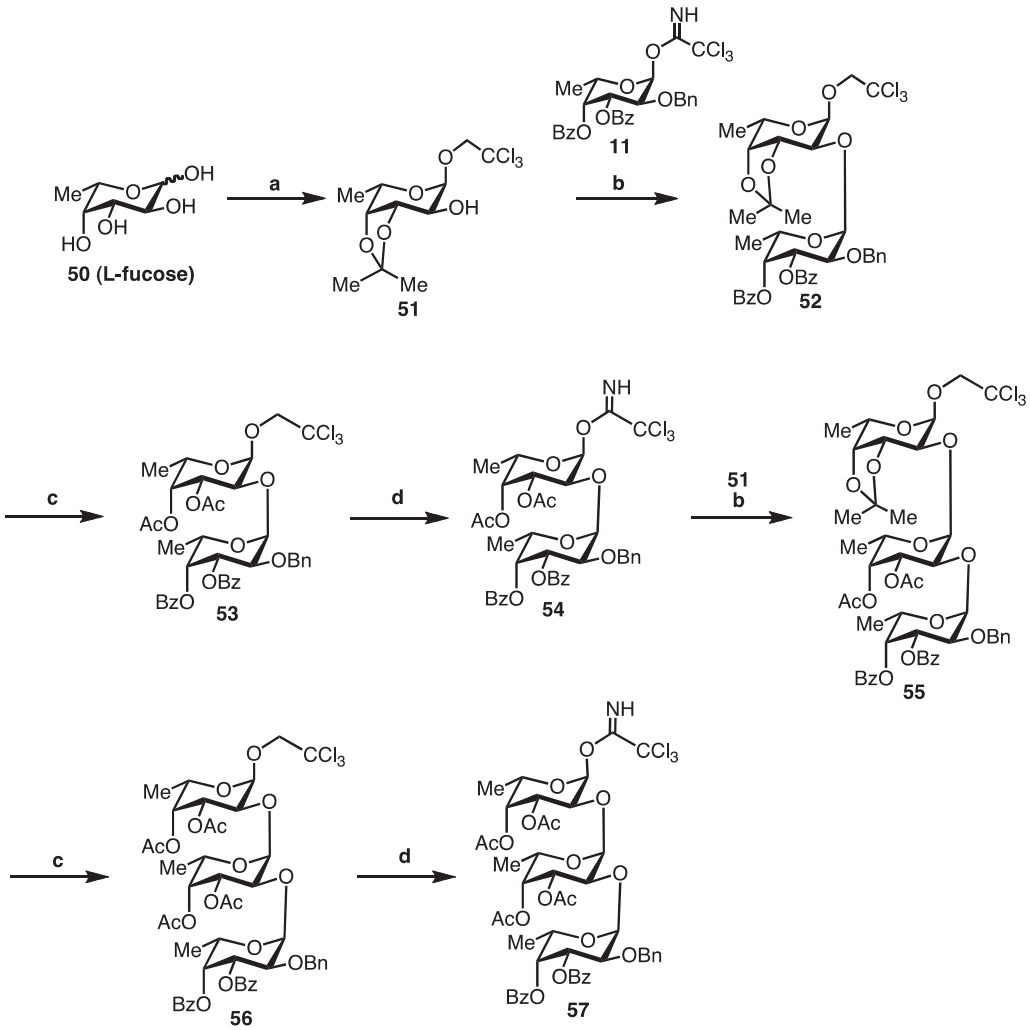
deoxy-2-(2,2,2-trichloroethoxy-carbonylamino)-1-thio-β-D-glucopyranoside (**34**).[20] At first chloroacetylation of the free hydroxyl group of **34** using standard conditions provided acetate **35**. The thioglycoside donor **35** was then condensed with the schisto core acceptor **14** using NIS/TfOH promoter to furnish trisaccharide **36** in 73% yield. Hydrolysis of the chloroacetyl group in **36** with aqueous pyridine produced trisaccharide acceptor **37** in 86% yield. Glycosylation of **37** with **13** produced hexasaccharide **38** which was further converted into glycosphingolipid **3** by a series of reactions as described previously. The structure and purity of **3** were demonstrated by its ^{1}H NMR and HR-FABMS data (Scheme 4).

2.4. Synthesis of oligosaccharide fragments 6–9

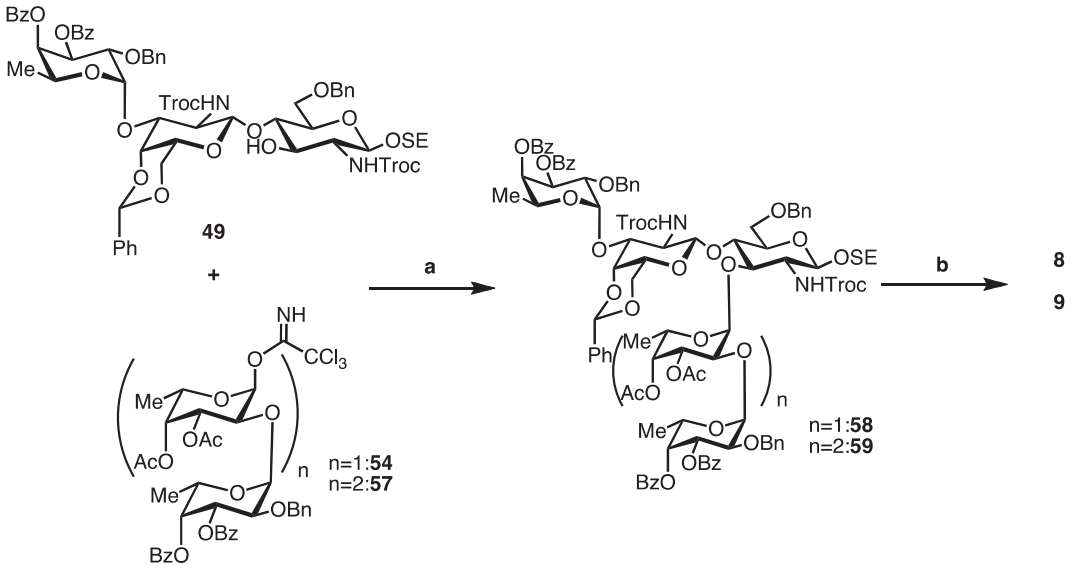
Glycosphingolipids **F–J** contain a common β-D-Glc*p*NAc-(1→3)-β-D-Gal*p*NAc-(1→4)-β-D-Glc*p*-sequence. The synthesis of glycosphingolipids **G–J** can be envisaged by coupling of the common trisaccharide sequence to oligosaccharide fragments **6–9** which corresponded to the non-reducing ends of **G–J**, respectively. Oligosaccharide fragments **6–9** are not only important intermediates toward the synthesis of glycosphingolipids **G–J** but also important molecular probes to explore their potential use as diagnostic tools for serum-based-antigen recognition in patients and



Scheme 6. Reagents and conditions: (a) (1) guanidinium nitrate, MeONa, MeOH/$CHCl_3$; (2) benzaldehyde dimethyl acetal, $NaHSO_4{\cdot}SiO_2$, CH_3CN 58% (two steps); (b) TMSOTf, MS 4 Å, CH_2Cl_2; (c) (1) Zn, Ac_2O, AcOH; (2) Pd-C/H_2, MeOH/AcOH; (3) Ac_2O/pyridine; 4) MeONa, MeOH, 23% (four steps).



Scheme 7. Reagents and conditions: (a) (1) 2,2,2-trichloroethanol, $NaHSO_4{\cdot}SiO_2$; (2) 2,2-dimethyl propane, $NaHSO_4{\cdot}SiO_2$, acetone 59% (two steps); (b) TMSOTf, MS 4 Å, CH_2Cl_2, **52** 75%, **55** 80%; (c) (1) 80% AcOH; 2) Ac_2O/pyridine, **53** 86%, **56** 63%; (d) (1) Zn, AcOH; (2), CF_3CO_2H/CH_2Cl_2; (3) DBU, CCl_3CN, CH_2Cl_2, **54** 77%, **57** 76% (three steps).



Scheme 8. Reagents and conditions: (a) TMSOTf, MS 4 Å, CH_2Cl_2, **58** 67%, **59** 43%; (b) (1) Zn, Ac_2O, AcOH; (2) Pd-C/H_2, MeOH/AcOH; (3) Ac_2O/pyridine; (4) MeONa, MeOH, **8** 32%, **9** 35% (four steps).

immunomodulator. The desired oligosaccharide fragments **6**–**9** were prepared by a systematic and integrated approach (Schemes 5–8). Trisaccharide fragment **6** is the LDN-F antigen {β-D-Gal*p*NAc-(1→4)-[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAc} while tetrasaccharide fragment **7** contains an additional α1→3 fucosyl Gal*p*NAc sequence at the non-reducing end. Oligosaccharide fragments **8** and **9**, precursors of glycosphingolipids **I** and **J**, can be derived from fragment **7** to which di and tri α1→2 fucopyranosyl repeating units are to be attached at the 3-position of Glc*p*NAc.

Trisaccharide **6** was synthesized by a coupling of the fucopyranosyl donor **11** with a disaccharide acceptor **44**. The acceptor **44** was obtained by a condensation of acceptor **23** with a known glycosyl imidate **42**[21] to afford disaccharide **43** followed by hydrolysis of chloroacetyl group. TMSOTf-promoted glycosylation of fucosyl imidate **11** with acceptor **44** produced trisaccharide **45** which was subjected to standard deblocking conditions as described for the preparation of **1** to afford unprotected trisaccharide **6** (Scheme 5).

Compound **47** was chosen as a common acceptor for the synthesis of oligosaccharide fragments **7**–**9**. It was obtained from disaccharide intermediate **43** by ester hydrolysis followed by benzylidenation[22] of 4′,6′-diol using benzaldehyde dimethyl acetal in 58% yield. Three glycosylation conditions of acceptor **47** with the fucosyl donor **11** were tested (Table 1). Tetrasaccharide **48**, which can be converted into **7**, was obtained by condensation of **47** with large excess of **11** (6 equiv) in the presence of TMSOTf. Deprotection of **48** as previously described for oligosaccharide **6** afforded target tetrasaccharide **7** (Scheme 6). On the other hand, regioselective fucosylation of acceptor **47** was achieved by using a reduced amount of **11** (3 equiv). In this case desired **49**, which is the intermediate to prepare **8** and **9**, was obtained in 66% yield together with recovered acceptor **47** (11%).

Difucosyl donor **54** and trifucosyl donor **57**, which are the building blocks of **8** and **9**, respectively, were obtained from fucosyl derivative **51** which was prepared by trichloroethylation and isopropylidenation of L-fucose **50**. TMSOTf-promoted glycosylation of **51** with the common fucosyl donor **11** provided disaccharide **52** in 75% yield. The α-glycosidic linkage between the fucose units in **52** was established from the homonuclear coupling constant (d, J = 3.3 Hz) of the newly introduced anomeric proton signal at δ = 5.58. Compound **52** was converted into **53** by deisopropylidenation followed by acetylation. The anomeric trichloroethyl protecting group in **53** was selectively cleaved by exposure to Zn/AcOH and resulted hemiacetal was converted into imidate **54** using standard conditions. Coupling of acceptor **51** to disaccharide donor **54** afforded trisaccharide **55** which was deprotected and activated to provide trisaccharide imidate **57** (Scheme 7). Similarly, TMSOTf-promoted glycosylation of trisaccharide acceptor **49** with glycosyl donors **54** and **57** afforded desired α-glycosides **58** (67%) and **59** (43%), respectively. Finally, standard deprotection of **58** and **59**, followed by purification by column chromatography on Sephadex LH-20 furnished penta- and hexasaccharides **8** and **9**, respectively (Scheme 8). All the intermediates and the unprotected target oligosaccharides were fully characterized by NMR spectroscopy and MS spectrometry.

Table 1
Fucosylation under various conditions

Ent. No.	Donor **11** (equiv)	Acceptor **47** (μmol)	Time (h)	Promoter (equiv)	Solvent	Temp (°C)	Yield %
1	6	62.7	18	TMSOTf (0.15)	CH_2Cl_2	−40	**48**: 78
2	1.5	94.9	3	TMSOTf (0.1)	CH_2Cl_2	−40	**49**: 28[a]
3	3	114	3	TMSOTf (0.15)	CH_2Cl_2	−40	**49**: 66[b]

[a] With 52% recovery of **47**.
[b] With 11% recovery of **47**.

3. Conclusions

In summary, a systematic and integrated approach for the synthesis of three glycosphingolipids **1**–**3** found in the parasite, *Schistosoma mansoni* and six non-reducing end oligosaccharide fragments **4**–**9** has been accomplished. Fragments **6**–**9** are expected to be probes to clarify structural requirements for antigen recognition in glycosphingolipids **G**, **H**, **I**, and **J**. Although, *S. mansoni* possesses unique carbohydrate antigens, so far it has not been possible to exploit them for diagnostic and therapeutic purposes. As isolation of carbohydrate antigens from natural sources requires time consuming procedures and skill, the demand for homogeneous synthetic carbohydrate antigens is growing. Effective

synthetic methods are expected to contribute toward development of rapid, cost-effective, and reliable diagnostic tools in the near future.

4. Experimental

4.1. General

Optical rotations were measured with a Jasco P-1020 digital polarimeter. ^{1}H and ^{13}C NMR spectra were recorded with a Varian 500 FT NMR spectrometer. Me_4Si and acetone were used as internal standards for $CDCl_3$ and CD_3OD, respectively. MALDI-TOFMS was recorded on an AB SCIEX Voyager RP mass spectrometer. High-resolution mass spectra were recorded on a JEOL JMS-700 under FAB conditions. TLC was performed on Silica Gel 60 F254 (E. Merck) with detection by quenching of UV fluorescence and by charring with 10% H_2SO_4. Column chromatography was carried out on Silica Gel 60 (E. Merck) and Iatrobeads 6RS-8060 (Iatron Lab., Tokyo). 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (**10**),[12] 2-(trimethylsilyl)ethyl 4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxy carbonylamino)-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (**14**),[11] phenyl 4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (**20**),[19] 2-(trimethylsilyl)ethyl 6-*O*-benzyl-3-*O*-chloroacetyl-2-deoxy-2-(2,2,2-trichloro-ethoxycarbonyl amino)-β-D-glucopyranoside (**23**),[11] were prepared as reported. Benzoylceramide **18** was prepared from phytosphingosine, which was purchased from Degussa (The Netherlands) by the conventional four-step procedure.[18]

4.2. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)]-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (12)

A mixture of **10** (335 mg, 0.38 mmol), **12** (581 mg, 0.96 mmol, 2.5 equiv), and MS 4 Å (500 mg) in dry CH_2Cl_2 (4 mL) was stirred for 2 h at room temperature, then cooled to −30 °C. TMSOTf (34.8 μL, 0.19 mmol) was added, and the mixture was stirred for 18 h at −30 °C, then neutralized with Et_3N. The precipitates were filtrated off and washed with $CHCl_3$. The combined filtrate and washings were washed with water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography (2:1 hexane–EtOAc) to give **12** (399 mg, 79%) as an amorphous powder. $[\alpha]_D$ −61.7 (*c* 3.2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95–7.21 (m, 20H, 4 Ph), 5.68–5.64 (m, 2H, H-3, 4 of Fuc), 5.37 (d, 1H, N*H*), 5.33 (d, 1H, $J_{1,2}$ = 4.9 Hz, H-1 of Fuc), 5.32 (d, 1H, $J_{3,4}$ = 3.8 Hz, H-4 of Gal), 5.13 (br dd, 1H, H-5 of Fuc), 5.05 (dd, 1H, $J_{1,2}$ = 8.2 Hz, $J_{2,3}$ = 10.2 Hz, H-2 of Gal), 4.92 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1 of GlcN), 4.82–4.76 (m, 4H, H-3 of Gal, benzylmethylene, NHCOCH_2CCl$_3$), 4.71–4.66 (m, 2H, 2 benzylmethylene), 4.65 (d, 1H, H-1 of Gal), 4.49–4.45 (m, 2H, H-6a of Gal, benzylmethylene), 4.37 (dd, 1H, $J_{5,6b}$ = 7.3 Hz, $J_{6b,6a}$ = 11.6 Hz, H-6b of Gal), 4.33 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.3 Hz, H-3 of GlcN), 4.15 (dd, 1H, $J_{1,2}$ = 3.9 Hz, $J_{2,3}$ = 10.2 Hz, H-2 of Fuc), 4.06 (t, 1H, $J_{4,5}$ = 9.1 Hz, H-4 of GlcN), 3.96–3.92 (m, 1H, CH_2CH$_2$Si(CH$_3$)$_3$), 3.81 (dd, 1H, $J_{5,6a}$ = 3.0 Hz, $J_{6a,6b}$ = 10.7 Hz, H-6a of GlcN), 3.77 (dd, 1H, $J_{5,6b}$ = 1.6 Hz, H-6b of GlcN), 3.55 (t, 1H, $J_{5,6a}$ = $J_{5,6b}$ = 6.9 Hz, H-5 of Gal), 3.53–3.48 (m, 1H, CH_2CH$_2$Si(CH$_3$)$_3$), 3.42 (br d, 1H, H-5 of GlcN), 3.16 (br d, 1H, H-2 of GlcN), 2.22, 2.06, 1.99, 1.96 (each s, 12H, 4 Ac), 1.25 (d, 3H, H-6 of Fuc), 0.95–0.88 (m, 2H, CH$_2$CH_2Si(CH$_3$)$_3$), −0.01 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR ($CDCl_3$):δ 170.6, 170.3, 170.0, 168.9, 165.9, 165.1, 153.6, 137.63, 137.60, 133.1, 132.7, 129.9, 129.8, 129.7, 129.5, 128.6, 128.43, 128.38, 128.13, 128.10, 128.07, 128.0, 127.8, 99.6 (C-1 of Gal), 98.7 (C-1of GlcN), 97.2 (C-1 of Fuc), 95.5, 74.8, 74.4, 74.1, 73.7, 73.6, 73.2, 72.8, 70.94, 70.88, 70.8, 69.2, 67.6, 67.2, 67.0, 64.8, 61.1, 60.3, 59.4, 21.0, 20.8, 20.7, 20.6, 18.0, 16.0, 14.2, −1.4. HR-FABMS: calcd for $C_{62}H_{74}Cl_3NO_{22}SiNa$: *m/z* 1340.3435; found: *m/z* 1340.3441 [M+Na]$^+$.

4.3. 2-(Trimethylsilyl)ethyl β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranoside (4)

A mixture of **12** (111 mg, 76.4 μmol) and zinc powder (1.2 g) in AcOH–Ac_2O (1:1, 12 mL) was stirred for 18 h at 55 °C. After completion of the reaction, the mixture was filtered and the filtrate was diluted with water and extracted with $CHCl_3$. The extract was washed with water, dried ($MgSO_4$), and concentrated. The residue was dissolved in THF–MeOH (1:1, 3 mL) and hydrogenolysed under hydrogen (0.4 MPa) in the presence of 10% Pd/C (300 mg) for 18 h at room temperature. The mixture was then filtered and concentrated. The residue was acetylated with acetic anhydride (2 mL) in pyridine (3 mL). The reaction mixture was poured into ice H_2O and extracted with $CHCl_3$. The extract was washed sequentially with 5% HCl, aq $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography using 2:1 $CHCl_3$–acetone as eluent to give acylated trisaccharide intermediate (48.3 mg, 58%). $[\alpha]_D$ −51.4 (*c* 0.3, MeOH); ^{1}H NMR (600 MHz, CD_3OD): δ 5.76 (d, 1H, $J_{3,4}$ = 3.3 Hz, H-4 of Fuc), 5.62 (d, 1H, N*H*), 5.60 (dd, 1H, $J_{2,3}$ = 10.7 Hz, H-3 of Fuc), 5.54 (d, 1H, $J_{1,2}$ = 4.1 Hz, H-1 of Fuc), 5.47 (d, 1H, $J_{3,4}$ = 3.8 Hz, H-4 of Gal), 5.34 (dd, 1H, H-2 of Fuc), 5.16 (dd, 1H, $J_{1,2}$ = 7.3 Hz, $J_{2,3}$ = 10.2 Hz, H-2 of Gal), 5.04–4.99 (m, 2H, H-3 of Gal, H-5 of Fuc), 4.69 (d, 1H, $J_{1,2}$ = 6.9 Hz, H-1 of GlcN), 4.62 (dd, 1H, $J_{5,6a}$ = 2.8 Hz, $J_{6a,6b}$ = 11.8 Hz, H-6a of GlcN), 4.58 (dd, 1H, $J_{5,6a}$ = 6.5 Hz, $J_{6a,6b}$ = 10.6 Hz, H-6a of Gal), 4.52 (d, 1H, H-1 of Gal), 4.41 (dd, 1H, $J_{5,6a}$ = 7.4 Hz, H-6b of Gal), 4.22–4.18 (m, 2H, H-3 of GlcN, H-6b of Gal), 3.93 (dd, 1H, H-5 of Gal), 3.91–3.86 (m, 2H, H-4 of GlcN, CH_2CH$_2$Si(CH$_3$)$_3$), 3.70 (br d, H-2 of GlcN), 3.63–3.60 (m, 1H, H-5 of GlcN), 3.54–3.49 (m, 1H, CH_2CH$_2$Si(CH$_3$)$_3$), 2.27, 2.17, 2.15, 2.10, 2.08, 2.01, 1.99 (each s, 21H, 7 Ac), 1.30 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6 of Fuc), 0.96–0.85 (m, 2H, CH$_2$CH_2Si(CH$_3$)$_3$), 0.001 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR ($CDCl_3$):δ 171.2, 170.6, 170.5, 170.3, 170.0, 169.3, 166.0, 165.3, 133.3, 133.0, 129.6, 129.51, 129.47, 128.5, 128.2, 100.5 (C-1 of Gal), 99.3 (C-1 of GlcN), 95.4 (C-1 of Fuc), 74.6, 73.1, 72.8, 72.00, 72.19, 70.9, 69.5, 69.0, 68.8, 68.6, 66.9, 66.8, 64.9, 64.8, 62.3, 61.0, 53.8, 31.7, 30.9, 29.7, 23.5, 20.97, 20.95, 20.8, 20.68, 20.65, 20.6, 20.5, 18.0, 16.0, −1.5. MALDI-TOFMS: calcd for $C_{51}H_{67}NO_{23}SiNa$ ([M+Na]$^+$), *m/z* 1112; found 1112. To a solution of the intermediate (17.3 mg) in MeOH (1.5 mL) was added NaOMe (15.0 mg) at 40 °C. The mixture was stirred for 5 h and then neutralized with Amberlite IR 120 [H$^+$]. The mixture was filtered and concentrated. The product was purified by Sephadex LH-20 column chromatography with MeOH to give **4** (5.3 mg, 86%). ^{1}H NMR (500 MHz, CD_3OD): δ 4.42 (d, 1H, $J_{1,2}$ = 4.5 Hz, H-1 of Fuc), 3.91 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1 of Gal), 3.84 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1 of GlcN). HR-FABMS: calcd for $C_{62}H_{74}Cl_3NO_{22}SiNa$: *m/z* 652.2613; found: *m/z* 652.2642 [M+Na]$^+$.

4.4. 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-[3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)]-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl trichloroacetimidate (13)

To a solution of **12** (247 mg, 0.19 mmol) in CH_2Cl_2 (3.0 mL) cooled to 0 °C was added CF_3CO_2H (1.5 mL), and the mixture was stirred for 3 h at room temperature and concentrated. EtOAc and toluene (1:2) were added and evaporated to give the reducing sugar. To a solution of the residue in CH_2Cl_2 (3.0 mL) cooled at 0 °C

were added DBU (42.0 μL, 0.28 mmol) and CCl_3CN (191 μL, 1.87 mmol). The reaction mixture was stirred for 6 h at room temperature. After completion of the reaction, the mixture was concentrated. The residue was purified by silica gel column chromatography using 100:1 chloroform–acetone as eluent to give **13** (187 mg, 73%). $[\alpha]_D$ −85.6 (*c* 1.3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.46 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1 of GlcN), 5.49 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1 of Fuc), 4.61 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1 of Gal). ^{13}C NMR ($CDCl_3$): δ 170.7, 170.4, 170.0, 169.3, 166.0, 165.2, 154.6, 137.5, 137.4, 137.3, 133.1, 132.7, 129.8, 128.74, 128.66, 128.6, 128.5, 128.4, 128.3, 128.22, 128.19, 128.1, 127.7, 99.8 (C-1 of Gal), 97.5 (C-1 of Fuc), 95.3, 91.7 (C-1of GlcN), 74.7, 74.2, 73.7, 73.1, 72.8, 72.6, 72.1, 70.9, 70.8, 70.4, 69.4, 67.5, 66.9, 65.0, 61.1, 61.0, 59.3, 20.8, 20.7, 20.64, 20.57, 16.0.

4.5. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)]-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (15)

A mixture of **14** (65.7 mg, 65.5 μmol), **13** (98.3 mg, 72.1 μmol), and MS 4 Å (120 mg) in dry CH_2Cl_2 (1 mL) was stirred for 5 h at room temperature, then cooled to −40 °C. TMSOTf (1.3 μL, 7.21 μmol) was added, and the mixture was stirred for 12 h at −40 °C, then neutralized with Et_3N. The precipitates were filtrated off and washed with $CHCl_3$. The combined filtrate and washings were washed with water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography (2:1 hexane–EtOAc) to give **15** (113 mg, 78%). $[\alpha]_D^{25}$ −37.0 (*c* 1.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.95 (d, 1H, N*H* of GlcN), 5.67 (d, 1H, N*H* of GalN), 5.30 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1 of Fuc), 4.99 (br d, 1H, H-1 of GalN), 4.72 (br d, 1H, H-1 of GlcN), 4.66 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of Glc), 4.64 (d, 1H, $J_{1,2}$ = 7.0 Hz, H-1 of Gal). ^{13}C NMR (150 MHz, $CDCl_3$):δ 100.4 (C-1 of Glc), 99.8 (C-1 of GalN), 99.3 (C-1 of Gal), 98.7 (C-1 of GlcN), 97.1 (C-1 of Fuc). MALDI-TOFMS: calcd for $C_{105}H_{114}Cl_6N_2O_{35}SiNa$: *m/z* 2224; found: *m/z* 2224c.

4.6. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[2-*O*-acetyl-3,4-di-*O*-benzoyl-α-L-fucopyranosyl-(1→3)]-2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-acetyl-2,3-di-*O*-benzoyl-β-D-glucopyranoside (16)

A mixture of **15** (113 mg, 51.3 μmol) and zinc powder (1.0 g) in AcOH–Ac_2O (1:1, 10 mL) was stirred for 18 h at 55 °C. After completion of the reaction, the mixture was filtered and the filtrate was diluted with water and extracted with $CHCl_3$.The extract was washed with water, dried ($MgSO_4$), and concentrated. The residue in MeOH–AcOH (1:1, 4 mL) was hydrogenolysed (0.4 MPa) under hydrogen in the presence of 10% Pd/C (300 mg) for 18 h at room temperature, then filtered and concentrated. The residue was acetylated with acetic anhydride (2 mL) in pyridine (3 mL). The reaction mixture was poured into ice H_2O and extracted with $CHCl_3$. The extract was washed sequentially with 5% HCl, aq $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography using 5:1 $CHCl_3$–acetone as eluent to give **16** (34.0 mg, 37%). $[\alpha]_D^{25}$ −26.4 (*c* 0.61, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.95 (d, 1H, N*H* of GlcN), 5.67 (d, 1H, N*H* of GalN), 5.43 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1 of Fuc), 4.82 (br d, 1H, H-1 of GalN), 4.72 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1 of GlcN), 4.68 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of Glc), 4.60 (d, 1H, $J_{1,2}$ = 8.4 Hz, H-1 of Gal). ^{13}C NMR (150 MHz, $CDCl_3$):δ 100.5 (C-1 of Glc), 100.5 (C-1 of Gal), 99.5 (C-1 of GalN), 99.4 (C-1 of GlcN), 95.6 (C-1 of Fuc). MALDI-TOFMS: calcd for $C_{85}H_{104}N_2O_{38}SiNa$: *m/z* 1812; found: *m/z* 1812 $[M+Na]^+$.

4.7. 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[2-*O*-acetyl-3,4-di-*O*-benzoyl-α-L-fucopyranosyl-(1→3)]-2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (17)

Compound **17** was prepared from **16** (34.0 mg, 18.8 μmol) as described for preparation of **13**. The product was purified by silica gel column chromatography (5:1 chloroform–methanol) to give **17** (34.4 mg, quant.). $[\alpha]_D^{25}$ −40.5 (*c* 0.85, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.70 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1 of Glc), 5.44 (d, 1H, $J_{1,2}$ = 4.1 Hz, H-1 of Fuc), 4.82 (d, 1H, $J_{1,2}$ = 8.5 Hz,H-1 of GalN), 5.09 (d, 1H, $J_{1,2}$ = 7.1 Hz, H-1 of GlcN), 4.88 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1 of Gal).

4.8. 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[2-*O*-acetyl-3,4-di-*O*-benzoyl-α-L-fucopyranosyl-(1→3)]-2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoy-β-D-glucopyranosyl-(1→1)-(2*S*,3*S*,4*R*)-3,4-di-*O*-benzoyl-2-hexadecanamido-octadecane-1,3,4-triol (19)

A mixture of **17** (54.4 mg, 36.5 μmol), (2*S*,3*S*,4*R*)-3,4-di-*O*-benzoyl-2-hexadecanamido-octadecane-1,3,4-triol **18** (55.7 mg, 72.8 μmol), and activated MS 4 Å (200 mg) in dry CH_2Cl_2 (0.4 mL) was stirred under an atmosphere of argon for 18 h at room temperature, then cooled to 0 °C. TMSOTf (5.3 μL, 29.2 μmol) was added, and the mixture was stirred for 3 h at room temperature, then neutralized with Et_3N. The solids were filtrated off and washed with $CHCl_3$. The combined filtrate and washings were washed with brine, dried ($MgSO_4$), and concentrated. The product was purified by flash silica gel column chromatography using 30:1 chloroform–methanol as eluent to give **19** (25 mg, 23%). $[\alpha]_D^{25}$ −13.6 (*c* 0.2, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12–7.26 (m, 30H, 6 Ph), 6.10 (d, 1H, N*H* of ceramide), 5.81 (d, 1H, N*H* of GlcN), 5.43 (d, 1H, $J_{1,2}$ = 4.1 Hz, H-1 of Fuc), 4.66 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1 of GlcN), 4.62 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1 of Glc), 4.60 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1 of GalN), 4.55 (d, 1H, $J_{1,2}$ = 7.4 Hz, H-1 of Gal). ^{13}C NMR (150 MHz, $CDCl_3$): δ 100.5 (C-1 of Glc, Gal), 99.3 (C-1 of GalN, GlcN), 95.6 (C-1 of Fuc). MALDI-TOFMS: Calcd for $C_{128}H_{167}N_3O_{43}Na$: *m/z* 2457.1; found: *m/z* 2458.4 $[M+Na]^+$.

4.9. β-D-Galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-D-galactopyranosyl-(1→4)-β-D-glucopyranosyl-(1→1)-(2*S*,3*S*,4*R*)-2-hexadecanamido-octadecane-1,3,4-triol (1)

To a solution of **19** (25 mg, 10.3 μmol) in MeOH (1.0 mL) was added dioxane (1.0 mL) and NaOMe (20 mg) at 40 °C. The mixture was stirred for 18 h and then neutralized with Amberlite IR 120 $[H^+]$. The mixture was filtered and concentrated. The product was purified by Sephadex LH-20 column chromatography with 1:1 $CHCl_3$–MeOH to give **1** (9.5 mg, 65%). $[\alpha]_D$ −7.0 (*c* 0.08, $CHCl_3$/MeOH = 1:1). ^{1}H NMR (600 MHz, $CDCl_3/CD_3OD$ = 1:1): δ 4.90 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1 of Fuc), 4.52 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1 of GlcN), 4.45 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of GalN), 4.36 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1 of Gal), 4.30 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1 of Glc). HR-FABMS: calcd for $C_{68}H_{125}N_3NaO_{28}$: *m/z* 1454.8347; found: *m/z* 1454.8300 $[M+Na]^+$.

4.10. Phenyl 4,6-*O*-benzylidene-3-*O*-chloroacetyl-1-thio-β-D-galactopyranoside (21)

A solution of **20** (2.17 g, 6.02 mmol) and dibutyltin oxide (2.3 g, 9.03 mmol) in 60 mL of dry toluene was stirred under reflux for 5 h. Toluene was distilled off, the stannylidene derivative was dissolved in DMF (15 mL) and Bu_4NBr (2.4 g, 7.23 mmol) and chloroacetyl chloride (0.72 mL, 9.03 mmol) were added at room temperature. After being stirred for 5 h, the solution was concentrated. The residue was dissolved with EtOAc, washed with aq NaCl, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography using 20:1 toluene–ethyl acetate to give **21** (1.97 g, 75%). $[\alpha]_D$ −22.0 (*c* 1.9, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.68–7.25 (m, 10H, 2Ph), 5.59 (s, 1H, PhC*H*), 5.09 (dd, 1H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 3.6 Hz, H-3), 4.81 (d, 1H, $J_{1,2}$ = 9.6, H-1), 4.64 (br s, 1H, O*H*), 4.46 (d, 1H, H-4), 4.25–4.22 (m, 3H, H-6a, $ClCH_2CO$), 4.14 (dd, 1H, $J_{5,6b}$ = 1.7 Hz, $J_{6a,6b}$ = 12.6 Hz, H-6b), 3.93 (t, 1H, H-2), 3.83 (dd, 1H, H-5). ^{13}C NMR (150 MHz, $CDCl_3$):δ 167.6, 139.5, 133.5, 133.2, 129.5, 128.7, 128.0, 127.3, 101.3, 87.7 (C-1), 77.6, 74.6, 70.2, 69.7, 66.5, 41.6.

HR-FABMS: calcd for $C_{21}H_{22}ClO_6S$: *m/z* 437.0826; found: *m/z* 437.0759 $[M]^+$.

4.11. Phenyl 2-*O*-benzoyl 4,6-*O*-benzylidene-3-*O*-chloroacetyl-thio-β-D-galactopyranoside (22)

To a solution of **21** (1.18 g, 2.70 mmol) in CH_2Cl_2 (8.0 mL) was added pyridine (4.8 mL) and benzoyl chloride (0.47 mL, 4.05 mmol), and the reaction mixture was stirred for 5 h at room temperature. Toluene was added and evaporated, then the residue was dissolved in $CHCl_3$, washed with 5% HCl, aq $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 3:1 hexane–EtOAc as eluent to give **22** (3.2 g, 85.1%). $[\alpha]_D$ +5.3 (*c* 3.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 8.02–7.23 (m, 15H, 3Ph), 5.60 (t, 1H, $J_{1,2}$ = $J_{2,3}$ = 9.9 Hz, H-2), 5.50 (s, 1H, PhC*H*), 5.24 (dd, 1H, $J_{3,4}$ = 3.6 Hz, H-3), 4.88 (d, 1H, H-1), 4.46 (d, 1H, H-4), 4.41 (dd, 1H, $J_{5,6a}$ = 1.4 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.06 (dd, 1H, $J_{5,6b}$ = 1.4 Hz, H-6b), 3.67 (d, 1H, H-5). ^{13}C NMR (150 MHz, $CDCl_3$):δ 167.1, 164.8, 137.3, 133.9, 133.4, 130.9, 129.8, 129.4, 129.2, 128.8, 128.5, 128.3, 128.2, 126.5, 101.1, 85.2 (C-1), 74.9, 73.3, 69.7, 69.0, 67.1, 40.6.

HR-FABMS: calcd for $C_{28}H_{25}ClO_7S$: *m/z* 541.1088; found: *m/z* 541.1055 $[M]^+$.

4.12. 2-(Trimethylsilyl)ethyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-chloroacetyl-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-3-*O*-chloroacetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (24)

A mixture of **22** (190 mg, 0.35 mmol), **23** (169 mg, 0.27 mmol), and powdered MS 4 Å (350 mg) in dry CH_2Cl_2 (3 mL) was stirred under Ar atmosphere for 2 h at room temperature, then cooled to −40 °C. NIS (119 mg, 0.53 mmol) and TfOH (3.1 μL, 35.2 μmol) were added and the mixture was stirred for 1 h at −40 °C, then neutralized with Et_3N. The precipitates were filtered off and washed with $CHCl_3$. The combined filtrate and washings were successively washed with saturated aqueous $Na_2S_2O_3$ and water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography (8:1 toluene–acetone) to give **24** (238 mg, 84%). $[\alpha]_D$ +17.6 (*c* 3.4, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.86–7.37 (m, 15H, 3 Ph), 5.49 (s, 1H, PhC*H*), 5.44 (dd, 1H, $J_{1,2}$ = 8.3 Hz, $J_{2,3}$ = 9.9 Hz, H-2 of Gal), 5.25 (d, 1H, N*H*), 5.17 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 10.5 Hz, H-3 of GlcN), 4.99 (dd, 1H, $J_{3,4}$ = 3.9 Hz, H-3 of Gal), 4.75–4.71 (m, 2H, benzylmethylene, $NHCOCH_2CCl_3$), 4.65 (d, 1H, $NHCOCH_2CCl_3$), 4.63 (d, 1H, H-1 of Gal), 4.41 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1 of GlcN), 4.38 (d 1H, benzylmethylene), 4.36 (d, 1H, H-4 of Gal), 4.32 (br d, 1H, H-6a of Gal), 4.25, 4.15 (each d, 2H, $COCH_2Cl$ of GlcN), 4.07–4.01 (m, 2H, H-4 of GlcN, H-6b of Gal), 3.97 (d, 1H, $COCH_2Cl$ of Gal), 3.93–3.87 (m, 2H, $COCH_2Cl$ of Gal, $CH_2CH_2Si(CH_3)_3$), 3.73 (dd, 1H, H-2 of GlcN), 3.59 (dd, 1H, $J_{5,6a}$ = 2.8 Hz, $J_{6a,6b}$ = 11.0 Hz, H-6[a] of GlcN), 3.51–3.45 (m, 2H, H-6b of GlcN, $CH_2CH_2Si(CH_3)_3$), 3.34 (br s, 1H, H-5 of Gal), 3.27 (br d, 1H, H-5of GlcN), 0.91–0.88 (m, 2H, $CH_2CH_2Si(CH_3)_3$), −0.06 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (150 MHz, $CDCl_3$):δ 167.7, 167.1, 164.3, 154.2, 138.0, 137.0, 133.4, 129.6, 129.3, 129.0, 128.6, 128.5, 128.4, 128.2, 128.1, 126.3, 101.3, 100.5 (C-1 of GlcN), 100.0 (C-1 of Gal), 95.5, 74.5, 74.29, 74.26, 74.0, 73.5, 73.0, 69.1, 68.7, 67.3, 67.2, 66.1, 55.9, 40.8, 40.5, 18.0, −1.4. HR-FABMS: calcd for $C_{45}H_{52}Cl_5NO_{15}Si$-Na: *m/z* 1072.1447; found 1072.1423: *m/z* $[M+Na]^+$.

4.13. 2-(Trimethylsilyl)ethyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-3-*O*-chloroacetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (25)

A solution of **24** (137 mg, 0.130 mmol) in pyridine (4.0 mL) and H_2O (2.0 mL) was stirred for 18 h at 80 °C. The mixture was diluted with $CHCl_3$, washed with aq 5%HCl, aq $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 10:1 chloroform–acetone to give **25** (81.7 mg, 70%). $[\alpha]_D$ −2.5 (*c* 3.0, CH_3COCH_3). ^1H NMR (600 MHz, CD_3COCD_3): δ 8.09–7.21 (m, 15H, 3 Ph), 6.83 (d, 1H, N*H*), 5.70 (s, 1H, PhC*H*), 5.43 (dd, 1H, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 10.2 Hz, H-2 of Gal), 4.88 (d, 1H, H-1 of Gal), 4.79, 4.70 (each d, 2H, $NHCOCH_2CCl_3$), 4.46 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of GlcN), 4.43 (d, 1H, $J_{3,4}$ = 3.0 Hz, H-4 of Gal), 4.40–4.37 (m, 2H, 2 OH), 4.25–4.23 (m, 2H, H-6 of Gal, benzylmethylene), 4.17 (d 1H, benzylmethylene), 4.09 (dt, 1H, H-3 of GlcN), 3.92–3.88 (m, 2H, H-3 of Gal, $CH_2CH_2Si(CH_3)_3$), 3.70 (d, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, H-3 of GlcN), 3.59 (d, 1H, H-4 of Gal), 3.55–3.46 (m, 3H, H-2, 6 of GlcN, $CH_2CH_2Si(CH_3)_3$), 3.39–3.36 (m, 1H, H-5 of GlcN), 0.94–0.82 (m, 2H, $CH_2CH_2Si(CH_3)_3$), −0.02 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (150 MHz, CD_3COCD_3):δ 165.8, 155.2, 139.7, 139.4, 134.1, 131.1, 130.5, 129.5, 129.4, 129.0, 128.7, 128.1, 127.2, 102.3 (C-1 of Gal), 101.6 (C-1 of GlcN), 101.5, 97.1, 82.1, 76.8, 74.8, 74.7, 73.64, 73.55, 73.3, 71.6, 69.41, 69.39, 68.0, 67.0, 58.3, 18.6, −1.2. HR-FABMS: calcd for $C_{41}H_{50}Cl_3NO_{13}SiNa$: *m/z* 920.2015; found: *m/z* 920.2032 $[M+Na]^+$.

4.14. 2-(Trimethylsilyl)ethyl 3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-[3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)]-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (26)

Compound **26** was prepared from **25** (81.6 mg, 90.7 μmol) and **11** (110 mg, 0.18 mmol) as described for preparation of **12**. The product was purified by silica gel column chromatography (2:1 hexane–ethyl acetate) to give **26** (132 mg, 82%). $[\alpha]_D$ −79.5 (*c* 2.04): ^1H NMR (600 MHz, $CDCl_3$): δ 8.01–6.86 (m, 45H, 9 Ph), 5.82 (dd, 1H, $J_{2,3}$ = 10.7 Hz, $J_{3,4}$ = 3.0 Hz, H-3 of Fuc a), 5.70 (dd, 1H, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 3.3 Hz, H-3 of Fuc b), 5.65 (d,1H, H-4 of Fuc a), 5.63 (d,1H, H-4 of Fuc b), 5.60–5.57 (m, 2H, H-2 of Gal, PhC*H*), 5.52 (br d, 1H, N*H*), 5.36 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1 of Fuc a), 5.22 (br dd, 1H, H-5 of Fuc a), 5.04 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1 of Fuc b), 4.89 (d, 1H, benzylmethylene), 4.83–4.79 (m, 4H, H-1 of GlcN, H-1, 6a of Gal, benzylmethylene), 4.83–4.79 (H-5 of Fuc b, $NHCOCH_2CCl_3$, benzylmethylene), 4.47 (d, 1H, benzylmethylene), 4.27 (d, 1H, $J_{3,4}$ = 3.6 Hz, H-4 of Gal), 4.20 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.1 Hz, H-3of GlcN), 4.16 (br d, H-6 of Gal), 4.12–4.09 (m, 2H, H-2 of Fuc a, benzylmethylene), 4.05 (t, 1H, $J_{4,5}$ = 8.8 Hz, H-4 of GlcN), 3.99–3.96 (m, 3H, H-6a of GlcN, H-2 of Fuc b, benzylmethylene),

3.86–3.82 (m, 1H, $CH_2CH_2Si(CH_3)_3$), 3.68 (br d, 1H, H-3 of Gal), 3.62 (br d, 1H, H-6b of GlcN), 3.39–3.35 (m, 1H, $CH_2CH_2Si(CH_3)_3$), 3.34 (s, 1H, H-5 of Gal), 3.27 (br d, 1H, H-5 of GlcN), 3.13 (br. dd, H-2 of GlcN), 1.07 (d, 3H, H-6 of Fuc b), 0.89–0.82 (m, 2H, $CH_2CH_2Si(CH_3)_3$), 0.79 (d, 3H, H-6 of Fuc a), −0.06 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$):δ 166.0, 165.6, 165.2, 165.0, 164.3, 153.4, 138.5, 137.7, 137.5, 137.1, 133.1, 132.8, 132.69, 132.65, 132.6, 139.4, 130.3, 130.1, 129.9, 129.71, 129.66, 129.6, 129.4, 128.5, 128.44, 128.39, 128.3, 128.2, 128.2, 128.11, 128.08, 128.0, 127.9, 127.8, 127.5, 100.3, 100.20 (C-1 of Fuc a), 100.16 (C-1 of Gal), 98.7 (C-1of GlcN), 97.5 (C-1 of Fuc b), 95.6, 79.8, 75.5, 75.1, 74.7, 74.5, 74.4, 73.8, 73.6, 73.1, 72.3, 71.8, 71.7, 71.5, 70.8, 70.3, 69.2, 68.0, 67.0, 66.9, 65.7, 65.5, 59.3, 29.6, 17.9, 16.2, 15.1, −1.4. MALDI-TOFMS: Calcd for $C_{95}H_{98}Cl_3NO_{25}SiNa$: *m/z* 1808.5; found: 1807.7 *m/z* [M+Na] $^+$.

4.15. 2-(Trimethylsilyl)ethyl α-L-fucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranoside (5)

A mixture of **26** (52.0 mg, 67.7 μmol) and zinc powder (600 mg) in AcOH–Ac_2O (2:1, 6 mL) was stirred for 18 h at 55 °C. After completion of the reaction, the mixture was filtered and the filtrate was diluted with water and extracted with $CHCl_3$. The extract was washed with water, dried ($MgSO_4$), and concentrated. A solution of the residue in MeOH–AcOH (2:1, 3 mL) was hydrogenolysed (0.4 MPa) under hydrogen in the presence of 10% Pd/C (300 mg) for 18 h at room temperature, then filtered and concentrated. The residue was de-acylated with NaOMe (20 mg) in MeOH (2 mL) at 40 °C. The mixture was stirred for 5 h and then neutralized with Amberlite IR 120 [H^+]. The mixture was filtered and concentrated. The product was purified by Sephadex LH-20 column chromatography with MeOH to give **5** (7.2 mg, 23%). $[\alpha]_D$ +88.0 (*c* 0.3, MeOH), ^{1}H NMR (600 MHz, CD_3OD) δ 4.90 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1 of Fuc b), 4.78 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1 of Fuc a), 4.29 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of Gal), 4.25 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of GlcN). ^{13}C NMR (125 MHz, $CDCl_3$) δ 101.7 (C-1 of Gal), 100.8 (C-1 of Fuc b), 99.7 (C-1 of GlcN), 98.2 (C-1 of Fuc a).

HR-FABMS: Calcd for $C_{31}H_{57}NO_{19}SiNa$: *m/z* 798.3192; found: *m/z* 798.3213 [M+Na]$^+$.

4.16. 2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-chloroacetyl-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-3-*O*-chloroacetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-D-glucopyranosyl trichloroacetimidate (27)

To a mixture of **24** (100.3 mg, 0.10 mmol) and MS 4 Å (150 mg) in CH_2Cl_2 (20 mL) cooled to 0 °C was added CF_3CO_2H (1.5 mL), and the mixture was stirred for 3 h at room temperature. The solids were filtrated off and concentrated. EtOAc and toluene (1:2) were added and evaporated to give the reducing sugar. To a solution of the residue in CH_2Cl_2 (2.0 mL) cooled at 0 °C were added DBU (14.7 μL, 98.6 μmol) and CCl_3CN (52.7 μL, 0.53 μmol). The reaction mixture was stirred for 6 h at room temperature. After completion of the reaction, the mixture was concentrated. The residue was purified by silica gel column chromatography using chloroform to give **27** (65.7 mg, 64%).

4.17. 2-(Trimethylsilyl)ethyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-chloroacetyl-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-3-*O*-chloroacetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonyl-amino)-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (28)

Compound **28** was prepared from **24** (123.2 mg, 112 μmol) and **14** (93.6 mg, 93.3 μmol) as described for preparation of **12**. The product was purified by silica gel column chromatography (5:1 chloroform–acetone) to give **28** (118 mg, 65%). $[\alpha]_D$ +21.4 (*c* 2.8), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96–7.23 (m, 35H, 7 Ph), 4.84 (br d, 1H, H-1 of GlcN), 4.67 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of Glc), 4.62 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1 of Gal), 4.58 (br d, 1H, H-1 of GalN). ^{13}C NMR (150 MHz, $CDCl_3$) δ 101.6 (C-1 of GalN), 100.3 (C-1 of Glc), 100.2 (C-1 of Gal), 99.2 (C-1 of GlcN). MALDI-TOFMS: Calcd for $C_{88}H_{92}Cl_8N_2O_{28}SiNa$: *m/z* 1955.3; found: *m/z* 1955.1[M+Na]$^+$.

4.18. 2-(Trimethylsilyl)ethyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (29)

Compound **29** was prepared from **28** (118 mg, 63.4 μmol) as described for preparation of **25**. The product was purified by silica gel column chromatography (5:1 chloroform–methanol) to give **29** (34.4 mg, quant.). $[\alpha]_D$ +12.9 (*c* 2.6), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07–7.20 (m, 35H, 7 Ph), 4.83 (br d, 1H, H-1 of GlcN), 4.62 (d, 2H, $J_{1,2}$ = 7.4 Hz, H-1 of Glc, Gal), 4.54 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1 of GalN). ^{13}C NMR (150 MHz, $CDCl_3$) δ 101.4 (C-1 of Glc), 100.7 (C-1 of GalN), 100.3 (C-1 of Gal), 99.3 (C-1 of GlcN). MALDI-TOFMS: Calcd for $C_{84}H_{90}Cl_6N_2O_{26}SiNa$: *m/z* 1803.4; found: *m/z* 1803.9 [M+Na]$^+$.

4.19. 2-(Trimethylsilyl)ethyl 3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-[3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)]-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonyl amino)-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (30)

Compound **30** was prepared from **11** (178 mg, 293 μmol) and **29** (104.3 mg, 58.5 μmol) as described for preparation of **12**. The product was purified by silica gel column chromatography (2:1 hexane–ethyl acetate) to give **30** (110 mg, 72%). $[\alpha]_D$ −23.5 (*c* 2.8, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02–6.85 (m, 60H, 12 Ph), 5.30 (br s, H-1 of Fuc a), 5.03 (d, $J_{1,2}$ = 3.6 Hz, H-1 of Fuc b), 4.96 (br, 1H, H-1 of GlcN), 4.80 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of Glc), 4.64 (d, 1H, $J_{1,2}$ = 7.4 Hz, H-1 of GalN), 4.63 (d, $J_{1,2}$ = 8.0 Hz, H-1 of Gal), 1.05 (d, 1H, H-6 of Fuc a), 0.75 (d, 1H, H-6 of Fuc b). ^{13}C NMR (150 MHz, $CDCl_3$) δ 100.5 (C-1 of Glc), 100.3 (C-1 of Fuc b), 100.2 (C-1 of Gal), 99.3 (C-1 of GalN, GlcN). MALDI-TOFMS: Calcd for $C_{138}H_{138}Cl_6N_2O_{38}SiNa$: *m/z* 2691.7; found: *m/z* 2692.1 [M+Na]$^+$.

4.20. 2-(Trimethylsilyl)ethyl 2-*O*-acetyl-3,4-di-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-[2-*O*-acetyl-3,4-di-*O*-benzoyl-α-L-fucopyranosyl-(1→3)]-2-acetramide-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamide-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-acetyl-2,3-di-*O*-benzoyl-D-glucopyranoside (31)

Compound **31** was prepared from **30** (110 mg, 41.2 μmol) as described for preparation of **16**. The product was purified by silica gel column chromatography (15:1 chloroform–methanol) to give **31** (39.1 mg, 43%). $[\alpha]_D^{25}$ −26.4 (*c* 0.61, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98–6.90 (m, 35H, 7 Ph), 5.40 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1 of Fuc a), 5.20 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1 of Fuc b), 4.84 (br d, 1H, H-1 of GalN), 4.75 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of GlcN), 4.66 (d, 1H, $J_{1,2}$ = 7.4 Hz, H-1 of Glc), 4.60 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of Gal), 0.98 (d, 1H, H-6 of Fuc a), 0.80 (d, 1H, H-6 of Fuc b). ^{13}C NMR (150 MHz, $CDCl_3$):δ101.3 (C-1 of Glc), 100.5 (C-1 of Gal), 100.0

(C-1 of Fuc b), 99.5 (C-1 of GalN), 99.2 (C-1 of GlcN), 95.4 (C-1 of Fuc a). MALDI-TOFMS: calcd for $C_{110}H_{124}N_2O_{44}SiNa$: *m/z* 2228.7; found: *m/z* 2227.9 $[M+Na]^+$.

4.21. 2-*O*-Acetyl-3,4-di-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-[2-*O*-acetyl-3,4-di-*O*-benzoyl-α-L-fucopyranosyl-(1→3)]-2-acetramide-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamide-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-acetyl-2,3-di-*O*-benzoyl-β-D-glucopyranosyl trichloroacetimidate (32)

Compound **32** was prepared from **31** (39.1 mg, 17.7 μmol) as described for preparation of **17**. The product was purified by silica gel column chromatography (20:1 chloroform–methanol) to give **32** (32.6 mg, 82%). $[\alpha]_D$ −1.5 (*c* 0.3, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 5.70 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1 of Glc), 5.44 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1 of Fuc a), 5.30 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1 of Fuc b), 4.91 (br d, 1H, H-1 of GalN), 4.82 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of GlcN), 4.68 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of Gal).

4.22. 2-*O*-Acetyl-3,4-di-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-2-deoxy-β-D-galactopyranosyl-(1→4)-[2-*O*-acetyl-3,4-di-*O*-benzoyl-α-L-fucopyranosyl-(1→3)]-2-acetramide-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamide-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoyl-β-D-glucopyranosyl-(1→1)-(2*S*,3*S*,4*R*)-3,4-di-*O*-benzoyl-2-hexadecanamido-octadecane-1,3,4-triol (33)

Compound **33** was prepared from **32** (32.6 mg, 14.5 μmol) and **18** (16.7 mg, 21.8 μmol) as described for preparation of **19**. The product was purified by silica gel column chromatography (20:1 hexane–ethyl acetate) to give **33** (11.6 mg, 28%) as an amorphous powder. $[\alpha]_D$ −23.4 (*c* 0.2, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 8.10–7.14 (m, 45H, 9 × Ph), 5.45 (d, 1H, $J_{1,2}$ = 4.1 Hz, H-1 of Fuc a), 5.32 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1 of Fuc b), 4.70 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1 of GlcN), 4.65 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1 of Glc), 4.60 (br d, 1H, H-1 of GalN), 4.56 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of Gal). ^{13}C NMR (150 MHz, $CDCl_3$):δ 100.8 (C-1 of Glc, Gal), 99.5 (C-1 of GalN, GlcN), 96.2 (C-1 of Fuc). MALDI-TOFMS: calcd for $C_{153}H_{187}N_3O_{49}Na$: *m/z* 2873.2; found 2873.4: *m/z* $[M+Na]^+$.

4.23. α-L-Fucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetramide-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamide-2-deoxy-β-D-galactopyranosyl-(1→4)-β-D-glucopyranosyl-(1→1)-(2*S*,3*S*,4*R*)-2-hexadecanamido-octadecane-1,3,4-triol (2)

Compound **2** was prepared from **33** (11.6 mg, 4.1 μmol) as described for preparation of **1**. The product was purified by Sephadex LH-20 column chromatography in 1:1 $CHCl_3$–MeOH to give **2** (6.8 mg, quant.). $[\alpha]_D$ −7.0 (*c* 0.08, $CHCl_3/CH_3OH$ = 1:1). ^1H NMR (600 MHz, $CDCl_3/CD_3OD$ = 1:1): δ 4.93 (d, 1H, $J_{1,2}$ = 4.1 Hz, H-1 of Fuc), 4.79 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1 of Fuc), 4.48 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1 of GlcN), 4.30 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of GalN), 4.28 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of Gal), 4.05 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1 of Glc). 0.99 (d, 2H, H-6 of Fuc). MALDI-TOFMS: calcd for $C_{74}H_{135}N_3O_{32}Na$: *m/z* 1600.9; found: *m/z* 1600.5 $[M+Na]^+$.

4.24. Phenyl 4,6-*O*-benzylidene-3-*O*-chloroacetyl-2-deoxy-2-(2,2,2-trichloro-ethoxycarbonyl amino)-thio-β-D-gulcopyranoside (35)

Compound **35** was prepared from **34** (1.93 g, 3.61 mmol) as described for preparation of **22**. The product was purified by silica gel column chromatography (20:1 chloroform–methanol) to give **35** (2.18 g, 99%). $[\alpha]_D$ −22.0 (*c* 1.9, $CHCl_3$). ^1H NMR (600 MHz, CD_3COCD_3): δ 7.54–7.31 (m, 10H, 2Ph), 7.29 (d, 1H, N*H*), 5.65 (s, 1H, PhC*H*), 5.46 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, H-3), 5.25 (d, 1H, $J_{1,2}$ = 10.4 Hz, H-1), 4.82 (q, 2H, $NHCOOCH_2CCl_3$), 4.33 (dd, 1H, $J_{5,6a}$ = 4.9 Hz, $J_{6a,6b}$ = 10.2 Hz, H-6a), 4.22 (q, 2H, $ClCH_2CO$), 3.88–3.82 (m, 3H, H-2, 4, 6b), 3.69 (dt, 1H, H-5). ^{13}C NMR (150 MHz, CD_3ODCD_3):δ 167.4, 155.2, 138.4, 133.8, 132.7, 129.8, 129.6, 128.8, 128.5, 127.0, 101.8, 96.8, 87.6 (C-1), 79.1, 75.3, 74.8, 71.1, 68.8, 56.1, 41.4. HR-FABMS: calcd for $C_{24}H_{23}Cl_4NO_7S$: *m/z* 610.0028; found: *m/z* 610.0039 $[M]^+$.

4.25. 2-(Trimethylsilyl)ethyl 4,6-*O*-benzylidene-3-*O*-chloroacetyl-2-deoxy-2-(2,2,2-trichloroethoxy-carbonylamino)-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (36)

Compound **36** was prepared from **35** (150 mg, 0.150 mmol) and **14** (183 mg, 0.300 mmol) as described for preparation of **24**. The product was purified by silica gel column chromatography (6:1 chloroform–acetone) to give **36** (165 mg, 73%). $[\alpha]_D$ +4.6 (*c* 3.6, $CHCl_3$). ^1H NMR (600 MHz, CD_3COCD_3): δ 6.87 (d, 1H, N*H* of GlcN), 6.66 (d, 1H, N*H* of GalN), 5.04 (1H, d, $J_{1,2}$ = 8.2 Hz, H-1 of GalN), 4.92 (1H, d, $J_{1,2}$ = 8.0 Hz, H-1 of Glc), 4.87 (1H, d, $J_{1,2}$ = 8.2 Hz, H-1 of GlcN). ^{13}C NMR (125 MHz, $CDCl_3$): δ178.8, 167.3, 165.7, 155.0, 139.9, 139.6, 138.4, 133.9, 133.6, 131.0, 130.9, 130.3, 129.6, 129.5, 129.24, 129.15, 129.1, 128.8, 128.7, 128.5, 128.4, 128.2, 127.3, 127.0, 103.0 (C-1 of GalN), 101.8, 101.6 (C-1 of GlcN), 101.2, 100.7 (C-1 of Glc), 97.0, 96.8, 79.3, 79.1, 78.0, 76.6, 76.0, 75.6, 75.3, 74.9, 74.8, 74.3, 73.7, 69.7, 69.0, 67.4, 67.2, 66.8, 57.4, 57.3, 54.5, 41.4, 18.4, −1.32. MALDI-TOFMS: calcd for $C_{66}H_{71}Cl_7N_2O_{21}SiNa$: *m/z* 1523; found: *m/z* 1523 $[M+Na]^+$.

4.26. 2-(Trimethylsilyl)ethyl 4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxy-carbonylamino)-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonyl-amino)-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (37)

Compound **37** was prepared from **36** (120 mg, 79.8 μmol) as described for preparation of **25**. The product was purified by silica gel column chromatography (6:1 chloroform–acetone) to give **37** (97.5 mg, 86%). $[\alpha]_D$ +36.1 (*c* 0.9, $CHCl_3$). ^1H NMR (600 MHz, CD_3COCD_3): δ 7.95–7.28 (m, 25H, 5 Ph), 6.74 (br d, 1H, N*H* of GalN), 6.64 (br d, 1H, N*H* of GlcN), 5.67 (1H, d, $J_{2,3}$ = $J_{3,4}$ = 9.1 Hz, H-3 of GlcN), 5.56 (s, 1H, PhC*H*), 5.40 (s, 1H, PhC*H*), 5.21 (1H, t, $J_{1,2}$ = 9.1 Hz, H-2 of Glc), 4.92 (1H, br. d, H-1 of Glc), 4.91–4.81 (m, 4H, H-1 of GalN, H-1 of GlcN, $NHCOCH_2CCl_3$, benzylmethylene), 4.72–4.63 (m, 3H, $NHCOCH_2CCl_3$, benzylmethylene, O*H*), 4.28 (1H, d, $J_{3,4}$ = 2.8 Hz, H-4 of GalN), 4.24–4.19 (m, 3H, H-4 of Glc, H-3 of GalN, H-4 of GlcN), 4.04–4.01 (m, 1H, $CH_2CH_2Si(CH_3)_3$), 4.00–4.93 (m, 2H, H-6 of Glc), 3.90–3.86 (m, 2H, H-5 of Glc, H-3 of GlcN), 3.75–3.63 (m, 3H, H-2, 6 of GalN, H-6a of GlcN, $CH_2CH_2Si(CH_3)_3$), 3.51 (t, 1H, H-6b of GlcN), 3.44–3.37 (m, 2H, H-3, 5 of GalN), 0.93–0.79 (m, 2H, $CH_2CH_2Si(CH_3)_3$), −0.08 (m, 9H, $Si(CH_3)_3$). ^{13}C NMR (125 MHz, CD_3COCD_3): δ 165.7, 155.2, 155.0, 139.9, 139.0, 133.8, 133.6, 131.0, 130.9, 130.3, 129.5, 129.21, 129.15, 129.1, 128.7, 128.5, 128.4, 128.2, 127.3, 127.2, 103.4 (C-1 of GalN), 102.0, 101.7 (C-1 of GlcN), 101.1, 100.7 (C-1 of Glc), 97.1, 82.5, 79.1, 77.3, 76.7, 76.2, 75.6, 75.4, 74.9, 73.7, 71.6, 69.8, 69.1, 69.0, 67.4, 67.3, 67.1, 59.6, 54.5, 18.4, −1.32. MALDI-TOFMS: calcd for $C_{64}H_{70}Cl_6N_2O_{20}SiNa$: *m/z* 1447; found: *m/z* 1447 $[M+Na]^+$.

4.27. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)]-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxy-carbonylamino)-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloro-ethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (38)

Compound **38** was prepared from **37** (97.5 mg, 68.4 μmol) and **13** (112.2 mg, 82.1 μmol) as described for preparation of **15**. The product was purified by silica gel column chromatography (3:1 hexane–ethyl acetate) to give **38** (114 mg, 63%). $[\alpha]_D$ +13.6 (*c* 1.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 8.03–7.24 (m, 45H, 9 Ph), 5.62 (br s, 1H, H-1 of Fuc), 4.95 (br d, 1H, H-1 of GalN), 4.91 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1 of GlcN a), 4.87 (br d, 1H, H-1 of GlcN b), 4.75 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1 of Glc), 4.69 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of Gal), 1.25 (d, 1H, H-6 of Fuc). ^{13}C NMR (150 MHz, $CDCl_3$):δ101.0 (C-1 of Glc), 100.8 (C-1 of GalN), 100.7 (C-1 of Gal, GlcN a, GlcN b), 96.7 (C-1 of Fuc). MALDI-TOFMS: calcd for $C_{121}H_{130}Cl_9N_3O_{41}SiNa$: *m/z* 2646.5; found: *m/z* 2647.5 $[M+Na]^+$.

4.28. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[2-*O*-acetyl-3,4-di-*O*-benzoyl-α-L-fucopyranosyl-(1→3)]-2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoyl-β-D-glucopyranoside (39)

Compound **39** was prepared from **38** (114 mg, 51.7 μmol) as described for preparation of **16**. The product was purified by silica gel column chromatography (10:1 chloroform–methanol) to give **39** (43.0 mg, 40%). $[\alpha]_D$ −23.4 (*c* 0.2, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 5.60 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1 of Fuc), 4.89 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of Glc), 4.85 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of GalN), 4.79 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1 of GlcN a), 4.70 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of GlcN b), 4.56 (d, 1H, H-1 of Gal), ^{13}C NMR ($CDCl_3$):δ 100.6 (C-1 of Glc, Gal), 99.9 (C-1 of GlcN a), 99.3 (C-1 of GalN, GlcN b), 96.1 (C-1 of Fuc). MALDI-TOFMS: calcd for $C_{97}H_{121}N_3O_{45}SiNa$: *m/z* 2098.6; found: *m/z* 2098.2 $[M+Na]^+$.

4.29. 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[2-*O*-acetyl-3,4-di-*O*-benzoyl-α-L-fucopyranosyl-(1→3)]-2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoyl-D-glucopyranosyl trichloroacetimidate (40)

Compound **40** was prepared from **39** (43.0 mg, 20.7 μmol) as described for preparation of **17**. The product was purified by silica gel column chromatography (20:1 chloroform–methanol) to give **40** (33.8 mg, 77%). $[\alpha]_D$ −1.5 (*c* 0.8, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 5.68 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1 of Glc), 5.45 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1 of Fuc), 4.86 (br d, 1H, H-1 of GalN), 4.71 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1 of GlcN a), 4.70 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of GlcN b), 4.60 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1 of Gal).

4.30. 2,3,4,6-Tetra-*O*acetyl-β-D-galactopyranosyl-(1→4)-[2-*O*-acetyl-3,4-di-*O*-benzoyl-α-L-fucopyranosyl-(1→3)]-2-acetamido-6-*O*acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-4,6-di-*O*acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-4,6-di-*O*acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-acetyl-2,3-di-*O*-benzoyl-β-D-glucopyranosyl-(1→1)-(2*S*,3*S*,4*R*)-3,4-di-*O*benzoyl-2-hexadecanamido-octadecane-1,3,4-triol (41)

Compound **41** was prepared from **40** (32.6 mg, 14.5 μmol) and **18** (16.7 mg, 21.8 μmol) as described for preparation of **19**. The product was purified by silica gel column chromatography (20:1 hexane–ethyl acetate) to give **41** (8.6 mg, 20%). $[\alpha]_D$ −23.4 (*c* 0.2, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 8.08–7.22 (m, 30H, 6 × Ph), 5.70 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1 of Fuc), 4.79 (br d, 1H, H-1 of GalN), 4.70 (br d, 1H, H-1 of GlcN a), 4.65 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of GlcN b), 4.59 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1 of Glc), 4.56 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of Gal). ^{13}C NMR (150 MHz, $CDCl_3$):δ100.8 (C-1 of Glc, Gal), 99.5 (C-1 of GalN, GlcN), 96.2 (C-1 of Fuc). MALDI-TOFMS: calcd for $C_{140}H_{184}N_4O_{50}Na$: *m/z* 2744.1; found: *m/z* 2744.5 $[M+Na]^+$.

4.31. β-D-Galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)-β-D-glucopyranosyl-(1→1)-(2*S*,3*S*,4*R*)-2-hexadecanamido-octadecane-1,3,4-triol (3)

Compound **3** was prepared from **41** (8.6 mg, 2.9 μmol) as described for preparation of **1**. The product was purified by Sephadex LH-20 column chromatography with 1:1 $CHCl_3$–MeOH to give **3** (3.4 mg, 79%). $[\alpha]_D$ −35.6 (*c* 0.09, $CHCl_3/CH_3OH$ = 1:1). ^1H NMR (600 MHz, $CDCl_3/CD_3OD$ = 1:1): δ 4.78 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1 of Fuc), 4.48 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1 of GlcN), 4.37 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of GlcN), 4.35 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of GalN), 4.20 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of Gal), 4.05 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1 of Glc). 0.92 (d, 1H, H-6 of Fuc). MALDI-TOFMS: calcd for $C_{76}H_{138}N_4O_{33}Na$: *m/z* 1657.9; found: *m/z* 1658.3 $[M+Na]^+$.

4.32. 2-(Trimethylsilyl)ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxy-carbonylamino)-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-3-*O*-chloroacetyl-2-deoxy-2-(2,2,2-trichloroethoxy-carbonylamino)-β-D-glucopyranoside (43)

Compound **43** was prepared from **23** (221 mg, 0.36 mmol) and **42** (266 mg, 0.43 mmol) as described for preparation of **15**. The product was purified by silica gel column chromatography (4:1 hexane–ethyl acetate) to give **43** (313 mg, 79%). $[\alpha]_D$ −15.2 (*c* 7.8, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.45–7.33 (m, 5H, Ph), 5.27 (d, 1H, N*H* of GlcN), 5.21 (d, 1H, $J_{3,4}$ = 3.3 Hz, H-4 of GalN), 5.16 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 8.6 Hz, H-3 of GlcN), 4.79, 4.35 (each d, 2H, 2 benzylmethylene), 4.69–4.60 (m, 5H, H-3 of GalN, 2 NHCOCH_2CCl_3), 4.48 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of GlcN), 4.26 (br d, 1H, H-1 of GalN), 4.10–4.01 (m, 5H, H-6 of GalN, 2 OCOCH_2Cl, N*H* of GalN), 3.96–3.89 (m, 2H, H-4 of GlcN, C$H_2CH_2Si(CH_3)_3$), 3.69 (br d, 1H, H-6a of GlcN), 3.62–3.56 (m, 3H, H-2, 6b of GlcN, H-5 of GalN), 3.53–3.48 (m, 2H, H-2 of GalN, C$H_2CH_2Si(CH_3)_3$), 3.39 (br d, 1H, H-5 of GlcN), 3.53–3.48 (m, 1H, C$H_2CH_2Si(CH_3)_3$), 3.42 (br d, 1H, H-5 of GlcN), 2.08, 2.05, 1.91 (each s, 9H, 3 Ac), 0.91–0.86 (m, 2H, $CH_2CH_2Si(CH_3)_3$), −0.03 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (150 MHz, $CDCl_3$):δ 170.3, 170.2, 170.0, 167.1, 154.1, 153.7, 137.4, 129.1, 129.0, 128.6, 100.4 (C-1of GlcN), 100.1 (C-1 of GalN), 95.5, 95.4, 74.4, 74.3, 73.8, 73.5, 70.4, 70.3, 69.8, 67.4, 67.0, 66.21, 66.15, 61.2, 60.0, 56.0, 52.4, 40.8, 20.7, 20.64, 20.58, 20.48, 20.45, 18.0, −1.4, −1.5. HR-FABMS: calcd for $C_{38}H_{51}Cl_7N_2O_{17}SiNa$: *m/z* 1103.0674; found: *m/z* 1103.0670 $[M+Na]^+$.

4.33. 2-(Trimethylsilyl)ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycar bonylamino)-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (44)

Compound **44** was prepared from **43** (0.64 g, 0.59 mmol) as described for preparation of **25**. The product was purified by silica gel column chromatography (4:1 toluene–ethyl acetate) to give **44** (0.43 g, 70%). $[\alpha]_D$ −23.5 (*c* 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.45–7.12 (m, 5H, Ph), 5.25 (d, 1H, $J_{3,4}$ = 3.3 Hz, H-4 of GalN), 5.16 (br s, 1H, N*H* of GlcN), 4.83, 4.32 (each d, 2H, 2 benzylmethylene),

4.73–4.70 (m, 2H, NHCOCH_2CCl$_3$), 4.65–4.58 (m, 4H, H-1 of GlcN, H-3 of GalN, NHCOCH_2CCl$_3$), 4.11 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of GalN), 4.09–4.06 (m, 2H, H-6 of GalN), 4.02 (br d, N*H* of GalN), 3.97–3.93 (m, 1H, CH_2CH$_2$Si(CH$_3$)$_3$), 3.86–3.80 (m, 3H, H-3 of GlcN, H-2,5 of GalN), 3.71 (dd, 1H, $J_{6a,5}$ = 3.8 Hz, $J_{6a,6b}$ = 10.7 Hz), 3.63 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.3 Hz, H-4 of GlcN), 3.59 (br d, 1H, H-6b of GlcN), 3.52–3.47 (m, 1H, CH_2CH$_2$Si(CH$_3$)$_3$), 3.38 (br d, 1H, H-5 of GlcN), 3.28 (br dd, 1H, H-2 of GalN), 2.10, 2.04, 1.94 (each s, 9H, 3 Ac), 0.96–0.85 (m, 2H, CH$_2$CH_2Si(CH$_3$)$_3$), −0.03 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (CDCl$_3$):δ 170.5, 170.0, 154.1, 154.0, 138.1, 129.1, 128.9, 128.6, 128.2, 101.9 (C-1of GalN), 99.9 (C-1 of GlcN), 95.5, 95.4, 81.4, 74.6, 74.4, 73.4, 71.5, 71.0, 70.0, 67.2, 66.2, 66.1, 61.3, 58.0, 51.9, 20.6, 18.0, −1.4. HR-FABMS: calcd for $C_{36}H_{50}Cl_6N_2O_{16}SiNa$: *m/z* 1027.0958; found: *m/z* 1027.0980 [M+Na]$^+$.

4.34. 2-(Trimethylsilyl)ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxy-carbonylamino)-β-D-galactopyranosyl-(1→4)-[3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)]-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (45)

Compound **45** was prepared from **44** (122 mg, 121 μmol) and **11** (147 mg, 242 μmol) as described for preparation of **15**. The product was purified by silica gel column chromatography (3:1 hexane–ethyl acetate) to give **45** (141 mg, 80%). [α]$_D$ +29.7 (*c* 3.2, CHCl$_3$). ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.94–7.21 (m, 20H, 4 Ph), 5.68 (d, 1H, $J_{3,4}$ = 2.5 Hz, H-4 of Fuc), 5.62 (dd, 1H, $J_{2,3}$ = 10.4 Hz, H-3 of Fuc), 5.40 (d, 1H, N*H* of GlcN), 5.34 (d, 1H, $J_{3,4}$ = 3.3 Hz, H-4 of GalN), 5.32 (d 1H, $J_{1,2}$ = 3.6 Hz, H-1 of Fuc), 5.09 (br. dd, 1H, H-5 of Fuc), 4.91 (d, 1H, $J_{1,2}$ = 7.4 Hz, H-1 of GlcN), 4.87 (d, 1H, benzylmethylene), 4.79–4.66 (m, 7H, N*H* of Gal, 2 NHCOCH_2CCl$_3$, 2 benzylmethylene), 4.57 (br d, 1H, H-3 of GalN), 4.50 (dd, 1H, $J_{6a,5}$ = 6.3 Hz, $J_{6a,6b}$ = 11.3 Hz, H-6a of GalN), 4.42–4.39 (m, 3H, H-1, 6b of GalN, benzylmethylene), 4.30 (br t, 1H, H-3 of GalN), 4.14 (dd, 1H, H-2 of Fuc), 3.97–3.92 (m, 3H, H-4,5 of GlcN, CH_2CH$_2$Si(CH$_3$)$_3$), 3.77 (dd, 1H, $J_{6a,5}$ = 2.2 Hz, $J_{6a,6b}$ = 10.7 Hz, H-6a of GlcN), 3.72–3.67 (m, 2H, H-2, 5 of GalN), 3.61 (br d, 1H, H-6b of GlcN), 3.52–3.47 (m, 1H, CH_2CH$_2$Si(CH$_3$)$_3$), 3.40 (br d, 1H, H-5 of GlcN), 3.14 (br d, 1H, H-2 of GlcN), 2.21, 2.08, 1.96 (each s, 9H, 3 Ac), 1.26 (d, 3H, H-6 of Fuc), 0.95–0.86 (m, 2H, CH$_2$CH_2Si(CH$_3$)$_3$), −0.01 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (150 MHz, CDCl$_3$):δ 170.7, 170.5, 170.1, 166.0, 165.9, 165.3, 154.0, 153.7, 137.6, 137.1, 133.1, 132.8, 129.9, 129.8, 129.7, 129.6, 129.4, 129.3, 128.8, 128.5, 128.4, 128.2, 128.1, 127.9, 100.4 (C-1 of GalN), 98.8 (C-1 of GlcN), 97.3 (C-1 of Fuc), 95.6, 74.7, 74.5, 74.4, 74.1, 73.8, 73.3, 72.8, 71.0, 70.7, 70.4, 67.8, 67.3, 66.1, 64.8, 61.2, 59.4, 52.4, 29.3, 20.9, 20.6, 18.1, 16.0, −0.02, −1.4. HR-FABMS: calcd for $C_{63}H_{74}Cl_6N_2O_{22}SiNa$: *m/z* 1471.2531; found: *m/z* 1471.2535 [M+Na]$^+$.

4.35. 2-(Trimethylsilyl)ethyl 2-acetamido-3,4,6-tri-*O*-acetyl-deoxyβ-D-galacto-pyranosyl-(1→4)-[2-*O*-acetyl-3,4-di-*O*-benzoyl-α-L-fucopyranosyl-(1→3)]-2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranoside (46)

A mixture of **45** (106 mg, 73.2 μmol) and zinc powder (900 mg) in AcOH–Ac$_2$O (2:1, 9 mL) was stirred for 18 h at 55 °C. After completion of the reaction, the mixture was filtered and the filtrate was diluted with water and extracted with CHCl$_3$. The extract was washed with water, dried (MgSO$_4$), and concentrated. A solution of the residue in MeOH–THF (1:1, 2 mL) was hydrogenolysed (0.4 MPa) under hydrogen in the presence of 10% Pd/C (150 mg) for 18 h at room temperature, then filtered and concentrated. The residue was acetylated with acetic anhydride (2 mL) in pyridine (3 mL). The reaction mixture was poured into ice H$_2$O and extracted with CHCl$_3$. The extract was washed sequentially with 5% HCl, aq NaHCO$_3$, and brine, dried (MgSO$_4$), and concentrated. The residue was purified by silica gel column chromatography using 3:1 CHCl$_3$–acetone to give **46** (36.5 mg, 44%). [α]$_D$ −86.3 (*c* 0.6, CHCl$_3$): ^{1}H NMR (600 MHz, CDCl$_3$): δ 5.54 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1 of Fuc), 4.61 (d, 1H, $J_{1,2}$ = 6.4 Hz, H-1 of GlcN), 4.61 (d, 1H, $J_{1,2}$ = 6.4 Hz, H-1 of GalN). ^{13}C NMR (150 MHz, CDCl$_3$):δ 171.2, 171.0, 170.8, 170.6, 166.0, 165.3, 133.3, 133.0, 129.8, 129.6, 129.48, 129.45, 128.5, 128.2, 101.2 (C-1 of GalN), 99.5 (C-1 of GlcN), 95.4 (C-1 of Fuc), 73.8, 73.6, 73.0, 72.0, 71.0, 70.3, 69.5, 68.9, 68.2, 66.8, 66.2, 65.1, 63.2, 61.2, 53.8, 50.8, 31.7, 29.7, 29.3, 23.3, 21.0, 20.9, 20.8, 20.7, 20.6, 18.0, 16.1, −0.04, −1.5. HR-FABMS: calcd for $C_{51}H_{68}N_2O_{22}SiNa$: *m/z* 1111.3931; found: *m/z* 1111.3956 [M+Na]$^+$.

4.36. 2-(Trimethylsilyl)ethyl 2-acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl- (1→3)]-2-acetamido-2-deoxy-β-D-glucopyranoside (6)

Compound **6** was prepared from **46** (36.5 mg, 33.5 μmol) as described for preparation of **1**. The product was purified by Sephadex LH-20 column chromatography with MeOH to give **6** (21.1 mg, 94%). [α]$_D$ −28.1 (*c* 0.4, MeOH). ^{1}H NMR (600 MHz, CD$_3$OD): δ 4.99 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1 of Fuc), 4.44 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of GalN), 4.41 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1 of GlcN). HR-FABMS: calcd for $C_{27}H_{50}N_2O_{15}SiNa$: *m/z* 693.2878; found: *m/z* 693.2898 [M+Na]$^+$.

4.37. 2-(Trimethylsilyl)ethyl 4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxy-carbonylamino)-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (47)

To a solution of **43** (311 mg, 0.287 mmol) in MeOH/CHCl$_3$ (25 mL, 9:1) was added guanidinium nitrate (311 mg) and MeONa (27.1 mg). The reaction mixture was stirred for 3 h at room temperature then neutralized with Amberlite IR 120 [H$^+$]. The mixture was filtered and the filtrate was washed with brine, dried (MgSO$_4$), and concentrated. A mixture of the residue (756 mg, 0.83 mmol) in CH$_3$CN (5 mL), NaHSO$_4$·SiO$_2$ (300 mg), and benzaldehyde dimethyl acetal (BDA) (87.6 μL, 574 μmol, 2.0 equiv) was stirred for 3 h at room temperature, then neutralized with Et$_3$N. The solids were filtrated off and the filtrated was concentrated. The product was purified by silica gel column chromatography using 5:1 toluene–acetone to give **47** (161 mg, 58%). [α]$_D$ −13.0 (*c* 2.0, CHCl$_3$). ^{1}H NMR (600 MHz, CD$_3$COCD$_3$): δ 7.54–7.12 (m, 10H, Ph), 6.82 (d, 1H, N*H* of GlcN), 6.68 (d, 1H, N*H* of GalN), 5.68 (s, 1H, PhC*H*), 4.80–4.78 (m, 2H, NHCOCH_2CCl$_3$), 4.72–4.69 (m, 2H, NHCOCH_2CCl$_3$), 4.67 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 of GalN), 4.63 (s, 2H, 2 benzylmethylene), 4.51 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of GlcN), 4.46 (s, 1H, O*H* of GlcN), 4.33 (d, 1H, $J_{3,4}$ = 3.0 Hz, H-4 of GalN), 4.20 (br d, 2H, H-6 of GalN), 4.14 (br d, O*H* of GalN), 3.97–3.93 (m, 1H, CH_2CH$_2$Si(CH$_3$)$_3$), 3.91–3.86 (m, 2H, H-2, 5 of GalN), 3.80–3.78 (m, 2H, H-6 of GlcN, H-3 of GalN), 3.71 (br t, 1H, H-3 of GlcN), 3.63 (br t, 1H, H-4 of GlcN), 3.59–3.55 (m, 1H, CH_2CH$_2$Si(CH$_3$)$_3$), 3.51–3.47 (m, 2H, H-2, 5 of GlcN), 0.95–0.86 (m, 2H, CH$_2$CH_2Si(CH$_3$)$_3$), 0.00 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (150 MHz, CD$_3$COCD$_3$): δ 155.5, 155.3, 154.1, 140.0, 139.5, 129.4, 129.1, 129.0, 128.7, 128.4, 128.1, 127.2, 103.1 (C-1of GalN), 101.7 (C-1 of GlcN), 101.4, 97.1, 96.9, 81.8, 76.2, 75.1, 75.0, 74.9, 73.7, 73.6, 70.8, 69.6, 67.84, 67.81, 67.1, 58.4, 56.0, 18.6, −1.2. HR-FABMS: calcd for $C_{37}H_{48}Cl_6N_2O_{13}SiNa$: *m/z* 989.0955; found: *m/z* 989.0976 [M+Na]$^+$.

4.38. 2-(Trimethylsilyl)ethyl 3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L–L-fucopyranosyl- (1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)-[3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)]-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (48) 2-(trimethylsilyl)ethyl 3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (49)

(Ent. 1) A mixture of **47** (60.8 mg, 62.7 μmol), **11** (228 mg, 376 μmol, 6.0 equiv), and MS 4 Å (250 mg) in dry CH_2Cl_2 (1.8 mL) was stirred for 3 h at room temperature, then cooled to −40 °C. TMSOTf (8.5 μL, 47.1 μmol, 0.15 equiv) was added, and the mixture was stirred for 18 h at −40 °C, then neutralized with Et_3N. The precipitates were filtrated off and washed with $CHCl_3$. The combined filtrate and washings were washed with water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography (2:1 hexane–EtOAc) to give **48** (91.0 mg, 78%).

(Ent. 2) A mixture of **47** (92.0 mg, 94.9 μmol), **11** (86.4 mg, 142 μmol, 1.5 equiv), and MS 4 Å (150 mg) in dry CH_2Cl_2 (1.2 mL) was stirred for 3 h at room temperature, then cooled to −40 °C. TMSOTf (2.6 μL, 14.2 μmol, 0.10 equiv) was added, and the mixture was stirred for 3 h at −40 °C, then neutralized with Et_3N. The precipitates were filtrated off and washed with $CHCl_3$. The combined filtrate and washings were washed with water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography (5:2 hexane–EtOAc) to give **49** (91.0 mg, 28%) as an amorphous powder and was recovered compound **47** (52%).

(Ent. 3) A mixture of **47** (110.5 mg, 114 μmol), **11** (208 mg, 342 μmol, 3.0 equiv), and MS 4 Å (200 mg) in dry CH_2Cl_2 (2.0 mL) was stirred for 3 h at room temperature, then cooled to −40 °C. TMSOTf (9.3 μL, 51.3 μmol, 0.15 equiv) was added, and the mixture was stirred for 3 h at −40 °C, then neutralized with Et_3N. The precipitates were filtrated off and washed with $CHCl_3$. The combined filtrate and washings were washed with water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography (5:2 hexane–EtOAc) to give **49** (106 mg, 66%) as an amorphous powder and was recovered compound **47** (11%). **48**: $[\alpha]_D$ −109.9 (*c* 1.6, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.36 (d, 1H, $J_{1,2}$ = 3.0 Hz, H-1 of Fuc a), 4.79 (br s, 1H, H-1 of Fuc b), 4.85 (br d, 1H, H-1 of GlcN), 4.65 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of GalN). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.9, 165.8, 165.5, 165.3, 165.2, 154.4, 153.6, 138.5, 137.8, 137.4, 137.2, 133.2, 132.9, 132.8, 130.3,3 130.26, 129.7, 129.64, 129.56, 128.6, 128.49, 128.45, 128.4, 128.23, 128.19, 128.0, 127.92, 127.86, 127.7, 125.6, 100.1, 99.7 (C-1 of GalN; Fuc b), 98.9 (C-1 of GlcN), 97.6 (C-1 of Fuc a), 95.7, 95.5, 76.1, 74.8, 74.6, 74.3, 74.1, 74.0, 73.3, 73.0, 72.9, 72.3, 71.5, 70.8, 69.4, 68.8, 66.9, 66.6, 66.0, 65.4, 60.4, 58.8, 53.6, 29.7, 18.0, 16.2,15.3, 14.2, −1.5. MALDI-TOFMS: calcd for $C_{91}H_{96}Cl_6N_2O_{25}SiNa$: *m/z* 1877; found: *m/z* 1877 $[M+Na]^+$. **49**: $[\alpha]_D$ −61.7 (*c* 0.95, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.47 (d, 1H, $J_{1,2}$ = 3.0 Hz, H-1 of Fuc), 4.79 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1 of GalN), 4.52 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of GlcN). ^{13}C NMR (150 MHz, $CDCl_3$):δ 166.4, 165.8, 154.3, 140.0, 139.4, 139.3, 134.1, 133.9, 130.8, 130.7, 130.2, 129.6, 129.5, 129.13, 129.07, 129.0, 128.9, 128.5, 128.3, 128.1, 127.1, 102.5 (C-1 of GalN), 101.8, 101.5 (C-1 of GlcN), 100.2 (C-1 of Fuc), 97.1, 96.8, 81.7, 79.7, 75.6, 75.2, 74.89, 74.85, 73.9, 73.8, 73.7, 73.2, 72.0, 71.2, 69.6, 69.5, 67.5, 67.1, 66.2, 58.4, 54.2, 18.6, 16.6, −1.2. HR-FABMS: calcd for $C_{64}H_{72}Cl_6N_2O_{19}SiNa$: *m/z* 1433.2527; found: *m/z* 1433.2567 $[M+Na]^+$.

4.39. 2-(Trimethylsilyl)ethyl α-L-fucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranoside (7)

Compound **7** was prepared from **48** 70.5 mg, 38.0 μmol) as described for preparation of **4**. The product was purified by Sephadex LH-20 column chromatography in MeOH to give **7** (7.2 mg, 23%). $[\alpha]_D$ −88.0 (*c* 0.3, MeOH). ^{1}H NMR (600 MHz, CD_3OD): δ 5.00 (d, 1H, $J_{1,2}$ = 4.1 Hz, H-1 of Fuc a), 4.87 (d, 1H, $J_{1,2}$ = 4.1 Hz, H-1 of Fuc b), 4.51 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1 of GalN), 4.40 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1 of GlcN). ^{13}C NMR (150 MHz, $CDCl_3$):δ 103.0 (C-1 of Fuc b), 101.9 (C-1 of GalN), 101.7 (C-1 of GlcN), 100.0 (C-1 of Fuc a). HR-FABMS:: calcd for $C_{101}H_{110}Cl_6N_2O_{31}SiNa$: *m/z* 839.3457; found: *m/z* 839.3489 $[M+Na]^+$.

4.40. 2,2,2-Trichloroethyl 3,4-*O*-isopropylidene-α-L-fucopyranoside (51)

A mixture of L-fucose **(50)** (200 mg, 1.22 mmol) and $NaHSO_4{\cdot}SiO_2$ (500 mg) in 2,2,2-trichloroethanol (5 mL) was stirred for 8 h at 50 °C, then neutralized with Et_3N. The solids were filtrated off and the filtrated was concentrated. A mixture of the residue in acetone (4.0 mL), $NaHSO_4{\cdot}SiO_2$ (500 mg), and 2,2-dimethoxypropane (2 mL) was stirred for 3 h at room temperature, then neutralized with Et_3N. The solids were filtrated off and the filtrated was concentrated. The product was purified by silica gel column chromatography using 10:1 toluene–acetone to give **51** (240 mg, 59%). ^{1}H NMR (600 MHz, CD_3COCD_3): δ 5.03 (d, $J_{1,2}$ = 3.6 Hz, H-1), 4.35, 4.26 (each d, 2H, CH_2CCl$_3$), 4.32–4.30 (m, 1H, H-5), 4.23 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 6.1 Hz, H-3), 4.15 (dd, 1H, H-4), 3.98 (d, 1H, OH), 3.79–3.76 (m, 1H, H-2), 1.41, 1.29 (each s, 6H, O(CH_3)$_2$), 1.26 (d, 3H, H-6). ^{13}C NMR (150 MHz, CD_3COCD_3): δ 109.2, 100.2 (C-1), 97.8, 80.2, 76.8, 76.4, 70.1, 65.5, 28.2, 26.2, 16.6.

4.41. 2,2,2-Trichloroethyl 3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranoside (52)

Compound **52** was prepared from **51** (175 mg, 0.522 mmol) and **11** (475 mg, 0.783 mmol, 5.0 eq.) as described for preparation of **15**. The product was purified by silica gel column chromatography (3:1 hexane–ethyl acetate) to give **52** (326 mg, 75%). $[\alpha]_D$ −114.0 (*c* 1.3, $CHCl_3$). ^{1}H NMR (600 MHz, CD_3COCD_3): δ 7.97–7.22 (m, 15H, 3 Ph), 5.74 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, $J_{3',4'}$ = 3.3 Hz, H-3′), 5.64 (d, 1H, H-4′), 5.58 (d, 1H, $J_{1',2'}$ = 3.3 Hz, H-1′), 5.30 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1), 4.76 (q, 2H, benzylmethelene), 5.70–5.69 (m, 1H, H-5′), 4.45–4.42 (m, 2H, H-3, 5), 4.33–4.26 (m, 4H, H-4, 2′, OCH_2CCl$_3$), 3.96 (dd, 1H, $J_{2,3}$ = 7.7 Hz, H-2), 1.52, 1.36 (each s, 6H, C(CH_3)$_2$), 1.31 (d, 1H, H-6), 1.19 (d, 1H, H-6′). ^{13}C NMR (150 MHz, CD_3COCD_3): δ 166.5, 165.9, 139.3, 134.2, 133.9, 130.8, 130.3, 130.2, 129.5, 129.2, 129.0, 128.6, 128.3, 109.4, 98.3 (C-1), 97.5, 96.5 (C-1′), 81.0, 76.7, 75.3, 75.2, 74.2, 73.3, 72.7, 71.4, 65.6, 16.6, 16.4.

4.42. 2,2,2-Trichloroethyl 3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4-di-*O*-acetyl-α-L-L-fucopyranoside (53)

A solution of **52** (131 mg, 0.168 mmol) in 80% AcOH (5 mL) was stirred at 50 °C for 5 h, then diluted with toluene and concentrated. The residue was acetylated with acetic anhydride (2.0 mL) in pyridine (3.0 mL). After the reaction was quenched with MeOH, toluene was added and co-evaporated several times. The product was purified by silica gel column chromatography (4:1 hexane–ethyl

acetate) to give **53** (118 mg, 86%). $[\alpha]_D$ −154.1 (*c* 1.4, $CHCl_3$). ^1H NMR (600 MHz, CD_3COCD_3): δ 8.00–7.23 (m, 15H, 3 Ph), 5.72 (dd, 1H, $J_{2',3'}$ = 9.4 Hz, $J_{3',4'}$ = 3.3 Hz, H-3′), 5.63 (d, 1H, H-4′), 5.43 (d, 1H, $J_{1',2'}$ = 3.6 Hz, H-1′), 5.37 (dd, 1H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 3.3 Hz, H-3), 5.32–5.31 (d, 2H, $J_{1,2}$ = 3.6 Hz, H-1, 4), 4.77 (q, 2H, benzylmethelene), 4.59–4.56 (m, 1H, H-5′), 4.26 (dd, 1H, H-2′), 4.20 (q, 2H, OCH_2CCl_3), 4.18 (dd, 1H, H-2), 2.15, 2.03 (each s, 6H, 2 Ac), 1.18 (d, 1H, H-6′), 1.14 (d, 1H, H-6). ^{13}C NMR (150 MHz, CD_3COCD_3):δ 170.9, 170.3, 170.0, 166.5, 165.9, 139.1, 134.2, 133.9, 130.8, 130.3, 130.2, 129.5, 129.2, 129.1, 128.9, 128.5, 99.0 (C-1), 98.9 (C-1′), 97.3, 81.0, 74.8, 74.4, 73.5, 73.3, 72.0, 71.6, 70.0, 66.4, 66.2, 20.9, 20.5, 16.3, 16.1.

4.43. 3,4-Di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4-di-*O*-acetyl-α-L-fucopyranosyl trichloroacetimidate (54)

A mixture of **53** (1.75 g, 0.13 mmol) and zinc powder (1.50 g) in AcOH (15.0 mL) was stirred for 18 h at 55 °C. After completion of the reaction, the mixture was filtered and the filtrate was diluted with toluene and concentrated to give the intermediate. To a solution of the residue in CH_2Cl_2 (5.0 mL) cooled at –20 °C were added DBU (120 μL, 0.822 mmol) and CCl_3CN (280 μL, 2.74 mmol). The reaction mixture was stirred for 5 h at −20 °C. After completion of the reaction, the mixture was concentrated. The residue was purified by silica gel column chromatography using chloroform to give **54** (350 mg, 77%). $[\alpha]_D$ −117.2 (*c* 3.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 8.52 (s, 1H, C(N*H*)CCl_3), 7.94–7.22 (m, 15H, 3 Ph), 6.56 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 5.63 (dd, 1H, $J_{2',3'}$ = 10.4 Hz, $J_{3',4'}$ = 3.3 Hz, H-3′), 5.59 (d, 1H, H-4′), 5.45–5.43 (m, 2H, H-3, 4), 5.06 (d, 1H, $J_{1',2'}$ = 3.5 Hz, H-1′), 4.58 (d, 2H, benzylmethelene), 4.42 (br dd, 1H, H-5′), 4.37 (br dd, 1H, H-5), 4.22 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-2), 4.07 (dd, 1H, H-2′), 2.19, 2.07 (each s, 6H, 2 Ac), 1.19 (d, 1H, H-6′), 1.17 (d, 1H, H-6). ^{13}C NMR (150 MHz, $CDCl_3$):δ 170.3, 169.8, 165.8, 165.3, 161.0, 137.8, 133.2, 132.9, 129.7, 129.6, 129.5, 128.4, 128.3, 128.2, 128.0, 127.8, 98.6 (C-1′), 94.3 (C-1), 73.1, 73.0, 72.8, 72.2, 70.9, 70.8, 70.6, 69.4, 67.3, 65.6, 60.3, 30.9, 21.0, 20.8, 20.6, 15.99, 15.95, −0.04.

4.44. 2,2,2-Trichloroethyl 3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4-di-*O*-acetyl-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranoside (55)

Compound **55** was prepared from **51** (151 mg, 0.18 mmol) and **54** (122 mg, 0.36 mmol) as described for preparation of **15**. The product was purified by silica gel column chromatography (2:1 hexane–ethyl acetate) to give **55** (141 mg, 80%). $[\alpha]_D$ −157.2 (*c* 1.8, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 5.21 (d, 1H, $J_{1',2'}$ = 3.3 Hz, H-1′), 5.16 (d, 1H, $J_{1,2}$ = 3.0 Hz, H-1), 5.05 (d, 1H, $J_{1'',2''}$ = 3.6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$):δ 170.4, 169.9, 165.7, 165.2, 137.4, 133.2, 132.9, 129.7, 129.6, 129.5, 128.5, 128.4, 128.2, 128.1, 128.04, 127.99, 108.7, 98.7 (C-1″), 98.0 (C-1), 97.8 (C-1′), 96.5, 80.4, 76.6, 76.0, 74.6, 74.5, 73.1, 72.3, 71.9, 70.6, 69.2, 65.5, 64.9, 64.6, 28.3, 26.3, 20.9, 20.6, 16.2, 15.98, 15.95, 15.7.

4.45. 2,2,2-Trichloroethyl 3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4-di-*O*-acetyl-α-L-fucopyranosyl-(1→2)-3,4-di-*O*-acetyl-α-L-fucopyranoside (56)

Compound **56** was prepared from **55** (131 mg, 0.17 mmol) as described for preparation of **53**. The product was purified by silica gel column chromatography (3:1 hexane–ethyl acetate) to give **56** (98.4 mg, 63%). $[\alpha]_D$ −138.2 (*c* 2.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 5.50 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 5.05 (d, 1H, $J_{1',2'}$ = 3.3 Hz, H-1′), 4.89 (d, 1H, $J_{1'',2''}$ = 3.6 Hz, H-1″). ^{13}C NMR (150 MHz, $CDCl_3$):δ 170.4, 170.3, 170.0, 169.6, 165.7, 165.2, 137.8, 137.4, 133.3, 133.0, 129.71, 129.6, 129.6, 129.0, 128.6, 128.5, 128.3, 128.23, 128.19, 128.16, 125.2, 99.5 (C-1′), 98.8 (C-1″), 98.7 (C-1), 96.4, 80.1, 76.0, 74.6, 73.2, 72.5, 72.4, 71.63, 71.56, 70.6, 69.8, 69.0, 65.7, 65.6, 65.2, 29.7, 21.4, 21.0, 20.8, 20.6, 20.5, 16.0, 15.8, 15.7.

4.46. 3,4-Di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4-di-*O*-acetyl-α-L-fucopyranosyl-(1→2)-3,4-di-*O*-acetyl-α-L-fucopyranosyl trichloroacetimidate (57)

Compound **57** was prepared from **56** (151 mg, 0.18 mmol) as described for preparation of **54**. The product was purified by silica gel column chromatography (chloroform) to give **57** (75.8 mg, 76%). $[\alpha]_D$ −156.3 (*c* 1.9, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 8.60 (s, 1H, C(N*H*)CCl_3), 6.61 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 5.06 (d, 1H, $J_{1',2'}$ = 3.5 Hz, H-1′). 4.96 (d, 1H, $J_{1'',2''}$ = 3.6 Hz, H-1″).

4.47. 2-(Trimethylsilyl)ethyl 3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)-[3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4-di-*O*-acetyl-α-L-fucopyranosyl-(1→3)]-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloro-ethoxycarbonylamino)-β-D-glucopyranoside (58)

Compound **58** was prepared from **49** (83.3 mg, 59.1 μmol) and **54** (59.4 mg, 70.9 μmol) as described for preparation of **15**. The product was purified by silica gel column chromatography (5:2 hexane–ethyl acetate) to give **58** (82.7 mg, 67%). $[\alpha]_D$ −101.4 (*c* 2.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 5.37 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1 of Fuc a), 5.16 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1 of Fuc c), 5.12 (d, 1H, $J_{1,2}$ = 3.0 Hz, H-1 of Fuc b), 4.65 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1 of GlcN). ^{13}C NMR (150 MHz, $CDCl_3$):δ 99.9 (C-1 of GlcN), 99.7 (C-1 of Fuc b), 98.5 (C-1 of GalN), 98.2 (C-1 of Fuc c), 96.7 (C-1 of Fuc a). MALDI-TOFMS: calcd for $C_{101}H_{110}Cl_6N_2O_{31}SiNa$: *m/z* 2108; found: *m/z* 2108 $[M+Na]^+$.

4.48. 2-(Trimethylsilyl)ethyl 3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)-[3,4-di-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4-di-*O*-acetyl-α-L-fucopyranosyl-(1→2)-3,4-di-*O*-acetyl-α-L-fucopyranosyl-(1→3)]-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (59)

Compound **59** was prepared from **49** (46.5 mg, 33.0 μmol) and **57** (82.7 mg, 39.6 μmol) as described for preparation of **15**. The product was purified by silica gel column chromatography (5:2 hexane–ethyl acetate) to give **59** (32.9 mg, 43%). $[\alpha]_D$ −101.4 (*c* 2.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 5.37 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1 of Fuc a), 5.20 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1 of Fuc d), 5.15 (d, 1H, $J_{1,2}$ = 3.0 Hz, H-1 of Fuc b), 5.12 (d, 1H, $J_{1,2}$ = 3.0 Hz, H-1 of Fuc c), 4.65 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1 of GlcN). ^{13}C NMR (150 MHz, $CDCl_3$):δ 99.9 (C-1 of GlcN), 99.7 (C-1 of Fuc b), 98.6 (C-1 of GalN), 98.2 (C-1 of Fuc c, d), 96.5 (C-1 of Fuc a). MALDI-TOFMS: calcd for $C_{111}H_{124}Cl_6N_2O_{37}SiNa$: *m/z* 2337.6; found: *m/z* 2337.1 $[M+Na]^+$.

4.49. 2-(Trimethylsilyl)ethyl α-L-fucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→2)-α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-gluco-pyranoside (8)

Compound **8** was prepared from **58** (57.6 mg, 27.6 μmol) as described for preparation of **4**. The product was purified by silica gel column chromatography on Iatrobeads (2:1 chloroform–methanol) to give **8** (8.5 mg, 32%). ^1H NMR (600 MHz, CD_3OD) δ 5.29 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1 of Fuc a), 4.91 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1 of Fuc c), 4.90 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1 of Fuc b), 4.60 (d, 1H, $J_{1,2}$ = 8.5 Hz,

H-1 of GalN), 4.48 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1 of GlcN). HR-FABMS: calcd for $C_{39}H_{70}N_2O_{23}SiNa$: *m/z* 985.4036; found: *m/z* 985.4062 $[M+Na]^+$.

4.50. 2-(Trimethylsilyl)ethyl α-L-fucopyranosyl-(1→3)-2-acetamido-β-D-galacto-pyranosyl-(1→4)-[α-L-fucopyranosyl-(1→2)-α-L-fucopyranosyl-(1→2)-α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranoside (9)

Compound **9** was prepared from **59** (32.9 mg, 14.2 μmol) as described for preparation of **4**. The product was purified by silica gel column chromatography on Iatrobeads (2:1 chloroform–methanol) to give **9** (5.0 mg, 35%). $[\alpha]_D$ −76.2 (*c* 0.06, MeOH). ^1H NMR (600 MHz, CD_3OD) δ 5.28 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1 of Fuc a), 4.92 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1 of Fuc d), 4.90 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1 of Fuc c), 4.88 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1 of Fuc b), 4.60 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1 of GalN), 4.50 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1 of GlcN). HR-FABMS: calcd for $C_{45}H_{80}N_2O_{27}SiNa$: *m/z* 1131.4615; found: *m/z* 1131.4631 $[M+Na]^+$.

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Supplementary data

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References

1. Pearce, E. J.; MacDonald, A. S. *Nat. Rev. Immunol* **2002**, *2*, 499–511.
2. Nyame, A. K.; Kawar, Z. S.; Cummings, R. D. *Arch. Biochem. Biophys.* **2004**, *426*, 182–200.
3. Kamerling, J. K. In *Comprehensive Glycoscience*; Elsevier: New York, 2007; Vol. 4, 473–492.
4. Nash, T. E.; Lunnde, M. N.; Cheever, A. W. *J. Immunol.* **1981**, *126*, 805–810.
5. (a) Hokke, C. H.; Yazdnbakhsh, M. *Parasite Immunol.* **2005**, *27*, 257–264; (b) Harnett, W. *Parasite Immunol.* **2005**, *27*, 357–359; (a) Hokke, C. H.; Deelder, A. M. *Glycoconjugate J.* **2001**, *18*, 573–587; (b) Dell, A.; Haslam, S. M.; Morris, H. R.; Khoo, K. H. *Biochim. Biophys. Acta* **1999**, *1455*, 353–362; (c) Cummings, R. D.; Nyame, A. K. *Biochim. Biophys. Acta* **1999**, *1455*, 363–374; (d) Khoo, K. H. *Trends Glycosci. Glycotech.* **2001**, *13*, 493–506.
6. (a) Nyame, A. K.; Cummings, R. D.; Damian, R. T. *Mol. Biochem. Parasitol.* **1988**, *28*, 265–274; (b) Nyame, A. K.; Smith, D. F.; Damian, R. T.; Cummings, R. D. *J. Biol. Chem.* **1989**, *264*, 3235–3243; (c) Srivatsan, J.; Smith, D. F.; Cummings, R. D. *Glycobiology* **1992**, *2*, 445–452.
7. Hung, H. H.; Tsai, P. L.; Khoo, K. H. *Glycobiology* **2001**, *11*, 395–406.
8. (a) Wuhrer, M.; Kantelhardt, S. R.; Dennis, R. D.; Doenhoff, M. J.; Lochnit, G.; Geyer, R. *Glycobiology* **2000**, *10*, 89–101; (b) Wuhrer, M.; Kantelhardt, S. R.; Dennis, R. D.; Doenhoff, M. J.; Lochnit, G.; Geyer, R. *Eur. J. Biochem.* **2000**, *269*, 481–493.
9. Makaaru, C. K.; Damian, R. T.; Cummings, R. D. *J. Biol. Chem.* **1992**, *267*, 2251–2257.
10. (a) Hada, N.; Hayashi, E.; Takeda, T. *Carbohydr. Res.* **1999**, *316*, 58–70; (b) Ohtsuka, I.; Hada, N.; Ohtaka, H.; Sugita, M.; Takeda, T. *Chem. Pharm. Bull.* **2002**, *50*, 600–604; (c) Yamamura, T.; Hada, N.; Kaburaki, A.; Yamano, K.; Takeda, T. *Carbohydr. Res.* **2004**, *339*, 2749–2759; (d) Yamano, K.; Hada, N.; Yamamura, T.; Takeda, T.; Honma, H.; Sawada, Y. *J. Helminthol.* **2006**, *80*, 387–391; (e) Koizumi, A.; Hada, N.; Kaburaki, A.; Yamano, K.; Schweizer, F.; Takeda, T. *Carbohydr. Res.* **2009**, *344*, 856–868; (f) Koizumi, A.; Yamano, K.; Schweizer, F.; Takeda, T.; Kiuchi, F.; Hada, N. *Eur. J. Med. Chem.* **2011**, *46*, 1768–1778.
11. Kanaya, T.; Yagi, S.; Schweizer, F.; Takeda, T.; Kiuchi, F.; Hada, N. *Chem. Pharm. Bull.* **2010**, *58*, 811–817.
12. Komba, S.; Ishida, H.; Kiso, M.; Hasegawa, A. *Bioorg. Med. Chem.* **1996**, *4*, 1833–1847.
13. (a) Veeneman, G. H.; van Leeuwen, S. H.; van Boom, J. H. *Tetrahedron Lett.* **1990**, *31*, 1331–1334; (b) Konradsson, P.; Udodong, U. E.; Fraser-Reid, B. *Tetrahedron Lett.* **1990**, *31*, 4313–4316.
14. (a) Schmidt, R. R.; Kinzy, W. *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21–123; (b) Werz, D. B.; Schuster, H. J.; Tietze, L. F. *Synlett* **2008**, 1969–1972.
15. Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 212–235.
16. Zhu, X.; Pachamuthu, K.; Schmidt, R. R. *Org. Lett.* **2004**, *6*, 1083–1085.
17. Schmidt, R. R.; Grundler, G. *Synthesis* **1981**, 885–887.
18. Xia, C.; Yao, Q.; Schümann, J.; Rossy, E.; Chen, W.; Zhu, L.; Zhang, W.; De Libero, G.; Wang, P. G. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 2195–2199.
19. Ellervik, U.; Magnusson, G. *J. Org. Chem.* **1998**, *63*, 9314–9322.
20. Benakli, K.; Zha, C.; Kerns, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 9461–9462.
21. Hada, N.; Nakashima, T.; Shrestha, S. P.; Masui, R.; Narukawa, Y.; Tani, K.; Takeda, T. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 5912–5915.
22. Niu, Y.; Wang, N.; Cao, X.; Ye, X.-S. *Synlett* **2007**, 2116–2120.