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Synthetic studies on the carbohydrate moiety of the antigen from the parasite *Echinococcus multilocularis*

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ABSTRACT

Stereocontrolled syntheses of branched tri-, tetra-, and pentasaccharides displaying a Galβ1→3GalNAc core in the glycan portion of the glycoprotein antigen from the parasite *Echinococcus multilocularis* have been accomplished. Trisaccharide Galβ1→3(GlcNAcβ1→6)GalNAcα1-OR (**A**), tetrasaccharide Galβ1→3(Galβ1→4GlcNAcβ1→6)GalNAcα1-OR (**D**), and pentasaccharides Galβ1→3(Galβ1→4Galβ1→4GlcNAcβ1→6)GalNAcα1-OR (**E**) and Galβ1→3(Galα1→4Galβ1→4GlcNAcβ1→6)GalNAcα1-OR (**F**) (R = 2-(trimethylsilyl)ethyl) were synthesized by block synthesis. The disaccharide 2-(trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-2-azido-4-*O*-benzyl-2-deoxy-α-D-galactopyranoside served as a common glycosyl acceptor in the synthesis of the branched oligosaccharides. Moreover, linear trisaccharide Galβ1→4Galβ1→3GalNAcα1-OR (**B**) and branched tetrasaccharide Galβ1→4Galβ1→3(GlcNAcβ1→6)GalNAcα1-OR (**C**) were synthesized by stepwise condensation.

1. Introduction

Infection by parasitic protozoans and helminthes constitutes a serious health problem all over the world, but no vaccines exist against major human parasitic diseases such as malaria, African trypanosomiasis, leishmaniasis, schistosomiasis, and alveolar echinococcosis.[1] Recent studies on a number of parasites revealed that immune responses to parasites in infected animals and humans are directed toward glycoconjugate glycan determinants on the cell surface where they play important roles in host–parasite interactions.[2] Moreover, evidence is mounting that carbohydrate antigens, rather than protein antigens, dominate the immune responses to many helminthic parasites.[3] Because of the prospect of developing conjugate vaccines and new diagnostics for parasite infections, parasite-derived glycans are compelling vaccine targets. In this context it is of particular interest that the glycan portion of parasite-derived glycoprotein-based antigens commonly possesses unique glycan sequences and sorts that distinguish them from mammalian glycans.[2a] Parasitic helminthes are divided into three major groups: the cestodes (tapeworms) I; the nematodes (roundworms) II; and the trematodes (flukes) III. Among the major parasites it has been shown that the extracellular matrixes of cestode *Spirometra erinacei* (I), the nematode *Ascaris suum* (II), and the trematode *Fasciola* sp (III) contain glycolipids, while those of the nematodes *Dirofilaria immitis* (II) and *Toxocara* sp. (II) contain glycoproteins. In contrast, glycolipids and glycoproteins were identified in the extracellular matrix of cestode *Echinococcus* sp. (I) and nematode *Caenorhabditis elegans* (II).[2a] Glycosphingolipids found in mammals are classified into different types on the basis of their basic carbohydrate structure; these types include the globo, lacto, ganglio, neolacto, and isoglobo series.[4] However, to the best of our knowledge, the carbohydrate structure of parasitic helminth including schisto, arthro, spirometo, and neogala series represents a different type of glycolipid core structure.[5] Due to these differences in the glycan structure, we have been interested in the relationships between the structure and biological activity of glycolipids from invertebrate species and have synthesized oligosaccharides from various helminths.[6] Recently, we have developed a strong interest in the structure and synthesis of glycosphingolipids from *Echinococcus multilocularis*. *E. multilocularis* is a parasite, which belongs to the class cestoda of the Phylum Platyhelminthes and causes alveolar echinococcosis (AE), a severe disease that can be fatal in the absence of efficient treatment. AE is endemic in the Alps and in Hokkaido (Japan), and it is known as a severe parasitic zoonosis caused by ingestion of the parasite's eggs. The adult parasites mainly reside in the intestine of the red fox, *Vulpes vulpes schrencki,* where they produce eggs. These eggs are released in feces and are usually ingested by rodents, the intermediate hosts of the parasite, or accidentally by humans. However,

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no perfect antigen exists for the serological detection of patients with echinococcosis. Persat et al. reported[7] in 1991 that sera from AE patients recognized a neutral glycosphingolipid fraction extracted from metacestodes of *E. multilocularis*. Structure determination of this glycosphingolipid fraction revealed that it belonged to the neogala series (Galβ1→6Gal). In addition, it was further shown that neogala-based glycosphingolipids show significant serodiagnostic potential in differentiating alveolar echinococcosis from cystic echinococcosis (CE).[8] Based on this information, we previously synthesized four kinds of glycosphingolipids [Galβ1→6(Fucα1→3)Galβ1→6Galβ1→6] and their precursors,[6a,6b] and described their serodiagnostic potential.[9]

Attachment of carbohydrates to protein occurs via three major types of linkages: (a) an N-glycosidic linkage between the reducing terminal sugar and the amide group of asparagines (N-glycans) (b) O-glycosidic linkage between the sugar and the hydroxyl group of an amino acid, most commonly serine and threonine (O-glycans), and (c) via ethanolamine phosphate groups between the C-terminal residue of the protein and an oligosaccharide attached to phosphatidylinositiol (GPI anchor). O-Glycans often possess characteristic cores, the most frequent of which are core-I type [Galβ1→3GalNAc] and core-II type [Galβ1→3(GlcNAcβ1→6)GalNAc]. Köhler and co-workers recently isolated novel mucin-type glycoforms from the metacestode of *E. multilocularis*.[10] These glycoforms contained mucin-type core-I type and core-II type structures that were further diversified by addition of GlcNAc or Gal residues. Although several approaches to core-II type structures have been reported,[11] none of them is suitable for conjugation to lipids and proteins. We report here on the synthesis of the glycan portions of the glycoprotein antigen of *E. multilocularis* in order to elucidate the interactions between oligosaccharides and sera of AE by enzyme-linked immunosorbent assay (ELISA).

2. Results and discussion

The exact anomeric linkages of the carbohydrate sequence of the glycoforms derived from *E. multilocularis* are currently unknown. Previous studies have indicated that the *E. multilocularis* antigen contains mucin-type core-I type [Galβ1→3GalNAc] and core-II type [Galβ1→3(GlcNAcβ1→6)GalNAc] and branched core-I and core-II structures attached to both serine and threonine. Although α-anomeric linkages in cores I and II cannot be ruled out, it was suggested that the β-linkage is more likely.[12] Based on this information we were interested in developing an approach that would permit the synthesis of the branched oligosaccharides **A**, **C**, **D**, **E**, and **F** exhibiting core-I and core-II structures and of the linear oligosaccharide **B** with only a core-I structure. Branched oligosaccharides **A**, **C**, and **D** differ in the number of sugar residues attached to core-II, while pentasaccharides **E** and **F** vary at the anomeric linkage of the terminal Gal residue (Fig. 1). The presence of oligosaccharide sequences **A**–**F** in *E. multilocularis* glycoprotein antigen was previously suggested on the basis of mass spectrometric O-glycan profiling and sequencing.[10]

In order to study the structure–activity relationships of the carbohydrate moiety in the antigenic glycoprotein, access to oligosaccharide sequences **A**–**F** is required. In particular, we were interested in developing a block synthesis approach that would enable the synthesis of oligosaccharides **A** and **C**–**F** from common suitably protected di- and trisaccharide acceptors and various mono-, di-, and trisaccharide donors. Due to the fact that the nature of the O-glycosidic linkage of the oligosaccharides to the polypeptide is unknown, a synthetic approach giving access to both α- and β-glycosidic linkages was selected. This was realized by preparing oligosaccharide analogs bearing a non-participating azido group at C-2 in the GalNAc portion. The temporary 2-(trimethylsilyl)ethyl-[13] protecting group was chosen to ensure future conjugation to proteins, lipids, and other macromolecular devices. Trisaccharides **A** and tetrasaccharide **D** have been previously prepared;[11b,11e] however, oligosaccharides **B**, **C**, **E**, and **F** are novel compounds.

2.1. Syntheses of compounds A, D, E, and F

The synthetic strategy for the synthesis of oligosaccharides is shown in Scheme 1. The disaccharide, 2-(trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-2-azido-4-*O*-benzyl-2-deoxy-β-D-galactopyranoside (**6**) was chosen as the acceptor, while suitably protected mono-, di-, and trisaccharide-based thioglycosides (**8**, **13**, **22**, and **28**) were selected as glycosyl donors.

2.1.1. Synthesis of trisaccharide A

The preparation of disaccharide acceptor **6** is shown in Scheme 2. Compound **2** was obtained by in situ conversion of glycosylnitrate **1**[14] into the glycosyl iodide, followed by coupling to 2-(trimethylsilyl)ethanol using a combination of tetrabutylammonium iodide (TBAI) and iodine (I_2) as activator. Activation of the glycosyl iodide using only TBAI[15] or iodine[16] resulted in lower yields and reduced α-stereoselectivity. Zemplén deacetylation, followed by protection of the 4- and 6-hydroxy group as the benzylidine acetal, provided an anomeric mixture of **3a–b** (α:β ratio 3:1) that was separable into the α- and β-glycosides at this stage. Glycosylation[17] of **3a** with the imidate donor **4**[18] was carried out in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and AW-300 molecular sieves in CH_2Cl_2 to afford the desired β-glycoside **5** in 90% yield. Reductive ring opening of the benzylidene acetal **5** was achieved by treatment with dichlorophenylborane ($PhBCl_2$) and triethylsilane (Et_3SiH) in CH_2Cl_2[19] to produce disaccharide acceptor **6** as a single regioisomer in 73% yield.

Initially, we studied the preparation of the type-II trisaccharide motif by regioselective glycosylation of acceptor 2-(trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-2-azido-2-deoxy-α-D-galactopyranoside with slight excess of thioglycoside donors (data not shown). This, however, resulted in the formation of regioisomeric mixtures. As a result, we employed acceptor **6** for further studies.

In order to complete the synthesis of trisaccharide **A**, we originally studied the glycosylation of acceptor **6** with phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside donor using *N*-iodosuccinimide (NIS)–trifluoromethanesulfonic acid (TfOH)[20] as promoter. However, this resulted in poor yields (26%) of the corresponding trisaccharide. Significantly improved yields were obtained by replacement of the bulky phthaloyl group by 2-trichloroethoxycarbonyl (Troc). Donor **8** was prepared from common compound **7**[21] using standard Lewis acid-catalyzed conditions. Glycosylation of donor **8** with acceptor **6** was achieved in the presence of NIS and TfOH to afford trisaccharide **9** in 47% yield. Subsequently, the azido group and Troc group were converted to an acetamido moiety by reduction with Zn–AcOH, followed by debenzylation and catalytic hydrogenolysis over 10% Pd/C in MeOH and acetylation to yield **10** in 37% yield. Finally, Zemplén-based deacetylation and column chromatography on Sephadex LH-20 furnished target trisaccharide **A** (Scheme 3).

2.1.2. Synthesis of tetrasaccharide D

The synthesis of tetrasaccharide **D** containing core-II type structure was achieved by glycosylation of disaccharide donor **13** with previously prepared acceptor **6** (Scheme 4). Disaccharide donor **13** was prepared from **8** in a five-step process. At first, compound **8** was deacetylated, protected as 4,6-benzylidene, and benzoylated to provide compound **11** in 65% yield. Regioselective acid-catalyzed reductive ring opening of the benzylidene acetal using

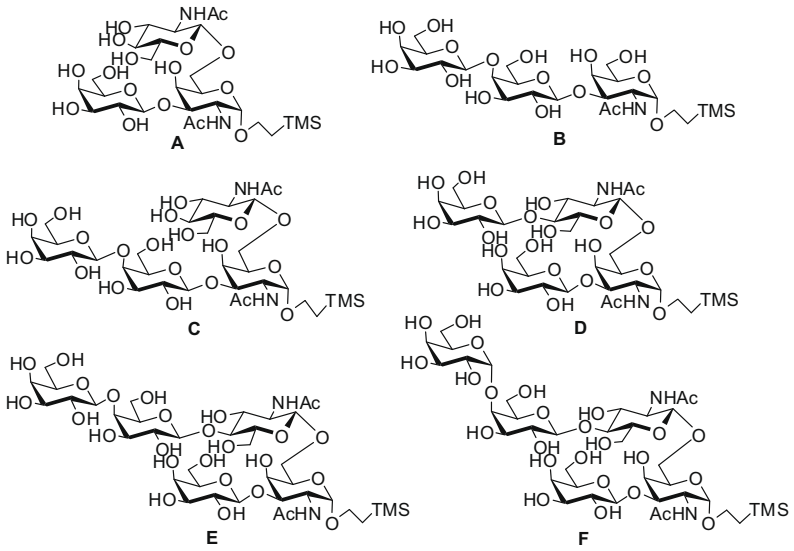
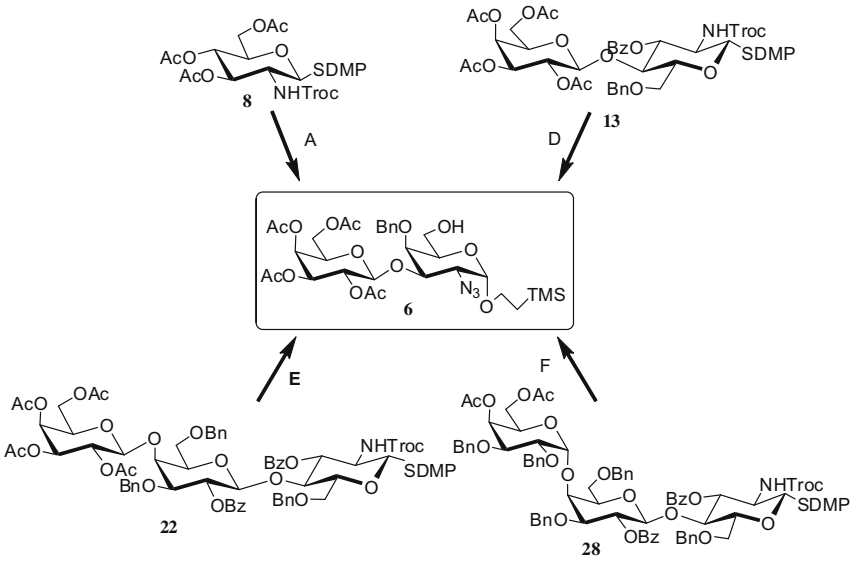
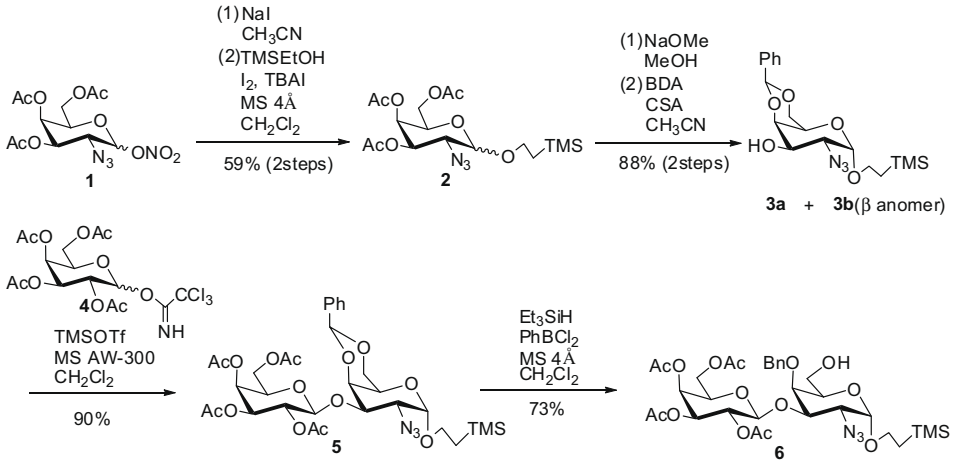


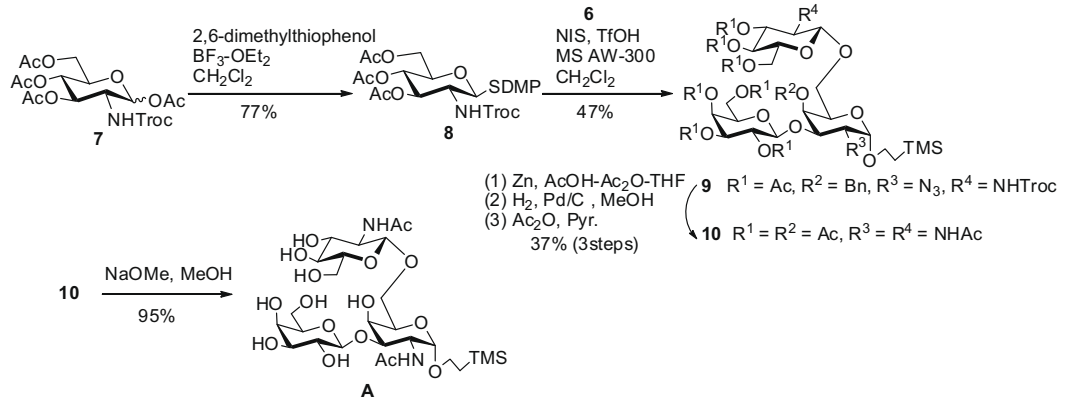
Figure 1. Structure of the target oligosaccharide derivatives, A–F from the parasite *Echinococcus multilocularis*.



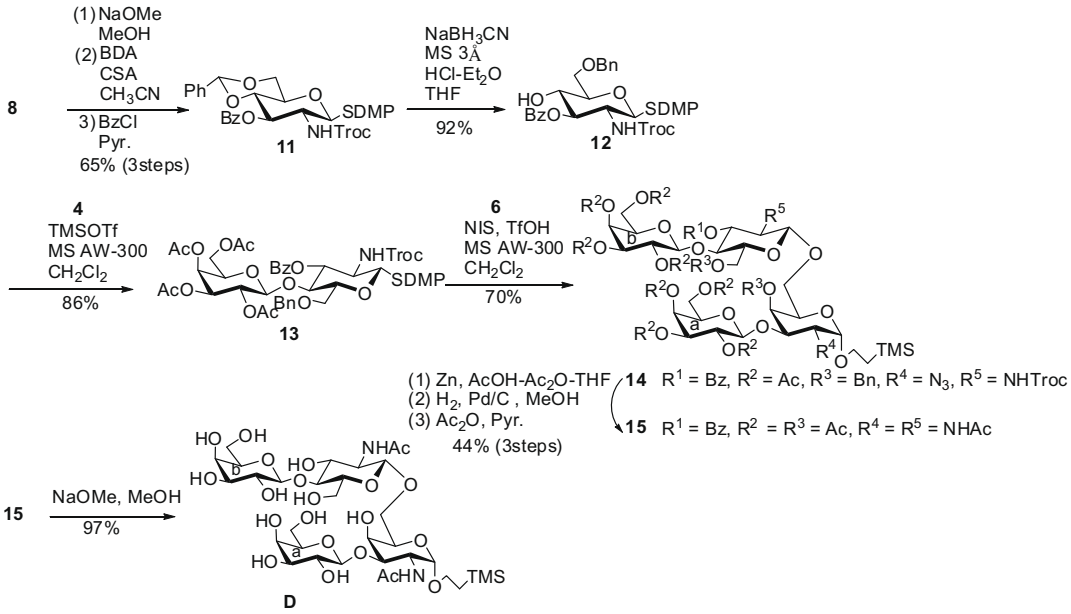
Scheme 1. Synthetic plan of the target oligosaccharides, A, D, E, and F.



Scheme 2. Preparation of disaccharide acceptor.



Scheme 3. Synthesis of trisaccharide A.

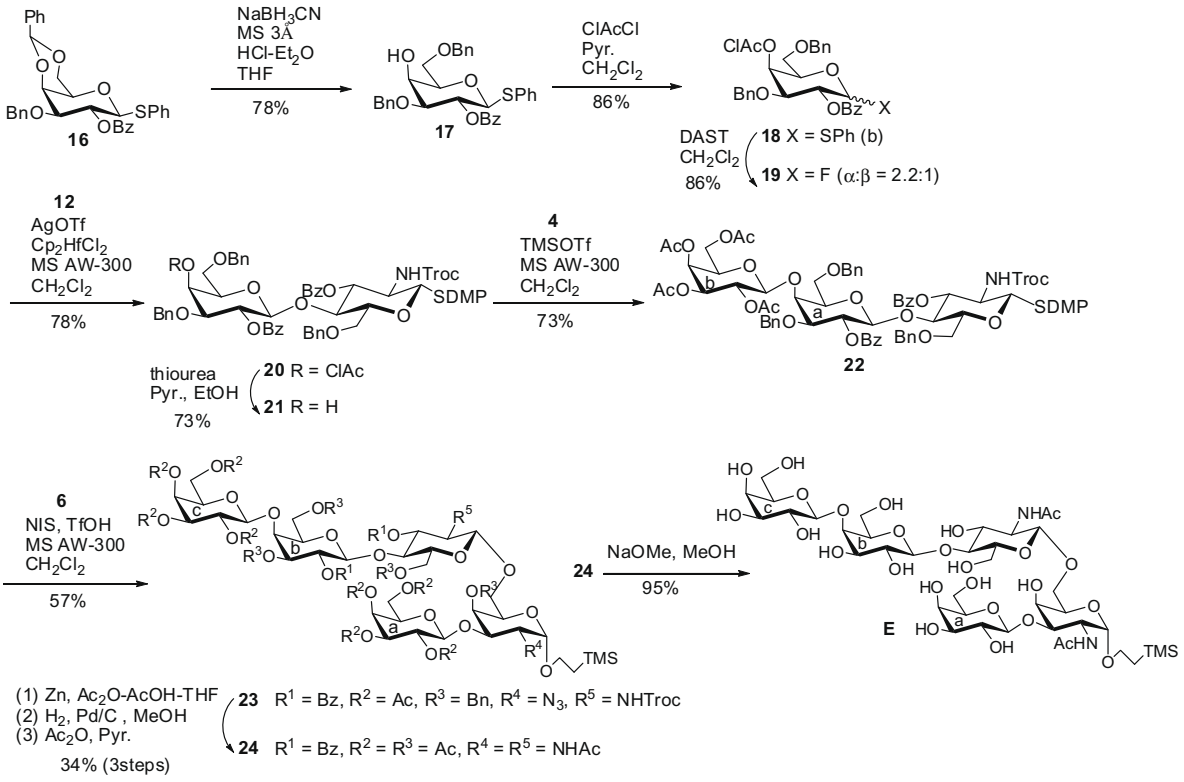


Scheme 4. Synthesis of tetrasaccharide D.

sodium cyanoborohydride in acidified ether afforded acceptor **12** in excellent yield (92%). Finally TMSOTf-catalyzed glycosylation of **12** with imidate donor **4** in the presence of AW-300 MS in CH_2Cl_2 produced the desired disaccharide **13** as the sole product in 86% yield. The β-glycosidic linkage was assigned on the basis of homonuclear coupling constants (H-1′, δ 4.49, $J_{H1',H2'}$ 7.9 Hz). With disaccharide donor **13** in hand, we then studied the glycosylation of donor **13** with acceptor **6**. We were pleased to see that NIS–TfOH-promoted glycosylation of **13** with **6** in the presence of AW-300 MS in CH_2Cl_2 afforded the desired tetrasaccharide **14** in 70% yield. The nature of the new glycosidic linkage was determined by measurements of the homonuclear coupling constants (H-1 of GlcNAc, δ 4.60, $J_{H1,H2}$ 7.9 Hz). Removal of the Troc-protecting group using Zn in a mixture containing Ac_2O and HOAc, followed by catalytic hydrogenation over 10% Pd–C in MeOH, and acetylation provided **15**. Finally, deacylation of **15** with NaOMe in MeOH afforded the desired target tetrasaccharide **D** in 97% yield (Scheme 4).

2.1.3. Synthesis of pentasaccharide E

Branched pentasaccharide **E** was synthesized by glycosylation of thioglycoside donor **22** with acceptor **6** (Scheme 5). The synthesis of trisaccharide **22** started from known phenylthio galactopyranoside **16**.[22] Regioselective reductive ring opening of the benzylidene acetal provided **17** in 78% yield, which was chloroacetylated by exposure to chloroacetyl chloride in pyridine to produce **18**. Thioglycoside **18** was converted to glycosyl fluoride **19** using *N*,*N*-diethylaminosulfur trifluoride[23] in CH_2Cl_2. Donor **19** was coupled to monosaccharide acceptor **12** by activation with AgOTf and Cp_2HfCl_2[24] to afford disaccharide **20** in 78% yield. Selective removal of the chloroacetyl group in **20** was achieved by treatment with thiourea in a solvent mixture containing pyridine and ethanol[25] to produce acceptor **21** in 73% yield. Accepor **21** served as precursor to prepare trisaccharide donor **22**. This was achieved by TMSOTf-promoted activation of imidate donor **4** and coupling to **21** to provide desired trisaccharide donor **22** in 73% yield. With donor **22** in hand we then studied the formation of pentasaccharide **E**. NIS–TfOH-promoted activation of donor **22** and coupling to disaccharide acceptor **6** afforded the desired β-glycoside **23** in 57% yield. Deprotection was performed as previously described for compound **D**. That is, sequential de(trichloroethoxycarbonyl)ation and N-acetylation, followed by debenzylation and O-acetylation, provided pentasaccharide **24** in 34% yield. Finally, Zemplén-based deacetylation



Scheme 5. Synthesis of pentasaccharide E.

and column chromatography on Sephadex LH-20 furnished target pentasaccharide **E** in 95% yield (Scheme 5).

2.1.4. Synthesis of pentasaccharide F

The synthesis of branched pentasaccharide **F** required access to trisaccharide donor **28** containing a Galα1→4Galβ1→4GlcNAc sequence. In order to prepare the Galα1→4Gal sequence with high α-stereoselectivity, we selected 4,6-*O*-di-*tert*-butylsilylene (DTBS)-protected galactose donor **26**. Previous studies have indicated that DTBS-protected galactose donors induce high α-selectivity in glycosylation reactions.[26] Donor **26** was prepared from known phenylthioglycoside donor **25**[27] by exposure to DAST and *N*-bromosuccinimide (NBS)[28] at −20 °C to form glycosyl fluoride **26** in 78% yield. Coupling of glycosyl fluoride **26** to previously prepared disaccharide acceptor **21** was achieved by activation with AgOTf–Cp_2HfCl_2 to produce trisaccharide **27** with complete α-selectivity in excellent yield (91%). The α-interglycosidic linkage in **27** was confirmed by ^{1}H NMR spectroscopy. The anomeric proton of galactose moiety (b) appeared as a doublet with a homonuclear coupling constant of 3.1 Hz. Selective removal of the DTBS group in **27** was achieved with HF–pyridine, and subsequent acetylation with Ac_2O in pyridine provided **28** in 93% yield. NIS–TfOH-promoted glycosylation of donor **28** and coupling to acceptor **6** afforded pentasaccharide derivative **29** in 46% yield. Deblocking as described above for oligosaccharides **A** and **D** provided target pentasaccharide **F** (Scheme 6).

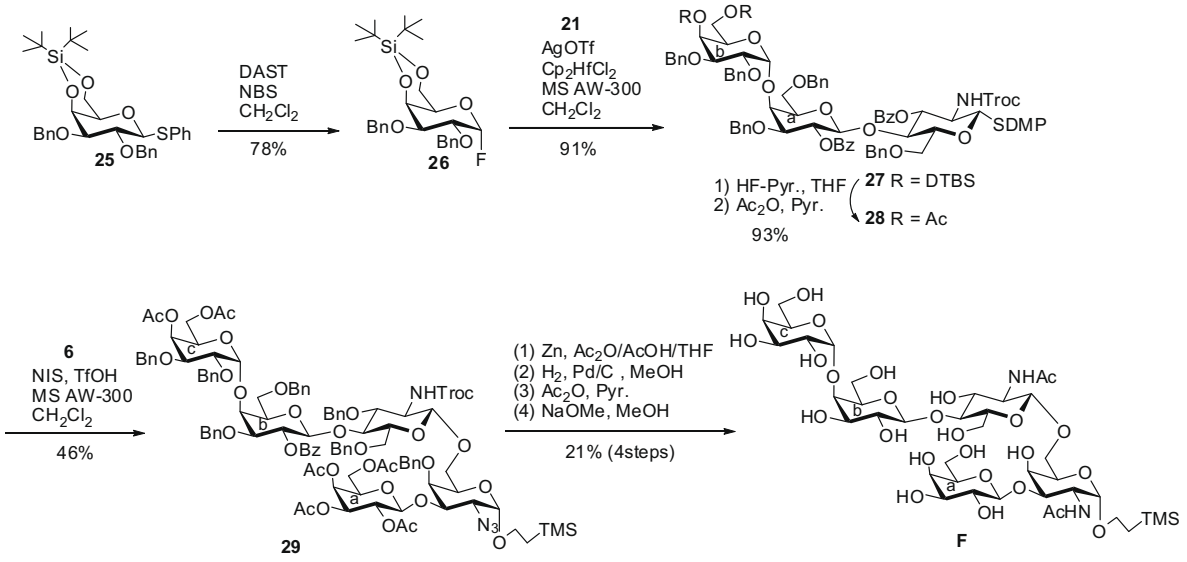
2.2. Syntheses of compounds B and C

Initial attempts to synthesize trisaccharide **B** by coupling of a disaccharide donor with acceptor **3a** failed because of the steric hindrance and low activities of the glycosyl donor. We therefore decided to prepare oligosaccharides **B** and **C** by stepwise condensation as outlined in Scheme 7. This required access to building blocks **4**, **18**, **3a**, and **8**. Both oligosaccharides **B** and **C** are derived from the common trisaccharide **32**.

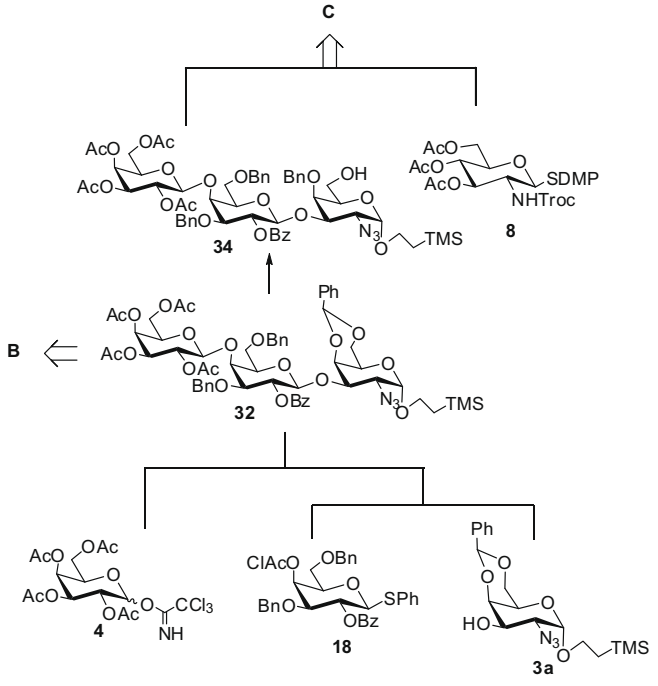
2.2.1. Synthesis of common intermediate 32 and conversion into trisaccharide B and tetrasaccharide C

Common intermediate **32** was synthesized by glycosylation of acceptor **3a** with donor **18** in the presence of NIS–TfOH to provide disaccharide **30** in 79% yield. The β-glycosidic linkage was confirmed by ^{1}H NMR spectroscopy. The anomeric proton of the newly formed interglycosidic linkage appeared as a doublet with a homonuclear coupling constant of 8.6 Hz (H-1′, δ 4.52, $J_{H1',H2'}$ 8.6 Hz). Selective removal of the chloroacetyl group in **30** with thiourea gave disaccharide acceptor **31**, which was used directly for the next glycosylation step. TMSOTf-promoted activation of imidate donor **4** and coupling to acceptor **31** generated trisaccharide **32** in 74% yield. The newly formed β-glycosidic linkage was confirmed by ^{1}H NMR spectroscopy. The anomeric proton of the galactose moiety in **32** appeared at δ 5.01 as a doublet with a homonuclear proton–proton coupling constant of 7.9 Hz (H-1 of Gal b, δ 5.01, $J_{H1b,H2b}$ 7.9 Hz). Catalytic hydrogenation followed by acetylation in pyridine produced trisaccharide **33** that was deblocked using sodium methoxide in methanol to produce target compound **B** in quantitative yield (Scheme 8).

To prepare the branched tetrasaccharide **C**, it was necessary to introduce the (1→6)-linked *N*-acetyl glucosamine moiety into trisaccharide **32**. In order to do so a reductive and regioselective ring opening of the benzylidene acetal group in **32** was necessary. This was achieved by exposure of **32** to Et_3SiH and $PhBCl_2$ in CH_2Cl_2 to afford trisaccharide acceptor **34**. Subsequently, acceptor **34** was glycosylated with thioglycoside donor **8** to generate protected tetrasaccharide **35** in 81% yield. Deblocking using reaction conditions that were the same as those described for oligosaccharides **A** and **D** afforded target tetrasaccharide **C** in 91% yield (Scheme 9).



Scheme 6. Synthesis of pentasaccharide F.



Scheme 7. Synthetic plan of the target oligosaccharides, B and C.

3. Conclusions

In summary, a systematic and integrated approach for the synthesis of six oligosaccharides **A**–**F** found in the metacestode of the parasite, *E. multilocularis* was developed. It is expected that these compounds will find use in future studies designed to reveal the relationships between the structure and biological activity for specific antibody detection in patients with alveolar echinococcosis.

4. Experimental

4.1. General methods

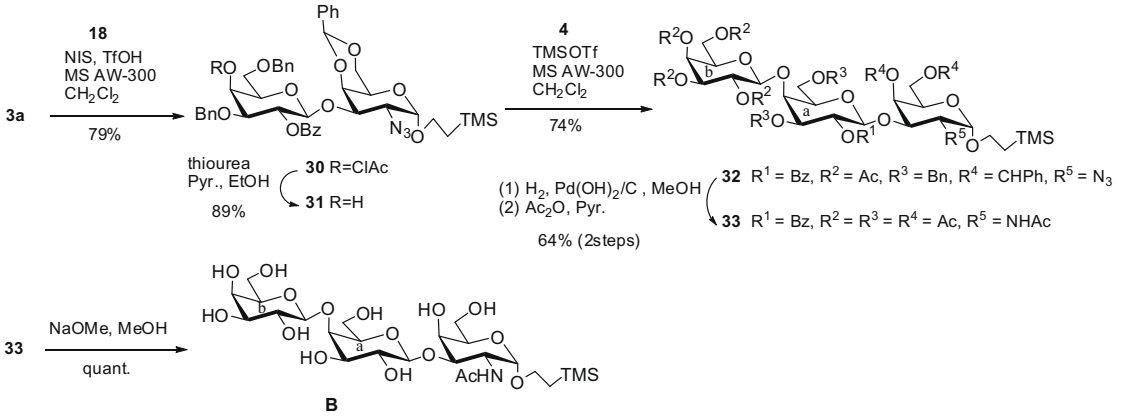
Optical rotations were measured with a Jasco P-1020 digital polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded with a JMN A500 FT NMR spectrometer with Me_4Si as the internal standard for solutions in $CDCl_3$. MALDI-TOFMS was recorded on a Perseptive Voyager RP mass spectrometer. High-resolution mass spectra were recorded on a JEOL JMS-700 under FAB conditions. TLC was performed on Silica Gel 60 F_{254} (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).

4.2. 2-(Trimethylsilyl)ethyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-D-galactopyranoside (2)

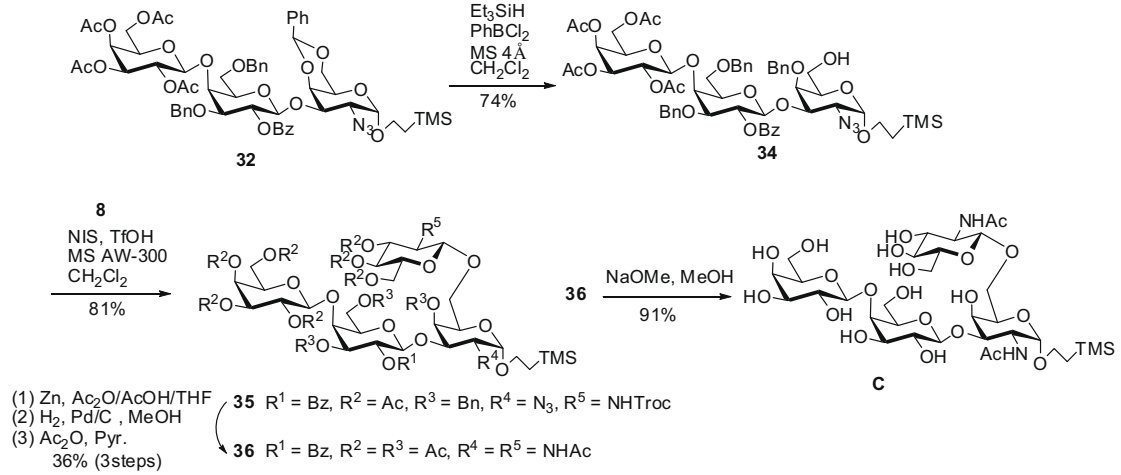
To a solution of **1** (1.00 g, 2.66 mmol) in CH_3CN (5.0 mL) was added NaI (2.78 g, 18.6 mmol). The reaction mixture was stirred for 1 h at room temperature, then extracted with Et_2O, washed with aq $Na_2S_2O_3$, dried ($MgSO_4$), and concentrated. To a solution of the residue in CH_2Cl_2 (5.0 mL) at room temperature were added 2-(trimethylsilyl)ethanol (TMSEtOH) (1.88 mL, 13.3 mmol), tetrabutylammonium iodide (TBAI) (196 mg, 0.53 mmol) and 4 Å MS (1.0 g). The reaction mixture was stirred under an atmosphere of argon for 2 h at room temperature, then iodine (I_2) (2.04 g, 7.98 mmol) was added and stirring was continued for 16 h. After that time, the reaction mixture was extracted with $CHCl_3$, washed with satd aq $Na_2S_2O_3$, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 6:1 hexane–AcOEt as eluent to give **2** (678 mg, 59%, two steps). MALDI-TOFMS: calcd for $C_{17}H_{29}N_3O_8$SiNa: ($[M+Na]^+$) 454.2, found 454.0.

4.3. 2-(Trimethylsilyl)ethyl 2-azido-4,6-*O*-benzylidene-2-deoxy-D-galactopyranoside (3)

To a solution of **2** (3.73 g, 8.64 mmol) in MeOH (40 mL) was added NaOMe (233 mg, 4.32 mmol), and the mixture was stirred for 30 min, and then neutralized with Amberlite IR 120 [H^+]. The mixture was filtered and concentrated. To a solution of the residue (2.64 g) in CH_3CN (5.0 mL) were added benzaldehyde dimethylacetal (2.58 mL, 17.3 mmol) and camphor-10-sulfonic acid (1.00 g, 4.32 mmol) at room temperature. The reaction mixture was stirred for 5 h, and then neutralized with Et_3N. After evaporation, column chromatography of the residue on silica gel (6:1→1:1 hexane–AcOEt) gave **3a** (2.25 g, 66%) and **3b**



Scheme 8. Synthesis of trisaccharide B.



Scheme 9. Synthesis of tetrasaccharide C.

(725 mg, 22%). Compound **3a** $[\alpha]_D^{24}$ +142 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.51–7.16 (m, 5H, Ar), 5.58 (s, 1H, PhCH), 5.03 (d, 1H, $J_{1,2}$ 3.1 Hz, H-1), 4.30–4.27 (m, 2H, H-4, H-6a), 4.18 (br, 1H, H-3), 4.10 (m, 1H, H-6b), 3.81 (m, 1H, Si$CH_2$$CH_2$), 3.76 (s, 1H, H-5), 3.63–3.57 (m, 2H, H-2, Si$CH_2$$CH_2$), 2.46 (br. d, 1H, OH), 1.08–0.93 (m, 2H, SiCH_2), 0.04 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR ($CDCl_3$): δ 137.4, 129.3, 128.3, 126.2, 101.3(Ph*C*H), 98.1(C-1), 75.6(C-4), 69.3(C-6), 67.7(C-3), 66.2(Si$CH_2$$CH_2$), 62.8(C-5), 60.8(C-2), 18.0(SiCH_2), −1.42(Si(CH_3)$_3$). HRFABMS: calcd for $C_{18}H_{28}NO_5Si$: ([M+H]$^+$) 394.1798, found 394.1765.

4.4. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranoside (5)

To a solution of **3a** (200 mg, 0.51 mmol) and **4** (376 mg, 0.77 mmol) in dry CH_2Cl_2 (2.0 mL) was added AW-300 MS (600 mg), and the mixture was stirred for 2 h at room temperature, and then cooled to −20 °C. TMSOTf (18.4 μL, 0.15 mmol) was added, and the mixture was stirred for 1 h at 0 °C, and then neutralized with Et_3N. The solids were filtered off and washed with $CHCl_3$. The combined filtrate and washings were successively washed with water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 2:1 hexane–EtOAc as eluent to give **5** (330 mg, 90%). $[\alpha]_D^{24}$ +75.8 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.47–7.20 (m, 5H, Ar), 5.49 (s, 1H, Ph*CH*), 5.34 (d, 1H, $J_{3',4'}$ 3.7 Hz H-4′), 5.22 (dd, 1H, $J_{1',2'}$ 7.9 Hz, $J_{2',3'}$ 10.4 Hz, H-2′), 4.99 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.96 (dd, 1H, $J_{2',3'}$ 10.4 Hz, $J_{3',4'}$ 3.7 Hz, H-3′), 4.72 (d, 1H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.29 (d, 1H, H-4), 4.19 (d, 1H, $J_{5,6}$12.2 Hz, H-6a), 4.14 (m, 1H, H-6′a), 4.07–4.03 (m, 2H, H-6′b, H-3), 3.99 (d, 1H, $J_{5,6}$12.2 Hz, H-6b), 3.86 (t, 1H, $J_{5',6'a}$ $J_{5',6'b}$ 6.7 Hz, H-5′), 3.78 (dd, 1H, $J_{1,2}$ 3.7 Hz, $J_{2,3}$ 11.0 Hz, H-2), 3.74 (m, 1H, Si$CH_2$$CH_2$), 3.62 (s, 1H, H-5), 3.56 (m, 1H, Si$CH_2$$CH_2$), 2.09–1.91 (s × 4, 12H, COCH_3),1.01–0.89 (m, 2H, SiCH_2), −0.03 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 170.1, 169.4, 137.7, 128.8, 128.1, 126.1, 102.4 (C-1′), 100.6 (*C*HPh) 97.9 (C-1), 75.9 (C-3), 75.8 (C-4), 71.0 (C-3′), 70.8 (C-5′), 69.2 (C-6), 68.7 (C-2″), 67.0 (C-4′), 66.0 (SiCH_2CH), 63.1 (C-5), 61.4 (C-6′), 59.0 (C-2), 20.7 (COCH_3), 20.5 (COCH_3), 18.1 (SiCH_2), −1.47 (Si(CH_3)$_3$). HRFABMS: calcd for $C_{32}H_{45}N_3O_{14}SiNa$: ([M+Na]$^+$) 746.2569, found 746.2579.

4.5. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-2-azido-4-*O*-benzyl-2-deoxy-α-D-galactopyranoside (6)

To a solution of **5** (123 mg, 0.51 mmol) in dry CH_2Cl_2 (2.0 mL) was added 4Å MS (500 mg), and the mixture was stirred for 2 h at room temperature, and then cooled to −78 °C. Et_3SiH (82.4 μL, 0.51 mmol) and $PhBCl_2$ (75.2 mL, 0.58 mmol) were added, and the mixture was stirred for 5 min, and then neutralized with Et_3N in MeOH. The solids were filtered off and washed with $CHCl_3$. The combined filtrate and washings were successively washed with water, dried ($MgSO_4$), and concentrated.

The product was purified by silica gel column chromatography using 15:1 toluene–acetone as eluent to give **6** (90.0 mg, 73%). $[\alpha]_D^{24}$ +32.3 (*c* 1.0, $CHCl_3$), ^1H NMR (500 MHz, $CDCl_3$): δ 7.42–7.18 (m, 5H, Ar), 5.45 (d, 1H, $J_{3',4'}$ 2.4 Hz H-4′), 5.33 (dd, 1H, $J_{1',2'}$ 7.9 Hz, $J_{2',3'}$ 10.4 Hz, H-2′), 5.08 (dd, 1H, $J_{2',3'}$ 10.4 Hz, $J_{3',4'}$ 3.7 Hz, H-3′), 4.97 (d, 1H, $J_{1,2}$ 4.3 Hz, H-1), 4.96 (d, 1H, J_{gem} 11.0 Hz, benzyl methylene a), 4.80 (d, 1H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.72 (d, 1H, J_{gem} 11.6 Hz, benzyl methylene b), 4.23 (m, 1H, H-6′a), 4.16 (m, 1H, H-6′b), 4.08 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 2.4 Hz, H-3), 3.99–3.97 (m, 2H, H-4, H-5′), 3.80–3.74 (m, 3H, H-2, H-5, $SiCH_2CH_2$), 3.66 (m, 1H, H-6a), 3.54 (m, 1H, $SiCH_2CH_2$), 3.47 (br d, 1H, H-6b), 2.15-2.00 (s × 4, 12H, $COCH_3$ × 4), 1.07–0.91 (m, 2H, $SiCH_2$), 0.02 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 170.1, 169.6, 138.1, 129.0, 128.5, 128.2, 102.6 (C-1′), 97.6 (C-1), 78.5 (C-3), 75.5 (C-4), 74.3 ($PhCH_2$), 71.0 (C-5′), 70.8 (C-5), 70.5 (C-3′), 68.9 (C-2′), 67.0 (C-4′), 65.9 (CH_2CH_2Si), 62.0 (C-6), 61.2 (C-6′), 59.9 (C-2), 20.7 ($COCH_3$), 20.6 ($COCH_3$), 20.5 ($COCH_3$), 18.1 ($SiCH_2$), −1.5($Si(CH_3)_3$). HRFABMS: calcd for $C_{32}H_{47}N_3O_{14}SiNa$: ($[M+Na]^+$) 748.2725, found 748.2700.

4.6. 2,6-Dimethylphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-thio-β-D-glucopyranoside (8)

To a solution of **7** (4.87 g, 9.32 mmol) in CH_2Cl_2 (50 mL) cooled at 0 °C were added 2,6-dimethylthiophenol (2.48 mL, 18.6 mmol) and $BF_3{\cdot}Et_2O$ (1.52 mL, 12.1 mmol). The mixture was stirred for 14 h at 40 °C. After completion of the reaction, the mixture was neutralized with Et_3N and concentrated. The residue was purified by silica gel column chromatography using 3:1 hexane–AcOEt as eluent to give **8** (4.30 g, 77%). $[\alpha]_D$ +12.0 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.26–7.09 (m, 3H, Ar), 5.39 (d, 1H, $J_{2,NH}$ 9.2 Hz, N*H*), 5.20 (t, 1H, $J_{2,3}$ $J_{3,4}$ 9.8 Hz, H-3), 5.05 (t, 1H, $J_{3,4}$ $J_{4,5}$ 9.8 Hz, H-4), 4.77 (s, 2H, Troc CH_2), 4.52 (d, 1H, $J_{1,2}$ 10.4 Hz, H-1), 4.15 (m, 1H, H-6a), 4.03 (m, 1H, H-6b), 3.87 (q, 1H, $J_{1,2}$ 10.4 Hz, $J_{2,3}$ 9.8 Hz, H-2), 3.53–3.50 (m, 1H, H-5), 2.53 (s, 6H, CH_3 × 2), 2.04–1.95 (s × 3, 9H, $COCH_3$ × 3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 129.3, 128.2, 89.0 (C-1), 75.4 (C-5), 74.7 (Troc CH_2), 73.2 (C-3), 68.7 (C-4), 62.4 (C-6), 56.0 (C-2), 22.3 (CH_3 × 2, $COCH_3$), 20.6 ($COCH_3$), 20.4 ($COCH_3$). MALDI-TOFMS: calcd for $C_{23}H_{28}Cl_3NO_9SNa$: ($[M+Na]^+$) 622.0, found 623.0. HRFABMS: calcd for $C_{23}H_{28}Cl_3NO_9SNa$: ($[M+Na]^+$) 622.0448, found 622.0486.

4.7. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→6)]-2-azido-4-*O*-benzyl-2-deoxy-α-D-galactopyranoside (9)

To a solution of **6** (83.8 mg, 0.115 mmol) and **8** (104 mg, 0.173 mmol) in dry CH_2Cl_2 (1 mL) was added powdered AW-300 MS (200 mg), and the mixture was stirred under an Ar atmosphere for 2 h at room temperature, and then cooled to −50 °C. NIS (117 mg, 0.52 mmol) and TfOH (3.0 μL, 17.3 μmol) were added to the mixture, which was stirred for 2 h at −50 °C, and then neutralized with Et_3N. The solids were filtered off and washed with $CHCl_3$. The combined filtrate and washings were successively washed with satd aq $Na_2S_2O_3$ and water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 1:1 hexane–EtOAc as eluent to give **9** (64.0 mg, 47%). $[\alpha]_D^{24}$ +20.8 (*c* 1.2, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 4.82 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.75 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of GlcNAc), 4.39 (br. d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal). ^{13}C NMR (125 MHz, $CDCl_3$): δ 102.3 (C-1 of GlcNAc), 100.5 (C-1 of Gal), 97.5 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{47}H_{65}Cl_3N_4O_{23}SiNa$: ($[M+Na]^+$) 1209.3, found 1210.0.

4.8. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-[2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)]-2-acetamido-4-*O*-acetyl-2-deoxy-α-D-galactopyranoside (10)

To a solution of **9** (102 mg, 85.7 μmol) in 3:2:1 AcOH–Ac_2O–THF (3.0 mL) was added Zn powder (1.0 g). The mixture was stirred for 1 h at room temperature. After completion of the reaction, the mixture was filtered through Celite. The filtrate was concentrated and purified by silica gel column chromatography (2:1 toluene–acetone) to give an acetamido residue. A solution of this compound (50 mg, 46.7 μmol) in MeOH (1.0 mL) was hydrogenolyzed in the presence of 10% Pd–C (60 mg) for 1 h at room temperature, then filtered, and concentrated. The residue was acetylated with Ac_2O (3.0 mL) in pyridine (5.0 mL). The reaction mixture was poured into ice-water and extracted with $CHCl_3$. The extract was washed sequentially with 5% HCl, aq $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 2:1 toluene–acetone as eluent to give **10** (32.0 mg, 37%). $[\alpha]_D^{24}$ +32.5 (*c* 0.8, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 4.84 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.67 (d, 1H, $J_{1,2}$ 8.6 Hz, H-1 of GlcNAc), 4.57 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal). ^{13}C NMR (125 MHz, $CDCl_3$): δ 100.6 (C-1 of GlcNAc), 100.5 (C-1 of Gal), 97.1 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{43}H_{66}N_2O_{24}SiNa$: ($[M+Na]^+$) 1045.4, found 1045.5.

4.9. 2-(Trimethylsilyl)ethyl β-D-galactopyranosyl-(1→3)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)]-2-acetamido-2-deoxy-α-D-galactopyranoside (A)

To a solution of **10** (32.0 mg, 31.3 μmol) in MeOH (2.0 mL) was added NaOMe (10.0 mg) at room temperature, and the mixture was stirred for 15 h, and then neutralized with Amberlite IR 120 [H^+]. The mixture was filtered off and concentrated. The product was purified by Sephadex LH-20 column chromatography in MeOH to give **A** (20.5 mg, 95%).$[\alpha]_D^{24}$ +33.6 (*c* 0.5, H_2O). ^1H NMR (500 MHz, D_2O): δ 4.76 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.40 (d, 1H, $J_{1,2}$ 8.6 Hz, H-1 of GlcNAc), 4.32 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal). ^{13}C NMR (125 MHz, D_2O): δ 102.8 (C-1 of GlcNAc), 101.7 (C-1 of Gal), 96.8 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{27}H_{50}N_2O_{16}SiNa$: ($[M+Na]^+$) 709.3, found 709.9. HRFABMS: calcd for $C_{27}H_{50}N_2O_{16}SiNa$: ($[M+Na]^+$) 709.2828, found 709.2847.

4.10. 2,6-Dimethylphenyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-thio-β-D-glucopyranoside (11)

To a solution of **8** (2.80 g, 4.66 mmol) in MeOH (30 mL) was added NaOMe (126 mg, 2.33 mmol), and the mixture was stirred for 1 h, and then neutralized with Amberlite IR 120 [H^+]. The mixture was filtered and concentrated. To a solution of the residue in CH_3CN (47 mL) were added benzaldehyde dimethylacetal (1.39 mL, 9.32 mmol) and camphor-10-sulfonic acid (1.00 g 2.33 mmol) at room temperature. The reaction mixture was stirred for 16 h at 40 °C, and then neutralized with Et_3N. After evaporation, the residue was recrystallized with 1,4-dioxane–*n*-hexane to give the benzylidene derivative. To a solution of this compound in pyridine (47 mL) was added benzoyl chloride (1.1 mL, 9.32 mmol), and the mixture was stirred for 16 h at room temperature. The reaction mixture was poured into ice-water and extracted with $CHCl_3$. The extract was washed sequentially with 5% HCl, satd aq $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 1:1 hexane–EtOAc as eluent to give **11** (2.03 g, 65%). $[\alpha]_D^{24}$ +0.98 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 8.07–7.02 (m, 13H, Ar), 6.07 (d, 1H, $J_{2,NH}$ 9.8 Hz, N*H*),

5.65 (t, 1H, $J_{2,3}$ $J_{3,4}$ 9.8 Hz, H-3), 5.42 (s, 1H, PhC*H*), 4.67 (s, 2H, Troc CH_2), 4.62 (d, 1H, $J_{1,2}$ 10.4 Hz, H-1), 4.18 (q, 1H, H-4), 3.94 (m, 1H, H-6a), 3.86 (t, 1H, $J_{3,4}$ $J_{4,5}$ 9.8 Hz, H-4), 3.67(t, 1H, $J_{5,6a}$ $J_{6a,6b}$ 10.4 Hz, H-6b), 3.61(m, 1H, H-5), 2.52 (s, 6H, $CH_3 \times 2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.6, 144.1, 136.8, 133.5, 129.3, 128.8, 128.5, 128.3, 127.9, 125.8, 100.8 (Ph*C*H), 89.9 (C-1), 78.6 (C-4), 74.5 (Troc *C*H_2), 73.4 (C-3), 70.2 (C-5), 68.1 (C-6), 56.3 (C-2), 22.4 (*C*$H_3 \times 2$). HRFABMS: calcd for $C_{31}H_{31}Cl_3NO_7S$: ([M+H]$^+$) 666.0887, found 666.0909.

4.11. 2,6-Dimethylphenyl 3-*O*-benzoyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-thio-β-D-glucopyranoside (12)

To a solution of **11** (2.03 g, 3.04 mmol) and $NaBH_3CN$ (1.72 g, 27.4 mmol) in dry THF (30 mL) was added powdered 3 Å MS (2 g), and the mixture was stirred for 2 h at room temperature, and then cooled to 0 °C. HCl–Et_2O was added until the solution was acidic (pH paper, gas evolution). After 30 min, the reaction mixture was poured into ice-water and extracted with $CHCl_3$. The extract was washed sequentially with satd aq $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. The product was purified by silica gel column chromatography using 20:1 toluene–acetone as eluent to give **12** (1.86 g, 92%). $[\alpha]_D^{24}$ +17.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02–7.06 (m, 13H, Ar), 5.75 (d, 1H, $J_{2,NH}$ 9.8 Hz, N*H*), 5.34 (t, 1H, $J_{2,3}$ $J_{3,4}$ 9.8 Hz, H-3), 4.69 and 4.63 (each d, 2H, J_{gem} 12.2 Hz, PhCH_2), 4.53 (d, 1H, $J_{1,2}$ 10.4 Hz, H-1), 4.51 and 4.47 (each d, 2H, J_{gem} 11.6 Hz, Troc CH_2), 4.08 (q, 1H, H-2), 3.90 (br, 1H, H-4), 3.69 (m, 2H, H-6a, H-6b), 3.44–3.40 (m, 1H, H-5), 3.07, (br d, 1H, O*H*), 2.53 (s, 6H, C$H_3 \times 2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.4, 154.5, 144.0, 137.6, 133.6, 131.1, 130.0, 129.1, 129.0, 128.44, 128.41, 127.8, 127.6, 125.3, 95.3, 89.3 (C-1), 77.9 (C-5), 76.7 (C-3), 74.5 (PhCH_2), 73.7 (Troc CH_2), 70.7 (C-4), 70.3 (C-6), 55.7 (C-2), 22.4(C$H_3 \times 2$). HRFABMS: calcd for $C_{31}H_{33}Cl_3NO_7S$: ([M+H]$^+$) 668.1043, found 668.1080.

4.12. 2,6-Dimethylphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3-*O*-benzoyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-thio-β-D-glucopyranoside (13)

To a solution of **4** (147 mg, 0.30 mmol) and **12** (100 mg, 0.15 mmol) in dry CH_2Cl_2 (1.0 mL) was added AW-300 MS (300 mg), and the mixture was stirred for 2 h at room temperature, then cooled to −20 °C. TMSOTf (5.4 μL, 29.8 μmol) was added, and the mixture was stirred for 1 h at −20 °C, and then neutralized with Et_3N. The solids were filtrated off and washed with $CHCl_3$. The combined filtrate and washings were successively washed with water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 4:1 hexane–EtOAc as eluent to give **13** (128 mg, 86%). $[\alpha]_D^{24}$ −14.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05–7.10 (m, 13H, Ar), 5.47 (d, 1H, $J_{2,NH}$ 9.8 Hz, N*H*), 5.31 (t, 1H, $J_{2,3}$ $J_{3,4}$ 9.8 Hz, H-3), 5.13 (d, 1H, $J_{3',4'}$ 3.7 Hz, H-4′), 4.93 (dd, 1H, $J_{1',2'}$ 7.9 Hz, $J_{2',3'}$ 10.4 Hz, H-2′), 4.77 (dd, 1H, $J_{2',3'}$ 10.4 Hz, $J_{3',4'}$ 3.7 Hz, H-3′), 4.73 and 4.50 (each d, 2H, J_{gem} 11.6 Hz, Troc CH_2), 4.72 and 4.62 (each d, 2H, J_{gem} 12.2 Hz, PhCH_2), 4.49 (d, 1H, $J_{1',2'}$ 7.9 Hz, H-1′′), 4.47 (d, 1H, $J_{1,2}$ 10.4 Hz, H-1), 4.16 (t, 1H, $J_{3,4}$ $J_{4,5}$ 9.8 Hz, H-4), 4.08 (q, 1H, H-2), 3.68 (m, 1H, H-6a), 3.61–3.58 (m, 2H, H-6b, H-6′a), 3.52 (m, 1H, H-5′), 3.47(m, 1H, H-6′b), 3.33(m, 1H, H-5), 2.56 (s, 6H, C$H_3 \times 2$), 2.00-1.87 (s × 4, 12H, COC$H_3 \times 4$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 168.9, 166.2, 154.4, 144.0, 137.8, 133.4, 129.9, 129.1, 128.5, 128.3, 128.2, 128.0, 100.1(C-1′), 89.4(C-1), 78.7(C-5), 74.5 (PhCH_2), 74.3 (C-4), 74.2 (C-3), 73.9 (TrocCH_2), 70.9 (C-3′), 70.5 (C-5), 69.2 (C-2′), 67.7 (C-6), 66.5 (C-4′), 60.6 (C-6′), 56,1 (C-2), 22.4 (Ph(CH_3)$_2$), 20.6 (COC$H_3 \times 2$), 20.5 (COCH_3), 20.4 (COCH_3). MALDI-TOFMS: calcd for $C_{45}H_{50}Cl_3NNaO_{16}S$: ([M+Na]$^+$) 1020.2, found 1020.8. HRFABMS: calcd for $C_{45}H_{50}Cl_3NO_{16}SNa$: ([M+Na]$^+$) 1020.1814, found 1020.1863.

4.13. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3-*O*-benzoyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→6)]-2-azido-4-*O*-benzyl-2-deoxy-α-D-galactopyranoside (14)

Compound **14** was prepared from **6** (53.6 mg, 73.8 μmol) and **13** (88.4 mg, 88.6 μmol) as described for preparation of **9**, yielding 82 mg (70%). $[\alpha]_D^{24}$ +8.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.89 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.79 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal a), 4.60 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of GlcNAc), 4.42 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal b). ^{13}C NMR (125 MHz, $CDCl_3$): δ 102.3 (C-1 of Gal a), 101.3 (C-1 of GlcNAc), 99.9 (C-1 of Gal), 97.5 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{69}H_{87}Cl_3N_4O_{30}SiNa$: ([M+Na]$^+$) 1607.4, found 1607.7.

4.14. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2-acetamido-6-*O*-acetyl-3-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl-(1→6)]-2-acetamido-4-*O*-acetyl-2-deoxy-α-D-galactopyranoside (15)

Compound **15** was prepared from **14** (132 mg, 83.2 mmol) as described for preparation of **10**, yielding 50.1 mg (44%). $[\alpha]_D^{24}$ +19.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.72 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.79 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal a), 4.60 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of GlcNAc), 4.42 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal b). ^{13}C NMR (125 MHz, $CDCl_3$): δ 102.3 (C-1 of Gal a), 101.3 (C-1 of GlcNAc), 99.9 (C-1 of Gal b), 97.5 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{60}H_{84}N_2O_{32}SiNa$: ([M+Na]$^+$) 1395.5, found 1395.8.

4.15. 2-(Trimethylsilyl)ethyl β-D-galactopyranosyl-(1→3)-[β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)]-2-acetamido-2-deoxy-α-D-galactopyranoside (D)

Compound **D** was prepared from **15** (50.1 mg, 36.5 μmol) as described for preparation of **A**, yielding 30.0 mg (97%). $[\alpha]_D^{24}$ +41.6 (*c* 0.5, H_2O). ^{1}H NMR (500 MHz, D_2O): δ 4.72 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.38 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1 of GlcNAc), 4.281 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal a), 4.276 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal b). ^{13}C NMR (125 MHz, D_2O): δ 104.1 (C-1 of GlcNAc), 102.5 (C-1 of Gal a), 101.0 (C-1 of Gal b), 96.2 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{33}H_{60}N_2O_{21}SiNa$: ([M+Na]$^+$) 871.3, found 871.7. HRFABMS: calcd for $C_{33}H_{60}N_2O_{21}SiNa$: ([M+Na]$^+$) 871.3356, found 871.3398.

4.16. Phenyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-1-thio-β-D-galactopyranoside (17)

Compound **17** was prepared from **16** (850 mg, 1.53 mmol) as described for preparation of **12**, yielding 666 mg (78%). $[\alpha]_D^{24}$ +33.6 (*c* 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02–7.12 (m, 20H, Ar), 5.50 (t, 1H, $J_{1,2}$ $J_{2,3}$ 9.8 Hz, H-2), 4.75 (d, 1H, H-1), 4.65 and 4.52 (each d, 2H, J_{gem} 12.2 Hz, PhCH_2), 4.59 (s, 2H, PhCH_2), 4.17 (br.d, 1H, H-4), 3.87–3.81 (m, 2H, H-6a, H-6b), 3.71 (t, 1H, H-5), 3.66 (dd, 1H, H-3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.0, 133.3, 133.1, 132.2, 129.9, 128.8, 128.4, 128.0, 127.9, 127.8, 127.6, 86.6 (C-1), 79.3 (C-3), 77.5 (C-5), 73.7, 71.3 (each PhCH_2), 69.6 (C-6), 69.3 (C-2), 66.4 (C-4). MALDI-TOFMS: calcd for $C_{33}H_{32}O_6SNa$: ([M+Na]$^+$) 579.2, found 579.4.

4.17. Phenyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-chloroacetyl-1-thio-β-D-galactopyranoside (18)

To a solution of **17** (1.92 g, 3.45 mmol) in 15:1 CH_2Cl_2–pyridine (32 mL) was added chloroacetyl chloride (550 μL, 6.90 mmol), and the mixture was stirred for 1 h at 0 °C. Toluene was added and evaporated, and the residue was extracted with $CHCl_3$. The extract was washed with 5% HCl, aq $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 7:1 hexane–EtOAc as the eluent to give **18** (1.88 g, 86%). $[\alpha]_D^{24}$ +47.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99–7.04 (m, 20H, Ar), 5.73 (d, 1H, $J_{3,4}$ 3.7 Hz, H-4), 5.36 (t, 1H, $J_{2,3}$ 9.8 Hz, H-2), 4.77(d, 1H, $J_{1,2}$ 10.4 Hz, H-1), 4.64 and 4.41 (each d, 2H, J_{gem} 12.8 Hz, PhCH_2), 4.58 and 4.46 (each d, 2H, J_{gem} 11.6 Hz, PhCH_2), 4.11 and 4.00 (each d, 2H, J_{gem} 14.6 Hz, COCH_2Cl), 3.86 (t, 1H, H-5), 3.70 (dd, 1H, $J_{2,3}$ 9.8 Hz, $J_{3,4}$ 3.1 Hz, H-3), 3.67–3.64 (m, 1H, H-6a), 3.57-3.54 (m, 1H, H-6b). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 165.1, 137.3, 136.9, 133.2, 132.7, 132.5, 129.9, 129.7, 128.8, 128.5, 128.33, 128.26, 128.15, 128.06, 128.02, 127.9, 127.8, 86.8 (C-1), 77.2 (C-3), 75.8 (C-5), 73.7 (PhCH_2), 71.1 (PhCH_2), 69.4 (C-2), 68.2 (C-4), 67.5 (C-6), 40.8 (COCH_2Cl). MALDI-TOFMS: calcd for $C_{35}H_{33}ClO_7SNa$: ([M+Na]$^+$) 655.2, found 655.5. HRFABMS: calcd for $C_{35}H_{33}ClO_7SNa$: ([M+Na]$^+$) 655.1534, found 655.1520.

4.18. 2-*O*-Benzoyl-3,6-di-*O*-benzyl-4-*O*-chloroacetyl-D-galactopyranosyl fluoride (19)

To a solution of **18** (1.88 g, 0,126 mmol) in CH_2Cl_2 (30 mL) was added DAST (1.19 mL) at 0 °C, and the mixture was stirred at 40 °C for 16 h. The reaction mixture was diluted with $CHCl_3$ and extracted with satd aq $NaHCO_3$, and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated. The residue was purified by chromatography on silica gel (9:1→8:1 hexane–EtOAc) to give **19α** (990 mg, 60%) and **19β** (422 mg, 25.6%) as pale-yellow syrups. Compound **19α**: $[\alpha]_D^{24}$ +113 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03–7.20 (m, 15H, Ar), 5.85 (dd, 1H, $J_{1,2}$ 2.4 Hz, $J_{1,F}$ 53.1 Hz, H-1), 5.83 (d, 1H, $J_{3,4}$ 2.4 Hz, H-4), 5.33 (ddd, 1H, $J_{1,2}$ 2.1 Hz, $J_{2,3}$ 10.4 Hz, $J_{2,F}$ 24.4 Hz, H-2), 4.72 and 4.51 (each d, 2H, J_{gem} 11.6 Hz, PhCH_2), 4.58 and 4.47 (each d, 2H, J_{gem} 11.6 Hz, PhCH_2), 4.34 (t, 1H, H-5), 4.10 and 4.02 (each d, 2H, J_{gem} 11.6 Hz, COCH_2Cl), 4.09 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.1 Hz, H-3), 3.62–3.51 (m, 2H, H-6a, H-6b). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7, 165.7, 137.2, 137.0, 133.5, 130.0, 129.2, 128.5, 128.4, 128.2, 128.0, 127.9, 104.8 (d, $J_{C-1,F}$ 226 Hz, C-1), 73.7 (PhCH_2), 72.1 (C-3), 71.5 (PhCH_2), 69.8 (C-5), 69.3 (d, $J_{C-2,F}$ 23 Hz, C-2), 68.6 (C-4), 67.0 (C-6). HRFABMS: calcd for $C_{29}H_{29}ClFO_7Na$: ([M+Na]$^+$) 543.1586, found 543.1562.

Compound **19β**: $[\alpha]_D^{24}$ +55.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500MHz, $CDCl_3$): δ 7.98–7.09 (m, 15H, Ar), 5.72 (s, 1H, H-4), 5.48–5.42 (m, 1H, H-2), 5.27 (dd, 1H, $J_{1,2}$ 7.3 Hz, $J_{1,F}$ 52.5 Hz, H-1), 4.67 and 4.44 (each d, 2H, J_{gem} 12.2 Hz, PhCH_2), 4.59 and 4.47 (each d, 2H, J_{gem}=12.8 Hz, PhCH_2), 4.15 and 4.04 (each d, 2H, J_{gem} 11.6 Hz, COCH_2Cl), 3.92 (t, 1H, H-5), 3.70 (dd, 1H, $J_{2,3}$ 9.8 Hz, $J_{3,4}$ 3.1 Hz, H-3), 3.68–3.58 (m, 2H, H-6a, H-6b). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.8, 165.0, 137.1, 136.7, 133.4, 129.9, 129.3, 128.6, 128.4, 128.2, 128.13, 128.05, 127.9, 107.3 (d, $J_{C-1,F}$ 219 Hz, C-1), 75.2 (d, $J_{C-3,F}$ 10.4 Hz, C-3), 73.8 (PhCH_2), 72.2 (C-5), 71.3 (PhCH_2), 70.8(d, $J_{C-2,F}$ 22.8 Hz, C-2), 67.3(C-4), 66.9(C-6), 40.7. HRFABMS: calcd for $C_{29}H_{29}ClFO_7Na$: ([M+Na]$^+$) 543.1586, found 543.1616.

4.19. 2,6-Dimethylphenyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-chloroacetyl-β-D-galactopyranosyl-(1→4)-3-*O*-benzoyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-thio-β-D-glucopyranoside (20)

A solution of compound **12** (200 mg, 0.30 mmol) and **19** (325 mg, 0.60 mmol) containing activated AW-300 MS (500 mg) in dry CH_2Cl_2 (8 mL) was stirred under an atmosphere of argon for 2 h at room temperature. After cooling to −20 °C, successively Cp_2HfCl_2 (460 mg, 1.79 mmol) and AgOTf (340 mg, 0.90 mmol) were added, and stirring was continued at −20 °C for 2 h. The mixture was then neutralized with Et_3N. The reaction mixture was filtered, and the filtrate was washed with $CHCl_3$ and brine, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 60:1 toluene–EtOAc as the eluent to give **20** (276 mg, 78%). $[\alpha]_D^{24}$ +12.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01–7.02 (m, 33H, Ar), 5.52 (d, 1H, $J_{3',4'}$ 3.7 Hz H-4′), 5.43 (d, 1H, $J_{2,NH}$ 9.8 Hz, N*H*), 5.24 (t, 1H, $J_{2,3}$ $J_{3,4}$ 9.8 Hz, H-3), 5.08 (dd, 1H, $J_{1',2'}$ 7.9 Hz, $J_{2',3'}$ 10.4 Hz, H-2′), 4.70 and 4.57 (each d, 2H, J_{gem} 12.2 Hz, PhCH_2), 4.57 and 4.31 (each d, 2H, J_{gem} 12.8 Hz, PhCH_2), 4.52 (d, 1H, $J_{1',2'}$ 8.6 Hz, H-1′), 4.50 and 4.36 (each d, 2H, J_{gem} 12.2 Hz, PhCH_2), 4.47 (d, 1H, $J_{1,2}$ 10.4 Hz, H-1), 4.22 (t, 2H, J_{gem} 11.6 Hz, Troc CH_2), 4.09–4.03 (m, 2H, H-4, H-2), 3.94 and 3.64 (each d, 2H, J_{gem} 14.6 Hz, COCH_2Cl), 3.44–3.41 (m, 2H, H-6a, H-6′a), 3.32(d, 1H, $J_{3,4}$ 11.0 Hz, H-6a), 3.14 (m, 1H, H-5), 3.07 (m, 1H, H-6′b), 2.84 (t, 1H, H-5), 2.49 (s, 6H, $CH_3 \times 2$),. ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7, 166.0, 164.6, 154.4, 144.0. 138.0, 137.1, 130.9, 130.0, 129.7, 129.5, 129.0, 128.5, 128.3, 128.2, 128.1, 128.02, 127.97, 127.90, 127.8, 127.7, 125.3, 100.5 (C-1′), 89.2 (C-1), 78.3 (C-5), 76.0 (C-6), 74.6 (C-3), 74.4 (C-2, PhCH_2), 73.5 (Troc CH_2), 73.4 (PhCH_2), 71.3 (C-2′), 71.2 (C-6′), 70.8 (PhCH_2), 67.8 (C-6), 67.2 (C-4′), 66.0 (C-4), 56.1 (CH_2Cl), 22.3 (Ph$(CH_3)_2$). MALDI-TOFMS: calcd for $C_{60}H_{59}Cl_4NO_{14}SNa$: ([M+Na]$^+$) 1212.2, found 1212.2. HRFABMS: calcd for $C_{60}H_{59}Cl_4NO_{14}SNa$: ([M+Na]$^+$) 1212.2308, found 1212.2349.

4.20. 2,6-Dimethylphenyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3-*O*-benzoyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-thio-β-D-glucopyranoside (21)

To a solution of **20** (514 mg, 0.431 mmol) in 5:1 EtOH–pyridine (12 mL) was added thiourea (98.4 mg, 1.29 mmol), and the mixture was stirred for 2 h at 80 °C. The mixture was diluted with $CHCl_3$, washed with satd aq $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 15:1 toluene–acetone as eluent to give **21** (350 mg, 73%). $[\alpha]_D^{24}$ +10.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00–7.00 (m, 33H, Ar), 5.54 (d, 1H, $J_{2,NH}$ 9.8 Hz, NH), 5.31–5.25 (m, 2H, H-3, H-2′), 4.67 and 4.58 (each d, 2H, J_{gem} 12.2 Hz, PhCH_2), 4.58 and 4.38 (each d, 2H, J_{gem} 12.8Hz, PhCH_2), 4.53 (d, 1H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.48 and 4.25 (each d, 2H, J_{gem} 12.2Hz, PhCH_2), 4.43 (d, 1H, $J_{1,2}$ 10.4 Hz, H-1), 4.35 and 4.30 (each d, 2H, J_{gem} 12.6 Hz, Troc CH_2), 4.11–4.05 (m, 2H, H-4, H-2), 4.00 (d, 1H, $J_{3',4'}$ 3.0 Hz H-4′), 3.50–3.47 (m, 1H, H-6a), 3.40 (dd, 1H, $J_{2,3}$ 9.8 Hz, $J_{3,4}$ 3.7 Hz, H-3), 3.32(d, 1H, $J_{3,4}$ 9.8 Hz, H-6a), 3.29–3.18 (m, 3H, H-5, H-5′, H-6′a), 3.12 (m, 1H, H-6′b), 2.49 (s, 6H, C$H_3 \times 2$),. ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.6, 164.8, 154.5, 144.0, 138.2, 138.0, 137.2, 133.0, 130.3, 130.0, 129.7, 129.0, 128.4, 128.3, 128.2, 128.1, 127.7, 127.62, 127.55, 100.7(C-1′), 89.3(C-1), 78.3(C-5), 78.1(C-3′), 74.8(C-2, C-2′), 74.4(PhCH_2), 73.4(PhCH_2), 73.3(Troc CH_2), 72.7(C-5′), 71.5(C-3), 70.5(PhCH_2), 68.0(C-6), 67.3(C-6′), 64.7(C-4,C-4′), 22.4(Ph$(CH_3)_2$). MALDI-TOFMS: calcd for $C_{58}H_{58}Cl_3NO_{13}S$-Na: ([M+Na]$^+$) 1136.3, found 1136.5. HRFABMS: calcd for $C_{58}H_{58}Cl_3NO_{13}SNa$: ([M+Na]$^+$) 1136.2592, found 1136.2632.

4.21. 2,6-Dimethylphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galacto-pyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3-*O*-benzoyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-thio-β-D-glucopyranoside (22)

Compound **22** was prepared from **21** (150 mg, 0.13 mmol) and **4** (528 mg, 0.54 mmol) as described for preparation of **13**, yielding

142 mg (73%). $[\alpha]_D^{24}$ −1.11 (*c* 1.4, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 4.88 (d, 1H, $J_{1,2}$ 7.9Hz, H-1 of Gal b), 4.45 (d, 1H, $J_{1,2}$ 7.9Hz, H-1 of Gal a), 4.27 (d, 1H, $J_{1,2}$ 11.0Hz, H-1 of GlcNAc). ^{13}C NMR (125 MHz, $CDCl_3$): δ 100.9 (C-1 of Gal a), 100.3 (C-1 of Gal b), 89.3 (C-1 of GlcNAc). MALDI-TOFMS: calcd for $C_{72}H_{76}Cl_3NO_{22}SNa$: ($[M+Na]^+$) 1466.4, found 1466.8.

4.22. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3-*O*-benzoyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→6)]-2-azido-4-*O*-benzyl-2-deoxy-α-D-galactopyranoside (23)

Compound **23** was prepared from **6** (64.8 mg, 89.3 μmol) and **22** (142 mg, 98.2 μmol) as described for preparation of **14**, yielding 104 mg (57%). $[\alpha]_D^{24}$ +17.2 (*c* 1.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 4.95 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1 of Gal c), 4.84 (d, 1H, $J_{1,2}$ 4.9 Hz, H-1 of GalNAc), 4.74 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1 of Gal a), 4.45 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1 of GlcNAc), 4.42 (d, 1H, $J_{1,2}$ 5.5 Hz, H-1 of Gal b). ^{13}C NMR (125 MHz, $CDCl_3$): δ 102.3 (C-1 of Gal b), 101.1 (C-1 of Gal a), 100.6 (C-1 of GlcNAc), 100.2 (C-1 of Gal c), 95.5 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{96}H_{113}Cl_3N_4O_{36}SiNa$: ($[M+Na]^+$) 2053.6, found 2053.8.

4.23. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2-acetamido-6-*O*-acetyl-3-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl-(1→6)]-2-acetamido-4-*O*-acetyl-2-deoxy-α-D-galactopyranoside (24)

Compound **24** was prepared from **23** (251 mg, 0.123 mmol) as described for preparation of **10**, yielding 73.3 mg (34%). $[\alpha]_D^{24}$ +25.9 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 4.82 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.59 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal c), 4.54 (d, 1H, $J_{1,2}$ 7.9Hz, H-1 of GlcNAc), 4.43 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1 of Gal a), 4.36 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal b). ^{13}C NMR (125 MHz, $CDCl_3$): δ 102.3 (C-1 of Gal b), 101.1 (C-1 of Gal a), 100.6 (C-1 of GlcNAc), 100.2 (C-1 of Gal c), 95.5 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{77}H_{102}N_2O_{40}SiNa$: ($[M+Na]^+$) 1745.5, found 1745.3.

4.24. 2-(Trimethylsilyl)ethyl β-D-galactopyranosyl-(1→3)-[β-D-galactopyranosyl-(1→4)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)]-2-acetamido-2-deoxy-α-D-galactopyranoside (E)

Compound **E** was prepared from **24** (69.7 mg, 40.4 μmol) as described for preparation of **A**, yielding 38.5 mg (95%). $[\alpha]_D^{24}$ +34.6 (*c* 1.0, H_2O). ^1H NMR (500 MHz, D_2O): δ 4.72 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.41 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal c), 4.37 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1 of GlcNAc) 4.31 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal a), 4.28 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal b). ^{13}C NMR (125 MHz, D_2O): δ 104.1 (C-1 of Gal c), 103.8 (C-1 of Gal b), 102.5 (C-1 of Gal a), 101.0 (C-1 of GlcNAc), 98.8 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{39}H_{70}N_2O_{26}SiNa$: ($[M+Na]^+$) 1033.4, found 1034.0. HRFABMS: calcd for $C_{39}H_{70}N_2O_{26}SiNa$: ($[M+Na]^+$) 1033.3884, found 1033.3920.

4.25. 2,3-Di-*O*-benzyl-4,6-di-*tert*-butylsilylene-α-D-galactopyranosyl fluoride (26)

To a solution of **25** (253 mg, 0.43 mmol) in CH_2Cl_2 (4 mL) were added DAST (84 μL, 0.64 mmol) and NBS (98.8 mg, 0.56 mmol) at −15 °C, and the mixture was stirred for 1.5 h. The reaction mixture was diluted with $CHCl_3$ and extracted with satd aq $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated. The residue was purified by chromatography on silica gel (20:1 hexane–EtOAc) to give **26** (167 mg, 78%). $[\alpha]_D^{24}$ +41.7 (*c* 1.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.43–7.25 (m, 10H, Ar), 5.54 (dd, 1H, $J_{1,2}$ 3.1 Hz, $J_{1,F}$ 53.7 Hz, H-1), 4.92–4.71 (m, 4H, $PhCH_2 \times 2$), 4.55 (d, 1H, $J_{3,4}$ 2.4 Hz, H-4), 4.22–4.14 (m, 2H, H-6a, H-6b), 3.99 (ddd, 1H, $J_{1,2}$ 2.4 Hz, $J_{2,3}$ 9.8 Hz, $J_{2,F}$ 26.2 Hz, H-2), 3.79 (s, 1H, H-5), 1.06 (s, 9H, $Si(CH_3)_3$), 0.97 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.5, 138.0, 128.4, 128.3, 127.9, 127.7, 106.9 (d, $J_{C\text{-}1,F}$ 226 Hz, C-1), 77.3 (C-3), 74.0 ($PhCH_2$), 73.7 (d, $J_{C\text{-}2,F}$ 23 Hz, C-2), 71.1 ($PhCH_2$), 70.5 (C-4), 69.6 (C-2), 66.7 (C-6), 27.6 ($Si(CH_3)_3$), 27.2 ($Si(CH_3)_3$). MALDI-TOFMS: calcd for $C_{28}H_{39}FO_5SiNa$: ($[M+Na]^+$) 525.2, found 525.4.

4.26. 2,6-Dimethylphenyl 2,3-di-*O*-benzyl-4,6-di-*tert*-butylsilylene-α-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3-*O*-benzoyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-thio-β-D-glucopyranoside (27)

Compound **27** was prepared from **21** (200 mg, 0.18 mmol) and **26** (135 mg, 0.27 mmol) as described for preparation of **20**, yielding 260 mg (91%). $[\alpha]_D^{24}$ +41.7 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 4.83 (d, 1H, $J_{1,2}$ 3.1 Hz, H-1 of Gal b), 4.72 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1 of Gal a), 4.37 (d, 1H, $J_{1,2}$ 10.4 Hz, H-1 of GlcNAc). ^{13}C NMR (125 MHz, $CDCl_3$): δ 101.6 (C-1 of Gal a), 100.7 (C-1 of Gal b), 89.5 (C-1 of GlcNAc). MALDI-TOFMS: calcd for $C_{86}H_{96}Cl_3NO_{18}SSiNa$: ($[M+Na]^+$) 1618.5, found1618.4.

4.27. 2,6-Dimethylphenyl 4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3-*O*-benzoyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-thio-β-D-glucopyranoside (28)

A solution of **27** (260 mg, 0.163 mmol) in THF (5 mL) was treated with HF–pyridine (500 μL) at 0 °C and then stirred for 2 h. The reaction mixture was added to water, extracted with EtOAc, and the organic layer was washed with satd aq $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. The residue was treated with Ac_2O (3 mL) in pyridine (5 mL). The reaction mixture was poured into ice-water and extracted with $CHCl_3$. The extract was washed sequentially with 5% HCl, satd aq $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 7:1 hexane–EtOAc as eluent to give **28** (234 mg, 93%). $[\alpha]_D^{24}$ +39.1 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 4.98 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of Gal b), 4.60 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1 of Gal a), 4.36 (d, 1H, $J_{1,2}$ 10.4 Hz, H-1 of GlcNAc). ^{13}C NMR (125 MHz, $CDCl_3$): δ 101. (C-1 of Gal a), 100.4 (C-1 of Gal b), 95.2 (C-1 of GlcNAc). MALDI-TOFMS: calcd for $C_{82}H_{84}Cl_3NO_{20}SNa$: ($[M+Na]^+$)1562.4, found 1562.5.

4.28. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-[4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3-*O*-benzoyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→6)]-2-azido-4-*O*-benzyl-2-deoxy-α-D-galactopyranoside (29)

Compound **29** was prepared from **6** (42.3 mg, 58.3 μmol) and **28** (108 mg, 70.0 μmol) as described for preparation of **14**, yielding 56.4 mg (46%). $[\alpha]_D^{24}$ +43.6 (*c* 1.0, $CHCl_3$).

^1H NMR (500 MHz, $CDCl_3$): δ 4.91 (d, 1H, $J_{1,2}$ 3.1 Hz, H-1 of Gal c), 4.79 (d, 1H, $J_{1,2}$ 4.3 Hz, H-1 of GalNAc), 4.68 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1 of Gal b), 4.51 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of GlcNAc), 4.37 (br d, 1H, $J_{1,2}$ 7.3 Hz, H-1 of Gal a). ^{13}C NMR (125 MHz, $CDCl_3$): δ 102.3(C-1 of Gal b), 101.2 (C-1 of GlcNAc), 101.12 (C-1 of Gal a), 100.4 (C-1 of Gal c), 97.4 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{106}H_{121}Cl_3N_4NaO_{34}Si$: ($[M+Na]^+$) 2149.7, found 2150.7.

4.29. 2-(Trimethylsilyl)ethyl β-D-galactopyranosyl-(1→3)-[α-D-galactopyranosyl-(1→4)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)]-2-acetamido-2-deoxy-α-D-galactopyranoside (F)

Compound **F** was prepared from **29** (122 mg, 57.3 μmol) as described for preparation of **A**, yielding 12.1 mg (21% four steps). $[\alpha]_D^{24}$ +41.9 (*c* 0.3, H_2O). ^1H NMR (500 MHz, D_2O): δ 4.76 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of Gal c), 4.72 (d, 1H, $J_{1,2}$ 3.7, H-1 of GalNAc), 4.38 (d, 1H, $J_{1,2}$ 7. 9Hz, H-1 of GlcNAc) 4.34 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1 of Gal b), 4.28 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal a). ^{13}C NMR (125 MHz, D_2O): δ 104.2 (C-1 of Gal b), 102.8 (C-1 of Gal a), 101.0 (C-1 of GlcNAc), 99.9 (C-1 of Gal c), 96.2 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{39}H_{70}N_2O_{26}SiNa$: ($[M+Na]^+$) 1033.4, found 1034.2. HRFABMS: calcd for $C_{39}H_{70}N_2O_{26}SiNa$: ($[M+Na]^+$) 1033.3884, found 1033.3907.

4.30. 2-(Trimethylsilyl)ethyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-chloroacetyl-β-D-galactopyranosyl-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranoside (30)

Compound **30** was prepared from **3a** (106 mg, 0.249 mmol) and **18** (256 mg, 0.408 mmol) as described for preparation of **9**, yielding 195 mg (79%). $[\alpha]_D$ +103 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 4.89 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.76 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal). ^{13}C NMR (125 MHz, $CDCl_3$): δ 102.3 (C-1 of Gal), 97.9 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{47}H_{54}ClN_3O_{12}SiNa$: ($[M+Na]^+$) 938.3, found: 939.0. HRFABMS: calcd for $C_{47}H_{54}ClN_3O_{12}$-SiNa: ($[M+Na]^+$) 938.3063, found 938.3097.

4.31. 2-(Trimethylsilyl)ethyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranoside (31)

Compound **31** was prepared from **30** (364 mg, 0.40 mmol) as described for preparation of **21**, yielding 297 mg (89%). $[\alpha]_D^{24}$ +81.6 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 4.88 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.72 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal). ^{13}C NMR (125 MHz, $CDCl_3$): δ 102.3 (C-1 of Gal), 97.9 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{45}H_{53}N_3O_{11}SiNa$: ($[M+Na]^+$) 862.3, found 863.1. HRFABMS: calcd for $C_{45}H_{53}N_3O_{11}SiNa$: ($[M+Na]^+$) 862.3347, found 862.3387.

4.32. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranoside (32)

Compound **32** was prepared from **31** (131 mg, 0.156 mmol) and **4** (308 mg, 0.624 mmol) as described for preparation of **13**, yielding 135 mg (74%). $[\alpha]_D^{24}$ +62.1 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 5.01 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal b), 4.93 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.77 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1 of Gal a). ^{13}C NMR (125 MHz, $CDCl_3$): δ 102.1 (C-1 of Gal a), 100.4 (C-1 of Gal b), 97.9 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{59}H_{71}N_4O_{20}SiNa$: ($[M+Na]^+$) 1192.4, found 1192.4. HRFABMS: calcd for $C_{59}H_{71}N_3O_{20}SiNa$: ($[M+Na]^+$) 1192.4298, found 1192.4354.

4.33. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-α-D-galactopyranoside (33)

A solution of **32** (132 mg, 0.113 mmol) in MeOH (3.0 mL) was hydrogenolyzed in the presence of 10% $Pd(OH)_2$–C (100 mg) for 20 h at room temperature, then filtered, and concentrated. The residue was acetylated with Ac_2O (3.0 mL) in pyridine (5.0 mL). The reaction mixture was poured into ice-water and extracted with $CHCl_3$. The extract was washed sequentially with 5% HCl, satd aq $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 3:1 toluene–acetone as eluent to give **33** (78.3 mg, 64%). $[\alpha]_D^{24}$ +67.5 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 4.96 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.74 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal a), 4.47 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal b). ^{13}C NMR (125 MHz, $CDCl_3$): δ 101.6 (C-1 of Gal b), 99.7 (C-1 of Gal a), 96.6 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{43}H_{66}N_2O_{24}SiNa$: ($[M+Na]^+$) 1108.4, found 1108.6.

4.34. 2-(Trimethylsilyl)ethyl β-D-galactopyranosyl-(1→4)-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (B)

Compound **B** was prepared from **33** (73.8 mg, 67.9 μmol) as described for preparation of **A**, yielding 48.6 mg (quant.). $[\alpha]_D^{24}$ +65.2 (*c* 1.0, H_2O). ^1H NMR (500 MHz, D_2O): δ 4.73 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.40 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1 of Gal b), 4.32 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal a). ^{13}C NMR (125 MHz, D_2O): δ 104.2 (C-1 of Gal a), 103.8 (C-1 of Gal b), 96.1 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{25}H_{47}NO_{16}SiNa$: ($[M+Na]^+$) 668.3, found 668.6. HRFABMS: calcd for $C_{25}H_{47}NO_{16}SiNa$: ($[M+Na]^+$) 668.2562, found 668.2602.

4.35. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→3)]-2-azido-4-*O*-benzyl-2-deoxy-α-D-galactopyranoside (34)

Compound **34** was prepared from **32** (189 mg, 0.16 mmol) as described for preparation of **6**, yielding 140 mg (74%). $[\alpha]_D^{24}$ +21.3 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 4.89 (d, 1H, $J_{1,2}$ 7.9Hz, H-1 of Gal b), 4.83 (d, 1H, $J_{1,2}$ 3.7Hz, H-1 of GalNAc), 4.79 (d, 1H, $J_{1,2}$ 7.9Hz, H-1 of Gal a). ^{13}C NMR (125 MHz, $CDCl_3$): δ 102.1 (C-1 of Gal a), 100.4 (C-1 of Gal b), 97.9 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{59}H_{73}N_3O_{20}SiNa$: ($[M+Na]^+$) 1194.5, found 1195.3. HRFABMS: calcd for $C_{59}H_{73}N_3O_{20}SiNa$: ($[M+Na]^+$) 1194.4454, found 1194.4517.

4.36. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→6)-]-2-azido-4-*O*-benzyl-2-deoxy-α-D-galactopyranoside (35)

Compound **35** was prepared from **34** (76.3 mg, 65.1 μmol) and **8** (78.2 mg, 0.130 mmol) as described for preparation of **14**, yielding 85.6 mg (81%). $[\alpha]_D^{24}$ +19.9 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 4.96 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.86 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal a), 4.77 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of GlcNAc), 4.60 (br d, 1H, $J_{1,2}$ 12.8 Hz, H-1 of Gal b). ^{13}C NMR (125 MHz, $CDCl_3$): δ 103.0 (C-1 of Gal a), 101.2 (C-1 of GlcNAc), 100.2 (C-1 of Gal b), 97.6 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{74}H_{91}Cl_3N_4O_{29}SiNa$: ($[M+Na]^+$) 1655.5, found 1655.2.

4.37. 2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-[2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-]-2-acetamido-4-*O*-acetyl-2-deoxy-α-D-galactopyranoside (36)

Compound **36** was prepared from **35** (119 mg, 72.9 μmol) as described for preparation of **10**, yielding 36.4 mg (36%). $[\alpha]_D^{24}$ +36.0 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 4.90 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1 of GalNAc), 4.75 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal b), 4.63 (d, 1H, $J_{1,2}$ 7.9

Hz, H-1 of GlcNAc), 4.48 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal a). ^{13}C NMR (125 MHz, $CDCl_3$): δ 101.6 (C-1 of Gal a), 100.7 (C-1 of GlcNAc), 99.6 (C-1 of Gal b), 96.6 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{60}H_{84}N_2O_{32}SiNa$: ($[M+Na]^+$) 1395.5, found 1396.1.

4.38. 2-(Trimethylsilyl)ethyl β-D-galactopyranosyl-(1→4)-β-D-galactopyranosyl-(1→3)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-]-2-acetamido-2-deoxy-α-D-galactopyranoside (C)

Compound **C** was prepared from **36** (36.4 mg, μmol) as described for preparation of **A**, yielding 20.4 mg (91%). $[\alpha]_D^{24}$ +52.0 (*c* 0.5, H_2O). ^{1}H NMR (500 MHz, D_2O): δ 4.72 (d, 1H, $J_{1,2}$ 3.7Hz, H-1 of GalNAc), 4.40 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1 of Gal b), 4.35 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1 of GlcNAc), 4.30 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Gal a). ^{13}C NMR (125 MHz, D_2O): δ 104.2 (C-1 of GlcNAc), 103.8 (C-1 of Gal b), 101.1 (C-1 of Gal a), 96.2 (C-1 of GalNAc). MALDI-TOFMS: calcd for $C_{33}H_{60}N_2O_{21}SiNa$: ($[M+Na]^+$) 871.3, found: 871.8. HRFABMS: calcd for $C_{33}H_{66}N_2O_{21}SiNa$: ($[M+Na]^+$) 871.3356, found 871.3376.

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Supplementary data

Supplementary data (Copies of the NMR spectra for all new compounds are provided) associated with this article can be found, in the online version, at doi:10.1016/j.carres.2009.02.019.

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